Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Alkanethiolate-Capped Palladium Nanoparticle for Selective Catalytic Hydrogenation of Dienes and Trienes

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1 Materials

All reagents are used as received from the following suppliers. 1-Bromooctane ($C_8H_{17}Br$), sodium thiosulfate pentahydrate ($Na_2O_3S_2.5H_2O$) and substrates (2,3-dimethyl-1,3-butadiene, isoprene, trans-1,3-pentadiene, 1,3-hexadiene, 2,4-dimethyl-1,3-pentadiene, 3-methyl-1,3-pentadiene, ocimene and myrcene) were obtained from Sigma-Aldrich. Tetra-n-octylammonium bromide (TOAB), sodium borohydride ($NaBH_4$), potassium tetrachloropalladate(II) (K_2PdCl_4), were obtained from Acros. Ethanol, methanol, acetone, and toluene were obtained from Fisher Scientific. Chloroform-d ($CDCl_3$) was purchased from Cambridge Isotope Laboratories, Inc.

2 Synthesis of Sodium S-Octylthiosulfate

A 20 mmol of 1-bromooctane and 20 mmol of sodium thiosulfate pentahydrate are refluxed in the mixture of 40 mL ethanol and 40 mL water for 3 h and recrystallized by hot ethanol. ^{1}H NMR (400 MHz, D_2O): triplet (δ 3.1 ppm, α-CH_2-S), quintet (δ 1.7 ppm, β-CH_2CH_2-S), broad peak (δ 1.3 ppm, -CH_2-) and another triplet (δ 0.90 ppm, CH_3-).[46,47]

3 Synthesis of Octanethiolate-Capped Palladium Nanoparticle

A 0.4 mmol of potassium tetrachloropalladate (II) (K_2PdCl_4) and 0.8 mmol of ocatanthiolsulfate ligand are transferred by a phase transfer agent, 4 mmol of tera-n-octylammonium bromide (TOAB), from aqueous phase to organic phase, and then reduced by 8 mmol of sodium borohydride ($NaBH_4$). Excess TOAB is washed away by ethanol and methanol after reaction is done.[48,49] Nanoparticle size is estimated to be 2.3±1.21 nm using TEM. Thermo gravimetric analysis showed the organic weight fraction of 19 % and palladium weight fraction of 81 %.

4 Catalysis Experiment

A 0.5 mmol of substrates with 5 mol % of octanethiolate-capped palladium nanoparticle are dissolved in 2.5 mL $CDCl_3$ in a 50 mL round bottle flask and purged with H_2 for 10 min. The compositions crude product containing octanethiolate-capped palladium nanoparticle are characterized by Bruker Fourier 400 MHz NMR.

5 Recycle Study

After 24 hour catalyst reaction, 5 mL of methanol solution is added to the crude product. Due to the increased solvent polarity, the solubility of hydrophobic C8 PdNP decreases. C8 PdNP are then centrifuged out from the mixture solution. The collected C8 PdNP are further washed with methanol and ethanol solution to make sure the free and unbound organic compounds are washed away. The washed C8 PdNP is placed under vacuum for ~1 week before next catalytic cycle.

6 Leaching Examination

The crude product mixture and nanoparticle catalyst are separated by silica gel column. The crude mixtures are dried under nitrogen gas and digested by sodium cyanide solution. The mixture solution is placed under sonication for 15 min in order to make sure the complete digestion of Pd^0 with cyanide. The solution is analyzed by Thermo Scientific ICAP 6000 Series, ICP Emission Spectrometers.

7. TEM and TGA charatorization of C8 PdNP:

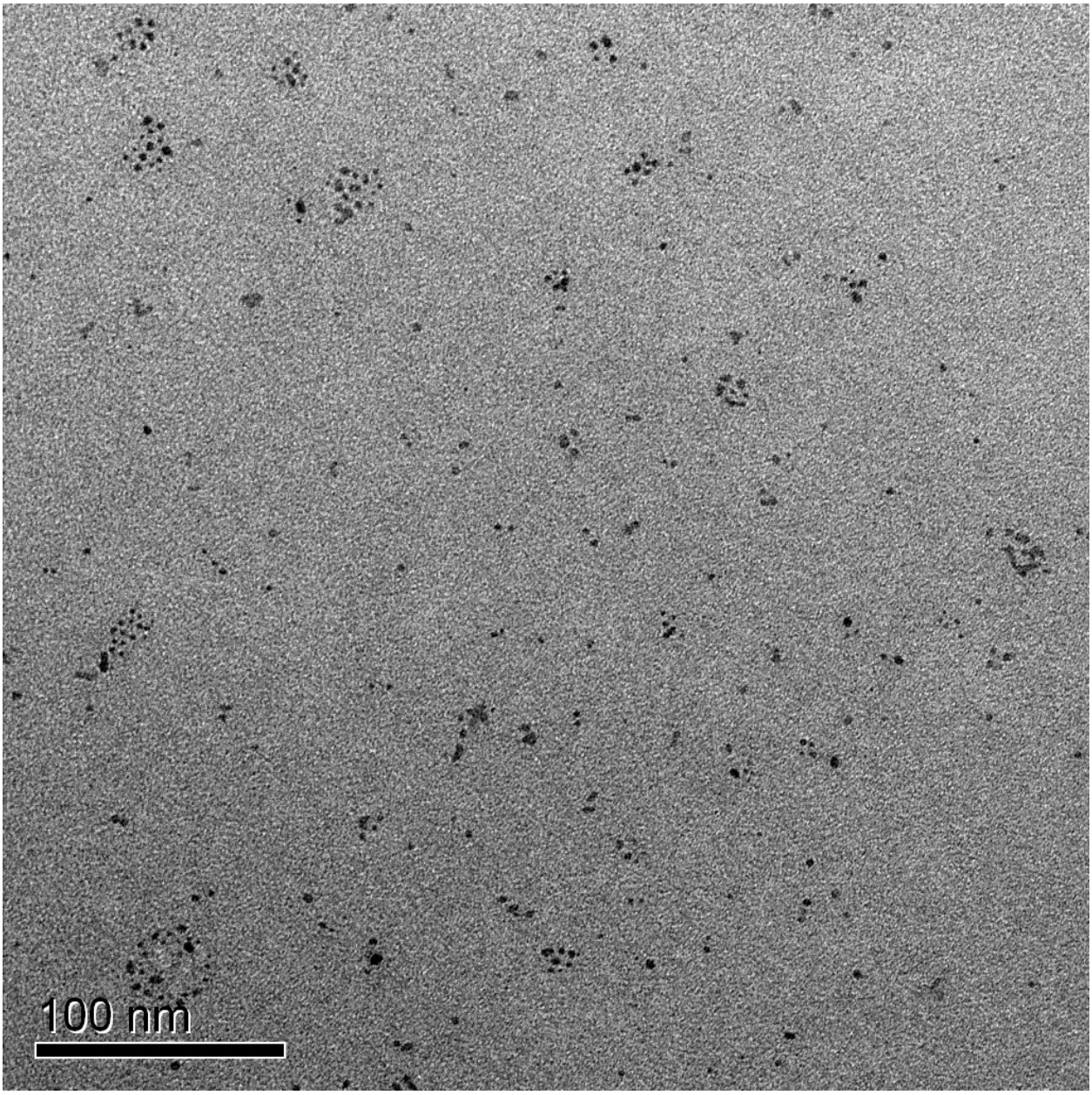

Figure S1. TEM image of C8 PdNP. Particle size is around 2.3 nm. Metal ligand ratio is 84 % of metal: 16 % ligand.

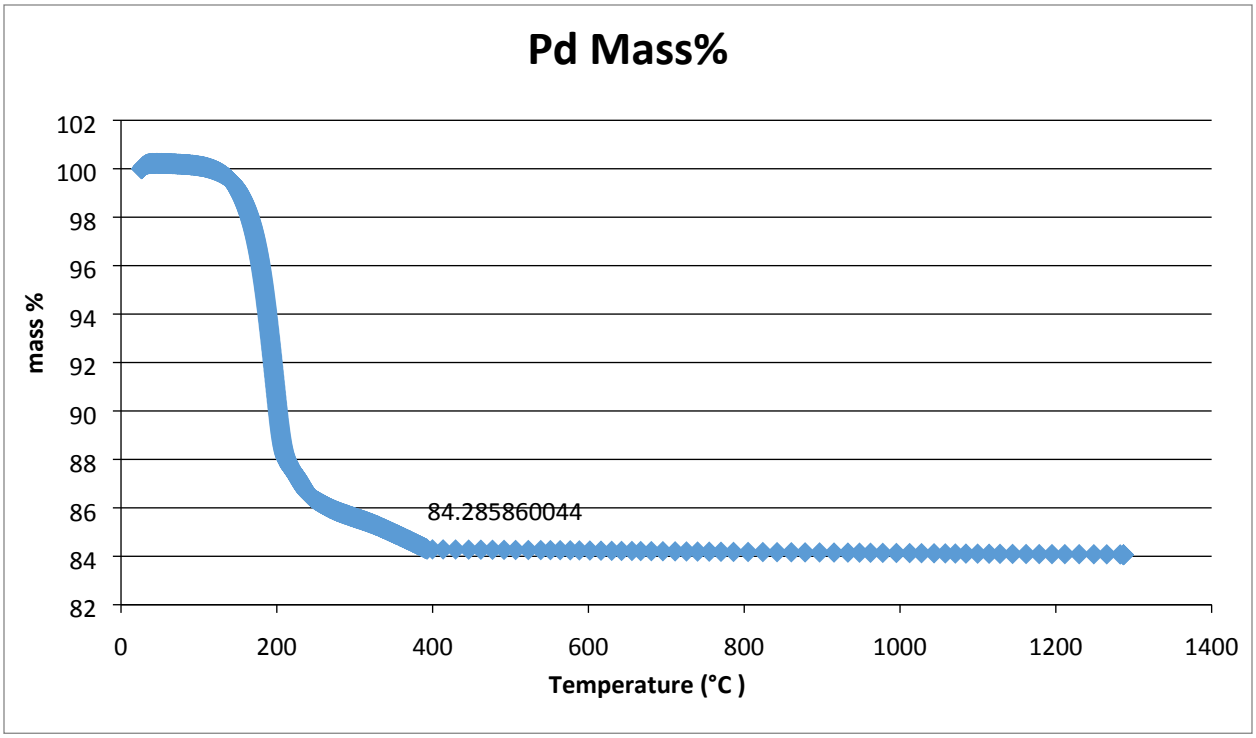

Figure S2. C8 PdNP TGA data. Metal ligand ratio is 84.3 % of metal: 15.7 % ligand.

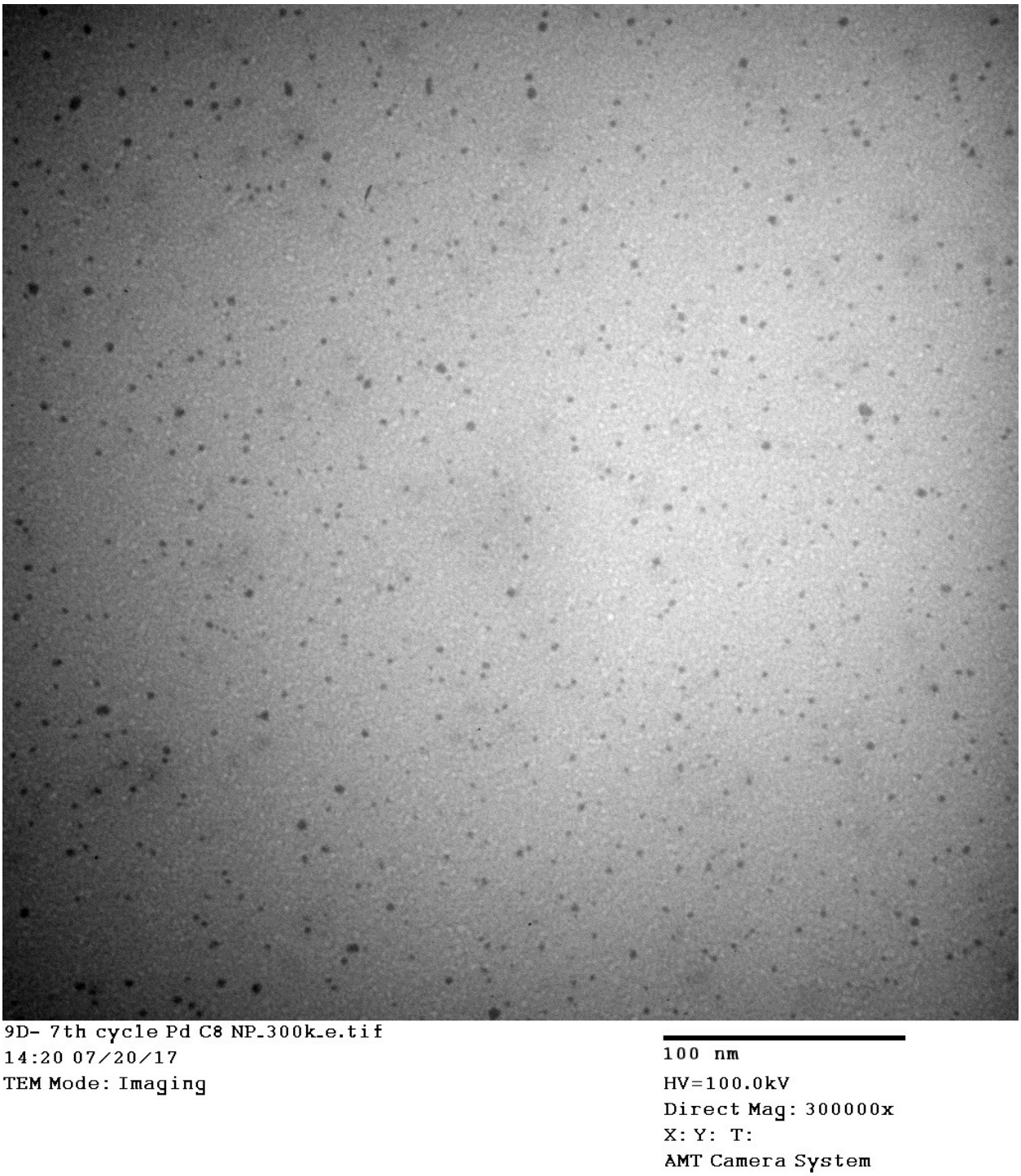

Figure S3. TEM image of C8 PdNP after the 7th cycle of reaction.

8. NMR Spectra

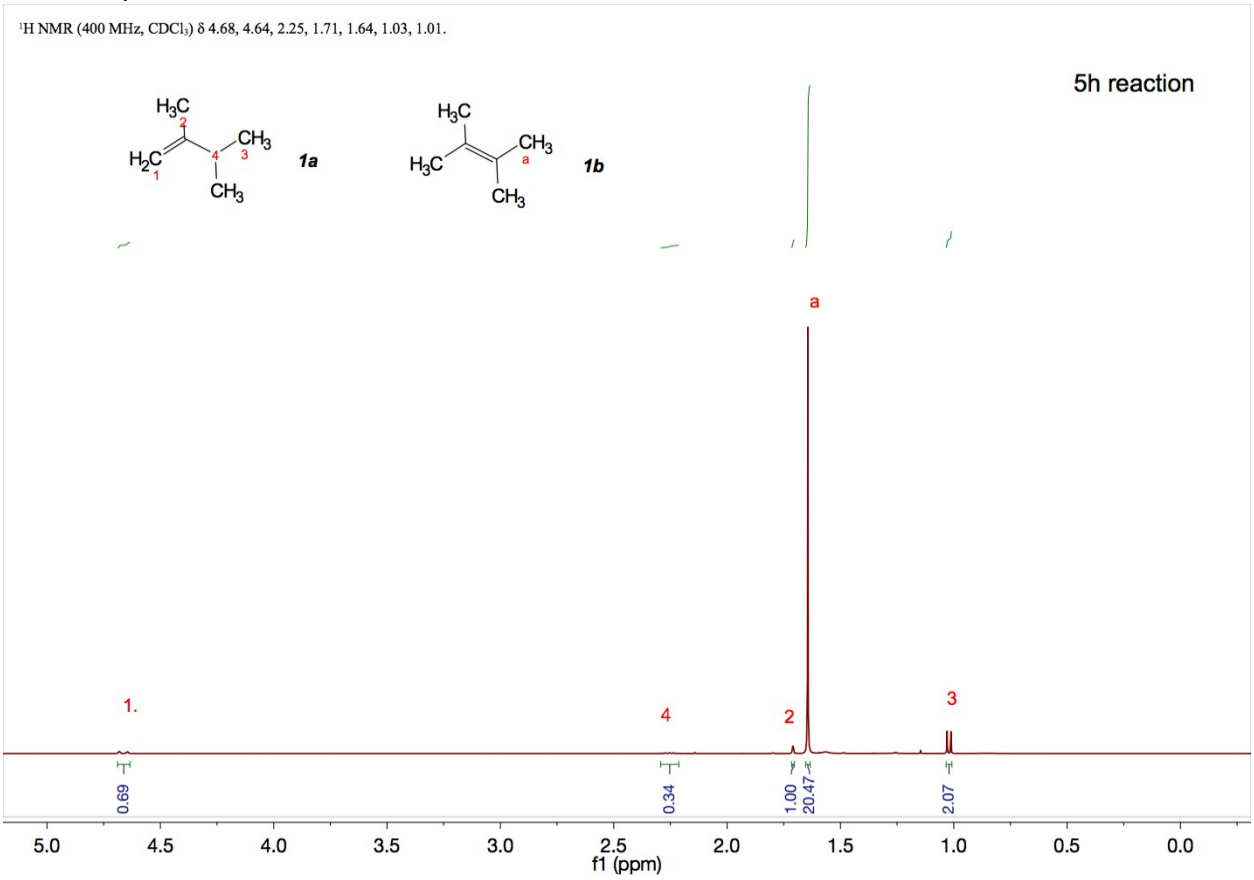

Figure S4. ^{1}H NMR spectrum obtained after reacting 2,3-dimtheyl buta-1,3-diene (**1**) with PdNP in $CDCl_3$ under H_2 conditions after 5 h. The spectrum shows **1a** as the minor product (16.34%) and **1b** as the major product (83.6%).

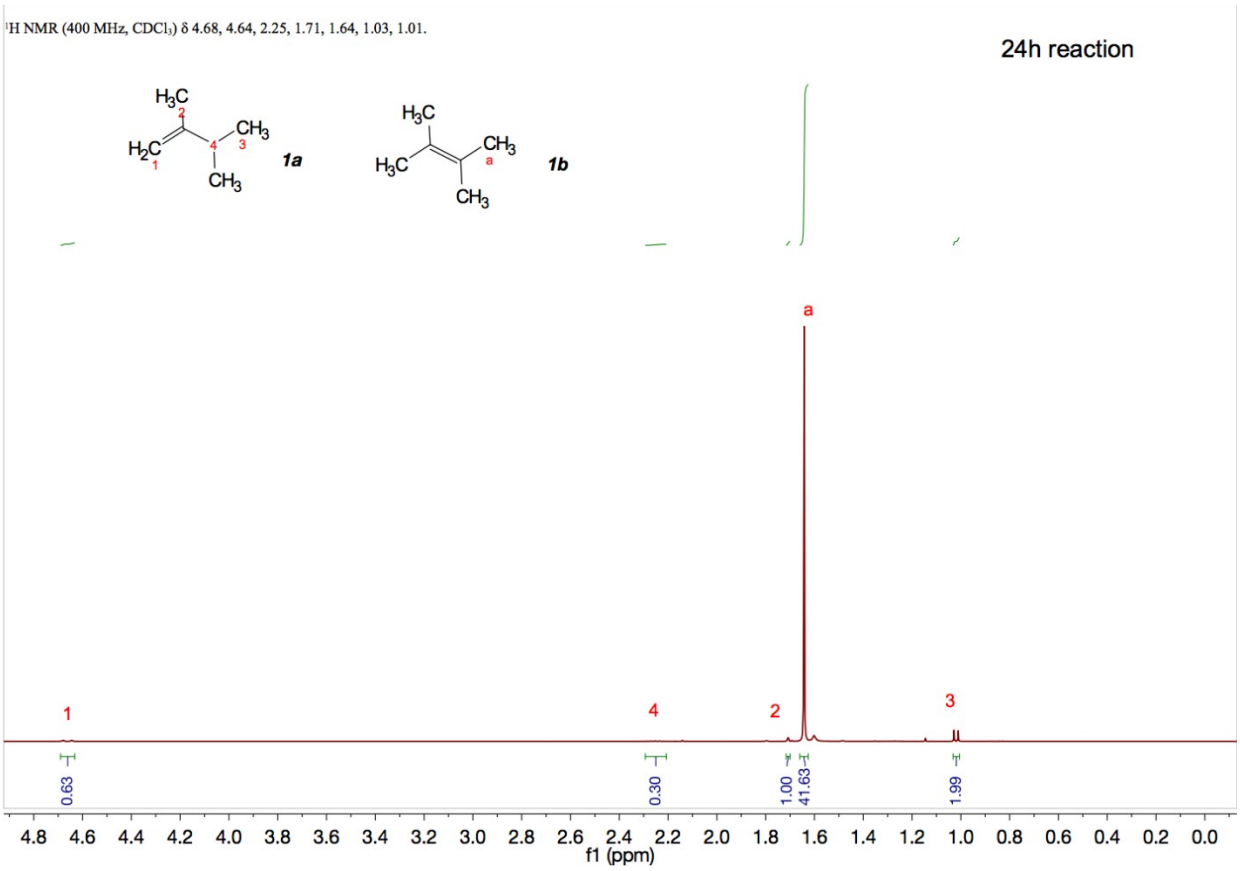

Figure S5. ^{1}H NMR spectrum obtained after reacting 2,3-dimtheyl buta-1,3-diene (**1**) with PdNP in $CDCl_3$ under H_2 conditions after 5 h. The spectrum shows ***1a***, 1,2-addition product, as the minor product (8.8 %) and ***1b***, 1,4-addition product, as the major product (91.2%).

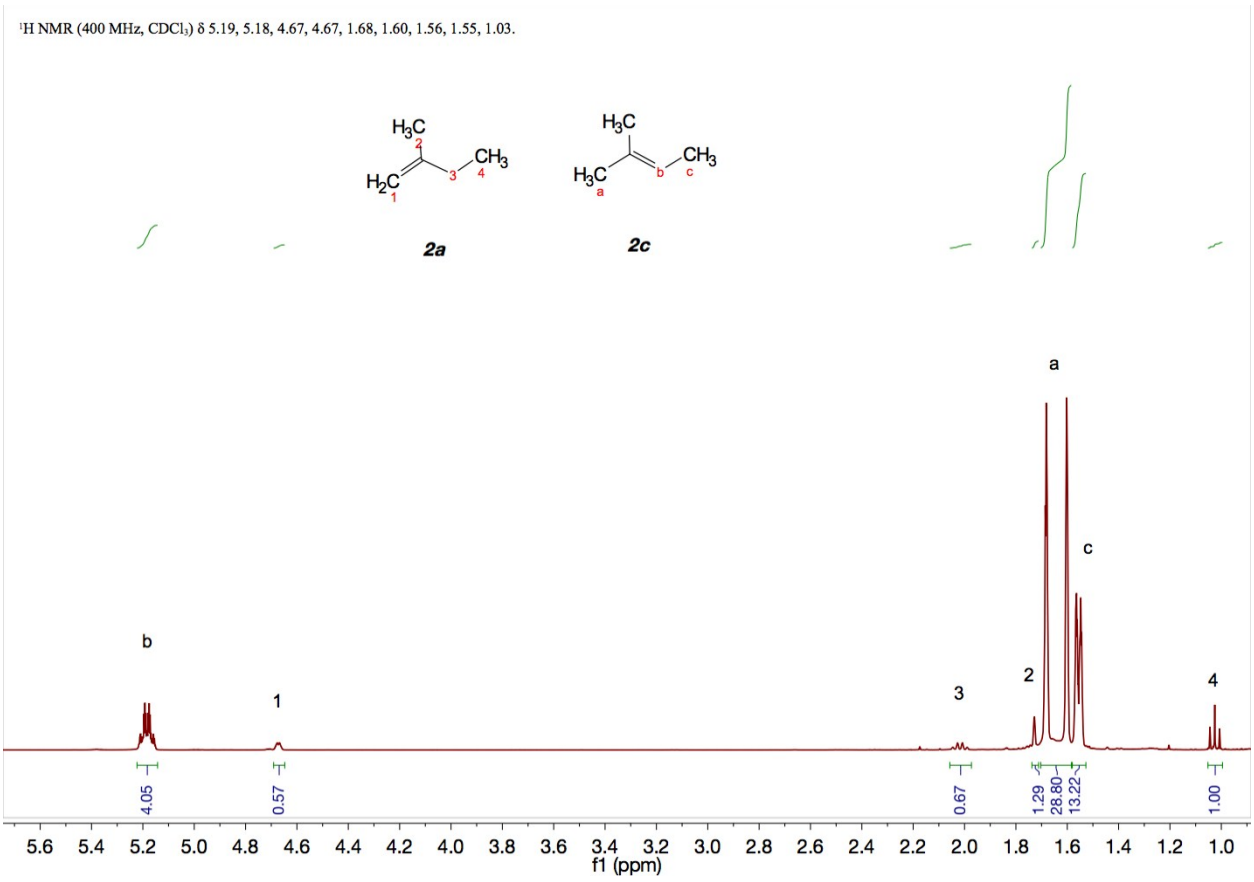

Figure S6. ^{1}H NMR spectrum obtained after reacting isoprene (**2**) with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows ***2a***, 1,2-addition product, as the minor product (6.6%) and ***2c***, 1,4-addition product as the major product (93.4%).

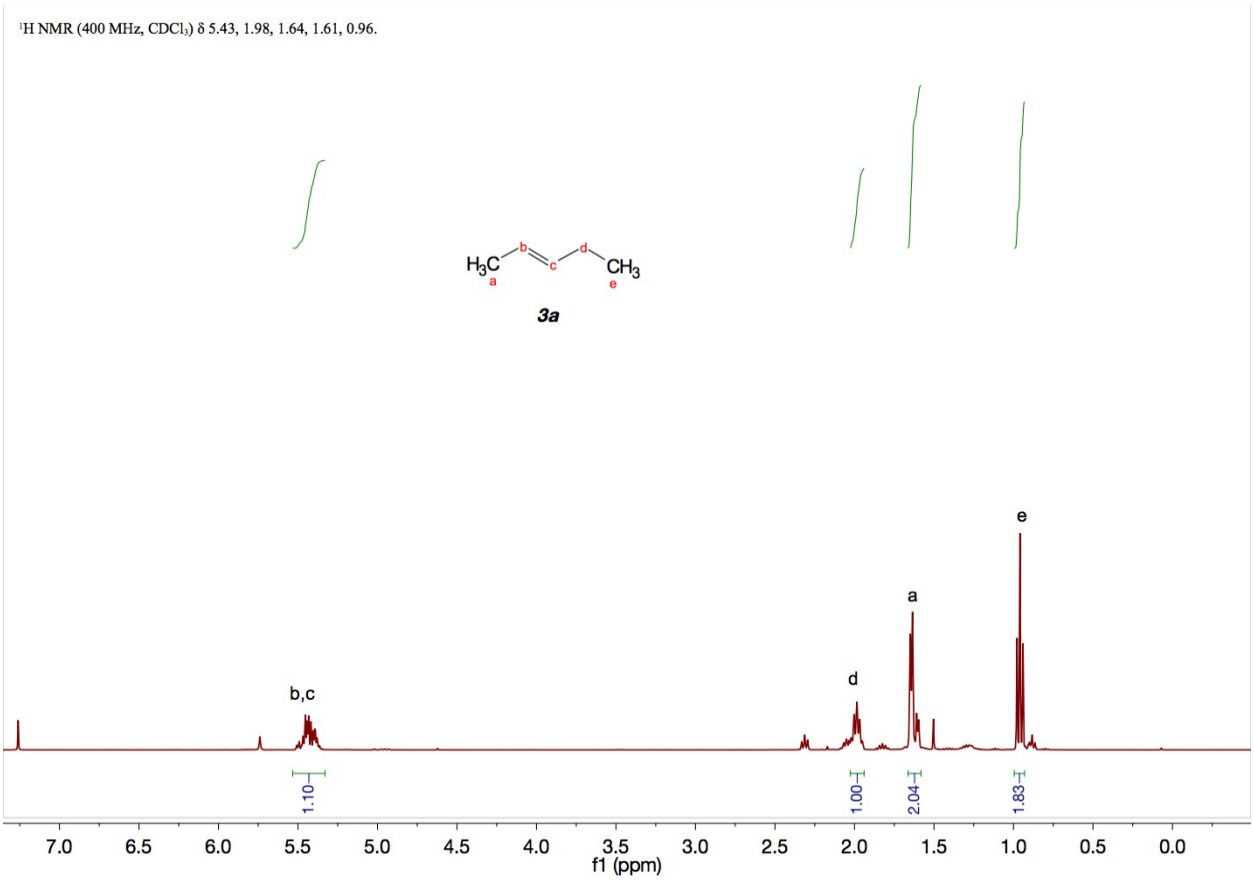

Figure S7. ^{1}H NMR spectrum obtained after reacting trans-1,3-pentadiene (**3**) with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows ***3a*** as the major product (98.2 %).

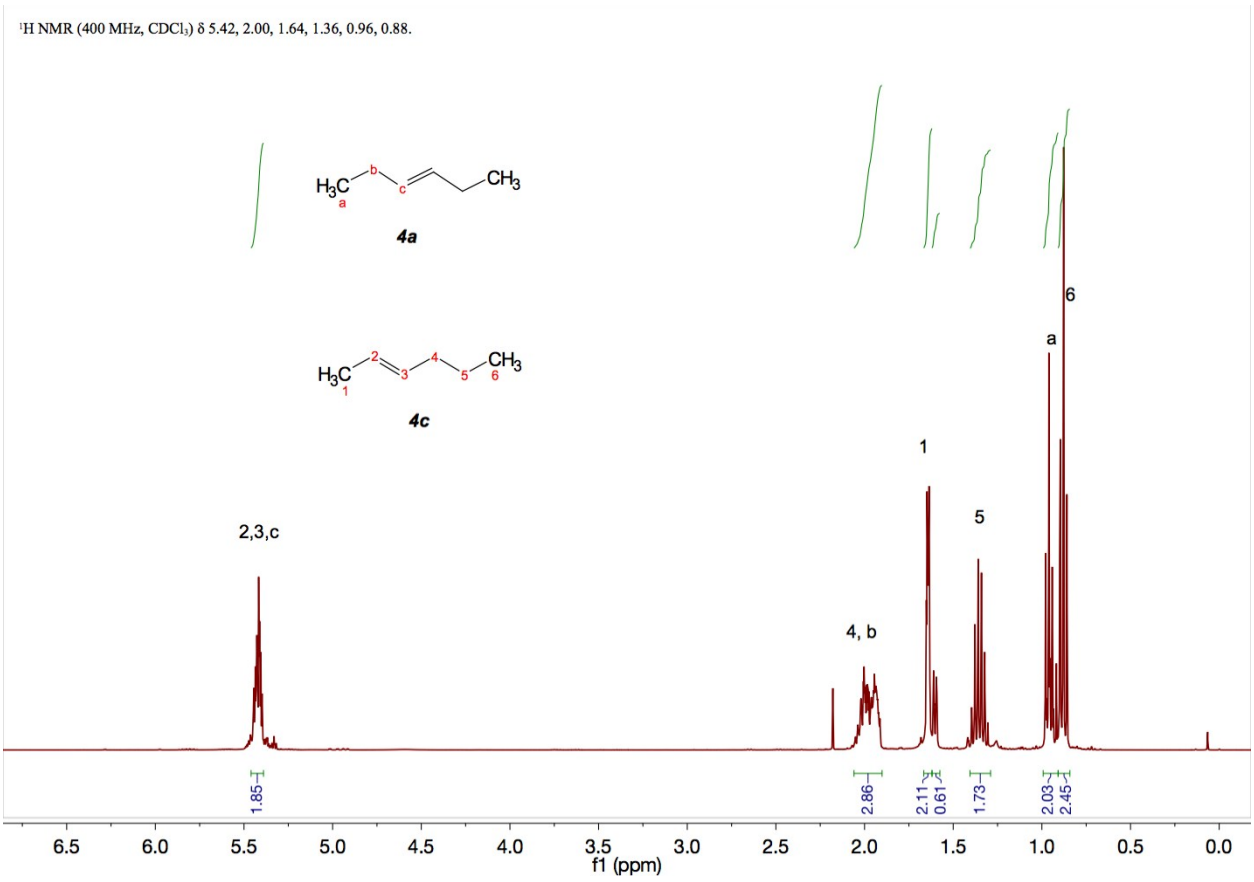

Figure S8. ^{1}H NMR spectrum obtained after reacting 1,3-hexadiene (**4**) with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows **4a**, 1,2-addition product, as the minor product (29.3 %) and **4c**, 1,4-addition product as the major product (70.7%).

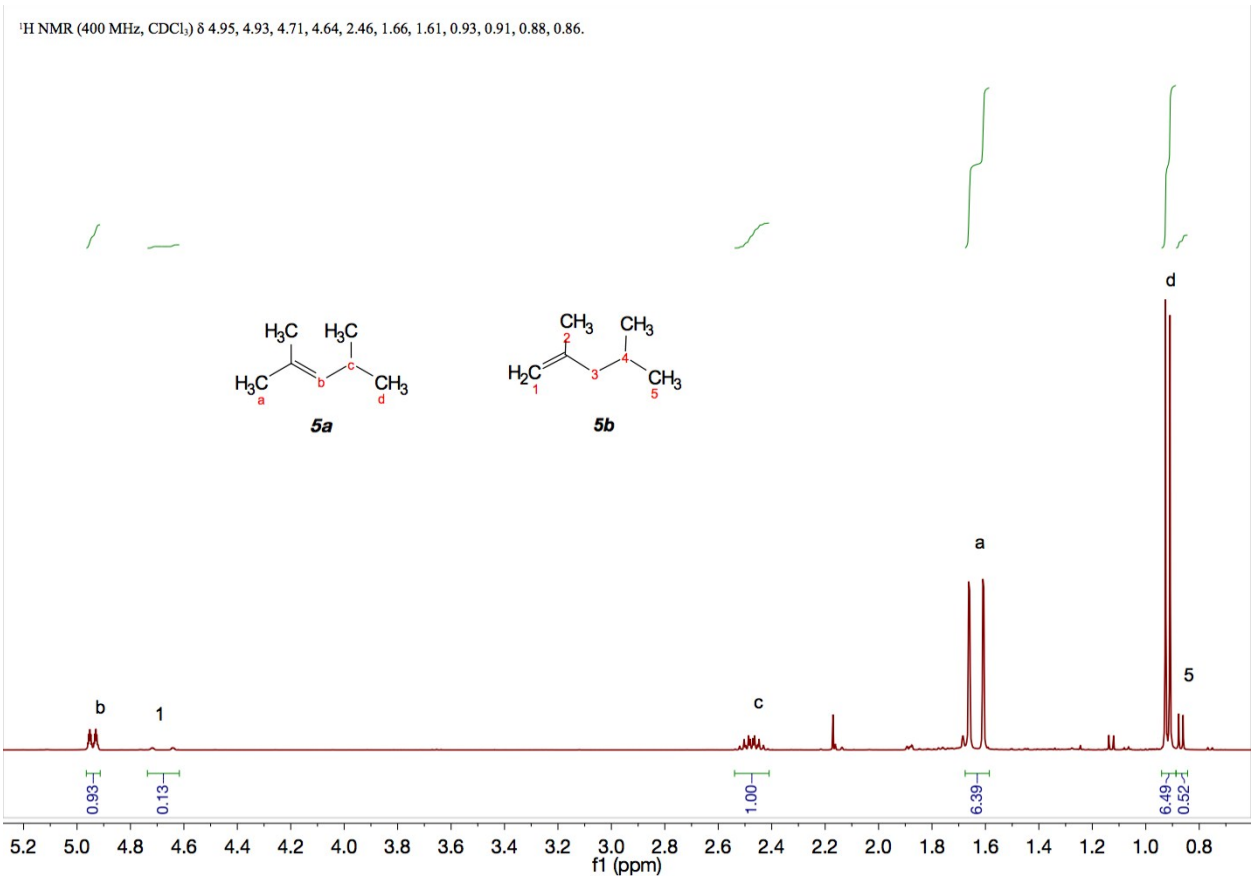

Figure S9. ^{1}H NMR spectrum obtained after reacting 2,4-dimethyl penta-1,3-diene (**5**) with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows ***5b*** as the minor product (6.5 %) and ***5a*** as the major product (93.5 %).

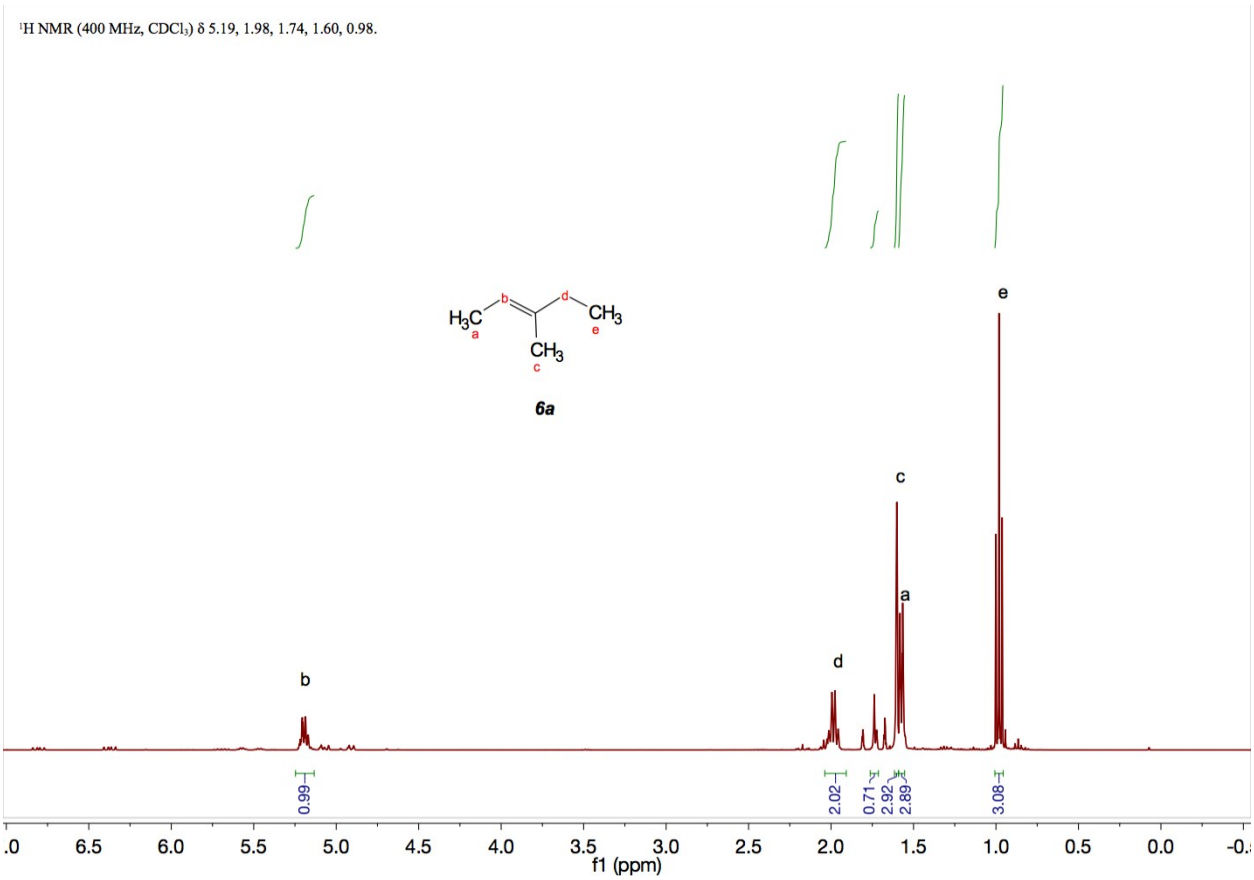

Figure S10. ^{1}H NMR spectrum obtained after reacting 3-methyl penta-1,3-daidene (**6**) with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows ***6a*** as the major product (90.6 %). Residual reactant still remained after reaction.

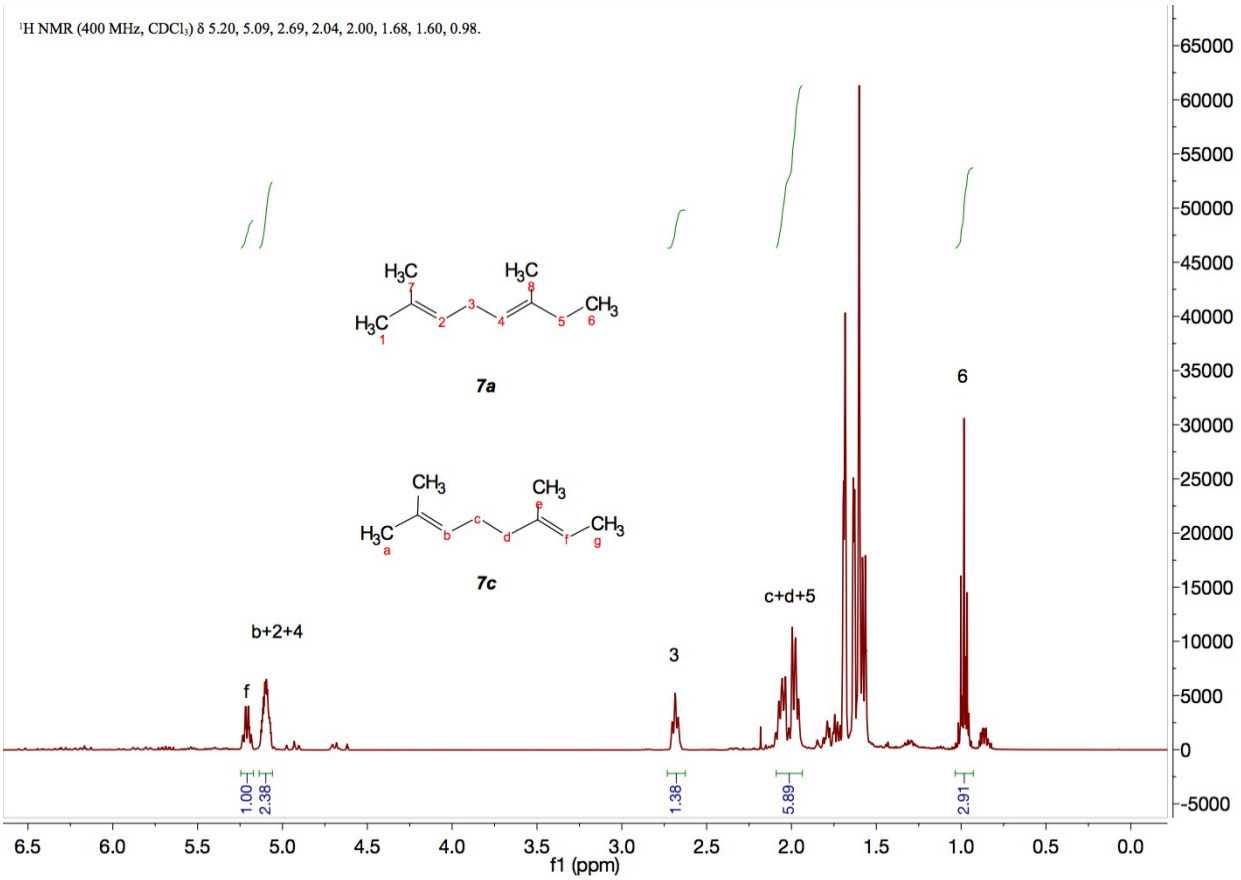

Figure S11. ^{1}H NMR spectrum obtained after reacting ocimene (**7**) with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows ***7a*** as the minor product (40.8 %), and **7c** as the major product (59.2 %).

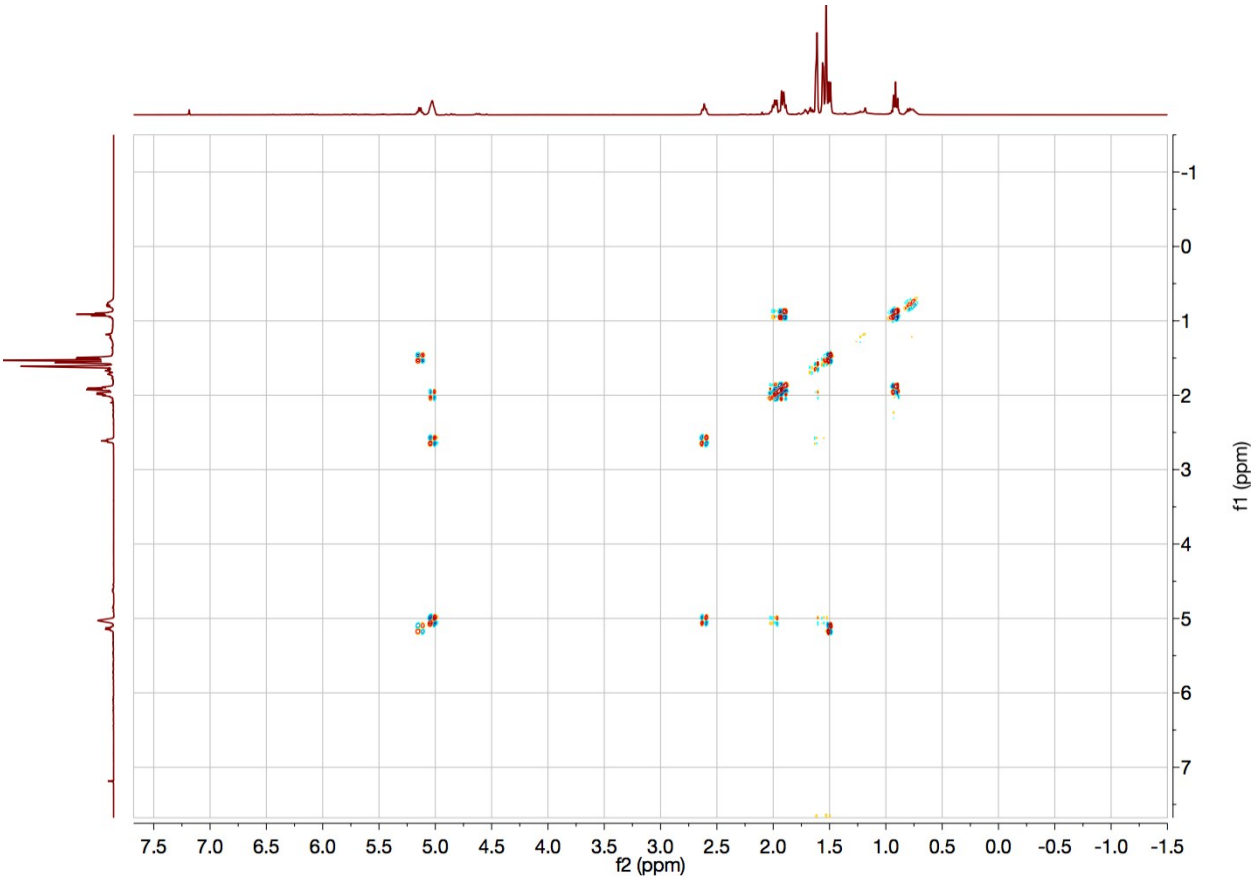

Figure S12. COSY NMR spectrum obtained after reacting ocimene (**7**) with PdNP in $CDCl_3$ under H_2 conditions after 24 h.

myrcene TC52.mnovamyrcene TC52.mnova

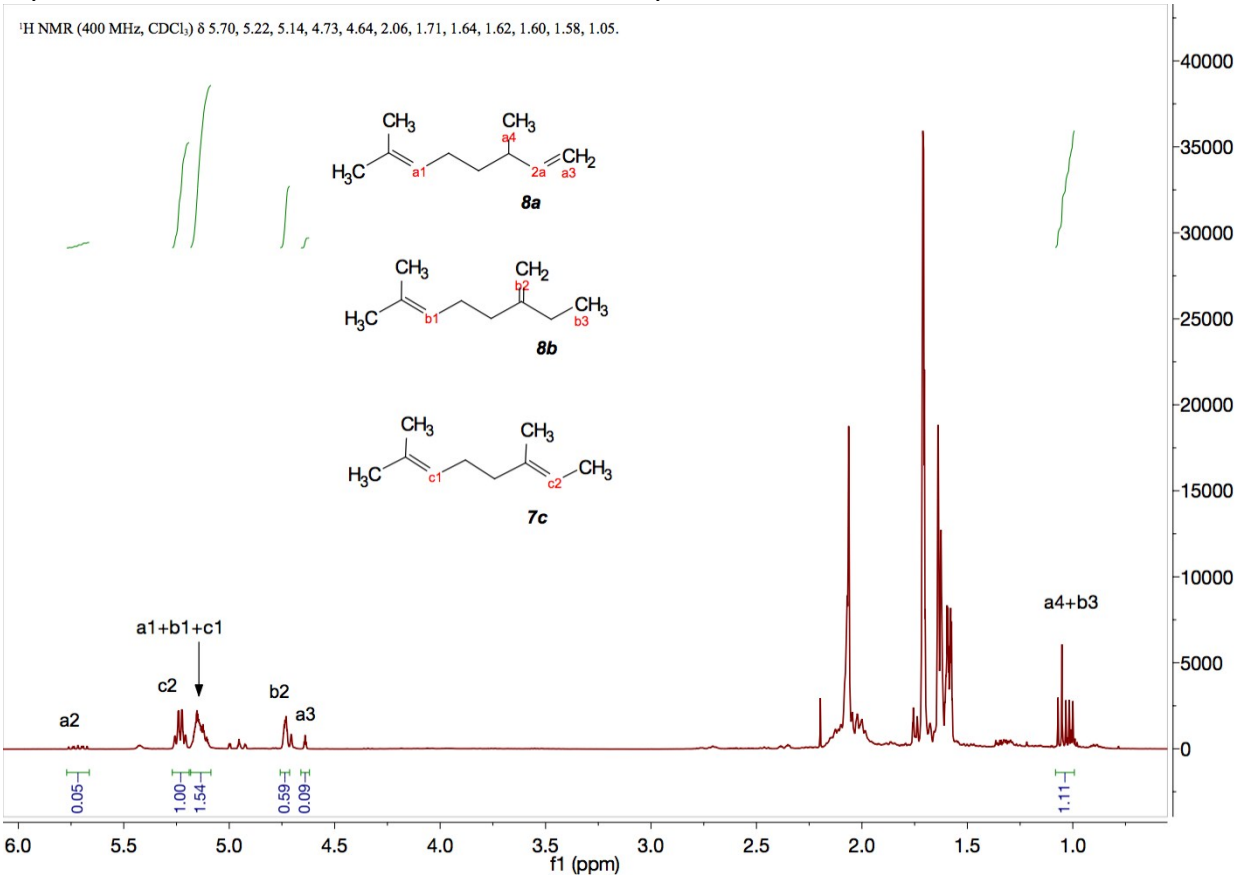

Figure S13. ^{1}H NMR spectrum obtained after reacting myrcene (**8**) with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows ***7c*** as the major product (75 %). Reactant still remained after reaction.

9. Leaching examination (ICP-AES) result:

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Custom ID1=
Custom ID2=
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Mode=CONC
CorrFactor=1.000
Repeats=3

[Results]
Elem,Units,Avg,Stddev,RSD,Rep1,Rep2,Rep3
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[Internal Standards]
Elem,Units,Avg,Stddev,RSD,Rep1,Rep2,Rep3
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