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Supporting Information for

Diruthenium(II)-NNN Pincer Complex Catalysts for Transfer Hydrogenation of Ketones

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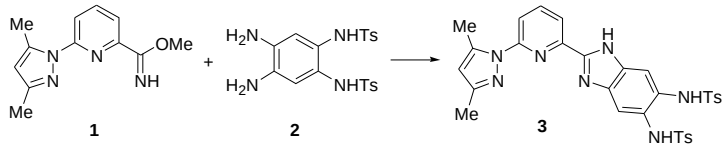
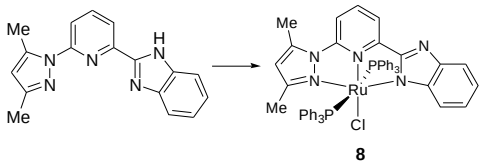
1. Experimental procedures



1.1 Synthesis of compound 3

A mixture of methyl 6-(3,5-dimethyl-1H-pyrazol- 1-yl)-picolinimidate (**1**) (377 mg, 1.6 mmol) and N,N‘-(4,5-diamino-1,2-phenylene)-bis(4-methylbenzenesulfonamide) (**2**) (730 mg, 1.6 mmol) in 10 mL glacial acetic acid was stirred at reflux under nitrogen atmosphere for 4 h. The resultant mixture was cooled to ambient temperature, and followed by addition of 30 mL water and neutralization with aqueous ammonia (25%, 5 mL). The resultant precipitate was collected by filtration and dried under vacuum to afford **3** as a brown solid (890 mg, 86% yield).

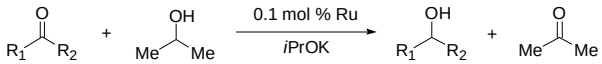


1.2 Synthesis of complex 8

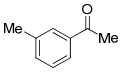
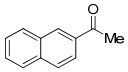
Under nitrogen atmosphere, a mixture of $RuCl_2(PPh_3)_3$ (480 mg, 0.5 mmol), pyrazolyl-imidazolyl-pyridine ligand (145 mg, 0.5 mmol), and triethylamine (505 mg, 5.0 mmol) in toluene (10 mL) was stirred at reflux for 2 h. The mixture was cooled to ambient temperature and the resultant precipitate was filtered off, successively rinsed with *i*PrOH (2×5 mL) and diethyl ether (5×5 mL), and dried under reduced pressure to afford complex **8** as an orange solid (403 mg, 85% yield). [Reference: F. L. Zeng, Z. K. Yu, *Organometallics* **2009**, *28*, 1855.]

1.3 Comparative investigation of the catalytic activities of complexes 6-9

Table S1. Transfer hydrogenation of ketones catalyzed by complexes **6-9**.[a]



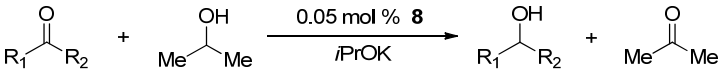
entry	catalyst	ketone	time (min)	yield[b] (%)
1	**6**		1	98
	7		1	98
	8		15[c]	97[c]
	9		15	97

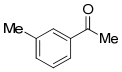
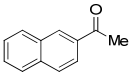
2	**6**		5	98
	7		5	98
	8		180	95
	9		180	95
3	**6**		1/2	99
	7		1/2	99
	8		120[c]	98[c]
	9		120	98
4	**6**		7	96
	7		7	96
	8		10[c]	96[c]
	9		10	96
5	**6**		10	99
	7		10	99
	8		240[c,d]	94[c,d]
	9		240[d]	94[d]

[a]Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); ketone/*i*PrOK/Ru = 1000:20:1; 0.1 MPa N_2, 82 °C. [b]Determined by GC analysis. [c]Cited from reference (F. L. Zeng and Z. K. Yu, *Organometallics* **2009**, 28, 1855). [d]Using 0.2 mol % Ru.

1.4 Transfer hydrogenation of ketones catalyzed by complex 8 at a low catalyst loading

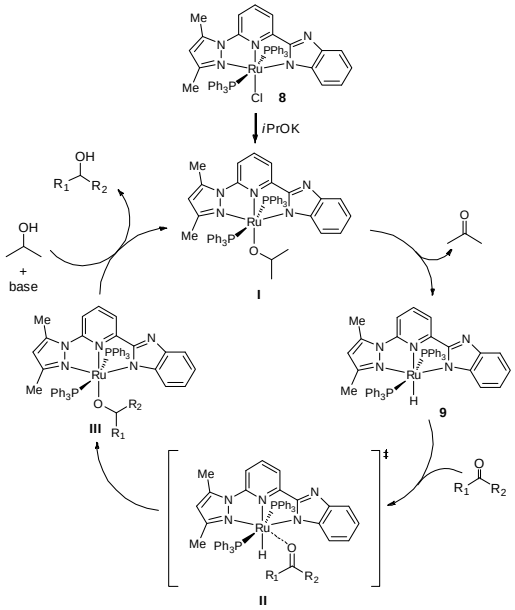
Table S2. Transfer hydrogenation of ketones catalyzed by complex **8**.[a]



entry	catalyst	ketone	time (min)	Yield[b] (%)
1	**8**		60	95
2	**8**		240	75
3	**8**		180	95
4	**8**		120	80

[a]Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); ketone/*i*PrOK/Ru = 2000:20:1; 0.1 MPa N_2, 82 °C. [b]Determined by GC analysis.

1.5 A proposed mechanism for transfer hydrogenation of ketones



Scheme S1. A proposed mechanism.

2. X-Ray crystallographic studies

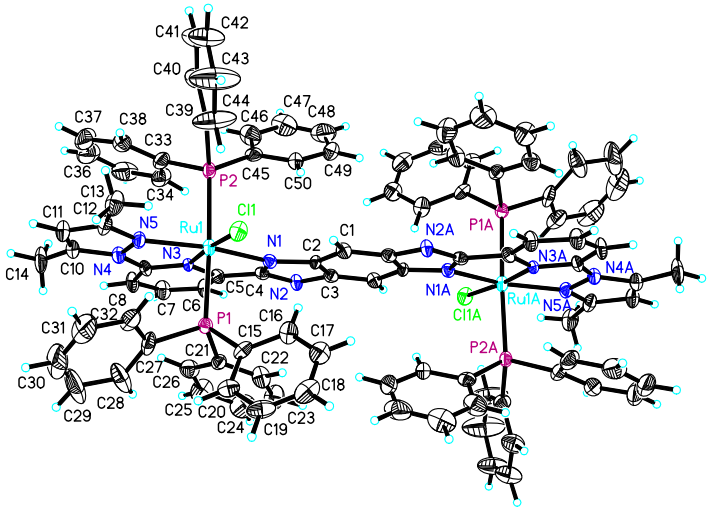


Figure S1. The molecular structure of complex **7**.

Table S3. Crystal data and structure refinement for 503_4_2 (complex **7**).

Identification code	503_4_2
Empirical formula	C50 H41 Cl N5 P2 Ru
Formula weight	910.34
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	P 21/n
Unit cell dimensions	a = 11.9390(7) Å α= 90°.
b = 18.9599(7) Å	β= 98.957(5)°.
c = 20.3416(7) Å	γ = 90°.
Volume	4548.4(3) $Å^3$
Z	4
Density (calculated)	1.329 Mg/m^3
Absorption coefficient	0.513 mm^{-1}
F(000)	1868
Crystal size	0.175 x 0.143 x 0.112 mm^3
Theta range for data collection	2.843 to 25.049°.
Index ranges	-14<=h<=13, -22<=k<=22, -24<=l<=18
Reflections collected	24054
Independent reflections	8041 [R(int) = 0.0596]
Completeness to theta = 25.242°	97.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.7557
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8041 / 72 / 522
Goodness-of-fit on F^2	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0887, wR2 = 0.2085
R indices (all data)	R1 = 0.1421, wR2 = 0.2302
Extinction coefficient	n/a
Largest diff. peak and hole	1.190 and -0.775 e.$Å^{-3}$

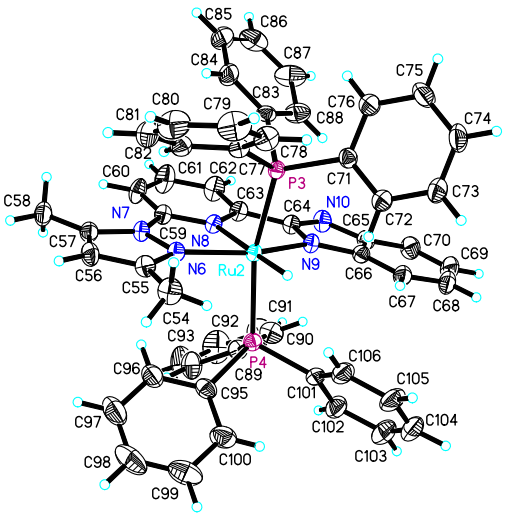


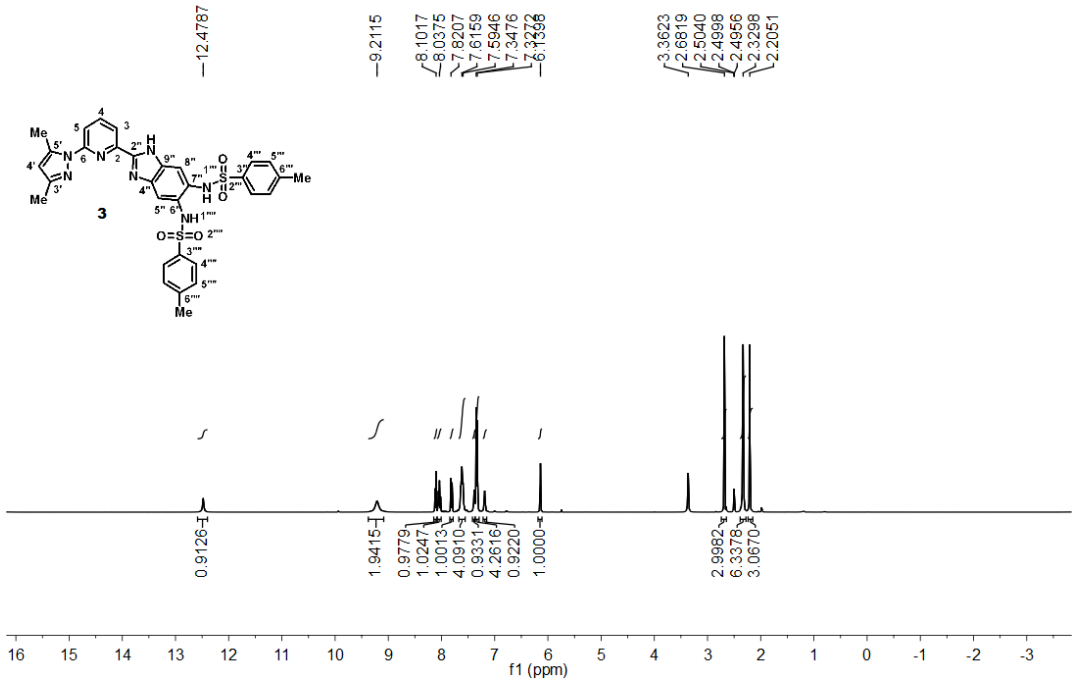
Figure S2. The molecular structure of complex **9**.

Table S4. Crystal data and structure refinement for cd214117 (complex **9**).

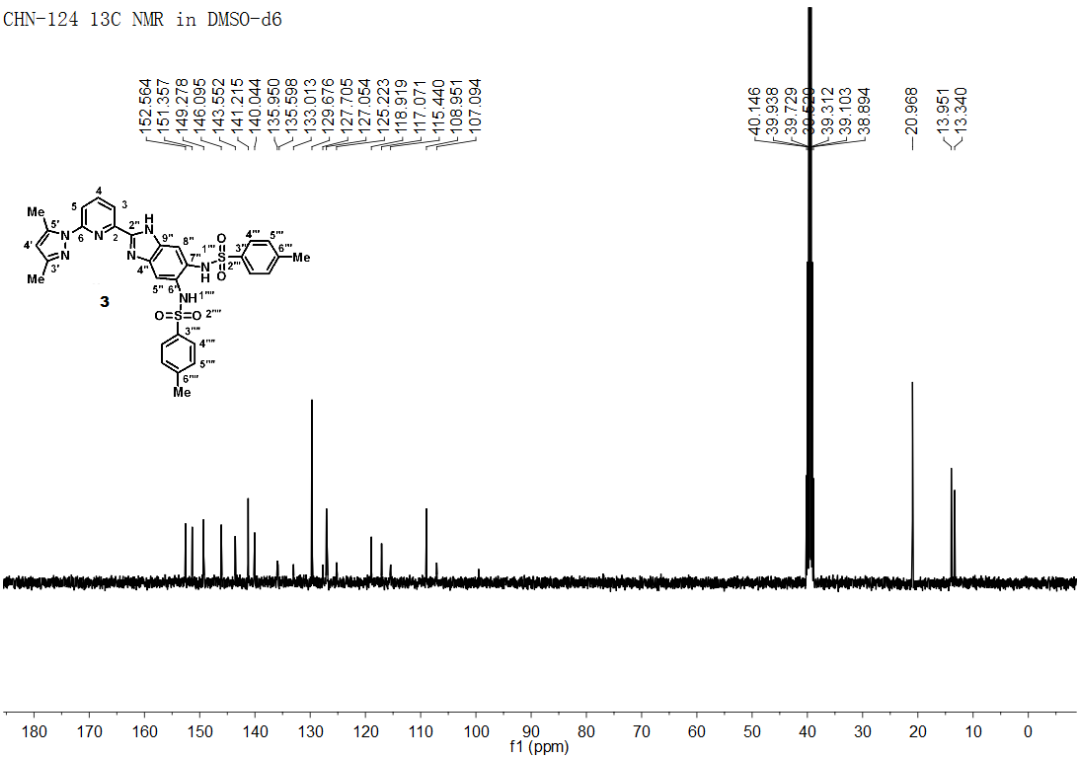
Identification code	cd214117	
Empirical formula	C115 H104 N10 O2 P4 Ru2	
Formula weight	1984.10	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.052(3) Å	α= 90.286(6)°.
	b = 20.350(6) Å	β= 94.702(6)°.
	c = 20.965(6) Å	γ = 97.737(6)°.
Volume	5077(2) $Å^3$	
Z	2	
Density (calculated)	1.298 Mg/m^3	
Absorption coefficient	0.416 mm^{-1}	
F(000)	2056	
Crystal size	0.187 x 0.101 x 0.056 mm^3	
Theta range for data collection	0.975 to 26.000°.	
Index ranges	?<=h<=?, ?<=k<=?, ?<=l<=?	
Reflections collected	?	
Independent reflections	19805 [R(int) = ?]	
Completeness to theta = 25.242°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5947	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19805 / 2 / 1213	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0566, wR2 = 0.1347	
R indices (all data)	R1 = 0.0748, wR2 = 0.1427	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.945 and -0.512 $e.Å^{-3}$	

3. Copies of NMR spectra

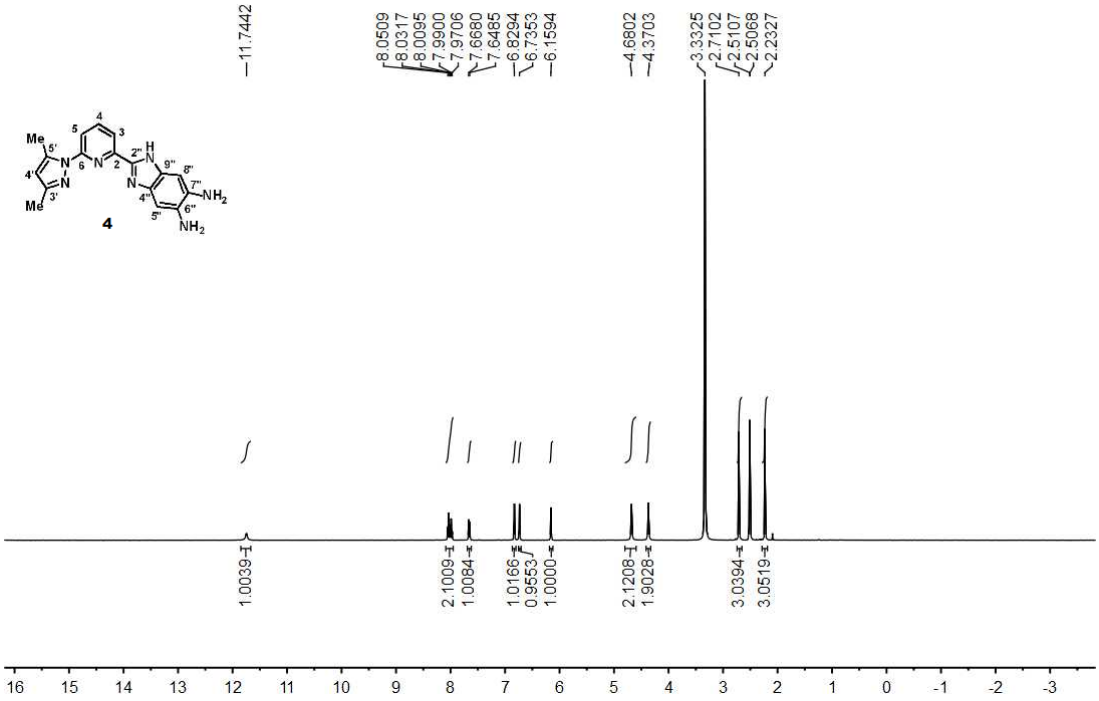
CHN-124 1H NMR in DMSO-d6



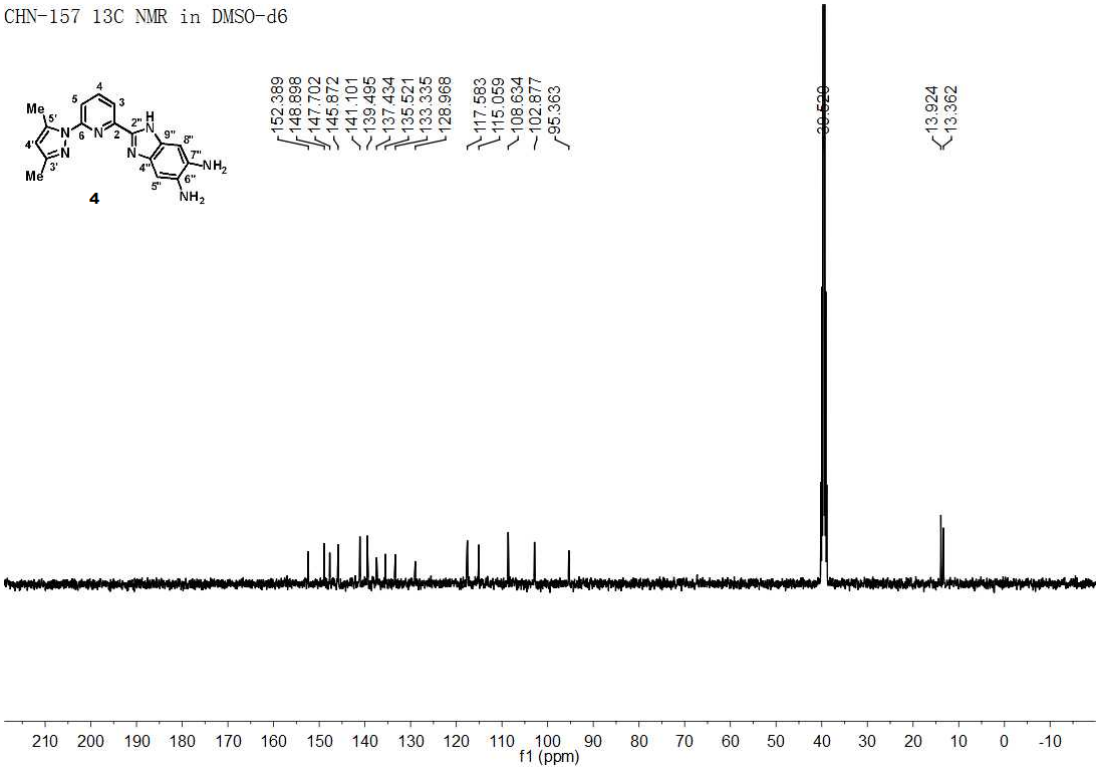
CHN-124 13C NMR in DMSO-d6



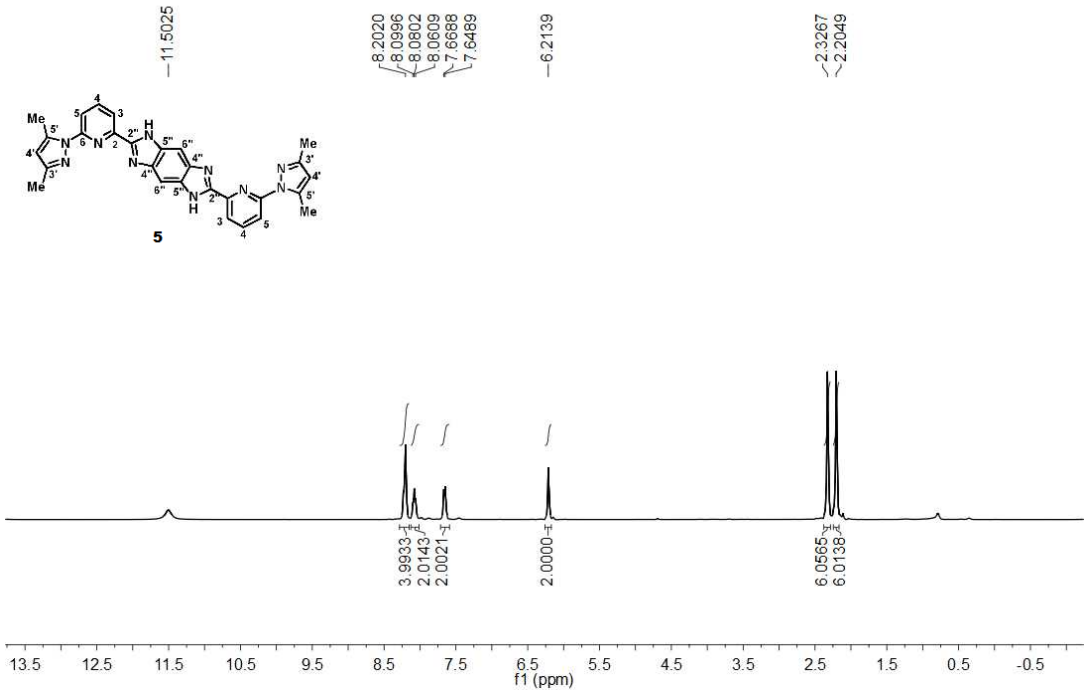
CHN-157 1H NMR in DMSO-d6



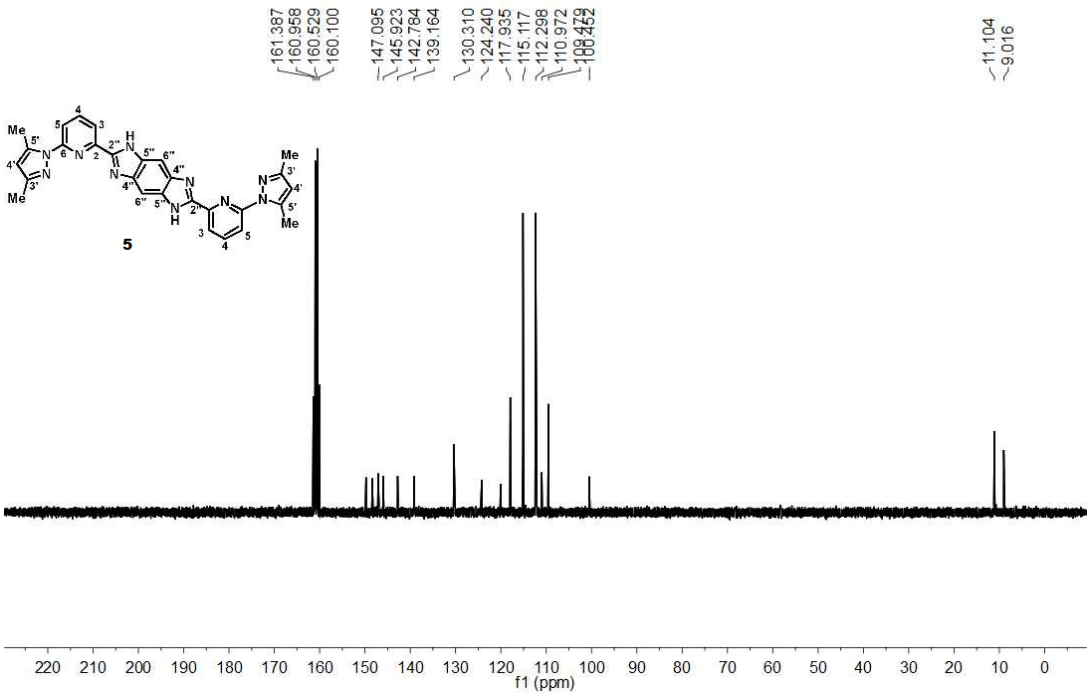
CHN-157 13C NMR in DMSO-d6



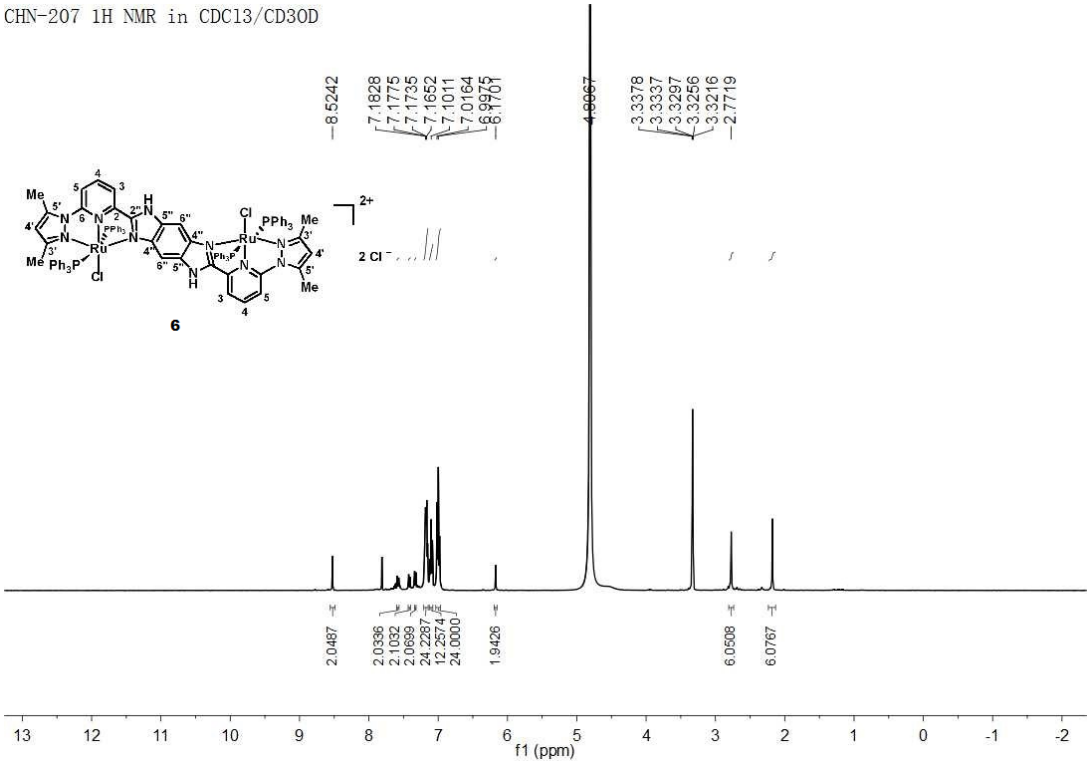
CHN-076 1H NMR in TFA-d



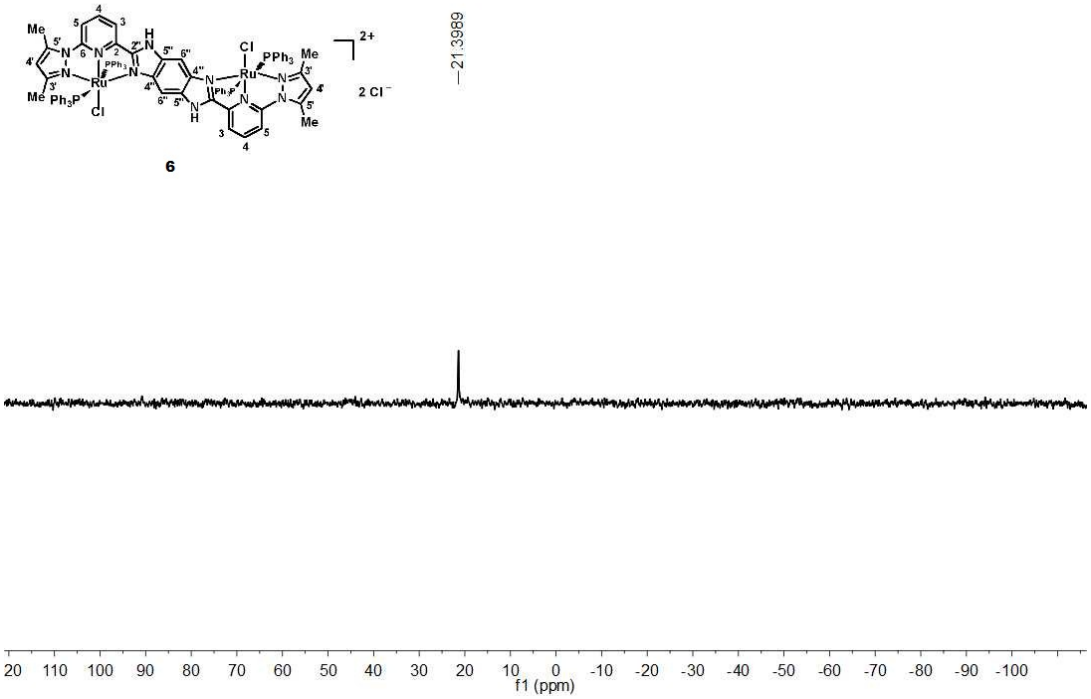
CHN-076 13C NMR in TFA-d



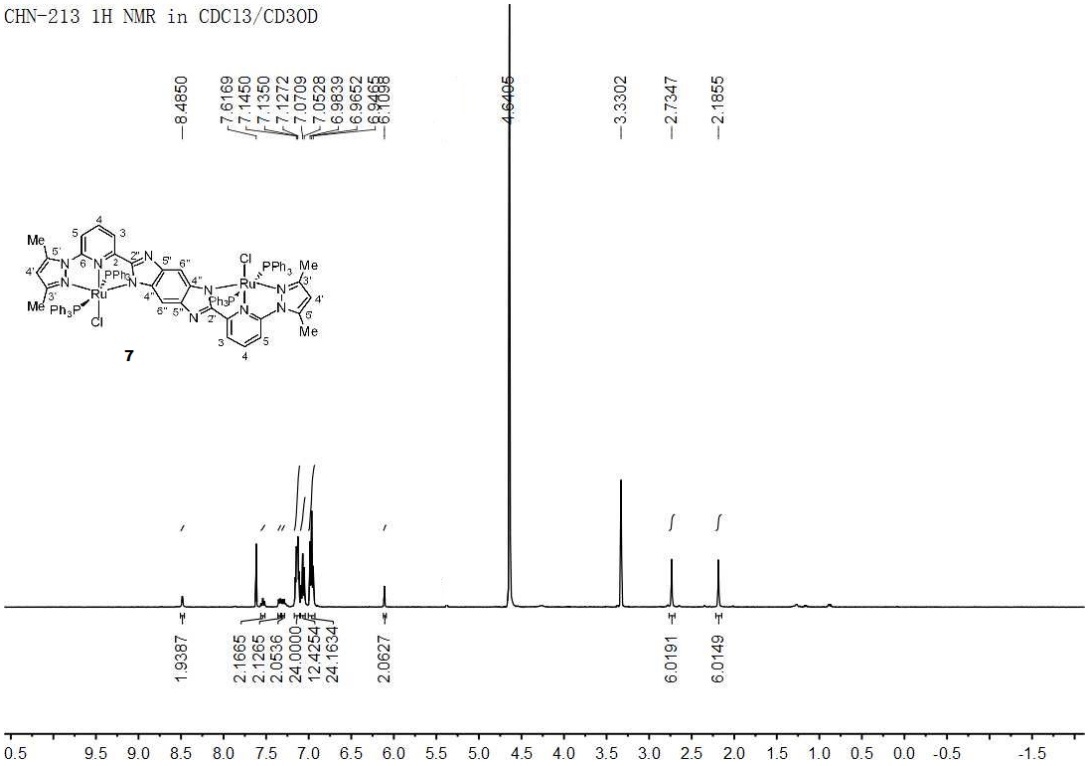
CHN-207 1H NMR in CDCl3/CD3OD



CHN-207 31P NMR in CDCl3/CD3OD



CHN-213 1H NMR in CDCl3/CD3OD



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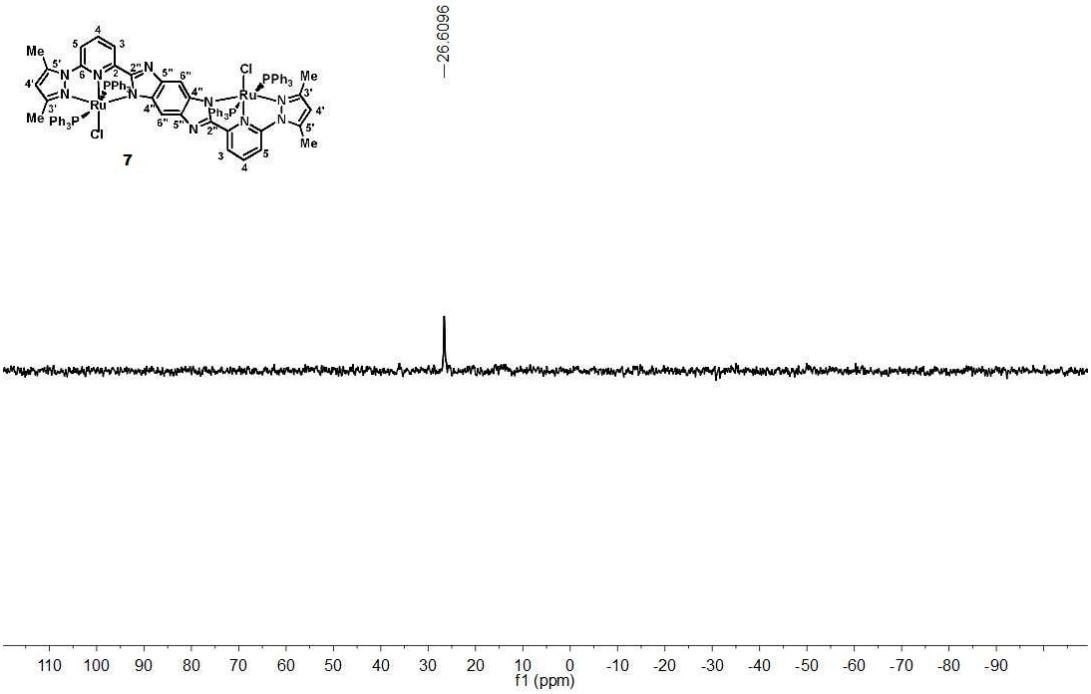

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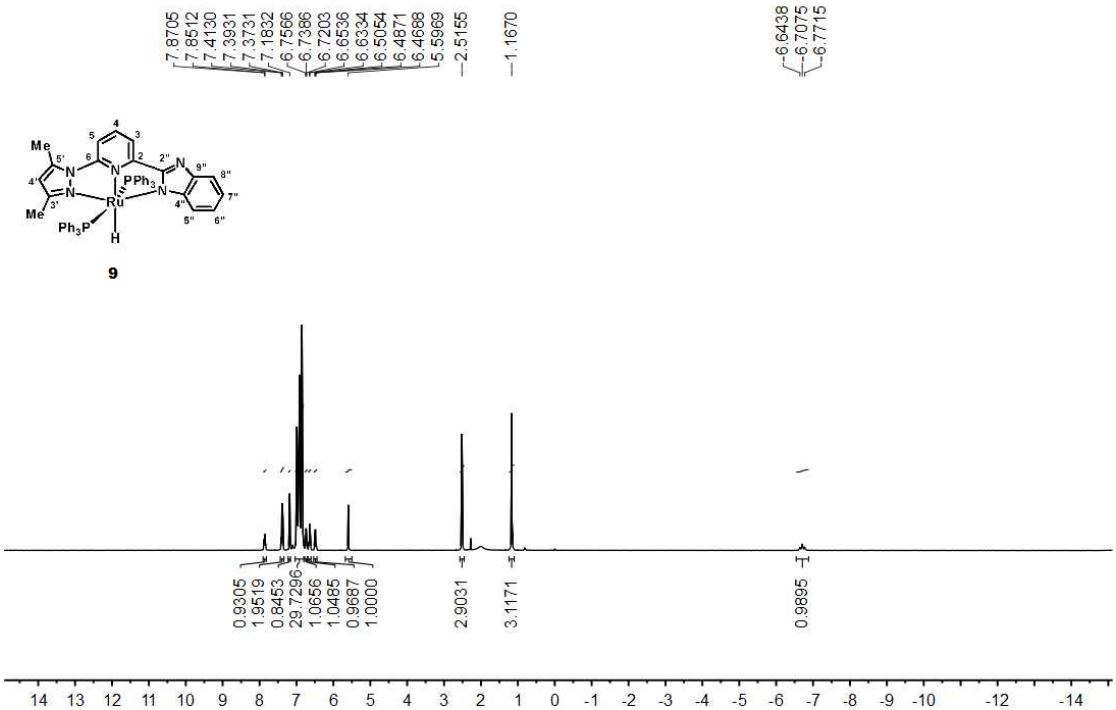
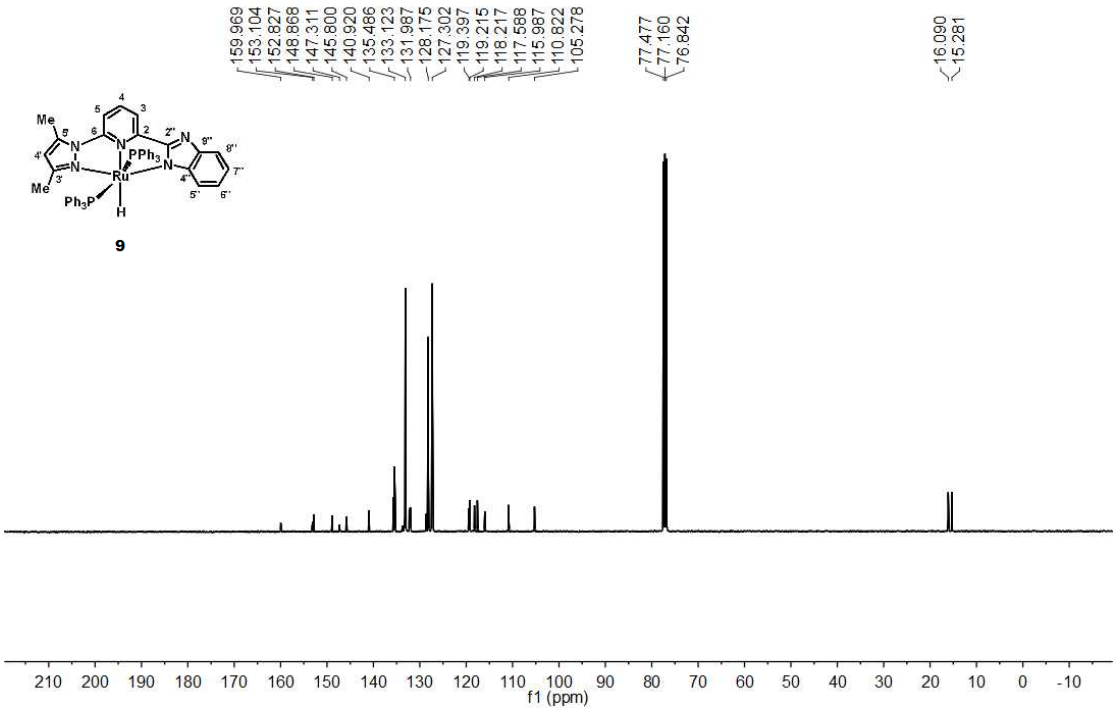
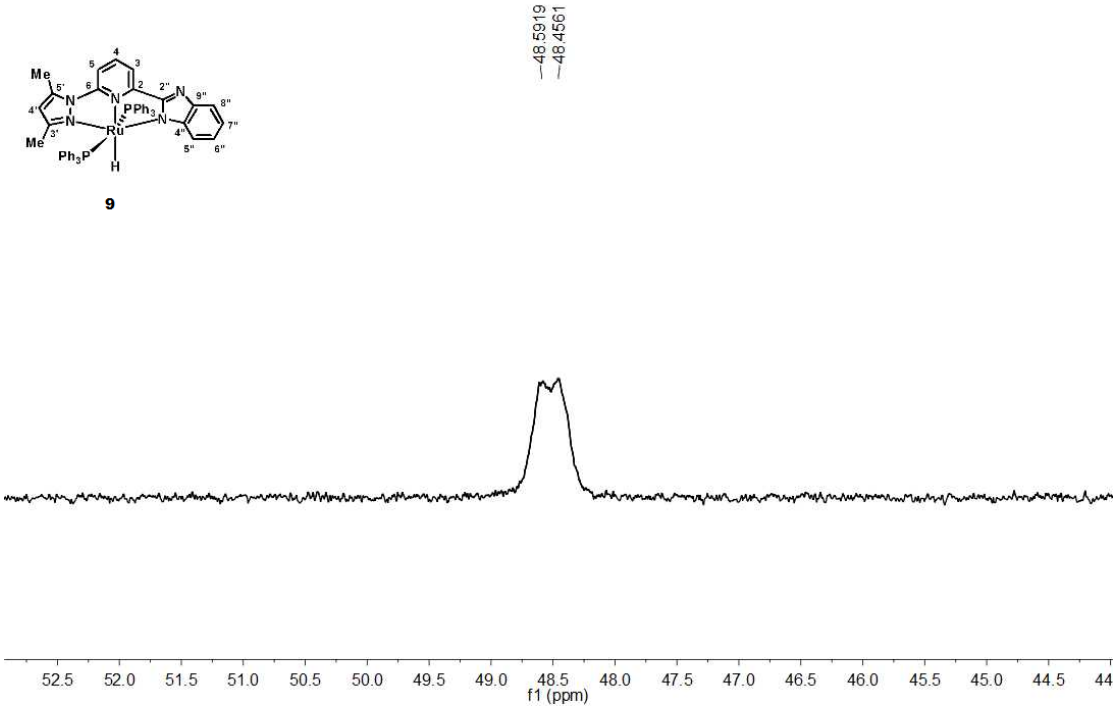


CHN-762 13C NMR in CDCl3



CHN-762 31P NMR in CDCl3

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