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Colour and constitution of conjugate bases of benzodifurantrione, its ring-opened derivatives, and benzodifuranone dye analogues

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Electronic Supplementary Information

Contents

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Experimental and characterisation data - general

All non-aqueous reactions were performed under an inert atmosphere of dry nitrogen using oven-dried glassware. Reagents were used as received. Solvents used for chemistry were of Analar quality.

Analytical TLC was carried out on pre-coated 0.2 mm silica plates. The plates were visualised by UV light at 254 and 330 nm.

Nuclear magnetic resonance (NMR) spectra were recorded using residual non-deuterated solvent as the internal standard. Proton spectra (^{1}H) were recorded at 400 or 500 MHz. Carbon spectra (^{13}C) were recorded at 100 or 125 MHz. All chemical shifts (δ_H and δ_C) are quoted in parts per million (ppm), using tetramethylsilane as a standard. Coupling constants *J* are given in Hertz (Hz).

UV/vis/NIR spectra were recorded at 25°C. A 1 cm path length quartz cell was used. Solvents were 99+% grade with <50 ppm water. Solutions were prepared at 10 micromolar level concentrations (10^{-5} M).

Mass spectra were recorded using chemical ionisation (CI) and electrospray (ES) techniques.

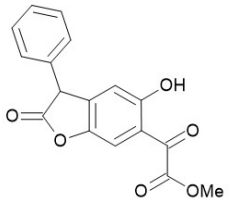
IR spectra were run either in solution in a sodium chloride cell dissolved in the stated solvent or dispersed in a solid KBr disc. Absorption maxima (ν_{max}) are quoted in wavenumbers (cm^{-1}).

BDF dyes **1a,b,c,d** were available from previous work.[1,2] Hplc and ^{1}H NMR confirmed their purity. BDT **2**, ester **6** and acid **7** were described in the earlier paper and its associated SI on phenylogous enolisation of BDT.[3]

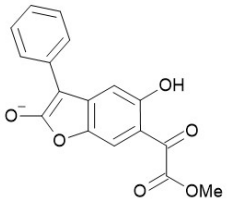
References

1. C. W. Greenhalgh, J. L. Carey and D. F. Newton, *Dyes and Pigments*, 1980**, 1**, 103-120
2. C. W. Greenhalgh, J. L. Carey, N. Hall and D. F. Newton, *J. Soc. Dyers Col*., 1994, **110**, 178-184
3. A. J. Lawrence, M. G. Hutchings, A. R. Kennedy and J. J. W. McDouall, *J. Org. Chem*., 2010, **75,** 690-701

Methyl (5-hydroxy-2-oxo-3-phenyl-2,3-dihydro-1-benzofuran-6-yl)(oxo)acetate (**6**) and 5-hydroxy-6-[methoxy(oxo)acetyl]-3-phenyl-1-benzofuran-2-olate (**16**)

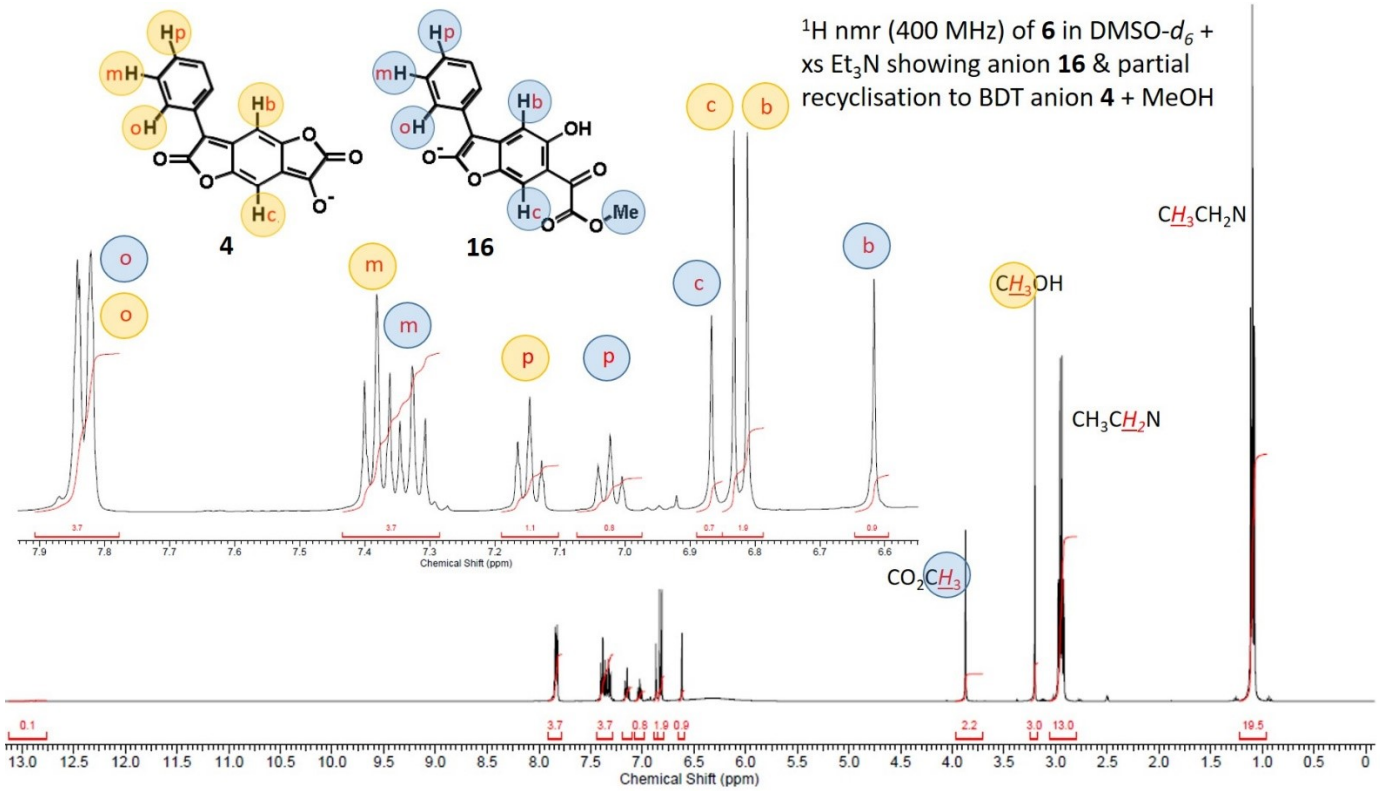


6

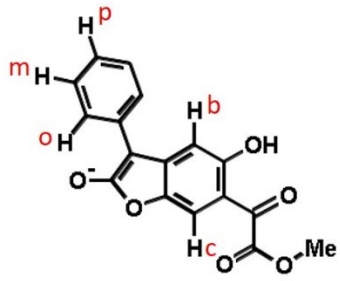


16

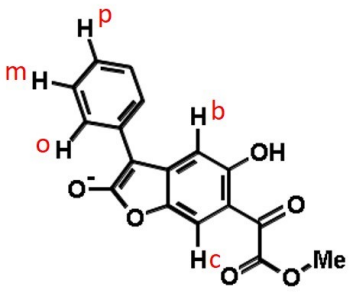
Details of the synthesis and characterisation of ester **6** were reported in the SI associated with reference 4 (main text). Conjugate base **16** was generated *in situ* by addition of triethylamine to solutions of **6**. In DMSO-d_6 excess amine led to partial ring closure back to the conjugate base **4** of BDT, as clearly evidenced by ^{1}H NMR, below. A slight molar deficiency of amine gave cleaner NMR spectra. HMQC and HMBC spectra led to unambiguous assignments. ^{1}H NMR (400 MHz, DMSO-d_6 + TEA) δ_H ppm 1.11 (tr, J = 7, $CH_3(Et_3NH^+)$), 3.02 (dq, J = 7 5, $CH_2(Et_3NH^+)$), 3.85 (s, 3H, $CH_3(CO_2Me)$), 6.62 (s, 1H, H*b*), 6.87 (s 1H, H*c*), 7.02 (tr, J = 9, 1H, H*p*), 7.33 (tr, J = 9, 2H, H*m*), 7.83 (d, J = 9, 2H, H*o*), 8.85 (br s, N^+H), 11.15 (br s, OH). ^{13}C NMR (100 MHz, DMSO-d_6 + TEA) δ_C ppm 8.5 ($CH_3(Et_3NH^+)$), 45.82 ($CH_2(Et_3NH^+)$), 52.44 ($CH_3(CO_2Me)$), 89.24 (C*a*), 96.13 (C*c*), 103.5 (C*h*), 104.37 (C*g*), 123.0 (C*n*), 124.82 (C*l*), 128.12 (C*m*), 136.12 (C*k*), 141.11 (C*i*), 142.7 (C*b*), 161.61 (C*d*), 165.51 (C*e*), 169.88 (C*j*), 181.41 (C*f*). λ_{max} (DCM +1 eqvt TEA) 451 nm (ε_{max} 4,800 M^{-1} cm^{-1}) (see also Table 2, main text). IR ν_{max} cm^{-1} (DCM + 1 eqvt TEA) 3100 (bw), 1720 (s), 1699 (s), 1530-1640 (m).

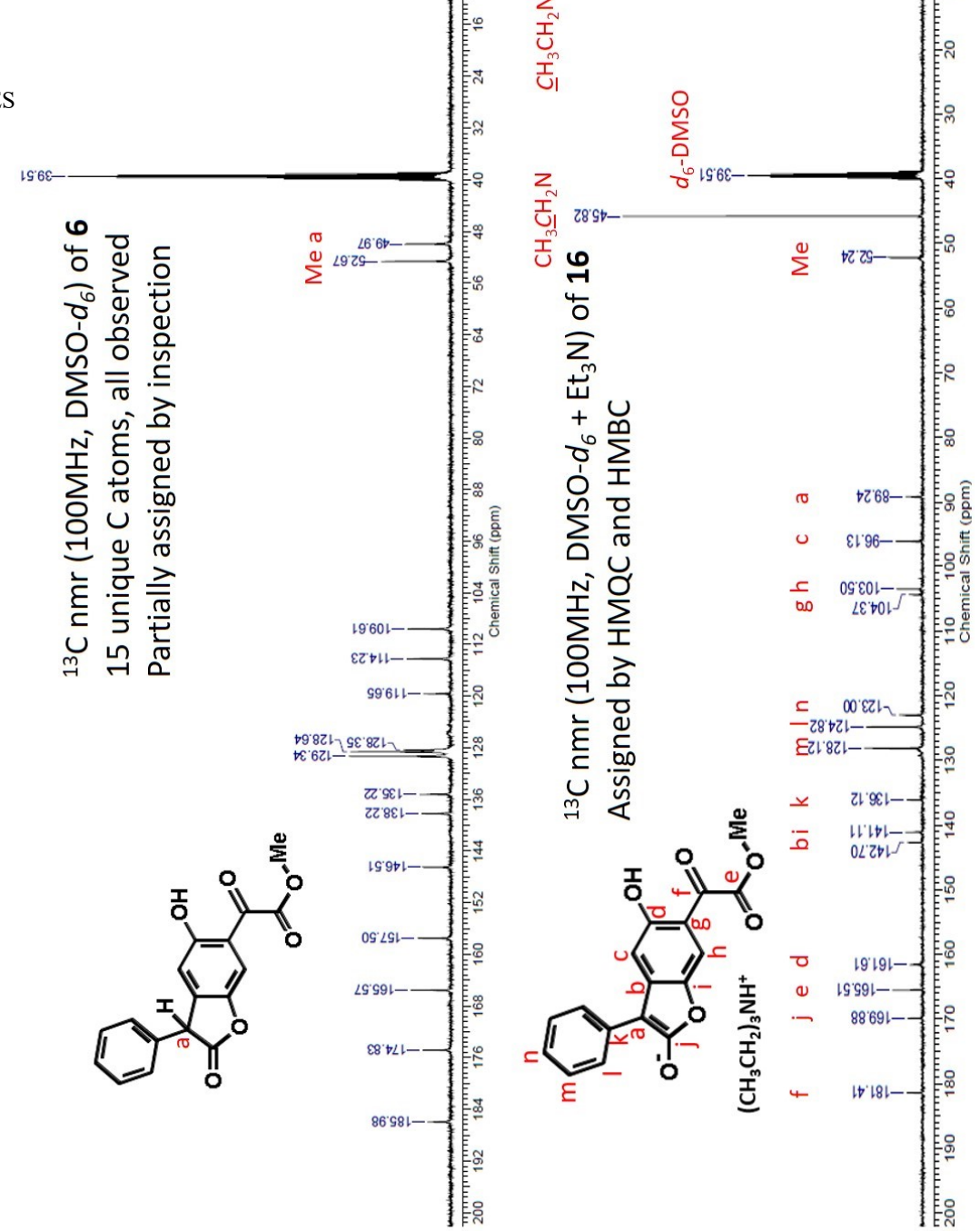


^{1}H nmr spectrum of **6** (400 MHz, DMSO-d_6 + <1 eqvt Et_3N)
Mainly anion **16** + minor parent material (*cf* Ha at δ_H 5.45)

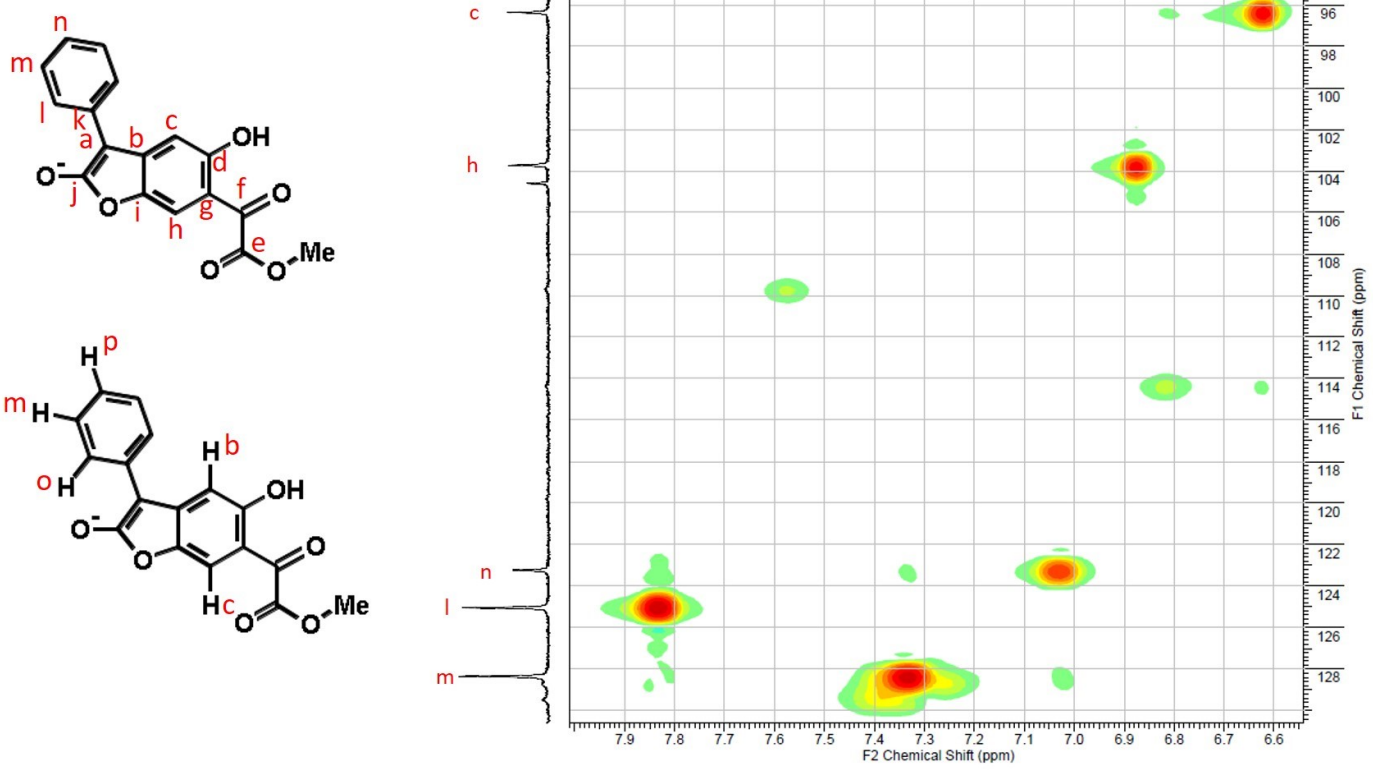


^{1}H nmr spectrum of **6** (400 MHz, DMSO-d_6 + <1 eqvt Et_3N)
Mainly anion **16** + minor parent material

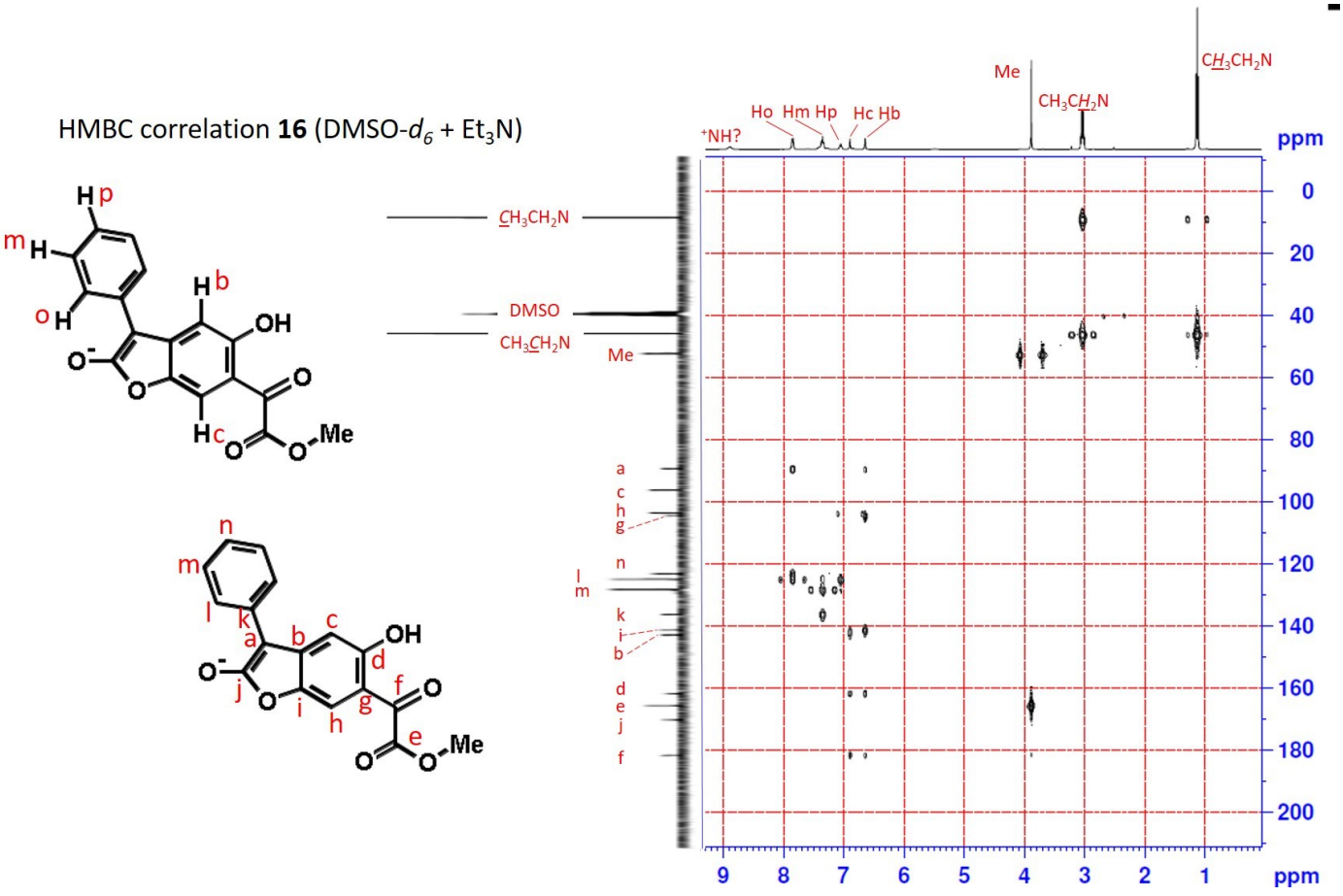



^{13}C nmr (100MHz, DMSO-d_6) of **6**
15 unique C atoms, all observed
Partially assigned by inspection
Me a
39.51
49.97
52.67
109.61
114.23
119.65
128.35
128.64
129.34
135.22
138.22
146.51
157.50
165.57
174.83
185.98
Chemical Shift (ppm)
^{13}C nmr (100MHz, DMSO-d_6 + Et_3N) of **16**
Assigned by HMQC and HMBC
$CH_3\underline{C}H_2N$
$\underline{C}H_3CH_2N$
d_6-DMSO
39.51
45.82
52.24
89.24
96.13
103.50
104.37
123.00
124.82
128.12
136.12
141.11
142.70
161.61
165.51
169.88
181.41
$(CH_3CH_2)_3NH^+$
Chemical Shift (ppm)

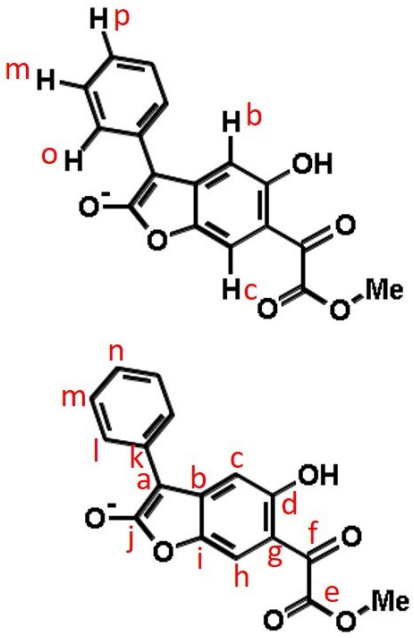
HMQC correlation **16** (DMSO-d_6 + Et_3N)



HMBC correlation **16** (DMSO-d_6 + Et_3N)



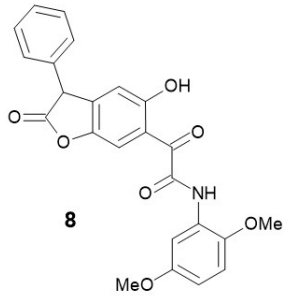
Summary of nmr assignments for **16** from HMQC and HMBC correlations (DMSO-d_6 +Et_3N)



		δ_H ppm & assignment					
		7.83	7.33	7.02	6.87	6.62	3.85
		Ho	Hm	Hp	Hc	Hb	Me
Assignment	δ_c ppm						
Me	52.44						HMQC
a	89.24	X				X	
c	96.13					HMQC	
h	103.5				HMQC		
g	104.37					X	
n	123	X		HMQC			
l	124.82	HMQC	w	X			
m	128.12		HMQC	w			
k	136.12		X				
i	141.11					X	
b	142.7				X		
d	161.61				X	X	
e	165.51						X
j	169.88						
f	181.41				X	w	w

HMBC: X =strong correlation, usually 3-bond; w = weak, usually 2-bond

N-(2,5-dimethoxyphenyl)-2-(5-hydroxy-2-oxo-3-phenyl-2,3-dihydro-1-benzofuran-6-yl)-2-oxoacetamide (**8**) and 6-[(2,5-dimethoxyanilino)(oxo)acetyl]-5-hydroxy-3-phenyl-1-benzofuran-2-olate (**17**)



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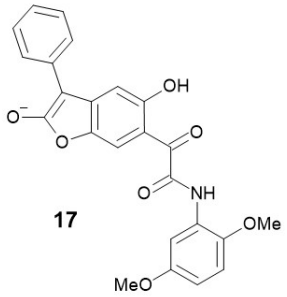


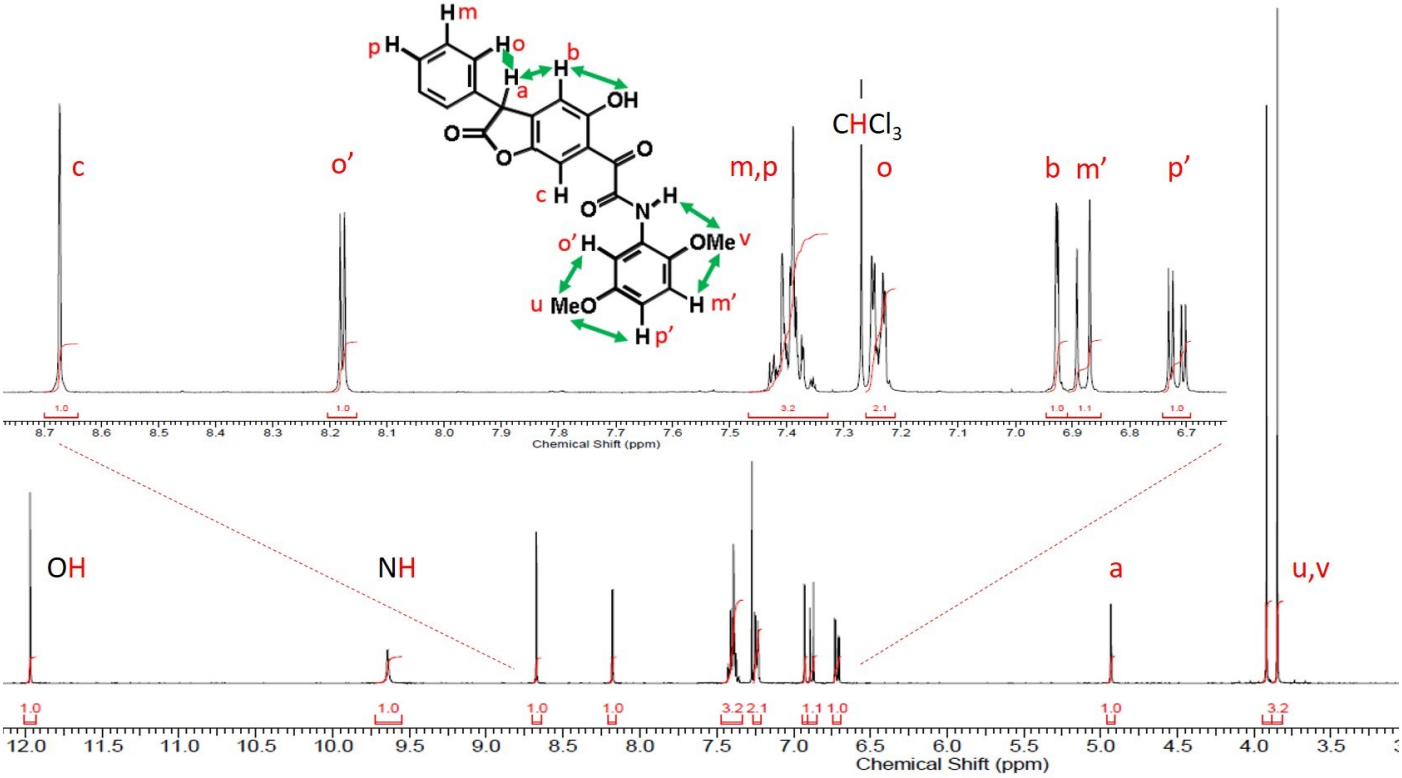
17

BDT (2g, 7.14mmol) and 2,5-dimethoxyaniline (1g, 6.53mmol) dissolved in acetic acid (20ml) were stirred at room temperature for 4 hours. The crude product was filtered and washed with acetic acid (50ml). The product was dried in a fan oven at 40°C overnight to give crude **8** as an orange solid (2.82g, 91.3%, mp 143°C). A sample (250mg) was purified by dissolving in chloroform (8ml) with sonication at room temperature, then filtered through glass wool to give a clear solution. On standing a small amount of solid precipitated. The solution was again filtered and then evaporated to give a yellow foam. The entire process was repeated. The product was dried under high vacuum for several hours to yield a final yellow foam (**8**; 141mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 3.85 (s, 3H, OMe), 3.92 (s, 3H, OMe), 4.94 (br s, 1H, H*a*), 6.72 (dd, *J* = 3.0, 9.0, 1H, H*p'*), 6.88 (d, *J* = 9.0, 1H, H*m'*), 6.93 (d, *J* = 1.3, 1H, H*b*), 7.23 (m, 2H, H*o*), 7.40 (m, 3H, H*m* and H*p*), 8.18 (d, *J* = 3.0, 1H, H*o'*), 8.68 (s, 1H, H*c*), 9.65 (br s, 1H, NH), 11.98 (s, 1H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 50.60, 56.12, 56.60, 106.56, 110.71, 111.29, 113.84, 115.94, 116.99, 126.66, 128.54, 128.89, 129.65, 134.10, 139.19, 143.35, 146.45, 154.03, 159.00, 162.53, 174.24, 188.81 ppm. Mass spec EI/CI, 433 (M^+). λ_{max} (DCM + trace MSA) 389 nm (ε_{max} 10,000 M^{-1} cm^{-1}). IR ν_{max} (KBr) 3370 (NH amide), 3000-3200 (bm, OH), 1801 (lactone), 1683 (amide), 1624 (H-bonded ketone), 1527 cm^{-1}; (DCM) 3347 (NH amide), 3100 (bw, OH)) 1818 (lactone), 1692 (amide), 1628 (H-bonded ketone), 1531 cm^{-1}. Found C, 66.16%; H, 4.23%; N, 3.12%. $C_{24}H_{19}NO_7$ requires C, 66.51%; H, 4.42%; N, 3.23%.

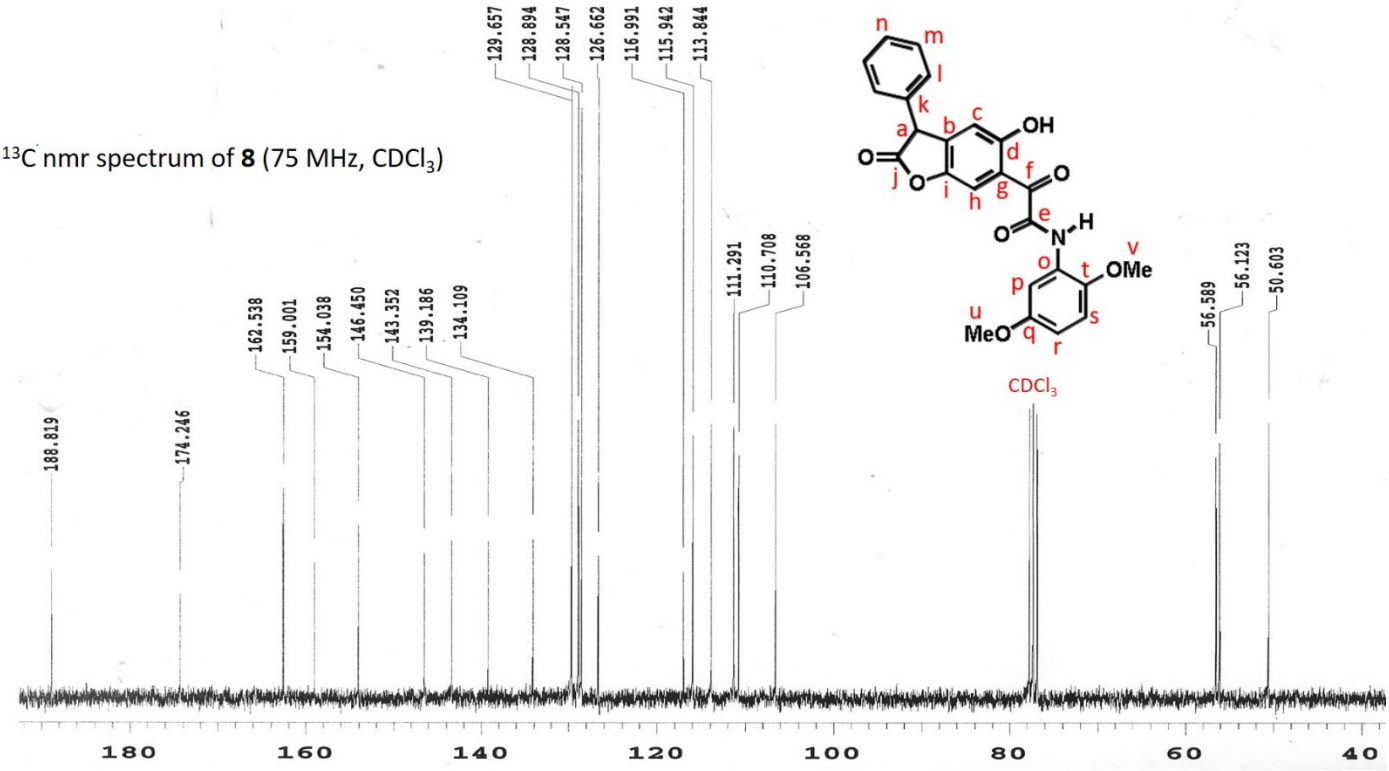
Conjugate base **17** was generated *in situ* by addition of one equivalent of triethylamine to solutions of **8**. HMQC and HMBC spectra led to unambiguous NMR assignments, following. ^{1}H NMR (500 MHz, DMSO-d_6 + 1 eqvt TEA) δ_H 1.08 (t *J* = 7, 9H, $CH_3(Et_3N^+H)$), 2.80 (q, *J* = 7, 6H, $CH_2(Et_3N^+H)$), 3.75 (s, 3H, Me*u*), 3.85 (s, 3H, Me*v*), 6.57 (s, 1H, H*b*), 6.68 (dd, *J* = 3 9, 1H, H*p'*), 7.00 (d, *J* = 9, 1H, H*m'*), 7.06 (tr, *J* = 9, 1H, H*p*), 7.35 (tr, *J* = 9, 2H, H*m*), 7.84 (d, *J* = 9, 2H, H*o*), 8.00 (s, 1H, H*c*), 8.01 (d, *J* = = 3, 1H, H*o'*), 10.00 (s, 1H, NH), 13.49 (bs, 1H, OH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6 + 1 eqvt TEA) δ_C 10.0 ($\underline{C}H_3CH_2N^+$), 45.05 ($CH_3\underline{C}H_2N^+$), 55.36 (C*u*), 56.25 (C*v*), 91.09 (C*a*), 95.8 (C*c*), 104.58 (C*h*), 105.88 (C*g*), 106.4 (C*p*), 108.35 (C*r*), 111.55 (C*s*), 123.24 (C*n*), 125.04 (C*l*), 127.13 (C*o*), 128.07 (C*m*), 135.83 (C*k*), 141.3 (C*i*), 142.82 (C*b*), 143.05 (C*t*), 153.12 (C*q*), 162.5 (C*e*), 163.92 (C*d*), 170.09 (C*j*), 177.51 (C*f*) ppm. λ_{max} (DCM + 1 eqvt Et_3N) 496 nm (ε_{max} 18,200 M^{-1} cm^{-1}). IR ν_{max} (DCM + 1 eqvt Et_3N) 3300 (w NH amide), 1681, 1649, 1620, 1598 cm^{-1}.

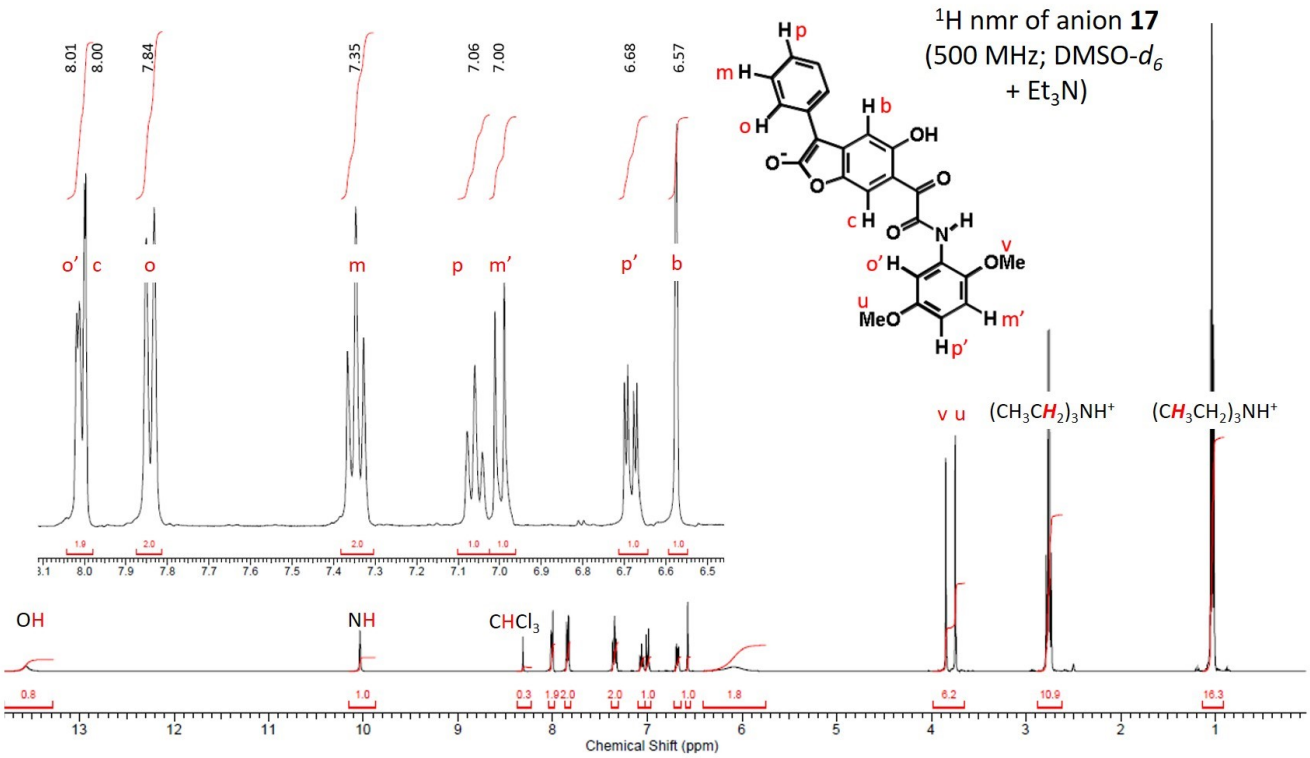
^{1}H nmr spectrum of amide (**8**) (500 MHz, $CDCl_3$)

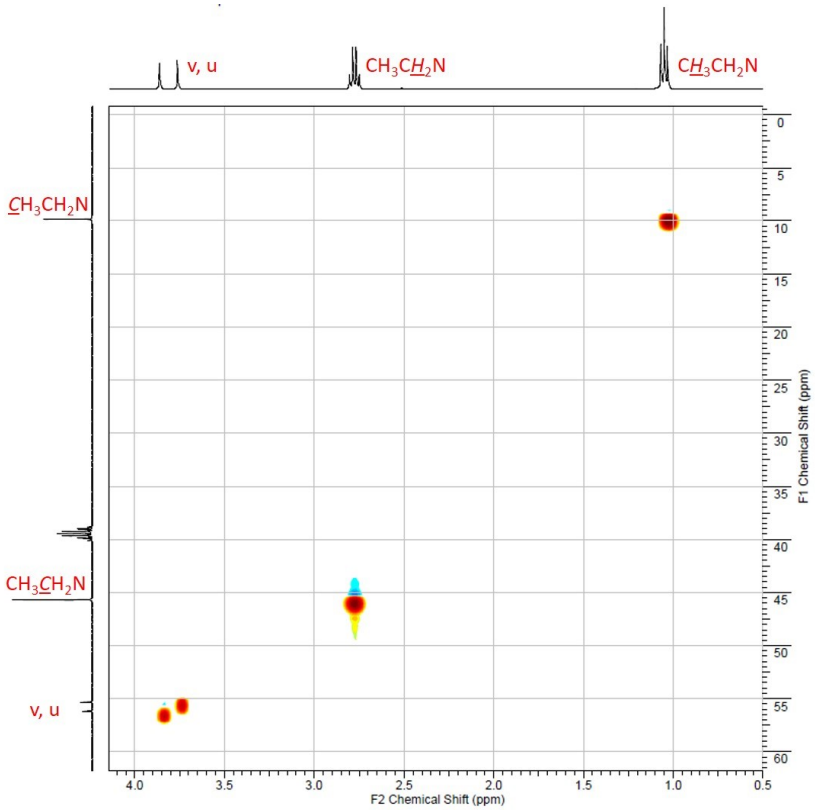
↔ NOE interactions from a NOESY spectrum (not shown)



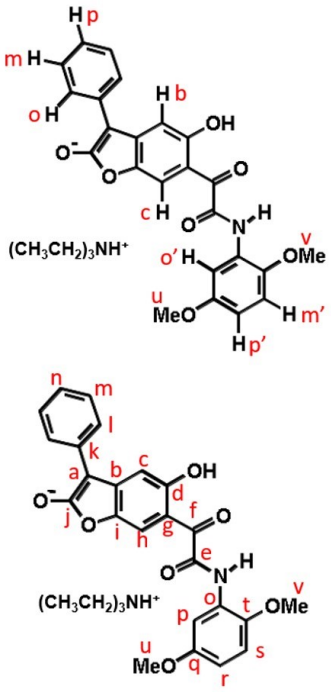
^{13}C nmr spectrum of **8** (75 MHz, $CDCl_3$)

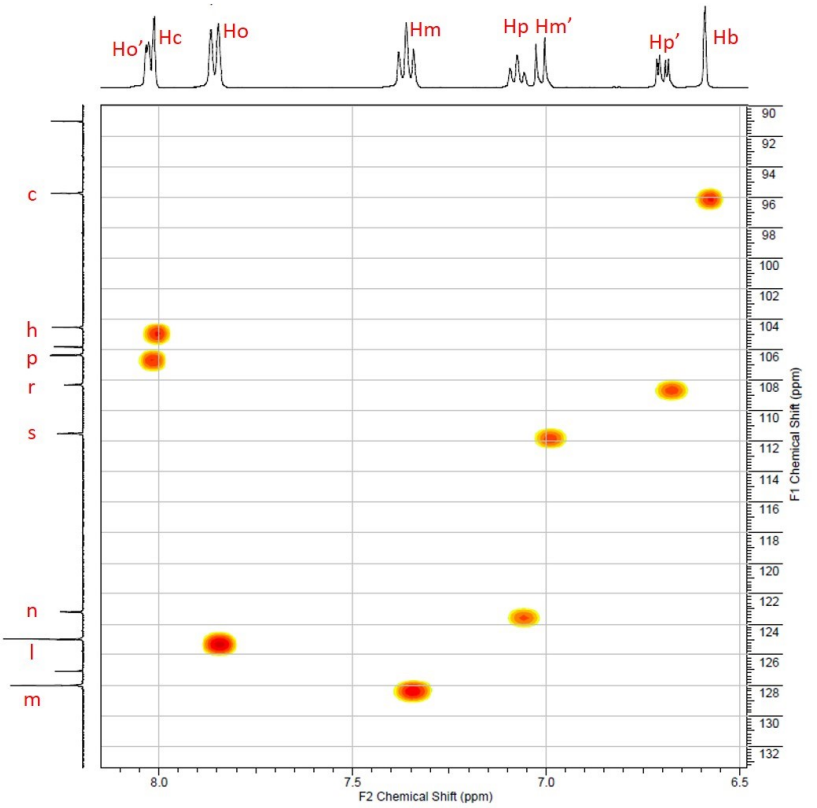



^{1}H nmr of anion **17**
(500 MHz; DMSO-d_6
+ Et_3N)
8.01
8.00
7.84
7.35
7.06
7.00
6.68
6.57
o′ c o m p m′ p′ b
v u
$(CH_3CH_2)_3NH^+$
$(CH_3CH_2)_3NH^+$
OH
NH
$CHCl_3$
Chemical Shift (ppm)

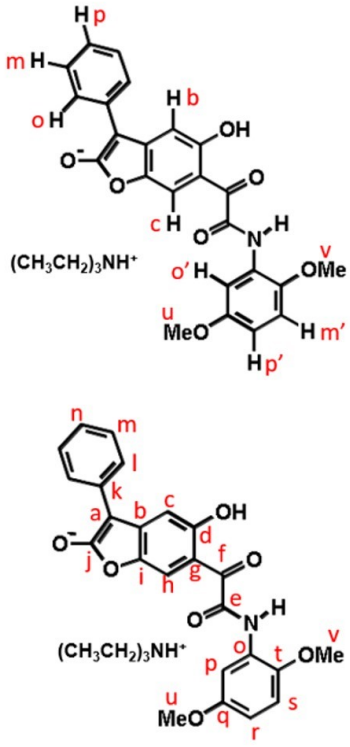


HMQC correlations for **17** (DMSO-d_6 +Et_3N)

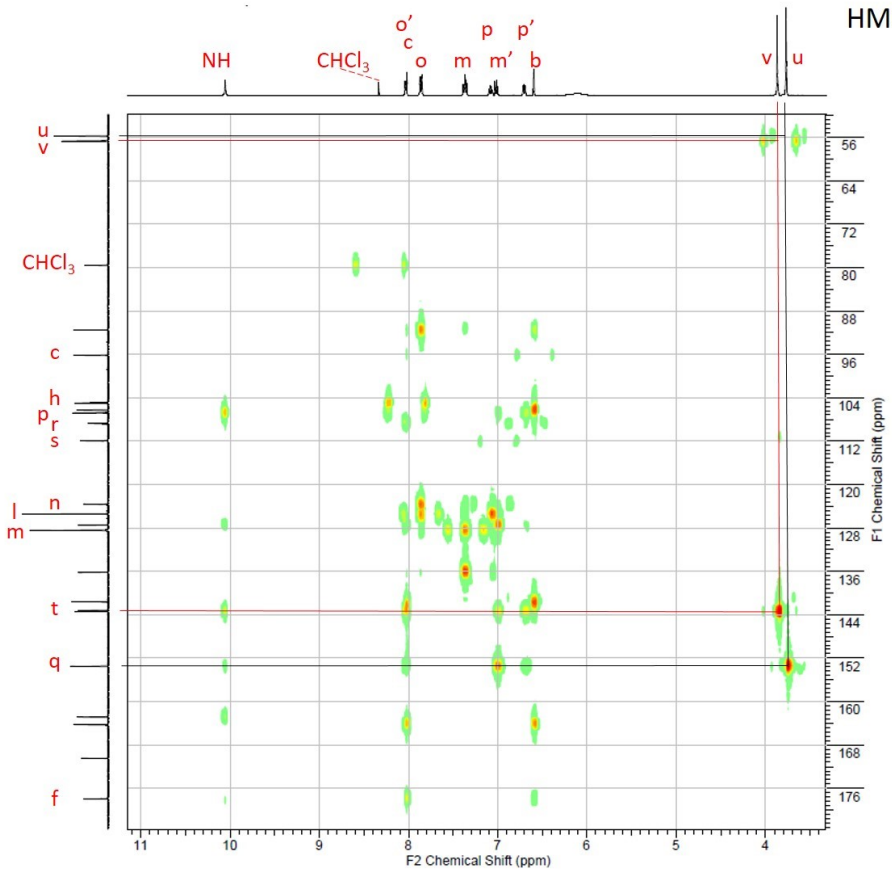


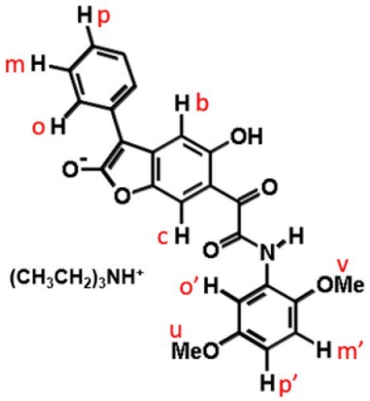


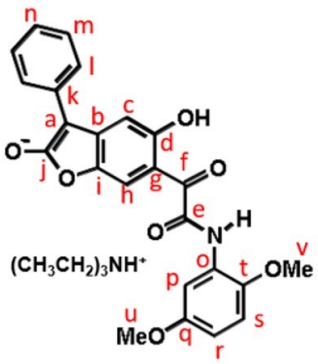
HMQC correlations for **17** (DMSO-d_6 +Et_3N)



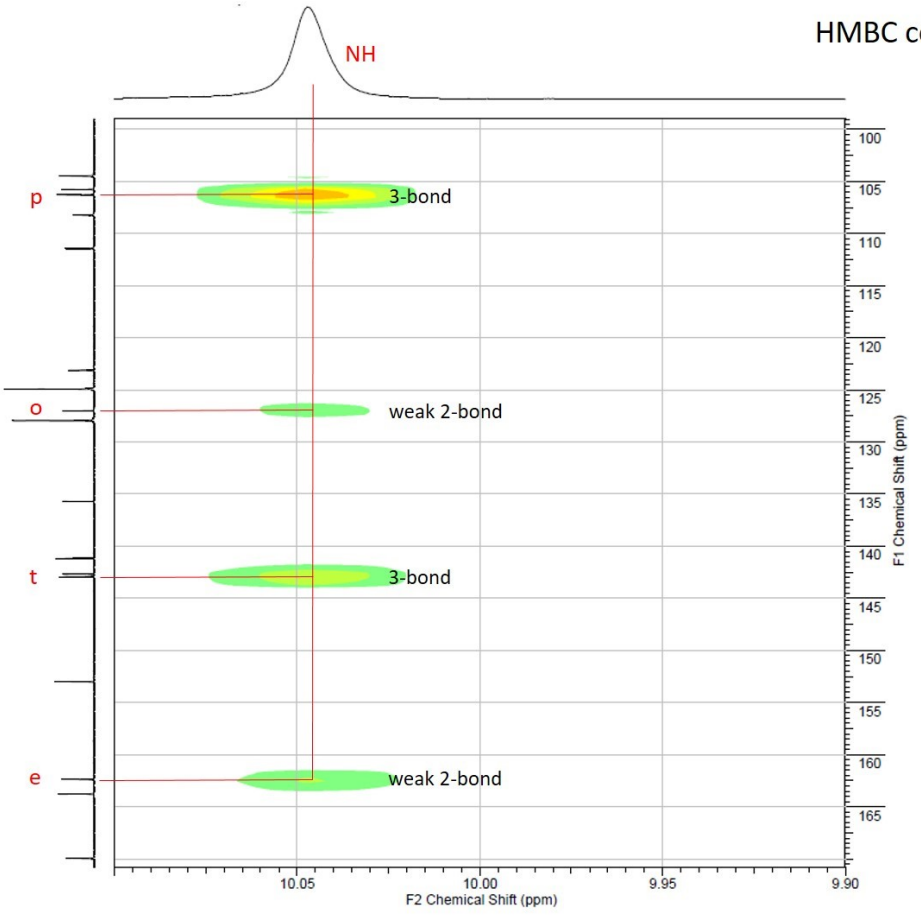
HMBC correlations for **17** (DMSO-d_6 +Et_3N)

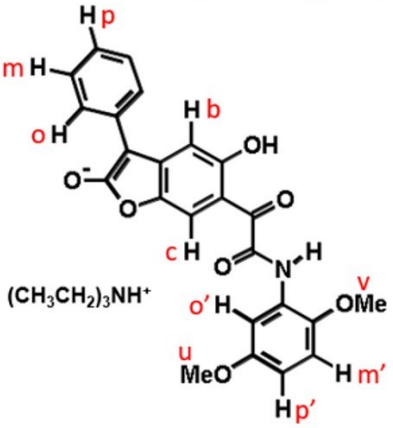


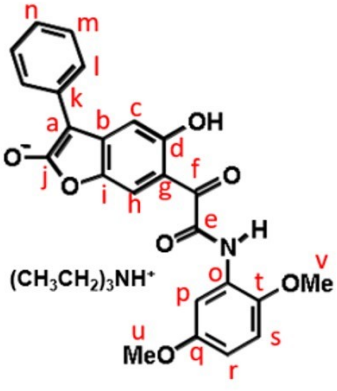




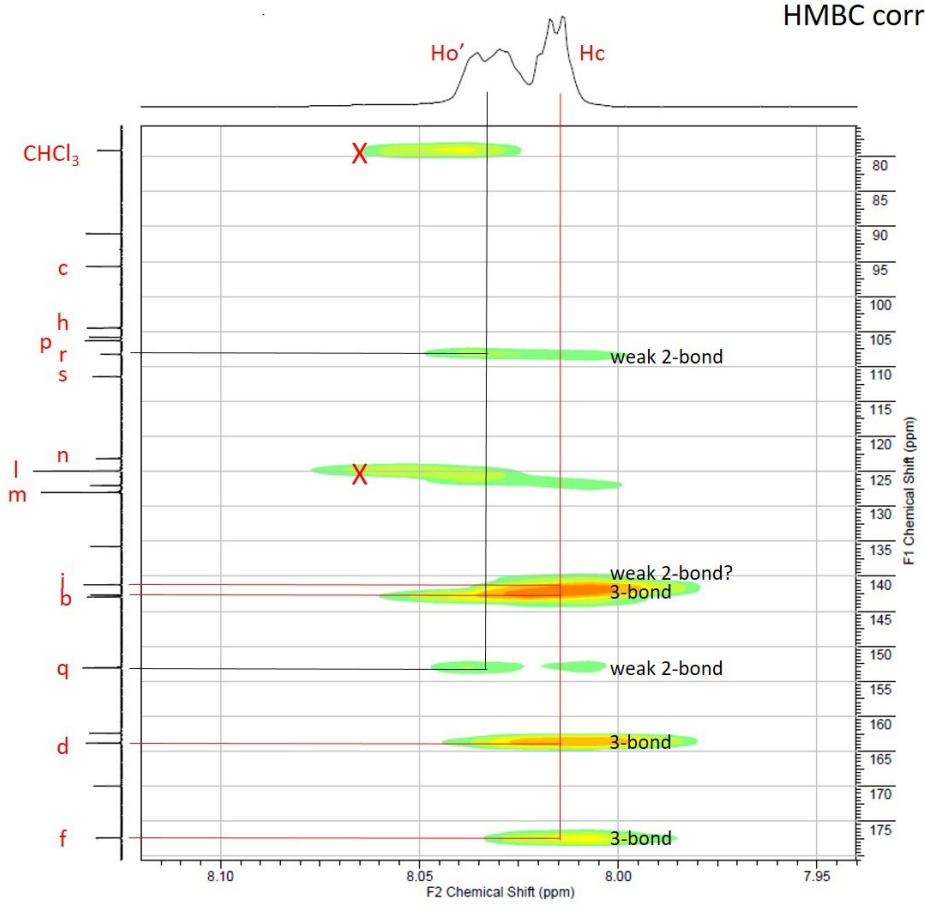
HMBC correlations for **17** (DMSO-d_6 +Et_3N)

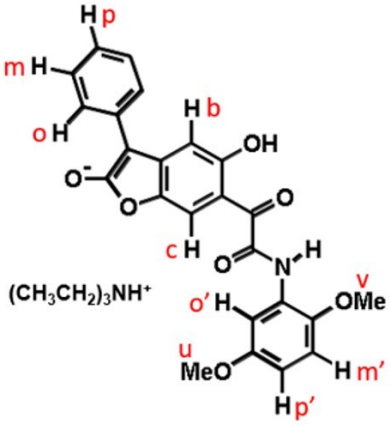


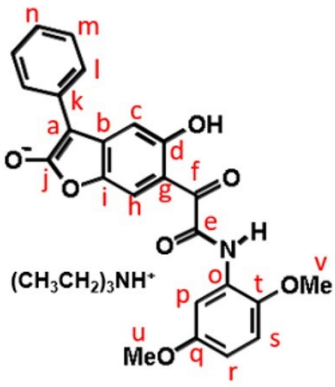


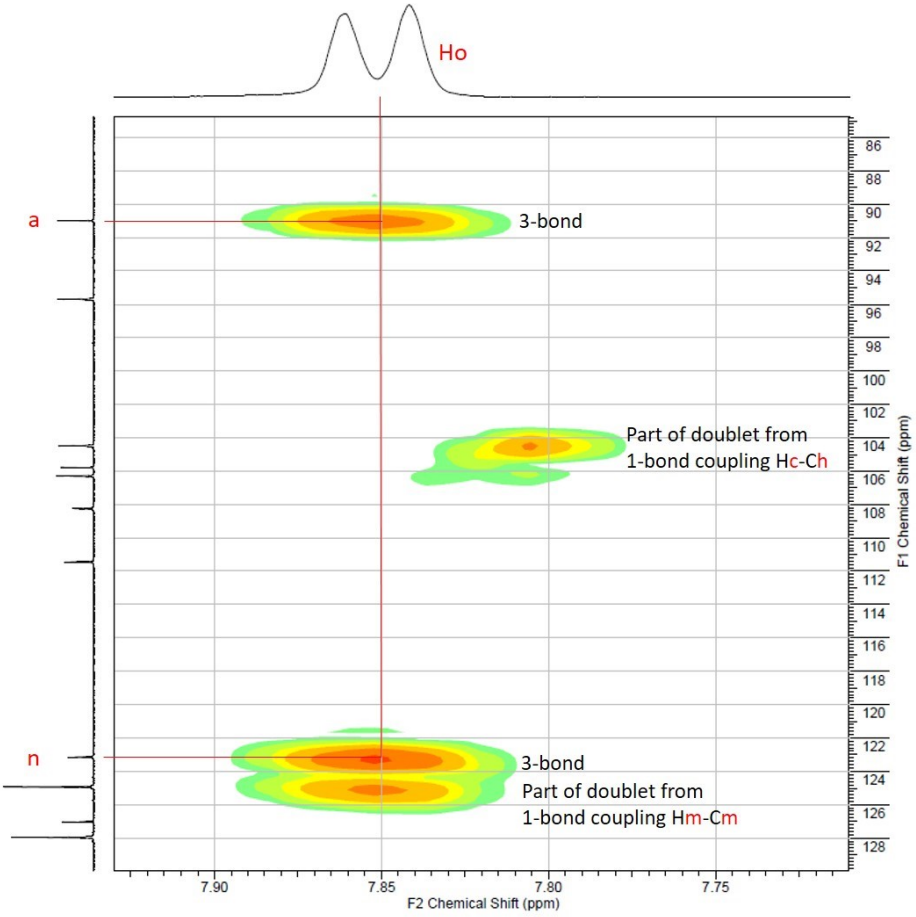


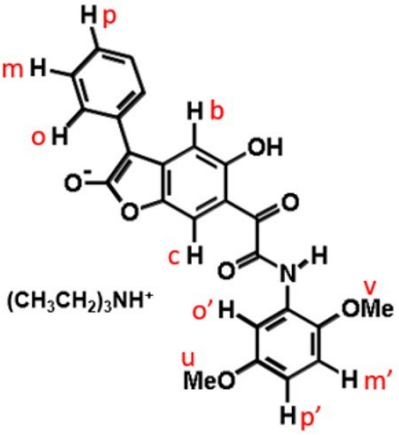
HMBC correlations for **17** (DMSO-d_6 +Et_3N)

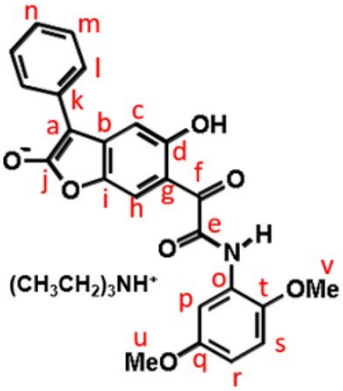




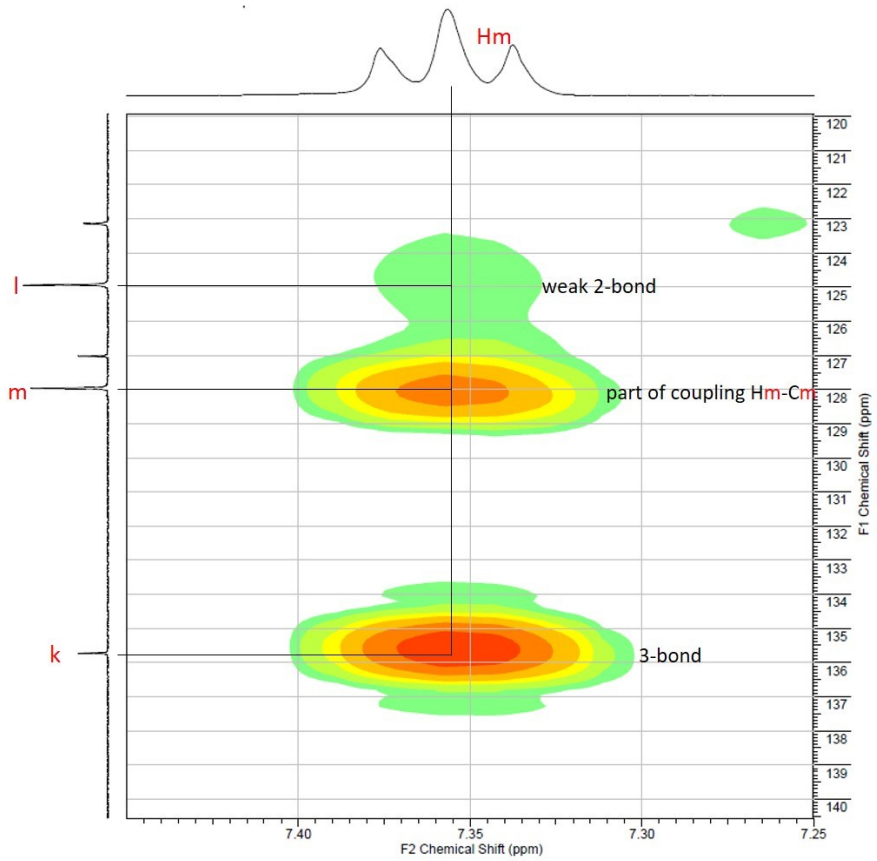


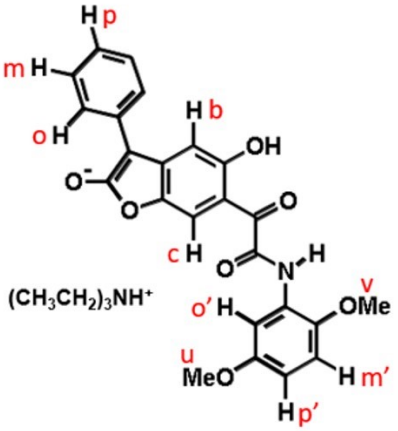


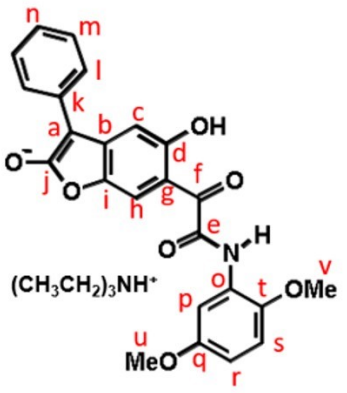




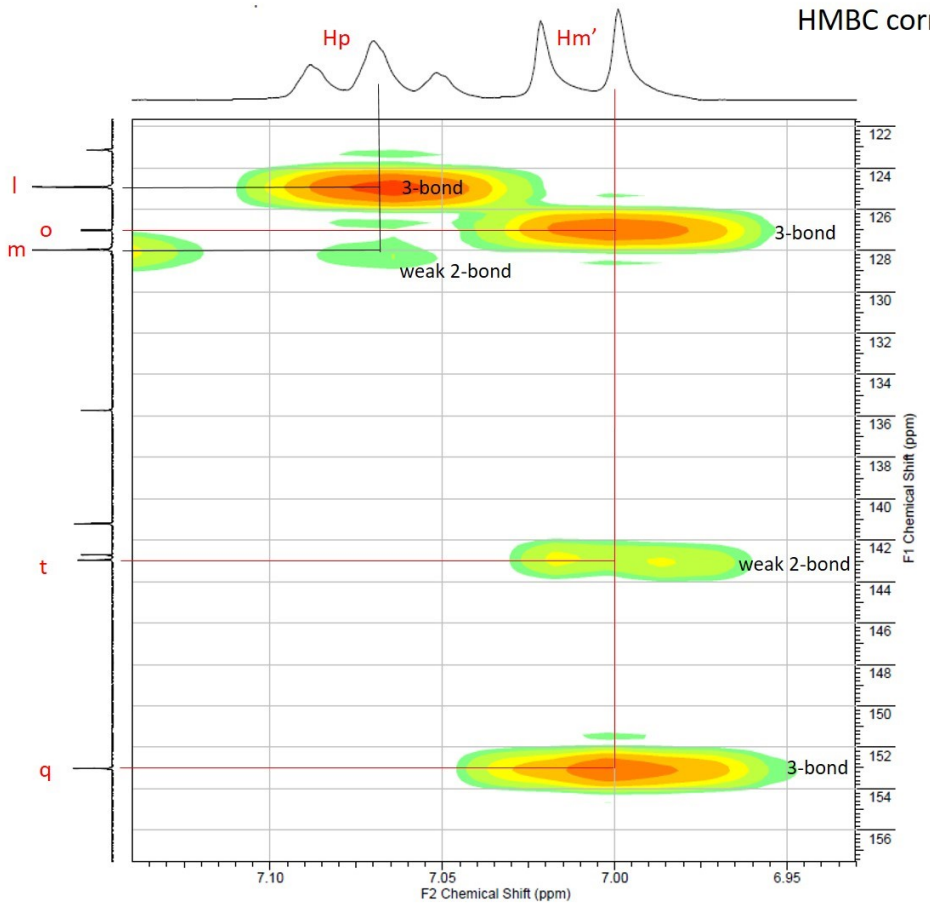
HMBC correlations for **17** (DMSO-d_6 +Et_3N)

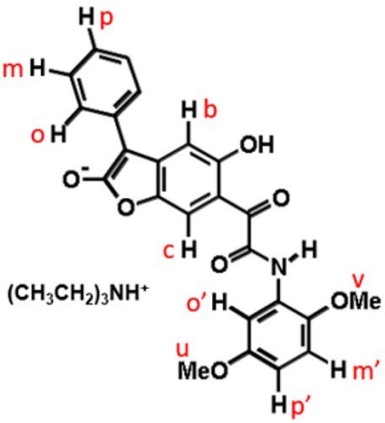


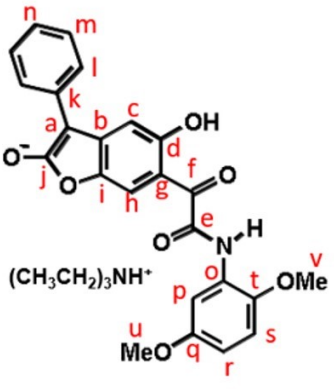




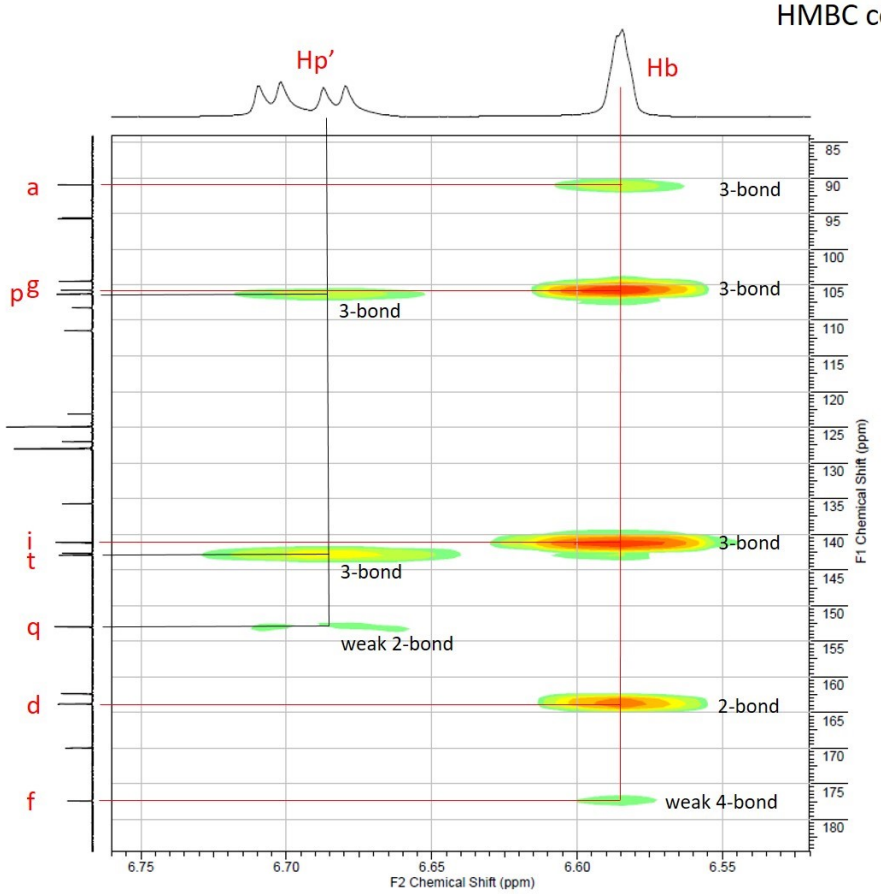
HMBC correlations for **17** (DMSO-d_6 +Et_3N)

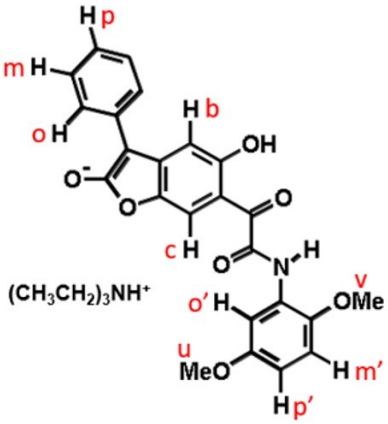


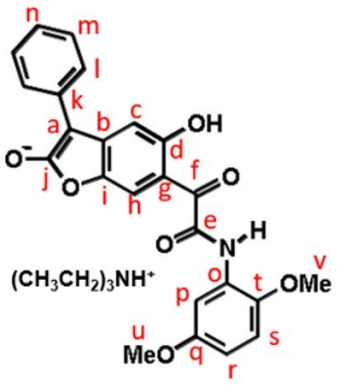




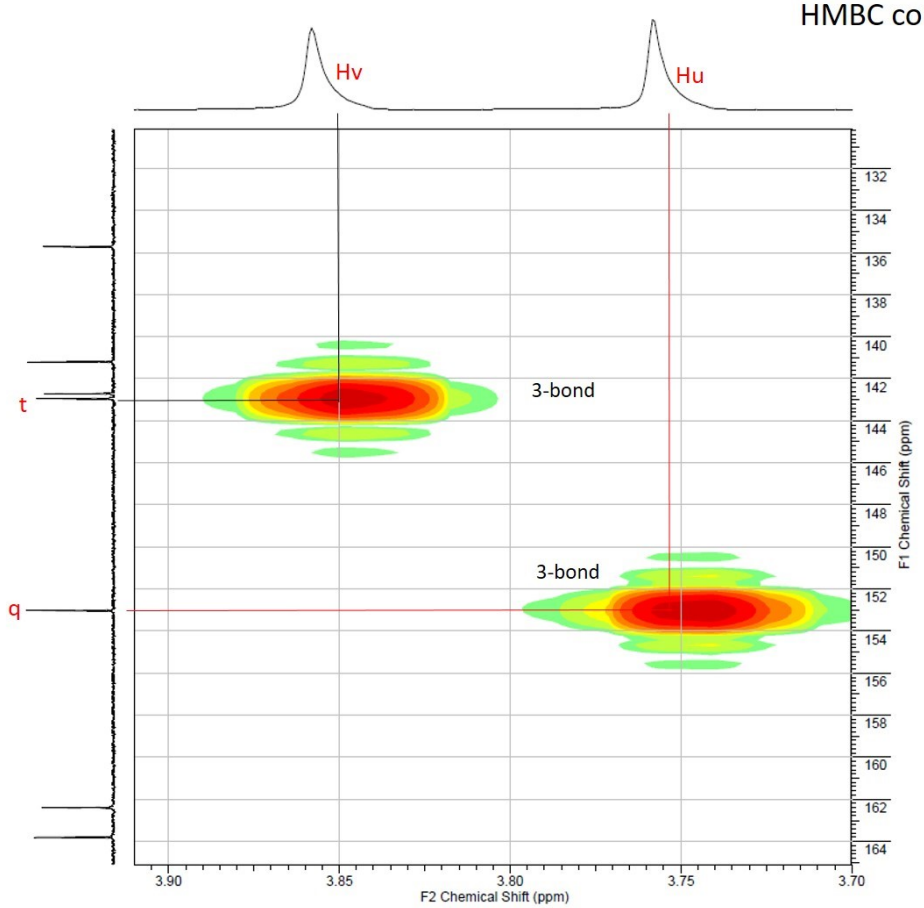
HMBC correlations for **17** (DMSO-d_6 +Et_3N)

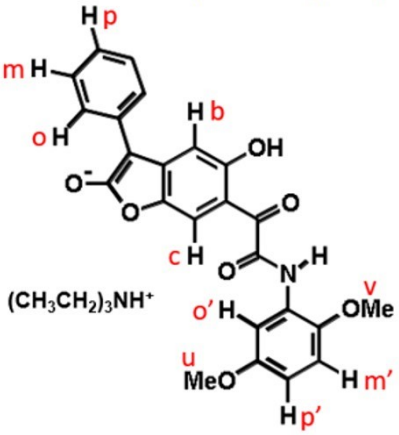


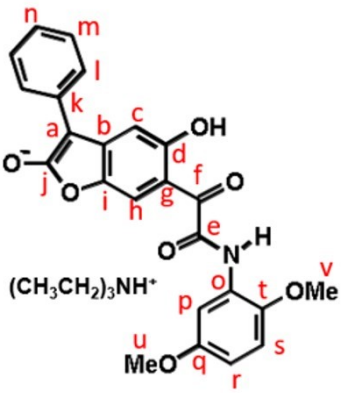




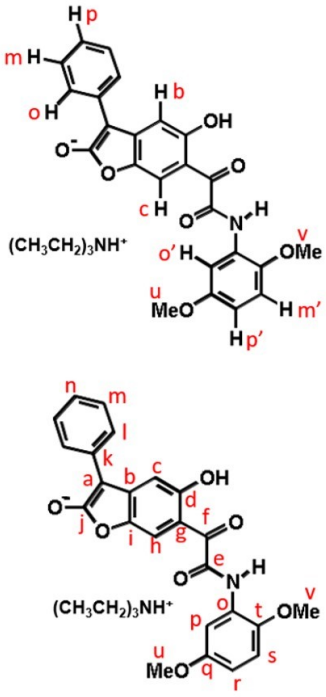
HMBC correlations for **17** (DMSO-d_6 +Et_3N)







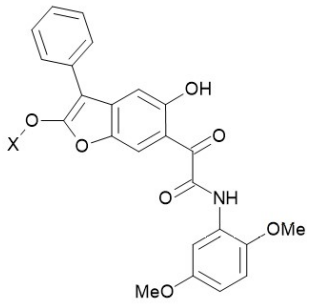
Summary of nmr assignments for **17** from HMQC and HMBC (DMSO-d_6 +Et_3N)



		δ_H ppm & assignment											
		13.49	10.00	8.01	8.00	7.84	7.35	7.06	7.00	6.68	6.57	3.85	3.75
		OH	NH	Ho'	Hc	Ho	Hm	Hp	Hm'	Hp'	Hb	Hv	Hu
Assignment	δ_C ppm												
u	55.36												HMQC
v	56.25											HMQC	
a	91.09				w	X	w				X		
c	95.8										HMQC		
h	104.58				HMQC						w?		
g	105.88										X		
p	106.4		X	HMQC					w	X			
r	108.35			X						HMQC			
s	111.55								HMQC			w	
n	123.24					X		HMQC					
l	125.04					HMQC	w	X					
o	127.13		X						X				
m	128.07						HMQC	w					
k	135.83					w	X	w					
i	141.3				X?						X		
b	142.82				X								
t	143.05		w						X	X		X	
q	153.12		X	w					X	w			X
e	162.5		X										
d	163.92				X						X		
j	170.09												
f	177.51		w		X						w		

^{1}H nmr spectrum assigned initially by inspection; Hb/Hc and Hu/Hv differentiated by HMBC correlations
HMBC: X = correlation; w = weak correlation; ? = unreliable: possible overlap with adjacent correlation

N-(2,5-dimethoxyphenyl)-2-(5-hydroxy-3-phenyl-2-trimethylsilylmethoxy-1-benzofuran-6-yl)-2-oxoacetamide (**12**) and *N*-(2,5-dimethoxyphenyl)-2-(5-hydroxy-2-methoxy-3-phenyl-1-benzofuran-6-yl)-2-oxoacetamide (**13**)



12 X = Me_3SiCH_2
13 X = CH_3

Amide **8** (0.5g, 1.15mmol) in toluene (50ml) was brought to 40°C. TMS-Diazomethane (0.5ml, 3.45mmol) was added dropwise. After 3hrs the reaction mixture was brought to room temperature and stirred in methanol (20ml) overnight. Tlc revealed 2 closely running yellow spots as products, and no starting material. The solvent was evaporated and the major product isolated by column chromatography to give **12** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H ppm 0.19 (s, 9H, Me_3Si), 3.85 (s, 3H, OMe), 3.92 (s, 3H, OMe), 4.31 (s, 2H, $SiCH_2$), 6.69 (dd *J* = 8.83, 2.84, 1H, H*p'*), 6.88 (d *J* = 8.83, 1H, H*m'*), 7.22 (s, 1H, H*b*), 7.29 (t *J* = 7.88, 1H, H*p*), 7.45 (t *J* = 7.88, 2H, H*m*), 7.66 (d *J* = 7.25, 2H, H*o*), 8.25 (d *J* = 2.84, 1H, H*o'*), 9.01 (s, 1H, H*c*), 9.75 (s, 1H, NH), 12.09 (s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C ppm -3.30 (Me_3Si), 55.46, 56.31, 58.71, 66.53, 93.36, 104.31, 108.33, 109.27, 112.23, 125.32, 126.76, 127.05, 128.20, 128.84, 128.89, 130.35, 130.58, 141.16, 144.06, 152.96, 158.55, 188.03 (C*f*). λ_{max} (acetone) 394nm. IR ($CHCl_3$) ν_{max} cm^{-1} 3400 (NH), 2920 (br, OH), 1688 (amide), 1598 (H-bonded aryl ketone), 1528. HRMS m/z Calcd for $C_{28}H_{29}NO_7Si$ [M+H$^+$]: 520.1792. Found: 520.1785

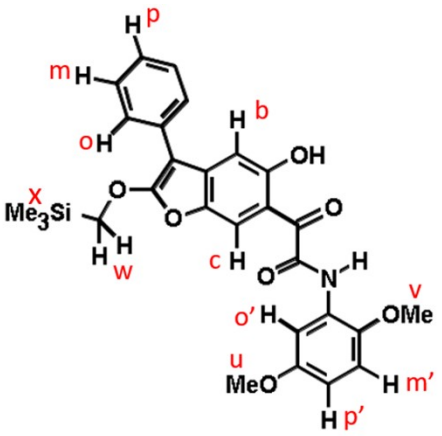
The minor product was not isolated pure. It is assigned the structure of the methyl ether analogue (**13**) of the TMS-substituted methyl ether (**12**) on the basis of the ^{1}H NMR spectra of enriched fractions; see example below. In a roughly 50/50 mixture of **12** and **13** the following features of the NMR spectrum ($CDCl_3$) stand out, and overall are consistent with the assigned methyl ether structure (**13**):

- A second OH resonance is observed of near equal integrated intensity (δ_H (**12**) 12.09, (**13**) 12.05 ppm)
- A second H*c* resonance is observed of near equal integrated intensity (δ_H (**12**) 9.01, (**13**) 9.05 ppm)
- All other aromatic ^{1}H resonances overlap more or less exactly
- The $TMSCH_2$ resonance (δ_H (**12**) 4.31 ppm) is accompanied by another (δ_H (**13**) 4.24 ppm) of 50% higher integrated intensity, assigned CH_3O
- The remaining TMS resonance (δ_H (**12**) 0.19 ppm) is 50% intensity of that expected for pure **12** based on ArH intensities

Additionally ^{1}H NMR spectra of different ratios of **12** and **13** gave relative peak intensities consistent with the above assignment.

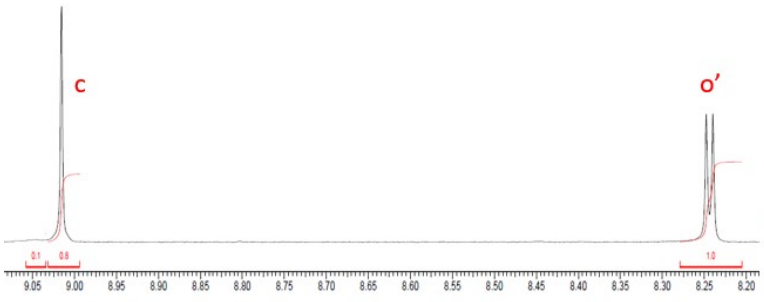
Small scale attempts to desilylate **12** to give **13** failed:

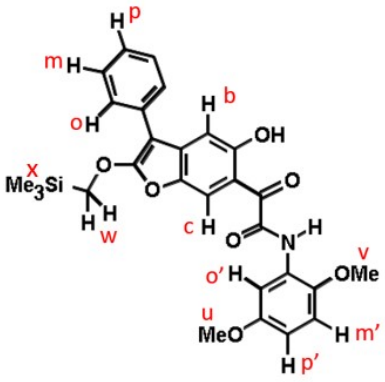
- 2N HCl gave decomposition to amide (**8**) and other products
- Methane sulfonic acid (trace) gave no conversion
- Biphasic $Me_4N^+Cl^-$/KF in water and **12** in DCM gave no conversion
- $PhEt_3N^+Cl^-$ in DCM plus KF plus one drop of water gave no conversion.

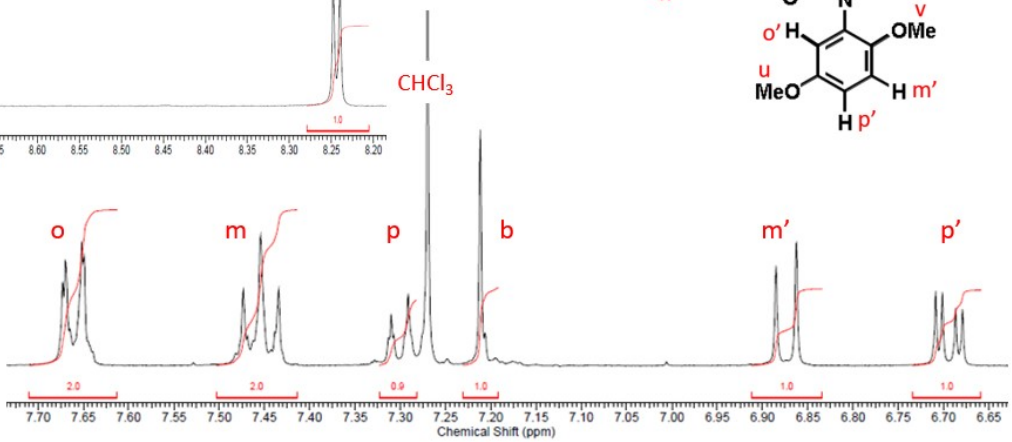


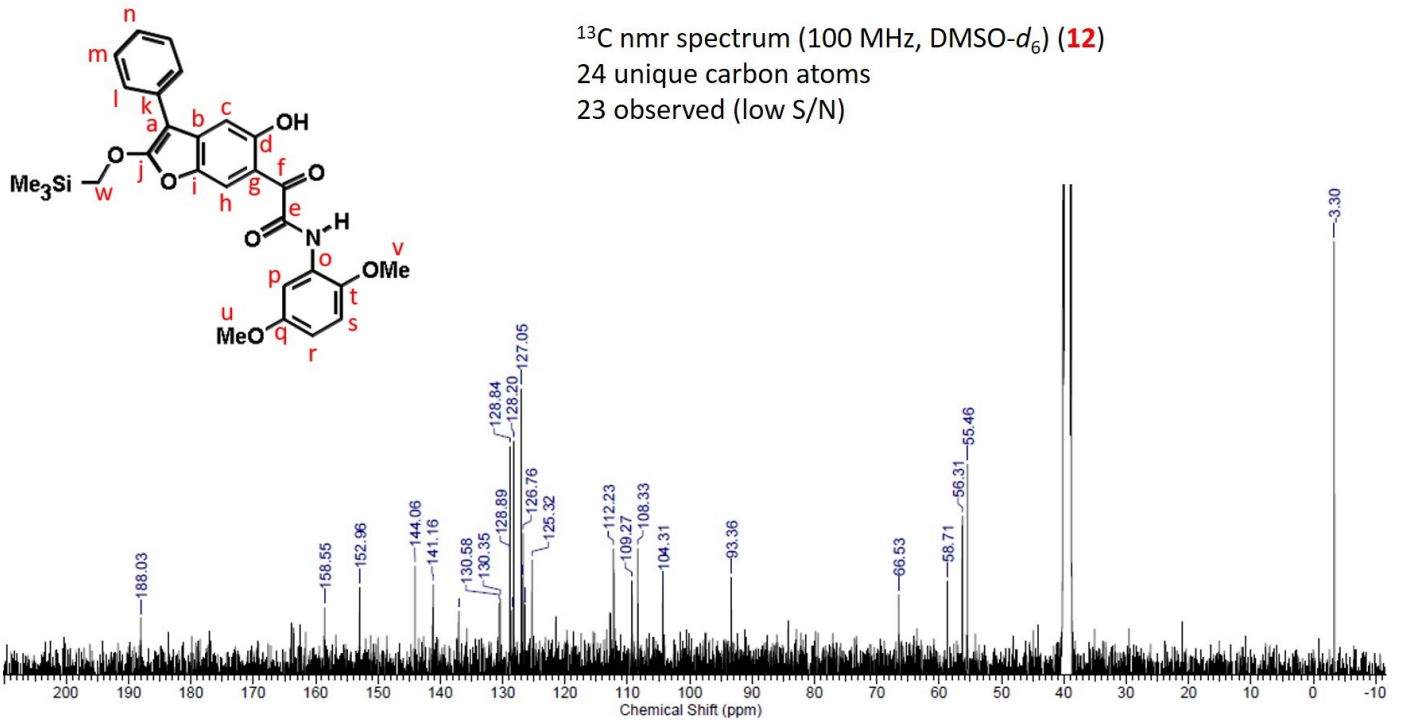
^{1}H nmr spectrum of **12** (400 MHz, $CDCl_3$)

^{1}H nmr spectrum of **12** (400 MHz, $CDCl_3$)
Expansions

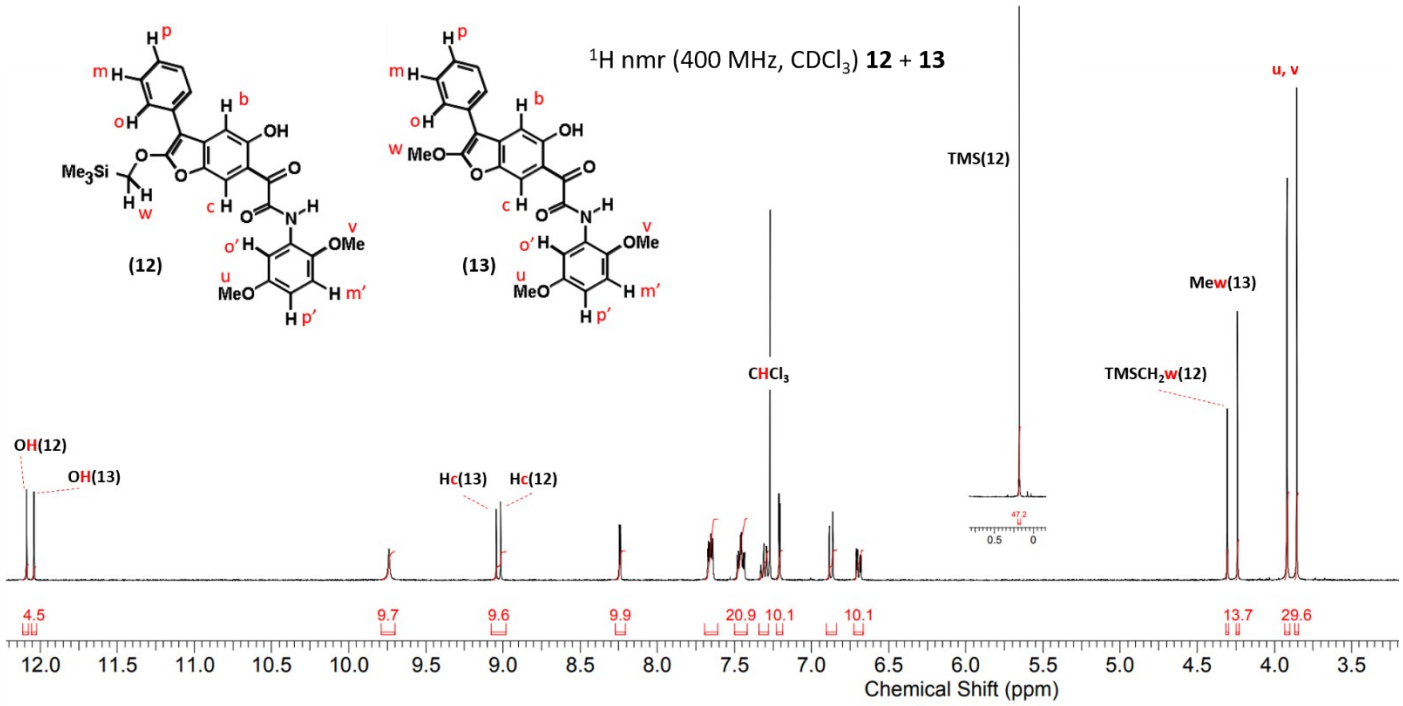




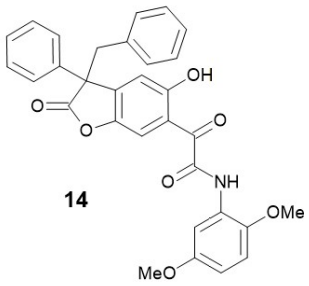




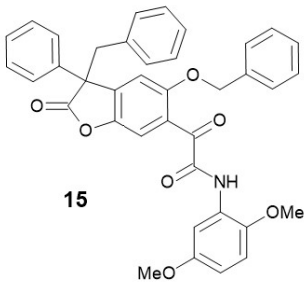
^{13}C nmr spectrum (100 MHz, DMSO-d_6) (**12**)
24 unique carbon atoms
23 observed (low S/N)



N-(2,5-dimethoxyphenyl)-2-(3-benzyl-5-hydroxy-2-oxo-3-phenyl-2,3-dihydro-1-benzofuran-6-yl)-2-oxoacetamide (**14**) and *N*-(2,5-dimethoxyphenyl)-2-[3-benzyl-5-(benzyloxy)-2-oxo-3-phenyl-2,3-dihydro-1-benzofuran-6-yl]-2-oxoacetamide (**15**)



14

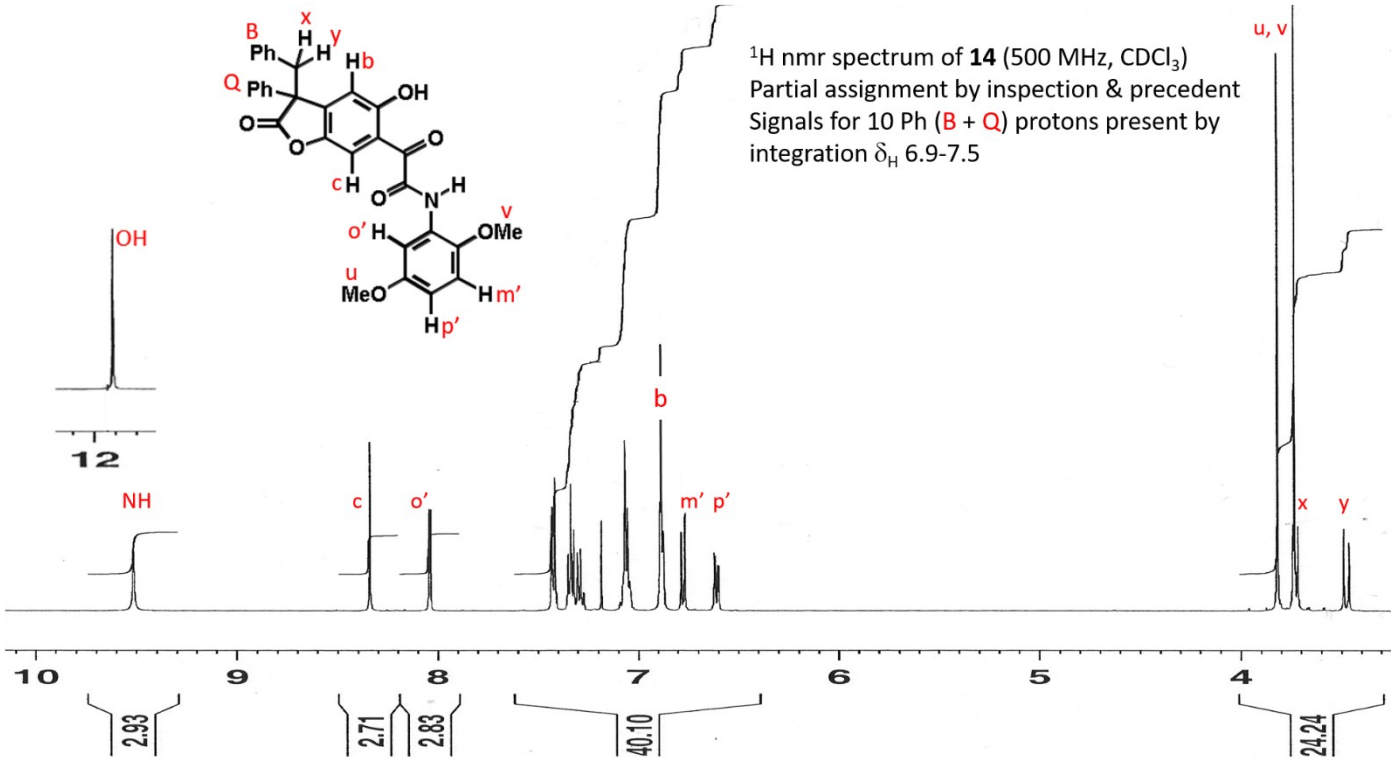


15

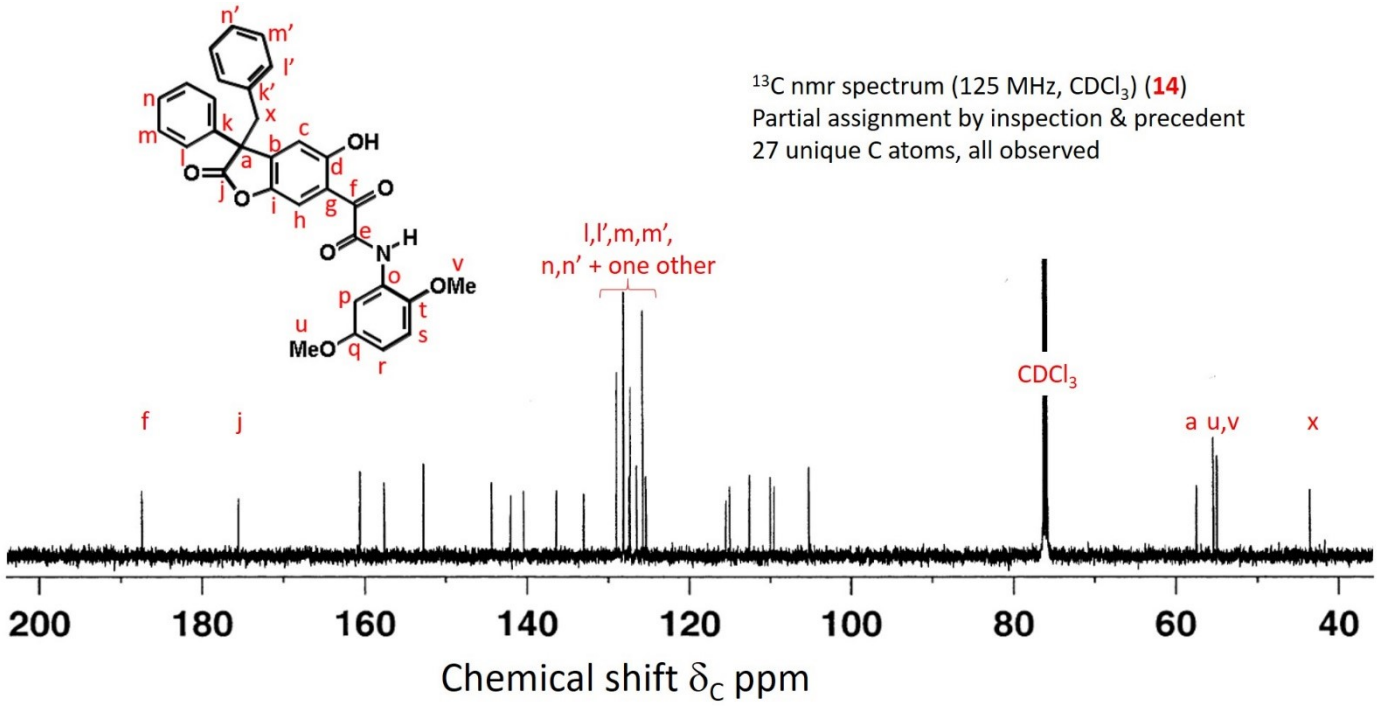
A mixture of amide **8** (1g, 2.30 mmol), benzyl bromide (3.4 ml, 27.6 mmol) and potassium carbonate (0.4g, 2.76 mmol) was stirred in DMF (10ml) at room temperature for 24 hrs. Water (50ml) and DCM (50ml) were added to the reaction mixture. The organic layer was washed with water and dried over magnesium sulphate. The DCM was evaporated and the resulting mixture was stirred in cyclohexane (3ml) and the cyclohexane decanted off. Remaining solvent was evaporated under vacuum to give a yellow liquid which was a mixture of two major products. The products were separated by flash column chromatography to give two yellow oils **14** (900mg, 75%) and **15** (200mg, 15%).

14: ^{1}H NMR (500 MHz, $CDCl_3$) δ_H ppm 3.48 (d, *J* = 13.2, 1H, H*y*), 3.72 (d, *J* = 13.2, 1H, H*x*), 3.73 (s, 3H, OMe), 3.82 (s, 3H, OMe), 6.61 (dd, *J* = 8.98, 2.99, 1H, H*p'*), 6.78 (d, *J* = 9.14, 1H, H*m'*), 6.88 (m, 2H, ArH), 6.89 (s, 1H, H*b*), 7.0-7.5 (m, 8H, ArH), 8.04 (d, *J* = 3.15, 1H, H*o'*), 8.34 (s, 1H, H*c*), 9.51 (s, 1H, NH), 11.91 (s, 1H, OH). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C ppm 43.39 (C*x*), 54.81 (OMe), 55.28 (OMe), 57.35 (C*a*), 105.16, 109.45, 109.97, 112.54, 114.99, 115.51, 125.34, 125.74, 126.50, 127.33, 127.45, 128.11, 128.94, 133.04, 136.37, 140.43, 142.00, 144.37, 152.74, 152.67, 160.64, 175.55, 187.52 (C*f*). λ_{max} (acetone) 390 nm. IR ($CHCl_3$) ν_{max} (cm^{-1}) 3346 (NH), 2960 (br, OH), 1805 (lactone), 1692 (amide), 1599 (H-bonded ketone), 1527. HRMS (EI/CI) m/z Calcd for $C_{31}H_{25}NO_7$ [M+H$^+$]: 524.1709. Found: 524.1714.

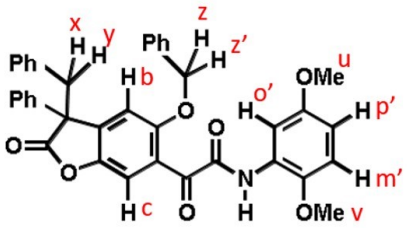
15: ^{1}H NMR (500 MHz, $CDCl_3$) δ_H ppm 3.49 (d, *J* = 15, 1H, H*y*), 3.59 (d, *J* = 15, 1H, H*x*), 3.71 (s, 3H, OMe), 3.77 (s, 3H, OMe), 4.96 (s, 2H, H*z, Hz'*), 6.59 (dd, *J* = 8.99, 2.99, 1H, H*p'*), 6.63 (s, 1H, H*b*), 6.71 (d, *J* = 7.25, 2H, *ortho*-ArH), 6.76 (d, *J* = 9.14, 1H, H*m'*), 7.0-7.5 (m, 13H, ArH), 7.22 (s, 1H, H*c*), 8.04 (d, *J* = 3.15, 1H, H*o'*), 8.88 (s, 1H, NH). λ_{max} (acetone) 342 nm. IR ($CHCl_3$) ν_{max} (cm^{-1}) 3350 (NH), 1802 (lactone), 1686, 1680 (amide, non-H-bonded ketone), 1600, 1536. HRMS (EI/CI) m/z Calcd for $C_{38}H_{31}NO_7$ [M+H$^+$]: 614.2179. Found: 614.2171.



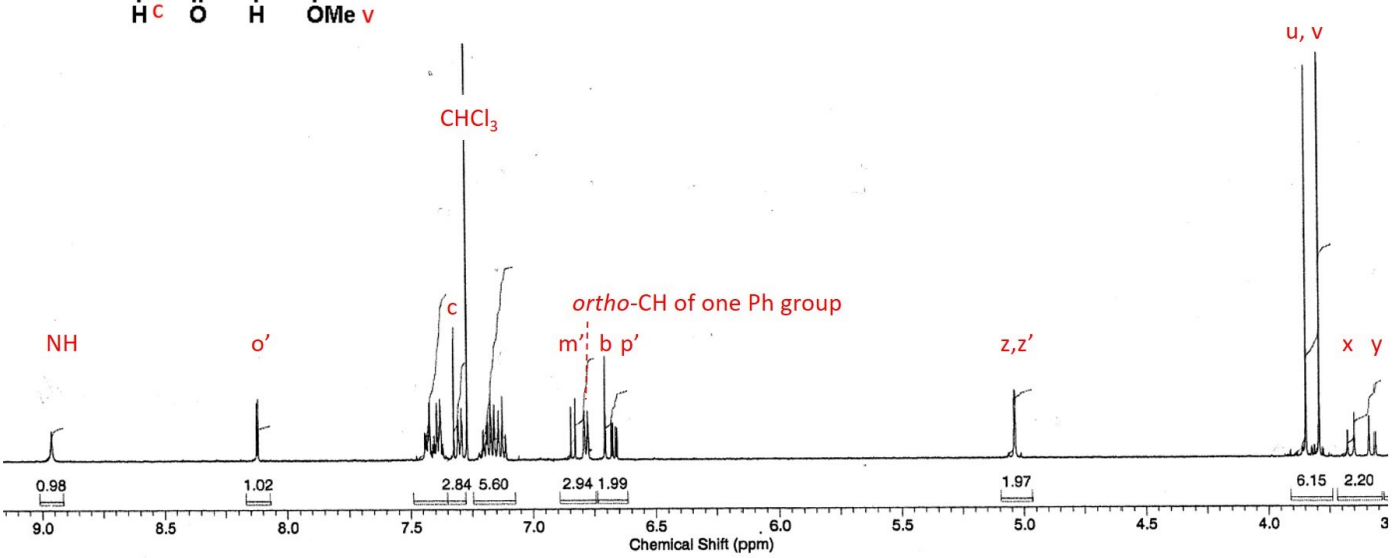
^{1}H nmr spectrum of **14** (500 MHz, $CDCl_3$)
Partial assignment by inspection & precedent
Signals for 10 Ph (B + Q) protons present by integration δ_H 6.9-7.5



^{13}C nmr spectrum (125 MHz, $CDCl_3$) (**14**)
Partial assignment by inspection & precedent
27 unique C atoms, all observed



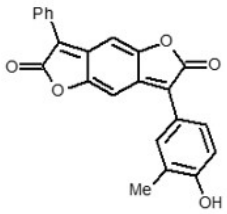
^{1}H nmr spectrum of **15** (500 MHz, $CDCl_3$)
Assignment by inspection & precedent
No signal at δ_H >9: phenol OH absent
13 Ph proton signals present by integration at δ_H 7.1-7.5



Visible/NIR spectra

Solutions were prepared from dry solvents with sample concentrations at 10^{-5} M, aimed at absorbance values, A, below unity. Graphics below were manipulated to show spectra with roughly equal absorbances.

BDF dye 1b and its conjugate base



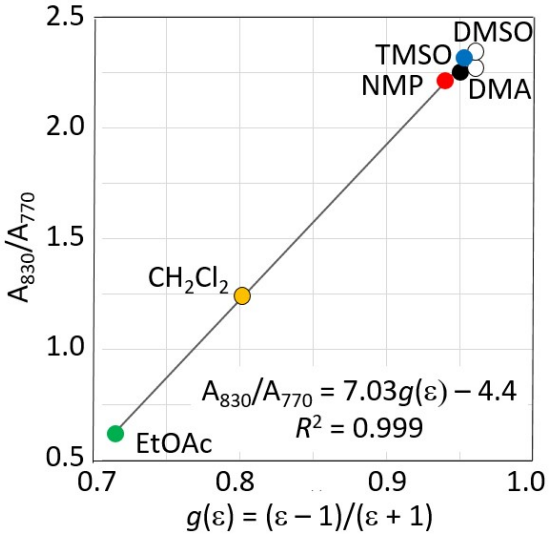
1b

The discussion in the main text of the visible-NIR spectra of **1b** gave qualitative arguments for conjugate base aggregation in solution, with a greater tendency for aggregation in less polar solvents. A preliminary quantitative exploration of solvent-dependent aggregation has been based on available data; see Table below. No attempt has been made to carry out a rigorous study. The following graphic shows a plot which relates the ratio of absorbances in the NIR of the conjugate base of dye **1b** to the solvent polarity as represented by the Kirkwood-Onsager reaction field parameter $g(\varepsilon)$ derived from solvent relative permittivity (ε) as $g(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 1)$.

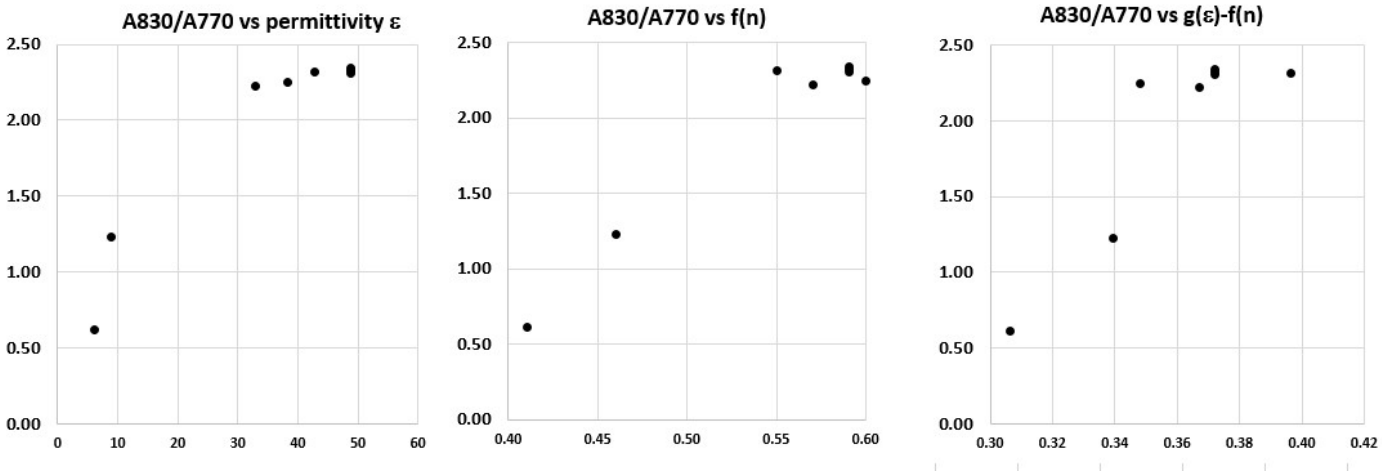
	Reaction field parameters [a]					λ_{max} (nm) and A [b]			Ratio [c]
Solvent	ε	$g(\varepsilon)$	$f(n)$	$g(\varepsilon) - f(n)$	Additive	Vis	NIR770	NIR830	A830/A770
DMSO[d]	48.71	0.958	0.372	0.59	DBU		770	831	
							0.86	2.00	2.33
					None	529.5	770	834.5	
						0.63	0.16	0.369	2.31
					DBU		770	834	
							0.61	1.429	2.34
TMSO	42.84	0.954	0.396	0.55	None	533	770	838	
						0.38	0.25	0.58	2.32
DMA	38.3	0.949	0.348	0.60	None		770	825	
							0.89	2.00	2.25
NMP	32.98	0.940	0.367	0.57	None	530	770	834	
						0.95	0.9	2.00	2.22
DCM	9.02	0.800	0.339	0.46	DBU		770	825	
							0.788	0.97	1.23
EtOAc	6.03	0.716	0.306	0.41	DBU		770	830	
							0.71	0.44	0.62

[a] Values from J.-L.M. Abboud and R.Notario, *Pure Appl.Chem.,* 1999, **71**, 645-718. See this reference and reference 7 of the main text for discussion of all these reaction field parameters. ε is the solvent relative permittivity, and should not be confused with the wholly unrelated ε_{max}, the molar extinction coefficient referred to elsewhere in the main text and ESI. n is the solvent refractive index from which $f(n) = (n^2 - 1)/(n^2 + 1)$. [b] Absorbance values, A, are recorded in blue below the corresponding λ_{max} values. In some cases they have been scaled to a maximum of A = 2. NIR770 and NIR830 are labels for the two main absorbances in the NIR. [c] The relative absorbances are given as ratios of values at the λ_{max} near 830 nm (A830) and τηατ measured at 770 nm (A770). [d] Three measurements are recorded for DMSO, in different

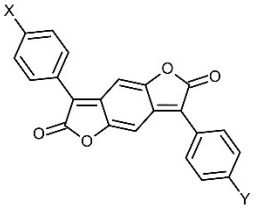
batches of dry solvent, with and without DBU, at different concentrations. The relative absorbance ratios are essentially unchanged.



There is a clear relationship between the degree of aggregation (lower ratio) and reduced solvent polarity as reflected by $g(\varepsilon)$. Plots of the absorbance ratios against alternative reaction field parameters show inferior trends; see below.



BDF dye 1d and its conjugate bases



1d X = Y = OH
1d-cb1 X = OH, Y = O^-
1d-cb2 X = Y = O^-

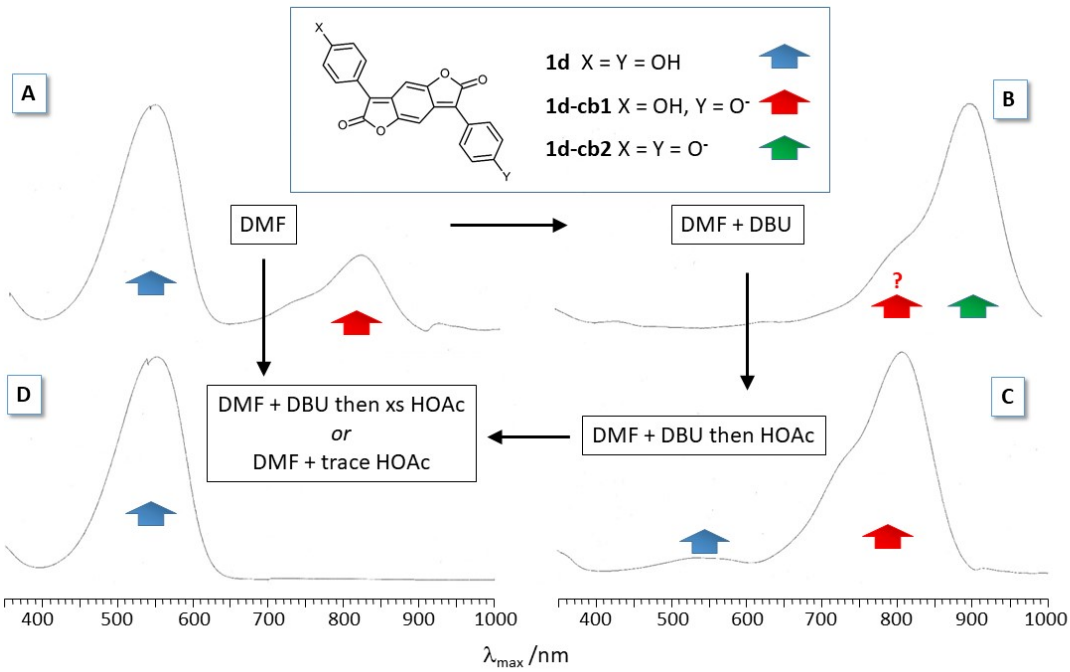
Absorption data for this BDF dye and its deprotonated derivatives are included in Table 1 of the main text. The following Figure reproduces a series of visible-NIR spectra recorded in DMF.

A is **1d** dissolved in dry DMF, showing maxima due to the parent dye and its mono-deprotonated conjugate base **1d-cb1**. The latter features a blue-shifted shoulder assigned to the aggregated anion.

B shows the effect of DBU addition (2 equivalents) to give the dianion **1d-cb2**. Its blue-shifted shoulder is ambiguous. It may be due to aggregated dianion, or to mono-deprotonated **1d-cb1**.

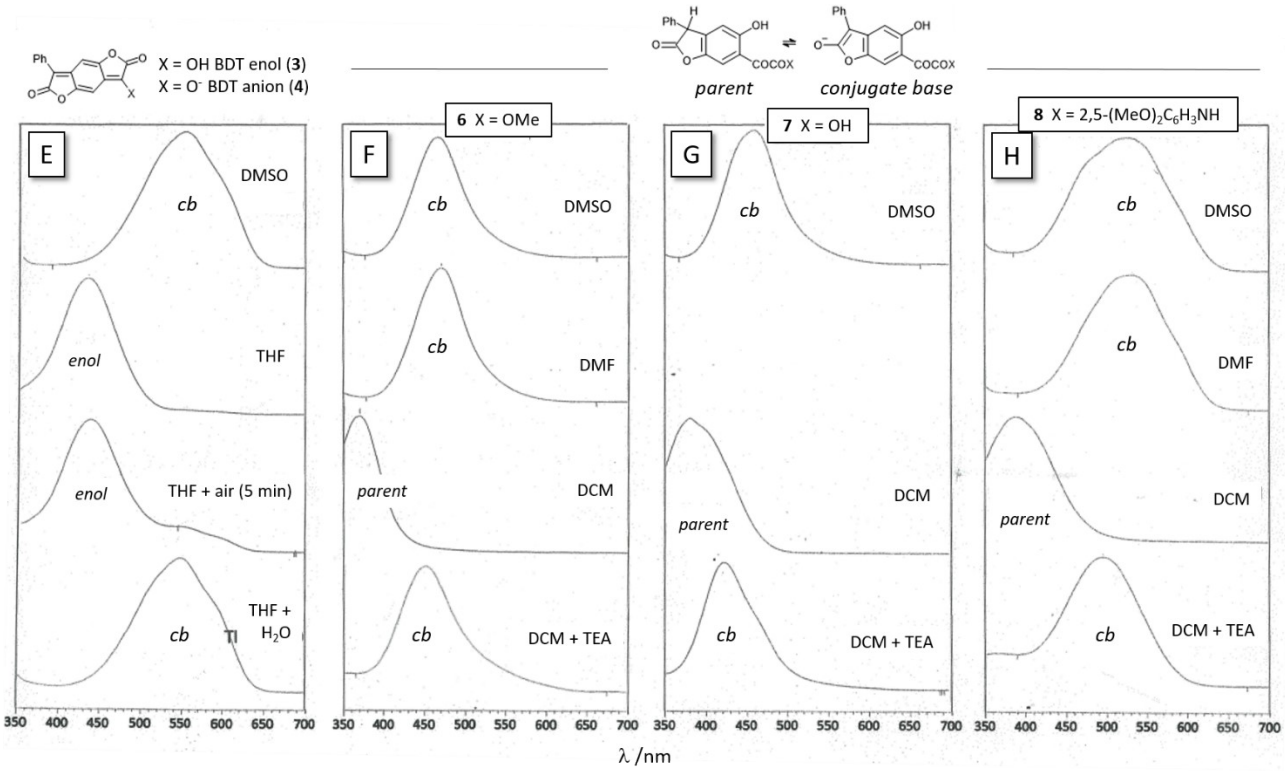
C Careful addition of one equivalent of acetic acid leads to **1d-cb1** plus an indication of formation of the parent dye **1d**.

D The parent dye **1d** free from any conjugate base is generated by further addition of acetic acid, or by direct acidification of the base-free DMF solution.



BDT and ring-opened analogues and their conjugate bases

Visible spectra data are recorded in Table 2 of the main text for **3**, **6**, **7** and **8**. Following are 4 panels of spectra.
Panel E from the top shows the conjugate base of BDT enol (**4**) in DMSO, then the parent BDT enol (**3**) in THF. On opening the sample cuvette to lab air a pink colour develops over minutes, due presumably to ionisation in the more polar medium once it has started to absorb ambient moisture. Addition of water (bottom) completes the ionisation.
Panels F, G, and H compare ring-opened analogues **6**, **7**, and **8** each in DMSO and DMF where ionisation is complete, then in DCM revealing the parent compounds, and finally in DCM after the addition of an equivalent of TEA to bring about full ionisation.



X-ray structure determination of compound 7

Crystallographic measurements on a weakly diffracting yellow plate of **7** were made with monochromatic Cu radiation (λ = 1.54184 Å) using an Oxford Diffraction Gemini E diffractometer. Data reduction utilised CrysalisPro.[1] The structure was solved using direct methods, and refined against F^2 to convergence using all unique reflections and the program Shelxl-2018 as implemented within WINGX.[2,3] Difference syntheses showed electron density peaks corresponding to two different chemically sensible positions for the carboxylic acid H atom. This was thus modelled as disordered over two sites, approximately corresponding to a 180 ° rotation about the C-O bond. Selected crystallographic and refinement parameters are given below. Full details in cif format have been deposited with the Cambridge Structural Database as CCDC 1994670. $C_{16}H_{10}O_6$; Monoclinic $P2_1/c$. 123(2) K, a, b, c = 13.653(6), 5.286(2), 17.808(7) Å, β = 100.77(5) °, V = 1262.6(9) Å^3. 6789 reflections of which 2082 are unique, R_{int} 0.0749, 207 refined parameters, R = 0.0619, R_w = 0.2197, S = 0.941.

1. *CrysalisPro*. (Rigaku Oxford Diffraction, 2019).
2. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* 2015, **71**, 3–8.
3. Farrugia, L. J., WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* 2012, **45**, 849–854.

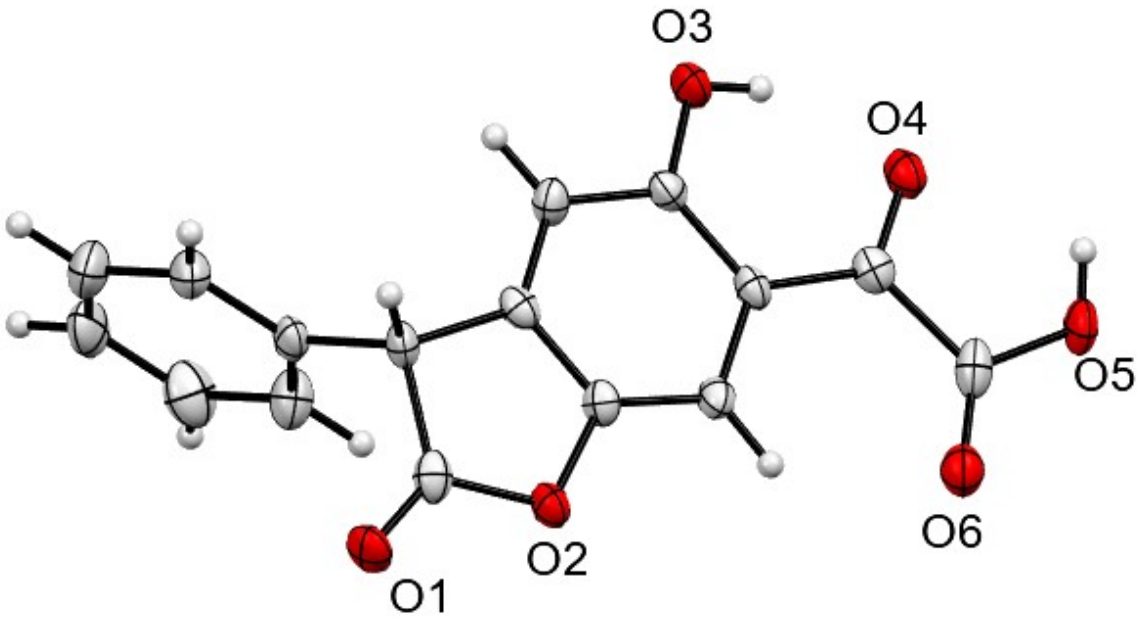


Figure ORTEP view of the molecular structure of **7**. Non-H atoms are drawn as 50% probability ellipsoids and H atoms are drawn as small spheres of arbitrary size. The disorder of the H atom bonded to O5 is not shown.

dyestar1009mono.cif

Datablock: shelx

```
Bond precision:      C-C = 0.0071 A              Wavelength=1.54180
Cell:        a=13.653(5)    b=5.286(2)     c=17.808(7)
             alpha=90       beta=100.77(5) gamma=90
Temperature: 123 K
                   Calculated                    Reported
Volume             1262.6(9)                     1262.6(9)
Space group        P 21/c                        P 21/c
Hall group         -P 2ybc                       -P 2ybc
Moiety formula     C16 H10 O6                    ?
Sum formula        C16 H10 O6                    C16 H10 O6
Mr                 298.24                        298.24
Dx,g cm-3          1.569                         1.569
Z                  4                             4
Mu (mm-1)          1.036                         1.036
F000               616.0                         616.0
F000'              618.27
h,k,lmax           16,6,21                       16,6,21
Nref               2281                          2082
Tmin,Tmax          0.865,0.969                   0.657,1.000
Tmin'              0.865
Correction method= # Reported T Limits: Tmin=0.657
Tmax=1.000 AbsCorr = MULTI-SCAN
Data completeness= 0.913       Theta(max)= 67.499
R(reflections)= 0.0619( 1089)                wR2(reflections)=
                                             0.2197( 2082)
S = 0.942            Npar= 207
```

Search of the Cambridge Crystal Structure Database

A search was made of the CSD version March 2021 for X-ray structures of molecules containing the substructure C*-CO-CO-R, where C* is a 3-coordinate carbon atom (*i.e.* sp^2), R is O or N, and the substructure is acyclic. All structures containing a metal were rejected. Only structures that had atom positions available and where R was 10% or less were accepted. The following lists include all the search results that underpin the statistics presented in Figure 4 and associated discussion in the main text. Dihedral angles are recorded for the α-dicarbonyl OC-CO unit present in each structure determined. The minus signs of negative dihedral angles are disregarded, and values reported as positive in the lists following. The Refcodes and Compound Names are as reported in the CSD.

The data underpinning the histograms in Figure 4 are as follows.

	Structures found / 15 degree bin												
Substructure	0-15	15-30	30-45	45-60	60-75	75-90	90-105	105-120	120-135	135-150	150-165	165-180	Total
C*-CO-CO-NH	0	0	0	0	0	3	6	6	8	20	30	49	122
C*-CO-CO-NC_2	0	0	0	0	1	20	60	23	4	1	0	0	109
C*-CO-CO-OH	1	0	1	0	0	0	2	0	4	1	2	7	18
C*-CO-CO-OC	4	2	5	7	6	17	19	15	12	6	9	12	114

Amide-types based on the substructure C*-CO-CO-N

Refcode	*Dihedral angle*	*Compound Name*
LITTEO	68.347	2-oxo-N,N-diphenyl-2-(6-methylpyridin-2-yl)acetamide
QUBNOR	80.304	2-Oxo-2-phenyl-N-[(R)-1-phenylethyl]acetamide
QUPWEE	80.408	N-(2-t-Butylphenyl)-N-isopropyl-2-oxo-2-phenylacetamide
NAJCEH	80.592	3-((Di-isopropylamino)oxalyl)-N-((S)-1-naphthalen-1-ylethyl)benzamide
VOMYAA	80.949	1-(cyclohex-1-en-1-yl)-2-[3,3-bis(propan-2-yl)triaz-1-en-1-yl]ethane-1,2-dione
RUHYEY	81.023	(4-Benzyloxyindol-3-yl)-glyoxylic acid N,N-di-isopropylamide
VOMXON	82.16	1-[3,3-bis(propan-2-yl)triaz-1-en-1-yl]-2-(4-methoxyphenyl)ethane-1,2-dione
ZIRWEF	84.707	2-(2-aminophenyl)-N-benzyl-N-[2-(1H-indol-3-yl)ethyl]-2-oxoacetamide
GIKYOO	85.355	1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol 1-(benzoylcarbonyl)piperidine clathrate
VIZTII	85.594	Methyl (((2-acetamidophenyl)(oxo)acetyl)amino)acetate
OHOLOO	85.982	N-Methoxy-N-methyl-2,3-dioxobutanamide
ZOHNOZ	87.057	m-Chlorophenyl-N,N-di-isopropylglyoxylamide
VAYKOY	87.177	N-(1-iminoethyl)-2-oxo-2-(4-oxo-4H-pyrido[1,2-a]pyrimidin-3-yl)acetamide
XONVEC	87.202	1-(2-Methoxyphenyl)-2-(2-oxo-4-phenyl-1,3-oxazolidin-3-yl)-1,2-ethanedione
NUDQAF	87.412	1-(3,5-Dimethylpiperazin-1-yl)-2-(4-fluoro-1H-indol-3-yl)ethane-1,2-dione monohydrate
XULCIT	87.668	3-[oxo(phenyl)acetyl]-1,1-bis(propan-2-yl)triaz-1-en-1-ium trifluoromethanesulfonate
XOGYEY	87.988	4,5-bis(Hydroxy(diphenyl)methyl)-2,2-(pentamethylene)-1,3-dioxolane 1-phenyl-2-(1-piperidinyl)-1,2-ethanedione clathrate
JAGLAE	88.046	(+)-N,N-Di-isopropylphenylglyoxylamide
ZELLOR	88.138	N-(Benzoylformyl)-N-benzyl-S-phenylthiocarbamate
KAHWIA	88.509	4-((Di-isopropylamino)oxalyl)-N-((R)-1-phenylethyl)benzamide
CECZIV	88.549	2-(1H-Indol-3-yl)-N,N-dimethyl-2-oxoacetamide
NAHZIG	88.815	4-((Di-isopropylamino)oxalyl)-N-((R)-1-phenylethyl)benzamide
NAHZUS	88.84	4-((Di-isopropylamino)oxalyl)-N-((R)-3-methylbutan-2-yl)benzamide
ZELLUX	88.909	N-(Benzoylformyl)-N-methyl-S-phenylthiocarbamate
AGIZAU	89.091	N,N-diethyl-3-(2-methyl-2-phenylhydrazinylidene)-2-oxobutanamide
ZUBVEZ	89.191	N-(4-Chlorophenyl)-N-(2-(cyclohexylamino)-1-(3-methoxyphenyl)-2-oxoethyl)-2-oxo-2-phenylacetamide
NAJBUW	89.227	4-((Di-isopropylamino)oxalyl)-N-((R)-1-phenyl-2-hydroxyethyl)benzamide
NAJBOQ	89.665	4-((Di-isopropylamino)oxalyl)-N-((1R,2S)-1-hydroxy-1-phenylpropan-2-yl)-N-methylbenzamide benzene solvate
WULZEJ	89.726	N-(2,5-Di-t-butylphenyl)-N-methyl-2-oxo-2-phenylacetamide
VOMYII	89.766	1-(3,3-dicyclohexyltriaz-1-en-1-yl)-2-(4-methoxyphenyl)ethane-1,2-dione

SAPFOF	90.118	2-(2,4-Dihydroxyphenyl)-N,N-dimethyl-2-oxoacetamide
FEMMEQ	90.151	trans-2,3-bis(Hydroxydiphenylmethyl)-1,4-dioxaspiro(4,5)decane 4-(oxophenylacetyl)morpholine clathrate
REPDOH	90.259	1-(4-Benzoylpiperazin-1-yl)-2-(4-fluoro-7-(1H-pyrazol-3-yl)-1H-pyrrolo[2,3-c]pyridin-3-yl)ethane-1,2-dione
WOLZIJ	90.498	N-[dimethyl(oxo)-lambda$6!-sulfanylidene]-2-oxo-2-phenylacetamide
POWMIX	90.713	(R)-(+)-N-Ethyl-N-isopropylphenylglyoxylamide
LUXRAY	90.735	2-(Biphenyl-4-yl)-N,N-dimethyl-2-oxoacetamide
XOMYOP	90.77	N-(2-(oxo(piperidin-1-yl)acetyl)phenyl)propanamide
XOGYEY	91.033	4,5-bis(Hydroxy(diphenyl)methyl)-2,2-(pentamethylene)-1,3-dioxolane 1-phenyl-2-(1-piperidinyl)-1,2-ethanedione clathrate
XONVEC	91.4	1-(2-Methoxyphenyl)-2-(2-oxo-4-phenyl-1,3-oxazolidin-3-yl)-1,2-ethanedione
NAJBAC	91.676	2-(4-((Di-isopropylamino)oxalyl)benzoylamino)-(S)-3-phenylpropionic acid methyl ester
XOBGUR	91.726	1,1,2,2-Tetraphenyl-1,2-ethanediol 1-phenyl-2-(1-piperidinyl)-1,2-ethanedione clathrate
FEMMEQ	91.943	trans-2,3-bis(Hydroxydiphenylmethyl)-1,4-dioxaspiro(4,5)decane 4-(oxophenylacetyl)morpholine clathrate
WIQKUC	91.991	N,N-Diisopropyl-(3-methylphenyl)glyoxylamide
GIKYUU	92.247	1-(Benzoylcarbonyl)piperidine
DUBKUI	92.612	1-(3-(4-Bromophenyl)-4,6-dimethoxy-1H-indol-7-yl)-2-(piperidin-1-yl)ethane-1,2-dione
DUBKUI	92.73	1-(3-(4-Bromophenyl)-4,6-dimethoxy-1H-indol-7-yl)-2-(piperidin-1-yl)ethane-1,2-dione
HOBJOX	92.782	N-(4-((4-Acetyl-1-piperazinyl)oxoacetyl)phenyl)-2-methyl-propanamide
XIMBUS	93.018	N-t-Butyl-2-(2-methoxyphenyl)-2-oxoacetamide
NAJBEG	93.173	2-(4-((Di-isopropylamino)oxalyl)benzoylamino)-3-((S)-4-hydroxyphenyl)propionic acid methyl ester
PEQHAU	93.45	2-(3'-(4''-Chlorophenyl)-4',6'-dimethoxyindol-7'-yl)glyoxyl-1-pyrrolidine
COSTIO	93.474	N,N-Dimethyl(6,8-dimethoxy-1,2-diphenylpyrrolo[3,2,1-hi]indol-4-yl)glyoxylamide
XIMBUS	93.502	N-t-Butyl-2-(2-methoxyphenyl)-2-oxoacetamide
WUGGIQ	93.799	1-(4-bromo-2-((2-(morpholin-4-yl)ethyl)amino)phenyl)-2-(morpholin-4-yl)ethane-1,2-dione
AVUMOT	94.301	3-(2-(N,N-Diethylamino)glyoxyloyl)-1H-indol-4-yl acetate monohydrate
YOWVUB	94.34	N,N-Di-isopropyl(o-methylphenyl)glyoxylamide
RIVZED	94.56	N,N-Dimethyl-2,3-dioxobutanamide
NAJBIK	94.823	4-((Di-isopropylamino)oxalyl)-N-((1S,2S)-2-hydroxy-1-methoxymethyl-2-phenylethyl)benzamide benzene solvate
XOMYEF	94.955	N-(2-(oxo(piperidin-1-yl)acetyl)phenyl)acetamide
QUBNUX	95.038	N,N-Dimethyl-2-(1-naphthyl)-2-oxoacetamide
DOXJEH	95.178	N,N'-bis(2-((t-butylamino)(oxo)acetyl)phenyl)hexanediamide
NUKSUH	95.193	N-Benzyl-N-methacryloylbenzoylformamide
IZANEE	95.426	1-(2-amino-3-fluorophenyl)-2-(3,4-dihydroisoquinolin-2(1H)-yl)ethane-1,2-dione
DUBKUI	95.654	1-(3-(4-Bromophenyl)-4,6-dimethoxy-1H-indol-7-yl)-2-(piperidin-1-yl)ethane-1,2-dione
FEXJUP	95.654	1-(Piperidin-1-yl)butane-1,2,3-trione
DUBKUI	95.817	1-(3-(4-Bromophenyl)-4,6-dimethoxy-1H-indol-7-yl)-2-(piperidin-1-yl)ethane-1,2-dione
WOVBEO	96.124	(R,R)-(-)-trans-2,3-bis(Hydroxydiphenylmethyl)-1,4-dioxaspiro(4.5)decane N-ethyl-N-methylbenzoylformamide clathrate
SUTTOR	97.431	1-(4-Benzoylpiperazin-1-yl)-2-(4,7-dimethoxy-1H-pyrrolo[2,3-c]pyridin-3-yl)ethane-1,2-dione
WOVBEO	97.577	(R,R)-(-)-trans-2,3-bis(Hydroxydiphenylmethyl)-1,4-dioxaspiro(4.5)decane N-ethyl-N-methylbenzoylformamide clathrate
YOWVUF	98.057	N,N-Di-isopropyl(p-methylphenyl)glyoxylamide
NUKSAN	98.112	N-Tigloylbenzoylformanilide
QEKCAK	98.165	N-(2-t-Butylphenyl)-N-allyl-phenyloxamide
IWIXAO	98.743	1-Benzoyl-4-(2-(4-methoxy-7-(3-methyl-1H-1,2,4-triazol-1-yl)-1-((phosphonooxy)methyl)-1H-pyrrolo(2,3-c)pyridin-3-yl)-1,2-dioxoethyl)p
IGIRUO	98.751	1-(4-chlorophenyl)-2-(4-methylpiperazin-1-yl)ethane-1,2-dione
QUPWII	99.333	N-(2-t-Butylphenyl)-N-cyclohexyl-2-oxo-2-phenylacetamide
QAKREB	99.392	N-(2-Oxo-2-phenylacetyl)benzamide
ZOHNUF	99.53	p-Chlorophenyl-N,N-di-isopropylglyoxylamide
POWMET	99.932	(R)-(+)-N-Ethyl-N-isopropylphenylglyoxylamide trans-2,3-bis(hydroxydiphenylmethyl)-1,4-dioxaspiro(5.4)decane clathrate
NAJCAD	100.029	3-((Di-isopropylamino)oxalyl)-N-((R)-1-phenylethyl)benzamide monohydrate
NUKTAO	100.188	N-Methacryloylbenzoylformanilide

DOXJUX	100.385	N,N'-bis(2-((hexylamino)(oxo)acetyl)-4-methylphenyl)ethanediamide
ZUBVAV	100.826	N-(4-Chlorophenyl)-N-(2-(cyclohexylamino)-1-(2,3-dimethoxyphenyl)-2-oxoethyl)-2-oxo-2-phenylacetamide dichloromethane solvate
GIMKIW	101.059	(S)(-)-1,6-bis(o-Chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol N,N-dimethyl-alpha-oxobenzenacetamide clathrate
YOWWAI	101.151	N,N-Di-isopropyl(3,4-dimethylphenyl)glyoxylamide
HAPCIN	101.176	N-(2-methoxyphenyl)-N-((4-methylphenyl)sulfonyl)-2-oxo-2-phenylacetamide
NUDPUY	101.449	1-(4-Benzoyl-3,5-dimethylpiperazin-1-yl)-2-(4-fluoro-1H-indol-3-yl)ethane-1,2-dione ethyl acetate solvate
RUYWEO	102.039	2-(2-Amino-3-bromophenyl)-N,N-diethyl-2-oxoacetamide
ZEDJUN	102.195	bis((R,R)-(-)-trans-2,3-bis(Diphenylhydroxymethyl)-1,4-dioxaspiro(4.5)decane) N-isopropyl-N-methylphenylglyoxylamide
HAPCOT	102.304	N-(4-methylphenyl)-N-((4-methylphenyl)sulfonyl)-2-oxo-2-phenylacetamide
ZEDJOH	102.344	bis((R,R)-(-)-trans-2,3-bis(Diphenylhydroxymethyl)-1,4-dioxaspiro(4.4)nonane) N-isopropyl-N-methylphenylglyoxylamide
RIYQUL01	102.609	1-(10,10-Dimethyl-3,3-dioxo-3-thia-4-azatricyclo[5.2.1.0$1,5!]decan-4-yl)-2-phenylethane-1,2-dione
JADTUG	102.822	ethyl (2-(1-((4-bromophenyl)(oxo(phenyl)acetyl)amino)-2-(t-butylamino)-2-oxoethyl)-1H-pyrrol-1-yl)acetate
XOBHAY	103.046	1,1,6,6-Tetraphenyl-2,4-hexadiyne-1,6-diol 1-(4-morpholinyl)-2-phenyl-1,2-ethanedione clathrate
SEMCOE	103.217	1-(4-Bromophenyl)-2-(piperidin-1-yl)ethane-1,2-dione
QUQNOH	103.41	t-butyl (2-(oxo(pyrrolidin-1-yl)acetyl)phenyl)carbamate
IWIXOC	104.322	1,3-Dihydroxy-2-(hydroxymethyl)propan-2-aminium (3-((4-benzoylpiperazin-1-yl)(oxo)acetyl)-4-methoxy-7-(3-methyl-1H-1,2,4-triazol-1-
IWIXIW	104.607	1,3-Dihydroxy-2-(hydroxymethyl)propan-2-aminium (3-((4-benzoylpiperazin-1-yl)(oxo)acetyl)-4-methoxy-7-(3-methyl-1H-1,2,4-triazol-1-
XOBGOL	104.632	2,5-Diphenylhydroquinone 1-(4-morpholinyl)-2-phenyl-1,2-ethanedione clathrate
VAFPEZ	104.691	(S)-N-(2-Methyl-1-phenylprop-2-en-1-yl)-2-oxo-2-phenylacetamide
PEMHAR	105.675	1-(Azepan-1-yl)-2-(1H-indol-3-yl)ethane-1,2-dione
NAJCAD	106.148	3-((Di-isopropylamino)oxalyl)-N-((R)-1-phenylethyl)benzamide monohydrate
POTDAE	106.358	N,N-Dimethyl-4,6-dimethoxy-1-(N,N-dimethylacetamido)-2,3-diphenylindol-7-ylglyoxylamide
OTODUX	106.677	Trimethyl (nitrilotris(ethane-2,1-diylimino(1,2-dioxoethane-2,1-diyl)-2,1-phenylene))triscarbamate dichloromethane solvate
MODLOJ	106.956	N-[(4-nitrophenyl)sulfonyl]-N-[(oxiran-2-yl)methyl]-2-oxo-2-phenylacetamide
ZOHNIT	107.786	o-Chlorophenyl-N,N-di-isopropylglyoxylamide
XOBGAX	108.174	1,6-bis(2-Chlorophenyl)-1,6-dihydroxy-1,6-diphenylhexa-2,4-diyne 1-(4-morpholinyl)-2-phenyl-1,2-ethanedione clathrate
WULZIN	109.113	N-(2-t-Butylphenyl)-N-methyl-2-oxo-2-phenylacetamide
WOTZUA	109.669	(R,R)-(-)-trans-2,3-bis(Hydroxydiphenylmethyl)-1,4-dioxaspiro(4.4)nonane N-ethyl-N-methylbenzoylformamide clathrate
WIHHIH	111.888	1-benzyl-N-(3-chlorophenyl)-4-(((3-chlorophenyl)amino)(oxo)acetyl)-2-methyl-3,5-bis(4-methylphenyl)-2,3-dihydro-1H-pyrrole-2-carbox
NUKSIV	111.931	N-Methacryloylbenzoylformyl(2,6-dimethyl)anilide
LAYWUE	111.981	10,10-dimethyl-3-p-tosyl-4-(2-oxo-2-phenylacetyl)-3,4-diazatricyclo(5.2.1.0$1,5!)decan-2-one
RUPCOV	111.99	N-(2,6-Dimethylphenyl)-2-(2-hydroxyphenyl)-2-oxoacetamide
TIRPAO	112.079	2-oxo-N,2-diphenyl-N-(propan-2-yl)acetamide
NUKTIW	112.473	N-Methacroylbenzoyl-2,6-dichloroformanilide
VAFPEZ	113.03	(S)-N-(2-Methyl-1-phenylprop-2-en-1-yl)-2-oxo-2-phenylacetamide
QOTNIW	113.965	(-)-trans-1,4-bis(3-(o-Chlorophenyl)-3-hydroxy-3-phenylprop-1-ynyl)-2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-diol N,N-dimethylpheny
DONRUV	114.271	N-benzyl-2-oxo-2-phenylacetamide
WEPCID01	114.652	N-Isopropyl-N-tigloylbenzoylformamide
QUBNOR	114.801	2-Oxo-2-phenyl-N-[(R)-1-phenylethyl]acetamide
NUKSER	115.766	N-Tigloylbenzoyl-o-methylformanilide
NUKTES	115.855	N-Tigloylbenzoyl-2,6-dimethylformanilide
NUKSOB	116.038	N-Isopropyl-N-methacryloylbenzoylformamide
ACMGHX	116.304	2'-Acetyl-2'-(p-chlorobenzoyl)-2-(p-methoxyphenyl)-glyoxylohydrazide
GIJBEJ	116.712	1-(3-methyl-1H-indol-1-yl)-2-(4-nitrophenyl)ethane-1,2-dione
GIJBEJ	116.927	1-(3-methyl-1H-indol-1-yl)-2-(4-nitrophenyl)ethane-1,2-dione
LUVBIN	117.987	N-(1-Cyclohexenecarbonyl)-N-(5,6,7,8-tetrahydronaphthalen-1-yl)benzoylformamide
ZIMTUM	119.171	(M)-N-(2-t-Butylphenyl)-2-methylene-N-(oxo(phenyl)acetyl)butanamide
ZIMVAU	119.213	(P)-N-(2-t-Butylphenyl)-2-methylene-N-(oxo(phenyl)acetyl)butanamide
WOGCUS	119.724	1-(4-Chlorophenyl)-2-(2-(diphenylmethylene)pyrrolidin-1-yl)ethane-1,2-dione

COSTOU	125.458	N,N-Dimethyl(6,8-dimethoxypyrrolo[3,2,1-hi]indol-2-yl)glyoxylamide
OTODUX	126.324	Trimethyl (nitrilotris(ethane-2,1-diylimino(1,2-dioxoethane-2,1-diyl)-2,1-phenylene))triscarbamate dichloromethane solvate
RUPCOV	126.866	N-(2,6-Dimethylphenyl)-2-(2-hydroxyphenyl)-2-oxoacetamide
LAYXEP	126.873	10,10-dimethyl-3-tosyl-4-(2-oxo-2-(thien-2-yl)acetyl)-3,4-diazatricyclo(5.2.1.0$1,5!)decan-2-one
ZIHQOW	128.643	Ethyl 2-(N'-(phenyloxalyl)hydrazino)-1-aza-azulene-3-carboxylate
LAYWUE	129.458	10,10-dimethyl-3-p-tosyl-4-(2-oxo-2-phenylacetyl)-3,4-diazatricyclo(5.2.1.0$1,5!)decan-2-one
PAXQEM	129.876	N-Cyclohexyl-2-oxo-2-phenylacetamide
TEGSIK	130.558	2-(4-methylphenyl)-2-oxoacetamide
XIMBOM	131.853	N-t-Butyl-2-(4-methoxyphenyl)-2-oxoacetamide
DOXJUX	133.262	N,N'-bis(2-((hexylamino)(oxo)acetyl)-4-methylphenyl)ethanediamide
OCUKUT	134.243	1-(10,10-Dimethyl-2-oxo-3-phenyl-3,4-diazatricyclo[5.2.1.0$1,5!]decan-4-yl)-2-phenylethane-1,2-dione
FEKYIG	134.853	N-(4-chloro-2-((2-(1H-indol-2-ylcarbonyl)hydrazino)(oxo)acetyl)phenyl)acetamide dimethyl sulfoxide solvate
CEKSES	136.405	Hexyl N-((2-acetamidophenyl)(oxo)acetyl)glycinate
WINFEG	136.589	N-(2-((Dodecylamino)(oxo)acetyl)-4-methylphenyl)octanamide
DOXJUX	136.593	N,N'-bis(2-((hexylamino)(oxo)acetyl)-4-methylphenyl)ethanediamide
XOVQOR	136.614	dimethyl 2,2'-{methylenebis[(6-acetamido-3,1-phenylene)(1,2-dioxoethane-2,1-diyl)azanediyl]}bis[4-(methylsulfanyl)butanoate]
WINDUU	137.036	Hexyl N-((2-(octanoylamino)phenyl)(oxo)acetyl)glycinate
WIGHEB	137.072	2-(2-Chlorophenyl)-N-cyclohexyl-2-oxoacetamide unknown solvate
RUBFOM	137.147	N-[2-(1H-benzimidazol-2-yl)phenyl]-2-oxo-2-phenylacetamide
FEKYIG	137.365	N-(4-chloro-2-((2-(1H-indol-2-ylcarbonyl)hydrazino)(oxo)acetyl)phenyl)acetamide dimethyl sulfoxide solvate
OTODUX	138.176	Trimethyl (nitrilotris(ethane-2,1-diylimino(1,2-dioxoethane-2,1-diyl)-2,1-phenylene))triscarbamate dichloromethane solvate
WINFIK	138.491	N-(4-Bromo-2-((dodecylamino)(oxo)acetyl)phenyl)octanamide
XOVQOR	139.612	dimethyl 2,2'-{methylenebis[(6-acetamido-3,1-phenylene)(1,2-dioxoethane-2,1-diyl)azanediyl]}bis[4-(methylsulfanyl)butanoate]
OCULEE	139.735	1-(10,10-Dimethyl-2-oxo-3-phenyl-3,4-diazatricyclo[5.2.1.0$1,5!]decan-4-yl)-2-(thiophen-2-yl)ethane-1,2-dione
WINFOQ	140.774	N-(2-((Hexylamino)(oxo)acetyl)-4-methylphenyl)octanamide
HUNCID	143.056	2-(1H-Indol-3-yl)-N-isopropyl-2-oxoacetamide
YEFXUD	144.76	1-(1H-Indol-3-ylcarbonyl)-N-(4-methoxybenzyl)formamide
HUNCUP	146.015	N-t-Butyl-2-(1H-indol-3-yl)-2-oxoacetamide
QUZQIM	147.037	N-(2-[N-(4-Methylphenyl)oxamoyl]phenyl)propanamide
JEGBIJ	148.346	2-(4-benzoyl-1-benzyl-3-methyl-6-phenyl-1H-pyrazolo[3,4-b]pyridin-5-yl)-N-(4-methylphenyl)-2-oxoacetamide
IJUHIF	148.448	N-Cyclohexyl-2-(5-methoxy-1H-indol-3-yl)-2-oxoacetamide
HUNCUP	149.123	N-t-Butyl-2-(1H-indol-3-yl)-2-oxoacetamide
CECZER	149.267	2-(1H-Indol-3-yl)-2-oxoacetamide
VONPAS	151.833	2-[4-(benzenecarbonyl)-5-oxo-2-phenyl-6,7-dihydro-5H-cyclopenta[b]pyridin-3-yl]-N-(4-methylphenyl)-2-oxoacetamide
PUFVOE	151.916	N-[(4-methylbenzene-1-sulfonyl)methyl]-2-oxo-2-phenylacetamide unknown solvate
DOXJIL	152.121	N,N'-bis(2-((butylamino)(oxo)acetyl)phenyl)hexanediamide
MILMUR	152.493	N-((1-Benzyl-1H-1,2,3-triazol-4-yl)methyl)-2-(1H-indol-3-yl)-2-oxoacetamide
WOCZIA	152.73	2-oxo-2-(thiophen-3-yl)acetamide
WATSEQ	153.902	5,11,17,23-Tetra-t-butyl-25,27-dihydroxy-26,28-bis(2-(2-oxo-2-(2-thienyl)acetamido)ethoxy)calix(4)arene
CATJOY	154.443	2-(2-Acetamidophenyl)-N-(4-methylphenyl)-2-oxoacetamide
FOKKAU	155.809	N-(2-formylphenyl)-2-oxo-2-phenylacetamide
WINFAC	157.217	Methyl N-((2-(octanoylamino)phenyl)(oxo)acetyl)glycinate
DOXJOR	157.342	N,N'-bis(2-((methylamino)(oxo)acetyl)phenyl)hexanediamide
TIFYAI	157.58	N-(Pyridin-4-yl)-(1-(4-chlorobenzyl)indol-3-yl)glyoxylamide
DOXJOR	158.084	N,N'-bis(2-((methylamino)(oxo)acetyl)phenyl)hexanediamide
YILDOM	158.115	3-Benzoylformamido-4-phenyl-1,2,5-thiadiazole
RUBFOM	158.455	N-[2-(1H-benzimidazol-2-yl)phenyl]-2-oxo-2-phenylacetamide
CATJIS	158.465	N-(2-(((4-Bromophenyl)amino)(oxo)acetyl)phenyl)propanamide
IZALIF	159.971	2-(3-Benzoyl-1-benzyl-5-phenyl-1H-pyrazol-4-yl)-N-(4-methoxyphenyl)-2-oxoacetamide

UPOROI	160.082	Methyl 4-(((4-methoxyphenyl)amino)(oxo)acetyl)-1,5-diphenyl-1H-pyrazole-3-carboxylate
OBOYEL	160.427	2-(2-Chlorophenyl)-2-oxo-N-phenylacetamide
MAXNIL	160.858	N-(4-chlorophenyl)-2,3-dioxo-3-phenylpropanamide
WINFUW	161.012	N-(2-((Methylamino)(oxo)acetyl)phenyl)octanamide
UPOROI	161.195	Methyl 4-(((4-methoxyphenyl)amino)(oxo)acetyl)-1,5-diphenyl-1H-pyrazole-3-carboxylate
TOPYUU	161.25	2-(2-Acetamidophenyl)-N-(4-nitrophenyl)-2-oxoacetamide
CEKSOC	161.516	2-(2-Acetamido-5-bromophenyl)-N-hexyl-2-oxoacetamide cyclohexane solvate
JEGBOP	162.229	methyl 5-(anilino(oxo)acetyl)-6-(4-methoxyphenyl)-3-methyl[1,2]oxazolo[5,4-b]pyridine-4-carboxylate
LEBBID	162.359	2'-(N-Isopropyloxamoyl)acetanilide
HUNCOJ	162.955	N-t-Butyl-2-(5-methoxy-1H-indol-3-yl)-2-oxoacetamide
CEKSUI	163.061	2-(2-Acetamido-5-bromophenyl)-N-hexyl-2-oxoacetamide
OXMBZS	163.364	Ammonium 2-oxamoyl-3-methyl-benzenesulfonate
GUNDOI	163.579	N-Phenyl phenylglyoxamide
YUVTEP	164.782	N-(4-Methylphenyl)-2-oxo-2-phenylacetamide
TIZZAD	165.157	2-(3'-(4''-Chlorophenyl)-4',6'-dimethoxyindol-2'-yl)glyoxylamide
JOTFIJ	165.315	N-(4-cyanophenyl)-2-oxo-2-phenylacetamide
HIKXII	165.337	(3,3-Dimethyl-1,2,3,4-tetrahydroisoquinol-1-ylidene)pyruvoylhydrazide
MEGKOY	165.387	(1S,5S,6S,8S,10R)-5(((2R,3R,4R)-2,3-Dimethyl-4-(phenylselenylmethyl)-3,4-dihydro-2H-pyran-6-yl)oxoethanamido)-9,9-dimethyl-10-met
MIBHOW	167.029	(Z)-4-[5-(2,6-Difluorobenzyl)-1-(2-fluorobenzyl)-2-oxo-1,2-dihydropyridin-3-yl]-4-hydroxy-2-oxo-N-(2-oxopyrrolidin-1-yl)but-3-enamide
ZIHQOW	168.289	Ethyl 2-(N'-(phenyloxalyl)hydrazino)-1-aza-azulene-3-carboxylate
YIVFIV	168.311	N-benzyl-2-oxo-2-(thiophen-2-yl)acetamide
BOPRUV	168.543	N-(5-(methylsulfanyl)-4-phenyl-1,3-thiazol-2-yl)-2-oxo-2-phenylacetamide
EVIFEV	168.768	N-Cyclohexyl-2-(5-fluoro-1H-indol-3-yl)-2-oxoacetamide
VOKSUM	169.018	2-[1-(4-chlorophenyl)-5-(4-nitrophenyl)-1H-pyrazol-4-yl]-N-methyl-2-oxoacetamide dichloromethane solvate
QOWZUA	169.277	3-(3,3-dimethyl-3,4-dihydroisoquinolin-1(2H)-ylidene)-N-hydroxy-2-oxopropanamide
IGERUH	169.536	2-(1-Cyclopent-2-enyl-1H-indol-3-yl)-N-(2-(1H-indol-3-yl)ethyl)-2-oxoacetamide
GIZYIY	169.646	(2-Furyl)oxoacetamide
YUVTEP	169.773	N-(4-Methylphenyl)-2-oxo-2-phenylacetamide
IJUSOW	169.815	2-(1-Ethyl-5-methoxy-1H-indol-3-yl)-N-(4-methoxyphenyl)-2-oxoacetamide
IJUSOW	170.185	2-(1-Ethyl-5-methoxy-1H-indol-3-yl)-N-(4-methoxyphenyl)-2-oxoacetamide
BATNUI	170.2	tetra-n-butylammonium 2-(2-acetamidophenyl)-N-(4-nitrophenyl)-2-oxoacetamide chloride
GLYXAN	170.205	p-Tolyl-glyoxylic acid m-trifluoroanilide
HAFTUF	171.018	2-(Imidazo[1,2-a]pyridin-2-yl)-2-oxo-N-(pyridin-2-yl)acetamide
JOTFIJ01	171.449	N-(4-cyanophenyl)-2-oxo-2-phenylacetamide
MPGCAN	172.562	p-Tolyl-glyoxylic acid p-chloroanilide
IJUSOW	172.858	2-(1-Ethyl-5-methoxy-1H-indol-3-yl)-N-(4-methoxyphenyl)-2-oxoacetamide
LOHPOO	173.331	4-Desoxy-4beta-((5-methoxy-1H-indol-3-yl)oxalylamino)podophyllotoxin methanol solvate
JOXVUP	173.682	2-Oxo-N-(2-oxo-2-(1H-pyrrol-2-yl)ethyl)-2-(3,4,5-trimethoxyphenyl)acetamide
IGERUH	173.742	2-(1-Cyclopent-2-enyl-1H-indol-3-yl)-N-(2-(1H-indol-3-yl)ethyl)-2-oxoacetamide
IJUSOW	174.368	2-(1-Ethyl-5-methoxy-1H-indol-3-yl)-N-(4-methoxyphenyl)-2-oxoacetamide
JOXVUP	174.577	2-Oxo-N-(2-oxo-2-(1H-pyrrol-2-yl)ethyl)-2-(3,4,5-trimethoxyphenyl)acetamide
UREBUP	174.913	2-(1-Ethyl-5-methoxy-1H-indol-3-yl)-N-isopropyl-2-oxoacetamide
ULAXIQ	175.055	N-(4-Methoxyphenyl)-2-oxo-2-(4-phenyl-1,3-thiazol-2-yl)acetamide
CILLOY	175.188	3-Methoxycarbonyl-1-p-tolyl-4-p-tolyloxamoyl-5-p-ethoxyphenylpyrazole
GIZYIY	175.308	(2-Furyl)oxoacetamide
NAWHID	175.372	2-(1H-Indol-3-yl)-N-methyl-2-oxoacetamide
YARFIJ	175.643	benzyl [(4-chlorophenyl)(oxo)acetyl]carbamate
KEKSUQ	175.682	Methyl 3-(2-anilino-1-hydroxy-2-oxoethylidene)-4-((4-methoxybenzoyl)hydrazono)-2-methyl-5-oxo-1-phenylprolinate
VILXOG	175.93	N-{4-[(4,6-dimethylpyrimidin-2-yl)sulfamoyl]phenyl}-4-hydroxy-4-(4-methylphenyl)-2-oxobut-3-enamide acetic acid solvate

ULAXIQ	176.148	N-(4-Methoxyphenyl)-2-oxo-2-(4-phenyl-1,3-thiazol-2-yl)acetamide
DURLEJ	176.215	4,4'-(ethane-1,2-diyldiimino)bis(N-(2-methylphenyl)-4-(4-methylphenyl)-2-oxobut-3-enamide)
VOMTAV	176.996	N',N'-diacetyl-3-(2,2-dimethyl-2,3-dihydrobenzo[f]isoquinolin-4(1H)-ylidene)-2-oxopropanehydrazide
LOHPOO	178.355	4-Desoxy-4beta-((5-methoxy-1H-indol-3-yl)oxalylamino)podophyllotoxin methanol solvate
ACOKOU	178.4	N-Benzyl-2-(1-methyl-1H-indol-3-yl)-2-oxoacetamide
WATSEQ	178.438	5,11,17,23-Tetra-t-butyl-25,27-dihydroxy-26,28-bis(2-(2-oxo-2-(2-thienyl)acetamido)ethoxy)calix(4)arene
TIZZEH	178.826	N-Methyl-2-(3'-(4''-chlorophenyl)-4',6'-dimethoxyindol-2'-yl)glyoxylamide
URIBED	178.929	3-Diazo-N-[(2S)-1-hydroxypropan-2-yl]-2-oxopropanamide
GIZYIY	179.098	(2-Furyl)oxoacetamide
GIZYIY01	179.193	(2-Furyl)oxoacetamide
KAYBOE	179.295	{3-[(methylamino)(oxo)acetyl]-1H-indol-7-yl}(2,4,6-trimethylphenyl)iodanium perchlorate acetone ethanol solvate
YICPEG	179.382	2-(5-Bromo-1-methyl-1H-indol-3-ylcarbonyl)-N-methylacetamide
KAYBOE	179.562	{3-[(methylamino)(oxo)acetyl]-1H-indol-7-yl}(2,4,6-trimethylphenyl)iodanium perchlorate acetone ethanol solvate
QOWZUA	179.676	3-(3,3-dimethyl-3,4-dihydroisoquinolin-1(2H)-ylidene)-N-hydroxy-2-oxopropanamide

Carboxylic acid and ester structures containing the substructure C*-CO-CO-O

Refcode	*Dihedral angle*	*Compound Name*
UBEPAS	0	t-Butyldiazopyruvate
PARVAH	2.971	2-(Carboxycarbonyl)imidazo[1,2-a]pyridin-1-ium chloride methanol solvate monohydrate
XEPJOR	4.485	4-Hydroxy-2-oxo-6-phenyl-3,5-hexadienoic acid
UWABAW	4.863	(E)-dimethyl 2-oxo-3-((4-oxo-4H-chromen-3-yl)methylene)succinate
DAJBIB	10.318	Imidazo[1,2-a]pyridin-1-ium-2-yl(oxo)acetate monohydrate
QUZTOV	14.183	(Z)-Ethyl 2-oxo-3-(1,2-dihydroquinolin-2-ylidene)propanoate
ACMDOC	14.432	(3-Chloro-4-hydroxyphenyl)-glyoxylic acid methyl ester
UPAHUQ	18.036	ethyl 5-(ethoxy(oxo)acetyl)-2-phenylpyrimidine-4-carboxylate
QUZTOV	26.242	(Z)-Ethyl 2-oxo-3-(1,2-dihydroquinolin-2-ylidene)propanoate
WOCTUD	31.396	alpha-Oxo-2,4,6-trimethylbenzeneacetic acid
DUWFUY	33.148	methyl (1-benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)(oxo)acetate
CUSWEV	35.668	ethyl [1-benzyl-4-(3-fluorophenyl)-1H-1,2,3-triazol-5-yl](oxo)acetate
ZADKAT	36.274	ammonium oxo(phenyl)acetate
XOMYAB	42.836	methyl (2-acetamidophenyl)(oxo)acetate
CUSVUK	44.161	ethyl {1-[(4-methylphenyl)methyl]-4-phenyl-1H-1,2,3-triazol-5-yl}(oxo)acetate
CUSVOE	44.228	Ethyl 2-(1-benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazol-5-yl)-2-oxoacetate
BOSRIM	45.895	ethyl (1-benzyl-4-phenyl-1H-1,2,3-triazol-5-yl)(oxo)acetate
DIVCES	46.521	Ethyl (1-(3-methylbutyl)-4-phenyl-1H-1,2,3-triazol-5-yl)(oxo)acetate
NETZIY	48.247	ethyl oxo(1-oxo-2-phenyl-1H-inden-3-yl)acetate
CUSWAR	48.61	ethyl {4-(4-chlorophenyl)-1-[(4-methylphenyl)methyl]-1H-1,2,3-triazol-5-yl}(oxo)acetate
BOPWOS	49.862	Dimethyl 2-((2-((diethylamino)-carbonyl)-2-methyl-3-phenyl-1-aziridinyl)-ethylidene)-3-oxobutanedioate
YUCWUQ	53.748	Ethyl (2-(3-nitrophenyl)-4-phenyl-1H-pyrrol-3-yl)(oxo)acetate
BISZUB	58.717	ethyl [2-(4-chlorophenyl)-1H-indol-3-yl](oxo)acetate
RIQKEH	60.159	Dimethyl 2-oxo-3-(1',2',2',4',4'-pentamethyl-3'-oxopyrrolidin-5'-ylidene)butane-1,4-dioate
COYDEB	61.159	Ethyl (1-cyclohexyl-4-phenyl-1H-1,2,3-triazol-5-yl)(oxo)acetate
WORYIL	64.561	exo-1-(Diphenyl(hydroxy)methyl)-7,7-dimethylbicyclo(2.2.1)heptan-2-yl alpha-benzoylformate
NERGAV	67.18	ethyl (Z)-4-(methylamino)-3-(4-nitrobenzene-1-carbonyl)-2-oxobut-3-enoate
NERTIQ	70.206	(Z)-4-(butylamino)-3-(4-nitrobenzoyl)-2-oxobut-3-enoic acid ethyl ester
HEVSAC	72.03	Benzamidinium (2-acetamidobenzoyl)formate
NULYOK	72.696	2-isopropyl-5-methylcyclohexyl oxo(phenyl)acetate
QUBCEX	76.163	diethyl 2,2'-perylene-3,9-diylbis(oxoacetate) ethyl acetate solvate

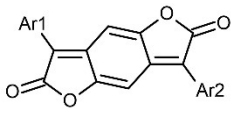
KAQPEX	77.351	Dimethyl 3,6-bis(triphenylphosphoranylidene)-2,4,5,7-tetraoxo-octanedioate deuterochloroform solvate
GIJXUU	79.585	Ethyl 3-((4-methylphenyl)hydrazono)-2,4-dioxopentanoate
NERTEM	79.768	(Z)-4-(benzylamino)-3-(4-nitrobenzoyl)-2-oxobut-3-enoic acid ethyl ester
VAYLEP	81.122	ethyl oxo(5-oxo-5H-[1,3]thiazolo[3,2-a]pyrimidin-6-yl)acetate
NERGEZ	81.129	ethyl (Z)-4-(t-butylamino)-3-(4-nitrobenzene-1-carbonyl)-2-oxobut-3-enoate
COQBIU	81.559	2-(1H-indol-3-yl)ethanaminium oxo(3,4,5-trimethoxyphenyl)acetate
HEBJAA	81.821	(Z)-1,4-Dimethoxy-3-[1-(4-methoxyphenyl)-2-phenyl-1,2-dihydroquinazolin-3-ium-3-yl]-1,4-dioxo-2-buten-2-olate monohydrate
GOQRUC	82.159	ethyl 2,4-dioxo-3-(phenylhydrazono)pentanoate
KEHGOT	82.26	Dimethyl 3-(2-phenyl-1,2-dihydrophthalazin-1-ylidene)-2-oxobutanedioate
HOCVAW	82.608	Ethyl 3-(3,3-dimethyl-1,2,3,4-tetrahydroisoquinolidenehydrazono)-2-oxobutanoate
VISKIT	82.994	Methyl 2,4-dioxo-3-(phenylhydrazono)pentanoate
HOTNIN	83.436	4-Methylamino-5-methoxycarbonyl-3-(2,3-bis(ethoxycarbonyl)-3-oxo-propenylamine)isoxazole
JOSTOD	84.119	t-butyl (4-nitrophenyl)(oxo)acetate
BOCNAJ	84.614	Dimethyl 2-oxo-3-(3,4,4,5,5-pentamethyl-1-phenylimidazolidin-2-ylidene)succinate
SURROO	86.164	1-(4-Bromo-3-(4-methoxyphenyl)isoquinolinium-2-yl)-1,2-bis(methoxycarbonyl)-2-oxoethanide
QUBCEX	87.463	diethyl 2,2'-perylene-3,9-diylbis(oxoacetate) ethyl acetate solvate
AVAGUZ	89.749	Dimethyl 2-(1-hydroxy-4,4,5,5-tetramethyl-imidazolidin-2-ylidene)-3-oxo-succinate
KASVEI	90.456	4-methoxy-3-(2,2,7,7,12,12,17,17-octaethyl-21,22,23,24-tetrathiapentacyclo[16.2.1.1$3,6!.1$8,11!.1$13,16!]tetracosa-1(20),3,5,8,10,13
SURROO	91.305	1-(4-Bromo-3-(4-methoxyphenyl)isoquinolinium-2-yl)-1,2-bis(methoxycarbonyl)-2-oxoethanide
IDIYOL	92.554	Methyl 2-(2-[(2-methylphenoxy)methyl]phenyl)-2-oxoacetate
MEPBGY10	92.589	(-)-Menthyl-p-bromophenyl-glyoxylate
IVEZOZ	92.873	Ethyl (1-methyl-1H-imidazol-2-yl)(oxo)acetate
BISTEF	93.209	ethyl {5-methyl-2-[(4-methylphenyl)sulfanyl]-1H-indol-3-yl}(oxo)acetate
NERSOV	95.414	ethyl 3-(4-nitrobenzene-1-carbonyl)-2-oxo-4-(phenylamino)but-3-enoate
VAYLAL	95.794	ethyl oxo(4-oxo-4H-pyrido[1,2-a]pyrimidin-3-yl)acetate
ISELAT	96.003	(1R,2S,5R)-Menthyl alpha-napthoylformate
MEPBGY10	96.476	(-)-Menthyl-p-bromophenyl-glyoxylate
WORYOR	97.413	exo-1-(Diphenyl(methoxy)methyl)-7,7-dimethylbicyclo(2.2.1)heptan-2-yl alpha-benzoylformate
BOCNEN	97.562	Dimethyl 2-(2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolidin-3-ylidene)-3-oxo-succinate
ZERRAP	98.127	1-(4,6,7-Trioxo-3,8-dioxadecanido)-5H,7H-dibenzo(b,g)(1,5)selenoniumoxocine
GADHEZ	99.836	Methyl 2-(methoxyoxalyl)-2-(1,4,4-trimethylpyrrolidin-2-ylidene)acetate
NERTAI	99.896	(Z)-4-(isopropylamino)-3-(4-nitrobenzoyl)-2-oxobut-3-enoic acid ethyl ester
YUCMEQ	101.905	1-oxo-1-phenylpropan-2-yl oxo(phenyl)acetate
XIWKEU	102.058	syn-(R)-(3,4-dimethoxyphenyl)((R)-2-oxo-1,3-oxazolidin-4-yl)methyl 2-oxo-2-phenylacetate
YUMLUN	102.205	Methyl 3-benzoyl-4-((4-methylphenyl)amino)-2-oxo-4-phenyl-3-butenoate
DUFJET10	103.284	(-)-(1R,2S,5R)-2-(1-Methyl-1-phenylethyl)-5-methylcyclohexyl phenylglyoxylate
KOFBOX	103.825	Methyl 2-(7-benzyloxy-1-naphthyl)-2-oxoacetate
NEHTIG	104.032	(4-(dimethylamino)phenyl)(oxo)acetic acid
BEXZUZ	107.166	(2-Benzoyloxy-4,6-di-t-butyl-phenyl)-phenylglyoxylate
NAWNIJ	109.044	Methyl (2-((t-butoxycarbonyl)amino)phenyl)(oxo)acetate
VEMBEX	109.401	methyl oxo(pyrido[2,1-a]isoindol-6-yl)acetate
NERGID	109.469	(Z)-4-(t-butylamino)-3-(4-methoxybenzoyl)-2-oxobut-3-enoic acid ethyl ester
DILHOW	110.78	Methyl (2-methyl-1-phenylsulfonyl-1H-indol-3-yl)glyoxylate
MEPBGY10	111.11	(-)-Menthyl-p-bromophenyl-glyoxylate
MEPBGY10	111.504	(-)-Menthyl-p-bromophenyl-glyoxylate
EYESIM	111.881	methyl 2,4-dioxo-3-(triphenylphosphoranylidene)pentanoate
AGUBAI	112.508	methyl (2-(2,5-dimethylpyrrolidin-1-yl)phenyl)(oxo)acetate
MAGSOE	113.056	Methyl oxo(4-oxo-4H-chromen-3-yl)acetate
AGUBAI	113.074	methyl (2-(2,5-dimethylpyrrolidin-1-yl)phenyl)(oxo)acetate

YUCWOK	113.48	Ethyl (2,4-diphenyl-1H-pyrrol-3-yl)(oxo)acetate
KIKFEQ	114.612	Ethyl (2-methyl-1-phenylsulfonyl-1H-indole-3-carbonyl)acetate
WIWFOA	115.496	methyl {4-[(acetyloxy)methyl]-1,4-dimethyl-7,8-dioxo-2,3-dihydro-1H,4H-3a,6a-(epoxyethano)pentalen-5-yl}(oxo)acetate
HEXTAG	117.989	2-bromocyclohexyl oxo(phenyl)acetate
TAMNUT	121.83	methyl (4-chlorophenyl)(oxo)acetate
KAQPEX	122.455	Dimethyl 3,6-bis(triphenylphosphoranylidene)-2,4,5,7-tetraoxo-octanedioate deuterochloroform solvate
QUGXAT	123.308	methyl (4-bromophenyl)(oxo)acetate
ODOFAR	123.832	(4-fluorophenyl)(oxo)acetic acid
ODOFAR	124.054	(4-fluorophenyl)(oxo)acetic acid
WUQHOH	124.15	ethyl (4-benzoyl-2-(4-fluorophenyl)-1-phenyl-5-thiocyanato-1H-pyrrol-3-yl)(oxo)acetate
VIZVEG	125.433	1-n-Butyl 4-ethyl 2-oxo-3-[phenyl(2-phenyl-1H-indol-3-yl)methylidene]butanedioate
CEBZAM	126.533	Methyl (6-bromo-2-oxo-2H-chromen-3-yl)(oxo)acetate
CEBZAM	126.567	Methyl (6-bromo-2-oxo-2H-chromen-3-yl)(oxo)acetate
NERSUB	127.841	ethyl 4-[(4-methoxyphenyl)amino]-3-(4-nitrobenzene-1-carbonyl)-2-oxobut-3-enoate
KEGMOB	129.191	ethyl 3-[({[5-methyl-2-(propan-2-yl)cyclohexyl]oxy}carbonyl)amino]-2-oxo-4-phenylbut-3-enoate
DIQZEK	131.497	Ethyl (6-(4-methylbenzoyl)-7-phenyl-2,3-dihydro-1H-pyrrolizin-5-yl)(oxo)acetate
RIFXAF	132.073	Methyl 2-(2-methoxycarbonyl-6-(4-methoxyphenyl)-2H-thiopyran-3-yl)glyoxylate
NEHTIG	132.582	(4-(dimethylamino)phenyl)(oxo)acetic acid
KEGMIV	133.248	ethyl 3-{[(benzyloxy)carbonyl]amino}-2-oxo-4-phenylbut-3-enoate
WOCTOX	134.295	Phenylglyoxylic acid
ZUYYID	135.382	Benzyl biphenyl-4-yl(oxo)acetate
FOGTAX	135.444	Methyl (4-methoxy-3-(methylsulfonyloxy)benzoyl)formate
DORSOV	136.865	methyl [3,3-dicyano-5-ethenyl-2-(4-methylphenyl)cyclopent-1-en-1-yl](oxo)acetate
TUFYUQ	142.929	methyl 3-(methoxy(oxo)acetyl)-1H-indole-1-carboxylate
SUWJOL	146.172	ethyl 4-(ethoxy(oxo)acetyl)-1-phenyl-1H-pyrazole-5-carboxylate
WOGXUN	148.282	(4-Chlorophenyl)(oxo)acetic acid monohydrate
YELPUD	149.245	ethyl (5-(4-nitrophenyl)-1,2-oxazol-4-yl)(oxo)acetate
WOGXUN	150.472	(4-Chlorophenyl)(oxo)acetic acid monohydrate
QARWOY	152.088	ethyl (5-bromo-1-(pyrimidin-2-yl)-2,3-dihydro-1H-indol-7-yl)(oxo)acetate
QARWOY	152.247	ethyl (5-bromo-1-(pyrimidin-2-yl)-2,3-dihydro-1H-indol-7-yl)(oxo)acetate
RIQJIK	153.236	Methyl 5,10,15,20-tetraphenylporphyrinyl-2-(1-keto)acetate
XIKHEH	156.237	methyl (3-nitrophenyl)(oxo)acetate
CIJWEX	159.695	2,8-Dimethoxy-4-methoxycarbonyl-6-methyloxalyl-5-n-pentyl-dibenzofuran
HUFBEQ	160.687	Diethyl 2-oxo-3-(2-oxo-2,3-dihydro-1H-indol-3-ylidene)butanedioate
SARQIM	161.938	Ethyl (Z)-4-chloro-4-(p-fluorophenyl)-2-oxo-3-butenoate
HUFYOX	164.816	Methyl 2-(5-fluoro-1H-indol-3-yl)-2-oxoacetate
GUGCER	164.973	4-(6-Bromo-1-(4-fluorobenzyl)-4-oxo-1,4-dihydroquinolin-3-yl)-4-hydroxy-2-oxobut-3-enoic acid dimethyl sulfoxide solvate
QOMMAI	165.085	(E)-Ethyl 4-(4-chlorophenyl)-4-methoxy-2-oxobut-3-enoate
CUQTOA	165.525	(1-methyl-1H-pyrazol-4-yl)(oxo)acetic acid
NESTEL	165.632	2,3,7,8-Tetraethyl-10H-dipyrrinone-9-glyoxylic acid
HUFBEQ	169.495	Diethyl 2-oxo-3-(2-oxo-2,3-dihydro-1H-indol-3-ylidene)butanedioate
XONJIU	170.012	(E)-Ethyl 4-(4-fluorophenyl)-4-methoxy-2-oxo-3-butenoate
NESTIP	170.817	3,4-Diethyl-1H-pyrrole-2-glyoxylic acid
PARTUZ	173.932	2-(Carboxycarbonyl)imidazo[1,2-a]pyridin-1-ium perchlorate monohydrate
SARQIM	174.885	Ethyl (Z)-4-chloro-4-(p-fluorophenyl)-2-oxo-3-butenoate
WACGIS	174.963	2-Oxo-2-(2-thienyl)acetic acid
PEPDIX	175.017	Methyl 9-anthrylglyoxylate
HOKVOT	175.97	4-(4-Bromophenyl)-2-oxo-3-butenoic acid monohydrate
PEPDIX	175.988	Methyl 9-anthrylglyoxylate

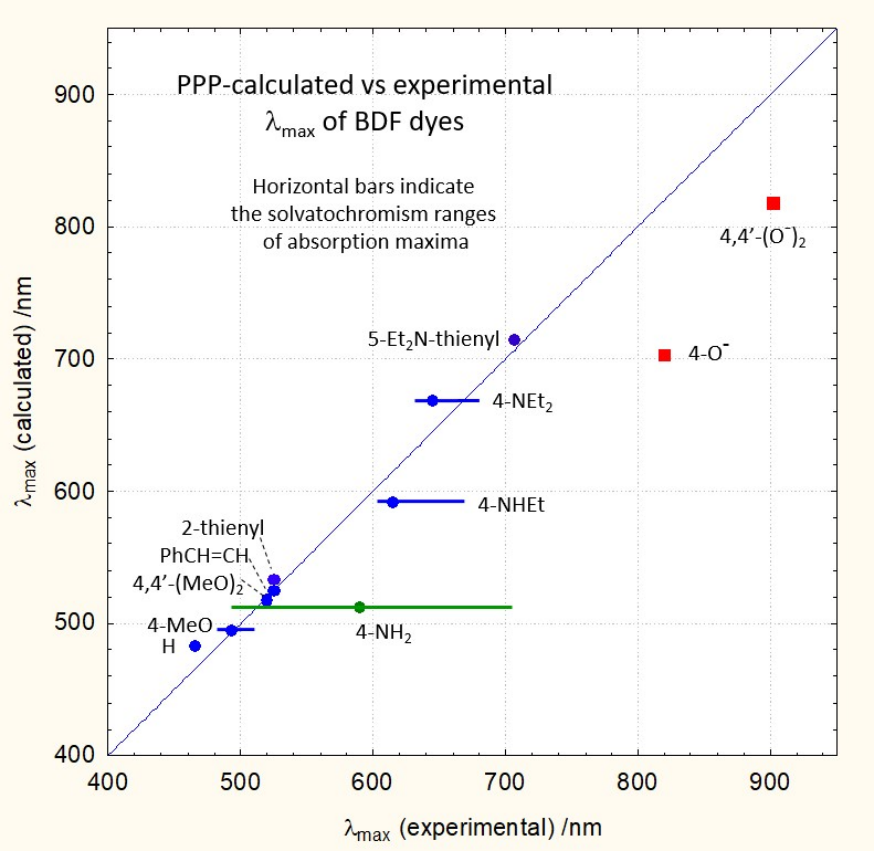
TUBCOK	176.069	bis(2-(carboxycarbonyl)imidazo[1,2-a]pyridin-1-ium) imidazo[1,2-a]pyridin-1-ium-2-yl(oxo)acetate bis(hydrogen sulfate) dihydrate
CEBMUR	176.247	(4-Methoxy-2-oxo-pentene)-carboxylic acid methyl ester
EYESAE	176.5	ethyl 2-oxo-3-(triphenylphosphoranylidene)propanoate
VEYROJ	177.115	methyl (4-hydroxy-3,4-diphenyl-3a,4-dihydro-3H-pyrrolo[2,1-c][1,4]benzothiazin-2-yl)(oxo)acetate
LOMKOP	177.386	methyl 2-(4-cyanophenyl)-5-(methoxy(oxo)acetyl)-3-furoate
NESTEL	177.506	2,3,7,8-Tetraethyl-10H-dipyrrinone-9-glyoxylic acid
AFUNIA	177.604	Ethyl (Z)-4'-(4-ethoxy-1-hydroxy-3,4-dioxobut-1-en-1-yl)biphenyl-3-carboxylate
YIFWAM	179.176	(E)-Methyl 2-oxo-4-phenylbut-3-enoate
TUBCOK	179.578	bis(2-(carboxycarbonyl)imidazo[1,2-a]pyridin-1-ium) imidazo[1,2-a]pyridin-1-ium-2-yl(oxo)acetate bis(hydrogen sulfate) dihydrate
TUBCOK	179.685	bis(2-(carboxycarbonyl)imidazo[1,2-a]pyridin-1-ium) imidazo[1,2-a]pyridin-1-ium-2-yl(oxo)acetate bis(hydrogen sulfate) dihydrate

Theoretical calculations

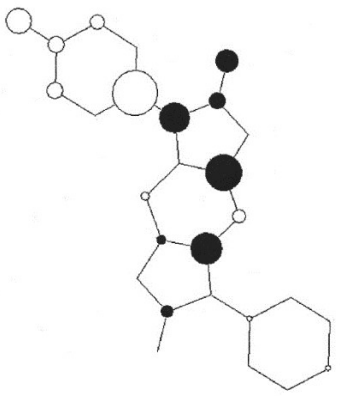
The main text references state of the art TD-DFT calculations that provide insight into the nature of excitation in BDF dyes.[1] It also refers to parallel application of lower level π-electron-only PPP theory for calculation of the same properties especially λ_{max} and π-electron charge transfer (CT) on excitation. The following Table lists in-house experimental results for BDF and related dyes, and corresponding values calculated by PPP-SCF-CI.[2] The data are compared in the plot. The degree of agreement between PPP-theory and experiment is reasonable and consistent with data from many other chromogens.[2b] (Note the problem associated with choice of experimental values for highly solvatochromic dyes. PPP does not make any allowance for data recorded in different solvents. The solvatochromism range of some of these dyes is unknown.) The deviations for the conjugate bases (red) from the ideal y = x line may be due to solvatochromic effects. Published comparison with TD-DFT for a different series of BDF dyes shows TD-DFT is superior, as to be expected.[1] However, this series does not include any anionic BDF or related derivatives.

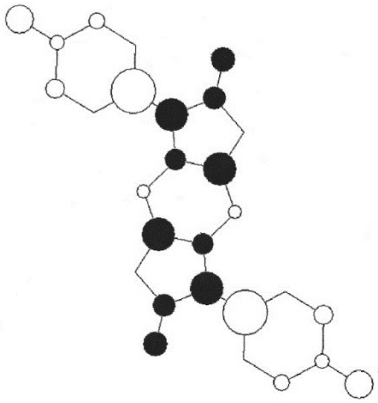


BDF derivative		λ_{max} /nm		
Ar1	Ar2	PPP	Expt	Solvent
Ph	Ph	483	466	$CHCl_3$
Ph	4-$MeOC_6H_4$	495	493	EtOAc
Ph	4-$NH_2C_6H_4$	513	590	EtOAc
Ph	4-$EtNHC_6H_4$	592	615	EtOAc
Ph	4-$Et_2NC_6H_4$	669	645	EtOAc
4-$MeOC_6H_4$	4-$MeOC_6H_4$	518	520	EtOAc
Ph	2-thienyl	533	525	acetone
Ph	5-Et_2N-2-thienyl	715	706	EtOAc
Ph	PhCH=CH	525	525	EtOAc
Ph	4-$O^{(-)}C_6H_4$	703	820	DMSO
4-$O^{(-)}C_6H_4$	4-$O^{(-)}C_6H_4$	818	902	DMSO



The graphics below show π-electron CT on excitation as calculated by PPP. Open circles represent sites of electron donation. Filled circles are electron-acceptor sites. The circle sizes reflect the relative amount of π-electron density transferred between ground state S_0 and first excited site S_1. That on the left is a 4-donor-substituted BDF. That on the right is the corresponding 4,4'-disubstituted BDF. Planar geometries were input in these runs, but the same CT pattern is found for nonplanar conformations. Electron density is transferred from electron rich pendant aryl substituents into the BDF tricyclic core, a novel complex delocalised electron acceptor.





Heteroatom identities are not shown in these diagrams. Refer to the generic structure in the Table above.

TD-DFT calculations[1] apparently give similar patterns of CT for S_1. Consequently we judge that PPP is sufficiently reliable to be also applied to the ring-opened conjugate bases **16** and **17** discussed in the main text. The key result is that both carbonyl units of their planar COCOR substituents act as π-electron acceptor centres on excitation, but that only the ketone is an acceptor when non-planar because of torsion about the CO-COR bond. Thus the planar conformation has a more bathochromic influence than nonplanar.

References

1. J. P. Cerón-Carrasco, A. Ripoche, F. Odobel, and D. Jacquemin, *Dyes and Pigments*, 2012, **92**, 1144-1152
2. (a) R. Naef, PiSystem98, Im Budler 6, CH-4419 Lupsingen, Switzerland; (b) M. G. Hutchings, *Dyes and Pigments*, 1995, **29**, 95-101