Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Synthesis and solid-state supramolecular chemistry of a series of pyridinium-derived zwitterions

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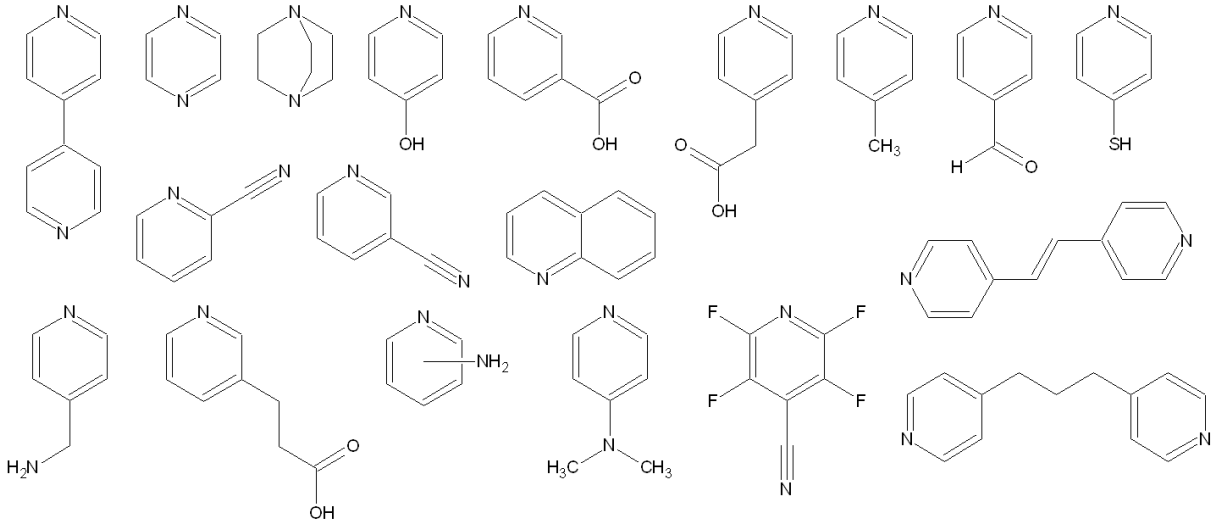
Experimental:

A variety of pyridyl-derivatives were tested for zwitterion formation using a one-pot crystallisation with acetylenedicarboxylic acid (Scheme S1).



Scheme S1 Pyridyl-derivates that have not produced crystals and are currently still under investigation for zwitterion formation: 1) 4,4′-bipyridine, 2) pyrazine, 3) DABCO, 4) 4-hydroxypyridine, 5) nicotinic acid 6) 4-pyridylacetic acid 7) 4-picoline, 8) 4-pyridinecarboxaldehyde, 9) 4-mercaptopyridine, 10) 2-cyanopyridine, 11) 3-cyanopyridine, 12) quinoline, 13) 4-(aminomethyl)pyridine, 14) 3-pyridinepropionic acid, 15) aminopyridine, 16) 4-(dimethylamino)pyridine, 17) 2,3,5,6-tetrafluoro-4-pyridinecarbonitrile, 18) 1,2-bis(4-pyridyl)ethylene, 19) 4,4′-trimethylenedipyridine.

Table S1 Selected crystallographic data for structures **1-7**

Structure	**1**	**2**	**3**	**4**	**5**	**5a**	**6_{H2O}**	**6_{MeOH}**	**6a**	**7**
Chemical formula	$C_9H_7NO_4$	$C_{13}H_9NO_4$	$C_9H_8NO_6$	$C_{10}H_6N_2O_4$	$C_{20}H_{14}N_2O_{12}$	$C_{10}H_9NO_7$	$C_{15}H_{15}NO_6$	$C_{16}H_{14}NO_5$	$C_{27}H_{24}N_2O_5$	$C_{16}H_{13}NO_4$
Formula weight	193.16	243.21	226.16	218.17	474.33	255.18	305.28	300.29	456.48	283.27
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$	$P2_1/c$	P-1	P-1	$C2/c$	$P2_1/n$	$P2_1/n$	$Pbca$
a/ Å	7.968 (4)	11.119 (3)	10.444 (3)	7.097 (3)	7.189 (5)	7.344 (5)	13.856 (6)	13.746 (5)	16.831 (7)	15.143 (1)
b/ Å	8.368 (5)	8.057 (2)	8.094 (2)	19.995 (8)	7.500 (5)	7.851 (5)	8.011 (3)	7.408 (2)	7.267 (3)	7.687 (5)
c/ Å	12.570 (7)	12.839 (3)	12.306 (4)	7.478 (3)	9.557 (7)	9.780 (6)	25.655 (1)	14.216 (5)	20.065 (8)	22.303 (2)
Σ/ °	90	90	90	90	82.788 (7)	91.428 (7)	90	90	90	90
β/ °	90	113.549 (3)	110.376 (6)	112.227 (5)	87.499 (7)	94.012 (7)	92.488 (7)	90.223 (4)	110.560 (6)	90
γ/ °	90	90	90	90	64.972 (7)	106.401 (7)	90	90	90	90
Z	4	4	4	4	1	2	8	4	4	8
Temperature / K	100(2)	100(2)	100(2)	150(2)	100(2)	100(2)	100(2)	150(2)	100(2)	100(2)
Calculated Density / $g.cm^{-1}$	1.531	1.532	1.547	1.475	1.700	1.572	1.401	1.382	1.320	1.450
μ / mm^{-1}	0.123	0.116	0.133	0.117	0.144	0.136	0.109	0.104	0.092	0.105
Independent Reflections	1888	2414	2235	2232	2117	2439	3169	3349	5190	3070

Table 2 Hydrogen bonding parameters for **1**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C3—H3···O3^{i}	0.95	2.58	3.336 (3)	137
O4—H4···O2^{ii}	0.99 (3)	1.49 (3)	2.474 (2)	172 (3)
C6—H6···O1^{iii}	0.95	2.35	3.156 (3)	142
C7—H7···O1^{iv}	0.95	2.52	3.120 (3)	121
C10—H10···O1^{v}	0.95	2.45	3.250 (3)	142
C10—H10···O4^{vi}	0.95	2.58	3.287 (3)	131
Symmetry codes: (i) −x+2, y−1/2, −z+1/2; (ii) x+1, y, z; (iii) −x+1, y+1/2, −z+1/2; (iv) x, y+1, z; (v) x+1/2, −y+1/2, −z+1; (vi) x−1/2, −y+1/2, −z+1.				

Table 3 Hydrogen bonding parameters for **2**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
O4—H4···O2^{i}	0.97 (3)	1.51 (3)	2.483 (2)	176 (3)
C6—H6···O1^{ii}	0.95	2.53	3.296 (2)	138
C14—H14···O1^{iii}	0.95	2.39	3.287 (2)	158
Symmetry codes: (i) x, y+1, z; (ii) −x+1, −y+1, −z+1; (iii) −x+3/2, y+1/2, −z+3/2.				

Table 4 Hydrogen bonding parameters for **3**

D*—H···*A	***D*—H**	***H*···*A***	***D*···*A***	***D*—H···*A***
O4—H1···O2^{i}	0.99 (3)	1.55 (4)	2.539 (2)	171 (3)
C3—H3···O6^{ii}	0.95	2.55	3.309 (3)	137
C7—H7···O3^{iv}	0.95	2.54	3.164 (3)	123
C9—H9···O1^{ii}	0.95	2.38	3.235 (3)	149
O6—H4···O2	0.79 (4)	2.09 (4)	2.851 (2)	162 (3)
O6—H2···O1^{v}	0.87 (5)	1.99 (4)	2.835 (2)	165 (4)
O7—H11···O6^{vi}	1.02 (2)	1.56 (2)	2.586 (3)	179 (3)
Symmetry codes: (i) x, y+1, z; (ii) −x+1, y+1/2, −z+1/2; (iii) −x+1, −y+1, −z; (iv) −x+2, y−1/2, −z+1/2; (v) −x+1, y−1/2, −z+1/2; (vi) −x+2, −y+1, −z+1.				

Table 5 Hydrogen bonding parameters for **4**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
O4—H4···O1^{ii}	0.98 (3)	1.52 (3)	2.501 (2)	177 (2)
C6—H6···O2^{iii}	0.95	2.18	3.088 (2)	160
C8—H8···O1^{iv}	0.95	2.23	3.094 (2)	150
C9—H9···O1^{v}	0.95	2.22	3.141 (2)	164
Symmetry codes: (i) −x, −y+1, −z+1; (ii) x, y, z+1; (iii) x, −y+1/2, z+1/2; (iv) x+1, y, z+1; (v) −x+1, −y+1, −z+1.				

Table 6 Hydrogen bonding parameters for **5**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C3—H3···O3^{i}	0.96 (2)	2.41 (2)	3.343 (2)	167 (1)
O4—H4···O1^{ii}	0.93 (2)	1.60 (2)	2.526 (2)	175 (2)
O5—H10···O2^{iii}	0.96 (2)	1.64 (2)	2.593 (2)	177 (2)
C5—H5···O6^{iv}	0.95	2.30	3.150 (2)	149
C6—H6···O4^{v}	0.95	2.46	3.388 (3)	167
C8—H8···O1^{vi}	0.95	2.37	3.177 (2)	143
C9—H9···O1^{vii}	0.95	2.34	3.235 (2)	157
Symmetry codes: (i) −x, −y+2, −z+1; (ii) x, y−1, z; (iii) −x+2, −y+1, −z+2; (iv) x−1, y+1, z; (v) −x+1, −y+1, −z+2; (vi) x+1, y−1, z; (vii) −x+1, −y+2, −z+1.				

Table 7 Hydrogen bonding parameters for **5a**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
O1A—H1A···O4A^{i}	1.02 (3)	1.48 (3)	2.494 (2)	173 (2)
C2B—H2B···O3A^{v}	0.95	2.43	3.245 (2)	143
C2B—H2B···O5B^{vi}	0.95	2.45	3.131 (3)	129
O1C—H1C···O2A	0.86 (2)	1.93 (2)	2.785 (2)	170 (2)
N1B—H1B···O1C^{iv}	0.94 (2)	1.81 (2)	2.684 (2)	153 (2)
C6B—H6B···O1C	0.95	2.42	3.299 (2)	154
Symmetry codes: (i) x, y+1, z; (ii) x+1, y, z; (iii) −x+1, −y+1, −z+1; (iv) −x+1, −y, −z+1; (v) x, y, z+1; (vi) x, y−1, z.				

Table 8 Hydrogen bonding parameters for $\mathbf{6_{MeOH}}$

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C5—H5···O2^{ii}	0.95	2.42	3.074 (2)	126
C6B—H6B···O2^{ii}	0.95	2.41	3.03 (2)	123
O6C—H2···O3^{iii}	0.84 (3)	1.97 (3)	2.798 (2)	167 (3)
O1—H1···O4^{iv}	0.86 (4)	1.59 (4)	2.446 (2)	171 (4)
Symmetry codes: (ii) −x+2, −y, −z+1; (iii) x-1, y, z; (iv) x, y-1, z.				

Table 9 Hydrogen bonding parameters for $\mathbf{6_{H2O}}$

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C5B—H5B···O1^{i}	0.95	2.26	3.16 (2)	157
C9B—H9B···O4^{ii}	0.95	2.60	3.395 (9)	142
C9B—H9B···O5	0.95	2.62	3.340 (1)	133
C9A—H9A···O1^{iii}	0.95	2.50	3.392 (9)	158
C9A—H9A···O5	0.95	2.62	3.171 (9)	117
C5A—H5A···O1^{i}	0.95	2.46	3.392 (1)	166
O5—H5···O1^{iii}	0.98 (3)	1.84 (3)	2.811 (2)	167 (3)
O4—H4···O2^{iv}	0.93 (5)	1.57 (5)	2.461 (2)	160 (4)
O5—H6···O3^{v}	0.95 (3)	1.93 (3)	2.843 (2)	162 (3)
O2—H2···O4^{vi}	0.96 (2)	1.51 (3)	2.461 (2)	168 (8)
Symmetry codes: (i) −x, y, −z+1/2; (ii) −x+1/2, y−1/2, −z+1/2; (iii) −x+1/2, y+1/2, −z+1/2; (iv) x, y+1, z; (v) x+1/2, y−1/2, z; (vi) x, y-1, z.				

Table 10 Hydrogen bonding parameters for **6a**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C2B—H2B···O2A^{i}	0.95	2.51	3.213 (3)	131
C3B—H3B···O1D^{i}	0.95	2.58	3.276 (3)	130
C5B—H5B···O1D^{ii}	0.95	2.46	3.399 (3)	172
C6B—H6B···O1A	0.95	2.60	3.219 (3)	123
C2C—H2C···O3A	0.95	2.31	3.231 (3)	163
C3C—H3C···O1A	0.95	2.47	3.392 (3)	163

C5C—H5C···O1A^{iii}	0.95	2.33	3.148 (3)	145
C6C—H6C···O4A^{iv}	0.95	2.66	3.292 (3)	125
N1B—H1···O1A	1.08 (3)	2.54 (3)	3.231 (3)	121 (2)
N1B—H1···O2A	1.08 (3)	1.53 (3)	2.603 (2)	178 (3)
N1C—H2···O3A^{iv}	1.09 (3)	1.53 (3)	2.618 (2)	173 (2)
N1C—H2···O4A^{iv}	1.09 (3)	2.56 (3)	3.298 (3)	124 (2)
O1D—H3···O4A^{v}	0.98 (3)	1.77 (3)	2.752 (2)	178 (3)
Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) x−1/2, −y+1/2, z−1/2; (iii) −x+3/2, y−1/2, −z+1/2; (iv) −x+2, −y+1, −z+1; (v) x, y−1, z.				

Table 11 Hydrogen bonding parameters for **7**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
O4—H4···O1^{i}	0.91 (2)	1.72 (2)	2.617 (1)	171 (2)
C5—H5···O1^{ii}	0.95	2.59	3.210 (1)	123
C5—H5···O2^{ii}	0.95	2.44	3.248 (2)	143
C6—H6···O1^{ii}	0.95	2.60	3.215 (2)	123
C9—H9···O2^{iii}	0.95	2.36	3.093 (2)	134
Symmetry codes: (i) x, y−1, z; (ii) −x, y−1/2, −z+1/2; (iii) −x+1/2, y−1/2, z.				

DSC and TG analysis

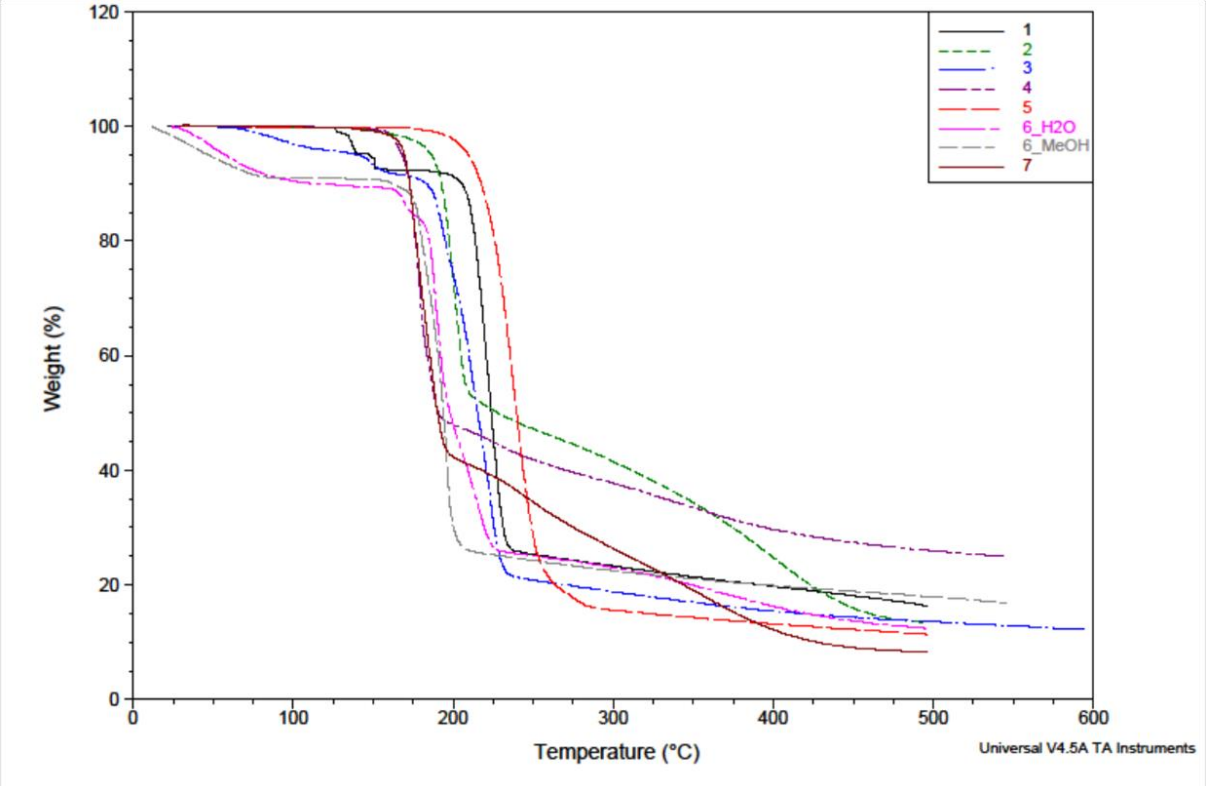


Figure S1 Overlay of TGA analysis of compounds **1-7**.

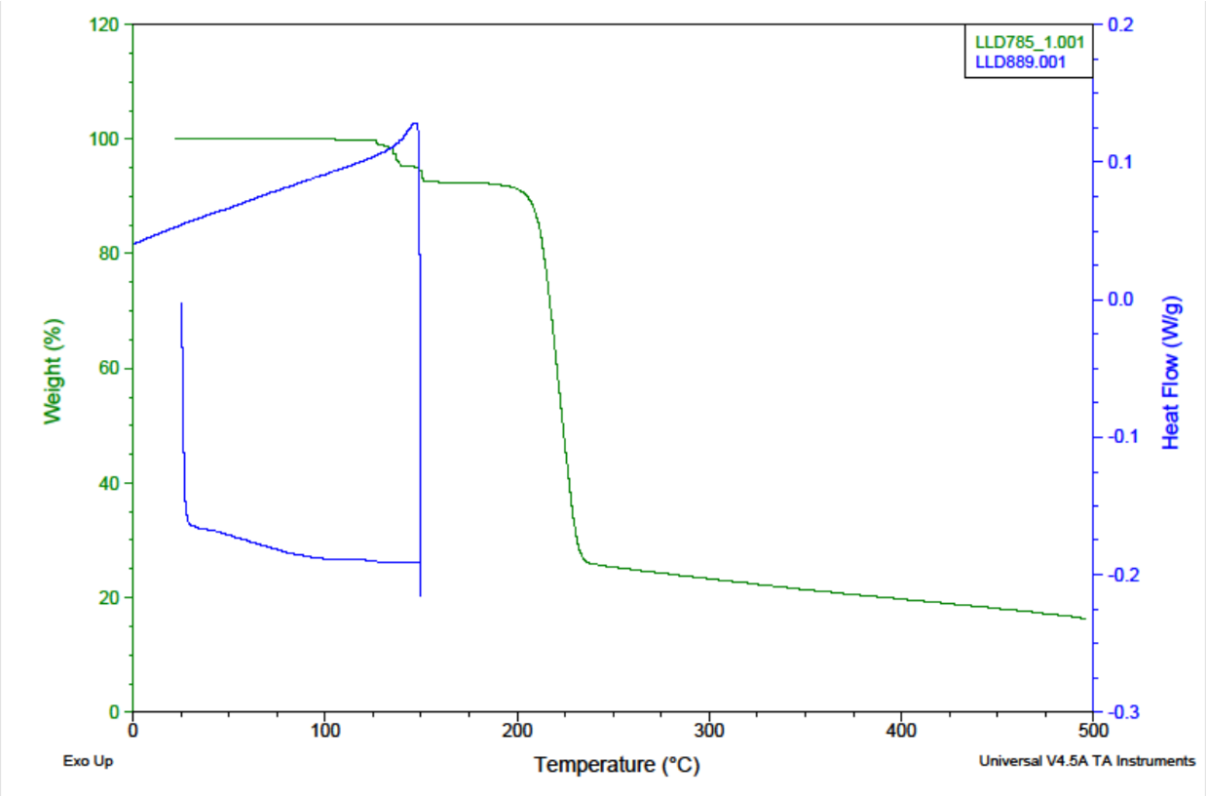


Figure S2 DSC (blue) and TG (green) analysis of **1**

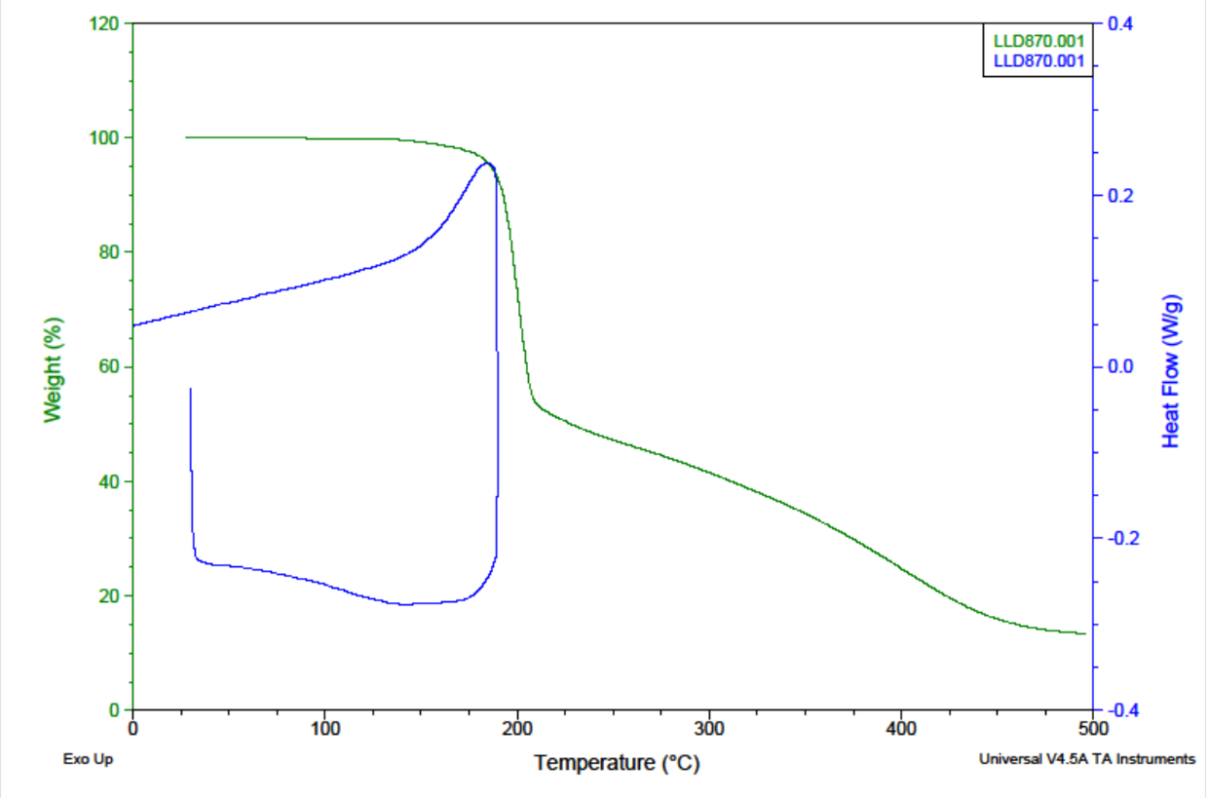


Figure S3 DSC (blue) and TG (green) analysis of **2**

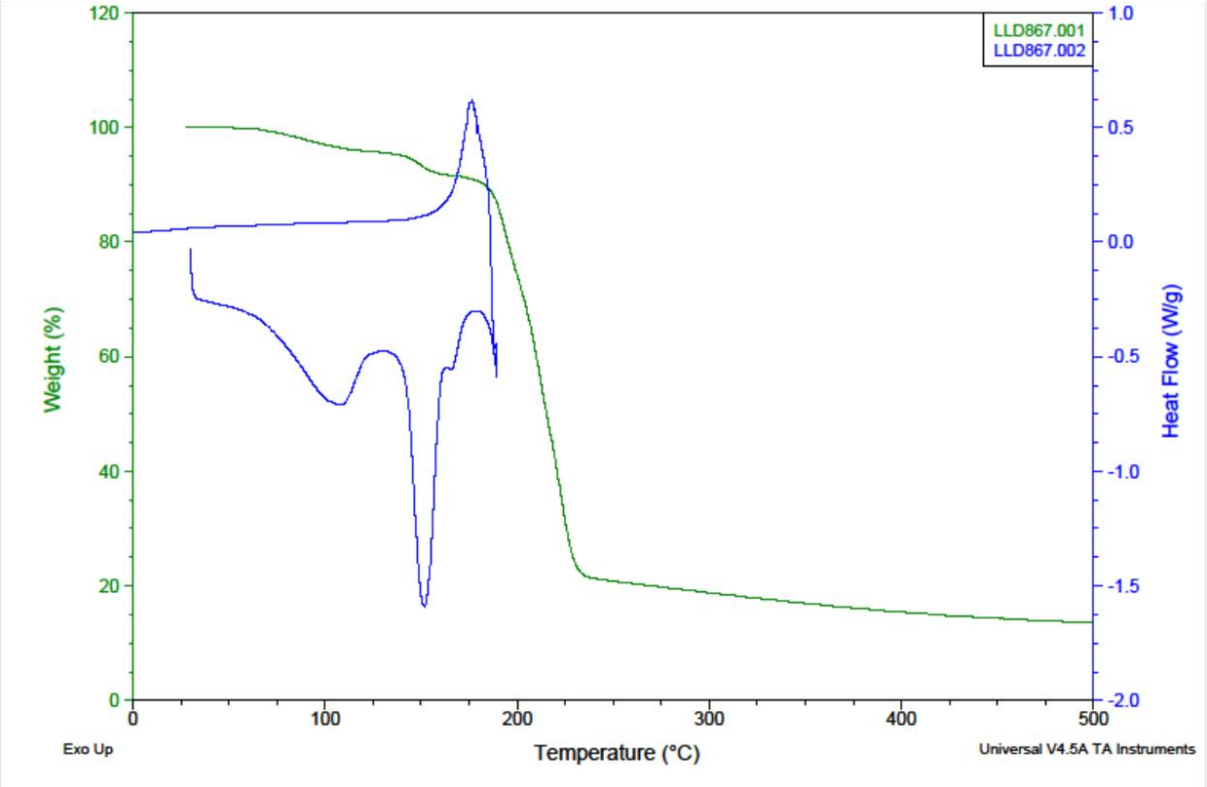


Figure S4 DSC (blue) and TG (green) analysis of **3**.

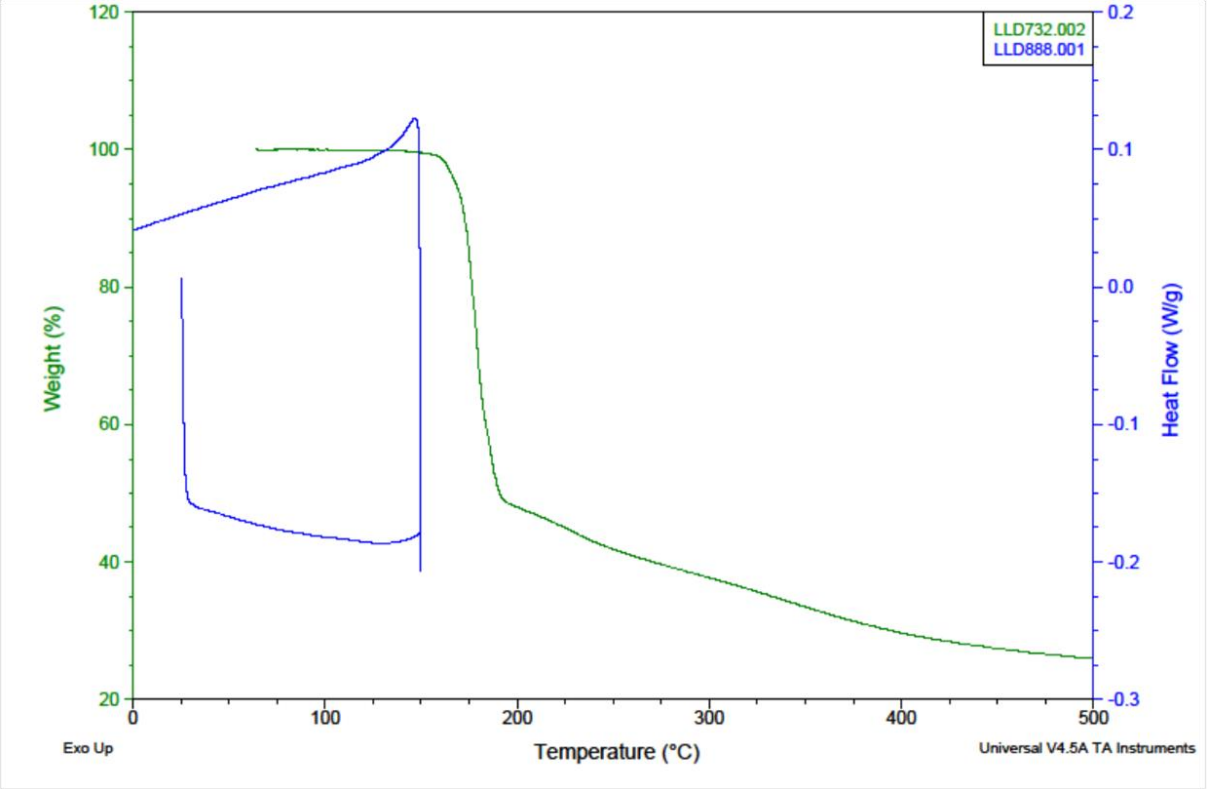


Figure S5 DSC (blue) and TG (green) analysis of **4**.

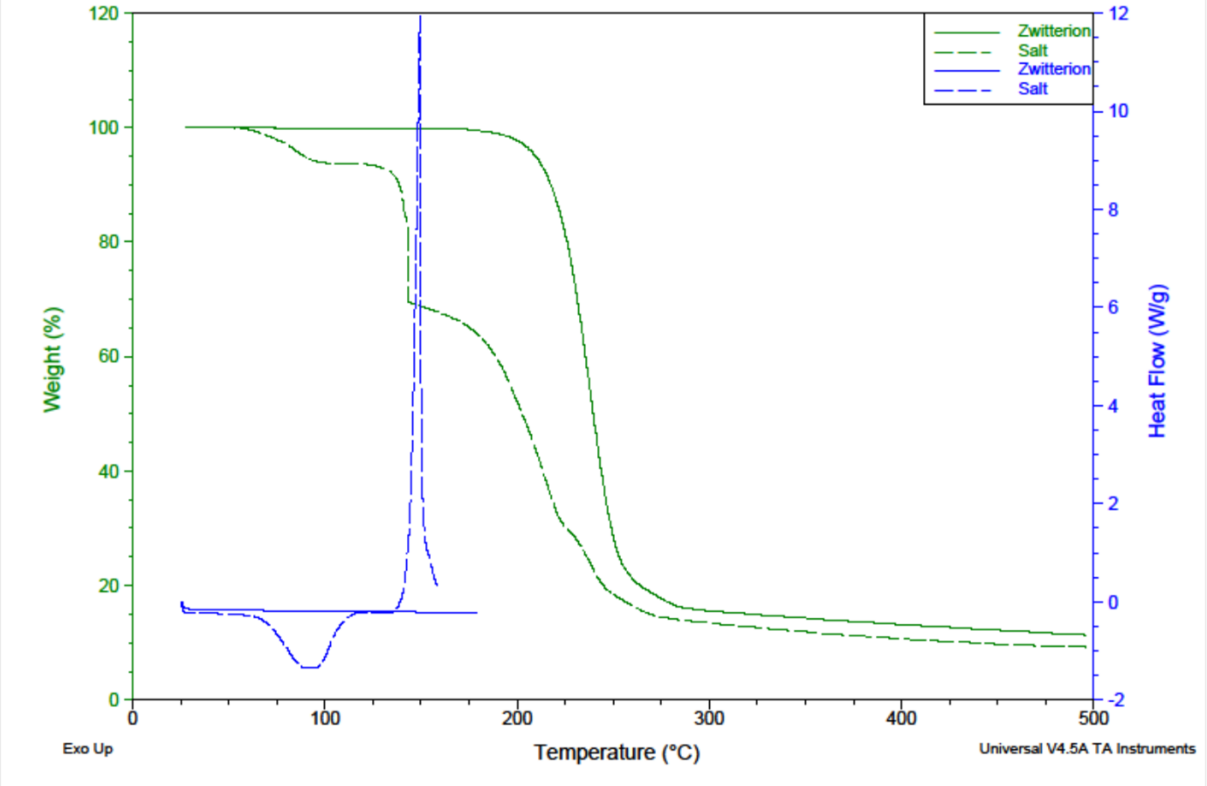


Figure S6 DSC (blue) and TG (green) analysis of **5** (solid line) and **5a** (dotted line).

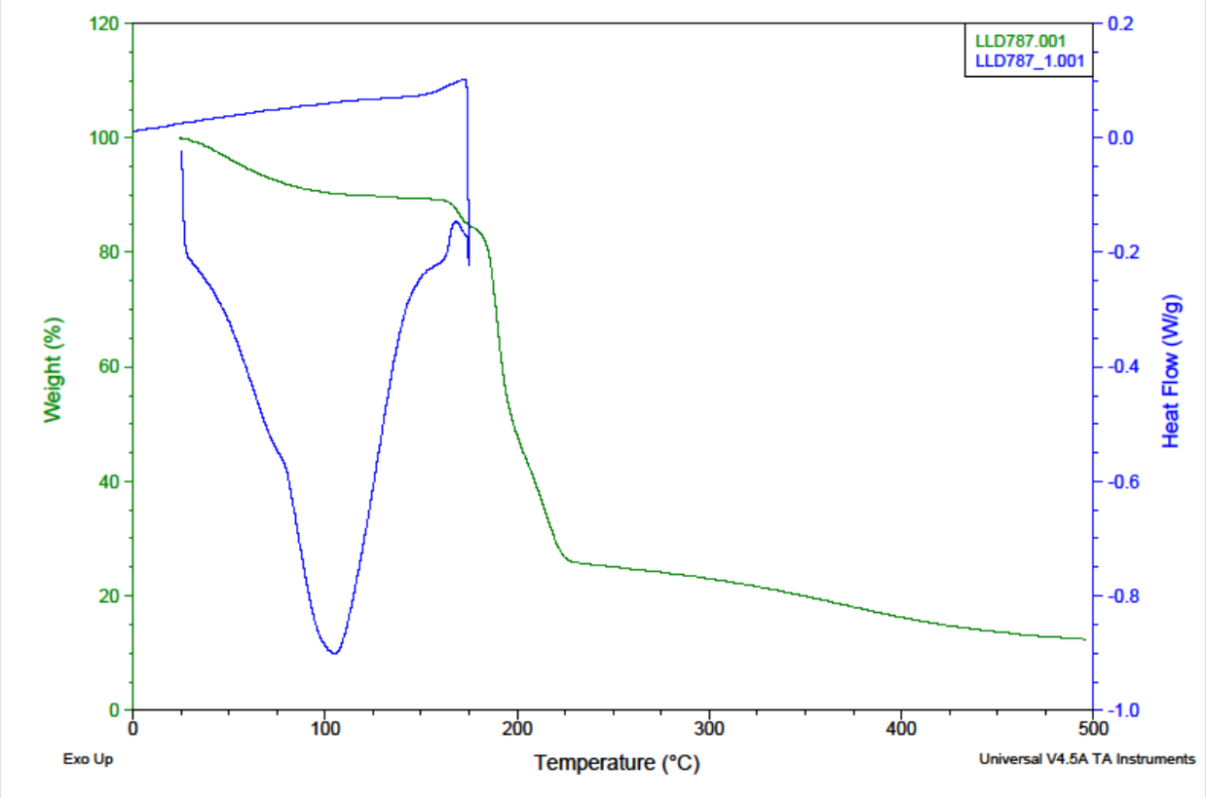


Figure S7 DSC (blue) and TG (green) analysis of $\mathbf{6}_{\mathbf{H2O}}$, 11.02% weight loss corresponds to the expected 11.1% for two molecules of water per 1 molecule of **6** as observed in the crystal structure (two partially occupied molecules).

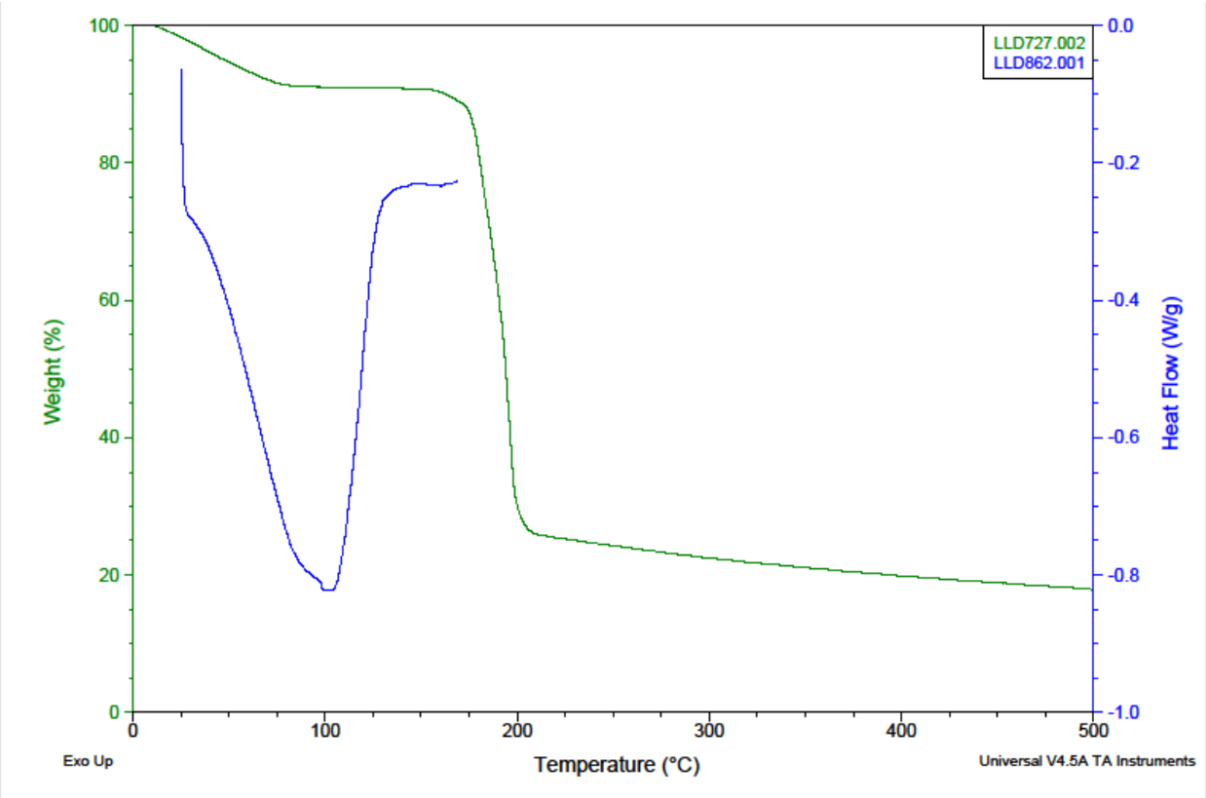


Figure S8 DSC (blue) and TG (green) analysis of $\mathbf{6}_{\mathbf{MeOH}}$. The TGA shows a 9.2% mass loss which corresponds to one methanol molecule per host molecule. This corresponds well with the crystal structure data.

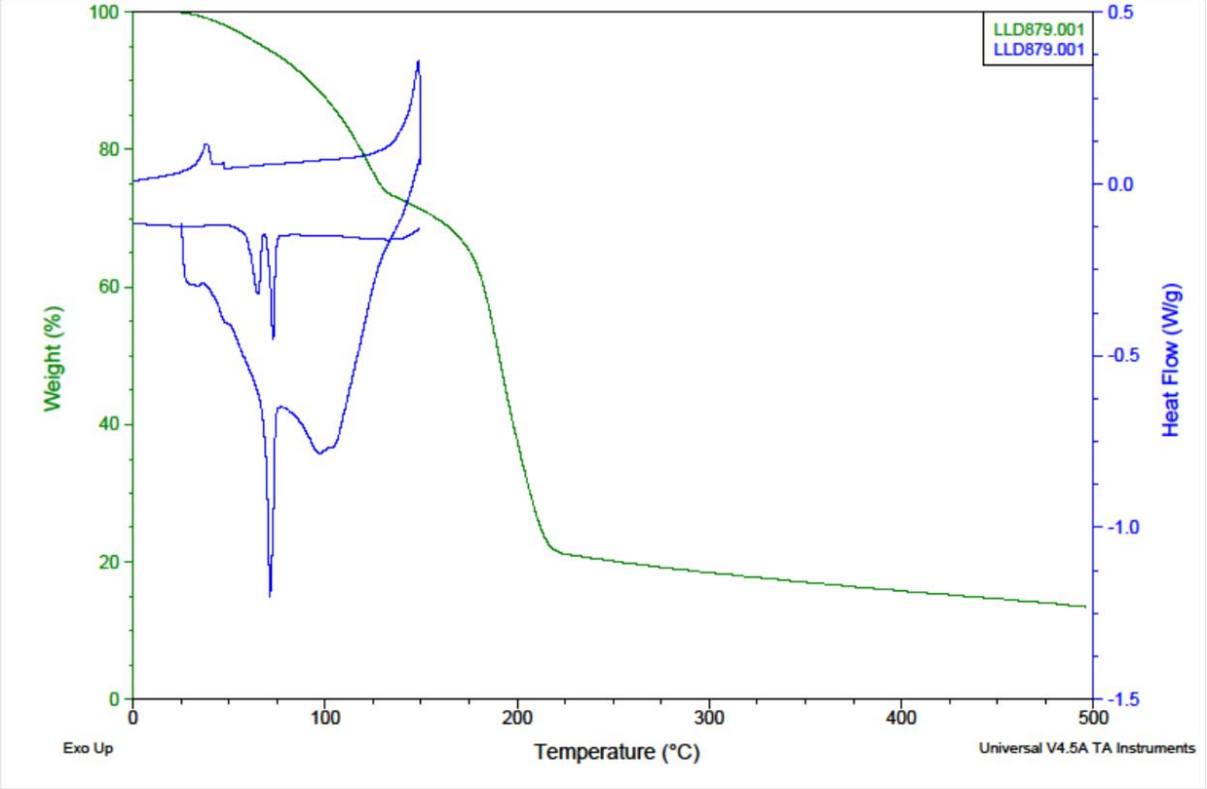


Figure S9 DSC (blue) and TG (green) analysis of **6a**. TGA shows a large mass loss (27%) starting at ambient temperature.

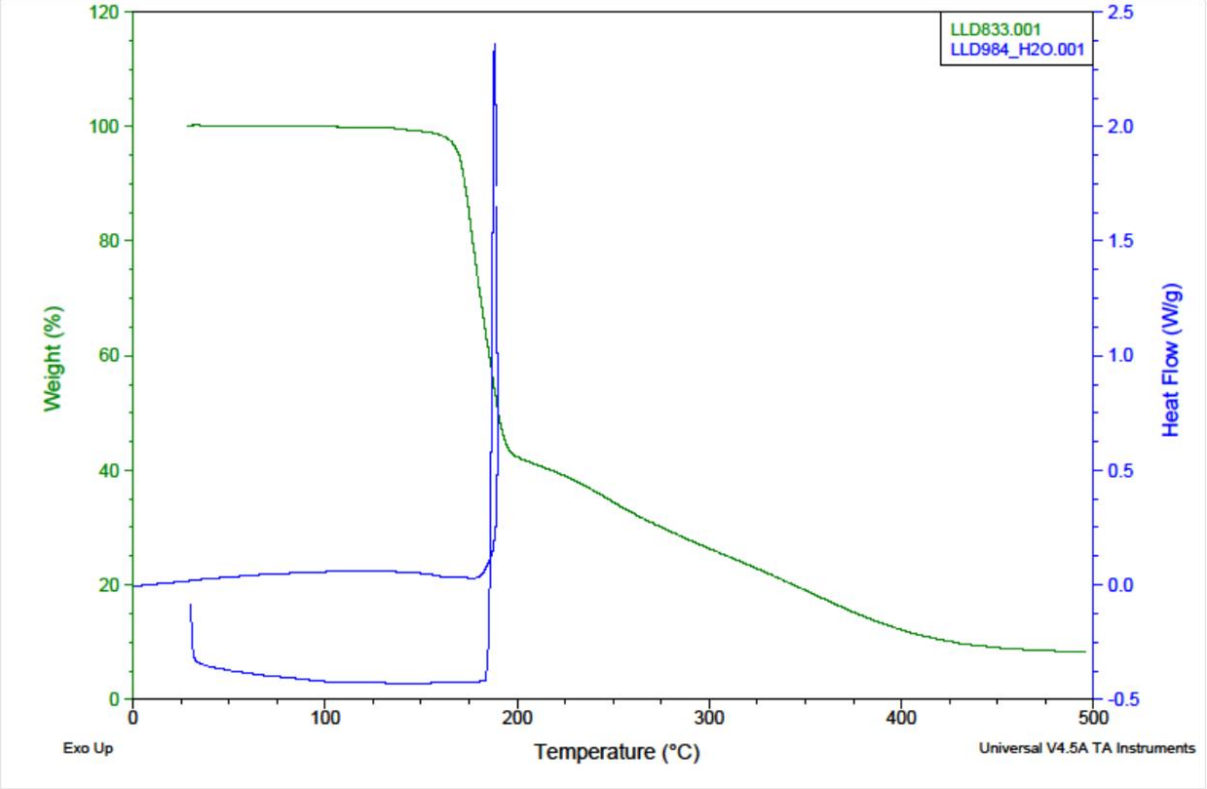


Figure S10 DSC (blue) and TG (green) analysis of **7**

PXRD Analysis:

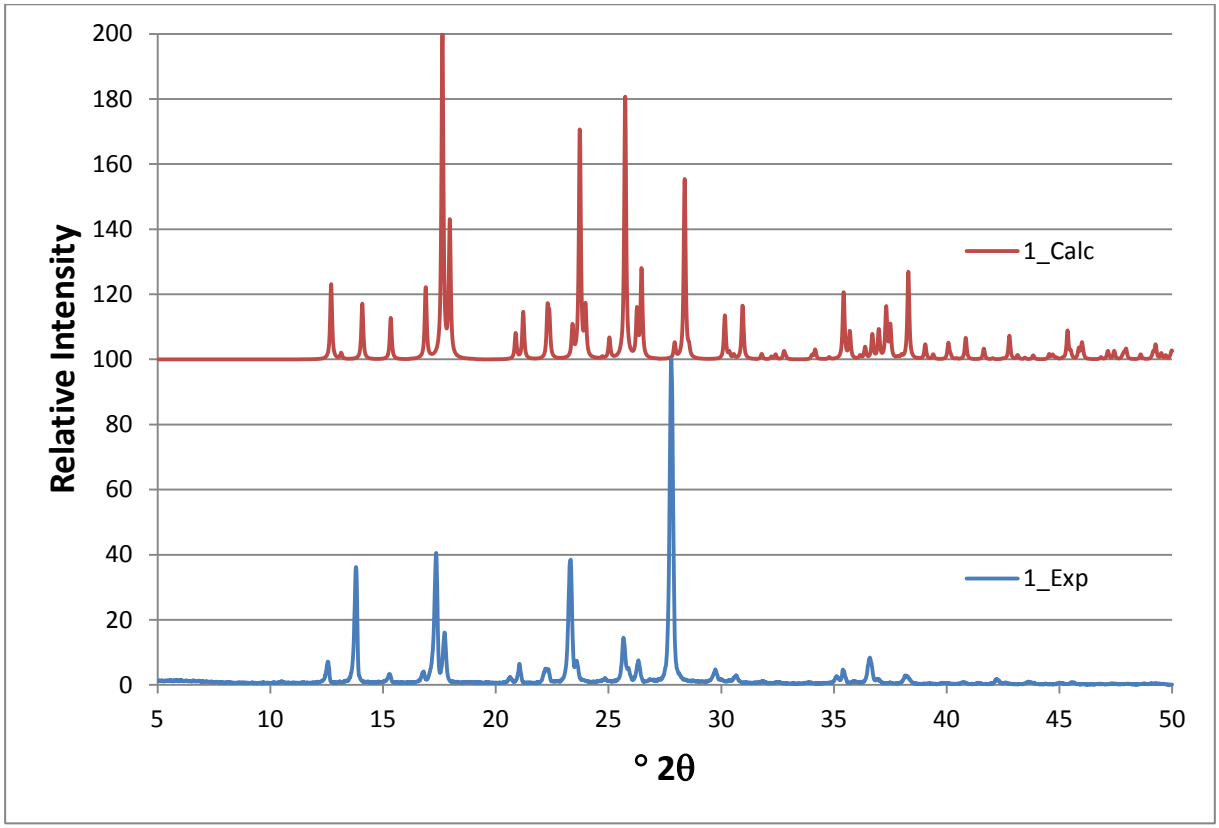


Figure S11 PXRD patterns for **1**, calculated (red) and experimental (blue)

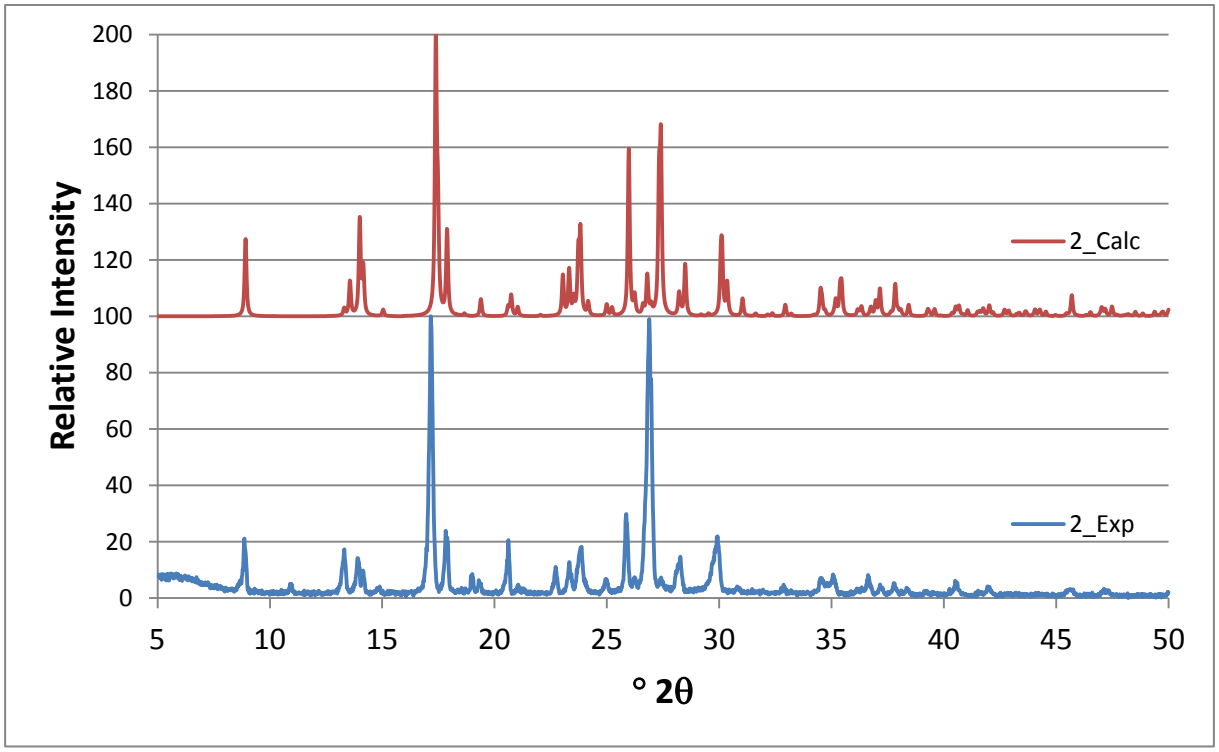


Figure S12 Calculated (red) and experimental (blue) PXRD patterns for compound **2**.

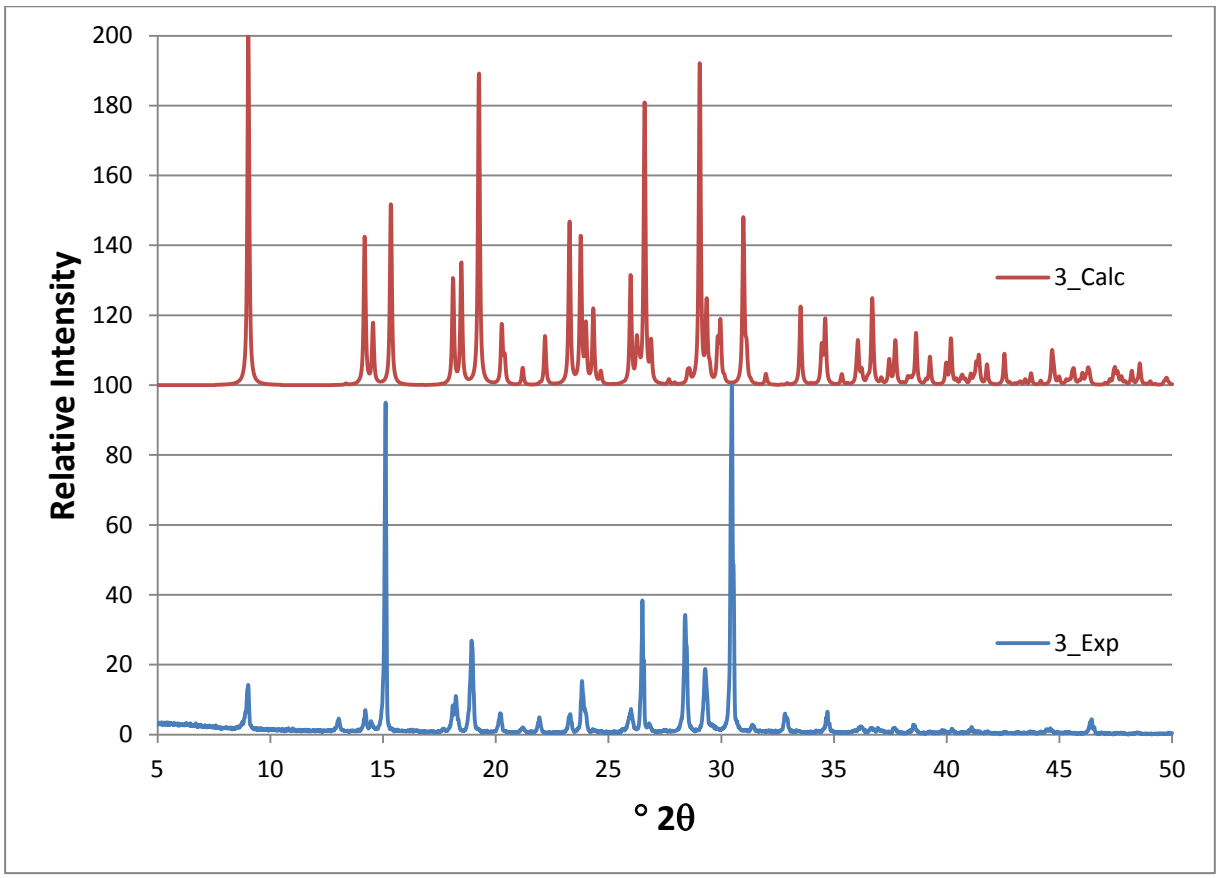


Figure S13 Calculated (red) and experimental (blue) PXRD patterns for compound **3**

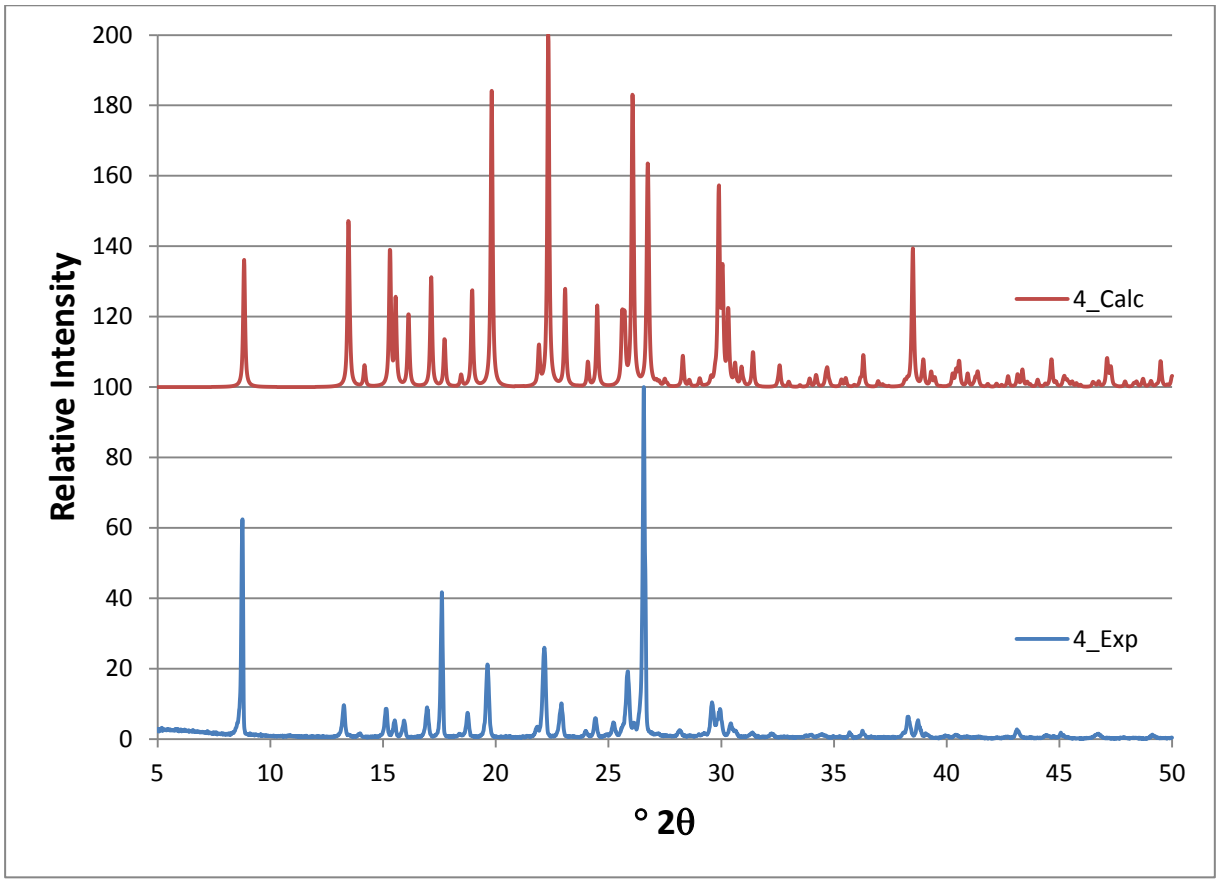


Figure S14 Calculated (red) and experimental (blue) PXRD patterns for compound **4**

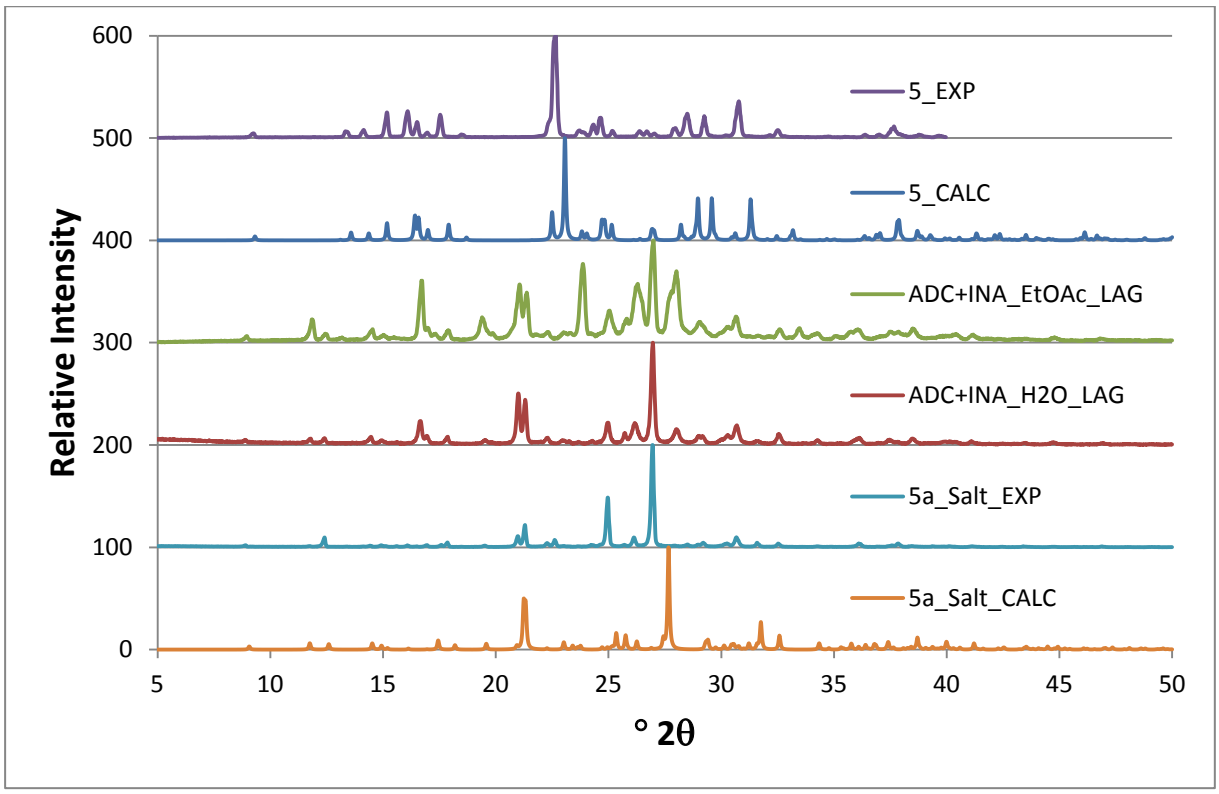


Figure S15 Experimental and calculated PXRD patterns for **5** and **5a** compared to the products obtained from liquid-assisted grinding (LAG) experiments using either ethyl acetate (EtOAc) or water (H_2O) as solvent.

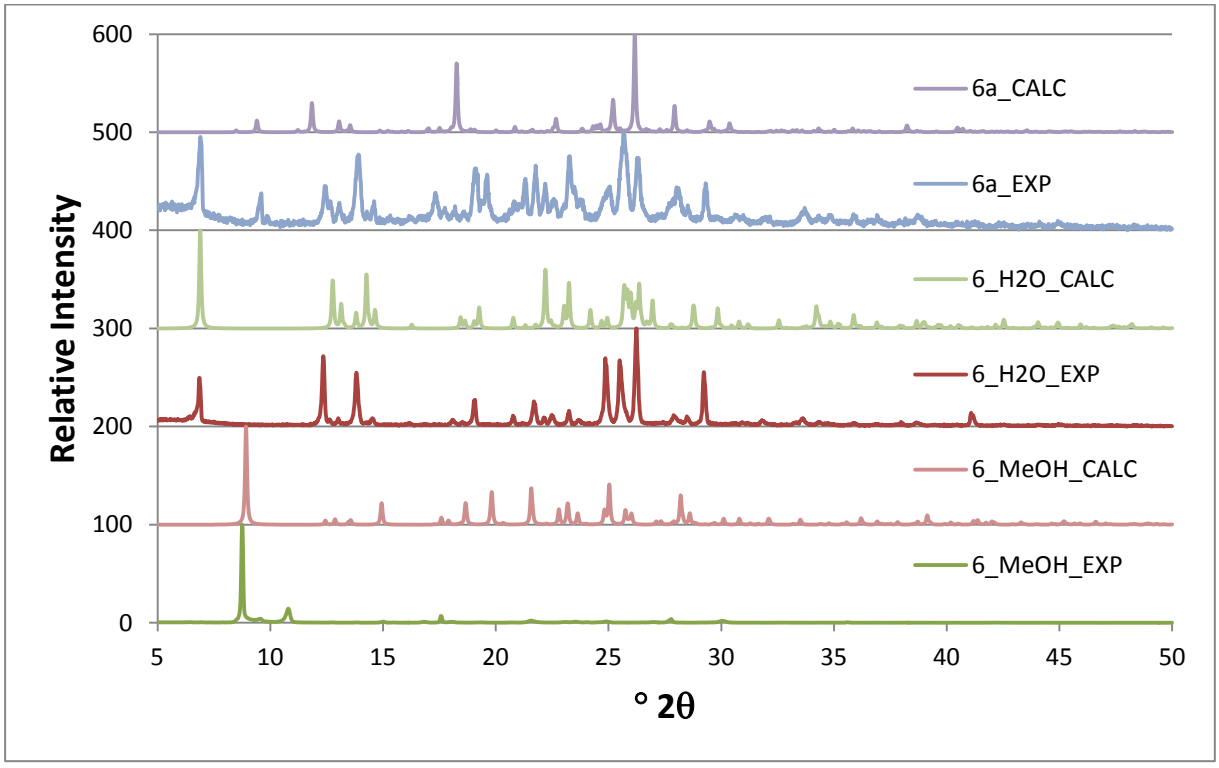


Figure S16 Comparison of experimental and calculated PXRD patterns for $\mathbf{6}_{\mathbf{H2O}}$, $\mathbf{6}_{\mathbf{MeOH}}$ and **6a** (salt). The experimental pattern for **6a** appears to be a physical mixture of **6a** as well as some of $\mathbf{6}_{\mathbf{H2O}}$. The experimental pattern for $\mathbf{6}_{\mathbf{MeOH}}$ contains a few peaks that do not correspond to the calculated pattern. These peaks can be attributed to a mixture of products – solvent loss occurs when $\mathbf{6}_{\mathbf{MeOH}}$ is exposed to the atmosphere resulting in an apohost product.

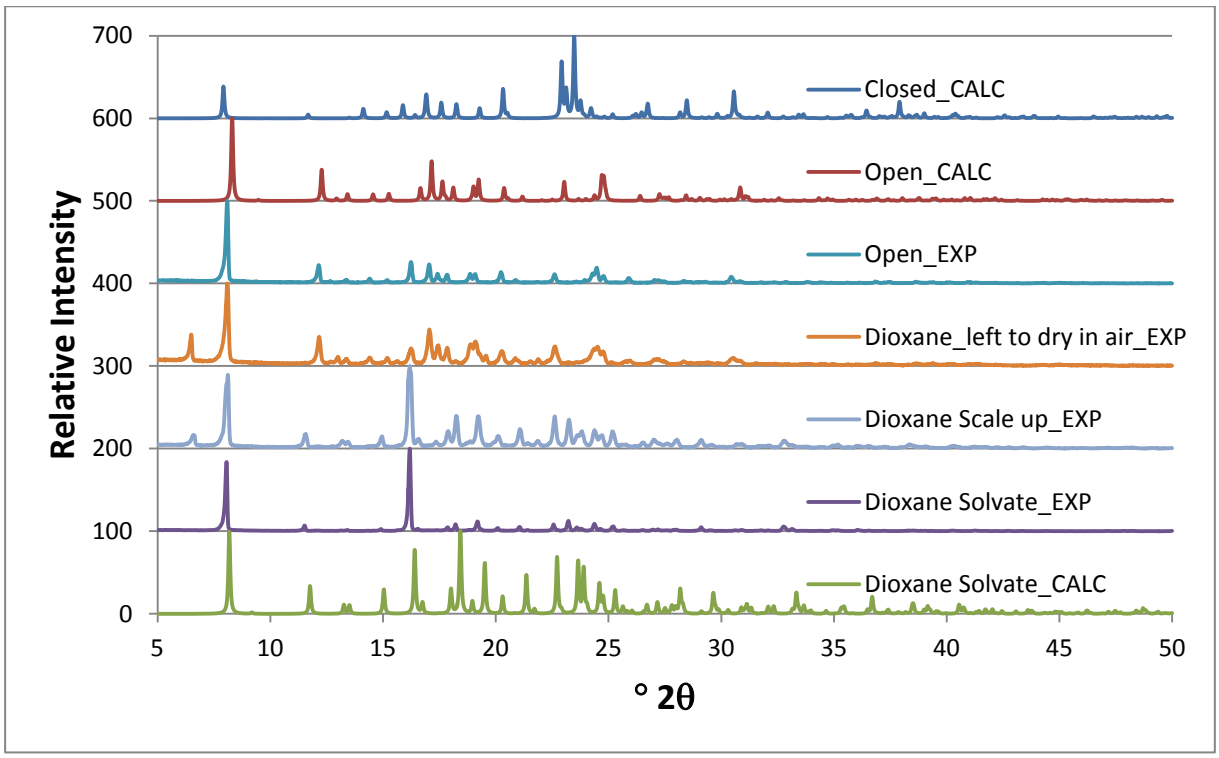


Figure S17 Comparison of experimental and calculated PXRD patterns for **7** (calc), $\mathbf{7}_{\mathbf{open}}$, $\mathbf{7}_{\mathbf{diox}}$ and $\mathbf{7}_{\mathbf{diox}}$ that was left in air for approximately 3 weeks

NMR Spectra

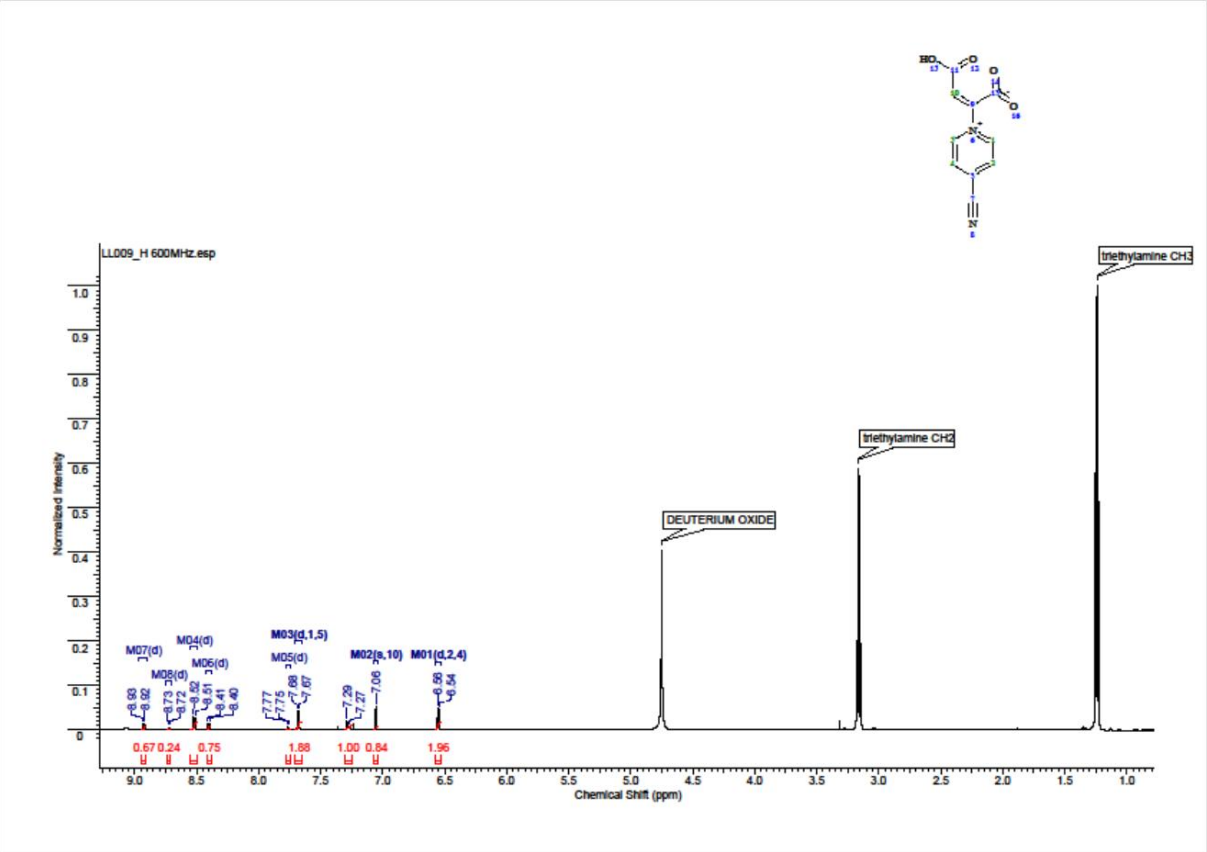


Figure S18 ^{1}H NMR spectrum for **4**, the zwitteric compound was identified by comparing the ratio of the intergrals of the resonance peaks.

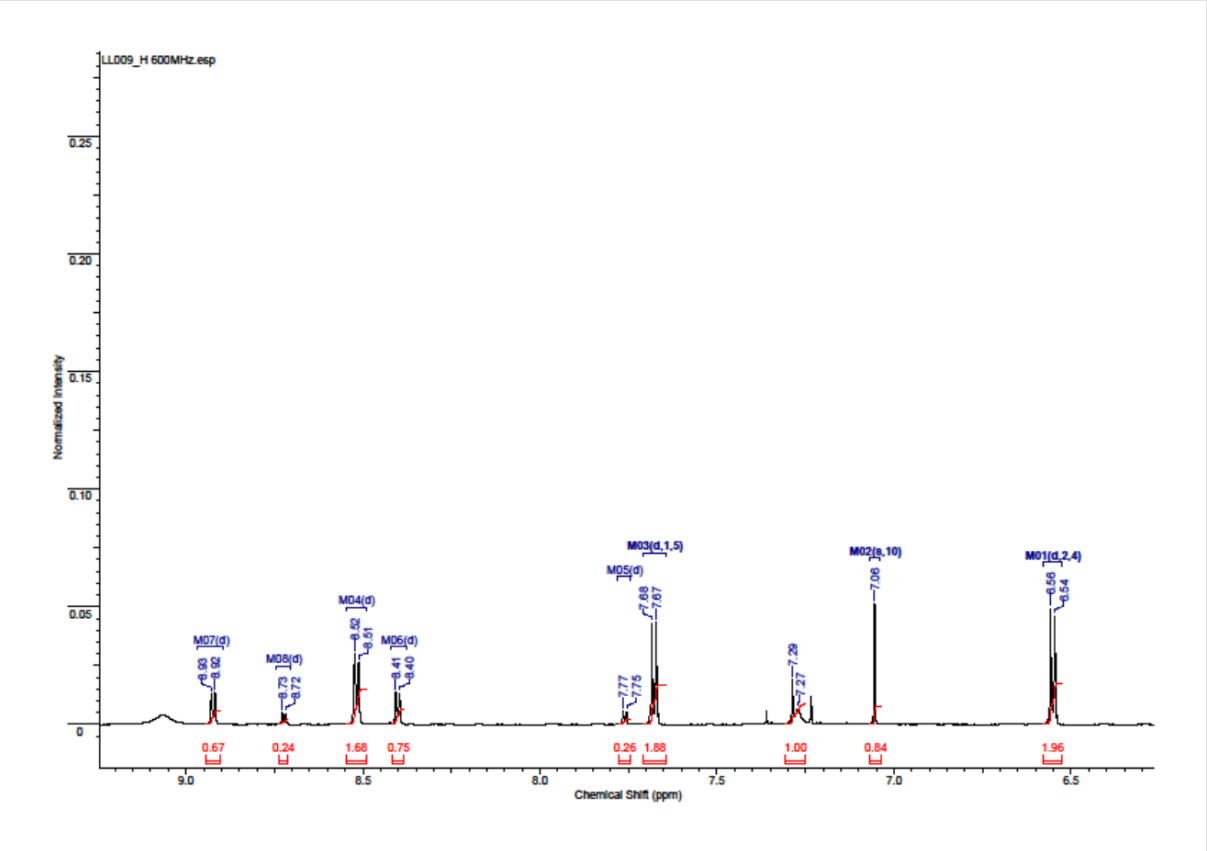


Figure S19 Zoomed in view of ^{1}H NMR spectrum for **4** showing chemical shifts in the area 6-9 ppm.

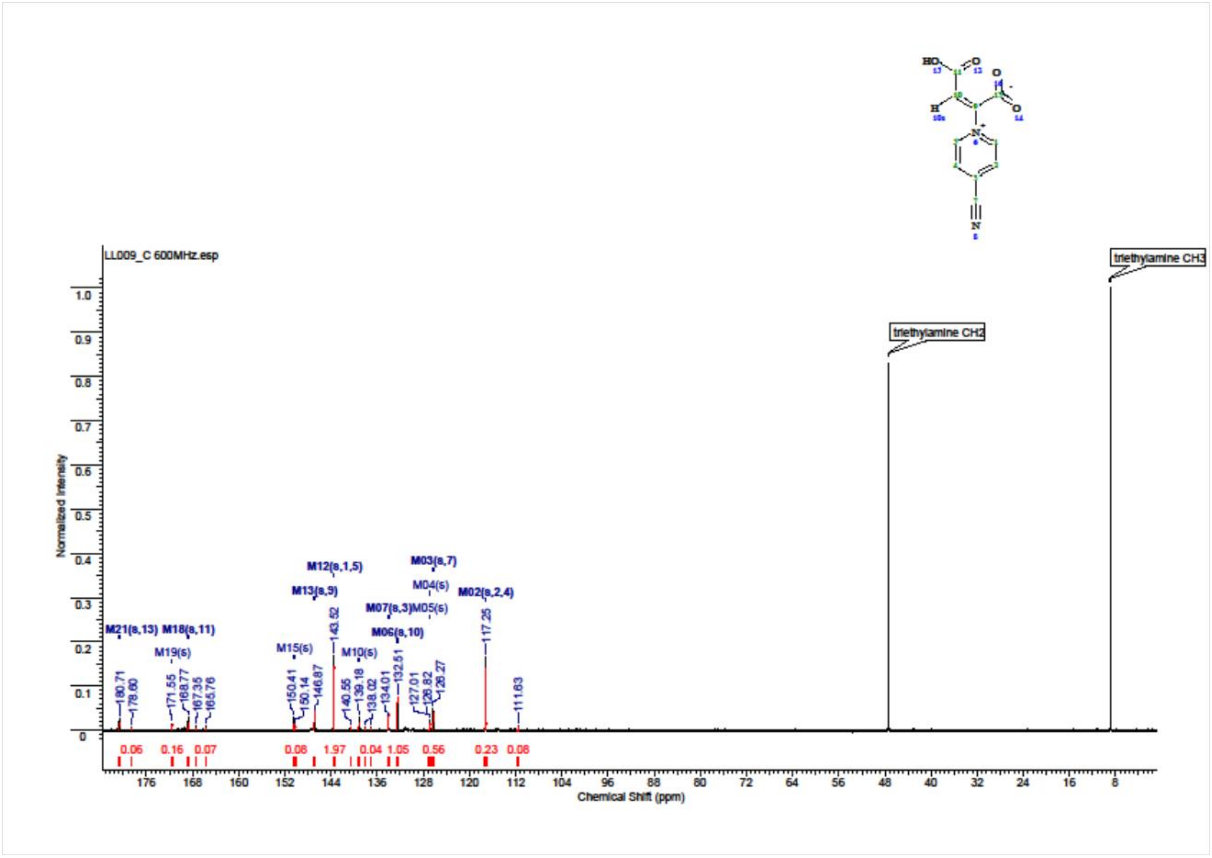


Figure S20 ^{13}C NMR spectrum for **4**, the zwitteric compound was identified by comparing the ratio of the intergrals of the resonance peaks.

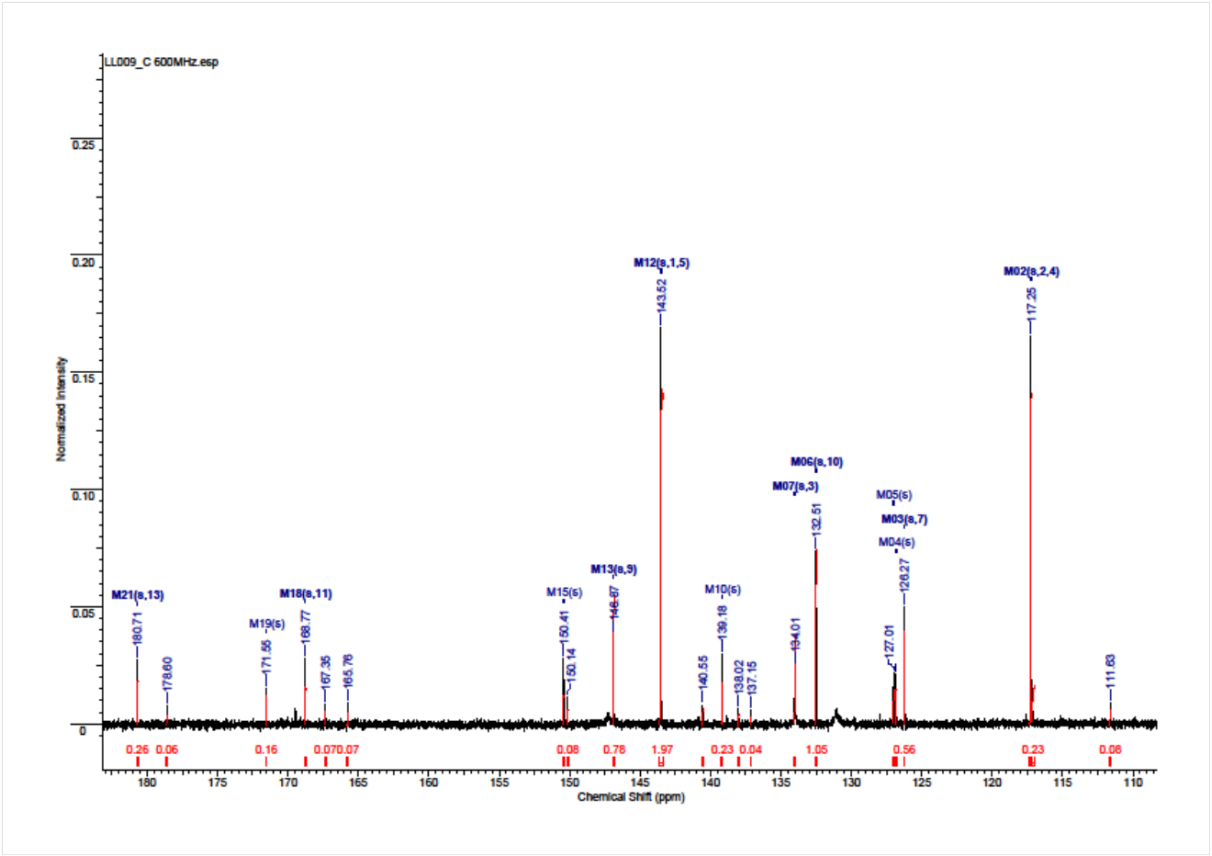


Figure S21 Zoomed in view of ^{13}C NMR spectrum for **4** showing chemical shifts in the area 110-180 ppm