

Supporting Information

H-Transfer reactions of internal alkenes with tertiary amines as H-donors on carbon supported noble metals

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Experimental procedures, materials

Chemicals The following chemicals were used as received, without any additional purification or further treatment: anhydrous *p*-xylene (Sigma-Aldrich $\geq 99.0\%$), CH_2Cl_2 (Sigma-Aldrich $\geq 99.8\%$), eicosane (Sigma-Aldrich 99.0%), butylcyclohexane (Sigma-Aldrich 99.0%), methyl oleate (Sigma-Aldrich 99.0%), *trans*-5-decene (Sigma-Aldrich 99.0%), triethylamine (Sigma-Aldrich $\geq 99.5\%$), tributylamine (Sigma-Aldrich $\geq 99.5\%$), tripropylamine (Sigma-Aldrich 98.0%), trihexylamine (Sigma-Aldrich $\geq 96.0\%$), *N,N*-diisopropylethylamine (Sigma-Aldrich $\geq 98.0\%$), 1-ethylpyrrolidine (Sigma-Aldrich 97.0%), 1-ethylpiperidine (Sigma-Aldrich 99.0%), nitrogen (Westfalen $> 99.999\%$), hydrogen (Westfalen $> 99.999\%$) and argon (Westfalen $> 99.996\%$). The catalysts Pd/C (10 wt%) (Sigma-Aldrich LOT: MKBV2219V), Pt/C (10 wt%) (Sigma-Aldrich LOT: MKBZ4050V), Rh/C (5 wt%) (Sigma-Aldrich LOT: MKBN5780V) were activated prior to their use.

Catalyst activation The commercial catalysts (Pd/C, Pt/C, Rh/C) were activated before usage. The reduction was performed in flowing H_2 at 120 °C for 1 h, then the temperature was increased to 400 °C with a heating rate of 1 °C min^{-1} and held for 3 hours (flow rate of H_2 : 100 mL min^{-1}), the samples were then flushed with N_2 for 1 h before collection. Afterwards, the catalysts were immediately transferred into the glovebox with a very brief exposure to air.

Catalytic reactions The catalytic reactions were carried out in a Schlenk-tube under inert conditions. All the reagent materials, the catalyst (0.10 mmol metal), *p*-xylene (1.50 mL), the corresponding amount of amines (2.20 mmol), the substrate (**1a** = methyl oleate / 1.00 mmol; **2a** = *trans*-5-decene) / 1.00 mmol) and an internal standard (**1a** / eicosane / 0.50 mmol; **2a** / butylcyclohexane / 0.50 mmol) were added to the Schlenk-tube in a glove box (*M Braun LABstar^{pro} ECO*). The reaction mixture was heated to 140 °C. After the required reaction time, it was cooled to room temperature. Sequentially, the catalyst was filtered out and an aliquot of the reaction mixture (50 μL) was taken and diluted with dichloromethane (1.15 mL). The sample was analysed by GC-MS (*Agilent 7890B* gas chromatograph with *Agilent 5977A* mass spectrometer).

GC-MS The filtered liquid samples were analysed via an *Agilent 7890B* gas chromatograph equipped with a flame ionization detector (FID) and an *Agilent 5977A* mass spectrometer. Eicosane and butylcyclohexane were used as internal standard for methyl oleate and *trans*-5-decene, respectively. The liquid sample (1 μL) was injected into a HP-5 MS column (30 m \times 0.32 mm \times 0.25 μm) at an inlet temperature of 280 °C using a split ratio of 50 (He). The column temperature was initially held at 80 °C (**1a**) (**2a**/ 50 °C) for 1 min, then increased to 200 °C (**1a**) (**2a**/80 °C) at a rate of 10 °C min^{-1} (**1a**) (**2a**/ 4 °C min^{-1}) and held at that temperature for 2 min; afterwards, the temperature was increased slowly to 210 °C (**1a**) (**2a**/85 °C), at a rate of 1 °C min^{-1} (**1a**) (**2a**/ 0.5 °C min^{-1}). After holding the temperature for 2 min, the temperature increased to a final 200 °C (**1a**) (**2a**/ 150 °C) at a rate of 10 °C min^{-1} (**1a**) (**2a**/ 5 °C min^{-1}). While the column flow was maintained constant at 1 mL min^{-1} (He) for the whole duration of the measurement. The FID was operated at 280 °C. Identification of the components was performed by using the molecular database (*NIST Spectrum Library 2.0*) of mass spectrometer or by the retention times of commercially available pure substances (methyl oleate (Sigma-Aldrich 99.0%, CAS: 112-62-9), methyl stearate (Sigma-Aldrich $\geq 99.0\%$, CAS: 112-61-8), *trans*-5-decene (Sigma-Aldrich 99.0%, CAS: 7433-56-9), decane (Sigma-Aldrich $\geq 99.0\%$, CAS: 124-18-5)). Quantification of reactants was analysed via the FID-signal. The carbon balance of hydrogenation was 99% for **1a** and 97% for **2a**.

Atomic Absorption Spectroscopy (AAS) Elemental analysis of the samples were performed by atomic absorption spectroscopy on a *UNICAM 939 AA-Spectrometer* equipped with a GF 95 graphite furnace to determine the Pd, Pt, Rh content of the catalysts. The samples were dissolved in a solution of hydrofluoric acid (48%) and nitro-hydrochloric acid at its boiling point before the measurement.

BET surface analysis Specific surface area of the support was determined from nitrogen adsorption-desorption isotherms recorded on an automated *PMI Sorptomatic 1990* instrument at liquid nitrogen temperature (77 K). The samples were outgassed in vacuum ($p = 1 \times 10^{-3}$ mbar) for 2 h at 475 K prior to adsorption. The specific surface areas were calculated by applying the *B.E.T.¹ theory*, the *t-plot method* was used to determine the micropore volumes and mesopore surface areas, while mesopore volumes was determined using the *B.J.H.² method*.

H₂ Chemisorption The active carbon supported metal (Pd, Pt and Rh) was pre-treated at 573 K under 0.1 MPa H₂ for 1 h, followed by evacuation in vacuum for 1 h. After the temperature was cooled to 298 K, the H₂ chemisorption and physisorption were subsequently determined in a pressure of H₂ from 5 to 350 Torr. Then, the physisorbed H₂ was removed by outgassing the sample at 298 K for 1 h. The concentration of chemisorbed hydrogen on the metal was obtained by extrapolating the isotherm to zero Torr of H₂ pressure. The metal (Pd, Pt and Rh) dispersion and TOF were deduced by assuming an average H/metal ratio of 1.

Transmission electron microscopy (TEM) TEM measurements were performed on a JEOL JEM-2011 equipment at 120 kV. The average particle size and its standard deviation was calculated based on the Pd, Pt and Rh particle size distribution of 300 metal particles measured in at least five different particle domains of the catalyst.

Mode of calculations

Conversion = (weight of converted reactant / weight of the starting reactant) × 100%. **The initial reaction rate** was deduced from the slope of the linear fit to the conversion *versus* time plot in the linear region at low conversions (≤ 40%). **TOF** = mole of converted reactant / (mole of accessible metal site × reaction time). **The carbon balance** = (mole of carbon in the product / mole of carbon of starting reactant) × 100%.

Particle size distribution of Pt, Pd and Rh in the catalysts

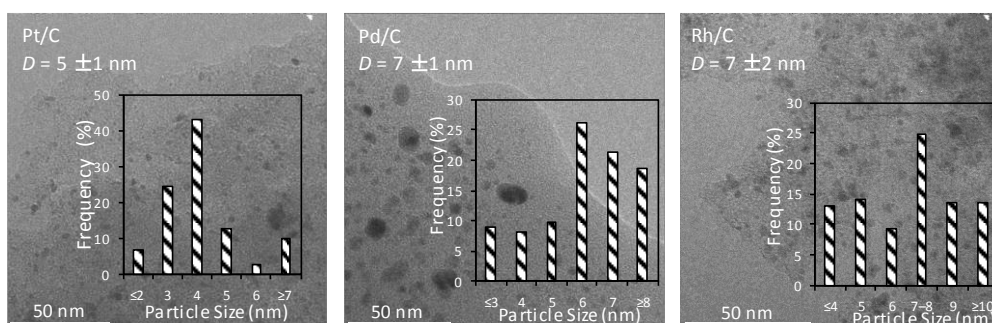


Fig. S1 Particle size distribution of Pt/C, Pd/C and Rh/C via TEM analysis.

For the particle size distribution each metal was estimated based on at least 300 metal particles from five different particle domains of each catalyst. The average particle size is 5 ± 1 nm, 7 ± 1 nm and 7 ± 2 nm for Pt/C, Pd/C and Rh/C, respectively.

Exclusion of mass transfer limitation under the present reaction conditions

Experiments with different agitating speeds were carried out to determine the impact of stirring speed on the reaction. As shown in Fig. S2, mass transfer limitations is considerable when the stirring speed is less than 100 rpm. Therefore, all further reactions have been conducted at a stirring speed of 500 rpm.

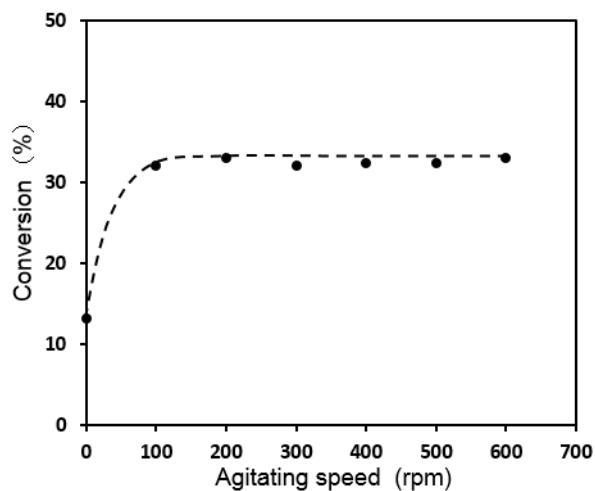


Fig. S2 Hydrogenation conversion of methyl oleate versus agitation speeds. Reaction conditions: 1.00 mmol of methyl oleate in 1.50 mL of *p*-xylene, over Pt/C (10 wt%, 0.10 mmol Pt), at 140°C, 10 min, under Ar, with a stirring speed of 0 – 600 rpm.

Formation of 1-ethyl-pyrrol in the studied system

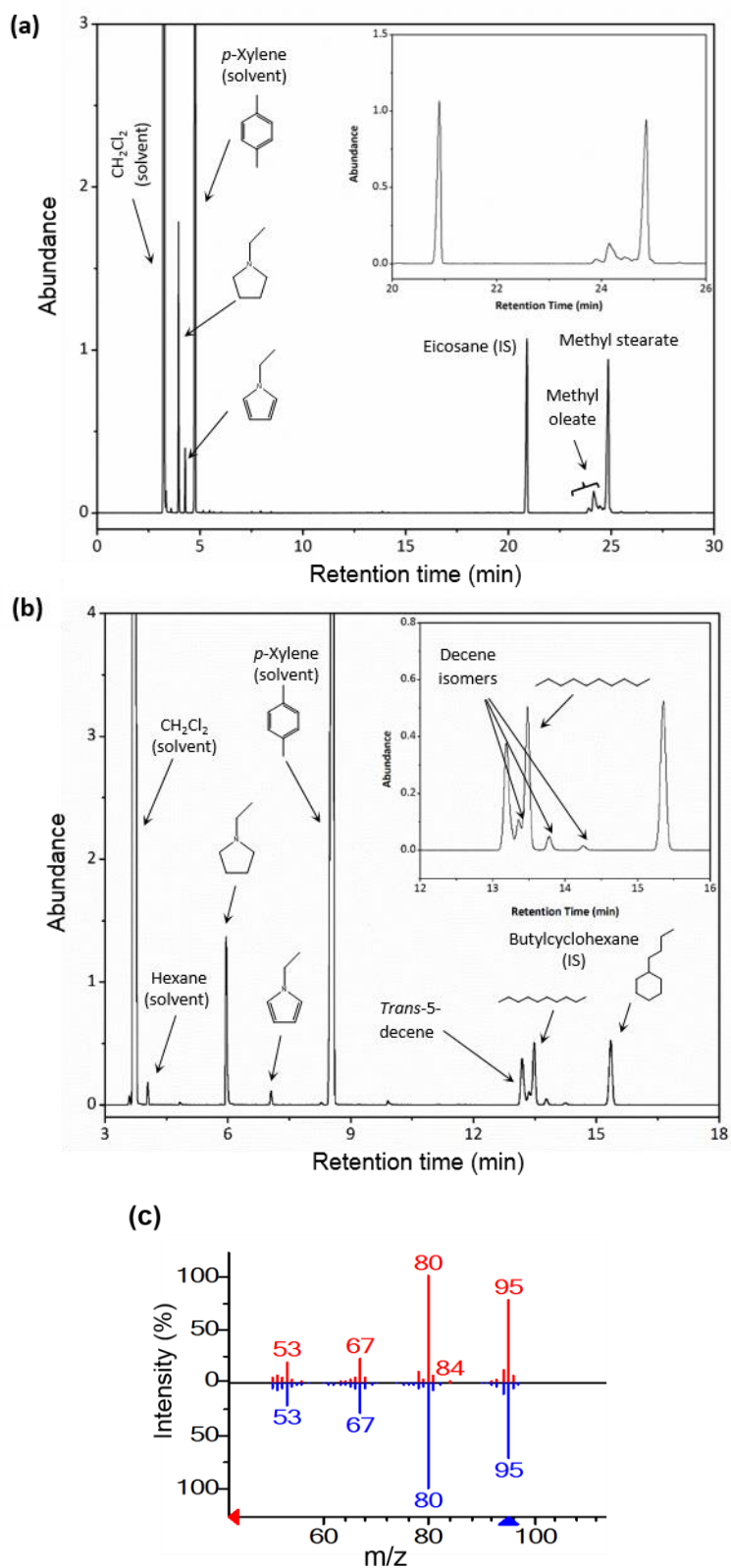


Fig. S3 Representative GC-MS chromatograms of reaction products from hydrogenation of methyl oleate over Pd/C **(a)** and *trans*-5-decene over Pt/C **(b)**, with the 1-ethyl-pyrrolidine (1-EPyr) as the H-donor. (IS) Represents the internal standards for methyl oleate and *trans*-5-decene. The shift of 1-ethyl-pyrrolidine and 1-ethyl-pyrrole peaks on Fig. S3 parts **(a)** and **(b)** are caused by the two different GC-MS methods applied to the different substrates. **(c)** MS pattern of 1-ethyl-pyrrole; the red MS is the spectra of 1-ethyl-pyrrole in the reaction mixture, the spectra in blue is the reference identification according to the NIST database.

Formation of pyridine in the studied system

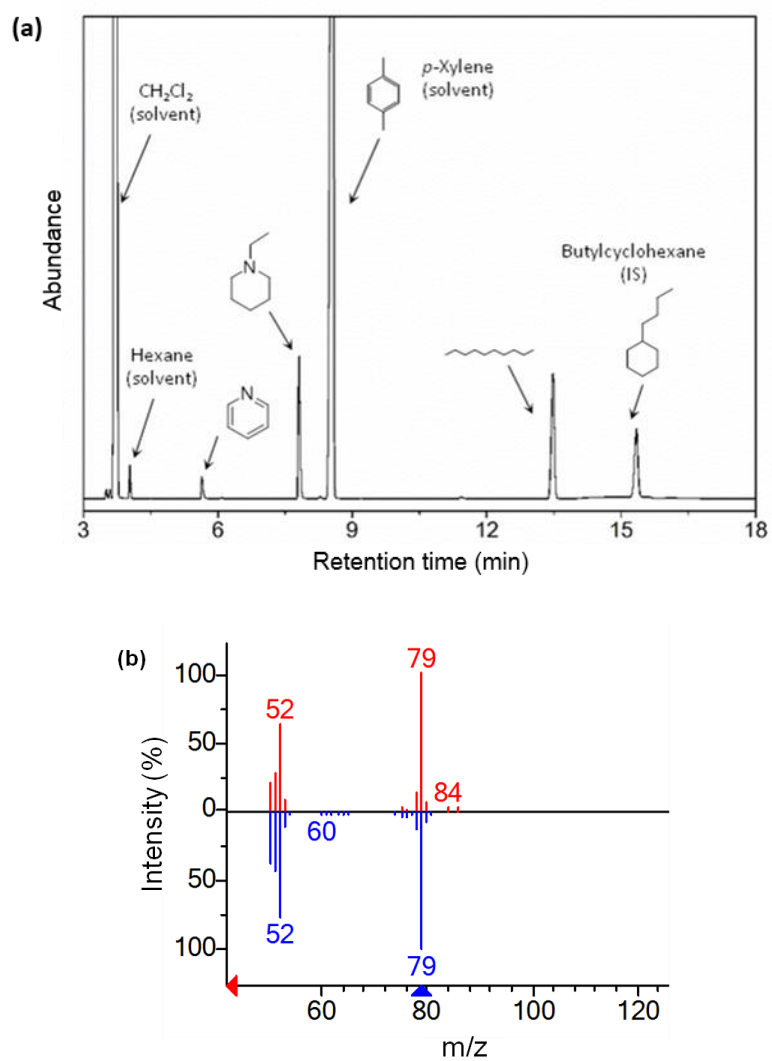


Fig. S4 Representative GC-MS chromatogram (a) of reaction products from hydrogenation of *trans*-5-decene over Pd/C with the 1-ethylpiperidine (1-EPip) as the H-donor. (IS) Represents the internal standards for *trans*-5-decene. (b) MS pattern of pyridine; the red MS is the spectra of the pyridine in the reaction mixture, the spectra in blue is the reference identification according to the NIST database.

The formation of an amine dimer in the presence of (*i*Pr)₂NEt

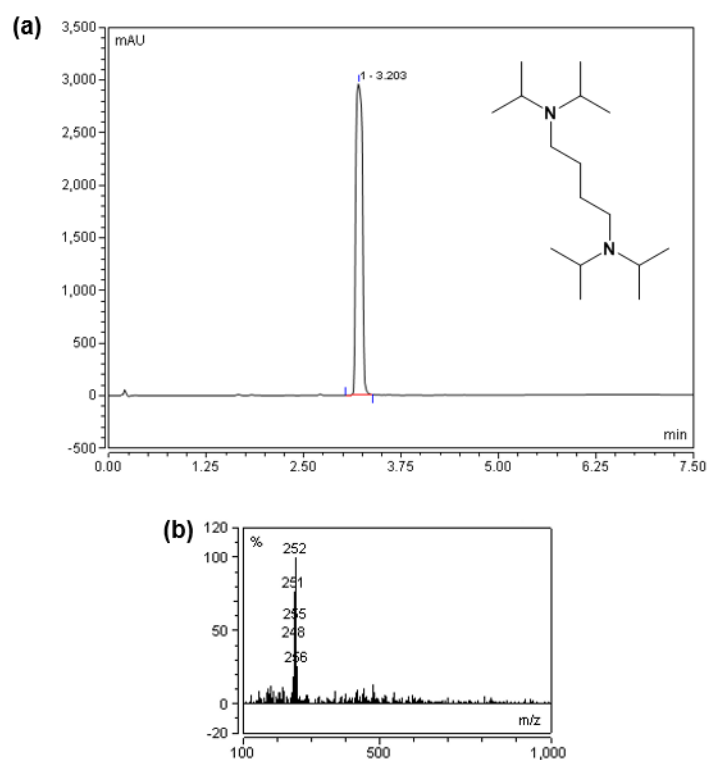


Fig. S5 Representative HPLC (a) and ESI⁺-MS (b) chromatogram of the formation of higher molecular weight compound of (*i*Pr)₂NEt. The HPLC spectra was recorded on *Ultimate3000* by ThermoFisher, column was *Accucore Polar Premium* (50mm x 2.1mm, 2,6μm) by ThermoFisher, gradient: 20% acetonitrile to 100% acetonitrile in 5 min, linear against water with a flow of 900μl min⁻¹, additive free solvents and UV detector (210 nm) were used. ESI⁺-MS spectra was recorded on a *MSQ Plus* by ThermoFisher (needle 3kV, 550 °C, 100 V).

Conversion versus reaction time plots for hydrogenation of methyl oleate and *trans*-5-decene

Typical plots of conversion versus time for hydrogenation of methyl oleate and *trans*-5-decene are shown in Figure S6A and S6B. Initial rates were calculated from the slopes of the curves at conversions less than 40 %.

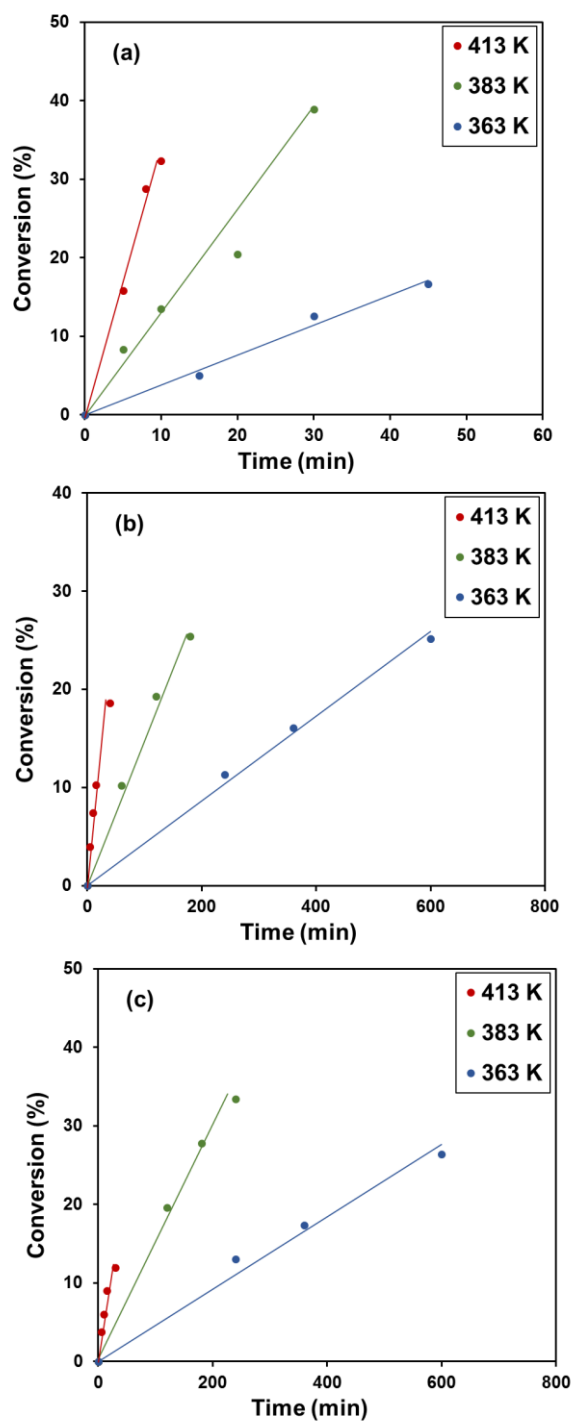


Fig. S6A Hydrogenation of methyl oleate over Pt/C (a), Pd/C (b) and Rh/C (c). Reaction conditions: methyl oleate (1.00 mmol), *p*-xylene (1.50 mL), *N,N*-diisopropyl-ethylamine (2.20 mmol) at a stirring speed of 500 rpm, over Pt/C (10 wt%, 0.10 mmol Pt), Pd/C (10 wt%, 0.10 mmol Pd) and Rh/C (5 wt%, 0.10 mmol Rh).

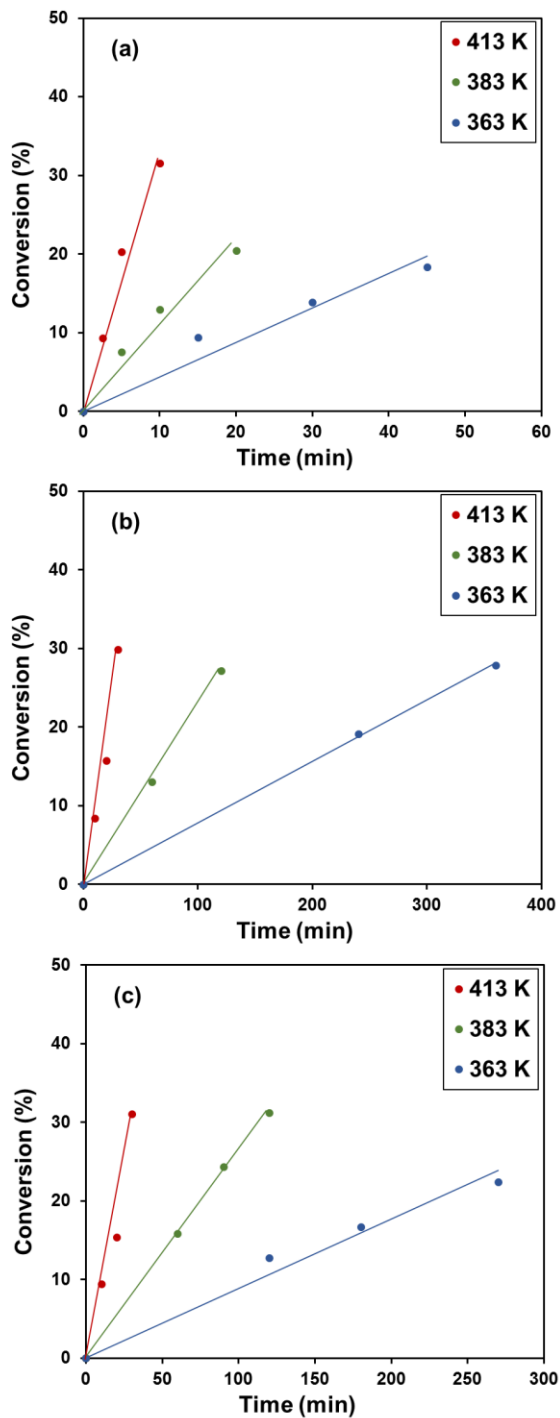


Fig. S6B Hydrogenation of *trans*-5-decene over Pt/C (a), Pd/C (b) and Rh/C (c). Reaction conditions: *trans*-5-decene (1.00 mmol), *p*-xylene (1.50 mL), *N,N*-diisopropyl-ethylamine (2.20 mmol) at a stirring speed of 500 rpm, over Pt/C (10 wt%, 0.10 mmol Pt), Pd/C (10 wt%, 0.10 mmol Pd) and Rh/C (5 wt%, 0.10 mmol Rh).

References

1. S. Brunauer, P. H. Emmett, E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309-319.
2. E. P. Barrett, L. F. Joyner, P. H. Holenda, *J. Am. Chem. Soc.*, 1951, **73**, 373-380.