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Phosphonate-containing polystyrene copolymer-supported Ru catalyst for asymmetric transfer hydrogenation in water

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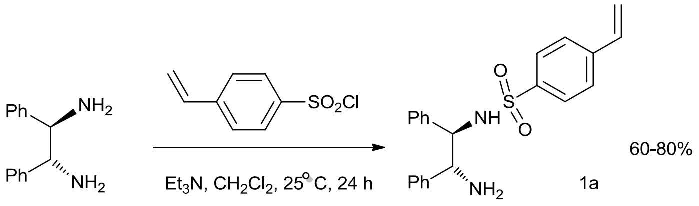
1. General Remarks

All chemicals were purchased and used without any further purification. Fourier transform infrared spectra were recorded on Perkin–Elmer Model GX Spectrometer using a KBr pellet method with polystyrene as a standard. Thermogravimetric analysis (TGA) was performed on a SBTQ600 Thermal Analyzer (USA) with a heating rate of 20 °C min^{-1} over a temperature range of 40–800 °C under flowing compressed N_2 (100 mL min^{-1}). ^1H, ^{13}C and ^{31}P NMR were performed on a Bruker AV–300 NMR instrument at 300.1, 75.0 and 121.5 MHz respectively, in which all chemical shifts were reported downfield in ppm relative to the hydrogen, carbon and phosphorus resonances of TMS, chloroform–d1 and H_3PO_4 (85 %) respectively. The morphologies of as-synthesized samples were determined by a Hitachi model H-800 transmission electron microscope (TEM). N_2 adsorption–desorption analysis was carried out at 77 K on an Autosorb-1 apparatus (Quantachrome). The specific surface areas and pore diameters were calculated by the B.E.T. and BJH model respectively. C, H, and N elemental analysis was obtained from an EATM 1112 automatic elemental analyzer instrument (Thermo, USA). Gel permeation chromatography (GPC) was performed using a 515 HPCC pump and a Waters styragel HT3 column (Mw 500-30,000) with a 2414 refractive index detector from Waters. Experiments were performed at 35 °C using THF as fluent, flow rate of 0.5 mL /min, and molecular weights are reported versus monodispersed polysaccharide standards. The enantiomeric excess (%ee) was determined on GC with a Chiral Cyclodex- B column (30 m× 0.25 nm×0.25 μm, Supelco) under 100 ℃, 5 min, 5 ℃·min^{-1};140 ℃, 15 min conditions. X-ray photoelectron spectroscopy measurements were carried out on a Physical Electronics ESCA 5701 instrument, equipped with a multichannel detector and a hemispherical analyzer. Mg Ka radiation (hm = 1253.6 eV) was used as the exciting source, and operated at a constant power of 300 W (15 kV, 20 mA). The data were acquired at a take-off angle of 45º and pass energy of 29.35 eV. The pressure in the analysis chamber was maintained at 8×10^{-7} Pa. Charge compensation was done with the adventitious C 1 s peak at 284.8 eV.

2. The synthesis of 1a-b with different arm chain lengths

2.1 The synthesis of monomer 1a



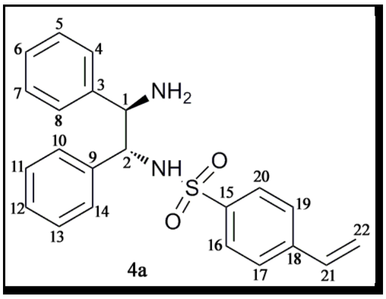
(1) *p*-vinylbenzenesulfonyl chloride

A dried flask (150 mL) containing *p*-hydroxyanisole (50 mg, 0.4 mmol), 36 mL of DMF and 30 mL of $SOCl_2$ was stirred at 25°C for 10 min, cooled to 0°C, and then added *p*-vinylbenzene sulfonate sodium (10.30 g, 50.0 mmol) in three separate doses with a one-hour interval, stirred overnight and poured into ice-water with stirring. The reaction mixture was extracted with toluene (100 mL×3), washed with water (100 mL×3), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford the yellow liquid *p*-vinylbenzene sulfonyl chloride (1.9 g, 94%).

(2) (R, R)-N- *p*-vinylbenzenesulfonyl-1,2-diphenylethylene-1, 2-diamine (1a)

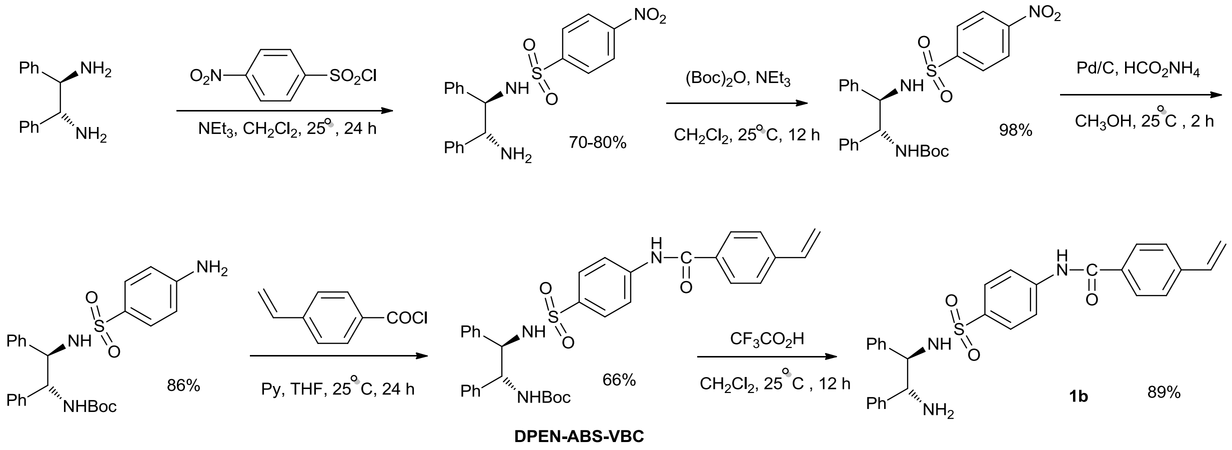
A dried flask (250 mL) containing (R, R)-1, 2-diphenylethylene-1, 2-diamine (6.4 g, 30.0 mmol was flushed three times with Ar_2 atmosphere, added 30 mL of CH_2Cl_2, 24 mL of Et_3N, stirred for 20 min, and then added dropwise 20 mL of *p*-vinylbenzene sulfonyl chloride (6.5 g, 32.0 mmol) CH_2Cl_2 solution and stirred at 25°C for 24 h. The reaction mixture was washed with saturated $NaHCO_3$ solution, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford light yellow solid. The crude solid was purified by flash column chromatography eluting with $CHCl_3$ to obtain the white product (R, R)-N-*p*-vinylbenzenesulfonyl-1,2-diphenylethylene-1, 2-diamine (**1a**) (7.4 g, 65%).

^1H NMR (300 MHz, DMSO) : δ 7.36-7.28 (Ar-H-16, 17, 19, 20, m, 4 H), 7.05 (Ar-H-10-14, s, 5 H), 6.92 (H-4-8, s, 5 H), 6.70-6.61 (H-21, dd, ^3J = 17.6, 11.0 Hz, 1 H), 5.85 (H-22, d, ^2J = 17.6 Hz, 1 H), 5.33 (H-22, d, ^2J = 10.9 Hz, 1 H), 4.29 (H-2, d, ^3J = 7.3 Hz, 1 H), 3.90 (H-1, d, ^3J = 7.3 Hz, 1 H). ^{13}C NMR (75 MHz, DMSO, TMS): δ 142.8 (C-15), 140.6 (C-18), 140.5, 140.1 (C-16, 17, 19, 20),



135.8 (21), 128.0, 127.9, 127.7, 127.6, 126.9, 126.7, 126.4 (C-3-8, 9-14), 117.4 (C-22), 65.1 (C-2), 60.9 (C-1). Anal. calcd for $C_{22}H_{22}N_2O_2S$: C, 69.81; H, 5.86; N, 7.40; O, 8.45; S, 8.47; Found: C, 69.80; H, 5.89; N, 7.38; O, 8.48; S, 8.43.

.2 The synthesis of monomer 1b



(1) (*R*,*R*)-*N*-(4-Nitrophenylsulfonyl)-1,2-diphenylethylenediamine

A dried flask (250 mL) containing (R, R)-1, 2-diphenylethylene-1, 2-diamine (4.3 g, 20.0 mmol) was flushed three times with Ar_2 atmosphere, added 80 mL of CH_2Cl_2, 5 mL of Et_3N, stirred for 20 min, cooled to 0°C and then added dropwise 20 mL of *p*-nitrobenzenesulfonyl chloride (6.5 g, 32.0 mmol) CH_2Cl_2 solution and stirred at 25°C for 24 h. After evaporated under reduced pressure, the crude yellow solid was recrystallized in ethyl acetate to afford the white solid (R, R)-*N*-(4-nitrophenylsulfonyl)-1, 2-diphenylethylenediamine (5.9 g, 74%).

(2) (*R*,*R*)-*N*-Boc-*N'*-(4-Nitrophenylsulfonyl)-1,2-diphenylethylenediamine

A dried flask (250 mL) containing (R, R)-*N*-(4-nitrophenylsulfonyl)-1, 2-diphenylethylenediamine (3.2 g, 8.0 mmol) was added 100 mL of CH_2Cl_2, 6 mL of Et_3N, stirred at 25°C for 20 min, and then added dropwise 20 mL of $(Boc)_2O$ (4.7 g, 21 mmol) CH_2Cl_2 solution. The reaction mixture was stirred at 25°C for 12 h, washed in turn with 10% citric acid aqueous solution (100 mL×3), water (100 mL×3), saturated sodium bicarbonate (100 mL×3) and saturated brine (100 mL×3). The organic phase was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford light yellow solid (R, R)-*N*-Boc-*N'*-(4-nitrophenylsulfonyl)-1, 2-diphenylethylenediamine (4.0 g, 98%).

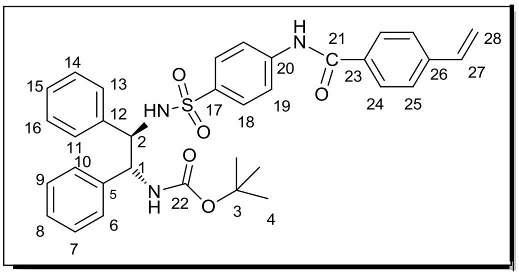
(3) (*R*,*R*)-*N*-Boc-*N′*-(4-Aminophenylsulfonyl)-1,2-diphenylethylenediamine

A dried flask (100 mL) was added (R, R)-*N*-Boc-*N′*-(4-nitrophenylsulfonyl)-1, 2-diphenylethylenediamine (1.0 g, 2 mmol), HCO_2NH_4 (0.6 g, 10 mmol), 10% Pd/C (200 mg), flushed three times with Ar_2 atmosphere, and then added 30 mL of MeOH. The reaction mixture was stirred at 25°C for 2 h and evaporated under reduced pressure to afford the white solid (R, R)-*N*-Boc-*N′*-(4-aminophenylsulfonyl)-1, 2-diphenylethylenediamine (0.8 g, 86%).

Above-mentioned three compounds were synthesized according to the reference: Y. C. Chen, T. F. Wu, J. G. Deng, H. Liu, X. Cui, J. Zhu,Y. Z. Jiang, M. C. K. Choi and A. S. C. Chan, *J. Org. Chem.* **2002**, *67*, 5301-5306.

(4) (R, R)-*N*-Boc-N′-[4-(*N′′*-vinylbenzoyl)aminophenylsulfonyl]-1, 2-diphenylethylene-1, 2-diamine (DPEN-ABS-VBC)

A dried flask (150 mL) containing (R, R)-*N*-Boc-*N′*-(4-aminophenylsulfonyl)-1, 2-diphenylethylenediamine (0.9 g, 2.0 mmol) was flushed three times with Ar_2 atmosphere, added 40 mL THF and 4 mL of Et_3N, stirred for 10 min, cooled to 0°C. To the reaction mixture was added dropwise 5 mL of *p*-vinylbenzoyl chloride (0.6 g, 3.0 mmol) CH_2Cl_2 solution, stirred at 25°C for 24 h and evaporated under reduced pressure to remove THF. The crude product was dissolved in 50 mL of CH_2Cl_2 and washed in turn with 10% citric acid aqueous solution (50 mL×3), water (50 mL×3), saturated sodium bicarbonate (50 mL×3) and saturated brine (50 mL×3). The organic phase was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford white solid. The crude white solid was recrystallized in mixed ethyl acetate/*n*-hexane (v/v=1/3) to afford the white solid (R, R)-*N*-Boc-N'-[4-(*N″*-vinylbenzoyl)aminophenylsulfonyl]-1, 2-diphenylethylene-1, 2-diamine (0.7 g, 66%).



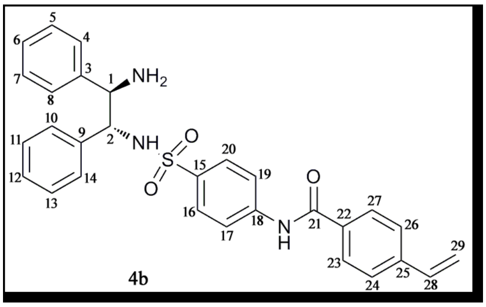
^{1}H NMR (300 MHz, DMSO) : δ10.37 (NHCO, s, 1 H), 8.12 (NHCO, d, ^3J = 9.6 Hz, 1 H), 7.91 (H-18, d, ^3J = 8.1 Hz, 2 H), 7.61 (H-19、24, d, ^3J =7.8 Hz, 4 H), 7.36-7.00 (H-6-10, 11-16, 25, m, 12 H), 6.84-6.75 (H-27, dd, ^3J =17.6, 11.0 Hz, 1 H), 5.97 (H-28, d, ^3J =17.7 Hz, 1 H), 5.39 (H-28, d, ^3J =11.0 Hz, 1 H), 4.78 (H-1, d, ^3J =6.1 Hz, 1 H), 3.93 (H-2, d, ^3J =6.1 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO, TMS): δ165.7 (C-22), 155.3 (C-21), 142.4, 140.8, 140.0, 139.8, 136.2, 136.0, 128.2 (C-5, 12, 27, 17, 20, 23, 26), 128.6, 128.2, 127.9, 127.5, 127.4, 127.2, 127.1, 126.5, 119.5 (C-6-10, 11, 12-16, 18, 19, 24, 25), 117.1 (C-28), 78.4 (C-3), 62.4, 59.5 (C-1, 2), 28.5

(C-4). Anal. calcd for $C_{34}H_{35}N_3O_4S$: C, 70.20; H, 6.06; N, 7.22; O, 11.00; S, 5.51; Found: C, 70.17; H, 6.11; N, 7.13; O, 11.12; S, 5.48.

(5) (R, R)- N-[4-(*N′*-vinylbenzoyl)aminophenylsulfonyl]-1, 2-diphenylethylene-1, 2-diamine (R, R) (1b)

To a flask (100 mL) was added (R, R)-*N*-Boc-N'-[4-(*N″*-vinylbenzoyl)aminophenylsulfonyl]-1, 2-diphenylethylene-1, 2-diamine (0.4 g, 0.6 mmol) and 30 mL of CH_2Cl_2, stirred and cooled to 0°C, added dropwise 2.0 mL of CF_3CO_2H, and then stirred at 25°C for 12 h. The reaction mixture was adjusted to pH=9 by using 10% NaOH aqueous solution, and the solid was filtered. The aqueous phase was extracted by ethyl acetate (30 mL×3), and the combined organic phases were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford light yellow solid **1b** (0.3 g, 89%).

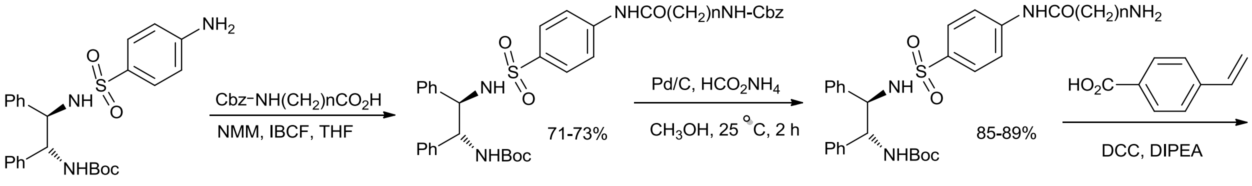


4b

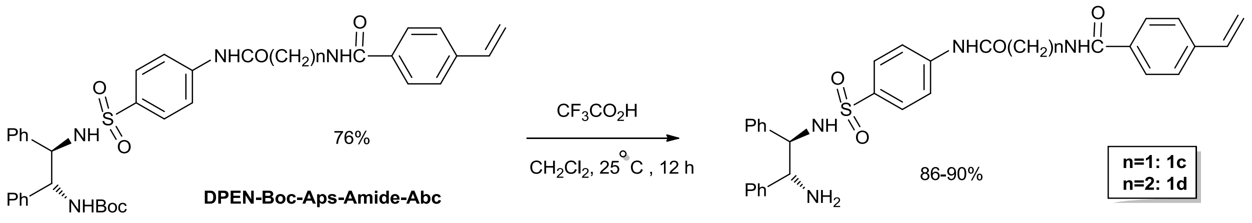
^{1}H NMR (300 MHz, DMSO) : δ10.40 (NHCO, s, 1 H), 7.92 (H-16、20, d, ^3J = 8.2 Hz, 2 H), 7.69 (H-23, 27, d, ^3J = 8.8 Hz, 2 H), 7.61 (H-17, 19, d, ^3J = 8.3 Hz, 2 H), 7.39 (H-24, 26, d, ^3J = 8.7 Hz, 2 H), 7.07 (H-10-14, s, 5 H), 6.97 (H-4-8, s, 5 H), 6.80 (H-28, dd, ^3J = 17.6, 11.0 Hz, 1 H), 5.98 (H-29, d, ^3J = 17.7 Hz, 1 H), 5.39 (H-29, d, ^3J = 11.0 Hz, 1 H), 4.31 (H-1, d, ^3J = 7.4 Hz, 1 H), 3.93 (H-2, d, ^3J = 7.4 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO, TMS): δ165.7 (C-21), 142.9, 142.5, 140.9, 140.4, 136,2, 136.1, 133.8 (C-18, 3, 9, 22, 15, 25, 28), 128.6, 128.0, 127.8, 127.7, 127.5, 127.0, 126.9, 126.5, 119.7 (C-4-8 、10-14、23、24、26、27, 16, 17, 19, 20), 117.1 (C-29), 65.2 (C-2), 61.1 (C-1). Anal. calcd for $C_{29}H_{27}N_3O_3S$: C, 70.00; H, 5.47; N, 8.44; O, 9.65; S, 6.44; Found: C, 69.92; H, 5.52; N, 8.40; O, 9.71; S, 6.39.

2.3 The synthesis of monomers 1c and 1d

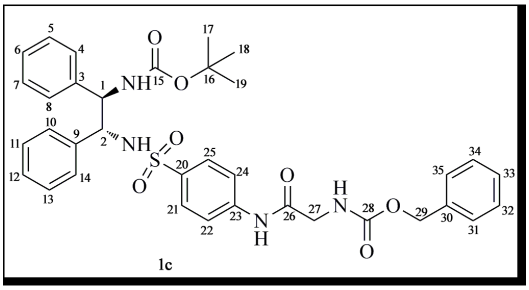


DPEN-Boc-Aps-Amide-Cbz **DPEN-Boc-Aps-Amide-Amino**



(1) DPEN-Boc-Aps-Amide-Cbz

A dried flask (50 mL) containing (R, R)-*N*-Boc-*N′*-(4- aminophenylsulfonyl)-1, 2-diphenyl-ethylenediamine (0.24 g, 0.5 mmol) and Cbz-$NHCH_2CO_2H$ (0.16 g, 0.8 mmol) was added 10 mL of NMM (0.09 g, 0.9 mmol) THF solution, cooled to 0°C, added dropwise 5 mL of IBCF (0.16 g, 0.8 mmol) THF solution and stirred at 25°C for 24 h. After evaporated under reduced pressure, the reaction residues was added 20 mL of water, extracted by ethyl acetate (30 mL×3). The combined organic phase was washed in turn with 10% citric acid aqueous solution (50 mL×3), water (50 mL×3), saturated sodium bicarbonate (50 mL×3) and saturated brine (50 mL×3), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford white solid. The crude white solid was recrystallized in mixed ethyl acetate/*n*-hexane (*v/v*=1/3) to obtain DPEN-Boc-Aps-Amide-Cbz (n=1) (0.24 g, 71%).

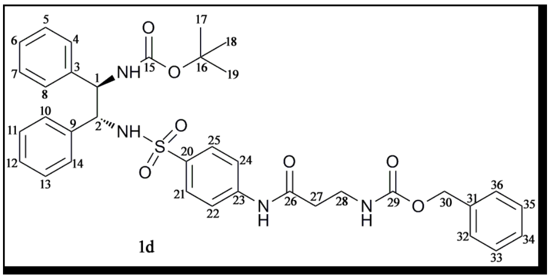


^{1}H NMR (300.1 MHz, DMSO) : δ 10.15 (NHCO, s, 1 H), 8.10 (HNCO, d, ^3J = 9.6 Hz, 1 H), 7.57 (HNCO, t, ^3J = 6.0 Hz, 1 H), 7.40–7.00 (Ar-H, HNCO, m, 19 H), 5.03 (H-29, s, 2 H), 4.81–4.77 (H-1, m, 1 H), 4.65-4.60 (H-2, m, 1 H), 3.79 (H-27, d, ^3J = 6.1 Hz, 2 H), 1.02 (H-17-19, s, 9 H). ^{13}C NMR (75.0 MHz, DMSO, TMS): δ 168.8 (C-28), 157.0 (C-15), 155.3 (C-26), 142.0, 140.8, 139.8, 137.4, 135.7 (C-20, 3, 9, 23, 30), 128.7, 128.1, 127.9, 127.5, 127.4, 127.1, 127.0, 118.5 (C-4-8, 10-14, 21, 22, 24, 25, 31-35), 78.4 (C-16), 65.9 (C-29), 62.5 (C-2), 59.5 (C-1), 44.5 (C-27), 28.5 (C-17-19). Anal. calcd for $C_{35}H_{38}N_4O_7S$: C, 63.81; H, 5.81; N, 8.50; O, 17.00; S, 4.87; Found: C, 63.79; H, 5.82; N, 8.43; O, 8.51; S, 4.79.

According to the same procedure, DPEN-Boc-Aps- Amide-Cbz (n=2) (0.28 g,73%) was obtained.

^{1}H NMR (300.1 MHz, DMSO) : δ10.12 (NHCO, s, 1 H), 8.09 (NHCO, d, 1 H), 7.40 – 7.00 (NHCO, Ar-H, m, 21 H), 4.99 (H-30, s, 2 H), 4.81-4.76

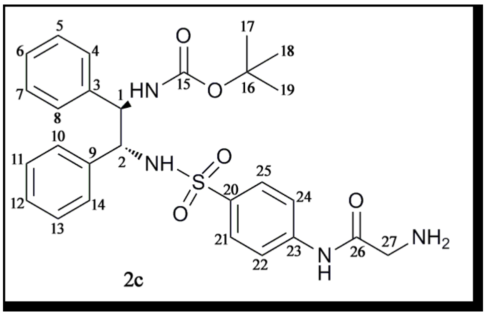
(H-1, m, 1 H), 4.64-4.59 (H-2, m, 1 H), 3.26 (H-28, t, ^3J = 7.5 Hz, 2 H), 2.49 (H-27, t, ^3J = 7.5 Hz, 2 H), 1.24 (H-17-19, s, 9 H).^{13}C NMR (75.0 MHz, DMSO, TMS): δ 170.1 (C-29), 156.5 (C-15), 155.3 (C-26), 142.3, 140.8, 139.9, 137.5, 135.5 (C-3, 9, 20, 23, 31), 128.7, 128.1, 128.0, 127.9, 127.5, 127.4, 127.1, 118.5 (C-4-8, 10-14, 21, 22, 32-36), 78.4 (C-16), 65.6 (C-30), 62.5 (C-2), 59.5 (C-1), 39.0 (C-28), 37.1 (C-27), 28.5 (C-17-19). Anal. calcd for $C_{36}H_{40}N_4O_7S$: C, 64.27; H, 5.99; N, 8.33; O, 16.65; S, 4.77; Found: C, 64.23; H, 6.02; N, 8.27; O, 8.38; S, 4.70.



1d

(2) DPEN-Boc-Aps-Amide-Amino

A dried flask (100 mL) containing DPEN-Boc-Aps-Amide-Cbz (n=1) (0.66 g, 1.0 mmol), 10% Pd/C (500 mg) was flushed three times with H_2 atmosphere, added 50 mL of MeOH with a syringe, and then stirred at 25°C for 12 h. The reaction mixture was filtered to recover the Pd/C catalyst and evaporated under reduced pressure to afford white solid. The crude product was purified by flash column chromatography eluting with $CHCl_3$/MeOH (*v*/*v*=100/1) to obtain the white product **DPEN-Boc-Aps-Amide-Amino** (n=1) (0.20 g, 89%).

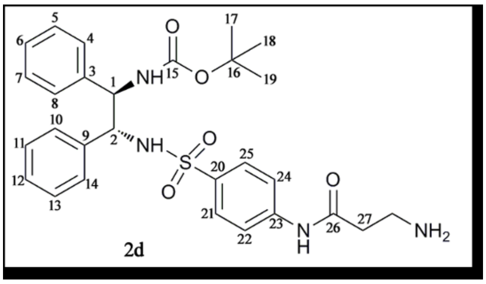


2c

^{1}H NMR (300.1 MHz, DMSO) : δ 7.43 (H-21, 25, d, ^3J = 8.4 Hz, 2 H), 7.19 – 6.99 (H-4-8, 10-14, 22, 24, m, 12 H), 4.75 (H-1, d, ^3J = 7.4 Hz, 1 H), 4.59 (H-2, d, ^3J =5.7 Hz, 1 H), 2.47 (H-27, s, 2 H), 1.23 (H-17-19, s, 9 H). ^{13}C NMR (75.0 MHz, DMSO, TMS): δ173.1 (C-15), 155.3 (C-26), 141.9, 141.0, 140.2, 136.0 (C-20, 3, 9, 23), 128.1, 127.8, 127.5, 127.4, 127.0, 118.4 (C-4-8, 10-14, 22, 24), 78.3 (C-16), 62.6 (C-2), 59.7 (C-1), 46.0 (C-27), 28.5 (C-17-19). Anal. calcd for $C_{27}H_{32}N_4O_5S$: C, 61.81; H, 6.15; N, 10.68; O, 15.25; S, 6.11; Found: C, 61.76; H, 6.22; N, 10.57; O, 15.32; S, 6.04.

According to the same procedure, **DPEN-Boc-Aps-Amide-Amino** (n=2) (0.19 g, 85 %) was obtained.

^{1}H NMR (300.1 MHz, DMSO) : δ 7.39 (H-21, NHCO,

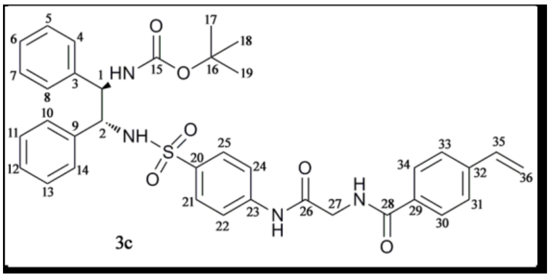


2d

25, d, ^3J = 7.5 Hz, 4 H), 7.19–7.00 (H-4-8, 10-14, 22, 24, m, 12 H), 4.77 (H-1, d, ^3J = 7.2 Hz, 1 H), 4.61 (H-2, d, ^3J =5.4 Hz, 1 H), 2.84 (H-27, 28, s, 4 H), 1.23 (H-17-19, s, 9 H). ^{13}C NMR (75 MHz, DMSO, TMS): δ 171.1 (C-15), 155.3 (C-26), 142.4, 140.9, 139.9, 135.5 (C-20, 23, 3, 9), 128.1, 127.9, 127.5, 127.3, 127.0, 126.9, 118.5(C-4-8, 10-14, 21, 22, 24, 25), 78.3 (C-16), 62.5 (C-2), 59.5 (C-1), 49.0 (C-28), 37.7 (C-27), 28.5 (C-17-19). Anal. calcd for $C_{28}H_{34}N_4O_5S$: C, 62.43; H, 6.36; N, 10.40; O, 14.85; S, 5.95; Found: C, 62.36; H, 6.42; N, 10.36; O, 14.91; S, 5.87.

(3) DPEN-Boc-Aps-Amide-Abc

To a dried flask (25 mL) was added in sequence p-vinylbenzoic acid (37 mg, 0.25 mmol), DCC (37 mg, 0.25 mmol), HOBt (42 mg, 0.28 mmol), DIPEA (32 mg, 0.25 mmol) and 5 mL of THF. After stirred at 0°C for 30 min, the reaction mixture was added dropwise **DPEN-Boc-Aps-Amide-Amino** (n=1) (0.16 g, 0.3 mmol) and stirred at 25°C for 12 h. After evaporated under reduced pressure, the reaction residues were added 30 mL of ethyl acetate. The organic phase was washed in turn with 10% citric acid aqueous solution (50 mL×3), water (50 mL×3), saturated sodium bicarbonate (50 mL×3) and saturated brine (50 mL×3), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford light yellow solid **DPEN-Boc-Aps-Amide-Abc** (n=1) (0.13 g, 76%).

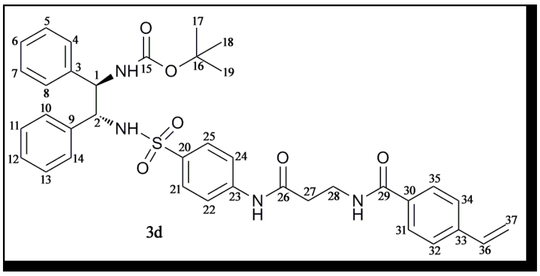


3c

^{1}H NMR (300.1 MHz, DMSO) : δ10.26 (NHCO, s, 1 H), 8.86 (HNCO, t, ^3J=3.4 Hz, 1 H), 8.12 (NHCO, d, ^3J=9.4 Hz,1 H), 7.86 (H-21, 25, d, ^3J=7.8 Hz, 2 H), 7.57 (H-22, 24, d, ^3J=7.8 Hz, 2 H), 7.39 (H-30, 34, d, ^3J=8.4 Hz, 2 H), 7.21-7.00 (H-4-8, 10-14, 32, 34, m, 12 H), 6.82-6.73 (H-35, m, 1 H), 5.95 (H-36, d, ^3J=17.7 Hz, 1 H), 5.35 (H-36, d, ^3J=10.5 Hz, 1 H), 4.78 (H-2, d, ^3J=7.8 Hz, 1 H), 4.63 (H-1, d, ^3J =8.4 Hz, 1 H), 4.05 (H-27, s, 2 H), 1.24 (H-17-19, s, 9 H).

^{13} C NMR (75.0 MHz, DMSO, TMS): δ 168.6(C-15), 166.6 (C-28), 155.2 (C-26), 141.9, 140.8, 140.4, 139.8, 136.3, 135.6, 133.4 (C-3, 9, 20, 23, 29, 32, 35), 128.2, 127.9, 127.5, 127.4, 127.1, 127.0, 126.3, 118.5 (C-4-8, 10-14, 21, 22, 30, 31), 116.5 (C-36), 78.4 (C-16), 62.3 (C-2), 59.5 (C-1), 47.7 (C-27), 28.5 (C-17-19). Anal. calcd for $C_{36}H_{38}N_4O_6S$: C, 66.04; H, 5.85; N, 8.56; O, 14.66; S, 4.90; Found: C, 65.96; H, 5.89; N, 8.49; O, 14.71; S, 4.86.

According to the same procedure, **DPEN-Boc-Aps-Amide-Abc** (n=2) (0.15 g, 75%) was obtained.

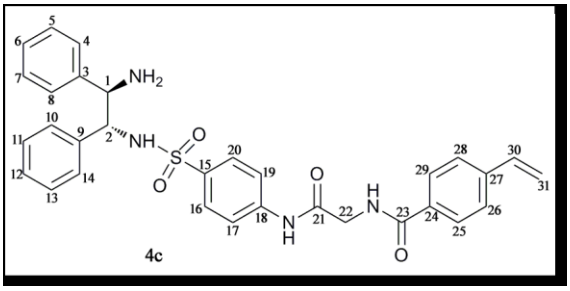


3d

^{1}H NMR (300.1 MHz, DMSO) : δ10.15 (NHCO, s, 1 H), 8.58 (HNCO, t, ^3J=3.4 Hz, 1 H), 7.78 (H-21, 25, d, ^3J = 8.2 Hz, 2 H), 7.52 (H-22, 24, d, ^3J=8.2 Hz, 2 H), 7.39 (H-31, 35, d, ^3J=8.7 Hz, 2 H), 7.28-6.97 (H-4-8, 10-14, 32, 34, NHCO, 14 H), 6.79-6.69 (H-36, m, 1 H), 5.90 (H-37, d, ^3J= 17.1 Hz, 1 H), 5.32 (H-27, d, ^3J=11.1 Hz, 1 H), 4.79 (H-2, d, ^3J=7.2 Hz, 1 H), 4.60 (H-1, d, ^3J = 6.3 Hz, 1 H), 3.52 (H-28, t, ^3J=5.7 Hz, 2 H), 2.61 (H-27, t, ^3J=6.6 Hz, 2 H), 1.23 (H-17-19, s, 9 H). ^{13} C NMR (75.0 MHz, DMSO, TMS): δ 170.3 (C-15), 166.3 (C-29), 155.3 (C-26), 142.2, 140.8, 140.1, 139.8, 136.3, 135.5, 134.0 (C-3, 9, 20, 23, 30, 33, 36), 128.1, 127.9, 127.5, 127.4, 127.1, 127.0, 126.3, 118.4 (C-4-8, 10-14, 21, 22, 31, 32), 116.5 (C-37), 78.4 (C-16), 62.3 (C-2), 59.5 (C-1), 36.7 (C-28), 36.2 (C-27), 28.5 (C-17-19). Anal. calcd for $C_{37}H_{40}N_4O_6S$: C, 66.45; H, 6.03; N, 8.38; O, 14.35; S, 4.79; Found: C, 66.38; H, 6.08; N, 8.34; O, 14.39; S, 4.76.

(4) Monomers 1c and 1d

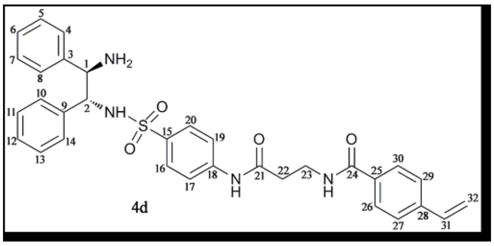
To a flask (100 mL) was added **DPEN-Boc-Aps-Amide-Abc** (n=1) (0.20 g, 0.3 mmol) and 40 mL of CH_2Cl_2, stirred and cooled to 0°C, added dropwise 1.4 mL of CF_3CO_2H, and then stirred at 25°C for 12 h. The reaction mixture was adjusted to pH=9 by using 10% NaOH aqueous solution, and the precipitate was filtered. The aqueous phase was extracted by ethyl acetate (50 mL×3), and the combined organic phases were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford light yellow solid **1c** (0.15 g, 90%).



4c

^{1}H NMR (300 MHz, DMSO) : δ10.31 (NHCO, s, 1 H), 8.84 (NHCO, t, ^3J=5.6 Hz, 1 H), 7.85 (H-16, 20, d, ^3J=8.2 Hz, 2 H), 7.56 (H-17, 19, d, ^3J=8.3 Hz, 2 H), 7.42 (H-25, 29, d, ^3J =8.7 Hz, 2 H), 7.33 (H-26, 28, d, ^3J = 8.7 Hz, 2 H), 7.21-6.85 (H-4-8, 10-14, m, 10 H), 6.79-6.70 (H-30, dd, ^3J =17.7, 11.0 Hz, 1 H), 5.94 (H-31, d, ^3J=29.5 Hz, 1 H), 5.35 (H-31, d, ^3J=11.1 Hz, 1 H), 4.48 (H-2, d, ^3J=7.5 Hz, 1 H), 4.22 (H-1, d, ^3J=7.5 Hz, 2 H), 4.02 (H-22, d, ^3J=6.4 Hz, 2 H). ^{13}C NMR (75.0 MHz, DMSO): δ166.6 (C-21), 157.0 (C-23), 141.9, 140.8, 140.4, 139.8, 136.3, 135.6, 133.4 (C-3, 9, 15, 18, 24, 27, 30), 128.2, 127.9, 127.5, 127.4, 127.1, 127.0, 126.3, 118.5 (C-4-8, 10-14, 16, 17, 25, 26), 116.5 (C-31), 62.3 (C-2), 59.5 (C-1), 47.7 (C-22). Anal. calcd for $C_{31}H_{30}N_4O_4S$: C, 67.13; H, 5.45; N, 10.10; O, 11.54; S, 5.78; Found: C, 67.10; H, 5.49; N, 10.09; O, 11.59; S, 5.76.

According to the same procedure, **1d** (0.14 g, 86 %) was obtained.

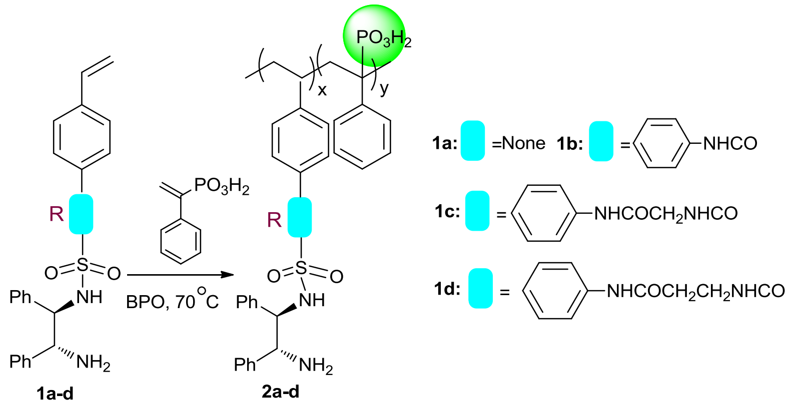


4d

^{1}H NMR (300 MHz, DMSO) : δ10.16 ($NHSO_2$, s, 1 H), 8.58 (HNCO, t, ^3J=5.4 Hz, 1 H), 7.79 (H-16, 20, d, ^3J=8.1 Hz, 2 H), 7.52 (H-17, 19, d, ^3J=8.1 Hz, 2 H), 7.46 (H-26, 30, d, ^3J =8.7 Hz, 2 H), 7.31(H-27, 29, d, ^3J = 8.7 Hz, 2 H), 7.21-6.92 (H-4-8, 10-14, m, 10 H), 6.79-6.70 (H-31, dd, ^3J =17.7, 11.0 Hz, 1 H), 5.91 (H-32, d, ^3J=29.5 Hz, 1 H), 5.33 (H-32, d, ^3J=11.1 Hz, 1 H), 4.28 (H-2, d, ^3J=7.5 Hz, 1 H), 3.93 (H-1, d, ^3J= 7.5 Hz, 2 H), 3.54-3.50 (H-23, m, 2 H), 2.61 (H-22, t, ^3J=6.6 Hz, 2 H). ^{13}C NMR (75.0 MHz, DMSO, TMS): δ170.2 (C-21), 166.1 (C-24), 142.2, 142.1, 139.9, 139.8, 136.1, 135.2, 133.8 (C-3, 9, 15, 18, 25, 28, 31), 127.8, 127.7, 127.5, 127.4, 126.8, 126.8, 126.1, 118.3 (C-4-8, 10-14, 16, 17, 26, 27), 116.3 (C-32), 64.9 (C-2), 60.7 (C-1), 56.7 (C-23), 35.8 (C-22). Anal. calcd for $C_{32}H_{32}N_4O_4S$: C, 67.58; H, 5.67; N, 9.85; O, 11.25; S, 5.64; Found: C, 67.53; H, 5.73; N, 9.84; O, 11.32; S, 5.56.

3. Synthesis of phosphonate-containing polystyrene copolymers

3.1 Synthesis of 2a-d



A dried flask (25 mL) containing **1a** (75.6 mg, 0.2 mmol) and 1-phosphonate styrene (184.0 mg, 1.0 mmol) was flushed three times with Ar_2 atmosphere, added 5 mL of THF and benzoy peroxide

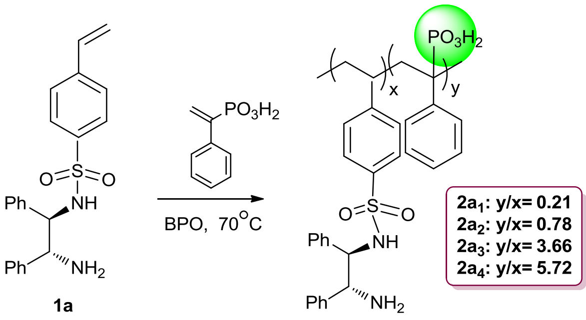
(BPO) (20.0 mg, 0.08 mmol) and heated to 80°C for 24 h. During the reaction process benzoy peroxide (5.0 mg) was added at eight hours interval. The reaction mixture was filtered, washed with THF (5 mL×3), ethyl acetate (5 mL×3) and acetone (5 mL×3) and dried at 60°C in a vacuum tank to afford white solid **2a** (105 mg, 40%).

The molar ratio of **1b-d** to 1-phosphonate styrene at 1:5 was maintained, the other phosphonate-containing polystyrene copolymers **2b-d** were prepared according to the procedure metioned above (Table 1).

Table 1 The yields of phosphonate-containing polystyrene copolymers 1a-d

Entry	The used amount of 1a-d (mg/mol)	1-phosphonate styrene (mg/mol)	molar ratio	Yield (mg/%)	y/x value
1a	75.6/0.2	147.2/1	1:4	105/47.1	3.66/1
1b	99.4/0.2	147.2/1	1:4	152/61.6	3.72/1
1c	43.0/0.08	58.9/0.32	1:4	90/88.3	3.92/1
1d	45.0/0.08	58.9/0.32	1:4	84/80.8	4.08/1

3.2 Synthesis of $2a_1$-a_4



A dried flask (25 mL) containing **1a** (151.4 mg, 0.4 mmol) and 1-phosphonate styrene (80.8 mg, 0.4 mmol) was flushed three times with Ar_2 atmosphere, added 5 mL of THF and benzoy peroxide (BPO) (20.0 mg, 0.08 mmol) and slowly heated to 80°C for 24 h. During the reaction process benzoy peroxide (5.0 mg) was added at eight hours interval. The reaction mixture was filtered, washed with THF (5 mL×3), ethyl acetate (5 mL×3) and acetone (5 mL×3) and dried at 60°C in a vacuum tank to afford white solid **$2a_2$** (105 mg, 40%).

According to the procedure metioned above, the other phosphonate-containing polystyrene copolymers **$2a_1$-a_4** were prepared at 4:1, 1:4 and 1:8 molar ratio of **1a** to 1-phosphonate styrene (Table 2).

Table 2 The yields of phosphonate-containing polystyrene copolymers **$2a_1$-a_4**

Entry	Used amount of 1a (mg/mol)	1-phosphonate styrene (mg/mol)	molar ratio	Yield (mg/%)	y/x value

$2a_1$	151.4/0.4	20.2/0.1	4:1	108.1/63.0	0.21/1
$2a_2$	151.4/0.4	80.8/0.4	1:1	167.5/72.1	0.78/1
$2a_3$ (2a)	151.4/0.4	323.2/1.6	1:4	220.3/46.4	3.66/1
$2a_4$	151.4/0.4	646.4/3.2	1:8	105.2/13.1	6.78/1

3.3 Characterization of $2a_1$-a_4

(1) ^{31}P NMR of $2a_1$-a_4

Due to NMR characteristic of phosphorus, it was easier to determine the structural feature and composition of phosphonate-containing polystyrene copolymer by ^{31}P NMR than other non-phosphonate-containing copolymer. ^{31}P NMR spectra of **$2a_1$-a_4** were shown **Fig.S1-1**. It was noted that 1-phosphonate styrene self-polymers prepared under the same conditions showed four groups of ^{31}P NMR peaks at 13.0-13.5 (m), 5.7 (s), 0.9 (s) and 0.3 (s) ppm, which illustrated four different structural arrangements of phosphonate ($-PO_3H_2$) by means of self polymerization. However, after 1-phosphonate styrene copolymerized with polystyrene, a new and wide ^{31}P NMR peak of phosphonate-containing polystyrene copolymers **$2a_1$-a_4** emerged in the range of 19.0-31.0 ppm, which was attributed to the newly generated chains upon the copolymerization of 1-phosphonate styrene with polystyrene (**Fig.S1-1**).

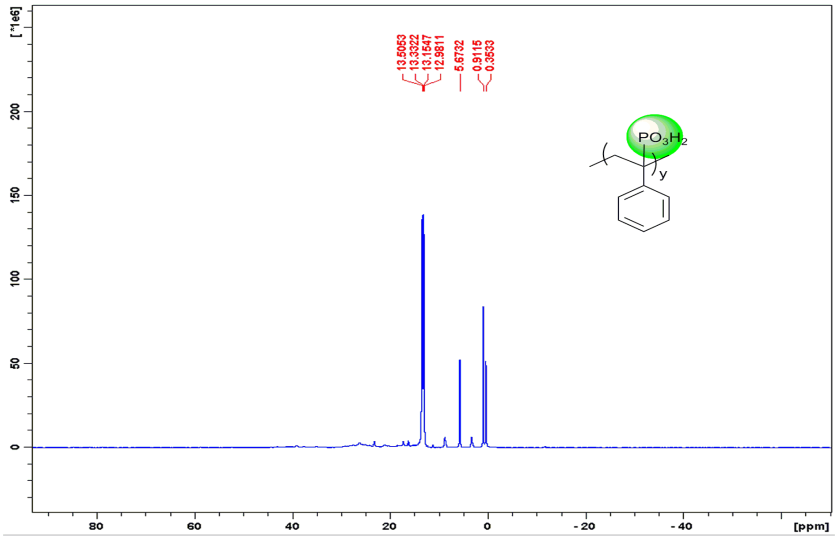
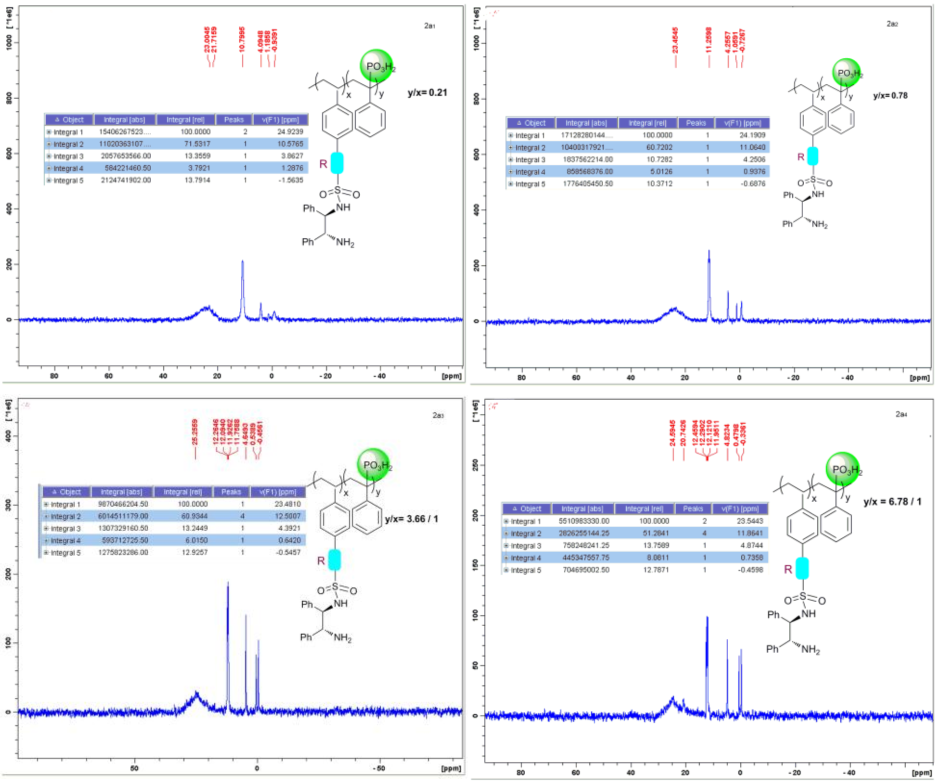


Fig.S1-1. The ^{31}P NMR spectra of 1-phosphonate styrene self-polymer



△ Object	Integral [abs]	Integral [rel]	Peaks	ν(F1) [ppm]
⊞ Integral 1	15406267523....	100.0000	2	24.9239
⊞ Integral 2	11020363107....	71.5317	1	10.5765
⊞ Integral 3	2057653566.00	13.3559	1	3.8627
⊞ Integral 4	584221460.50	3.7921	1	1.2876
⊞ Integral 5	2124741902.00	13.7914	1	-1.5635

△ Object	Integral [abs]	Integral [rel]	Peaks	ν(F1) [ppm]
⊞ Integral 1	17128280144....	100.0000	1	24.1909
⊞ Integral 2	10400317921....	60.7202	1	11.0640
⊞ Integral 3	1837562214.00	10.7282	1	4.2506
⊞ Integral 4	858568376.00	5.0126	1	0.9376
⊞ Integral 5	1776405450.50	10.3712	1	-0.6876

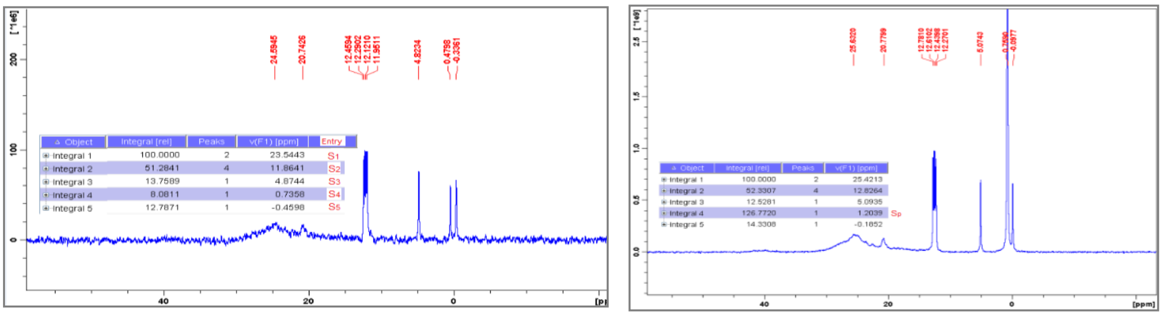
△ Object	Integral [abs]	Integral [rel]	Peaks	ν(F1) [ppm]
⊞ Integral 1	9870466204.50	100.0000	1	23.4810
⊞ Integral 2	6014511179.00	60.9344	4	12.5007
⊞ Integral 3	1307329160.50	13.2449	1	4.3921
⊞ Integral 4	593712725.50	6.0150	1	0.6420
⊞ Integral 5	1275823286.00	12.9257	1	-0.5457

△ Object	Integral [abs]	Integral [rel]	Peaks	ν(F1) [ppm]
⊞ Integral 1	5510983330.00	100.0000	2	23.5443
⊞ Integral 2	2826255144.25	51.2841	4	11.8641
⊞ Integral 3	758248241.25	13.7589	1	4.8744
⊞ Integral 4	445347557.75	8.0811	1	0.7358
⊞ Integral 5	704695002.50	12.7871	1	-0.4598

Fig.S1-2. The ^{31}P NMR spectra of phosphonate-containing polystyrene copolymers **$2a_1$-a_4**

(2) Quantitative ^{31}P NMR

Due to P-31 high natural abundance and magnetic resonance sensitivity as hydrogen, ^{31}P NMR was used as a quantitative method to determine the phosphorus content in copolymers **$2a_1$-a_4**. Determination procedure: In sample tube was quantitatively charged phosphonate-containing copolymer **$2a_4$** (m_s) and added 0.5 mL of d_6-DMSO. After completely dissolved in d_6-DMSO, 85% H_3PO_4 (m_1) was quantitatively charged, mixed well and then ^{31}P NMR were performed on a Bruker AV–300 NMR instrument at 121.511 MHz. As an example, the ^{31}P NMR spectra of **$2a_4$** and sample (85% H_3PO_4 + **$2a_4$**) was shown in Fig.S2.



△ Object	Integral [rel]	Peaks	ν(F1) [ppm]	Entry
⊞ Integral 1	100.0000	2	23.5443	S1
⊞ Integral 2	51.2841	4	11.8641	S2
⊞ Integral 3	13.7589	1	4.8744	S3
⊞ Integral 4	8.0811	1	0.7358	S4
⊞ Integral 5	12.7871	1	-0.4598	S5

△ Object	Integral [rel]	Peaks	ν(F1) [ppm]	
⊞ Integral 1	100.0000	2	25.4213	
⊞ Integral 2	52.3307	4	12.8264	
⊞ Integral 3	12.5281	1	5.0935	
⊞ Integral 4	126.7720	1	1.2039	Sp
⊞ Integral 5	14.3308	1	-0.1852	

Fig.S2. The ^{31}P NMR spectra of **2a$_4$** and sample (85% H_3PO_4 + **2a$_4$**)

The chemical compositions (x/y) in the copolymers **2a$_1$-a$_4$** could be determined by ^{31}P NMR method. By the comparative investigation of ^{31}P NMR of **2a$_4$** and sample (85% H_3PO_4 + **2a$_4$**), the inreased peak area at 0.7 ppm was attributed to the added H_3PO_4 (85%). Then, the x and y values could be calculated according to the following equations.

$$\frac{S_p}{S_{all}} = \frac{m_1 * 85\% * \frac{M_p}{M_{H_3PO_4}}}{m_2}$$

$$x = \frac{m_s - \frac{m_2 * M_{pps}}{M_p}}{M_{1a}}$$

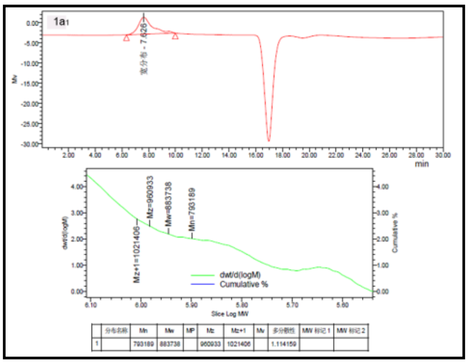
$$y = \frac{m_2}{M_P}$$

S_{all}: The sum of peak areas of 2a4
S_p : Peak area at 0.7 ppm owing to H3PO4
m_1 : The mass of added 85% H3PO4
m_2 : The mass of phosphorus in 2a4
m_S : The total mass of 2a4
M_P : The molar mass of phosphorus
M_{PPS} :The molar mass of1-phosphonatestyrene
M_{1a} : The molar mass of1a

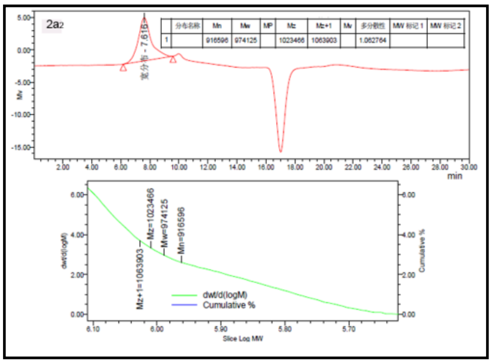
The chemical compositions (x/y) of the copolymers **2a-b** and **2a$_1$-a$_4$** were calculated and shown in Table 1 and Table 2.

(3) Determination of molecular weights of 2a$_1$-a$_4$

Gel permeation chromatography (GPC) was performed using a 515 HPCC pump and a Waters styragel HT3 column (Mw 2000-1000,000) with a 2414 refractive index detector from Waters. Experiments were performed at 35 °C using THF as fluent, flow rate of 0.7 mL /min, and molecular weights are reported versus monodispersed polysaccharide standards. From Fig.S3, it was found that the weight-average molecular weights (M_n) of the copolymers **2a$_1$-a$_4$** increased as the increase of y values, and then decreased at y=3.66 between 595.2 and 916.6 kDa. The good PDI values between 1.06 and 1.28, which illustrated controlled molecular weight and narrow polydispersity, were obtained under a mild and easily operating experiment conditions.



	分布名称	Mn	Mw	MP	Mz	Mz+1	Mv	多分散性	MW 标记 1	MW 标记 2
1		793189	883738		960933	1021406		1.114159		



	分布名称	Mn	Mw	MP	Mz	Mz+1	Mv	多分散性	MW 标记 1	MW 标记 2
1		916596	974125		1023466	1063903		1.062764		

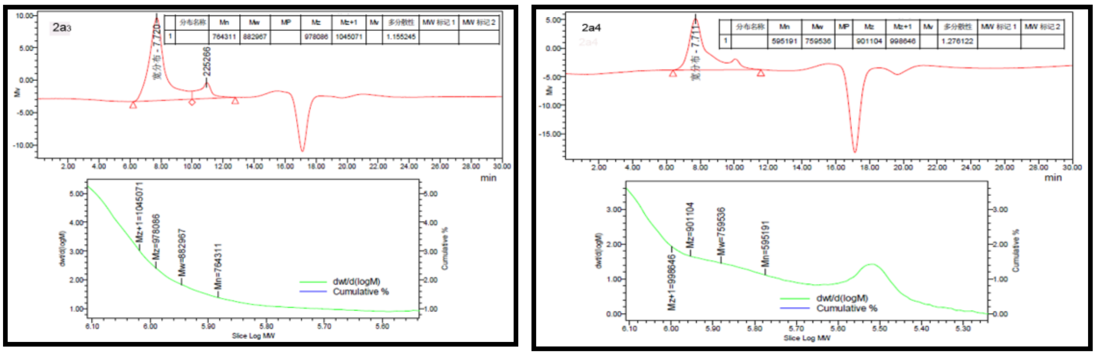


Fig.S3. The GPC spectra of the copolymers **2a$_1$-a$_4$**

(4) TGA

On heating the copolymers **2a$_1$–a$_4$**, the similar thermolysis curves over a broad temperature range of 40–800 ^{o}C with a three-step weight loss behavior were observed, which were shown in **Fig. S4**. The first slope curve of **2a$_1$–a$_4$** below 150 ^{o}C was attributed to the desorption of the surface-bound or intercalated water in the pores with weight losses of 3.8, 3.8, 3.2 and 3.1 wt.% respectively, followed by the sharp second curve with a single DTG peak between 150 and 330 ^{o}C, while the third stage appeared from 330 to 700 ^{o}C. From **Fig. S4**, it was found that the second weight losses successively decreased from 30.8 to 17.1%. On the contrary, the third weight losses increased from 33.0 to 57.9%. This could be due to an association with the mount of 1-phosphonate styrene fragments (y value). Owing to the higher y value of 2**a$_4$**, it possessed the more weight loss in the third curve, which was accordance with the composition of phosphonate-containing polystyrene copolymer determined by ^{31}P NMR.

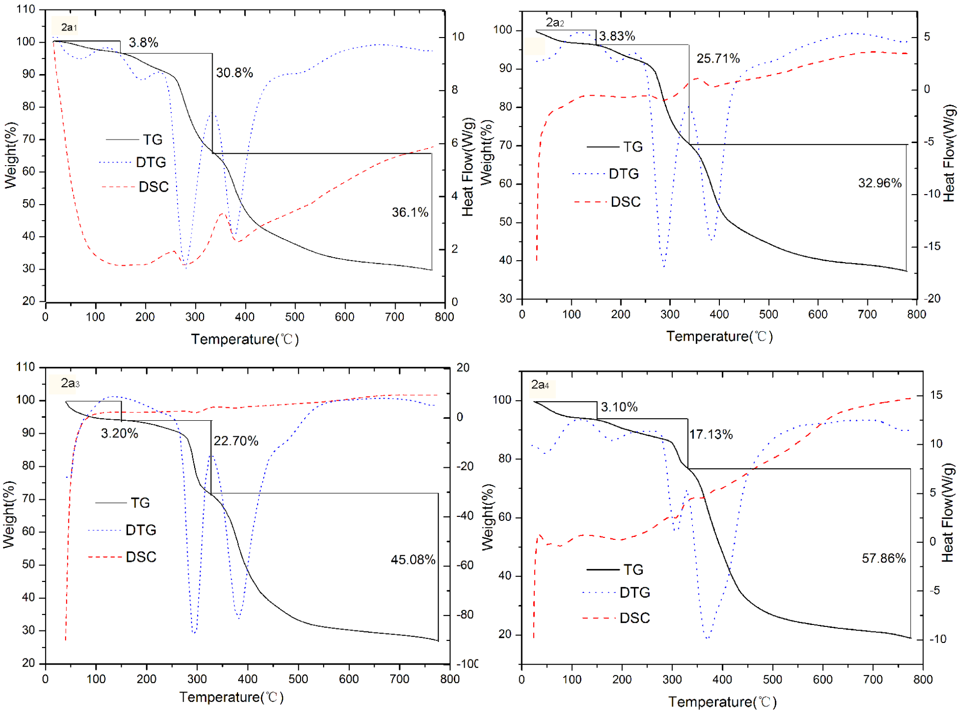
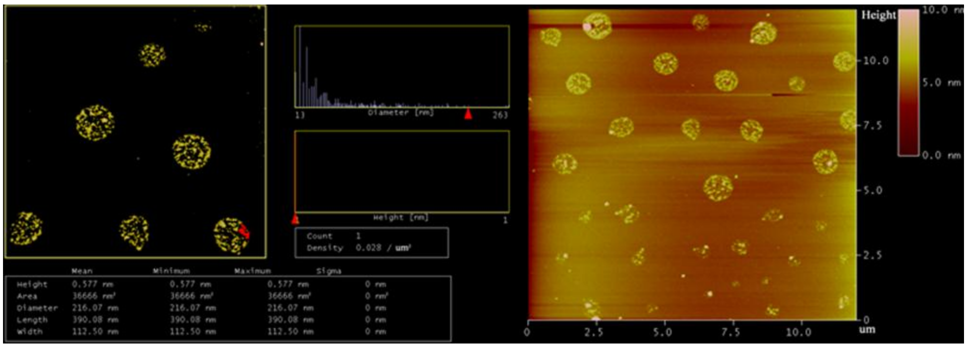


Fig.S4. The thermal gravimetric curves of the copolymers **$2a_1$-a_4**

(5) Surface morphology

As an example, the copolymer **$2a_3$** was well clarified by AFM (**Fig.S5-1**) and SEM (**Fig.S5-2**) to understand the surface morphology and particle size. After being well-dispersed in water (1 mg sample in 5 mL of H_2O) for 10 min under ultrasonic radiation, a thin film of the suspension on mica was prepared by spin coating, and the particles were left on the mica surface after volatilization of water for three days. Due to being well-dispersed in water, the AFM images could be identified as being efficiently elaborated the surface morphology of the copolymer **$2a_3$** in aqueous solution, which seemed to simulate the "true" states of **$2a_3$** in water. From **Fig.S5-2**, it can be seen that the aggregates were observed with 0.58 nm mean height, 390.1 nm mean length and 112.5 nm mean width. The SEM images showed that the aggregates with 1-5 um in size dispered in THF could be considered to mirror surface morphology of **$2a_3$** in solid state.



Count 1
Density 0.028 / um²

	Mean	Minimum	Maximum	Sigma
Height	0.577 nm	0.577 nm	0.577 nm	0 nm
Area	36666 nm²	36666 nm²	36666 nm²	0 nm²
Diameter	216.07 nm	216.07 nm	216.07 nm	0 nm
Length	390.08 nm	390.08 nm	390.08 nm	0 nm
Width	112.50 nm	112.50 nm	112.50 nm	0 nm

Fig.S5-1. The AFM images of the copolymer **$2a_3$**

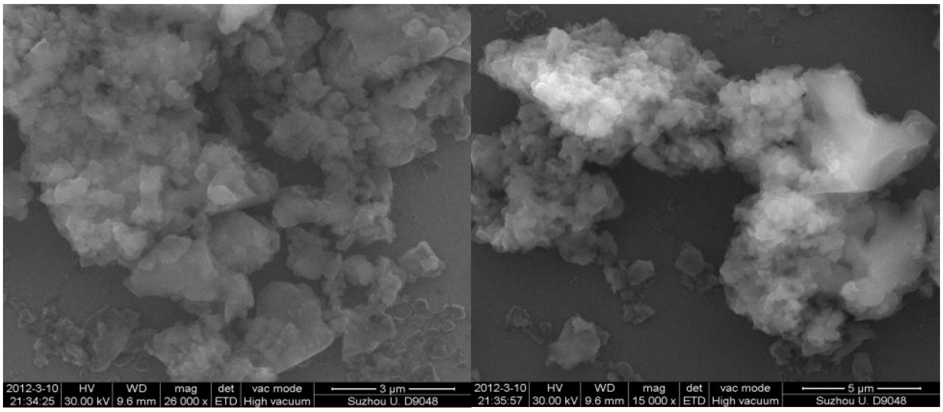


Fig.S5-2. The SEM images of the copolymer **$2a_3$**

(6) Porous structure

The nitrogen adsorption–adsorption isotherm plots of **$2a_1$–a_4**, performed at 77 K, were shown in Fig. S6. The isotherm plots of **$2a_1$–a_4** were linear to the P/P_0 axis at relative low P/P_0 range (0~0.8) and convex to the P/P$_0$ axis at high P/P$_0$ range (0.8~1.0), which were beyond to the classic definitions. From the calculated data in Table 3 and Fig.S6, these pore size distributions (PSDs) of as-synthesized **2a$_1$–a$_4$** suggested the existence of 0.8-10 nm irregular micropores, having two sharp peaks at about 1.2 and 2.0 nm. As expected, the surface areas, average pore diameters and pore volumes of **2a$_1$–a$_4$** increased from 3.1 to 8.3 m^2 g^{-1}, 8.1 to 10.2 Å and 1.2 to 8.3×10^{-3} cc/g, respectively with the increase of the content of 1-phosphonate styrene (y) in the copolymers **2a$_1$-a$_4$** from 0.21 to 6.78. Thus it can be seen that the introduction of functional phosphonate groups was advantageous to the construction of pore structure owing to the action of hydrogen bond between phosphonate groups.

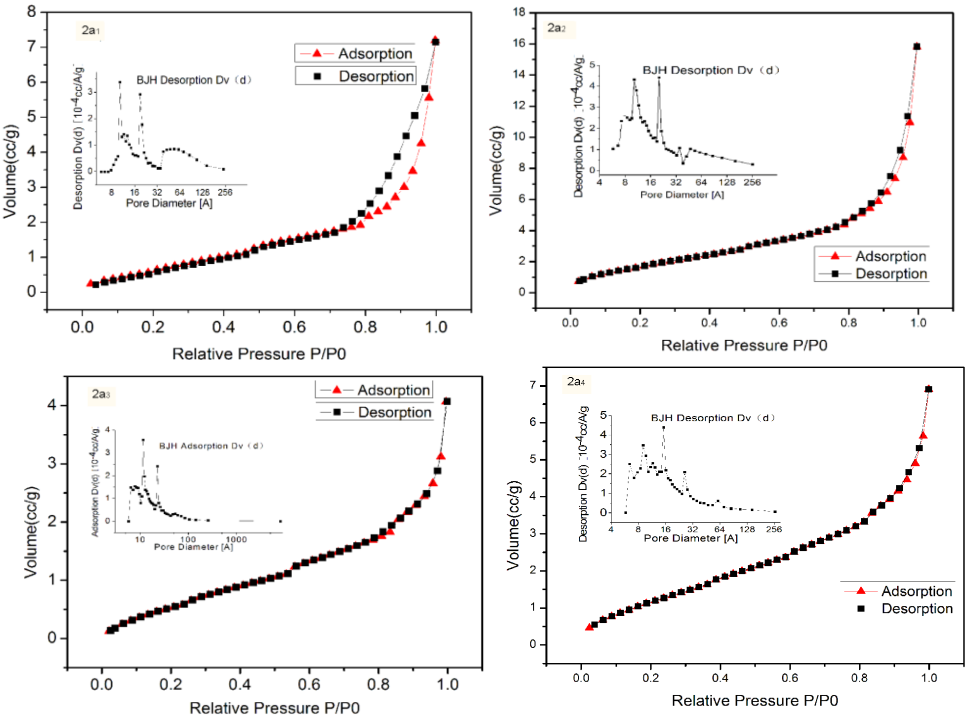


Fig.S6. Nitrogen adsorption–desorption isotherm plots obtained with **2a$_1$–a$_4$**

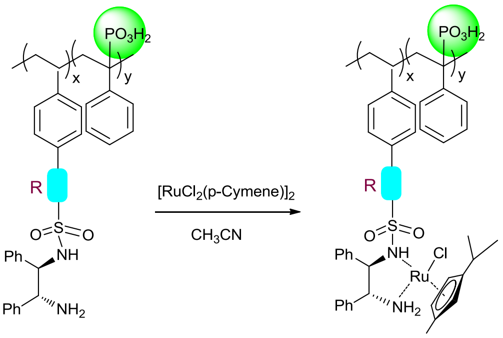
Table 3 The mesoporous properties of the as-synthesized **2a$_1$-a$_4$**^{a}

Entry	Surface Area [m^2/g]^b	Average Pore Diameter [Å]^c	Pore Volume [10^{-3} cc/g]^d
2a$_1$	3.1	8.1	1.2
2a$_2$	3.3	7.0	4.6
2a$_3$ (2a)	5.0	9.2	6.1
2a$_4$	8.3	10.2	8.3

^{a} The sample was degassed at 100 ºC for 5 h. ^{b} based on multipoint BET method. ^{c} Based on the desorption data using BJH method. ^{d} Based on the desorption data of BJH method.

4. Preparation of copolymer-supported Ru catalysts

4.1. Preparation of copolymer-supported Ru catalyst 3a-d

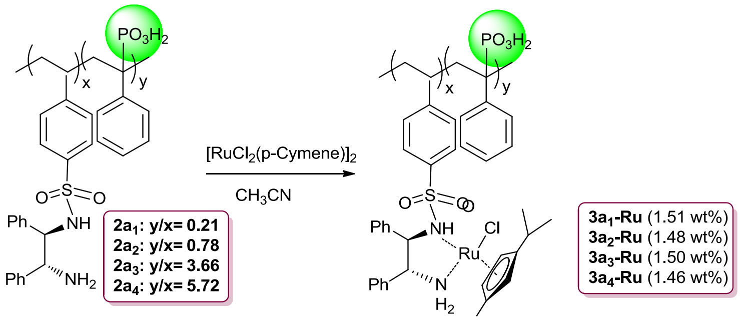


2a-d (y/x= 3.66-4.08) **3a-d** (y/x= 3.66-4.08)

A dried flask (25 mL) containing **2a** (20.0 mg) and [$RuCl_2$(*p*-cymene)]$_2$ (9.0 mg, 0.015 mmol) was flushed three times with Ar_2 atmosphere, added 0.4 mL of Et_3N and 5 mL of methyl cyanide, stirred and heated to 82 °C for 5 h (the color of the solution changed from orange to yellow). The orange solid was filtered, washed with CH_2Cl_2 (5 mL×3) and dried at 40°C in a vacuum tank to afford copolymer-supported Ru catalyst **3a** in 72.4% yield.

According to the same procedure, the other copolymer-supported Ru catalysts **3b-d** were prepared in 74.1-76.0% yields.

4.2. Preparation of copolymer-supported Ru catalysts 3a$_1$-a$_4$



A dried flask (25 mL) containing **2a$_1$** (20.0 mg) and [$RuCl_2$(*p*-cymene)]$_2$ (9.0 mg, 0.015 mmol) was flushed three times with Ar_2 atmosphere, added 0.4 mL of Et_3N and 5 mL of methyl cyanide, stirred and heated to 82 °C for 5 h (the color of the solution changed from orange to yellow). The orange solid was filtered, washed with CH_2Cl_2 (5 mL×3) and dried at 40°C in a vacuum tank to afford copolymer-supported Ru catalyst **3a$_1$** in 75.9% yield.

According to the same procedure, the other copolymer-supported Ru catalysts **3a$_2$-a$_4$** were prepared in 76.1-78.5% yields.

4.3 Characterization of 3a$_1$-a$_4$

(1) XPS spectra

The contents of immobolized ruthenium in **3a-d** and **3a$_1$-a$_4$** were determined by X-ray photoelectron spectroscopy measurement (XPS). The XPS spectra and data were carried out on a Physical Electronics ESCA 5701 instrument, equipped with a multichannel detector and a hemispherical analyzer. Mg Ka radiation (hm = 1253.6 eV) was used as the exciting source, and operated at a constant power of 300 W (15 kV, 20 mA). The data were acquired at a take-off angle of 45º and pass energy of 29.35 eV. The pressure in the analysis chamber was maintained at 8×10^{-7} Pa. Charge compensation was done with the adventitious C 1 s peak at 284.8 eV. As an example, the spectra of support **2a$_3$** and its supported Ru catalyst **3a$_3$** were shown in **Fig.S7** and **Table 4**.

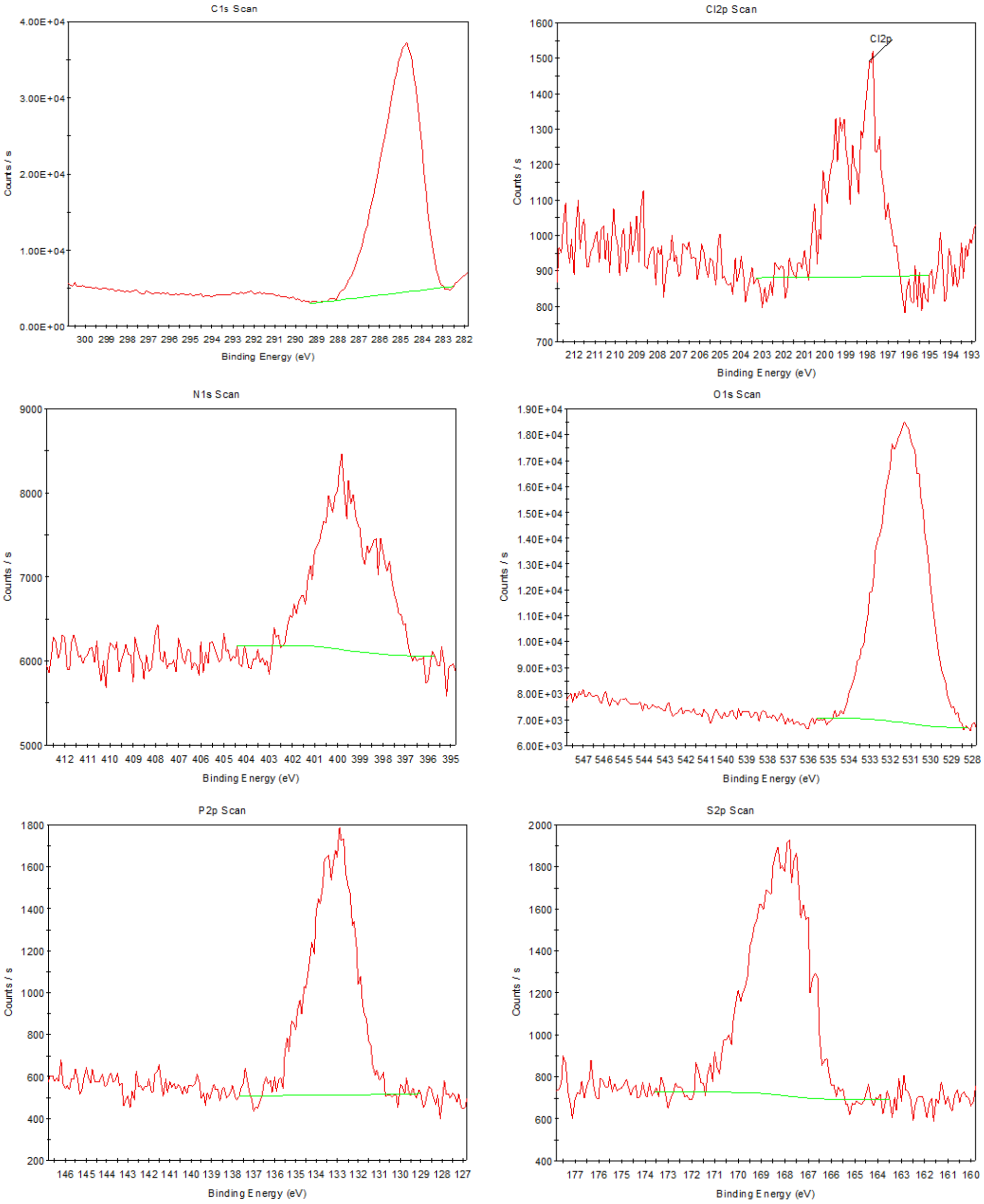
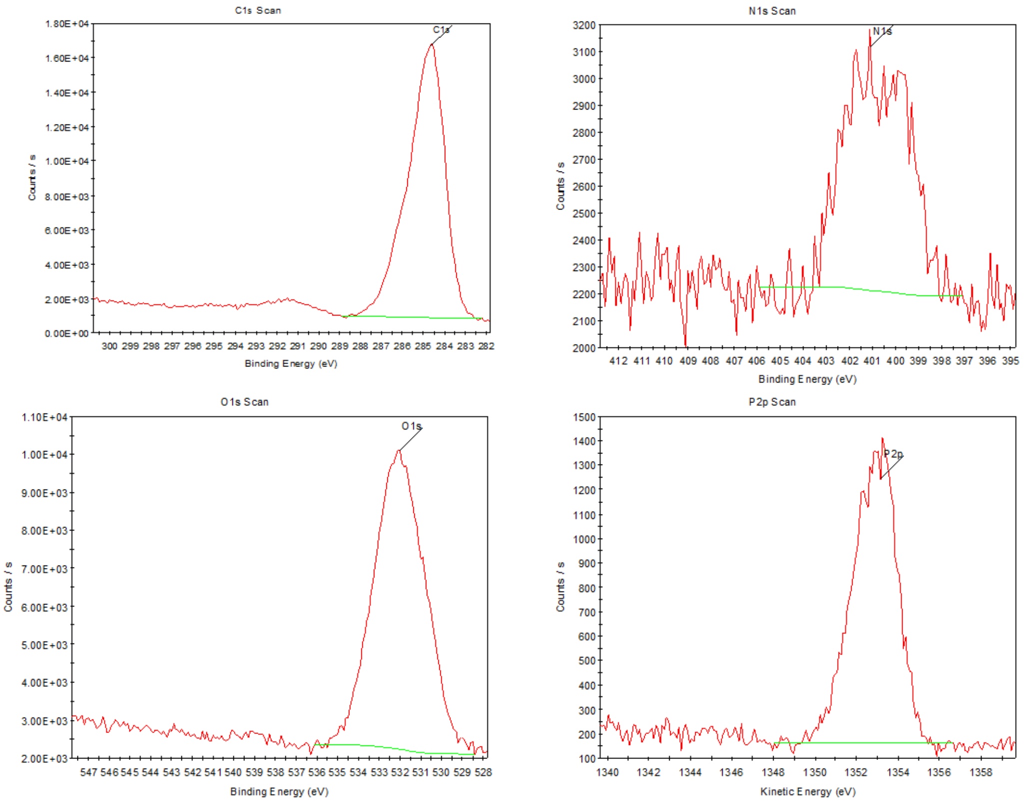


Fig.S7-1. The XPS spectra of support **2a$_3$**



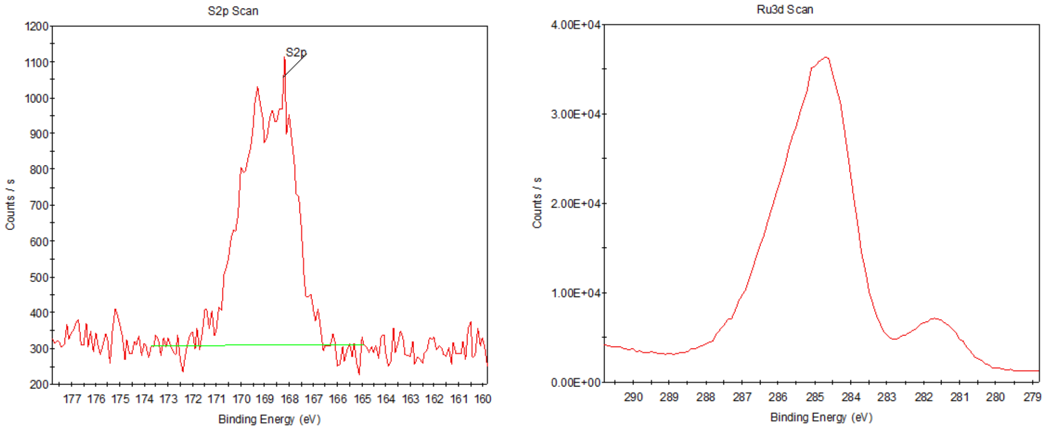


Fig.S7-2. The XPS spectra of Ru catalyst **3a$_3$**

Table 4 The XPS data of support **2a$_3$** and its supported Ru catalyst **3a$_3$**

Sample	C_{1s}/wt.%	Cl_{2p}/wt.%	N_{1s}/wt.%	O_{1s}/wt.%	P_{2p}/wt.%	S_{2p}/wt.%	Ru_{3d}/wt.%
2a$_3$	167.9/71.0		399.8/3.5	532.2/17.7	132.9/5.5	167.9/2.3	
3a$_3$	168.2/77.5	197.9/0.6	401.1/3.5	532.1/12.2	133.1/2.7	168.1/2.1	284.7/1.4

(2) IR

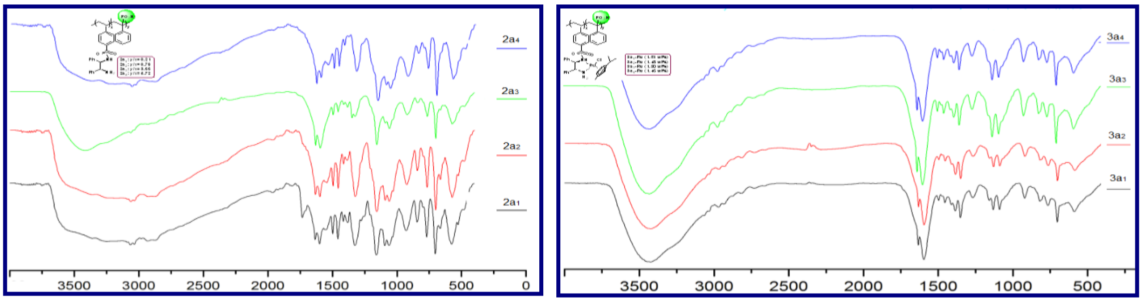


Fig.S8 IR spectra of copolymer-supported Ru catalysts **$3a_1$–a_4**

After $RuCl_2$(*p*-cymene)]$_2$ was stirred with **$2a_1$–a_4** at 82 °C in 0.4 mL of Et_3N and 5 mL of methyl cyanide, there are two major changes in IR spectra of **$3a_1$–a_4**. First, from **Fig.S8**, it was found that IR spectra in the range of 1570-1640 cm^{-1} were strengthened markedly, which resulted from Ar-H stretching vibration in *p*-cymene moiety and indirectly illustrated that Ru had been immobolized onto the backbone of supports **$2a_1$–a_4**. Secondly, the characteristic stretching vibration of PO_3H_2 in the range of 1000-1200 cm^{-1} were reshaped and became two absorption peaks at 1155 and 1058 cm^{-1} with equal absorbing intensity, which was related to the decreased formation of hydrogen bond between PO_3H_2 and NH_2 groups upon the coordination reaction of $RuCl_2$(*p*-cymene)]$_2$ with NH_2 groups.

(3) TGA

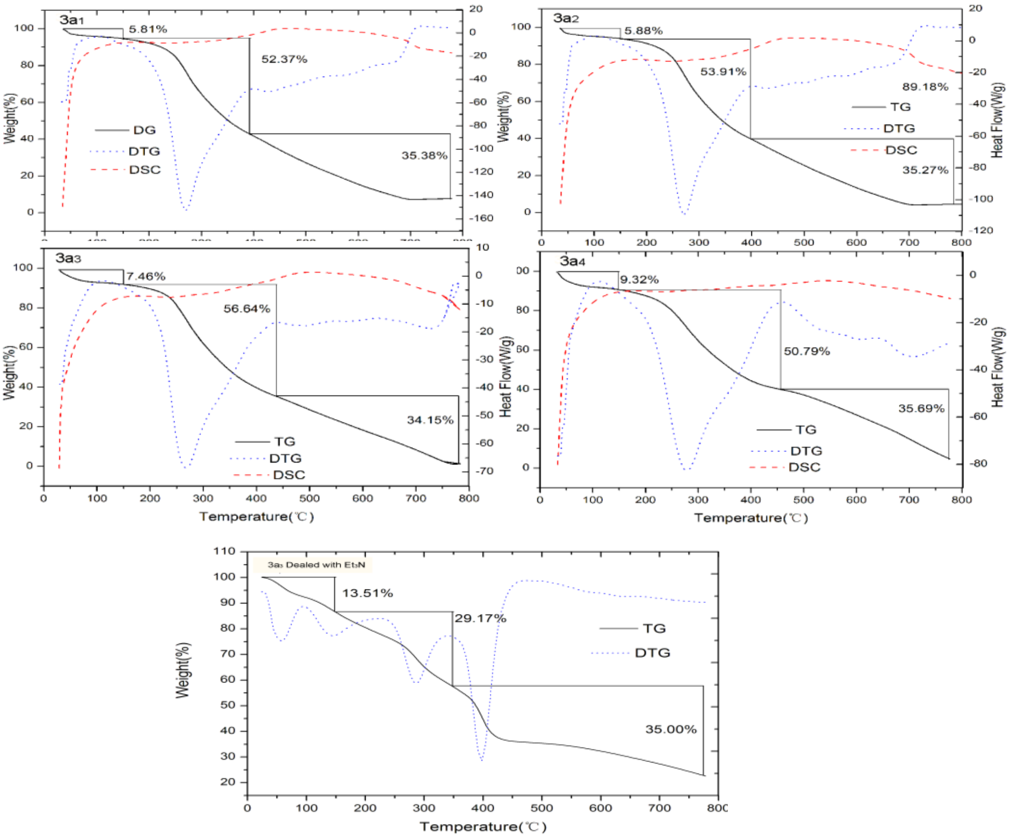
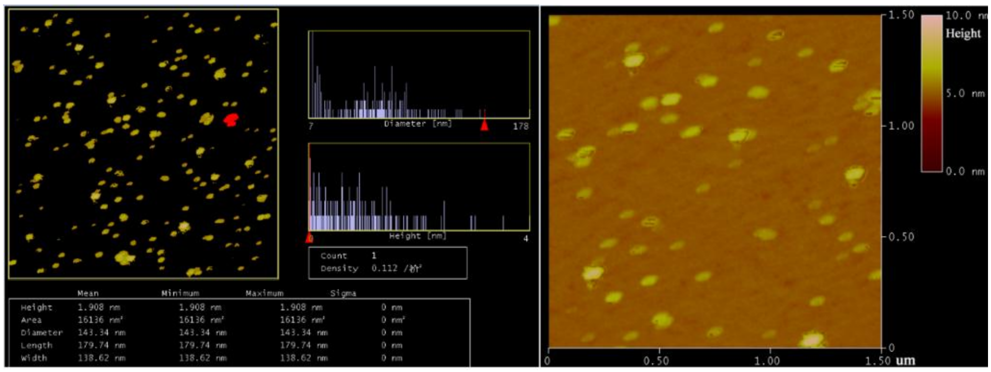


Fig.S9. The thermal gravimetric curves of copolymers-supported Ru catalysts **$3a_1$-a_4**

On heating supported Ru catalysts **3a$_1$–a$_4$** as the copolymers **2a$_1$–a$_4$**, the first slope curves of **3a$_1$–a$_4$** below 150 ºC showed that the desorption of the surface-bound or intercalated water in the pores increased from 3.1-3.9 to 5.8-9.3 wt%. Furthermore, the total weight losses of **3a$_1$–a$_4$** in the temperature range of 150-800 ºC also increased from 58.7-75.0 to 86.5-90.8 wt%.

(4) Surface morphology



Count 1
Density 0.112 /[illegible]

	Mean	Minimum	Maximum	Sigma
Height	1.908 nm	1.908 nm	1.908 nm	0 nm
Area	16136 nm²	16136 nm²	16136 nm²	0 nm²
Diameter	143.34 nm	143.34 nm	143.34 nm	0 nm
Length	179.74 nm	179.74 nm	179.74 nm	0 nm
Width	138.62 nm	138.62 nm	138.62 nm	0 nm

Fig.S10-1. The AFM images of the copolymer **3a$_3$**

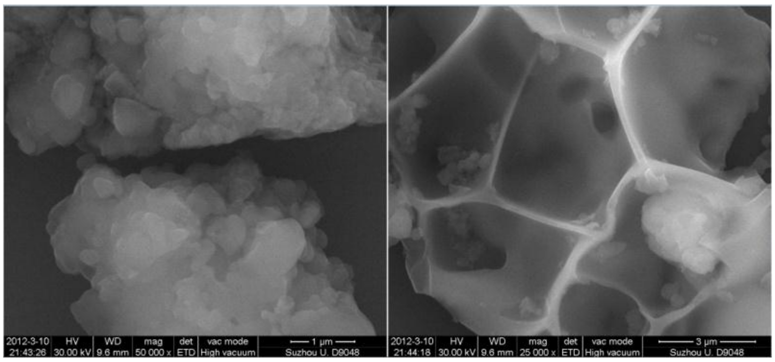
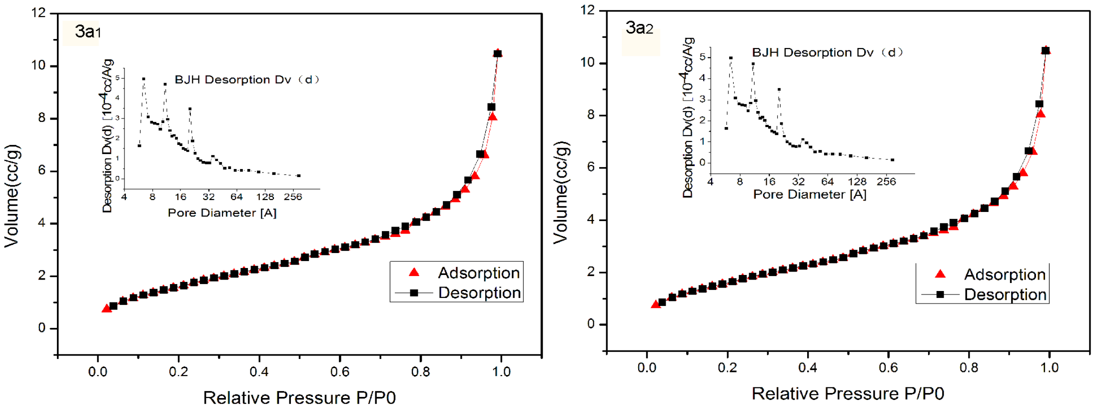


Fig.S10-2. The SEM images of the copolymer **3a$_3$**

As an example, the copolymer-supported Ru catalyst **3a$_3$** was well clarified by AFM (**Fig.S10-1**) and SEM (**Fig.S10-2**) to understand the surface morphology and particle size. After being well-dispersed in water, it can be seen that the mean width and height of supported Ru catalyst **3a$_3$** increased from 112.5 and 0.58 nm to 138.6 and 1.9 nm respectively, compared with copolymer support **2a$_3$**. However, its mean length decreased from 390.1 to 179.7nm. The SEM images showed the powder **2a$_3$** dispersed in THF consisted of primary particles of approximately 1-8 um in size, which mirrored surface morphology of **2a$_3$** in poor solvent.

(5) Porous structure



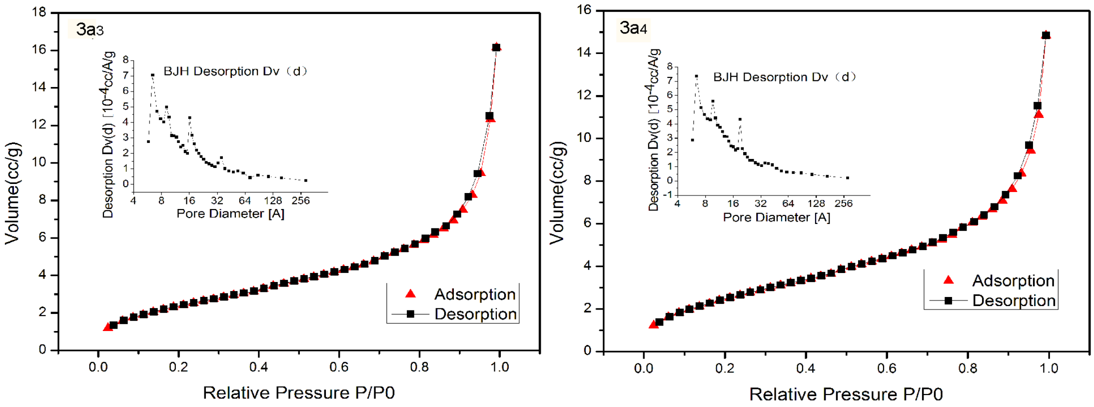
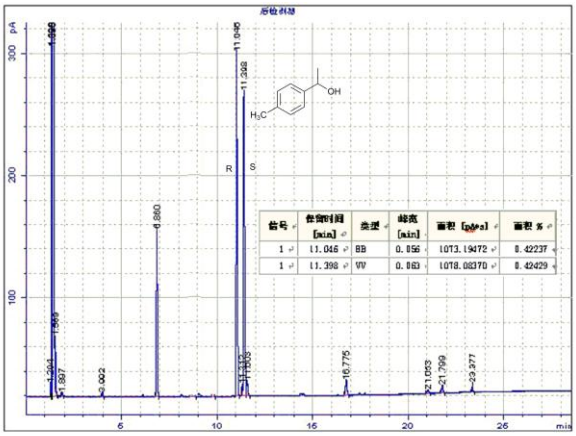


Fig.S11. Nitrogen adsorption–desorption isotherm plots obtained with **$3a_1$–a_4**

Upon the immobilization of [$RuCl_2$(*p*-cymene)]$_2$ into polystyrene copolymers **$2a_1$-a_4**, some nanopores in the range of 0.8-8 nm disappeared, especially at about 6.4 nm, which demonstrated that [$RuCl_2$(p-cymene)]$_2$ particles had been trapped inside those nanopores. It was particularly worth noting that four typical nanopores inside **$2a_1$-a_4** at about 0.6-0.7, 1.0-1.3, 1.8-2.4 and 3.2-4.0 nm were reconstructed. Those nanopores beneficially provided the diffusional channels for substrates to smoothly access the catalytic sites of the trapped Ru(p-cymene) in the catalytic process.

4.4 Asymmetric transfer hydrogenation in water

A dried flask (25 mL) containing **$3a_3$** (1.4 wt%, 15.0 mg, 2.1×10^{-3} mmol) was added 0.5 mL of HCO_2H/Et_3N (HCO_2H/Et_3N, *v/v*=1:3), 0.5 mL of H_2O and 0.1 mL of acetophenone (120.0 mg, 1.0 mmol), slowly heated to 50°C and stirred for 6 h (catalyst **$3a_3$** was well-dispered during the reaction process). The reaction mixture was centrifugated, the catalyst **$3a_3$** was recovered in quatitative yield. The conversion and chemoselectivity of acetophenone, and enantioselectivity of (R) or (S)-1-phenylethanol in the upper organic phase was directly determined on an Agilent 6820 gas chromatograph (USA) using a Chiral Cyclodex-B capillary column (30 m× 0.25 nm×0.25 um, Supelco). Temperature program: 100 ºC, 5 min, 5 ºC·min^{-1};140 ºC,15 min. The retention times of (R) or (S)-1-phenylethanol were t_R=8.95 min and t_S=9.26 min respectively. The other derivatives were shown as follows:



峰号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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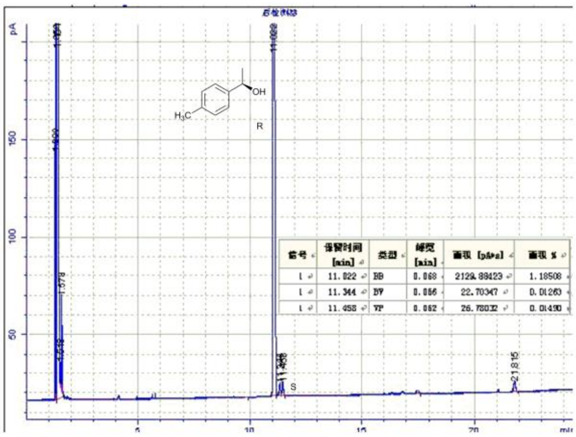
1	11.398	VV	0.063	1078.08370	0.42429



峰号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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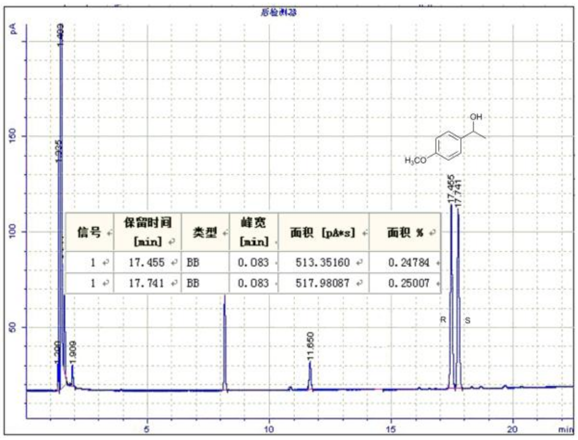
1	11.344	BV	0.066	22.70347	0.01263
1	11.458	VP	0.062	26.78032	0.01490



信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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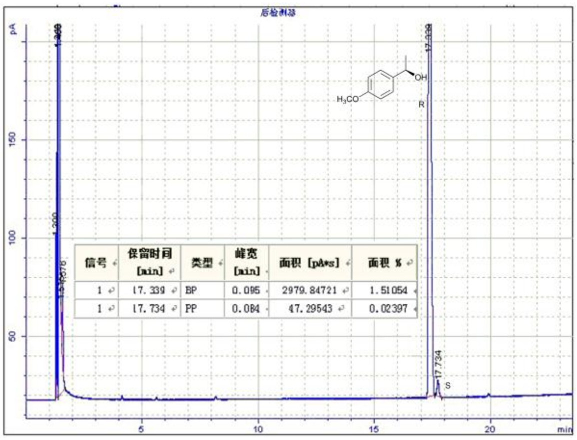
1	17.741	BB	0.083	517.98087	0.25007



信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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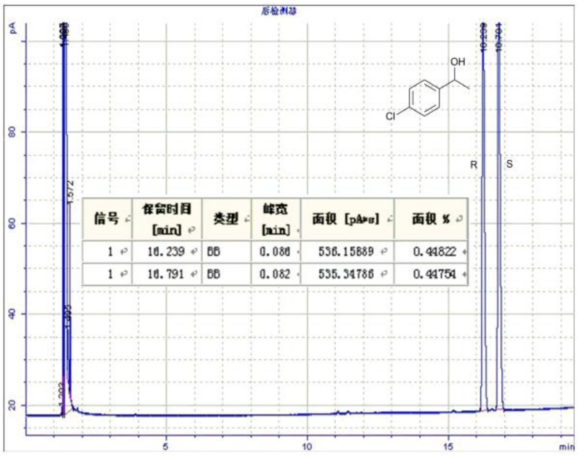
1	17.734	PP	0.084	47.29543	0.02397



信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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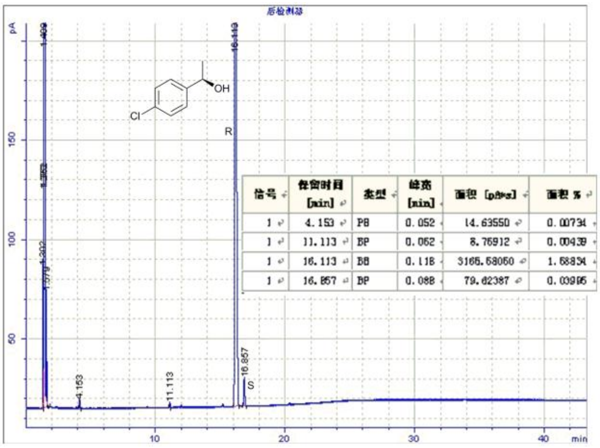
1	16.791	BB	0.082	535.34786	0.44754



信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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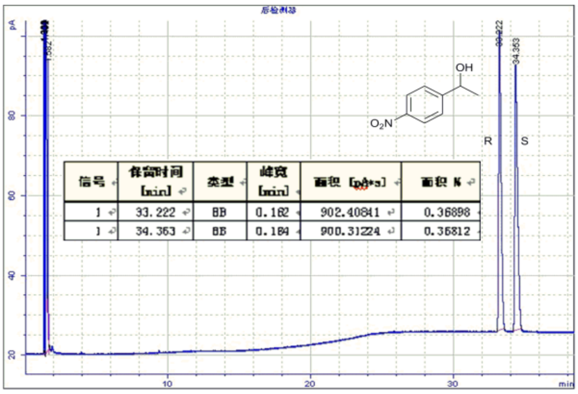
1	11.113	BP	0.062	8.76912	0.00439
1	16.113	BB	0.118	3166.58060	1.58834
1	16.857	BP	0.088	79.62387	0.03995



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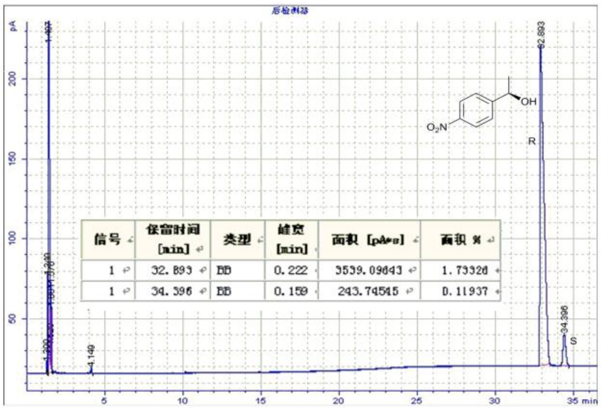

信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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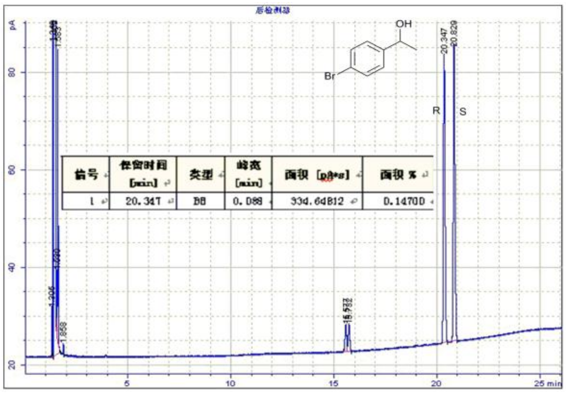

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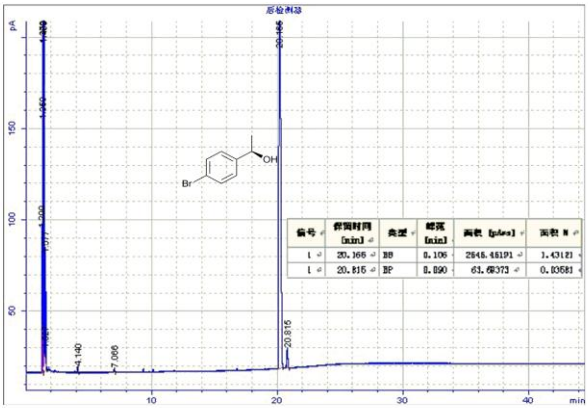

信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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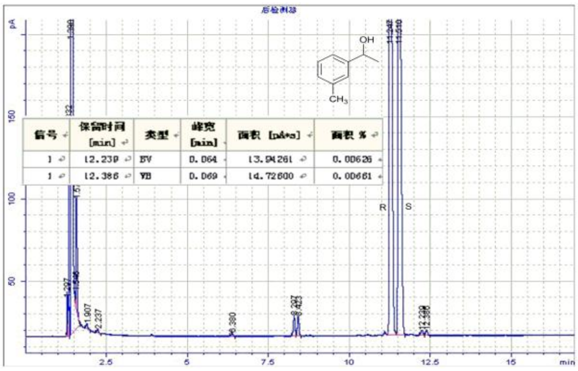
1	20.816	BP	0.090	61.69373	0.03581



信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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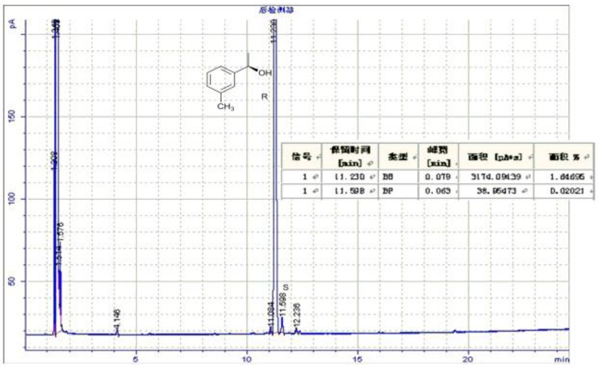

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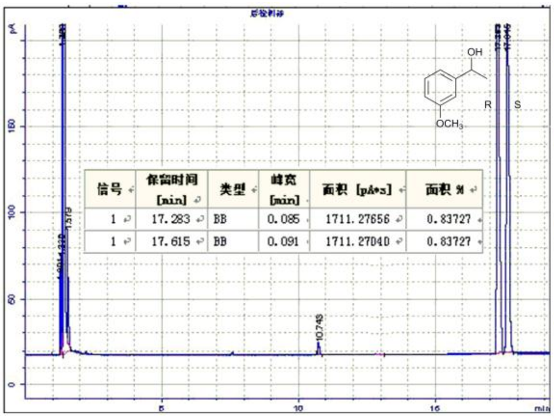

信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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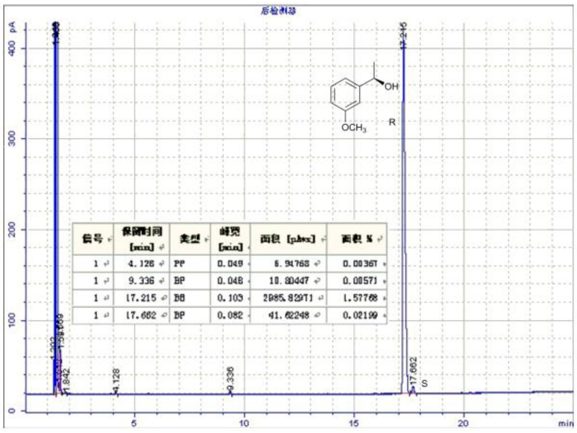

信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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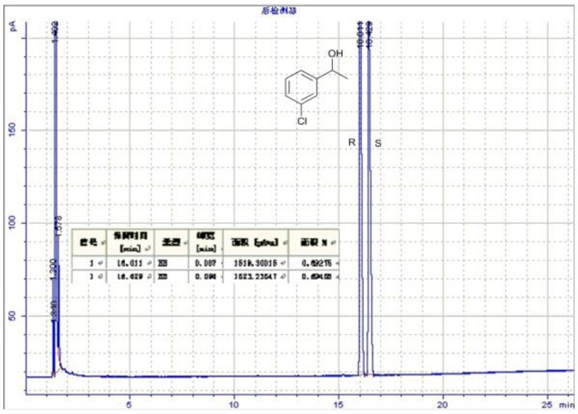
1	9.336	BP	0.048	10.80447	0.00571
1	17.215	BB	0.103	2985.82971	1.57768
1	17.662	BP	0.082	41.62248	0.02199



信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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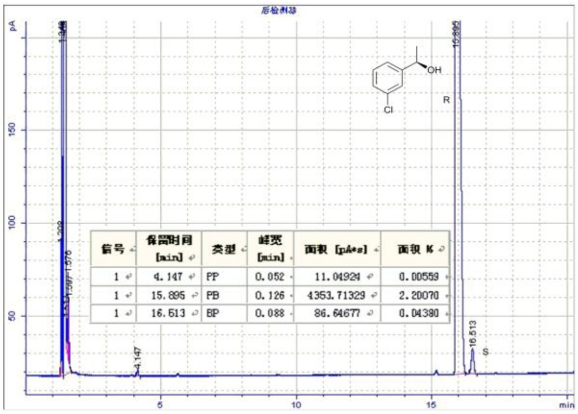

信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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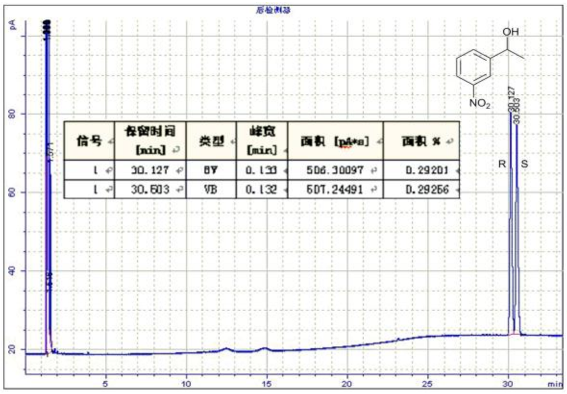
1	15.895	PB	0.126	4353.71329	2.20070
1	16.513	BP	0.088	86.64677	0.04380



信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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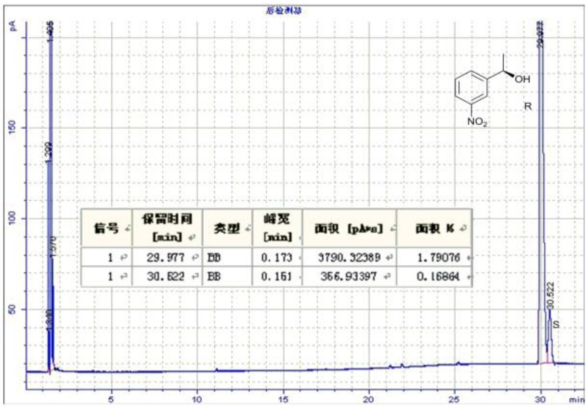
1	30.603	VB	0.132	507.24491	0.29256



信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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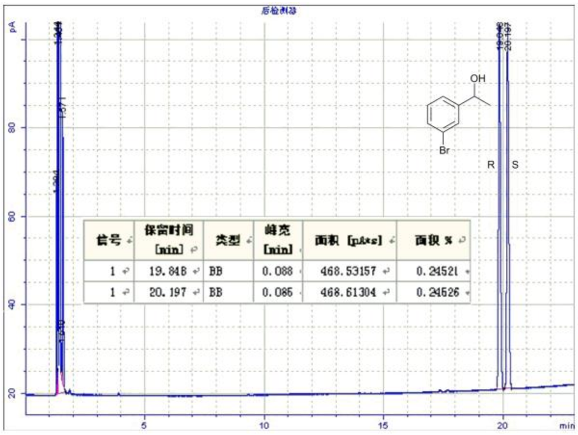
1	30.622	BB	0.161	356.93397	0.16864



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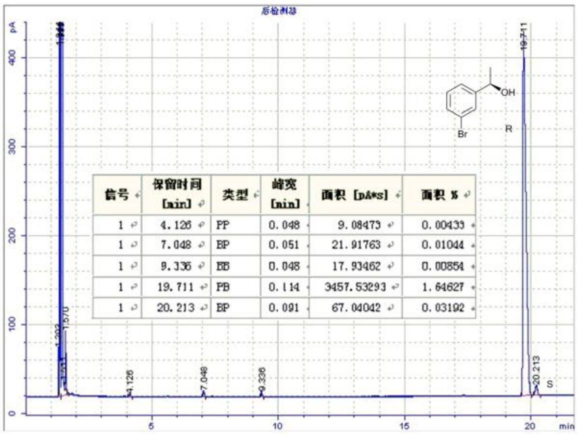

信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
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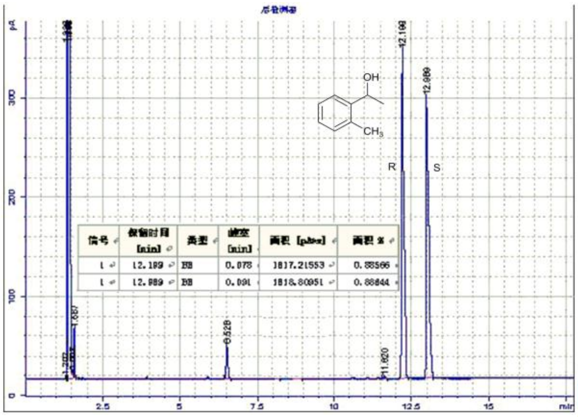
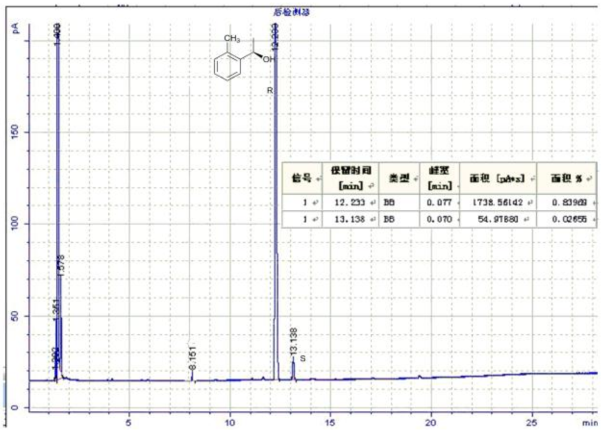
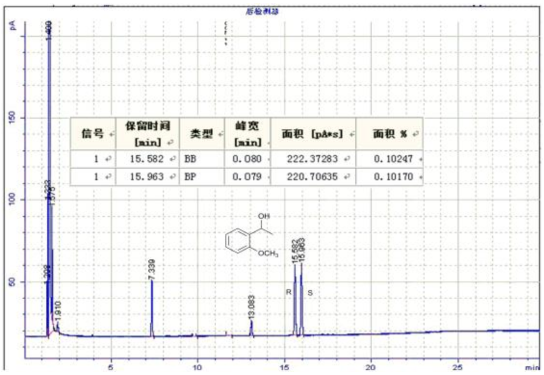
1	7.048	BP	0.051	21.91763	0.01044
1	9.336	BB	0.048	17.93462	0.00854
1	19.711	PB	0.114	3457.53293	1.64627
1	20.213	BP	0.091	67.04042	0.03192



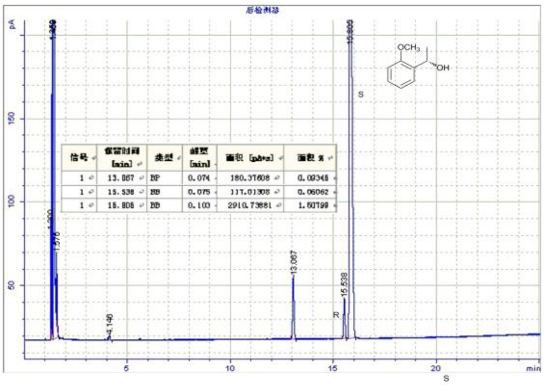
信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
1	12.189	BB	0.078	1817.21553	0.88566
1	12.989	BB	0.091	1818.80951	0.88844



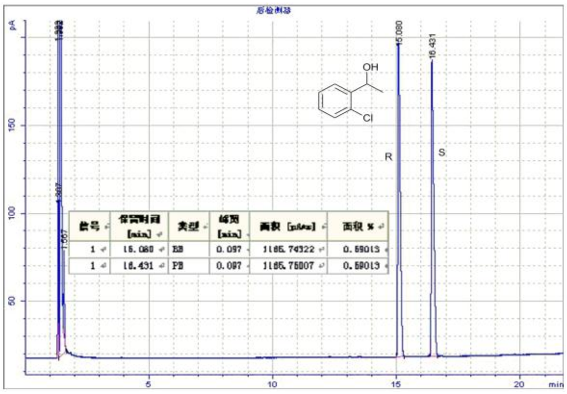
信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
1	12.233	BB	0.077	1738.56142	0.83969
1	13.138	BB	0.070	54.97880	0.02656



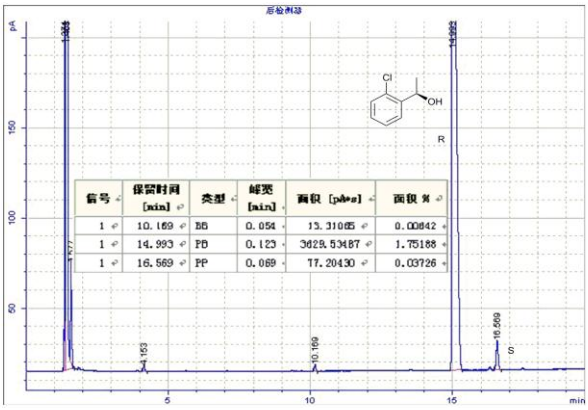
信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
1	15.582	BB	0.080	222.37283	0.10247
1	15.963	BP	0.079	220.70635	0.10170



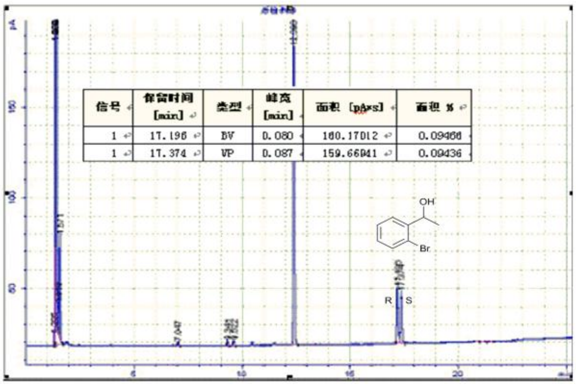
信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
1	13.067	BP	0.074	180.37608	0.09345
1	15.538	BB	0.075	117.01308	0.06062
1	15.806	BB	0.103	2910.73881	1.60799



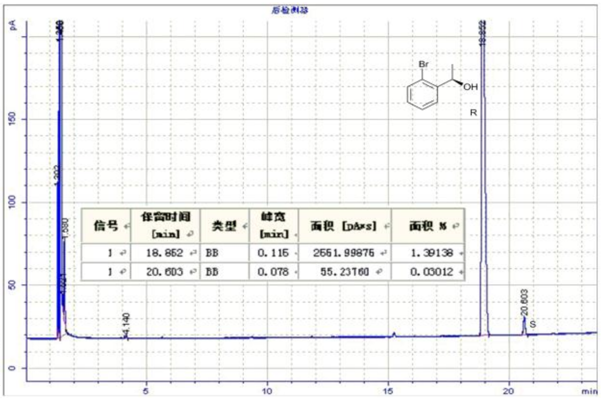
信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
1	15.080	BB	0.097	1165.74322	0.59013
1	16.431	PB	0.097	1165.75807	0.59013



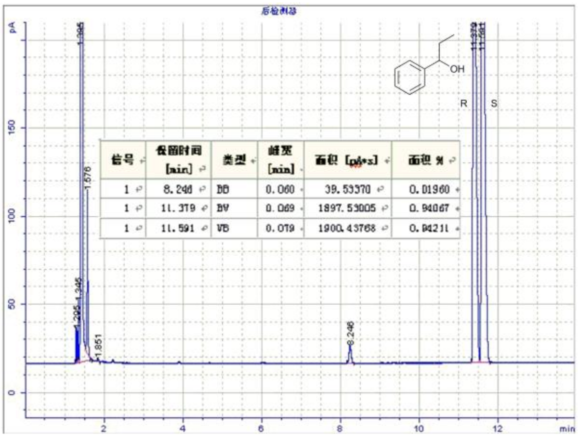
信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
1	10.169	BB	0.054	13.31065	0.00642
1	14.993	PB	0.123	3629.53487	1.75188
1	16.569	PP	0.069	77.20430	0.03726



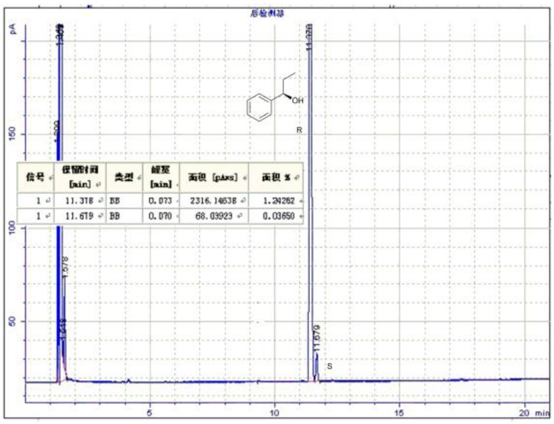
信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
1	17.196	BV	0.080	160.17012	0.09466
1	17.374	VP	0.087	159.66941	0.09436



信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
1	18.852	BB	0.115	2551.99876	1.39138
1	20.603	BB	0.078	55.23760	0.03012



信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
1	8.246	BB	0.060	39.53370	0.01960
1	11.379	BV	0.069	1897.53005	0.94067
1	11.591	VB	0.079	1900.43768	0.94211



信号	保留时间 [min]	类型	峰宽 [min]	面积 [pA*s]	面积 %
1	11.318	BB	0.073	2316.14638	1.24262
1	11.679	BB	0.070	68.03923	0.03650

5. Reuse of copolymer-supported Ru catalyst

Catalyst **3a$_3$** could be easily and quantitatively recycled by centrifugal separation, dried in reduced pressure and reused. The conversion and enantioselectivity of each reaction (5 runs) were shown in the following Table 3.

Table 3. The conversion and enantioselectivity of in each reused reaction[a]

Run	Cat.	S/C	Solvent	Conv.(%) [b]	Yield (%)[c]	(%ee) [d]
1	**3a$_3$(3a)**	660	H_2O	100	98	97.2 (R)
2			H_2O	97	95	96.8 (R)
3			H_2O	98	96	97.0 (R)
4			H_2O	95	92	96.5 (R)
5			H_2O	90	86	96.6 (R)

[a] Reaction conditions: (1.5 wt% Ru, 9 mg, 1.3×10^{-3} mmol), acetophenone (0.1 mL, 0.86 mmol), HCO_2H/Et_3N (0.5 mL, *v*/*v*=1:3), 50 °C, 6 h. [b] Monitored by GC. [c] Isolated yield. [d] Determined by chrial GC, Chiral Cyclodex-B (30 m× 0.25 nm×0.25 μm, Supelco). [d] *v*/*v*=1:1.