

# Ruthenium and iridium dipyridylamine catalysts for the efficient synthesis of $\gamma$ -valerolactone by transfer hydrogenation of Levulinic acid.

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## General Information:

Levulinic acid (98%), formic acid (98%) and 2,2'-dipyridylamine (98%) were purchased from Sigma-Aldrich. Solvents (methanol, diethyl ether) were HPLC grade and used as received. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance (400 MHz) spectrometer and reported in ppm with reference to CHCl<sub>3</sub> (7.26 ppm). Data are reported as follows: s=singlet, d=doublet, t= triplet, q= quartet, m= multiplet. Coupling constants are reported in Hz. <sup>13</sup>C NMR spectra were recorded at 100 MHz on the same spectrometer and reported in ppm with reference to CDCl<sub>3</sub> (77.16 ppm).

## Ligand syntheses

### Synthesis of known (2,2'-dipyridyl)benzylamine **2**<sup>1</sup>

2-Bromopyridine (0.32 g, 2 mmol), benzylamine (0.11 g, 1 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.023 g, 2.5 mol%), BINAP (0.025 g, 4 mol%), tBuOK (0.17 g, 1.5 mmol) and 10 ml of toluene were combined in a Schlenk tube under an argon atmosphere. The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the crude reaction mixture was filtrated over Celite. Purification by column chromatography on silica gel (petroleum ether:ethyl acetate = 1/3, v/v). The target product was obtained as a white solid (0.25 g, 96%). NMR data were consistent with reported data.<sup>2</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.31 (d, <sup>3</sup>J<sub>H-H</sub> = 4.8 Hz, 2H, pyr NCH), 7.53-7.49 (m, 2H, CH), 7.35 (d, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 2H, CH), 7.28-7.22 (m, 2H, CH), 7.20-7.14 (m, 3H, CH), 6.87-6.82 (m, 2H, CH), 5.51 (s, 2H, NCH<sub>2</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 157.2, 148.3, 139.4, 137.4, 128.4, 127.1, 126.7, 117.3, 114.7, 51.5.

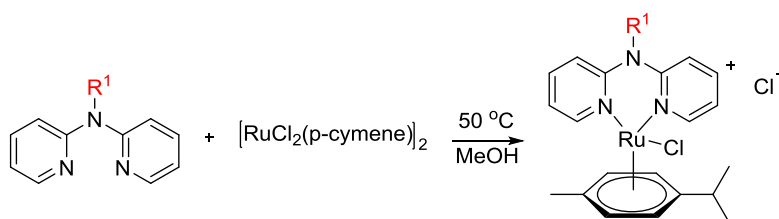
### Synthesis of known (2,2'-dipyridyl)methylbenzylamine **3**

2-Bromopyridine (0.32 g, 2 mmol), 1-phenylethylamine (0.12 g, 1 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.023 g, 2.5 mol%), BINAP (0.025 g, 4 mol%), tBuOK (0.17 g, 1.5 mmol) and 10 ml of toluene were combined in a Schlenk tube under an argon atmosphere. The reaction mixture was stirred for 24 h at 80 °C. The crude reaction mixture was allowed to cool down to r. t. and filtrated over Celite. Purification by column chromatography on silica gel (petroleum ether : ethyl acetate = 1/3, v/v). The target product was obtained as a yellow solid (0.25 g, 91%). NMR data were consistent with reported data.<sup>3</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.35 (dd, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.2 Hz, 2H, pyr NCH), 7.46-7.38

(m, 4H, CH), 7.28-7.22 (m, 2H, CH), 7.20-7.15 (m, 2H, CH), 6.86-6.84 (m, 2H, CH), 6.66 (d,  $^3J_{\text{H-H}} = 8.4$  Hz, 2H, CH), 6.53 (q,  $^3J_{\text{H-H}} = 7.2$  Hz, NCH), 1.67 (d,  $^3J_{\text{H-H}} = 7.2$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 157.2, 148.5, 143.3, 137.3, 128.2, 127.5, 126.6, 117.7, 117.0, 54.3, 18.1.

### Syntheses of ruthenium complexes



	Ru1	Ru2	Ru3
	1	2	3
R <sup>1</sup>	H	Benzyl	1-phenylethyl

Scheme S1. Synthesis of ruthenium compounds **Ru1-Ru3**.

#### Synthesis of known **Ru1**: [(dpa)(*p*-cymene)RuCl]Cl<sup>4</sup>

**1** (0.068 g, 0.4 mmol) was added to a suspension of [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (0.034 g, 0.2 mmol) in methanol (5 mL). The mixture was stirred for 12 h at 50 °C. After evaporation to dryness, the residue was washed with diethylether (3 × 2 mL) to give the expected product **Ru1** 0.085 g (yield: 89%) as a yellow solid. NMR data were consistent with reported data.<sup>4</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 12.82 (s, 1H, NH), 8.42-8.41 (d,  $J = 6.0$  Hz, 2H, pyr NCH), 8.12 (d,  $J = 8.4$  Hz, 2H, CH), 7.75-7.68 (m, 2H, CH), 7.05-6.99 (m, 2H, CH), 5.41 (d,  $^3J_{\text{H-H}} = 6.0$  Hz, 2H, *p*-cymene CH), 5.27 (d,  $^3J_{\text{H-H}} = 6.0$  Hz, 2H, *p*-cymene CH), 2.76-2.73 (hept,  $^3J_{\text{H-H}} = 6.8$  Hz, 1H, iPr CH), 1.94 (s, 3H, CH<sub>3</sub>), 1.22 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 6H, iPr CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 154.5, 152.6, 139.8, 119.3, 116.3, 106.6, 99.6, 84.6, 84.5, 30.8, 22.4, 18.2.

#### Synthesis of **Ru2**: [(bdpa)(*p*-cymene)RuCl]Cl

Using the same procedure as for the synthesis of **Ru1**, **Ru2** was obtained as a yellow powder (0.081 g, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.67 (m, 2H, pyr NCH), 7.76 - 7.71 (m, 2H, CH), 7.38-7.32 (m, 7H, CH), 7.16-7.13 (m, 2H, CH), 5.93 (s, 2H, benzyl, CH<sub>2</sub>), 5.89 (d,  $^3J_{\text{H-H}} = 6.0$  Hz,

2H, *p*-cymene CH), 5.80 (d,  $^3J_{\text{H-H}} = 6.0$  Hz, 2H, *p*-cymene, CH), 2.78-2.75 (hept, 1H,  $^3J_{\text{H-H}} = 7.6$  Hz, *i*Pr CH), 1.81 (s, 3H, CH<sub>3</sub>), 1.23 (d,  $^3J_{\text{H-H}} = 7.6$  Hz, 6H, *i*Pr CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 156.4, 153.5, 140.3, 134.8, 129.2, 127.9, 126.8, 120.4, 116.2, 105.8, 100.8, 86.4, 84.2, 57.4, 30.7, 22.6, 18.0.

Elemental Analysis: Calculated for C<sub>27</sub>H<sub>29</sub>N<sub>3</sub>Cl<sub>2</sub>Ru·H<sub>2</sub>O (%) : C, 55.38, H, 5.34, N, 7.18. Found: C, 55.45, H, 5.14, N, 7.14.

HRMS (ESI): m/z Calculated for C<sub>27</sub>H<sub>29</sub>N<sub>3</sub>ClRu: 532.1088; m/z measured: 532.1087

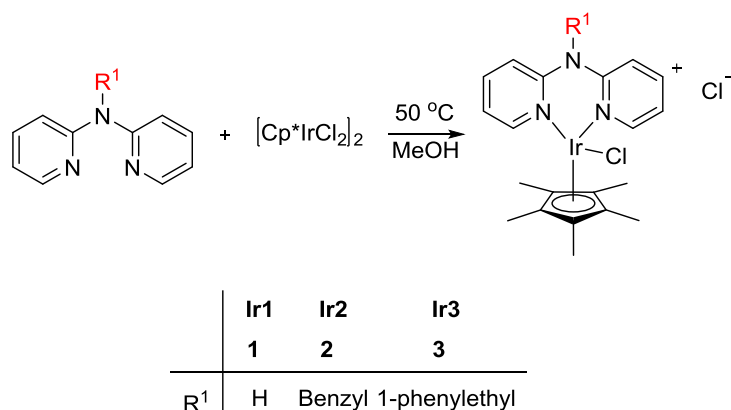
### Synthesis of **Ru3**: [(*mbdpa*)(*p*-cymene)RuCl]Cl

Using the same procedure as for the synthesis of **Ru1**, **Ru3** was obtained as a yellow powder (0.076 g, Yield: 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.78 (d,  $^3J_{\text{H-H}} = 5.2$  Hz, 1H, pyr NCH), 8.64 (d,  $^3J_{\text{H-H}} = 5.6$  Hz, 1H, py CH), 7.75 (m 1H, CH), 7.63 (m, 1H, pyr CH), 7.37-7.16 (m, 9H, CH), 6.63 (m 1H, CH), 6.12 (d,  $^3J_{\text{H-H}} = 6.0$  Hz, 1H, *p*-cymene CH), 5.95 (d,  $^3J_{\text{H-H}} = 6.0$  Hz, 1H, *p*-cymene CH ), 5.86 (d,  $^3J_{\text{H-H}} = 5.6$  Hz, 1H, *p*-cymene CH), 5.82 (d,  $^3J_{\text{H-H}} = 5.6$  Hz, 1H, *p*-cymene CH ), 2.73-2.67(hept,  $^3J_{\text{H-H}} = 6.8$  Hz, 1H, *i*Pr CH), 2.09 (s, 1.5H, CH<sub>3</sub> ), 2.11 (s, 1.5H, CH<sub>3</sub> ), 1.82 (s, 3H, CH<sub>3</sub>), 1.29 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 3H, CH<sub>3</sub>), 1.27 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 158.0, 154.2, 154.1, 152.9, 140.5, 139.7, 138.8, 129.1, 127.7, 126.9, 120.8, 120.7, 118.9, 117.3, 103.9, 103.0, 88.6, 87.4, 83.1, 82.3, 61.9, 30.5, 23.2, 22.1, 21.8, 18.2.

Elemental Analysis: C<sub>28</sub>H<sub>31</sub>N<sub>3</sub>Cl<sub>2</sub>Ru (%) : C, 57.83, H, 5.37, N, 7.23. Found: C, 57.68, H, 5.28, N, 7.05.

HRMS (ESI): m/z Calculated for C<sub>28</sub>H<sub>31</sub>N<sub>3</sub>ClRu: 546.1250; m/z measured: 546.1251

## Syntheses of Iridium complexes



Scheme S2. Synthesis of ruthenium compounds **Ir1-Ir3**.

### Synthesis of known **Ir1**: [(dpa)Cp\*IrCl]Cl

**1** (0.019 g, 0.12 mmol) was added to a suspension of [Cp\*IrCl<sub>2</sub>]<sub>2</sub> (0.045 g, 0.056 mmol) in methanol (5 mL). The mixture was stirred for 12 h at 50 °C. After evaporation to dryness, the residue was washed with diethyl ether (3 × 2 mL) to give the expected product **Ir1** (0.056 g, yield: 89%) as a yellow powder. NMR data were consistent with reported data.<sup>5</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.79 (s, 1H, NH), 8.26-8.20 (m, 4H, pyr NCH), 7.74- 7.69 (m, 2H, py CH), 7.03-6.99 (m, 2H, py CH), 1.42 (s, 15H, Cp\* CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 153.2, 150.6, 140.2, 120.3, 116.5, 87.8, 8.65.

Elemental Analysis: C<sub>20</sub>H<sub>24</sub>N<sub>3</sub>Cl<sub>2</sub>Ir (%) : C, 42.18, H, 4.25, N, 7.38. Found: C, 41.70, H, 4.25, N, 7.16.

HRMS (ESI): m/z Calculated for C<sub>20</sub>H<sub>24</sub>N<sub>3</sub>ClIr: 534.1288; m/z measured: 534.1280

### Synthesis of **Ir2**: [(bdpa)Cp\*IrCl]Cl

Using the same procedure as for the synthesis of **Ir1**, **Ir2** was obtained as a yellow powder (0.06 g, 91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.54 (d, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 1H, py CH), 7.82-7.77 (m, 2H, CH), 7.38-7.35 (m, 5H, CH), 7.28-7.27 (m, 2H, CH), 7.22 - 7.18 (m, 2H, CH), 5.88 (s, 2H, NCH<sub>2</sub>), 1.50 (s, 15H, Cp\* CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 154.7, 152.3, 141.4, 133.9, 129.3, 128.1, 126.4, 121.8, 116.2, 88.7, 57.4, 8.9.

HRMS (ESI): m/z Calculated for C<sub>27</sub>H<sub>30</sub>N<sub>3</sub>ClIr: 624.1752; m/z measured: 624.1760

Accurate elemental analyses could not be obtained. We assume that the high hydrophilicity of this

compound is responsible for this issue. X-ray quality crystals failed to provide accurate elemental analyses

### Synthesis of **Ir3**: [(bmdpa)Cp\*IrCl]Cl

Using the same procedure as for the synthesis of **Ir1**, **Ir3** was obtained as a yellow powder (0.092 g, Yield: 86 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.61 (dd, <sup>3</sup>J<sub>H-H</sub> = 6.0 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.6 Hz, 1H, py CH), 8.50 (dd, <sup>3</sup>J<sub>H-H</sub> = 6.0 Hz, <sup>3</sup>J<sub>H-H</sub> = 1.6 Hz, 1H, py CH), 7.88-7.84 (m, 1H, CH), 7.71-7.67 (m, 1H, CH), 7.48 (d, <sup>3</sup>J<sub>H-H</sub> = 8.4 Hz, 1H, py CH), 7.49 - 7.30 (m, 6H, CH), 7.21-7.17 (m, 2H, CH), 6.37 (q, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, 1H, CH), 1.96 (d, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, 3H, CH<sub>3</sub>), 1.60 (s, 15H, Cp\* CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 156.4, 153.6, 152.8, 152.1, 141.8, 139.9, 139.0, 129.2, 128.0, 126.7, 122.4, 121.9, 119.5, 117.2, 88.7, 61.6, 22.1, 9.2.

HRMS (ESI): m/z Calculated for C<sub>28</sub>H<sub>32</sub>N<sub>3</sub>ClIr: 638.1914; m/z measured: 638.1907

Accurate elemental analyses could not be obtained. We assume that the high hydrophilicity of this compound is responsible for this issue. X-ray quality crystals failed to provide accurate elemental analyses.

### General Experimental Procedure for transfer hydrogenation of Levulinic acid

LA (2 mmol), FA (2-8 mmol), Et<sub>3</sub>N (0-4 mmol), catalyst (0.05-0.1 mol%) were added to a Schlenk tube with a Teflon screw cap. The mixture of substrates and catalyst was heated to the desired temperature in less than 15 min. The crude mixtures were analyzed by <sup>1</sup>H NMR using anisole as internal standard. Volatile compounds were removed under vacuum and the crude product was purified by column chromatography using petroleum ether / ethyl acetate (3/1; v/v) as eluent.

### Base screening

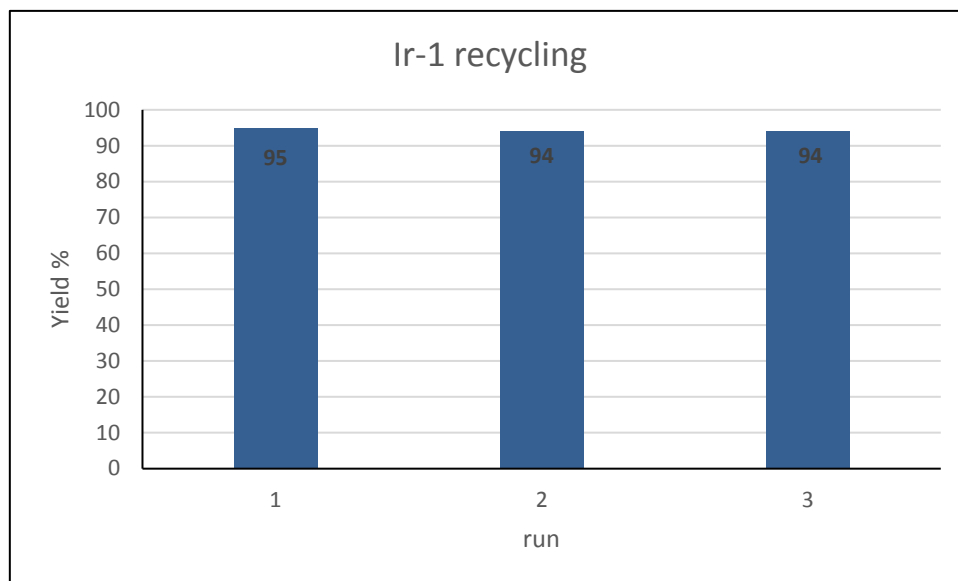
**Table S1** Transfer hydrogenation of LA by different base. <sup>a</sup>

Entry	Base	LA Conv. (%) <sup>b</sup>	GVL Yield(%) <sup>b</sup>
1	iPr <sub>2</sub> NH	30	30
2	HCOONa	75	43
3	K <sub>2</sub> CO <sub>3</sub>	73	61
4	K <sub>3</sub> PO <sub>4</sub>	92	41
5	Et <sub>3</sub> N	82	82

<sup>a</sup> conditions: LA (0.232 g, 2 mmol), Base (0.5 eq), FA (2 eq), **Ru1** 0.1 mol %, 150 °C, 16 h.

<sup>b</sup>determined by <sup>1</sup>H NMR

## Recycling of Ir-1

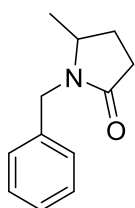


Recycling of Ir-1(0.1 mol%, 120 °C, LA:FA:Et<sub>3</sub>N = 1:4:2)

### General procedure for the reductive amination of LA

Benzylamine (4-8 mmol), catalyst (0.05-0.1 mol%), levulinic acid (2-4 mmol), formic acid (4-8 mmol) and a magnetic stirring bar were placed in a Schlenk tube. The mixture was stirred at 120-150 °C for 16 h. After cooling to room temperature, the reaction was basified with saturated NaOH solution, and extracted with DCM (10 × 3 mL). The organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After removing DCM in vacuo, the product was purified by flash column chromatography using petroleum ether and ethyl acetate with 1% triethylamine as eluent.

### Analytic data of 1-Benzyl-5-methylpyrrolidin-2-one.



**1-Benzyl-5-methylpyrrolidin-2-one:** Yellow oil;

NMR data were consistent with reported data<sup>6</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.33-7.22 (m, 5H), 4.96 (d, <sup>2</sup>J<sub>H-H</sub> = 15.2 Hz, 1H), 3.98 (d, <sup>2</sup>J<sub>H-H</sub> = 14.8 Hz, 1H), 3.52 (m, 1H), 2.50-2.40 (m, 2H), 2.16-2.14 (m, 1H), 1.60-1.58 (m, 1H), 1.15 (d, <sup>3</sup>J<sub>H-H</sub> = 6.4 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 175.0, 137.0, 128.7, 128.1, 127.5, 52.9, 44.0, 30.4, 26.8, 19.7.

## NMR spectra

Figure S1  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K) of compound **2**

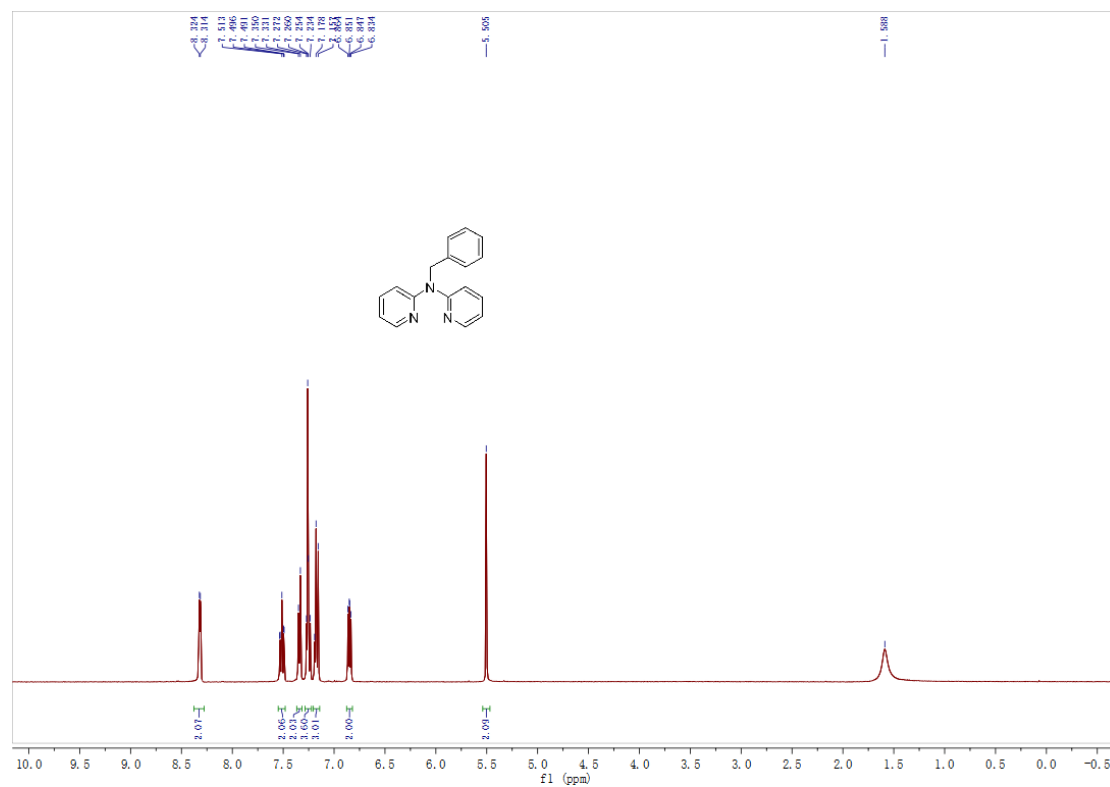


Figure S2  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz, J mod,  $\text{CDCl}_3$ ) of compound **2**

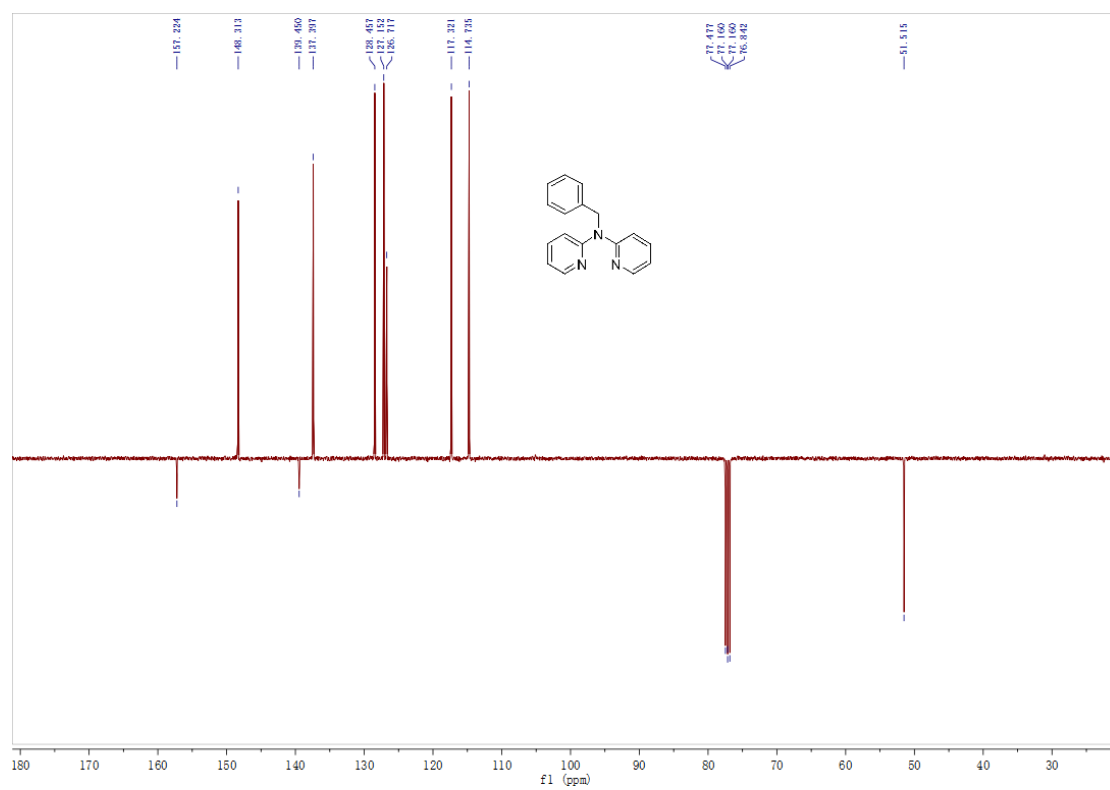




Figure S3  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K) of compound **3**

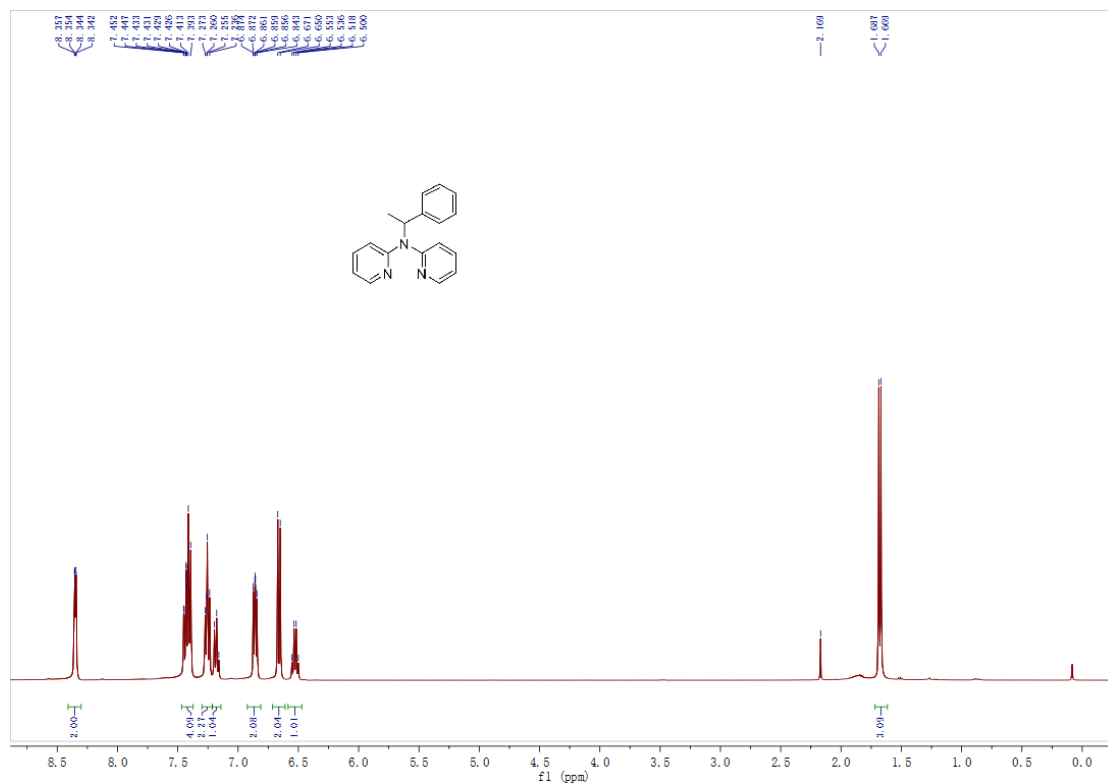


Figure S4  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz, J mod,  $\text{CDCl}_3$ ) of compound **3**

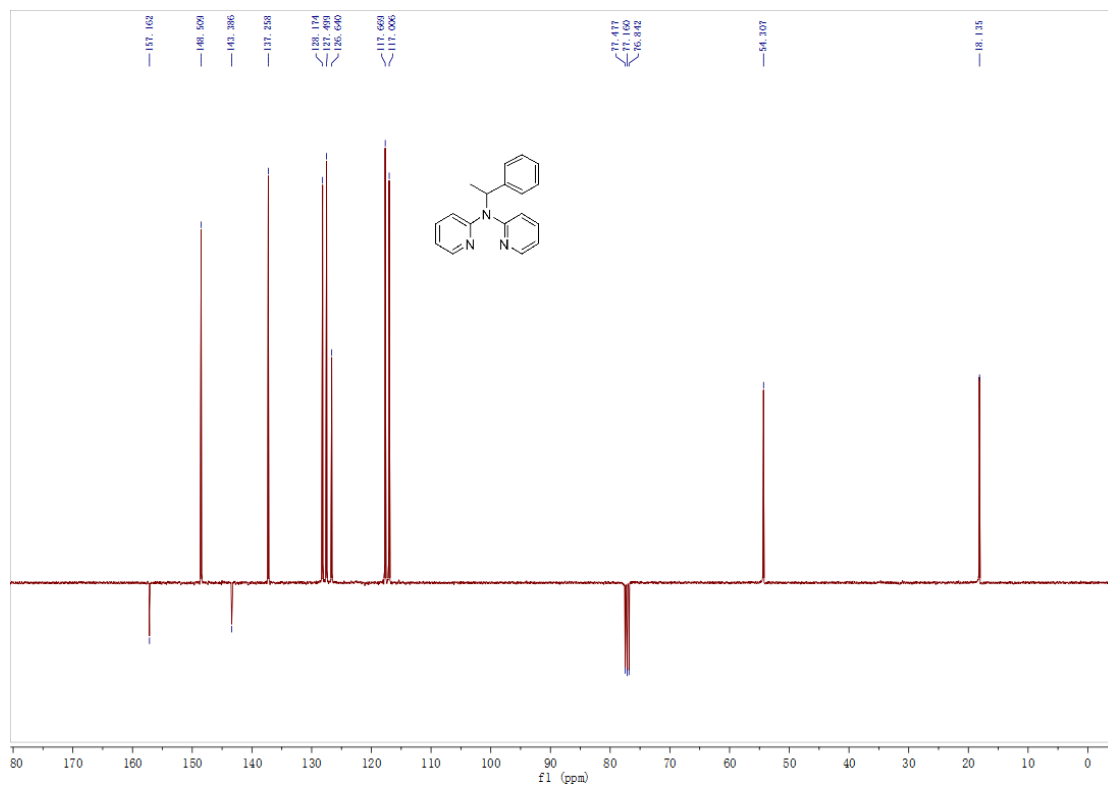


Figure S5  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K) of **Ru1**

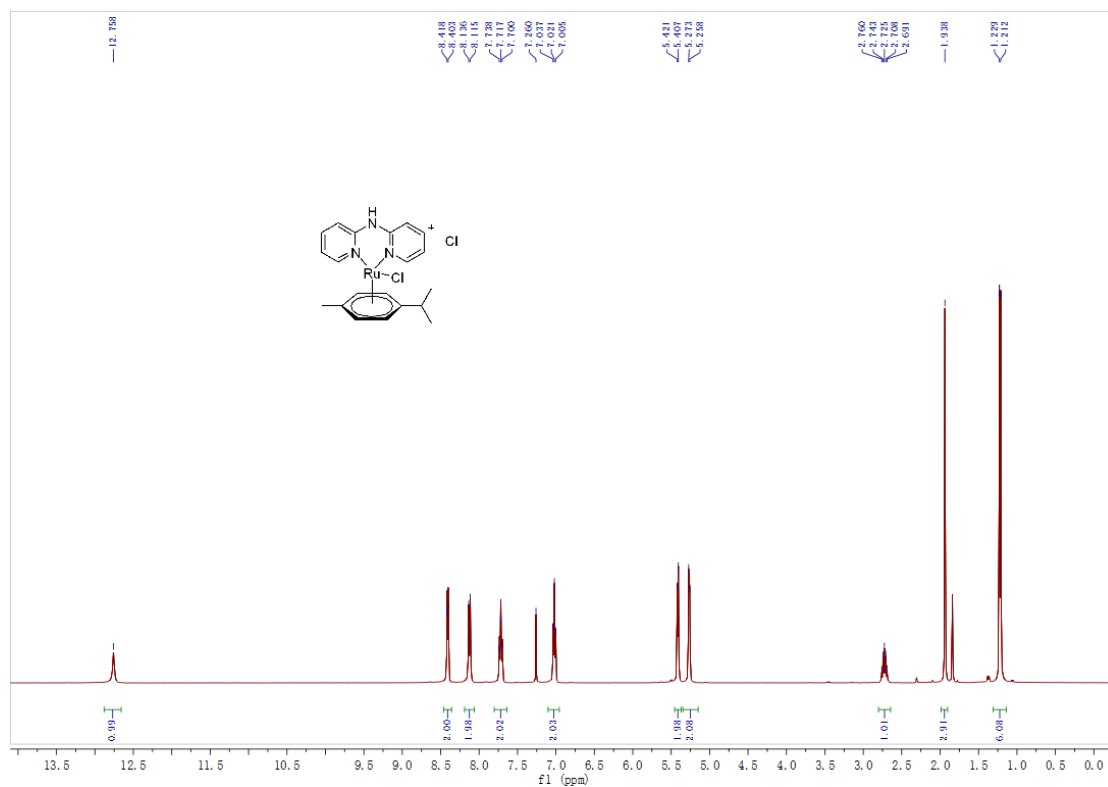


Figure S6  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz, J mod,  $\text{CDCl}_3$ ) of **Ru1**

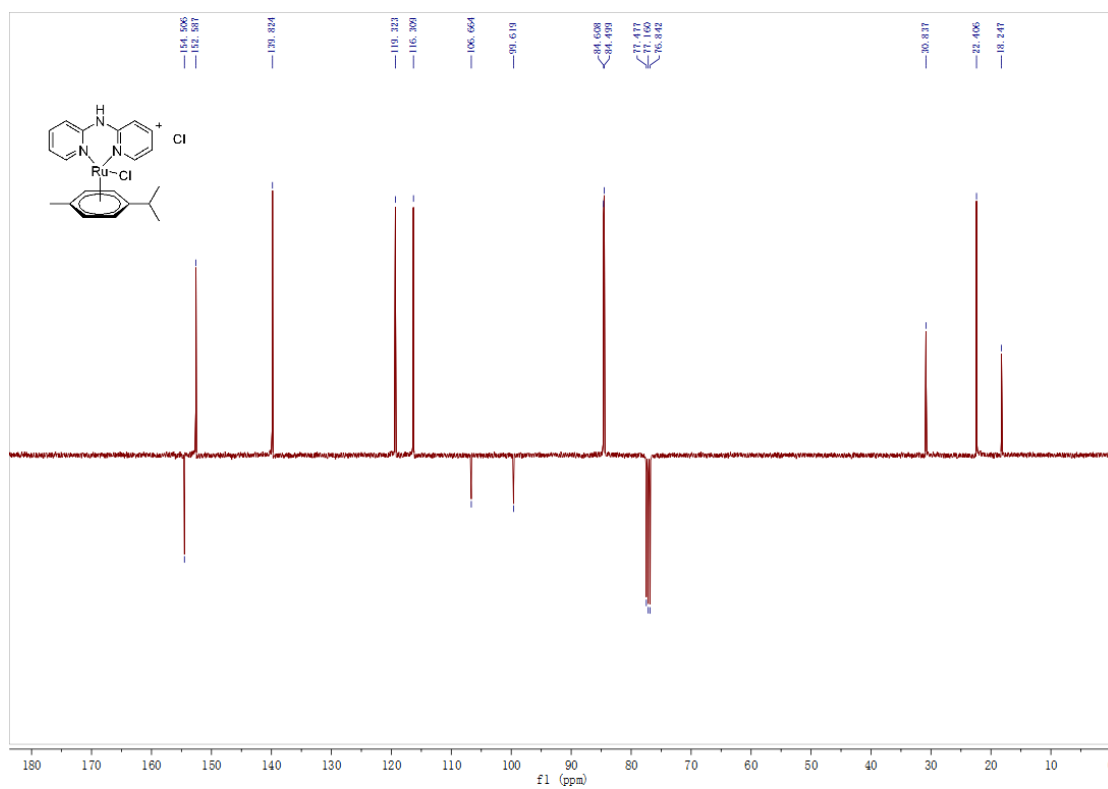


Figure S7  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K) of **Ru2**

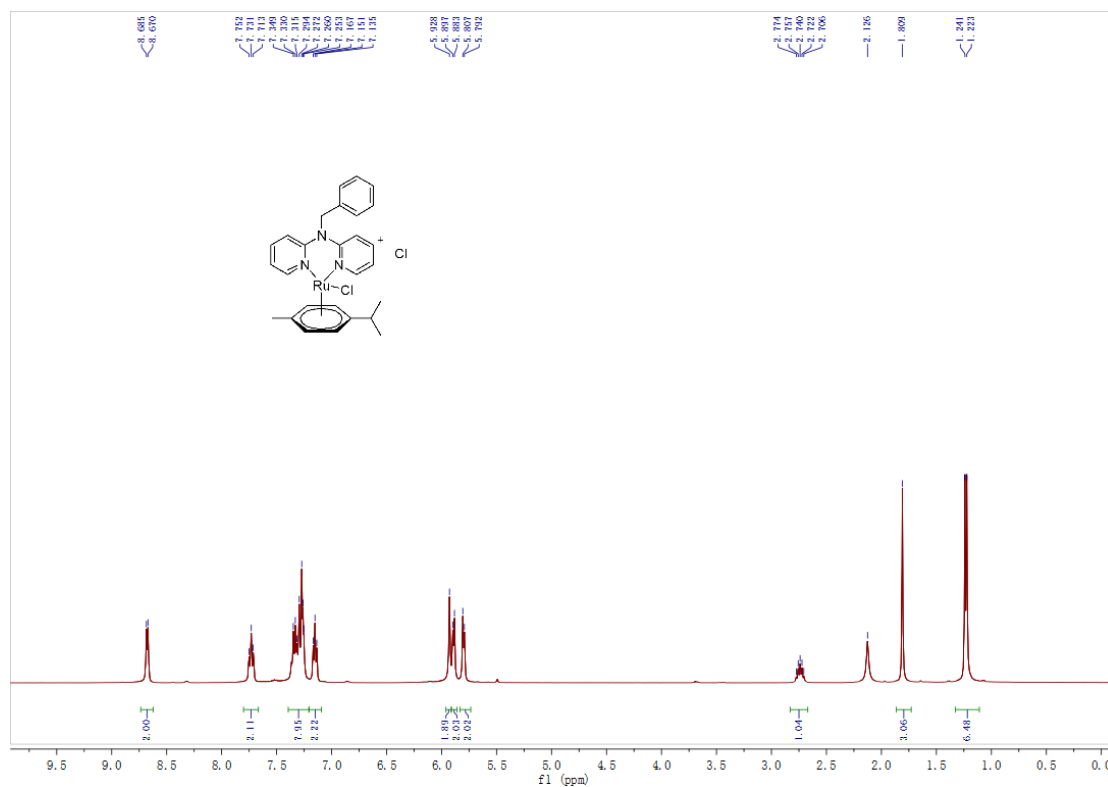


Figure S8  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz, J mod,  $\text{CDCl}_3$ ) of **Ru2**

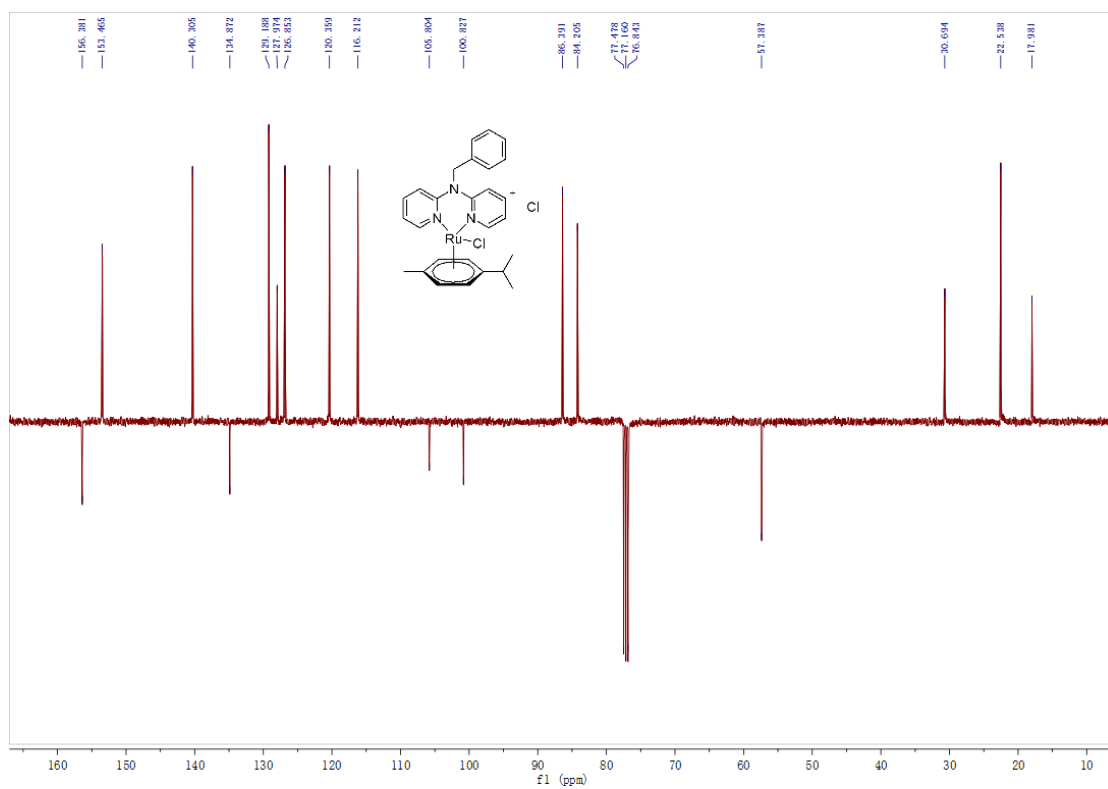


Figure S9  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K) of **Ru3**

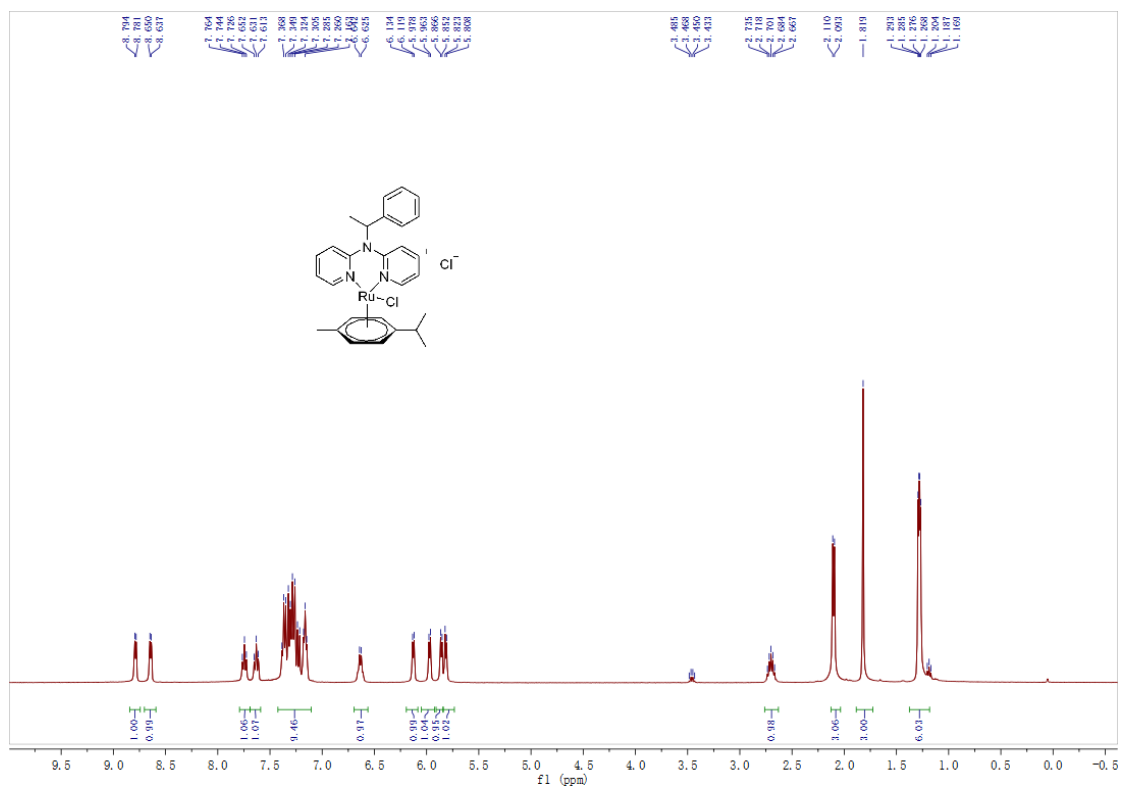


Figure S10  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz, J mod,  $\text{CDCl}_3$ ) of **Ru3**

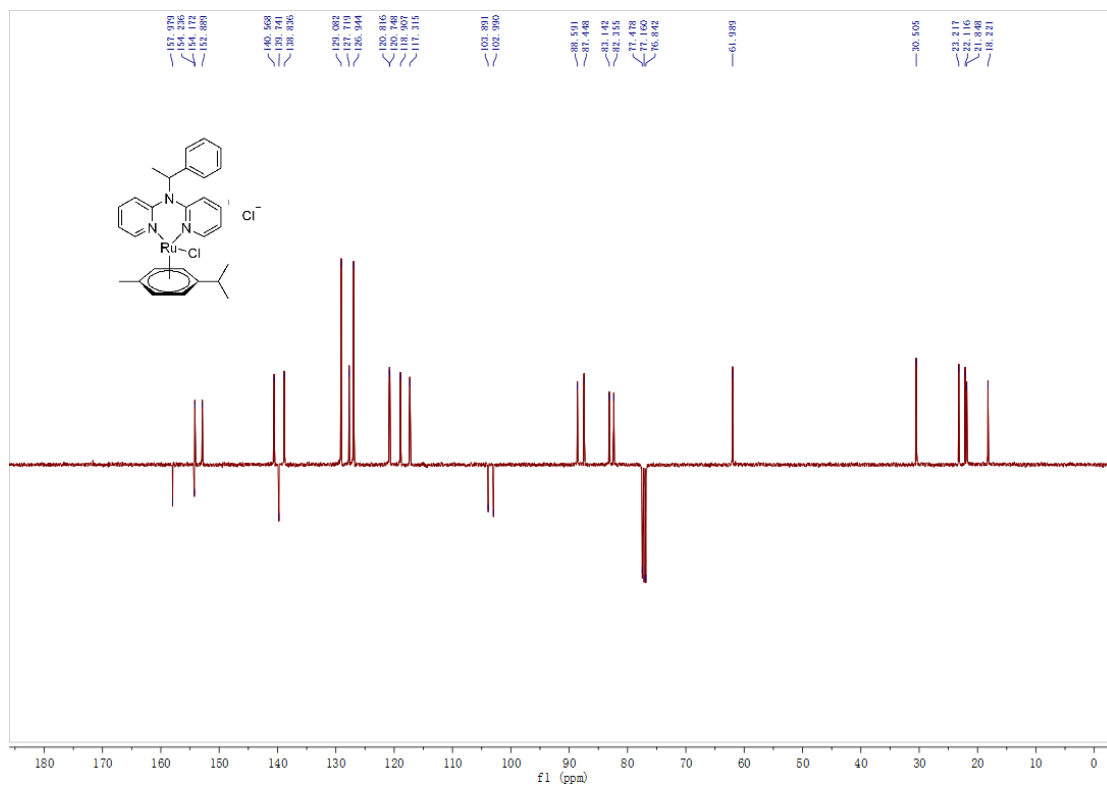


Figure S11  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K) of **Ir1**

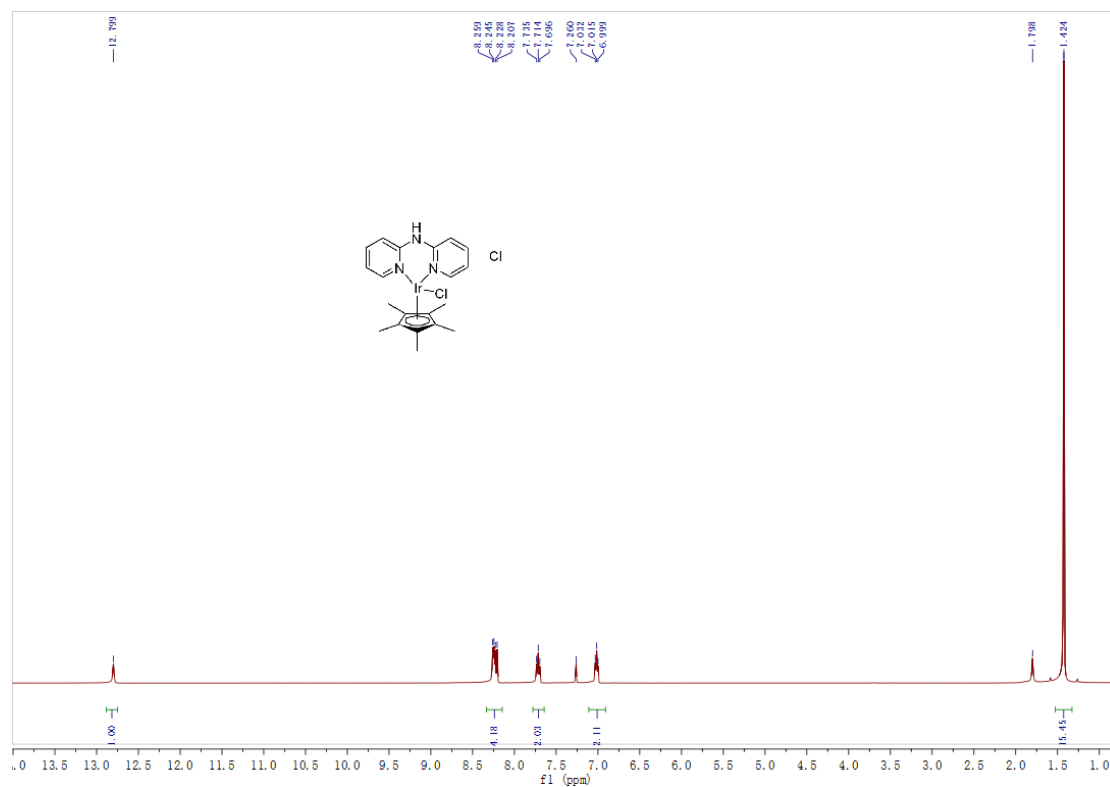


Figure S12  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz, J mod,  $\text{CDCl}_3$ ) of **Ir1**

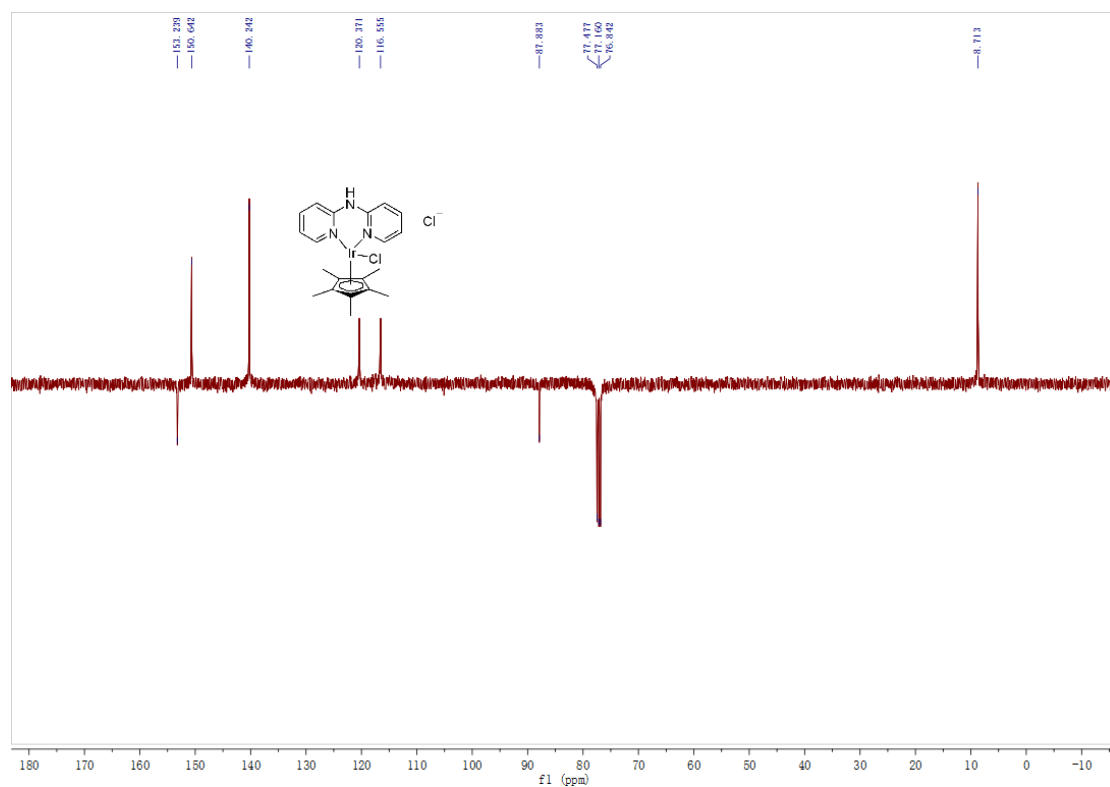


Figure S13  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K) of **Ir2**

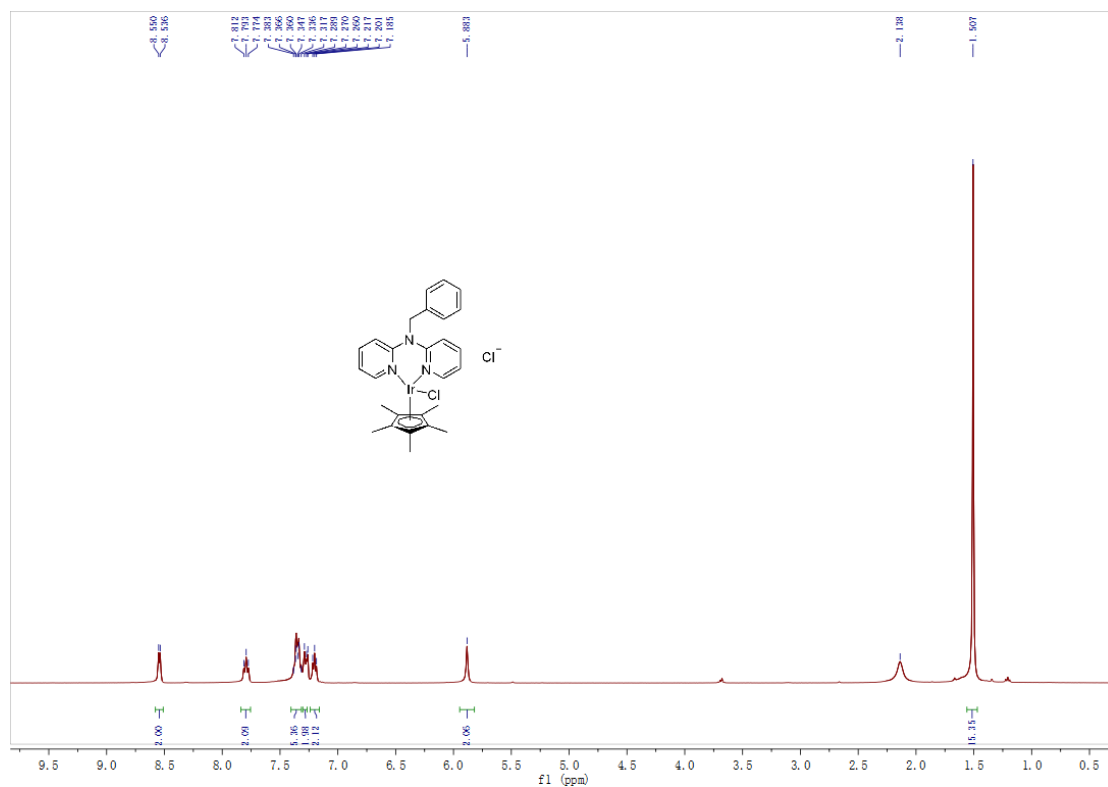


Figure S14  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz, J mod,  $\text{CDCl}_3$ ) of **Ir2**

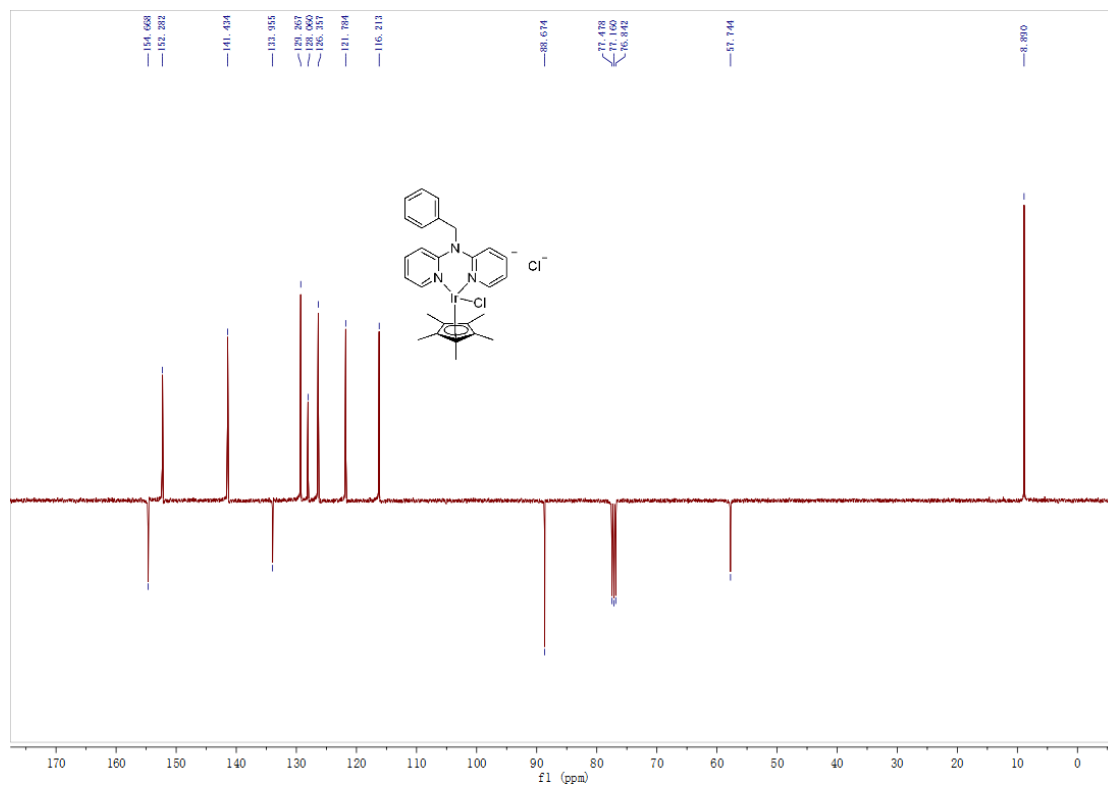




Figure S17  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K) of 1-Benzyl-5-methylpyrrolidin-2-one

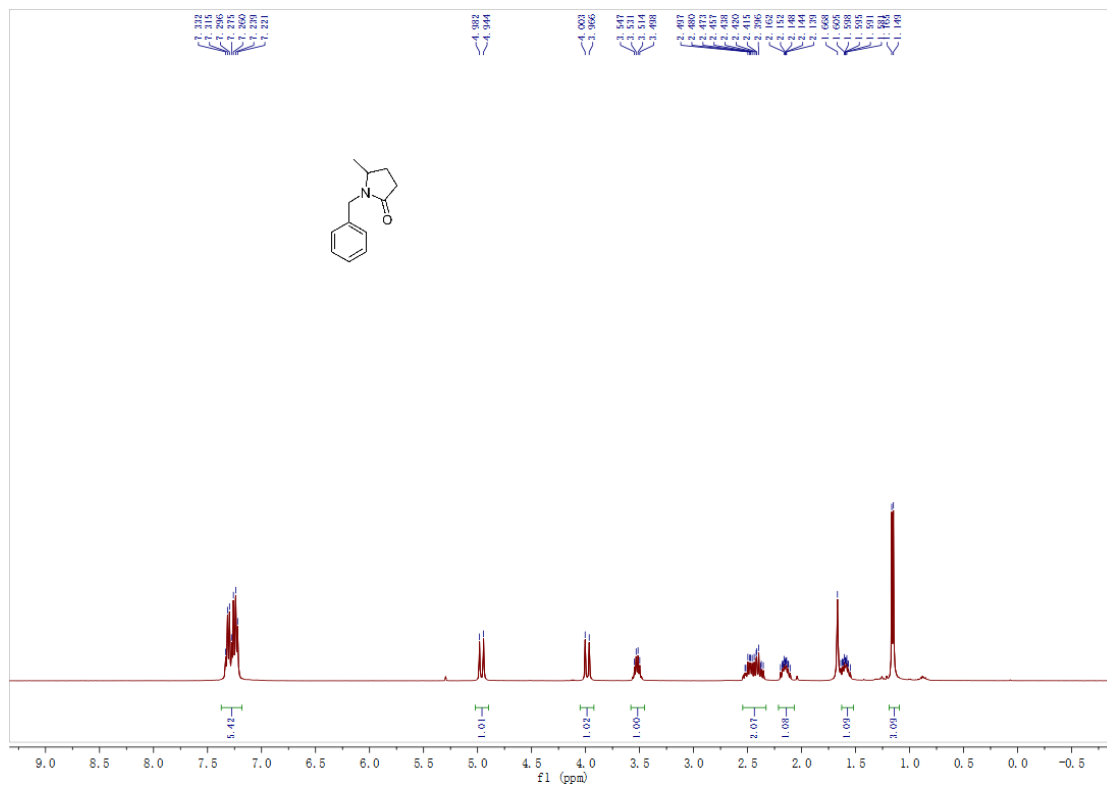
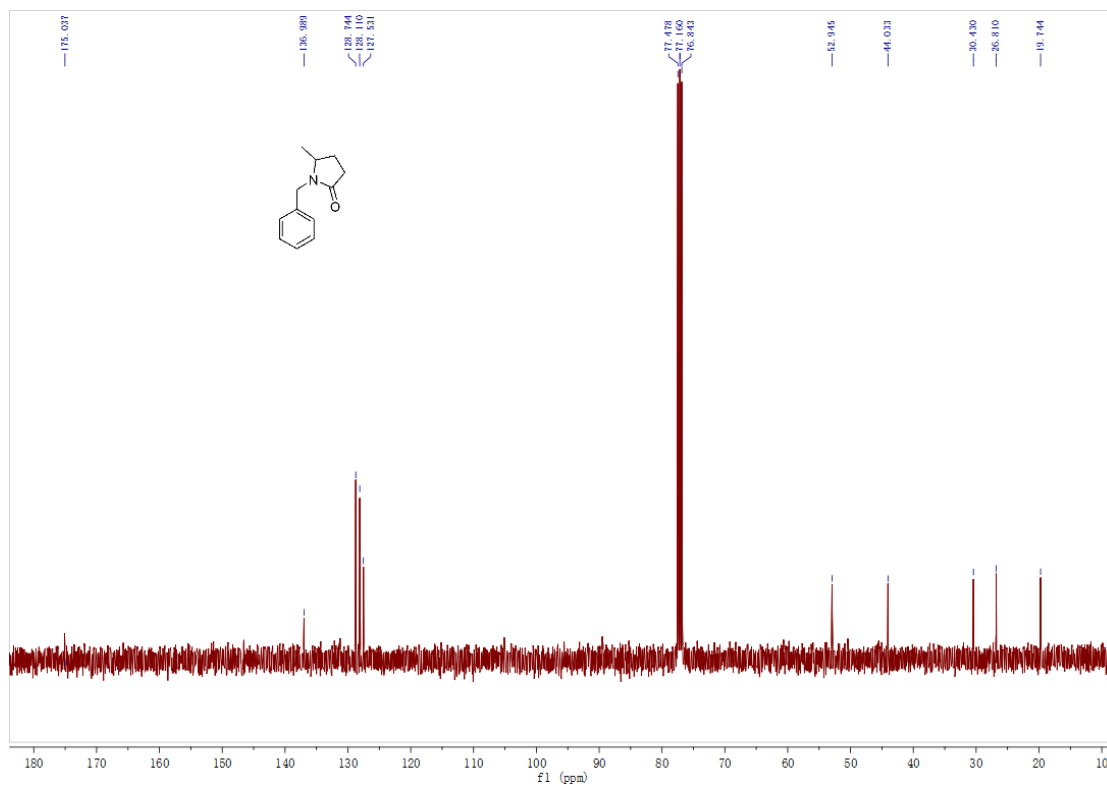


Figure S18  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ ) of 1-Benzyl-5-methylpyrrolidin-2-one





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