Electronic Supplementary Material (ESI) for Nanoscale.

Mechanistic Interpretation of Selective Catalytic Hydrogenation and Isomerization of Alkenes and Dienes by Ligand Deactivated Pd Nanoparticles

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1. Materials and Instrumentation

All chemicals purchased from Sigma-Aldrich were reagent grade and used without further purification. Deuterated $CDCl_3$ was purchased from Cambridge Isotope Laboratories and stored over 4 Å molecular sieves. Nanopure H_2O was obtained by purification to 18.2 MΩ resistance using a Barnstead NANOpure Diamond Life Science (UV/UF) purification system equipped with a D50280 Organic free Ro/Dis filter. NMR experiments were performed using Bruker 300 or 400 MHz NMR instruments and processed using MestReNova. Chemical shifts were referenced to the residue solvent peaks and reported as chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, or m = multiplet), and integration ratio. GC/MS experiments were performed using an Agilent G1701EA GC/MSD Chemstation equipped with a HP-5 fused silica capillary column with 5% phenylmethylsiloxane (30m length x 250 μM internal diameter). He gas was used as a carrier with a flow rate of 1.5 mL/min. The injector mode was set to pulsed splitless with 2 μL injections with injector temperature at 285^{o}C and split flow rate of 225 mL/min. A temperature program of 45^{o}C for 5 min, ramp to 180^{o}C with a rate of 20^{o}C/min, ramp to 220^{o}C with a rate of 10^{o}C, ramp to 295^{o}C with a rate of 12^{o}C/min and hold for 4 mins, ramp to 315^{o}C with a rate of 10^{o}C/min and hold for 3 mins. Mass spectrum was obtained in m/z range of 45-550 with a 3 minute solvent delay. The temperature of the ion source was 230^{o}C and the temperature of the quadrapole was 150^{o}C.

2. Procedure for the Preparation of Thiolate-capped PdNP:

K_2PdCl_4 (0.1306 g, 0.4 mmol) and tetraoctylammonium bromide (1.094 g, 2 mmol) was combined in 25 ml toluene and 12 ml nanopure H_2O. The solution was stirred for 10 minutes and the organic layer was separated then transferred to a 500 mL round bottom flask. Sodium S-octylthiosulfate (0.1984 g, 0.8 mmol) in 25% MeOH in nanopure H_2O solution was added followed by tetraoctylammonium bromide (1.094 g, 2 mmol). This solution was stirred for 10 minutes and a freshly prepared solution of sodium borohydride (0.3026 g, 8 mmol) in 7 mL nanopure H_2O was added over ~10 seconds. The bubbling black solution was stirred for 3 hours then organic layer was separated. The solvent was removed under reduced pressure at less than 30^{o}C. The crude PdNPs transferred to a 10 mL Falcon tube and sonicated in 5 mL ethanol for 10 minute followed by 10 minutes of centrifugation. The supernatant was discarded and this process was repeated 2 times and then with acetone 3 times. The PdNPs were allowed to dry in a vacuum desiccator over night before use.

Thermal gravimetric analysis of the PdNP showed an organic weight fraction of 19.7%; Pd weight fraction 80.3% (average of two batches of particles synthesized).

The average size of the particles, based on previously optimized synthesis of dodecanethiolate-capped palladium nanoparticles,[1] was 2.59±1.15 nm

3. General procedure for the hydrogenation of alkene:

Alkene (0.5 mmol) and PdNP (3.3 mg, 5 mol%) were stirred in $CDCl_3$ (2.5 mL) in a 50 mL round bottom flask with a rubber septum. The flask was purged with hydrogen gas for 10 minutes and the septum was quickly replaced with a polyethylene stopper. The resulting solution was then stirred for 24h. The $CDCl_3$ was removed by evaporation and approximately 2 mL of methanol was used to transfer crude mixture into a 2 mL Eppendorf vial. The vial was centrifuged to separate the PdNP and products.

4. NMR spectra and GC/MS charts

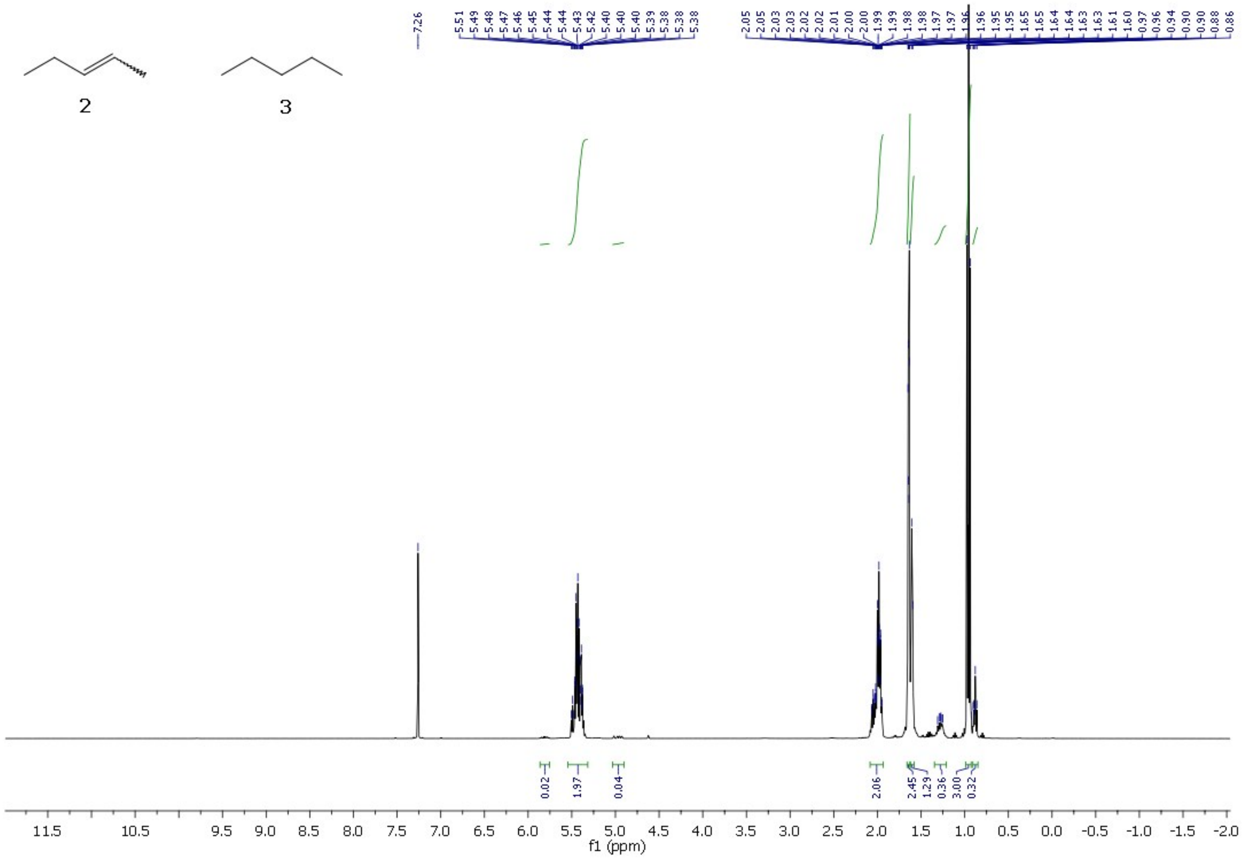

Figure S1. ^{1}H NMR spectrum obtained after reacting 1-pentene (**1**) with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows **2** as the major product (90%) and **3** as the minor product (9%).

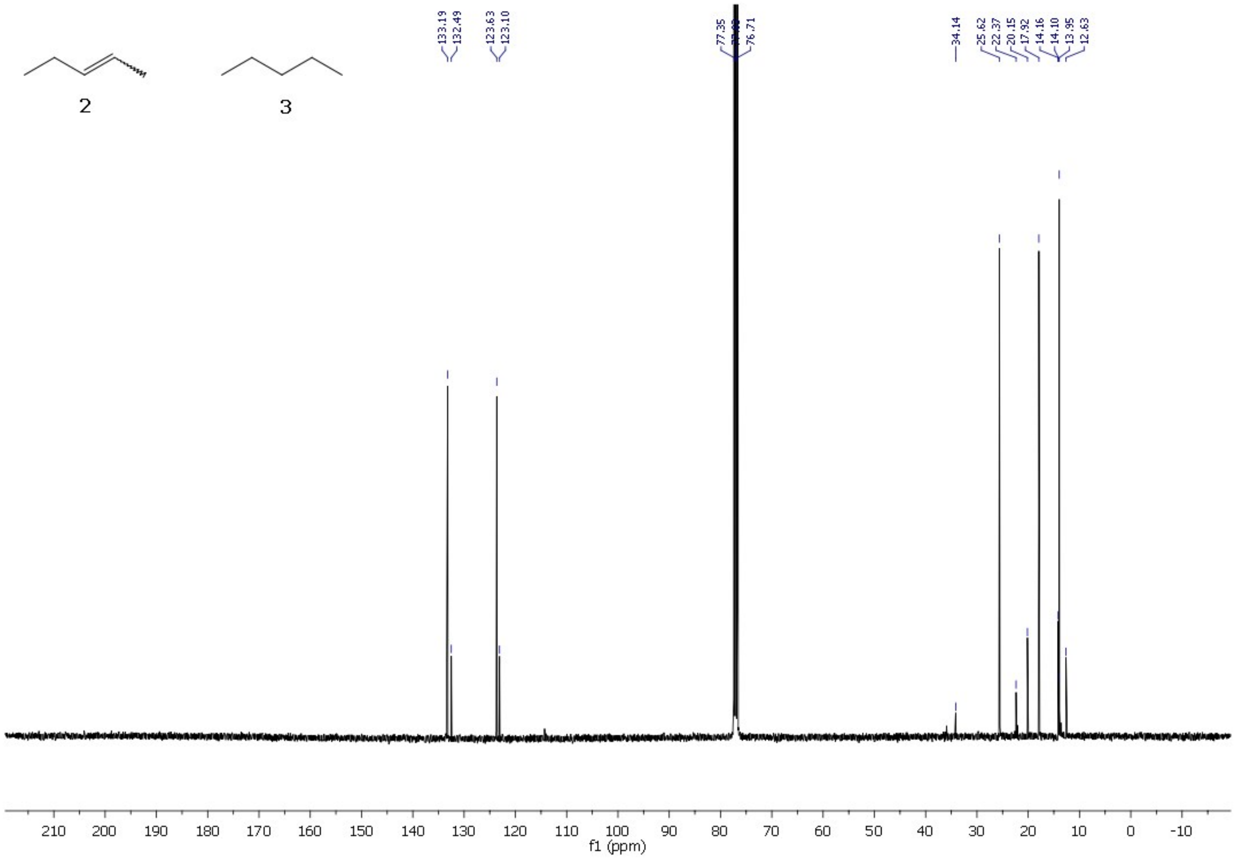

Figure S2. ^{13}C NMR spectrum obtained after reacting 1-pentene (**1**) with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows a mixture of *cis*- and *trans*- **2** and **3**.

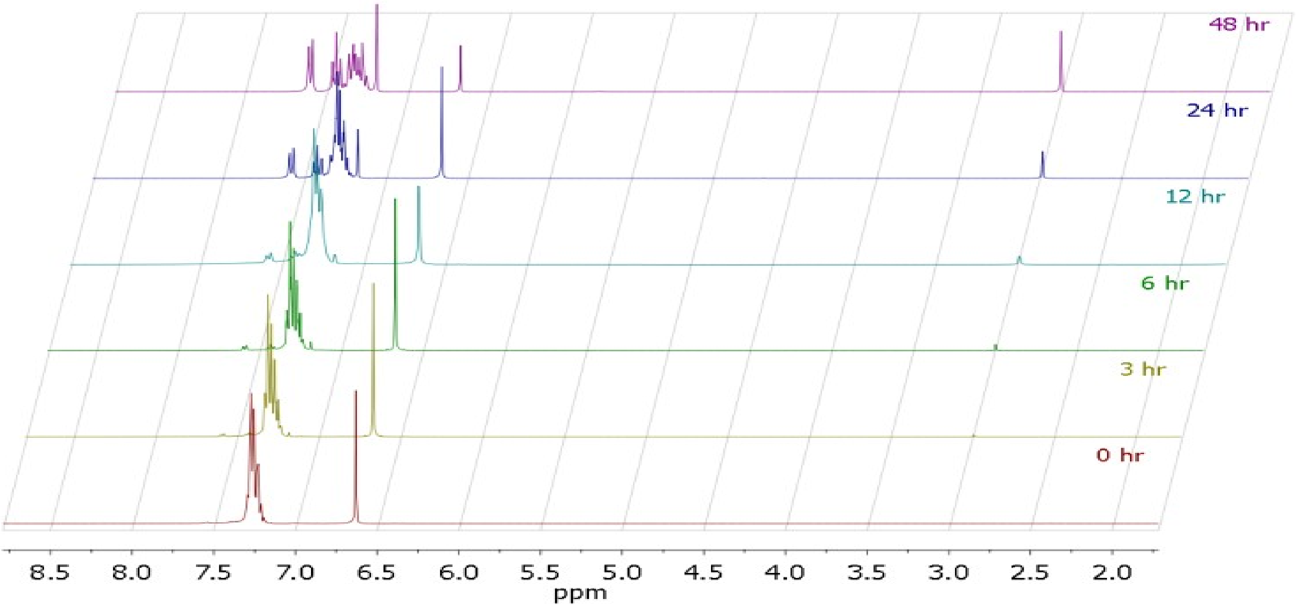

Figure S3. ^1H NMR spectra obtained after reacting *cis*-stilbene (**10**) with PdNP in $CDCl_3$ under H_2 conditions after 48 h at various time intervals. The spectrum shows *trans*-stilbene (**11**) as the major product and 1,2-diphenylethane (**9**) as the minor product.

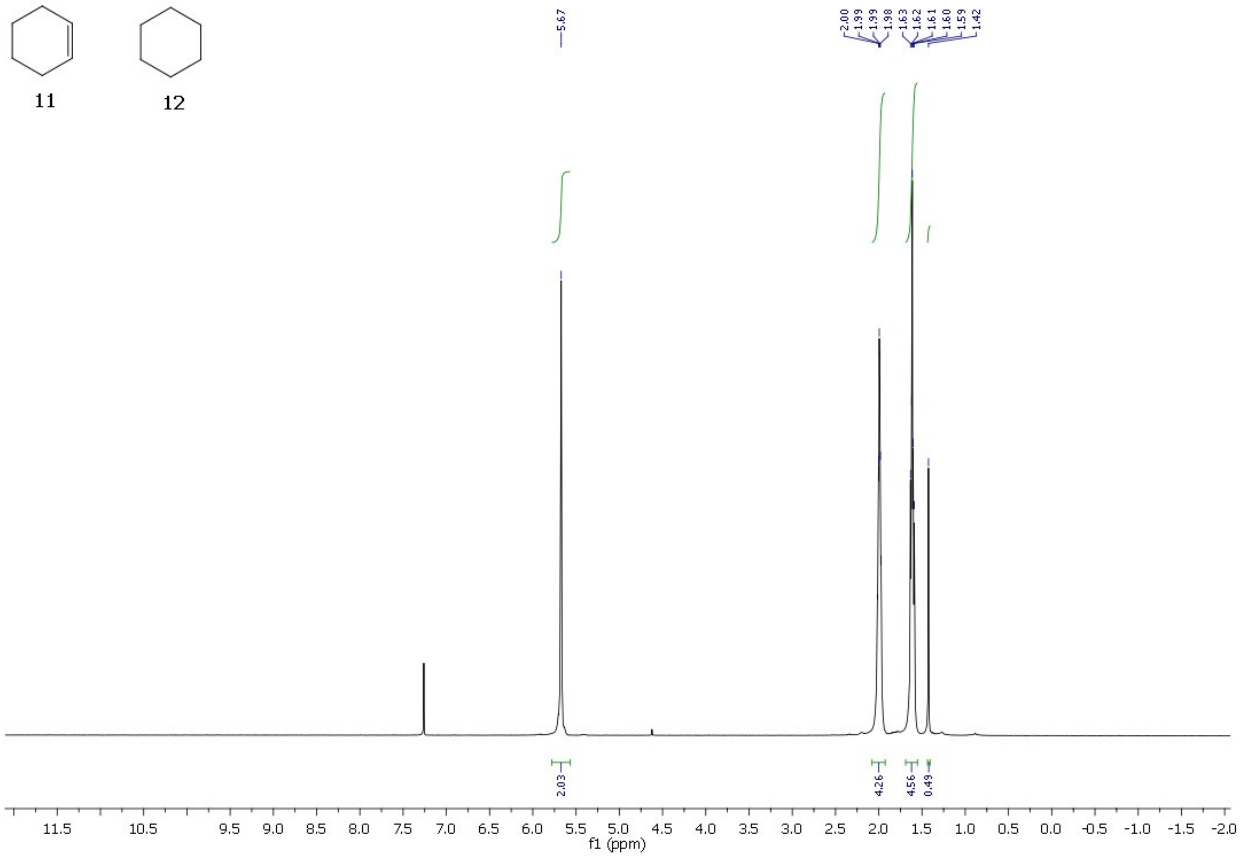

Figure S4. ^{1}H NMR spectrum obtained after reacting **11** with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows **12** as a minor product (4%) and **11** as the unreacted starting material (96%).

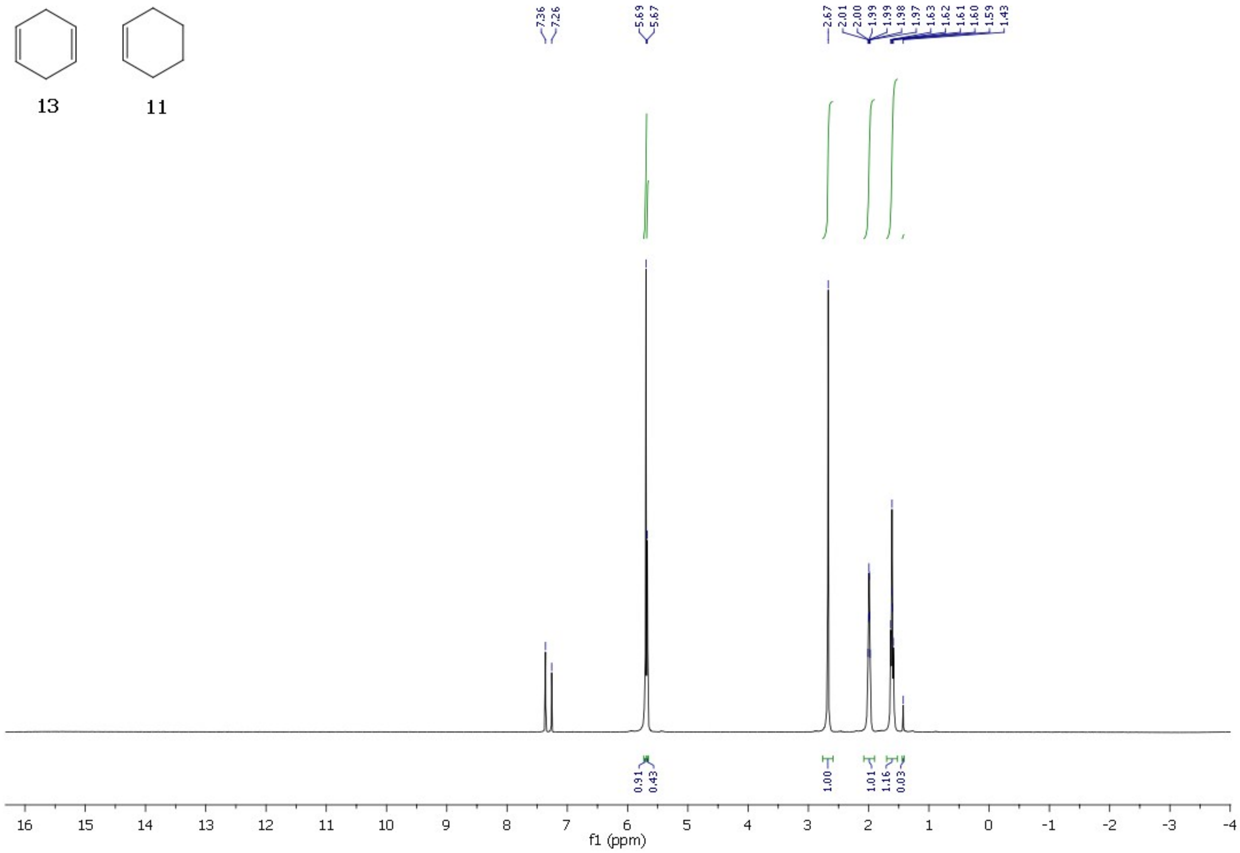

Figure S5. ^{1}H NMR spectrum obtained after reacting **13** with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows **11** as the major product (33%) and **12** as the minor product, and **13** as the unreacted starting material (67%).

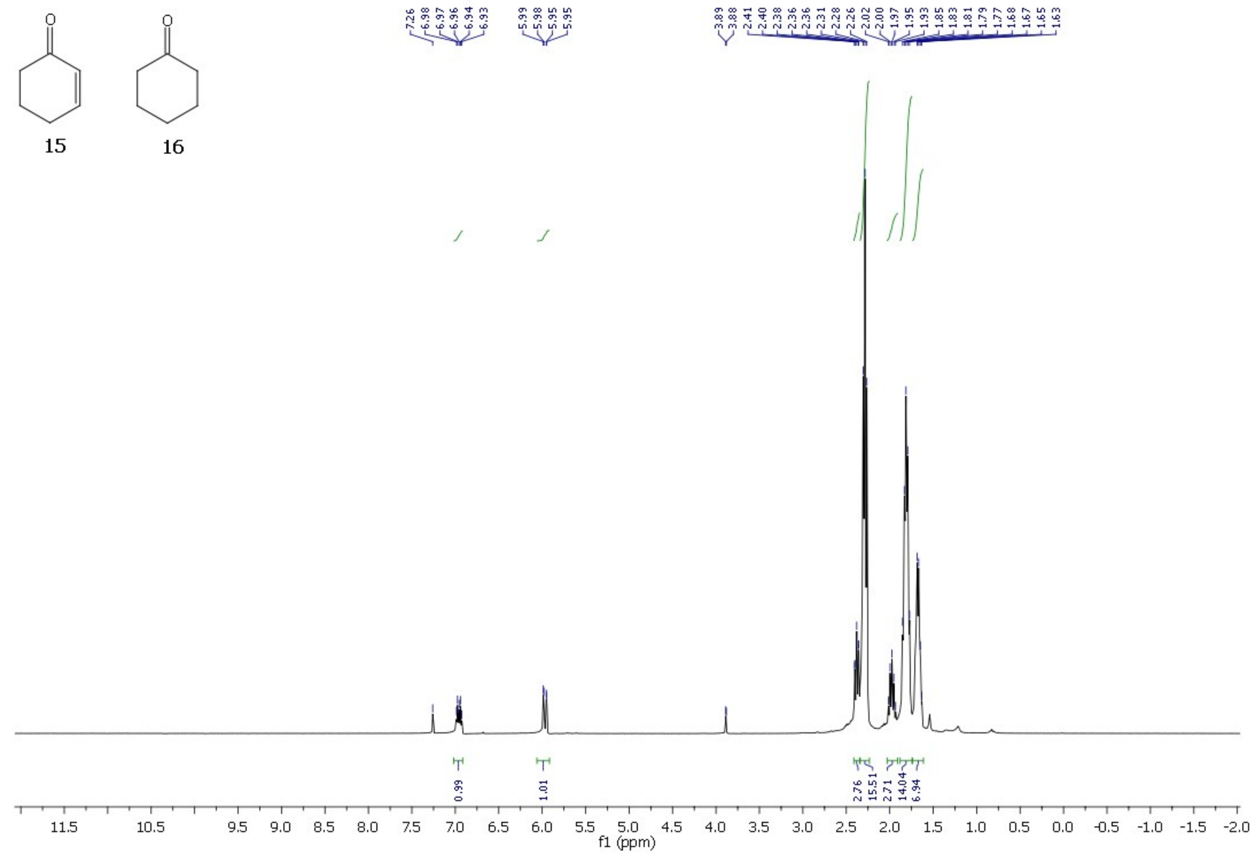

Figure S6. ^{1}H NMR spectrum obtained after reacting **15** with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows **16** as the major product (83%) and **15** as the unreacted starting material (17%).

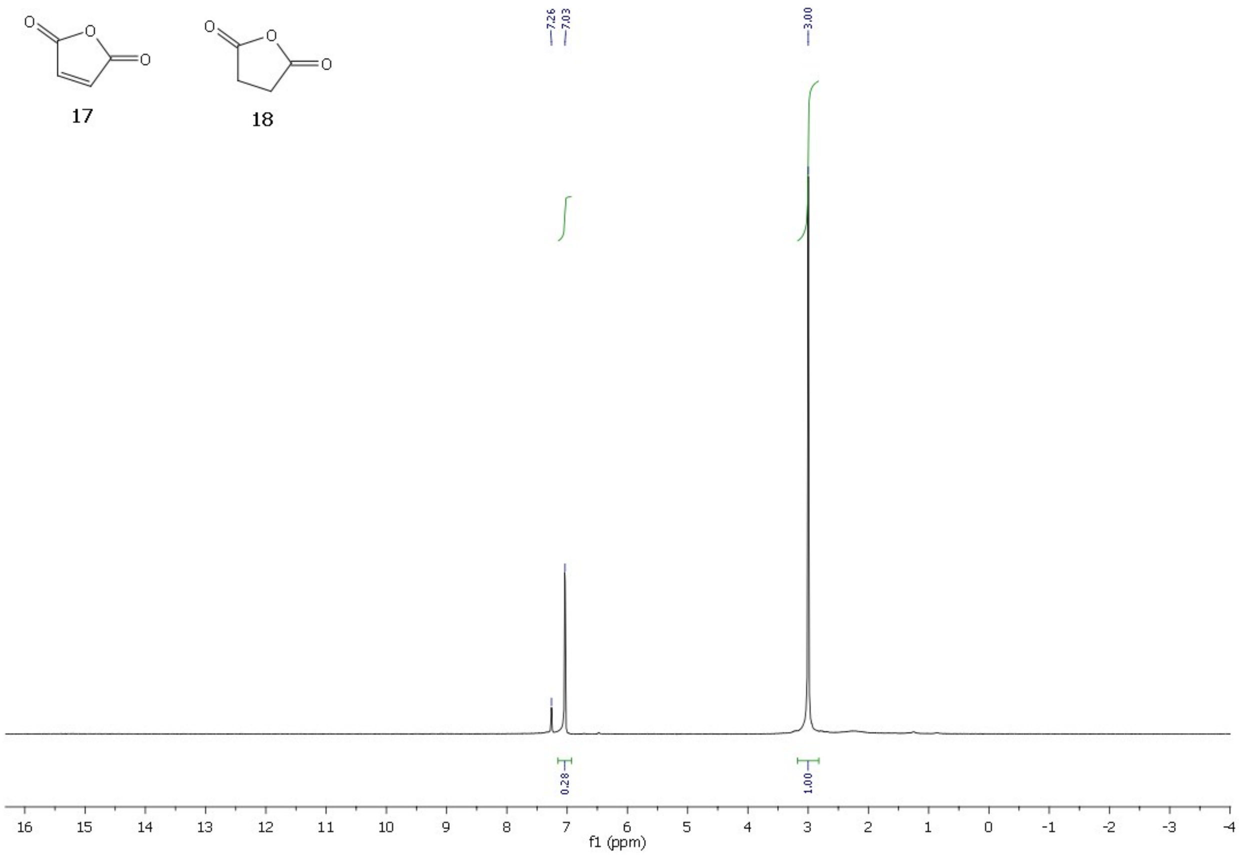

Figure S7. ^{1}H NMR spectrum obtained after reacting **17** with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows **18** as the major product (64%) and **17** as the unreacted starting material (36%).

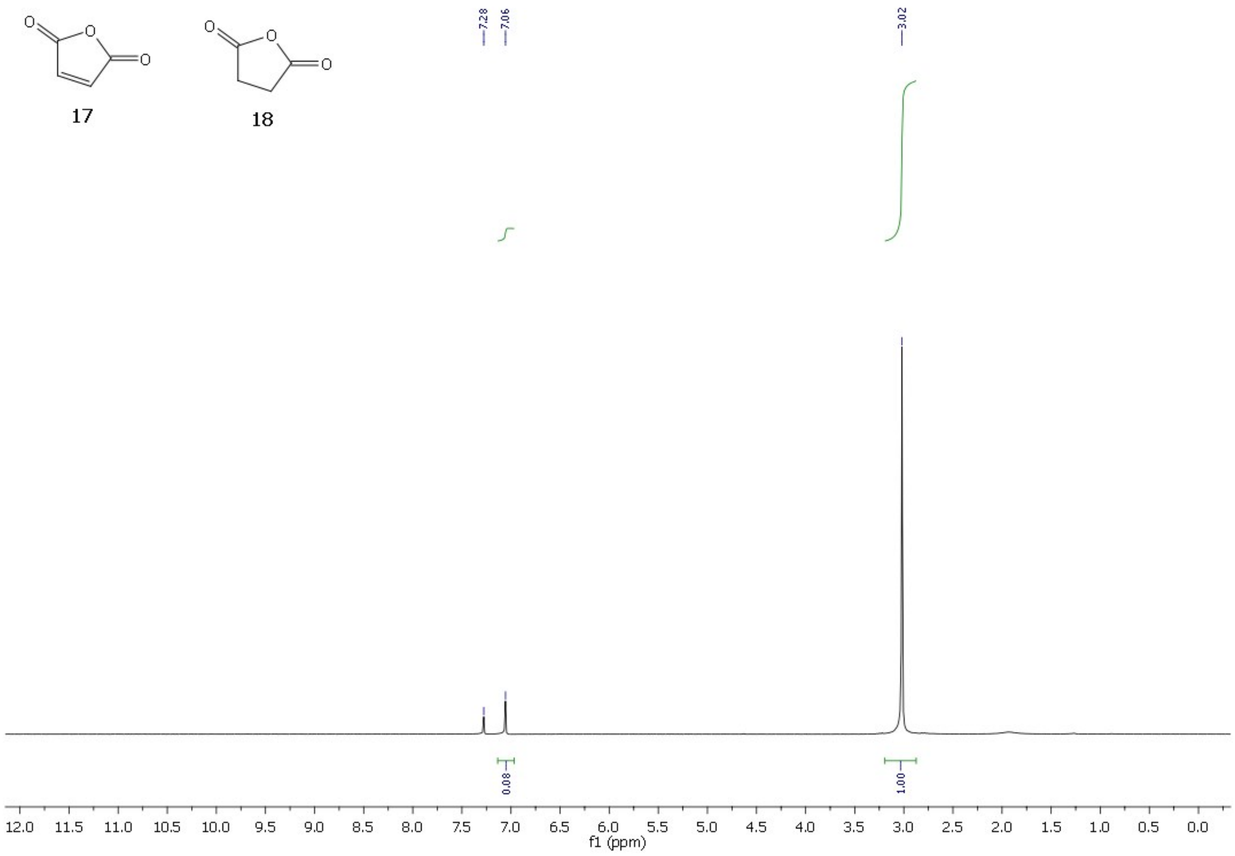

Figure S8. ^{1}H NMR spectrum obtained after reacting **17** with PdNP in $CDCl_3$ under H_2 conditions after 48 h. The spectrum shows **18** as the major product (87%) and **17** as the unreacted starting material (13%).

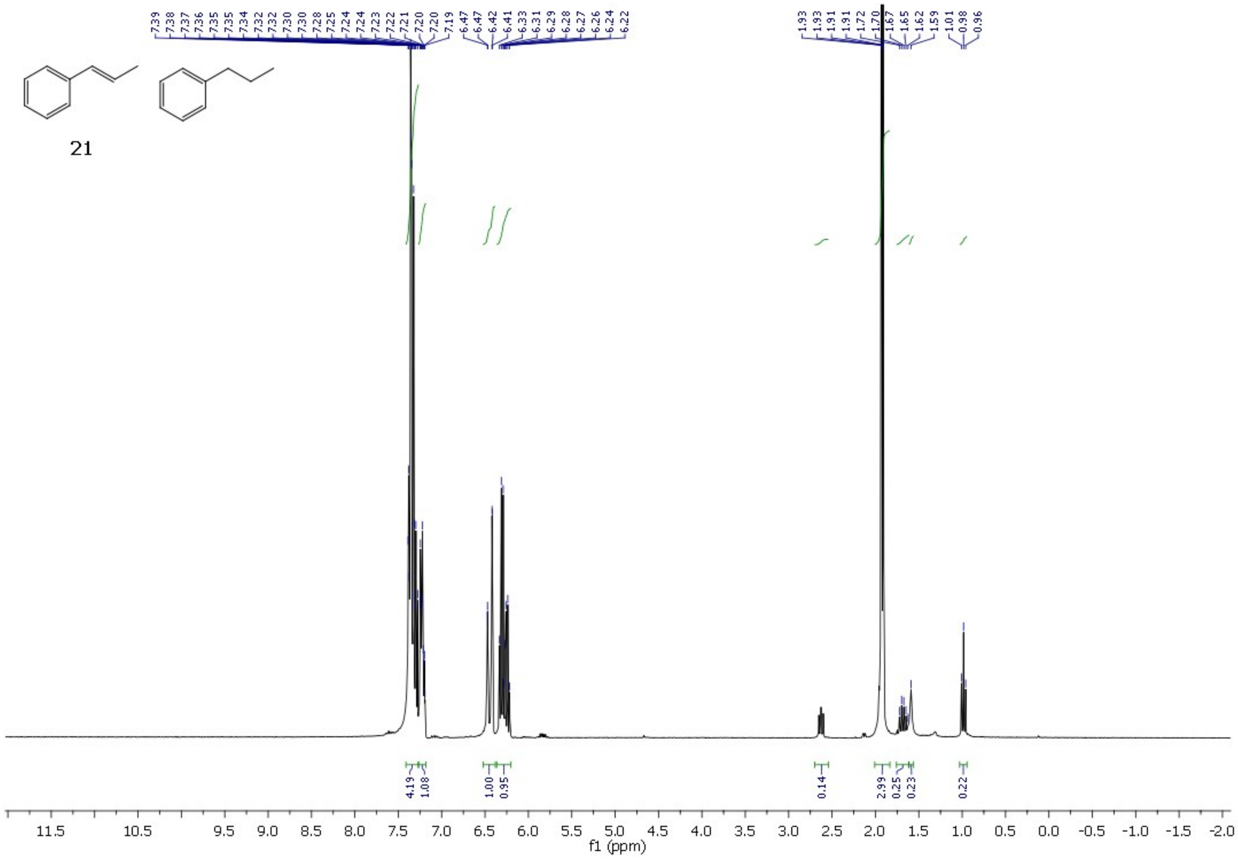

Figure S9. ^{1}H NMR spectrum obtained after reacting **21** with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows **21** as the unreacted starting material (90%) and minute amounts of **22** (2%) and propylbenzene (8%)

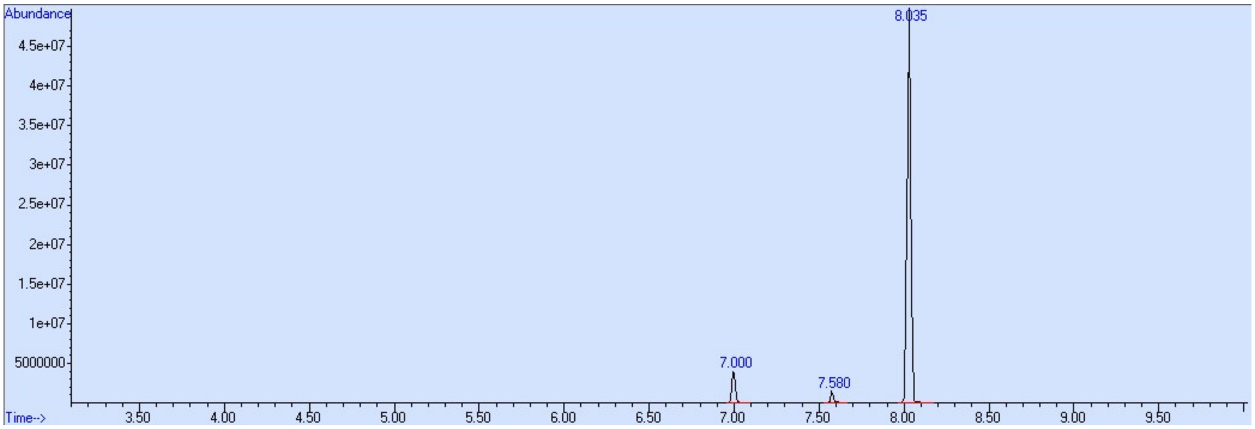

Figure S10. GC/MS spectrum obtained after reacting **21** with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The integration of the peaks on spectrum shows **21** as the unreacted starting material (90.48%) and minute amounts of **21** (2.16%) and propylbenzene (8.73%).

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
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1	7	345	349	358	BB	4051920	61301260	8.14%	7.37%
2	7.58	396	401	409	BB	1307357	17962648	2.39%	2.16%
3	8.035	435	441	454	BB	45912269	753038115	100.00%	90.48%

Sum of corrected areas: 832302023

Table S1. Retention times and integration of the peaks shown in **Figure S9**.

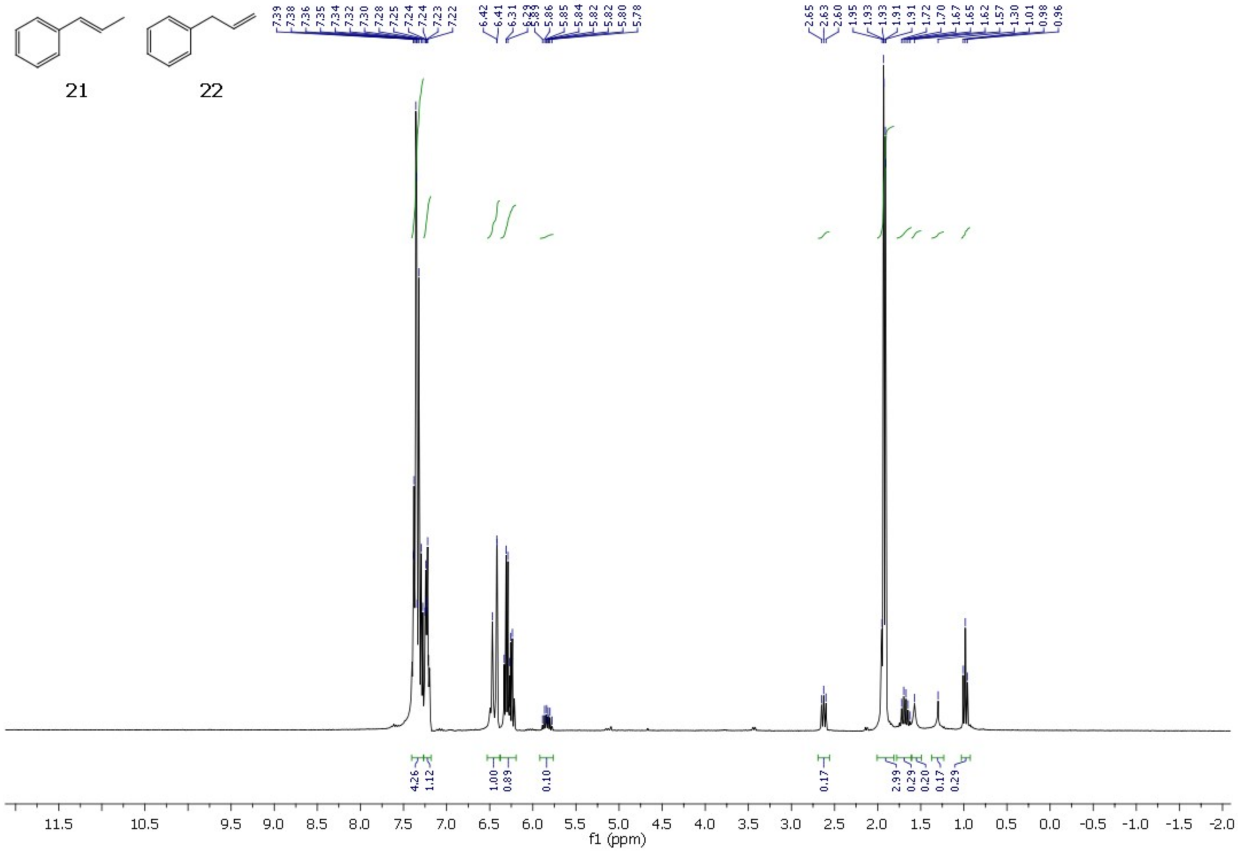

Figure S11. ^{1}H NMR spectrum obtained after reacting **22** with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows **21** as the major product (83%), propylbenzene as the minor product (9%), and unreacted **22** (8%).

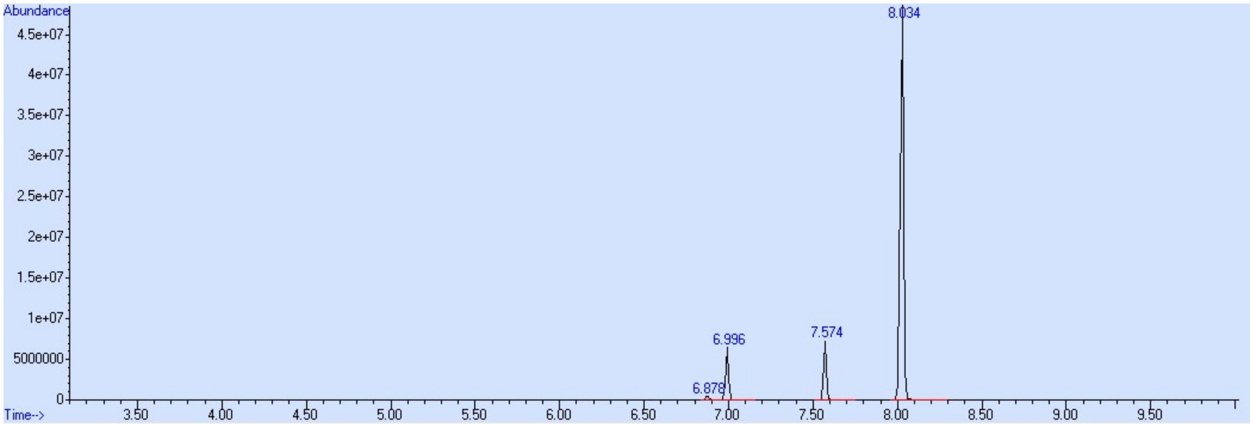

Figure S12. GC/MS spectrum obtained after reacting **22** with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The integration of the peaks on spectrum shows **21** as the major product (82.47%), propylbenzene as the minor product (9.05%), and unreacted **22** (7.70%).

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
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1	6.878	334	338	344	BV	404111	6711009	0.94%	0.77%
2	6.996	344	349	364	VB	5662672	78523038	10.97%	9.05%
3	7.574	394	400	416	BB	7145437	66840562	9.34%	7.70%
4	8.034	434	441	464	BB	45923752	7.16E+08	100.00%	82.47%

Sum of corrected area: 867641632

Table S2. Retention times and integration of the peaks shown in **Figure S11**.

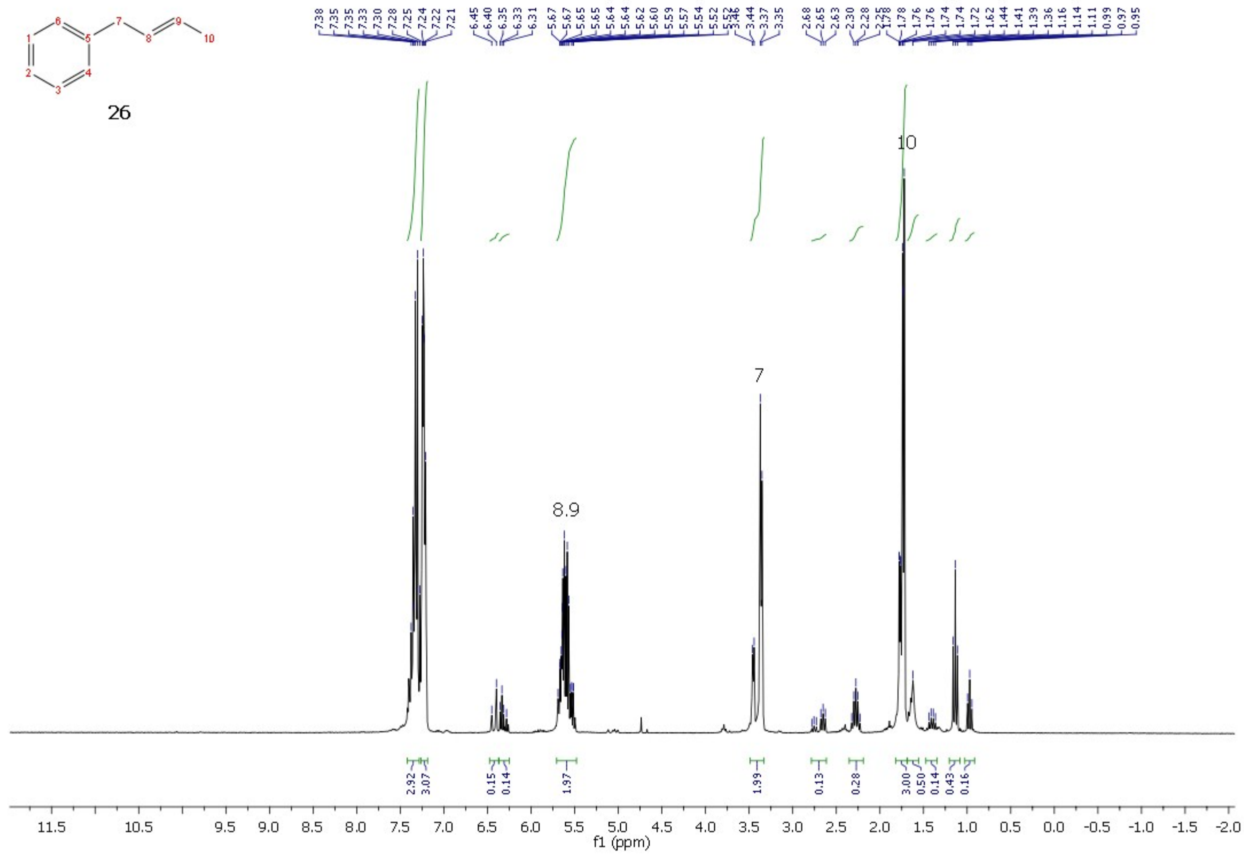

Figure S13. ^{1}H NMR spectrum obtained after reacting **23** with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows *trans*-**26** as the major product (65%).

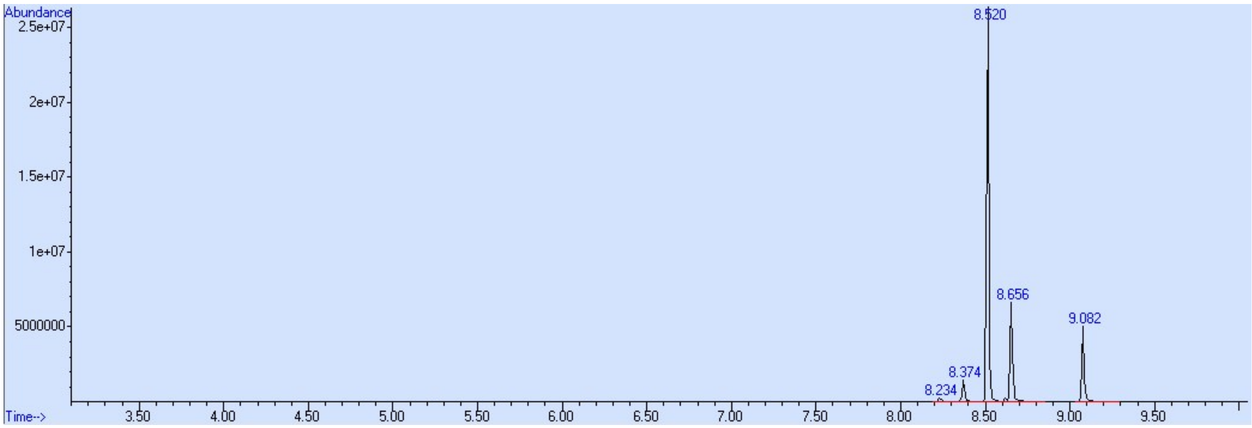

Figure S14. GC/MS spectrum obtained after reacting **23** with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The integration of the peaks on spectrum shows *trans*-**26** as the major product (64.72%), and *cis*-**26** (18.39%), **25** (12.06%), and **27** (3.80%) as the minor products.

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
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1	8.234	455	459	468	BV	218158	4192691	1.58%	1.02%
2	8.374	468	471	480	PV	1167863	15626788	5.87%	3.80%
3	8.52	480	484	491	VV	23073226	2.66E+08	100.00%	64.72%
4	8.656	491	497	514	VB	5473168	75629651	28.42%	18.39%
5	9.082	530	535	554	BB	4372764	49600077	18.64%	12.06%

Sum of corrected areas: 411174108

Table S3. Retention times and integration of the peaks shown in **Figure S13**.

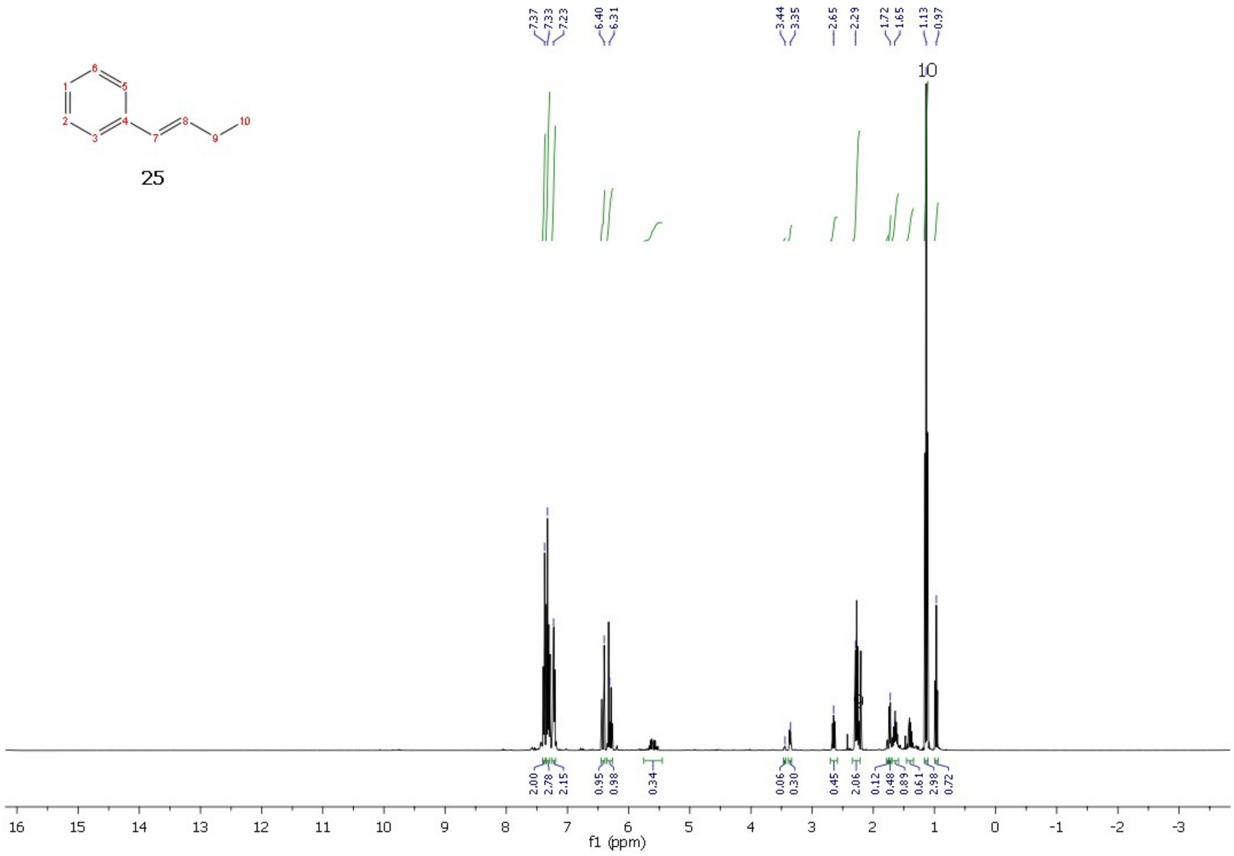

Figure S15. ^{1}H NMR spectrum obtained after reacting **24** with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The spectrum shows **25** as the major product (72%).

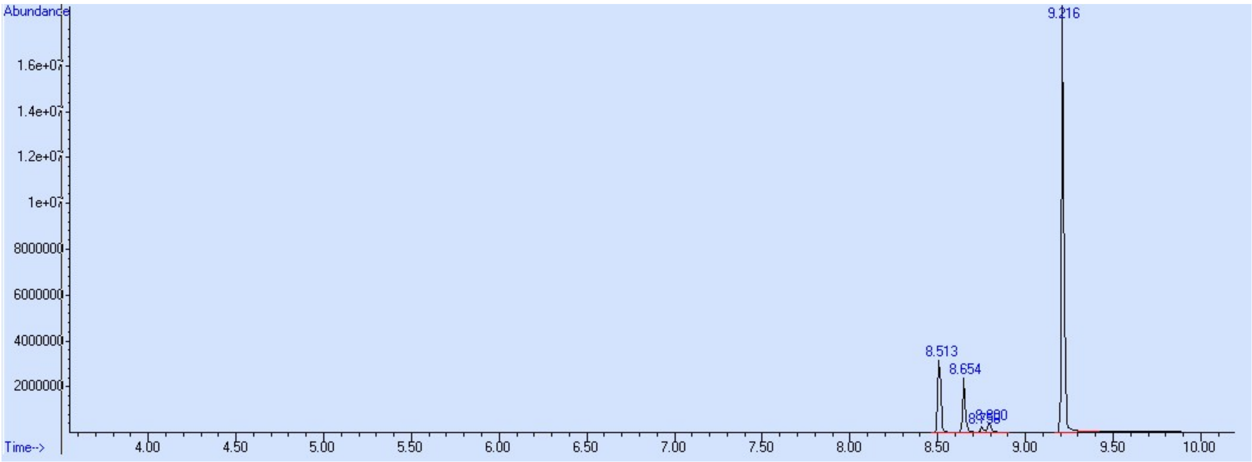

Figure S16. GC/MS spectrum obtained after reacting **23** with PdNP in $CDCl_3$ under H_2 conditions after 24 h. The integration of the peaks on spectrum shows **25** as the major product (71.84%), **23** (0.91%), *cis*-**26** (2.08%), *trans*-**26** (9.81%) and **27** (15.37 %) as the minor products.

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
---	-----	-----	----	----	---	-------	-------	------	-------
1	8.513	479	484	493	BV	2947632	38851397	21.39%	15.37%
2	8.654	493	496	503	VV	1966777	24799639	13.65%	9.81%
3	8.756	503	505	507	VV	193964	2298370	1.27%	0.91%
4	8.8	507	509	520	VB	349513	5245991	2.89%	2.08%
5	9.216	542	546	565	BV	15156858	1.82E+08	100.00%	71.84%

Sum of corrected areas:
252852430

Table S4. Retention times and integration of the peaks shown in **Figure S15**.

6. References

D. J. Gavia, Y.-S. Shon, *Langmuir* **2012**, *28*, 14502-14508