

Supporting information

Organosoluble Zirconium Phosphonate Nanocomposites and their Supported Chiral Ruthenium Catalysts: the first Example of Homogeneization of Inorganic-Supported Catalyst in Asymmetric Hydrogenation

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1. ^1H NMR, ^{13}C and ^{31}P NMR of compounds **1a-e** (Figure S1-S5)

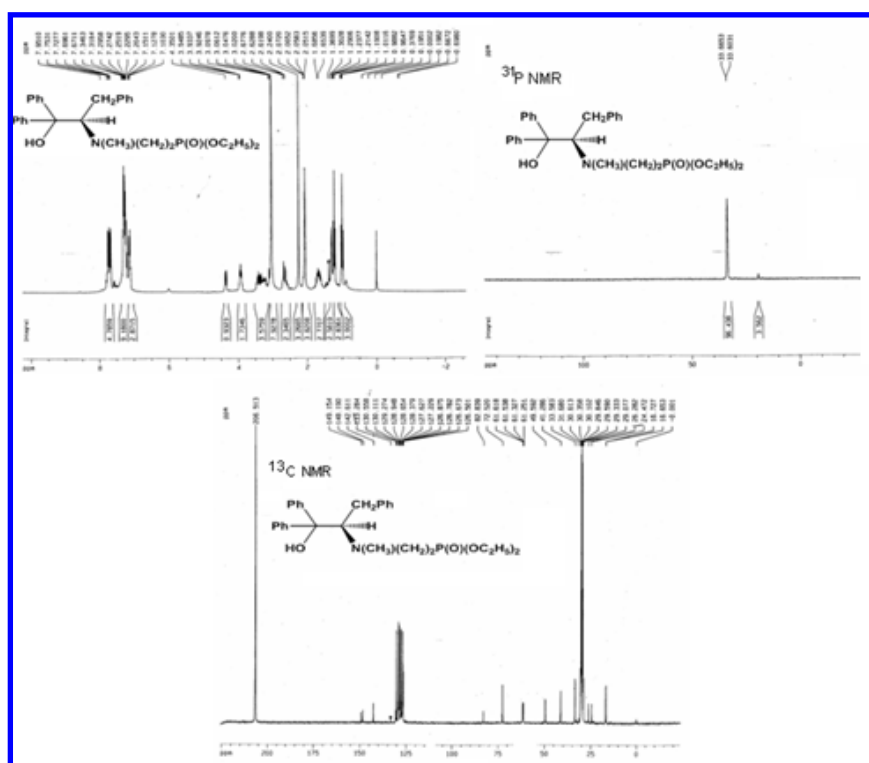


Figure S1. ^1H NMR, ^{13}C NMR and ^{31}P NMR of phosphonate **1a**

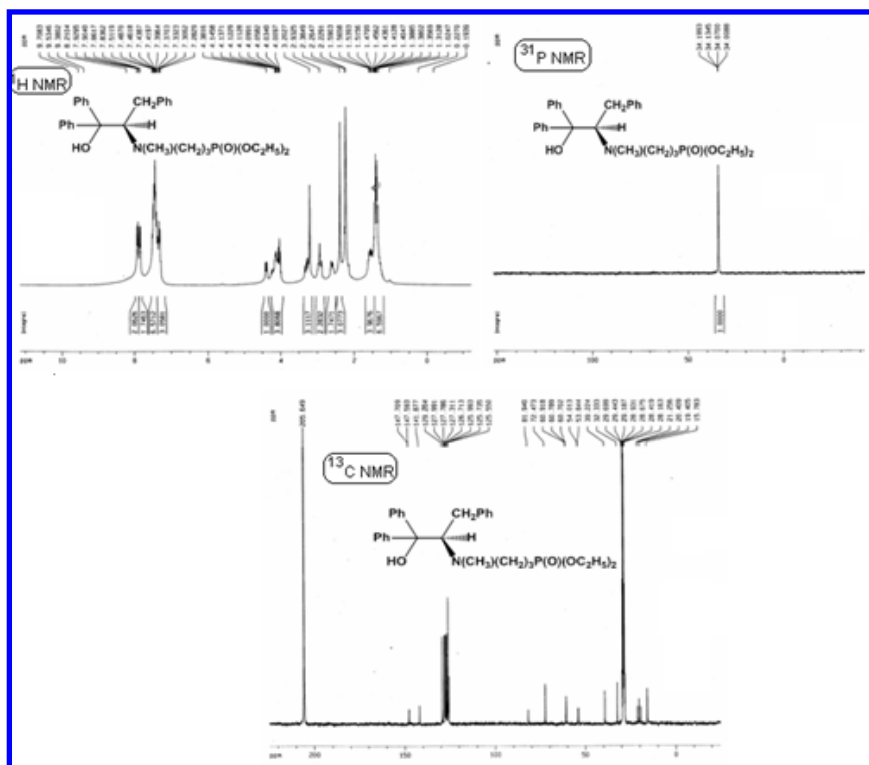


Figure S2. ¹H NMR, ¹³C NMR and ³¹P NMR of phosphonate **1b**

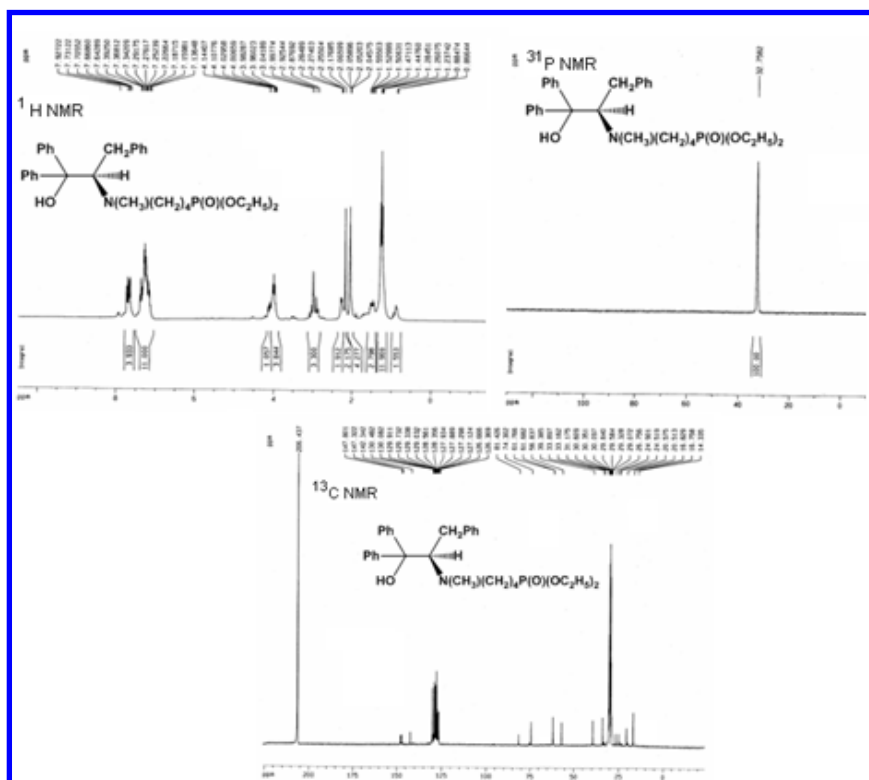


Figure S3. ¹H NMR, ¹³C NMR and ³¹P NMR of phosphonate **1c**

¹H NMR

Chemical shift (ppm): 8.458, 8.451, 8.447, 8.443, 8.439, 8.435, 8.431, 8.427, 8.423, 8.419, 8.415, 8.411, 8.407, 8.403, 8.399, 8.395, 8.391, 8.387, 8.383, 8.379, 8.375, 8.371, 8.367, 8.363, 8.359, 8.355, 8.351, 8.347, 8.343, 8.339, 8.335, 8.331, 8.327, 8.323, 8.319, 8.315, 8.311, 8.307, 8.303, 8.299, 8.295, 8.291, 8.287, 8.283, 8.279, 8.275, 8.271, 8.267, 8.263, 8.259, 8.255, 8.251, 8.247, 8.243, 8.239, 8.235, 8.231, 8.227, 8.223, 8.219, 8.215, 8.211, 8.207, 8.203, 8.199, 8.195, 8.191, 8.187, 8.183, 8.179, 8.175, 8.171, 8.167, 8.163, 8.159, 8.155, 8.151, 8.147, 8.143, 8.139, 8.135, 8.131, 8.127, 8.123, 8.119, 8.115, 8.111, 8.107, 8.103, 8.099, 8.095, 8.091, 8.087, 8.083, 8.079, 8.075, 8.071, 8.067, 8.063, 8.059, 8.055, 8.051, 8.047, 8.043, 8.039, 8.035, 8.031, 8.027, 8.023, 8.019, 8.015, 8.011, 8.007, 8.003, 7.999, 7.995, 7.991, 7.987, 7.983, 7.979, 7.975, 7.971, 7.967, 7.963, 7.959, 7.955, 7.951, 7.947, 7.943, 7.939, 7.935, 7.931, 7.927, 7.923, 7.919, 7.915, 7.911, 7.907, 7.903, 7.899, 7.895, 7.891, 7.887, 7.883, 7.879, 7.875, 7.871, 7.867, 7.863, 7.859, 7.855, 7.851, 7.847, 7.843, 7.839, 7.835, 7.831, 7.827, 7.823, 7.819, 7.815, 7.811, 7.807, 7.803, 7.799, 7.795, 7.791, 7.787, 7.783, 7.779, 7.775, 7.771, 7.767, 7.763, 7.759, 7.755, 7.751, 7.747, 7.743, 7.739, 7.735, 7.731, 7.727, 7.723, 7.719, 7.715, 7.711, 7.707, 7.703, 7.699, 7.695, 7.691, 7.687, 7.683, 7.679, 7.675, 7.671, 7.667, 7.663, 7.659, 7.655, 7.651, 7.647, 7.643, 7.639, 7.635, 7.631, 7.627, 7.623, 7.619, 7.615, 7.611, 7.607, 7.603, 7.599, 7.595, 7.591, 7.587, 7.583, 7.579, 7.575, 7.571, 7.567, 7.563, 7.559, 7.555, 7.551, 7.547, 7.543, 7.539, 7.535, 7.531, 7.527, 7.523, 7.519, 7.515, 7.511, 7.507, 7.503, 7.499, 7.495, 7.491, 7.487, 7.483, 7.479, 7.475, 7.471, 7.467, 7.463, 7.459, 7.455, 7.451, 7.447, 7.443, 7.439, 7.435, 7.431, 7.427, 7.423, 7.419, 7.415, 7.411, 7.407, 7.403, 7.399, 7.395, 7.391, 7.387, 7.383, 7.379, 7.375, 7.371, 7.367, 7.363, 7.359, 7.355, 7.351, 7.347, 7.343, 7.339, 7.335, 7.331, 7.327, 7.323, 7.319, 7.315, 7.311, 7.307, 7.303, 7.299, 7.295, 7.291, 7.287, 7.283, 7.279, 7.275, 7.271, 7.267, 7.263, 7.259, 7.255, 7.251, 7.247, 7.243, 7.239, 7.235, 7.231, 7.227, 7.223, 7.219, 7.215, 7.211, 7.207, 7.203, 7.199, 7.195, 7.191, 7.187, 7.183, 7.179, 7.175, 7.171, 7.167, 7.163, 7.159, 7.155, 7.151, 7.147, 7.143, 7.139, 7.135, 7.131, 7.127, 7.123, 7.119, 7.115, 7.111, 7.107, 7.103, 7.099, 7.095, 7.091, 7.087, 7.083, 7.079, 7.075, 7.071, 7.067, 7.063, 7.059, 7.055, 7.051, 7.047, 7.043, 7.039, 7.035, 7.031, 7.027, 7.023, 7.019, 7.015, 7.011, 7.007, 7.003, 6.999, 6.995, 6.991, 6.987, 6.983, 6.979, 6.975, 6.971, 6.967, 6.963, 6.959, 6.955, 6.951, 6.947, 6.943, 6.939, 6.935, 6.931, 6.927, 6.923, 6.919, 6.915, 6.911, 6.907, 6.903, 6.899, 6.895, 6.891, 6.887, 6.883, 6.879, 6.875, 6.871, 6.867, 6.863, 6.859, 6.855, 6.851, 6.847, 6.843, 6.839, 6.835, 6.831, 6.827, 6.823, 6.819, 6.815, 6.811, 6.807, 6.803, 6.799, 6.795, 6.791, 6.787, 6.783, 6.779, 6.775, 6.771, 6.767, 6.763, 6.759, 6.755, 6.751, 6.747, 6.743, 6.739, 6.735, 6.731, 6.727, 6.723, 6.719, 6.715, 6.711, 6.707, 6.703, 6.699, 6.695, 6.691, 6.687, 6.683, 6.679, 6.675, 6.671, 6.667, 6.663, 6.659, 6.655, 6.651, 6.647, 6.643, 6.639, 6.635, 6.631, 6.627, 6.623, 6.619, 6.615, 6.611, 6.607, 6.603, 6.599, 6.595, 6.591, 6.587, 6.583, 6.579, 6.575, 6.571, 6.567, 6.563, 6.559, 6.555, 6.551, 6.547, 6.543, 6.539, 6.535, 6.531, 6.527, 6.523, 6.519, 6.515, 6.511, 6.507, 6.503, 6.499, 6.495, 6.491, 6.487, 6.483, 6.479, 6.475, 6.471, 6.467, 6.463, 6.459, 6.455, 6.451, 6.447, 6.443, 6.439, 6.435, 6.431, 6.427, 6.423, 6.419, 6.415, 6.411, 6.407, 6.403, 6.399, 6.395, 6.391, 6.387, 6.383, 6.379, 6.375, 6.371, 6.367, 6.363, 6.359, 6.355, 6.351, 6.347, 6.343, 6.339, 6.335, 6.331, 6.327, 6.323, 6.319, 6.315, 6.311, 6.307, 6.303, 6.299, 6.295, 6.291, 6.287, 6.283, 6.279, 6.275, 6.271, 6.267, 6.263, 6.259, 6.255, 6.251, 6.247, 6.243, 6.239, 6.235, 6.231, 6.227, 6.223, 6.219, 6.215, 6.211, 6.207, 6.203, 6

Figure S5. ^1H NMR, ^{13}C NMR and ^{31}P NMR of phosphonate **1e**

2. The solid state ^{13}C and ^{31}P NMR of zirconium phosphonate **2b** (Figure S6)

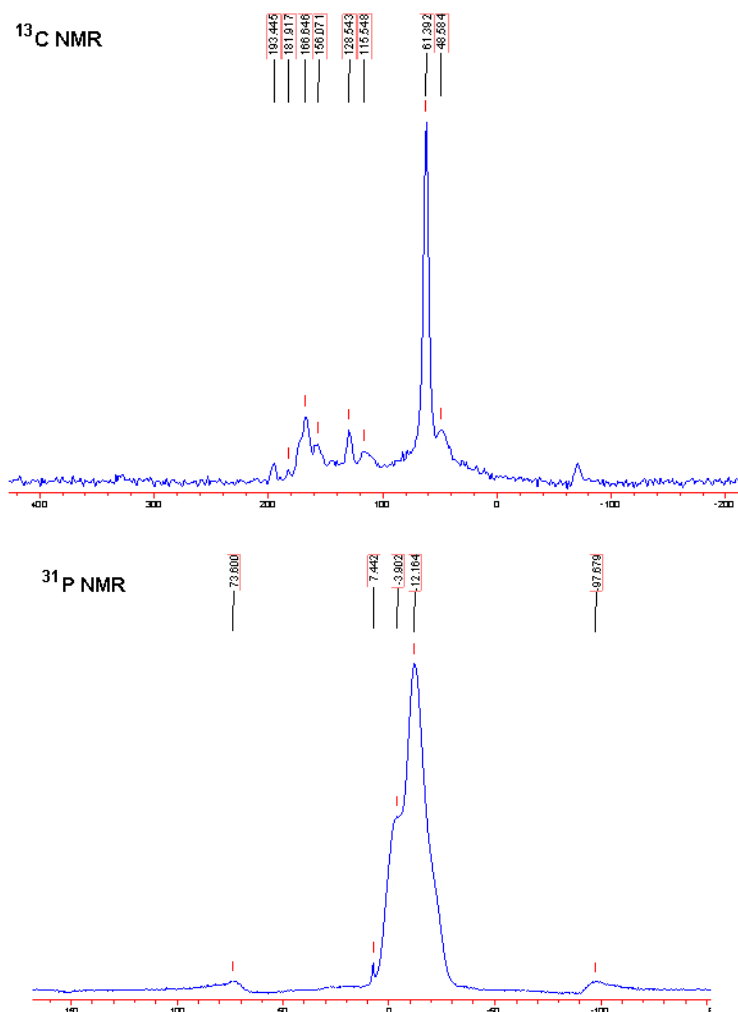


Figure S6. The solid state ^{13}C NMR and ^{31}P NMR of zirconium phosphonate **2b**

3. The solution ^{13}C and ^{31}P NMR of compounds **2b** and **2c** (Figure S7-S8)

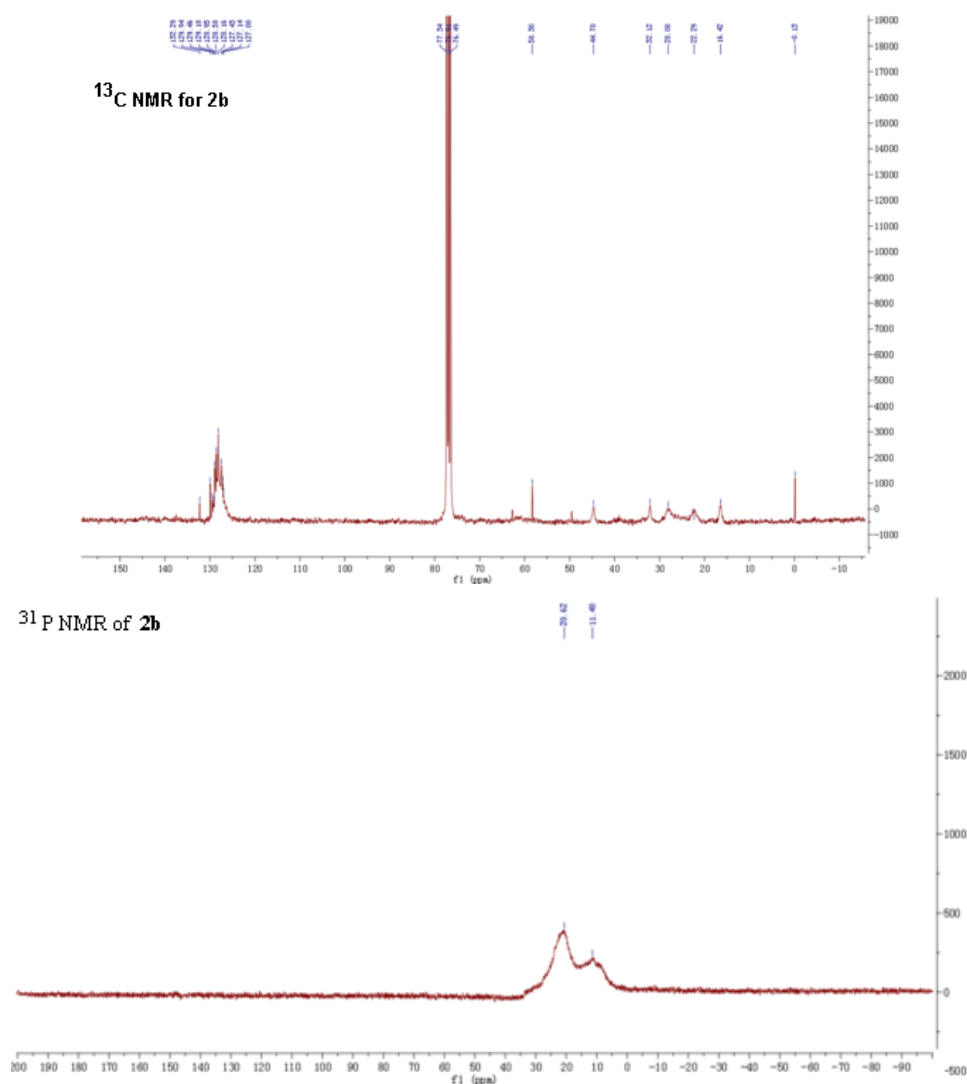


Figure S7. The solution ^{13}C NMR and ^{31}P NMR of zirconium phosphonate **2b**

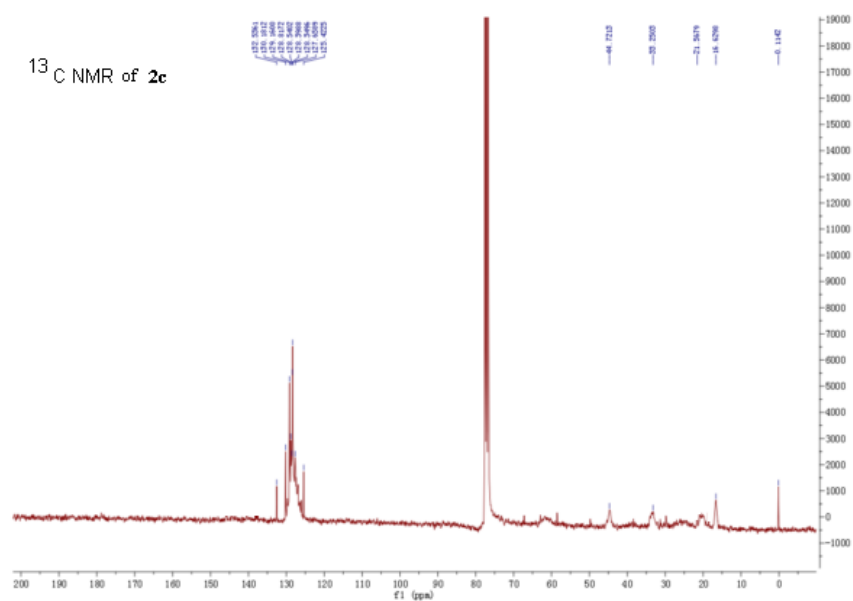


Figure S7. The solution ^{13}C NMR of zirconium phosphonate **2c**

4. The thermogravimetric curves of the other supports and their supported ruthenium catalysts (**Figure S9-S12**)

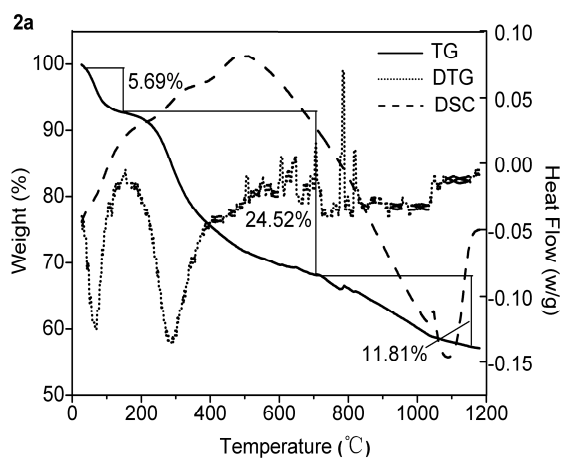


Figure S9. The thermogravimetric curves of the support **2a**

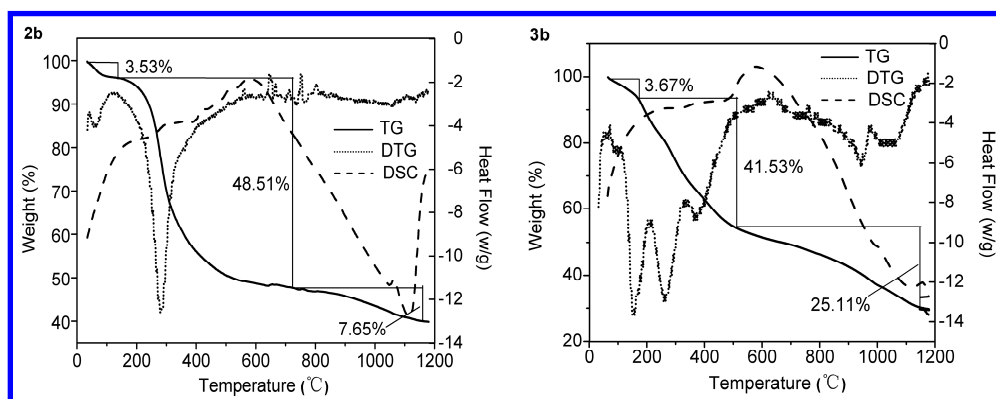


Figure S10. The thermogravimetric curves of the support **2b** and its supported catalyst **3b**

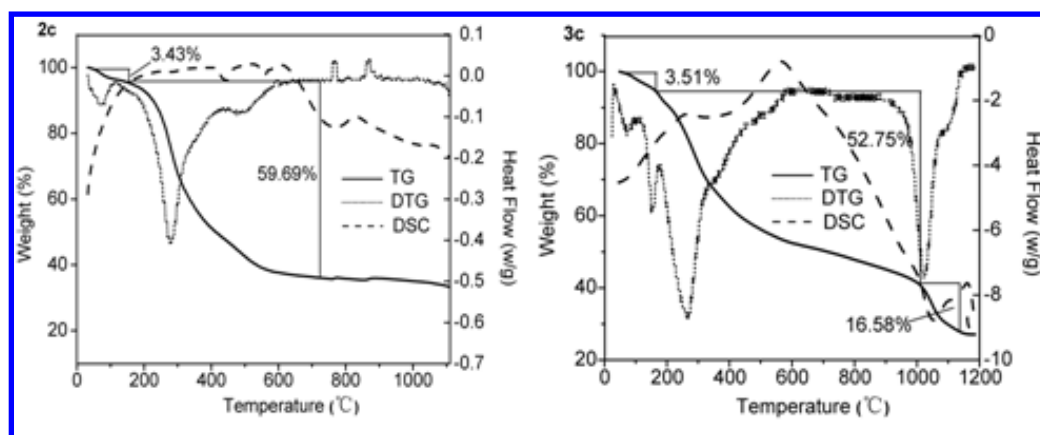


Figure S11. The thermogravimetric curves of the support **2c** and its supported ruthenium catalyst

3c

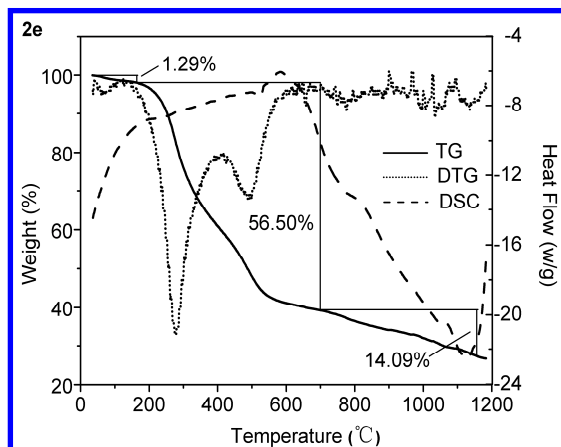


Figure S12. The thermogravimetric curves of the support **2e**

5. Isotherms and distributions of pore diameter of the other supports and their supported ruthenium catalysts (**Figure S13-S17**)

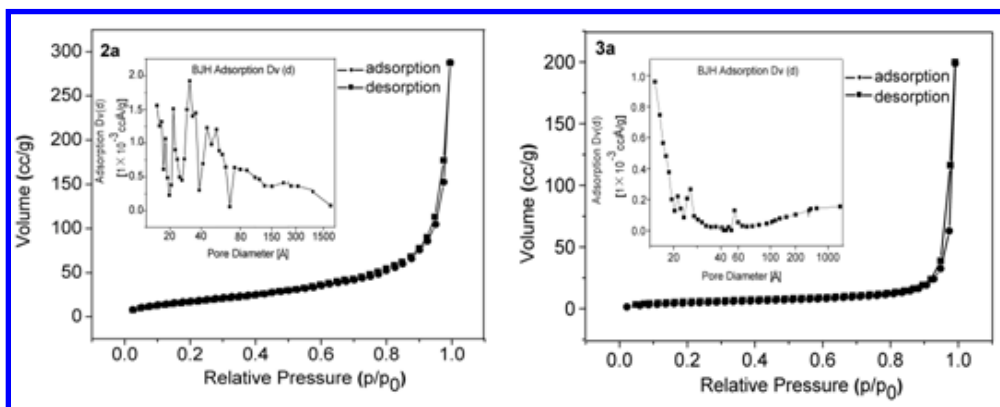


Figure S13. Isotherms and distributions of pore diameter of support **2a** and its supported ruthenium catalyst **3a**

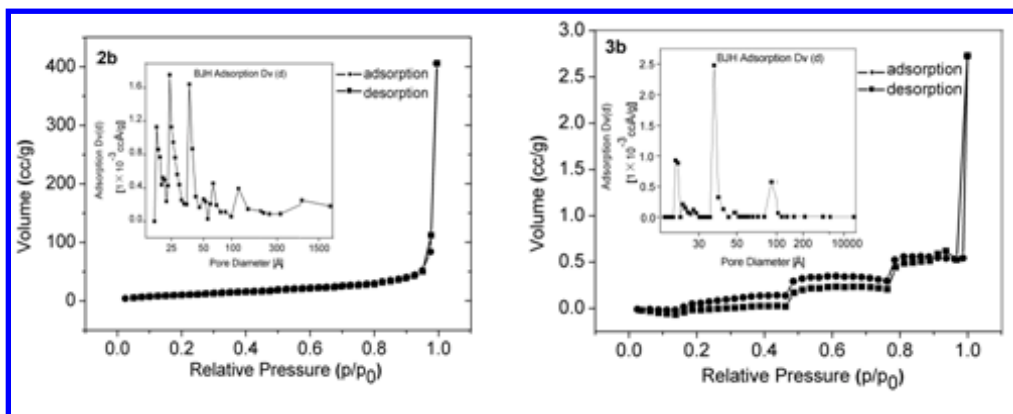


Figure S14. Isotherms and distributions of pore diameter of support **2b** and its supported ruthenium catalyst **3b**

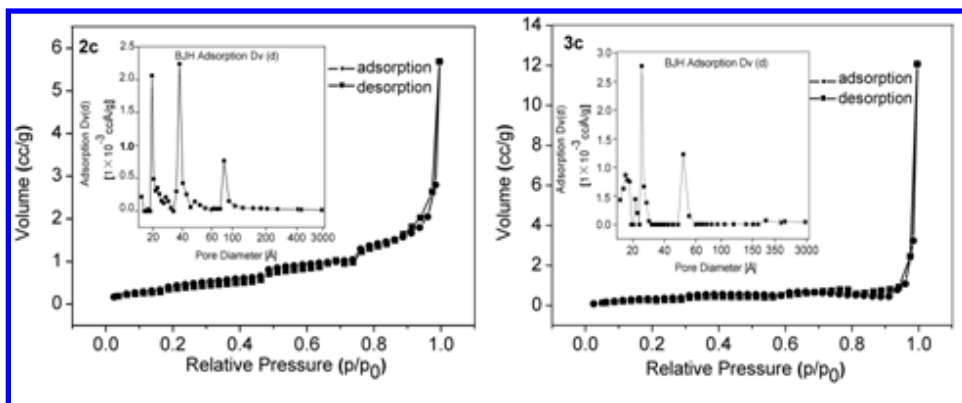


Figure S16. Isotherms and distributions of pore diameter of support **2c** and its supported ruthenium catalyst **3c**

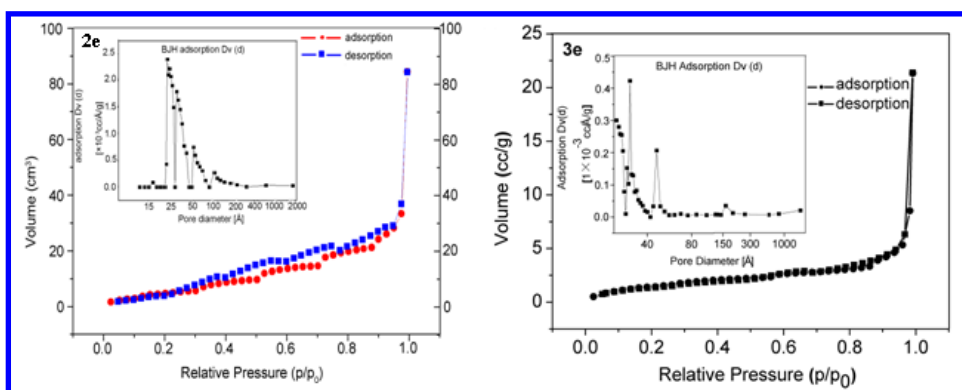


Figure S17. Isotherms and distributions of pore diameter of support **2e** and its supported ruthenium catalyst **3e**

6. Particle analysis picture of **2a** (Figure S18)

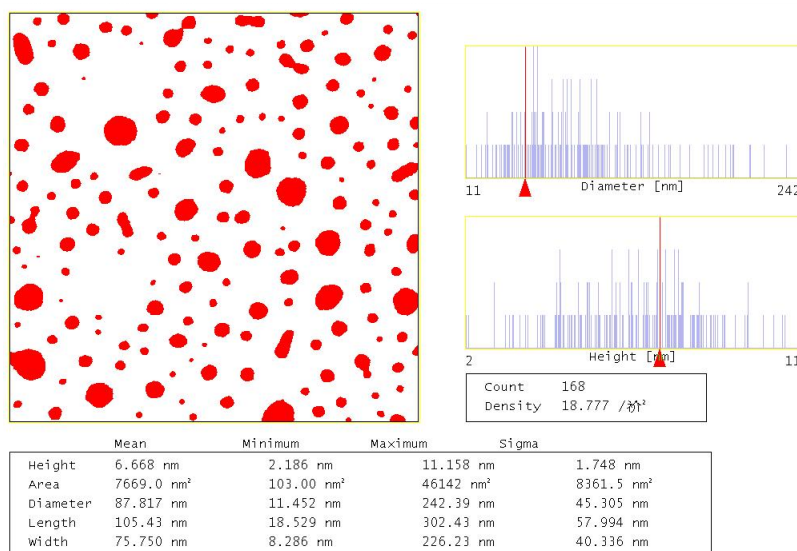


Figure S18. The particle analysis picture of **2a**: scan scale 3000nm×3000nm, scan rate:1.40Hz

5. The diameter of the particles (**Table ST1**) and the height of the particles ranges (**Table ST2**)

Table ST1. The diameter distribution of particles **2a** **Table ST2.** The height of particle **2a** ranges

Diameter	number
11-30	6
30-50	15
50-70	40
70-90	30
90-110	32
110-130	16
130-150	10
150-170	5
170-195	5
195-210	4
210-230	3

Height (nm)	number
1.0-2.0	3
3.0-4.0	2
4.0-5.0	9
5.0-6.0	18
6.0-7.0	25
7.0-8.0	29
8.0-9.0	43
9.0-10.0	26
10.0-11.0	7
11.0-13.0	6

7. Composition of as-prepared zirconium phosphonate nanocomposites (**Table ST3**)

Table ST3. The organic weight loss, x and y values of zirconium phosphonates **2a-e** bearing different arm lengths (*n*)

<i>n</i>	2	3	4	5	6
Water weight loss(%)	5.69	3.53	3.43	2.50	1.29
organic weight loss (%)	36.33	56.16	59.69	67.36	70.59
x value	0.44	0.95	1.00	1.37	1.50

y value	1.11	1.83	1.14	1.07	0.60
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Based on the data of thermogravimetric analysis (TGA) and zirconium phosphonate **2b** as an example, the above values were calculated as follows: the 3.53 % weight loss was observed below 180 °C, which illustrated the presence of adsorbed interlayer water. The end product of the thermal reaction at 1200 °C is zirconium pyrophosphate (Formula Weight= 266.2), and the organic weight loss in the temperature 180-1200 °C range was 56.16 %. The value of x in the formula $\text{Zr}(\text{OH})_{4-2x}(\text{O}_3\text{PR})_x$ was determined from eq 1 and eq 2.

$$\left\{ \begin{array}{l} \frac{\text{The theoretic water weight loss}}{\text{Formula weight}} = (W_{25^\circ\text{C}} - W_{180^\circ\text{C}}) \% \quad (1) \\ \frac{\text{The theoretic organic weight loss}}{\text{Formula weight}} = (W_{180^\circ\text{C}} - W_{1200^\circ\text{C}}) \% \quad (2) \end{array} \right.$$

Combined with the formula of **2b**, eq 3 and eq 4 were obtained.

$$\frac{18y}{403x+18y+159.25} = 3.53\% \quad (3)$$

$$\frac{372x-30}{403x+18y+159.25} = 56.16\% \quad (4)$$

Then, $x=0.95$, $y=1.83$. The other x , y values were calculated according to the same method.