

**Electronic supplementary information (ESI)**

for

**Bimetallic Pd-Ag nanoclusters decorated micro-cellulose bio-template  
towards efficient catalytic Suzuki-Miyaura coupling reaction of nitrogen-  
rich heterocycles**

Prantika Bhattacharjee,<sup>a,b</sup> Anindita Dewan,<sup>\*a</sup> Purna K. Boruah,<sup>c</sup> Manash R. Das,<sup>c,d</sup> Sanjeev P.  
Mahanta,<sup>a</sup> Ashim J. Thakur<sup>a</sup> and Utpal Bora<sup>\*a</sup>

<sup>a</sup>*Department of Chemical Sciences, Tezpur University, Napaam-784028, Assam, India*

<sup>b</sup>*Department of Chemistry, Bahona College, Jorhat-785101, Assam, India*

<sup>c</sup>*Advanced Materials Group, Materials Sciences and Technology Division, CSIR-North East  
Institute of Science and Technology, Jorhat-785006 Assam, India*

<sup>d</sup>*Academy of Scientific and Innovative Research, Ghaziabad-201002, India*

*\*Corresponding author email: utbora@yahoo.co.in, ubora@tezu.ernet.in*

**Table of contents**

|   |  |     |
|---|--|-----|
| 1 | General experimental information                               | S2  |
| 2 | Preparation of catalysts                                       | S2  |
| 3 | Characterization of catalysts                                  | S3  |
| 4 | General procedure for Suzuki-Miyaura coupling reaction         | S4  |
| 5 | Physical and spectroscopic data of products                    | S7  |
| 6 | <sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of products | S10 |
| 7 | References   | S29 |

## 1. General experimental information

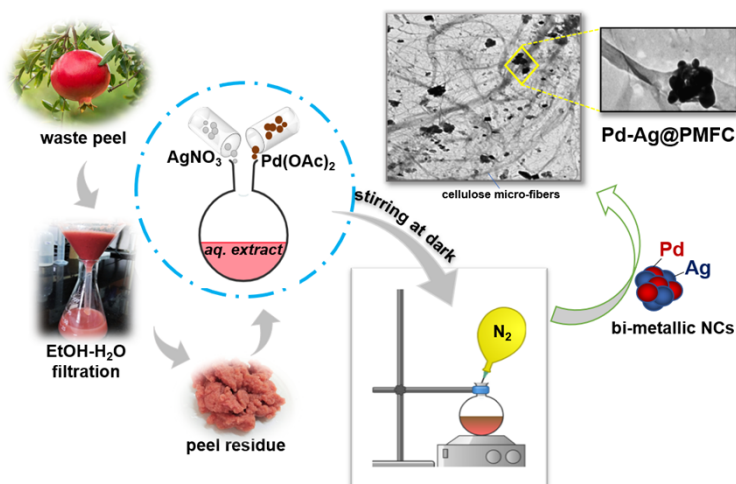
Reactions were carried out in Tarsons spinot digital magnetic stirrer and EYELA Process Station Personal Synthesizer PPS-CTRL1 under standard conditions. Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel 60F<sub>254</sub> plates using short wave (254 nm) UV light. Column chromatography purifications were performed over silica gel (100-200 mesh). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL JNM 400ECS NMR spectrometer (400 and 100 MHz respectively) using CDCl<sub>3</sub> as solvent and TMS as internal standard. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to the central peak of the solvent and multiplicities are indicated as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets) and br (broad). Coupling constants ( $J$  values) are given in hertz (Hz). All chemicals used were purchased commercially from either Sigma Aldrich, Merck or Alfa Aesar and used without further purification. Solvents used for extraction and chromatographic separations were distilled prior use.

## 2. Preparation of catalysts

**Preparation of PMFC:** 20 g of waste peels of pomegranate fruit were collected and washed properly, finely chopped, ground and mixed with 100 ml distilled water. The water extract of fruit peel was filtered using Whatman filter paper (grade 41) and stored in refrigerator. Then, the peeled residue on the filter paper was washed with 300 ml distilled water-ethanol 1:1 (v/v) mixture and allowed to dry in a vacuum. The finely powdered white mass of PMFC was obtained.

**Preparation of Pd-Ag@PMFC:** 4 g dried powder of PMFC was mixed with 20 ml of aqueous peel extract in a 50 ml round-bottom flask. To the mixture, 50 mM (0.112 g) Pd(OAc)<sub>2</sub> and 50 mM (0.085 g) AgNO<sub>3</sub> were added. The mixture was completely de-gassed and charged with N<sub>2</sub> gas. The reaction flask was covered with black paper and stirred at room temperature for 72 h. A gradual change in the colour of the solution from brown to black indicated the reduction of Pd<sup>2+</sup> and Ag<sup>+</sup> ions to Pd<sup>0</sup> and Ag<sup>0</sup> respectively. Thereafter, the mixture was centrifuged (600 rpm) and washed with H<sub>2</sub>O and EtOH and dried under vacuum to obtain the bi-metal loaded Pd-Ag@PMFC.

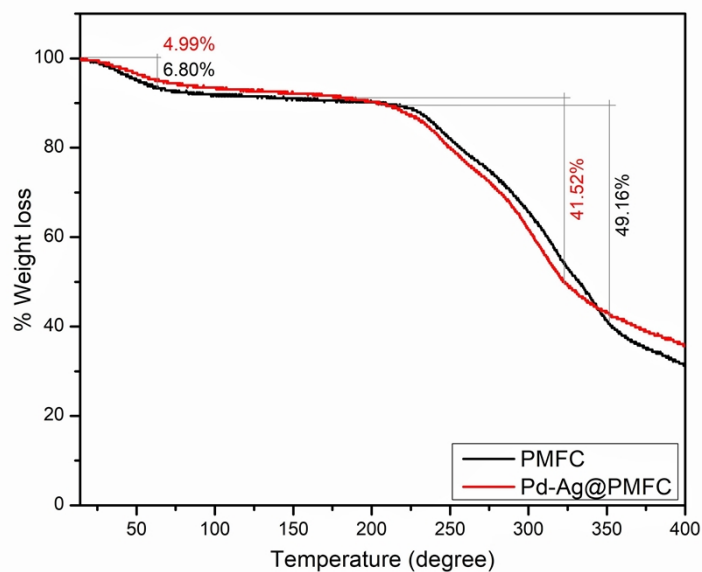
**Preparation of Pd@PMFC and Ag@PMFC:** As mentioned above for Pd-Ag@PMFC, same procedure was followed for Pd@PMFC and Ag@PMFC using 4 g PMFC with 20 ml aqueous extract and 100 mM Pd(OAc)<sub>2</sub> or AgNO<sub>3</sub> respectively.



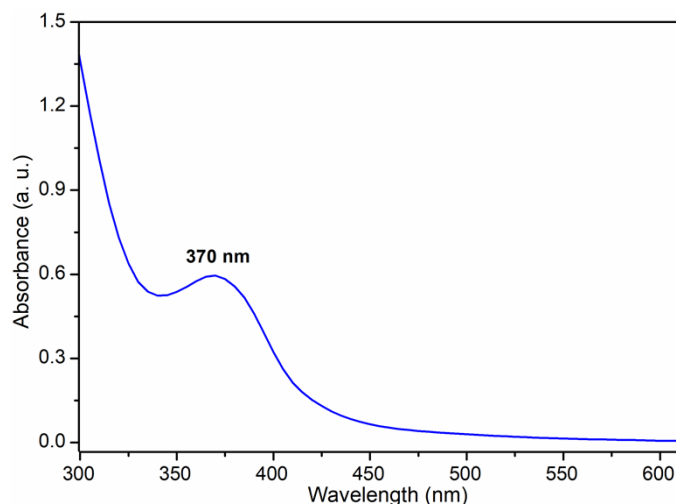
**Fig. S1** Schematic preparation method of Pd-Ag@PMFC from waste pomegranate peels

### 3. Characterization of Pd-Ag@PMFC

The X-ray diffraction (XRD) patterns were measured with the help of a Rigaku MultiFlex instrument using a nickel-filtered Cu  $K\alpha$  radiation source operating at a wavelength of 0.154 nm. The surface structures and morphologies of the catalyst system were observed by scanning electron microscopy (SEM) (model: JEOL JSM 6390 LV) and transmission electron microscopy (TEM) (model: JEOL JEM 2100 at 200kV) analyses. The elemental composition of the nanostructure was determined by energy dispersive X-Ray (EDX) analysis using the same SEM instrument. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Thermo-Scientific ESCALAB Xi+ spectrometer with a monochromatic Al  $K\alpha$  X-ray source (1486.6 eV) and a spherical energy analyzer that operates in the CAE (constant analyzer energy) mode. The CAE for the survey spectrum is 200 eV and for high-resolution spectra is 50 eV. Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Frontier MIR/FIR spectrometer, the wavenumbers ( $\nu$ ) of recorded IR signals are reported in  $\text{cm}^{-1}$ . The real content of Ag and Pd was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis on an ACROS ICP spectrometer. Thermogravimetric analyses (TGA) were performed on a Shimadzu 60 thermal analyzer at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  under continuous nitrogen flow. The Brunauer-Emmett-Teller (BET) surface area and porosity were measured, and its  $\text{N}_2$  adsorption-desorption isotherms were recorded with a Quanta Chrome Novae-2200 surface area analyzer. Ultraviolet-visible (UV-Vis) spectrum was recorded on Shimadzu UV-2600i spectrophotometer.



**Fig. S2** TGA curves of PMFC and Pd-Ag@PMFC



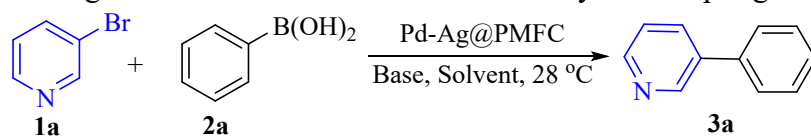
**Fig. S3** UV-vis spectrum of Pd-Ag@PMFC (0.01 g dispersed in H<sub>2</sub>O-EtOH 1:1 (10 ml))

#### 4. General procedure for Suzuki-Miyaura coupling of heteroaryl compounds

In an oven-dried 50 ml round-bottom flask, a mixture of aryl/heteroaryl halide (0.5 mmol), aryl/heteroarylboronic acid (0.6 mmol), Pd-Ag@PMFC (10 wt%, 0.001 mmol of Pd) and K<sub>2</sub>CO<sub>3</sub> (1.2 mmol) were stirred in H<sub>2</sub>O-EtOH 1:1 (4 ml) at room temperature (28 °C). After completion of reaction (confirmed by TLC), the reaction mixture was diluted with distilled water and extracted with ethyl acetate (3 × 10 ml), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel 100-200 mesh by using ethyl acetate and hexane (1:9) as the eluent to give the corresponding cross-coupling products. The purity of isolated products was confirmed by comparing <sup>1</sup>H and <sup>13</sup>C NMR data. The reactions were performed under general

lighting conditions of the laboratory (average intensity value 2.92 W/m<sup>2</sup>) recorded on a solar power meter (Model: KM-SPM-11).

**Table S1** Screening of reaction conditions for Suzuki-Miyaura coupling<sup>a</sup>



| Entry | Catalyst (wt%) | Solvent                     | Base                            | Time (h) | Yield <sup>b</sup> (%) |
|-------|----------------|-----------------------------|---------------------------------|----------|------------------------|
| 1     | 15             | EtOH                        | K <sub>2</sub> CO <sub>3</sub>  | 12       | 76                     |
| 2     | 15             | i-PrOH                      | K <sub>2</sub> CO <sub>3</sub>  | 12       | 72                     |
| 3     | 15             | CH <sub>3</sub> CN          | K <sub>2</sub> CO <sub>3</sub>  | 12       | 70                     |
| 4     | 15             | H <sub>2</sub> O            | K <sub>2</sub> CO <sub>3</sub>  | 10       | 83                     |
| 5     | 15             | H <sub>2</sub> O-EtOH (1:1) | K <sub>2</sub> CO <sub>3</sub>  | 6        | 93                     |
| 6     | 15             | H <sub>2</sub> O-EtOH (1:1) | Na <sub>2</sub> CO <sub>3</sub> | 7        | 87                     |
| 7     | 15             | H <sub>2</sub> O-EtOH (1:1) | Cs <sub>2</sub> CO <sub>3</sub> | 6        | 92                     |
| 8     | 15             | H <sub>2</sub> O-EtOH (1:1) | NaHCO <sub>3</sub>              | 7        | 73                     |
| 9     | 15             | H <sub>2</sub> O-EtOH (1:1) | NaOH                            | 7        | 60                     |
| 10    | 15             | H <sub>2</sub> O-EtOH (1:1) | KOH                             | 7        | 63                     |
| 11    | 15             | H <sub>2</sub> O-EtOH (1:1) | Et <sub>3</sub> N               | 12       | 35                     |
| 12    | 15             | H <sub>2</sub> O-EtOH (1:1) | -                               | 24       | nr                     |
| 13    | 10             | H <sub>2</sub> O-EtOH (1:1) | K <sub>2</sub> CO <sub>3</sub>  | 6        | 93                     |
| 14    | 8              | H <sub>2</sub> O-EtOH (1:1) | K <sub>2</sub> CO <sub>3</sub>  | 12       | 81                     |
| 15    | 5              | H <sub>2</sub> O-EtOH (1:1) | K <sub>2</sub> CO <sub>3</sub>  | 12       | 65                     |
| 16    | -              | H <sub>2</sub> O-EtOH (1:1) | K <sub>2</sub> CO <sub>3</sub>  | 24       | nr                     |

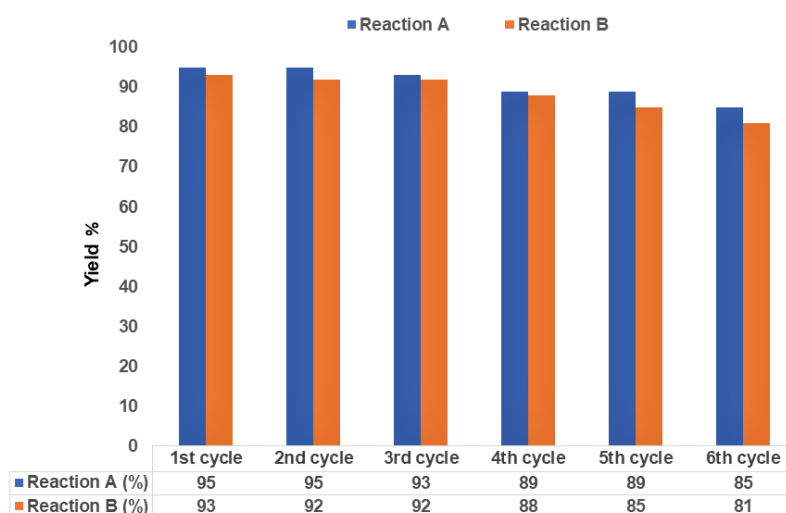
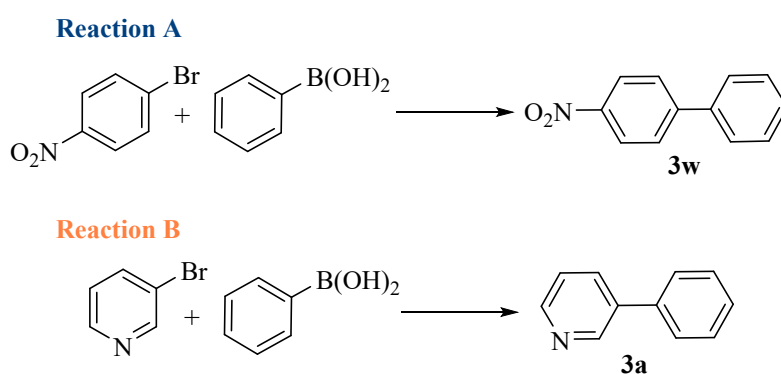
<sup>a</sup>Reaction conditions: 3-bromopyridine (0.5 mmol), phenylboronic acid (0.6 mmol), Pd-Ag@PMFC, base (1.2 mmol), solvent (4 ml), room temperature (28 °C); catalyst amount: 15 wt% (0.012 g), 10 wt% (0.008 g), 8 wt% (0.006 g), 5 wt% (0.004 g); <sup>b</sup>yield.

#### **Hot-filtration test:**

The heterogeneity of the present catalyst and the real active species in the catalytic reaction was determined by performing a hot filtration test. Pd-Ag@PMFC (10 wt%) was pre-treated with K<sub>2</sub>CO<sub>3</sub> (1.2 mmol) in H<sub>2</sub>O-EtOH 1:1 (4 ml) in a round bottom flask at 28 °C. After 2 h, the solid catalyst phase was filtered off using Whatman filter paper (grade 41). The filtrate was collected in another round-bottom flask and employed for Suzuki-Miyaura coupling of 3-

bromopyridine (0.5 mmol) and phenylboronic acid (0.6 mmol) for 10 h. However, only a trace amount of product formation was detected even after an extended reaction time. The ICP-OES analysis of the liquid phase reveals a residual amount (less than 0.01 ppm) of leached Pd and Ag species in the reaction medium. This inferior leaching suggests the heterogeneous nature of the active catalyst species.

**Reusability study of Pd-Ag@PMFC:** For the recycle experiments, the used catalyst was recovered from the reaction media by centrifugation (600 rpm) and washed with EtOAc, H<sub>2</sub>O and EtOH. The catalyst was dried in a vacuum desiccator for 24 h and the catalyst was ready for the next cycle.



<sup>a</sup>Reaction conditions: aryl/heteroaryl bromide (0.5 mmol), phenylboronic acid (0.6 mmol), Pd-Ag@PMFC (0.008 g, 0.001 mmol of Pd), K<sub>2</sub>CO<sub>3</sub> (1.2 mmol), H<sub>2</sub>O-EtOH 1:1 (4 ml), room temperature (28 °C), reaction time: **A**: 25 min; **B**: 6 h.

**Fig. S4** Reusability test for Pd-Ag@PMFC

## 5. Physical and spectroscopic data of products

**3-phenylpyridine (3a).** Colourless liquid, 73 mg, 93% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.85 (d, *J*=2.6 Hz, 1H), 8.59 (dd, *J*=4.9, 1.6 Hz, 1H), 7.89-7.86 (m, 1H), 7.59-7.57 (m, 2H), 7.50-7.46 (m, 2H), 7.42-7.35 (m, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 148.4, 148.2, 137.7, 136.6, 134.4, 129.0, 128.1, 127.1, 123.4 ppm.

**3-(4-methoxyphenyl)pyridine (3b).** White solid, 81 mg, 88% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.82 (d, *J*=1.5 Hz, 1H), 8.54 (dd, *J*=4.8, 1.7 Hz, 1H), 7.84-7.81 (m, 1H), 7.51 (d, *J*=8.9 Hz, 2H), 7.33 (dd, *J*=7.4, 4.4 Hz, 1H), 7.01 (d, *J*=8.9 Hz, 2H), 3.85 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.7, 147.8, 147.7, 136.2, 133.8, 130.1, 128.1, 123.5, 114.5, 55.3 ppm.

**3-(4-(*tert*-butyl)phenyl)pyridine (3c).** Colourless liquid, 94 mg, 89% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.85 (d, *J*=2.2 Hz, 1H), 8.57 (dd, *J*=4.9, 1.7 Hz, 1H), 7.92-7.89 (m, 1H), 7.54-7.49 (m, 4H), 7.38 (dd, *J*=7.9, 4.9 Hz, 1H), 1.35 (s, 9H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 151.4, 147.4, 147.3, 136.8, 134.7, 134.5, 126.7, 126.0, 123.7, 34.5, 31.0 ppm.

**3-(4-chlorophenyl)pyridine (3d).** Colourless liquid, 77 mg, 81% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.83 (d, *J*=2.6 Hz, 1H), 8.61 (dd, *J*=4.8, 1.6 Hz, 1H), 7.89-7.86 (m, 1H), 7.52-7.39 (m, 5H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 148.0, 147.4, 135.9, 135.8, 134.7, 134.5, 129.3, 128.3, 123.8 ppm.

**5-phenylpyrimidine (3e).** Colourless liquid, 73 mg, 93% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.21 (s, 1H), 8.96 (s, 2H), 7.60-7.47 (m, 5H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 157.3, 154.8, 134.2, 134.1, 129.3, 128.9, 126.8 ppm.

**5-(4-methoxyphenyl)pyrimidine (3f).** White solid, 80 mg, 88% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.16 (s, 1H), 8.92 (s, 2H), 7.53 (d, *J*=8.8 Hz, 2H), 7.05 (d, *J*=8.8 Hz, 2H), 3.88 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 160.4, 156.8, 154.3, 133.9, 128.1, 126.5, 114.7, 55.4 ppm.

**5-(4-(*tert*-butyl)phenyl)pyrimidine (3g).** Colourless liquid, 90 mg, 85% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.19 (s, 1H), 8.95 (s, 2H), 7.57-7.52 (m, 4H), 1.37 (s, 9H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 157.4, 154.7, 152.3, 134.1, 131.2, 126.7, 126.4, 34.7, 31.2 ppm.

**5-(4-chlorophenyl)pyrimidine (3h).** Colourless liquid, 76 mg, 80% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.22 (s, 1H), 8.93 (s, 2H), 7.54-7.49 (m, 4H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 157.6, 154.6, 135.3, 133.1, 132.6, 129.6, 128.1 ppm.

**5-(4-fluorophenyl)pyrimidine (3i).** Colourless liquid, 70 mg, 81% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.20 (s, 1H), 8.92 (s, 1H), 7.57-7.53 (m, 2H), 7.25-7.19 (m, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 163.5 (d, *J*=250.2 Hz), 157.4, 154.7, 133.5, 130.4, 128.8 (d, *J*=5.8 Hz), 116.6 (d, *J*=21.1 Hz) ppm.

**3-phenylquinoline (3j).** Colourless liquid, 85 mg, 83% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.20 (d, *J*=2.2 Hz, 1H), 8.31 (d, *J*=2.3 Hz, 1H), 8.16 (d, *J*=8.5 Hz, 1H), 7.89 (d, *J*=8.2 Hz, 1H), 7.75-7.71 (m, 3H), 7.60-7.52 (m, 3H), 7.47-7.42 (m, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 149.9, 147.3, 137.9, 133.8, 133.2, 129.4, 129.2, 129.2, 128.1, 128.0, 128.0, 127.4, 127.0 ppm.

**5-(*m*-tolyl)-1H-indole (3k).** Colourless liquid, 88 mg, 86% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.05 (br, s, 1H), 7.92 (m, 1H), 7.54-7.49 (m, 3H), 7.44-7.37 (m, 2H), 7.21-7.18 (m, 2H), 6.65-6.64 (m, 1H), 2.49 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 142.5, 138.2, 135.2, 133.4, 128.5, 128.3, 127.0, 124.8, 124.8, 124.4, 121.8, 119.2, 111.1, 103.0, 21.5 ppm.

**2-methoxy-5-(4-methoxyphenyl)pyridine (3n).** White solid, 90 mg, 85% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.34 (d, *J*=3.0 Hz, 1H), 7.73 (dd, *J*=8.6, 2.6 Hz, 1H), 7.45-7.43 (m, 2H), 6.99-6.95 (m, 2H), 6.79 (dd, *J*=8.4, 0.8 Hz, 1H), 3.96 (s, 3H), 3.84 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 163.1, 159.1, 144.4, 137.2, 130.3, 129.7, 127.7, 114.3, 110.7, 55.3, 53.5 ppm.

**2-methoxy-5-(4-nitrophenyl)pyridine (3o).** Yellow solid, 102 mg, 89% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.44 (dd, *J*=2.6, 0.7 Hz, 1H), 8.36-8.27 (m, 2H), 7.83-7.77 (m, 1H), 7.72-7.65 (m, 2H), 6.86 (dd, *J*=8.7, 0.7 Hz, 1H), 3.99 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 164.6, 147.0, 145.6, 144.4, 137.3, 128.3, 127.1, 124.3, 111.4, 53.8 ppm.

**1-(4-(6-methoxypyridin-3-yl)phenyl)ethan-1-one (3p).** Colourless liquid, 92 mg, 81% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.44 (d, *J*=2.6 Hz, 1H), 8.04 (d, *J*=8.1 Hz, 2H), 7.83 (dd, *J*=8.6, 2.5 Hz, 1H), 7.63 (d, *J*=8.1 Hz, 2H), 6.85 (d, *J*=8.6 Hz, 1H), 4.00 (s, 3H), 2.64 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 197.5, 164.2, 145.3, 142.5, 137.3, 135.8, 129.1, 126.5, 111.0, 99.8, 53.7, 26.6 ppm.

**5-(*o*-tolyl)-1H-indole (3q).** Colourless liquid, 83 mg, 81% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.07 (br, s, 1H), 7.59 (m, 1H), 7.39 (d, *J*=8.4 Hz, 1H), 7.33-7.24 (m, 4H), 7.21-7.16 (m, 2H), 6.59-6.57 (m, 1H), 2.32 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 143.0,



135.7, 134.7, 133.8, 130.3, 130.2, 127.7, 126.7, 125.6, 124.7, 123.8, 121.0, 110.4, 102.7, 20.7 ppm.

**6-methoxy-3,3'-bipyridine (3s).** Colourless liquid, 81 mg, 88% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.80 (d,  $J=2.4$  Hz, 1H), 8.60 (dd,  $J=4.8, 1.6$  Hz, 1H), 8.39 (d,  $J=2.6$  Hz, 1H), 7.84-7.78 (m, 2H), 7.38 (dd,  $J=7.9, 4.8$  Hz, 1H), 6.87 (d,  $J=8.6$  Hz, 1H), 3.99 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.1, 148.5, 147.7, 145.1, 137.3, 133.9, 133.5, 126.7, 123.7, 111.2, 53.7 ppm.

**5-(6-methoxypyridin-3-yl)pyrimidine (3t).** Colourless liquid, 77 mg, 83% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.21 (s, 1H), 8.92 (s, 2H), 8.40 (d,  $J=2.6$  Hz, 1H), 7.79 (dd,  $J=8.6, 2.6$  Hz, 1H), 6.90 (d,  $J=8.6$  Hz, 1H), 4.00 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.7, 157.4, 154.4, 145.1, 137.0, 131.5, 123.2, 111.6, 53.8 ppm.

**3-(6-methoxypyridin-3-yl)quinoline (3u).** Colourless liquid, 94 mg, 80% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.12 (d,  $J=2.1$  Hz, 1H), 8.51 (d,  $J=2.2$  Hz, 1H), 8.22 (d,  $J=2.1$  Hz, 1H), 8.14 (d,  $J=8.4$  Hz, 1H), 7.89 (dd,  $J=8.6, 2.6$  Hz, 1H), 7.86 (d,  $J=8.1$  Hz, 1H), 7.74-7.70 (m, 1H), 7.59-7.55 (m, 1H), 6.89 (d,  $J=8.6$  Hz, 1H), 4.01 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.0, 149.1, 147.2, 145.3, 137.4, 132.6, 130.6, 129.4, 129.1, 127.7, 127.0, 126.7, 111.3, 99.9, 53.6 ppm.

**5-(6-methoxypyridin-3-yl)-1H-indole (3v).** Colourless liquid, 86 mg, 78% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.44-8.41 (m, 2H), 7.84 (dd,  $J=8.6, 2.6$  Hz, 1H), 7.77 (s, 1H), 7.44 (d,  $J=8.5$  Hz, 1H), 7.35 (dd,  $J=8.4, 1.8$  Hz, 1H), 7.23 (dd,  $J=3.3, 2.5$  Hz, 1H), 6.82 (d,  $J=8.5$  Hz, 1H), 6.61-6.59 (m, 1H), 3.99 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  163.0, 144.8, 138.0, 135.3, 131.5, 129.8, 128.4, 125.0, 121.3, 118.8, 111.5, 110.6, 102.9, 53.5 ppm.

## 6. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of products

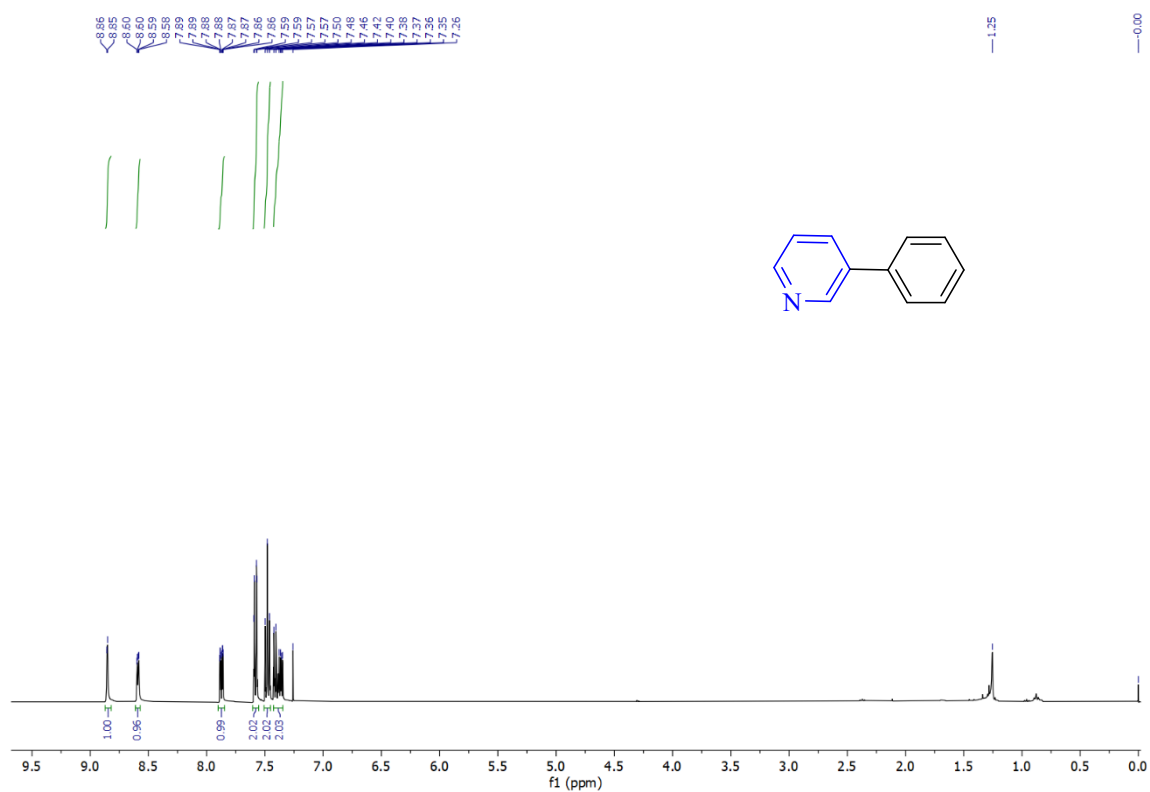


Fig. S5  $^1\text{H}$  NMR spectrum of 3a in  $\text{CDCl}_3$

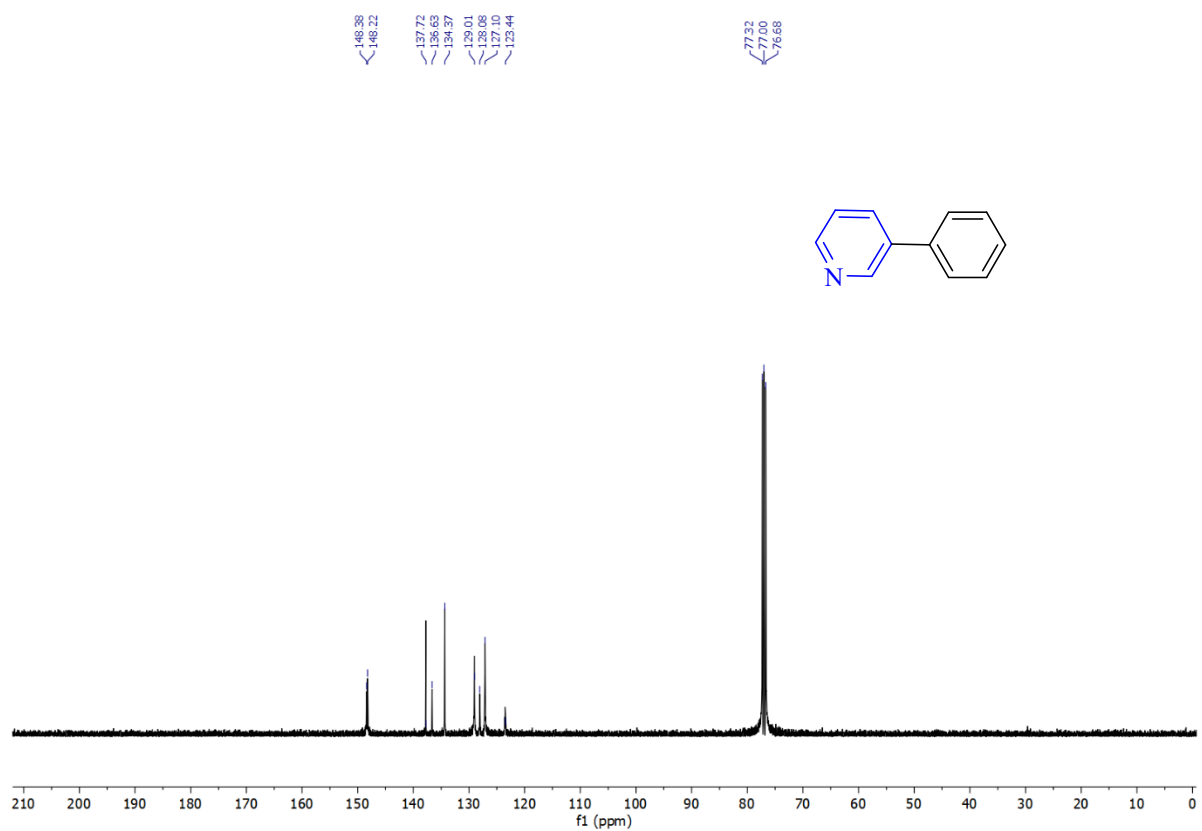


Fig. S6  $^{13}\text{C}$  NMR spectrum of 3a in  $\text{CDCl}_3$

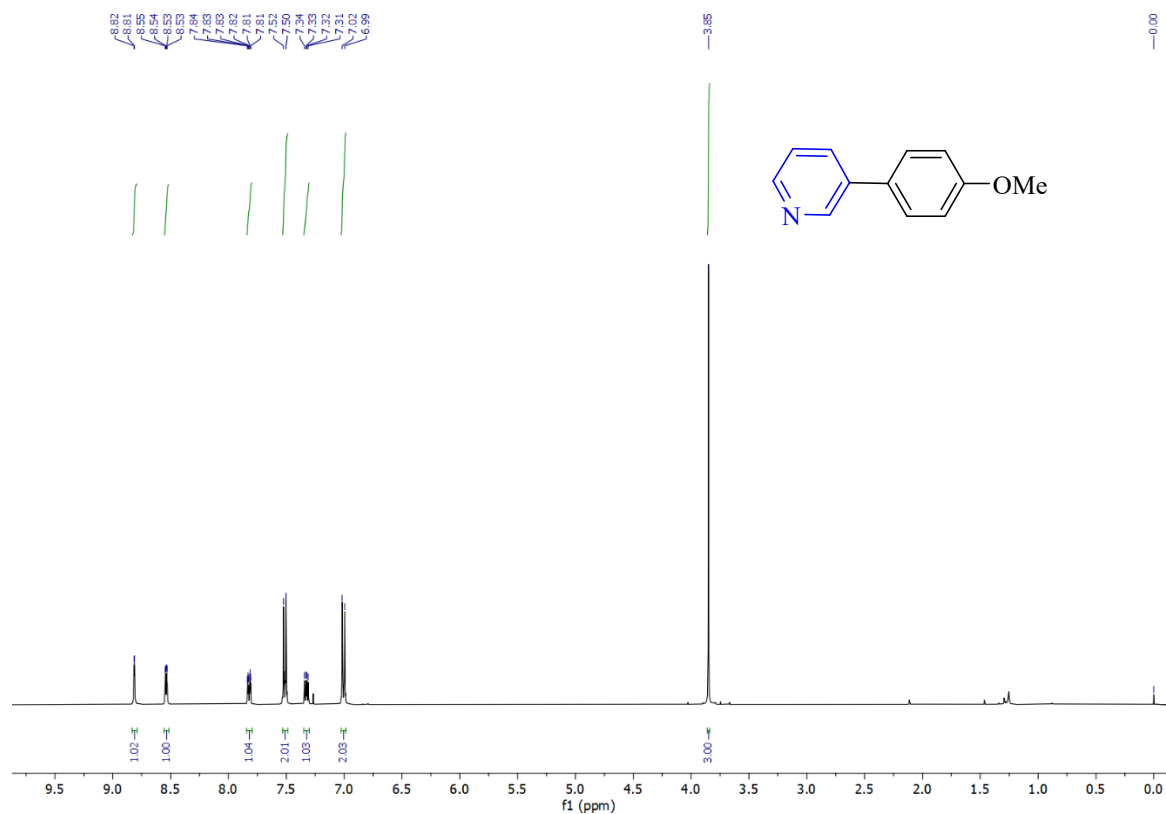


Fig. S7  $^1\text{H}$  NMR spectrum of 3b in  $\text{CDCl}_3$

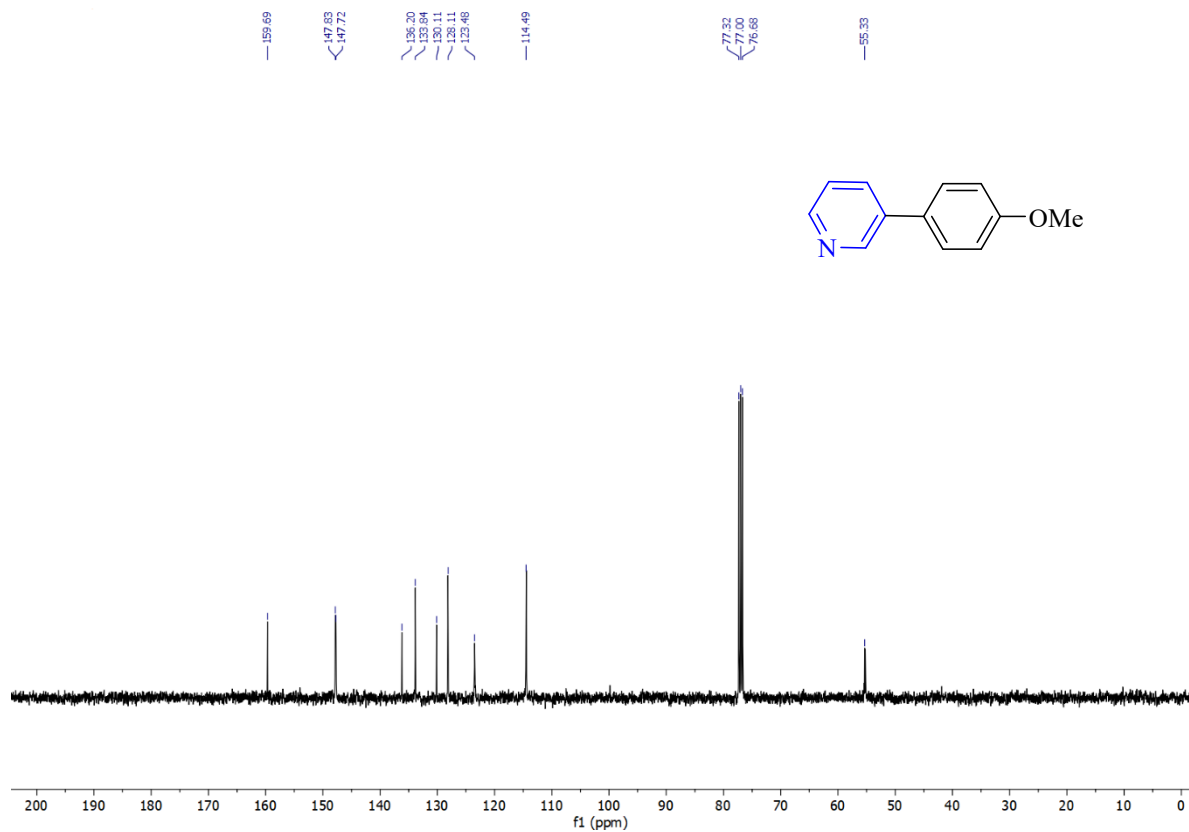
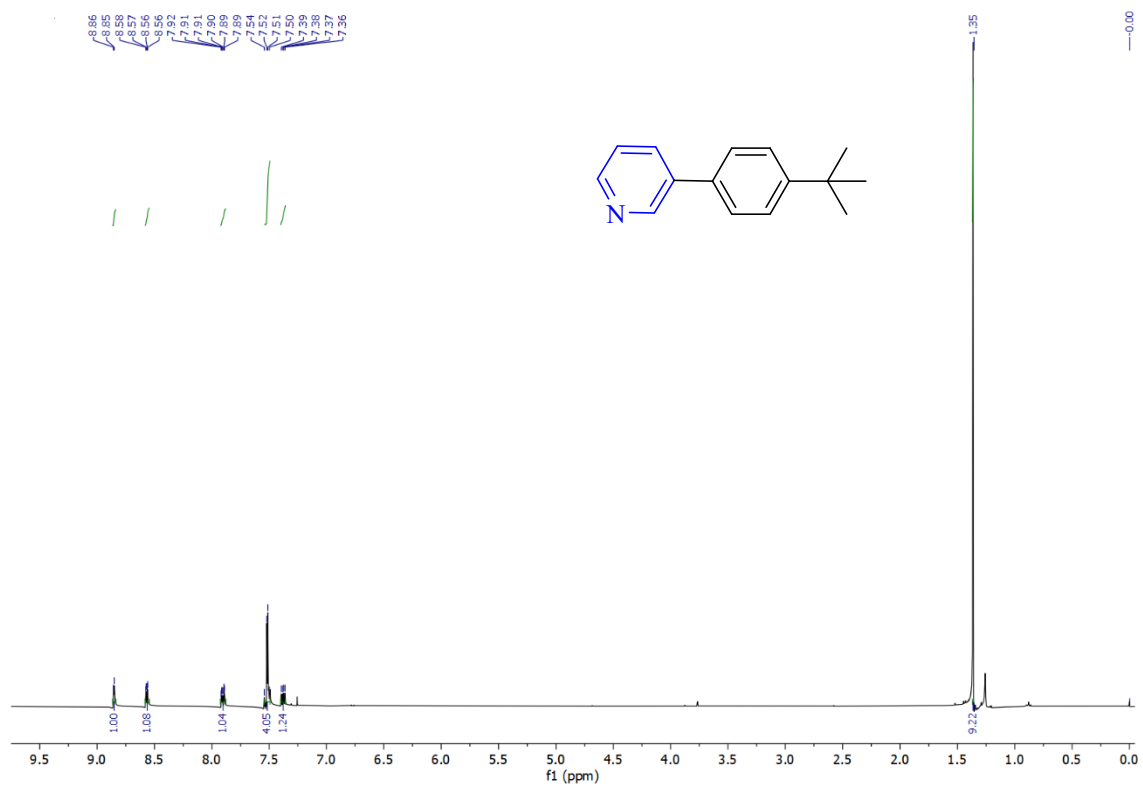
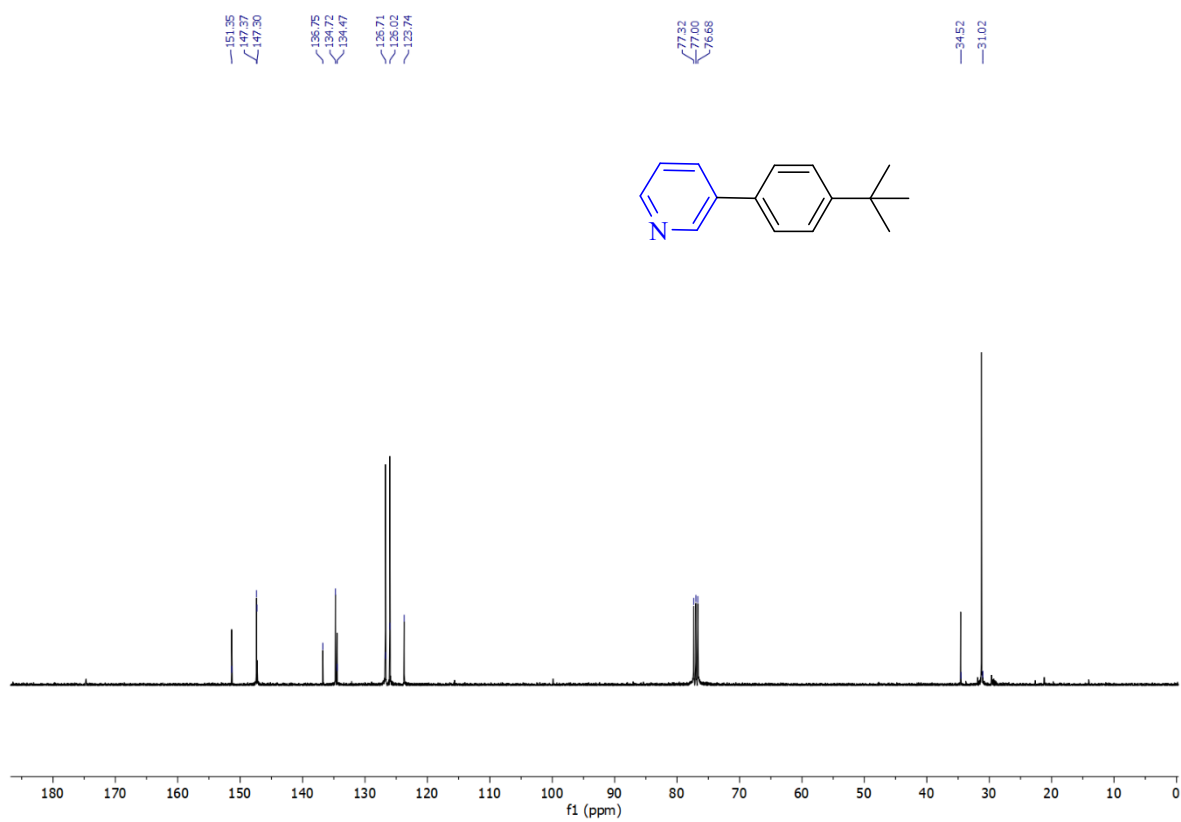


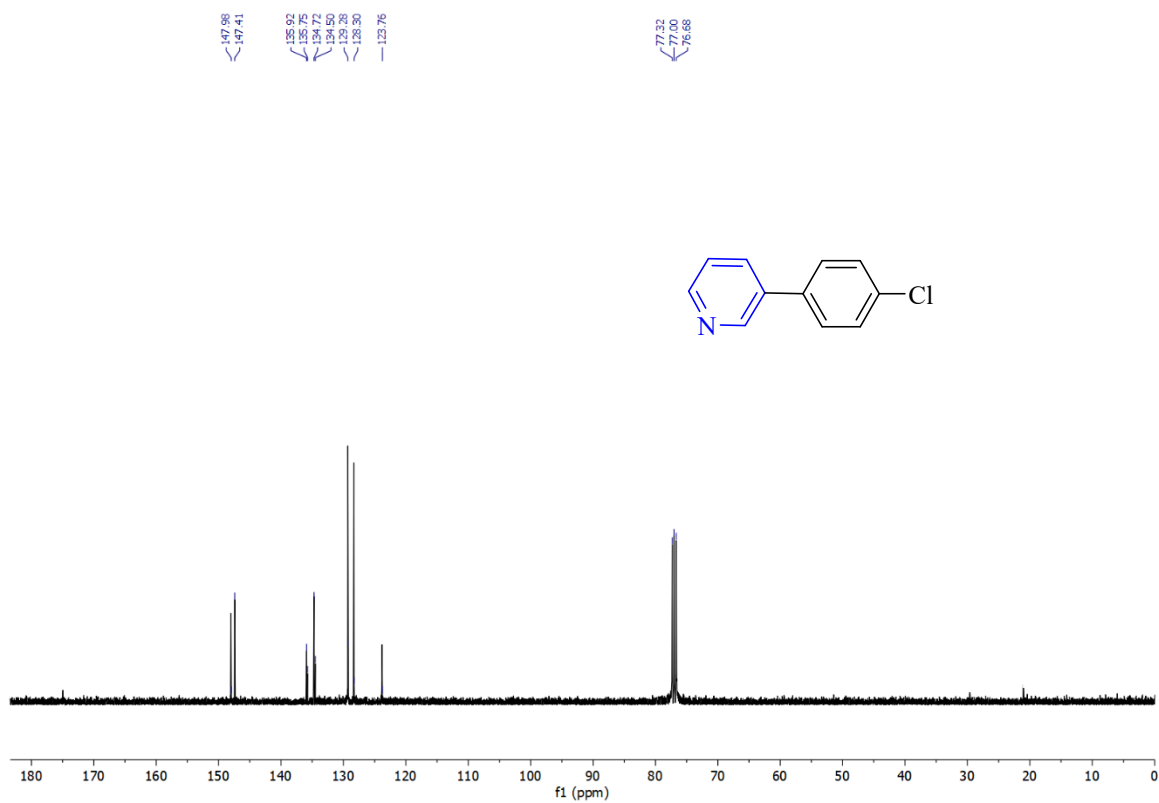
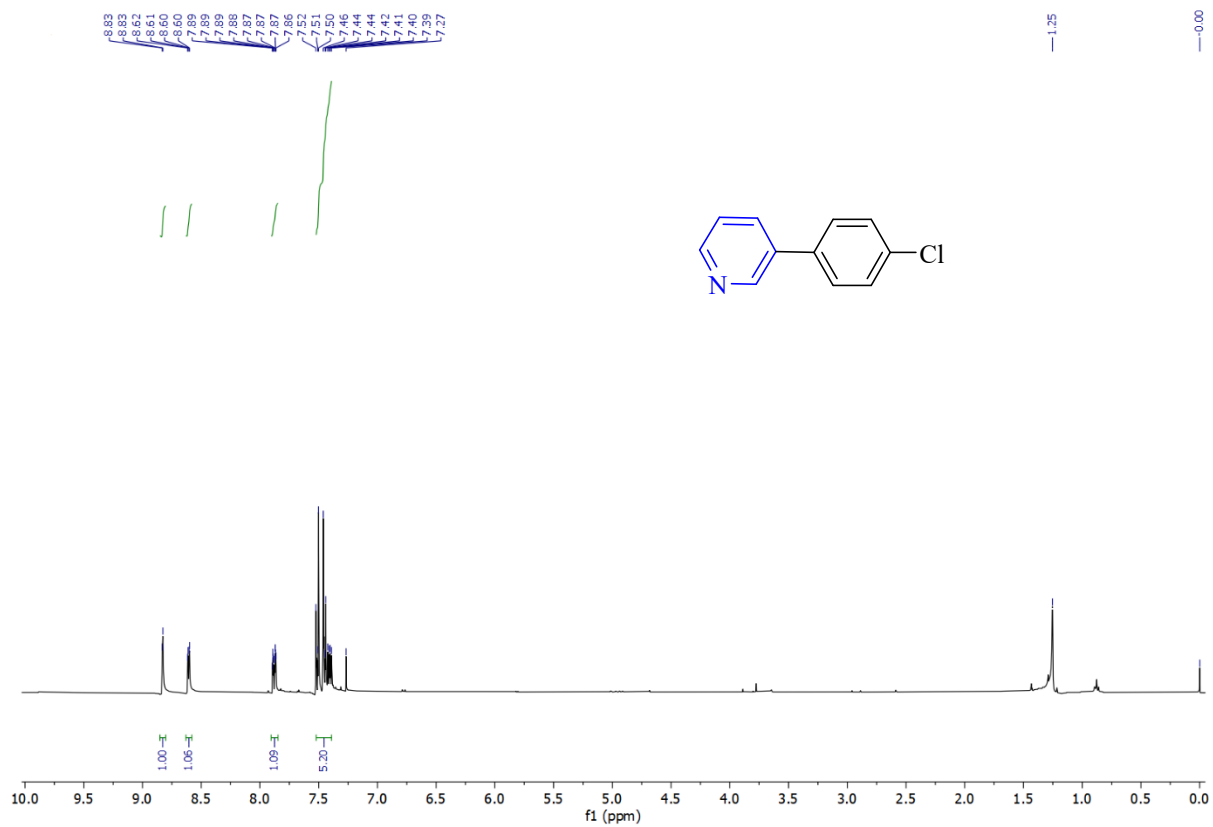
Fig. S8  $^{13}\text{C}$  NMR spectrum of 3b in  $\text{CDCl}_3$

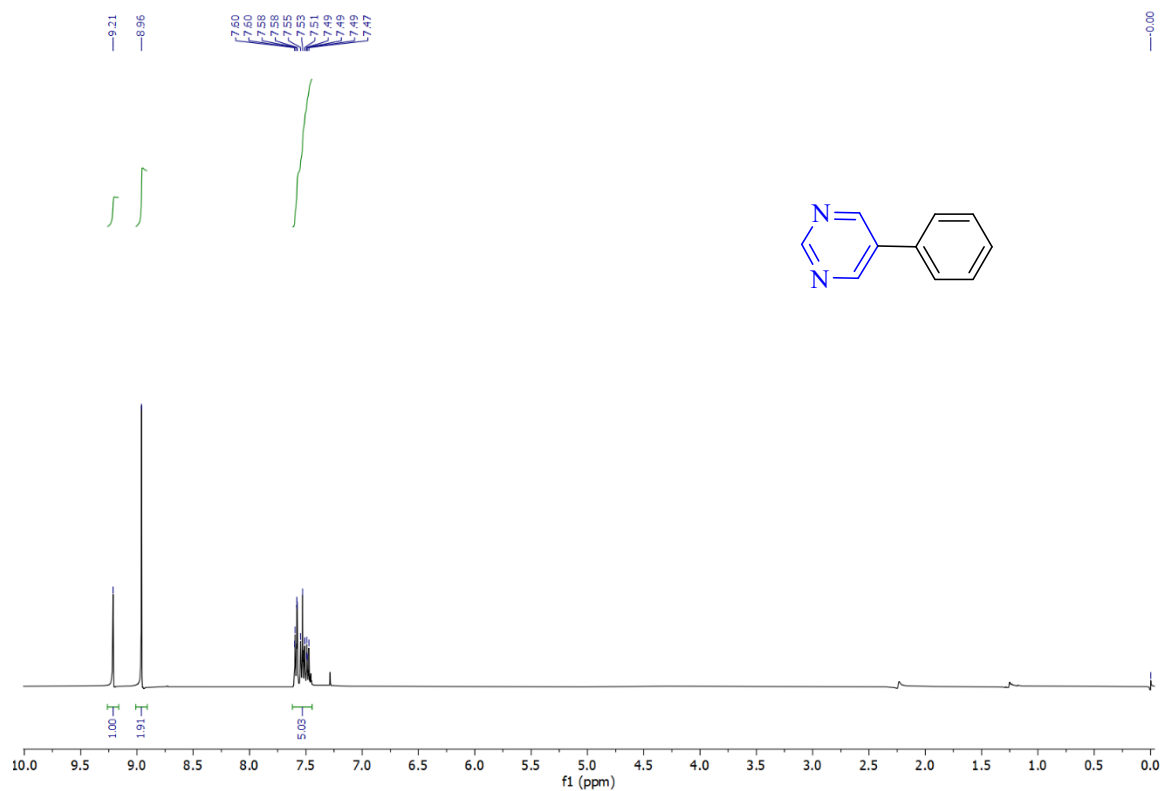


**Fig. S9** <sup>1</sup>H NMR spectrum of 3c in CDCl<sub>3</sub>

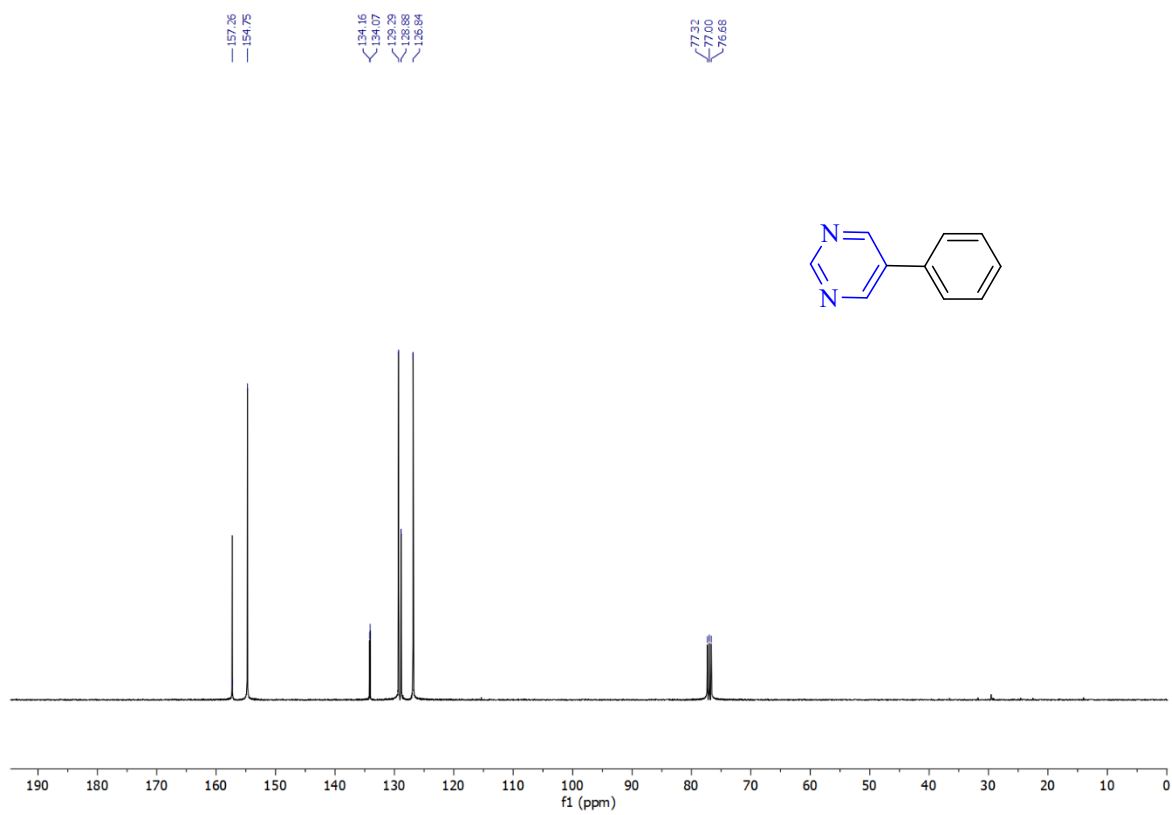


**Fig. S10** <sup>13</sup>C NMR spectrum of 3c in CDCl<sub>3</sub>



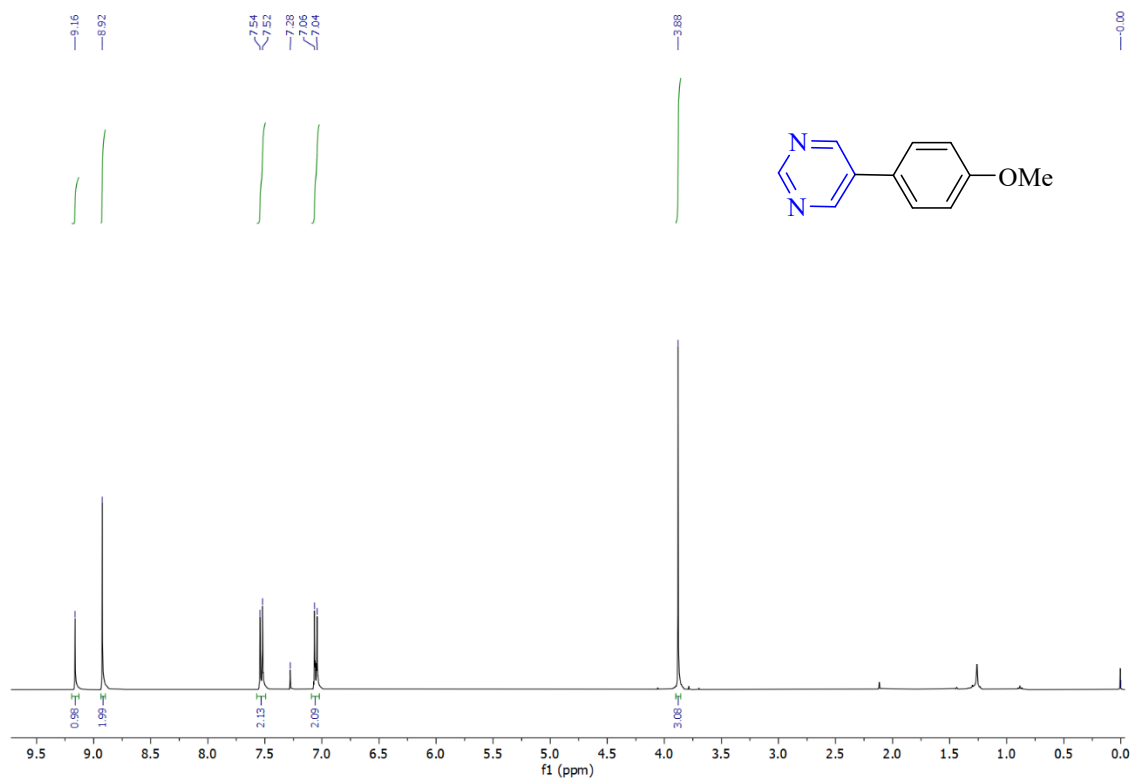


**Fig. S13**  $^1\text{H}$  NMR spectrum of 3e in  $\text{CDCl}_3$

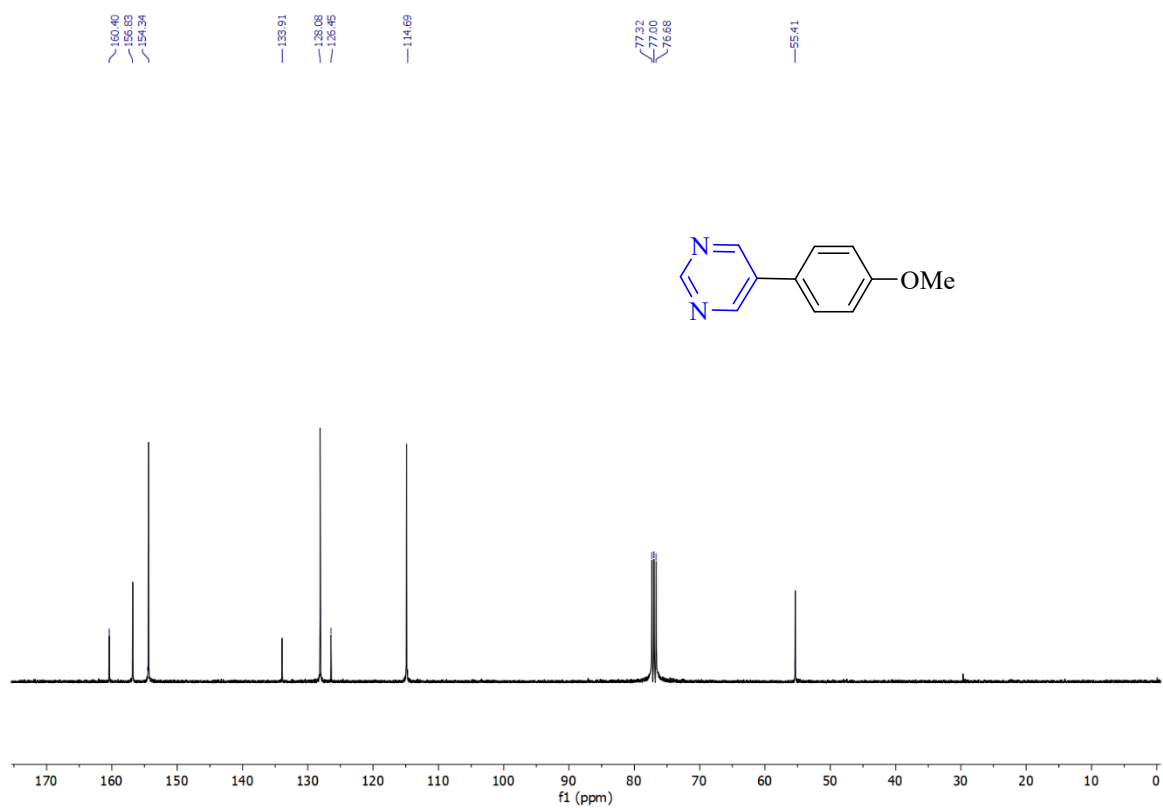


**Fig. S14**  $^{13}\text{C}$  NMR spectrum of 3e in  $\text{CDCl}_3$

7.

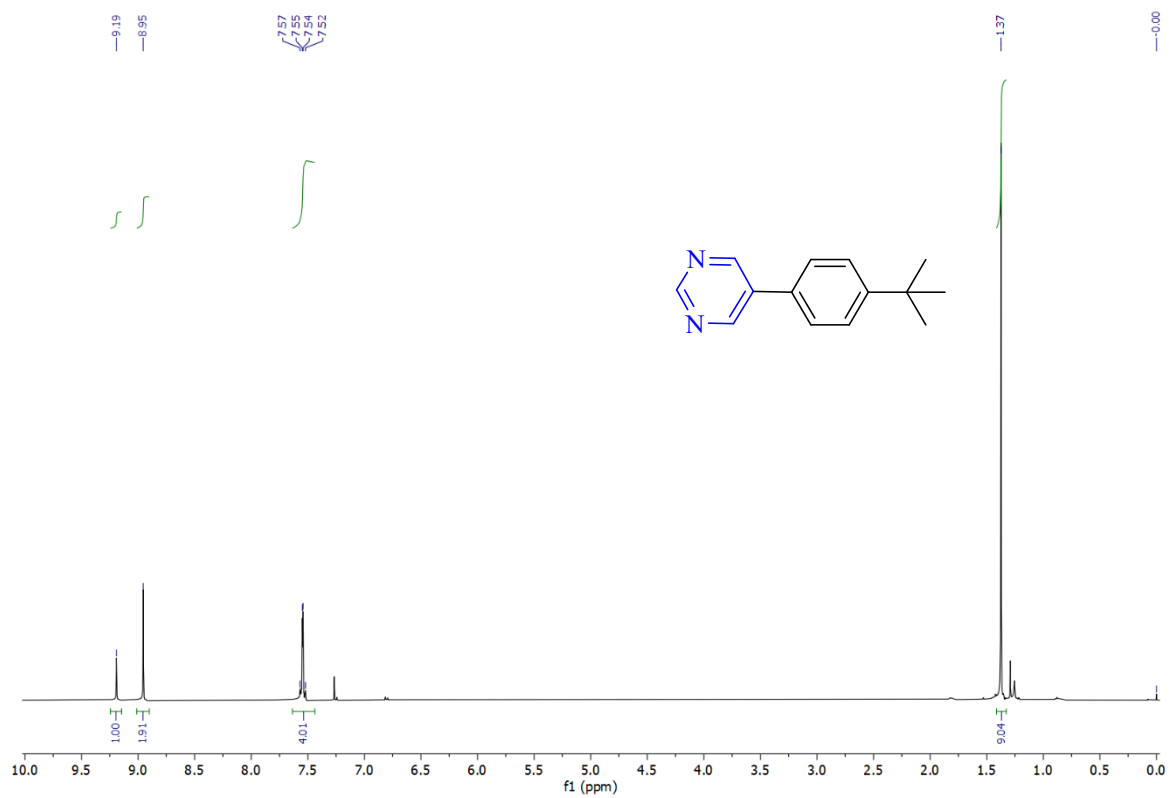


**Fig. S15**  $^1\text{H}$  NMR spectrum of 3f in  $\text{CDCl}_3$

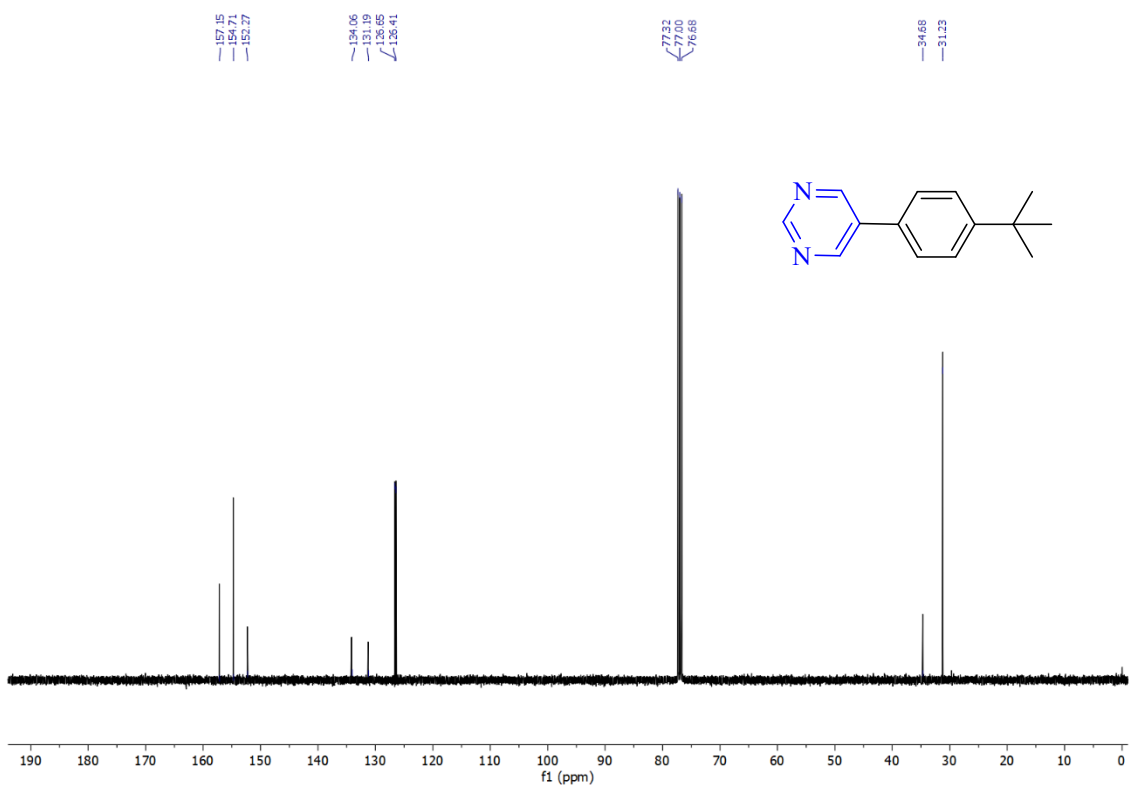


**Fig. S16**  $^{13}\text{C}$  NMR spectrum of 3f in  $\text{CDCl}_3$

8.

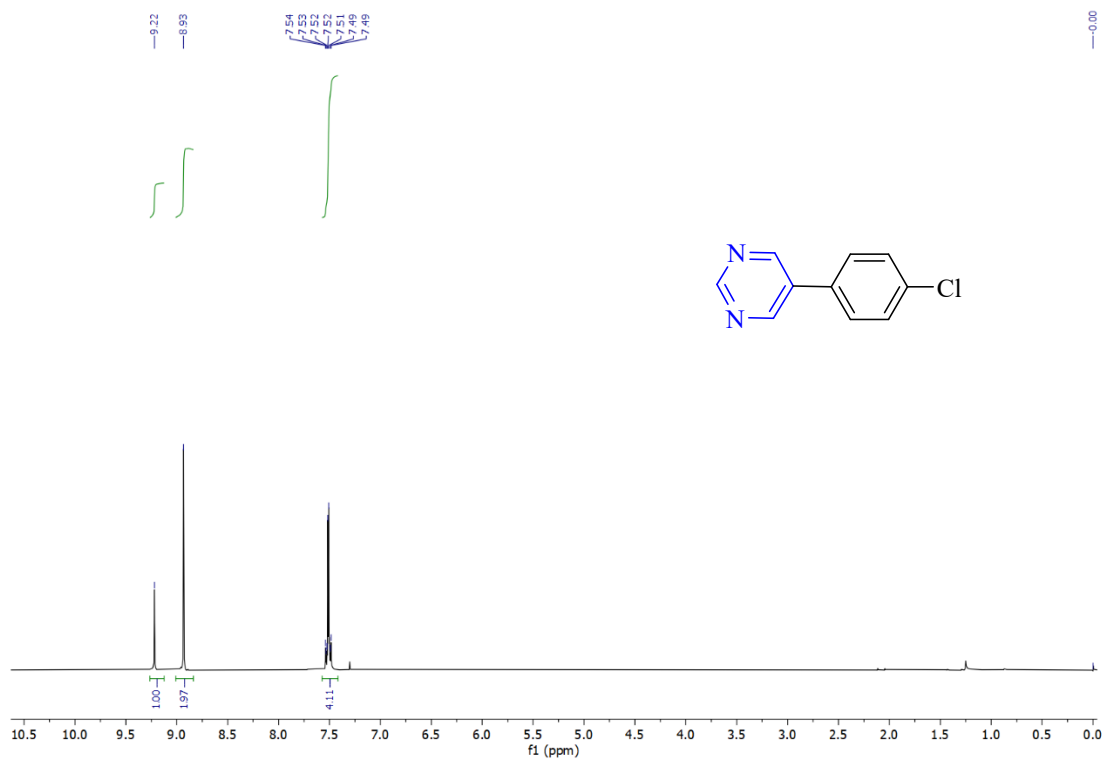


**Fig. S17** <sup>1</sup>H NMR spectrum of 3g in CDCl<sub>3</sub>

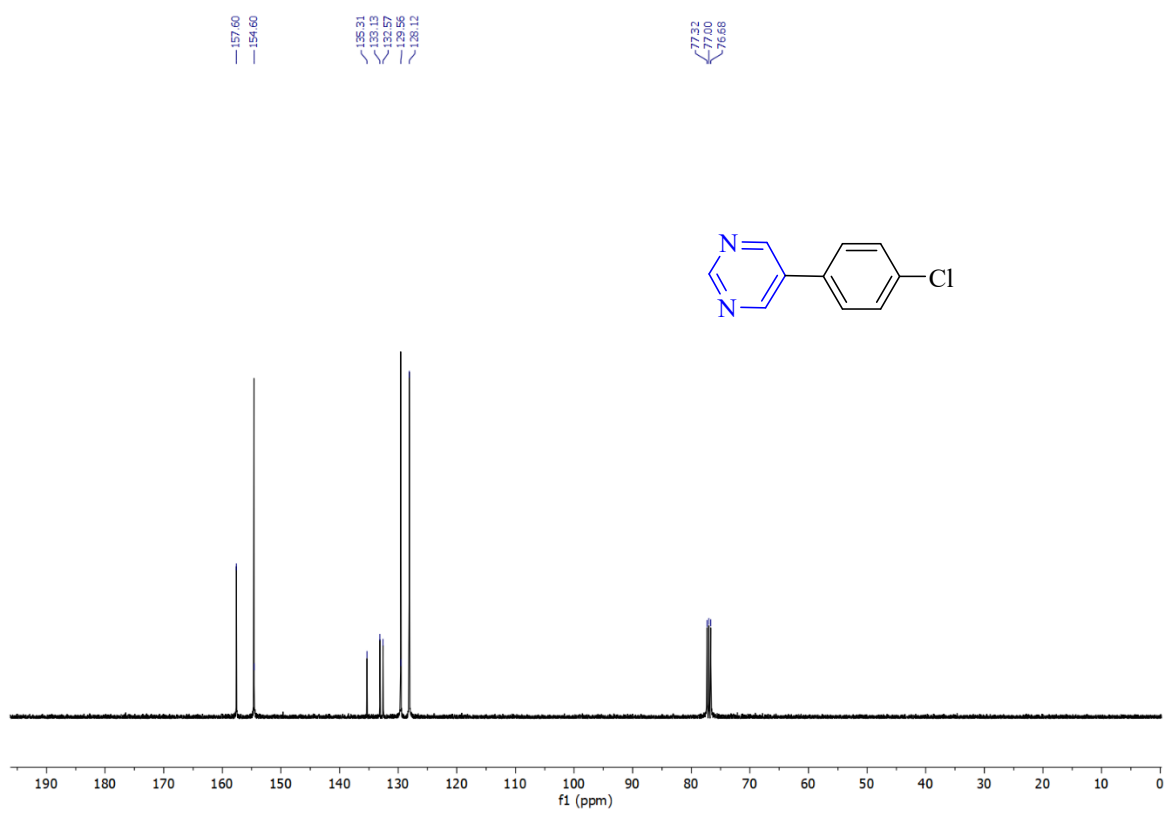


**Fig. S18** <sup>13</sup>C NMR spectrum of 3g in CDCl<sub>3</sub>

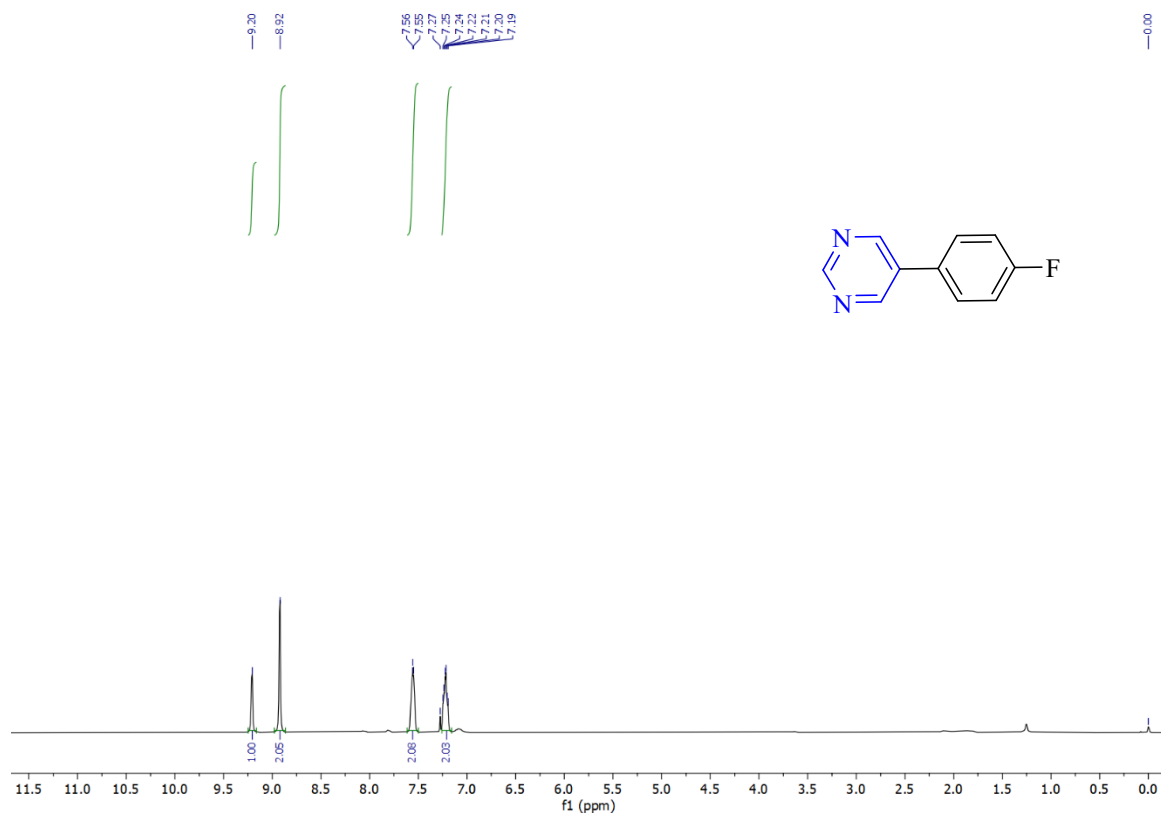




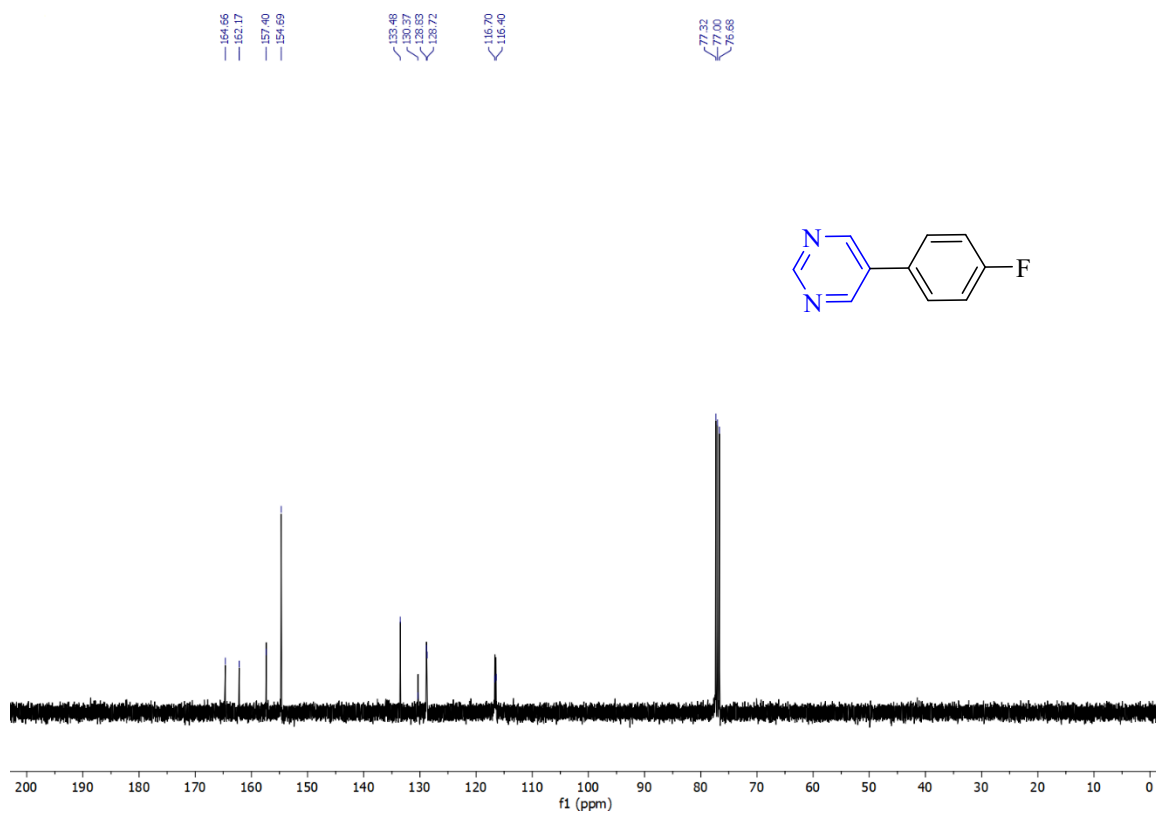
**Fig. S19** <sup>1</sup>H NMR spectrum of 3h in CDCl<sub>3</sub>



**Fig. S20** <sup>13</sup>C NMR spectrum of 3h in CDCl<sub>3</sub>



**Fig. S21**  $^1\text{H}$  NMR spectrum of 3i in  $\text{CDCl}_3$



**Fig. S22**  $^{13}\text{C}$  NMR spectrum of 3i in  $\text{CDCl}_3$

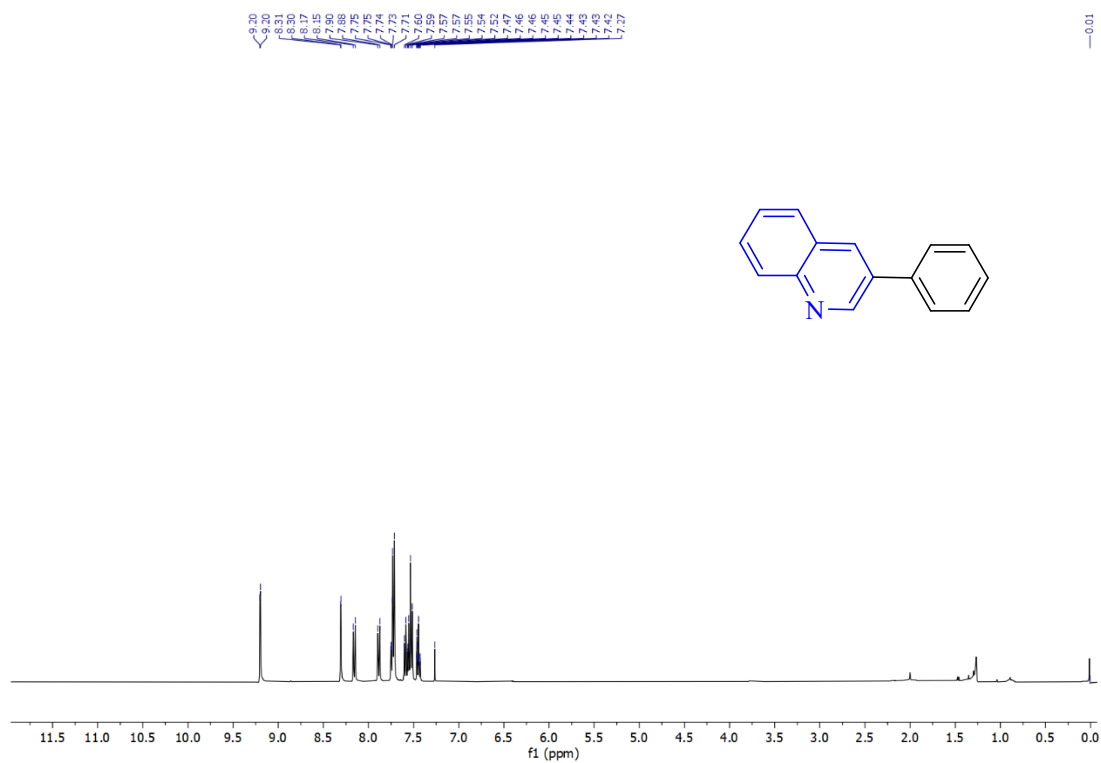


Fig. S23  $^1\text{H}$  NMR spectrum of 3j in  $\text{CDCl}_3$

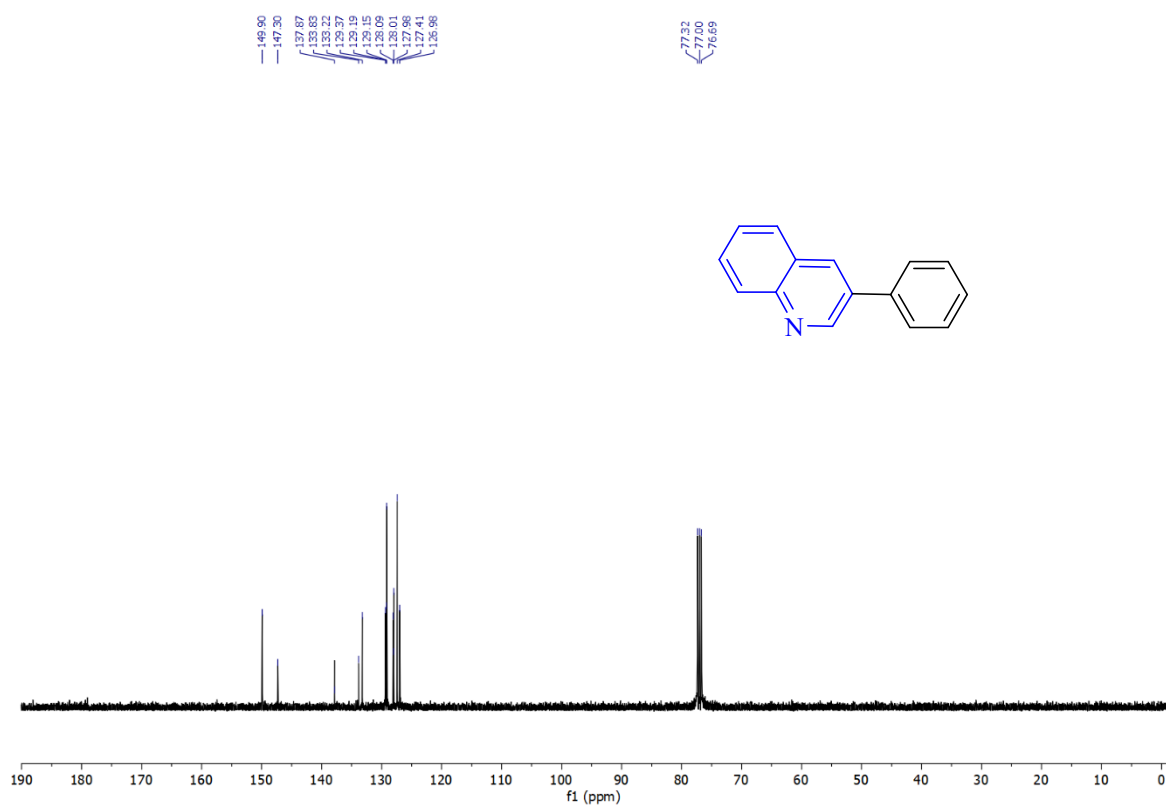
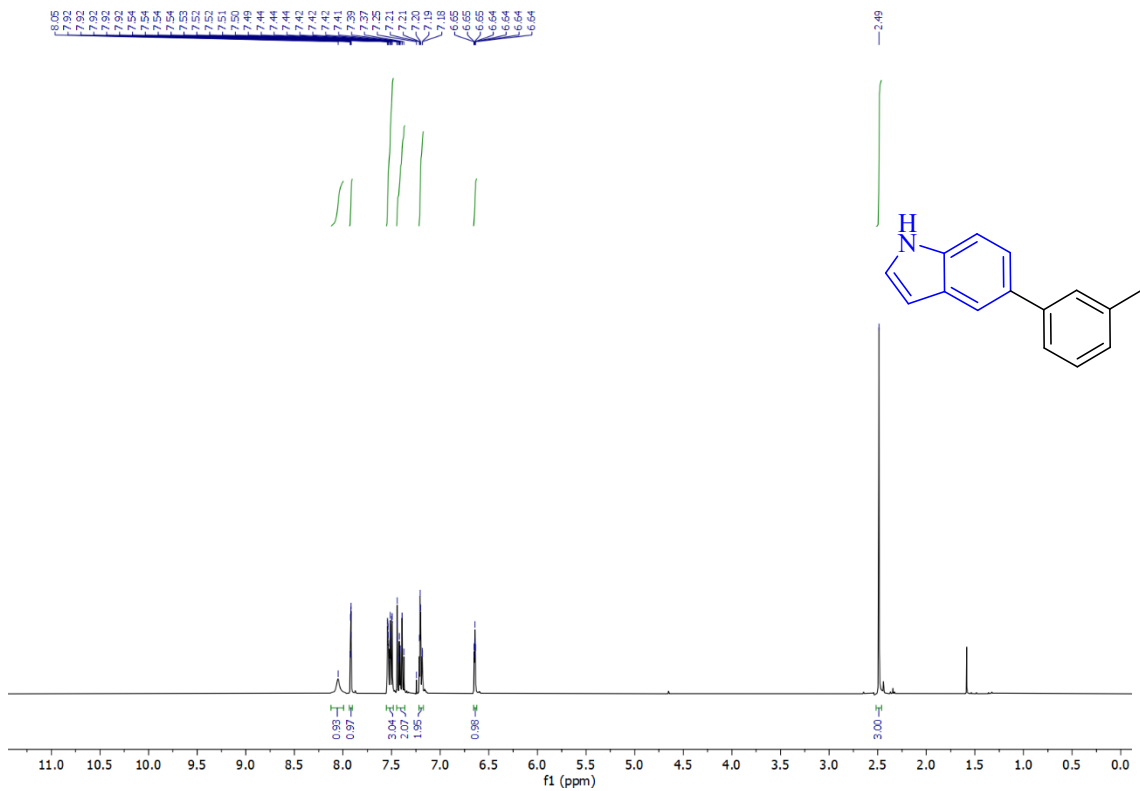
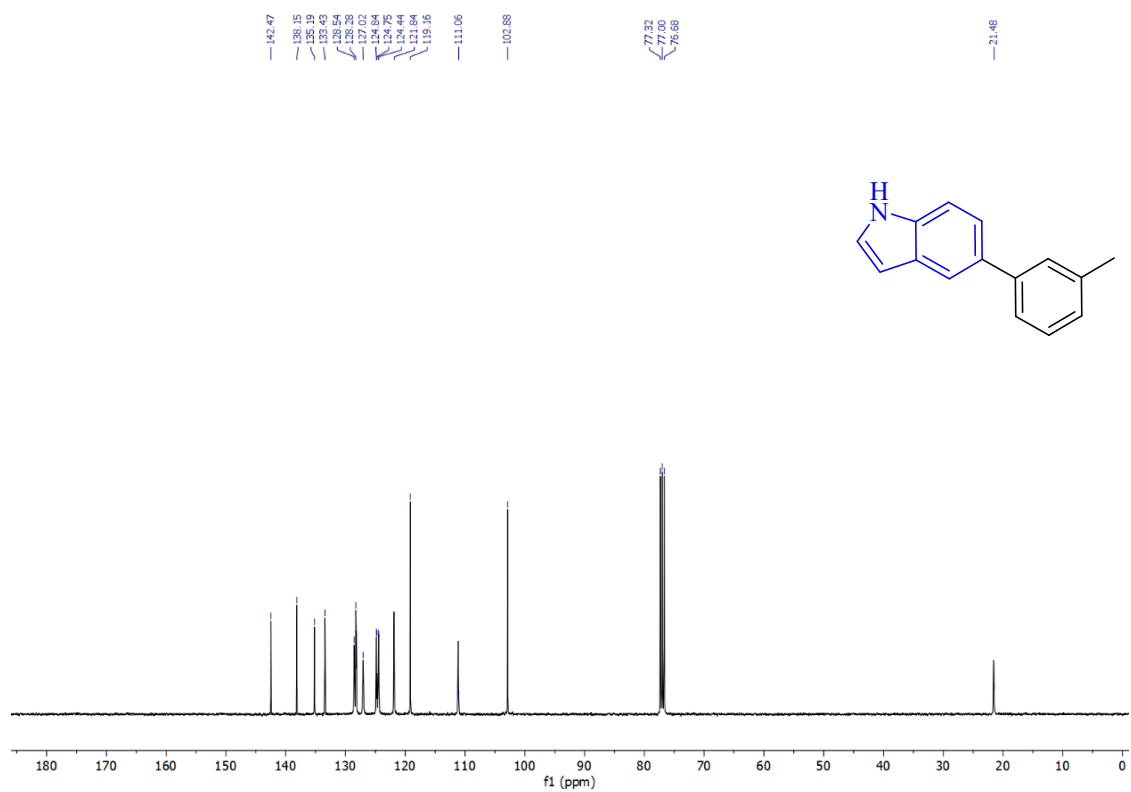


Fig. S24  $^{13}\text{C}$  NMR spectrum of 3j in  $\text{CDCl}_3$



**Fig. S25** <sup>1</sup>H NMR spectrum of 3k in CDCl<sub>3</sub>



**Fig. S26** <sup>13</sup>C NMR spectrum of 3k in CDCl<sub>3</sub>

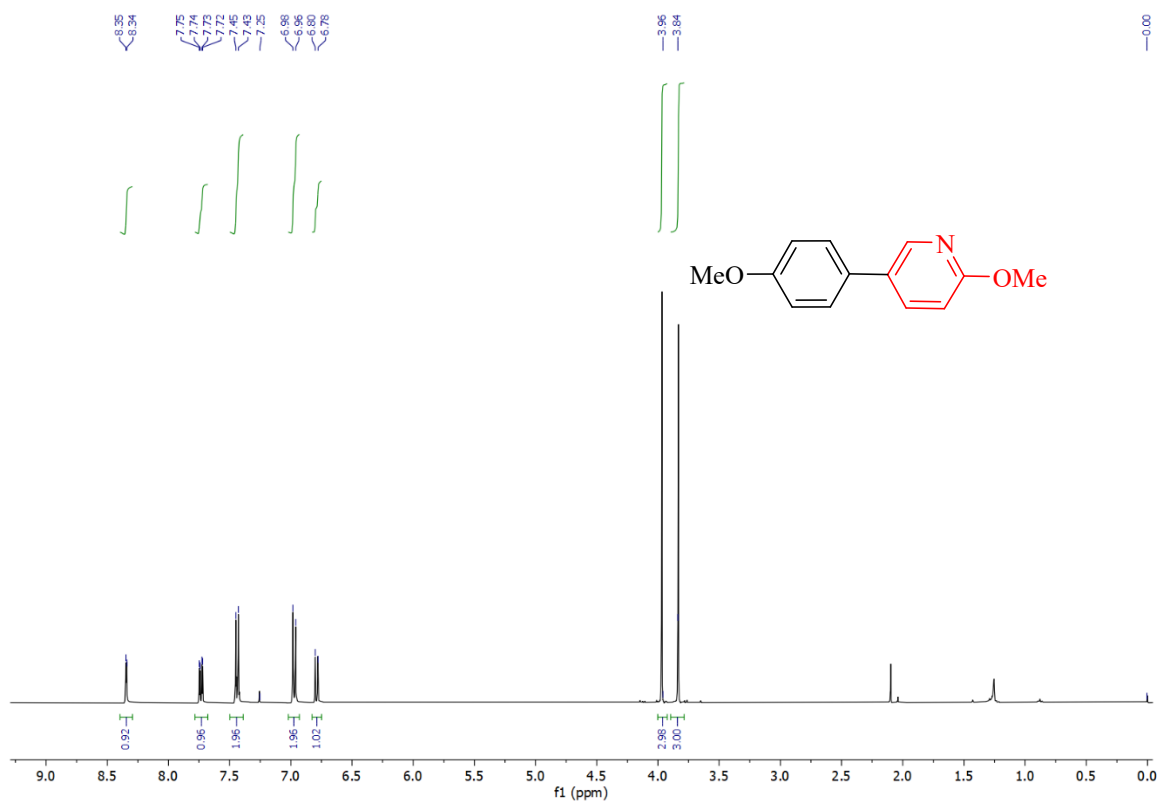


Fig. S27 <sup>1</sup>H NMR spectrum of 3n in CDCl<sub>3</sub>

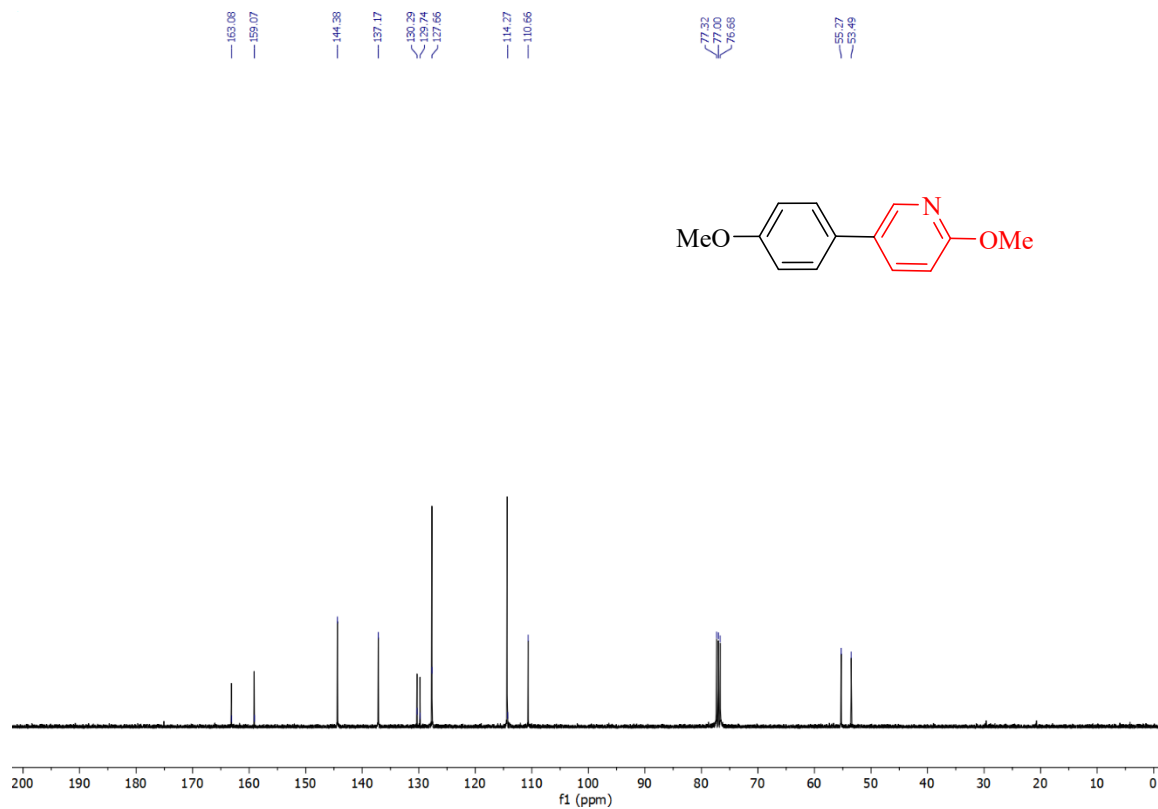


Fig. S28 <sup>13</sup>C NMR spectrum of 3n in CDCl<sub>3</sub>

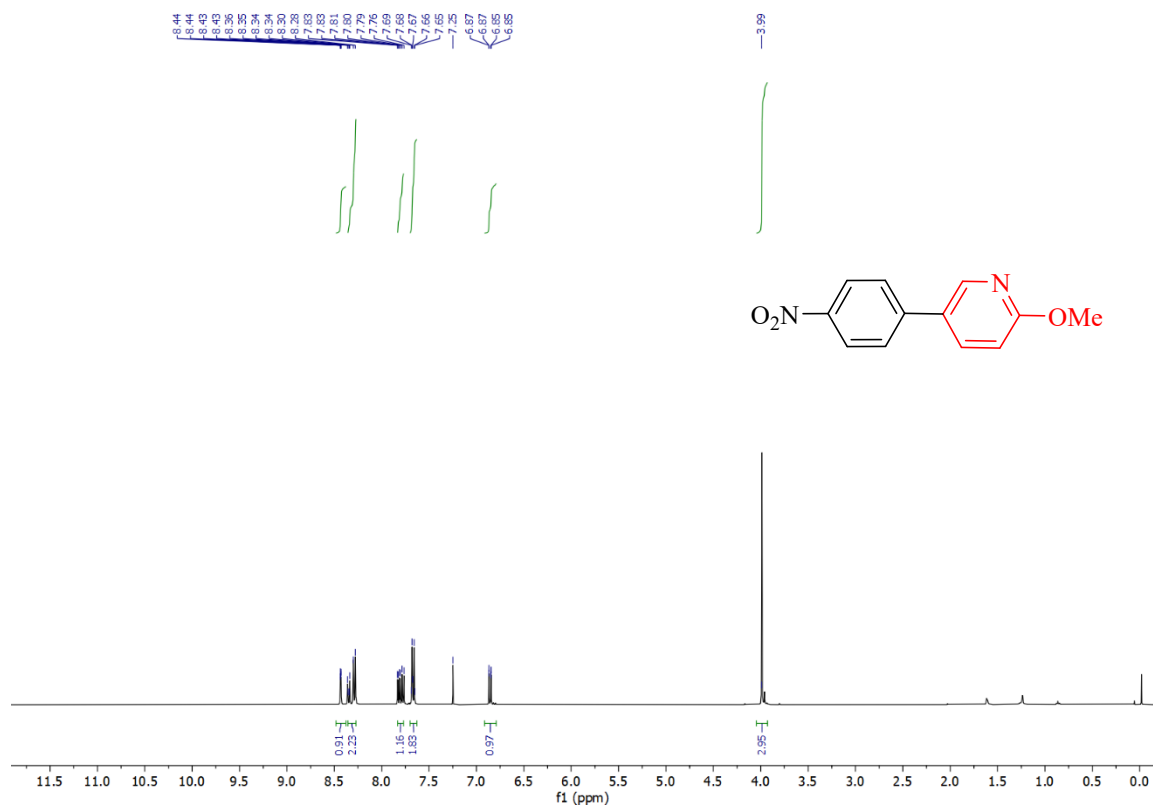


Fig. S29 <sup>1</sup>H NMR spectrum of 3o in CDCl<sub>3</sub>

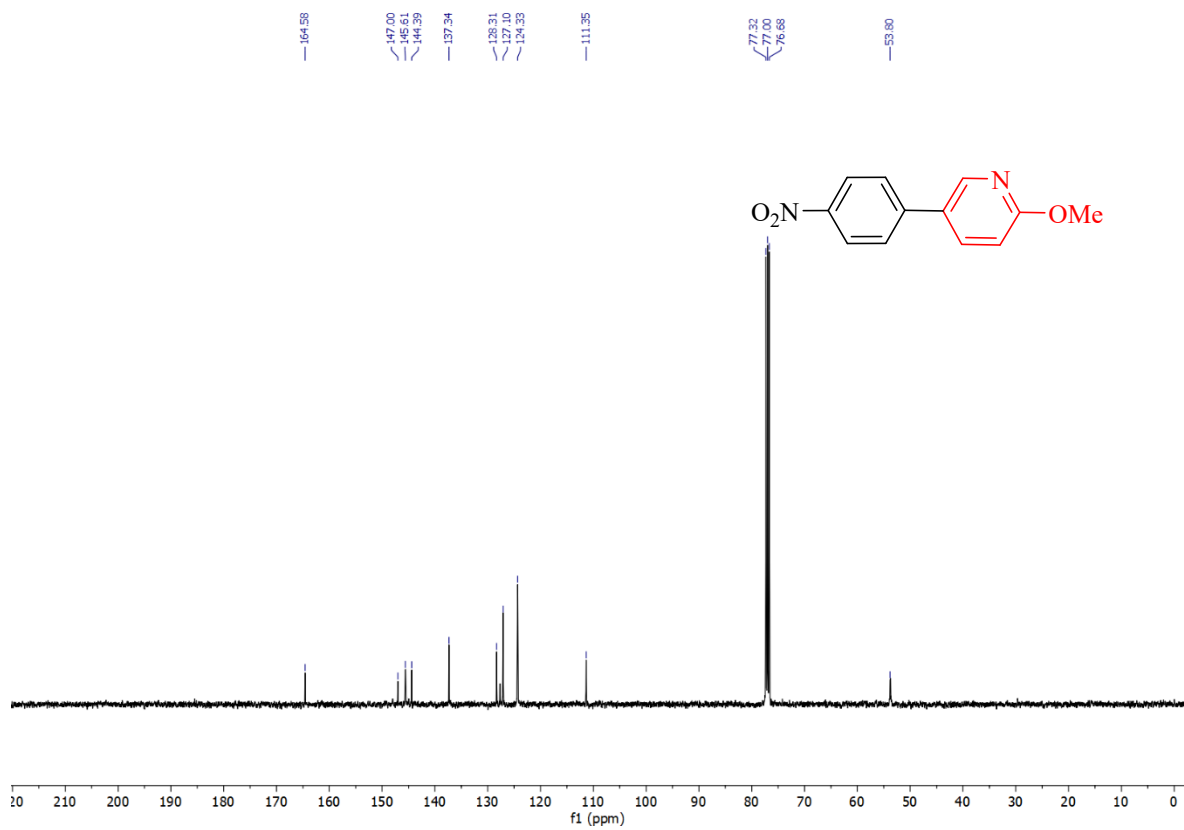


Fig. S30 <sup>13</sup>C NMR spectrum of 3o in CDCl<sub>3</sub>

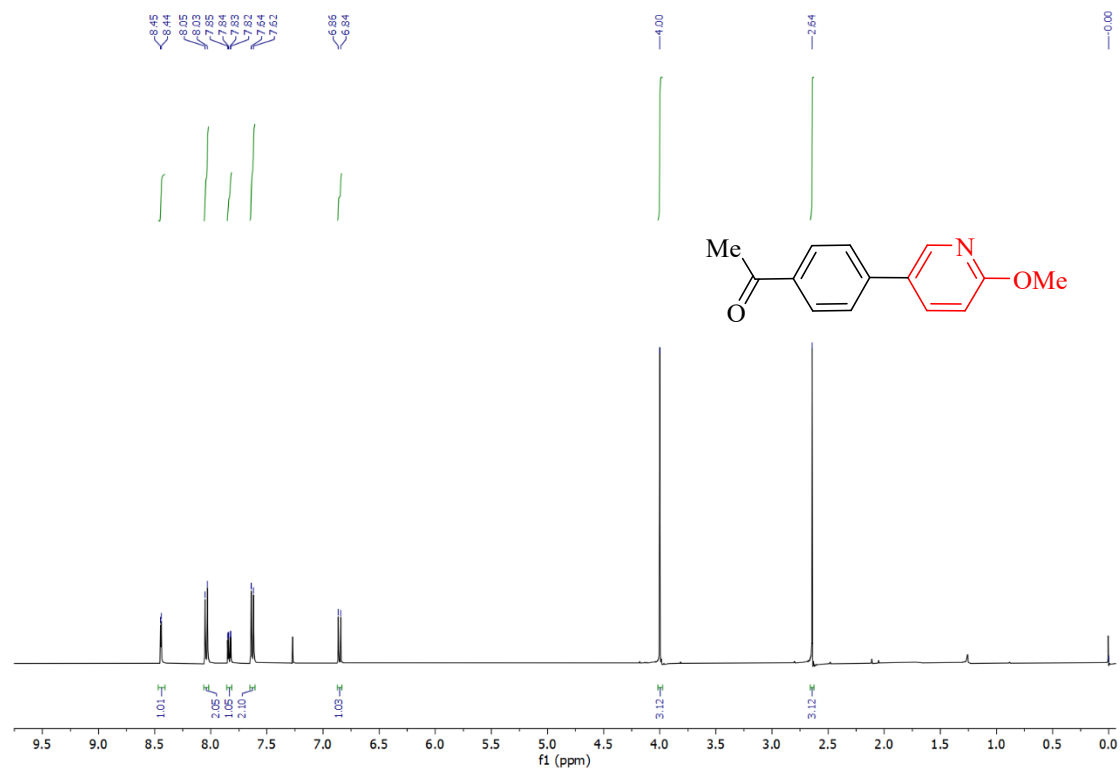


Fig. S31  $^1\text{H}$  NMR spectrum of 3p in  $\text{CDCl}_3$

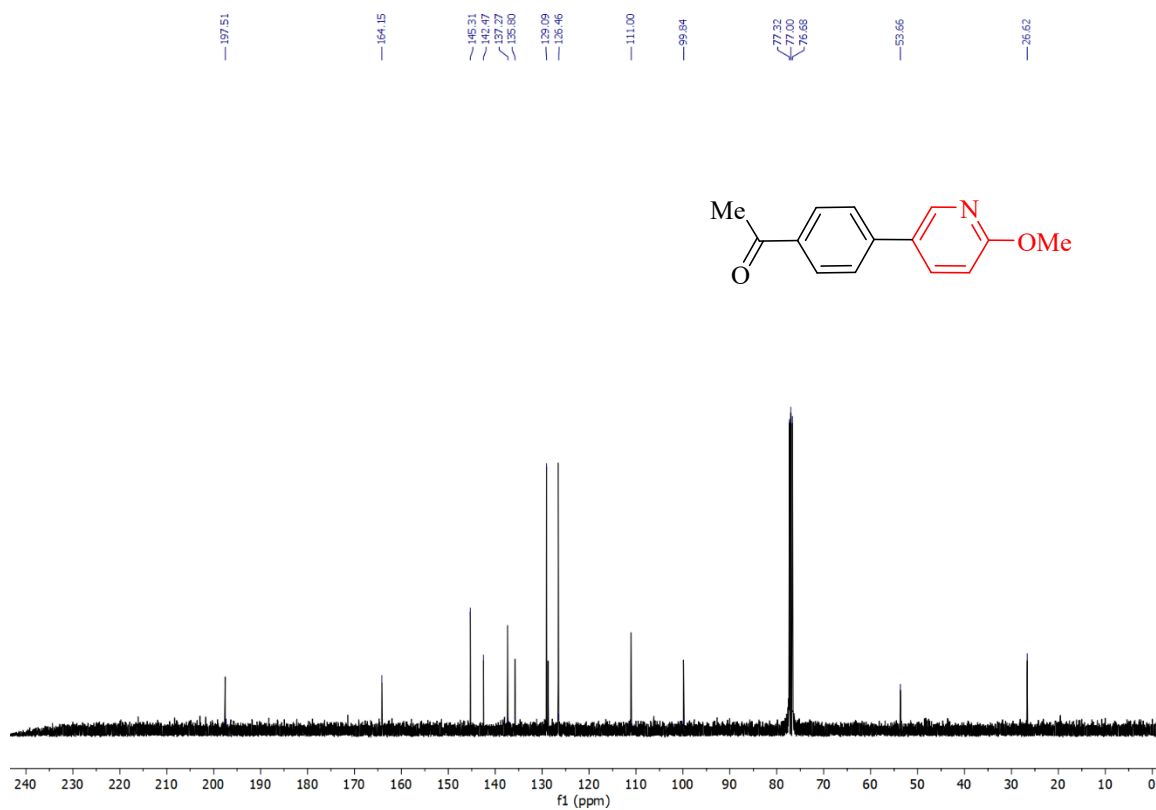


Fig. S32  $^{13}\text{C}$  NMR spectrum of 3p in  $\text{CDCl}_3$





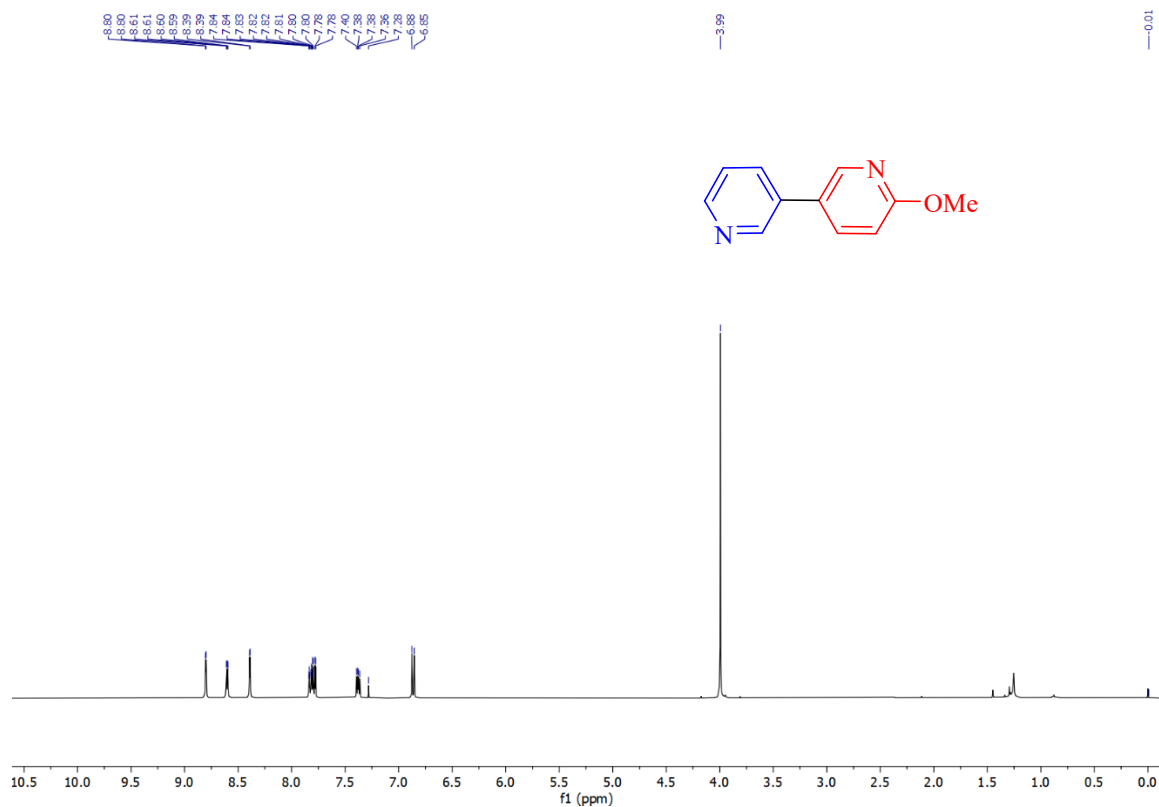


Fig. S35 <sup>1</sup>H NMR spectrum of 3s in CDCl<sub>3</sub>

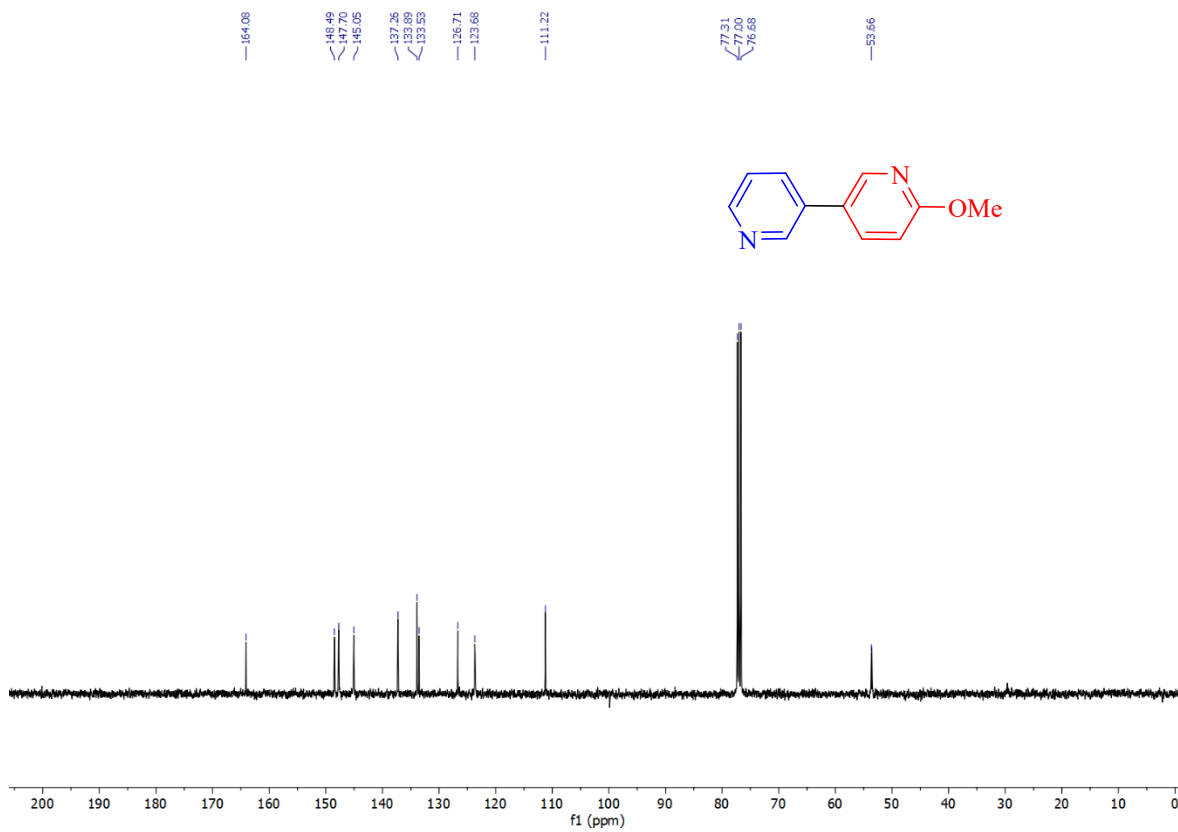


Fig. S36 <sup>13</sup>C NMR spectrum of 3s in CDCl<sub>3</sub>

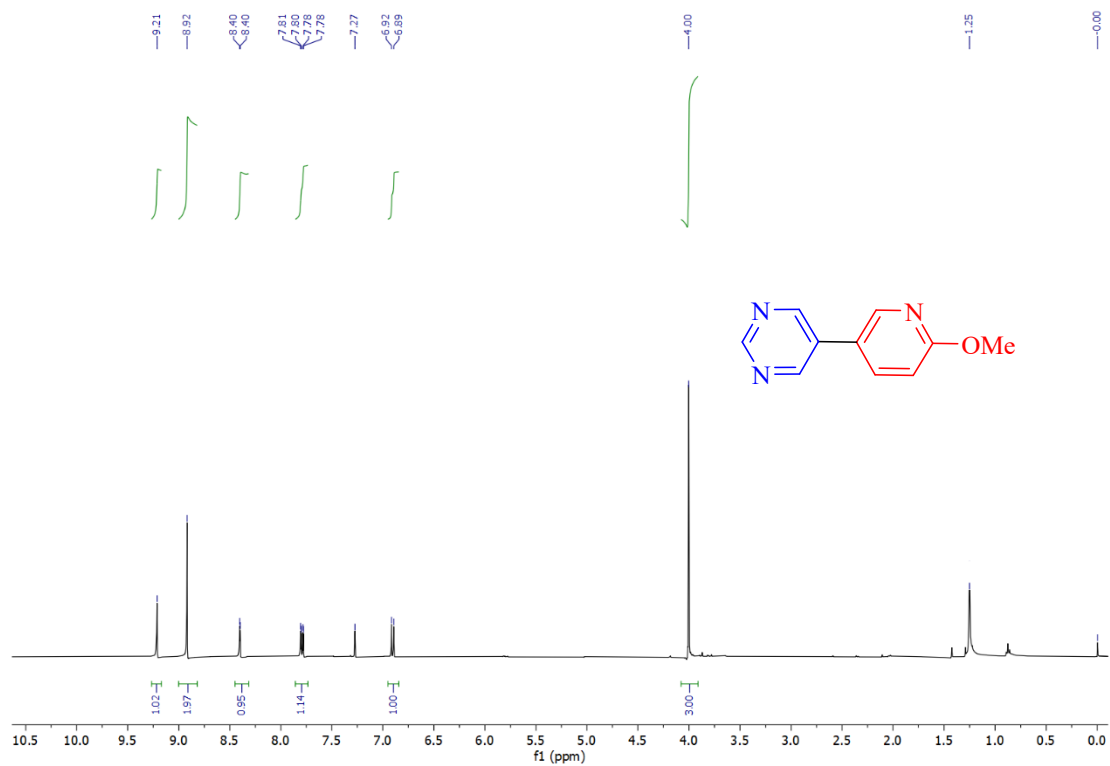


Fig. S37  $^1\text{H}$  NMR spectrum of 3t in  $\text{CDCl}_3$

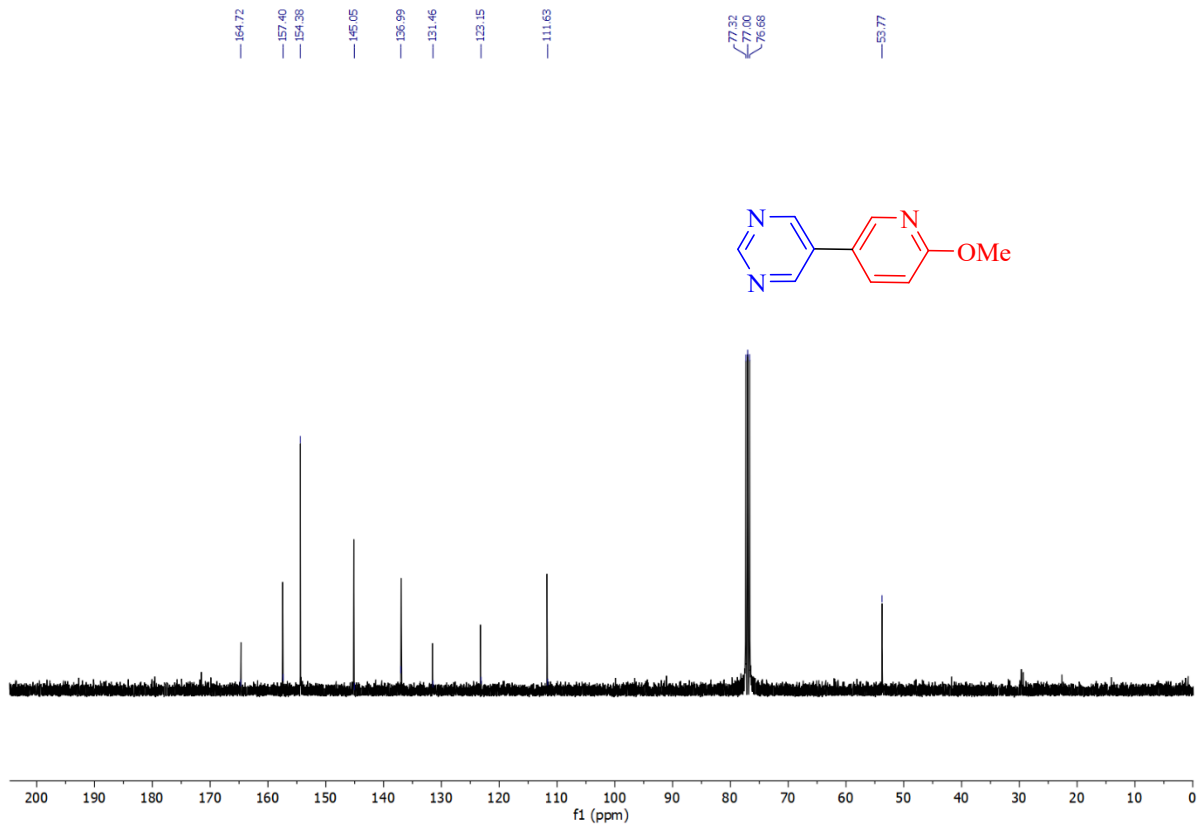
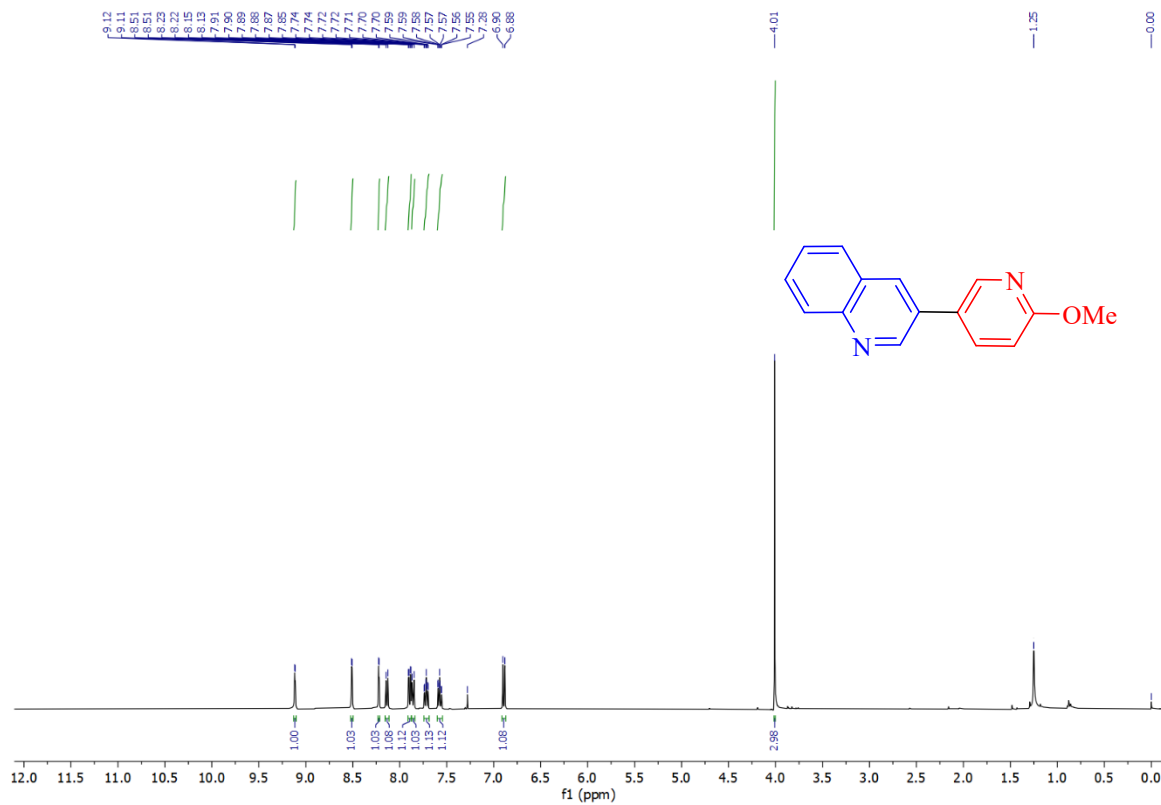
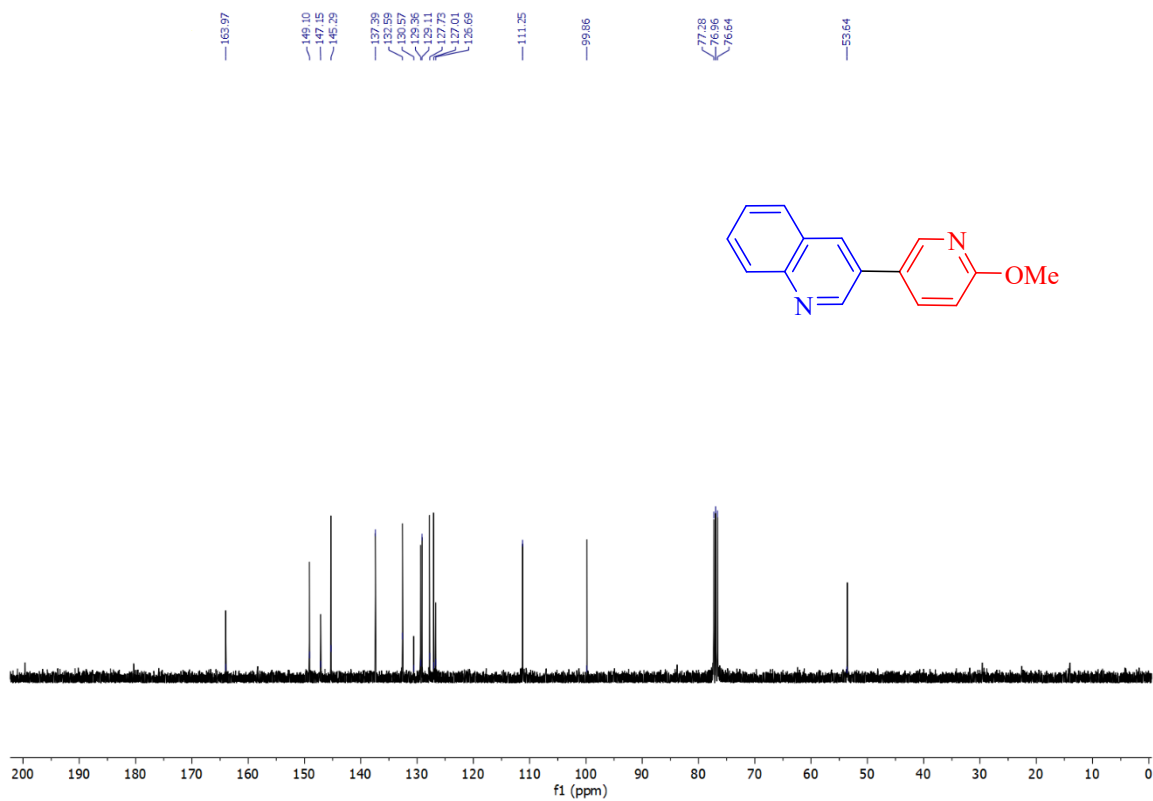


Fig. S38  $^{13}\text{C}$  NMR spectrum of 3t in  $\text{CDCl}_3$



**Fig. S39** <sup>1</sup>H NMR spectrum of 3u in CDCl<sub>3</sub>



**Fig. S40** <sup>13</sup>C NMR spectrum of 3u in CDCl<sub>3</sub>

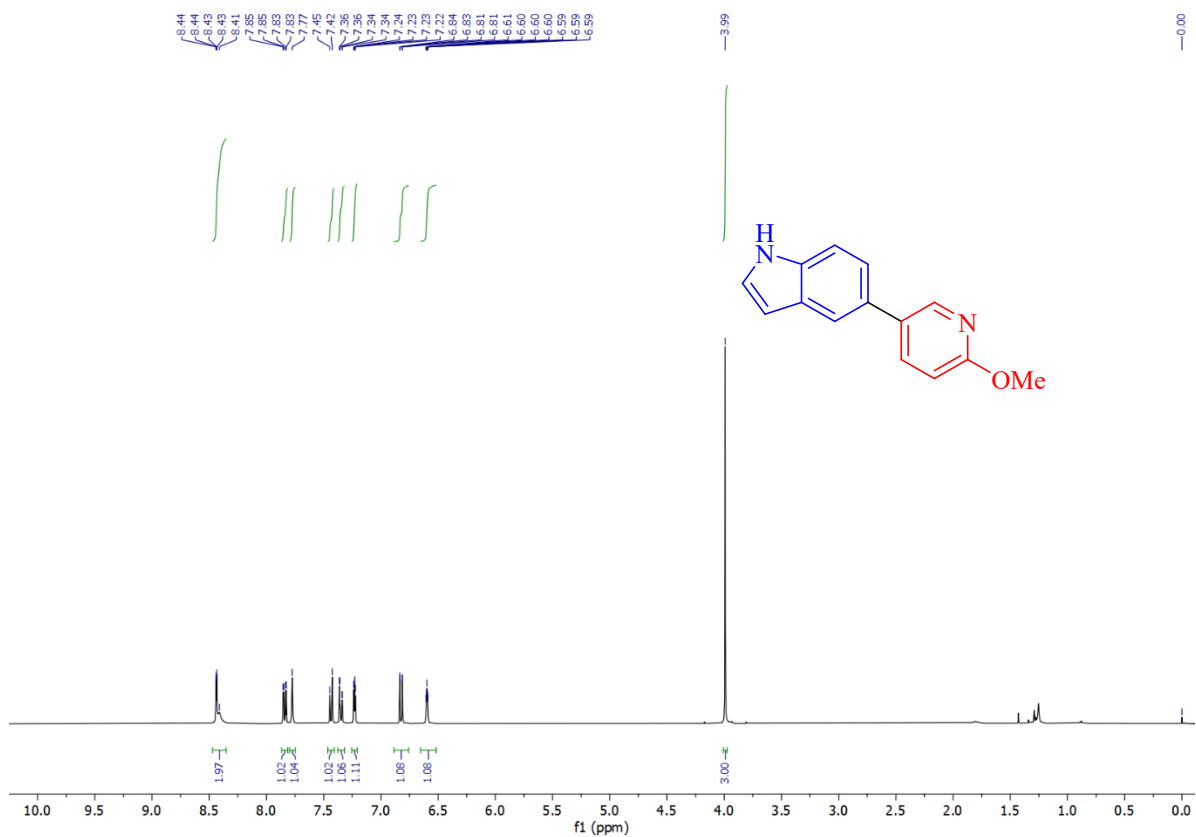


Fig. S41  $^1\text{H NMR}$  spectrum of 3v in  $\text{CDCl}_3$

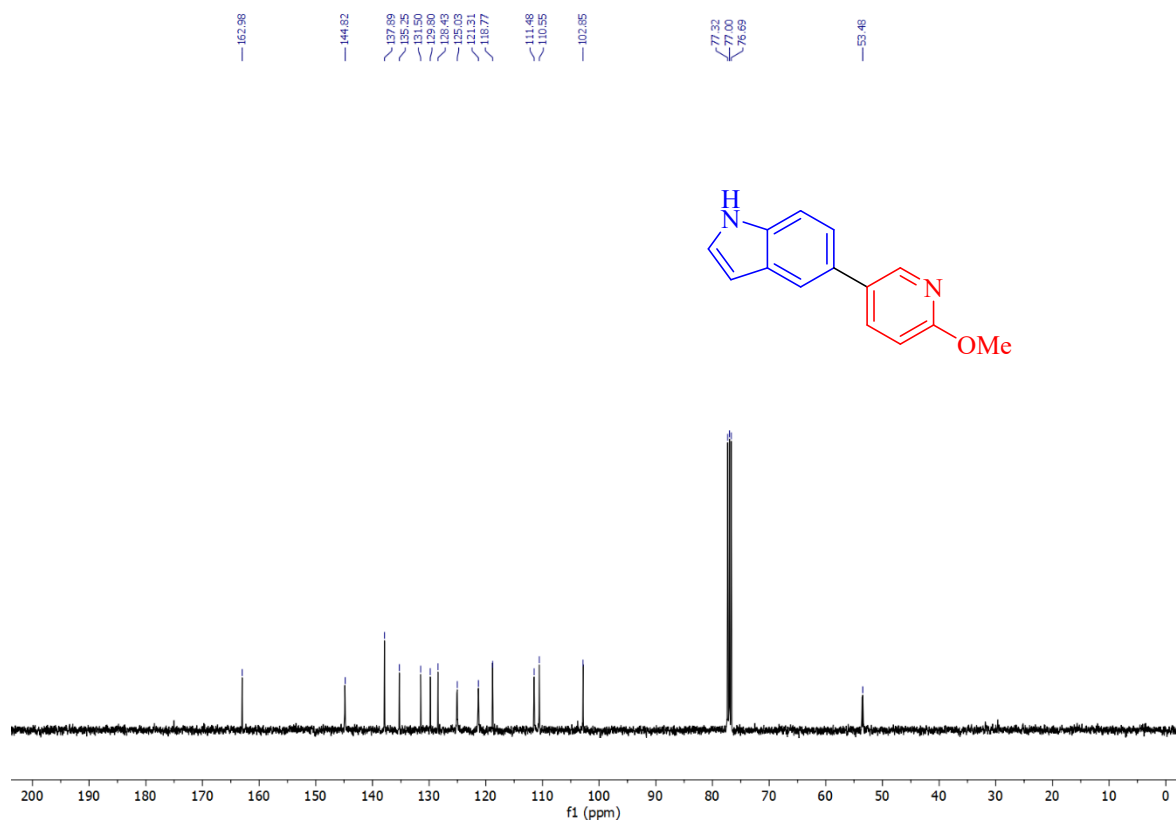


Fig. S42  $^{13}\text{C NMR}$  spectrum of 3v in  $\text{CDCl}_3$

## 7. References

1. C. Liu, Q. Ni, F. Bao and J. Qiu, *Green Chem.*, 2011, **13**, 1260-1266.
2. S. Shi and Y. Zhang, *Green Chem.*, 2008, **10**, 868-872.
3. A. Dewan, M. Sarmah, P. Bharali, A. J. Thakur, P. K. Boruah, M. R. Das and U. Bora, *ACS Sustainable Chem. Eng.*, 2021, **9**, 954-966.
4. G. K. Rao, A. Kumar, J. Ahmed and A. K. Singh, *Chem. Commun.*, 2010, **46**, 5954-5956.
5. Y. Kitamura, S. Sako, T. Udzu, A. Tsutsui, T. Maegawa, Y. Monguchi and H. Sajiki, *Chem. Commun.*, 2007, **47**, 5069-5071.