

Supporting Information for

**Exceptionally Active Assembled Dinuclear Ruthenium(II)-NNN Complex  
Catalysts for Transfer Hydrogenation of Ketones**

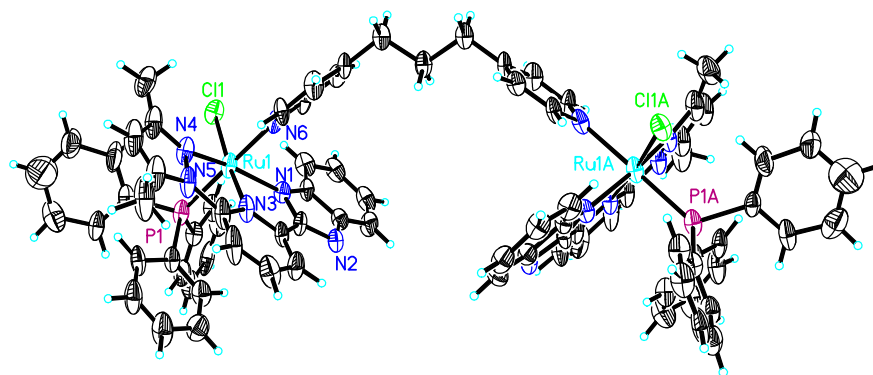
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## 1. X-Ray crystallographic data for complex 3d



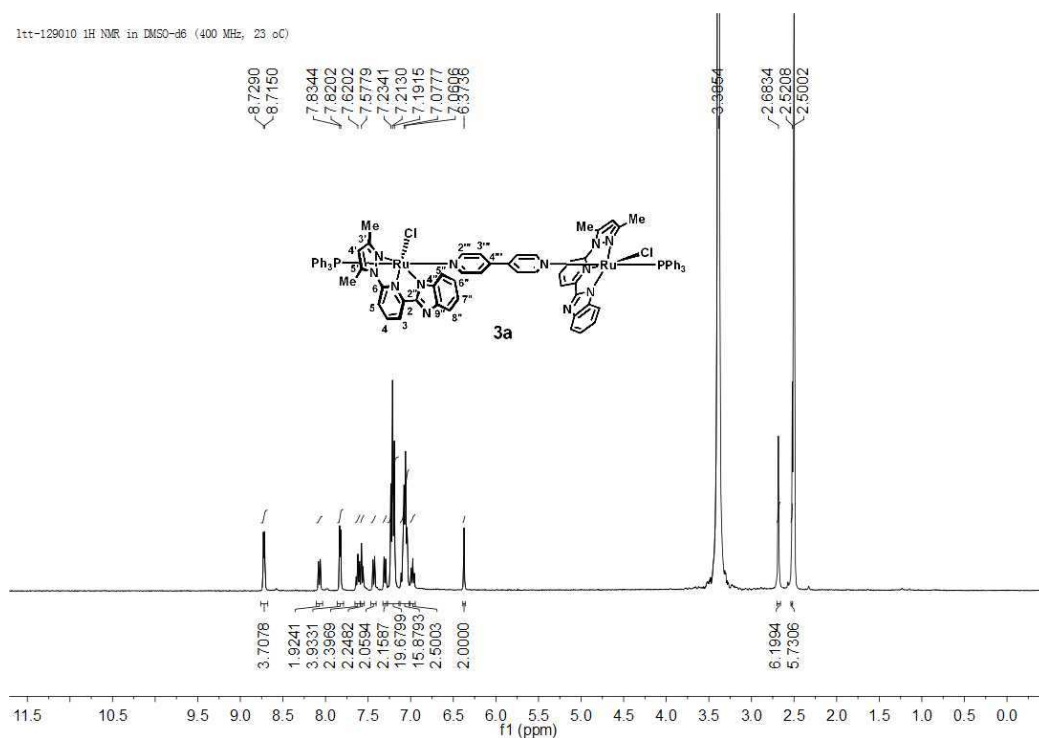
**Figure S1.** Molecular structure of complex **3d**.

**Table S1.** Crystal data and structure refinement for complex **3d**.

|                                 |                                                                                                |                |
|---------------------------------|------------------------------------------------------------------------------------------------|----------------|
| Identification code             | mo_dm14386_0m                                                                                  |                |
| Empirical formula               | C <sub>83</sub> H <sub>72</sub> Cl <sub>2</sub> N <sub>12</sub> P <sub>2</sub> Ru <sub>2</sub> |                |
| Formula weight                  | 1572.50                                                                                        |                |
| Temperature                     | 140(2) K                                                                                       |                |
| Wavelength                      | 0.71073 Å                                                                                      |                |
| Crystal system                  | Monoclinic                                                                                     |                |
| Space group                     | C 2/c                                                                                          |                |
| Unit cell dimensions            | a = 39.654(5) Å                                                                                | α = 90°        |
|                                 | b = 12.7311(17) Å                                                                              | β = 93.851(2)° |
|                                 | c = 38.082(5) Å                                                                                | γ = 90°        |
| Volume                          | 19182(4) Å <sup>3</sup>                                                                        |                |
| Z                               | 8                                                                                              |                |
| Density (calculated)            | 1.089 Mg/m <sup>3</sup>                                                                        |                |
| Absorption coefficient          | 0.446 mm <sup>-1</sup>                                                                         |                |
| F(000)                          | 6448                                                                                           |                |
| Crystal size                    | 0.250 × 0.200 × 0.060 mm <sup>3</sup>                                                          |                |
| Theta range for data collection | 1.029 to 26.000°.                                                                              |                |
| Index ranges                    | -42 ≤ h ≤ 48, -15 ≤ k ≤ 15, -46 ≤ l ≤ 46                                                       |                |
| Reflections collected           | 68464                                                                                          |                |

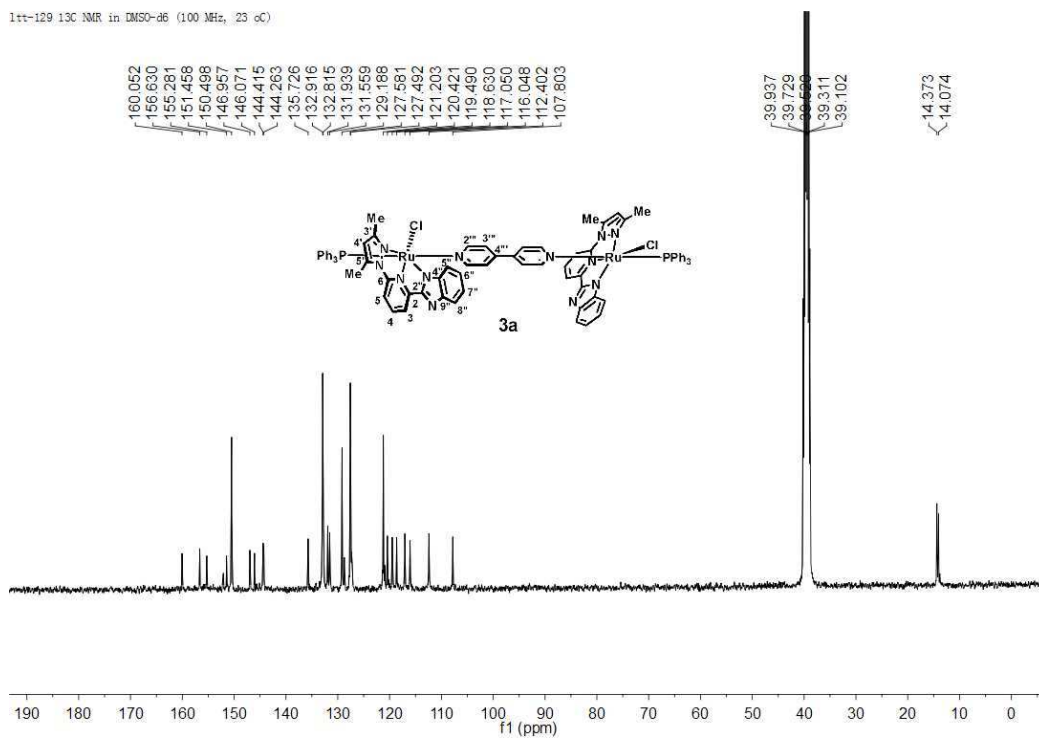
|                                   |                                             |
|-----------------------------------|---------------------------------------------|
| Independent reflections           | 18853 [R(int) = 0.0822]                     |
| Completeness to theta = 25.242°   | 99.9 %                                      |
| Absorption correction             | Semi-empirical from equivalents             |
| Max. and min. transmission        | 0.7456 and 0.5427                           |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup> |
| Data / restraints / parameters    | 18853 / 269 / 917                           |
| Goodness-of-fit on F <sup>2</sup> | 1.139                                       |
| Final R indices [I>2sigma(I)]     | R1 = 0.0894, wR2 = 0.2411                   |
| R indices (all data)              | R1 = 0.1479, wR2 = 0.2594                   |
| Extinction coefficient            | n/a                                         |
| Largest diff. peak and hole       | 1.378 and -0.705 e.Å <sup>-3</sup>          |

## 2. Copies of NMR spectra



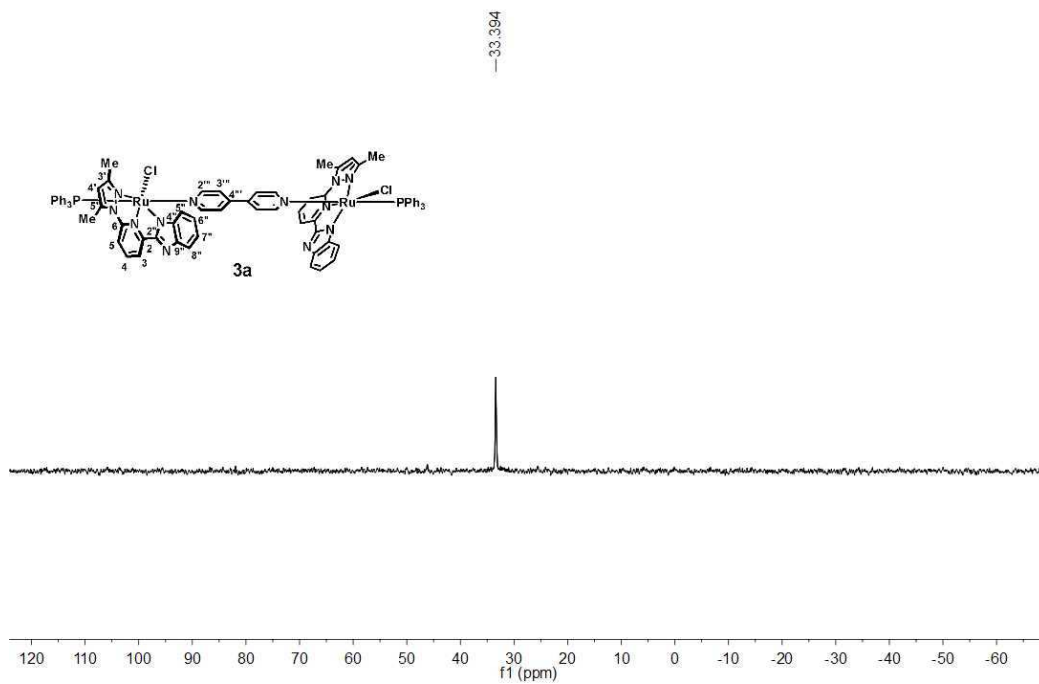
**Figure S2.** <sup>1</sup>H NMR spectrum of complex **3a** (DMSO-*d*<sub>6</sub>, 400 MHz, 23 °C).

1tt-129 13C NMR in DMSO-d6 (100 MHz, 23 °C)

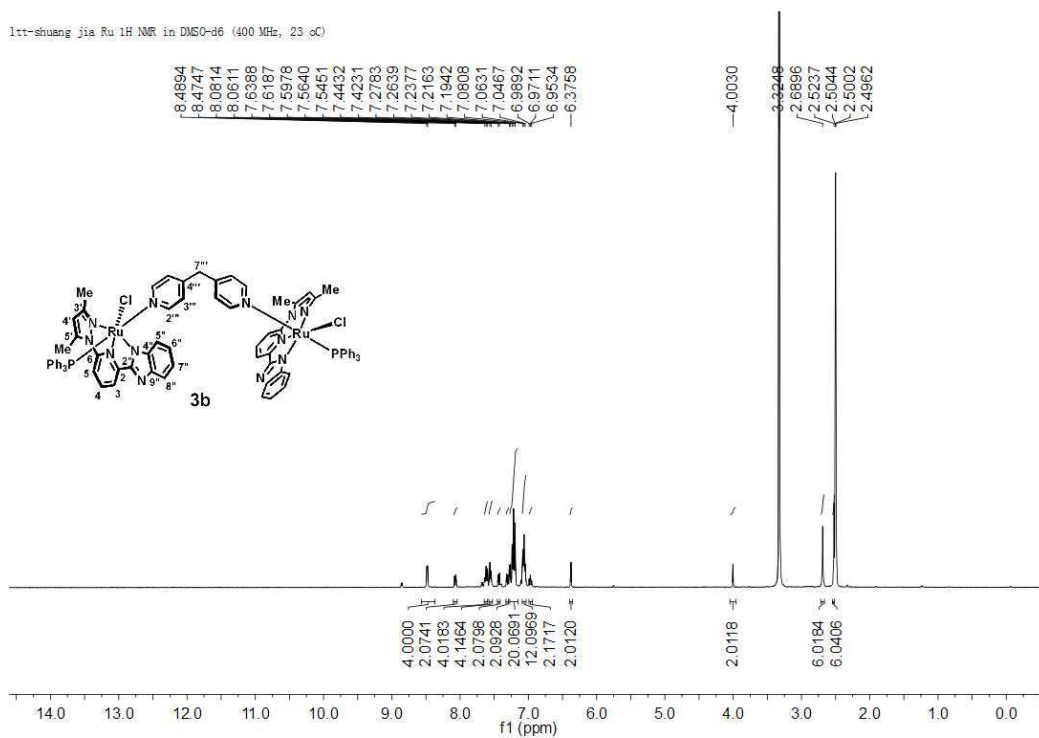


**Figure S3.** <sup>13</sup>C NMR spectrum of complex **3a** (DMSO-*d*<sub>6</sub>, 100 MHz, 23 °C).

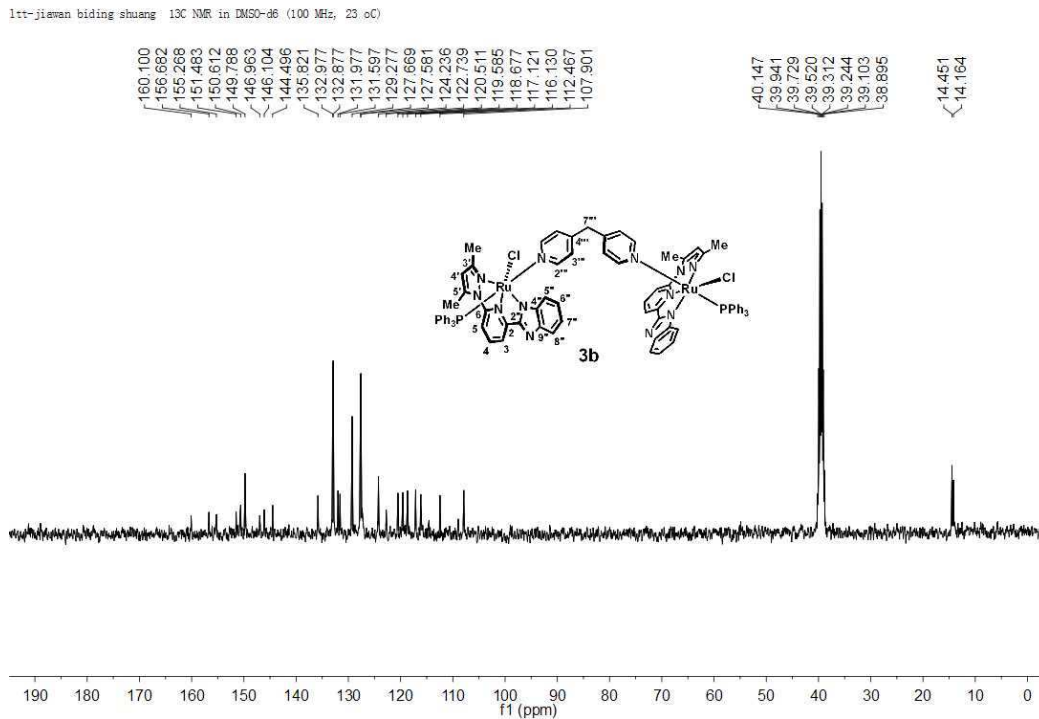
1tt-129 31P NMR in DMSO-d6 (162 MHz, 23 °C)



**Figure S4.** <sup>31</sup>P NMR spectrum of complex **3a** (DMSO-*d*<sub>6</sub>, 162 MHz, 23 °C).

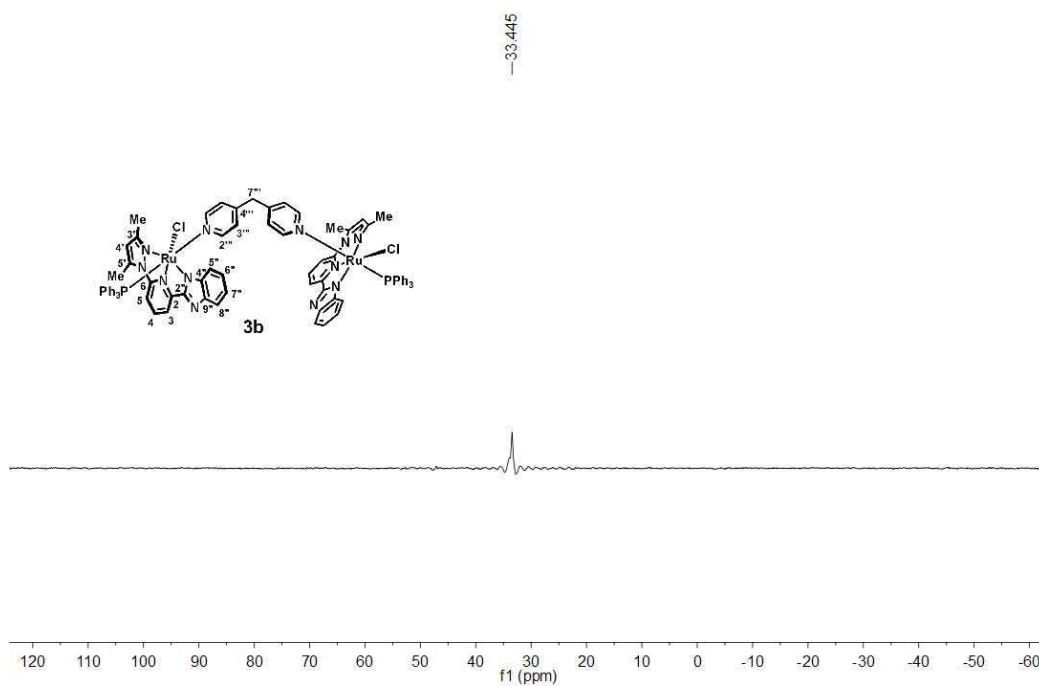


**Figure S5.**  $^1\text{H}$  NMR spectrum of complex **3b** ( $\text{DMSO}-d_6$ , 400 MHz, 23 °C).



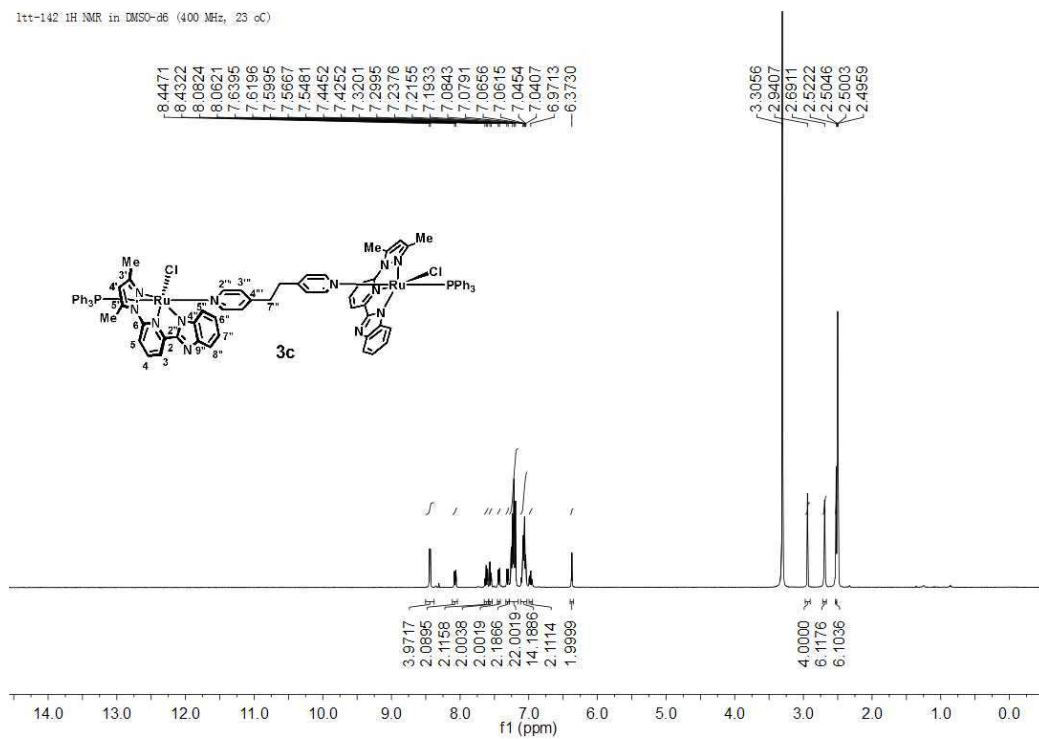
**Figure S6.**  $^{13}\text{C}$  NMR spectrum of complex **3b** ( $\text{DMSO}-d_6$ , 100 MHz, 23 °C).

1tt-jiewan biding shuang-1 31P NMR in DMSO-d6 (162 MHz, 23 °C)



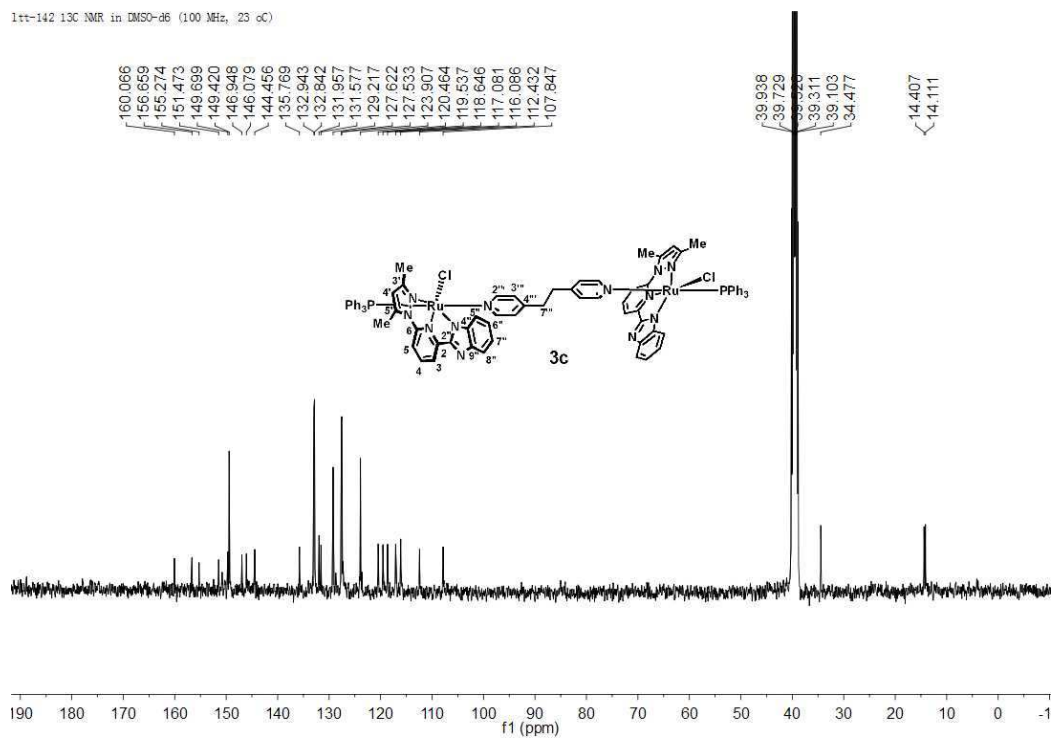
**Figure S7.**  $^{31}\text{P}$  NMR spectrum of complex **3b** (DMSO- $d_6$ , 162 MHz, 23 °C).

1tt-142 1H NMR in DMSO-d6 (400 MHz, 23 °C)



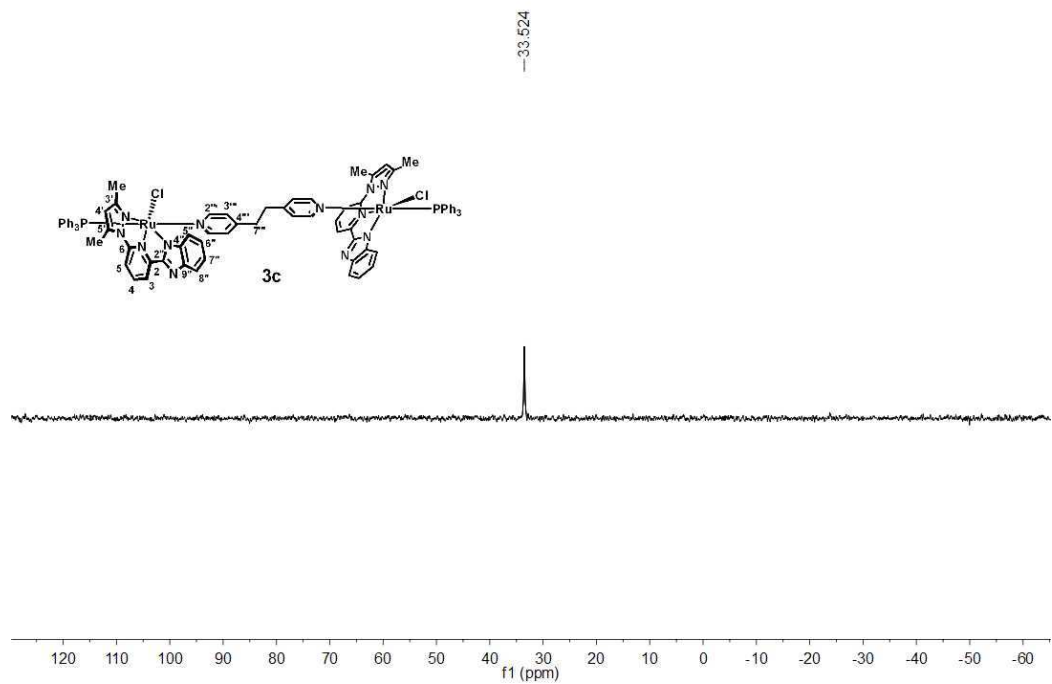
**Figure S8.**  $^1\text{H}$  NMR spectrum of complex **3c** (DMSO- $d_6$ , 400 MHz, 23 °C).

1tt-142  $^{13}\text{C}$  NMR in DMSO- $d_6$  (100 MHz, 23 °C)

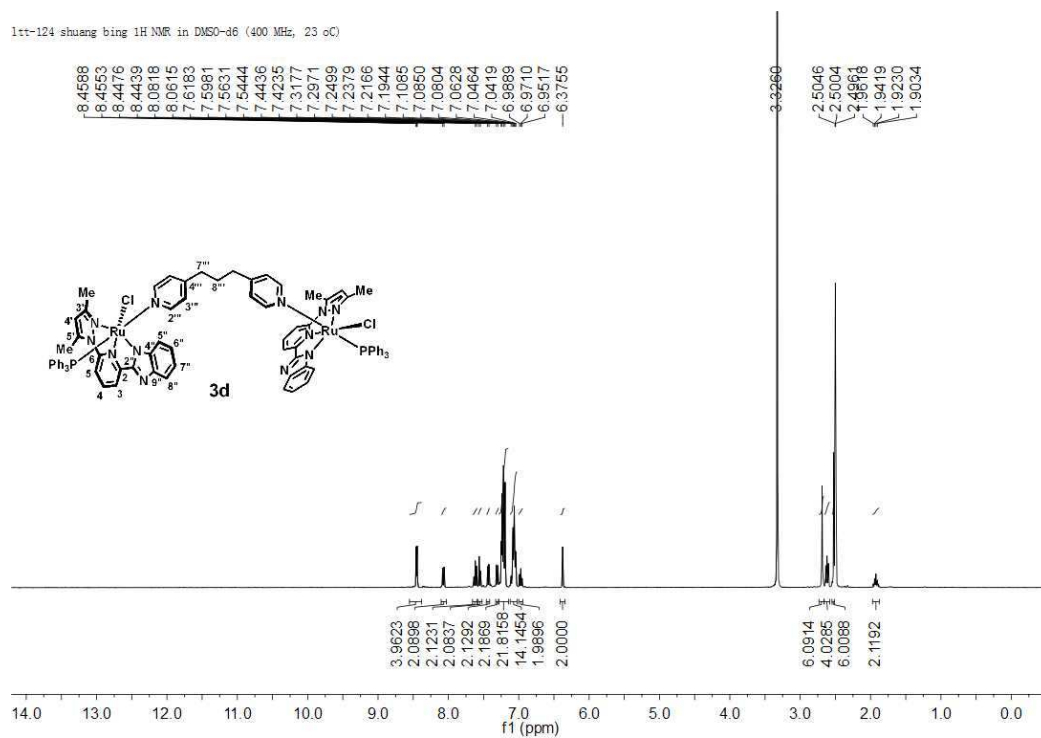


**Figure S9.**  $^{13}\text{C}$  NMR spectrum of complex **3c** (DMSO- $d_6$ , 100 MHz, 23 °C).

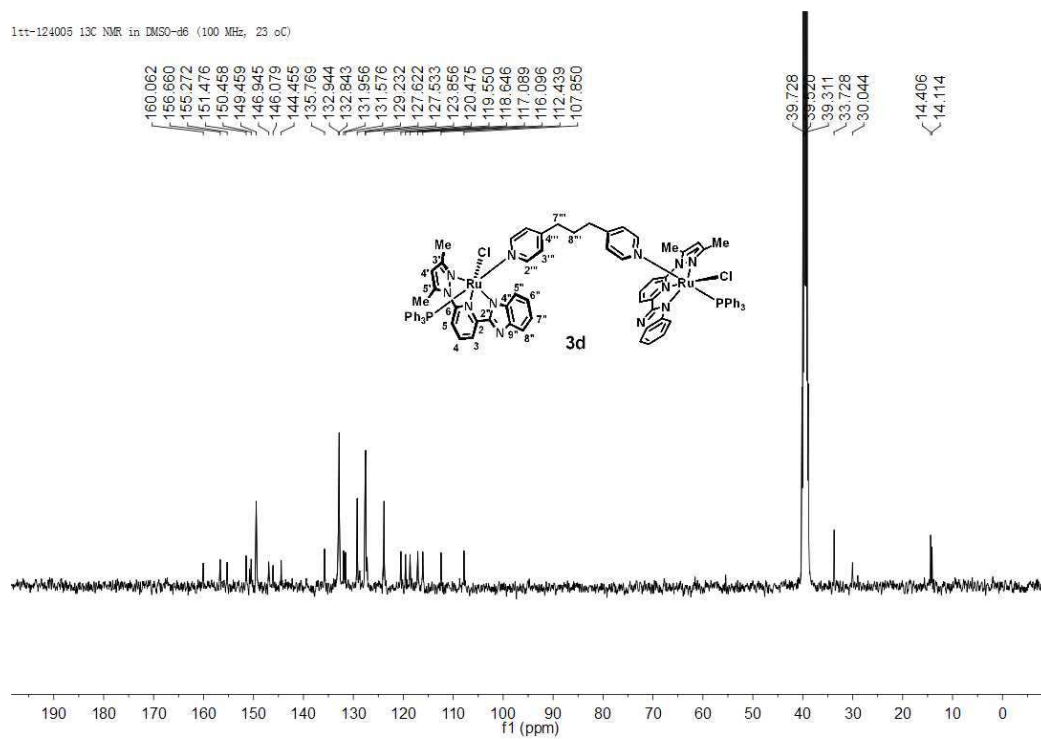
1tt-142  $^{31}\text{P}$  NMR in DMSO- $d_6$  (162 MHz, 23 °C)



**Figure S10.**  $^{31}\text{P}$  NMR spectrum of complex **3c** (DMSO- $d_6$ , 162 MHz, 23 °C).

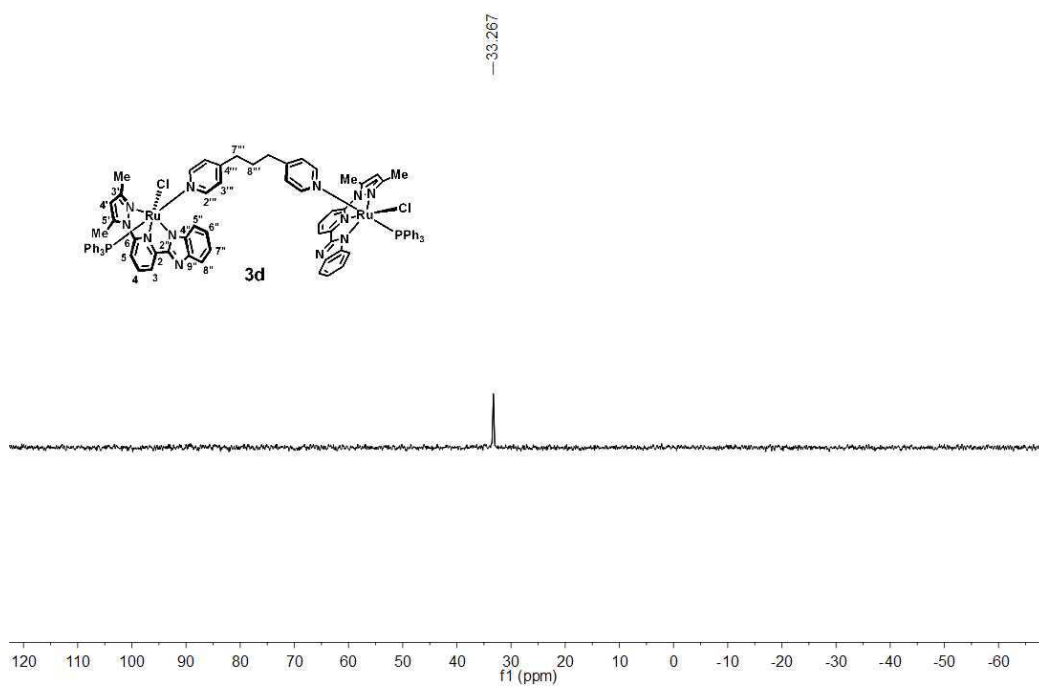


**Figure S11.**  $^1\text{H}$  NMR spectrum of complex **3d** (DMSO- $d_6$ , 400 MHz, 23 °C).



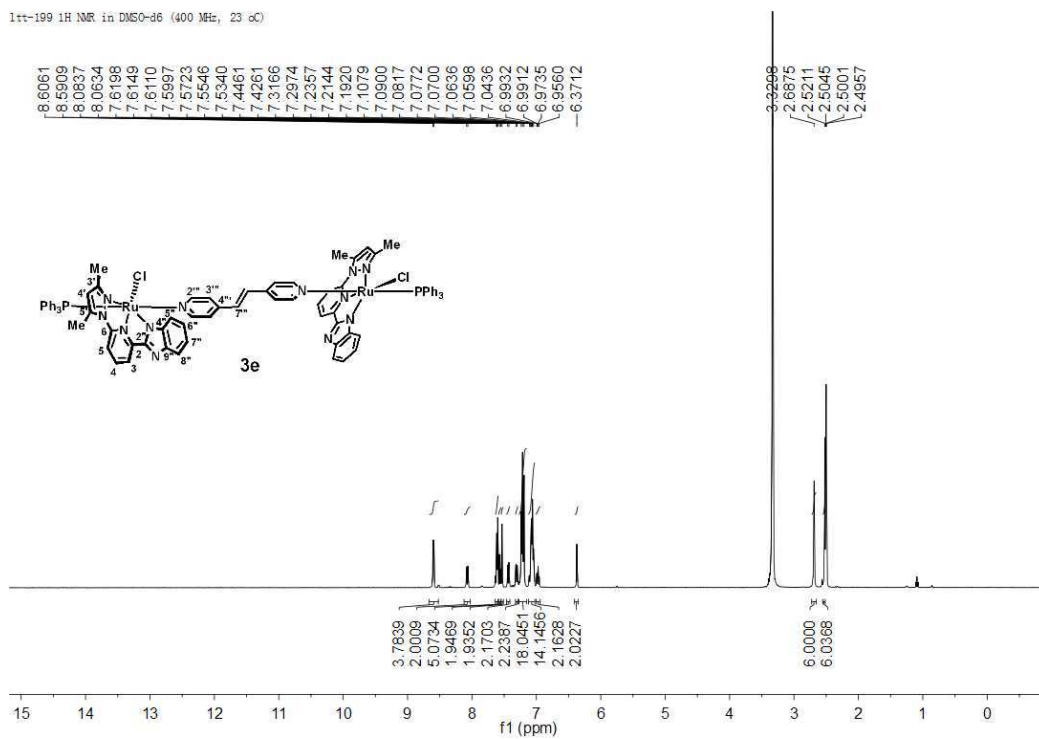
**Figure S12.**  $^{13}\text{C}$  NMR spectrum of complex **3d** (DMSO- $d_6$ , 100 MHz, 23 °C).

1tt-124-04 31P NMR in DMSO-d6 (162 MHz, 23 °C)



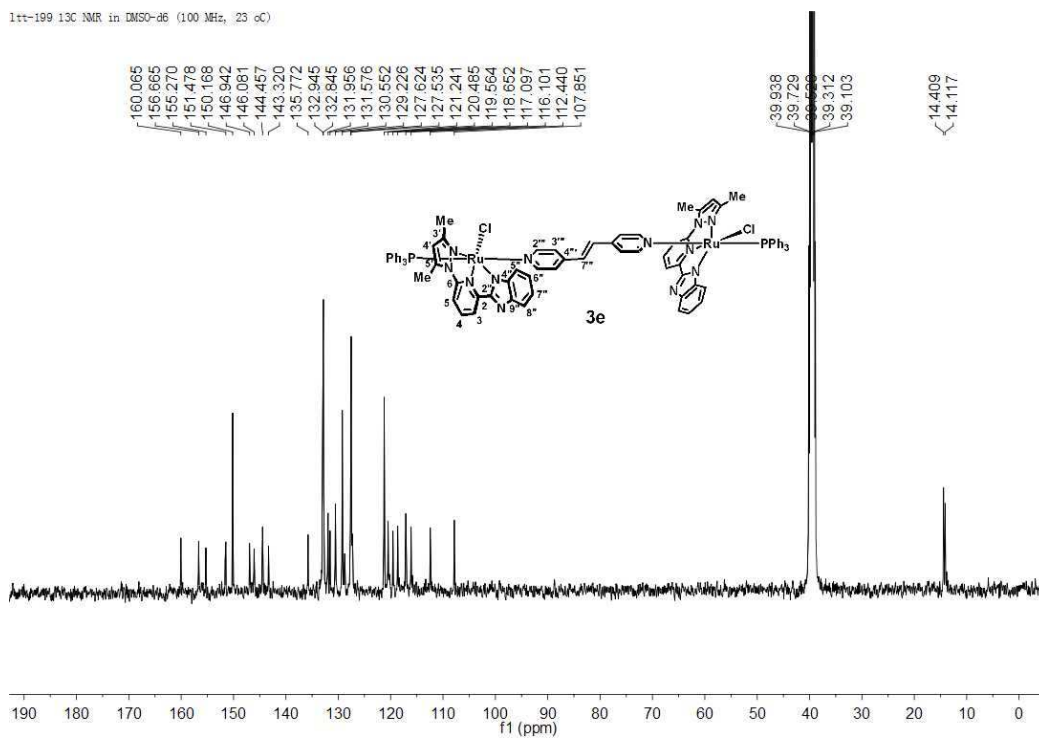
**Figure S13.** <sup>31</sup>P NMR spectrum of complex **3d** (DMSO-*d*<sub>6</sub>, 162 MHz, 23 °C).

1tt-199 1H NMR in DMSO-d6 (400 MHz, 23 °C)



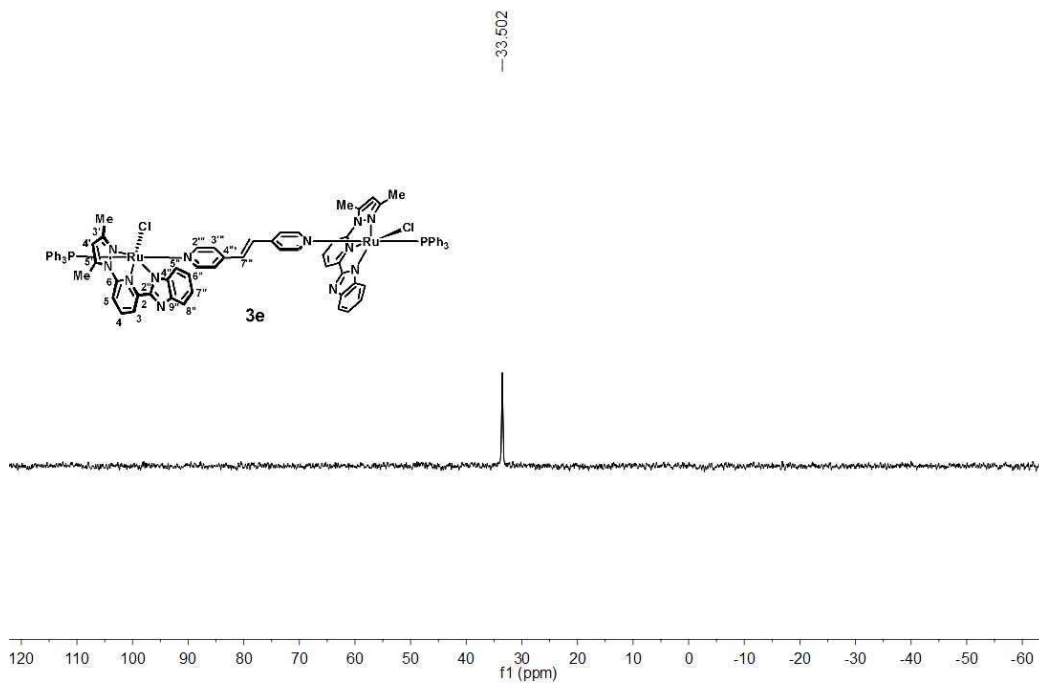
**Figure S14.** <sup>1</sup>H NMR spectrum of complex **3e** (DMSO-*d*<sub>6</sub>, 400 MHz, 23 °C).

1tt-199  $^{13}\text{C}$  NMR in DMSO- $d_6$  (100 MHz, 23  $^{\circ}\text{C}$ )

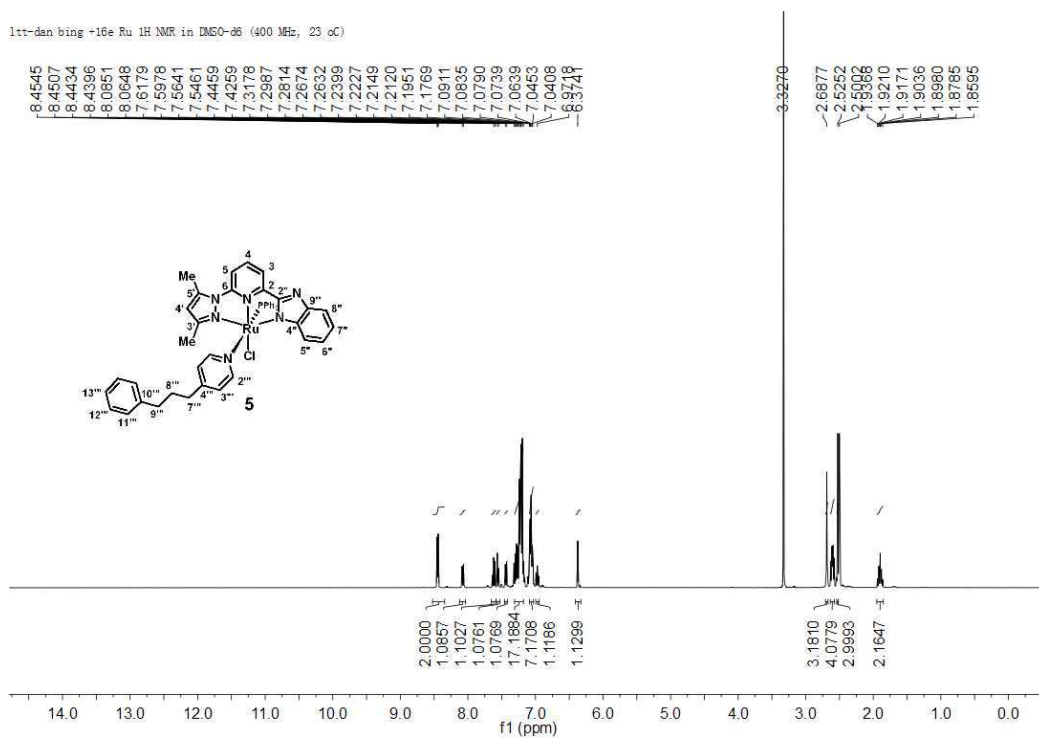


**Figure S15.**  $^{13}\text{C}$  NMR spectrum of complex **3e** (DMSO- $d_6$ , 100 MHz, 23  $^{\circ}\text{C}$ ).

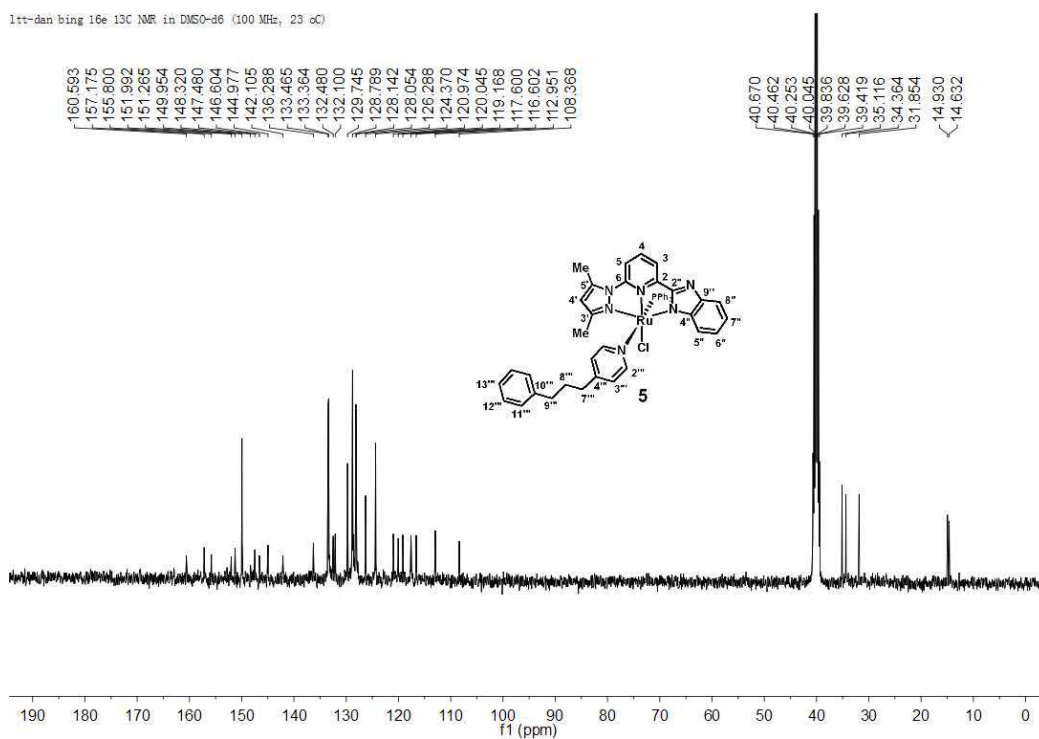
1tt-199  $^{31}\text{P}$  NMR in DMSO- $d_6$  (162 MHz, 23  $^{\circ}\text{C}$ )



**Figure S16.**  $^{31}\text{P}$  NMR spectrum of complex **3e** (DMSO- $d_6$ , 162 MHz, 23  $^{\circ}\text{C}$ ).



**Figure S17.** <sup>1</sup>H NMR spectrum of complex **5** (DMSO-*d*<sub>6</sub>, 400 MHz, 23 °C).



**Figure S18.** <sup>13</sup>C NMR spectrum of complex **5** (DMSO-*d*<sub>6</sub>, 100 MHz, 23 °C).

—33.542

