

**Boosting the activity of Mizoroki-Heck cross-coupling reactions  
with a supramolecular palladium catalyst favouring remote  
Zn $\cdots$ pyridine interactions**

**Naba Abuhafez and Rafael Gramage-Doria**

e-mail: [rafael.gramage-doria@univ-rennes1.fr](mailto:rafael.gramage-doria@univ-rennes1.fr)

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## 1. General methods.

Solvents were purified with an MB SPS-800 purification system or dried with  $\text{CaH}_2$  and distilled prior to use.  $\text{CDCl}_3$  was filtered through alumina and stored under argon over molecular sieves. All chemicals were purchased from commercial sources and used as received. Unless otherwise specified, reactions were carried out under argon atmosphere by employing standard Schlenk and vacuum-line techniques.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker GPX (400 MHz) spectrometer.  $^1\text{H}$  NMR spectra were referenced to residual protiated solvent ( $\delta = 7.26$  ppm for  $\text{CDCl}_3$ ).  $^{13}\text{C}$  NMR spectra were referenced to  $\text{CDCl}_3$  ( $\delta = 77.00$  ppm). Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; q, quadruplet; p, pentuplet; hept, heptuplet; m, multiplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; tt, triplet of triplets; tdd, doublet of doublet of triplets. Coupling constants,  $J$ , were reported in hertz unit (Hz). The reactions were monitored by using a Shimadzu 2014 gas chromatograph equipped with an Equity<sup>TM</sup>-1 Fused Silica capillary column (30 m x 0.25 mm x 0.25  $\mu\text{m}$ ) and an FID detector. Purifications were done by combiflash nextgen 300 teledyne flash chromatography.

## 2. Synthesis of the supramolecular ligand L.

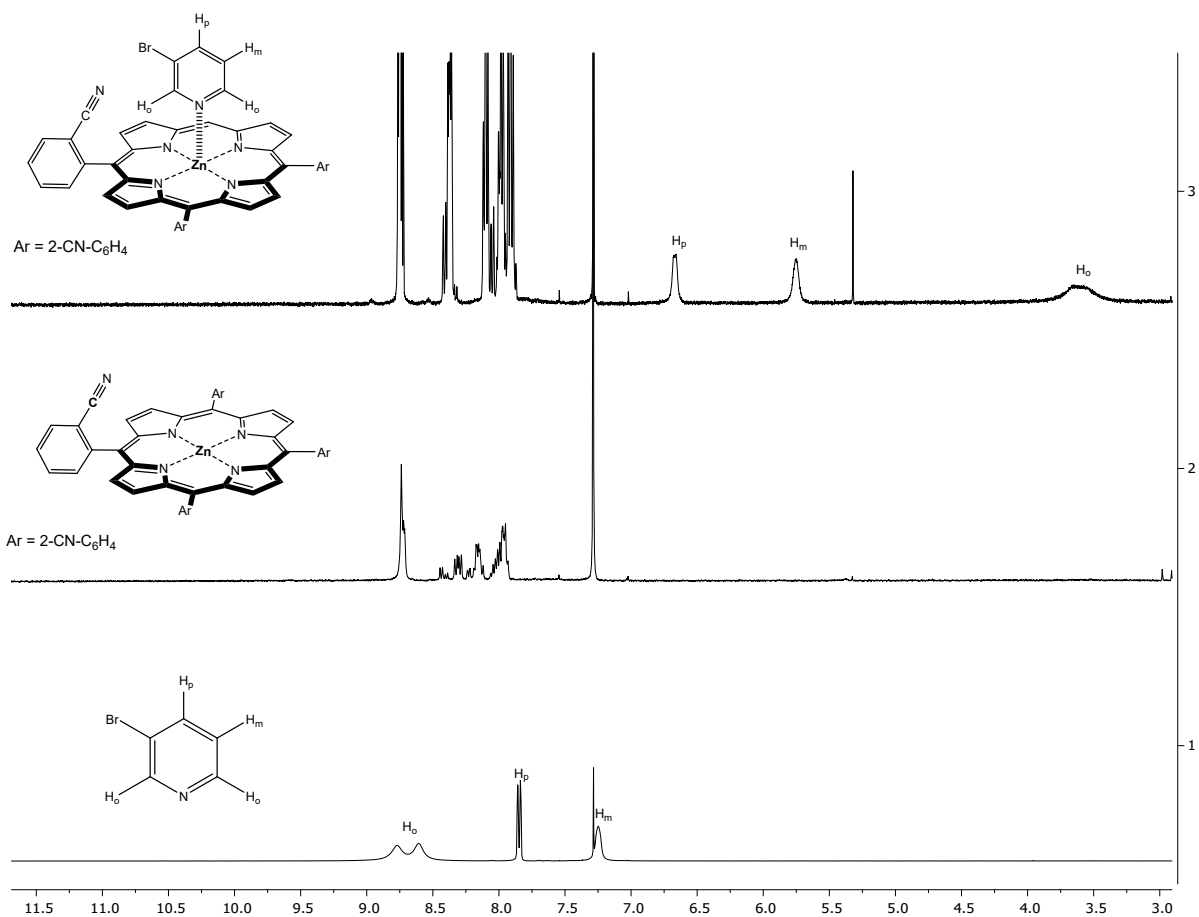
With exclusion of light, 2-cyanobenzaldehyde (1.89 g, 14 mmol) was dissolved in propionic acid (100 mL) and the mixture heated to reflux. Pyrrole (1.0 mL, 14 mmol) was added and the thus-obtained dark mixture was further heated at reflux for 2 h. The solvent was removed by vacuum distillation and the crude product was purified by chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$  as eluent). The fraction containing the porphyrin was evaporated to dryness and crystallized from  $\text{CH}_2\text{Cl}_2$ /heptane to give free-base porphyrin as a dark violet solid (121 mg, 4.7 %). In air atmosphere, the free-base porphyrin (0.16 mmol) and  $\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$  (140 mg, 0.64 mmol) were dissolved in  $\text{CHCl}_3$ /MeOH (4:1, 25 mL). The mixture was heated to reflux for 2 h, after which no free-base porphyrin was detected by TLC analysis, and evaporated to dryness. The crude reaction mixture was filtered through a short pad of alumina with  $\text{CH}_2\text{Cl}_2$  as eluent. The fraction containing L evaporated to dryness. The NMR data is in agreement with the literature.<sup>1</sup>

### 3. NMR experiments.

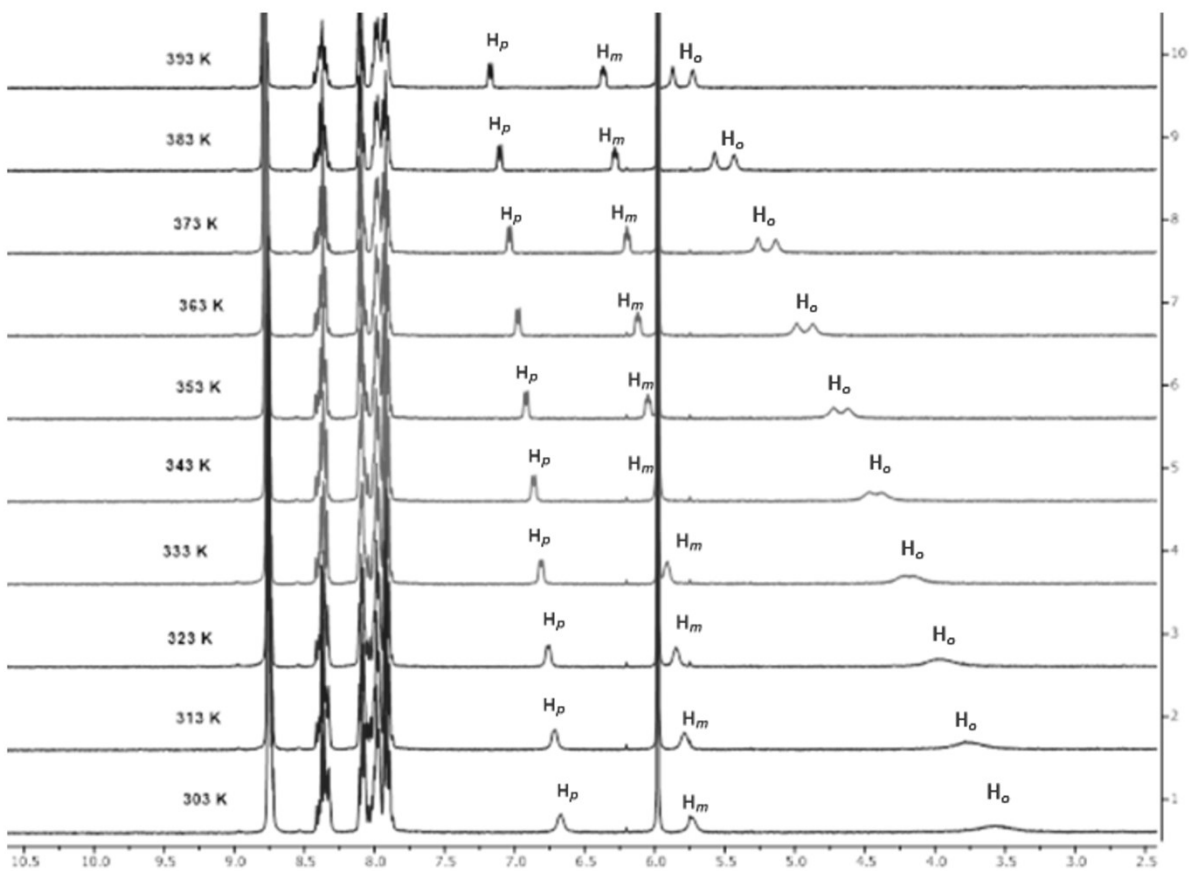
All experiments were performed in a dried NMR tube.

- For experiments described in *Section 3.1* and *3.2.*, **L** ( $2.3 \times 10^{-3}$  mmol) was dissolved in deuterated solvent (1.0 mL). A  $2.3 \times 10^{-2}$  M solution of **1a** and **2a** in deuterated solvent  $\text{CDCl}_3$  were added and a  $^1\text{H}$  NMR spectrum was recorded at room temperature.
- The competition experiment in *Section 3.3.* between **1a** and **2a** for **L** coordination was performed by dissolving an equimolar amount of **L** and **1a** ( $2.3 \times 10^{-3}$  mmol) in 1,1,2,2-tetrachloroethane- $d_2$  (0.6 mL) and by adding **2a** ( $2.3 \times 10^{-3}$  mmol).  $^1\text{H}$  NMR spectra were before and after **2a** addition.

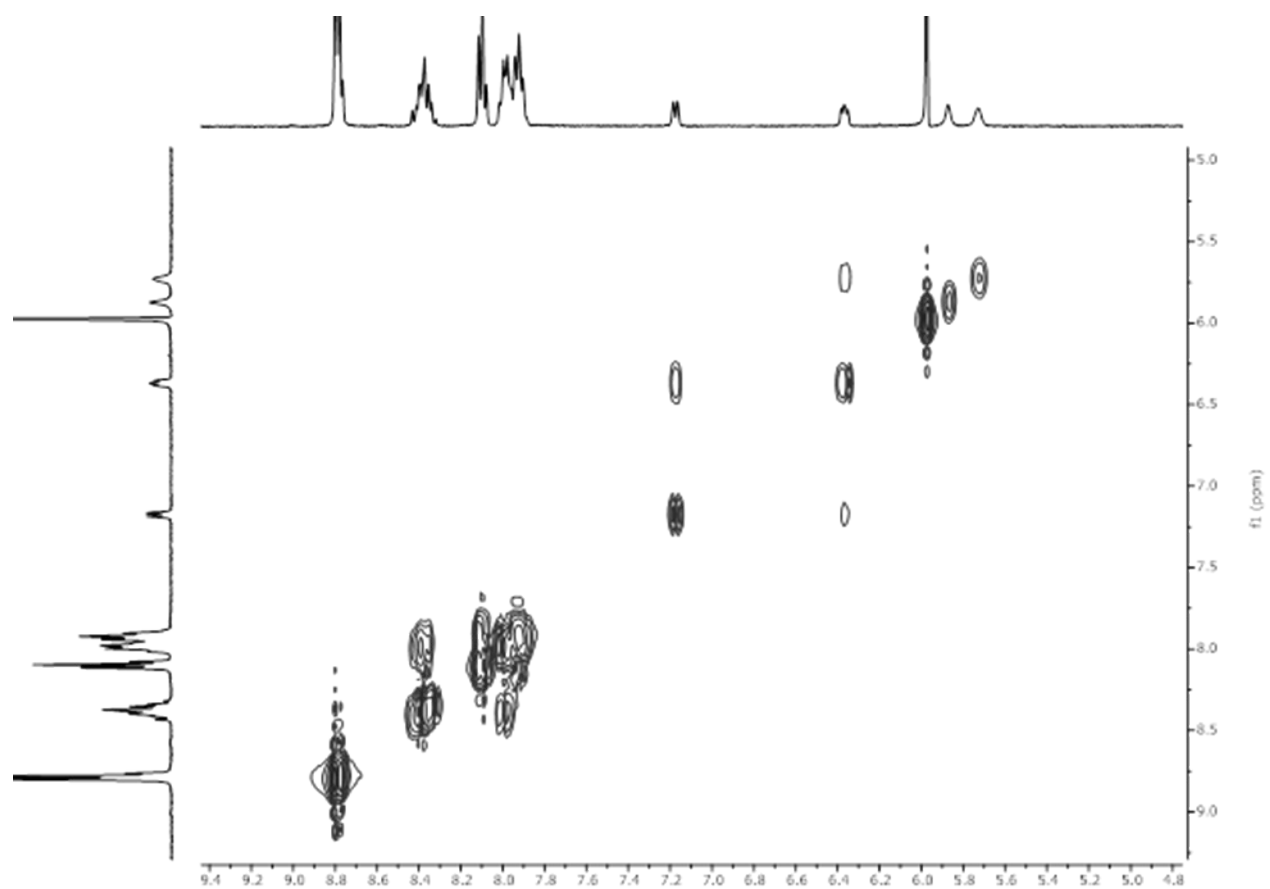
### 3.1. NMR binding experiment between L and 1 (1:1 ratio).



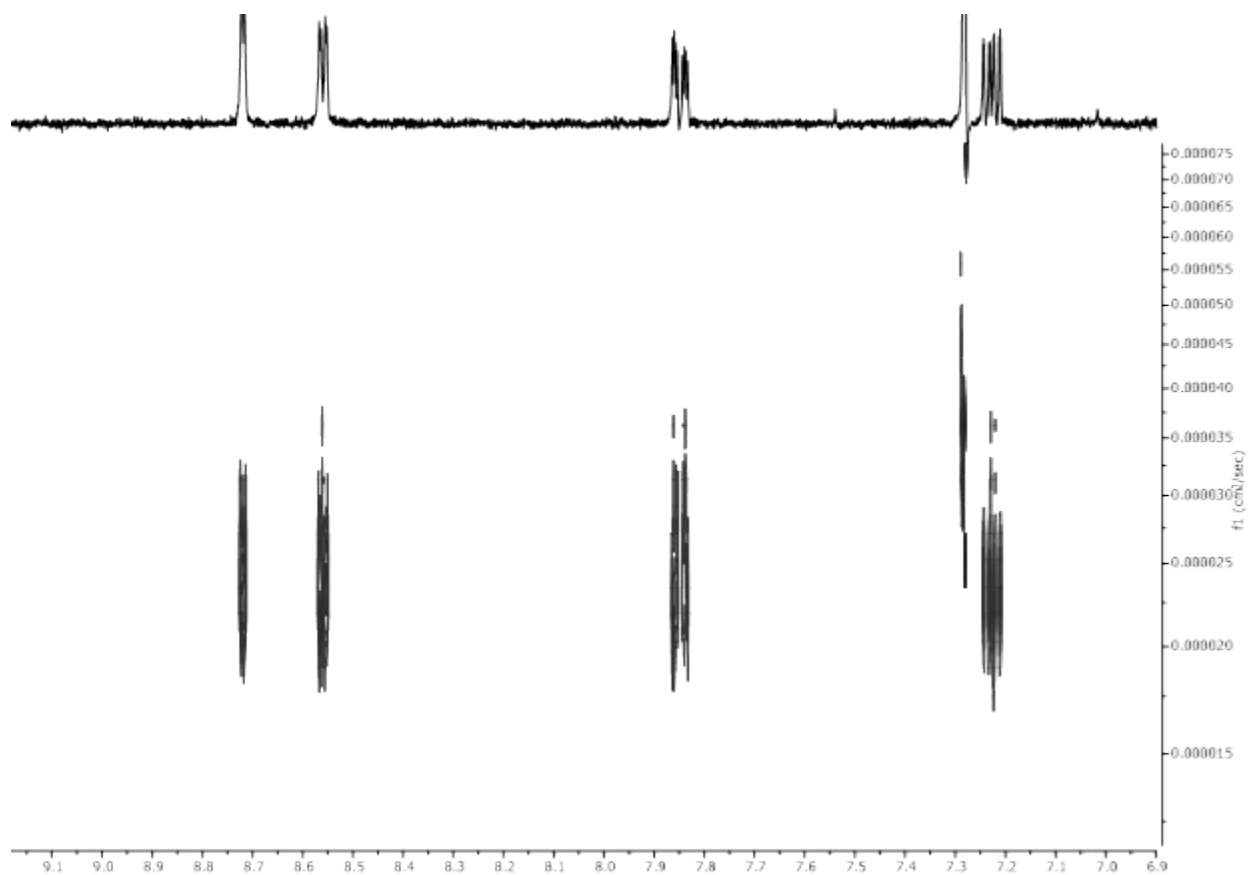
**Figure S1.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectra of pure 3-bromopyridine **1** (bottom), **L** (middle) and self-assembly  $[\text{L} \subset \text{1}]$  in an equimolar ratio (top).



**Figure S2.** Variable high-temperature <sup>1</sup>H NMR (1,1,2,2-tetrachloroethane-*d*<sub>2</sub>, 400 MHz) spectra of **1** and **L** in an equimolar ratio in the range 30-120 °C (bottom to top).

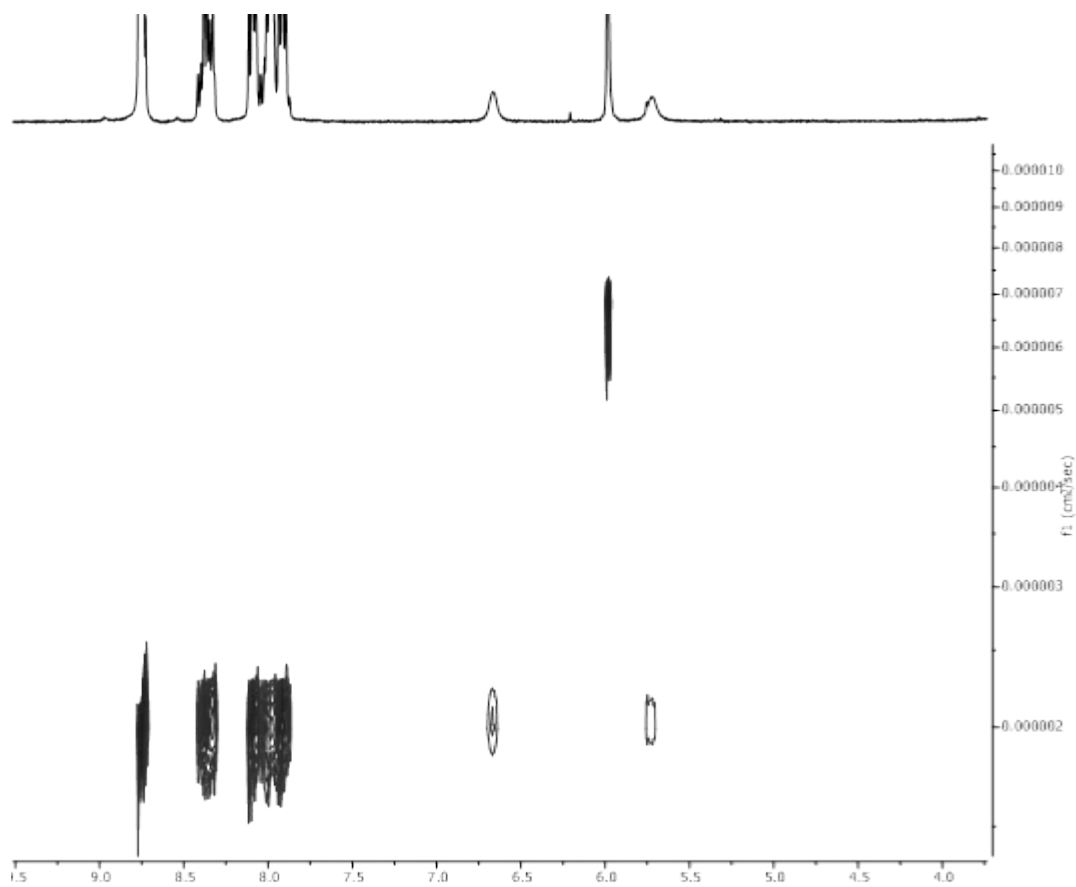


**Figure S3.**  $^1\text{H}$ - $^1\text{H}$  COSY (1,1,2,2-tetrachloroethane- $d_2$ , 400 MHz) experiment of **1** and **L** combined in equimolar ratio.



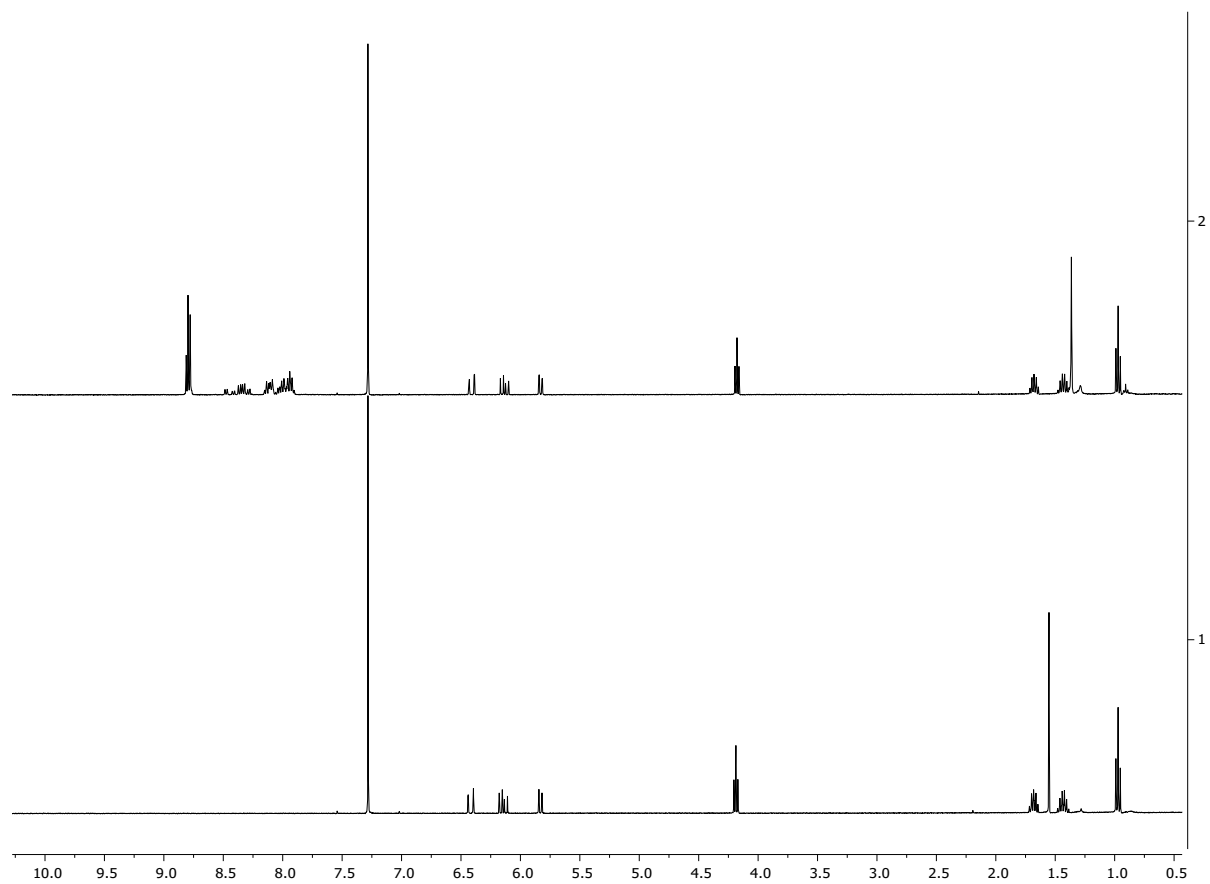
**Figure S4.** DOSY (1,1,2,2-tetrachloroethane-d<sub>2</sub>, 400 MHz) experiment of pure **1**.



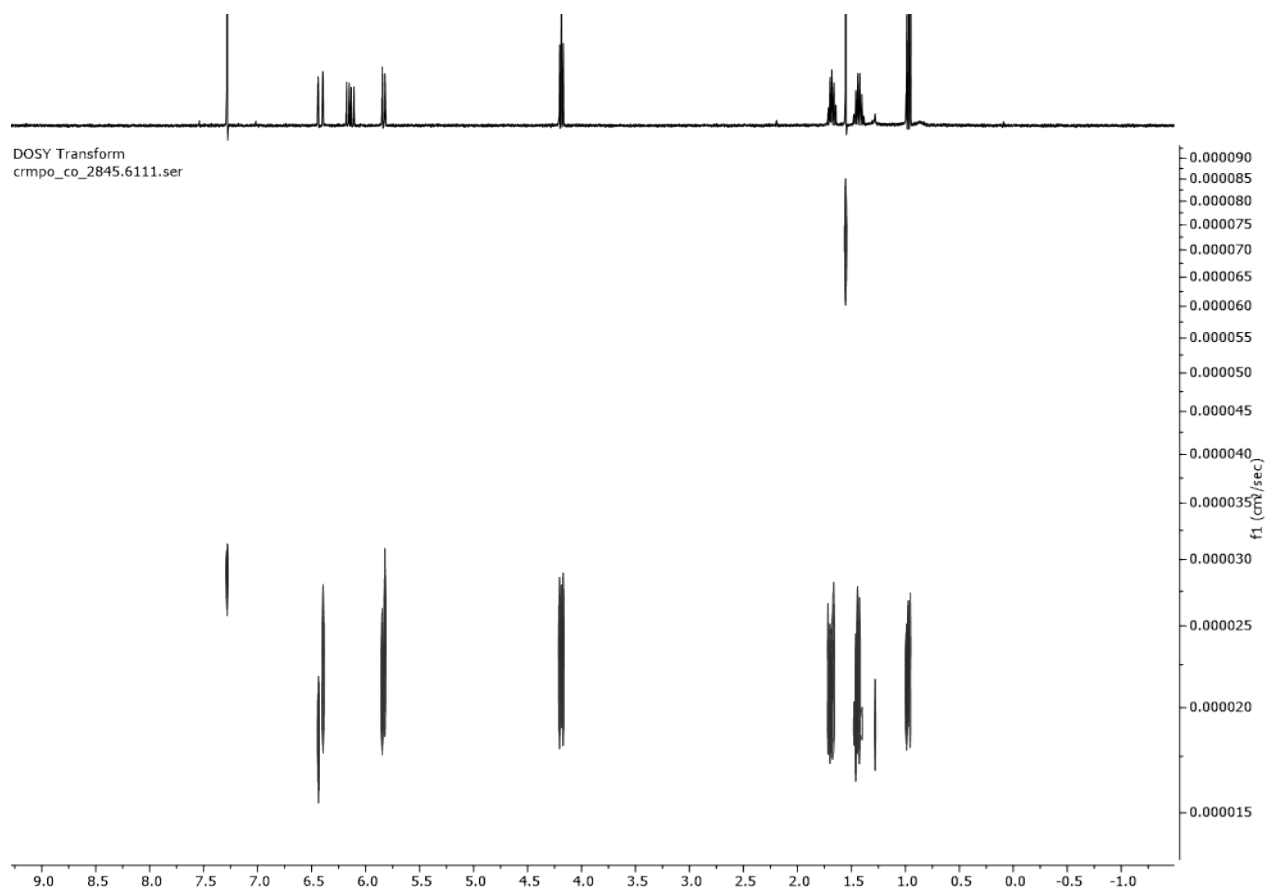


**Figure S5.** DOSY (1,1,2,2-tetrachloroethane- $d_2$ , 400 MHz) experiment of **1** and **L** combined in equimolar ratio.

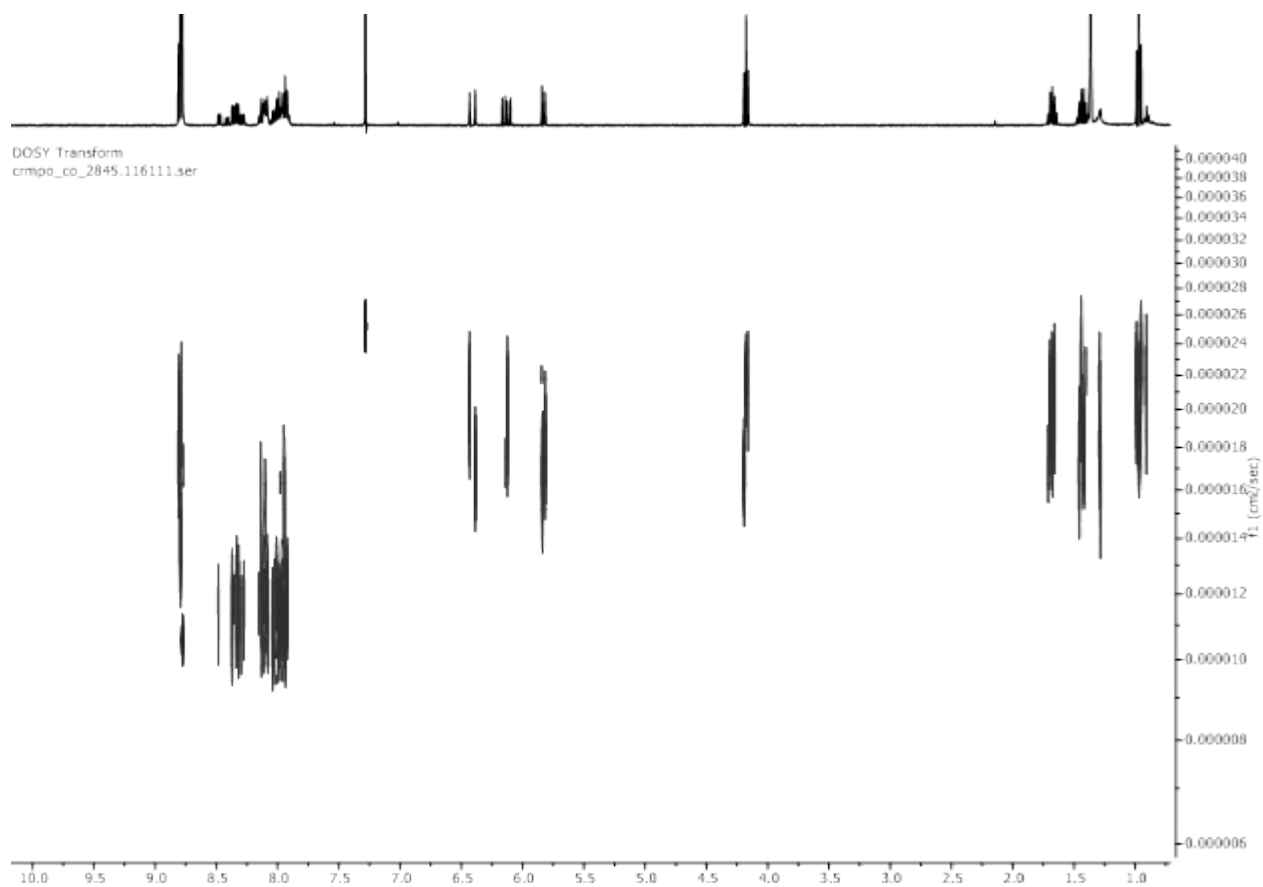
### 3.2. NMR binding experiment between L and butylacrylate (1:1 ratio).



**Figure S6.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) spectra of 1.0 equivalent of **2a** combined with **L** solution (top) and pure **2a** (bottom).

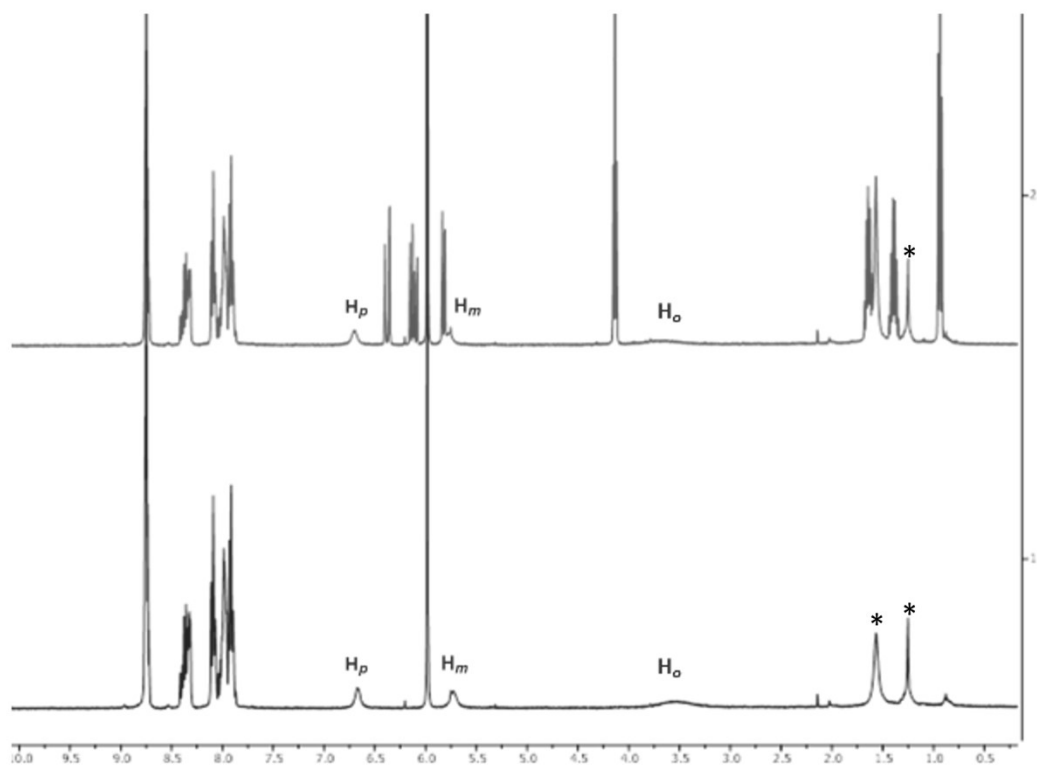


**Figure S7.** DOSY (CDCl<sub>3</sub>, 400 MHz) experiment of pure **2a**.

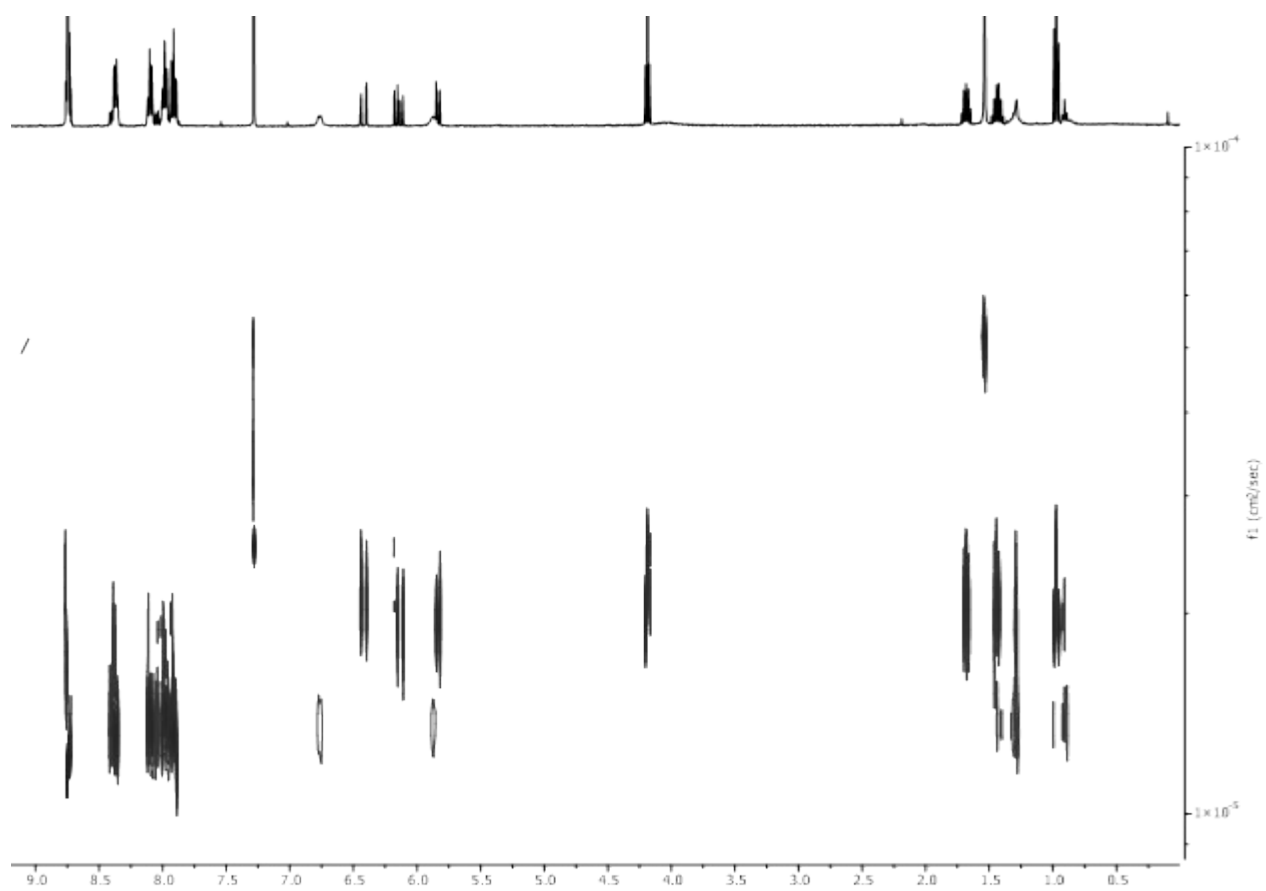


**Figure S8.** DOSY (CDCl<sub>3</sub>, 400 MHz) experiment of **2a** and **L** combined in equimolar ratio.

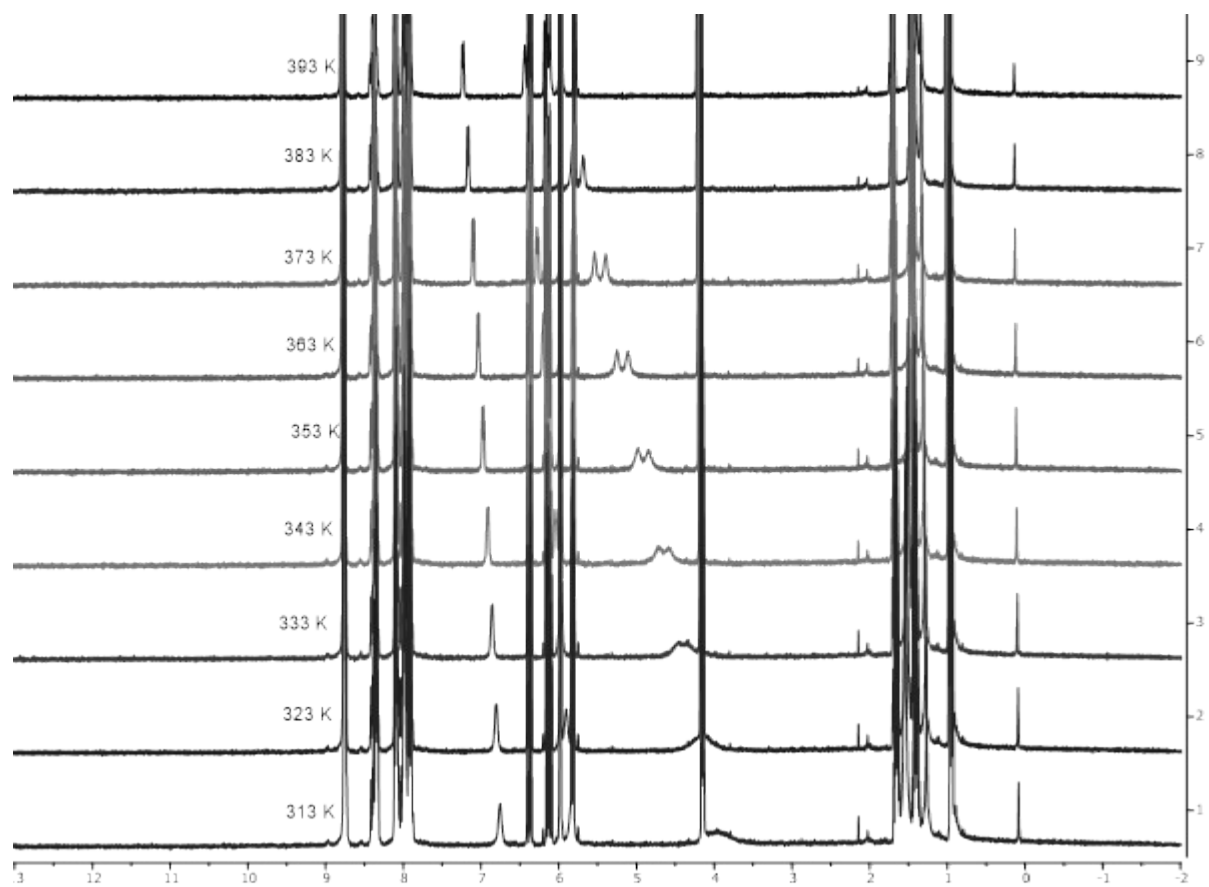
### 3.3. Competition experiment between 1a and 2a for coordination to L.



**Figure S9.** <sup>1</sup>H NMR (1,1,2,2-tetrachloroethane-*d*<sub>2</sub>, 400 MHz) spectra of 1.0 equivalent of **1** combined with 1.0 equivalent **L** solution (bottom) and after addition of 1.0 equivalent of **2a** (top) at room temperature. Asterisks (\*) denote traces of solvents (water and heptane).



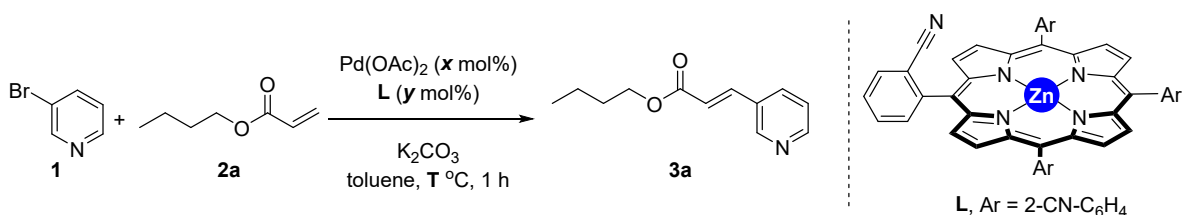
**Figure S10.** DOSY ( $\text{CDCl}_3$ , 400 MHz) experiment of equimolar amounts of **1** : **2a** : **L** at room temperature.



**Figure S11.** Variable high-temperature  $^1\text{H}$  NMR (1,1,2,2-tetrachloroethane- $d_2$ , 400 MHz) spectra of equimolar amounts of **1** : **2a** : **L** in the range 40-120  $^\circ\text{C}$  (bottom to top).

#### 4. General procedure for heck cross-coupling reactions:

An overnight-dried Schlenk tube was filled, under an argon atmosphere, with 3-bromopyridine **1** (7.9 mg, 4.8  $\mu$ L, 0.05 mmol, 1 equiv.), butyl acrylate **2a** (19.2 mg, 21.6  $\mu$ L, 0.15 mmol, 3 equiv.), potassium carbonate (20.7 mg, 0.15 mmol, 3 equiv.), the supramolecular ligand **L** (7.8 mg, 0.01 mmol, 0.2 equiv.), Pd(OAc)<sub>2</sub> (1.12 mg, 0.005 mmol, 0.1 equiv.) and toluene (1 mL). After 5 min stirring at room temperature the mixture was placed in a preheated oil bath at 130 °C and stirred for one hour. The reaction mixture was cooled down to room temperature and further analyzed



by GC-MS.

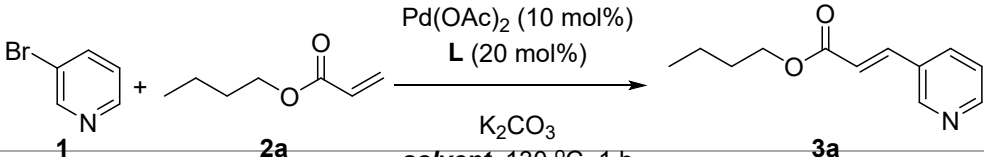
**Table S1.** Reaction optimization.

entry	Pd(OAc) <sub>2</sub> ( <i>x</i> mol%)	L ( <i>y</i> mol%)	Base	Temperature (°C)	Yield of <b>3a</b> (%)
1	5	10	K <sub>2</sub> CO <sub>3</sub>	130	50
2	5	10	DIPEA	130	5
3	5	10	CsCO <sub>3</sub>	130	12
4	5	10	tBuOK	130	-
5	5	10	NaOAc	130	5
6	5	10	2,6-lutidine	130	7
7	5	10	K <sub>2</sub> CO <sub>3</sub>	80	21
8	5	10	K <sub>2</sub> CO <sub>3</sub>	100	26
9	5	10	K <sub>2</sub> CO <sub>3</sub>	120	32
10	5	10	K <sub>2</sub> CO <sub>3</sub>	140	60
11	10	20	K <sub>2</sub> CO <sub>3</sub>	130	78



Table S2.

Study

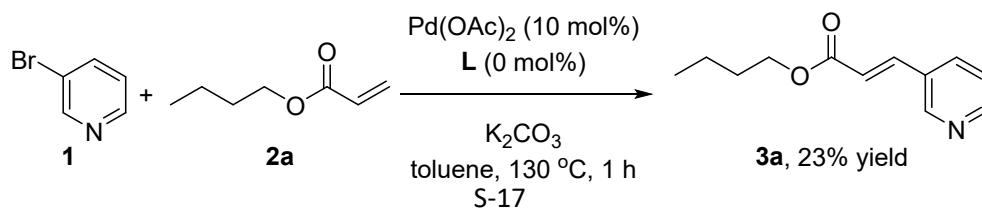


Entry	toluene:DMF	Yield of <b>3a</b> with L (%)	Yield of <b>3a</b> w/o L (%)	Relative Reactivity
1	100:0	50	10	6
2	80:20	30	10	3
3	70:30	34	16	2
4	50:50	90	70	1.3

concerning polarity of the solvent.

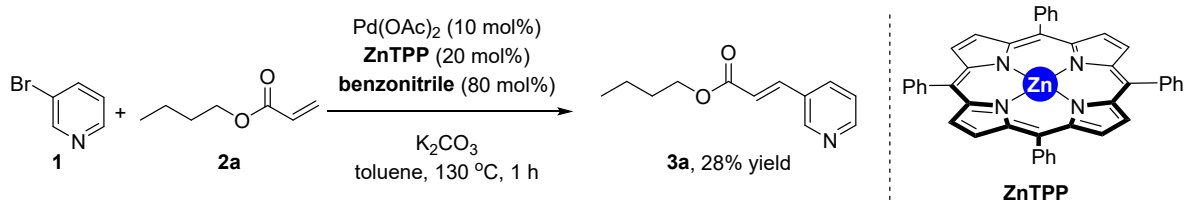
## 5. Control experiments.

**Control experiment without L:** An overnight-dried Schlenk tube was filled, under an argon atmosphere, with 3-bromopyridine **1** (7.9 mg, 4.8  $\mu$ L, 0.05 mmol, 1 equiv.), butyl acrylate **2a** (19.2 mg, 21.6  $\mu$ L, 0.15 mmol, 3 equiv.), potassium carbonate (20.7 mg, 0.15 mmol, 3 equiv.), Pd(OAc)<sub>2</sub> (1.12 mg, 0.005 mmol, 0.1 equiv.) and toluene (1 mL). After 5 min stirring at room temperature the mixture was placed in a preheated oil bath at 130 °C and stirred for one hour. The reaction mixture was cooled down to room temperature and further analyzed by GC-MS showing 23%



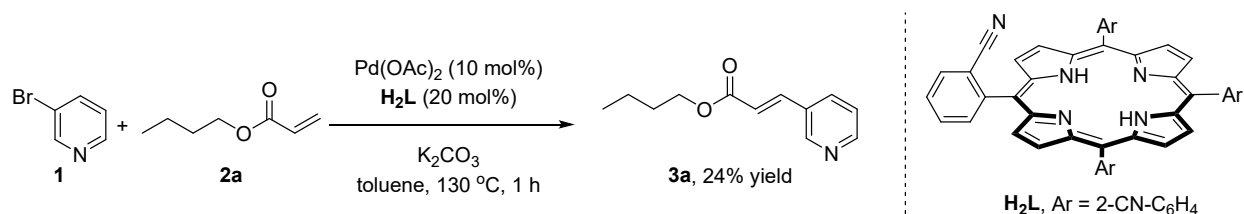
yield formation of **3a**.

**Control experiment with ZnTPP and benzonitrile:** An overnight-dried Schlenk tube was filled, under an argon atmosphere, with 3-bromopyridine **1** (7.9 mg, 4.8  $\mu$ L, 0.05 mmol, 1 equiv.), butyl acrylate **2a** (19.2 mg, 21.6  $\mu$ L, 0.15 mmol, 3 equiv.), potassium carbonate (20.7 mg, 0.15 mmol, 3 equiv.), zinc(II)tetraphenylporphyrin (6.78 mg, 0.010 mmol, 0.2 equiv.), benzonitrile (4.12 mg, 4.1



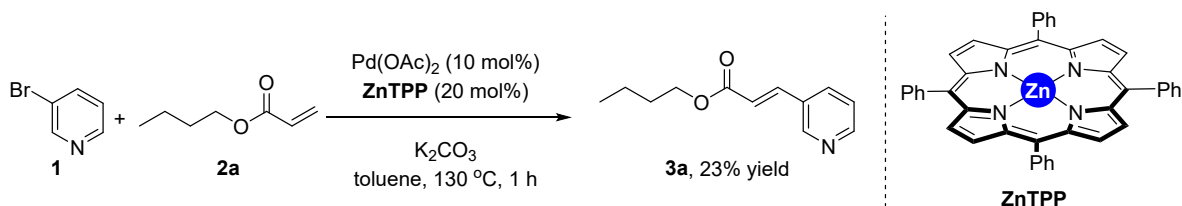
$\mu$ L, 0.040 mmol, 0.8 equiv.), Pd(OAc)<sub>2</sub> (1.12 mg, 0.005 mmol, 0.1 equiv.) and toluene (1 mL). After 5 min stirring at room temperature the mixture was placed in a preheated oil bath at 130 °C and stirred for one hour. The reaction mixture was cooled down to room temperature and further analyzed by GC-MS showing 28% yield formation of product **3a**.

**Control experiment with H<sub>2</sub>L:** An overnight-dried Schlenk tube was filled, under an argon atmosphere, with 3-bromopyridine **1** (7.9 mg, 4.8  $\mu$ L, 0.05 mmol, 1 equiv.), butyl acrylate **2a** (19.2 mg, 21.6  $\mu$ L, 0.15 mmol, 3 equiv.), potassium carbonate (20.7 mg, 0.15 mmol, 3 equiv.), H<sub>2</sub>L (7.14 mg, 0.01 mmol, 0.2 equiv.), Pd(OAc)<sub>2</sub> (1.12 mg, 0.005 mmol, 0.1 equiv.) and toluene (1 mL). After 5 min stirring at room temperature the mixture was placed in a preheated oil bath at 130 °C and



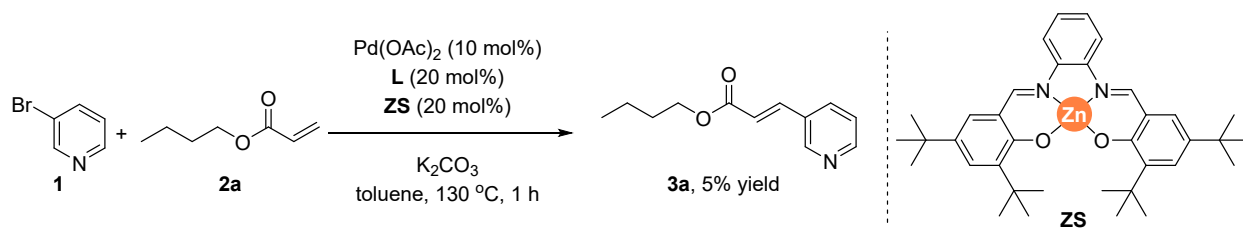
stirred for one hour. The reaction mixture was cooled down to room temperature and further analyzed by GC-MS showing 24% yield formation of **3a**.

**Control experiment with ZnTPP:** An overnight-dried Schlenk tube was filled, under an argon



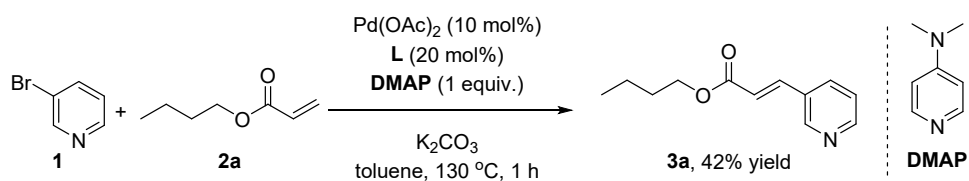
atmosphere, with 3-bromopyridine **1** (7.9 mg, 4.8  $\mu\text{L}$ , 0.05 mmol, 1 equiv.), butyl acrylate **2a** (19.2 mg, 21.6  $\mu\text{L}$ , 0.15 mmol, 3 equiv.), potassium carbonate (20.7 mg, 0.15 mmol, 3 equiv.), zinc(II)tetraphenylporphyrin (6.78 mg, 0.010 mmol, 0.2 equiv.),  $\text{Pd(OAc)}_2$  (1.12 mg, 0.005 mmol, 0.1 equiv.) and toluene (1 mL). After 5 min stirring at room temperature the mixture was placed in a preheated oil bath at 130 °C and stirred for one hour. The reaction mixture was cooled down to room temperature and further analyzed by GC-MS showing 23% yield formation of product **3a**.

**Competition between ligand L and zinc(II)-salphen:** An overnight-dried Schlenk tube was filled, under an argon atmosphere, with 3-bromopyridine **1** (7.9 mg, 4.8  $\mu\text{L}$ , 0.05 mmol, 1 equiv.), butyl acrylate **2a** (19.2 mg, 21.6  $\mu\text{L}$ , 0.15 mmol, 3 equiv.), potassium carbonate (20.7 mg, 0.15 mmol, 3 equiv.), the supramolecular ligand **L** (7.8 mg, 0.01 mmol, 0.2 equiv.), zinc(II)-salphen **ZS** (6.04 mg, 0.01 mmol, 0.2 equiv.),  $\text{Pd(OAc)}_2$  (1.12 mg, 0.005 mmol, 0.1 equiv.) and toluene (1 mL). After 5 min stirring at room temperature the mixture was placed in a preheated oil bath at 130 °C and stirred for one hour. The reaction mixture was cooled down to room temperature and further



analyzed by GC-MS showing 5% yield formation of product **3a**.

**Competition between 1a and 4-dimethylaminopyridine (DMAP):** An overnight-dried Schlenk tube was filled, under an argon atmosphere, with 3-bromopyridine **1** (7.9 mg, 4.8  $\mu$ L, 0.05 mmol, 1 equiv.), DMAP (6.10 mg, 0.05 mmol, 1 equiv.), butyl acrylate **2a** (19.2 mg, 21.6  $\mu$ L, 0.15 mmol, 3 equiv.), potassium carbonate (20.7 mg, 0.15 mmol, 3 equiv.), the supramolecular ligand **L** (7.8 mg, 0.01 mmol, 0.2 equiv.), zinc(II)-salphen **ZS** (6.04 mg, 0.01 mmol, 0.2 equiv.), Pd(OAc)<sub>2</sub> (1.12 mg, 0.005 mmol, 0.1 equiv.) and toluene (1 mL). After 5 min stirring at room temperature the mixture was placed in a preheated oil bath at 130 °C and stirred for one hour. The reaction mixture was cooled down to room temperature and further analyzed by GC-MS showing 42% yield formation of product **3a**.



6.

Preliminary  
study.

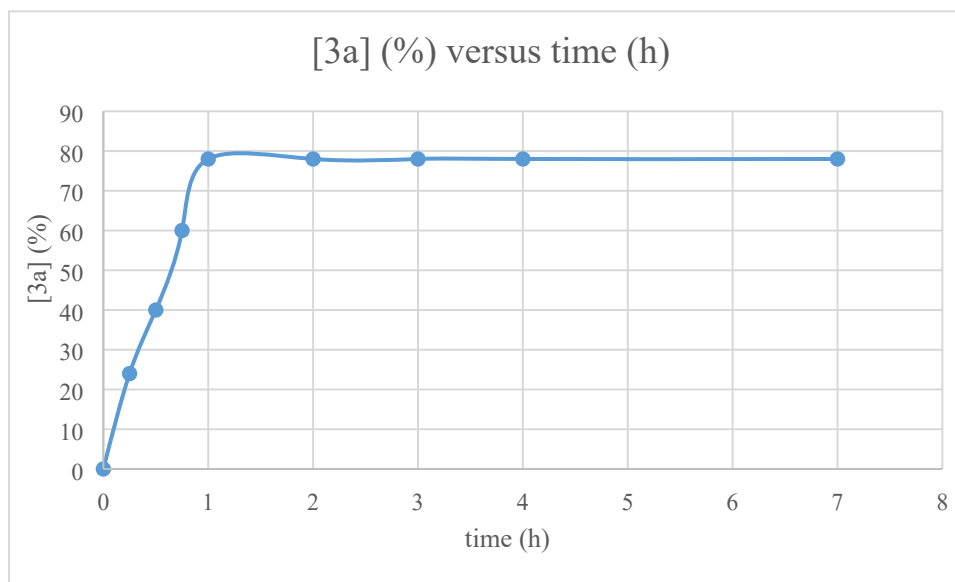


Figure S12.  
production  
time with L  
mol%).

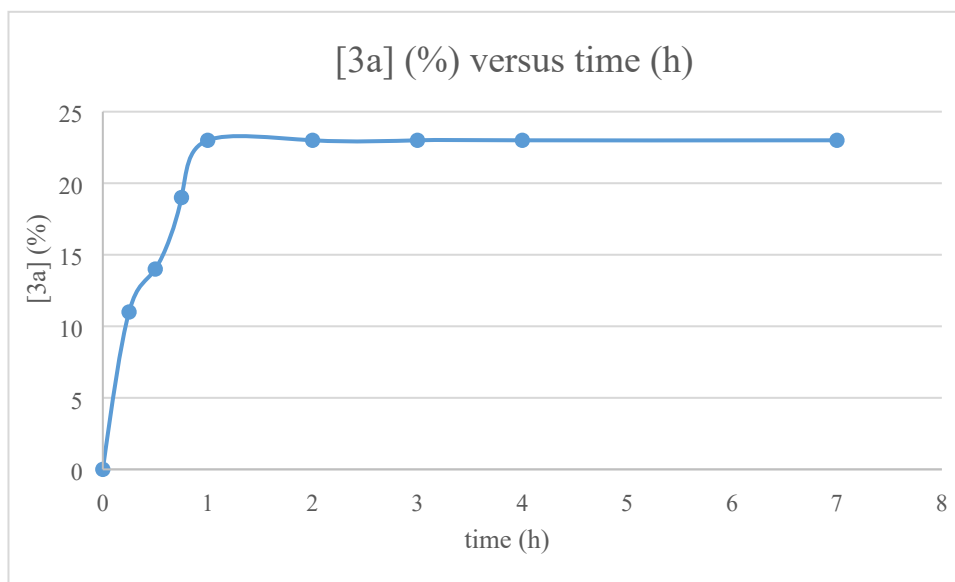
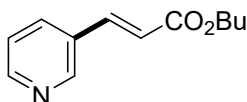


Figure S13. [3a] production versus time without L.

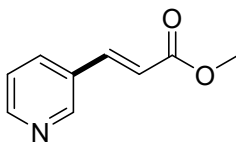
## 7. Characterization of products.

### Butyl (*E*)-3-(pyridin-3-yl)acrylate (**3a**)



Following the optimized conditions, 78% yield was estimated by GC-MS analysis. Purification was done by flash chromatography with a mixture of heptane and ethyl acetate as the eluent affording analytically pure product **3a**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.74 (d,  $J$  = 2.3 Hz, 1H), 8.59 (dd,  $J$  = 4.8, 1.6 Hz, 1H), 7.83 (dt,  $J$  = 8.0, 2.0 Hz, 1H), 7.65 (d,  $J$  = 16.1 Hz, 1H), 7.41–7.14 (m, 1H), 6.50 (d,  $J$  = 16.1 Hz, 1H), 4.22 (t,  $J$  = 6.7 Hz, 2H), 1.69 (dq,  $J$  = 8.5, 6.8 Hz, 2H), 1.43 (h,  $J$  = 7.4 Hz, 2H), 0.96 (t,  $J$  = 7.4 Hz, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.37, 150.92, 149.67, 140.79, 134.18, 130.25, 123.71, 120.53, 64.70, 30.73, 19.17, 13.71 ppm. The data match those reported previously.<sup>2</sup>

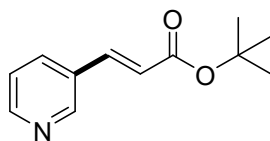
### Methyl (*E*)-3-(pyridin-3-yl)acrylate (**3b**)



Following the optimized conditions, 48% yield was estimated by GC-MS analysis. Purification was done by flash chromatography with a mixture of heptane and ethyl acetate as the eluent affording analytically pure product **3b**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.74 (d,  $J$  = 2.3 Hz, 1H), 8.60 (dd,  $J$  = 4.9, 1.7 Hz, 1H), 7.83 (dt,  $J$  = 8.0, 2.0 Hz, 1H), 7.68 (d,  $J$  = 16.1 Hz, 1H), 7.33 (dd,  $J$  = 8.0, 4.8 Hz, 1H), 6.51 (d,  $J$  = 16.1 Hz, 1H), 3.82 (s, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.74, 151.02,

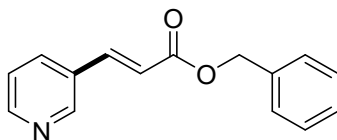
149.71, 141.15, 134.22, 130.18, 123.74, 120.05, 51.83 ppm. The data match those reported previously.<sup>3</sup>

*tert*-Butyl (*E*)-3-(pyridin-3-yl)acrylate (**3c**)



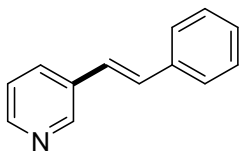
Following the optimized conditions, 59% yield was estimated by GC-MS analysis. Purification was done by flash chromatography with a mixture of heptane and ethyl acetate as the eluent affording analytically pure product **3c**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.73 (d, *J* = 2.3 Hz, 1H), 8.59 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.81 (dt, *J* = 8.0, 2.1 Hz, 1H), 7.56 (d, *J* = 16.0 Hz, 1H), 7.31 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.44 (d, *J* = 16.1 Hz, 1H), 1.54 (s, 9H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ = 165.59, 150.72, 149.60, 139.77, 134.12, 123.69, 122.45, 81.01 ppm. The data match those reported previously.<sup>4</sup>

(Benzyl (*E*)-3-(pyridin-3-yl)acrylate (**3d**)



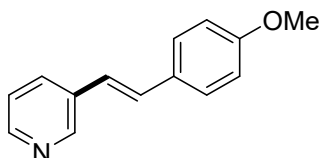
Following the optimized conditions, 87% yield was estimated by GC-MS analysis. Purification was done by flash chromatography with a mixture of heptane and ethyl acetate as the eluent affording analytically pure product **3d**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.77 (s, 1H), 8.63 (d, *J* = 4.8 Hz, 1H), 7.85 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.74 (d, *J* = 16.1 Hz, 1H), 7.50–7.32 (m, 6H), 7.28 (s, 1H), 6.58 (d, *J* = 16.1 Hz, 1H), 5.29 (s, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ = 166.13, 151.10, 149.77, 141.46, 135.79, 134.24, 130.14, 128.67, 128.42, 128.39, 123.77, 120.11 ppm. The data match those reported previously.<sup>5</sup>

(*E*)-3-Styrylpyridine (**3e**)



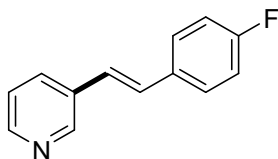
Following the optimized conditions, 95% yield was estimated by GC-MS analysis. Purification was done by flash chromatography with a mixture of heptane and ethyl acetate as the eluent affording analytically pure product **3e**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.69 (d, *J* = 2.2 Hz, 1H), 8.45 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.79 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.54–7.45 (m, 2H), 7.39–7.30 (m, 2H), 7.28–7.23 (m, 2H), 7.13 (d, *J* = 16.4 Hz, 1H), 7.03 (d, *J* = 16.4 Hz, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ = 148.70, 136.80, 133.14, 132.79, 130.99, 128.93, 128.36, 126.80, 125.05, 123.66 ppm. The data match those reported previously.<sup>6</sup>

#### 3-(4-methoxystyryl)pyridine (**3f**)



Following the optimized conditions, 89% yield was estimated by GC-MS analysis. Purification was done by flash chromatography with a mixture of heptane and ethyl acetate as the eluent affording analytically pure product **3f**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.82–8.61 (m, 1H), 8.54–8.37 (m, 1H), 7.80 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.54–7.40 (m, 2H), 7.26 (q, *J* = 4.8 Hz, 1H), 7.11 (d, *J* = 16.4 Hz, 1H), 6.99–6.84 (m, 3H), 3.84 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ = 159.78, 148.33, 148.14, 133.37, 132.40, 130.38, 129.49, 127.96, 123.52, 122.73, 114.26, 55.35 ppm. The data match those reported previously.<sup>7</sup>

#### 3-(4-Fluorostyryl)pyridine (**3g**)

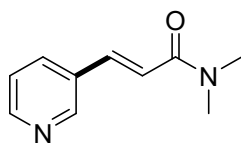


Following the optimized conditions, 43% yield was estimated by GC-MS analysis. Purification was done by flash chromatography with a mixture of heptane and ethyl acetate as the eluent affording



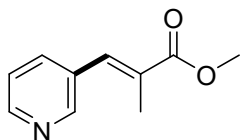
analytically pure product **3g**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.76–8.68 (m, 1H), 8.55–8.45 (m, 1H), 7.80 (dt,  $J$  = 7.9, 2.1 Hz, 1H), 7.49 (ddq,  $J$  = 10.5, 5.2, 3.0 Hz, 2H), 7.34–7.22 (m, 1H), 7.16–7.02 (m, 3H), 6.98 (dd,  $J$  = 16.4, 2.1 Hz, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 163.72, 161.25, 148.46, 148.32, 132.72, 132.69, 132.67, 132.40, 129.42, 128.08, 128.00, 124.56, 124.54, 123.36, 115.71, 115.49 ppm. The data match those reported previously.<sup>8</sup>

*N,N*-dimethyl 3-(pyridin-3-yl)acrylamide (**3h**)



Following the optimized conditions, 26% yield was estimated by GC-MS analysis. Purification was done by flash chromatography with a mixture of heptane and ethyl acetate as the eluent affording analytically pure product **3f**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.75 (s, 1H), 8.55 (d,  $J$  = 4.8 Hz, 1H), 7.80 (dt,  $J$  = 8.0, 1.9 Hz, 1H), 7.63 (d,  $J$  = 15.5 Hz, 1H), 7.35–7.23 (m, 1H), 6.95 (d,  $J$  = 15.5 Hz, 1H), 3.17 (s, 3H), 3.07 (s, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.97, 150.26, 149.21, 138.68, 134.26, 131.12, 123.60, 119.61, 37.43, 35.96 ppm. The data match those reported previously.<sup>9</sup>

Methyl (*E*)-2-methyl-3-(pyridin-3-yl)acrylate (**3i**)

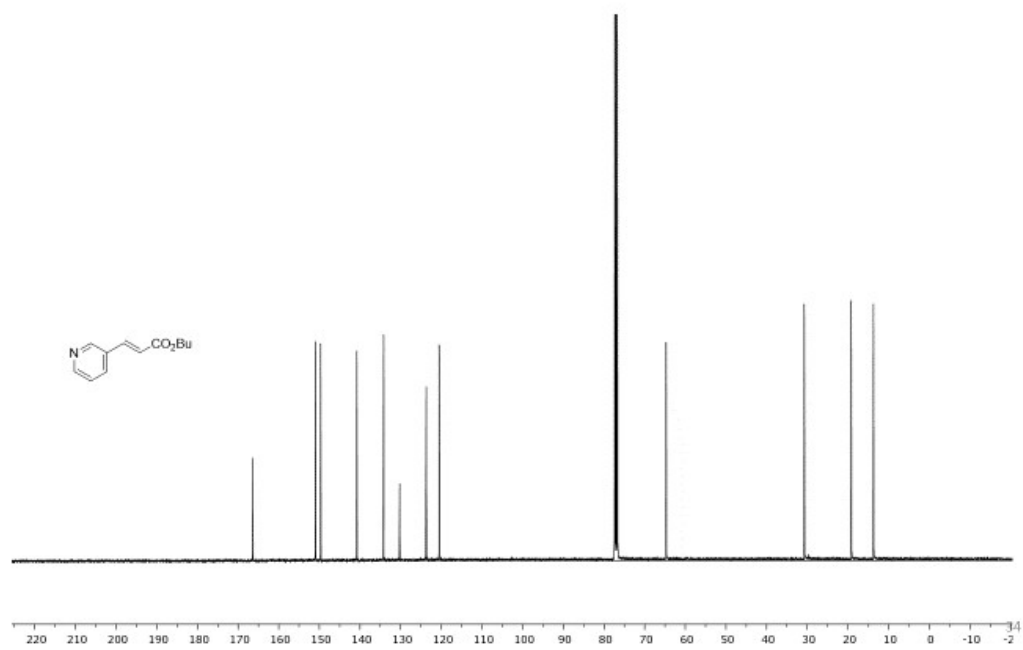
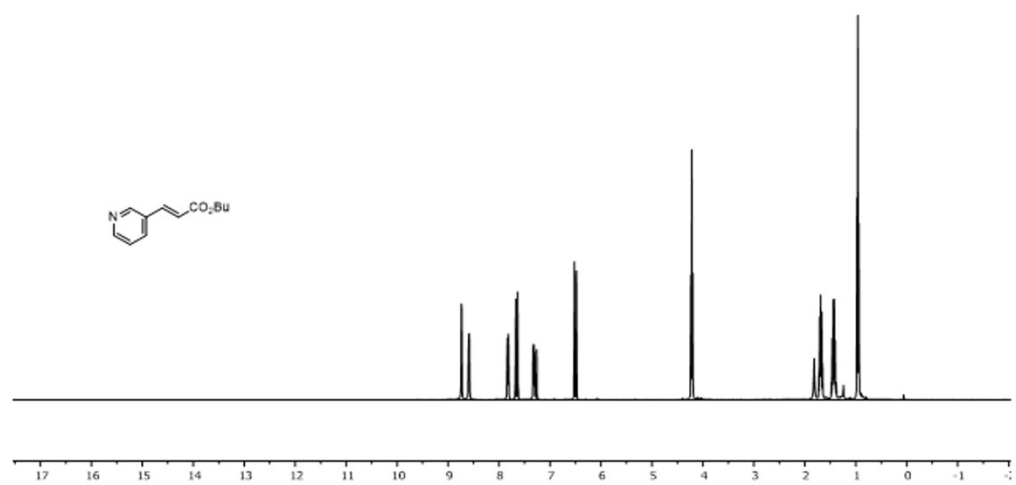


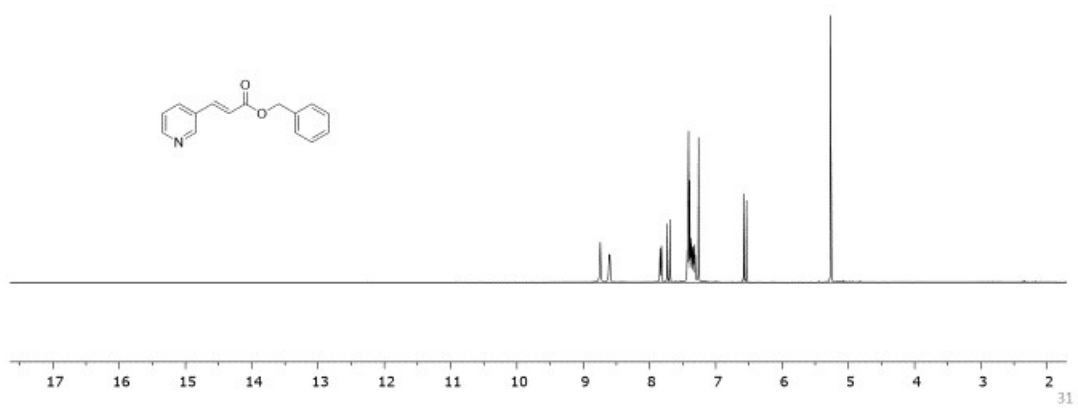
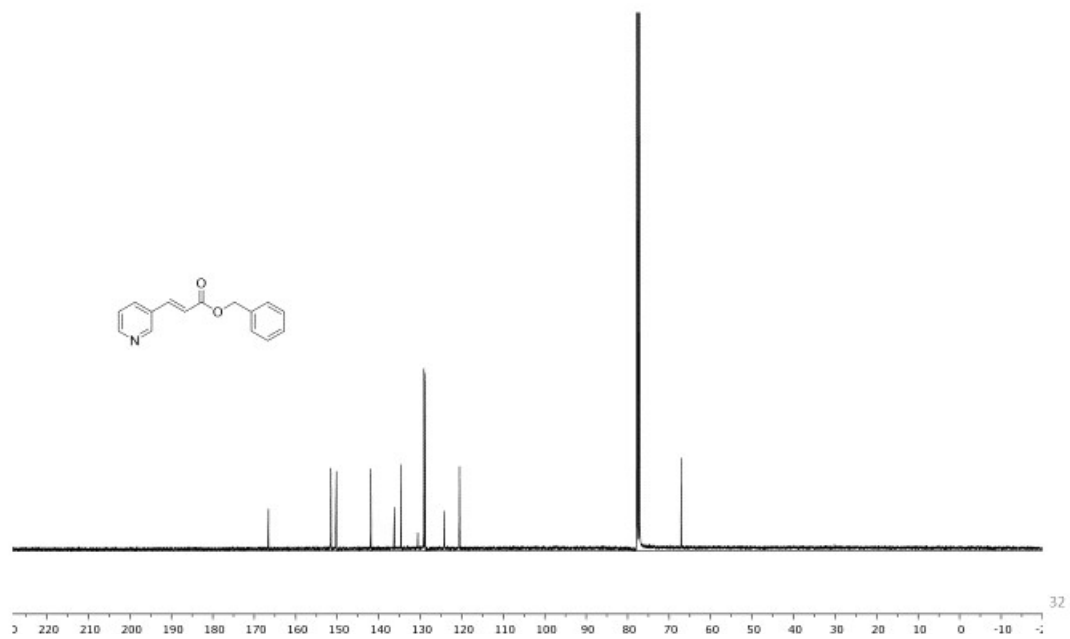
Following the optimized conditions, 50% yield was estimated by GC-MS analysis. Purification was done by flash chromatography with a mixture of heptane and ethyl acetate as the eluent affording analytically pure product **3g**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.65 (s, 1H), 8.56 (s, 1H), 7.71 (d,  $J$  = 7.9 Hz, 1H), 7.64 (s, 1H), 7.34 (dd,  $J$  = 7.9, 4.9 Hz, 1H), 3.84 (s, 3H), 2.13 (d,  $J$  = 1.5 Hz, 3H) ppm. The data match those reported previously.<sup>10</sup>

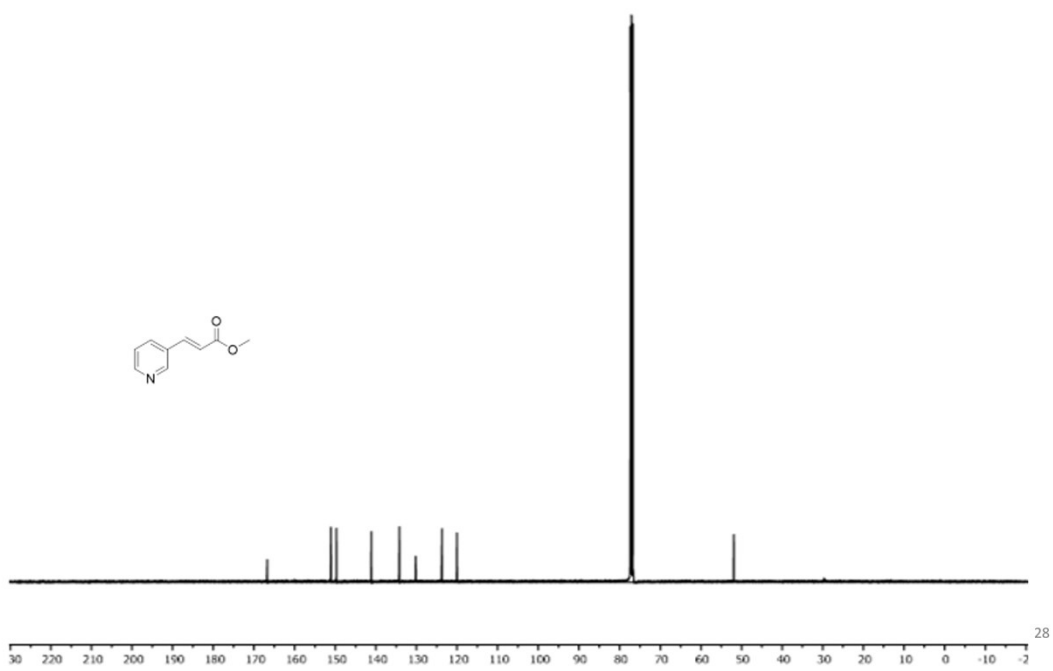
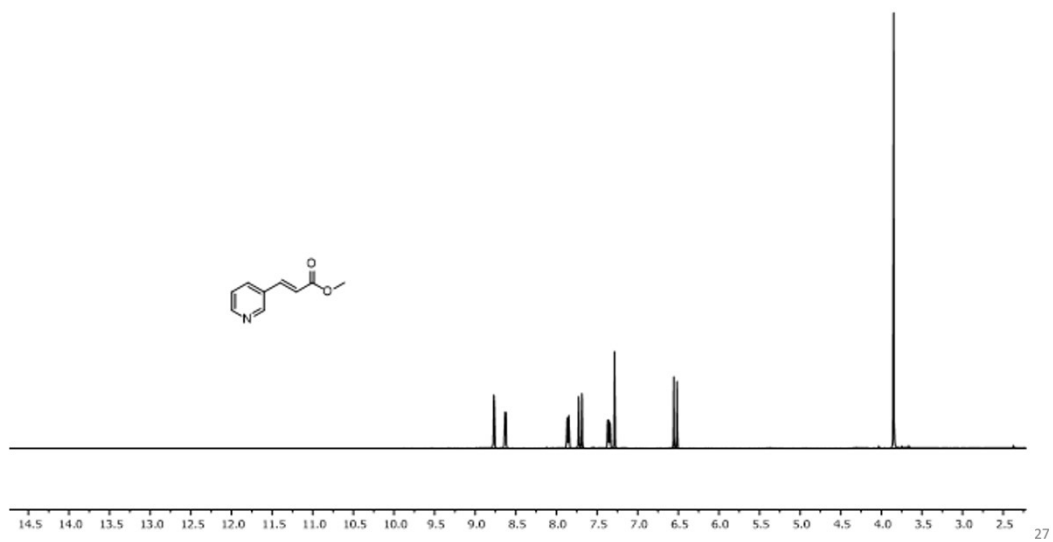
## 8. References.

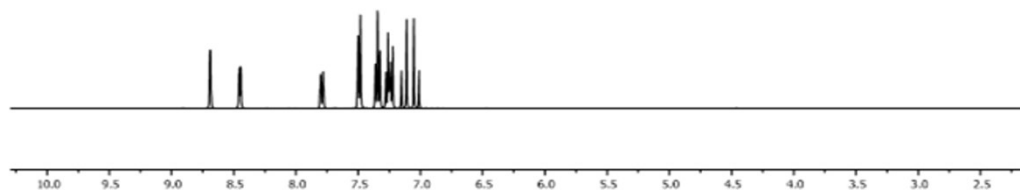
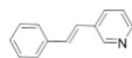
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## 9. NMR data.

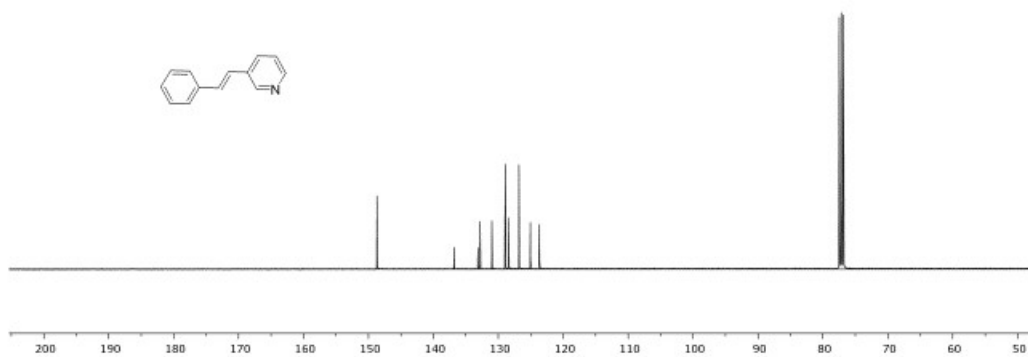
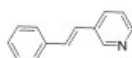




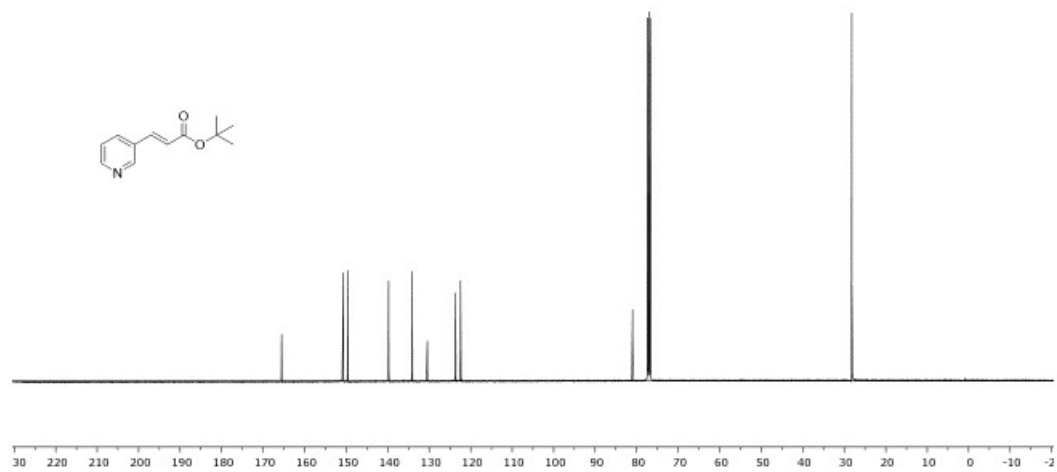
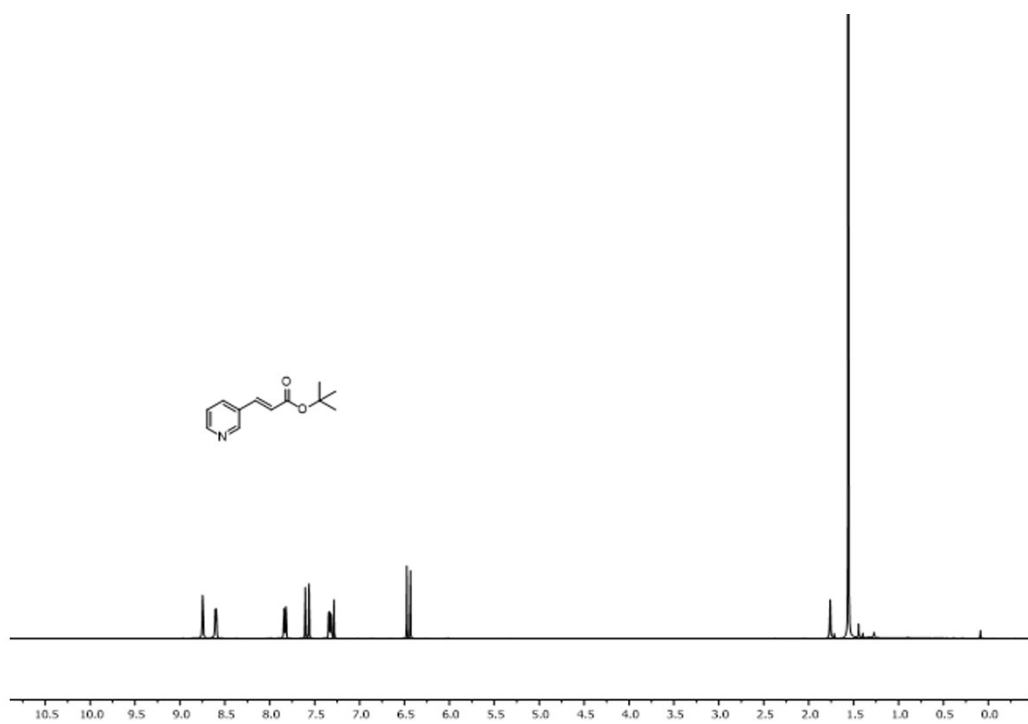


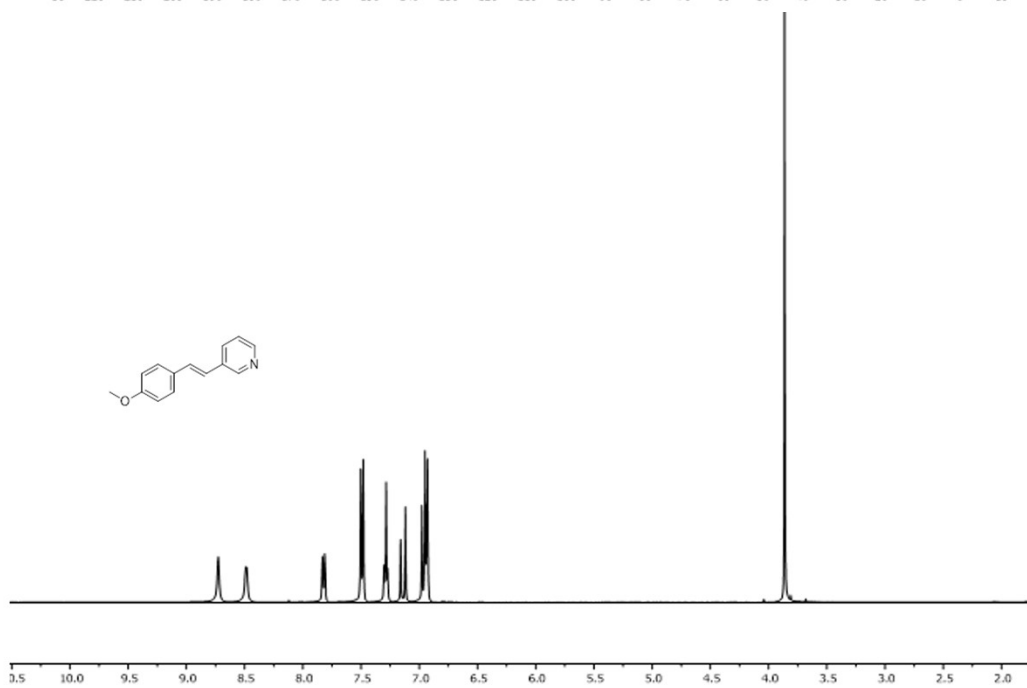
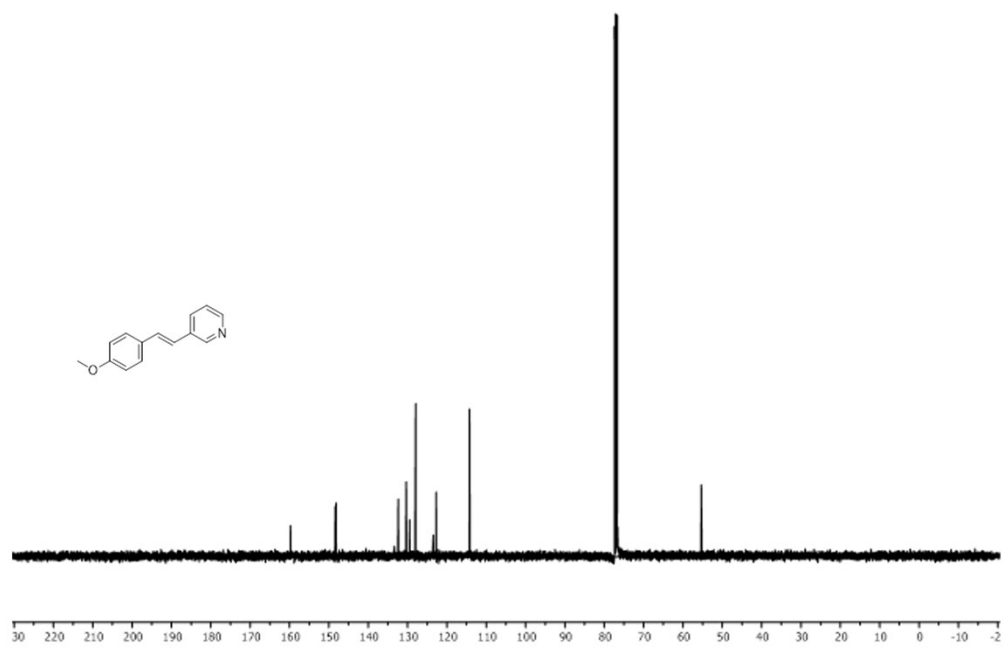


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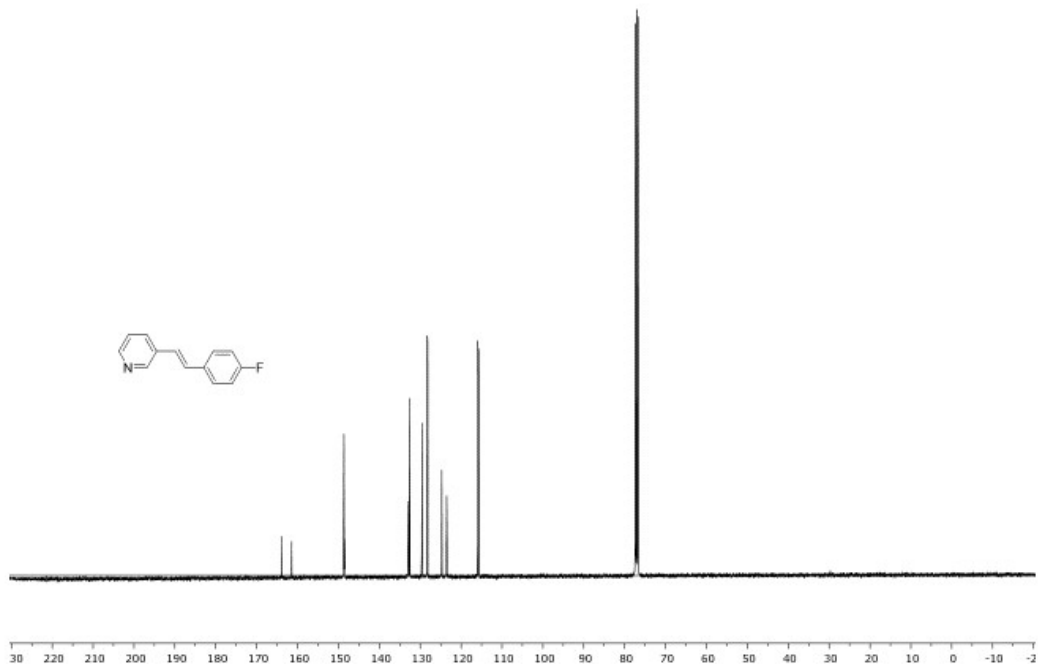
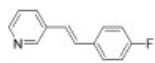
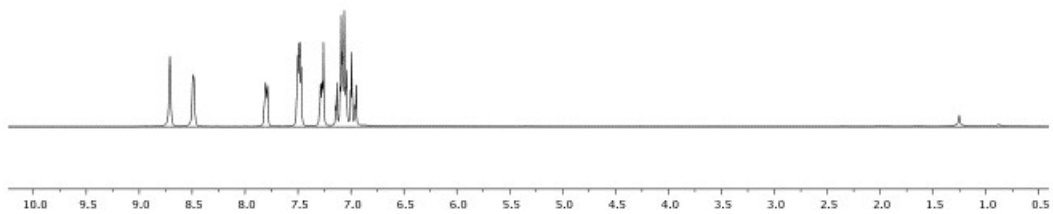
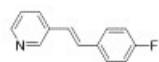


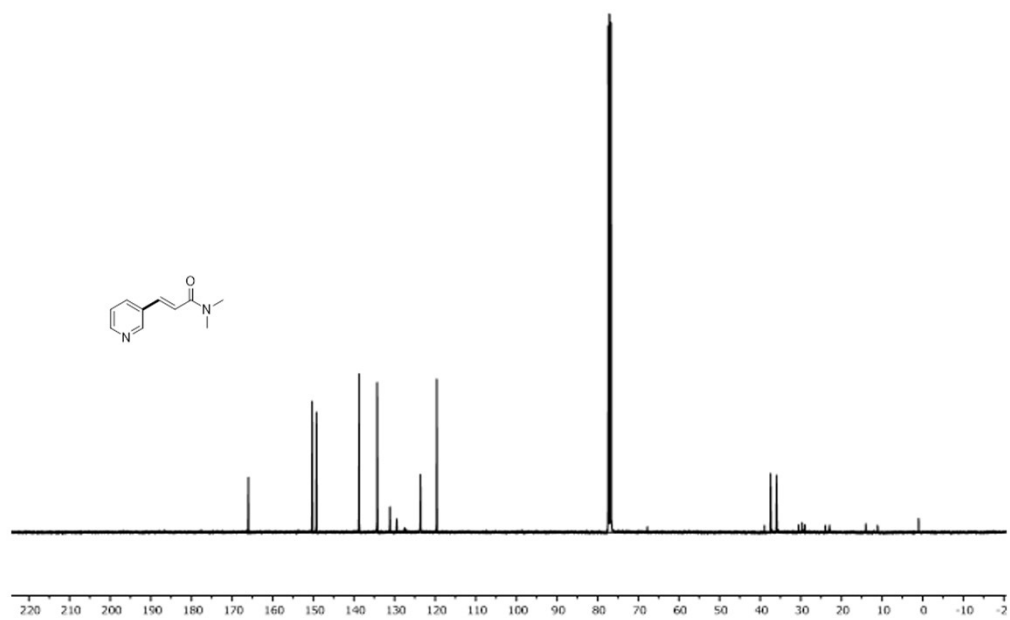
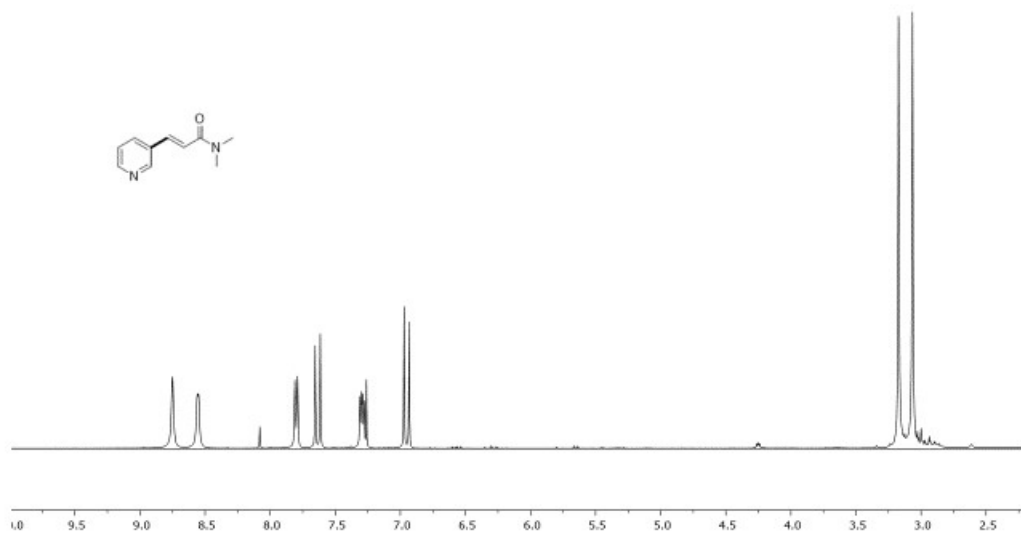
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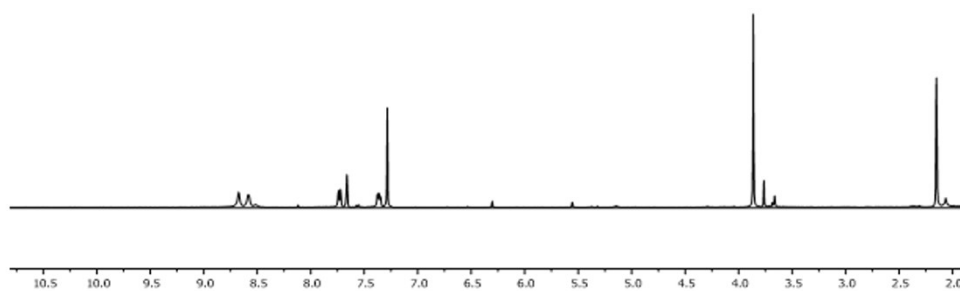
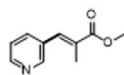












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