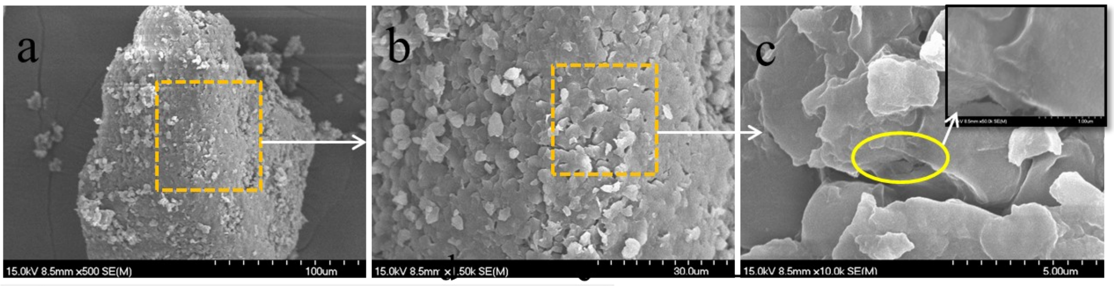
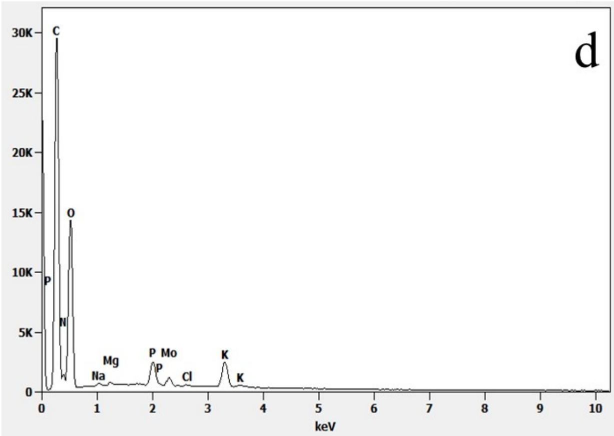
Electronic Supplementary Information (ESI)

Table S1 the hydrogenation performance of nitrobenzene or halogenated nitrobenzene over metal-free carbon materials catalysts

Catalysts	Substrate	Product	Hydrogen source	T or P_{H2}(°C or MPa)	t(h)	Yield (%)	Ref.
graphite	nitrobenzene	aniline	N_2H_4•H_2O	/	2	95.0	1
C_{60}	nitrobenzene	aniline	H_2	150/5	4	10.0	2
AC	3-nitrostyrene	3-aminostyrene	N_2H_4•H_2O	100	2	21.1	3
AC-H_2O_2	3-nitrostyrene	3-aminostyrene	N_2H_4•H_2O	100	2	56.3	3
C_{60}-EDAC	ρ-CNB	ρ-CAN	N_2H_4•H_2O	100	2	99.0	4
C_{60}-EDAC	o-CNB	o-CAN	N_2H_4•H_2O	100	2	99.0	4
NC-950	ρ-CNB	ρ-CAN	N_2H_4•H_2O	90	4	93.4	5
CNS-900	o-CNB	o-CAN	H_2	140/5	24	100.0	6
NSHC	ρ-CNB	ρ-CAN	N_2H_4•H_2O	100	4	93.1	7
NSHC	ρ-bromonitrobenzene	ρ-bromoaniline	N_2H_4•H_2O	100	4	98.0	7
NSHC	ρ-iodonitrobenzene	ρ-iodoaniline	N_2H_4•H_2O	100	4	93.0	7
NPG	ρ-CNB	ρ-CAN	NaBH4	35	2	98.5	8
NPG	ρ-bromonitrobenzene	ρ-bromoaniline	NaBH4	35	2	85.1	8
g-C3N4	m-CNB	m-CAN	N_2H_4•H_2O	90 (visible-light)	18	88.0	9
BNC	ρ-CNB	ρ-CAN	N_2H_4•H_2O	80	10	98.7	10
NC-700	ρ-CNB	ρ-CAN	N_2H_4•H_2O	100	2.5	83.2	11
NC-700	o-CNB	o-CAN	N_2H_4•H_2O	100	2	90.8	11
NC-700	m-CNB	m-CAN	N_2H_4•H_2O	100	2	92.5	11
ONPC	m-CNB	m-CAN	N_2H_4•H_2O	80	4	96.3	12
ONPC	ρ-bromonitrobenzene	ρ-bromoaniline	N_2H_4•H_2O	80	4	90.2	12
ONPC	ρ-iodonitrobenzene	ρ-iodoaniline	N_2H_4•H_2O	80	4	52.8	12
PNC	ρ-CNB	ρ-CAN	N_2H_4•H_2O	Xenon lamp	24	95.7	13
N-CNT_{900}	nitrobenzene	aniline	H_2	50/3	15	˂1.0	14
N-CNT_{900}	nitrobenzene	aniline	H_2	120/3	18	95.0	14
P-CNT_{900}	ρ-CNB	ρ-CAN	H_2	50/3	15	97.0	14
P-CNT_{900}	ρ-bromonitrobenzene	ρ-bromoaniline	H_2	50/3	15	94.0	14
P-CNT_{900}	ρ-iodonitrobenzene	ρ-iodoaniline	H_2	50/3	15	94.0	14
OZG-800	nitrobenzene	aniline	H_2	170/3	26	94.1	15
CN-900	nitrobenzene	aniline	HCOOH	160	12	68.5	16





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Element	Weight %	Atom %
C	**49.36**	**57.38**
N	**9.98**	**9.95**
O	**35.14**	**30.67**
Na	0.21	0.12
Mg	0.09	0.05
P	**1.46**	**0.66**
Cl	0.26	0.10
K	2.61	0.93
Mo	0.90	0.13
Total	100.00	100.00

Fig. S1 SEM image (a-c) and EDS element analysis (de) of yeasts after adding water.

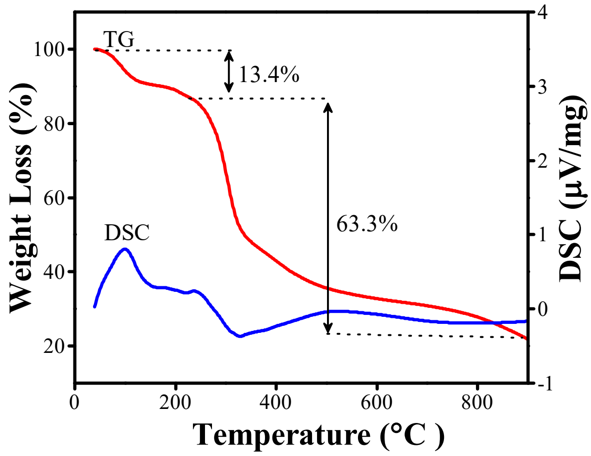


Fig. S2 TG-DSC curve of yeast.

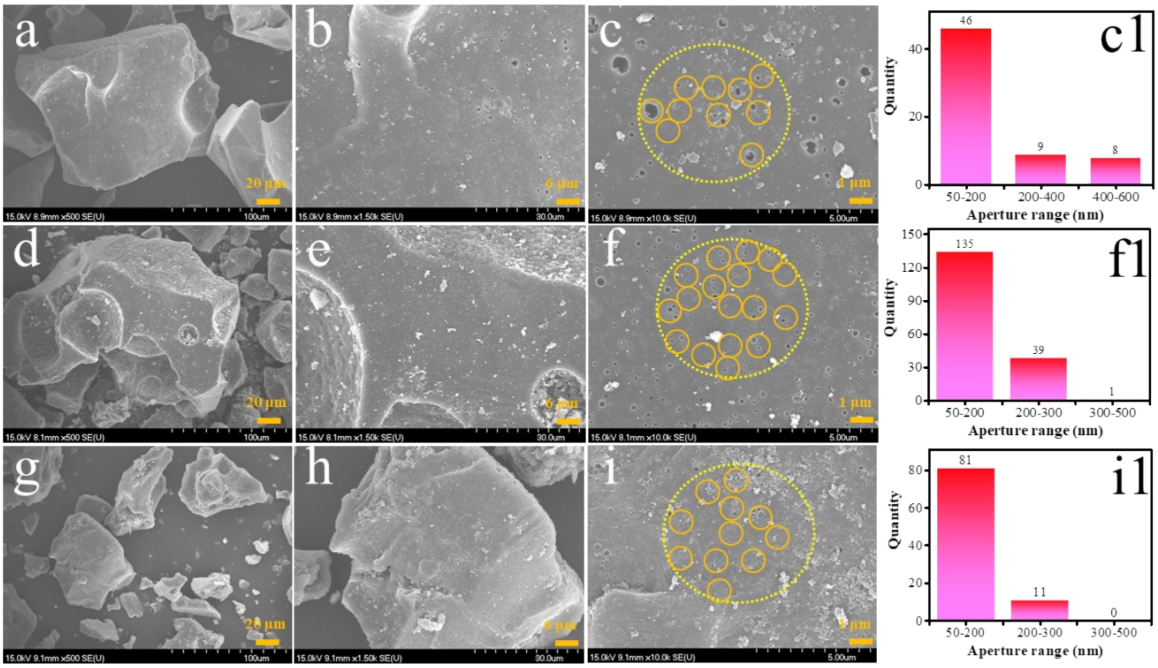


Fig. S3 SEM images and macropore size distribution of the catalysts (Y-NPC-800 ℃ (a-c, c1); Y-NPC-900 ℃ (d-f, f1); Y-NPC-950 ℃ (g-i, i1)).

Table S2 Surface area (S_{BET}), pore volume and average pore size values of the samples

Samples	S_{BET} (m^2g^{-1})	Total pore volume [a] (cm^3g^{-1})	BJH desorption average pore size (nm)
Y-NPC-800 ℃	226	0.13	4.5
Y-NPC-900 ℃	255	0.16	4.7
Y-NPC-950 ℃	355	0.23	4.8

[a] Single point adsorption total pore volume of pores less than 196.2 nm diameter at P/Po 0.99.

Table S3 Crystal plane spacing and full width at half maximum (FWHM) of the samples[17]

Samples	2θ(˚)	d-spacing of (002) (nm)	FWHM (nm)	2θ(˚)	d-spacing of (100) (nm)	FWHM (nm)
Y-NPC-800 ºC	25.056	0.355	0.655	44.497	0.206	0.281
Y-NPC-900 ºC	25.311	0.352	0.555	43.433	0.203	0.185
Y-NPC-950 ºC	24.577	0.361	0.512	43.425	0.208	0.687

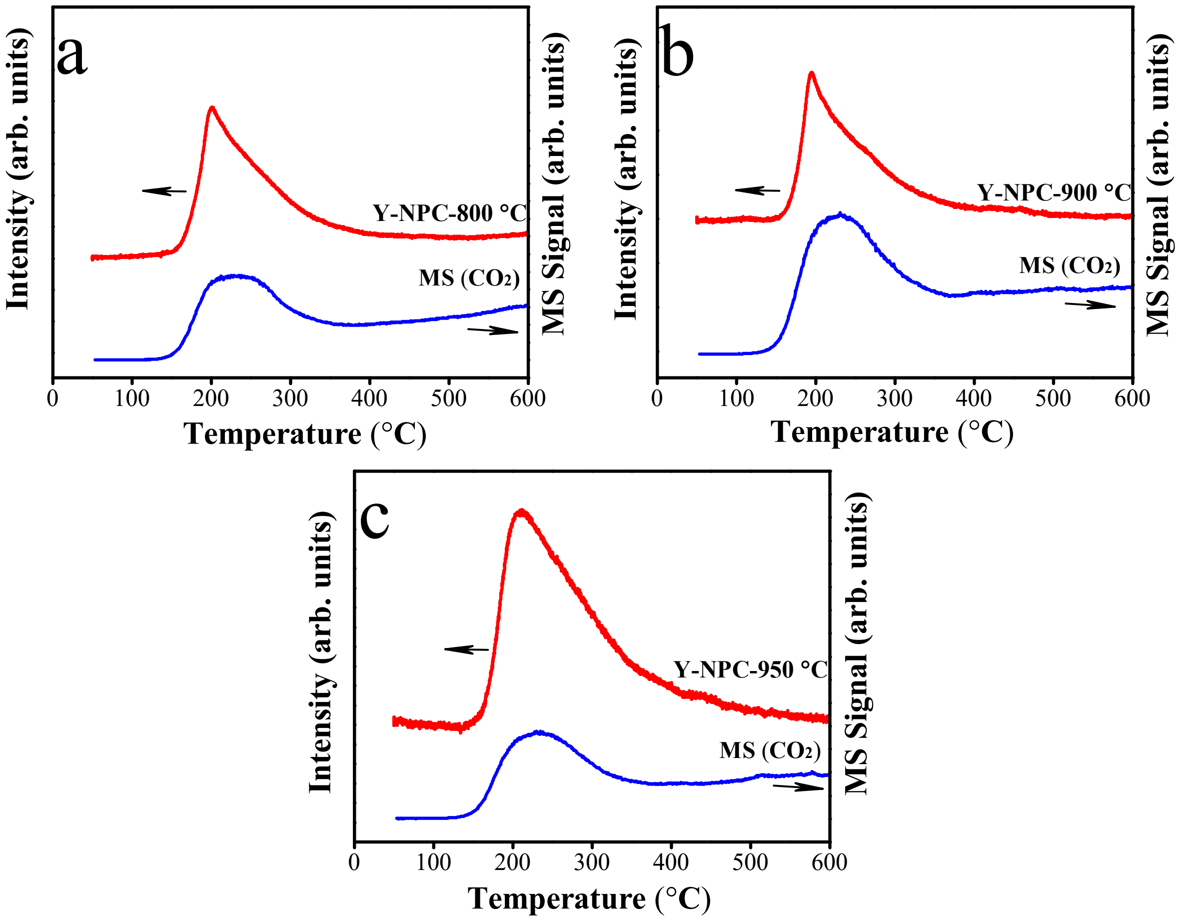


Fig. S4 CO_2-TPD profiles associated with the samples and CO_2-TPD profiles with MS of the samples (a-c).

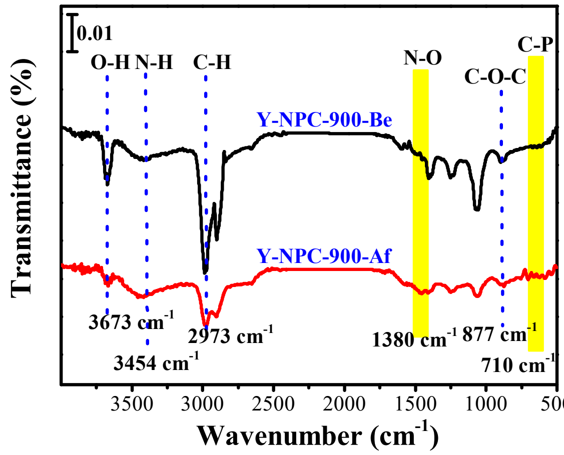


Fig. S5 FTIR spectra of Y-NPC-900 °C.

Table S4 Elemental analysis of the samples by XPS

Atomic Content%	C	O	N	P	N-Q	P-O	P-C	P-N
Y-NPC-800 °C	80.09	14.87	4.39	0.65	2.23	0.12	0.46	0.07
Y-NPC-900 °C	87.30	9.16	3.17	0.37	1.68	0.09	0.15	0.13
Y-NPC-950 °C	88.24	9.20	2.36	0.24	1.25	0.05	0.11	0.08

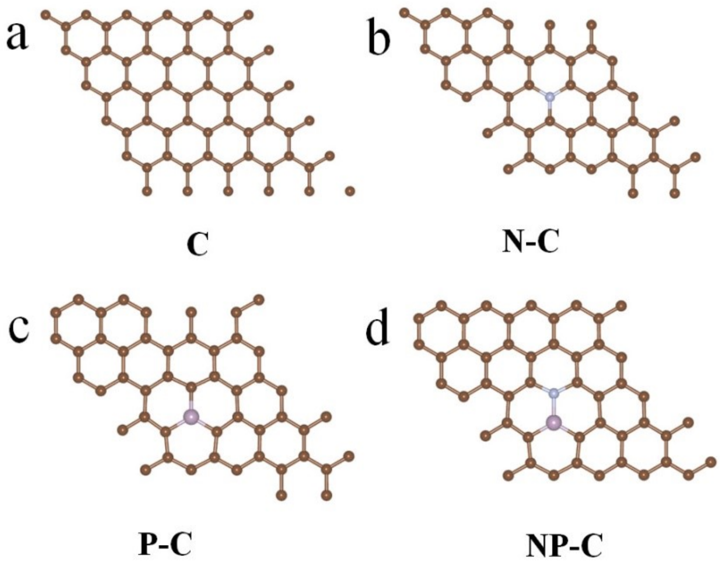


Fig. S6 Structures of C, N-C, P-C and NP-C (a-d) contain 50 carbon atoms, 1 nitrogen atom and 1 phosphorus atom. Carbon: brown, nitrogen: light blue, and phosphorus: purple.

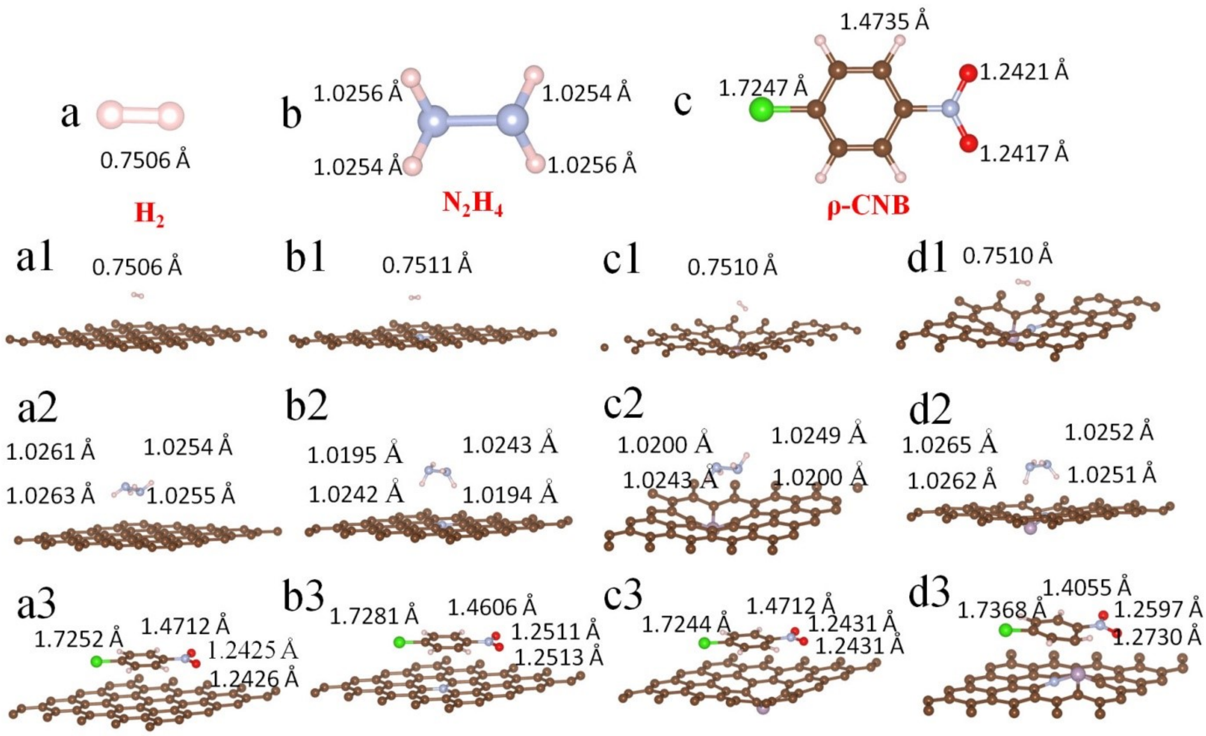


Fig. S7 Optimized free molecules for H_2(a), N_2H_4 (b)and ρ-CNB(c); adsorption model of H_2, N_2H_4, ρ-CNB molecules over C-C (a1, a2, a3), N-C (b1, b2, b3), P-C (c1, c2, c3) and NP-C (d1, d2, d3), respectively.

Table S5 Adsorption energy of H_2 over C-C, N-C, P-C and NP-C

System	*	H_2	$*H_2$	ΔE_{ads} (eV)
C	-462.31	-6.77	-469.14	-0.06
N-C	-460.20	-6.77	-467.05	-0.08
P-C	-453.72	-6.77	-462.40	-1.91
NP-C	-452.24	-6.77	-461.99	-2.98

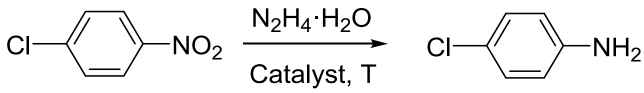
Table S6 Adsorption energy of N_2H_4 over C-C, N-C, P-C and NP-C

System	*	N_2H_4	$*N_2H_4$	ΔE_{ads} (eV)
C	-462.31	-30.18	-492.70	-0.21
N-C	-460.20	-30.18	-490.70	-0.32
P-C	-453.72	-30.18	-486.02	-2.12
NP-C	-452.24	-30.18	-485.71	-3.29

Table S7 Adsorption energy of ρ-CNB over C-C, N-C, P-C and NP-C

System	*	ρ-CNB	*ρ-CNB	ΔE_{ads} (eV)
C	-462.31	-90.16	-553.11	-0.64
N-C	-460.20	-90.16	-551.06	-0.70
P-C	-453.72	-90.16	-546.40	-2.52
NP-C	-452.24	-90.16	-544.93	-2.53

Table S8 Catalytic transfer hydrogenation performance of catalyst[a]



Entry	Catalyst	$m_{Catalyst}$(mg)	S_{BET} ($m^2 \cdot g^{-1}$)	T(℃)	ρ-CNB Con.(%)	ρ-CAN Sel.(%)	PR [b] ($molg^{-1}h^{-1}$)	PR [b] /S_{BET} ($molh^{-1}m^{-2}$)	PR [b] /S_{BET}P-N[c] ($molh^{-1}m^{-2}$)
1[11]	--	--	--	100	1.2	99	--	--	--
2[11]	NC-700	40	601	100	100	83.2	4.2×10^{-3}	6.9×10^{-6}	/
3[11]	Graphite	40	/	100	30.2	>99	1.1×10^{-3}	/	/
4[11]	CNTs	40	/	100	27.7	>99	9.9×10^{-4}	/	/
5[11]	g-C_3N_4	40	/	100	42.5	>99	1.5×10^{-3}	/	/
6	CSs	40	4.3	100	12.8	>99	6.4×10^{-4}	1.4×10^{-4}	/
7	Y-NPC-800 ℃	40	226	100	46.7	91.8	2.1×10^{-3}	0.9×10^{-5}	1.3×10^{-4}
8	Y-NPC-900 ℃	40	255	100	100	>99.0	5.0×10^{-3}	2.0×10^{-5}	1.5×10^{-4}
9	Y-NPC-950 ℃	40	354	100	75.4	98.4	3.8×10^{-3}	1.0×10^{-5}	1.3×10^{-4}
10	Y-NPC-900 ℃	40	255	90	96.0	>99.0	4.8×10^{-3}	1.9×10^{-5}	1.5×10^{-4}
11	Y-NPC-900 ℃	40	255	80	90.0	>99.0	4.5×10^{-3}	1.8×10^{-5}	1.4×10^{-4}
12	Y-NPC-900 ℃	40	255	60	44.6	>99.0	3.0×10^{-3}	1.2×10^{-5}	9.2×10^{-5}
13	Y-NPC-900 ℃	20	255	100	79.2	>99.0	7.9×10^{-3}	3.0×10^{-5}	2.3×10^{-4}
14[18d]	1.36%Pd/CSs	0.53	/	80	100	86.2	1.1×10^{-2}	/	/

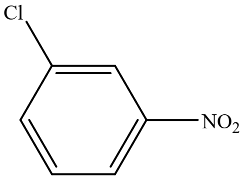
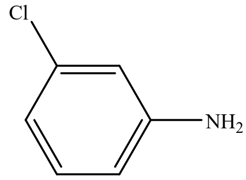
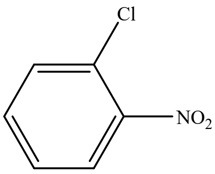
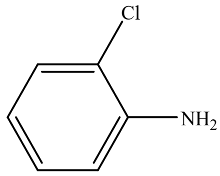
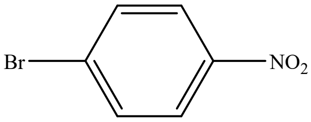
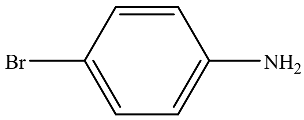
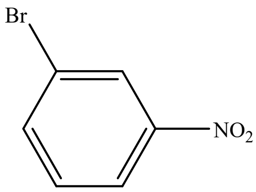
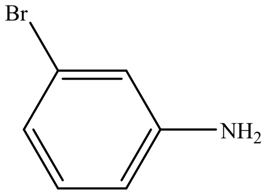
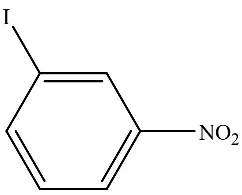
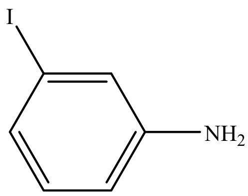
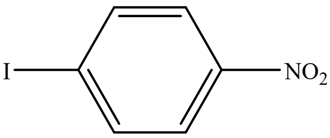
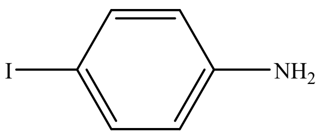
[a] Reaction conditions: 0.5 mmol reactant, 5 mmol hydrazine hydrate ($N_2H_4 \bullet H_2O$, 85 wt.%), 40 mg Y-NPC-900 ℃, 4 mL solvent ($V_{ethanol}/V_{water}$ = 1/3), 100 ℃, 2.5 h.

[b] Production rate per catalyst weight (PR) = mole of converted substrate × ρ-CAN Sel. (%)/ g catalyst × h reaction time (mol $g^{-1}h^{-1}$).

[c] The P-N content is in Table S4.

[d] Reaction conditions: substrate (1 mmol), hydrazine hydrate (10 mmol), 1.36 wt.% Pd (5 $\times10^{-4}$ mmol), solvent (ethanol/H_2O: 1 mL/1 mL), air, 1.5 h.

Table S9 The catalytic performance of Y-NPC-900 ℃ for the transfer hydrogenation of halonitrobenzenes

Entry	Substrate	Product	Con. (%)	Sel. (%)
1			96.7	>99.9
2			99.3	>99.9
3			98.0	97.1
4			83.1	98.9
5			82.5	97.2
6			100	80.2

Reaction conditions: 0.5 mmol reactant, 5 mmol hydrazine hydrate ($N_2H_4 \cdot H_2O$, 85 wt.%), 40 mg Y-NPC-900 ℃, 4 mL solvent ($V_{ethanol}/V_{water}$ = 1/3), 100 ℃, 2.5 h.

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