Supporting Information

A simple synthesis of [$RuCl_2$(NHC)(*p*-cymene)] complexes and their use in olefin oxidation catalysis

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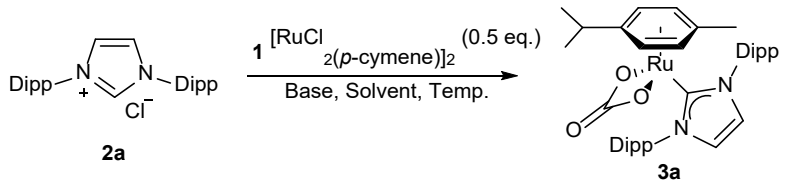
SUPPORTING INFORMATION

Selected Optimization of the Reaction Conditions

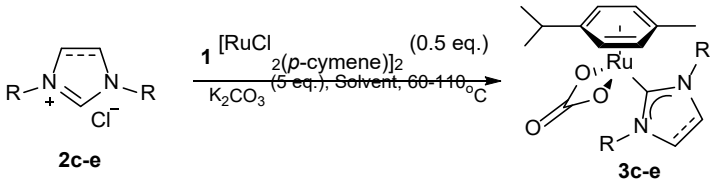
*Table S1 Optimization of the reaction conditions for **3a***



Entry	K_2CO_3(eq.)	Solvent	T(°C)	Time (h)	Yield (%)[b]
1	3	Acetone	60	17	64
2	*5*	*Acetone*	*60*	*17*	*72*
3	7	Acetone	60	12	58
5	5	EtOAc	60	24	54
6	5	DCM	40	24	0
7	5	PhMe	60	22	62
8	5	PhMe	80	3	51
9	5	PhMe	110	3	0
10	3	PhMe	80	17	53
11	4	PhMe	80	3	54

[a] Reaction conditions: **1** (0.12 mmol, 0.5 eq.), **2a** (0.24 mmol, 1 eq.), K_2CO_3, solvent (1.0 mL) in a 4 mL vial. [b] Isolated yields.

*Table S2 Selected optimization of the reaction conditions for **3c** - **3e***

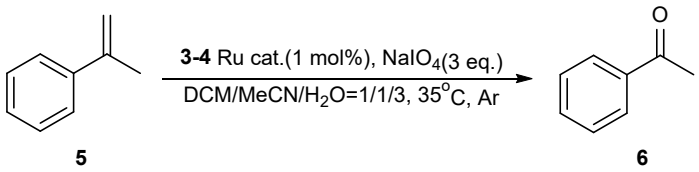


Entry	NHC	Solvent	T (°C)	Time (h)	Yield (%)[b]
1	ICy	Acetone	60	22	19
2	ICy	DCM	40	7	0
3	ICy	PhMe	60	12	41
5	ICy	PhMe	80	3	52
6	*ICy*	*PhMe*	*110*	*3*	*63*
7	IMe	Acetone	60	24	0
8	IMe	DCM	40	20	0
9	IMe	PhMe/Acetone	60	4	43
10	IMe	PhMe	60	14	47
11	*IMe*	*PhMe*	*80*	*26*	*67*
12	IMe	PhMe	110	3	36
13	SIMes	Acetone	60	17	33
14	SIMes	DCM	40	22	0
15	SIMes	PhMe	60	12	41
16	SIMes	PhMe	80	12	37
17	*SIMes*	*PhMe/Acetone*	*60*	*3*	*38*

[a] Reaction conditions: **1** (0.12 mmol, 0.5 eq.), **2** (0.24 mmol, 1 eq.), K_2CO_3 (1.18 mmol, 5 eq.), solvent (1.0 mL) in a 4 mL vial. [b] Isolated yields.

Typical procedure for catalytic olefin oxidation

*Table S3 Olefin oxidation with complexes **3-4**.*



5 **6**

Entry	NHC-Ru	Time(min)	Conv.(%)[b]
1	**3a**	20	100
2[c]	**3a**	120	100 (53)
3[d]	**3a**	35	100
4	**3b**	20	100 (62)
5	**3c**	30	100
6	**3d**	10	100 (60)
7	**3e**	25	100
8	**4a**	20	100
9	**4b**	20	100
10	**4c**	35	100
11	***4d***	*5*	*100 (65)*
12	**4e**	30	100
13	-	30	0

[a] Reaction conditions: 5 (0.2 mmol, 1 eq.), **3-4** (0.002 mmol, 1 mol%), $NaIO_4$ (0.6 mmol, 3 eq.), DCM/MeCN/H_2O (v/v/v = 1/1/3, 1.5 mL) in a 4 mL vial. [b] Conversion determined by ^1H NMR spectroscopy (1,3,5-trimethoxybenzene as internal standard) or TLC. Between brackets are isolated yields. [c] 0.5 mmol of **5**, 0.05 mol% of **3a**. [d] Room temperature.

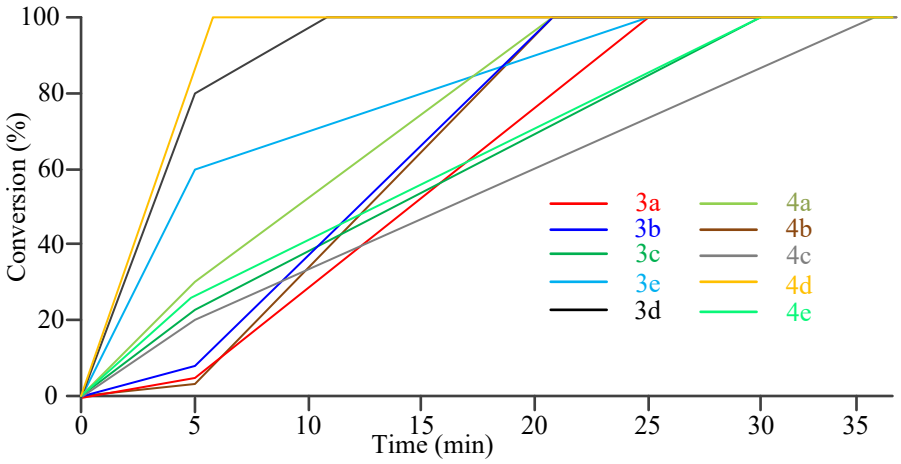


Figure S1. Using catalyst precursors **3**-**4** for olefin oxidation of *α*-methylstyrene. **4d** has the fastest initial reaction rate in the first five minutes, and the trend of the conversion over time shows that the compound **4d** had the best catalytic performance in olefin oxidation.

Molecular structures of complexes

Crystals that were of suitable quality for single crystal X-ray diffraction analysis were obtained in all cases by slow vapor diffusion of the antisolvent into saturated solutions of the complexes at 4 ºC. CCDC2045651-2045650 (**3a** and **3d**) contain the crystallographic data for this paper and can be obtained via http://www.ccdc.cam.ac.uk/data_request/cif.

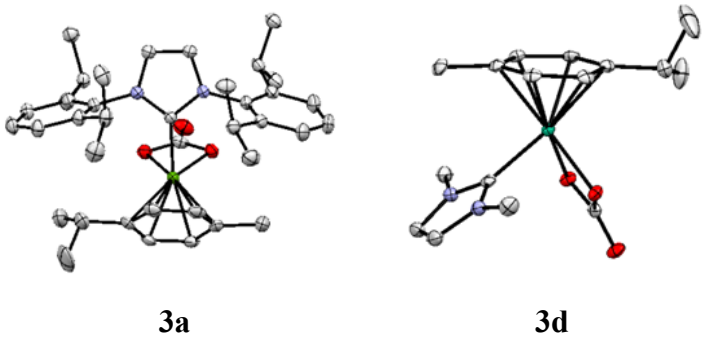


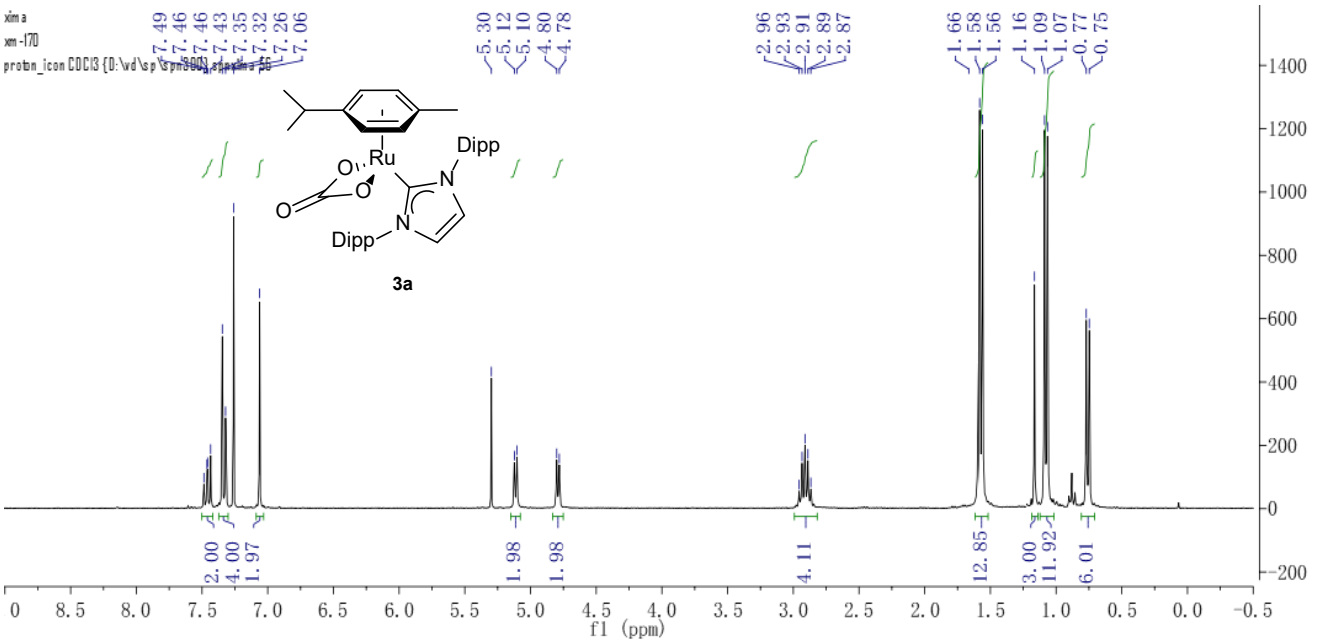
Figure S2. X-ray molecular structure of complexes **3a** and **3d**. Hydrogen atoms and free molecule (including the water molecules in 3d) omitted for clarity.

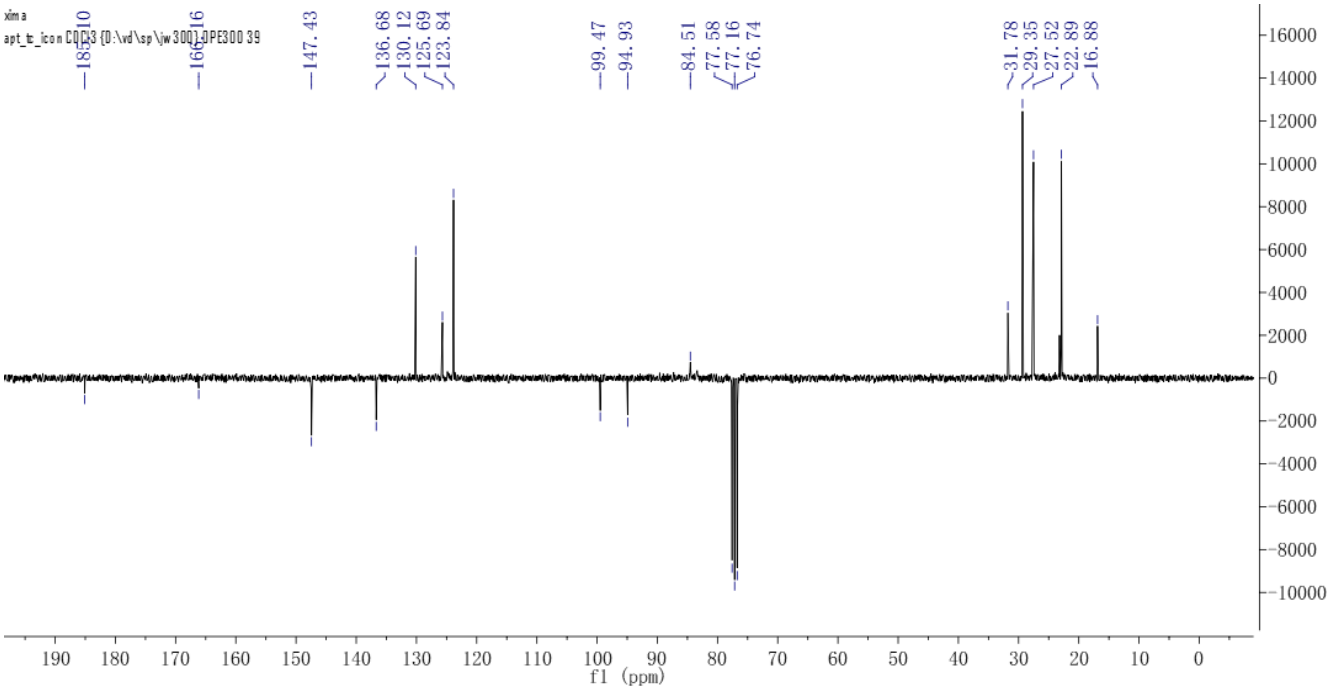
*Table S4. Crystallographic data for complexes **3a** and **3e***

	Complex **3a**·2$CHCl_2$	Complex **3e**·2H_2O
Empirical formula	$C_{40}H_{54}Cl_4N_2O_3Ru$	$C_{16}H_{26}N_2O_5Ru$
Formula weight	853.72	427.46
Temperature/K	100(2)	100.28(16)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	14.8188(2)	11.4295(2)
b/Å	12.79860(10)	10.48900(10)
c/Å	22.2382(3)	15.6396(2)
α/°	90	90
β/°	102.6790(10)	104.0610(10)
γ/°	90	90
Volume/$Å^3$	4114.85(9)	1818.76(4)
Z	4	4
$\rho_{calc}g/cm^3$	1.378	1.561
μ/mm^{-1}	5.769	7.218
F(000)	1776.0	880.0
Crystal size/mm^3	0.119 × 0.085 × 0.045	0.172 × 0.068 × 0.034
Radiation	CuKα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.114 to 147.78	7.974 to 147.384
Index ranges	-18 ≤ h ≤ 18, -13 ≤ k ≤ 15, -27 ≤ l ≤ 23	-13 ≤ h ≤ 12, -12 ≤ k ≤ 12, -19 ≤ l ≤ 19
Reflections collected	31252	17699
Independent reflections	8213 [R_{int} = 0.0460, R_{sigma} = 0.0381]	3629 [R_{int} = 0.0425, R_{sigma} = 0.0296]
Data/restraints/parameters	8213/0/462	3629/4/234
Goodness-of-fit on F^2	1.022	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0810	R_1 = 0.0248, wR_2 = 0.0576
Final R indexes [all data]	R_1 = 0.0417, wR_2 = 0.0861	R_1 = 0.0309, wR_2 = 0.0605
Largest diff. peak/hole / e $Å^{-3}$	1.15/-1.37	0.52/-0.56

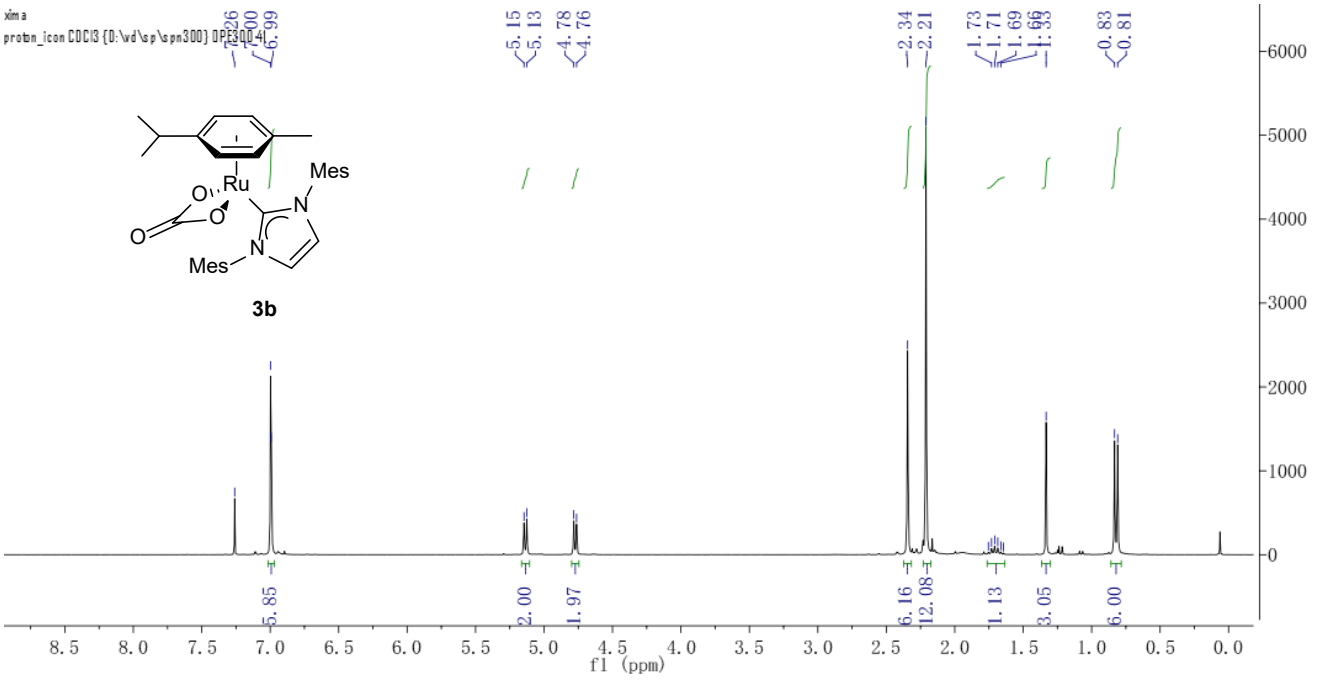
NMR spectra

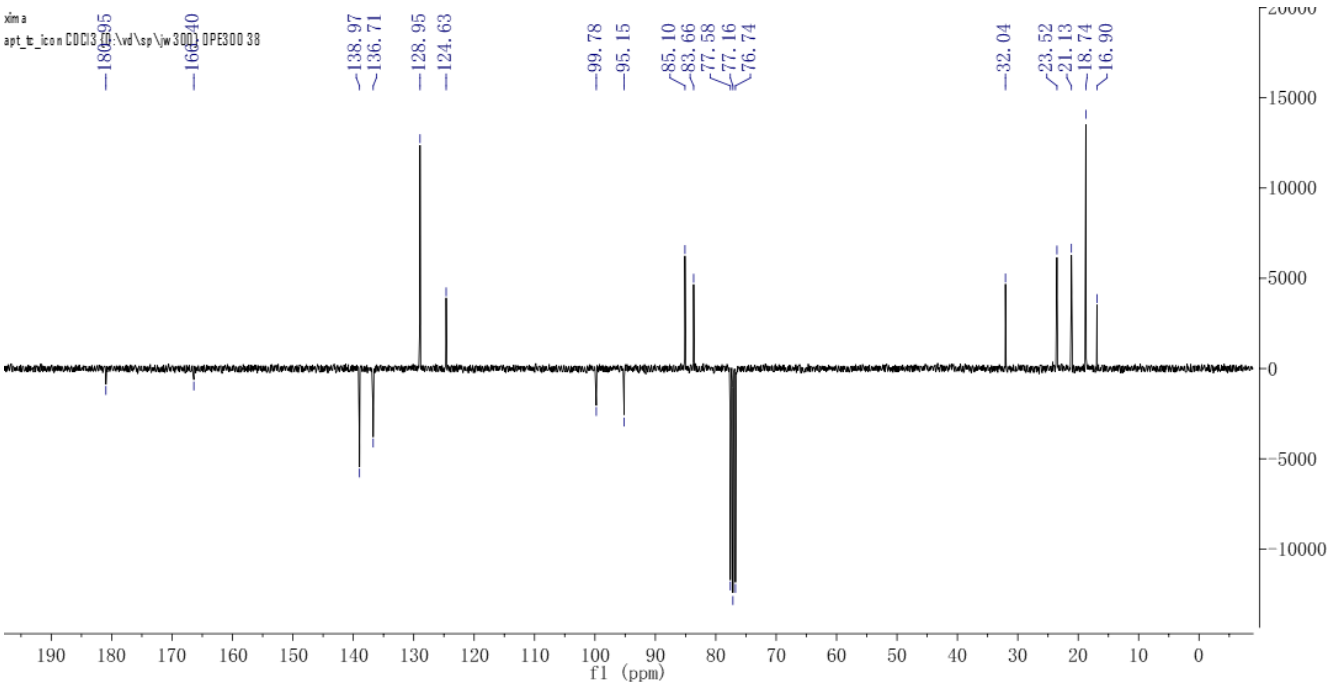
^{1}H and $^{13}C\{^{1}H\}$ apt NMR of [Ru(CO_3)(IPr)(*p*-cymene)] (**3a**)



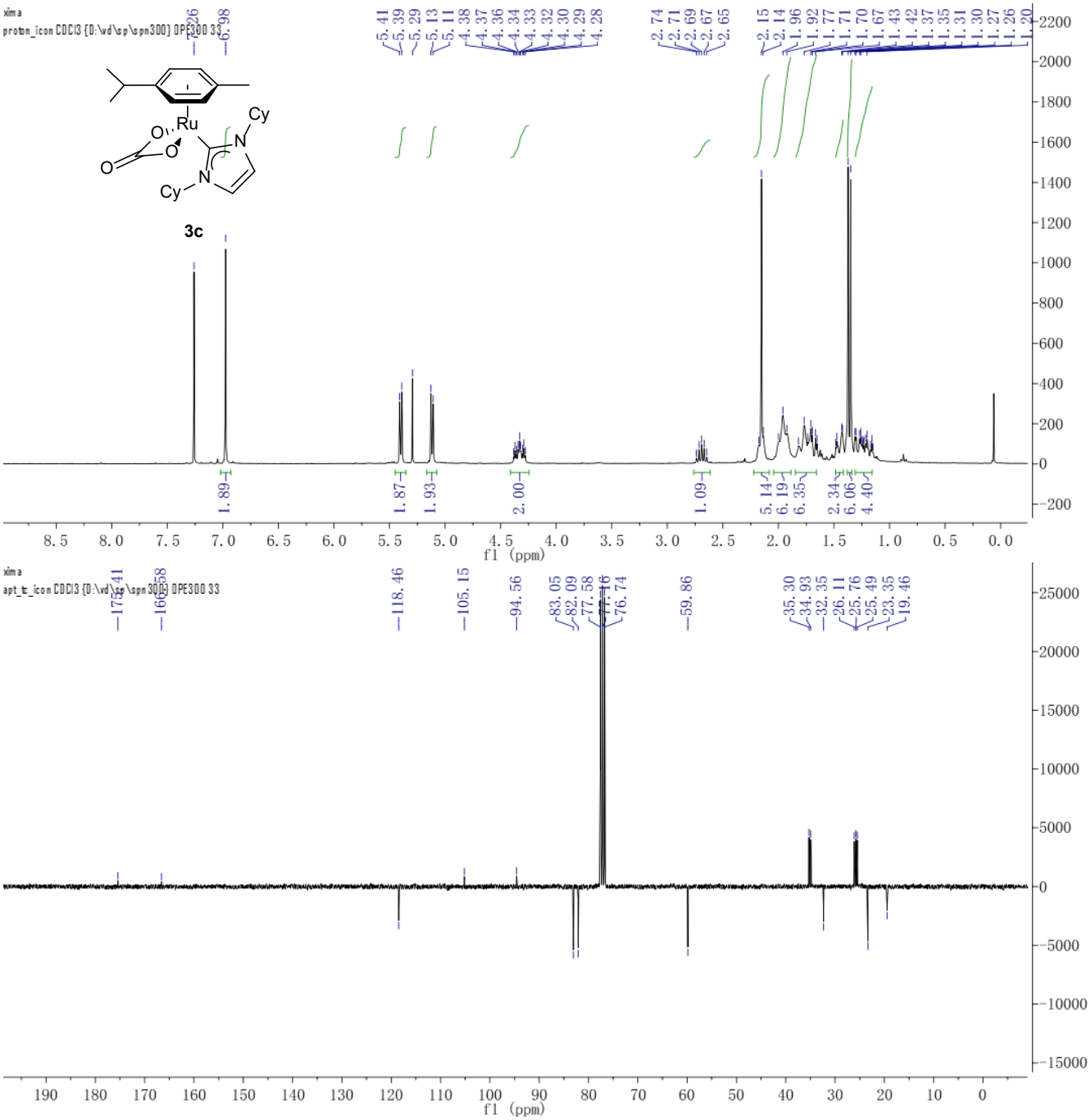


^{1}H and $^{13}C\{^{1}H\}$ apt NMR of [Ru(CO_3)(IMes)(*p*-cymene)] (**3b**)

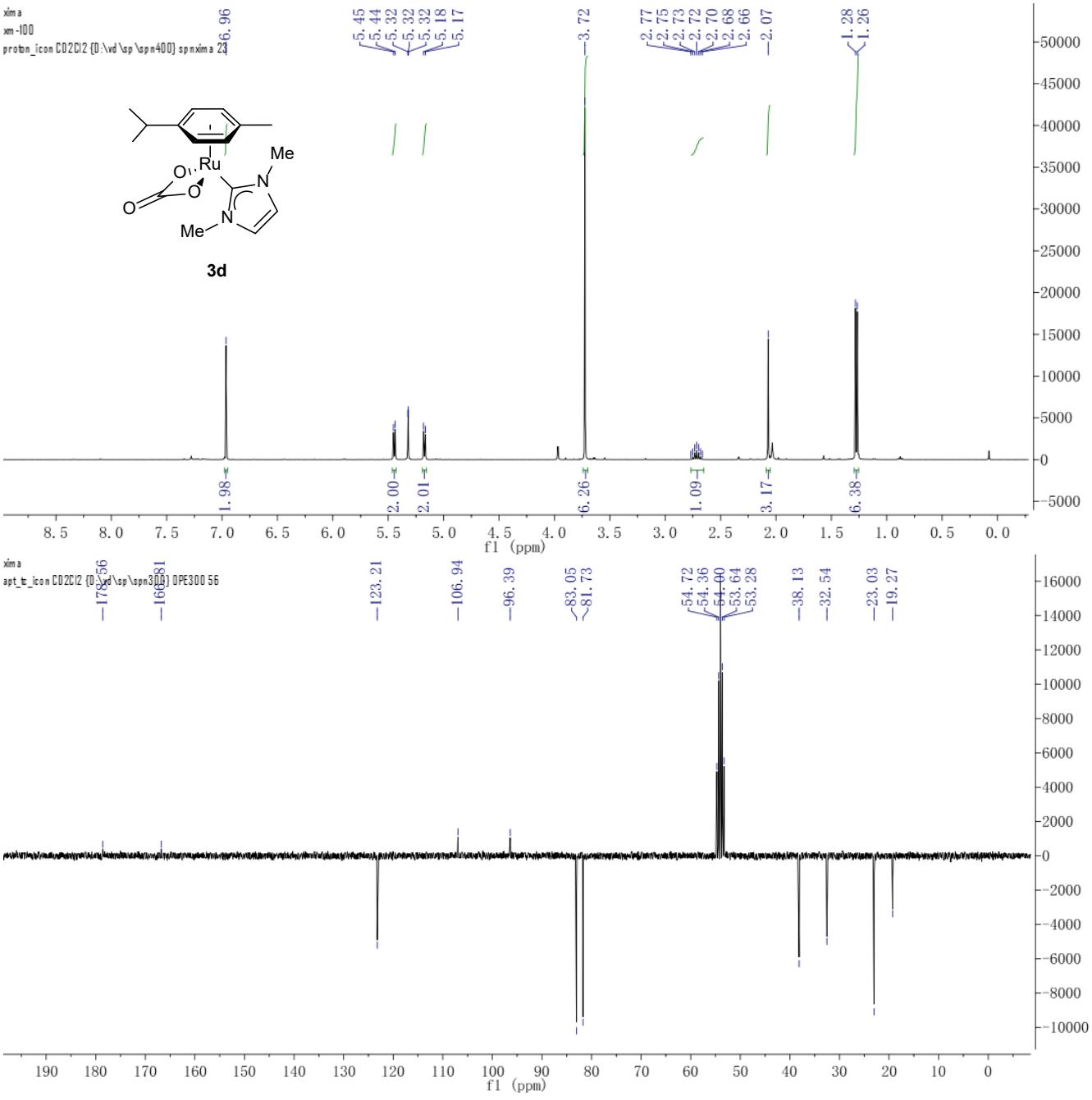




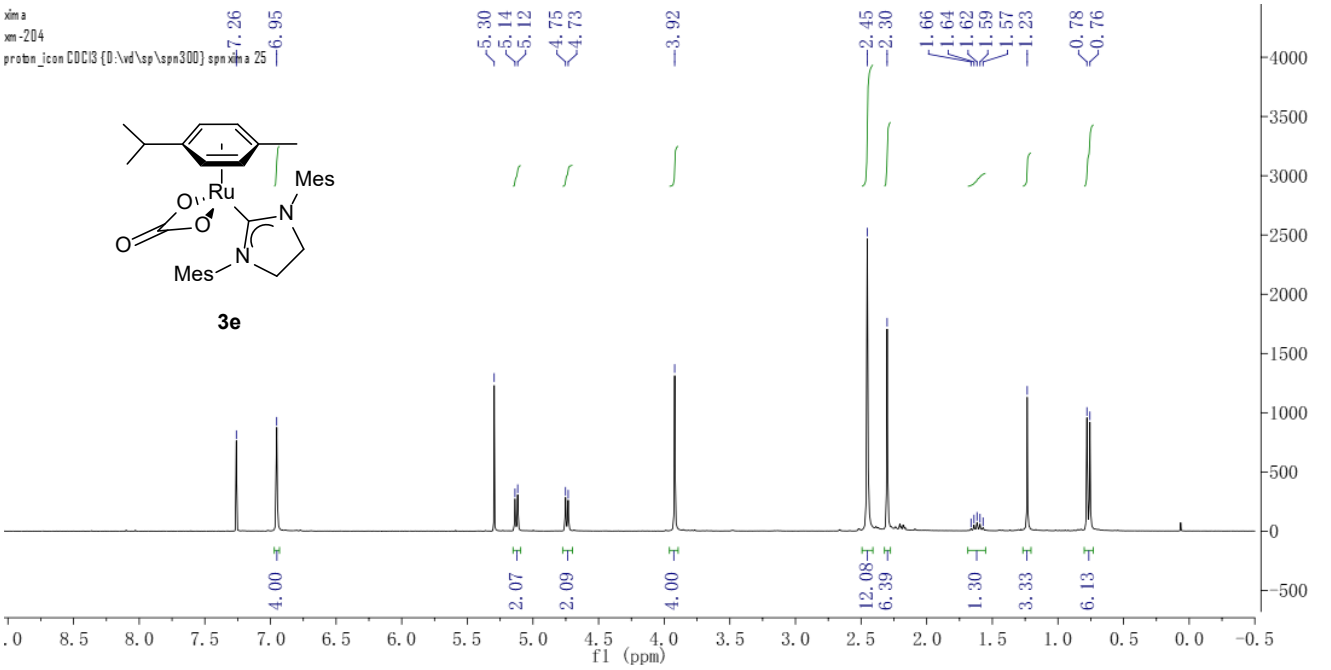
^{1}H and $^{13}C\{^{1}H\}$ apt NMR of [Ru(CO_3)(ICy)(*p*-cymene)] (**3c**)

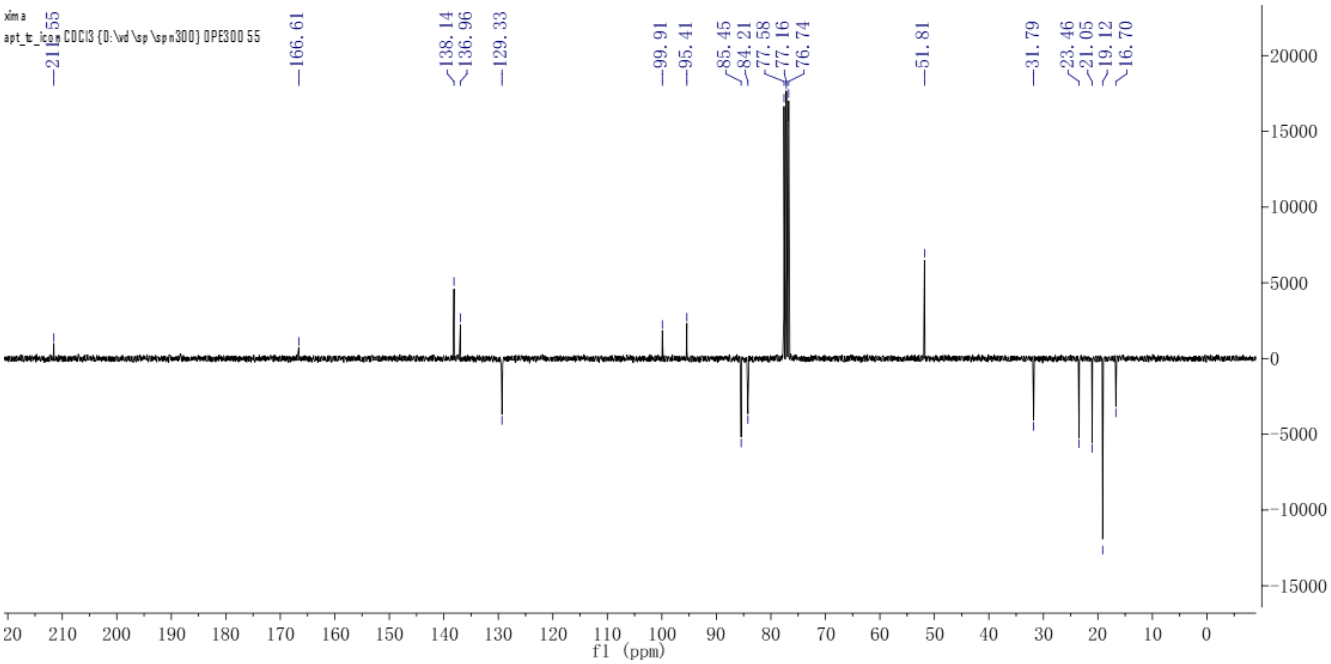


^{1}H and $^{13}C\{^{1}H\}$ apt NMR of [Ru(CO_3)(IMe)(*p*-cymene)] (**3d**)

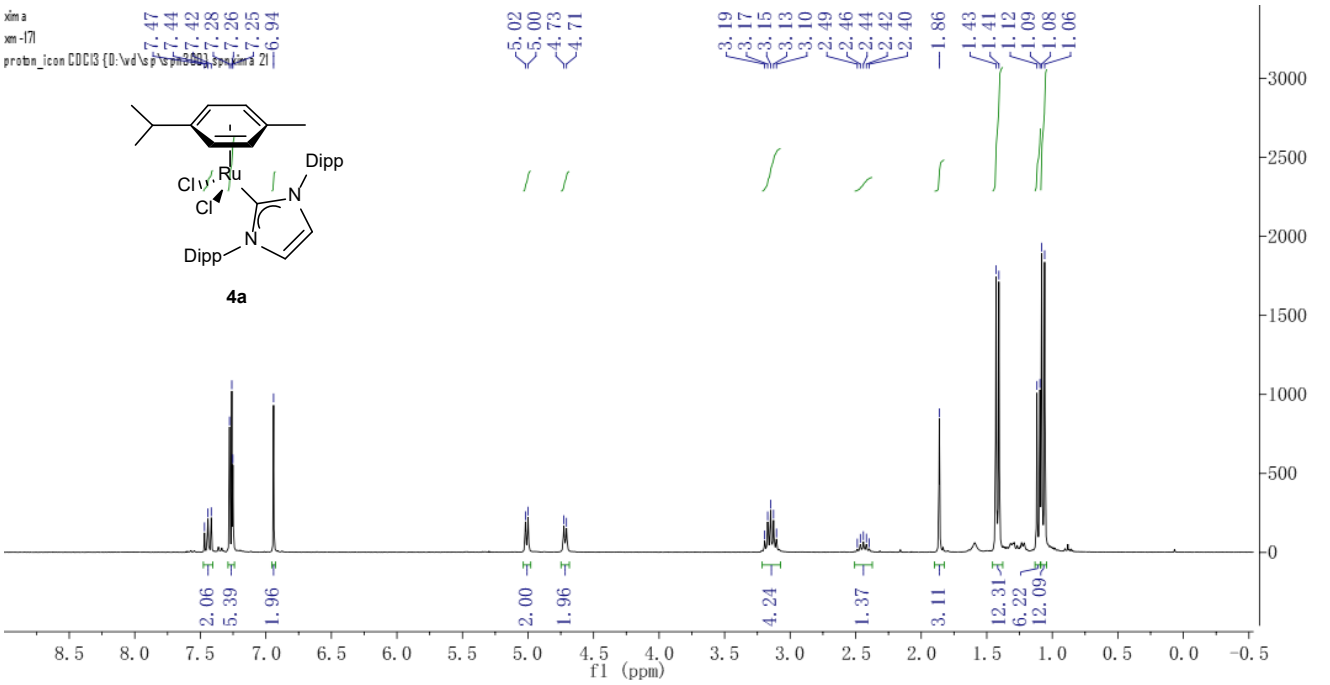


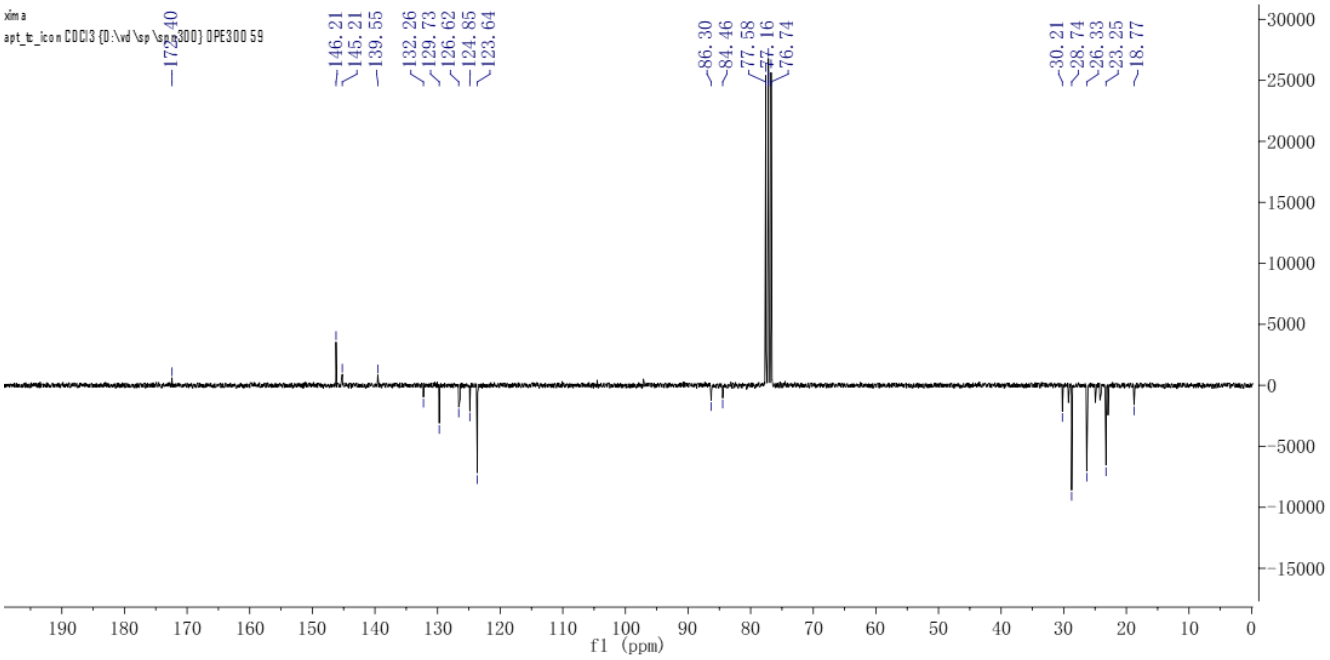
^{1}H and $^{13}C\{^{1}H\}$ apt NMR of [Ru(CO_3)(SIMes)(*p*-cymene)] (**3e**)



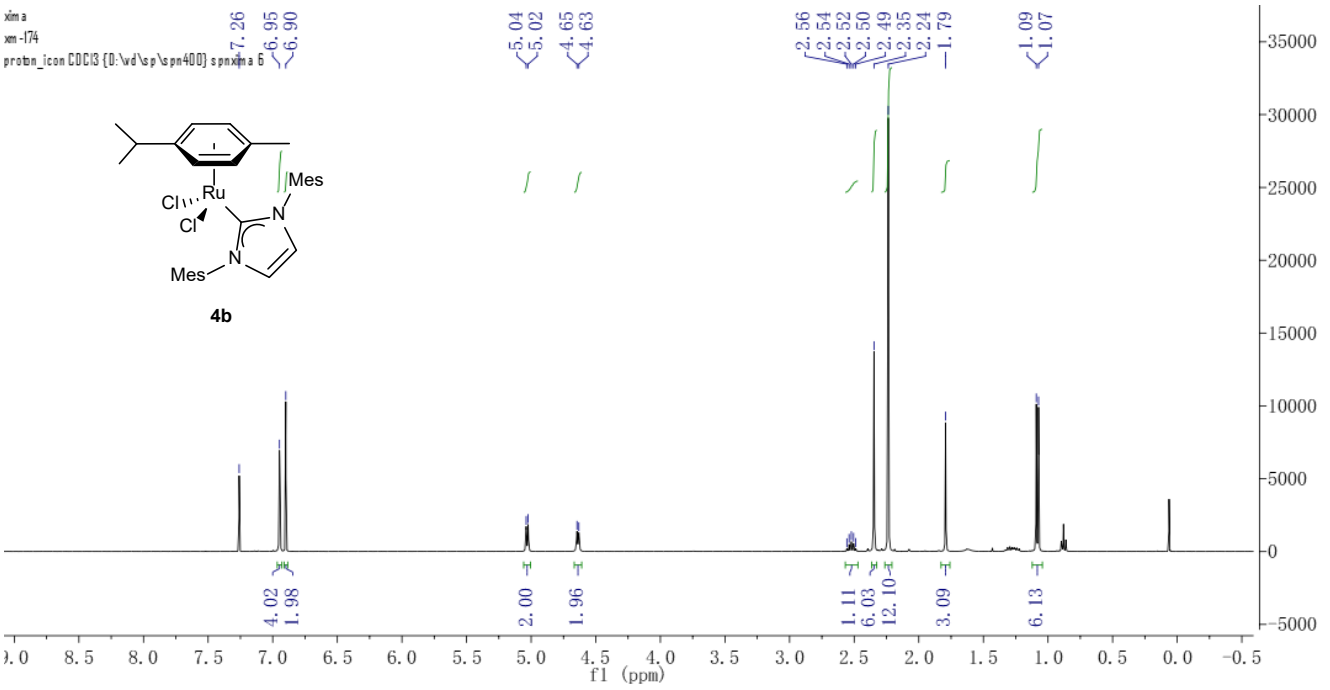


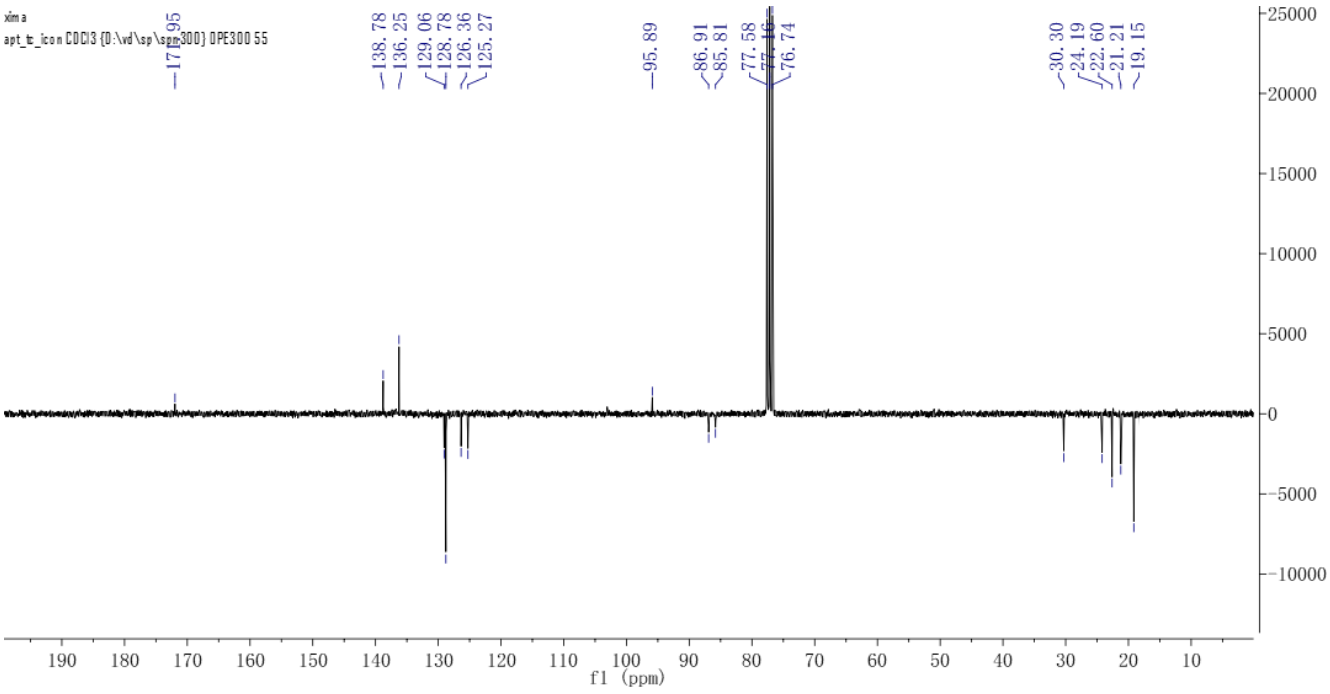
^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[RuCl_2(IPr)(p\text{-cymene})]$ (**4a**)



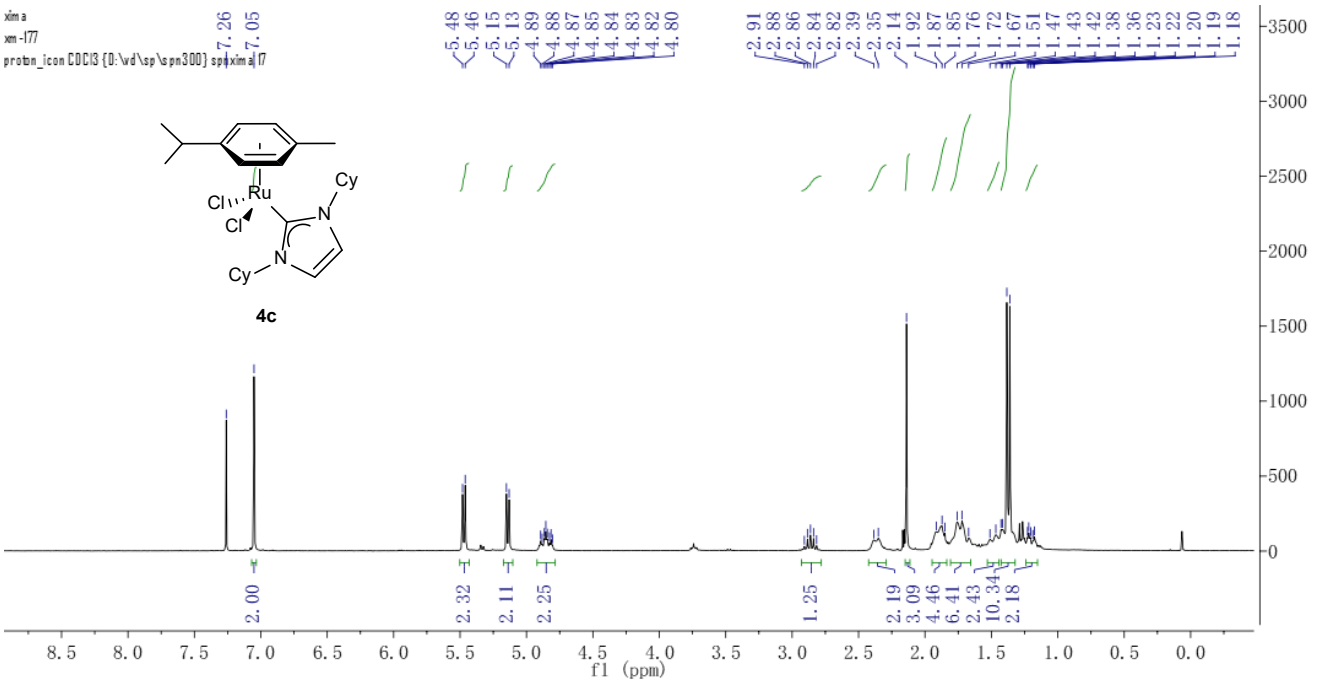


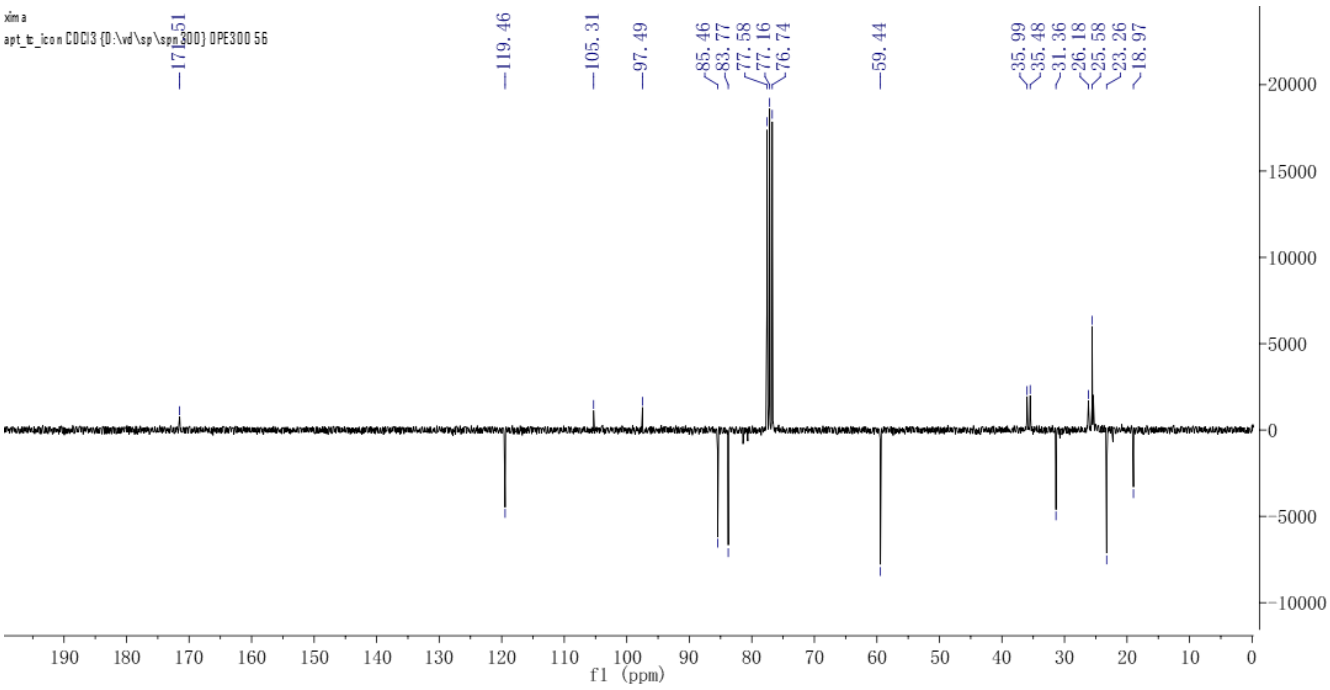
^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[RuCl_2(IMes)(p\text{-cymene})]$ (**4b**)



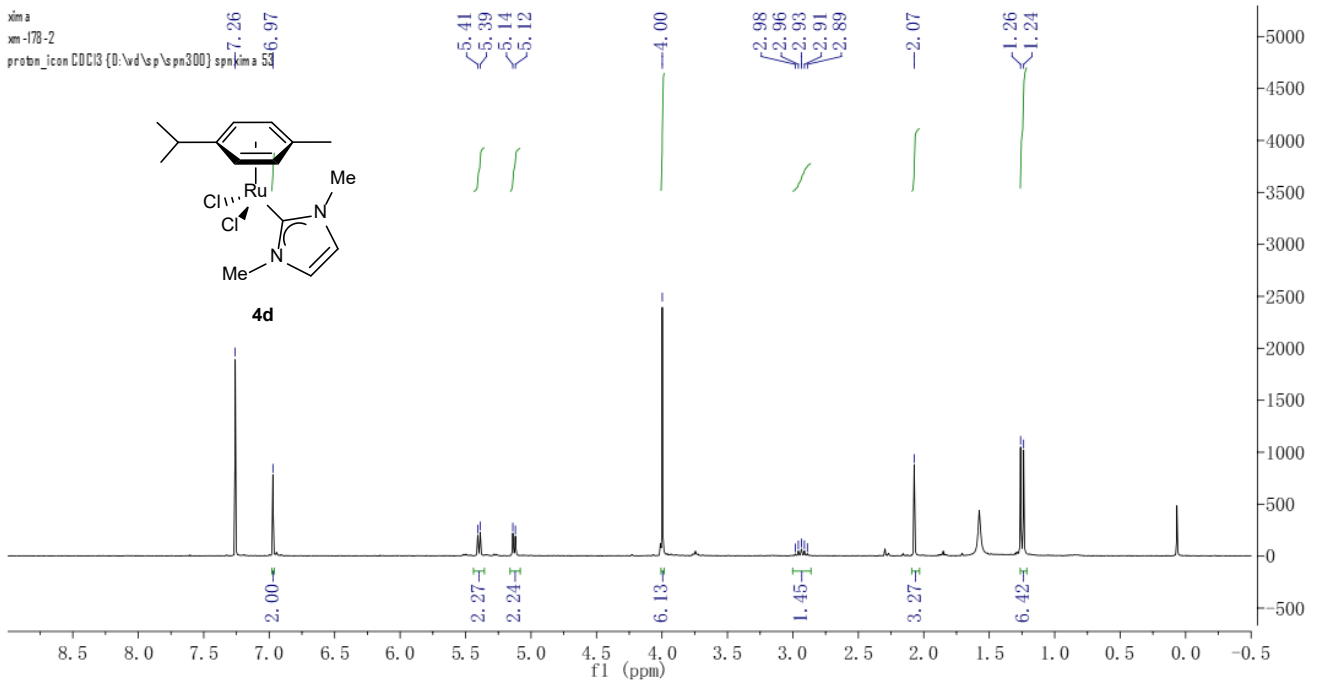


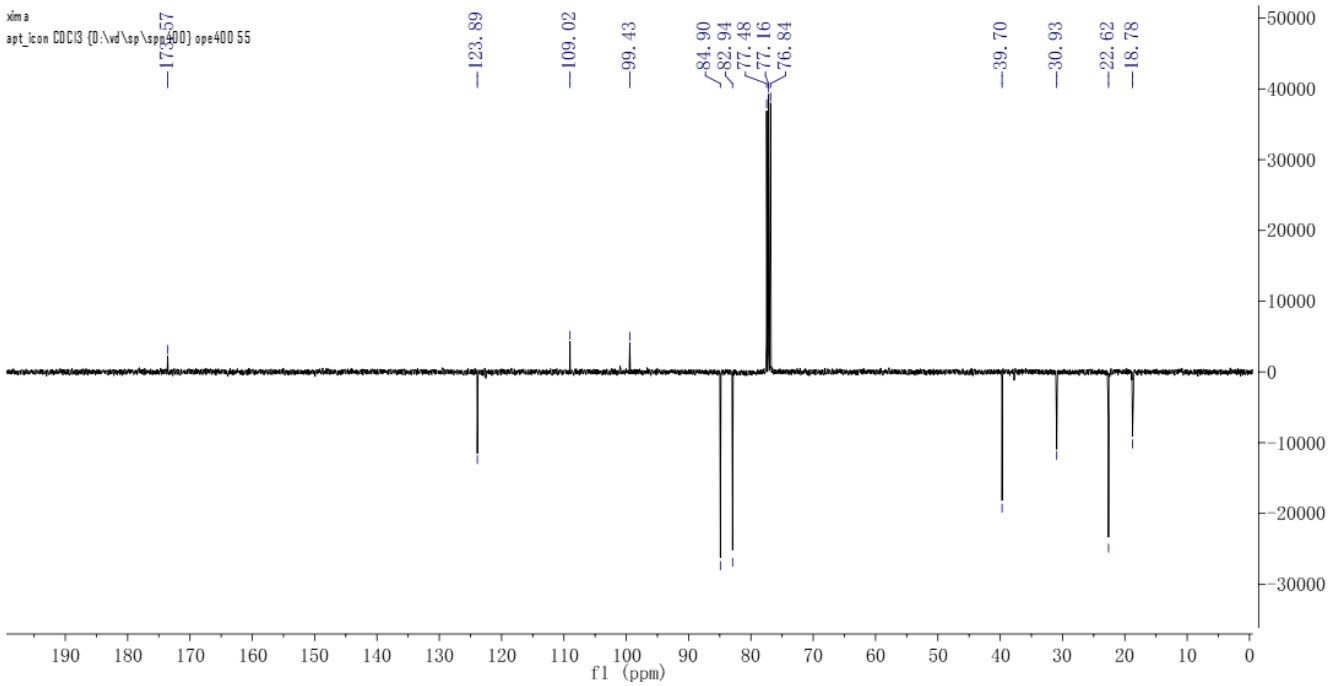
^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[RuCl_2(ICy)(p\text{-cymene})]$ (**4c**)



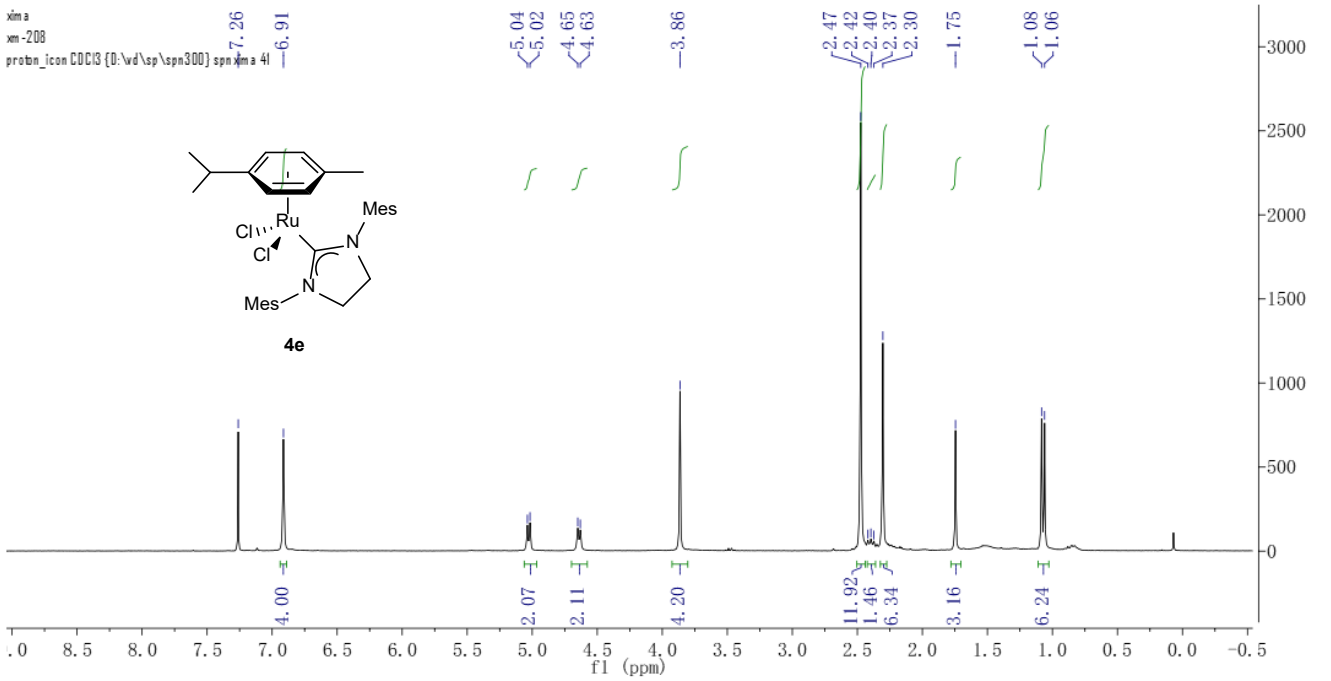


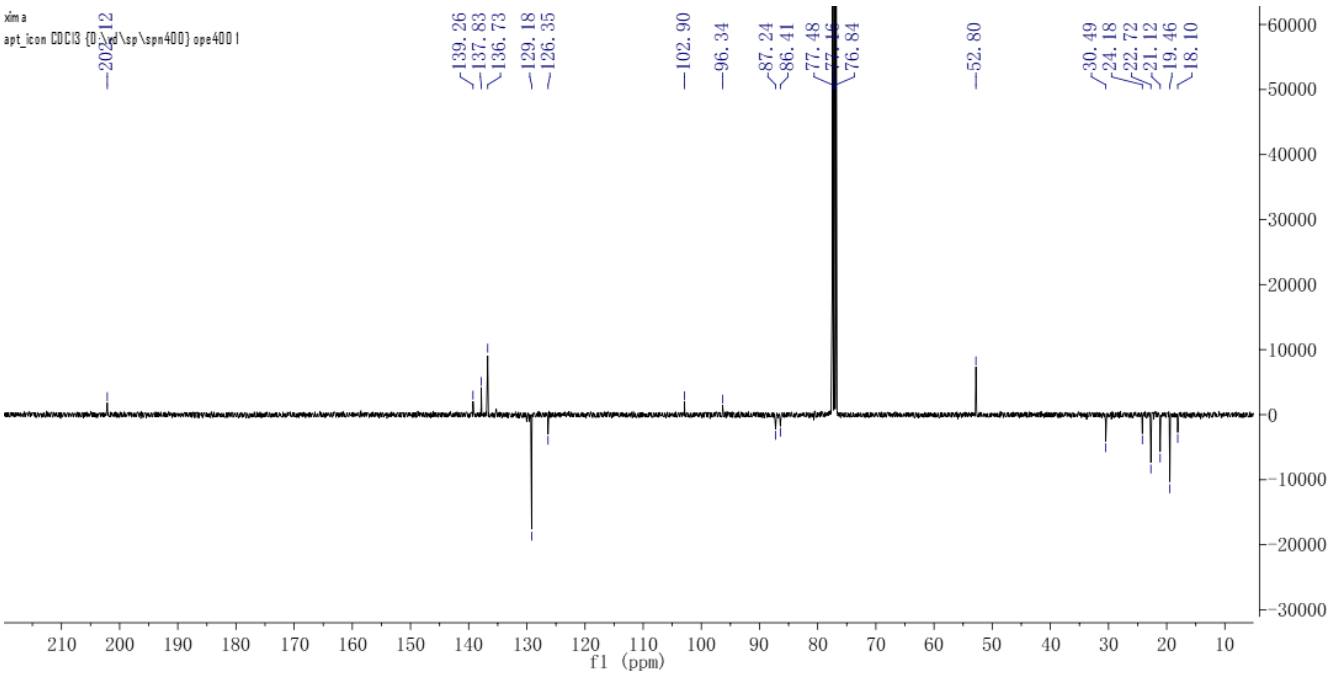
^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[RuCl_2(IMe)(p\text{-cymene})]$ (**4d**)





^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[RuCl_2(SIMes)(p\text{-cymene})]$ (**4e**)





^{1}H and $^{13}C\{^{1}H\}$ apt NMR of acetophenone (**6**)