Supplementary Information

Transfer Hydrogenation of Alkynes into Alkenes by Ammonia Borane over Pd-MOF Catalyst

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S1. General information

S1.1 Reagents

Palladium (II) acetate (Pd (CH₃COO) ₂, 98%), phenylacetylene (99%), styrene (99%) and halfniumchloride (HfCl₄, 98%) were purchased from Sigma-Aldrich. Tetrahydrofuran (99.9%) and 1, 4-benzenedicarboxylate (H₂BDC, 98%) were brought from SDFCL, Mumbai, India. Ammonium sulphate ((NH₄)₂SO₄, 99%) and sodiumborohydride (NaBH₄, >95%) were purchased from Merck Life Science Pvt. Ltd. Mumbai, India. Polyvinylpyrrolidone K30 (PVP, Mw=55000, 90%) and ethyl benzene (99%) were purchased from Spectrochem Pvt. Ltd, Mumbai, India. Ethylene glycol (EG, 99.8%), and N, N-dimethylformamide (DMF, 99 wt %) were purchased by Avra Synthesis Pvt. Ltd. Hyderabad, India. All chemicals were used without further purification. **S2. Synthesis methods**

S2.1. Synthesis of ammonia borane (AB)

In a typical synthesis procedure¹, equal molar ratio of NaBH₄ (0.945g, 0.0249 mol) and $(NH_4)_2SO_4$ (3.303 g, 0.0249 mol) were dissolved in a 150 mL of THF solvent and transferred into 250 mL of RB flask with two neck (one neck for condenser and second one for maintaining inert atmosphere by injecting N₂ gas in order to remove released hydrogen during reaction. The reaction was carried at 40 °C (oil bath) for 2 h under vigorous stirring. After completion of reaction time, the solvent was removed by rotary evaporator at room temperature and finally white crystalline powder was formed.

S2.2. Synthesis of UiO-66(Hf) MOF

In a typical solvothermal synthesis², 300 mg (0.94 mmol) of HfCl₄·6H₂O and 174 mg (1.04 mmol) of H₂BDC were dissolved in 10 mL of DMF solvent containing 0.1M H₂O in a 30 mL screw capped bottle and sealed. The synthesis was carried out in a pre-heated oven at 100°C for 24 h. On completion of the reaction time, the reaction mixture was brought to room temperature and the supernatant was decanted. The solid product was washed with fresh DMF (50 mL) once, twice with ethanol (2 x 50 mL) using centrifuge. Finally, the powder was dried under vacuum at room temperature.

S2.3. Synthesis of Pd nanoparticles

The nanoparticles were synthesized according to reported procedure elsewhere³,

Solution 1: 1.114 g (10 mmol) of PVP polymer was weighted and placed into to a three-necked round bottom flask. This polymer was dissolved by adding of 120 mL of ethylene glycol. The solution was kept under stirring at 80 $^{\circ}$ C (pre-heated oil bath) for 2 h.

Solution 2: 0.2245 g (1 mmol) of the palladium acetate was weighted and dissolved in 50mL of dioxane. The solution was kept under stirring at room temperature until become homogeneous solution (15 min) .Solution was in light orange in color.

Solution 1 was brought to 0 $^{\circ}$ C using ice bath and to this 3 mL of 1M sodium hydroxide solution was added drop wise under stirring. Solution 2 was poured into solution 1 under vigorous stirring at room temperature and the resulting solution was placed in pre-heated oil bath at 100 $^{\circ}$ C for 2 h. After a few minutes, the solution color was changed from light orange to dark brown, indicating the formation of metallic zerovalent nanoparticles. The nanoparticles were washed with acetone and dried under vacuum at room temperature.

S2.4. Synthesis of supported Pd NPs onto the UiO-66(Hf)

~10 mg of Pd NPs were dispersed in a 10 mL of DMF using sonication for 15 minutes. Afterwards, around ~200 mg of activated UiO-66(Hf) sample was transferred into Pd solution. The mixture solution was kept for stirring at room temperature for 2 h. After this, supernatant was removed from dark brown precipitate after centrifugation and the dark brown precipitate was washed twice with 50 mL of EtOH. Finally, the solid product was dried under vacuum at room temperature.



S3. Characterization of UiO-66(Hf) and Pd/UiO-66(Hf) material

Figure S1. Characterization of Pd/UiO-66(Hf) material and their individual counter parts using a) powder XRD, b) N_2 isotherms, and c) Bright field-TEM image. d) Size distribution histogram of Palladium nanoparticles present in Pd supported UiO-66 (Hf) material.

Pd/UiO-66(Hf) catalyst was synthesized by stirring activated UiO-66(Hf) MOF with colloidal Pd nanoparticles for 2 h at room temperature. The obtained brown color solid was first characterized with powder X-ray diffraction (PXRD). PXRD pattern of the material showed reflections corresponding to only UiO-66(Hf)(Figure S1a). Reflections due to Pd was not observed because of smaller particle size as well as low amount of Pd. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis confirmed the presence of 1.05 wt % of Pd in the material. Bright field-TEM image revealed presence Pd nanoparticles over external surface of UiO-66(Hf) (Figure S1c). The BET surface area measured using N₂ isotherms at 77 K(Figure S1b) decreased to 865 m²/g from 895 m²/g slightly lowered for the hybrid material when compared pristine MOF due to the presence of Pd. The calculated average Pd nanoparticle size is 3.5 ± 0.15 nm (Figure S1d).

S4. Effect of hydrogen source on transfer hydrogenation of phenylacetylene

In a typical reaction, 0.5 mmol of hydrogen source was dissolved in 1 mL of 1,4-dioxane solvent in a 30 mL glass vial and to this 27.6 μ L(0.25 mmol) of phenylacetylene was added. Finally the container was closed immediately and placed in a prehaeted alumina block under stirring at different temperatures for 1h. After completion of reaction, the reaction vessel was cooled to room temperature and the ammonia borane derivative which is in white solid material was separated by centrifugation and the seperated product reaction mixture was analyzed by gas chromatography (GC, Agilent-7820A, and column: HP-5, 30 m × 0.32 mm × 0.25 μ m). Here, the reactions were carried using different hydrogen sources, namely ethanol, isopropanol and formic acid, N₂H₄·H₂O, and NaBH₄.

S4.1. Hydrogenation of phenyl acetylene using molecular H₂

In a typical hydrogenation reaction, 27.6 μ L (0.25 mmol) of phenylacetylene was transferred into 1 mL of 1, 4-dioxane solvent in a Fischer bottle. The vessel was evacuated and refilled with H₂ for 3 times, finally the H₂ pressure adjusted to 0.5 bar before reaction. The reaction mixture was stirred at 350 rpm at 110 °C. On completion of the reaction time, the reaction vessel was cooled to room temperature and the reaction mixture was analyzed by gas chromatography.

S5. Effect of solvent in the transfer hydrogenation of phenylacetylene



Figure S2: Effect of solvent: transfer hydrogenation in both protic and non-protic solvents. Significant PA conversions were observed with non-protic solvents. Reaction conditions: 0.50 mmol of AB, 1 mL of solvent and 0.25 mmol of PA. Reaction carried for 1 h at 110 °C.

In corporation of 1,4- dioxane into computations revealed that the lowest energy barrier (TS1) for the reduction of phenylacetylene into styrene is 32.6 kcal mol⁻¹. On the other hand, incorporation of water as solvent into the computations indicated enhancement of the barrier energies of TS1 (36.0 kcal mol⁻¹). Consistent with these results experimentally we did not observe any PA conversion in water at 110 °C.

S 5.1. GC chromatograms of reaction mixture



Figure S3: Gas chromatogram of uncatalyzed reaction products analysis. Order of the peaks were labeled as ethyl benzene (retention time -2.99) and styrene (R.T-3.63). Reaction conditions: 0.50 mmol of AB, 1 mL of 1, 4-dioxane and 27.8 uL (0.252 mmol) of PA. Reaction carried for 30 min at 110 °C in a closed system.

S 5.2. NMR data of uncatalyzed product mixture

Transfer hydrogenation of phenylacetylene has been carried out in a NMR tube by dissolving 0.25 mmol of NH₃-BH₃ in 0.4 mL of 1, 4-Dioxane solvent and to this 0.125 mmol of phenylacetylene was added. The NMR tube was sealed and placed in oil bath which was preheated at 110 °C. Finally, reaction was carried for 1h. After completion of reaction time, the temperature of NMR tube was brought it to room temperature and analyzed for NMR analysis. In the NMR data we found major product is styrene (> 99.9 %).



Figure S4: ¹H NMR data of uncatalyzed reaction. Reaction conditions: 0.25 mmol of AB source, 0.4 mL of 1, 4dioxane, 0.125 mmol of PA reaction carried at 110 °C for 1h.

S6. Computational methods

Density functional theoretical (DFT) computations were performed using Gaussian09 program⁴. The geometry optimizations were performed using Minnesota functional M06-2X in conjunction with cc-pVTZ basis set ⁵. In computations, implicit solvent effect of 1, 4-dioxane was considered by polarizable continuum model (PCM). The harmonic vibrational frequency of the optimized

geometries was analyzed to check the nature of stationary points. The optimized ground state structures possess no imaginary vibrational mode whereas each transition state contains one imaginary frequency. Gibbs free energies after thermally corrected unscaled zero point vibrational energies at 110 $^{\circ}$ C are reported in kcal mol⁻¹.



Scheme S1. M06-2X/cc-pVTZ (PCM, 1, 4-dioxane) calculated energies for the reduction of phenylacetylene with NH₃BH₃.



Scheme S2. M06-2X/cc-pVTZ (PCM, 1, 4-dioxane) calculated energies for the reduction of phenylacetylene with NH₂BH₂.



Scheme S3. M06-2X/cc-pVTZ (PCM, 1, 4-dioxane) calculated energies for the reduction of styrene with NH₃BH₃.



Scheme S4. M06-2X/cc-pVTZ (PCM, 1, 4-dioxane) calculated energies for the reduction of styrene with NH₂BH₂.

S6.1. Optimized Structures and Energies

Ethylbenzene

•	
Zero-point correction=	0.158048 (Hartree/Particle)
Thermal correction to energy=	0.165212
Thermal correction to enthalpy=	0.166157
Thermal correction to Gibbs free energy	rgy= 0.126374
Sum of electronic and zero-point energy	rgies= -310.683209
Sum of electronic and thermal energi	es= -310.676045
Sum of electronic and thermal enthal	pies= -310.675100
Sum of electronic and thermal free er	nergies= -310.714883
C 2.304700 0.000000 0.23860	0
C 1.620400 -1.199200 0.09510	00
C 0.262000 -1.196000 -0.18920	00
C -0.435700 -0.000000 -0.33680	00
C 0.261900 1.195900 -0.18930	00
C 1.620400 1.199300 0.09500	0
Н 3.363800 0.000000 0.45770	0
Н 2.145400 -2.139300 0.20180	00
Н -0.266500 -2.135300 -0.3033	00
Н -0.266600 2.135300 -0.30340	00
Н 2.145300 2.139300 0.20170	0
C -1.918900 -0.000000 -0.59400	00
Н -2.186100 -0.877600 -1.1849	00
Н -2.186100 0.877400 -1.18500)0
C -2.716700 0.000000 0.71130	00
Н -3.789000 0.000000 0.51780	00
Н -2.474500 -0.880700 1.30690)0
Н -2.474500 0.880800 1.30680	00

NH₂BH₂

Charge = 0, Multiplicity = 1, Number of imaginary frequency = 0 Zero-point correction= 0.048373 (Hartree/Particle)

The	rmal correct	ion to energ	y=	0.051603
The	rmal correct	ion to entha	lpy=	0.052547
The	rmal correct	ion to Gibbs	s free energy=	0.025979
Sun	n of electron	ic and zero-	point energies=	-81.983486
Sun	n of electron	ic and therm	nal energies=	-81.980256
Sun	n of electron	ic and therm	nal enthalpies=	-81.979312
Sun	n of electron	ic and therm	nal free energie	s= -82.005880
Ν	0.609700	-0.000000	0.000000	
Η	1.162000	-0.841000	0.000100	
Η	1.162000	0.841000	0.000100	
В	-0.776300	0.000000	-0.000100	
Η	-1.355100	-1.040500	0.000100	
Η	-1.355100	1.040500	0.000100	

NH₃BH₃

Char	ge = 0, Mul	tiplicity $= 1$, Number of im	aginary frequency $= 0$
Zero	-point corre	ction=	0.0	70751 (Hartree/Particle)
The	rmal correct	ion to energ	y=	0.074505
The	rmal correct	ion to entha	lpy=	0.075450
The	rmal correct	ion to Gibbs	s free energy=	0.048366
Sun	n of electron	ic and zero-	point energies=	-83.135543
Sun	n of electron	ic and therm	nal energies=	-83.131789
Sun	n of electron	ic and therm	nal enthalpies=	-83.130844
Sun	n of electron	ic and therm	nal free energie	s= -83.157928
Ν	0.000000	0.000000	0.720600	
Н	0.763200	0.558300	1.089700	
Н	0.102000	-0.940100	1.089700	
Н	-0.865100	0.381700	1.089700	
В	0.000000	0.000000	-0.916300	
Н	1.060800	-0.475100	-1.243700	
Н	-0.941800	-0.681100	-1.243700	
Н	-0.119000	1.156200	-1.243700	

NHBH

Charge = 0, Multiplicity = 1, Number of imaginary frequency = 0Zero-point correction=0.025496 (Hartree/Particle)Thermal correction to energy=0.028482Thermal correction to enthalpy=0.029427Thermal correction to Gibbs free energy=0.005676Sum of electronic and zero-point energies=-80.774792

Sum of electronic and thermal energies=	-80.771805
Sum of electronic and thermal enthalpies=	-80.770861
Sum of electronic and thermal free energies=	-80.794612

Н	0.000000	0.000000	-1.85//00
Η	0.000000	0.000000	1.533500
Ν	0.000000	0.000000	0.540500
В	0.000000	0.000000	-0.691900

Phenylacetylene

Char	ge = 0, Mul	tiplicity = 1,	Number of in	naginary frequency $= 0$
Zero	-point corre	ction=	0.1	10579 (Hartree/Particle)
The	rmal correct	tion to energ	y=	0.116893
The	rmal correct	ion to entha	lpy=	0.117838
The	rmal correct	ion to Gibbs	s free energy=	0.080237
Sum	of electron	ic and zero-	point energies=	-308.261104
Sum	of electron	ic and therm	al energies=	-308.254789
Sum	of electron	ic and therm	al enthalpies=	-308.253845
Sum	of electron	ic and therm	al free energie	es= -308.291445
С	-2.199200	-0.000000	-0.000000	
С	-1.504200	-1.202100	-0.000000	
С	-0.119100	-1.206000	-0.000000	
С	0.584500	0.000000	0.000000	
С	-0.119100	1.206000	-0.000000	
С	-1.504200	1.202100	-0.000000	
Н	-3.280600	-0.000000	-0.000000	
Н	-2.042700	-2.139800	-0.000000	
Н	0.429300	-2.137700	0.000000	
Н	0.429300	2.137700	0.000000	
Н	-2.042700	2.139800	-0.000000	
С	2.016800	0.000000	0.000000	
С	3.216000	0.000000	0.000100	
Н	4.279100	-0.000000	0.000100	

Styrene

Charge = 0, Multiplicity = 1, Number of imaginary frequency = 0Zero-point correction=0.134251 (Hartree/Particle)Thermal correction to energy=0.140974Thermal correction to enthalpy=0.141918Thermal correction to Gibbs free energy=0.102605Sum of electronic and zero-point energies=-309.481284

Sum of electronic and thermal energies=-309.474561Sum of electronic and thermal enthalpies=-309.473617Sum of electronic and thermal free energies=-309.512930

С	2.249300	0.264300	0.000000
С	1.773100	-1.037700	0.000100
С	0.406000	-1.275900	0.000000
С	-0.509000	-0.223600	-0.000100
С	-0.014500	1.083000	-0.000100
С	1.348300	1.323600	-0.000000
Η	3.313700	0.455700	0.000100
Η	2.464200	-1.869700	0.000100
Η	0.036400	-2.294000	0.000000
Η	-0.699800	1.919800	-0.000200
Η	1.712700	2.342100	-0.000100
С	-1.948000	-0.533000	-0.000100
Η	-2.183400	-1.592600	-0.000300
С	-2.950900	0.337900	0.000100
Η	-2.793000	1.408400	0.000400
Н	-3.976900	-0.001900	0.000100

TS1

Charg	ge = 0, Mul	tiplicity $= 1$, Number of ima	aginary frequency = 1
Zero-	point corre	ction=	0.17	8710 (Hartree/Particle)
Ther	mal correct	tion to energ	y=	0.188646
Ther	mal correct	tion to entha	lpy=	0.189590
Ther	mal correct	ion to Gibbs	s free energy=	0.142811
Sum	of electron	ic and zero-	point energies=	-391.361535
Sum	of electron	ic and therm	nal energies=	-391.351600
Sum	of electron	ic and therm	nal enthalpies=	-391.350656
Sum	of electron	ic and therm	nal free energies	= -391.397435
С	3.140900	-0.469900	-0.000000	
С	2.150100	-1.440000	0.000000	
С	0.811600	-1.074900	0.000000	
С	0.450400	0.268700	0.000000	
С	1.454000	1.242800	-0.000000	
С	2.787600	0.874500	-0.000000	
Η	4.183600	-0.757400	-0.000000	
Η	2.417200	-2.488100	0.000000	
Η	0.039000	-1.831600	0.000100	
Н	1.171400	2.286900	-0.000100	

Η	3.554300	1.637500	-0.000100
С	-0.933100	0.733300	0.000000
С	-1.763700	1.661800	0.000000
Η	-1.883200	2.726100	0.000000
Ν	-3.728300	-0.213500	-0.000000
В	-2.666600	-1.339000	0.000000
Η	-4.319900	-0.190100	0.822100
Η	-4.319900	-0.190100	-0.822100
Η	-2.639700	-1.951800	-1.028700
Η	-2.639700	-1.951800	1.028800
Η	-3.132100	0.728100	-0.000000
Η	-1.586600	-0.605300	-0.000000

TS2

Charg	ge = 0, Mul	tiplicity $= 1$,	, Number of imag	ginary frequency = 1
Zero-	point corre	ction=	0.178	8865 (Hartree/Particle)
Ther	mal correct	tion to energ	y= 0	.188885
Ther	mal correct	ion to entha	lpy= ().189829
Ther	mal correct	tion to Gibbs	s free energy=	0.142277
Sum	of electron	ic and zero-	point energies=	-391.359483
Sum	of electron	ic and therm	nal energies=	-391.349462
Sum	of electron	ic and therm	al enthalpies=	-391.348518
Sum	of electron	ic and therm	nal free energies=	-391.396070
С	-3.207100	-0.000100	-0.362100	
С	-2.524900	-1.197600	-0.190900	
С	-1.180900	-1.203300	0.144000	
С	-0.487200	0.000100	0.325100	
С	-1.180900	1.203300	0.143800	
С	-2.525000	1.197500	-0.191200	
Η	-4.255800	-0.000100	-0.624800	
Η	-3.042900	-2.139100	-0.318300	
Н	-0.657000	-2.140200	0.277600	
Н	-0.657000	2.140300	0.277100	
Н	-3.042900	2.139000	-0.318800	
С	0.910100	0.000100	0.652900	
С	1.864100	0.000200	1.455500	
Н	2.189600	0.000300	2.479700	
Н	4.540700	1.033100	-0.120400	
Н	4.540700	-1.033100	-0.120100	
Н	2.837700	-0.822500	-1.865300	

Η	2.837700	0.821900	-1.865600
В	3.944500	-0.000000	-0.188300
Ν	2.847100	-0.000200	-1.273000
Η	3.154500	0.000100	0.898700
Η	1.894000	-0.000100	-0.709700

TS3

Charge = 0, Multiplicity = 1, Number of imaginary frequency = 1						
Zero-point correction=			0.	0.154341 (Hartree/Particle)		
Thermal correction to energy=			gy=	0.163516		
Thermal correction to enthalpy=			0.164460			
Thermal correction to Gibbs free energy=				= 0.119608		
Sum of electronic and zero-point energies= -390.1780						
Sum of electronic and thermal energies= -390.168850						
Sum of	electron	nic and thern	nal enthalpies	-390.167905		
Sum of	electron	nic and thern	nal free energ	ies= -390.212757		
C -3.	069500	-0.409100	0.000000			
C -2.	119600	-1.419200	0.000000			
C -0.	768300	-1.105700	0.000000			
C -0.	350500	0.221800	-0.000000			
C -1.	313400	1.235200	-0.000000			
C -2.	660800	0.919800	-0.000000			
Н -4.	123100	-0.652700	0.000000			
Н -2.	429600	-2.455400	0.000000			
Н -0.	029500	-1.896700	0.000000			
Н -0.	990000	2.267500	-0.000000			
Н -3.	395900	1.713200	-0.000000			
C 1.	061000	0.596300	-0.000000			
C 1.	913200	1.531800	-0.000000			
H 1.	861000	2.606000	-0.000000			
N 3.	756300	-0.301500	0.000000			
B 2.	867600	-1.269400	0.000000			
Н 4.	758900	-0.266700	-0.000000			
Н 2.	731100	-2.438500	0.000000			
Н 3.	169000	0.747800	-0.000000			
H 1.	664200	-0.593000	0.000000			

TS4

Charge = 0, Multiplicity = 1, Number of imaginary frequency = 1 Zero-point correction= 0.201573 (Hartree/Particle)

Thermal correction to energy=				0.211370		
Thermal correction to enthalpy= 0.21				0.212315		
The	Thermal correction to Gibbs free energy= 0.165878					
Sur	n of electron	ic and zero-	point energies=	-392.577199		
Sur	n of electron	ic and therm	nal energies=	-392.567401		
Sur	n of electron	ic and therm	nal enthalpies=	-392.566457		
Sum of electronic and thermal free energies= -392.61289						
С	2.959700	0.637300	0.126100			
С	2.717800	-0.665800	0.534100			
С	1.448700	-1.212400	0.401700			
С	0.409700	-0.469900	-0.150900			
С	0.660500	0.841600	-0.549800			
С	1.924500	1.391400	-0.413200			
Н	3.946400	1.067000	0.233200			
Н	3.516400	-1.258600	0.959500			
Н	1.261200	-2.228700	0.725600			
Н	-0.144300	1.439200	-0.960000			
Η	2.103400	2.412600	-0.722300			
С	-0.938200	-1.075500	-0.305600			
Η	-1.024800	-2.067300	0.124400			
С	-1.763300	-0.753400	-1.392500			
Н	-1.372400	-0.091000	-2.154500			
Н	-2.460400	-1.504500	-1.741000			
Η	-3.011300	-0.341700	2.245500			
Н	-1.677500	1.208900	1.933900			
Н	-4.158600	0.525800	0.256700			
Н	-3.101300	1.761000	0.011000			
Ν	-3.179800	0.784200	0.265100			
В	-2.389600	0.352600	1.491500			
Н	-1.526600	-0.493300	0.927700			
Н	-2.661000	0.157500	-0.651000			

TS5

Charge = 0, Multiplicity = 1, Number of imaginary frequency = 1						
Zero-point correction=	0.178342 (Hartree/Particle)					
Thermal correction to energy=	0.187688					
Thermal correction to enthalpy=	0.188632					
Thermal correction to Gibbs free energy	gy= 0.143183					
Sum of electronic and zero-point energy	gies= -391.392267					
Sum of electronic and thermal energies	s= -391.382921					

Su	-391.381977			
Sum of electronic and thermal free energies= -391.42742				
С	-2.875600	-0.662200	0.028100	
С	-2.677200	0.640000	0.462100	
С	-1.407000	1.199500	0.427800	
С	-0.325100	0.468900	-0.052500	
С	-0.531300	-0.842200	-0.479400	
С	-1.797100	-1.403600	-0.439500	
Н	-3.863800	-1.100500	0.058400	
Н	-3.511400	1.222600	0.829300	
Н	-1.254100	2.215700	0.769400	
Н	0.312300	-1.424100	-0.831400	
Н	-1.943900	-2.423200	-0.769800	
С	1.033500	1.076500	-0.110300	
Н	1.097000	2.045600	0.374900	
С	1.872700	0.845000	-1.236500	
Н	1.424000	0.313300	-2.067500	
Η	2.527000	1.658100	-1.526700	
Η	2.357000	-0.815800	2.500900	
Н	3.943300	-1.433500	0.022400	
Ν	3.190300	-0.824400	0.282400	
В	2.501900	-0.553800	1.360100	
Н	1.611700	0.415900	0.952000	
Н	2.701800	-0.064800	-0.687200	

S7. Transfer hydrogenation of phenylacetylene over Pd supported on UiO-66(Hf) MOF at room temperature.

In a typical transfer hydrogenation reaction, 15.5 mg (0.5 mmol) of AB was dissolved in 1 mL of 1,4-dioxane solvent in a 30 mL glass vial and to this 27.6 μ L (0.25 mmol) of phenylacetylene was added. To this mixture respective mol % of catalysts was added and carried out reaction at room temperature for 30 min.



Figure S5: Transfer hydrogenation of phenylacetylene over Pd/UiO-66(Hf) catalyst at room temperature. *Reaction conditions:* Respective mol% of catalyst (Pd mol% with respect to PA), 0.5 mmol AB source, 1 mL of solvent, 0.25 mmol of PA.



S7.1. GC chromatogram of reaction mixture

Figure S6: Gas chromatogram of transfer hydrogenation products analysis. Order of the peaks were labeled as ethyl benzene (retention time -3.02), phenylacetylene (R.T- 3.17) and styrene (R.T-3.67). Column is HP-5. *Reaction conditions*: 1 mol% of catalyst (0.0027 mmol of Pd), 0.25 mmol of AB source, 1 mL of solvent, 0.25 mmol of PA.

S7.3. Literature table

Catalyst	Substrate	Solvent	Temp. (°C)	Con (%)	Alkenes Sel.(%)	Ref.	
	Homogeneous catalysis						
[Pd(NHC)(PR3)] complexes	diphenylacetylene	Iso-propanol	50	100	88:12(Z/E)	<i>Chem. Commun.,</i> 2013 , <i>49</i> , 1005.	
Pincer complex [Mn(II)- PNP][Cl] ₂	diphenylacetylene	1,4-Dioxane	60	63	79:21(Z/E)	ACS Catal., 2018 , 8, 4103–4109.	
Ni(0) complex	phenylacetylene	THF	80	97	3:97(Z/E)	10.1016/j.apcata.201 0.06.052	
Copper(I)/NHC complexe	diphenylacetylene	THF	50	57	>99:0(Z/E)	<i>Chem. Commun.</i> 2017 , <i>53</i> , 732.	
[Si(II)L ₁]MnCl ₂	diphenylacetylene	THF	50	97	8:92(Z/E)	<i>Chem. Eur. J.</i> 2018 , 24, 4780 – 4784.	
Uncatalyzed	phenylacetylene	1,4-Dioxane	110	>99.9	>99.9	This work	
	Heterogeneous catalysis						
Au/TiO ₂	p-methoxy phenylacetylene	Ethanol	25	100	>94	Chem.Com. 2015 , <i>51</i> , 2384-2387.	
TiO ₂ /Pt/TiO ₂	phenylacetylene	H ₂ O/EtOH	30	98	96	ACS Catalysis. 2017, 7, 6567-6572.	
Cu/CuO	diphenylacetylene	EtOH	50	100	99.5	<i>Chemical</i> science, 2018 , 9, 2517-2524.	
Ni NPs	diphenylacetylene	MeOH	25	94	92	Chem. Commun. 2017 , 53, 5372—5375.	
Au/TiO ₂	p-methoxy phenylacetylene	THF	25	11	>99	<i>Chem.Com.</i> 2015 , <i>51</i> , 2384-2387.	
Pd/UiO-66(Hf)	phenylacetylene	1,4- Dioxane	25	>99.9	98.7	This work	

Table S1: Transfer semihydrogenation of alkynes using ammonia borane as a hydrogen sources.

S7.4. Phenylacetylene hydrogenation with molecular H₂ over Pd/UiO-66(Hf) catalyst

In a typical hydrogenation reaction, 1 mol % of containing Pd catalyst was dispersed in 1, 4dioxane solvent and to this 0.252 mmol of phenylacetylene was added. The Fischer port pressure bottle was washed twice with H_2 in order to remove moisture in the reactor. Finally, reactor was filled with 0.3 bar H_2 and carried reaction at room temperature for 30 min. Products were analyzed using GC.



Figure S7: Hydrogenation of phenylacetylene over Pd/UiO-66(Hf) catalysts. *Reaction conditions*: 1 mol % of catalyst (0.0027 mmol of Pd), 1 mL of 1, 4-dioxane and 27.8 uL(0.252 mmol) of PA. Reaction carried under 0.3 bar H_2 pressure and at R.T in a closed system for 30 min.

S8. Transfer hydrogenation of phenylacetylene over Pd/UiO-66(Zr) Catalyst

S8.1 synthesis and Characterization of Pd/UiO-66(Zr) Catalyst

In a 10 mL of DMF solvent ~10 mg of Pd NPs were dispersed using sonication for 15 minutes. Afterwards, around ~200 mg of activated UiO-66(Zr) sample was transferred into Pd solution. The mixture solution was kept for stirring at room temperature for 2 h. After completion of reaction time, supernatant was removed from dark brown precipitate after centrifugation and the dark brown precipitate was washed twice with 50 mL of EtOH. Finally, the solid product was dried under vacuum at room temperature.



Figure S8: XRD data of UiO-66(Zr) and Pd/UiO-66(Zr) supported materials.



Figure S9: Gas chromatography of product analysis. The retention time of styrene and phenylacetylene has been lablled at 5.1 min and 6.8 min, respectively. *Reaction conditions:* 1 mol % of Pd/UiO-66(Zr) catalyst (0.0027 mmol of Pd), 0.50 mmol of hydrogen source, 1 mL of 1, 4-dioxane and 0.25 mmol of substrate at R.T for 30 min.

S9. Leaching, recyclability test and characterization of spent catalyst

The Pd/UiO-66(Hf) catalyst found to be recyclable and maintained its performance up to three cycles (Figure S9). We also filtered out the catalyst from the reaction mixture after 15 min of reaction time. After this, reaction did not progress further suggesting heterogeneous nature of the catalysis (Figure S8). Further, ICP-OES analysis did not show any detectable amounts Pd and Hf in the supernatants collected from reaction mixtures. These observations along PXRD data of used catalyst (Figure S10) suggest that catalyst is highly stable under present reaction conditions.

S9.1. Leaching test:

Leaching test was performed at room temperature after isolating the catalyst from reaction mixture. Initially the reaction has been carried out for 15 min and then catalyst was separated from the reaction mixture and further reaction carried for another 15 min. During the reaction for every 5 min product was collected and analyzed by gas chromatography. As shown in leaching test plot no further conversion of phenyl acetylene has been observed and it suggests that no leaching of catalyst took place during course of the reaction. And also, we have tested isolated product mixture using ICP-OES analysis and no Pd was identified in the product mixture.



Figure S10: Leaching test. Reaction conditions: 1 mol% of catalyst (0.0027 mmol of Pd), 7.8 mg (0.252 mmol) of AB source , 1 mL of solvent and 27.8 uL(0.252 mmol) of PA. Reaction carried at R.T in a closed system.

S9.2. Recyclability test:

The recyclability test was performed for three cycles. In a typical procedure, after first cycle the catalyst was isolated from supernatant and then catalyst was washed with ethanol for three times. Finally, catalyst was dried at room temperature under vacuum and it was used for next cycle.



Figure S11: Recyclability study over Pd/UiO-66(Hf) catalysts *.Reaction conditions:* 1 mol% of catalyst (0.0027 mmol of Pd), 7.8 mg (0.252 mmol) of AB source, 1 mL of solvent and 27.8 uL(0.252 mmol) of PA. Reaction carried at R.T in a closed system for 30 min.

S9.3. Characterization of spent catalyst

After 3rd cycle, the catalyst was washed three times with ethanol and dried under vacuum at room temperature. Finally dried catalyst was characterized using PXRD. Spent catalyst maintained its crystalline nature even after three cycles.



Figure S12: Powder-XRD patterns of fresh and spent Pd/UiO-66(Hf) catalyst.

S9. References

1. P.V. Ramachandran, P.D. Gagare, Inorg. Chem. 2007, 46, 7810-7817.

2. V.R. Bakuru, B. Velaga, N.R. Peela, S.B. Kalidindi, Chem. Eur. J, 2018, 24, 15978-15982.

3. I. Miguel-García, Á. Berenguer-Murcia, D. Cazorla-Amorós, *Appl. Catal. B: Enviro.* **2010**, *98*, 161-170.

Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Jr. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.V. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D.J. Fox, *Gaussian, Inc., Wallingford CT*, 2009.
 X. Yang, L. Zhao, T. Fox, Z. –X. Wang, H. Berke, *Angew. Chem. Int. Ed.* 2010, *49*, 2058.