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[Supporting Information]

Use of Steric Encumbrance to Develop Conjugated Nanoporous Polymers for Metal-free Catalytic Hydrogenation

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3. Tables

Table S1 Structural parameters for **CNPs**.

Table S2 Catalyst recycling data for **CNP-1/B**-catalyzed hydrogenation of AP to EB.

4. References

1. Experimental Section

Chemicals: All commercially available solvents and other chemicals were purchased and used without further purification. 1,3-Bis(N-carbazolyl)benzene was purchased from Sigma Aldrich. 2,6-di(9H-carbazol-9-yl)pyridine (**2,6-Cz**) and 3,5-di(9H-carbazol-9-yl)pyridine (**3,5-Cz**) are synthesized following the reported procedures.[1] Their ^{1}H NMR spectrum were shown in Figure S6 and Figure S7.

1.1 Preparation of CNPs

Synthesis of Task-Specific CNP-1: Under an inert atmosphere, **2,6-Cz** (366 mg) was dissolved in anhydrous dichloromethane (50 mL). The solution was subsequently added dropwise to a mixture of anhydrous $FeCl_3$ (1.716 g) and anhydrous dichloromethane (60 mL). The resulting mixture was kept stirring under N_2 for 24 h at room temperature. Methanol was then added to quench the reaction. The obtained polymer was filtered and washed with water, methanol, and acetone. The polymer is insoluble in common organic solvents. The solid was further purified using Soxhlet extraction with methanol for 24 h and then with tetrahydrofuran for another 24 h. Finally, the desired polymer was collected and dried in a vacuum oven at 100 °C overnight. Yield: ~90 %.

CNP-2 and **CNP-3** were synthesized following the same method described above for **CNP-1** using the 1,3-Bis(N-carbazolyl)benzene and **3,5-Cz** as reagents, respectively.

1.2 Synthesis of CNPs/B

$B(C_6F_5)_3$ was introduced into the **CNPs** using a wet impregnation method. Typically, 0.1 g of $B(C_6F_5)_3$ was dissolved into 2 mL CH_2Cl_2. Subsequently, 0.1 g of the as-synthesized **CNP**s was added and the mixture was stirred at 25 °C for 1 h. The temperature was then increased to 40 °C and placed under vacuum to completely evaporate CH_2Cl_2. **CNPs/B** was obtained as heterogeneous FLP catalysts for hydrogenation. [Note: **CNP-1/B** equals to CNP-1-B (1/1). CNP-1-B (1/2) indicates that the mass ratio of **CNP-1** and $B(C_6F_5)_3$ is 0.5 during the synthetic process.]

1.3 Characterization

The powder X-ray diffraction (XRD) data were recorded with a PANalytical Empyrean diffractometer, operated at 45 kV and 40 mA (scanning step: 0.02 ° per step). The diffraction patterns were recorded in the range of 10–80° 2θ. The nitrogen adsorption and desorption isotherms were measured at 77 K under a Gemini 2375 surface area analyzer. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer. Solid-state ^{13}C magic-angle spinning (MAS) NMRs were performed using a Solid State Varian INOVA 400 MHz. The ^{11}B (I=3/2) MAS NMR experiments were performed on a 600 MHz NMR spectrometer (Agilent, USA) at the Larmor frequency of 192.4 MHz equipped with 4 mm HFXY MAS probe using single pulse excitation with π/20 degree pulse of 0.3 μs at ambient temperature with a spinning speed of 10 kHz. The ^{11}B chemical shift of 0 ppm from 0.1 M boric acid solution was used as an external reference. X-ray photoelectron spectroscopy (XPS) measurements: XPS experiments were performed with a PHI 3056 spectrometer equipped with an Al anode source operated at 15 KV and an applied power of 350 W and a pass energy of 93.5 eV.

The conversion of acetophenone (AP) and yield of ethylbenzene (EB) in the acetophenone hydrogenation reaction were determined using a GC-MS system (HP/Agilent 6890GC/5973MSD) equipped with a HP-5MS (30 m × 0.25 mm, film: 0.25 μm) capillary column and a FID detector. Prior to the measurements, the samples were diluted with CH_2Cl_2.

1.4 Catalytic hydrogenation of acetophenone

0.30 g of AP and 0.20 g of **CNPs/B** was added into 5 mL of hexane in a teflon-lined hydrogenation vessel. Upon sealing, the system was charged to a pressure of 5 bar with H_2 and heated at 100 °C. After the reaction proceeded for the desired period of time, the reactor was cooled down rapidly with an ice bath and the reaction mixture was filtered.

The conversion of acetophenone was analyzed by a GC-MS system (HP/Agilent 6890GC/5973MSD) equipped with a HP-5MS (30 m × 0.25 mm, film: 0.25 μm) capillary column and FID detector, based on

the standard curve obtained with pure acetophenone. The integrations of the peaks were used to determine the quantity of acetophenone. All experiments were performed three times to obtain an average peak area. The temperature program was as follows: hold at 60 °C 5 min, increase from 60 to 150 °C at 10 °C/min. The peak of acetophenone appears at 9.52 min. The conversion of acetophenone was calculated by (%) = $[(n_A - n_B)/n_A] \times 100$, where n_A (2.5 mmol) and n_B denote the initial and final molar amounts of acetophenone. GC samples were prepared from 0.035g of reaction solution and diluted with 1.0 g of CH_2Cl_2.

The yield of ethylbenzene was estimated by GC-MS based on the conversion of acetophenone through an internal standard method. Various mass ratios of ethylbenzene (EB) and acetophenone (AP) were prepared for the standard curve. AP was used as the internal standard to estimate the yield of EB in the same reaction mixture. The ratio of peak areas of AP and EB were used to calculate their mass ratio. The yield of ethylbenzene was calculated by (%) = $(n_{EB}/n_A) \times 100$, where n_{EB} denotes the molar amount of ethylbenzene produced. The temperature program is the same as above. The peak of EB will be shown at 5.76 min. GC samples were prepared as above.

A typical analysis of GC-MS data was shown in Table S1. As displayed in the following figure,

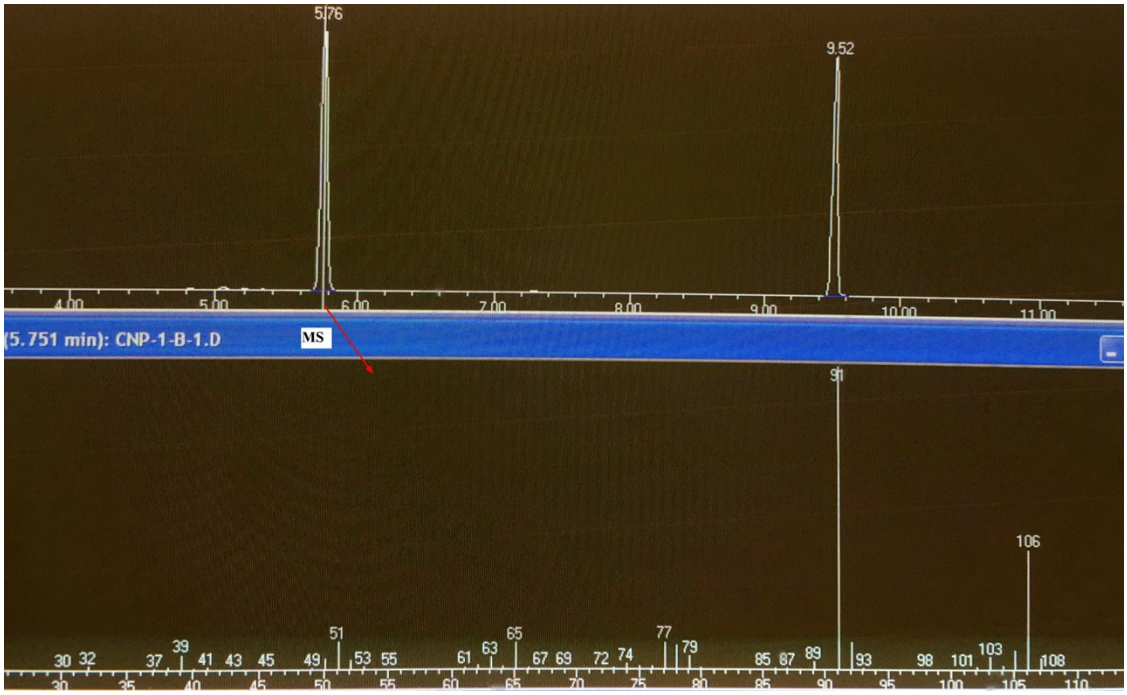
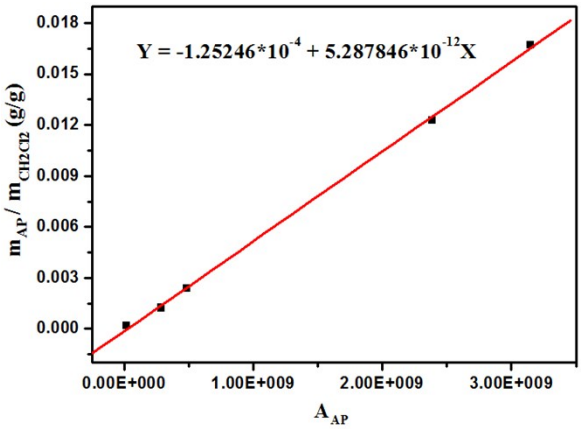


Table S1 The GC-MS data for the AP hydrogenation catalyzed by **CNP-1/B** at 100 °C for 24 h.

Sample	R.T. (min)	corr. area	corr. % max	% of total
EB	5.757	416403985	100.00%	52.76
AP	9.516	372787986	89.53%	47.24

The standard curve of various concentration of pure AP in the CH_2Cl_2 (external standard method) as follows:



After being diluted, A_{AP} *= 372787986,* m_{CH2Cl2}*= 1.0 g*

$m_{AP\ diluted} = (-1.25246*10^{-4} + 5.287846*10^{-12}\ A_{AP}) * m_{CH2Cl2} = 1.846 *10^{-3}$ *g*

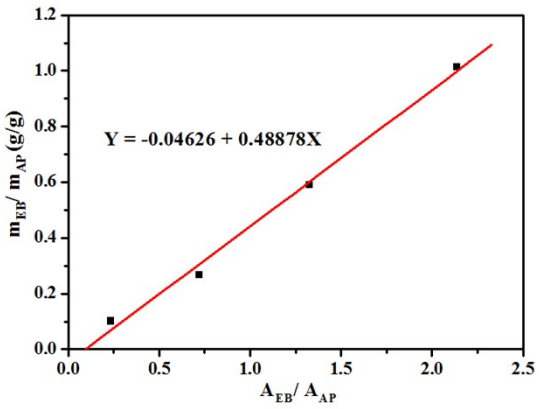
Because 0.035g of samples were took out from the produts (m = 3.6 g),

m_{AP} *= (3.6/0.035)* $m_{AP\ diluted}$ = 0.1899 g*

n_A *= 2.5 mmol,* n_B*=* m_{AP} */ 120 = 1.582 mmol*

The conversion of acetophenone (%) = $[(n_A - n_B)/n_A] \times 100 = 36.7\ \%$

The standard curve of various mass ratio of EB and AP in the CH_2Cl_2 (internal standard method) as follows:



A_{EB} / A_{AP} *= 1.117*

m_{EB} / m_{AP} *= -0.04626 + 0.48878* (A_{EB} / A_{AP}) = 0.4997, according to the above result,* m_{AP} *= 0.1899 g*

m_{EB}*= 0.4997 ** m_{AP} *= 0.0949 g,* n_{EB} *=* m_{EB}*/ 106 = 0.895 mmol*

The yield of ethylbenzene (%) = $(n_{EB}/n_A) \times 100 = 0.895/2.5=35.8\%$

For recycling experiments of catalysts, the reaction time for hydrogenation of AP was set at 24 h and the reaction was performed in the same manner. The recovered catalyst was collected by filtration, washed with hexane several times and dried at 70 °C for the next run. Because of the loss of $B(C_6F_5)_3$ during the recycling and separation process, after the second recycling, the catalysts were regenerated by adding 0.05 g $B(C_6F_5)_3$ in each round. The conversion and yield was measured by GC-MS.

1.5 Catalytic hydrogenation of other substrates

2.5 mmol g of substrate and 0.20 g of **CNP-1/B** were added into 5 mL of hexane in a teflon-lined hydrogenation vessel. Upon sealing, the system was charged to a pressure of 5 bar with H_2 and heated at 100 °C. After the reaction proceeded for the desired period of time, the reactor was cooled down rapidly with an ice bath and the reaction mixture was filtered. The conversion and yield was measured by GC-MS.

1.6 DFT calculations

Structures of all the moieties and complexes were optimized at RI-B-LYP-D3/def2-TZVPP level in the Turbomole 6.5 software package. Natural bond orbital analysis was further employed to obtain atomic partial charges.

2. Figures

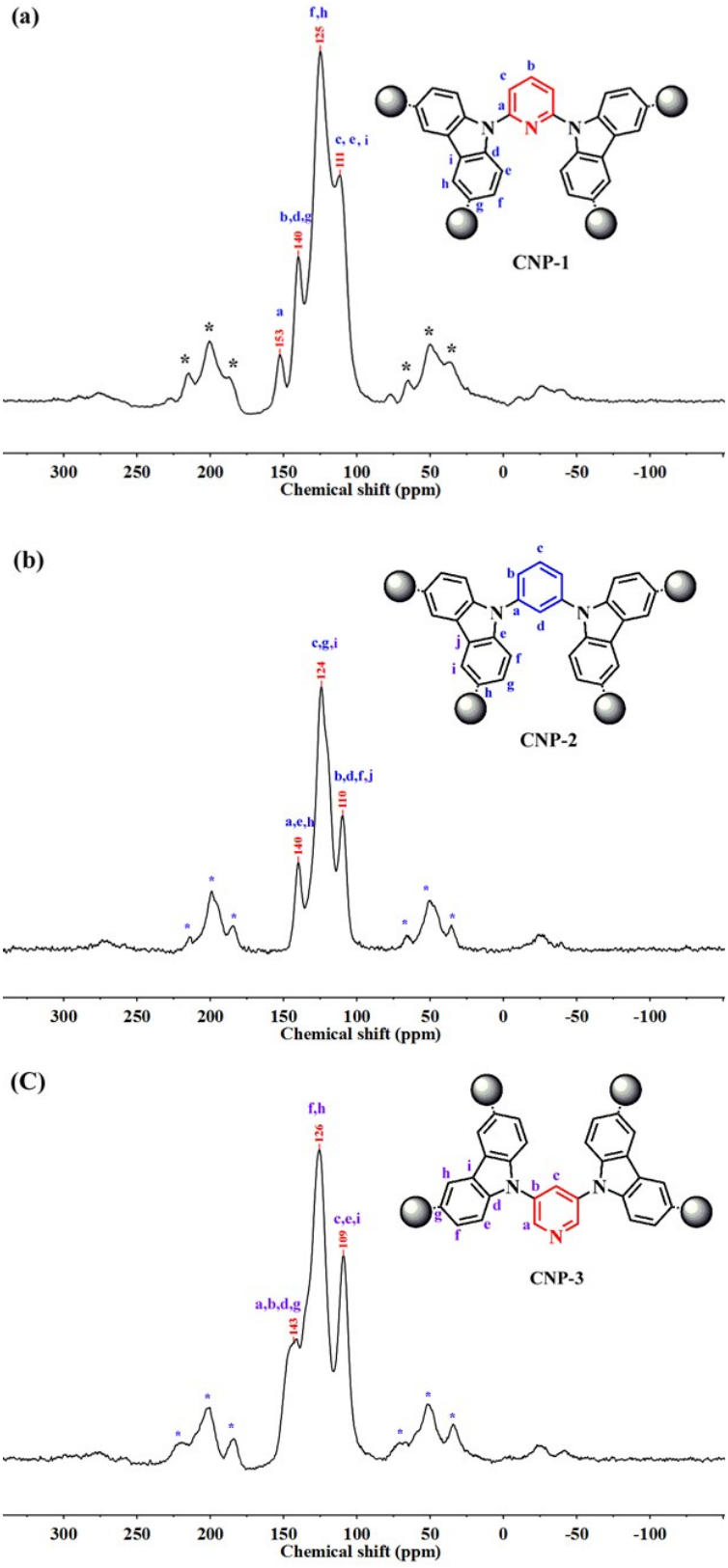

(a)
f,h
125
c, e, i
111
b,d,g
140
a
153
CNP-1
300 250 200 150 100 50 0 -50 -100
Chemical shift (ppm)
(b)
c,g,i
124
b,d,f,j
110
a,e,h
140
CNP-2
300 250 200 150 100 50 0 -50 -100
Chemical shift (ppm)
(C)
f,h
126
c,e,i
109
a,b,d,g
143
CNP-3
300 250 200 150 100 50 0 -50 -100
Chemical shift (ppm)

Figure S1. ^{13}C MAS ssNMR spectra of **CNPs**.

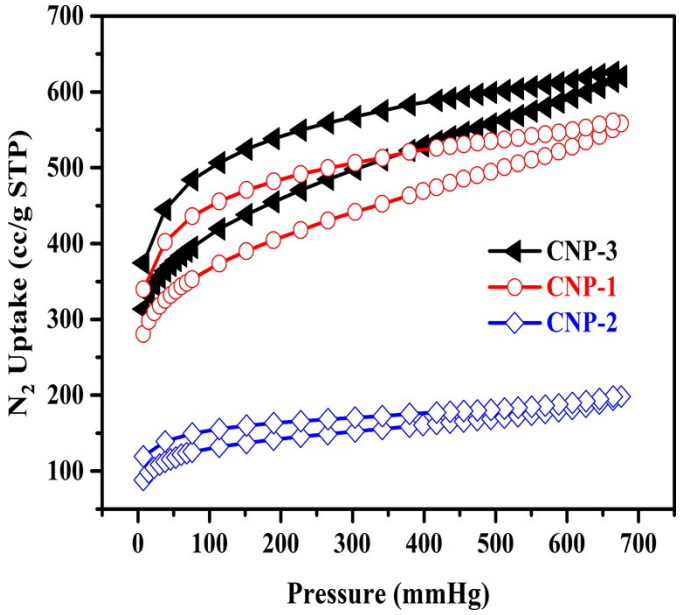


Figure S2. Nitrogen adsorption-desorption isotherms of **CNPs.** [**CNP-2** displayed a BET surface area of 483 m^2 g^{-1} (Table S1), similar to what has been shown in other polycarbazoles[2].]

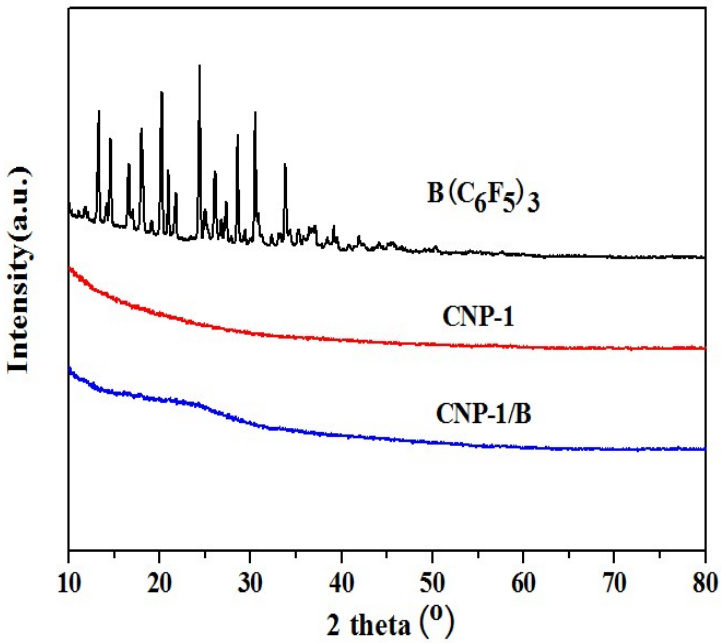


Figure S3. Wide-angle XRD patterns of $B(C_6F_5)_3$, **CNP-1** and **CNP-1/B**.

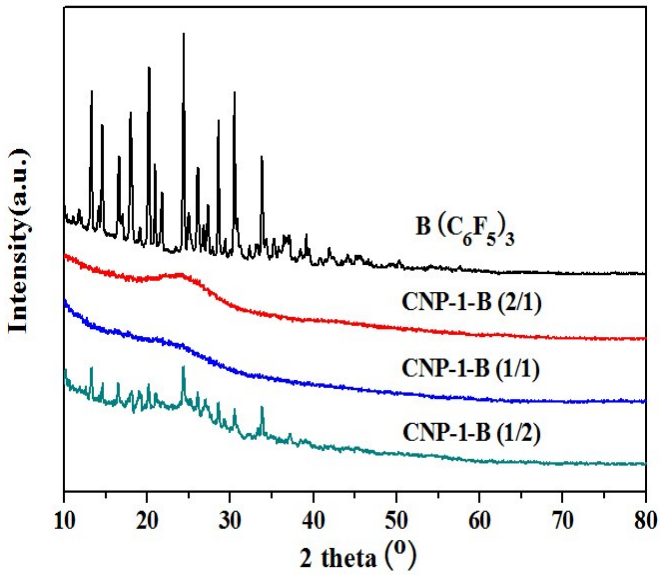


Figure S4. Wide-angle XRD patterns of **CNP-1-B** with different amount of $B(C_6F_5)_3$. CNP-1-B (1/2) indicates that the mass ratio of **CNP-1** and $B(C_6F_5)_3$ is 0.5 during the synthetic process.

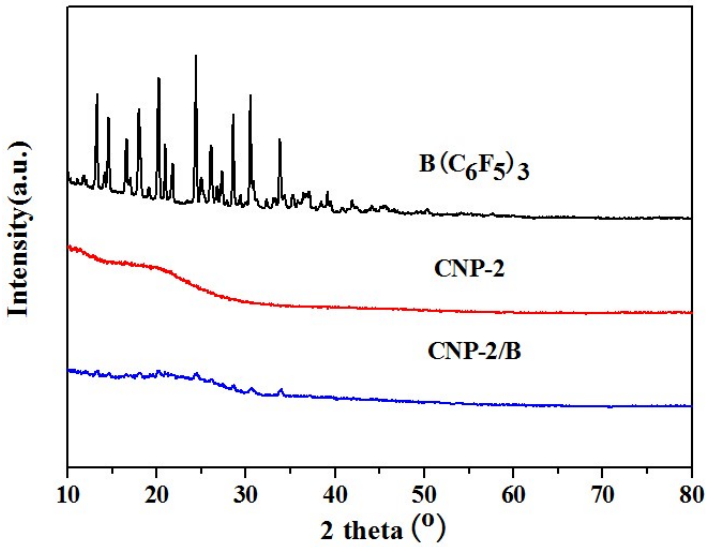


Figure S5. Wide-angle XRD patterns of $B(C_6F_5)_3$, **CNP-2** and **CNP-2/B**.

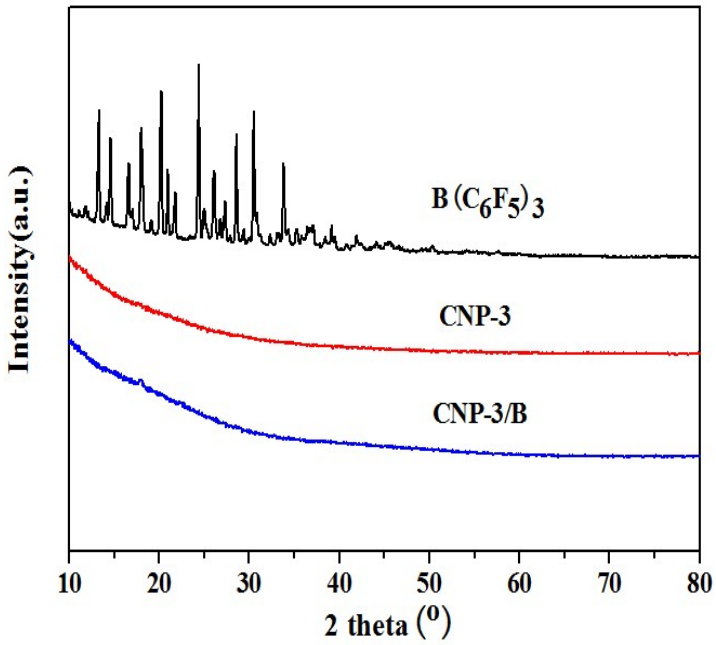


Figure S6. Wide-angle XRD patterns of $B(C_6F_5)_3$, **CNP-3** and **CNP-3/B.**

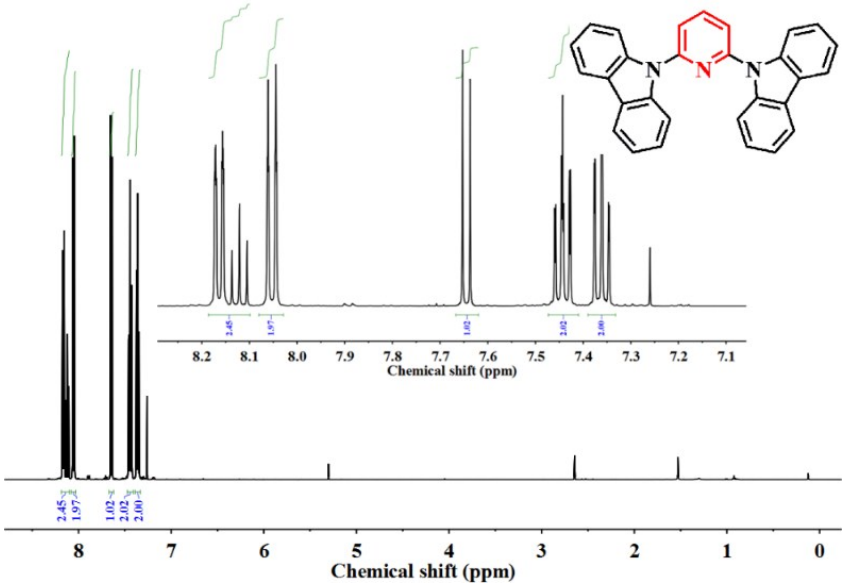


Figure S7. ^1H NMR spectra of 2,6-di(9H-carbazol-9-yl)pyridine (**2,6-Cz**) (Solvent: $CDCl_3$).

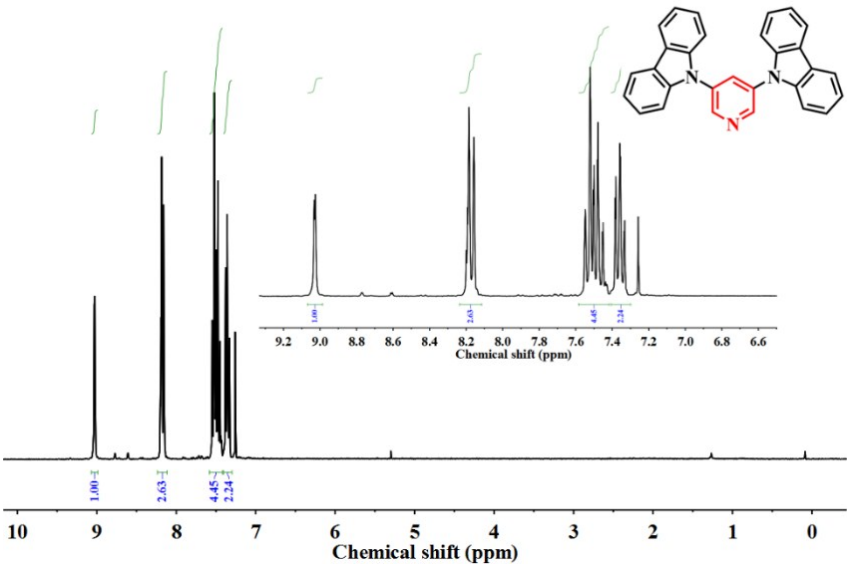


Figure S8. ^{1}H NMR spectra of 3,5-di(9H-carbazol-9-yl)pyridine (**3,5-Cz**) (Solvent: $CDCl_3$).

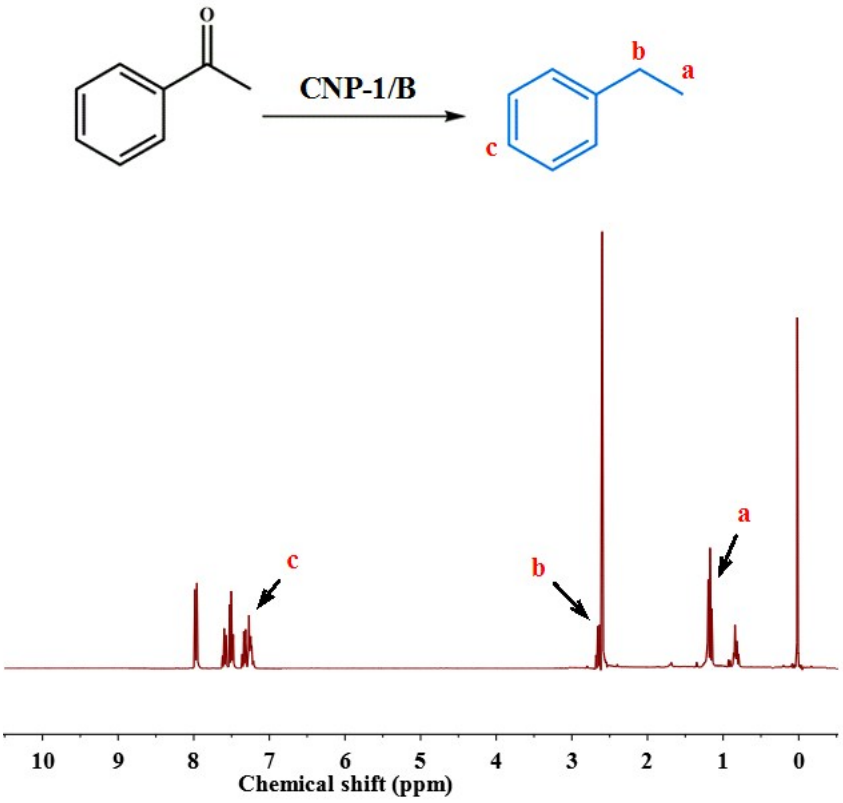


Figure S9. ^{1}H NMR spectra of **CNP-1/B**-catalyzed hydrogenation of acetophenone in $CDCl_3$.

3. Tables

Table S1. Structural parameters for **CNPs.**

Polymers	S_{BET} (m^2 g^{-1})	V_{total} (cm^3 g^{-1}) [a]
CNP-1	1368	0.86
CNP-2	483	0.31
CNP-3	1538	0.96

[a] Total Pore Volume measured at P/Po=0.89.

Table S2 Catalyst recycling data for **CNP-1/B**-catalyzed hydrogenation of AP to EB.

Catalyst	Conversion (%)	Yield (%)
Run 1	36.7	35.8
Run 2[a]	8.6	8.2
Run 3[b]	30.2	29.4
Run 4[b]	29.4	28.1

[a] Direct recycling; [b] Recycling with the addition of 0.05 g of $B(C_6F_5)_3$.

4. References

(1) Tang, C.; Bi, R.; Tao, Y.; Wang, F.; Cao, X.; Wang, S.; Jiang, T.; Zhong, C.; Zhang, H.; Huang, W. *Chem. Commun.* **2015**, *51*, 1650.

(2) Chen, Q.; Liu, D.-P.; Luo, M.; Feng, L.-J.; Zhao, Y.-C.; Han, B.-H. *Small* **2014**, *10*, 308.