Electronic Supplementary information

$PhICl_2$ is activated by chloride ions

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1. EXPERIMENTAL SECTION

I. Experimental Details

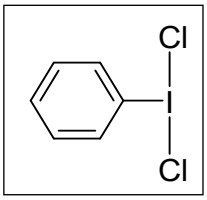
All reagents were purchased from Sigma Aldrich and used as received. $CDCl_3$ was stirred over CaH_2 for 24 hours, distilled and stored over 3 angstrom molecular sieves in the glovebox, although used as received had no effect on conversions. The BindFit experiments were prepared in an N_2 filled glove box. The reagents and solvents used for these experiments were air and water free. NMR spectra for all experiments were recorded using Bruker Ultrashield Plus 500 MHz and Ascend 400 MHz

spectrometers. The abbreviations used to report NMR signal multiplicity are s = singlet, d = doublet, t = triplet, m = multiplet.

II. Reaction Procedures

i. Syntheses

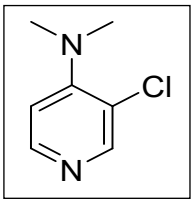
a. Iodobenzene dichloride[1]



In a conical flask, PhI (0.5 mL, 5mmol) was cooled to 0 °C on ice bath. HCl (10 mL, 10M) was added dropwise while stirring followed by 3-4 drops of H_2O_2 (30%). Gradually, a yellow solid sticking to the walls of flask was observed. After two hours, solid was collected by filtration and washed free of chloride with water. The air-dried solid was then dissolved in minimal CH_2Cl_2 and dried over anhydrous $MgSO_4$. The filtered solution was stored at -20 °C resulting in overnight formation of crystals. The yellow needle like crystals were collected and identified as title compound (1.10 g, 89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.18 (2H, d), 7.62-7.58 (1H, t), 7.48-7.46 (2H, t).

b. 3-Chloro-4-dimethylaminopyridine[1]



Iodobenzene 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 4-dimethylaminopyridine.HCl by ^{1}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 as a $CHCl_3$ solution, 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 $MgSO_4$ and filtered. Volatiles were removed in vacuo to give the title compound as a colourless liquid (70 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (1H, s), 8.22-8.20 (1H, d), 6.75-6.74 (IH, d), 2.99 (6H, s).

^{13}C NMR (400 MHz, CDCl3): δ 155.50, 150.24, 147.68, 121.66, 112.82, 42.32.

c. Pyridine hydrochloride salts

A reaction flask was charged with the respective pyridine (2 mmol) and dissolved in Et_2O (2 mL). 2M HCl.Et_2O (1.1 eq., 2.20 mmol) was added dropwise while continuously stirring. White precipitates were formed immediately. The solid was isolated *via* centrifugation, washed with Et_2O (3 × 2 mL) and dried under vacuum to give an HCl salt of the respective pyridine.

Pyridine.HCl ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88-8.87 (2H, d), 8.49-8.45 (1H, t), 7.48-7.46 (2H, t).

4-DMAP.HCl ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12-8.08 (2H, t), 6.77-6.75 (2H, d), 3.23 (6H, s).

3-Cl-4-DMAP.HCl ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (1H, s), 8.14-8.12 (1H, d), 6.88-6.87 (1H, d), 3.37 (6H, s).

d. Pyridine hydrotriflate salt

A reaction flask was charged with respective pyridine (2 mmol) and dissolved in Et_2O (2 mL). Triflic acid (1.1 eq., 2.20 mmol) dissolved in Et_2O was added dropwise while continuously stirring. White precipitates were formed immediately. The solid was isolated *via* centrifugation, washed with Et_2O (3 × 2 mL) and dried under vacuum to give an HOTf salt of the respective pyridine.

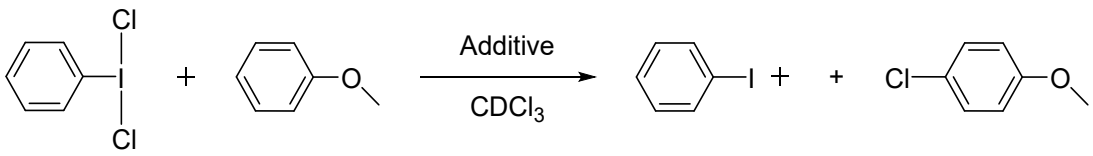
Pyridine.HOTf ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94-8.93 (2H, d), 8.53-8.51 (1H, t), 8.06-8.02 (2H, t).

4-DMAP.HOTf ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15-8.12 (2H, t), 6.77-6.75 (2H, d), 3.26 (6H, s).

e. Crystals of $PhICl_2$-NEt_4Cl

Tetraethylammonium chloride (3 mg, 0.018 mmol) was added to a warm solution of $PhICl_2$ (5 mg, 0.018 mmol) in minimum dichloromethane. The reaction mixture was stirred until the solution turned clear before cooling (-20 °C). Pale yellow needle-like crystals (91%) were obtained overnight.

ii. Conversion of Anisole to p-Chloroanisole

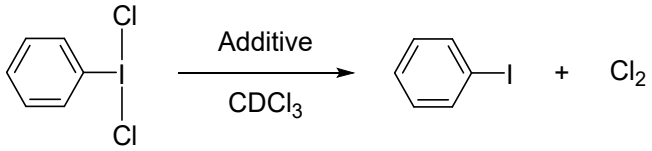


$PhICl_2$ was dissolved in $CDCl_3$ to obtain a 0.09 M solution. Subsequently, anisole (1 eq.) and the additive were added to the solution. The reaction was stirred for 1 hour. An aliquot (600 µL) was taken at t = 1 hour and ^1H NMR was recorded. The amounts of $PhICl_2$, anisole, $CDCl_3$ and respective additive used in each reaction are summarised in Table S1.

Table S1. Amounts of $PhICl_2$, anisole, $CDCl_3$ and respective additive used.

Additive Name	**mol% of additive**	**Amount of $PhICl_2$ (mg)**	**Amount of Anisole (mg)**	**Amount of $CDCl_3$ (mL)**	**Amount of additive**
None	0	25	9.8	1	-
Pyridine	20%	50	19.6	2	2.9 µL
Pyridine.HCl	20%	50	19.6	2	4.2 mg
Pyridine.HOTf	20%	25	9.8	1	4.2 mg
Pyridine.HOTf	50%	25	9.8	1	10.4 mg
NBu_4Cl	20%	25	9.8	1	5.0 mg
$HCl.Et_2O$	20%	100	39.3	4	36 µL
NBu_4OTf	20%	25	9.8	1	7.1 mg
4-DMAP	20%	50	19.6	2	4.4 mg
4-DMAP.HCl	20%	50	19.6	2	5.8 mg
4-DMAP.HOTf	20%	25	9.8	1	5.0 mg
3-Cl-4-DMAP	20%	50	19.6	2	5.7 mg
3-Cl-4-DMAP.HCl	20%	50	19.6	2	7.0 mg
NBu_4Cl	5%	100	39.3	4	5.0 mg
NaCl	20%	50	19.6	2	2.1 mg
LiCl	20%	100	39.3	4	3.1 mg
LiCl	50%	50	19.6	2	7.7 mg

iii. Decomposition of $PhICl_2$ with time



$PhICl_2$ was dissolved in $CDCl_3$ to obtain a 0.09 M solution. Subsequently, the additive was added to the solution. The amount of solution in vial was marked as initial volume. The reaction was stirred in an open vial. Aliquots (600 µL) were taken from reaction vial for periodic NMR analysis at t = 10 minutes, 30 minutes, 1 hour, 2 hours, 3 hours and 4 hours. Then, the vial was covered with perforated parafilm to minimize $CDCl_3$ loss to evaporation. The reaction was continuously stirred for 20 hours. $CDCl_3$ was

topped up to initial volume mark and another NMR was recorded. The amounts of $PhICl_2$, $CDCl_3$ and respective additive used in each reaction are summarised in Table S2.

Table S2. Amounts of $PhICl_2$, $CDCl_3$ and respective additive used.

Additive Name	**Amount of $PhICl_2$**	**Amount of $CDCl_3$**	**Amount of additive**
None	100 mg	1 mL	0 mg
Pyridine	50 mg	2 mL	2.9 µL
Pyridine.HCl	50 mg	1 mL	4.2 mg
Pyridine.HOTf	25 mg	1 mL	4.2 mg
NBu_4Cl	25 mg	2 mL	5 mg
$HCl.Et_2O$	100 mg	4 mL	36 µL
NBu_4OTf	25 mg	1 mL	7.12 mg
LiCl	100 mg	4 mL	3.1 mg

iv. BindFit NMR titrations procedure

$PhICl_2$ was dissolved in $CDCl_3$ to form a stock solution. Aliquots (600 µL) of stock solution were then transferred to six different vials. To each vial, amount of additive corresponding to 1, 2, 3, 4, 5 and 10 equivalents was added. The reaction mixtures were taken for NMR analysis. The concentration of $PhICl_2$ for each reaction was calculated by comparing ratio of $PhICl_2$ and PhI by NMR integration with actual concentration of stock solution. The corresponding amounts of all components used for each manipulation are summarised in Table S3 and Table S4 for NBu_4Cl and NBu_4OTf, respectively. The data obtained from NMR investigation was processed using BindFit[2] to calculate the binding constant.

Table S3. Amounts of components involved in $PhICl_2$-NBu_4Cl BindFit experiment.

Stock Solution Concentration: 0.036M $PhICl_2$ in $CDCl_3$					
NMR Tube no.	$PhICl_2$ equivalent	NBu_4Cl equivalent	NBu_4Cl (mg)	NBu_4Cl Concentration (M)	$PhICl_2$ Concentration (M)
1	1	1	6.1	0.037	0.022
2	1	2	12.2	0.074	0.020
3	1	3	18.3	0.111	0.014
4	1	4	24.4	0.148	0.015
5	1	5	30.5	0.185	0.016
6	1	10	60.6	0.370	0.006

Table S4. Amounts of components involved in $PhICl_2$-NBu_4OTf BindFit experiment.

Stock Solution Concentration: 0.023M $PhICl_2$ in $CDCl_3$					
NMR Tube no.	$PhICl_2$ equivalent	NBu_4OTf equivalent	NBu_4OTf (mg)	NBu_4OTf Concentration (M)	$PhICl_2$ Concentration (M)
1	1	1	5.3	0.023	0.023
2	1	2	10.6	0.045	0.023
3	1	3	15.9	0.068	0.023
4	1	4	21.2	0.091	0.023
5	1	5	26.5	0.114	0.023
6	1	10	53.0	0.227	0.023

v. Electrochemical procedure

An electrochemical cell was set-up using a CH instruments 660E potentiostat, using a GC electrode as the working, Au wire as auxiliary, and an Ag/Ag^+ reference electrode was sheathed with an internal solution of 0.1 M $TBAPF_6$. The electrolyte solutions were prepared under an inert atmosphere to minimise the amount of water and oxygen in the solution.

The GC electrode was cleaned prior with acetone and ethanol washes, and polished using 0.3 μm alumina. The Au wire was cleaned prior to use with acetone and ethanol washes and sanded back with P3000 silicon carbide sandpaper. Each experiment contained 1 ml of 0.1 M $TBAPF_6$ electrolyte, with 1.5 mM of $PhICl_2$. Potentials were scanned between -3 V to +4 V to determine electroactive working window, and 0 to -3 V for observing reductions of $PhICl_2$ at 200 mV/s. To calibrate the redox potentials, ferrocene was added and $Ep^{1/2}$ determined for Fc/Fc^+ for each experiment.

III. NMR Investigations

(a = $PhICl_2$, b = PhI, c = Anisole, d = 4-Chloroanisole, e = 2-chloroanisole, f = corresponding pyridinium chloride)

i. Conversion of anisole to p-chloroanisole

a. $PhICl_2$ only

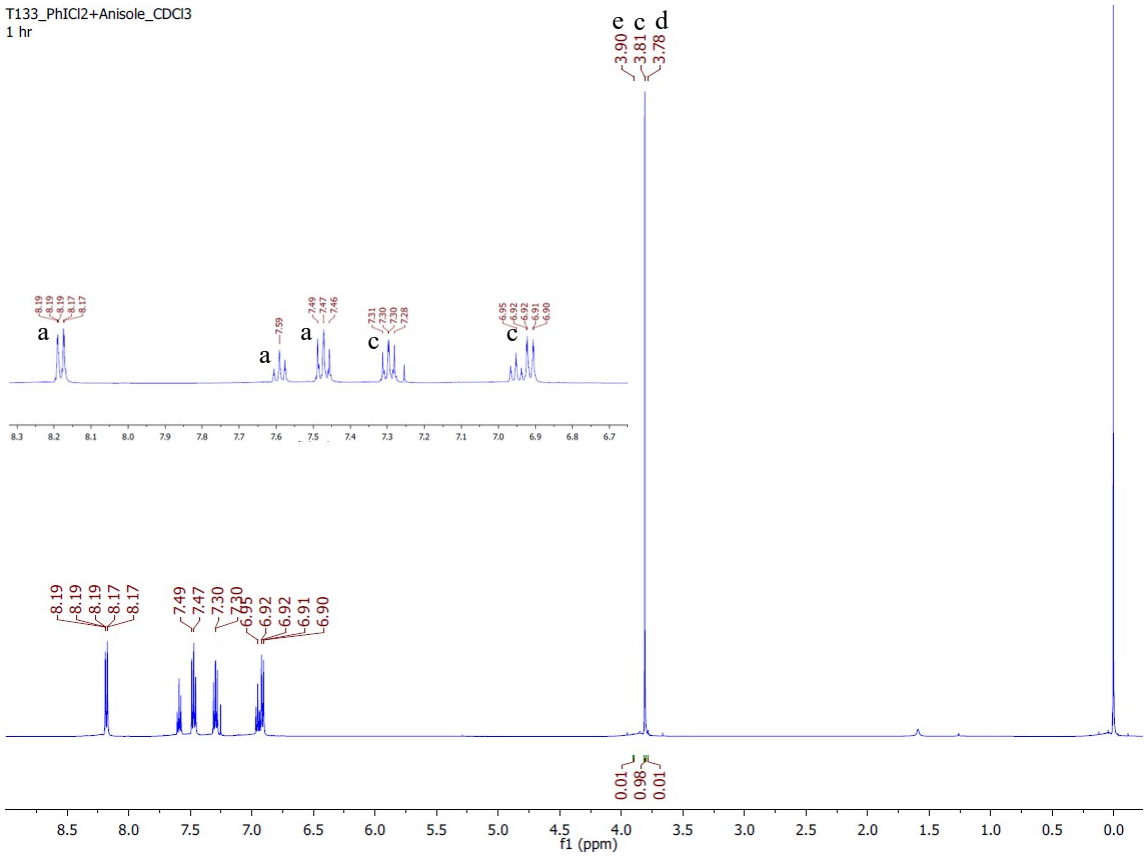


Figure S1. ^1H NMR spectrum of $PhICl_2$ and anisole at t = 1 hour in $CDCl_3$.

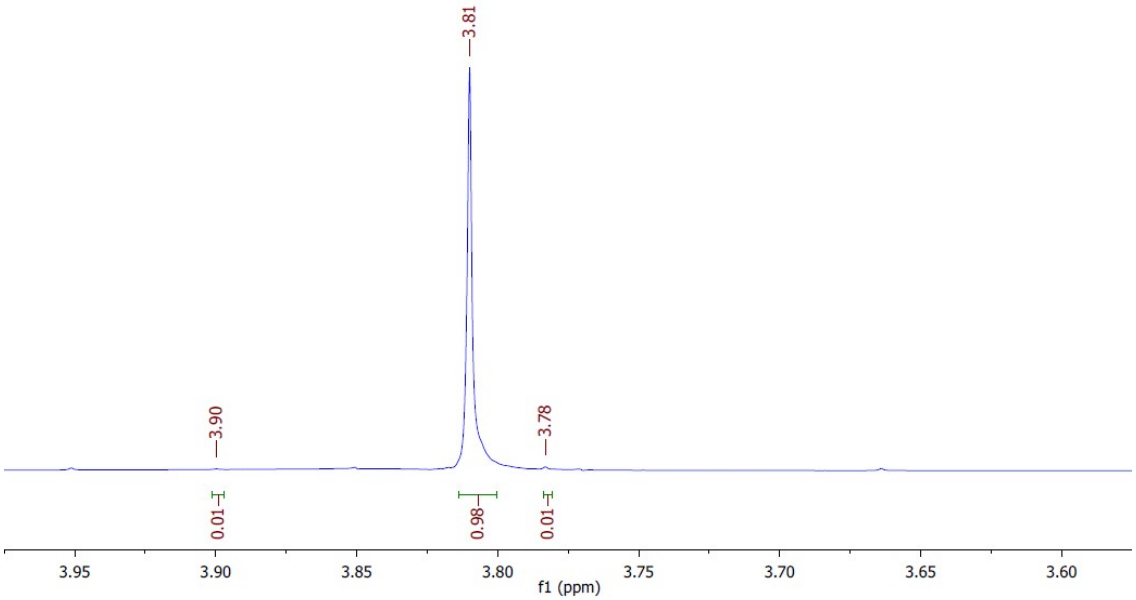


Figure S2. ^{1}H NMR spectrum of $PhICl_2$ and anisole at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

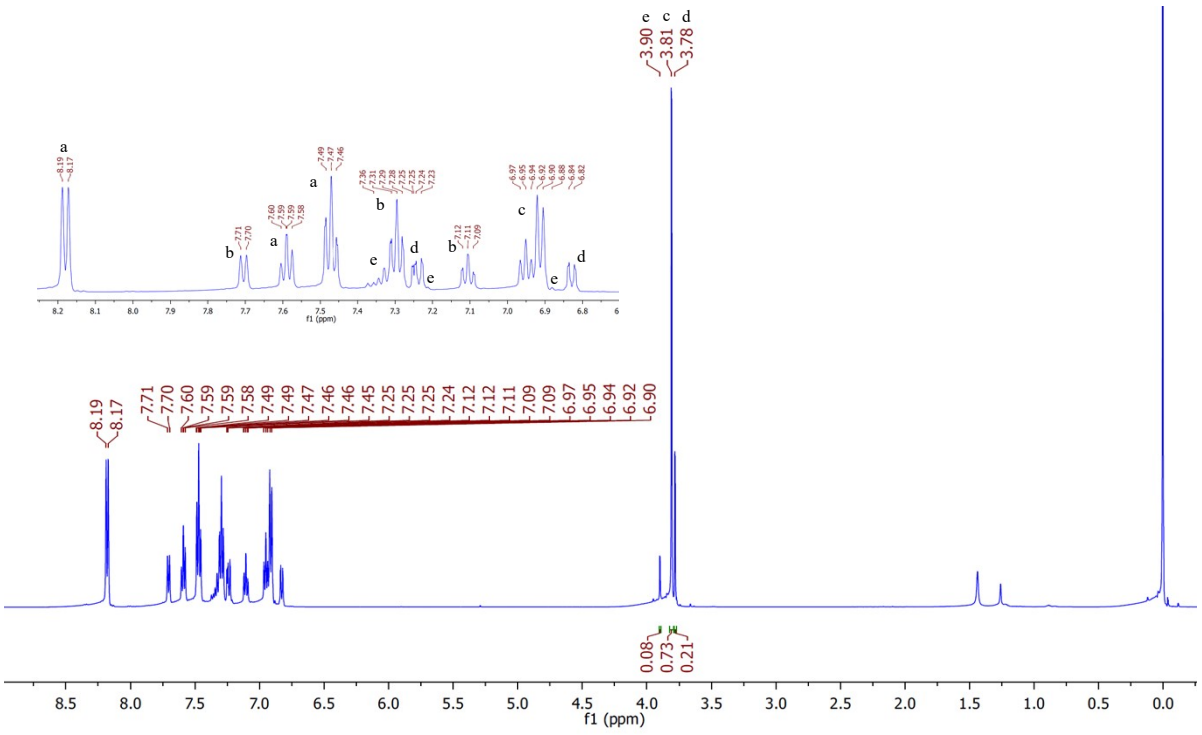


Figure S3. ^{1}H NMR spectrum of $PhICl_2$ and anisole at t = 20 hours in $CDCl_3$.

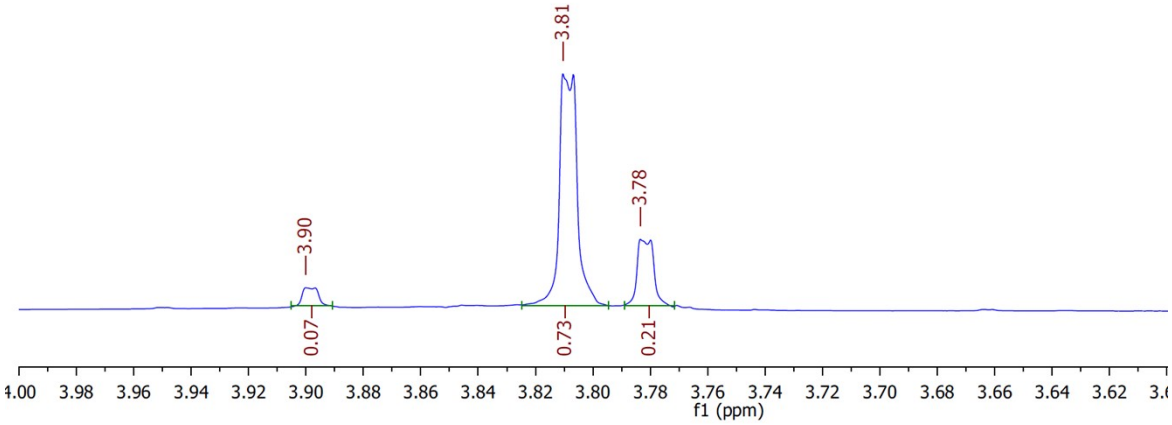


Figure S4. ^{1}H NMR spectrum of $PhICl_2$ and anisole at t = 20 hours in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

b. $PhICl_2$ + Pyridine (20%)

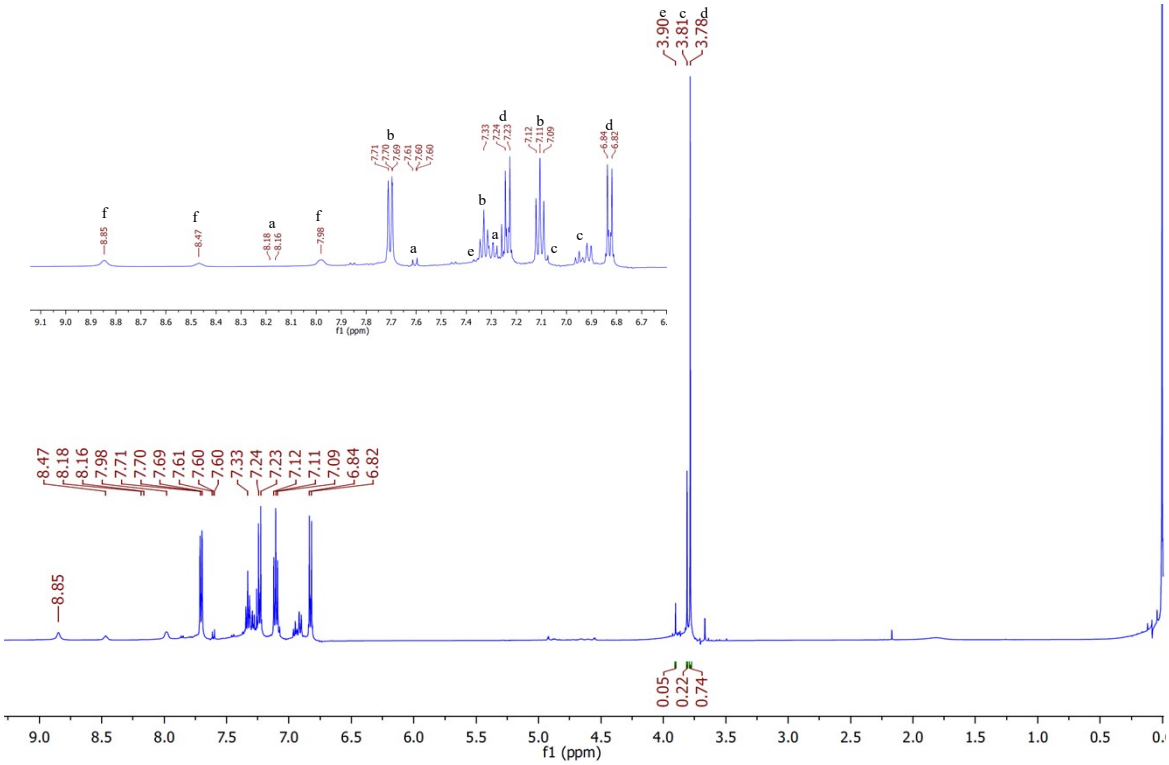


Figure S5. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% pyridine at t = 1 hour in $CDCl_3$.

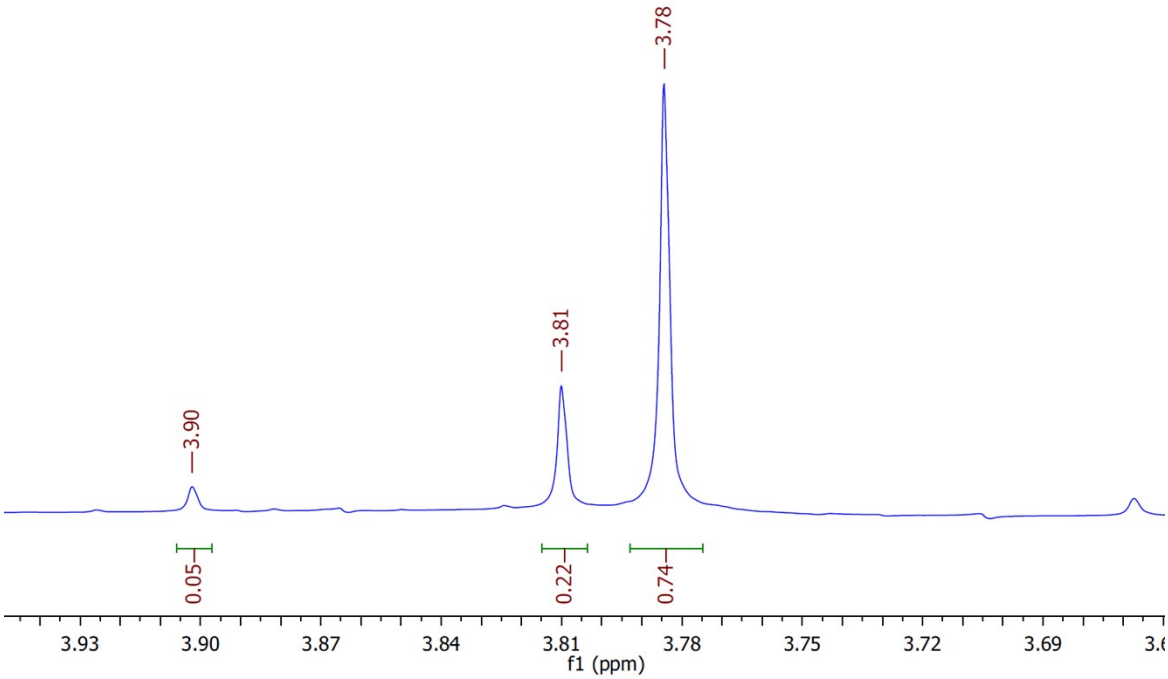


Figure S6. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% pyridine at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

c. $PhICl_2$ + Pyridine.HCl (20%)

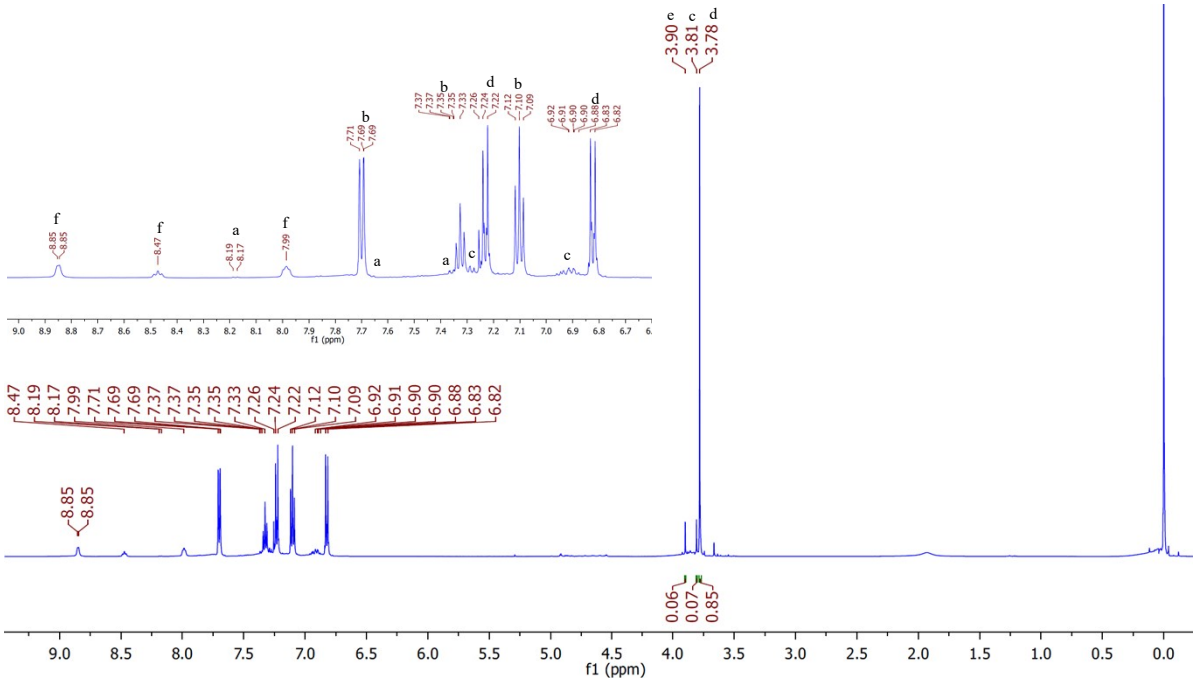


Figure S7. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% pyridine.HCl at t = 1 hour in $CDCl_3$.

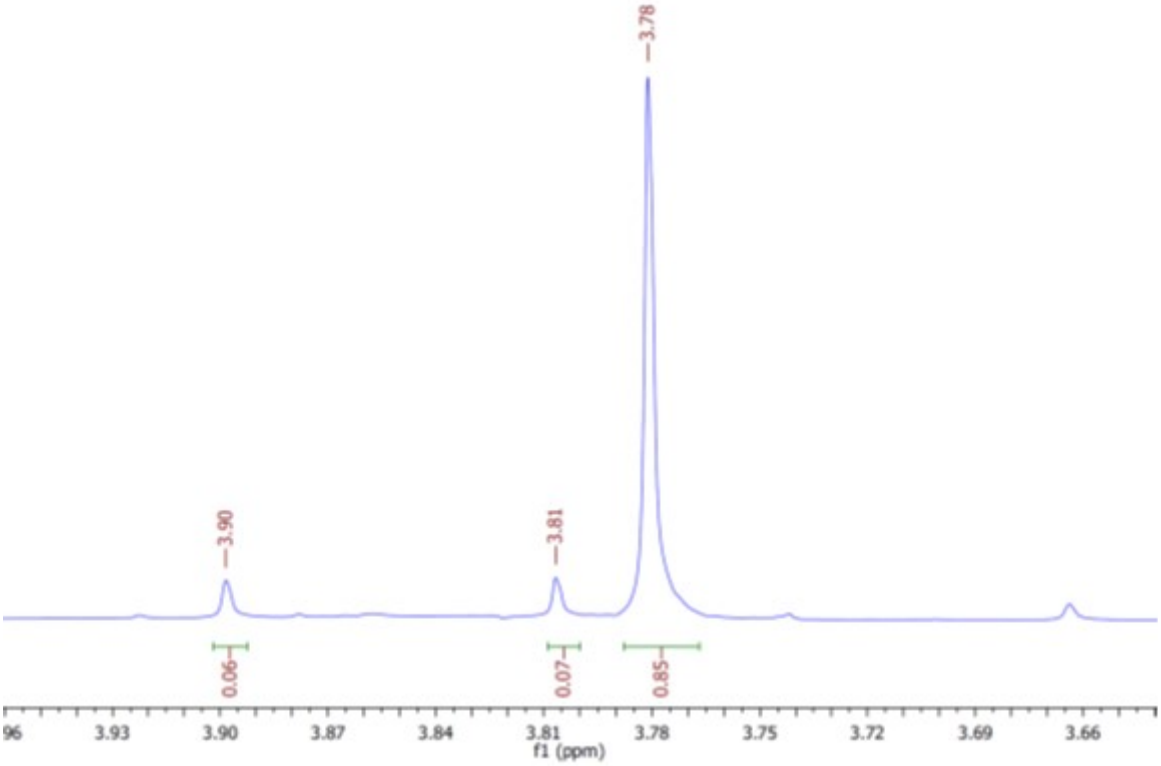


Figure S8. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% pyridine.HCl at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

d. $PhICl_2$ + Pyridine.HOTf (20%)

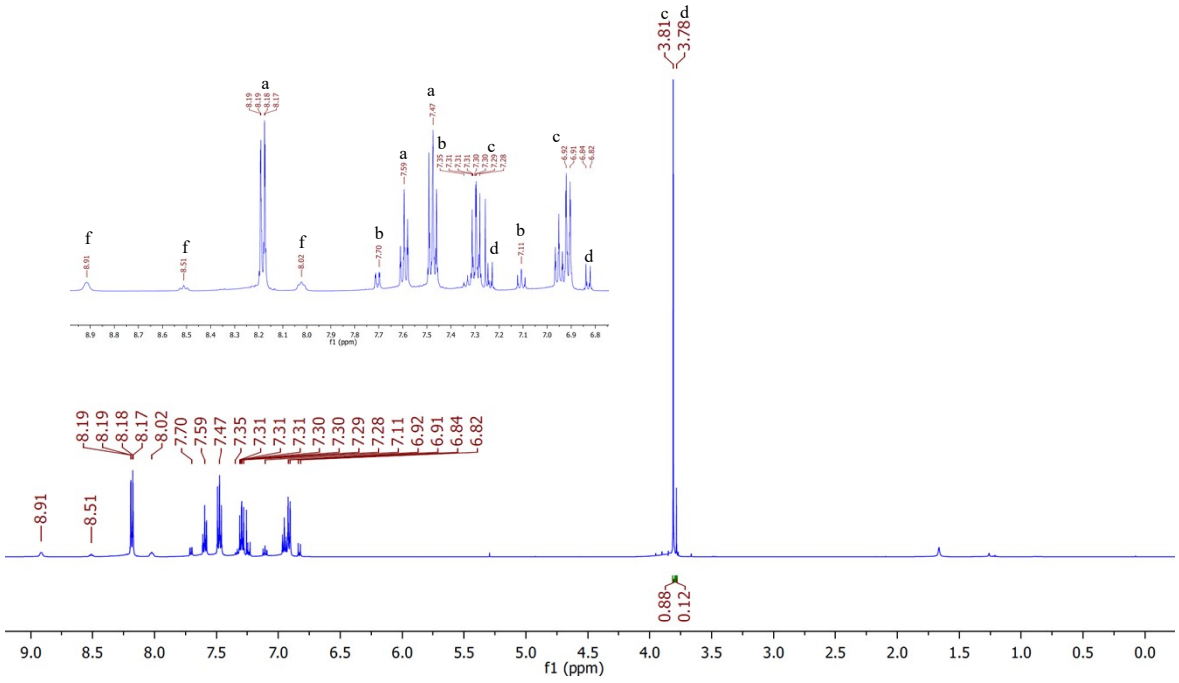


Figure S9. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% pyridine.HOTf at t = 1 hour in $CDCl_3$.

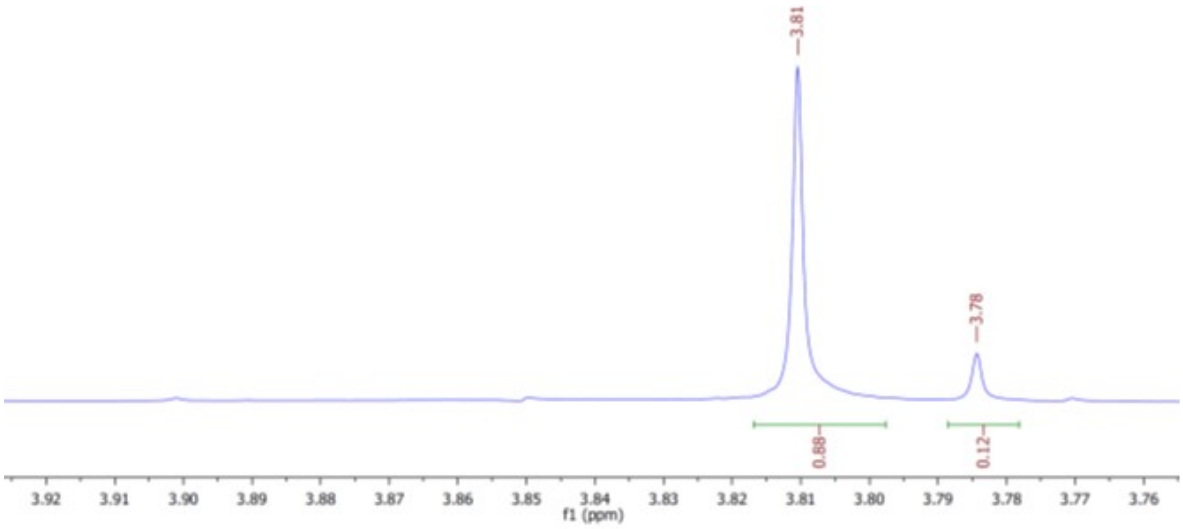


Figure S10. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% pyridine.HOTf at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

e. $PhICl_2$ + Pyridine.HOTf (50%)

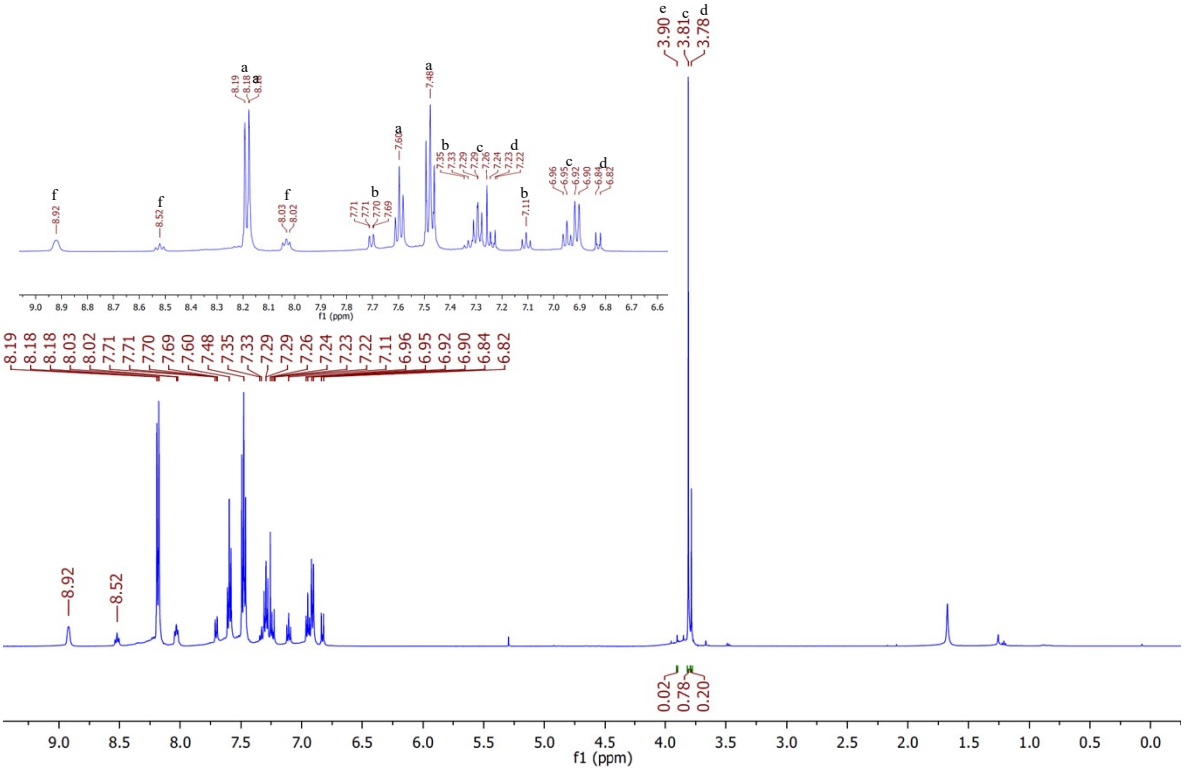


Figure S11. ^{1}H NMR spectrum of $PhICl_2$, anisole and 50% pyridine.HOTf at t = 1 hour in $CDCl_3$.

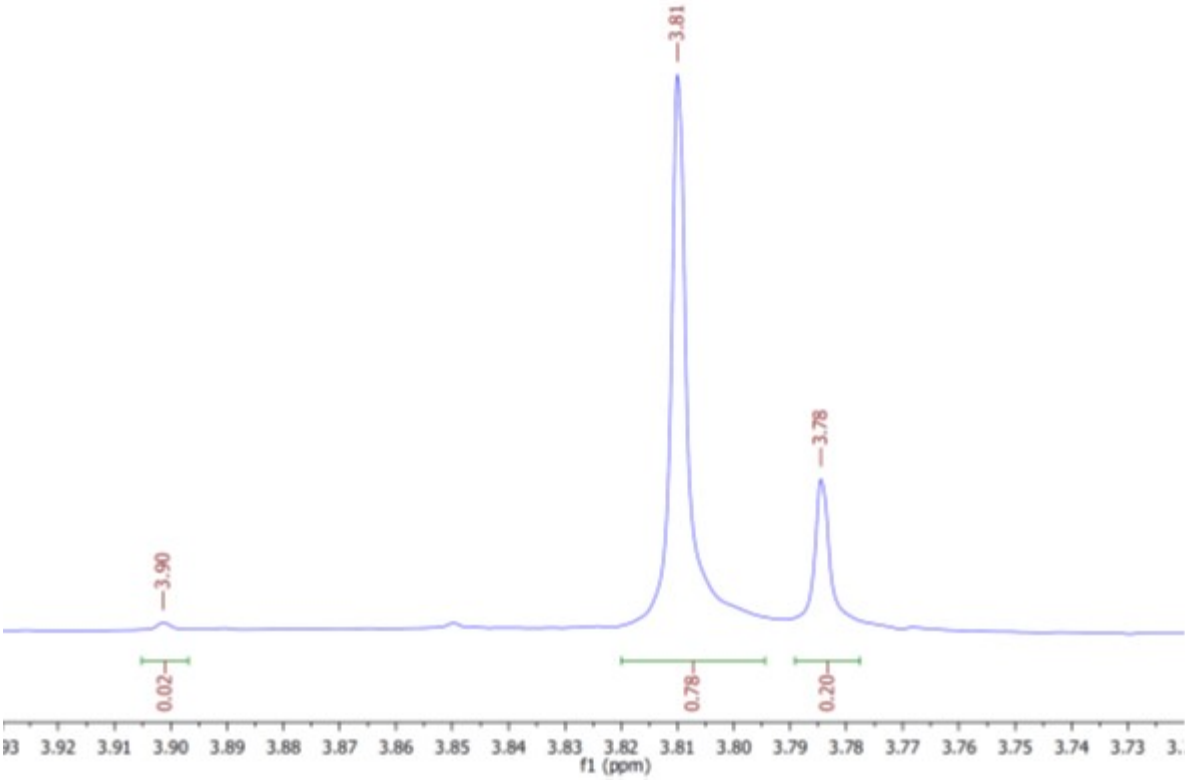


Figure S12. ^{1}H NMR spectrum of $PhICl_2$, anisole and 50% pyridine.HOTf at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

f. $PhICl_2$ + NBu_4Cl (20%)

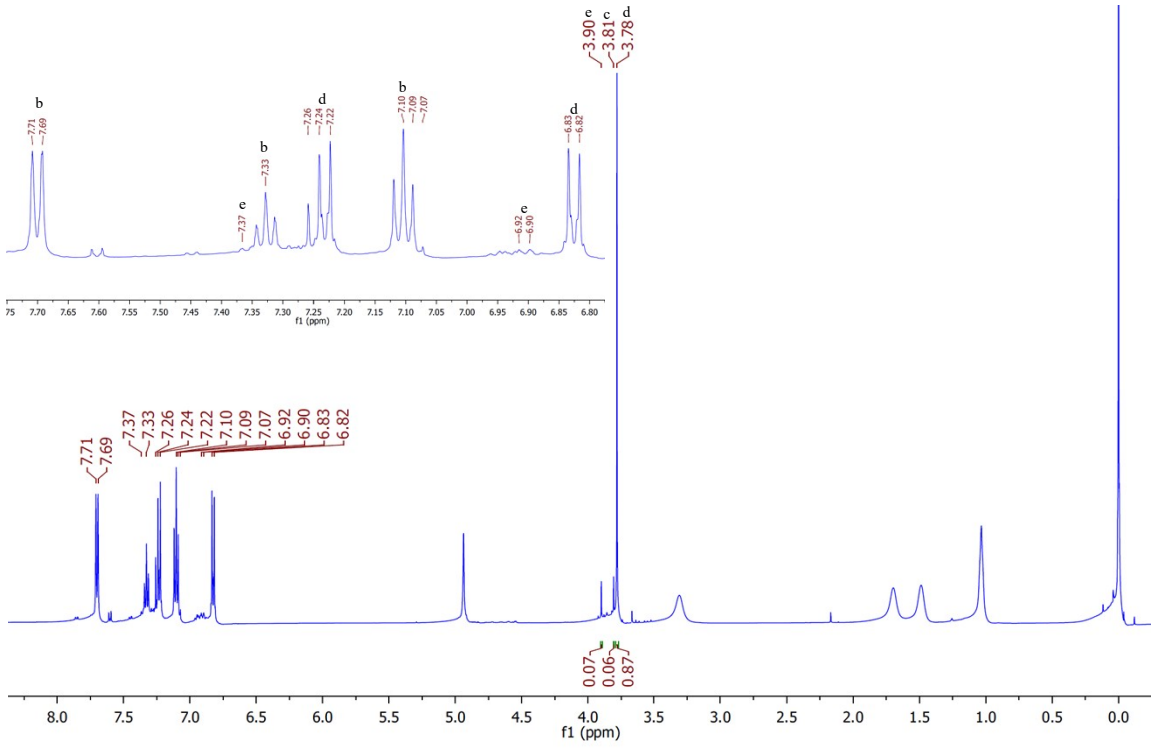


Figure S13. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% NBu_4Cl at t = 1 hour in $CDCl_3$.

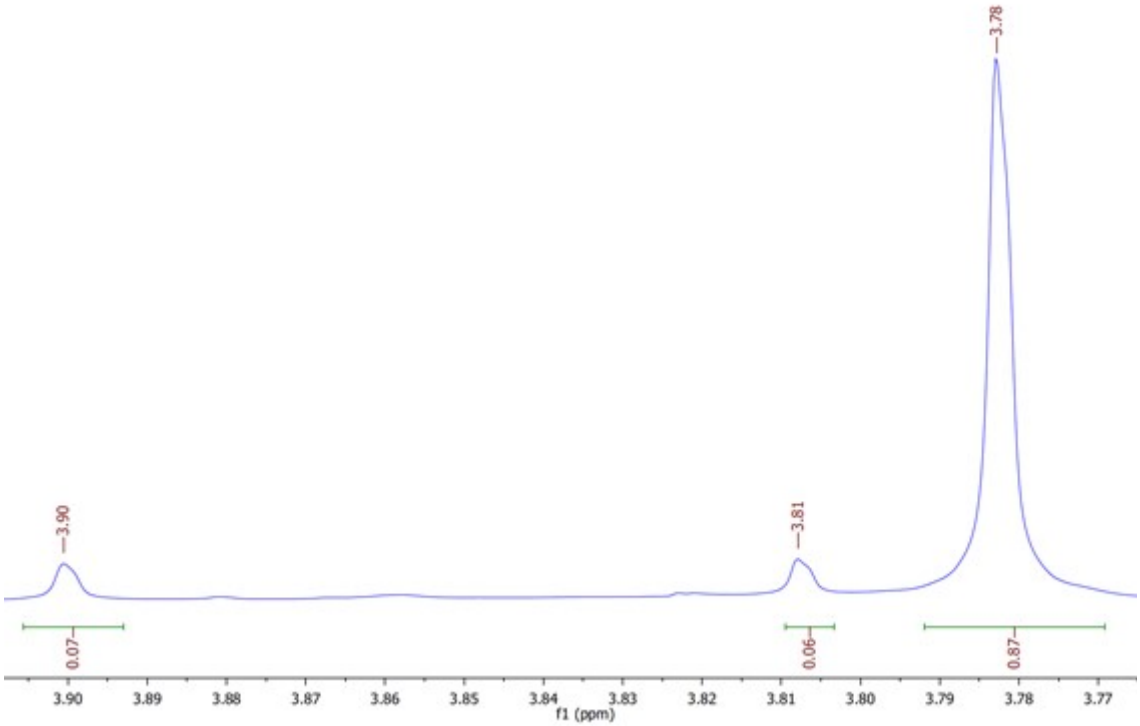


Figure S14. Methyl region ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% NBu_4Cl at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

g. $PhICl_2$ + $HCl.Et_2O$ (20%)

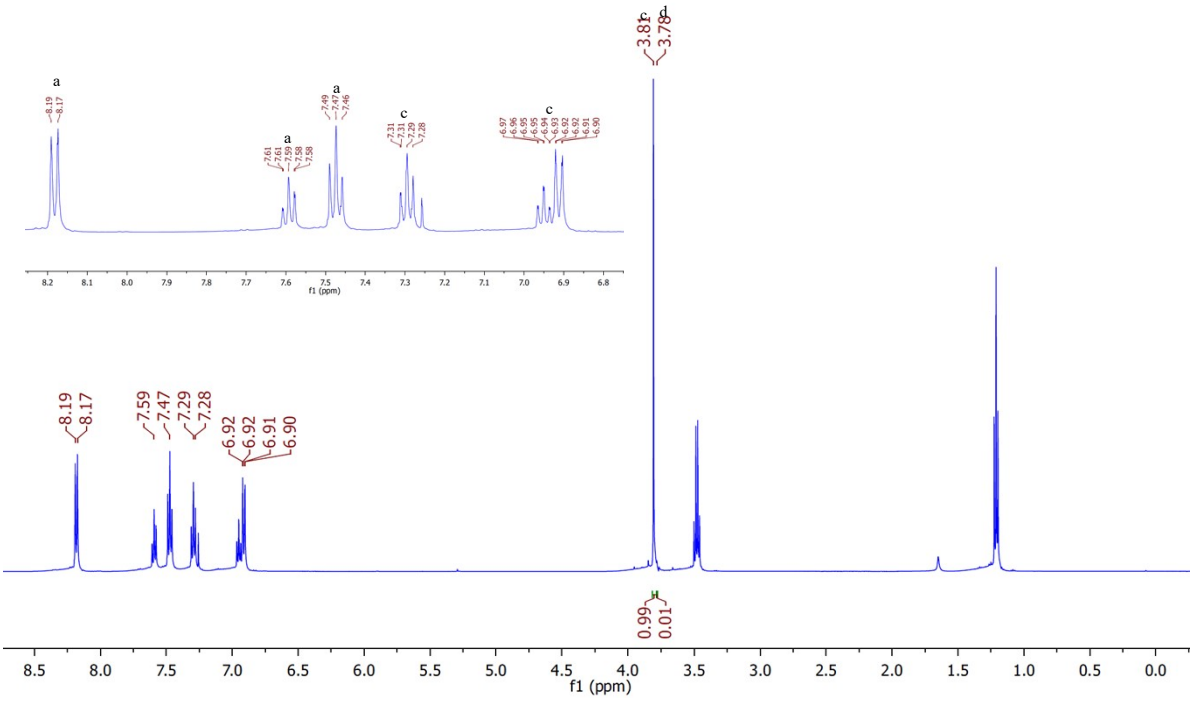


Figure S15. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% $HCl.Et_2O$ at t = 1 hour in $CDCl_3$.

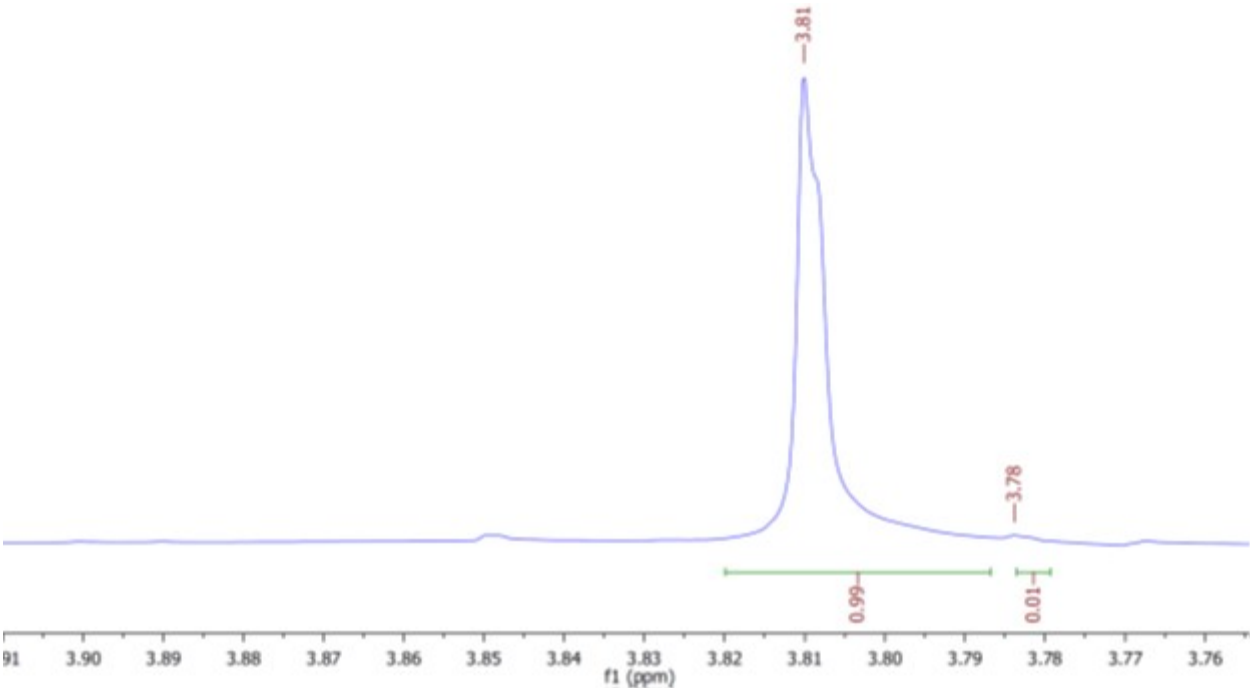


Figure S16. Methyl region ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% $HCl.Et_2O$ at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

h. $PhICl_2$ + NBu_4OTf (20%)

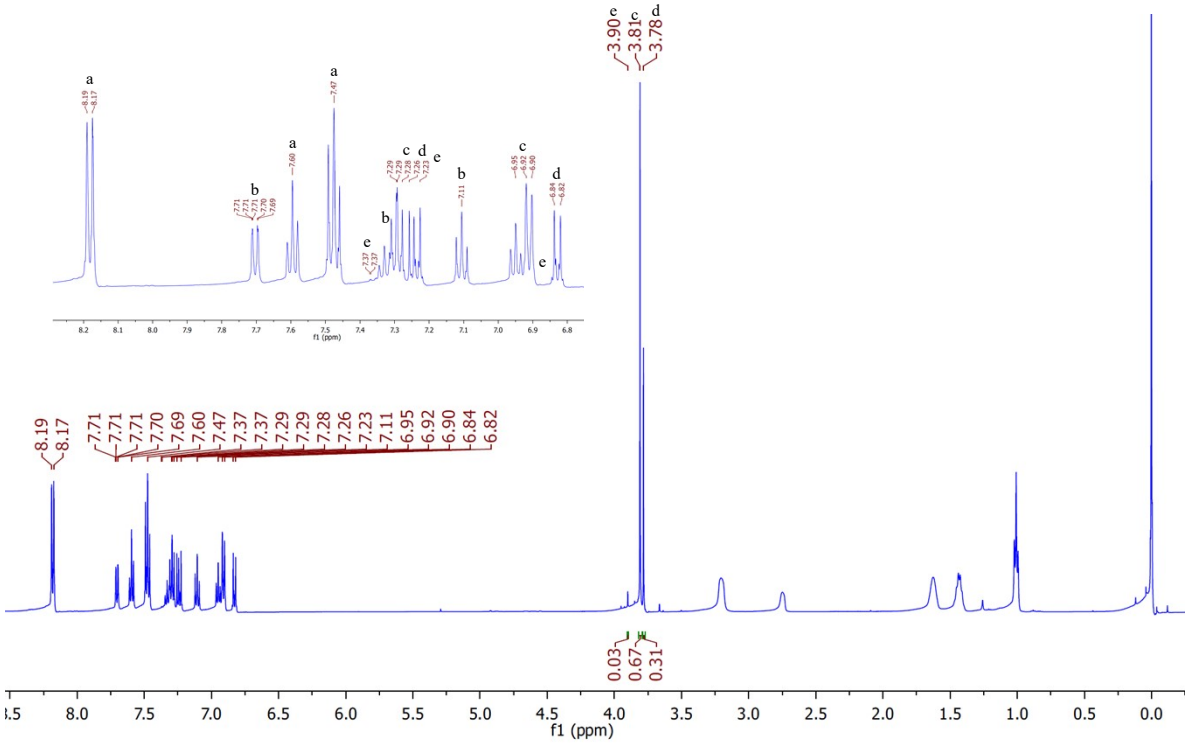


Figure S17. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% NBu_4OTf at t = 1 hour in $CDCl_3$.

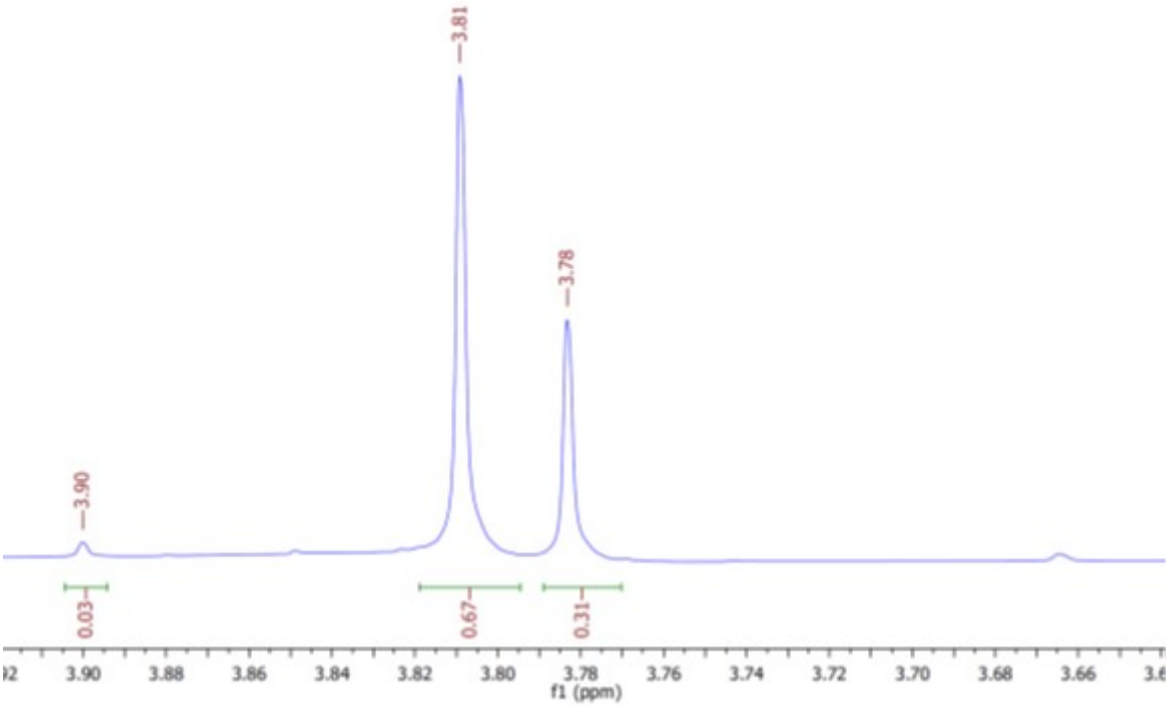


Figure S18. Methyl region ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% NBu_4OTf at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

i. $PhICl_2$ + 4-DMAP (20%)

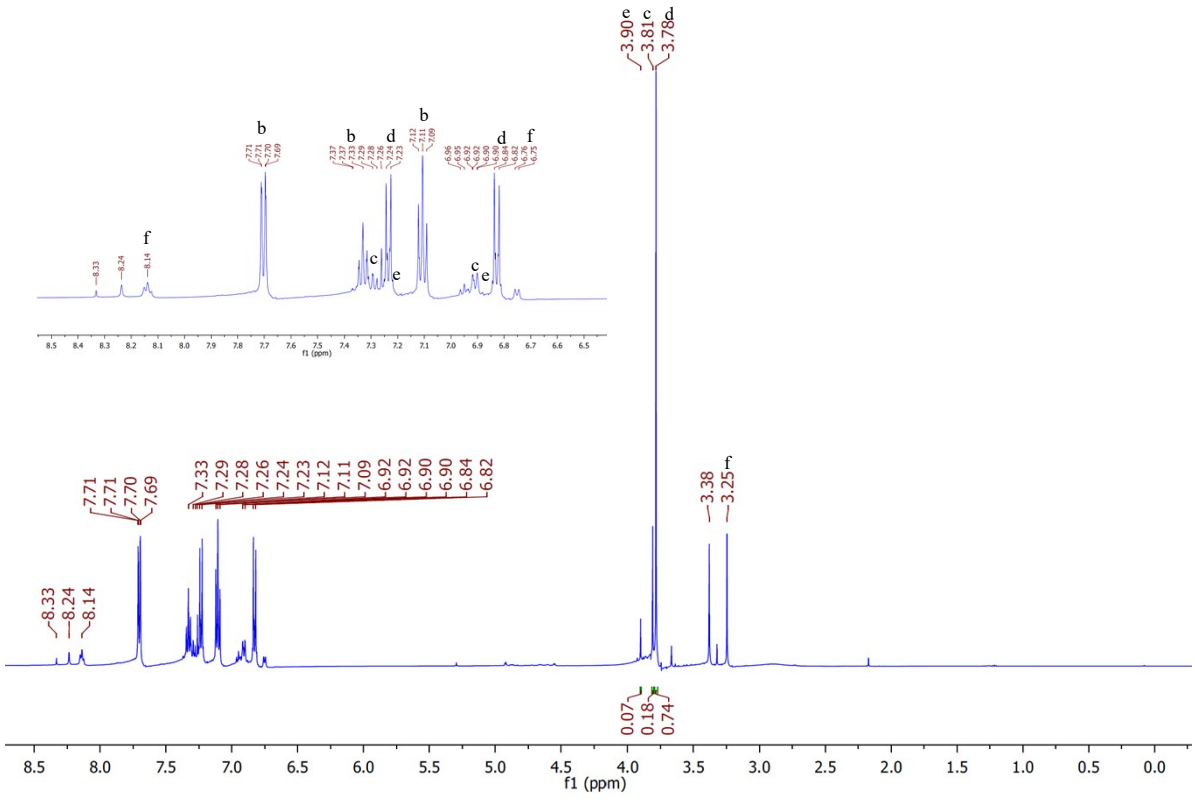


Figure S19. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% 4-DMAP at t = 1 hour in $CDCl_3$.

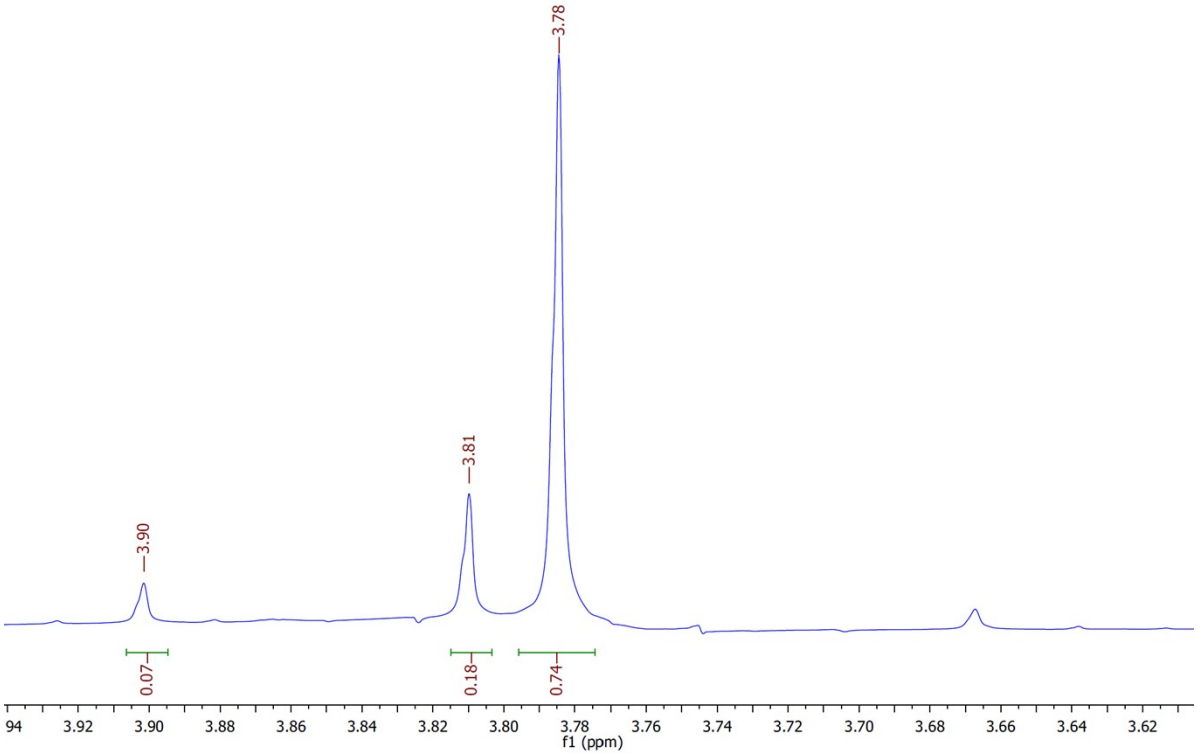


Figure S20. Methyl region ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% 4-DMAP at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

j. $PhICl_2$ + 4-DMAP.HCl (20%)

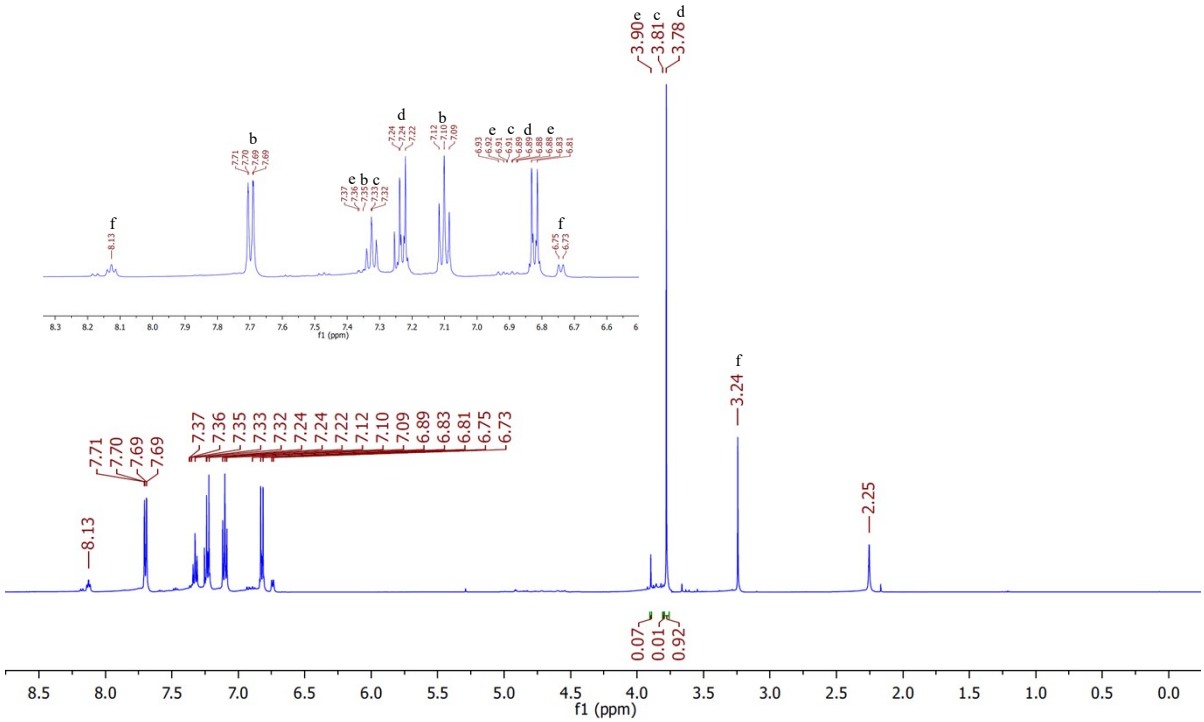


Figure S21. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% 4-DMAP.HCl at t = 1 hour in $CDCl_3$.

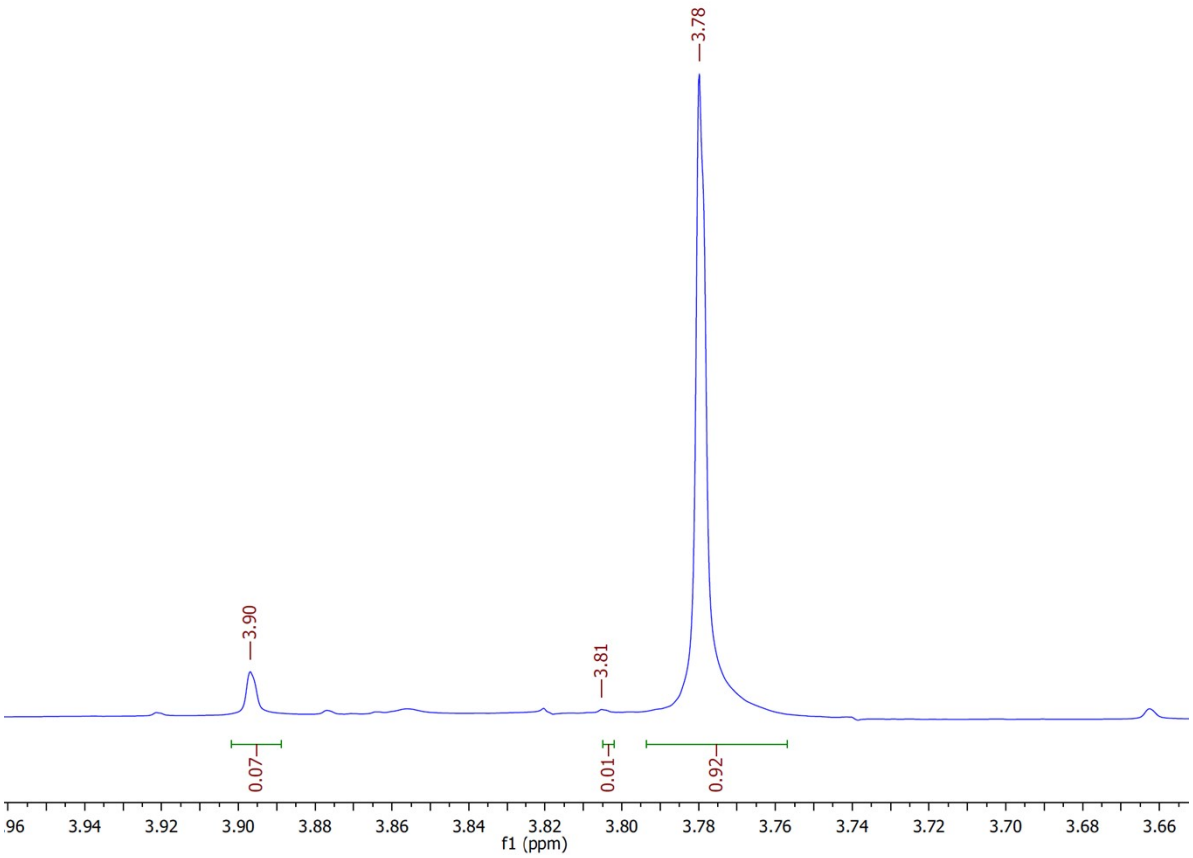


Figure S22. Methyl region ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% 4-DMAP.HCl at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

k. $PhICl_2$ + 4-DMAP.HOTf (20%)

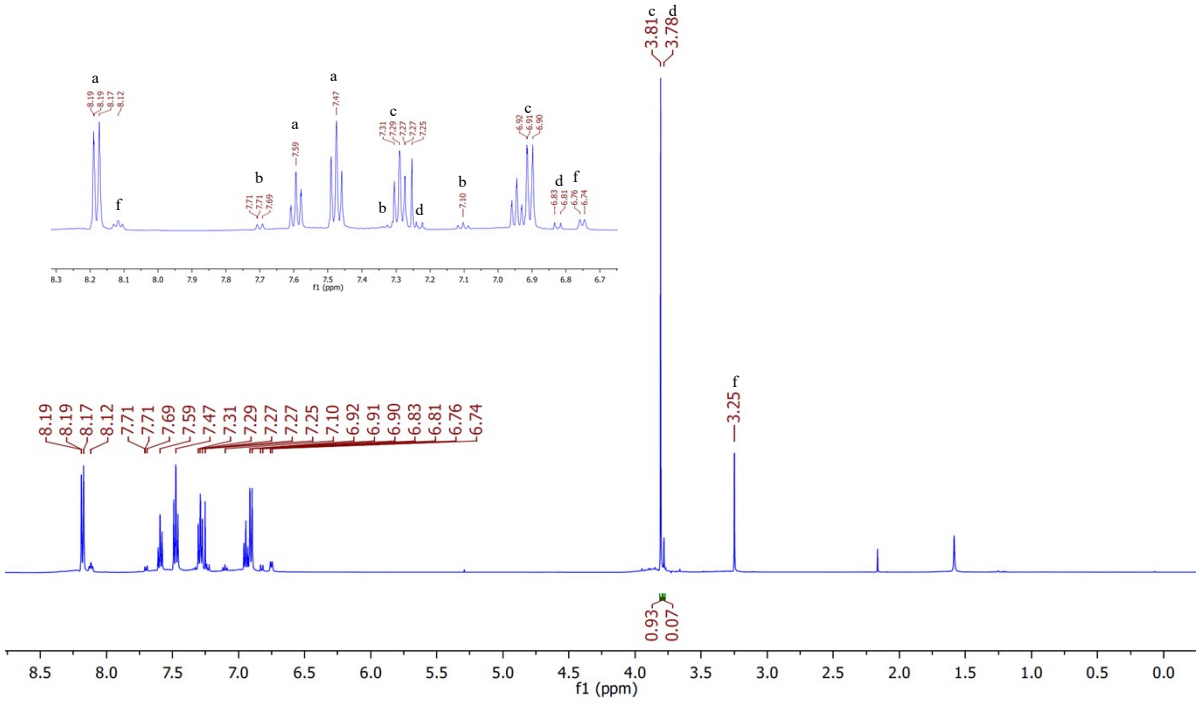


Figure S23. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% 4-DMAP.HOTf at t = 1 hour in $CDCl_3$.

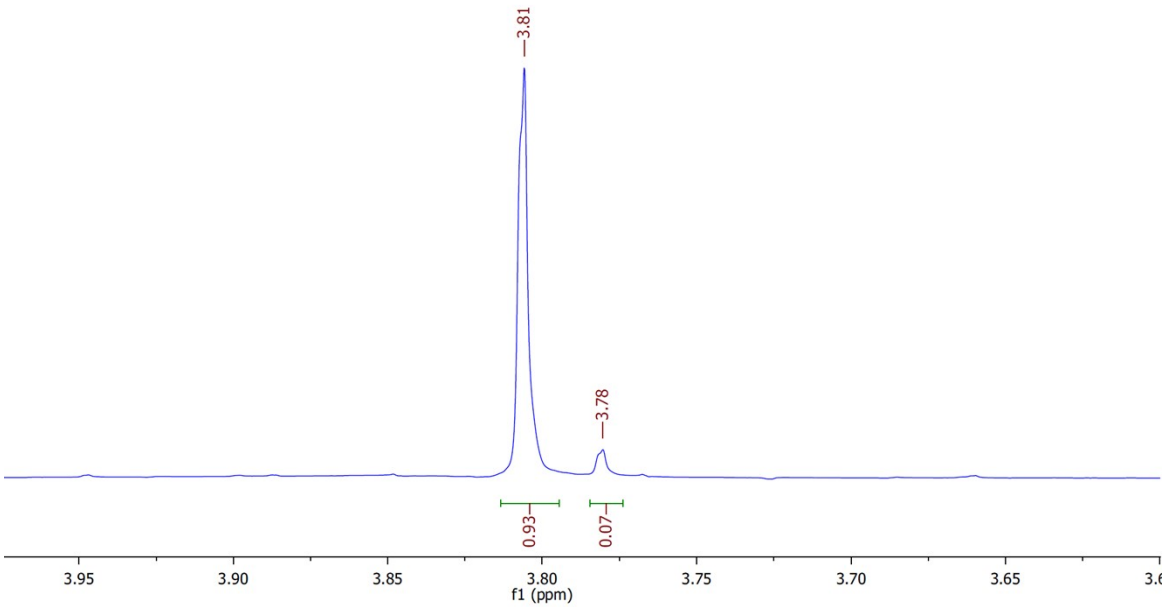


Figure S24. Methyl region ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% 4-DMAP.HOTf at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

l. $PhICl_2$ + 3-Cl-4-DMAP (20%)

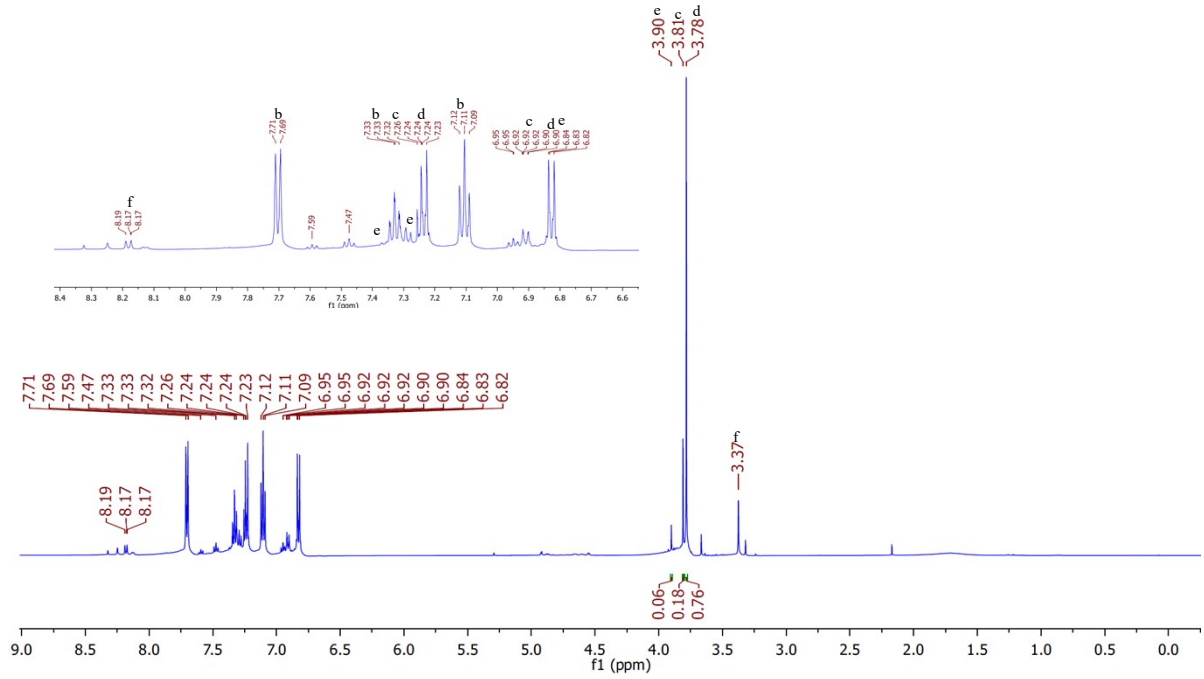


Figure S25. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% 3-Cl-4-DMAP at t = 1 hour in $CDCl_3$.

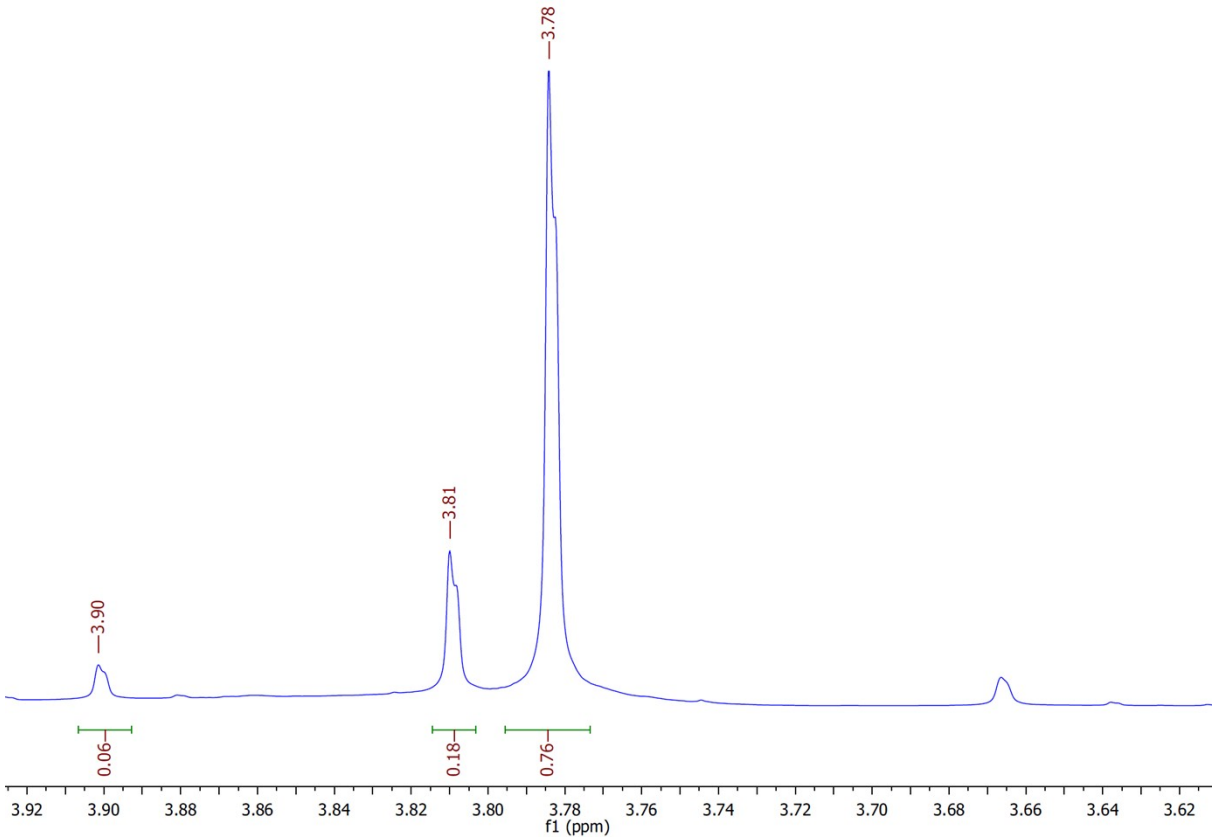


Figure S26. Methyl region ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% 3-Cl-4-DMAP at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

m. $PhICl_2$ + 3-Cl-4-DMAP.HCl (20%)

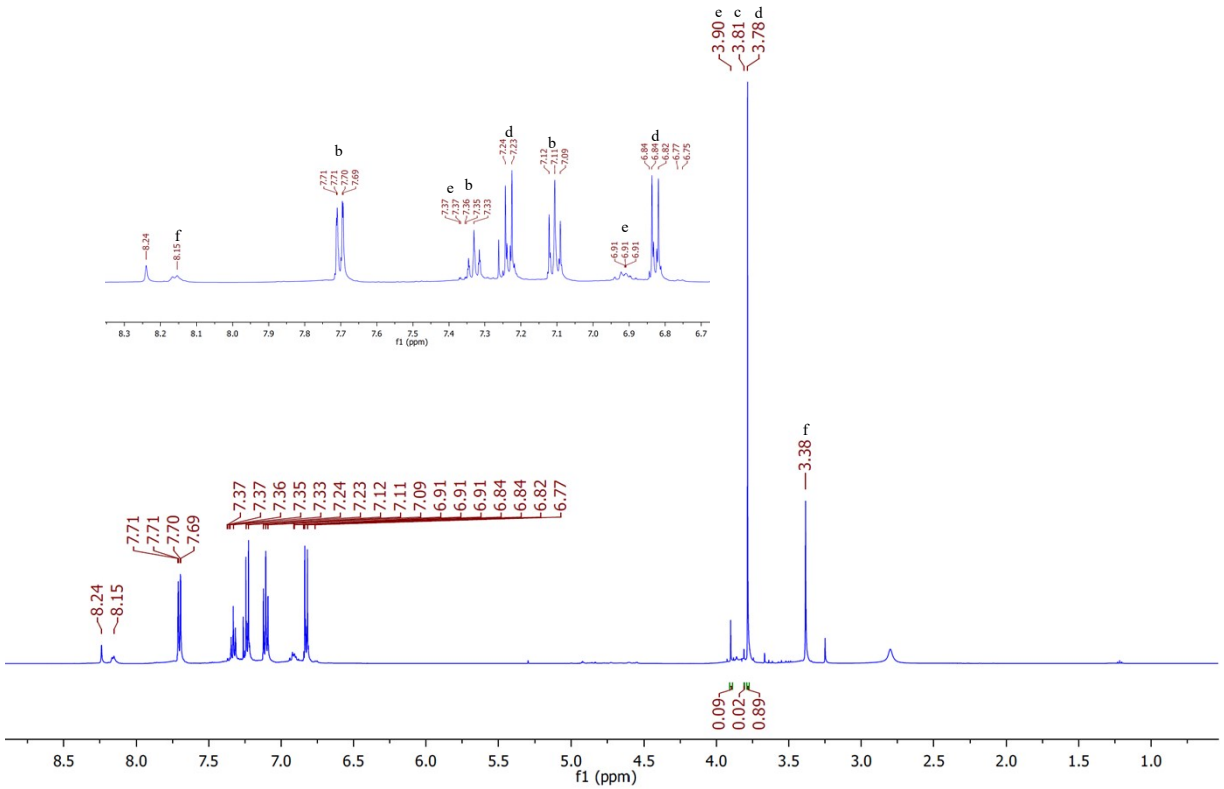


Figure S27. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% 3-Cl-4-DMAP.HCl at t = 1 hour in $CDCl_3$.

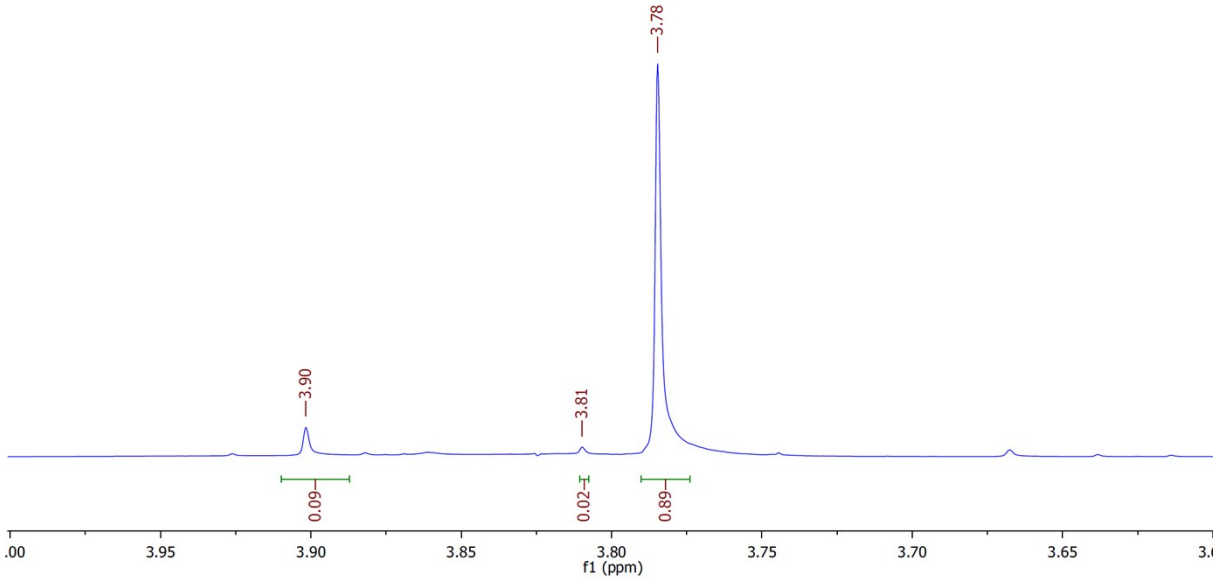


Figure S28. Methyl region ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% 3-Cl-4-DMAP.HCl at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

n. $PhICl_2$ + NBu_4Cl (5%)

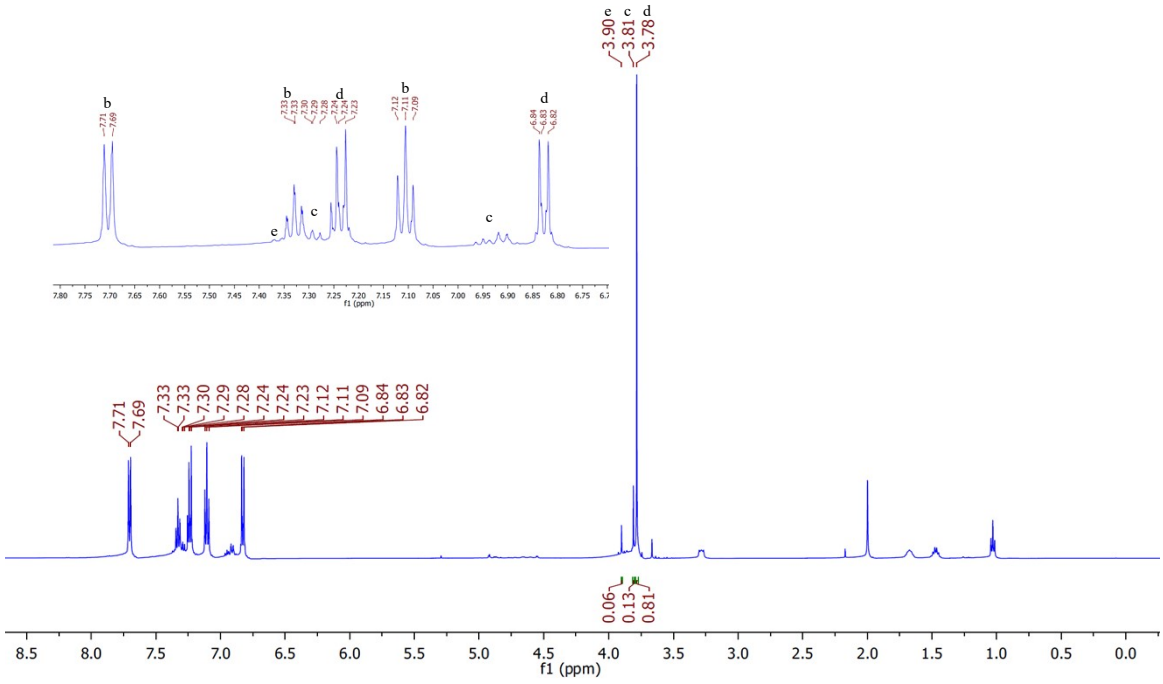


Figure S29. ^{1}H NMR spectrum of $PhICl_2$, anisole and 5% NBu_4Cl at t = 1 hour in $CDCl_3$.

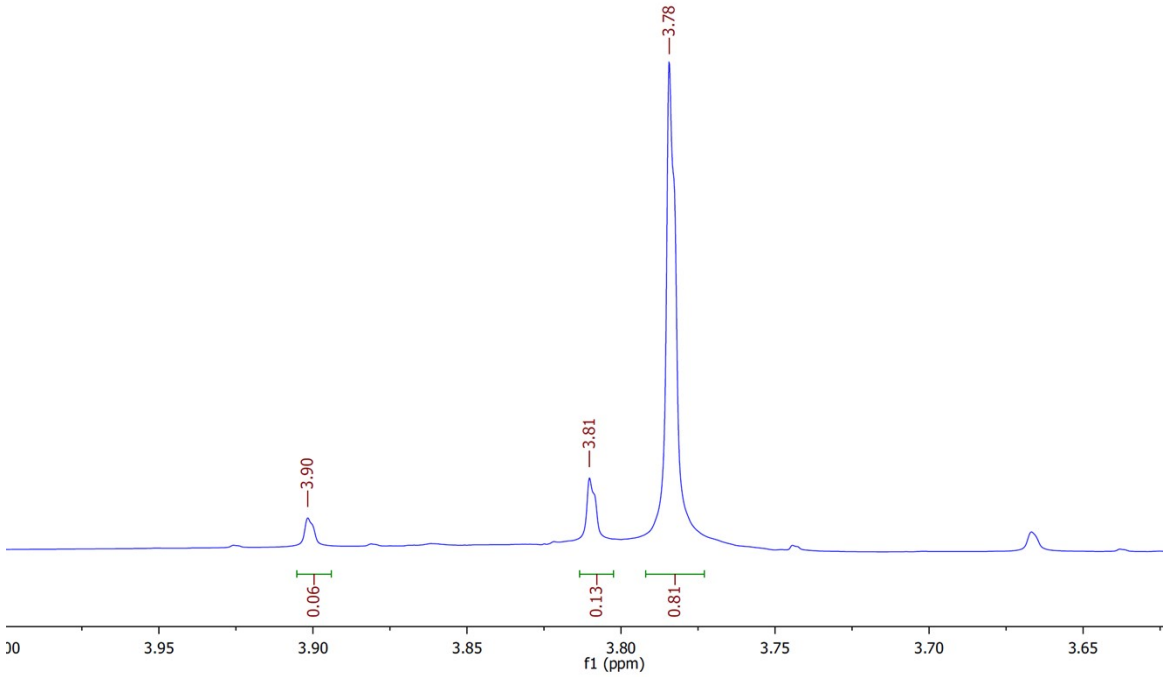


Figure S30. Methyl region ^{1}H NMR spectrum of $PhICl_2$, anisole and 5% NBu_4Cl at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

o. $PhICl_2$ + NaCl (20%)

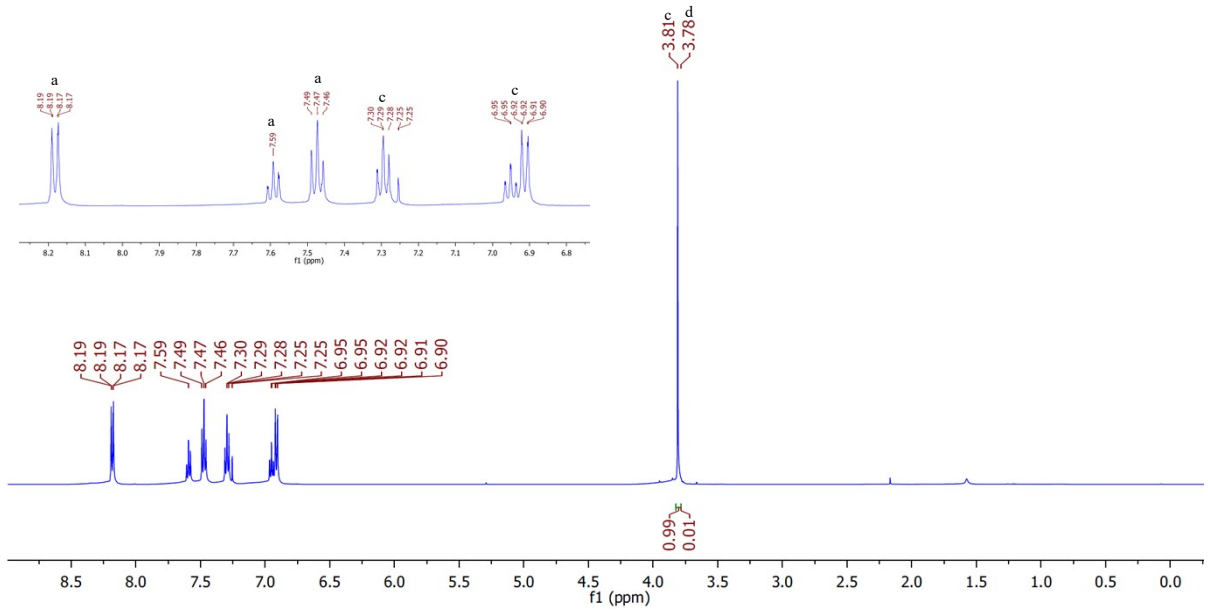


Figure S31. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% NaCl at t = 1 hour in $CDCl_3$.

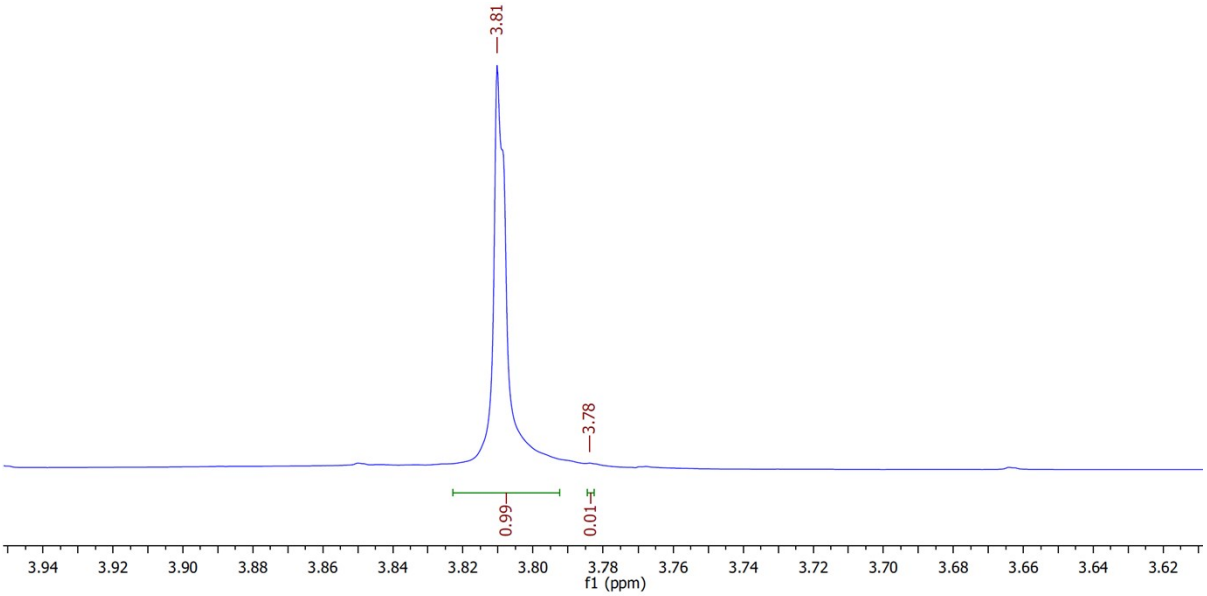


Figure S32. Methyl region ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% NaCl at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

p. $PhICl_2$ + LiCl (20%)

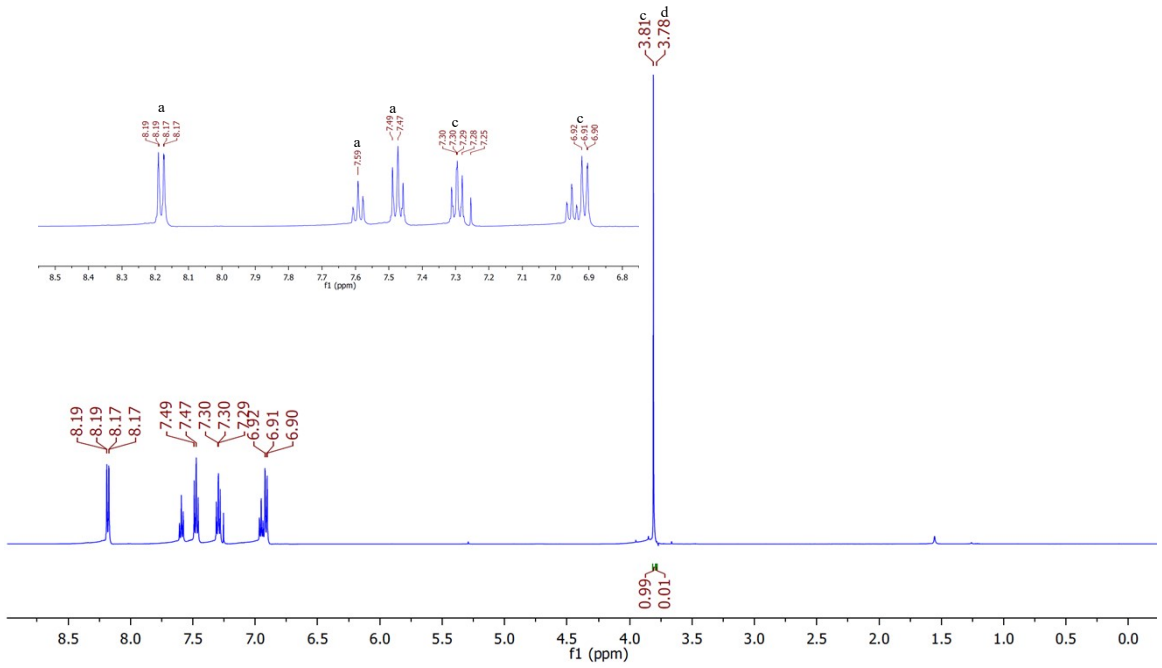


Figure S33. ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% LiCl at t = 1 hour in $CDCl_3$.

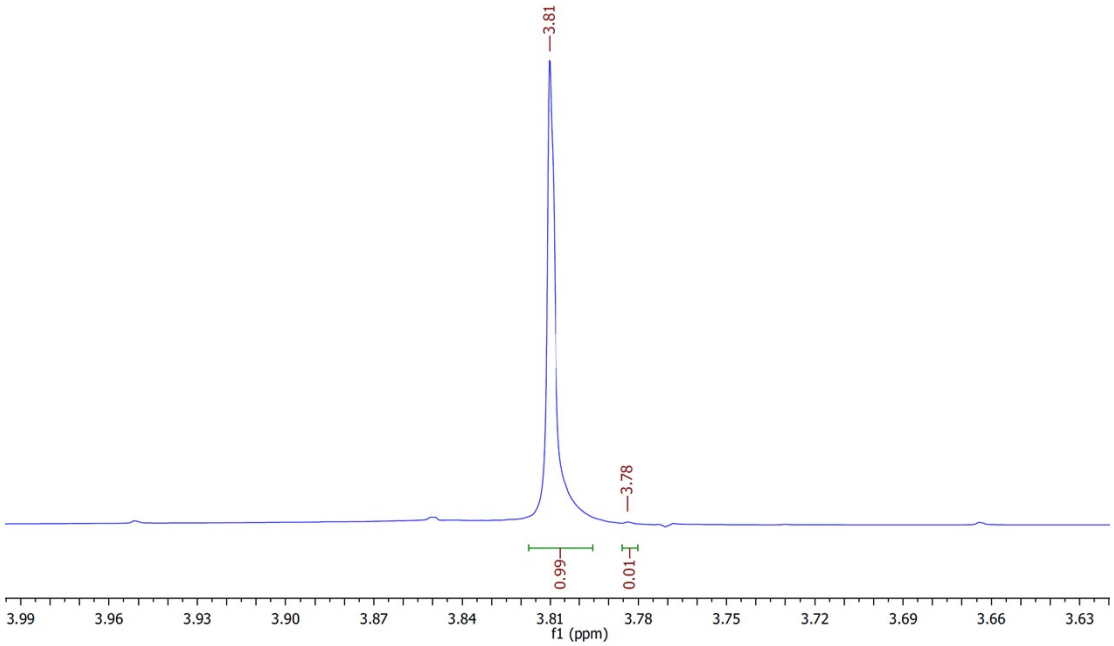


Figure S34. Methyl region ^{1}H NMR spectrum of $PhICl_2$, anisole and 20% LiCl at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

q. $PhICl_2$ + LiCl (50%)

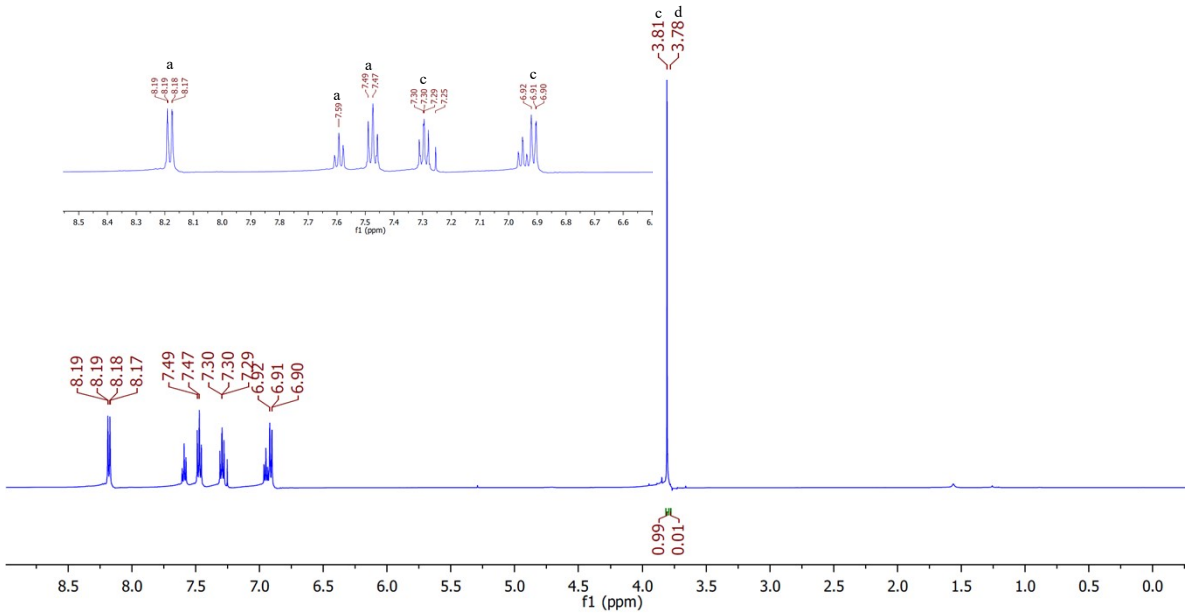


Figure S35. ^{1}H NMR spectrum of $PhICl_2$, anisole and 50% LiCl at t = 1 hour in $CDCl_3$.

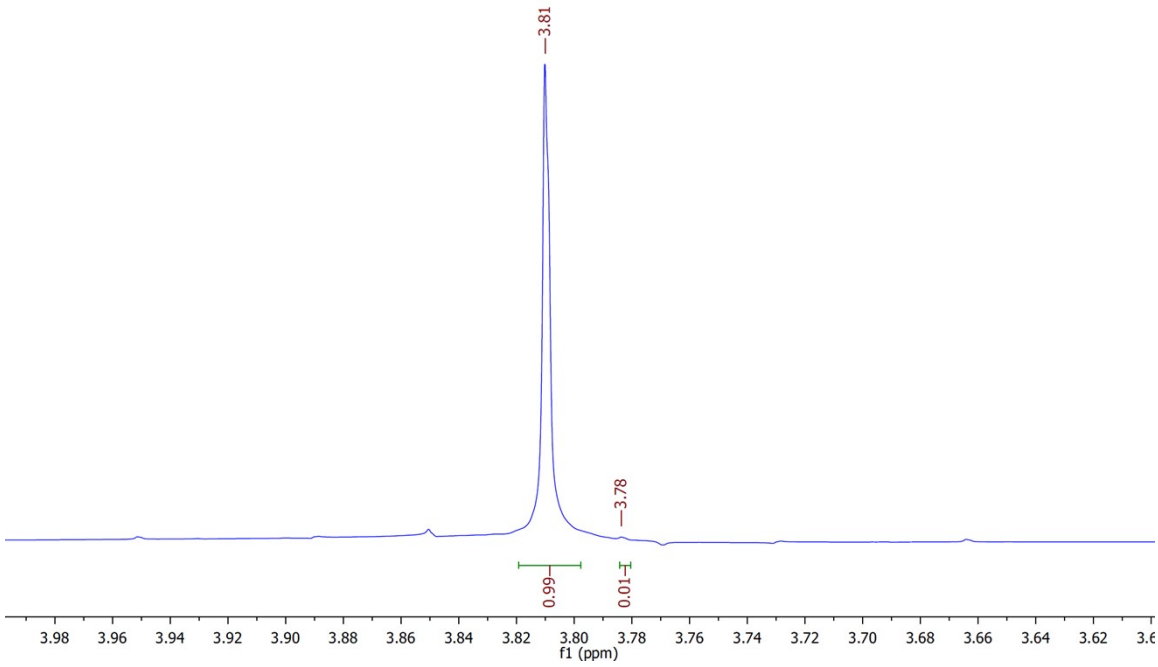


Figure S36. Methyl region ^{1}H NMR spectrum of $PhICl_2$, anisole and 50% LiCl at t = 1 hour in $CDCl_3$ showing normalised integrals for anisole methyl (3.81 ppm), 2-chloroanisole methyl (3.90 ppm) and 4-chloroanisole methyl (3.78 ppm) protons.

ii. Decomposition of $PhICl_2$

a. $PhICl_2$ only

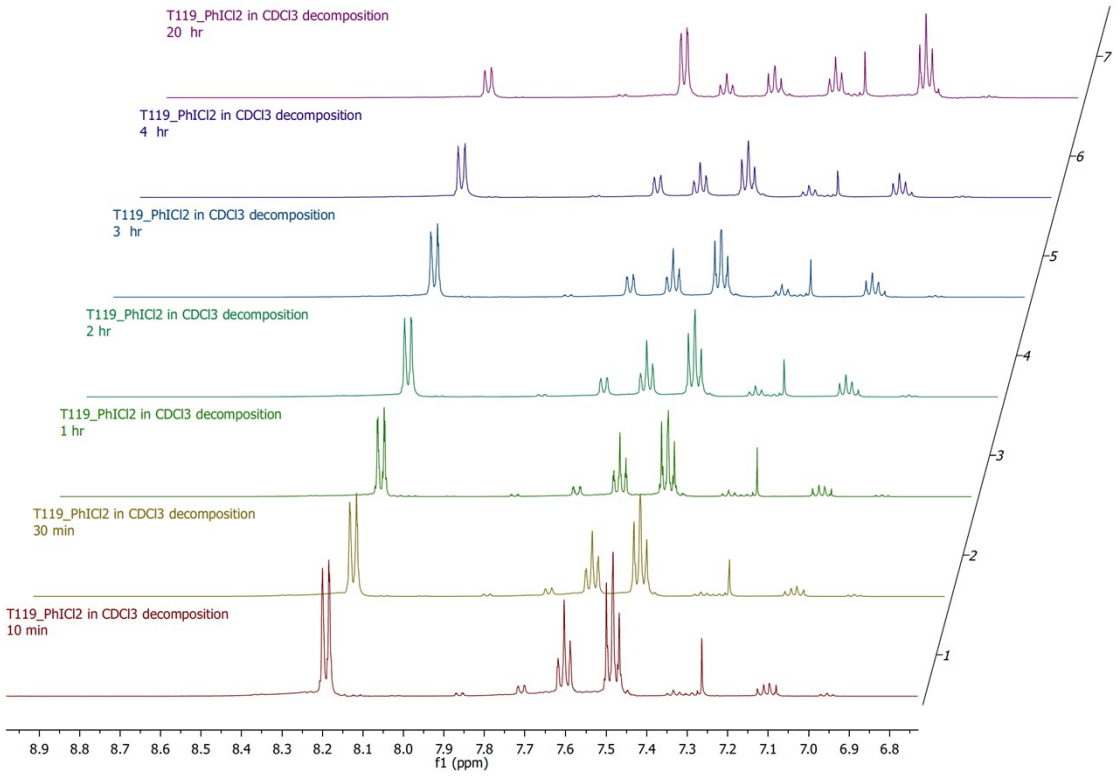


Figure S37. ^{1}H NMR spectra overlay for $PhICl_2$ in $CDCl_3$ at t = 10 min (red), 30 min (yellow), 1 hr (green), 2 hrs (cyan), 3 hrs (blue), 4 hrs (violet) and 20 hrs (magenta).

b. $PhICl_2$ + Pyridine (20%)

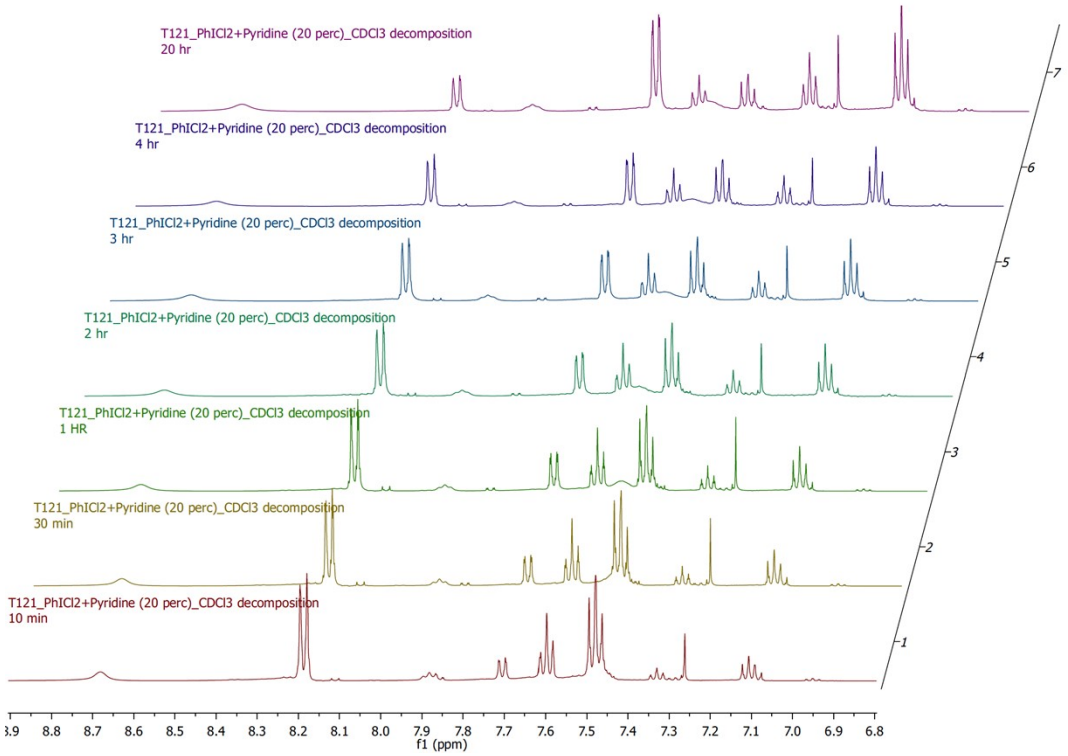


Figure S38. ^{1}H NMR spectra for $PhICl_2$ and 20% pyridine in $CDCl_3$ at t = 10 min (red), 30 min (yellow), 1 hr (green), 2 hrs (cyan), 3 hrs (blue), 4 hrs (violet) and 20 hrs (magenta).

c. $PhICl_2$ + Pyridine.HCl (20%)

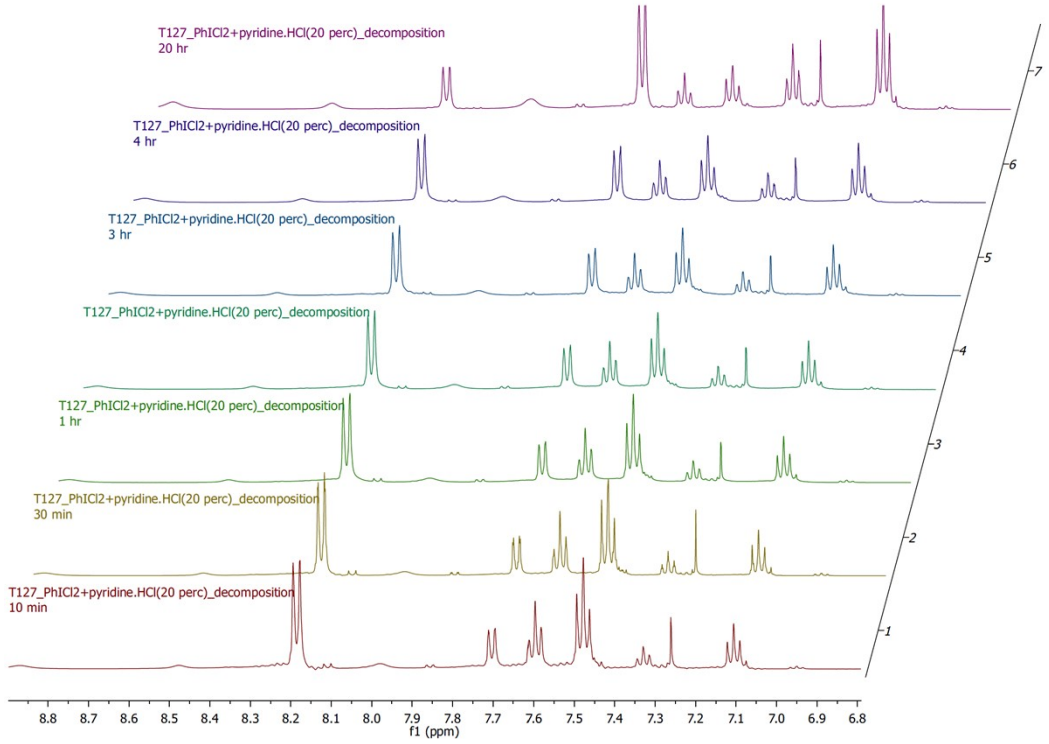


Figure S39. ^{1}H NMR spectra for $PhICl_2$ and 20% pyridine.HCl in $CDCl_3$ at t = 10 min (red), 30 min (yellow), 1 hr (green), 2 hrs (cyan), 3 hrs (blue), 4 hrs (violet) and 20 hrs (magenta).

d. $PhICl_2$ + Pyridine.HOTf (20%)

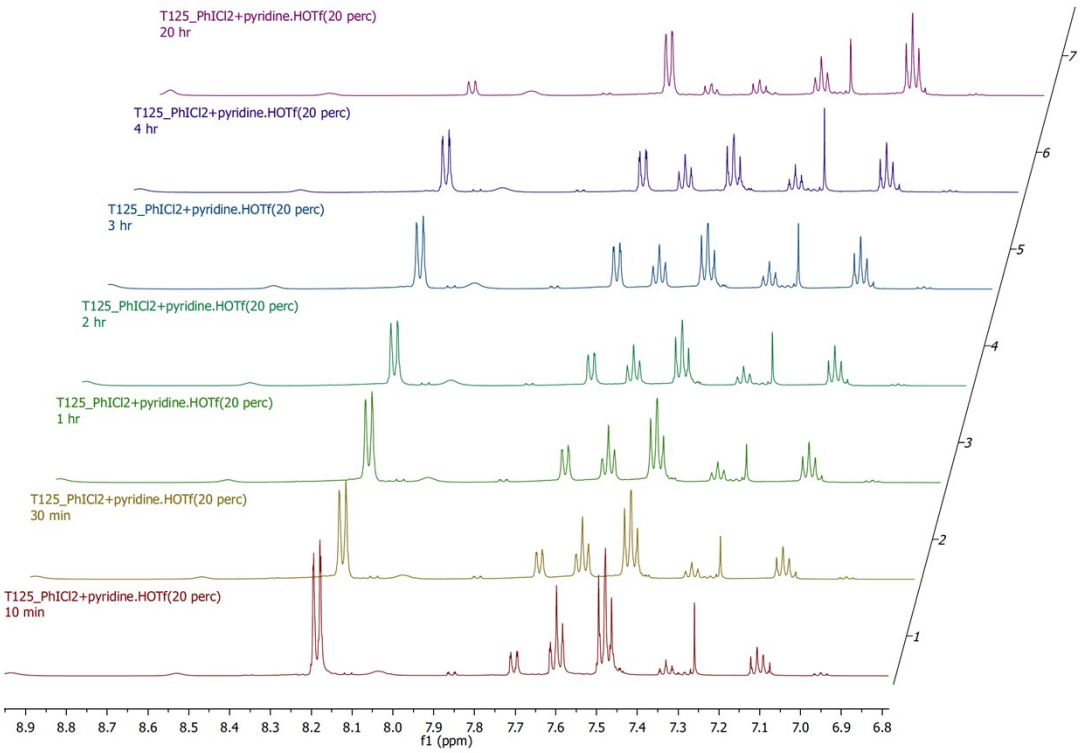


Figure S40. ^{1}H NMR spectra for $PhICl_2$ and 20% pyridine.HOTf in $CDCl_3$ at t = 10 min (red), 30 min (yellow), 1 hr (green), 2 hrs (cyan), 3 hrs (blue), 4 hrs (violet) and 20 hrs (magenta).

e. $PhICl_2 + NBu_4Cl$ (20%)

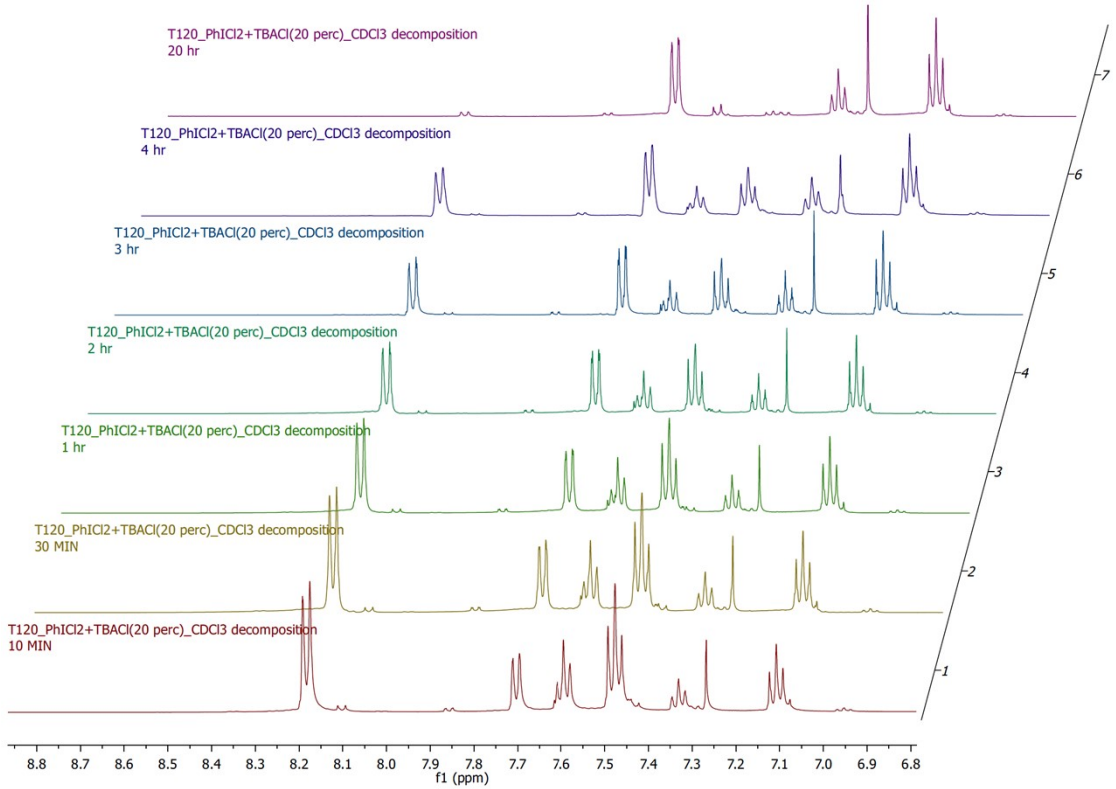


Figure S41. ^{1}H NMR spectra for $PhICl_2$ and 20% NBu_4Cl in $CDCl_3$ at t = 10 min (red), 30 min (yellow), 1 hr (green), 2 hrs (cyan), 3 hrs (blue), 4 hrs (violet) and 20 hrs (magenta).

f. $PhICl_2 + HCl.Et_2O$ (20%)

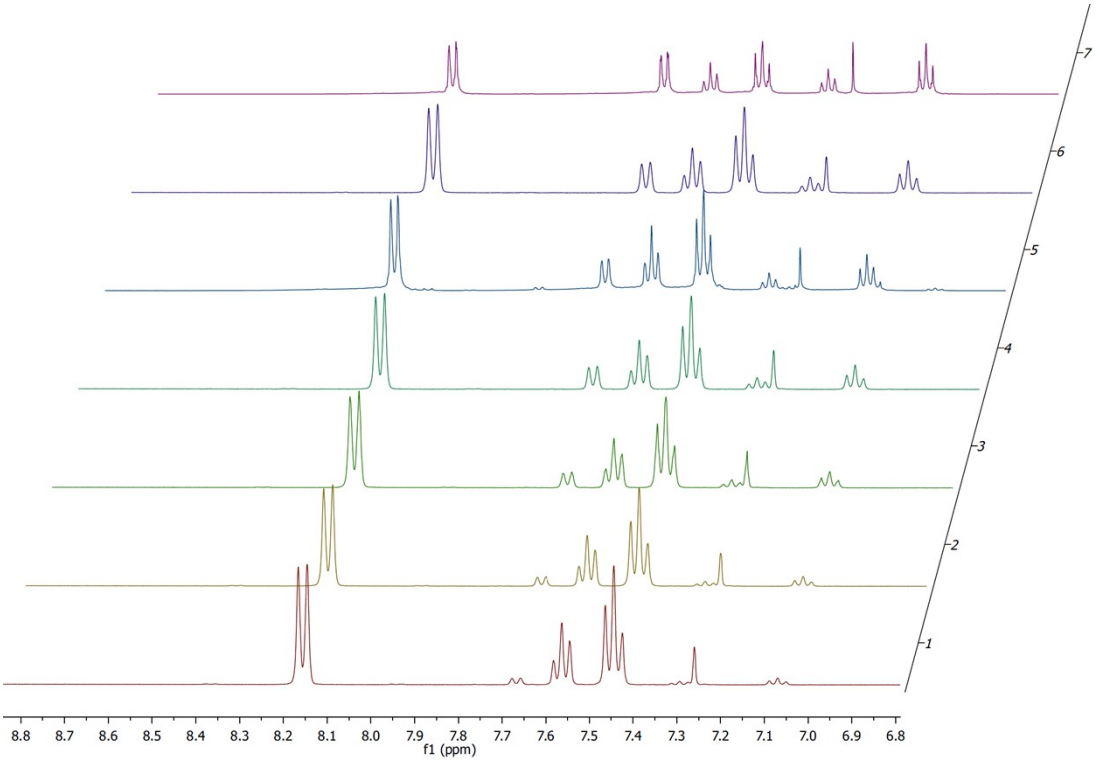


Figure S42. ^{1}H NMR spectra for $PhICl_2$ and 20% $HCl.Et_2O$ in $CDCl_3$ at t = 10 min (red), 30 min (yellow), 1 hr (green), 2 hrs (cyan), 3 hrs (blue), 4 hrs (violet) and 20 hrs (magenta).

g. $PhICl_2$ + NBu_4OTf (20%)

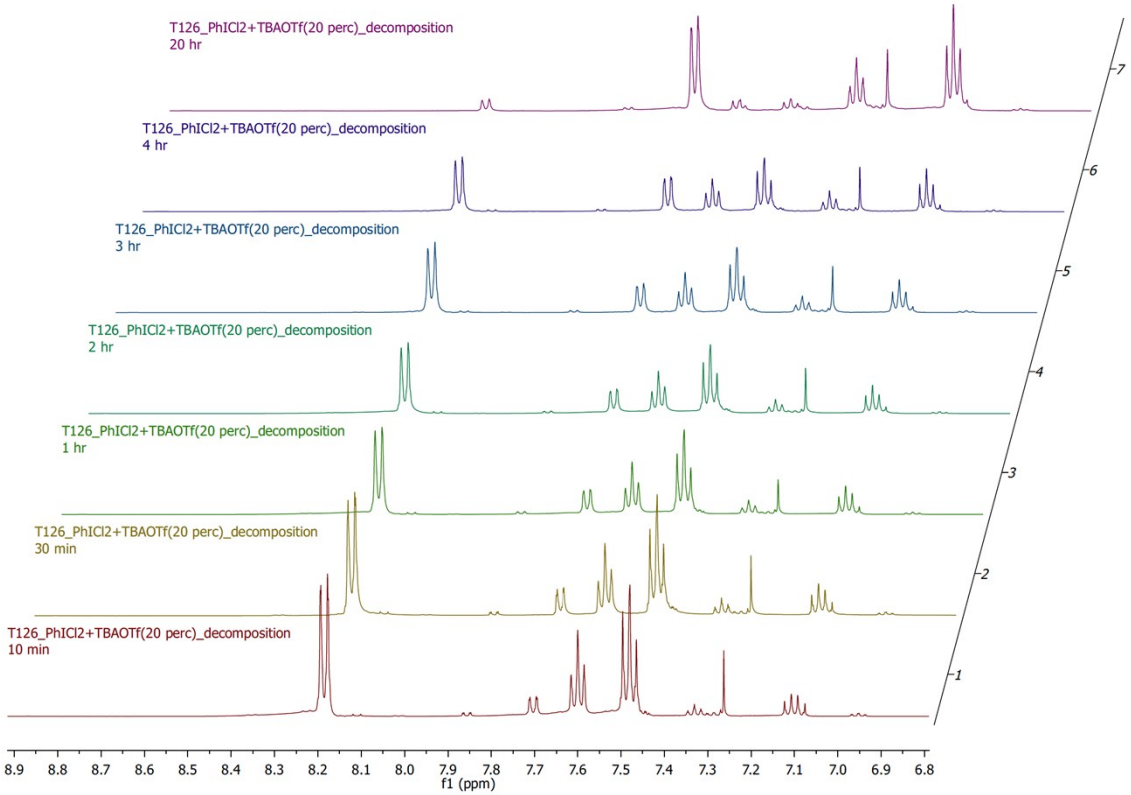


Figure S43. ^{1}H NMR spectra for $PhICl_2$ and 20% NBu_4OTf in $CDCl_3$ at t = 10 min (red), 30 min (yellow), 1 hr (green), 2 hrs (cyan), 3 hrs (blue), 4 hrs (violet) and 20 hrs (magenta).

h. $PhICl_2$ + LiCl (20%)

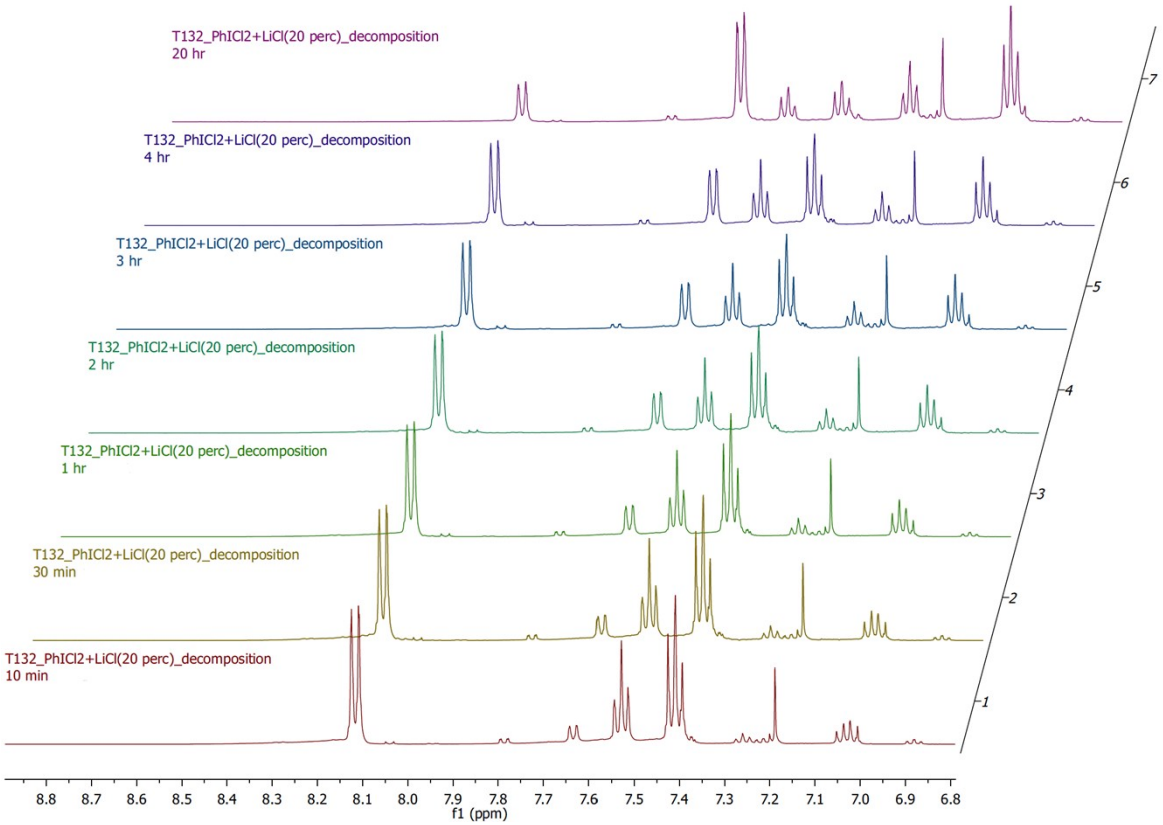


Figure S44. ^{1}H NMR spectra for $PhICl_2$ and 20% LiCl in $CDCl_3$ at t = 10 min (red), 30 min (yellow), 1 hr (green), 2 hrs (cyan), 3 hrs (blue), 4 hrs (violet) and 20 hrs (magenta).

iii. BindFit experiment

a. $PhICl_2$ + NBu_4Cl (20%)

Link: http://app.supramolecular.org/bindfit/view/7dbfd70a-44d3-43da-9974-49dc3782779e

Table S5. Excel data used for BindFit experiment.

Host concentration / M	Guest concentration / M	Proton 1	Proton 2	Proton 3
2.20E-02	0.037	8.164	7.572	7.456
2.00E-02	0.074	8.123	7.530	7.418
1.40E-02	0.111	8.092	7.499	7.390
1.50E-02	0.148	8.060	7.468	7.360
1.60E-02	0.185	8.033	7.442	7.336
6.00E-03	0.370	7.888	7.306	7.203

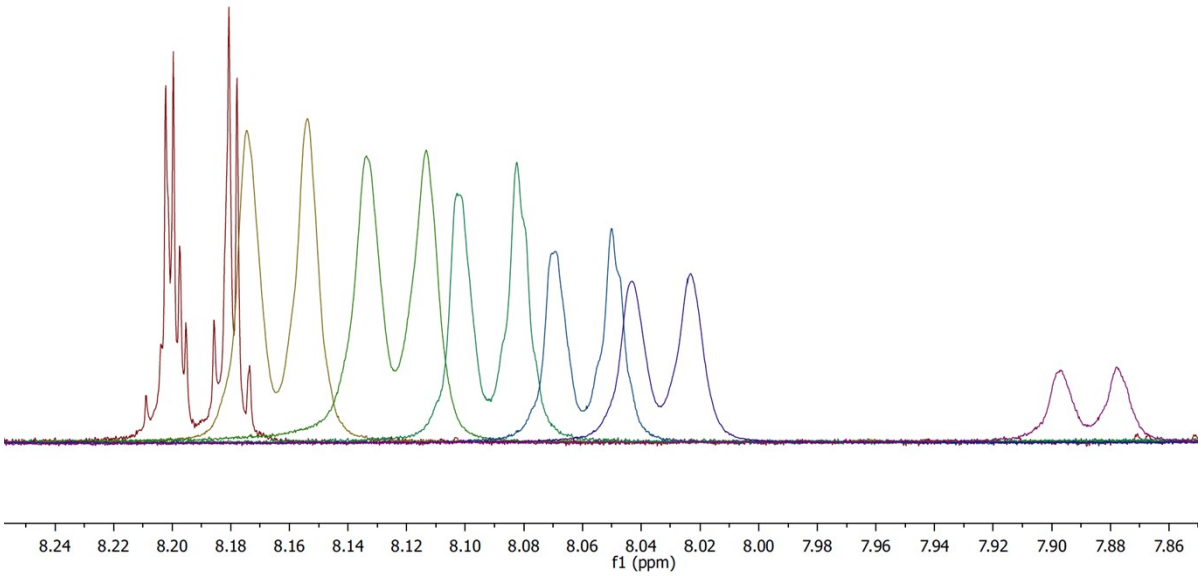


Figure S45. ^{1}H NMR spectrum overlay for ortho proton of $PhICl_2$ and 0 (red), 1 (yellow), 2 (green), 3 (cyan), 4 (blue), 5 (purple) and 10 (magenta) equivalents of NBu_4Cl in $CDCl_3$.

b. $PhICl_2$ + NBu_4OTf (20%)

Link: http://app.supramolecular.org/bindfit/view/b78d3215-d747-4b10-aa2b-4d7887163379

Table S6. Excel data used for BindFit experiment.

Host concentration / M	Guest concentration / M	Proton 1	Proton 2	Proton 3
0.023	0.023	8.184	7.600	7.479
0.023	0.045	8.180	7.599	7.477
0.023	0.068	8.174	7.596	7.474
0.023	0.091	8.169	7.594	7.471
0.023	0.113	8.165	7.592	7.469
0.023	0.227	8.138	7.576	7.451

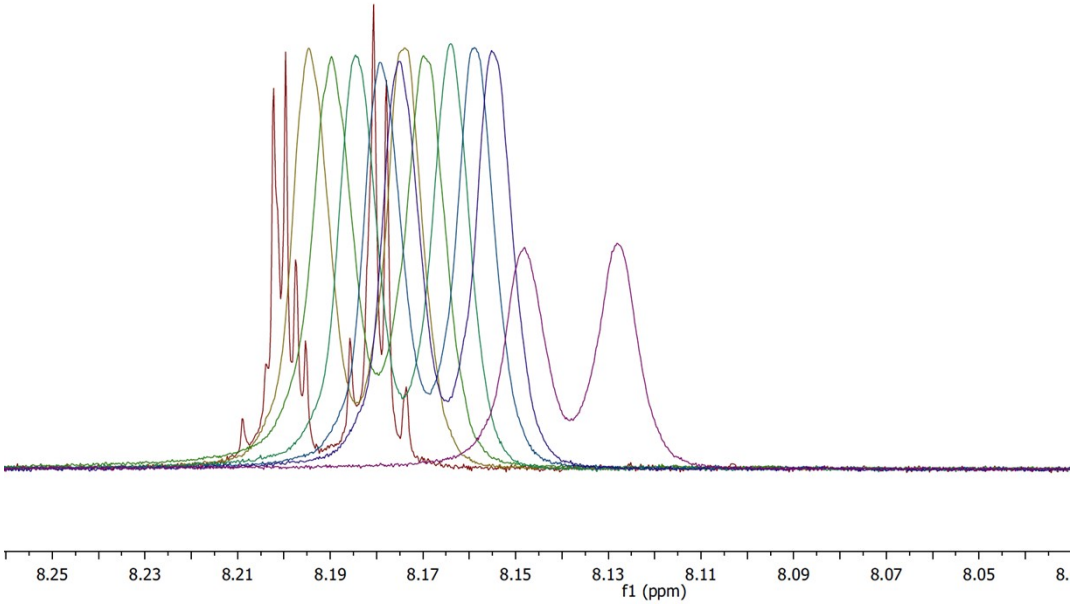


Figure S46. ^{1}H NMR spectrum overlay for ortho proton of $PhICl_2$ and 0 (red), 1 (yellow), 2 (green), 3 (cyan), 4 (blue), 5 (purple) and 10 (magenta) equivalents of NBu_4OTf in $CDCl_3$.

IV. Electrochemical Analysis

Table S7. Reduction potential values for $PhICl_2$ with different mol% of NBu_4Cl added.

	0% Cl^-	**5 mol% Cl^-**	**20 mol% Cl^-**
$Ep^{1/2}$ (ferrocene)	+0.408 V	+0.407 V	+0.500 V
R-**ICl_2** (vs Ag/Ag^+)	-0.493 V	-0.688 V	-0.698 V
R-**ICl_2** (vs Fc/Fc^+)	-0.901 V	-1.095 V	-1.198 V
Difference from 0% Cl^-	0 V	-0.195 V	-0.205 V
PhI-$(X)_2$ (vs Ag/Ag^+)	-2.744 V	-2.785 V	-2.762 V
PhI-$(X)_2$ (vs Fc/Fc^+)	-3.152 V	-3.192 V	-3.262 V

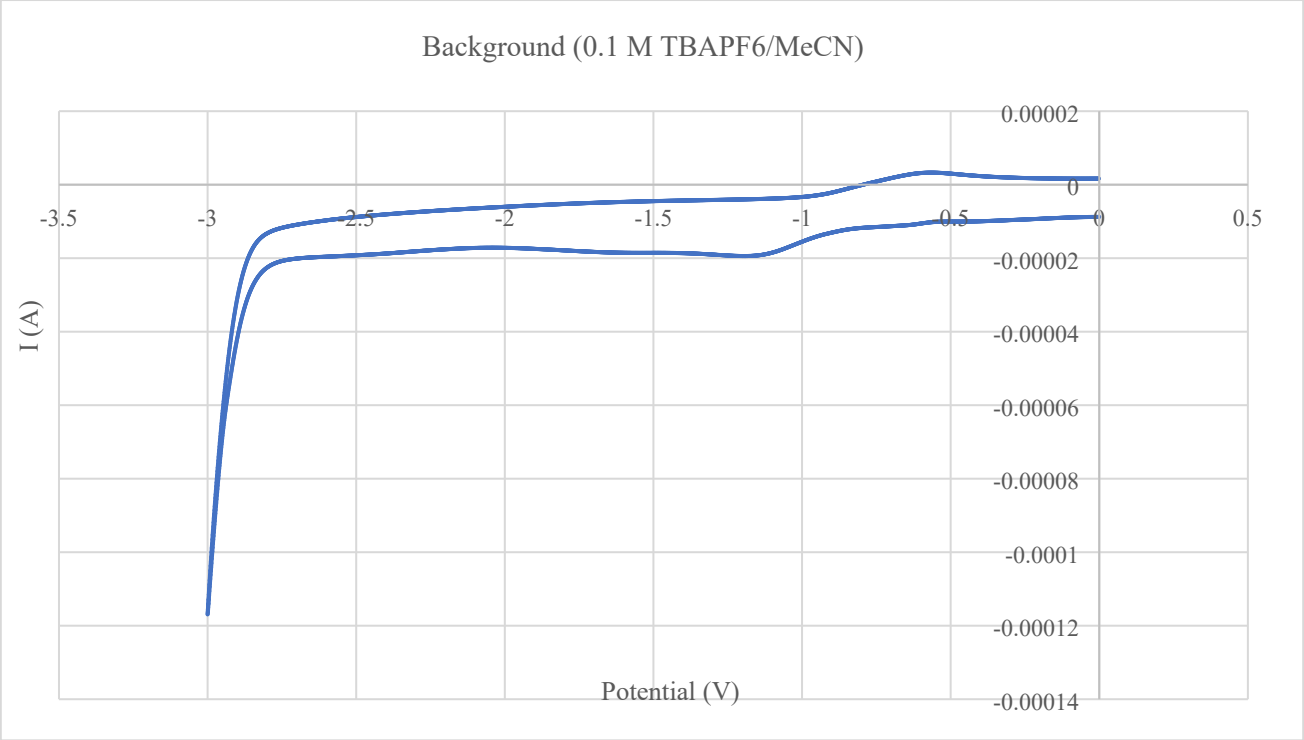


Figure S47. Cyclic voltammogram of $TBAPF_6$ in MeCN. Scan rate of 200mV/s. Redox peak at $Ep^{1/2}$ at ~-0.85 V is indicative of O_2.

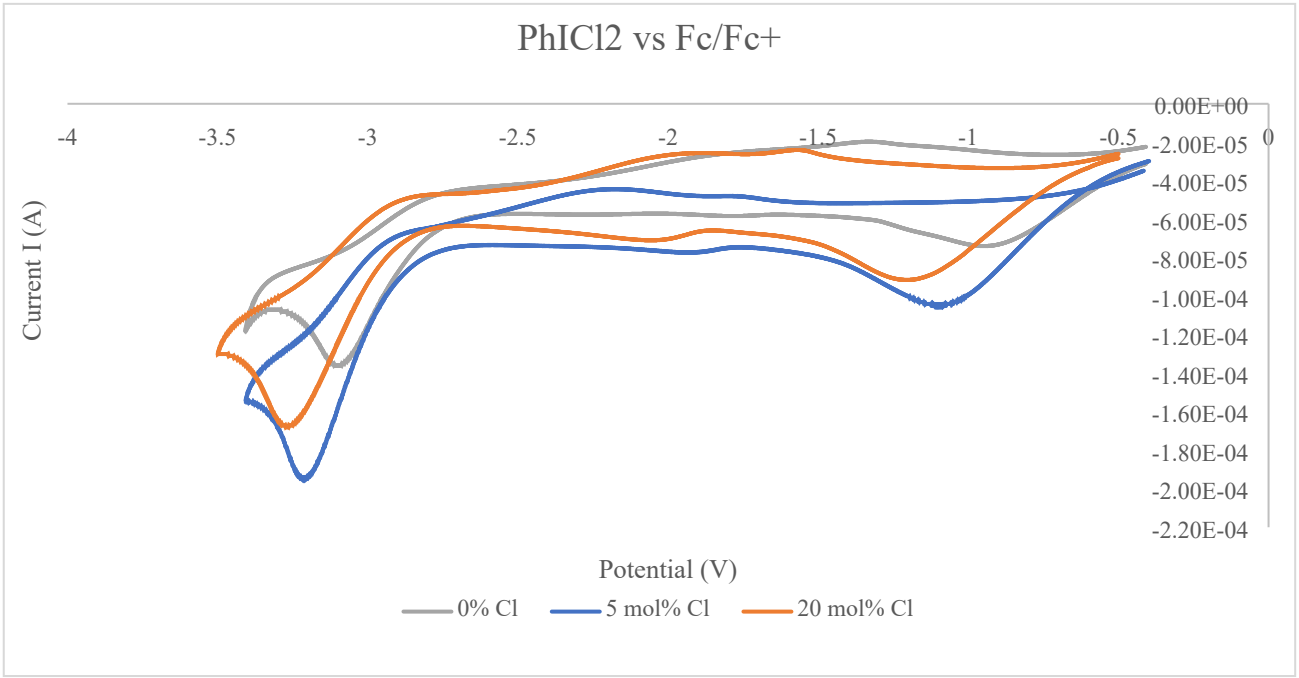


Figure S48. Cyclic voltammogram of $PhICl_2$ with differing concentrations of NBu_4Cl in MeCN (0.1 M $TBAPF_6$). Scan rate of 200mV/s.

V. X-ray Crystallographic Details

Tetraethylammonium chloride (3 mg, 0.018 mmol) was added to a warm solution of $PhICl_2$ (5 mg, 0.018 mmol) in minimum dichloromethane. The reaction mixture was stirred until the solution turned clear before cooling (-20 °C). Pale yellow needle-like crystals (91%) were obtained overnight.

X-ray data were collected using a Rigaku XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer employing monochromated Mo-Kα radiation at 100(2) K and solved using SHELXT with further structural refinements carried out using SHELXL within the OLEX2 graphical user interface. Non-hydrogen atoms were refined anisotropically and hydrogen atoms placed using a riding model. The CIF has been deposited with the CSD (CCDC 2091146).

Crystal Data for $C_{20}H_{30}Cl_5I_2N$ (M =715.50 g/mol): monoclinic, space group $I2/a$ (no. 15), a = 9.8786(4) Å, b = 17.2644(6) Å, c = 15.6853(6) Å, β = 101.359(4)°, V = 2622.70(18) Å^3, Z = 4, T = 100(2) K, μ(Mo Kα) = 2.916 mm^{-1}, *Dcalc* = 1.812 g/cm^3, 16675 reflections measured (4.822° ≤ 2Θ ≤ 56.562°), 3242 unique (R_{int} = 0.0390, R_{sigma} = 0.0290) which were used in all calculations. The final R_1 was 0.0239 (I > 2σ(I)) and wR_2 was 0.0506 (all data).

2. COMPUTATIONAL SECTION

All the calculations were carried out using Gaussian 16 revision C.01 unless noted.[3] Geometry optimisation was carried out at the B3LYP-D3(BJ)/def2-TZVPPD (PCM, SMD, chloroform) level of theory.[4-8] Some geometries were also calculated with dichloromethane solvation for comparison. 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. Molecular orbital (MO) and Natural Bond Orbital (NBO) analysis was caried out on the optimised geometries at the same level of theory. NBO analysis was performed using NBO 6.0.[9]

ORCA 5.0.0 was used to perform single point calculations at the DLPNO-CCSD(T)/ma-def2-QZVPP level of theory (inclusive of CPCM solvation).[10] The single point electronic energies were converted to free energies

(Δ*G*) by adding the free energy correction calculated at the B3LYP-D3(BJ)/def2-TZVPPD (SMD) level of theory.

Cartesian coordinates computed at the B3LYP-D3(BJ)/def2-TZVPPD (SMD, chloroform) level of theory. Units of Ångstrøm.

$PhICl_2$
Ee = -1450.02927382

I	-1.132833	0.000002	-0.000004
C	0.976397	0.000005	-0.000003
C	1.635160	-0.154816	-1.209932
C	3.025212	-0.155760	-1.197176
C	3.715721	-0.000005	0.000000
C	3.025210	0.155756	1.197175
C	1.635158	0.154820	1.209928
H	1.089019	0.274700	2.133647
H	3.563654	0.277115	2.126987
H	4.797174	-0.000009	0.000002
H	3.563657	-0.277124	-2.126986
H	1.089022	-0.274693	-2.133652
Cl	-1.125847	-2.533300	-0.001334
Cl	-1.125869	2.533303	0.001348

$PhICl_3^-$
Ee = -1910.42958712

I	-0.691279	0.016262	0.000012
C	1.449401	0.006666	0.000838
C	2.124877	0.014625	-1.211372
C	3.515774	-0.007873	-1.204282
C	4.209024	-0.037673	0.001422
C	3.514813	-0.042909	1.207295
C	2.123767	-0.020032	1.213647
H	1.578676	-0.026934	2.146986
H	4.053509	-0.066464	2.145301
H	5.290775	-0.057026	0.001486
H	4.055172	-0.003758	-2.142171
H	1.580671	0.034861	-2.145029
Cl	-0.565638	-2.526505	-0.012108
Cl	-0.562970	2.569762	0.005873
Cl	-3.668273	-0.056161	0.003147

PhI
Ee = -529.569713507

I	0.000000	0.000000	1.550509
C	0.000000	0.000000	-0.564319
C	0.000000	1.210860	-1.246275
C	0.000000	1.202771	-2.637601
C	0.000000	0.000000	-3.334931
C	0.000000	-1.202771	-2.637601
C	0.000000	-1.210860	-1.246275
H	0.000001	-2.146340	-0.706061
H	0.000000	-2.142883	-3.173156
H	0.000000	0.000000	-4.416516
H	0.000000	2.142883	-3.173156
H	-0.000001	2.146340	-0.706061

Cl_2
Ee = -920.429940367

Cl	0.000000	0.000000	1.006207
Cl	0.000000	0.000000	-1.006207

$[PhICl_2\text{-}Cl\text{-}PhICl_2]^-$
Ee = -3360.47333631

I	-2.191071	-0.646178	0.111409
C	-3.683042	0.868162	0.160534
C	-4.787054	0.702381	0.984270
C	-5.752135	1.703106	1.013421
C	-5.602251	2.842398	0.229415
C	-4.487587	2.988225	-0.589882
C	-3.514302	1.995725	-0.630185
H	-2.644515	2.101256	-1.262881
H	-4.371326	3.874088	-1.199784

H	-6.355740	3.618143	0.257119
H	-6.618975	1.590048	1.650718
H	-4.895278	-0.184715	1.591889
Cl	-3.518509	-1.762577	-1.747078
Cl	-1.017347	0.610720	1.992236
Cl	0.000139	-2.795352	0.000690
I	2.191495	-0.646720	-0.111351
C	3.682664	0.868405	-0.160835
C	4.786992	0.703037	-0.984224
C	5.751501	1.704311	-1.013391
C	5.600753	2.843737	-0.229741
C	4.485773	2.989161	0.589199
C	3.513048	1.996111	0.629501
H	2.643026	2.101321	1.261928
H	4.368829	3.875125	1.198821
H	6.353814	3.619897	-0.257451
H	6.618582	1.591580	-1.650419
H	4.895898	-0.184172	-1.591559
Cl	1.017681	0.608167	-1.993430
Cl	3.519040	-1.761403	1.748174

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