

Supporting Information

Complex Electronic interplay of σ -hole and π -hole interactions in crystals of halogen substituted 1,3,4-oxadiazol-2(3*H*)-thiones

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Table S1: Selected Torsion Angles for OT2, OT3, OT5, OT6.

	$\tau_1(^{\circ})$	$\tau_2(^{\circ})$	$\tau_1(^{\circ})$	$\tau_2(^{\circ})$
OT2	O1-C5-C6-C1'	C6'-C1'-C6-C5		
	-171.33(12)	109.64(16)		
OT3	O1-C15-C16-C11'	C16'-C11'-C16-C15	O2-C25-C26-C21'	C26'-C21'-C26-C25
	-43.49(23)	83.88(22)	-38.52(21)	-80.21(21)
OT5	O1-C5-C6-C1'	C6'-C1'-C6-C5		
	-57.55(14)	100.86(13)		
OT6	O1-C5-C6-C1'	C6'-C1'-C6-C5		
	77.61(20)	43.94(23)		

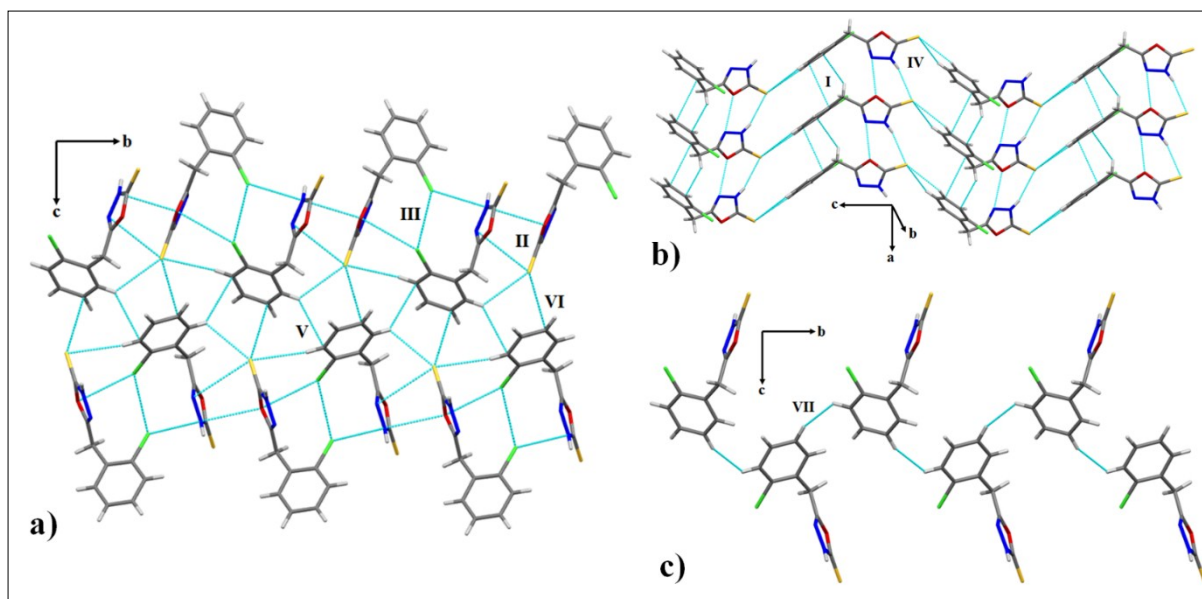


Figure S1: Crystal packing of OT2 showing the utilization of different molecular motifs.

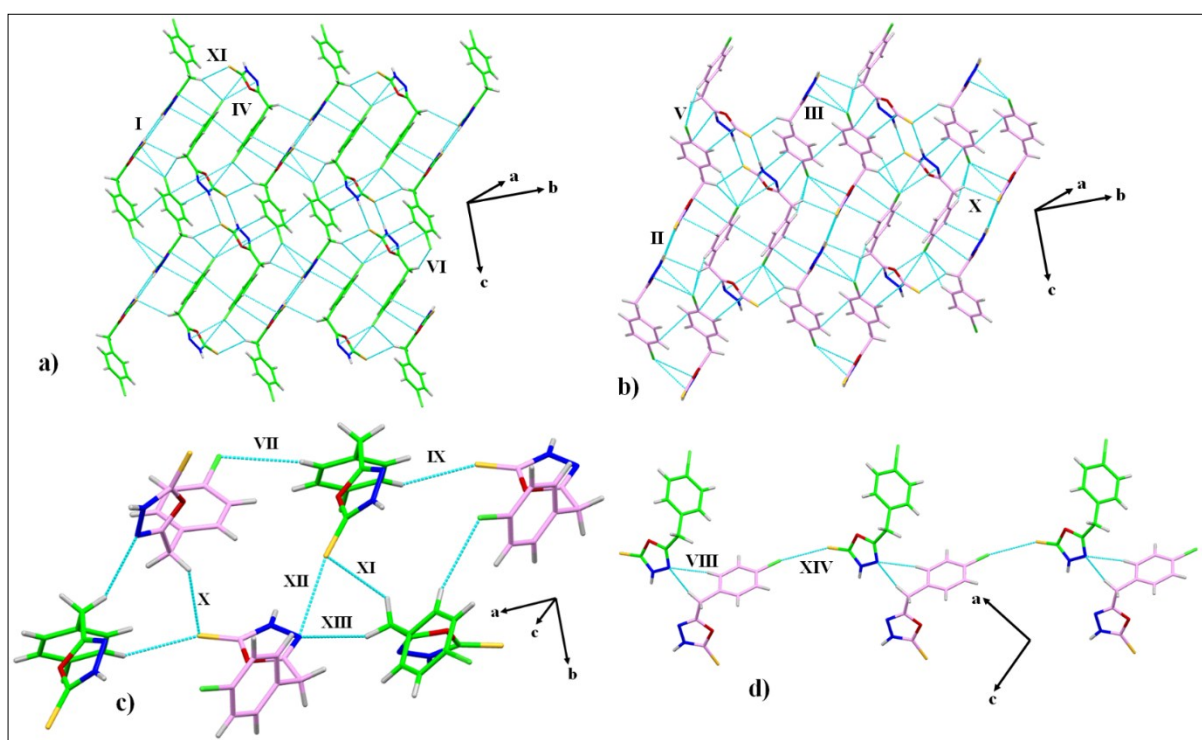


Figure S2: Crystal packing of OT3 showing the utilization of different molecular motifs.

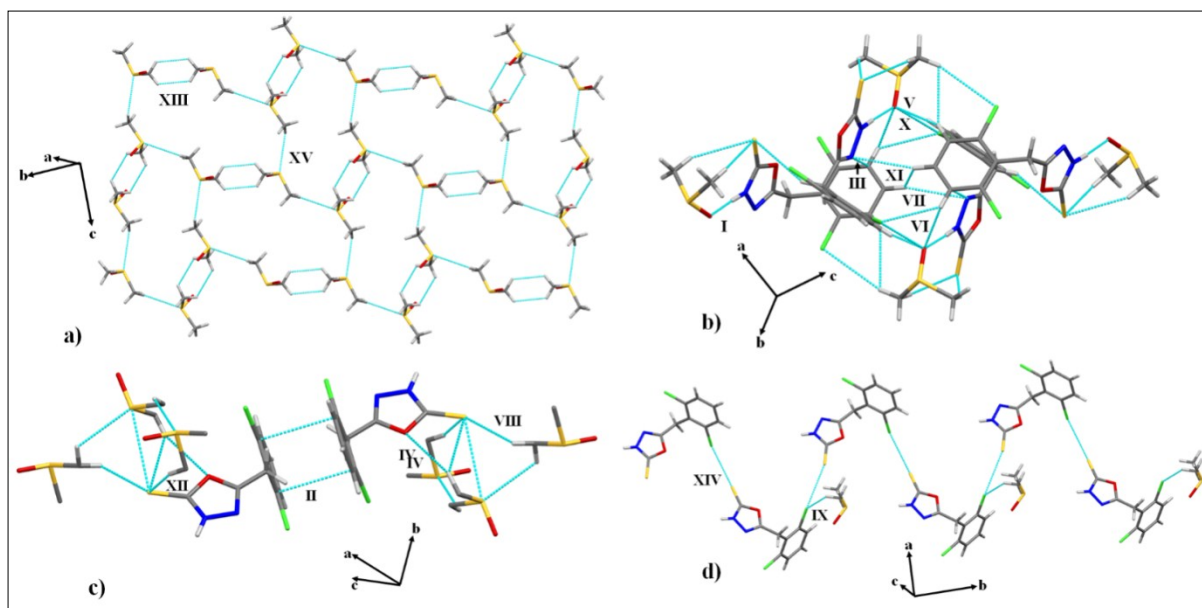


Figure S3: Crystal packing of OT5 showing the utilization of different molecular motifs.

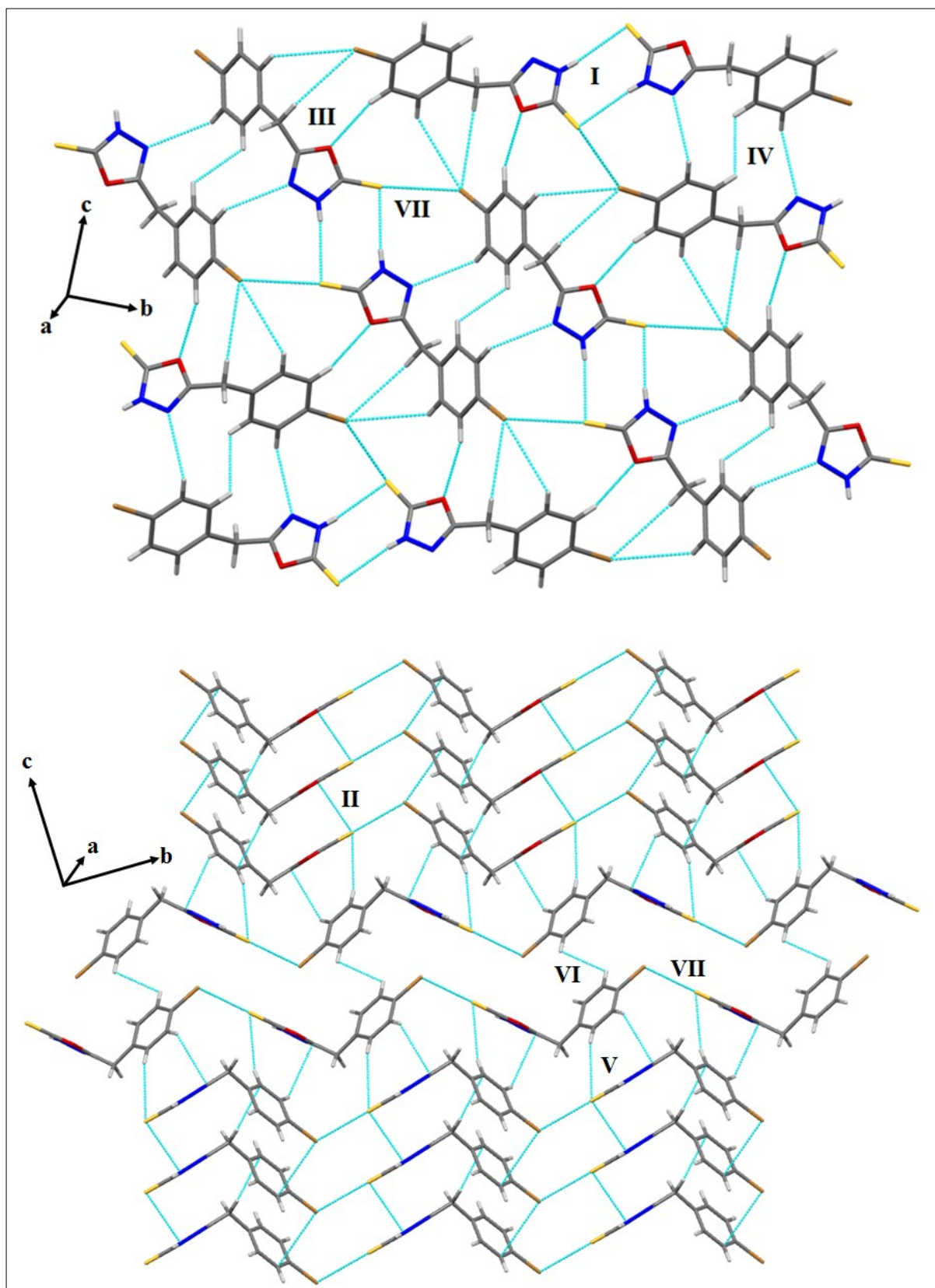


Figure S4: Crystal packing of OT6 showing the utilization of different molecular motifs.

Table S2: Intermolecular interactions along with their topological parameters.

	Interaction	BPL (Å)	ρ (e/Å ³)	∇^2 (e/Å ⁵)	$ V_b /G_b$
OT2					
I	N3-H3N...S2	2.61	0.111	0.978	0.909
	C5-N4...O1	2.84	0.079	1.083	0.864
	C6-H6A...C3'	3.05	0.024	0.253	0.718
	C1'...C4'	3.570	0.030	0.301	0.810
II	C5-O1...N3	3.320	0.033	0.406	0.881
	C2-S2...N4	3.962	0.038	0.395	0.772
	C6'-H6'...S2	3.11	0.023	0.227	0.732
III	C2'-Cl2'...Cl2'-C2'	3.753	0.029	0.371	0.647
	C3'-H3'...S2	3.12	0.044	0.443	0.804
	C2'-Cl2'...N3	3.299	0.048	0.654	0.772
	C2'-Cl2'...O1	3.535	0.029	0.387	0.765
IV	C4'-H4'...S2	3.13	0.042	0.456	0.781
	C5'-H5'...S2	3.30	0.034	0.359	0.752
V	C6'-H6'...C3'	3.02	0.040	0.387	0.821
VI	C2-S2...C5'	3.554	0.035	0.388	0.755
VII	C3'-H3'...H5'-C5'	2.69	0.026	0.300	0.819
OT3					
I	N13-H13N...S12	2.52	0.168	1.230	1.077
II	N23-H23N...S22	2.43	0.163	1.206	1.063
III	C25'...C25'	3.368	0.044	0.440	0.793
	C24-Cl24...N23	3.537	0.034	0.429	0.781
	C24-Cl24...N24	3.674	0.030	0.381	0.765
IV	C14'-Cl14...N14	3.401	0.043	0.586	0.789
	C14'-Cl14...N13	3.987	0.049	0.614	0.761
	C13'...C13'	3.471	0.038	0.369	0.820
V	C22'-H22'...Cl24	3.12	0.036	0.410	0.754
	C26-H26B...Cl24	3.07	0.040	0.456	0.774

	C24'...C25	3.526	0.030	0.345	0.794
	C23'...C22	3.268	0.047	0.535	0.791
VI	C16-H16B...Cl14	3.04	0.041	0.472	0.772
	C12...C15'	3.575	0.036	0.374	0.793
	O1...C14'	3.731	0.028	0.334	0.835
VII	C16'-H16'...Cl24	3.16	0.034	0.389	0.752
VIII	C26'-H26'...N14	2.64	0.070	0.752	0.853
	C26-H26A...N14	2.53	0.080	0.878	0.848
IX	C13'-H13'...S22	3.04	0.045	0.493	0.800
X	C26-H26B...S22	2.91	0.063	0.670	0.820
XI	C16-H16B...S12	3.07	0.046	0.480	0.790
XII	C12-S12...N24	3.231	0.055	0.682	0.841
XIII	C16-H16A...N24	2.95	0.037	0.378	0.858
XIV	C12-S12...Cl24-C24'	3.436	0.045	0.688	0.755
OT5					
I	N3-H3N...O1S	1.79	0.317	3.611	1.124
	C1S-H2S1...S2	3.12	0.046	0.434	0.800
	C1S-H3S3...S2	3.03	0.053	0.505	0.803
II	C2'...C6'	3.500	0.037	0.361	0.835
	C6-H6A...C5'	3.17	0.041	0.450	0.791
III	C5-N4...C5'	3.473	0.042	0.470	0.829
	C6-H6B...S2	3.06	0.048	0.495	0.802
IV	C1S-H2S2...S2	2.99	0.057	0.600	0.815
	C1S-H2S2...O1	2.81	0.038	0.462	0.867
	O1S-S1S...S2	3.729	0.041	0.488	0.768
V	C3'-H3'...O1S	2.52	0.080	0.872	0.902
	C2S-H3S1...Cl2'	3.27	0.025	0.277	0.741
VI	C5'-H5'...O1S	2.61	0.065	0.771	0.876
VII	C5'-H5'...Cl2'	2.98	0.044	0.552	0.749
	C4'-H4'...N4	2.93	0.036	0.397	0.854
VIII	C2S-H3S2...S3	3.12	0.040	0.484	0.755
IX	C2S-H3S3...Cl6'	3.20	0.029	0.376	0.701

X	C2'-Cl2'...O1S	3.275	0.046	0.641	0.826
XI	C4'-H4'...H4'-C4'	2.79	0.030	0.368	0.726
XII	C1S-H2S3...S2	3.10	0.044	0.450	0.798
XIII	C1S-H2S3...H2S1-C1S	2.42	0.046	0.522	0.809
XIV	C6'-Cl6'...S2-C2	3.638	0.034	0.523	0.691
XV	C2S-H3S1...S1S	3.01	0.047	0.539	0.755
OT6					
I	N3-H3N...S2	2.56	0.172	1.239	1.090
II	C6-H6B...C2'	2.75	0.060	0.673	0.825
	C4'-Br4'...C5'	3.735	0.039	0.400	0.776
	C2-S2...N3	3.462	0.046	0.492	0.824
III	C3'-H3'...O1	2.57	0.063	0.761	0.863
	C6-H6A...Br4'	3.29	0.032	0.326	0.777
	C2'-H2'...Br4'	3.41	0.026	0.287	0.739
IV	C5'-H5'...N4	2.82	0.049	0.525	0.846
	C6'-H6'...H6'	2.42	0.049	0.564	0.809
V	C3'-H3'...C5	3.16	0.024	0.291	0.736
	C2'-H2'...S2	3.19	0.047	0.481	0.801
VI	C5'-H5'...H5'-C5'	2.87	0.035	0.460	0.735
VII	C4'-Br4'...S2-C2	3.871	0.033	0.403	0.695
VIII	C2-S2...Br4'-C4'	3.531	0.054	0.656	0.792

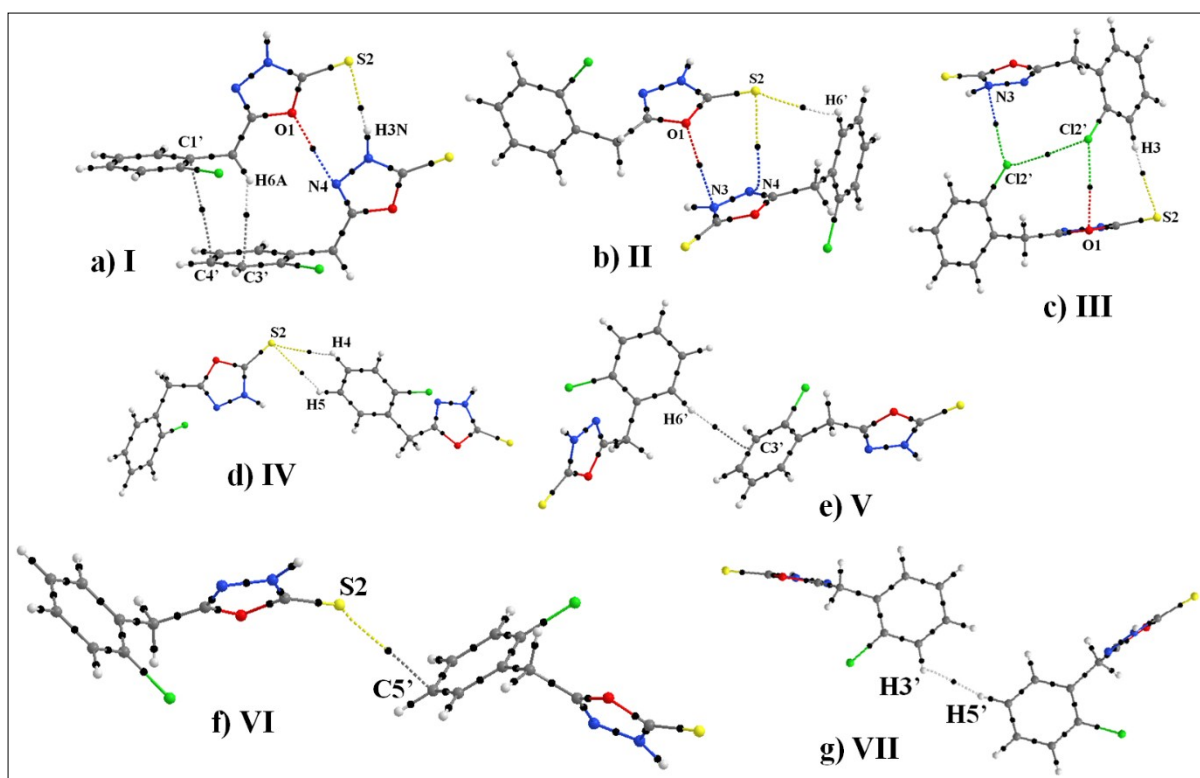


Figure S5: Molecule graph depicting the presence of bcp between interacting atoms in OT3.

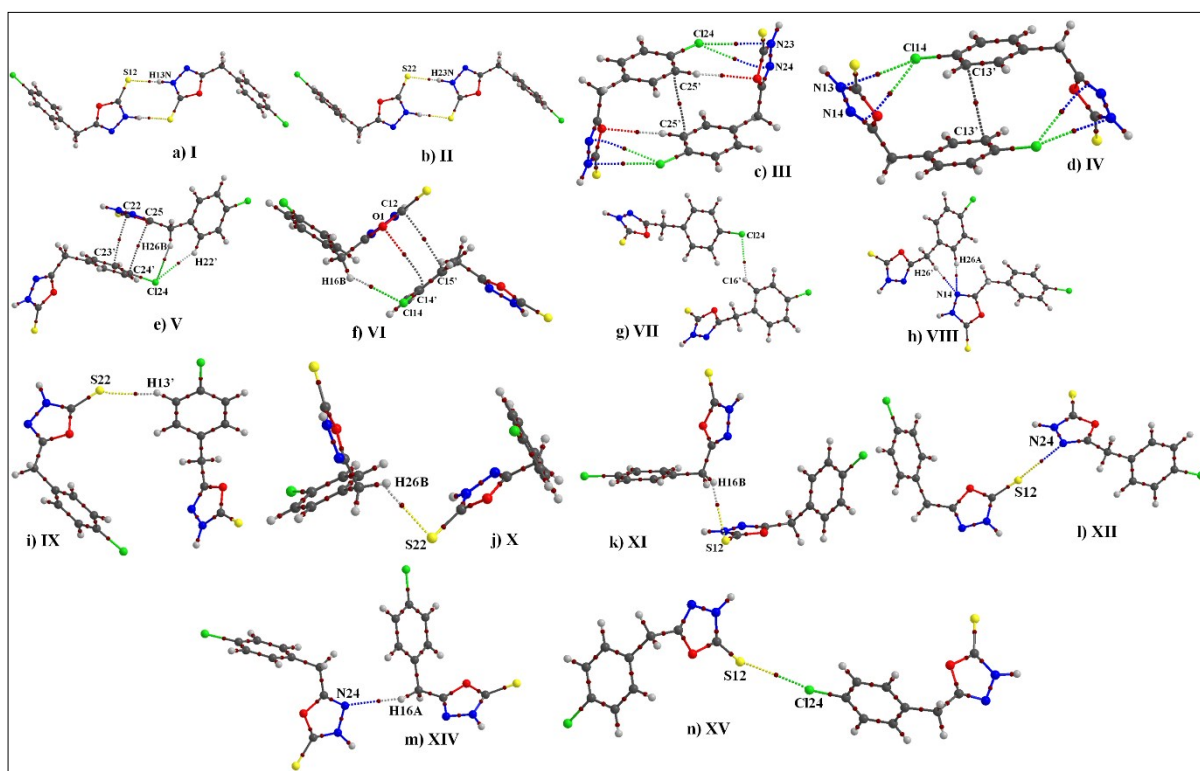


Figure S6: Molecule graph depicting the presence of bcp between interacting atoms in OT3.

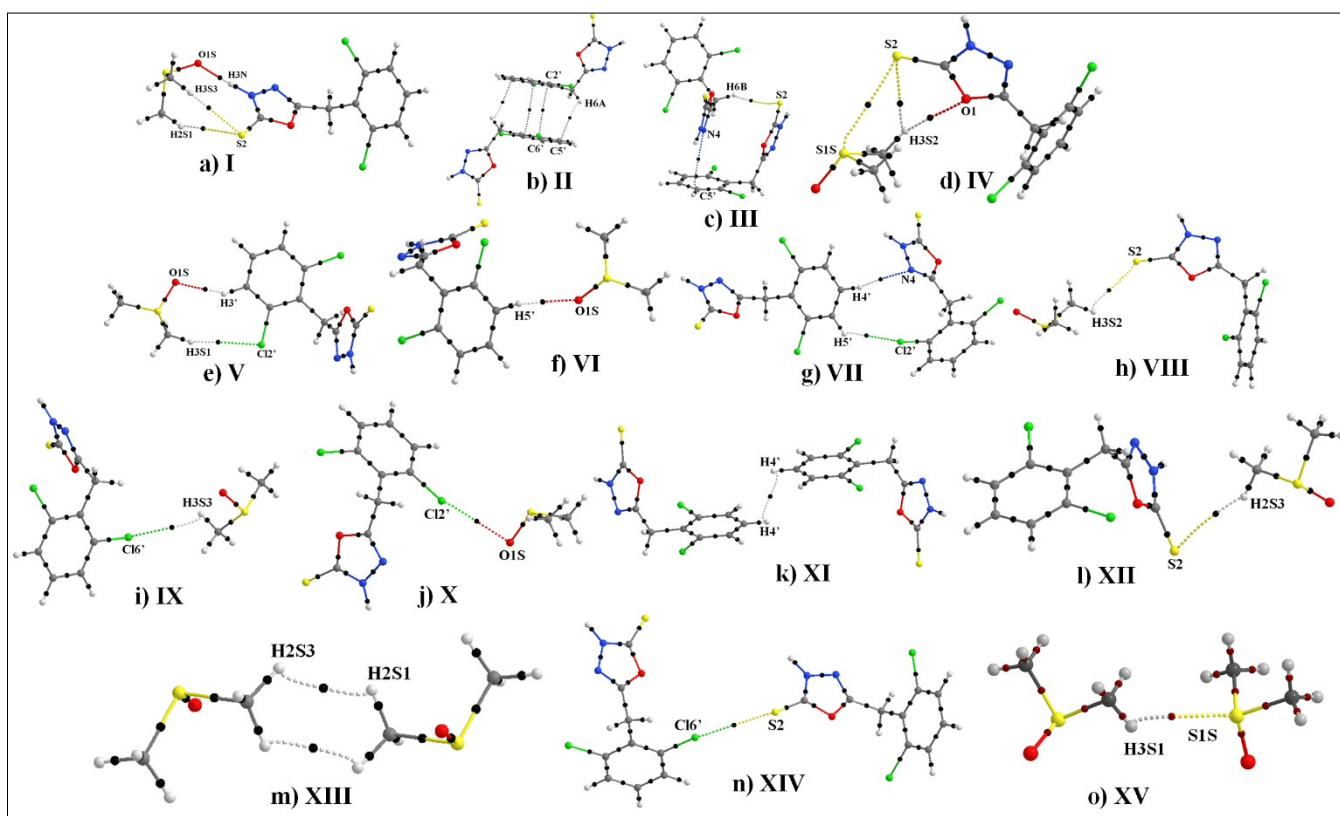


Figure S7: Molecule graph depicting the presence of bcp between interacting atoms in OT5.

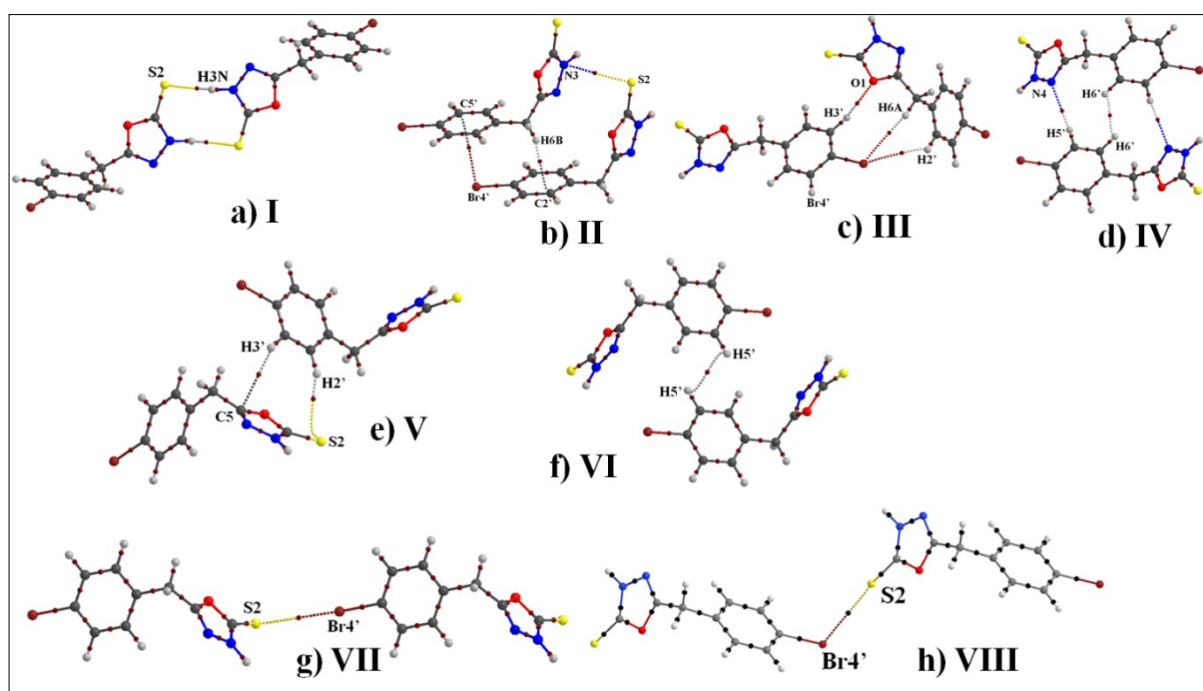


Figure S8: Molecule graph depicting the presence of bcp between interacting atoms in OT6.

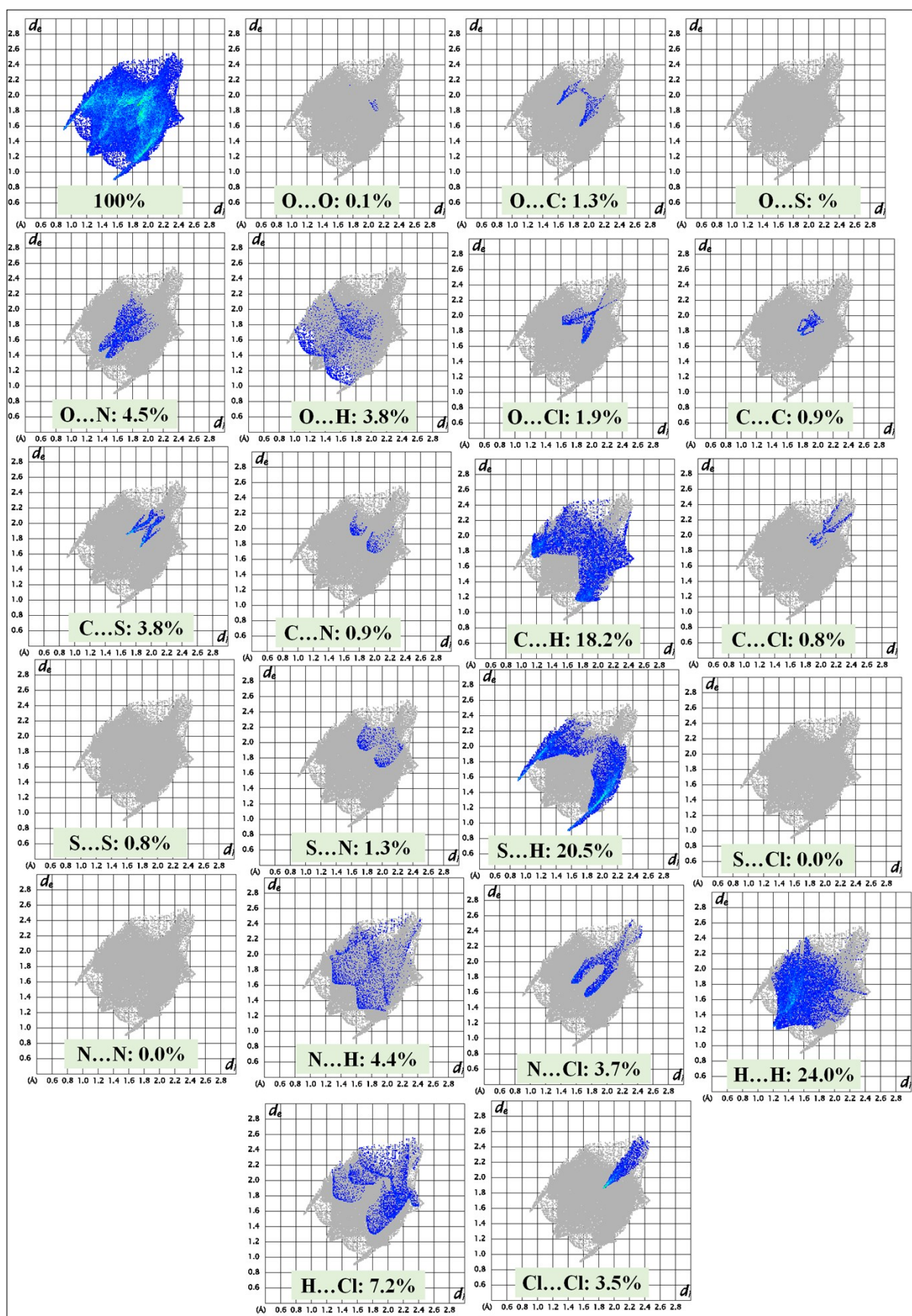


Figure S9: 2D Fingerprint plots for OT2

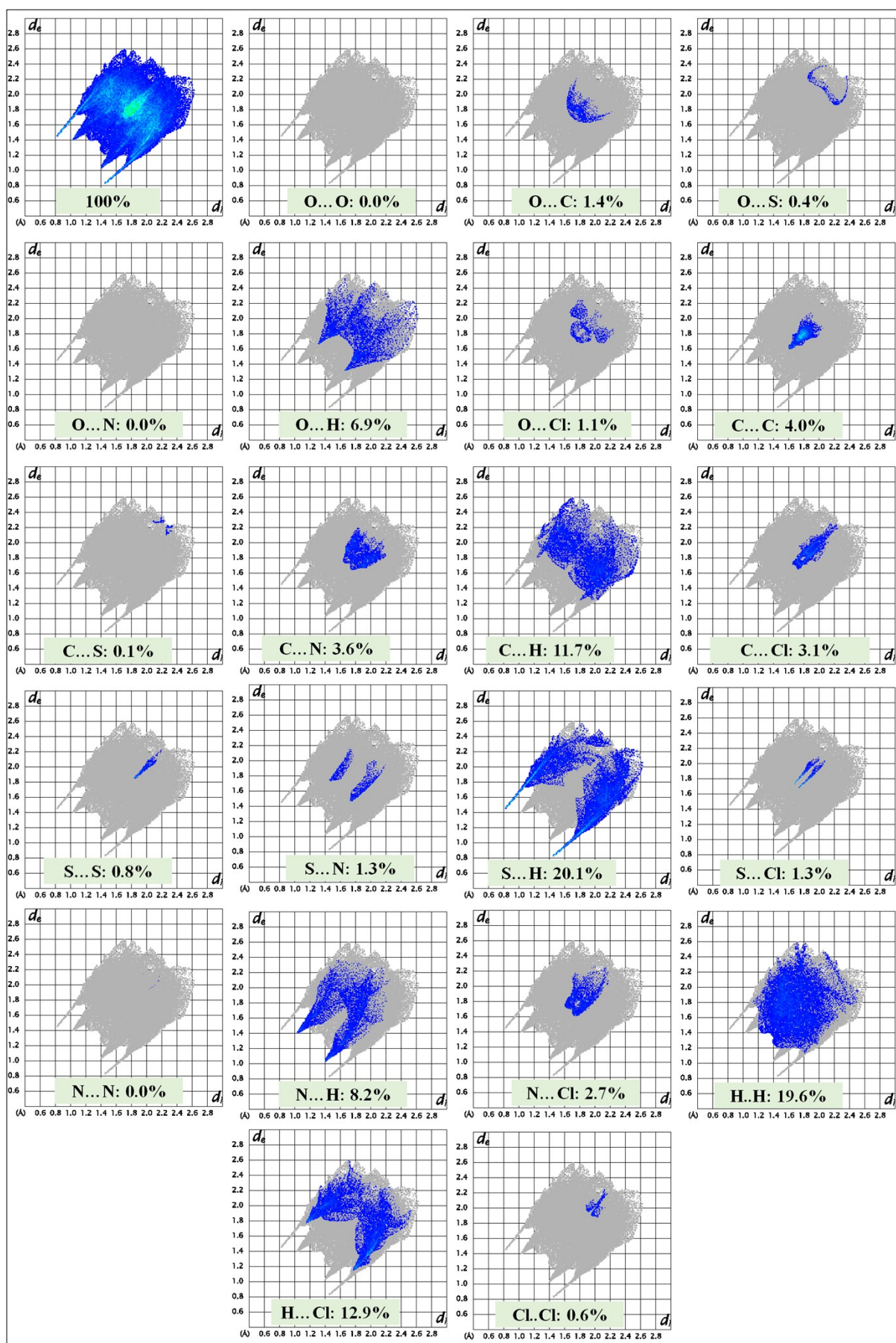


Figure S10: 2D Fingerprint plots for OT3

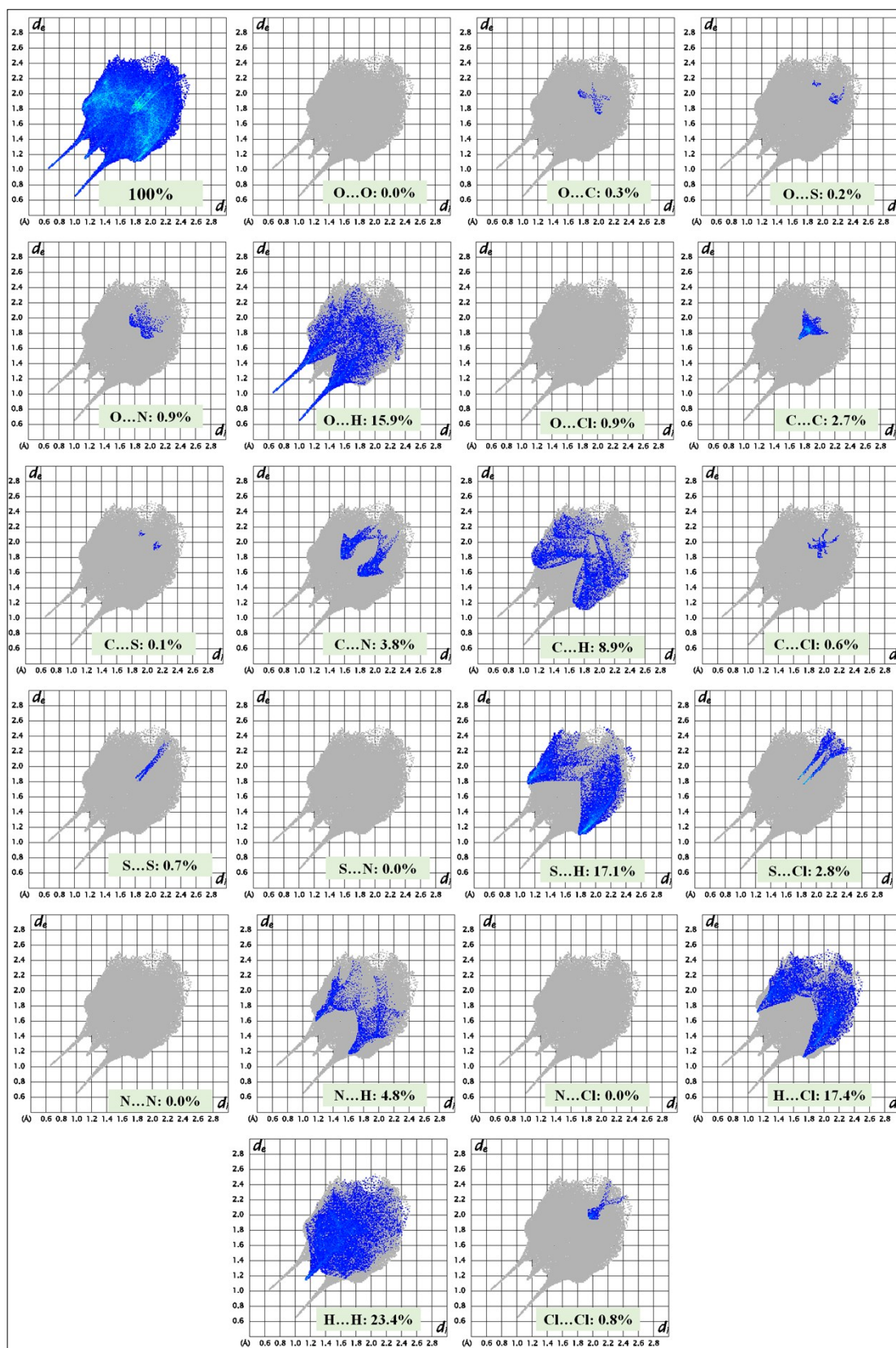


Figure S11: 2D Fingerprint plots for OT5

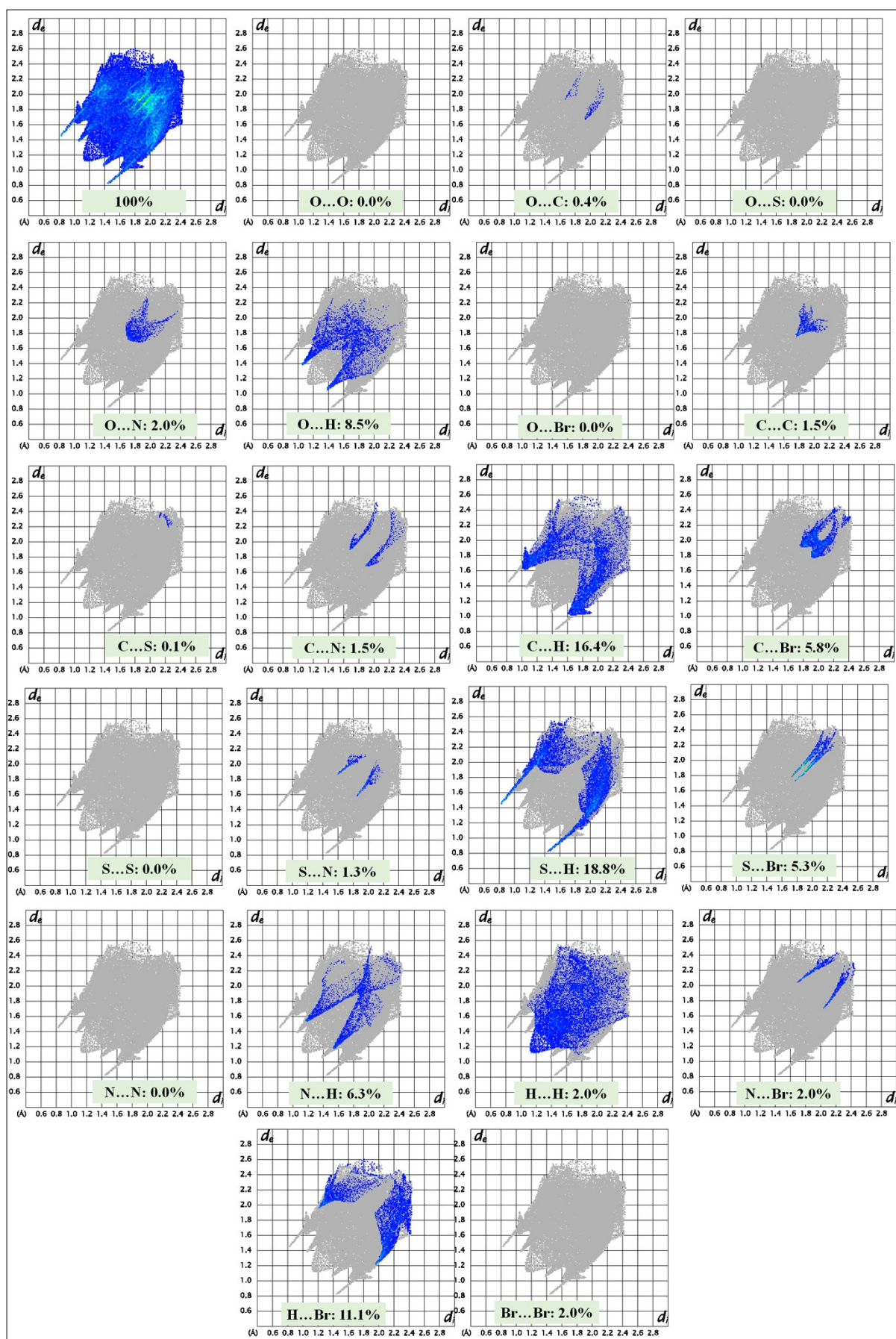


Figure S12: 2D Fingerprint plots for OT6