# **Electronic Supplementary information**

## On the activation of PhICl<sub>2</sub> with pyridine

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#### 1. Experimental methods 1.1. Synthesis and crystallisation

Preparation of Iodobenzene dichloride (PhICl<sub>2</sub>)

Concentrated HCl (10 mL, 10M) was added into ice-cold iodobenzene (0.5 mL, 5 mmol) followed by 2-3 drops of 30%  $H_2O_2$ . Then the reaction mixture was allowed to stir for 2 hrs at 0 °C. The resulting orange solution gradually formed a yellow precipitate of solid product. The yellow precipitate was collected by filtration and  $CH_2Cl_2$  was slowly added to precipitate until completely dissolved. Dried the product using MgSO<sub>4</sub>. The solution was then filtered into a 50 mL flask and stored in freezer to obtained pale yellow crystals. Yield, 1.23 g (99%).

Reaction of iodobenzene dichloride and pyridine for generation of crystalline 2

Dichloroiodobenzene (PhICl<sub>2</sub>) (20 mg, 0.08 mmol) was dissolved in minimum amount of pyridine and stored in freezer to obtained yellow crystals.

Reaction of iodobenzene dichloride and pyridine for NMR analysis of 2

Iodobenzene dichloride (20 mg, 0.0728 mmol) was dissolved in  $CDCl_3$  (0.6 mL) and rapidly stirred to give a pale-yellow solution. To this, pyridine (5.75 mg, 0.0728 mmol) was added in one portion and the reaction was left to stir. At t = 15 m, the reaction mixture was transferred to an NMR tube and taken for analysis.

Reaction of iodobenzene dichloride and 2,6-dimethylpyridine (lutidine)

Iodobenzene dichloride (22 mg, 0.0808 mmol) was dissolved in  $CDCl_3$  (0.6 mL) and rapidly stirred to give a pale-yellow solution. To this, 2,6-dimethylpyridine (9 mg, 0.0808 mmol) was added in one portion and the reaction was left to stir. At t = 15 m, the reaction mixture was transferred to an NMR tube and taken for analysis.

#### Reaction of iodobenzene dichloride and 4-dimethylaminopyridine

lodobenzene dichloride (200 mg, 0.728 mmol) was dissolved in  $CHCl_3$  (6 mL) in a reaction flask. 4-Dimethylaminopyridine (178 mg, 1.46 mmol) dissolved in  $CHCl_3$  (0.5 mL) was added to the flask. The mixture was stirred for 15 minutes. Subsequently, hexane was added to reaction mixture and a white solid precipitated. The precipitate was removed via centrifugation and identified as identified as 4dimethylaminopyridine.HCl by <sup>1</sup>H NMR via comparison with a genuine sample. The supernatant was collected, and volatiles were removed in vacuo to give a colourless liquid. The liquid was dissolved in  $CHCl_3$  (1 mL), and triflic acid (64 µL, 0.728 mmol) was added dropwise with stirring. Diethyl ether (5 mL) was added to yield a white precipitate which was collected via centrifugation (m/z = 157.13). The solid was dissolved in  $H_2O$  (1 mL) and basified with 1M NaOH (approx. 1 mL) until pH 14. The aqueous solution was extracted with  $CH_2Cl_2$  (3 x 5 mL). The organic layers were combined and washed with  $H_2O$  (3 x 10 mL) and subsequently dried over MgSO4 and filtered. Volatiles were removed in vacuo to give **3** as a colourless liquid (70 mg, 61%).

 $^{1}\text{H}$  NMR, ppm (CDCl\_3, 400 MHz):  $\delta$  8.32 (1H, s), 8.22-8.20 (1H, d), 6.75-6.74 (1H, d), 2.99 (6H, s).

 $^{13}\text{C}$  NMR, ppm (CDCl\_3):  $\delta$  155.50, 150.24, 147.68, 121.66, 112.82, 42.32.

#### 2. Data collection and details of structure refinement

X-ray data were collected using either a Rigaku XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer or a Rigaku SuperNova. Using Olex2<sup>1</sup>, the structures were solved with the SHELXT<sup>2</sup> structure solution program using Intrinsic Phasing and refined with the SHELXL<sup>3</sup> refinement package using Least Squares minimisation. Crystal data and information concerning data collection is shown in the following table. CCDC Deposition Numbers 2071297-2071290 may be used to access the Crystallographic Information Files (.cif) from the Cambridge Crystallographic Data Centre.

Identification codePinCl223Empirical formulaC <sub>8</sub> H <sub>5</sub> C <sub>1</sub> IC <sub>11</sub> H <sub>10</sub> C <sub>1</sub> NC <sub>8</sub> H <sub>10</sub> CF <sub>3</sub> N <sub>2</sub> O <sub>3</sub> SFormula weight74.90354.00306.69Temperature/K100(2)102(2)150(2)Cystal systemmonoclinicmonoclinicmonoclinicSpace group21.021.021.0A/Å12.0910(2)8.9394(3)7.7784(2)b/Å5.3579(10)5.5397(4)9.3743(2)c/Å2.42400(10)9.5747(3)5.923(3)a/Å909.09.0a/Å10.1870(10)107.39(4)5.923(3)a/Å10.870(10)107.39(4)5.923(3)a/Å10.870(10)102.09(6)122.09(6)a/Å10.870(10)102.01122.09(6)a/Å10.870(10)102.01122.09(6)a/Å10.870(10)102.01122.09(6)a/Å10.870(10)102.01122.09(6)a/Å10.870(10)102.01122.09(6)a/Å10.870(10)102.01122.09(6)a/m <sup>1</sup> 2.48102.1140.01a/m <sup>1</sup> 10.810(10)122.0010.01a/m <sup>1</sup> 10.810(10)122.0010.810(10)a/m <sup>1</sup> 2.4810110.510(10)a/m <sup>1</sup> 10.810(10)10.810(10)10.810(10)a/m <sup>1</sup> 10.810(10)10.810(10)10.810(10)a/m <sup>1</sup> 10.810(10)10.810(10)10.810(10)a/m <sup>1</sup> 10.810(10)10.810(10)10.810(10				
Empirical formulaC <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> lC <sub>11</sub> H <sub>10</sub> Cl <sub>1</sub> NQC <sub>6</sub> H <sub>10</sub> Cl <sub>3</sub> N <sub>2</sub> O <sub>5</sub> SFormula weight274.90354.00306.69Temperature/K100(2)100(2)150(2)Crystal systemmonoclinicmonoclinicP2./na/Å2.0910(2)8.9394(3)7.784(2)b/Å5.35790(10)5.5397(4)9.3743(2)c/Å104.2400(10)9.5747(3)6.8499(5)a/°909090a/°90.009090b/Å10.8700(10)107.339(4)9.5923(3)v/°909090Volume/Å3787.65(2)1669.3(7)122.09(6)z444p <sub>cale</sub> g/cm <sup>3</sup> 2.318852.11667u/m <sup>1</sup> 2.4489.114.807F(000)51.20.040.12 × 0.09 × 0.040.18 × 0.15 × 0.06Crystal size/mm <sup>3</sup> 0.15 × 0.12 × 0.040.12 × 0.09 × 0.040.18 × 0.15 × 0.06RadiationAg Ka (A = 0.56087)Mo Ka (A = 0.71073)Cu Ka (A = 1.54184)20 range for data collections3.1 × h ≤ 3.1, -14 × k ≤ 14, -210.5 × 1.0 × 1.1 × s10 range-3.1 × h ≤ 3.1, -14 × k ≤ 14, -21.5 × 1.0 × 1.1	Identification code	PhICl <sub>2</sub>	2	3
Formula weight274.90354.00306.69Temperature/K100(2)100(2)150(2)Crystal systemmonoclinicmonoclinicmonoclinicSpace groupP2,1nP2,1nP2,1na/Å12.0910(2)8.9394(3)7.784(2)b/Å5.35790(10)15.5397(4)9.3743(2)c/Å12.42400(10)9.5747(3)16.8499(5)a/*909090a/*91.8700(10)107.339(4)9.523(3)a/*90.99090b/h12.8200(2)1269.63(7)1222.09(6)z/v90909090Volume/Å378.75(2)1269.63(7)1222.09(6)z444p <sub>rate</sub> g/cm³2.3181.8521.667p(mm¹¹2.4482.9114.807f(D00)155.0.12 × 0.040.12 × 0.09 × 0.041.8 × 0.15 × 0.06RadiationAgka (\abela 0.56087)Mca (\abela 0.71073)Cu Ka (\abela 1.54184)collection/*alles size size size1.05 < 1.01 < 1.05 < 1.01 < 1.05 < 1.01 < 2.01 < 2.00	Empirical formula	C <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> I	$C_{11}H_{10}CI_2IN$	$C_8H_{10}CIF_3N_2O_3S$
Temperature/K100(2)100(2)150(2)Crystal systemmonoclinicmonoclinicmonoclinicSpace groupP21/nP21/nP21/na/Å12.0910(2)8.9394(3)7.7784(2)b/Å5.5397(10)15.5397(4)9.3743(2)c/Å12.42400(10)9.5747(3)16.8499(5)a/°909090β/°101.8700(10)107.339(4)95.923(3)v/°909090Volume/Å378.65(2)1269.63(7)1222.09(6)z41269.63(7)1222.09(6)z4.80716671220.09(6)z12.086.062.40Crystal size/ma³0.15 × 0.12 × 0.040.12 × 0.09 × 0.040.18 × 0.15 × 0.05RadiationAg Ka (\alpha = 0.56087)10.5 × 0.040.18 × 0.15 × 0.05collection/°2.18 × 0.51.2.14 × 6.51.2.1310.5 × 1.0.70.3012.65 to 142.59collection/°2.88 to 95.11410.5 × 1.0.70.302.96 (0.14.2.59)collection/°11.267012.64511.583ndex ranges13.5 × 3.1.74.54 × 54.9.3.210.5 × 1.0.512. Raigena2.360 (Rint = 0.0328, Raigena)collections collection12.070822.633 (Rint = 0.0512.Raigena)3.600 (Albert = 1.583)ndex ranges15.02.7 [Nint = 0.0387, Raigena]2.633 (Rint = 0.0512.Raigena)2.630 (Rint = 0.0512.Raigena)collections collection15.07 (Nint = 0.0387, Raigena)2.630 (Nint = 0.0512.Raigena)2.600 (Rint = 0.0328, Raigena)collections collecti	Formula weight	274.90	354.00	306.69
Crystal system         monoclinic         monoclinic         monoclinic         monoclinic           Space group         P21/n         P21/n         P21/n           a/Å         12.0910(2)         8.9394(3)         7.7784(2)           b/Å         5.35790(10)         15.5397(4)         9.3743(2)           c/Å         12.42400(10)         9.5747(3)         16.8499(5)           a/°         90         90         90           b/Å         101.8700(10)         107.339(4)         95.923(3)           y/°         90         90         90           Volume/Å3         787.65(2)         1269.63(7)         1222.09(6)           Z         4         4         4           p <sub>cat</sub> g/cm <sup>3</sup> 2.318         1.852         1.6677           y/mm <sup>-1</sup> 2.448         2.911         4.807           Crystal size/nm <sup>3</sup> 0.15× 0.12× 0.04         0.12× 0.09× 0.04         0.18× 0.15× 0.06           Radiation         Ag Kα (λ = 0.56087)         Mo Kα (λ = 0.71073)         Cu Kα (λ = 1.54184)           20 arange for data collection <sup>2</sup> 5.13 to 50.21× 0.04         1.055 to 142.59           Independent reflection         12670         2636 [R <sub>int</sub> = 0.0512, R <sub>sigma</sub> = 0.0303]         2360 [R <sub>int</sub>	Temperature/K	100(2)	100(2)	150(2)
Space group         P2₁/n         P2₁/n         P2₁/n           a/Å         12.0910(2)         8.9394(3)         7.7784(2)           b/Å         5.35790(10)         15.5397(4)         9.3743(2)           c/Å         12.42400(10)         9.0747(3)         16.8499(5)           a/°         90         90         90           g/°         101.8700(10)         107.339(4)         95.923(3)           y/°         90         90         90           Volume/Å3         787.65(2)         1269.63(7)         1222.09(6)           Z         4         4         4           p <sub>alk</sub> g/m³         2.318         1.852         1.667           K(000)         12.0         680.0         624.0           Crystal size/m³         0.15 × 0.12 × 0.04         0.12 × 0.09 × 0.04         0.18 × 0.15 × 0.06           Radiation         Ag Kα ( > 0.56087)         Mo Kα ( > 0.71073)         Cu Kα ( > 1.54184)           20 range for data collection?         -31 < h < 31.14 ≤ k ≤ 14.2	Crystal system	monoclinic	monoclinic	monoclinic
a/Å       12.0910(2)       8.9394(3)       7.7784(2)         b/Å       5.35790(10)       15.5397(4)       9.3743(2)         c/Å       12.42400(10)       9.5747(3)       16.8499(5)         a/°       90       90       90         b/Å       101.8700(10)       107.339(4)       95.923(3)         y/°       90       90       90       90         Volume/Å3       787.65(2)       1269.63(7)       1222.09(6)         Z       4       4       4         pcacg/cm³       2.318       1.852       1.667         V/mm <sup>-1</sup> 2.448       2.911       4.807         K(000)       512.0       680.0       624.0         Crystal size/mm³       0.15× 0.12 × 0.04       0.12 × 0.09 × 0.04       0.18 × 0.15 × 0.06         Radiation       Ag K (\Lambda = 0.56087)       Mok (\Lambda = 0.71073)       Cu K (\Lambda = 1.54184)         20 range for data       -132 × 0.5114       -125 × 0.04       0.12 × 0.09 × 0.04       0.158 × 0.15 × 0.06         Radiation       Ag K (\Lambda = 0.56087)       Mok (\Lambda = 0.71073)       Cu K (\Lambda = 1.54184)       20         ander ange for data       -12637       -216 × 5114       -215 × 514       -215 × 514       -215 × 514 <td>Space group</td> <td>P2<sub>1</sub>/n</td> <td>P2<sub>1</sub>/n</td> <td>P2<sub>1</sub>/n</td>	Space group	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n
b/Å5.35790(10)15.5397(4)9.3743(2)c/Å12.42400(10)9.5747(3)16.8499(5)α/°909090β/°101.8700(10)107.339(4)95.923(3)γ/°909090Volume/Å3787.65(2)1269.63(7)1222.09(6)Z444ρ <sub>calc</sub> g/cm32.3181.8521.667μ/mm142.4482.9114.807(f000)512.0680.0624.0Crystal size/mm30.15× 0.12 × 0.040.12 × 0.09 × 0.040.18 × 0.15 × 0.06RadiationAg Kα (λ = 0.56087)Mo Kα (λ = 0.71073)Cu Kα (λ = 1.54184)20 range for data collection/*-31 ≤ h ≤ 31, -14 ≤ k ≤ 14, -32-10 ≤ h ≤ 10, -18 ≤ k ≤ 18, -11-9 ≤ h ≤ 9, -11 ≤ k ≤ 10, -19 ≤ i ≤ 1 ≤ 32-11 ≤ h ≤ 10, -18 ≤ k ≤ 18, -11-9 ≤ h ≤ 9, -11 ≤ k ≤ 10, -19 ≤ i ≤ 1 ≤ 32-12 ≤ 20263 [kint = 0.0512, Raigma = 0.0303]2360 [Rint = 0.0324, Raigma = 0.0253]Independent reflections15027 [Rint = 0.0387, Raigma = 0.0180]2263 [Rint = 0.0512, Raigma = 0.0303]2360 [Rint = 0.0324, Raigma = 0.0253]Data/restraints/parametes15027 [Rint = 0.0387, Raigma = 0.0180]2360 (D/169.0253]Goodness-of-fit on F21.0511.0551.063Final R indexes [I>=20(1)]R_1 = 0.0162, wR_2 = 0.0394R_1 = 0.0338, wR_2 = 0.0773R_1 = 0.0788, wR_2 = 0.2045Final R indexes [I=20(1)]R_1 = 0.0268, wR_2 = 0.0403R_1 = 0.0358, wR_2 = 0.0786R_1 = 0.0857, wR_2 = 0.2133Largest diff, peak/ho	a/Å	12.0910(2)	8.9394(3)	7.7784(2)
c/Å12.42400(10)9.5747(3)16.8499(5) $\alpha/^{\circ}$ 909090 $\beta/^{\circ}$ 101.8700(10)107.339(4)95.923(3) $\gamma'^{\circ}$ 909090Volume/Å <sup>3</sup> 787.65(2)1269.63(7)1222.09(6)Z444 $\rho_{ealc}/cm^3$ 2.3181.8521.667 $\mu/mm^{-1}$ 2.4482.9114.807(600)512.0680.0624.0Crystal size/mm <sup>3</sup> 0.15× 0.12 × 0.040.12 × 0.09 × 0.040.18 × 0.15 × 0.06RadiationAg Ka ( $\lambda$ = 0.56087)Mo Ka ( $\lambda$ = 0.71073)Cu Ka ( $\lambda$ = 1.54184)20 range for data collection/° $-31 \le h \le 31, -14 \le k \le 14, -32$ $-10 \le h \le 10, -18 \le k \le 18, -11$ $-9 \le 9, -11 \le k \le 10, -19 \le 1$ 1ndex ranges $-31 \le h \le 31, -14 \le k \le 14, -32$ $-10 \le h \le 10, -18 \le k \le 18, -11$ $-9 \le 9, -11 \le k \le 10, -19 \le 1$ Independent reflections $15027$ ( $R_{int} = 0.0387, R_{sigma} = 0.0303$ ) $0.0253$ ] $0.0253$ ]Data/restraints/parametra $15027/0/82$ $263/0/136$ $2360/0/169$ Goodness-of-fit on F <sup>2</sup> 1.0511.0551.063Final R indexes [ $k = 2\sigma$ (I)] $R_1 = 0.0162, wR_2 = 0.0394$ $R_1 = 0.0338, wR_2 = 0.0773$ $R_1 = 0.0788, wR_2 = 0.2045$ Final R indexes [addat] $R_1 = 0.0208, wR_2 = 0.0394$ $R_1 = 0.0338, wR_2 = 0.0776$ $R_1 = 0.0857, wR_2 = 0.2133$ Largest diff. peak/hole / eÅ <sup>3</sup> 1.99/-0.902.87/-1.861.87/-0.53	b/Å	5.35790(10)	15.5397(4)	9.3743(2)
α/°         90         90         90           β/°         101.8700(10)         107.339(4)         95.923(3)           γ/°         90         90         90           Volume/ų         787.65(2)         1269.63(7)         1222.09(6)           Z         4         4         4           ρ <sub>cal</sub> g/cm³         2.318         1.852         1.667           µ/mm¹         2.448         2.911         4.807           F(000)         512.0         680.0         624.0           Crystal size/mm³         0.15× 0.12× 0.04         0.12× 0.09× 0.04         0.18× 0.15× 0.06           Radiation         Ag Kα (λ = 0.56087)         Mo Kα (λ = 0.71073)         Cu Kα (λ = 1.54184)           20 range for data collecton/°         5.288 to 95.114         5.17 to 50.244         10.556 to 142.59           Index ranges         -31 ≤ h ≤ 31, -14 ≤ k ≤ 14, -23         -10 ≤ h ≤ 10, -18 ≤ k ≤ 18, -11         -9 ≤ h ≤ 9, -11 ≤ k ≤ 10, -19 ≤             Index ranges         -31 ≤ h ≤ 31, -14 ≤ k ≤ 14, -23         -10 ≤ h ≤ 10, -18 ≤ k ≤ 18, -11         -9 ≤ h ≤ 9, -11 ≤ k ≤ 10, -19 ≤             Index ranges         112670         12645         11583           Indegendent reflections         0.0303         0.0253           Data/restraints/parametes	c/Å	12.42400(10)	9.5747(3)	16.8499(5)
$\beta/^{\circ}$ 101.8700(10)107.339(4)95.923(3) $\gamma'^{\circ}$ 909090Volume/ų787.65(2)1269.63(7)1222.09(6)Z444 $\rho_{calc}g/cm^3$ 2.3181.8521.667 $\mu/mm^{-1}$ 2.4482.9114.807 $F(000)$ 512.0680.0624.0Crystal size/mm³0.15× 0.12× 0.040.12× 0.09× 0.040.18× 0.15× 0.06RadiationAg Ka ( $\lambda = 0.56087$ )Mo Ka ( $\lambda = 0.71073$ )Cu Ka ( $\lambda = 1.54184$ )20 range for data collection/°-328 to 95.114-5.17 to 50.244-9 sh $\leq 9, -11 \leq k \leq 10, -19 <  $ $\leq 1 \leq 32$ -10 sh $\leq 10, -18 \leq k \leq 18, -11$ $-9 < h < 9, -11 \leq k \leq 10, -19 <  $ $\leq 1 \leq 32$ -200Index ranges-31 sh $\leq 31, -14 \leq k \leq 14, -2$ $-10 < h < 10, -18 \leq k \leq 18, -11$ $-9 < h < 9, -11 \leq k \leq 10, -19 <  $ 	α/°	90	90	90
γ/°909090Volume/ų787.65(2)1269.63(7)1222.09(6)Z444ρ <sub>calc</sub> /cm³2.3181.8521.667µ/mm¹2.4482.9114.807F(000)512.0680.0624.0Crystal size/mm³0.15× 0.12× 0.040.12× 0.09× 0.040.18× 0.15× 0.06RadiationAg Kα (λ = 0.56087)Mo Kα (λ = 0.71073)Cu Kα (λ = 1.54184)20 range for data collection/°5.288 to 95.1145.17 to 50.244.0.556 to 142.591ndex ranges-31 < h < 31, +1 < st < 14, < 12	β/°	101.8700(10)	107.339(4)	95.923(3)
Volume/Å3787.65(2)1269.63(7)1222.09(6)Z444 $p_{calc}B/cm^3$ 2.3181.8521.667 $\mu/mm^1$ 2.4482.9114.807 $F(000)$ 512.0680.0624.0Crystal size/mm³0.15×0.12×0.040.12×0.09×0.040.18×0.15×0.06RadiationAg Ka ( $\lambda$ = 0.56087)Mo Ka ( $\lambda$ = 0.71073)Cu Ka ( $\lambda$ = 1.54184)20 range for data collection/° $-31 \le h \le 31, -14 \le k \le 10, -15$ $-10 \le h \le 9, -11 \le k \le 10, -19 \le 1$ 1ndex ranges $-31 \le h \le 31, -14 \le k \le 14, -32$ $-10 \le h \le 10, -18 \le k \le 18, -11$ $-9 \le h \le 9, -11 \le k \le 10, -19 \le 1$ Reflections collected1126701264511583Independent reflections15027 (R <sub>int</sub> = 0.0387, R <sub>sigma</sub> = 0.0180]263 (R <sub>int</sub> = 0.0512, R <sub>sigma</sub> = 0.0303]2360 (R <sub>int</sub> = 0.0324, R <sub>sigma</sub> = 0.0253]Data/restraints/parameters15027/0/822263 / 0.1362360 / 0.169Goodness-of-fit on F21.0511.0551.063Final R indexes [I=>20 (J)]R <sub>1</sub> = 0.0162, wR <sub>2</sub> = 0.0394R <sub>1</sub> = 0.0338, wR <sub>2</sub> = 0.0773R <sub>1</sub> = 0.0788, wR <sub>2</sub> = 0.2045Final R indexes [all data]R <sub>1</sub> = 0.0208, wR <sub>2</sub> = 0.0403R <sub>1</sub> = 0.0388, wR <sub>2</sub> = 0.0786R <sub>1</sub> = 0.0857, wR <sub>2</sub> = 0.2133Largest diff. peak/hole / e Å <sup>3</sup> 1.99/-0.902.87/-1.861.87/-0.53	γ/°	90	90	90
Z         4         4         4           ρ <sub>cle</sub> g/cm <sup>3</sup> 2.318         1.852         1.667           μ/mm <sup>-1</sup> 2.448         2.911         4.807           F(000)         512.0         680.0         624.0           Crystal size/mm <sup>3</sup> 0.15× 0.12× 0.04         0.12× 0.09× 0.04         0.18× 0.15× 0.06           Radiation         Ag Ka (λ = 0.56087)         Mo Ka (λ = 0.71073)         Cu Ka (λ = 1.54184)           20 range for data collection/°         3.288 to 95.114         5.17 to 50.244         0.556 to 142.59           Index ranges         -31 ≤ h ≤ 31, -14 ≤ k ≤ 14, -23 ≤ l ≤ 32         10 ≤ h ≤ 10, -18 ≤ k ≤ 18, -11         -9 ≤ h ≤ 9, -11 ≤ k ≤ 10, -19 ≤ l ≤ l ≤ 32         -20           Reflections collected         112670         12645         11583         -20           Independent reflections         5027 [Rint = 0.0387, Rigma = 0.0180]         263 [Rint = 0.0512, Rigma = 0.0303]         360 [Rint = 0.0324, Rigma = 0.0253]           Data/restraints/parametes         15027/082         263/0/136         1.063           Goodness-of-fit on F <sup>2</sup> 1.051         1.063         .0253]           Final R indexes [I>>20(I)]         R <sub>1</sub> = 0.0162, wR <sub>2</sub> = 0.0394         R <sub>1</sub> = 0.0338, wR <sub>2</sub> = 0.0778         R <sub>1</sub> = 0.0788, wR <sub>2</sub> = 0.2045           Final R indexes [all da	Volume/Å <sup>3</sup>	787.65(2)	1269.63(7)	1222.09(6)
pcadeg/cm³2.3181.8521.667μ/mm⁻¹2.4482.9114.807F(00)512.0680.0624.0Crystal size/mm³0.15×0.12×0.040.12×0.09×0.040.18×0.15×0.06RadiationAg Kα (λ = 0.56087)Mo Kα (λ = 0.71073)Cu Kα (λ = 1.54184)20 range for data collection/°5.288 to 95.1145.17 to 50.2440.1556 to 142.59Index ranges-31 ≤ h ≤ 31, -14 ≤ k ≤ 14, -32 ≤   ≤ 32-10 ≤ h ≤ 10, -18 ≤ k ≤ 18, -11 ≤   ≤ 32-9 ≤ h ≤ 9, -11 ≤ k ≤ 10, -19 ≤   ≤ 20Reflections collected1126701264511583Independent reflections Goodness-of-fit on F²15027 [Rint = 0.0387, Rsigma = 0.0180]2263 [Rint = 0.0512, Rsigma = 0.0303]2360 [Rint = 0.0324, Rsigma = 0.0253]Final R indexes [I>=2σ (II)R_1 = 0.0162, wR_2 = 0.0394R_1 = 0.0338, wR_2 = 0.0773R_1 = 0.0788, wR_2 = 0.2045Final R indexes [all data]R_1 = 0.0208, wR_2 = 0.0403R_1 = 0.0358, wR_2 = 0.0786R_1 = 0.0857, wR_2 = 0.2133Largest diff. peak/hole / e ų1.99/-0.902.87/-1.861.87/-0.53	Z	4	4	4
$\mu$ /mm <sup>-1</sup> 2.4482.9114.807F(000)512.0680.0624.0Crystal size/mm³0.15× 0.12× 0.040.12× 0.09× 0.040.18× 0.15× 0.06RadiationAg Ka ( $\lambda$ = 0.56087)Mo Ka ( $\lambda$ = 0.71073)Cu Ka ( $\lambda$ = 1.54184)20 range for data collection/°5.288 to 95.1145.17 to 50.2440.556 to 142.591ndex ranges-31 ≤ h ≤ 31, -14 ≤ k ≤ 14, -32 ≤ l ≤ 32-10 ≤ h ≤ 10, -18 ≤ k ≤ 18, -11 ≤ l ≤ 11-9 ≤ h ≤ 9, -11 ≤ k ≤ 10, -19 ≤ l ≤ 20Reflections collected11267012645115831ndependent reflections5027 (R <sub>int</sub> = 0.0387, R <sub>sigma</sub> = 0.0180]2263 (R <sub>int</sub> = 0.0512, R <sub>sigma</sub> = 0.0303]360 (R <sub>int</sub> = 0.0324, R <sub>sigma</sub> = 0.0253]Data/restraints/parameter10511.0551.063Final R indexes [l>=2\sigma (l)]R <sub>1</sub> = 0.0162, wR <sub>2</sub> = 0.0394 R <sub>1</sub> = 0.0338, wR <sub>2</sub> = 0.07768 R <sub>1</sub> = 0.0385, wR <sub>2</sub> = 0.2785 R <sub>1</sub> = 0.0358, wR <sub>2</sub> = 0.0786 R <sub>1</sub> = 0.0857, wR <sub>2</sub> = 0.2133Largest diff. peak/hole / e Å <sup>3</sup> 1.99/-0.902.87/-1.861.87/-0.53	$\rho_{calc}g/cm^3$	2.318	1.852	1.667
F(00)512.0680.0624.0Crystal size/mm³0.15 × 0.0240.12 × 0.09 × 0.040.18 × 0.15 × 0.06RadiationAg Ka ( $\lambda$ = 0.56087)Mo Ka ( $\lambda$ = 0.71073)Cu Ka ( $\lambda$ = 1.54184)20 range for data collection/° $2.88$ to 95.114 $5.17$ to 50.244 $0.556$ to 142.591mdex ranges $-31 \le h \le 31, -14 \le k \le 14, -32$ $\le l \le 32$ $-10 \le h \le 10, -18 \le k \le 18, -11$ $\le l \le 32$ $-9 \le h \le 9, -11 \le k \le 10, -19 \le l$ $\le l \le 11$ Reflections collected11267012645115831mdependent reflection $5027$ (R <sub>int</sub> = 0.0387, R <sub>sigma</sub> = $0.0180$ ) $2263$ (R <sub>int</sub> = 0.0512, R <sub>sigma</sub> = $0.0303$ ) $2360$ (R <sub>int</sub> = 0.0324, R <sub>sigma</sub> = $0.0253$ )Data/restraints/parametes $15027$ (Naz $1.051$ $2263$ (Nat $1.055$ $2360$ (Nat $1.063$ Final R indexes [I>=20 (II) $R_1 = 0.0162, wR_2 = 0.0394$ $R_1 = 0.0338, wR_2 = 0.0786$ $R_1 = 0.0857, wR_2 = 0.2133$ $1.67.0857, wR_2 = 0.2133$ Largest diff. peak/hole / e Å <sup>3</sup> $1.99$ -0.90 $2.87/-1.86$ $1.87/-0.53$	µ/mm⁻¹	2.448	2.911	4.807
Crystal size/mm³ $0.15 \times 0.02 \times 0.04$ $0.12 \times 0.09 \times 0.04$ $0.18 \times 0.15 \times 0.06$ RadiationAg K $\alpha$ ( $\lambda$ = 0.56087)Mo K $\alpha$ ( $\lambda$ = 0.71073)Cu K $\alpha$ ( $\lambda$ = 1.54184)20 range for data collection/° $5.288$ to 95.114 $5.17$ to 50.244 $10.556$ to 142.59Index ranges $-31 \le h \le 31, -14 \le k \le 14, -32$ $\le 1 \le 32$ $-10 \le h \le 10, -18 \le k \le 18, -11$ $\le 1 \le 11$ $-9 \le h \le 9, -11 \le k \le 10, -19 \le 1$ $\le 20$ Reflections collected1126701264511583Independent reflections $5027$ (R <sub>int</sub> = 0.0387, R <sub>sigma</sub> = $0.0180$ ) $263$ (R <sub>int</sub> = 0.0512, R <sub>sigma</sub> = $0.0303$ ) $2360$ (R <sub>int</sub> = 0.0324, R <sub>sigma</sub> = $0.0253$ )Data/restraints/parameters $15027$ (Ng2 $263$ (N136) $2360$ (Nint = 0.0324, R <sub>sigma</sub> = $0.0253$ )Goodness-of-fit on F <sup>2</sup> $1.051$ $1.055$ $1.063$ Final R indexes [I>=2 $\sigma$ (II) $R_1 = 0.0162, wR_2 = 0.0394$ $R_1 = 0.0338, wR_2 = 0.0773$ $R_1 = 0.0788, wR_2 = 0.2045$ Final R indexes [all data] $R_1 = 0.0208, wR_2 = 0.0403$ $R_1 = 0.0358, wR_2 = 0.0786$ $R_1 = 0.0857, wR_2 = 0.2133$ Largest diff. peak/hole / e Å <sup>-3</sup> $1.99$ -0.90 $2.87/-1.86$ $1.87/-0.53$	F(000)	512.0	680.0	624.0
RadiationAg Ka ( $\lambda = 0.56087$ )Mo Ka ( $\lambda = 0.71073$ )Cu Ka ( $\lambda = 1.54184$ )20 range for data collection/° $5.288$ to 95.114 $5.17$ to 50.244 $10.556$ to 142.591ndex ranges $-31 \le h \le 31, -14 \le k \le 14, -32$ $\le   \le 32$ $-10 \le h \le 10, -18 \le k \le 18, -11$ $\le   \le 20$ $-9 \le h \le 9, -11 \le k \le 10, -19 \le l$ $\le 20$ Reflections collected1126701264511583Independent reflections15027 [R <sub>int</sub> = 0.0387, R <sub>sigma</sub> = $0.180$ ]2263 [R <sub>int</sub> = 0.0512, R <sub>sigma</sub> = $0.0303$ ]2360 [R <sub>int</sub> = 0.0324, R <sub>sigma</sub> = $0.0253$ ]Data/restraints/parameters15027/0/822263/0/1362360/0/169Goodness-of-fit on F <sup>2</sup> 1.0511.0551.063Final R indexes [I>=20 (I)]R <sub>1</sub> = 0.0162, wR <sub>2</sub> = 0.0394R <sub>1</sub> = 0.0338, wR <sub>2</sub> = 0.0773R <sub>1</sub> = 0.0788, wR <sub>2</sub> = 0.2045Final R indexes [all data]R <sub>1</sub> = 0.0208, wR <sub>2</sub> = 0.0403R <sub>1</sub> = 0.0358, wR <sub>2</sub> = 0.0786R <sub>1</sub> = 0.0857, wR <sub>2</sub> = 0.2133Largest diff. peak/hole / e Å <sup>-3</sup> 1.99/-0.902.87/-1.861.87/-0.53	Crystal size/mm <sup>3</sup>	$0.15 \times 0.12 \times 0.04$	$0.12 \times 0.09 \times 0.04$	$0.18 \times 0.15 \times 0.06$
20 range for data collection/° $5.288 to 95.114$ $5.17 to 50.244$ $10.556 to 142.59$ Index ranges $-31 \le h \le 31, -14 \le k \le 14, -32$ $\le 1 \le 32$ $-10 \le h \le 10, -18 \le k \le 18, -11$ $\le 1 \le 11$ $-9 \le h \le 9, -11 \le k \le 10, -19 \le 1$ $\le 20$ Reflections collected1126701264511583Independent reflections $15027 [R_{int} = 0.0387, R_{sigma} = 0.0303]$ $263 [R_{int} = 0.0512, R_{sigma} = 0.0253]$ $0.0253]$ $263/0/136$ Data/restraints/parameters $15027/0/82$ $2263/0/136$ $2360/0/169$ Goodness-of-fit on F <sup>2</sup> $1.051$ $1.055$ $1.063$ Final R indexes [I>=2 $\sigma$ (I)] $R_1 = 0.0162, wR_2 = 0.0394$ $R_1 = 0.0338, wR_2 = 0.0773$ $R_1 = 0.0788, wR_2 = 0.2045$ Final R indexes [all data] $R_1 = 0.028, wR_2 = 0.0403$ $R_1 = 0.0358, wR_2 = 0.0786$ $R_1 = 0.0857, wR_2 = 0.2133$ Largest diff. peak/hole / e Å <sup>-3</sup> $1.99/-0.90$ $2.87/-1.86$ $1.87/-0.53$	Radiation	Ag Kα (λ = 0.56087)	Μο Κα (λ = 0.71073)	Cu Kα (λ = 1.54184)
Index ranges $-31 \le h \le 31, -14 \le k \le 14, -32$ $-10 \le h \le 10, -18 \le k \le 18, -11$ $-9 \le h \le 9, -11 \le k \le 10, -19 \le 1$ Reflections collected112670 $\le l \le 11$ $\le 20$ Independent reflections $15027 [R_{int} = 0.0387, R_{sigma} = 0.0303]$ $2263 [R_{int} = 0.0512, R_{sigma} = 0.0253]$ $2360 [R_{int} = 0.0324, R_{sigma} = 0.0303]$ Data/restraints/parameters $15027/0/82$ $2263/0/136$ $2360/0/169$ Goodness-of-fit on F <sup>2</sup> $1.051$ $1.055$ $1.063$ Final R indexes [l>= $2\sigma$ (l)] $R_1 = 0.0162, wR_2 = 0.0394$ $R_1 = 0.0338, wR_2 = 0.0773$ $R_1 = 0.0788, wR_2 = 0.2045$ Final R indexes [all data] $R_1 = 0.0208, wR_2 = 0.0403$ $R_1 = 0.0358, wR_2 = 0.0786$ $R_1 = 0.0857, wR_2 = 0.2133$ Largest diff. peak/hole / e Å <sup>-3</sup> $1.99/-0.90$ $2.87/-1.86$ $1.87/-0.53$	20 range for data collection/°	5.288 to 95.114	5.17 to 50.244	10.556 to 142.59
Reflections collected1126701264511583Independent reflections $15027 [R_{int} = 0.0387, R_{sigma} = 0.0303]$ $2263 [R_{int} = 0.0512, R_{sigma} = 0.0253]$ $2360 [R_{int} = 0.0324, R_{sigma} = 0.0253]$ Data/restraints/parameters $15027/0/82$ $2263/0/136$ $2360/0/169$ Goodness-of-fit on F <sup>2</sup> $1.051$ $1.055$ $1.063$ Final R indexes [l>= $2\sigma$ (l)] $R_1 = 0.0162, wR_2 = 0.0394$ $R_1 = 0.0338, wR_2 = 0.0773$ $R_1 = 0.0788, wR_2 = 0.2045$ Final R indexes [all data] $R_1 = 0.0208, wR_2 = 0.0403$ $R_1 = 0.0358, wR_2 = 0.0786$ $R_1 = 0.0857, wR_2 = 0.2133$ Largest diff. peak/hole / e Å <sup>-3</sup> $1.99/-0.90$ $2.87/-1.86$ $1.87/-0.53$	Index ranges	$-31 \le h \le 31, -14 \le k \le 14, -32$ $\le l \le 32$	$\begin{array}{l} -10 \leq h \leq 10,  -18 \leq k \leq 18,  -11 \\ \leq l \leq 11 \end{array}$	$\begin{array}{l} -9 \leq h \leq 9,  -11 \leq k \leq 10,  -19 \leq l \\ \leq 20 \end{array}$
Independent reflections $15027 [R_{int} = 0.0387, R_{sigma} = 0.0303]$ $2263 [R_{int} = 0.0512, R_{sigma} = 0.0253]$ $2360 [R_{int} = 0.0324, R_{sigma} = 0.0253]$ Data/restraints/parameters $15027/0/82$ $2263/0/136$ $2360/0/169$ Goodness-of-fit on F <sup>2</sup> $1.051$ $1.055$ $1.063$ Final R indexes [I>= $2\sigma$ (I)] $R_1 = 0.0162, wR_2 = 0.0394$ $R_1 = 0.0338, wR_2 = 0.0773$ $R_1 = 0.0788, wR_2 = 0.2045$ Final R indexes [all data] $R_1 = 0.0208, wR_2 = 0.0403$ $R_1 = 0.0358, wR_2 = 0.0786$ $R_1 = 0.0857, wR_2 = 0.2133$ Largest diff. peak/hole / e Å-3 $1.99/-0.90$ $2.87/-1.86$ $1.87/-0.53$	Reflections collected	112670	12645	11583
Data/restraints/parameters15027/0/822263/0/1362360/0/169Goodness-of-fit on $F^2$ 1.0511.0551.063Final R indexes [I>=2 $\sigma$ (I)]R1 = 0.0162, wR2 = 0.0394R1 = 0.0338, wR2 = 0.0773R1 = 0.0788, wR2 = 0.2045Final R indexes [all data]R1 = 0.0208, wR2 = 0.0403R1 = 0.0358, wR2 = 0.0786R1 = 0.0857, wR2 = 0.2133Largest diff. peak/hole / e Å-31.99/-0.902.87/-1.861.87/-0.53	Independent reflections	15027 [R <sub>int</sub> = 0.0387, R <sub>sigma</sub> = 0.0180]	2263 [R <sub>int</sub> = 0.0512, R <sub>sigma</sub> = 0.0303]	2360 [R <sub>int</sub> = 0.0324, R <sub>sigma</sub> = 0.0253]
Goodness-of-fit on $F^2$ 1.0511.0551.063Final R indexes [I>=2 $\sigma$ (I)]R1 = 0.0162, wR2 = 0.0394R1 = 0.0338, wR2 = 0.0773R1 = 0.0788, wR2 = 0.2045Final R indexes [all data]R1 = 0.0208, wR2 = 0.0403R1 = 0.0358, wR2 = 0.0786R1 = 0.0857, wR2 = 0.2133Largest diff. peak/hole / e Å-31.99/-0.902.87/-1.861.87/-0.53	Data/restraints/parameters	15027/0/82	2263/0/136	2360/0/169
Final R indexes [l>=2 $\sigma$ (l)]R1 = 0.0162, wR2 = 0.0394R1 = 0.0338, wR2 = 0.0773R1 = 0.0788, wR2 = 0.2045Final R indexes [all data]R1 = 0.0208, wR2 = 0.0403R1 = 0.0358, wR2 = 0.0786R1 = 0.0857, wR2 = 0.2133Largest diff. peak/hole / e Å-31.99/-0.902.87/-1.861.87/-0.53	Goodness-of-fit on F <sup>2</sup>	1.051	1.055	1.063
Final R indexes [all data] $R_1 = 0.0208$ , $wR_2 = 0.0403$ $R_1 = 0.0358$ , $wR_2 = 0.0786$ $R_1 = 0.0857$ , $wR_2 = 0.2133$ Largest diff. peak/hole / e Å-31.99/-0.902.87/-1.861.87/-0.53	Final R indexes [I>=2σ (I)]	$R_1 = 0.0162$ , $wR_2 = 0.0394$	R <sub>1</sub> = 0.0338, wR <sub>2</sub> = 0.0773	R <sub>1</sub> = 0.0788, wR <sub>2</sub> = 0.2045
Largest diff. peak/hole / e Å <sup>-3</sup> 1.99/-0.90 2.87/-1.86 1.87/-0.53	Final R indexes [all data]	$R_1 = 0.0208$ , $wR_2 = 0.0403$	R <sub>1</sub> = 0.0358, wR <sub>2</sub> = 0.0786	R <sub>1</sub> = 0.0857, wR <sub>2</sub> = 0.2133
	Largest diff. peak/hole / e Å <sup>-3</sup>	1.99/-0.90	2.87/-1.86	1.87/-0.53

Table S1. Crystal data and structure refinement for PhICl<sub>2</sub>, 2 and 3



Figure S1: Crystal packing in PhICl<sub>2</sub>. Angles:  $\theta_1$ (C-I  $\star \star \star$ Cl) =166.38°,  $\theta_2$ (Cl-I  $\star \star \star$ Cl) = 100.24°,  $\theta_3$ (Cl-I-Cl) = 176.70°; bond distances d(I-Cl1) = 2.48319(12) Å and d(I-Cl2) = 2.505926(11) Å). The slightly asymmetrical I-Cl distances can be attributed to different intermolecular interactions. The Cl2 atom interacts with the iodine I1 *via* a type II  $\beta$  halogen bonding ( $\psi$  = 0.33)<sup>4</sup> while Cl1 atom undergoes exclusively hydrogen bonding interactions with two aryl C-Hs.



Figure S2: Crystal structure of the PhICl<sub>2</sub>  $\star$  Py aggregate **2**. Selected angles ( $\theta_1$ (C-I  $\star$   $\star$   $\star$  CI) =177.97°,  $\theta_2$ (Cl-I  $\star$   $\star$   $\star$  CI) = 175.38°) show a type II  $\beta$  halogen bonding ( $\psi$  = 0.98)<sup>4</sup> with an intermolecular short contact distance of d(N1  $\star$   $\star$   $\star$  I1) = 2.750 Å.

## 3. Experimental electron density study

## **3.1.** Multipole refinement of $PhICl_2$

The multipolar refinement was carried out on *F*<sup>2</sup> according to the Hansen & Coppens formalism for aspherical atomic density expansion as implemented in *MoProSuite*.<sup>5</sup> <sup>6</sup>Multipole coefficients up to hexadecapoles were refined for non-H atoms. H-atoms were constrained to C-H bond distances of 1.083 Å based on neutron diffraction data reported by Allen and Bruno.<sup>7</sup>Refinement results have been compiled in Table 2. Electron density maps were obtained using *MoProViewer*.<sup>8</sup>

Table S2: Refinement results.

Refinement	IAM	MM
Resolution	0.38 – 10 Å	0.38 – 6.079 Å
R <sub>1</sub> [I>=2σ (I)]	0.0162	0.01296 (RF factor)
$wR_2[I >= 2\sigma(I)]$	0.0394	0.01360 (wR2F factor)
R <sub>1</sub> [all data]	0.0208	0.01910 (RI factor)
wR <sub>2</sub> [all data]	0.0403	0.02.668 (wR2I factor)
Nvar/Nref	-	301/11758
Largest diff. peak/hole / e Å <sup>-3</sup>	1.99/-0.90	-
Goodness-of-fit on F <sup>2</sup>	1.051	1.028
Weighting scheme	0.0177 0.0497	0.52372 (MoPro gof1)

### 3.2. Topological analysis





c)



d)



Figure S3: Logarithmic Laplacian maps of the intermolecular halogen bonding  $I1 \rightarrow Cl2$  along the ZX plane *a*) and *c*) and XY plane *b*) and *d*). Red denotes charge depletion (VSCD) and blue denotes charge concentration (VSCC).



**Figure S4:** Experimental two-dimensional electron density maps of **1** at a resolution range of 0.38 < d (Å) > 6.079. *a*) shows the ZX plane used for 2D maps, *b*) corresponds to the residual density (0.10 e Å<sup>-1</sup>, 0.08 <  $\sin\theta/\lambda < 0.80$ ), *c*) full deformation of the static electron density (contour 0.05 e Å<sup>-1</sup>). Positive density is shown in blue and negative in red; grey dotted lines represent zero density. The Laplacian map of lodobenzene dichloride *d*) was drawn on a logarithmic scale. Red denotes charge depletion (VSCD) and blue denotes charge concentration (VSCC).



**Figure S5:** Experimental two-dimensional electron density maps of **1** at a resolution range of 0.38 < d(Å) > 6.079. *a*) shows the XY plane used for 2D maps, *b*) corresponds to the residual density (0.10 e Å<sup>-1</sup>,0.08 <  $\sin\theta/\lambda < 0.80$ ), *c*) full deformation of the static electron density (contour 0.05 e Å<sup>-1</sup>). Positive density is shown in blue and negative in red; grey dotted lines represent zero density. The Laplacian map of Iodobenzene dichloride *d*) was drawn on a logarithmic scale. Red denotes charge depletion (VSCD) and blue denotes charge concentration (VSCC).



**Figure S6:** Non-covalent • and covalent • critical points of **1** illustrated with *MoProViewer*.

СР	Туре	Atom1	Atom2	d <sub>ij</sub>	d1	d <sub>2</sub>	p	Δ² ρ	Gcp	Vср	ellip
				(Å)	(Å)	(Å)	(eÅ-³)	(eÅ⁻⁵)	$\left(\frac{\text{kJmol}^{-1}}{\text{Bohr}^{3}}\right)$	(kJmol <sup>-1</sup> /Bohr <sup>3</sup>	
Cp1	(3,-1)	11	Cl2	2.5047	1.2731	1.2419	0.51441	1.766	135.38	-222.65	0.7375
Cp2	(3,-1)	11	Cl1	2.4825	1.2625	1.2201	0.46643	2.182	127.37	-195.31	0.3985
СрЗ	(3,-1)	11	C1	2.0971	1.1676	0.9295	0.88623	-0.447	247.65	-507.49	0.07
Cp4	(3,-1)	C2	H2	1.0829	0.7024	0.3805	1.90408	-18.461	579.79	-1662.41	0.0799
Cp5	(3,-1)	C2	C1	1.3886	0.6897	0.6992	2.13437	-18.325	774.05	-2047.22	0.2031
Cp6	(3,-1)	C2	C3	1.3951	0.6983	0.6969	2.15537	-20.183	758.53	-2066.78	0.1993
Cp7	(3,-1)	C1	C6	1.3905	0.6919	0.6987	2.09699	-16.678	771.84	-1997.94	0.2287
Cp8	(3,-1)	C3	H3	1.083	0.6784	0.4046	1.86365	-18.703	543.25	-1595.92	0.0757
Ср9	(3,-1)	C3	C4	1.3923	0.6839	0.7084	2.12597	-18.986	754.8	-2026.72	0.2236
Cp10	(3,-1)	C4	H4	1.0829	0.6924	0.3905	1.85767	-15.146	603.13	-1618.79	0.0499
Cp11	(3,-1)	C4	C5	1.3942	0.7265	0.6677	2.15773	-19.632	770.58	-2075.88	0.189
Cp12	(3,-1)	C5	H5	1.0829	0.6735	0.4094	1.90234	-18.483	578	-1659.43	0.0873
Ср13	(3,-1)	C5	C6	1.3959	0.678	0.7179	2.18753	-19.819	793.25	-2126.3	0.2011
Cp14	(3,-1)	C6	H6	1.0828	0.7321	0.3507	1.76012	-17.602	483.03	-1445.48	0.0435

Table S3. Bond critical points details of covalent interactions.

 $d_{ij}$  is the bond path,  $d_1$  and  $d_2$  its components,  $\rho$  the electron density and  $\Delta^2$  the Laplacian of bcp; Gcp and Vcp correspond to the kinetic and potential energy, respectively.

Table S4. Bond critical p	points details of non-	<ul> <li>-covalent interactions.</li> </ul>
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СР	Туре	Atom1	Atom2	d <sub>ij</sub>	d1	d <sub>2</sub>	ρ	Δ² ρ	Gcp	Vcp	ellip
				(Å)	(Å)	(Å)	(eÅ⁻³)	(eÅ⁻⁵)	(kJmol <sup>-1</sup> / <sub>Bohr<sup>3</sup></sub> )	$\left(\frac{\text{kJmol}^{-1}}{\text{Bohr}^{3}}\right)$	
Cn15	(3 -1)	11	CI2	3 1216	1 0867	1 07/6	0 15080	-0.257	10.06	_27.13	0.6651
Chip	(3,-1)	11	CIZ	5.4210	1.9807	1.9740	0.13989	-0.237	10.00	-27.15	0.0051

 $d_{ij}$  is the bond path,  $d_1$  and  $d_2$  its components,  $\rho$  the electron density and  $\Delta^2$  the Laplacian in the intermolecular bcp; Gcp and Vcp correspond to the kinetic and potential energy, respectively.

Table S5. Electron density properties of various reported intermolecular contacts.

Bond	Туре	dist(Å)	d <sub>ij</sub> (Å)	d <sub>1</sub> (Å)	d₂(Å)	ρ(eÅ⁻³)	Δ² ρ(eÅ⁻₅)	Ref.
Cl(1)…Cl(3)a	CICI	3.1912(6)	3.1912	1.5779	1.6133	0.107(2)	1.102(4)	9
Cl2…Cl2i (1)inter	CICI	3.7641 (3)	3.764	1.888	1.877	0.023 (2)	0.307 (2)	10
Cl1…Cl1a	CICI	3.3651(6)	3.3650	1.6825	1.6825	0.048(2)	0.576(2)	9
Cl1…Cl1b	CICI	3.5480(6)	3.5480	1.7738	1.7742	0.041(2)	0.489(2)	9
Br…Br1ii (2)inter	BrBr	3.5834 (2)	3.608	1.898	1.710	0.038 (3)	0.456 (5)	10
Br2…Br2iii(5)inter	BrBr	3.9082 (2)	3.908	1.946	1.963	0.040 (2)	0.547 (2)	10
I(1)N(2)	IN	2.833(3)	2.8527	1.5223		0.154(12)	1.708(11)	11
I(2)O(7)a	10	3.026(6)	3.0818	1.6303		0.092(7)	0.856(9)	11
I(3)O(1)	10	3.157(2)	3.1702	1.7442		0.082(4)	1.063(7)	11
Br…Oa	BrO	2.9217(9)	2.922	1.343	1.579	0.117(2)	1.330(4)	12
Br1…Cl1i (1)	BrCl	3.3652(3)	3.3653	1.7227	1.6426	0.081(2)	0.862(2)	13
Cl1…Cl6 (2)	CICI	3.2219(4)	3.2258	1.5992	1.6266	0.084(2)	1.006(2)	13
Cl2…Cl3 (2)	CICI	3.2871(4)	3.2895	1.6302	1.6593	0.073(2)	0.867(2)	13
Cl1…Cl2(3)	CICI	3.2411(3)	3.2730	1.5980	1.6750	0.109(3)	0.930(3)	13
I1…N1	IN	2.6622(4)	2.6625	1.2351	1.4274	0.359(5)	1.95(2)	14
I(1)…O(1)i	10	2.9826(9)	2.9824	1.5992	1.3832	0.102(2)	1.307(3)	15
I(1)…O(1)	10	2.1241(9)	2.1270	1.1470	0.9800	0.64(2)	7.91(6)	15
I1…N1	IN	2.7374 (11)	2.7616	1.4660		0.19 (2)	2.071 (5)	16
I2…N2i	IN	2.7453 (11)	2.8461	1.5145		0.16 (2)	1.807 (5)	16
I1…N1	IN	2.9301(4)	2.9354	1.6145	1.3209	0.186(4)	1.713(2)	17

 $d_{ij}$  is the bond path,  $d_1$  and  $d_2$  its components,  $\rho$  the electron density and  $\Delta^2$  the Laplacian in the intermolecular bcp.

## 4. NMR Investigations



Figure S7: lodobenzene dichloride in CDCl<sub>3</sub>.



Figure S2: Reaction mixture of PhICl<sub>2</sub> and 2,6-dimethylpyridine (blue) overlayed with PhICl<sub>2</sub> (red) and 2,6-dimethylpyridine (green) in CDCl<sub>3</sub>.



**Figure S3:** Downfield region of reaction mixture of PhICl<sub>2</sub> and 2,6-dimethylpyridine (blue) overlayed with PhICl<sub>2</sub> (red) and 2,6-dimethylpyridine (green). **Note:** Free iodobenzene is present owing to gradual decomposition of PhICl<sub>2</sub>.



**Figure S4:** Upfield region of reaction mixture of PhICl<sub>2</sub> and 2,6-dimethylpyridine (blue) overlayed with PhICl<sub>2</sub> (red) and 2,6-dimethylpyridine (green).



**Figure S5:** Reaction mixture of PhICl<sub>2</sub> and pyridine (blue) overlayed with PhICl<sub>2</sub> (green) and pyridine (red). **Note:** Free iodobenzene is present owing to gradual decomposition of PhICl<sub>2</sub>



Figure S6: <sup>1</sup>H spectrum of 3-chloro-4-dimethylaminopyridine in CDCl<sub>3</sub>.



Figure S7: <sup>13</sup>C spectrum of 3-chloro-4-dimethylaminopyridine in CDCl<sub>3</sub>



Figure S8: <sup>1</sup>H NMR spectrum of 1 equivalent of PhICl<sub>2</sub> and 1 equivalent of pyridine in CDCl<sub>3</sub>.



Figure S9: <sup>1</sup>H NMR spectrum of 1 equivalent of PhICl<sub>2</sub> and 2 equivalents of pyridine in CDCl<sub>3</sub>.



Figure S10: <sup>1</sup>H NMR spectrum of 1 equivalent of PhICl<sub>2</sub> and 3 equivalents of pyridine in CDCl<sub>3</sub>.



Figure S11: <sup>1</sup>H NMR spectrum of 1 equivalent of PhICl<sub>2</sub> and 4 equivalents of pyridine in CDCl<sub>3</sub>.



Figure S12: <sup>1</sup>H NMR spectrum of 1 equivalent of PhICl<sub>2</sub> and 5 equivalents of pyridine in CDCl<sub>3</sub>.



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Figure S14: <sup>1</sup>H NMR spectrum overlay of PhICl<sub>2</sub> and 1-5, 10 equivalents of pyridine in CDCl<sub>3</sub>.



Figure S15: <sup>1</sup>H NMR spectrum overlay (most downfield signal) of PhICl<sub>2</sub> and 1-5, 10 equivalents of pyridine in CDCl<sub>3</sub>.

#### 5. Computational details

All calculations were performed using Gaussian 16 revision A.03 unless noted.<sup>18</sup> Geometry optimizations were performed with the B3LYP density functional<sup>19, 20</sup> with Grimme's empirical D3 dispersion with Becke-Johnson (BJ) damping,<sup>21</sup> together with the def2-TZVPPD basis set, which includes an ECP for iodine.<sup>21, 22</sup> Harmonic vibrational frequencies were computed analytically at the same level of theory in order to characterise the stationary points as minima on the potential energy surface and determine thermochemical properties. Geometry optimization and harmonic frequency calculations inclusive of solvent effects using the polarizable continuum model (IEF-PCM) with Truhlar's SMD model<sup>23</sup> with parameters for acetonitrile.

All subsequent property and electronic structure calculations were carried out at the optimized geometries. Molecular orbital (MO), population analysis (CM5 charges<sup>24</sup>) and Natural Bond Orbital (NBO) analysis was caried out at the same B3LYP-D3(BJ)/def2-TZVPPD (SMD, acetonitrile) level of theory. NBO analysis was performed using NBO 6.0.<sup>25</sup>

For thermochemistry analysis, single point calculations were carried out at the  $\omega$ B97XD/def2-TZVPPD, B3LYP-D3(BJ)/def2-QZVPPD level of theory.<sup>23</sup> All calculations included SMD solvation with acetonitrile, while B3LYP-D3(BJ)/def2-QZVPPD calculations were also carried out with dichloromethane and pyridine solvation. Single-point DLPNO-CCSD(T)/def2-QZVPP calculations (inclusive of CPCM acetonitrile solvation) were computed using ORCA 4.2.1.<sup>26</sup> The single point energies were converted to free energies ( $\Delta G$ ) by adding the free energy correction calculated at the B3LYP-D3(BJ)/def2-TZVPPD (SMD, acetonitrile) level of theory in the harmonic frequency calculation. Thermochemistry analysis with quasi-harmonic analysis was carried out in GoodVibes 3.0.2.<sup>27</sup>

Method	Basis Set	Solvation	Geometry	$\Delta G$	$\Delta G(QH)^{a}$
B3LYP-D3(BJ)	Def2-TZVPPD	Gas phase	opt	-10.1	-14.0
B3LYP-D3(BJ)	Def2-TZVPPD	ACN	opt	+11.6	+9.3
ωB97XD	Def2-TZVPPD	ACN	opt	+17.1	+15.1
B3LYP-D3(BJ)	Def2-QZVPPD	ACN	b	+12.1	+9.3
B3LYP-D3(BJ)	Def2-QZVPPD	$CH_2Cl_2$	b	+10.8	+8.5
B3LYP-D3(BJ)	Def2-QZVPPD	pyridine	b	+10.5	+8.2
DSDPBeP86	Def2-QZVPPD	ACN	b	+9.8	+7.5
DLPNO-CCSD(T)	Def2-TZVPPD	ACN (CPCM)	b	+14.7	+12.4
DLPNO-CCSD(T)	Def2-QZVPP	ACN (CPCM)	b	+18.2	+16.0

Table S6. Calculated  $\Delta G$  of reaction (kJ/mol) for addition of pyridine to PhICl<sub>2</sub> to form four-coordinate PhICl<sub>2</sub>pyr (compound **2**).

<sup>a</sup> Quasi-harmonic analysis using GoodVibes, with cutoff of 200 cm<sup>-1</sup>. Temp = 40 K. Scale factor = 0.9857.

<sup>b</sup> B3LYP-D3(BJ)/def2-TZVPPD (SMD, acetonitrile) optimized geometry.

## Cartesian coordinates of optimized geometries

B3LYP-D3(BJ)/def2-TZVPPD (SMD, acetonitrile)

PhICl<sub>2</sub>

0, 1	(charge and multip	olicity)	
53	1.131766	-0.000004	-0.000000
6	-0.975580	0.000006	-0.000001
6	-1.635117	0.143262	1.212082
6	-3.025476	0.143532	1.199343
6	-3.716031	0.000008	0.000000
6	-3.025477	-0.143516	-1.199343
6	-1.635118	-0.143248	-1.212083
1	-1.086864	-0.252499	-2.135994
1	-3.564335	-0.254851	-2.130252
1	-4.797518	0.000007	0.000001
1	-3.564333	0.254869	2.130252
1	-1.086862	0.252515	2.135993
17	1.123314	-2.541657	0.073063
17	1.123340	2.541650	-0.073062

PhICl<sub>2</sub>Pyr (compound 2)

0,1			
53	0.000000	-0.000000	0.196272
6	0.000000	-0.000000	2.313853
6	0.000000	1.216995	2.983585
6	0.000000	1.207588	4.374049
6	0.000000	-0.000000	5.065697
6	-0.000000	-1.207588	4.374049
6	-0.000000	-1.216995	2.983585
1	0.000000	-2.148907	2.436713
1	0.000000	-2.144809	4.913867
1	0.000000	-0.000000	6.147333
1	0.000000	2.144809	4.913867
1	0.000000	2.148907	2.436713
17	2.549053	-0.000000	0.197059
17	-2.549053	0.000000	0.197059
7	-0.000000	0.000000	-2.659603
6	-0.000000	-1.148088	-3.340006
6	0.000000	1.148088	-3.340006
6	-0.000000	-1.196462	-4.727436
1	-0.000000	-2.057460	-2.751144
6	0.000000	1.196462	-4.727436
1	0.000000	2.057460	-2.751144
6	-0.000000	0.000000	-5.433616
1	-0.000000	-2.149671	-5.236993
1	0.000000	2.149671	-5.236993
1	-0.000000	0.000000	-6.515320

[PhI(Pyr)Cl]+

+1,1	
53	0.486317 -1.169889 -0.000002
6	0.934986 0.887802 -0.000003
6	1.067814 1.531011 1.221088
6	1.348856 2.892885 1.208070
6	1.488152 3.568830 0.000005
6	1.348828 2.892898 -1.208064
6	1.067785 1.531024 -1.221090
1	0.958339 0.993744 -2.151135
1	1.458814 3.420427 -2.145534
1	1.708132 4.627615 0.000008
1	1.458867 3.420404 2.145543
-	0.958390 0.993721 2.151130
- 17	2.942480 -1.703405 -0.000004
7	-1 695138 -0 496673 0 000004
, 6	-2 316237 -0 288764 -1 168006
6	-2 316240 -0 288773 1 168012
6	-2.510240 -0.288775 1.108012
1	1745440 0480212 2064600
6	2622927 0 157249 1 100622
1	
0	-4.286466 0.385418 0.000003
1	-4.106176 0.321886 -2.151683
1	-4.106181 0.321869 2.151690
1	-5.308506 0.737247 0.000004
PhiCit	
+1,1	
53	-1.131895 -0.595398 0.016331
6	0.895851 -0.164664 0.004565
6	1.542992 0.001142 1.228007
6	2.904067 0.264658 1.205856
6	3.579814 0.356192 -0.009126
6	2.907424 0.184290 -1.217191
6	1.546274 -0.079356 -1.225425
1	1.005888 -0.214001 -2.150318
1	3.441788 0.255643 -2.154051
1	4.641035 0.563845 -0.014604
1	3.435766 0.399214 2.137310
1	1.000296 -0.071276 2.158443
17	-1.987815 1.602888 -0.044850
Pyridine	
0,1	
7	0.000000 -0.000000 1.411136
6	-0.000000 1.143467 0.719344
6	-0.000000 -1.143467 0.719344
6	-0.000000 1.194428 -0.669087

1	-0.000000 2.058703 1.299784
6	-0.000000 -1.194428 -0.669087
1	-0.000000 -2.058703 1.299784
6	-0.000000 0.000000 -1.377832
1	-0.000000 2.148854 -1.176961
1	-0.000000 -2.148854 -1.176961
1	-0.000000 0.000000 -2.459688
PhI	
0,1	
53	0.000000 1.550968 0.000000
6	0.000000 -0.564602 -0.000000
6	0.000000 -1.246551 1.211368
6	0.000000 -2.638410 1.203289
6	0.000000 -3.335937 -0.000000
6	0.000000 -2.638410 -1.203289
6	0.000000 -1.246551 -1.211368
1	0.000000 -0.706566 -2.147082
1	0.000000 -3.173920 -2.143486
1	0.000000 -4.417578 -0.000000
1	0.000000 -3.173920 2.143486
1	0.000000 -0.706566 2.147082
PhI(py	r) <sub>2</sub> <sup>2+</sup>
+2.1	/_
53	-0.000002 -0.888190 -0.068558
6	0.000003 1.213713 0.045939
6	-0.000031 1.795847 1.304182
6	-0.000028 3.184806 1.372909

0.000010 3.944732 0.207471

6

0.000046	3.327779	-1.039519
0.000042	1.940541	-1.135480
0.000067	1.448126	-2.095931
0.000075	3.921357	-1.943273
0.000012	5.024232	0.271364
-0.000054	3.667728	2.340307
-0.000058	1.193127	2.199761
2.249772	-0.776310	-0.042667
2.915341	-0.544131	-1.182642
2.893826	-0.958528	1.118644
4.295107	-0.482127	-1.189778
2.321518	-0.408588	-2.074341
4.273299	-0.908268	1.171950
2.283776	-1.140248	1.991111
4.983853	-0.666583	0.002873
4.813203	-0.292933	-2.118060
4.773776	-1.056461	2.117168
6.063727	-0.622433	0.020905
-2.249776	-0.776304	-0.042673
-2.893836	-0.958562	1.118628
-2.915340	-0.544085	-1.182643
-4.273309	-0.908299	1.171930
-2.283791	-1.140314	1.991092
-4.295106	-0.482079	-1.189783
-2.321513	-0.408514	-2.074335
-4.983858	-0.666572	0.002858
-4.773791	-1.056523	2.117141
-4.813197	-0.292853	-2.118062
-6.063731	-0.622421	0.020887
	0.000046 0.000042 0.000067 0.000075 0.000012 -0.000058 2.249772 2.915341 2.893826 4.295107 2.321518 4.273299 2.283776 4.983853 4.813203 4.773776 6.063727 -2.249776 -2.893836 -2.915340 -4.273309 -2.283791 -4.295106 -2.321513 -4.983858 -4.773791 -4.813197 -6.063731	0.0000463.3277790.0000421.9405410.0000671.4481260.0000753.9213570.0000125.024232-0.0000543.667728-0.0000581.1931272.249772-0.7763102.915341-0.5441312.893826-0.9585284.295107-0.4821272.321518-0.4085884.273299-0.9082682.283776-1.1402484.983853-0.6665834.813203-0.2929334.773776-1.0564616.063727-0.622433-2.249776-0.776304-2.893836-0.958562-2.915340-0.544085-4.273309-0.908299-2.283791-1.140314-4.295106-0.482079-2.321513-0.408514-4.983858-0.666572-4.773791-1.056523-4.813197-0.292853-6.063731-0.622421

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