

Electronic Supplementary Information for

Impact of Molecular and Crystal Structure on the Melting Points in Halo-Substituted Phenyl-Quinazolinones

Ivica Đilović¹, Nenad Judaš¹, Mario Komar², Maja Molnar², Marta Počkaj³ and Tomislav Balić^{4,*}

¹ Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia; idilovic@chem.pmf.hr (I.Đ.); judas@chem.pmf.hr (N.J.)

² Faculty of Food Technology Osijek, Josip Juraj Strossmayer University of Osijek, Franje Kuhača 18, 31000 Osijek, Croatia; mario.komar@ptfos.hr (M.K.); mmolnar@ptfos.hr (M.M.)

³ Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna Pot 113, 1000 Ljubljana, Slovenia; marta.pockaj@fkkt.uni-lj.si

⁴ Department of Chemistry, Josip Juraj Strossmayer University of Osijek, Cara Hadrijana 8/A, 31000 Osijek, Croatia

* Correspondence: tombalic@kemija.unios.hr

Contents

Figure S1. The 2D resolved fingerprint plots for the whole asymmetric unit of 1	3
Figure S2. The 2D resolved fingerprint plots for molecule A of 1	4
Figure S3. The 2D resolved fingerprint plots for molecule B of 1	5
Comment on the major differences in 1	5
Figure S4. The 2D resolved fingerprint plots for the whole asymmetric unit of 2	6
Figure S5. The 2D resolved fingerprint plots for molecule A of 2	6
Figure S6. The 2D resolved fingerprint plots for molecule B of 2	7
Comment on the major differences in 2	7
Figure S7. The 2D resolved fingerprint plots for the whole asymmetric unit of 3	8
Figure S8. The 2D resolved fingerprint plots for molecule A (occupancy 60%) of 3	9
Figure S9. The 2D resolved fingerprint plots for molecule B of 3	10
Comment on the major differences in 3	10
Figure S10. TG (black) and DSC (red) curves of 1	11
Figure S11. TG (black) and DSC (red) curves of 2	11
Figure S12. TG (black) and DSC (red) curves of 3	12
Table S1. Thermodynamic data of the DSC measurements for all compounds.....	12
Table S2. Results of CSD database search.....	12
Figure S13. Linear Gibbs free energy functions for 1 forms I and II	16
Figure S14. Representation of Cl···O halogen bond in WULMIB	17
Figure S15. Representation of C–Br···O halogen bond in <i>rac</i> -NEPNOO.....	17

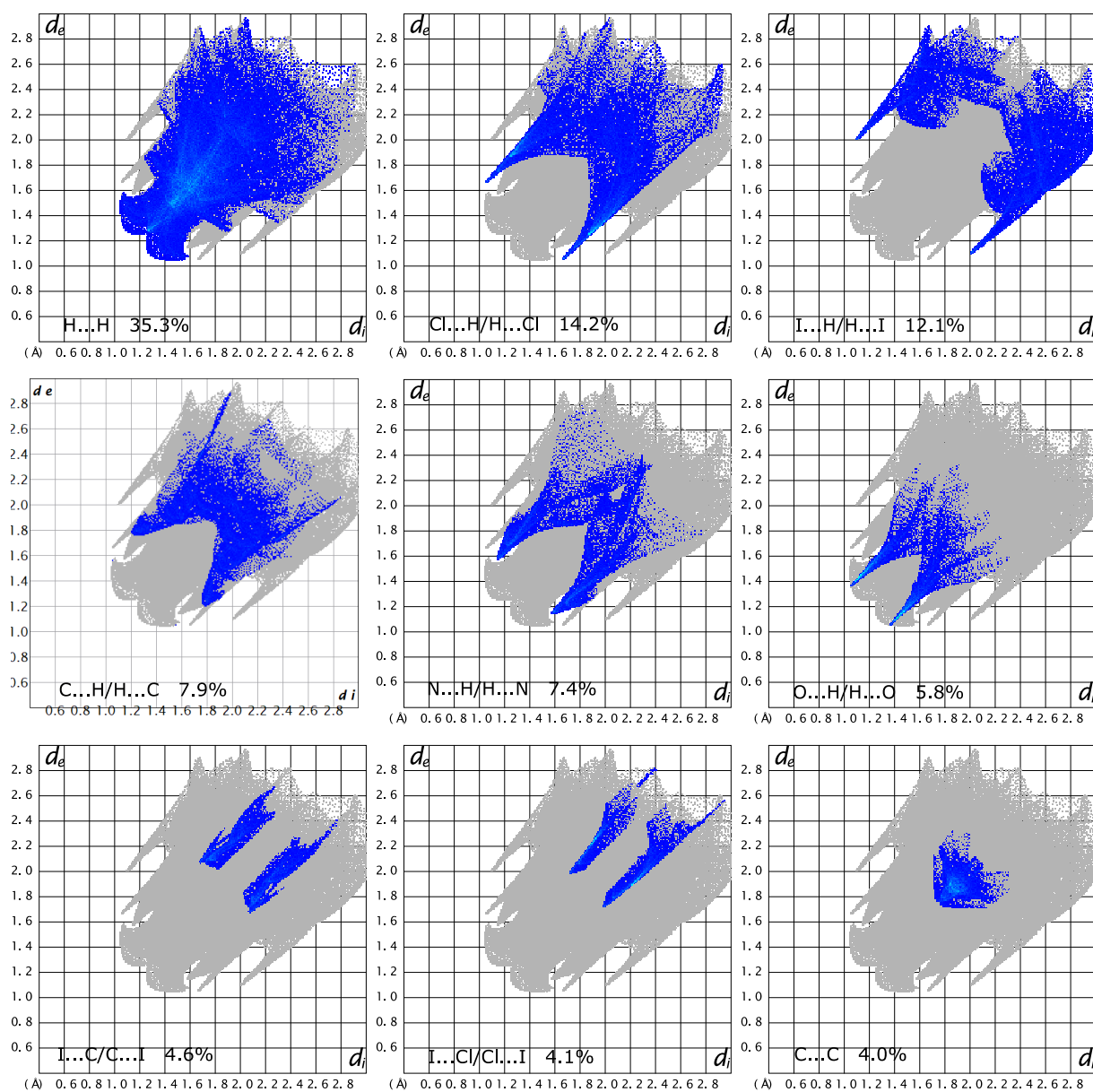


Figure S1. The 2D resolved fingerprint plots for the whole asymmetric unit of **1**.

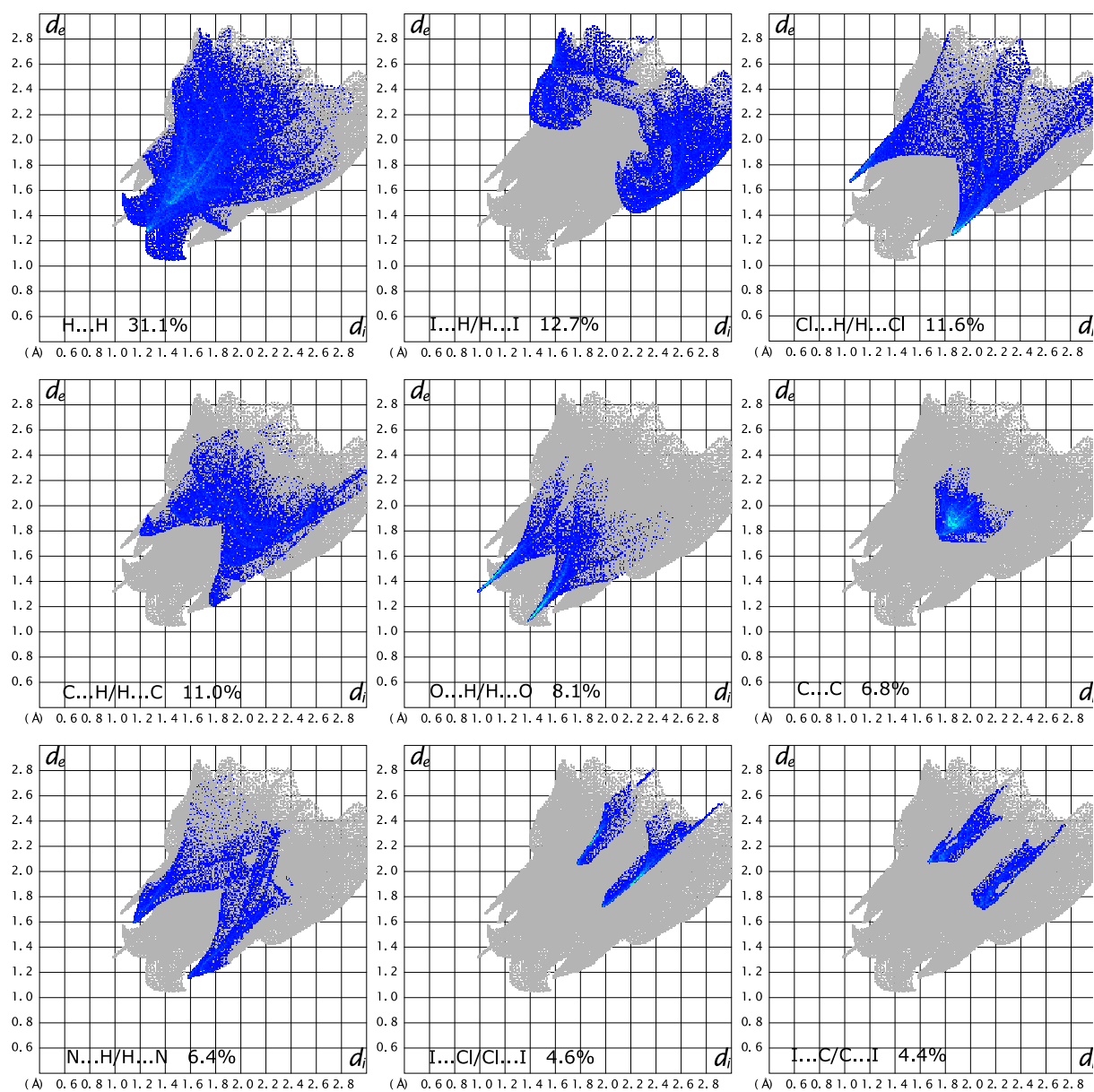


Figure S2. The 2D resolved fingerprint plots for molecule A of **1**.

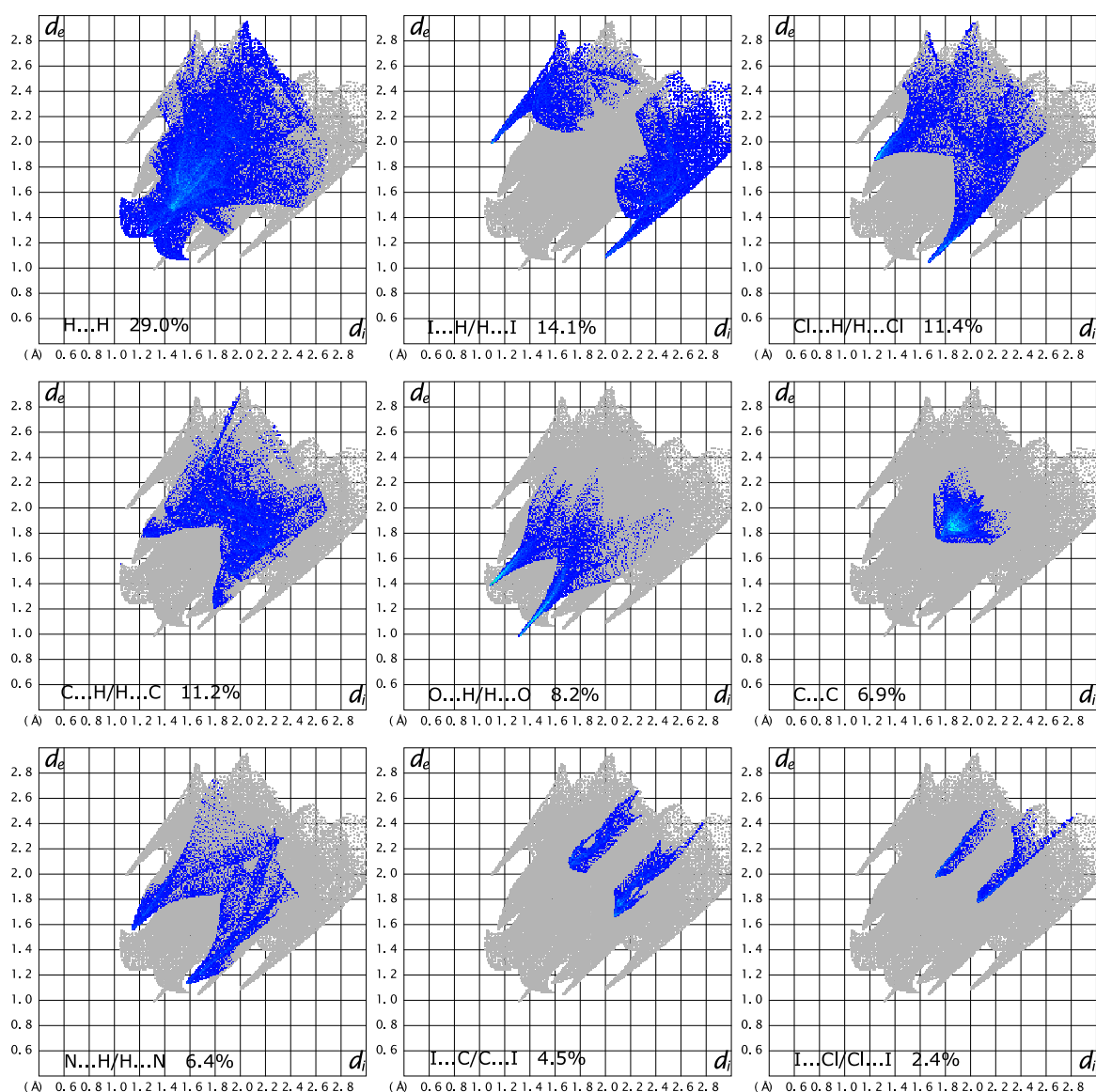


Figure S3. The 2D resolved fingerprint plots for molecule B of **1**.

Comment on the major differences in **1**:

In molecule A, the I...H/H...I interactions are more scattered than in B and in the asymmetric unit, where two sharp spikes at $d_i+d_e \sim 3.1$ Å represent them. The second most noticeable difference is a significant reduction in the contribution of I...C/C...I interactions in B compared to A. All other interactions do not differ much between A and B. In the whole asymmetric unit, the contribution of Cl...H/H...Cl contacts dominates over I...H/H...I interactions, which is just the opposite of the individual molecules. The contribution of C...C interactions also decreases in the asymmetric unit compared to A and B.

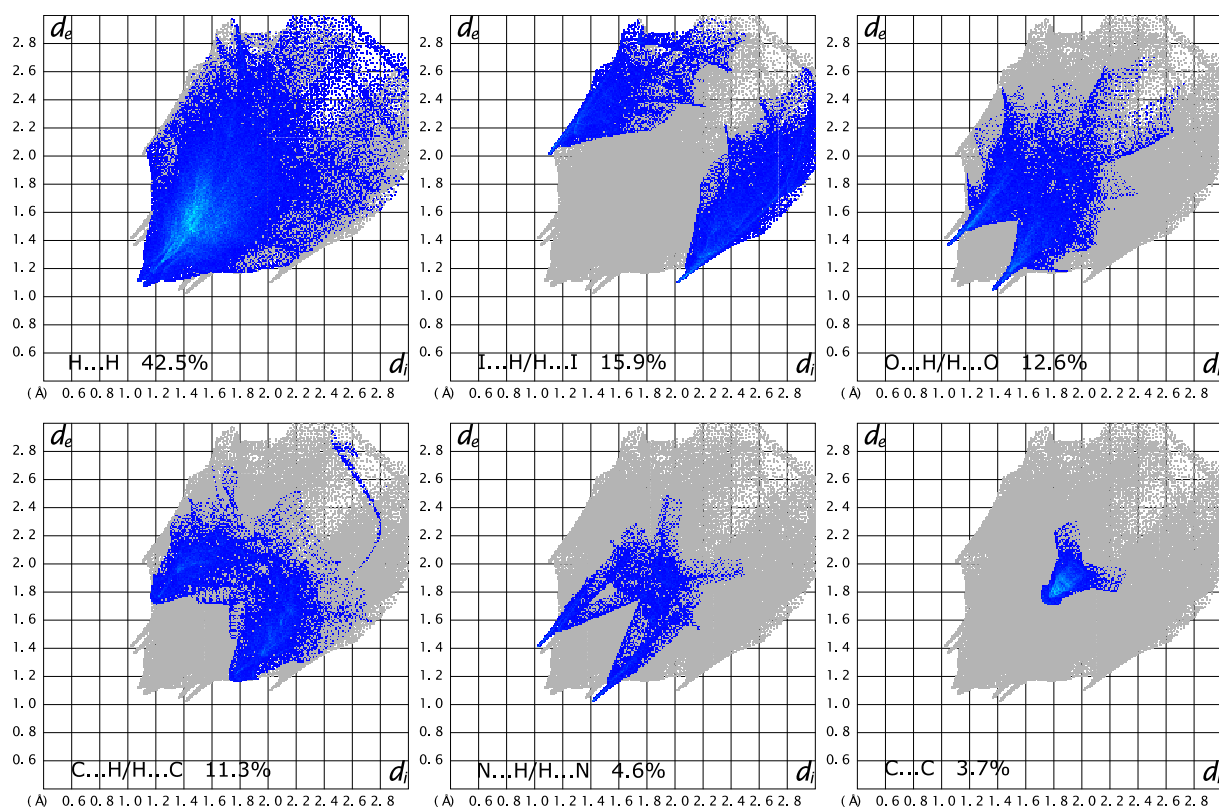


Figure S4. The 2D resolved fingerprint plots for the whole asymmetric unit of 2.

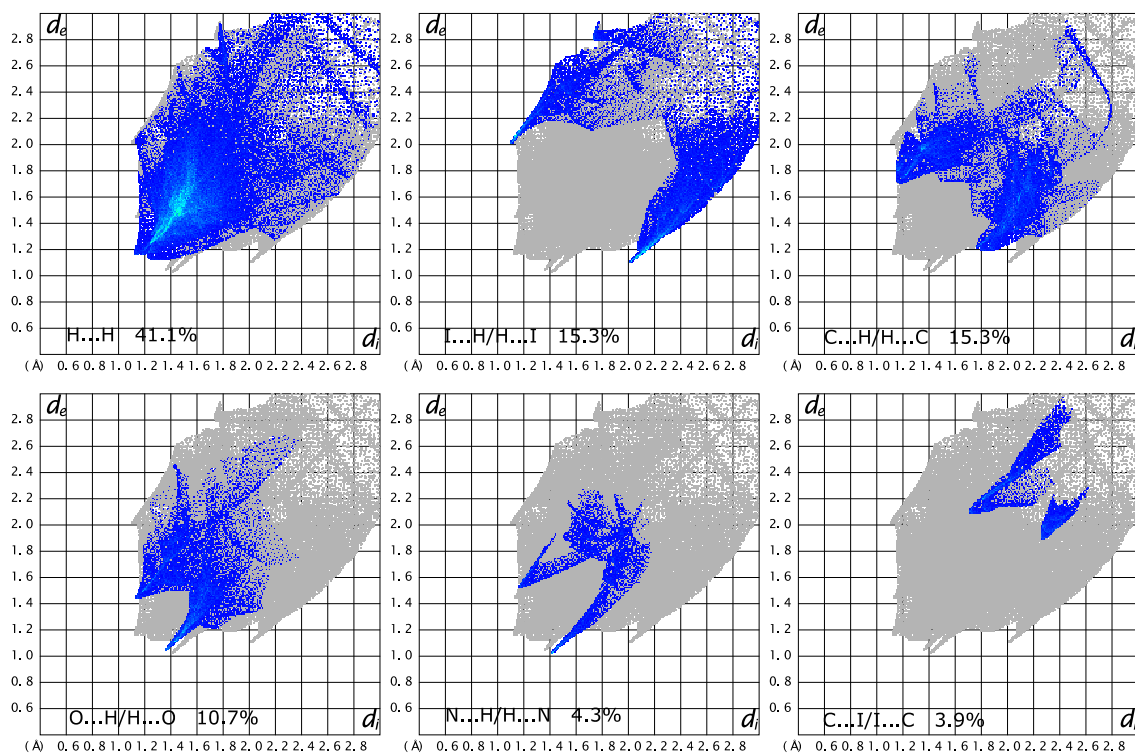


Figure S5. The 2D resolved fingerprint plots for molecule A of 2.

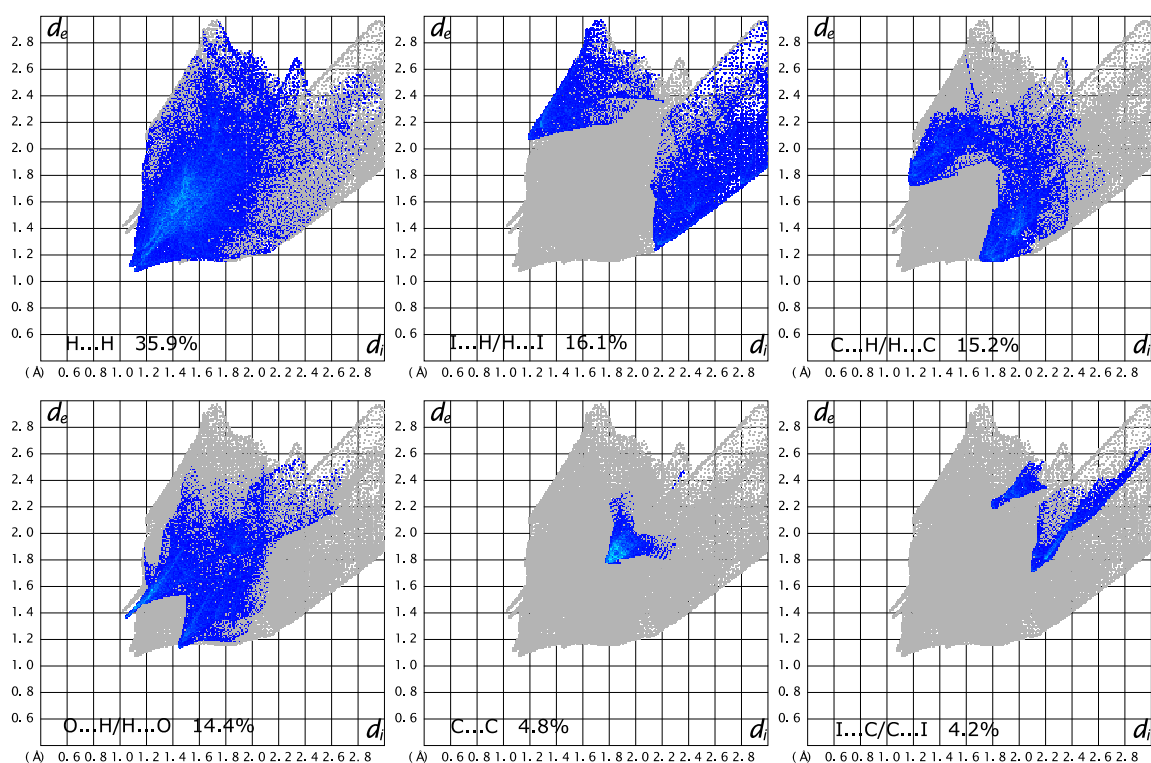


Figure S6. The 2D resolved fingerprint plots for molecule B of 2.

Comment on the major differences in 2:

When comparing molecules A and B, the contribution of H...H interactions is significantly larger in B. The opposite holds true for O...H/H...O interactions, which are more pronounced in B. The difference is also present in C...C interactions originating from $\pi\cdots\pi$ stacking, which holds together adjacent molecules B (in A, its contribution is only 2.4%). The fingerprint plots of the asymmetric unit are more similar to A than B. The difference when compared with A is the domination of O...H/H...O over C...H/H...C contacts, and the C...C interactions show a greater contribution to the total HS than in A.

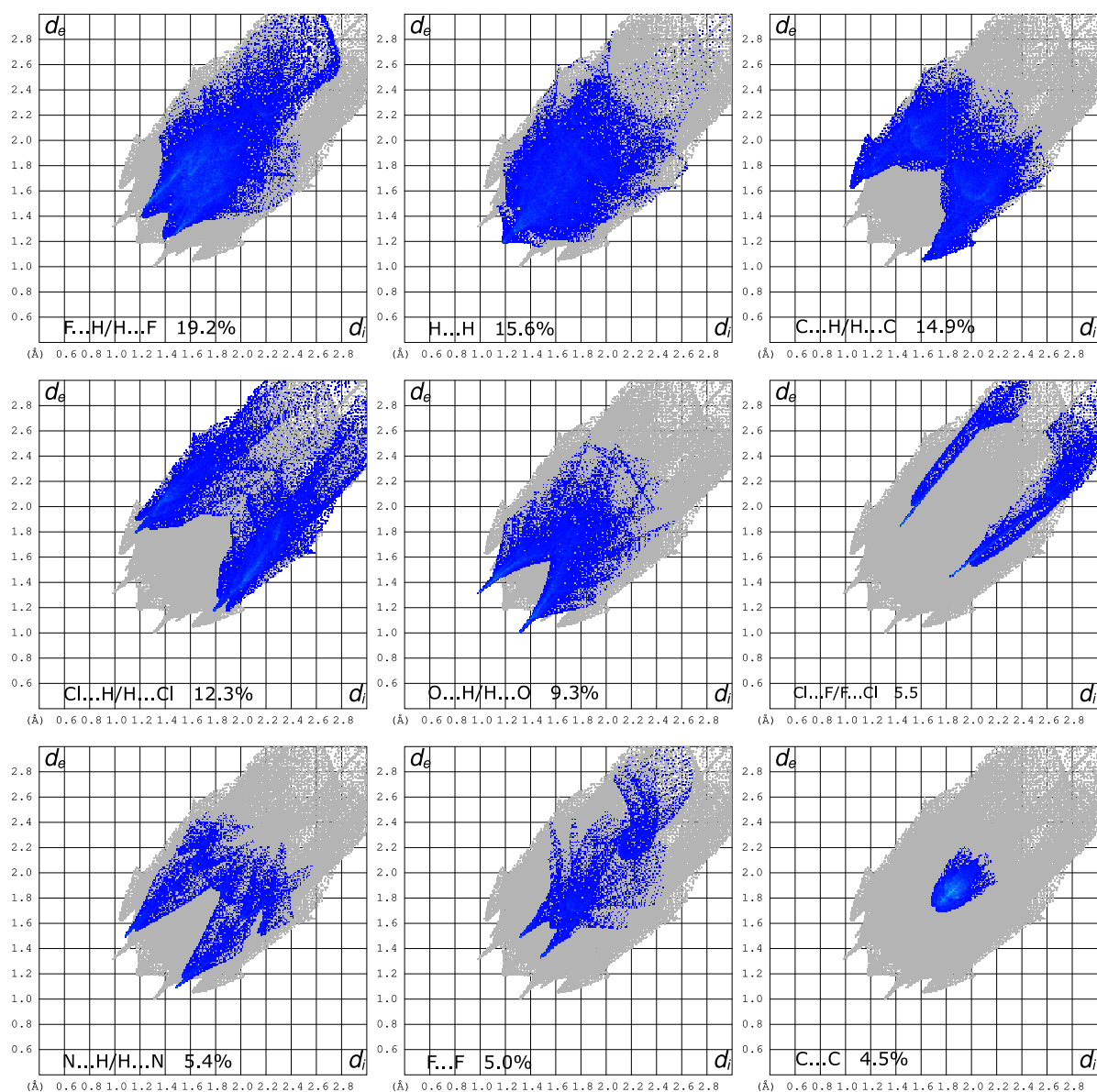


Figure S7. The 2D resolved fingerprint plots for the whole asymmetric unit of **3**.

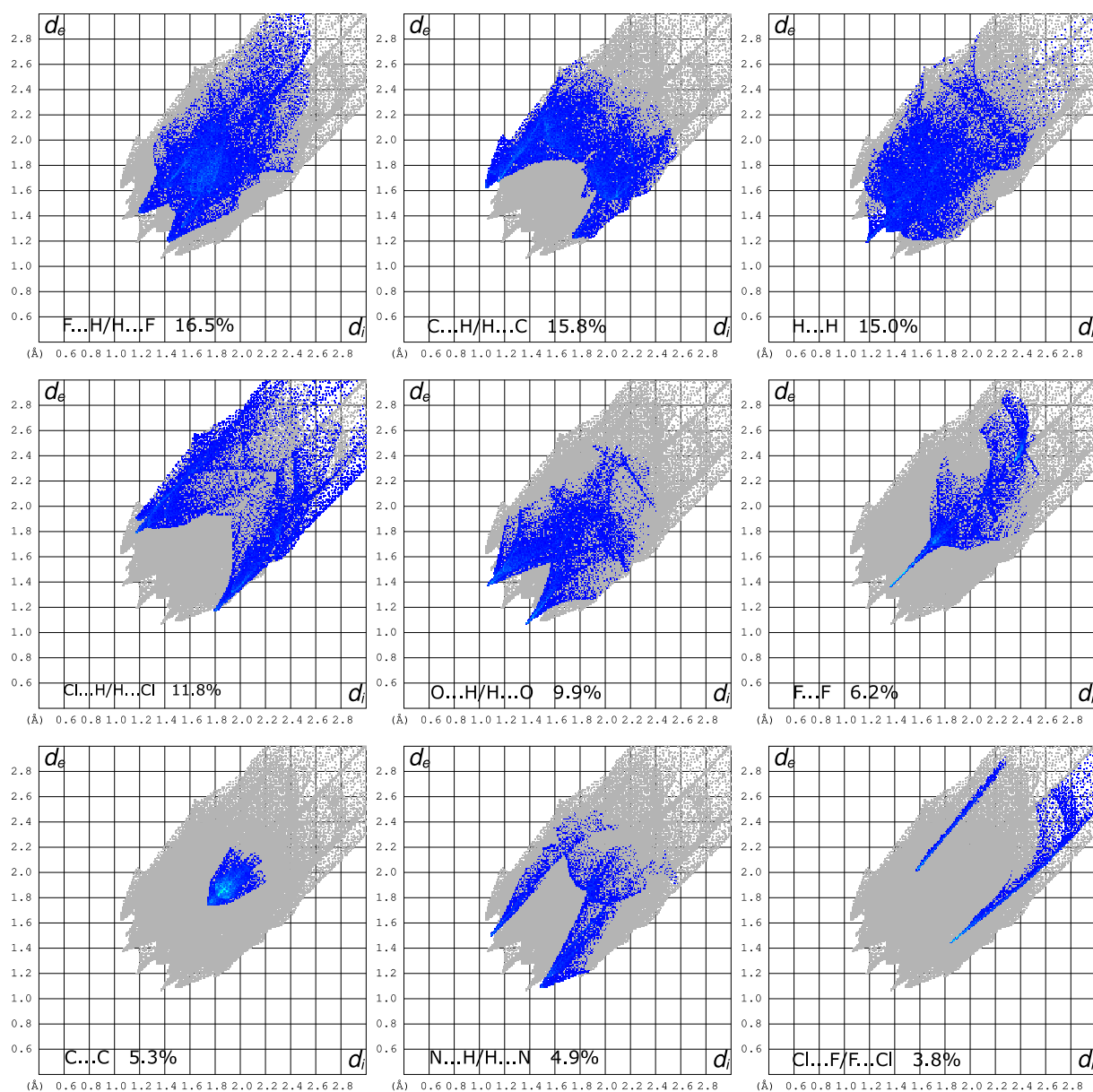


Figure S8. The 2D resolved fingerprint plots for molecule A (occupancy 60%) of 3.

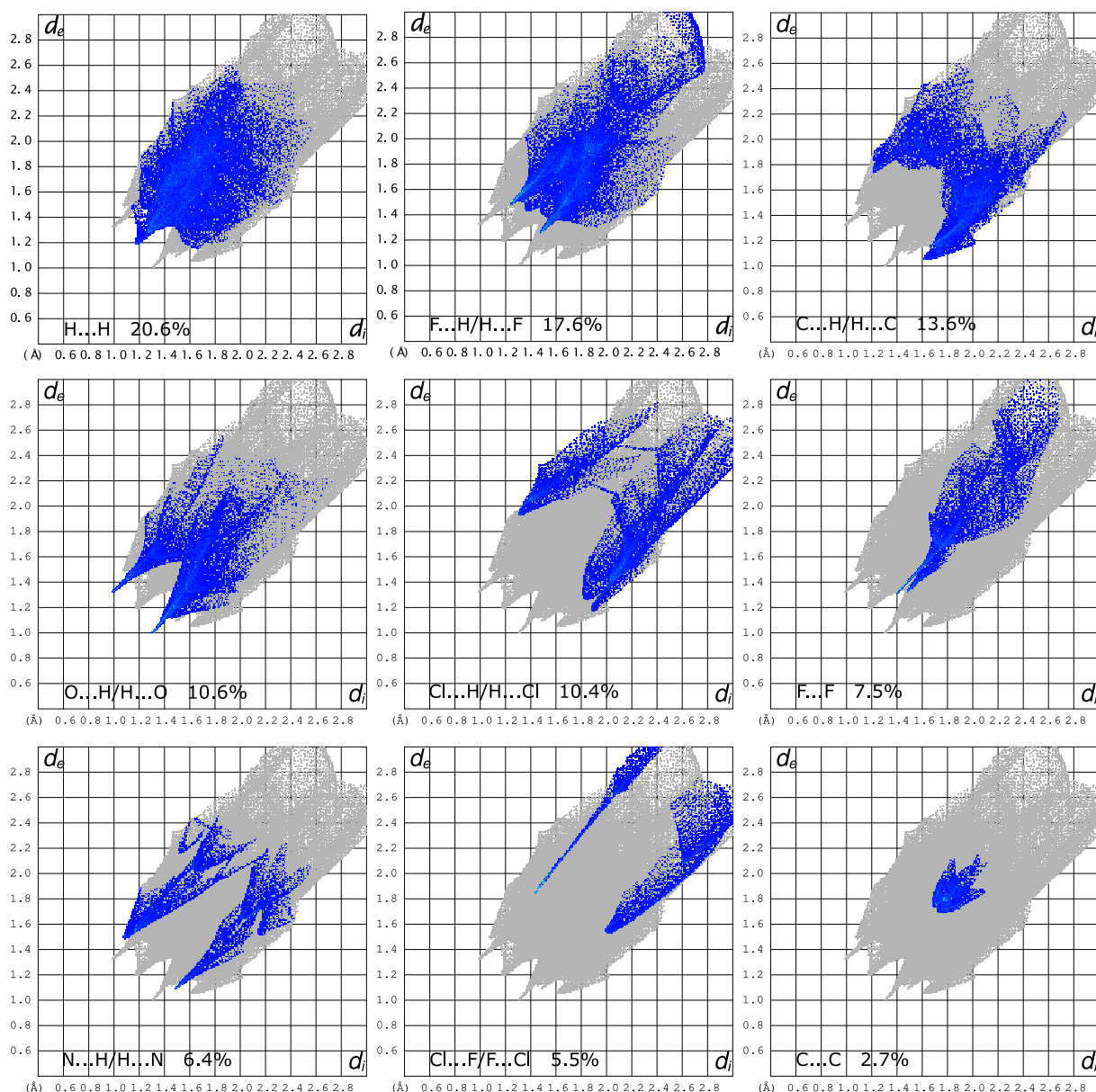


Figure S9. The 2D resolved fingerprint plots for molecule B of **3**.

Comment on the major differences in **3**:

In the asymmetric unit and in molecule A, F...H/H...F contacts are dominant over H...H and C...H/H...C contacts, which is just the opposite of that in B, where the most contributing factor is the H...H interaction. In B, the contribution of F...F interactions is the largest and the contribution of C...C the smallest in comparison with the asymmetric unit and molecule B.

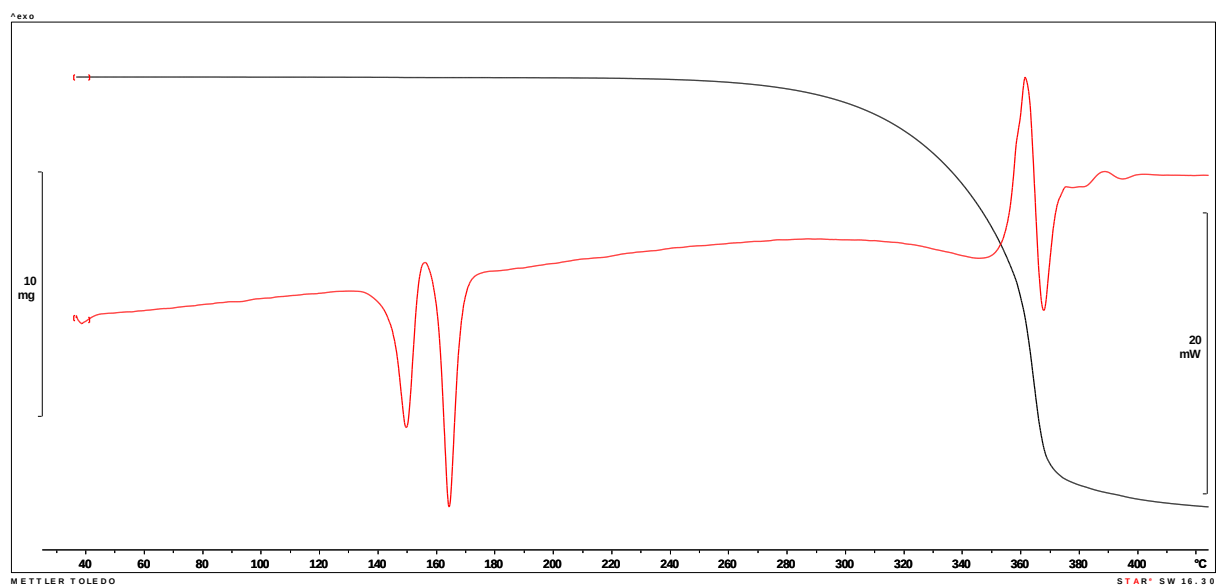


Figure S10. TG (black) and DSC (red) curves of **1**.

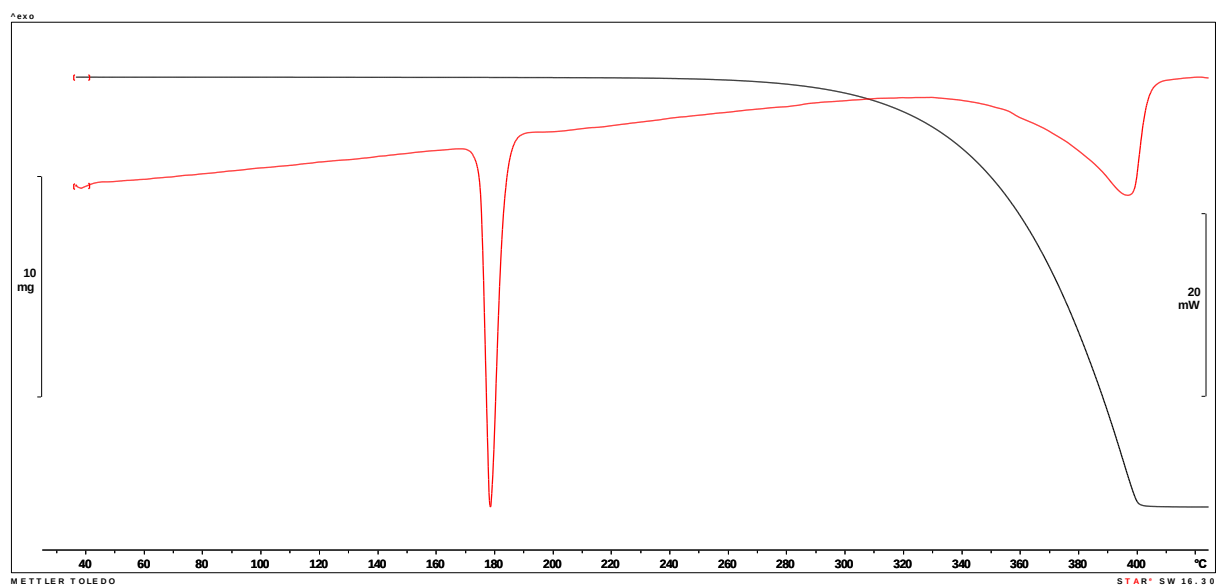


Figure S11. TG (black) and DSC (red) curves of **2**.

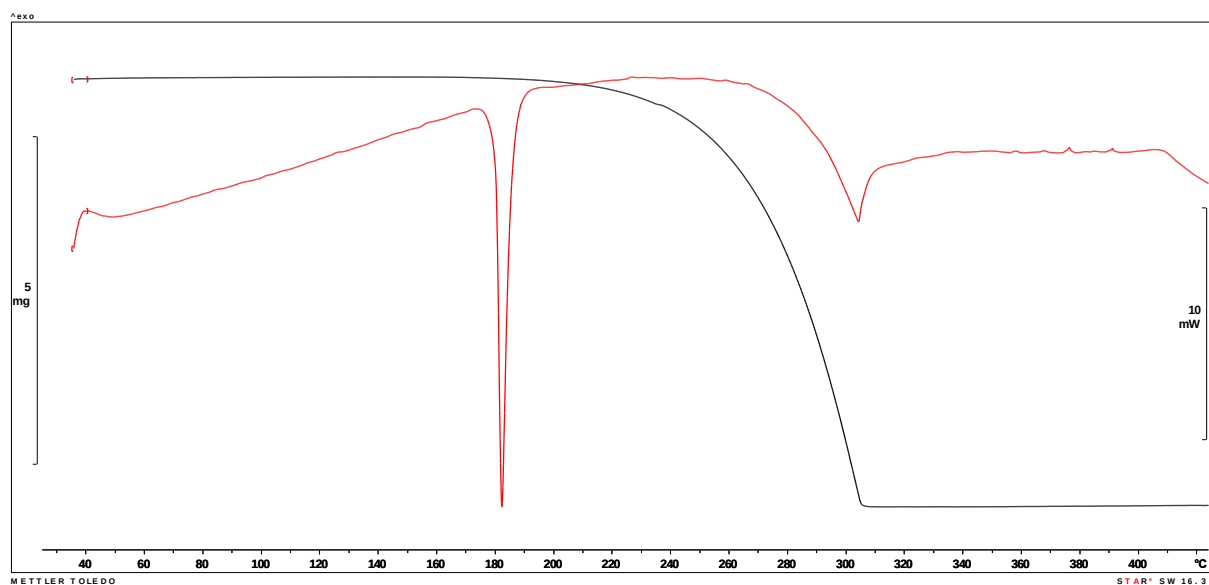


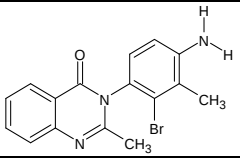
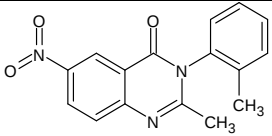
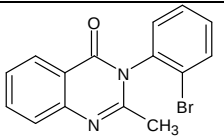
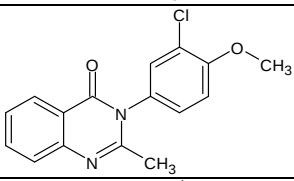
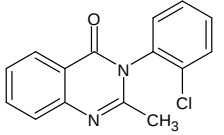
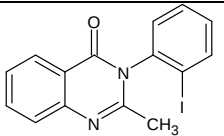
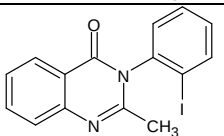
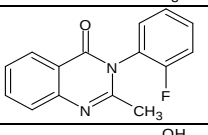
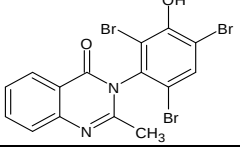
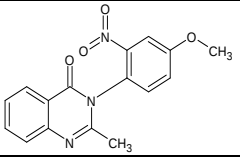
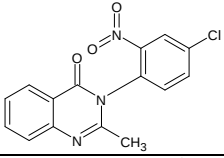
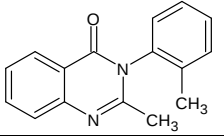
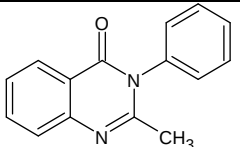
Figure S12. TG (black) and DSC (red) curves of **3**.

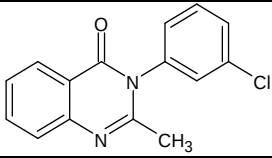
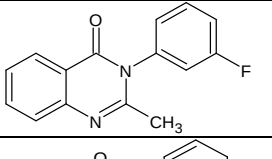
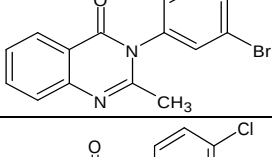
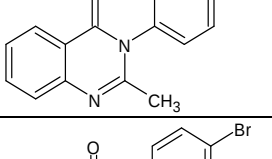
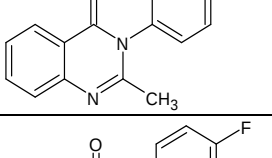
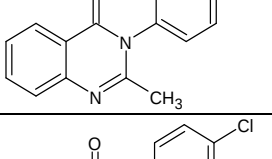
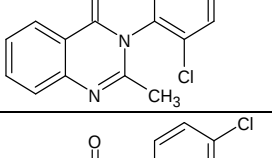
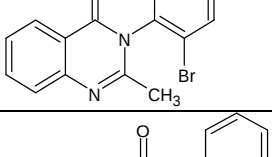
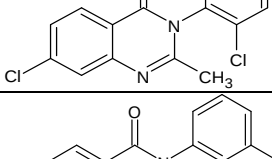
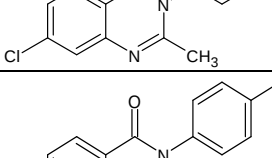
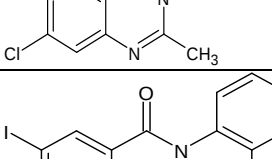
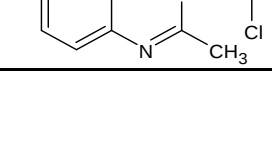
Table S1. Thermodynamic data of the DSC measurements for all compounds.

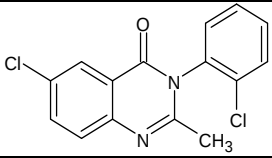
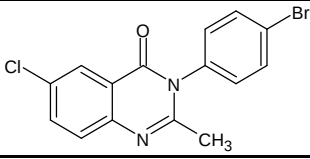
Compound	$T_{fus}/^{\circ}\text{C}$	T_{fus}/K	$\Delta H_{fus}/\text{kJ mol}^{-1}$	$\Delta S_{fus}/\text{kJ mol}^{-1}\text{K}^{-1}$
1 (Form I)	150	423.15	7.97	0.0188
1 (Form II)	164	437.15	9.43	0.0216
2	178	451.15	25.23	0.0559
3	182	455.15	21.11	0.0464

Table S2. Results of CSD database search.

Compound/Reference	Melting Point/ $^{\circ}\text{C}$	Molecular Structure	Substituents	Major Inter-Molecular Interactions	Halogen Interactions
1/this work	150/164		6-I, 4-Cl	C-H...N, C-H...O, $\pi\cdots\pi$	Cl...Cl, Cl...I
2/this work	178		6-I, 4-OCH ₃	C-H...N, C-H...O, $\pi\cdots\pi$	
3/this work	182		7-Cl, 4-OCF ₃	C-H...N, C-H...O, $\pi\cdots\pi$	F...F
DUJSIN/[36]	173-175		6-phenyl	C-H...N, C-H... π	
ent-EZUHUE/[38]	149-151		2-Br	C-H...O	

KELGOB/[29]	n.a.		2-Br, 3-CH ₃ , 4-NH ₂	N-H...O, C-H...O	
LAQHES/[34]	281		6-NO ₂ , 2-CH ₃	$\pi \cdots \pi$, C-H...O	
rac-NEPNOO/[16]	104-105		2-Br	C-H...O, C-H...N	C=O...Br
SOHCIE/[30]	n.a.		3-Cl, 4-OCH ₃	C-H...O, C-H...N	
SOKQER/[39]	127		2-Cl	C-H...O, C-H...N	C=O...Cl
rac-SOKQOB/[39]	54-57		2-I	C-H...N	C=O...I
ent-SOKQUH/[39]	132-133		2-I	C-H...O	C=O...I, I...N
SOKRAO/[39]	116-117		2-F	C-H...N, C-H...O, $\pi \cdots \pi$	
TUXLIJ/[31]	n.a.		2,4,6-Br, 3-OH	C-H...O, O-H...N	C=O...Br
WULKOF/[33]	171-173		2-NO ₂ , 4-OCH ₃	C-H...O	
WULMIB/[33]	220-222		2-NO ₂ , 4-Cl	C-H...O	C=O...Cl
ZIYYUE/[37]	120		2-CH ₃	C-H...O, C-H...N	
Unsubstituted/[39]	145-146				

3-Cl/[40]	152		3-Cl
3-F/[41]	131		3-F
3-Br/[42]	134-136		3-Br
4-Cl/[43]	157-158		4-Cl
4-Br/[44]	171-172		4-Br
4-F/[43]	132-134		4-F
2,4-Cl/[45]	156		2, 4-Cl
2-Br-4Cl/[31]	170-180		2-Br, 4-Cl
2-Cl-7-Cl/[46]	230		7-Cl, 2-Cl
3-Cl-7-Cl/[46]	190		7-Cl, 3-Cl
4-Cl-7-Cl/[18]	198		7-Cl, 4-Cl
2-Cl-6-I/[47]	164		6-I, 2-Cl

2-Cl-6-Cl/[48]	150-152		6-Cl, 2-Cl
4-Br-6-Cl/[48]	175-177		6-Cl, 4-Br

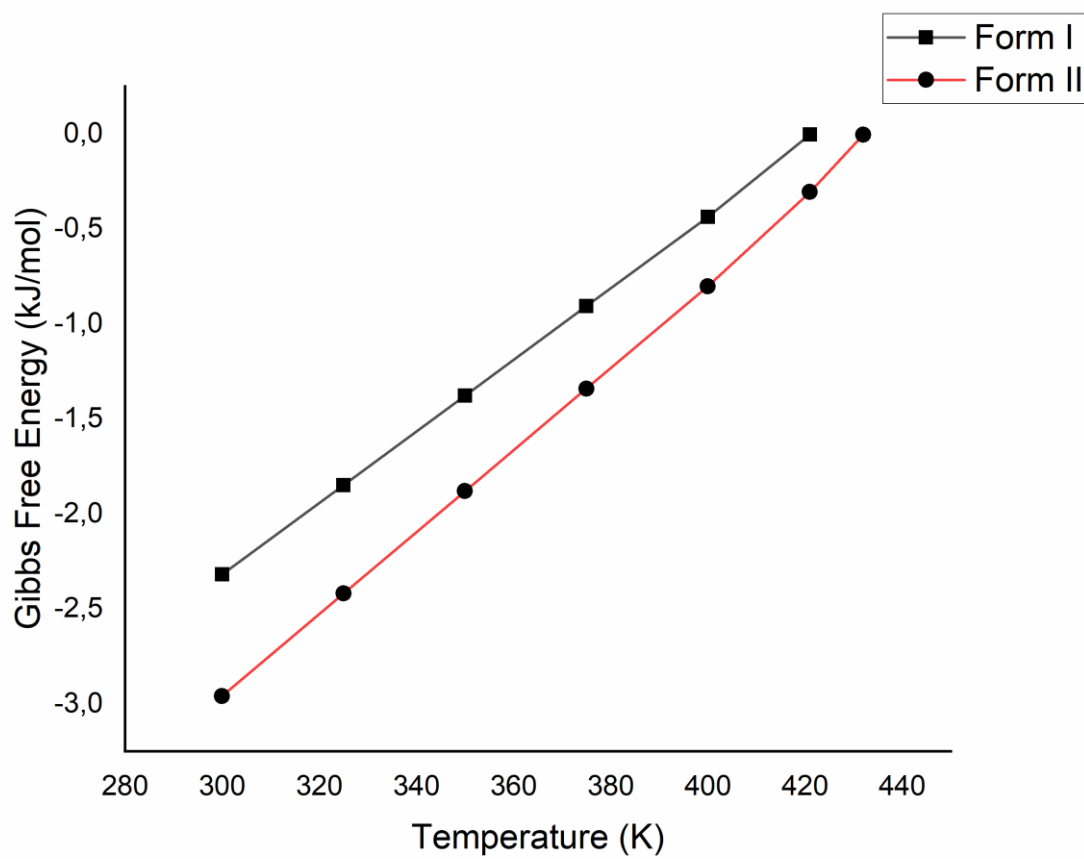


Figure S13. Linear Gibbs free-energy functions for **1** forms **I** and **II**.

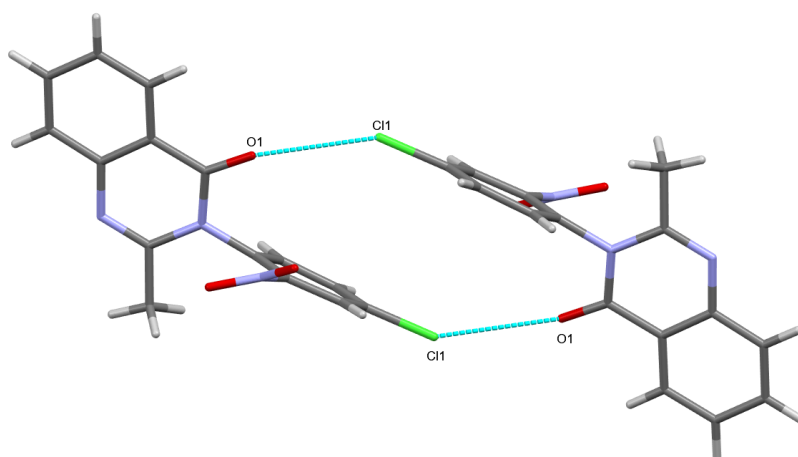


Figure S14. Representation of Cl $\cdots$ O halogen bond in WULMIB.

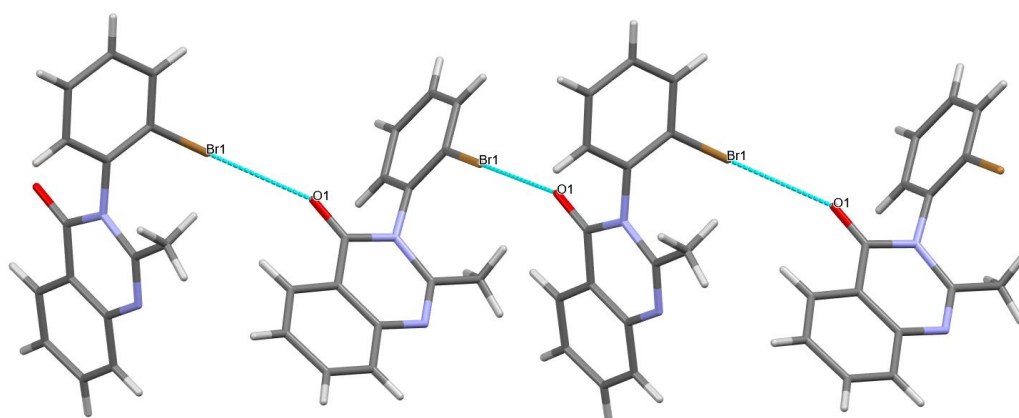


Figure S15. Representation of C-Br $\cdots$ O halogen bond in *rac*-NEPNOO.