# (Pyridyl)benzoazole palladium(II) complexes as homogeneous catalysts for the hydrogenation of alkenes and alkynes

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## Supplementary materials and information

### Synthesis of cationic ((2-(2-pyridyl)benzimidazole) Pd(II) Complexes

*[{2-(2-pyridyl)benzimidazole}PdPPh$_3$Cl]Cl* ***(5)***

To a suspension of **1** (0.05 g, 0.13 mmol) in $CH_2Cl_2$ (5 mL), was added a solution of $PPh_3$ (0.04 g, 0.14 mmol) in $CH_2Cl_2$ (5 mL) and the precipitate formed was stirred for 24 h. After the reaction period the mixture filtered and the precipitate washed with $CH_2Cl_2$ (10 mL) to afford compound **5** as a light yellow solid. Yield = 0.04 g (52%). $^1$H NMR (DMSO-d$_6$): δ 7.39 (t, 1H, bz$_{im}$, $^3J_{HH}$ = 7.2 Hz); 7.49 (t, 1H, py, $^3J_{HH}$ = 14.0 Hz); 7.68-7.44 (m, $PPh_3$) 7.76 (d, 1H, bz$_{im}$, $^3J_{HH}$ = 8.0 Hz); 7.82 (t, 2H, bz$_{im}$, $^3J_{HH}$ = 6.0 Hz); 8.34 (d, 1H, bz$_{im}$, $^3J_{HH}$ = 7.2 Hz); 8.42 (t, 1H, py, $^3J_{HH}$ = 8.0 Hz); 8.71(d, 1H, py, $^3J_{HH}$ = 8.4 Hz); 9.11 (d, 1H, py, $^3J_{HH}$= 5.2 Hz). $^{31}$P {H} NMR ($CDCl_3$): δ 23.71 (s, 1P, $PPh_3$). Anal. Calcd. For $C_{30}H_{24}Cl_2N_3PPd$: C, 56.76; H, 3.81; N, 6.62%. Found C, 56.54; H, 4.10; N, 6.71%. Positive mode (ESI-MS) *m/z* 600.08 (M +1,100).

*[{2-(2-pyridyl)benzimidazole}PdMePPh$_3$]BAr$_4$* ***(6)***

To a solution of **4** (0.03 g, 0.09 mmol) in $CH_2Cl_2$ (5 mL), was added $NaBAr_4$ (0.08 g, 0.09 mmol) and $PPh_3$ (0.02 g, 0.09 mmol) in $CH_2Cl_2$ (5 mL). The resultant clear orange solution was

stirred for 12 h. The solution was filtered and concentrated *in vacuo* and hexane (15 mL) added to precipitate an orange solid.

Yield = 0.09 g (75%). $^{1}$H NMR ($CDCl_3$): δ 1.23 (s, 3H, Pd-Me); 7.02 (d, 1H, py, $^{3}J_{HH}$ = 4.8 Hz); 7.50 (s, 8H, $BAr_4$); 7.88-7.41 (Ph); 7.73 (s, 4H, $BAr_4$); 8.09 (d, 1H, $bz_{im}$, $^{3}J_{HH}$ = 8.0 Hz); 8.72 (d, 1H, bzim,$^{3}J_{HH}$ = 6.0 Hz); 9.44 (d, 1H, py, $^{3}J_{HH}$ = 4.4 Hz); 10.72 (s, NH). $^{31}$P {H} NMR ($CDCl_3$): δ 33.74 (s, 1P, $PPh_3$). Anal. Calcd. For $C_{63}H_{40}BF_{24}N_3PPd$: C, 52.47; H, 2.73; N, 2.91%. Found C, 53.36; H, 2.91; N, 2.85%.

**X-ray crystallographic analysis of complex 6**

***Data collection***

X-ray data were recorded on a Bruker Apex Duo equipped with an Oxford instrument Cryojet operating at 100(2) K and an Incoatec microsource operating at 30 W. The data were collected with Mo Kα (λ = 0.71073 Å) radiation at a crystal-to-detector distance of 50 mm.
The following conditions were used for the data collection: omega and phi scans with exposures taken at 30 W X-ray power and 0.50° frame widths using APEX2 [i]. The data were reduced with the programme SAINT [ii] using outlier rejection, scan speed scaling, as well as standard Lorentz and polarisation correction factors. A SADABS semi-empirical multi-scan absorption correction was applied to the data.

***Structure solution and refinement***

Direct methods, SHELXS-97 and WinGX [iii] were used to solve the structures at the University of KwaZulu-Natal, South Africa. All non-hydrogen atoms were located in the difference density map and refined anisotropically with SHELXL-97. All hydrogen atoms were included as idealised contributors in the least squares process. Their positions were calculated

using a standard riding model with C-$H_{aromatic}$ distances of 0.93 Å and $U_{iso}$ = 1.2 Ueq. The imidazole N-H were located in the difference density map, and refined isotropically.

**Table S1**: Data collection and structural refinement parameters of complex **6**

| **Parameter** | **6** |
|---|---|
| Empirical formula | $C_{63}$ $H_{39}$ $BF_{24}N_3PPd$ |
| Formula weight | 1442.15 |
| Temperature(K) | 100(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Triclinic |
| Space group | P-1 |
| *a* (Å)<br>*b (*Å)<br>*c* (Å)<br>α ($^0$)<br>β ($^0$)<br>γ ($^0$) | 12.7129(8)<br>13.3917(8)<br>17.6166(11)<br>93.824 (3)<br>90.923 (2)<br>93.204 (2) |
| Volume($A^3$) | 2987.23 (3) |
| Z | 2 |
| $D_{calcd}$ ($mg/m^3$) | 1.603 |
| Absorption coefficient ($mm^{-1}$) | 0.457 |
| F(000) | 1440 |
| Theta range for data collection (°) | 1.50 -26.40 |
| Reflections collected / unique | 13981 |
| Completeness to theta (%)<br>Goodness-of-fit on $F^2$<br>R indices (all data)<br><br>Largest diff. peak and hole (e $Å^{-3}$) | 97.3<br>0.838<br>$R_1$ = 0.0208<br>$wR_2$ = 0.0929<br>1.69 and<br>-0.96 |

**Table S2**: Dependence of catalytic activities of **1-6** on the average Pd-$N_{py/bz}$ bond lengths and HOMO-LUMO gaps

| Entry | Complex | (Pd-$N_{py}$+ Pd-$N_{bz}$)/2 (Å) | HOMO-LUMO GAP (ΔeV) | $k_{obs}$ ($h^{-1}$) |
|---|---|---|---|---|
| 1 | **1** | 2.0857 | 2.854 | 6.24 |
| 2 | **2** | 2.1062 | 2.733 | 3.02 |
| 3 | **3** | 2.0914 | 2.751 | 4.26 |
| 4 | **4** | 2.1468 | 2.730 | 0.30 |
| 5 | **5** | 2.1165 | 2.443 | 0.72 |
| 6 | **6** | 2.1953 | 2.360 | 0.21 |

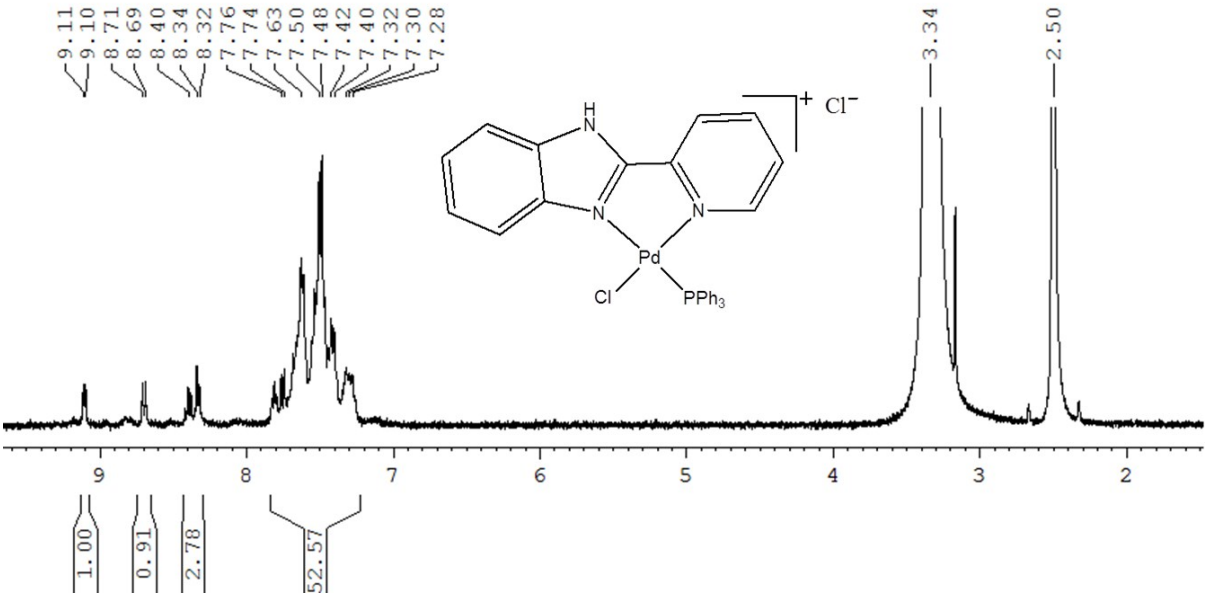



**Figure S1**: $^{1}H$ NMR spectrum for complex **5**

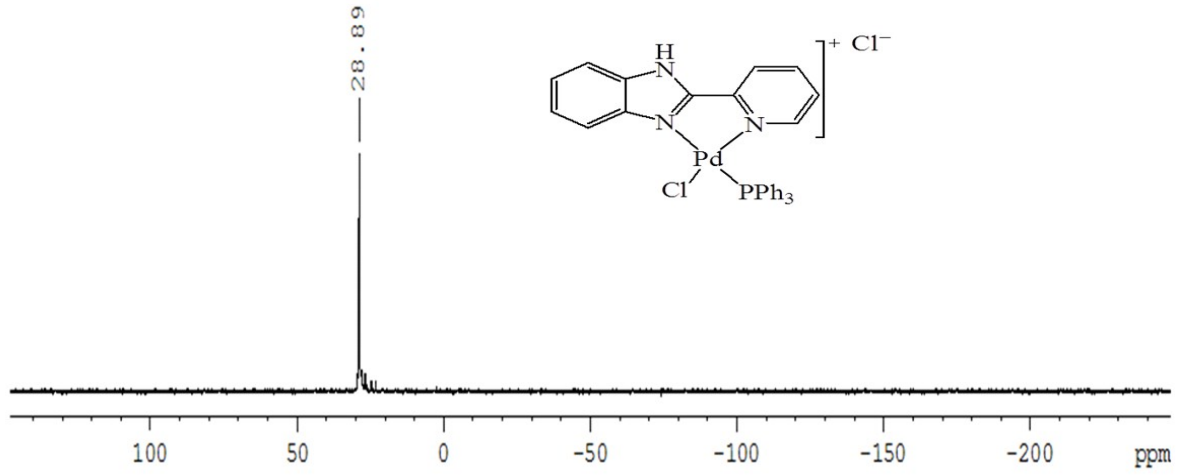



**Fig. S2**: $^{31}P$ $\{^{1}H\}$ NMR spectrum for complex **5** showing a peak of a coordinated $PPh_3$ ligand.

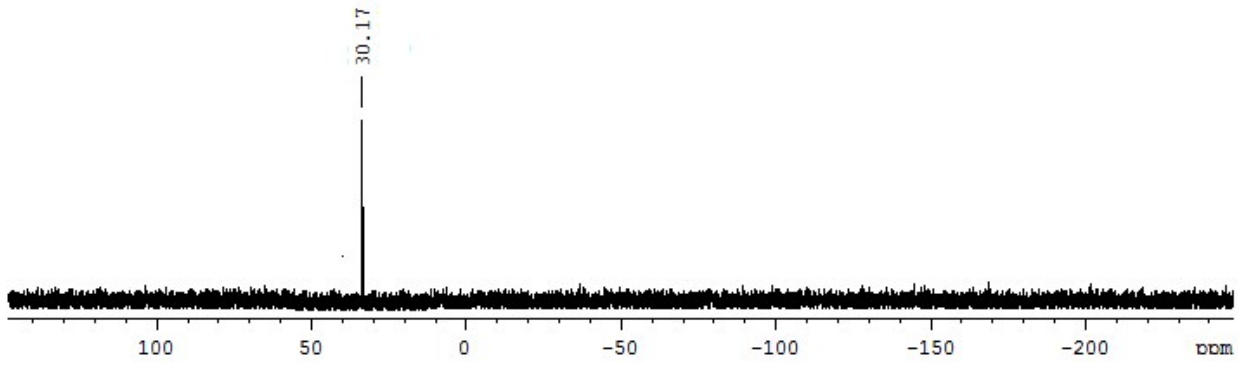
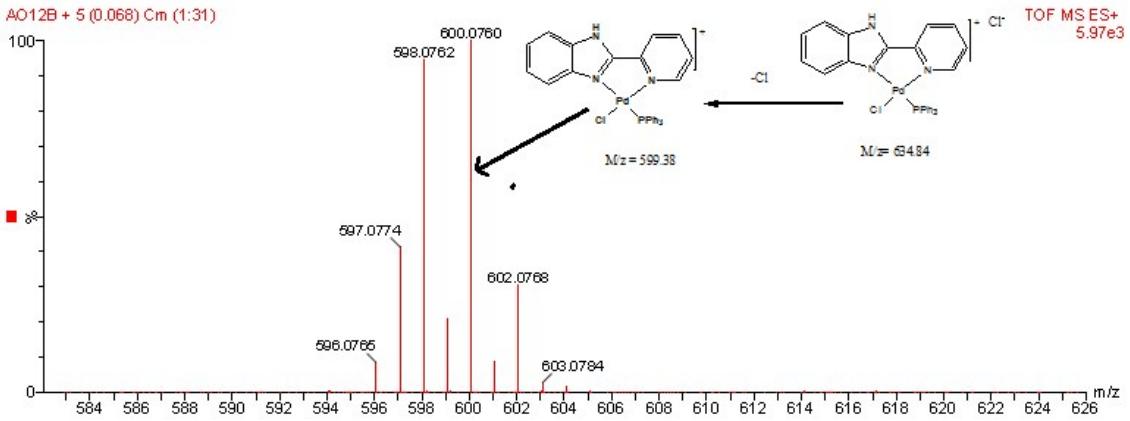
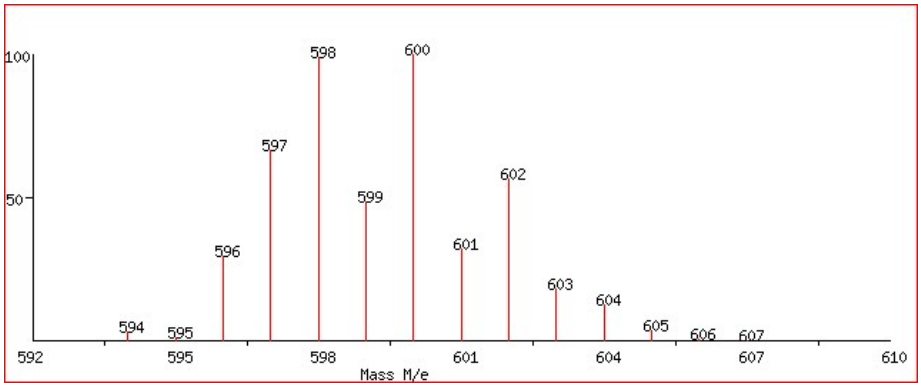



**Figure S3**: $^{31}P$ $\{^{1}H\}$ NMR spectrum for complex **6** showing a peak of a coordinated $PPh_3$ ligand.




**(a)**




**(b)**

**Figure S4**: **(a)** ESI mass spectrum showing *m/z* peak of molecular cation of complex **5**. (**b**) Calculated isotopic distribution of the cation of complex **5**.

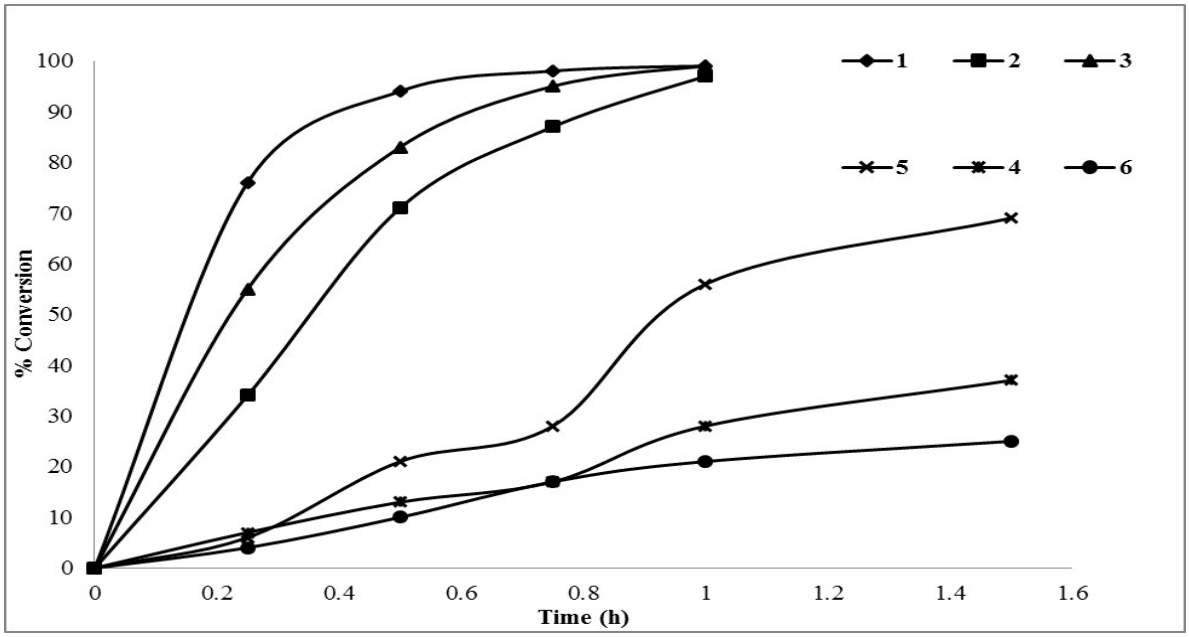
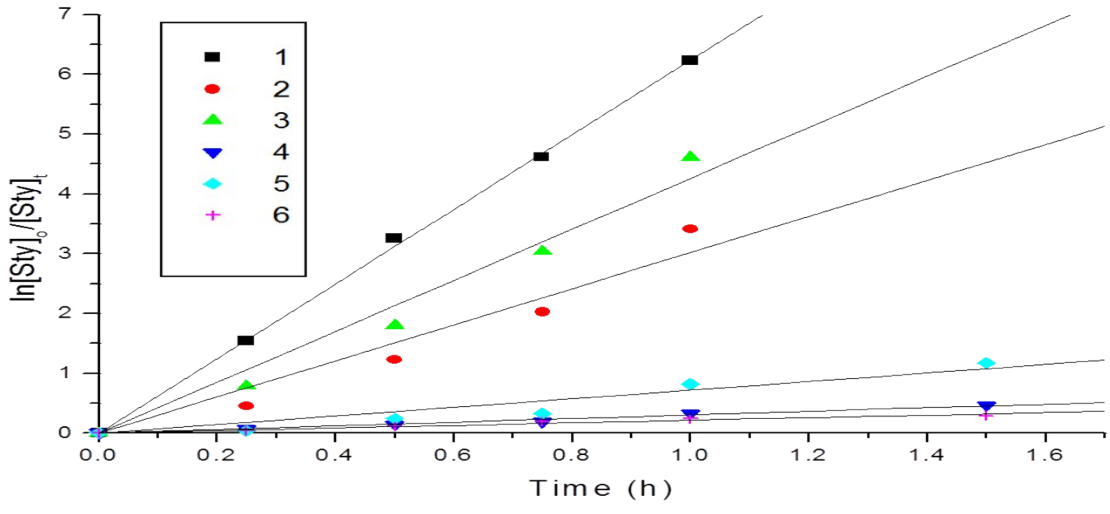
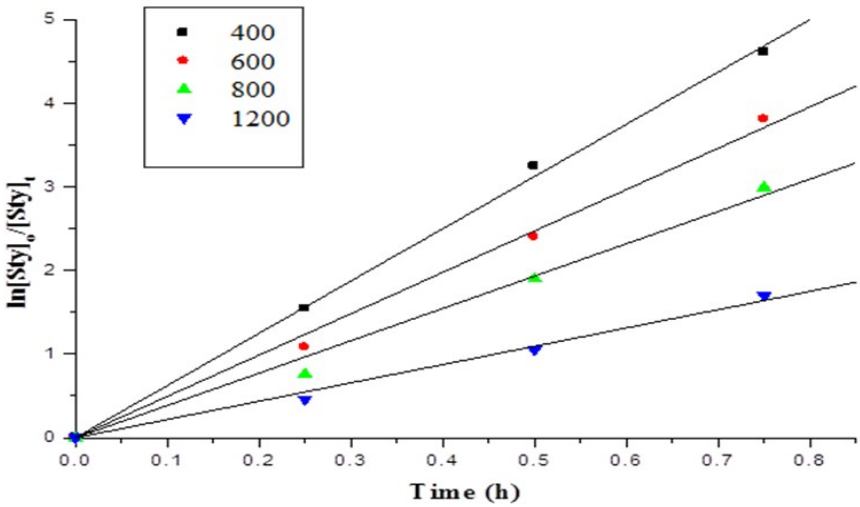



**Figure S5**: Time-dependence of molecular hydrogenation of styrene catalyzed by complexes **1-6**



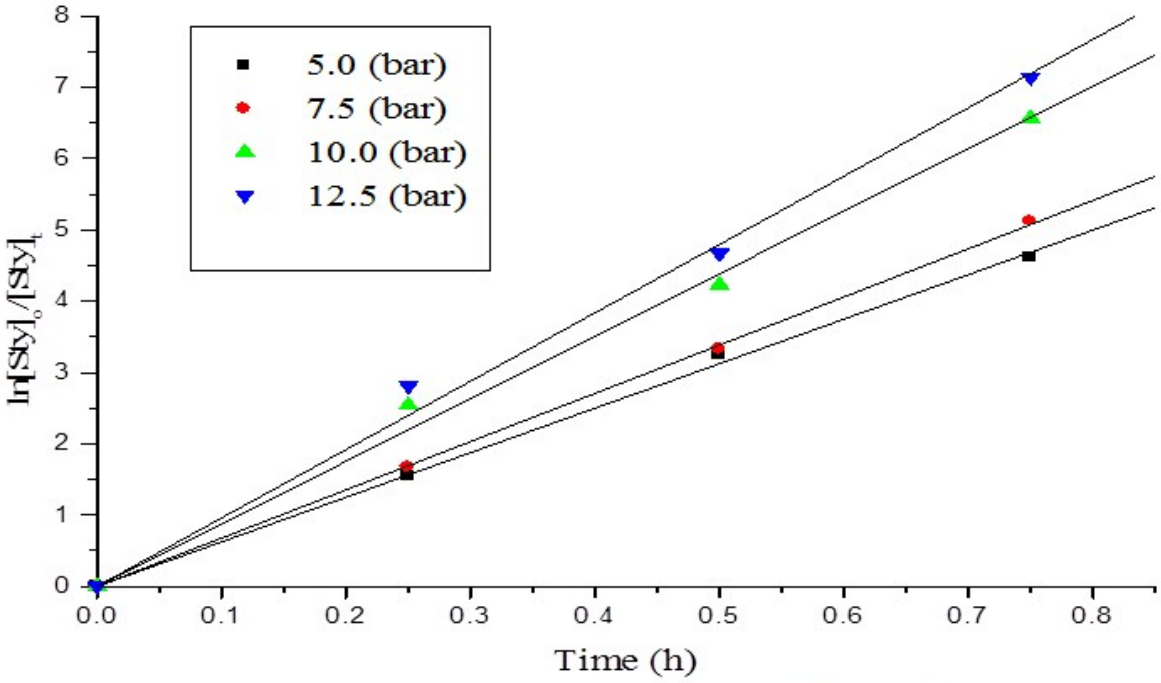

| Complex | Rate constant (k) | Regression ($R^2$) | Error |
|---|---|---|---|
| 1 | 6.24 | 0.99 | (±) 0.055 |
| 2 | 3.01 | 0.98 | (±) 0.225 |
| 3 | 4.26 | 0.95 | (±) 0.021 |
| 4 | 0.30 | 0.91 | (±) 0.011 |
| 5 | 0.72 | 0.98 | (±) 0.068 |
| 6 | 0.21 | 0.96 | (±) 0.011 |

**Figure S6**: Plot of $\ln[Sty]_o/[Sty]_t$ *vs* time for styrene hydrogenation with complexes **1-6.**




| S/C | Rate constant (k) | Regression ($R^2$) | Error |
|---|---|---|---|
| 400 | 6.24 | 0.99 | 0.091 |
| 600 | 4.94 | 0.99 | 0.123 |
| 800 | 3.86 | 0.99 | 0.140 |
| 1200 | 2.19 | 0.99 | 0.070 |

**Figure S7**: Effect of catalyst loading: Styrene (6.45 mmol). Pressure: 5 bar. Catalyst: **1** Temperature: 30 °C. Solvent: toluene (50 mL). Stirring speed: 600 rpm.




| Pressure (bar) | Rate constant (k) | Regression ($R^2$) | Error |
|---|---|---|---|
| 5 | 6.24 | 0.99 | 0.091 |
| 7.5 | 6.76 | 0.99 | 0.045 |
| 10 | 8.77 | 0.99 | 0.234 |
| 12.5 | 9.59 | 0.99 | 0.268 |

**Figure S8**: Effect of hydrogen presure on hydrogenation of styrene: Styrene (6.45 mmol). Pressure: 5 bar. Catalyst: **1** Temperature: 30 °C. Solvent: toluene (50 mL). Stirring speed: 600 rpm.

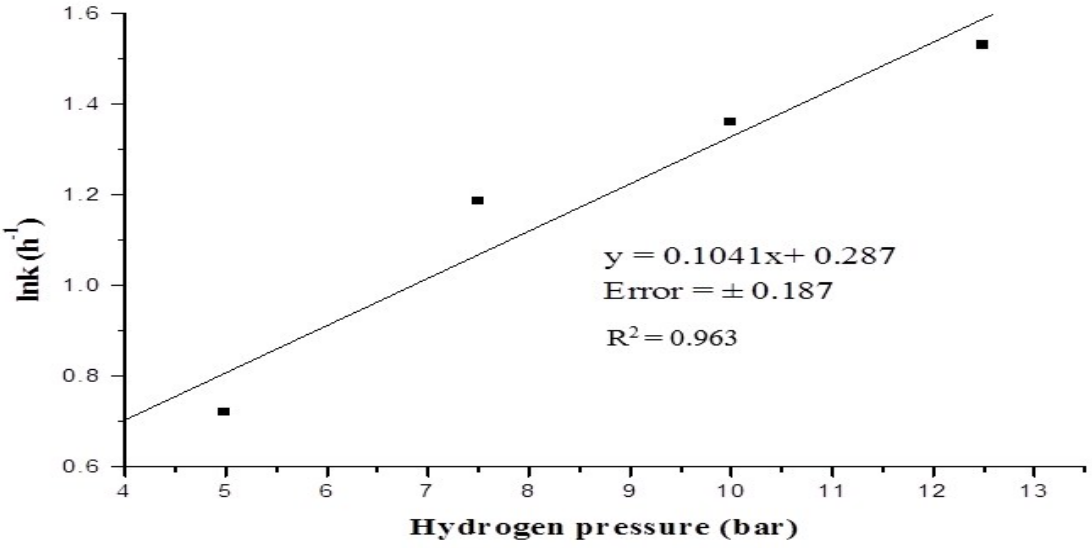
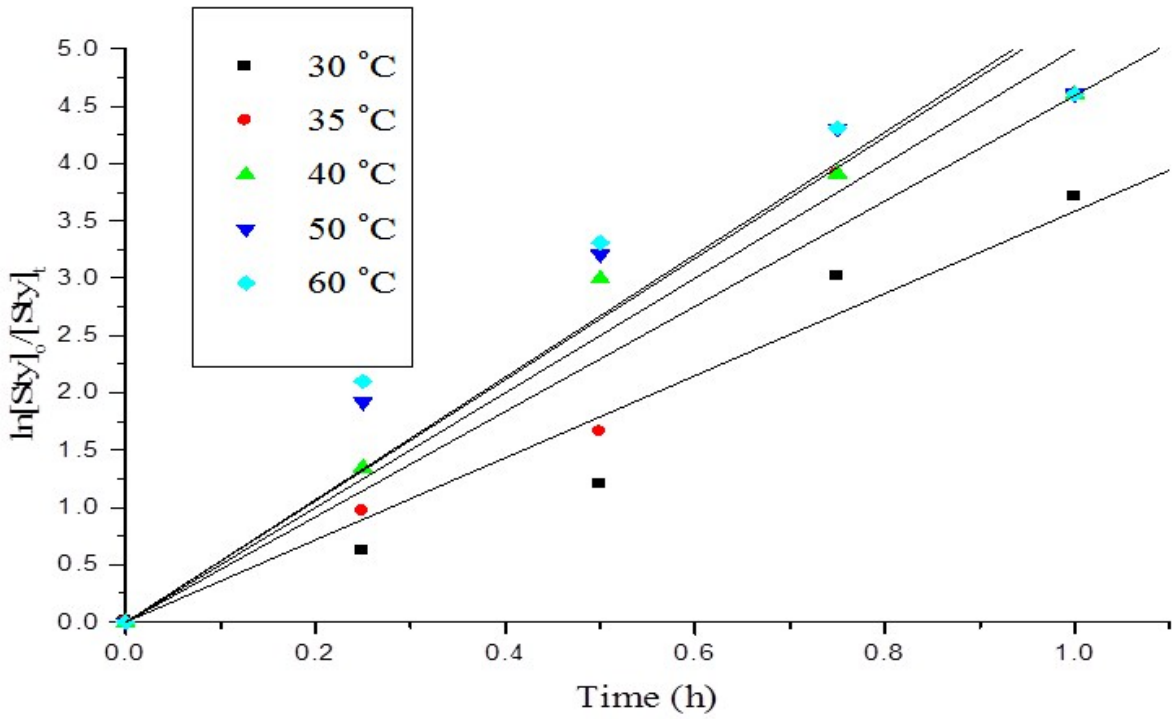
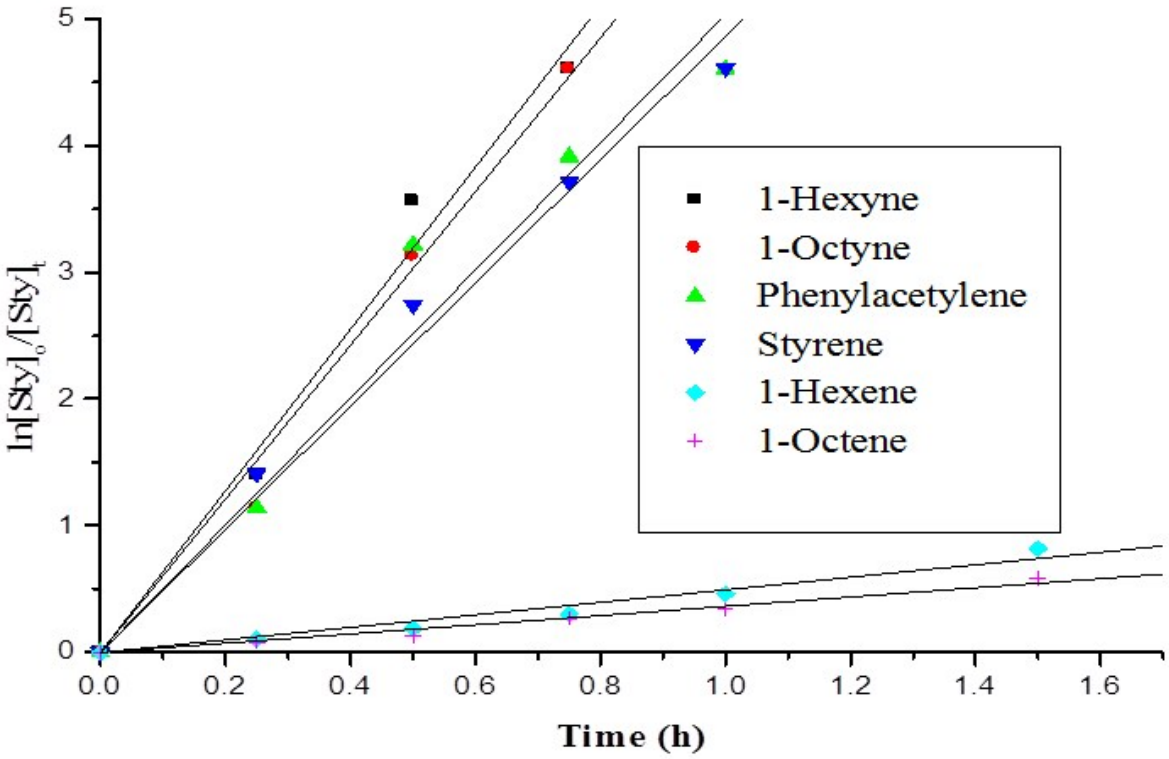



**Figure S9**: Plot of rate constants ($k_{obs}$) versus hydrogen pressure for the determination of order of reaction with respect to $H_2$ pressure using catalyst **1**.




| Reaction Temp (°C) | Rate constant | Regression ($R^2$) | Error |
|---|---|---|---|
| 30 | 3.583 | 0.97 | ± 0.269 |
| 35 | 4.592 | 0.98 | ± 0.295 |
| 40 | 4.999 | 0.98 | ± 0.241 |
| 50 | 5.288 | 0.96 | ± 0.408 |
| 60 | 5.340 | 0.96 | ± 0.466 |

**Figure S10**: Effect of temperature on the kinetics of hydrogenation reaction of styrene: Substrate (6.45 mmol). Pressure: 5 bar; Catalyst: **1**; Solvent: toluene (50 mL); Stirring speed: 600 rpm.




| Substrate | Rate constant (k) | Regression ($R^2$) | Error |
|---|---|---|---|
| 1-hexyne | 6.38 | 0.99 | 0.281 |
| 1-octyne | 6.06 | 0.99 | 0.242 |
| Phenylacetylene | 5.03 | 0.97 | 0.307 |
| Styrene | 4.86 | 0.99 | 0.163 |
| 1-Hexene | 0.49 | 0.98 | 0.027 |
| 1-Octene | 0.36 | 0.99 | 0.015 |

**Figure S11**: Effect of substrate on the kinetics of reaction of hydrogenation of alkenes and alkynes; Substrate (6.45 mmol). Pressure; 5 bar. Catalyst; **1**. Temperature; 30 °C. Solvent; toluene (50 mL). Stirring speed; 600 rpm.

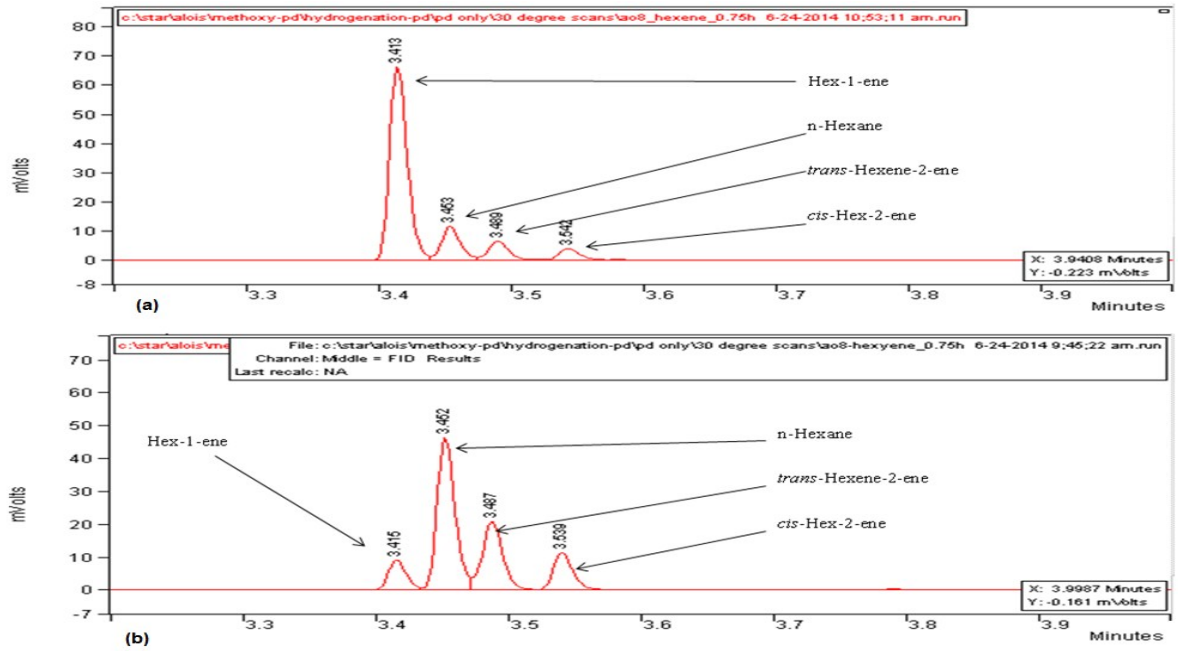



**Figure S12**: GC chromatogram showing isomerization of (a) 1-hexene and (b) 1-hexyne.

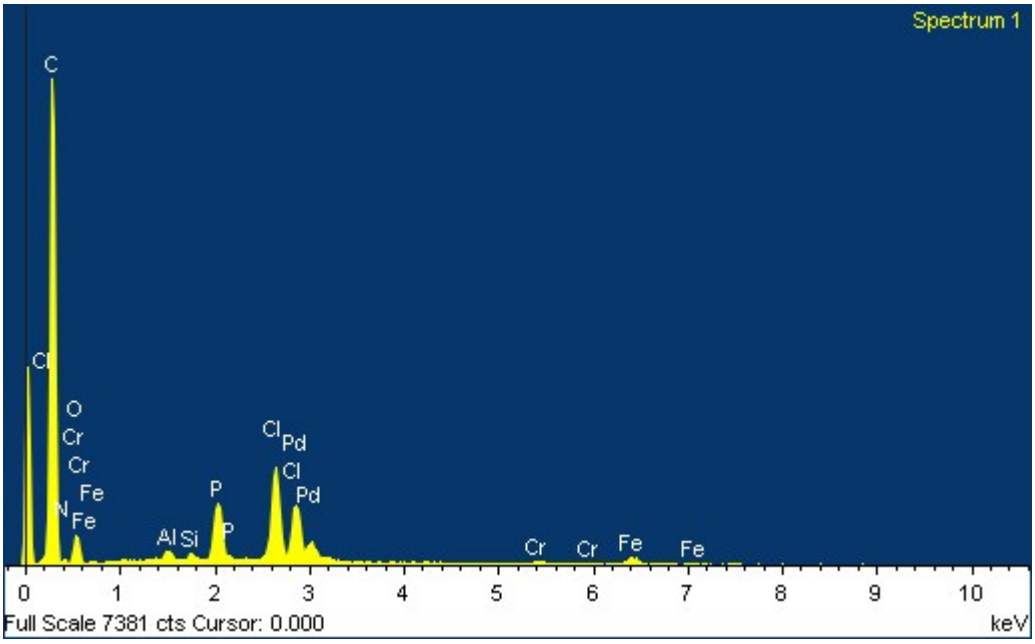



**Figure S13**: EDX spectrum of palladium nanoparticles obtained from the catalytic mixture of complex **1**. The high carbon content in addition to the presence of N established the formation of ligand stabilized palladium nanoparticles.

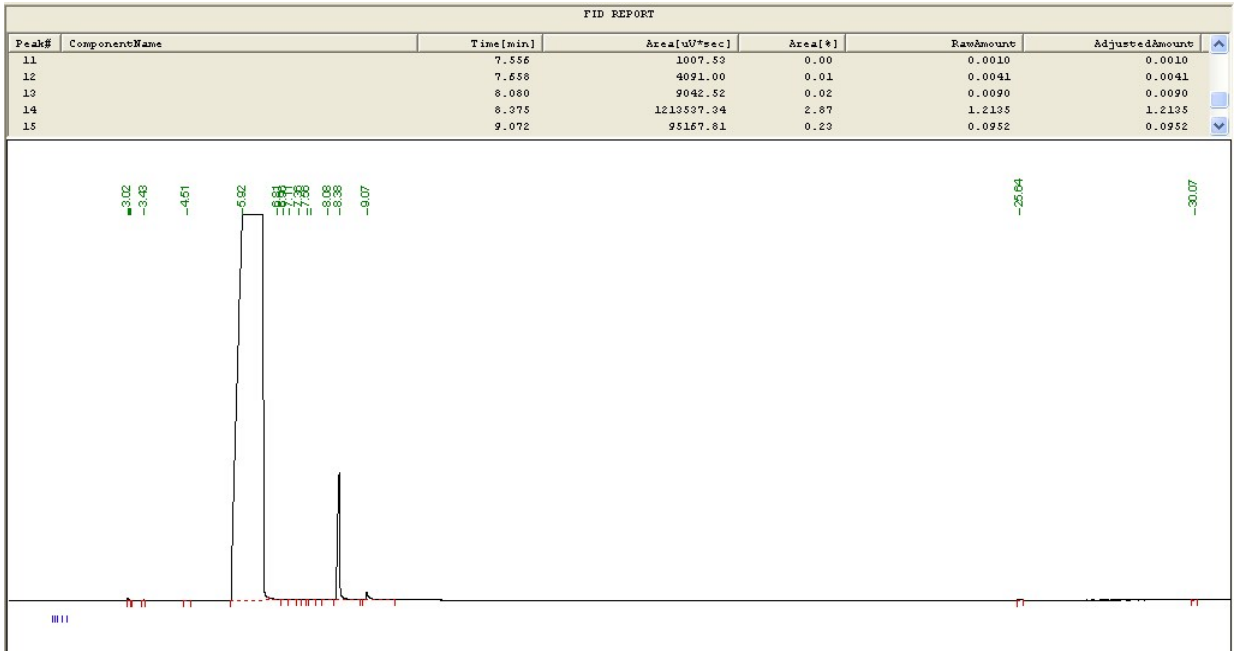



**Figure S14**: A GC chromatogram of styrene hydrogenation carried out by isolated nanoparticles of complex **1**. Conditions: styrene, substrate/catalyst = 400; substrate, 8.00 mmol; catalyst; 0.02 mmol (0.25 mol%); solvent, toluene; pressure, 5 bar; toluene, temperature, 30 oC;, time 45 min. ( Styrene peak : 8.38 min and ethylbenzene peak: 9.07 min.

**References**

i. Bruker (2010). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.

ii. G. M. Sheldrick, Acta Cryst. A64 (2008) 112.

iii. L. J. Farrugia, J. Appl. Cryst. 32 (1999) 837.