

Supporting Information

Efficient synthesis of zirconium poly(styrene- phenylvinylphosphonate)phosphate-supported proline as a recyclable catalyst for direct asymmetric aldol reactions in water

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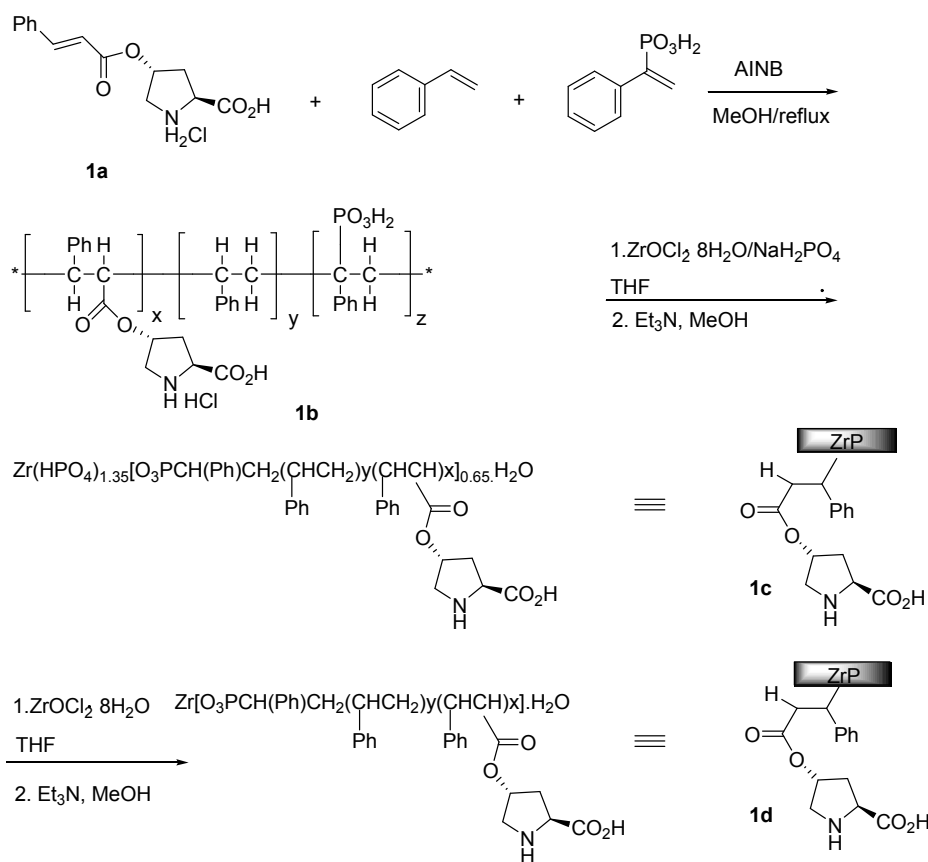
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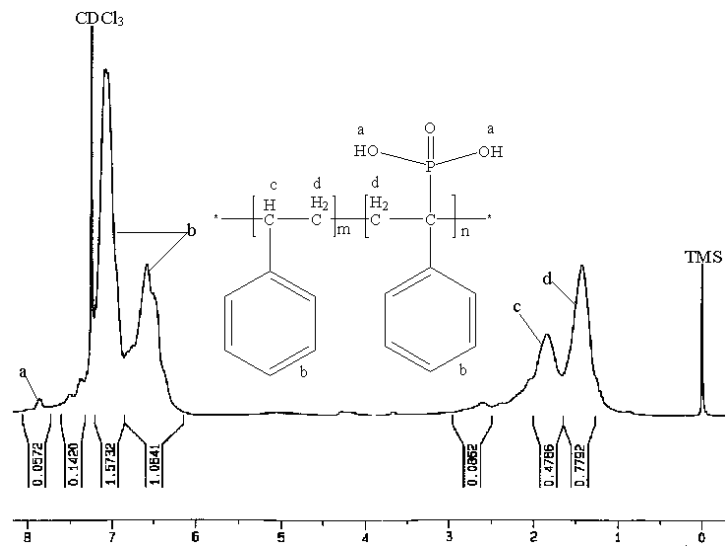
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Scheme 1. Synthesis of catalyst **1**.



^1H NMR of copolymer

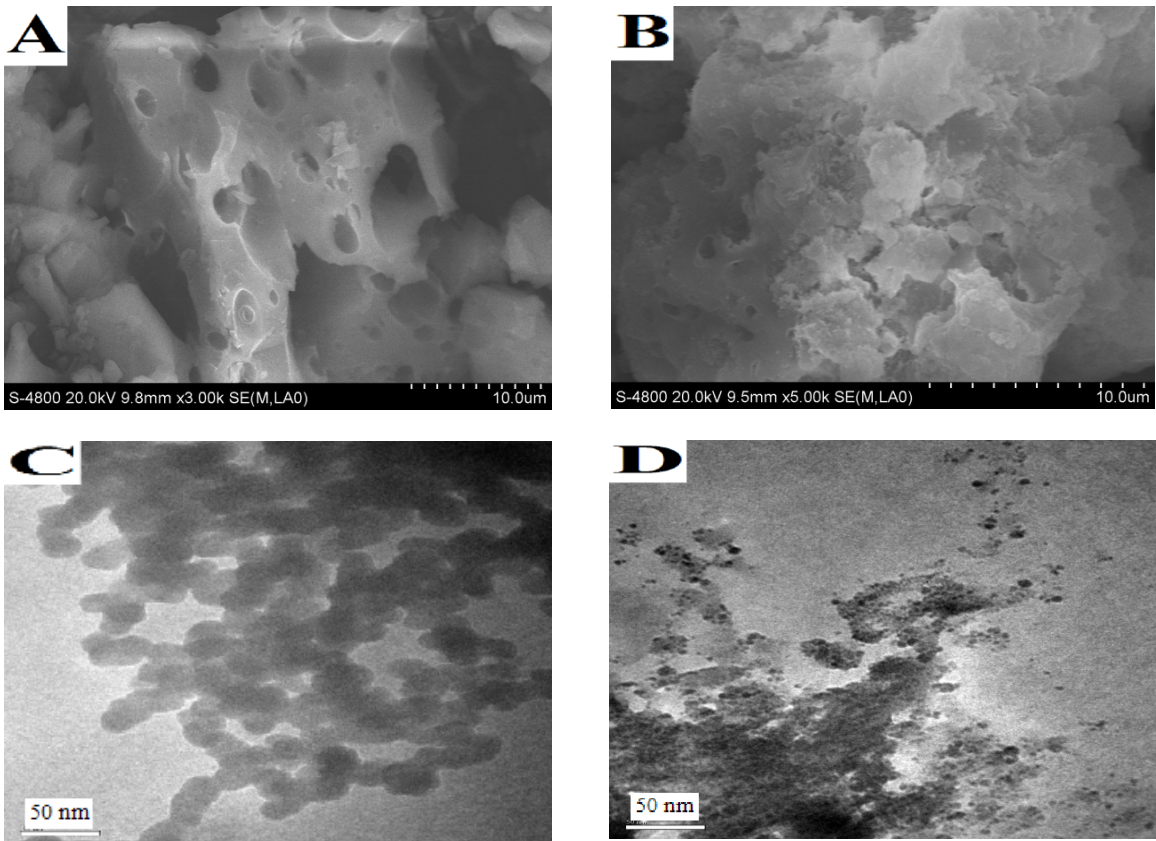


Figure 2. SEM and TEM analysis of catalyst **1**.

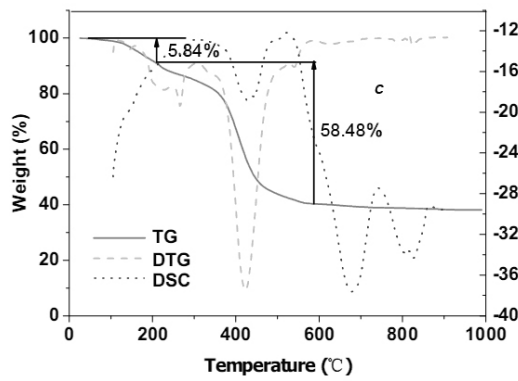


Figure 3. The TG curves of the catalyst.

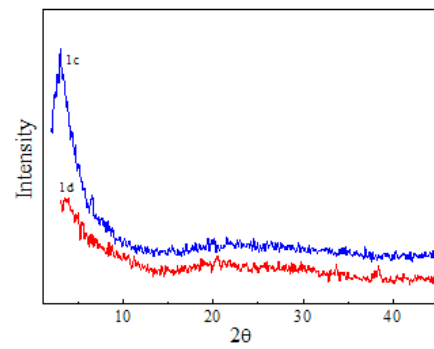


Figure 4. XRD pattern of the catalyst **1**.

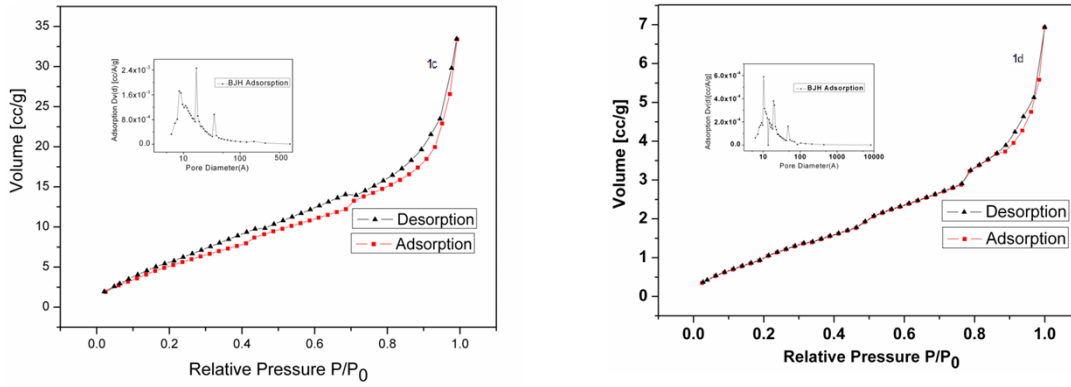


Figure 5. N₂ adsorption-desorption analysis of catalyst 1.

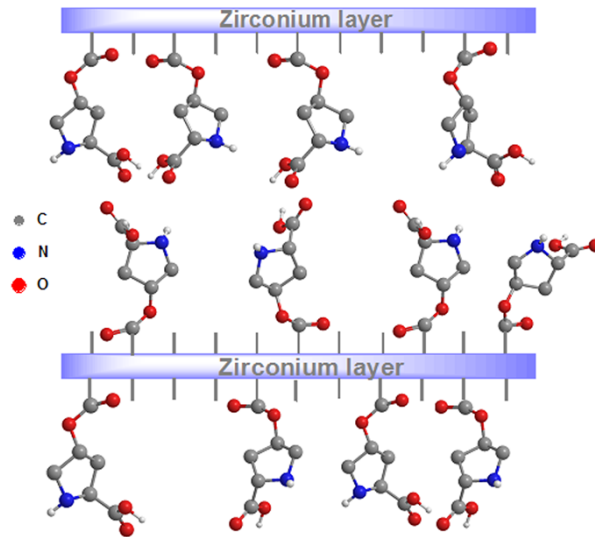


Figure 1. The ideal structure model of ZrPS-PVPA-Pr

(2S, 10R)-2-[Hydroxy(4-nitrophenyl)methyl]cyclohexan-1-one (2):¹

Yield: 98%; *anti/syn* = 98:2, enantiomeric excess: 99% (*anti* diastereomer) determined by HPLC (Daicel Chiralpak AD-H column; *i*-PrOH/hexane = 20:80; 0.5 mL/min; 20 °C; λ = 254 nm) t_R = 42.5 min (*anti*, major) and t_R = 32.8 min (*anti*, minor).

(2S, 10R)-2-[Hydroxy(2-nitrophenyl)methyl]cyclohexan-1-one (3):¹

Yield: 9%; *anti/syn* = 99:1, enantiomeric excess: 99% (*anti* diastereomer) determined by HPLC (Daicel Chiralpak OD-H column; *i*-PrOH/hexane = 5:95; 0.5 mL/min; 20 °C; λ = 254 nm) t_R = 41.9 min (*anti*, major) and t_R = 50.7 min (*anti*, minor).

(2S, 10R)-2-[Hydroxy(3-nitrophenyl)methyl]cyclohexan-1-one (4):¹

Yield: 97%; *anti/syn* = 97:3, enantiomeric excess: 99% (*anti* diastereomer) determined by HPLC (Daicel Chiralpak AD-H column; *i*-PrOH/hexane = 20:80; 0.5 mL/min; 20 °C; λ = 254 nm) t_R = 41.9 min (*anti*, major) and t_R = 32.4 min (*anti*, minor).

(2S, 10R)-2-[(4-Cyanophenyl)hydroxymethyl]cyclohexan-1-one (5):¹

Yield: 97%; *anti:syn* = 97:3, enantiomeric excess: 98% (*anti* diastereomer) determined by HPLC (Daicel Chiralpak AD-H column; *i*-PrOH/hexane = 20:80; 0.5 mL/min; 20 °C; λ = 254 nm) t_R = 22.5 min (*anti*, major) and t_R = 18.1 min (*anti*, minor).

(2S, 10R)-2-{Hydroxy[4-(trifluoromethyl)methyl]}cyclohexan-1-one (6):¹

Yield: 98%; *anti/syn* = 98:2, enantiomeric excess: 97% (*anti* diastereomer) determined by HPLC (Daicel Chiralpak AD-H column; *i*-PrOH/hexane = 10:90; 0.5 mL/min, 20 °C, λ = 254 nm) t_R = 34.4 min (*anti*, major) and t_R = 26.9 min (*anti*, minor).

(2S, 10R)-2-[(4-Bromophenyl)hydroxymethyl]cyclohexan-1-one (7):¹

Yield: 95%; *anti/syn* = 97:3, enantiomeric excess: 98% (*anti* diastereomer) determined by HPLC (Daicel Chiralpak AD-H column; *i*-PrOH/hexane = 10:90; 0.5 mL/min, 20 °C, λ = 220 nm) t_R = 43.1 min (*anti*, major) and t_R = 35.5 min (*anti*, minor).

(2S, 10R)-2-[(4-Chlorophenyl)hydroxymethyl]cyclohexan-1-one (8):¹

Yield: 96%; *anti/syn* = 98:2, enantiomeric excess: 99% (*anti* diastereomer) determined by HPLC (Daicel Chiralpak AD-H column; *i*-PrOH/hexane = 10:90; 0.5 mL/min, 20 °C, λ = 221 nm) t_R = 39.2 min (*anti*, major) and t_R = 33.4 min (*anti*, minor).

(2S, 10R)-2-[(2-Chlorophenyl)hydroxymethyl]cyclohexan-1-one (9):¹

Yield: 95%; *anti/syn* = 96:4, enantiomeric excess: 99% (*anti* diastereomer) determined by HPLC (Daicel Chiralpak OD-H column; *i*-PrOH/hexane = 5:95; 1.0 mL/min, 20 °C, λ = 221 nm) t_R = 9.7 min (*anti*, major) and t_R = 12.3 min (*anti*, minor).

(2S, 10R)-2-[(3-Chlorophenyl)hydroxymethyl]cyclohexan-1-one (10):¹

Yield: 92%; *anti/syn* = 94:6, enantiomeric excess: 98% (*anti* diastereomer) determined by HPLC (Daicel Chiralpak OD-H column; *i*-PrOH/hexane = 5:95; 1.0 mL/min, 20 °C, λ = 221 nm) t_R = 9.7 min (*anti*, major) and t_R = 12.3 min (*anti*, minor).

(2S, 10R)-2-(Hydroxy-(4-fluor-phenyl)methyl)cyclohexan-1-one (11):¹

Yield: 95%; *anti/syn* = 96:4, enantiomeric excess: 98% (*anti* diastereomer) determined by HPLC (Daicel Chiralpak AD-H column; *i*-PrOH/Hexane = 5:95; flow rate 1.0 mL/min, 20 °C, λ = 221 nm; t_R = 28.3 min (*anti*, major), t_R = 24.7 min (*anti*, minor)).

(2*S*, 10*R*)-2-[Hydroxy(4-methoxyphenyl)methyl]cyclohexan-1-one (12):¹

Yield: 84%; *anti/syn* = 93:7, enantiomeric excess: 96% (*anti* diastereomer) determined by HPLC (Daicel Chiralpak AD-H column; *i*-PrOH/hexane = 10:90; 0.8 mL/min, 20 °C, λ = 221 nm) t_R = 32.5 min (*anti*, major) and t_R = 30.8 min (*anti*, minor).

(2*S*, 10*R*)-2-[Hydroxy(3-methoxyphenyl)methyl]cyclohexan-1-one (13):¹

Yield: 85%; *anti/syn* = 94:6, enantiomeric excess: 97% (*anti* diastereomer) determined by HPLC (Daicel Chiralpak AD-H column; *i*-PrOH/hexane = 10:90; 0.5 mL/min, 20 °C, λ = 221 nm) t_R = 56.3 min (*anti*, major) and t_R = 51.1 min (*anti*, minor).

(2*S*, 10*R*)-2-[Hydroxy(2-naphthyl)methyl]cyclohexan-1-one (14):¹

Yield: 86%; *anti/syn* = 94:6, enantiomeric excess: 94% (*anti* diastereomer) determined by HPLC (Daicel Chiralpak OD-H column; *i*-PrOH/hexane = 10:90; 1.0 mL/min, 20 °C, λ = 221 nm) t_R = 15.7 min (*anti*, major) and t_R = 22.2 min (*anti*, minor).

(2*S*, 10*R*)-2-[Hydroxy(1-naphthyl)methyl]cyclohexan-1-one (15):¹

Yield: 87%; *anti/syn* = 95:5, enantiomeric excess: 97% (*anti* diastereomer) determined by HPLC (Daicel Chiralpak AD-H column; *i*-PrOH/hexane = 5:95; 1.0 mL/min, 20 °C, λ = 254 nm) t_R = 45.9 min (*anti*, major) and t_R = 36.7 min (*anti*, minor).

(2*S*, 10*R*)-2-[Hydroxy(phenyl)methyl]cyclohexan-1-one (16):¹

Yield: 85%; *anti/syn* = 92:8, enantiomeric excess: 93% (*anti* diastereomer) determined by HPLC (Daicel Chiralpak OD-H column; *i*-PrOH/hexane = 10:90; 0.5 mL/min, 20 °C, λ = 220 nm) t_R = 19.6 min (*anti*, major) and t_R = 30.6 min (*anti*, minor).

1 (a) C. L. Wu, X. K. Fu, X. B. Ma, S. Li. *Tetrahedron: Asymmetry*. 2010, **21**, 2465-2470.

(b) C. L. Wu, X. K. Fu, S. Li. *Eur. J. Org. Chem.* 2011, **7**, 1291–1299

(c) C. L. Wu, X. K. Fu, S. Li. *Tetrahedron*. 2011, **67**, 4283-4290

(d) C. L. Wu, X. K. Fu, S. Li. *Tetrahedron: Asymmetry*. 2011, **22**, 1063-1073.