

## Supporting Information

# Silylated Organometals: A Family of Recyclable Homogeneous Catalysts

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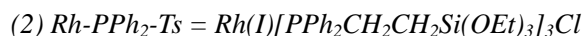
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### 15 Silylated organometal catalysts preparation

(1)  $Pd\text{-}PPh_2\text{-}Ts = Pd(II)[PPh_2CH_2CH_2Si(OEt)_3]_2Cl_2$ .

In a typical run of synthesis, 2.7 g  $PPh_2CH_2CH_2Si(OEt)_3$  was added dropwise into a suspension comprised of 1.0 g  $Pd(COD)Cl_2$  (COD=1,5-cyclooctadiene) and 25 ml toluene. The mixture was kept stirring until reaching a clear orange solution for 24 h. The solution was concentrated to 5.0 ml, followed by 25 ml pentane to extract those soluble  
20 organic substances. The yellow solid was recovered by filtration and washed thoroughly with distilled pentane. Finally, the yellow solid was dried at 60°C and 0.10 Torr to remove residue solvents, leading to the solid  $Pd\text{-}PPh_2\text{-}Ts$  catalyst.



0.54 g  $[RhCl(COD)]_2$  was dissolved in 10 ml toluene in a Schlenk tube, followed by adding dropwise 10 ml toluene containing 2.6 g  $PPh_2CH_2CH_2Si(OEt)_3$ . The mixture was kept stirring for 3 h, during which the solution color changed from red-orange to red. Then, toluene solvent was distilled at 60°C and 0.10 Torr, followed by adding 25 ml pentane to extract those soluble organic substances. After cooling to -20°C, the clear solution in up-layer was decanted and the left red-orange oil layer was dried at 60°C and 0.10 Torr to remove residue solvents, leading to the solid  $Rh\text{-}PPh_2\text{-}Ts$  catalyst.



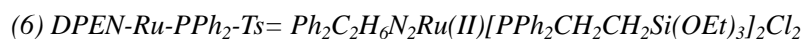
2.1 g  $PPh_2CH_2CH_2Si(OEt)_3$  was added dropwise into a suspension comprised of 1.0 g  $Pt(COD)Cl_2$  and 20 ml toluene. The mixture was kept stirring at 25°C until reaching a clear yellow-green solution. After being concentrated to 5.0 ml, 25 ml pentane was added. The white solid was recovered by filtration and washed thoroughly with distilled pentane, followed by drying at 60°C and 0.10 Torr to remove residue solvents, leading to the solid  $Pt\text{-}PPh_2\text{-}Ts$  catalyst.



0.25 g  $[Ir(COD)Cl]_2$  was dissolved in 10 ml toluene in a Schlenk tube, followed by adding dropwise into 5.0 ml toluene containing 0.96 g  $PPh_2CH_2CH_2Si(OEt)_3$ . The mixture was kept stirring at 25°C for 3 h, during which the solution color changed from red to orange. Then, toluene solvent was distilled at 60°C and 0.10 Torr, followed by adding 25 ml pentane. After cooling to -20°C, the clear solution in up-layer was decanted and the left red-orange oil layer was dried at 60°C and 0.10 Torr to remove residue solvents, leading to the solid  $Ir\text{-}PPh_2\text{-}Ts$  catalyst.



0.60 g  $RuCl_3 \cdot xH_2O$  was dissolved in 75 ml methanol in a Schlenk tube, followed by adding 5.2 g  $PPh_2CH_2CH_2Si(OEt)_3$  under stirring. Then, sodium borohydride was added gradually until the solution color changed to brown. After further stirring for 15 h at 25°C, methanol was evaporated at 60°C and 0.50 Torr. Then, 50 ml  $CH_2Cl_2$  was added and the mixture was shaken for 30 min. After filtrating the solid, the  $CH_2Cl_2$  solvent was evaporated at 50°C and 0.50 Torr. Finally, the oil layer was extracted with pentane for two times to remove soluble organic substances, followed by drying at 60°C and 0.10 Torr to remove residue solvents, leading to the solid  $Ru\text{-}PPh_2\text{-}Ts$  catalyst.



1.0 mmol Ru-PPh<sub>2</sub>-Ts and 1.2 mmol DPEN were dissolved in 6.0 ml CH<sub>2</sub>Cl<sub>2</sub> and kept stirring for 5 h at room temperature, followed by evaporating CH<sub>2</sub>Cl<sub>2</sub> solvent at 50°C and 0.50 Torr. Then, the oil layer was washed with fresh pentane for two times to remove soluble organic substances, followed by drying at 60°C and 0.10 Torr to remove residue solvents, leading to the solid DPEN-Ru-PPh<sub>2</sub>-Ts catalyst.

5 For comparison, the Pd-PPh<sub>2</sub>-PMO (Ph) and Ru-PPh<sub>2</sub>-PMO (Ph) catalysts were used from our paper before reported.<sup>1</sup> As well as, the Pd(PPh<sub>3</sub>)<sub>4</sub>, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, Pt(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, [Ir (COD)Cl]<sub>2</sub>, Pt(COD)Cl<sub>2</sub>, Pd(COD)Cl<sub>2</sub>, [RhCl(COD)]<sub>2</sub>, Rh(PPh<sub>3</sub>)<sub>3</sub>Cl, Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub> and DPEN homogeneous catalysts were also used as references in the different organic reactions. All these catalysts and other chemical reagents were commercially available and purified before use according to the standard methods.

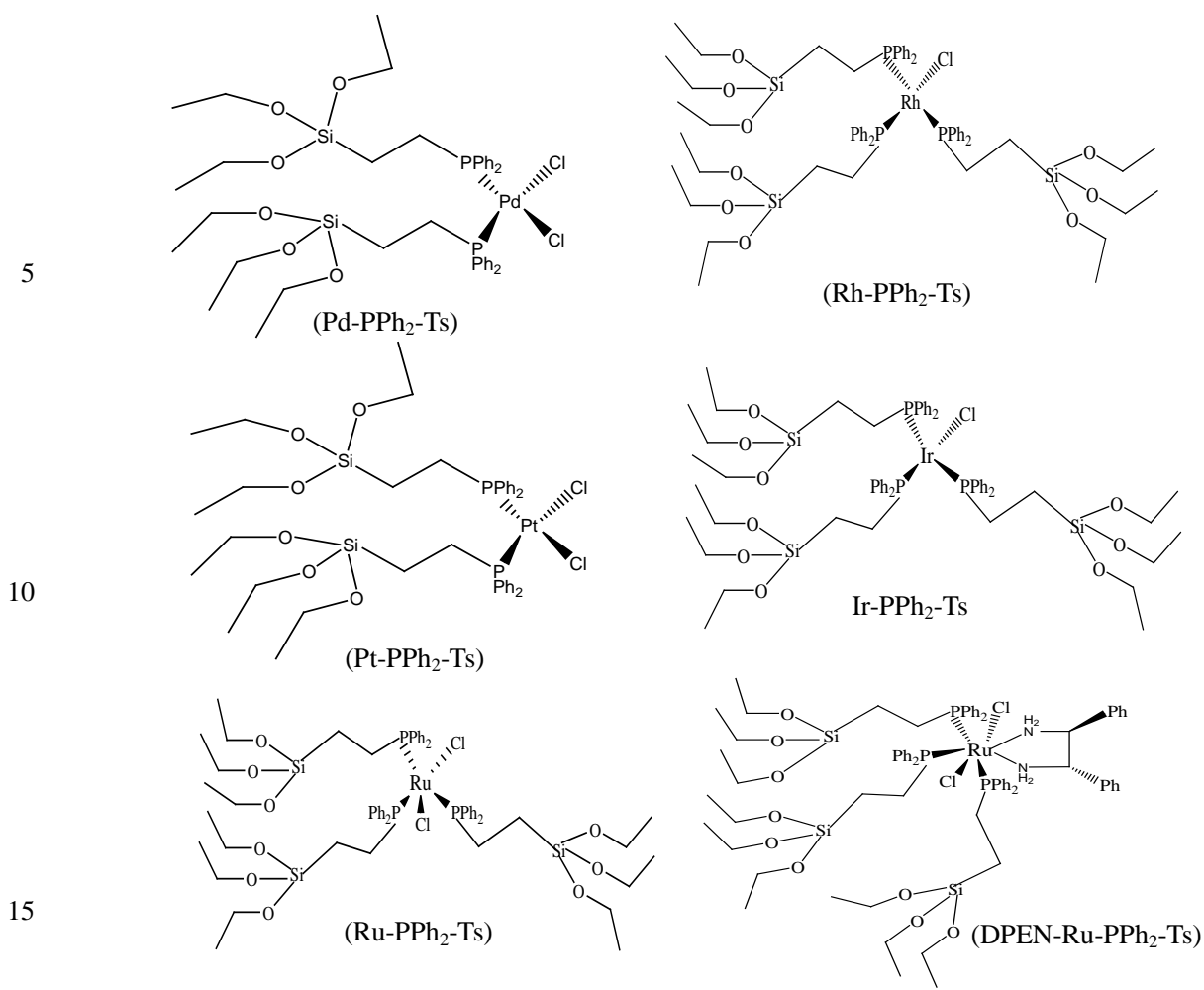
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1 J.-L. Huang, F. Zhu, W. He, F. Zhang, W. Wang, H.-X. Li, *J. Am. Chem. Soc.* 2010, **132**, 1492-1493.

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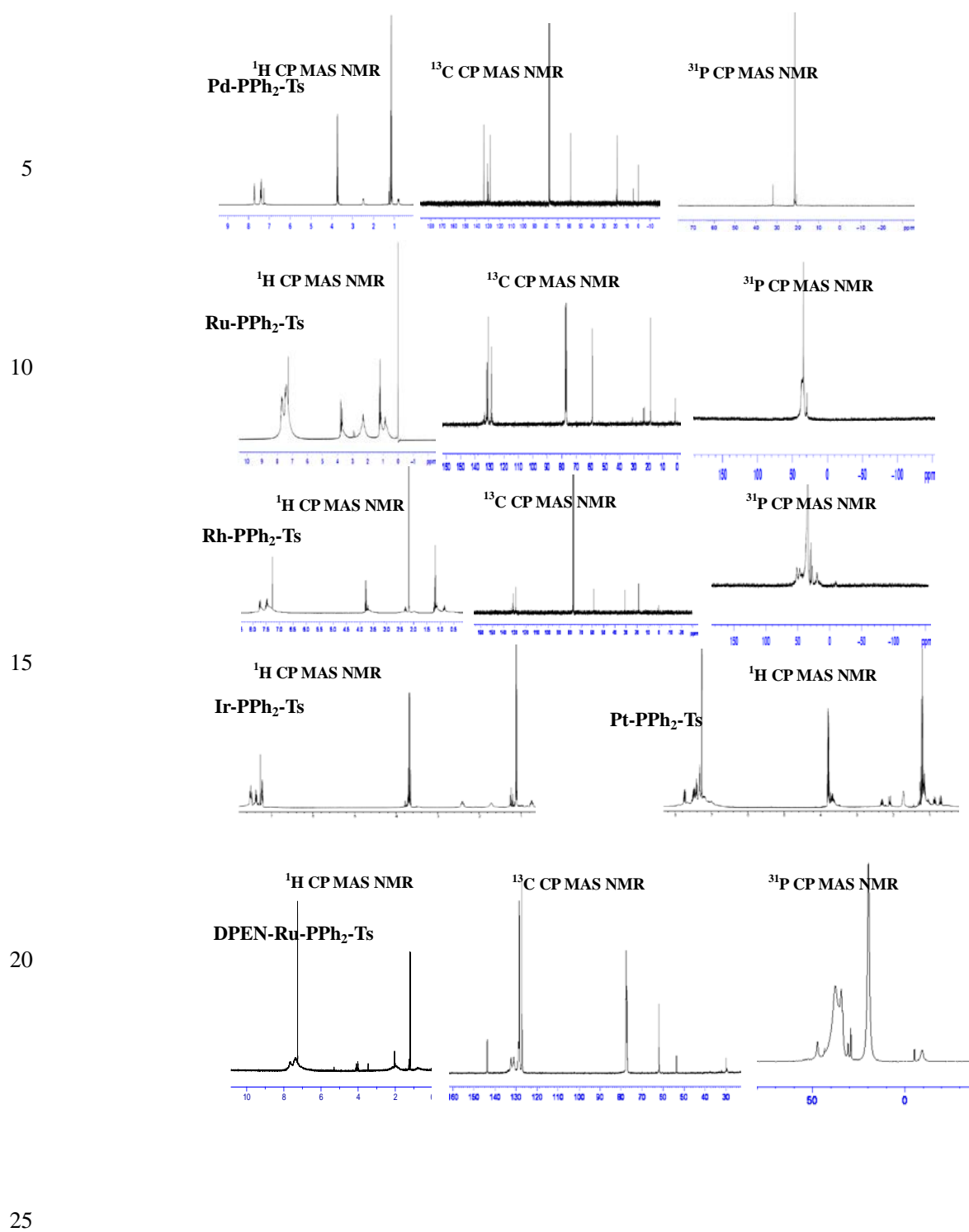
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**Scheme S1.** Illustration of the silylated organometallic catalysts structural formula.

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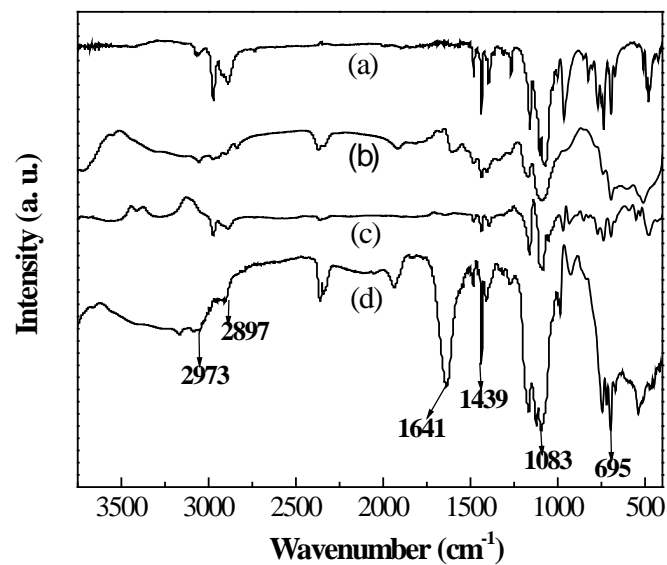


**Fig. S1** NMR spectra of different samples in CDCl<sub>3</sub>.

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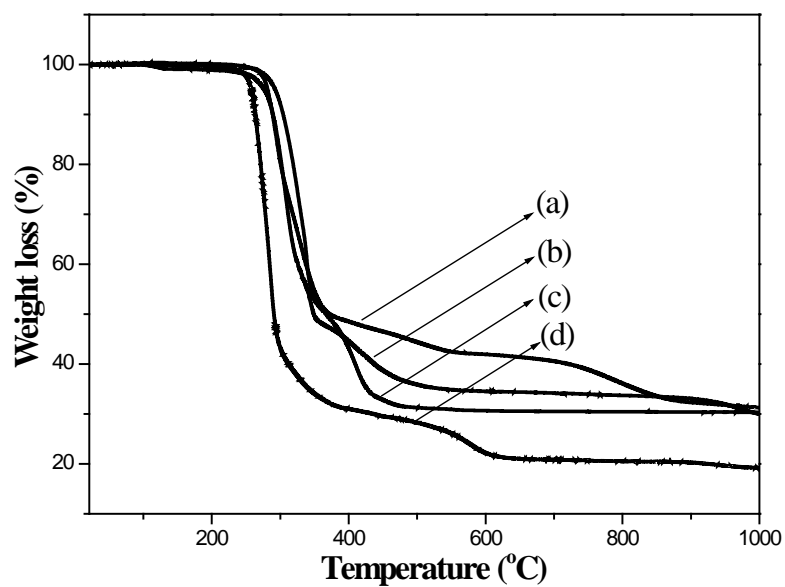
**Fig. S2** FTIR spectra of (a) Pd-PPh<sub>2</sub>-Ts, (b) Ru-PPh<sub>2</sub>-Ts, (c) Rh-PPh<sub>2</sub>-Ts, and (d) DPEN-Ru-PPh<sub>2</sub>-Ts.

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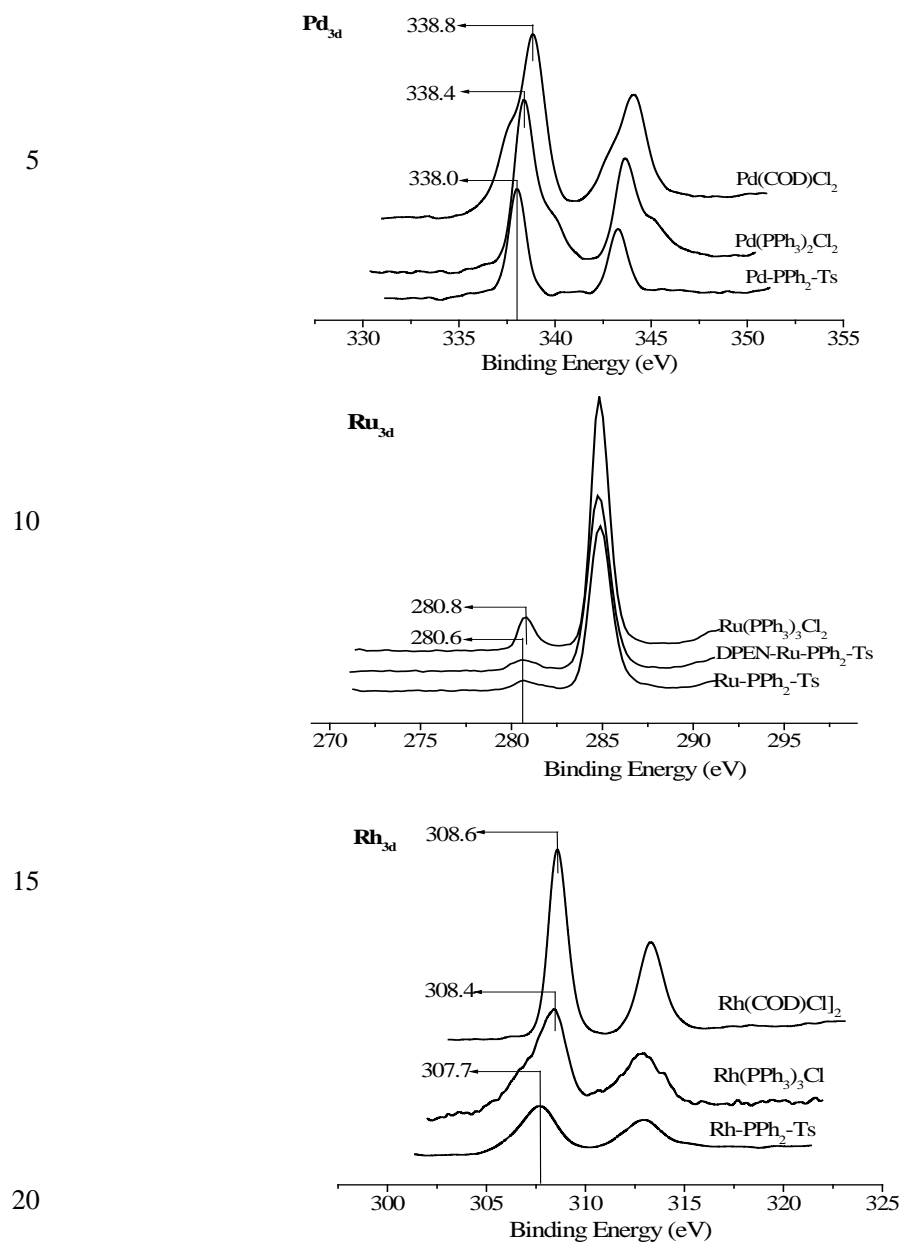
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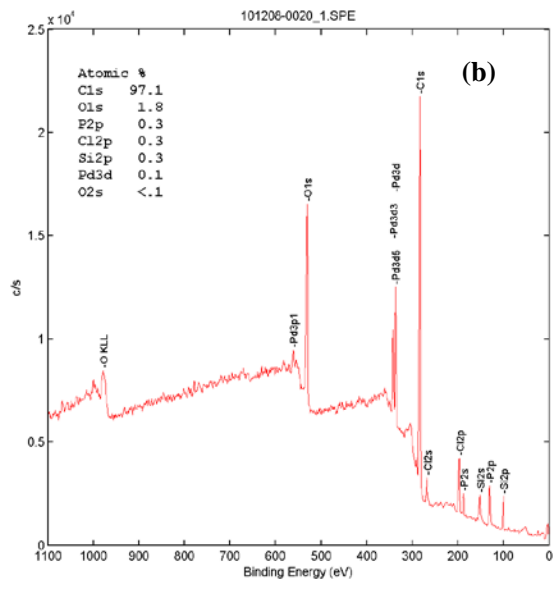
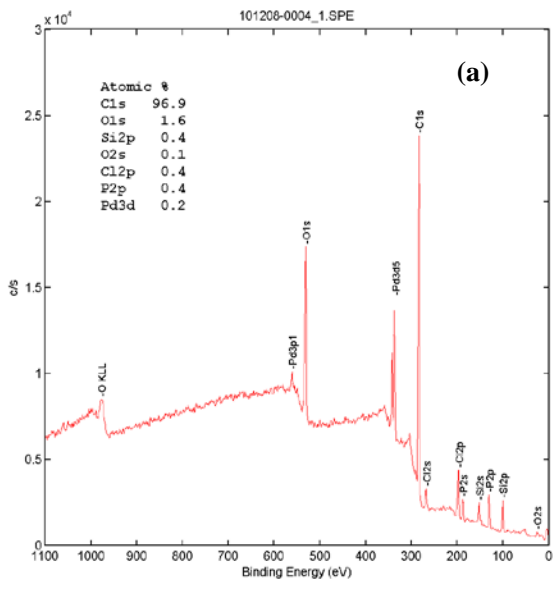
**Fig. S3** TG curves of (a) Pd-PPh<sub>2</sub>-Ts, (b) Rh-PPh<sub>2</sub>-Ts, (c) Ru-PPh<sub>2</sub>-Ts, and (d) DPEN-Ru-PPh<sub>2</sub>-Ts.



**Fig. S4** XPS spectra of different samples.

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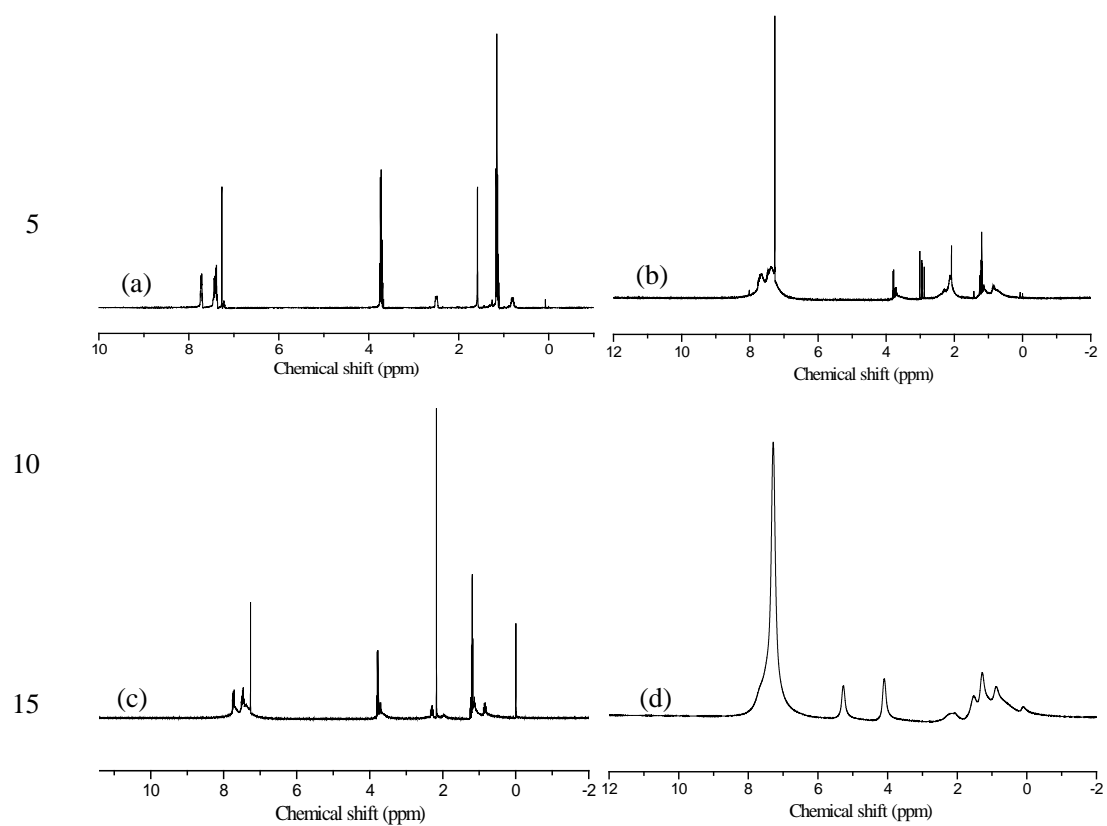
**Fig. S5** XPS spectra of Pd-PPh<sub>2</sub>-Ts catalyst (a) fresh and (b) after being used repetitively for 6 times.

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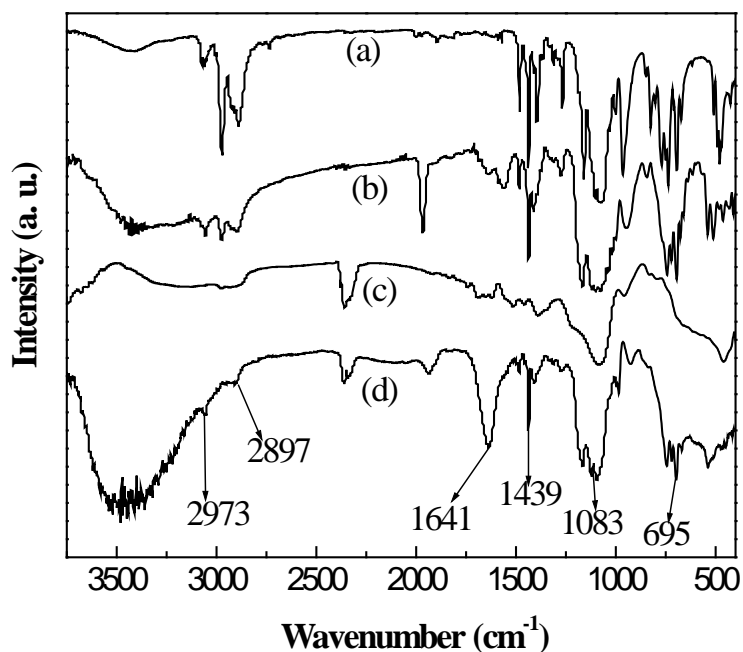


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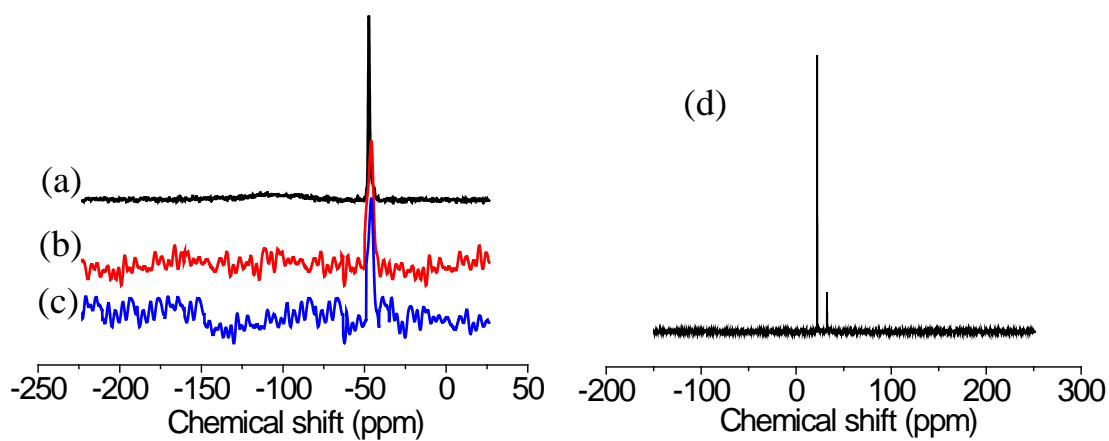
**Fig. S6**  $^1\text{H}$  CP MAS NMR spectra of (a) Pd-PPh<sub>2</sub>-Ts (b) Ru-PPh<sub>2</sub>-Ts, as well as (c) Rh-PPh<sub>2</sub>-Ts after being used repetitively for 6 times and (d) DPEN-Ru-PPh<sub>2</sub>-Ts after being reused for 3 times repetitively.

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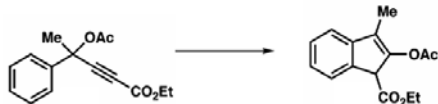
**Fig. S7** FTIR spectra of (a) Pd-PPh<sub>2</sub>-Ts (b) Ru-PPh<sub>2</sub>-Ts, as well as (c) Rh-PPh<sub>2</sub>-Ts after being used repetitively for 6 times and (d) DPEN-Ru-PPh<sub>2</sub>-Ts after being reused for 3 times repetitively.



**Fig. S8** <sup>29</sup>Si CP MAS NMR spectra of (a) PPh<sub>2</sub>-Ts (b) Pd-PPh<sub>2</sub>-Ts, and (c) Pd-PPh<sub>2</sub>-Ts after being used repetitively for 6 times (d) <sup>31</sup>P CP MAS NMR of Pd-PPh<sub>2</sub>-Ts after being used repetitively for 6 times.

Table S1. Reaction efficiencies of Pt-catalyzed cyclization of propargylic esters<sup>a</sup>

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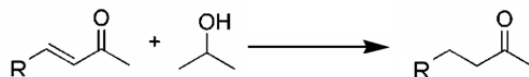
Catalyst	Reactant	Product	Yield(%)
Pt(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>			85
Pt-PPh <sub>2</sub> -Ts			81
Pt(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>			65
Pt-PPh <sub>2</sub> -Ts			61
Pt(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>			79
Pt-PPh <sub>2</sub> -Ts			75
Pt(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>			73
Pt-PPh <sub>2</sub> -Ts			73

<sup>a</sup>Reaction conditions: catalyst (0.10 equiv), PhIO (0.20 equiv), PhMe (0.20 M), 5.0 ml toluene, 100°C, 8 h.

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Table S2. Reaction efficiencies of Ir-catalyzed transfer hydrogenation reactions<sup>a</sup>

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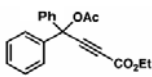
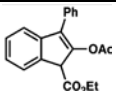



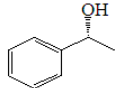


entry	Reactant	Product	Conversion(%)	Selectivity(%)
1			95(98)	95(97)
2			96(98)	94(95)
3			73(76)	70(71)

<sup>a</sup>Reaction conditions: 5.0 mmol substrate, 50 mol 2-propanol, a Ir-PPh<sub>2</sub>-Ts catalyst containing 0.10 mmol Ir, 0.10 mmol Cs<sub>2</sub>CO<sub>3</sub>, 5.0 ml toluene, 80°C, 4 h. The values in the bracket were obtained by using [Ir(COD)Cl]<sub>2</sub> and phosphine as a homogeneous catalyst system.

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Table S3. Recycling test of different catalysts<sup>a</sup>

Catalyst	Reactant	Product	Recycling No	Yield(%)	ee(%)
Pt-PPh <sub>2</sub> -Ts			1	85	/
			3	85	/
Ir-PPh <sub>2</sub> -Ts			1	90	/
			3	90	/
DPEN-Ru-PPh <sub>2</sub> -Ts			1	97	70
			3	96	69

<sup>a</sup>Reaction conditions are given in Table 4 and Table S1-S2.