

Supporting Information for

**A Highly Active Ruthenium(II) Pyrazolyl-Pyridyl-Pyrazole Complex Catalyst
for Transfer Hydrogenation of Ketones**

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Experimental procedures and analytical data:

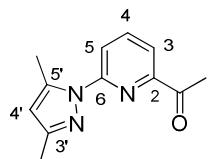
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1. General Considerations

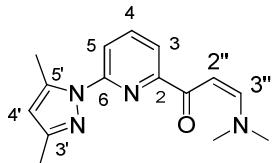
The solvents were dried and distilled prior to use by the literature methods. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker DRX-400 spectrometer and all chemical shift values refer to $\delta_{\text{TMS}} = 0.00$ ppm or CDCl_3 ($\delta(^1\text{H})$, 7.26 ppm; $\delta(^{13}\text{C})$, 77.16 ppm). The HRMS analysis was obtained on a Waters GC-TOF CA156 mass spectrometer. All the melting points were uncorrected. Analytical TLC plates, Sigma-Aldrich silica gel 60_{F200} were viewed by UV light (254 nm). Column chromatographic purifications were performed on SDZF silica gel 160. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated.

2. Experimental Procedures

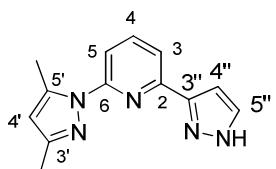


Synthesis of 2-acetyl-6-(3,5-dimethylpyrazol-1-yl)pyridine (2): Under nitrogen atmosphere, to a suspension of 2-bromo-6-(3,5-dimethylpyrazol-1-yl)pyridine (10.00 g, 39.7 mmol) in 150 mL Et_2O was added 17.5 mL $n\text{BuLi}$ (2.5 M in hexane, 43.6 mmol) at -78 °C over a period of 30 minutes. The resultant mixture was stirred at -40 °C for 1 h and then cooled to -78 °C. *N,N*-Dimethylacetamide (6.0 mL, 67.4 mmol) was added, and the mixture was allowed to warm up to room temperature. The reaction was quenched with 45 mL saturated aqueous NH_4Cl solution. The resultant mixture was extracted with diethyl ether (3×50 mL) and the organic phase was separated, dried over anhydrous Na_2SO_4 and filtered. All the volatiles were removed under reduced pressure and the resultant residue was purified by flash silica gel column chromatography (petroleum ether (60-90 °C)/ethyl acetate, v/v = 30:1) to afford compound **2** as a white solid (5.60 g, 65%). M.p.: 105-107 °C. ^1H NMR (CDCl_3 , 23 °C) δ 8.11 (d, $J = 7.8$ Hz, 1 H, 5-H), 7.88 (t, 1 H, 4-H), 7.85 (d, $J = 7.5$ Hz, 1 H, 3-H), 6.02 (s, 1 H, 4'-H), 2.73 (s, 3 H, CO-CH_3), 2.68 and 2.29 (s each, 3:3 H,

3' and 5'-CH₃). ¹³C{¹H} NMR (CDCl₃, 23 °C) δ 199.5 (s, C=O), 152.8, 151.2, 150.4, and 141.6 (Cq each, C=N and C-N), 139.3 (s, C4), 119.0 and 118.3 (C3 and C5), 109.8 (s, C4'), 26.3 (CO-CH₃), 15.3 and 13.7 (3' and 5'-CH₃). HRMS Calcd for C₁₂H₁₃N₃O: 215.1059. Found: 215.1062.

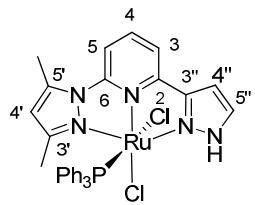


Synthesis of 1-(6-(3,5-dimethyl-1H-pyrazol-1-yl)pyridin-2-yl)-3-(dimethylamino)prop-2-en-1-one (3): A mixture of compound **2** (3.00 g, 13.9 mmol) and 15 mL dimethylformamide dimethyl acetal was heated to reflux for 14 h under nitrogen atmosphere, yielding a dark brown solution. After cooled to ambient temperature, excessive dimethylformamide dimethyl acetal was removed *in vacuo* to give a brown solid which was subject to purification by flash silica gel column chromatography (petroleum ether (60-90 °C)/ethyl acetate, v/v = 20:1) to afford compound **3** as a yellow solid (3.30 g, 88%). M.p.: 142- 143 °C. ¹H NMR (CDCl₃, 23 °C) δ 7.99 and 7.96 (d each, *J* = 7.5 and 8.2 Hz, 1:1 H, 3-H and 5-H), 7.90-7.85 (m, 2 H, 4-H and 3''-H), 6.42 (d, *J* = 12.7 Hz, 1 H, 2''-H), 6.00 (s, 1 H, 4'-H), 3.16 and 2.93 (s each, 3:3 H, N(CH₃)₂), 2.76 and 2.29 (s each, 3:3 H, C3' and 5'-CH₃). ¹³C{¹H} NMR (CDCl₃, 23 °C) δ 186.2 (Cq, C=O), 154.6 (s, C3''), 154.0, 152.2, 149.9 and 141.2 (Cq each, C=N and C-N), 139.1 (C4), 118.8 and 117.4 (C3 and C5), 109.3 (C4'), 91.6 (s, C2''), 45.2 and 37.4 (N(CH₃)₂), 15.1 and 13.8 (C3' and C5'-CH₃). HRMS Calcd for C₁₅H₁₈N₄O: 270.1481. Found: 270.1476.

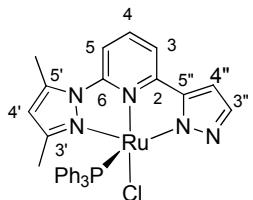


Synthesis of 2-(1H-pyrazol-3-yl)-6-(3,5-dimethylpyrazol-1-yl)- pyridine (4): A mixture of compound **3** (1.10 g, 4.1 mmol) and 7 mL hydrazine monohydrate in ethanol (15 mL) was heated to reflux for 1.5 h. Water (15 mL) was added and the mixture was cooled to ambient temperature. The white precipitate was collected by

filtration, successively washed with cold water and pentane, and dried *in vacuo*. Recrystallisation from CH₂Cl₂/hexane (v/v = 1:2) afforded **4** as a white solid (0.80 g, 82%). M.p.: 114-116 °C. ¹H NMR (CDCl₃, 23 °C) δ 11.16 (br, 1 H, NH), 7.77-7.74 (m, 2 H, 3-H and 5"-H), 7.62 (m, 2 H, 5-H and 4-H), 6.81 (br, 1 H, 4"-H), 6.01 (s, 1 H, 4'-H), 2.69 and 2.31 (s each, 3:3 H, C3' and 5'-CH₃). ¹³C{¹H} NMR (CDCl₃, 23 °C) δ 153.1, 150.1, 147.8, 146.1, and 141.6 (Cq each, C=N and C-N), 139.2 (C4), 136.1 (C5"), 116.8 and 114.7 (C3 and C5), 109.3 (C4'), 104.0 (C4"), 15.0 and 13.7 (C3' and C5'-CH₃). HRMS Calcd for C₁₃H₁₃N₅: 239.1171. Found: 239.1174.



Synthesis of complex 5: Under nitrogen atmosphere, a mixture of RuCl₂(PPh₃)₃ (0.81 g, 0.84 mmol) and compound **4** (0.20 g, 0.84 mmol) in toluene (40 mL) was refluxed for 2 h. The mixture was cooled to ambient temperature to precipitate a red-brown microcrystalline solid. The solid was filtered off, washed with diethyl ether (3×50 mL), and dried under reduced pressure to afford complex **5** (0.48 g, 85%) as a red-brown crystalline solid. M.p.: dec. > 230 °C. ¹H NMR (CDCl₃, 23 °C) δ 14.54 (s, 1 H, NH), 7.64 and 7.56 (d each, *J* = 6.3 and 7.0 Hz, 1:1 H, 3-H and 5-H), 7.29-7.04 (m, 16 H, 4-H, and Ph in PPh₃), 7.05 (d, *J* = 6.8 Hz, 1 H, 5"-H), 6.77 (br, 1 H, 4"-H), 6.11 (s, 1 H, 4'-H), 2.56 and 2.16 (s each, 3:3 H, C3' and C5'-CH₃). ¹³C{¹H} NMR (CDCl₃, 23 °C) δ 157.8, 155.6, 153.3, 150.7, and 132.0 (Cq each, C=N and C-N), 144.7 (C4), 135.6 (C5"), 133.3 (d, *J* = 9.6 Hz), 129.6, and 128.0 (d, *J* = 9.3 Hz) (CH of 3×Ph), 131.2 (Cq and d, *J* = 82.6 Hz, *i*-C of PPh₃), 116.7 and 113.1 (C3 and C5), 107.8 (C4'), 105.3 (s, C4"), 15.3 and 14.6 (C3' and C5'-CH₃). ³¹P{¹H} NMR (CDCl₃, 23 °C) δ 46.1. Anal. Calcd for C₃₁H₂₈Cl₂N₅PRu: C, 55.28; H, 4.19; N, 10.40. Found: C, 51.81; H, 4.81; N, 9.69.

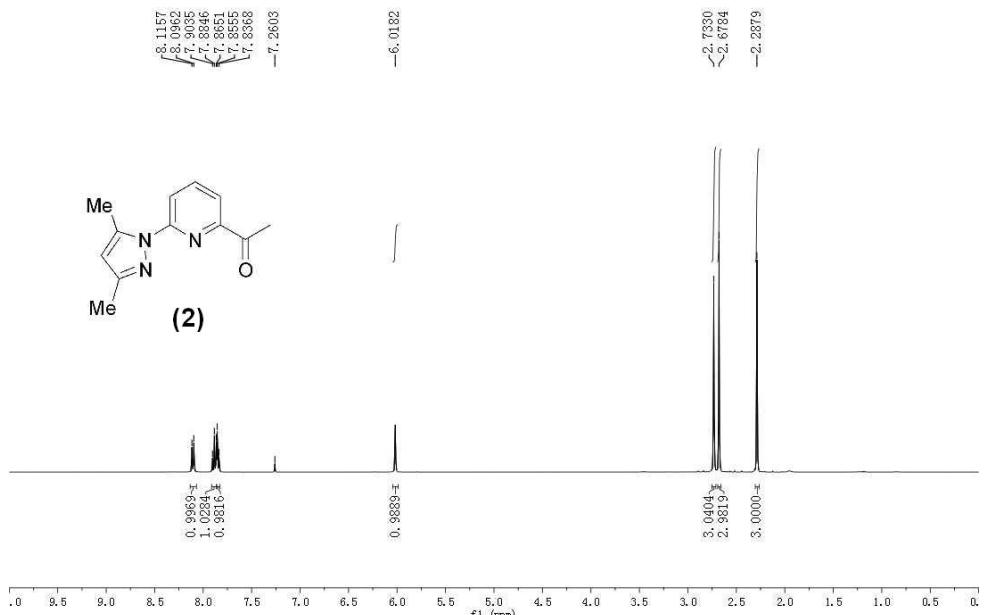


Synthesis of complex 6: Under nitrogen atmosphere, a mixture of complex **5** (0.240 g, 0.36 mmol) and K_2CO_3 (0.500 g, 3.6 mmol) in CH_2Cl_2 (30 mL) was stirred at ambient temperature for 10 h and then passed through a short pad of celite which was rinsed with 2×5 mL CH_2Cl_2 . The filtrate was combined and all the volatiles were removed under reduced pressure to afford complex **6** (0.205 g, 90%) as a red-brown crystalline solid. M.p.: dec. > 170 °C. 1H NMR ($CDCl_3$, 23 °C) δ 7.65 (t, 1 H, 4-H), 7.54-7.46 and 7.32-7.28 (m each, 9:7 H, 3-H and CH of PPh_3), 7.17 (d, J = 7.8 Hz, 1 H, 5-H), 6.53 (s, 1 H, 4'-H), 6.45 (d, J = 2.3 Hz, 1 H, 3''-H), 6.28 (d, J = 2.2 Hz, 1 H, 4''-H), 2.96 and 2.92 (s each, 3:3 H, C3' and C5'-CH₃). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C) δ 158.2, 154.8, 152.7, 149.7, and 144.0 (Cq each, C=N and C-N), 140.2 (C4), 134.4 (s, C3''), 133.8 (Cq, *i*-C of PPh_3), 133.4 (d, J = 9.8 Hz), 129.4, and 127.7 (d, J = 9.0 Hz) (CH of PPh_3), 114.5 and 111.6 (C3 and C5), 106.4 and 105.8 (C4' and C4''), 16.1 and 15.2 (C3' and C5'-CH₃). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 23 °C) δ 46.6. Anal. Calcd for $C_{31}H_{27}ClN_5PRu$: C, 58.44; H, 4.27; N, 10.99. Found: C, 57.61; H, 4.31; N, 10.89.

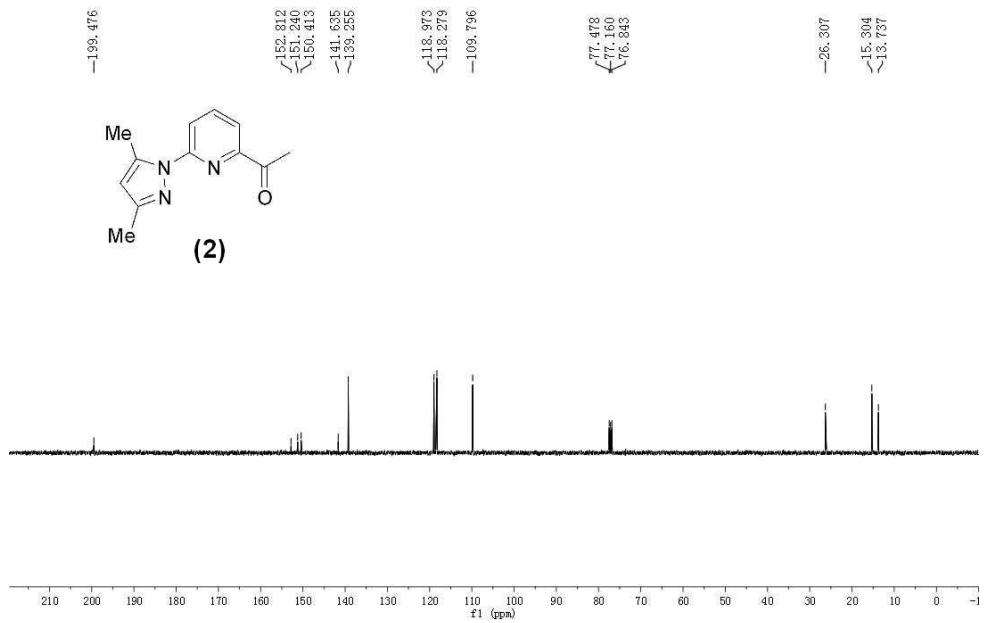
A general procedure for transfer hydrogenation of ketones: A catalyst solution was prepared by dissolving complex **5** (6.7 mg, 10.0 μ mol) in *iso*-propanol (198.0 mL). Under nitrogen atmosphere, the mixture of a ketone (2.0 mmol) and 19.8 mL of the catalyst solution containing 1.0 μ mol of **5** was stirred at 82 °C for 5 minutes. Then 0.2 mL of a 0.1 M *iPrOK* solution in *iso*-propanol was introduced to initiate the transfer hydrogenation reaction. At the stated time, 0.05 mL of the reaction mixture was sampled and immediately diluted with 0.5 mL of *iso*-propanol at ambient temperature for GC analysis. After the reaction was complete, the reaction mixture was condensed under reduced pressure and subject to purification by flash silica gel column chromatography to afford the alcohol product. All of the alcohol products were identified by comparison with the authentic samples and/or by proton NMR measurements.

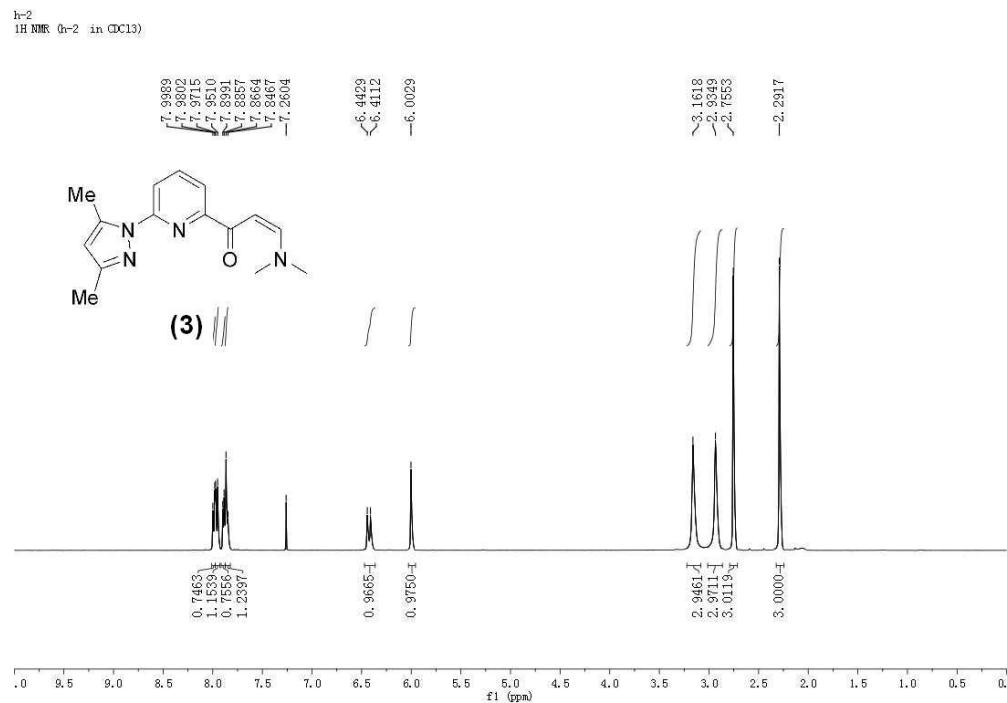
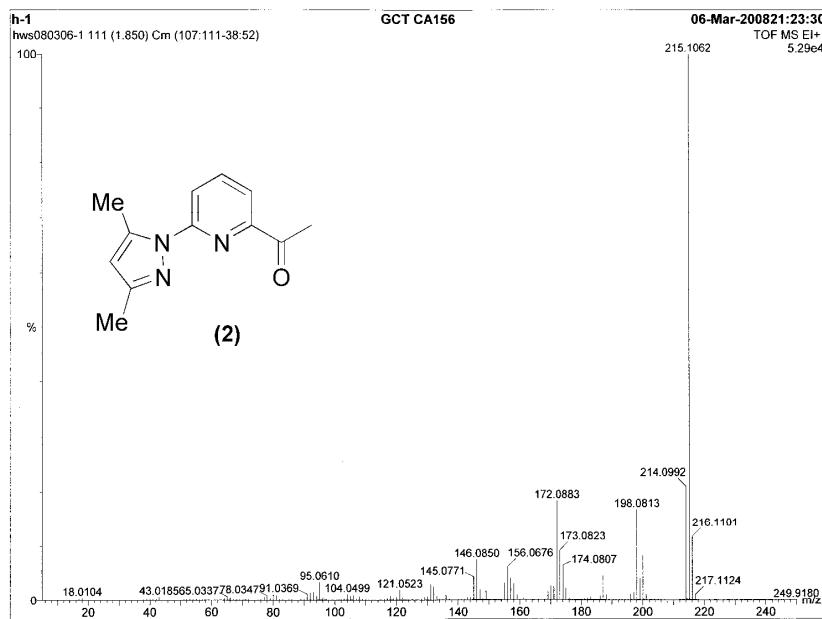
3. Copies of NMR and HRMS spectra

hr-1
1H NMR (hr-1 in CDCl_3)

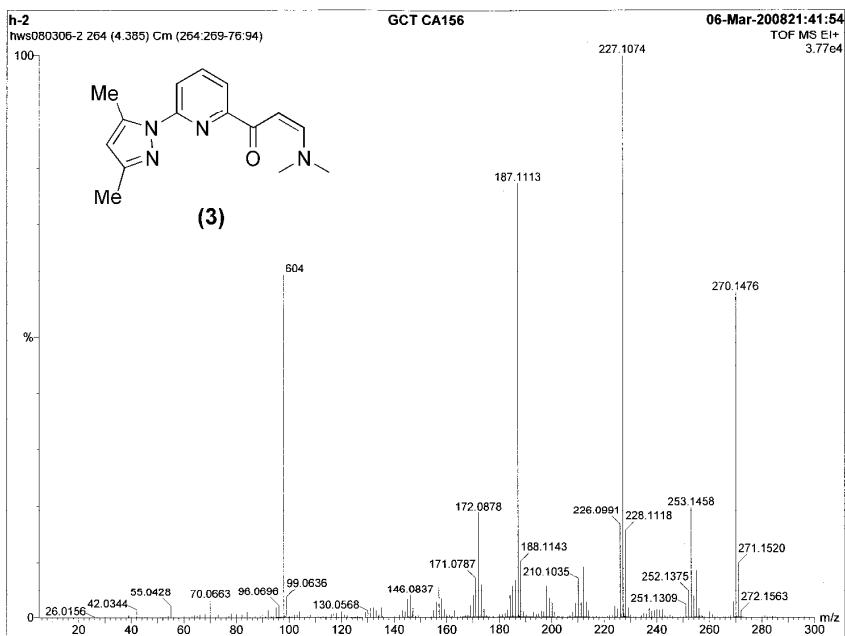
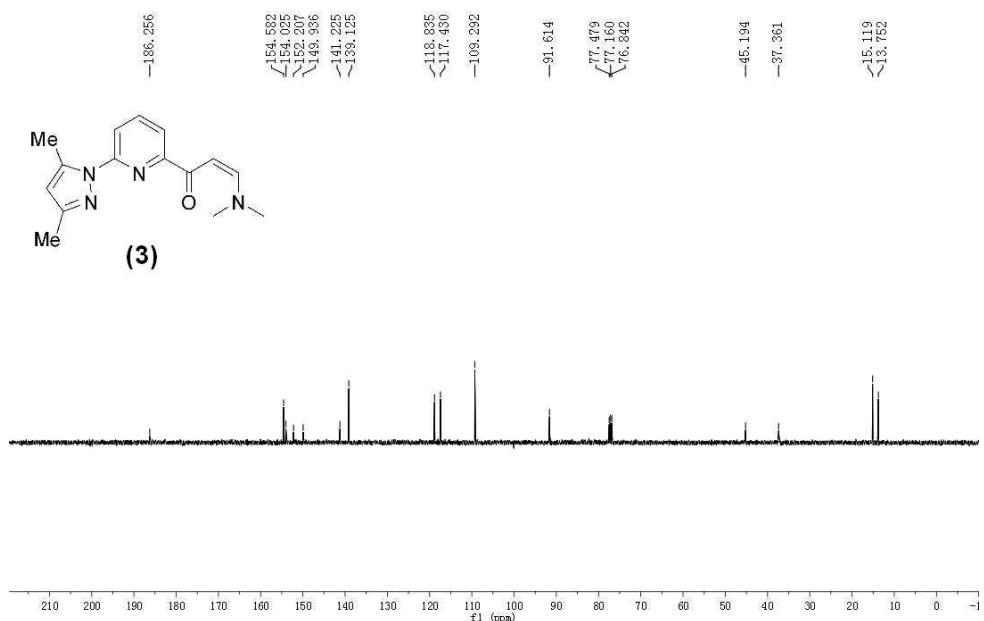


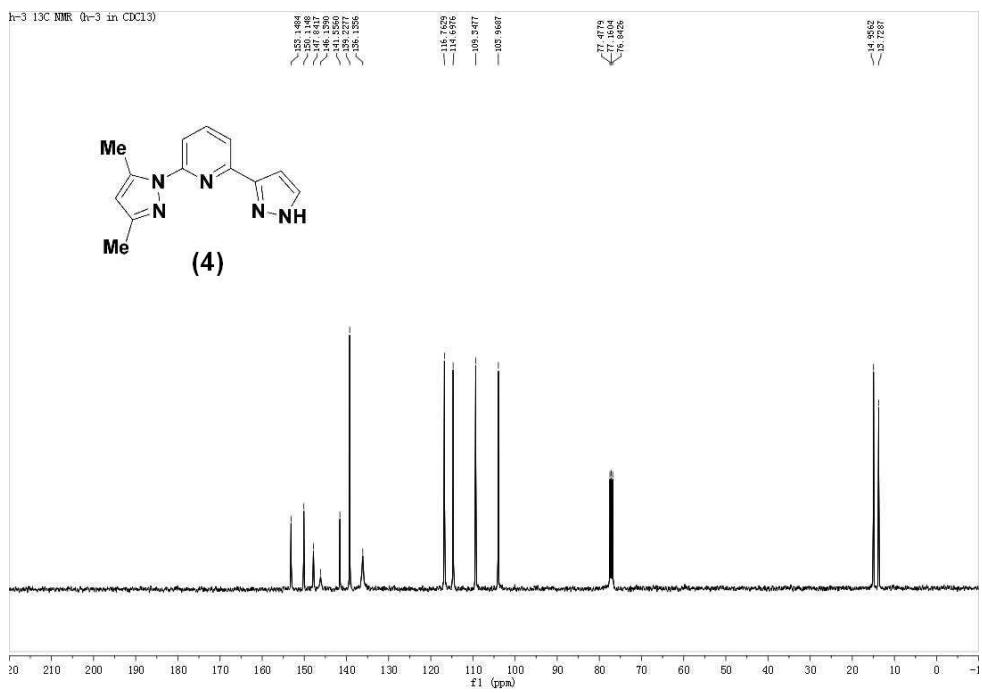
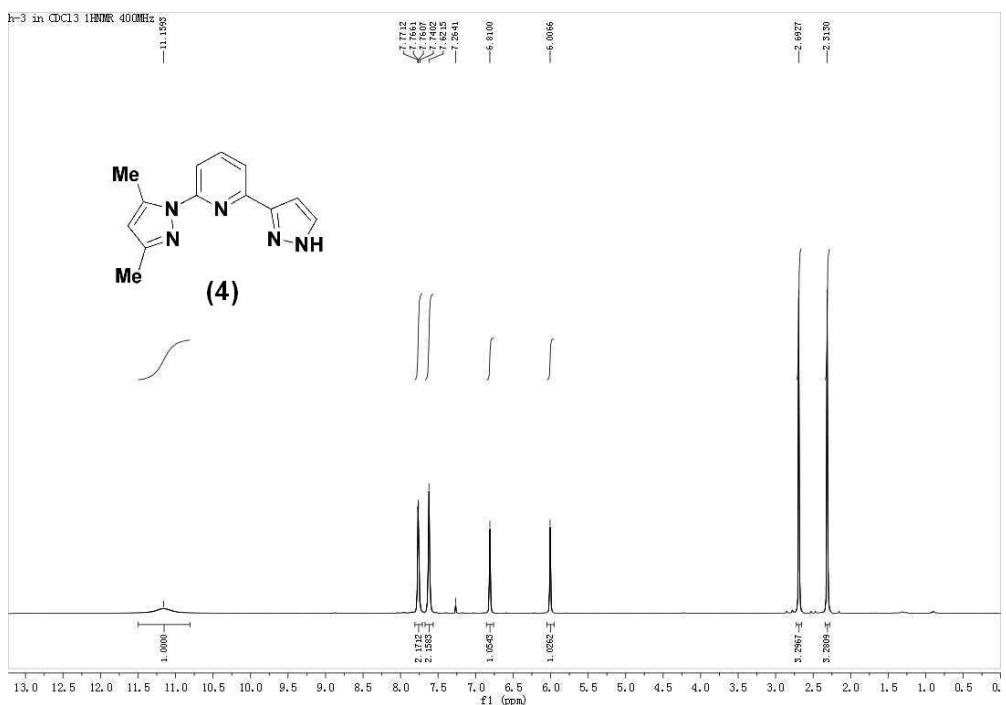
hr-1
13C NMR (hr-1 in CDCl_3)

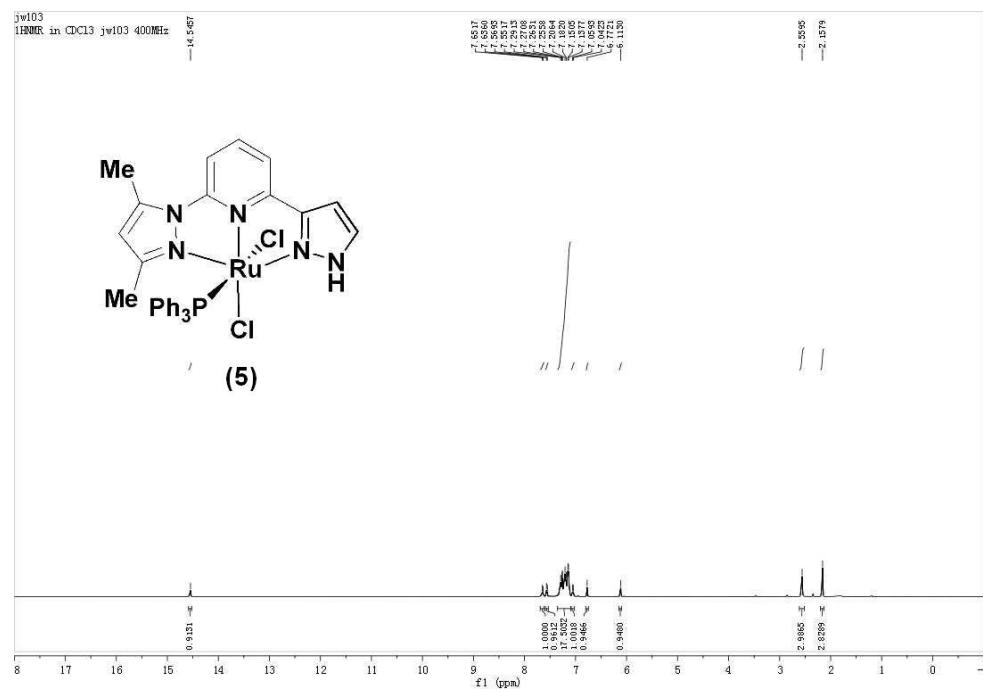
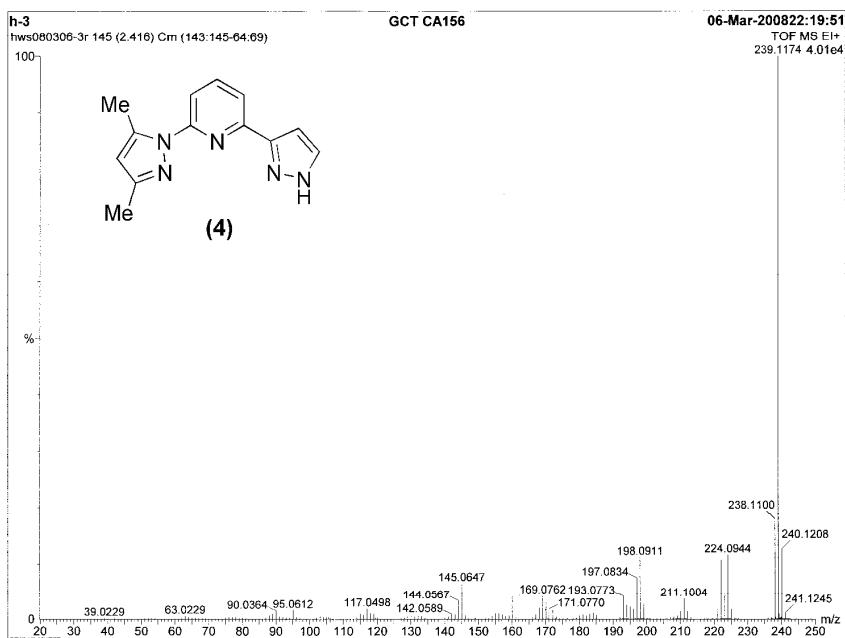


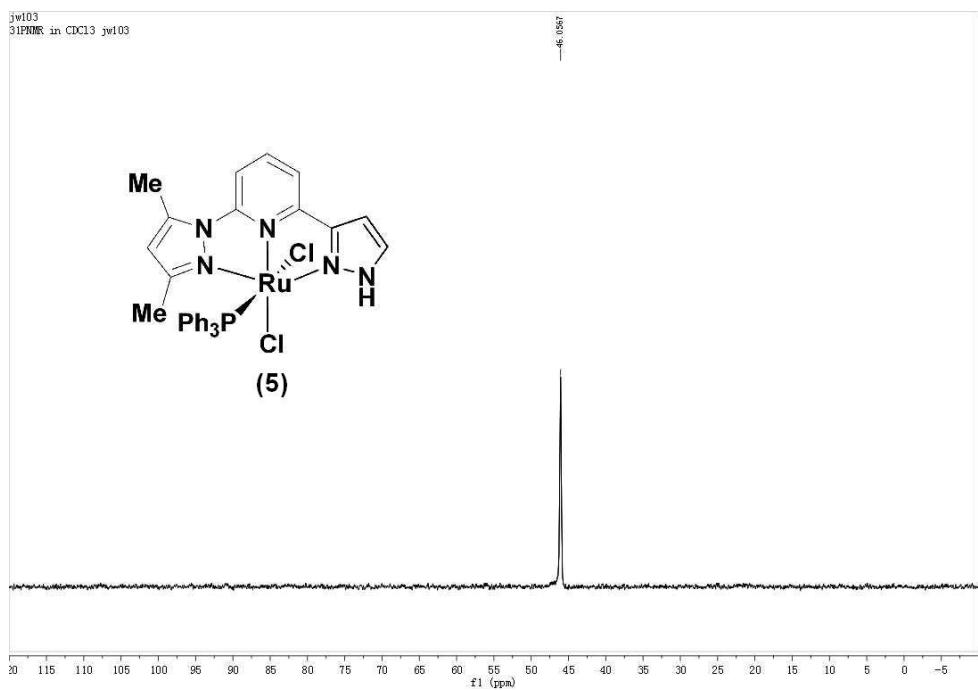
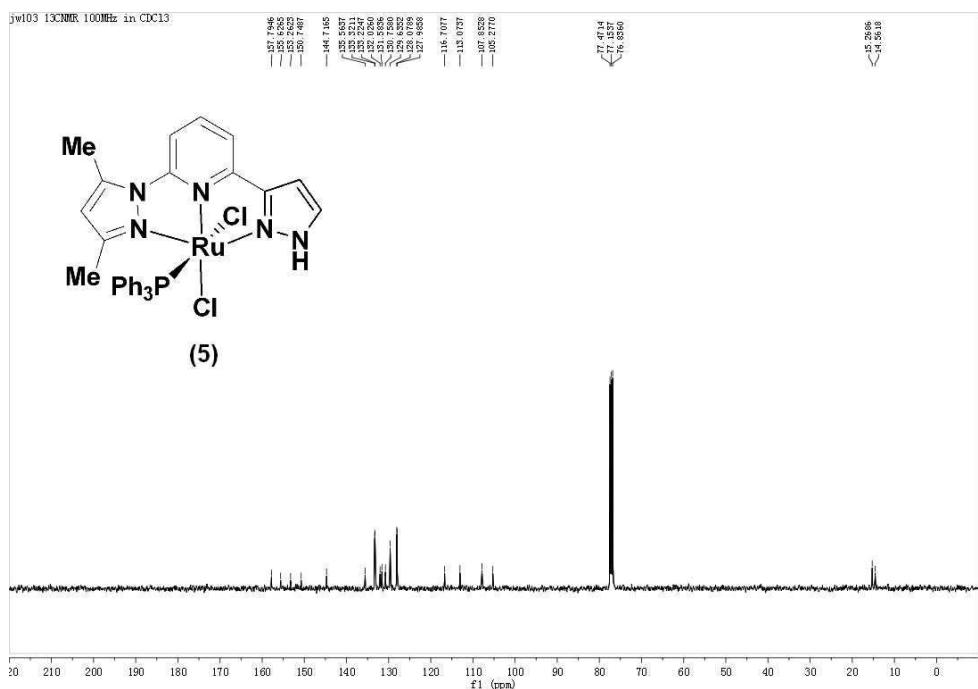


h-2
¹³C NMR (h-2 in CDCl₃)

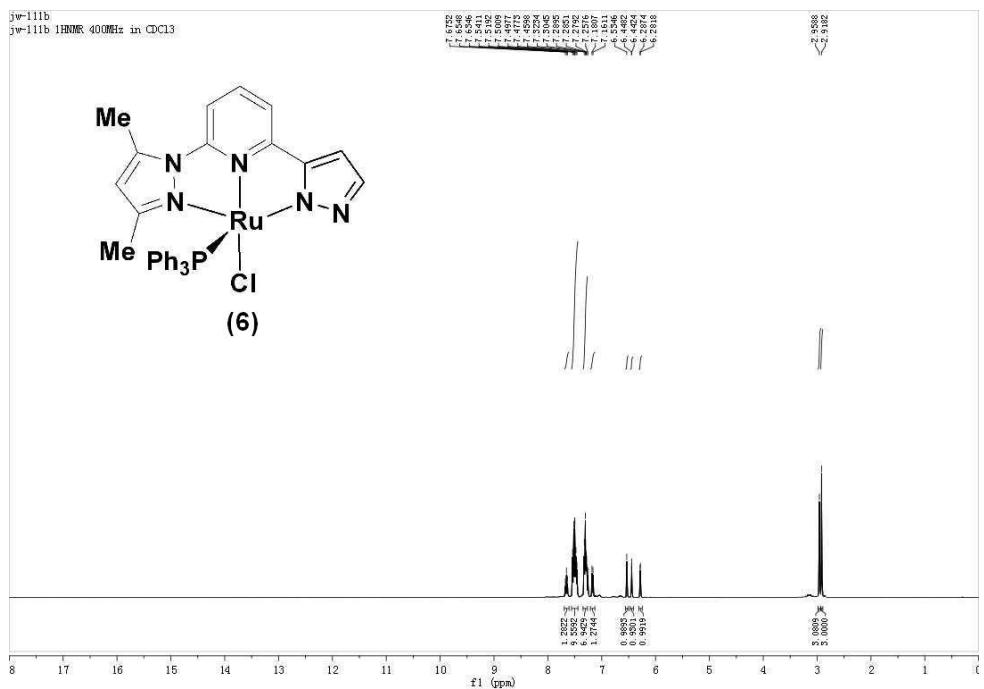








JPW-111b
JPW-111b 1H NMR 400MHz in CDCl₃



JPW-111b
JPW-111b 13C NMR 100MHz in CDCl₃

