Supporting Information

Effect of Halogen Bonding Interaction on Supramolecular Assembly of Halogen-Substituted Phenylpyrazinamides

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Lattice Energy Calculations. Lattice energy of polymorph 3-Brα and 3-Brβ were calculated using the Forcite module of Material Studio 4.4 with COMPASS force field [S1]. The Ewald summation employed to compute the non-bonded interactions that include van der Waals and electrostatic interactions. Finally, lattice energies were computed per molecule based on the number of molecules present in the unit cell. Lattice energy calculations are also consistent with 3-Brα as the thermodynamically stable form (3-Brα: -39.09; and 3-Brβ: -32.34 Kcal/mol).

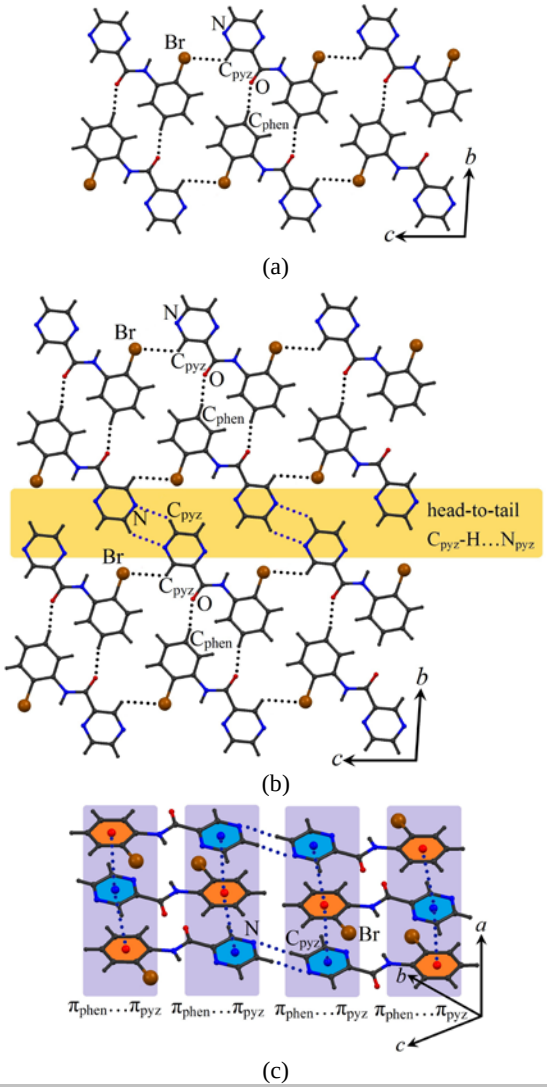


Figure S1. A side view representation of *N*-(2-bromophenyl)pyrazine-2-carboxamide, **2-Br**, in *bc*-plane, showing the association of the adjacent molecules through C_{phen}-H…O=C and C_{pyz}-H…Br non-classical hydrogen bonds and weak Br…N halogen bonds as red band which generates of linear chain (a). Presence of head-to-tail C_{phen}-H...N_{pyz}

non-classical hydrogen bonds between adjacent chains, (b). π-π stacking interactions in *a*-direction, (c).

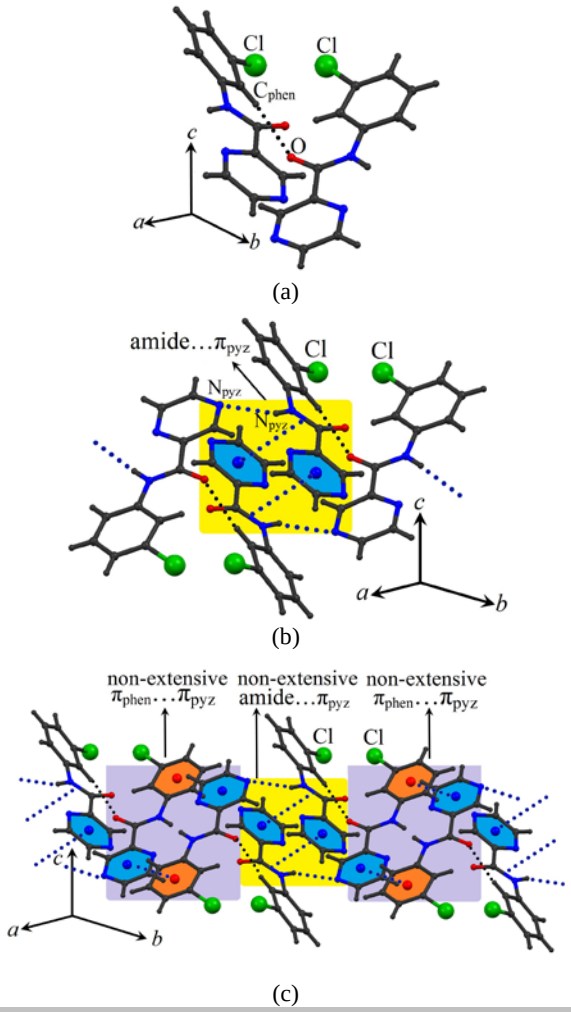
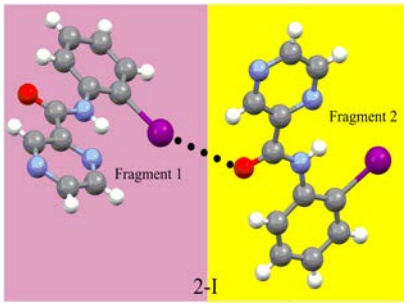
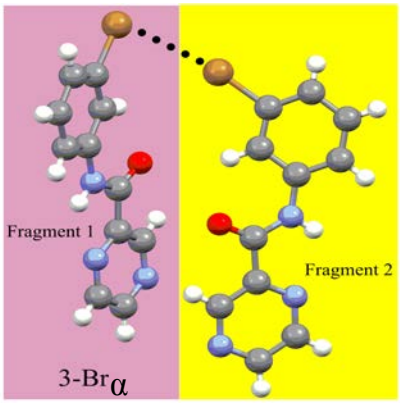
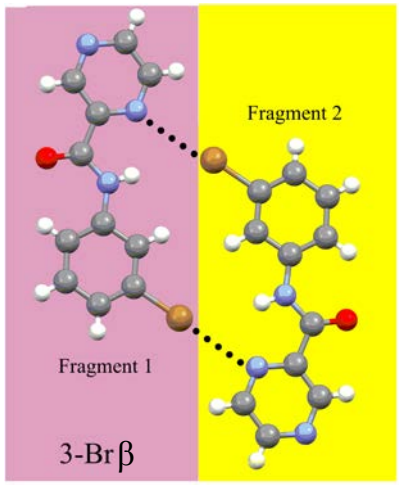


Figure S2. A side view representation of *N*-(3-chlorophenyl)pyrazine-2-carboxamide, **3-Cl**, showing the presence of C_{phen}-H…O=C interactions between two crystallographically independent molecules, (a). Presence of N_{amide}-H…N_{pyz} hydrogen bond and amide…π_{pyz} interaction between adjacent units, (b). Resulted units are linked to each other by head-to-tail π_{phen}…π_{pyz} interactions which generate linear chain, (c).







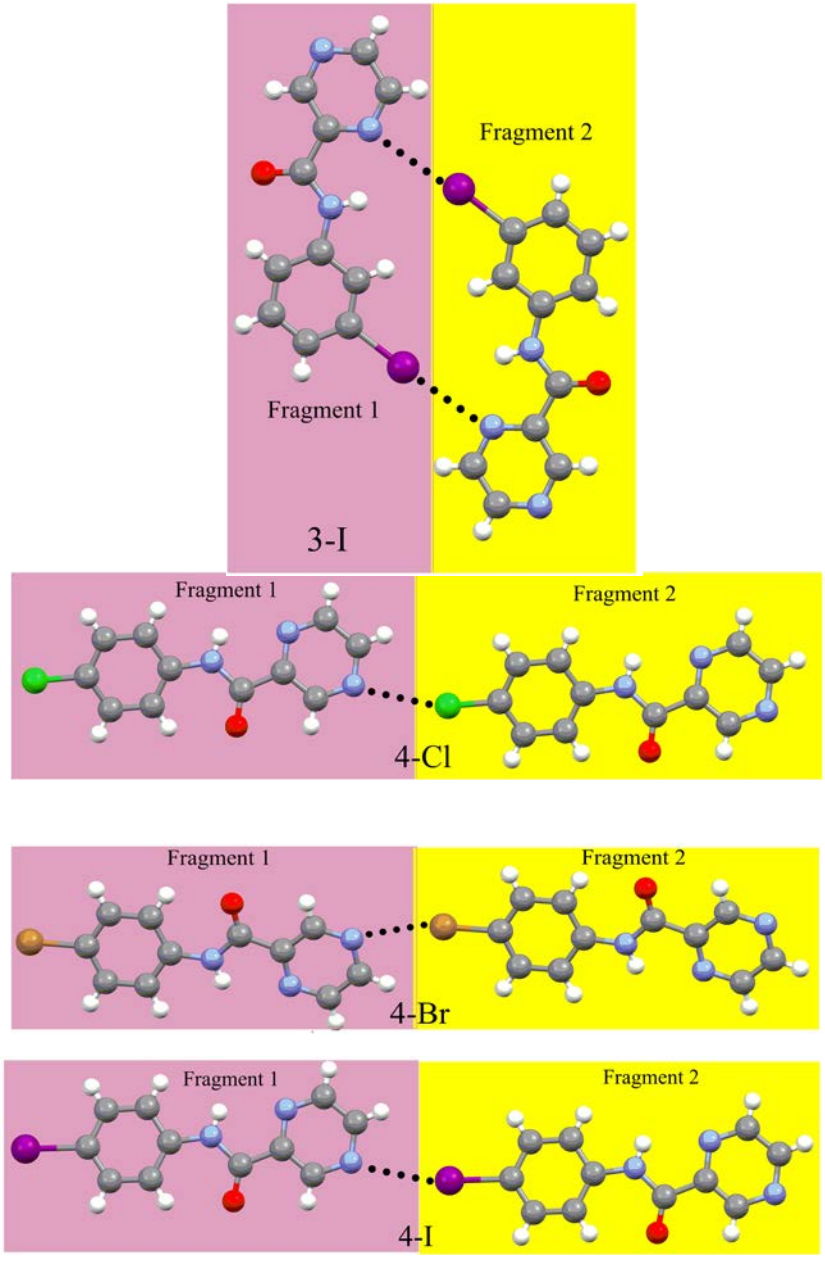
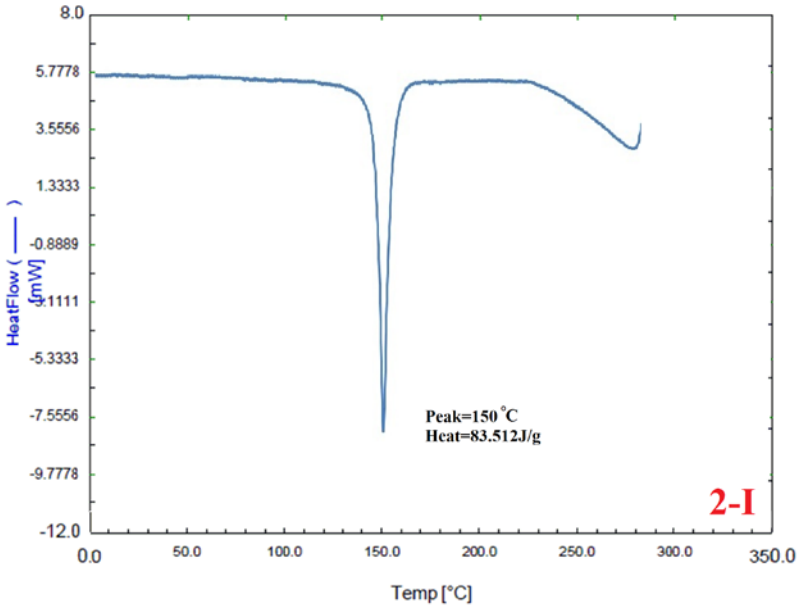
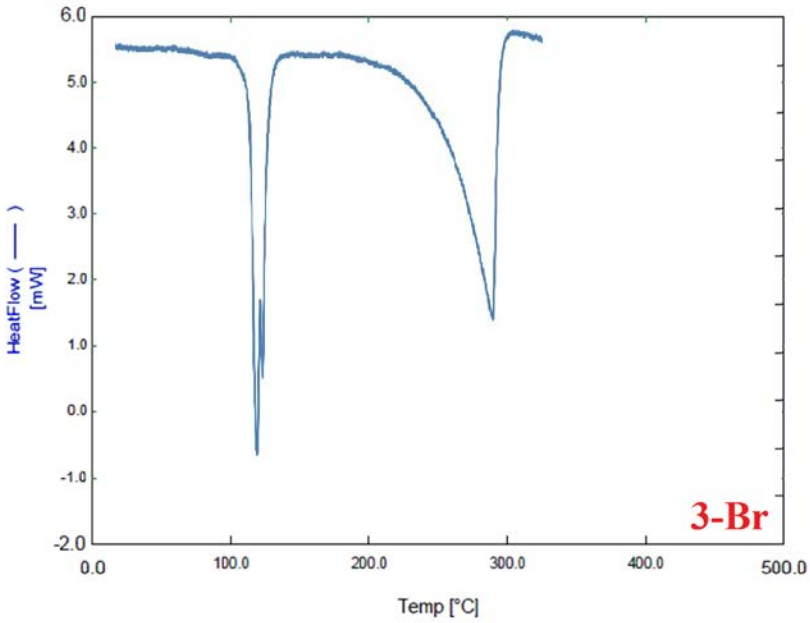


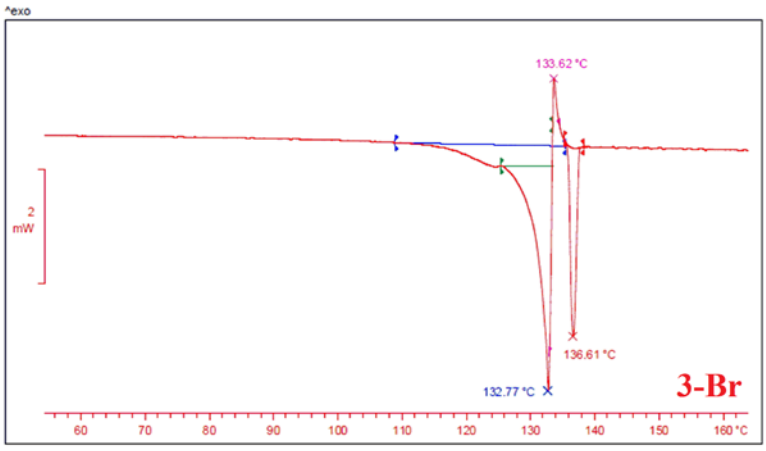
Figure S3. Fragments selected for halogen bonding interaction energy analysis in compounds **2-I, 3-Brα, 3-Brβ, 3-I, 4-Cl, 4-Br** and **4-I**.



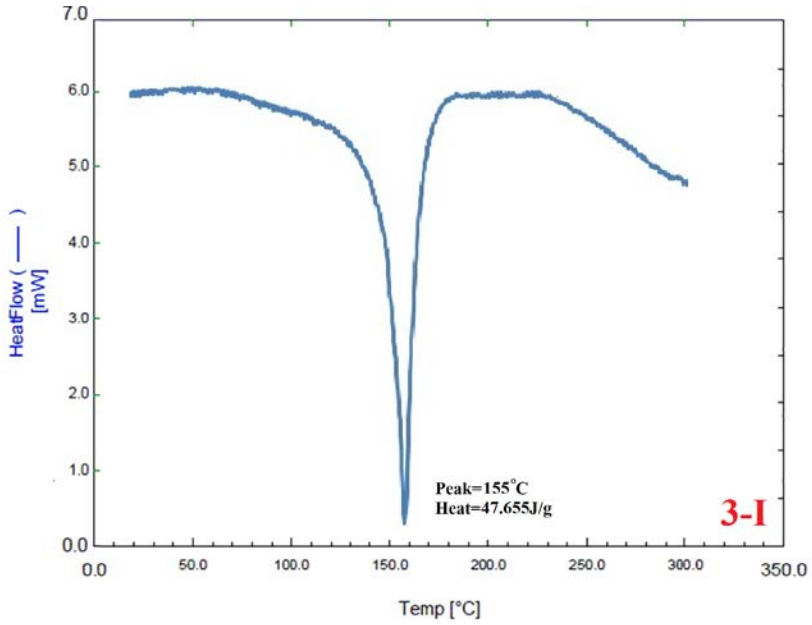
(a)



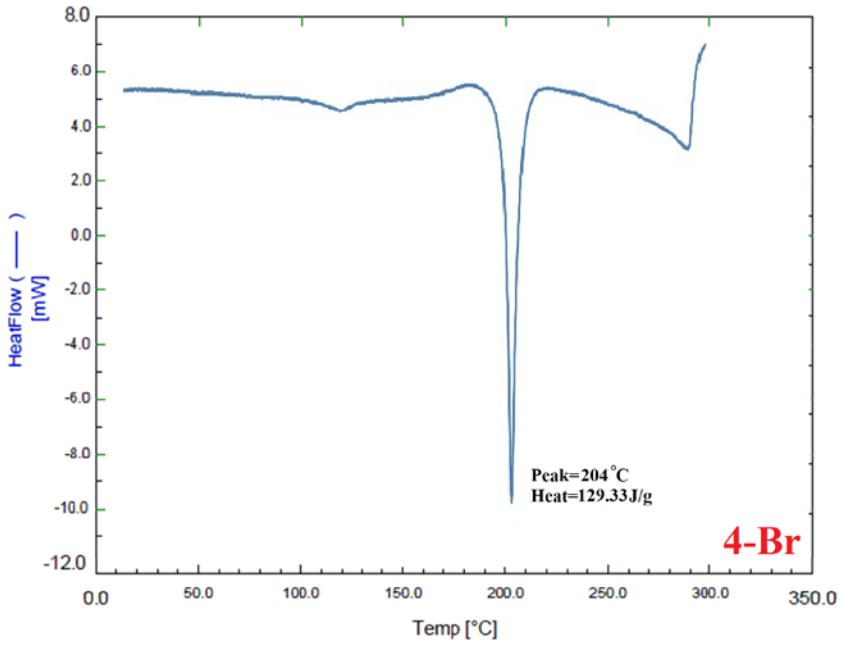
(b)



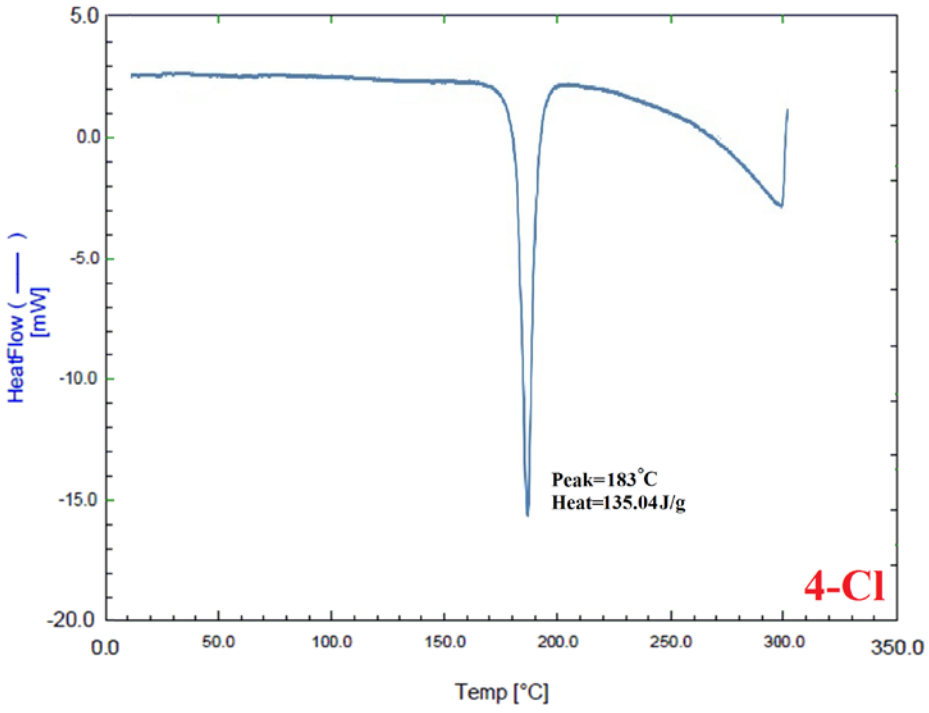
(c)



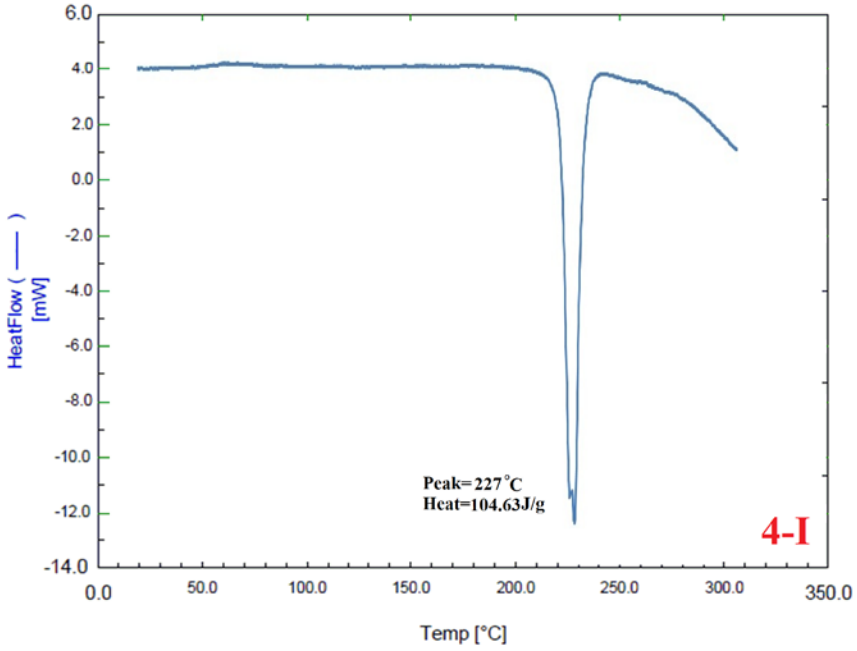
(d)



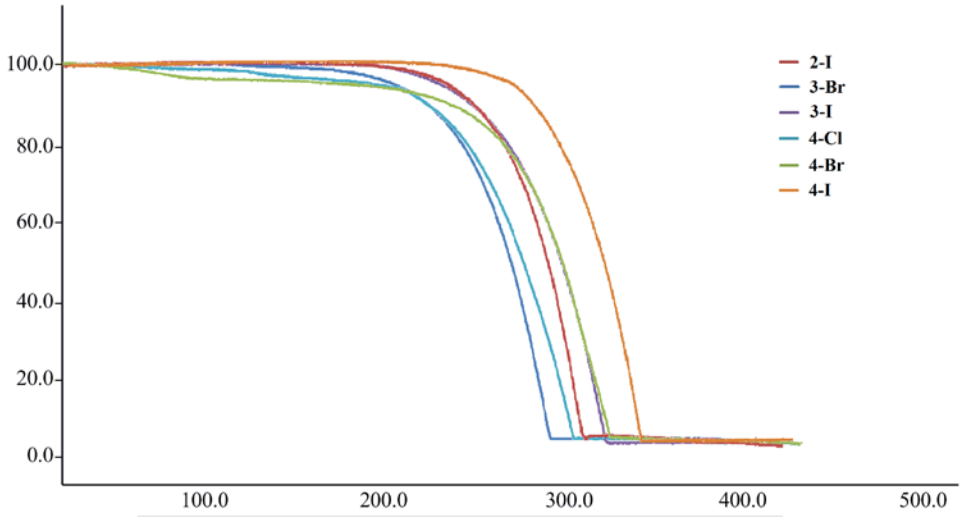
(e)



(f)

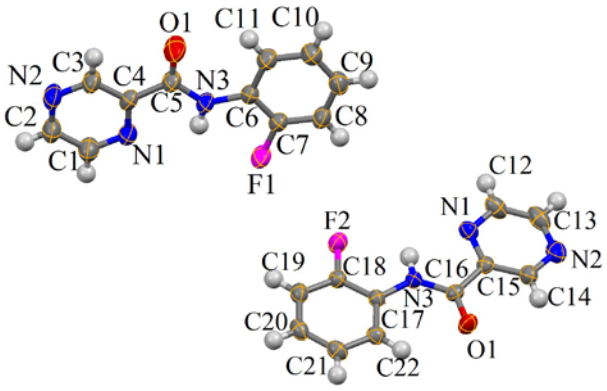


(g)

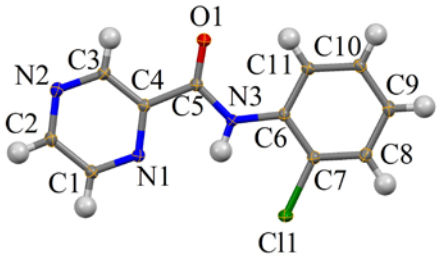


(h)

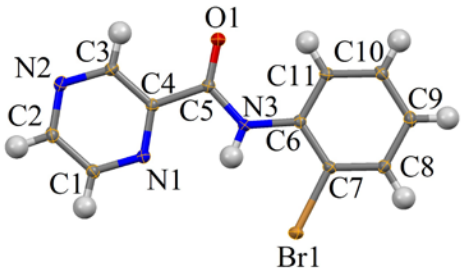
Figure S4. DSC plots of compounds **2-I**, **3-Br**, **3-I**, **4-Cl**, **4-Br** and **4-I**, (a) to (g) respectively and superimposed TGA plot of these compounds, (h).



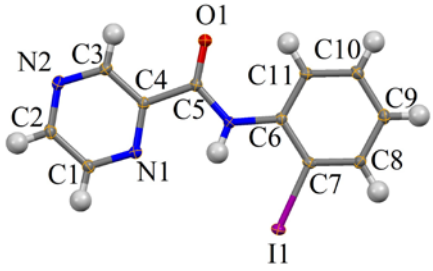
2-F



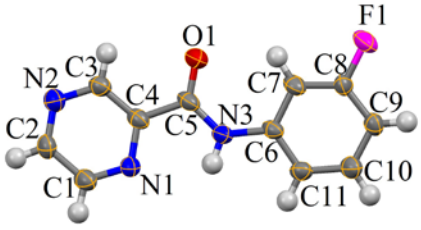
2-Cl



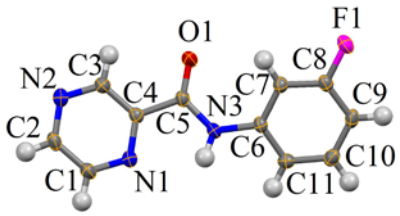
2-Br



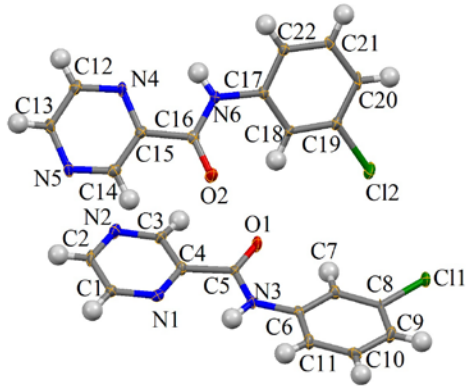
2-I



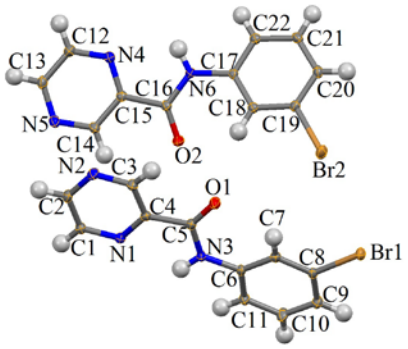
3-Fα



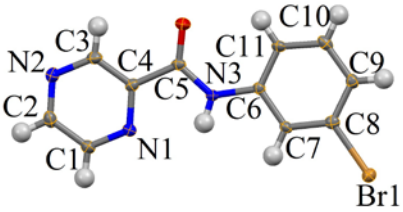
3-Fβ



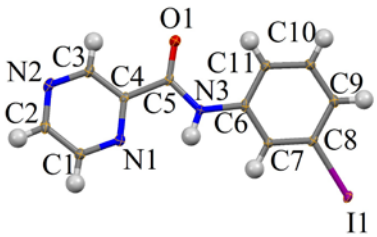
3-Cl



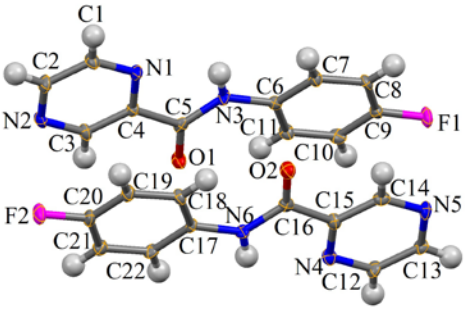
3-Brα



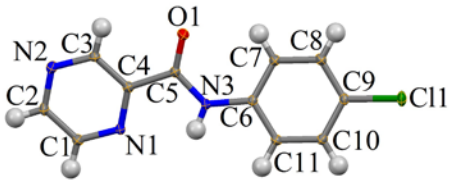
3-Brβ



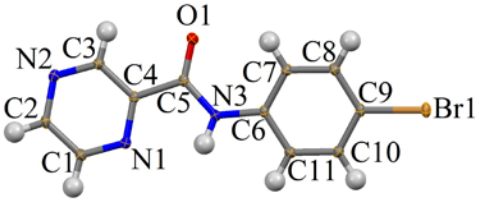
3-I



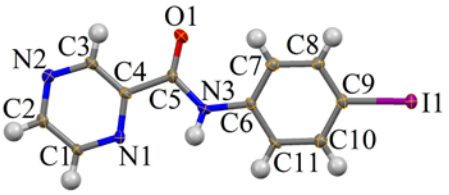
4-F



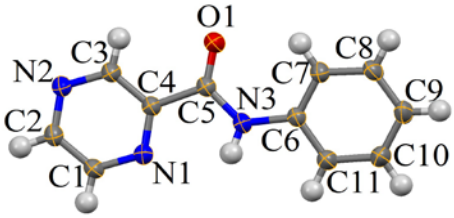
4-Cl



4-Br



4-I



H

Figure S5: *ORTEP* diagrams of compounds **n-X** drawn with 30% ellipsoid probability.

REFERENCE:

S1. H. Sun, *J. Phys. Chem. B*, 1998, **102**, 7338.