Electronic Supplementary Material (ESI) for CrystEngComm.
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Structural landscape of heteroaryl-2-imidazoles: Competing halogen- and hydrogen- bond interactions

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Supplementary Information

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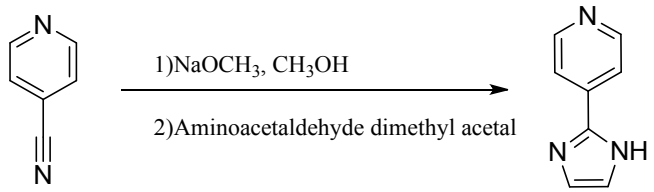
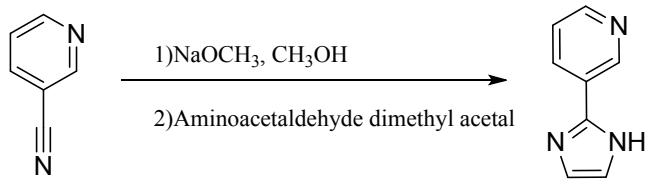
1. Experimental data - Synthesis

Synthesis of 4-(imidazol-2-yl)pyridine[1], A1



To a flask containing 4-cyanopyridine (2.00 g, 0.019 mol) and MeOH (20 mL) a 30% solution of NaOMe in MeOH (0.36 mL, 1.90 mmol) was added. The reaction mixture was stirred for one hour at room temperature. Aminoacetaldehyde dimethyl acetal (2.07 ml, 1 eq) followed by AcOH (2.09 mL, 37 mmol) was added dropwise. The reaction mixture was heated to reflux for 30 min. After cooling the reaction mixture to room temperature, MeOH (15 mL) and 6 N HCl in H_2O (10 ml) were added, and the mixture was heated to reflux for 3 hours. Once the cyclization was complete, the solution was evaporated to dryness on a rotary evaporator. A freshly prepared warm solution of K_2CO_3 (50% w/w in water) was added carefully, bringing pH to 10. The resulting suspension was allowed to cool to room temperature and recrystallized from boiling water to obtain 4-(imidazol-2-yl)pyridine**, A1** as an off-white solid (1.98 g, 72%): mp 197-200°C (lit. 210–211 °C)[1]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.90 (br s, 1H), 8.62 (dd, 2H), 7.86 (dd, 2H), 7.39 (br s, 1H), 7.13 (br s, 1H).

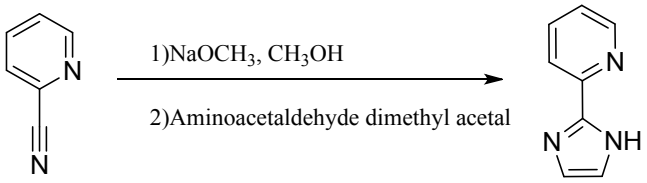
Synthesis of 3-(imidazol-2-yl)pyridine[1], A2



To a flask containing 3-cyanopyridine (2.00 g, 0.019 mol) and MeOH (20 mL) a 30% solution of NaOMe in MeOH (0.36 mL, 1.90 mmol) was added. The reaction mixture was stirred for one hour at room temperature. Aminoacetaldehyde dimethyl acetal (2.07 ml, 1 eq) followed by AcOH (2.09 mL, 37 mmol) was added dropwise. The reaction mixture was heated to reflux for

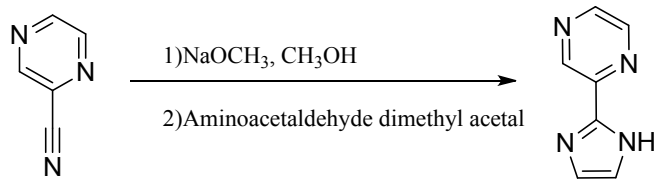
30 min. After cooling the reaction mixture to room temperature, MeOH (15 mL) and 6 N HCl in H_2O (10 ml) were added, and the mixture was heated to reflux for 8 hours. Once the cyclization was complete, the solution was evaporated to dryness on a rotary evaporator. A freshly prepared warm solution of K_2CO_3 (50% w/w in water) was added carefully, bringing pH to 10. The resulting suspension was allowed to cool to room temperature and recrystallized from boiling water to obtain 3-(imidazol-2-yl)pyridine, **A2** as an off-white solid (2.33 g, 85%): mp 197–201 °C (lit. 208–209 °C)1; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.71 (br s, 1H), 9.14 (d, 1H), 8.53 (dd, 1H), 8.26 (dt, 1H), 7.47 (dd, 1H), 7.21 (br s, 2H).

Synthesis of 2-(imidazol-2-yl)pyridine1, A3



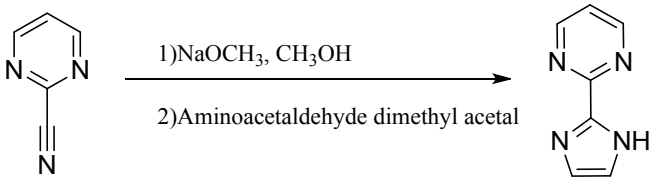
To a flask containing 2-cyanopyridine (2.00 g, 0.019 mol) and MeOH (20 mL) a 30% solution of NaOMe in MeOH (0.36 mL, 1.90 mmol) was added. The reaction mixture was stirred for one hour at room temperature. Aminoacetaldehyde dimethyl acetal (2.07 ml, 1 eq) followed by AcOH (2.09 mL, 37 mmol) was added dropwise. The reaction mixture was heated to reflux for 30 min. After cooling the reaction mixture to room temperature, MeOH (15 mL) and 6 N HCl in H_2O (10 ml) were added, and the mixture was heated to reflux for 5 hours. Once the cyclization was complete, the solution was evaporated to dryness on a rotary evaporator. A freshly prepared warm solution of K_2CO_3 (50% w/w in water) was added carefully, bringing pH to 10. The resulting suspension was allowed to cool to room temperature and recrystallized from boiling EtOAc to afford 2-(imidazol-2-yl)pyridine, **A3** as an off-white solid: mp 132–135 °C (lit.137–138 °C)1; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.74 (br s, 1H), 8.57 (d, 1H), 8.03 (d, 1H), 7.86 (td, 1H), 7.34 (m, 1H), 7.20 (br s, 1H), 7.06 (br s, 1H).

Synthesis of 2-(imidazol-2-yl)pyrazine[1], A4



A 100-mL flask was charged with pyrazine-2-carbonitrile (1.05 g, 10 mmol), MeOH (10 mL), and a 30% solution of NaOMe in MeOH (0.38 mL, 1 mmol). The reaction mixture was stirred for 40 minutes at room temperature. Aminoacetaldehyde dimethyl acetal (1.09 ml, 1 eq) was added to the reaction mixture followed by AcOH (1.2 mL, 20 mmol). The reaction mixture was heated to 50 °C for 1 h and then cooled to room temperature. MeOH (20 mL) and 6 N HCl in H_2O (5 mL) were added, and the reaction mixture was heated to reflux for 5 hours. Once the cyclization was complete, the solution was removed on a rotary evaporator, and the residue was taken up in a 1:1 mixture of H_2O and Et_2O. The layers were separated and the pH of the aqueous layer was adjusted to pH 9 with 2 N aqueous NaOH. Then the aqueous mixture was stirred for 30 min to allow complete precipitation of the product. The solid was collected by filtration and dried under vacuum to obtain pure 2-(1H-imidazol-2-yl)pyrazine, **A4** (0.83 g, 57%) as a white solid. mp 196-198 °C (lit. 199–201 °C)[1]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (br s, 1H), 9.44 (d, 1H), 8.53 (d, 1H), 8.49 (m, 1H), 7.31 (br s, 1H), 7.23 (br s, 1H).

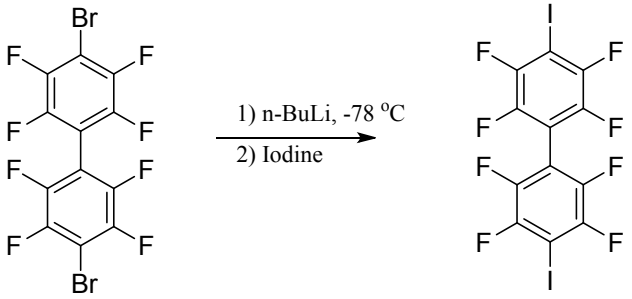
Synthesis of 2-(imidazol-2-yl)pyrimidine[1], A5



To a flask containing pyrimidine-2-carbonitrile (2.00 g, 0.019 mol) and MeOH (20 mL) a 30% solution of NaOMe in MeOH (0.36 mL, 1.90 mmol) was added. The reaction mixture was stirred for two hours at room temperature. Aminoacetaldehyde dimethyl acetal (2.07 ml, 1 eq) followed by AcOH (2.09 mL, 37 mmol) was added dropwise. The reaction mixture was heated to reflux

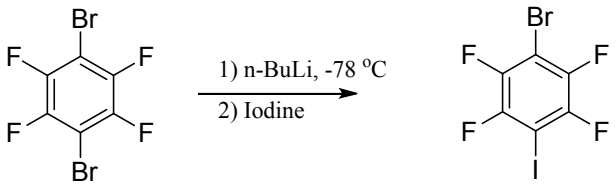
for 30 min. After cooling the reaction mixture to room temperature, MeOH (15 mL) and 6 N HCl in H_2O (10 ml) were added, and the mixture was heated to reflux for 5 hours. Once the cyclization was complete, the solution was evaporated to dryness on a rotary evaporator. A freshly prepared warm solution of K_2CO_3 (50% w/w in water) was added carefully, bringing pH to 10. The resulting suspension was allowed to cool to room temperature and washed with ice-cold water to obtain pure 2-(1H-imidazol-2-yl)pyrimidine, **A5** as a white solid (2.61 g, 36%): mp 193-195 °C (lit. 196–197 °C)1; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.97 (br s, 1H), 8.86 (d, 2H), 7.44 (t, 1H), 7.22 (s, 2H).

Synthesis of 4,4'-diiodo-perfluorobiphenyl[2], D10



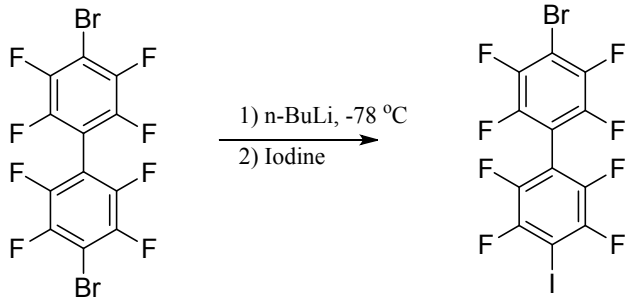
In an oven dried flask, 4,4'-dibromoperfluorobiphenyl (152 mg, 0.52 mmol) was dissolved in 10 mL of freshly distilled tetrahydrofuran under nitrogen. The solution was cooled in an acetone/dry ice bath and a solution of n-butylithium in hexane (1.6 M, 0.78 mL, 1.25 mmol) was slowly added over 15 min. After 20 minutes, I2 (326 mg, 1.28 mmol) was added. The reaction mixture was slowly warmed to room temperature and saturated sodium thiosulfate solution was added to obtain a clear solution. The product was extracted with methylene chloride (3x50 mL). The organic phase was dried using anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator to yield pure 4,4'-diiodoperfluorobiphenyl as an off-white solid. (1.54 g, 55%): mp 135-137 °C. ^{19}F NMR (400 MHz, $CDCl_3$) δ -119.09 (m, 4H), -136.62 (m, 4H).

Synthesis of 1-bromo-4-iodotetrafluorobenzene[3], D14



In an oven dried flask, 1,4-dibromotetrafluorobenzene (1.00 g, 3.2 mmol) was dissolved in 70 mL of freshly distilled tetrahydrofuran under nitrogen. The solution was cooled in an acetone/dry ice bath and a solution of n-butyllithium (1.6 M solutions in hexanes, 2.06 mL, 3.3 mmol) was slowly added over 15 min. After 20 minutes, I_2 (2.06g, 8 mmol) was added. The reaction mixture was slowly warmed to room temperature and saturated sodium thiosulfate solution was added to obtain a clear solution. The product was extracted with methylene chloride (3x100 mL). The organic phase was dried using anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator to yield pure1-bromo-4-iodotetrafluorobenzene as an off white solid (0.86 g, 75% yield). m.p. 87-89 °C. (lit. 87–89 °C)[3]; ^{19}F NMR (δH; 400 MHz, $CDCl_3$): -119.01 (m, 2F), -131.89 (m, 2F).

Synthesis of 4-bromo-4'-iodoperfluorobiphenyl[3], D15



In an oven dried flask, 4,4'-dibromoperfluorobiphenyl (1.00 g, 2.2 mmol) was dissolved in 40 mL of freshly distilled tetrahydrofuran under nitrogen. The solution was cooled in an acetone/dry ice bath and a solution of n-butyllithium (1.6 M solutions in hexanes, 1.4 mL, 2.26 mmol) was slowly added over 15 min. After 20 minutes, I_2 (0.57 g, 2.2 mmol) was added. The reaction mixture was slowly warmed to room temperature and saturated sodium thiosulfate solution was added to obtain a clear solution. The product was extracted with methylene chloride (3x100 mL). The organic phase was dried using anhydrous magnesium sulfate. The solvent was removed on a

rotary evaporator to yield pure 4-bromo-4'-iodoperfluorobiphenyl as an off white solid (0.95 g, 87 % yield). m.p. 105-108 ^{o}C. (lit. 104–108 °C); ^{19}F NMR (δH; 400 MHz, $CDCl_3$): -119.01 (m, 2F), -131.91 (m, 2F), -136.53(M, 2F), -136.87(m, 2F).

2. NMR data

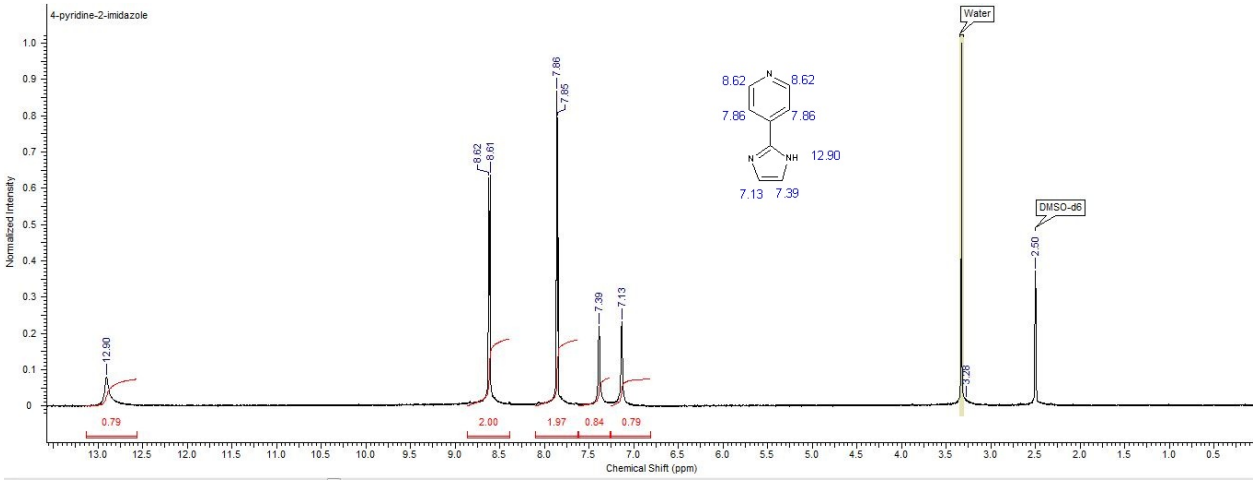


Figure S1: ^{1}H NMR spectrum of 4-(imidazol-2-yl)pyridine, **A1**

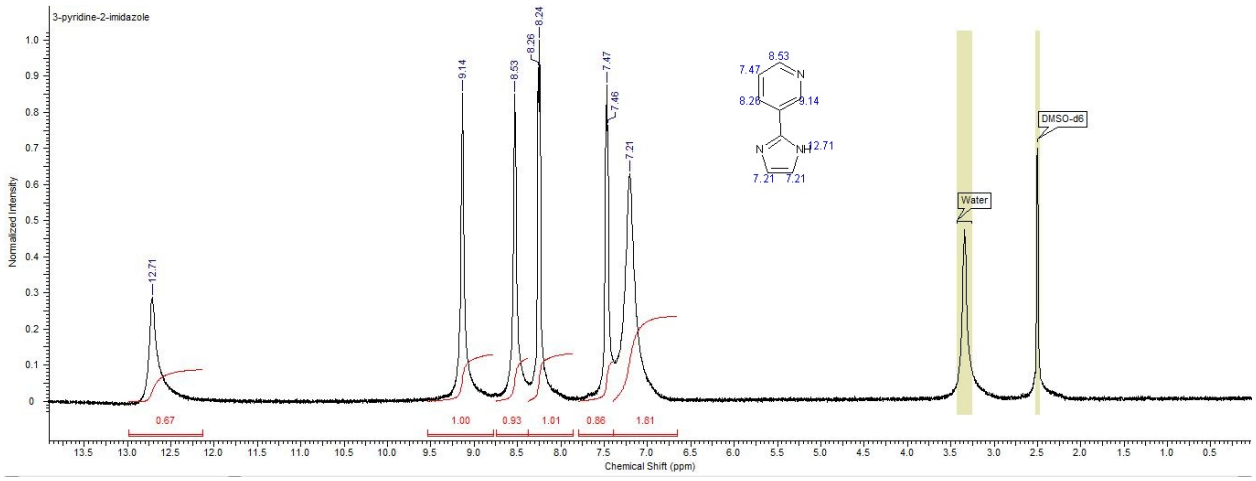


Figure S2: ^{1}H NMR spectrum of 3-(imidazol-2-yl)pyridine, **A2**

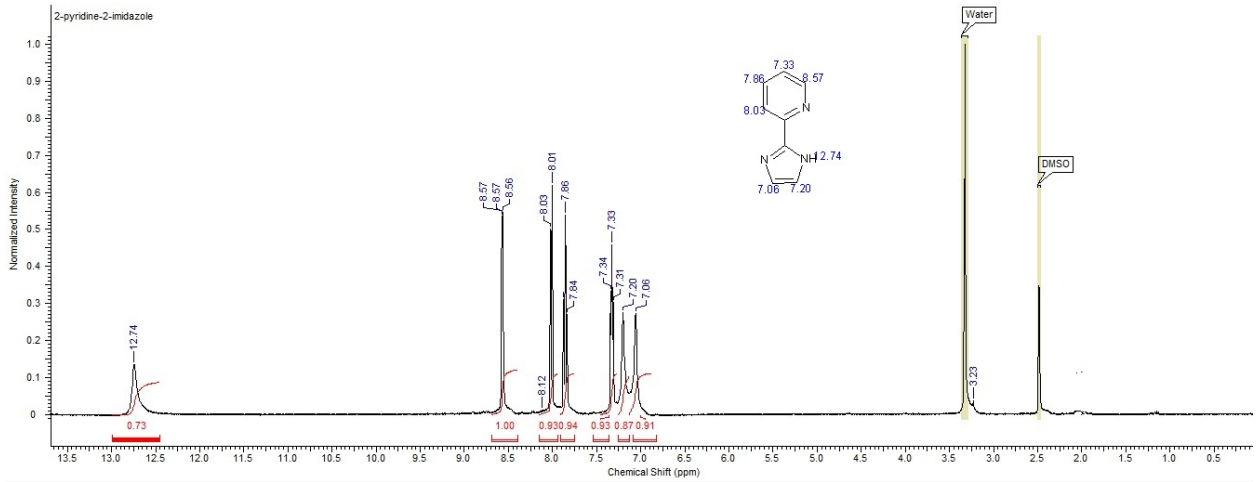


Figure S3: ^{1}H NMR spectrum of 2-(imidazol-2-yl)pyridine, **A3**

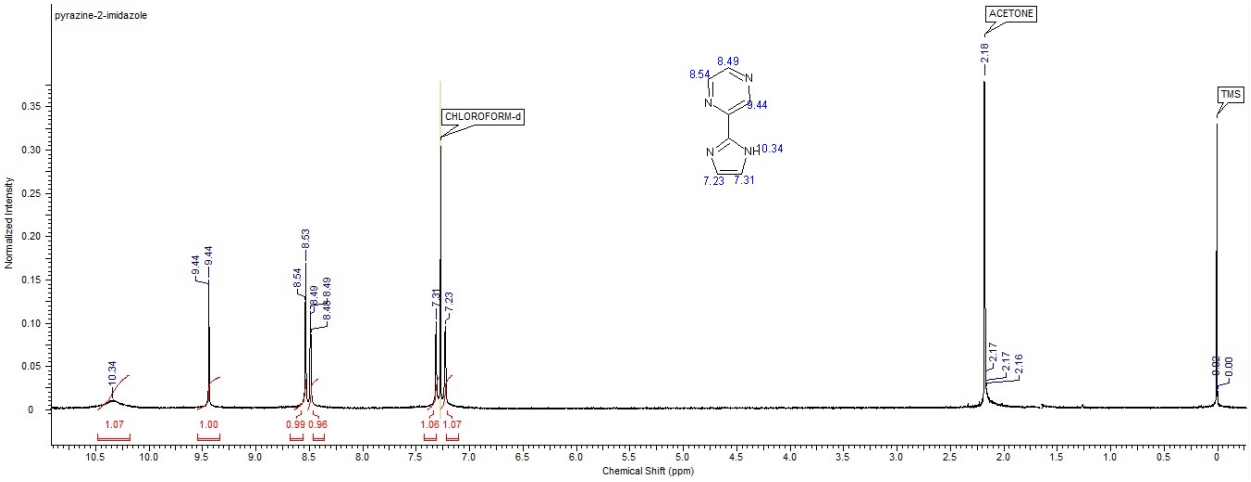


Figure S4: ^{1}H NMR spectrum of 2-(imidazol-2-yl)pyrazine, **A4**

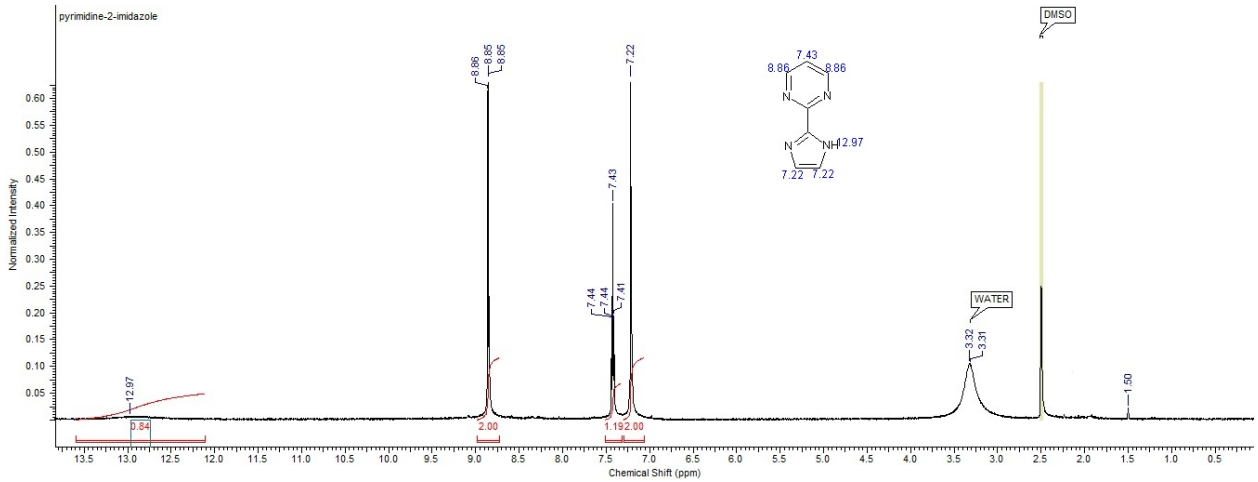


Figure S5: ^{1}H NMR spectrum of 2-(imidazol-2-yl)pyrimidine, **A5**

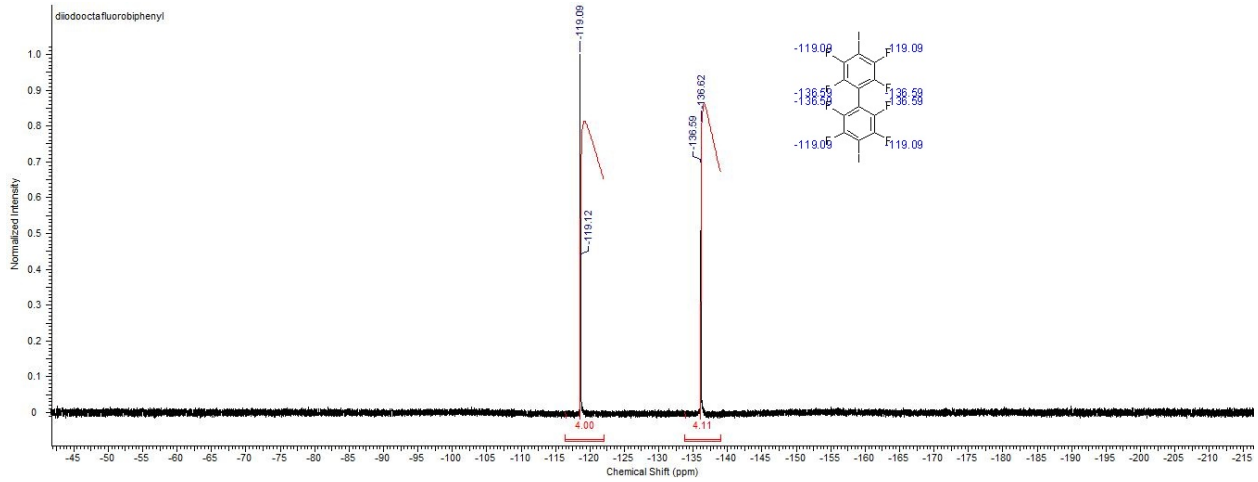


Figure S6: ^{19}F NMR spectrum of 4,4'-diiodo-perfluorobiphenyl, **D10**

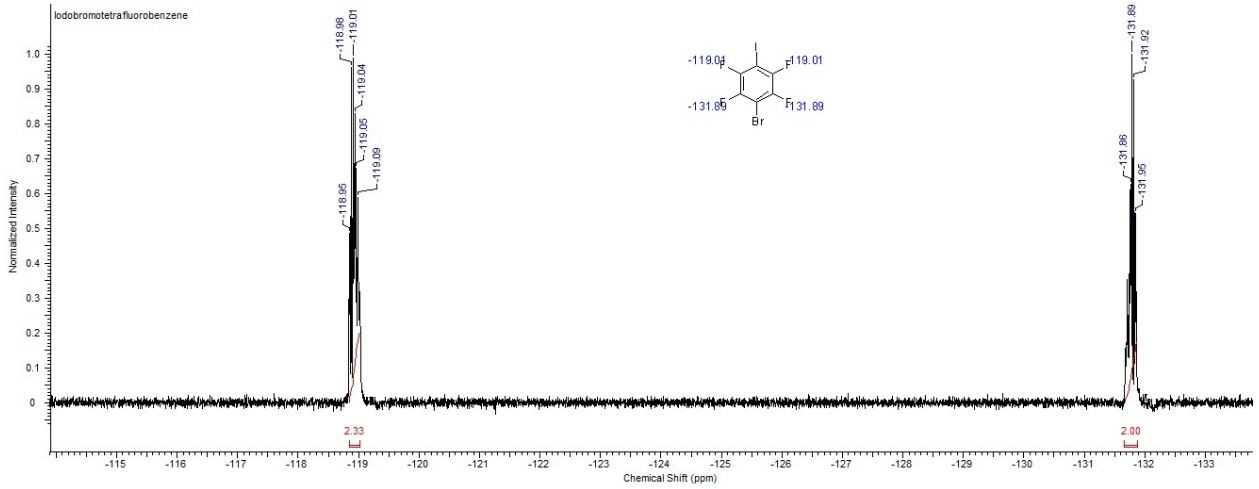


Figure S7: ^{19}F NMR spectrum of 1-bromo-4-iodotetrafluorobenzene, **D14**

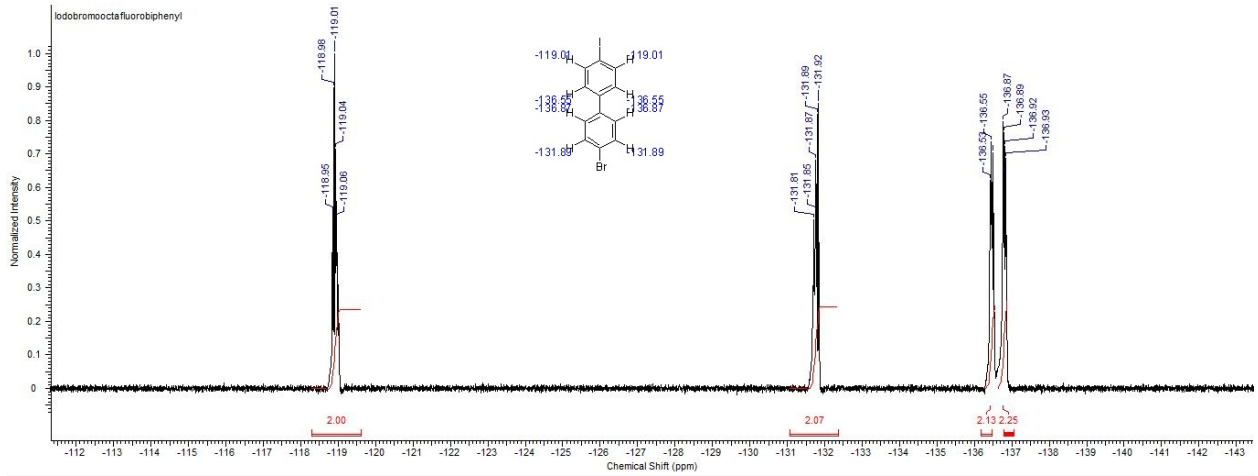


Figure S7: ^{19}F NMR spectrum of 4-bromo-4'-iodoperfluorobiphenyl, **D15**

3. IR data

Mixture	IR bands (cm^{-1})		Shifts Δcm^{-1}
	Halogen bond donors	Grounded Mixture	
A1D2	1192 1041	1178 1048	-14 +7
A1D6	1488 805	1481 796	-7 -9
A1D7	1309 772	1305 765	-4 -7
A1D8	1459 941	1456 937	-3 -4
A1D10	1459 954	1456 950	-3 -4
A2D1	1100 693	1095 700	-5 +7
A2D2	1192 634	1184 637	-7 +3
A2D3	1199 1086	1201 1078	+3 -8
A2D6	1488 805	1485 800	-3 -5
A2D7	1489 1438	1484 1432	-5 -6
A2D8	1459 759	1456 751	-3 -7
A2D9	1403 1049	1398 1045	-5 -4
A2D10	1219 954	1216 950	-3 -4
A2D14	1471 772	1459 769	-11 -3
A2D15	1464 955	1468 959	-4 +3
A3D3	1199 1141	1191 1153	-7 +11
A3D7	1489 1438	1484 1435	-5 -4
A3D8	1459 759	1453 751	-6 -7
A3D10	1459 954	1456 944	-3 -10
A3D14	1471 772	1465 769	-6 -3
A4D1	1100 693	1096 702	-4 +9
A4D2	1192 1133	1188 1125	-3 -7
A4D3	1199 1086	1209 1079	+10 -7
A4D4	1204 834	1216 830	+12 -4
A4D6	1488	1484	-4

	805	798	-7
A4D8	1459 759	1455 752	-4 -7
A4D9	1563 1049	1560 1044	-3 -5
A4D10	1459 954	1453 949	-6 -7
A5D7	1110 1438	1104 1442	-6 +4
A5D8	1212 1460	1215 1451	+3 -9

4. Crystallographic data

Datasets were collected on a Bruker Kappa APEX II system using CuKα radiation (**A3D3**), or a on a Bruker APEX II system using MoKα radiation (all others). Data were collected using APEX2 software.(a) Initial cell constants were found by small widely separated "matrix" runs. Data collection strategies were determined using COSMO.(b) Scan speed and scan widths were chosen based on scattering power and peak rocking curves. All datasets were collected at -153 °C using an Oxford Croystream low-temperature device.

Unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with SAINT,(c) using this improved unit cell as a starting point. Precise unit cell constants were calculated in SAINT from the final merged dataset. Lorenz and polarization corrections were applied. Multi-scan absorption corrections were performed with SADABS(d).

Data were reduced with SHELXTL.(e) The structures were solved in all cases by direct methods without incident. Except as noted, hydrogen atoms were located in idealized positions and were treated with a riding model. All non-hydrogen atoms were assigned anisotropic thermal parameters. Refinements continued to convergence, using the recommended weighting schemes.

A2D1 The single crystal X-ray diffraction studies were carried out on a Bruker D8 Smart Apex CCD diffractometer equipped with Mo K_α radiation (λ = 0.71073 Å) and . A 0.44 x 0.20 x 0.14 mm colorless rod was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 60 mm and exposure time was 10 seconds per frame using a scan width of 0.4°. Data collection was 100% complete to 25.00° in θ. A total of 15508 reflections were collected covering the indices, -15<=h<=16 -11<=k<=11, -12<=l<=12. 2435 reflections were found to be symmetry independent, with a Rint of 0.0315. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P21/c. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXS) produced a complete phasing model consistent with the proposed structure. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97.

A2D7 Colorless crystal of KSU11c, mounted on a Cryoloop with Paratone-N oil and data collected at 100 K using a Bruker APEX I CCD with Mo K alpha radiation. Data corrected for absorption with SADABS and structure solved by direct methods. All non-hydrogen atoms were refined anisotropically by full matrix least squares on F^2. Hydrogen atom H1N was found from a Fourier difference map and was allowed to refined with a N-H distance of 0.87 (2) angstroms

and isotropic displacement parameters set to 1.20 Ueq of the parent N atom. All other H atoms were placed in calculated positions with appropriate riding modes.

A1D8 The halo compound sits on a crystallographic inversion center, giving an overall 2 : 1 amine : halo compound stoichiometry. Two alternate protonation schemes for the imidazole moiety were observed, corresponding to oppositely directed translation-related linear hydrogen bonding chains in the y direction. Two PARTs were assembled to account for the two schemes, with EADP and EXYZ instructions pairwise included for superimposed nitrogen atoms (N11A & N11B and N13A & N13B). The proportion of the two sites was allowed to refine by using a free variable; this free variable refined to 0.20(4), representing a ~ 20:80 proportion for the two schemes.

A2D2 The halo compound sits on a crystallographic inversion center, giving an overall 2 : 1 amine : halo compound stoichiometry. Two alternate protonation schemes for the imidazole moiety were observed, corresponding to oppositely directed linear hydrogen bonding chains along the c glide plane. A hydrogen atom was included at both imidazole nitrogen atoms (N21 and N23) in idealized positions, and the occupancy of these two hydrogen atoms was allowed to refine, while summing to 1.0, by using a free variable; this free variable refined to 0.81(4), representing a ~ 81:19 proportion for the two schemes.

A2D8 The halo compound sits on a crystallographic inversion center, giving an overall 2 : 1 amine : halo compound stoichiometry. Coordinates for the amine proton H11 were allowed to refine.

A2D9 The halo compound sits on a crystallographic twofold axis, giving an overall 2 : 1 amine : halo compound stoichiometry. Coordinates for the amine proton H11 were allowed to refine.

A2D10 The compound crystallizes with an overall 2 : 1 amine : halo compound stoichiometry. The structure was solved and refined in the noncentrosymmetric space group Pc, and was treated as a racemic twin, with the batch scale factor refining to 0.129(11). For each imidazole moiety, two alternate protonation schemes were observed, corresponding to oppositely directed linear hydrogen bonding chains along the c glide plane. For each imidazole moiety, PARTs were assembled to account for the two schemes, with EADP and EXYZ instructions pairwise included for superimposed nitrogen atoms (N11A & N11B; N13A & N13B; N31A & N31B; N33A & N33B).

A2D14 The halo compound sits on a crystallographic inversion center, giving an overall 2 : 1 amine : halo compound stoichiometry. Occupancies of the bromine and the iodine atoms were fixed to 0.50 to accommodate disorder on the inversion center. Two alternate protonation schemes for the imidazole moiety were observed, corresponding to oppositely directed linear hydrogen bonding chains along the c glide plane. For each imidazole moiety, the proportion of the two sites was allowed to refine by using free variables; this free variables refined to 0.64(6) and 0.33(6) for the two sites. Two PARTs were assembled to account for the two schemes, with

EADP and EXYZ instructions pairwise included for superimposed nitrogen atoms (N11A & N11B and N13A & N13B). The proportion of the two sites was allowed to refine by using a free variable; this free variable refined to 0.23(20).

A3D3 The halo compound sits on a crystallographic inversion center. There are two different amine species present: the first sits on a general position, and the second straddles a crystallographic inversion center and was modeled as a complete molecule having an occupancy of 50%. The overall stoichiometry was therefore 2 : 1 amine : halo compound. The geometry of the second amine was restrained to approximate the fully ordered first amine by using the SHELXL SAME command, and the EADP command was used to pairwise constrain thermal parameters of atoms in the partially occupied amine that are located in proximity to each other.

A3D8 The asymmetric unit contains two amines on general positions, one halo compound on a general position, and two half-halo compounds sitting adjacent to crystallographic inversion centers. Overall stoichiometry in the asymmetric unit is therefore 2 : 2 amine : halo compound. Coordinates for the amine protons H11 and H31 were allowed to refine.

A3D10 The halo compound sits on a crystallographic 2-fold axis, giving an overall 2 : 1 amine : halo compound stoichiometry. Coordinates for the amine proton H11 were allowed to refine.

A4D2 The halo compound sits on a crystallographic inversion center, giving an overall 2 : 1 amine : halo compound stoichiometry. The amine was disordered over two distinct sites. Occupancies for the two species were set to 0.50, and the SAME command was used to restrain geometries. Thermal parameters for certain closely positioned atoms were constrained by using the EADP command. Two alternate protonation schemes for both imidazole moieties were observed. For each imidazole molecule, N-H hydrogen atoms were added in idealized positions, and the population of the two hydrogen atoms was controlled with a free variable. The halo compound was disordered over two closely located sites. The SAME command was used to restrain geometries, the EADP command was used to pairwise constrain closely located atoms, and the proportion of the two species was controlled with a free variable.

A4D8 The halo compound sits on a crystallographic inversion center, giving an overall 2 : 1 amine : halo compound stoichiometry. Coordinates for the amine proton H11 were allowed to refine.

A4D9 The halo compound sits on a crystallographic 2-fold axis, giving an overall 2 : 1 amine : halo compound stoichiometry. Two alternate protonation schemes for the imidazole moiety were observed, corresponding to oppositely directed linear hydrogen bonding chains along the ba glide plane. Two PARTs were assembled to account for the two schemes, with EADP and EXYZ instructions pairwise included for superimposed nitrogen atoms (N11A & N11B and N13A & N13B). The proportion of the two sites was allowed to refine by using a free variable; this free variable refined to 0.80(3), representing a ~ 80:20 proportion for the two schemes.

A4D10 The compound crystallizes with an overall 2 : 1 amine : halo compound stoichiometry. Coordinates for the amine protons H11 and H31 were allowed to refine.

(a) APEXII v2009. 5-1, © 2009, Bruker Analytical X-ray Systems, Madison, WI.

(b) COSMO v1. 60, © 1999 - 2009, Bruker Analytical X-ray Systems, Madison, WI.

(c) SAINT v7. 60a, © 1997 - 2008, Bruker Analytical X-ray Systems, Madison, WI.

(d) SADABS v2008/1, © 2008, Bruker Analytical X-ray Systems, Madison, WI.

(e) SHELXTL v2008/4, © 2008, Bruker Analytical X-ray Systems, Madison, WI.

	A1D8	**A2D1**	**A2D2**	**A2D7**	**A2D8**	**A2D9**	**A2D10**	**A2D14**
Systematic name	TW-1-107 [2-(4-pyridyl)-imidazole]$_2$, 1,4-diiodo-tetra-fluorobenzene	TW-2-02[2-(3-pyridyl)-imidazole]$_2$, I-$(CF_2)_2$-I	TW-2-07 [2-(3-pyridyl)-imidazole]$_2$, I-$(CF_2)_4$-I	TW-2-22[2-(3-pyridyl)-imidazole]$_2$, I-$(CF_2)_3$-I	TW-2-27 [2-(3-pyridyl)-imidazole]$_2$, 1,4-diiodotetra-fluorobenzene	TW-1-57 [2-(3-pyridyl)-imidazole]$_2$, 1,3,5-F_3-2,4,6-I_3-benzene	TW-1-67 [2-(3-pyridyl)-imidazole], 4,4'-diiodo-F_8-biphenyl	TW-1-47 [2-(3-pyridyl)-imidazole]$_2$, 1-bromo-4-iodotetra-fluorobenzene
Formula moiety	$(C_8H_7N_3)_2$ $(C_6F_4I_2)$	$(C_8H_7N_3)_2$, $(C_2F_4I_2)$	$(C_8H_7N_3)_2$ $(C_4F_8I_2)$	$(C_8H_7N_3)_2$, $(C_6F_4I_2)$	$(C_8H_7N_3)_2$ $(C_6F_4I_2)$	$(C_8H_7N_3)_2$ $(C_6F_3I_3)$	$(C_8H_7N_3)_2$ $(C_{12}F_8I_2)$	$(C_8H_7N_3)_2$ (C_6BrF_4I)
Empirical formula	$C_{22}H_{14}F_4I_2N_6$	$C_{18}H_{14}F_4I_2N_6$	$C_{20}H_{14}F_8I_2N_6$	$C_{22}H_{14}F_4I_2N_6$	$C_{22}H_{14}F_4I_2N_6$	$C_{22}H_{14}F_3I_3N_6$	$C_{28}H_{14}F_8I_2N_6$	$C_{22}H_{14}BrF_4IN_6$
Molecular weight	692.19	644.15	744.17	692.19	692.19	800.09	840.25	645.20
Color, Habit	colourless needle	Colourless, Rod	colourless prism	Colourless, Block	colourless plate	colourless plate	colourless prism	colourless rod
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group, Z	P2(1)/n, 2	P2(1)/c, 2	P2(1)/c, 2	Cm, 2	P2(1)/c, 2	Pbcn, 4	Pc, 2	P2(1)/c, 2
a, Å^3	12.9720(11)	12.3214(7)	14.3500(9)	10.0009(13)	4.1462(3)	32.4147(16)	4.2333(3)	4.0019(11)
b, Å^3	5.0426(4)	8.9036(5)	8.7642(5)	28.964(4)	27.9646(17)	9.9354(5)	32.768(2)	28.546(8)
c, Å^3	17.0878(15)	9.8742(6)	9.9637(6)	4.1036(6)	9.9124(6)	7.4776(4)	9.9627(8)	9.972(3)
α, °	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
β, °	92.470(4)	100.4930(10)	106.551(2)	100.997(2)	100.094(2)	90.00	93.7600(10)	98.464(8)
γ, °	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
Volume, Å^3	1116.72(16)	1065.13(11)	1201.18(12)	1166.8(3)	1131.52(13)	2408.2(2)	1379.00(18)	1126.7(5)
Density, g/cm^3	2.059	2.008	2.058	1.970	2.032	2.207	2.024	1.902
Crystal size, min x mid x max	0.06 x 0.10 x 0.42	0.44 x 0.20 x 0.14	0.16 x 0.22 x 0.30	0.30 x 0.20 x 0.10	0.06 x 0.18 x 0.26	0.06 x 0.20 x 0.28	0.12 x 0.20 x 0.28	0.06 x 0.14 x 0.26
μ, mm^{-1}	2.874	3.004	2.702	2.750	2.836	3.941	2.367	3.251
Trans min / max	0.3782 / 0.8465	0.3515/ 0.6784	0.4978 / 0.6717	0.4925/ 0.7705	0.5259 / 0.8483	0.4050 / 0.7979	0.5570 / 0.7643	0.4853 / 0.8288
θ_{min}, °	1.93	1.68	1.48	2.81	1.46	2.14	5.40	2.18
θ_{max}, °	32.56	27.49	33.14	26.40	32.58	32.58	30.97	29.61
Reflections								
collected	17748	15508	21724	8684	13291	18651	15349	14624
independent	3962	2435	4223	2217	3850	3961	7025	3088
observed	3386	2327	3853	2118	3433	3361	6767	2657
Threshold expression	>2□(I)	>2□(I)	>2□(I)	>2□(I)	>2□(I)	>2□(I)	>2□(I)	>2□(I)
R_1 (observed)	0.0256	0.0215	0.0284	0.0203	0.0254	0.0343	0.0205	0.1103
wR_2 (all)	0.0622	0.0570	0.0639	0.0470	0.0607	0.0805	0.0480	0.2432
Goodness of fit (all)	1.058	1.037	1.110	1.023	1.022	1.158	1.027	1.348
Δρ max / min	1.046 / -0.910	0.913/-0.609	1.394 / -0.763	0.408/ 0.452	0.734 / -0.545	1.906 / -0.858	0.625 / -0.414	1.180 / -1.820
2θ limit	30.00	25.00	27.50	25.00	30.00	30.00	27.50	25.00
Completeness to 2θ limit	0.994	1.000	0.986	1.000	0.983	0.988	0.978	0.991

	A3D3	**A3D8**	**A3D10**	**A4D2**	**A4D8**	**A4D9**	**A4D10**
Systematic name	TW-2-13 [2-(2-pyridyl)-imidazole]$_3$, I-$(CF_2)_6$-I	TW-1-107 [2-(4-pyridyl)-imidazole]$_2$, 1,4-diiodotetra-fluorobenzene	TW-1-68 [2-(2-pyridyl)-imidazole]$_2$, 4,4'-diiodo-F_8-biphenyl	TW-2-09 2-(2-pyrazinyl)-imidazole, I-$(CF_2)_4$-I	TW-1-M1 2-(2-pyrazinyl)-imidazole, 1,4-diiodotetra-fluorobenzene	TW-1-59 [2-(2-pyrazinyl)-imidazole]$_2$, 1,3,5-F_3-2,4,6-I_3-benzene	TW-1-69 [2-(2-pyrazinyl)-imidazole]$_2$, 4,4'-diiodo-F_8-biphenyl
Formula moiety	$(C_8H_7N_3)_3$ $(C_6F_{12}I_2)$	$(C_8H_7N_3)_2$ $(C_6F_4I_2)$	$(C_8H_7N_3)_2$ $(C_{12}F_8I_2)$	$(C_7H_6N_4)_2$ $(C_4F_8I_2)$	$(C_7H_6N_4)_2$ $(C_6F_4I_2)$	$(C_7H_6N_4)_2$ $(C_6F_3I_3)$	$(C_7H_6N_4)_2$ $(C_{12}F_8I_2)$
Empirical formula	$C_{30}H_{21}F_{12}I_2N_9$	$C_{22}H_{14}F_4I_2N_6$	$C_{28}H_{14}F_8I_2N_6$	$C_{18}H_{12}F_8I_2N_8$	$C_{20}H_{12}F_4I_2N_8$	$C_{20}H_{12}F_3I_3N_8$	$C_{26}H_{12}F_8I_2N_8$
Molecular weight	989.36	692.19	840.25	746.16	694.18	802.08	842.24
Color, Habit	colourless prism	colourless needle	colourless prism	colourless prism	colourless plate	colourless rod	yellow prism
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space group, Z	P-1, 1	P2(1)/n, 2	C2/c, 4	P-1, 1	P2(1)/c, 2	Pbcn, 4	P-1, 2
a, Å^3	5.1393(6)	12.9720(11)	24.4359(12)	6.1488(7)	11.0717(6)	33.0655(16)	7.6527(4)
b, Å^3	11.0259(12)	5.0426(4)	7.2667(4)	6.3967(7)	10.6250(6)	9.8284(5)	12.7331(7)
c, Å^3	15.2795(17)	17.0878(15)	16.3695(8)	15.8942(19)	10.1858(6)	7.3176(3)	15.4446(9)
α, °	92.084(3)	90.00	90.00	81.861(4)	90.00	90.00	67.3200(10)
β, °	91.221(3)	92.470(4)	109.7130(10)	85.950(4)	108.814(2)	90.00	88.558(2)
γ, °	100.093(3)	90.00	90.00	72.388(3)	90.00	90.00	81.6160(10)
Volume, Å^3	851.52(17)	1116.72(16)	2736.4(2)	589.59(12)	1134.20(11)	2378.08(19)	1372.95(13)
Density, g/cm^3	1.929	2.059	2.040	2.101	2.033	2.240	2.037
Crystal size, min x mid x max	0.08 x 0.14 x 0.22	0.06 x 0.10 x 0.42	0.18 x 0.24 x 0.32	0.04 x 0.12 x 0.22	0.10 x 0.26 x 0.34	0.04 x 0.10 x 0.28	0.22 x 0.26 x 0.32
μ, mm^{-1}	15.460	2.874	2.386	2.755	2.832	3.993	2.380
Trans min / max	0.1321 / 0.3710	0.3782 / 0.8465	0.5157 / 0.6734	0.5824 / 0.8978	0.4460 / 0.7649	0.4010 / 0.8566	0.5164 / 0.6226
θ_{min}, °	2.90	1.93	2.64	1.29	1.94	2.16	1.75
θ_{max}, °	69.25	32.56	33.13	32.70	32.64	32.52	33.45
Reflections							
collected	13661	17748	14274	3658	10920	36207	40305
independent	2928	3962	4778	3658	3791	4246	9826
observed	2797	3386	4451	3313	3467	3689	9163
Threshold expression	>2□(I)	>2□(I)	>2□(I)	>2□(I)	>2□(I)	>2□(I)	>2□(I)
R_1 (observed)	0.0368	0.0256	0.0231	0.0314	0.0219	0.0212	0.0210
wR_2 (all)	0.1302	0.0622	0.0570	0.1144	0.0595	0.0480	0.0516
Goodness of fit (all)	1.241	1.058	1.029	1.135	1.077	1.046	1.041
Δρ max / min	0.769 / -0.997	1.046 / -0.910	1.073 / -0.856	2.122 / -0.925	0.620 / -0.677	0.684 / -0.719	0.646 / -0.545
2θ limit	67.50	30.00	30.00	27.50	30.00	32.52	30.00
Completeness to 2θ limit	0.942	0.994	0.985	0.984	0.983	0.983	0.987

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