Experimental

General Methods

All chemicals purchased from SigmaAldrich and were used as received, without further purification. Solvents were dried by passage through a column of activated alumina prior to use. Reactions were monitored by thin layer chromatography (TLC) with DCM as the eluent. Silica coated aluminium TLC plates used were purchased from Merck (Kieselgel 60 F-254) and visualised using either UV light (254 nm and 365 nm), or by oxidation with either iodine or aqueous potassium permanganate solution. Yields refer to chromatographically (HPLC) and spectroscopically (^{1}H NMR and ^{13}C{^{1}H} NMR) homogenous material. NMR spectra were recorded on a JEOL ECS spectrometer operating at 400 MHz (^{1}H) or 100.5 MHz (^{13}C{^{1}H}). Coupling constants are quoted in units of Hz.

Mass spectra were recorded on a Bruker micrOTOF MS-Agilent series 1200LC spectrometer. FTIR spectroscopy was performed using a Shimadzu IR Prestige-21 with Specac Golden Gate diamond ATR IR insert. High-performance liquid chromatography was performed on a Shimadzu Prominence modular HPLC system comprising a LC-20A liquid chromatograph, a DGU-20A$_5$ and DGU-20B degasser, a SIL-20A autosampler, a CBM-20A communication bus, a CTO-20A column oven, and a SPO-20A dual wavelength UV-vis detector. 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. The mobile phase was 5% chloroform in acetonitrile and the detector wavelengths of 226 and 254 nm were selected.

Computational chemistry was performed using the using Gaussian G09 revision d01 on the York Advanced Research Computing Cluster (YARCC) as described in the text. [1]

Polarised optical microscopy was performed on a Zeiss Axioskop 40Pol microscope using a Mettler FP82HT hotstage controlled by a Mettler FP90 central processor. Cells with both homogenous and homeotropic alignment layers were obtained from Instec. Photomicrographs were captured with an InfinityX-21 MP digital camera. Differential scanning calorimetry was performed on a Mettler DSC822^e fitted with an autosampler operating with Mettler Star^e software and calibrated before use each

day using an indium standard (onset = 156.55 ± 0.2 °C, ΔH = 28.45 ± 0.40 Jg^{-1}) under an atmosphere of dry nitrogen.

An INSTEC ALCT Property Tester was used to determine the parallel and perpendicular dielectric capacitance of the materials in their nematic phases via the "one-cell method" first reported by Clark. [2-4] The thickness of a cell coated with a buffed polyimide for homogenous alignment was determined by UV-Vis interferometry. Using this value, the capacitance of the empty cell was determined using the ALCT and the value of parasitic capacitance for the cell adjusted so that the value of d obtained by this method matched that obtained from interferometry. [5] The cell was then filled by capillary action with a target material heated into the isotropic phase. At applied voltages below the threshold ($V_{threshold}$) the capacitance measured gave $C_\perp$ which gave $\varepsilon_\perp$ according to equation (1). For applied voltages above the threshold voltage ($V > 5V_{threshold}$) a linear fit of capacitance as a function of 1/V extrapolated to 1/V = 0 gave $C_\parallel$ which in turn gave $\varepsilon_\parallel$ according to equation (2).

$$\varepsilon_\perp = \frac{C_\perp}{C_0}$$
(1)

$$\varepsilon_\parallel = \frac{C_\parallel}{C_0}$$
(2)

The Maier-Meier equations (4, 5 and 6) were used to calculate dielectric anisotropy using dipole moments and molecular polarisabilities calculated at the B3LYP/6-31G(d) level of theory. The effective dipole moment (μ_{eff}) is the molecular dipole moment mediated by the Kirkwood 'g' factor, as shown in equation (3)

$$\mu_{eff}^{\;2} = g\mu_{mol}^{\;2}$$
(3)

Solving these equations so the calculated dielectric anisotropy matches that measured experimentally for a range of order parameters (S = 0.4 – 0.6) allows an empirical measurement of the Kirkwood factor (g), which reflects the degree of anti (g<1) or parallel (g>1) dipole correlations in a system. A more detailed description is given elsewhere. [6]

$$\varepsilon_\parallel = 1 + \frac{NFh}{\varepsilon_0}\left\{\alpha - \frac{2}{3}\Delta\alpha S + \frac{F\mu_{eff}^{\;2}}{3k_BT}[1 - (1 - 3cos^2\beta)S]\right\}$$
(4)

$$\varepsilon_\perp = 1 + \frac{NFh}{\varepsilon_0}\left\{\bar{\alpha} - \frac{1}{3}\Delta\alpha S + \frac{F\mu_{eff}^2}{3k_BT}\left[1 + \frac{1}{2}(1 - 3cos^2\beta)S\right]\right\} \quad (5)$$

$$\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp = \frac{NFh}{\varepsilon_0}\left\{\Delta\alpha - \frac{F\mu_{eff}^2}{2k_BT}(1 - (3cos^2\beta))\right\}S \quad (6)$$

The reaction field vector (F) and cavitation factor (h) were calculated using equations 7 and 8.

$$F = \frac{1}{1 - \bar{\alpha}\cdot f} \quad (7)$$

where $$f = \frac{2\bar{\varepsilon} - 1}{2\bar{\varepsilon} + 1}\cdot\frac{N}{3\varepsilon_0}$$

$$h = \frac{3\bar{\varepsilon}}{2\bar{\varepsilon} + 1} \quad (8)$$

As described by Kazynski $et.$ $al.$ the correctness of the calculations was checked by back calculating the order parameter (S) and Kirkwood factor (g) using equations (9) and (10) respectively. [6]

$$S = \frac{2\Delta\varepsilon\varepsilon_0}{NFh[2\Delta\alpha + 3\bar{\alpha}(1 - 3cos^2\beta)] - 3(\bar{\varepsilon} - 1)\varepsilon_0(1 - 3cos^2\beta)} \quad (9)$$

$$g = \frac{[(\varepsilon_\parallel - 1)\varepsilon_0 - \bar{\alpha}NHf - \frac{2}{3}\Delta\alpha NFSh]3K_BT}{NF^2h\mu^2[1 - (1 - 3cos^2\beta)S]} \quad (10)$$

Small angle X-ray diffraction 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. Diffraction patterns were recorded on a 2048x2048 pixel Bruker VANTEC 500 area detector set at a distance of 121 mm from the sample, allowing simultaneous collection of small angle and wide angle scattering data. Samples were

filled into 1mm capillary tubes and aligned with a pair of 1T magnets. Diffraction patterns were collected as a function of temperature and the data processed using Matlab. Raw data are available upon request from the University of York data catalogue.
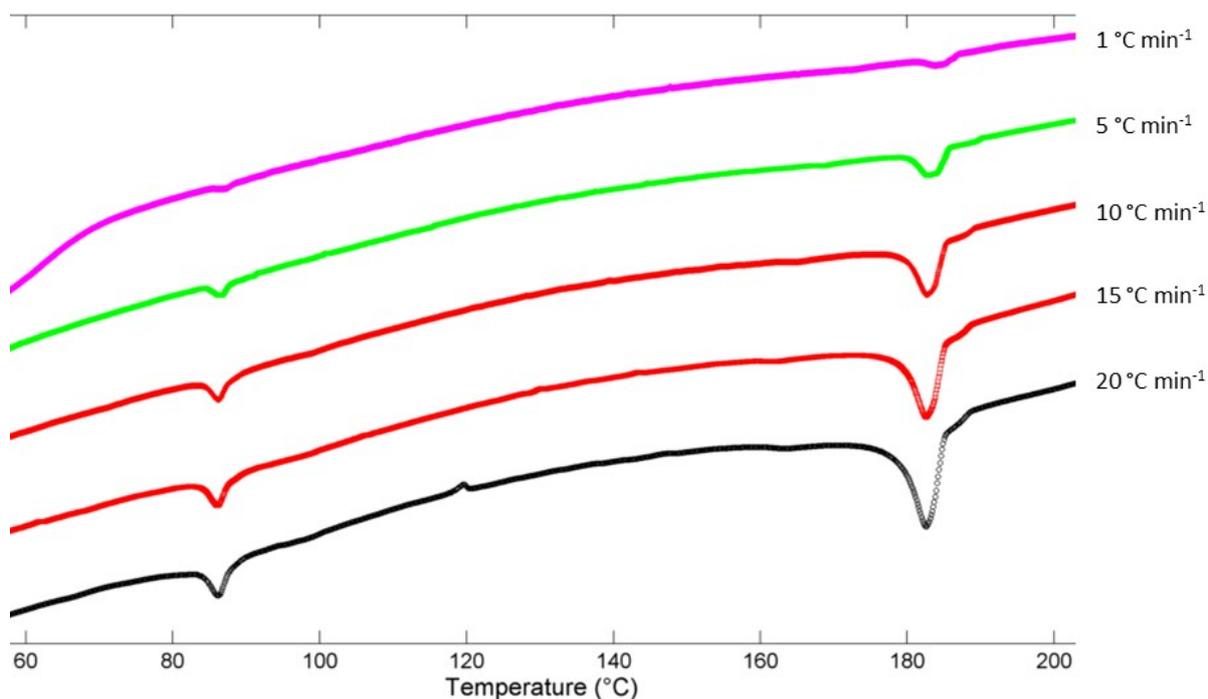

Figure SI1: DSC thermograms (mW vs temperature) of compound **1** obtained at the indicated cooling rates. The rightmost peak is the nematic to isotropic (N-Iso) transition, the left most is the nematic to nematic (N-N_X) transition.
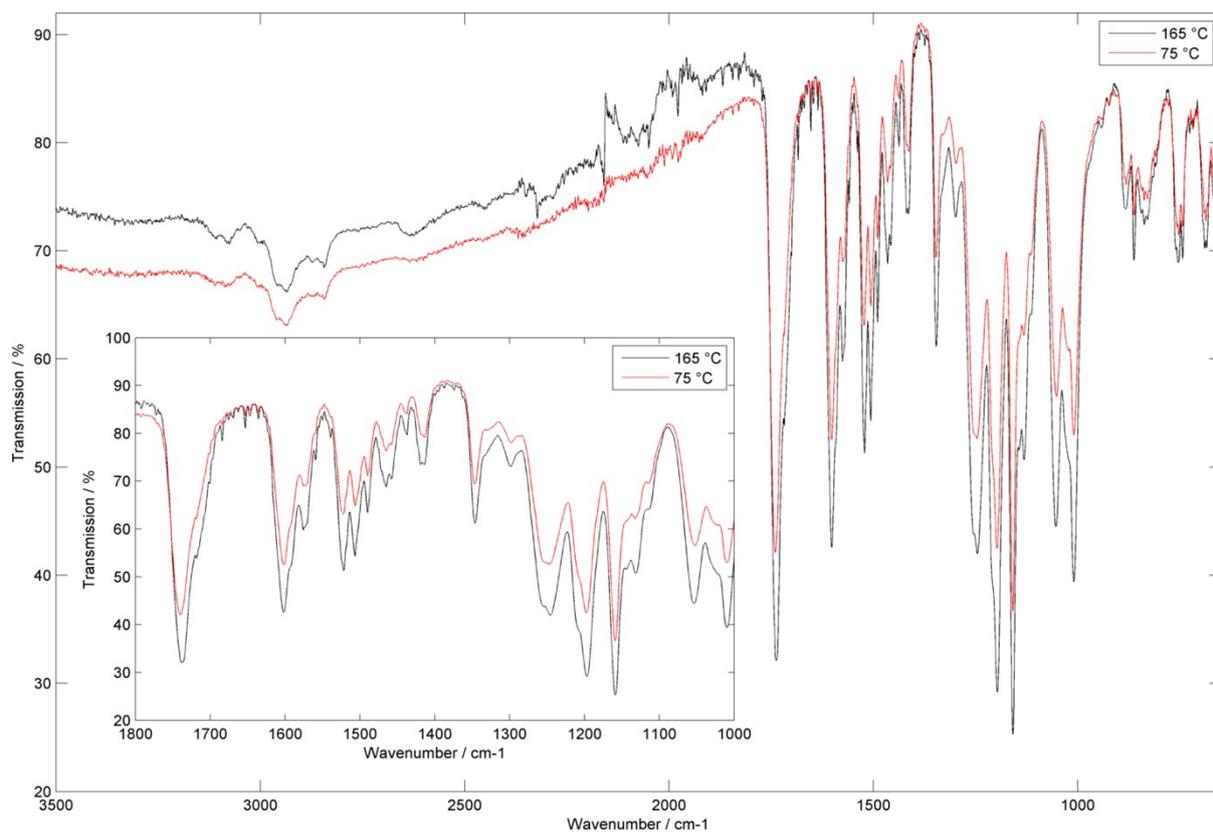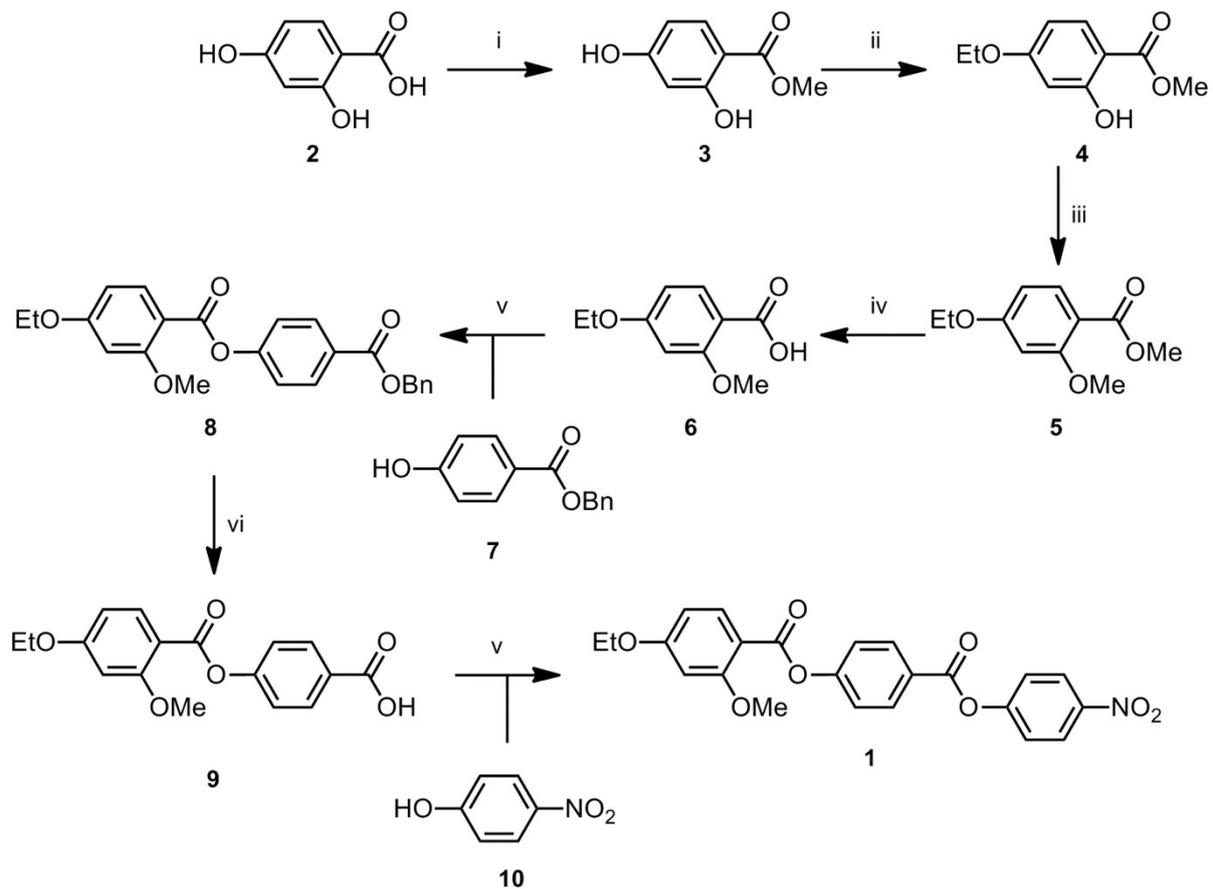
Figure SI2: FT-IR spectra recorded in the upper temperature nematic phase of compound **1** (165 °C, black line) and in the lower temperature nematic phase of **1** (75 °C, red line). Temperature control was afforded by a SEPAC temperature controlled FT-IR stage. The temperature accuracy is better than ± 3°C.

i... MeI, KHCO$_3$, DMF
ii... EtBr, K$_2$CO$_3$, Acetone
iii... MeI, K$_2$CO$_3$, Acetone
iv... KOH, MeOH, H$_2$O
v... EDAC, DMAP, DCM
vi... H$_2$, Pd/C, THF
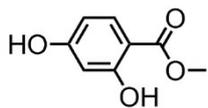
Methyl 2,4-dihydroxybenzoate (3)

Methyl iodide (50.4 g, 22.2 ml, 0.3557 mmol) was added dropwise to a stirred solution of compound **2** (50 g, 0.324 mmol) and potassium hydrogen carbonate (64.8 g, 0.648 mmol) in anhydrous DMF (300 ml) under an atmosphere of dry argon at 40 °C. The reaction was monitored by TLC and reached completion after 4h, at which point the solution was cooled to ambient temperature and poured onto water (1 L) and the product extracted into diethyl ether (3 x 100 ml). The combined organic extracts were washed with water (5 x 200 ml) and brine (2 x 100 ml). The ethereal extract was dried over anhydrous $MgSO_4$ and the solvent removed *in vacuo* to give an off white solid that was recrystallised from ethanol/water to afford the title compound as white crystals.
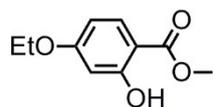
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Yield:	49.1 g (92%)
Melting Point (°C):	119
^{1}H NMR (400 MHz, CDCl$_3$):	3.21 (3H, s, CH$_3$O), 5.75 (2H, m, Ar), 7.02 (1H, d, J = 8.4, Ar), 9.43 (1H, s, OH), 10.21 (1H, s, OH)
^{13}C{^{1}H} NMR (100.5 MHz, CDCl$_3$):	51.45, 102.35, 103.75, 107.99, 131.15, 163.08, 164.07, 169.87
MS (m/z, ESI +):	169.0497 (100%, C$_8$H$_9$O$_4$ M+H)

Methyl 4-ethoxy-2-hydroxybenzoate (4)

Bromoethane (21.4 g, 0.166 mol) was added dropwise to a stirred solution of compound **3** (30 g, 0.179 mol) and potassium carbonate (49.28 g, 0.357 mol) in acetone (400 ml) heated under reflux at 70 °C. After addition of the bromoethane the reaction was left to stir for 24h. The potassium carbonate was then removed by filtration and the solvent removed *in vacuo*. The crude material was purified by recrystallisation from 9:1 ethanol/H_2O giving **4** as white plates.

Yield:	29.4 g (84%)
Melting Point (°C):	77.0
^{1}H NMR (400 MHz, CDCl$_3$):	1.34 (3H, t, J = 7.0, CH$_3$), 3.86 (3H, s, CH$_3$O), 4.00 (2H, quart, J = 7.0, CH$_2$O), 6.36 - 6.39 (2H, m, J = 2.4, J = 9.5, Ar), 7.68 (1H, d, J = 9.5, Ar), 10.93 (1H, s, OH)
^{13}C{^{1}H} NMR (100.5 MHz, CDCl$_3$):	14.65, 52.02, 63.84, 101.16, 105.32, 107.99, 131.25, 163.82, 165.08, 170.50
IR (v$_{max}$ cm^{-1}):	524, 640, 694, 779, 902, 956, 1041, 1095, 1141, 1180, 1203, 1334, 1442, 1573, 1612, 1666, 2322, 2461, 2507, 2615, 2746, 2877, 3062, 3155, 3348, 3741
MS (m/z, ESI +):	197.0808 (100%, C$_{10}$H$_{13}$O$_4$, M+H), 165.05, 138.52, 122.51
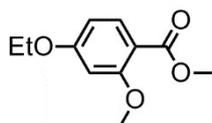
Methyl 2-methoxy-4-ethoxybenzoate (5)

Quantities used: Compound **4** (2.0 g, 10.2 mmol), methyl iodide (1.7 g, 0.76 ml, 12.2 mmol), potassium carbonate (2.9 g, 20.4 mmol), potassium iodide (100 mg) and acetone (30 ml).The experimental procedure was as described in the preparation of compound **4** . The product was isolated from the crude residue by gradient elution column chromatography over silica with DCM as the eluent gave compound **5** as a colourless oil.
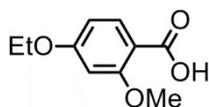
Yield:	1.59 g (71.5%)
^{1}H NMR (400 MHz, CDCl$_3$):	1.26 (3H, t, J = 7.0, CH$_3$), 3.70 (3H, s, CH$_3$O), 3.72 (3H, s, CH$_3$O), 3.89 (2H, quart, J = 7.0, CH$_2$O), 6.32 (2H, m, J = 2.4, J = 8.5, Ar), 7.68 (1H, d, J = 8.5, Ar)
^{13}C{^{1}H} NMR (100.5 MHz, CDCl$_3$):	13.97, 50.86, 53.09, 55.18, 63.08, 98.16, 104.42, 111.43, 131.12, 160.70, 163.09, 165.34
IR (v_{max} cm^{-1}):	540, 663, 771, 817, 840, 902, 972, 1033, 1126, 1211, 1365, 1435, 1581, 1604, 1743, 2839, 2985, 3456
MS (m/z, ESI +):	233.0711 (100%, C$_{11}$H$_{14}$NaO$_4$, M+Na)

2-Methoxy-4-ethoxybenzoic acid (6)

To a solution of compound **5** (1.5 g, 7.14 mmol) in ethanol (20 ml), heated under reflux, was added lithium hydroxide (0.5 g, 21.4 mmol) in water (20 ml) in one portion. After heating the solution under reflux for 2 h the solution was cooled to ambient temperature and acidified with 36% HCl, affording compound **6** as a voluminous white precipitate which was collected by filtration, washed with water (2 x 50 ml) and recrystallised from ethanol, to give the title compound as colourless needles.

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Yield:	1.3 g (95%)
Melting Point (°C):	122.4

^{1}H NMR (400 MHz, DMSO-D6): 1.33 (3H, t, J = 7.0, CH_3), 3.79 (3H, s, CH_3O), 4.06 (2H, quart, J = 7.0, CH_2O), 6.50 (1H, dd, J = 2.1, J = 8.5, Ar), 6.54 (1H, d, J = 2.1, Ar), 7.68 (1H, d, J = 8.5, Ar)

^{13}C{^{1}H} NMR (100.5 MHz, DMSO-D6): 14.44, 55.64, 66.37, 99.10, 105.26, 112.31, 133.30, 160.58, 162.96, 166.33

IR (v_{max} cm^{-1}): 555, 632, 686, 763, 817, 879, 918, 1033, 1095, 1157, 1203, 1265, 1373, 1427, 1566, 1612, 1666, 1743, 1921, 2144, 2314, 2546, 2615, 2816, 2947, 2970, 3464

MS (ESI +): 219.0626 (100%, $C_{10}H_{12}NaO_4$, M+Na)
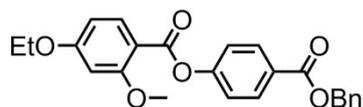
4-((Benzyloxy)carbonyl)phenyl 2-methoxy-4-ethoxybenzoate (8)

Compound **6** (0.6 g, 3.06 mmol), compound **7** (0.76 g, 3.36 mmol), EDAC (0.87 g, 4.59 mmol) and DMAP (56 mg, 0.46 mmol) were dissolved into DCM (25 ml) and stirred for 16 h. The solvent was removed *in vacuo* and the crude residues purified by column chromatography with 1:1 DCM/hexanes as the eluent, followed by recrystallisation from 11:2 ethanol/water gave compound **8** as white needles.

Yield:	0.7 g (56%)

^{1}H NMR (400 MHz, CDCl$_3$): 1.43 (3H, t, J = 7.0, CH$_3$), 3.88 (3H, s, CH$_3$O), 4.08 (2H, quart, J = 7.0, CH$_2$O), 5.33 (2H, s, Bn), 6.52 (1H, d, J = 2.1, Ar), 6.55 (1H, dd, J = 2.1, J = 8.5, Ar), 7.29 (2H, ddd, J = 1.8, J = 2.4, J = 8.9, Ar), 7.31 - 7.47 (5H, m, Bn), 8.08 (1H, d, J = 8.5, Ar), 8.14 (2H, ddd, J = 1.8, J = 2.4, 8.9, Ar)

^{13}C{^{1}H} NMR (100.5 MHz, CDCl$_3$): 14.46, 63.78, 66.21, 66.66, 99.20, 105.22, 109.89, 121.38, 127.08, 127.87, 127.95, 128.38, 131.79, 134.46, 136.09, 154.81, 162.34, 163.07, 165.76, 166.40

IR (ν_{max} cm^{-1}): 694, 756, 833.25, 894, 1010, 1087, 1149, 1195, 1373, 1566, 1604, 1735, 2623, 2885, 2947, 3070, 3456

MS m/z (ESI+): 429.1331 (M+Na), 407.1499 (100%, C$_{24}$H$_{23}$O$_6$, M+H)
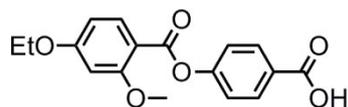
4-(4-Ethoxy-2-methoxybenzoyloxy)benzoic acid (9)

THF (20 ml) and ethanol (20 ml) were added to compound **8** (0.7 g, 1.72 mmol) and 10% palladium on carbon (10 mg) under an atmosphere of dry nitrogen. The resulting suspension was back purged with hydrogen gas delivered *via* a balloon, before stirring under an atmosphere of hydrogen for 24 h, at which point TLC analysis showed that no starting material remained, with a new spot present (Rf = 0, DCM). The reaction solution was filtered through a pad of compressed celite which was subsequently washed with THF (2 x 50 ml) before removal of the solvent *in vacuo* to yield a white solid. Recrystallisation of the crude residues from ethanol gave compound **9** as colourless needles.

Yield:	0.42 g (77%)

^{1}H NMR (400 MHz, DMSO-D6): 1.36 (3H, t, *J* = 7.0, CH$_3$), 3.83 (3H, s, CH$_3$O), 4.12 (2H, quart, *J* = 7.0, CH$_2$O), 6.57 (1H, dd, *J* = 2.4, *J* = 8.5, Ar), 6.61 (1H, d, *J* = 2.4, Ar), 7.26 (2H, ddd, *J* = 2.1, *J* = 2.4, *J* = 8.9, Ar), 7.92 (1H, d, *J* = 8.5, Ar), 7.99 (2H, ddd, *J* = 2.1, *J* = 2.4, *J* = 8.9, Ar)

^{13}C{^{1}H} NMR (100.5 MHz, DMSO-D6): 14.31, 55.68, 63.50, 99.08, 105.57, 109.65, 121.83, 127.96, 130.59, 133.84, 154.14, 161.61, 162.29, 164.09, 166.54,

IR (v_{max} cm^{-1}): 516, 640, 756, 833, 871, 1002, 1111, 1149, 1203, 1365, 1419, 1566, 1604, 1681, 1735, 2314, 2546, 2661, 2947, 2970, 3456

MS m/z (ESI+): 317.1017 (100%, C$_{17}$H$_{17}$O$_6$, M+H), 179.06
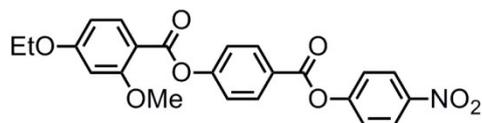
4-((4-Nitrophenoxy)carbonyl)phenyl 4-ethoxy-2-methoxybenzoate (1)

Quantities used: Compound **9** (250 mg, 0.792 mmol), compound **10** (139 mg, 1 mmol), EDAC (191 mg, 1 mmol), DMAP (6 mg, 50 µmol) and DCM (5 ml). The experimental procedure was as described in the preparation of compound **8**. Column chromatography over silica with DCM as the eluent followed by recrystalisation from ethanol/THF (8:1) gave the title compound as a fine white solid.

Yield:	280 mg (81%)

^{1}H NMR (400 MHz, CDCl$_3$): 1.40 (3H, t, J = 7.0, CH$_3$), 3.85 (3H, s, CH$_3$O), 4.06 (2H, quart, J = 7.0, CH$_2$O), 6.48 (1H, d, J = 2.1, Ar), 6.50 (1H, dd, J = 2.1, J = 8.9, Ar), 7.32 (2H, ddd, J = 2.1, J = 2.4, J = 8.9, Ar), 7.36 (2H, ddd, J = 2.1, J = 3.1, J = 9.2, Ar), 8.02 (1H, d, J = 8.9, Ar), 8.18 (2H, ddd, J = 2.1, J = 2.4, J = 2.9, Ar, 8.26 (2H, ddd, J = 2.1, J = 3.1, J = 9.2, Ar)

^{13}C{^{1}H} NMR (100.5 MHz, CDCl$_3$): 14.74, 56.11, 64.07, 99.51, 105.47, 110.18, 122.60, 122.74, 125.37, 125.61, 131.96, 134.71, 145.49, 155.77, 156.07, 162.62, 162.89, 163.71, 164.89

IR (v_{max} cm^{-1}): 532, 617, 686, 748, 825, 1002, 1056, 1149, 1195, 1257, 1350, 1411, 1519, 1604, 1735, 2985, 3086, 3116

MS (m/z, ESI +): 460.10 (M+Na), 438.1185 (100%, C$_{23}$H$_{20}$NO$_8$, M+H), 179.08

Assay (HPLC): >99.9% (only one peak detected)

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