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Enhancing catalytic activity in hydrogenation reaction by decorating Pd nanoparticles with N-heterocyclic carbenes

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Contents

General experimental information

General procedures.

All reagents were purchased and used as received except when indicated. Chemical shifts (δ) are given in ppm downfield from Me_4Si and refer to the internal standard to the residual solvent (unless indicated) $CDCl_3$: ($\delta = 7.26$ for ^{1}H and 77.00 for ^{13}C). The coupling constants, J, are reported in hertz (Hz).

NMR study.

NMR spectra were recorded via Bruker Fourier 300HD spectrometers operating at 300.1 MHz for ^{1}H and 76 MHz for ^{13}C. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to the solvent signals as internal standards: 2.50 ppm/39.5 ppm for DMSO-*d*6. All the measurements were performed at room temperature.

TEM studies.

TEM was carried out on a Hitachi HT7700 transmission electron microscope. The images were acquired in bright-field TEM mode at an accelerating voltage of 100 kV. Before measurements the samples were deposited on the 3 mm a standard carbon-coated copper or Lacey Carbon grids from isopropanol suspension.

General method for obtaining catalysts.

*Method for producing Pd NPs(standard) in Figure 1(*a*), Entry 1:* $Pd_2(dba)_3\cdot CHCl_3$ (1 mg), the carbon material (20 mg) graphite powder (Sigma Aldrich, <20μm, synthetic) and 2 ml of $CHCl_3$ were placed into a 4 ml vail with an equipped with a magnetic stir bar. The reaction mixture was stirred until the solution became colorless at room temperature (22 °C). The material was filtered, washed with acetone and dried. (1% Pd NPs/Graphite).

Other materials were prepared by varying the condition: Varying the support *NPs (Halloysite)* and *NPs (T900);* varying the chemical additive *NPs(acid)* and *NPs(base);* varying the amount of palladium*; NPs(0.1Pd)* and *NPs(5Pd)* and *NPs(10Pd);* varying the dilution *NPs(2c)* and *NPs(10c);* varying the temperature *NPs(40°C)* and *NPs(80°C);* varying the solvent *NPs(acetone)* and *NPs(toluene)* and *NPs(DMF)* compared to the standard methodology.

*Conditions for producing NPs (Halloysite) in Figure 1(*a*), Entry 2:* As a support (20 mg) was a material called Halloysite formula of which $Al_2Si_2O_5(OH)_4\bullet 2H_2O$.

*Conditions for producing NPs (T900) in Figure 1(*a*), Entry 3:* As a support (20 mg), a carbon material called T900 was used. T900 is a commercially available, low-activity carbon black derived from natural gas, characterized by low dispersibility and low structuring.

*Conditions for producing NPs(acid) in Figure 1(*a*), Entry 4:* 500 μL of acetic acid was added to the reaction mixture during the application of palladium.

*Conditions for producing NPs(base) in Figure 1(*a*), Entry 5:* 500 μL of triethylamine was added to the reaction mixture during the application of palladium.

*Conditions for producing NPs(0.1Pd) in Figure 1(*a*), Entry 6:* $Pd_2(dba)_3 \cdot CHCl_3$ (0.1 mg)

*Conditions for producing NPs(5Pd) in Figure 1(*a*), Entry 7:* $Pd_2(dba)_3 \cdot CHCl_3$ (5 mg)

*Conditions for producing NPs(10Pd) in Figure 1(*a*), Entry 8:* $Pd_2(dba)_3 \cdot CHCl_3$ (10 mg)

*Conditions for producing NPs(2c) in Figure 1(*a*), Entry 9:* 4 ml of $CHCl_3$ were placed into a 4 ml vail with an equipped with a magnetic stir bar.

*Conditions for producing NPs(10c) in Figure 1(*a*), Entry 10:* 20 ml of $CHCl_3$ were placed into a 50 ml round-bottom flask with an equipped with a magnetic stir bar.

*Conditions for producing NPs(40°C) in Figure 1(*a*), Entry 11:* The reaction mixture was stirred until the solution became colorless at 40℃ temperature.

*Conditions for producing NPs(80°C) in Figure 1(*a*), Entry 12:* The reaction mixture was stirred until the solution became colorless at 80℃ temperature.

*Conditions for producing NPs(acetone) in Figure 1(*a*), Entry 13:* 2 ml of acetone were placed into a 4 ml vail with an equipped with a magnetic stir bar.

*Conditions for producing NPs(toluene) in Figure 1(*a*), Entry 14:* 2 ml of toluene were placed into a 4 ml vail with an equipped with a magnetic stir bar.

*Conditions for producing NPs(DMF) in Figure 1(*a*), Entry 15:* 2 ml of DMF were placed into a 4 ml vail with an equipped with a magnetic stir bar.

*Method for producing Pt NPs/*Graphite *in Figure 1(*e*):* $Pt_2(dba)_3 \cdot CHCl_3$ (0.65 mg), the carbon material (20 mg) graphite powder (Sigma Aldrich, <20μm, synthetic) and 2 ml of $CHCl_3$ were placed into a 4 ml vial with an equipped with a magnetic stir bar. The reaction mixture was stirred until the solution became colorless at room temperature (80 ℃). The carbon material was filtered, washed with acetone and dried.

General methodology for catalytic reactions.

Glass vials containing 1 equivalent of DPA (210 mg, 1.18 mmol), 1 mL of solvent (DMF : H_2O = 3:1 v/v), 1.5 equivalents of KOH (99 mg, 1.77 mmol), 5 mg of Pd/Support catalyst, and magnetic stir bars were placed in autoclaves. Prior to the experiment, the autoclaves were purged with argon to remove air and then pressurized with hydrogen to 10 bar. The reactions were conducted at room temperature (22 °C) with vigorous stirring using magnetic stirrers. After completion, the reaction mixtures were filtered, and the resulting solutions were analyzed by ^1H NMR as described previously.

In the initial stages of the hydrogenation reaction of diphenylacetylene, the primary product formed is (*Z*)-1,2-diphenylethylene, with no detectable amounts of (*E*)-1,2-diphenylethylene or 1,2-diphenylethane observed by NMR (Figure S4). Conversions were measured after 10 minutes, as this timeframe approximately corresponds to the half-conversion point and serves as an indicator of the catalytic activity of the material. During this period, the conversion equals the yield of (*Z*)-1,2-diphenylethylene, the sole product of the hydrogenation reaction.

General methodology the effect of NHC addition on catalytic activity in the hydrogenation reaction.

In comparison to the general methodology for catalytic reactions, 5 equivalents (Pd) of NHC·HCl (5 mg of IMes·HCl) was dissolved in 500 µL of DMF, and an 80 µL aliquot of the solution was added to the reaction mixture. Alternatively, 6.35 mg of IPr·HCl was dissolved in 500 µL of DMF, and an 80 µL aliquot of this solution was added to the reaction mixture) were added to the reaction mixture, which contained DPA (210 mg, 1.18 mmol), 1 mL of solvent (DMF : H_2O = 3:1 v/v), 1.5 equivalents of KOH (99 mg, 1.77 mmol), and 5 mg of the NPs(80°C) or Pr NPs/Graphite catalyst. All other procedures followed the general methodology for catalytic reactions.

General methodology the effect of pre-activation with the addition of NHC on catalytic activity.

In a 2 mL glass vial, while stirring, 1 equivalent of DPA (210 mg, 1.18 mmol), 1 mL of solvent (DMF:H_2O = 3:1 v/v), 1.5 equivalents of KOH (99 mg, 1.77 mmol), and NHC·HCl (5 mg of IMes·HCl dissolved in 500 µL of DMF, with an 80 µL aliquot added to the reaction mixture, or alternatively, 6.35 mg of IPr·HCl dissolved in 500 µL of DMF, with an 80 µL aliquot added) were combined. The reaction mixture was then heated at 80 °C for 30 minutes. After cooling, the reaction mixture was transferred to an autoclave. Prior to the experiment, the autoclaves were purged with argon to remove air and then pressurized with hydrogen to 10 bar. The reactions were performed at room temperature (22 °C) under vigorous stirring with magnetic stirrers for 5 min. After completion, the reaction mixtures were filtered, and the resulting solutions were analyzed by ^{1}H NMR as previously described.

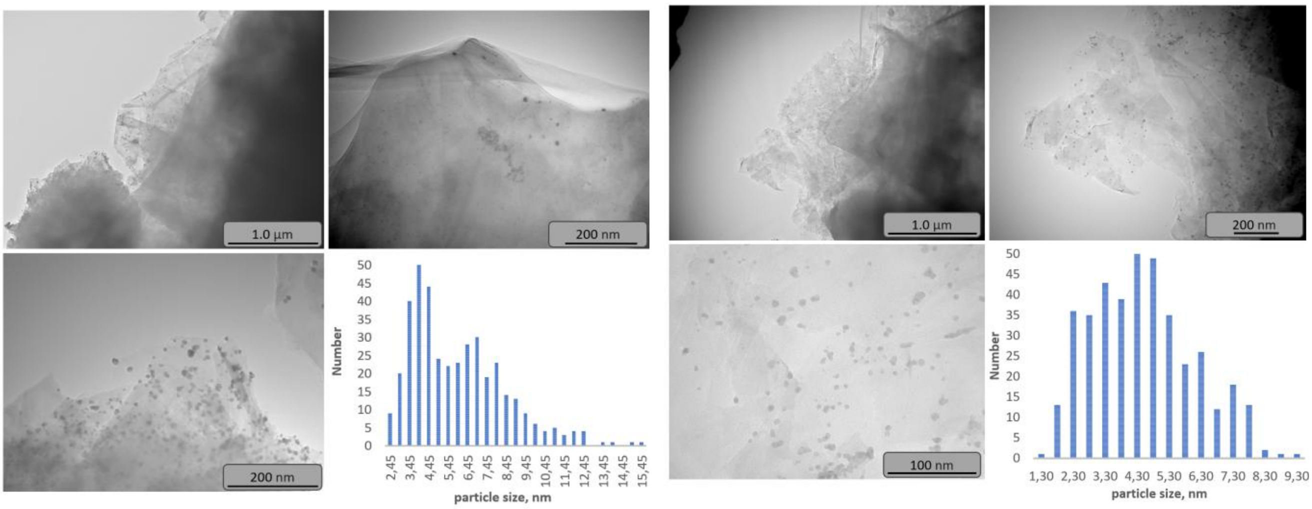
General methodology of the hot filtration test.

In a 2 mL glass vial, while stirring, 1 equivalent of DPA (210 mg, 1.18 mmol), 1 mL of solvent (DMF:H_2O = 3:1 v/v), 1.5 equivalents of KOH (99 mg, 1.77 mmol), and NHC·HCl (5 mg of IMes·HCl dissolved in 500 µL of DMF, with an 80 µL aliquot added to the reaction mixture, or alternatively, 6.35 mg of IPr·HCl dissolved in 500 µL of DMF, with an 80 µL aliquot added) were combined. The reaction mixture was then heated at 80 °C for 30 minutes. Then quickly filtered the reaction mixture and 200 µl were taken from the profiled reaction mixture for ICP-MS. After cooling, the filtered reaction mixture was transferred to an autoclave. Prior to the experiment, the autoclaves were purged with argon to remove air and then pressurized with hydrogen to 10 bar. The reactions were performed at room temperature (22 °C) under vigorous stirring with magnetic stirrers for 5 min. After completion, the reaction mixtures were filtered, and the resulting solutions were analyzed by ^{1}H NMR as previously described. (Figure S11-S13).

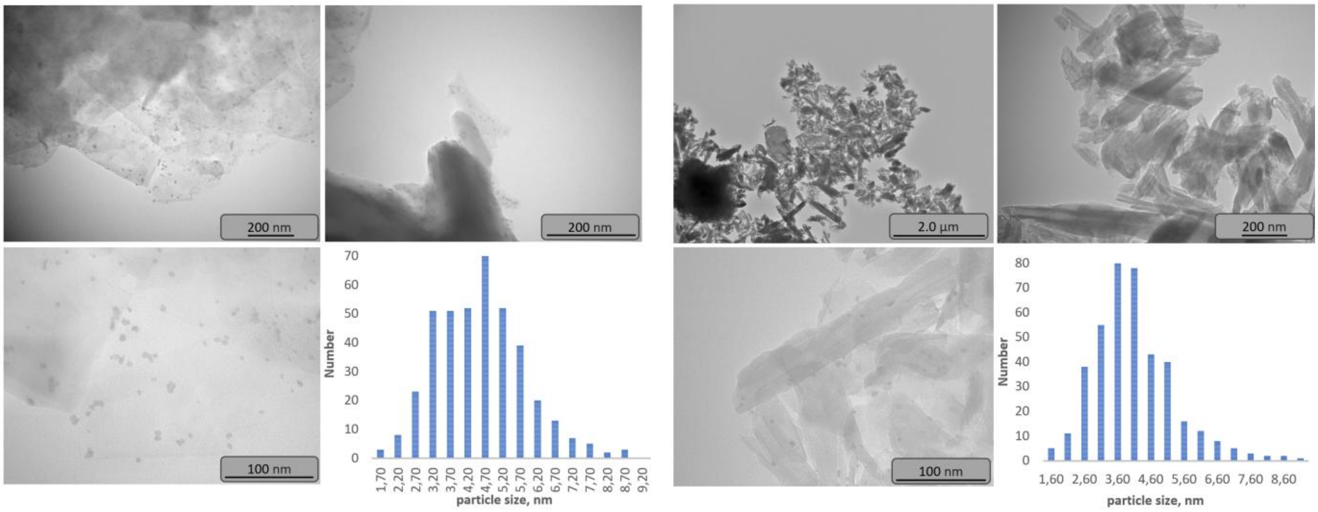
Inductively coupled plasma mass spectrometry analysis.

The analysis is performed on a PlasmaQuant MS Elite AMR instrument. The sample was diluted with 0.5 mL of concentrated nitric acid. Then 0.4 ml of the sample was diluted with 9 ml of deionized water. For the analysis, a slightly acidic environment is a prerequisite and a volume of about 10 ml is optimum. The calibration was carried out in various ranges from 5 to 500 µg/liter.

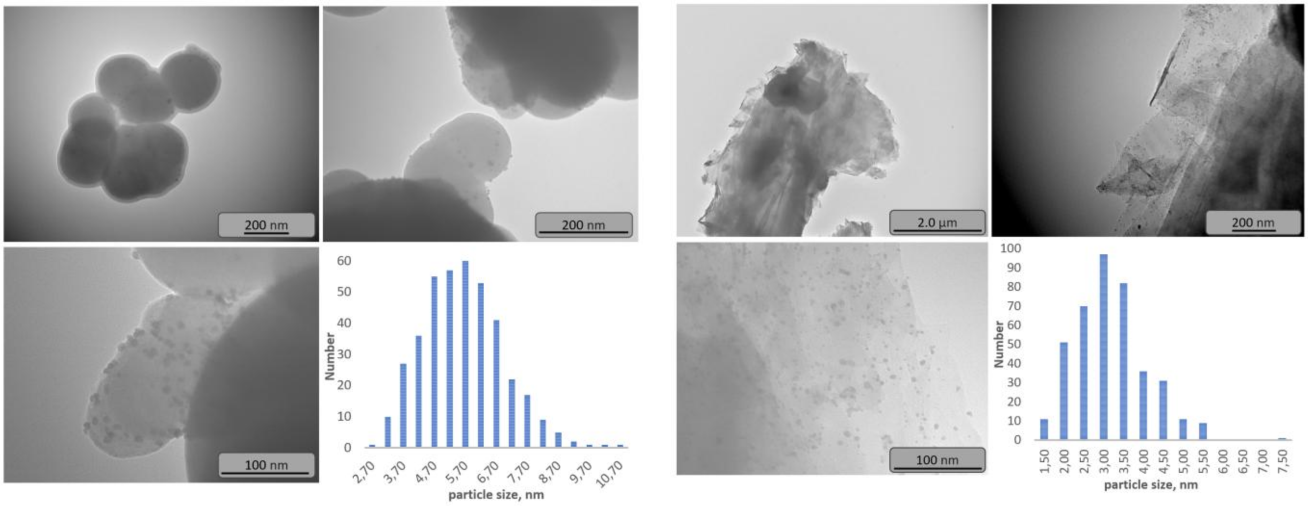
TEM studies



A NPs(acid) **B** NPs(standard)

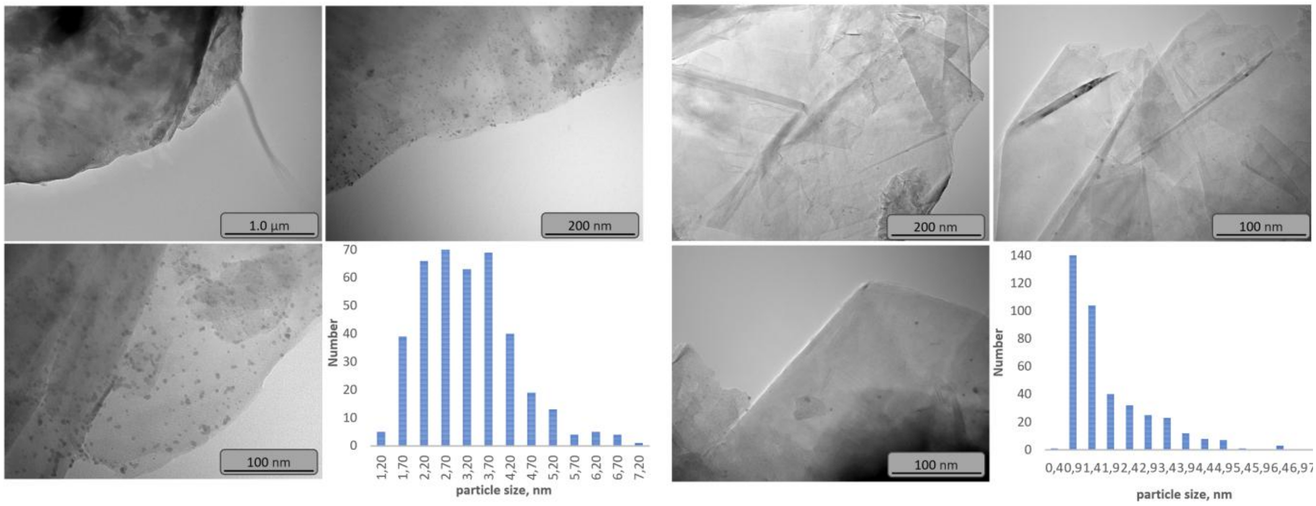


C NPs(base) **D** NPs(Halloysite)

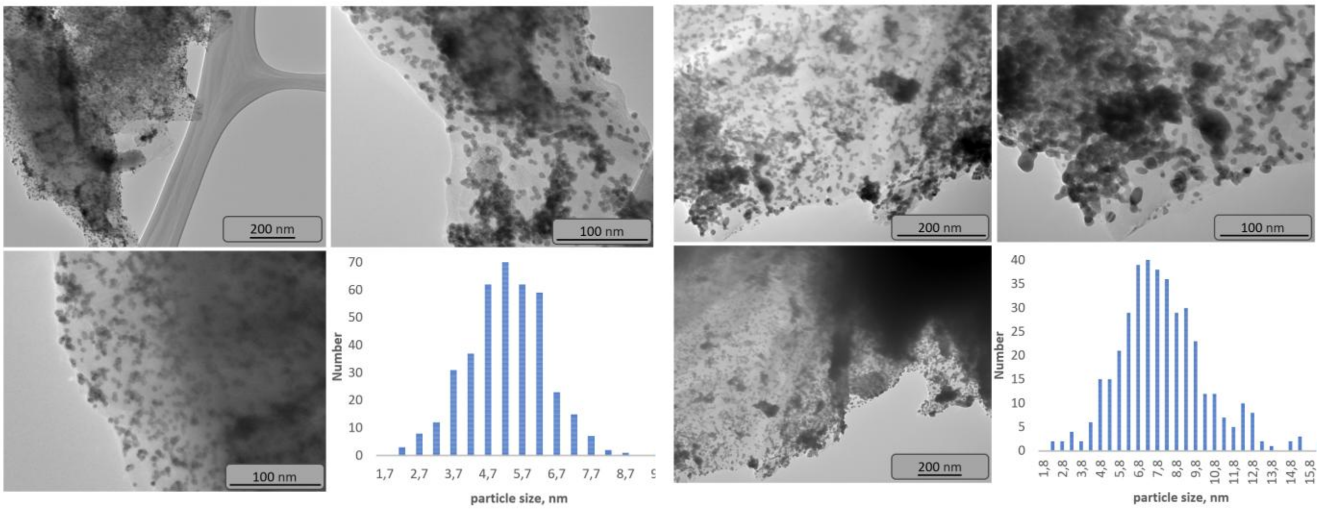


E NPs(T900) **F** NPs(40°C)

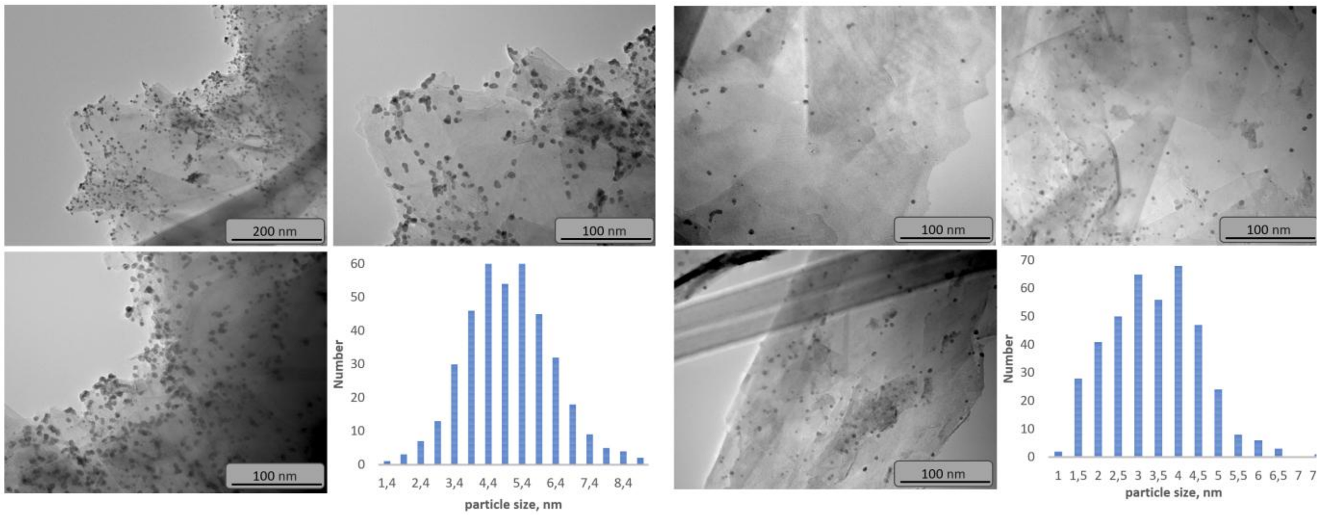
Figure S1 TEM images and histograms of particle distribution.



A NPs(80°C) **B** NPs(0.1Pd)

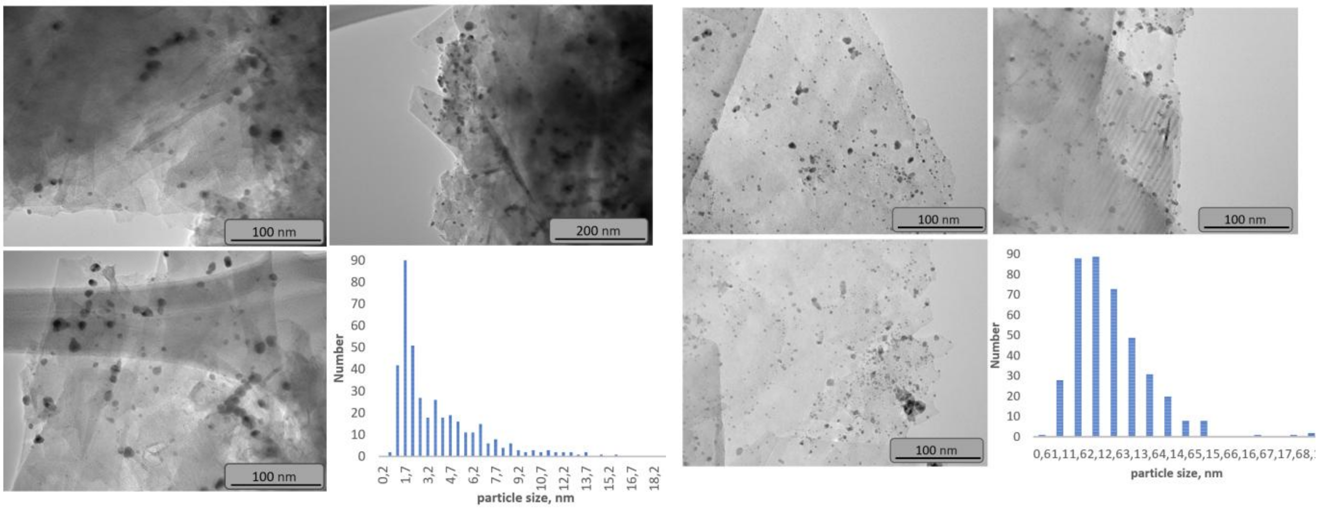


C NPs(5Pd) **D** NPs(10Pd)



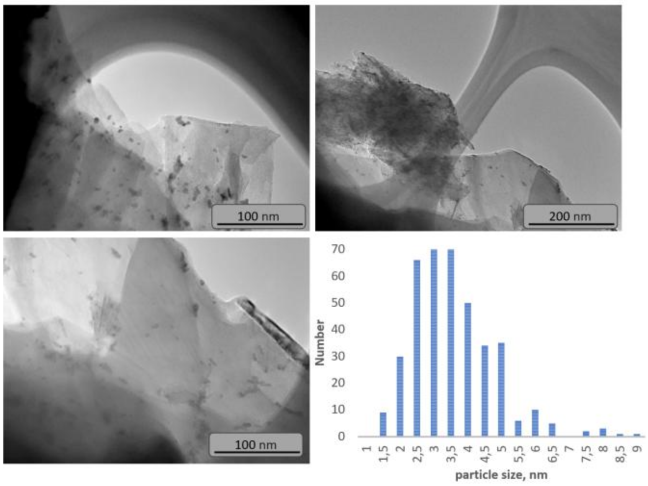
E NPs(2c) **F** NPs(10c)

Figure S2 TEM images and histograms of particle distribution.



A NPs(acetone)

B NPs(toluene)



C NPs(DMF)

Figure S3 TEM images and histograms of particle distribution.

Table S1 Maximum and minimum particle sizes.

Name of sample	Min size NPs (nm)	Max size NPs (nm)
NPs(toluene)	0.6	8.0
NPs(40°C)	1.0	7.5
NPs(80°C)	0.8	7.1
NPs(0.1Pd)	0.4	7.0
NPs(10c)	1.0	7.3
NPs(DMF)	1.0	9.0
NPs(acetone)	0.2	19.3
NPs(Halloysite)	1.1	8.9
NPs(standard)	1.3	8.9
NPs(base)	1.7	8.6
NPs(2c)	1.4	8.7
NPs(5Pd)	1.8	9.4
NPs(T900)	2.7	10.6
NPs(acid)	2.0	15.1
NPs(10Pd)	1.9	16.5

Catalytic study

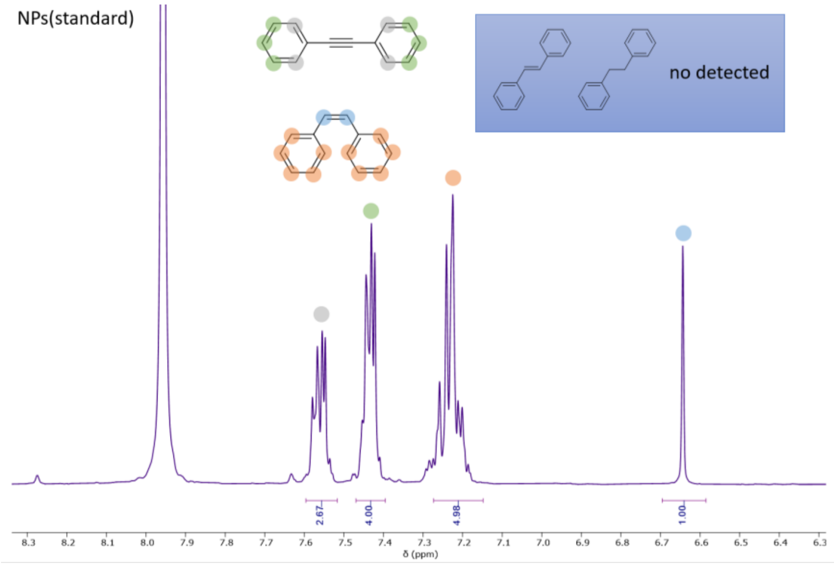
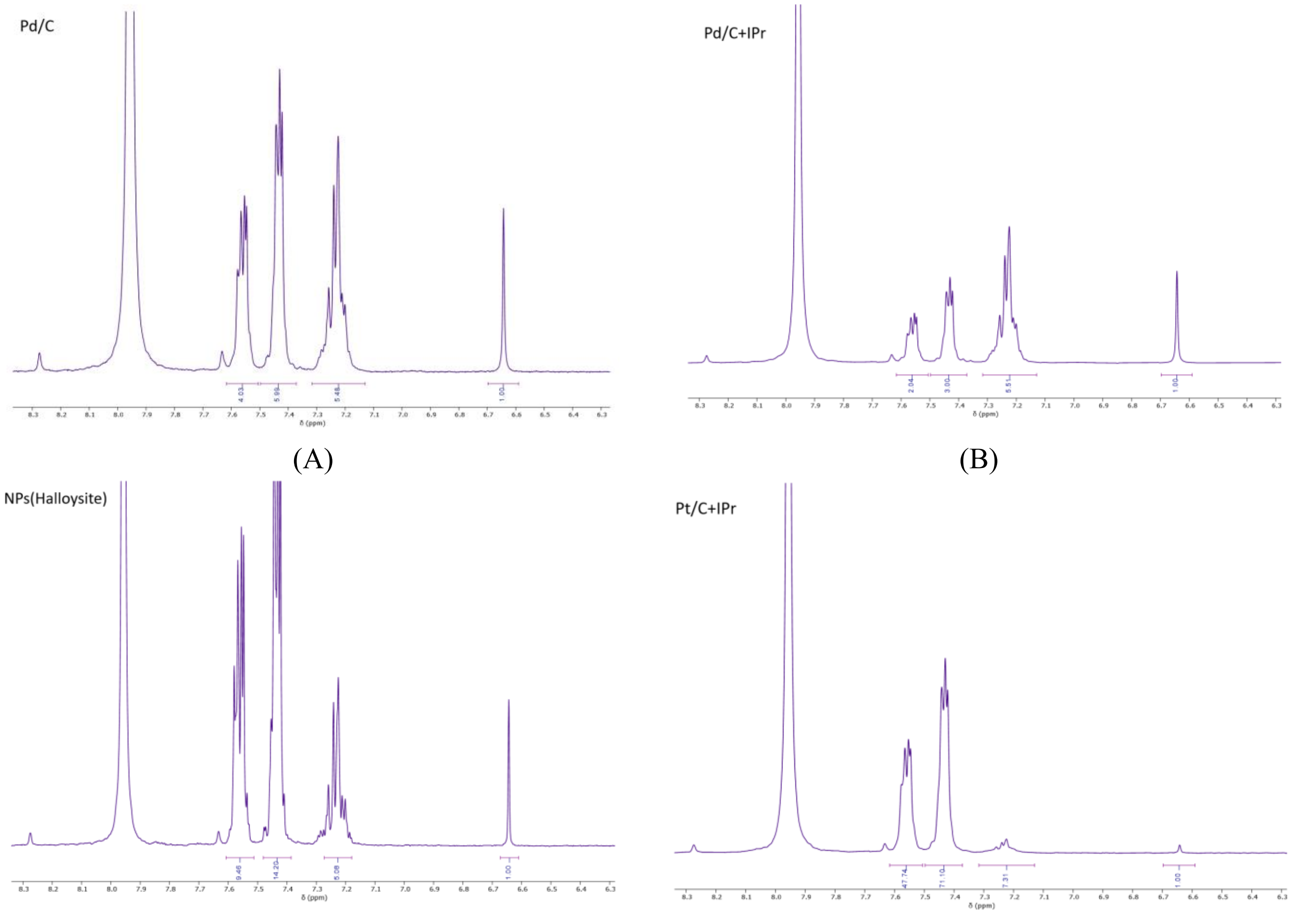


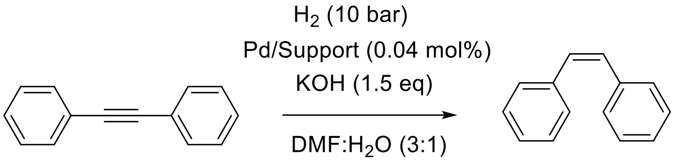
Figure S4 Fragment of the ^1H NMR spectrum of the reaction mixture at 10 min. Reaction conditions: 0.1 mmol 1,2-diphenylacetylene DPA (210 mg, 1.18 mmol), 1.5 equivalents of KOH (99 mg, 1.77 mmol), 5 mg of 1% Pd NPs/Graphite, 1 mL of solvent (DMF : H_2O = 3:1 v/v), 10 bar H_2, 22 °C.



(A) (B)

(C) (D)

Figure S5 Fragments of the ^1H NMR spectra of the reaction mixtures. Effect of pre-activation with the addition of NHC on catalytic activity of (A) Pd/C, (B) Pd/C+IPr, (C) NPs(Halloysite) and (D) Pt/C+IPr at (A),(B),(D) 5 and (C) 10 min.



Name of sample	Conversion rate after 5 min	Conversion rate after 10 min	Conversion rate after 2 hours
NPs(acid)	4%	14%	100%
NPs(standard)	16%	42%	100%
NPs(base)	10%	39%	100%
NPs(Halloysite)	5%	18%	100%
NPs(T900)	13%	32%	100%
NPs(40°C)	14%	52%	100%
NPs(80°C)	17%	69%	100%
NPs(0.1Pd)	5%	16%	100%
NPs(5Pd)	11%	74%	100%
NPs(10Pd)	34%	77%	100%
NPs(2c)	5%	18%	100%
NPs(10c)	3%	9%	100%
NPs(acetone)	14%	36%	100%
NPs(toluene)	16%	37%	100%
NPs(DMF)	4%	11%	100%

Figure S6 Conversions in hydrogenation reactions on different catalysts.

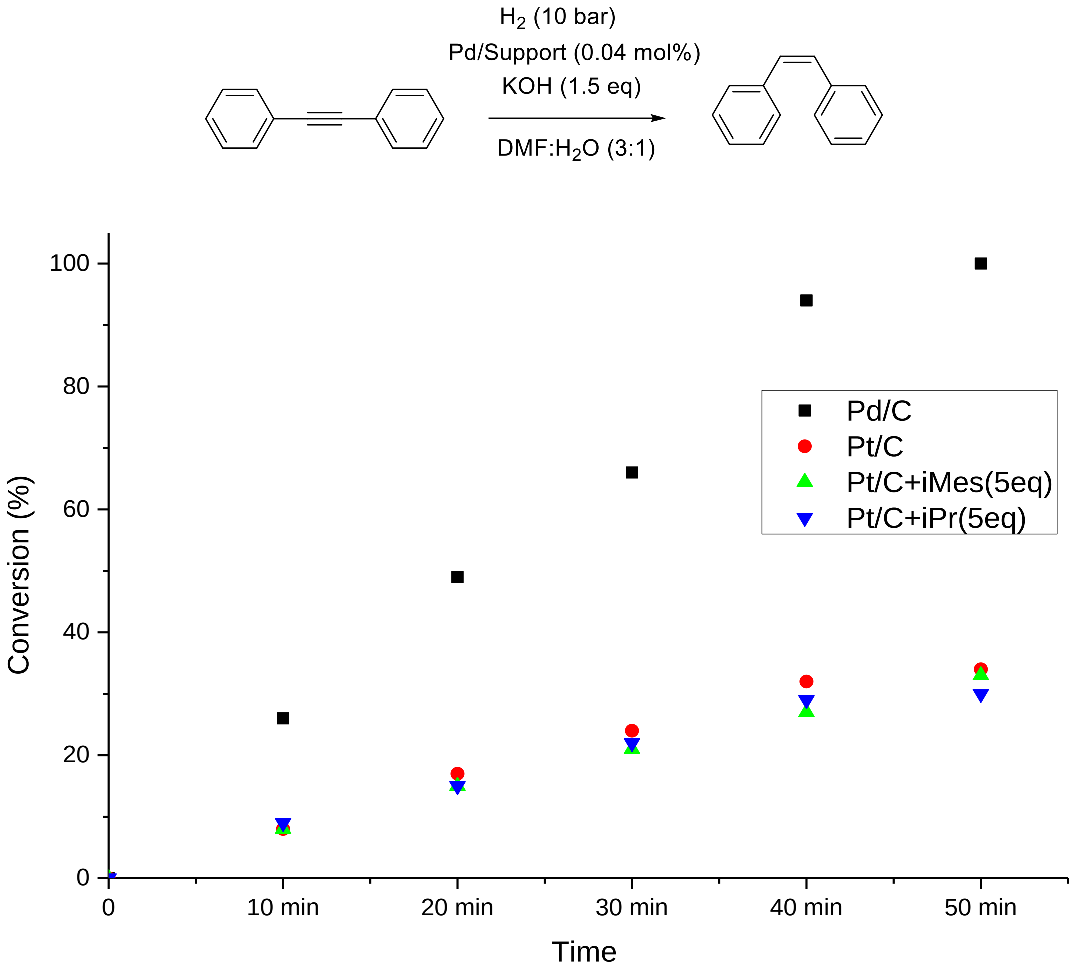
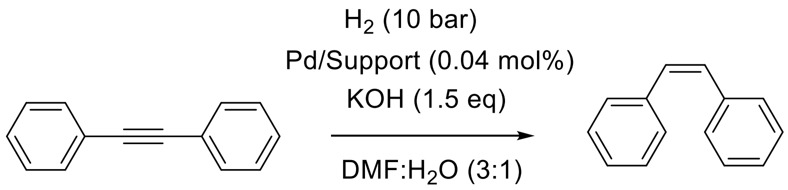


Figure S7 Effect of adding NHC on catalytic activity in the reaction of diphenylacetylene.



Name of sample	Conversion after preactivation 80 °C 1 hour (not H_2)	Conversion rate after 10 min
Pd/C	trace	34%
Pd/C+iMesNHC*HCl (5eq)	trace	28%
Pd/C+iPrNHC*HCl (5eq)	trace	51%
Pt/C	trace	5%
Pt/C+iMesNHC*HCl (5eq)	trace	5%
Pt/C+iPrNHC*HCl (5eq)	trace	5%

Figure S8 Effect of pre-activation with the addition of NHC on catalytic activity in the reaction of diphenylacetylene hydrogenation.

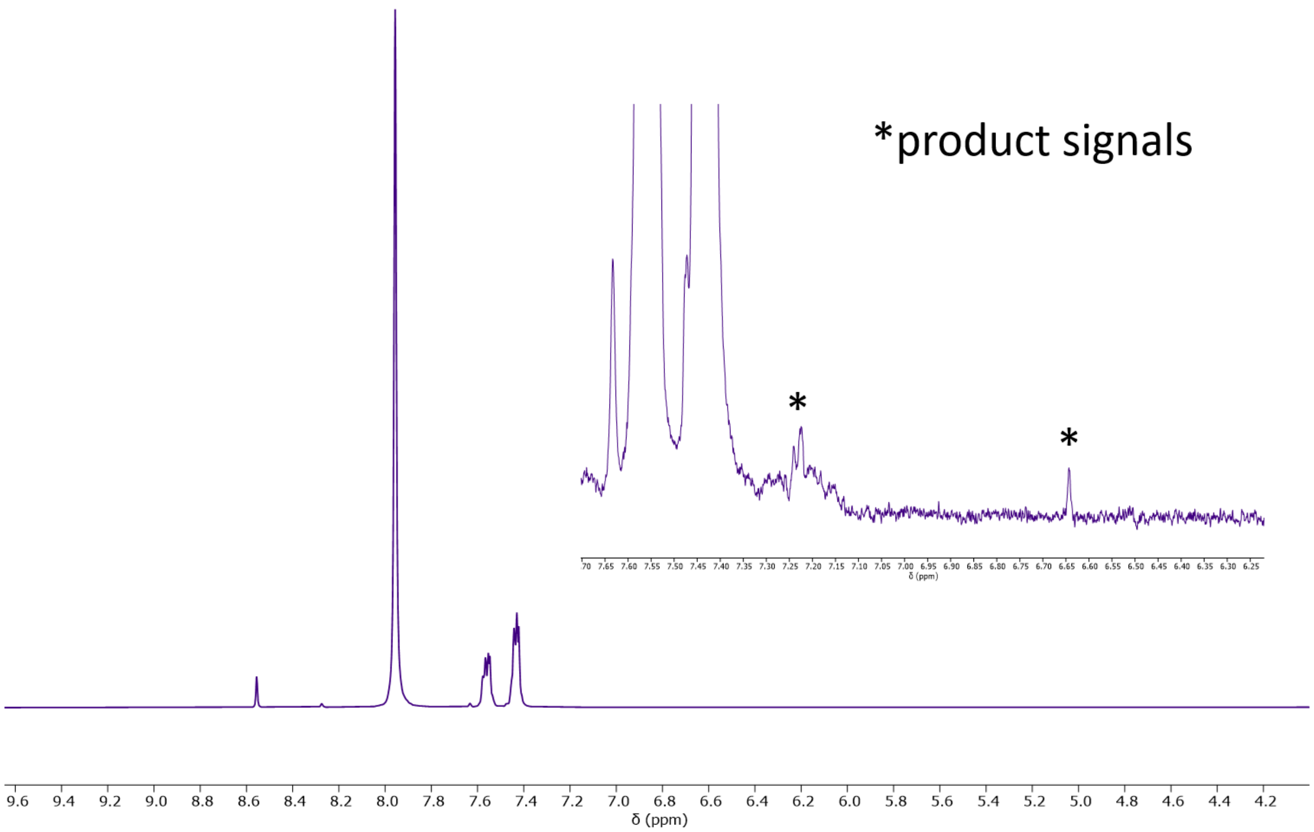


Figure S9 ^{1}H NMR of the reaction mixture after pre-activation.

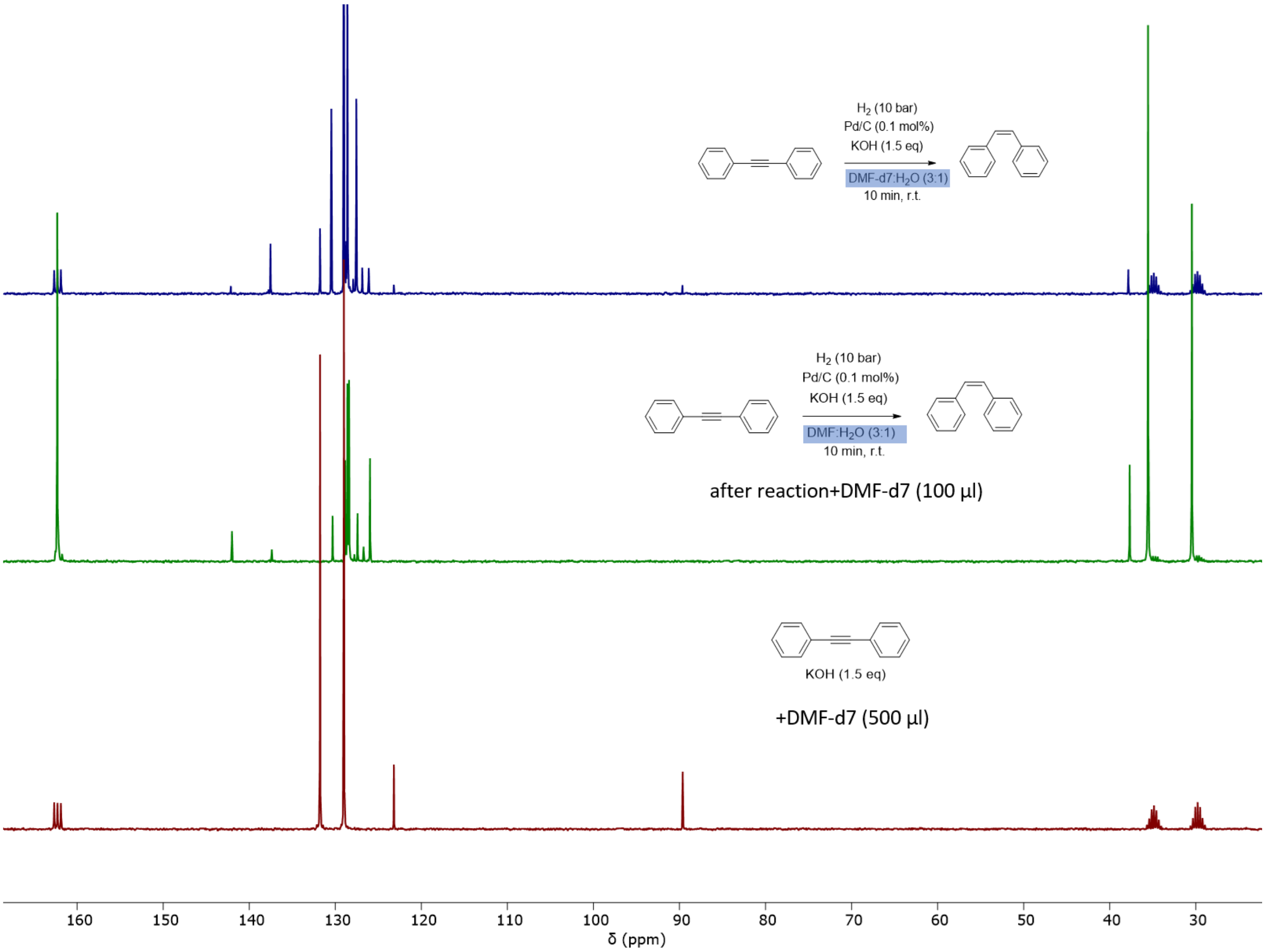


Figure S10 ^{13}C NMR experiments in fully deuterated DMF (DMF-*d*7). Deuterated form is absent.

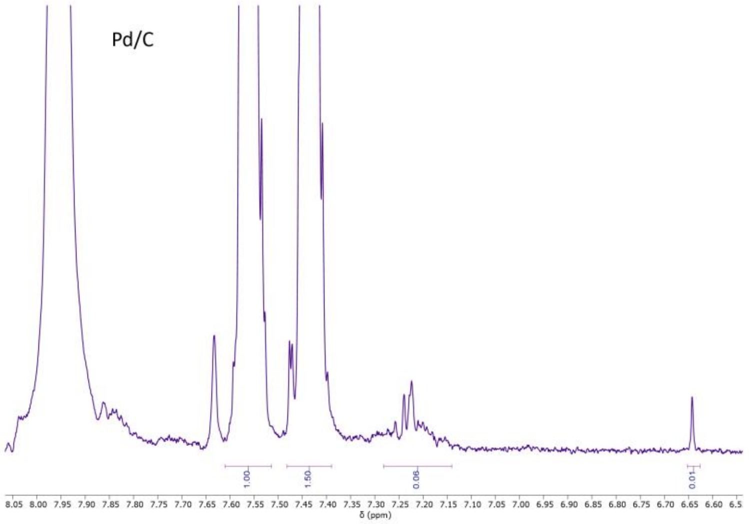


Figure S11 The hot filtration test on Pd/C.

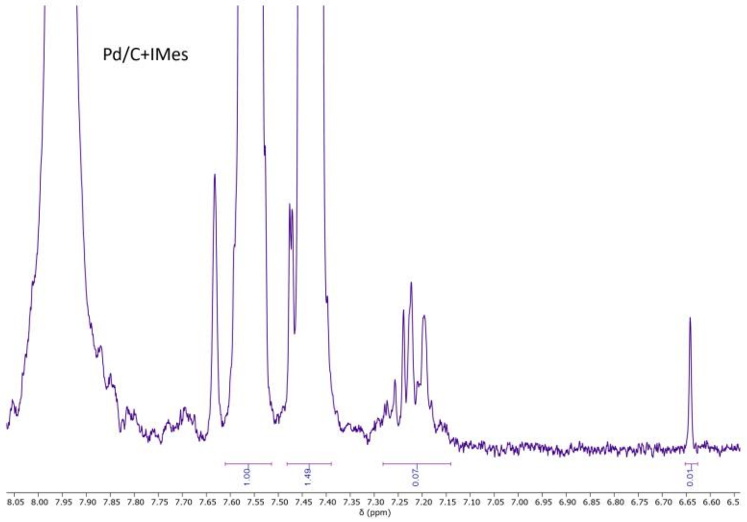


Figure S12 The hot filtration test on Pd/C+IMes.

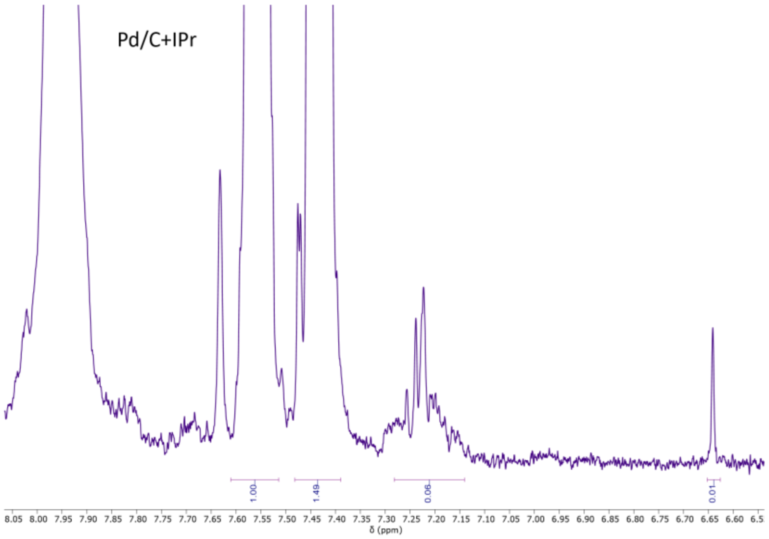


Figure S13 The hot filtration test on Pd/C+IPr.