SUPPORTING INFORMATION

Double-doped Pd/$C_{N\text{-}B}$ nano-architectures for hydrogen evolution and hydrogenation reaction in water

Adam W. Augustyniak

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland
adam.augustyniak@uwr.edu.pl

Experimental Section

The phenylacetylene conversion, styrene and ethylbenzene selectivity, were estimated in accordance with the formula below by analyzing the peak areas and factors of the reactants and products calibrated by gas chromatography:

$$\alpha = \frac{A_{wz} \cdot n_s}{A_s \cdot n_{wz}}$$

α - *correction factors*, **A_{wz}** - *internal standard area*, **A_s** - *substrate area*, **n_{wz}** - *number of moles of internal standard*, **n_s** - *number of moles of substrate*

$$Conversion\ (\%) = 100\% - (\frac{n_k}{n_p} \cdot 100\%)$$

n_k - *number of moles of unreacted substrate*

$$n_k = \frac{\alpha \cdot n_{wz} \cdot A_s}{A_{wz}}$$

n_s - *initial number of substrate moles*

$$Selectivity\ (\%) = A_p(\%) \cdot \frac{100\%}{A_{ST}(\%) + A_{EB}\ (\%)}$$

A_p- *product area (styrene (ST) or ethylbenzene (EB))*

A_{ST} - styrene area

A_{EB} - ethylbenzene area

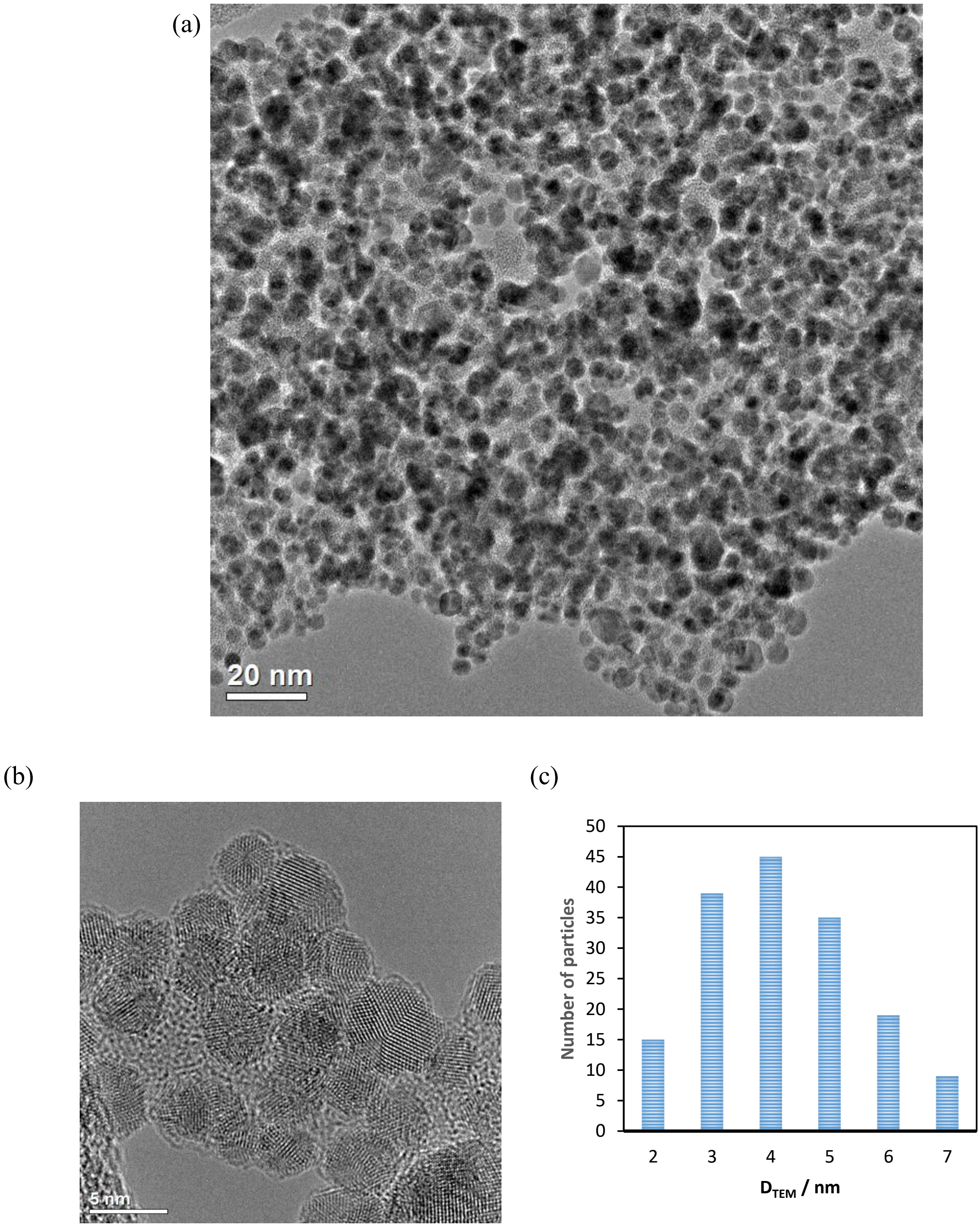


Fig. S1 TEM images of Pd/$C_{N\text{-}B}$ (a-b) and particle size distribution (c).

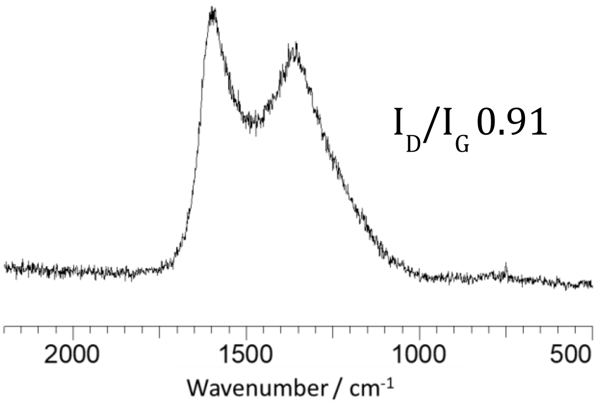


Fig. S2 Raman spectrum of Pd/C$_{PYMO}$.

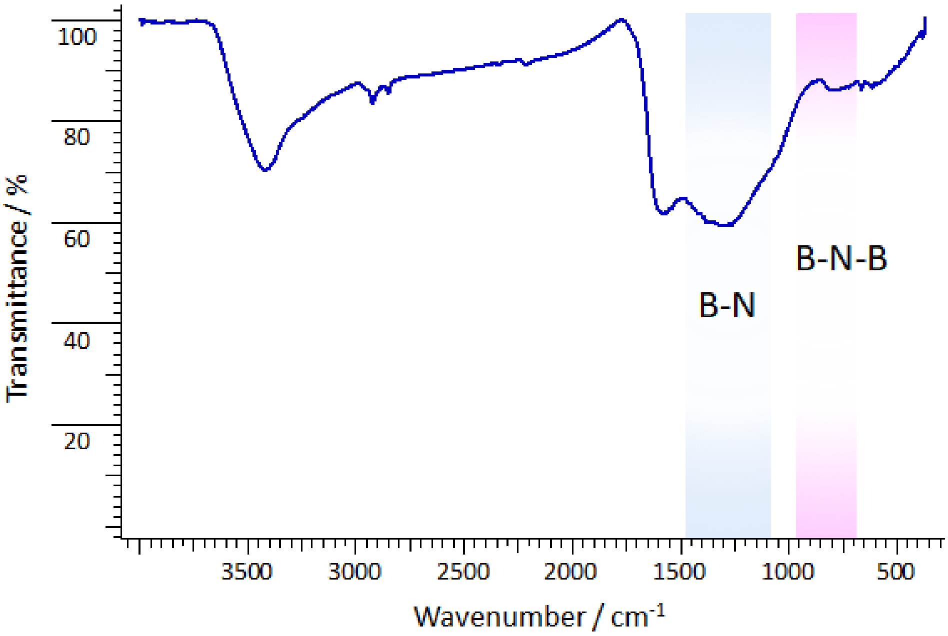


Fig. S3 IR spectrum of **Pd/C$_{N-B}$**.

Table S1. N, C, H, and B elements content.

Catalyst	N (%)[a]	C (%)[a]	H (%)[a]	B (%)[b]
Pd/C$_{N-B}$	5.39	17.28	0.78	5.7
Pd/C$_{PYMO}$	5.22	37.82	2.226	-

[a] Elemental analysis, [b] ICP-OES

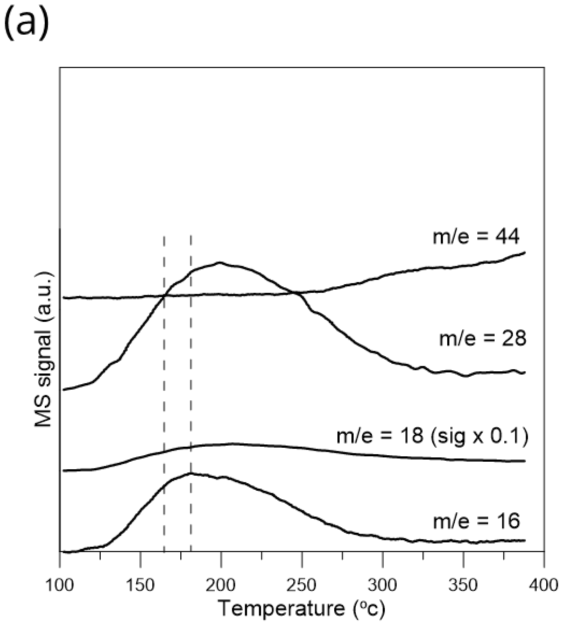


Fig. S4 (a) NH_3-TPD–MS and (b) CO_2-TPD–MS profiles for **Pd/C$_{N\text{-}B}$**

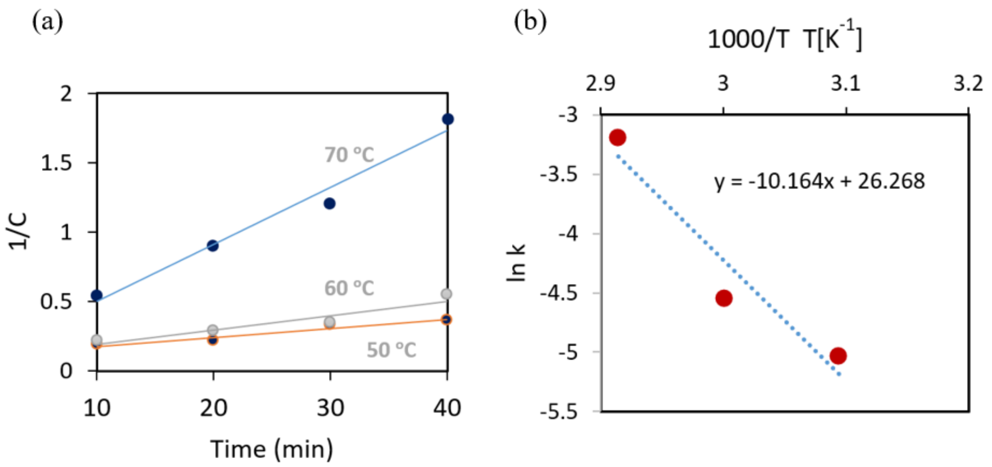


Fig. S5 (a) Time dependency of the (1/C) ratio for the second-order phenylacetylene hydrogenation at 50-70 °C. **(b)** Arrhenius plot for the hydrogenation of phenylacetylene using the rate constants calculated from the second-order plots.

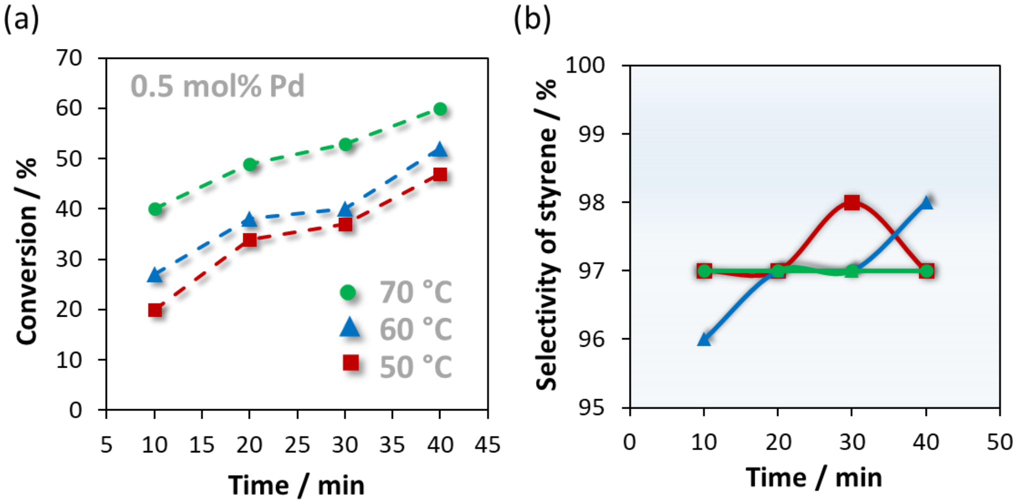
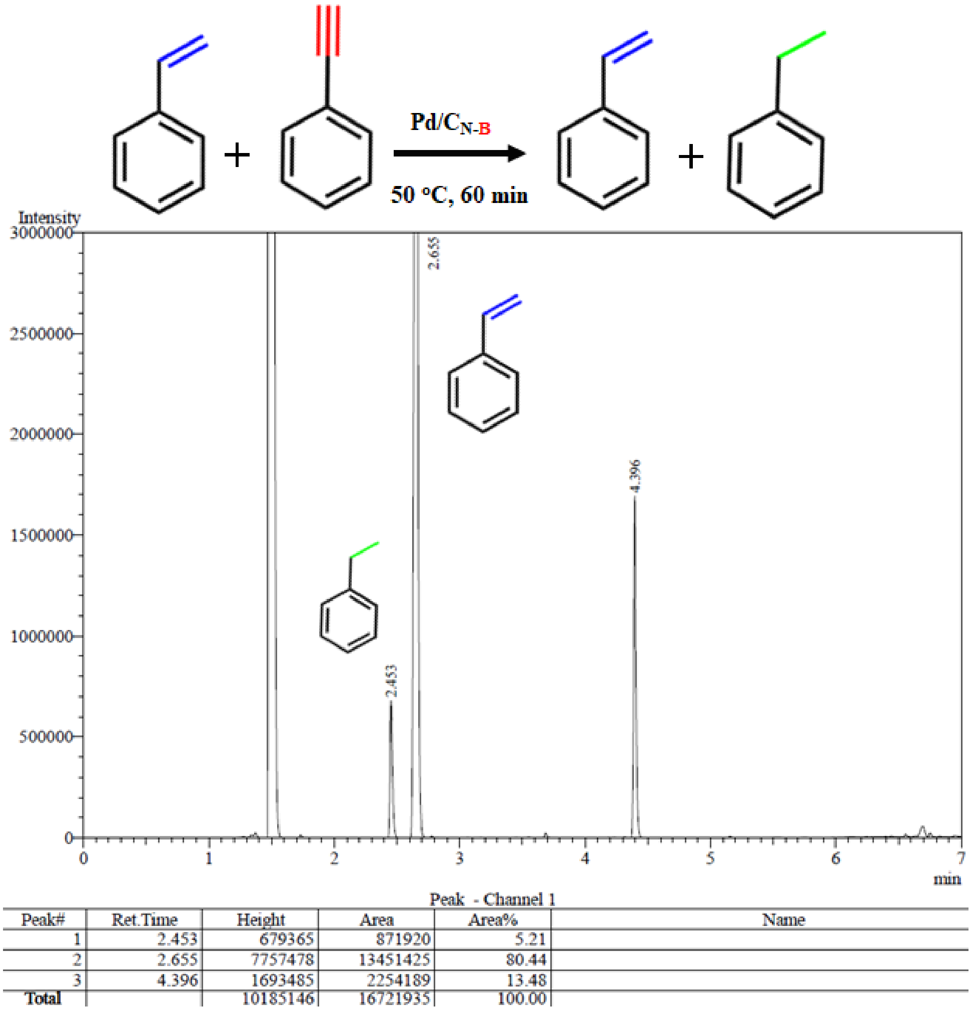
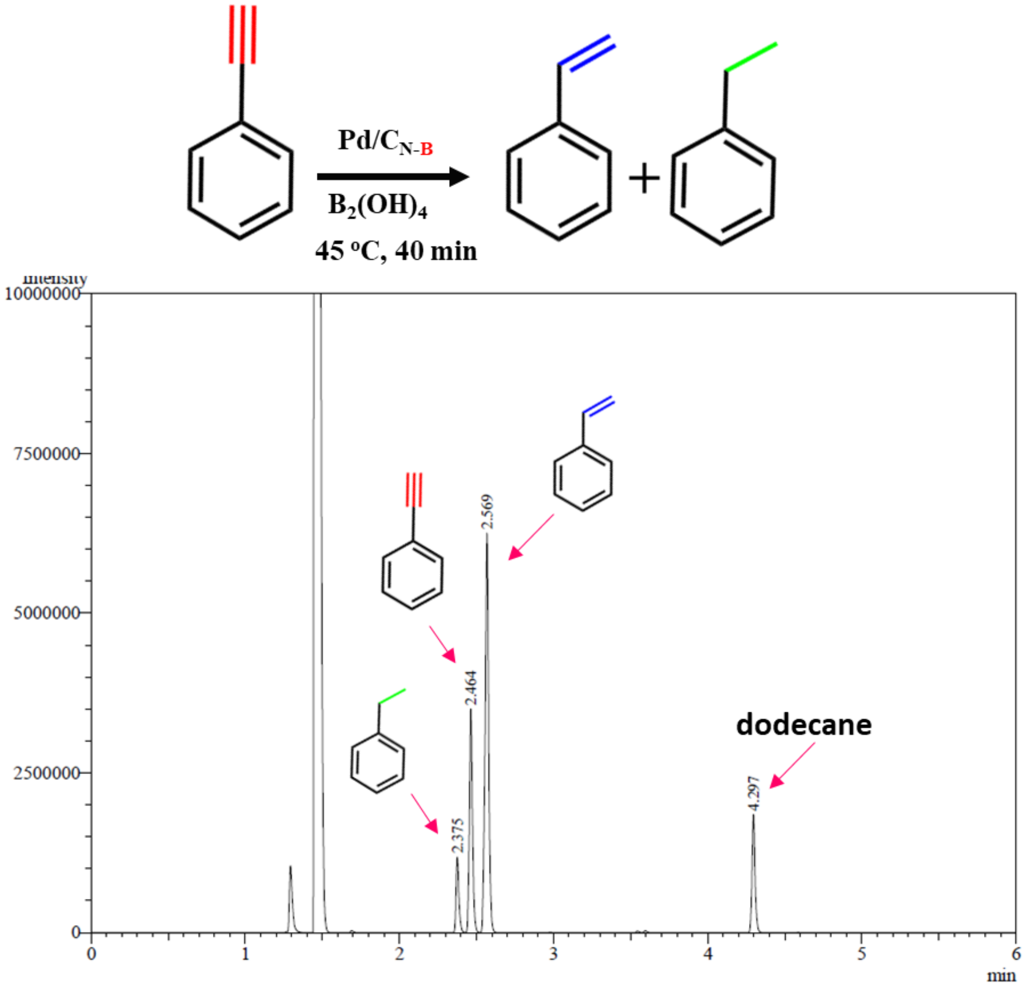


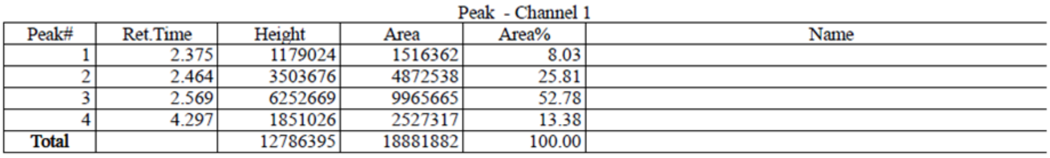
Fig. S6 Tme profiles of conversion of phenylacetylene catalyzed by **Pd/C$_{N-B}$** (a) and selectivity to styrene profile (b). Reaction conditions: 0.91 mmol of phenylacetylene, catalyst **Pd/C$_{N-B}$** (0.5 mol% Pd), 1 mmol of NH_3BH_3, 2 mL of H_2O.



Peak#	Ret.Time	Height	Area	Area%	Name
1	2.453	679365	871920	5.21	
2	2.655	7757478	13451425	80.44	
3	4.396	1693485	2254189	13.48	
Total		10185146	16721935	100.00	

Fig. S7 GC-FID chromatogram of the hydrogenation of a mixture of phenylacetylene and styrene using **Pd/C$_{\text{N-B}}$** as the catalyst. Reaction conditions: 1 mmol of phenylacetylene and 1 mmol of styrene, 1 mmol of BH_3NH_3 catalyst **Pd/C$_{\text{N-B}}$** (1 mol% Pd), 2 mL of H_2O.



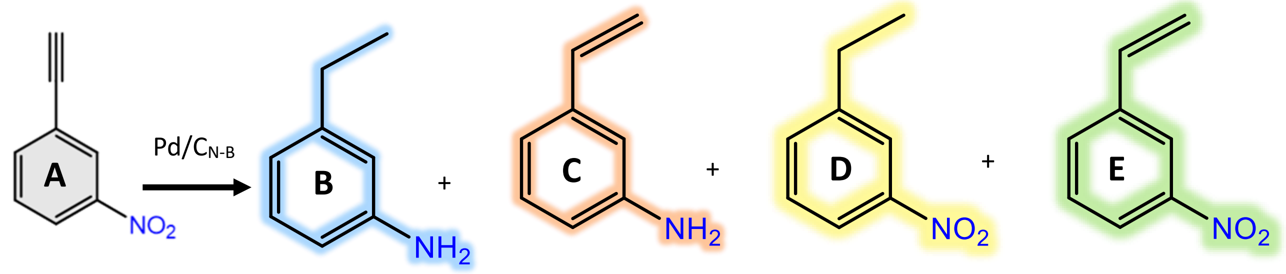


Peak - Channel 1

Peak#	Ret.Time	Height	Area	Area%	Name
1	2.375	1179024	1516362	8.03	
2	2.464	3503676	4872538	25.81	
3	2.569	6252669	9965665	52.78	
4	4.297	1851026	2527317	13.38	
Total		12786395	18881882	100.00	

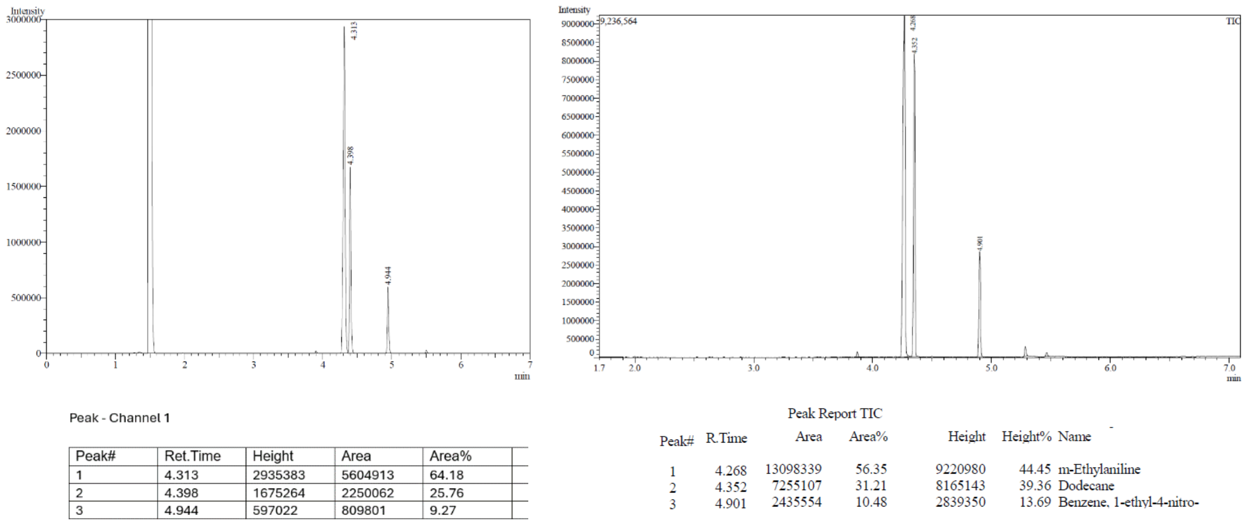
Fig. S8 GC-FID chromatogram of the hydrogenation of phenylacetylene using **Pd/C$_{N-B}$** as the catalyst. Reaction conditions: 0.91 mmol of phenylacetylene and 1 mmol of $B_2(OH)_4$, catalyst **Pd/C$_{N-B}$** (1 mol% Pd), 2 mL of H_2O.

Table S2 Hydrogenation of 3-nitrophenylacetylene.



	Conversion (%) A	Selectivity (%) B	C	D	E
40 °C	100	37.6	4.6	18.4	39.4
50 °C	100	36.7	4.8	17.7	40.8
60 °C	100	87.4	-	12.6	-

Reaction conditions: The catalyst (0.5 mol%), 3-nitrophenylacetylene (0.91 mmol), NH_3BH_3 (1 mmol), water (2 mL), 40 °C, 30 min.


(a) (b)

Peak - Channel 1

Peak#	Ret.Time	Height	Area	Area%
1	4.313	2935383	5604913	64.18
2	4.398	1675264	2250062	25.76
3	4.944	597022	809801	9.27

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                    Peak Report TIC
Peak#  R.Time     Area    Area%        Height  Height%  Name

  1     4.268  13098339   56.35       9220980    44.45  m-Ethylaniline
  2     4.352   7255107   31.21       8165143    39.36  Dodecane
  3     4.901   2435554   10.48       2839350    13.69  Benzene, 1-ethyl-4-nitro-
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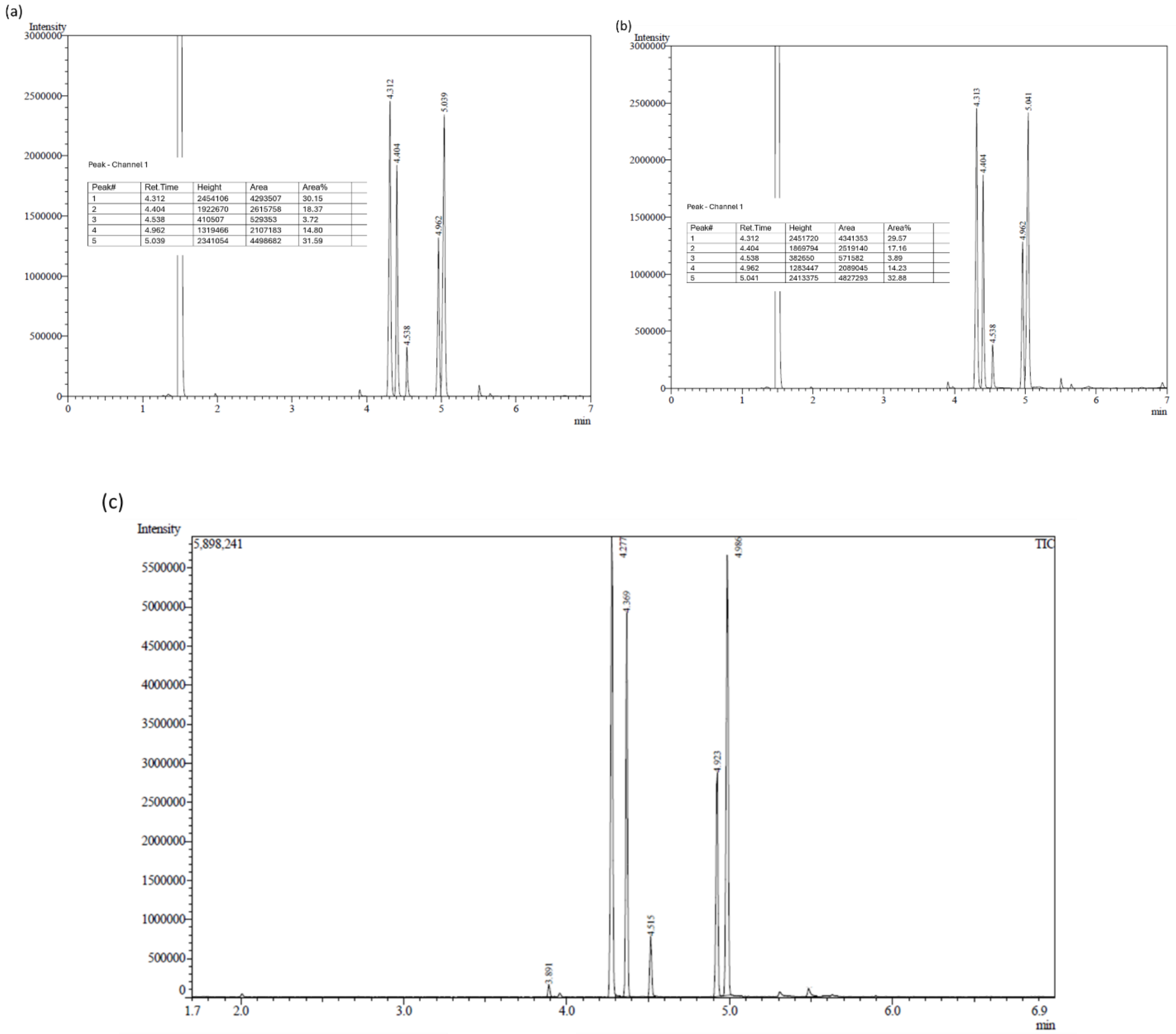
Fig. S9 GC-FID chromatogram (a) and GC-MS spectrum (b) for the 3-nitrophenylacetylene hydrogenation at 60 °C for 30 min.



Peak - Channel 1

Peak#	Ret.Time	Height	Area	Area%
1	4.312	2454106	4293507	30.15
2	4.404	1922670	2615758	18.37
3	4.538	410507	529353	3.72
4	4.962	1319466	2107183	14.80
5	5.039	2341054	4498682	31.59

Peak - Channel 1

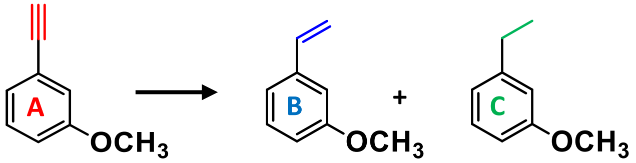
Peak#	Ret.Time	Height	Area	Area%
1	4.312	2451720	4341353	29.57
2	4.404	1869794	2519140	17.16
3	4.538	382650	571582	3.89
4	4.962	1283447	2089045	14.23
5	5.041	2413375	4827293	32.88

Peak Report TIC

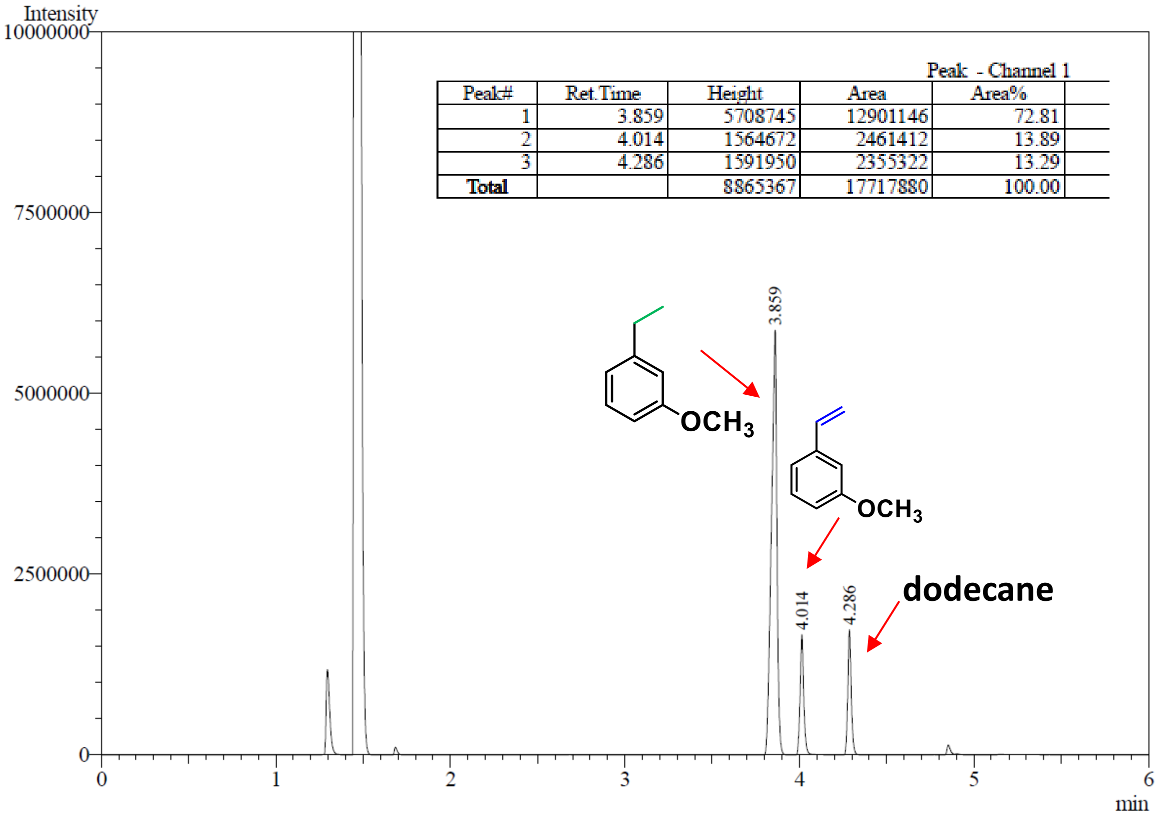
Peak#	R.Time	Area	Area%	Height	Height%	Name
1	4.277	5323696	30.28	5894478	28.98	m-Ethylaniline
2	4.369	3683921	20.95	4913546	24.15	Dodecane
3	4.515	620009	3.53	768985	3.78	4-Aminostyrene
4	4.923	2526089	14.37	2864959	14.08	1-Ethyl-3-nitrobenzene
5	4.986	5165398	29.38	5634461	27.70	Benzene, 1-ethenyl-3-nitro-

Fig. S10 GC-FID chromatogram for the 3-nitrophenylacetylene hydrogenation at 40 ^{o}C (a), 50 ^{o}C (b), and GC-MS spectrum for 50 ^{o}C (c).

Table S3 Hydrogenation of 3-ethynylanisole

		
Conversion (%)	Selectivity (%)	
A	**B**	**C**
100	16	84

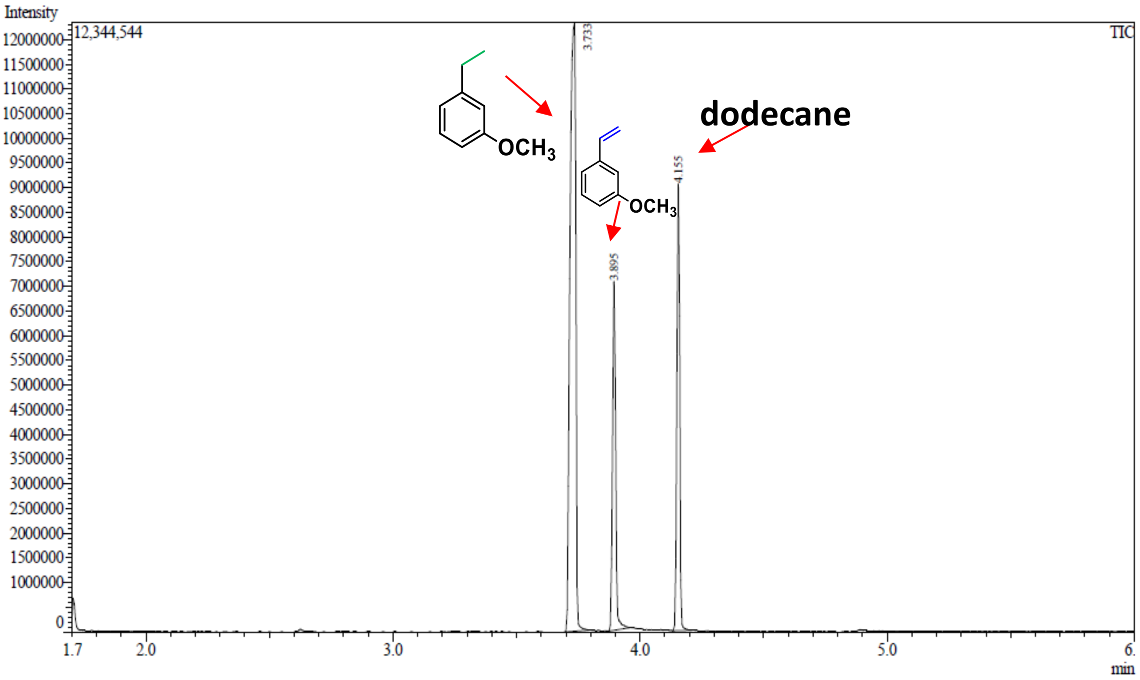
Reaction conditions: The catalyst (1 mol%), 3-ethynylanisole (0.91 mmol), NH_3BH_3 (1 mmol), water (2 mL), 70 °C, 40 min.



Peak - Channel 1

Peak#	Ret.Time	Height	Area	Area%
1	3.859	5708745	12901146	72.81
2	4.014	1564672	2461412	13.89
3	4.286	1591950	2355322	13.29
Total		8865367	17717880	100.00

Fig. S11 GC-FID chromatogram for the 3-ethynylanisole hydrogenation.

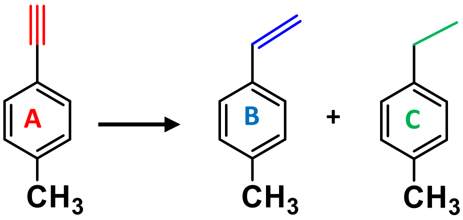


Peak Report TIC

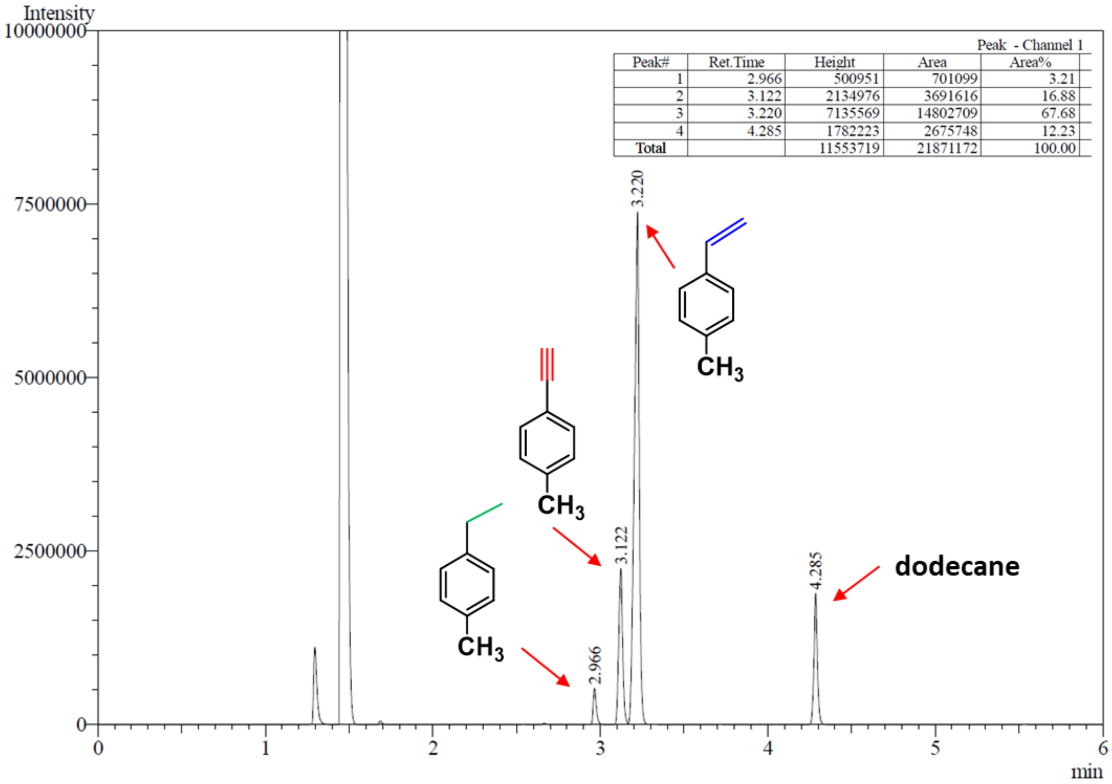
Peak#	R.Time	Area	Area%	Height	Height%	Name
1	3.733	20218924	60.24	12329236	43.36	3-Ethylanisole
2	3.895	6169733	18.38	7062642	24.84	Benzene, 1-ethenyl-3-methoxy-
3	4.155	7175330	21.38	9045620	31.81	Dodecane
		33563987	100.00	28437498	100.00	

Fig. S12 GC-MS spectrum for the 3-ethynylanisole hydrogenation.

Table S4 Hydrogenation of 4-ethynyltoluene

		
Conversion (%)	Selectivity (%)	
A	**B**	**C**
79	95	5

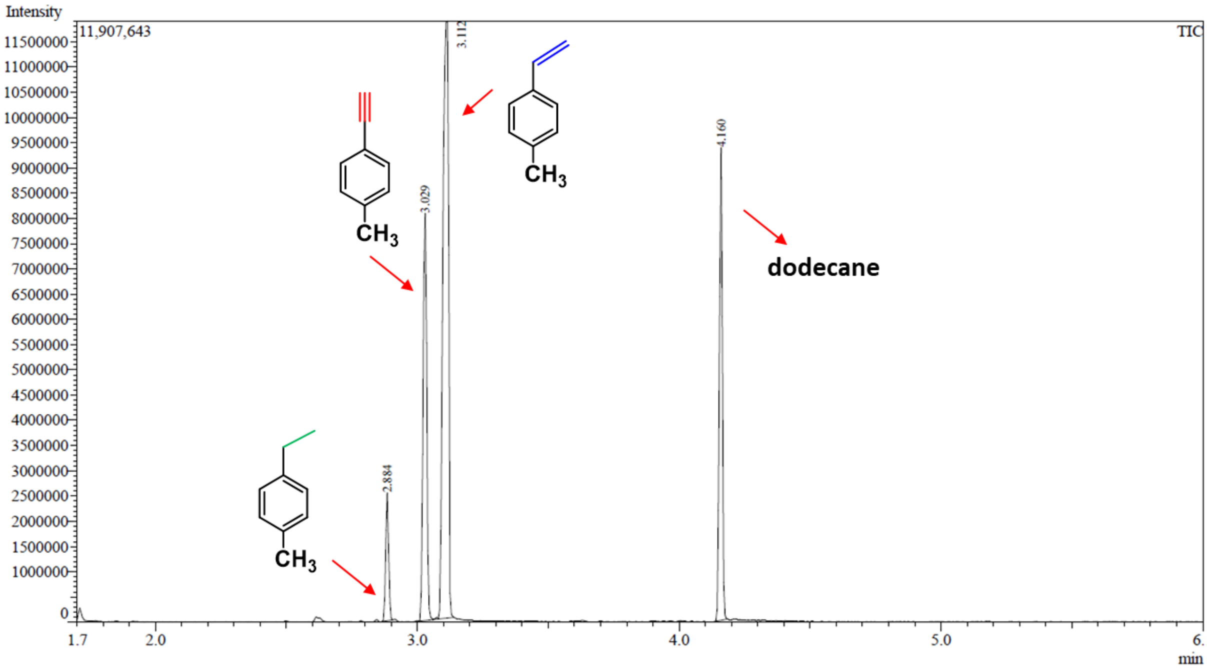
Reaction conditions: The catalyst (1 mol%), 4-ethynyltoluene (0.91 mmol), NH_3BH_3 (1 mmol), water (2 mL), 70 °C, 40 min.



Peak - Channel 1

Peak#	Ret.Time	Height	Area	Area%
1	2.966	500951	701099	3.21
2	3.122	2134976	3691616	16.88
3	3.220	7135569	14802709	67.68
4	4.285	1782223	2675748	12.23
Total		11553719	21871172	100.00

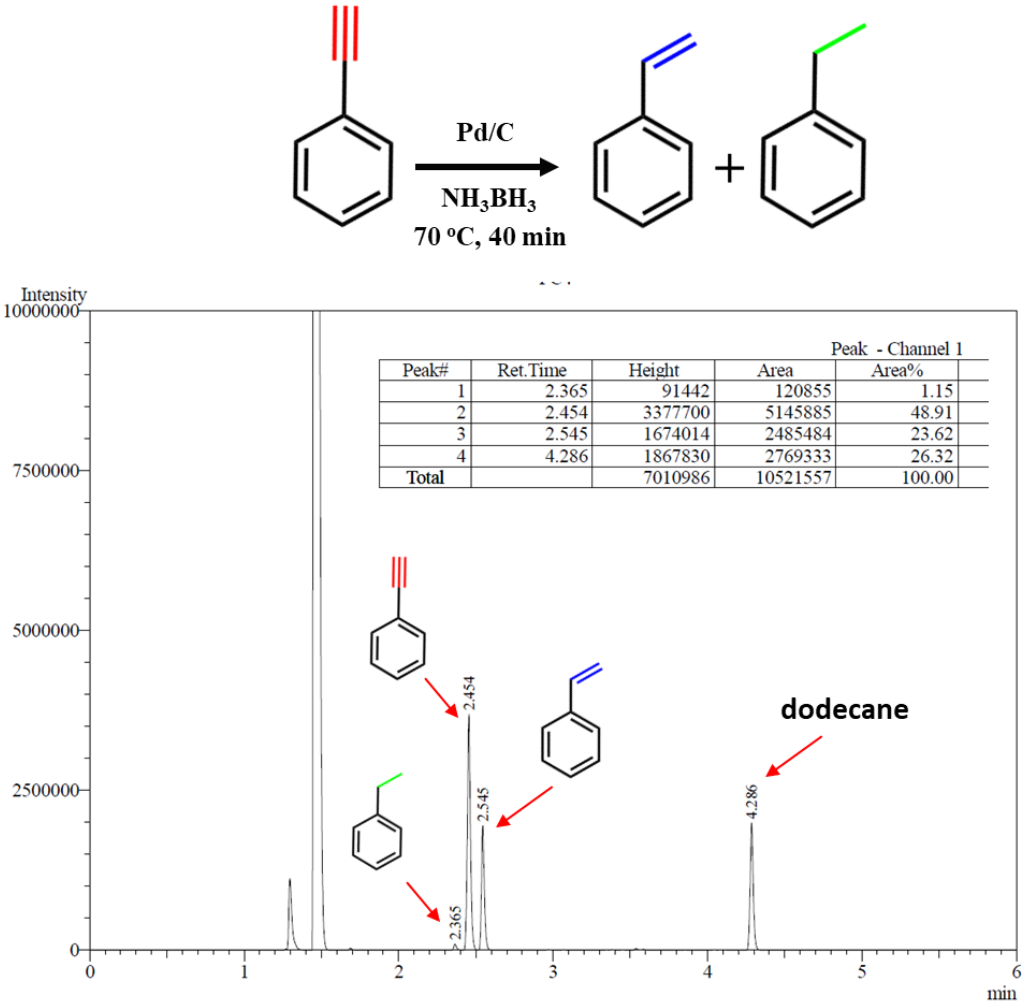
Fig. S13 GC-FID chromatogram for the 3-ethynylanisole hydrogenation.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name
1	2.884	1965752	5.59	2534017	7.97	Benzene, 1-ethyl-4-methyl-
2	3.029	7795515	22.17	8066982	25.38	Benzene, 1-ethynyl-4-methyl-
3	3.112	17878863	50.84	11826513	37.20	Benzene, 1-ethenyl-4-methyl-
4	4.160	7525673	21.40	9362724	29.45	Dodecane
		35165803	100.00	31790236	100.00	

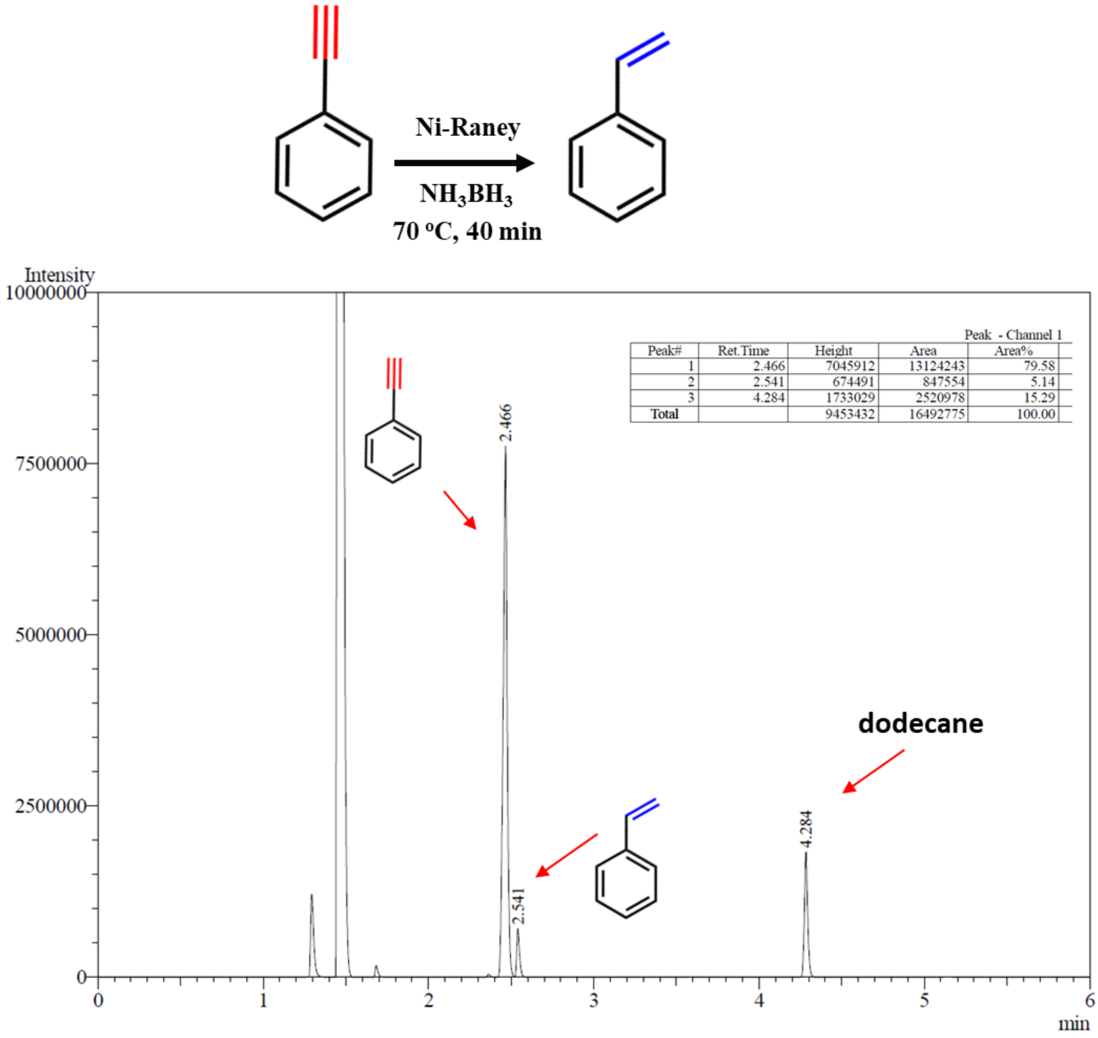
Fig. S14 GC-MS spectrum for the 3-ethynylanisole hydrogenation.



Peak - Channel 1

Peak#	Ret.Time	Height	Area	Area%
1	2.365	91442	120855	1.15
2	2.454	3377700	5145885	48.91
3	2.545	1674014	2485484	23.62
4	4.286	1867830	2769333	26.32
Total		7010986	10521557	100.00

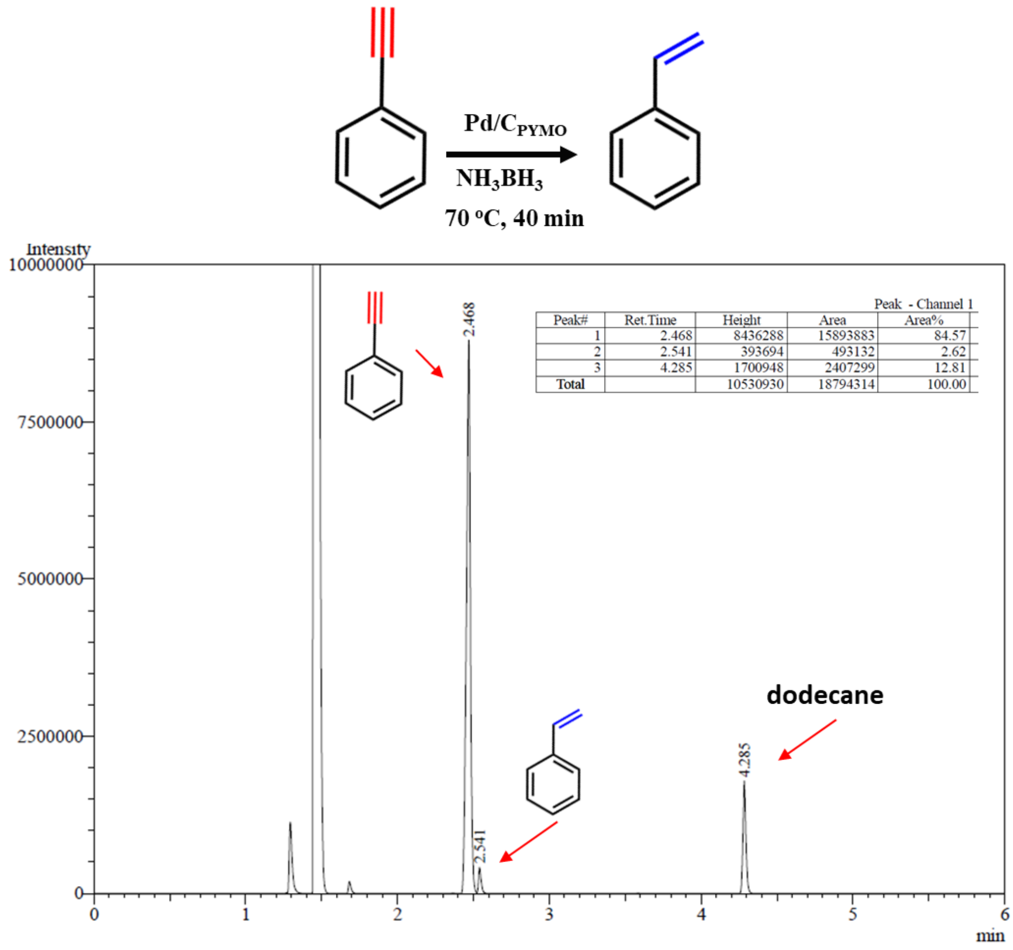
Fig. S15 GC-FID chromatogram of the hydrogenation of phenylacetylene using **Pd/C** as the catalyst. Reaction conditions: 0.91 mmol of phenylacetylene and 1 mmol of NH_3BH_3, catalyst **Pd/C** (1 mol% Pd), 2 mL of H_2O.



Peak - Channel 1

Peak#	Ret.Time	Height	Area	Area%
1	2.466	7045912	13124243	79.58
2	2.541	674491	847554	5.14
3	4.284	1733029	2520978	15.29
Total		9453432	16492775	100.00

Fig. S16 GC-FID chromatogram of the hydrogenation of phenylacetylene using **Raney®-Nickel** as the catalyst. Reaction conditions: 0.91 mmol of phenylacetylene and 1 mmol of NH_3BH_3, catalyst **Raney®-Nickel** (5 mol% Ni), 2 mL of H_2O.



Peak - Channel 1

Peak#	Ret.Time	Height	Area	Area%
1	2.468	8436288	15893883	84.57
2	2.541	393694	493132	2.62
3	4.285	1700948	2407299	12.81
Total		10530930	18794314	100.00

Fig. S17 GC-FID chromatogram of the hydrogenation of phenylacetylene using **Pd/C$_{PYMO}$** as the catalyst. Reaction conditions: 0.91 mmol of phenylacetylene and 1 mmol of NH_3BH_3, catalyst **Pd/C$_{PYMO}$** (1 mol% Pd), 2 mL of H_2O.

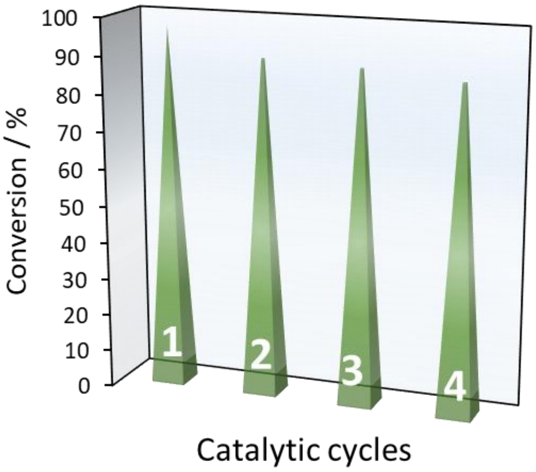


Fig.S18 Recycling test of hydrogenation of phenylacetylene using **Pd/C$_{N-B}$** catalyst. Reaction conditions: 0.91 mmol of phenylacetylene and 1 mmol of BH_3NH_3, catalyst **Pd/C$_{N-B}$** (1 mol% Pd), 2 mL of H_2O.

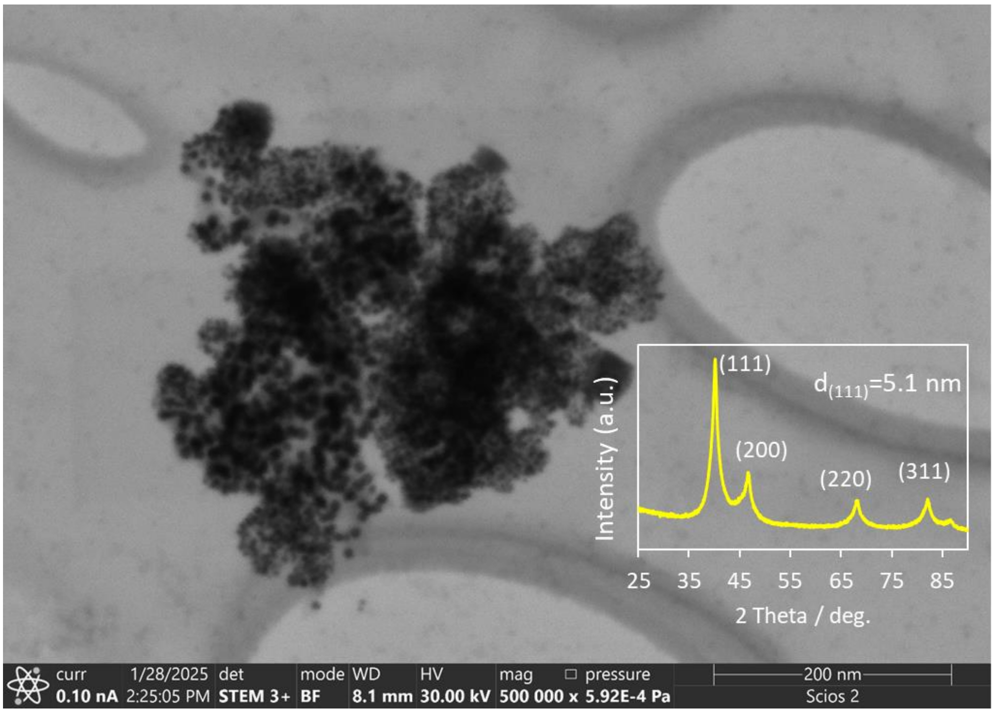


Fig. S19 STEM image (inset: XRD diffractogram) of Pd/$C_{N\text{-}B}$ after after hydrolysis of NH_3BH_3 and H_2 evolution.

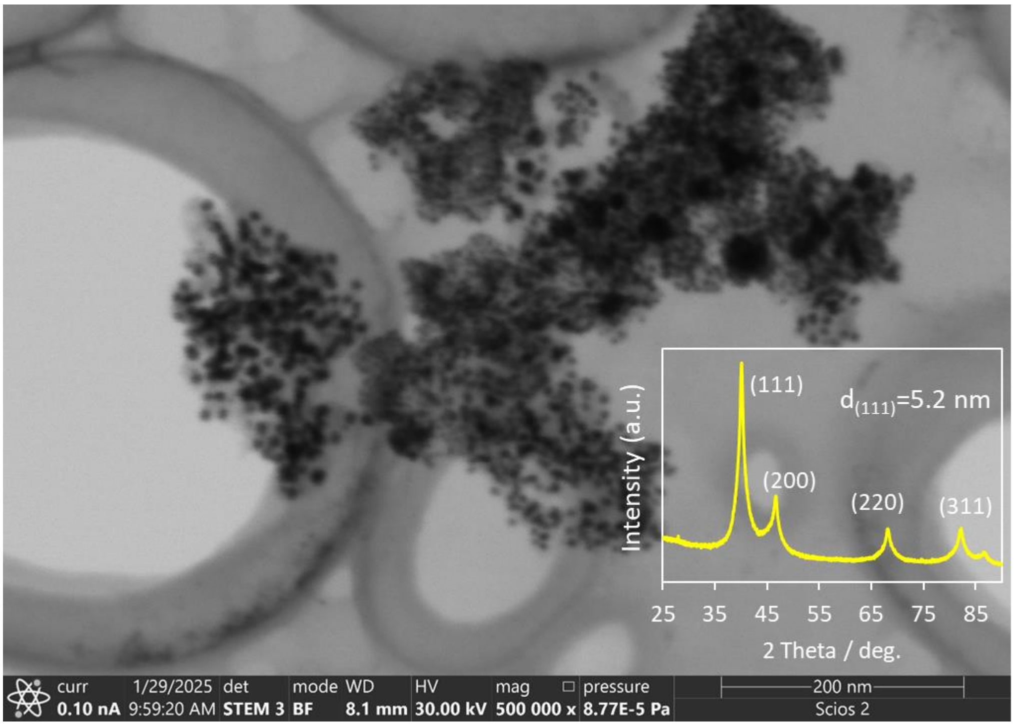


Fig. S20 STEM image (inset: XRD diffractogram) of Pd/$C_{N\text{-}B}$ after hydrolysis of $B_2(OH)_4$ and H_2 evolution.

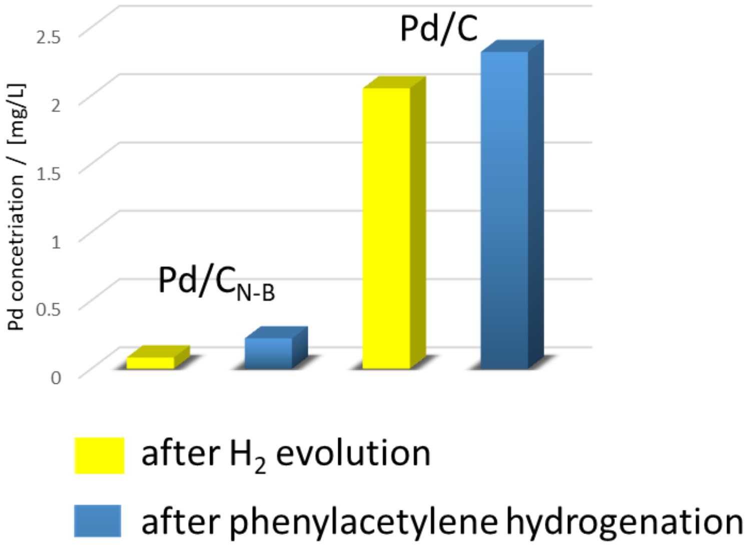


Fig.S21 ICP-OES of liquid phase after H_2 evolution from NH_3BH_3 and phenylacetylene hydrogenation by Pd/C$_{N-B}$ and commercial Pd/C

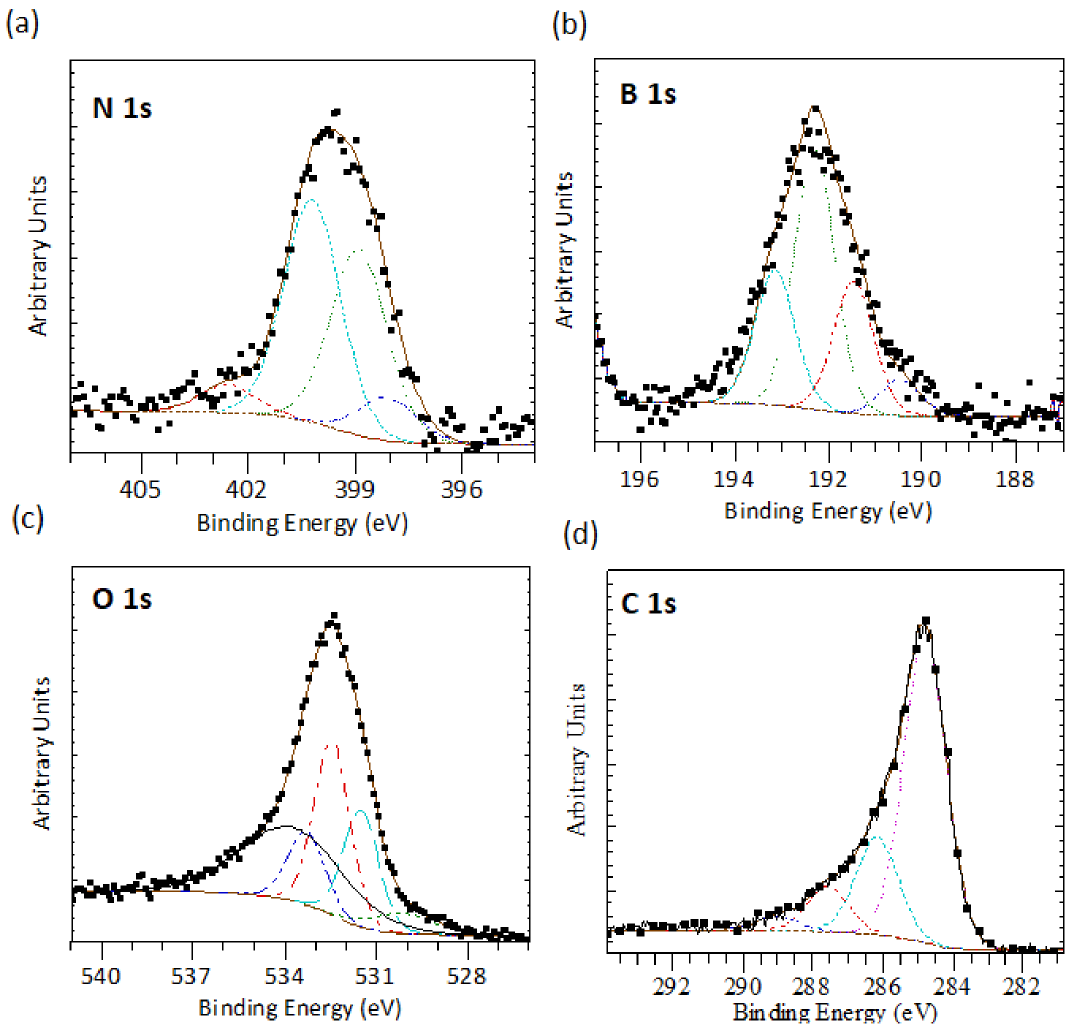


Fig. S22 High-resolution XPS spectra of N 1s (a), B 1s (b), O 1s (c), and C1s (d) for **Pd/C$_{N\text{-}B}$** after reaction.

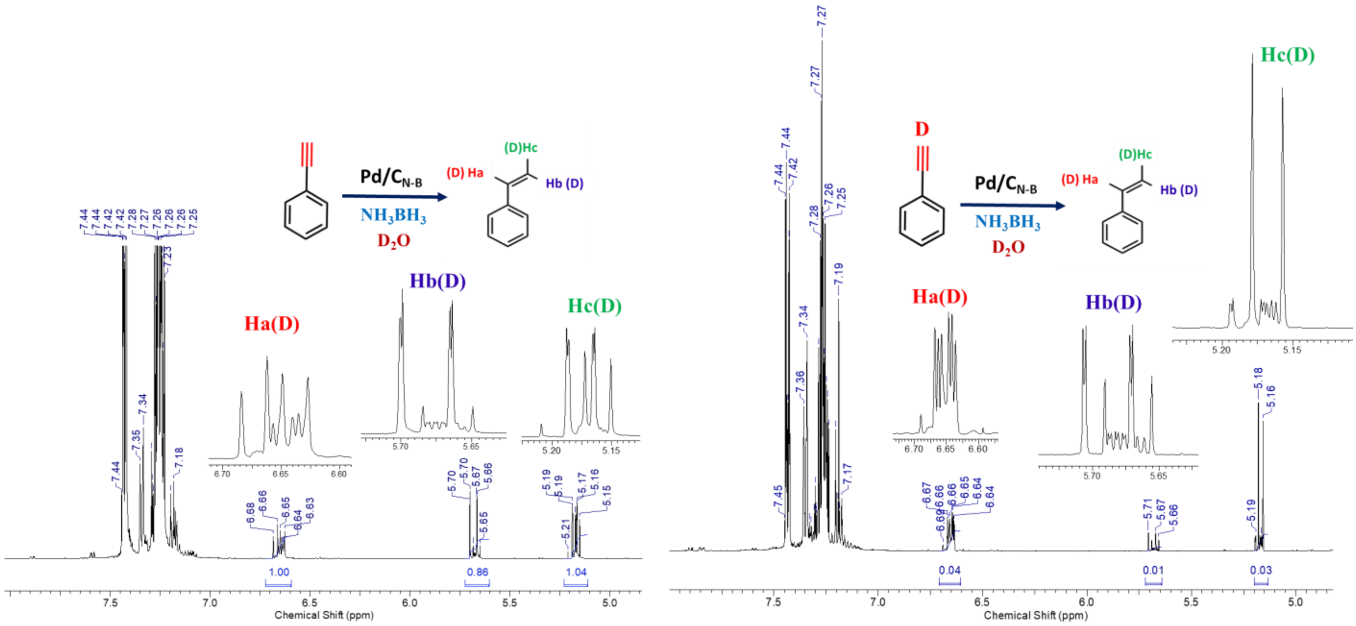


Fig.S23 ^{1}H NMR spectra for the hydrogenation of phenylacetylene/d1-phenylacetylene using H_2O/D_2O as a solvent BH_3NH_3 and **Pd/C$_{N-B}$** as the catalyst during 40 min at 50 °C.

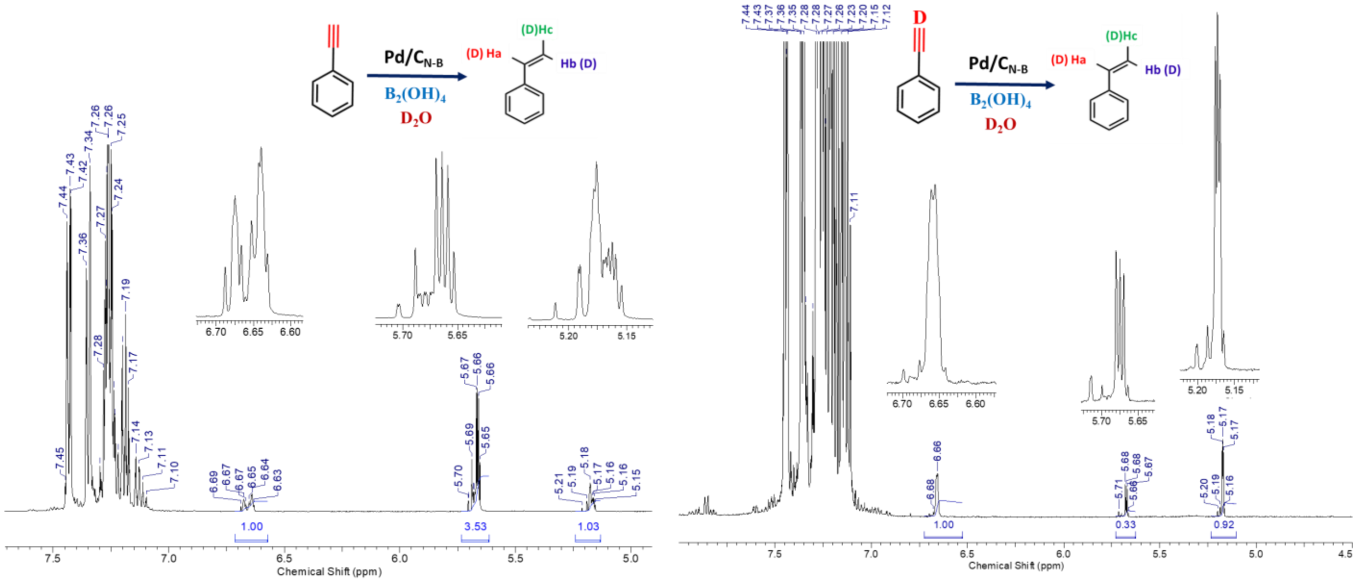
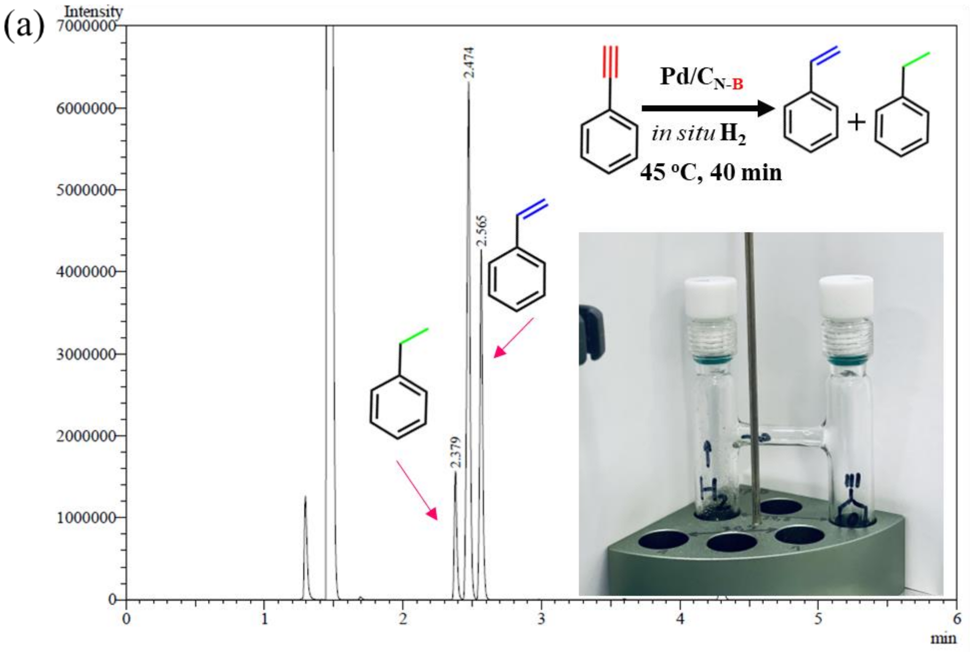


Fig.S24 ^{1}H NMR spectra for the hydrogenation of phenylacetylene/d1-phenylacetylene using H_2O/D_2O as a solvent $B_2(OH)_4$ and **Pd/C$_{N-B}$** as the catalyst during 40 min at 45 °C.



Peak - Channel 1

Peak#	Ret.Time	Height	Area	Area%	Name
1	2.379	1567664	2072473	10.02	
2	2.474	6322482	10011939	48.41	
3	2.565	4271292	6080772	29.40	
4	4.298	1845794	2516656	12.17	
Total		14007232	20681840	100.00	

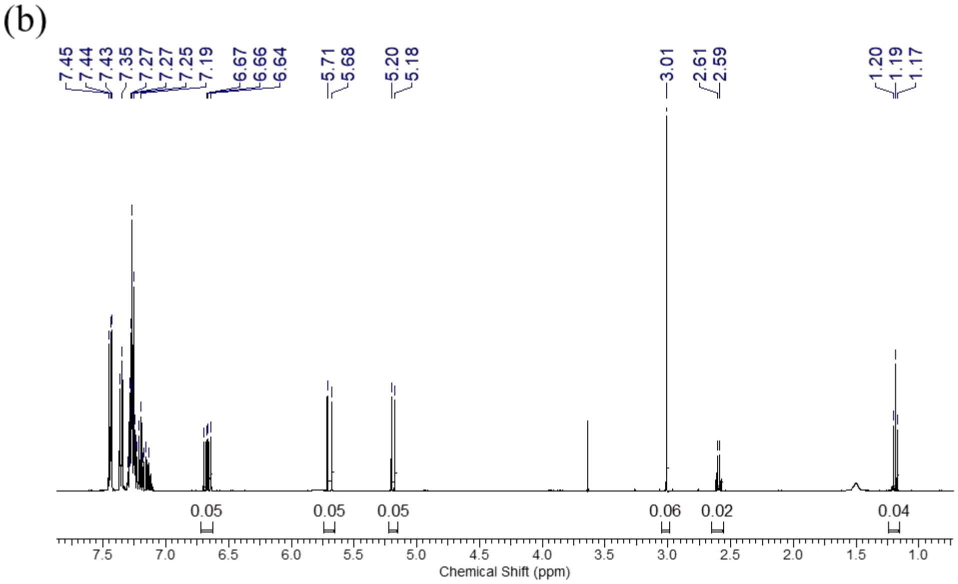


Fig.S25 Tandem reaction of $B_2(OH)_4$ dehydrogenation in H_2O and hydrogenation of phenylacetylene in H_2O. GC-FID chromatogram (a) and ^1H NMR spectrum (b). Reaction conditions: 0.91 mmol of phenylacetylene and 1 mmol of $B_2(OH)_4$, catalyst **Pd/C$_{N-B}$** (1 mol% Pd), 2 mL of H_2O, 40 min at 45 ^oC.

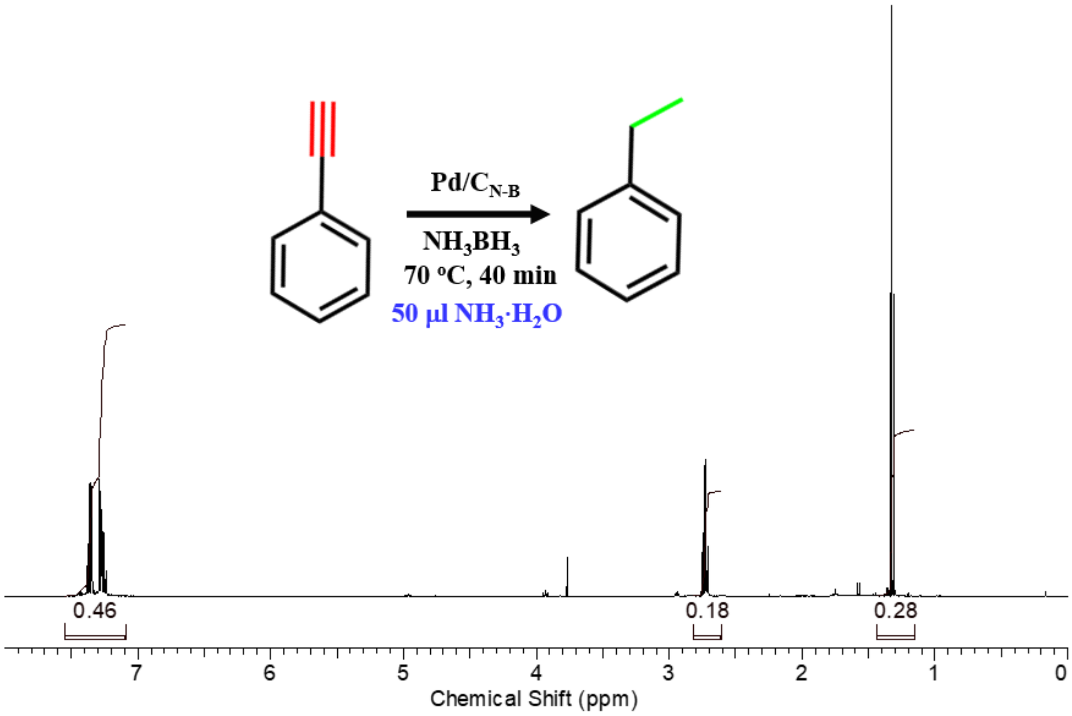


Fig.S26 ^{1}H NMR spectrum of phenylacetylene hydrogenation with **ammonia water.** Reaction conditions: 0.91 mmol of phenylacetylene and 1 mmol of NH_3BH_3, catalyst **Pd/C$_{N-B}$** (1 mol% Pd), 2 mL of H_2O, 40 min at 70 °C, 50 μl $NH_3 \cdot H_2O$.