Electronic Supplementary Material (ESI) for CrystEngComm.

Steric influence on solvate formation – A comparison of resorcylic acid and two brominated derivatives

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Supporting Information

Contents

Crystallographic data

Table S1 Crystallographic information of the single crystal structures of **RA**.

Crystal form	**RA S_{DMF}**	**RA S_{DIO}0.5**	**RA S_{AcOH}**
CCDC number	2120727	2120724	2120730
Identifier	RA_DMF	RA_DIO	ke064
Formula	$C_7H_6O_4$ x C_3H_7NO	$C_7H_6O_4$ x 0.5 $C_4H_8O_2$	$C_7H_6O_4$ x $C_2H_4O_2$
M_r [g/mol]	227.21	198.17	214.17
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
Temperature [K]	120	120	120
a [Å]	12.320(4)	13.2219(17)	4.6177(5)
b [Å]	24.910(7)	6.4624(8)	17.933(2)
c [Å]	7.009(2)	11.2303(14)	11.6033(15)
α [°]	90	90	90
β [°]	96.322(7)	111.089(2)	99.898(4)
γ [°]	90	90	90
V [Å^3]	2137.8(11)	895.3(2)	946.6(2)
Z	8	4	4
Wavelength (Å)	0.71073	0.71073	0.71073
F(000)	960	416	448
Θ range for data collection	1.663 - 28.950	1.651 - 28.500	2.271 - 25.998
Index ranges	-16 < h < 16 -33 < k < 33 -9 < l < 9	-17 < h < 17 -8 < k < 8 -15 < l < 15	-5 < h < 5 -22 < k < 22 -14 < l < 14
Reflections observed	32606	12446	16041
Unique reflections	5627	2269	1868
Final R indices ($I \geq 2\sigma I$)	R1 = 0.0928 wR2 = 0.2140	R1 = 0.0816 wR2 = 0.2186	R1 = 0.0417 wR2 = 0.0886
R indices (all data)	R1 = 0.1352 wR2 = 0.2537	R1 = 0.0873 wR2 = 0.2268	R1 = 0.0683 wR2 = 0.0979

Table S2. Crystallographic information of the single crystal structures of **5-BRA**.

Crystal form	**5-BRA S_{MeOH}**	**5-BRA S_{EtOH}**	**5-BRA S_{Ace}**	**5-BRA S_{DMF}**	**5-BRA S_{DMSO}**
CCDC number	2120725	2120722	2120714	2120715	2120717
Identifier	ke057	ke055	ke049	ke047	ke050
Formula	$C_7H_5BrO_4$ x CH_4O	$C_7H_5BrO_4$ x C_2H_6O	$C_7H_5BrO_4$ x C_3H_6O	$C_7H_5BrO_4$ x C_3H_7NO	$C_7H_5BrO_4$ x C_2H_6SO
M_r [g/mol]	265.06	279.09	291.10	306.12	311.15
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	P-1
Temperature [K]	120	120	120	120	120
a [Å]	4.8463(3)	10.7541(10)	4.8141(5)	10.8995(4)	7.8467(5)
b [Å]	14.8609(10)	5.1393(5)	27.892(2)	17.2454(6)	8.5738(5)
c [Å]	13.0678(8)	18.7589(19)	8.7246(8)	13.5191(5)	9.3115(6)
α [°]	90	90	90	90	73.0626(18)
β [°]	95.0313(19)	91.411(3)	104.630(3)	111.328(5)	68.6204(18)
γ [°]	90	90	90	90	83.6321(19)
V [Å^3]	937.52(10)	1036.46(17)	1133.51(18)	2367.10(17)	558.02(6)
Z	4	4	4	8	2
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
F(000)	528	560	584	1232	311.9
Θ range for data collection	2.74 – 26.65	2.85 – 25.99	2.52 – 26.73	2.00 – 27.357	2.44 – 26.00
Index ranges	-5 < h < 5 -18 < k < 18 -16 < l < 16	-13 < h < 12 -6 < k < 6 -23 < l < 23	-6 < h < 5 -34 < k < 35 -10 < l < 11	-12 < h < 13 -21 < k < 20 -16 < l < 14	-10 < h < 9 -11 < k < 11 -11 < l < 11
Reflections observed	19982	19118	8599	10853	11487
Unique reflections	1833	2042	2390	4656	2195
Final R indices ($I \geq 2\sigma I$)	R1 = 0.0315 wR2 = 0.0590	R1 = 0.0372 wR2 = 0.0513	R1 = 0.0469 wR2 = 0.0753	R1 = 0.0431 wR2 = 0.0763	R1 = 0.0200 wR2 = 0.0498
R indices (all data)	R1 = 0.0434 wR2 = 0.0625	R1 = 0.0631 wR2 = 0.0561	R1 = 0.0783 wR2 = 0.0821	R1 = 0.0675 wR2 = 0.0860	R1 = 0.0244 wR2 = 0.0520

Table S3 Crystallographic information of the single crystal structures of **5-BRA** continued.

Crystal form	**5-BRA S_{EMK}**	**5-BRA $S_{DIO}0.5$**	**5-BRA $S_{DIO}1$**	**5-BRA S_{THF}**
CCDC number	2120720	2120716	2120729	2120723
Identifier	ke061	ke056	ke062	ke048
Formula	$C_7H_5BrO_4$ x 0.5 C_4H_8O	$C_7H_5BrO_4$ x 0.5 $C_4H_8O_2$	$C_7H_5BrO_4$ x $C_4H_8O_2$	$C_7H_5BrO_4$ x C_4H_8O
M_r [g/mol]	269.07	277.072	321.12	305.13
Crystal system	Triclinic	Triclinic	Orthorhombic	Monoclinic
Space group	P-1	P-1	P*nma*	$P2_1/c$
Temperature [K]	120	120	120	120
a [Å]	4.9186(7)	4.2750(4)	22.7597(16)	4.8148(4)
b [Å]	14.079(2)	10.1068(9)	6.6011(5)	15.5203(12)
c [Å]	14.695(2)	12.626(1)	16.731(1)	15.6723(12)
α [°]	97.214(4)	108.660(3)	90	90
β [°]	91.367(3)	98.455(3)	90	96.448(2)
γ [°]	98.717(4)	97.857(3)	90	90
V [Å^3]	996.9(2)	501.32(8)	2513.6(3)	1163.74(16)
Z	4	2	8	4
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
F(000)	535.2	275.8	1296	615.26
Θ range for data collection (°)	2.80 - 26.81	3.22 – 25.99	2.44 – 26.77	2.62 – 27.20
Index ranges	-6 < h < 6 -17 < k < 16 -18 < l < 18	-4 < h < 5 -12 < k < 12 -15 < l < 15	-28 < h < 28 -8 < k < 8 -20 < l < 21	-6 < h < 6 -19 < k < 19 -20 < l < 20
Reflections observed	17196	8977	71370	25375
Unique reflections	4245	1975	2914	2578
Final R indices ($I \geq 2\sigma I$)	R1 = 0.0627 wR2 = 0.0740	R1 = 0.0340 wR2 = 0.0776	R1 = 0.0434 wR2 = 0.0880	R1 = 0.0526 wR2 = 0.1279
R indices (all data)	R1 = 0.1426 wR2 = 0.0897	R1 = 0.0426 wR2 = 0.0815	R1 = 0.0693 wR2 = 0.0970	R1 = 0.0801 wR2 = 0.1442

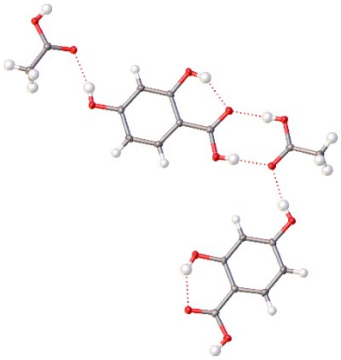
Table S4 Crystallographic information of the single crystal structures of **3,5-BRA**.

Crystal form	**3,5-BRA S_{DIO}**	**3,5-BRA S_{THF}**	**3,5-BRA S_{DMF}**	**3,5-BRA S_{PeOH}**	**3,5-BRA S_{AcOH}**
CCDC number	2120718	2120719	2120721	2120728	2120726
Identifier	ke031	ke033	ke034	ke037	ke042
Formula	$C_7H_4Br_2O_4$ x $C_4H_8O_2$	$C_7H_4Br_2O_4$ x C_4H_8O	$C_7H_4Br_2O_4$ x C_3H_7NO	$C_7H_4Br_2O_4$ x $C_5H_{12}O$	$C_7H_4Br_2O_4$ x $C_2H_4O_2$
M_r [g/mol]	400.03	384.03	385.02	400.07	371.97
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$Pna2_1$	$P2_1/c$	$I2/a$
Temperature [K]	120	120	120	120	120
a [Å]	5.0921(3)	4.9275(3)	17.6810(12)	8.1238(4)	17.2749(9)
b [Å]	9.6935(6)	16.6356(9)	3.8913(3)	24.7317(15)	3.9072(2)
c [Å]	27.0491(16)	15.8268(8)	18.1986(14)	7.2459(4)	35.441(2)
α [°]	90	90	90	90	90
β [°]	91.041(2)	97.1838(17)	90	93.5848(19)	98.9201(16)
γ [°]	90	90	90	90	90
V [Å^3]	1334.93(14)	1287.17(12)	1252.10(16)	1452.96(14)	2363.2(2)
Z	4	4	4	4	8
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
F(000)	784	752	752	792	1440
Θ range for data collection	2.232 - 25.988	2.449 - 26.777	2.238 - 25.987	2.512 - 25.998	2.327 – 32.019
Index ranges	-5 < h < 6 -11 < k < 11 -33 < l < 33	-6 < h < 6 -21 < k < 21 -20 < l < 20	-19 < h < 21 -4 < k < 4 -22 < l < 19	-10 < h < 9 -30 < k < 30 -8 < l < 8	-25 < h < 25 -5 < k < 5 -52 < l < 51
Reflections observed	13871	19514	11495	21736	48462
Unique reflections	2628	2740	2315	2841	4111
Final R indices ($I \geq 2\sigma I$)	R1 = 0.0250 wR2 = 0.0443	R1 = 0.0211 wR2 = 0.0470	R1 = 0.0212 wR2 = 0.0466	R1 = 0.0291 wR2 = 0.0553	R1 = 0.0465 wR2 = 0.1078
R indices (all data)	R1 = 0.0347 wR2 = 0.0462	R1 = 0.0277 wR2 = 0.0491	R1 = 0.0224 wR2 = 0.0468	R1 = 0.0361 wR2 = 0.0568	R1 = 0.0642 wR2 = 0.1167

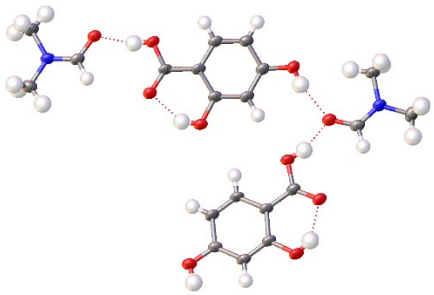
Supporting tables and figures to the main manuscript

Table S5 Packing motifs in the structurally determined solvates of **RA**, **5-BRA** and **3,5-BRA**.

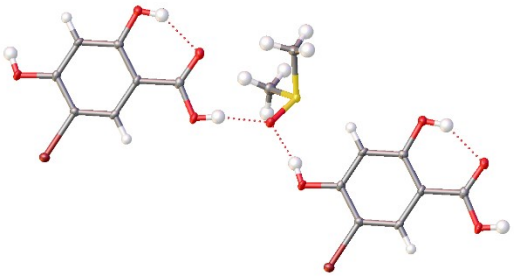
Solvate	No acid dimer	Acid dimer	Finite tetramer	Infinite tetramer chain
RA $S_{DMSO}0.5$		X		x
RA S_{AcOH}	X			
RA S_{DMF}	X			
RA $S_{DIO}0.5$		X		X
5-BRA S_{MeOH}		X		X
5-BRA S_{EtOH}		X		X
5-BRA S_{Ace}		X	X	
5-BRA S_{DMF}		X	X	
5-BRA S_{DMSO}	X			
5-BRA S_{EMK}		X	X	
5-BRA $S_{DIO}1$	X			
5-BRA $S_{DIO}0.5$		X		X
5-BRA S_{THF}		X	X	
3,5-BRA S_{DIO}	X			
3,5-BRA S_{THF}		X	X	
3,5-BRA S_{DMF}	X			
3,5-BRA S_{PeOH}	X			
3,5-BRA S_{AcOH}		X		X



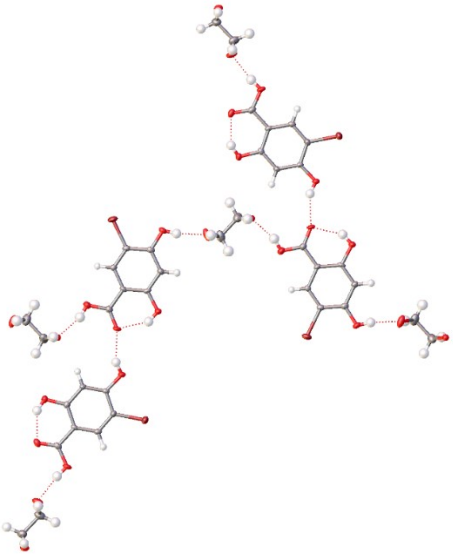
RA S_{AcOH}



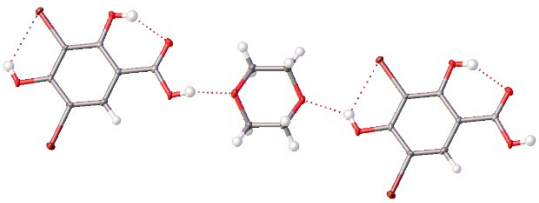
RA S_{DMF}



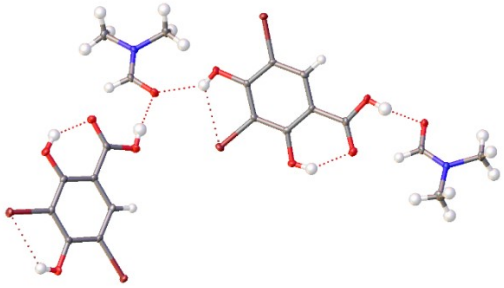
5-BRA S_{DMSO}



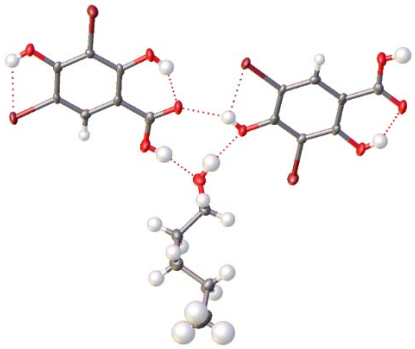
5-BRA $S_{DIO}1$



3,5-BRA S_{DIO}



3,5-BRA S_{DMF}



3,5-BRA S_{PeOH}

Figure S1 Hydrogen bonding motifs of the solvates not showing acid-acid homodimers. Only one position of the disordered solvent of **3,5-BRA S_{PeOH}** is shown for clarity.

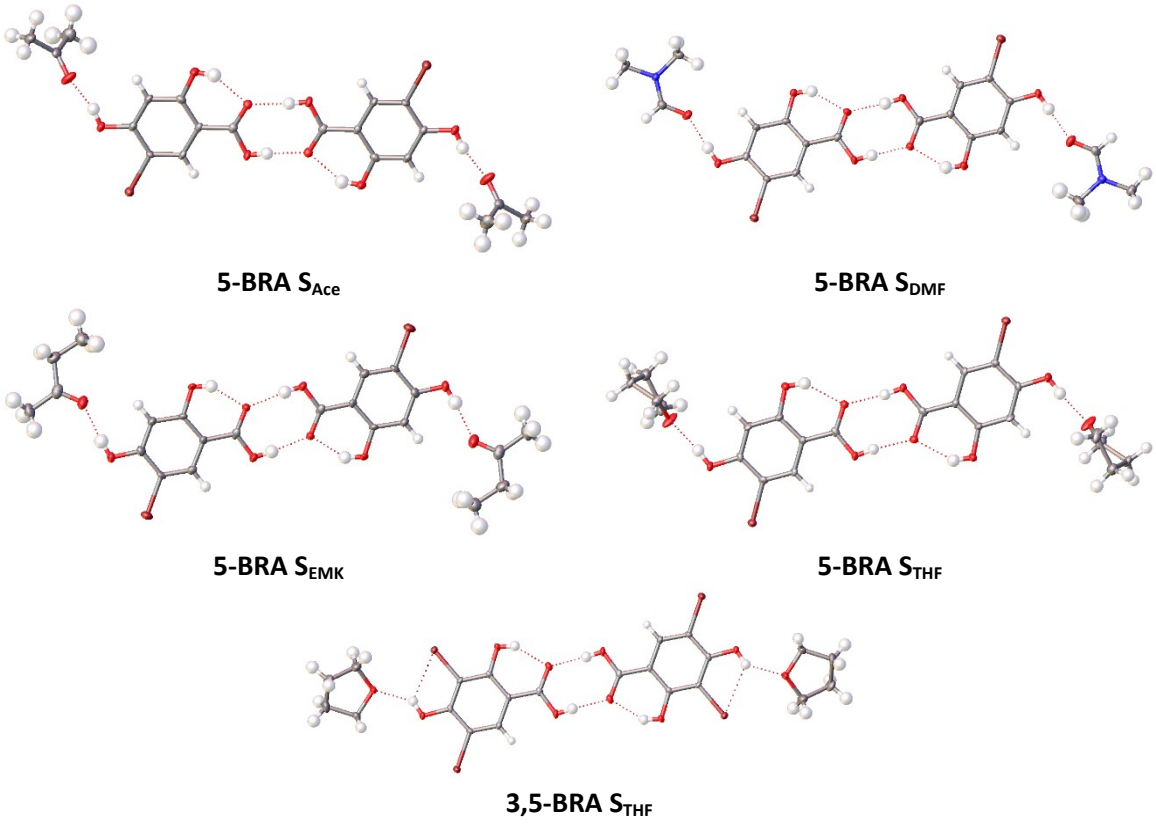


Figure S2 Hydrogen bonding motifs of the solvates showing acid-acid homodimers in finite tetramers with the guest molecules.

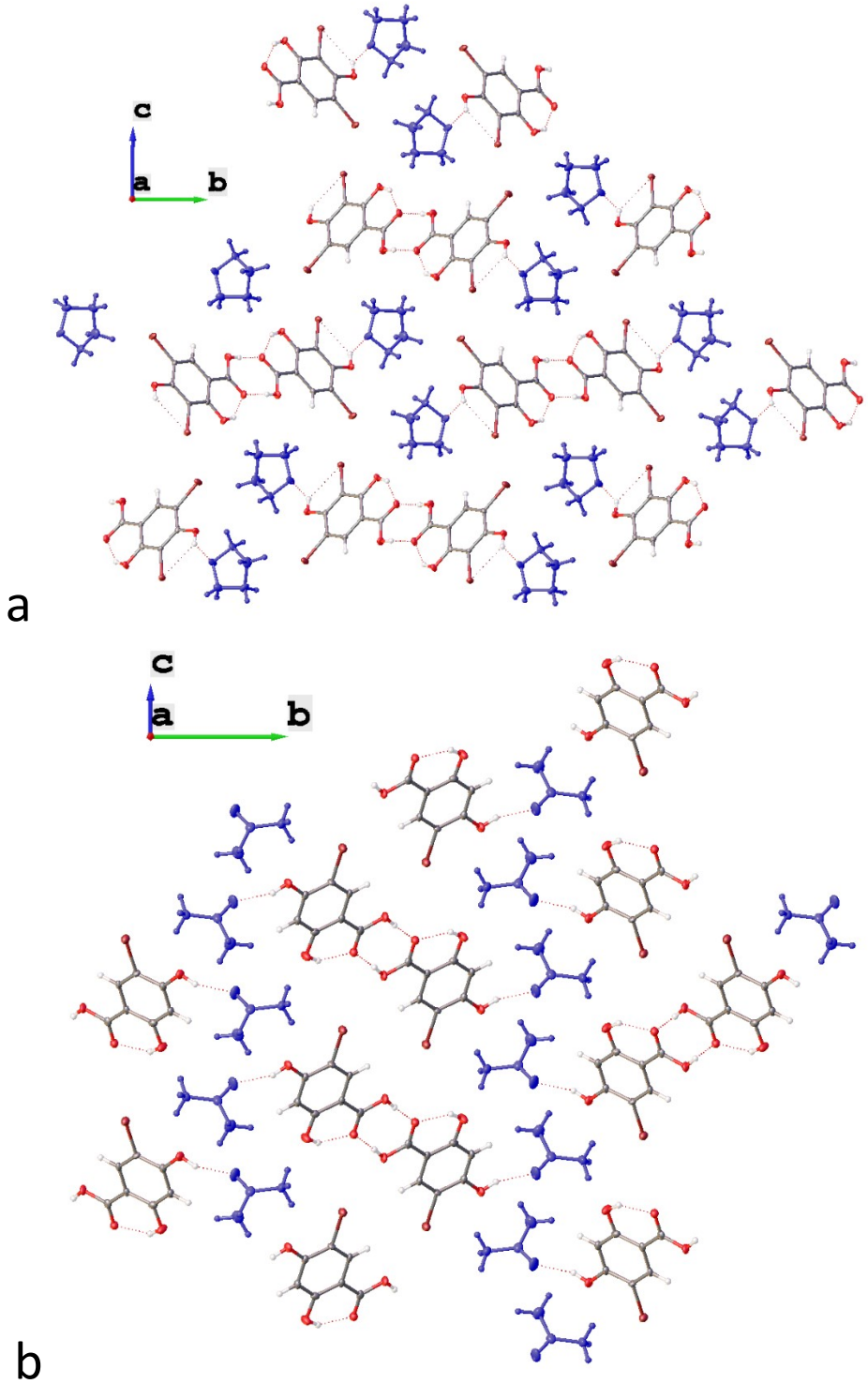


Figure S3 Packing representations of a) **3,5-BRA S_{THF}** and b) **5-BRA S_{Ace}** showing the packing of finite tetramers with the solvent in distinct channels or as phase separated layers. Solvent molecules are coloured in blue for clarity.

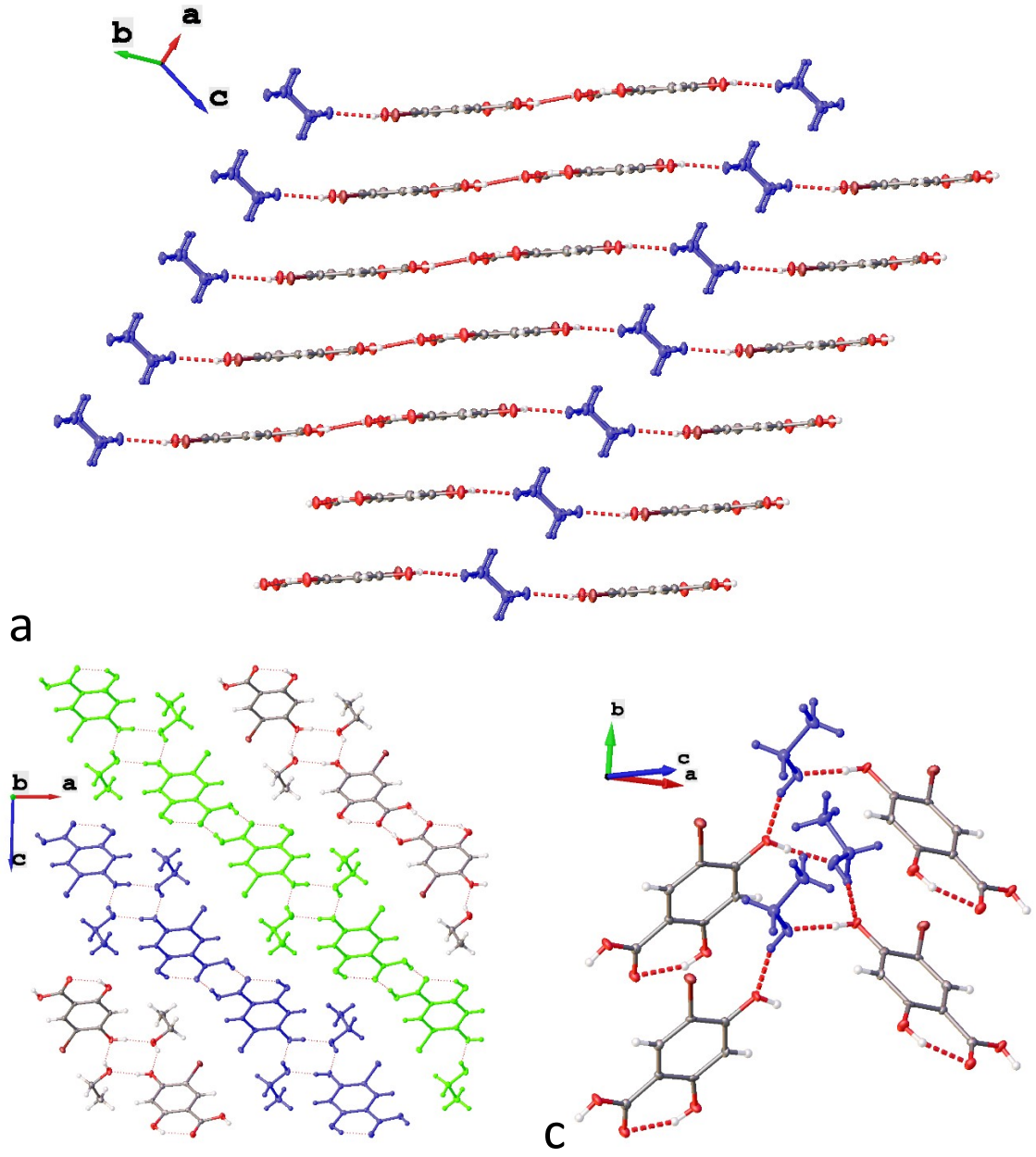
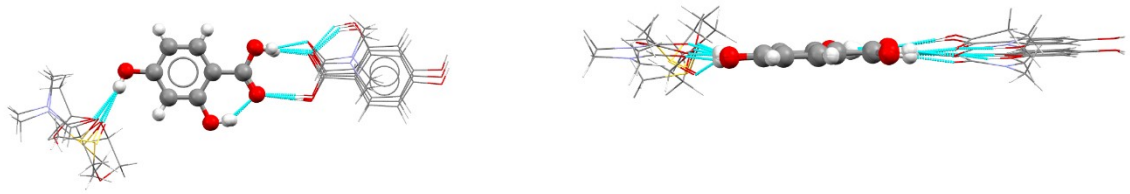
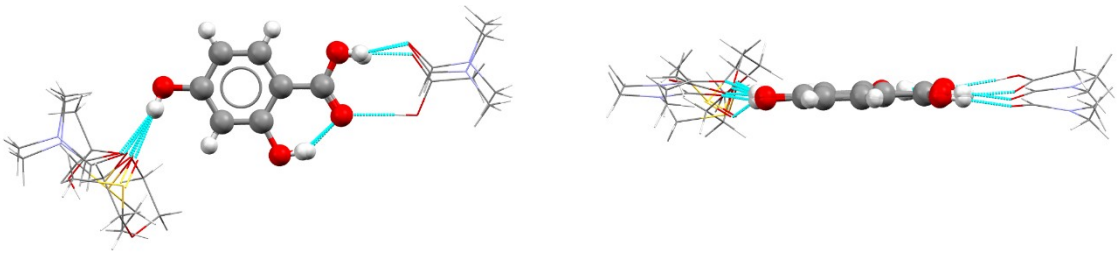


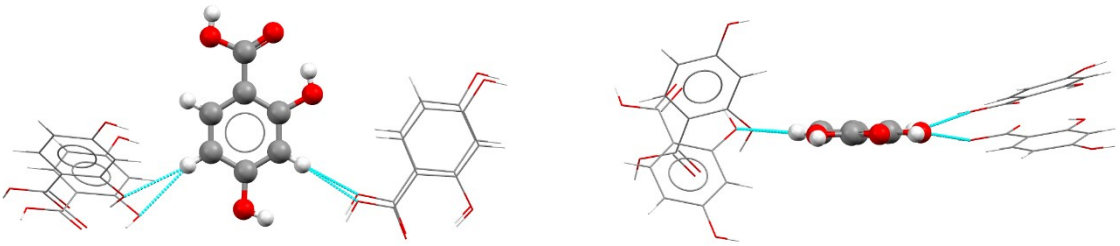
Figure S4 Packing representations of a) **5-BRA S_{DIO}1**, b) **5-BRA S_{EtOH}** showing the packing of infinite chains along [1 0 1] with neighbouring chains coloured in blue and green for clarity, and c) **5-BRA S_{EtOH}** showing the hydrogen bonded connection between the layers through the 2_1-screw axis along [0 1 0]. Solvent molecules in a) and c) are coloured blue for clarity.



All hydrogen bonding short contacts

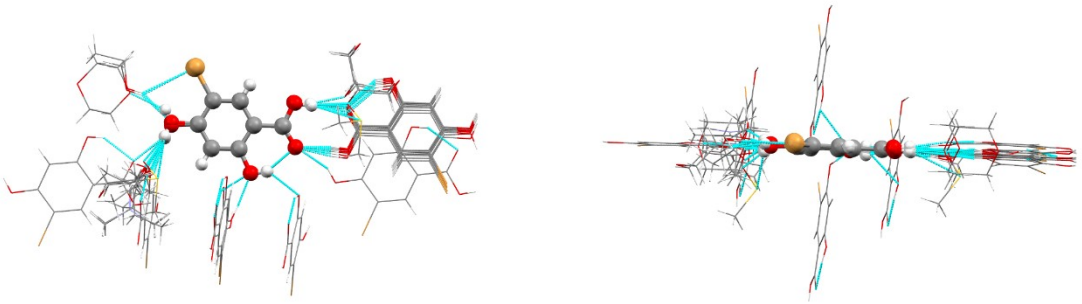


Hydrogen bonds to solvent

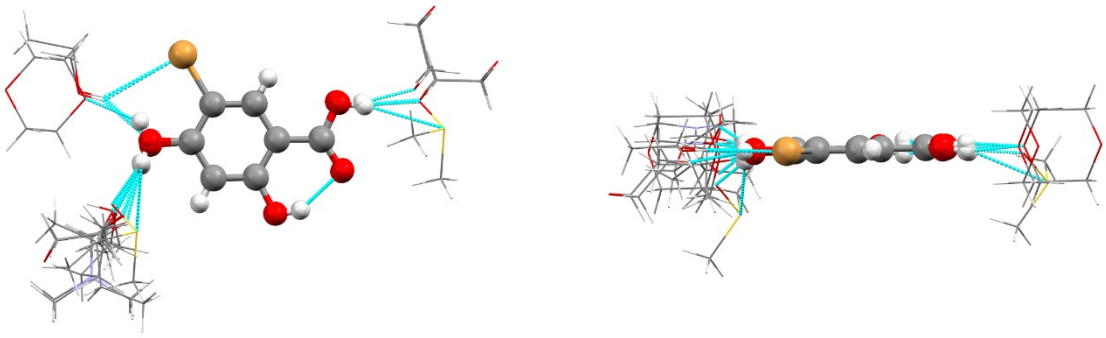


Non-classical hydrogen bonds in the meta position

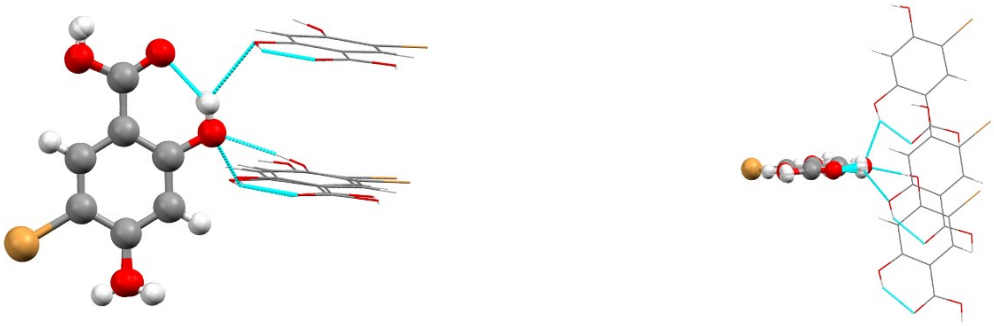
Figure S5 Radial distribution of short contacts (≤ sum of van-der-Waals radii of adjacent atoms) around central **RA** molecule for all four solvates.



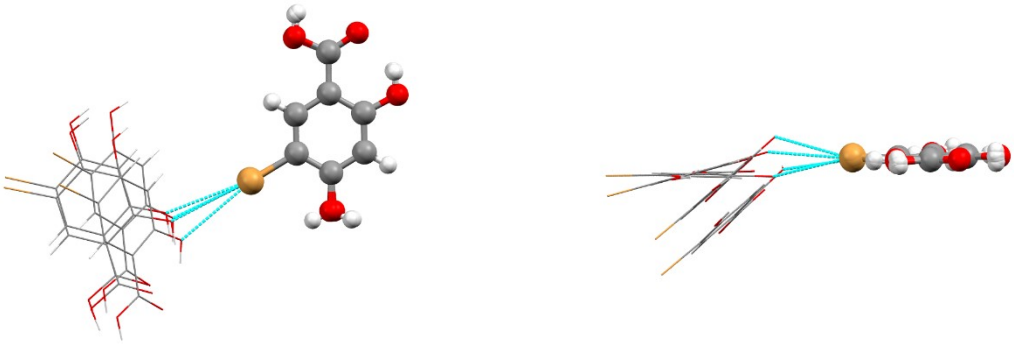
All hydrogen bonding close contacts



Solvent contacts

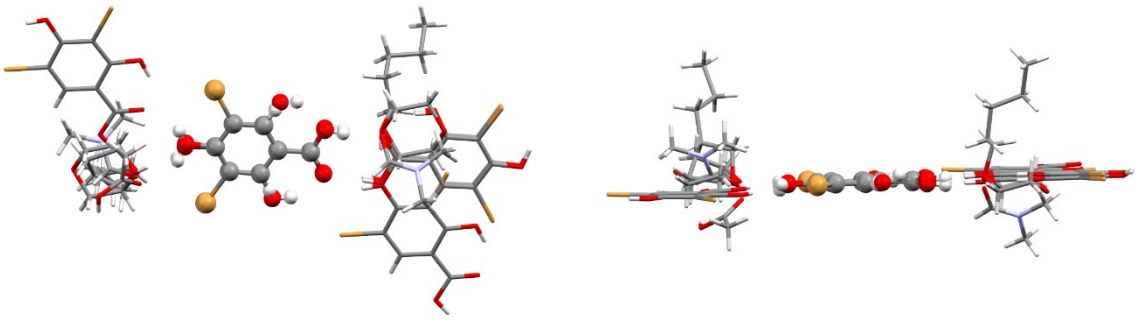


5-BRA contacts through 4-hydroxyl group



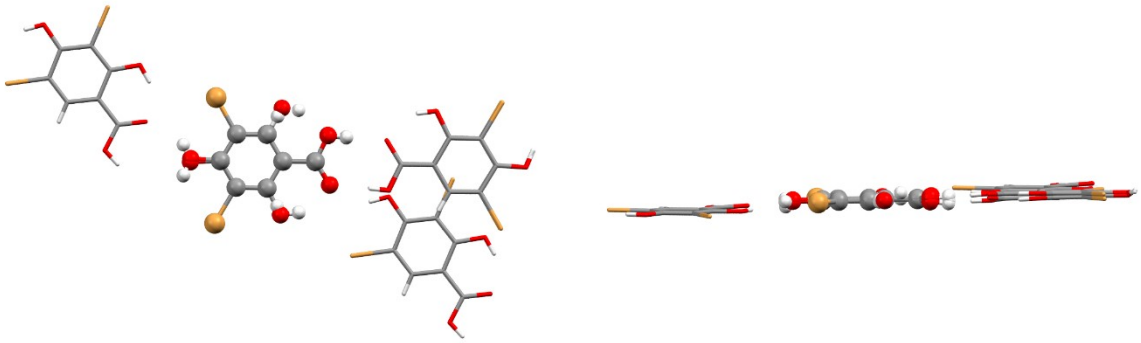
Halogen bonding

Figure S6 Radial distribution of short contacts (≤ sum of van-der-Waals radii of adjacent atoms) around central **5-BRA** molecule for all nine solvates.



All short contacts

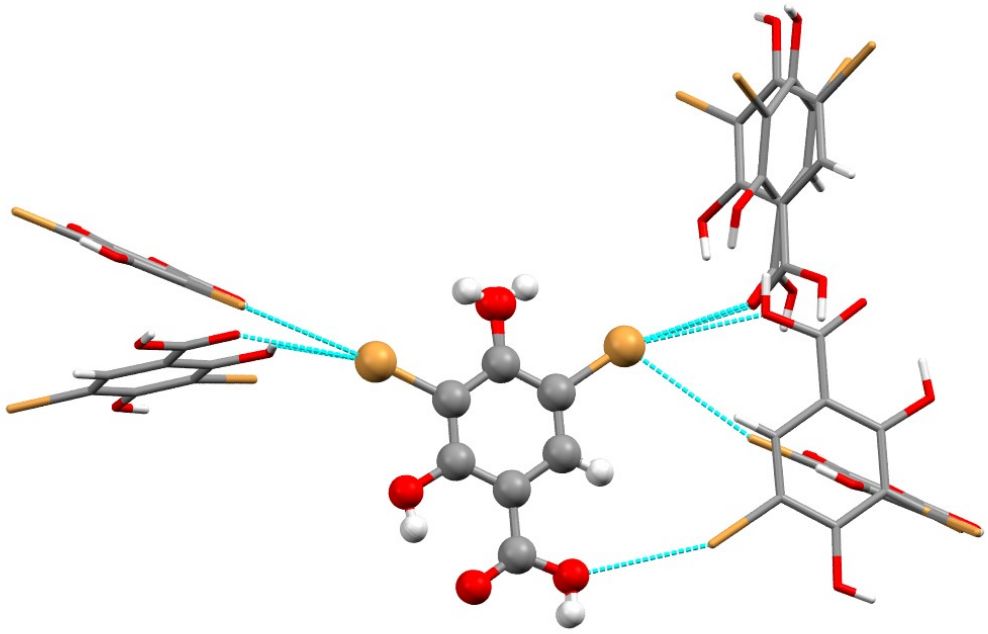
Solvent contacts



3,5-BRA contacts

Figure S7 Radial distribution of short contacts (≤ sum of van-der-Waals radii of adjacent atoms) around the carboxylic acid and para-hydroxyl group of a central **3,5-BRA** molecule for all five solvates.

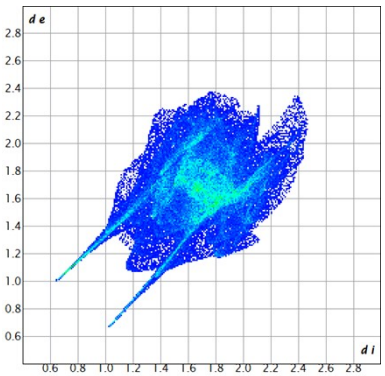
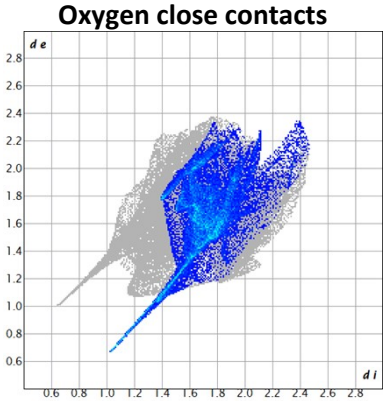
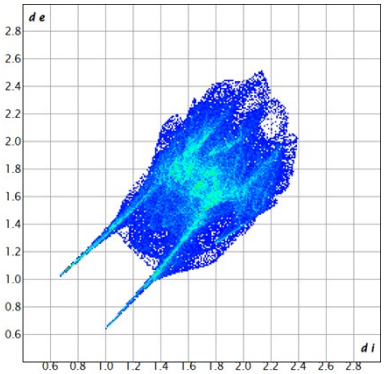
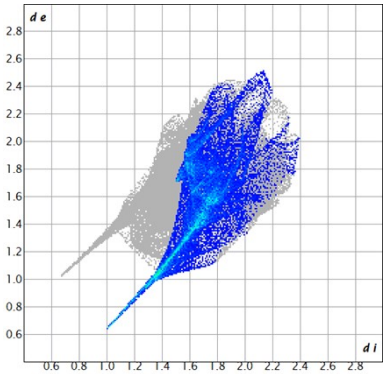
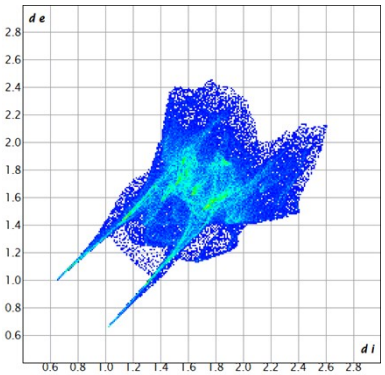
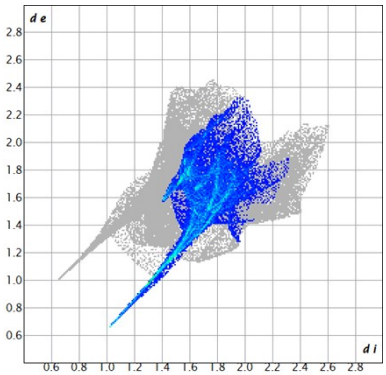
Contacts around 4-hydroxyl group

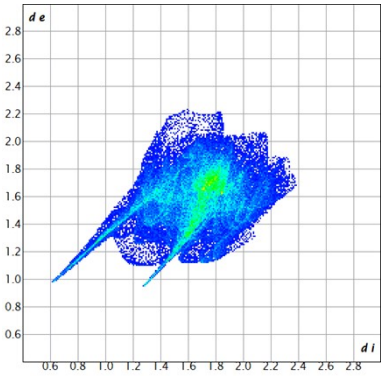


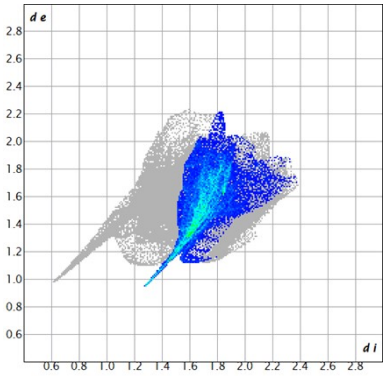
Halogen bonds

Figure S8 Radial distribution of short contacts (≤ sum of van-der-Waals radii of adjacent atoms) around the ortho-hydroxyl group and halogen bonding of a central **3,5-BRA** molecule for all five solvates.

Table S6. Hirshfeld surface fingerprints of the solvated crystal forms of **RA**

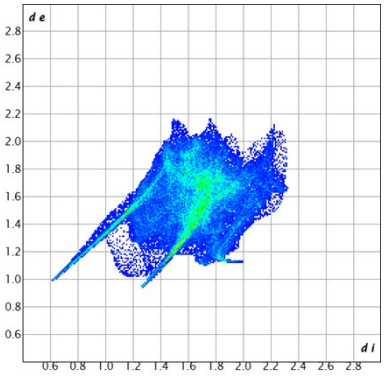
All contacts	Oxygen close contacts
	
	29.1%
RA S_{DMSO}0.5 molecule 1	
	
	28.5%
RA S_{DMSO}0.5 molecule 2	
	
	28.9%
RA S_{AcOH}	

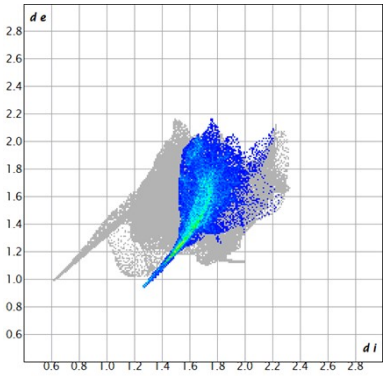




29. 9%

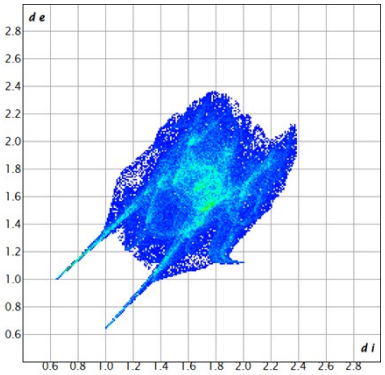
RA S_{DMF} molecule 1

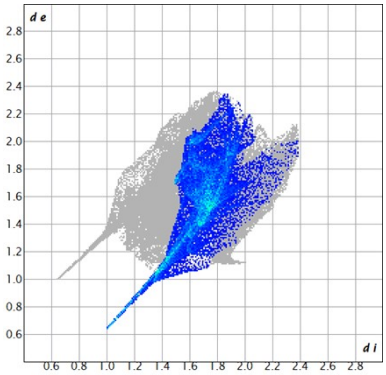




29.6%

RA S_{DMF} molecule 2

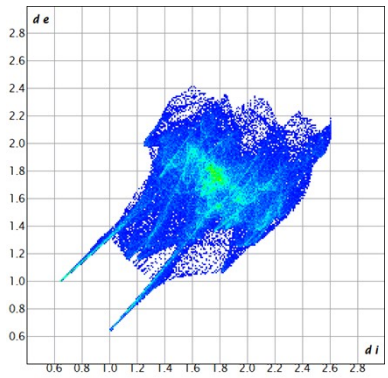
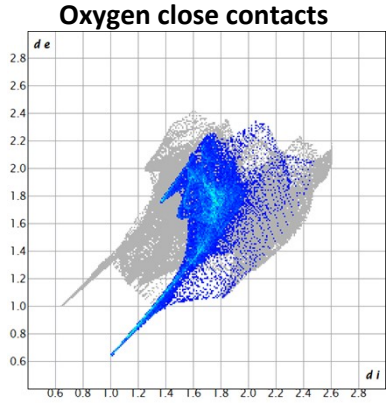
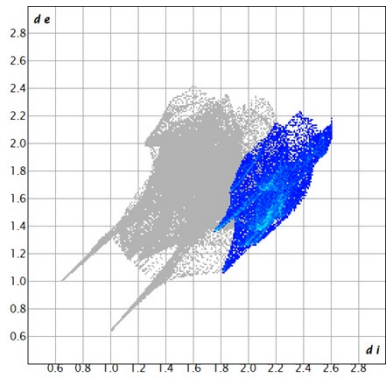
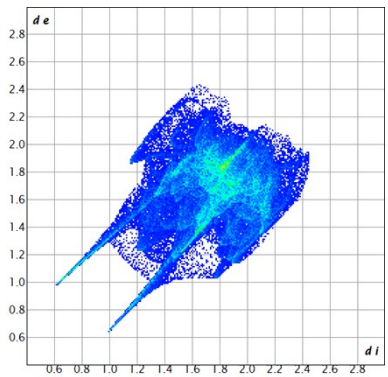
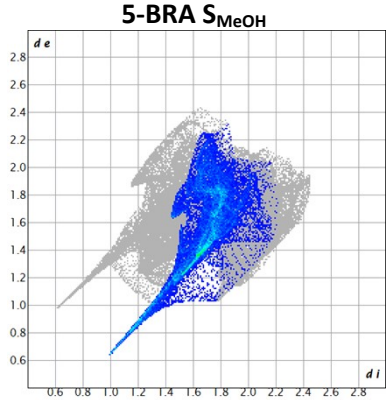
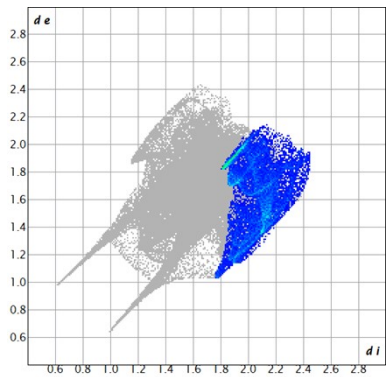
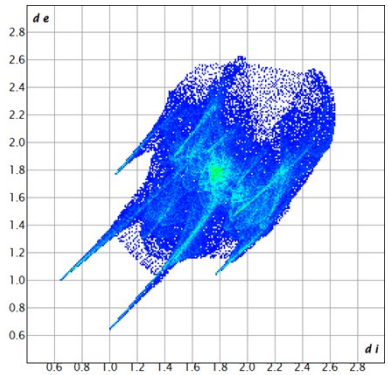
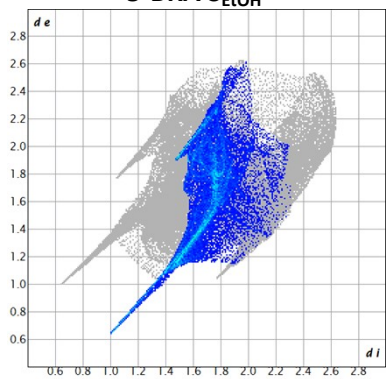
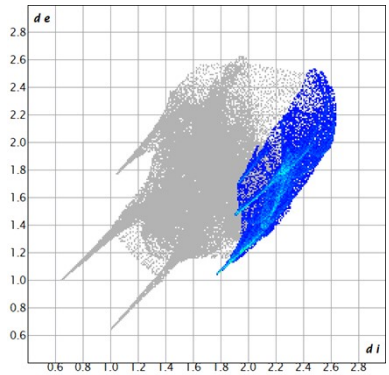


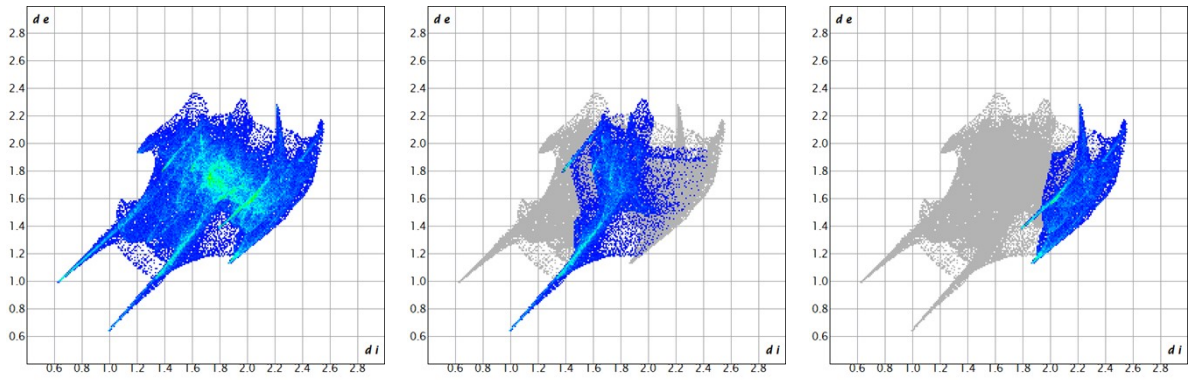


28.9%

RA S_{DIO}0.5

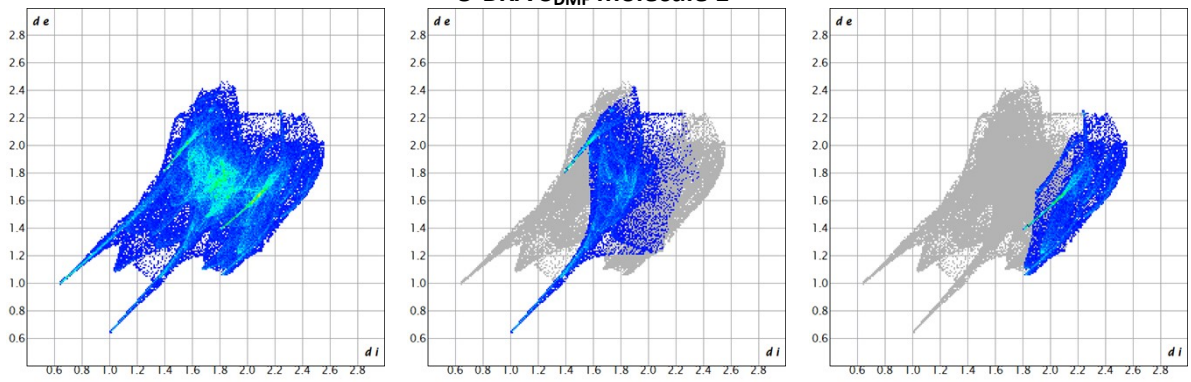
Table S7. Hirshfeld surface fingerprints of the solvated crystal forms of **5-BRA**

All contacts	Oxygen close contacts	Bromine close contacts
		
	26.0%	19.6%
	5-BRA S_{MeOH}	
		
	25.9%	18.5%
	5-BRA S_{EtOH}	
		
	25.8%	20.0%
	5-BRA S_{Ace}	



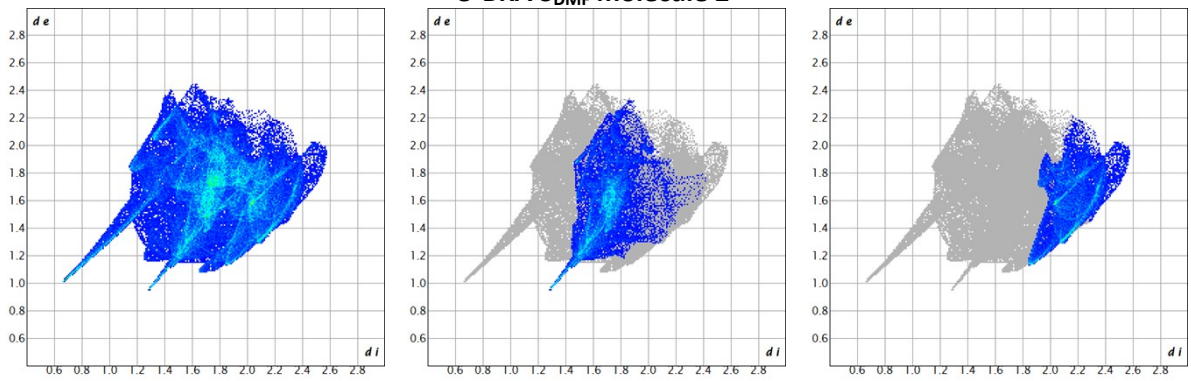
25.8% 19.1%

5-BRA S_{DMF} molecule 1



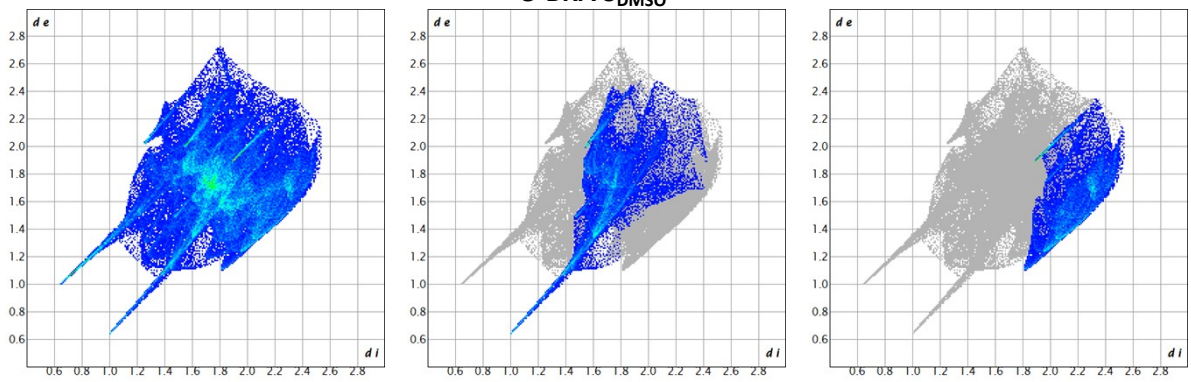
25.4% 19.0%

5-BRA S_{DMF} molecule 2



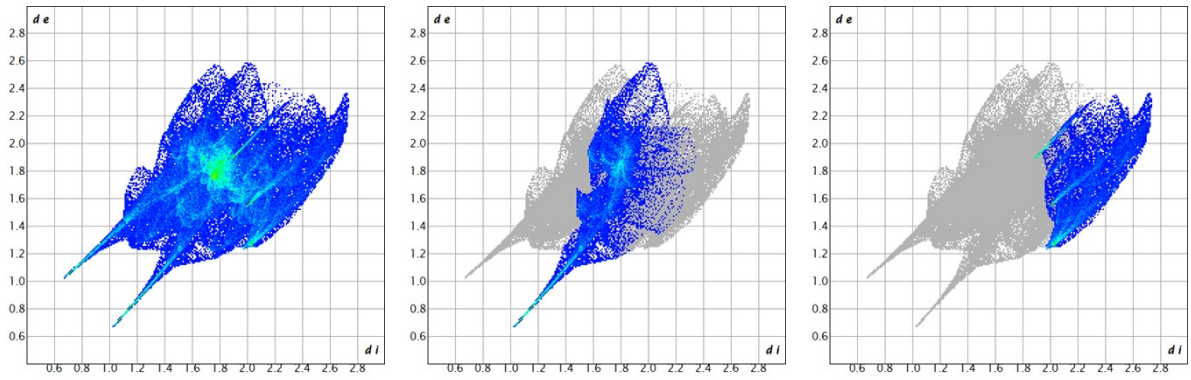
25.9% 19.4%

5-BRA S_{DMSO}



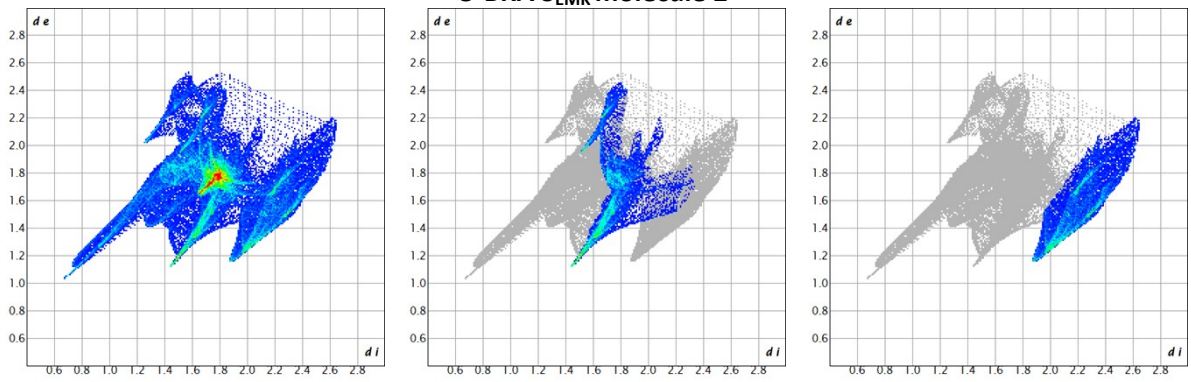
26.0% 18.8%

5-BRA S_{EMK} molecule 1



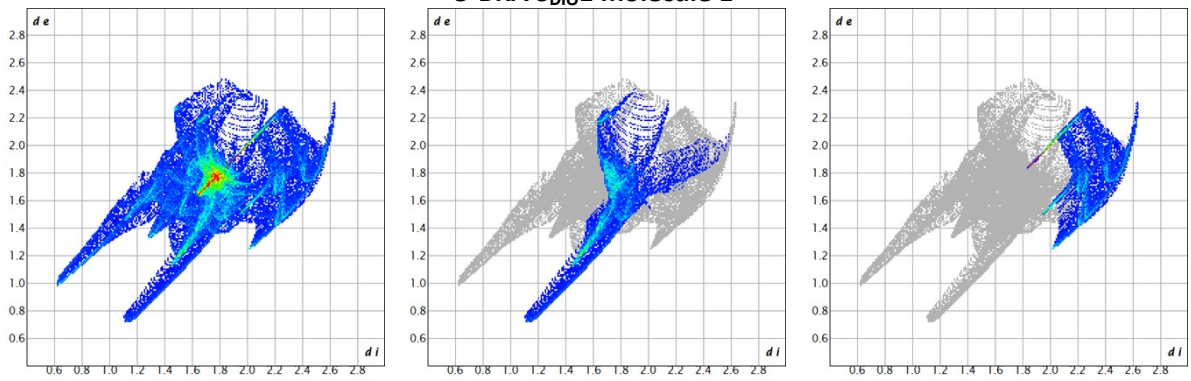
24.8% 19.9%

5-BRA S_{EMK} molecule 2



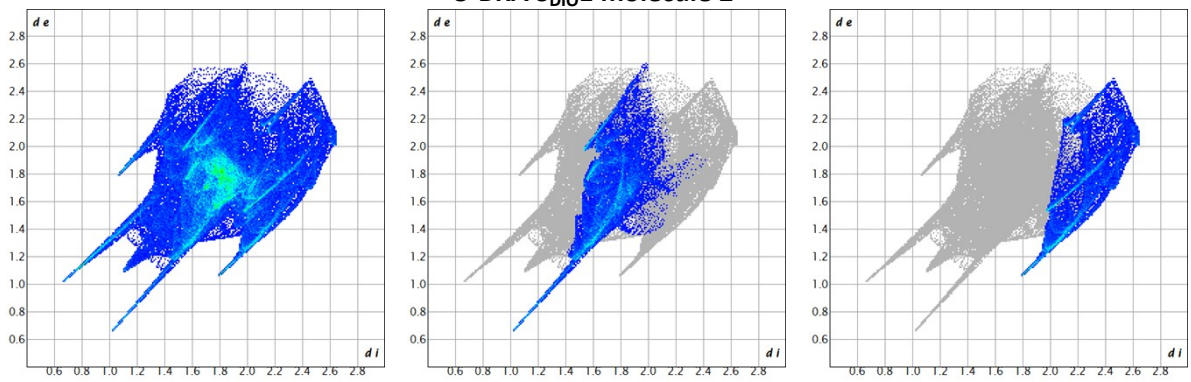
22.6% 19.2%

5-BRA $S_{DIO}1$ molecule 1



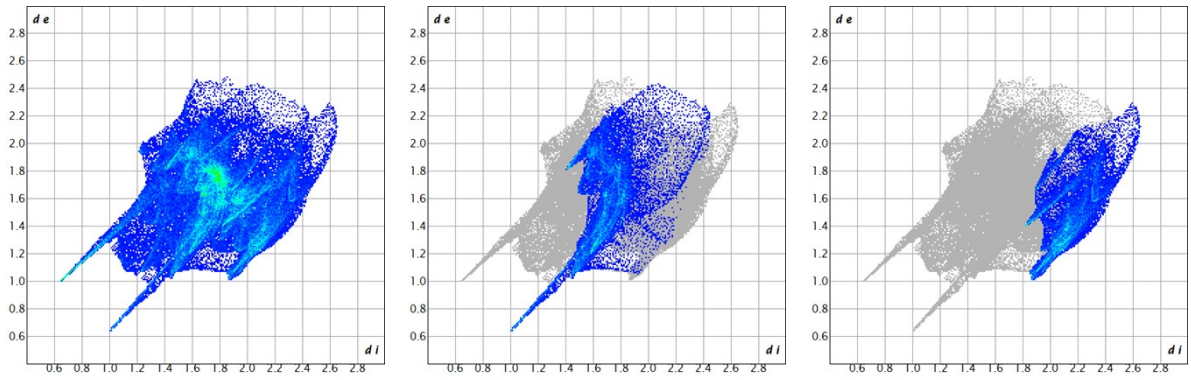
25.0% 19.4%

5-BRA $S_{DIO}1$ molecule 2



25.4% 18.4%

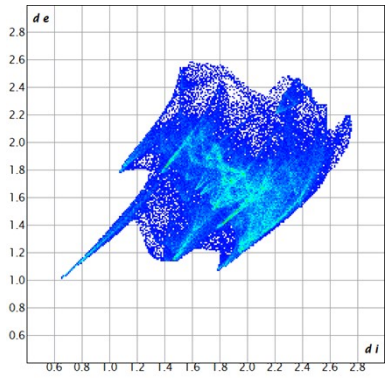
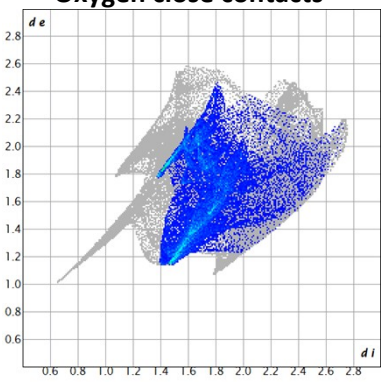
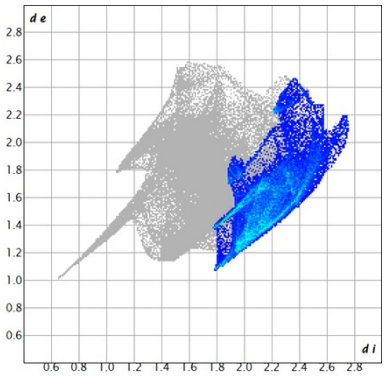
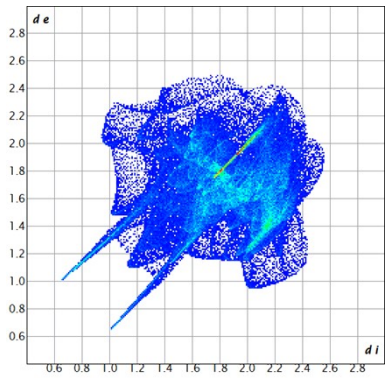
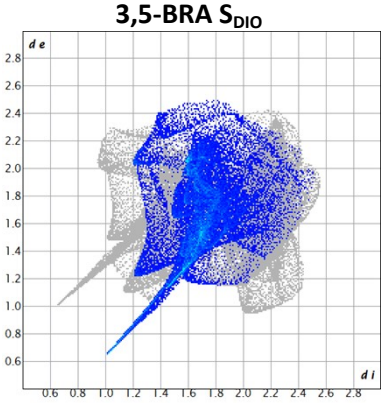
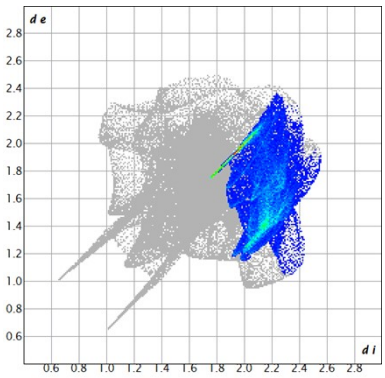
5-BRA $S_{DIO}0.5$

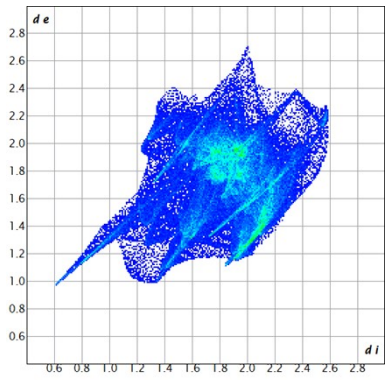


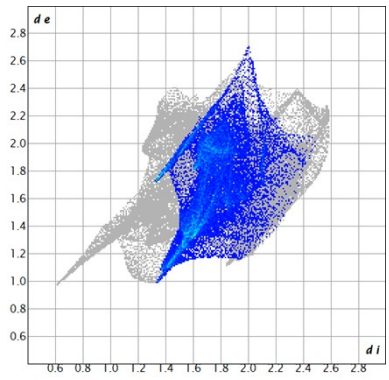
26.1% 19.6%

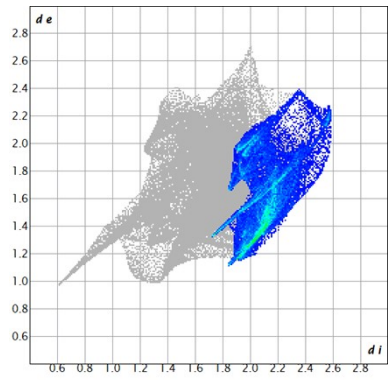
5-BRA S_{THF}

Table S8. Hirshfeld surface fingerprints of the solvated crystal forms of **3,5-BRA**

All contacts	**Oxygen close contacts**	**Bromine close contacts**
		
23.9%		32.9%
3,5-BRA S_{DIO}		
		
25.2%		31.9%
3,5-BRA S_{THF}		

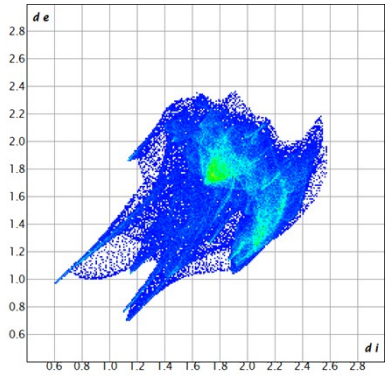


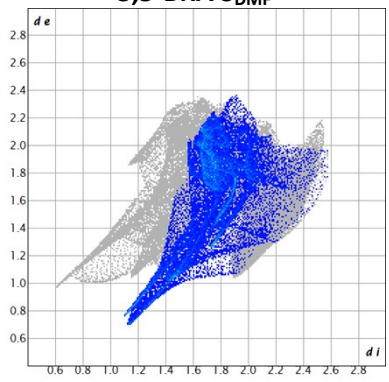


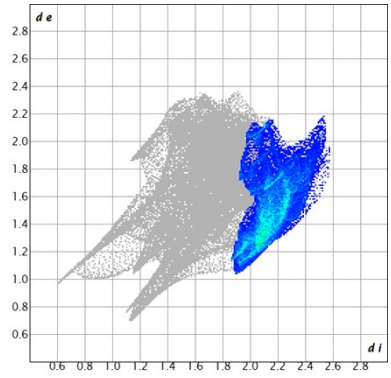


23.7% 32.2%

3,5-BRA S_{DMF}

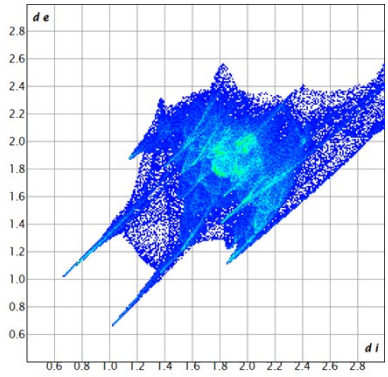


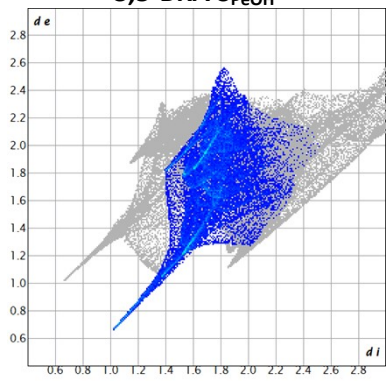


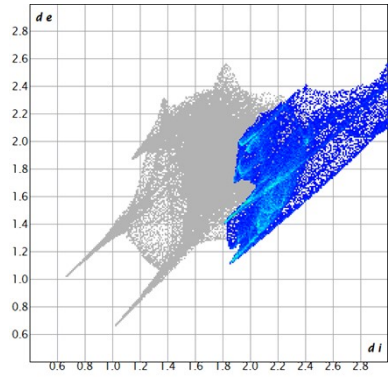


23.6% 32.5%

3,5-BRA S_{PeOH}







22.7% 33.8%

3,5-BRA S_{AcOH}

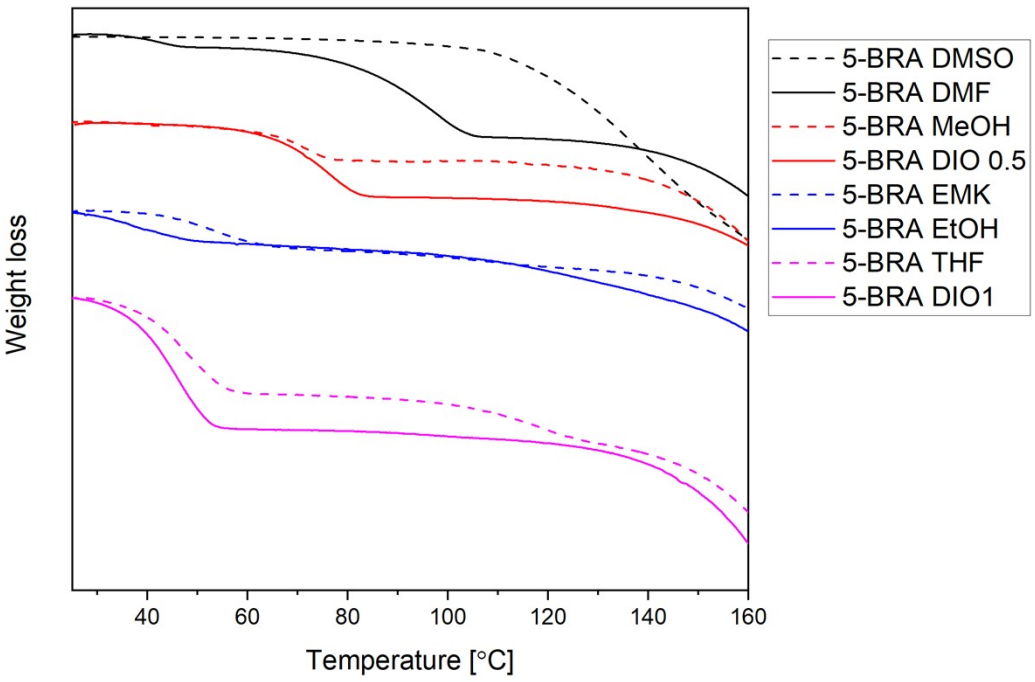


Figure S9 Thermogravimetric thermograms of **5-BRA** solvates for which crystal structures could be obtained. Initial weights are all at 100% but offset to visualise the different temperature range of the weight loss

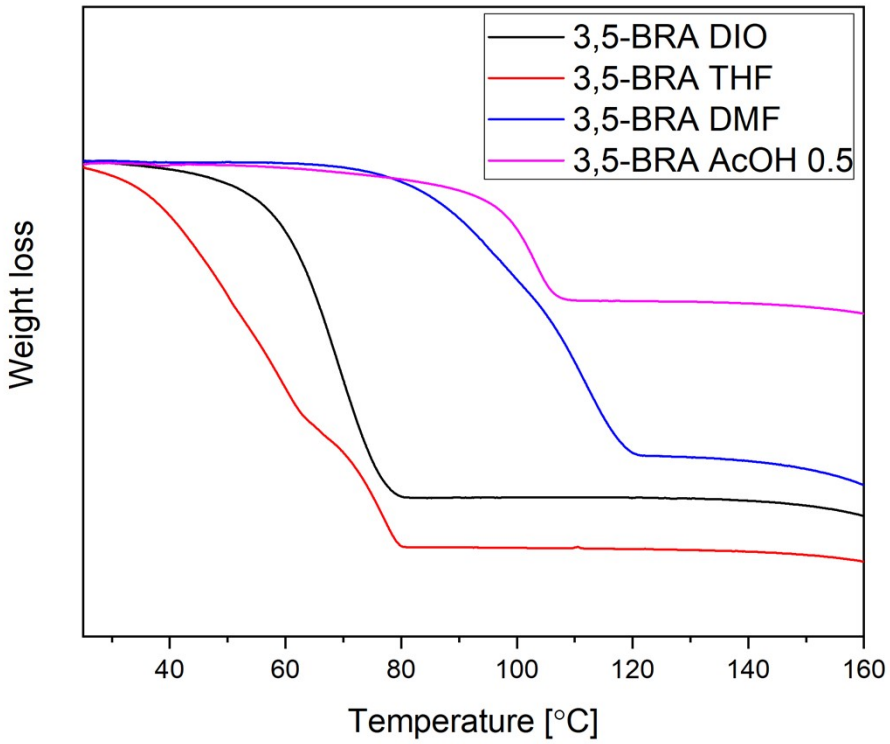


Figure S10 Thermogravimetric thermograms of **3,5-BRA** solvates stable enough to obtain reliable data. **3,5-BRA S_{THF}** has been submitted to measurement as damp paste to avoid desolvation before measurement.

Table S9 Packing motifs in the structurally determined solvates of **RA**, **5-BRA** and **3,5-BRA**. All crystallisations were carried out with the same set of the following solvents: acetone, acetonitrile, pentanol, 1-butanol, 2-butanol, 2-butanone, chloroform, dimethyl sulfoxide, 1,4-dioxane, *N,N*-dimethyl formamide, dichloromethane, diethyl ether, ethyl acetate, ethanol, hexane, methanol, nitromethane, 1-propanol, 2-propanol, tetrahydrofuran, and toluene.

Solvate	Fast cooling	Slow cooling	Evaporation	precipitation
RA $S_{DMSO}0.5$	X[a]	X[a]	X[a]	
RA S_{AcOH}	X[a]	X	X[a]	X[a]
RA S_{DMF}	X[a]			
RA $S_{DIO}0.5$			X[a]	X[a]
5-BRA S_{MeOH}	X	X		
5-BRA S_{EtOH}	X			
5-BRA S_{Ace}				X
5-BRA S_{DMF}	X	X		X
5-BRA S_{DMSO}	X	X	X	X
5-BRA S_{EMK}	X			
5-BRA $S_{DIO}1$	X	X		
5-BRA $S_{DIO}0.5$				X
5-BRA S_{THF}	X	X		
3,5-BRA S_{DIO}	X	X	X	
3,5-BRA S_{THF}	X	X		
3,5-BRA S_{DMF}	X	X		
3,5-BRA S_{PeOH}	X			
3,5-BRA S_{AcOH}	X	X		

[a] data extracted from Braun *et al*.[1]

Additional information

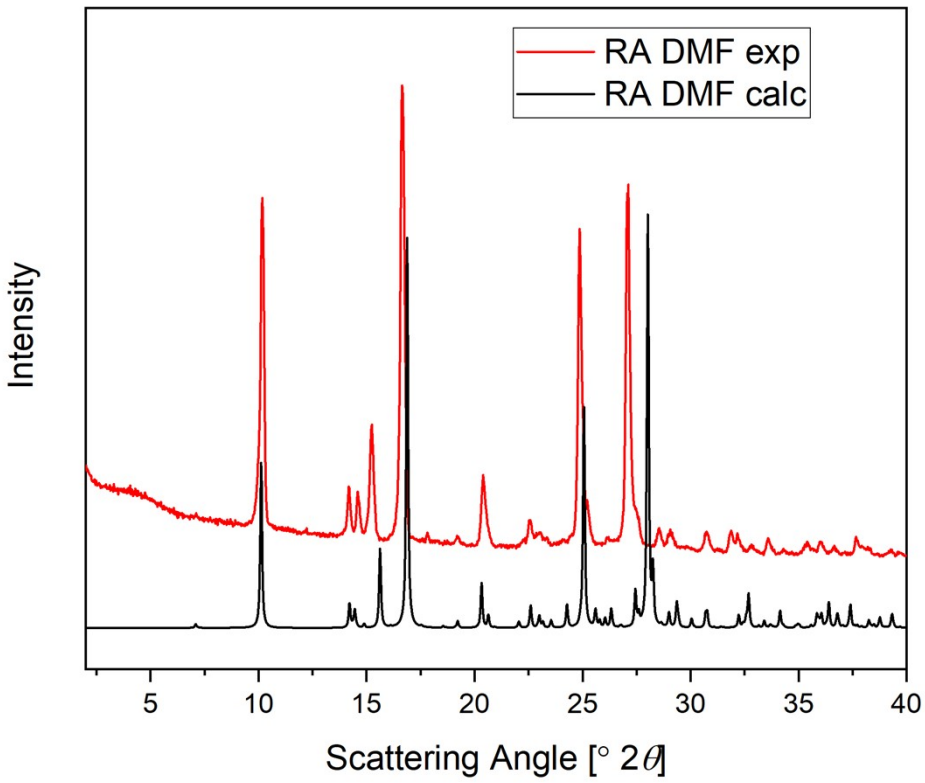


Figure S11 Calculated (black, bottom) and experimental (red, top) PXRD patterns of **RA S_{DMF}**.

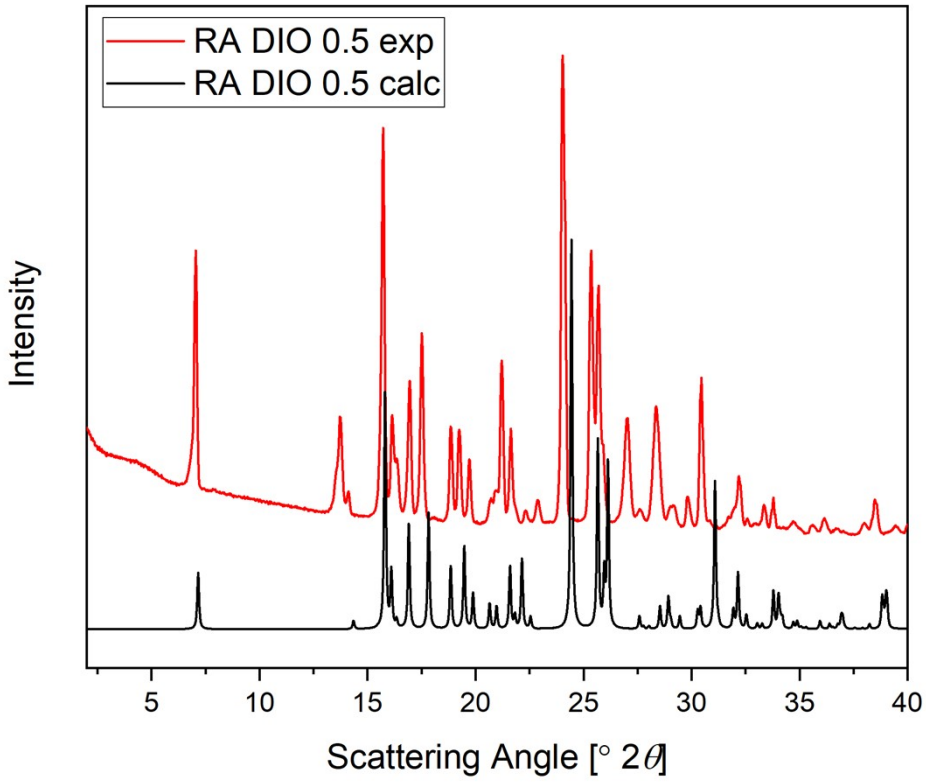


Figure S12 Calculated (black, bottom) and experimental (red, top) PXRD patterns of **RA S_{Dio}0.5**. The bulk sample contains traces of a second crystalline phase.

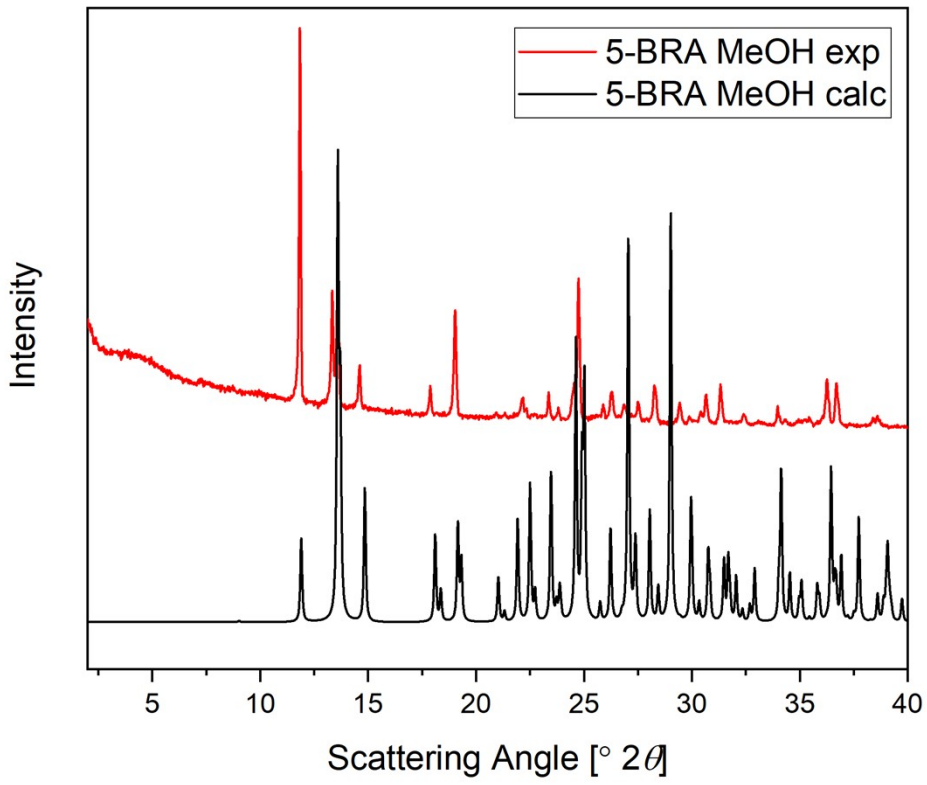


Figure S13 Calculated (black, bottom) and experimental (red, top) PXRD patterns of **5-BRA S_{MeOH}**.

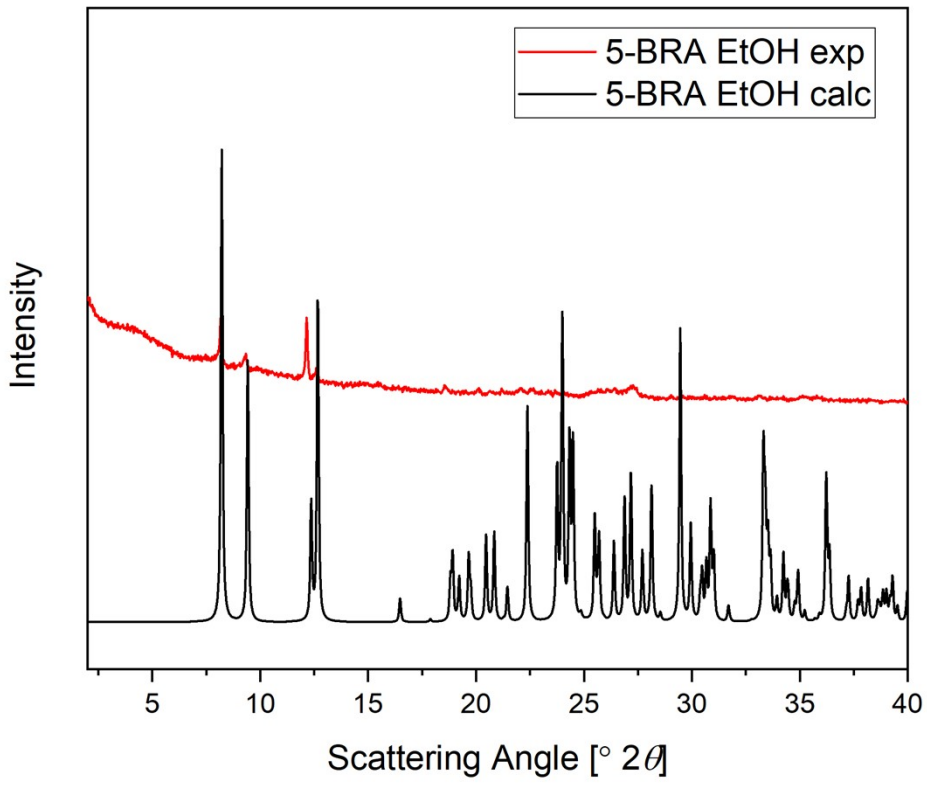


Figure S14 Calculated (black, bottom) and experimental (red, top) PXRD patterns of **5-BRA S_{EtOH}**.

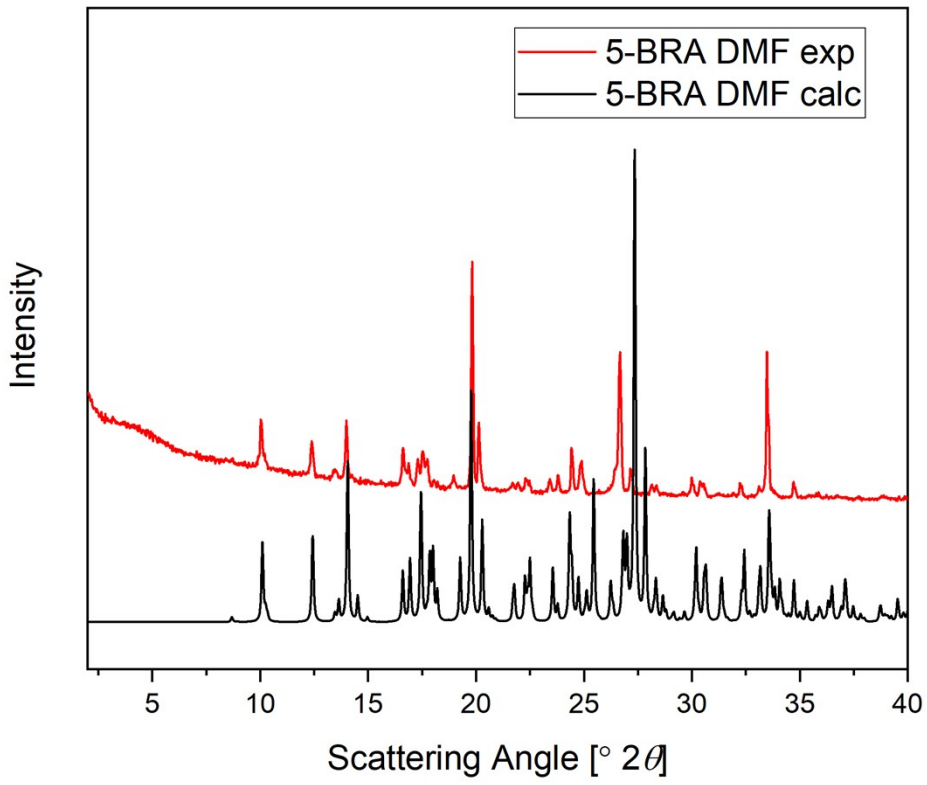


Figure S15 Calculated (black, bottom) and experimental (red, top) PXRD patterns of **5-BRA S_{DMF}**.

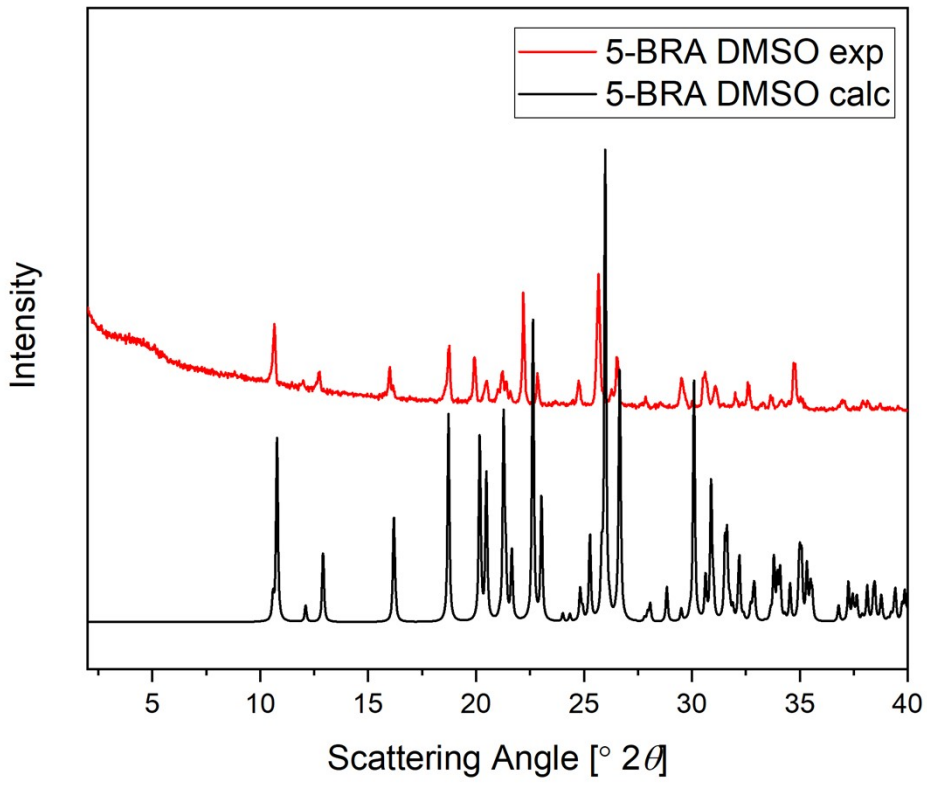


Figure S16 Calculated (black, bottom) and experimental (red, top) PXRD patterns of **5-BRA S_{DMSO}**.

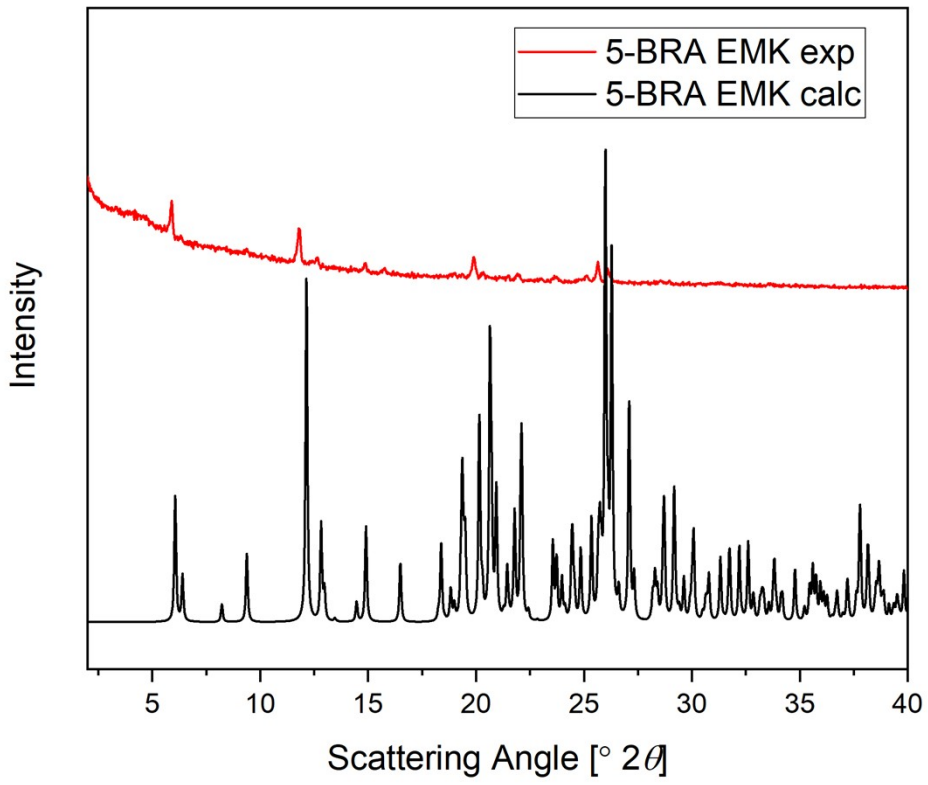


Figure S17 Calculated (black, bottom) and experimental (red, top) PXRD patterns of **5-BRA S_{EMK}**.

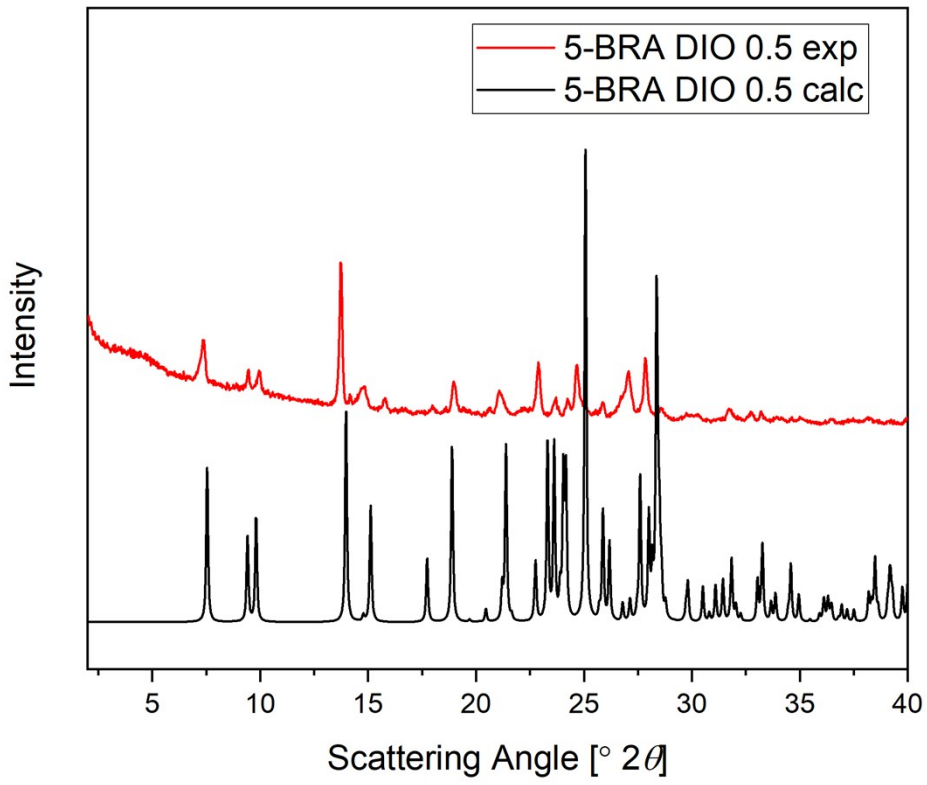


Figure S18 Calculated (black, bottom) and experimental (red, top) PXRD patterns of **5-BRA S_{DIO}0.5**.

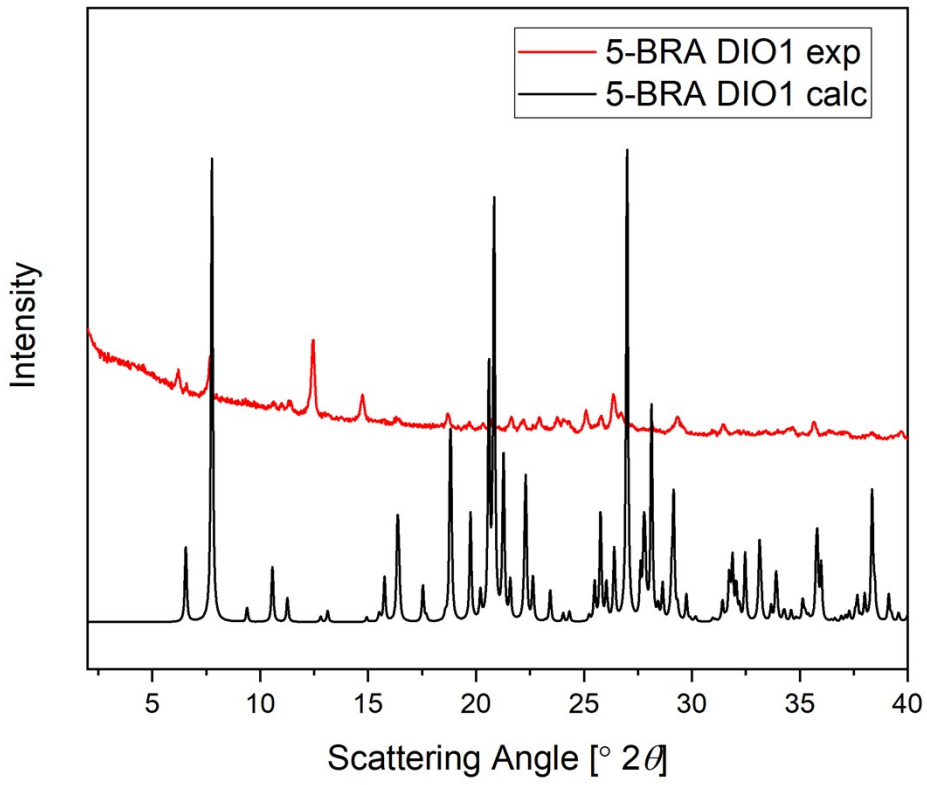


Figure S19 Calculated (black, bottom) and experimental (red, top) PXRD patterns of **5-BRA S_{DIO}1**.

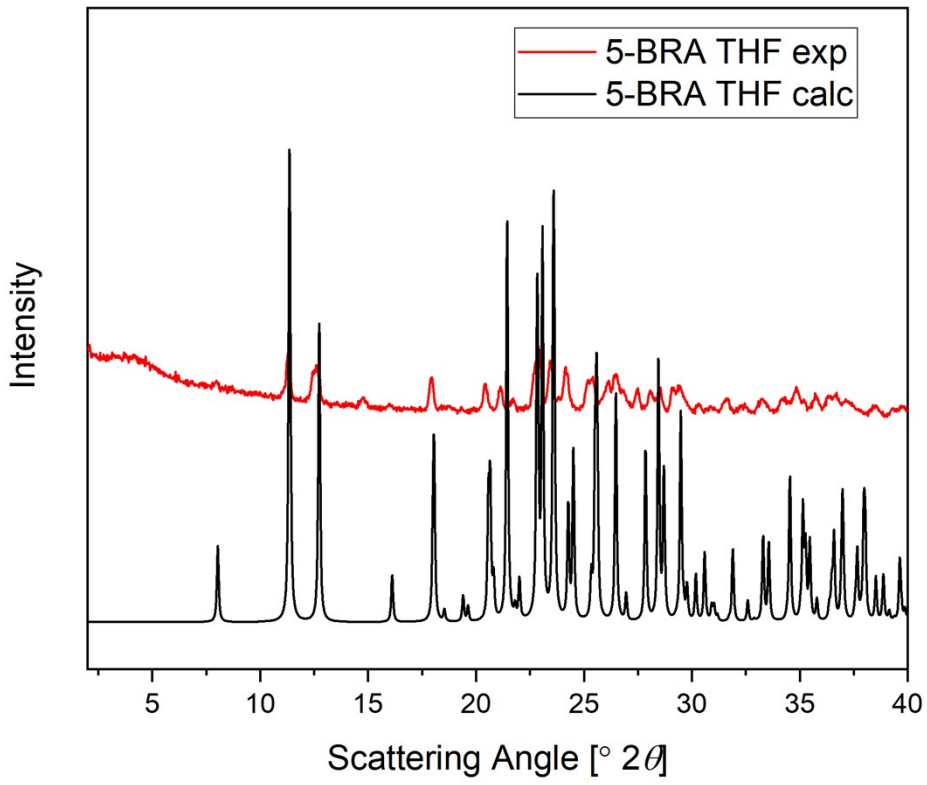


Figure S20 Calculated (black, bottom) and experimental (red, top) PXRD patterns of **5-BRA S_{THF}**.

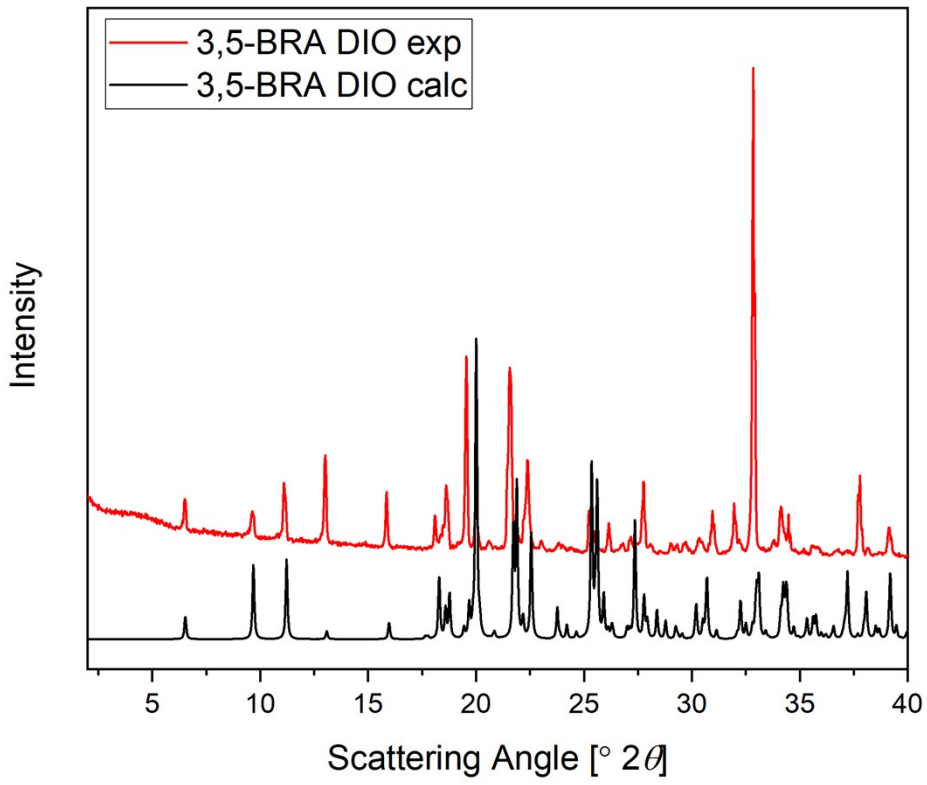


Figure S21 Calculated (black, bottom) and experimental (red, top) PXRD patterns of **3,5-BRA S_{DIO}**.

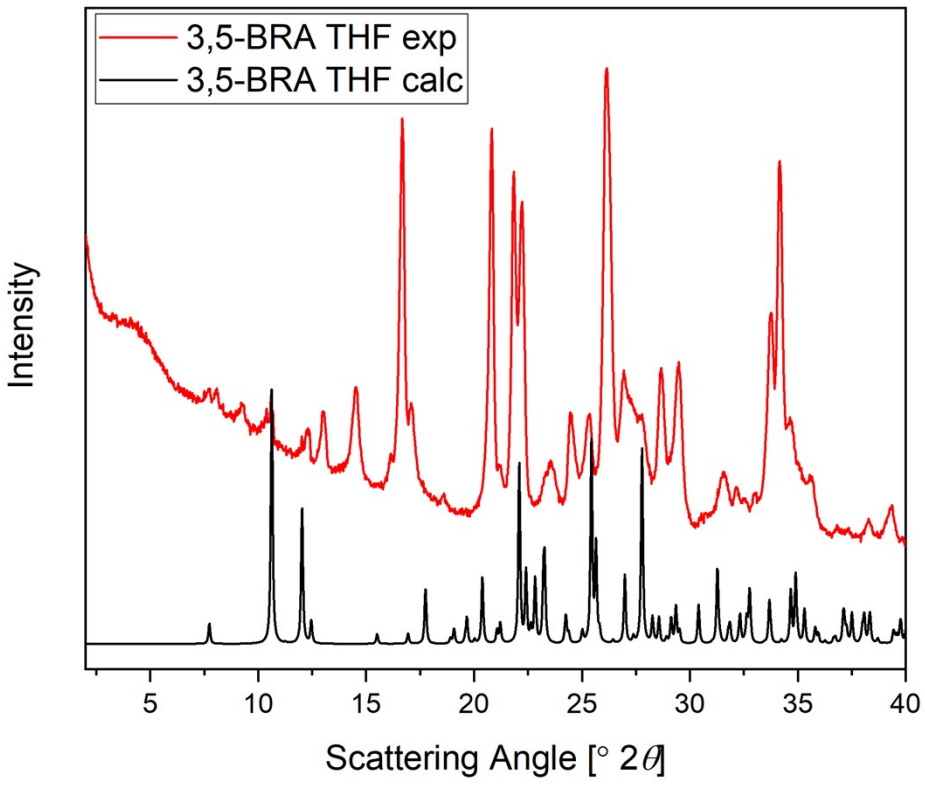


Figure S22 Calculated (black, bottom) and experimental (red, top) PXRD patterns of **3,5-BRA S_{THF}**. The bulk sample shows peaks of another crystal form as impurity, likely due to the low stability and thus starting transformation of the solvate (see Figure S10).

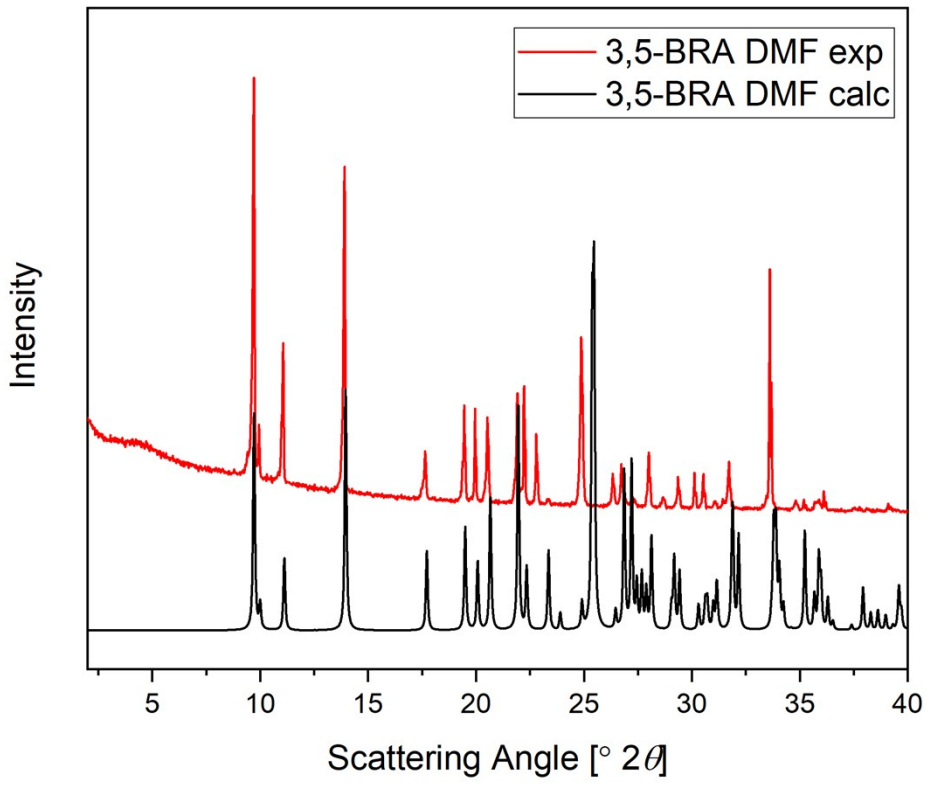


Figure S23 Calculated (black, bottom) and experimental (red, top) PXRD patterns of **3,5-BRA S_{DMF}**.

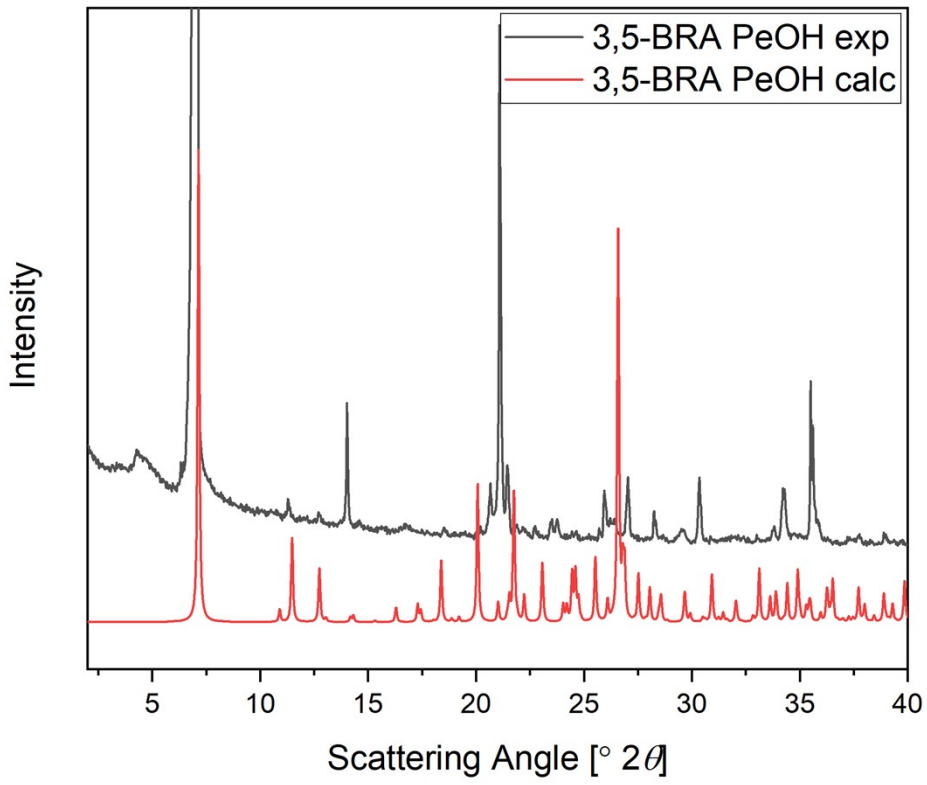


Figure S24 Calculated (black, bottom) and experimental (red, top) PXRD patterns of **3,5-BRA S_{PeOH}**.

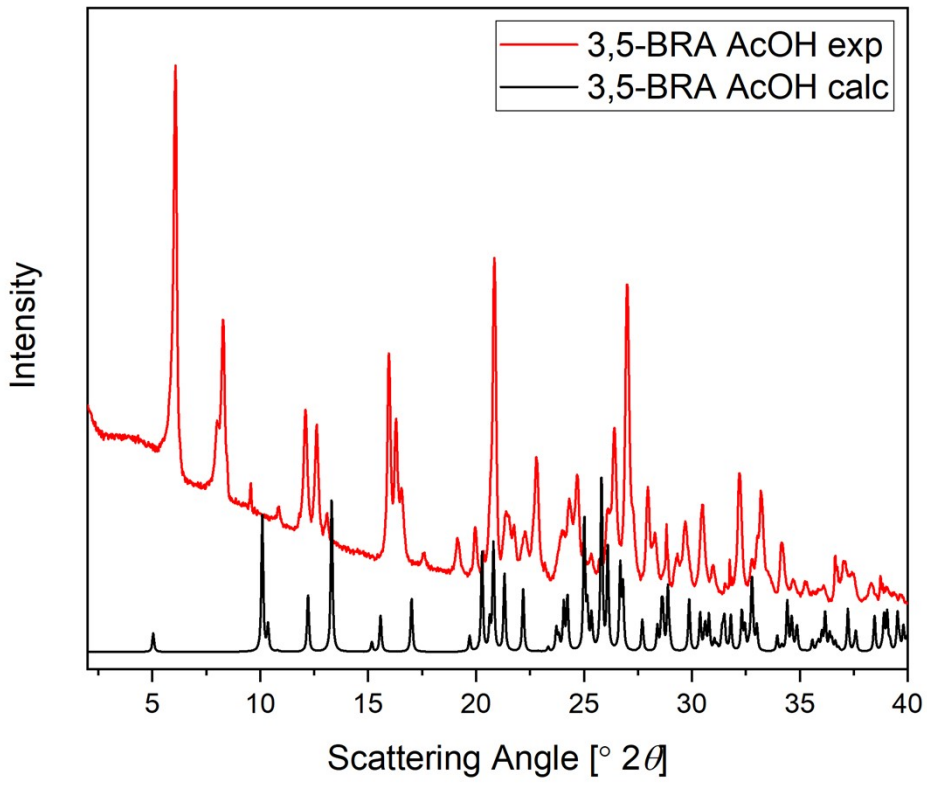


Figure S25 Calculated (black, bottom) and experimental (red, top) PXRD patterns of 3,5-BRA S_{AcOH}. The bulk material represents the partially desolvated sample with the majority of the phase presented by the acetic acid hemisolvate (see Figure S10).

References

1. D. E. Braun, P. G. Karamertzanis, J. B. Arlin, A. J. Florence, V. Kahlenberg, D. A. Tocher, U. J. Griesser and S. L. Price, *Crystal Growth & Design*, 2011, **11**, 210-220.