Electronic Supplementary Material (ESI) for CrystEngComm.

Design of solvatomorphic structures based on polyboronated tetraphenyladamantane molecular tecton

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SUPPORTING INFORMATION

1. Single-crystal X-ray diffraction of studied compounds

Table S1. Selected crystal data, data collection and refinement parameters for **1-DMF**, **1-DMSO**, **1-A** and **1-Diox-W**.

	1-DMF	**1-DMSO**	**1-A**	**1-Diox-W**
Formula	$C_{46}H_{63}B_4N_4O_{12}$	$C_{44}H_{60}B_4O_{13}S_5$	$C_{49}H_{66}B_4O_{13}$	$C_{42}H_{54}B_4O_{13}$
Molecular mass, M_r / a.u.	907.24	1000.46	906.25	810.09
Temperature, T / K	100.0(1)	100.0(1)	100.0(1)	100.0(1)
Crystal system	monoclinic	tetragonal	tetragonal	tetragonal
Space group	*C2/c*	*P4/n*	*P4/n*	$I4_1/a$
a / Å	30.202(13)	18.8442(15)	18.51710(10)	17.4201(7)
b/ Å	7.1631(2)	18.8442(15)	18.51710(10)	17.4201(7)
c/ Å	25.2857(5)	7.0478(6)	7.06700(10)	26.248(3)
α / °	90	90	90	90
β / °	117.95(4)	90	90	90
γ / °	90	90	90	90
Volume, V / Å^3	4941(3)	2502.7(5)	2423.15(4)	7965.2(12)
Z / Z'	4	2	2	8
d_{calc} / g·cm^{-3}	1.221	1.328	1.242	1.351
F(000)	1936.0	1056.0	968.0	3440.0
θ range / °	6.626 to 133.706	6.634 to 77.948	6.75 to 134.074	6.09 to 80.698
Absorption coefficient, μ / mm^{-1}	0.703	2.634	0.707	0.796
Index ranges	$-36 \le h \le 35$, $-6 \le k \le 8$, $-30 \le l \le 30$	$-13 \le h \le 14$, $-15 \le k \le 15$, $-5 \le l \le 5$	$-22 \le h \le 21$, $-21 \le k \le 21$, $-8 \le l \le 7$	$-9 \le h \le 14$, $-14 \le k \le 8$, $-21 \le l \le 19$
No. of reflections collected / unique	13019	3272	16021	4974
Independent reflections	4347 [R_{int} = 0.0317, R_{sigma} = 0.0368]	698 [R_{int} = 0.0436, R_{sigma} = 0.0336]	2162 [R_{int} = 0.0254, R_{sigma} = 0.0138]	1222 [R_{int} = 0.0359, R_{sigma} = 0.0287]
No. of parameters / restrains	4347/4/311	698/90/162	2162/1/169	1222/5/271
GooF	1.020	1.205	1.214	1.670
$R[F]$ / $wR[F^2]$ ($I > 2\sigma(I)$) / %	R_1 = 7.59, wR_2 = 21.33	R_1 = 11.68, wR_2 = 24.42	R_1 = 9.58, wR_2 = 19.64	R_1 = 11.18, wR_2 = 34.83
$R[F]$ / $wR[F^2]$ (all data) / %	R_1 = 10.33, wR_2 = 23.91	R_1 = 0.13.17, wR_2 = 25.22	R_1 = 9.47, wR_2 = 19.70	R_1 = 12.70, wR_2 = 36.37
Max. and min. residual density/ e·Å^{-3}	0.82/–0.41	0.41/–0.31	0.36/–0.48	0.48/–0.30

Table S2. Selected crystal data, data collection and refinement parameters for **1'-W**, **1'-Urea** and **1-DMSO-ACN**.

	1'-W	**1'-Urea**	**1-DMSO-ACN**
Formula	$C_{38}H_{48}B_4O_{10}$	$C_{19.5}H_{24}B_2NO_{4.5}$	$C_{43}H_{61.5}B_4N_{0.5}O_{12}S_4$
Molecular mass, M_r / a.u.	708.00	366.02	948.90
Temperature, T / K	100.0(1)	100.0(1)	100.0(1)
Crystal system	tetragonal	tetragonal	tetragonal
Space group	*P*-4	*P4/n*	*P4/n*
a / Å	11.2591(7)	16.1648(15)	18.7776(3)
b/ Å	11.2591(7)	16.1648(15)	18.7776(3)
c/ Å	7.1282(5)	7.1212(12)	7.0172(3)
α / °	90	90	90
β / °	90	90	90
γ / °	90	90	90
Volume, V / Å^3	903.62(13)	1860.8(5)	2474.25(13)
Z / Z'	1	4	2
d_{calc} / g·cm^{-3}	1.301	1.307	1.274
F(000)	376.0	776.0	1006.0
θ range / °	7.852 to 140.272	7.734 to 145.4	6.656 to 153.43
Absorption coefficient, μ / mm^{-1}	0.736	0.729	2.238
Index ranges	$-13 \le h \le 12$, $-13 \le k \le 8$, $-8 \le l \le 8$	$-11 \le h \le 19$, $-18 \le k \le 17$, $-5 \le l \le 8$	$-17 \le h \le 23$, $-23 \le k \le 21$, $-8 \le l \le 8$
No. of reflections collected / unique	3220	3415	8918
Independent reflections	1510 [R_{int} = 0.0436, R_{sigma} = 0.0374]	1784 [R_{int} = 0.0556, R_{sigma} = 0.0799]	2558 [R_{int} = 0.0480, R_{sigma} = 0.0509]
No. of parameters / restrains	1510/0/120	1784/12/185	2558/38/161
GooF	1.122	1.114	1.055
$R[F]$ / $wR[F^2]$ ($I > 2\sigma(I)$) / %	R_1 = 6.57, wR_2 = 18.53	R_1 = 15.08, wR_2 = 39.39	R_1 = 8.25, wR_2 = 24.22
$R[F]$ / $wR[F^2]$ (all data) / %	R_1 = 7.58, wR_2 = 19.58	R_1 = 19.46, wR_2 = 42.35	R_1 = 11.26, wR_2 = 26.99
Max. and min. residual density/ e·Å^{-3}	0.27/–-0.32	0.62/–0.40	1.41/–0.44

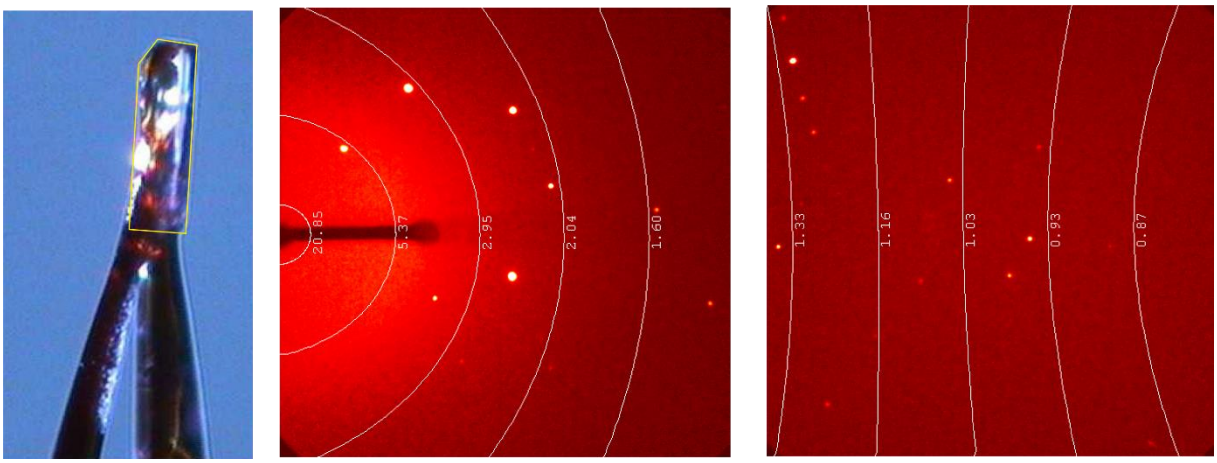


Figure S1. 1-A crystal snapshot together with two exemplary X-Ray diffraction frames.

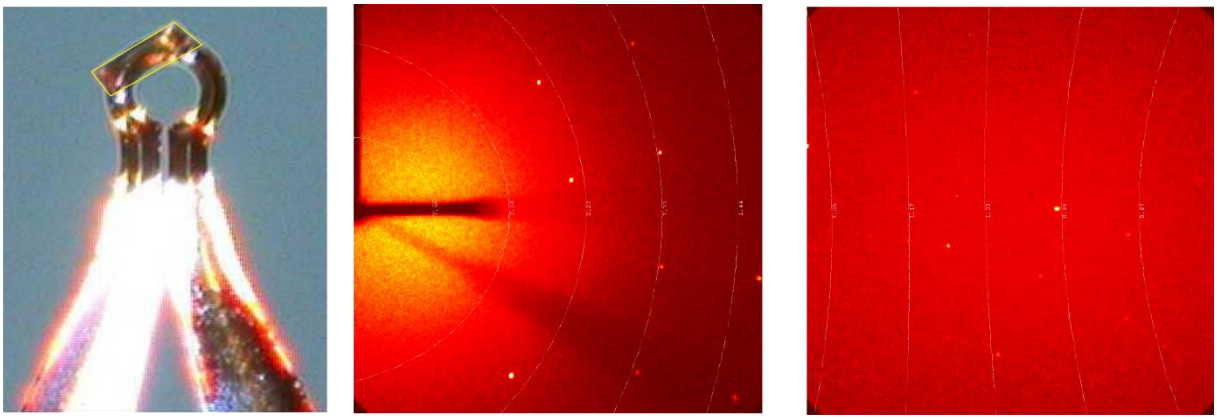


Figure S2. 1-DMF crystal snapshot together with two exemplary X-Ray diffraction frames.

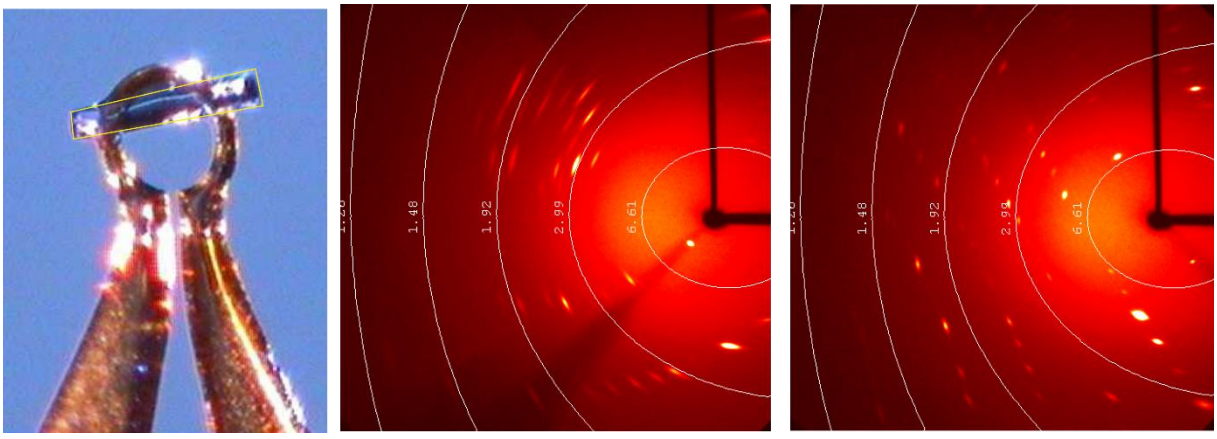


Figure S3. 1-DMSO crystal snapshot together with two exemplary X-Ray diffraction frames.

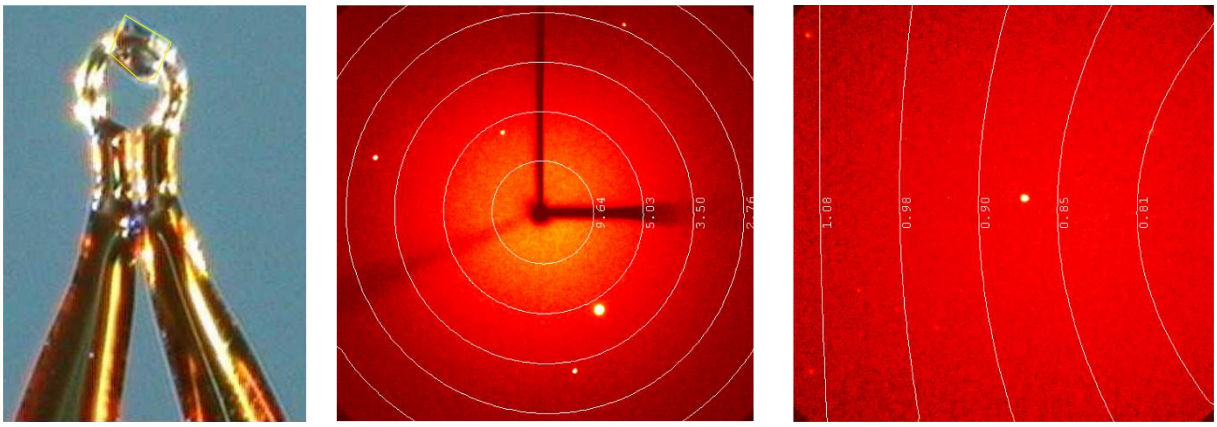


Figure S4. 1-DMSO-ACN crystal snapshot together with two exemplary X-Ray diffraction frames.

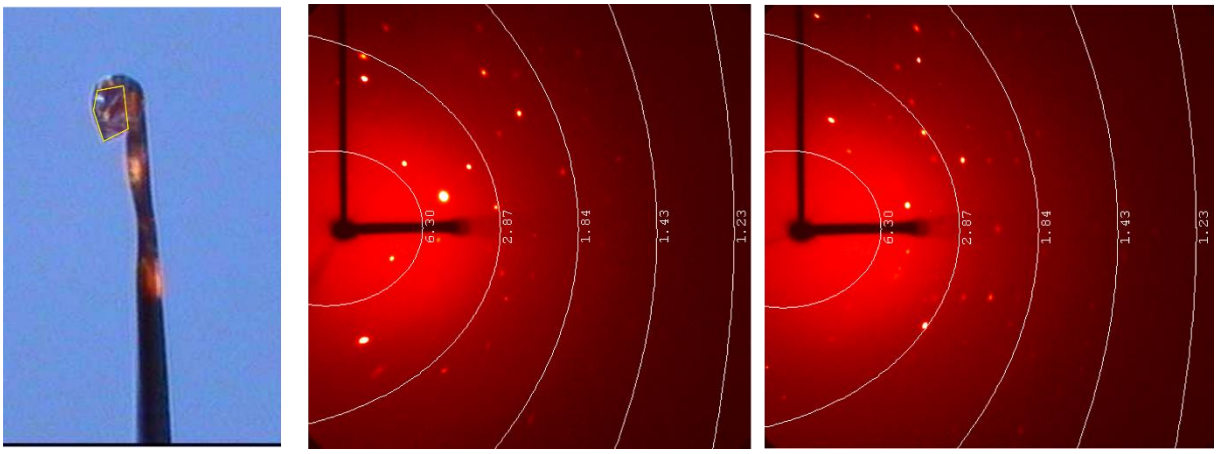


Figure S5. 1-Diox-W crystal snapshot together with two exemplary X-Ray diffraction frames.

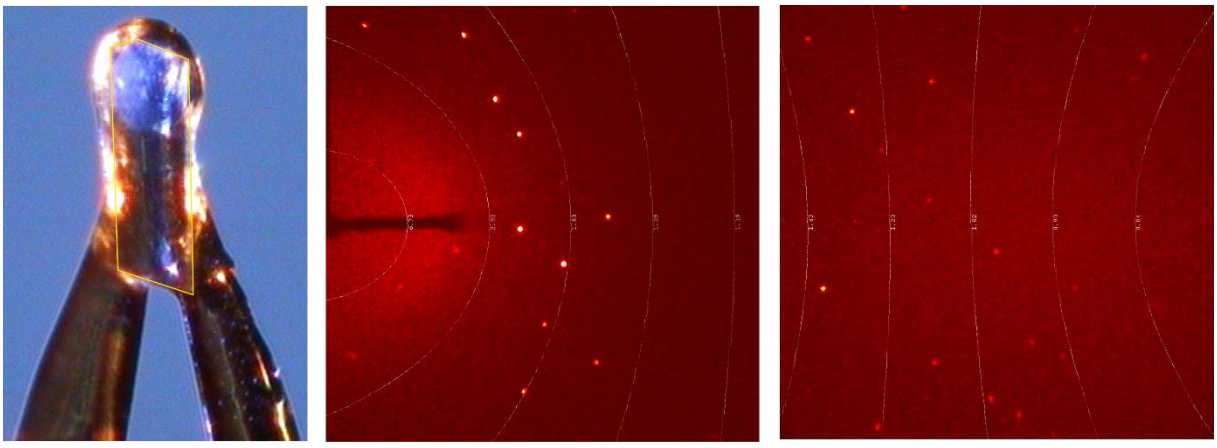


Figure S6. 1'-Urea crystal snapshot together with two exemplary X-Ray diffraction frames.

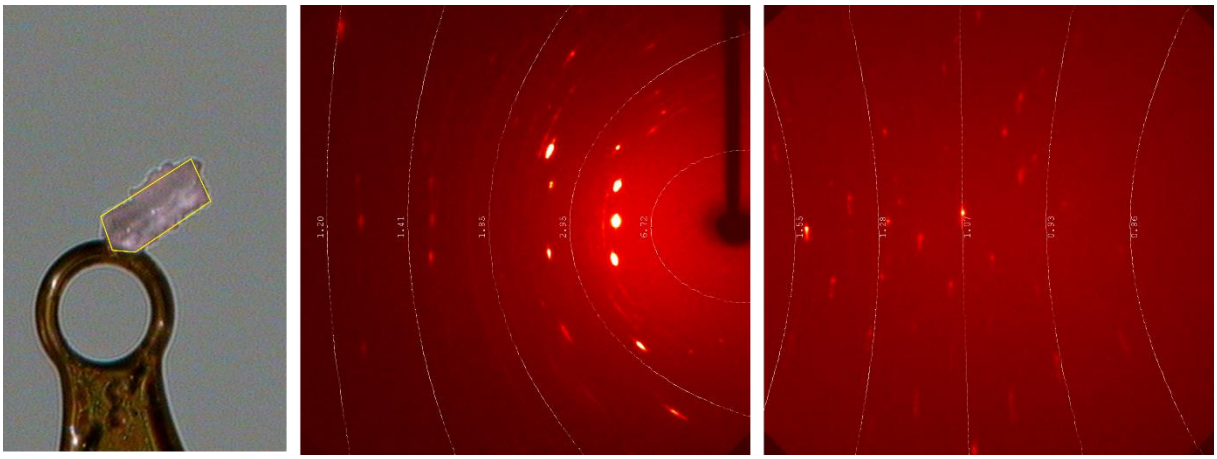


Figure S7. 1'-W crystal snapshot together with two exemplary X-Ray diffraction frames.

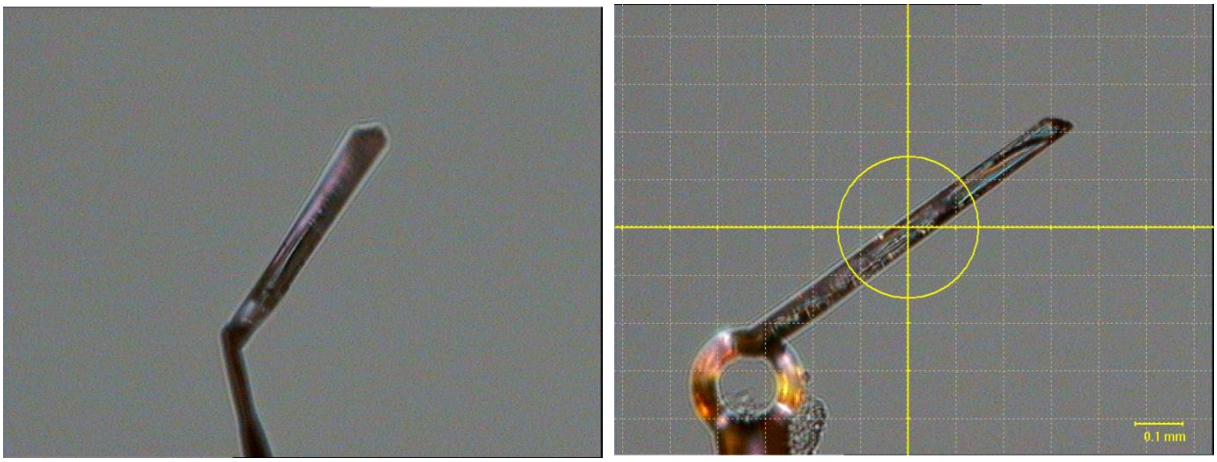
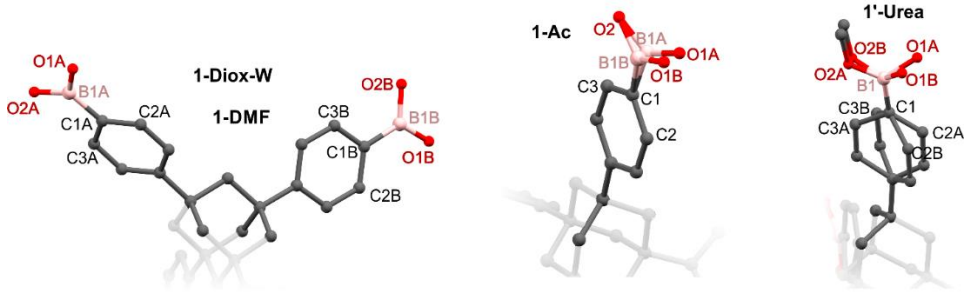


Figure S8. Snapshot of crystals obtained from MeOH-ACN crystallization attempt together with two exemplary X-Ray diffraction frames.

Table S3. Comparison of basic geometric parameters of the studied structures.



Bond / Å	1-DMF		1-Diox-W		1-DMSO
	A	B	A – *anti-anti*	B – *syn-syn*	
B1-C1	1.547(6)	1.555(5)	1.53(2)	1.67(3)	1.52(3)
B1-O1	1.358(5) *anti*	1.349(5) *anti*	1.343(19)	1.31(3) *anti*	1.40(3) *anti*
B1-O2	1.357(5) *syn*	1.380(5) *syn*	1.383(16)	1.33(3) *syn*	1.35(3) *syn*
Dihedral / °					
O1-B1-C1-C2	–1.4(6)	1.9(7)	12.2(18)	20(2)	-6(3)
O2-B1-C1-C2	177.1(3)	–179.0(4)	–167.0(10)	–165.0(18)	171.1(19)
O1-B1-C1-C3	179.8(3)	–176.6(4)	–167.7(11)	–150(2)	173.4(18)
O2-B1-C1-C3	–1.7(5)	2.5(7)	13.1(18)	25(3)	-9(3)

Bond / Å	1-Ac		1-DCM-ACN	1'-Urea		1'-W
	A	B		A	B	
B1-C1	1.56(3)	1.60(3)	1.572(6)	1.555(11)		1.575(7)
B1-O1	1.36(3) *anti*	1.36(3) *anti*	1.367(6) *anti*	1.425(13) *anti*	1.436(16) *anti*	1.348(8) *anti*
B1-O2	1.37(3) *syn*	1.41(3) *syn*	1.364(6) *syn*	1.34(3) *syn*	1.32(4) *syn*	1.346(8) *syn*
Dihedral / °						
O1-B1-C1-C2	6.9(19)	15.0(15)	–4.7(7)	19.2(13)	15.1(17)	9.9(7)
O2-B1-C1-C2	–176.0(7)	–176.0(7	175.3(4)	–172.1(13)	–145.6(18)	–168.7(5)
O1-B1-C1-C3	–164.1(11)	–175.5(9)	175.5(5)	–159.2(9)	–170.1(18)	–174.0(5)
O2-B1-C1-C3	–6.6(14)	-6.6(14)	–4.5(6)	9.5(15)	29(2)	7.3(7)

Table S4. Symmetrically independent C-C bond lengths (Å) in adamantane core.

1-DMF	1-Diox-W	1-DMSO	1-Ac	1-DMSO-ACN	1'-Urea	1'-W
1.547(4)	1.533(11)	1.52(2)	1.538(4)	1.553(4)	1.525(8)	1.538(6)
1.538(4)	1.540(12)	1.55(2)	1.544(4)	1.540(4)	1.538(8)	1.551(6)
1.543(4)	1.538(13)	1.53(2)	1.543(4)	1.539(4)	1.544(7)	1.542(5)
1.539(4)	1.529(11)	1.55(2)	1.543(4)	1.553(4)	1.525(8)	
1.540(4)	1.534(13)	1.52(2)	1.544(4)	1.539(4)	1.544(7)	
1.536(4)	1.521(13)					
	1.530(11)					
	1.533(11)					

Table S5. Geometric parameters of hydrogen bond interactions in crystal structure **1-DMF**.

D-H…A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C20-H20…O2[a]	0.95	2.43	3.344(5)	161.0
C21-H21C…O4[b]	0.98	2.59	3.420(6)	142.6
C22-H22A…O4	0.98	2.57	3.458(7)	150.8
O1-H1…O5[c]	0.850(10)	1.84(2)	2.646(4)	158(5)
O2-H2…O1[d]	0.847(10)	1.88(2)	2.686(4)	159(5)
O3-H3…O6[e]	0.852(10)	1.885(13)	2.732(4)	172(5)
O4-H4…O5[f]	0.846(10)	1.90(2)	2.736(4)	168(9)
O5-H5…O4[b]	0.845(10)	2.05(6)	2.736(4)	137(8)

[1]1/2-x,1/2+y,3/2-z; [2]+x,-1+y,+z; [3]+x,-y,1/2+z; [4]1/2-x,-1/2-y,2-z; [5]+x, 2-y,1/2+z; [6]+x,1+y,+z

Table S6. Geometric parameters of hydrogen bond interactions in crystal structure **1-DMSO**.

D-H…A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C11-H11A…S3	0.98	2.80	3.49(4)	128.2
C11-H11B…O2[a]	0.98	2.52	3.30(3)	136.9
O1-H1…O3[b]	0.84	1.94	2.759(18)	164.0
O2-H2…O3[c]	0.84	2.01	2.760(19)	148.7
O2-H2…S1[c]	0.84	2.90	3.454(16)	125.3

[a]+x,+y,1+z; [b]+x,+y,-1+z; [c]+y,3/2-x,-1+z

Table S7. Geometric parameters of hydrogen bond interactions in crystal structure **1-Ac**.

D-H…A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2A-H2X…O3[a]	1.14(5)	1.84(5)	2.893(9)	151(4)
O1-H1…O3[b]	0.846(10)	2.040(12)	2.884(4)	175(6)
C10-H10A…O2A[c]	0.98	2.59	3.391(10)	139.1
C10-H10A…O2B[c]	0.98	2.57	3.370(9)	139.1
C10-H10B…O4[d]	0.98	2.56	3.270(7)	129.4

[a]1-y,-1/2+x,1-z; [b]1-x,1-y,1-z; [c]1/2+y,1-x,1-z; [d]1-x,1-y,-z

Table S8. Geometric parameters of hydrogen bond interactions in crystal structure **1-Diox-W**.

D-H…A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C20-H20B…O1[a]	0.99	2.61	3.53(2)	155.1
O5-H5…O3[b]	0.842(11)	1.91(5)	2.720(10)	162(14)
O4-H4…O6[c]	0.84	2.07	2.775(14)	141.9
O1-H1…O5[a]	0.84	2.35	3.090(15)	147
O1-H1…O4[d]	0.84	2.47	2.980(16)	119.9
O2-H2…5[a]	0.84	2.06	2.85(2)	154.8

[a]1-x,-y,-z; [b]3/2-x,1/2-y,1/2-z; [c]1/2+x,+y,1/2-z; [d]3/2-x,-y,-1/2+z

Table S9. Geometric parameters of hydrogen bond interaction in crystal structure **1'-Urea**.

D-H…A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C10A-H10A…O1A[a]	0.98	2.61	3.53(4)	156.9
C10A-H10C…N1[b]	0.98	2.33	3.19(4)	146.5
C10B-H10E…O2B[c]	0.98	2.55	3.46(3)	153.6
O2A-H2X…O3	1.12(18)	1.92(17)	2.724(13)	125(13)
N1-H1D…O2B[d]	0.88	2.09	2.83(3)	140.7

[a]1-x,1-y,-1-z; [b]+y,3/2-x,-1+z; [c]3/2-y,+x,+z; [d]3/2-y,+x,1+z

Table S10. Geometric parameters of hydrogen bond interactions in crystal structure **1-DMSO-ACN**.

D-H…A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2-H2…S1	0.84	2.89	3.456(4)	126.3
O2-H2…O1	0.84	1.97	2.730(5)	150.4
O3-H3…O1[a]	0.842(10)	1.909(12)	2.750(4)	176(6)
O3-H3…S1A[a]	0.842(10)	1.85(5)	2.503(15)	134(6)
C11-H11D…O3[b]	0.98	2.63	3.604(7)	173.0
C10-H10A…O2[c]	0.98	2.47	3.317(8)	144.2
C10-H10C…N2[d]	0.98	2.69	3.322(9)	122.3

[a]1/2-y,1+x,+z; [b]-1+y,1/2-x,-1+z; [c]-1+y,1/2-x,+z; [d]+x,+y,-1+z

2. NMR spectra

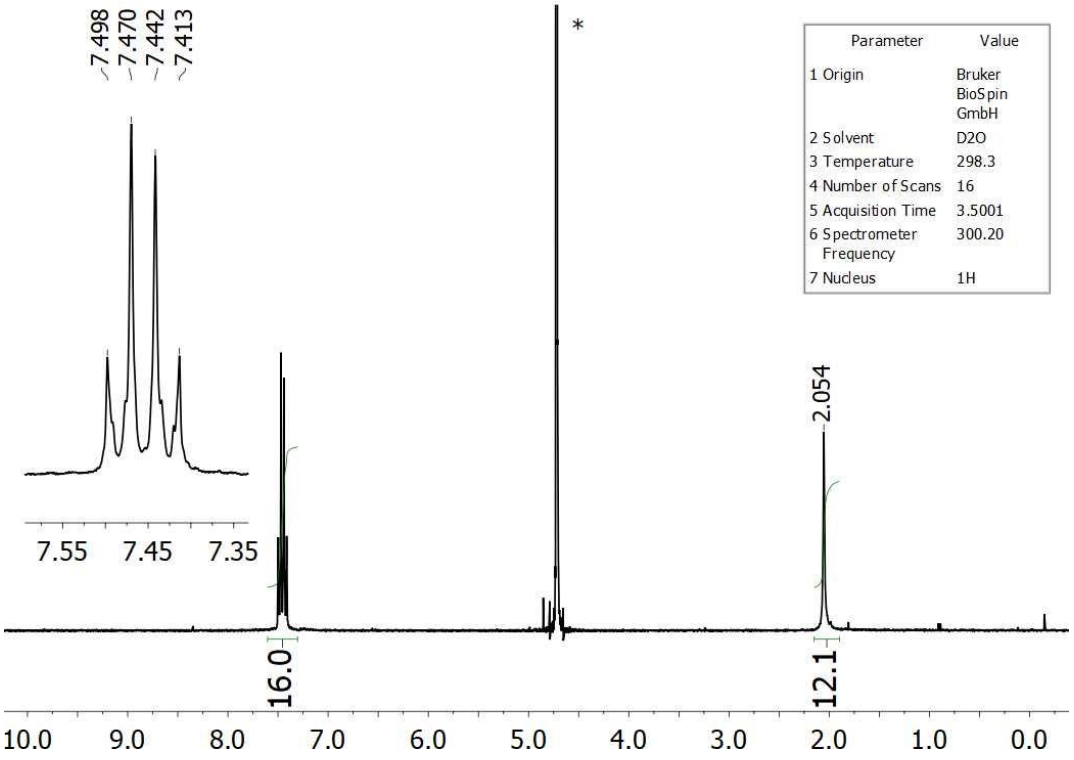


Figure S9. ^{1}H NMR spectrum of **1** in D_2O + NaOH. *signal of HDO.

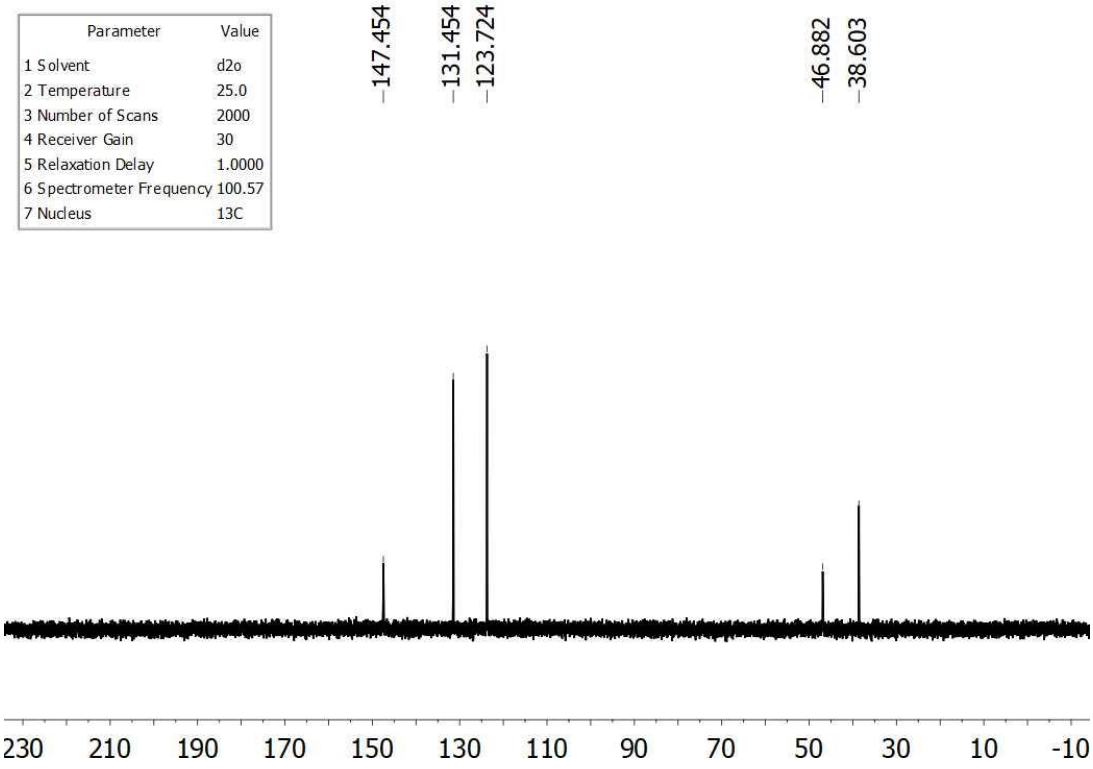


Figure S10. ^{13}C{1H} NMR spectrum of **1** in D_2O + NaOH.

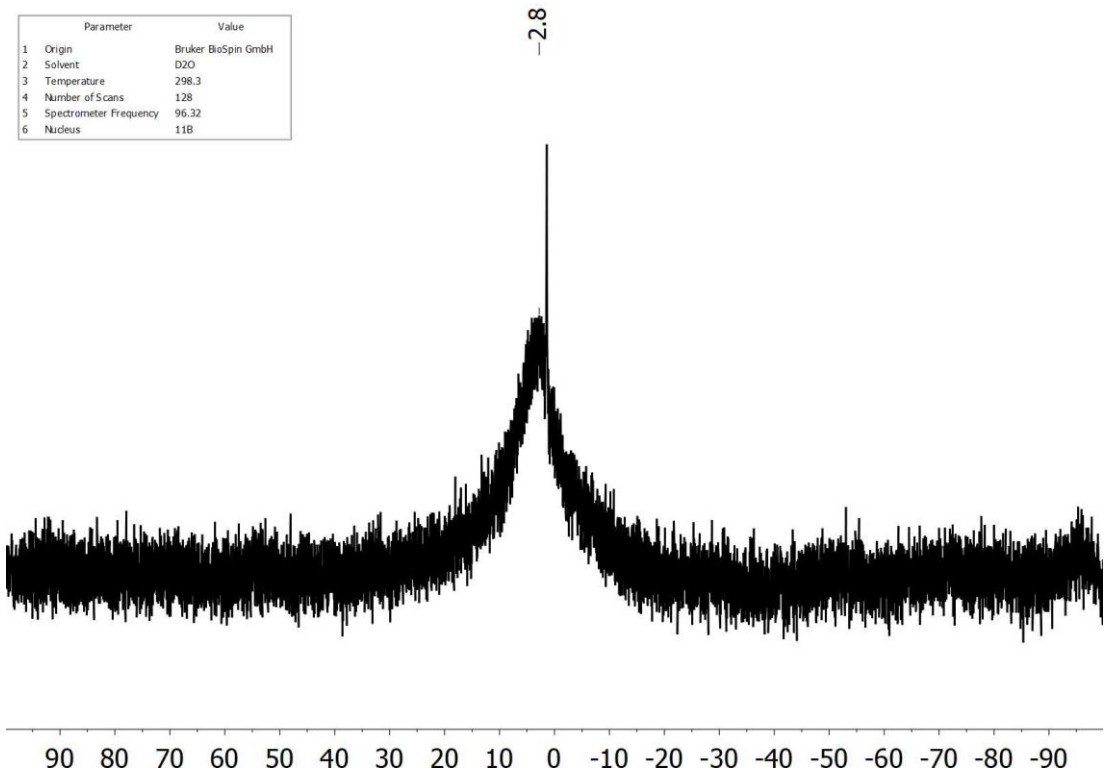


Figure S10. ^{11}B NMR spectrum of **1** in D_2O + NaOH.

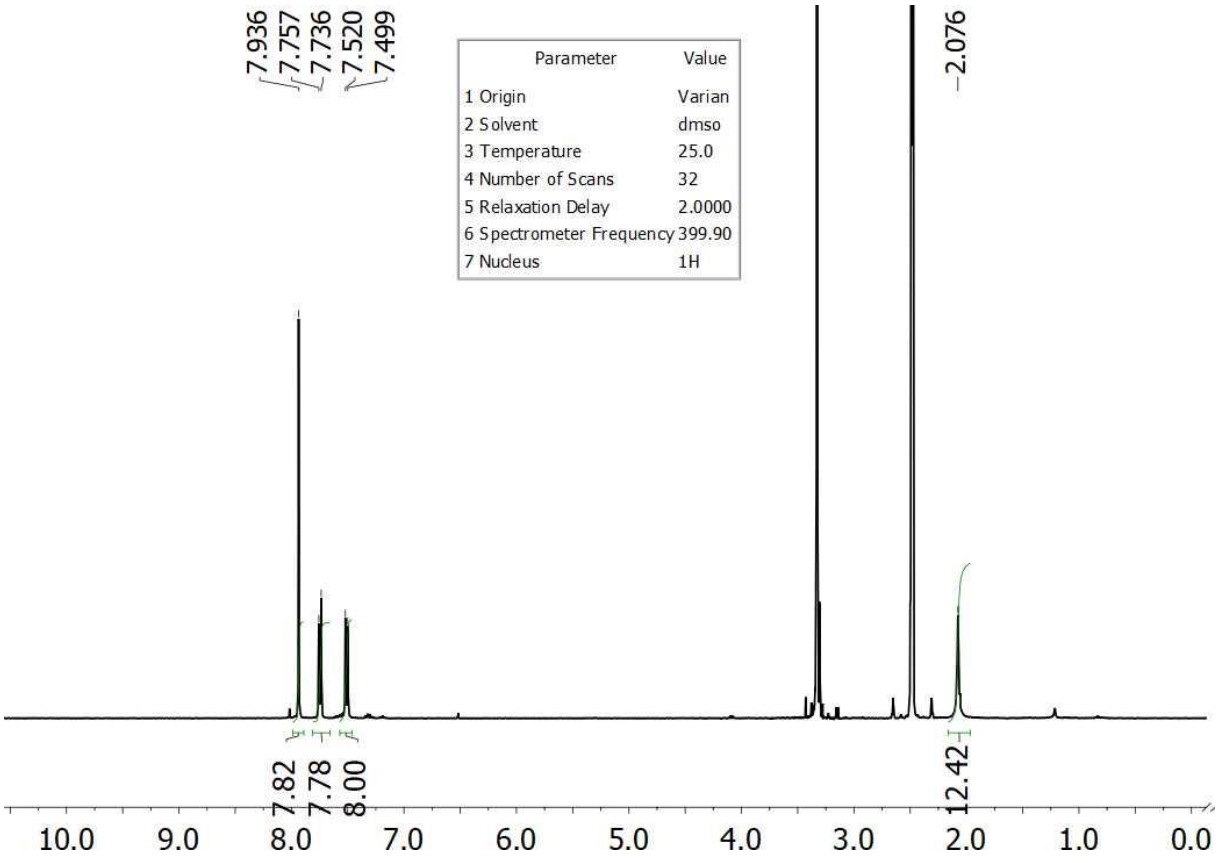


Figure S11. ^{1}H NMR spectrum of **1** in DMSO-d_6.

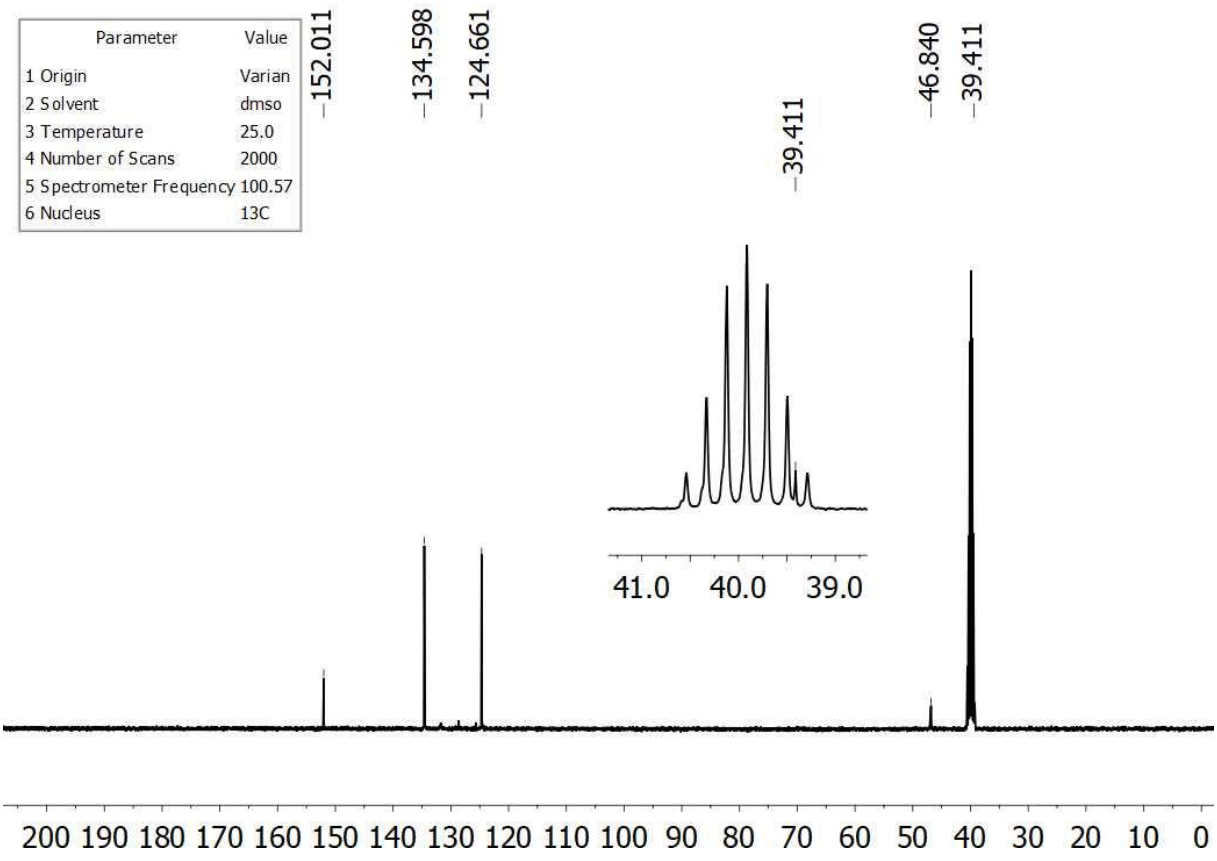


Figure S12. $^{13}C\{1H\}$ NMR spectrum of **1** in in DMSO-d_6.

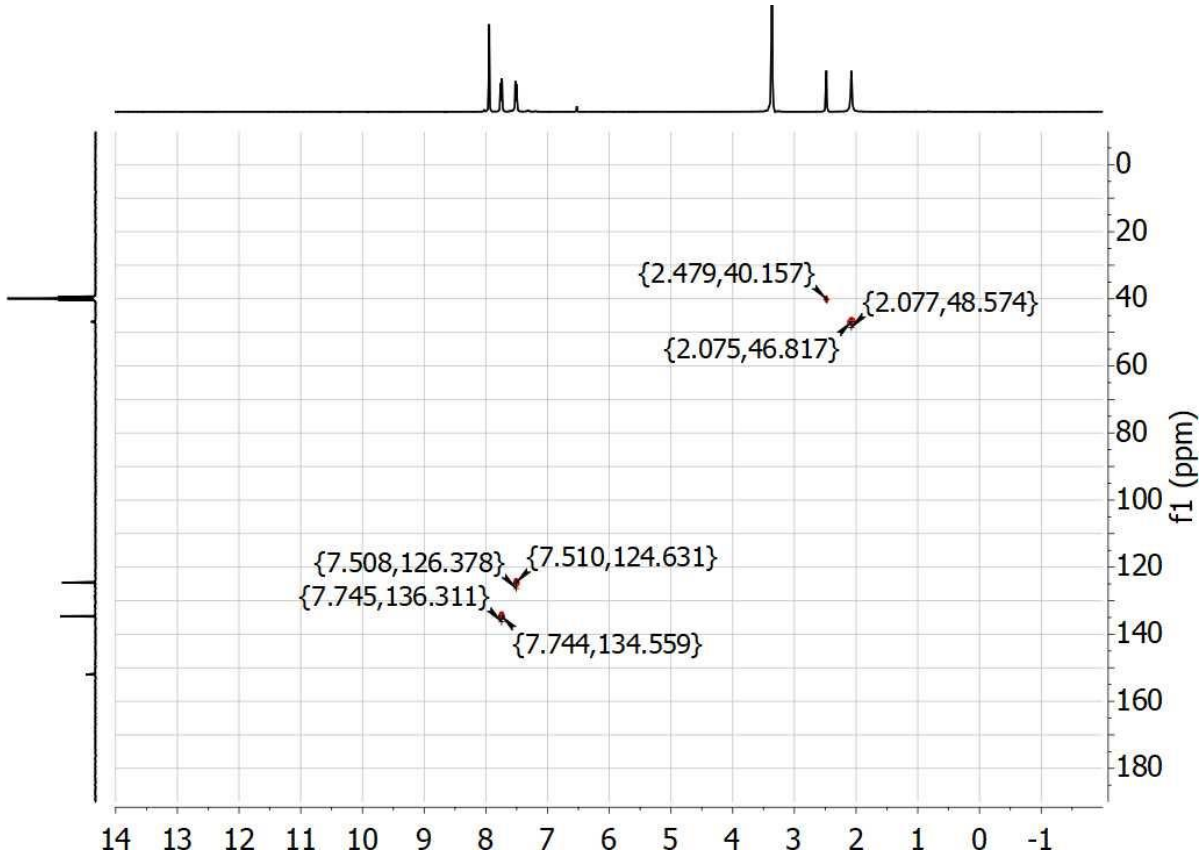


Figure S13. HSQC NMR spectrum of **1** in in DMSO-d_6.

3. Theoretical calculations

Table S11. Computed total energy values (in atomic units) for 1(1')-solvent dimers.

Compound	*OH(syn)-solvent (in vacuo)*	*OH(anti)-solvent (in vacuo)*	*OH(syn)-solvent (MeOH)*	*OH(anti)-solvent (MeOH)*
1-DMF	-2267.29179974	-2267.29288845	-2267.33164212	-2267.33244272
1-A	-2211.93861842	-2211.93988529	-2211.97575795	-2211.97670209
1-DMSO	-2571.97702326	-2571.97904313	-2572.01965242	-2572.01989695
1-DMSO-CAN	-2151.54742287	-2151.55000040	-2151.58804639	-2151.58915671
1-Diox	-2326.42619400	-2326.42663165	-2326.47126157	-2326.47238403
1-W	-2095.23038536	-2095.22761136	-2095.27524791	-2095.27460344
1-Urea	-2244.07694620	-2244.07681993	-2244.12065386	-2244.11886838
1-MeOH	-2134.51407230	-2134.52537876	-2134.55734816	-2134.56163059
1'-W	-	-2252.37883621	-	-2252.41220177
1'-Urea	-	-2401.21576741	-	-2401.25304236

Table S12. Computed total energy values (in atomic units) for the crystal motifs.

1(1') opt	*1-1(1'-1') C-H…C(π) dimer*	*Tetrameric motifs*	*Other motifs*
-2018.79799134	-4037.62672230	-9069.15375475	-4037.61112745
-2018.78102086	-4037.59486396	-8847.67667872	-
-2018.77713525	-4037.58675484	-10287.8257335	-
-2018.80197583	-4037.63628446	-10420.6712820	-
-2018.72291285	-4037.48116036	-	-8151.36592745 -8074.91256675
-	-	-	-
-	-	-	-
-	-	-	-
-2175.92207886	-4351.89595070	-	-4504.73057449
-2175.87817831	-4351.80333852	-8928.80879335	-

4. TG analysis

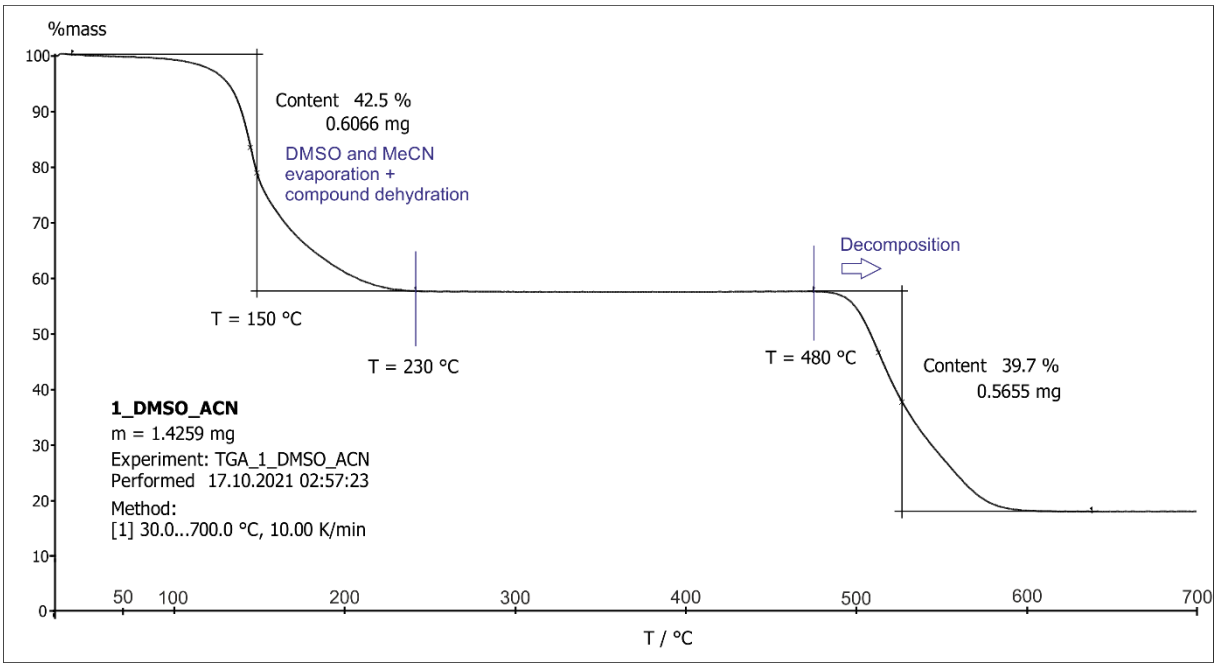


Figure S14. TGA curve of **1-DMSO-ACN**.

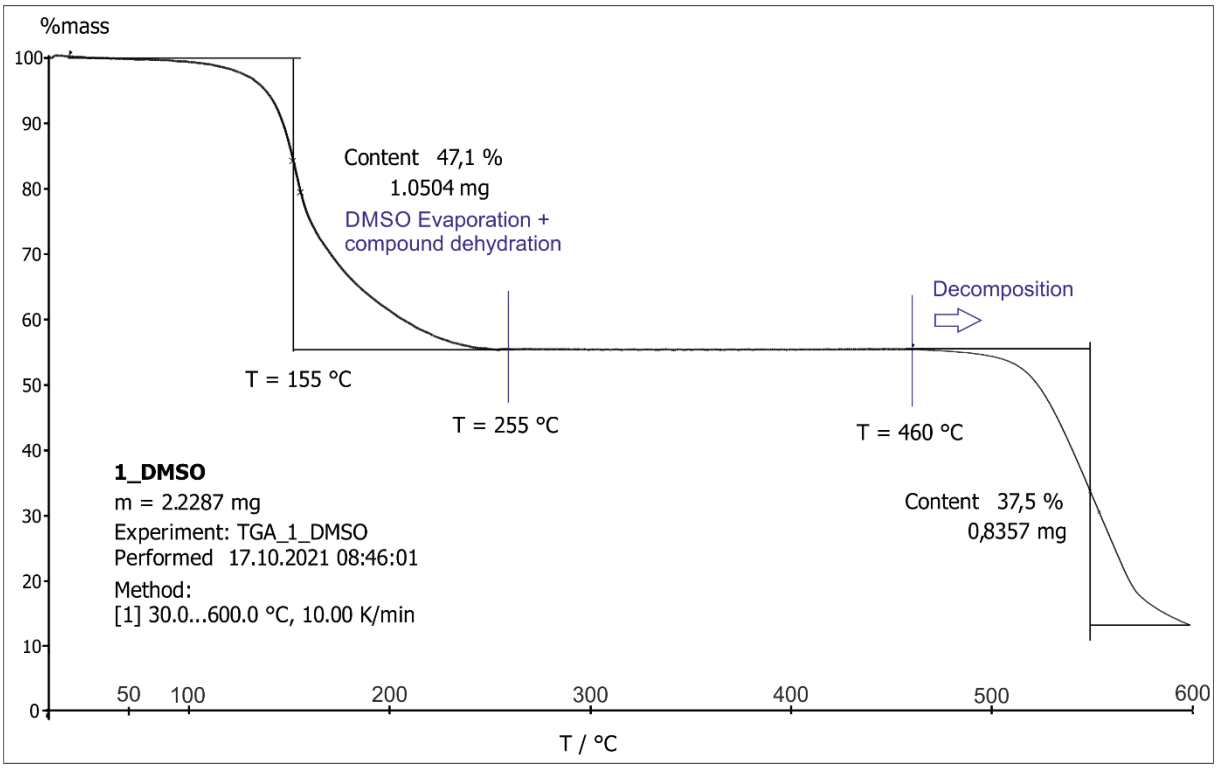


Figure S15. TGA curve of **1-DMSO**.

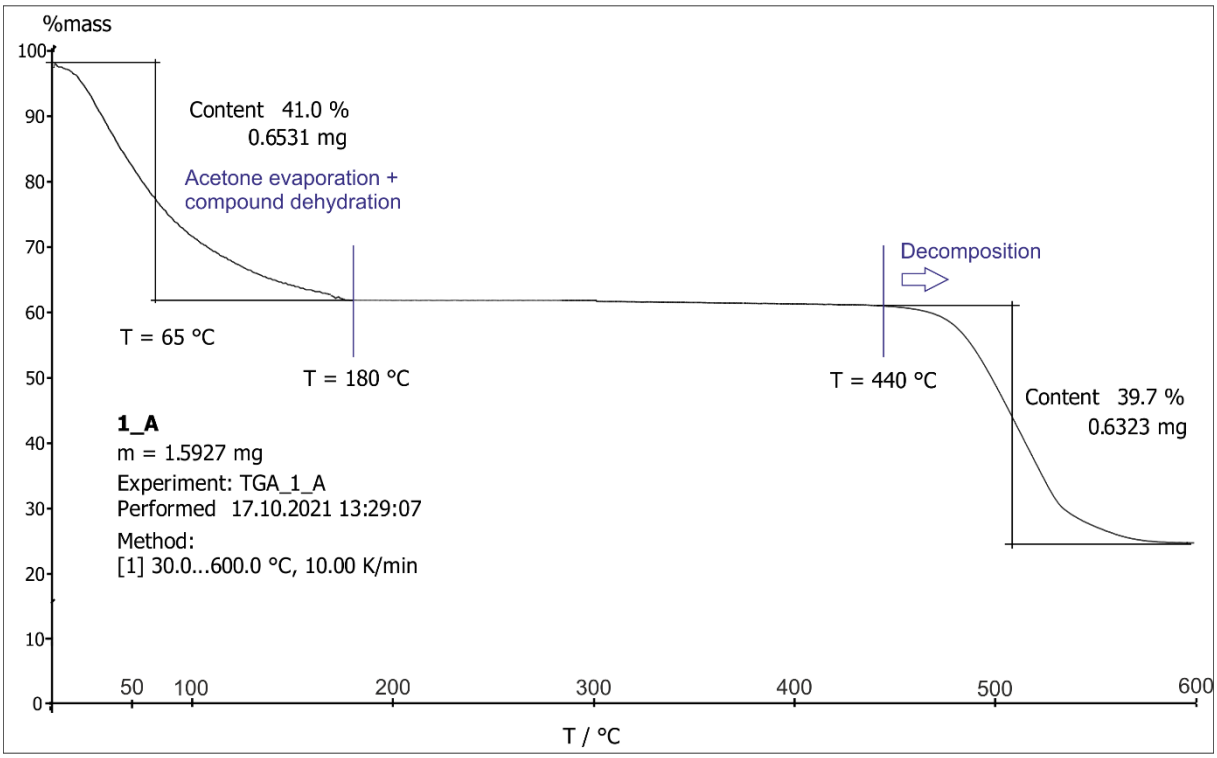


Figure S16. TGA curve of **1-A.**

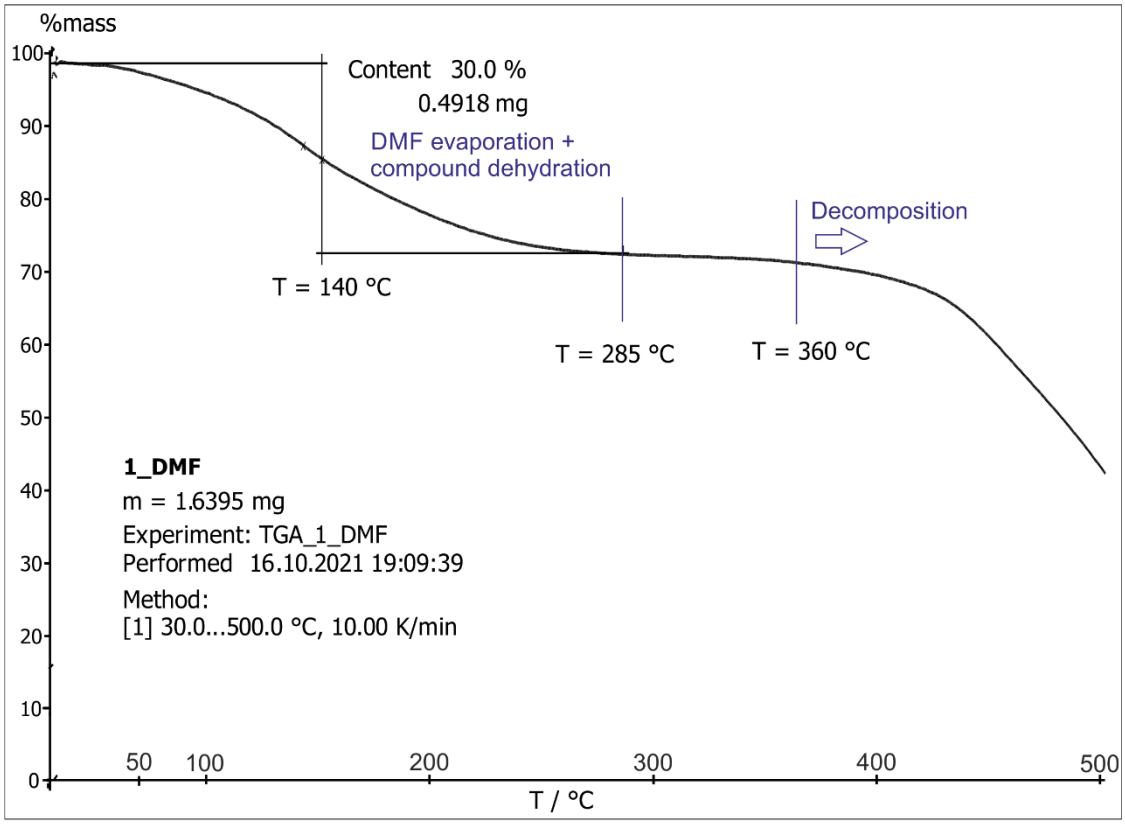


Figure S17. TGA curve of **1-DMF**.

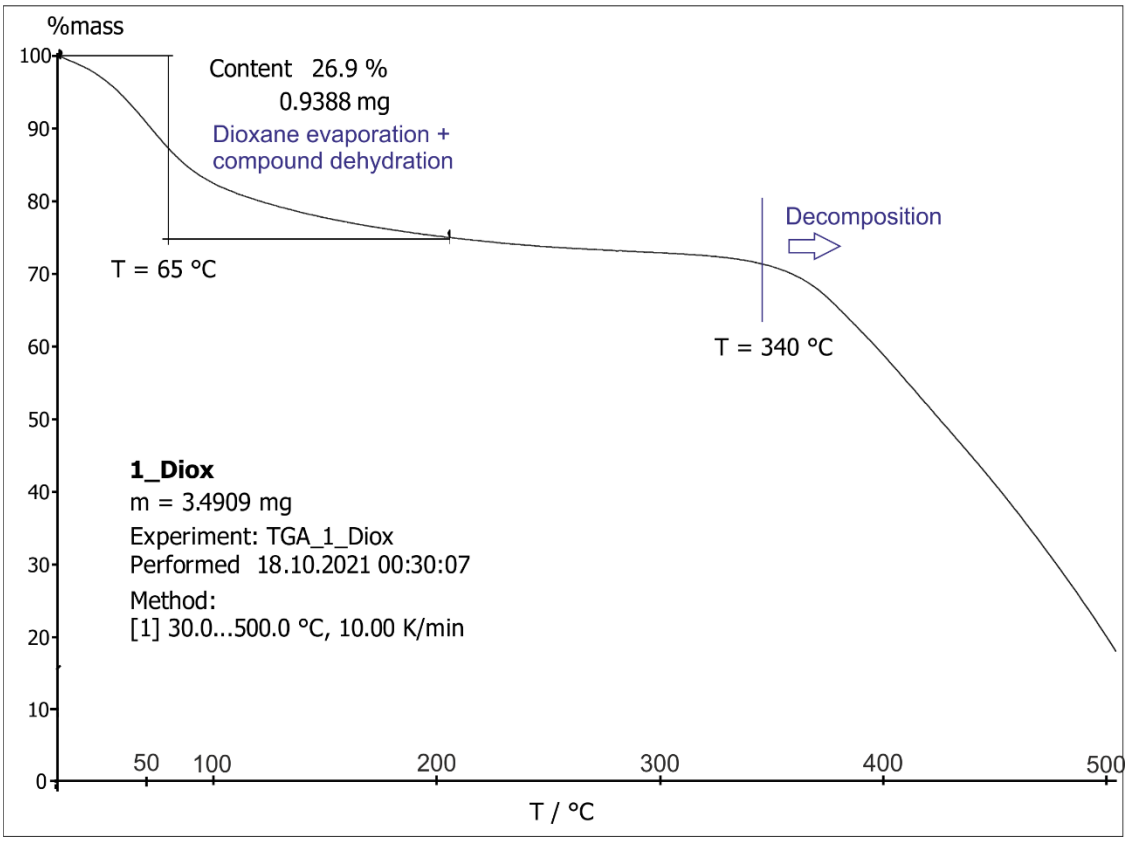


Figure S18. TGA curve of **1-Diox-W**.

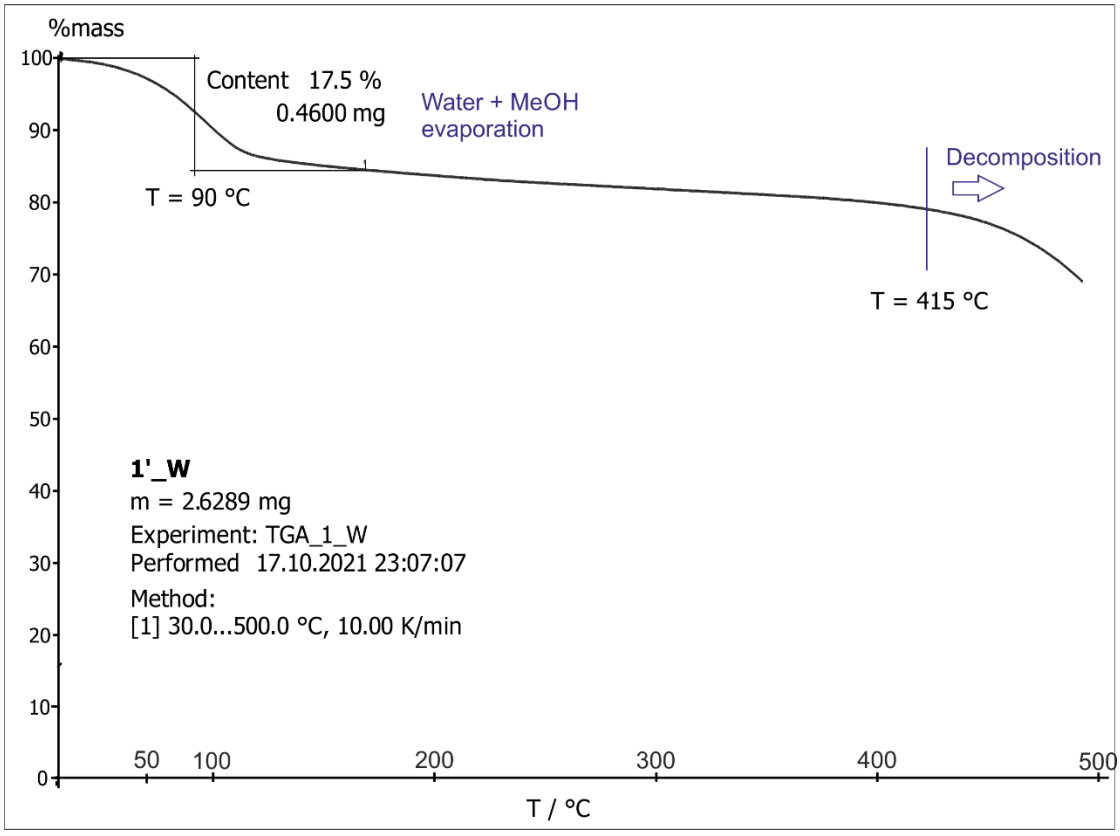


Figure S19. TGA curve of **1'-W.**

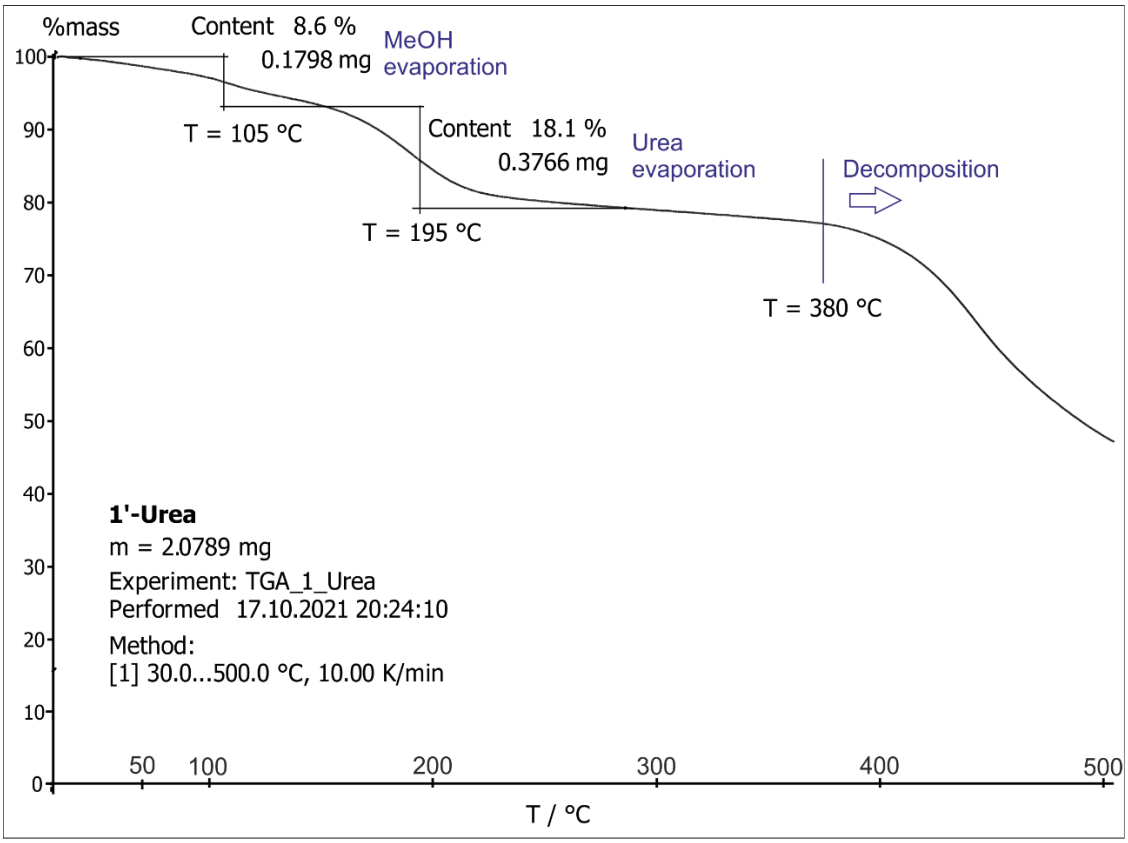


Figure S20. TGA curve of **1'-Urea.**