Supporting Information

Design and development of hydrogen bonded molecular assemblies based on pyromellitic diimides tethered carboxylic acids as optical materials

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Experimental

Computational Details

Hydrogen bond motifs were derived from formic acid and its interaction with DMF, DMSO and Dioxsolvent molecules as a model system. All the calculations were performed using the Gaussian09 program package in the gas phase.[S1] The energies of the geometries of these models were calculated by DFT[S2] using Becke's three-parameter exchange functional[S3] along with the gradient-corrected functional of Lee, Yang and Parr (B3LYP functional).[S4] Single point calculations at the 6-31+G*, 6-31++G* and 6-31++G** level were performed on the fully optimized geometries of level B3LYP/6-31+G*. The Interaction energy (E_{int}) for each bimolecular motif was obtained by $E_{int} = [E_{\text{for bimolecular structure}} - (E_{\text{for formic acid}} + E_{\text{for interacting solvent molecule}})]$. The relative stability of a particular motif over another motif was calculated by subtracting the value of lower energy motif from the higher energy motif.

Crystal Structure Determination

Crystals were coated with Paratone oil, and the diffraction data were collected at 173 K with MoKα radiation on a Rigaku Rapid AutoDiffractometer equipped with a graphitecrystalincidentbeam monochromator. The RapidAuto software [S5]was used for data collection and data processing. The

structures were solved by direct method and refined by full-matrix least-squares calculation with the SHELXTL software package.[S6] All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U (C) and 1.5U (C_{methyl}), and their coordinates were allowed to ride on their respective atoms.In the structures of solvates **2a**, **2b** and **2c**, all three carbon atoms in the aliphatic part attached with cyclic imide cores were found to be disordered. These disordered atoms were refined by sharing two carbon atoms at one position having half occupancies and then hydrogen atoms were fixed at respective positions.Crystallographic details and hydrogen bond parameters are listed in Table S4 and Table S5, respectively.

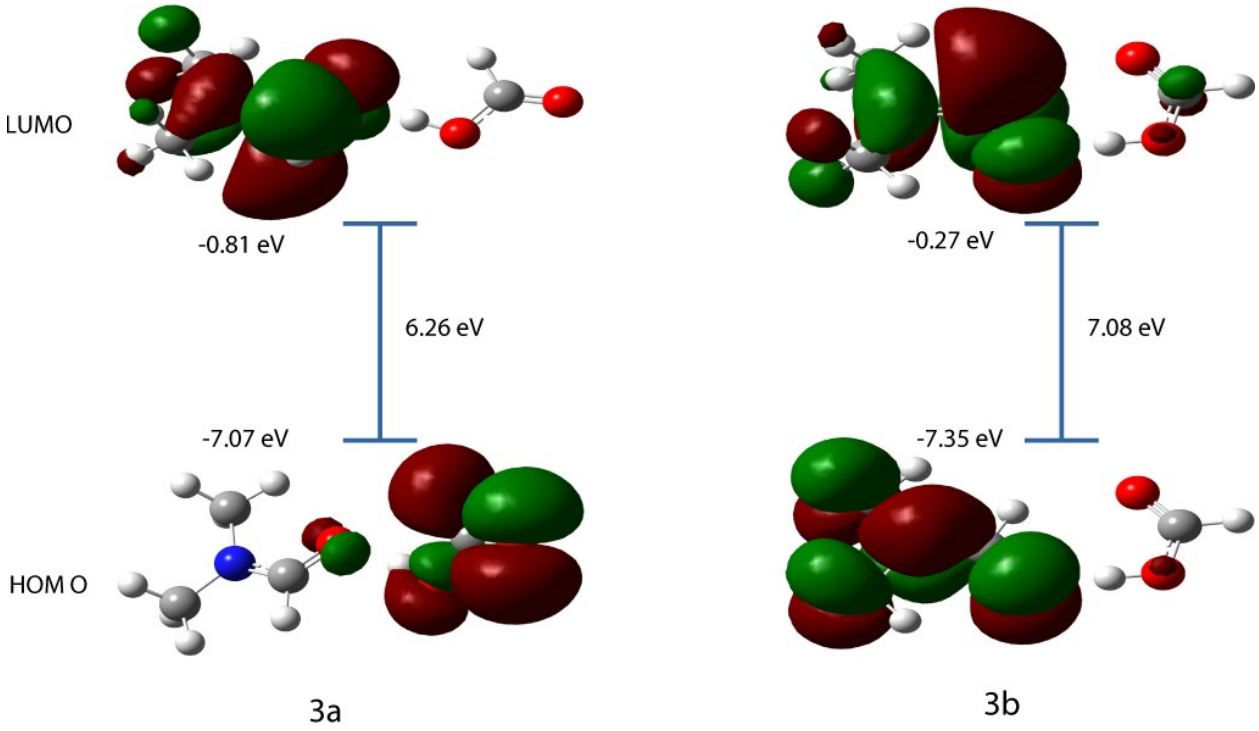


Figure S1. HOMO and LUMO frontier molecular orbitals of structures **3a** and **3b** at B3LYP/631+G∗ level.

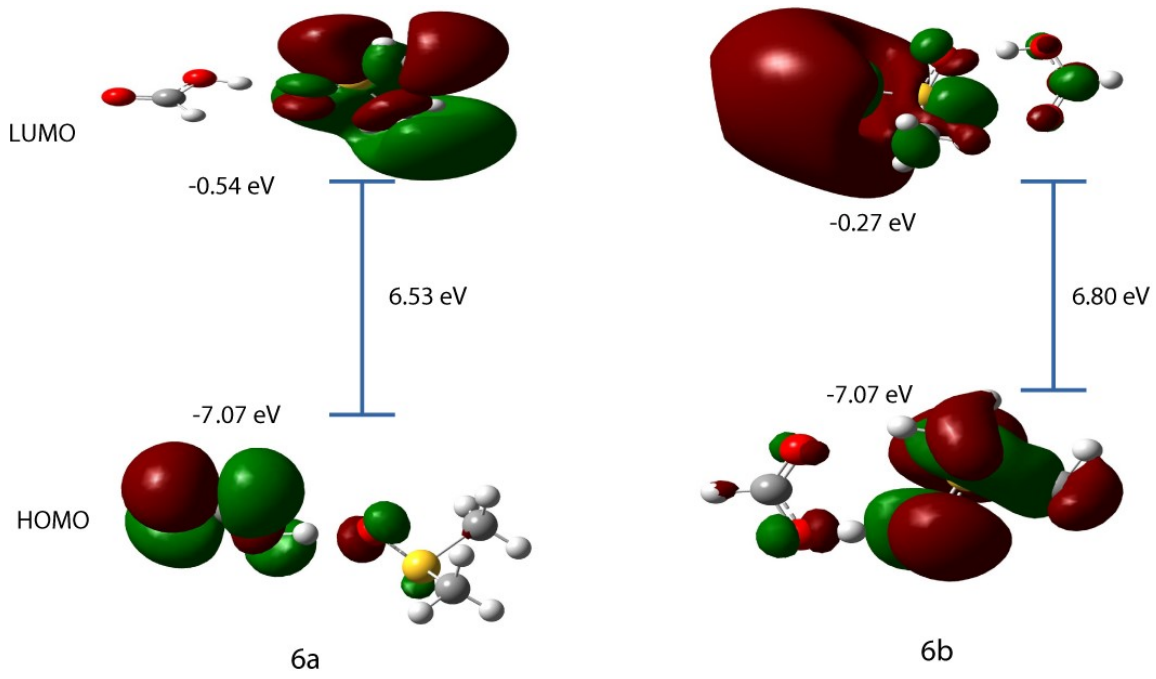


Figure S2. HOMO and LUMO frontier molecular orbitals of structures **6a** and **6b** at B3LYP/631+G∗ level.

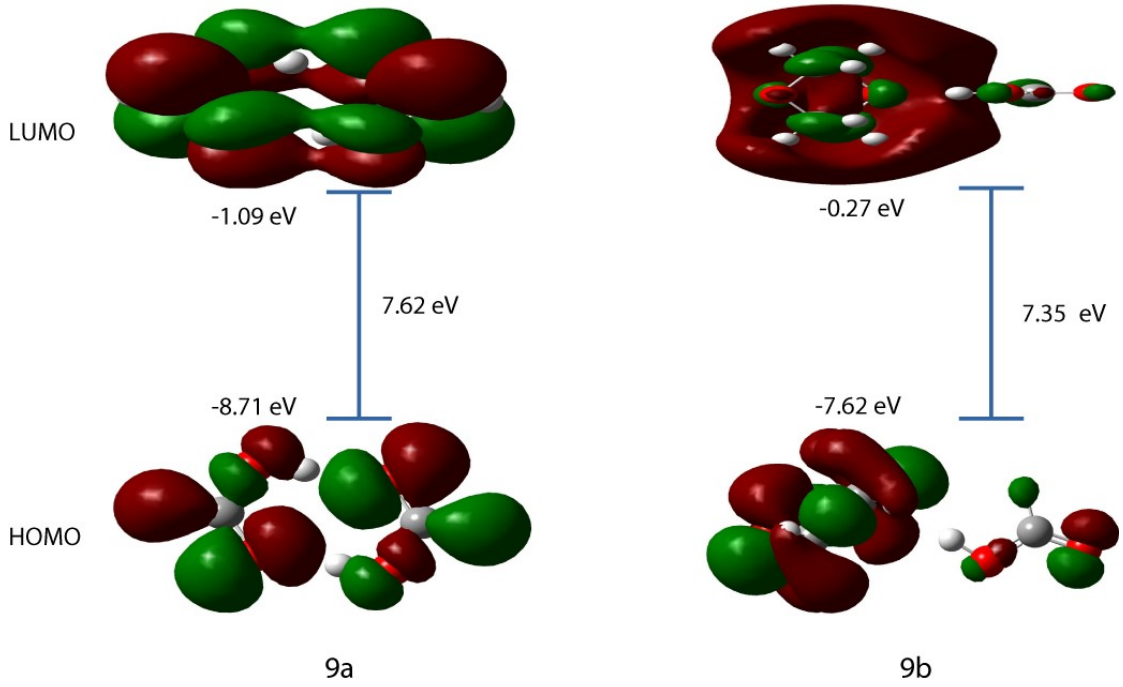


Figure S3. HOMO and LUMO frontier molecular orbitals of structures **9a** and **9b** at B3LYP/6-31+G∗ level.

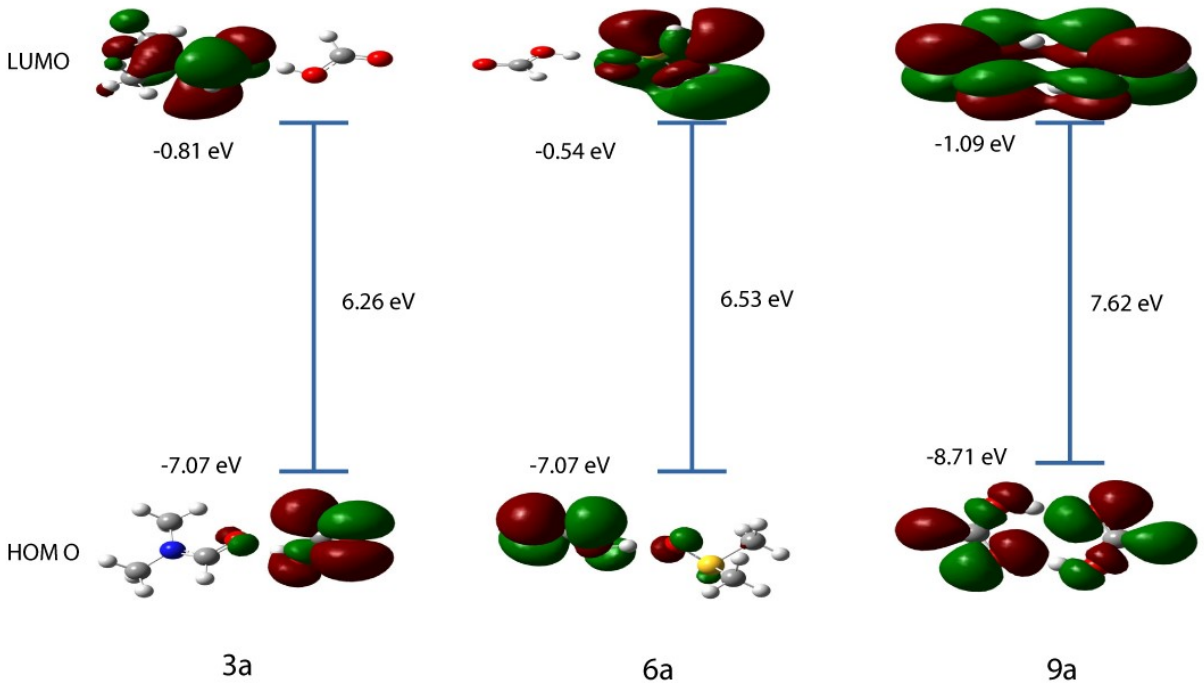


Figure S4. HOMO and LUMO frontier molecular orbitals of structures **3a**, **6a** and **9a** at B3LYP/6-31+G* level.

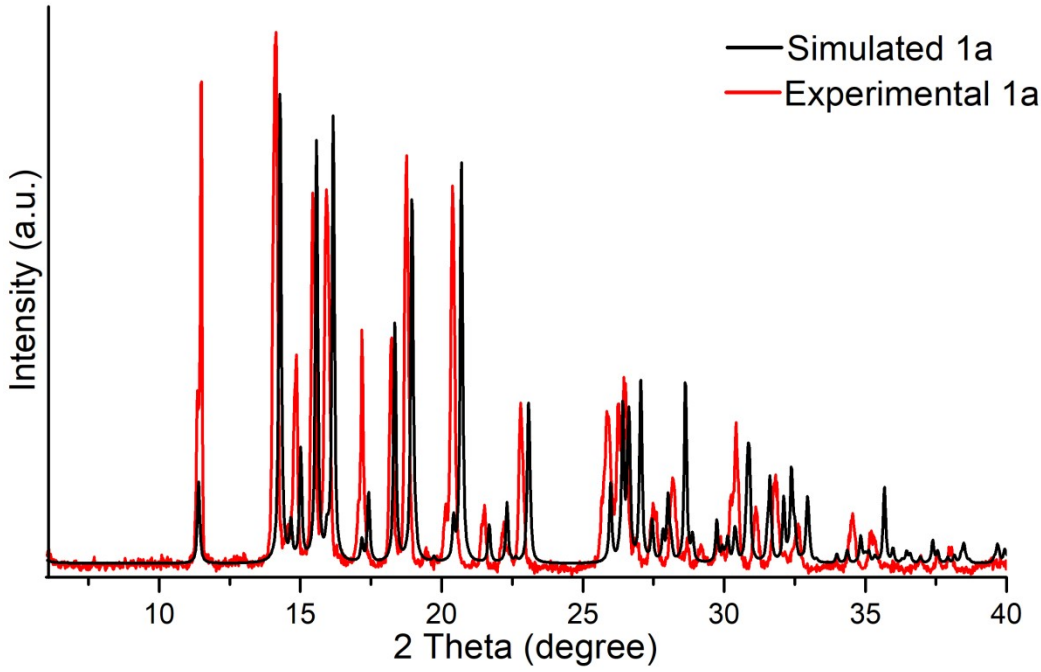


Figure S5. Simulated (black) and experimental (red) PXRD patterns of solvate **1a**.

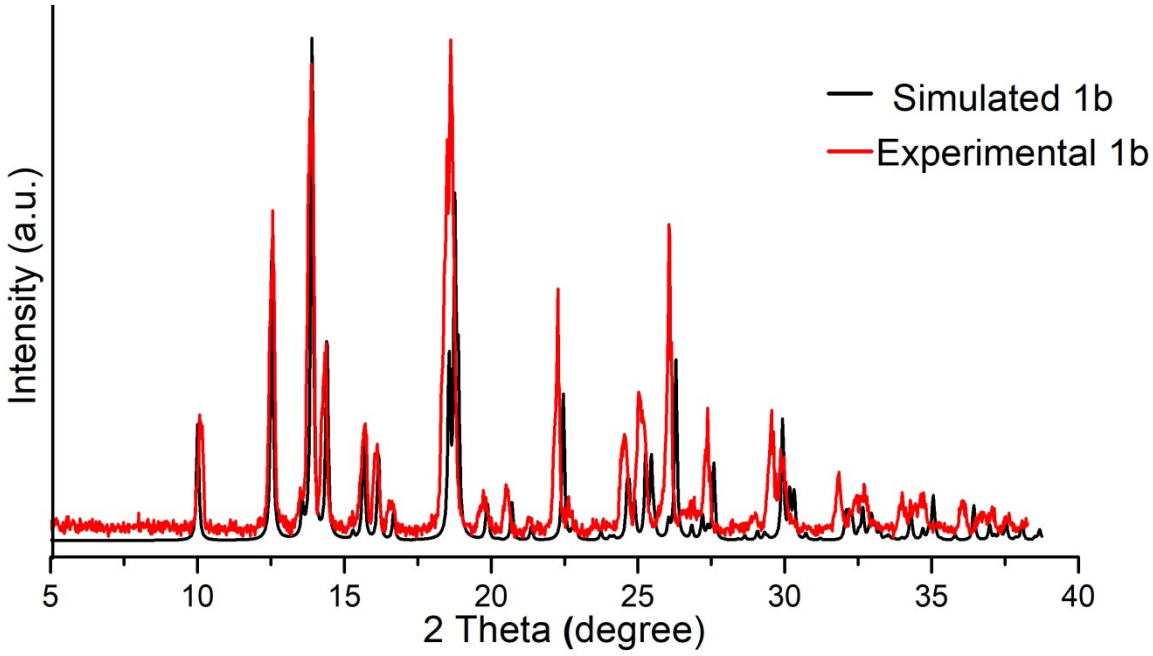


Figure S6. Simulated (black) and experimental (red) PXRD patterns of solvate **1b**.

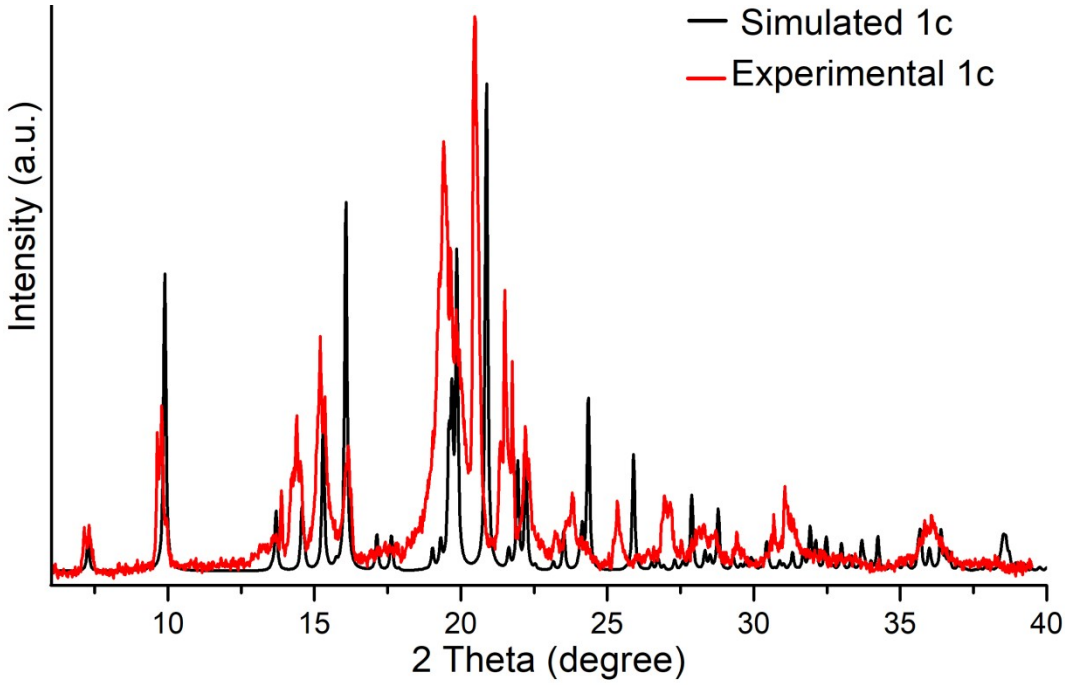


Figure S7. Simulated (black) and experimental (red) PXRD patterns of solvate **1c**.

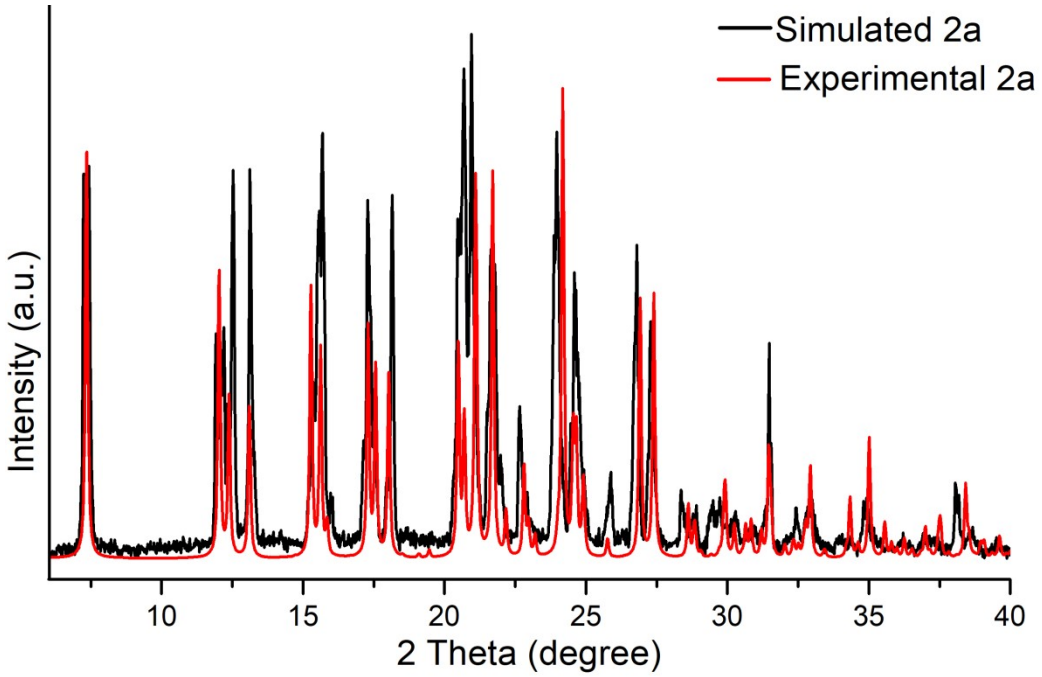


Figure S8. Simulated (black) and experimental (red) PXRD patterns of solvate **2a**.

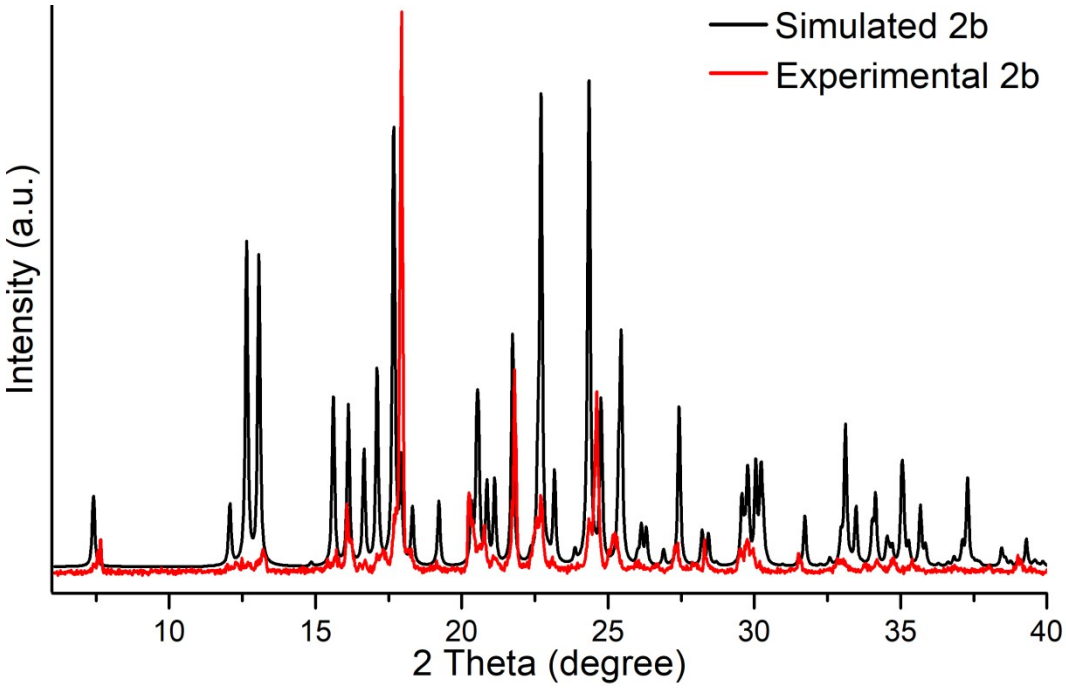


Figure S9. Simulated (black) and experimental (red) PXRD patterns of solvate **2b**.

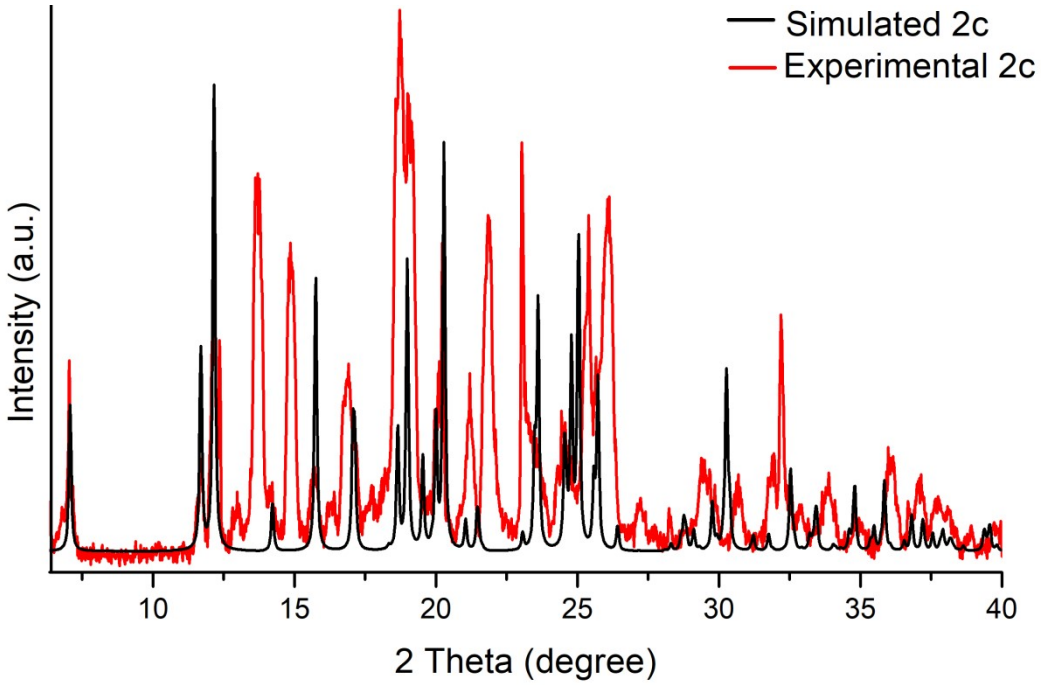


Figure S10. Simulated (black) and experimental (red) PXRD patterns of solvate **2c**.

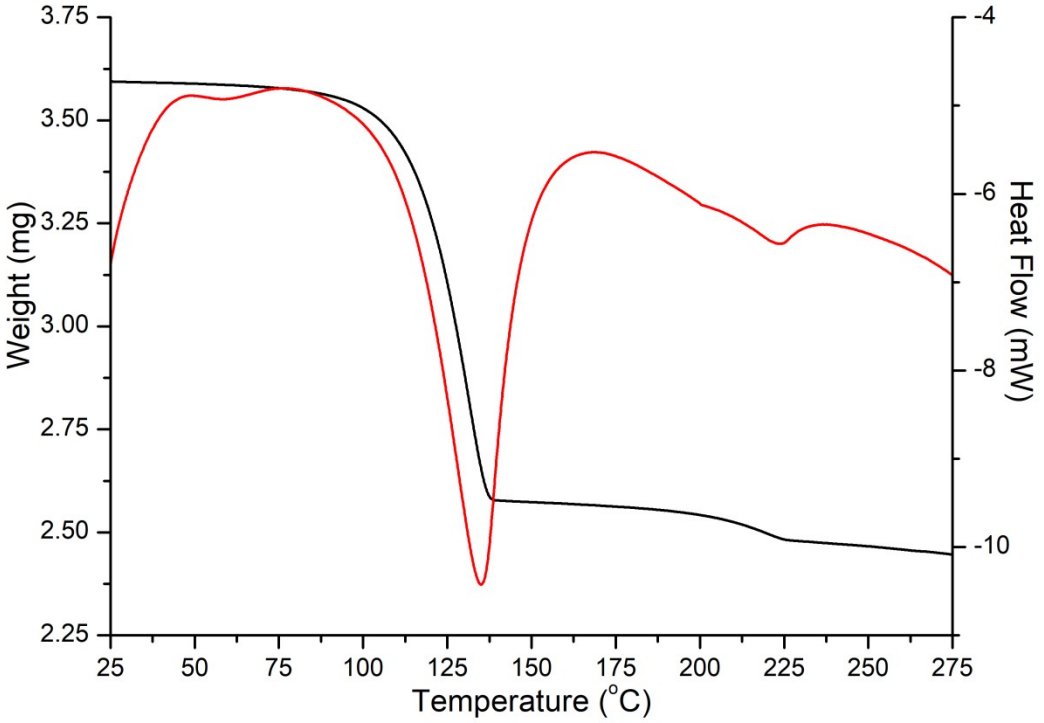


Figure S11. TGA (black) and DSC (red) curves of solvate **1a**.

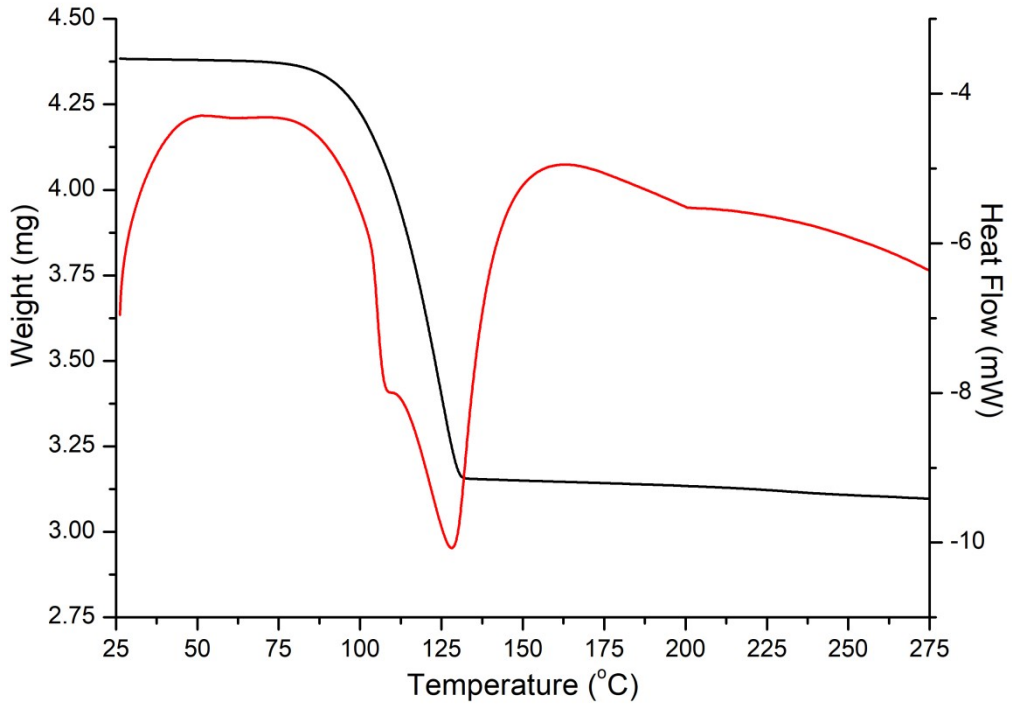


Figure S12. TGA (black) and DSC (red) curves of solvate **1b**.

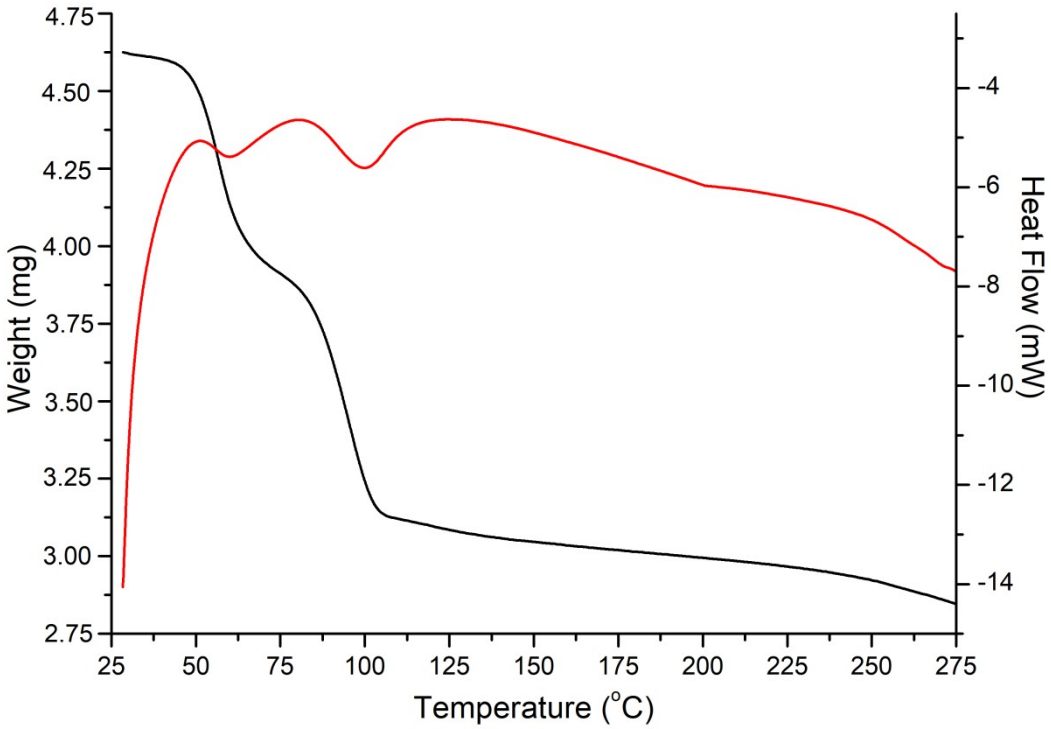


Figure S13. TGA (black) and DSC (red) curves of solvate **1c**.

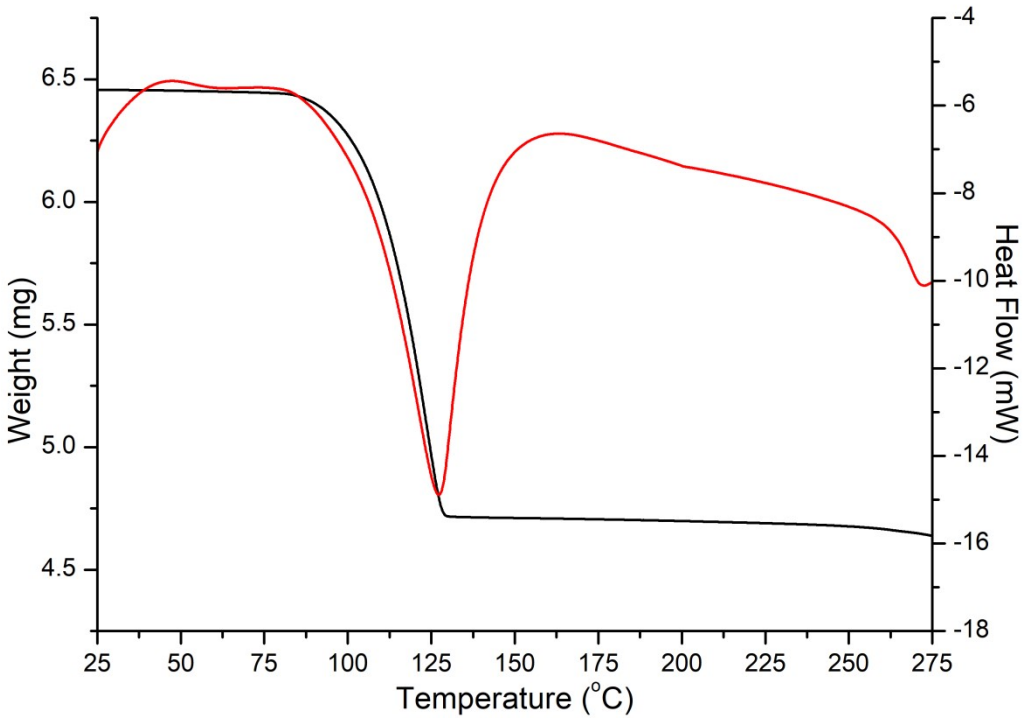


Figure S14. TGA (black) and DSC (red) curves of solvate **2a**.

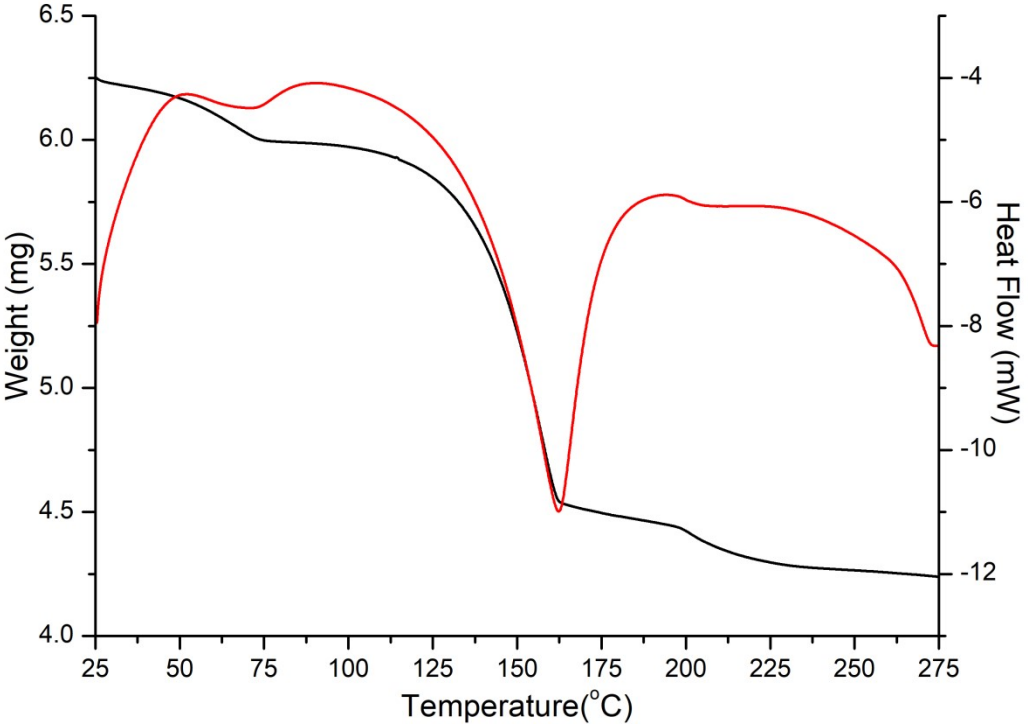


Figure S15. TGA (black) and DSC (red) curves of solvate **2b**.

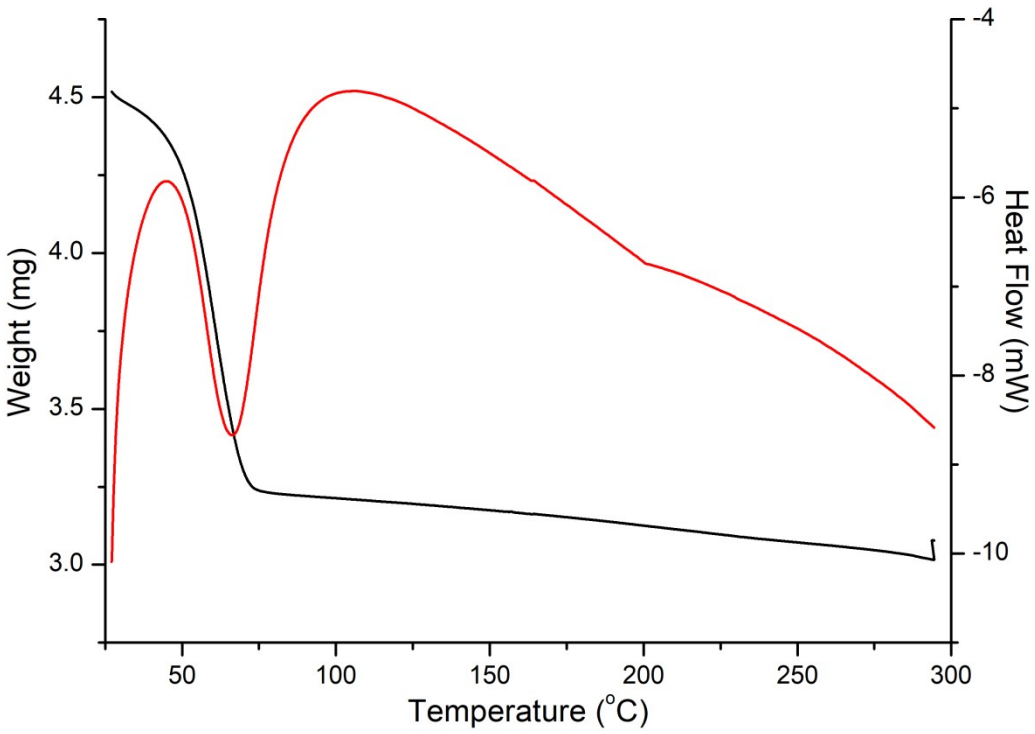
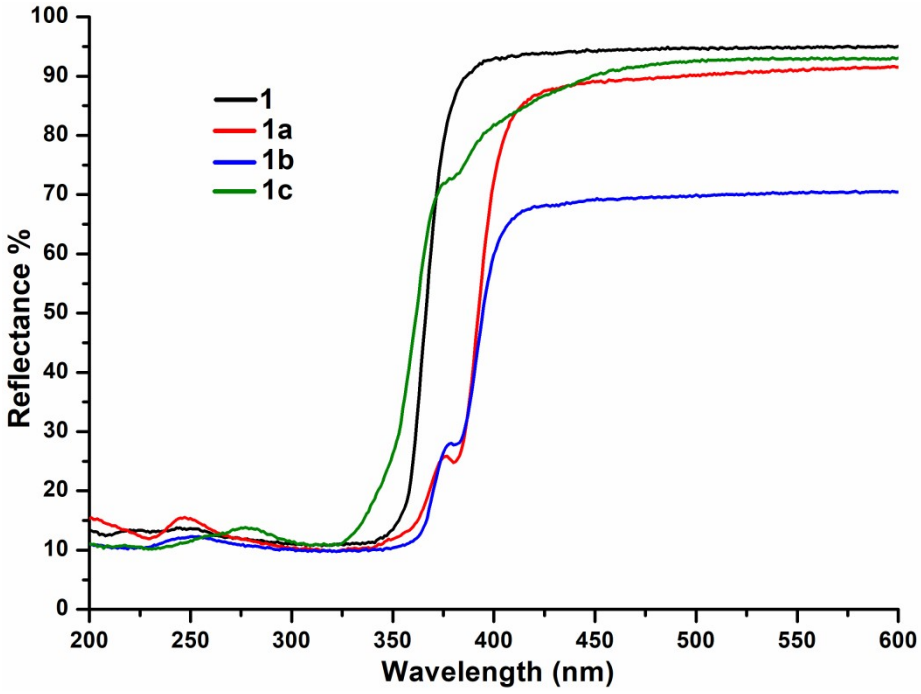
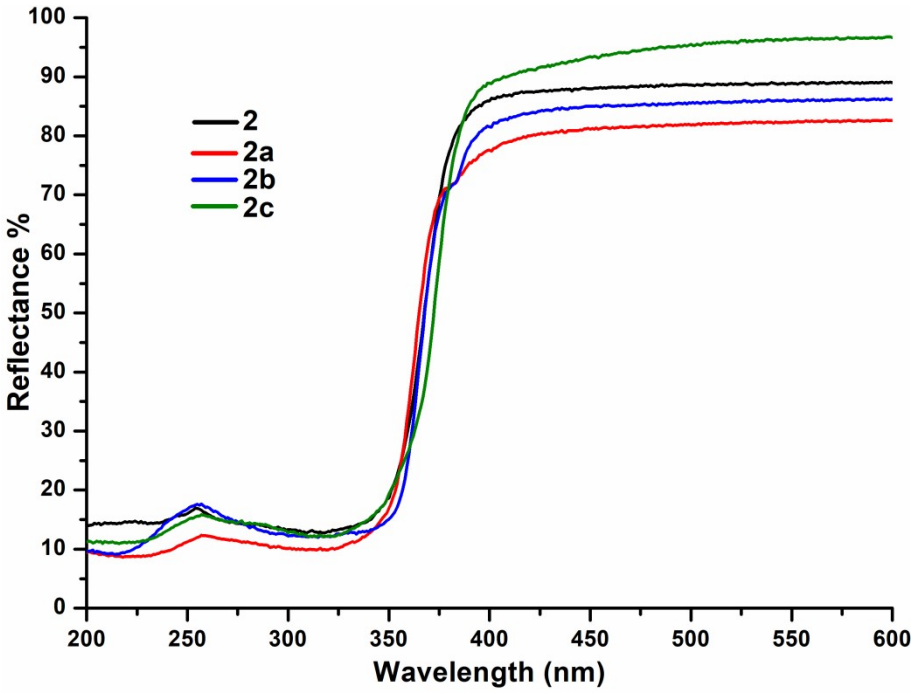


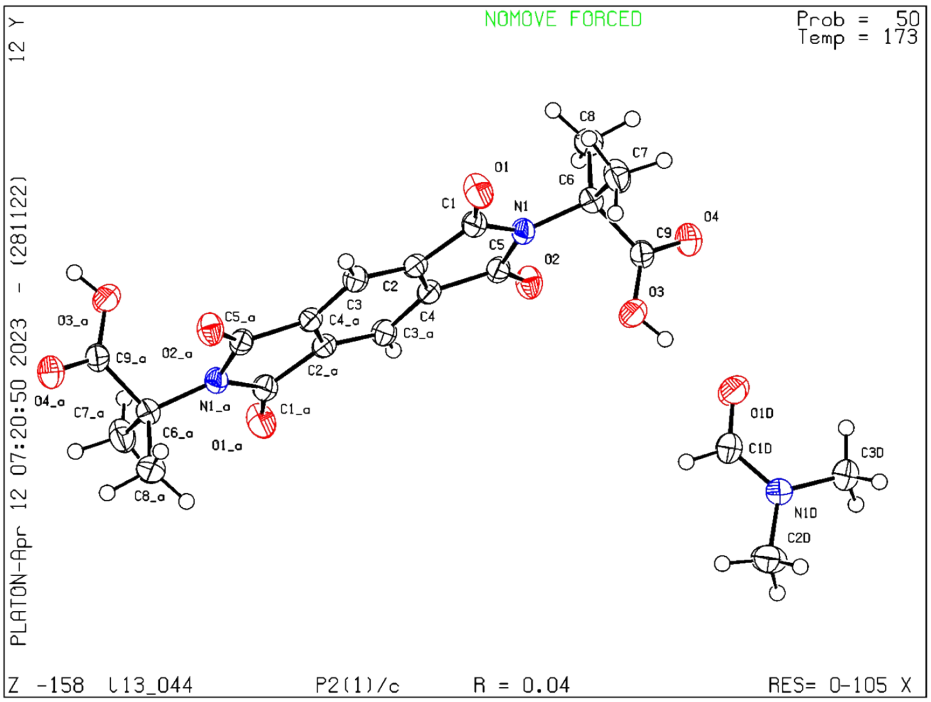
Figure S16. TGA (black) and DSC (red) curves of solvate **2c**.



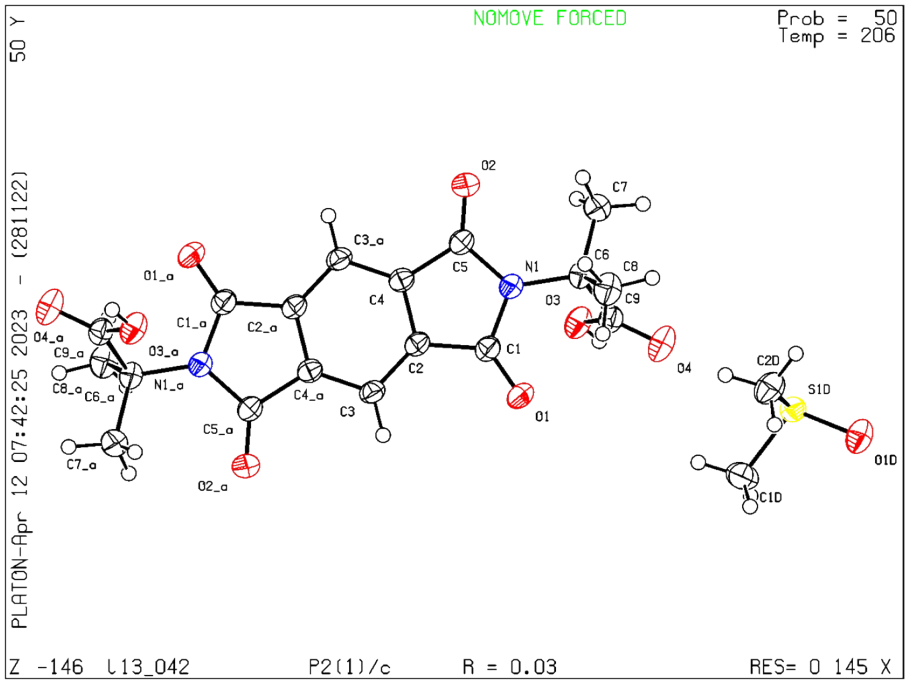
FigureS17. Solid state UV-Vis spectra of host **1** and its solvates **1a**, **1b** and **1c**.



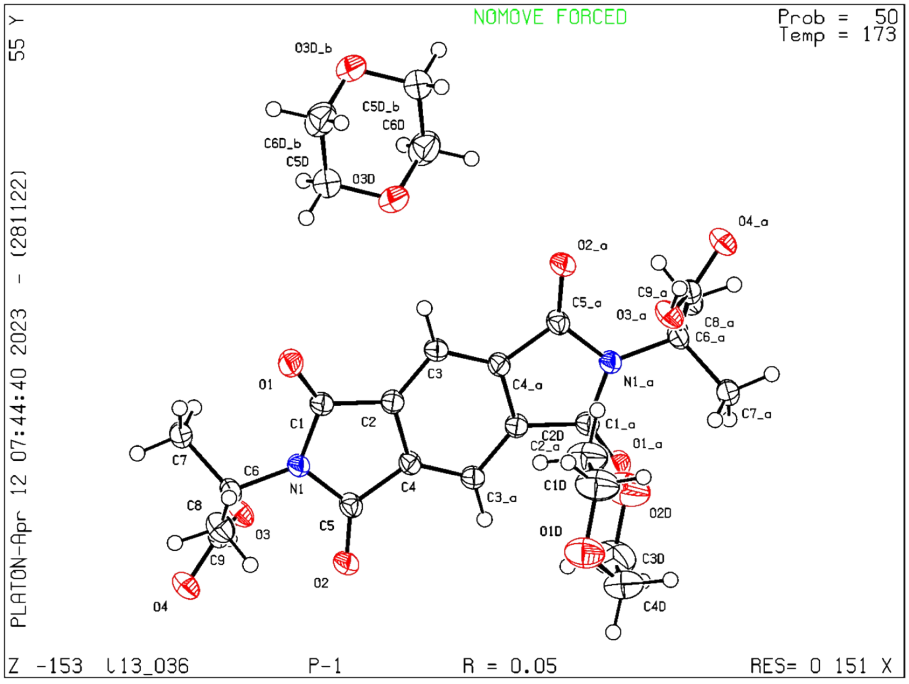
FigureS18. Solid state UV-Vis spectra of host **2** and its solvates **2a**, **2b** and **2c**.



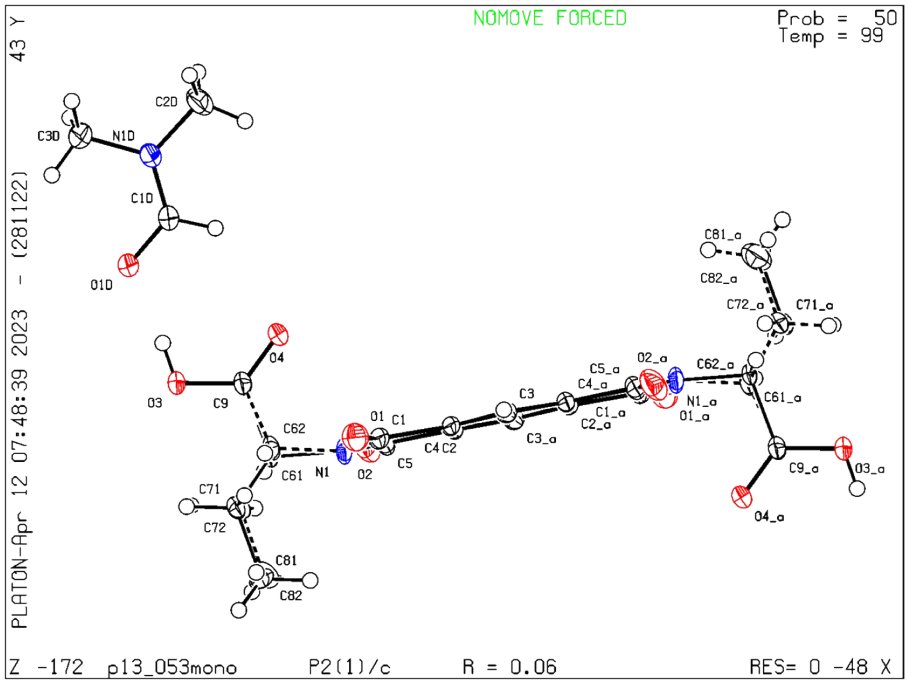
FigureS19. Atomic displacement (ellipsoid plot) structure of solvate **1a**.



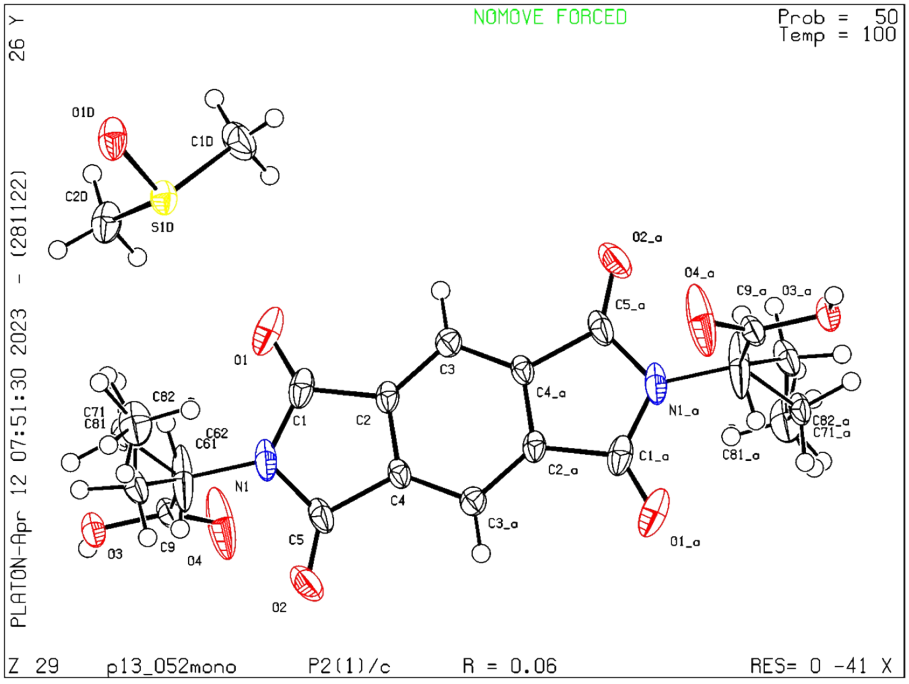
FigureS20. Atomic displacement (ellipsoid plot) structure of solvate **1b**.



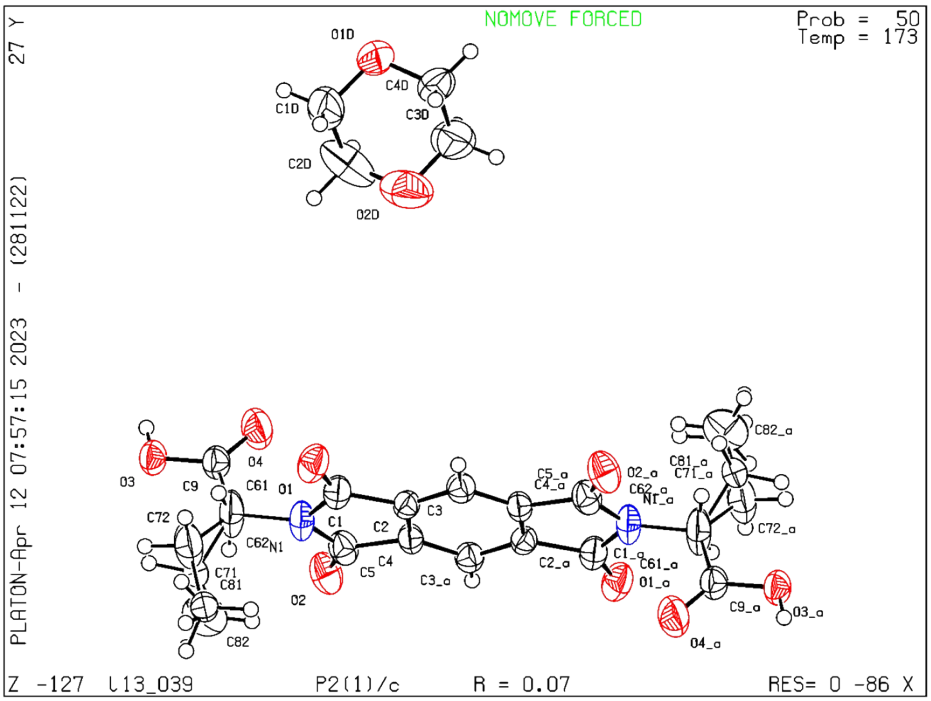
FigureS21. Atomic displacement (ellipsoid plot) structure of solvate **1c**.



FigureS22. Atomic displacement (ellipsoid plot) structure of solvate **2a**.



FigureS23. Atomic displacement (ellipsoid plot) structure of solvate **2b**.



FigureS24. Atomic displacement (ellipsoid plot) structure of solvate **2b**.

Table S1. Interaction energies (E_{int}) and relative stabilities of optimized structures **9a**, **9b** and **9c** (in kcal/mol).

Functional/Basis sets	Interaction energies of **9c**	Stability of **9a** over **9c**	Stability of **9b** over **9c**
B3LYP/6-31+G*	-4.58	11.26	4.21
B3LYP/6-31++G*	-4.58	11.31	4.21
B3LYP/6-31++G**	-4.52	11.14	4.15

Table S2:Interaction energies (E_{int}) of optimized structures **3a**, **3b** and **6a**, **6b** at different basis sets of B3LYP-D3functional.

Functional/Basis sets	Interaction energy (kcal/mol)			
	Structures		Structures	
	3a	**3b**	**6a**	**6b**
B3LYP-D3/6-31+G*	-18.82	-25.10	-18.83	-25.10
B3LYP-D3/6-31++G*	-18.83	-25.10	-18.83	-25.10
B3LYP-D3/6-31++G**	-25.10	-31.38	-18.83	-18.83

Gibbs free energy of structure 9a:

Δ r G° (298 K) = Σ (ε 0 + G corr) product - Σ (ε 0 + G corr) reactant

= [-379.53 – 2 x (-189.76)] a.u.

= -0.01 a.u.= -6.28 kcal/mol

where, Σ (ε 0 + G corr) product = Sum of electronic and thermal Free Energies of dimer **9a**

and Σ (ε 0 + G corr) reactant = Sum of electronic and thermal Free Energies of acid monomer.

The negative value of change in free energy suggests that the dimer **9a** is thermodynamically more stable compared to its monomers.

Table S3:Interaction energies of structures **6a** and **6b** both in the gas and solvent (DMSO) phases.

Functional/Basis sets	Interaction energy (kcal/mol)			
	Gas phase		Solvent phase	
	6a	**6b**	**6a**	**6b**
B3LYP/6-31+G*	-8.12	-13.79	-8.85	-12.55
B3LYP/6-31++G*	-8.37	-13.73	-25.10	-25.10
B3LYP/6-31++G**	-8.37	-13.79	-25.10	-25.10

Table S4. Crystallographic parameters ofsolvates**1a**, **1b**, **1c**and **2a, 2b, 2c**.

Compounds	**1a**	**1b**	**1c**	**2a**	**2b**	**2c**
Empirical formula	$C_{24}H_{30}N_4O_{10}$	$C_{22}H_{28}N_2O_{10}S_2$	$C_{30}H_{40}N_2O_{14}$	$C_{24}H_{30}N_4O_{10}$	$C_{22}H_{28}N_2O_{10}S_2$	$C_{26}H_{32}N_2O_{12}$
Formula weight	534.52	544.58	652.64	534.52	544.58	564.54
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.70000 Å	0.70000 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	P-1	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å)	a = 15.625(3) b = 6.8164(14) c = 12.177(2)	a = 16.231(3) b = 7.0373(14) c = 11.685(2)	a = 6.4872(13) b = 9.976(2) c = 12.810(3)	a = 12.632(3) b = 9.2860(19) c = 11.744(2)	a = 12.768(3) b = 9.2840(19) c = 11.394(2)	a = 12.514(3) b = 9.5933(19) c = 11.344(2)
Volume ($Å^3$)	1296.2(4)	1292.6(4)	783.2(3)	1310.5(5)	1260.7(5)	1361.4(5)
Z	2	2	1	2	2	2
Density (Mg/m^3)	1.370	1.399	1.384	1.355	1.435	1.377
Abs coeff (mm^{-1})	0.108	0.263	0.110	0.068	0.269	0.110
F(000)	564	572	346	564	572	596
Index ranges	–20<=h<=20, –8<=k<=8, –15<=l<=15	–21<=h<=21, –9<=k<=9, –13<=l<=15	–8<=h<=8, –11<=k<=12, –16<=l<=16	–17<=h<=17, –12<=k<=12, –16<=l<=16	–17<=h<=17, –13<=k<=13, –16<=l<=16	–16<=h<=16, –12<=k<=12, –14<=l<=14
Completeness to 2θ	99.8 %	98.7 %	99.2 %	99.0 %	99.3 %	99.9 %
Data / restraints / parameters	2958 / 0 / 177	2919 / 0 / 168	3560 / 0 / 211	3782 / 1 / 215	3664 / 1 / 203	3117 / 0 / 212
Gof (F^2)	1.077	1.063	1.102	1.065	1.075	1.083
R indices [I>2σ(I)]	R1 = 0.0408, wR2 = 0.1026	R1 = 0.0339, wR2 = 0.0880	R1 = 0.0493, wR2 = 0.1284	R1 = 0.0554, wR2 = 0.1434	R1 = 0.0517, wR2 = 0.1442	R1 = 0.0662, wR2 = 0.1670
R indices (all	R1 = 0.0579,	R1 = 0.0420,	R1 = 0.1026,	R1 = 0.0599,	R1 = 0.0584,	R1 = 0.1405,

data)	wR2 = 0.1148	wR2 = 0.0934	wR2 = 0.1691	wR2 = 0.1469	wR2 = 0.1506	wR2 = 0.2197
CCDC No.	2205752	2205753	2205754	2205755	2205756	2205757

Table S5. Hydrogen bond parameters (Å and °) ofsolvates**1a**, **1b**, **1c**and **2a, 2b, 2c**.

Compounds	D-H···A	d_{D-H}	$d_{H\cdots A}$	$d_{D\cdots A}$	∠D-H···A
1a	O3-H3···O1D [-x+2, -y, -z+1]	0.84	1.71	2.55(16)	172.7
	C1D-H1D···O4 [2-x, -y, 1-z]	0.95	2.33	3.24	159.6
	C2D-H2D3···O4 [1+x, y, z]	0.98	2.56	3.50	162.8
	C7-H7C···O2 [x, -1+y, z]	0.98	2.49	3.27	136.8
1b	O3-H3···O1D [-x, -y, -z+2]	0.83	1.71	2.54(15)	173.7
	C1D-H1D2···O4	0.97	2.65	3.29	123.3
	C7-H7A···O1[x, -1+y, z]	0.97	2.69	3.40	130.5
	C1D-H1D3···O1D [-x, -½+y, ½-z]	0.97	2.64	3.57	161.8
1c	O3-H3···O4 [-x, -y+1, -z+1]	0.84	1.80	2.64(2)	173.6
	C8-H8C···O2 [-1+x, y, z]	0.98	2.69	3.48	137.2
	C7-H7B···O4[1+x, 1+y, -1+z]	0.98	2.62	3.42	139.5
	C2D-H2D2···O3 [-x, 1-y, 1-z]	0.98	2.58	3.46	149.2
	C4DH4D2···O3[x, y, 1+z]	0.99	2.68	3.49	139.4
	C7-H7C···O2D [-x, 1-y, 1-z]	0.98	2.61	3.50	150.5
	C3-H3A···O3D [-x, 1-y, 1-z]	0.95	2.39	3.34	174.6
2a	O3-H3···O1D [-x+1, -y+2, -z+1]	0.84	1.69	2.53(14)	175.0
	C1D-H1D···O4	0.95	2.46	3.18	132.5
	C3D-H3D3···O3	0.98	2.70	3.26	117.1
	C2D-H2D3···O1 [x, 1+y, z]	0.98	2.54	3.27	131.1
	C3D-H3D2···O1 [1-x, 2-y, 1-z]	0.98	2.59	3.45	146.02
	C71-H71B···O4	0.99	2.65	3.44	137.4
	C2D-H2D3···O1D [x, ½-y, -½+z]	0.98	2.66	3.18	113.2
2b	O3-H3···O1D [-x+1, -y+1, -z]	0.84	1.72	2.56(19)	168.7
	C1D-H1D3···O4 [x, -1+y, z]	0.98	2.71	3.52	140.1
	C1D-H1D2···O1	0.98	2.625	3.3	126.2
	C2D-H2D2···O1	0.98	2.60	3.28	126.8
	C71-H71A···O4 [x, ½-y, -½+z]	0.99	2.51	3.35	143.0
	C2D-H2D1···O1D [-x, -½+y, ½-z]	0.98	2.63	3.38	133.2

2c	O3-H3···O1D [-x+1, -y, -z+1]	0.84	1.86	2.70(3)	178.3
	C1D-H1D1···O4 [x, 1-y, 1-z]	0.99	2.48	3.25	134.5
	C1D-H1D2···O1 [-x, 1-y, 1-z]	0.99	2.50	3.48	169.7
	C3D-H3D1···O1 [-x, 1-y, 1-z]	0.99	2.66	3.32	123.8
	C3-H3A···O1D	0.95	2.64	3.42	140.0
	C71-H71B···O4 [-x, -½+y, ½-z]	0.99	2.40	3.21	139.0

Table S6: Coordinates of the studied compounds (in Angstroms) optimized in gas phase at B3LYP/6-31+G* level of theory.

Structure - 3a

Atoms Coordinates (Å)

	X	**Y**	**Z**
C	3.350190	-0.263226	-0.136799
O	4.532268	-0.024300	-0.197305
O	2.440669	0.607668	0.316184
H	2.918239	-1.231407	-0.453824
H	1.529497	0.214035	0.272964
C	-1.035411	0.400187	0.045051
O	-0.088381	-0.387730	0.156996
N	-2.333321	0.044307	-0.027631
H	-0.875187	1.489172	-0.004274
C	-2.730353	-1.358443	0.025765
H	-3.395435	-1.528688	0.880933

H	-3.259552	-1.635594	-0.893930
H	-1.835786	-1.972514	0.131225
C	-3.389867	1.037696	-0.160736
H	-3.956032	0.873764	-1.085733
H	-4.081485	0.978540	0.688534
H	-2.954816	2.040149	-0.189168

Structure - 3b

C	3.097583	0.302312	0.000185
O	2.364588	1.275425	0.001388
O	2.716408	-0.967419	-0.000722
H	4.195196	0.378919	-0.000224
H	1.709972	-1.033568	-0.000451
C	-0.555920	-0.025882	-0.000775
O	0.032164	-1.118150	-0.000552
N	-1.896373	0.119101	0.000234
H	0.009176	0.917074	-0.001685
C	-2.780018	-1.040074	0.001199
H	-3.420484	-1.026434	0.891760
H	-3.418177	-1.029993	-0.891096
H	-2.170584	-1.944126	0.003706

C	-2.514062	1.437218	-0.000830
H	-3.140671	1.567765	-0.892039
H	-3.141642	1.568580	0.889551
H	-1.738951	2.207794	-0.000743

Structure - 6a

C	-3.106102	-0.114932	0.299247
O	-4.299406	-0.093333	0.112220
O	-2.207746	0.301449	-0.599878
H	-2.654028	-0.484507	1.239050
H	-1.286405	0.192458	-0.242873
S	1.559688	0.022151	-0.427597
O	0.282421	-0.024132	0.423661
C	2.551043	-1.415766	0.110068
H	2.017835	-2.310935	-0.218688
H	3.538452	-1.377052	-0.360478
H	2.630754	-1.408459	1.200939
C	2.596251	1.329781	0.318372
H	3.581491	1.333029	-0.158311
H	2.090951	2.280562	0.132751
H	2.676629	1.154115	1.395014

Stucture - 6b

C	-2.768033	0.105779	-0.123458
O	-2.079638	1.091381	-0.326584
O	-2.332028	-1.094542	0.226003
H	-3.864663	0.113366	-0.215235
H	-1.326020	-1.086341	0.313821
S	1.107987	-0.047966	-0.399339
O	0.332190	-1.069607	0.454491
C	2.859362	-0.501383	-0.152413
H	3.006605	-1.478327	-0.618704
H	3.500820	0.243167	-0.634223
H	3.064948	-0.565810	0.919872
C	1.113188	1.513178	0.547723
H	1.779164	2.230780	0.057614
H	0.084096	1.877713	0.530771
H	1.435970	1.309611	1.573111

Structure - 9a

C	-0.122807	1.923667	-0.000065
O	-1.125429	1.219859	-0.000592
O	1.125429	1.501625	0.000604

H	-0.179719	3.019192	-0.000087
H	1.159035	0.499306	0.000381
C	0.122807	-1.923667	-0.000065
O	1.125429	-1.219859	-0.000592
O	-1.125429	-1.501625	0.000604
H	0.179719	-3.019192	-0.000087
H	-1.159035	-0.499306	0.000381

Structure - 9b

C	3.141116	-0.033762	-0.214549
O	2.543556	-0.362523	-1.218905
O	2.584186	0.308944	0.948701
H	4.237914	0.019176	-0.146622
H	1.588194	0.257580	0.870352
C	-0.558103	-1.127291	0.265038
C	-2.078744	-1.189105	0.214085
C	-2.180154	1.128875	-0.156655
C	-0.659949	1.214528	-0.106000
H	-0.120915	-1.305102	-0.726488
H	-2.412933	-2.135412	-0.221879
H	-2.584952	1.861356	-0.861452

H	-0.331014	2.158826	0.338134
H	-0.230116	1.113500	-1.112428
H	-2.600833	1.324543	0.842910
H	-2.494158	-1.097542	1.231116
H	-0.155798	-1.855549	0.975576
O	-0.136961	0.168859	0.734677
O	-2.600829	-0.152886	-0.614564

Structure - 9c

C	3.171204	0.000031	-0.160487
O	4.328826	-0.000463	0.175988
O	2.148249	0.000817	0.708427
H	2.852672	-0.000209	-1.220325
H	1.284583	0.000294	0.226013
C	-2.072999	-1.175528	0.463676
C	-1.053175	-1.190351	-0.668097
C	-1.053584	1.190271	-0.668334
C	-2.073188	1.175340	0.463618
H	-1.557831	-1.222705	1.436565
H	-0.362883	-2.034015	-0.576070
H	-0.363554	2.034180	-0.576644

H	-2.755828	2.026581	0.382539
H	-1.557732	1.222530	1.436341
H	-1.560054	1.241516	-1.642788
H	-1.559503	-1.241996	-1.642603
H	-2.755463	-2.026888	0.382338
O	-2.877157	-0.000178	0.397127
O	-0.246662	0.000092	-0.629995

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