

# Halogen Bonding in New Dichloride-Cobalt(II) Complex with Iodo Substituted Chalcone Ligands

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## 1. NMR and ESI-MS spectra's data of ligand 4I-L and complex 1a.

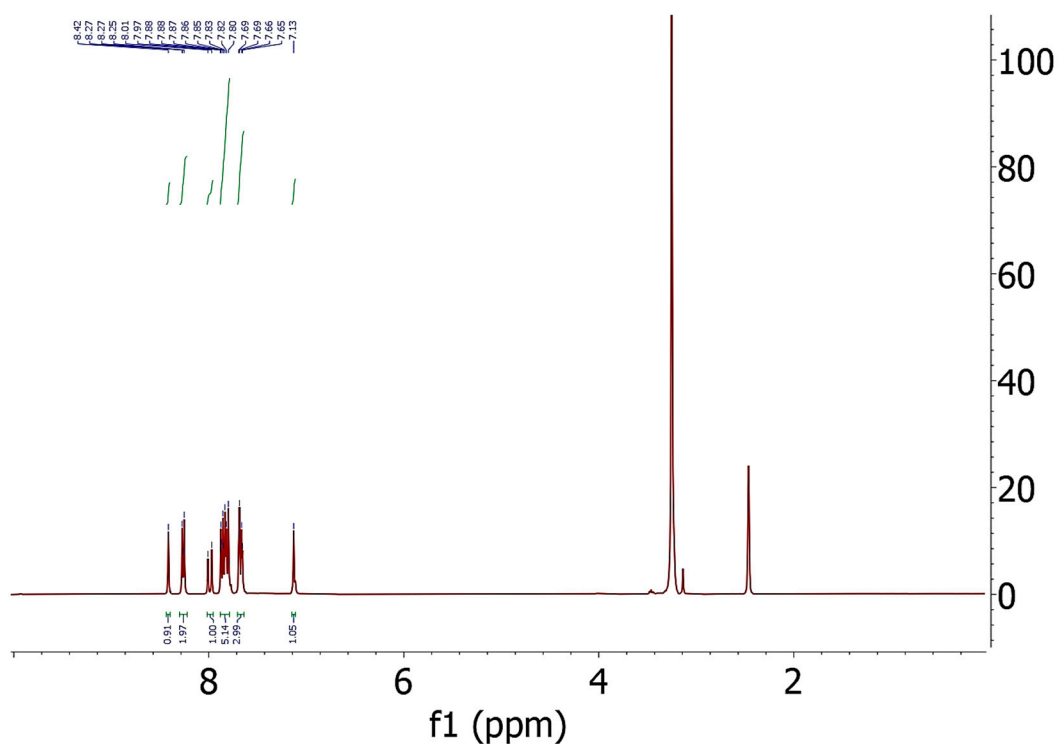


Figure S1. <sup>1</sup>H NMR spectrum of ligand 4I-L in DMSO-*d*<sub>6</sub>.

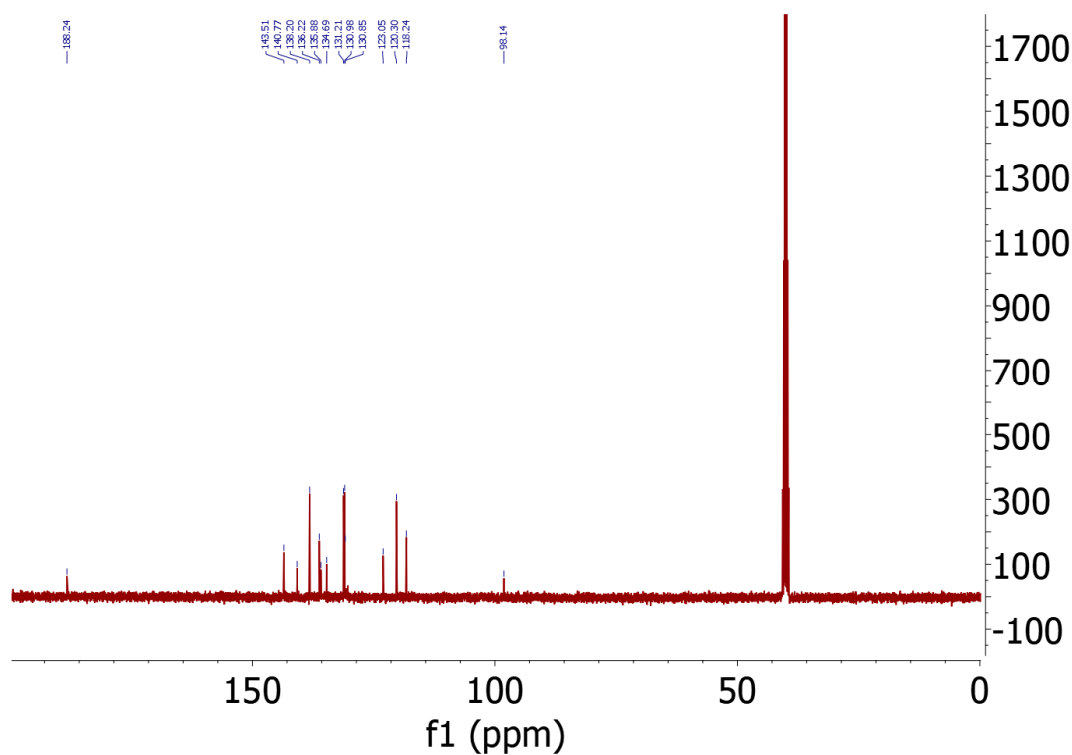


Figure S2.  $^{13}\text{C}$  NMR spectrum of ligand 4I-L in  $\text{DMSO-}d_6$ .

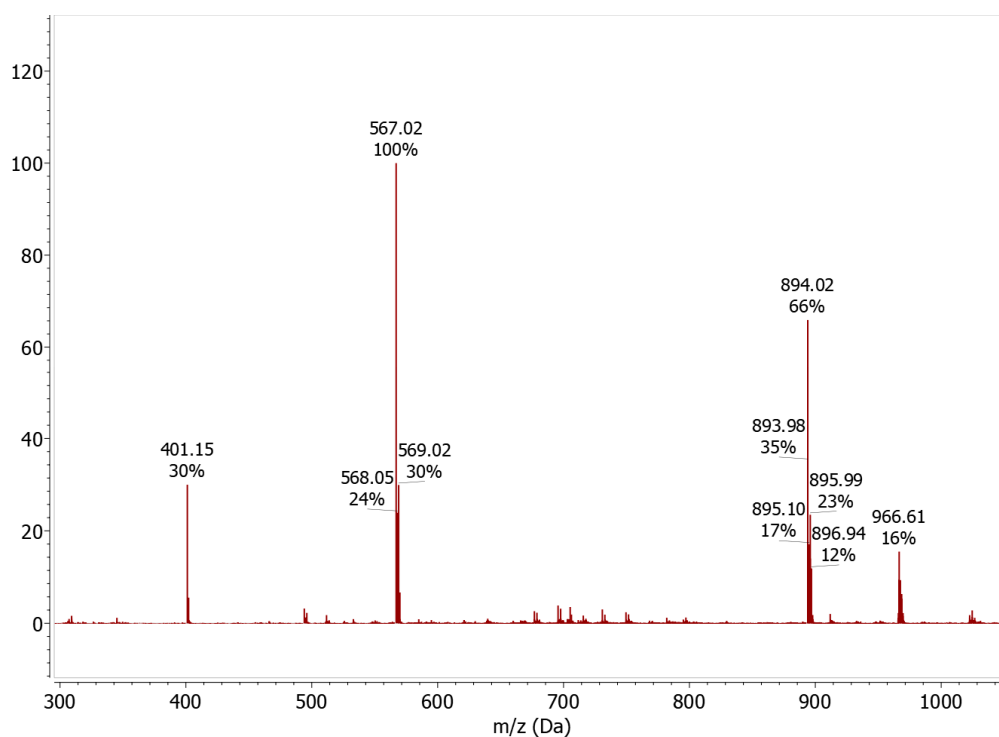
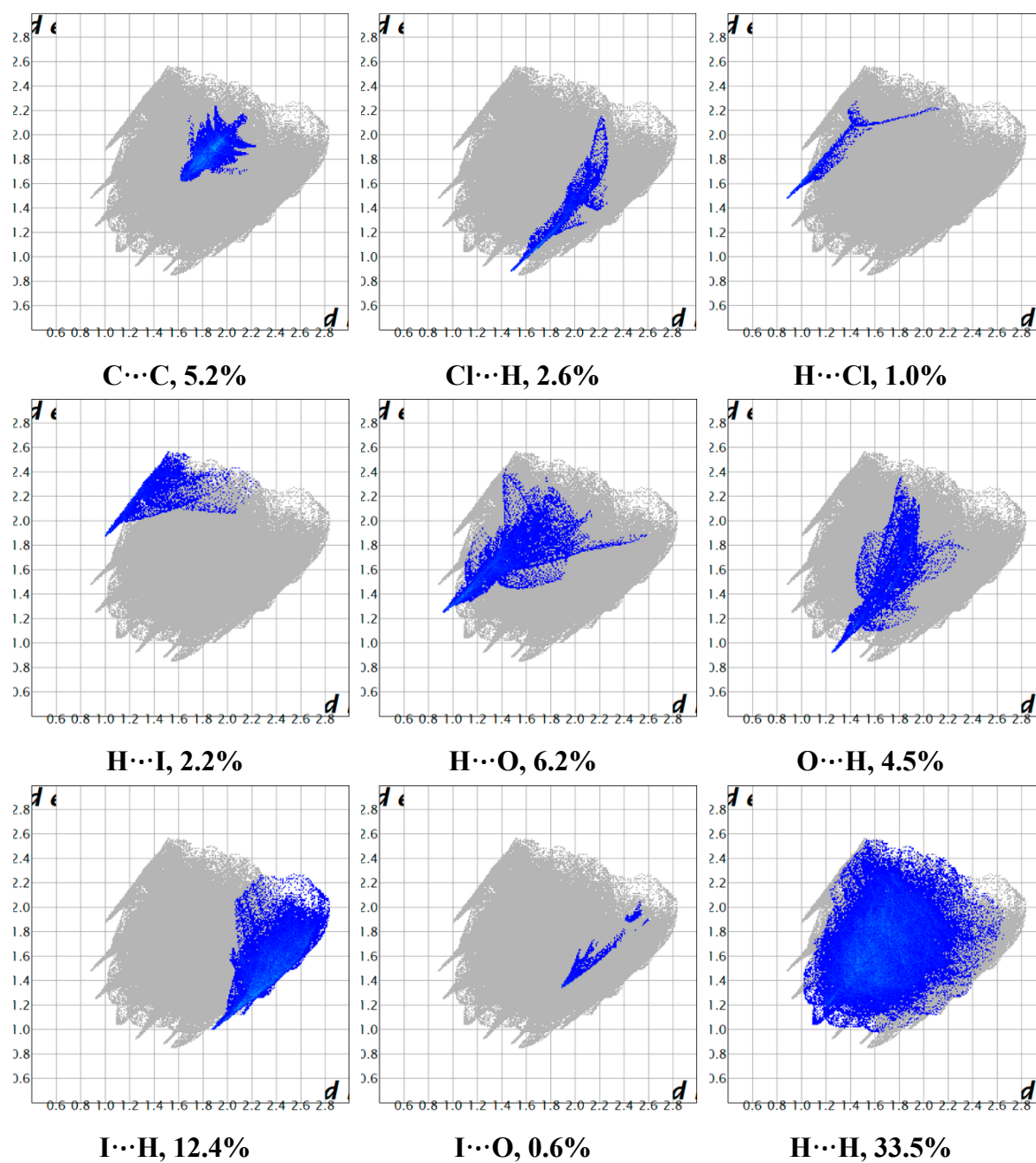
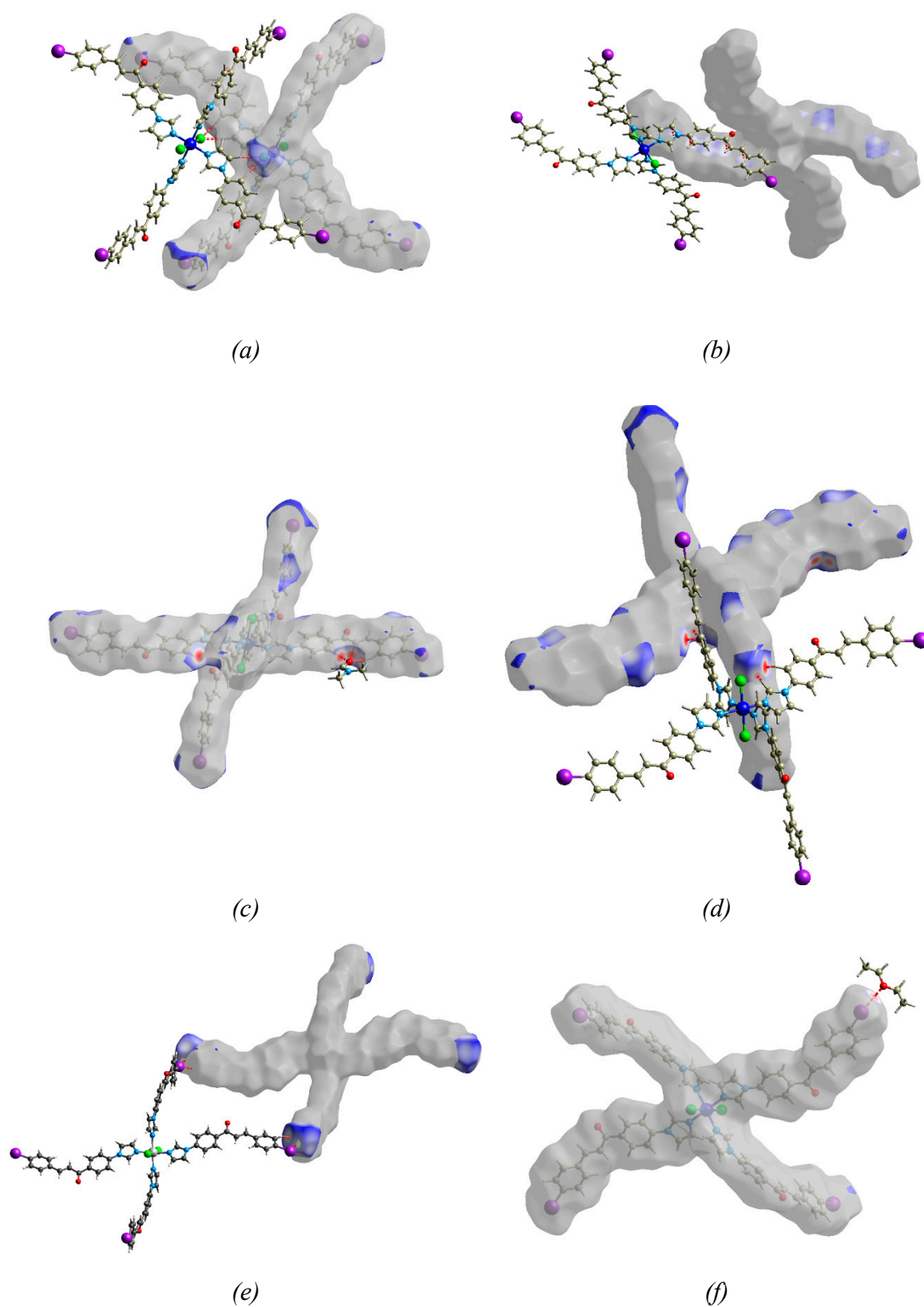


Figure S3. ESI-MS mass spectrum of complex 1a in methanol.

## 2. Hirshfeld surfaces



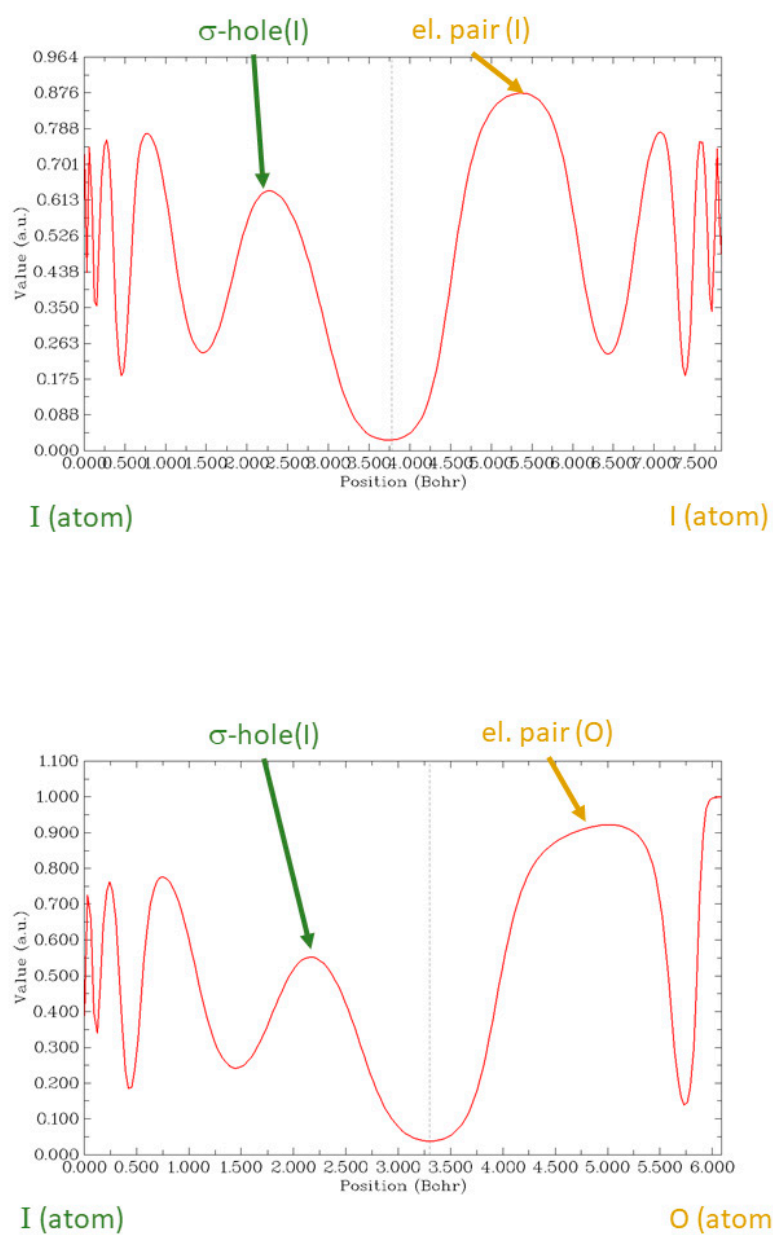
**Figure S4.** 2D fingerprint plots generated for the complex molecule [Co(4I-L)<sub>4</sub>Cl<sub>2</sub>] in crystal structure of **1b**. The percentage contribution to the Hirshfeld surface areas for selected intermolecular contacts is listed below each fingerprintplot, while the first atom label stands always for the atom on molecular surface, whereas the second is located outside the molecule.



**Figure S5.** Hirshfeld surface calculated for the complex molecule [Co(4I-L)<sub>4</sub>Cl<sub>2</sub>] in crystal structure of **1b** with highlighted areas of surface involved in selected non-covalent interactions: (a) supramolecular dimer via C-H...Cl hydrogen bonding, (b)  $\pi$ - $\pi$  stacking interactions, (c) stabilization of DMF molecule by C-H...O hydrogen bonding, (d) C-H...O hydrogen bonds of the chalcone keto group, (e) I...I and C-H...I interactions, (f) O...I halogen bonding. Non-covalent interactions are drawn as red dashed lines.

Table S1. Parameters of non-covalent interactions in 1b.

Hydrogen bond	$d(\text{H}\cdots\text{A})/\text{\AA}$	$d(\text{H}\cdots\text{A})/\text{\AA}$	$d(\text{D}\cdots\text{A})/\text{\AA}$	$\angle(\text{D}-\text{H}\cdots\text{A})^\circ$	Symm. code
C2-H2...Cl1	0.950	2.526	3.466(5)	170.47	-x, -y+1, -z+1
C3-H3...O2	0.950	2.574	3.420(4)	148.58	x, y+1, z
C5-H5...O4	0.950	2.383	3.324(6)	172.0	x, y, z
C8-H8...O2	0.950	2.316	3.193(5)	153.33	x, y+1, z
C10-H10...O4	0.950	2.444	3.388(5)	172.05	x, y, z
C13-H13...O4	0.950	2.516	3.394(5)	153.8	x, y, z
C16-H16...I2	0.950	3.029	3.918(5)	156.27	x+1, y+2, z+1
C18-H18...Cl1	0.950	2.699	3.273(4)	119.54	x, y, z
C19-H19...Cl1	0.950	2.775	3.319(4)	117.19	-x-1, -y+1, -z+1
C20-H20...I2	0.950	3.234	3.732(4)	114.71	-x, -y, -z+1
C35-H35...Cl1	0.950	2.878	3.807(4)	166.35	-x, -y+1, -z+1
C37-H37B...I1	0.980	3.181	4.088(5)	154.7	-x+2, -y+2, -z+2
C37-H37B...I2	0.980	3.298	3.944(5)	125.14	-x+1, -y, -z+1
C43-H43...Cl11	0.950	2.740	3.673(5)	167.19	-x-1, -y+1, -z+1
C46A-H46A...O4	0.990	2.538	3.300(2)	133.48	-x+2, -y+2, -z+2
C47A-H47B...I1	0.980	3.232	4.060(2)	142.86	x, y, z
C47B-H47F...I1	0.980	3.13	4.000(2)	149.39	x, y, z



**Figure S6.** The calculated Electron localization function (ELF) along calculated bond paths for the molecular fragments  $\{(4I-L)\cdots(4I-L)\}$  (*top*) and  $\{(4I-L)\cdots(Et_2O)\}$  (*bottom*) showing halogen bonds of the types  $I\cdots I$  and  $O\cdots I$ . The dotted line locates the BCP (3,-1).