Supporting Information

Synthesis of Carbazole-based Microporous Polymer Networks via Oxidative Coupling Mediated Self-assembly Strategy: From Morphology Regulation to Application Analysis

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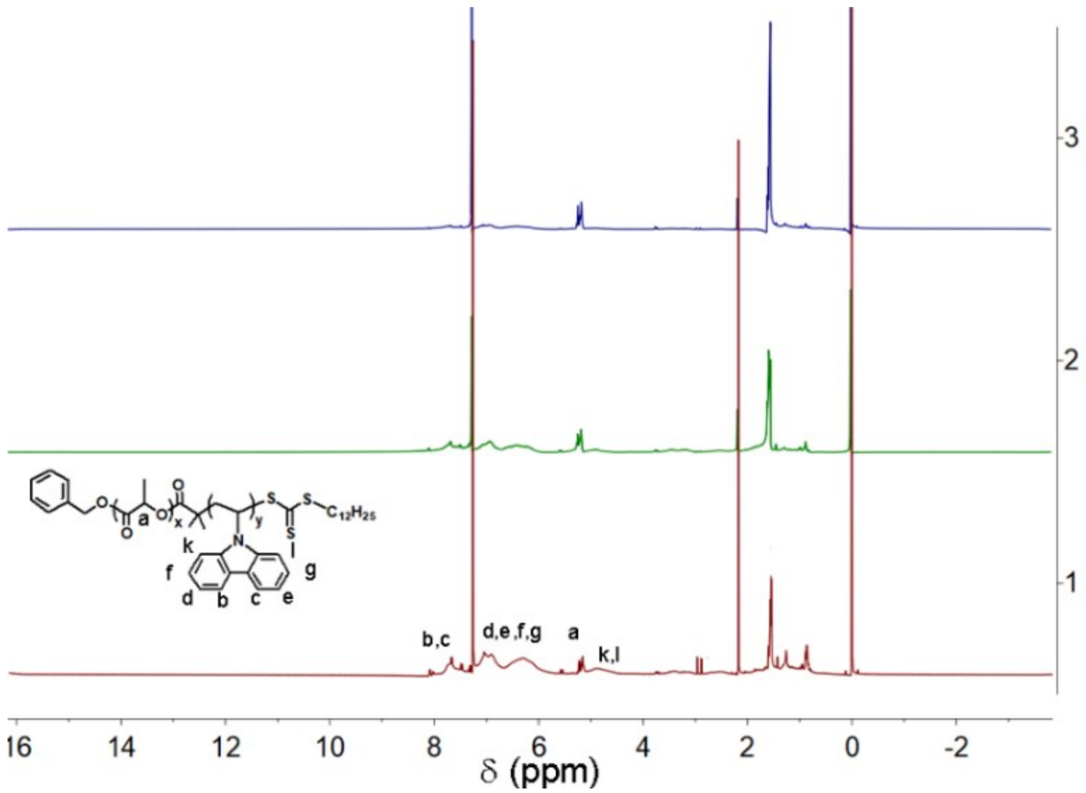


Fig. S1 ^{1}H NMR characterization of PLA_x-b-$PNVC_y$: (1) x=184, y=400; (2) x=184, y=190; (3) x=184, y=70.

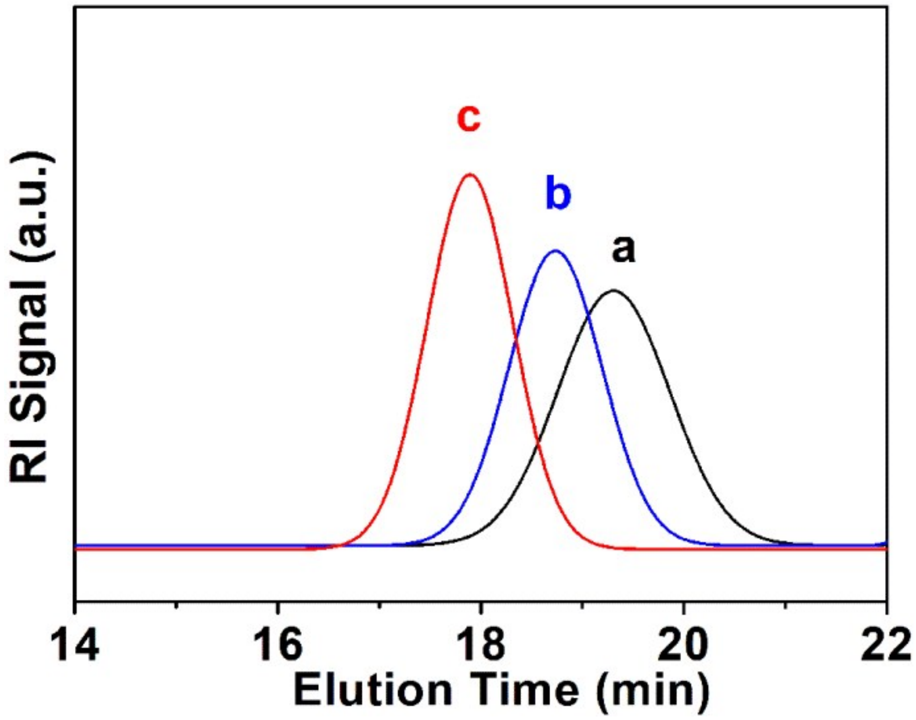


Fig. S2 GPC traces recorded for (a) PLA_{184}-b-$PNVC_{70}$, (b) PLA_{184}-b-$PNVC_{190}$ and (c) PLA_{184}-b-$PNVC_{400}$.

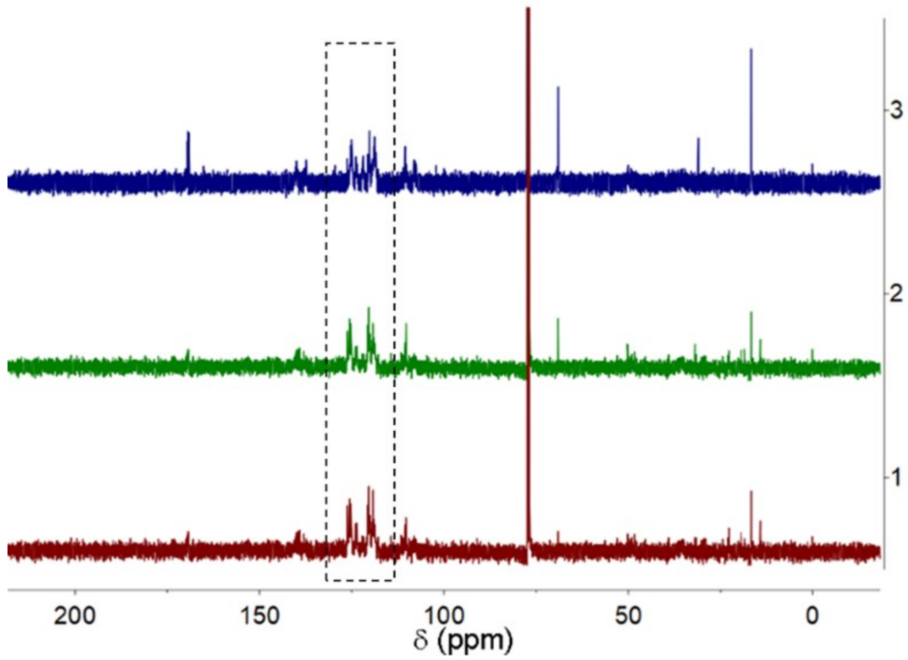


Fig. S3 ^{13}C NMR characterization of PLA_x-b-$PNVC_y$: (1) x=184, y=400; (2) x=184, y=190; (3) x=184, y=70.

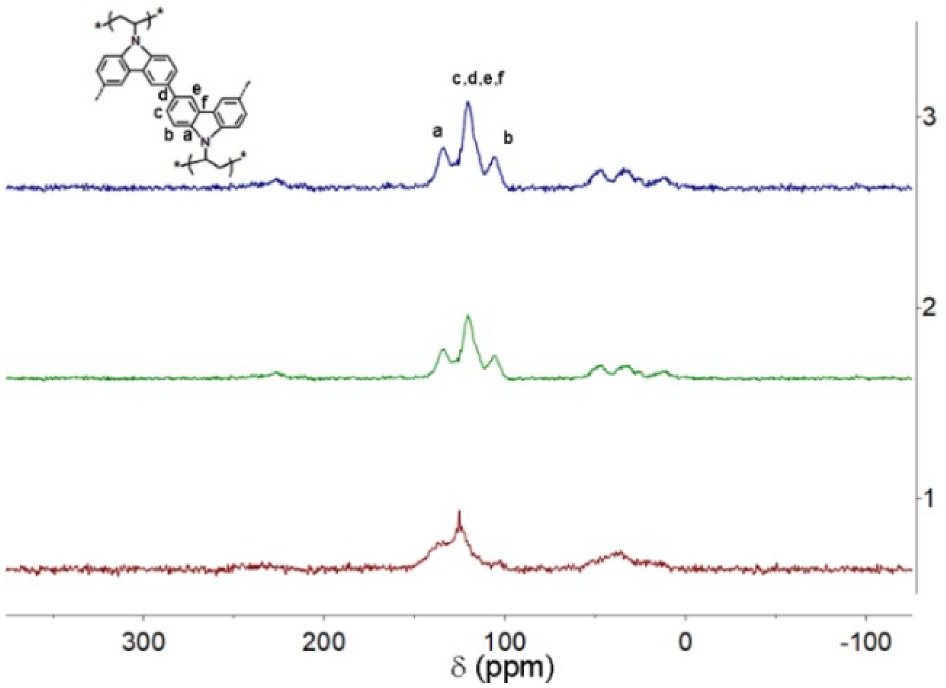


Fig. S4 ^{13}C CP/MAS NMR characterization of (1) S-C-MPNs, (2) B-C-MPNs and (3) H-C-MPNs, repectively.

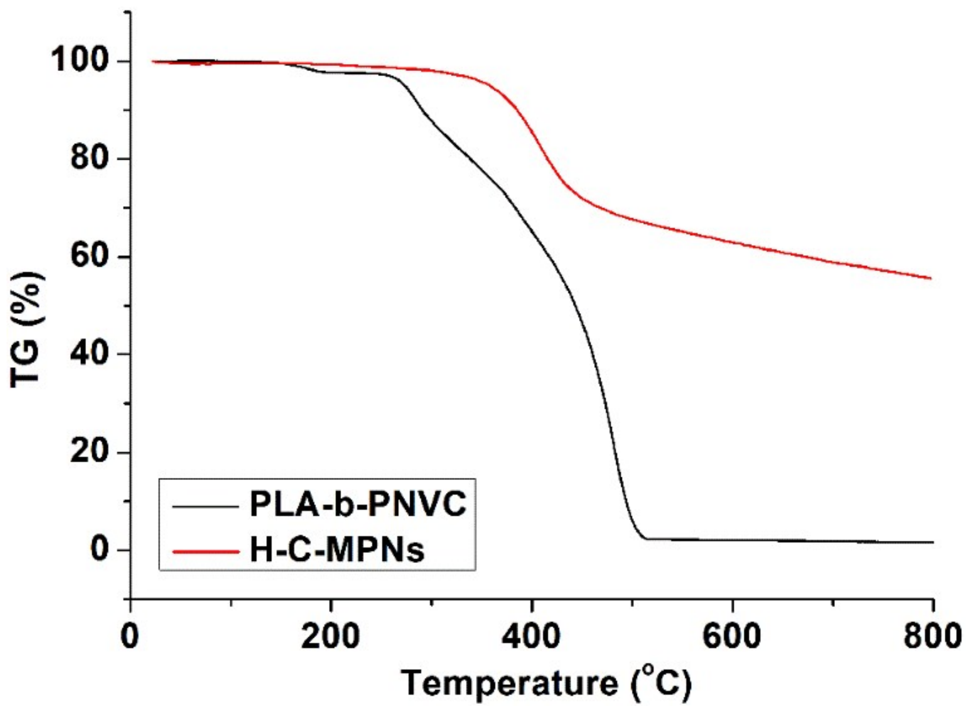


Fig. S5 TGA curves of PLA-b-PNVC (x=184, y=190) and H-C-MPNs.

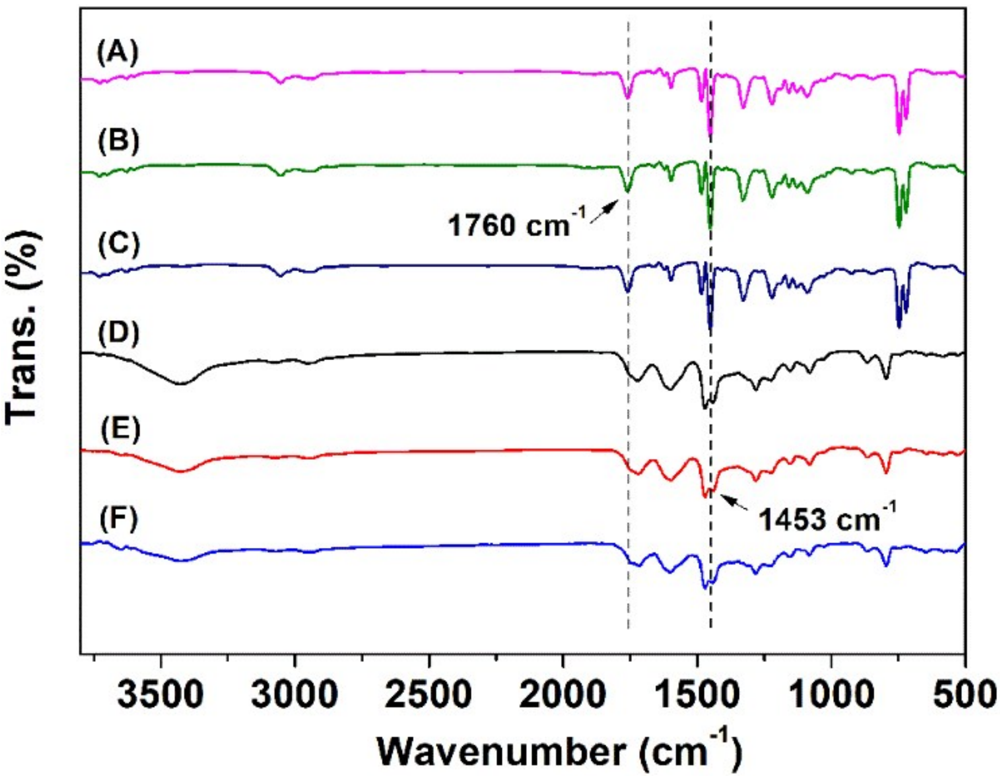


Fig. S6 FT-IR spectra of (A) PLA_{184}-b-$PNVC_{70}$, (B) PLA_{184}-b-$PNVC_{190}$, (C) PLA_{184}-b-$PNVC_{400}$ polymer and the corresponding (D) S-C-MPNs, (E) B-C-MPNs and (F) H-C-MPNs, repectively.

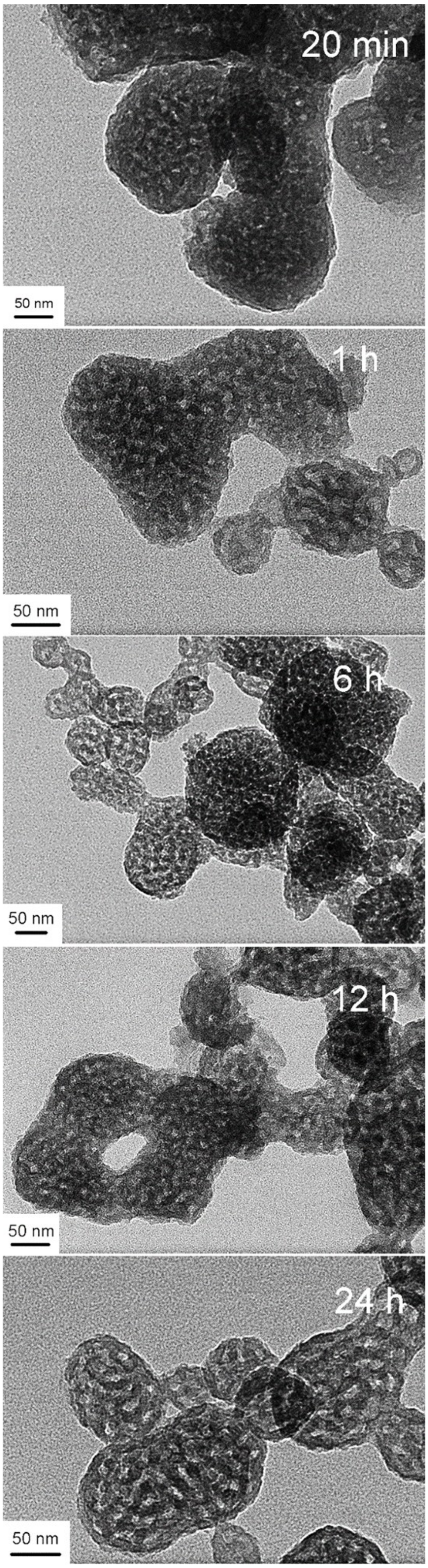


Fig. S7 TEM images of B-C-MPNs with different oxidative coupling times.

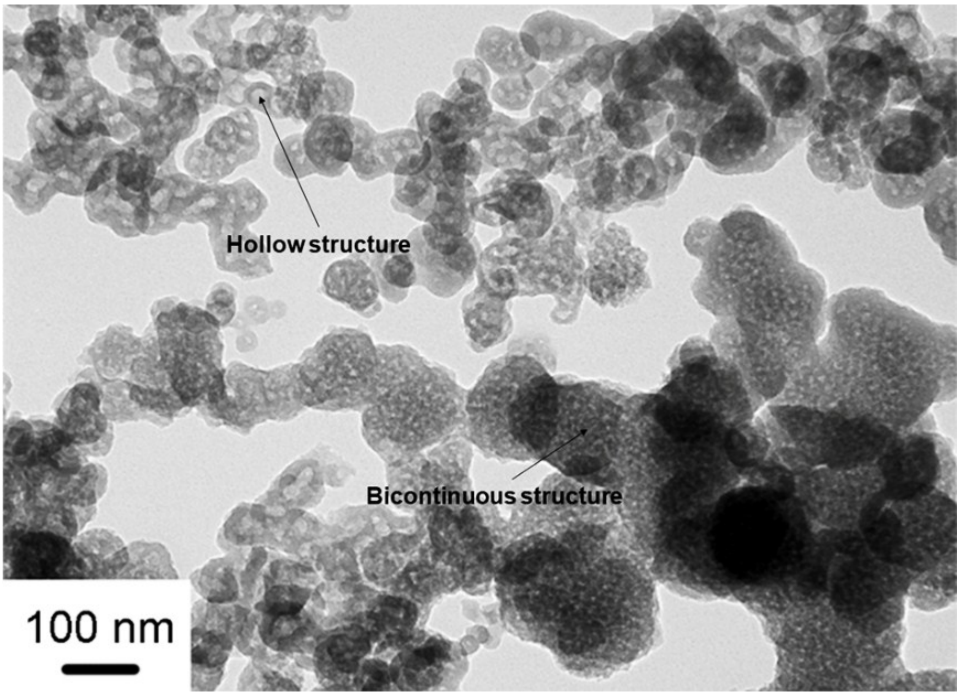


Fig. S8 TEM image of the sample from PLA_{184}-b-$PNVC_{300}$ precursor.

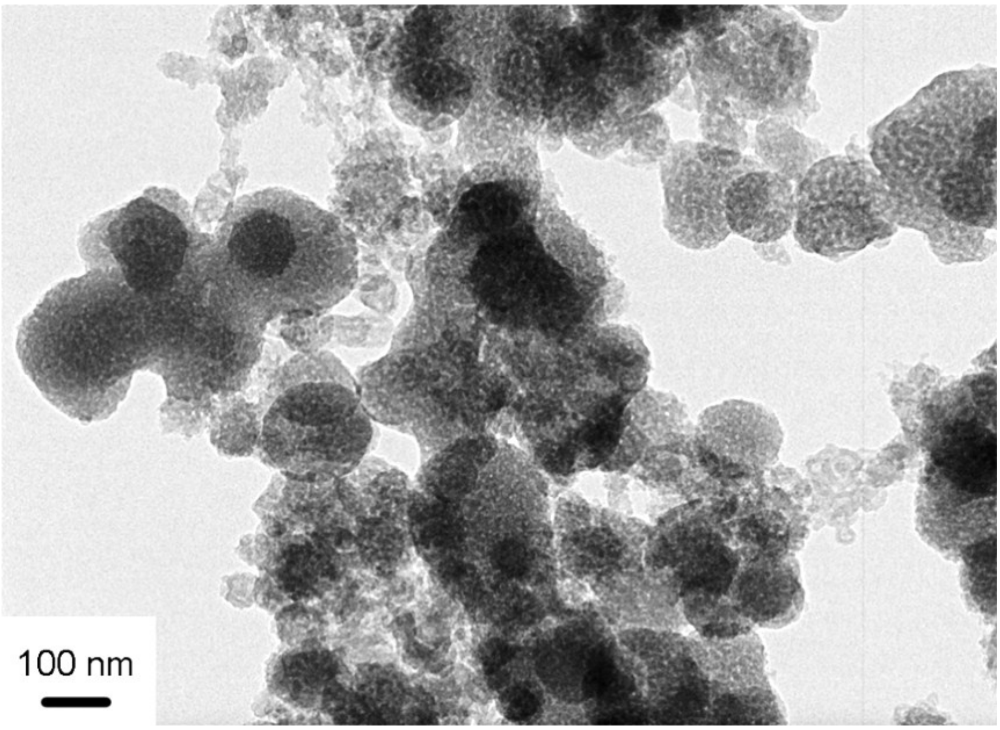


Fig. S9 TEM image of the sample from PLA_{90}-b-$PNVC_{95}$ precursor.

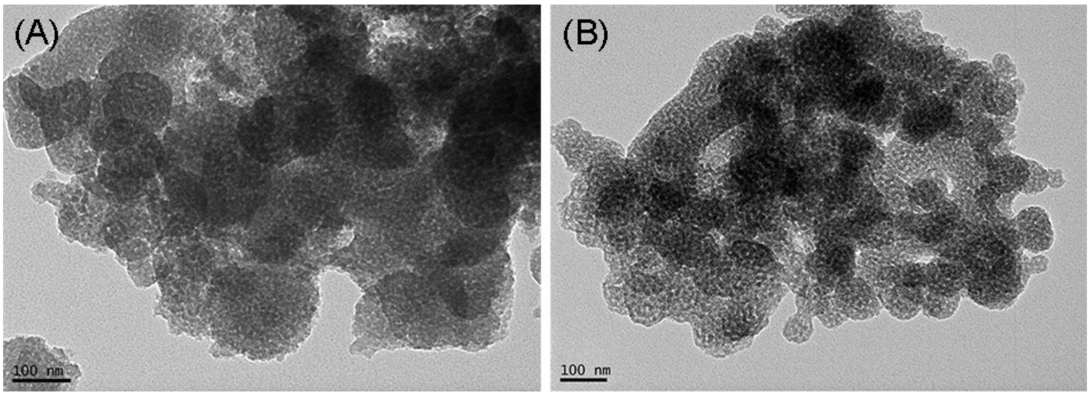


Fig. S10 TEM images of the obtained oxidative coupling polymers from different molar ratio of $FeCl_3$ to carbazole unit of PLA_{184}-b-$PNVC_{184}$: (A) ratio = 2; (B) ratio = 8.

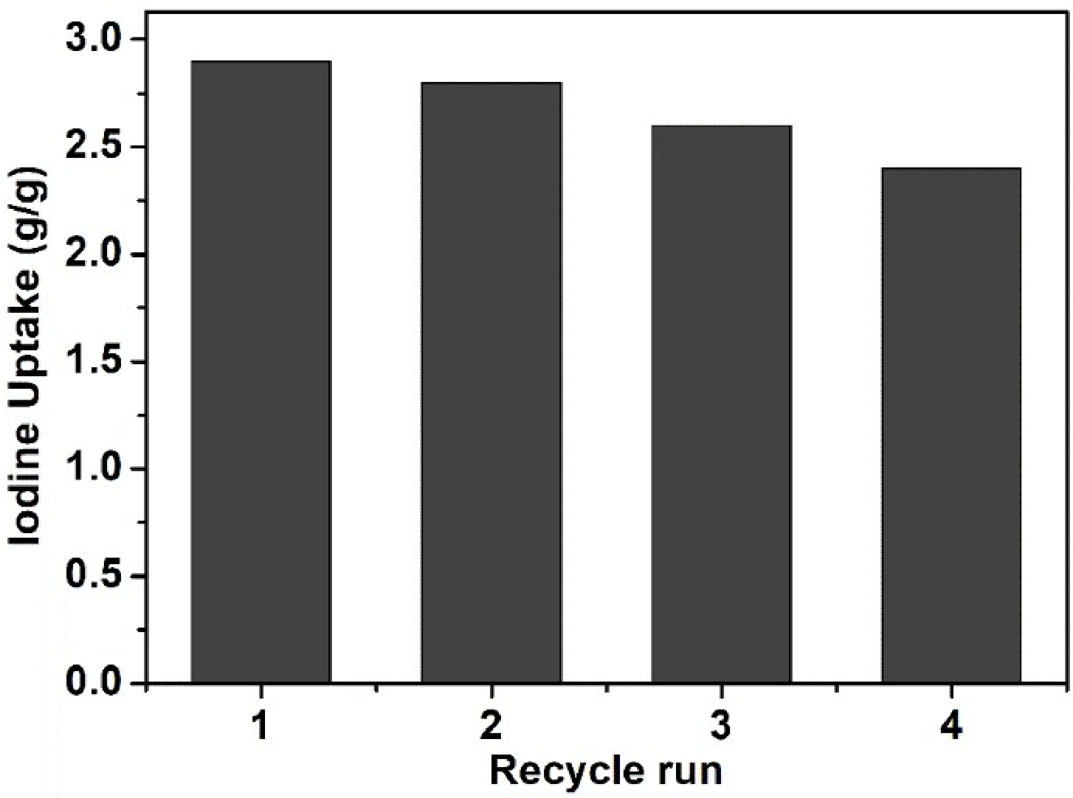


Fig. S11 Reusability of H-C-MPNs for iodine adsorption.

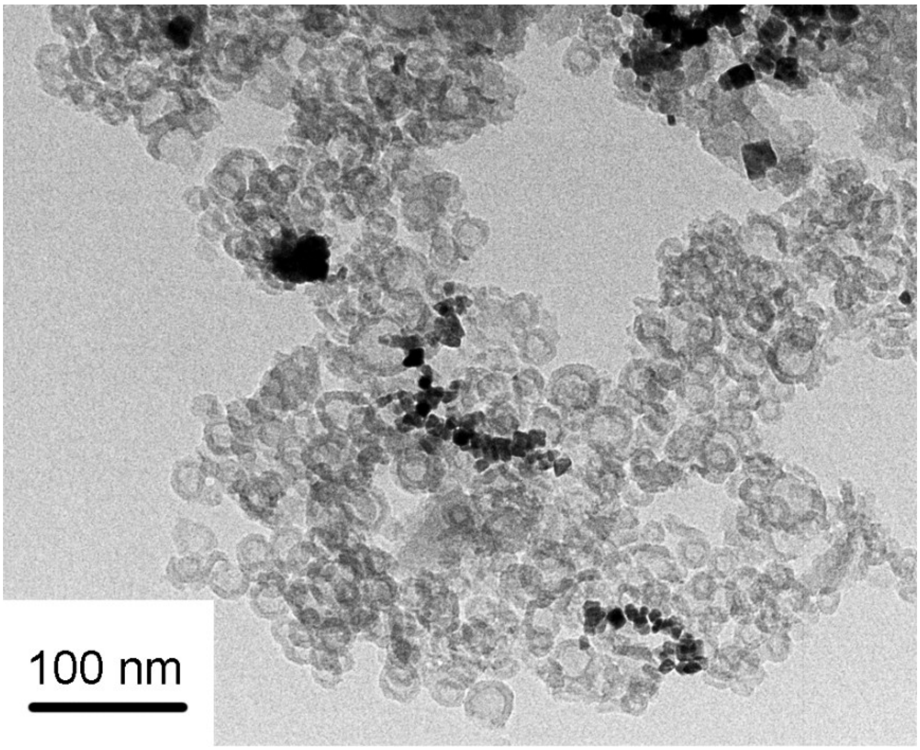


Fig. S12 TEM image of Pd@H-C-MPNs.

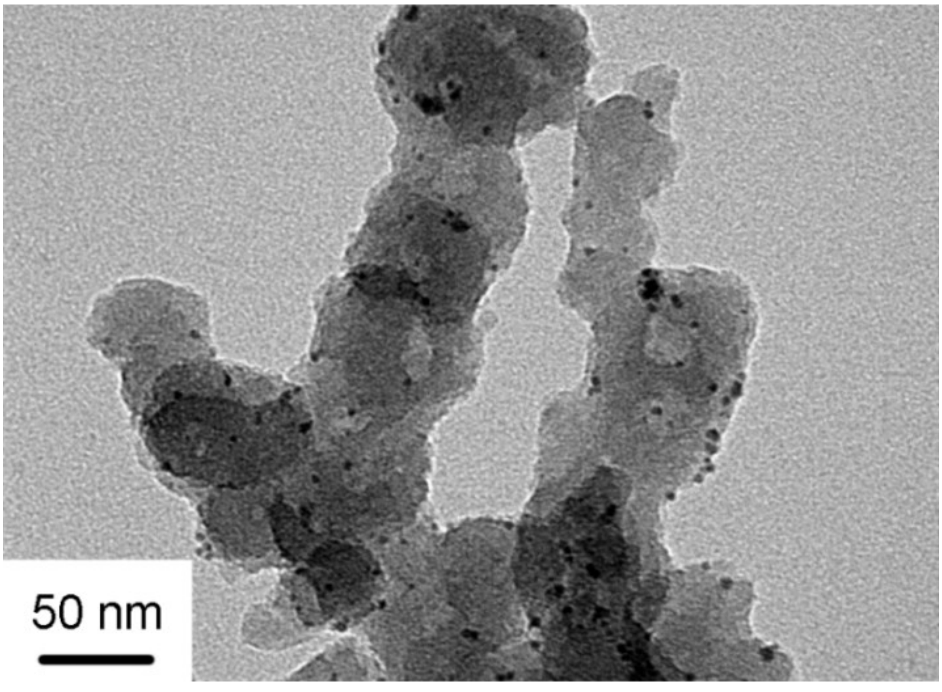


Fig. S13 TEM image of Pd@H-N-PCNs after recycle used.

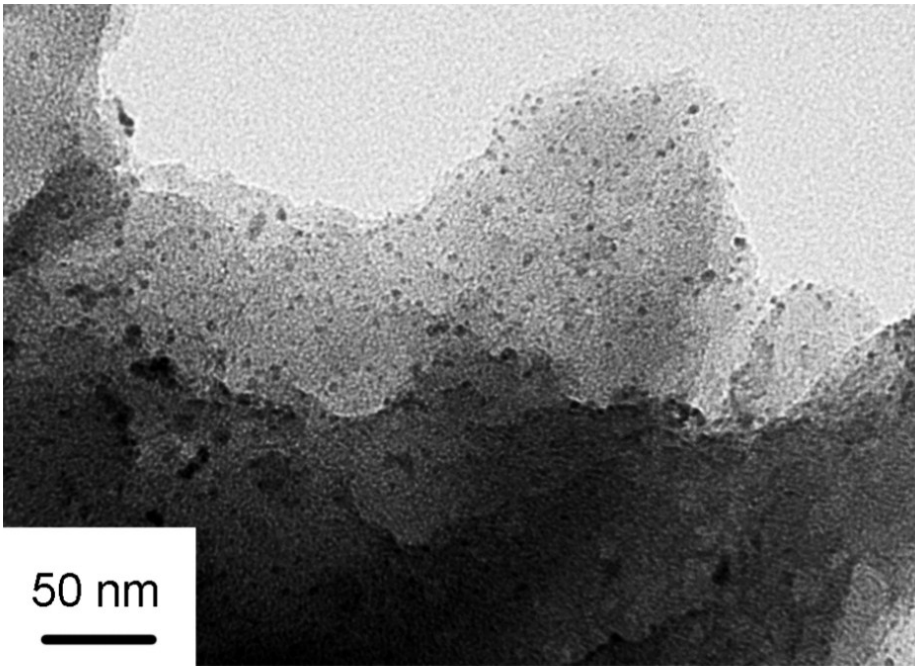


Fig. S14 TEM image of Pd@S-N-PCNs.

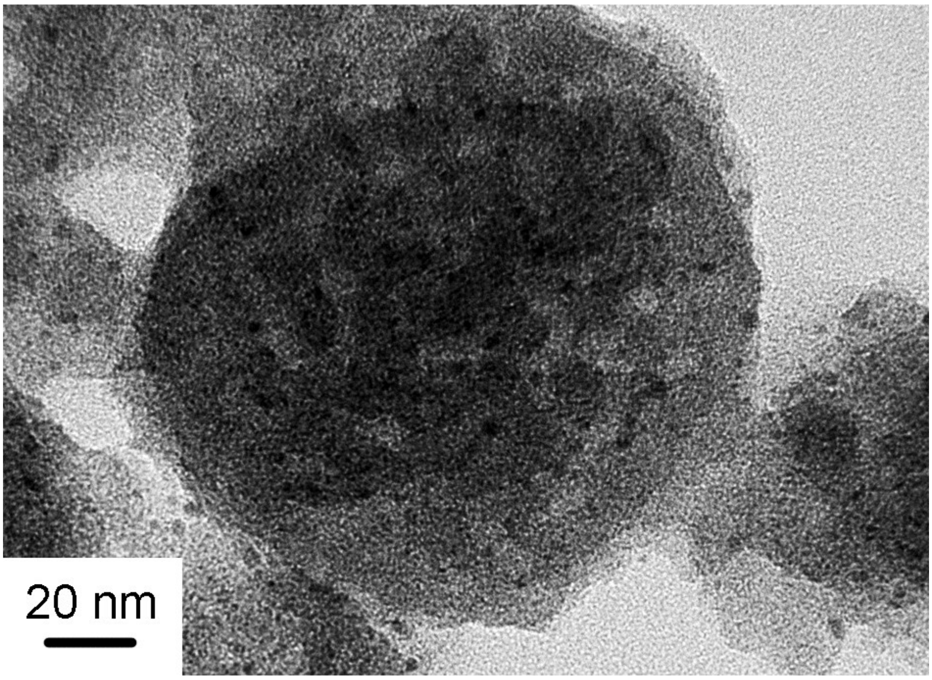


Fig. S15 TEM image of Pd@B-N-PCNs.

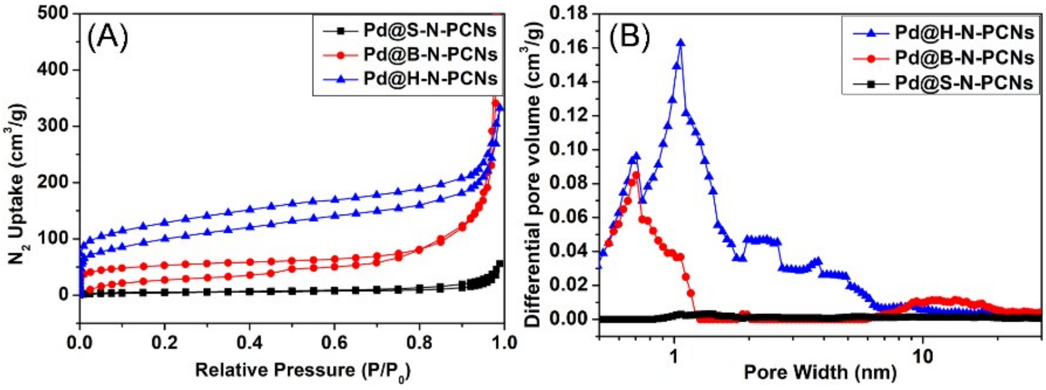


Fig. S16 (A) N_2 adsorption/desorption isotherms and (B) NLDFT pore size distribution of Pd@H-N-PCNs, Pd@B-N-PCNs and Pd@S-N-PCNs, respectively.

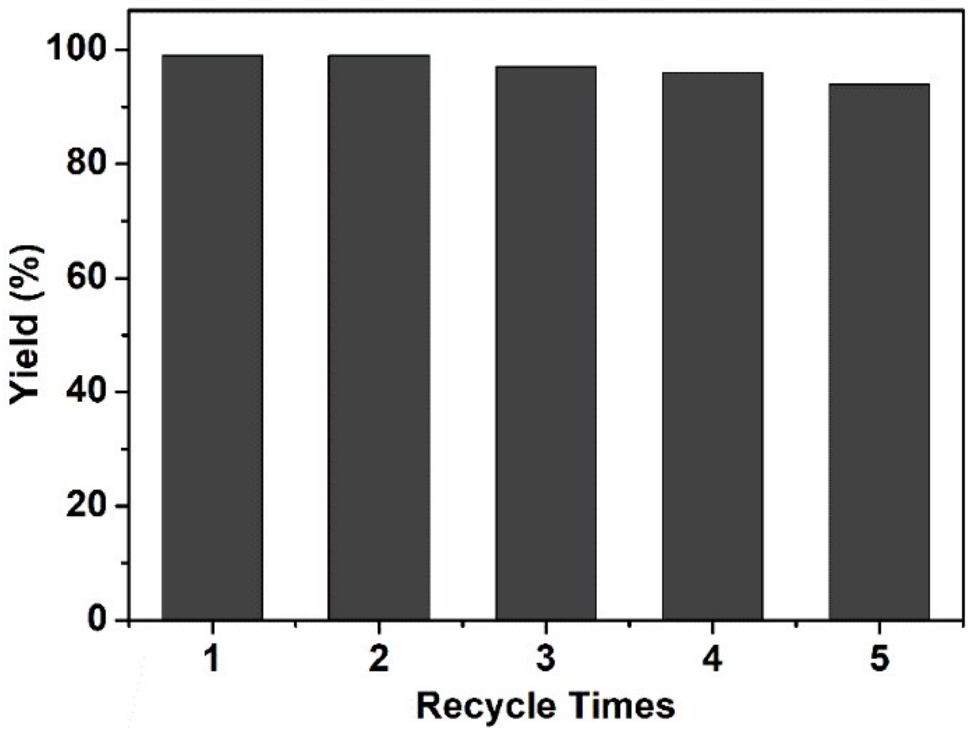


Fig. S17 Recycling tests of Pd@H-N-PCNs for quinolin selective hydrogenation.

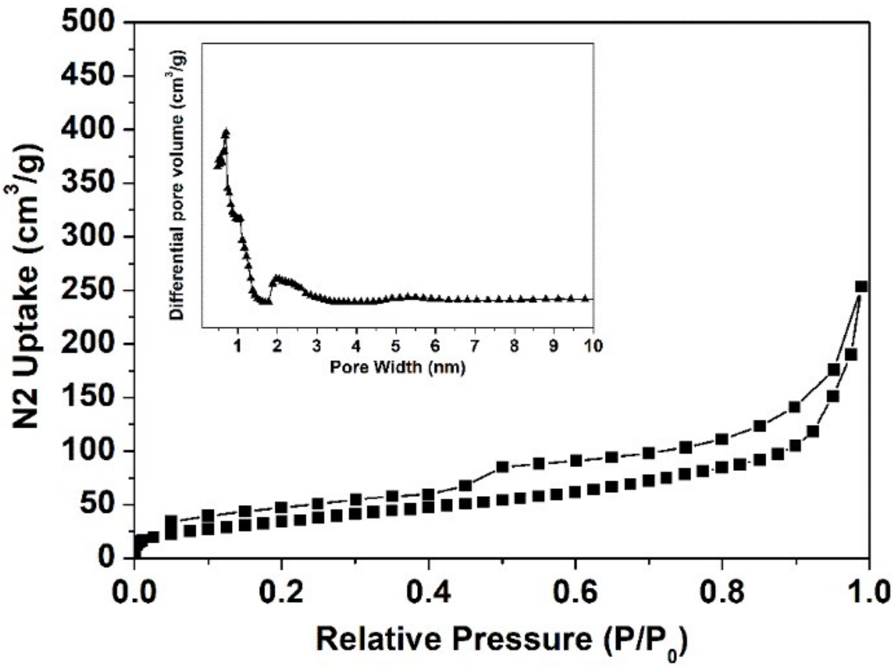


Fig. S18 N_2 adsorption/desorption isotherms and NLDFT pore size distribution of Pd@H-N-PCNs after recycle used.

Table S1. Elemental analysis of various materials.

Sample	Content (%)				
	N	C	H	C:N	C:N by NMR
PLA_{184}-b-$PNVC_{70}$	3.49	62.20	5.78	17.82	17.71
PLA_{184}-b-$PNVC_{190}$	5.15	78.70	5.46	15.28	14.49
PLA_{184}-b-$PNVC_{400}$	6.01	81.58	5.15	13.57	13.18
S-C-MPNs	8.78	82.31	7.12	9.37	--
B-C-MPNs	8.65	84.73	6.99	9.80	--
H-C-MPNs	8.46	85.66	5.87	10.13	--
S-N-PCNs	5.32	92.02	--	17.30	--
B-N-PCNs	5.05	90.36	--	17.89	--
H-N-PCNs	5.10	90.15	--	17.68	--

Table S2. Comparison of the iodine adsorption performance of selected outstanding absorbents reported in the literature.

Absorbents	T (°C)	Iodine (g/g)	Ref.
NiP-CMPs	77	2.02	*Chem. Commun.* **2014**, 50, 8495-8498.
PAF-1	25	1.86	*J. Mater. Chem. A*, **2014**, 2, 7179-7187.
CMPN-3	70.3	2.08	*J. Mater. Chem. A*, **2015**, 3, 87-91.
PAF-24	75	2.76	*Angew. Chem. Int. Ed*, **2015**, 54, 12733-12737.
Azo-Trip	77	2.33	*Polym. Chem.*, **2016**, 7, 643-647.
SCMP-2	80	2.22	*ACS Appl. Mater. Interfaces*, **2016**, 8, 21063-21069.
NTP	75	1.80	*ACS Macro Lett.*, **2016**, 5, 1039-1043.
AzoPPN	77	2.90	*Chem. Eur. J.*, **2016**, 22(33), 11863-11868.
NCMP1	85	2.15	*ACS Appl. Mater. Interfaces*, **2017**, 1944-8244.
NRPP-2	80	2.22	*ACS Appl. Mater. Interfaces,* **2018**, 10,

			16049-16058.
MFM-300(Sc)	80	1.54	*J. Am. Chem. Soc.* **2017**, 139, 16289-16296.
HCNPs	80	3.36	*Macromolecules,* **2016**, 49, 6322-6333.
Cu-BTC	75	1.75	*Chem. Mater.* **2013**, 25, 2591-2596.
H-C-MPNs	**75**	**2.90**	**This work**

Table S3. Catalytic activities comparison for the selective hydrogenation of nitrobenzene catalyzed by selected outstanding heterogeneous catalysts.

Catalysts	Hydrogen sources	Reaction conditions	Time	Recycle runs	Yield (%)	TOF (h^{-1})	References.
Pd/H_2N-SiO_2/Fe_2O_3	1 atm of H_2	2-propanol, Pd (2 μmol) room temperature	90 min	14 (87%)	99	--	*Chem. Mater.*, **2006**, 18, 2459
Pd/HS-SiO_2/Fe_2O_3	1 atm of H_2	2-propanol, Pd (2 μmol) room temperature	290 min	14 (76%)	99	--	*Chem. Mater.*, **2006**, 18, 2459
SiO_2-BisILs[PF_6]-Pd^0	1 atm of H_2	Pd (5 μmol) room temperature	8.5 h	15	100	--	*ACS Catal.*, **2011**, 1, 657.
Pd/PEG4000	1 atm of H_2	Catalyst (100 mg) room temperature	180 min	10 (67%)	100	83	*J.Catal.*, **2012**, 286,184.
Co@Pd/NC	1 atm of H_2	EtOAc, Pd (0.2 mol%)	45 min	7 (~80%)	98	--	*ACS Catal.*, **2015**, 5, 5264

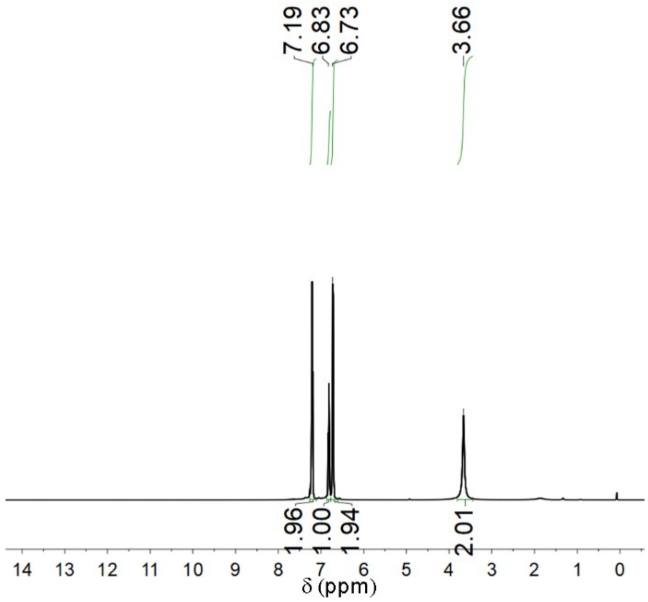
		room temperature					
Pt/ZSM-5	1.0 MPa H_2	EtOH, Catalyst (100 mg) 80 °C	60	--	100	--	*ACS Catal.,* **2015**, 5, 6893
Ru@C_{60}	30 bar of H_2	EtOH, Catalyst (5 mg) 80 °C	4 h	--	90	55.7	*ACS Catal.,* **2016**, 6, 6018
Pd-H-MOF-5	1 atm of H_2	EtOH, Catalyst (0.01 equiv) 60 °C	1.5 h	--	95.6	--	*Chem. Sci.,* **2016**, 7, 7101
Pd/TiO_2-NH_3	0.25 vol % NB, 2.5 vol %, He balance	Catalyst (10 mg) 200 °C	240 min	--	100	876	*ACS Catal.,* **2017**, 7, 1197
Co-Mo-S	11 bar of H_2	Toluene, Catalyst (4.9 mg) 150 °C	7 h	7	99	--	*ACS Catal.,* **2017**, 7, 2698
Zr_{12}-TPDC-Co	40 bar of H_2	Toluene, Catalyst (0.5 mg) 110 °C	42 h	8	100	--	*J. Am. Chem. Soc.,* **2017**, 139, 7004
$LaCu_{0.67}Si_{1.33}$	3.0 MPa H_2	2-propanol, Catalyst (50 mg) 120 °C	9 h	10	100	--	*J. Am. Chem. Soc.,* **2017**, 139, 17089
Pd/PPh3@FDU-12	10 bar of H_2	EtOH, Pd (8 x 10^{-3} mmol) 60 °C	60 min	5	100	11020	*ACS Catal.,* **2018**, 8, 6476

(MeCp)PtH/Zn/SiO_2	50 psi H_2	Toluene, Pd (0.04 mol%) 40 ^oC	24 h	3	99	--	*J. Am. Chem. Soc.,* **2018**, 140, 3940
Fe_3O_4@N-C@Pd Y-S(B)	$NaBH_4$	H_2O:EtOH (1:1), Pd (1 mol%) room temperature	45 min	10 (94%)	81	108	*J.Catal.,* **2018**, 364, 69.
Co-SiCN	5.0 MPa H_2	H_2O:EtOH (4:1), Co (0.024 mmol) 110 ^oC	15 h	5	99	--	*Angew. Chem. Int. Ed.* **2016**, 55, 15175
Pd/C@HCS-H_2O_2	10 bar of H_2	Cyclohexane, Catalyst (50 mg) 120 ^oC	30 min	6 (47%)	100	--	*Chem. Mater.,* **2018,** 30, 2483
Pd@HBPs-1	1 atm of H_2	EtOH, Pd (0.6 mol%) room temperature	60 min	8	100	167	*Macromolecules* **2017**, 50, 9626
Pd@H-N-PCNs	**1 atm of H_2**	**EtOH, Pd (0.0012 mmol) room temperature**	**30 min**	**15 (92%)**	**100**	**833**	***This work***

^{1}H NMR data for compounds of the hydrogenation products.

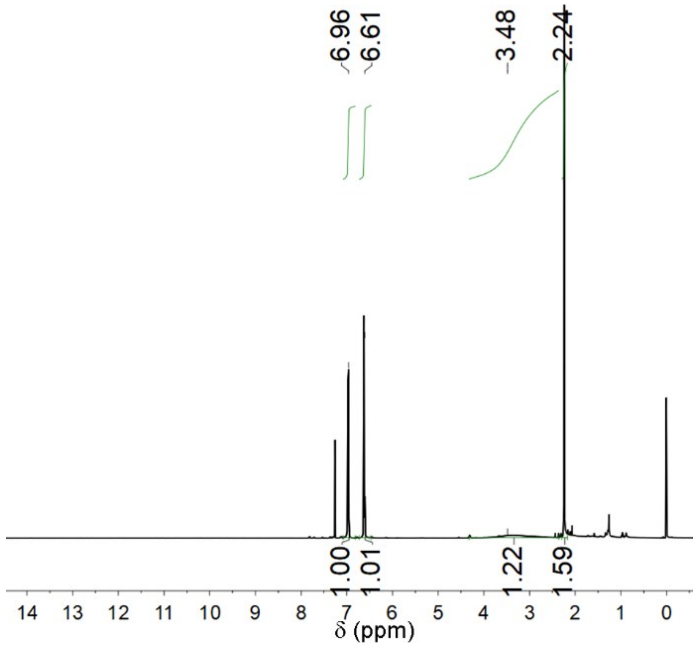
Aniline

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (t, J = 8.0 Hz, 2H); 6.83 (t, J = 7.5 Hz, 1H); 6.73 (d, J = 7.5 Hz, 2H); 3.66 (s, 2H). Isolated yield= 99%.



p-Toluidine:

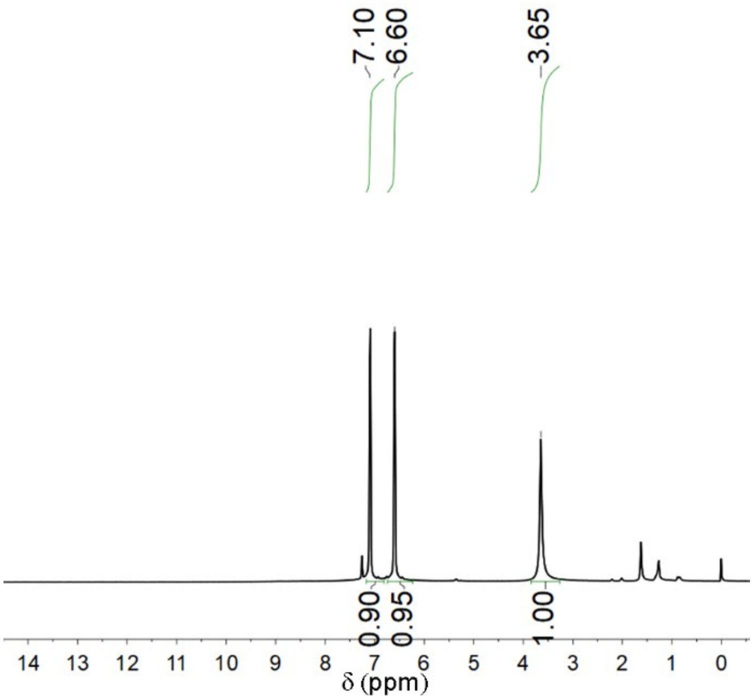
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.96 (d, J = 8.0 Hz, 2H), 6.61 (d, J = 8.0 Hz, 2H), 3.48 (w, 2H), 2.24 (s, 3H). Isolated yield= 99%.



4-Chloroaniline

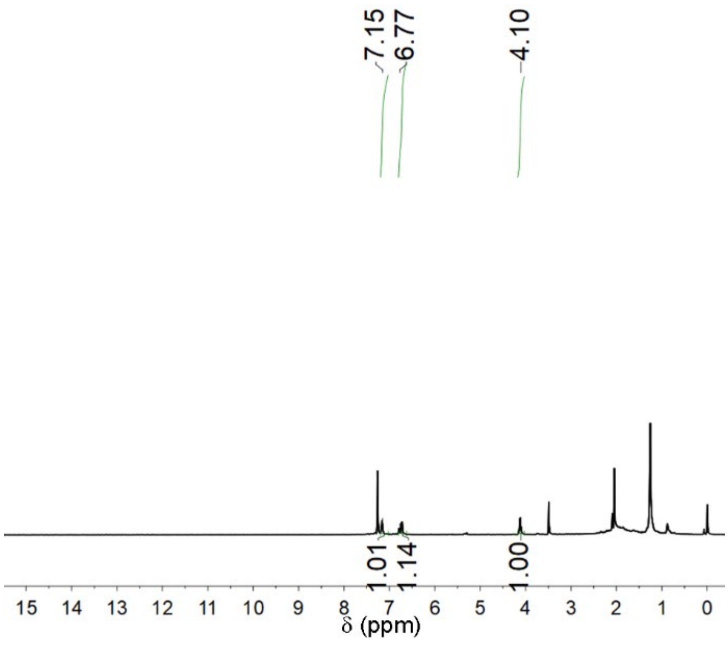
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.10 (d, J = 6.5 Hz, 2H); 6.60 (d, J = 6.5 Hz, 2H); 3.65 (s, 2H).

Isolated yield= 99%.



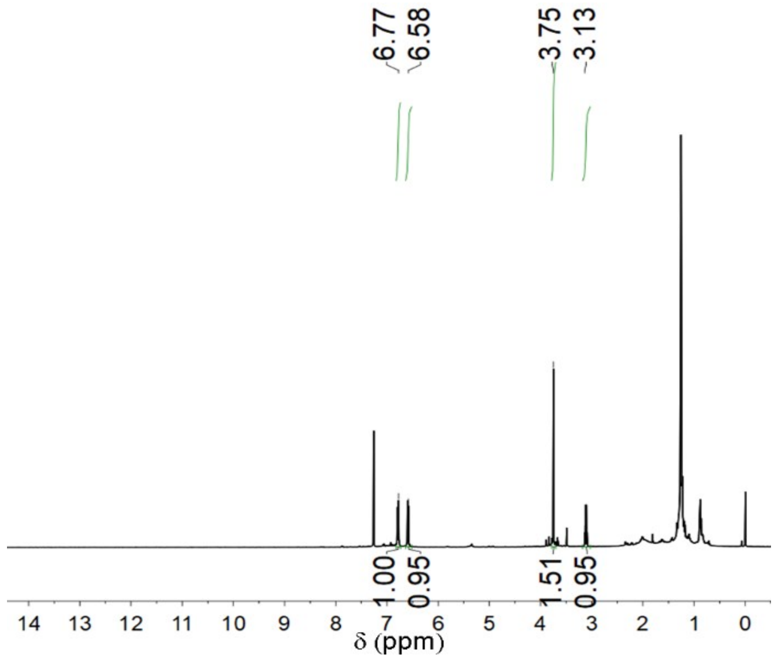
2-Chloroaniline

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.15 (m, 2H); 6.77 (d, J = 7.5 Hz, 2H); 4.10 (bs, 2H). Isolated yield= 90%.



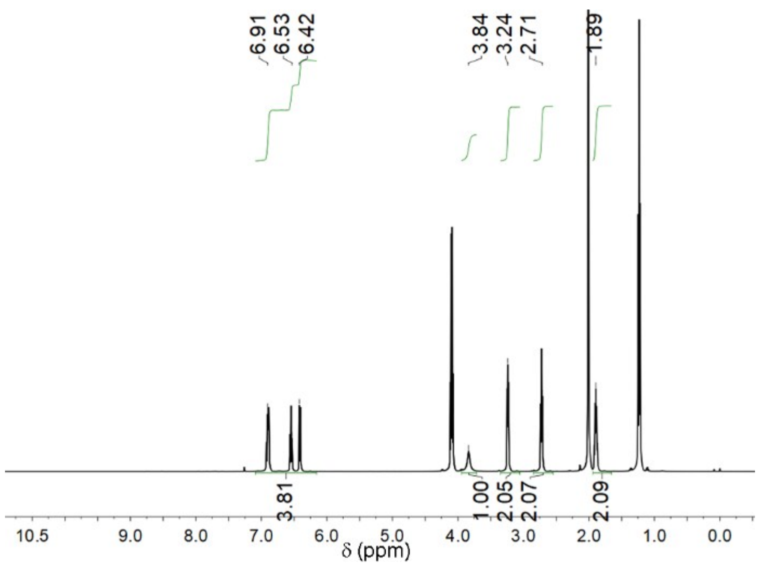
4-Aminoanisole

[1]H NMR (500 MHz, $CDCl_3$): δ 6.77 (d, J = 8.0 Hz, 2H); 6.58 (d, J = 8.0 Hz, 2H); 3.75 (s, 3H); 3.13 (bs, 2H). Isolated yield= 98%.



1,2,3,4-Tetrahydroquinoline

[1]H NMR (500 MHz, $CDCl_3$): δ 6.91-6.42 (m, 4H); 3.84 (s, 1H); 3.24 (t, J = 8.0 Hz, 2H); 2.71 (t, J = 8.0 Hz, 2H); 1.89 (q, J = 8.0 Hz, 2H). Isolated yield: Pd@H-N-PCNs, 92%; Pd@B-N-PCNs, 82%; Pd@S-N-PCNs, 78%.



5,6,7,8-Tetrahydroquinoline

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (m, 1H); 7.29 (d, J = 9.5 Hz, 1H); 7.00 (m, 1H); 2.88 (t, J = 8.0 Hz, 2H); 2.75 (t, J = 8.0 Hz, 2H); 1.89 (m, 2H); 1.78 (m, 2H). Isolated yield: Pd@H-N-PCNs, 8%; Pd@B-N-PCNs, 18%; Pd@S-N-PCNs, 22%.