

Supporting Information for

**A New Designed Hydrazine Group-contained Ruthenium Complex
Used for Catalytic Hydrogenation of Esters**

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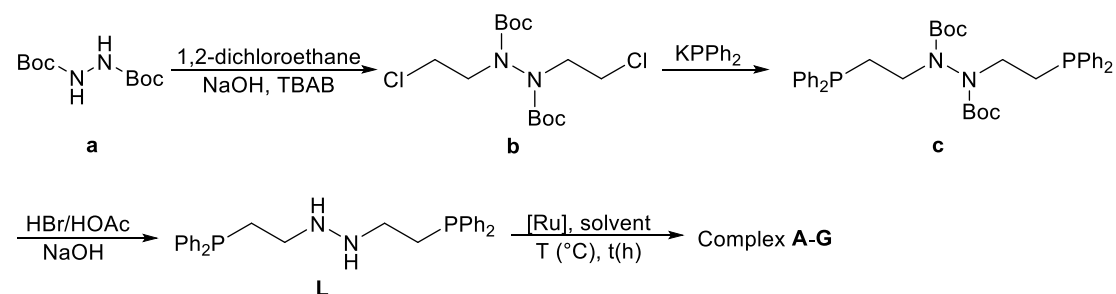
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1. General information

Unless mentioned otherwise, all experiments were carried out under an atmosphere of argon or using standard Schlenk techniques. Solvents were dried with standard procedures and degassed with N₂. ¹H, ¹³C, ³¹P NMR spectrum were recorded on NMR spectra were recorded on Bruker ADVANCE III (400 MHz) spectrometers for ¹H, ¹³C, ³¹P NMR. With CDCl₃ or CD₂Cl₂ as the solvent and tetramethylsilane as the internal standard. Chemical shifts were reported upfield to TMS (0.00 ppm) for ¹H NMR and relative to CDCl₃ (77.0 ppm) for ¹³C NMR. Column Chromatography was performed with silica gel Merck 60 (300-400 mesh). GC analysis was carried out on Angilent 1200 Series instrument using achiral capillary columns.

2. Synthetic details



Compound **a** and **b** were synthesized according to the literature procedure.^{1,2}

Preparation of **c**:

HPPH₂ (8.19 g, 44 mmol) was added to a suspension of KO^tBu (6.72 g, 60 mmol) in THF (120 mL) at room temperature. The mixture was stirred at room temperature for 15 minutes, then a solution of compound **b** (7.14 g, 20 mmol) in 10 mL THF was added dropwise. After stirred at room temperature for 4 hours, saturated NaCl solution (50 mL) was added. Remove most of the THF under vacuo, the aqueous phase was extracted with ethyl acetate (3 × 50 mL). Dried with anhydrous Na₂SO₄ and purified by column chromatography. A viscous liquid (7.89 g, 60%) was obtained. The product was obtained as a mixture of more than three conformations, due to the interaction of carbonyl group in –Boc substitute, which may exist as (cis, cis-**c**), (cis, trans-**c**) and (trans, trans-**c**). Reference 3 explained this phenomenon clearly. ¹H NMR (400 MHz, CDCl₃): δ = 7.29–7.50 (m, 20H), 3.38–3.64 (m, 4H), 2.28–2.54 (m, 4H), 1.38–1.52 (m, 18H); ¹³C NMR (101 MHz, CDCl₃) It's difficult to recognize each peak as there exists more than one conformation; ³¹P NMR (161.7 MHz, CDCl₃): δ -20.50 (s), -21.08 (s), -21.21 (s), -21.37 (s). HRMS (ESI+), m/z 657.3041 ([M+H]⁺), calcd for C₃₈H₄₇N₂O₄P₂⁺: 657.3006.

Preparation of **L**:

Compound **c** (2.63 g, 4 mmol) was dissolved in 20 mL dichloromethane, HBr/HOAc (5.6 mL, 40% wt.) was added to the solution at 0 °C. During 4 hours, a white solid precipitated out. Solvent was removed under vacuum and the solid was washed with ethyl ether (15 mL × 3). Under a nitrogen atmosphere, the solid was suspended in

toluene (30 mL), a solution of NaOH (3.2 mL, 10% wt.) was added and stirred for 30 min. The organic phase was separated and washed with water (10 mL*2). Dried with anhydrous Na₂SO₄ and concentrated, a viscous liquid (1.65 g) was obtained, which can be used in the next step without further purification. ¹H NMR(400 MHz, CDCl₃): δ = 7.44-7.50 (m, 8H), 7.32-7.40 (m, 12H), 3.10-3.21 (br, 2H), 2.84-3.00 (dt, J¹ = 6.8 Hz, J² = 8.4 Hz, 4H), 2.23-2.33 (t, J = 8.0 Hz, 4H); ¹³C NMR (101 MHz, CDCl₃) δ = 138.5, 138.3, 132.8, 132.7, 128.7, 128.6, 128.5, 48.2, 48.0, 27.2, 27.1; ³¹P NMR (161.7 MHz, CDCl₃): δ = -20.5(s). HRMS (ESI+), m/z 457.1971 ([M+H]⁺), calcd for C₂₈H₃₁N₂P₂⁺: 457.1957.

Preparation of **Complex A-G**:

All complexes were prepared used a same procedure. Under a nitrogen atmosphere, ruthenium precursors (0.5 mmol, see Table 1) were added to a 25 mL schlenk vessel, a solution of d (0.55 mmol) in corresponding solvent (10 mL, see Table 1) was added. The mixture was heated to required temperatures and stirred for required time (Table 1). The reaction mixture was cooled to room temperature and concentrated. Ethyl ether (10 mL) was added and stirred for 5 min in an ice bath. The precipitates was filtered under a nitrogen atmosphere and washed with ethyl ether for two times. Corresponding complexes were obtained after dried under vacuum and used directly without further purification.

Table 1. Reaction conditions of preparation of complex A-G.

Entry	[Ru]	Solvent	T (°C)	t (h)	Complex
1	RuCl ₂ (PPh ₃) ₃	DCM	25	12	A
2	RuCl ₂ (PPh ₃) ₃	THF	70	20	B
3	RuCl ₂ (PPh ₃) ₃	Toluene	110	24	C
4	[RuCl ₂ (p-cymene)] ₂	THF	70	20	D
5	[RuCl ₂ (p-cymene)] ₂	Dioxane	100	12	E
6	RuHCl(CO)(PPh ₃) ₃	Toluene	110	10	F
7	RuCl ₂ (DMSO) ₄	THF	70	12	G

NMR spectra of Complex A and B have the same conformation as follow:

¹H NMR(400 MHz, CDCl₃): δ = 6.80-7.54 (m, 35H, *aryl-H*), 5.69-5.92 (br, 1H, *NH*), 5.22-5.32 (br, 1H, *NH*), 3.51-3.76 (br, 2H, *NHCH₂*), 3.26-3.47 (br, 2H, *NHCH₂*), 2.66-2.85 (br, 1H, *PCH₂*), 2.42-2.64 (br, 2H, *PCH₂*), 2.16-2.29 (br, 1H, *PCH₂*); ³¹P NMR (161.7 MHz, CDCl₃): δ = 40.9 (t, 1P, J = 28.6 Hz, **L_{P1}**), δ = 28.4 (dd, 1P, J¹ = 308.8 Hz, J² = 29.1 Hz, **L_{P2}**), δ = -3.8 (d-br, 1P, J = 308.8 Hz, PPh₃), δ = -5.6 (s, free PPh₃). The free and two broad peaks of PPh₃ revealed an equilibrium between the five- and six-coordinated species and the existence of interconversion between those species. The distinction between J_{P1-P2} (29.1 Hz) and J_{P2-PPh₃} (308.8 Hz) revealed P1 hold the cis-position to P2, and P2 hold the trans-position to PPh₃, the small coupling constant of P1 (28.6 Hz) revealed P1 hold the cis-position to P2 and PPh₃.

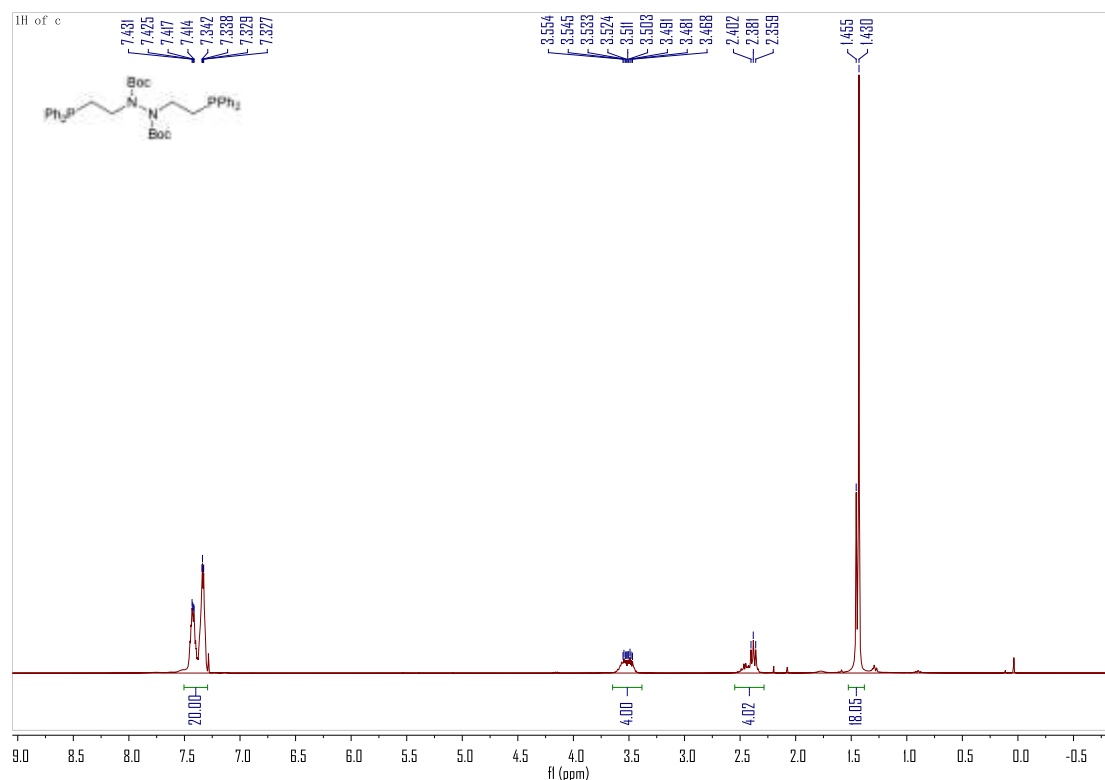
¹H and ³¹P NMR spectra showed the structure of catalysts **C - G** are extremely complicated, ¹H and ³¹P NMR spectra showed the structure of catalysts **C - G** are

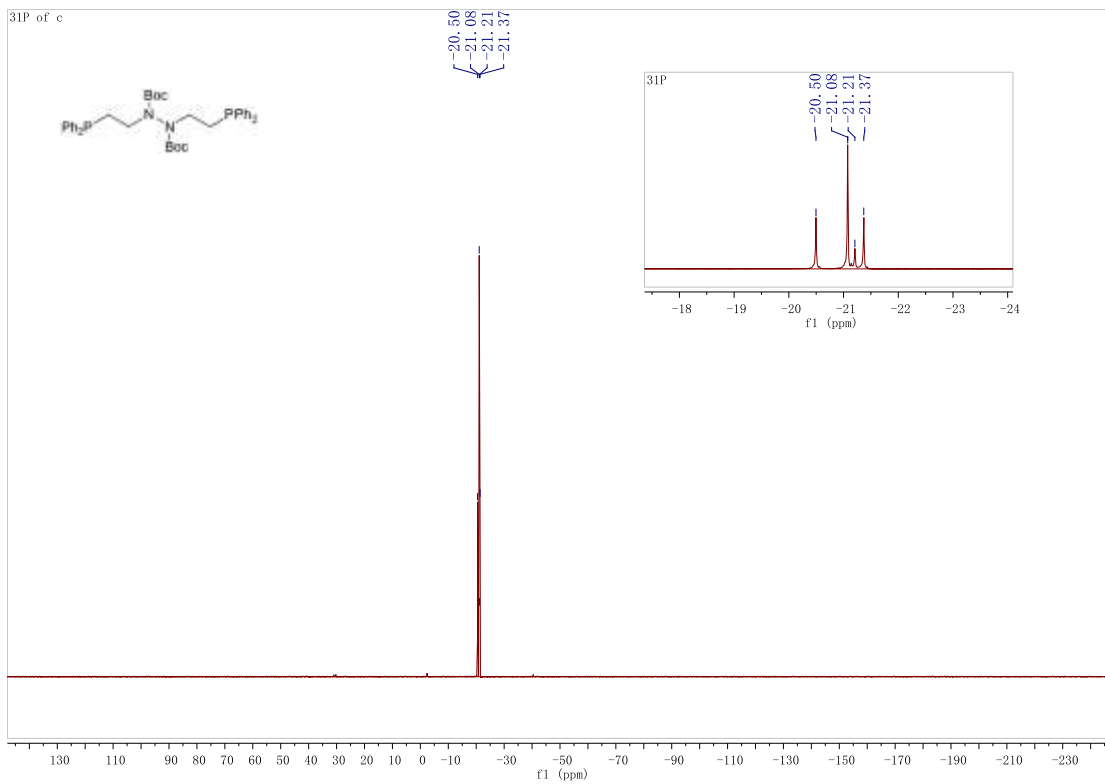
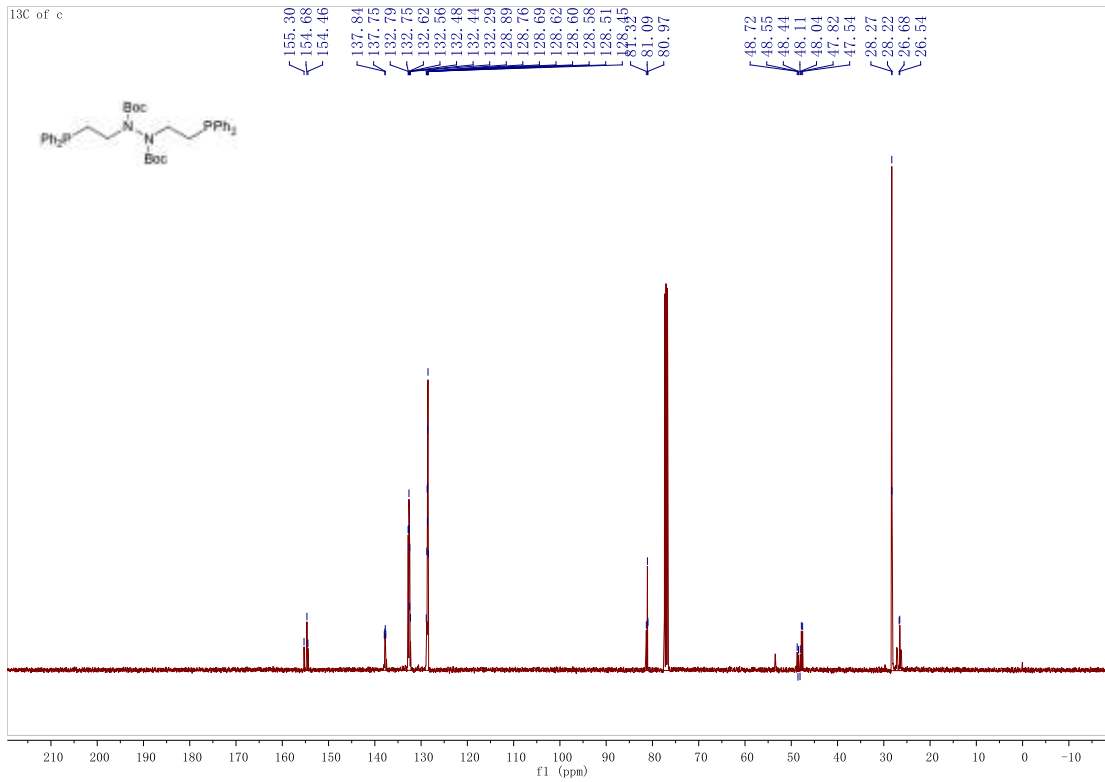
extremely complicated, and high-resolution mass spectra revealed there existed $\text{RuCl}_2(\text{L})$ and its dimer or trimer. This may be due to the deficient coordinating atoms to fulfill the 18 electron compositions and solvents participated the coordination or even one hydrazine group coordinated with two ruthenium to form the dimer, trimer or oligomer complexes.

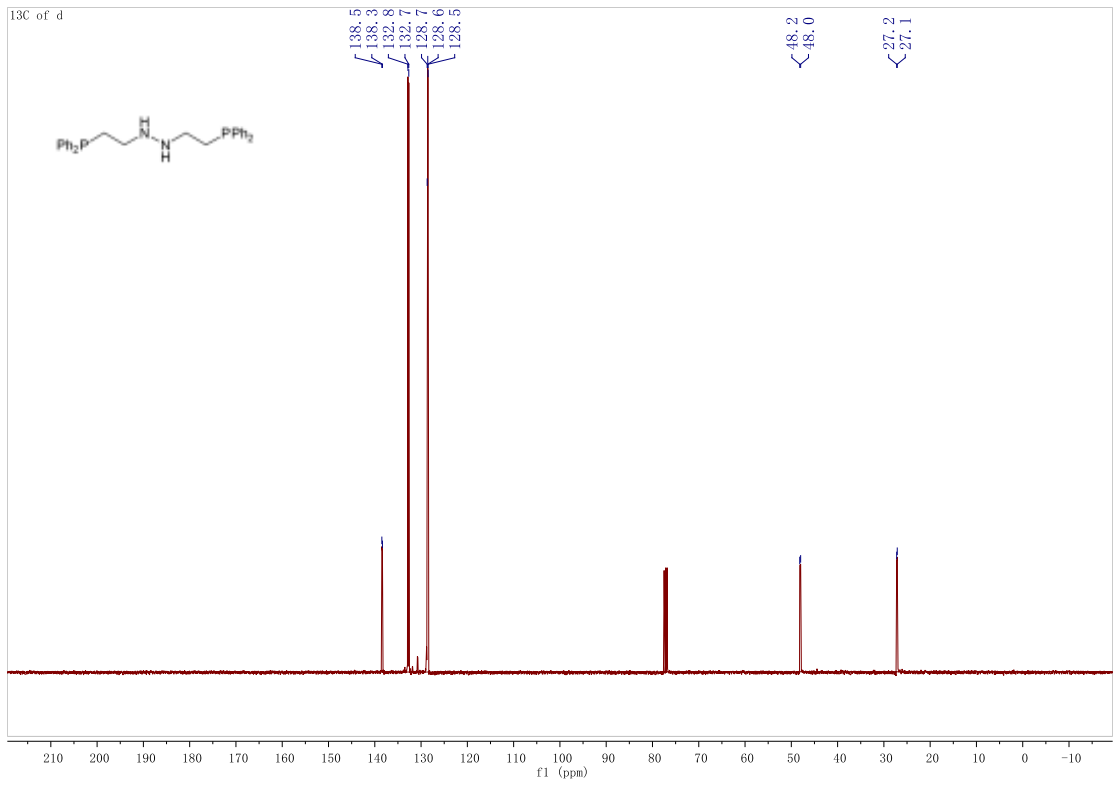
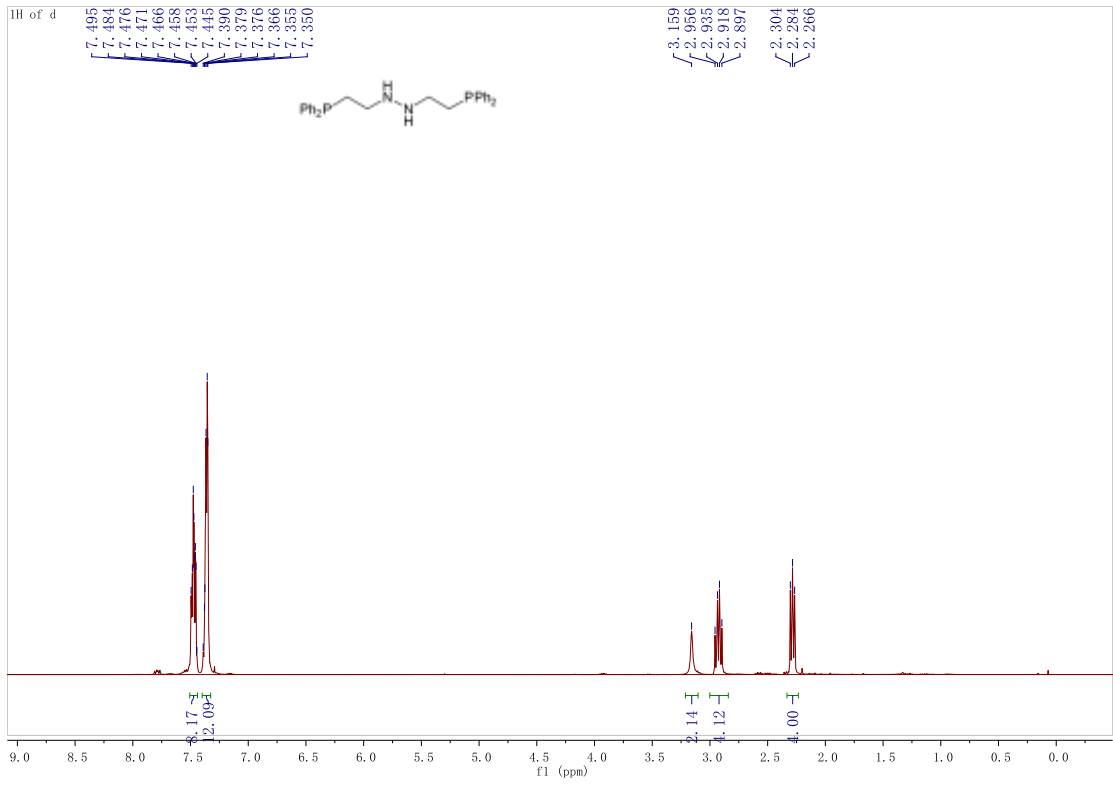
3. Catalytic study details

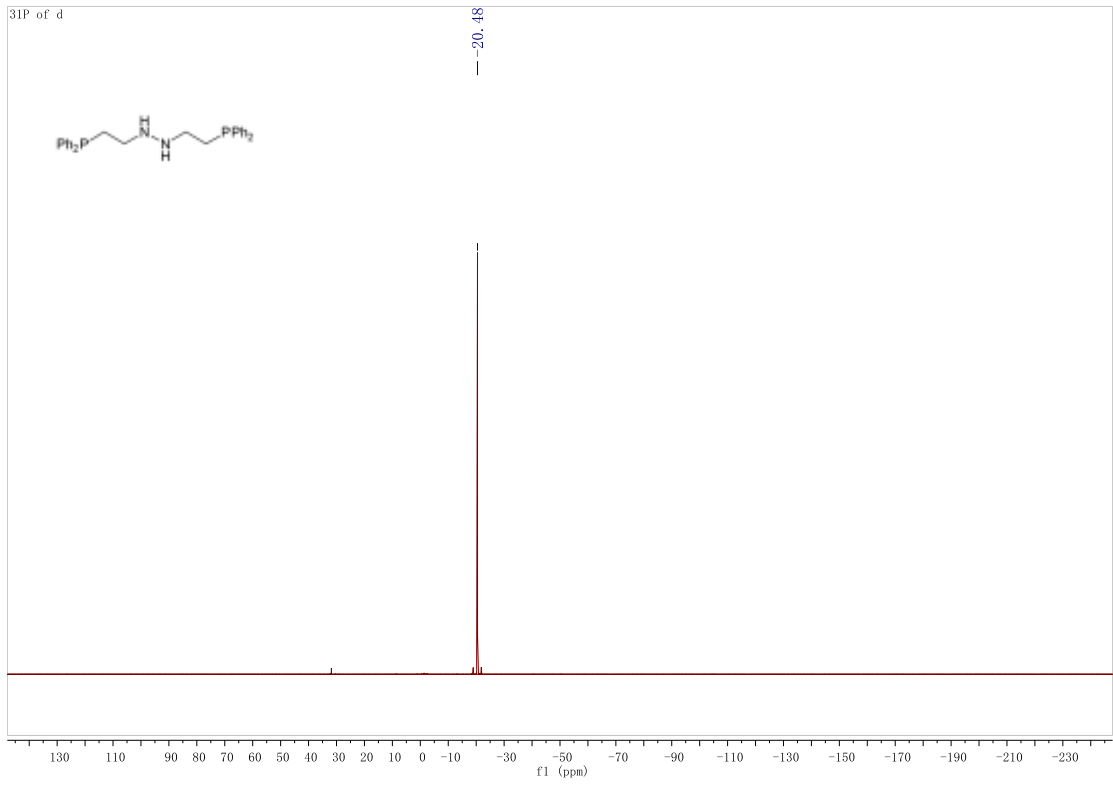
In an argon glovebox, a 5 mL vial equipped with a magnetic stirring bar, was added the required amount of complex **A-G** (1 mg/mL in used solvent) and base successively, the mixture was shaken homogeneously. To the mixture was added substrate (5 mmol) and the necessary amount of solvent (plus the solution of complex, 3 mL in all). The mixture was transferred to a stain-less autoclave and then was purged by three cycles of pressurization/venting with H_2 (10 atm) then pressurized with H_2 (50 atm) and disconnected from the H_2 source. Then the autoclave was placed in an oil bath preheated to the desired temperature. After the desired reaction time, the autoclave was cooled in an ice bath, and the pressure was released slowly. The resulting mixture was filtered with a plug of silica gel and then analyzed by GC.

4. NMR and mass spectra

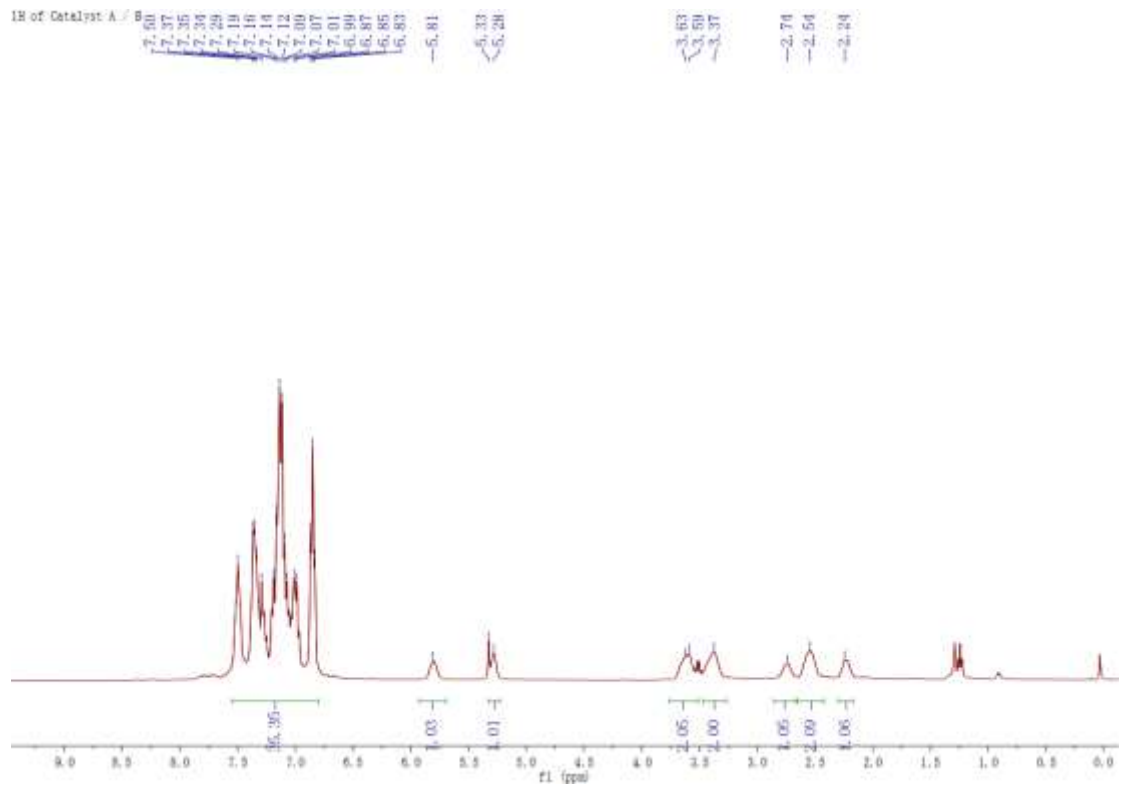






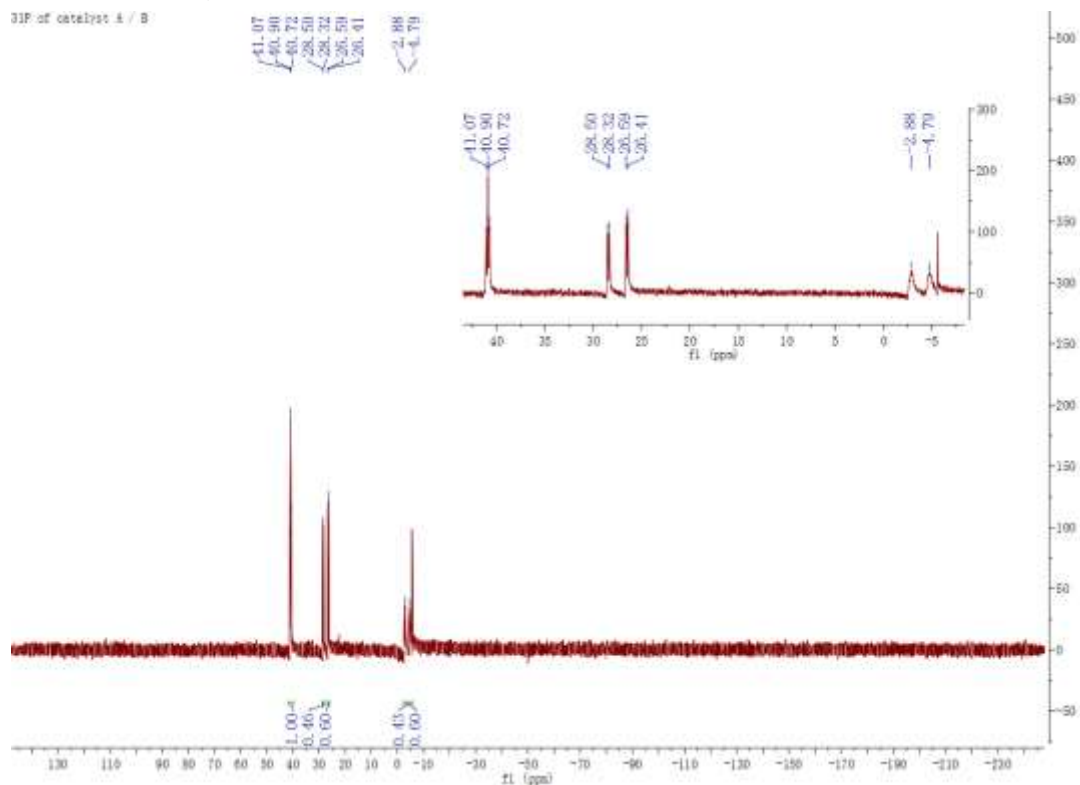


¹H NMR of catalyst A/B



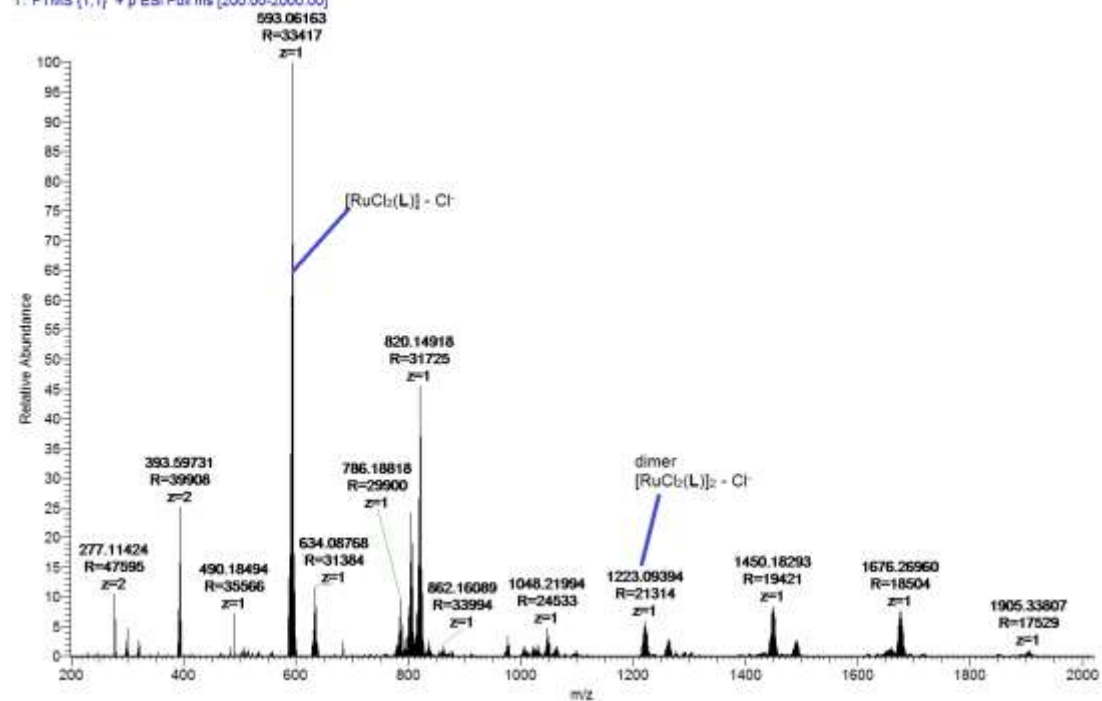
^{31}P NMR of catalyst A/B

^{31}P of catalyst A / B

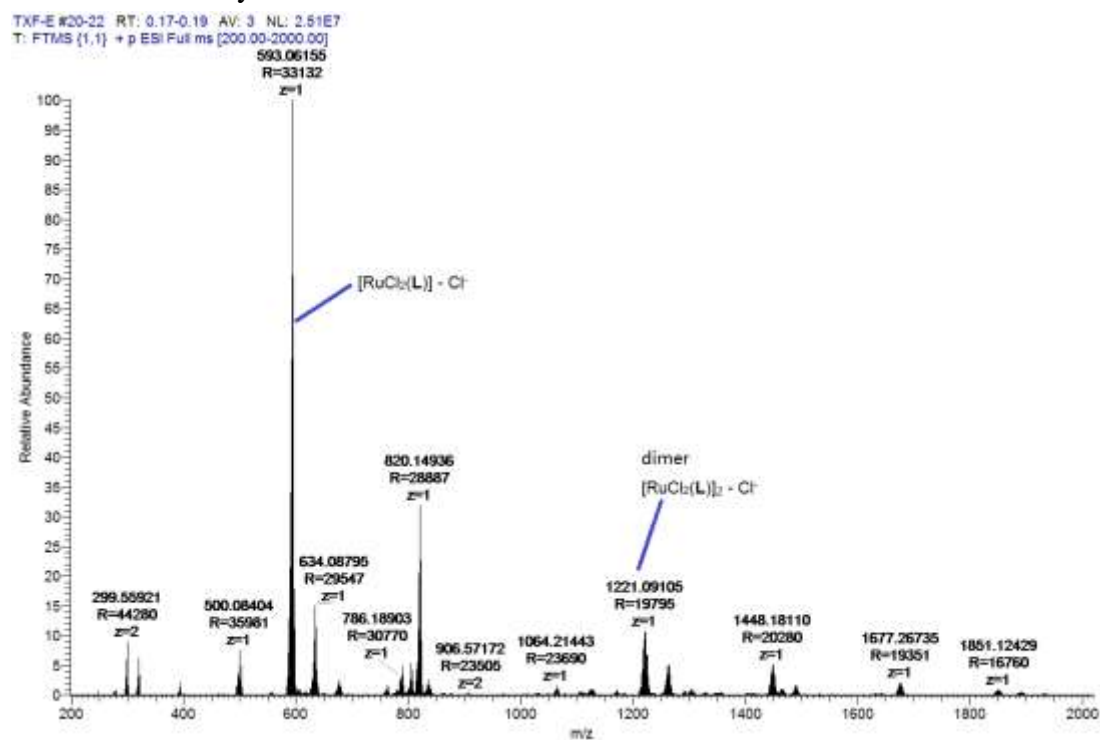


Full Mass of catalyst C

TXF-C#12-13 RT: 0.11-0.12 AV: 2 NL: 2.22E7
T: FTMS (1,1) + p ESI Full ms [200.00-2000.00]



Full Mass of catalyst E



5. Reference

- (1) Pérez Luna, A.; Ceschi, M. A.; Bonin, M.; Micouin, L.; Husson, H. P.; Gougeon, S.; Estenne-Bouhtou, G.; Marabout, B.; Sevrin, M.; George, P. *The Journal of organic chemistry* **2002**, *67*, 3522.
- (2) Muehlebach, M.; Boeger, M.; Cederbaum, F.; Cornes, D.; Friedmann, A. A.; Glock, J.; Niderman, T.; Stoller, A.; Wagner, T. *Biorg. Med. Chem.* **2009**, *17*, 4241.
- (3) Nielsen, A. T.; Lawrence, G. W. *The Journal of organic chemistry* **1977**, *42*, 2900.