

Supporting Information for
Establishing a hierarchy of halogen bonding by engineering crystals
without disorder

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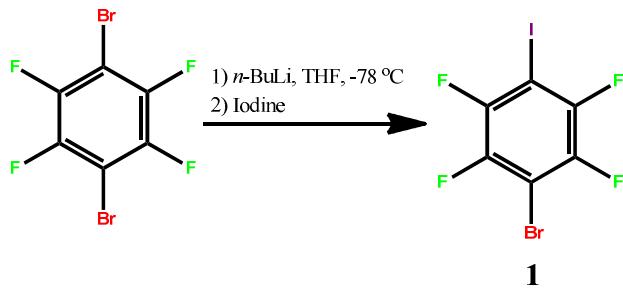
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1. Experimental section

¹H NMR spectra were recorded on a Varian Unity plus 400 MHz spectrometer in CDCl₃ or *d*-DMSO. Data is expressed in parts per million (ppm) downfield shift from tetramethylsilane or residual protiosolvent as internal reference and are reported as position (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (*J* in Hz) and integration (number of protons). Chemical shift for ¹⁹F fluorine were recorded in parts per million (ppm) relative to trifluorotoluene ($\delta = -63.72$ ppm) as an internal standard in CDCl₃ or *d*-DMSO. Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectroscopy (IR) was done on a Nicolet 380 FT-IR. All chemicals were purchased from Aldrich and Fisher and used without further purification, unless otherwise noted. Solvents and reagents were purified according to the procedures outlined by Perrin and Armarego. [Purification of Laboratory Chemicals; D. D. Perrin, W.L.F. Armarego; 3rd Ed., Pergamon Press, 1988]. 4-bromotetrafluorobenzoic acid and 4-iodoterafluorobenzoic acid were prepared from previously reported procedure.¹

1.1 Experimental Procedures and Product Characterization Data

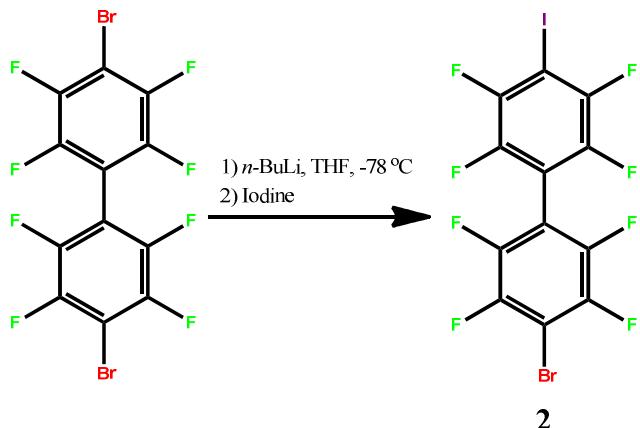
1.1.1 Synthesis of 1-bromo-2,3,5,6-tetrafluoro-4-iodobenzene, 1



To an oven dried flask was added 1,4-dibromo-2,3,5,6-tetrafluorobenzene (1g, 3.2 mmol) under a stream of argon and sealed the flask with rubber septum. To this flask was added dry, freshly distilled THF (70mL) via canula. This solution was cooled to -78 °C by immersing into dry ice–acetone bath for 5-7 mins. To this solution was then slowly added *n*-butyllithium (1.6 M solutions in hexanes, 2.06 mL, 3.3 mmol). After 20 minutes, iodine (2.06g, 8 mmol) was added and the reaction mixture was slowly warmed to room temperature and saturated sodium

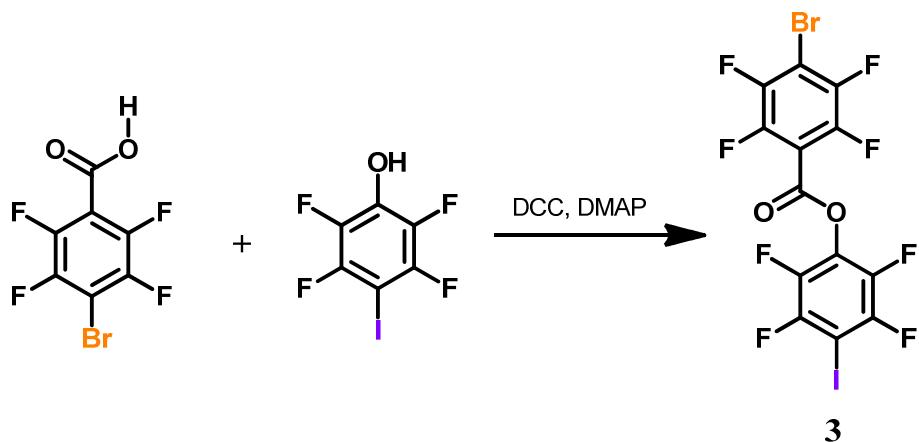
thiosulfate solution was added to obtain a clear solution. The product was extracted with methylene chloride (3x100 mL). The organic phase was dried using anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator to yield pure **1** (0.95g, 82% yield). M.p. 87-89 °C. ^{19}F NMR (δ_{H} ; 400 MHz, CDCl_3): -118.74 – -118.94 (m, 2F), -131.06 – -131.47 (m, 2F). IR: 2919, 2361, 1667, 1469, 1440, 1356, 1224, 976, 948, 771, 757, 572.

1.1.2 Synthesis of 4-bromo-2,2',3,3',5,5',6,6'-octafluoro-4'-iodo-1,1'-biphenyl, **2**



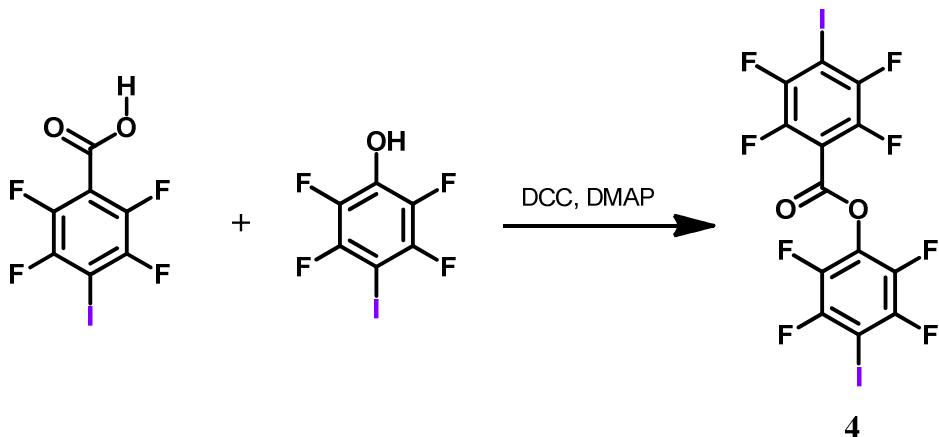
To an oven dried flask was added 4,4'-dibromo-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (1g, 2.2 mmol) under stream of argon and the flask was sealed with rubber septum. To this flask was added dry, freshly distilled THF (40mL) via canula. This solution was cooled to -78 °C by immersing into dry ice –acetone bath for 5-7 mins. To this solution was then slowly added n-butyllithium (1.6 M solutions in hexanes, 1.4 mL, 2.26 mmol). After 20 minutes, iodine (0.57 g, 2.2 mmol) was added into a reaction mixture. 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 rotary evaporator to yield pure **2** (1.02g, 93 % yield). M.p. 104-108 °C. ^{19}F NMR (δ_{H} ; 400 MHz, CDCl_3): -119.78 - -120.10 (m, 2F), -132.60 - -132.93 (m, 2F), -137.30 - -137.64 (M, 2F), -137.70 - -137.98 (m, 2F). IR: 2940, 2856, 1631, 1465, 1366, 1221, 1221, 1109, 975, 954, 861, 716, 582.

1.1.3 Synthesis of 4-bromo-2,3,5,6-tetrafluorophenyl 2,3,5,6-tetrafluoro-4-iodobenzoate, 3



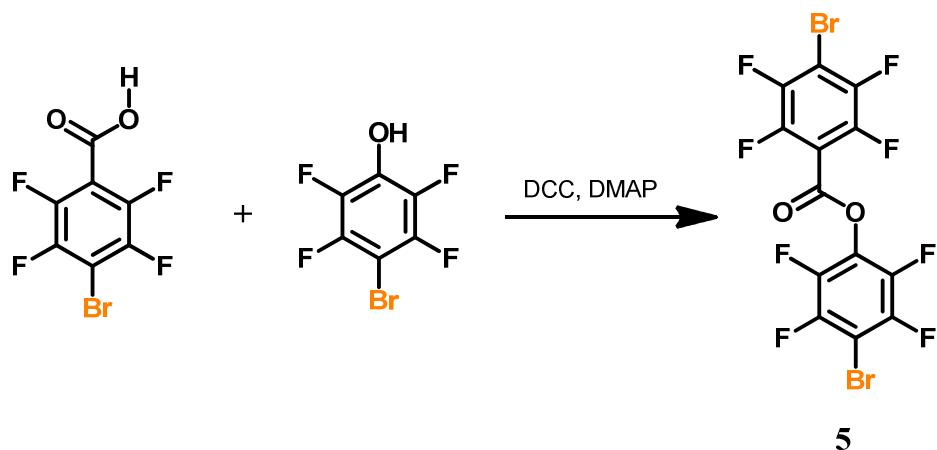
To an oven dried 50 mL flask was added 4-bromotetrafluorobenzoic acid (1.07g, 3.9 mmol), 4-iodotetrafluorophenol (1.14g, 3.9mmol) and 20 mL dry methylene chloride under a nitrogen atmosphere. To this solution DCC (0.89g, 4.32 mmol) and DMAP (0.04g, 34.4 mmol) were added. The reaction mixture was allowed to stir at room temperature for 48 hours. The white precipitate was filtered off and was washed with aqueous acetic acid (5%, 100 mL). The organic layer was separated; the solvent removed by rotary evaporation and a yellow solid was collected. The crude product was purified by column chromatography (100 g silica, hexane → hexane: ethyl acetate 100:1) to give pure **3** (0.80g, 40%). M. p. 58-60 °C. ^{19}F NMR (δ_{H} ; 400 MHz, CDCl_3): -118.96 - -119.53 (m, 2F), -130.29 - -130.75 (m, 2F), -135.05 - -135.50 (m, 2F), -150.03 - -150.46 (m, 2F). IR: 1775, 1634, 1473, 1401, 1299, 1266, 1133, 1067, 984, 970, 854, 807.

1.1.4 Synthesis of 2,3,5,6-tetrafluoro-4-iodophenyl 2,3,5,6-tetrafluoro-4-iodobenzoate, 4



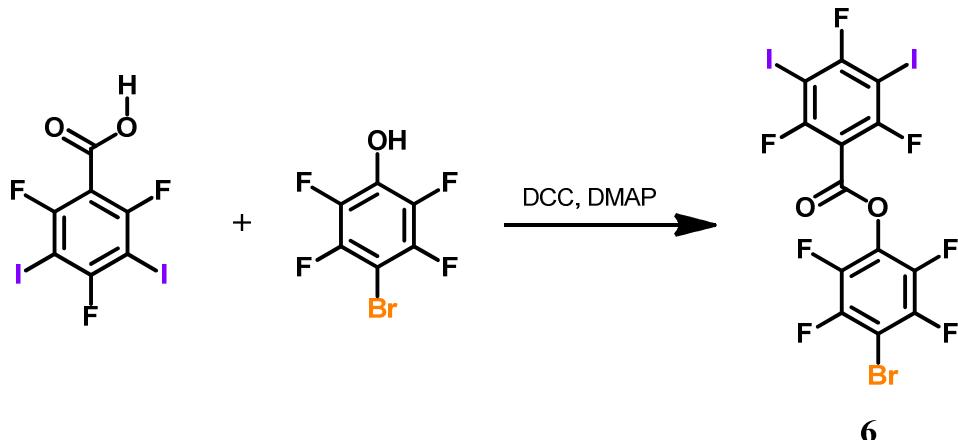
To an oven dried 50 mL flask was added 4-iodotetrafluorobenzoic acid (0.2g, 0.46 mmol), 4-iodotetrafluorophenol (0.14g, 0.46 mmol) and 10 mL dry methylene chloride under nitrogen atmosphere. To this solution DCC (0.11g, 0.5 mmol) and DMAP (0.005g, 0.04 mmol) were added. The reaction mixture was allowed to stir at room temperature for 48 hours. The white precipitate was filtered off and washed with aqueous acetic acid (5%, 100 mL). The organic layer was separated; the solvent removed by rotary evaporation and a yellow solid was collected. The crude product was purified by column chromatography (100 g silica, hexane → hexane: ethyl acetate 97:3) to give pure **4** (0.12g, 42%). M. p. 80-82 °C. ^{19}F NMR (δ_{H} ; 400 MHz, CDCl_3): -117.48 - -117.78 (m, 2F), -119.16 - -119.41 (m, 2F), -135.01 - -135.23 (m, 2F), -150.09 - -150.35 (m, 2F). IR: 1771, 1623, 1467, 1291, 1263, 1142, 1134, 970, 806, 771.

1.1.5 Synthesis of 4-bromo-2,3,5,6-tetrafluorophenyl 4-bromo-2,3,5,6-tetrafluorobenzoate, **5**



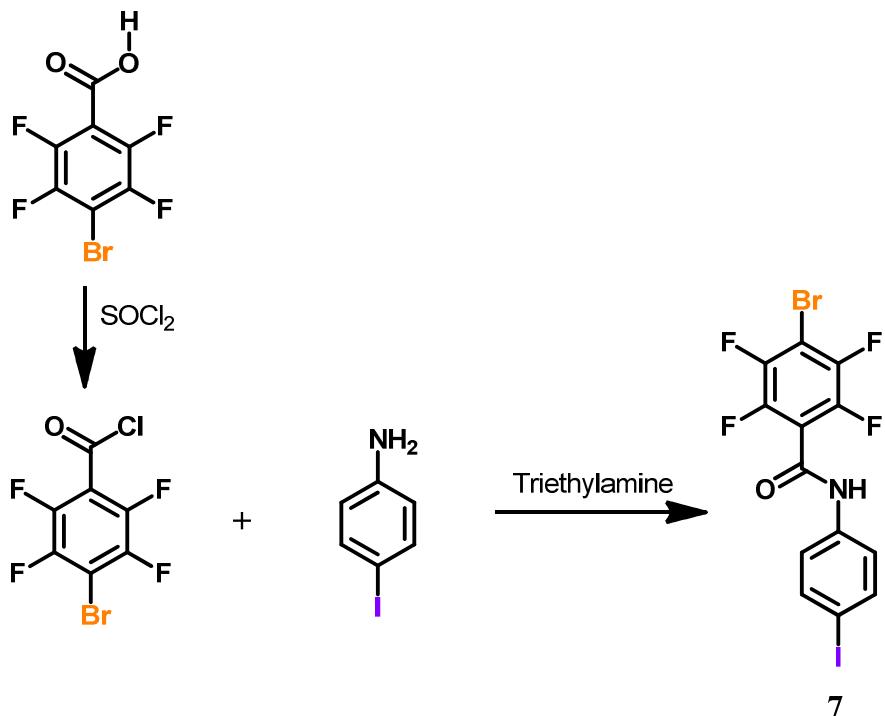
To an oven dried 50 mL round bottom flask was added 4-bromotetrafluorobenzoic acid (0.5g, 1.8 mmol), 4-bromotetrafluorophenol (0.45g, 1.8 mmol) and 10 mL dry methylene chloride under nitrogen atmosphere. To above solution DCC (0.42g, 2 mmol) and DMAP (0.02g, 0.16 mmol) were added. The reaction mixture was allowed to stir at room temperature for 48 hours. The white precipitate was filtered off and the filtrate was washed with aqueous acetic acid (5%, 100 mL). The organic layer was separated; the solvent removed by rotary evaporation and a yellow solid was collected. The crude product was purified by column chromatography (100 g silica, hexane → hexane: ethyl acetate 95:5) to give pure **5** (0.43g, 46%). M. p. 81-83 °C. ^{19}F NMR (δ_{H} ; 400 MHz, CDCl_3): -130.17 - -130.72 (m, 2F), -132.21 - -132.52 (m, 2F), -135.07 - -135.38 (m, 2F), -150.48 - -151.02 (m, 2F). IR: 1758, 1633, 1477, 1402, 1305, 1156, 1138, 1065, 977, 938, 833, 782.

1.1.6 Synthesis of 4-bromo-2,3,5,6-tetrafluorophenyl 2,4,6-trifluoro-3,5-diiodobenzoate, 6



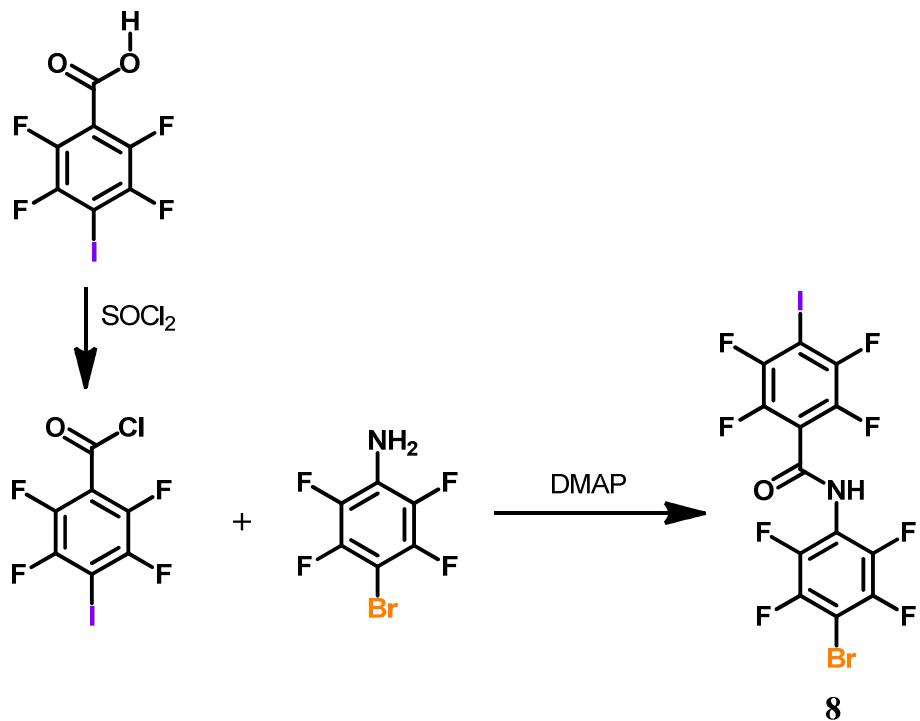
To an oven dried 50 mL flask was added 2,4,6-trifluoro-3,5-diiodobenzoic acid (1g, 2.31mmol), 4-bromotetrafluorophenol (0.57g, 2.31mmol) and 10 mL dry methylene chloride under nitrogen atmosphere. To this solution DCC (0.53g, 2.54mmol) and DMAP (0.012g, 0.1 mmol) were added. The reaction mixture was allowed to stir at room temperature for 48 hours. The white precipitate was filtered off and the filtrate was washed with aqueous acetic acid (5%, 100 mL). The organic layer was separated; the solvent removed by rotary evaporation and a yellow solid was collected. The crude product was purified by column chromatography (100 g silica, hexane → hexane: ethyl acetate 97:3) to give pure **6** (0.46g, 30%). M. p. 125-127 °C. ^{19}F NMR (δ_{H} ; 400 MHz, CDCl_3): -59.73 - -59.92 (m, 1F), -84.26 - -84.49 (m, 2F), -132.39 - -133.34 (m, 2F), -140.61 - -141.10 (m, 2F). IR: 1764, 1594, 1489, 1210, 1101, 1064, 977, 835, 665.

1.1.7 Synthesis of 4-bromo-2,3,5,6-tetrafluoro-N-(4-iodophenyl)benzamide, 7



To an oven dried 50 mL round bottom flask was added 4-bromotetrafluorobenzoic acid (0.5g, 1.8 mmol) and 10 mL dichloromethane under nitrogen atmosphere. An excess of oxalyl chloride (1.50 mL) and catalytic amount of DMF were added via syringe to the reaction flask. The reaction mixture was stirred until all the acid had gone into solution (typically 1-2 h), and the methylene chloride and excess oxalyl chloride were removed under reduced pressure. The acid chloride was used without further purification. To another oven dried 100 mL round bottom flask 4-iodoaniline (0.40g, 1.82mmol) and triethylamine (0.254 mL, 1.82 mmol) were added under nitrogen atmosphere. To this flask was added acid chloride (dissolved in 5 mL methylene chloride) via syringe in lots over 10 minutes. The reaction mixture was stirred at room temperature for 5 hours. The white precipitate was filtered off and washed with methylene chloride to yield white solid of **7** (0.64g, 98%). Single crystals of **7** were grown from ethanol as a solvent via slow evaporation. M. p. > 250 $^{\circ}\text{C}$. ^1H NMR (δ_{H} ; 400 MHz, $\text{D}_6\text{-DMSO}$): 11.11 (s, 1H), 7.74 (d, $J = 8\text{Hz}$, 2H), 7.51 (d, $J = 8\text{Hz}$, 2H). ^{19}F NMR (δ_{F} ; 400 MHz, $\text{D}_6\text{-DMSO}$): -132.78 - -133.34 (m, 2F), -140.61 - -141.10(m, 2F). IR: 3247, 3179, 3108, 3059, 1669, 1637, 1597, 1584, 1537, 1473, 1391, 1323, 1247, 1004, 974, 817, 788, 729.

1.1.8 Synthesis of *N*-(4-bromo-2,3,5,6-tetrafluorophenyl)-2,3,5,6-tetrafluoro-4-iodobenzamide, **8**



To an oven dried 50 mL flask was added 4-iodotetrafluorobenzoic acid (0.5g, 1.6 mmol) under nitrogen atmosphere. An excess of thionyl chloride (2 mL) was added via syringe to the reaction flask. The reaction mixture was refluxed at 90 °C for 20 hours, and excess thionyl chloride was removed under reduced pressure. The acid chloride was used without further purification. To another oven dried 100 mL flask was added 4-bromotetrafluoroaniline (0.763g, 3.12 mmol), DMAP (0.190g, 1.76 mmol) and dry methylene chloride under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 48 hours. The white precipitate was filtered, to yield white solid of **8** (0.55g, 65%). Dec. 225 °C. ^{19}F NMR (δ_{H} ; 400 MHz, D_6 -DMSO): -120.82 - -121.02 (m, 2F), -134.40 - -134.93 (m, 2F), -140.47 - -141.00(m, 2F), -143.54 - -144.07. IR: 3213, 1686, 1632, 1540, 1474, 1313, 1219, 979, 966, 863, 830, 786, 775, 693.

1.1.9 Synthesis of 1-bromo-2,3,5,6-tetrafluoro-4-iodobenzene tetramethylpyrazine (1:1), 1·A

1-Bromo-2,3,5,6-tetrafluoro-4-iodobenzene (10 mg, 0.02 mmol) and tetramethylpyrazine (1.9mg, 0.01 mmol) were placed in a 2 dram borosilicate vial and dissolved in 2 mL of methanol

After two days of slow evaporation, plate-shaped colorless crystals were obtained. M. p. 104-106 °C.

1.1.10 Synthesis of 4-bromo-2,2',3,3',5,5',6,6'-octafluoro-4'-iodo-1,1'-biphenyl tetramethylpyrazine (1:1), 2·A

4-Bromo-2,2',3,3',5,5',6,6'-octafluoro-4'-iodo-1,1'-biphenyl (10 mg, 0.01 mmol) and tetramethylpyrazine (0.68 mg, 0.005 mmol) were placed in a 2 dram borosilicate vial and dissolved in 2 mL of methanol. After three days of slow evaporation, plate-shaped colorless crystals were obtained. M. p. 144-146 °C.

1.1.11 Synthesis of 1-bromo-2,3,5,6-tetrafluoro-4-iodobenzene tetramethylpyrazine mono-N-oxide (1:1), 1·B

1-Bromo-2,3,5,6-tetrafluoro-4-iodobenzene (10 mg, 0.02 mmol) and tetramethylpyrazine mono-*N*-oxide (3.04 mg, 0.02 mmol) were placed in a 2 dram borosilicate vial and dissolved in 2 mL of methylene chloride. After one day of slow evaporation, plate-shaped crystals were obtained. M. p. 106-108 °C.

1.1.12 Synthesis of 4-bromo-2,2',3,3',5,5',6,6'-octafluoro-4'-iodo-1,1'-biphenyl tetramethylpyrazine mono-N-oxide (1:1), 2·B

4-Bromo-2,2',3,3',5,5',6,6'-octafluoro-4'-iodo-1,1'-biphenyl (10 mg, 0.01 mmol) and tetramethylpyrazine mono-*N*-oxide (1.52 mg, 0.01 mmol) were placed in a 2 dram borosilicate vial and dissolved in 2 mL of methylene chloride. After two days of slow evaporation, plate-shaped colorless crystals were obtained. M. p. 140-142 °C.

1.1.13 Synthesis of 1-bromo-2,3,5,6-tetrafluoro-4-iodobenzene 4,4'-bipyridine mono N-oxide (1:1), 1·C

1-Bromo-2,3,5,6-tetrafluoro-4-iodobenzene (10 mg, 0.02 mmol) and 4,4'-bipyridine mono *N*-oxide (3.44 mg, 0.02 mmol) were placed in a 2 dram borosilicate vial and dissolved in 2 mL of methylene chloride. After five days of slow evaporation, plate-shaped crystals were obtained. M. p. 107-109 °C.

1.1.14 Synthesis of 4-bromo-2,2',3,3',5,5',6,6'-octafluoro-4'-iodo-1,1'-biphenyl 5,6-dimethyl-1-(pyridin-4-ylmethyl)-1H-benzo[d]imidazole (1:1), 2·D

4-Bromo-2,2',3,3',5,5',6,6'-octafluoro-4'-iodo-1,1'-biphenyl (10 mg, 0.01 mmol) and 6-dimethyl-1-(pyridin-4-ylmethyl)-1H-benzo[d]imidazole (2.37 mg, 0.01 mmol) were placed in a 2 dram borosilicate vial and dissolved in 2 mL of ethanol:nitromethane (1:1). After five days of slow evaporation, block-shaped colorless crystals were obtained. M. p. 185-187 °C.

1.1.15 Synthesis of 4-bromo-2,2',3,3',5,5',6,6'-octafluoro-4'-iodo-1,1'-biphenyl 4-(N-pyrrolidinyl)pyridine (1:1), 2·E

4-Bromo-2,2',3,3',5,5',6,6'-octafluoro-4'-iodo-1,1'-biphenyl (10 mg, 0.01 mmol) and 4-(N-pyrrolidinyl)pyridine (1.48 mg, 0.01 mmol) were placed in a 2 dram borosilicate vial and dissolved in 2 mL of methanol. After three days of slow evaporation, plate-shaped crystals were obtained. M. p. 144-146 °C.

1.1.16 Synthesis of 4-bromo-2,2',3,3',5,5',6,6'-octafluoro-4'-iodo-1,1'-biphenyl 4-(N,N-dimethylamino)pyridine (1:1), 2·F

4-Bromo-2,2',3,3',5,5',6,6'-octafluoro-4'-iodo-1,1'-biphenyl (10 mg, 0.01 mmol) and 4-(N,N-dimethylamino)pyridine (1.22 mg, 0.01 mmol) were placed in a 2 dram borosilicate vial and dissolved in 2 mL of methanol. After three days of slow evaporation, plate-shaped colorless crystals were obtained. M. p. 95-97 °C.

1.1.17 Synthesis of N-(4-bromo-2,3,5,6-tetrafluorophenyl)-2,3,5,6-tetrafluoro-4-iodobenzamide 1,2-bis(4-pyridyl)ethylene (1:1), 8·G

N-(4-bromo-2,3,5,6-tetrafluorophenyl)-2,3,5,6-tetrafluoro-4-iodobenzamide (10 mg, 18.3 μmol) and 1,2-bis(4-pyridyl)ethylene (1.33 mg, 73.2 μmol) were placed in a clear 2 dram borosilicate vial and dissolved in 2 mL of ethyl acetate:nitromethane (1:1). After six days of slow evaporation, plate-shaped colorless crystals were obtained. M. p. 215-217 °C.

1.1.18 Synthesis of N-(4-bromo-2,3,5,6-tetrafluorophenyl)-2,3,5,6-tetrafluoro-4-iodobenzamide 1,2-bis(4-pyridyl)ethane (1:1), 8·H

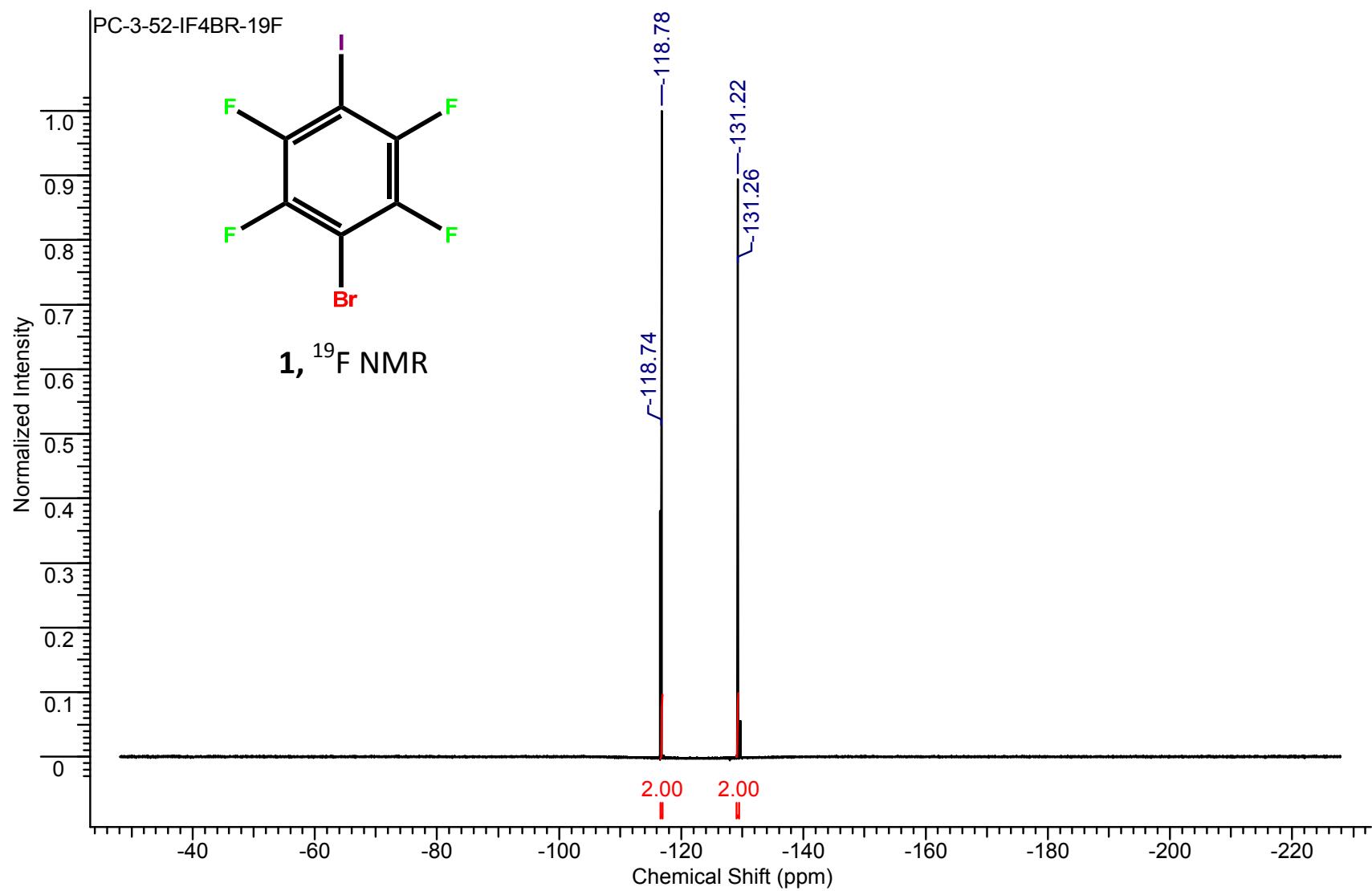
N-(4-bromo-2,3,5,6-tetrafluorophenyl)-2,3,5,6-tetrafluoro-4-iodobenzamide (10 mg, 18.3 μmol) and 1,2-bis(4-pyridyl)ethane (1.34 mg, 73.2 μmol) were placed in a clear 2 dram

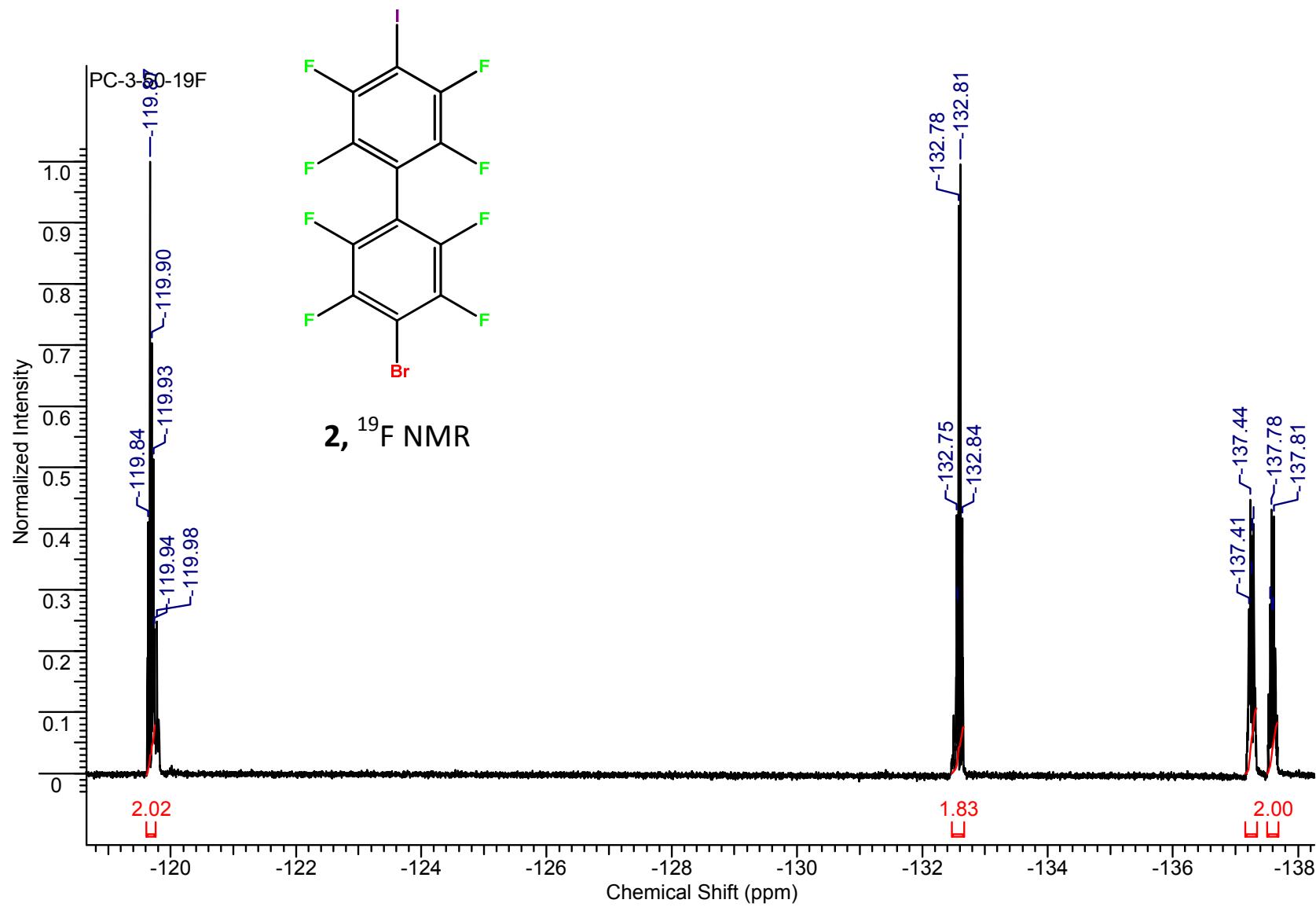
borosilicate vial and dissolved in 2 mL of ethyl acetate:nitromethane (1:1). After five days of slow evaporation, plate-shaped colorless crystals were obtained. M. p. 205-207 °C.

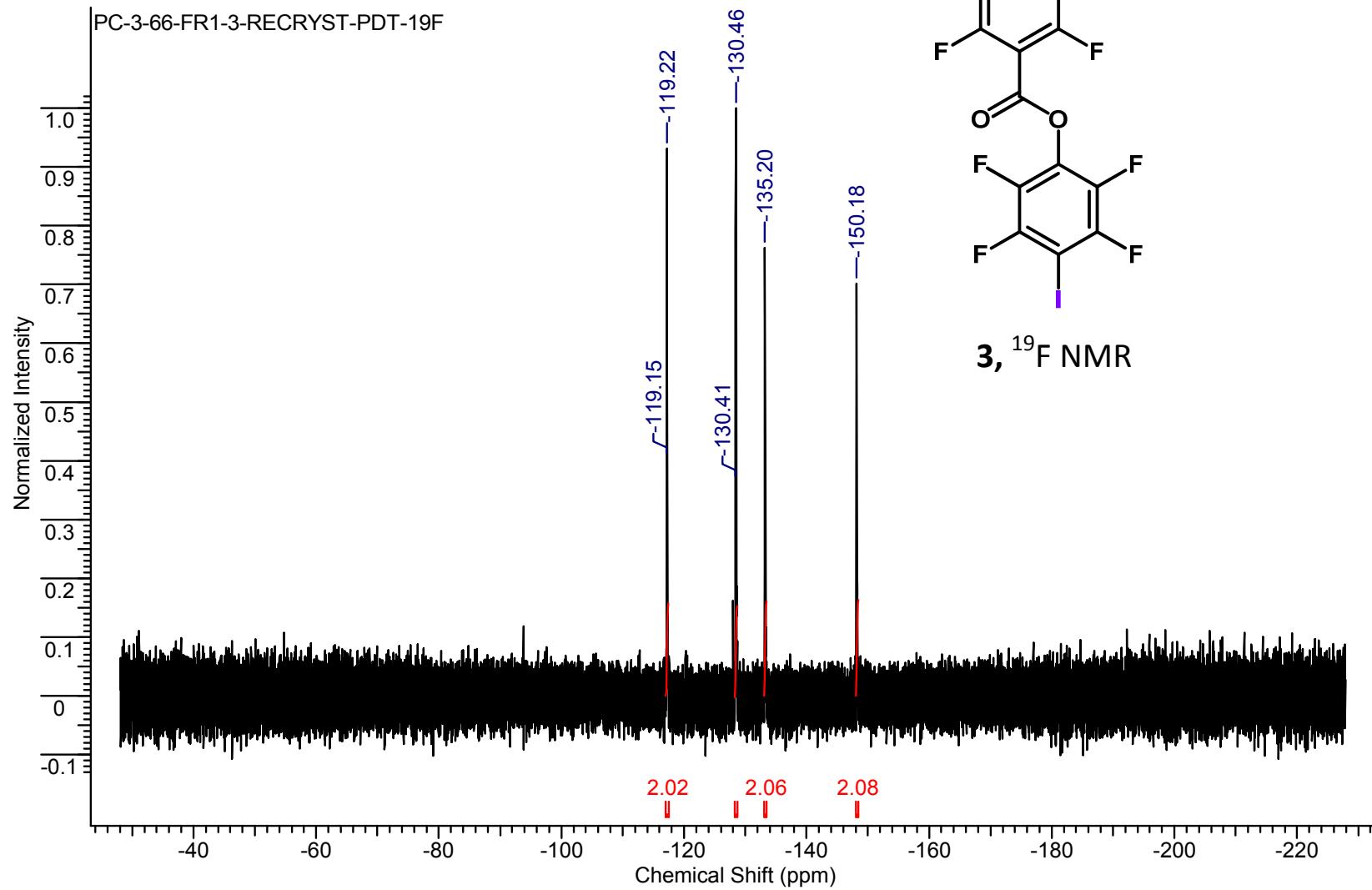
1.1.19 Synthesis of N-(4-bromo-2,3,5,6-tetrafluorophenyl)-2,3,5,6-tetrafluoro-4-iodobenzamide 4,4'-bipyridine (1:1), 8·I

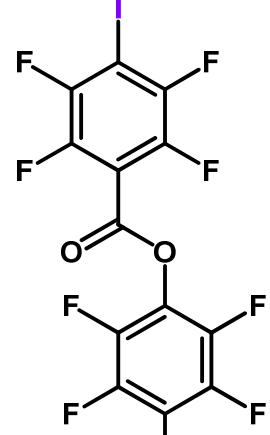
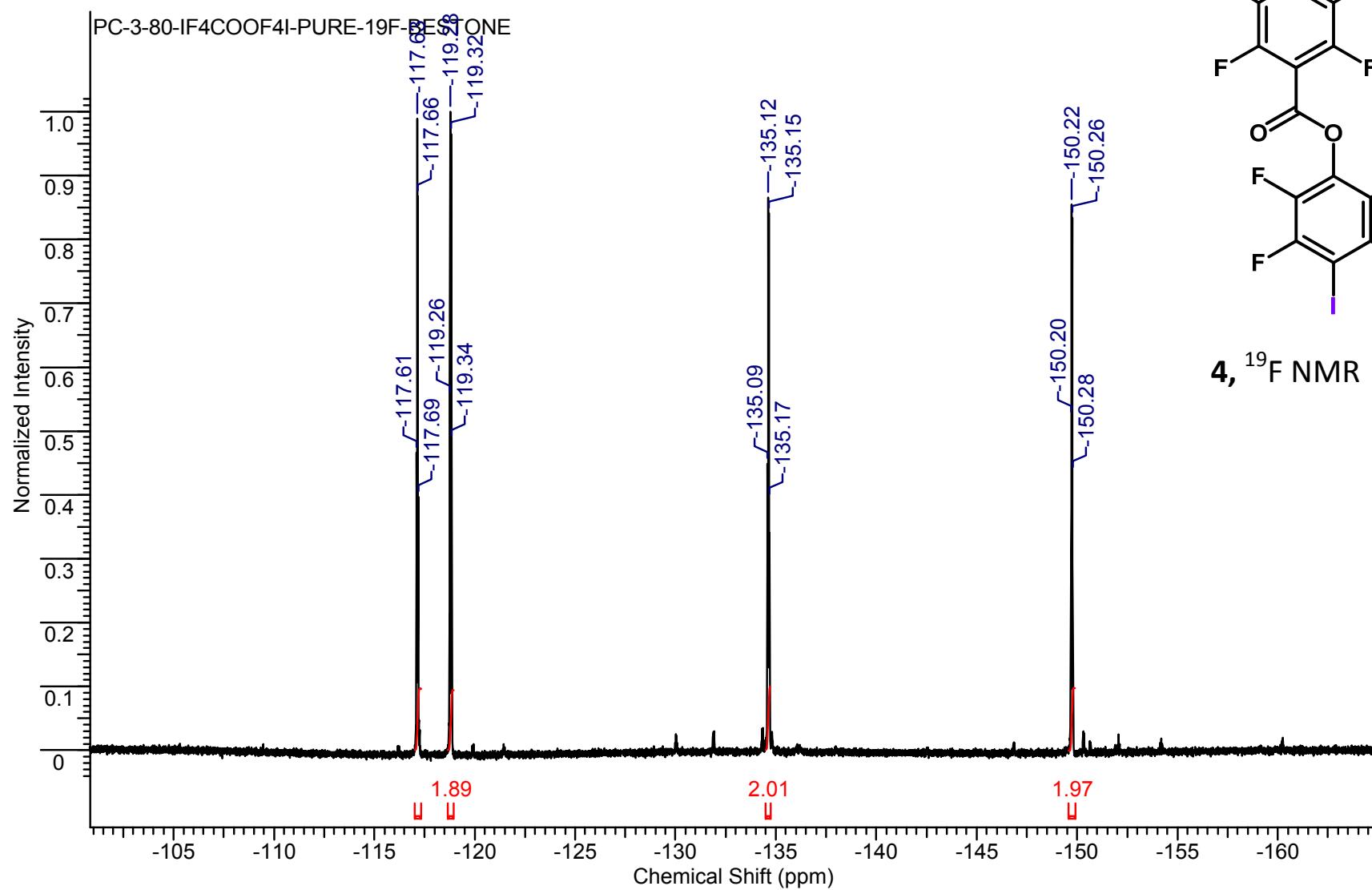
N-(4-bromo-2,3,5,6-tetrafluorophenyl)-2,3,5,6-tetrafluoro-4-iodobenzamide (10 mg, 18.3 μ mol) and 4,4'-bipyridine (1.14 mg, 73.2 μ mol) were placed in a clear 2 dram borosilicate vial and dissolved in 2 mL of ethyl acetate:nitromethane (1:1). After six days of slow evaporation, plate-shaped colorless crystals were obtained. M. p. 175-177 °C.

1.2 NMR spectra of 1-8

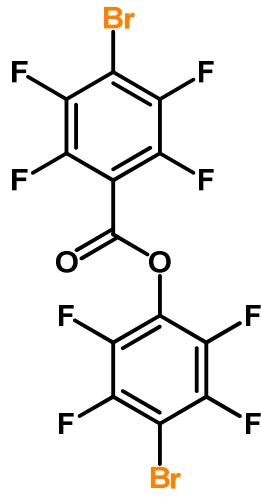
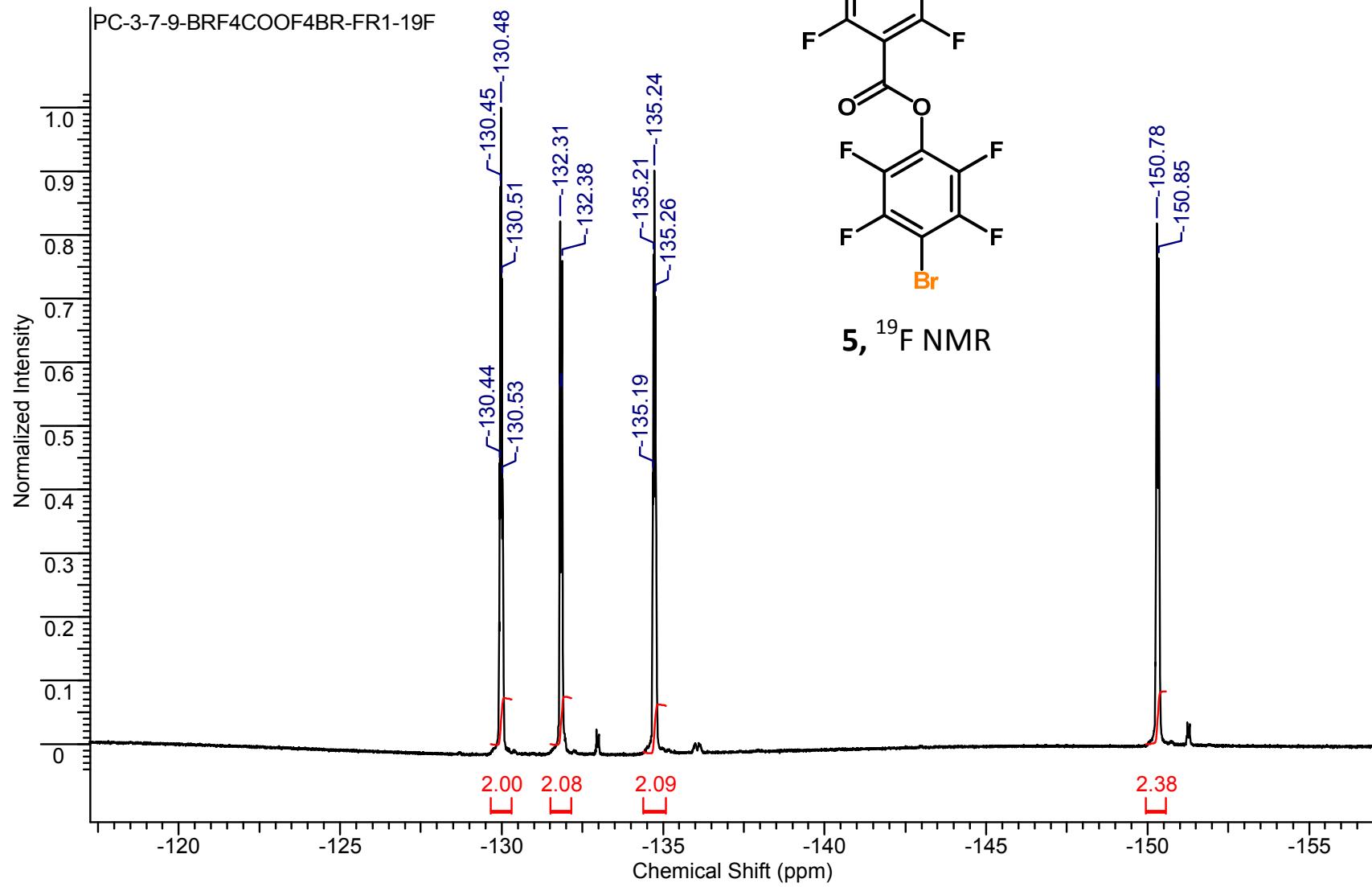




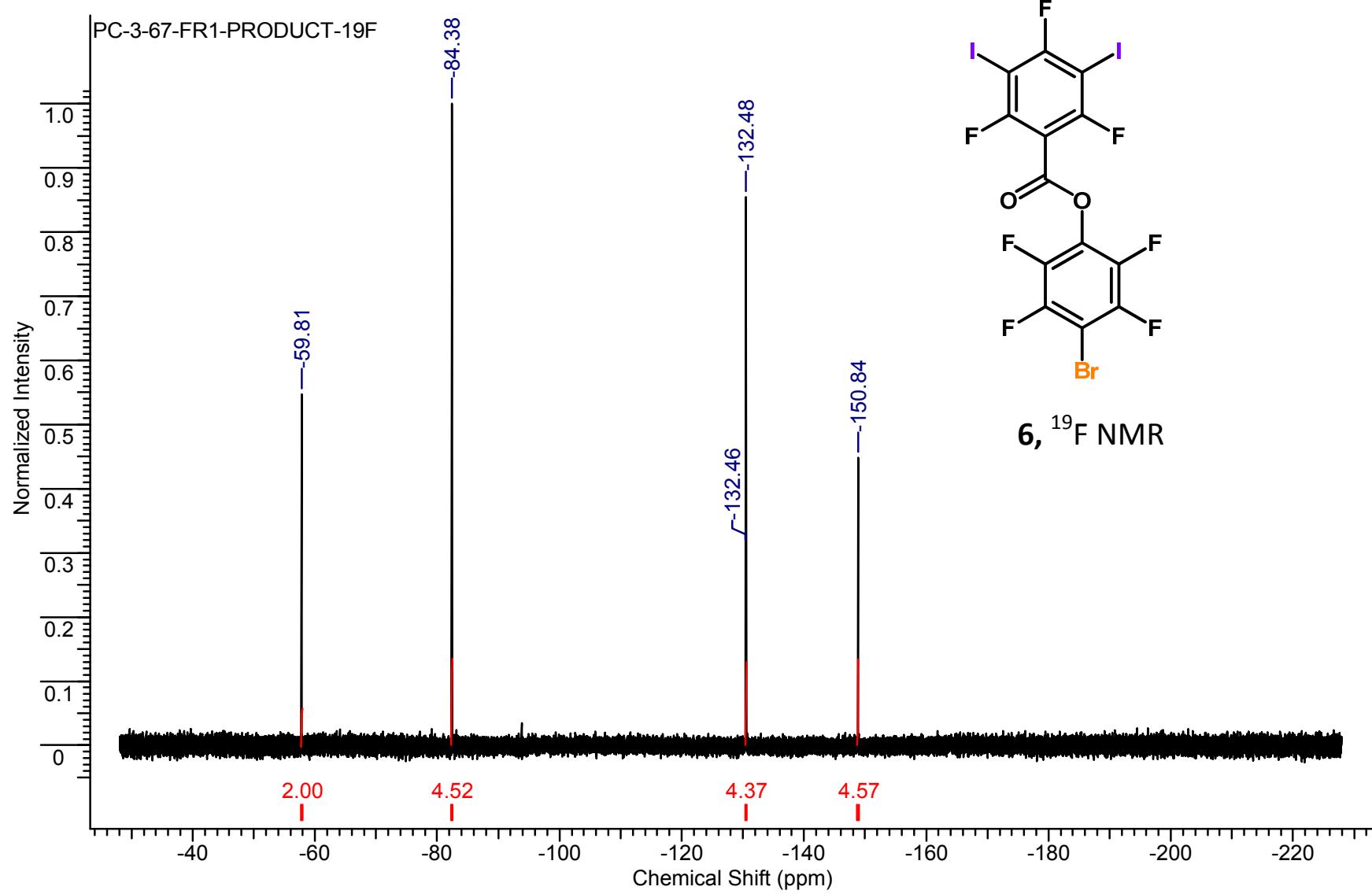


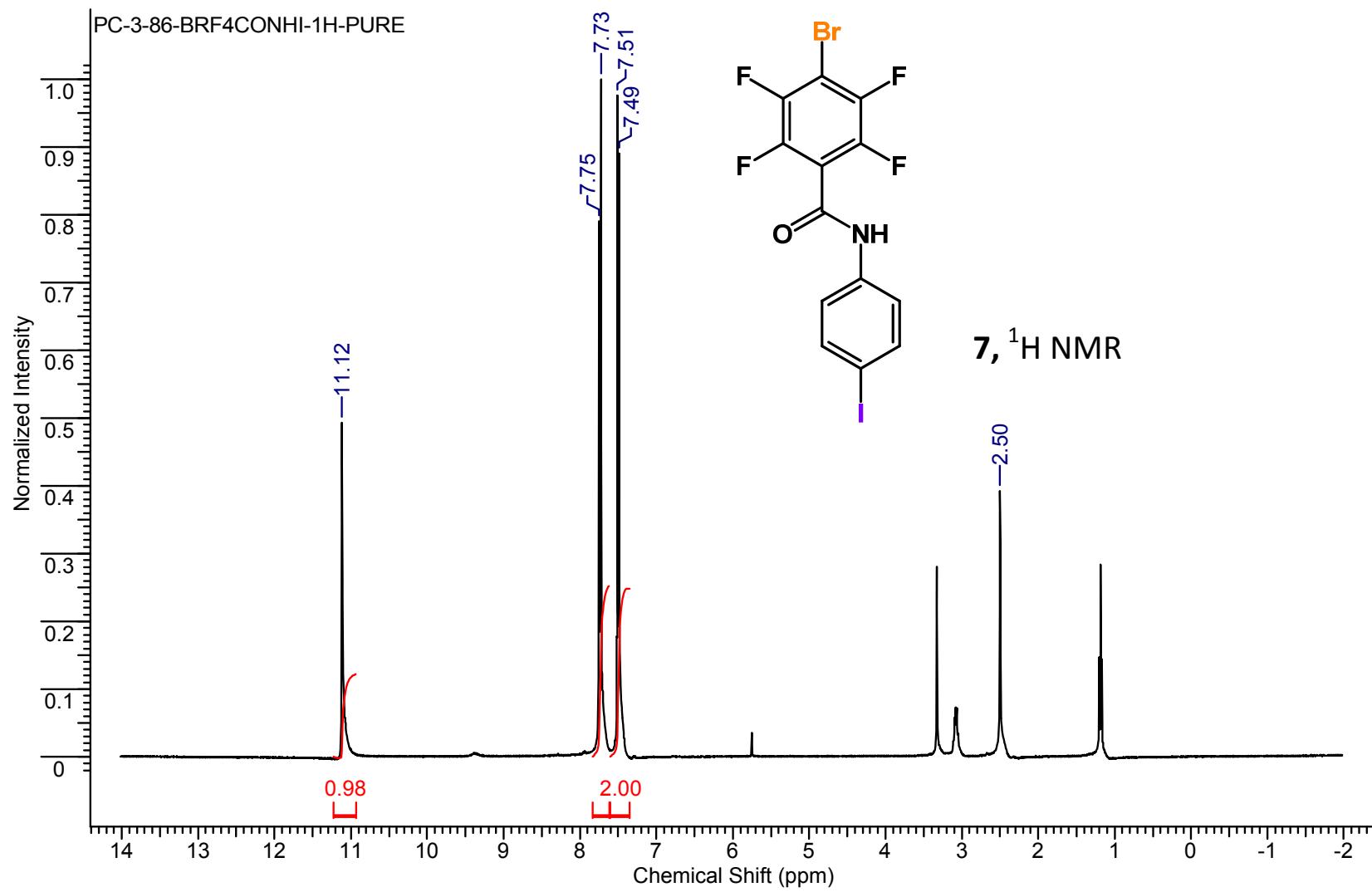


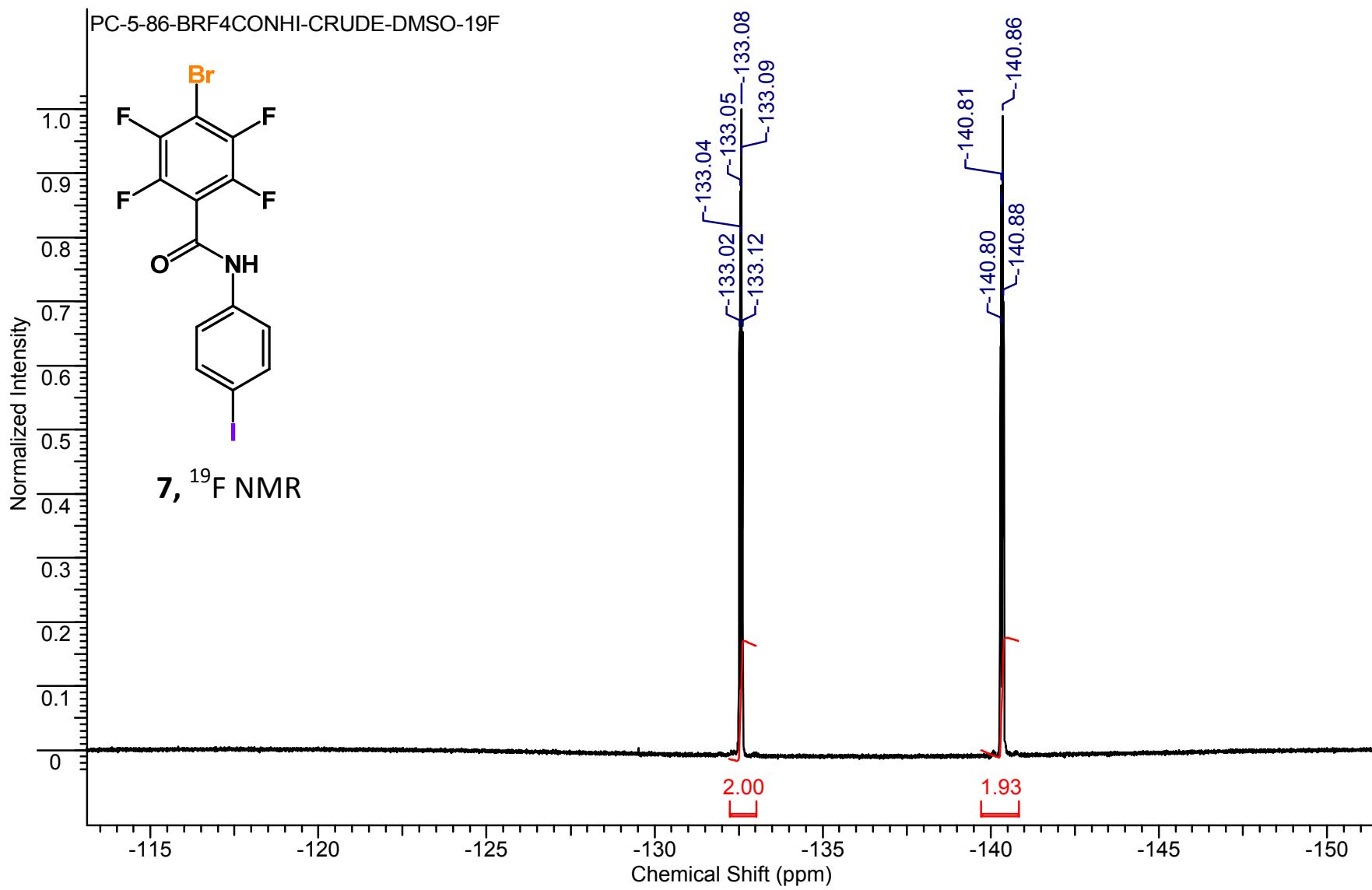
4, ^{19}F NMR

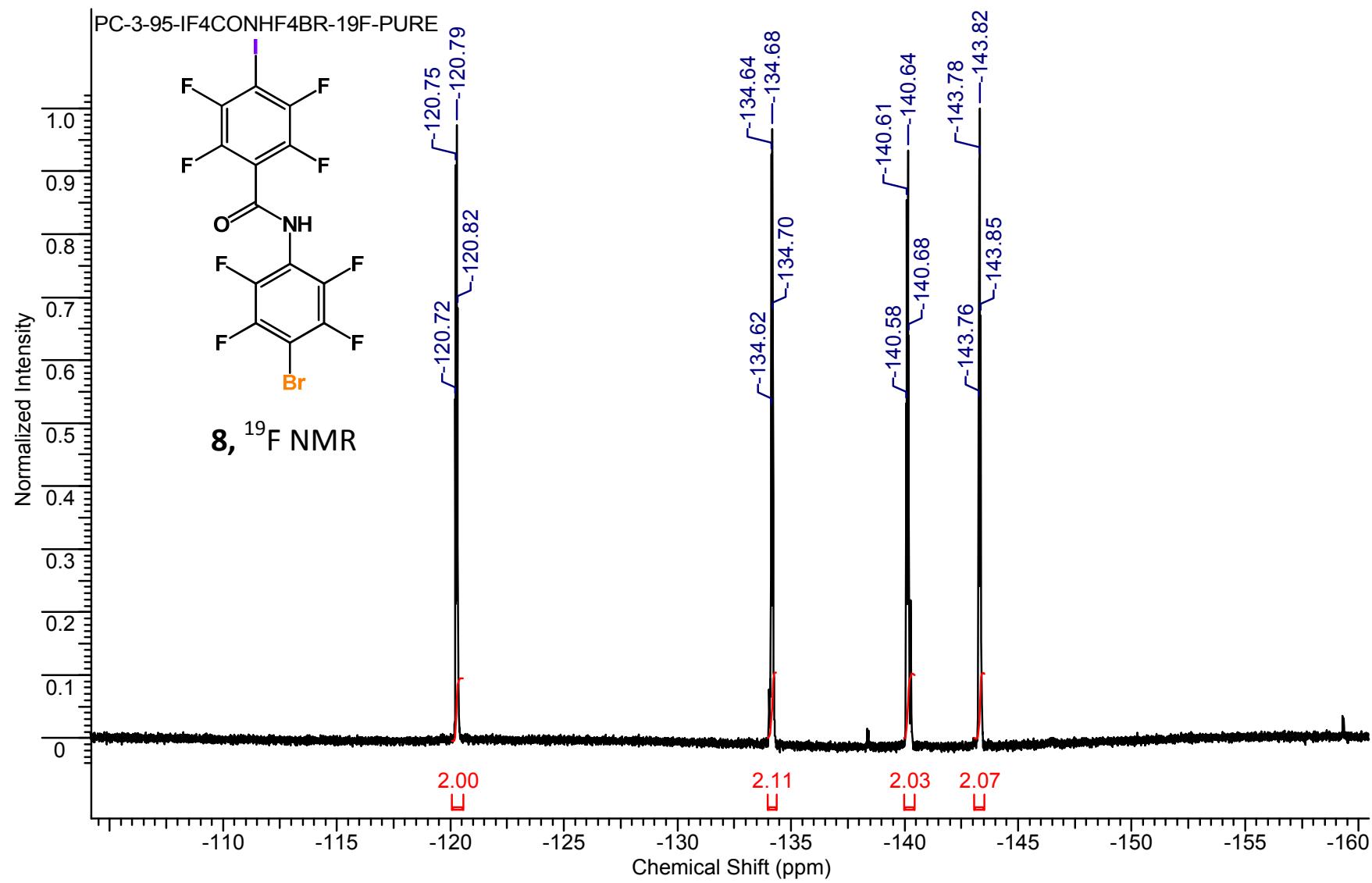


5, ¹⁹F NMR









2. Molecular electrostatic surface potential calculations

Molecular structures and their geometries were optimized using DFT, maximum value of the molecular electrostatic potential surface calculated at the DFT/B3LYP level of theory with the 6-311+G** using Spartan '08(Wavefunction, Inc. Irvine, CA).

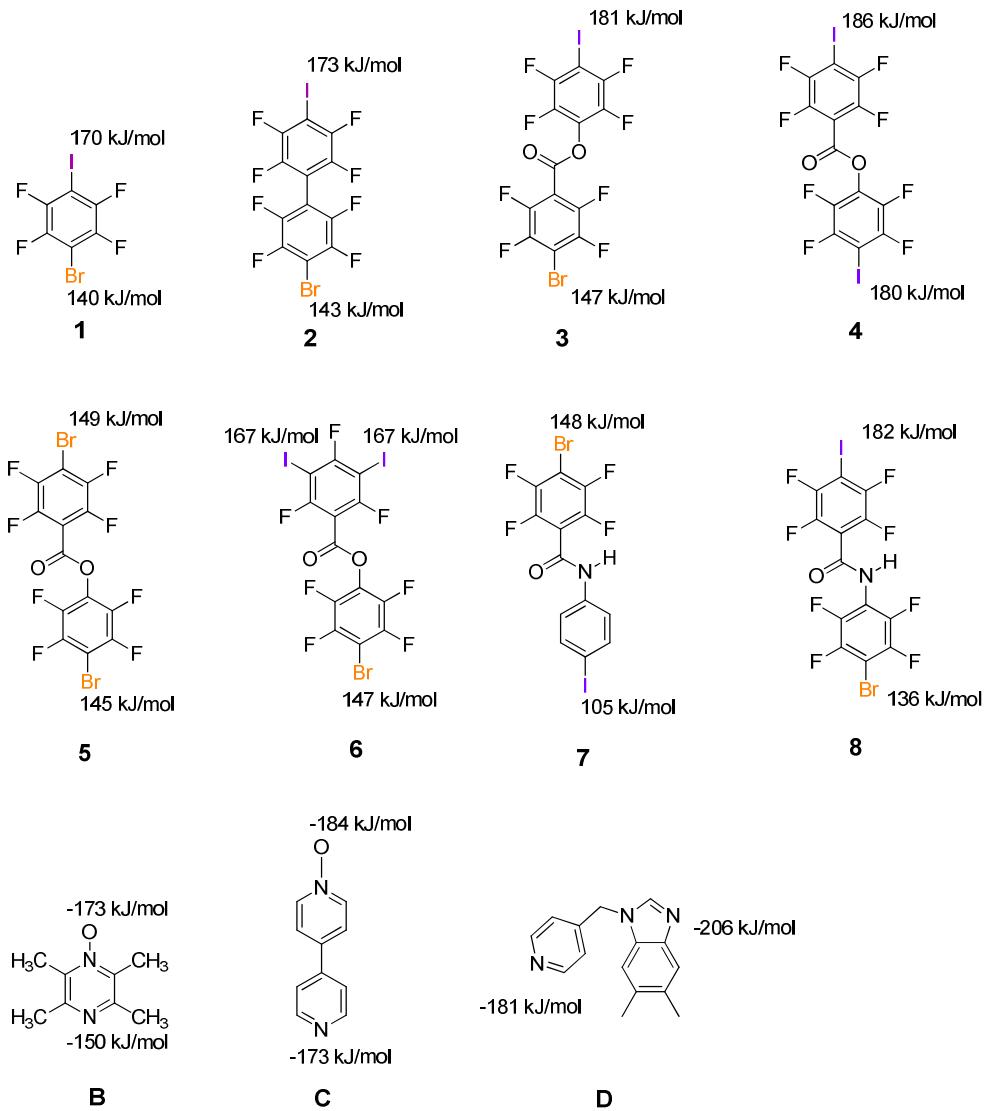
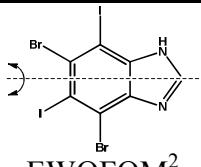
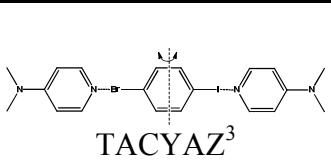
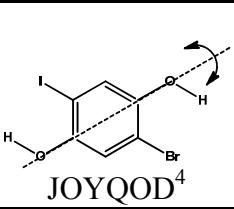
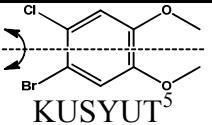
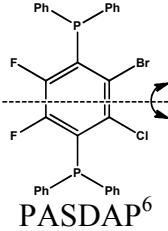
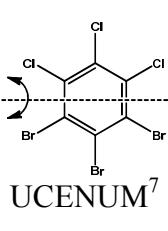
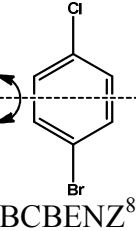
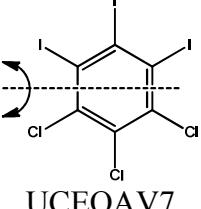
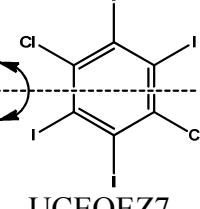
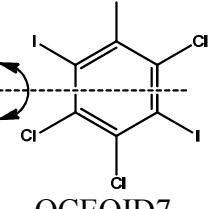
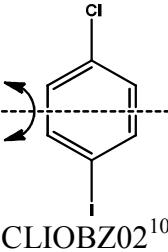
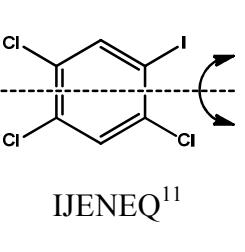


Figure S1. Ditopic halogen-bond donor and acceptor probe molecules with electrostatic charges on activated halogens and XB acceptors calculated using DFT/B3LYP level of theory with the 6-311+G** basis set using Spartan '08.

3. CSD survey

Table S1. CSD survey for heavy halogen atoms located *ortho* or *para* to each other on phenyl ring. All the CSDCODES represent disordered structures. The axis with the arrow indicates the disorder along that axis.

4. A library of ester-bridged XB donor molecules

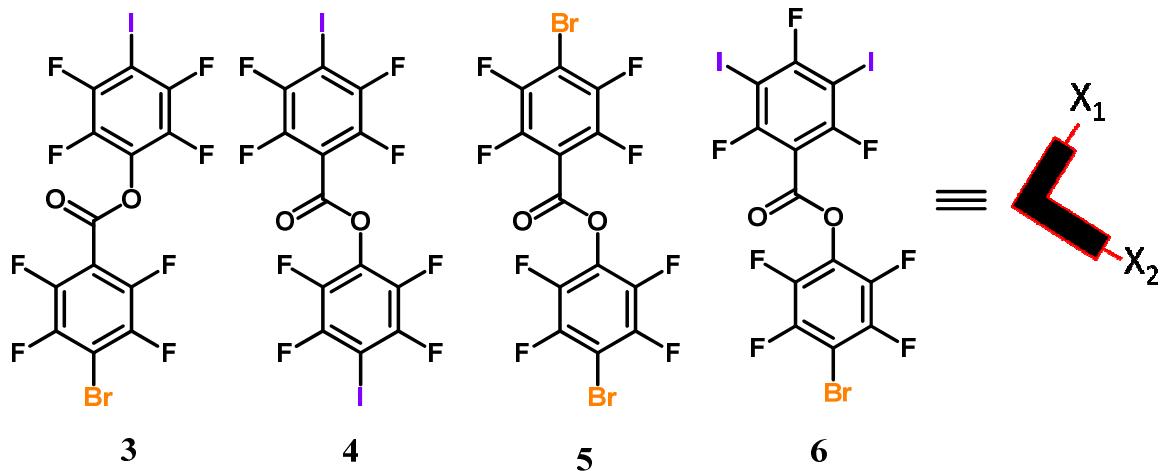


Figure S2. A library of ester-bridged XB donor molecules (For electrostatic charge calculations, see supporting information).

Table S2. Comparison of the key geometric parameters from the relevant reported structures and our work (distances and angles are averaged).

	Distance (Å)	Angle (°)
	$\text{N}_{\text{aromatic}} \cdots \text{X}_{\text{I/Br}} - \text{C}_{\text{aromatic}}$	
Reported	2.97	170.82
Current study	2.97	170.52
	$\text{N}_{\text{aromatic}} - \text{O} \cdots \text{X}_{\text{I/Br}}$	
Reported	2.91	131.66
Current Study	2.61	136.17

We analyzed the XB geometries for six structures and compared with the literature values, Table S2. The $\text{N} \cdots \text{X}_{\text{I/Br}} - \text{C}$ angle is linear and the $\text{N}-\text{O} \cdots \text{X}_{\text{I/Br}}$ angle is close to 120° (the angle at which the lone pairs of the oxygen atom are located).

As a result of this extensive structural study, we have established a tentative halogen-bond hierarchy that can be tracked in the flowchart presented in Figure S3.

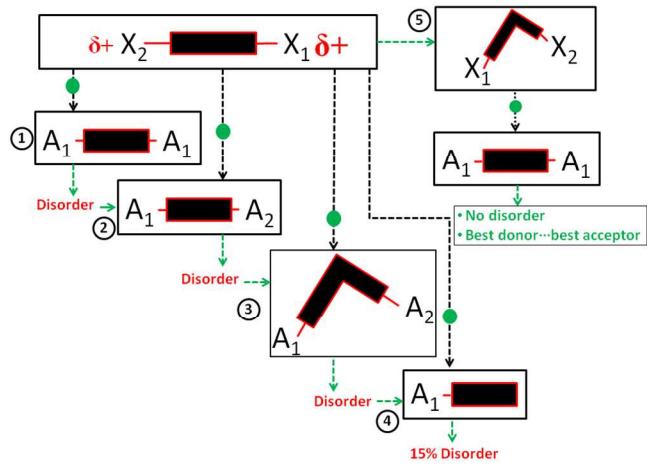


Figure S3. Flow chart summarizing the current work. Numbers indicate path direction and green circles represent co-crystallization reaction.

5. Crystallographic Experimental Details

Table S3. Summary of X-ray data

Mss name	2-F	7	8-G	8-H	8-I
Machine	Kappa	Kappa	Kappa	SMART	Kappa
Formula moiety	(C ₁₂ BrF ₈ I) (C ₉ H ₁₂ N ₂)	C ₁₃ H ₅ BrF ₄ INO	(C ₁₃ HBrF ₈ IN) (C ₁₂ H ₁₀ N ₂ O)	(C ₁₃ HBrF ₈ INO) (C ₁₂ H ₁₂ N ₂)	(C ₁₃ HBrF ₈ INO) ₂ (C ₁₀ H ₈ N ₂)
Empirical formula	C ₂₁ H ₁₂ BrF ₈ IN ₂	C ₁₃ H ₅ BrF ₄ INO	C ₂₅ H ₁₁ BrF ₈ IN ₃ O	C ₂₅ H ₁₃ BrF ₈ IN ₃ O	C ₃₆ H ₁₀ Br ₂ F ₁₆ I ₂ N ₄ O ₂
Molecular weight	651.14	473.99	728.18	730.19	1248.10
Color, Habit	colourless plate	colourless plate	colourless plate	colourless prism	colourless plate
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group, Z	C2/c, 4	P2 ₁ /n, 4	P1, 1	P2 ₁ /n, 4	P-1, 1
a, Å	13.3208(8)	7.1847(7)	4.6568(3)	15.2758(8)	4.7774(7)
b, Å	23.8060(14)	25.234(3)	11.0639(6)	7.9588(4)	7.9111(10)
c, Å	7.8323(4)	8.0401(8)	12.2258(7)	20.3245(10)	25.928(4)
α, °	90.00	90.00	98.373(2)	90.00	89.199(8)
β, °	123.017(3)	107.157(5)	100.443(2)	99.899(2)	85.294(9)
γ, °	90.00	90.00	97.995(2)	90.00	75.073(8)
V, Å ³	2082.6(2)	1392.8(2)	603.94(6)	2434.2(2)	943.6(2)
X-ray wavelength	0.71073	0.71073	0.71073	0.71073	0.71073
μ, mm ⁻¹	3.540	5.210	3.068	3.045	3.905
Absorption corr	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Trans min / max	0.4373 / 0.8157	0.3444 / 0.6806	0.5026 / 0.7914	0.4827 / 0.6752	0.4542 / 0.7995
Reflections					
collected	8039	18273	18953	26829	22718
independent	3701	4613	8253	8265	6177
observed	3063	3583	8105	6418	4033
Threshold expression	>2σ(I)	>2σ(I)	>2σ(I)	>2σ(I)	>2σ(I)
R ₁ (observed)	0.0435	0.0525	0.0518	0.0371	0.0842
wR ₂ (all)	0.1137	0.1387	0.1302	0.1030	0.2117
S	1.028	1.024	1.034	1.087	1.094
Δρ max / min	2.394 / -1.053	1.385 / -2.852	1.242 / -0.789	1.287 / -0.710	3.006 / -3.682

Mss name	2-F	7	8-G	8-H	8-I
Machine	Kappa	Kappa	Kappa	SMART	Kappa
Formula moiety	(C ₁₂ BrF ₈ I) (C ₉ H ₁₂ N ₂)	C ₁₃ H ₅ BrF ₄ INO	(C ₁₃ HBrF ₈ IN) (C ₁₂ H ₁₀ N ₂ O)	(C ₁₃ HBrF ₈ INO) (C ₁₂ H ₁₂ N ₂)	(C ₁₃ HBrF ₈ INO) ₂ (C ₁₀ H ₈ N ₂)
Empirical formula	C ₂₁ H ₁₂ BrF ₈ IN ₂	C ₁₃ H ₅ BrF ₄ INO	C ₂₅ H ₁₁ BrF ₈ IN ₃ O	C ₂₅ H ₁₃ BrF ₈ IN ₃ O	C ₃₆ H ₁₀ Br ₂ F ₁₆ I ₂ N ₄ O ₂
Molecular weight	651.14	473.99	728.18	730.19	1248.10
Color, Habit	colourless plate	colourless plate	colourless plate	colourless prism	colourless plate
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group, Z	C2/c, 4	P2 ₁ /n, 4	P1, 1	P2 ₁ /n, 4	P-1, 1
a, Å	13.3208(8)	7.1847(7)	4.6568(3)	15.2758(8)	4.7774(7)
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μ , mm ⁻¹	3.540	5.210	3.068	3.045	3.905
Absorption corr	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Trans min / max	0.4373 / 0.8157	0.3444 / 0.6806	0.5026 / 0.7914	0.4827 / 0.6752	0.4542 / 0.7995
Reflections					
collected	8039	18273	18953	26829	22718
independent	3701	4613	8253	8265	6177
observed	3063	3583	8105	6418	4033
Threshold expression	>2σ(I)	>2σ(I)	>2σ(I)	>2σ(I)	>2σ(I)
R ₁ (observed)	0.0435	0.0525	0.0518	0.0371	0.0842
wR ₂ (all)	0.1137	0.1387	0.1302	0.1030	0.2117
S	1.028	1.024	1.034	1.087	1.094
Δρ max / min	2.394 / -1.053	1.385 / -2.852	1.242 / -0.789	1.287 / -0.710	3.006 / -3.682

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