

Characteristic redshift and intensity enhancement as Far-IR fingerprints of the halogen bond involving aromatic donors

Vera Vasylyeva,^a Luca Catalano,^a Carlo Nervi,^b Roberto Gobetto,^b Pierangelo Metrangolo^{a,c} and Giuseppe Resnati^{a*}*

^a Laboratory of Nanostructured Fluorinated Materials (NFMLab), Department of Chemistry, Materials, and Chemical Engineering “Giulio Natta”, Politecnico di Milano, Via L. Mancinelli 7, 20131 Milan, Italy.

^b Department of Chemistry and NIS, University of Turin, via P. Giuria 7, 10125 Turin, Italy.

^c VTT-Technical Research Centre of Finland, Biologinkuja 7, 02150 Espoo, Finland.

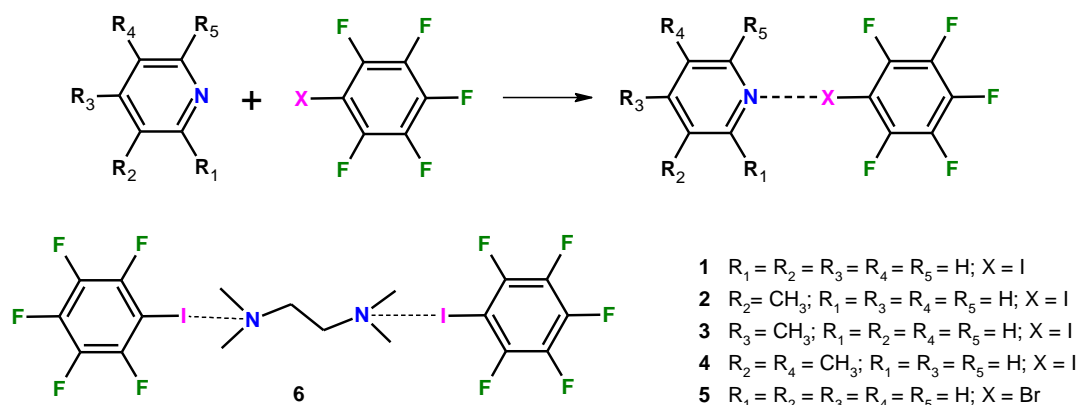
Electronic Supplementary Information

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S.1 Supramolecular synthesis

Starting materials pyridine, 3-methylpyridine, 4-methylpyridine, 3,5-dimethylpyridine, iodopentafluorobenzene (**IPFB**) and bromopentafluorobenzene (**BrPFB**) were purchased from commercial suppliers (Sigma-Aldrich, Apollo Scientific, and ABCR) and used without further purification. The six halogen-bonded cocrystals were synthesized by direct mixing of the liquid starting materials in either 1:1 (**1**, **2**, **3**, **4**, and **5**) and 1:2 (**6**) molar ratios, taking into account the pairing of the respective halogen-bond donor and acceptor sites. The liquid mixtures were stirred for 1h at room temperature. **2**, **3**, **4**, and **6** crystallized during mixing somewhere between 1 - 30 minutes.



S.2 Crystallization procedure and crystal structure determination

1 and **5** were *in situ* cryo-crystallized on the diffractometer in sealed 0.3 mm Lindemann capillaries according to a reported procedure.¹ Suitable crystals of **2**, **3**, **4** and **6** were, instead, chosen directly from the crystallized starting mixtures.

The crystals were diffracted using Mo-K α radiation on a Bruker KAPPA APEX II diffractometer with a Bruker KRYOFLEX low temperature device. The formation of cocrystals **3** and **4** was confirmed by the unit cell determination and comparison with previously reported data.²

Crystal structures of **1**, **2**, **5**, and **6** were solved by direct method and refined against F^2 using SHELXL97.³ Packing diagrams were generated using Mercury 3.5.⁴ Intermolecular interactions were analyzed with PLATON.⁵ The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using difference Fourier map or positioned geometrically.

S.3 Differential Scanning Calorimetry (DSC) data

DSC analyses were performed using a Mettler Toledo DSC 823e. 12-26 mg of each sample were enclosed in aluminum pans and measured with heating/cooling rates of 5 °C/min.

All the mixtures melted with single peaks at temperatures higher than both pure precursors indicating cocrystal formation.

Table S1. Experimental melting points (m.p.) of the starting compounds and the obtained cocrystals. Also indicated are the masses (mg) of the samples measured. Onset temperatures are given.

Compound/cocrystal	m.p. (°C)	m (mg)
Pyridine	-40	13.3
3-methylpyridine	-26	23.0
4-methylpyridine	-6	25.0
3,5-dimethylpyridine	-9	13.3
Tetramethylethylenediamine	-60	12.9
Iodopentafluorobenzene	-15	23.0
Bromopentafluorobenzene	-30	21.6
1	18	26.1
2	35	13.0
3	30	15.0
4	53	12.0
5	-22	15.3
6	50	14.2

S.4 Infrared (IR) spectroscopic data

IR spectra were obtained using a Nicolet iS50 FTIR spectrometer equipment with ATR device. For each sample, spectra were collected in the far-IR region (128 scans, 80-400 cm^{-1}) using solid-state substrate beam splitter. All the spectra were measured with a resolution of $\pm 4 \text{ cm}^{-1}$ and corrected with the baseline correction tool of the OMNIC[®] software.

The experimental intensity increase was calculated following the equation:

$$\Delta I = (I_{\text{C-I stretch.}} / I_{\text{ref.}})_{\text{co-crystal}} / (I_{\text{C-I stretch.}} / I_{\text{ref.}})_{\text{XB pure donor}}$$

Where $I_{\text{C-I stretch.}}$ is the intensity of the vibration band associated to the symmetric C-I in plane stretching and $I_{\text{ref.}}$ is the intensity of a reference peak, centered at around 310 cm^{-1} , which does not change passing from the starting material to the final adducts. To partially correct peak overlapping, all the spectra were deconvoluted using OMNIC[®] software tools to calculate the intensities. Partial band overlapping and deconvolution methods may affect intensity measurements, therefore these intensity variations have to be considered indicative. Calculated intensity increase (see herein after), instead, are not affected by peak overlapping.

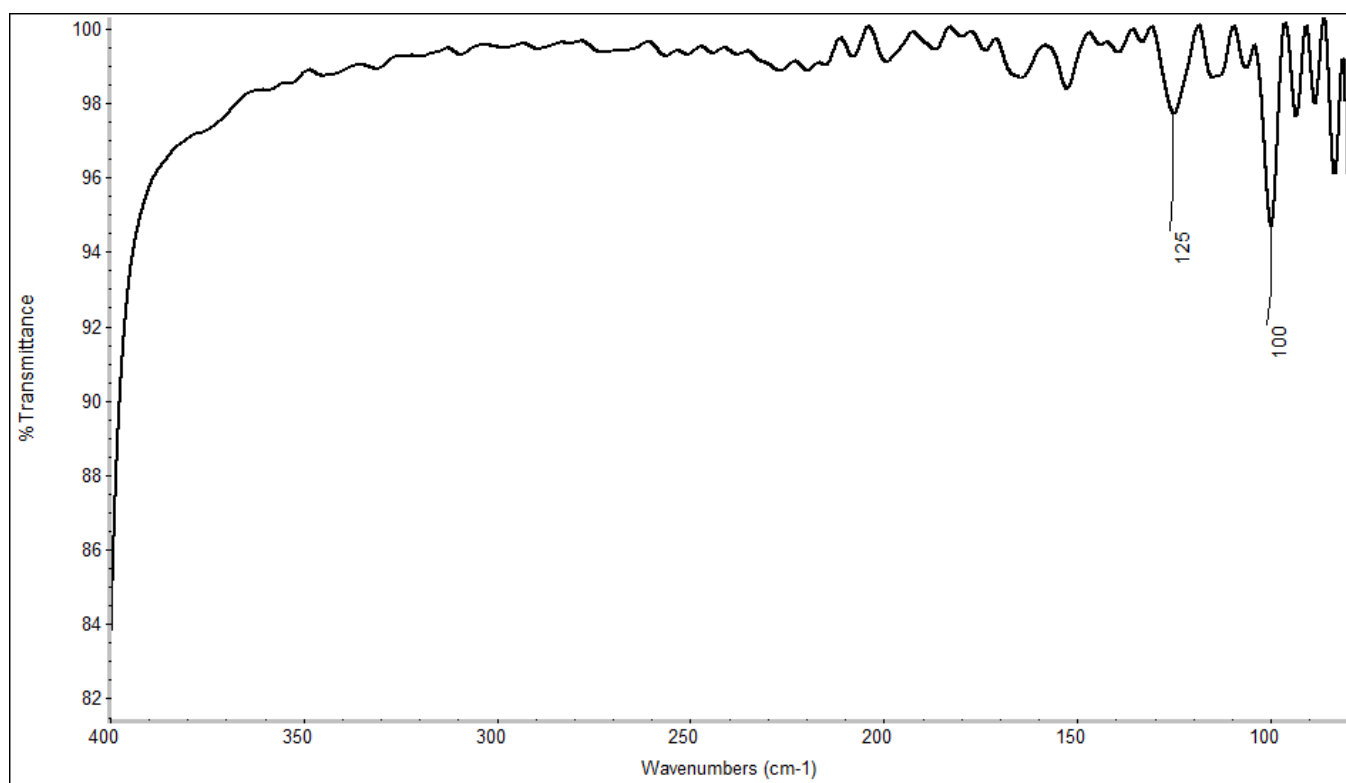


Figure S8. IR-spectra of pyridine from 80 to 400 cm^{-1} .

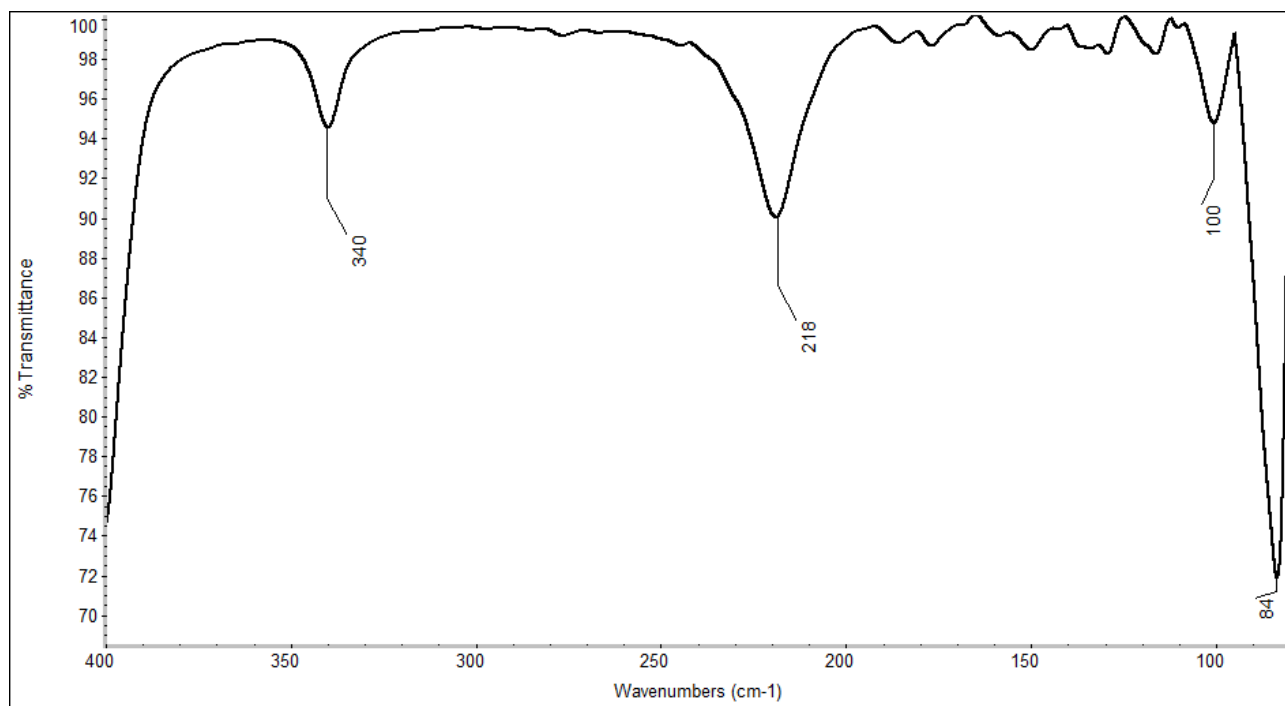


Figure S9. IR-spectra of 3-methylpyridine from 80 to 400 cm⁻¹.

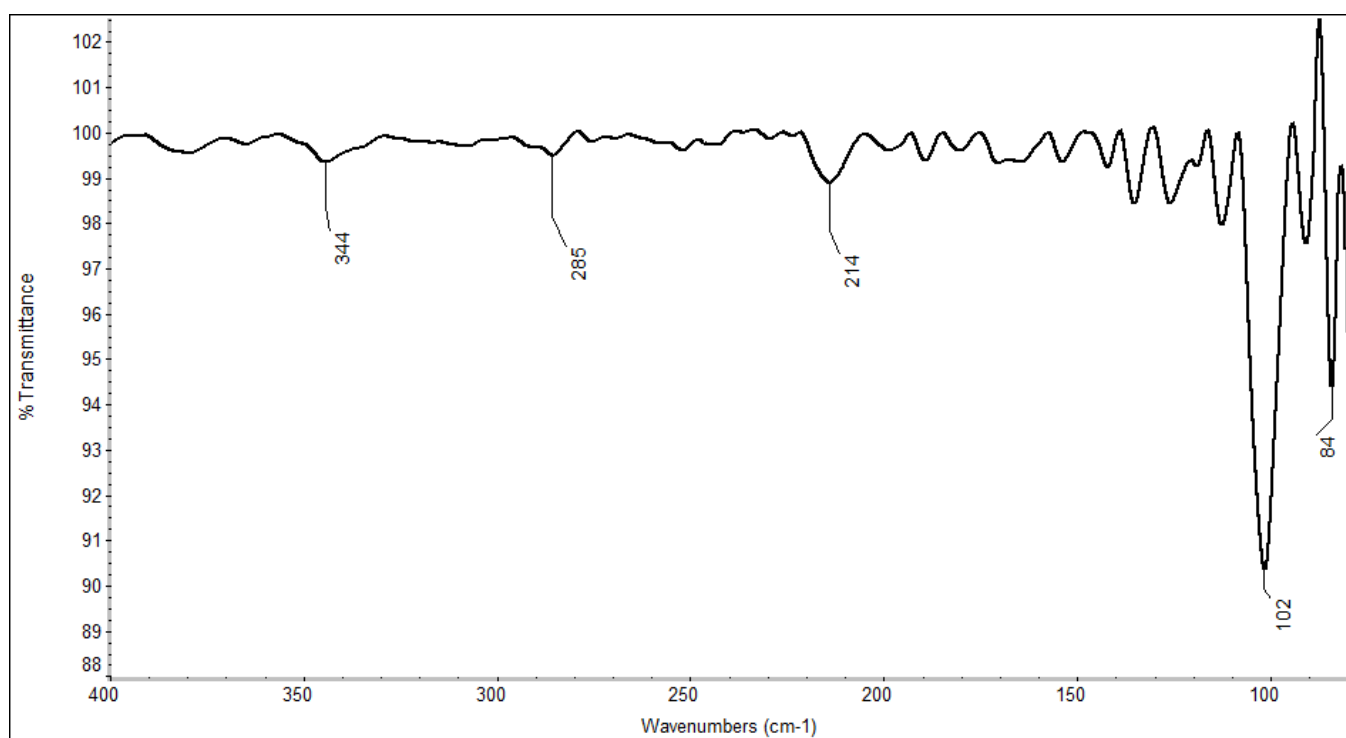


Figure S10. IR-spectra of 4-methylpyridine from 80 to 400 cm⁻¹.

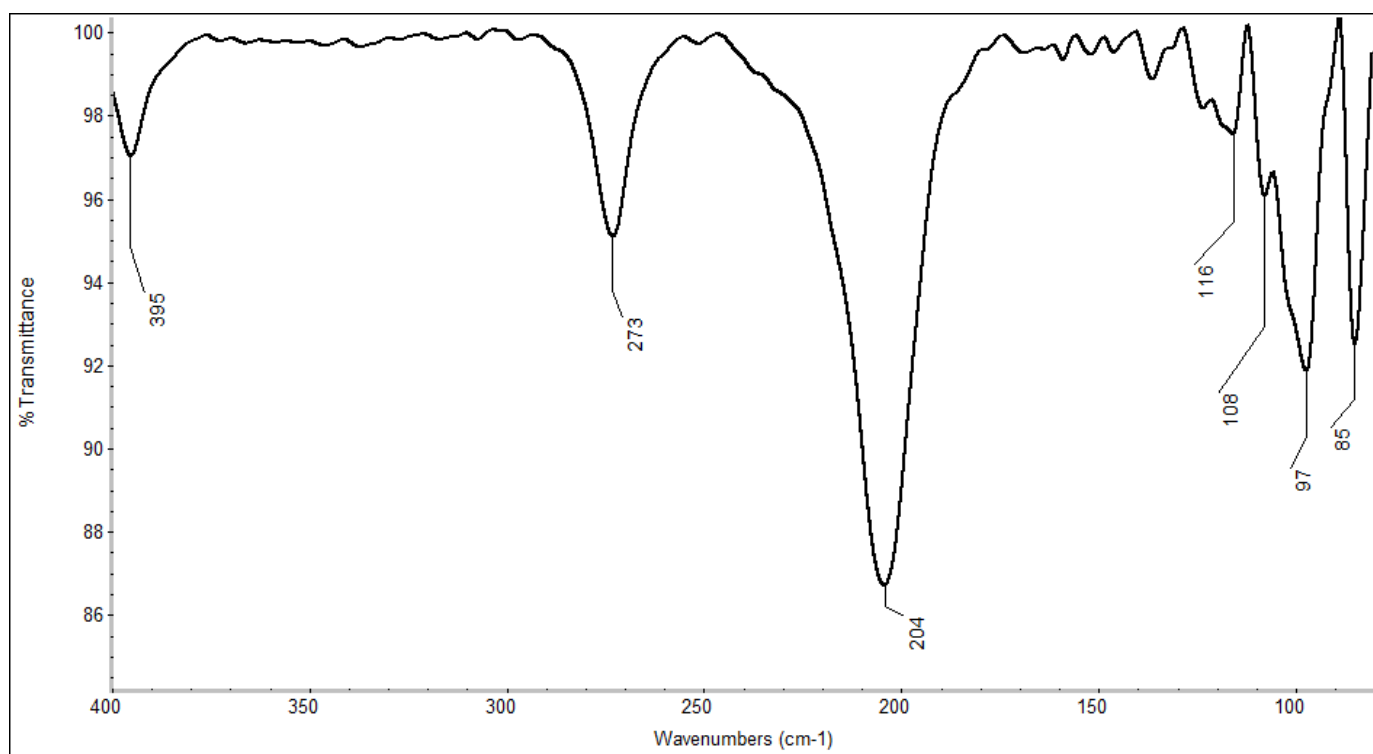


Figure S11. IR-spectra of 3,5-dimethylpyridine from 80 to 400 cm⁻¹.

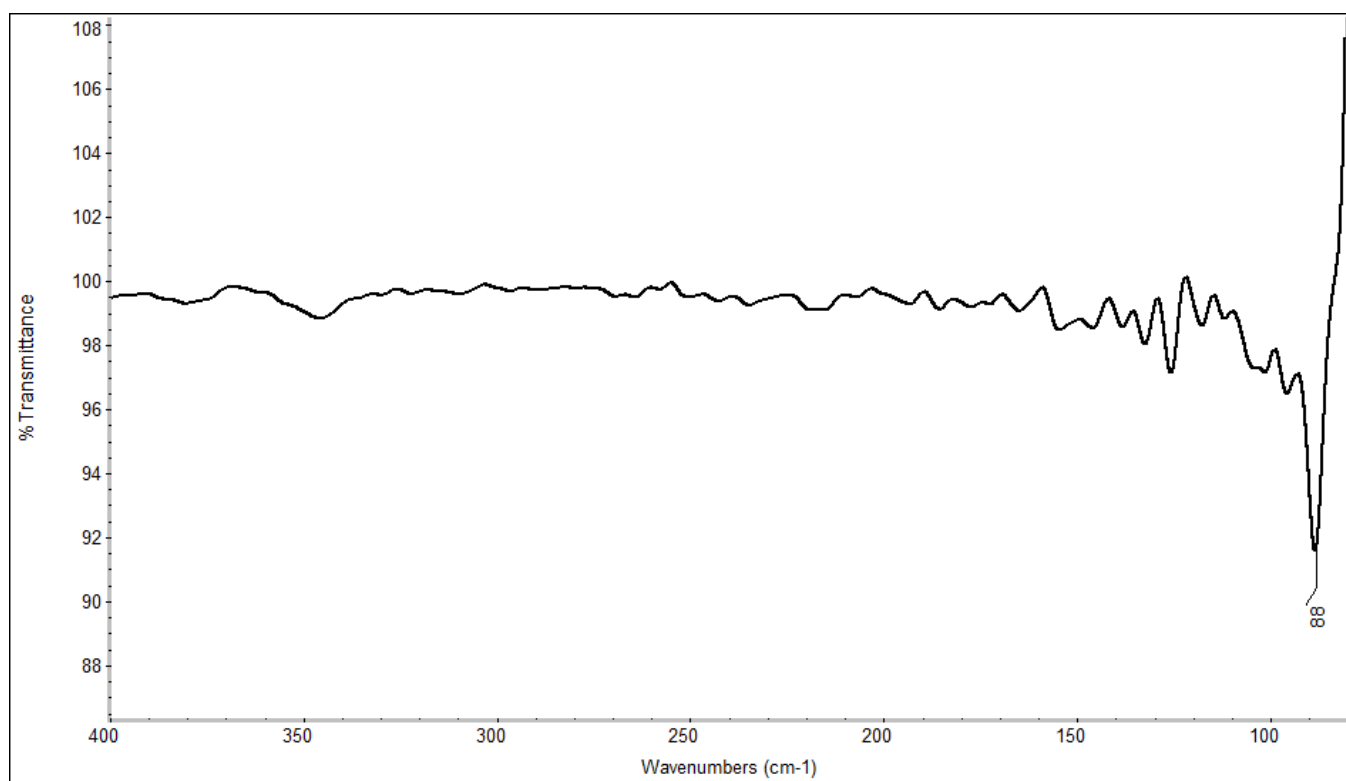


Figure S12. IR-spectra of tetramethylethylenediamine from 80 to 400 cm⁻¹.

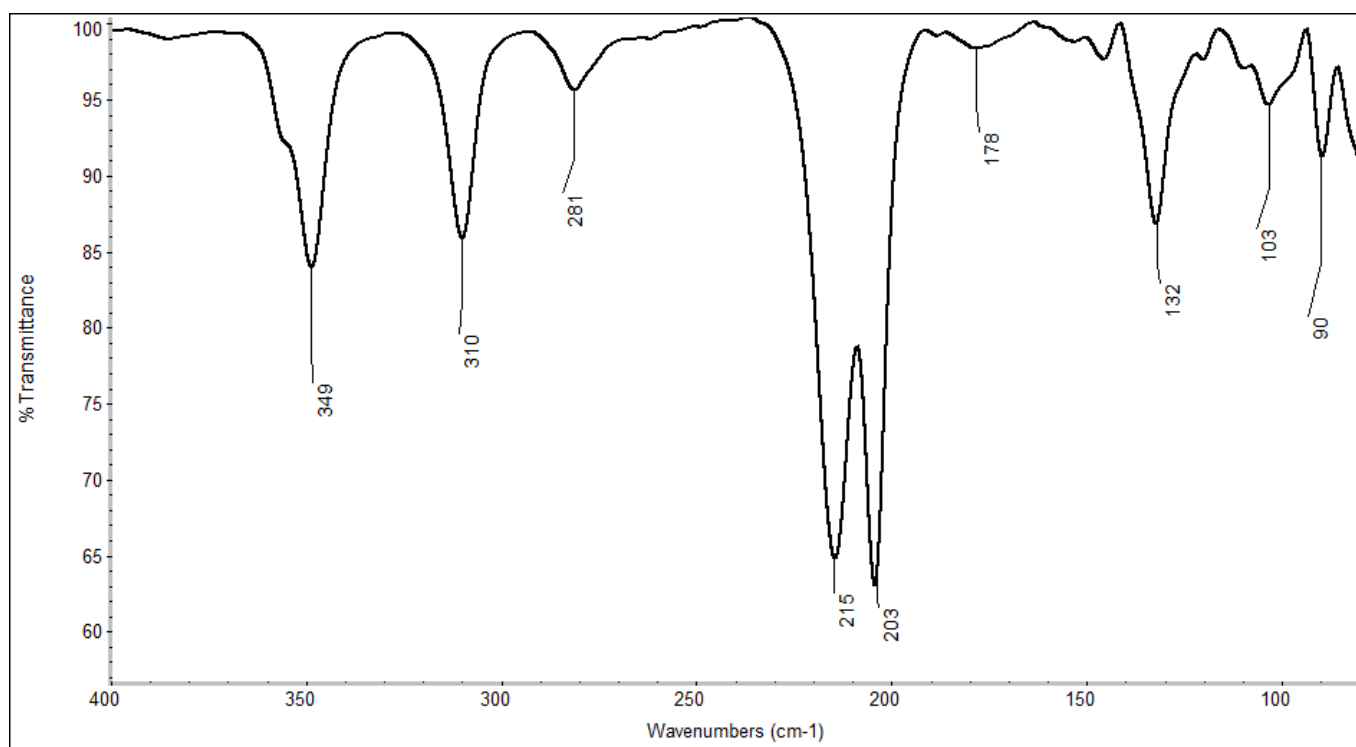


Figure S13. IR-spectra of iodopentafluorobenzene from 80 to 400 cm⁻¹.

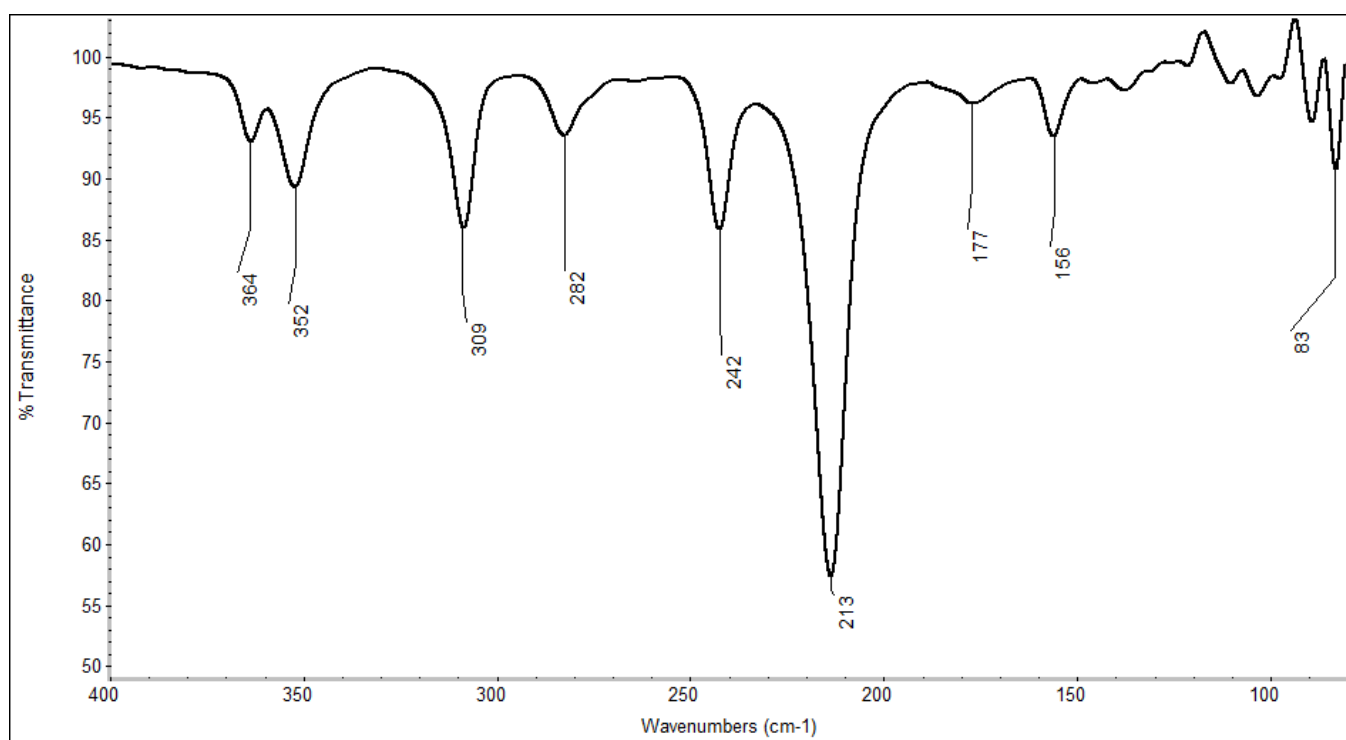


Figure S14. IR-spectra of bromopentafluorobenzene from 80 to 400 cm⁻¹.

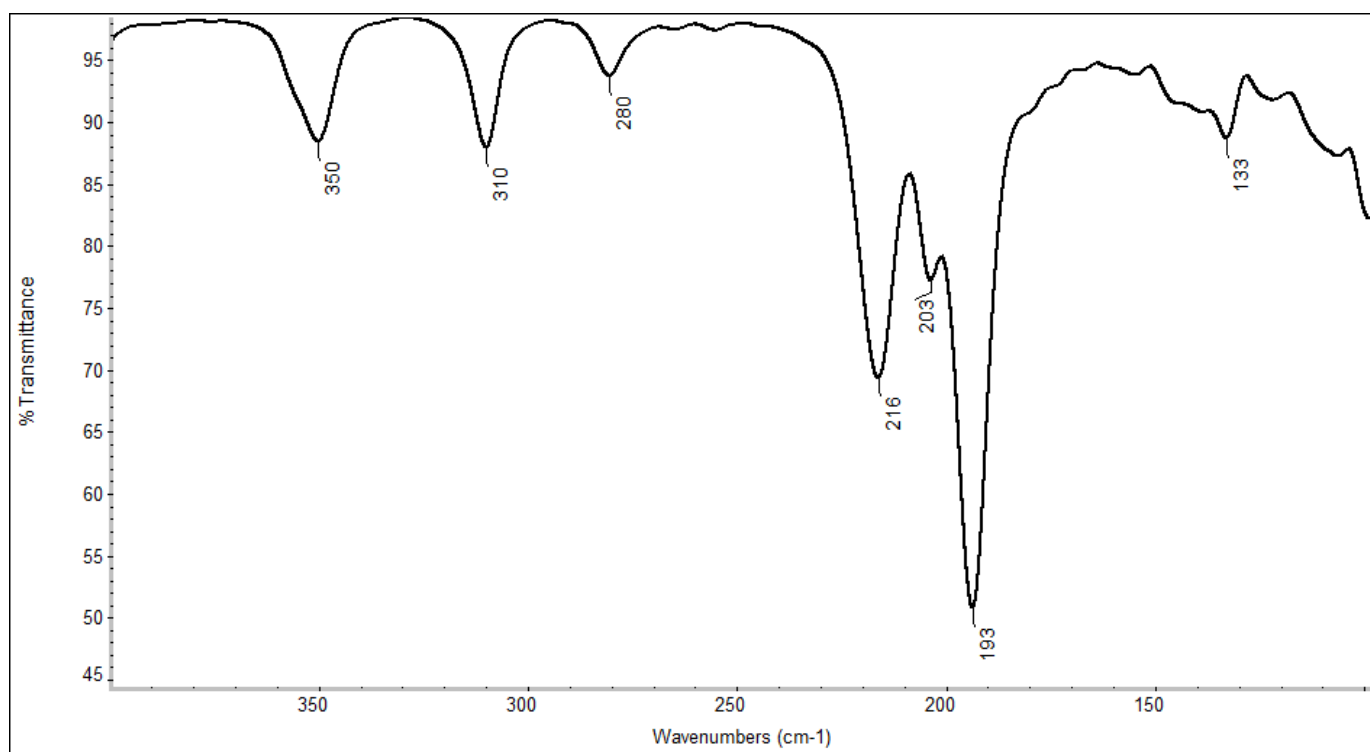


Figure S15. IR-spectra of **1** from 80 to 400 cm^{-1} .

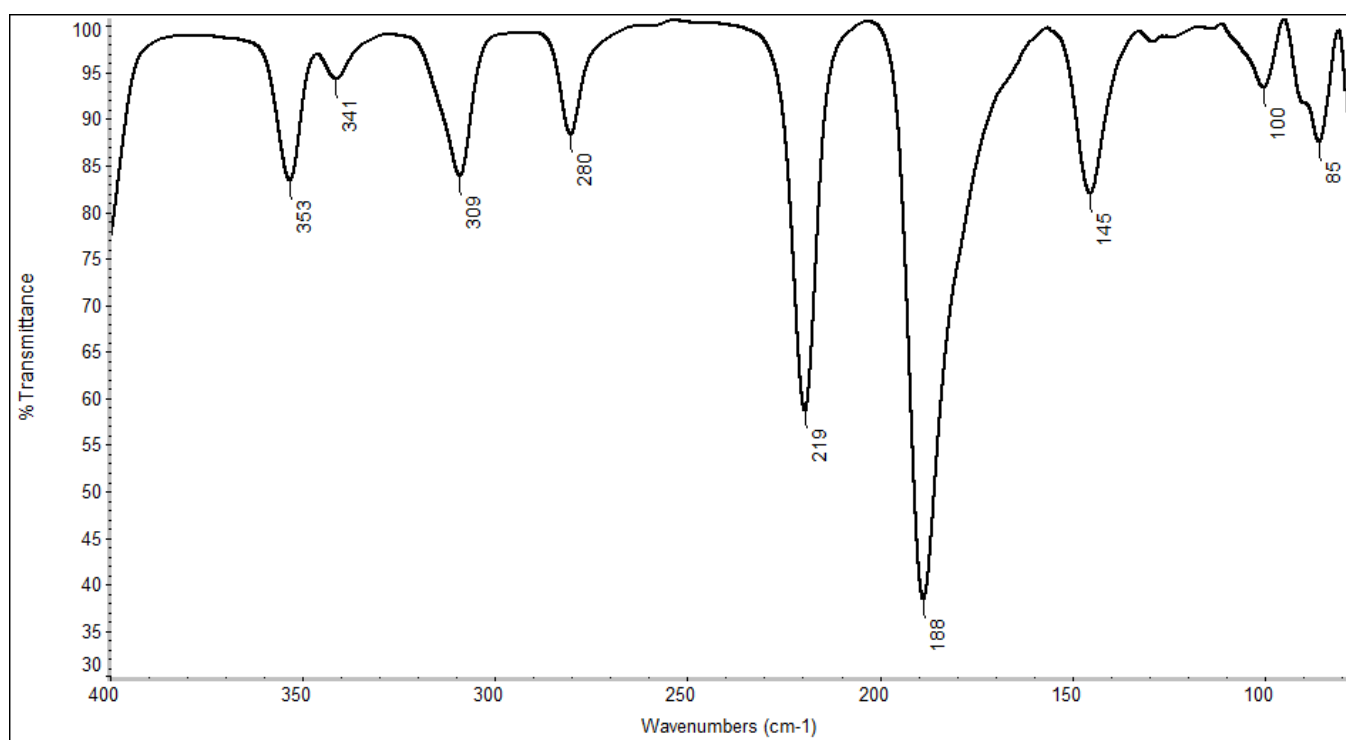


Figure S16. IR-spectra of **2** from 80 to 400 cm^{-1} .

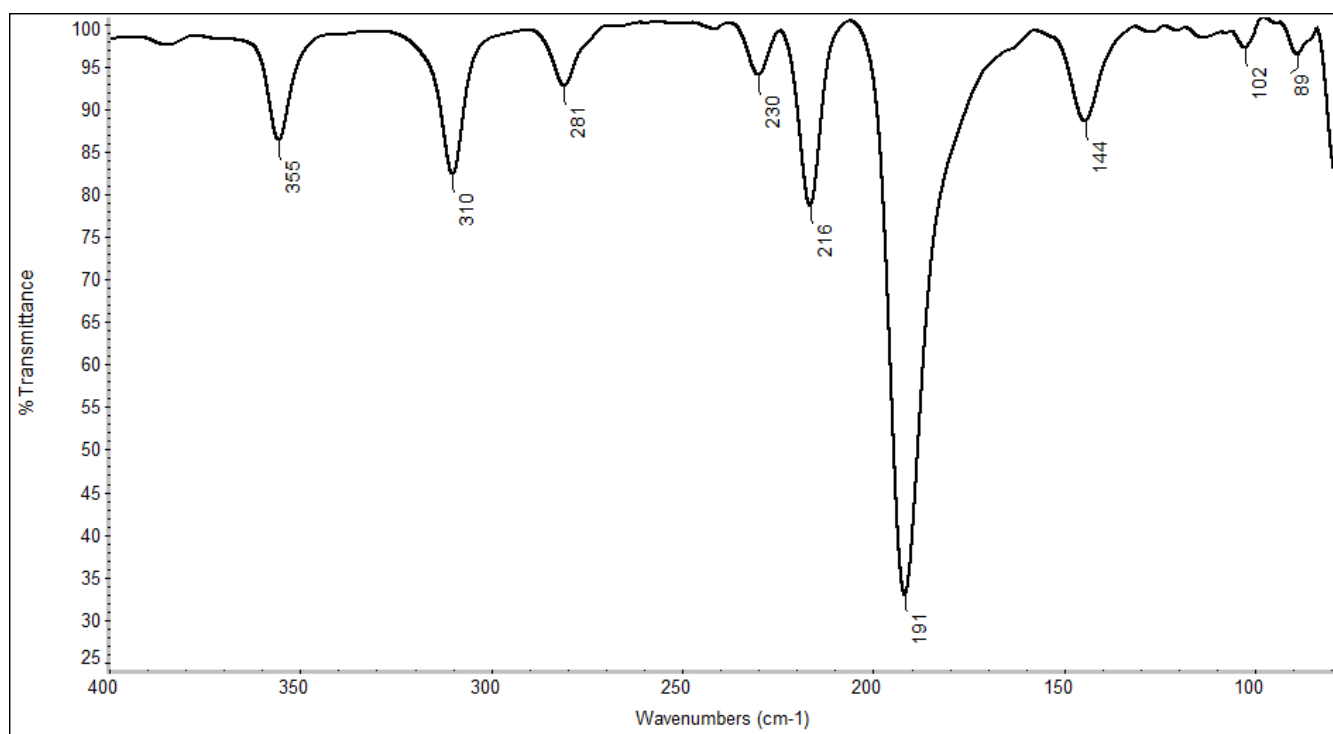


Figure S17. IR-spectra of **3** from 80 to 400 cm⁻¹.

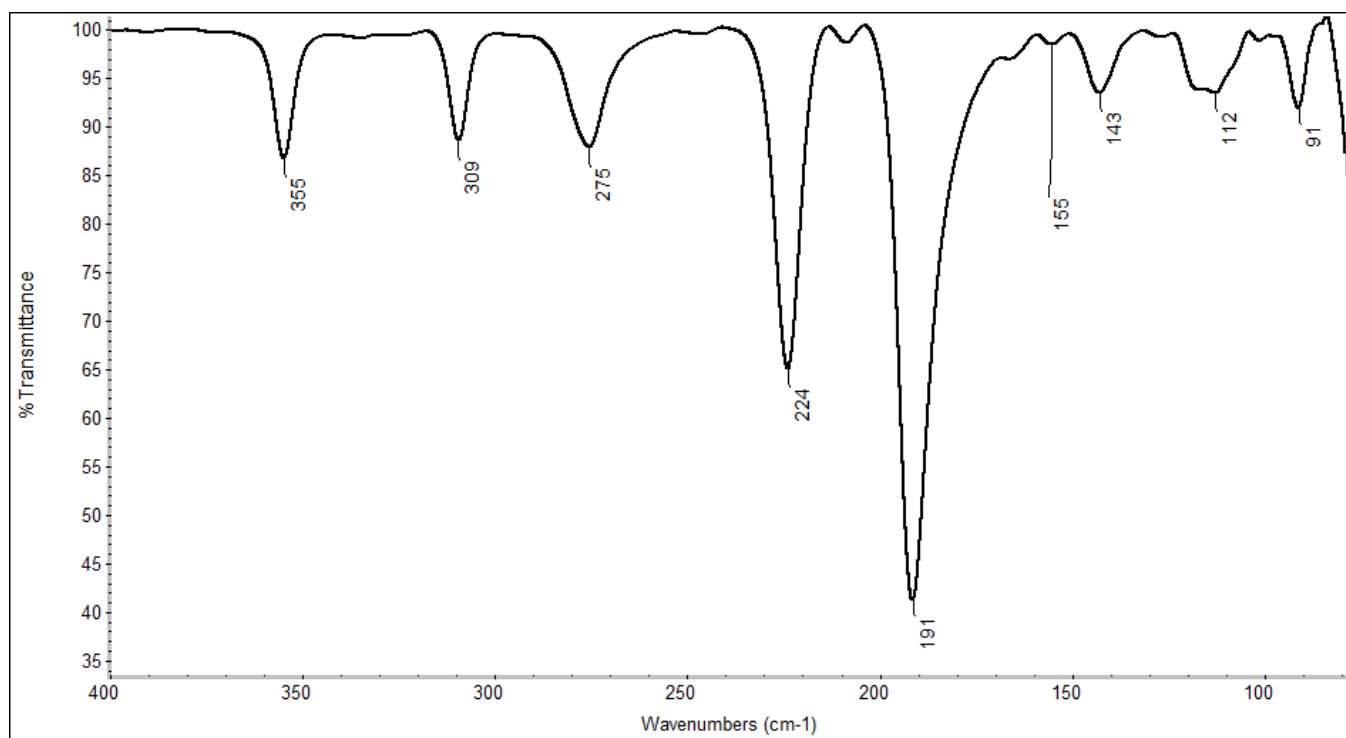


Figure S18. IR-spectra of **4** from 80 to 400 cm⁻¹.

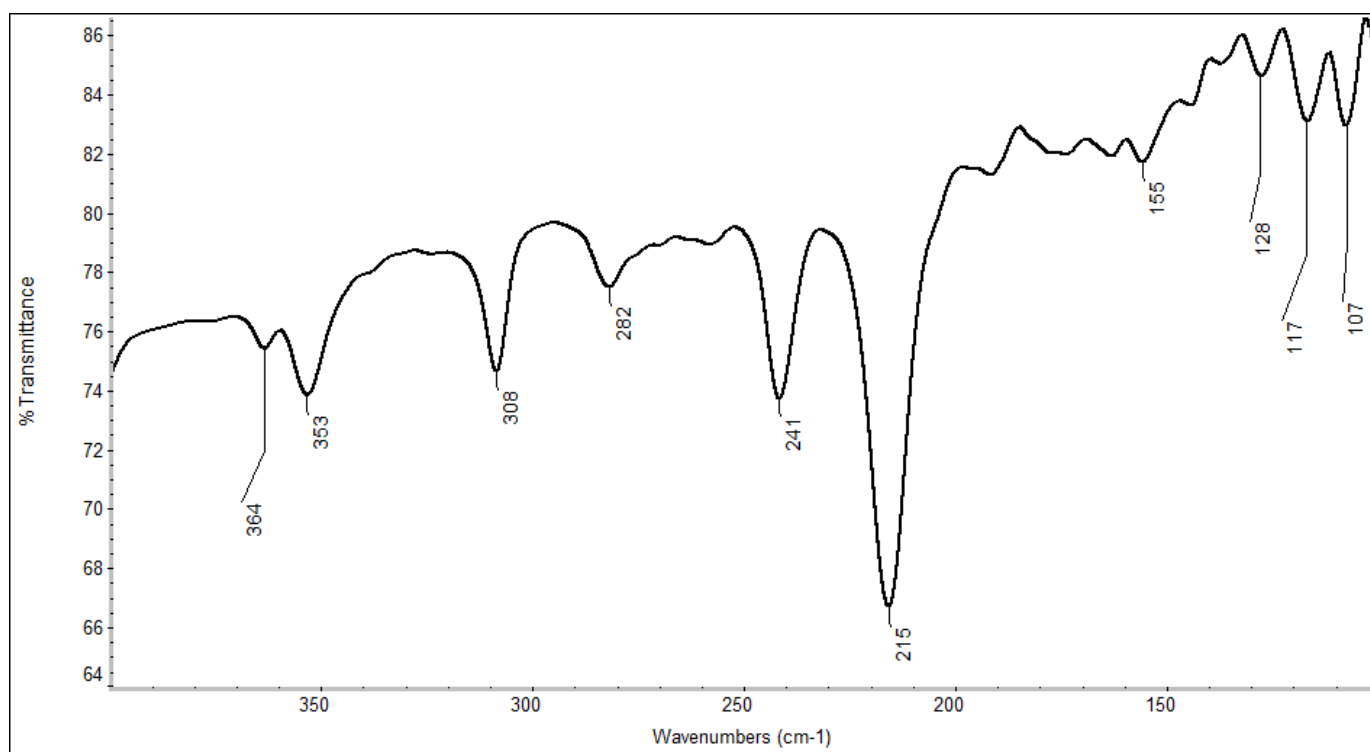


Figure S19. IR-spectra of **5** from 80 to 400 cm⁻¹.

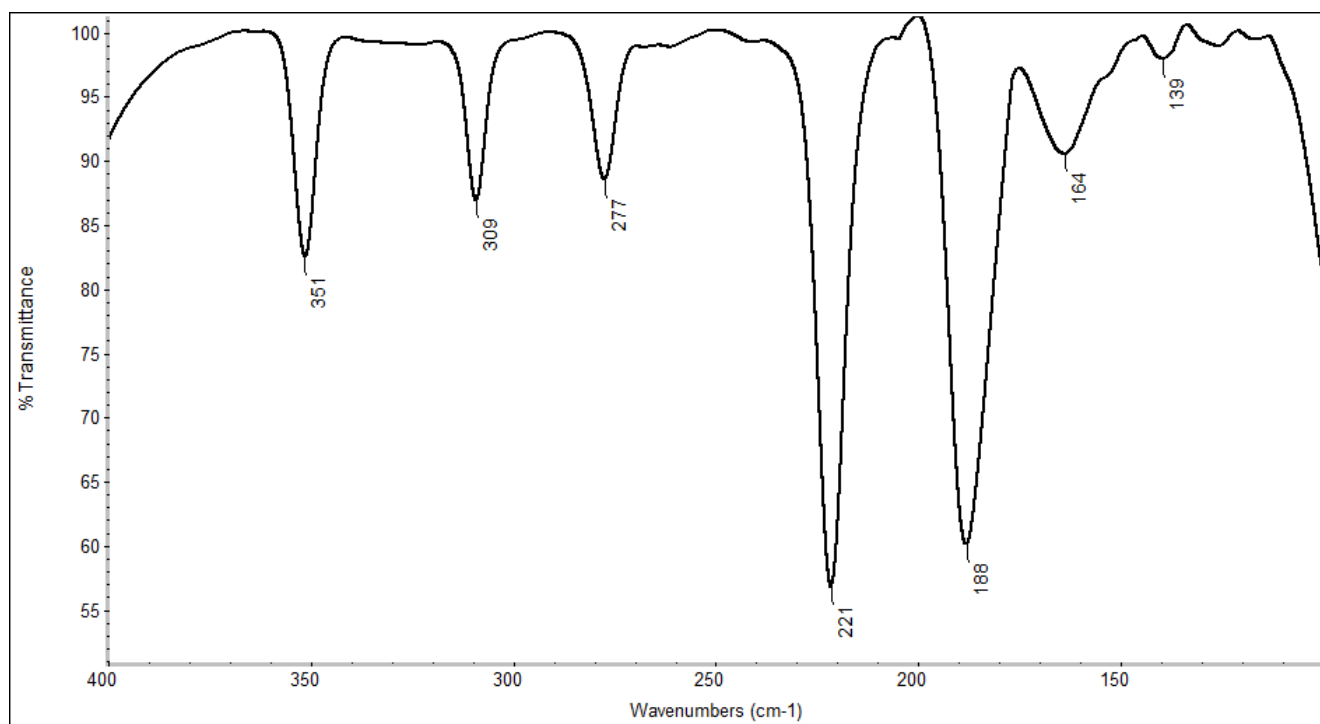


Figure S20. IR-spectra of **6** from 80 to 400 cm⁻¹.

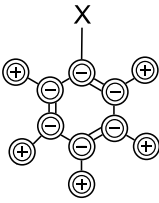
S.5 Theoretical calculations of IR spectra. Computational Details.

All calculations were performed with the Gaussian 09 (G09) program package⁶ employing the density functional theory (DFT) method with Becke's three parameter hybrid functional⁷ and Lee-Yang-Parr's gradient-corrected correlation functional (B3LYP).⁸ For iodine and bromine atoms the Los Alamos double- ζ (LanL2Dz)⁹ basis set and effective core potential, augmented with polarization functions of d symmetry and diffuse functions of p symmetry,¹⁰ were used. The 6-31+G(d,p) basis set was applied for all other atoms. The ground-state geometries of the adducts were optimized in the gas phase. This approximation does not take into account some weak interactions of the solid state, which would require a periodic plane-wave computational approach, but the results appear to be in good agreement with the experimental data, probably because in these class of complexes the nitrogen-halogen interactions observed in the adducts are very similar in the gas and in the solid state phases. The nature of all stationary points was confirmed by performing a normal-mode analysis, which finally gave the wave numbers of carbon-halogen stretching and bending modes.

For comparison purposes, in Table S2 calculations with the set base LanL2DZ (as implemented in Gaussian 09) are also reported.

Significant improvements are obtained adopting diffuse and polarization functions, i.e. passing from the B3LYP/LanL2DZ to the B3LYP/6-31+G(d,p)-LanL2DZdp basis set. As we focused on the vibrational analysis, counterpoise¹¹ correction has not been considered. On the other hand, the frequencies of the adduct **2**, computed for the single (1:1) or for the double (2:2) adducts are nearly equivalent in positions and intensities.

Table S3. Experimental and calculated IR vibrations (cm^{-1}) involving halogen bond with their calculated IR intensities (km mol^{-1}) and Raman scattering activities ($\text{\AA}^4 \text{amu}^{-1}$).

	Out of Plane C-X Bending		In plane C-X bending			In plane C-X stretching					
	Calc. ^{a)} IR Raman	Calc. ^{b)} IR Raman	Exp.	Calc. ^{a)}	Calc. ^{b)}	Exp.	Calc. ^{a)}	Calc. ^{b)}	Exp.	Calc. ^{a)}	Calc. ^{b)}
IPFB	80	80		132	132		203	204		205	212
	0.1217	0.0191	132	0.2467	0.2850	204	1.1451	0.9615	214	3.8759	3.2444
	0.0164	0.0597		2.3042	0.8032		2.8932	2.8986		1.1434	0.1841
BrPFB	88	90		152	155		237	243		205	212
	0.0569	0.0038	155	0.0723	0.1302	242	0.7576	0.4251	*	4.4098	3.7118
	0.0021	0.0211		2.0896	0.8445		2.8079	2.1457		0.5846	0.1269
1	109	103		151	149		185	192		208	215
	1.7179	0.4927	141	0.5846	0.3099	193	21.8538	16.2261	216.5	3.3296	3.1765
	2.3910	0.9563		1.0594	0.4550		32.4097	30.3179		1.8172	0.6853
2	110	104		149	147		184	191		208	215
	1.6271	0.4816	146	0.5900	0.3080	188	23.8546	17.7118	219	3.0826	3.5131
	1.9420	0.8968		1.1592	0.5127		34.7700	32.9400		1.7269	0.8192
2^{c)}		104			147			190			215
		0.4343	146		0.3962	188		17.1949	219		3.0070

		0.9430			0.5924			29.2215			0.5769
		106			148			191			216
		0.4426			0.3258			17.9952			4.5085
		0.9002			0.4407			32.5548			0.9734
3	102	98	143	150	148	192	184	191	216	207	213
	0.7985	0.1692		0.5300	0.2922		24.5695	18.2823		3.4257	2.7401
	0.5821	0.1725		1.4967	0.6817		36.5004	34.5285		0.8829	0.0922
4	109	104	143	147	146	191	183	190	223.5	208	215
	1.5691	0.4436		0.4144	0.2307		25.9622	19.2274		3.7960	3.2827
	1.2573	0.5974		1.1048	0.4621		37.1966	35.6561		2.0601	0.7730
5	107	106	155	167	168	241	224	236	*	208	214
	0.8515	0.2070		0.2200	0.1180		17.8165	9.4157		4.0193	3.6991
	1.2606	0.4811			0.6153		53.5201	29.0803		1.1202	0.4773
6	84 IR	83	*	137	139	188	183	189	221	208	215
	0.9968	10.4422		1.0439	0.4451		24.0720	36.8477		7.2474	6.4791

* too low intensity to be detected ^{a)} B3LYP/LanL2DZ; ^{b)} B3LYP/6-31+G(d,p)-LanL2DZdp; ^{c)} This is the adduct **2** with ratio 2:2 computed with four molecules (two XB interactions). ^{d)} Raman intensities are zero because symmetry.

The pyridine ring stretching mode that involves the N atom computed at 1010 (IR intensity 5.6304) is shifted to 1020 cm^{-1} (19.3638) in the **1** adduct, whereas the other pyridine ring stretching mode (that does not involve the N atom) at 1045 cm^{-1} (4.6134) are not shifted after adduct formation (IR intensity 1.1338). In the **1** adduct an intense iodopentafluorobenzene ring stretching is computed at 1088 cm^{-1} (137.0467).

Optimized geometry at B3LYP/6-31+G(d,p) level, with LanL2Dz basis set, with polarization functions of d symmetry and diffuse functions of p symmetry, for I and Br atoms:

Iodopentafluorobenzene

C	0.00000000	0.00000000	-2.59460000
C	0.00000000	1.20571400	-1.89600200
C	0.00000000	1.19758100	-0.50231800
C	0.00000000	0.00000000	0.21751000
C	0.00000000	-1.19758100	-0.50231800
C	0.00000000	-1.20571400	-1.89600200
F	0.00000000	2.37758100	0.13384800
F	0.00000000	-2.36543500	-2.56586000
F	0.00000000	-2.37758100	0.13384800
F	0.00000000	0.00000000	-3.93136600
F	0.00000000	2.36543500	-2.56586000
I	0.00000000	0.00000000	2.30567700

Bromopentafluorobenzene

C	0.00000000	0.00000000	-2.17670500
C	0.00000000	1.20604900	-1.47839100
C	0.00000000	1.20045600	-0.08469900
C	0.00000000	0.00000000	0.63111500
C	0.00000000	-1.20045600	-0.08469900
C	0.00000000	-1.20604900	-1.47839100
F	0.00000000	2.37541500	0.55690200

F	0.00000000	-2.36550700	-2.14786900
F	0.00000000	-2.37541500	0.55690200
F	0.00000000	0.00000000	-3.51344000
F	0.00000000	2.36550700	-2.14786900
Br	0.00000000	0.00000000	2.52254200

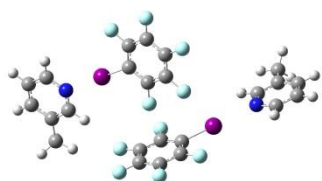
Pyridine•Iodopentafluorobenzene (1)

I	-0.74764800	-0.00003500	0.00001700
F	1.46072300	-2.37845500	0.00003500
C	1.36671500	-0.00001000	0.00000500
F	4.15893400	-2.36626900	0.00001800
F	5.52657400	0.00004600	-0.00002100
F	1.46066000	2.37843900	-0.00002700
F	4.15887000	2.36632400	-0.00004400
C	2.09380400	-1.19197400	0.00001500
C	3.48739200	-1.20449200	0.00000700
C	4.18717900	0.00002800	-0.00001300
C	3.48735900	1.20453000	-0.00002400
C	2.09377100	1.19197400	-0.00001500
C	-4.31381400	1.15058300	0.00007600
N	-3.62490200	-0.00000500	0.00002300
C	-4.31385300	-1.15057100	-0.00006200
H	-3.72221900	2.06310400	0.00014500
C	-5.70924600	1.20146300	0.00004700
H	-6.21898300	2.15965800	0.00009200
C	-6.42051200	0.00004100	-0.00004200
H	-7.50669500	0.00006000	-0.00006800
C	-5.70928600	-1.20140500	-0.00009800
H	-6.21905500	-2.15958200	-0.00016700
H	-3.72228700	-2.06311000	-0.00010300

3-Methylpyridine•Iodopentafluorobenzene (2)

H	-3.53494900	1.70487200	0.00012400
C	-4.07466700	0.75953100	0.00007500
C	-5.47534700	0.74943300	0.00005900
H	-7.18227100	-0.57676800	-0.00002400
C	-6.09692300	-0.50729100	-0.00000700
H	-5.77829700	-2.64867100	-0.00010300
C	-5.32006300	-1.66463200	-0.00005200
H	-3.28447600	-2.41317800	-0.00006300
C	-3.92934700	-1.53777200	-0.00003000
N	-3.31721200	-0.34687600	0.00003200
C	-6.26901200	2.03273800	0.00011200
H	-6.91490200	2.09915600	-0.88277500
H	-6.91487700	2.09909800	0.88302200
H	-5.61131400	2.90639600	0.00013200
I	-0.46077900	-0.15691400	0.00001400
F	1.90682600	-2.37897400	-0.00010800
F	4.59786600	-2.18263400	-0.00013700
F	5.80090900	0.27153000	-0.00005500

F	4.27470100	2.53902100	0.00005800
F	1.58212000	2.36695600	0.00008800
C	1.65017200	-0.01251600	-0.00000800
C	2.45723300	-1.15179300	-0.00006500
C	3.84845100	-1.06933000	-0.00008100
C	2.29454600	1.22605300	0.00003300
C	3.68399900	1.33392600	0.00001800
C	4.46446600	0.18008000	-0.00003900



3-Methylpyridine•Iodopentafluorobenzene (2), 2:2 adduct

I	3.45010000	-1.05687100	0.39034600
F	0.76818700	-2.68657700	-0.45097600
F	-1.52284200	-3.23609800	0.86440700
F	-1.88660000	-2.35687400	3.42514400
F	0.07786000	-0.91425400	4.66607800
F	2.37721000	-0.35472000	3.37069100
C	1.65378300	-1.49996800	1.41461800
C	0.63254400	-2.23333600	0.80871000
C	-0.55555100	-2.52465800	1.47401300
C	1.43787900	-1.06562600	2.72380600
C	0.25684300	-1.34599000	3.40838200
C	-0.74569300	-2.07944300	2.77913200
H	-3.65526700	-2.60567300	-0.45569600
C	-4.57370800	-2.55868400	-1.03666900
C	-5.28026500	-3.73224800	-1.33063700
H	-7.04282000	-4.46844300	-2.34202400
C	-6.45382000	-3.59120600	-2.08418100
H	-7.76730700	-2.19066900	-3.08523200
C	-6.86233300	-2.32503900	-2.50095000
H	-6.36191400	-0.21523900	-2.45480800
C	-6.08186200	-1.22121900	-2.15170500
N	-4.95802500	-1.33612900	-1.43272500
C	-4.79290800	-5.07802600	-0.85281100
H	-5.53119300	-5.55653900	-0.19913400
H	-4.61425200	-5.75600100	-1.69520000
H	-3.85885900	-4.98500100	-0.29244000
C	6.10343600	-0.86912300	-2.24375300
C	6.83208200	0.30832500	-0.40516900
N	5.88705300	-0.43574300	-0.99353000
I	-3.38147400	0.91723200	-0.72315900
H	5.30862100	-1.46962500	-2.68273900
C	7.26298200	-0.59188700	-2.97901900
H	9.16155700	0.43553600	-2.86749900
C	8.24033900	0.18816400	-2.34499300
H	8.76817900	1.25056800	-0.53399100

C	8.02676200	0.64474600	-1.04545600
H	6.62279500	0.64340400	0.60780300
C	7.44325300	-1.11034300	-4.38458700
H	8.33087600	-1.74862900	-4.46091100
H	7.57051300	-0.28743000	-5.09715600
H	6.57898000	-1.69912800	-4.70440700
F	-0.79794400	1.22932700	1.21674400
F	0.72338600	3.34527100	1.91306900
F	0.17412000	5.82873600	0.90965400
F	-1.92552300	6.17226300	-0.80557200
F	-3.46206300	4.07062700	-1.51489200
C	-2.18382300	2.57569800	-0.17433600
C	-1.10414200	2.43433400	0.69871200
C	-0.30679000	3.51482100	1.07053500
C	-2.43863600	3.85612000	-0.66866500
C	-1.65589300	4.95305500	-0.31304500
C	-0.58488100	4.78112800	0.56092900

4-Methylpyridine•Iodopentafluorobenzene (3)

I	0.39686900	0.00000500	-0.00324500
F	-1.81389800	2.37852700	-0.00024300
F	-4.51197600	2.36635100	0.00345600
F	-5.87979200	-0.00000700	0.00535000
F	-4.51196600	-2.36635900	0.00350100
F	-1.81388900	-2.37852500	-0.00019800
C	-1.71921400	0.00000100	-0.00033900
C	-2.44671400	1.19164800	0.00063000
C	-3.84030500	1.20441800	0.00254300
C	-4.54018700	-0.00000400	0.00350800
C	-3.84030000	-1.20442400	0.00256600
C	-2.44670900	-1.19164800	0.00065300
N	3.25682200	-0.00000100	-0.00547400
C	3.95200900	1.14673600	-0.00627200
H	3.36606500	2.06302300	-0.00919100
C	5.34570200	1.19416700	-0.00694900
H	5.85122400	2.15584300	-0.01187400
C	6.07954300	-0.00000200	-0.00472600
C	5.34570100	-1.19417000	-0.00705600
H	5.85122200	-2.15584600	-0.01206600
C	3.95200800	-1.14673800	-0.00637500
H	3.36606300	-2.06302500	-0.00937400
C	7.58734000	-0.00000400	0.02493300
H	7.99676100	-0.88740100	-0.46651900
H	7.99676200	0.88745100	-0.46641200
H	7.95052100	-0.00006800	1.06024500

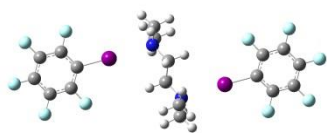
3,5-Dimethylpyridine•Iodopentafluorobenzene (4)

N	0.00000000	0.00000000	3.06539800
C	0.00000000	1.15113000	3.74880200
H	0.00000000	2.06240000	3.15376600

C	0.00000000	1.21740300	5.14805200
C	0.00000000	0.00000000	5.83870900
H	0.00000000	0.00000000	6.92772800
C	0.00000000	-1.21740300	5.14805200
C	0.00000000	-1.15113000	3.74880200
H	0.00000000	-2.06240000	3.15376600
C	0.00000000	2.54276400	5.87021100
H	0.00000000	3.37871000	5.16516200
H	0.88290800	2.64502700	6.51140400
H	-0.88290800	2.64502700	6.51140400
C	0.00000000	-2.54276400	5.87021100
H	-0.88290800	-2.64502700	6.51140400
H	0.88290800	-2.64502700	6.51140400
H	0.00000000	-3.37871000	5.16516200
I	0.00000000	0.00000000	0.21452000
F	0.00000000	-2.37859200	-1.99782900
F	0.00000000	-2.36638800	-4.69584600
F	0.00000000	0.00000000	-6.06373300
F	0.00000000	2.36638800	-4.69584600
F	0.00000000	2.37859200	-1.99782900
C	0.00000000	0.00000000	-1.90278500
C	0.00000000	-1.19146600	-2.63049500
C	0.00000000	-1.20437400	-4.02408800
C	0.00000000	0.00000000	-4.72402100
C	0.00000000	1.20437400	-4.02408800
C	0.00000000	1.19146600	-2.63049500

Pyridine•Bromopentafluorobenzene (5)

Br	0.71049800	-0.00001000	0.00002800
F	-1.27559100	-2.37627600	-0.00002000
F	-3.97836300	-2.36610400	-0.00009000
F	-5.34607300	0.00001100	-0.00012900
F	-3.97834600	2.36611700	-0.00009700
F	-1.27557500	2.37627100	-0.00002700
C	-1.19234200	-0.00000300	-0.00002000
C	-1.91431000	-1.19641400	-0.00003700
C	-3.30783100	-1.20493300	-0.00007400
C	-4.00726700	0.00000600	-0.00009400
C	-3.30782300	1.20494100	-0.00007700
C	-1.91430200	1.19641300	-0.00004100
N	3.62446400	-0.00000900	0.00009500
C	4.31664300	1.14824100	0.00005300
H	3.72693900	2.06236100	0.00001400
C	5.71270400	1.20096000	0.00005900
H	6.22223500	2.15947200	0.00002400
C	6.42471100	0.00001500	0.00011100
H	7.51101400	0.00002400	0.00011600
C	5.71272500	-1.20094200	0.00015400
H	6.22227200	-2.15944600	0.00019500
C	4.31666300	-1.14824800	0.00014400
H	3.72697500	-2.06237700	0.00017700



Tetramethylethylenediamine•Iodopentafluorobenzene (6)

I	3.70498200	-0.73058500	0.01461100
F	5.15269200	2.17624700	0.00749900
C	5.74007200	-0.13048800	0.00611200
F	7.74455300	2.93046300	-0.00218000
C	6.09780900	1.21839900	0.00429300
F	9.72670100	1.04918600	-0.00871300
C	7.43038100	1.62620400	-0.00062600
F	9.08732000	-1.60758000	-0.00554000
F	6.50210300	-2.38495300	0.00403400
C	8.44299200	0.66925700	-0.00398700
C	6.77400000	-1.06790400	0.00261200
C	8.11403000	-0.68461000	-0.00235200
N	0.94966400	-1.66089400	-0.00064000
C	0.66618600	-2.19941400	1.33662900
C	0.98652700	-2.75175100	-0.98443700
C	-0.02511600	-0.63771300	-0.42504800
H	-1.04976700	-1.04808100	-0.40845100
H	0.21108000	-0.39645900	-1.46552600
H	1.74184300	-3.48561800	-0.69038600
H	0.01332800	-3.26534200	-1.07007600
H	1.25872600	-2.35572700	-1.96685700
H	1.39977100	-2.97463200	1.57334100
H	-0.34321600	-2.64198700	1.39819700
H	0.75315300	-1.41911800	2.09543600
H	1.04976700	1.04808100	0.40845100
H	-0.21108000	0.39645900	1.46552600
N	-0.94966400	1.66089400	0.00064000
H	-1.74184300	3.48561800	0.69038600
H	-0.01332800	3.26534200	1.07007600
H	-1.25872600	2.35572700	1.96685700
H	-1.39977100	2.97463200	-1.57334100
H	0.34321600	2.64198700	-1.39819700
H	-0.75315300	1.41911800	-2.09543600
C	-0.66618600	2.19941400	-1.33662900
C	-0.98652700	2.75175100	0.98443700
C	0.02511600	0.63771300	0.42504800
I	-3.70498200	0.73058500	-0.01461100
F	-5.15269200	-2.17624700	-0.00749900
C	-5.74007200	0.13048800	-0.00611200
F	-7.74455300	-2.93046300	0.00218000
C	-6.09780900	-1.21839900	-0.00429300
F	-9.72670100	-1.04918600	0.00871300
C	-7.43038100	-1.62620400	0.00062600
F	-9.08732000	1.60758000	0.00554000
F	-6.50210300	2.38495300	-0.00403400
C	-8.44299200	-0.66925700	0.00398700
C	-6.77400000	1.06790400	-0.00261200
C	-8.11403000	0.68461000	0.00235200

S.6 Crystallographic data and intermolecular interactions

Table S4. Selected crystallographic and refinement parameters for the cocrystals.

	1	2	5	6
Formula	(C ₆ F ₅ I) (C ₅ H ₅ N)	(C ₆ F ₅ I) (C ₆ H ₇ N)	(C ₆ F ₅ I Br) (C ₅ H ₅ N)	(C ₆ F ₅ I) (C ₆ H ₁₆ N ₂)
Formula weight	373.1	387.09	326.1	352.06
Temperature (K)	223 (2)	100(2)	173(2)	100(2)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	11.9726(5)	8.0031(4)	8.8544(4)	11.7434(7)
<i>b</i> (Å)	9.2769(4)	12.0310(6)	9.3356(4)	5.8599(3)
<i>c</i> (Å)	11.5812(5)	13.4501(6)	14.0154(6)	16.7329(10)
α (°)	90	90	90	90
β (°)	112.372(2)	100.731(2)	101.4780(10)	99.173(2)
γ (°)	90	90	90	90
Volume (Å³)	1189.49(9)	1272.40(11)	1135.36(9)	1136.75(11)
<i>Z</i>	4	4	4	4
Density (gcm⁻³)	2.08	2.02	1.91	2.06
μ (mm⁻¹)	2.736	2.562	3.666	2.856
<i>F</i> (000)	704	736	632	668
$\theta_{\min, \max}$ (°)	(1.8, 27.5)	(2.3, 25.1)	(2.6, 24.9)	(3.5, 25.0)
<i>h</i>_{min, max}	(-15, 15)	(-9, 7)	(-10, 10)	(-12, 13)
<i>k</i>_{min, max}	(-12, 10)	(-14, 14)	(-9, 11)	(-6, 5)
<i>l</i>_{min, max}	(-15, 14)	(-15, 16)	(-16, 11)	(-18, 19)
No. of refl. measured	9611	6134	5249	5132
No. unique refl.	2731	2257	1994	1999
No of parameter	184	200	163	177
Data compl. (%)	99.3	99.7	99.5	99.6
<i>R</i>_{all}, <i>R</i>_{obs}	0.0224, 0.0202	0.017, 0.015	0.019, 0.018	0.019, 0.018
<i>wR</i>_{2-all}, <i>wR</i>_{2-obs}	0.0457, 0.0443	0.036, 0.035	0.049, 0.048	0.038, 0.038
$\Delta\rho_{\max, \min}$ (eÅ⁻³)	0.648, -0.492	0.337, -0.330	0.237, -0.241	0.498, -0.414
G.o.F	1.140	1.022	1.070	1.175
CCDC no.s	1432990	1432991	1432992	1432993

Table S5. Halogen-bond distances in **1-6**.

	X...Y	X...Y/Å
1	I...N	2.783
2	I...N	2.728
3	I...N	2.806 ^a
4	I...N	2.831 ^b 2.841 ^c
5	Br...N	2.882
6	I...N	2.765

^a CCDC: LEZQAJ; ^b CCDC: LEZPUC; ^c CCDC: LEZPUC 01

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- [1] R. Boese, M. Nussbaumer, in *Organic Crystal Chemistry* (Eds.: J. B. Garbarczyk, D. W. Jones), Oxford University Press, Oxford, **1994**, pp. 20-37.
- [2] A. Wasilewska, M. Gdaniec, T. Polonski, *CrystEngComm*, **2007**, *9*, 203–206.
- [3] G.M. Sheldrick, *Acta Crystallogr. Sect. A*. **2008**, *64*, 112-122.
- [4] C. F. Macrae, I. J. Bruno, J.A. Chisholm, P. R. Edgington, P.McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Cryst.* **2008**, *41*, 466-470.
- [5] A. L. Spek, *Acta Crystallogr. Sect. D* **2009**, *65*, 148-155.
- [6] *Gaussian 09*, Revision C.01; Gaussian, Inc.: Wallingford CT, 2009.
- [7] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
- [8] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785-789.
- [9] Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82* (1), 270-283.
- [10] Check, C. E.; Faust, T. O.; Bailey, J. M.; Wright, B. J.; Gilbert, T. M.; Sunderlin, L. S. *J. Phys. Chem. A* **2001**, *105*, 8111–8116.
- [11] Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.