

Electronic Supplementary Information

Porous Brønsted Superacid as an Efficient and Durable Solid Catalyst

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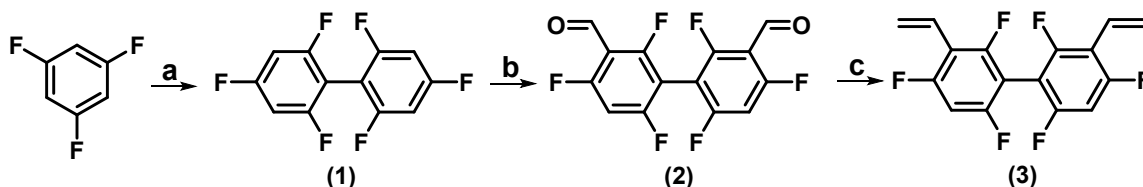
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Material synthesis

Synthesis of vinyl-functionalized hexafluorobiphenyl



Reagents: (a) *n*-BuLi, CuCl₂; (b) *n*-BuLi, DMF; (c) PPh₃CH₃I, (CH₃)₃COK

2,2',4,4',6,6'-hexafluorobiphenyl (1): To an anhydrous THF (200 mL) solution of 1,3,5-trifluorobenzene (6.92 g, 52.4 mmol), *n*-butyllithium in hexane (2.5 M, 21 mL, 52.5 mmol) was added dropwise at 0 °C under N₂ atmosphere. After 3 h, anhydrous copper chloride (14.6 g, 109 mmol) was added in portion and the resulting mixture was stirred at room temperature overnight. After that, the reaction was quenched by diluted H₂SO₄ and the resulting mixture was extracted with ether, washed with brine, and evaporated under reduced pressure, giving the crude compound which was purified by flash chromatography using hexane as eluent to afford the title product as a white powder (2.35 g, 34 %). ¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ 6.78-6.82 (m, 4H) ppm.

2,2',4,4',6,6'-hexafluoro-[1,1'-biphenyl]-3,3'-dicarbaldehyde (2): To an anhydrous THF (100 mL) solution of **1** (2.62 g, 10 mmol), *n*-butyllithium in hexane (2.5 M, 8.8 mL, 22 mmol) was added dropwise at 0 °C under N₂ atmosphere. After one hour, DMF (3 mL) was added and the resulting mixture was stirred overnight at room temperature. The reaction was quenched by the addition of an excess of NH₄Cl solution and the mixture was extracted twice by ethyl acetate. The combined organic phase was washed with brine, dried over MgSO₄, and concentrated to give the crude product which was purified by flash chromatography using hexane/ethyl acetate (V/V = 10/1) as eluent, giving **2** as a light yellow solid (2.04 g, 64%). ¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ 10.31 (s, 2H), 6.98 (t, 2H, *J* = 8.8 Hz) ppm.

2,2',4,4',6,6'-hexafluoro-3,3'-divinyl-1,1'-biphenyl (3): Methyltriphenylphosphonium iodide (8.08 g, 20 mmol) was added to a suspension of (CH₃)₃COK (2.46 g, 22 mmol) in THF (50 mL) under N₂ atmosphere at room temperature. After 0.5 h, THF solution (10 mL) of **2** (1.57 g, 5 mmol) was added and the mixture was stirred overnight. After the reaction was quenched by the addition of NH₄Cl solution, the resulting mixture was extracted with an excess of ether, washed with brine, dried over MgSO₄, and evaporated. The residue was purified by flash chromatography using hexane as eluent to afford **3** as a white solid (1.22 g, 78%). ¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ 6.79-6.84 (m, 2H), 6.64-6.71 (m, 2H), 6.02 (d, 2H, *J* = 18 Hz), 5.61 (d, 1H, *J* = 12 Hz) ppm. ¹⁹F NMR

(376 MHz, CDCl₃) δ -109.3, -109.38, -109.39, -110.57, -110.58 ppm. A very low intensity of ¹³C NMR signals in the title compound was observed due to the following reasons: a) the signals split as a result of the existence of the F species; and b) the quaternary carbons do not enjoy the large Overhauser enhancement by proton decoupling as the CH carbons do.

Synthesis of fluorinated porous polymer (FPOP)

1.0 g of **3** was dissolved in 10 mL of THF, followed by addition of 25 mg of azobisisobutyronitrile (AIBN). The mixture was transferred into an autoclave at 100 °C for 24 h. The title material was obtained after being washed with CH₂Cl₂ and dried under vacuum.

Synthesis of sulfonated FPOP (FPOP-SO₃H)

Fuming sulfonic acid (20%, 40 mL) was added dropwise to a 100 mL flask containing 500 mg of FPOP. The mixture was stirred at room temperature for 48 h, and then 50 °C for another 48 h, after which the mixture was poured into ice water and washed with an excess of water until the pH of the filtration tuned to around 7.

Synthesis of 4,4'-divinyl-1,1'-biphenyl

4,4'-dibromo-1,1'-biphenyl (3.09 g, 10 mmol), potassium vinyltrifluoroborate (3.22 g, 24 mmol), K₂CO₃ (4.14 g, 30 mmol), and Pd(PPh₃)₄ (0.22 g, 0.2 mmol) were dissolved in a mixture of toluene (25 mL), THF (25 mL) and H₂O (5 mL) and the resulting mixture was refluxed at 90 °C under N₂ atmosphere for 24 h. The residue was extracted with ethyl acetate, washed with brine, dried over Na₂SO₄, and evaporated under reduced pressure, giving the crude compound which was purified by flash chromatography with hexane as eluent to afford the title compound as a white solid (1.75 g, 85%). ¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ 7.46-7.58 (m, 8H), 6.72-6.79 (m, 2H), 5.79 (d, 2H, *J*=17.6 Hz), 6.02 (d, 2H, *J*=16.0 Hz), 5.27 (d, 2H, *J*=10.8 Hz) ppm.

Synthesis of polymerized 4,4'-divinyl-1,1'-biphenyl

1.0 g of 4,4'-divinyl-1,1'-biphenyl was dissolved in 10 mL of THF, followed by addition of 25 mg of AIBN. The mixture was transferred into an autoclave at 100 °C for 24 h. The title material was obtained after being washed with CH₂Cl₂ and dried under vacuum.

Synthesis of sulfonated polymerized 4,4'-divinyl-1,1'-biphenyl (POP-SO₃H)

Concentrated sulfonic acid (40 mL) was added dropwise to a 100 mL flask containing 500 mg of polymer. The mixture was stirred at room temperature for 48 h, and then 50 °C for another 48 h, after which the mixture was poured into ice water and washed with an excess of water until the pH of the filtration tuned to around 7.

Catalytic tests

Esterification of palmitic acid with ethanol: the reactions were carried out in a 50 mL Schlenk flask with a magnetic stirrer. As a typical run, palmitic acid (0.513 g, 2 mmol), ethanol (2.0 mL), internal standard (dodecane), and catalyst listed in Figure 3 (containing 0.04 mmol of accessible H⁺ ions) were transferred into the reactor. The tube was placed in a preheated oil bath and stirred for a desired time. After a predetermined period of time, ethyl acetate (20 mL) was added and the solid catalyst was taken out from the system by centrifugation. The yield of ethyl laurate was analyzed by gas chromatography (Kexiao gas chromatography equipped with a flame ionization detector and a HP-INNOWax capillary column) and calculated based upon the amount of palmitic acid. For recycling the catalysts, they were separated by centrifugation, washed with ethanol (5×5 mL) and used directly for the next run without drying.

Turnover frequencies were calculated using the first time point for each run and the equation:

$$\text{TOF} = (\text{moles of product})/(\text{moles of H}^+ \times \text{amount of time})$$

Friedel-Crafts acylation: In a typical run, benzoyl chloride (2 mmol, 0.28 g), anisole (1.0 g), internal standard (dodecane), and catalyst listed in Table 1 (containing 0.04 mmol of accessible H⁺ ions) were stirred in a flask equipped with a condenser at 100 °C. After a predetermined period of time, ethyl acetate (20 mL) was introduced and the solid catalyst was taken out from the system by centrifugation. The yields of various products were analyzed by gas chromatography as described above and calculated based upon the amount of benzoyl chloride. For recycling the catalysts, they were separated by centrifugation, washed with anisole (5×5 mL), and used directly for the next run without drying.

The conversion of the reaction was calculated based upon benzoyl chloride which was defined as follows:

$$\text{conversion} = \text{moles of benzoyl chloride left} / \text{moles of starting benzoyl chloride}$$

The selectivity of the reaction was defined as follows:

$$\text{selectivity} = \text{moles of product A} / \text{moles of starting benzoyl chloride}$$

Friedel-Crafts alkylation: In a typical run, benzyl alcohol (0.216 g, 2 mmol), toluene (10.0 mL), internal standard (dodecane), and catalyst listed in Table 2 (containing 0.04 mmol of accessible H⁺ ions) were stirred in a Schlenk tube at 80 °C. After a predetermined period of time, ethyl acetate (20 mL) was added and the catalyst was taken out from the system by centrifugation. The yields were analyzed by gas chromatography as described above and calculated based upon the amount of benzyl alcohol. For

recycling the catalysts, they were separated by centrifugation, washed with toluene (5×5mL) and used directly for the next run without drying.

The conversion of the reaction was calculated based upon benzyl alcohol which was defined as follows:

conversion = moles of benzyl alcohol left/ moles of starting benzyl alcohol

The selectivity of the reaction was defined as follows:

selectivity = moles of product A/ moles of starting benzyl alcohol

Detailed procedures for catalytic experiments carried out using a fixed-bed reactor:

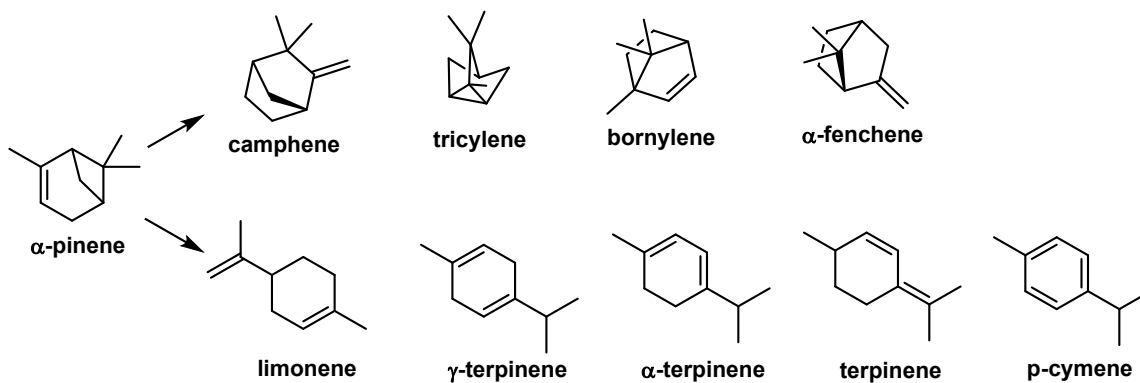
The reactions for benzylation of benzene with benzyl alcohol were carried out in a fixed-bed reactor homemade by a stainless steel tube with 10 mm inner diameter and 530 mm length. The reactor was heated by a high temperature furnace with three-section automatic controller. FPOP-SO₃H, POP-SO₃H, and Amberlyst-15 (50 mg) or Nafion® NR50 (300 mg) mixed with 1.0 g quartz sand (20~40 mesh) was filled into the reactor between quartz wool plugs. Before reaction, all catalysts were in-situ activated by heating at 100 °C for 5 h in air. Then, the temperature of the reaction system was decreased to the desired reaction temperature. Meanwhile, N₂ with a flow rate of 10 mL min⁻¹ was introduced into the system to replace air. The mixture of benzene and benzoyl alcohol (their molar ratio is 80) was fed by a HPLC pump (Series 1, Lab Alliance) with a liquid rate of 0.06 mL min⁻¹. The reactions were carried out under atmospheric pressure. Liquid samples were withdrawn at regular intervals from the storage silo. The products were analyzed by gas chromatography on an Agilent 7890A GC with an FID detector using a 30 m packed HP5 column and identified by GC-MS (5975C-7890A) analysis. Since aromatic reactant was in excess, conversion was calculated based on benzyl alcohol. The selectivity to the product was expressed as the amount of particular product divided by the amount of total products and multiplied by 100. The yield of the product is the conversion multiplied by selectivity. The product amount y (mg) during a period time

$$y = M \times \int_{t_1}^{t_2} f(t) dt$$

was calculated based on the following equation: M stands for the theoretical product amount produced at unit time (mg min⁻¹), (t) stands for the curve of reaction yield (assuming the yield between two monitor points are linear), t stands for the reaction time.

α -Pinene isomerization: Before catalytic tests each catalyst was activated under dynamic vacuum at 80 °C for 10 h. The α -pinene isomerization reactions were carried out in a Pyrex tube measuring o.d. × i.d. = 9.5 × 7.5 mm² loaded with 50 mg of activated catalysts. After adding 1 mL of α -pinene to the tube in a glovebox, the tube was flame sealed and placed in a pre-heated oil bath at 120 °C with stirring. After 2 h, the reaction samples

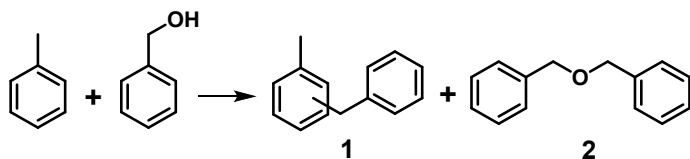
were cooled in an ice bath and diluted by ethyl acetate. The catalyst was taken out from the system by centrifugation and the conversion and selectivity were analyzed by GC-MS Agilent 7890 equipped with a HP-5 capillary column. The quantification using standard internal method was calibrated with the commercially available α -pinene, camphene and limonene. Conversions of α -pinene were calculated by dividing the amount of α -pinene left in the reaction mixture over the initial amount of α -pinene added. Selectivity towards camphene and limonene (Scheme S1) was calculated by dividing the amount of camphene and limonene produced in the reaction mixture over the amount of the α -pinene that had been converted to that time.



Scheme S1 Involved products in α -pinene isomerization.

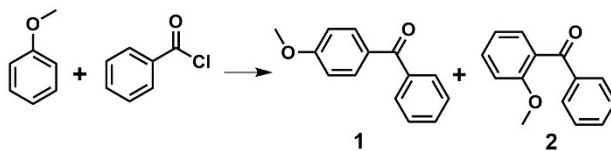
Table S1 Summary of accessible H⁺ ions in various samples.

Sample	H ⁺ ions contents (mmol g ⁻¹)
FPOP-SO ₃ H	3.56
POP-SO ₃ H	3.84
Amberlyst-15	4.70
Nafion [®] NR50	0.89

Table S2 Catalytic data in the Friedel-Crafts alkylation of benzyl alcohol and toluene.^a

Entry	Catalyst	Conv. (%)	Select. (%)	
			1	2
1	FPOP-SO ₃ H	>99.5	76.8	23.2
2	POP-SO ₃ H	80.0	61.7	38.3
3	Amberlyst-15	58.7	65.1	34.9
4	Nafion [®] NR50	49.7	83.4	16.6
5	H ₂ SO ₄	4.1	51.2	48.8

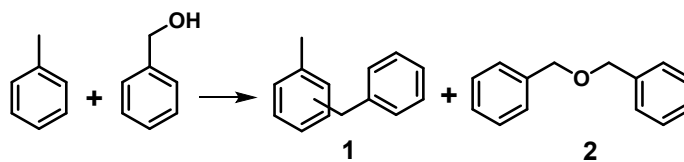
^a Reaction conditions: benzyl alcohol (2.0 mmol), toluene (10 mL), 80 °C, 6 h, catalyst (0.04 mmol accessible H⁺).

Table S3 Recycling tests of FPOP-SO₃H in the Friedel-Crafts acylation of benzoyl chloride and anisole.^a

Recycle times	Conv. (%)	Select. (%)	
		1	2
0	95.3	>99.5	n.d.
1	95.8	>99.5	n.d.
2	94.3	>99.5	n.d.
3	95.0	>99.5	n.d.
4	95.5	>99.5	n.d.
5	95.1	>99.5	n.d.

^a Reaction conditions: benzoyl chloride (2.0 mmol), anisole (1.0 g), 100 °C, 10 h, FPOP-SO₃H (11 mg containing 0.04 mmol accessible H⁺). ^b Not detectable.

Table S4 Recycling tests of FPOP-SO₃H in the Friedel-Crafts alkylation of benzyl alcohol and toluene.^a



Recycle times	Conv. (%)	Select. (%)	
		1	2
0	>99.5	76.8	23.2
1	>99.5	77.2	22.8
2	>99.5	76.9	23.1
3	>99.5	76.5	23.5
4	>99.5	77.8	22.2
5	>99.5	77.3	22.7

^a Reaction conditions: benzyl alcohol (2.0 mmol), toluene (10 mL), 80 °C, 6 h, FPOP-SO₃H (11 mg containing 0.04 mmol accessible H⁺).

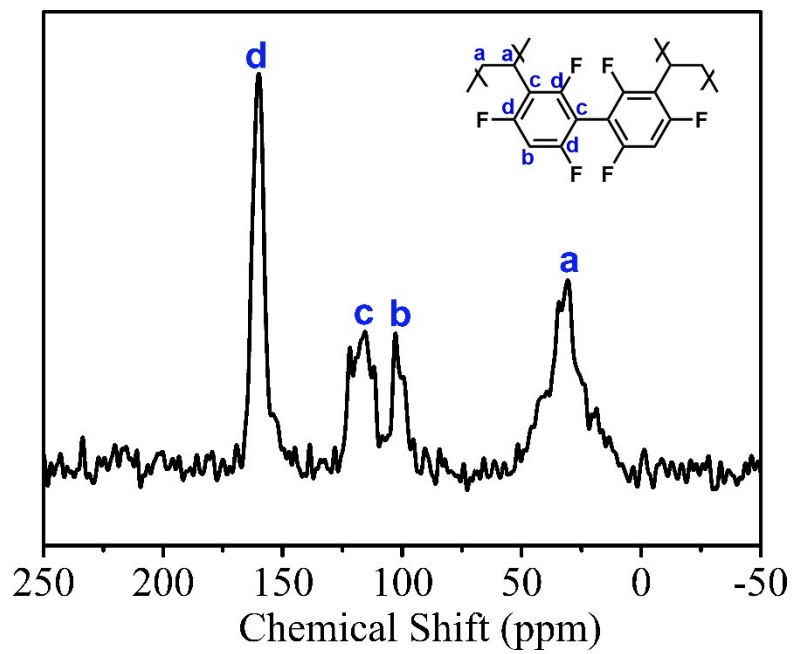


Fig. S1 ^{13}C MAS NMR of FPOP and corresponding peak assignment.

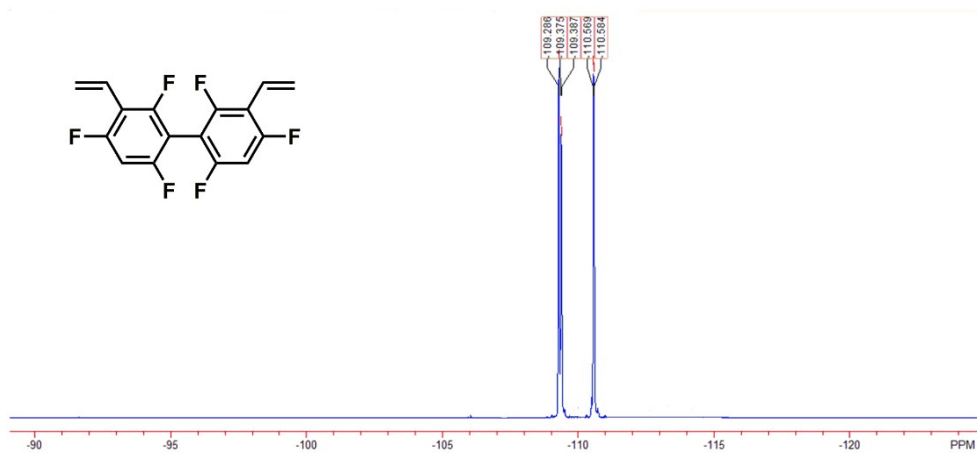
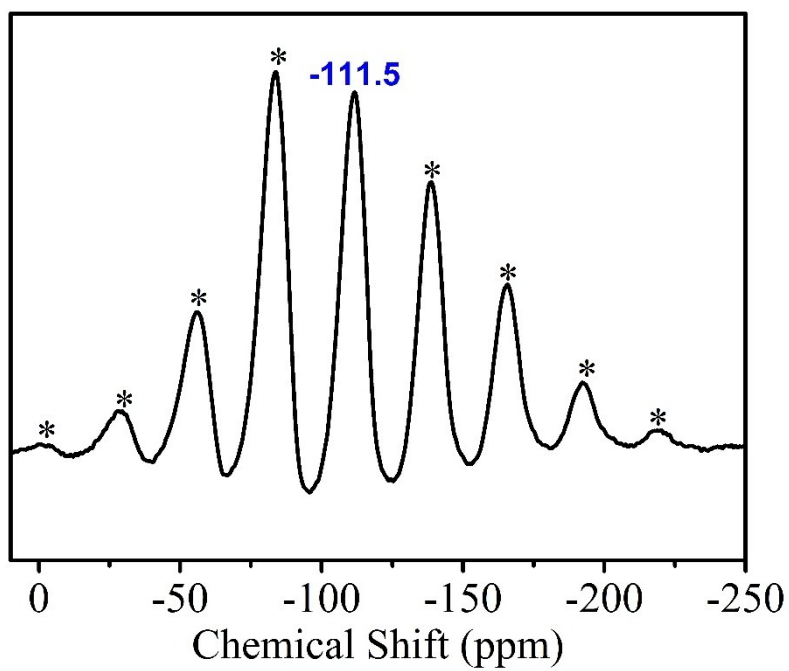


Fig. S2 ^{19}F MAS NMR of FPOP (top) and ^{19}F liquid NMR of corresponding monomer (bottom).

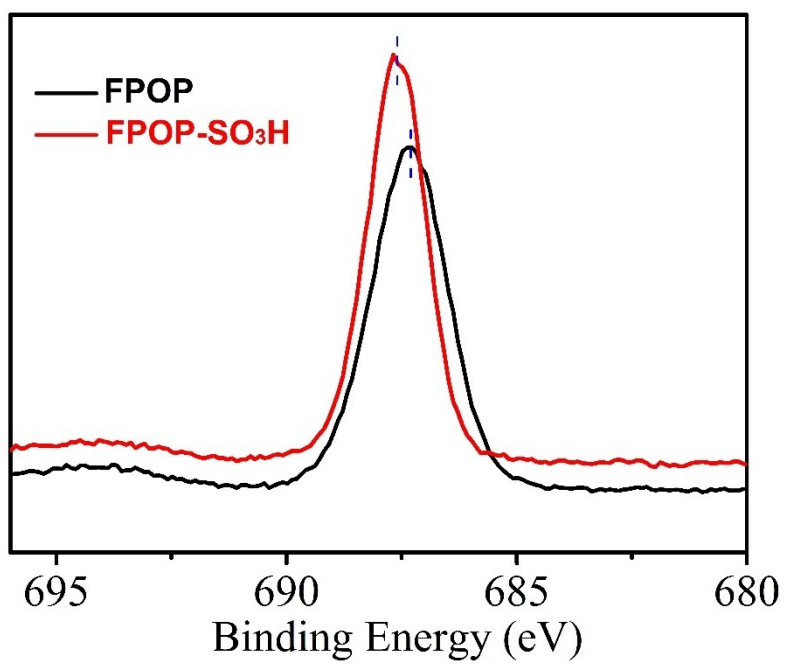
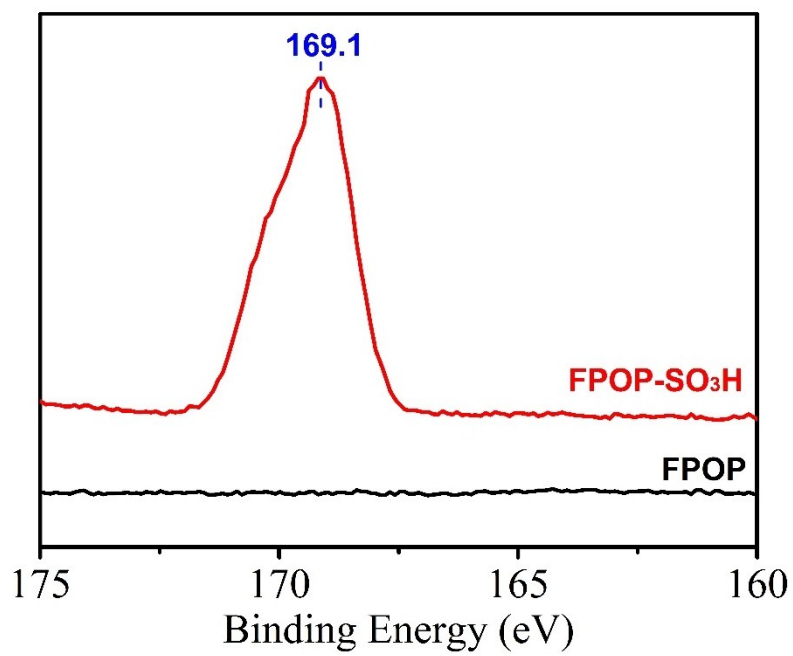


Fig. S3 S2p (top) and F1s (bottom) XPS spectra of FPOP and FPOP-SO₃H.

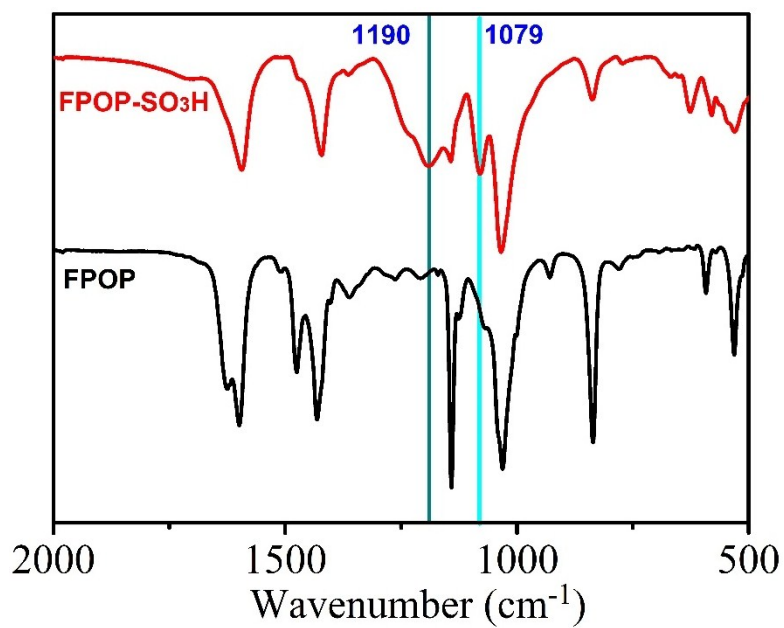


Fig. S4 IR spectra of FPOP and FPOP-SO₃H.

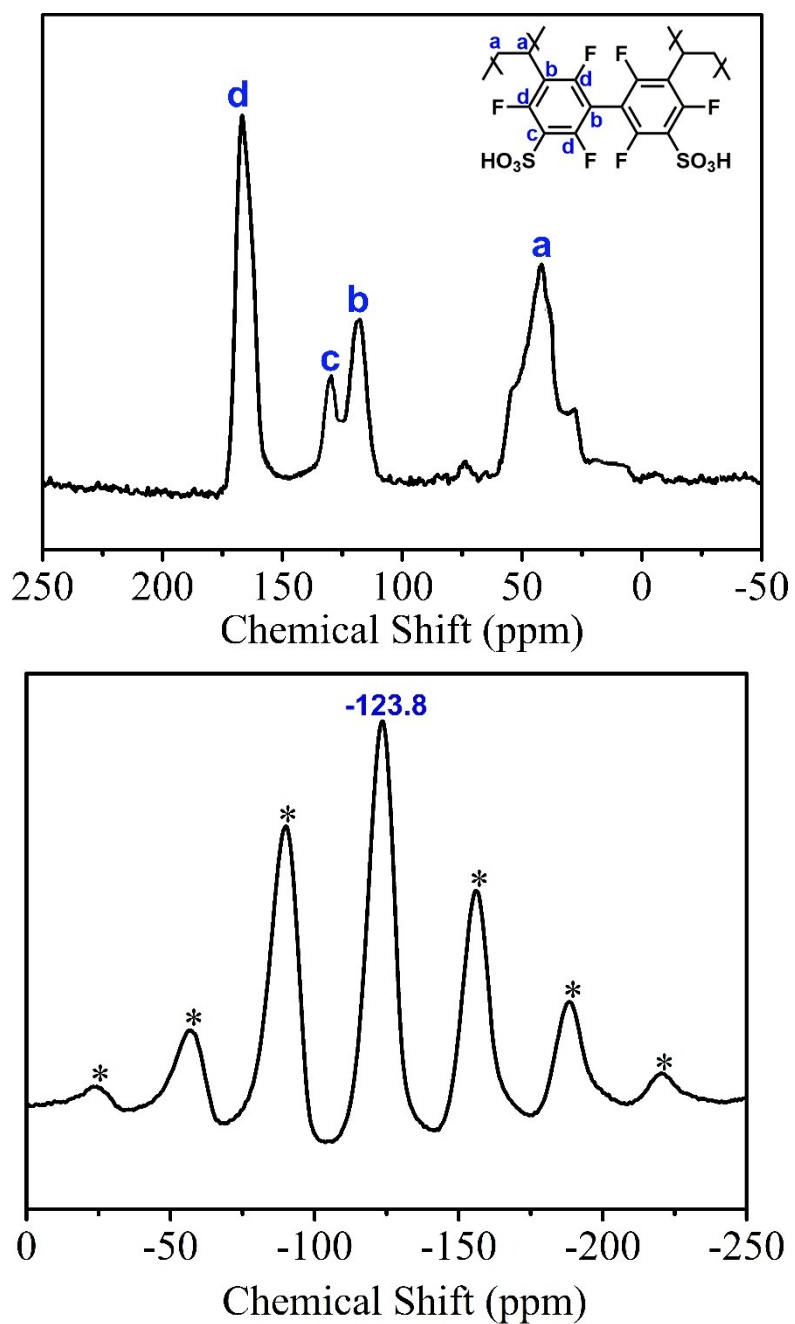


Fig. S5 ¹³C MAS NMR (top) and ¹⁹C MAS NMR (bottom) of FPOP-SO₃H.

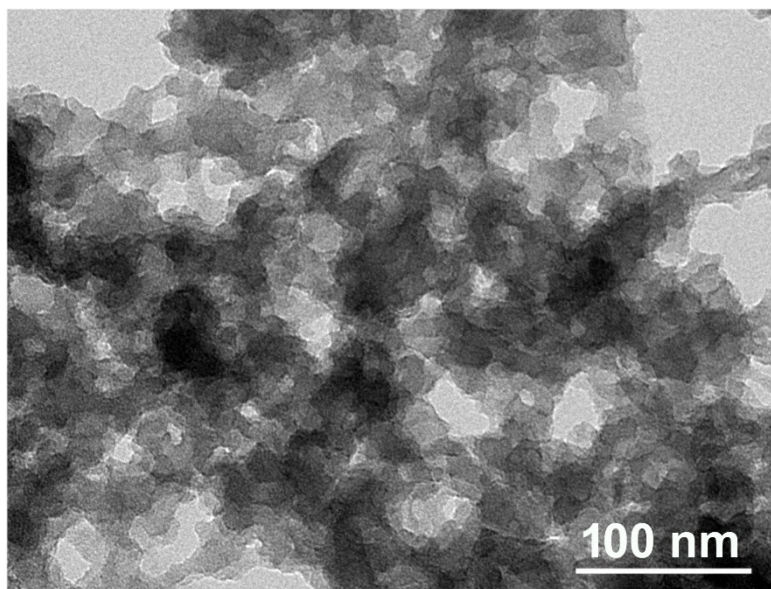
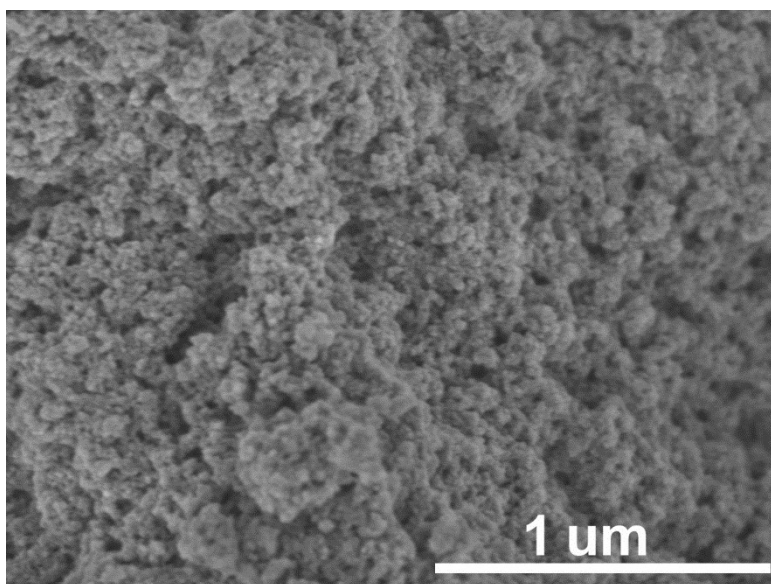


Fig. S6 SEM (top) and TEM (bottom) of FPOP-SO₃H.

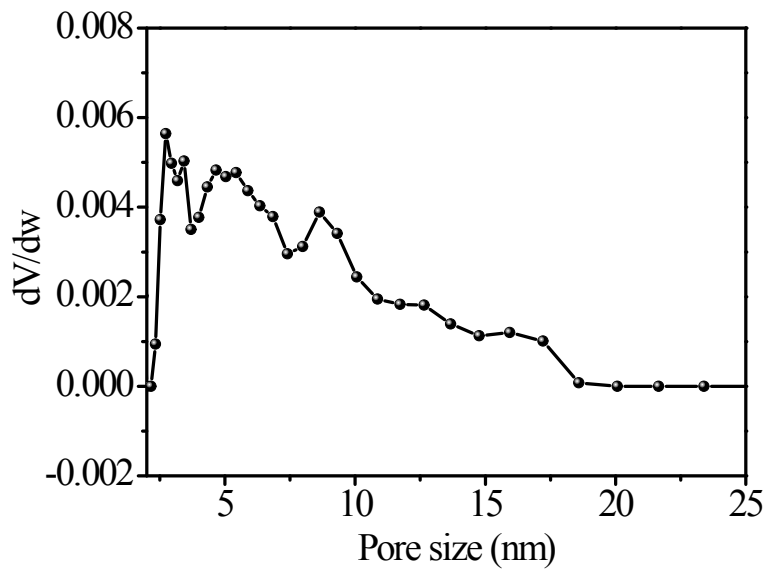


Fig. S7. Pore size distribution of FPOP-SO₃H calculated based upon nonlocal density functional theory.

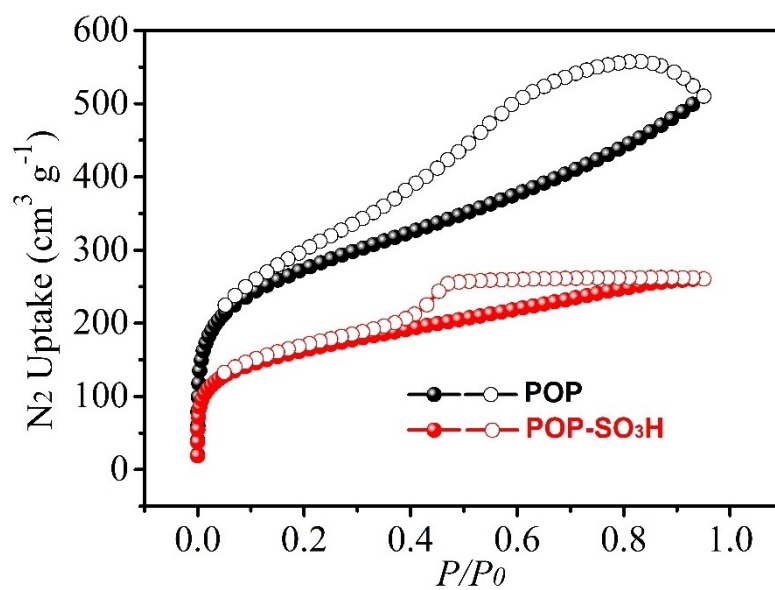


Fig. S8 N₂ sorption isotherms collected at 77 K. The BET surface area of POP and POP-SO₃H were calculated to be 942 cm³ g⁻¹ and 561 cm³ g⁻¹, respectively.

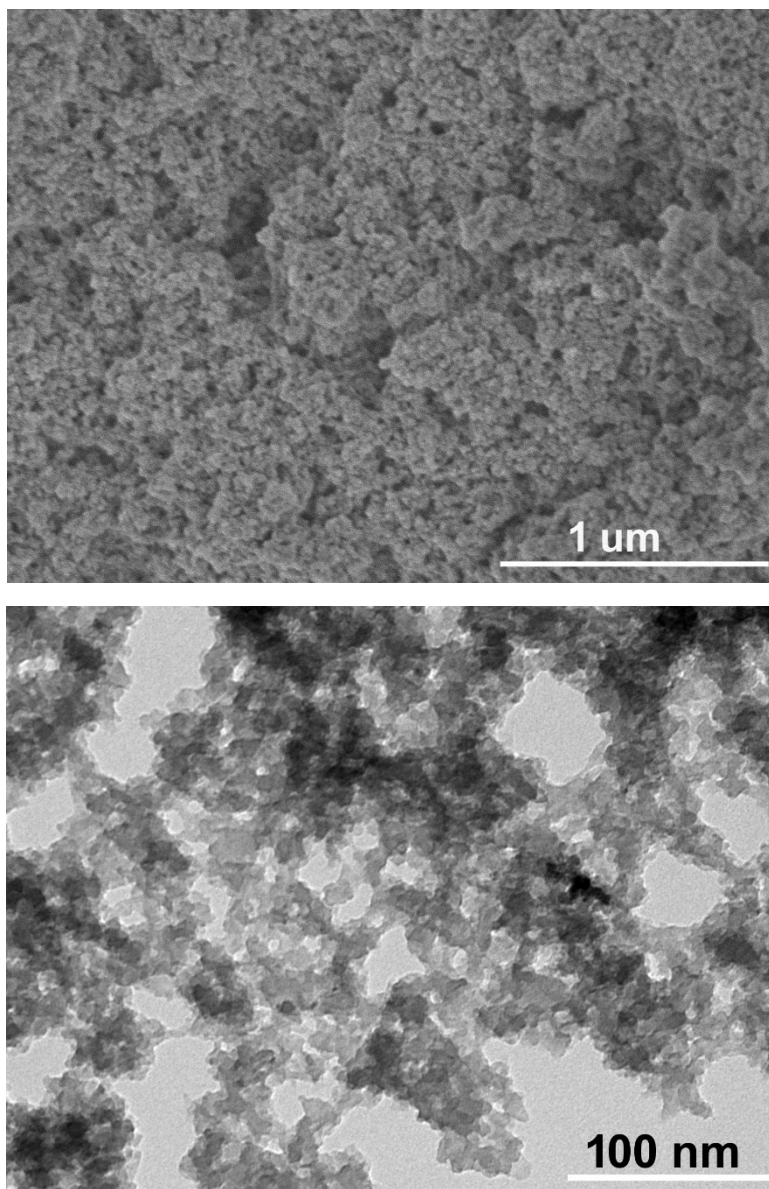


Fig. S9 SEM (top) and TEM (bottom) of polymerized 4,4'-divinyl-1,1'-biphenyl (POP).

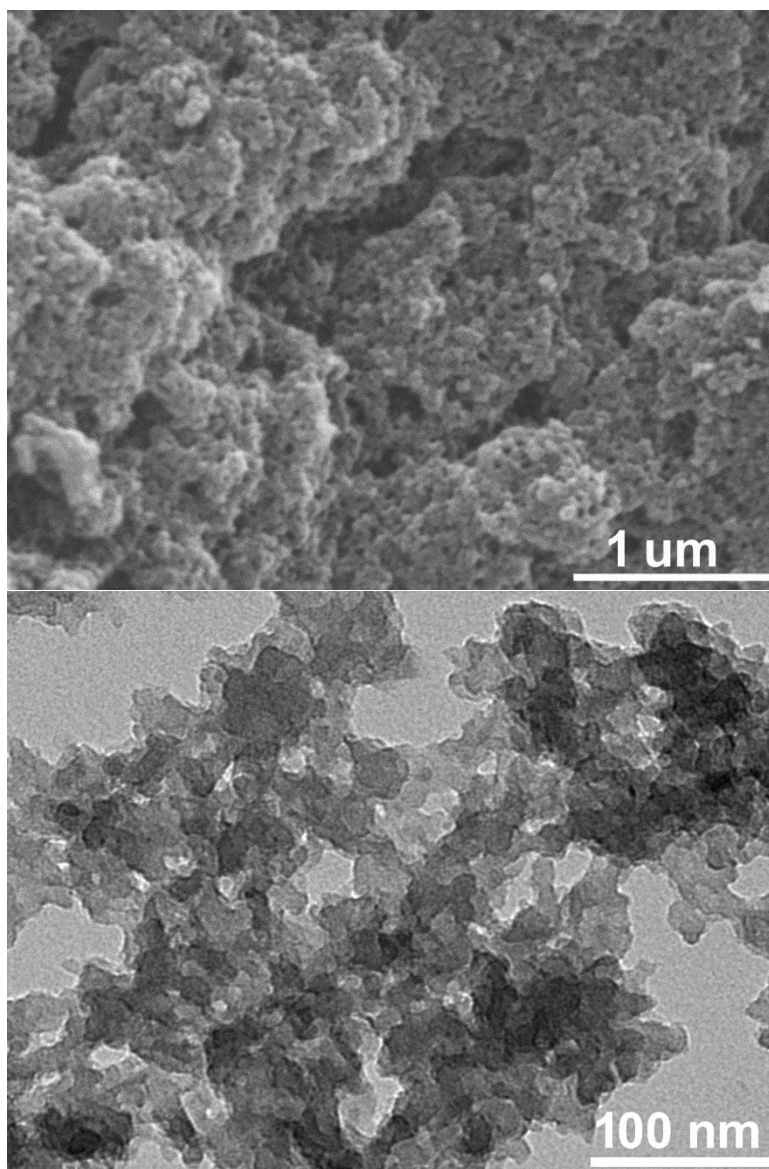


Fig. S10 SEM (top) and TEM (bottom) of POP-SO₃H.

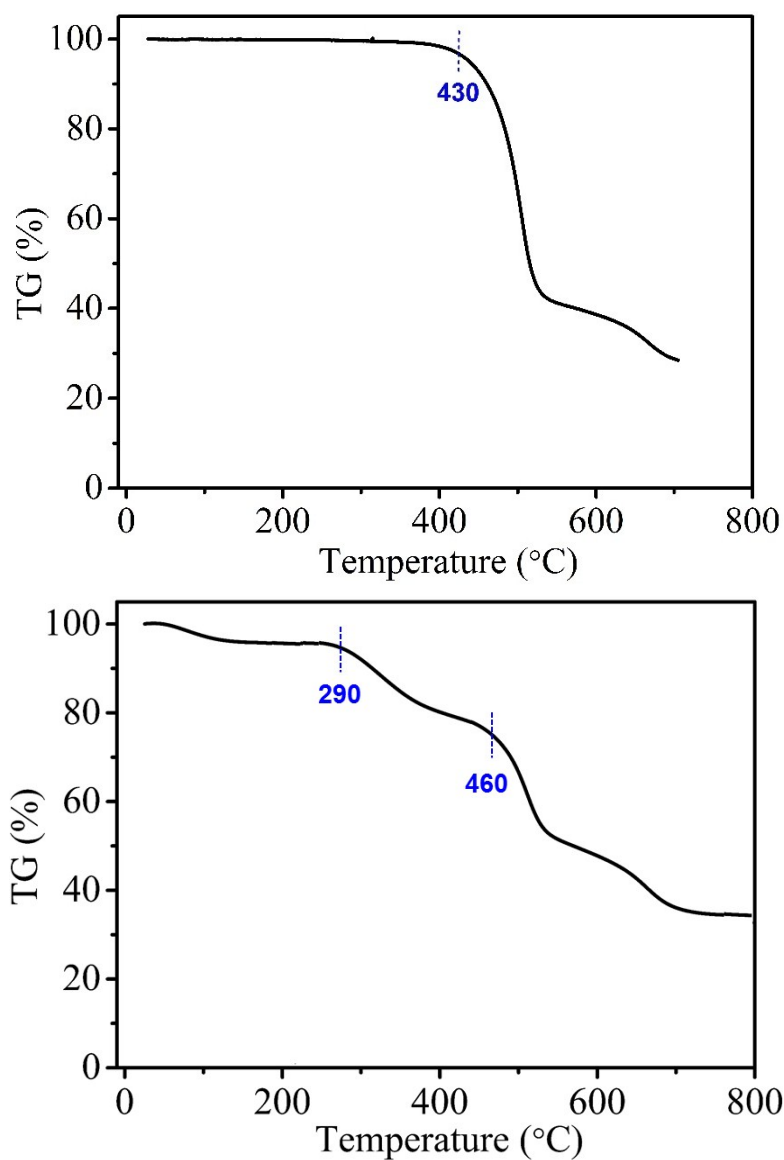


Fig. S11 TG curves of FPOP (top) and FPOP-SO₃H (bottom), respectively.

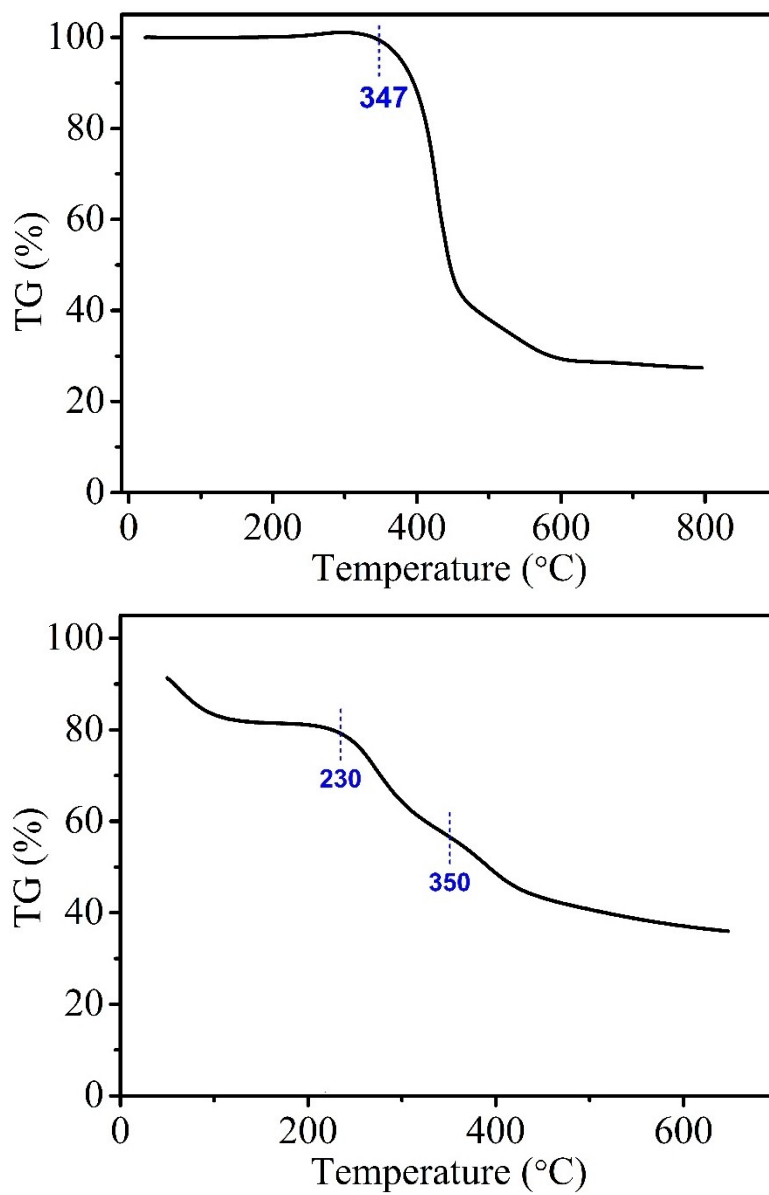


Fig. S12 TG curves of POP (top) and POP-SO₃H (bottom), respectively.

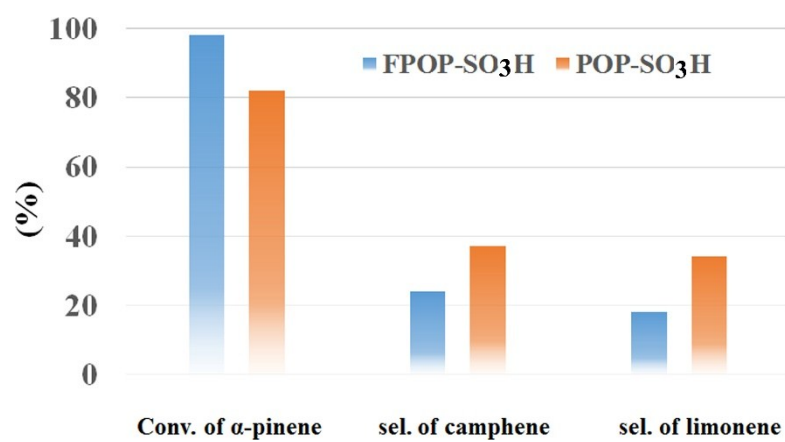


Fig. S13 Catalytic performance of α -pinene isomerization over FPOP-SO₃H and POP-SO₃H.

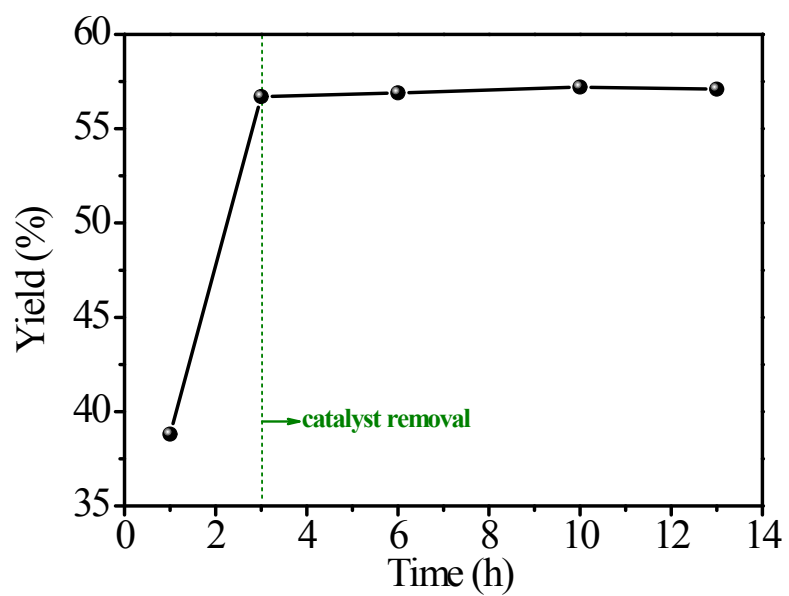


Fig. S14 Ethyl palmitate yield verse time plots after FPOP-SO₃H removal after 3 h.

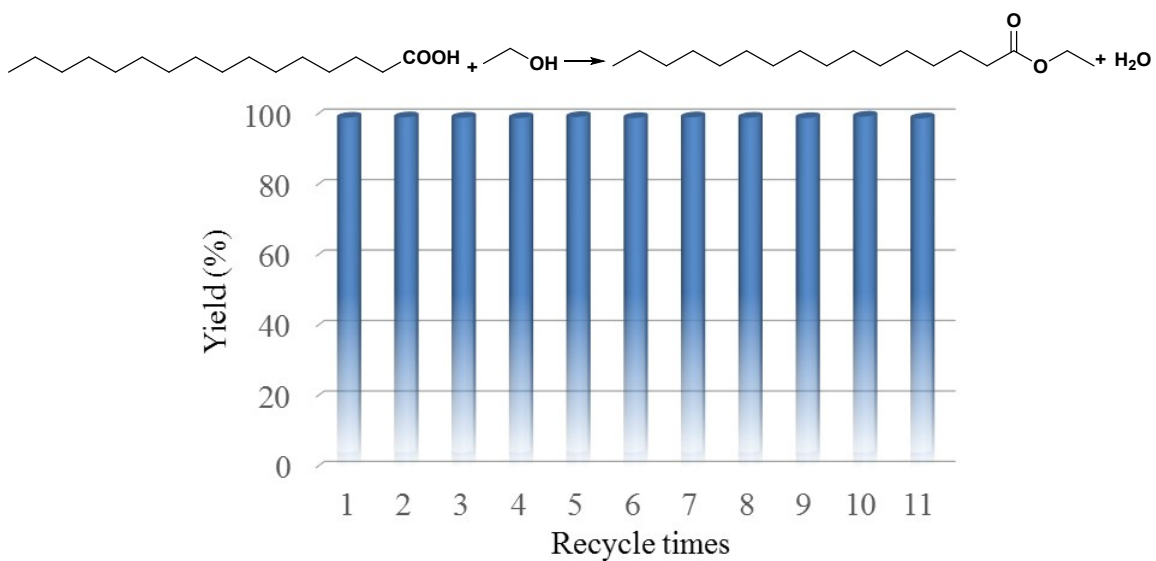


Fig. S15 Recycling tests for FPOP-SO₃H in the esterification of palmitic acid with ethanol. Reaction conditions: palmitic acid (2.0 mmol), ethanol (2.0 mL), FPOP-SO₃H (11 mg containing 0.04 mmol accessible H⁺), and 60 °C for 13 h.

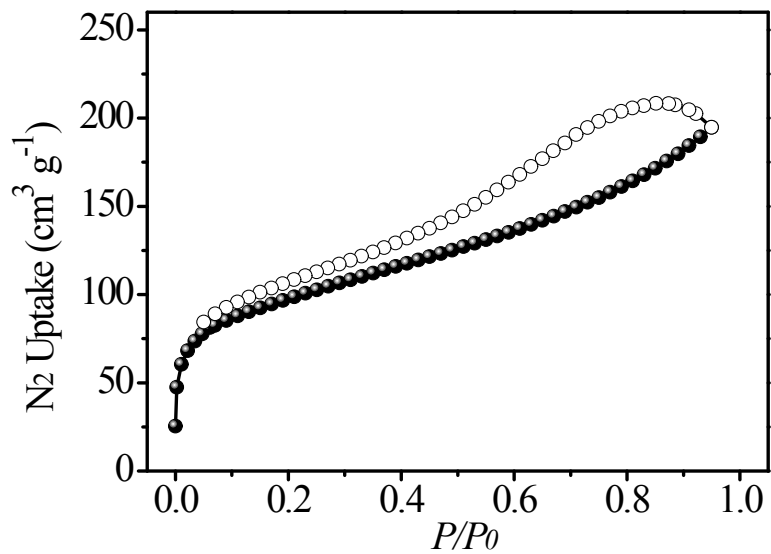


Fig. S16 N₂ sorption isotherms of the reused FPOP-SO₃H catalyst in the esterification of palmitic acid with ethanol, giving a BET surface area of 328 m² g⁻¹ and a pore volume of 0.3 cm³ g⁻¹.

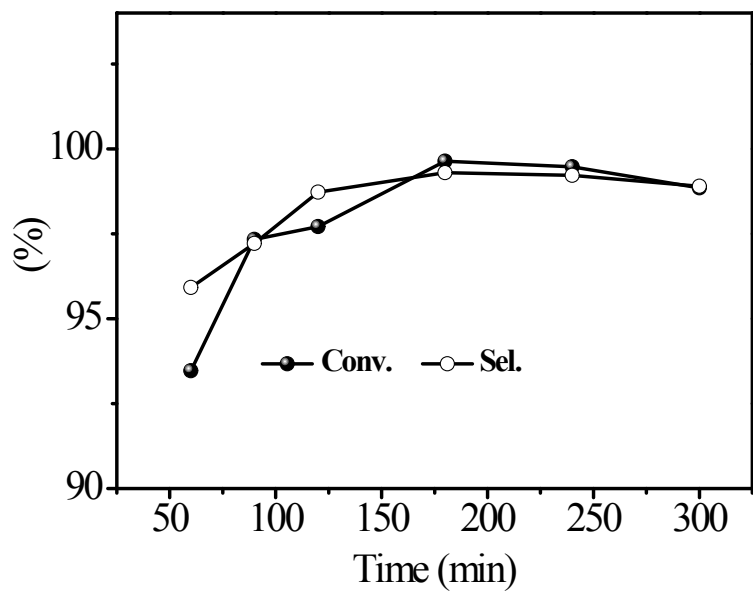
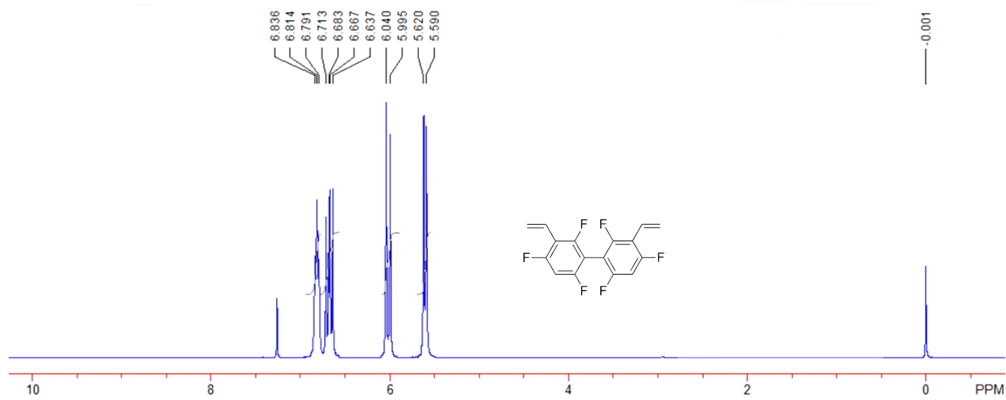
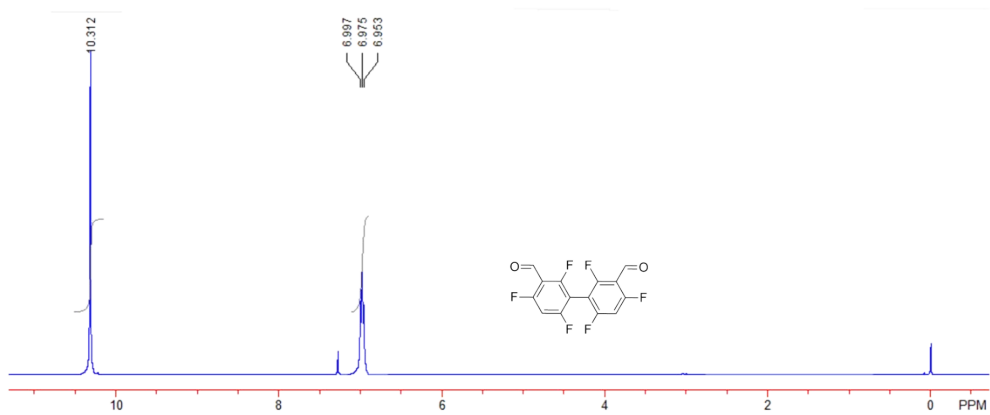
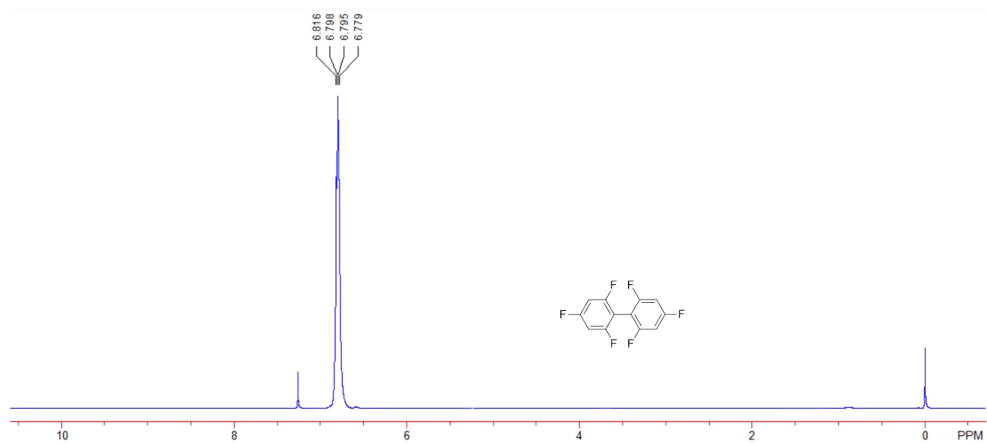


Fig. S17 Fixed-bed reaction evaluation. Conversion of benzyl alcohol and selectivity of diphenylmethane in the benzylation reaction of benzene with benzyl alcohol, in the presence of 50 mg of FPOP-SO₃H. Reaction conditions were detailed in the catalytic tests section except that a liquid injection rate of 0.07 mL min⁻¹ was employed. It was found that a benzyl alcohol conversion of 93% was achieved within 60 min, indicating that mass transfer limitations are negligible in the case of FPOP-SO₃H catalyst and the observed induction period of catalytic data shown in Fig. 3a is not due to slow mass transfer inside pores, and this delay is likely because when the instrument is initially started it requires time to be stabilized.



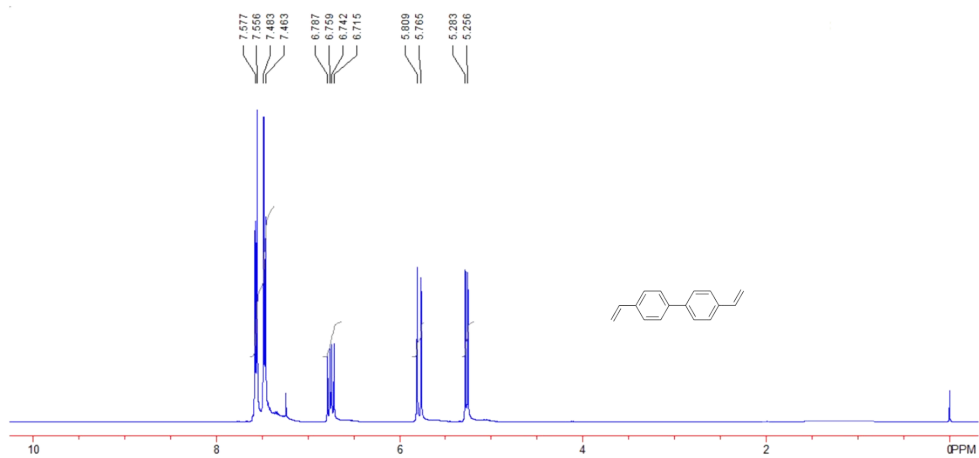
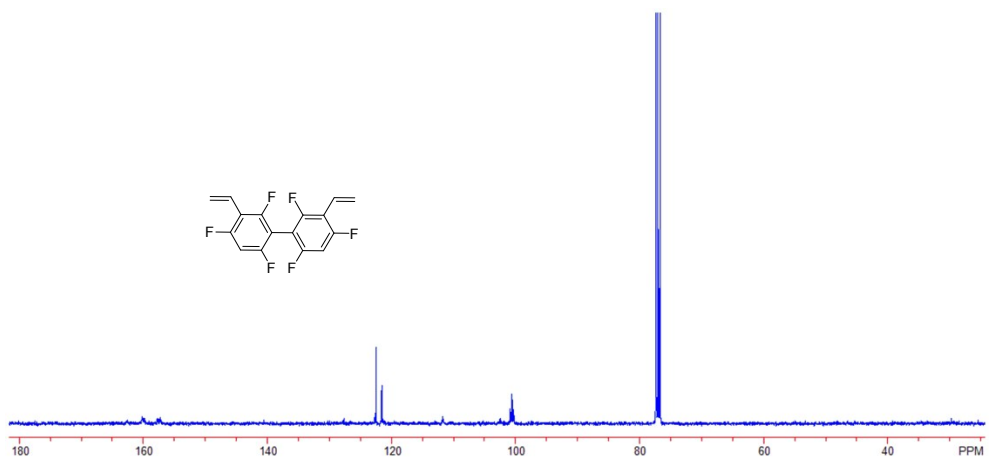


Fig. S18 Liquid NMR spectra of various compounds.