$O^{(-)}$---C Interactions and Bond Formation in 1-Naphtholate Anions with *Peri*-Located Electrophilic Carbon Centres.

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Supporting Information.

Synthetic Chemistry……. p S2-S17

X-ray Crystallography……. p S18-S24

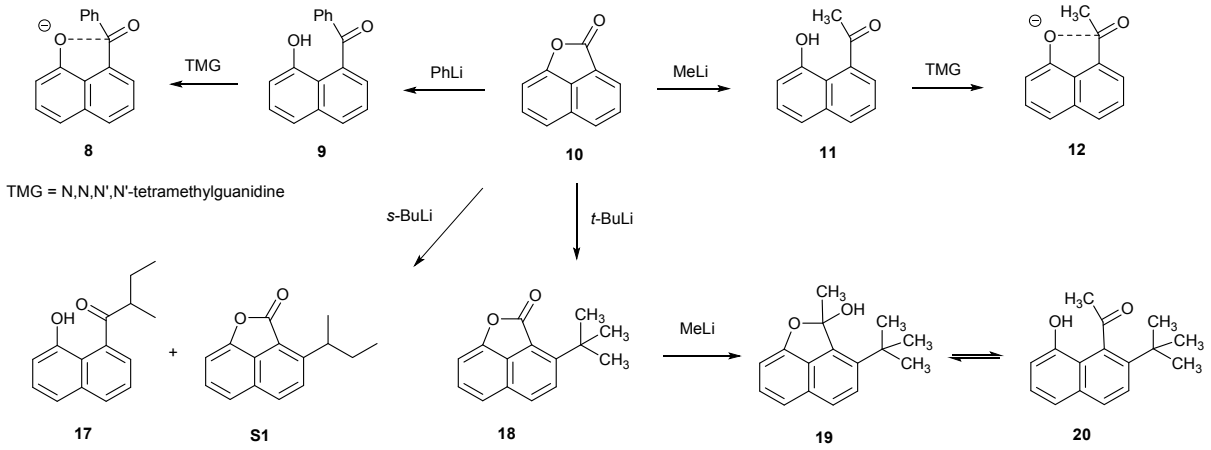
Calculations……... p S25-S26

References…….. p S27

Synthetic Chemistry.

Synthesis and molecular structures of hindered lactone 18 and lactol 19.

Reaction with phenyl lithium gave the phenyl ketone **9**, and with methyl lithium gave the methyl ketone **11** along with the dimethylated alcohol formed by a second addition of methyl lithium. In contrast, *t*-butyl lithium did not give the expected ketone but added to the ring carbon *ortho* to the carbonyl group to give, after oxidation in the air, the hindered lactone



Scheme S1.

18 in 14% yield as the only isolated product (Scheme S1). Protonation of the initial addition product, rather than oxidation, is disfavoured by the strain this would bring to the lactone ring. The structure of the product was confirmed by X-ray crystallography and is shown in Fig. S1. Steric pressure between the *t*-butyl and lactone groups has displaced the groups apart from their expected positions[S1] by (1.5-2°) so that the two shortest O---H-C contacts between the carbonyl and *t*-butyl groups are 2.42 Å. Reaction of *sec*-butyl-lithium with lactone **10** gave a mixture of the ring-opened ketone **17** and the *ortho* substitution product **S1**.

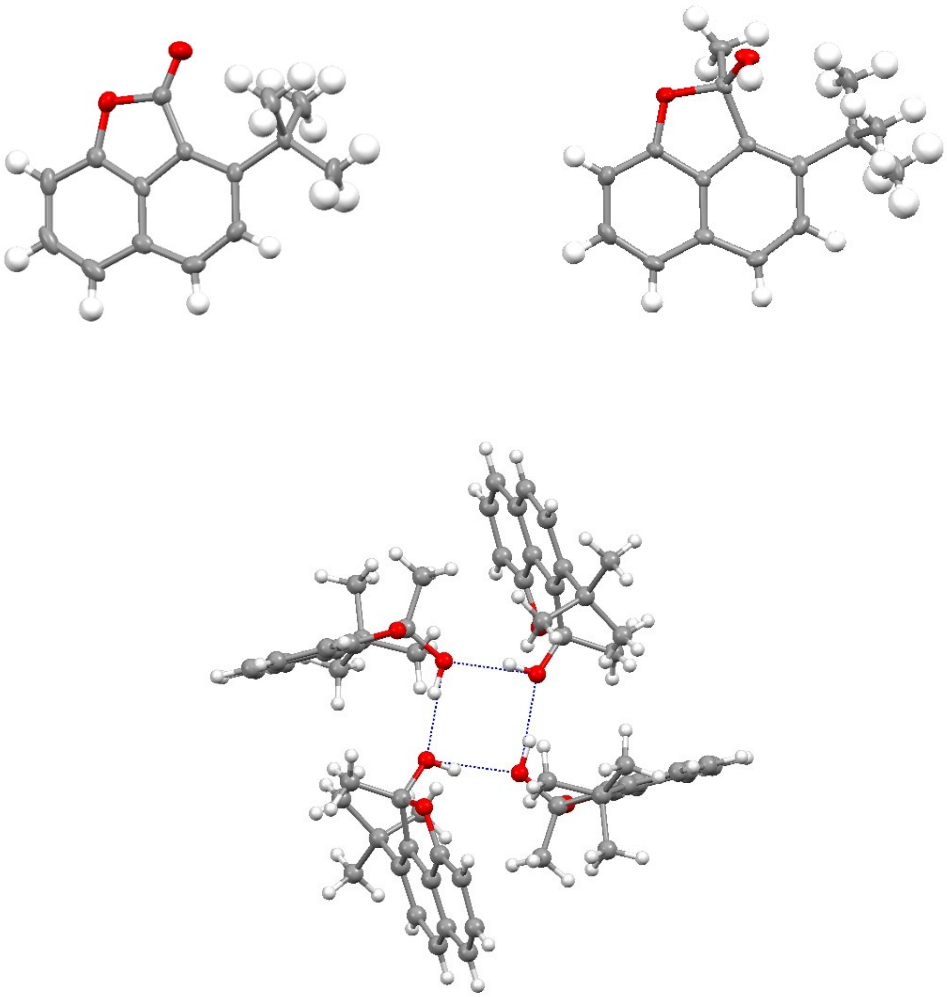


Figure S1. Molecular structures of the hindered lactone **18** (top left), one of the two crystallographically unique molecules of the lactol **19** formed from **18** with methyl lithium (top right), and the crystal packing arrangement for lactol **19** (bottom) in which four molecules are linked together by hydrogen bonds.

The *ortho* t-butyl substituted lactone **18** reacted with methyl lithium to give the lactol **19** in 75% yield, rather than the corresponding ring opened methyl ketone **20**. The ^{13}C NMR shows a resonance at δ_C: 114.5 for the hemi-ketal carbon, and no carbonyl resonance is observed. The product's structure was confirmed by X-ray crystallography (Fig. S1); by adopting the lactol structure rather than the ring-opened ketone, steric pressure with the *t*-butyl group is reduced. There are two crystallographically unique molecules of **18**, one of which has a disordered *t*-butyl group, though the overall molecular geometries are very similar. In the ordered molecule the *t*-butyl group is oriented so that two methyl groups lie to either side of the lactone. In both molecules the *t*-butyl group is bent away in-plane from the lactol by 4.9 and 5.1°, and the lactol is compressed so that the exocyclic angle at the naphthalene skeleton is widened to 136.0° and 136.2°. There is an anomeric effect between the exocyclic OH group

and the ring C-O bond, so that the C-OH bond is shortened to 1.394-1.399 Å, the ring O-C bond is lengthened to 1.480-1.485 Å, and the C(aryl)-C-CH_3 angles at the anomeric centres are widened to 119.4 and 116.3° to reduce the steric interaction between t-butyl and methyl groups. In the crystal structure four molecules of lactol **18** are organised in a square by hydrogen bonding between the hydroxyl groups (Fig. S1).

Experimental.

General. Solution NMR spectra were measured on a Jeol ECLIPSE 400 spectrometer at 400 MHz for ^{1}H and at 100.6 MHz for ^{13}C using $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard unless otherwise stated, and measured in p.p.m. downfield from TMS with coupling constants reported in Hz. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer using Attenuated Total Reflection sampling on solids or oils and are reported in cm^{-1}. Mass spectra were recorded at the EPSRC Mass Spectrometry Centre at the University of Swansea. Chemical analysis data were obtained from Mr Stephen Boyer, London Metropolitan University.

NMR of Naphth-1-ol and its Sodium Salt.

Naphth-1-ol: *δH* (400 MHz, THF-d_8, 24 °C): 8.98 (1H, s, O*H*), 8.27 (1H, m, 8-*H*), 7.77 (1H, m, 5-*H*), 7.39-7.46 (2H, m, 6-,7-*H*), 7.34 (1H, d, J = 7.3 Hz, 4-*H*), 7.27 (1H, t, J = 7.3 Hz, 3-*H*), 6.77 (1H, dd, J = 7.3, 0.9 Hz, 2-*H*); *δC* (100 MHz, THF-d_8, 24 °C): 154.9 (1-*C*), 136.5 (4a-*C*), 128.6 (5-*C*), 127.3 (3-*C*), 127.2 (6-*C*), 126.6 (8a-*C*), 125.5 (7-*C*), 123.6 (8-*C*), 120.1 (4-*C*), 109.1 (2-*C*). Naphth-1-ol, dissolved in THF-d_8, was treated with excess sodium hydride, stirred for 10 min and filtered. *δH* (400 MHz, THF-d_8, 24 °C): 8.48 (1H, d, J = 8.2 Hz, 8-*H*), 7.63 (1H, d, J = 8.2 Hz, 5-*H*), 7.22 (1H, t, J = 8.0 Hz, 6-*H*), 7.18 (1H, t, J = 8.0 Hz, 3-*H*), 7.09 (1H, t, J = 6.9 Hz, 7-*H*), 6.81 (1H, d, J = 7.8 Hz, 4-*H*), 6.61 (1H, d, J = 8.2 Hz, J = 7.8 Hz, 2-*H*); *δC* (100 MHz, THF-d_8, 24 °C): 168.8 (1-*C*), 138.0 (4a-*C*), 132.0 (8a-*C*), 129.4 (3-*C*), 128.8 (5-*C*), 125.8 (6-*C*), 124.2 (8-*C*), 123.2 (7-*C*), 111.7 (4-*C*), 110.9 (2-*C*).

Reaction of Naphth-1-ol with 1-,1-,3-,3-Tetramethylguanidine.

Naphth-1-ol (35 mg), dissolved in THF-d_8, was treated with TMG (28 mg), *δH* (400 MHz, THF-d_8, 24 °C): 8.40 (2H, br, 1-O*H*, TMG: N*H*), 8.29 (1H, d, J = 7.2 Hz, 8-*H*), 7.66 (1H, d, J = 7.3 Hz, 5-*H*), 7.26-7.34 (2H, m, 6-,7-*H*), 7.11-7.18 (2H, m, 3-,4-*H*), 6.85 (1H, dd, J = 6.9,

1.4 Hz, 2-*H*), 2.69 (12H, s, TMG: 4 x CH_3); *δC* (100 MHz, THF-d_8, 24 °C): 167.4 (TMG: -*C*=NH), 157.5 (1-*C*), 136.2 (4a-*C*), 127.9 (5-*C*), 127.5 (8a-*C*), 127.2 (3-*C*), 126.1 (6-*C*), 124.0 (7-*C*), 123.9 (8-*C*), 117.1 (4-*C*), 108.8 (2-*C*), 39.4 (TMG-H^+: 4 x CH_3), corresponds to *ca*. 20% deprotonation of naphthol by TMG.

8-Benzoylnaphth-1-ol, 9.

Lactone **10**[S2] (1.00 g, 5.88 mmol) was dissolved in anhydrous THF (15 mL) under nitrogen and cooled to -78℃. Phenyl lithium (1.8M in dibutyl ether, 2.61 mL, 4.71 mmol) was steadily added and the bright orange solution was allowed to warm to room temperature overnight. After 16 h. the resulting dark yellow solution was quenched with EtOAc (10 mL) and H_2O added. The aqueous solution was washed with DCM (3 x 40 mL) and the combined organic layers washed with H_2O (2 x 40 mL), brine (1 x 40 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to give a crude oil which was purified by flash column chromatography (1:4 EtOAc/petrol 40-60), to give **9** as a brown solid (370 mg, 32%) m.p. 183-185℃ (lit.[S3] 184-187 °C). δH (400 MHz, $CDCl_3$, 24 °C): 8.01 (1H, d, J = 7.8 Hz, 7-*H*), 7.81 (2H, d, J = 8.2 Hz, 2'-,6'-*H*), 7.58 (1H, t, J = 8.7 Hz, 4'-*H*), 7.50 - 7.55 (2H, m, 4-,5-*H*), 7.38 - 7.49 (4H, m, 3-,6-,3'-,5'-*H*), 7.12 (1H, br s, O*H*), 6.99 (1H, d, J = 7.8 Hz, 2-*H*); δC (100 MHz, $CDCl_3$, 24 °C): 201.7 (C=O), 152.3 (1-*C*), 138.5 (1'-*C*), 135.6, 134.6 (Ar-C_2), 133.1 (4'-*C*), 132.4 (Ar-C_1), 130.5 (2'-,6'-*C*), 129.9 (Ar-C_1), 128.3 (3'-,5'-*C*), 127.4, 124.2, 122.0, 121.5 (Ar-C_4), 113.7 (2-*C*); ν_{max}/cm^{-1} 3050 (OH), 1638 (C=O), 1574, 1432, 1345, 1270; *HRMS* (ESI) calcd for $C_{17}H_{13}O_2$ ($[M+H]^+$): 249.0910, found: 249.0912.

Sodium 8-benzoylnaphth-1-olate, Na^+.8.

8-Benzoylnaphth-1-ol (25 mg) was dissolved in THF (3 mL) and the solution treated with sodium hydride (60% dispersion in oil, *ca*. 4 mg) until there was no more effervescence. After stirring for a further 5 min. the solution was evaporated i*n vacuo*, DMSO-d_6 (1 ml) added, and the solution filtered, and the NMR spectra recorded. δH (400 MHz, DMSO-d_6, 24 °C): 7.49 (1H, d, J = 7.3 Hz, 5-*H*), 7.45 (2H, d, J = 7.6 Hz, 2'-, 6'-*H*), 7.35 (1H, t, J = 6.0 Hz, 4'-*H*), 7.28 (2H, t, J = 7.3 Hz, 3'-,5'-*H*), 7.14 (1H, t, J = 7.0 Hz, 6-*H*), 6.99 (1H, t, J = 8.0 Hz, 3-*H*), 6.65 (1H, dd, J = 6.9, 0.9 Hz, 7-*H*), 6.39 (1H, d, J = 7.3 Hz, 4-*H*), 5.79 (1H, dd, J = 7.8, 0.9 Hz, 2-*H*); δC (100 MHz, DMSO-d_6, 24 °C): 197.8 (*C*=O), 168.3 (1-*C*), 140.6 (1'-*C*), 139.5 (8-*C*), 136.3(4a-*C*), 130.1 (4'-*C*), 129.7 (3-*C*), 129.5 (8a-*C*), 127.5 & 127.4 (2'-,3'-,5'-,6'-*C*), 126.7 (5-*C*), 123.8 (6-*C*), 118.1 (7-*C*), 108.1 (2-*C*), 103.7 (4-*C*).

1-,1-,3-,3-Tetramethylguanidium 8-benzoylnaphth-1-olate, TMG-H$^+$.8.

8-Benzoylnaphth-1-ol (100 mg, 0.42 mmol) was dissolved in chloroform (2 mL) and TMG (0.05 mL, 0.42 mmol) was added. The solvent was removed *in vacuo* and the solid dissolved in DCM. Nitrogen was passed over the surface of the solution, yielding yellow crystals of the salt TMG-H$^+$.**8**, m.p. 100-103℃. δH (400 MHz, DMSO-d_6 24 °C): 7.53 (1H, d, J = 8.2 Hz, 5-*H*), 7.38 (2H, d, J = 7.8 Hz, 2'-,6'-*H*), 7.30 (1H, t, J = 6.8 Hz, 4'-*H*), 7.20 (2H, t, J = 6. Hz, 3'-,5'-*H*), 7.15 (1H, t, J = 7.8 Hz, 6-*H*), 6.81 (1H, t, J = 7.8 Hz, 3-*H*), 6.77 (1H, d, J = 6.9 Hz, 7-*H*), 6.70 (1H, d, J = 8.2 Hz, 4-*H*), 5.67 (1H, d, J = 7.3 Hz, 2-*H*), 2.66 (12H, s, TMG-H$^+$: 4 x CH_3); δC (100 MHz, $CDCl_3$, 24 °C): 197.9 (*C*=O), 163.6 (TMG-H$^+$: *C*=NH_2^+), 161.4 (1-*C*), 139.8 (1'-*C*), 138.3 (8-*C*), 135.4 (4a-*C*), 131.5 (4'-*C*), 128.6 (3-*C*), 128.4 (2'-,6'-*C*), 128.1 (3'-,5'-*C*), 128.0 (5-*C*), 125.6 (8a-*C*), 124.4 (6-*C*), 120.9 (7-*C*), 111.3 (4-*C*), 108.7 (2-*C*), 39.3 (TMG-H$^+$: 4 x *C*H_3); ν_{max}/cm^{-1} 3083, 3083, 2891, 1654 (C=O), 1594, 1568, 1491, 1442, 1385, 1318, 1270, 1106; *HRMS* (ESI): calcd for $C_{17}H_{11}O_2$ ([M-H]$^-$): 247.0765, found: 247.0771.

8-(2'-Methylbutanoyl)naphth-1-ol, 17.

Lactone **10** (1.00 g, 5.88 mmol) was dissolved in anhydrous THF (15 mL) under nitrogen and cooled to -78℃. *sec*-BuLi (1.4M in cyclohexane, 4.20 mL, 5.88 mmol) was steadily added, and the bright orange solution was allowed to warm to room temperature overnight. After 16 h. the resulting dark yellow solution was quenched with EtOAc (10 mL) and H_2O added. The aqueous solution was washed with DCM (3 x 40 mL) and the combined organic layers washed with H_2O (2 x 40 mL), brine (1 x 40 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to give a crude oil which was purified by flash column chromatography (1:19 EtOAc/petrol 40-60), to give **17** as a yellow solid (320 mg, 24%), m.p. 71-74℃. δH (400 MHz, $CDCl_3$, 24 °C): 8.19 (1H, s, O*H*), 8.00 (1H, dd, J = 8.2, 1.4 Hz, 7-*H*), 7.83 (1H, dd, J = 7.3, 0.9 Hz, 5-*H*), 7.42 - 7.52 (3H, m, 3-,4-,6-*H*), 7.11 (1H, dd, J = 7.3, 1.8 Hz, 2-*H*), 3.51 (1H, sxt, J = 6.9 Hz, 2'-*H*), 1.89 (1H, m, 3'-H_α), 1.56 (1H, m, 3'-H_β), 1.28 (3H, d, J = 6.9 Hz, 2'-CH_3), 0.97 (3H, t, J = 7.3 Hz, 4'-H_3); δC (100 MHz, $CDCl_3$, 24 °C): 215.0 (*C*=O), 152.9 (1-*C*), 136.0, 135.7 (Ar-C_2), 134.0 (7-*C*), 129.1, 127.6, 124.0, 121.5, 121.4 (Ar-C_5), 114.9 (2-*C*), 47.0 (2'-*C*), 27.1 (3'-*C*), 17.1 (2'-*C*H_3), 11.8 (4'-*C*); ν_{max}/cm^{-1} 3131 (OH), 3047, 2967, 2931, 1668 (C=O), 1620, 1577, 1523, 1439, 1346, 1239; *HRMS* (ESI): calcd for $C_{15}H_{17}O_2$ ([M+H]$^+$): 229.1223, found: 229.1223. A preceding fraction yielded a small amount (120 mg, 18%) of *3-(sec-butyl)-2H-naphtho[1,8-bc]furan-2-one,* δH (400 MHz, $CDCl_3$, 24 °C): 8.02 (1H, d, J = 8.5 Hz, Ar-*H*), 7.62 (1H, d, J = 8.4 Hz, Ar-*H*), 7.56 (1H, d, J = 8.4 Hz, Ar-*H*), 7.43 (1H, dd, J = 8.4, 7.2 Hz, 7-

H), 7.06 (1H, d, J = 7.3 Hz, 8-*H*), 3.74 (1H, sxt, J = 7.2 Hz, 2'-*H*), 1.72 (1H, quin, J = 7.4 Hz *3'*-H_2), 1.32 (3H, d, J = 7.0 Hz, 2'-CH_3), 0.79 (3H, t, J = 7.3 Hz, 4'-H_3); δC (100 MHz, $CDCl_3$, 24 °C): 167.3 (*C*=O), 151.8 (8a-*C*), 149.5, 132.4, 129.1, 128.2, 128.1, 128.0, 120.5, 117.3, 105.8 (Ar-C_9), 36.3 (2'-*C*), 30.2 (3'-*C*), 20.8 (2'-*C*H_3), 12.1 (4'-*C*).

8-(2'-Methylbutanoyl)naphth-1-ol . 4-Dimethylaminopyridine Molecular Complex, 17.DMAP.

Ketone **17** (63 mg, 0.28 mmol) was dissolved in THF (5 mL), DMAP (33 mg, 0.28 mmol) was added and the reaction stirred for 30 min. at room temperature. The solvent was removed *in vacuo* and the solid dissolved in acetone. The solution was left to evaporate slowly, yielding **17.**DMAP as a brown crystalline solid, m.p. 83-86℃. δH (400 MHz, $CDCl_3$, 24 °C): 8.17 (2H, dd, J = 5.0, 1.4 Hz, DMAP: 2-,6-*H*), 7.80 (1H, d, J = 8.2 Hz, 7-*H*), 7.40 (1H, t, J = 6.9 Hz, 6-*H*), 7.22 - 7.36 (3H, m, 3-,4-,5-*H*), 6.91 (1H, dd, J = 6.9, 1.8 Hz, 2-*H*), 6.49 (2H, dd, J = 5.5, 1.4 Hz, DMAP: 3-,5-*H*), 3.11 - 3.21 (1H, m, 2'-*H*), 2.99 (6H, s, DMAP: N(CH_3)$_2$), 1.77 - 1.90 (1H, m, 3'-H_α), 1.38 - 1.53 (1H, m, 3'-H_β), 1.21 (3H, d, J = 6.9 Hz, 2'-H_3), 0.90 (3H, t, J = 7.3 Hz, 4'-H_3); δC (100 MHz, $CDCl_3$, 24 °C): 212.3 (*C*=O), 154.7 & 154.4 (1-*C*, DMAP: 4-*C*) 148.3 (DMAP: 2-,6-*C*), 138.5, 135.5 (Ar-C_2), 129.5 (7-*C*), 127.2, 124.9, 124.1, 122.5, 118.8 (Ar-C_5), 110.4 (2-*C*), 106.7 (DMAP: 3-,5-*C*), 48.4 (2-*C*), 39.2 (DMAP, N(*C*H_3)$_2$), 25.8 (3'-*C*), 15.6 (2'-*C*H_3), 11.6 (4'-*C*); ν_{max}/cm^{-1} 2913, 2450, 1681 (C=O), 1602, 1526, 1445, 1343, 1223.

8-Acetylnaphth-1-ol, 11.

Lactone **10** (1.00 g, 5.88 mmol) was dissolved in anhydrous THF (15 mL) under nitrogen and cooled to -78℃. MeLi (1.6M in diethyl ether, 2.94 mL, 4.71 mmol) was steadily added, and the bright orange solution was kept at -78 °C for 1 h. The resulting yellow solution was quenched with saturated ammonium chloride (10 mL) and acidified with 1M aqueous hydrochloric acid. The aqueous solution was washed with ethyl acetate (3 x 40 mL) and the combined organic layers washed with H_2O (2 x 40 mL), brine (1 x 40 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to give a crude oil which was purified by flash column chromatography (1:9 EtOAc/petrol 40-60), to give **11** as a yellow solid (460 mg, 42%), %), m.p. 82-84 °C (lit.[S3] 81-83 °C). δH (400 MHz, $CDCl_3$, 24 °C): 9.67 (1H, s, O*H*), 8.00 (1H, dd, J = 8.2, 0.9 Hz, 5-*H*) 7.96 (1H, dd, J = 7.3, 0.9 Hz, 7-*H*), 7.41 - 7.45 (3H, m, 3-,4-,6-*H*), 7.10 (1H, dd, J = 6.0, 2.7 Hz, 2-*H*), 2.78 (3H, s, CH_3)*;* δC (100 MHz, $CDCl_3$, 24 °C): 207.3 (*C*=O), 153.3 (1-*C*), 136.1 (4a-*C*), 135.4 (5-*C*), 135.0 (8-*C*), 131.3 (7-*C*), 127.9 & 124.0 (3-,6-*C*), 121.3 (8a-*C*), 121.1 (4-*C*), 115.0 (2-*C*), 30.5 (*C*H_3); ν_{max}/cm^{-1} 3114 br, 3056, 2959, 1671

(C=O), 1620, 1577, 1522, 1438, 1346, 1292, 1257, 1189, 1165, 1142, 1091, 946, 821, 790. Found: C, 77.48; H, 5.47. Calc. for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41%.

Sodium 8-acetylnaphth-1-olate, Na^+.12.

8-Acetylnaphth-1-ol (20 mg) was dissolved in THF (4 ml) and the solution treated with sodium hydride (60% dispersion in oil, *ca*. 4.5 mg) until there was no more effervescence. After stirring for a further 5 min. the solution was evaporated i*n vacuo*, THF-d_8 (1 ml) added, and the solution filtered, and the NMR spectra recorded. δH (400 MHz, THF-d_8, 24 °C): 7.49 (1H, d, J = 8.2 Hz, 5-*H*), 7.06 (1H, t, J = 7.8 Hz, 3-*H*), 7.09 (1H, t, J = 7.3 Hz, 6-*H*), 6.71 (1H, d, J = 6.9 Hz, 7-*H*), 6.63 (1H, d, J = 8.2 Hz, 4-*H*), 6.29 (1H, d, J = 7.8 Hz, 2-*H*), 2.54 (3H, s, CH_3); δC (100 MHz, THF-d_8, 24 °C): 213.5 (*C*=O), 168.2 (1-*C*), 142.7 (8-*C*), 137.6 (4a-*C*), 129.9 (3-*C*), 128.3 (5-*C*), 128.2 (8a-*C*), 124.2 (6-*C*), 117.1 (7-*C*), 110.7 (2-*C*), 109.0 (4-*C*), 33.6 (*C*H_3).

8-Acetylnaphth-1-ol . 4-Dimethylaminopyridine Molecular Complex, 11.DMAP.

8-Acetylnaphth-1-ol (32 mg, 0.17 mmol) was dissolved in THF (3 mL), DMAP (22 mg, 0.17 mmol) was added and the reaction stirred for 30 min. at room temperature. The solvent was removed *in vacuo* and the solid dissolved in DCM. The solution was left to evaporate slowly, yielding **11.**DMAP as a brown crystalline solid, m.p. 110-112℃. δH (400 MHz, $CDCl_3$, 24 °C): 8.08 (2H, dd, J = 5.0, 1.4 Hz, DMAP: 2-,6-*H*), 7.75 (1H, m, 7-*H*), 7.29-7.34 (2H, m, 5-,6-*H*), 7.22 - 7.27 (2H, m, 3-,4-*H*), 7.17 (1H, br s, O), 6.87 (1H, dd, J = 5.5, 2.7 Hz, 2-*H*), 6.40 (2H, dd, J = 5.0, 1.4 Hz, DMAP: 3-,5-*H*), 2.90 (6H, s, DMAP: N(CH_3)$_2$), 2.58 (3H, s, CH_3); δC (100 MHz, $CDCl_3$, 24 °C): 206.0 (*C*=O), 154.6 & 154.2 (1-*C*, DMAP-H^+: 4-*C*), 148.0 (DMAP: 2-,6-*C*), 135.4, 138.6 (Ar-C_2), 130.6 (7-*C*), 127.4, 124.8, 124.2, 121.8, 118.9 (Ar-C_5), 111.1 (2-*C*), 106.6 (DMAP: 3-,5-*C*), 39.0 (DMAP: N(*C*H_3)$_2$), 31.8 (*C*H_3); ν_{max}/cm^{-1} 2921, 2345 br, 1687 (C=O), 1604, 1567, 1528, 1437, 1345, 1255, 1223, 1186, 1062, 1001, 808, 781, 750.

1-,1-,3-,3-Tetramethylguanidinium 8-acetylnaphth-1-olate, TMG-H^+.12.

8-Acetylnaphth-1-ol **11** (250 mg, 1.34 mmol) was dissolved in THF (5 mL) and 1, 1, 3, 3-tetramethylguanidine (0.17 mL, 1.34 mmol) was added. Nitrogen was passed over the surface of the solution, yielding a bright yellow oil. Maintenance of the oil under nitrogen eventually yielded yellow crystals of the salt, TMG-H^+**.12**, m.p. 88-90 °C. δH (400 MHz, $CDCl_3$, 24 °C): 7.64-7.74 (3H, m (d + br s), 7-*H*, TMG-H^+: NH_2), 7.25-7.31 (2H, m, 3-,6-*H*), 7.08 (1H, d, J = 7.3 Hz), & 7.00 (1H, dd, J = 6.9, 1.4 Hz) (4-,5-*H*), 6.80 (1H, dd, J = 7.3, 0.9 Hz, 2-*H*), 2.70

(12H, s, TMG-H^+: 4 x CH_3), 2.57 (3H, s, CH_3); δC (100 MHz, $CDCl_3$, 24 °C): 208.6 (*C*=O), 166.1 (TMG-H^+: *C*=N), 158.8 (1-*C*), 140.6, 135.5 (Ar-C_2), 128.5 (7-*C*), 128.1, 128.0, 124.5, 120.0, 114.4 (Ar-C_5), 110.2 (2-*C*), 39.2 (TMG-H^+: 4 x *C*H_3), 32.9 (-*C*H_3); ν_{max}/cm^{-1} 3319, 3020, 2940 br, 2906, 1676 (C=O), 1594, 1560, 1445, 1407, 1379, 1348, 1315, 1259, 1093, 1061, 1033, 944, 821, 760.

3-(*t*-Butyl)-2H-naphtho[1,8-bc]furan-2-one, 18.

Lactone **10** (0.75 g, 4.41 mmol) was dissolved in anhydrous THF (15 mL) under nitrogen and cooled to -78℃ (CO_2/acetone bath). *t*-BuLi (1.6M in pentane, 2.75 mL, 4.41 mmol) was steadily added, and the bright orange solution was allowed to warm to room temperature. After 72 h. the resulting dark brown solution was quenched with EtOAc (10 mL) and H_2O (5 mL) added. The aqueous solution was washed with DCM (3 x 40 mL) and the combined organic layers washed with H_2O (2 x 40 mL), brine (1 x 40 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to give a crude oil which was purified by flash column chromatography (1:49 EtOAc/petrol 40-60), to give **18** as a light brown solid (140 mg, 14%) m.p. 106-109℃. δH (400 MHz, $CDCl_3$, 24 °C): 8.08 (1H, d, J = 8.6 Hz, 4-*H*), 7.83 (1H, d, J = 8.6 Hz, 5-*H*), 7.61 (1H, d, J = 8.4 Hz, 6-*H*), 7.49 (1H, dd, J = 8.4, 7.3 Hz, 7-*H*), 7.12 (1H, d, J = 7.3 Hz, 8-*H*), 1.60 (9H, s, 3 x CH_3); δC (100 MHz, $CDCl_3$, 24 °C): 167.1 (*C*=O), 155.8 (8a-*C*), 149.7 (Ar-C_1), 132.7 (4-*C*), 130.4, 128.5 (Ar-C_2), 127.9 (5-,7-*C*), 120.5 (6-*C*), 117.8 (Ar-C_1), 105.4 (8-*C*), 36.3 (*C*$(CH_3)_3$), 29.6 (C(*C*$H_3)_3$); ν_{max}/cm^{-1} 2958, 2870, 1768 (C=O), 1748, 1461, 1361. Found: C, 79.84; H, 6.33. Calc. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24%.

3-(*tert*-Butyl)-2-methyl-2H-naphtho[1,8-bc]furan-2-ol, 19.

Ortho-substituted lactone **18** (75 mg, 0.33 mmol) was dissolved in anhydrous THF (5 mL) under nitrogen and cooled to -78℃. MeLi (1.2M in diethyl ether, 0.33 mL, 0.39 mmol) was steadily added, and the reaction was allowed to warm to room temperature overnight. After 24 h. the resulting solution was quenched with EtOAc (10 mL) and H_2O (5 mL) added. The aqueous solution was washed with DCM (3 x 40 mL) and the combined organic layers washed with H_2O (2 x 40 mL), brine (1 x 40 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to give a crude oil which was purified by flash column chromatography (1:19 EtOAc/petrol 40-60) to give a pink oil. The oil was heated to 50℃ under a high vacuum for 4 h. and cooled to -20℃ to give **19** as a pink solid (60 mg, 75%), m.p. 108-110℃. δH (400 MHz, $CDCl_3$, 24 °C): 7.67 - 7.75 (2H, m, 4-,5-*H*), 7.36 (1H, t, J = 7.8 Hz, 7-*H*), 7.25 (1H, d, J = 8.2

Hz, 6-*H*), 6.67 (1H, d, J = 7.3 Hz, 8-*H*), 3.65 (1H, br s, O*H*), 2.12 (3H, s, CH_3), 1.55 (9H, s, (CH_3)$_3$); *δC* (100 MHz, $CDCl_3$, 24 °C): 156.4 (8a-*C*), 144.2, 136.2, 130.2 (Ar-C_3), 129.4 (4- or 5-*C*), 128.6 (7-*C*), 127.2 (Ar-C_1), 126.3 (4- or 5-*C*), 115.5 (6-*C*), 114.5 (2-*C*), 101.1 (8-*C*), 36.8 (3-*C*(CH$_3$)$_3$), 33.0 (3-C(*C*H$_3$)$_3$), 28.4 (2-*C*H$_3$); ν_{max}/cm^{-1} 3350 (OH), 2957, 2919, 1688 (w), 1571, 1457, 1364, 1215, 1197, 1161, 1139, 1051, 939, 821, 749; Found: C, 79.16; H, 7.54. Calc. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

3-(*tert*-Butyl)-2-methyl-2H-naphtho[1,8-bc]furan-2-ol. 4-Dimethylamino- pyridine Molecular Complex, 20.DMAP (solid) /19.DMAP (solution).

Lactol **16** (28 mg, 0.12 mmol) was dissolved in DCM (3 mL), DMAP (14 mg, 0.12 mmol) was added and the reaction stirred for 30 min. at room temperature. The solvent was removed *in vacuo* and the oil dissolved in acetone. The solution was cooled to -78℃ in a CO_2/acetone bath and a stream of nitrogen blown over it, resulting in **20**.DMAP a pink crystalline solid, m.p. 93-96℃. This material exists as the DMAP complex with the hindered lactol **19** in $CDCl_3$ solution. δH (400 MHz, $CDCl_3$, 24 °C): 7.86 - 7.99 (2H, m, DMAP: 2-,6-*H*), 7.62 - 7.71 (2H, AB system, J = 8.7 Hz, 4-,5-*H*), 7.31 (1H, t, J = 8.2 Hz, 7-*H*), 7.21 (1H, d, J = 7.8 Hz, 6-*H*), 6.69 (1H, d, J = 6.9 Hz, 8-*H*), 6.38 (2H, d, J = 6.4 Hz, DMAP: 3-,5-*H*), 2.95 (6H, s, DMAP: N(CH_3)$_2$), 2.23 (3H, s, CH_3), 1.50 (9H, s, 3-C(CH_3)$_3$); δC (100 MHz, $CDCl_3$, 24 °C): 156.3 (8a-*C*), 154.5 (DMAP: 4-*C*), 148.6 (DMAP: 2-,6-*C*), 143.4, 136.9, 130.9 (Ar-C_3), 128.7 (4- or 5-*C*), 128.1 (7-*C*), 126.5 (Ar-C_1), 126.3 (4- or 5-*C*), 115.7 (2-,6-*C*), 106.5 (DMAP: 3-,5-*C*), 102.6 (8-*C*), 39.1 (DMAP: N(*C*H$_3$)$_2$), 36.8 (3-*C*(CH$_3$)$_3$), 32.9 (3-C(*C*H$_3$)$_3$), 30.0 (2-*C*H$_3$); ν_{max}/cm^{-1} (solid state) 2962, 2410, 1700 (C=O), 1604, 1536, 1380, 1362, 1216.

Ethyl (*E*)-2-cyano-3-(8'-hydroxynaphthalen-1'-yl)propenoate, 22.

1-Hydroxy-8-naphthaldehyde **21** (250 mg, 1.45 mmol) was dissolved in anhydrous MeOH (20 mL) under nitrogen. Ethyl cyanoacetate (197 mg, 1.74 mmol) and ethylenediamine diacetate (39 mg, 0.22 mmol) were added and the reaction heated to reflux for 6h. The solvent was removed *in vacuo* to give **22** as a crude yellow solid which was purified by flash column chromatography (1:9 EtOAc:petrol 40-60), to give a yellow solid (224 mg, 72%) m.p. 189-192 ℃; δH (400 MHz, (CD$_3$)$_2$CO, 24 °C): 9.61 (1H, s, O*H*), 9.55 (1H, s, 1-*H*), 8.03 (1H, d, J = 8.2 Hz, 7'-*H*), 7.80 (1H, d, J = 6.9 Hz, 5'-*H*), 7.58 (1H, t, J = 7.3 Hz, 6'-*H*), 7.48 (1H, d, J = 8.2 Hz, 4'-*H*), 7.40 (1H, d, J = 7.3 Hz, 3'-*H*), 7.06 (1H, dd, J = 7.8, 0.9 Hz, 2'-*H*), 4.36 (2H, q, J = 7.3 Hz, CH_2CH$_3$), (3H, t, J = 7.3 Hz, CH$_2$CH_3); δC (100 MHz, (CD$_3$)$_2$CO, 24 °C): 162.9 (*C*=O),

161.9 (1-*C*), 154.6 (1'-*C*), 136.7 (4a'-*C*), 132.8 (7'-*C*), 130.2 (8'-*C*), 128.4 (5'-*C*), 128.0 (3'-*C*), 126.3 (6'-*C*), 123.1 (8a'-*C*), 121.1 (4'-*C*), 115.8 (*C*≡N), 112.1 (2'-*C*), 104.6 (2-*C*), 62.8 (*C*$H_2$$CH_3$), 14.4 ($CH_2$*C*$H_3$); ν_{max}/cm^{-1} 3251, 3071, 2253 (C ≡N), 1708, 1600, 1436, 1370, 1344, 1263, 1240, 1088, 1084, 1013, 830, 770, 748; Found: C, 71.67; N, 5.25; H, 4.95. Calc. for $C_{16}H_{13}NO_3$: C, 71.90; N, 5.24; H, 4.90%.

2-Cyano-3-(8'-hydroxynaphthalen-1'-yl)propenenitrile, 23.

1-Hydroxy-8-naphthaldehyde **21** (150 mg, 0.87 mmol) was dissolved in anhydrous MeOH (10 mL) under nitrogen and malononitrile (70 mg, 1.05 mmol) added, and the deep orange solution was heated to reflux. After 2 h. the solvent was removed *in vacuo* to give a crude yellow solid which was purified by flash column chromatography (1:9 EtOAc:petrol 40-60), to give **23**[S4] as a yellow solid (140 mg, 73%), m.p. 145-148℃. δH (400 MHz, $CDCl_3$, 24 °C): 9.21 (1H, s, 3-*H*), 7.98 (1H, d, J = 7.9 Hz, 2'-*H*), 7.81 (1H, d, J = 7.3 Hz, 4'-*H*), 7.49-7.58 (2H, m, 3'-,5'-*H*), 7.41 (1H, t, J = 7.6 Hz, 6'-*H*), 6.92 (1H, dd, J = 7.4, 0.8 Hz, 7'-*H*), 5.85 (1H, br s, O*H*); δC (100 MHz, $CDCl_3$, 24 °C): 166.0 (3-*C*), 151.8 (8'-*C*), 135.7 (4a'-*C*), 133.5 (2'-*C*), 128.5 (4'-*C*), 127.8 (1'-*C*), 127.1 (6'-*C*), 125.7 (3'-*C*), 121.9 (8a'-*C*), 121.4 (5'-*C*), 113.9 & 112.5 (2 x *C*≡N), 112.1 (7'-*C*), 83.3 (2-*C*); ν_{max}/cm^{-1} 3374, 3068, 2237 (C≡N), 1582, 1562, 1368, 1244; Found: C, 76.31; N, 12.54; H, 3.53. Calc. for $C_{14}H_8N_2O$: C, 76.35; N, 12.72; H, 3.66%.

Sodium Dicyano-(2-(2*H*-naphtho(1,8-bc)furan-2'-yl)methanide, Na^+.29.

Dinitrile **23** (35 mg, 0.05 mmol) was dissolved in THF (4 mL) under nitrogen and excess sodium hydride (10 mg, 60% dispersion in oil) was added to give an immediate red-brown colour. The mixture was stirred for 5 min, the solvent evaporated *in vacuo* and THF-d_8 (*ca*. 0.4 ml) added to the purple residue followed by sufficient DMSO-d_6 to completely dissolve the product. δH (400 MHz, THF-d_8 and DMSO-d_6, 24 °C): 7.54 (1H, d, J = 8.2 Hz, 3'-*H*), 7.44 (1H, t, J = 7.8 Hz, 4'-*H*), 7.25 (1H, t, J = 7.8 Hz, 7'-*H*), 7.15 (1H, d, J = 6.9 Hz, 5'-*H*), 7.04 (1H, d, J = 8.2 Hz, 6'-*H*), 6.67 (1H, s, 2'-*H*), 6.41 (1H, d, J = 7.3 Hz, 8'-*H*); δC (100 MHz, THF-d_8 and DMSO-d_6, 24 °C): 162.3 (8a'-*C*), 141.6 (2a'-*C*), 132.8 (5a'-*C*), 131.6 (8b'-*C*), 130.3 (7'-*C*), 129.1 (4'-*C*), 128.0 (2 x *C*≡N), 123.9 (3'-*C*), 118.3 (5'-*C*), 114.0 (6'-*C*), 101.8 (2'-*C*), 100.7 (8'-*C*), 23.2 (2-*C*).

Reaction of 23 with 1-,1-,3-,3-Tetramethylguanidine.

Dinitrile **23** (35 mg) dissolved in THF-d_6 (0.6 ml) was treated with TMG (18 mg) to give an instant dark brown solution whose NMR spectra were recorded immediately, and indicated a dynamic partial deprotonation of the naphthol with the equilibrium strongly towards the naphthol form. δH (400 MHz, THF-d_8, 24 °C): 9.31 (1H, s, 3-*H*), 7.73 (1H, d, J = 7.8 Hz, 4'-*H*), 7.37 (1H, d, J = 7.3 Hz, 2'-*H*), 7.30 (1H, t, J = 7.6 Hz, 3'-*H*), 7.20 (1H, t, J = 7.8 Hz, 6'-*H*), 6.91 (1H, d, J = 8.2 Hz, 5'-*H*), 6.68 (1H, d, J = 7.8 Hz, 7'-*H*), 2.74 (6H, s, TMG: 4 x CH_3); δC (100 MHz, THF-d_8, 24 °C): 164.3 (8'-*C*), 164.0 (TMG: *C*=N), 158.4 (br, 3-*C*), 136.7 (4a'-*C*), 133.1 (2'-*C*), 131.7 (4'-*C*), 129.7 (6'-*C*), 127.9 (8a'-C), 125.4 (3'-*C*), 124.0 (2'-*C*), 117.4 (2 x *C*N), 113.2 (5'-*C*), 110.8 (7'-*C*), 68.9 (br, 2-*C*), 39.7 (TMG: 4 x *CH_3*).

5-((8'-Hydroxynaphthalen-1'-yl)methylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione, 24.

1-Hydroxy-8-naphthaldehyde **21** (800 mg, 4.65 mmol) was dissolved in anhydrous DMSO (25 mL) under nitrogen and Meldrum's acid (804 mg, 5.58 mmol) added and the deep orange solution was stirred at room temperature. After 7 days, H_2O (100 mL) was added producing an orange precipitate. The precipitate was dissolved by the addition of DCM (30 mL) and the organic layer separated. The aqueous solution was extracted further with DCM (3 x 30 mL) and the combined organic fractions were washed with H_2O (30 mL) and brine (30 mL), dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give a crude orange solid which was purified by flash column chromatography (1:9 EtOAc:petrol 40-60), to give **24** as an orange solid (1.19 g, 86%), m.p. 169-172℃. δH (400 MHz, DMSO-d_6, 24 °C): 10.58 (1H, s, O*H*), 9.27 (1H, s, 5-=C*H*), 7.89 (1H, d, J = 8.2 Hz, 2'-*H*), 7.28 - 7.47 (4H, m, 3'-, 4'-,5'-,6'-*H*), 6.88 (1H, d, J = 8.7 Hz, 7'-*H*), 1.77 (6H, s, 2 x -CH_3); δC (100 MHz, DMSO-d_6, 24 °C): 163.5 (5-=*C*H), 162.9, 159.9 (2 x *C*=O), 154.3 (8'-*C*), 135.5 (Ar-C_1), 131.1 (2'-*C*), 130.3, 127.5, 127.4, 125.6, 122.5, 119.8 (Ar-C_6), 114.4 (5-*C*), 110.9 (7'-C), 105.2 (*C*$(CH_3)_2$), 27.7 (2 x *C*H_3); ν_{max}/cm^{-1} 3276 (OH), 1697 (C=O), 1594, 1372, 1292, 1200; Found: C, 68.50; H, 4.64. Calc. for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73%.

Sodium 2,2-dimethyl-5-(2H-naphtho[1,8-bc]furan-2'-yl)-4,6-dioxo-1,3-dioxan-5-ide, Na^+. 30.

Knoevenagel product **21** (30 mg) was dissolved in THF (4 ml) and the solution treated with sodium hydride (60% dispersion in oil, *ca*. 4 mg) until the solution turned from yellow to colourless. After stirring for a further 5 min., the solution was evaporated i*n vacuo*. CD_3CN (1 ml) was added, the solution filtered, and the NMR spectra recorded. δH (400 MHz, CD_3CN, 24 °C): 7.51 (1H, d, J = 8.2 Hz, 3'-*H*), 7.41 (1H, t, J = 7.6 Hz, 4'-*H*), 7.30 (1H, t, J = 7.8 Hz, 7'-

H), 7.13 (1H, d, J = 8.2 Hz, 6'-*H*), 7.04 (1H, d, partially obscured, 5'-*H*), 7.00 (1H, s, 2'-*H*), 6.48 (1H, d, J = 7.3 Hz, 8'-*H*), 1.59 (6H, s, 2 x 2-CH_3); δC (100 MHz, CD_3CN, 24 °C): 166.8 (2 x *C*=O), 162.8 (8a-*C*), 145.4, 132.6, 130.4 (Ar-C_3), 130.1 (7'-*C*), 129.4 (4'-*C*), 122.3 (3'-*C*), 115.5 (5'-*C*), 114.7 (6'-*C*), 101.6 (2-*C*), 99.9 (8'-*C*), 89.6 (2'-*C*), 74.7 (5-C^-), 26.2 (2 x 2-*C*H_3).

1,4-Diazabicyclo[2.2.2]octan-1-ium 2,2-Dimethyl-5-(2H-naphtho[1,8-bc]furan-2-yl)-4,6-dioxo-1,3-dioxan-5-ide, DABCO-H^+. 30.

Knoevenagel product **24** (20 mg, 0.067 mmol) was dissolved in CD_3CN (2 mL), 1,4-diazabicyclo- [2.2.2]octane (7.5 mg, 0.067 mmol) was added and the reaction stirred for 30 min. at room temperature. The yellow solution became paler upon addition. Removal of the solvent resulted in the formation of a solidified foam, δH (400 MHz, CD_3CN, 24 °C): 7.53 (1H, d, J = 7.7 Hz, 3'-*H*), 7.42 (1H, t, J = 6.8 Hz, 4'-*H*), 7.30 (1H, t, J = 8.2 Hz, 7'-*H*), 7.13 (1H, d, J = 8.2 Hz, 6'-*H*), 7.04 (1H, d, J = 8.2 Hz, 5'-*H*), 7.00 (1H, s, 2'-*H*), 6.50 (1H, d, J = 7.3 Hz, 8'-*H*), 6.14 (1H, br s, DABCO-H^+ N*H*), 2.88 (12H, s, DABCO-H^+: 6 x NCH_2), 1.63 (6H, s, 2 x 2-CH_3); δC (100 MHz, CD_3CN, 24 °C): 167.1 (2 x *C*=O), 162.8 (8a'-*C*), 145.2, 132.7, 130.4 (Ar-C_3), 130.2 (7'-*C*), 129.5 (4'-*C*), 122.5 (3'-*C*), 115.6 (5'-*C*), 114.8 (6'-*C*), 102.1 (2-*C*), 100.1 (8'-*C*), 89.7 (2'-*C*), 75.7 (5-C^-),45.4 (DABCO-H^+: 6 x N*C*H_2), 26.2 (2 x 2-*C*H_3); ν_{max}/cm^{-1} 2943, 2881, 2258, 1765, 1709, 1615, 1591, 1369, 1054; *HRMS* (ESI): calcd for $C_{17}H_{13}O_5$ ([M-H]$^-$): 297.0768, found: 297.0844.

3-Hydroxy-2-(2'H-naphtho[1,8-bc]furan-2'-yl)cyclohex-2-en-1-one, 25.

1-Hydroxy-8-naphthaldehyde **21** (250 mg, 1.45 mmol) was dissolved in anhydrous MeOH (20 mL) under nitrogen. 1, 3-Cyclohexandione (195 mg, 1.74 mmol) and ethylenediamine diacetate (26 mg, 0.15 mmol) were added and the reaction heated to reflux for 6h. The solvent was removed *in vacuo* to give a crude yellow solid which was purified by flash column chromatography (3:1 EtOAc:Pet 40-60), to give **25** as a brown solid (200 mg, 52%), m.p. 186-189℃; in solution it exists in two forms: ring closed **25** and a minor component in *ca*. 17:3 ratio. δH (400 MHz, ($CDCl_3$, 24 °C): main component (ring closed) 85%: 9.11 (1H, br, O*H*), 7.62 (1H, d, J = 7.8 Hz, 3'-*H*), 7.49 (1H, t, J = 7.8 Hz, 4'-*H*), 7.33-7.41 (2H, m, 6'-,7'-*H*), 7.29 (1H, dd, J = 6.9, 1.4 Hz, 5'-*H*), 7.16 (1H, s, 2'-*H*), 6.82 (1H, d, J = 6.9 Hz, 8'-*H*), 2.25-2.52 (4H, m, 4-, 6-H_2), 1.85-2.00 (2H, m, 5-H_2), minor component, 15%, spectrum obscured apart from: 7.96 (1H, s), 7.91 (1H, d, J = 7.7 Hz), 7.72 (1H, d, J = 7.3 Hz); δC (100 MHz, ($CDCl_3$,

24 °C): 197.5 br (*C*=O), 174.2 br (3-*C*), 158.4 (8a'-*C*), 140.5, 131.6 (Ar-C_2), 129.4 (4'-*C*), 128.9 (7'-*C*), 127.6 (Ar-C_1), 123.4 (3'-*C*), 117.9 (5'-*C*), 117.2 (6'-*C*), 112.2 (2-*C*), 101.8 (8'-*C*), 87.8 (2'-*C*), 36.8 br (6-*C*), 29.5 br (4-*C*), 20.3 (5-*C*); ν_{max}/cm^{-1} 2917 (OH), 2849, 1622 (C=O), 1574, 1465, 1414, 1360, 1282. Found: C, 76.47; H, 5.37. Calc. for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30%.

4-(Dimethylamino)pyridin-1-ium 1-(2H-naphtho[1,8-bc]furan-2-yl)-2,6-dioxocyclohexan-1-ide, DMAP-H$^+$. 31.

Cyclohexenone derivative **25** (40 mg, 0.16 mmol) was dissolved in CD_3CN (2 mL), DMAP (18 mg, 0.16 mmol) was added and the reaction stirred for 30 min. at room temperature. The brown solution became paler upon addition. Removal of the solvent resulted in the formation of a solidified foam, δH (400 MHz, CD_3CN, 24 °C): 10.61 (1H, br s, DMAP-H$^+$: N*H*), 7.80 (2H, d, J = 6.9 Hz, DMAP-H$^+$: 2-,6-*H*), 7.45 (1H, d, J = 8.2 Hz, 3'-*H*), 7.34 (1H, t, J = 6.9 Hz, 4'-*H*), 7.27 (1H, t, J = 7.8 Hz, 7'-*H*), 7.13 (1H, s, 2'-*H*), 7.09 (1H, d, J = 8.2 Hz, 6'-*H*), 6.86 (1H, dd, J = 8.2, 1.4 Hz, 5'-*H*), 6.56 (2H, d, J = 7.3 Hz, DMAP-H$^+$: 3-,5-*H*), 6.46 (1H, d, J = 7.3 Hz, 8'-*H*), 2.98 (6H, s, DMAP-H$^+$: N(CH_3)$_2$), 2.12 (4H, t, J = 6.0, 1.4 Hz, 3-,5-H_2), 1.89 - 1.94 (2H, m, 4-H_2); δC (100 MHz, CD_3CN, 24 °C): 192.0 (2 x *C*=O), 163.3 (8a'-*C*), 156.8 (DMAP-H$^+$: 4-*C*), 146.2 (Ar-C_1), 144.8 (DMAP-H$^+$: 2-,6-*C*), 132.6, 130.6 (Ar-C_2), 130.1 (7'-*C*), 129.4 (4'-*C*), 122.0 (3'-*C*), 114.8 (5'-*C*), 114.7 (6'-*C*), 111.1 (1-*C*), 107.5 (DMAP-H$^+$: 3-,5-*C*), 100.0 (8'-*C*), 85.7 (2'-*C*), 39.8 (DMAP-H$^+$: N(*C*H$_3$)$_2$), 35.9 (3-,5-*C*), 22.0 (4-*C*); ν_{max}/cm^{-1} 2930, 1644, 1598, 1557, 1471, 1401, 1342, 1219, 1182, 1129; *HRMS* (ESI): calcd for $C_{17}H_{13}O_3$ ([M-H]$^-$): 265.0870, found: 265.0869.

1,4-Diazabicyclo[2.2.2]octan-1-ium 1-(2H-naphtho[1,8-bc]furan-2-yl)-2,6-dioxocyclohexan-1-ide, DABCO-H$^+$. 31.

Cyclohexenone derivative **25** (40 mg, 0.16 mmol) was dissolved in CD_3CN (2 mL), 1,4-diazabicyclo-[2.2.2]octane (17 mg, 0.16 mmol) was added and the reaction stirred for 30 min. at room temperature. The brown solution became paler upon addition. Removal of the solvent resulted in the formation of a solidified foam, δH (400 MHz, CD_3CN, 24 °C): 9.25 (1H, br s, DABCO-H$^+$: N*H*), 7.54 (1H, d, J = 8.2 Hz, 3'-*H*), 7.42 (1H, t, J = 6.9 Hz, 4'-*H*), 7.35 (1H, t, J = 8.2 Hz, 7'-*H*), 7.17 (1H, d, partially obscured, 6'-*H*), 7.19 (1H, s, 2'-*H*), 6.93 (1H, dd, J = 6.8, 1.4 Hz, 5'-*H*), 6.53 (1H, d, J = 7.3 Hz, 8'-*H*), 2.71 (12H, s, DABCO-H$^+$: 6 x NCH_2), 2.18

(4H, t, J = 6.3 Hz, 3-,5-H_2), 1.84 - 1.92 (2H, quin, J = 6.3 Hz, 4-CH_2); δC (100 MHz, CD_3CN, 24 °C): 192.4 (2 x *C*=O), 163.5 (8a-*C*), 146.7, 132.6, 130.8 (Ar-C_3), 130.1 (7'-*C*), 129.4 (4'-*C*), 121.8 (3'-*C*), 114.6 (5'-,6'-*C*), 110.8 (1-*C*), 99.9 (8'-*C*), 86.1 (2'-*C*), 45.8 (DABCO-H^+: 6 x N*C*H_2), 36.8 (3-,5-*C*), 22.2 (4-*C*); ν_{max}/cm^{-1} 3044, 2938, 2882, 2471, 1619, 1593, 1488, 1460, 1372; *HRMS* (ESI): calcd for $C_{17}H_{13}O_3$ ([M-H]$^-$): 265.0870, found: 265.0863.

7a-Hydroxy-9-phenyl-7a,8,9,10-tetrahydro-11H-benzo[f]naphtho[1,8-bc]oxepin-11-one, 27 (solid form) /3-Hydroxy- 2-(2'H-naphtho[1,8-bc]furan-2'-yl)-5-phenyl-cyclohex-2-en-1-one, 28 (solution form).

1-Hydroxy-8-naphthaldehyde **21** (100 mg, 0.58 mmol) was dissolved in anhydrous DMSO (25 mL) under nitrogen and 5-phenyl-1,3-cyclohexandione (120 mg, 0.64 mmol) added and the deep orange solution was stirred at room temperature. After 5 days, H_2O (100 mL) was added to produce a yellow precipitate. The precipitate was dissolved by the addition of DCM (30 mL) and the organic layer separated. The aqueous solution was extracted further with DCM (3 x 30 mL). The combined organics were washed with H_2O (30 mL) and brine (30 mL), dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give a crude yellow solid which was purified by flash column chromatography (1:4 EtOAc:petrol 40-60), to give **27** as a yellow solid (150 mg, 75%), m.p. 172-175℃. This compound exists as the fused oxepine **27** in the solid state but as the naphthofuran **28** in solution in DMSO-d_6. δH (400 MHz, DMSO-d_6, 24 °C): 7.57 (1H, d, J = 8.2 Hz, 3'-*H*), 7.41 (1H, t, J = 6.9 Hz, 4'-*H*), 7.28 - 7.35 (5H, m, 7'-*H*, 2 x *ortho*-Ph-*H*, 2 x *meta*-Ph-*H*), 7.15 - 7.24 (2H, m, 6'-*H*, *para*-Ph-*H*), 7.02 (1H, s, 2'-*H*), 6.98 (2H, br d, J = 6.4 Hz, 5'-*H*), 6.56 (1H, br d, J = 6.9 Hz, 8'-*H*), 3.16 - 3.51 (1H, m, 5-*H*), 2.65 - 2.85 (2H, m, 6-H_2), 2.48 - 2.57 (1H, m, 4-H_2); δC (100 MHz, DMSO, 24 °C): 197.1 (*C*=O), 162.0 (3-*C*), 151.8 (8a'-*C*), 143.7 & 143.3 (*ipso*-Ph-*C*, Ar-C_1), 131.6 (Ar-C_1), 129.8 (7'-*C*), 129.1 (4'-*C*), 129.1 (2 x *meta*-Ph-*C*), 127.5 (2 x *ortho*-Ph-*C*), 127.2 (*para*-Ph-*C*), 122.4 (3'-*C*), 115.0 (6'-*C*), 114.9 (5'-*C*), 112.3 (Ar-C_1), 101.1 (2-*C*), 100.2 (8'-*C*), 81.9 (2'-*C*), 47.0 (6-*C*), 40.2 (4-*C*), 38.4 (5-*C*); ν_{max}/cm^{-1} 3395 (OH), 3067, 3040, 2950, 1676 (C=O), 1592, 1581, 1388, 1227; Found: C, 80.63; H, 5.16. Calc. for $C_{17}H_{14}O_5$: C, 80.68; H, 5.30%.

Sodium 1-(2H-naphtho[1,8-bc]furan-2-yl)-2,6-dioxo-4-phenylcyclohexan-1-ide, Na^+. 32.

The fused oxepine **27** (20 mg) was dissolved in THF (4 ml) and the solution treated with sodium hydride (60% dispersion in oil, *ca*. 4 mg) until the solution turned from yellow to colourless. After stirring for a further 5 min., the solution was evaporated i*n vacuo*. THF-d_8 (1 ml) was added, the solution filtered, and the NMR spectra recorded. δH (400 MHz, THF-d_8, 24 °C):

7.27 (1H, d, J = 8.2 Hz, 3'-*H*), 7.01 - 7.20 (7H, m, 4'-,7'-*H*, -C_6H_5), 7.20 (1H, s, 2'-*H*), 6.91 (1H, d, J = 8.2 Hz, 6'-*H*), 6.74 (1H, dd, J = 8.2, 1.5 Hz, 5'-*H*), 6.31 (1H, d, J = 6.8 Hz, 8'-*H*), 3.06 - 3.26 (1H, m, 4-*H*), 2.14 - 2.34 (4H, m, 3-,5-H_2); δC (100 MHz, THF-d_8, 24 °C): 191.7 (*C*=O), 163.7 (8a'-*C*), 147.3 (*ipso*-Ph-C and Ar-C_1), 146.8, 132.7 (Ar-C_2), 131.0, 129.5 (4'- or 7'-*C*), 129.0 (2 x *meta*-Ph-*C*), 128.8 (4'- or 7'-*C*), 127.7 (2 x *ortho*-Ph-*C*), 126.5 (*para*-Ph-*C*), 121.1 (3'-*C*), 114.4 (5'-*C*), 114.0 (6'-*C*), 108.4 (1-C^-),99.5 (8'-*C*), 87.6 (2'-*C*), 44.6 (3-,5-*C*), 40.6 (4-*C*).

4-(Dimethylamino)pyridin-1-ium 1-(2H-naphtho[1,8-bc]furan-2-yl)-2,6-dioxo-4-phenylcyclohexan-1-ide, DMAP-H^+. 32.

The fused oxepine **27** (10 mg, 0.029 mmol) was dissolved in CD_3CN (2 mL), 4-dimethylaminopyridine (3.6 mg, 0.029 mmol) was added and the reaction stirred for 30 min. at room temperature. The yellow solution became paler upon addition. Removal of the solvent resulted in the formation of a solidified foam, δH (400 MHz, CD_3CN, 24 °C): 7.71 (2 H, d, J = 7.3 Hz, DMAP-H^+: 2-,6-*H*), 7.38 (1 H, d, J = 8.2 Hz, 3'-*H*), 7.16-7.34 (7H, m, C_6H_5, 4'-,7'-*H*), 7.15 (1H, s, 2'-*H*), 7.05 (1H, d, J = 8.2 Hz, 6'-*H*), 6.83 (1H, dd, J = 6.9, 1.8 Hz, 5'-*H*), 6.53 (2H, d, J = 7.3 Hz, DMAP-H^+: 3-,5-*H*), 6.42 (1H, d, J = 7.3 Hz, 8'-*H*), 3.25 - 3.33 (1H, m, 4-*H*), 2.97 (6H, s, DMAP-H^+: N(CH_3)$_2$), 2.49 (2H, dd, J = 16.5, 11.4 Hz , 3-H_α, 5-H_α), 2.37 (2H, dd, J = 16.5, 4.6 Hz, 3-H_β, 5-H_β); δC (100 MHz, CD_3CN, 24 °C): 190.8 (2 x *C*=O), 163.3 (8a'-*C*), 157.0 (DMAP-H^+: 4-*C*), 146.1 and 145.8 (*ipso*-Ph-*C*, Ar-C_1), 143.7 (DMAP-H^+: 2-,6-*C*), 132.5, 130.6, 130.1, 129.4 (2 x *meta*-Ph-*C* & Ar-C_1), 128.0 (2 x *ortho*-Ph-*C*), 127.3 (*para*-Ph-*C*), 122.0 (3'-*C*), 114.8 (6'-*C*), 114.7 (5'-*C*), 110.6 (1-*C*), 107.5 (DMAP-H^+: 3-,5-*C*), 100.0 (8'-*C*), 85.7 (2'-*C*), 43.4 (3-,5-*C*), 40.0 (DMAP-H^+: N(CH_3)$_2$), 39.9 (4-*C*); ν_{max}/cm^{-1} 3394, 3067, 3040, 2950, 1679, 1617, 1593, 1581, 1388, 1267, 1202; *HRMS* (ESI): calcd for $C_{23}H_{17}O_3$ ([M-H]$^-$): 341.1183, found: 341.1180.

1,4-Diazabicyclo[2.2.2]octan-1-ium 1-(2H-naphtho[1,8-bc]furan-2-yl)-2,6-dioxo-4-phenylcyclohexan-1-ide, DABCO-H^+. 32.

The fused oxepine **27** (20 mg, 0.058 mmol) was dissolved in CD_3CN (2 mL), 1,4-diazabicyclo-[2.2.2]octane (6.5 mg, 0.058 mmol) was added and the reaction stirred for 30 min. at room temperature. The yellow solution became paler upon addition. Removal of the solvent resulted in the formation of a solidified foam, δH (400 MHz, CD_3CN, 24 °C): 7.36 (1H, d, J = 8.7 Hz, 3'-*H*), 7.14 - 7.29 (6H, m, 4'-,7'-*H*, 2 x *ortho*-Ph-*H*, 2 x *meta*-Ph-*H*), 7.08 - 7.14 (1H, m, *para*-Ph-*H*), 7.05 (1H, s, 2'-*H*), 7.01 (1H, d, J = 8.2 Hz, 6'-*H*), 6.77 (1H, dd, J = 8.2, 1.5 Hz, 5'-*H*), 6.37

(1H, d, J = 7.3 Hz, 8'-*H*), 3.16 - 3.27 (1H, m, 4-*H*), 2.55 (12H, s, DABCO-H^+: 6 x NCH_2), 2.18 - 2.45 (4H, m, 3-,5-H_2); δC (100 MHz, CD_3CN, 24 °C): 191.2 (*C*=O), 163.3 (8a'-*C*), 146.7 and 146.1 (*ipso*-Ph-*C,* Ar-C_1), 132.7, 130.8 (Ar-C_2), 130.1 (4'-*C*), 129.5 (7'-*C*), 129.4 (2 x *meta*-Ph-*C*), 128.0 (2 x *ortho*-Ph-*C*), 127.3 (*para*-Ph-*C*), 121.8 (3'-C), 114.6 (5'-,6'-*C*), 110.3 (1-C^-), 99.9 (8'-*C*), 86.1 (2'-*C*), 45.6 (DABCO-H^+: 6 x NCH_2), 44.2 (3-,5-*C*), 40.2 (4-*C*); ν_{max}/cm^{-1} 3300 (NH), 3028 , 2939, 2887, 2479, 1620 (C=O), 1593, 1489, 1372, 1247; *HRMS* (ESI): calcd for $C_{23}H_{17}O_3$ ([M-H]$^-$): 341.1183, found: 341.1176.

X-ray Crystallography.

Low temperature (100-150 K) X-ray diffraction data (Mo Kα) were measured on an Rigaku Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire detector and an 700 series Cryostream low temperature system using the CrysAlis-Pro software package.[S5] Structures were solved and refined using the SHELXS and SHELXL suite of programs[S6] using the XSEED interface.[S7] Molecular illustrations were made with Mercury.[S8] Data are deposited at the Cambridge Crystallographic Data Centre with code numbers CCDC 1849340-1849345, 1849617-1849619, 1849628-1849632.

Table S1. Crystallographic data for ketones, **9** and **11**, salts TMG-H^+ **8** and TMG-H^+ **12**, lactone **18**, and lactol **19**.

	9	**11**	**TMG-H^+ 8**	**TMG-H^+ 12**	**18**	**19**
Formula	$C_{17}H_{12}O_2$	$C_{12}H_{10}O_2$	$C_5H_{14}N_3.$ $C_{17}H_{11}O_2.$ $0.05\,H_2O$	$C_5H_{14}N_3.$ $C_{12}H_9O_2$	$C_{15}H_{14}O_2$	$C_{16}H_{18}O_2$
Formula weight	248.27	186.20	364.35	301.38	226.26	242.30
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Triclinic	Orthorhombic	Monoclinic
Space group	*Iba*2	$P2_12_12_1$	*P*-1	*P*-1	*Pnma*	$P2_1/c$
a[Å]	17.3065(5)	9.9122(2)	8.2578(4)	15.1117(6)	14.0730(6)	12.4248(5)
b[Å]	17.6303(4)	13.8433(3)	10.5748(5)	15.6707(7)	6.8273(4)	22.9673(7)
c[Å]	8.0817(2)	13.9018(3)	23.1819(12)	16.4672(7)	12.0491(7)	9.8566(4)
α[°]	90	90	99.596(4)	80.552(4)	90	90
β [°]	90	90	91.720(4)	69.591(4)	90	112.446(5)
γ[°]	90	90	104.122(4)	61.179(4)	90	90
V [Å^3]	2465.88(11)	1907.57(7)	1930.40(17)	3202.1(3)	1157.68(11)	2599.63(19)
Z	4	8	4	8	4	8
ρ [gcm^{-3}]	1.34	1.297	1.25	1.250	1.298	1.238
T [*K*]	110(2)	150.01(10)	110(2)	100.01(10)	150(2)	110(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ[mm^{-1}]	0.087	0.088	0.082	0.083	0.085	0.080
unique refl.	3039	4651	9106	11729	1484	5334
Refl, I > 2σI	2920	4090	6926	8260	1268	4107
R_1 (I > 2σI)	0.033	0.0418	0.067	0.0555	0.0538	0.0611
wR_2(all)	0.079	0.0953	0.126	0.1291	0.1437	0.1450
Δρ(r) [e Å^{-3}]	0.210/ -0.194	0.210/ -0.232	0.236/ -0.235	0.345/ -0.226	0.330/ -0.257	0.267/ -0.228
Cryst. solvent.	CH_2Cl_2	EtOAc	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	$(CH_3)_2CO$

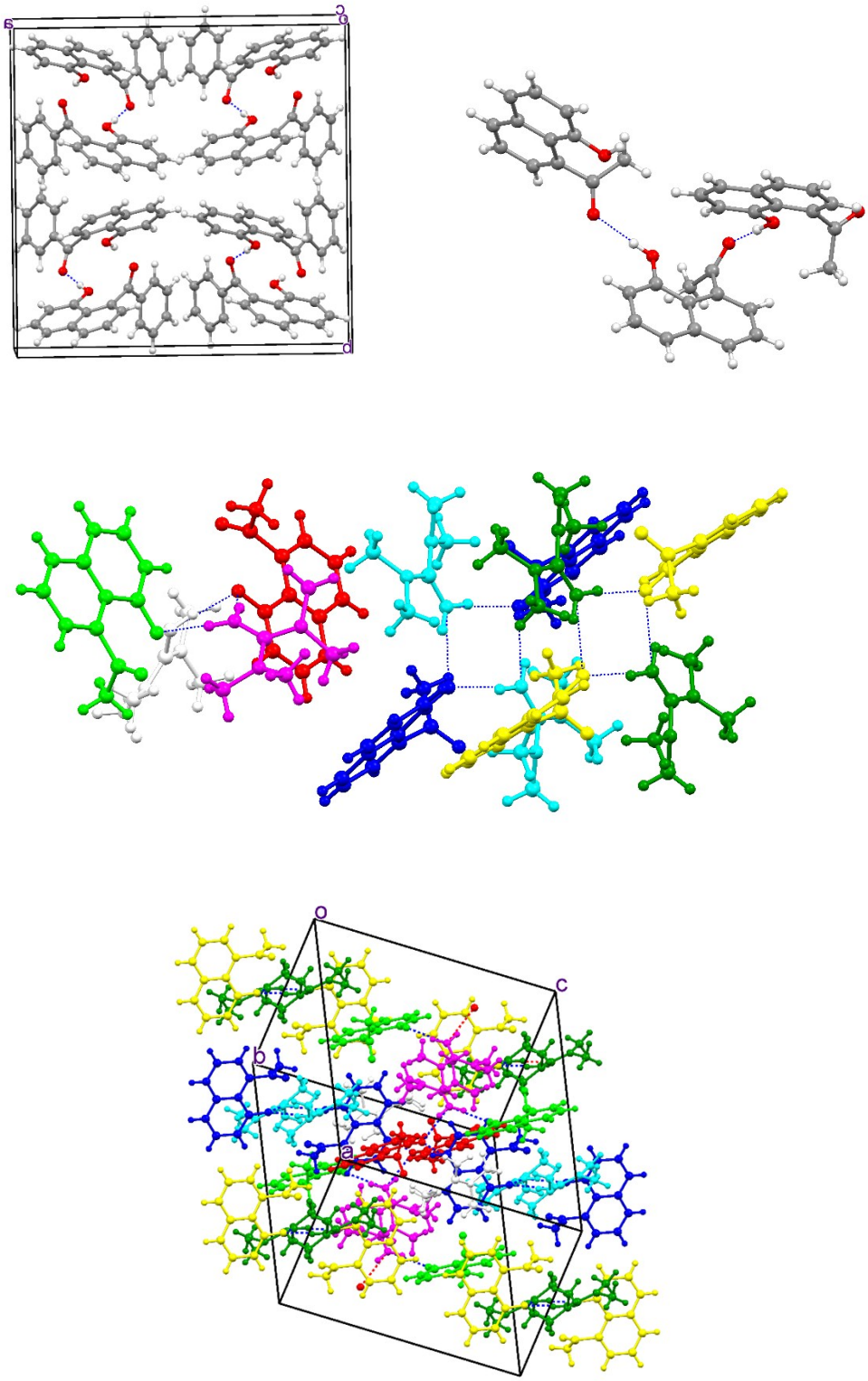


Figure S2. Packing diagram for the phenyl ketone **9** (top left), hydrogen bonding in the crystal structure of methyl ketone **11** (top right), arrangement of the four unique cations and four unique anions into hydrogen bonded square motifs for TMG-H^+. **12**, with two motifs involving pairs of one unique cation and anion, and one involving two unique cations and anions (middle and bottom)

Table S2. Crystallographic data for DMAP complexes of **11**, **17**, and **20**.

	DMAP.11	**DMAP.17**	**DMAP.20**
Formula	$C_7H_{10}N_2$. $C_{12}H_{10}O_2$	$C_7H_{10}N_2$. $C_{15}H_{16}O_2$	$C_7H_{10}N_2$. $C_{16}H_{18}O_2$
Formula weight	308.37	350.45	364.47
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/c$	$P2_1/c$
a[Å]	27.588(4)	8.4313(5)	10.1265(11)
b[Å]	8.2227(4)	26.5593(11)	25.804(3)
c[Å]	19.874(3)	9.5945(5)	7.9261(7)
α[°]	90	90	90
β [°]	132.66(3)	114.586(7)	105.497(10)
γ[°]	90	90	90
V [Å^3]	3315.6(13)	1953.7(2)	1995.9(4)
Z	8	4	4
ρ [g cm^{-3}]	1.236	1.191	1.213
T [*K*]	149.97(12)	150.01(10)	150.00(10)
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	0.081	0.076	0.077
unique refl.	3819	4523	4601
Refl, I > 2σI	2427	3146	2813
R_1	0.0723	0.0738	0.0691
wR_2	0.1398	0.1790	0.1364
Δρ(r) [e Å^{-3}]	0.166/ -0.229	0.437/ -0.292	0.203/ -0.185
Cryst. Solvent.	CH_2Cl_2	$(CH_3)_2CO$	$(CH_3)_2CO$

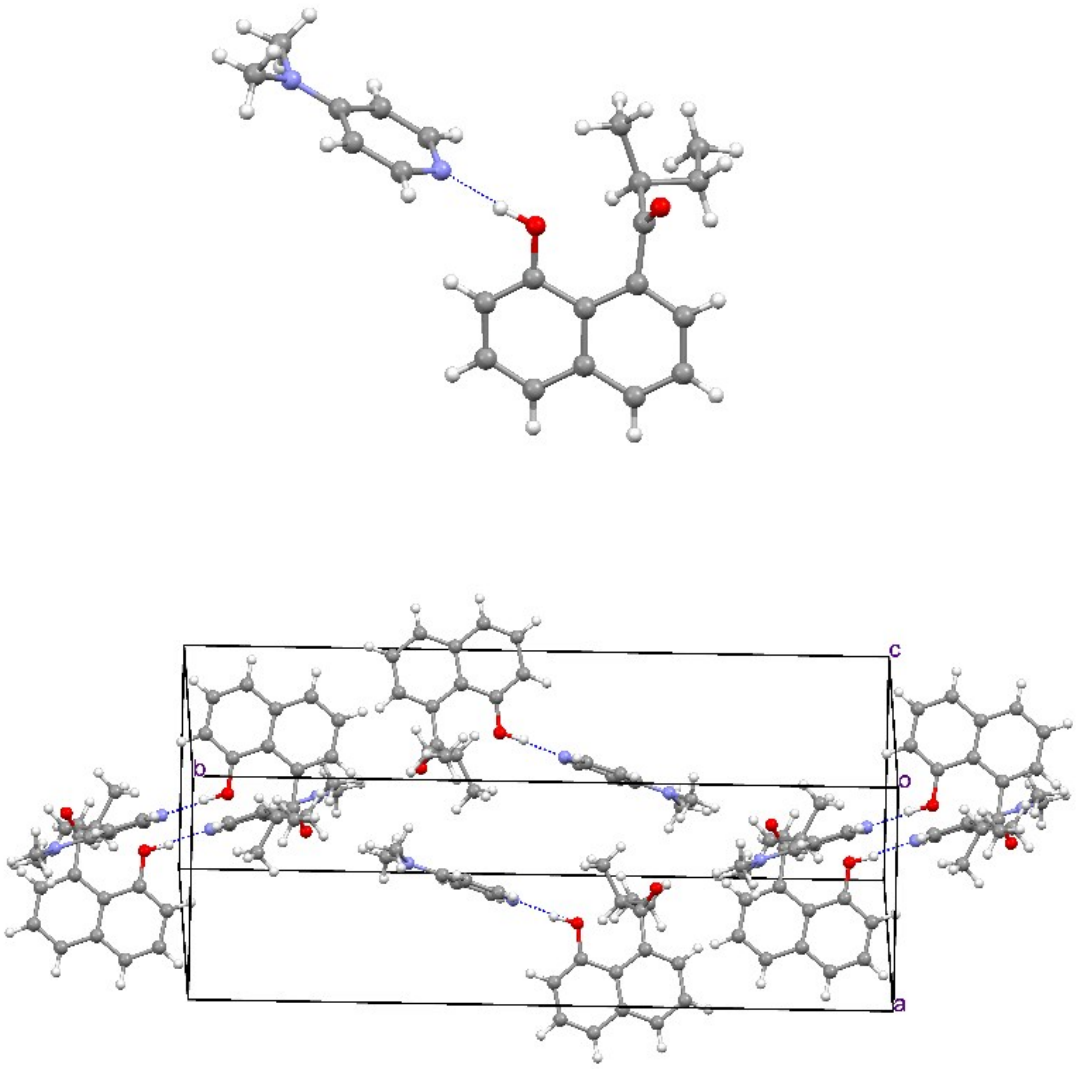


Figure S3: Molecular structure of **17**.DMAP (top) and its crystal packing arrangement (bottom).

Table S3. Crystallographic data for Knoevenagel products **22**-**25** and **27**.

	22	**23**	**24**	**25**	**27**
Formula	$C_{16}H_{13}NO_3$	$C_{14}H_8N_2O$	$C_{17}H_{14}O_5$	$C_{17}H_{14}O_3$	$C_{23}H_{18}O_3$
Formula weight	267.27	220.22	298.28	266.28	342.37
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	P-1
a[Å]	10.8607(7)	9.9169(5)	7.3963(3)	13.4588(5)	6.9441(4)
b[Å]	8.0882(5)	7.4879(2)	14.2452(4)	9.4421(3)	8.8146(4)
c[Å]	15.3629(9)	15.8768(6)	13.5274(5)	20.9855(9)	14.8418(8)
α[°]	90	90	90	90	77.773(4)
β [°]	100.510(5)	108.096(5)	105.187(4)	95.122(4)	78.744(4)
γ[°]	90	90	90	90	76.371(4)
V [Å^3]	1326.89(14)	1120.64(8)	1375.49(9)	2656.17(17)	852.70(8)
Z	4	4	4	8	2
ρ [g cm^{-3}]	1.338	1.305	1.440	1.332	1.333
T [*K*]	150(2)	150.00(10)	100(2)	100(2)	150.01(10)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	0.093	0.085	0.107	0.091	0.088
unique refl.	3097	2465	3198	6253	3941
Refl, I > 2σI	2604	1936	2640	4538	3040
R_1	0.0553	0.0527	0.0573	0.0763	0.0690
wR_2	0.1235	0.1102	0.1198	0.2046	0.1519
Δρ(r) [e Å^{-3}]	0.273/ -0.230	0.208/ -0.171	0.304/ -0.216	1.007/ -0.301	0.323/ -0.178
Cryst. Solvent.	$(CH_3)_2CO$	EtOAc	CH_2Cl_2/ $(CH_3)_2CO$	EtOAc	EtOAc

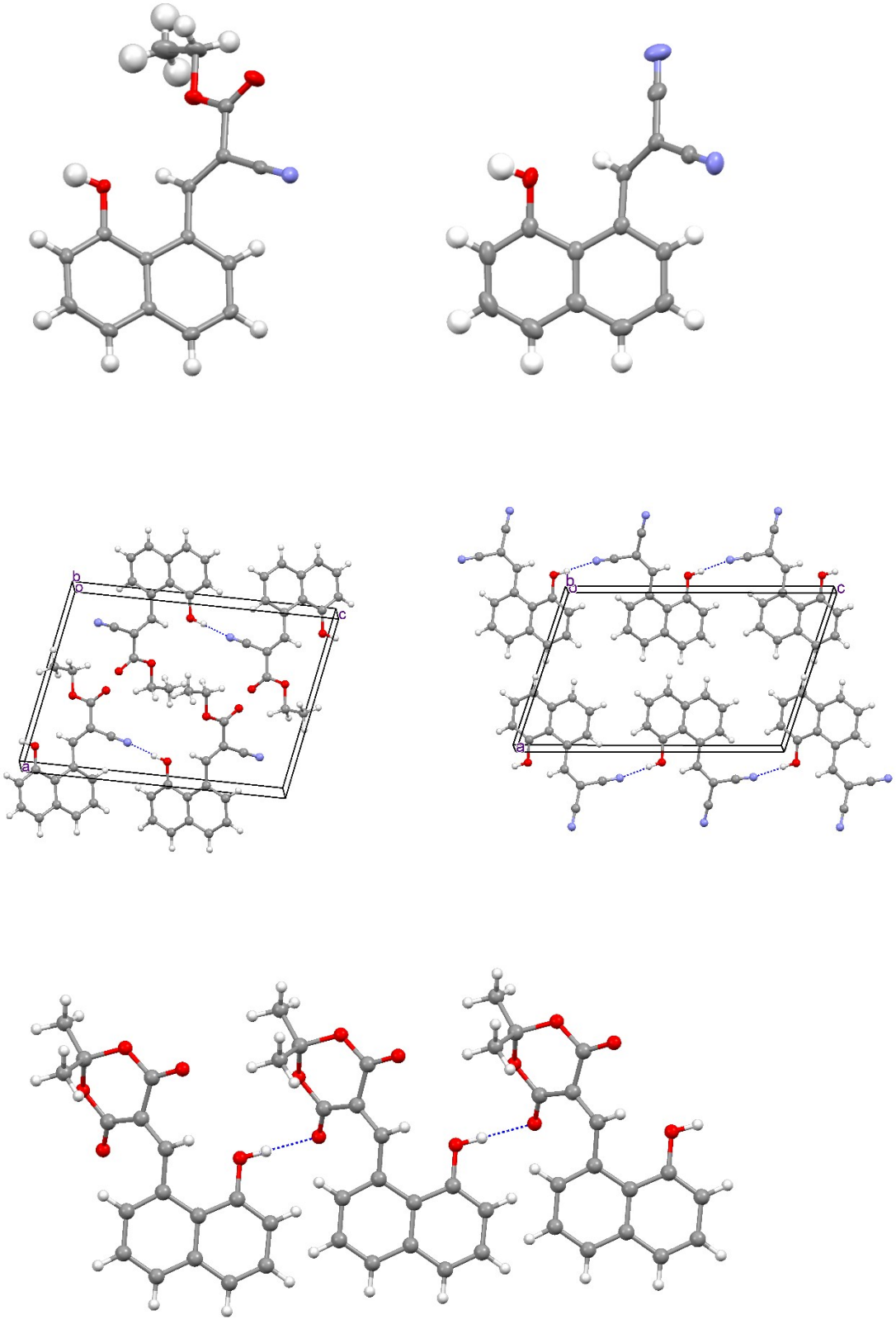
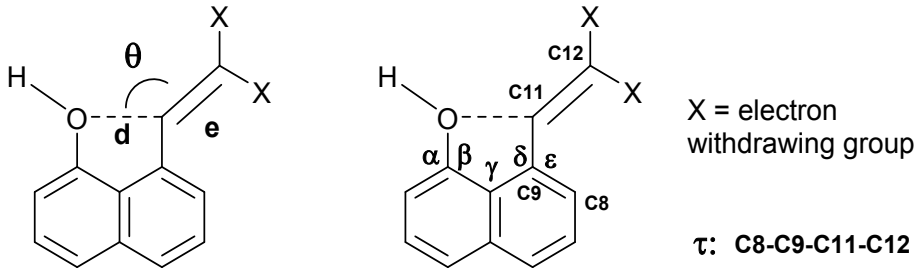


Figure S4: Molecular structures of Knoevenagel products **22** (top left) and **23** (top right), their crystal packing arrangements showing hydrogen bonding between OH groups and nitriles (middle) and hydrogen bonding in crystal structure of the Knoevenagel product **24** (bottom).

Table S4. Selected Molecular Geometry for Knoevenagel Products **22**-**25**.



	d / Å	**e** / Å	**θ**/°	**α** /°	**β** /°	**γ** /°	**δ** /°	**ε** /°	**τ** /°
22	2.6150(19)	1.343(2)	124.69(12)	122.36(15)	116.80(14)	123.40(14)	122.91(14)	117.70(14)	48.8(2)
23	2.6244(18)	1.351(2)	127.35(8)	122.43(15)	116.79(14)	123.42(15)	122.00(13)	118.71(13)	41.1(2)
24	2.623(2)	1.350(3)	125.13(13)	121.31(16)	117.36(17)	124.19(17)	120.73(16)	119.42(17)	45.63(6)
25	1.521(3)	1.500(3)	108.0(2)	130.6(3)	110.7(2)	109.5(2)	108.2(2)	134.7(2)	60.6(4)
	1.508(3)	1.496(3)	111.4(2)	128.7(3)	110.9(2)	110.0(2)	107.3(2)	134.0(2)	53.3(4)

Calculations.

To identify open and closed minima of the anions of **23** and **24**, the closed form of each was optimised using B3LYP/6-31++g(d,p). From each optimised structure the *peri* O-C bond length was scanned in 0.01 Å increments in both directions, allowing the rest of the molecule to relax at each step. The anion of dinitrile **23** was shown to have two minima, separated by a very small barrier for open and closed structures **33** and **29** (Figure S5). Optimisation starting from the point r_{OC} = 2.4 Å, resulted in the open form minimum (r_{OC} = 2.362 Å). All minima

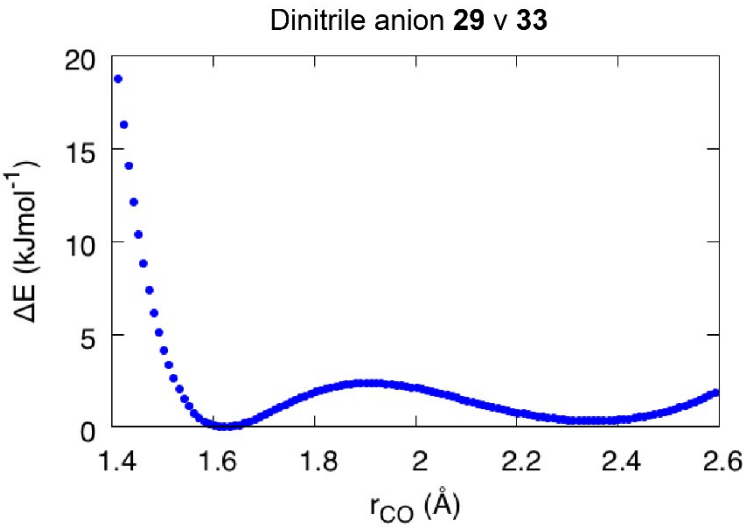


Figure S5. Plot of energy v O-C distance for the anion of **20**, with minima at 1.622 Å (for closed structure **29**) and 2.362 Å (for open structure **31**).

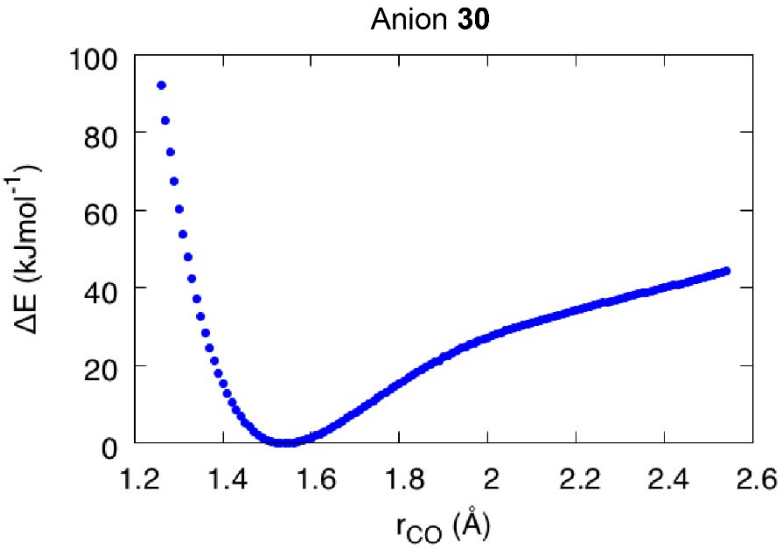


Figure S6. Plot of energy v O-C distance for the anion of **21**, with a minimum at 1.540 Å (for closed structure **30**).

were confirmed to have zero imaginary frequencies. In contrast, for the anion of the Meldrum's acid derivative, **30**, only a closed form was identified (Figure S6). Charge density distributions for the anions are shown in Figure S7.

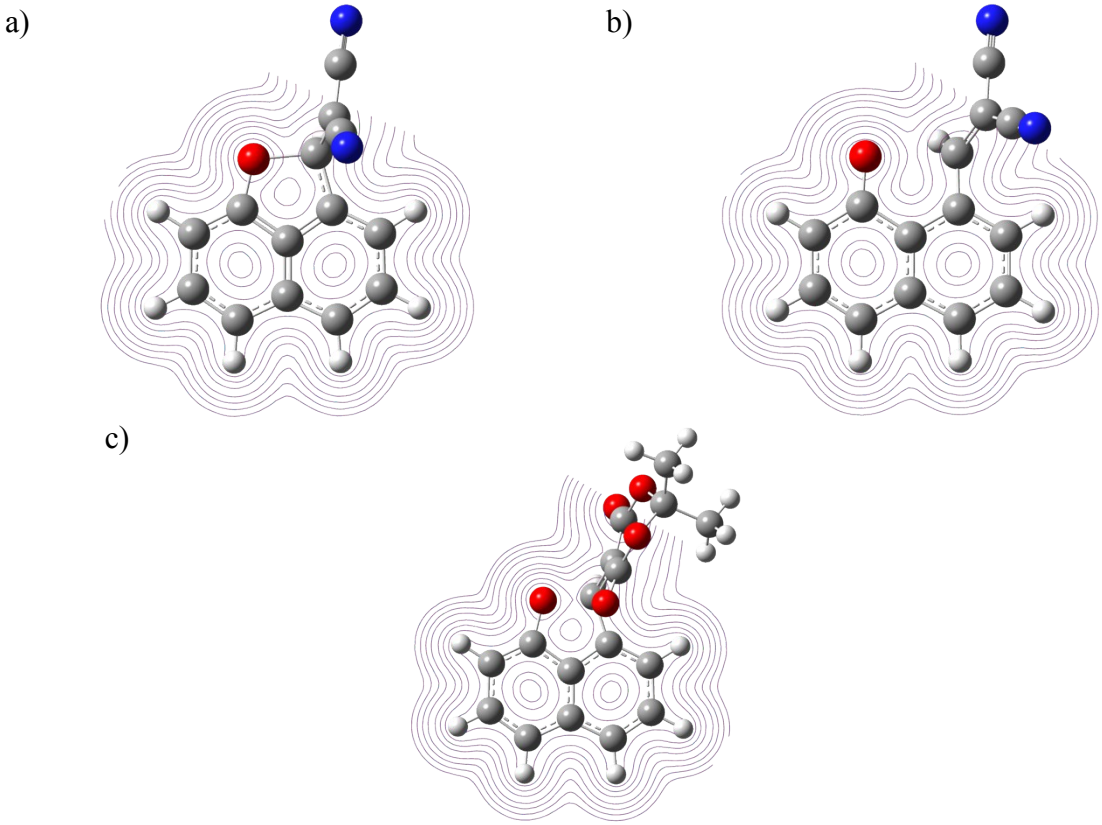


Figure S7. Charge density projected into the naphthalene plane of a) dinitrile closed structure **29**, b) dinitrile open structure **33** and c) the anion **30**.

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S1. Y. Bourdreux, S. Nowaczyk, C. Billaud, A. Mallinger, C. Willis, M. D.-E. Murr, L. Toupet, C. Lion, T. Le Gall, C. Mioskowski, *J. Org. Chem*., **2008**, *73*, 22-26.

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