

Supplementary Information

Influence of multiple binding sites on the supramolecular assembly of *N*-[(3-pyridinylamino) thioxomethyl] carbamates

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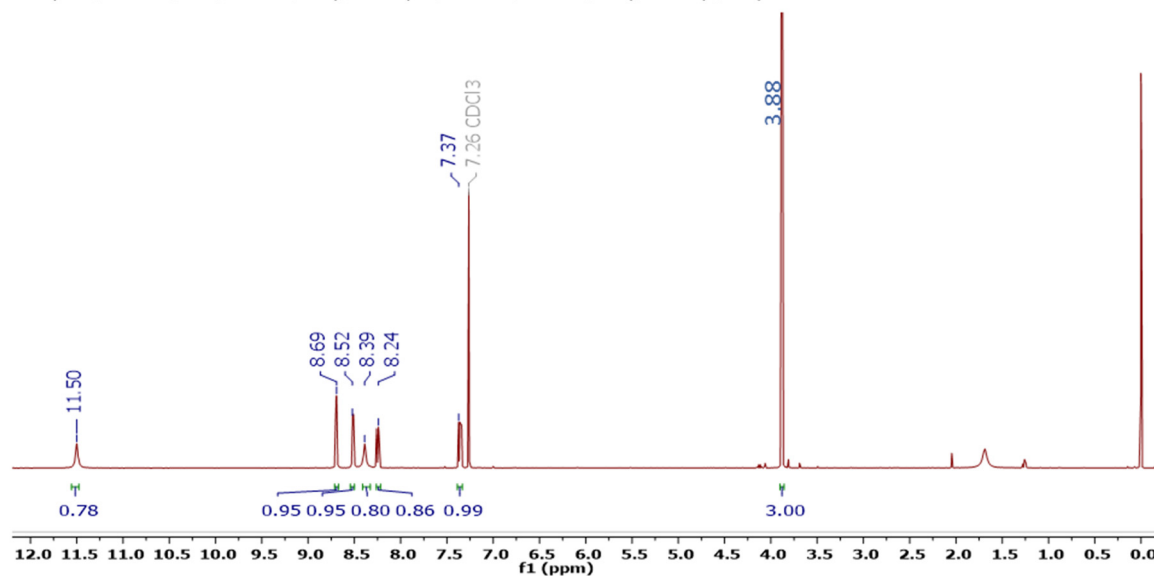
1. General Remarks

Commercial reagents were purchased as reagent-grade and used without further purification. All solvents utilized in this study were purchased commercially as technical grade and used as is without further purification. Targets were synthesized by modified versions of previously reported synthetic routes as described when referenced. Melting points were measured using a TA Instruments DSC Q20 differential scanning calorimeter. Nuclear magnetic resonance (NMR) data were collected using either a Bruker Ascend 400 MHz or Varian Unity Plus 400 MHz spectrometer. The residual solvent peak was used as the internal reference for ¹H and ¹³C NMR (CDCl₃: δ_H=7.26ppm, δ_C=77.16ppm). Single crystal X-ray diffraction data were collected using a Rigaku XtaLAB Synergy-S1 diffractometer. Data collection parameters are outlined in crystallographic information table. The structure was solved using Olex23 with the SHELXT4 structure solution program using Intrinsic Phasing and refined with the SHELXL5 refinement package using Least Squares minimization.

2. Spectral Data

2.1. Synthesis of methyl-*N*-[(3-pyridinylamino) thioxomethyl] carbamate (A1)

^1H NMR (400 MHz, Chloroform- d) δ 11.50 (s, 1H), 8.70 (d, J = 2.6 Hz, 1H), 8.51 (dd, J = 4.9, 1.5 Hz, 1H), 8.39 (s, 1H), 8.25 (ddd, J = 8.3, 2.8, 1.5 Hz, 1H), 7.36 (dd, J = 8.3, 4.8 Hz, 1H), 3.88 (s, 3H)



^{13}C NMR (101 MHz, CDCl_3) δ 178.57, 153.31, 147.68, 145.60, 134.52, 131.73, 123.29, 53.74.

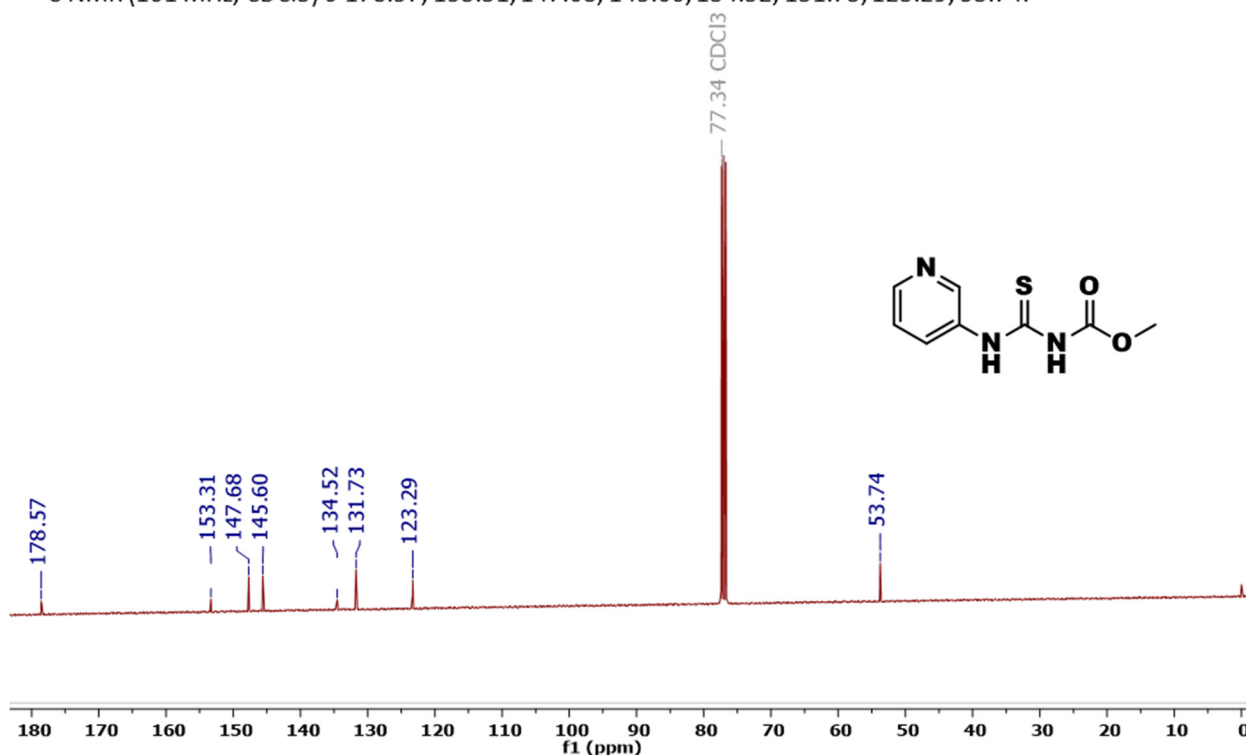
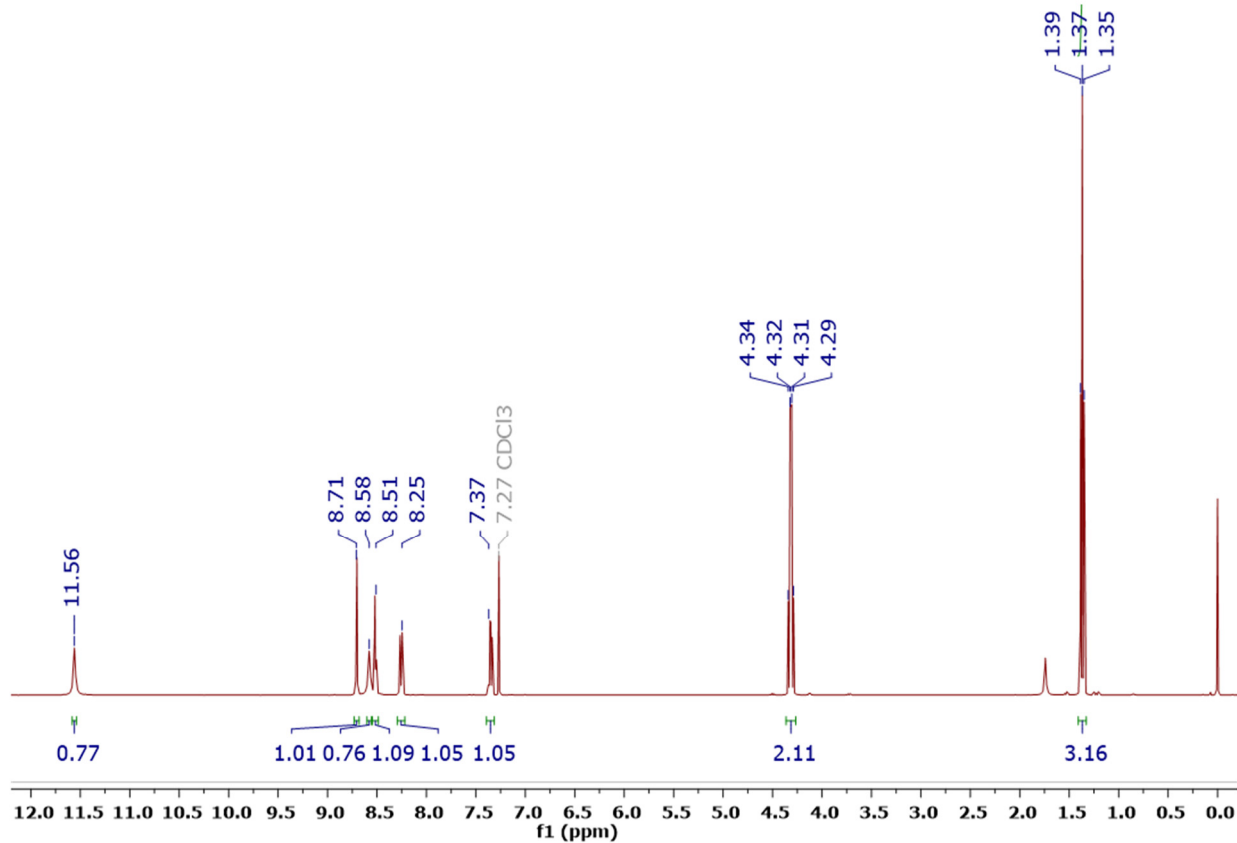


Figure S1 ^1H -NMR (top) and ^{13}C -NMR (bottom) of methyl-*N*-[(3-pyridinylamino) thioxomethyl] carbamate (A1)

2.2. Synthesis of ethyl-N-[(3-pyridinylamino) thioxomethyl] carbamate (A2)

^1H NMR (400 MHz, Chloroform- d) δ 11.56 (s, 1H), 8.71 (d, J = 2.6 Hz, 1H), 8.60–8.56 (m, 1H), 8.52 (dd, J = 4.8, 1.5 Hz, 1H), 8.26 (ddd, J = 8.4, 2.8, 1.6 Hz, 1H), 7.39–7.31 (m, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H).



^{13}C NMR (101 MHz, CDCl_3) δ 178.81, 152.98, 147.59, 145.60, 134.59, 131.72, 123.26, 63.31, 14.21

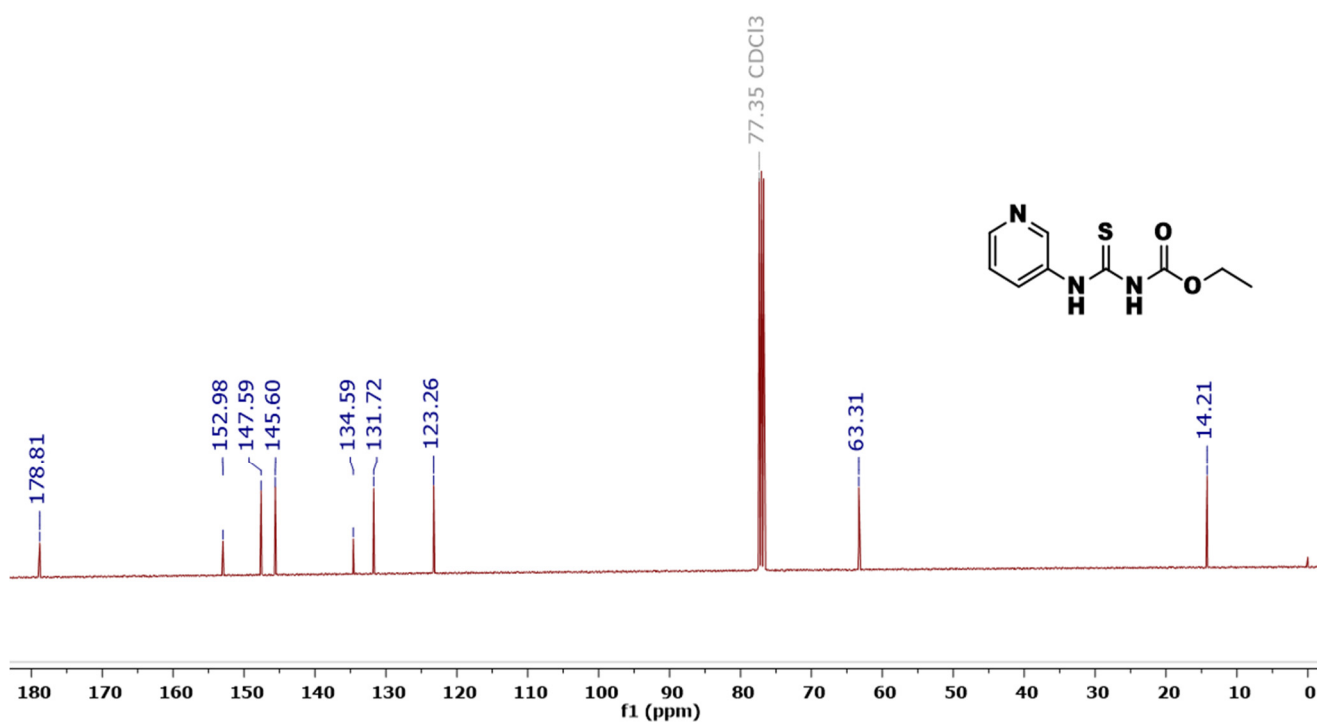
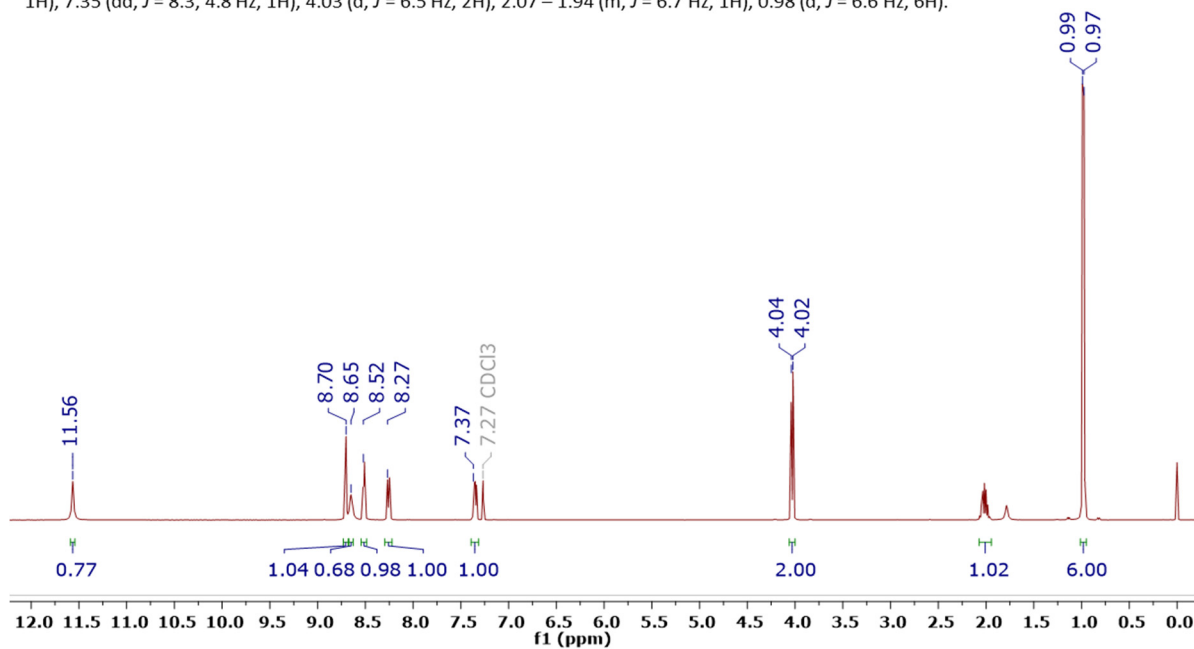


Figure S2 ^1H -NMR (top) and ^{13}C -NMR (bottom) of ethyl-N-[(3-pyridinylamino) thioxomethyl] carbamate (A2)

2.3. Synthesis of isobutyl-N-[(3-pyridinylamino) thioxomethyl] carbamate (A3)

^1H NMR (400 MHz, Chloroform- d) δ 11.56 (s, 1H), 8.71 (d, J = 2.6 Hz, 1H), 8.65 (s, 1H), 8.51 (d, J = 4.8 Hz, 1H), 8.26 (dt, J = 8.4, 2.0 Hz, 1H), 7.35 (dd, J = 8.3, 4.8 Hz, 1H), 4.03 (d, J = 6.5 Hz, 2H), 2.07–1.94 (m, J = 6.7 Hz, 1H), 0.98 (d, J = 6.6 Hz, 6H).



^{13}C NMR (101 MHz, Chloroform- d) δ 178.83, 153.09, 147.59, 145.59, 134.58, 131.71, 123.26, 73.06, 77.04, 27.75, 18.85.

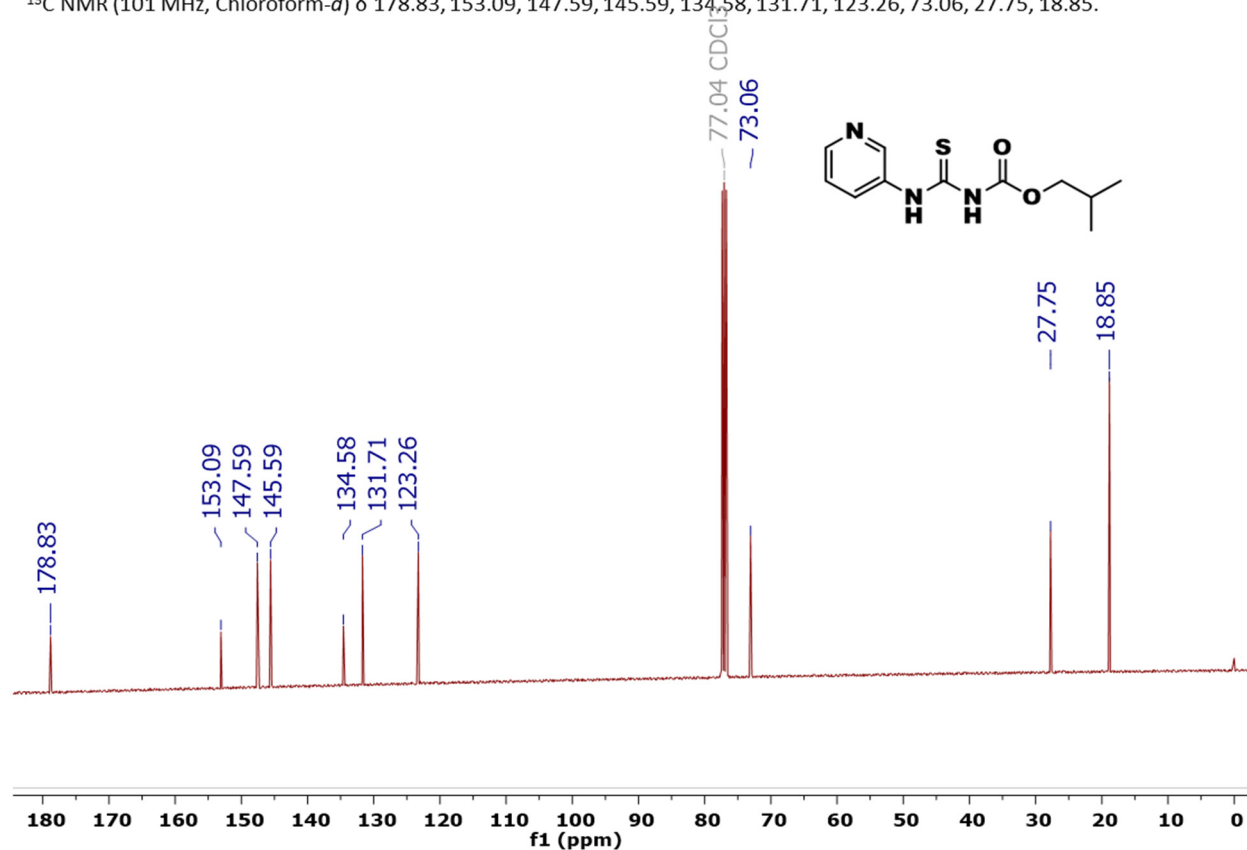


Figure S3 ^1H -NMR (top) and ^{13}C -NMR (bottom) of isobutyl-N-[(3-pyridinylamino) thioxomethyl] carbamate (A3)

3. Crystallographic information

Table S1 Crystallographic information of targets explored in this study

Compounds	A1	A3
Identification code	exp_231	Exp_334
Molecular formula	C ₈ H ₉ N ₃ O ₂ S	C ₁₁ H ₁₅ N ₃ O ₂ S
Formula weight (g mol ⁻¹)	211.24	253.32
Crystal system	orthorhombic	triclinic
Space group (No.)	<i>Fdd2</i>	<i>P</i> - 1 (No. 2)
a (Å)	28.61372(17)	9.5250(3)
b (Å)	19.21403(12)	10.2023(2)
c (Å)	6.92761(4)	14.3104(2)
α (°)	90	73.7596(18)
β (°)	90	78.554(2)
γ (°)	90	78.444(2)
V (Å ³)	3808.70(4)	1293.01(6)
Z	16	4
ρ _{calc} (g cm ⁻³)	1.474	1.301
μ (Cu Kα) (mm ⁻¹)	2.866	2.195
F (000)	1760.0	536.0
Crystal size (mm)	0.328 × 0.231 × 0.111	0.150 × 0.050 × 0.020
Temperature (K)	200 (10)	140 (2)
Radiation (Å)	CuKα, 1.54184	CuKα, 1.54174
Theta range for data collection	5.547 to 77.019°	3.254 to 77.577°
Index ranges	-35 ≤ h ≤ 36, -23 ≤ k ≤ 23, -8 ≤ l ≤ 8	-11 ≤ h ≤ 12, -12 ≤ k ≤ 12, -18 ≤ l ≤ 16
Final R indices [I > 2.0 σ(I)]	R ₁ =0.0225, wR ₂ =0.0645	R ₁ =0.0524, wR ₂ =0.1537
Final R indices [all data]	R ₁ =0.0225, wR ₂ =0.0645	R ₁ =0.0577, wR ₂ = 0.1577
Tot ref., uniq. ref, R (int)	16723, 1972, 0.0181	22321, 5358, 0.0438
Max. and min. transmission	1.000 and 0.265	1.00000 and 0.74851
Data/restraints/parameters	1972/1/137	5358 / 1 / 322
Goodness-of-fit on F ²	1.072	1.038
Largest diff. peak/hole (e. Å ⁻³)	0.192/-0.246	0.688/-0.717

Table S2 Crystallographic information of cocrystals obtained in this study

Compounds	A1·D1	(A2) ₂ ·D1	A3·D1	(A1) ₂ ·D2	A2·D2	(A3) ₂ ·D2
Identification code	exp_335c	exp_248	exp_308	exp_363	exp_351	Exp_393
Empirical formula	C ₁₄ F ₃ I ₃ H ₉ N ₃ O ₂ S	C ₁₂ H ₁₁ F _{1.5} I _{1.5} N ₃ O ₂ S	C ₁₇ F ₃ I ₃ H ₁₅ N ₃ O ₂ S	C ₁₂ F ₂ Cl ₃ I H ₁₀ N ₃ O ₂ S	C ₁₅ F ₄ I ₂ H ₁₁ N ₃ O ₂ S	C ₁₄ F ₂ I H ₁₅ N ₃ O ₂ S
Formula weight (g mol ⁻¹)	721.00	480.15	763.08	531.54	627.13	454.25
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic
Space group (No.)	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> nna	<i>P</i> -1 (No. 2)	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	4.3912(3)	17.4398(3)	9.19100(10)	4.20680(10)	4.40696(4)	19.6991(9)
<i>b</i> (Å)	14.6099(10)	35.2133(6)	11.04700(10)	26.0337(5)	27.4127(3)	4.78474(13)
<i>c</i> (Å)	15.3389(9)	5.09340(10)	12.41600(10)	15.3735(3)	15.48356(14)	20.6316(10)
α (°)	90	90	64.5040(10)	90	90	90
β (°)	96.621(6)	90	88.3510(10)	94.498	91.4598(9)	116.983(6)
γ (°)	90	90	79.9240(10)	90	90	90
<i>V</i> (Å ³)	977.50(11)	3127.92(10)	1118.78(2)	1678.50(6)	1869.91(3)	1732.94(15)
<i>Z</i>	2	8	2	4	4	4
ρ_{calc} (g cm ⁻³)	2.450	2.039	2.265	2.103	2.228	1.741
μ (Cu K α) (mm ⁻¹)	4.945	25.315	34.185	20.875	27.990	15.941
<i>F</i> (000)	664	1832.0	712	1028	1184	892
Crystal size (mm)	0.16 × 0.01 × 0.01	0.155 × 0.06 × 0.035	0.159 × 0.108 × 0.059	0.121 × 0.013 × 0.01	0.098 × 0.052 × 0.033	0.255 × 0.031 × 0.022
Temperature (K)	140.00(10)	170.00(10)	130.00(10)	139.7(6)	140.00(10)	200.00(10)
Radiation (Å)	CuK α , 1.54184	CuK α , 1.54184	CuK α , 1.54184	CuK α , 1.54184	CuK α , 1.54184	CuK α , 1.54184
Theta range for data collection/°	2.674 to 30.814	2.510 to 77.122	3.950 to 77.463	4.457 to 77.733	3.224 to 77.545	2.517 to 77.810
Index ranges	-5 ≤ <i>h</i> ≤ 5, -20 ≤ <i>k</i> ≤ 20, -19 ≤ <i>l</i> ≤ 21	-21 ≤ <i>h</i> ≤ 16, -44 ≤ <i>k</i> ≤ 39, -6 ≤ <i>l</i> ≤ 6	-11 ≤ <i>h</i> ≤ 11, -13 ≤ <i>k</i> ≤ 13, -15 ≤ <i>l</i> ≤ 15	-5 ≤ <i>h</i> ≤ 3, -32 ≤ <i>k</i> ≤ 32, -19 ≤ <i>l</i> ≤ 19	-5 ≤ <i>h</i> ≤ 5, -33 ≤ <i>k</i> ≤ 34, -18 ≤ <i>l</i> ≤ 19	-24 ≤ <i>h</i> ≤ 24, -6 ≤ <i>k</i> ≤ 4, -26 ≤ <i>l</i> ≤ 25
Final R indices [<i>I</i> > 2.0 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0439, <i>wR</i> ₂ = 0.0439	<i>R</i> ₁ = 0.0213 <i>wR</i> ₂ = 0.0598	<i>R</i> ₁ = 0.0237 <i>wR</i> ₂ = 0.0648	<i>R</i> ₁ = 0.0403 <i>wR</i> ₂ = 0.1071	<i>R</i> ₁ = 0.0198 <i>wR</i> ₂ = 0.0511	<i>R</i> ₁ = 0.0517 <i>wR</i> ₂ = 0.1312
Final R indices [all data]	<i>R</i> ₁ = 0.0514 <i>wR</i> ₂ = 0.1130	<i>R</i> ₁ = 0.0220 <i>wR</i> ₂ = 0.0603	<i>R</i> ₁ = 0.0239 <i>wR</i> ₂ = 0.0650	<i>R</i> ₁ = 0.0417 <i>wR</i> ₂ = 0.1082	<i>R</i> ₁ = 0.0203 <i>wR</i> ₂ = 0.0515	<i>R</i> ₁ = 0.0575 <i>wR</i> ₂ = 0.1344
Tot ref., uniq. ref, <i>R</i> (int)	15121, 4704, 0.0596	17973, 3307, 0.0256	42499, 4731, 0.0493	26685, 3561, 0.0459	22839, 4000, 0.47941	18918, 3609, 0.0625
Max. and min. transmission	1.00000 and 0.60523	1.00000 and 0.50257	1.00000 and 0.22072	0.920 and 0.327	1.00000 and 0.47941	1.000 and 0.408
Data/restraints/parameters	4704 / 2 / 236	3307/0/193	4731 / 0 / 265	3561/142/262	4000 / 0 / 246	3609 / 0 / 210
Goodness-of-fit	1.006	1.062	1.050	1.100	1.047	1.118
Largest diff. peak/hole (e. Å ⁻³)	1.309/-1.013	0.664/-1.096	1.165/-1.053	1.206/-0.929	0.933/-0.945	1.210/-1.471

Table S3 Hydrogen and halogen bond parameters of the eight crystal structures

	DH/X---A	D/X/Ch---A (Å)	<[DH/X/Ch---A] (°)
A1	C(3)-H(3)···S(9)	3.821(2)	153.0
	C(4)-H(4)···O(12)	3.436(2)	172.3
	N(7)-H(7)···O(12)	2.674(2)	140.0
	N(10)-H(10)···N(2)	2.891(2)	174.0
A3	C(4A)-H(4A)···S(9A)	3.666(2)	131.9
	N(7)-H(7)···O(12)	2.633(3)	140.9
	N(10)-H(10)···N(2A)	2.899(3)	172.5
A1·D1	C(3)-H(3)···S(9)	3.623(1)	134.7
	N(7)-H(7)···O(12)	2.664(1)	134.4
	N(10)-H(10)···N(2)	2.877(1)	171.6
	I(16)···S(9)	3.310(3)	
	C(15)-I(16)···S(9)		161.9(3)
	I(24)···O(12)	3.168(9)	
	C(24)-I(24)···O(12)		154.2(4)
(A2)₂·D1	C(1)-H(1)···S(9)	3.695(3)	159.2
	N(7)-H(7)···O(12)	2.713(3)	132.9
	N(7)-H(7)···O(12)	3.095(3)	131.2
	N(10)-H(10)···S(9)	3.311(2)	169.3
	I(21)···N(2)	2.877(2)	
	C(20)-I(21)···N(2)		177.2(8)
A3·D1	C(4)-H(4)···S(9)	3.774(3)	151.5
	C(5)-H(5)···F(25)	3.396(3)	165.4
	N(7)-H(7)···N(2)	3.282(3)	128.1
	N(7)-H(7)···O(12)	2.670(3)	134.2
	N(10)-H(10)···S(9)	3.366(2)	160.9
	I(27)···S(9)	3.363(6)	
	C(26)-I(27)···S(9)		171.9(7)
	I(19)···N(2)	2.927(3)	
	C(18)-I(19)···N(2)		176.2(1)
(A1)₂·D2	N(7)-H(7)···O(12)	2.653(5)	136.4
	N(10)-H(10)···N(2)	2.880(5)	173.9
	I(16)···S(9)	3.222(1)	
	C(15)-I(16)···S(9)		169.2(1)
A2·D2	N(7)-H(7)···O(12)	2.639(3)	135.9
	N(10)-H(10)···N(2)	2.889(3)	167.3
	I(17)···S(9)	3.248(7)	
	C(16)-I(17)···S(9)		170.0(6)
(A3)₂·D2	C(5)-H(5)···S(9)	3.199(6)	126.2
	N(7)-H(7)···O(12)	2.680(7)	141.6
	N(10)-H(10)···S(9)	3.320(5)	169.3
	I(19)···N(2)	2.802(6)	
	C(18)-I(19)···N(2)		177.8(2)

4. CSD analysis of $I\cdots N$ pyr, $I\cdots S=C$, and $I\cdots O=C$ bond lengths

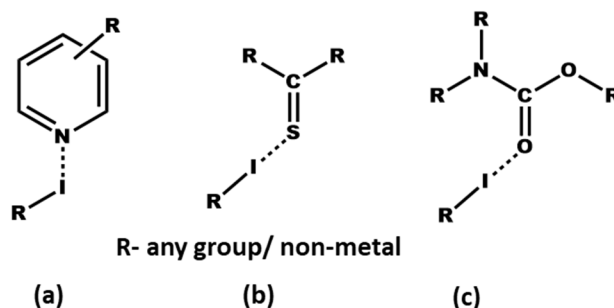


Figure S4 Contact descriptor used for CSD search (a) $I\cdots N$ pyr contact, (b) $I\cdots S=C$ contact, and (c) $I\cdots O=C$ contact

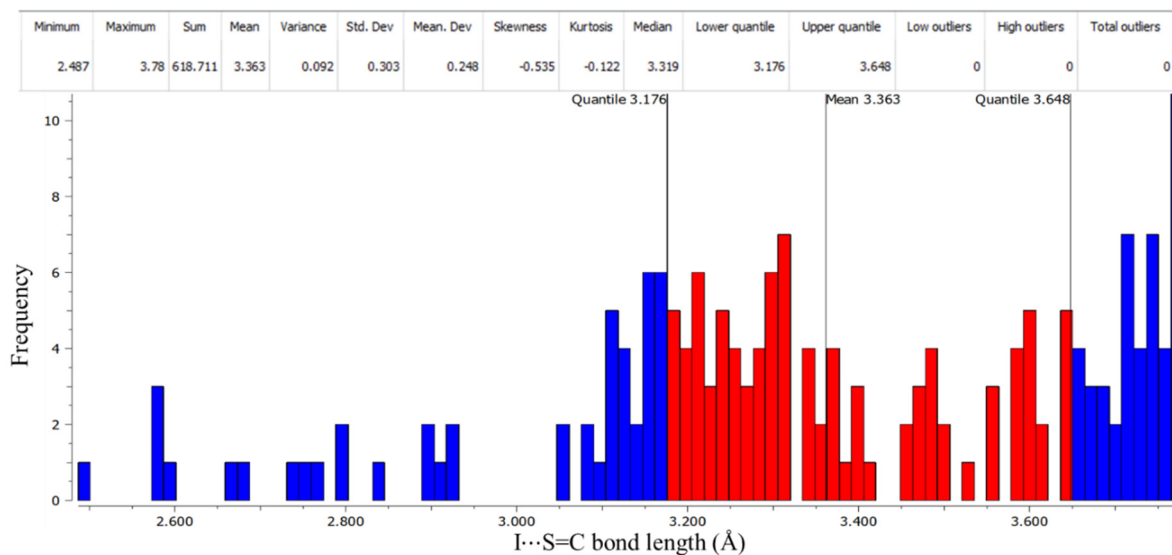


Figure S5 Histogram showing bond length against frequency for $I\cdots S=C$ halogen bond

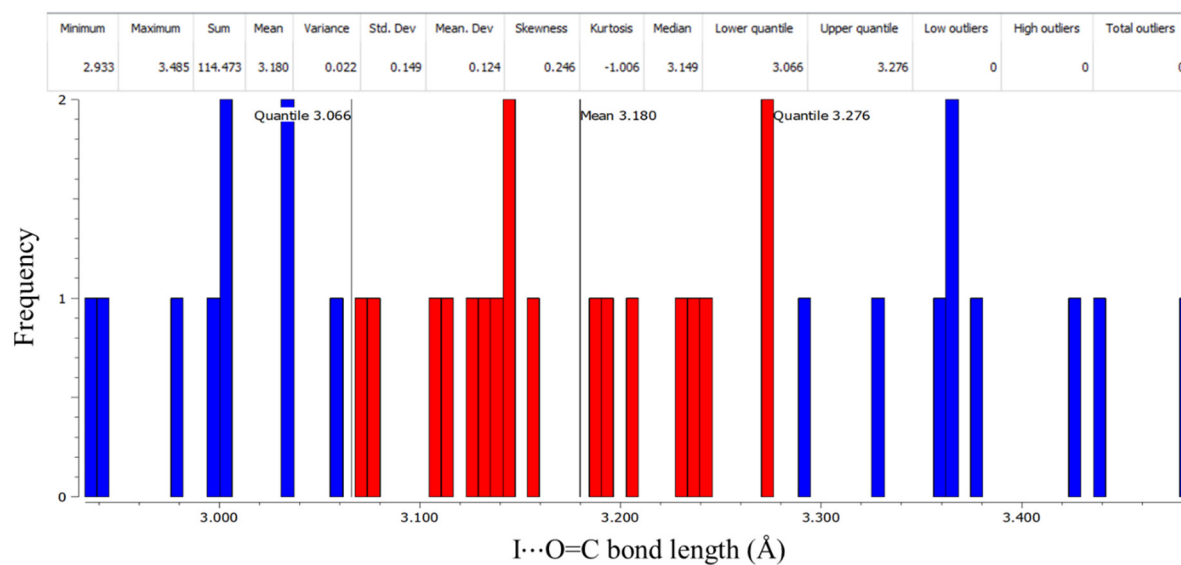


Figure S6 Histogram showing bond length against frequency for $I\cdots O=C$ halogen bond