Supporting Information for:

Remote *meta*-Selective C-H Bromination of Arenes Using a Recyclable Ru-based Aminopropyl Bifunctional PMO with Robust Imidazolium Bridges

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Contents:

Experimental Section

All chemicals including (Chloromethyl)triethoxy silane (CMTES), sodium hydride (95 %), Pluronic P-123, tetraethyl orthosilicate (TEOS), hydrochloric acid (37%), (3-aminopropyl)trimethoxysilane(APTMS), ruthenium(III) chloride trihydrate, potassium perrhenate and also solvents were purchased from Sigma-Aldrich, Merck, and TCI (Tokyo Chemical Industry) Companies. All the chemicals were used without additional purification. Philips CM-200 and Titan Krios transmission electron microscopes were utilized for studying the pore system of the materials. The nitrogen adsorption-desorption analyses were achieved with a BELSORP-MAX analyzer at 77 K. Degasification was operated for all materials at 353 K for 6 h before the assessment. The specific surface area of the samples was determined from the BET plot at the relative pressures (P/P0) of 0.05-0.15, and the pore size distribution (PSD) was assessed from the adsorption branch using the Barrett-Joyner-Halenda (BJH) and DH methods. Moreover, total pore volume was allocated by the adsorbed volume at P/P0 ≈ 0.995. The surface morphology of the materials was investigated with a TeScan-Mira III ultrahigh resolution cold field emission scanning electron microscope (FESEM). XPS spectra of the materials were obtained by α-Kratos Analytical X-ray photoelectron spectrometer. To correct possible deviation caused by electric charge, the C1s line at 285.0 eV was used

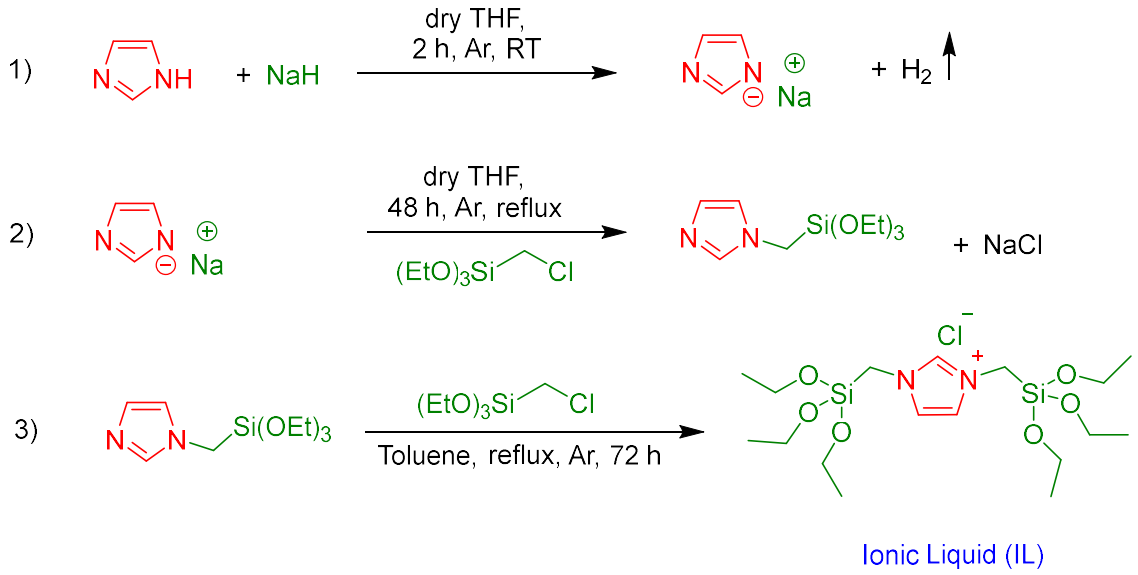
as the internal standard. The main elemental composition was measured using vario-EL CHNS instrument. Thermogravimetric analysis (TGA) was achieved by a NETZSCH STA-409 PC/PG instrument between the temperatures of 25 to 600 °C under O_2 and N_2 atmospheres. Fourier transform infrared (FTIR) spectrum was attained by a Bruker vector device in the ranges of 400 and 4000 cm-1. NMR spectra were reported with a Bruker instrument (1H frequency: 400 MHz, 13C frequency: 100 MHz). Cross-polarization (CP) technique was used for both ^{13}C and ^{29}Si spectra, which were referenced to tetramethylsilane. Rigaku Japan/Ultima-IV diffractometer was used to carry out low angle X-ray diffraction (LA-XRD) analysis. GC-MS spectrums were obtained by Bruker scion 456-GC equipment. A Varian CP-3800 gas chromatograph (GC) equipped with a capillary column [Teknokroma Meta. BLOOD 2 (30 m × 0.53 mm × 2.0 μm)] and a flame ionization detector (FID) were used to analyze the initial meta-bromination reaction progressing.

Special Notice: *We are deeply committed to addressing environmental pollution and climate change. Therefore, in all conducted experiments, the solvents have been individually separated, purified according to established fractional distillation procedures, and reused in subsequent applications.*

A typical procedure for the Preparation of the 1, 3-bis(triethoxysilyl)methyl imidazolium chloride ionic liquid (BTESMICl):

The ionic liquid precursor (BTESMICl) was prepared following a modified version of our previously established protocol for the synthesis of BTMSPICl.[1] In the initial step, imidazole was recrystallized in absolute CH_2Cl_2 and dried under vacuum over silica blue at room temperature for 3 days. Subsequently, the well-dried imidazole (2 g) was combined with a mixture 0.77 g of NaH (95%) in 40 mL of freshly dried THF under an argon atmosphere. Following 2 hours of stirring at room temperature, chloromethyl triethoxysilane (CMTES, 5.4 mL) was injected to the above suspension and, the resulting mixture was refluxed for 48 hours. The resulting mixture was allowed to cool to room temperature, and the solvent was subsequently removed under reduced pressure until an oily mixture containing NaCl was obtained. Freshly dried toluene (20 mL) and CMTES (5.4 mL) were successively added to the mixture, which was then refluxed under an argon atmosphere for 72 h until a two-phase mixture of toluene and the crude ionic liquid 1, 3-bis(triethoxysilylmethyl)imidazolium chloride (BTESMICl) was obtained. The toluene phase was removed, and 50 mL of dry CH_2Cl_2 was added to eliminate precipitated NaCl. The CH_2Cl_2 phase was then transferred to a well-dried two-neck flask, and the volatiles were removed under reduced pressure to obtain the ionic liquid (BTESMICl) along with any unreacted starting material. Finally, the ionic liquid was washed several times with dry toluene (5 × 15 mL) to remove the unreacted starting

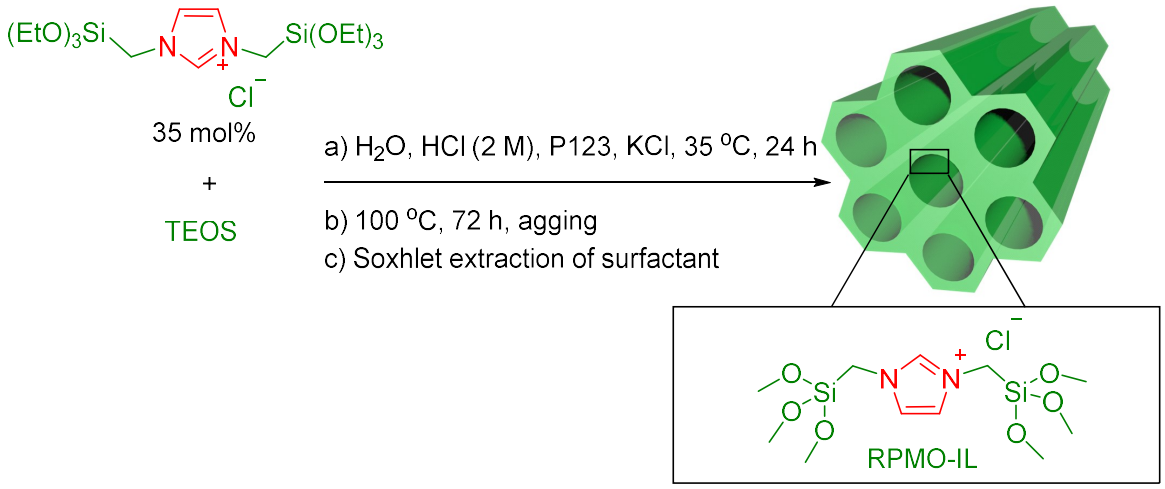
material under an argon atmosphere, yielding BTESMICl in pure form. The purity of BTESMICl was further assessed by NMR spectroscopy (Figures S23, S24).



Scheme S1: Preparation of 1, 3-bis(triethoxysilyl)methyl imidazolium chloride ionic liquid (BTESMICl).

Preparation of the Robust ordered periodic mesoporous organosilica (R-PMO-IL) with 35 % ionic liquid.

The R-PMO-IL was synthesized following a method developed within our group to produce a previously reported PMO-IL with 10% propyl imidazolium group, with minor adjustments.[1] In a typical procedure, Pluronic P123 (1.67 g) was introduced into a solution containing H_2O (10.5 g) and HCl (2 M, 46.2 g). After 4 hours, KCl (8.8 g) was added, and the mixture was stirred for an additional 2 hours at 35 °C until a homogeneous solution was obtained. A pre-mixture of tetraethyl orthosilicate (TEOS, 2.7 g, 13 mmol) and BTESMICl ionic liquid (3.2 g, 7 mmol) in dry MeOH (6 mL) was then added to the above solution, followed by continuous vigorous stirring at 40 °C for 24 hours. The resulting mixture was then subjected to an aging process at 100 °C for 72 hours without agitation. The resultant white precipitate was separated through vacuum filtration, and the surfactants were extracted using a Soxhlet apparatus by utilizing a solution comprising 100 mL ethanol and 3 mL concentrated HCl, repeated using a fresh solution four times within 12 hours. The final powder was then desiccated in an oven at 100 ºC overnight and identified as R-PMO-IL bearing high methylene imidazolium bridges of approximately 1.8-2 mmol.g-1 within the framework as determined by TGA and CHN analysis.



Scheme S2: Synthesis of robust periodic mesoporous organosilica with the ionic liquid framework (RPMO-IL).

A typical procedure for the Preparation of Ru@PMO-IL-1 catalyst[2]:

10 mg $KRuO_4$ was completely dissolved in 20 mL deionized water under sonication for 20 min followed by 1 hour of vigorous stirring at room temperature. In another flask, 200 mg of PMO-IL substrate was dispersed in 20 mL of deionized water by sonication for 20 minutes. Subsequently, the solution containing perruthenate ions was gradually added to the vigorously rotating suspension containing the PMO-IL material. The mixture was then vigorously stirred for an additional 24 hours at room temperature, and then washed with a sufficient quantity of deionized water to remove unreacted RuO_4 ions. The black crude product dried at 70°C for 24 hours. Subsequently, 100 mg of the dried RuO_4@PMO-IL IL (or RuO_4@R-PMO-IL) was dispersed in 10 mL of deionized water, and a freshly prepared $NaBH_4$ solution (0.05 M, 3 mL) was gently injected dropwise to reduce the RuO_4 ions. The resultant was washed with water and ethanol and dried at 70°C for 24 hours. The exact amount of Ru species was calculated to be 0.19 mmol/g by ICP-AES analysis.

Typical procedure for the Preparation of Ru@PMO-IL-2 and Ru@PMO-IL-3 catalysts:

17.4 mg $RuCl_3.3H_2O$ was completely dissolved in 20 mL acetone under sonication for 20 min followed by vigorous rotation at room temperature. In another flask, 200 mg of PMO-IL substrate was dispersed in 20 mL of acetone by sonication for 20 minutes. Subsequently, the solution containing ruthenium chloride was gradually added to the vigorously rotating suspension containing the PMO-IL (or R-PMO-IL) substrate. The mixture was then vigorously rotated for 24 hours at room temperature, and the resulting gray-black crude was washed with acetone (3 × 20) to remove unreacted $RuCl_3$ species and give **Ru@PMO-IL-3** catalyst. Subsequently, 100 mg of the dried **Ru@PMO-IL-3** was dispersed in 10 mL of absolute EtOH, and a freshly prepared $NaBH_4$ solution (0.05 M, 3 mL) was gently injected dropwise to reduce the $RuCl_3$

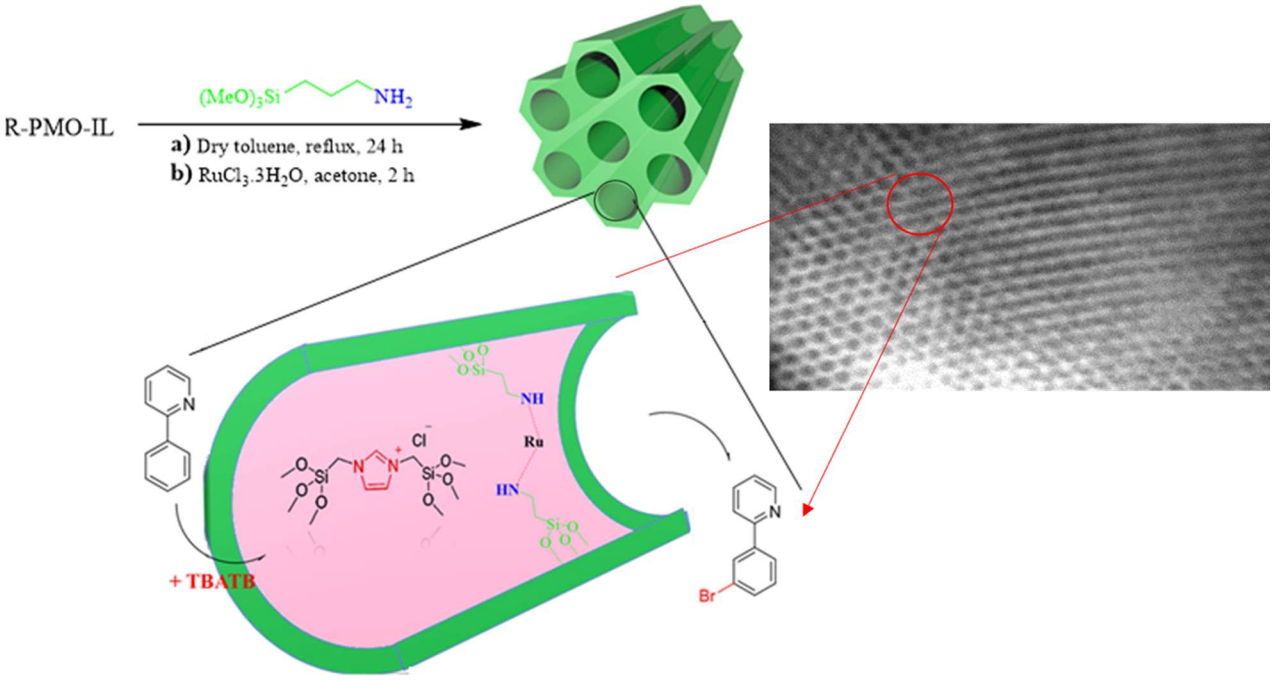
species. The resulting material was successively washed with water and ethanol and dried at 70°C for 24 hours to give **Ru@PMO-IL-2** catalyst. The exact amount of Ru species was calculated to be 0.12 mmol/g for Ru@PMO-IL-3 and 0.10 mmol/g for Ru@PMO-IL-2 respectively by ICP-AES analysis.

A typical procedure for the Preparation of $PrNH_2$@R-PMO-IL[3]:

In a typical protocol, 3-(aminopropyl)trimethoxysilane (1 mmol, 0.23 mL) was introduced into a vigorously stirred mixture of R-PMO-IL (1 g) in freshly anhydrous toluene (30 mL) under an argon atmosphere. Following 2 hours of stirring at room temperature under an argon atmosphere, the mixture underwent reflux for 16 hours. The beige solid obtained was subjected to vacuum filtered and washed multiple times with toluene (3 × 30 mL) and ethanol (3 × 30 mL) to eliminate any unreacted 3-(aminopropyl)trimethoxysilane and physisorbed residues. Subsequently, the material was dried at 105° C in an oven, resulting in the production of $PrNH_2$@R-PMO-IL in the form of a pale-yellow powder with an aminopropyl loading of 0.85 mmol g^{-1}, as determined through thermogravimetric and CHN analysis.

Preparation of Ru@$PrNH_2$@R-PMO-IL catalyst

In a typical procedure, $RuCl_3.3H_2O$ (87 mg, 0.33 mmol) was added to a well-stirred mixture of $PrNH_2$@R-PMO-IL (1 g) in acetone (30 mL) for 2 hours at room temperature under an argon atmosphere. The resulting black powder was washed with acetone (4 × 20 mL) to remove any unreacted ruthenium species, followed by drying at 70 °C for 12 hours under vacuum. The catalyst loading was determined to be 0.24 mmol.g-1 through ICP-AES analysis. Notably, this procedure allows for an increase in Ru loading of up to 0.6 mmol.g^{-1} However, for practical considerations such as accuracy in catalyst weighting, the catalyst comprising 0.24 mmol.g^{-1} was chosen for this study.



Scheme S3. Synthesis of Ruthenium catalyst supported on mesoporous organosilica (Ru@PrNH$_2$@R-PMO-IL).

Procedure for synthesis of Ackermann's catalyst (Ru@SiO$_2$)[4]

This catalyst was prepared following the procedure reported by Ackermann and his co-workers. In a typical procedure, $RuCl_3 \cdot 3H2O$ (150 mg, 0.53 mmol) was dissolved in ethanol (2.4 mL), followed by the addition of ethylene glycol (6.0 mL, 99.5% purity) and water (0.1 mL). The red-colored solution was stirred at 65 °C for 30 minutes, during which the color slightly changed to pale red. Si(OEt)4 (6.0 mL, 26.9 mmol) was then added, and the mixture was stirred for 3 hours at 65 °C. Water (3.0 mL, 167 mmol) was added while stirring at 65 °C for 75 minutes. The mixture was then stirred for 24 hours at 27 °C. The volatiles were removed under reduced pressure, and the mixture was heated to 100 °C overnight in an oven. The catalyst was dried at 100 °C in a vacuum oven. The catalyst was purified by first grinding it into a fine powder and washing it with CH_2Cl_2 (3 × 10 mL). The solid was separated by decantation after centrifugation (40 minutes, 8000 rpm). The wash phase was analyzed for residues, yielding a yellowish powder. (*The protocol text was slightly changed in order to avoid plagiarism*)

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A typical reaction procedure of selective *meta*-bromination of 2-phenylpyridine using Ru@PrNH$_2$@R-PMO-IL as catalyst (Condition A)[5]

A 5-mL two-necked round bottom flask, equipped with a condenser, was charged with Ru@PrNH$_2$@R-PMO-IL (21 mg, 0.005 mmol, 4 mol%), 2-Phenylpyridine (18 µl, 0.125 mmol, 1.0 eq), and TBATB (90 mg, 0.1875 mmol, 1.5 eq) in dry 1,4-dioxane (0.7 mL). The top of the condenser was sealed using a rubber septum. The entire system was purged three-times using vacuum-oxygen couples, and in the final stage, a balloon filled with oxygen was attached to the top of the condenser. The mixture was refluxed while gently stirring for 12 h under a balloon-filled oxygen atmosphere (625 Torr). After this period, the reaction mixture was allowed to cool to room temperature, and sodium thiosulfate (5 mL,10 wt% solution) was added and stirred for 10 minutes. The aqueous phase was subsequently extracted with ethyl acetate (3 × 10 mL). The combined organic layers were gathered and thoroughly rinsed with brine (25 mL) and water (2 × 15 mL), followed by drying over Na_2SO_4. After the removal of solvents under reduced pressure, the conversion was assessed through GC or NMR analysis. The crude product was subjected to purification via preparative TLC chromatography (solvent) to determine the isolated yield of the corresponding meta-C-H brominated products.

Important note: In those particular cases where small by-products have appeared in the product mixtures, to obtain an isolated yield of all reaction constituents, the reactions were carried out with a 0.5 mmol scale of 2-phenyl pyridine, and the crude products were combined, and the reaction products were precisely separated on the plate by a thin-layer chromatography method.

Typical reaction procedure of selective *meta*-bromination of 2-phenylpyridine using Ru@PrNH$_2$@R-PMO-IL as catalyst (Condition B)

A 5-mL two-necked round bottom flask, equipped with a condenser, was charged with Ru@PrNH$_2$@ HL-PMO-IL (21 mg, 0.005 mmol, 4 mol%), 2-Phenylpyridine (18 µl, 0.125 mmol, 1.0 eq), K_2CO_3 (35 mg, 2 eq), and TBATB (90 mg, 0.1875 mmol, 1.5 eq) in dry 1,4-dioxane (0.7 mL). The top of the condenser was sealed using a rubber septum. The entire system was purged three-times using vacuum-oxygen couples, and in the final stage, a balloon filled with oxygen was attached to the top of the condenser. The mixture was refluxed while gently stirring for 12 h under a balloon-filled oxygen atmosphere (625 Torr). After this period, the reaction mixture was allowed to cool to room temperature, and sodium thiosulfate (5 mL,10 wt% solution) was added and stirred for 10 minutes. The aqueous phase was subsequently extracted with ethyl acetate (3 × 10 mL). The combined organic layers were gathered and thoroughly rinsed with brine (25 mL) and water (2 × 15 mL), followed by drying over Na_2SO_4. After the removal of solvents under reduced pressure, the conversion was assessed through GC or NMR analysis. The crude product was subjected to purification via column chromatography (solvent) to determine the isolated yield of the corresponding meta-C-H brominated products.

Typical reaction procedure of selective meta-bromination of 1-phenylpyrazole using Ru@PrNH$_2$@R-PMO-IL as catalyst (Condition C)

The reaction was carried out under condition A (84 mg catalyst, 3 mL 1,4-dioxane, and 0.5 mmol 1-phenylpyrazole) without TBATB. The TBATB (360 mg, eq. 1.5) was dissolved in 0.8 mL of 1,4-dioxane and then injected into the above mixture 4 drops per hour during 20 hours. The reaction was then stirred for a further 4 hours under the same conditions. The reaction was cooled and after quenching the remaining TBATB with 20 mL $Na_2S_2O_3$ solution (10%), the reaction mixture was filtered under vacuum, and the catalyst was washed with ethyl acetate (3×50 mL). The filtrate was dried over sodium sulfate and concentrated under reduced pressure. Thin layer chromatography (TLC) (n-Hexane:CH_2CL_2:EtOAC - 20:5:3) was used to monitor reaction progress. The isolated yield was calculated after separating different spots on plate thin-layer chromatography.

Typical procedure for the catalyst recycling

In the initial run of catalyst recycling, the reaction was conducted under optimized conditions (Conditions A) using 105 mg of catalyst along with the appropriate amounts of starting materials: 90 µL (0.625 mmol)

of 2-phenylpyridine **1a** and 450 mg of TBATB. After cooling to room temperature, the reaction mixture was centrifuged for 10 minutes at 6000 rpm, allowing for the separation of the catalyst, which was then washed with 4 x 15 mL of ethyl acetate through multiple centrifugation steps. The catalyst was dried overnight at 70 °C and reused in the subsequent reaction run. The collected organic phases were successively washed with a 30 mL solution of $Na_2S_2O_3$ (10%) and then with 2 x 15 mL of water to eliminate TBATB. Finally, the product was separated and purified from the collected organic phase following the procedures outlined in previous protocols.

Run	1st	2nd	3rd	4th	5th	6th	7th
Amount of **2a**	126.0 mg	124.4 mg	124.5 mg	125.8 mg	123.0 mg	102.5 mg	72.0 mg
Yield of **2a** %	86	85	85	86	84	70	49

Typical procedure for TEMPO Test

Two typical reactions were conducted using 2-phenylpyridine (**1a**, 0.5 mmol), TBATB (360 mg, 1.5 equivalents), and Ru@PrNH$_2$@R-PMO-IL (84 mg, 4 mol%) as the catalyst. One reaction was performed in the presence of the radical scavenger (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (7.8 mg, 10 mol%), while the other was conducted without TEMPO, both under an argon atmosphere for 12 hours. No desired product was observed in the presence of TEMPO, in contrast to the 84% yield obtained in the absence of TEMPO. This result confirms the radical mechanism of the meta-bromination reaction with the ruthenium catalyst, which has been previously proposed in the literature for *meta*-C-H activation reactions of arenes[6-8].

Typical procedure for Hg poisoning test

Two typical reactions were conducted using 2-phenylpyridine (**1a**, 0.5 mmol), TBATB (360 mg, 1.5 equivalents), and Ru@PrNH$_2$@R-PMO-IL (84 mg, 4 mol%) as the catalyst under the outlined reaction conditions **A**. The yield of the first reaction, conducted in the absence of mercury, was calculated to be 58%. In the second reaction, metallic mercury (120 µL, 400 equivalents to catalyst, 8 mmol) was carefully introduced at the beginning and allowed to proceed for 6 hours as well. After cooling the second reaction to room temperature, the mercury was quenched with additional sulfur, and the crude product was washed with EtOAc (3 × 50 mL). The yield of this reaction was also calculated and compared with that of the first reaction. The nearly identical yield (60%) for the second reaction indicated that no free Ru nanoclusters were generated or leached into the solution during the catalysis.

Typical procedure for hot filtration test

A reaction was carried out using 2-phenylpyridine (**1a**, 0.5 mmol), TBATB (360 mg, 1.5 eq), and Ru@PrNH$_2$@R-PMO-IL (84 mg, 4mol%) as catalyst under oxygen for 6 hours, where the yield of **2a** was 58% by GC analysis through an standard addition method. The catalyst was then centrifuged and separated from the reaction medium and the filtrate was allowed to proceed for a further 6 hours under optimized condition A. The desired product was extracted with EtOAc (3 × 50) mL and purified by thin-layer chromatography after concentration.The yield of **2a** was measured to be 64%.

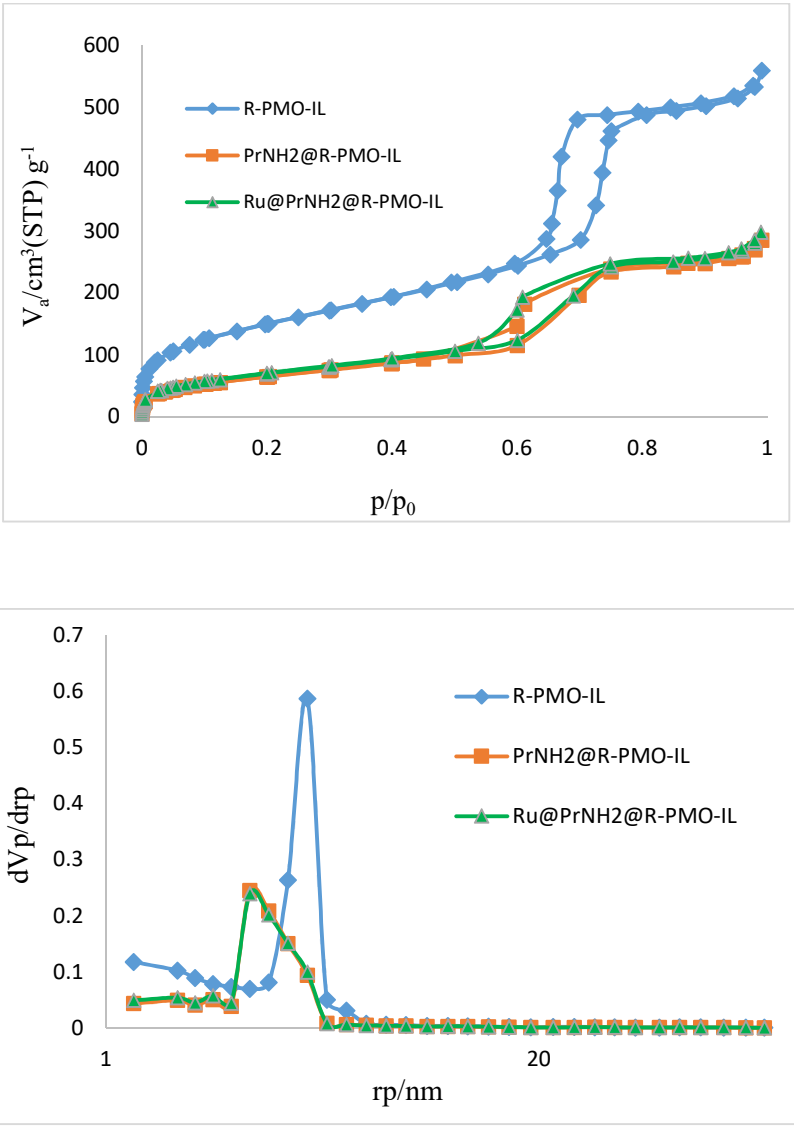
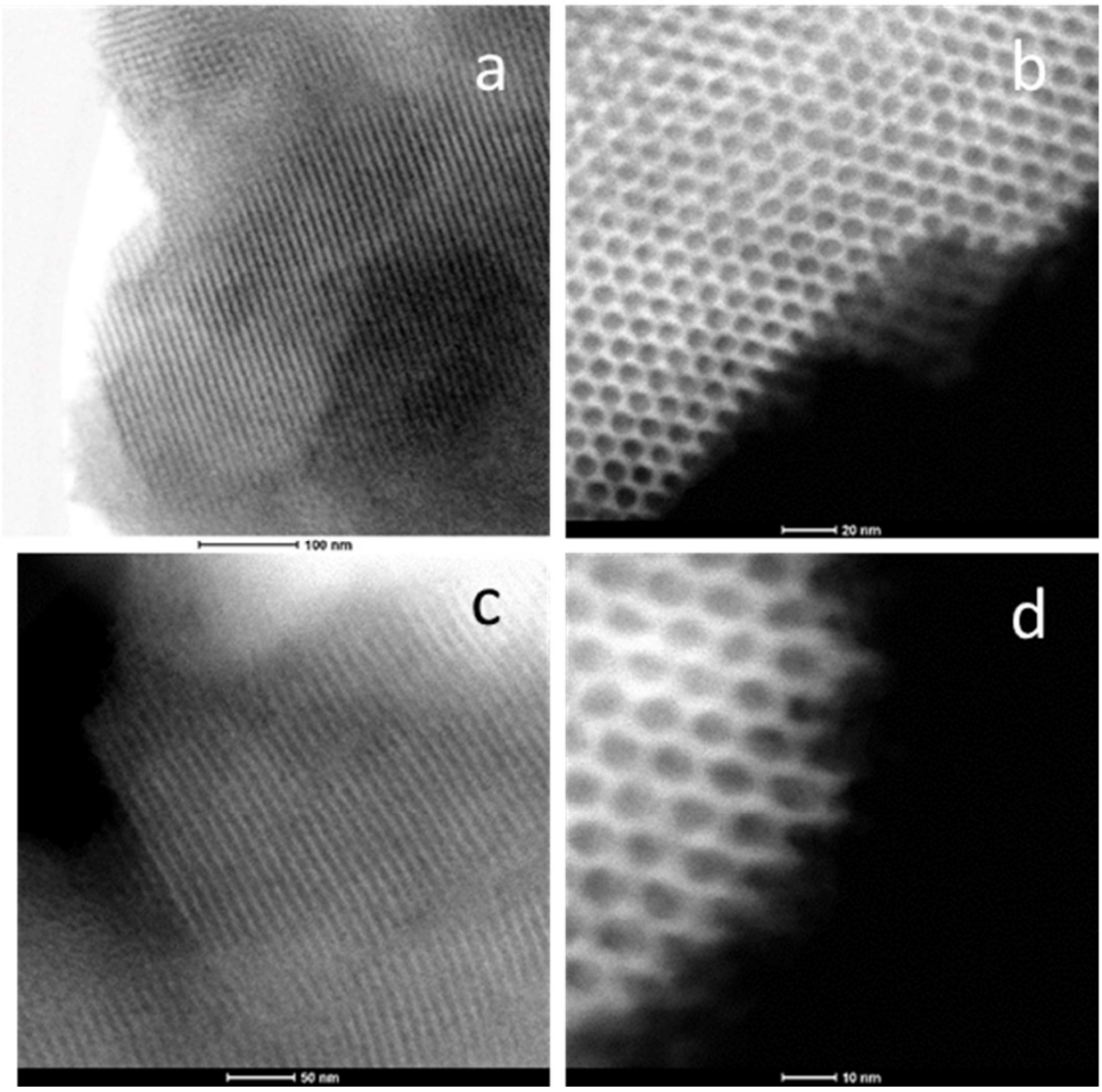


Figure S1. N_2 adsorption−desorption isotherms and BJH Pore size distributions (a and b) for R-PMO-IL (blue diamonds), PrNH$_2$@R-PMO-IL (orange squares), and Ru@PrNH$_2$@R-PMO-IL (green triangles).


a
100 nm
b
20 nm
c
50 nm
d
10 nm

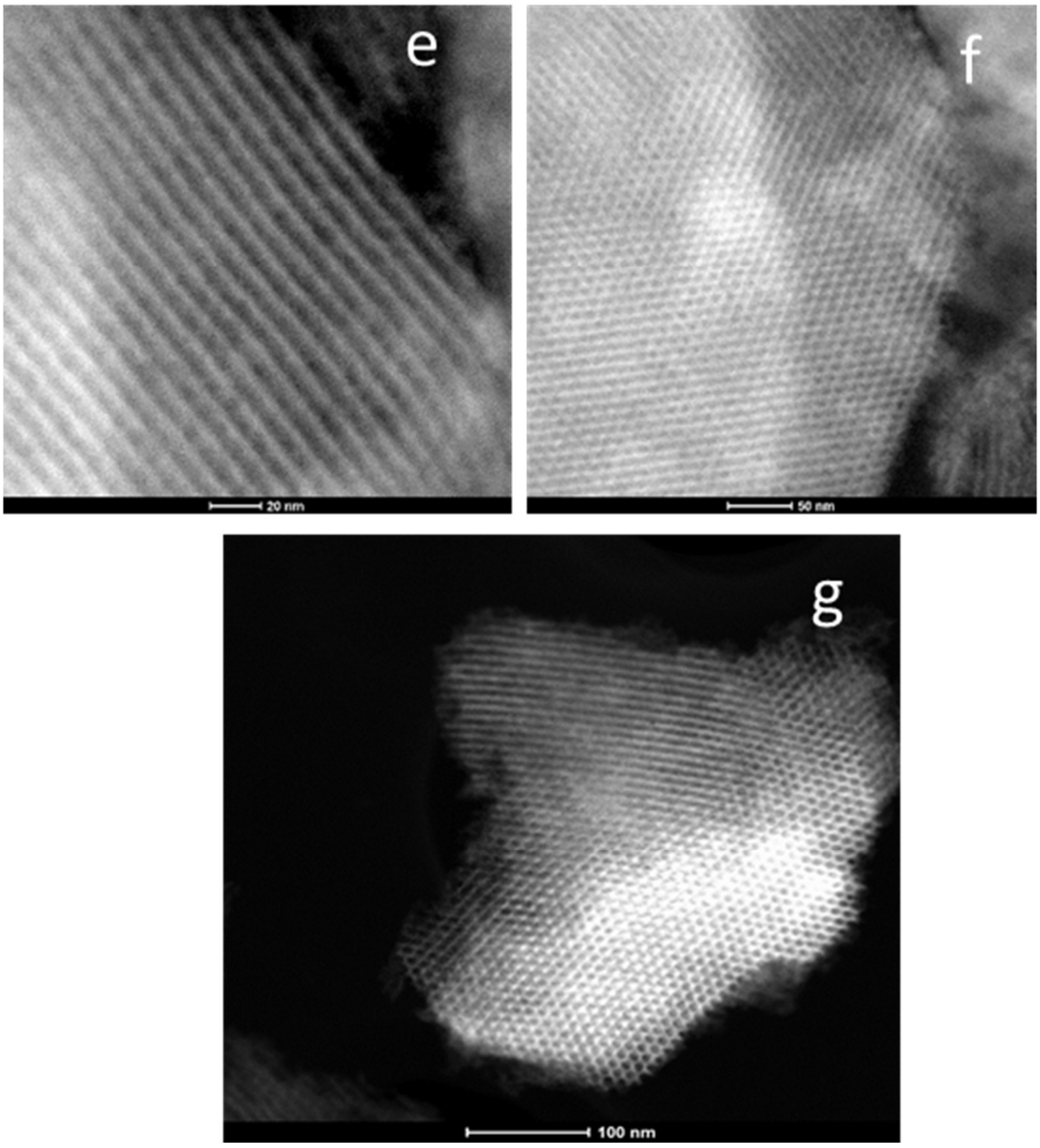


Figure S2. TEM images of R-PMO-IL (a, b), $PrNH_2$@R-PMO-IL (c, d) and Ru@$PrNH_2$@R-PMO-IL (e, f). STEM of Ru@$PrNH_2$@R-PMO-IL (g).

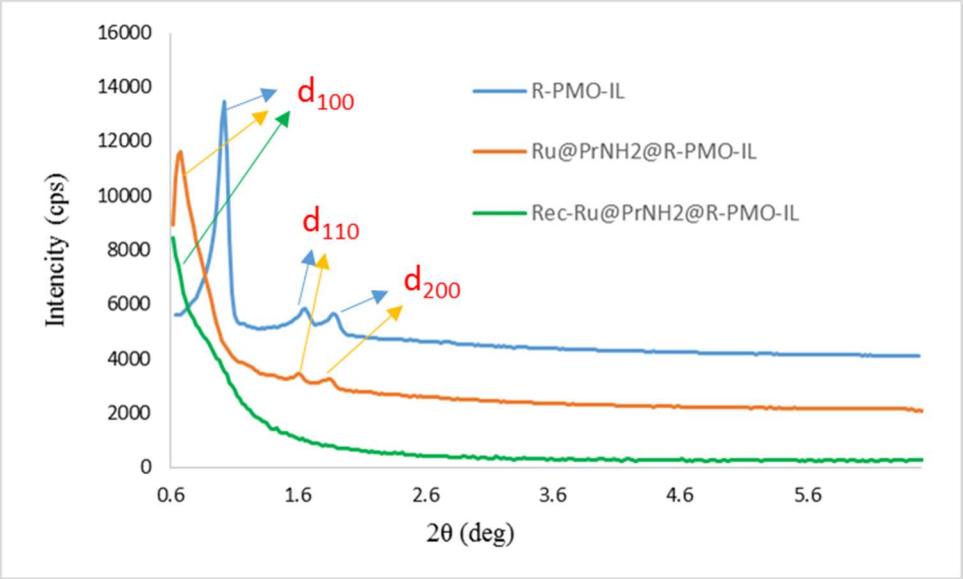


Figure S3. Low angle powder XRD of R-PMO-IL (blue diagram), Ru@PrNH$_2$@R-PMO-IL catalyst (orange diagram), and recovered-Ru@PrNH$_2$@R-PMO-IL catalyst (green diagram).

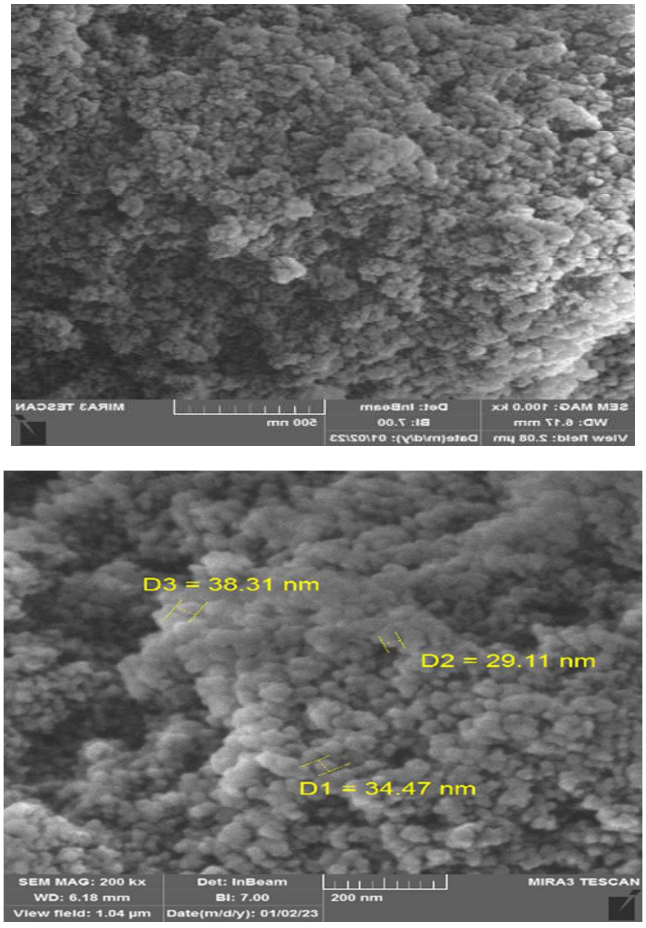


Figure S4. Scanning electron microscopy (SEM) images of R- PMO-IL.

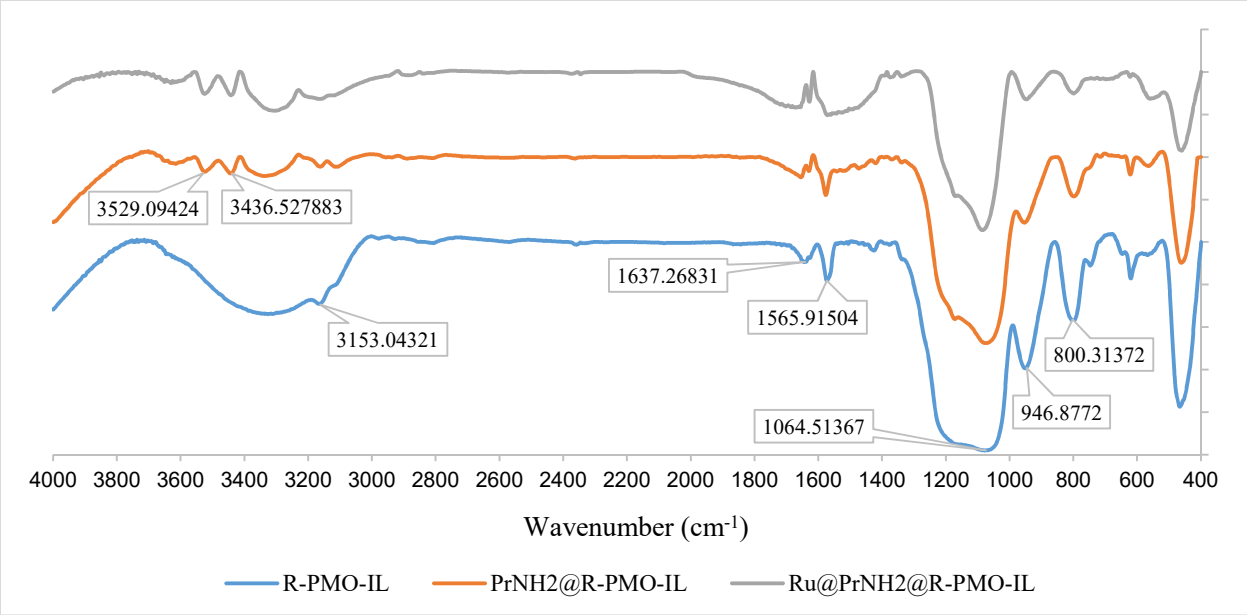
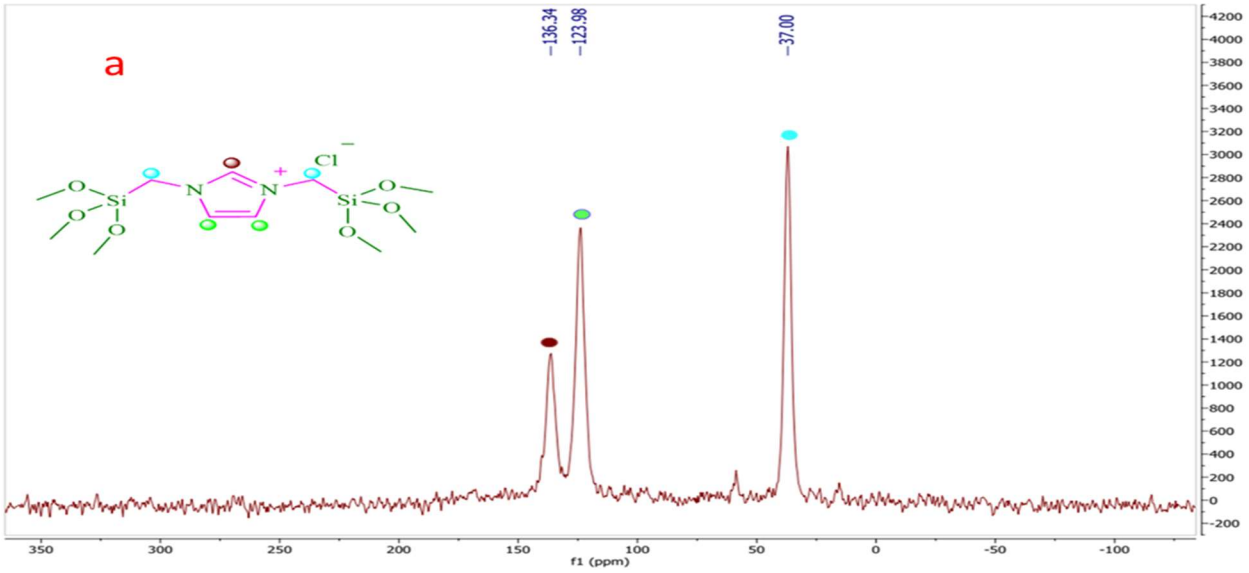


Figure S5. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of R-PMO-IL (blue) $PrNH_2$@R-PMO-IL (orange) and Ru@$PrNH_2$@R-PMO-IL (gray).



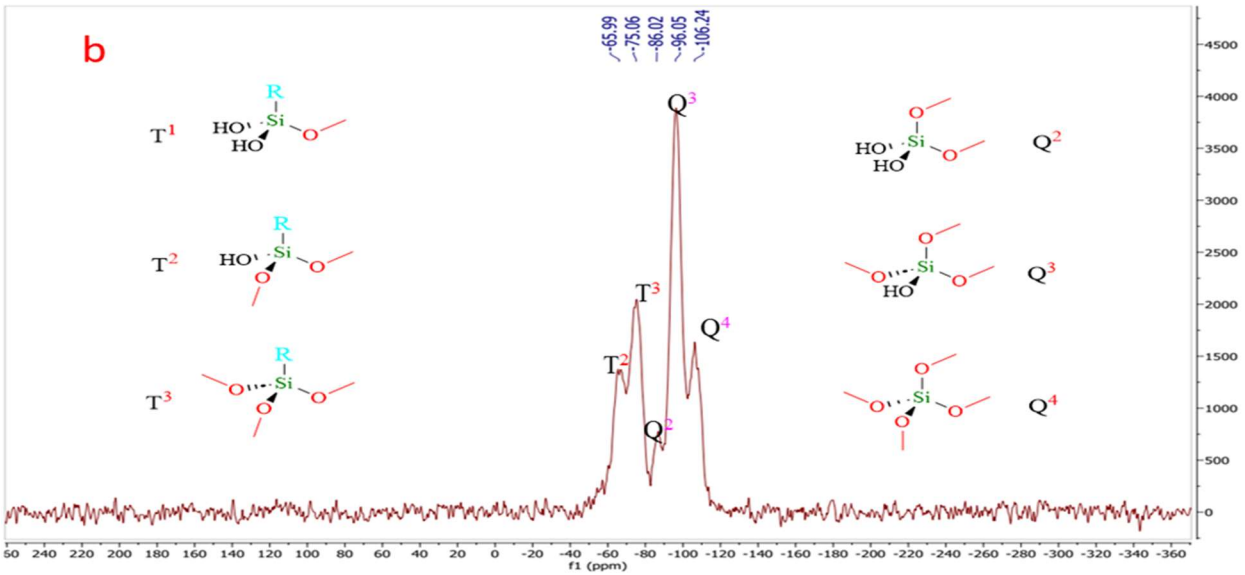
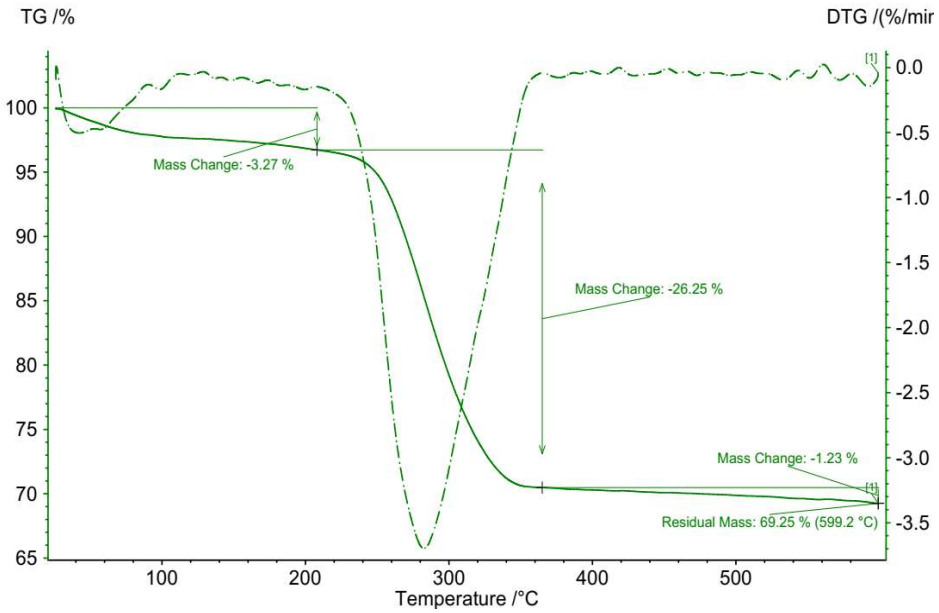


Figure S6. ^{13}C CP-MAS NMR (a) and ^{29}Si CP-MAS NMR (b) spectrum of R-PMO-IL.



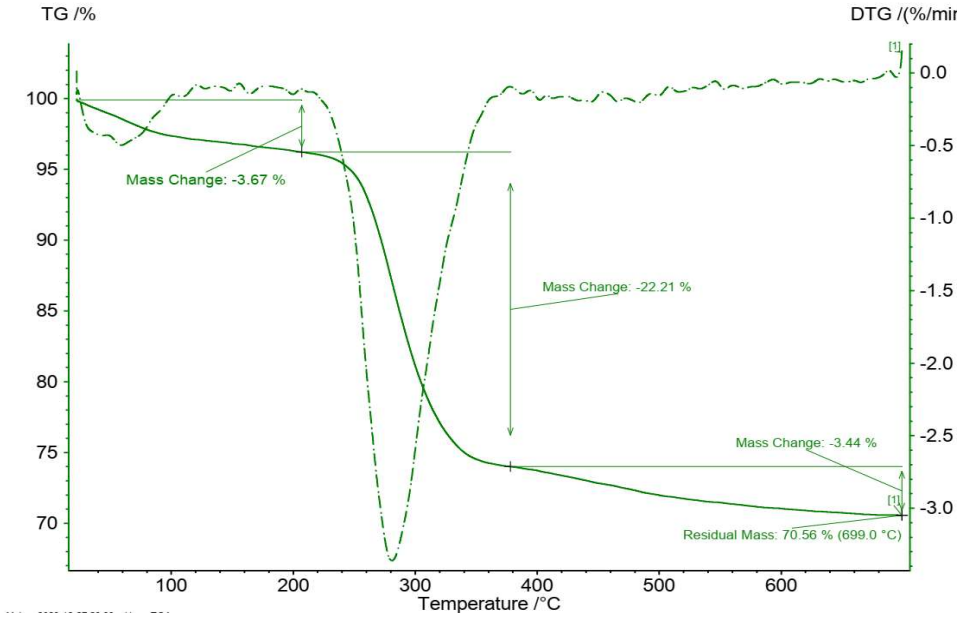


Figure S7. Thermogravimetric analysis of R-PMO-IL in O_2 (top) and N_2 (down) atmosphere.

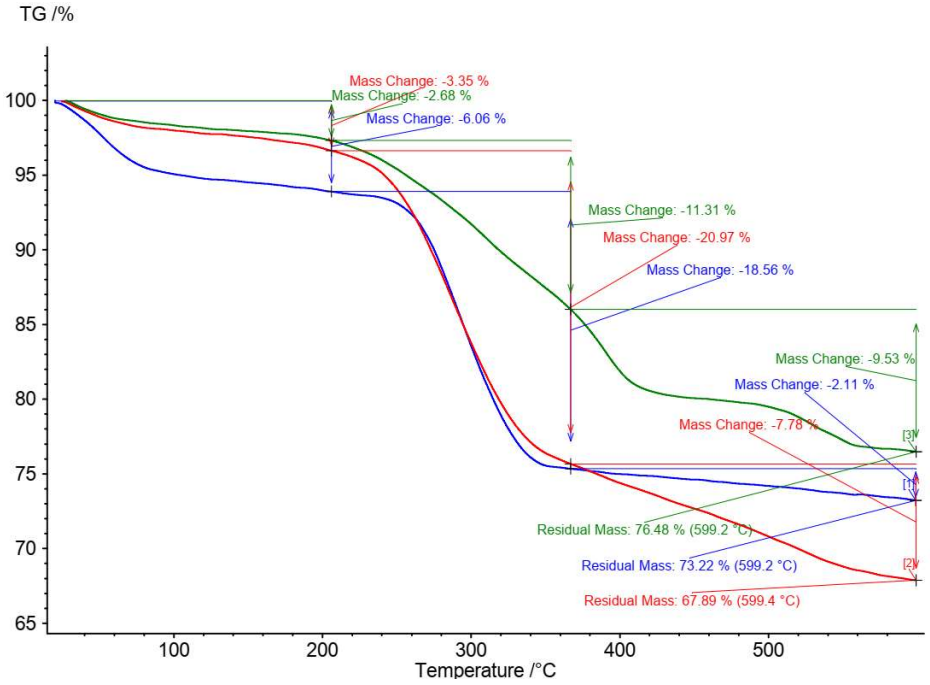


Figure S8. Thermogravimetric analysis of R-PMO-IL (green) $PrNH_2$@R-PMO-IL (red) and Ru@$PrNH_2$@R-PMO-IL (blue).

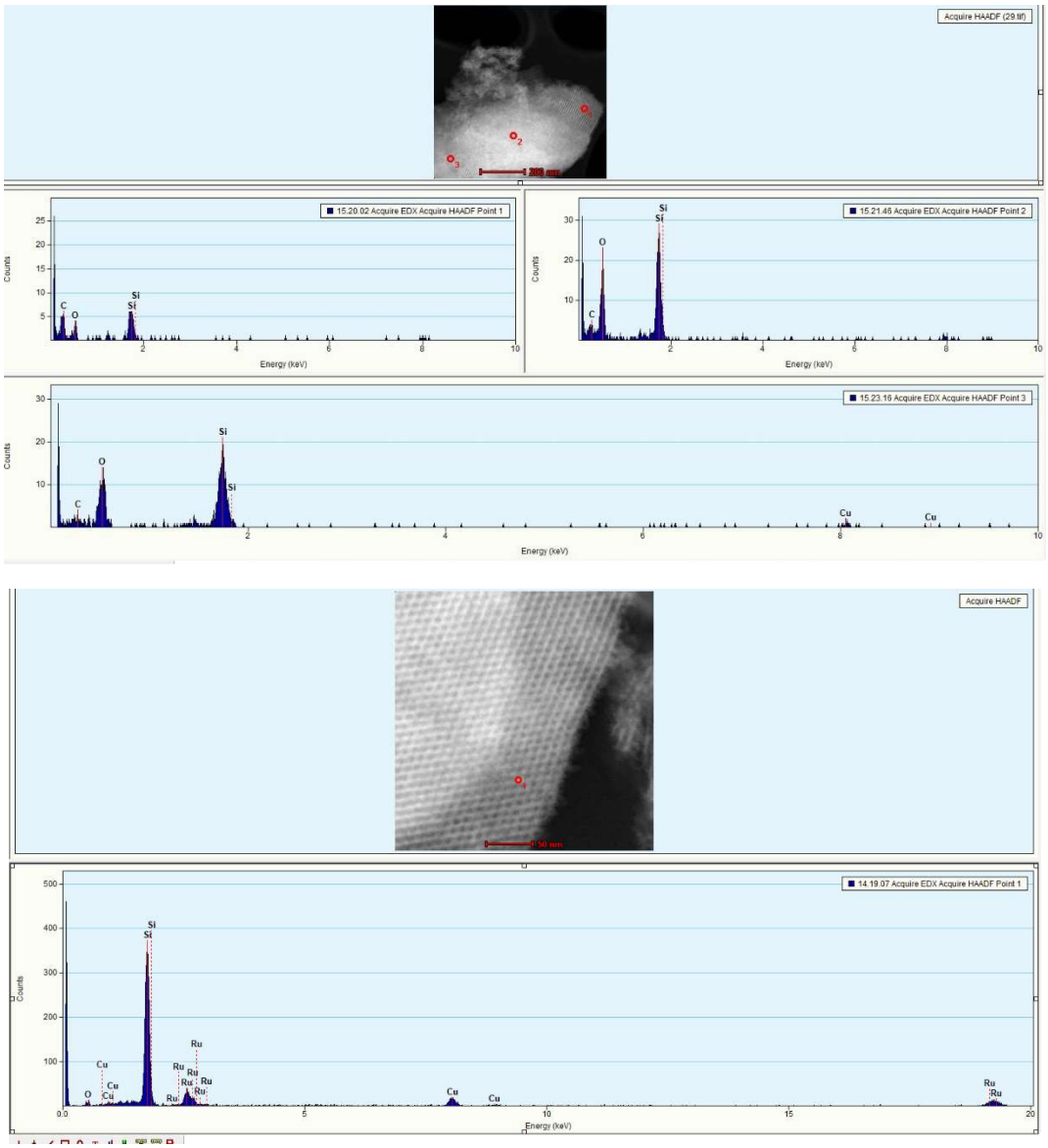


Figure S9. EDS images of R-PMO-IL (top) and Ru@PrNH$_2$@R-PMO-IL (down).

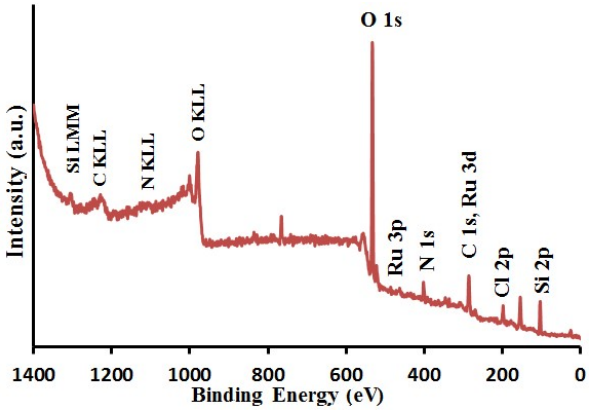


Figure S10. survey scans XPS spectra.

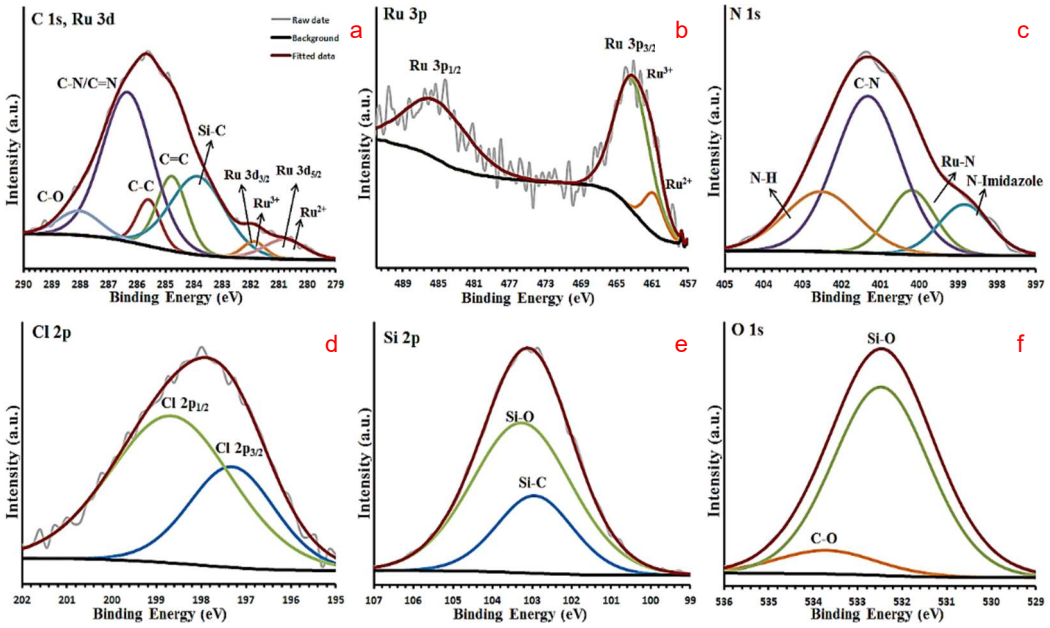


Figure S11. High resolution spectra of C1s, Ru3d (a), Ru3p (b), N1s (c), Cl2p (d), Si2p (e) and, O1s (f).

Table S1. The percentage of constituent elements in the R-PMO-IL based on XPS analysis.

R-PMO-IL	Atomic Constitutes					
	C	O	Ru	N	Si	Cl
(%)	26.04	39.37	2.1	5.43	22.71	4.37

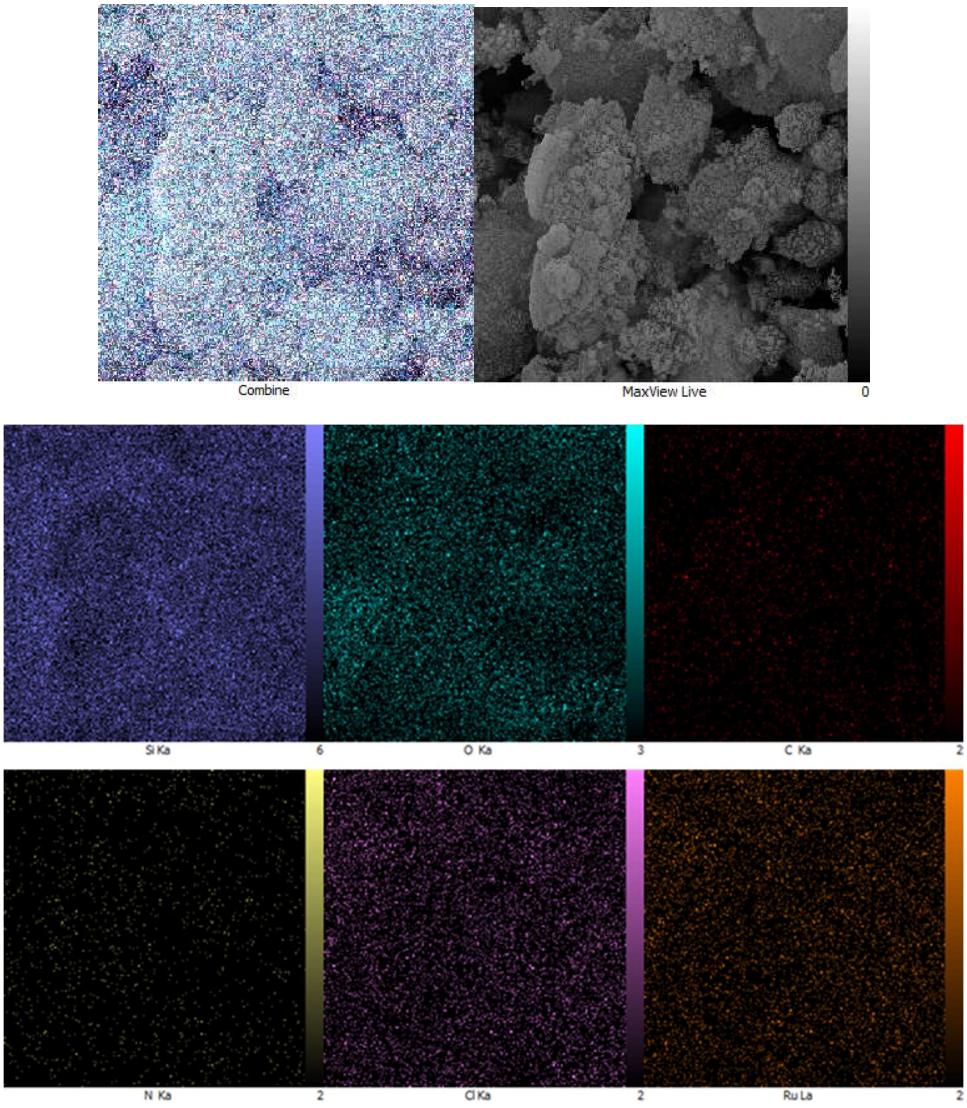


Figure S12. Elemental mapping of Ru@PrNH$_2$@R-PMO-IL.

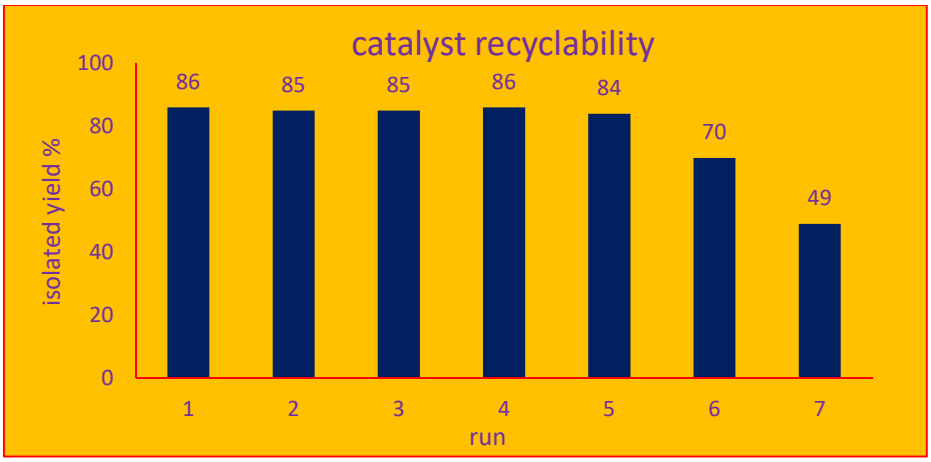


Figure S13. catalyst recyclability

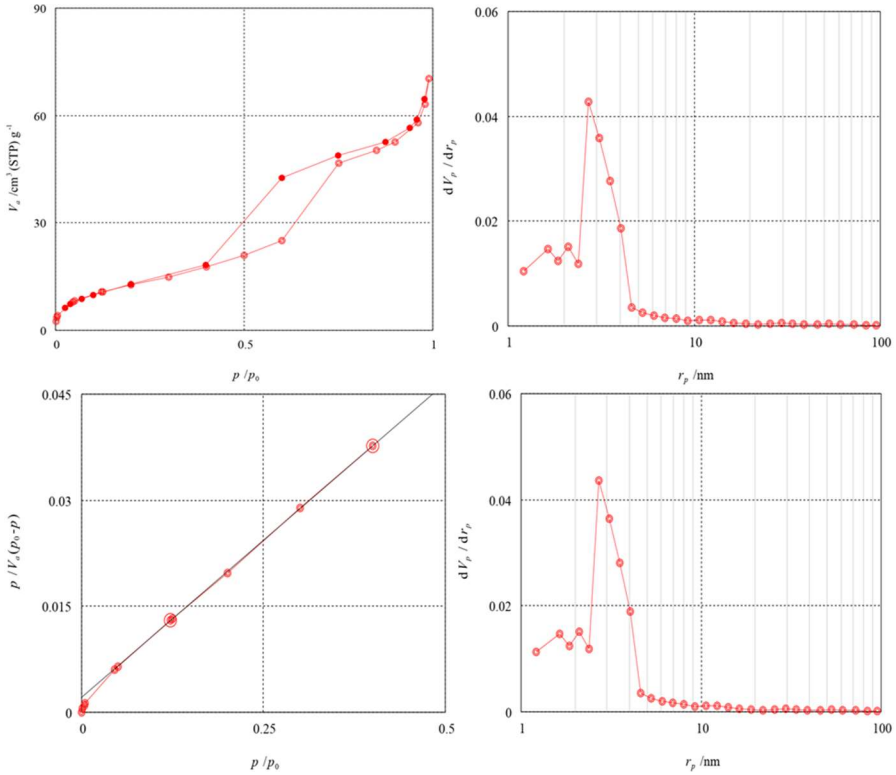
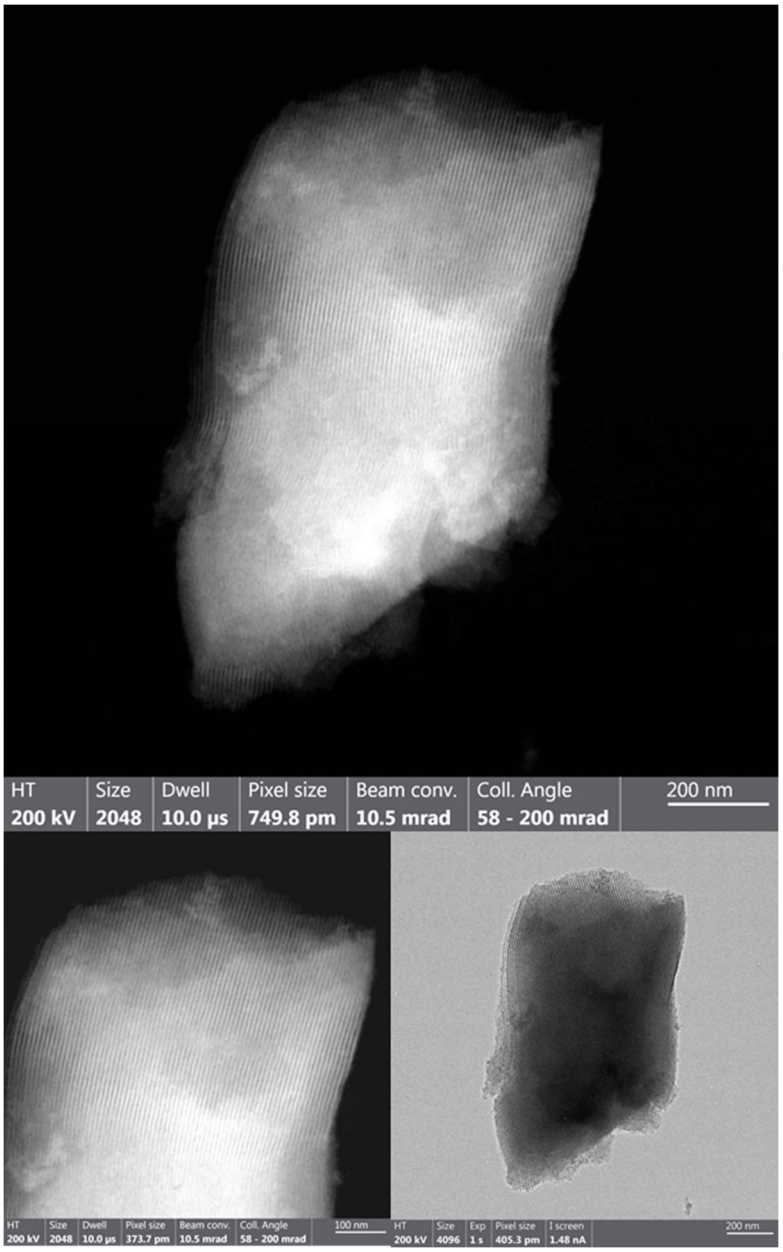


Figure S14. N_2 adsorption−desorption isotherm (top-left), BJH Pore size distribution (top-right) DH Pore size distribution (down-right) and BET surface area diagrams for of recovered Ru@PrNH$_2$@R-PMO-IL (Rec-Ru@PrNH$_2$@R-PMO-IL).


HT
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Size
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Dwell
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Pixel size
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Beam conv.
10.5 mrad
Coll. Angle
58 - 200 mrad
200 nm
HT
200 kV
Size
2048
Dwell
10.0 µs
Pixel size
373.7 pm
Beam conv.
10.5 mrad
Coll. Angle
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200 nm

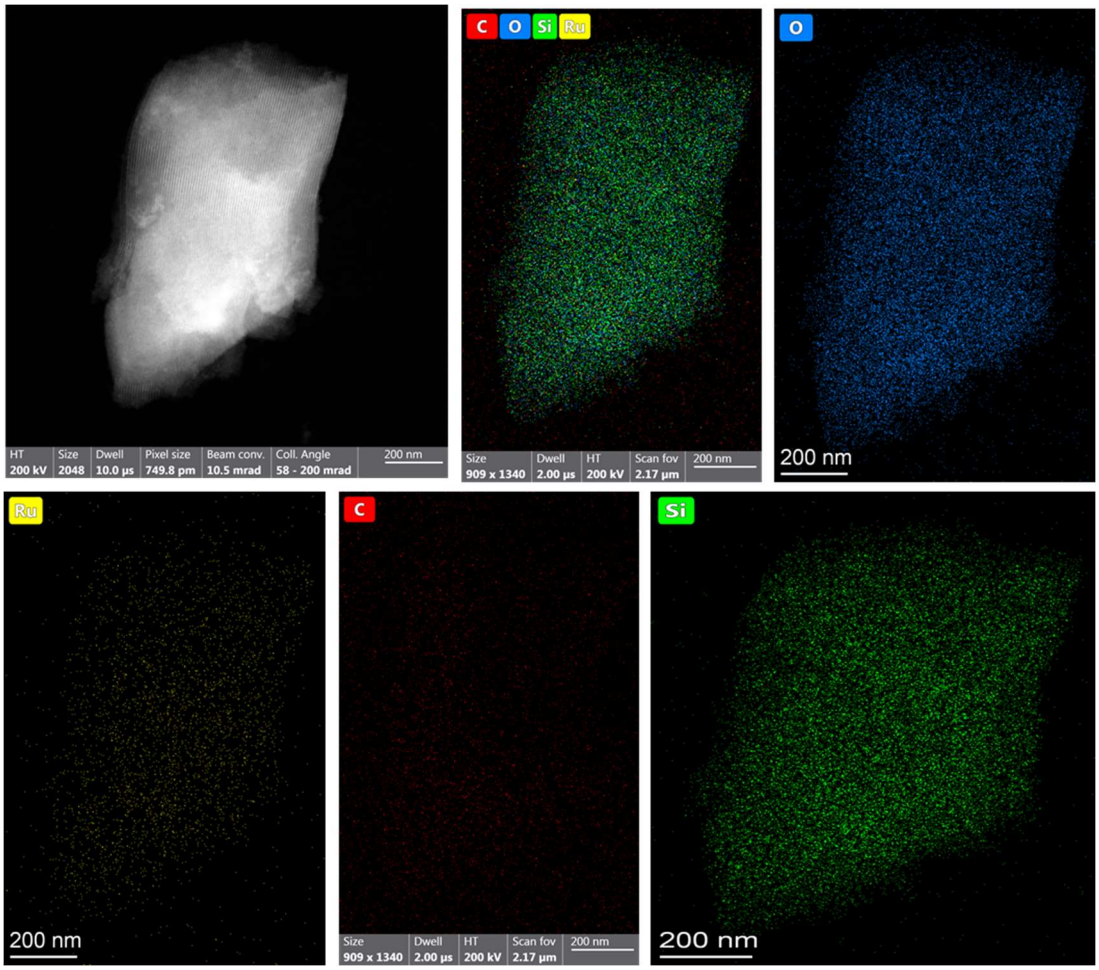


Figure S15. TEM images and elemental mapping of recovered Ru@PrNH$_2$@RPMO-IL catalyst ofter 7th run.

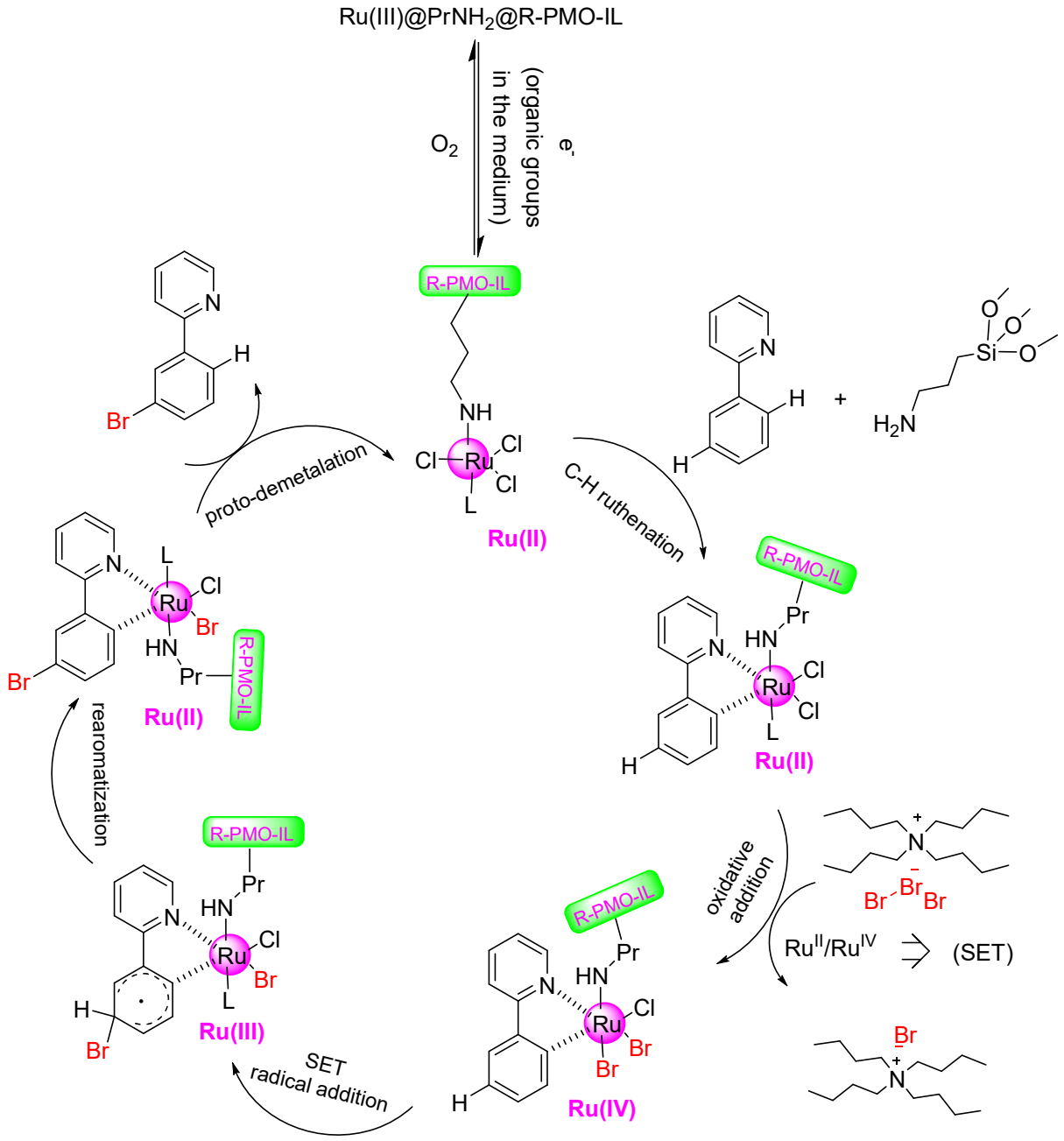
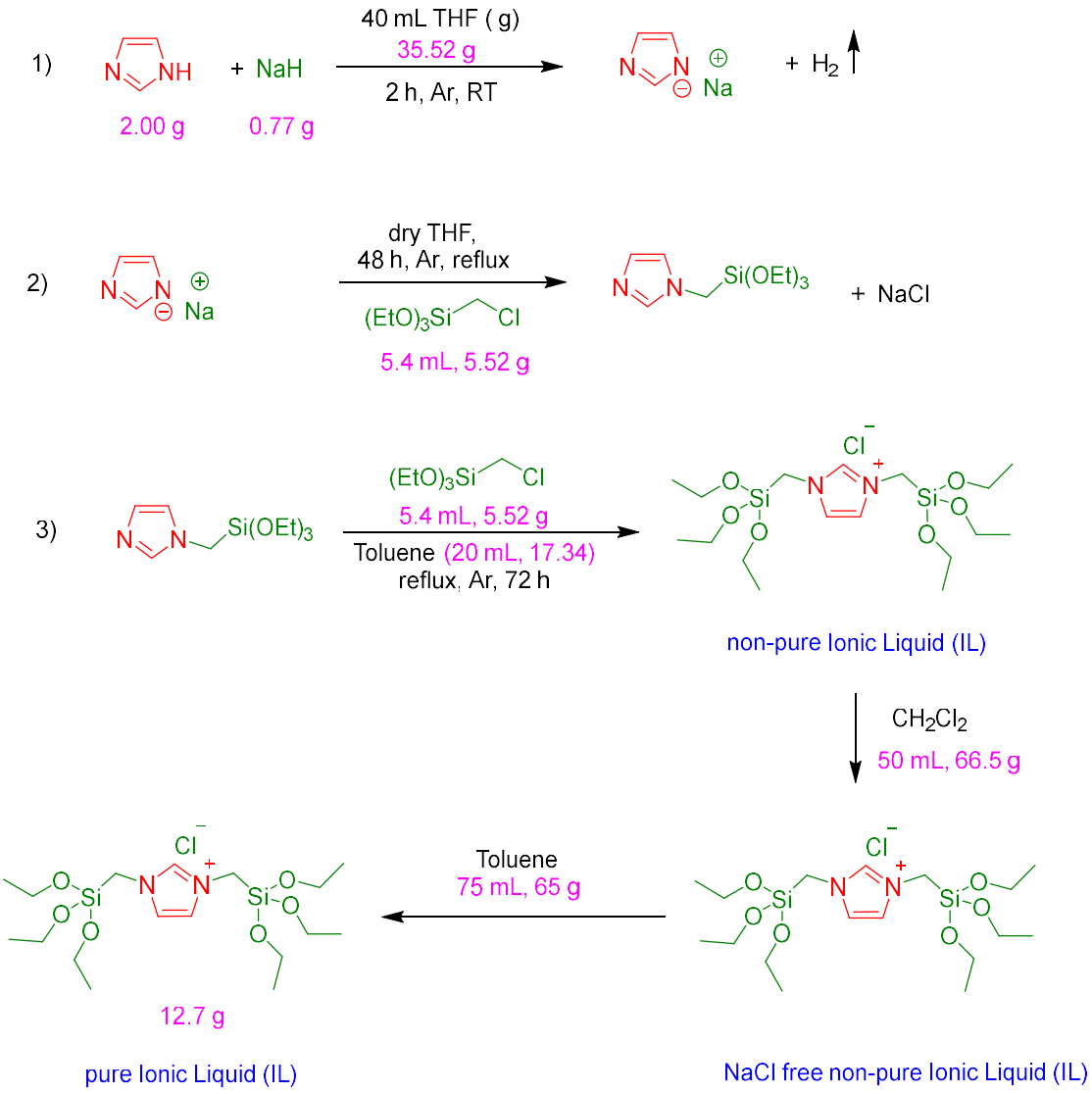


Figure S16: The proposed mechanistic cycle for the *meta*-bromination reaction of 2-phenylpyridine in the presence of Ru@PrNH$_2$@R-PMO-IL catalyst in condition A.

The E-factor and EcoScale factor calculations:



S17: Substrate weights for synthesis of IL

E-factor for ionic liquid synthesis reactions:

Substrates:
Imidazolium: 2 g
Sodium hydride: 0.77 g

(Chloromethyl)triethoxysilane: 11.04 g (2*5.52)

Reaction solvent:
THF (40 mL) (density 0.889 g/mL) = 35.52 g
Toluene (20 mL) (density 0.867 g/mL) = 17.34 g (80 % (13.87 g) of combined toluene was distilled and recovered; waste = 3.47 g)

Workup solvent:
Dichloromethane (50 mL) (density 1.33 g/mL) = 66.5 g
Toluene (75 mL (5*15 mL)) (density 0.867 g/mL) = 65.02 g (80 % (52.02 g) of combined toluene was distilled and recovered; waste = 13.00 g)

Product: 12.7 g IL

$$\text{E factor} = \frac{mass\ of\ waste}{mass\ of\ product} = \frac{2\ g\ (Imidazolium)+0.77\ g\ (Sodium\ hydride)+11.04\ (Chloromethyl)trimethoxysilane+35.52\ (THF)+16.47\ Toluene + 66.5\ Dichloromethane}{12.7\ g\ Iionic\ Liquid\ (IL)} =$$

$$\frac{132.3}{12.7} = 10.42 \text{ kg waste / 1kg product}$$

Calculation of EcoScale score of the Ionic Liquid synthesis
Eco Scale = 100 – Sum of individuals penalties
Score on EcoScale: >75, Excellent; >50, Acceptable; <50, Inadequate

A) Calculations of Penalty Points
Parameters Penalty Points

Table S2 : The penalty points for the synthesis of 12.7 g (**27.8 mmol**) (Ionic Liquid (BTESMICl)

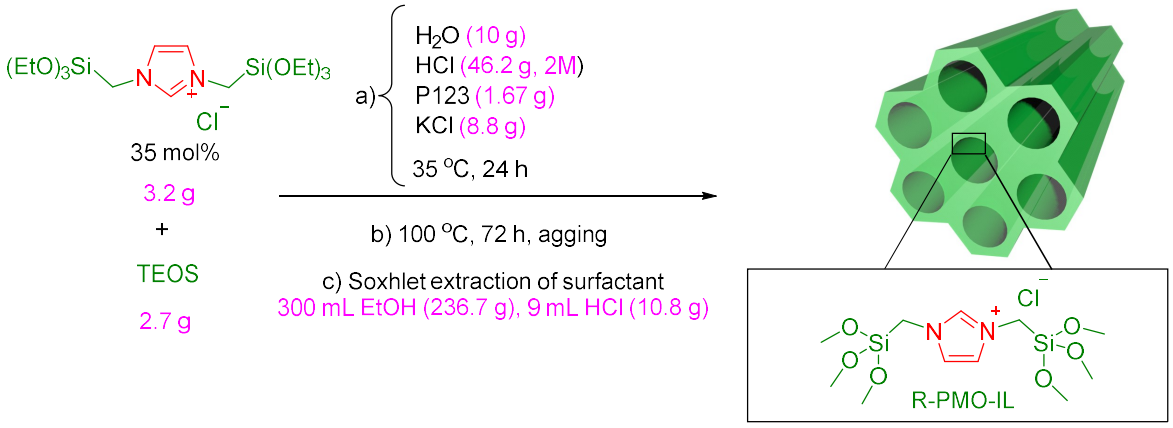
Ent.	Penalty parameter	The effective factor on the penalty point	To obtain 27.8 mmol IL	Penalty point
1	Yield	(100 – % yield)/2	95	2.5
2	Reaction components	Price of reaction components (to obtain 10 mmol of end product) Inexpensive (< $10) 0 Expensive (> $10 and < $50) 3 Very expensive (> $50) 5	Imidazole	0[a]
			NaH (0.77 g)	0[a]
			(Chloromethyl)triethoxysilane	3[a]
3	Safety	N (dangerous for environment) 5 T (toxic) 5 **F (highly flammable) 5** E (explosive) 10 F^+ (extremely flammable) 10 T^+ (extremely toxic) 10	NaH (F)	5
			(Chloromethyl)triethoxysilane (F)	5
			Imidazole	0

4	Technical Setup	**Common setup 0** Instruments for controlled addition of chemicals 1 Unconventional activation technique 2 Pressure equipment, > 1 atm. 3 Any additional special glassware 1 **(Inert) gas atmosphere 1** Glove box 3	Common setups	0
			Inert gas atmosphere	1
5	Temperature /time	Room temperature, < 1 h 0 **Room temperature, < 24 h 1** Heating, < 1 h 2 **Heating, > 1 h 3** Cooling to 0°C 4 Cooling, < 0°C 5	Room temperature, < 24 h (NaH addition)	1
			Heating, > 1 h (first step)	3
6	Workup and purification	None 0 Cooling to room temperature 0 **Adding solvent 0** Simple filtration 0 **Removal of solvent with bp < 150°C 0** **Crystallization and filtration 1** Removal of solvent with bp > 150°C 2 Solid phase extraction 2 Distillation 3 Sublimation 3 **Liquid-Liquid extraction 3** Classical chromatography 10	Crystallization of imidazole	1
			Adding solvent	0
			Removal of solvent with bp < 150°C	0
			Liquid-Liquid extraction (purification of IL)	3
Total Penalty Points				24.5
[a] Based on the amount needed to synthesize 10 mmol of the IL				

B) EcoScale calculation:

EcoScale score = 100 – 24.5 = 75.5 (>75; it is an Excellent synthesis)

……..



S18: Substrate weights for synthesis of R-PMO-IL

E-factor for R-PMO-IL preparation:

Substrates:
Ionic liquid: 3.2 g
TEOS: 2.7 g
HCl: 46.2 mL (2M); (8.212 mL concentrated HCl (density = 1.2 g/ml) in 50 mL deionized water gives 2M HCl solution) = (8.212*1.2) 9.85 g
P123: 1.67 g
KCl: 8.8 g

Wash-up solvent:
Ethanol (EtOH) (3*100 mL) (density 0.789 g/mL) = 236.7 g (90 % (213.03 g) of combined EtOH was distilled and recovered; waste = 23.67 g)

Product: 2.5 g R-PMO-IL

$$\text{E factor} = \frac{mass\ of\ waste}{mass\ of\ product} = \frac{3.2\ g\ (IL)+2.7\ g\ (TEOS)+20.65\ g\ HCl\ (C)+1.67\ g\ (P123)+8.8\ g\ (KCl) + 23.67\ g\ (EtOH)}{2.5\ g\ R-PMO-IL} = \frac{60.69}{2.5} = 24.28 \text{ kg waste / 1kg product}$$

Calculation of EcoScale score of the R-PMO-IL synthesis

A) Calculations of Penalty Points
Parameters Penalty Points

Table S3 : The penalty points for the synthesis of 2.5 g R-PMO-IL

Ent.	Penalty parameter	The effective factor on the penalty point	To obtain 2.5 g R-PMO-IL	Penalty point
1	Yield	(100 – % yield)/2	90	5[a]
2	Reaction components	Price of reaction components (to obtain 10 mmol of end product) Inexpensive (< $10) 0 Expensive (> $10 and < $50) 3 Very expensive (> $50) 5	BTESMICl (IL)	0[b]
			TEOS	0[b]
			P123	0[b]
			HCl	0[b]
			KCl	0[b]
3	Safety	**N (dangerous for environment) 5** T (toxic) 5 **F (highly flammable) 5** E (explosive) 10 F^+ (extremely flammable) 10 T^+ (extremely toxic) 10	TEOS (F)	5
			HCl (N)	5
4	Technical Setup	**Common setup 0** Instruments for controlled addition of chemicals 1 Unconventional activation technique 2 Pressure equipment, > 1 atm. 3 **Any additional special glassware 1** (Inert) gas atmosphere 1 Glove box 3	Common setups	0
			soxhlet apparatus	1

5	Temperature/ time	Room temperature, < 1 h 0 **Room temperature, < 24 h 1** Heating, < 1 h 2 **Heating, > 1 h 3** Cooling to 0°C 4 Cooling, < 0°C 5	Room temperature, 24 h	1
			Heating, > 1 h (aging step)	3
			Heating, > 1 h (Surfactant extraction step)	3
6	Workup and purification	None 0 Cooling to room temperature 0 Adding solvent 0 **Simple filtration 0** Removal of solvent with bp < 150°C 0 Crystallization and filtration 1 Removal of solvent with bp > 150°C 2 Solid phase extraction 2 Distillation 3 Sublimation 3 Liquid-Liquid extraction 3 Classical chromatography 10	Simple filtration	0
Total Penalty Points				23

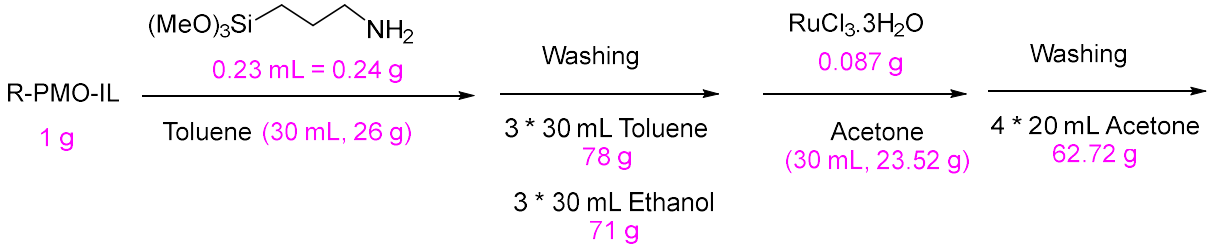
[a] Since the molecular mass is not available, it is not possible to calculate the yield. However, based on the loading of the ionic liquid and taking into account the average penalty point, we have assumed an efficiency of 90% for the production of the R-PMO-IL. [b] Based on the amount needed to synthesize 10 mmol of the R-PMO-IL

B) EcoScale calculation:

EcoScale score = 100 – 23 = 77 (>75; it is an excellent synthesis)

……

***E*-factor for Ru@PrNH$_2$@R-PMO-IL preparation:**



S19: Substrate weights for synthesis of Ru@PrNH$_2$@R-PMO-IL

Substrates:

R-PMO-IL: 1 g

Aminopropyltrimethoxy silane (APTMS): 0.24 g

$RuCl_3.3H_2O$: 0.087 g

Reaction solvent:
Toluene (30 mL) (density 0.867 g/mL) = 26 g (90 % (23.4 g) of combined toluene was distilled and recovered; waste = 2.6 g)
Acetone (30 mL) (density 0.784 g/mL) = 23.52 g (90 % (21.17 g) of combined acetone was distilled and recovered; waste = 2.4 g)

Wash-up solvent:
Toluene (3*30 mL) (density 0.867 g/mL) = 78 g (90 % (70.2 g) of combined toluene was distilled and recovered; waste = 7.8 g)
Ethanol (EtOH) (3*30 mL) (density 0.789 g/mL) = 71 g (90 % (63.9 g) of combined EtOH was distilled and recovered; waste = 7.1 g)
Acetone (4*20 mL) (density 0.784 g/mL) = 62.72 g (90 % (56.45 g) of combined acetone was distilled and recovered; waste = 6.3 g)

Product: 1.2 g Ru@PrNH$_2$@R-PMO-IL

E factor = $\frac{mass\ of\ waste}{mass\ of\ product}$ = $\frac{1\ g\ R{-}PMO{-}IL + 0.24\ g\ APTMS + 0.087\ g\ RuCl\ .3H2O + 1\ .4\ g\ (Toluene) + 8.7 g\ (Acetone) + 7.1\ g\ (EtOH)}{1.2\ g\ R{-}PMO{-}IL}$ = $\frac{20.43}{1.2}$ = 17.02 kg waste / 1kg product

……..

Calculation of EcoScale score of the Ru@PrNH$_2$@R-PMO-IL synthesis

A) Calculations of Penalty Points
Parameters Penalty Points

Table S4: The penalty points for the synthesis of 1.2 g Ru@PrNH$_2$@R-PMO-IL

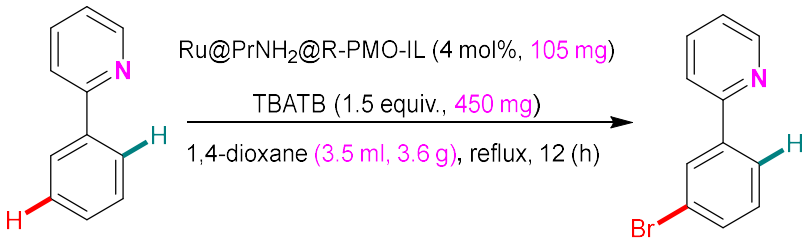
Ent.	Penalty parameter	The effective factor on the penalty point	To obtain 1.2 g Ru@PrNH$_2$@R-PMO-IL	Penalty point
1	Yield	(100 – % yield)/2	80	10[a]
2	Reaction components	Price of reaction components (to obtain 10 mmol of end product) Inexpensive (< $10) 0 Expensive (> $10 and < $50) 3 Very expensive (> $50) 5	APTMS (0.23 mL)	0
			$RuCl_3.3H_2O$ (0.087 g)	0
3	Safety	**N (dangerous for environment) 5** T (toxic) 5 F (highly flammable) 5 E (explosive) 10 F^+ (extremely flammable) 10 T^+ (extremely toxic) 10	APTMS	0
			$RuCl_3.3H_2O$ (N)	5

4	Technical Setup	**Common setup 0** Instruments for controlled addition of chemicals 1 Unconventional activation technique 2 Pressure equipment, > 1 atm. 3 Any additional special glassware 1 **(Inert) gas atmosphere 1** Glove box 3	Common setup	0
			gas atmosphere (Ar)	1
5	Temperature/time	Room temperature, < 1 h 0 **Room temperature, < 24 h 1** Heating, < 1 h 2 **Heating, > 1 h 3** Cooling to 0°C 4 Cooling, < 0°C 5	Heating, > 1 h (APTMS grafting)	3
			Room temperature, < 24 h (Ruthenium stabilization)	1
6	Workup and purification	None 0 Cooling to room temperature 0 Adding solvent 0 **Simple filtration 0** Removal of solvent with bp < 150°C 0 Crystallization and filtration 1 Removal of solvent with bp > 150°C 2 Solid phase extraction 2 Distillation 3 Sublimation 3 Liquid-Liquid extraction 3 Classical chromatography 10	Simple filtration of the catalyst	0
Total Penalty Points				20
[a] based on loading of Ru.				

B) EcoScale calculation:

EcoScale score = 100 – 20 = 80 (>75; it is an excellent synthesis)

.....



1a

90µl, 97 mg

2a

126 mg

S20: Substrate weights for synthesis of 2-(3-bromophenyl)pyridine

***E*-factor for meta-selective C-H bromination of 2-phenylpyridine**

Substrates:

2-phenylpyridine: 0.625 mmol; 97 mg

Ru@PrNH$_2$@R-PMO-IL (catalyst): 105 mg

TBATB: 450 mg

Reaction solvent:
1,4-dioxane (3.5 mL) (density 1.03 g/mL)= 3.6 g

Work-up solvent:
Ethyl Acetate (EtOAc) (4*15 mL) (density 0.902 g/mL) = 54.12 g; (95 % (51.4 g) of EtOAc was distilled and recovered using rotary); waste = 2.71 g
$Na_2S_2O_3$ (30 mL) (10 g $Na_2S_2O_3$ in 100 mL water gives 10% w/v $Na_2S_2O_3$ solution): 3g

Product:
126 mg 2-(3-bromophenyl)pyridine in first run
798.2 mg 2-(3-bromophenyl)pyridine after 7th cycle (1st cycle: 126.0 mg; 2nd cycle: 124.4 mg; 3rd cycle: 124.5 mg; 4th cycle: 125.8 mg; 5th cycle: 123.0 mg; 6th run: 102.5 mg; 7th cycle: 72.0 mg)

$$\text{E factor} = \frac{mass\ of\ waste}{mass\ of\ product} = \frac{0.097\ g\ 2{-}phenylpyridine + 0.105\ g\ Ru@PrNH2@R{-}PMO{-}IL + 0.450\ g\ TBATB + 3.6\ g\ Dioxane + 2.71\ g\ (EtOAc) + 3\ g\ (Na2S2O3)}{0.126\ g\ R{-}PMO{-}IL} =$$

$$\frac{9.958}{0.126} = 79.03 \text{ kg waste / 1kg product}$$

E factor after 7th run of catalyst usage= $\frac{9.958}{0.798} = 12.48$

Calculation of EcoScale score of the meta-selective C-H bromination of 2-phenylpyridine

A) Calculations of Penalty Points
Parameters Penalty Points

Table S5 : The penalty points for the synthesis of 10 mmol of 2-(3-bromophenyl)pyridine

Ent.	Penalty parameter	The effective factor on the penalty point	10 mmol of 2-(3-bromophenyl)pyridine	Penalty point
1	Yield	(100 – % yield)/2	86	7
2	Reaction components	Price of reaction components (to obtain **10 mmol of end product**) Inexpensive (< $10) 0 Expensive (> $10 and < $50) 3 Very expensive (> $50) 5	61.6 mg Ru@$PrNH_2$@R-PMO-IL (3.8 mg $RuCl_3.3H_2O$)[a]	0
			2-phenylpyridine (11.62 mmol)	0
			TBATB (264 mg)	0
3	Safety	N (dangerous for environment) 5 T (toxic) 5 F (highly flammable) 5 E (explosive) 10 F^+ (extremely flammable) 10 T^+ (extremely toxic) 10	2-phenylpyridine	0
			TBATB	0

4	Technical Setup	**Common setup 0** Instruments for controlled addition of chemicals 1 Unconventional activation technique 2 Pressure equipment, > 1 atm. 3 Any additional special glassware 1 (Inert) **gas atmosphere** 1 Glove box 3	Common setup	0
			gas atmosphere (O_2)	1
5	Temperature/ time	Room temperature, < 1 h 0 Room temperature, < 24 h 1 Heating, < 1 h 2 **Heating, > 1 h 3** Cooling to 0°C 4 Cooling, < 0°C 5	Heating, > 1 h (APTMS grafting)	3
6	Workup and purification	None 0 **Cooling to room temperature 0** **Adding solvent 0** **Simple filtration 0** **Removal of solvent with bp < 150°C 0** Crystallization and filtration 1 Removal of solvent with bp > 150°C 2 Solid phase extraction 2 Distillation 3 Sublimation 3 **Liquid-Liquid extraction 3** **Classical chromatography 10**	Cooling to room temperature	0
			Simple filtration of the catalyst	0
			Liquid-Liquid extraction (Extraction with AcOEt)	3
			Washing with aq. $Na_2S_2O_3$	3
			Washing with water and brine	3
			Drying over sodium sulfate	0
			Removal of AcOEt	0
			Silica gel chromatography	10
Total Penalty Points				30
[a]Due to the recyclability of the catalyst and the selective production of 798.2 mg (3.41 mmol) of the 2-(3-bromophenyl)pyridine, 61.6 mg of the synthesized catalyst (containing 3.8 mg of ruthenium) is sufficient to produce 10 mmol of the product.				

B) EcoScale calculation:

EcoScale score = 100 – 30 = 70 (>50, it is an Acceptable synthesis)

……..

Table S6. The average integral of **4-(2-pyridyl)benzaldehyde /2-bromo-4-(pyridin-2-yl)benzaldehyde** in different solutions

Entry	Theoretical ratio of 4-(2-pyridyl)benzaldehyde /2-bromo-4-(pyridin-2-yl)benzaldehyde	practical ratio of 4-(2-pyridyl)benzaldehyde /2-bromo-4-(pyridin-2-yl)benzaldehyde
1	(1 :1) = 1	(55.00) ÷ (45.00) = 1.22
Second injection	(1 :1) = 1	(55.22) ÷ (44.77) = 1.23
2	(2 :1) = 2	(72.45) ÷ (27.54) = 2.63
Second injection	(2 :1) = 2	(72.59) ÷ (27.41) = 2.65
3	(3 :1) = 3	(78.96) ÷ (21.04) = 3.75
Second injection	(3 :1) = 3	(78.82) ÷ (21.18) = 3.72

Theoretical ratio	GC ratio
1	1.22
2	2.63
3	3.75

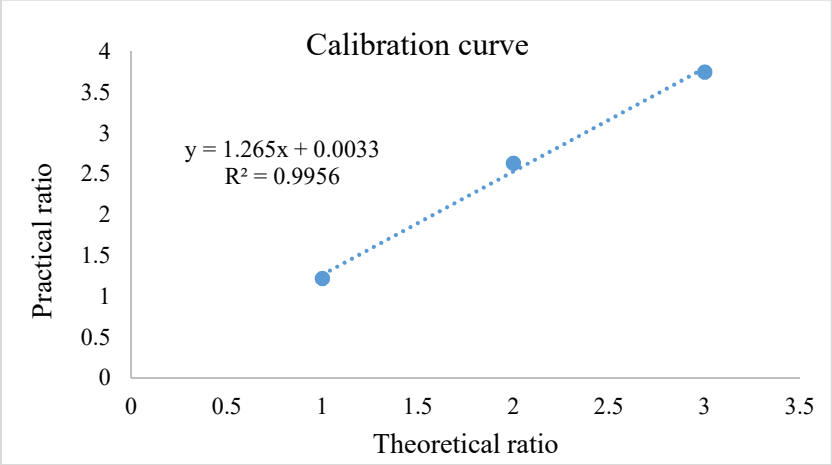


Figure S21. The calibrating curve of GC analysis in different molar ratios of 4-(2-pyridyl)benzaldehyde.

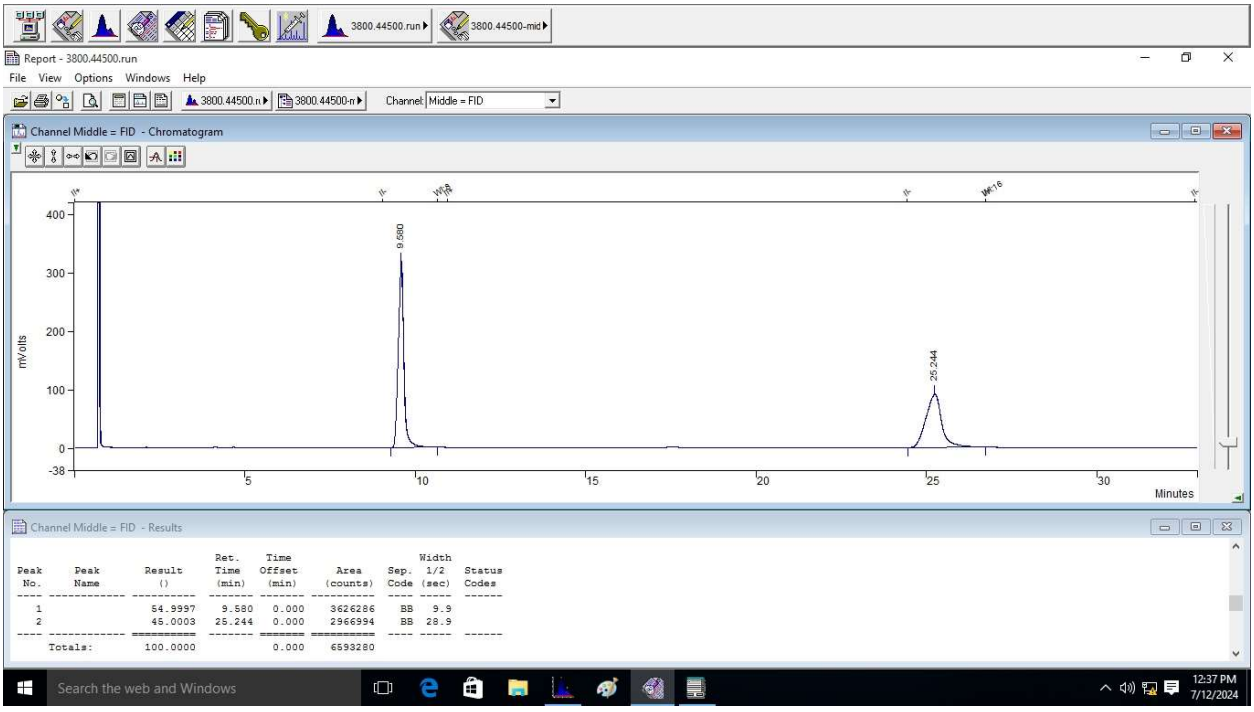


Figure S22. Gas chromatogram of the solution contains 0.1 mmol 4-(2-pyridyl)benzaldehyde and 2-bromo-4-(pyridin-2 yl)benzaldehyde (1: 1)- first injection.

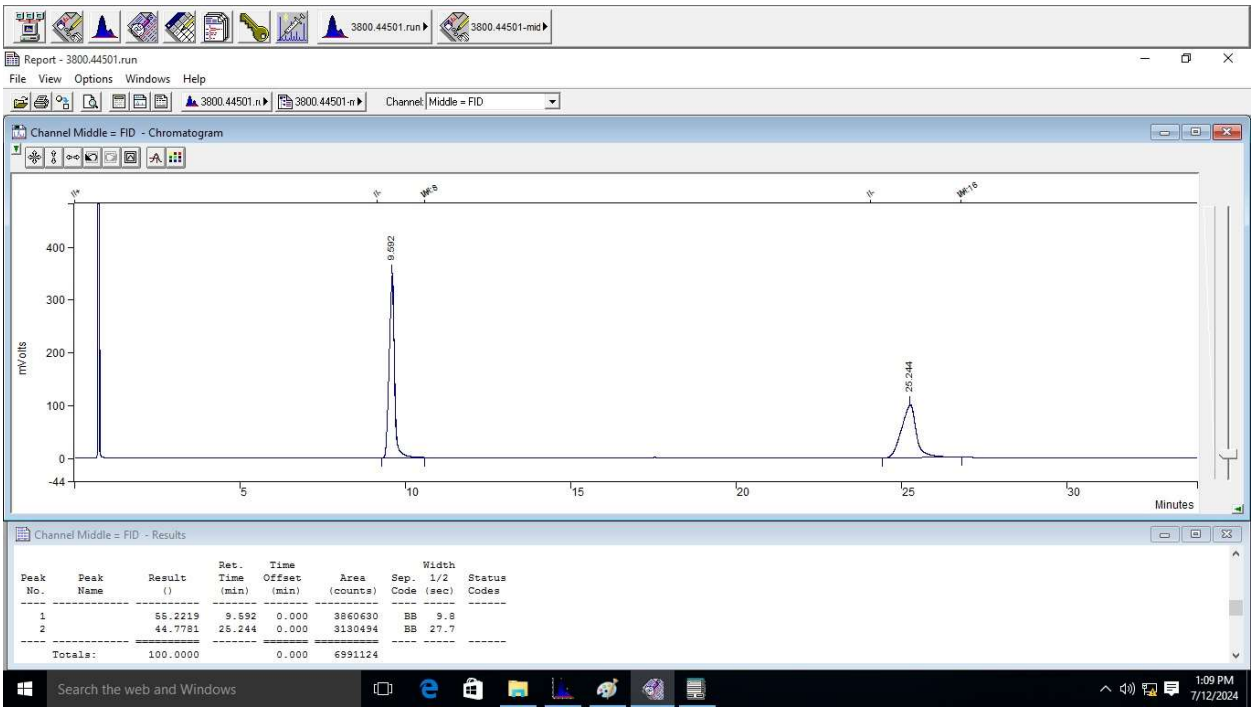


Figure S23. Gas chromatogram of the solution contains 0.1 mmol 4-(2-pyridyl)benzaldehyde and 2-bromo-4-(pyridin-2 yl)benzaldehyde (1: 1)- 2nd injection.

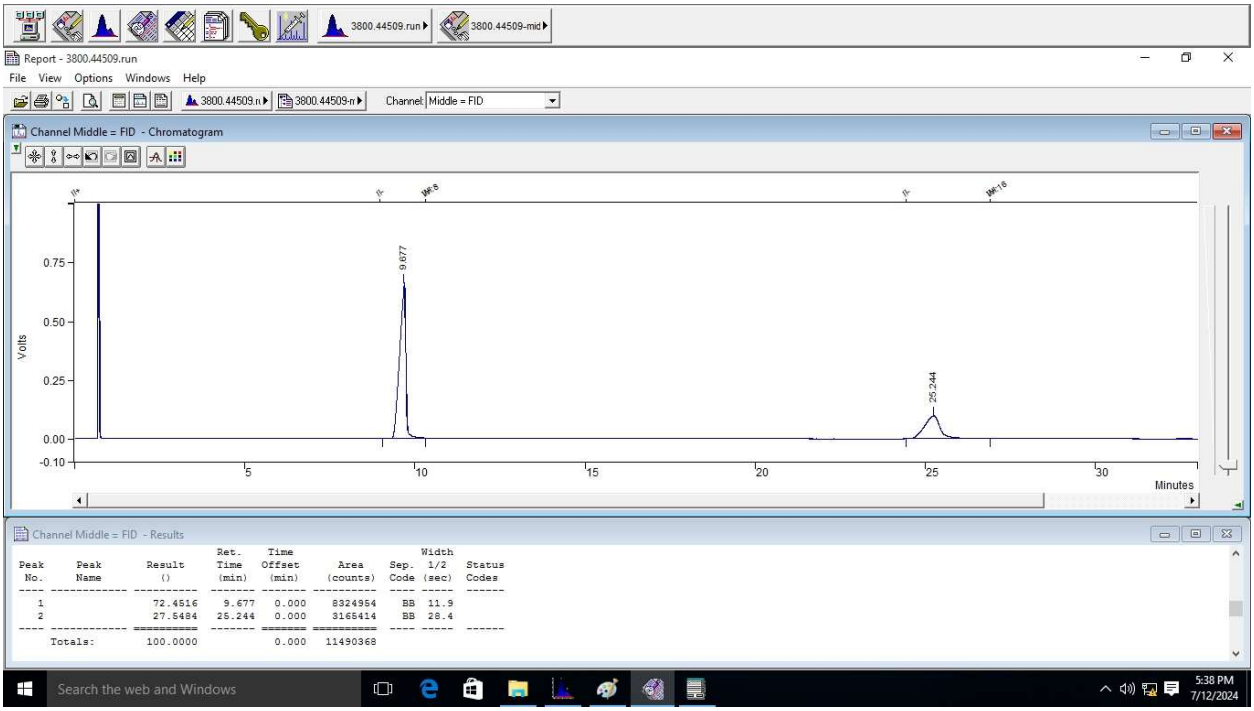


Figure S24. Gas chromatogram of the solution contains 0.2 mmol 4-(2-pyridyl)benzaldehyde and 0.1 mmol 2-bromo-4-(pyridin-2 yl)benzaldehyde (2: 1)- first injection.

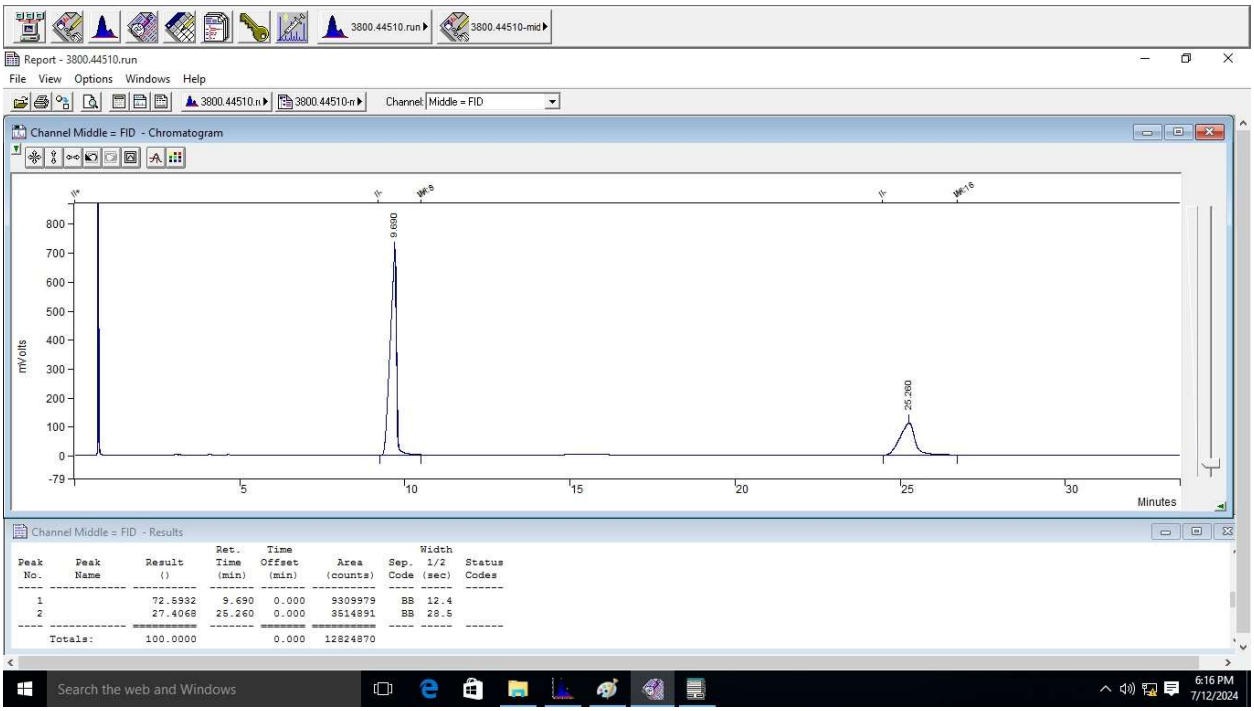


Figure S25. Gas chromatogram of the solution contains 0.2 mmol 4-(2-pyridyl)benzaldehyde and 0.1 mmol 2-bromo-4-(pyridin-2 yl)benzaldehyde (2: 1)- 2nd injection.

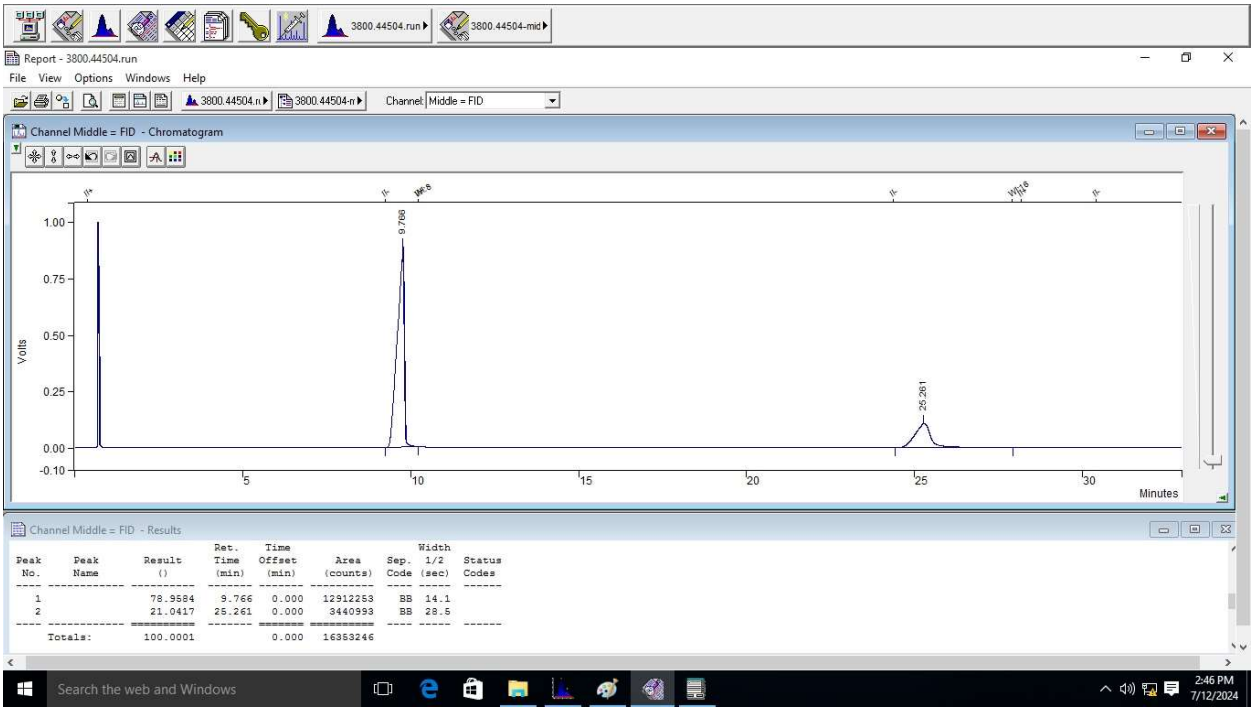


Figure S26. Gas chromatogram of the solution contains 0.3 mmol 4-(2-pyridyl)benzaldehyde and 0.1 mmol 2-bromo-4-(pyridin-2 yl)benzaldehyde (3: 1)- first injection.

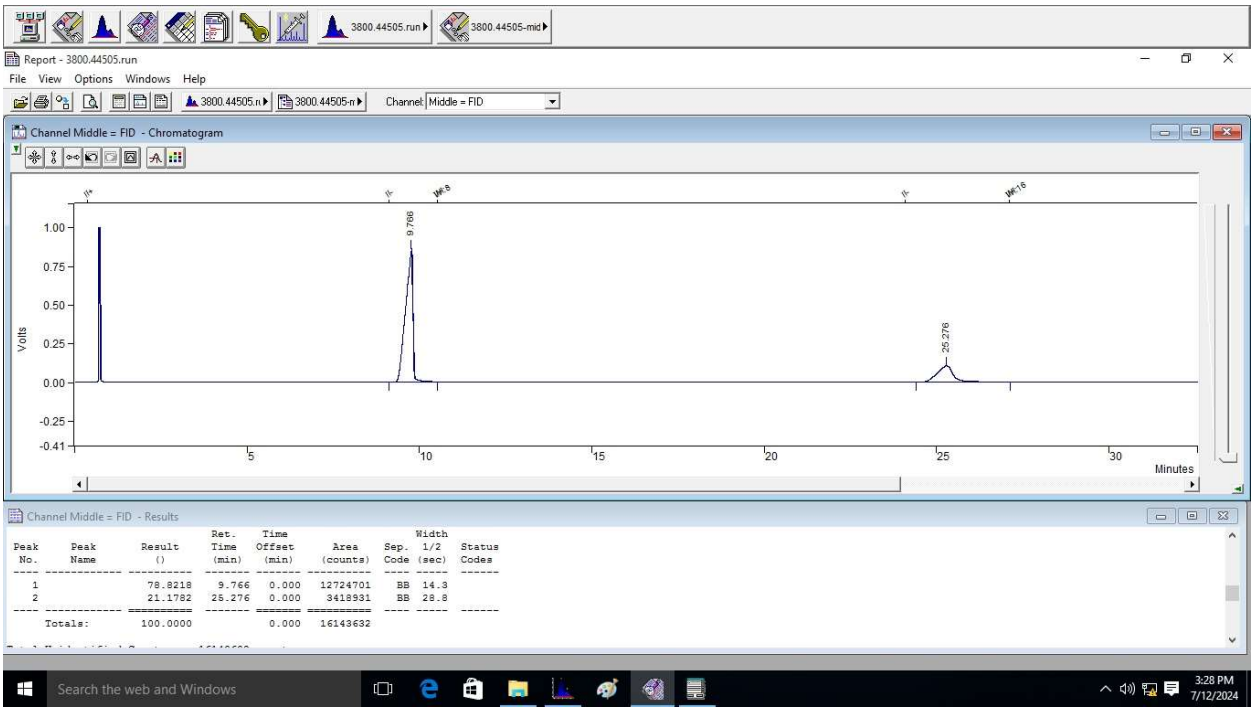
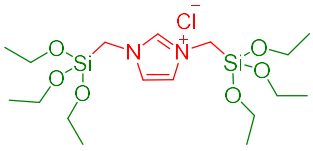


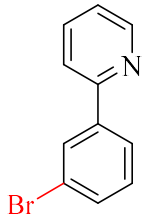
Figure S27. Gas chromatogram of the solution contains 0.3 mmol 4-(2-pyridyl)benzaldehyde and 0.1 mmol 2-bromo-4-(pyridin-2 yl)benzaldehyde (3: 1)- 2nd injection.

1, 3-bis(triethoxysilyl)methyl imidazolium chloride ionic liquid (BTESMICl)



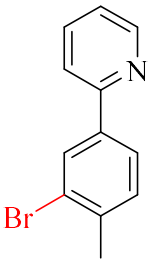
Brown viscous liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.36 (d, J = 1.2 Hz, 2H).δ 4.13 (s, 2H), δ 3.75 – 3.84 (m, 12H), 3.51 (s, 2H), δ 1.15 (t, J = 7.0 Hz, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 118.7, 58.4, 31.1, 18.5.

2-(3-bromophenyl)pyridine (2a)



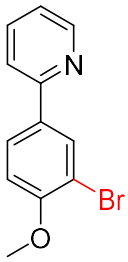
Yellow oil, procedure A, 86% (101 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (ddd, J = 4.8, 1.8, 1.0 Hz, 1H), 8.17 (t, J = 1.9 Hz, 1H), 7.90 (ddd, J = 7.8, 1.7, 1.0 Hz, 1H), 7.76 (ddd, J = 8.0, 7.4, 1.8 Hz, 1H), 7.69 (dt, J = 8.0, 1.1 Hz, 1H), 7.54 (ddd, J = 8.0, 2.0, 1.1 Hz, 1H), 7.34 (t, J = 7.9 Hz, 1H), 7.25 (ddd, J = 7.3, 4.7, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.96, 149.9, 141.5, 137.0, 131.98, 130.4, 130.1, 125.5, 123.2, 122.8, 120.7.

2-(3-bromo-4-methylphenyl)pyridine (2b)



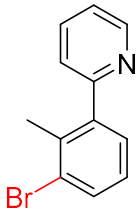
Yellow oil, procedure A, 89% (110 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 8.20 (d, *J* = 1.9 Hz, 1H), 7.82 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.73 (ddd, *J* = 8.0, 7.3, 1.8 Hz, 1H), 7.67 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.32 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.22 (ddd, *J* = 7.3, 4.8, 1.3 Hz, 1H), 2.44 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 149.8, 138.9, 138.7, 136.9, 131.1, 130.8, 125.7, 125.6, 122.5, 120.4, 22.9.

2-(3-bromo-4-methoxyphenyl)pyridine (2c)



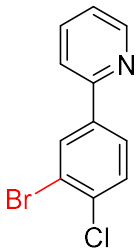
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 3.5 Hz, 1.2Hz 1H), 8.22 (d, *J* = 2.3 Hz, 1H), 7.85 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.63 (td, *J* = 7.7, 1.9 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.15 – 7.09 (m, 2H), 6.90 (d, *J* = 8.6 Hz, 1H), 3.86 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 155.56, 149.6, 136.8, 133.2, 131.8, 127.0, 122.0, 119.8, 112.1, 111.8, 56.3.

2-(3-Bromo-2-methylphenyl)pyridine (2d)



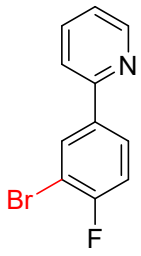
colorless oil, procedure B and 48 h, 38% (47 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.5 Hz, 1H), 7.81 (td, *J* = 7.7, 1.8 Hz, 1H), 7.65 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.17 (t, *J* = 7.8 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 149.4, 142.6, 136.4, 135.8, 132.6, 128.9, 126.98, 126.6, 124.3, 122.1, 20.7.

2-(3-bromo-4-chlorophenyl)pyridine (2e)



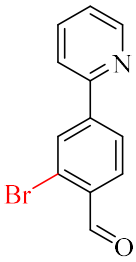
Off-white solid, procedure A, 60% (81 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 8.30 (d, *J* = 2.1 Hz, 1H), 7.87 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.77 (ddd, *J* = 8.0, 7.4, 1.8 Hz, 1H), 7.69 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.29 – 7.24 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.96, 150.00, 139.48, 137.14, 135.24, 132.22, 130.65, 126.79, 123.13, 122.99, 120.52. m.p. 60 – 62.

2-(3-bromo-4-fluorophenyl)pyridine (2f)



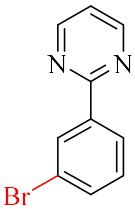
Colourless Solid, mp 47-49 °C, procedure A, 53% (67 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.23 (dd, *J* = 6.7, 2.3 Hz, 1H), 7.89 (ddd, *J* = 8.6, 4.7, 2.3 Hz, 1H), 7.75 (td, *J* = 7.7, 1.9 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.27 – 7.22 (m, 1H), 7.19 (t, *J* = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7 (d, J_{C-F} = 249.6 Hz), 155.1, 149.9, δ 137.1, 137.0 (d, J_{C-F} = 6.0 Hz), 132.3, 127.5 (d, J_{C-F} = 7.5 Hz), 122.7, 120.4, 116.7 (d, J_{C-F} = 22.6 Hz), 109.7 (d, J_{C-F} = 21.1 Hz).

2-bromo-4-(pyridin-2-yl)benzaldehyde (2g)



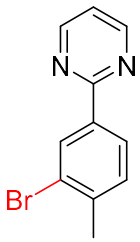
Off-white solid, procedure A, 51% (66 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (d, *J* = 0.7 Hz, 1H), 8.72 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 8.34 (d, *J* = 1.6 Hz, 1H), 8.06 – 7.92 (m, 2H), 7.85 – 7.75 (m, 2H), 7.31 (ddd, *J* = 6.8, 4.8, 1.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 154.4, 150.1, 145.9, 137.2, 133.3, 132.2, 130.1, 127.6, 126.1, 123.7, 121.2.

2-(3-bromophenyl)pyridine (2j)



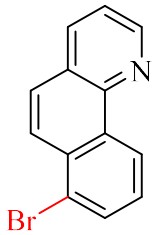
colorless solid, procedure A, 56% (66 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 4.9 Hz, 2H), 8.67 (t, *J* = 1.9 Hz, 1H), 8.43 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.66 (ddd, *J* = 7.9, 2.1, 1.1 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.26 (t, *J* = 4.8 Hz, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 163.4, 157.4, 139.6, 133.7, 131.2, 130.2, 126.7, 122.9, 119.6.

2-(3-Bromo-4-methylphenyl)pyrimidine (2k)



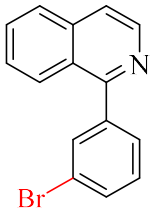
colorless solid, procedure A, 62% (77 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.9 Hz, 2H), 8.63 (d, *J* = 1.8 Hz, 1H), 8.27 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 4.8 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 157.4, 140.8, 137.1, 132.1, 131.0, 126.99, 125.5, 119.4, 23.1.

7-bromobenzo[h]quinolone (2h)



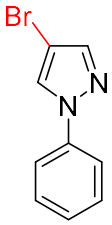
Off-white solid, procedure A, 47% (61 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (dt, *J* = 8.3, 1.0 Hz, 1H), 9.02 (dd, *J* = 4.4, 1.8 Hz, 1H), 8.26 (dd, *J* = 9.2, 0.8 Hz, 1H), 8.21 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.98 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.79 (d, *J* = 9.2 Hz, 1H), 7.70 – 7.52 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 146.2, 136.1, 133.4, 132.4, 132.2, 127.6, 126.9, 126.3, 126.3, 124.3, 122.9, 122.5.

1-(3-bromophenyl)isoquinoline (2i)



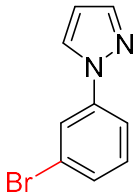
Colorless oil, procedure A and 24 h, 32% (45 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 5.7, 1.2 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.79 – 7.66 (m, 2H), 7.66 – 7.47 (m, 5H), 7.41 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 142.3, 142.2, 136.5, 134.3, 134.3, 134.2, 133.2, 132.99, 131.2, 130.6, 127.8, 127.2, 127.0, 121.2.

4-bromo-1-phenyl-1H-pyrazole (2l)



Colourless Solid, procedure A, 66% (74 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 0.7 Hz, 1H), 7.68 (s, 1H), 7.66 – 7.62 (m, 2H), 7.48 – 7.43 (m, 2H), 7.35 – 7.29 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 139.6, 129.5, 126.96, 118.9, 95.6.

1-(3-Bromophenyl)-*1H*-pyrazole (3l)



colorless oil, procedure C and 24 h, 26% (29 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (t, *J* = 2.4 Hz, 1H), 7.72 (d, *J* = 1.8 Hz, 0H), 7.62 (ddd, *J* = 8.1, 2.2, 1.0 Hz, 1H), 7.40 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 6.47 (t, *J* = 2.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 141.3, 130.8, 129.5, 126.9, 123.2, 122.4, 117.6, 108.2.

1, 3-bis(triethoxysilyl)methyl imidazolium chloride ionic liquid (BTESMICl)

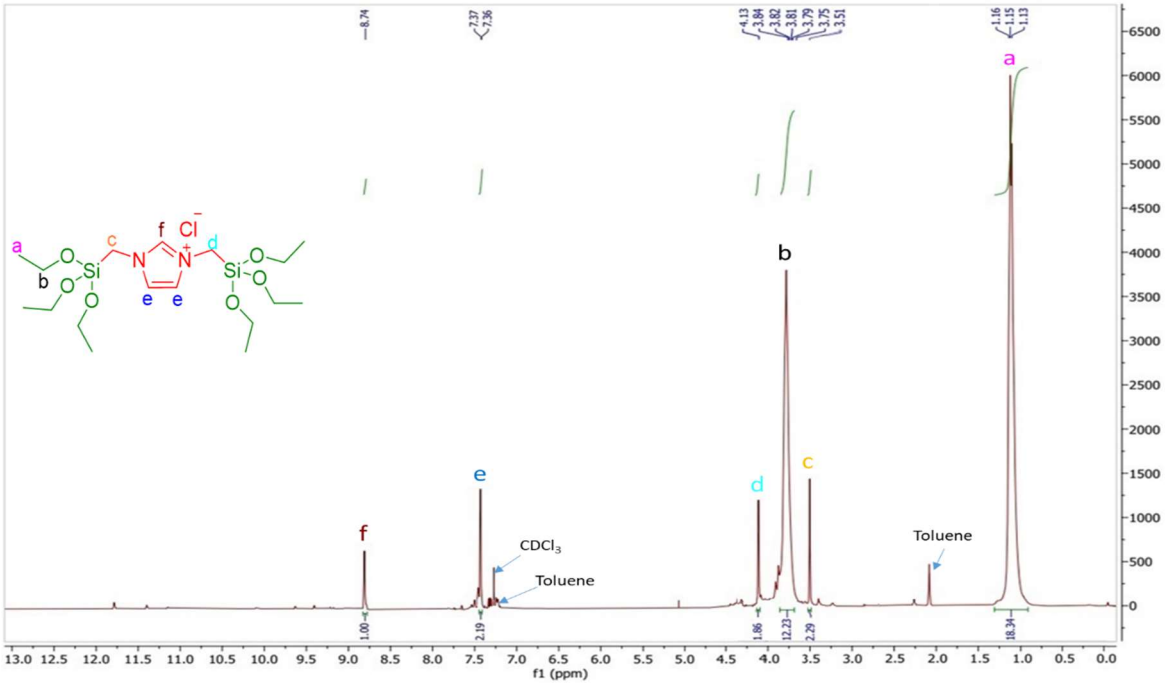


Figure S28. ^{1}H-NMR Spectrum of 1, 3-bis(triethoxysilyl)methyl imidazolium chloride ionic liquid (BTESMICl) in $CDCl_3$.

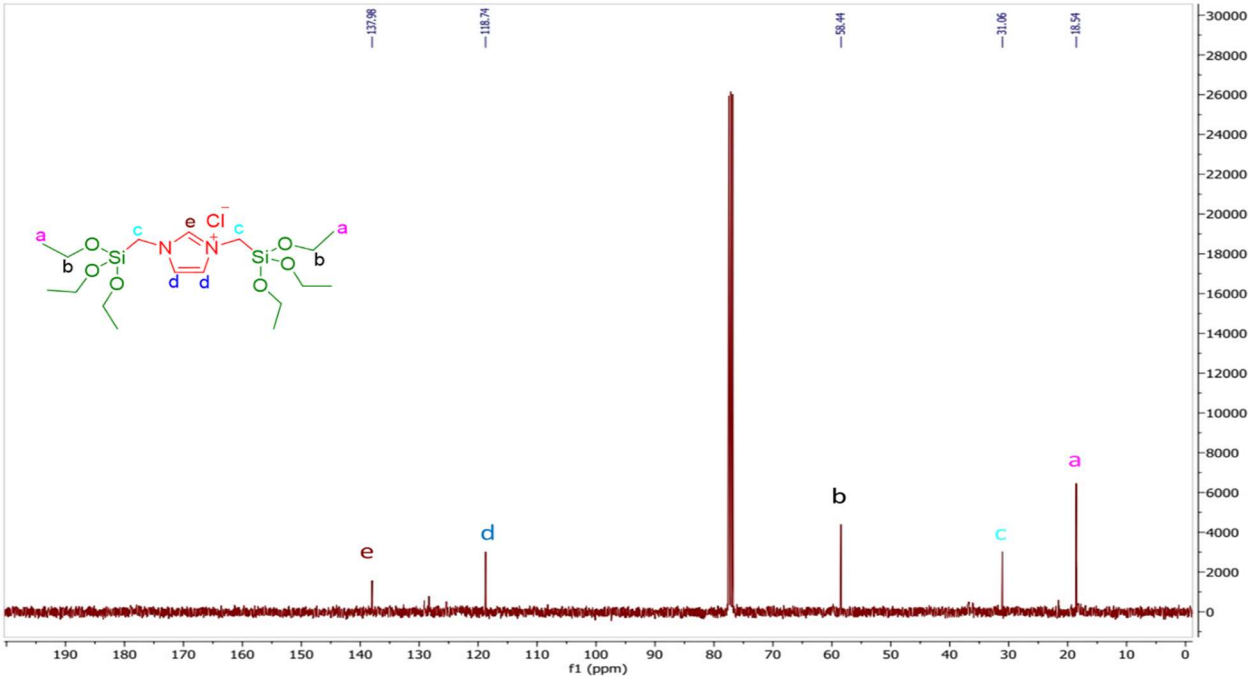


Figure S29. ^{13}C-NMR Spectrum of 1, 3-bis(triethoxysilyl)methyl imidazolium chloride ionic liquid (BTESMICl) in $CDCl_3$.

2-(3-bromophenyl)pyridine

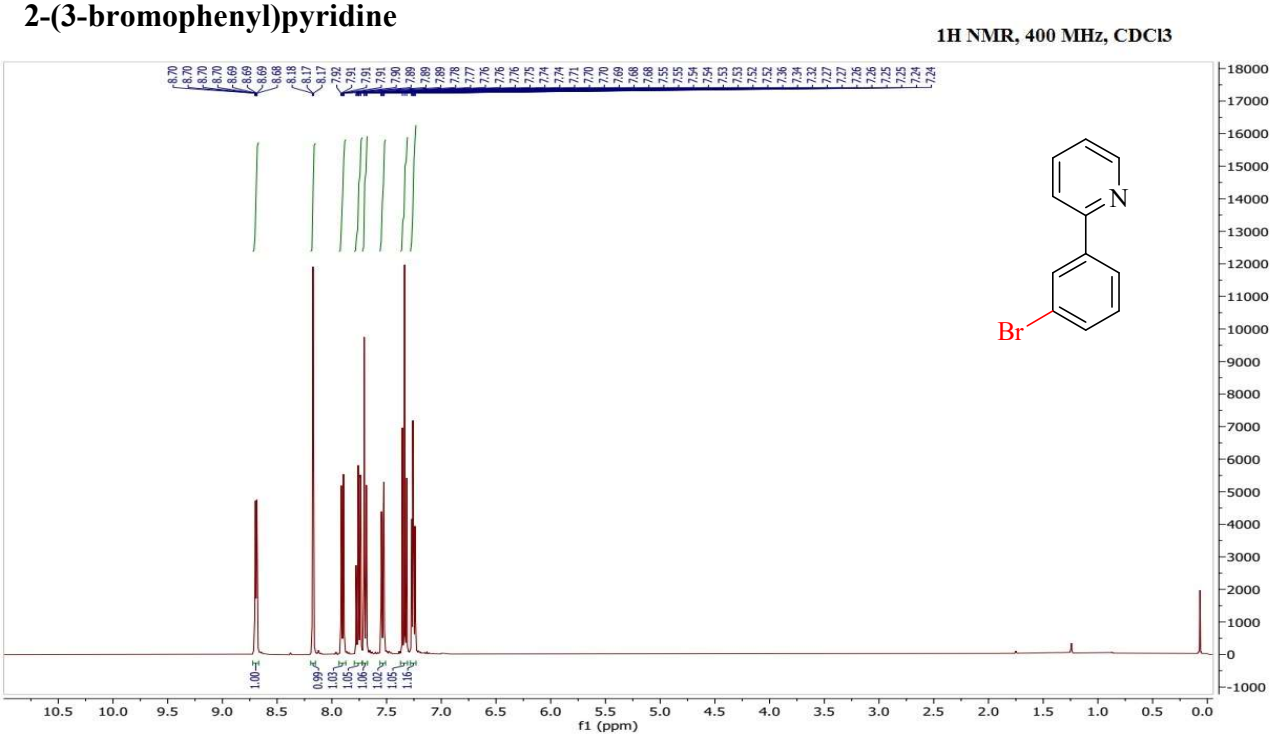


Figure S30. ^{1}H-NMR Spectrum of isolated pure 2-(3-bromophenyl)pyridine in $CDCl_3$.

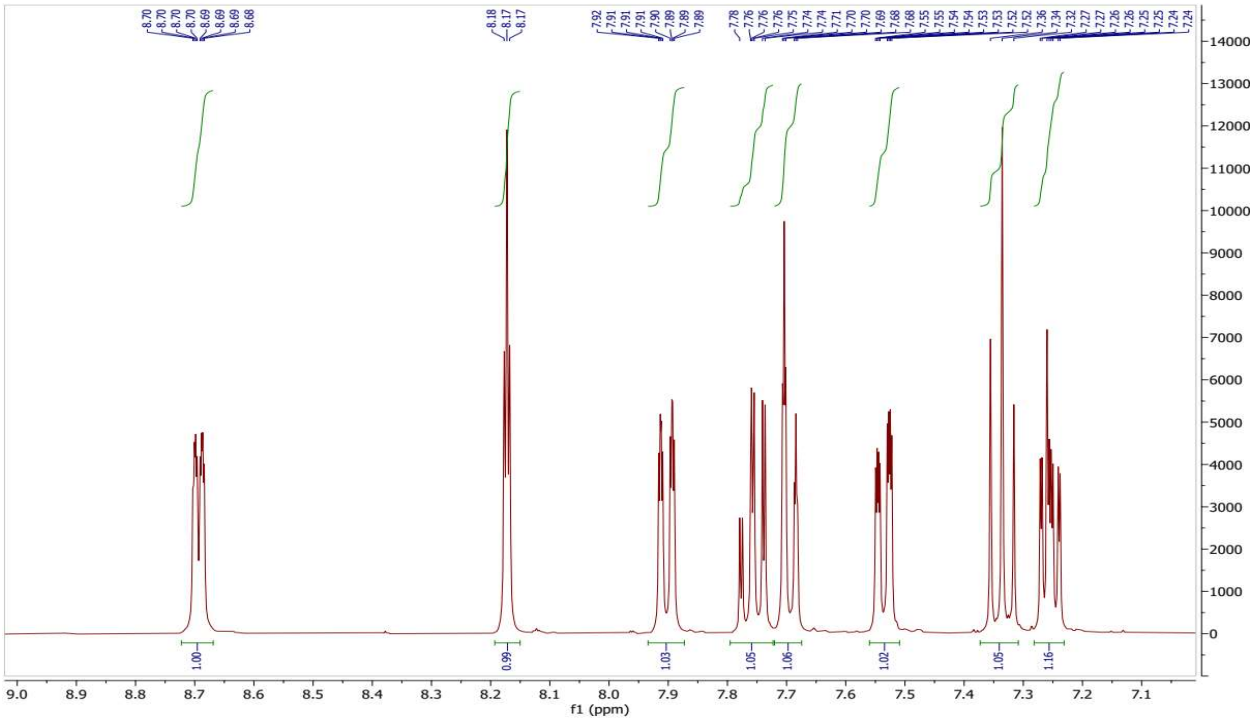


Figure S31. ^{1}H-NMR Spectrum of isolated pure 2-(3-bromophenyl)pyridine in $CDCl_3$ (Expanded).

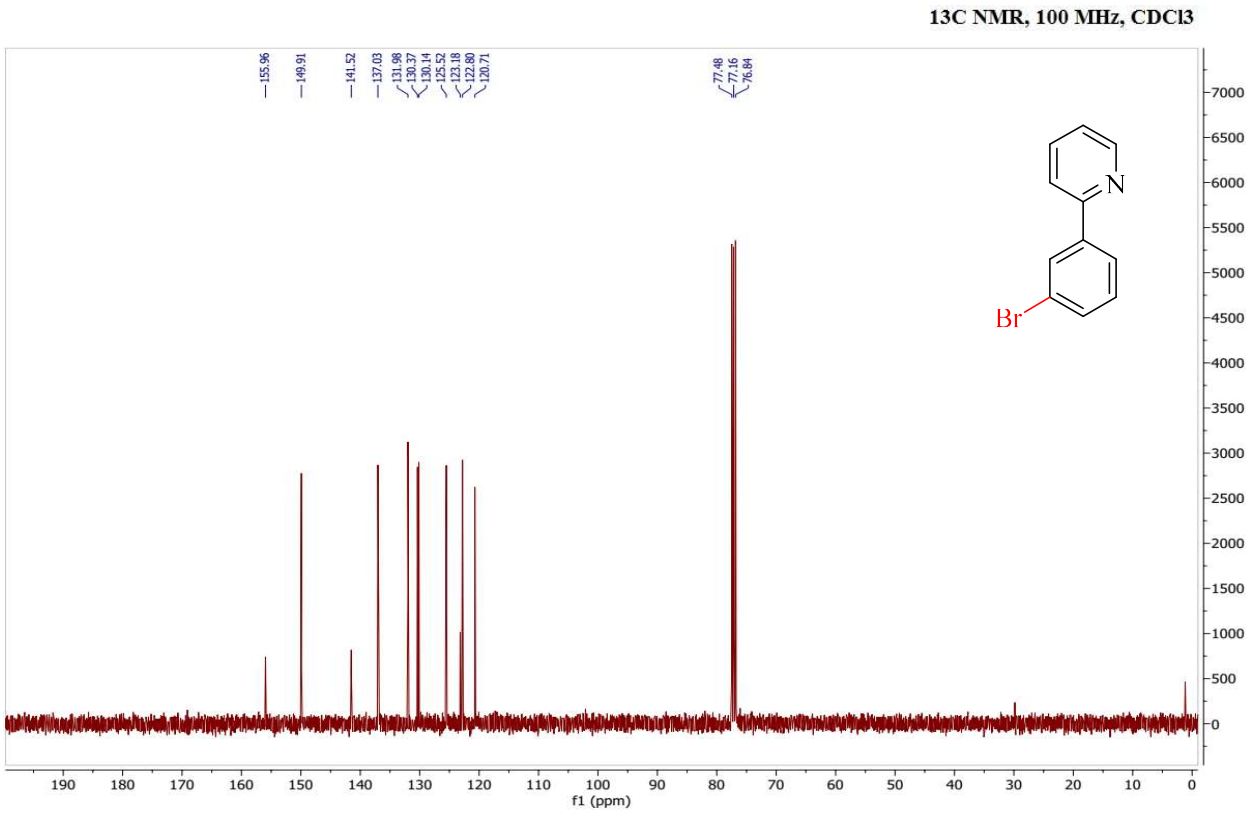
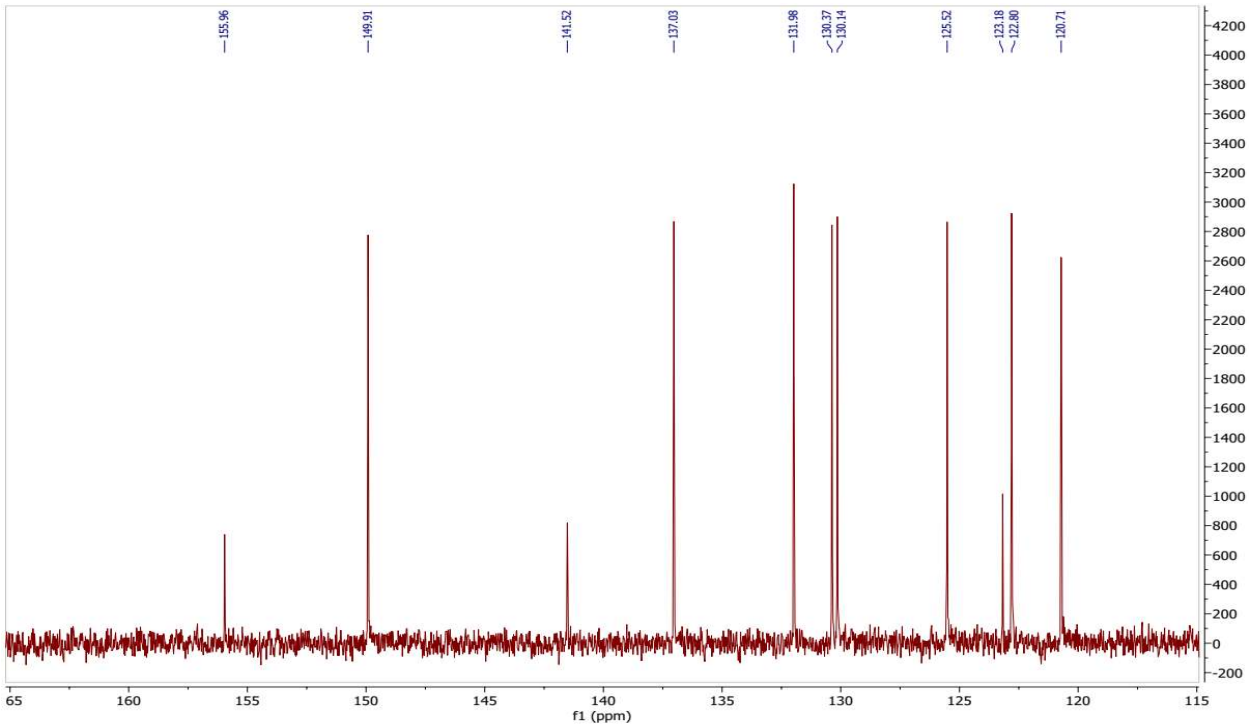
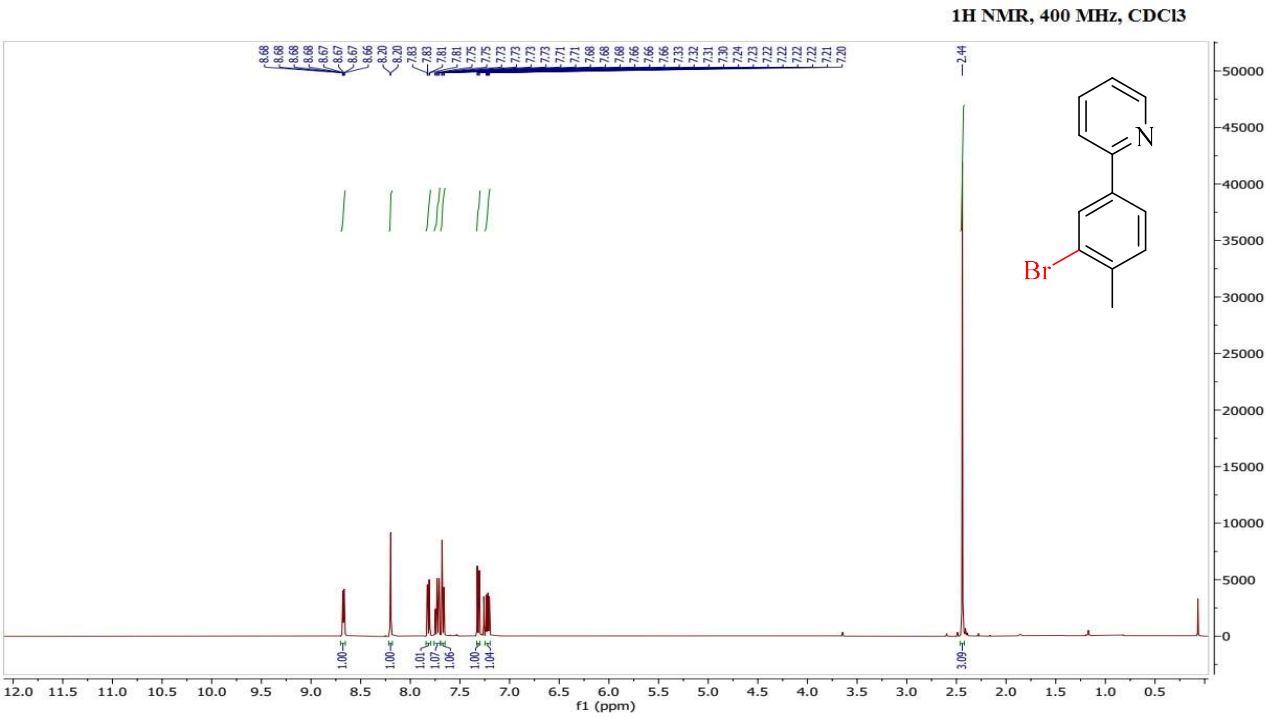


Figure S32. ^{13}C-NMR Spectrum of isolated pure 2-(3-bromophenyl)pyridine in $CDCl_3$.

Figure S33. ^{13}C-NMR Spectrum of isolated pure 2-(3-bromophenyl)pyridine in $CDCl_3$ (Expanded).

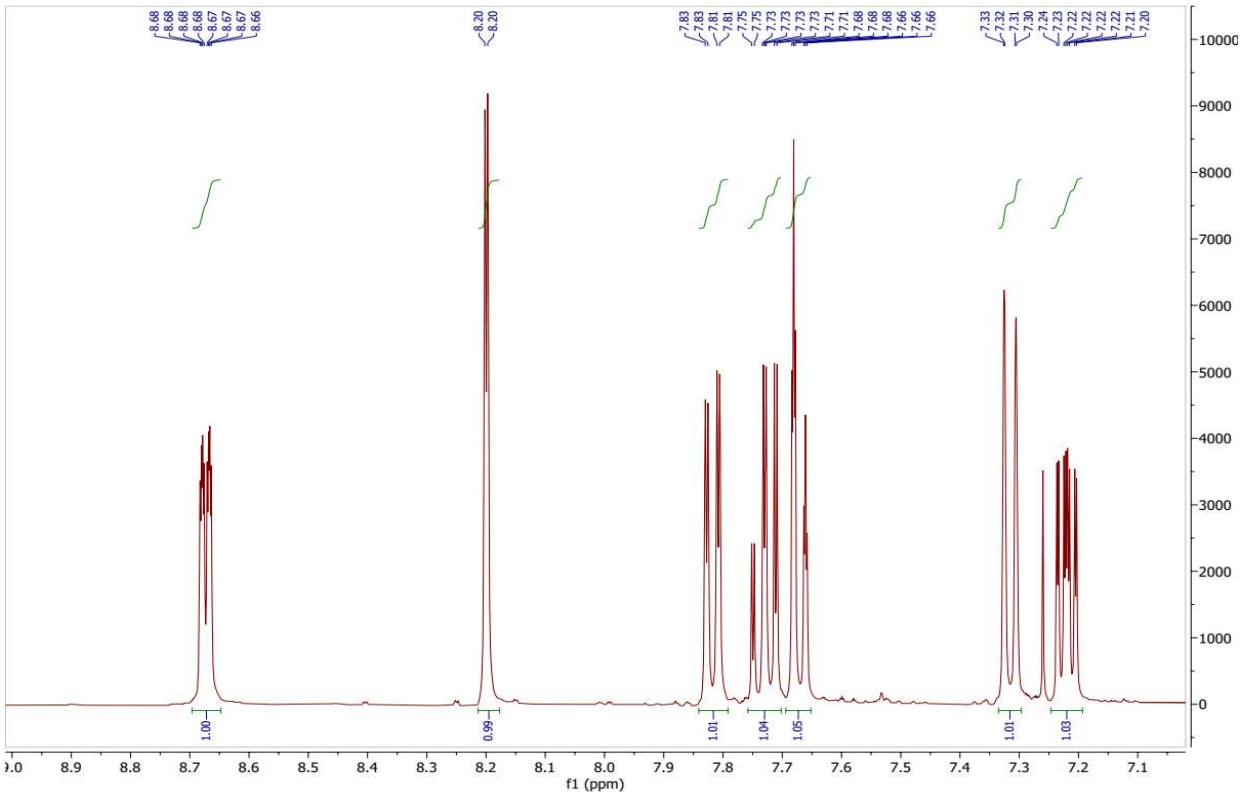




2-(3-bromo-4-methylphenyl)pyridine

Figure S34. ^{1}H-NMR Spectrum of isolated pure 2-(3-bromo-4-methylphenyl)pyridine in $CDCl_3$.

Figure S35. ^{1}H-NMR Spectrum of isolated pure 2-(3-bromo-4-methylphenyl)pyridine in $CDCl_3$ (Expanded).



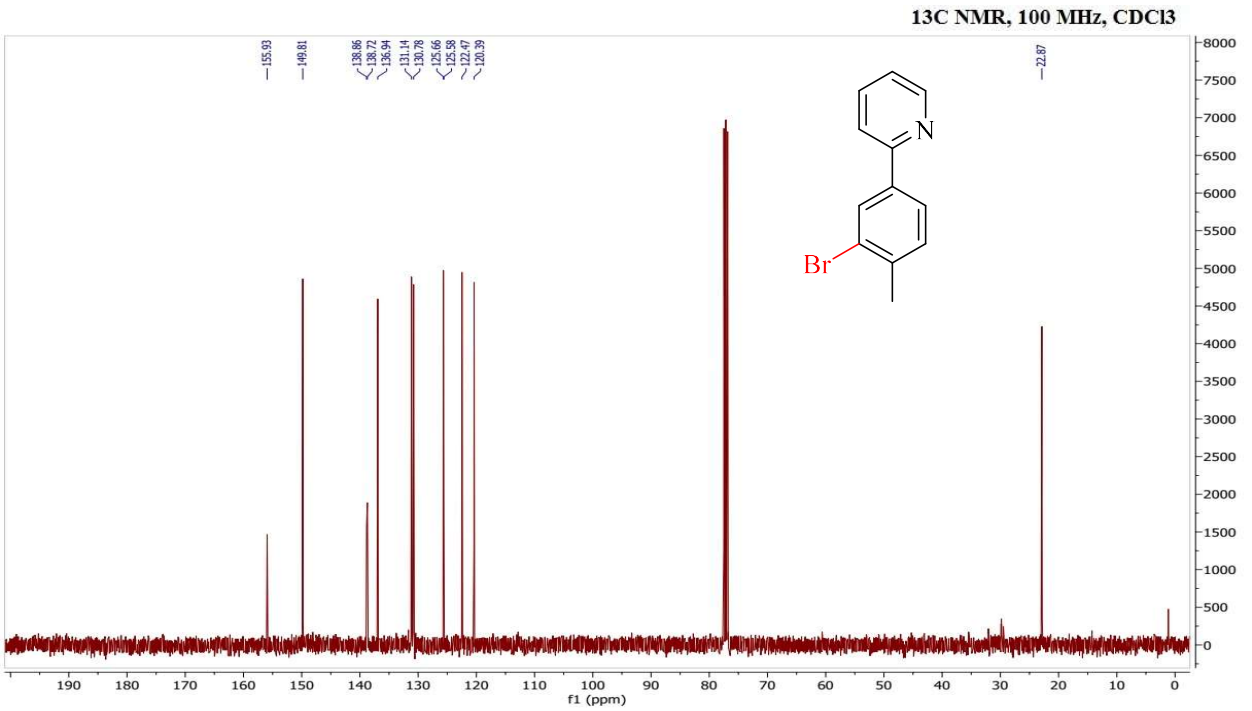


Figure S36. ^{13}C-NMR Spectrum of isolated pure 2-(3-bromo-4-methylphenyl)pyridine in $CDCl_3$.

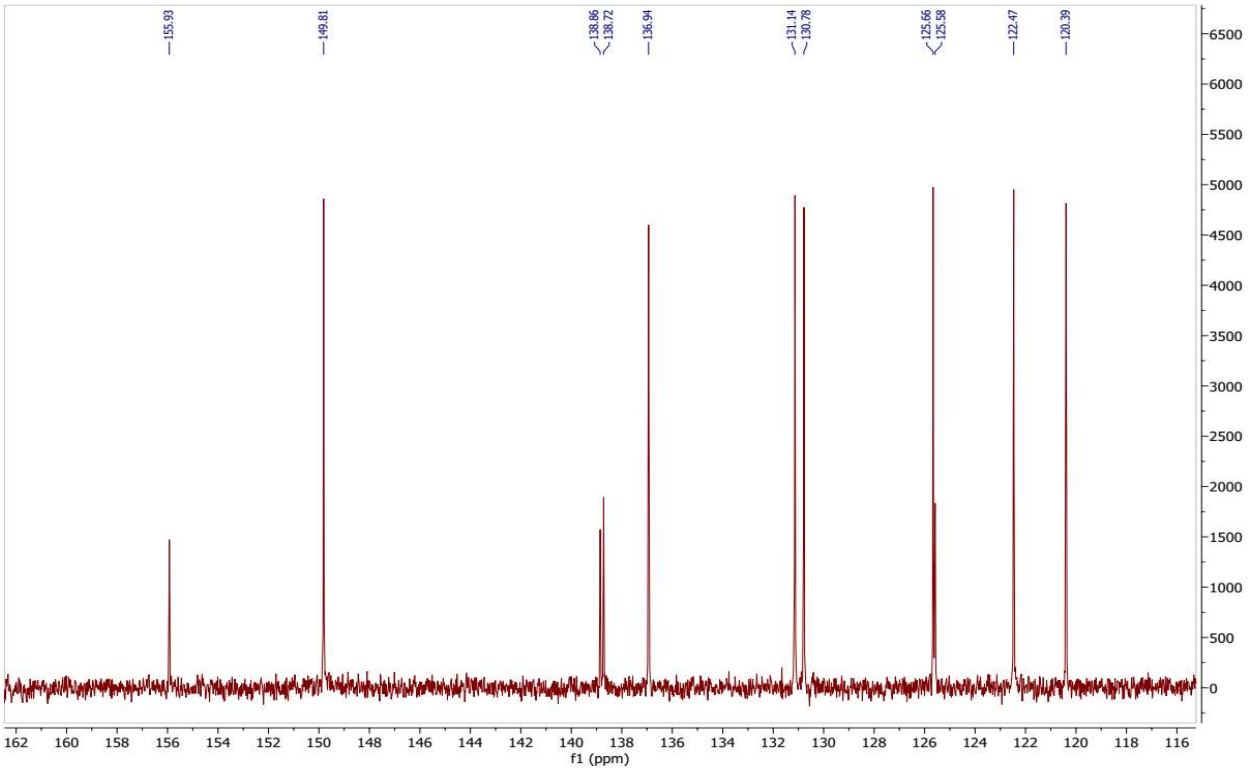


Figure S37. ^{13}C-NMR Spectrum of isolated pure 2-(3-bromo-4-methylphenyl)pyridine in $CDCl_3$ (Expanded).

2-(3-bromo-4-methoxyphenyl)pyridine **1H NMR, 400 MHz, CDCl3**

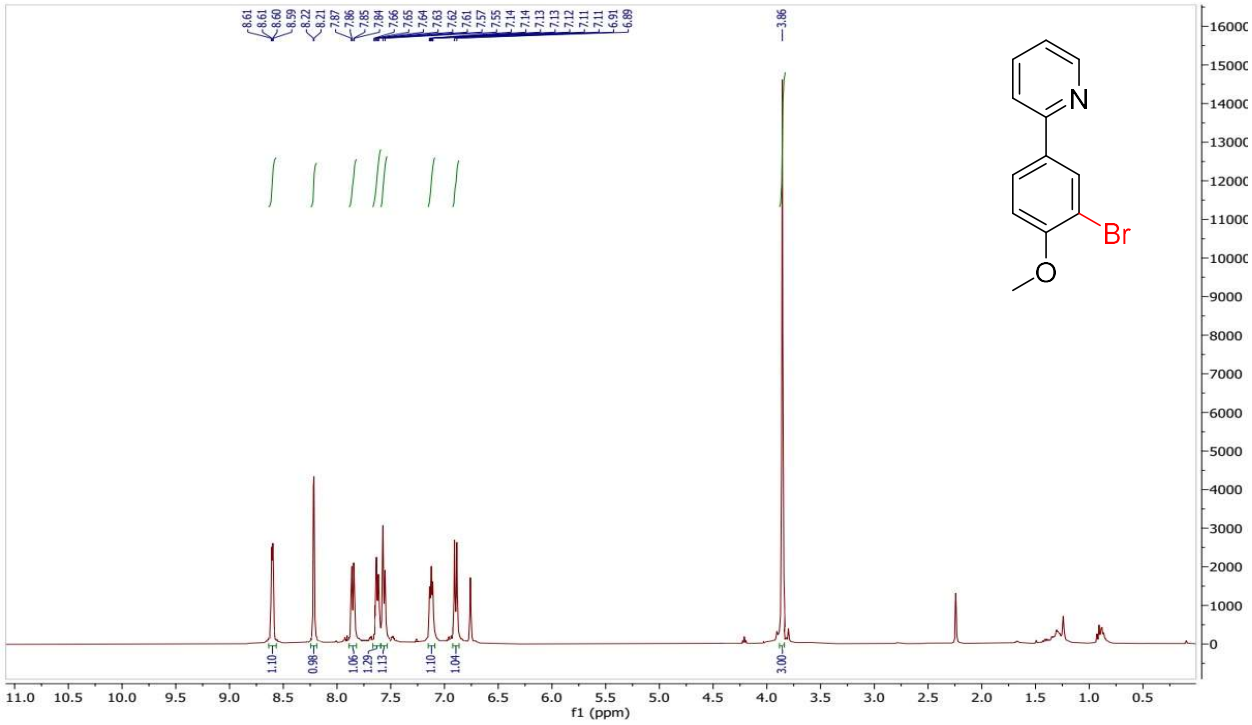


Figure S38. ^{1}H-NMR Spectrum of isolated pure 2-(3-bromo-4-methoxyphenyl)pyridine in $CDCl_3$.

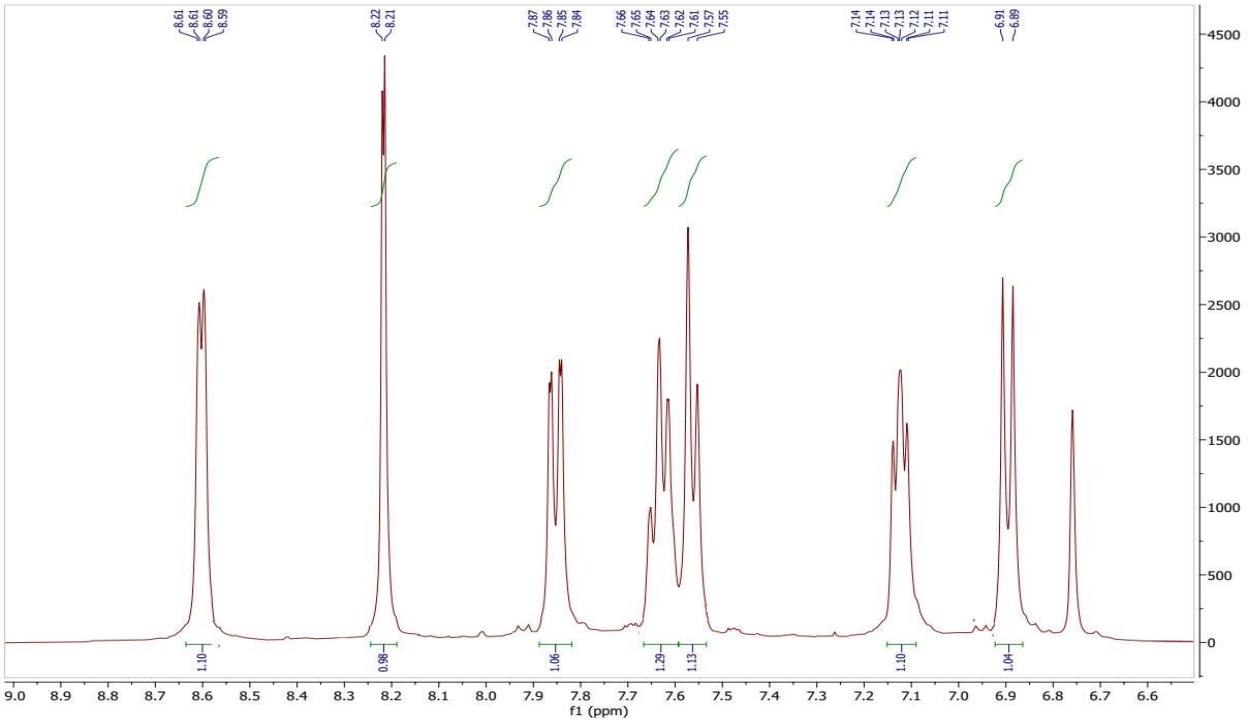


Figure S39. ^{1}H-NMR Spectrum of isolated pure 2-(3-bromo-4-methoxyphenyl)pyridine in $CDCl_3$ (Expaned)

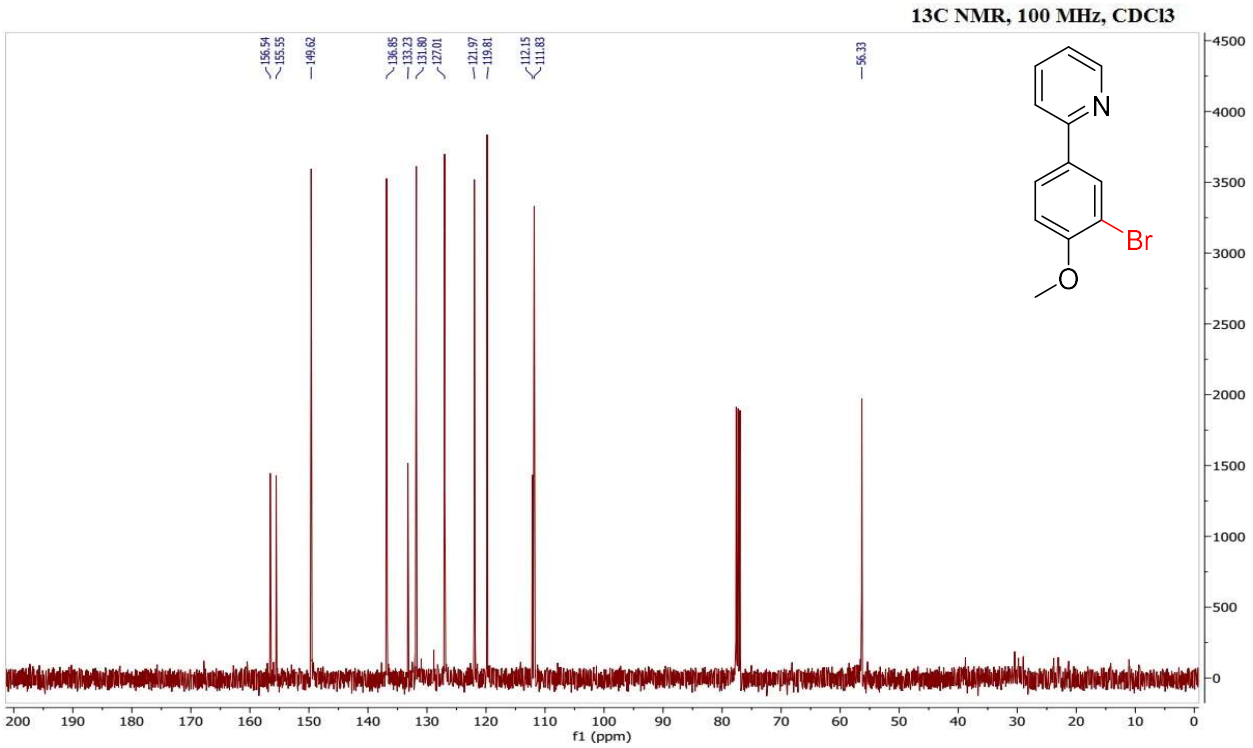


Figure S40. ^{13}C-NMR Spectrum of isolated pure 2-(3-bromo-4-methoxyphenyl)pyridine in $CDCl_3$.

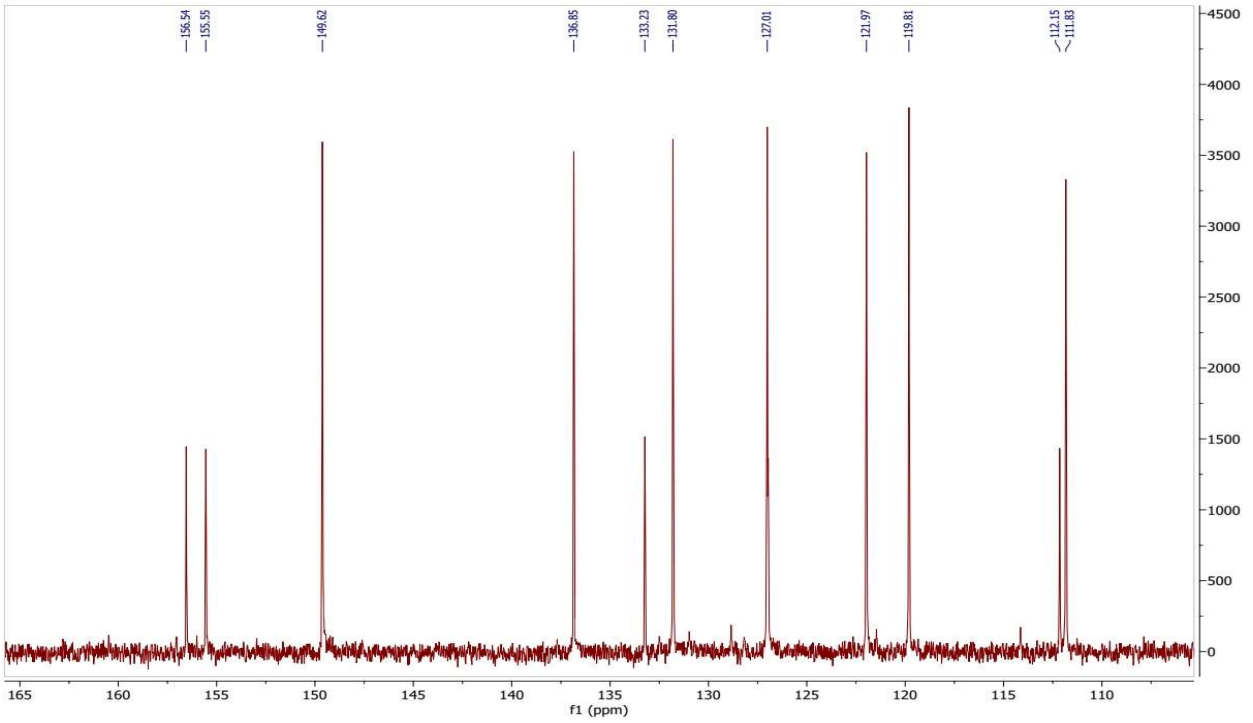
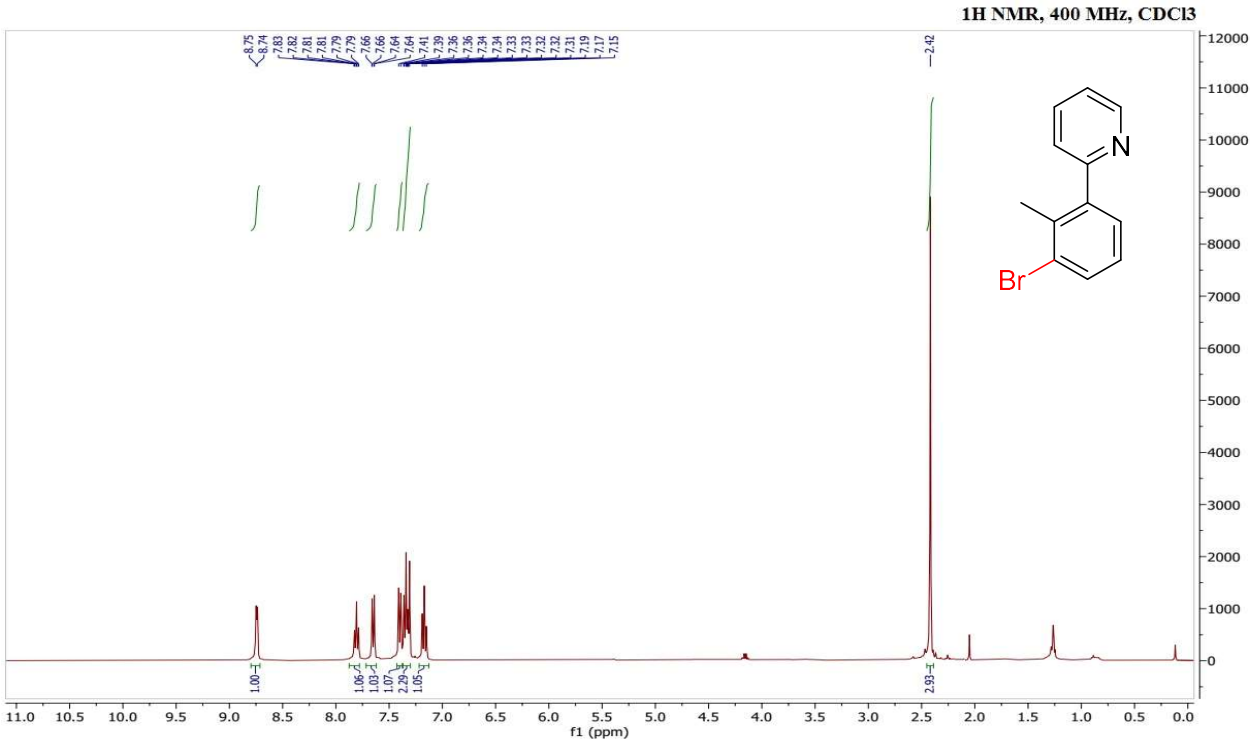


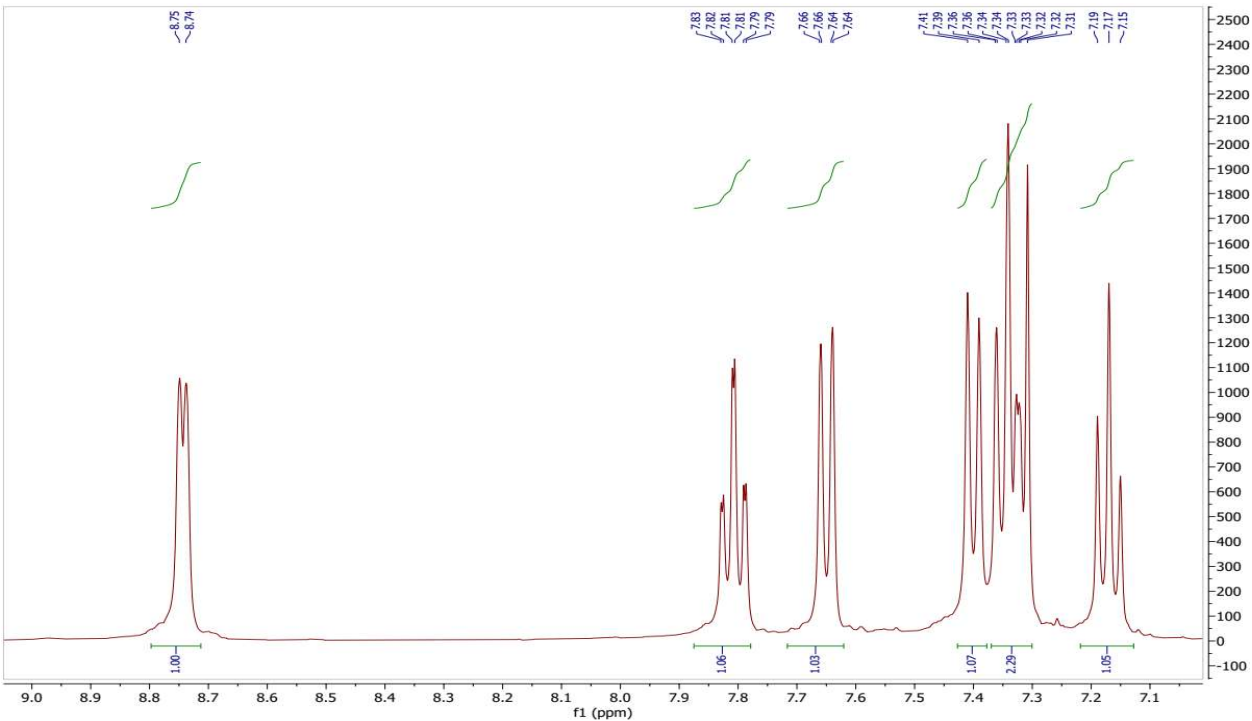
Figure S41. ^{13}C-NMR Spectrum of isolated pure 2-(3-bromo-4-methoxyphenyl)pyridine in $CDCl_3$ (Expaned).



2-(3-Bromo-2-methylphenyl)pyridine

Figure S42. ^{1}H-NMR Spectrum of isolated pure 2-(3-Bromo-2-methylphenyl)pyridine in $CDCl_3$.

Figure S43. ^{1}H-NMR Spectrum of isolated pure 2-(3-Bromo-2-methylphenyl)pyridine in $CDCl_3$ (Expanded).



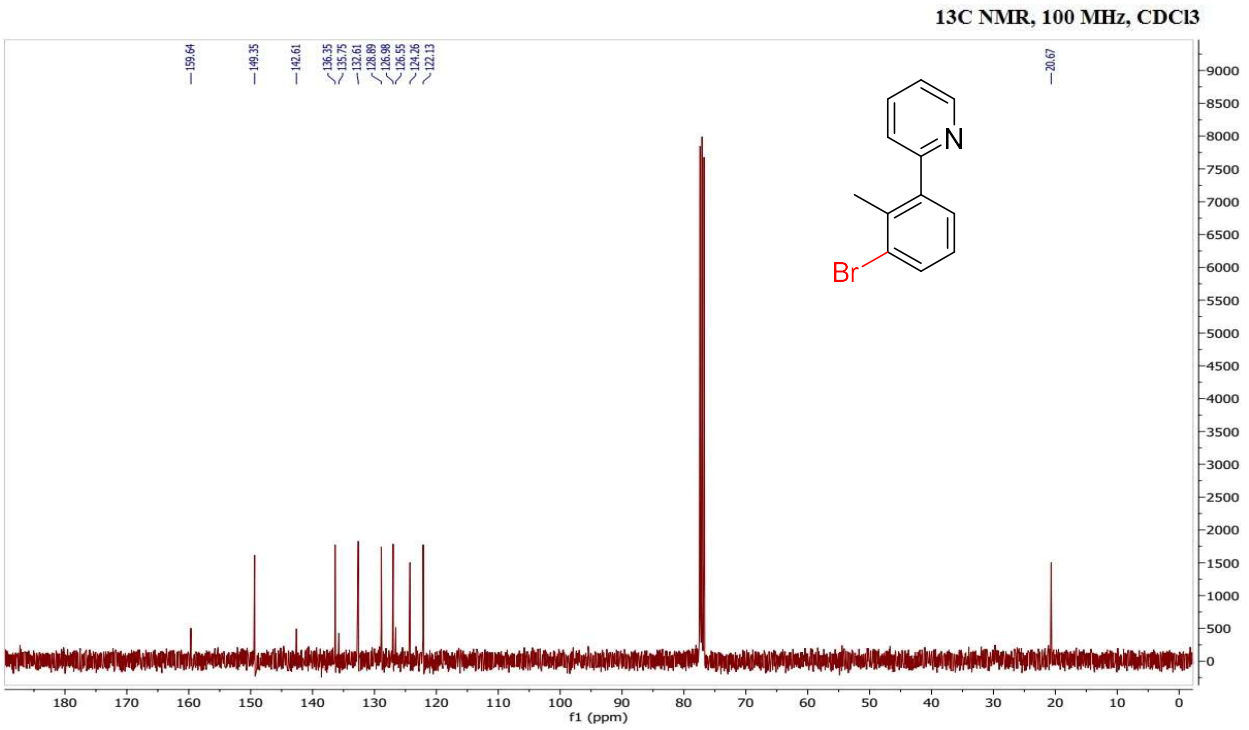


Figure S44. ^{13}C-NMR Spectrum of isolated pure 2-(3-Bromo-2-methylphenyl)pyridine in $CDCl_3$.

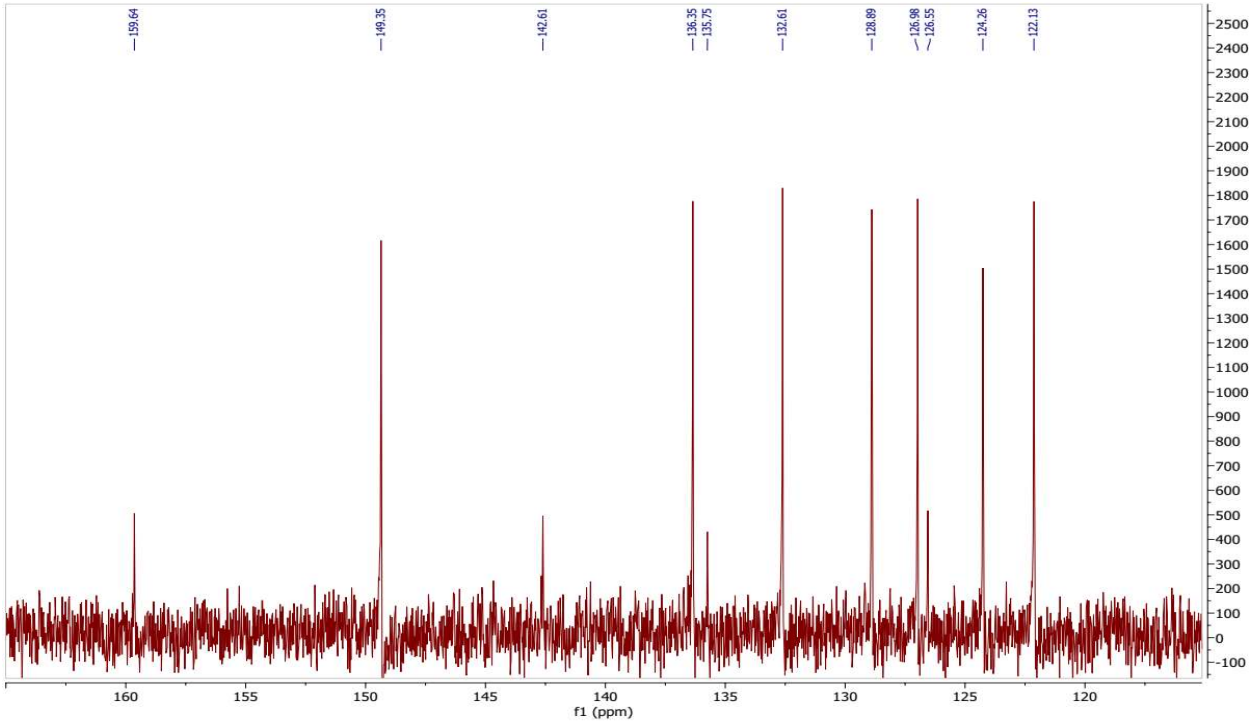
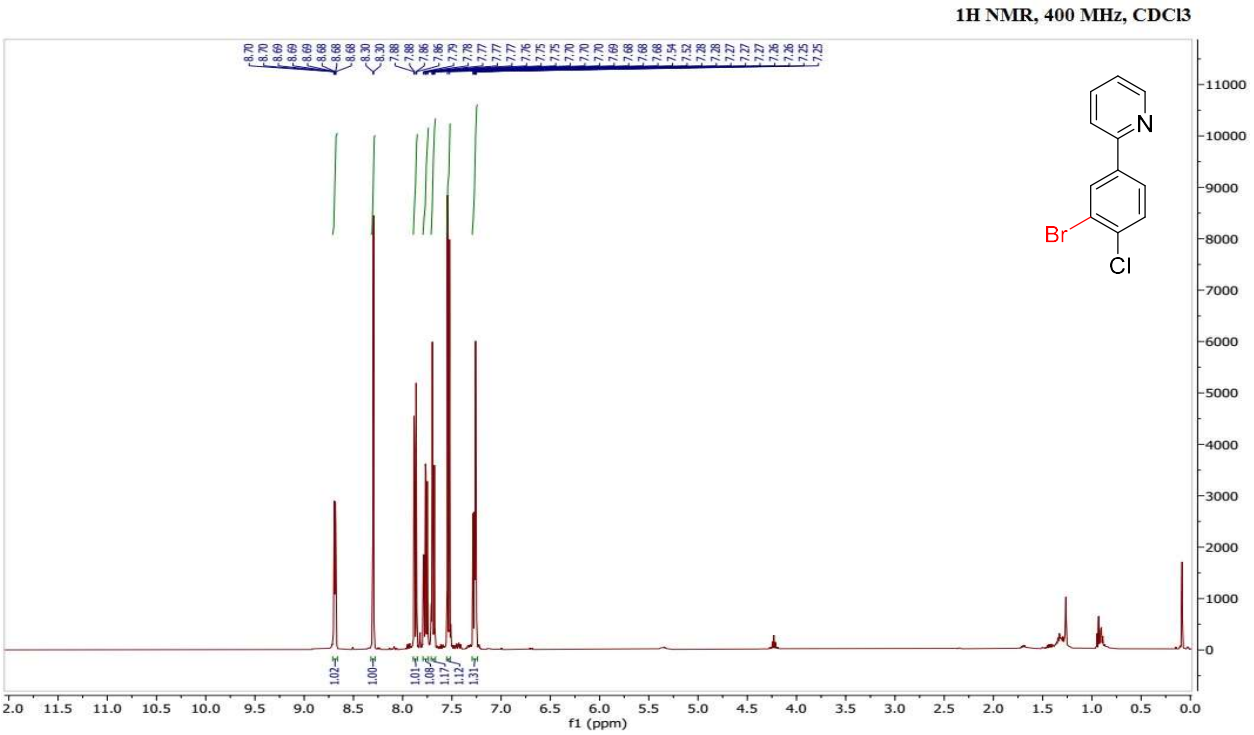


Figure S45. ^{13}C-NMR Spectrum of isolated pure 2-(3-Bromo-2-methylphenyl)pyridine in $CDCl_3$ (Expanded).



2-(3-bromo-4-chlorophenyl)pyridine

Figure S46. ^{1}H-NMR Spectrum of isolated pure 2-(3-bromo-4-chlorophenyl)pyridine in $CDCl_3$.

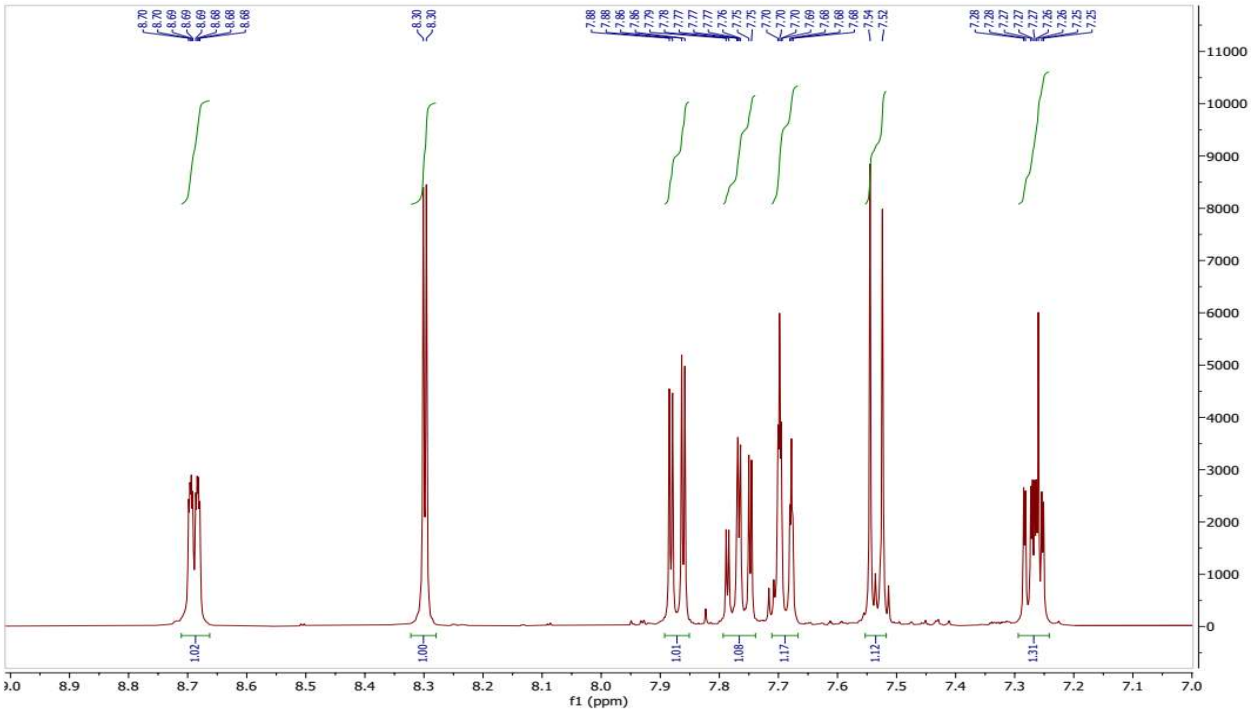


Figure S47. ^{1}H-NMR Spectrum of isolated pure 2-(3-bromo-4-chlorophenyl)pyridine in $CDCl_3$ (Expanded).

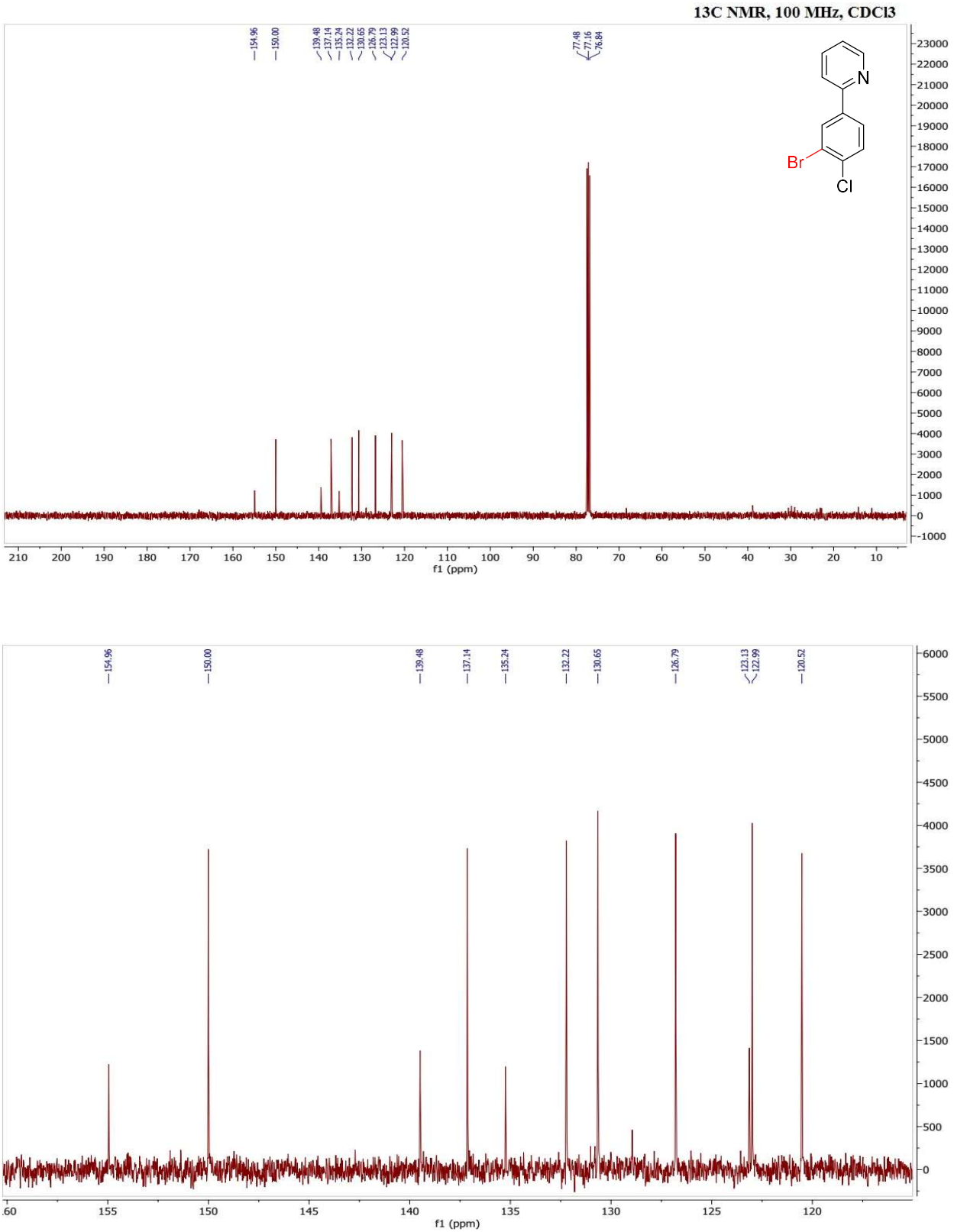
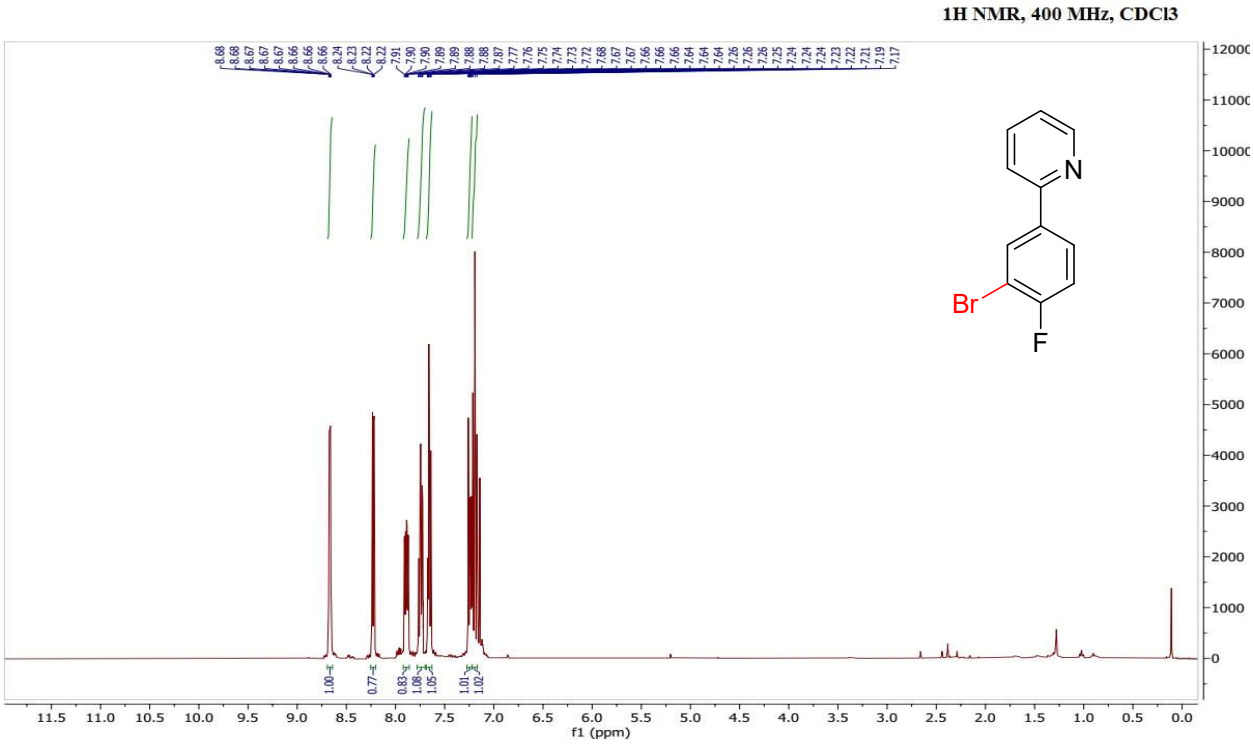


Figure S48. ^{13}C-NMR Spectrum of isolated pure 2-(3-bromo-4-chlorophenyl)pyridine in $CDCl_3$.

Figure S49. ^{13}C-NMR Spectrum of isolated pure 2-(3-bromo-4-chlorophenyl)pyridine in $CDCl_3$ (Expanded).



2-(3-bromo-4-fluorophenyl)pyridine

Figure S50. ^{1}H-NMR Spectrum of isolated pure 2-(3-bromo-4-fluorophenyl)pyridine in $CDCl_3$.

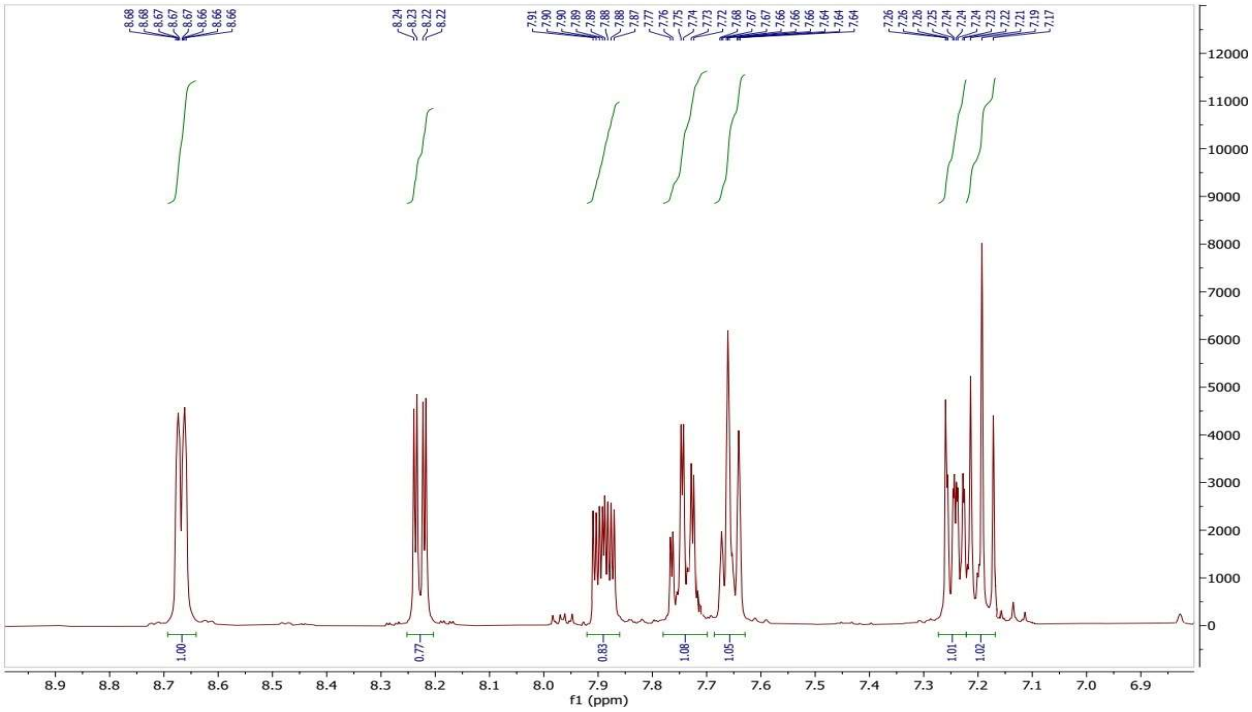


Figure S51. ^{1}H-NMR Spectrum of isolated pure 2-(3-bromo-4-fluorophenyl)pyridine in $CDCl_3$ (Expanded).

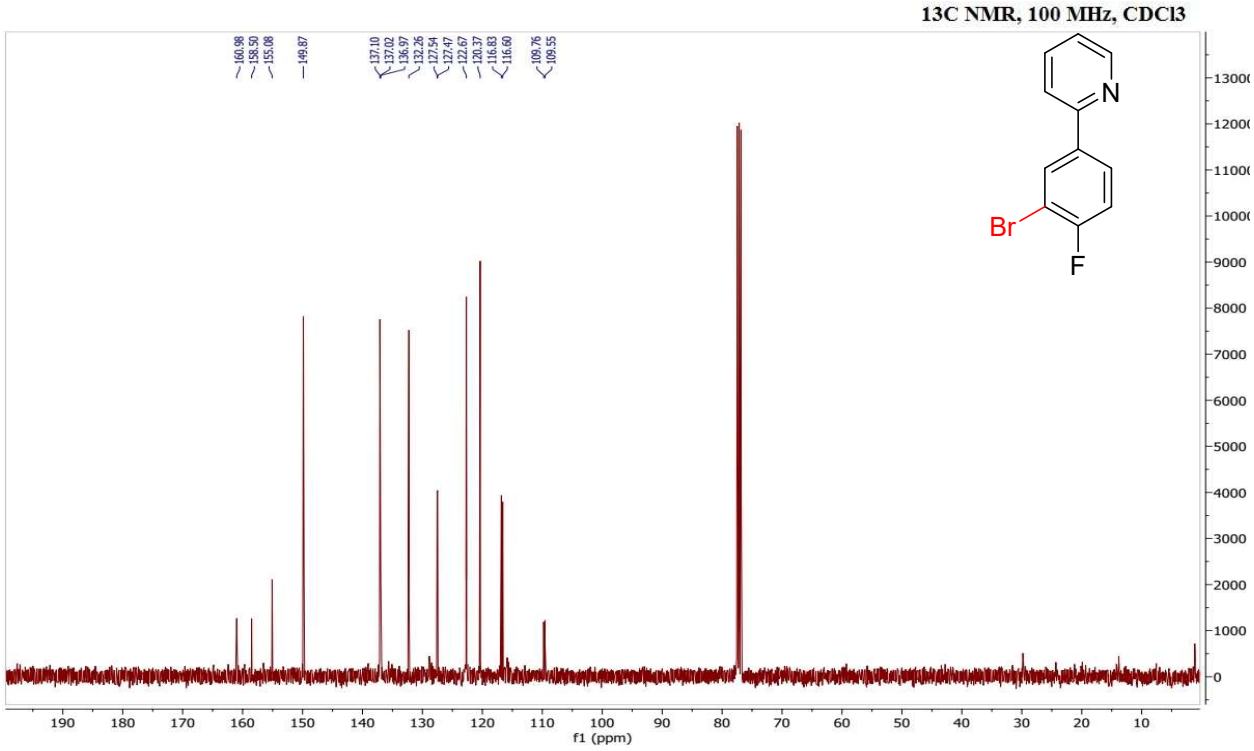


Figure S52. ^{13}C-NMR Spectrum of isolated pure 2-(3-bromo-4-fluorophenyl)pyridine in $CDCl_3$.

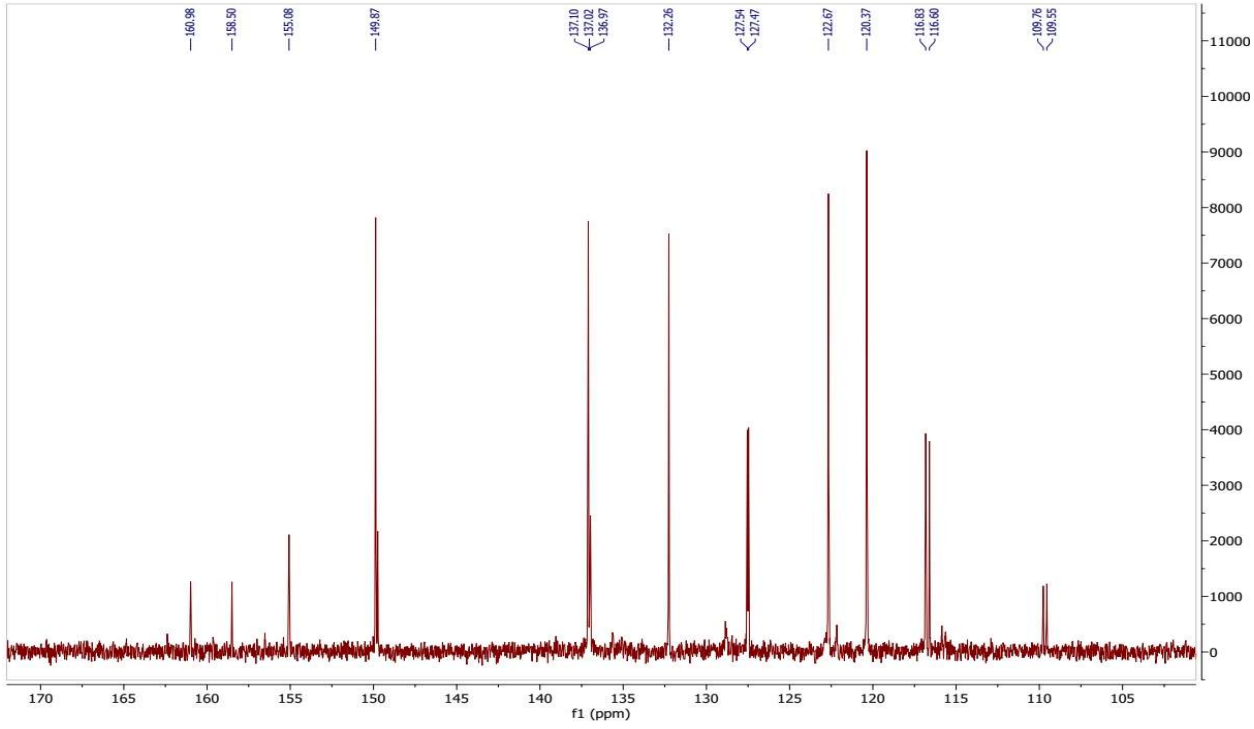
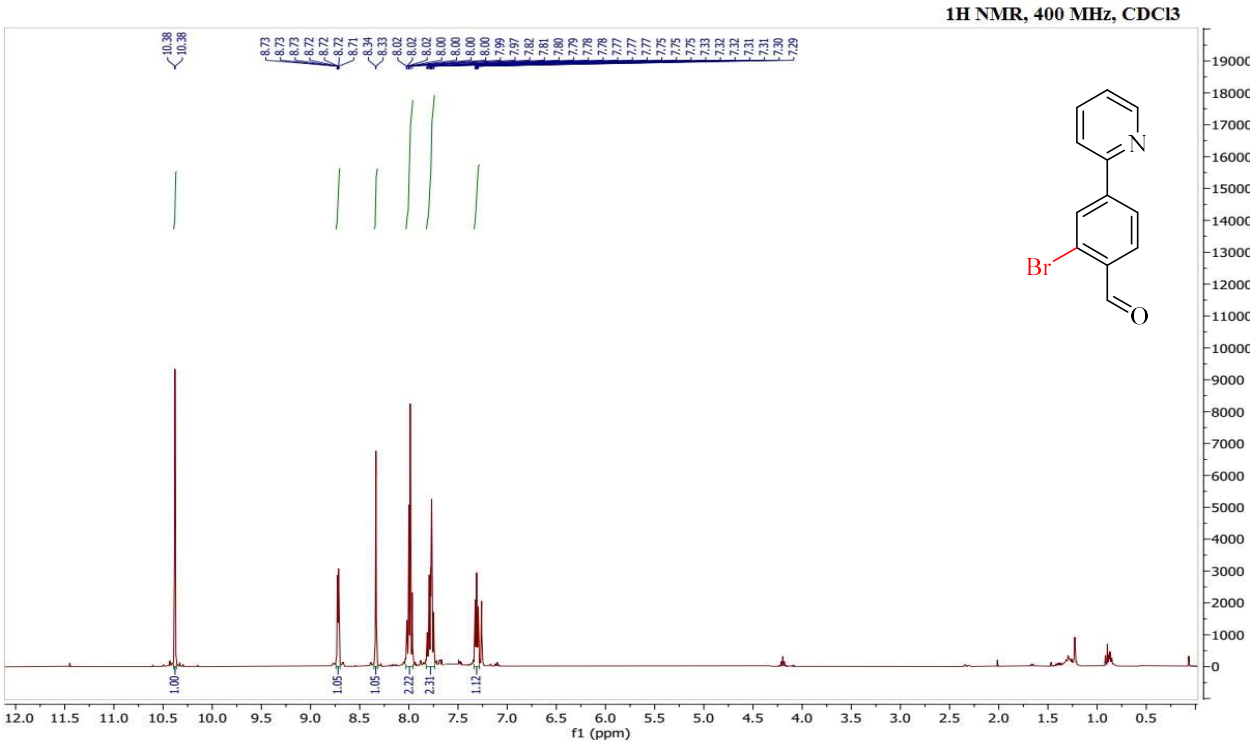


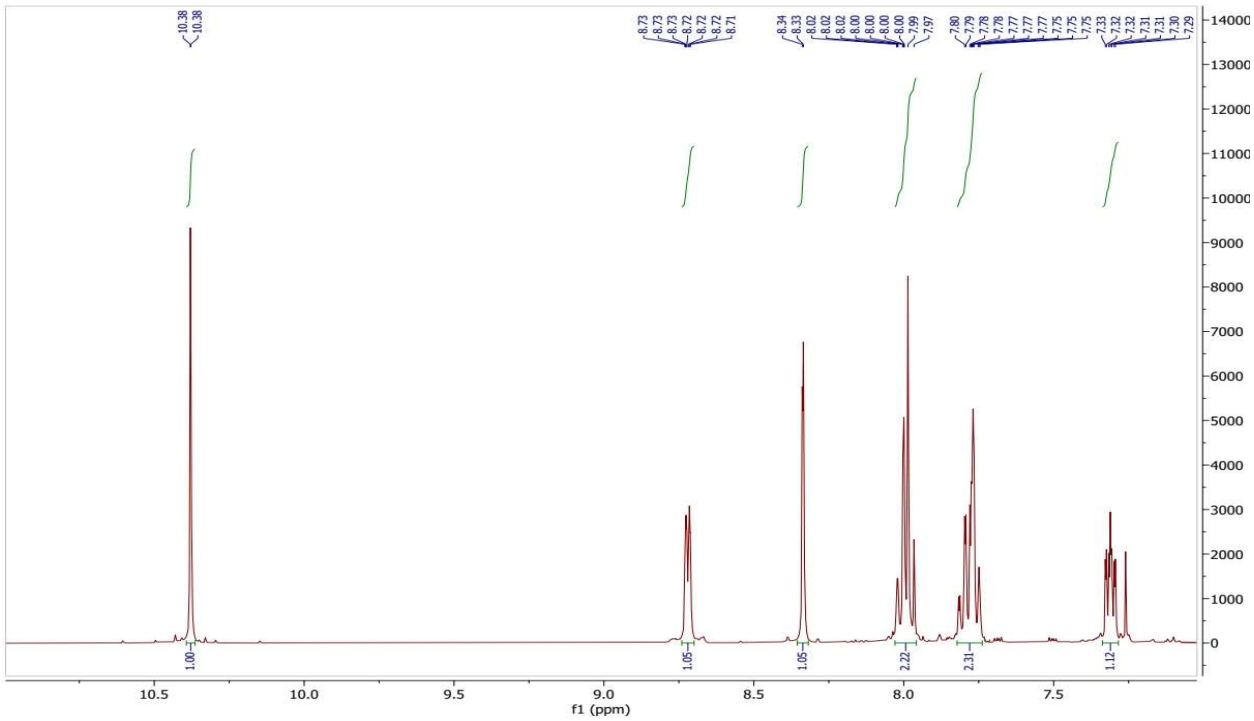
Figure S53. ^{13}C-NMR Spectrum of isolated pure 2-(3-bromo-4-fluorophenyl)pyridine in $CDCl_3$ (Expanded).



2-bromo-4-(pyridin-2-yl)benzaldehyde

Figure S54. ^{1}H-NMR Spectrum of isolated pure 2-bromo-4-(pyridin-2-yl)benzaldehyde in $CDCl_3$.

Figure S55. ^{1}H-NMR Spectrum of isolated pure 2-bromo-4-(pyridin-2-yl)benzaldehyde in $CDCl_3$ (Expanded).



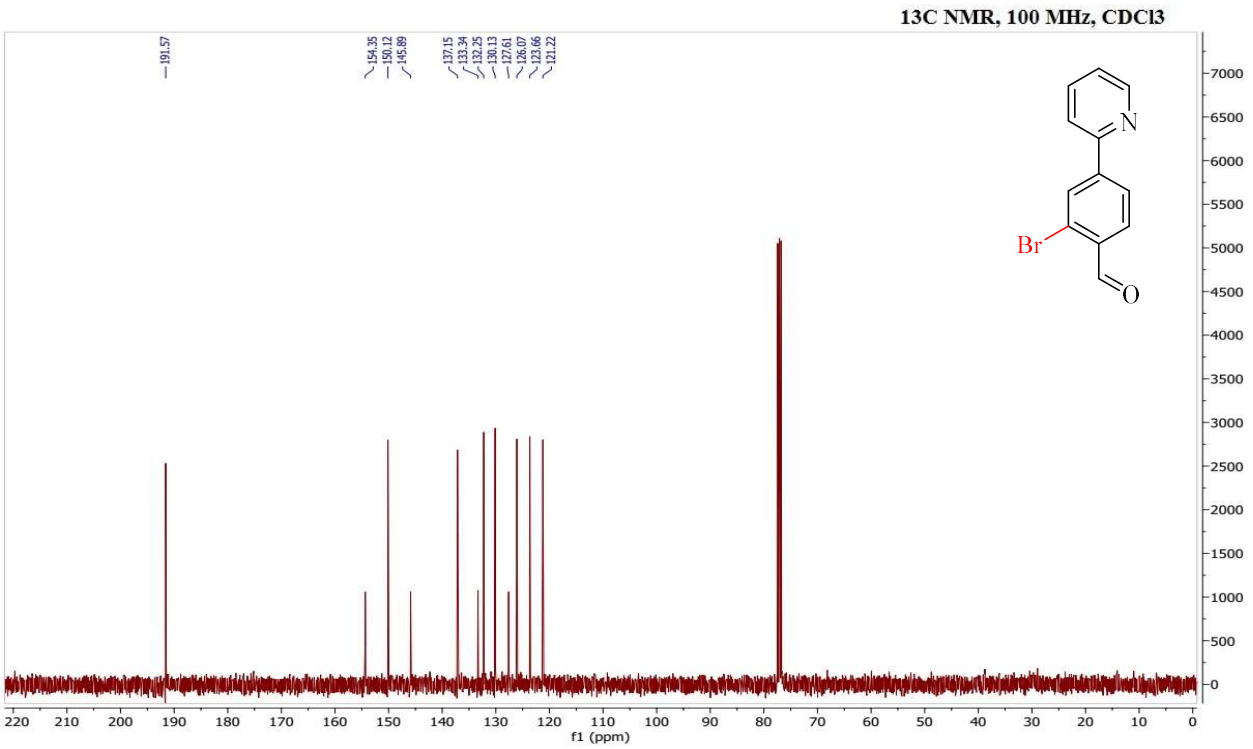


Figure S56. ^{13}C-NMR Spectrum of isolated pure 2-bromo-4-(pyridin-2-yl)benzaldehyde in $CDCl_3$.

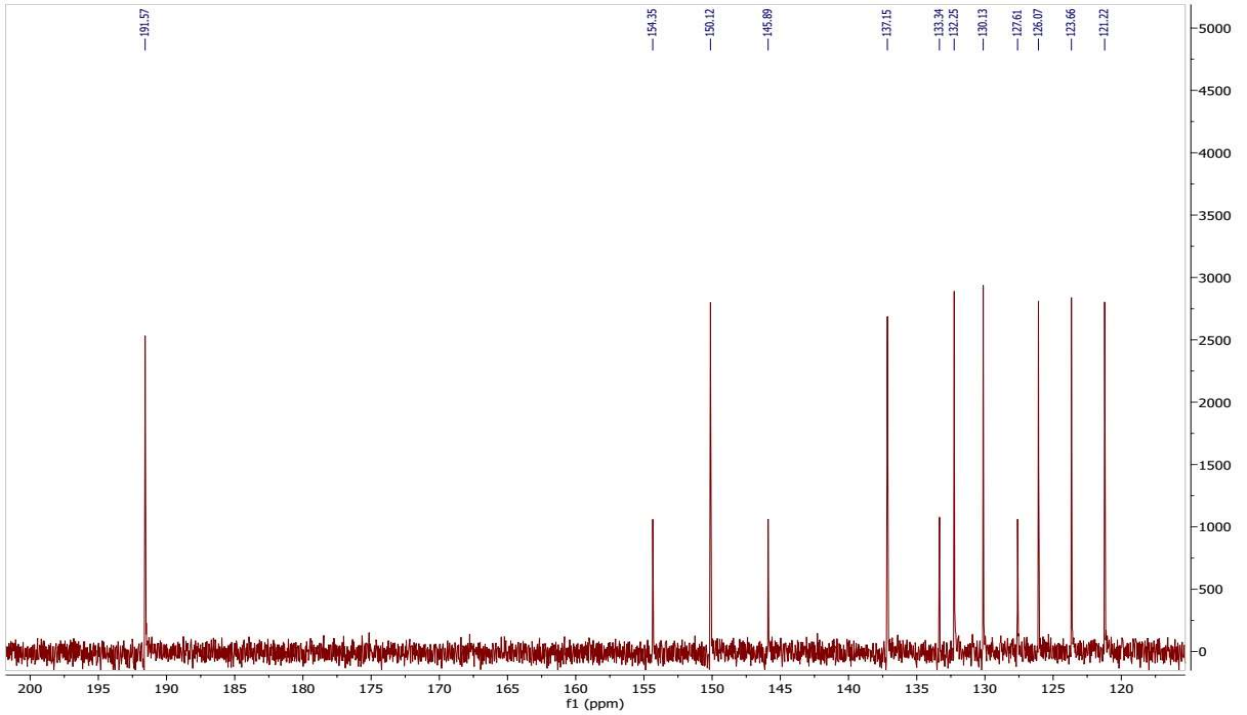


Figure S57. ^{13}C-NMR Spectrum of isolated pure 2-bromo-4-(pyridin-2-yl)benzaldehyde in $CDCl_3$ (Expanded).

2-(3-bromophenyl)pyridine

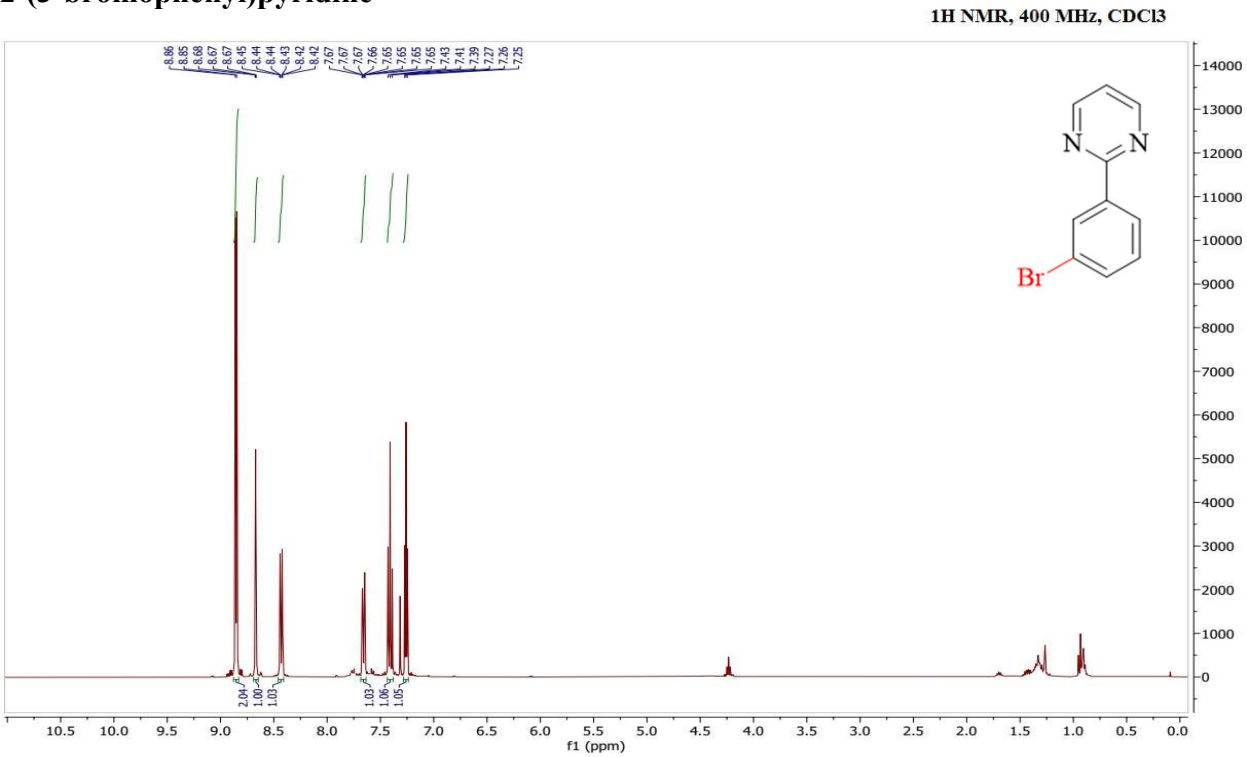


Figure S58. ^{1}H-NMR Spectrum of isolated pure 2-(3-bromophenyl)pyrimidine in in $CDCl_3$.

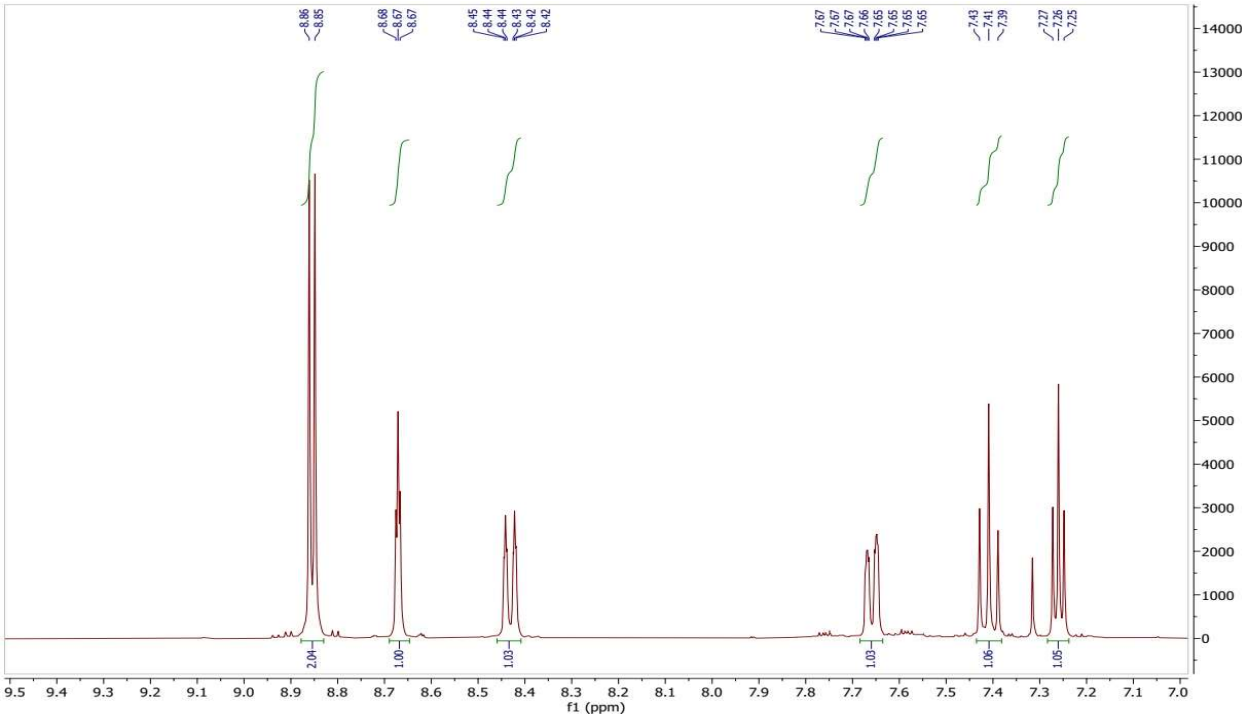


Figure S59. ^{1}H-NMR Spectrum of isolated pure 2-(3-bromophenyl)pyrimidine in $CDCl_3$ (Expanded).

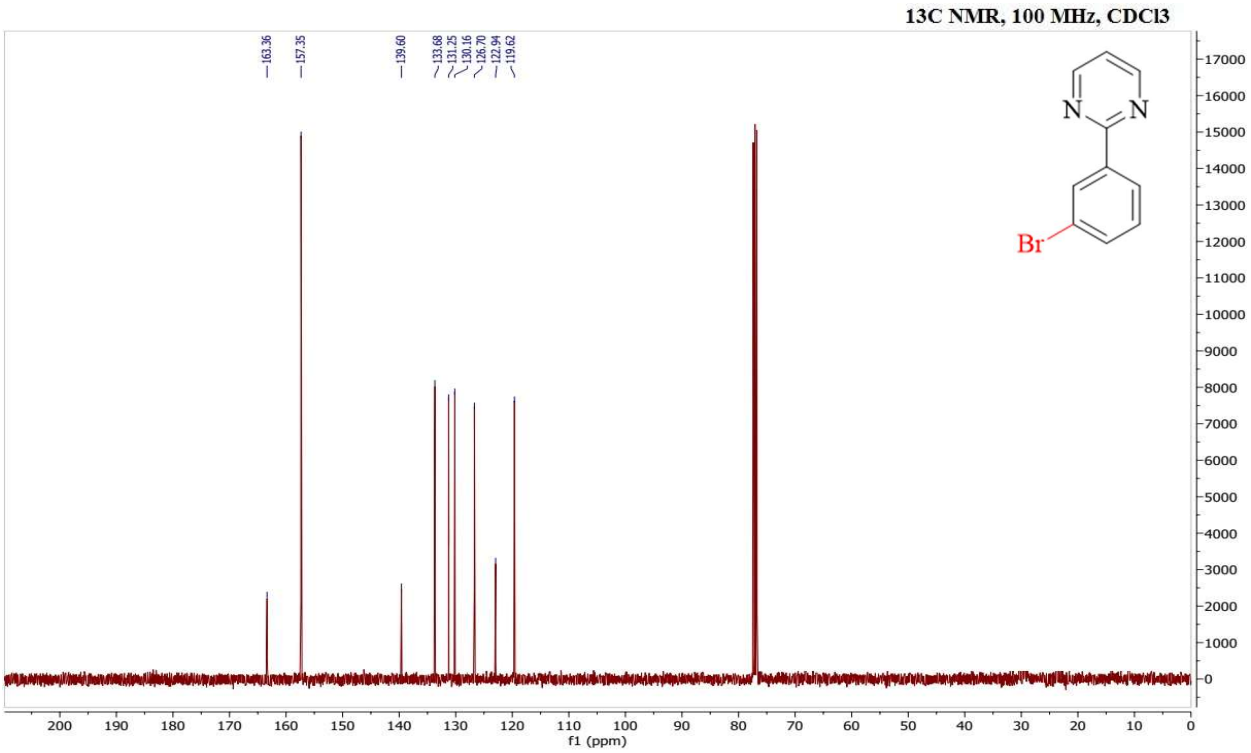


Figure S60. ^{13}C-NMR Spectrum of isolated pure 2-(3-bromophenyl)pyrimidine in $CDCl_3$.

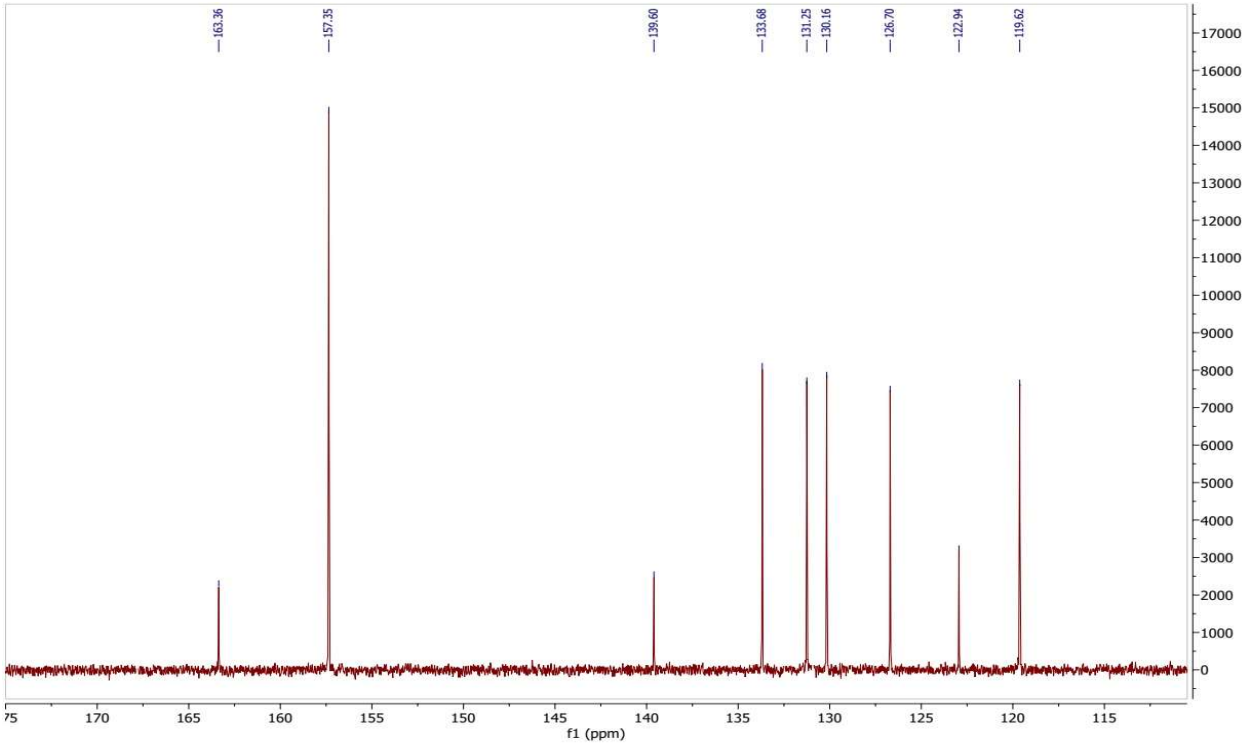
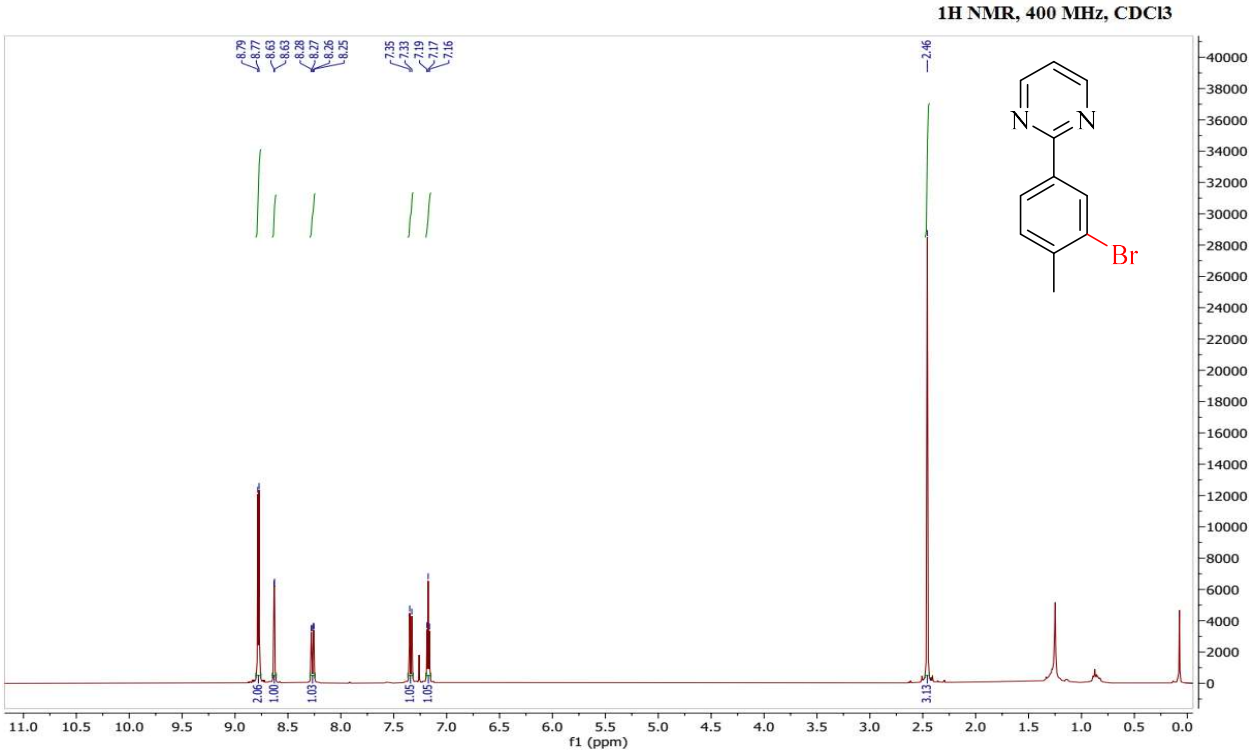


Figure S61. ^{13}C-NMR Spectrum of isolated pure 2-(3-bromophenyl)pyrimidine in $CDCl_3$ (Expanded).



X2-(3-Bromo-4-methylphenyl)pyrimidine

Figure S62. ^{1}H-NMR Spectrum of isolated pure 2-(3-Bromo-4-methylphenyl)pyrimidine in $CDCl_3$.

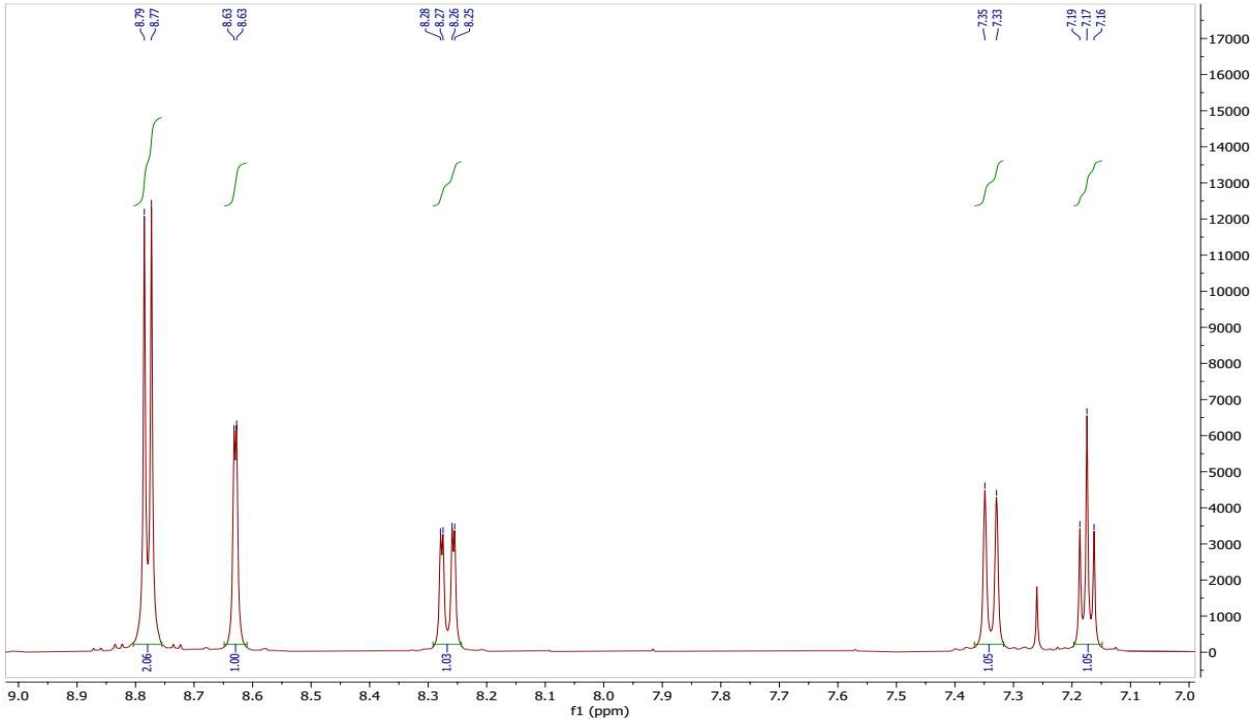


Figure S63. ^{1}H-NMR Spectrum of isolated pure 2-(3-Bromo-4-methylphenyl)pyrimidine in $CDCl_3$ (Expanded).

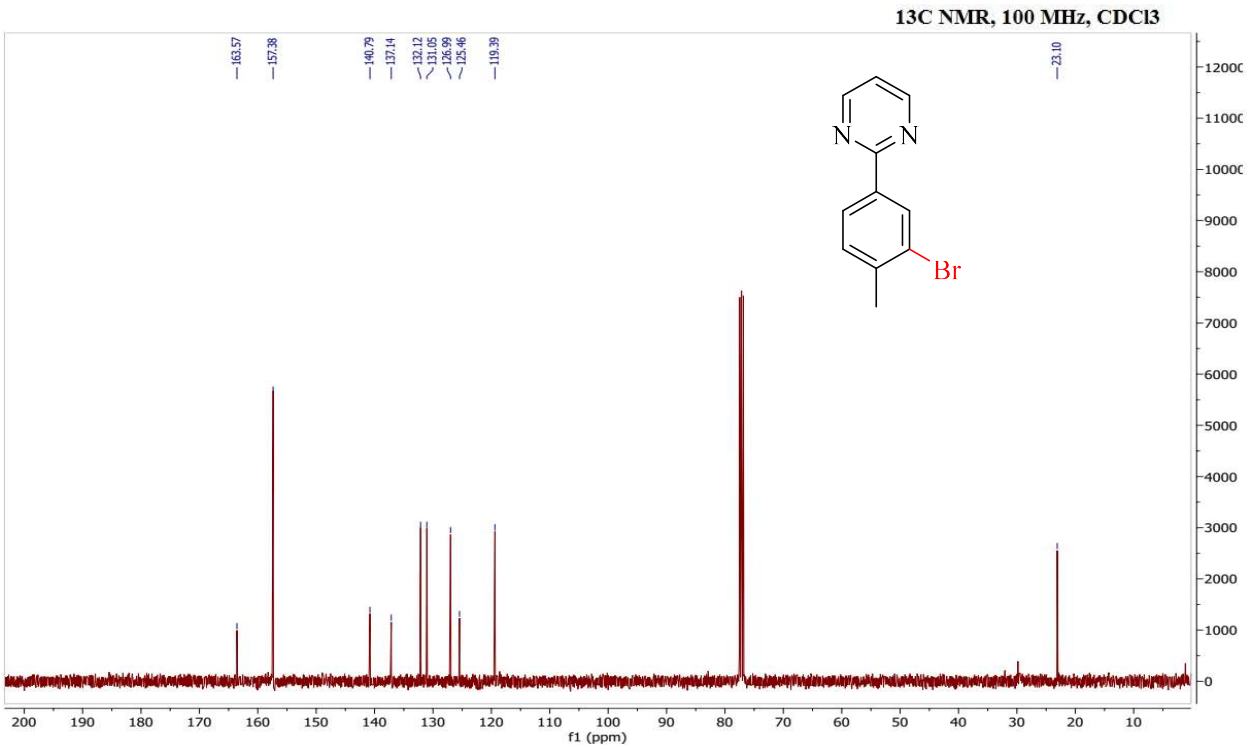


Figure S64. ^{13}C-NMR Spectrum of isolated pure 2-(3-Bromo-4-methylphenyl)pyrimidine in $CDCl_3$.

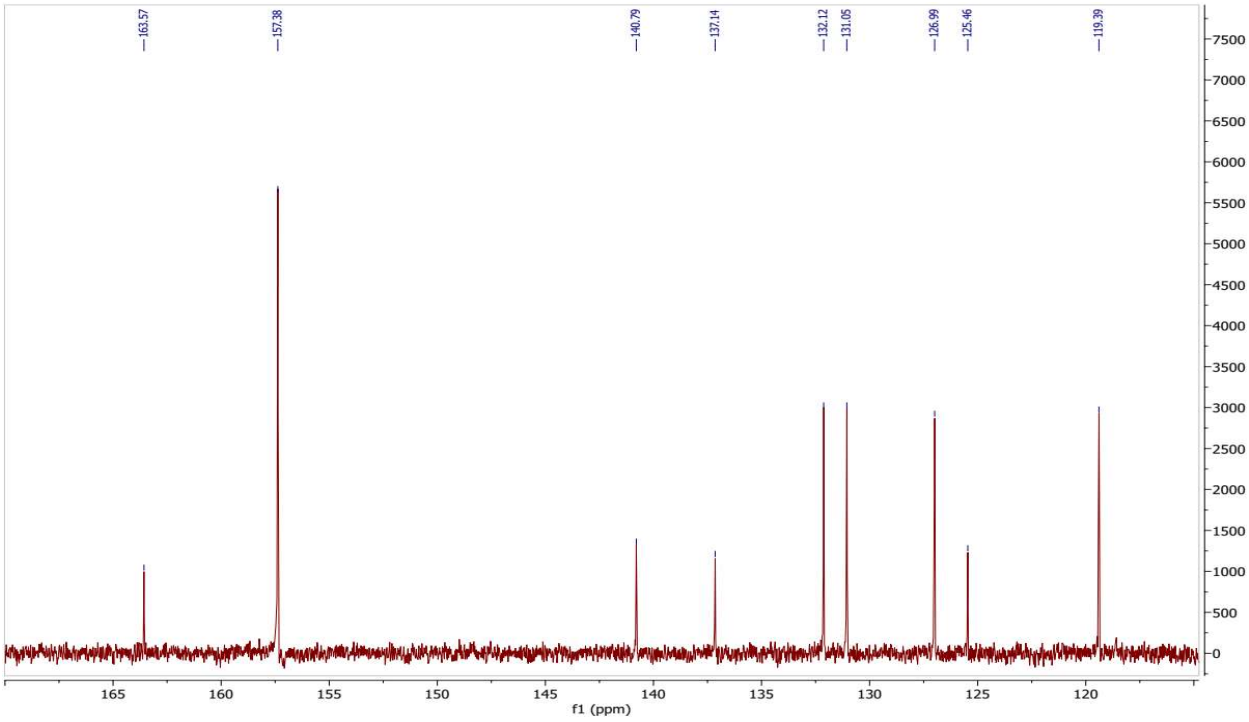
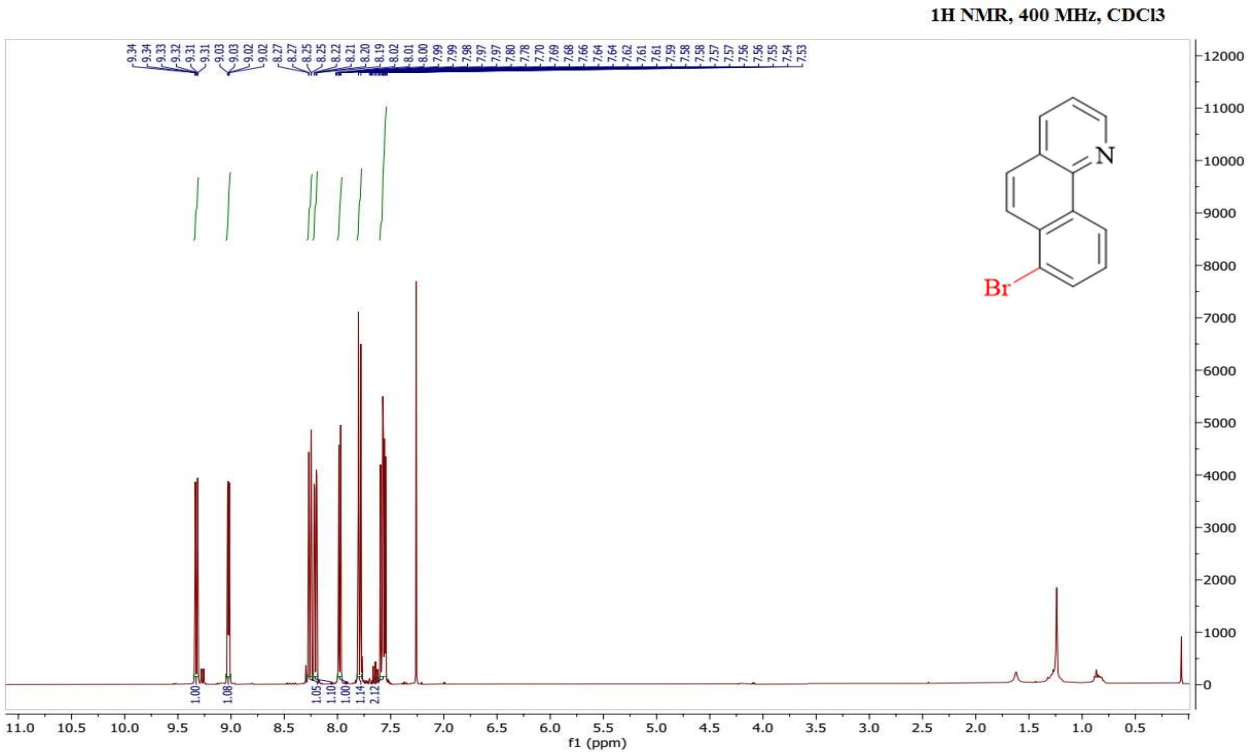


Figure S65. ^{13}C-NMR Spectrum of isolated pure 2-(3-Bromo-4-methylphenyl)pyrimidine in $CDCl_3$ (Expanded).



7-bromobenzo[h]quinolone

Figure S66. ^{1}H-NMR Spectrum of isolated pure 7-bromobenzo[h]quinolone in $CDCl_3$.

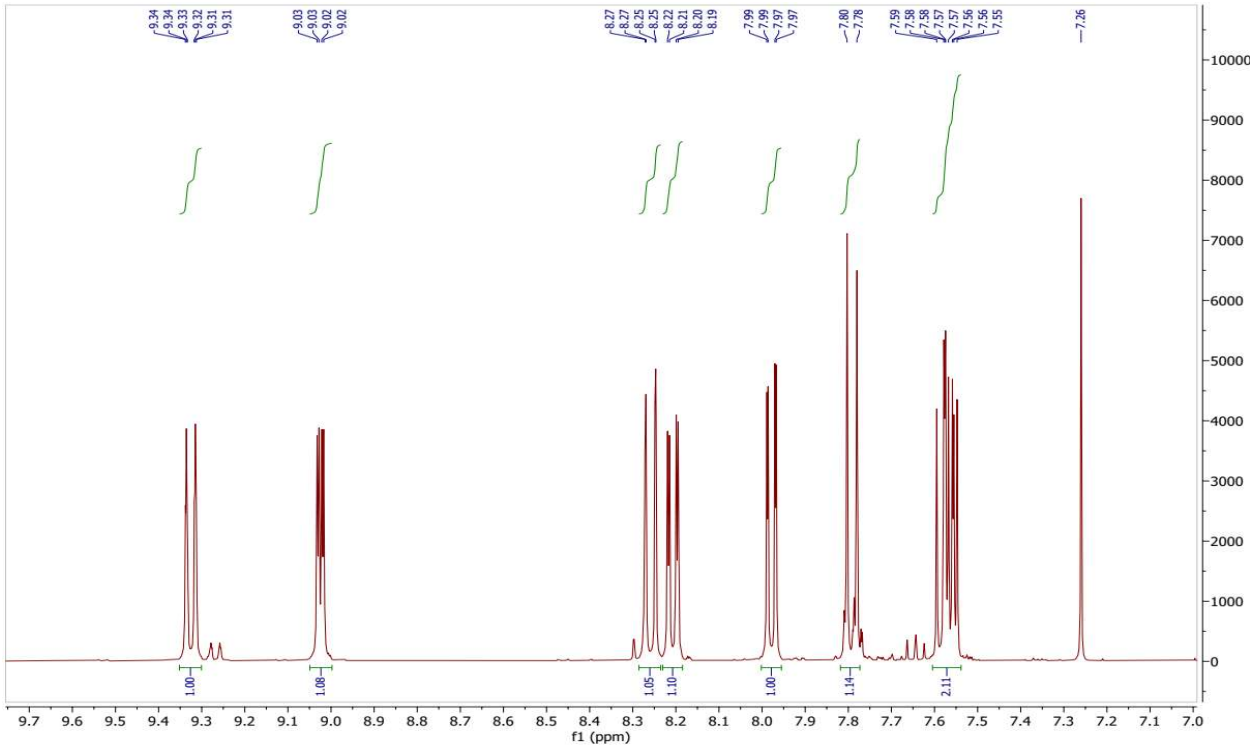


Figure S67. ^{1}H-NMR Spectrum of isolated pure 7-bromobenzo[h]quinolone in $CDCl_3$ (Expanded).

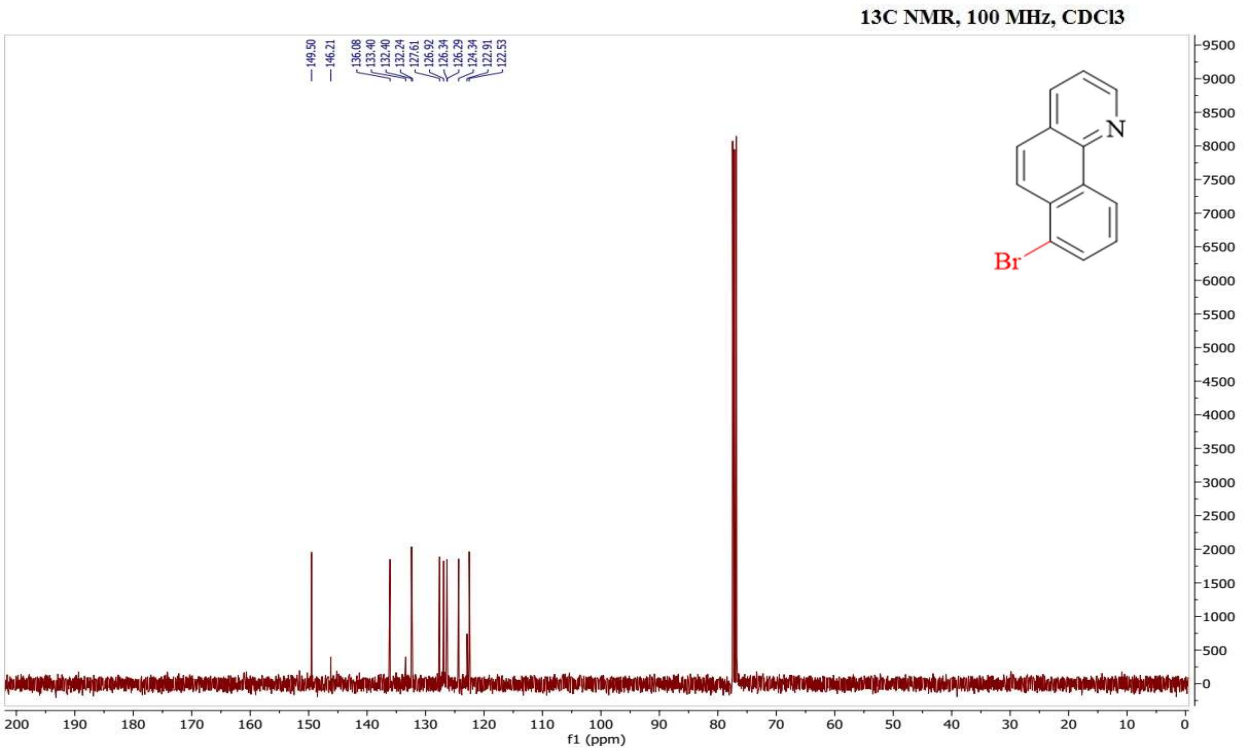


Figure S68. ^{13}C-NMR Spectrum of isolated pure 7-bromobenzo[h]quinolone in $CDCl_3$.

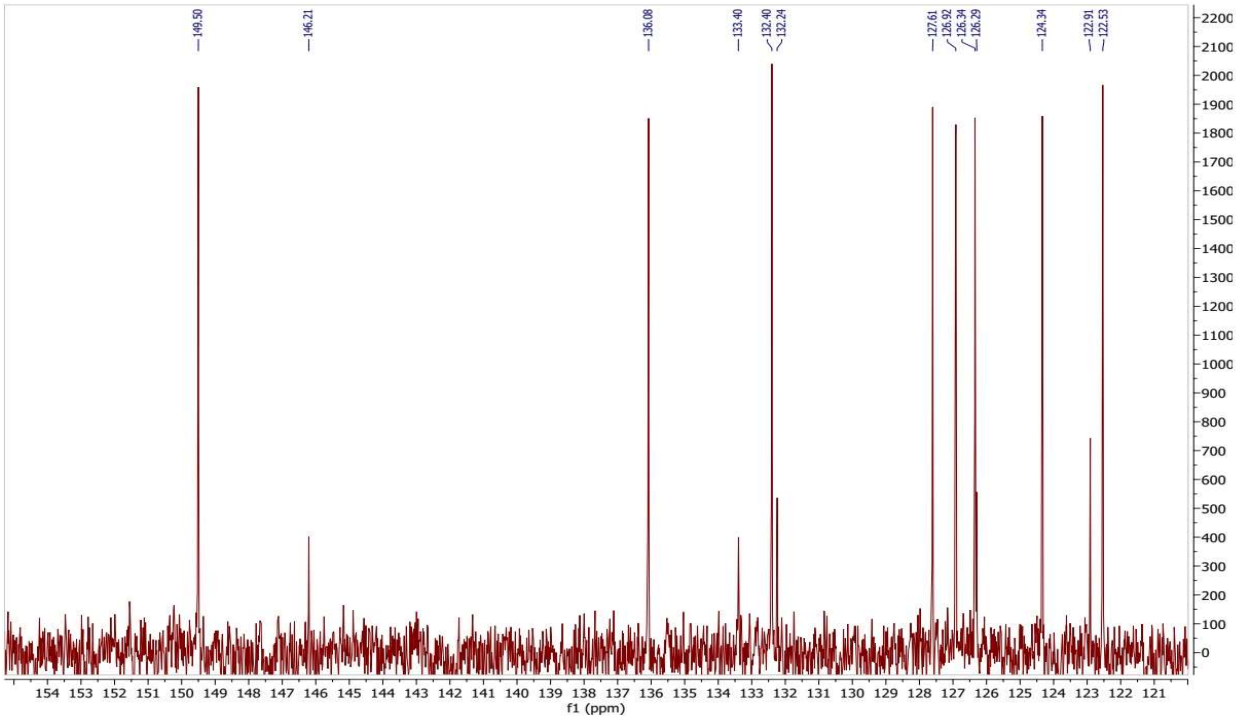
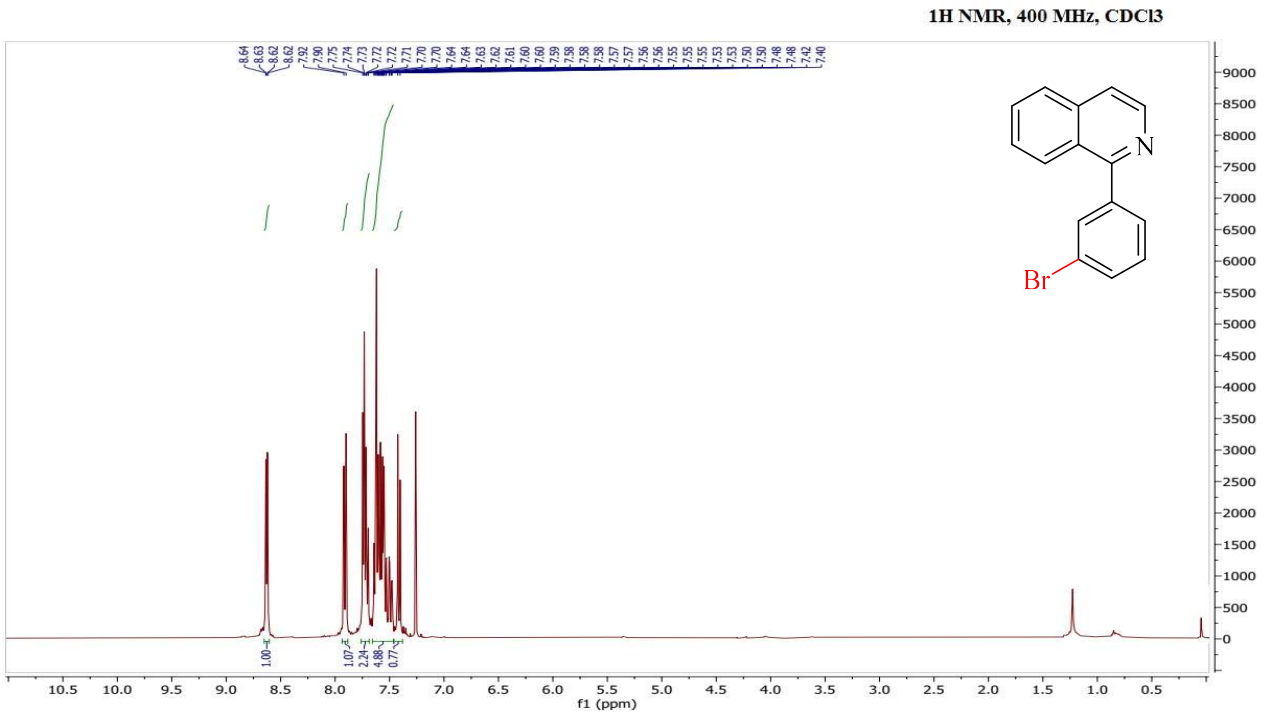


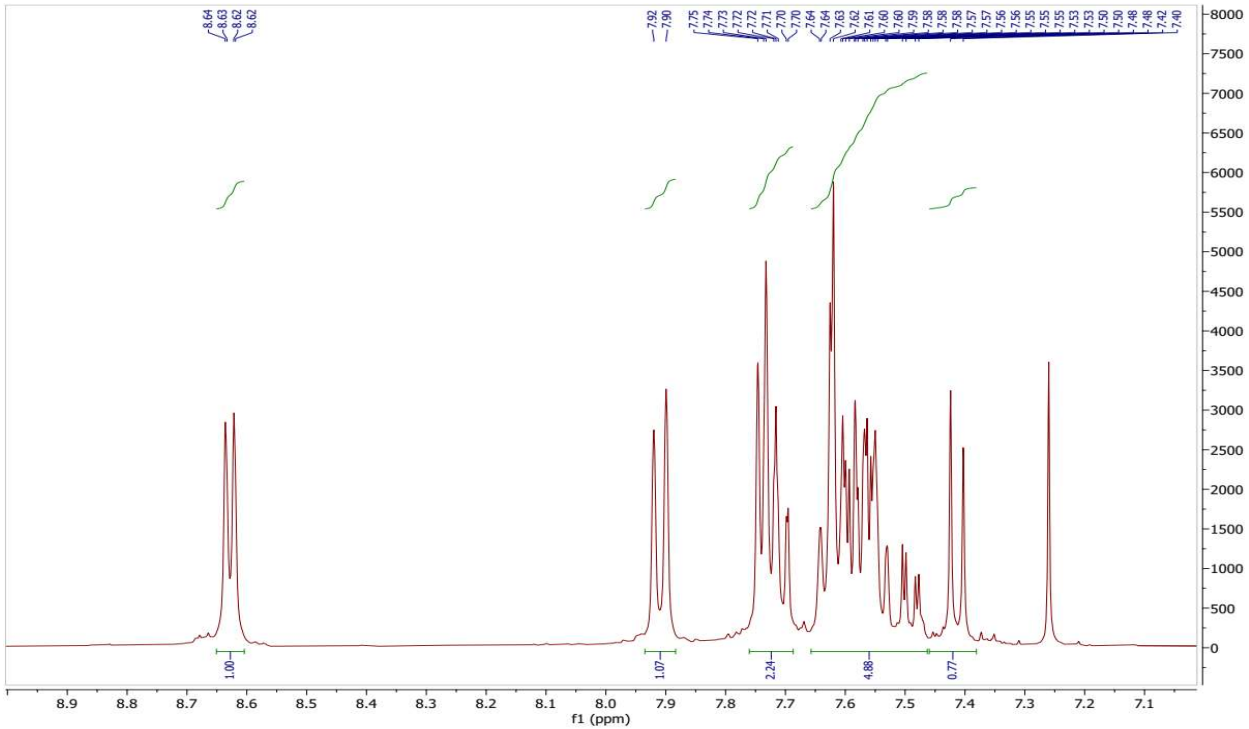
Figure S69. ^{13}C-NMR Spectrum of isolated pure 7-bromobenzo[h]quinolone in $CDCl_3$ (Expanded).



1-(3-bromophenyl)isoquinoline

Figure S70. ^{1}H-NMR Spectrum of isolated pure 1-(3-bromophenyl)isoquinoline in $CDCl_3$.

Figure S71. ^{1}H-NMR Spectrum of isolated pure 1-(3-bromophenyl)isoquinoline in $CDCl_3$ (Expanded).



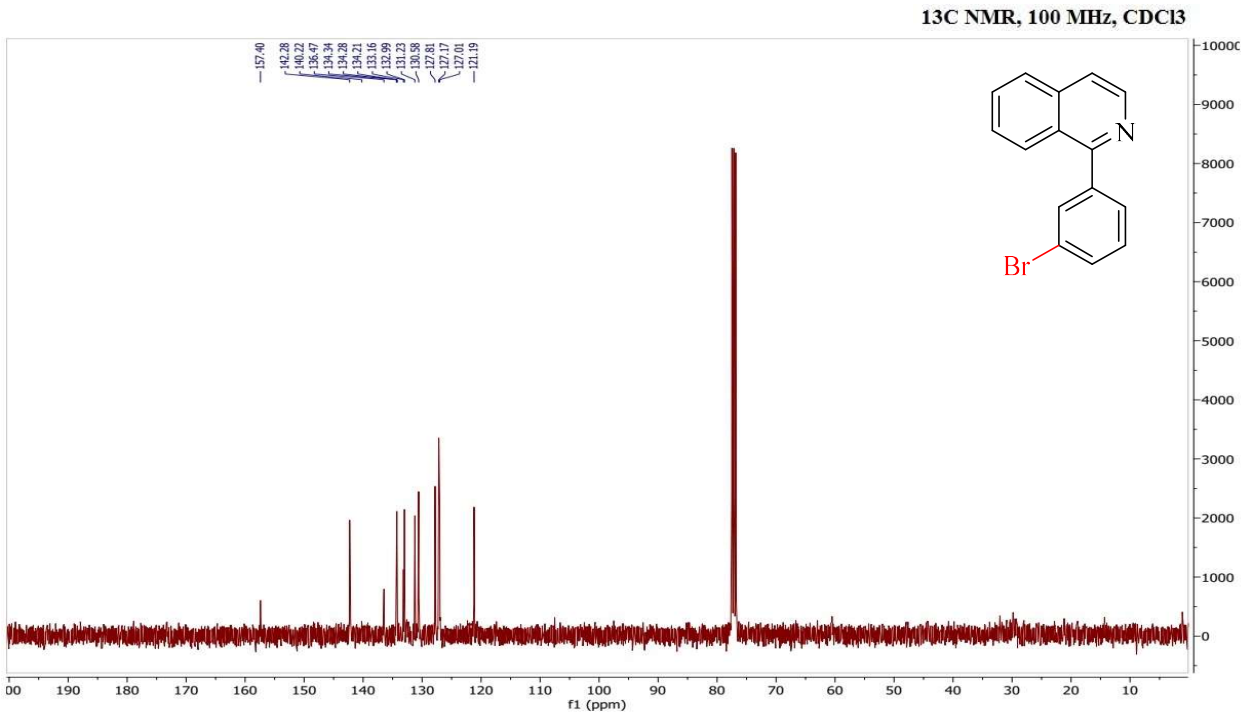


Figure S72. ^{13}C-NMR Spectrum of isolated pure 1-(3-bromophenyl)isoquinoline in $CDCl_3$.

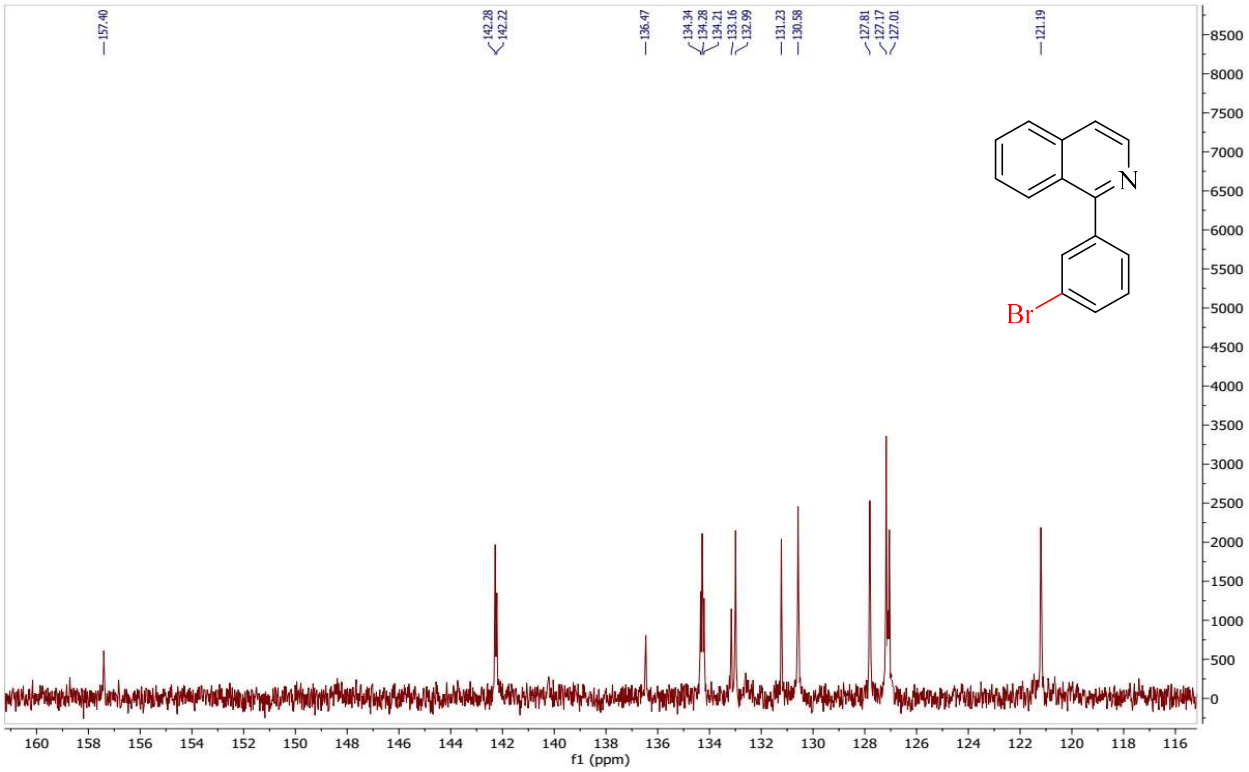
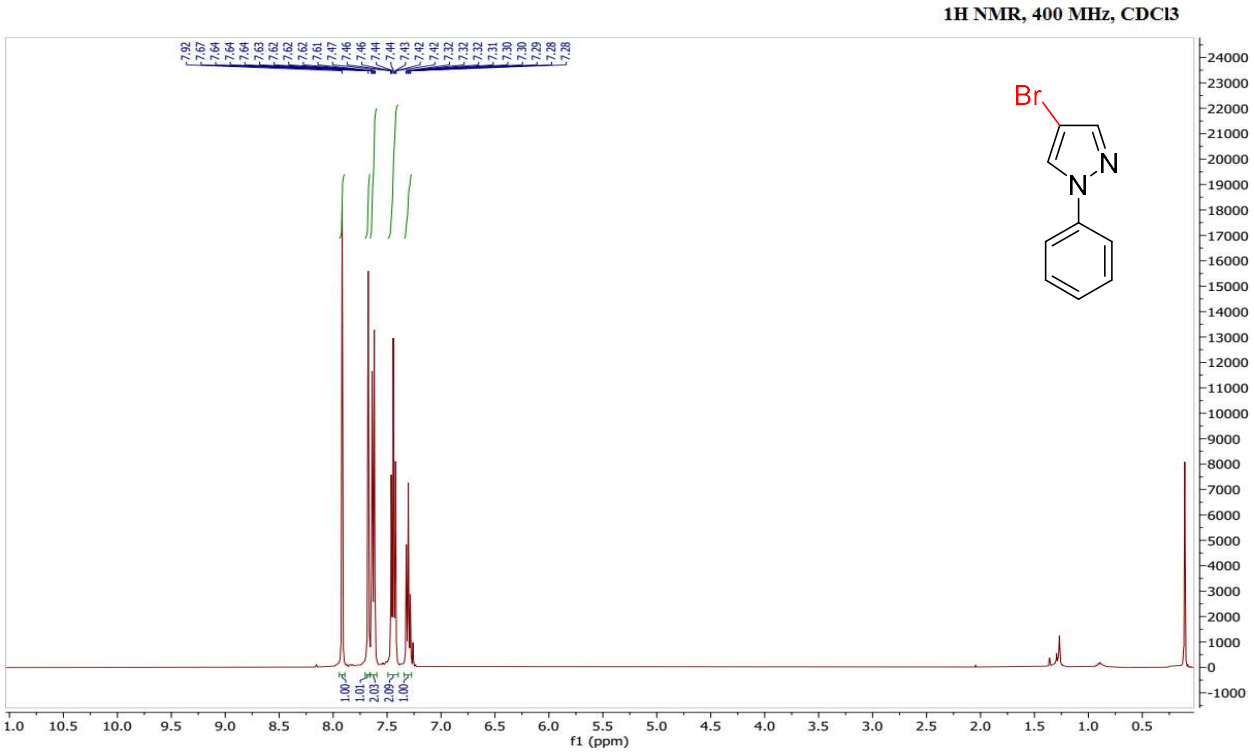


Figure S73. ^{13}C-NMR Spectrum of isolated pure 1-(3-bromophenyl)isoquinoline in $CDCl_3$ (Expanded).



14-bromo-1-phenyl-1H-pyrazole

Figure S74. ^{1}H-NMR Spectrum of isolated pure 4-bromo-1-phenyl-1H-pyrazole in $CDCl_3$.

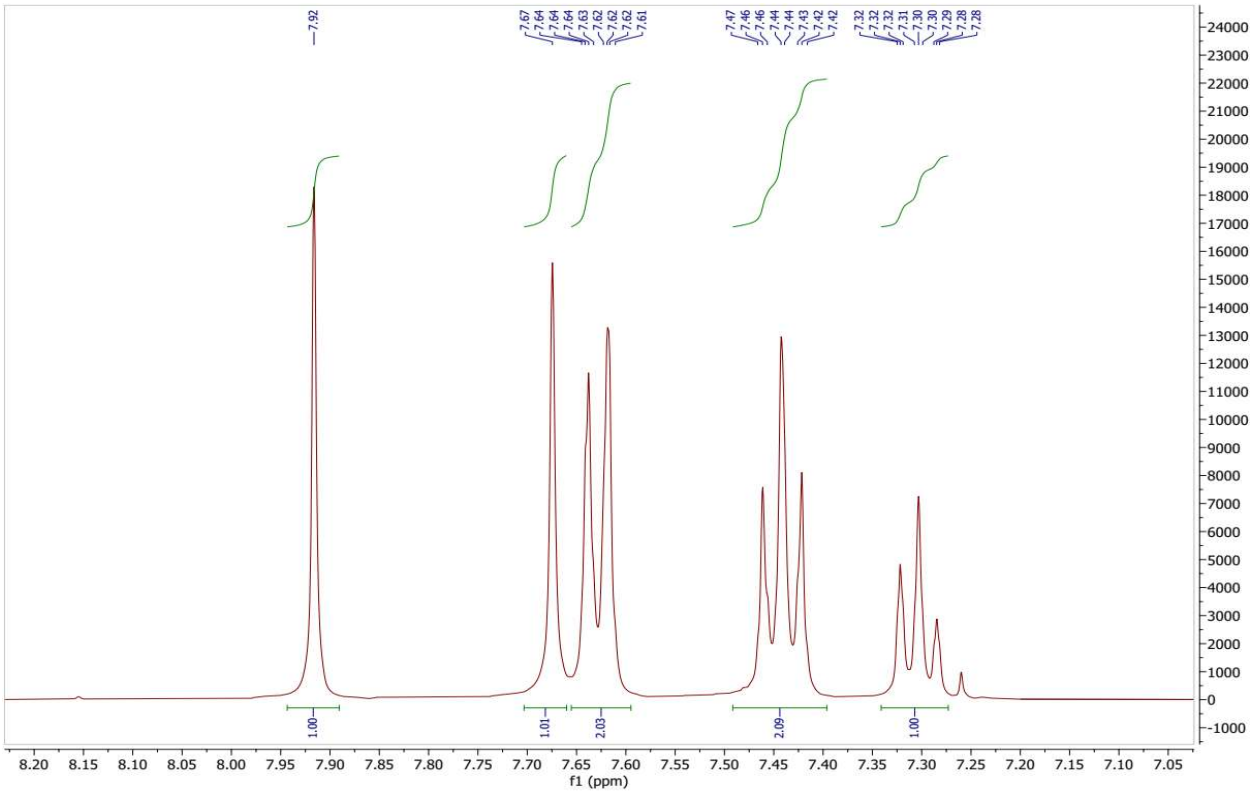


Figure S75. ^{1}H-NMR Spectrum of isolated pure 4-bromo-1-phenyl-1H-pyrazole in $CDCl_3$ (Expanded).

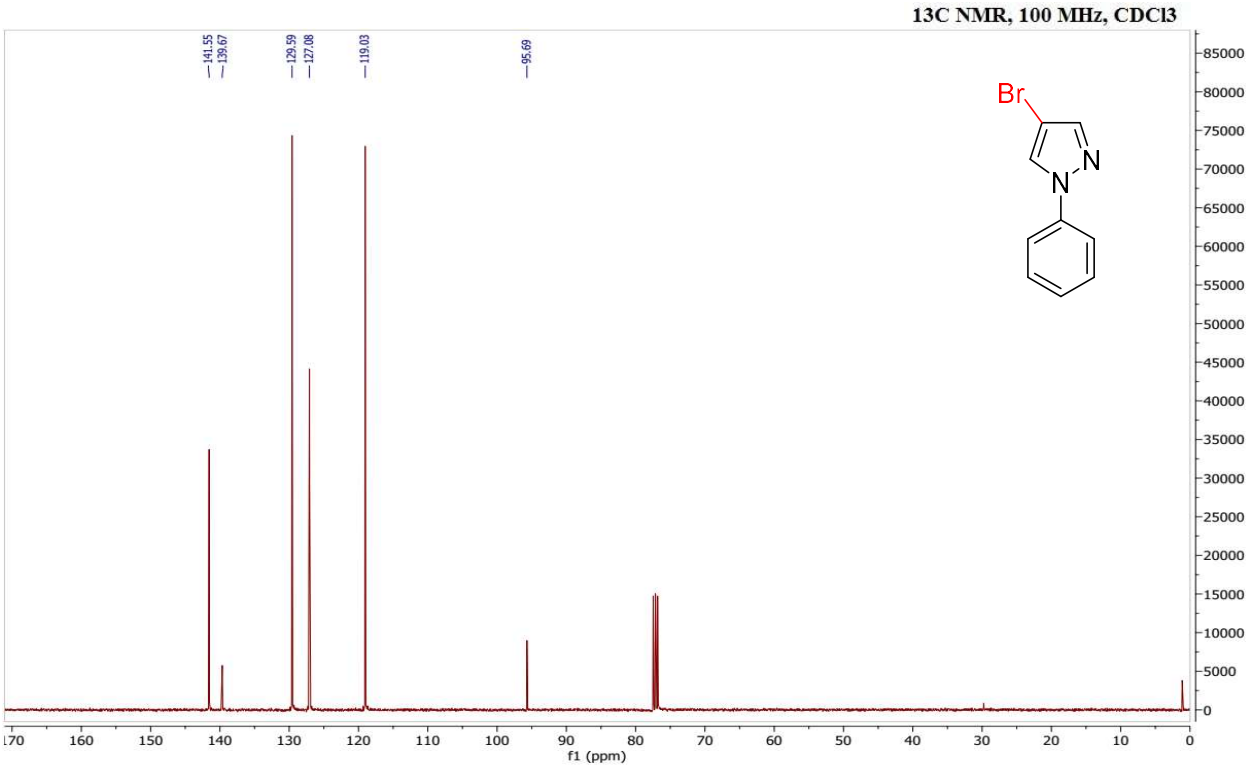


Figure S76. ^{13}C-NMR Spectrum of isolated pure 4-bromo-1-phenyl-1H-pyrazole in $CDCl_3$.

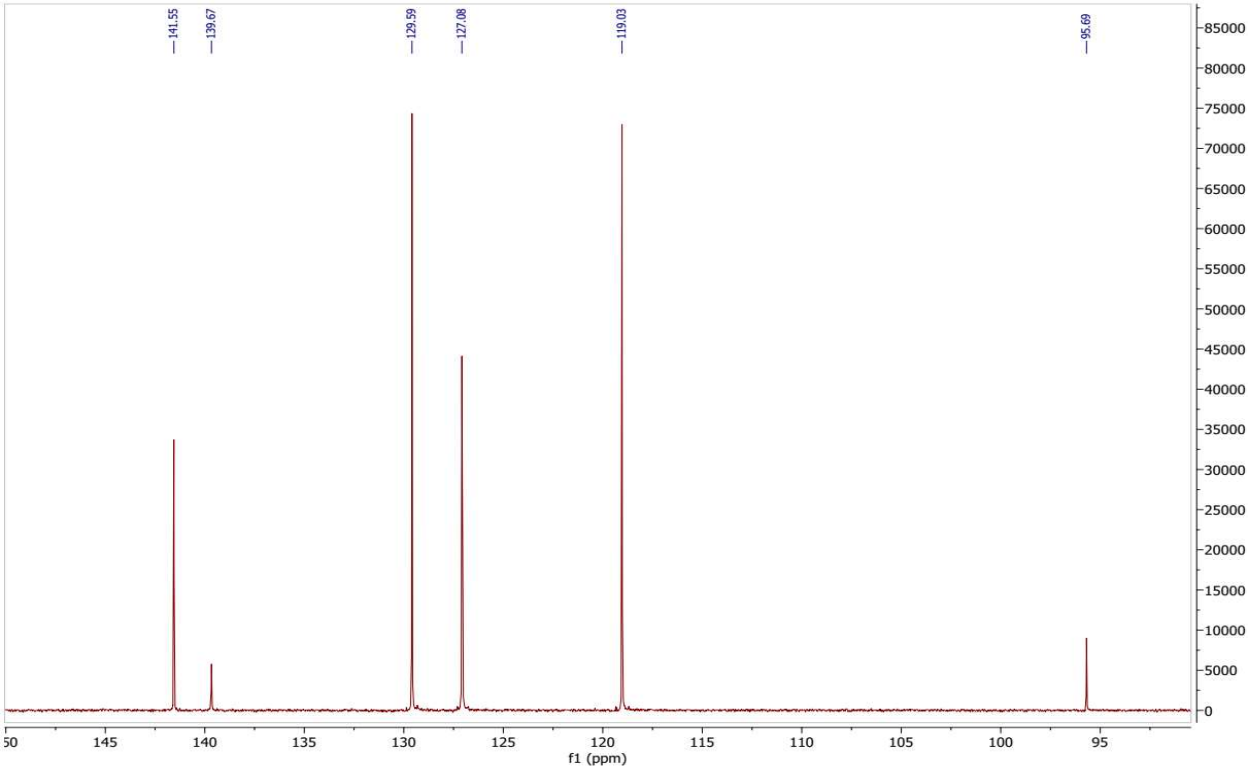
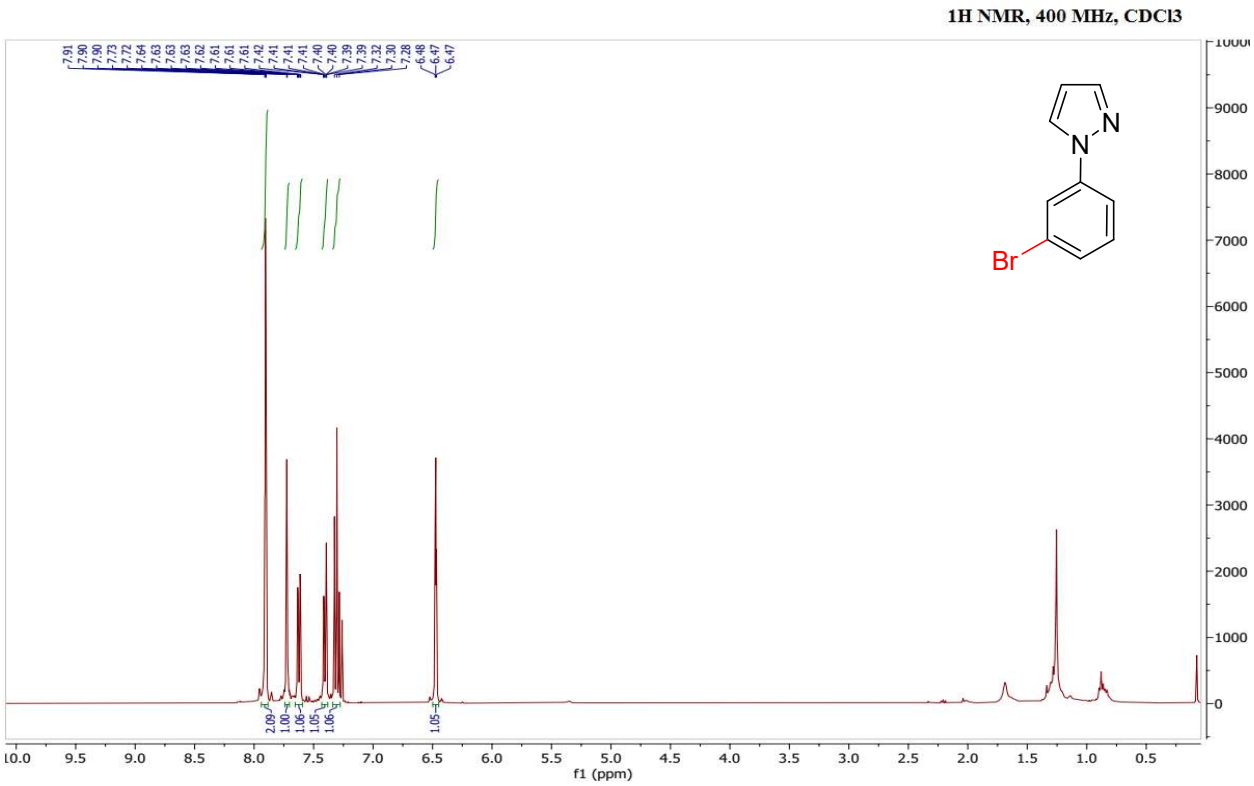


Figure S77. ^{13}C-NMR Spectrum of isolated pure 4-bromo-1-phenyl-1H-pyrazole in $CDCl_3$ (Expanded).



1-(3-Bromophenyl)-*1H*-pyrazole

Figure S78. ^{1}H-NMR Spectrum of isolated pure 1-(3-Bromophenyl)-*1H*-pyrazole in $CDCl_3$.

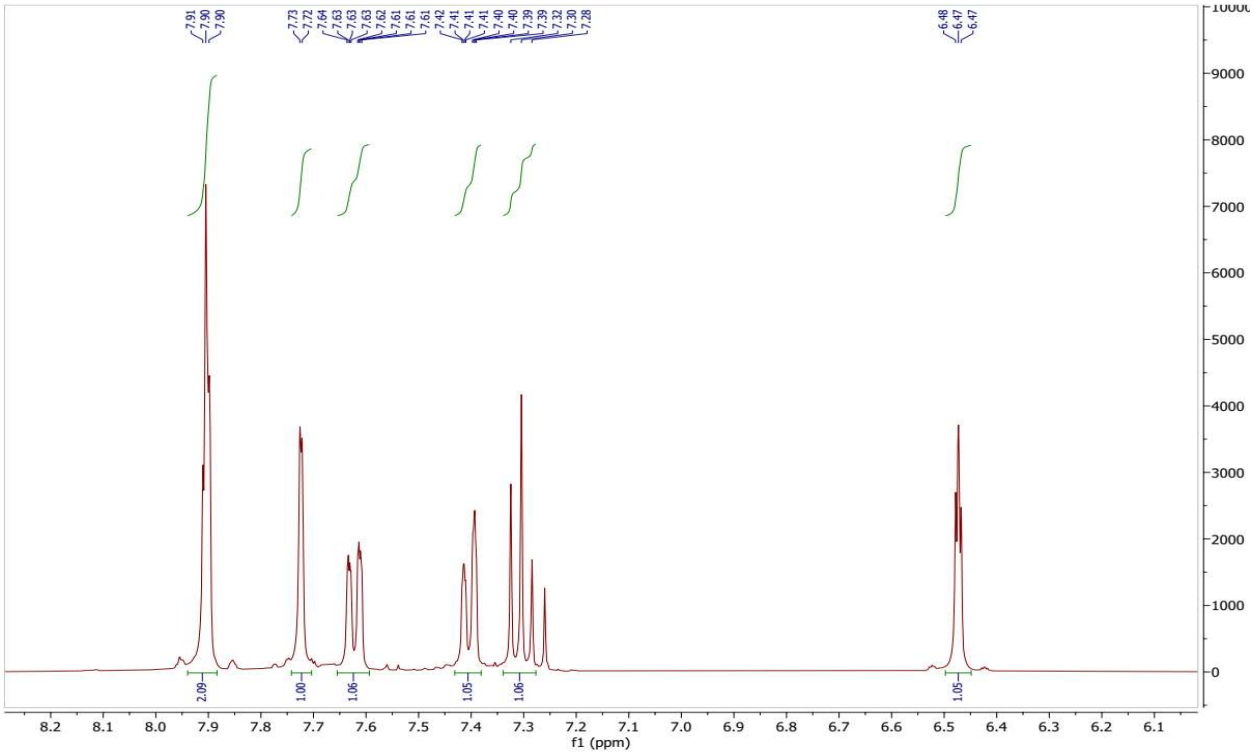


Figure S79. ^{1}H-NMR Spectrum of isolated pure 1-(3-Bromophenyl)-*1H*-pyrazole in $CDCl_3$ (Expanded).

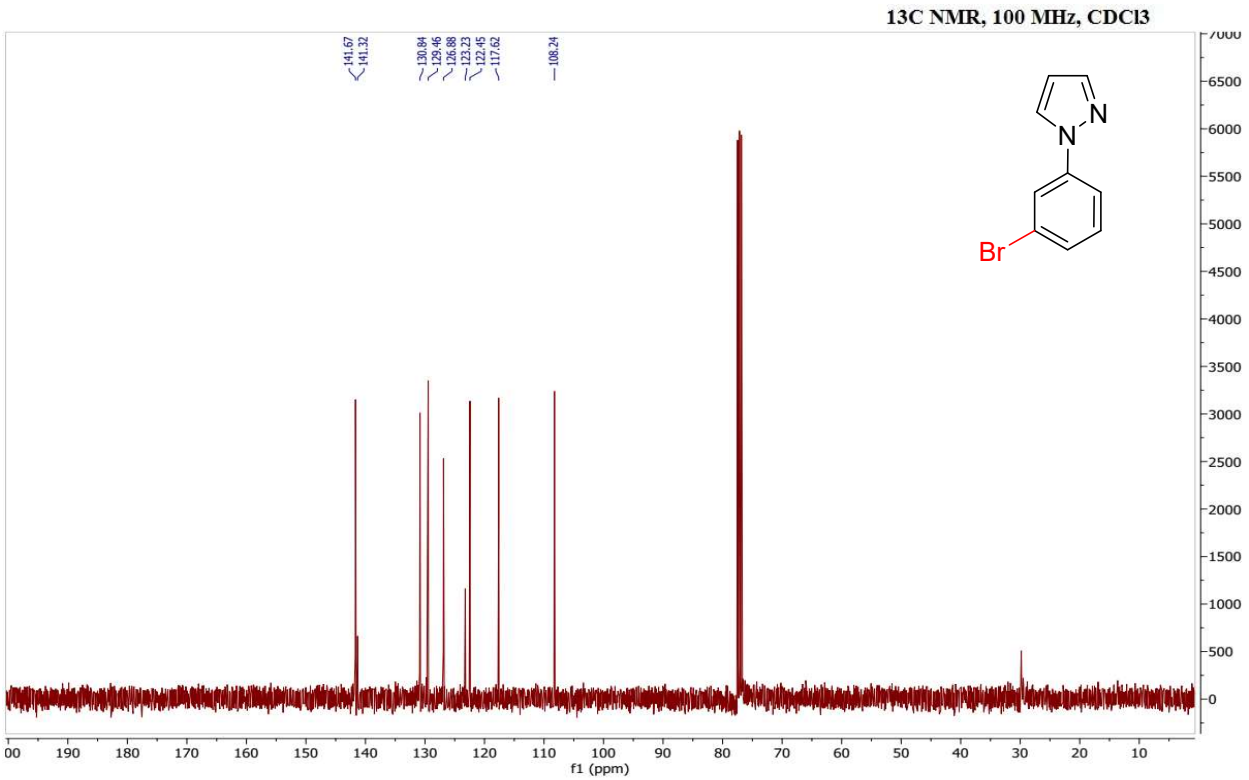


Figure S80. ^{13}C-NMR Spectrum of isolated pure 1-(3-Bromophenyl)-*1H*-pyrazole in $CDCl_3$.

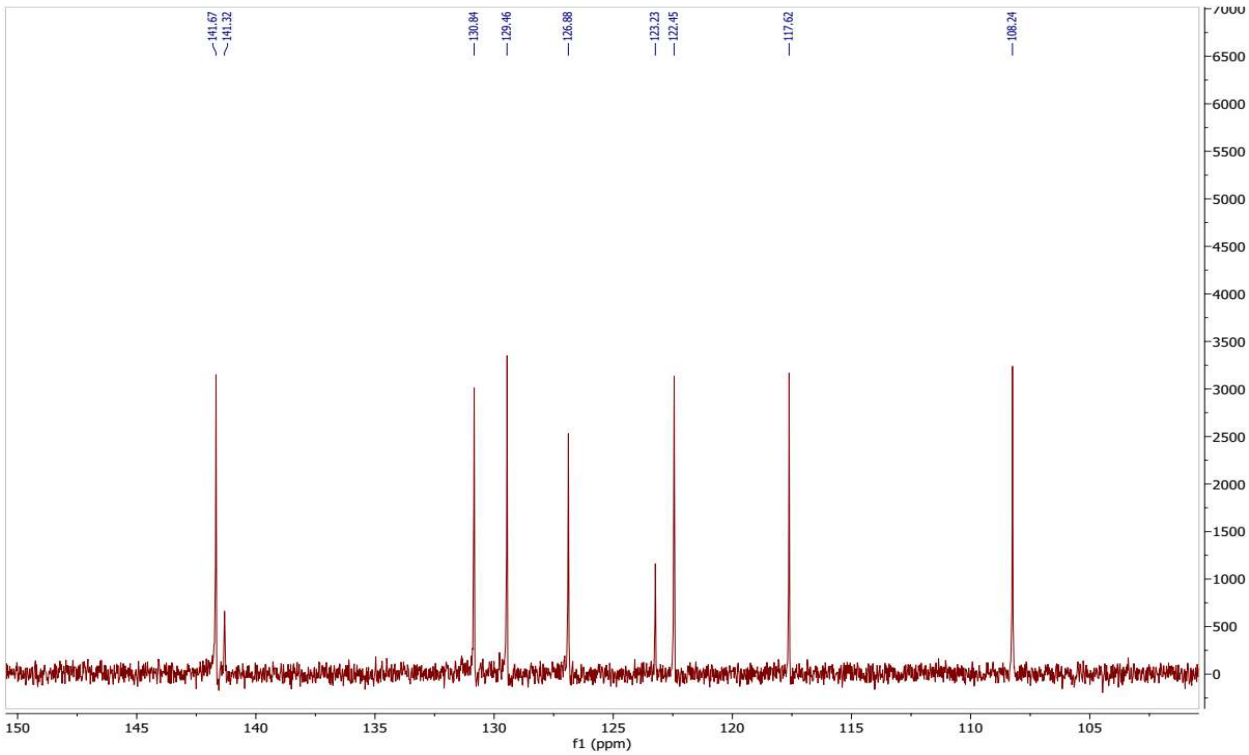


Figure S81. ^{13}C-NMR Spectrum of isolated pure 1-(3-Bromophenyl)-*1H*-pyrazole in $CDCl_3$ (Expanded).

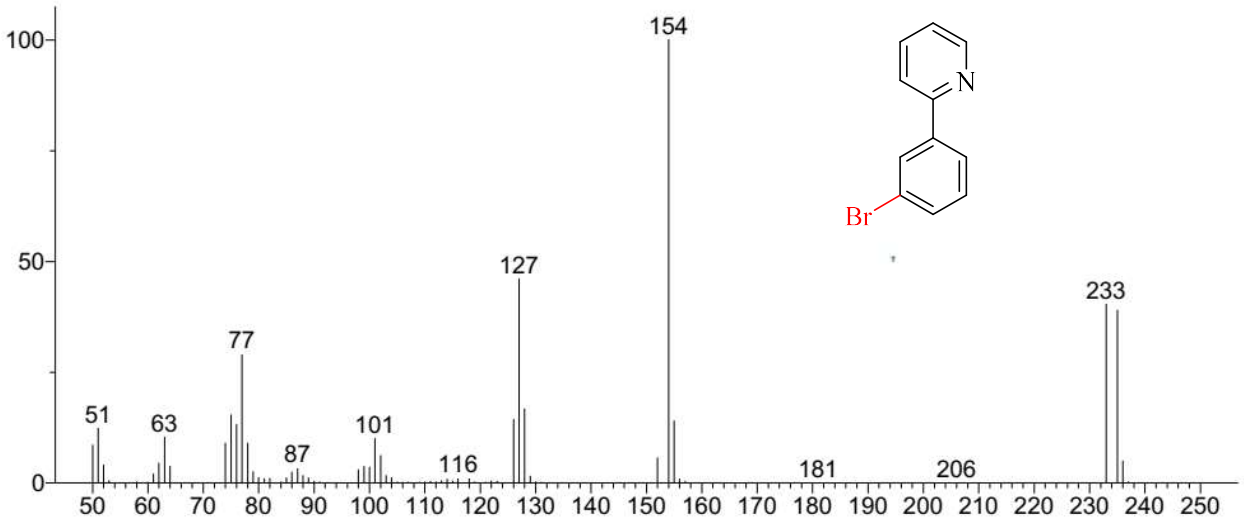


Figure S82. Gas-Chromatography Mass Spectroscopy (GC-MS) spectrum of 2-(3-bromophenyl)pyridine

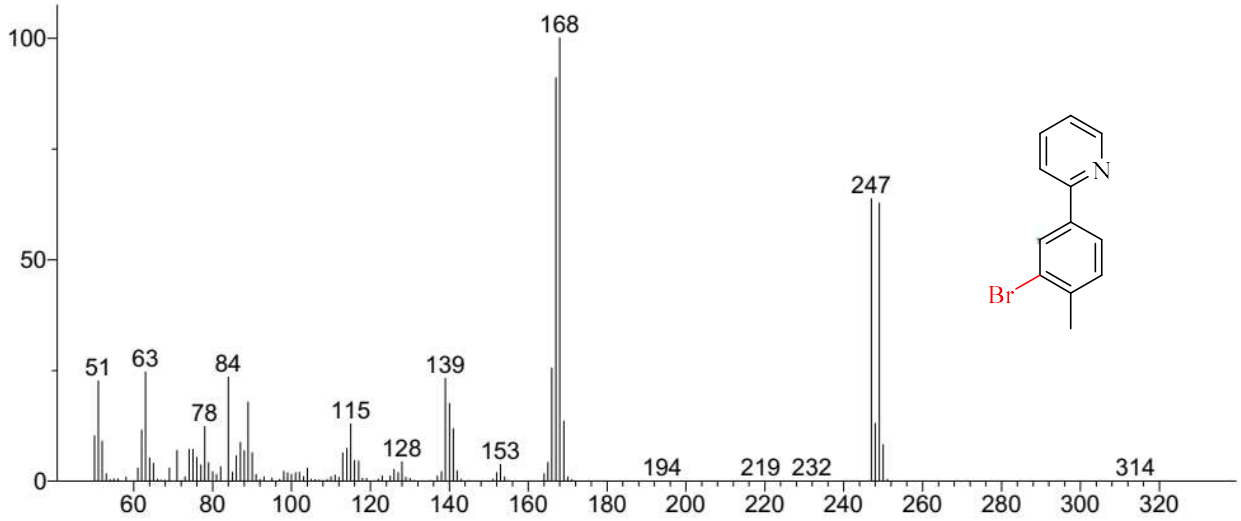


Figure S83. Gas-Chromatography Mass Spectroscopy (GC-MS) spectrum of 2-(3-bromo-4-methylphenyl)pyridine.

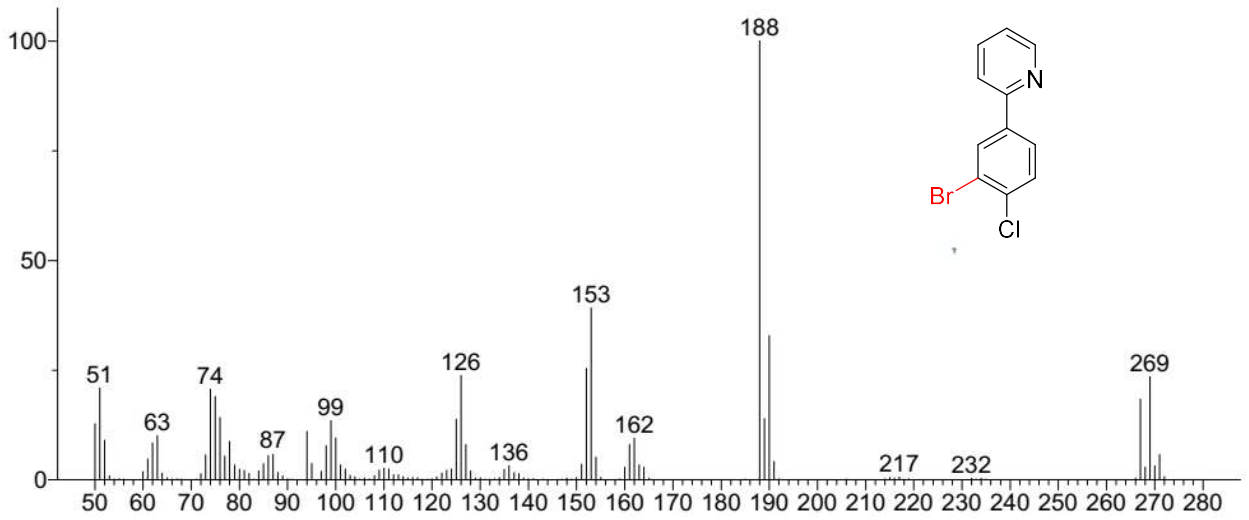


Figure S84. Gas-Chromatography Mass Spectroscopy (GC-MS) spectrum of 2-(3-bromo-4-chlorophenyl)pyridine.

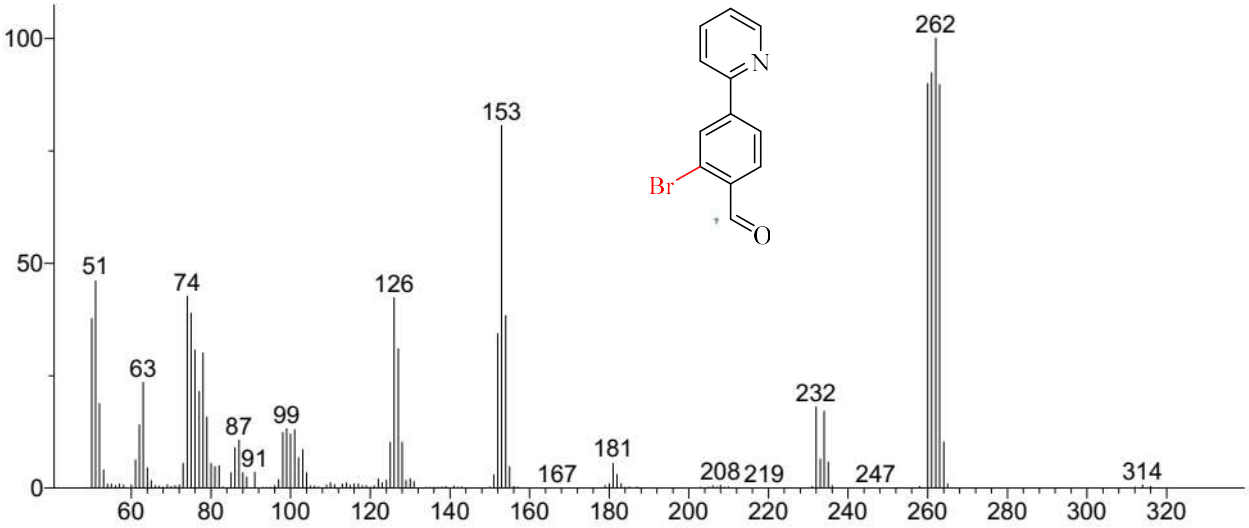


Figure S85. Gas-Chromatography Mass Spectroscopy (GC-MS) spectrum of 2-bromo-4-(pyridin-2-yl)benzaldehyde.

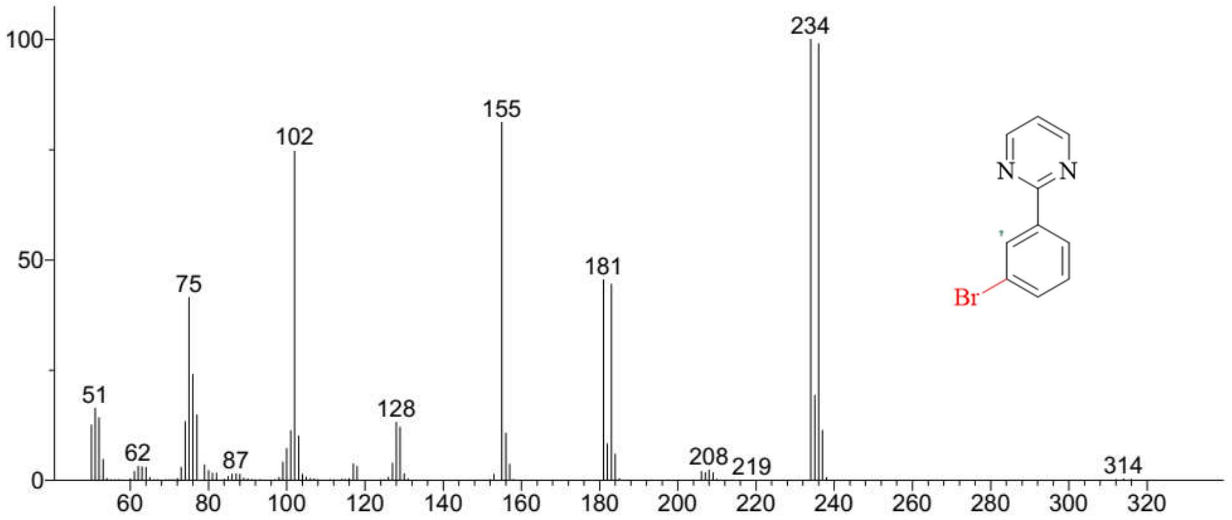


Figure S86. Gas-Chromatography Mass Spectroscopy (GC-MS) spectrum of 2-(3-bromophenyl)pyrimidine.

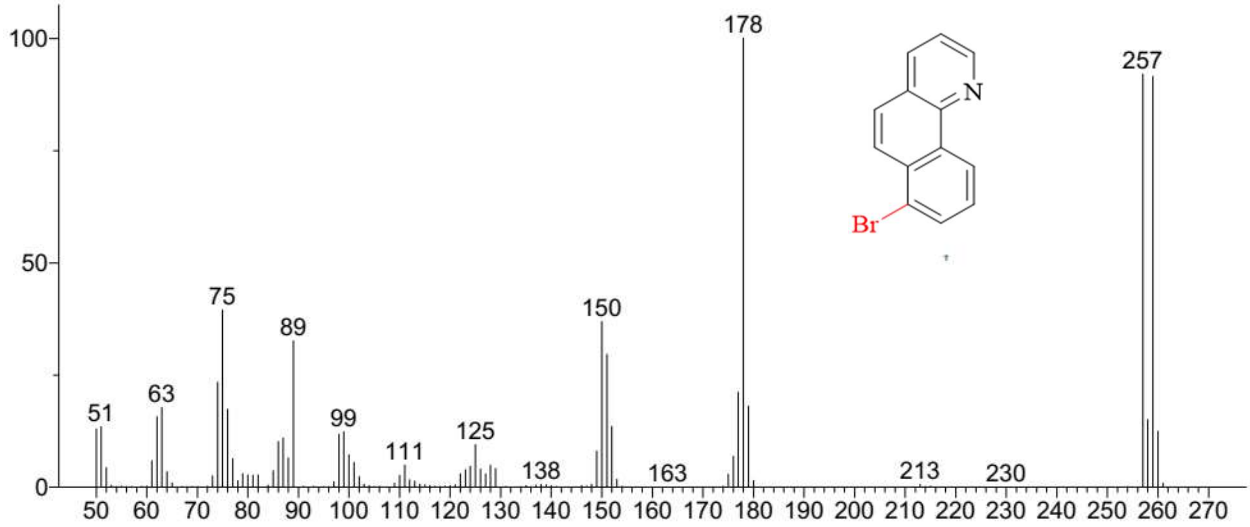


Figure S87. Gas-Chromatography Mass Spectroscopy (GC-MS) spectrum of 7-bromobenzo[h]quinolone.

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