Supporting Information

Large Stokes' Shift Fluorescent Dyes based on a Highly Substituted Terephthalic Acid Core

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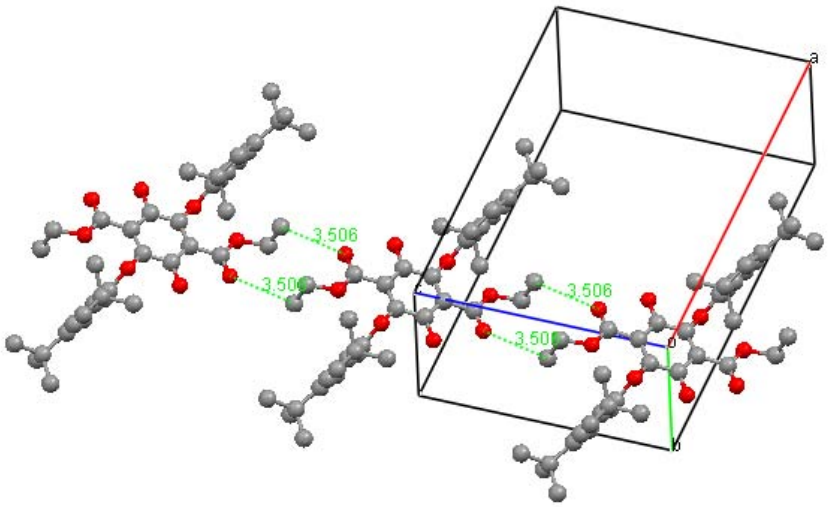
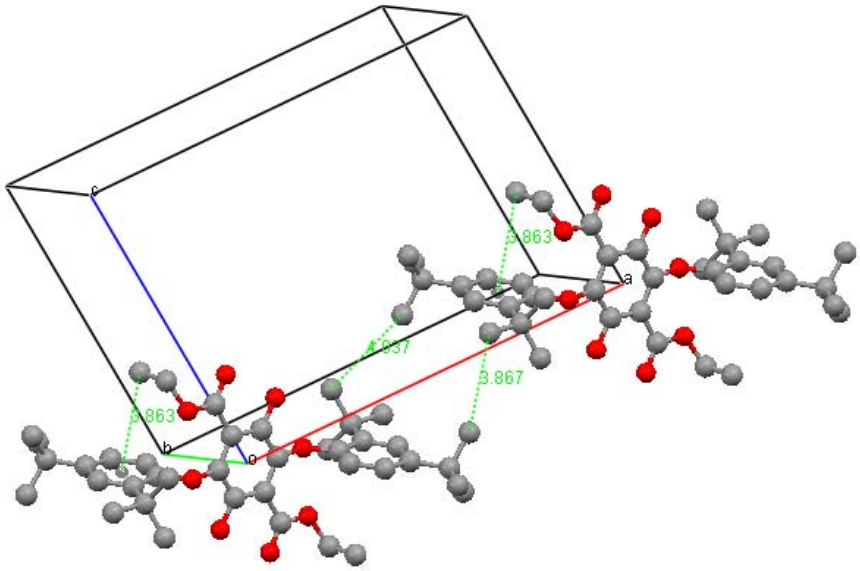
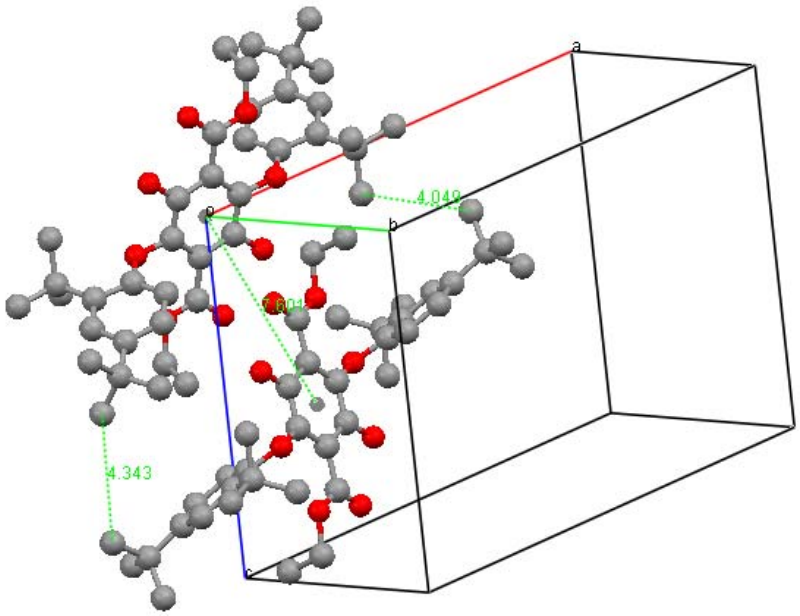


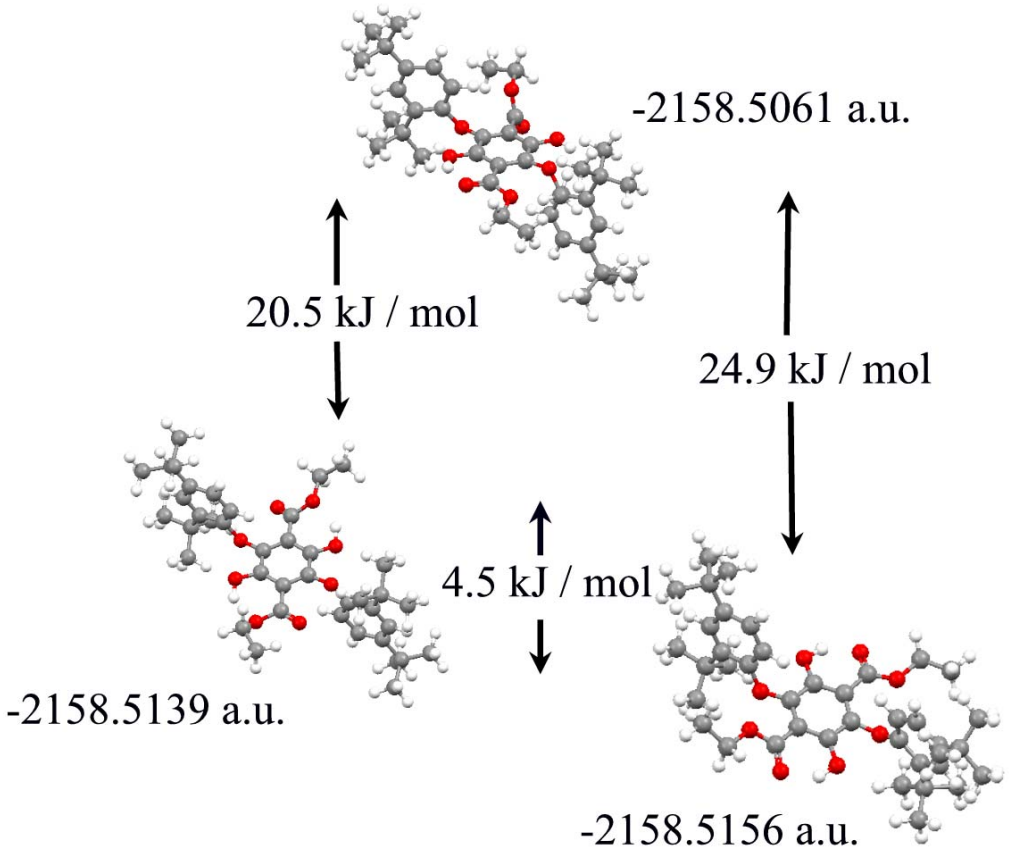
S1. Crystal packing diagram for **3a** along the c-axis. Hydrogen atoms omitted for clarity



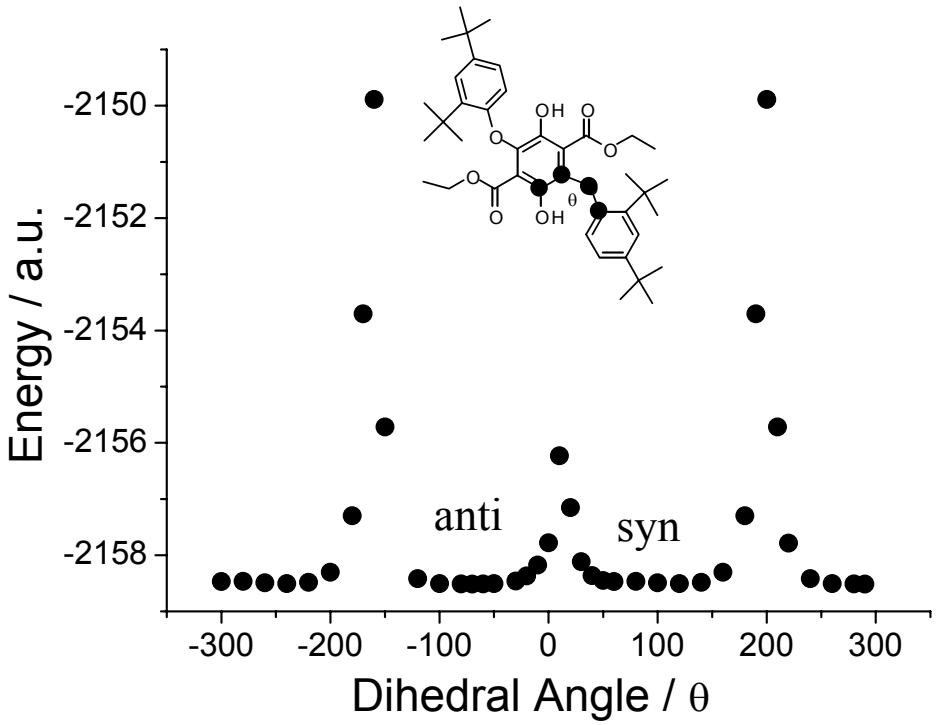
S2. Crystal packing diagram for **3a** along the a-axis. Hydrogen atoms omitted for clarity



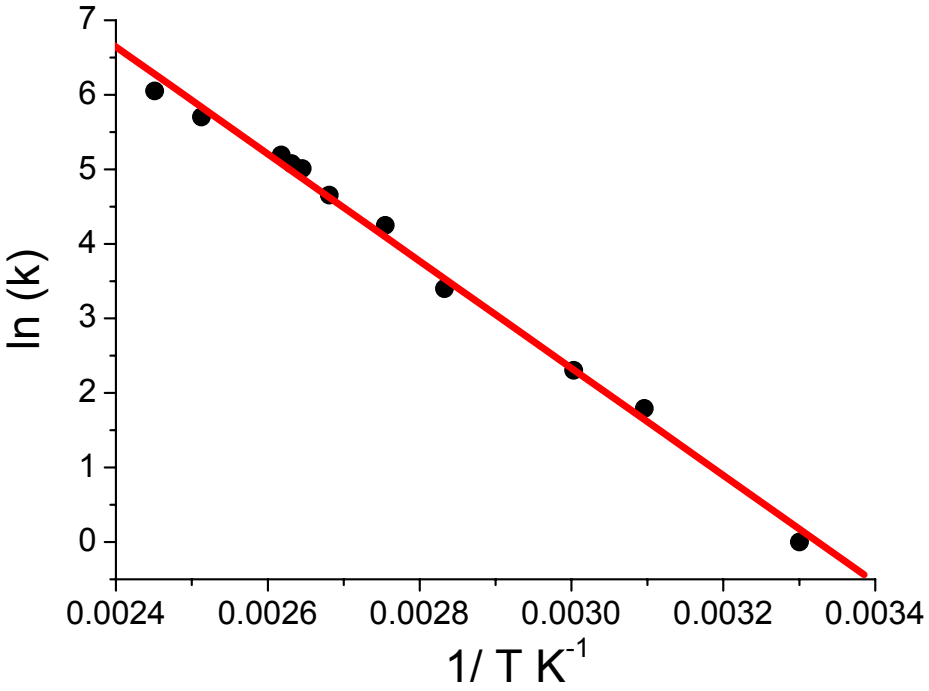
S3. Crystal packing diagram for **3a** along the b-axis. Hydrogen atoms omitted for clarity.



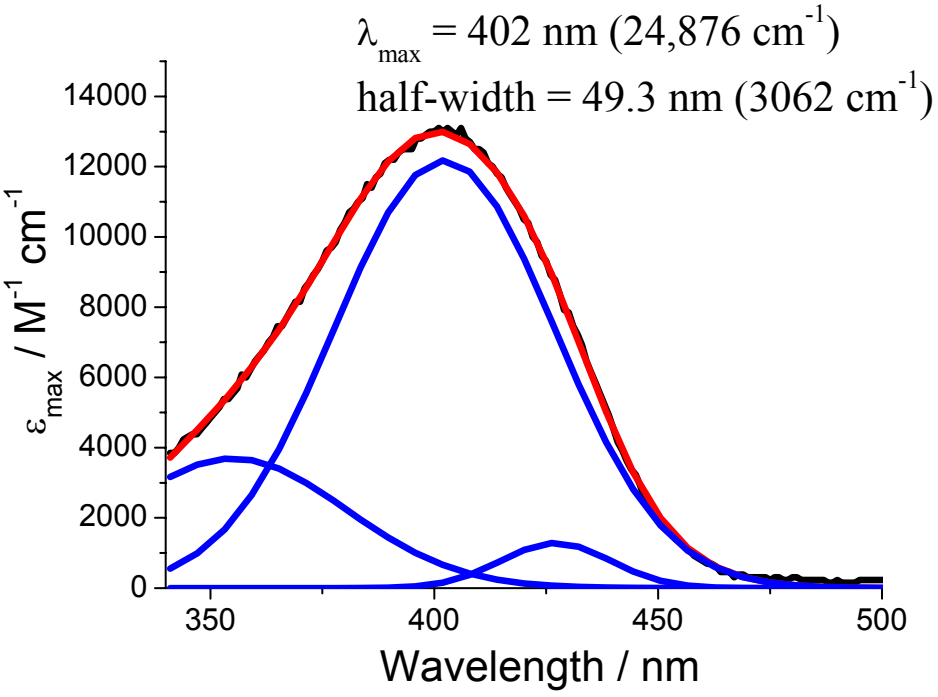
S4. Computer calculated energy-minimized structures for **3a** using B3LYP and the 6-311G basis set.



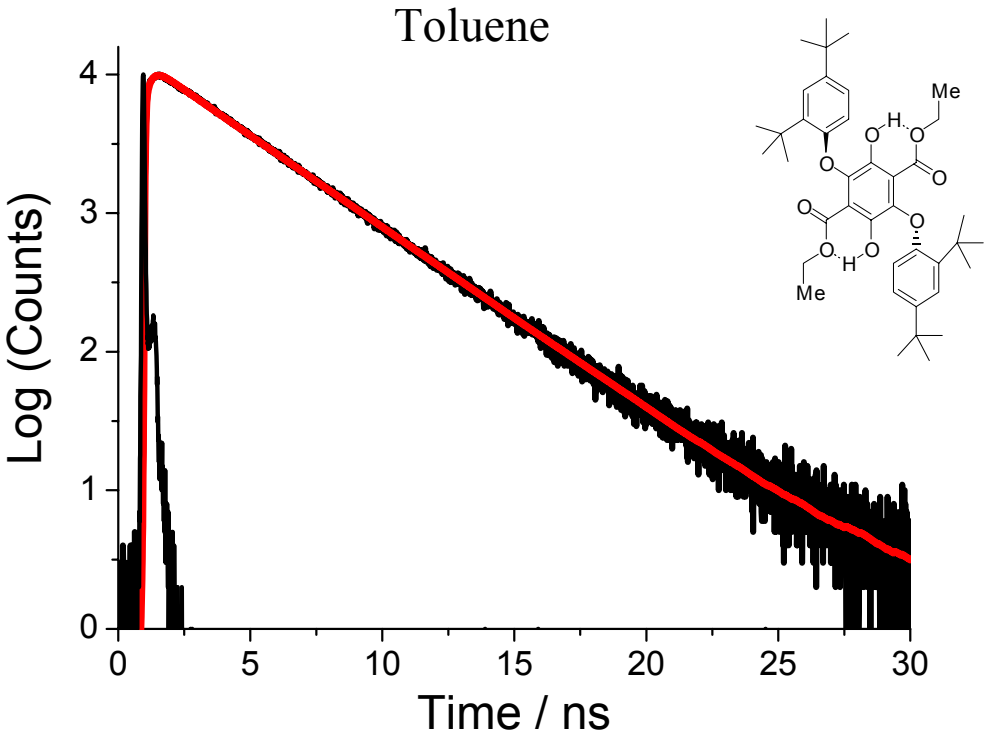
S5. Calculated energies for conformations of **3a** following alteration in the torsion angle (θ).



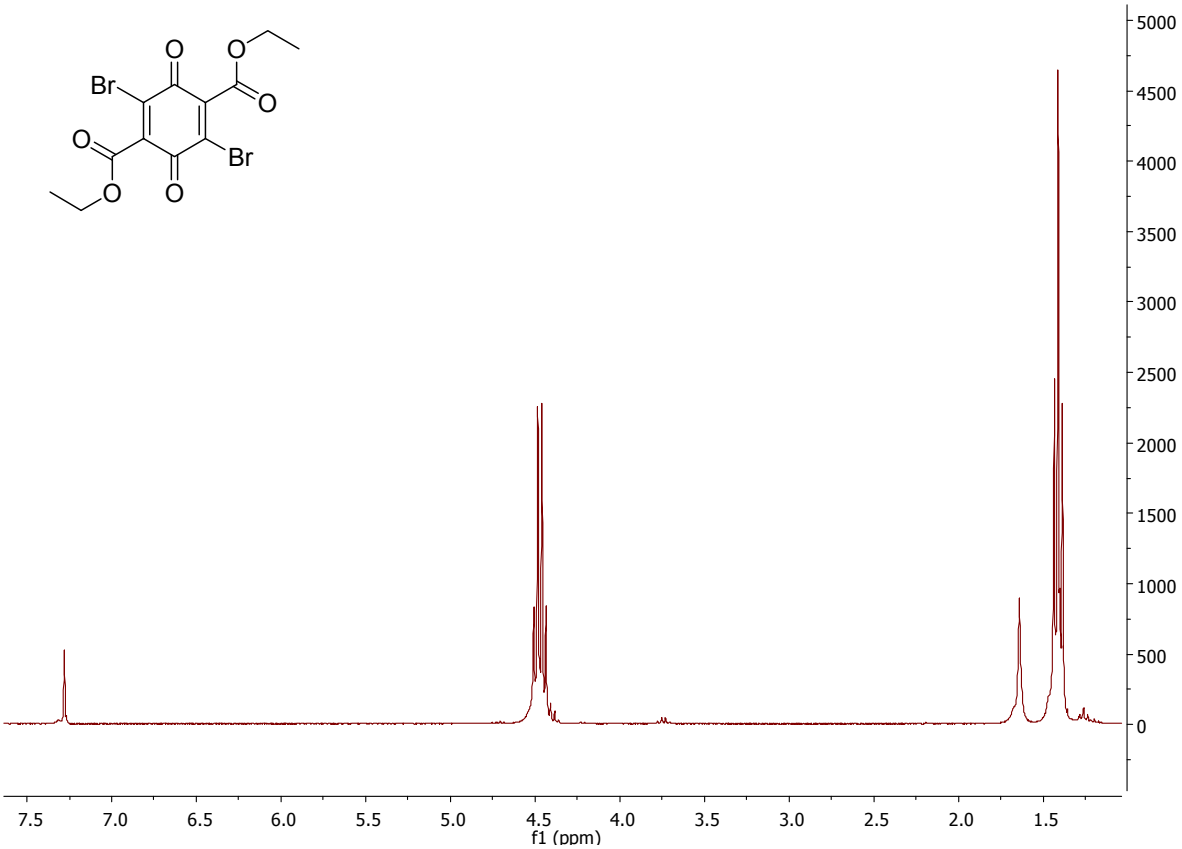
S6. Arrhenius plot for **3a** in d_{10}-o-xylene



S7. Absorption spectrum (black), Gaussian fits (blue) and simulated spectrum (red) for **3a** in toluene.



S8. Time-correlated single photon counting decay trace recorded for **3a** in toluene at room temperature.

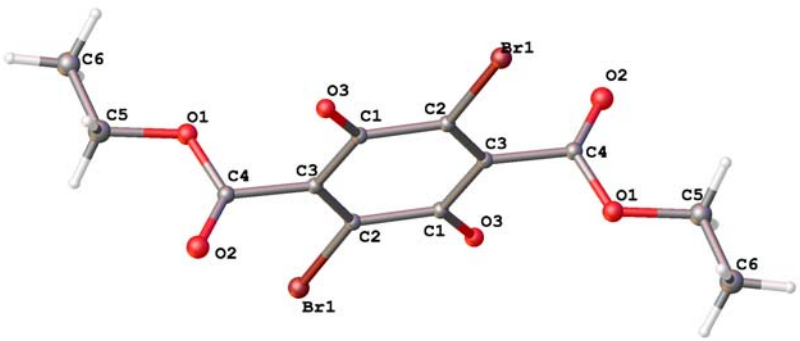


Preparation of 1

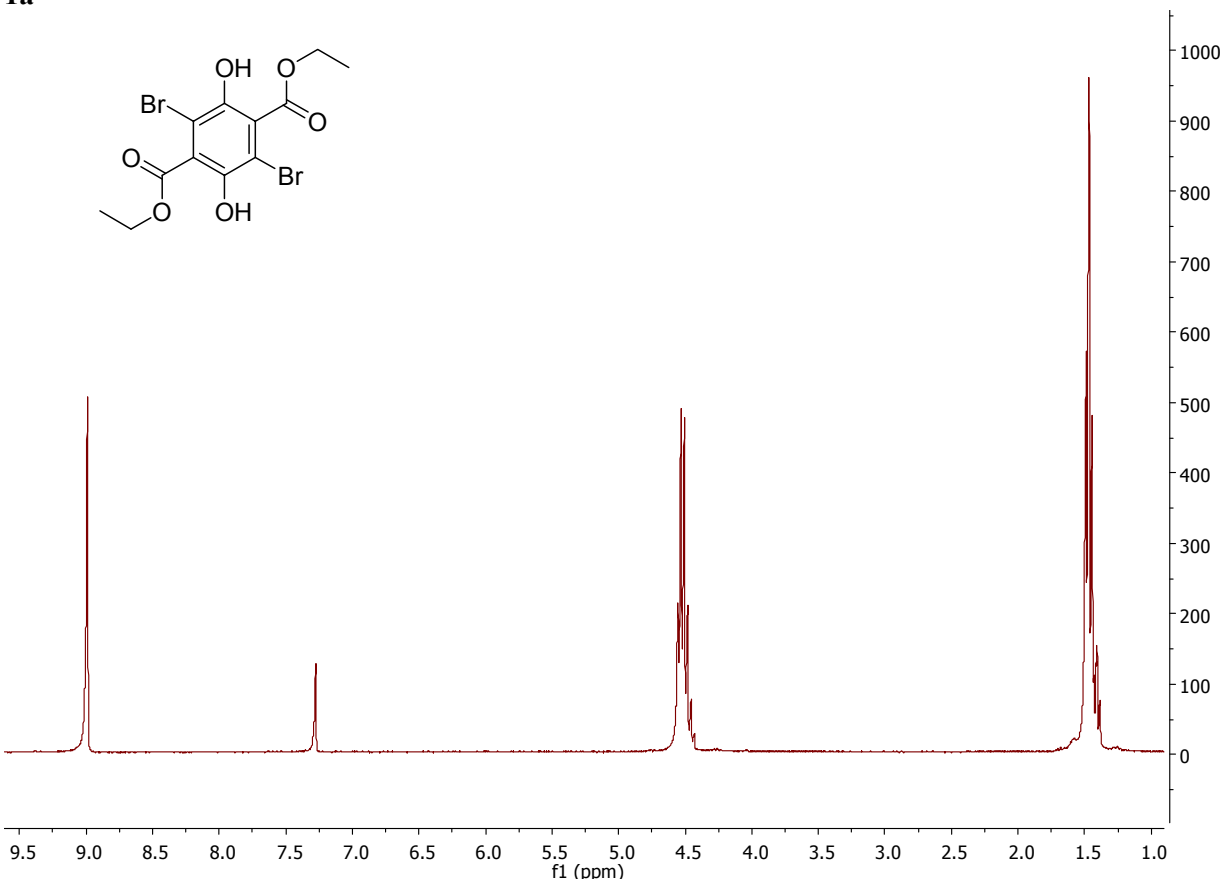
Diethyl-2,5-dihydroxyterephthalate (25.0 g, 0.098 mol) was placed on a petri dish which in turn was placed in a vacuum desiccator along with a sample vial containing liquid bromine (10 mL). The desiccator was closed, evacuated and the material left under a bromine atmosphere for 4 days. The reaction progress was monitored via 1H NMR spectroscopy daily until there was no sign of starting material. Once complete the product was recrystallised from ethanol and HNO_3 (5 mL). The HNO_3 was used to oxidise any material that had formed the dibromohydroquinone **1a** (see below). The product was a yellow needle-like crystal in excellent yield (39.8 g, 99%, 0.097 mol).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.47 (q, *J* = 7.2 Hz, 4H), 1.41 (t, *J* = 7.2 Hz, 6H)
^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.6, 161.3, 140.9, 133.5, 63.5, 14.1.
MP = 226 ^oC
IR – 2991, 1731, 1677, 1284 cm^{-1}
MS – calc. for $C_{12}H_{10}Br_2O_6$ = 410 fnd. 410 (M^+)

Crystal structure for **1**

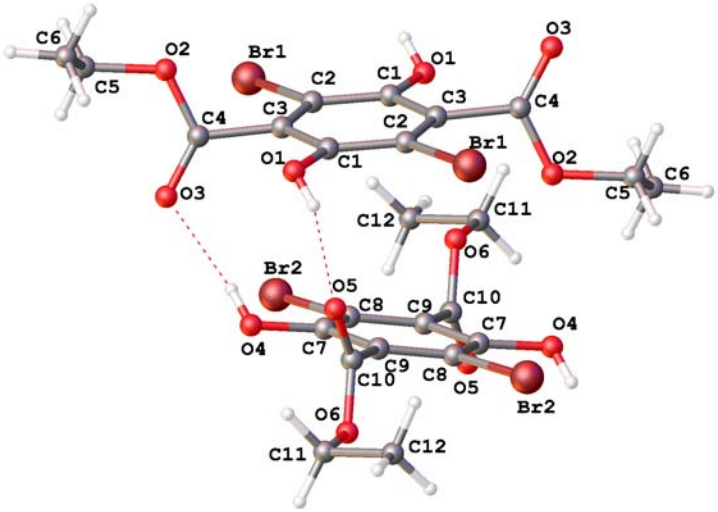


1a



^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.0 (s, 2H), 4.51 (td, J = 7.2, 1.9 Hz, 4H), 1.47 (td, J = 7.1, 2.0 Hz, 6H)

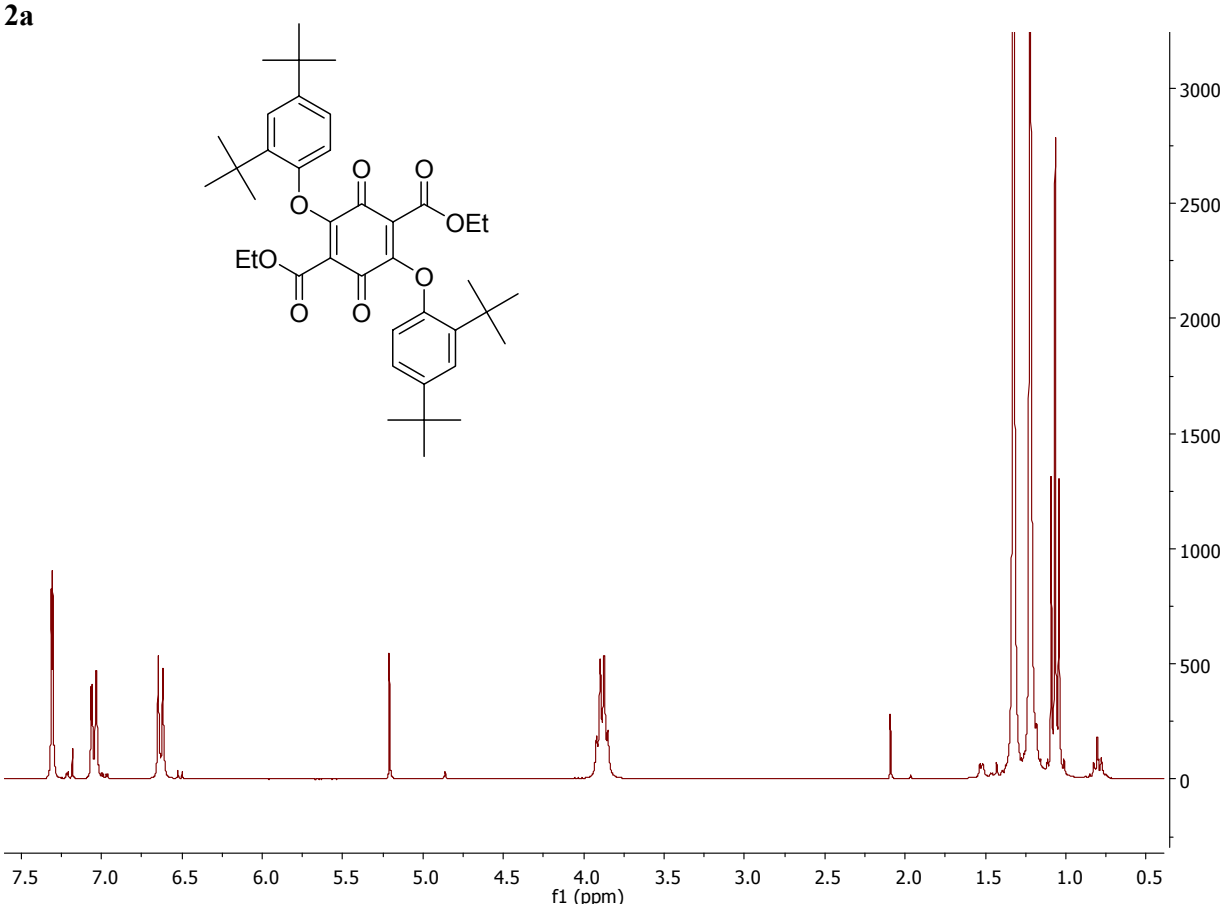
Crystal structure for **1a**



General procedure for synthesis of 2a-e

Compound **1** (1.5 g, 3.7 mmol), 2,4-ditertbutylphenol (1.5 g, 7.2 mmol), pyridine (1.5 mL, 18.5 mmol) and acetone (15 mL) was charged to a 100 mL round bottomed flask and refluxed for 10 minutes. The clear/ yellow suspension quickly turned dark red/ brown upon addition of pyridine and application of heat. The reaction mixture was diluted with water (100 mL) causing a precipitate to form. The precipitate was filtered off and washed with water, air dried and dissolved in DCM (100 mL). The oganic mixture was dried over $MgSO_4$, which was filtered and the cake washed with excess DCM. The combined organic solvents were removed under reduced pressure to give a dark red solid (1.6 g, 2.4 mmol, 66 %).

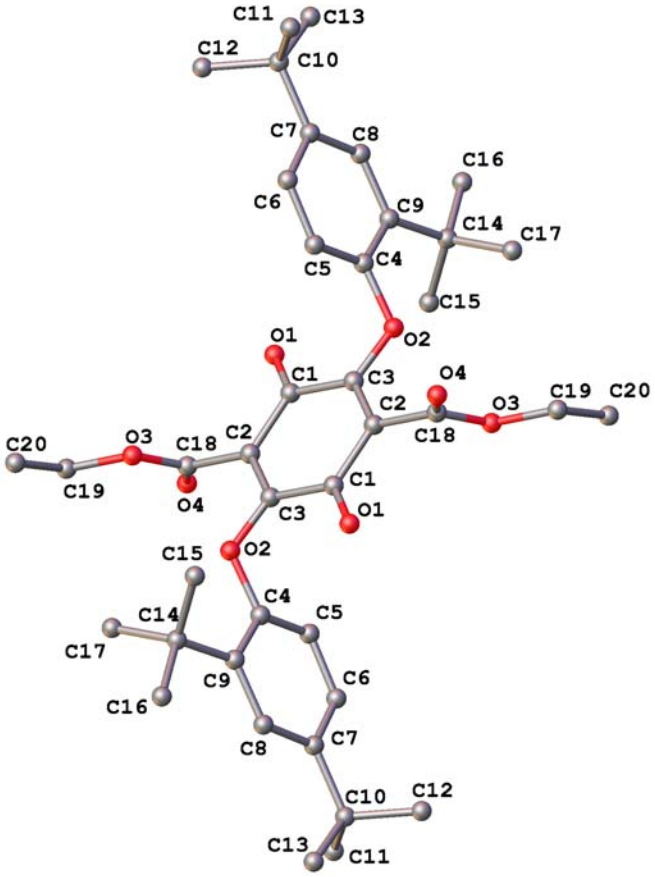
2a



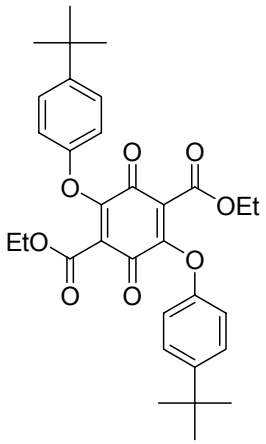
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.31 (d, *J* = 2.5 Hz, 2H), 7.05 (dd, *J* = 8.4, 2.4 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 2H), 3.89 (q, *J* = 7.1 Hz, 4H), 1.33 (s, 18H), 1.22 (s, 18H), 1.07 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.1, 161.3, 151.7, 151.1, 147.6, 138.4, 124.7, 123.7, 117.7, 62.4, 35.1, 34.7, 31.5, 30.1, 13.9.
MP = >250^{o}C
MS – calc. for $C_{40}H_{52}O_8$ = 660.8 fnd. 661 (M^+)
IR – 2963, 1731, 1674, 1175 cm^{-1}.

Crystal structure for **2a**



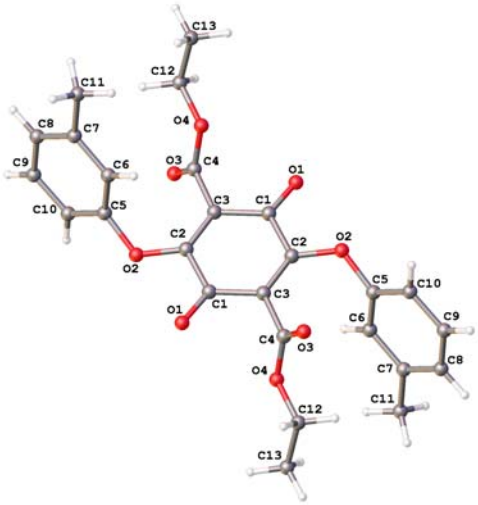
2b



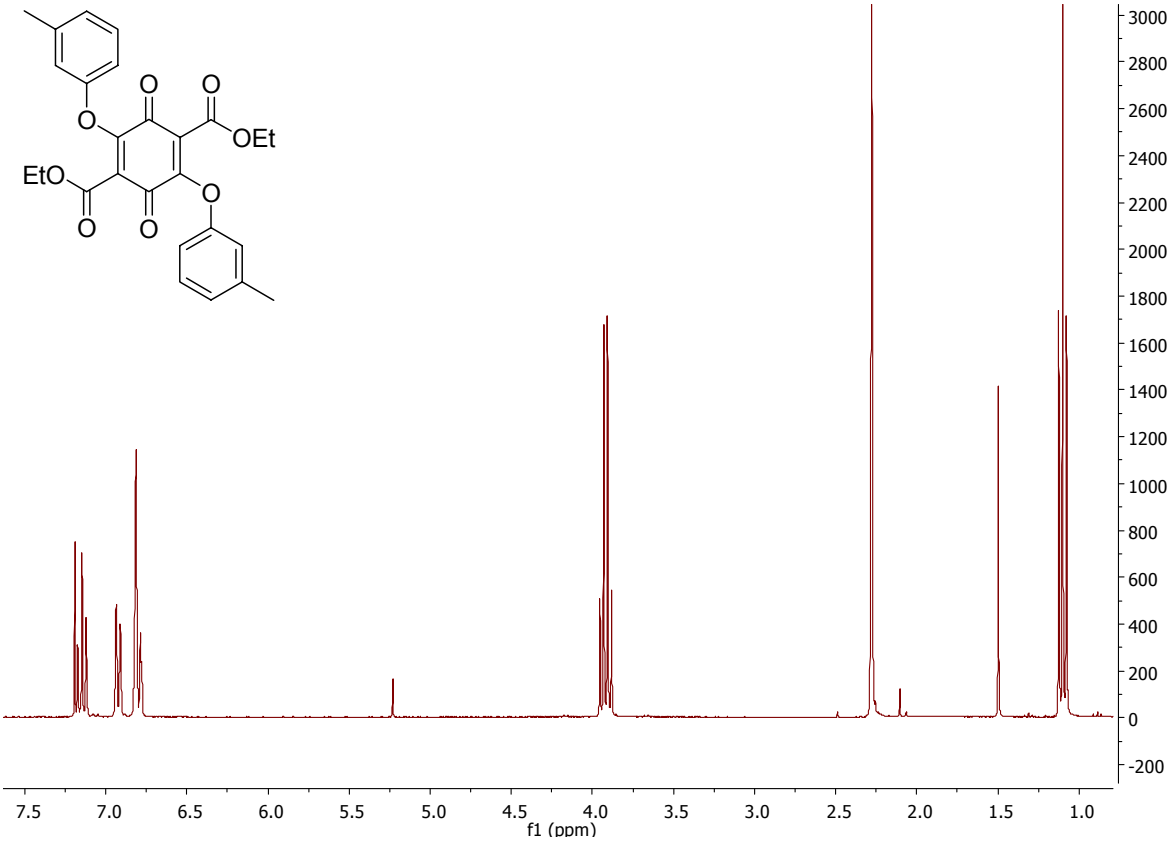
Yield = 96%

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.28 – 7.17 (m, 4H), 7.00 – 6.78 (m, 4H), 4.11 (q, *J* = 7.1 Hz, 4H), 1.24 (s, 18H), 1.00 (t, *J* = 7.1 Hz, 6H).
MP = >250^{o}C

Crystal Structure for **2b**



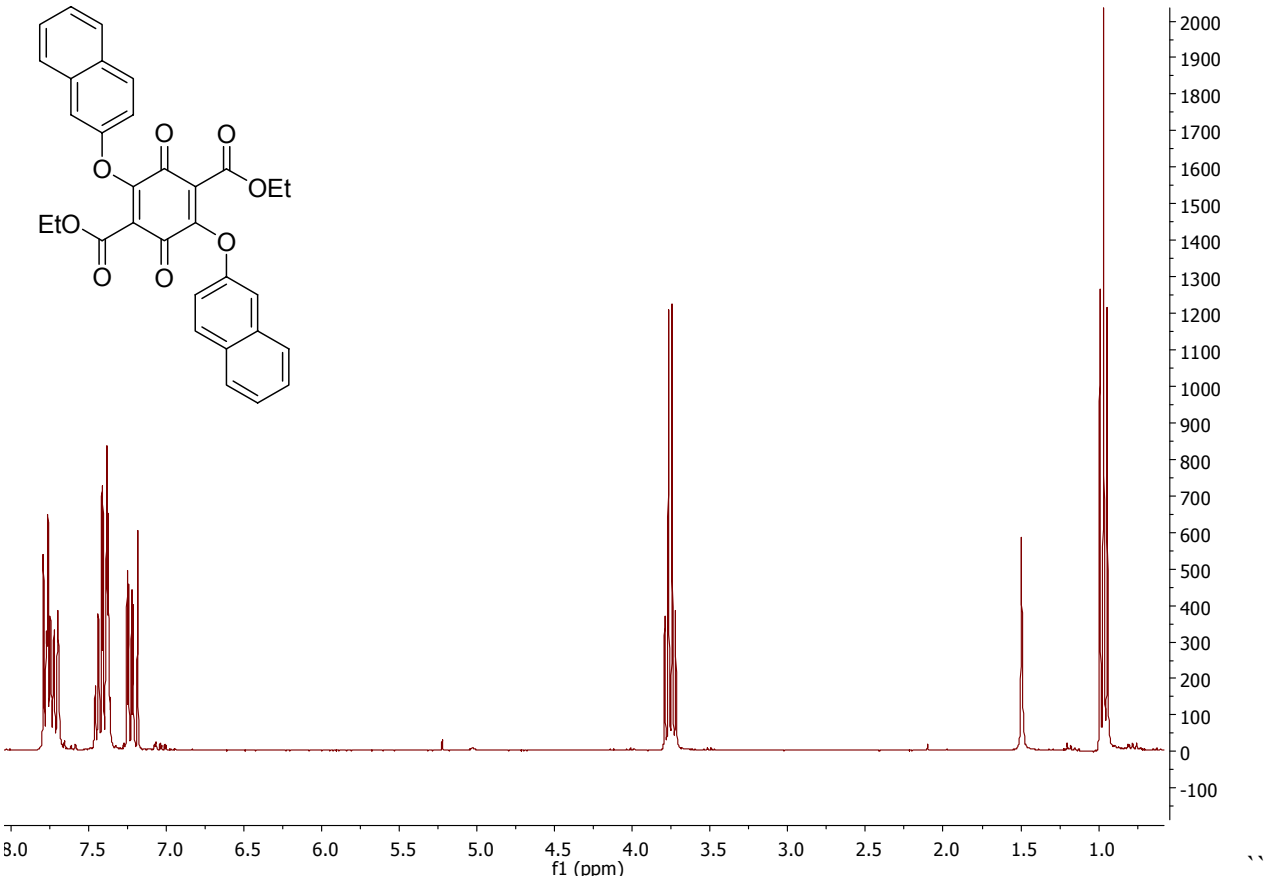
2c



Yield = 67 %

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.15 (t, *J* = 7.7 Hz, 2H), 6.92 (ddd, *J* = 7.5, 1.6, 0.8 Hz, 2H), 6.84 – 6.76 (m, 4H), 3.92 (q, *J* = 7.1 Hz, 4H), 2.28 (s, 6H), 1.10 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.4, 161.0, 155.1, 151.5, 147.8, 140.1, 129.4, 126.3, 122.7, 119.5, 115.9, 62.5, 21.4, 13.9.
MP = 162^{o}C

2d



Yield = 75%

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.78 (d, *J* = 8.9 Hz, 2H), 7.71 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.78 – 7.74 (m, 2H), 7.48 – 7.34 (m, 6H), 7.24 (dd, *J* = 8.9, 2.5 Hz, 2H), 3.76 (q, *J* = 7.1 Hz, 4H), 0.97 (t, *J* = 7.2 Hz, 6H).

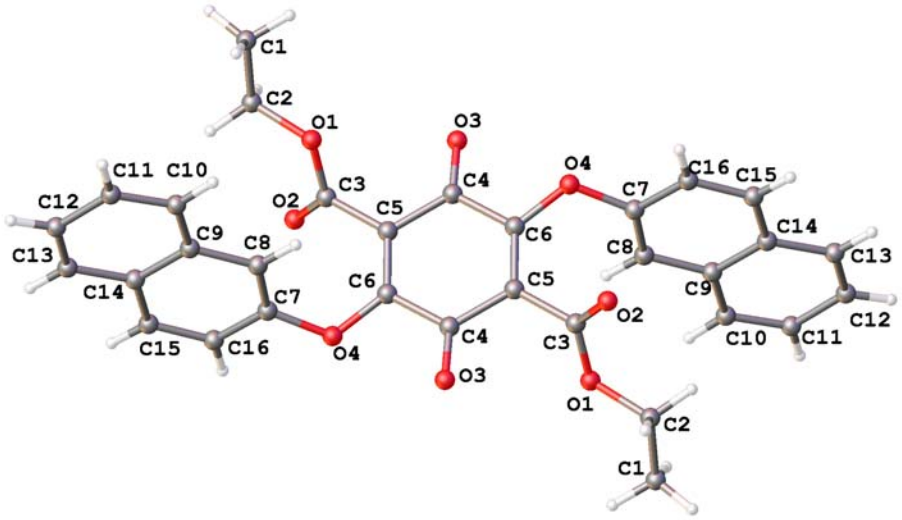
^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.9, 152.9, 151.7, 133.6, 131.1, 130.1, 127.9, 127.6, 127.1, 125.9, 123.1, 119.1, 115.2, 62.5, 13.7.

MP = 180^{o}C

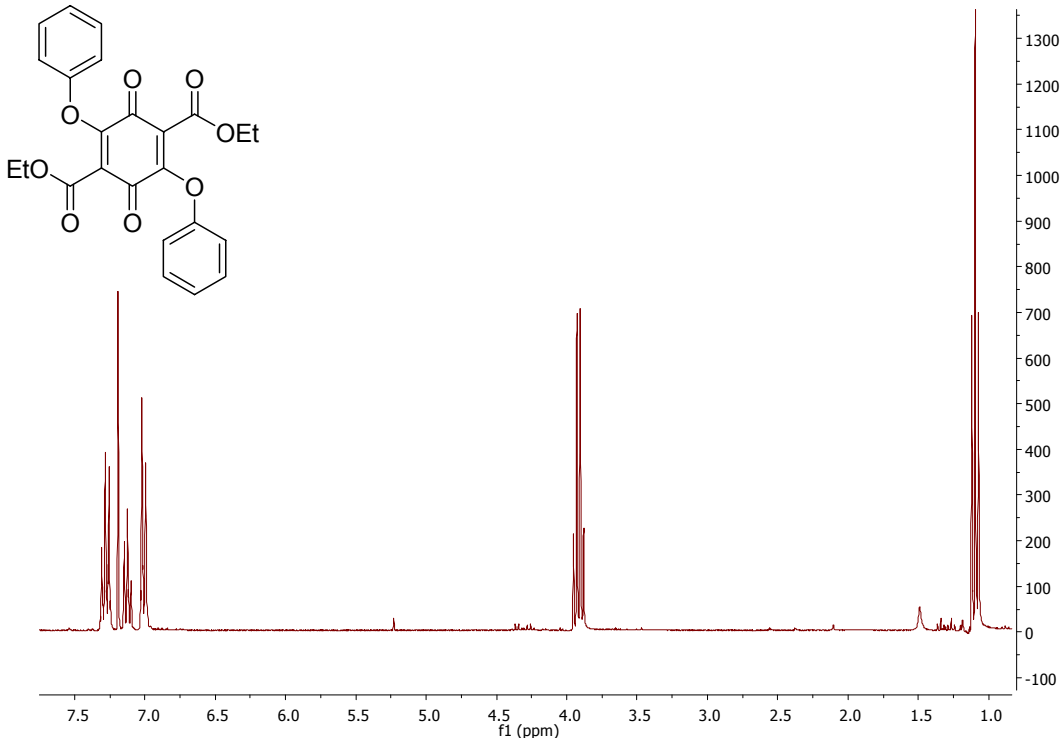
MS – calc. for $C_{32}H_{24}O_8$ = 536.5 fnd. 537 (M^{+})

IR – 2987, 1717, 1670, 1191 cm^{-1}

Crystal structure for **2d**.



2e

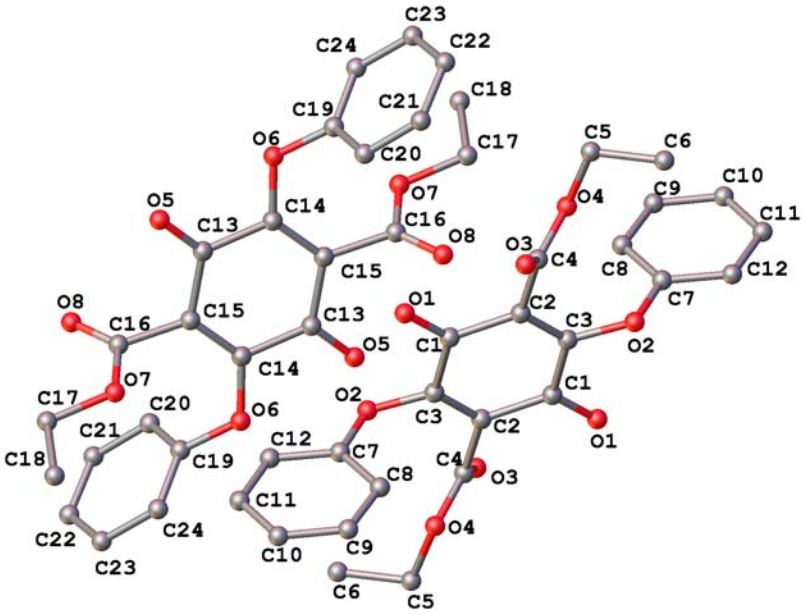


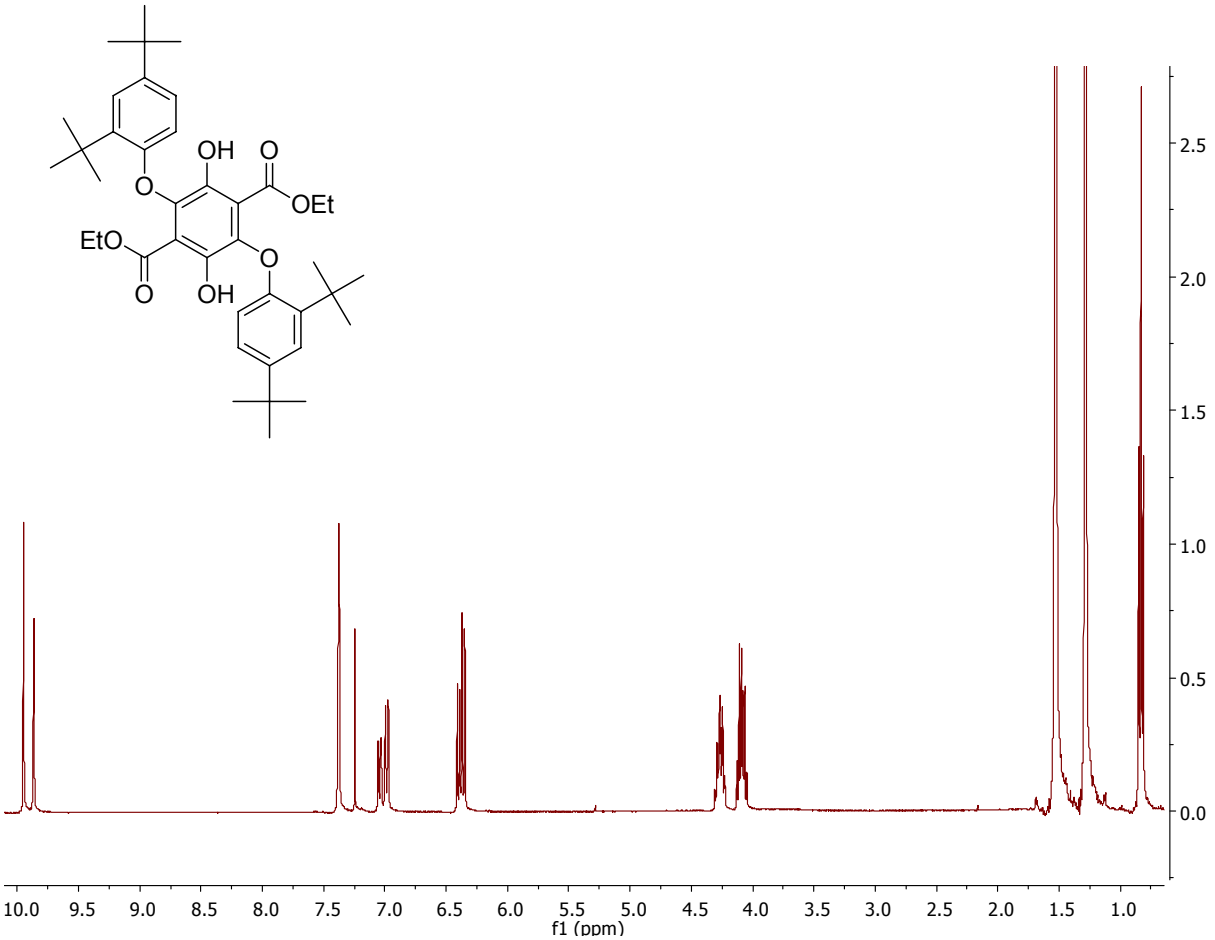
Yield = 95%

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.32 – 7.23 (m, 4H), 7.16 – 7.08 (m, 2H), 7.08 – 6.95 (m, 4H), 3.92 (q, *J* = 7.2 Hz, 4H), 1.10 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.3, 160.9, 155.1, 151.5, 129.8, 125.5, 122.9, 118.9, 62.5, 13.9.
MP = 171°C
IR – 2980, 1731, 1672, 1185
MS – calc. for $C_{24}H_{20}O_8$ = 436.4 fnd. 437 (M^+)

Crystal structure for **2e**.



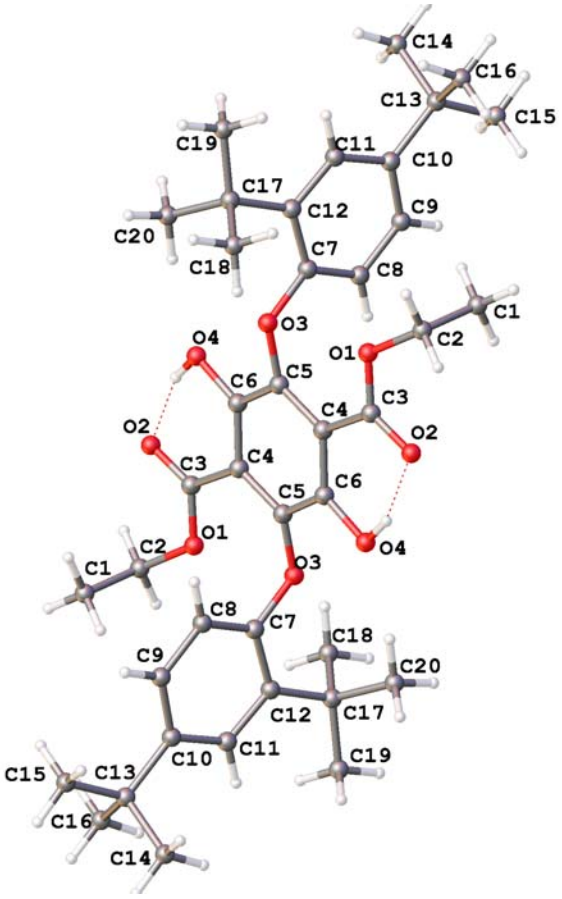


General procedure for synthesis of 3a-e

2c (2.00 g, 3.0 mmol), zinc powder (0.50 g, excess) and acetic acid (75 mL) was charged to a 100 mL round bottomed flask and the reaction mixture was placed in a sonicator for 60 minutes. The red/brown suspension quickly turned to a clear yellow solution with a zinc precipitate. Product was extracted using DCM (100 mL) and (water 3 x 150 mL). The organic phase was dried over $MgSO_4$, which was filtered and the cake washed with DCM (as required). The solvent was removed under reduced pressure giving a yellow solid (2.00 g, 3.0 mmol, 100 %).

^{1}H NMR ($CDCl_3$, 75 MHz): δ = 10.57 (s, 1H) 10.55 (s, 1H) 7.53 (t, *J* = 2.2 Hz, 2H) 6.95 (dq, *J* = 5.9, 2.9, 2.4 Hz, 2H) 6.57 (d, *J* = 8.4 Hz, 1H) 6.35 (d, *J* = 8.5 Hz, 1H) 3.90 – 3.75 (m, 2H) 3.74 – 3.63 (m, 2H) 1.72 (s, 9H) 1.72 (s, 9H) 1.26 (s, 9H) 1.25 (s, 9H) (t, *J* = 7.1 Hz, 3H)
^{13}C NMR (d_8-toluene, 296 K, 125.765 MHz): δ = 168.9, 155.4, 147.3, 143.5, 138.7, 136.0, 123.8, 123.3, 115.0, 112.6, 61.9, 35.2, 34.1, 31.4, 30.2, 12.9.
MP = 166^{o}C
MS – calc. for $C_{40}H_{54}O_8$ = 662.9 fnd. 663 [M^+]
IR – 2979, 1667, 1193 cm^{-1}.

Crystal structure for **3a**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C15
C19
C11
C10
C17
C12
C9
C20
C7
C18
C8
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O4
O1
C2
C6
C5
C3
C4
O2
O2
C3
C4
C5
C6
O1
O4
C2
C1
O3
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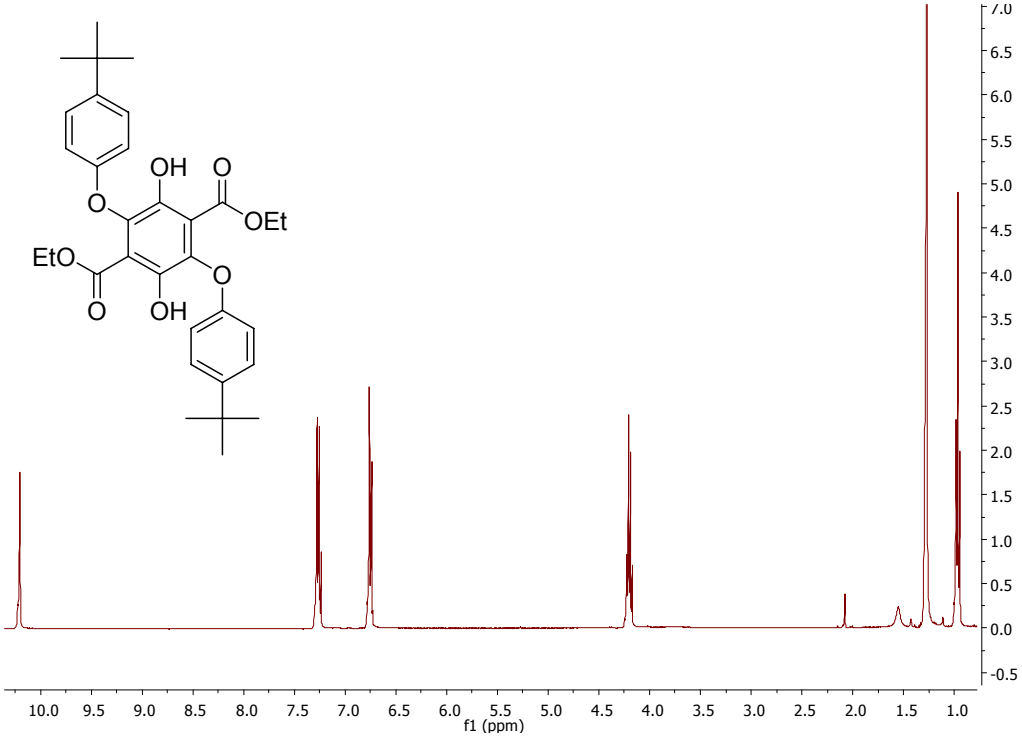
C11
C19
C15
C13
C16
C14

3b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f1 (ppm)
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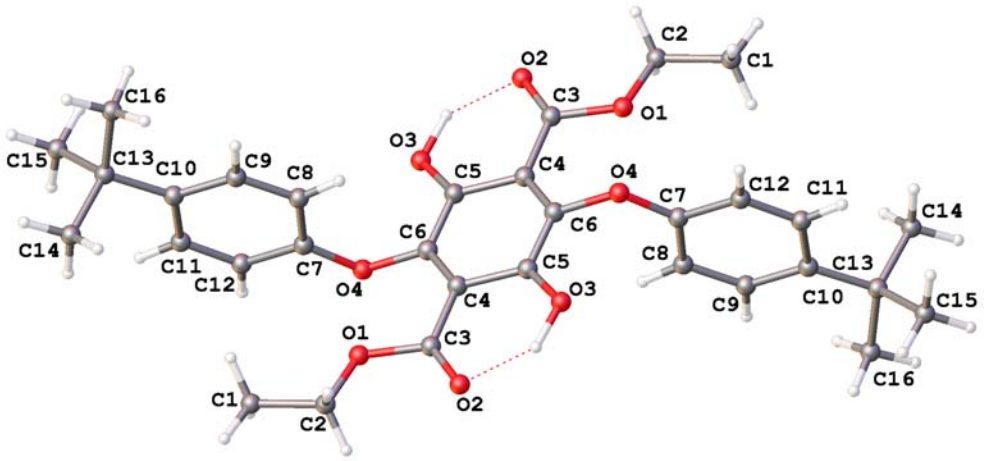
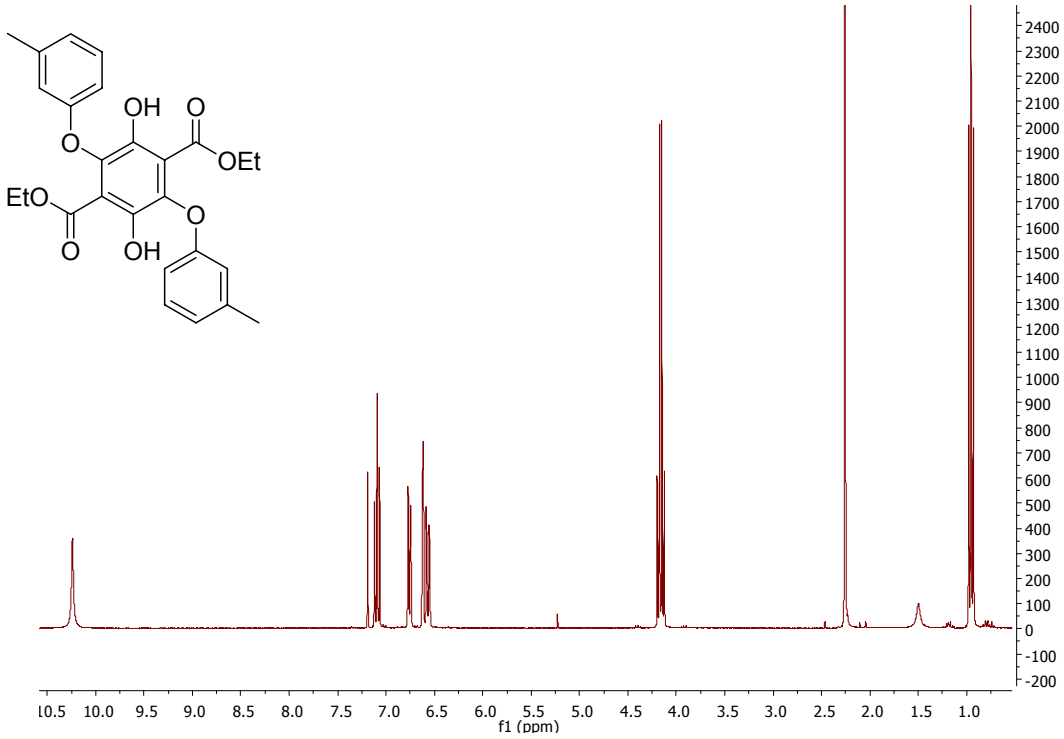
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

Yield = 100 %

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 10.21 (s, 2H), 7.27 (d, *J* = 8.8 Hz, 4H), 6.75 (d, *J* = 8.9 Hz, 4H), 4.20 (q, *J* = 7.1 Hz, 4H), 1.27 (s, 18H), 0.96 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.5, 156.1, 147.2, 144.7, 138.7, 126.3, 114.8, 113.9, 62.6, 34.2, 31.6, 13.4.
MP = 175°C
IR – 2961, 1165, 1194 cm^{-1}.

Crystal structure for **3b**.



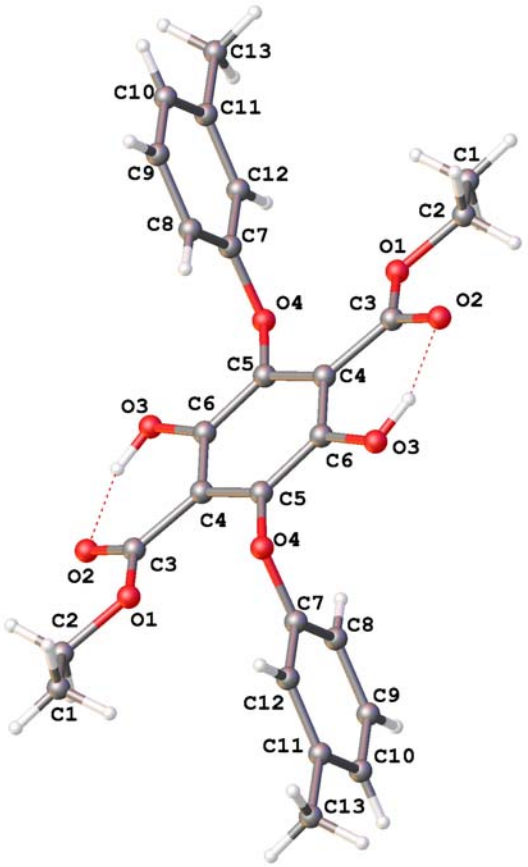


3c

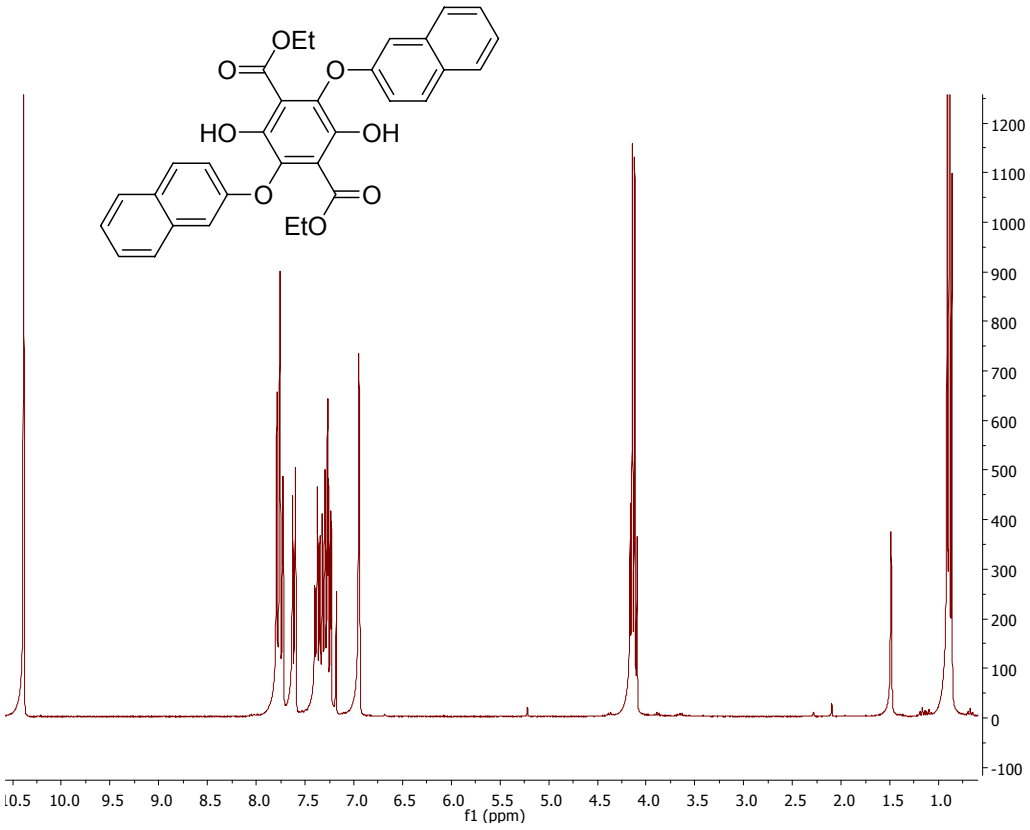
Yield = 100 %

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 10.24 (s, 2H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 7.7 Hz, 2H), 6.62 (s, 2H), 6.57 (dd, *J* = 8.1, 2.2 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 4H), 2.26 (s, 6H), 0.95 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.6, 158.3, 147.2, 139.7, 138.7, 129.2, 122.9, 115.4, 114.8, 111.6.
MP = 156 ^{o}C

Crystal structure for **3c**.



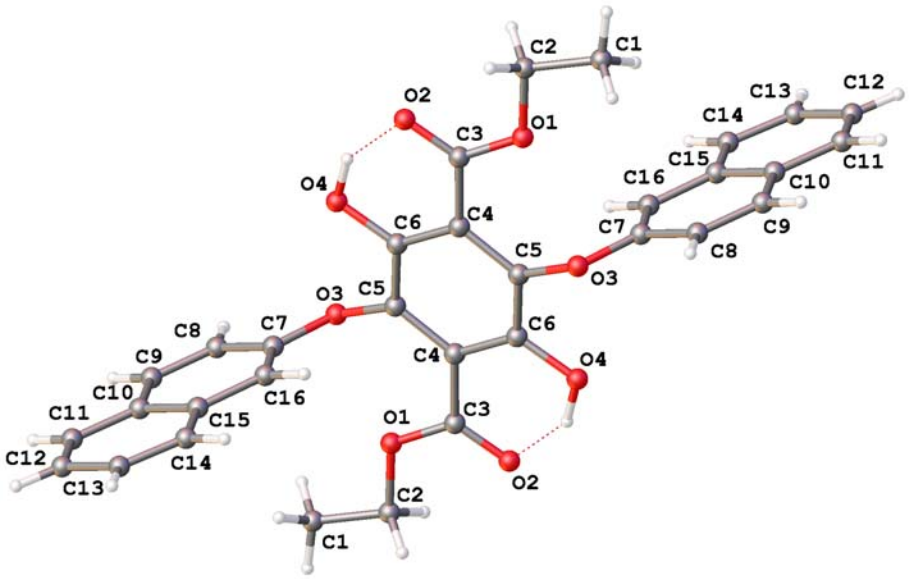
3d



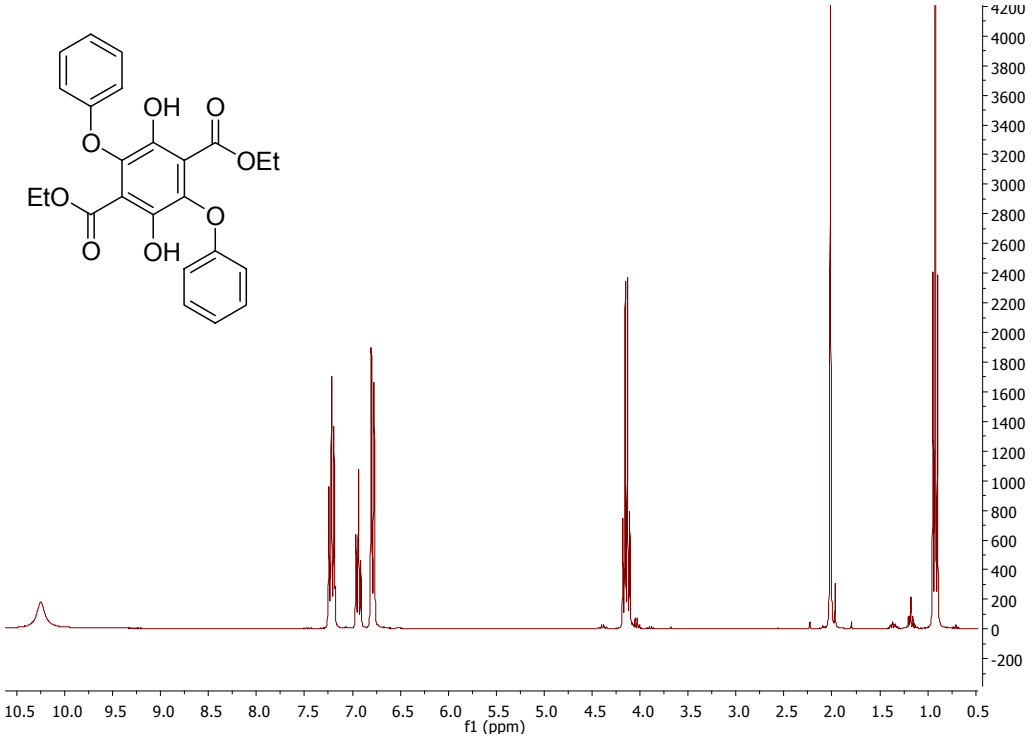
Yield = 95 %

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 10.39 (s, 2H), 7.76 (t, *J* = 9.3 Hz, 4H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.33 (m, 2H), 7.33 – 7.22 (m, 4H), 6.95 (d, *J* = 2.6 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 4H), 0.89 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) : δ = 168.6, 156.3, 147.4, 138.9, 134.3, 129.8, 129.7, 127.8, 127.0, 126.6, 124.2, 117.5, 114.8, 108.7, 62.7, 13.6.
MP = 192 ^{o}C
IR – 2980, 1665, 1186 cm^{-1}

Crystal structure for **3d**.

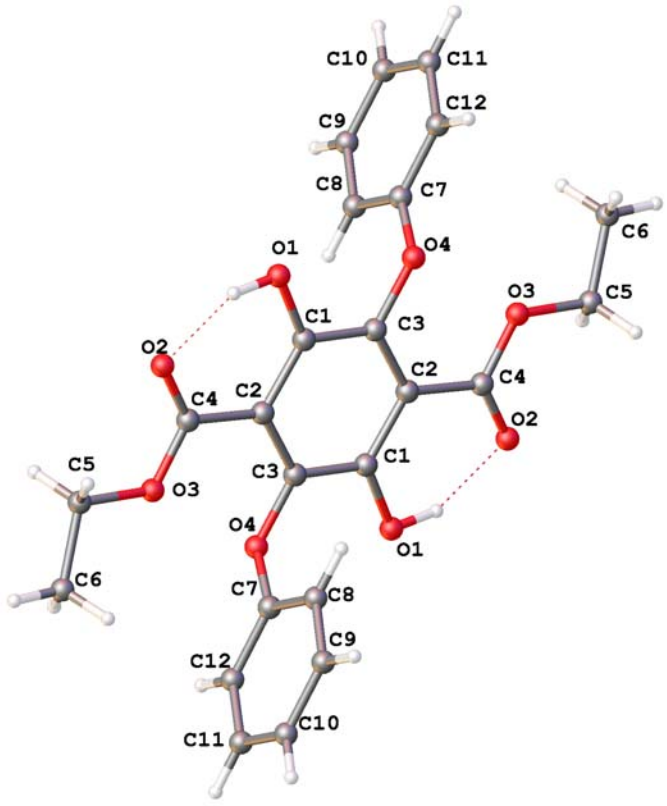


3e



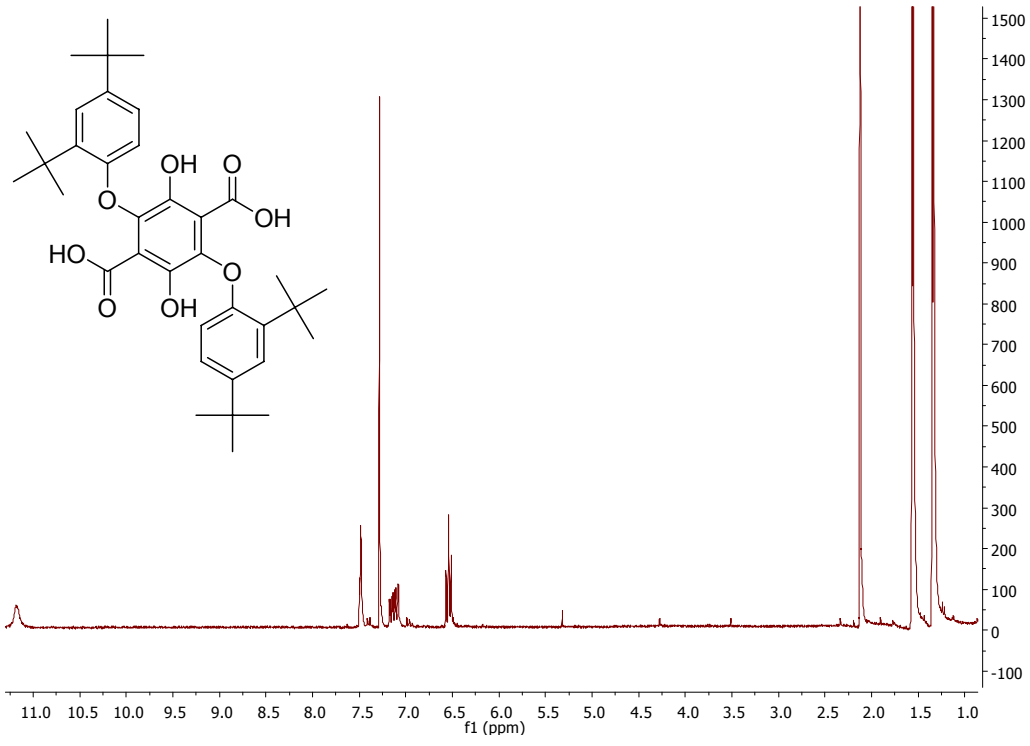
Yield = 100%
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 10.25 (s, 2H), 7.22 (dt, *J* = 7.2, 1.4 Hz, 4H), 6.94 (t, *J* = 7.3 Hz, 2H), 6.79 (d, *J* = 7.6 Hz, 4H), 4.14 (q, *J* = 7.1 Hz, 4H), 0.92 (t, *J* = 7.1 Hz, 6H)
^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.6, 168.5, 158.3, 147.2, 138.6, 129.5, 122.0, 114.7, 62.7, 13.5.
MP = 176 ^{o}C
IR = 3077, 2980, 1658, 1206

Crystal structure for **3e**.



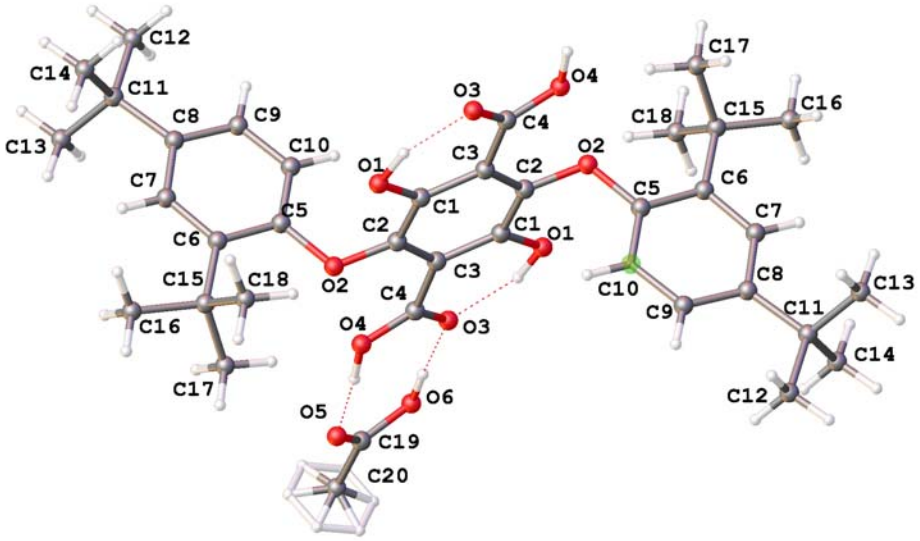
General procedure to make **4a-b**

4a

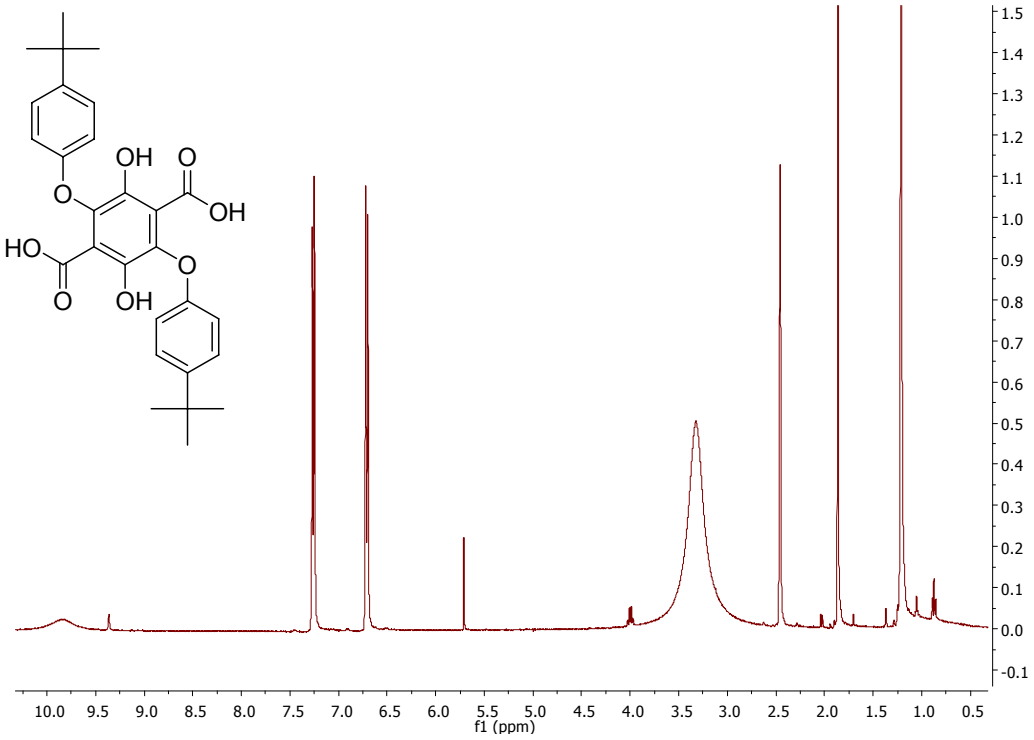


3a (2.0 g, 3.0 mmol), ethanol (0.5 mL) and 10% KOH (50 mL) was charged to a 100 mL round bottomed flask and the reaction mixture was heated at reflux for 24 hours. The yellow suspension changed colour to a dark red solution upon heating. The reaction mixture was removed from the heat source and allowed to cool to RT. Once at RT HCl was added to the reaction mixture until the pH was acidic. Once acidic the product crashed out of solution as a yellow solid. The product was filtered off and washed with water and air dried. The solid was recrystallized from acetic acid to give yellow needle-like crystals (0.5 g, 0.77 mmol, 25 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 11.17 (s, 2H), 7.49 (m, 2H), 7.15 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.10 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.55 (d, *J* = 8.2 Hz, 1H), 6.53 (d, *J* = 8.3 Hz, 1H), 1.56 (s, 9H), 1.55 (s, 9H), 1.35 (s, 9H), 1.33 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.8, 168.8, 153.0, 147.1, 145.9, 138.6, 137.2, 125.1, 124.1, 114.0, 35.2, 34.6, 31.5, 30.5.
MP = >250^{o}C
MS – calc. for $C_{36}H_{46}O_8$ = 606.8 fnd. 605 $(M-H)^-$
IR – 2962, 1652, 1191 cm^{-1}
Crystal structure for **4a**.

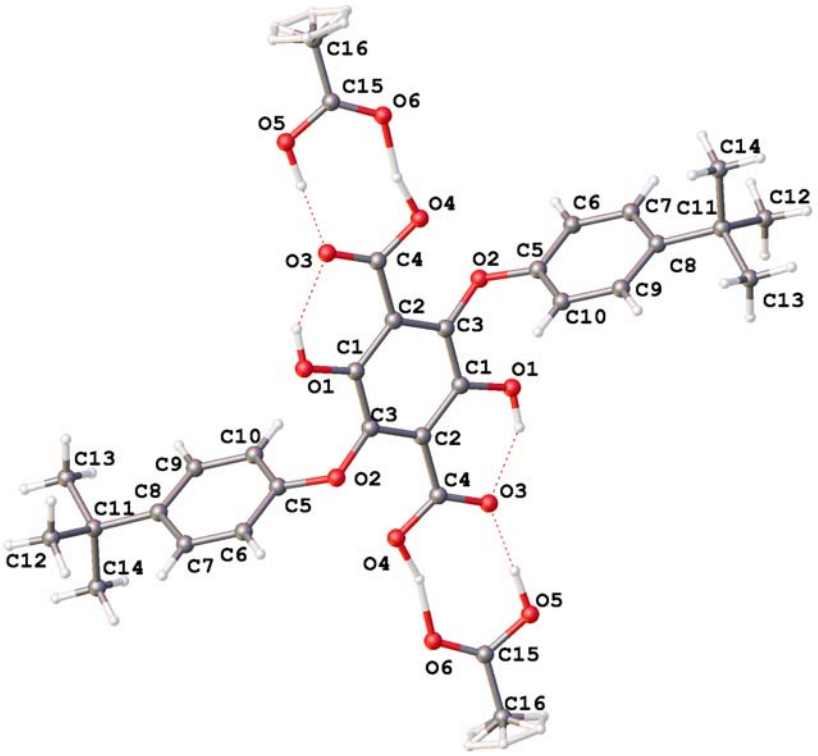


4b

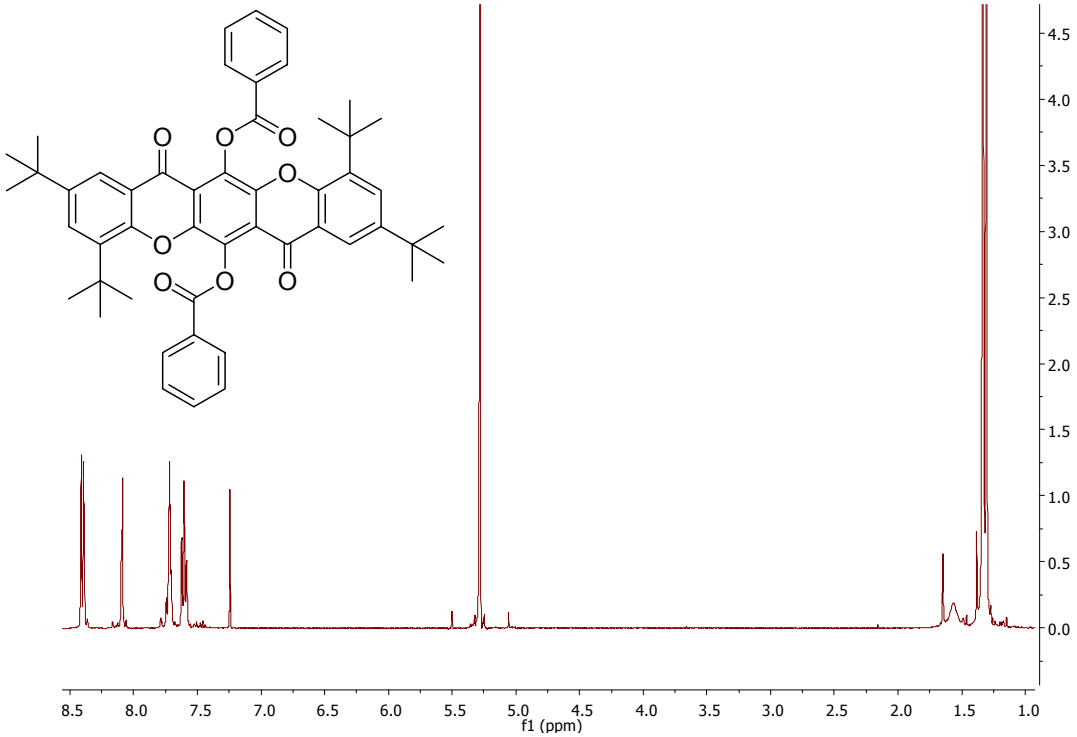


Yield = 60%

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.82 (brs, 2H), 7.26 (dd, *J* = 8.8, 2.0 Hz, 4H), 6.71 (dd, *J* = 8.7, 2.0 Hz, 4H), 2.46 (s, 2H), 1.21 (s, 18H)
^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.4, 156.3, 144.4, 142.7, 137.4, 126.5, 120.1, 115.1, 34.4, 31.9.
MP = >250^{o}C
MS – calc. for $C_{28}H_{30}O_8$ = 494.5 fnd. 493 $(M-H)^-$
IR – 2969, 2538, 1690, 1190 cm^{-1}
Crystal structure for **4b**.

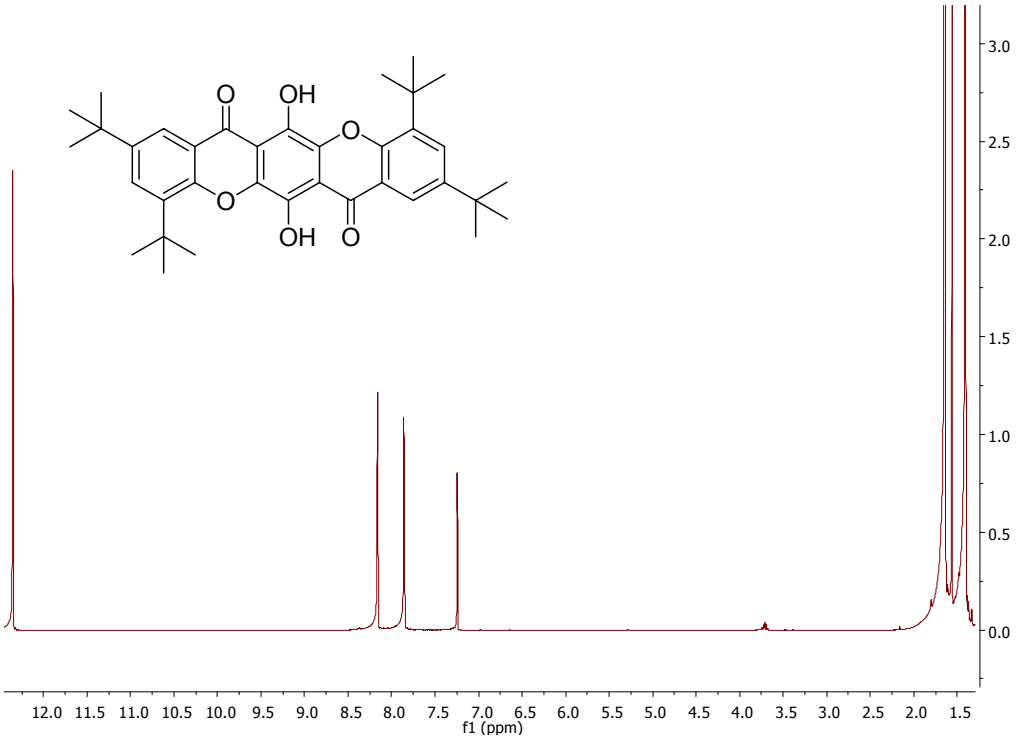

C16
C15
O6
O5
O4
O3
C4
C2
C3
C1
O1
O2
C5
C6
C7
C11
C14
C12
C8
C9
C10
C13

5a


O
O
O
O
O
O
O
O
O
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

4a (1.54 g, 2.5 mmol), benzoyl chloride (10 mL) and H_2SO_4 (1 drop) were charged to a 100 mL round bottomed flask and the reaction mixture was heated at reflux for 1 hour. The yellow solution changed colour to brown upon heating. The reaction mixture was removed from the heat source and allowed to cool to RT. Once at RT, water (50 mL) was added and the reaction heated at reflux for 30 minutes. After this time the reaction was allowed to cool to RT. Once cool a yellow/ brown precipitate formed. This was filtered off and washed with water, ethanol and ether. The yellow solid was crystallised via slow vapour diffusion (chloroform/ petrol ether) to give yellow needle-like crystals (1.59 g, 1.8 mmol, 72 %).
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.40 (d, *J* = 7.6 Hz, 4H), 8.10 – 8.07 (m, 2H), 7.74 – 7.69 (m, 4H), 7.60 (t, *J* = 7.5 Hz, 4H), 1.34 - 1.33 (m, 18H), 1.31 – 1.30 (m, 18H)
^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.1, 165.0, 164.6, 152.5, 146.9, 143.7, 138.3, 135.9, 134.0, 133.9, 130.9, 129.2, 129.1, 128.8, 128.8, 121.7, 120.9, 118.8, 53.5, 35.2, 35.0, 31.4, 29.7.
MP = >250^{o}C
MS – calc. for $C_{50}H_{50}O_8$ = 778.9 fnd. 779 (M^+)
IR – 2961, 1739, 1228

6a



5a (1.50 g, 1.8 mmol) and aniline (15 mL) were charged to a 100 mL round bottomed flask and the reaction mixture was heated at reflux for 2 hours. The yellow/ orange solution changed colour to a dark red solution upon heating. The reaction mixture was removed from the heat source and allowed to cool to RT. Once at RT, ethanol (50 mL) was added and the reaction heated at reflux for a further hour. After this time the reaction was allowed to cool to RT. Once at RT, water was added to the mixture forming a red precipitate. The precipitate was filtered off and washed with water and air dried. The solid was dissolved in DCM and dried over $MgSO_4$. The slurry was filtered and the solvent removed under reduced pressure. The red solid was recrystallized from ethanol to give red crystals (0.98 g, 1.7 mmol, 95 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 12.35 (s, 2H), 8.16 (d, *J* = 2.4 Hz, 2H), 7.85 (d, *J* = 2.3 Hz, 2H), 1.64 (s, 18H), 1.40 (s, 18H)
^{13}C NMR (75 MHz, $CDCl_3$): δ = 183.6, 153.8, 146.7, 140.2, 139.2, 136.8, 131.8, 129.4, 119.9, 119.7, 118.6, 115.2, 112.0, 35.7, 35.1, 31.4, 29.9.
MP = >250^{o}C
MS – calc. for $C_{36}H_{42}O_6$ = 570.7 fnd. 571 (M^+)
IR – 2956, 1652, 1475.

Crystal structure for **6a**.