Electronic Supplementary Material (ESI) for Dalton Transactions.

Kinetic studies on the activation of $PhICl_2$ with Lewis Bases for aromatic chlorinations

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Experimental Section

1.1 Experimental Details

All reagents were purchased from Sigma Aldrich and used as received. Deuterated solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories and stored in a desiccator over 3 Å molecular sieves. NMR spectra for all experiments were recorded using Bruker Ultrashield Plus 500 MHz and Ascend 400 MHz spectrometers. All data was referenced according to their corresponding solvent resonances for residual protons; $CDCl_3$: ^1H at δ 7.26. The abbreviations used to report NMR signal multiplicity are s = singlet, d = doublet, t = triplet, m = multiplet.

1.2 Experimental Procedure

a) Synthesis of $PhICl_2$[1]
In a conical flask, Iodobenzene (0.5 mL, 5mmol) was cooled to 0 °C on an 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 formed. 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%).

b) Generation of Cl_2 gas[2]
A two necked flask was charged with powdered $KMnO_4$ and equipped with a dropping funnel containing 10.18 M HCl. The acid was added to the solid dropwise leading to generation of Cl_2 gas according to following equation.

$$2\ KMnO_4 + 16\ HCl \rightarrow 2\ KCl + 2\ MnCl_2 + 8\ H_2O + 5\ Cl_2 \uparrow$$

c) Reaction of substrate and Cl_2

The Cl_2 gas generated in part (b) was displaced through 0.3 mm Teflon tubing, with the Teflon tubing directly immersed into the receiving flask by bubbling into a reaction flask containing substrate dissolved in $CDCl_3$. The experimental setup for this manipulation is shown in figure S1, where the joining between the flasks for gas flow is Teflon tubing only.

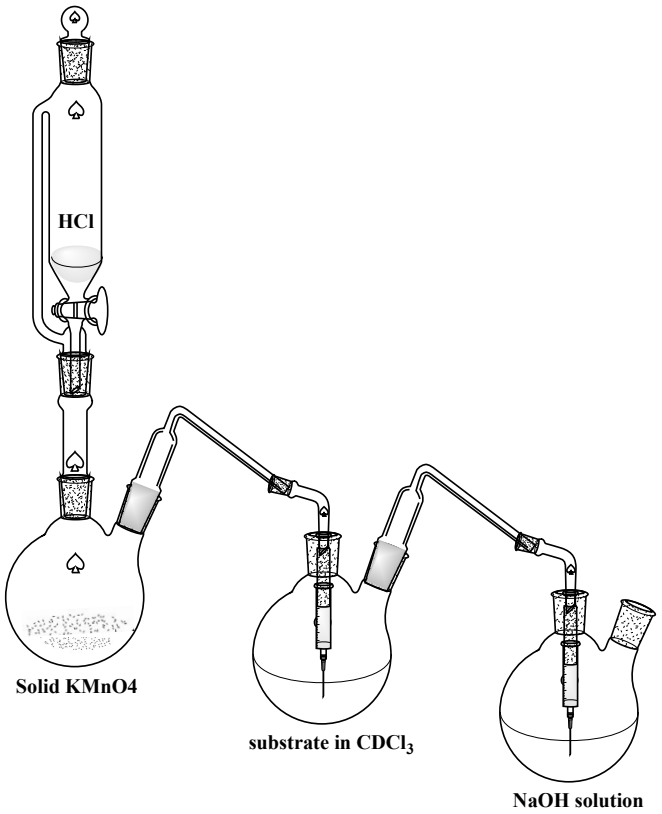

Figure S 1: Experimental setup for reaction of substrate with in-situ generated Cl_2 gas.

d) Reaction of Substrate and $PhICl_2$

In a reaction flask, 1 mL aliquot of freshly prepared solution of 90.9 mM $PhICl_2$ in $CDCl_3$ was stirred with 1 equivalent of aryl substrate for 1 hr at room temperature. The reaction aliquot was taken to record NMR.

This experiment was also repeated with same amount of $PhICl_2$ and aryl substrate in presence of 1 mol% TBACl and 20 mol% pyridine, respectively.

e) VT NMR Experiments

The reactions mentioned in part (d) were also performed at variable temperature and corresponding NMR spectra were recorded at respective temperatures. Reactants were mixed in a sample preparation room close to the NMR spectrometer. The NMR scans at fixed interval to follow reaction overtime.

Any attempts to replicate this data or methodology should take note of the initial reaction rate and ensure that catalytic concentrations are accurately controlled for.

1.3 NMR Spectra

a) $PhICl_2$

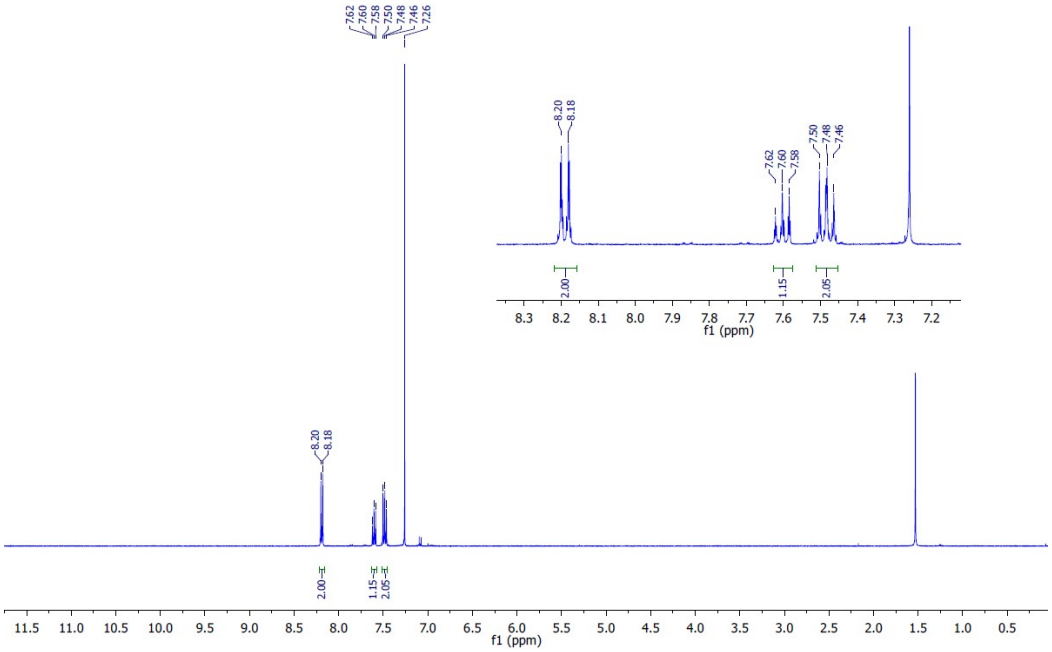

Figure S 2: ^1H NMR spectrum of $PhICl_2$ in $CDCl_3$ (inset) aryl region of the spectrum.

b) $PhICl_2$ + Catalyst + Aryl substrate

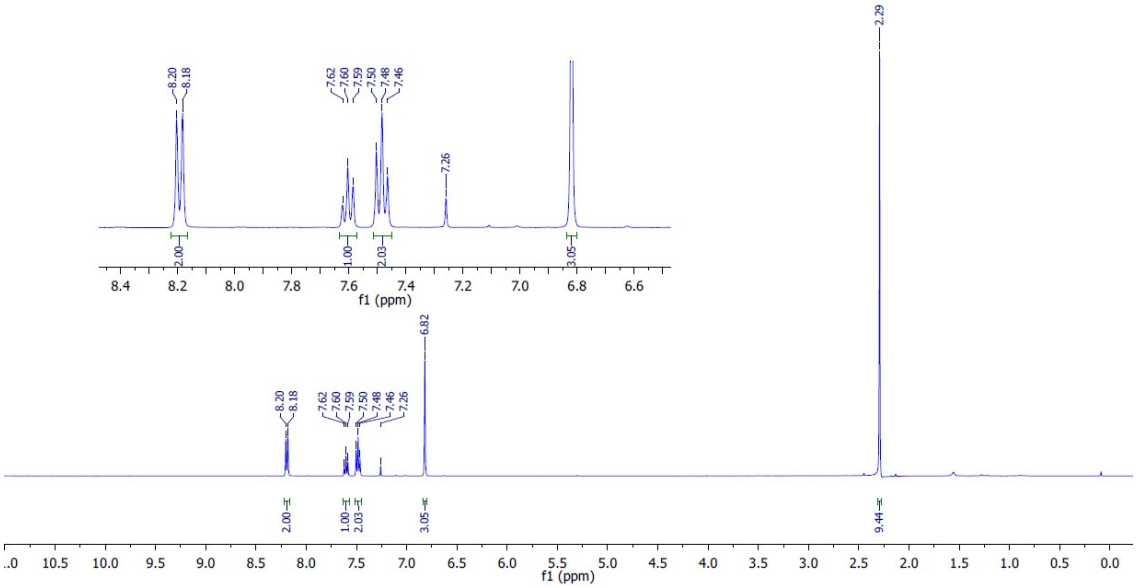

Figure S 3: ^1H NMR spectrum of reaction of $PhICl_2$ and mesitylene in $CDCl_3$ (inset) aryl region of the spectrum.

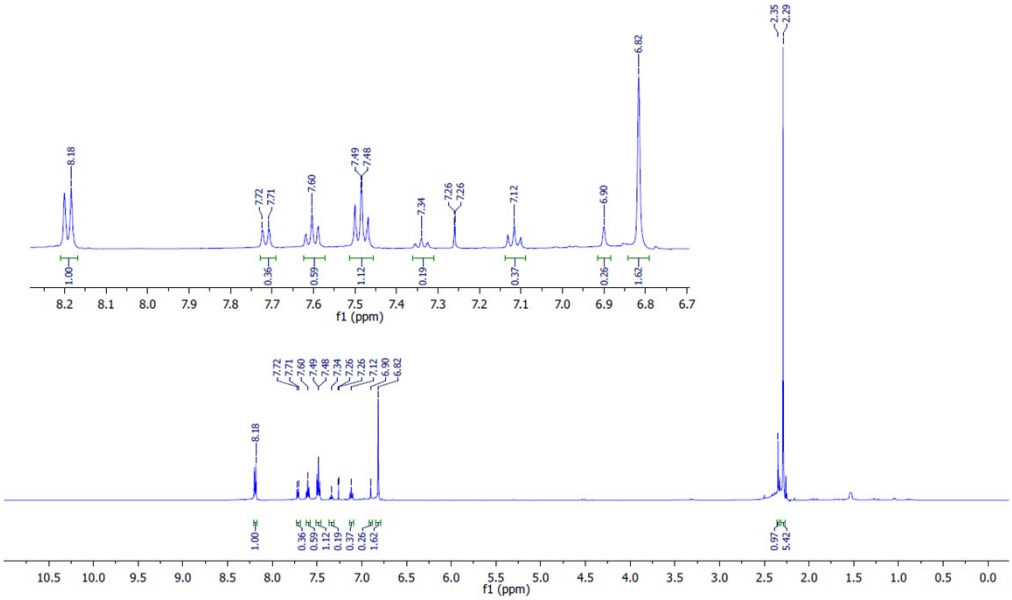

Figure S 4: ^{1}H NMR spectrum of reaction of $PhICl_2$ and mesitylene in presence of 1 mol% TBACl in $CDCl_3$ (inset) aryl region of the spectrum.

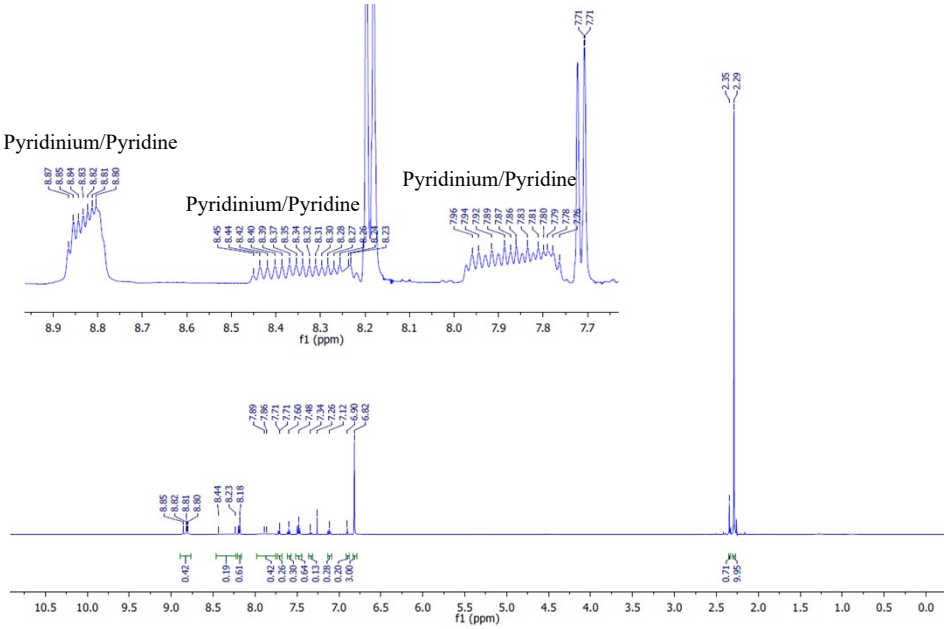

Figure S 5: ^{1}H NMR spectrum of reaction of $PhICl_2$ and mesitylene in presence of 20 mol% pyridine in $CDCl_3$ (inset) transition of pyridine to pyridinium signals.

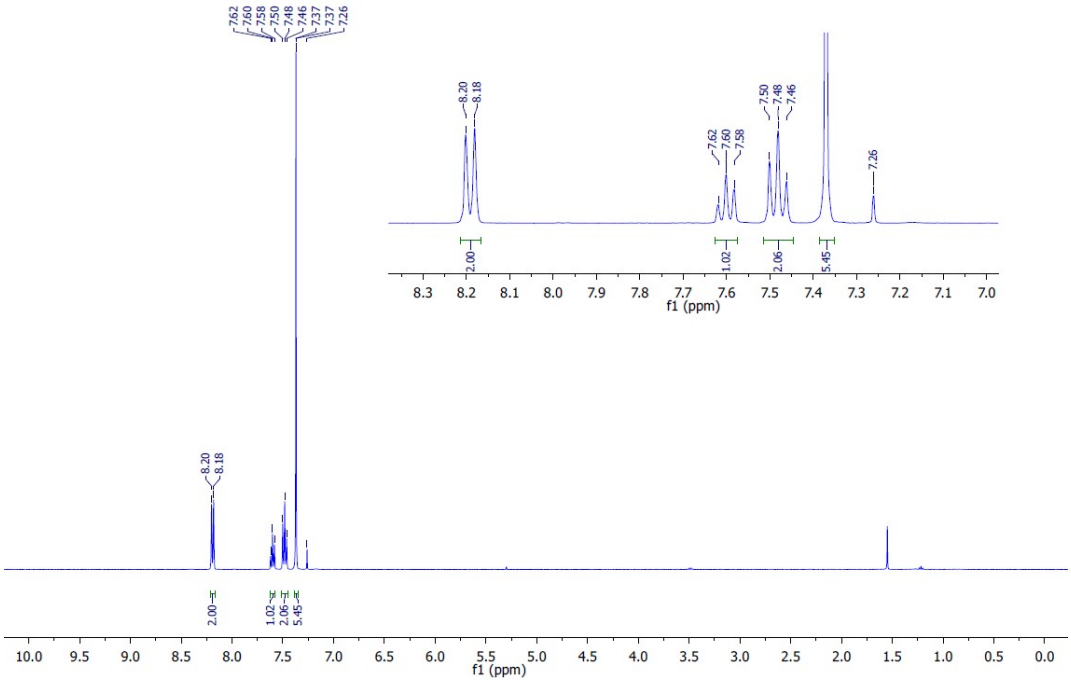

Figure S 6: ^{1}H NMR spectrum of reaction of 90 mM $PhICl_2$ and benzene in $CDCl_3$.

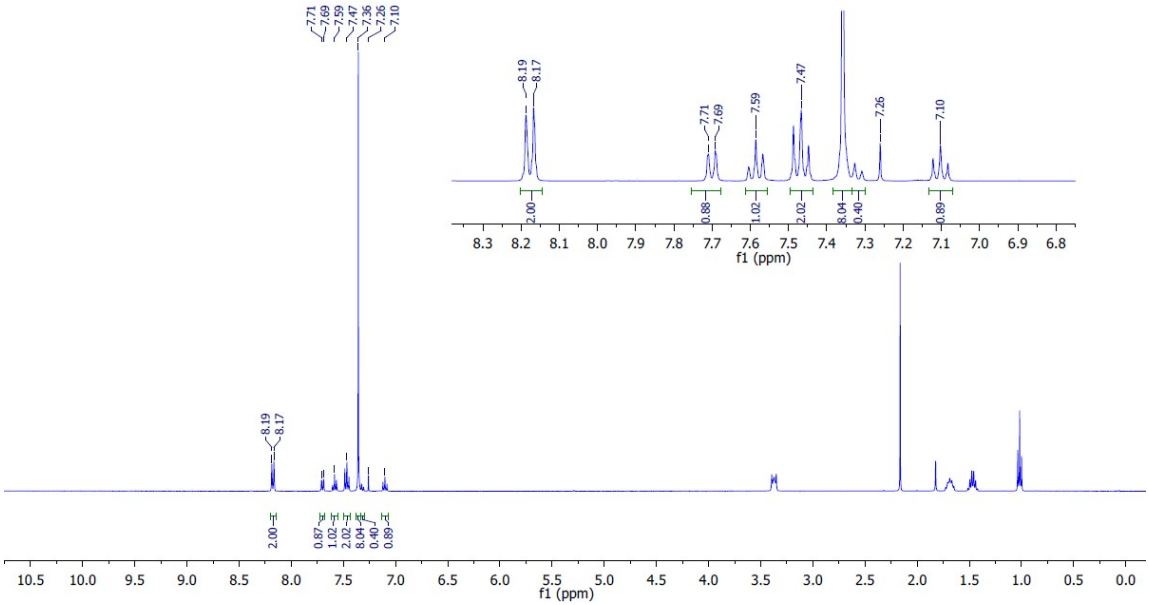

Figure S 7: ^{1}H NMR spectrum of reaction of 90 mM $PhICl_2$ and benzene in presence of 20 mol% TBACl in $CDCl_3$.

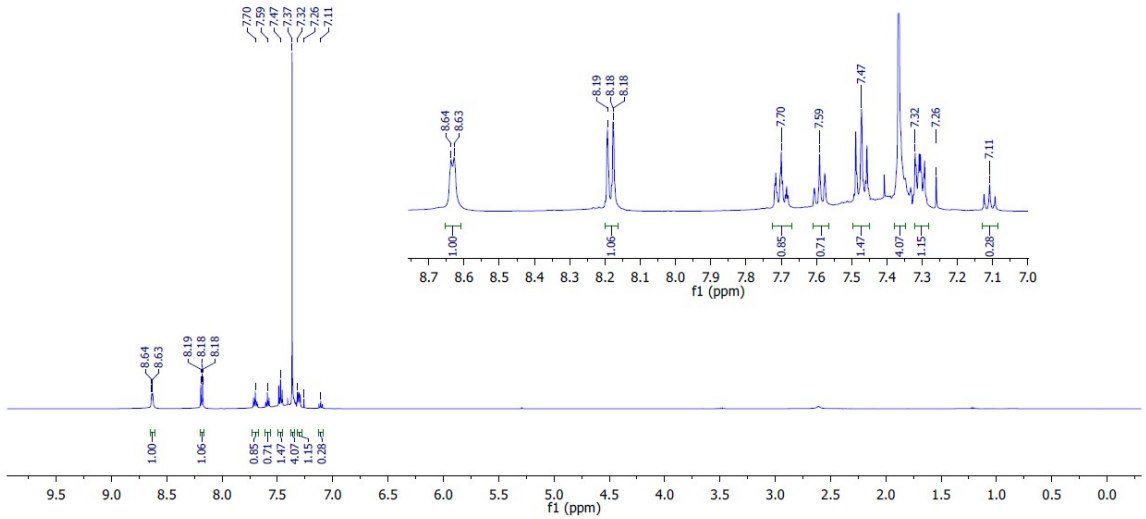

Figure S 8: ^{1}H NMR spectrum of reaction of 90 mM $PhICl_2$ and benzene in presence of 20 mol% pyridine in $CDCl_3$.

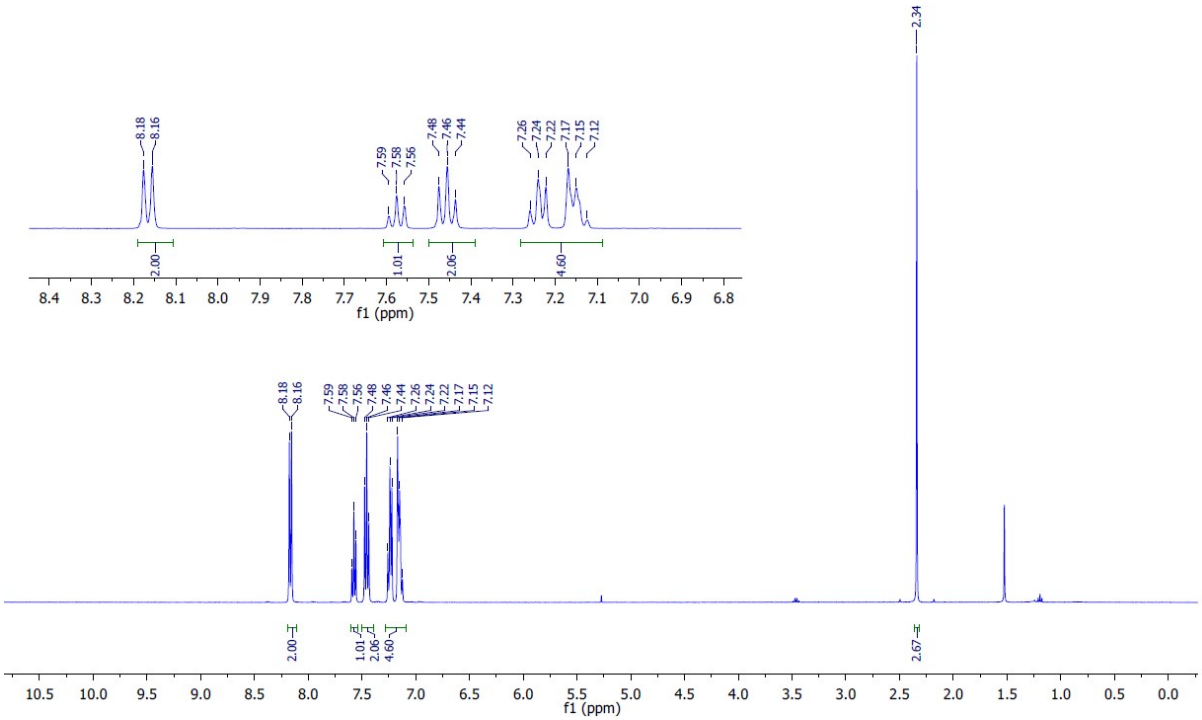

Figure S 9: ^{1}H NMR spectrum of reaction of $PhICl_2$ and toluene in $CDCl_3$.

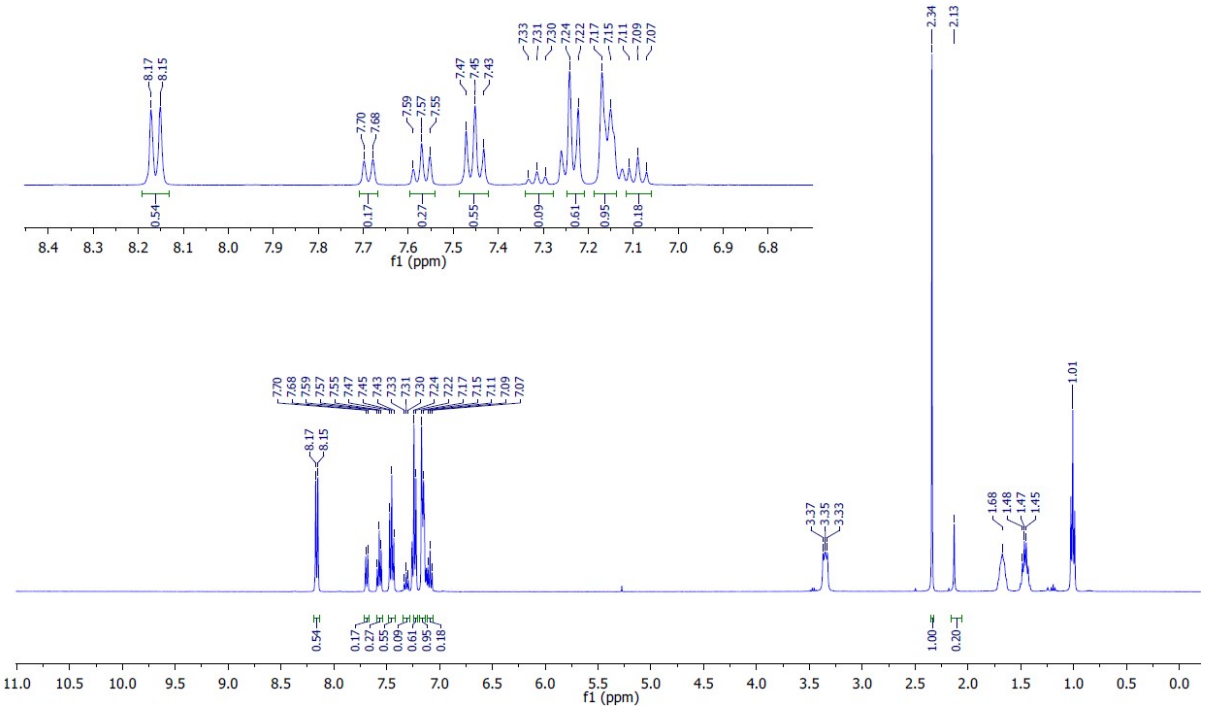

Figure S 10: ^{1}H NMR spectrum of reaction of 90 Mm $PhICl_2$ and toluene in presence of 20 mol% TBACl in $CDCl_3$.

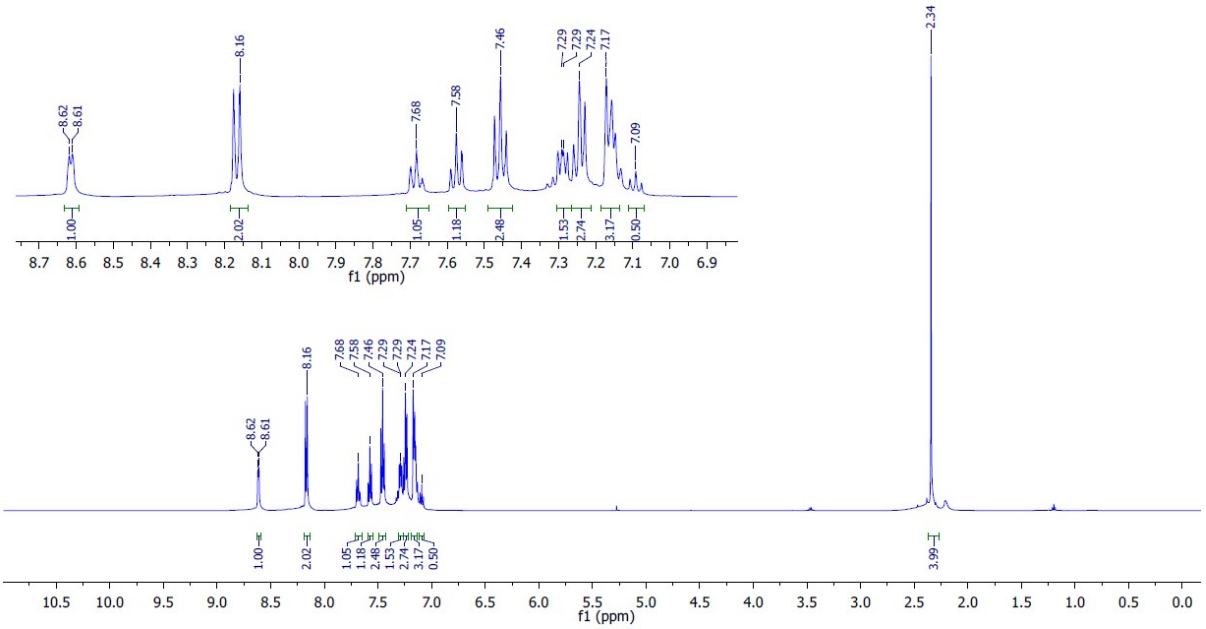

Figure S 11: ^{1}H NMR spectrum of reaction of 90 mM $PhICl_2$ and toluene in presence of 20 mol% pyridine in $CDCl_3$.

c) Order of Reaction w.r.t. $PhICl_2$

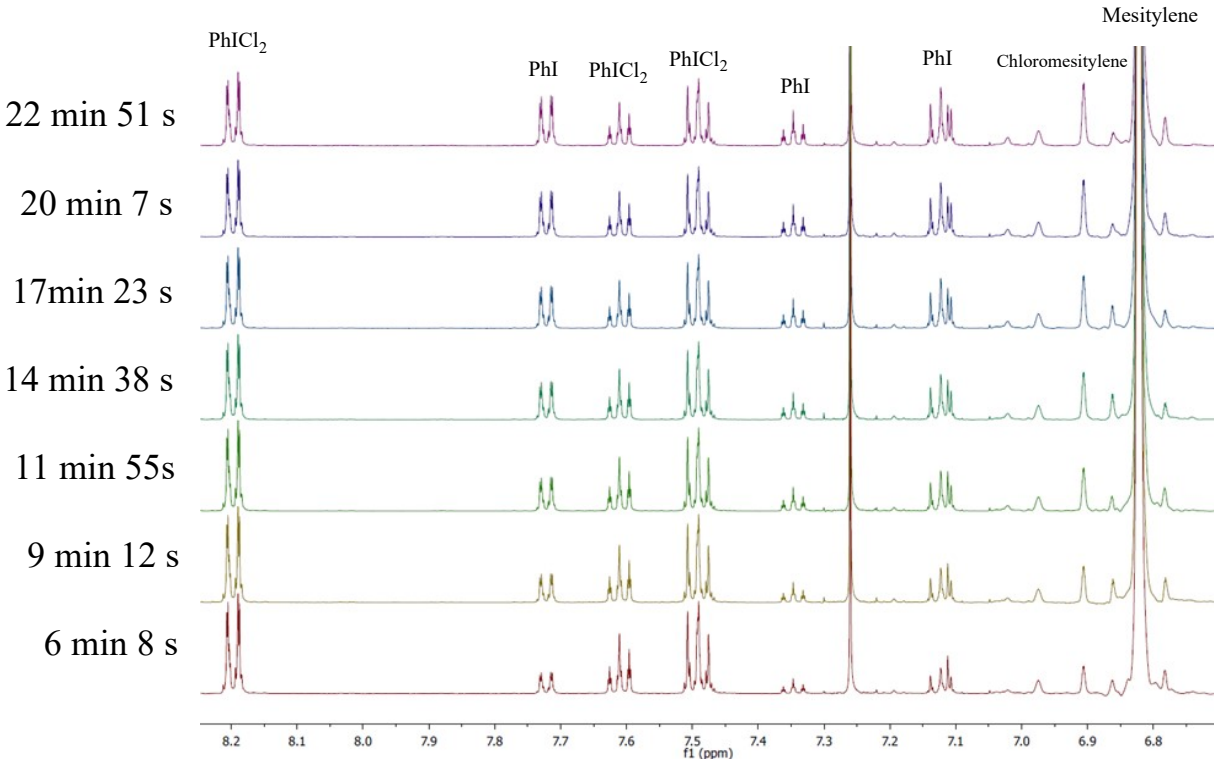

Figure S 12: ^1H NMR spectrum of reaction of 12 mM $PhICl_2$ and 122 mM mesitylene in presence of 0.261 mM (2 mol%) TBACl in $CDCl_3$ over time.

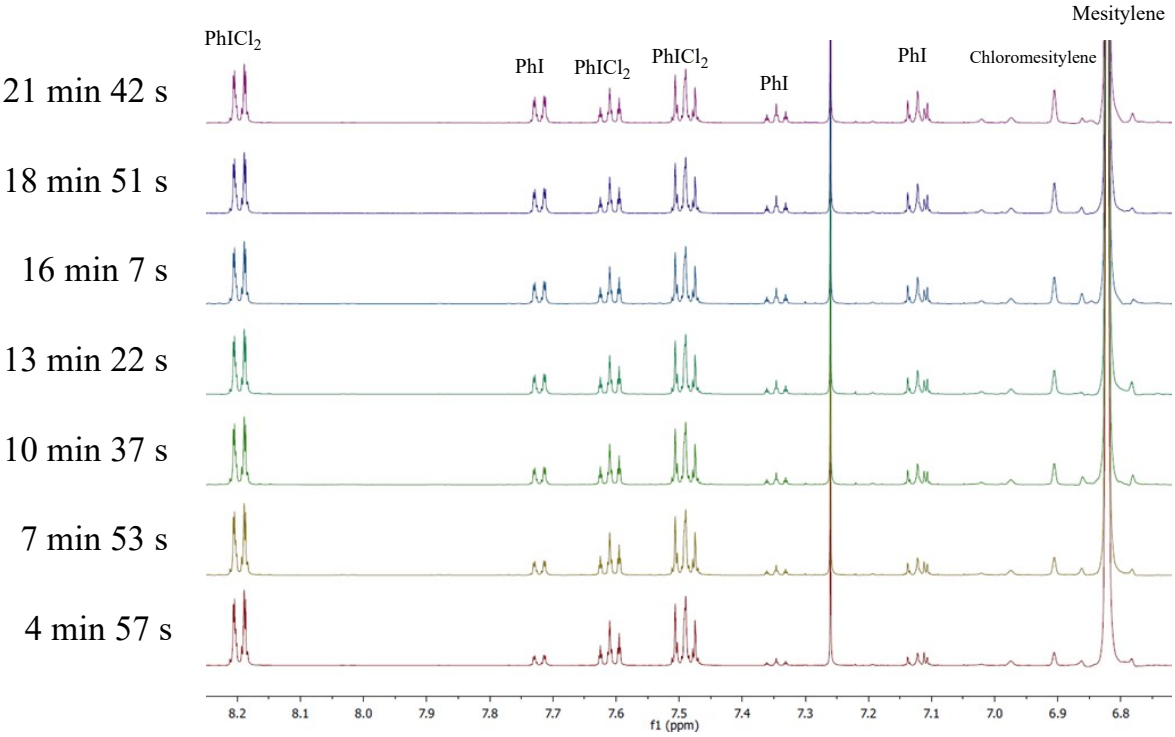

Figure S 13: ^1H NMR spectrum of reaction of 24 mM $PhICl_2$ and 122 mM mesitylene in presence of 0.261 mM (1 mol%) TBACl in $CDCl_3$ over time.

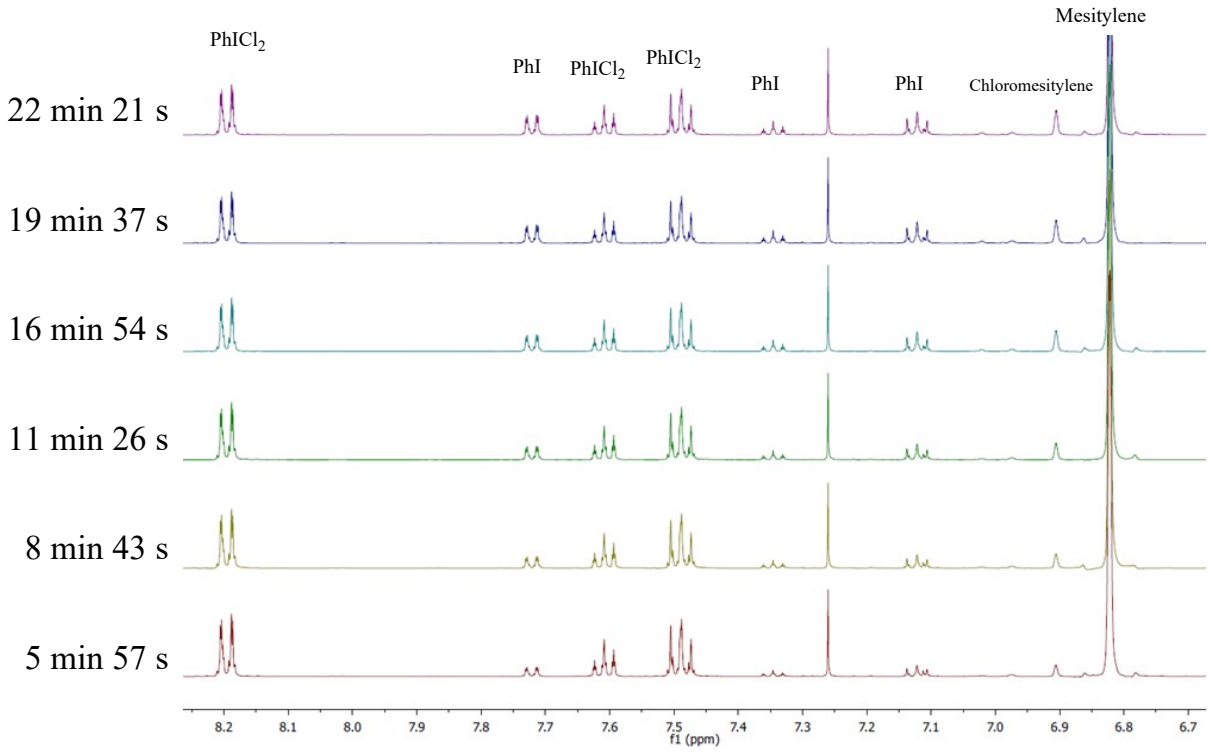

Figure S 14: ^{1}H NMR spectrum of reaction of 48 mM $PhICl_2$ 122 mM mesitylene in presence of 0.261 mM (0.5 mol%) TBACl in $CDCl_3$ over time.

d) Order of Reaction w.r.t. TBACl

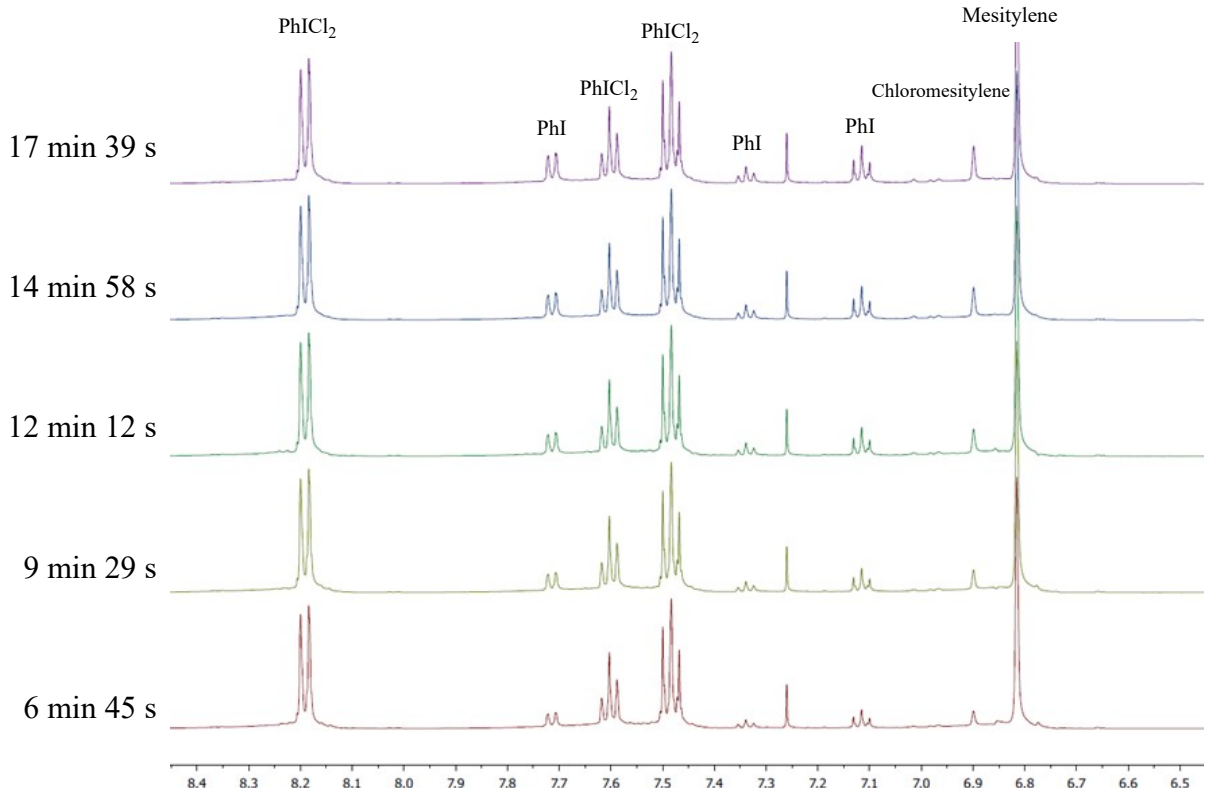

Figure S 15: ^{1}H NMR spectrum of reaction of 90.9 mM $PhICl_2$ and 90.9 mM mesitylene in presence of 0.25 mol% TBACl in $CDCl_3$ over time.

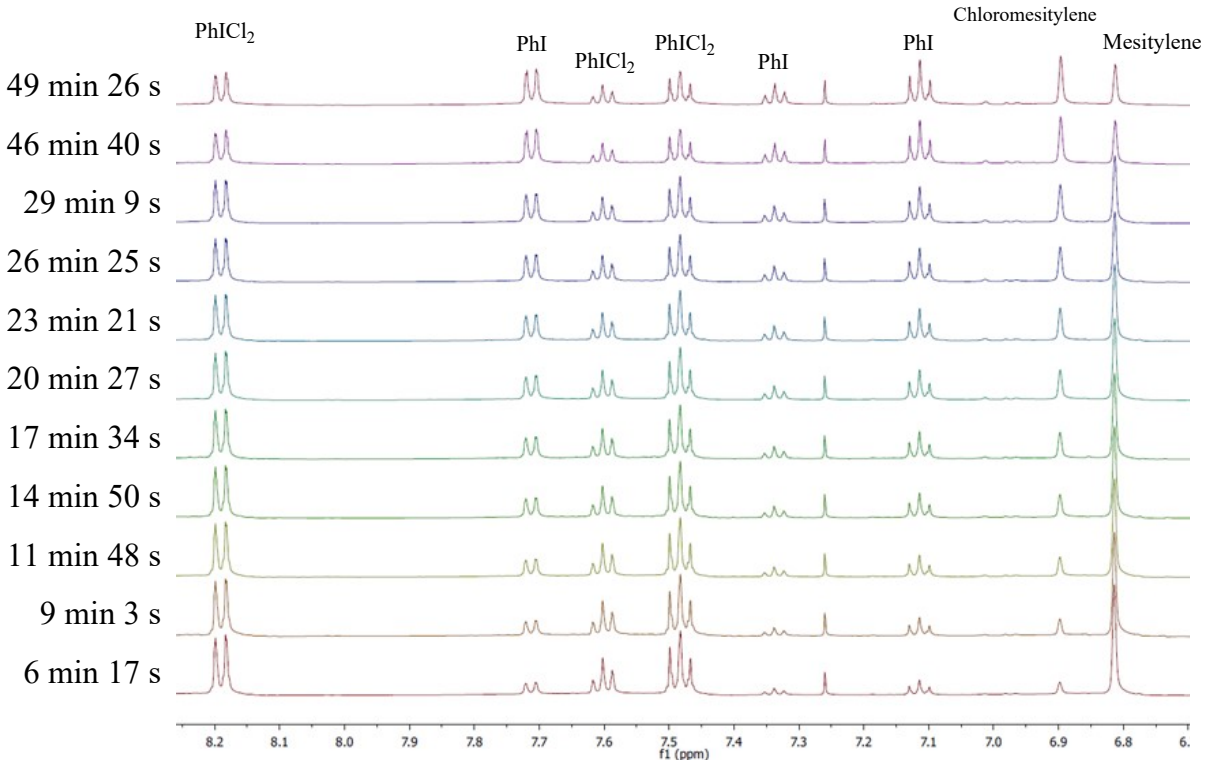

Figure S 16: ^{1}H NMR spectrum of reaction of 90.9 mM $PhICl_2$ and 90.9 mM mesitylene in presence of 0.50 mol% TBACl in $CDCl_3$ over time.

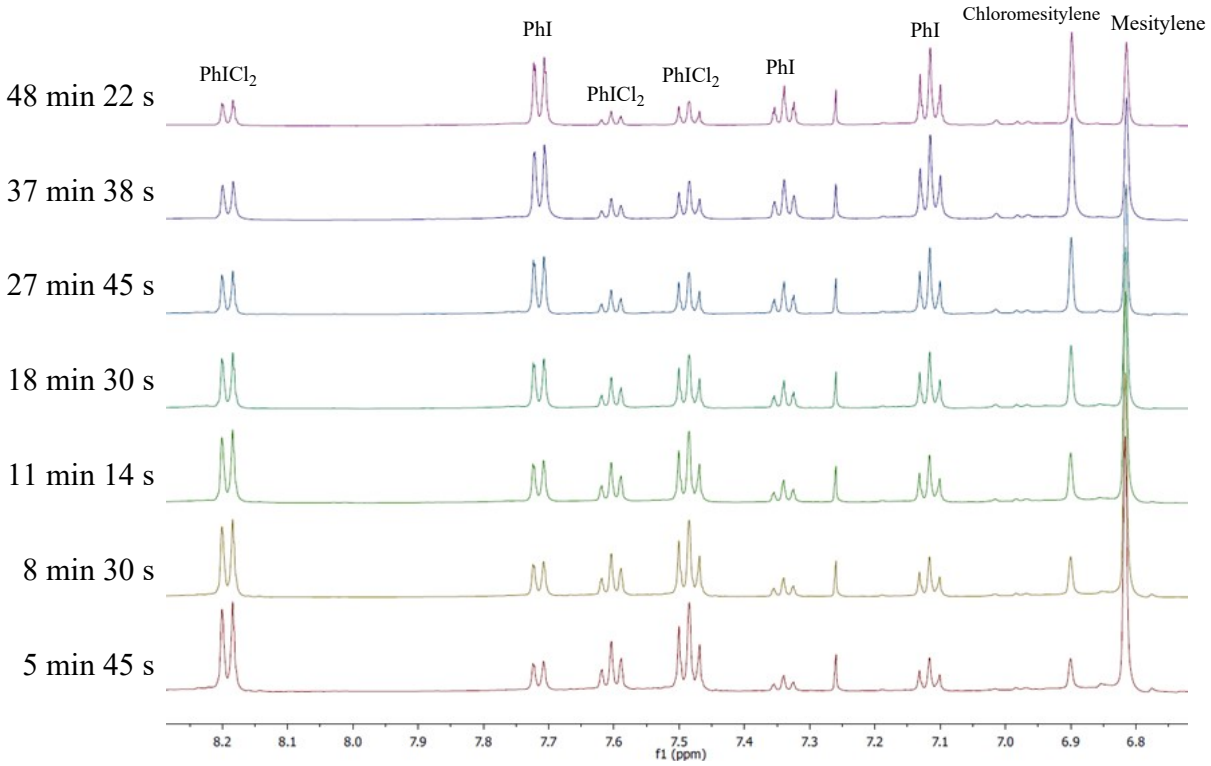

Figure S 17: ^{1}H NMR spectrum of reaction of 90.9 mM $PhICl_2$ and 90.9 mM mesitylene in presence of 1 mol% TBACl in $CDCl_3$ over time.

e) Order of Reaction w.r.t. Mesitylene

Figure S 18: ^{1}H NMR spectrum of reaction of 90.9 mM $PhICl_2$ and 90 mM mesitylene in presence of 0.455 mM (0.5 mol%) TBACl in $CDCl_3$ over time.

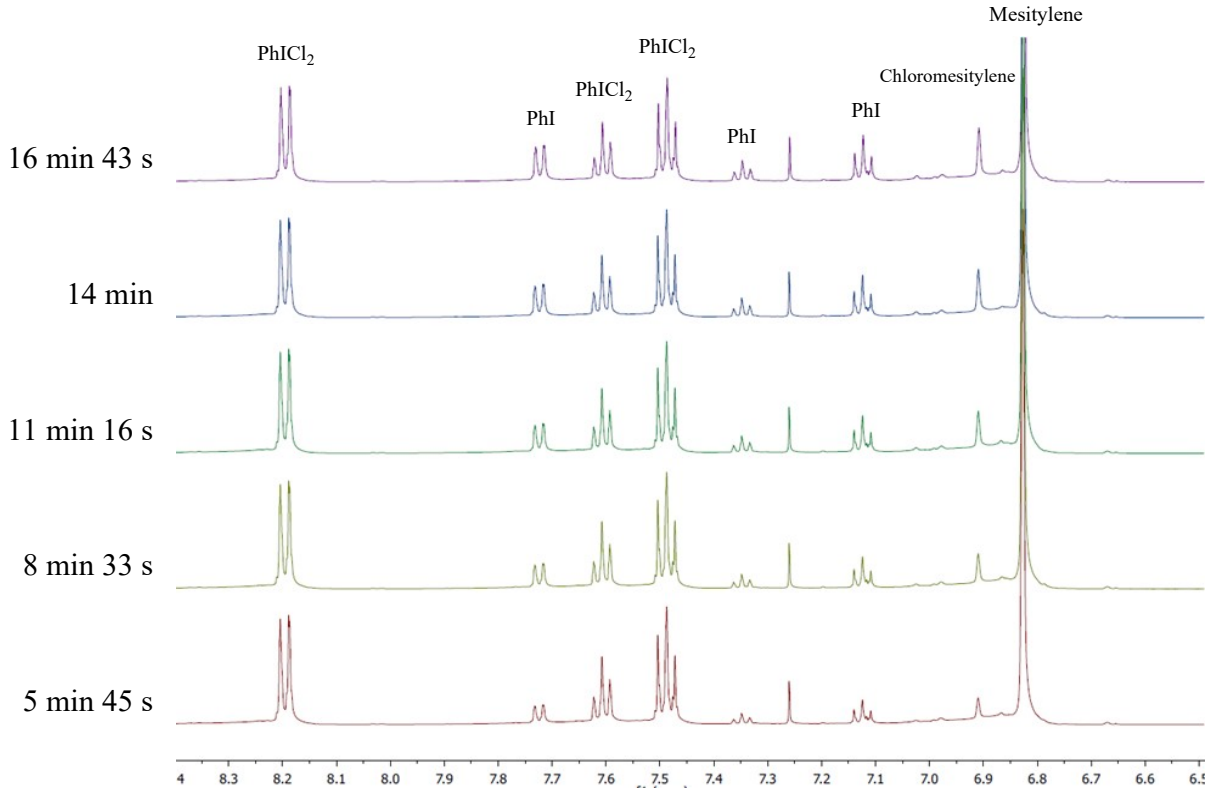

Figure S 19: ^{1}H NMR spectrum of reaction of 90.9 mM $PhICl_2$ and 180 mM mesitylene in presence of 0.455 mM (0.5 mol%) TBACl in $CDCl_3$ over time.

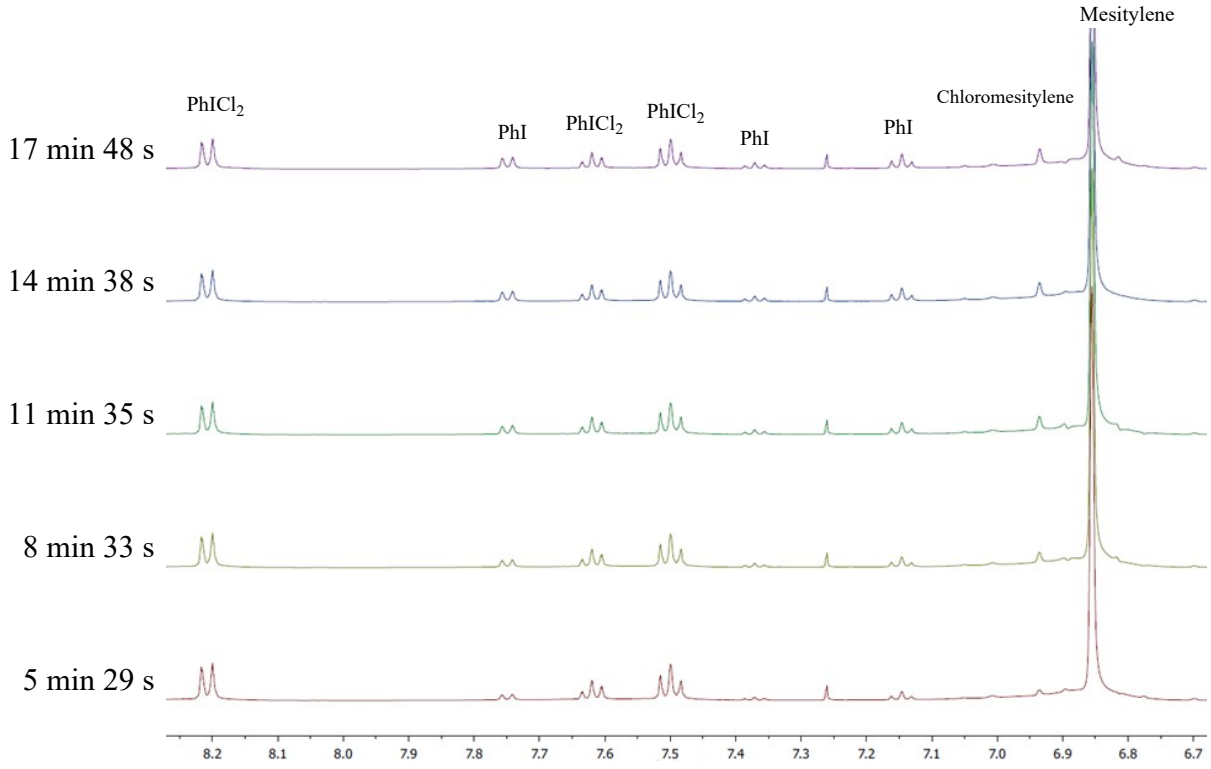

Figure S 20: ^{1}H NMR spectrum of reaction of 90.9 mM $PhICl_2$ and 360 mM mesitylene in presence of 0.455 mM (0.5 mol%) TBACl in $CDCl_3$ over time.

f) Order of Reaction w.r.t. Pyridine

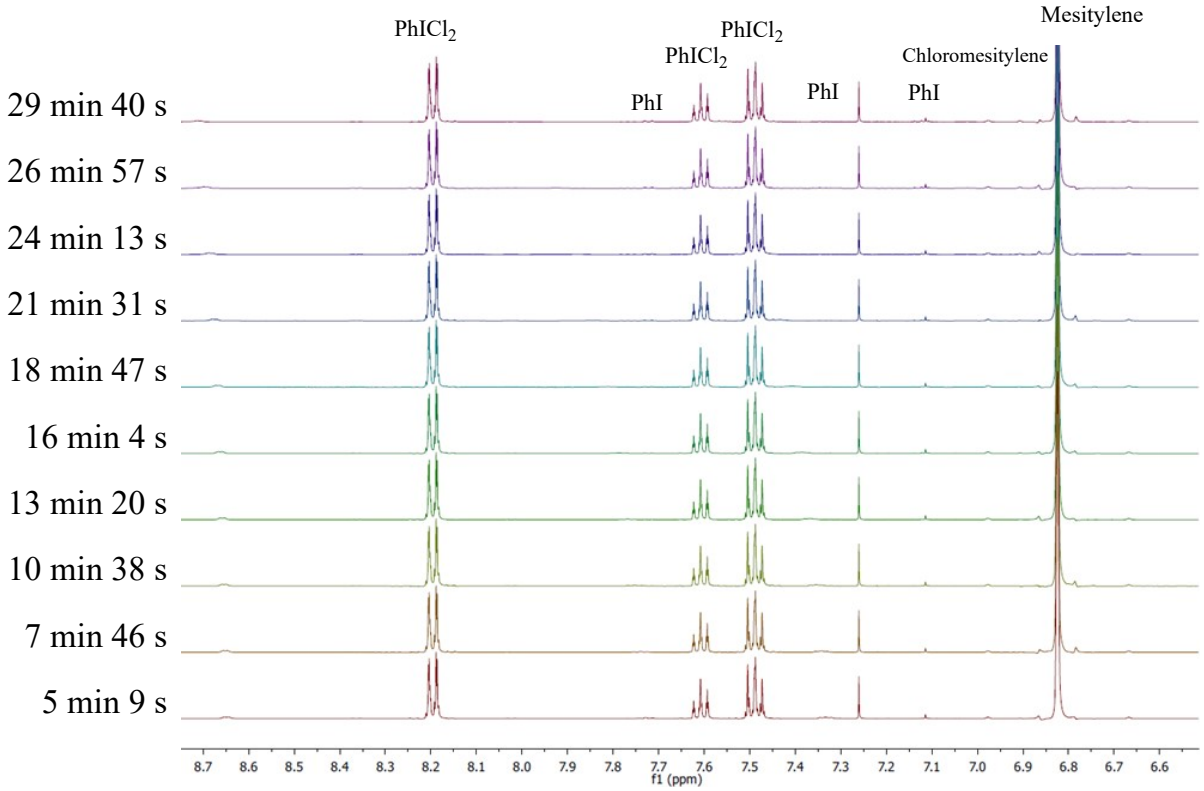

Figure S 21: ^{1}H NMR spectrum of reaction of 48 mM $PhICl_2$ and 134.2 Mm mesitylene in presence of 5 mol% pyridine in $CDCl_3$ over time.

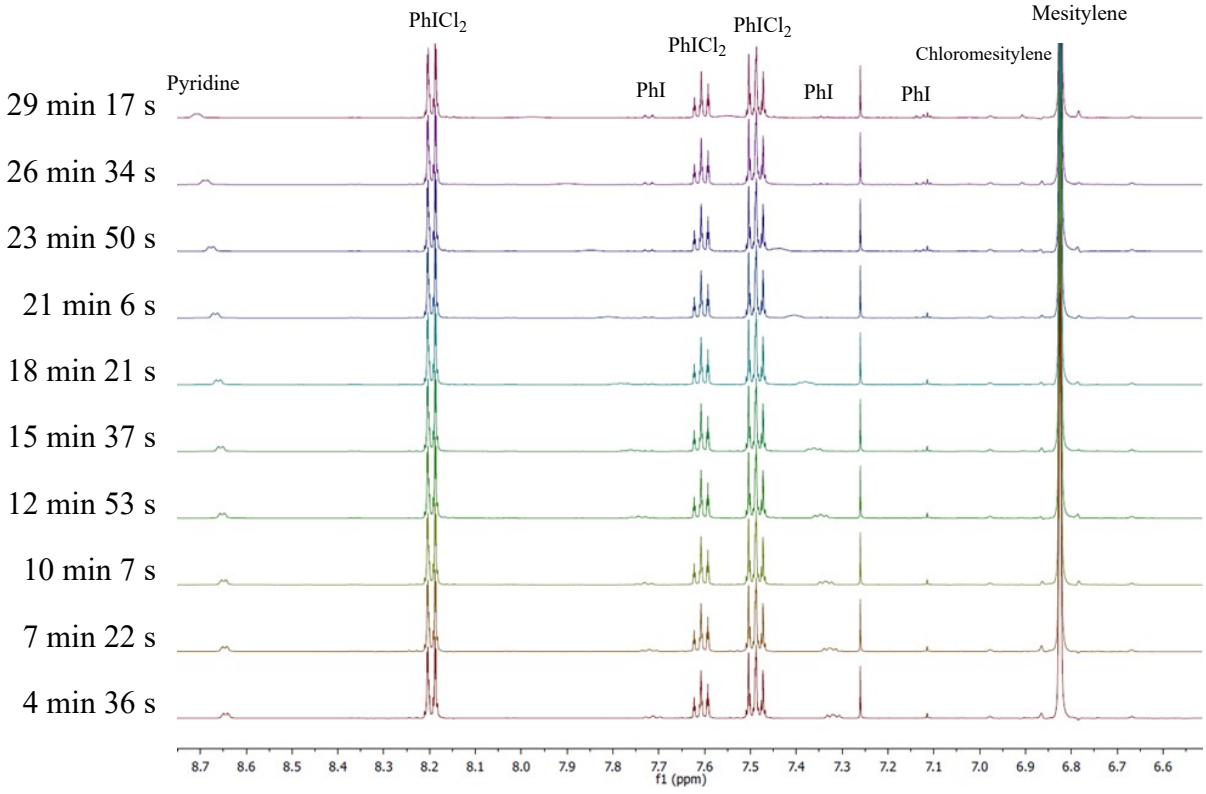

Figure S 22: ^{1}H NMR spectrum of reaction of 48 mM $PhICl_2$ and 134.2 Mm mesitylene e in presence of 10 mol% pyridine in $CDCl_3$ over time.

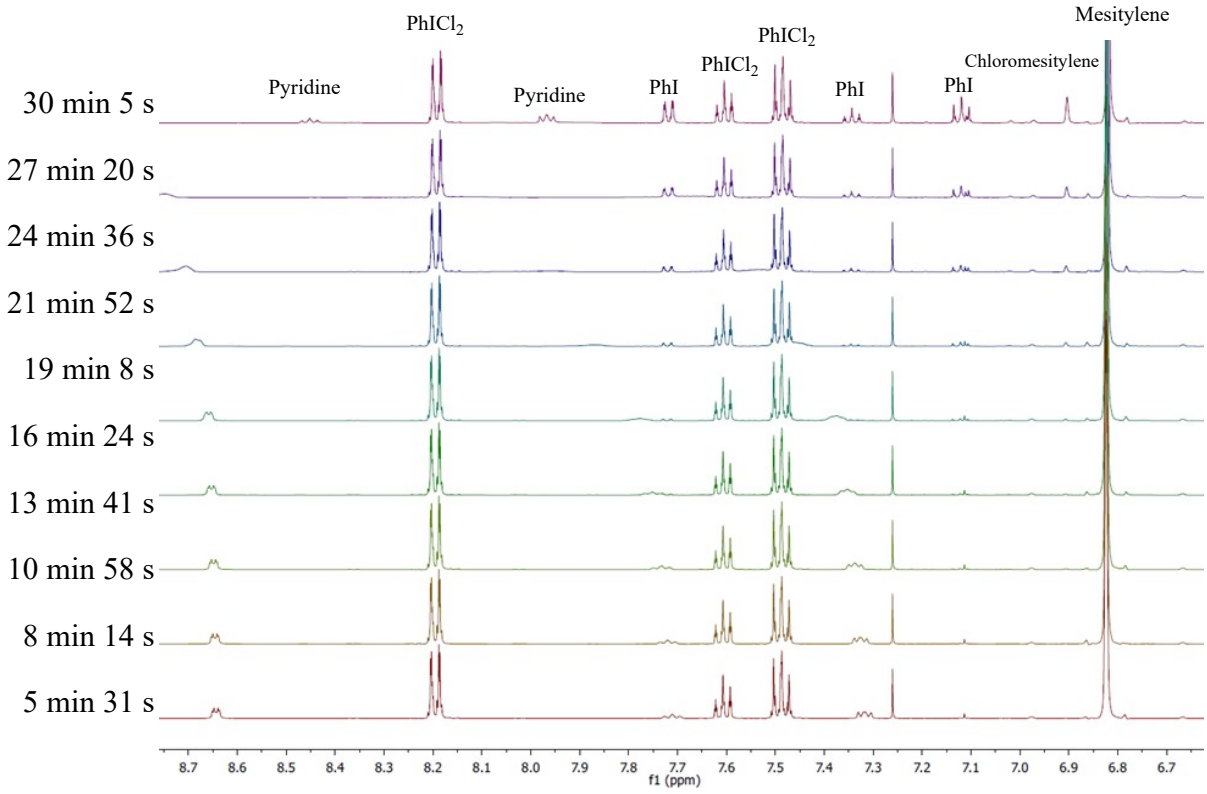

Figure S 23: ^{1}H NMR spectrum of reaction of 48 mM $PhICl_2$ and 134.2 Mm mesitylene in presence of 20 mol% pyridine in $CDCl_3$ over time.

g) Order of Reaction w.r.t. Anisole

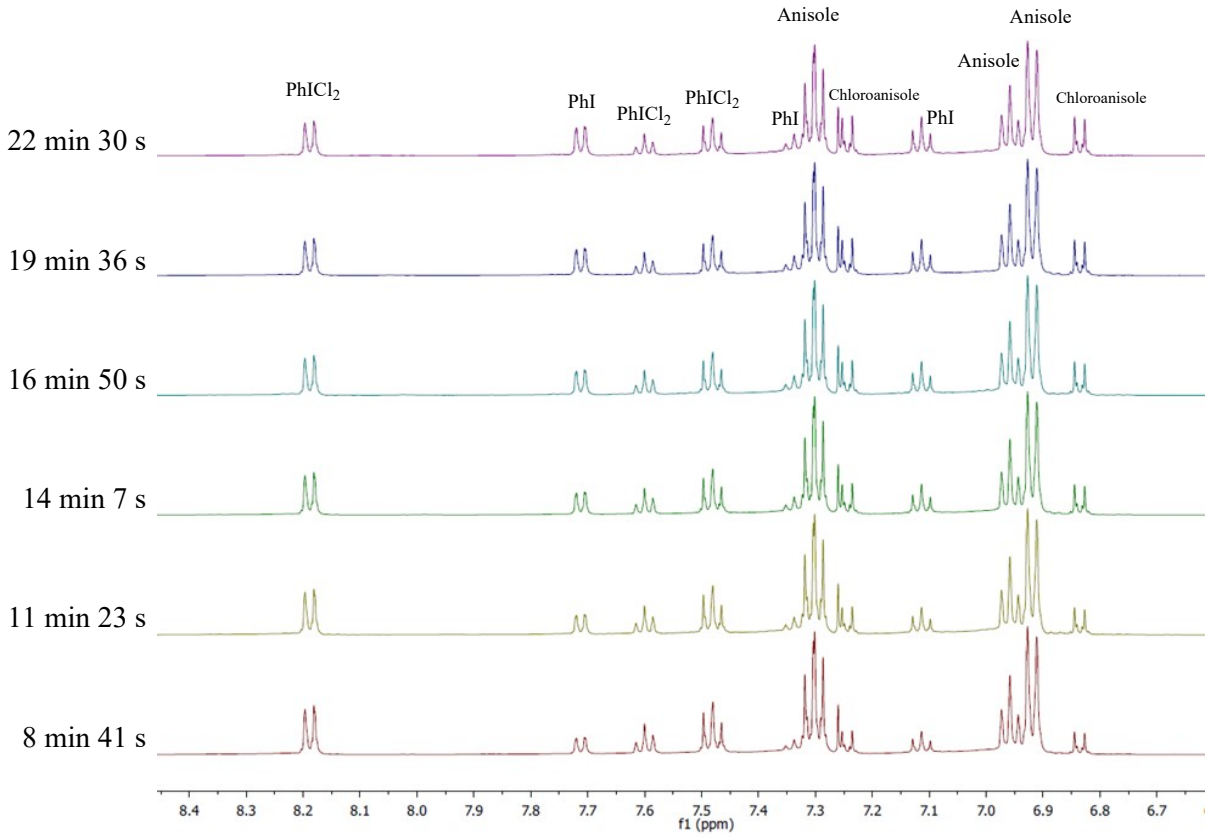

Figure S 24: ^{1}H NMR spectrum of reaction of 60.6 mM $PhICl_2$ and 121 mM anisole in presence of 0.606 mM (1mol%) TBACl in $CDCl_3$ over time.

h) VT NMR

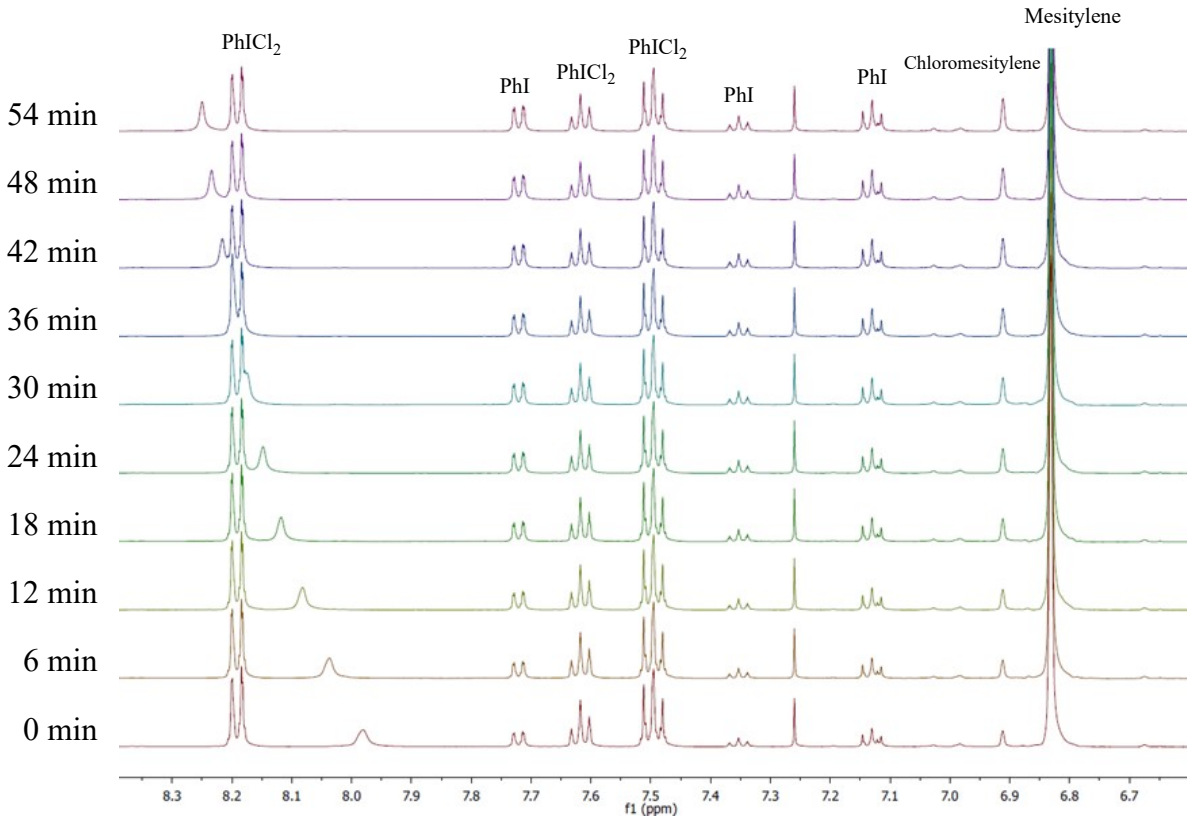

Figure S 25: ^{1}H NMR spectrum of reaction of 60 mM $PhICl_2$ and excess mesitylene in presence of 0.5 mol% TBACl in $CDCl_3$ at 278 K over time.

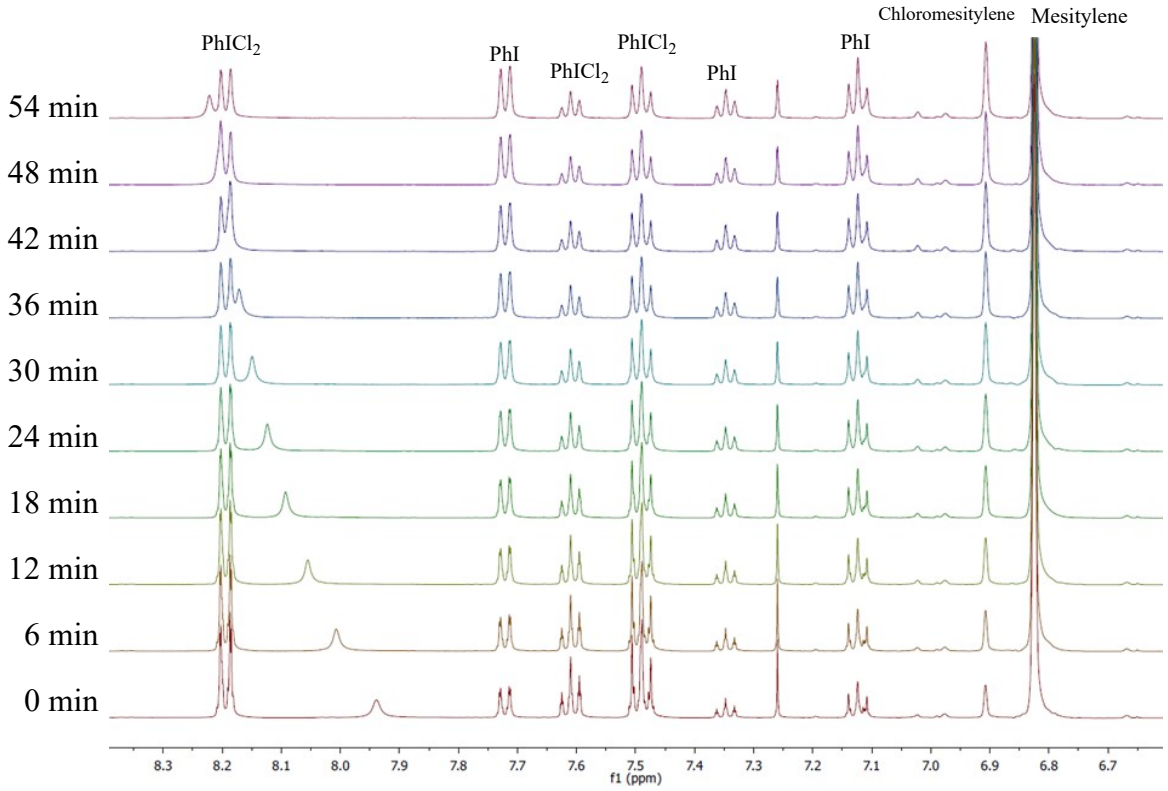

Figure S 26: ^{1}H NMR spectrum of reaction of 60 mM $PhICl_2$ and excess mesitylene in presence of 0.5 mol% TBACl in $CDCl_3$ at 293 K over time.

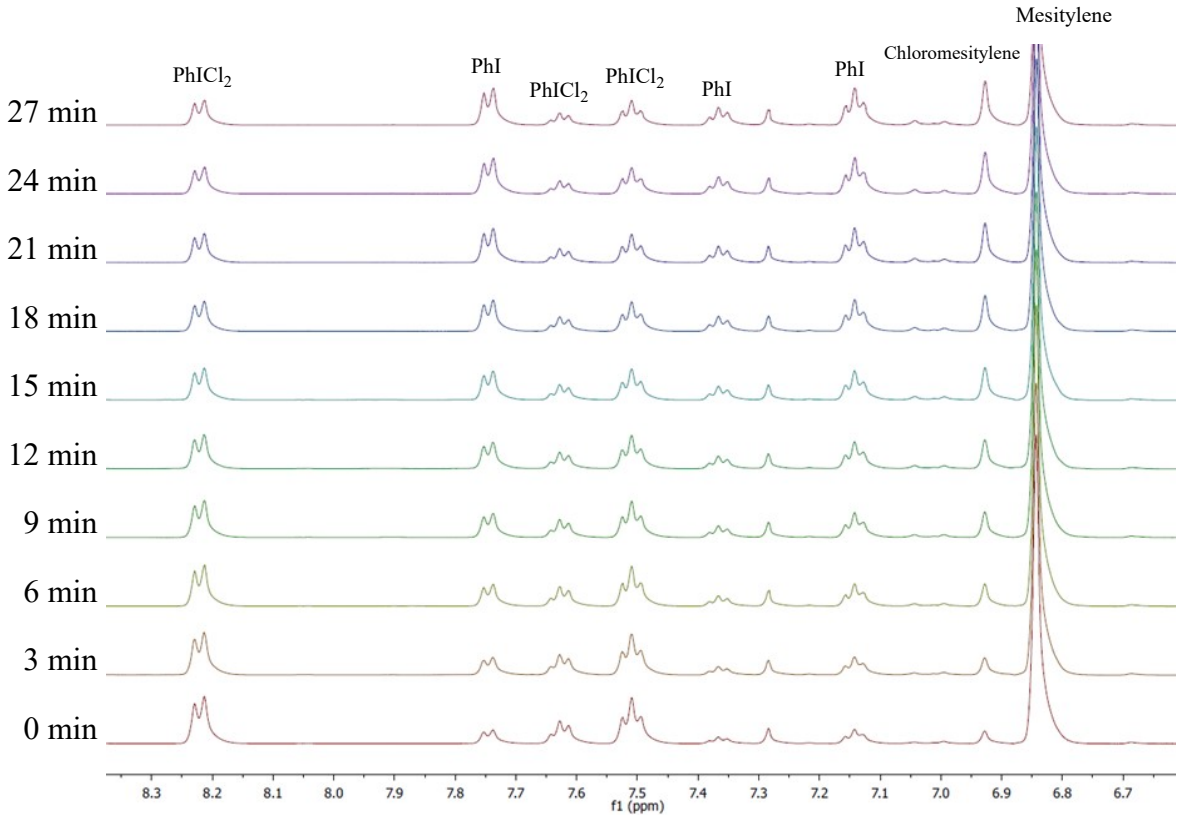

Figure S 27: ^{1}H NMR spectrum of reaction of 60 mM $PhICl_2$ and excess mesitylene in presence of 0.5 mol% TBACl in $CDCl_3$ at 308 K over time.

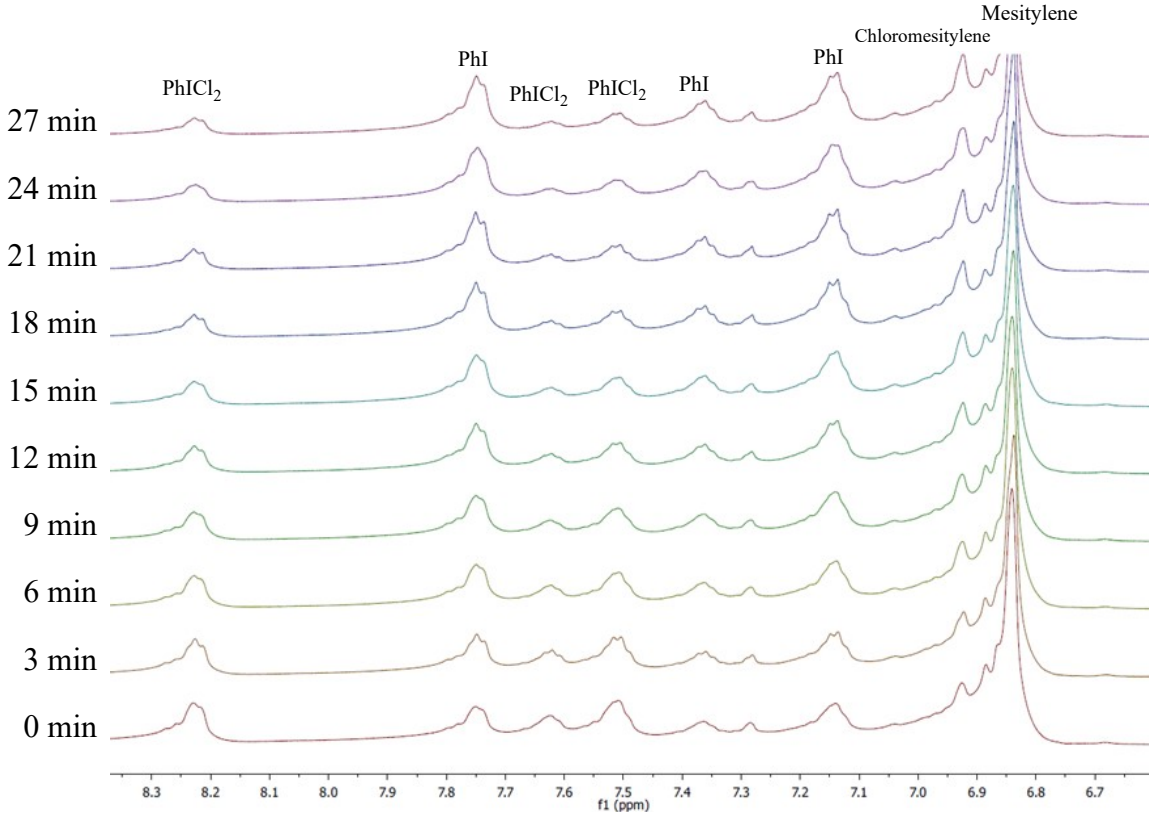

Figure S 28: ^{1}H NMR spectrum of reaction of 60 mM $PhICl_2$ and excess mesitylene in presence of 0.5 mol% TBACl in $CDCl_3$ at 318 K over time.

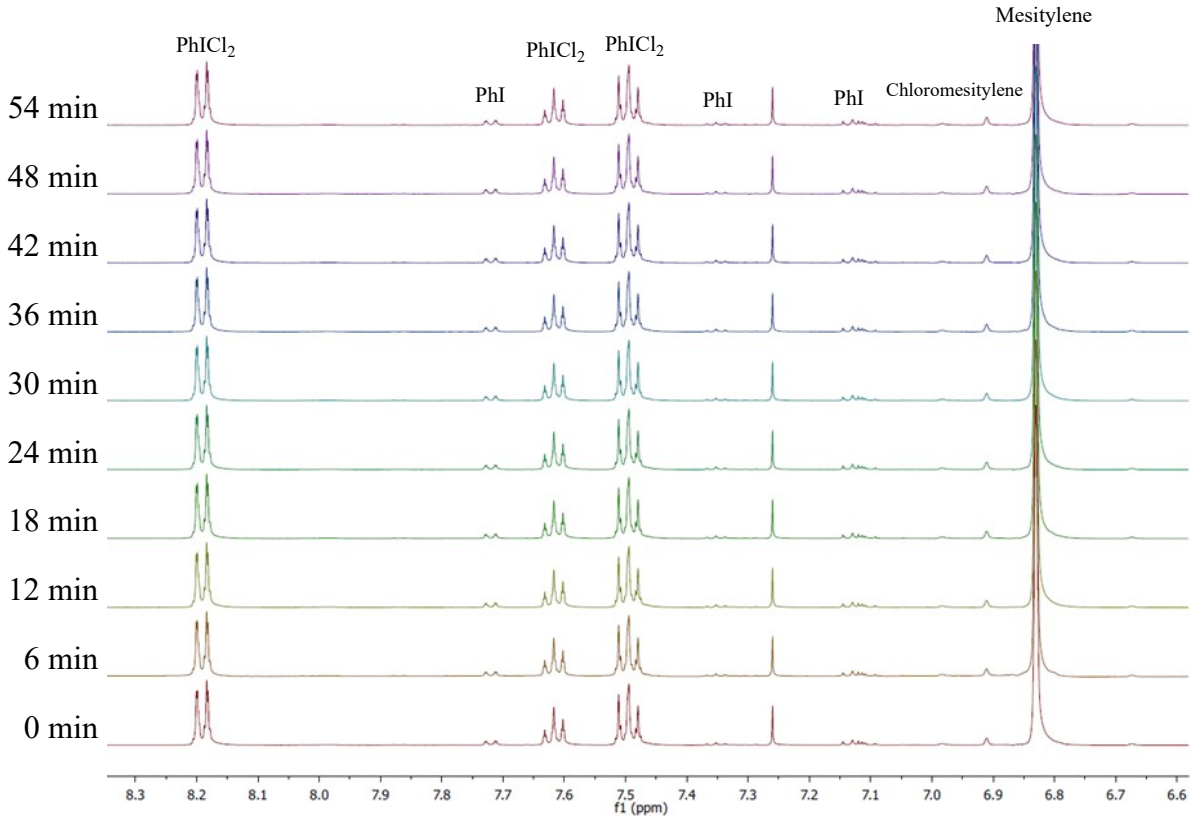

Figure S 29: ^{1}H NMR spectrum of reaction of 60 mM $PhICl_2$ and excess mesitylene in presence of 1 mol% pyridine in $CDCl_3$ at 278 K over time.

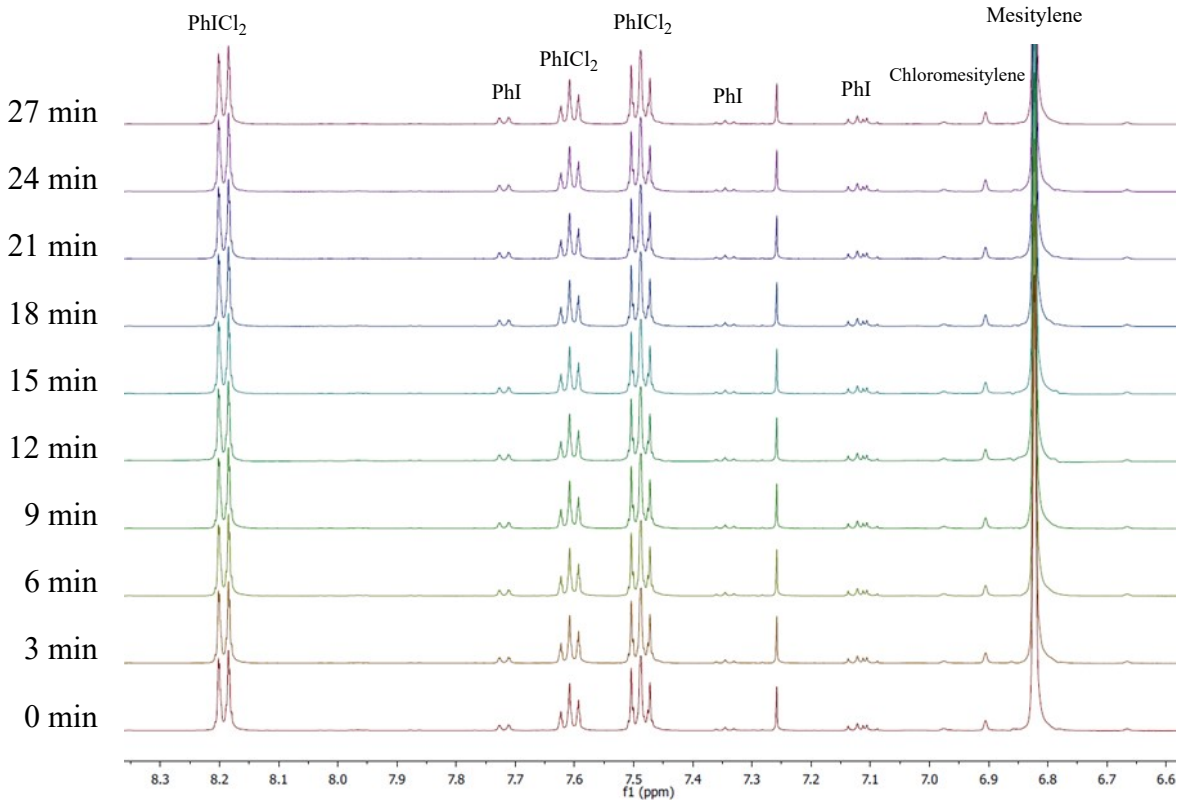

Figure S 30: ^{1}H NMR spectrum of reaction of 60 mM $PhICl_2$ and excess mesitylene in presence of 1 mol% pyridine in $CDCl_3$ at 293 K over time.

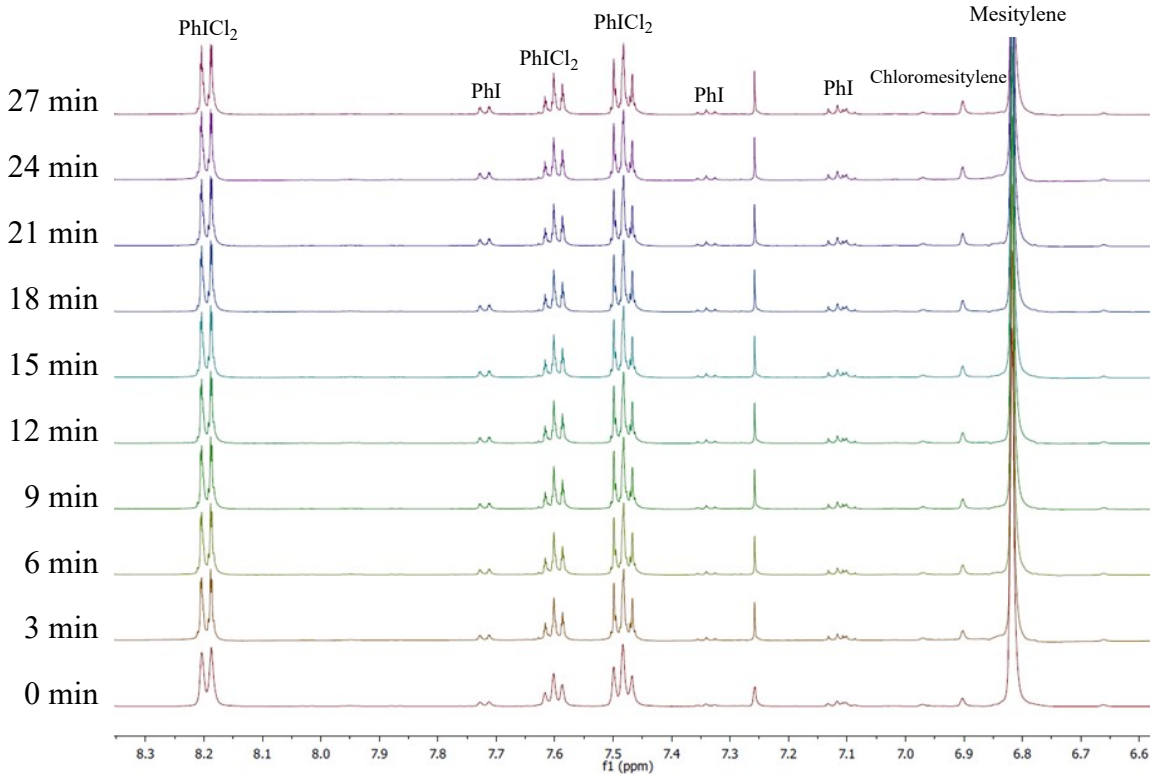

Figure S 31: ^{1}H NMR spectrum of reaction of 60 mM $PhICl_2$ and excess mesitylene in presence of 1 mol% pyridine in $CDCl_3$ at 308 K over time.

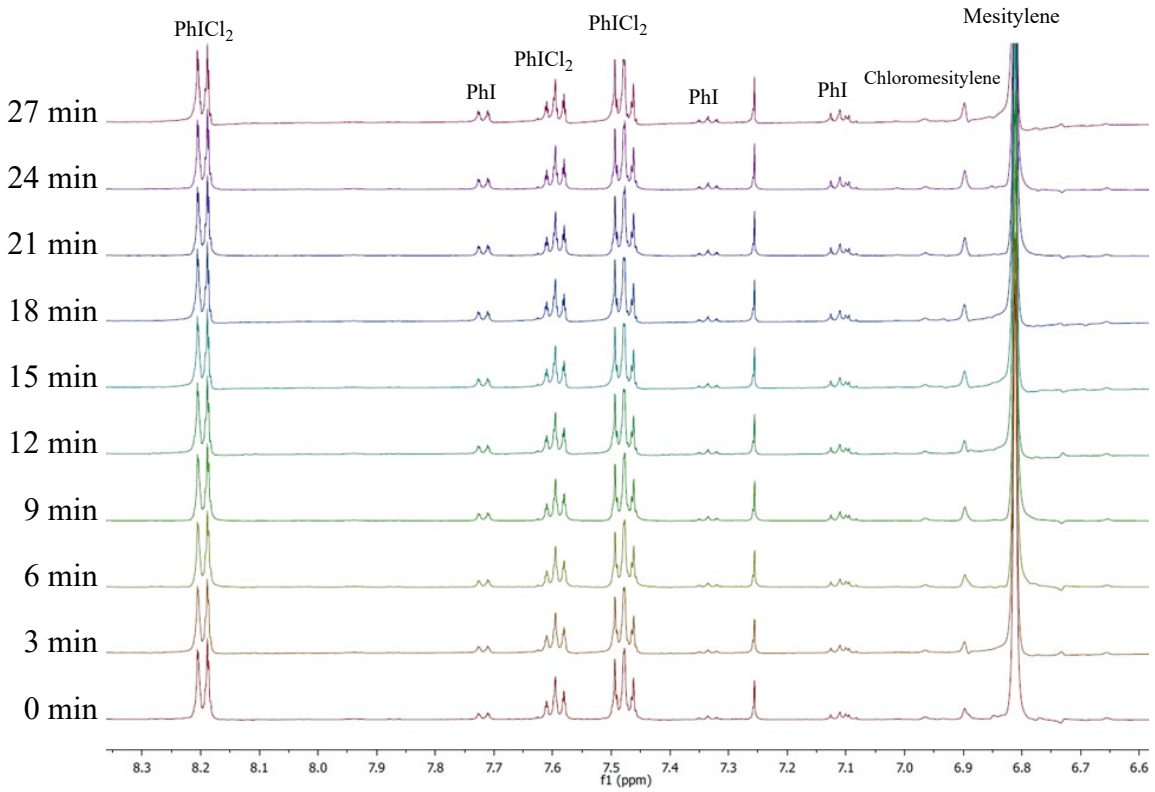

Figure S 32: ^{1}H NMR spectrum of reaction of 60 mM $PhICl_2$ and excess mesitylene in presence of 1 mol% pyridine in $CDCl_3$ at 318 K over time.

1.4 Kinetic Calculations and data

a) Comparison between mesitylene and anisole

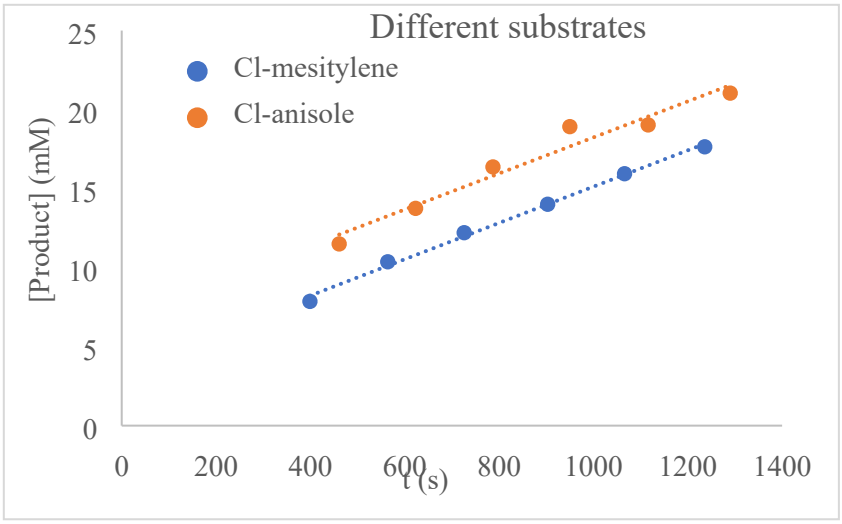

Figure S 33: Comparison of rate of reaction obtained for mesitylene and anisole. Experimental conditions; [PhICl2]: 60.6 mM [TBACl]: 0.606 mM (1 mol%) [Mesitylene]: 121 mM [Anisole]: 121 mM.

b) Log k

$$\log \frac{[PhICl2]}{[PhICl2]0} = kt$$

a. TBACl

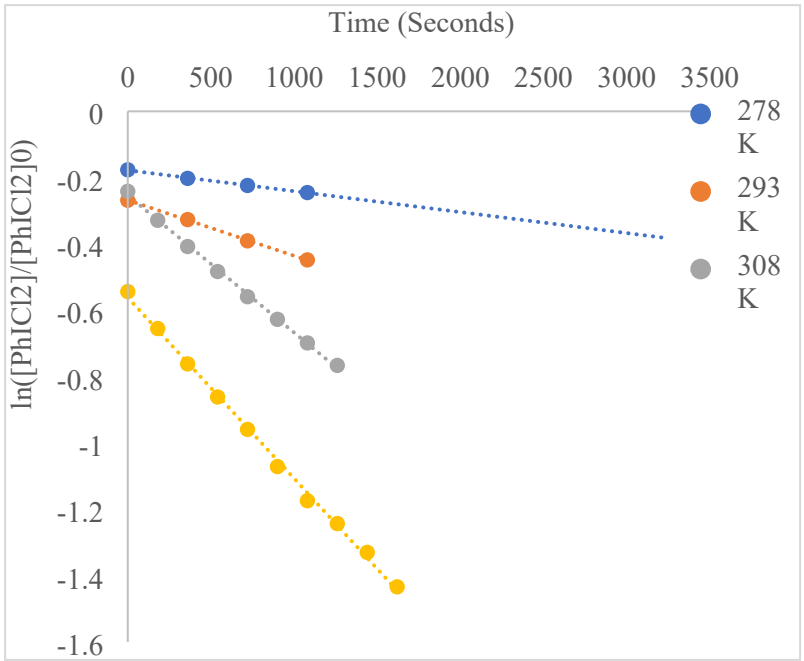

Figure S 34: Plot of ln([$PhICl_2$]/[$PhICl_2$]$_0$) vs. time (seconds) at variable temperature for reaction of $PhICl_2$ with mesitylene in presence of 0.5% TBACl. The slope of graph gives rate of reaction. Experimental conditions: [$PhICl_2$] 60.6 mM; [TBACl] 0.5 mol%; excess [Mesitylene].

Table S 1: Rate constant for reaction of $PhICl_2$ and mesitylene in presence of 0.5 mol% TBACl at variable temperatures.

Temperature (K)	Rate Constant (k) (Slope of graph)
273	0.210 ± 0.01345
298	0.550 ± 0.01912
308	1.374 ± 0.04752
318	1.812 ± 0.08274

b. Pyridine

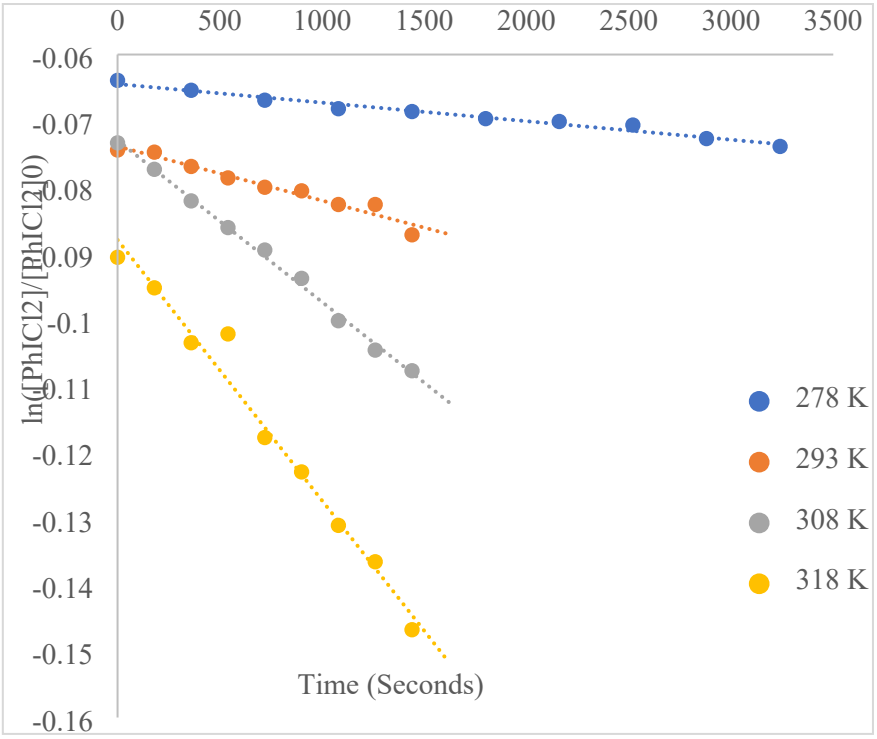

Figure S 35: Plot of $ln([PhICl_2]/[PhICl_2]_0)$ vs. time (seconds) at variable temperature for reaction of $PhICl_2$ with mesitylene in presence of 1 mol% pyridine. The slope of graph gives rate of reaction. Experimental conditions: $[PhICl_2]$ 60.6 mM; [pyridine] 1 mol%; excess [Mesitylene].

Table S 2: Rate constant for reaction of $PhICl_2$ and mesitylene in presence of 1 mol% pyridine at variable temperatures.

Temperature (K)	Rate Constant (k) (Slope of graph)
273	0.005 ± 0.00075
298	0.015 ± 0.00433
308	0.036 ± 0.00276
318	0.059 ± 0.01258

1. Activation Energy (ΔE_a) calculation using Arrhenius plots

$$\ln(k) = \frac{-\Delta Ea}{RT} + ln(A)$$

$$\text{Slope of reaction} = \frac{-\Delta Ea}{RT}$$

a. TBACl

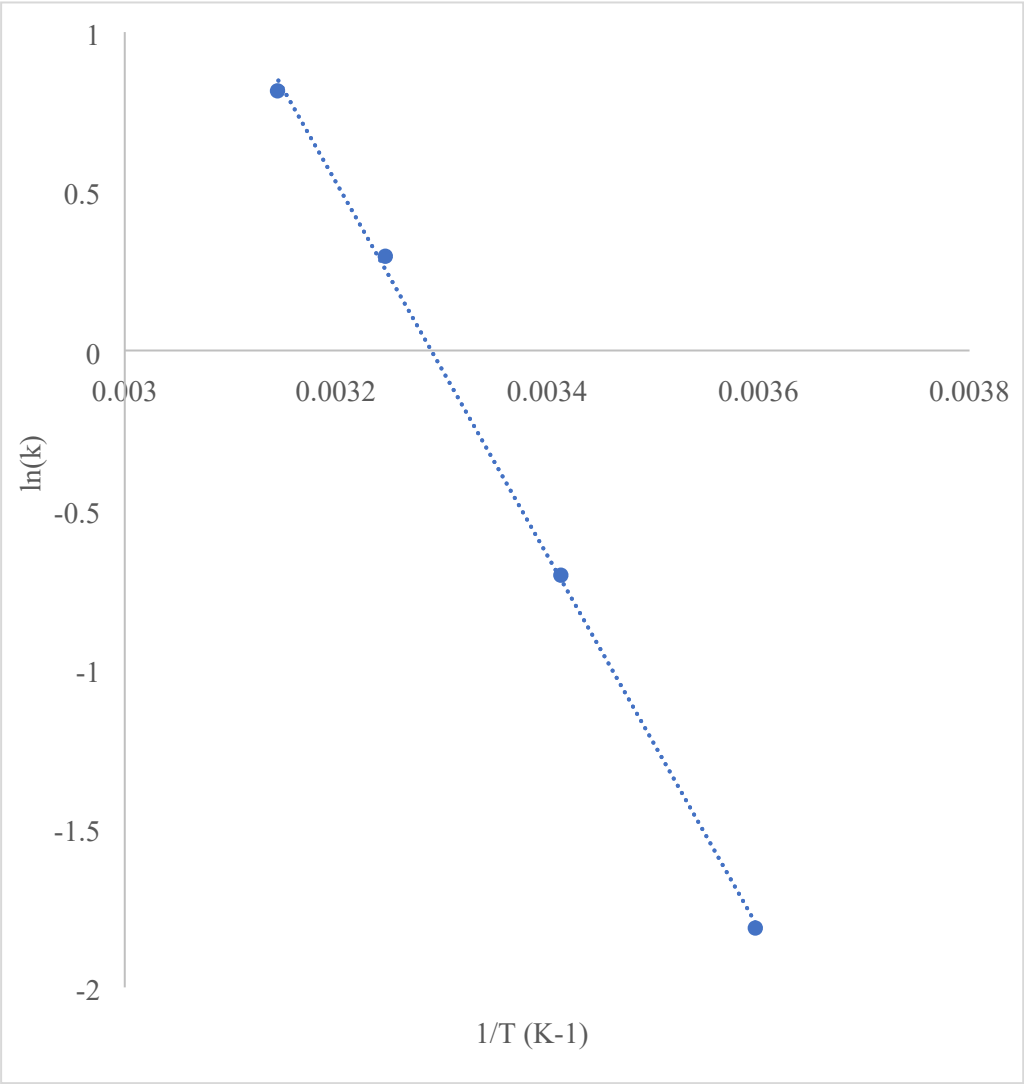

Figure S 36: Plot of ln(k) vs. 1/T (K^{-1}) for reaction of $PhICl_2$ with mesitylene in presence of 0.5 mol% TBACl. Experimental conditions: [$PhICl_2$] 60.6 mM; [TBACl] 0.5 mol%; excess [Mesitylene].

Table S 3: Activation Energy (ΔE_a) for reaction of $PhICl_2$ and mesitylene in presence of 0.5 mol% TBACl.

Temperature (T) (K)	1/T (K^{-1})	Rate Constant (k)	ln(k)	Slope of graph	Activation Energy (ΔE_a) (kJ/mol)
273	0.0036	0.210	-1.562 ± 0.064	-5855.05	44 ± 2
298	0.0034	0.550	-0.599 ± 0.035		
308	0.0032	1.374	0.318 ± 0.035		

318	0.0031	1.812	0.595 ± 0.046		

b. Pyridine

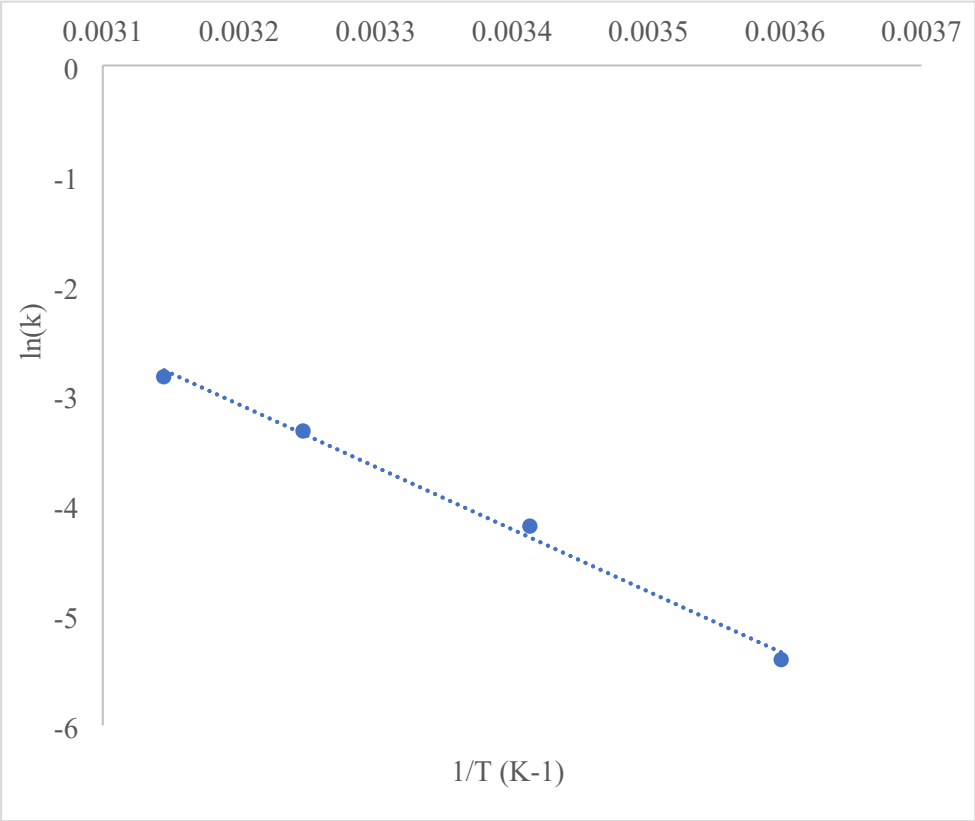

Figure S 37: Plot of ln(k) vs. 1/T (K^{-1}) for reaction of $PhICl_2$ with mesitylene in presence of 0.5 mol% TBACl. Experimental conditions: [$PhICl_2$] 60.6 mM; [TBACl] 0.5 mol%; excess [Mesitylene].

Table S 4: Activation Energy (ΔE_a) for reaction of $PhICl_2$ and mesitylene in presence of 1 mol% pyridine.

Temperature (T) (K)	1/T (K^{-1})	Rate Constant (k)	ln(k)	Slope of graph	Activation Energy (ΔE_a) (kJ/mol)
273	0.0036	0.005	-5.403 ± 0.167	-5672.87	46 ± 2
298	0.0034	0.015	-4.189 ± 0.254		
308	0.0032	0.036	-3.323 ± 0.076		
318	0.0031	0.059	-2.831 ± 0.213		

References

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