

Electronic Supplementary information

On the activation of PhICl_2 with pyridine

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1. Experimental methods

1.1. Synthesis and crystallisation

Preparation of Iodobenzene dichloride (PhICl₂)

Concentrated HCl (10 mL, 10M) was added into ice-cold iodobenzene (0.5 mL, 5 mmol) followed by 2-3 drops of 30% H₂O₂. 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 CH₂Cl₂ was slowly added to precipitate until completely dissolved. Dried the product using MgSO₄. 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**

Dichloriodobenzene (PhICl₂) (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 CDCl₃ (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 CDCl₃ (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

Iodobenzene dichloride (200 mg, 0.728 mmol) was dissolved in CHCl₃ (6 mL) in a reaction flask. 4-Dimethylaminopyridine (178 mg, 1.46 mmol) dissolved in CHCl₃ (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 4-dimethylaminopyridine.HCl by ¹H 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 CHCl₃ (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 H₂O (1 mL) and basified with 1M NaOH (approx. 1 mL) until pH 14. The aqueous solution was extracted with CH₂Cl₂ (3 x 5 mL). The organic layers were combined and washed with H₂O (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%).

¹H NMR, ppm (CDCl₃, 400 MHz): δ 8.32 (1H, s), 8.22-8.20 (1H, d), 6.75-6.74 (1H, d), 2.99 (6H, s).

¹³C NMR, ppm (CDCl₃): δ 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 Olex2¹, the structures were solved with the SHELXT² structure solution program using Intrinsic Phasing and refined with the SHELXL³ 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.

Table S1. Crystal data and structure refinement for PhICl₂, **2** and **3**

Identification code	PhICl ₂	2	3
Empirical formula	C ₆ H ₅ Cl ₂ I	C ₁₁ H ₁₀ Cl ₂ IN	C ₈ H ₁₀ ClF ₃ N ₂ O ₃ S
Formula weight	274.90	354.00	306.69
Temperature/K	100(2)	100(2)	150(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /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)
α/°	90	90	90
β/°	101.8700(10)	107.339(4)	95.923(3)
γ/°	90	90	90
Volume/Å ³	787.65(2)	1269.63(7)	1222.09(6)
Z	4	4	4
ρ _{calc} /g/cm ³	2.318	1.852	1.667
μ/mm ⁻¹	2.448	2.911	4.807
F(000)	512.0	680.0	624.0
Crystal size/mm ³	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)
2θ range for data collection/°	5.288 to 95.114	5.17 to 50.244	10.556 to 142.59
Index 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 ≤ 20
Reflections collected	112670	12645	11583
Independent reflections	15027 [R _{int} = 0.0387, R _{sigma} = 0.0180]	2263 [R _{int} = 0.0512, R _{sigma} = 0.0303]	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 ²	1.051	1.055	1.063
Final R indexes [I > 2σ (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

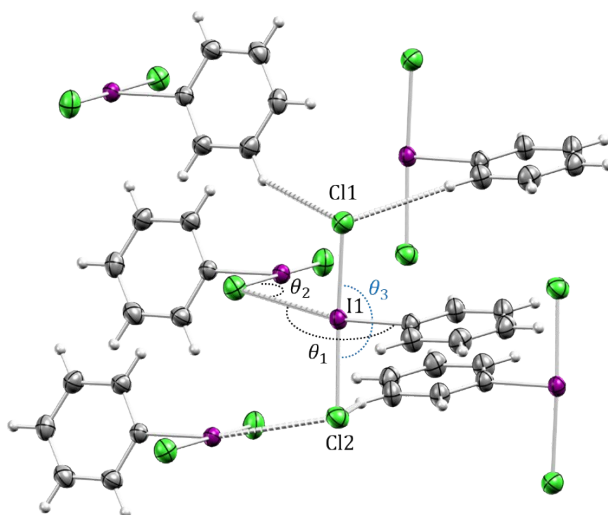


Figure S1: Crystal packing in PhICl_2 . Angles: $\theta_1(\text{C-I} \cdots \text{Cl}) = 166.38^\circ$, $\theta_2(\text{Cl-I} \cdots \text{Cl}) = 100.24^\circ$, $\theta_3(\text{Cl-I-Cl}) = 176.70^\circ$; bond distances $d(\text{I-Cl1}) = 2.48319(12) \text{ \AA}$ and $d(\text{I-Cl2}) = 2.505926(11) \text{ \AA}$. 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 β halogen bonding ($\psi = 0.33$)⁴ while Cl1 atom undergoes exclusively hydrogen bonding interactions with two aryl C-Hs.

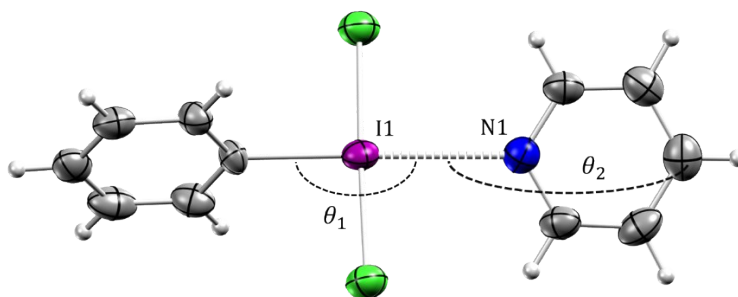


Figure S2: Crystal structure of the $\text{PhICl}_2 \cdots \text{Py}$ aggregate **2**. Selected angles ($\theta_1(\text{C-I} \cdots \text{Cl}) = 177.97^\circ$, $\theta_2(\text{Cl-I} \cdots \text{Cl}) = 175.38^\circ$) show a type II β halogen bonding ($\psi = 0.98$)⁴ with an intermolecular short contact distance of $d(\text{N1} \cdots \text{I1}) = 2.750 \text{ \AA}$.

3. Experimental electron density study

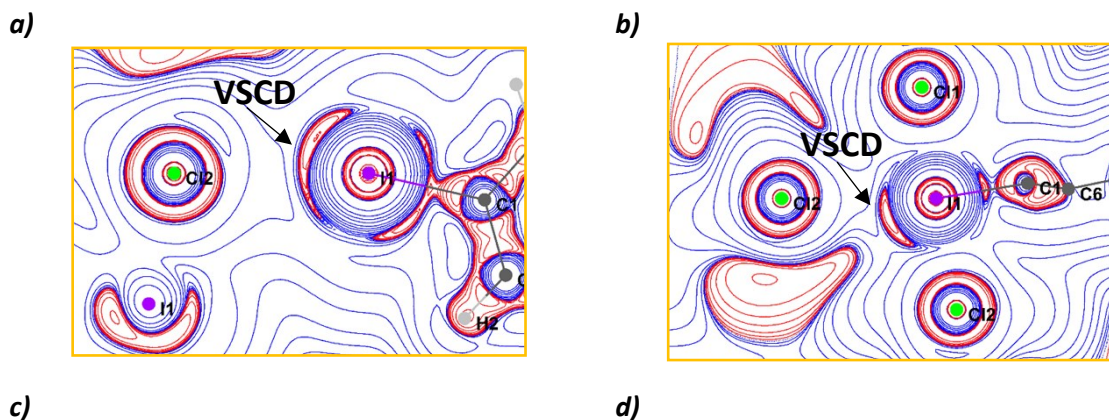
3.1. Multipole refinement of PhICl_2

The multipolar refinement was carried out on F^2 according to the Hansen & Coppens formalism for aspherical atomic density expansion as implemented in *MoProSuite*.⁵ 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.⁷ Refinement results have been compiled in Table 2. Electron density maps were obtained using *MoProViewer*.⁸

Table S2: Refinement results.

Refinement	IAM	MM
Resolution	0.38 – 10 Å	0.38 – 6.079 Å
R_1 [$I \geq 2\sigma(I)$]	0.0162	0.01296 (RF factor)
wR_2 [$I \geq 2\sigma(I)$]	0.0394	0.01360 (wR2F factor)
R_1 [all data]	0.0208	0.01910 (RI factor)
wR_2 [all data]	0.0403	0.02.668 (wR2I factor)
Nvar/Nref	-	301/11758
Largest diff. peak/hole / $e \text{ Å}^{-3}$	1.99/-0.90	-
Goodness-of-fit on F^2	1.051	1.028
Weighting scheme	0.0177 0.0497	0.52372 (MoPro gof1)

3.2. Topological analysis



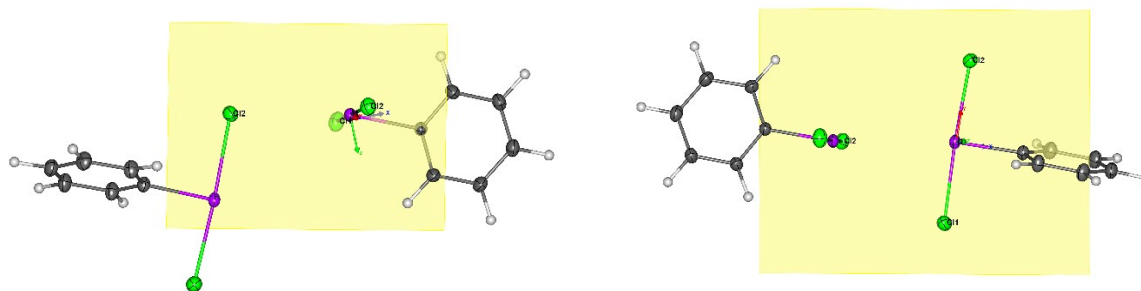
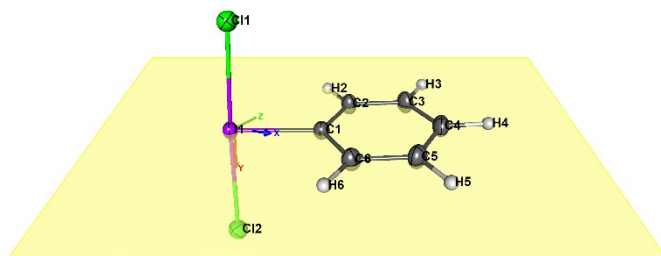
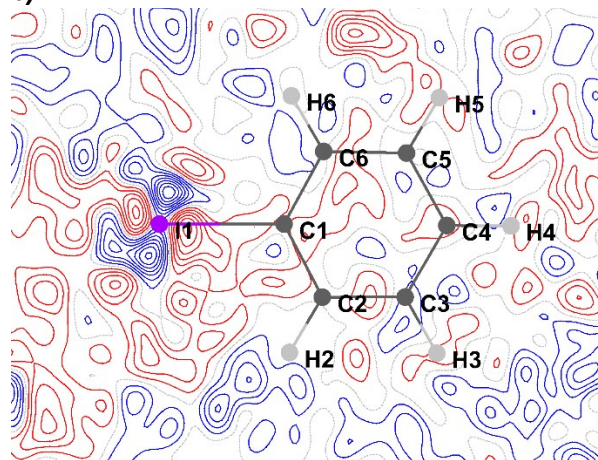


Figure S3: Logarithmic Laplacian maps of the intermolecular halogen bonding $I1 \rightarrow Cl2$ along the ZX plane **a)** and **c)** and XY plane **b)** and **d)**. Red denotes charge depletion (VSCD) and blue denotes charge concentration (VSCC).

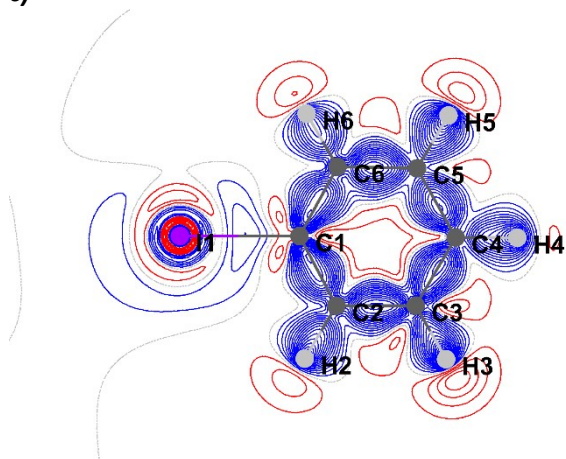
a)



b)



c)



d)

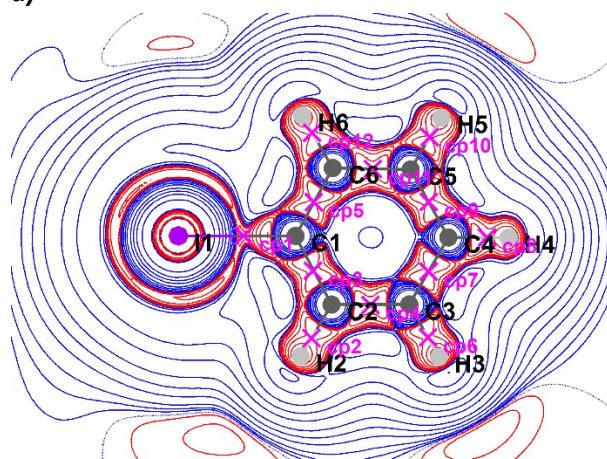


Figure S4: Experimental two-dimensional electron density maps of **1** at a resolution range of $0.38 < d \text{ (\AA)} < 6.079$. **a)** shows the ZX plane used for 2D maps, **b)** corresponds to the residual density ($0.10 \text{ e \AA}^{-1}$, $0.08 < \sin\theta/\lambda < 0.80$), **c)** full deformation of the static electron density (contour $0.05 \text{ e \AA}^{-1}$). 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).

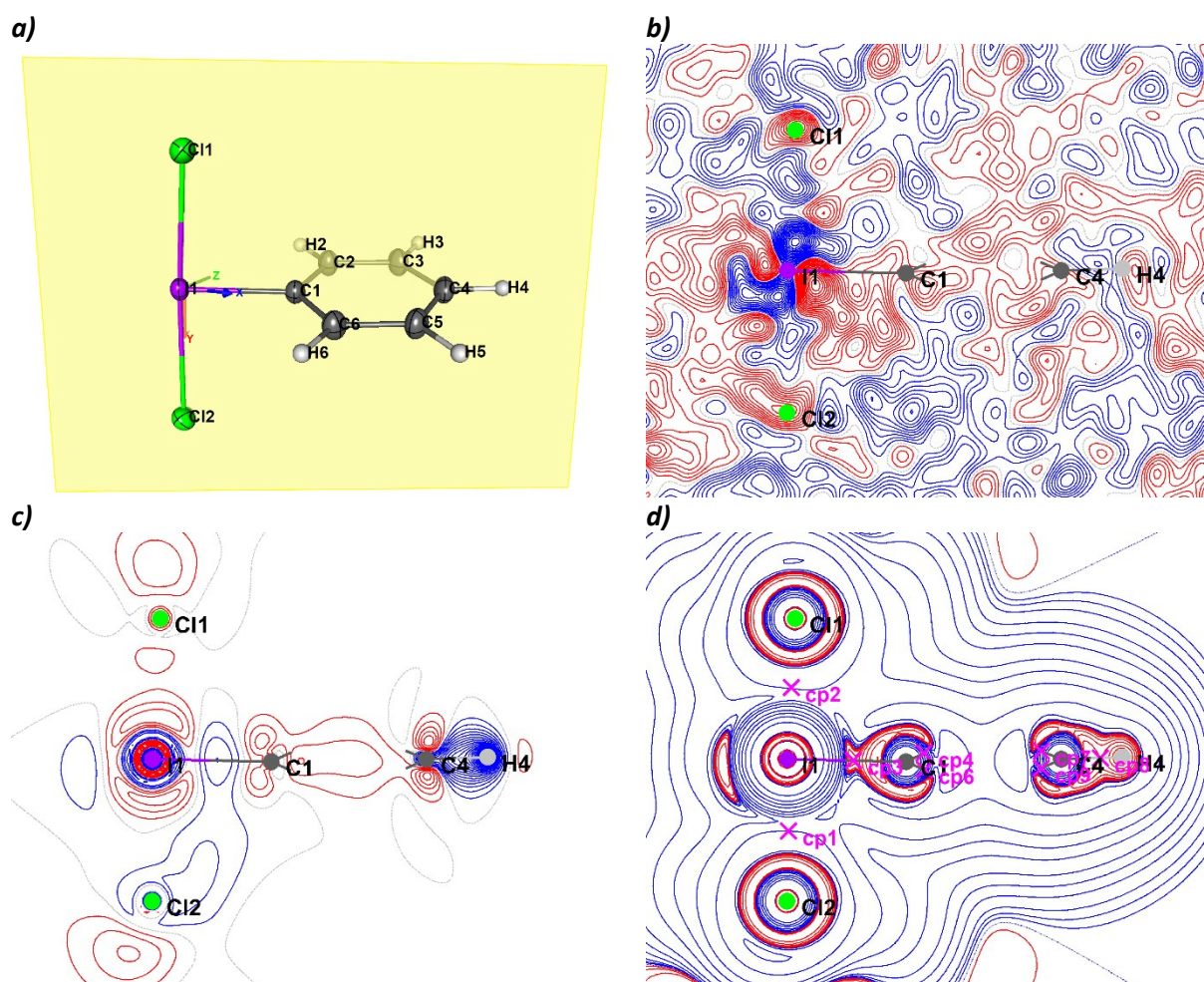


Figure S5: Experimental two-dimensional electron density maps of **1** at a resolution range of $0.38 < d \text{ (Å)} < 6.079$. **a)** shows the XY plane used for 2D maps, **b)** corresponds to the residual density (0.10 e Å^{-1} , $0.08 < \sin\theta/\lambda < 0.80$), **c)** full deformation of the static electron density (contour 0.05 e Å^{-1}). 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).

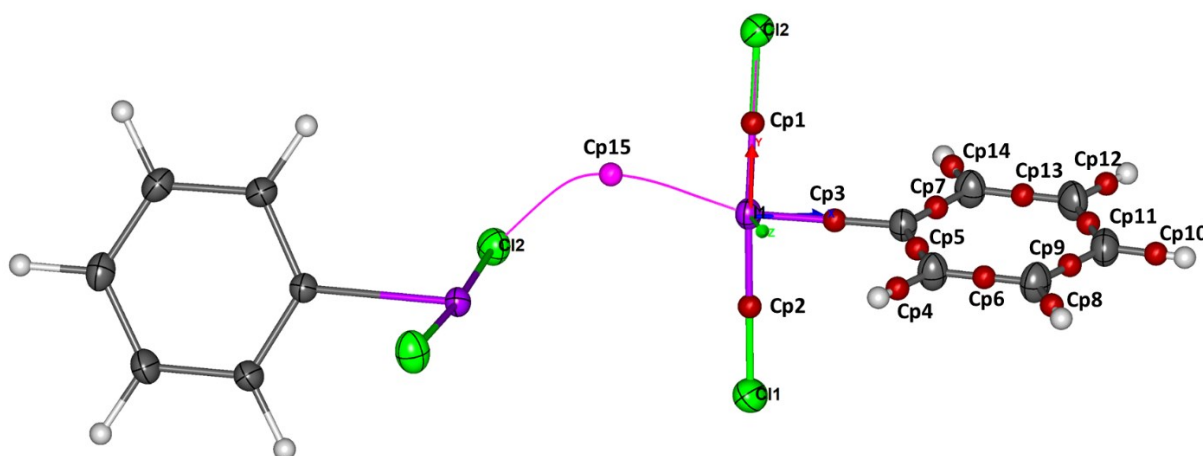


Figure S6: Non-covalent (pink) and covalent (red) critical points of **1** illustrated with *MoProViewer*.

Table S3. Bond critical points details of covalent interactions.

CP	Type	Atom1	Atom2	d_{ij} (Å)	d_1 (Å)	d_2 (Å)	ρ (eÅ ⁻³)	$\Delta^2 \rho$ (eÅ ⁻⁵)	Gcp (kJmol ⁻¹ /Bohr ³)	Vcp (kJmol ⁻¹ /Bohr ³)	ellip
Cp1	(3,-1)	I1	Cl2	2.5047	1.2731	1.2419	0.51441	1.766	135.38	-222.65	0.7375
Cp2	(3,-1)	I1	Cl1	2.4825	1.2625	1.2201	0.46643	2.182	127.37	-195.31	0.3985
Cp3	(3,-1)	I1	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
Cp9	(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
Cp13	(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

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

Table S4. Bond critical points details of non-covalent interactions.

CP	Type	Atom1	Atom2	d_{ij} (Å)	d_1 (Å)	d_2 (Å)	ρ (eÅ ⁻³)	$\Delta^2 \rho$ (eÅ ⁻⁵)	Gcp (kJmol ⁻¹ /Bohr ³)	Vcp (kJmol ⁻¹ /Bohr ³)	ellip
Cp15	(3,-1)	I1	Cl2	3.4216	1.9867	1.9746	0.15989	-0.257	10.06	-27.13	0.6651

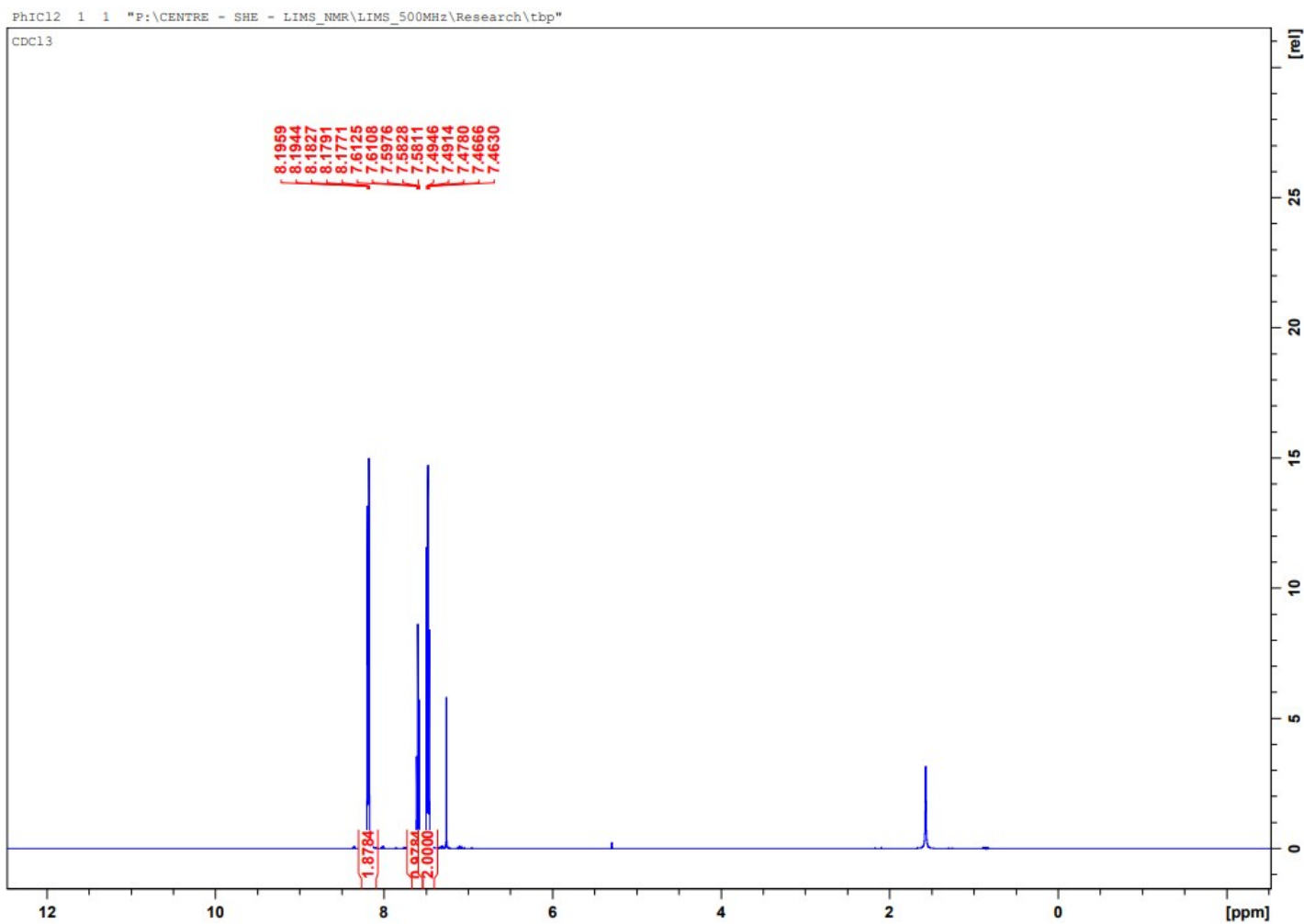
d_{ij} is the bond path, d_1 and d_2 its components, ρ the electron density and Δ^2 the Laplacian in the intermolecular bcp; Gcp and Vcp correspond to the kinetic and potential energy, respectively.

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

Bond	Type	dist(Å)	d_{ij} (Å)	d_1 (Å)	d_2 (Å)	ρ (eÅ ⁻³)	$\Delta^2 \rho$ (eÅ ⁻⁵)	Ref.
Cl(1)···Cl(3)a	ClCl	3.1912(6)	3.1912	1.5779	1.6133	0.107(2)	1.102(4)	9
Cl2···Cl2i (1)inter	ClCl	3.7641 (3)	3.764	1.888	1.877	0.023 (2)	0.307 (2)	10
Cl1···Cl1a	ClCl	3.3651(6)	3.3650	1.6825	1.6825	0.048(2)	0.576(2)	9
Cl1···Cl1b	ClCl	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	IO	3.026(6)	3.0818	1.6303		0.092(7)	0.856(9)	11
I(3)···O(1)	IO	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)	ClCl	3.2219(4)	3.2258	1.5992	1.6266	0.084(2)	1.006(2)	13
Cl2···Cl3 (2)	ClCl	3.2871(4)	3.2895	1.6302	1.6593	0.073(2)	0.867(2)	13
Cl1···Cl2(3)	ClCl	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	IO	2.9826(9)	2.9824	1.5992	1.3832	0.102(2)	1.307(3)	15
I(1)···O(1)	IO	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, ρ the electron density and Δ^2 the Laplacian in the intermolecular bcp.

4. NMR Investigations

Figure S7: Iodobenzene dichloride in CDCl₃.

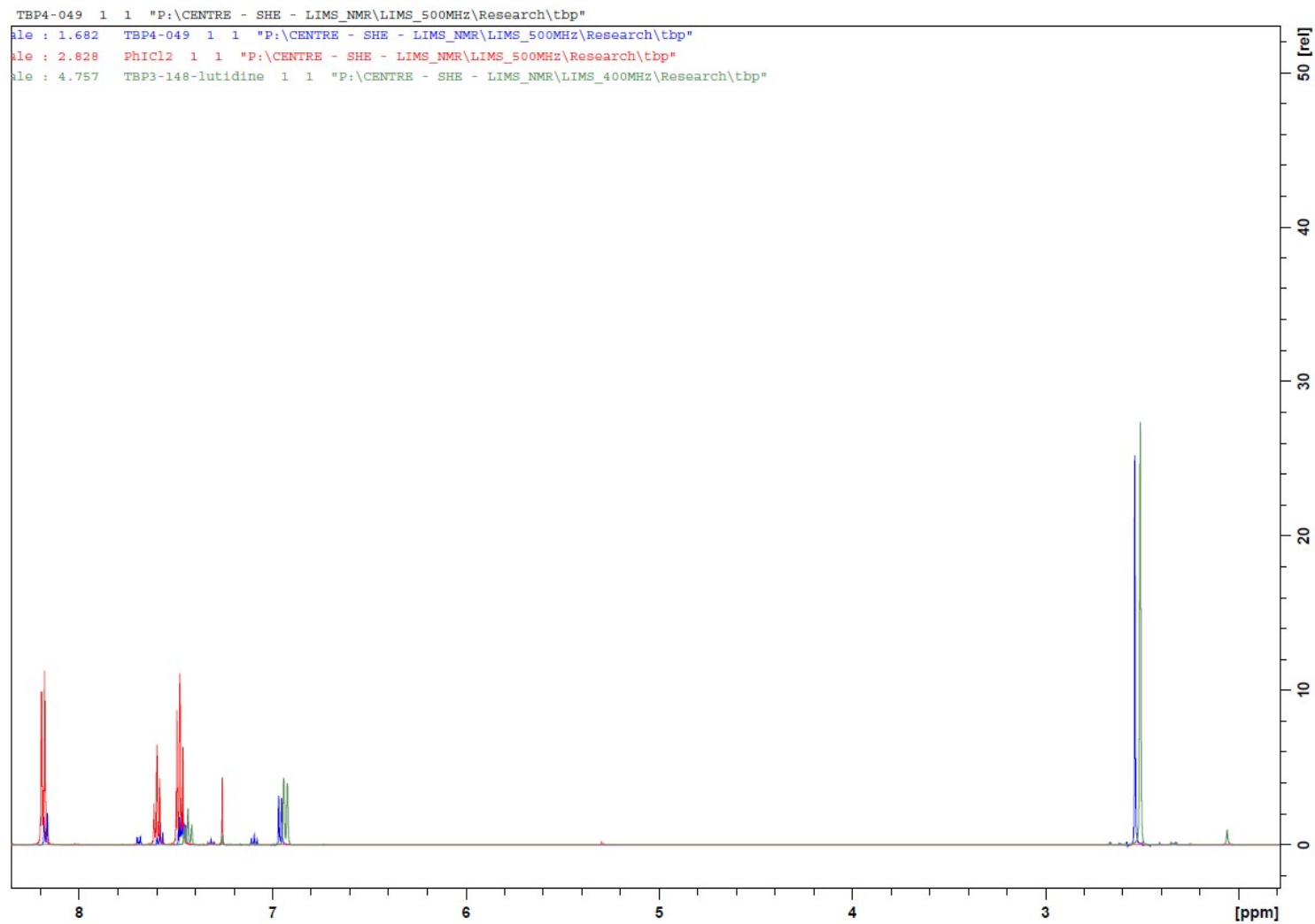


Figure S2: Reaction mixture of PhICl₂ and 2,6-dimethylpyridine (blue) overlaid with PhICl₂ (red) and 2,6-dimethylpyridine (green) in CDCl₃.

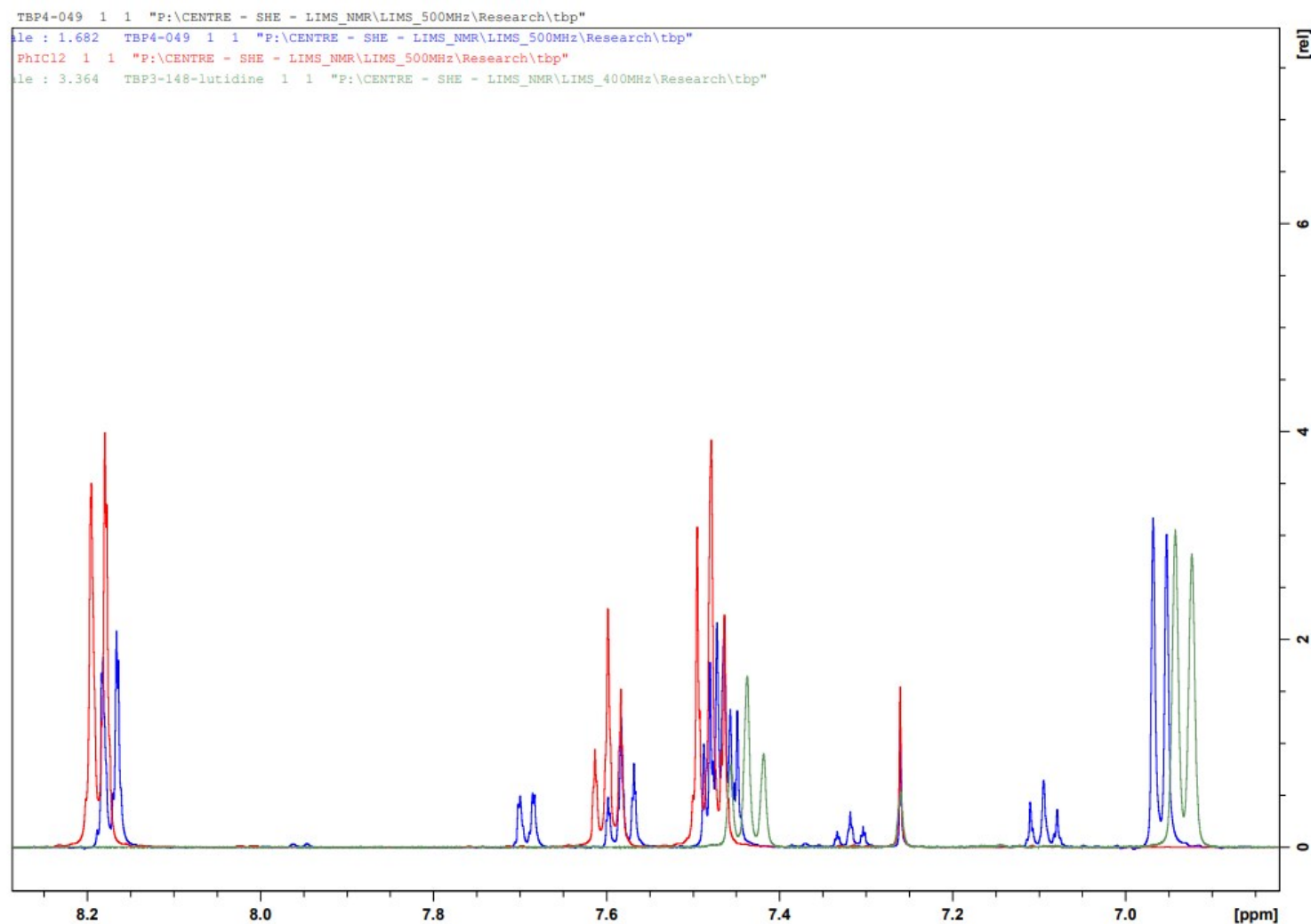


Figure S3: Downfield region of reaction mixture of PhICl_2 and 2,6-dimethylpyridine (blue) overlayed with PhICl_2 (red) and 2,6-dimethylpyridine (green).
Note: Free iodobenzene is present owing to gradual decomposition of PhICl_2 .

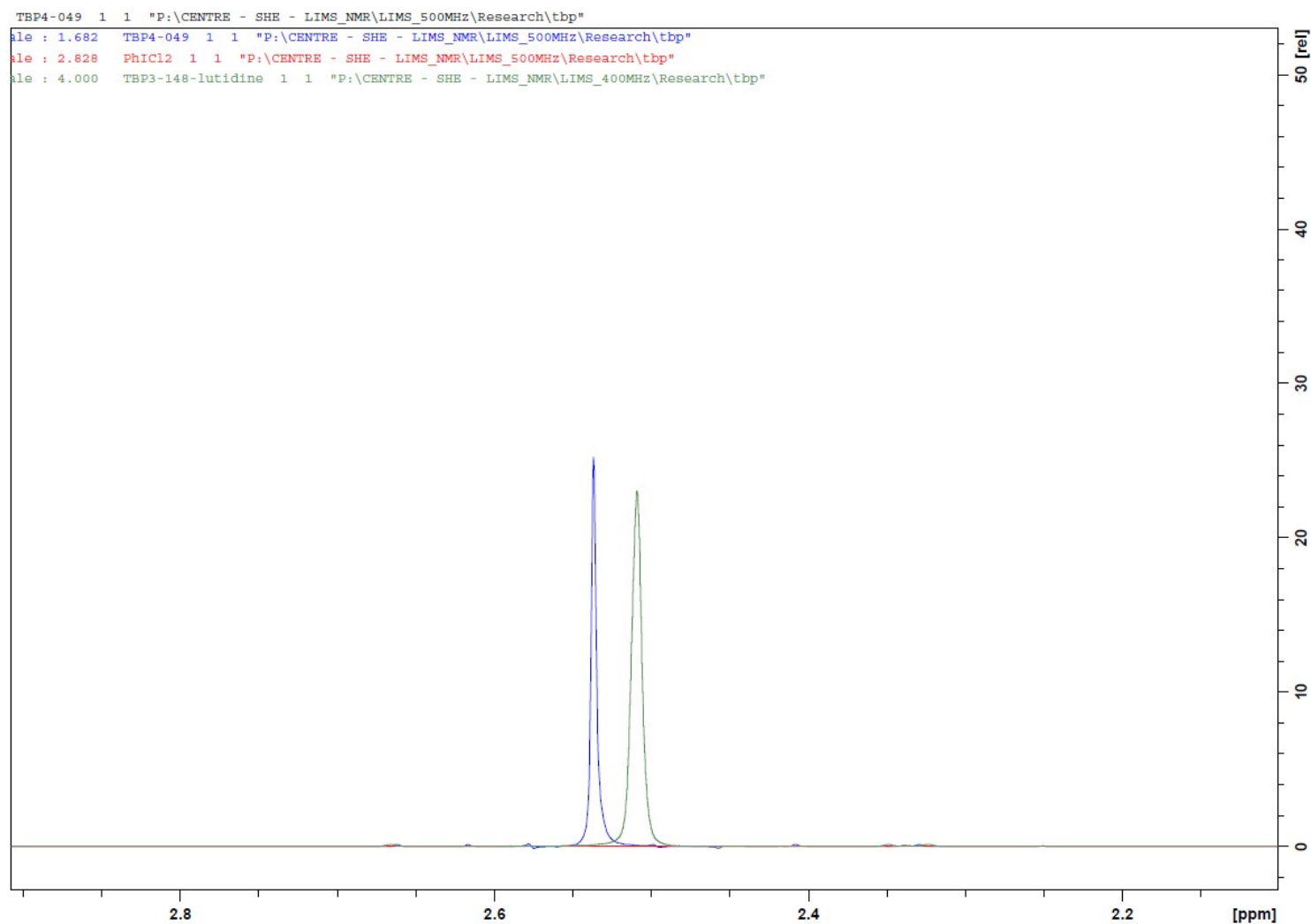


Figure S4: Upfield region of reaction mixture of PhICl₂ and 2,6-dimethylpyridine (blue) overlayed with PhICl₂ (red) and 2,6-dimethylpyridine (green).

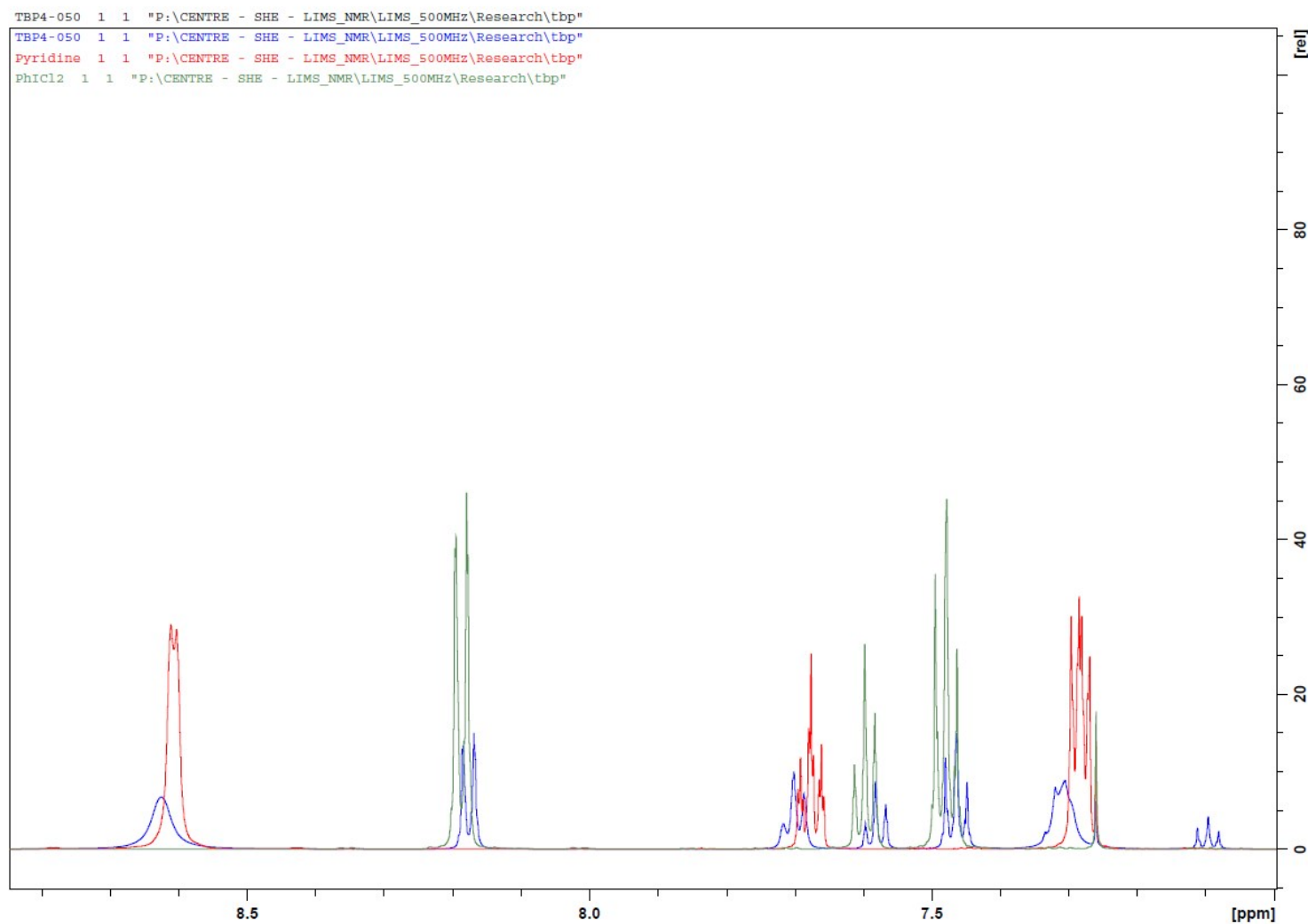


Figure S5: Reaction mixture of PhICl₂ and pyridine (blue) overlaid with PhICl₂ (green) and pyridine (red).

Note: Free iodobenzene is present owing to gradual decomposition of PhICl₂

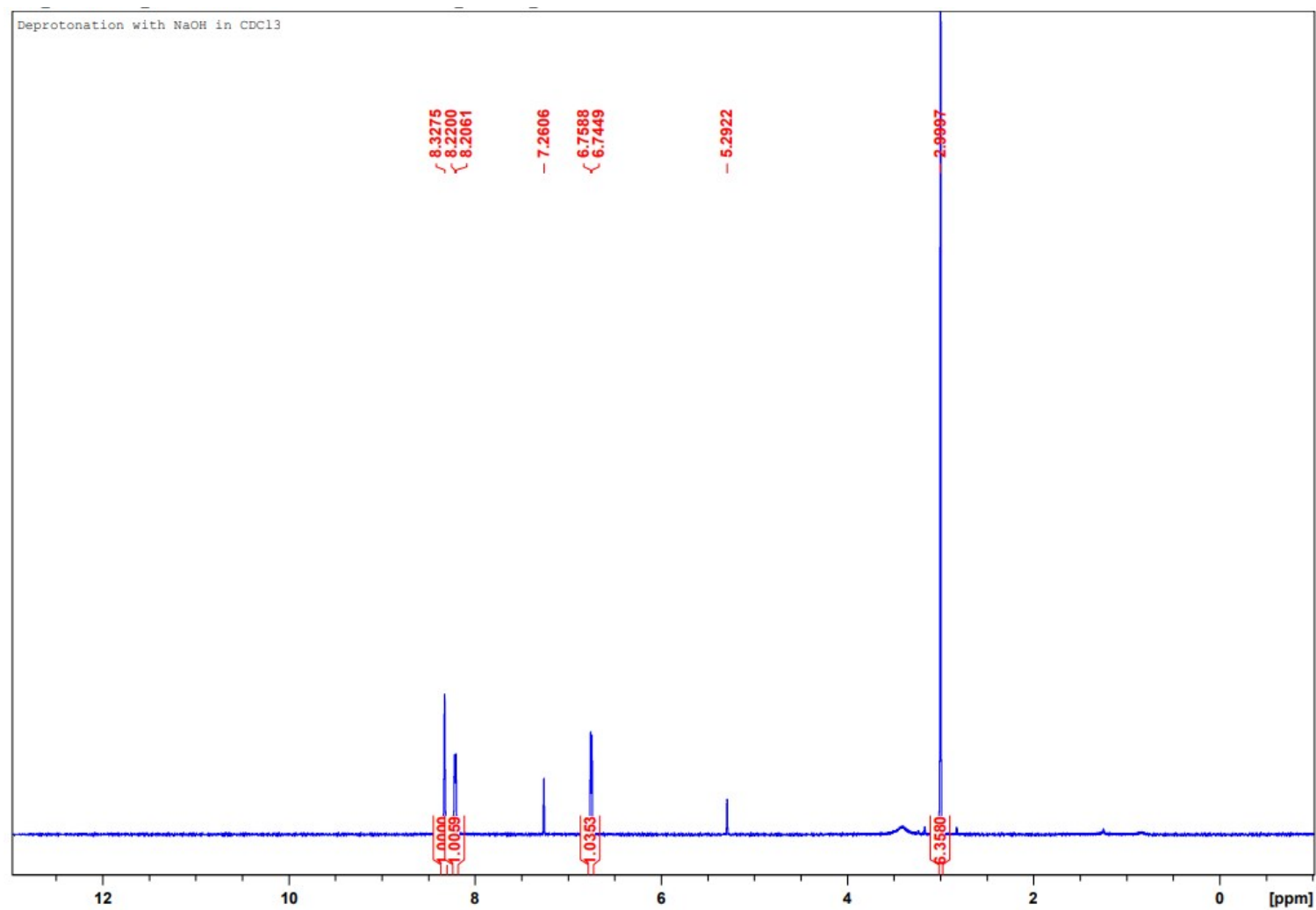


Figure S6: ¹H spectrum of 3-chloro-4-dimethylaminopyridine in CDCl₃.

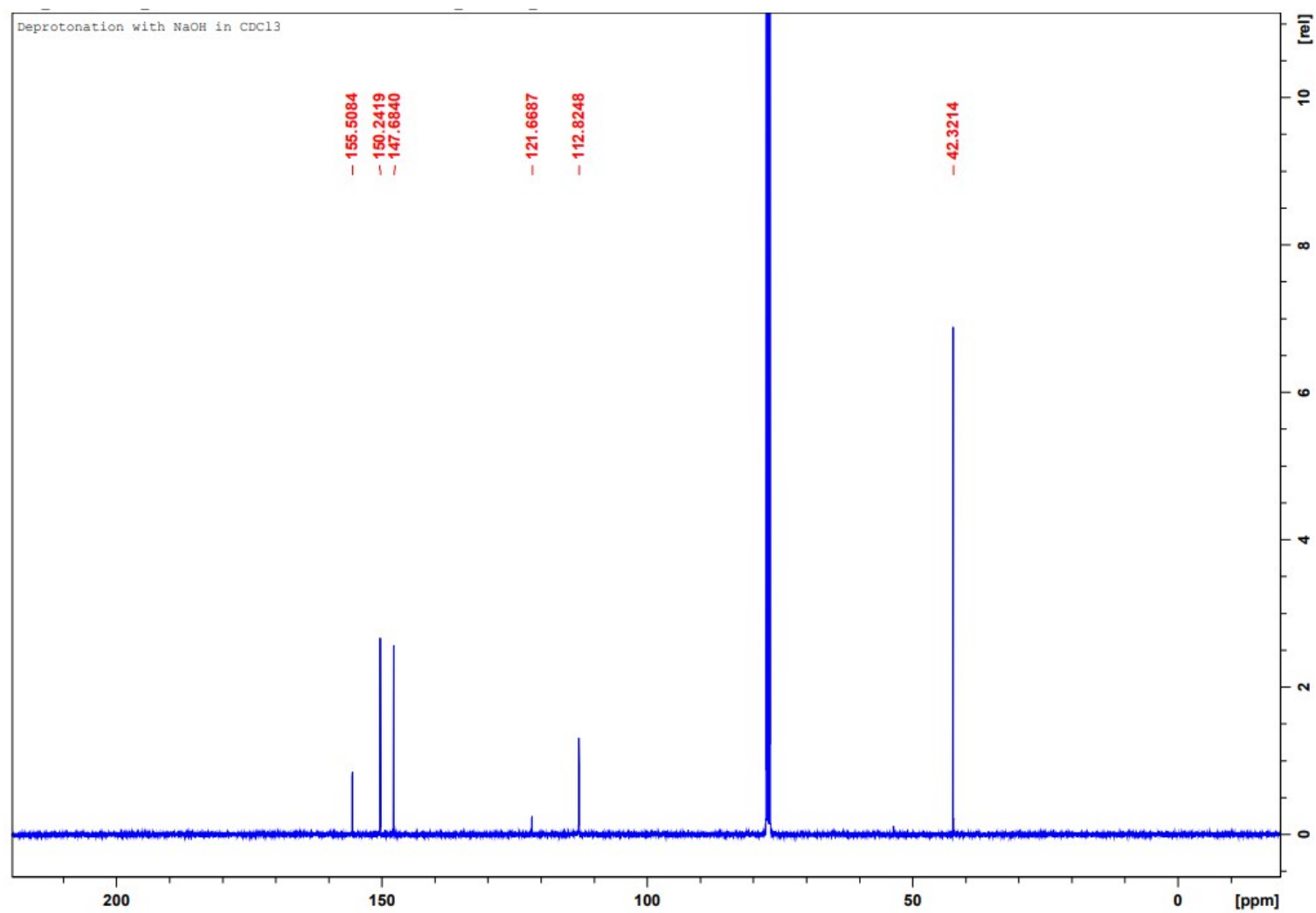


Figure S7: ¹³C spectrum of 3-chloro-4-dimethylaminopyridine in CDCl₃

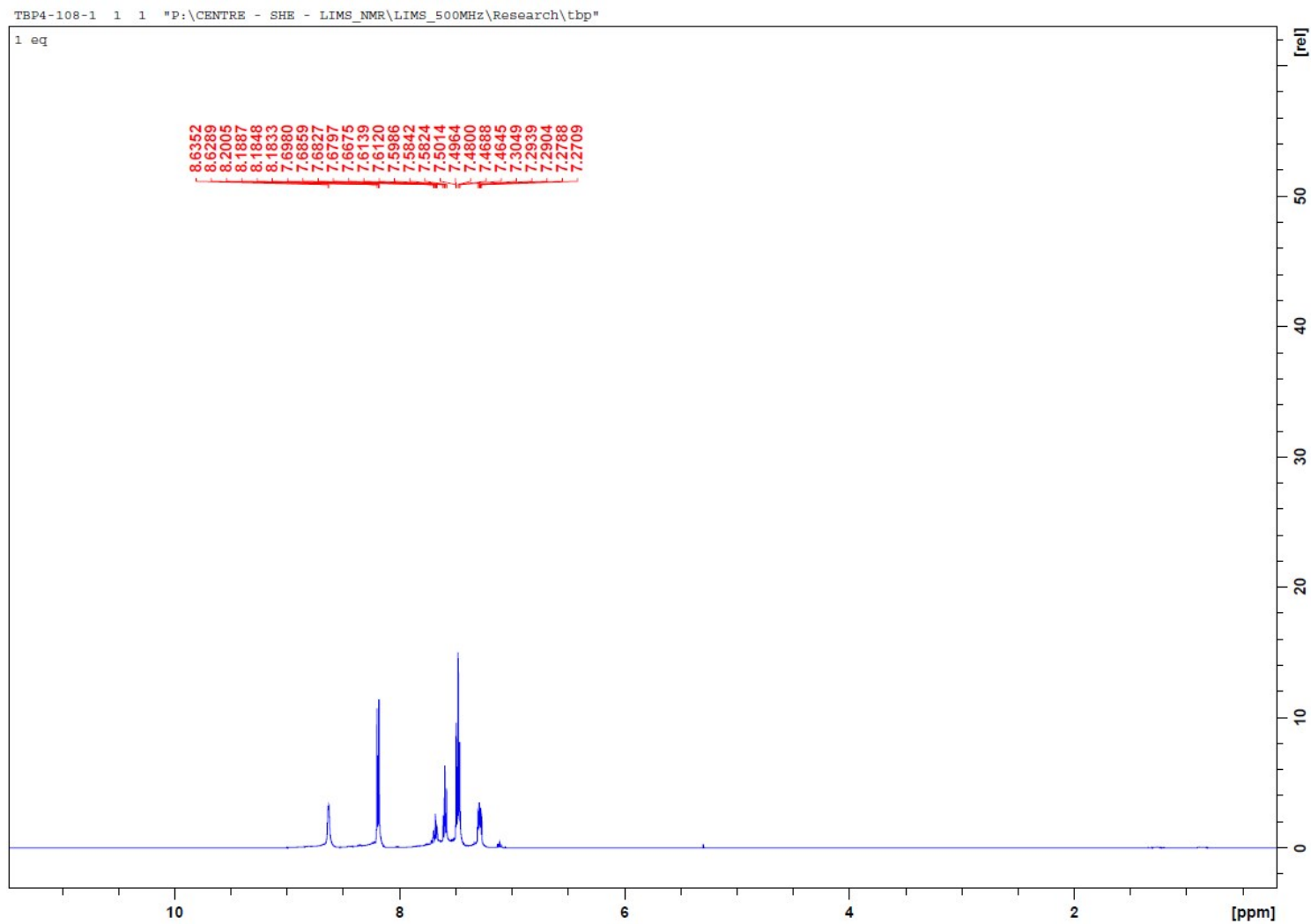


Figure S8: ^1H NMR spectrum of 1 equivalent of PhICl_2 and 1 equivalent of pyridine in CDCl_3 .

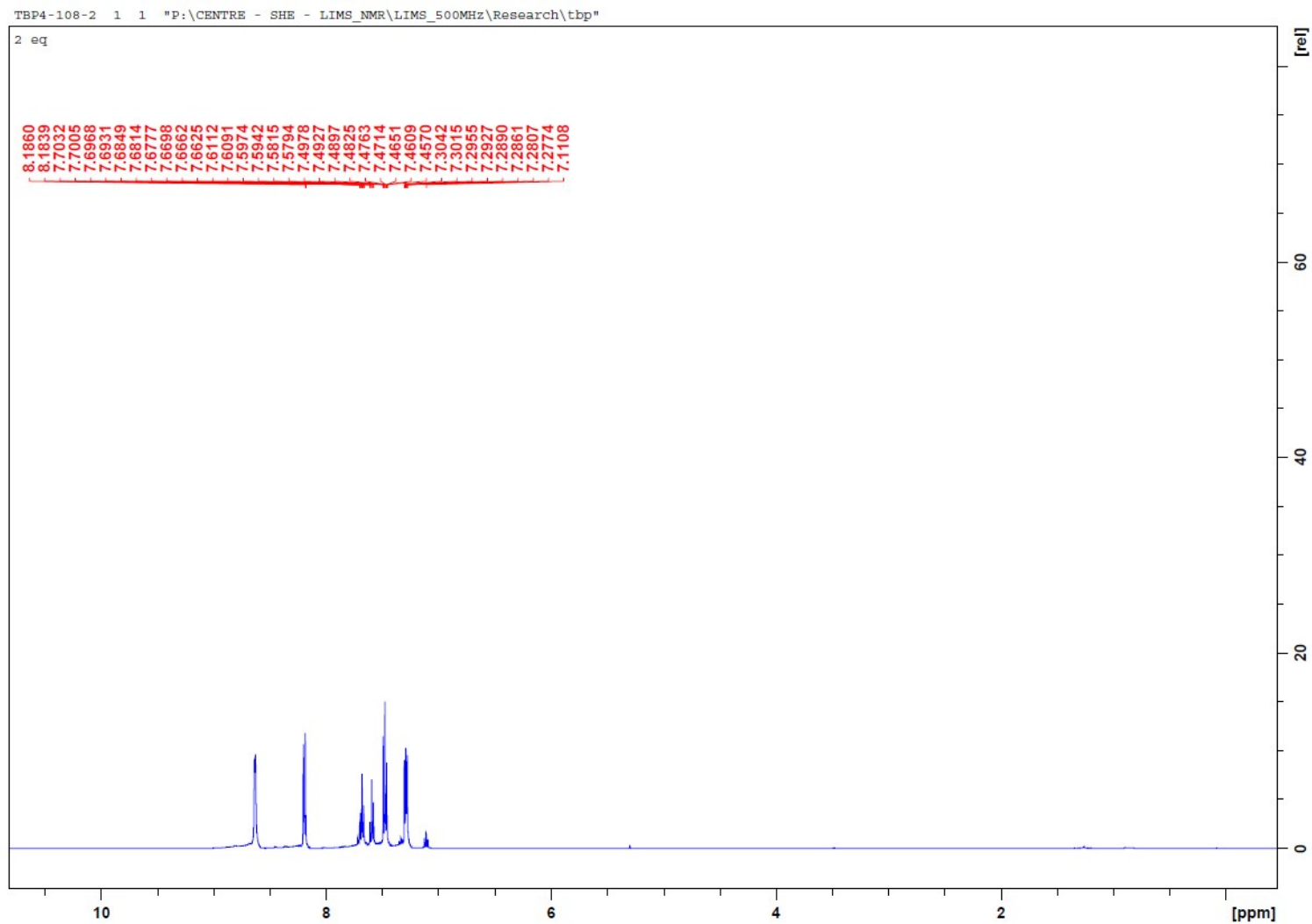


Figure S9: ^1H NMR spectrum of 1 equivalent of PhICl_2 and 2 equivalents of pyridine in CDCl_3 .

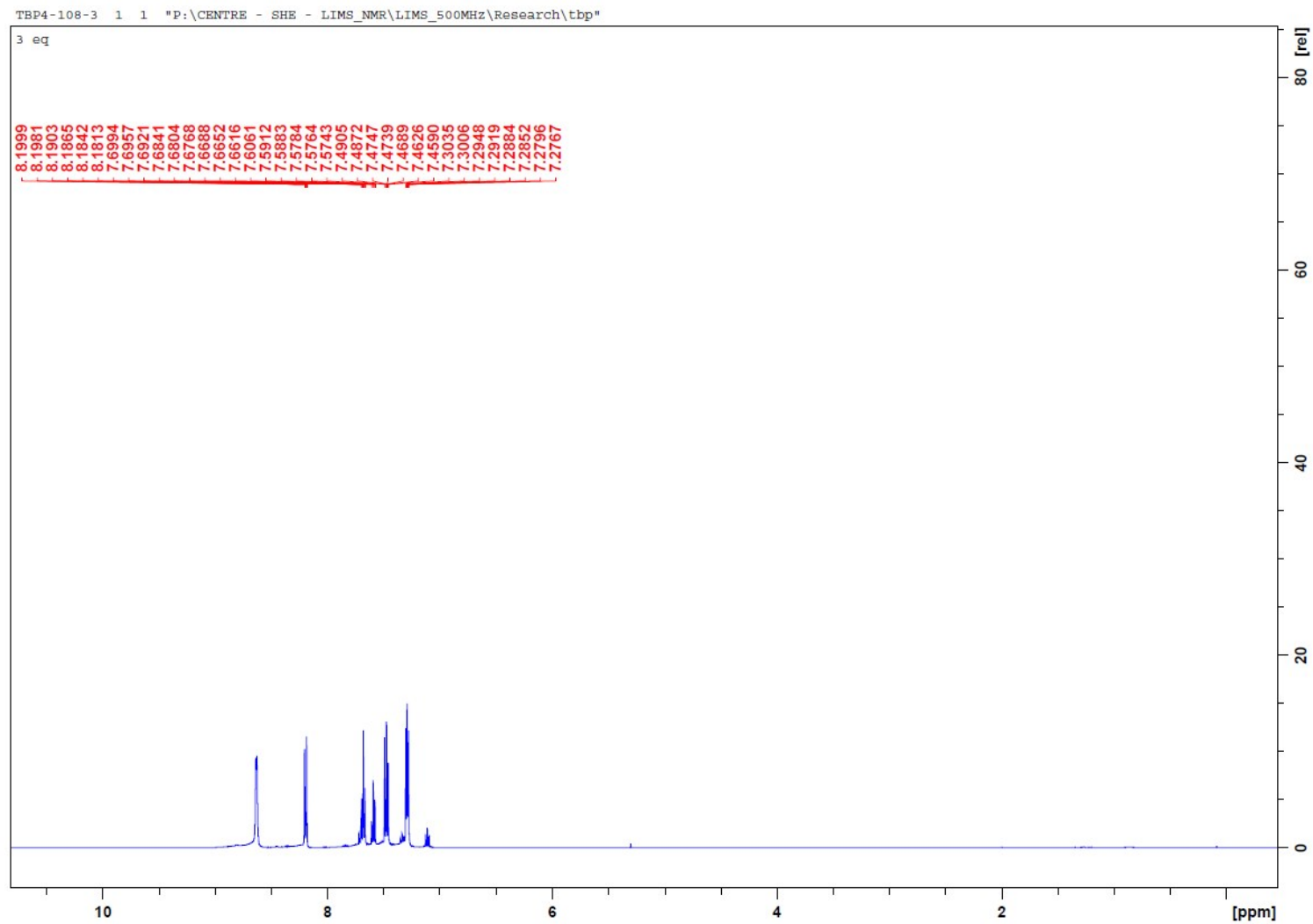


Figure S10: ^1H NMR spectrum of 1 equivalent of PhICl_2 and 3 equivalents of pyridine in CDCl_3 .

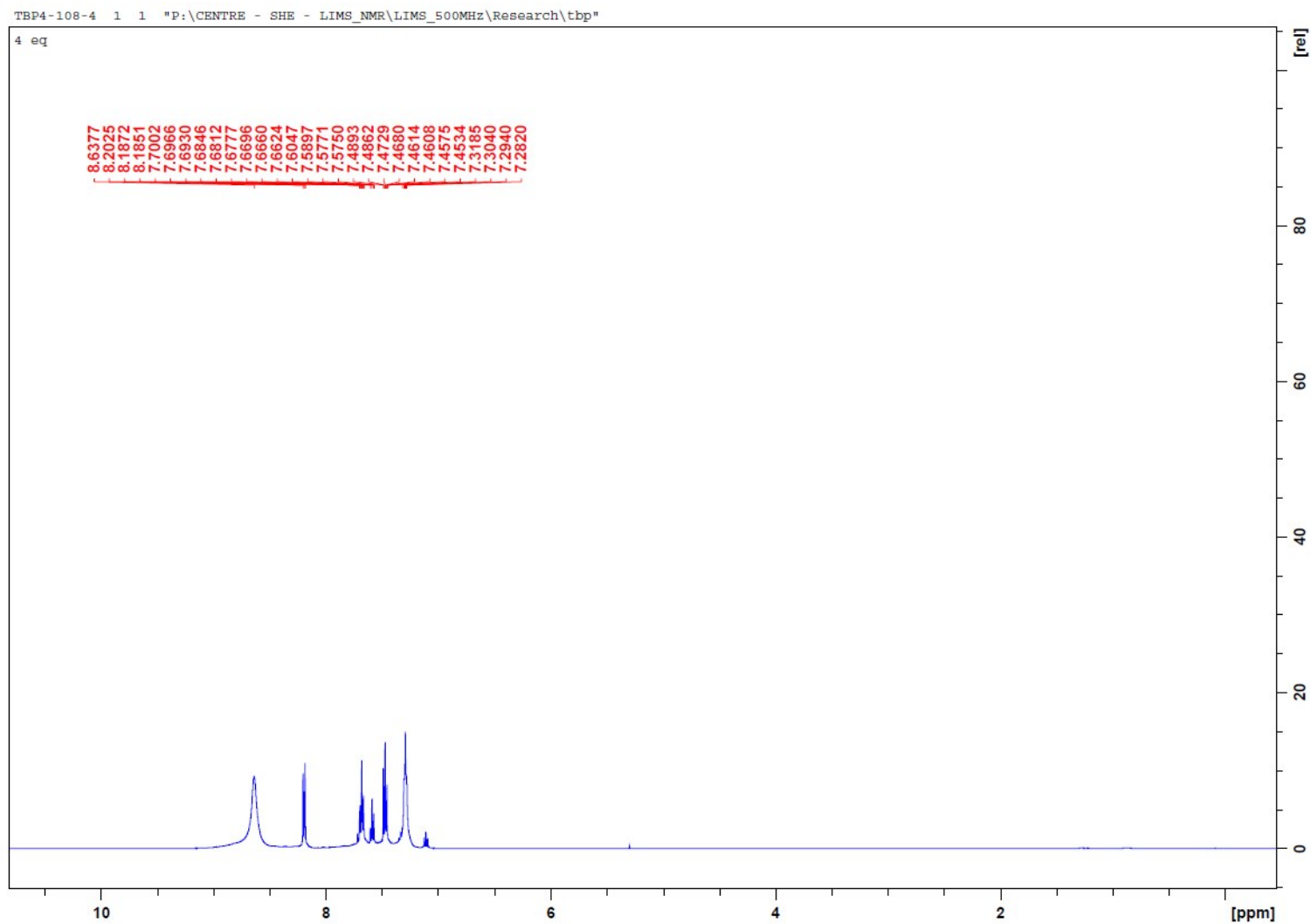


Figure S11: ^1H NMR spectrum of 1 equivalent of PhICl_2 and 4 equivalents of pyridine in CDCl_3 .

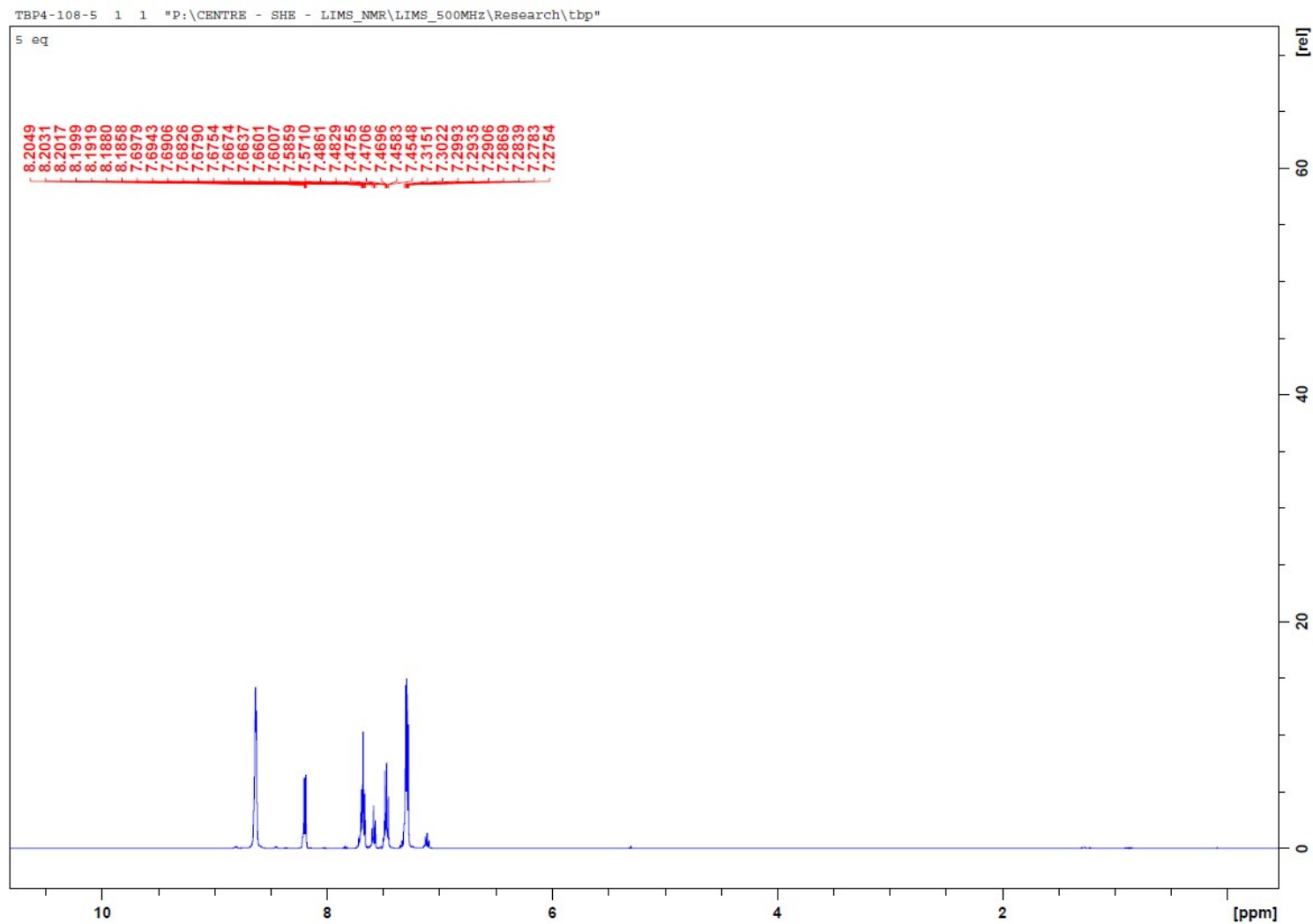


Figure S12: ^1H NMR spectrum of 1 equivalent of PhICl_2 and 5 equivalents of pyridine in CDCl_3 .

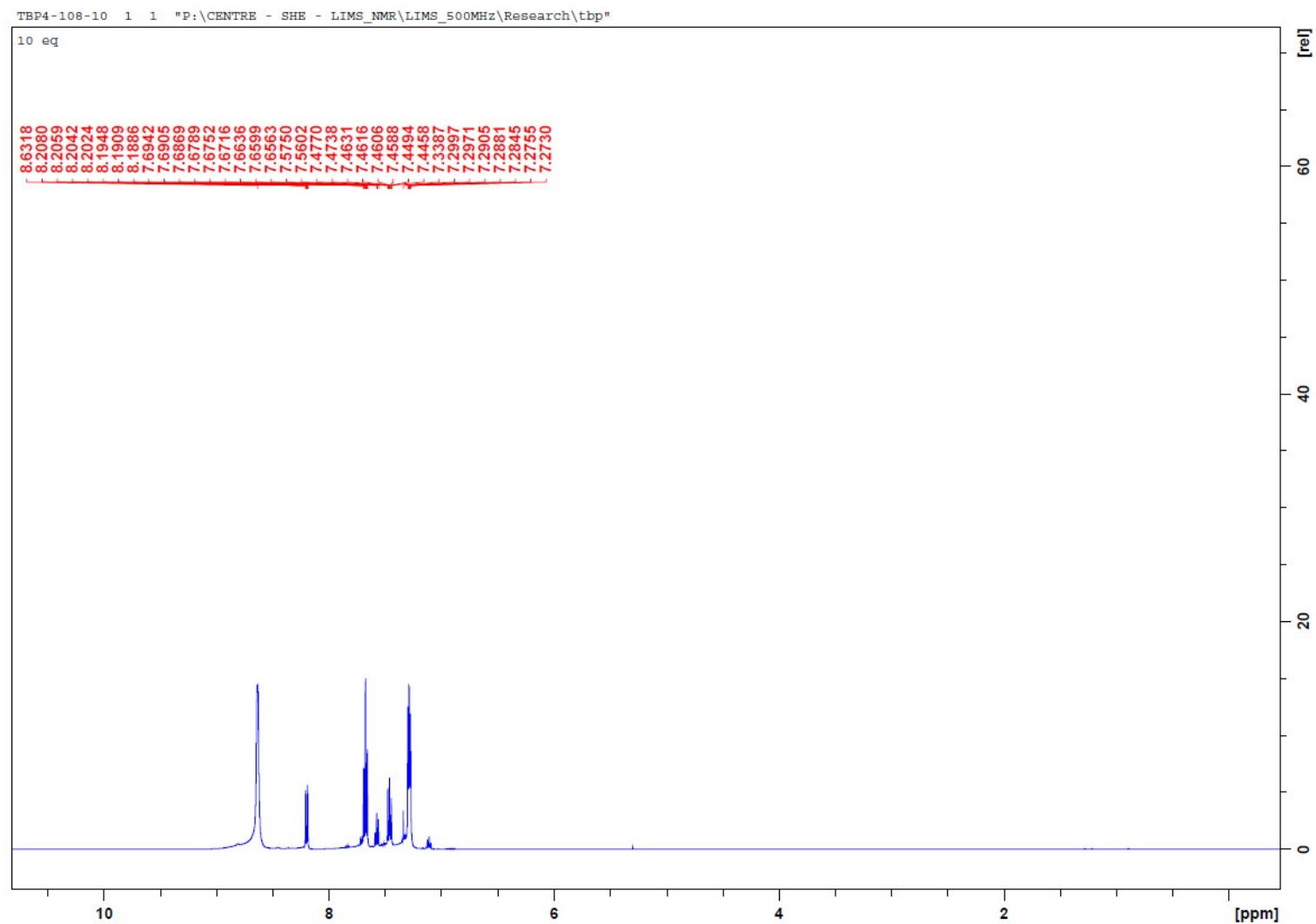


Figure S13: ^1H NMR spectrum of 1 equivalent of PhICl_2 and 10 equivalents of pyridine in CDCl_3 .

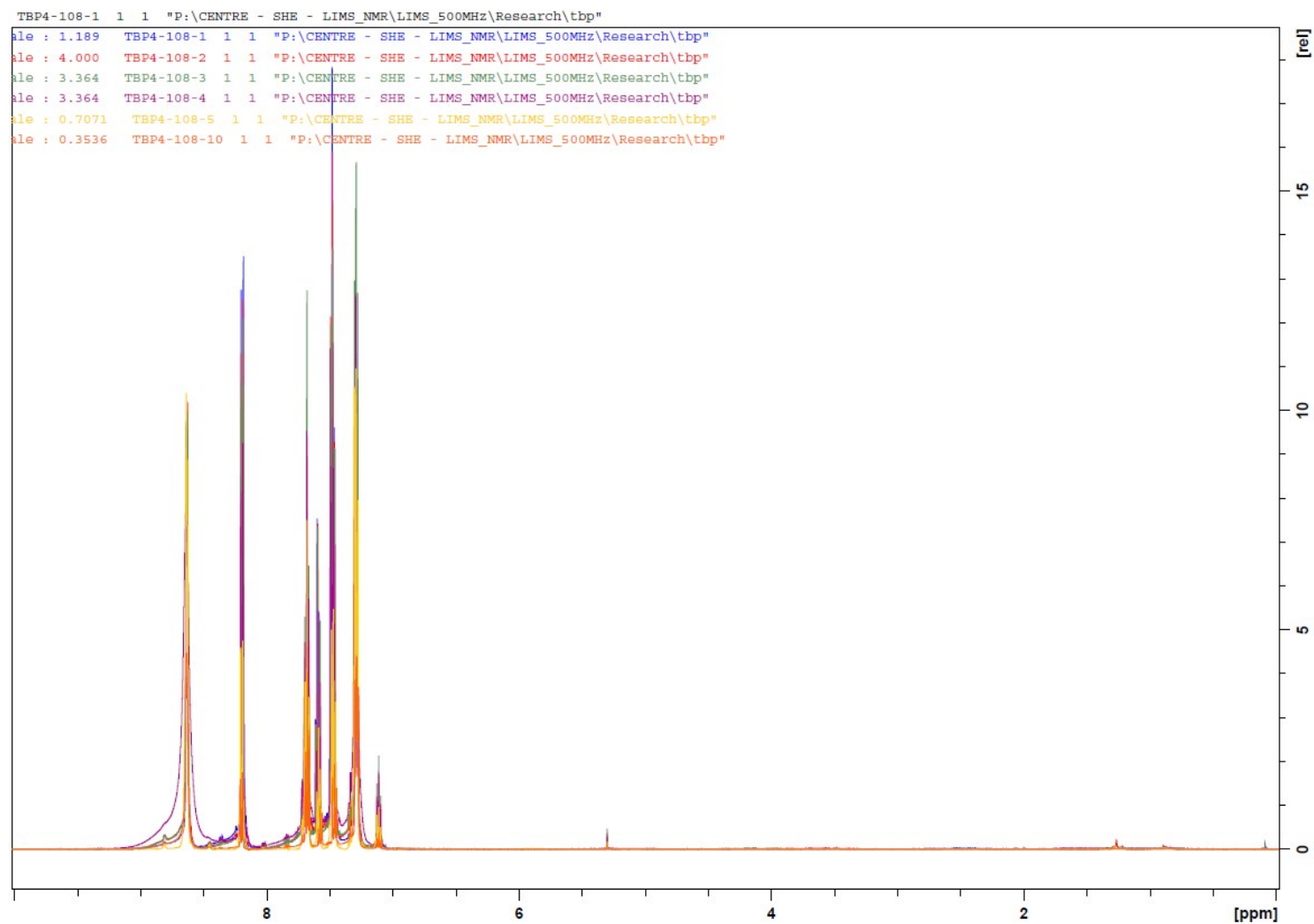


Figure S14: ^1H NMR spectrum overlay of PhICl_2 and 1-5, 10 equivalents of pyridine in CDCl_3 .

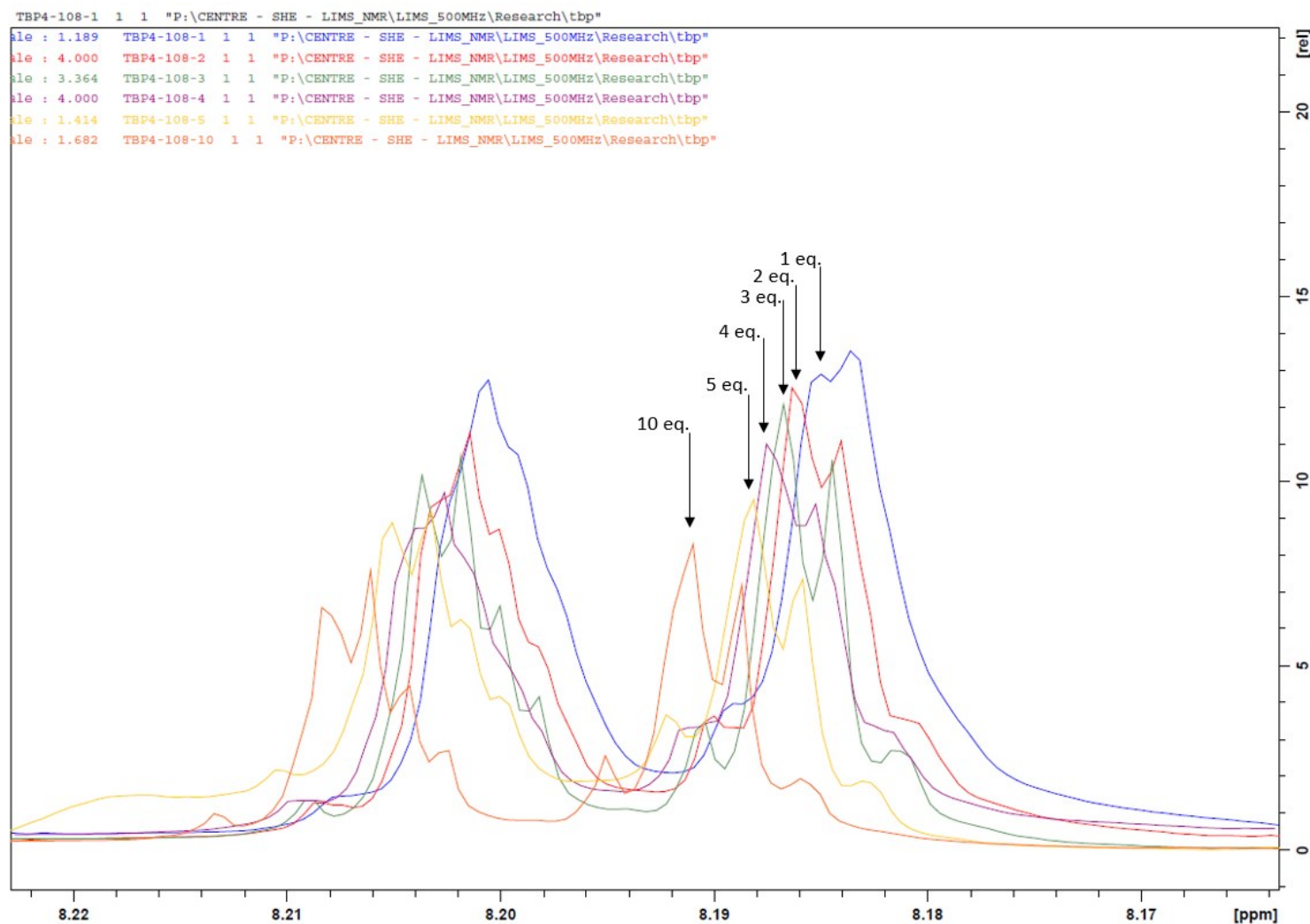


Figure S15: ^1H NMR spectrum overlay (most downfield signal) of PhICl_2 and 1-5, 10 equivalents of pyridine in CDCl_3 .

5. Computational details

All calculations were performed using Gaussian 16 revision A.03 unless noted.¹⁸ Geometry optimizations were performed with the B3LYP density functional^{19, 20} with Grimme's empirical D3 dispersion with Becke-Johnson (BJ) damping,²¹ together with the def2-TZVPPD basis set, which includes an ECP for iodine.^{21, 22} 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 model²³ with parameters for acetonitrile.

All subsequent property and electronic structure calculations were carried out at the optimized geometries. Molecular orbital (MO), population analysis (CM5 charges²⁴) and Natural Bond Orbital (NBO) analysis was carried out at the same B3LYP-D3(BJ)/def2-TZVPPD (SMD, acetonitrile) level of theory. NBO analysis was performed using NBO 6.0.²⁵

For thermochemistry analysis, single point calculations were carried out at the ω B97XD/def2-TZVPPD, B3LYP-D3(BJ)/def2-QZVPPD level of theory.²³ 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 4.2.1.²⁶ The single point energies were converted to free energies (ΔG) 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 3.0.2.²⁷

Table S6. Calculated ΔG of reaction (kJ/mol) for addition of pyridine to PhICl_2 to form four-coordinate PhICl_2pyr (compound **2**).

Method	Basis Set	Solvation	Geometry	ΔG	$\Delta G(\text{QH})^a$
B3LYP-D3(BJ)	Def2-TZVPPD	Gas phase	opt	-10.1	-14.0
B3LYP-D3(BJ)	Def2-TZVPPD	ACN	opt	+11.6	+9.3
ω B97XD	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

^a Quasi-harmonic analysis using GoodVibes, with cutoff of 200 cm^{-1} . Temp = 40 K. Scale factor = 0.9857.

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

Cartesian coordinates of optimized geometries
B3LYP-D3(BJ)/def2-TZVPPD (SMD, acetonitrile)

PhICl₂

+1,1

0, 1 (charge and multiplicity)

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

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
1	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	-3.623884	0.157357	-1.199616
1	-1.745449	-0.480212	-2.064600
6	-3.623887	0.157348	1.199623
1	-1.745453	-0.480227	2.064605
6	-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

PhICl₂Pyr (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

PhICl⁺

+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

[PhI(Pyr)Cl]⁺

1	-0.000000	2.058703	1.299784	6	0.000046	3.327779	-1.039519
6	-0.000000	-1.194428	-0.669087	6	0.000042	1.940541	-1.135480
1	-0.000000	-2.058703	1.299784	1	0.000067	1.448126	-2.095931
6	-0.000000	0.000000	-1.377832	1	0.000075	3.921357	-1.943273
1	-0.000000	2.148854	-1.176961	1	0.000012	5.024232	0.271364
1	-0.000000	-2.148854	-1.176961	1	-0.000054	3.667728	2.340307
1	-0.000000	0.000000	-2.459688	1	-0.000058	1.193127	2.199761
PhI				7	2.249772	-0.776310	-0.042667
0,1				6	2.915341	-0.544131	-1.182642
53	0.000000	1.550968	0.000000	6	2.893826	-0.958528	1.118644
6	0.000000	-0.564602	-0.000000	6	4.295107	-0.482127	-1.189778
6	0.000000	-1.246551	1.211368	1	2.321518	-0.408588	-2.074341
6	0.000000	-2.638410	1.203289	6	4.273299	-0.908268	1.171950
6	0.000000	-3.335937	-0.000000	1	2.283776	-1.140248	1.991111
6	0.000000	-2.638410	-1.203289	6	4.983853	-0.666583	0.002873
6	0.000000	-1.246551	-1.211368	1	4.813203	-0.292933	-2.118060
1	0.000000	-0.706566	-2.147082	1	4.773776	-1.056461	2.117168
1	0.000000	-3.173920	-2.143486	1	6.063727	-0.622433	0.020905
1	0.000000	-4.417578	-0.000000	7	-2.249776	-0.776304	-0.042673
1	0.000000	-3.173920	2.143486	6	-2.893836	-0.958562	1.118628
1	0.000000	-0.706566	2.147082	6	-2.915340	-0.544085	-1.182643
PhI(pyr) ₂ ²⁺				6	-4.273309	-0.908299	1.171930
+2,1				1	-2.283791	-1.140314	1.991092
53	-0.000002	-0.888190	-0.068558	6	-4.295106	-0.482079	-1.189783
6	0.000003	1.213713	0.045939	1	-2.321513	-0.408514	-2.074335
6	-0.000031	1.795847	1.304182	6	-4.983858	-0.666572	0.002858
6	-0.000028	3.184806	1.372909	1	-4.773791	-1.056523	2.117141
6	0.000010	3.944732	0.207471	1	-4.813197	-0.292853	-2.118062
				1	-6.063731	-0.622421	0.020887

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