

Electronic Supplementary Information (ESI) for

---

**A simple method for the preparation of ultra-small palladium nanoparticle and their utilization for the hydrogenation of terminal alkyne groups to alkanes**

Jhumur Seth<sup>a</sup>, Chandrababu Naidu Kona,<sup>b</sup> Shyamsundar Das<sup>b</sup> and B. L. V. Prasad<sup>\*a</sup>

**Table of Contents:**

<b>Serial No.</b>	<b>Contents</b>	<b>ESI No.</b>
1	Procedure for ultra-small sized Pd-nanoparticle synthesis	ESI-1
2	General Remarks	ESI-2
3	Sample preparation for the characterizations	ESI-3
4	Procedure for hydrogenation reactions	ESI-4
5	TEM image of the Pd nanoparticles after using as catalyst	ESI-5
6	XRD pattern of the nanoparticles after using as catalyst	ESI-6
7	TGA of the Pd nanoparticles after using as catalyst	ESI-7
8	Gas Chromatography Characterizations	ESI-8
9	Characterization of product molecules	ESI-9
10	Copy of <sup>1</sup> NMR, <sup>13</sup> C NMR and DEPT spectra of product molecules	ESI-10

**ESI-1. Procedure for ultra-small sized Pd-nanoparticle Synthesis:** Here, Palladium acetate dimer has been used as the Pd-nanoparticle precursor and toluene has been used as the solvent of the reaction. The whole reaction was carried out in Ar gas atmosphere and the toluene has been degassed by purging Ar gas ~30 minutes before using. 0.025M Di-dodecyl dimethyl ammonium bromide (DDAB) has been taken in 10 mL toluene and sonicated for 10 minutes. 0.01M Pd-acetate dimer was added to that solution and it was allowed to sonicate over ~30 minutes. This brown color solution of Pd ions has been reduced by adding NaBH<sub>4</sub> aqueous solution (80 μL of 9.4M) under vigorous stirring condition. This attiring has been continued for ~1 hour for the complete reduction. Dodecanethiol (DDT) has been added to this solution (metal and DDT ratio is 1:30) and allowed to stir another 10 minutes. Now the whole solution has been refluxed under toluene boiling temperature for 1 hour. This Pd-nanoparticle dispersion in toluene has been cooled at room temperature followed by the addition of 30 mL pure ethanol. This has been kept for ~12 hours for the complete precipitation of the Pd nanoparticles. Then the supernatant has been discarded and the precipitate of Pd-nanoparticles has been collected as powder. This powder Pd nanoparticles could be re-dispersed in toluene or any other nonpolar organic solvent.

**ESI-2. General Remarks:** The as prepared powder Pd nanoparticles have been characterized by PXRD, XPS and TGA. The powder Pd nanoparticles has been re-dispersed in toluene. This solution (very dilute) has been drop-casted upon the carbon coated Cu grid and dried for ~12 hours for the TEM characterization. Similarly for XRD the sample dispersed in toluene was drop casted on a glass slide.

**ESI-3. Sample preparation for the characterizations:** The sample were analysed by powder X-ray diffraction using a PANalytical X'PRET PRO instrument and the iron-filtered Cu-K<sub>α</sub> radiation ( $\lambda=1.5406 \text{ \AA}$ ). TEM analysis for the sample was done using FEI Technai G2 TF20 which was operated at 200 kV. TEM samples were prepared by drop casting the Pd-nanoparticles dispersion in toluene on the carbon coated Cu grid of 200 mesh. After which, the grid was dried for ~12 hours for the complete evaporation of the solvent. The particle size distribution was determined by measuring the size of 300 particles and using GATAN software. X-ray photoelectron spectroscopy (XPS) measurement of Pd nanoparticles was carried out by a VG Microtech, model ESCA 3000 instrument equipped with ion gun (EX-05) for cleaning the surface. The binding energy resolution was 0.1 eV for the XPS measurement. The general scan and C 1s, Pd 3d, O 1s core level spectra were recorded with un-monochomatized Mg K<sub>α</sub> radiation (photon energy 1253.6 eV) and electron take off angle (angle between electron emission direction and surface plane) of 60°. The backgrounds of the XPS spectra were corrected using Shirley Algorithm. The core level binding energies (BE) were fixed with the carbon binding energy of 284.6 eV. The thermogravimetric analysis (TGA) was done by using SDT model Q600 of TA Instruments Inc. USA at a heating rate of 10 °C/m under nitrogen flow at 100 mL/m. FTIR measurements were done using the instrument Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600-4000 cm<sup>-1</sup> region. X-ray photoelectron spectroscopy (XPS) analysis for carbon peak analysis of Pd-nanoparticle, phenyl acetylene, styrene, Pd-nanoparticles incubated with phenyl acetylene (Figure 2C-2F), was performed using an ambient pressure X-ray photoelectron spectrometer from Prevac, Poland. The spectra were collected at 50 eV pass energy using a monochromatic AlK<sub>α</sub> X-ray source. All the core-level were corrected using C1s as reference at 284.6 eV. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy measurements were carried out on Bruker AC 200 MHz or Bruker DRX 400 and Bruker DRX 500 MHz spectrometers, and TMS was used as an internal standard. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported in parts per million (ppm) downfield from chloroform-d ( $\delta=7.27$ ) or TMS and coupling constants (*J*) are reported in hertz (Hz). The following abbreviations are used to designate signal multiplicity: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, b=broad. The multiplicity of <sup>13</sup>C NMR signals was assigned with the help of DEPT spectra and the abbreviations used: s=singlet, d=doublet, t=triplet, q=quartet, represent C (quaternary), CH, CH<sub>2</sub>, and CH<sub>3</sub>, respectively. GC analyses were carried out on Agilent Technologies 7890. All the chemicals used have been purchased from sigma Aldrich. Toluene and ethanol has been used from Merck. For hydrogenation reactions, commercial reagents were used without purification.

**ESI-4. Procedure for the hydrogenation reactions and the characterization of the products formed:** All the hydrogenation reactions have been done in the "Thales Nano" reactor. This reactor contains a cylindrical cartridge chamber, which contains the catalysts. For the reactions reported in this manuscript, the cartridge has been filled with ~150 mg of Pd nanoparticles in powder form and sealed at either end using valve. The reactants have been dissolved in methanol in 10<sup>-3</sup>M concentration. Then these reactants were allowed to pass through this cartridge in 1 mL/min rate at 35°C and 35 bar pressure of hydrogen. Once the reactants have been passed through this cartridge are collected in a conical flask on the other side. **Then NMR spectra and GC spectra have been taken of the crude products without any column chromatography.** This cartridge was washed with acetone for minimum 1 hour after each reaction. The same cartridge has been used ~12 times for these hydrogenation reactions with promising results, whereas each reaction contains 50 mg of the reactants.

ESI-5. TEM image of the Pd nanoparticles after using as catalyst:

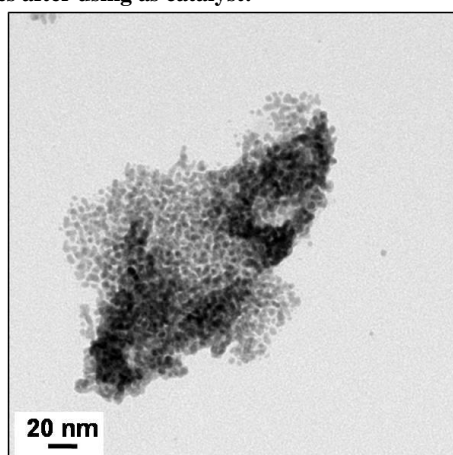


Figure ESI-5-1: TEM image of the Pd nanoparticles after using as catalyst

ESI-6. XRD pattern of the Pd nanoparticles after using as catalyst

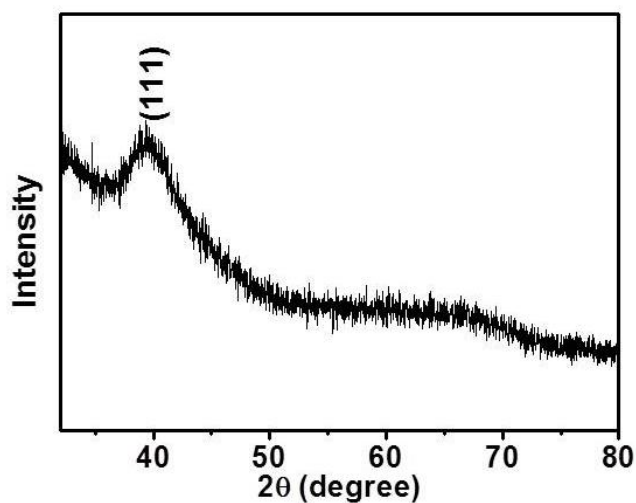


Figure ESI-6-1: PXRD pattern of the Pd nanoparticles after using as catalyst

ESI-7. TGA of the Pd nanoparticles after using as catalyst:

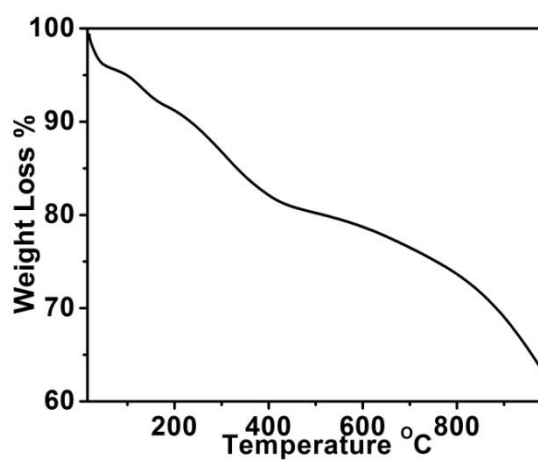


Figure ESI-7-1: TGA of the Pd nanoparticles after using as catalysis

ESI-8. Gas-Chromatography Characterizations of the molecules of table 1:

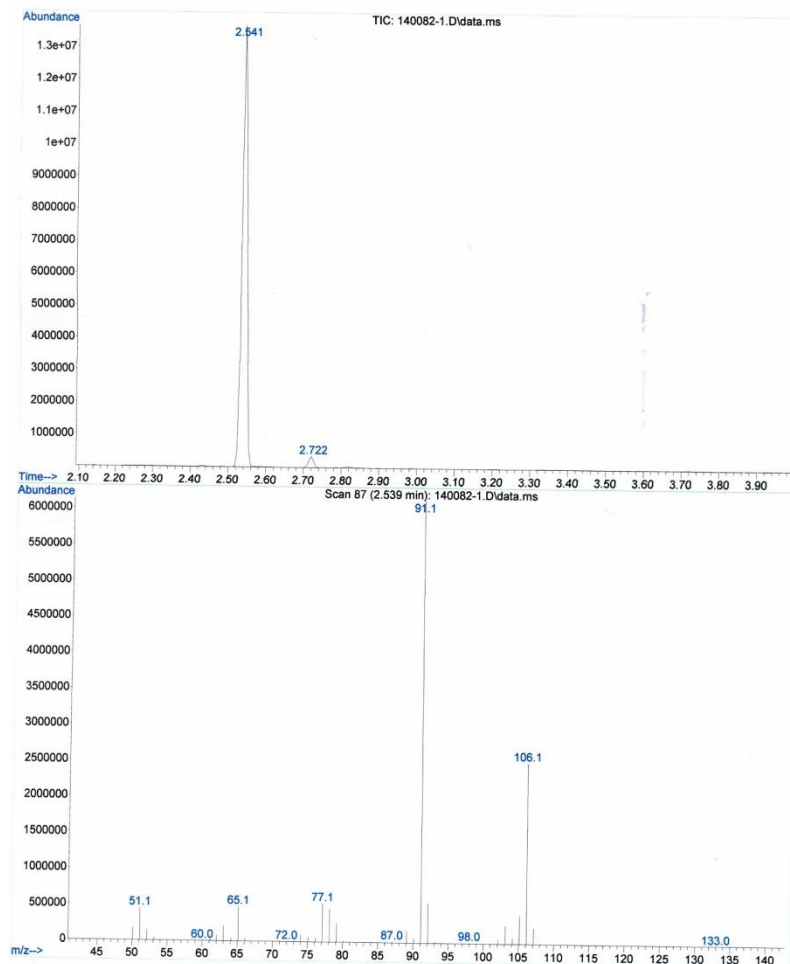


Figure ESI-8-1: GCMS data for the product of the hydrogenation reaction of Phenyl acetylene with the Pd nanoparticles

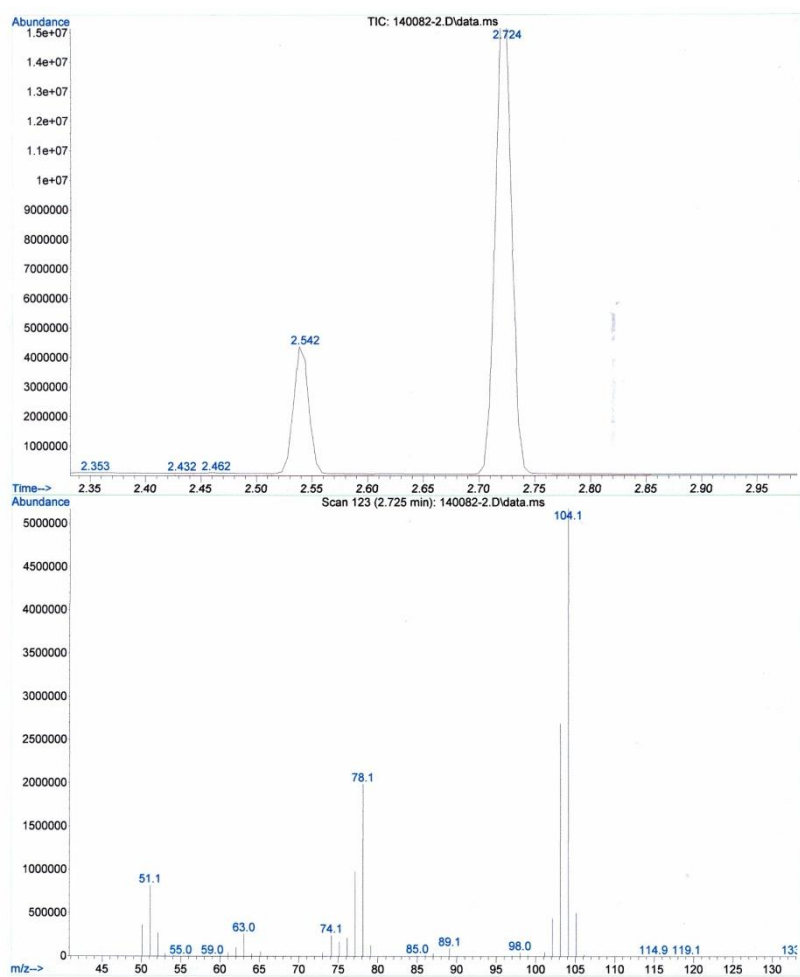


Figure ESI-8-2: GCMS data for the product of the hydrogenation reaction of Styrene with the Pd nanoparticles

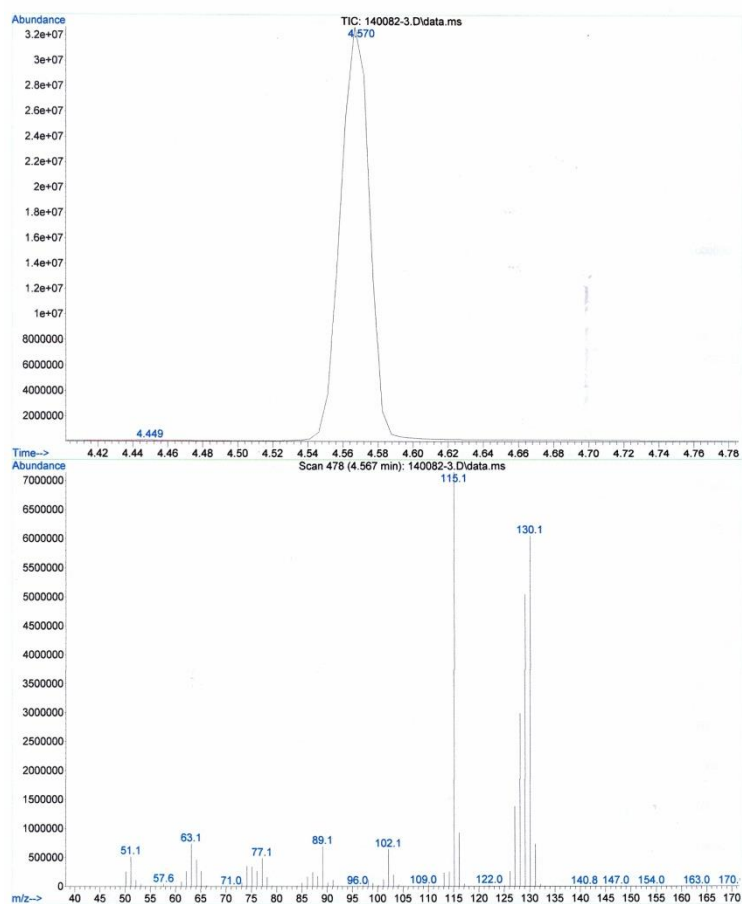


Figure ESI-8-3: GCMS data for the product of the hydrogenation reaction of 1-Phenyl-1-butyne with the Pd nanoparticles

The above GCMS graphs (Fig ESI-8-1 to ESI-8-3) are for the products of Table 1 by using as prepared Pd-nanoparticles as catalyst. From the above GCMS spectra, it is observed that, ethyl benzene has been formed only in the hydrogenation reaction of Phenyl acetylene in presence of Pd-nanoparticles. In case of styrene and 1-phenyl-1-butyne, the substrates have remained unreacted. To calculate the conversion of the reaction, GC spectra have been taken.

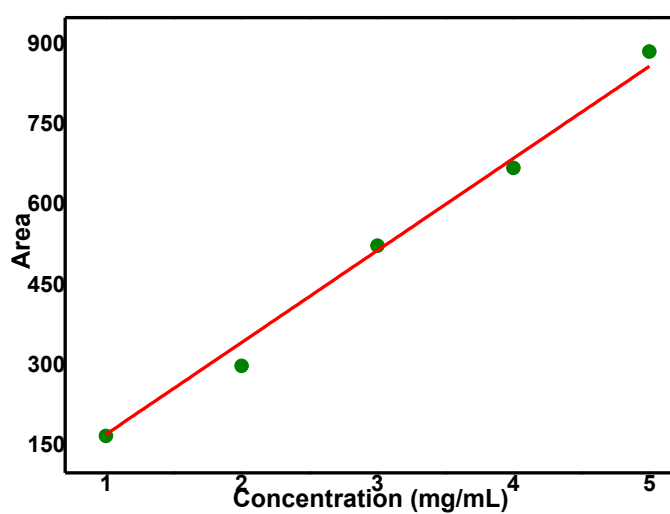
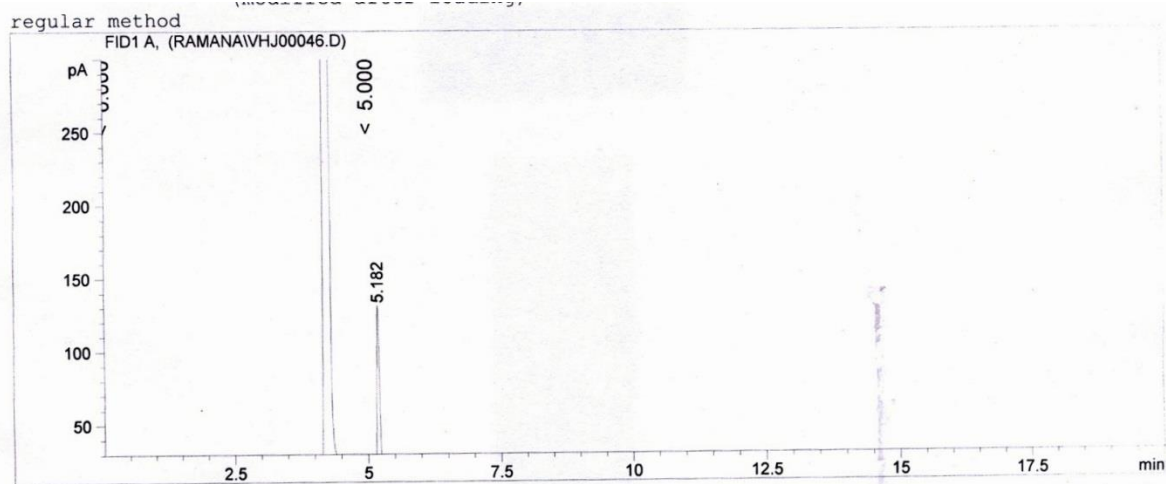


Figure ESI-8-4: Area vs concentration plot for the different concentrations of ethyl benzene



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.182	BB	0.0536	343.06833	106.55627	1.000e2

Totals : 343.06833 106.55627

Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*

Figure ESI-8-5: GC for pure ethyl benzene

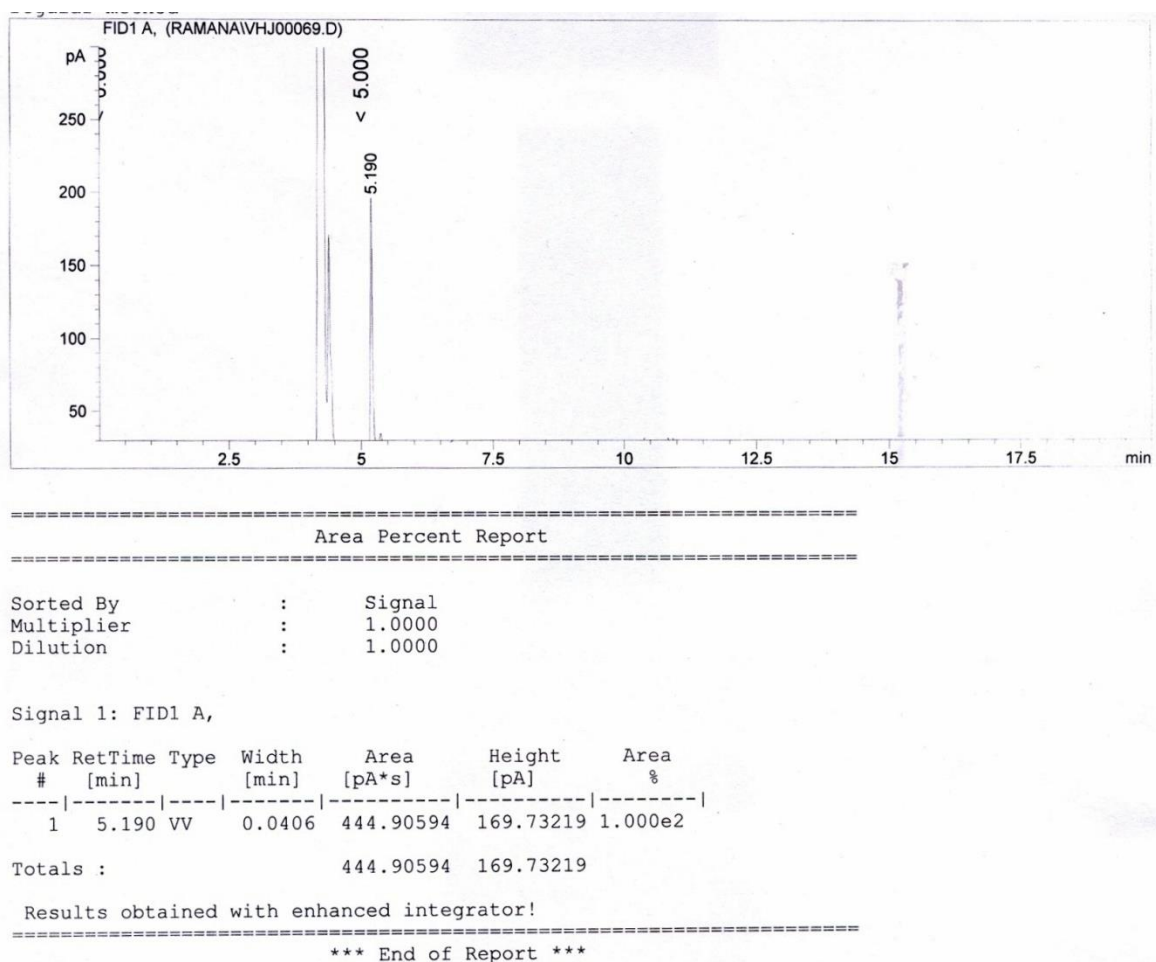


Figure ESI-8-6: GC for the product of the hydrogenation reaction of phenyl acetylene in presence of Pd-nanoparticle as catalyst

Figure ESI-8-4, represents the plot for area vs concentration for the ethyl benzene at different concentrations. Pure ethyl benzene gives peak at 5.19 in the temperature range 100-280 °C. The area of the peak varies with different concentrations for the equal volume of samples. The graph has been fitted with the straight line which shows the slope 168. Now, the product of hydrogenation reaction of phenyl acetylene in presence of Pd-nanoparticles, gives peak at 5.19 having an area 445 (from Fig ESI-8-5). The concentration of the ethyl benzene produced in this reaction is  $(445/168) = 2.65$  mg/mL. The amount of the phenyl acetylene was taken in the reaction is 3 mg/mL. Therefore the percentage yield of this reaction is  $\{(2.65/3) \times 100\} = 88.3\%$ . The crude product does not contain any peak of phenyl acetylene, which indicates 100% conversion.



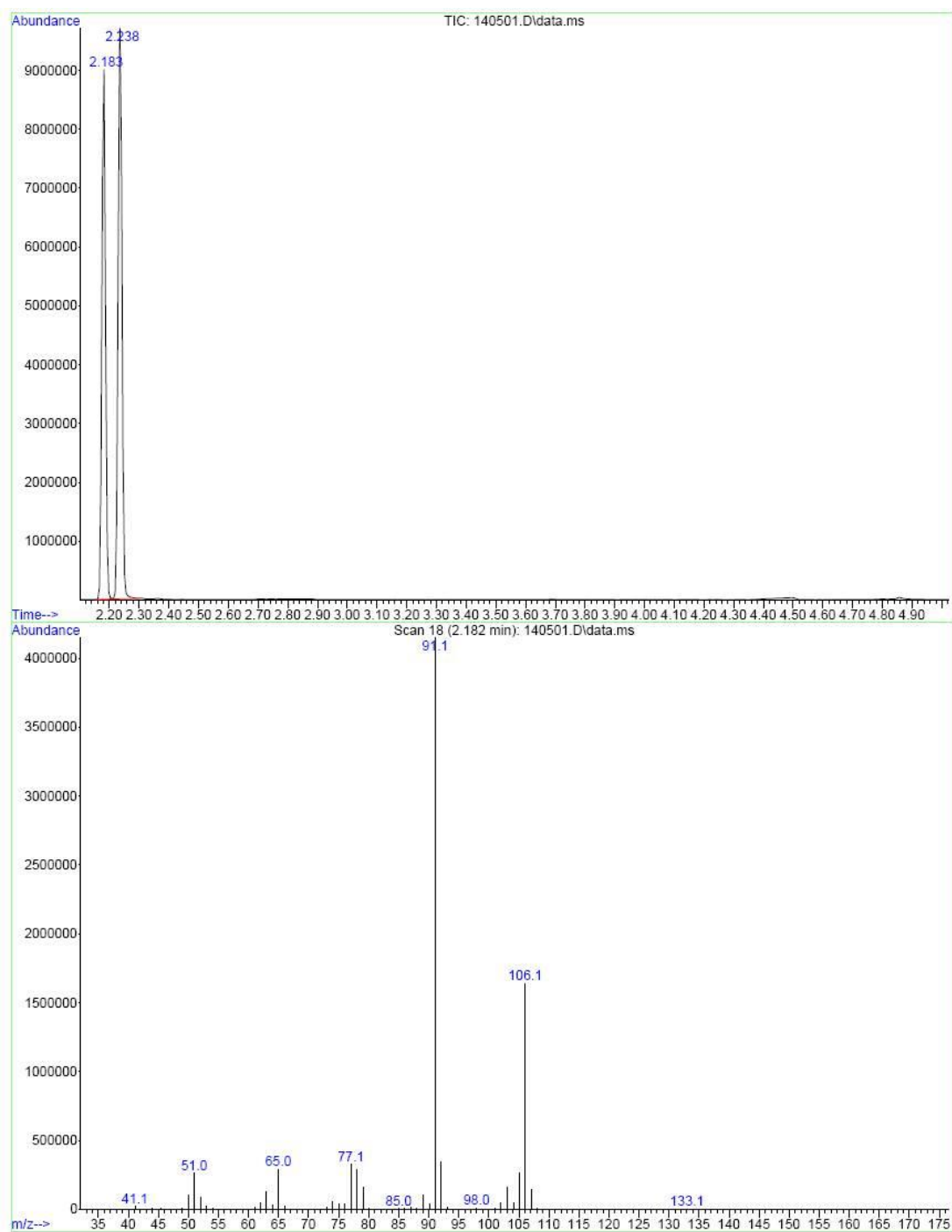


Figure ESI-8-7(a): GCMS data for the aliquot of the hydrogenation reaction of Phenyl acetylene with the Pd nanoparticles at the half time of the reaction.

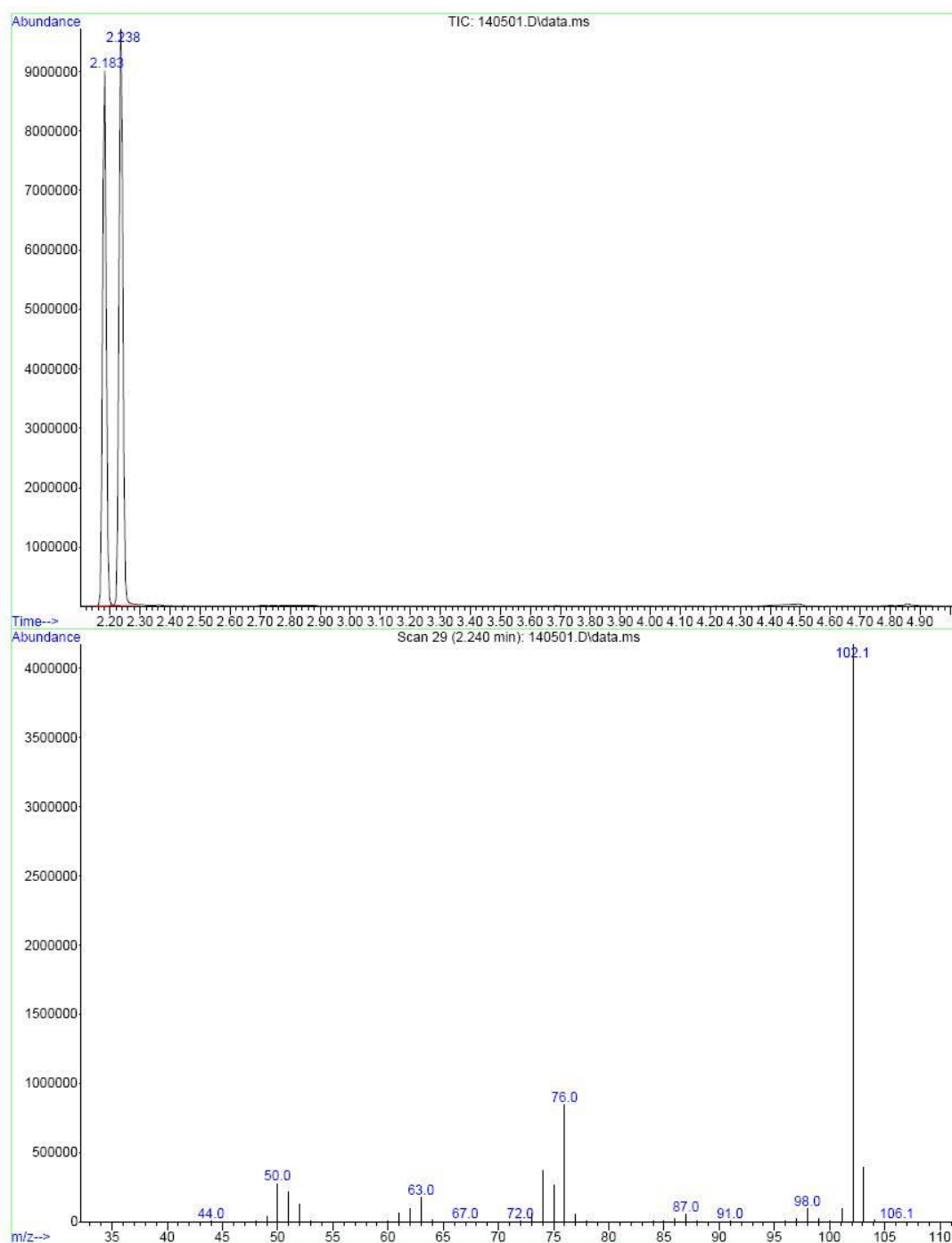
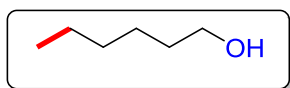


Figure ESI-8-7(b): GCMS data for the aliquot of the hydrogenation reaction of Phenyl acetylene with the Pd nanoparticles at the half time of the reaction.

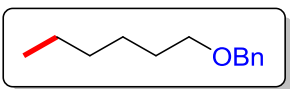
#### ESI-9. Characterizations of the product molecules of the hydrogenation reactions by Pd-nanoparticles catalyst:

The entry molecules Table-2, Set1, 1-6, have been synthesized by conventional method following the reference ESI 1. The entry molecule set-2, compound 7-9, have been readily purchased from Sigma-Aldrich chemicals. The entry molecules Set-3, 10-13 have been synthesized by following the reference ESI 2-3. The entry molecule set-4, compound 14-17 were prepared by Grignard reaction following conventional procedure.

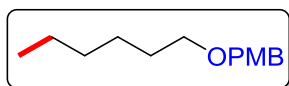
1. S. Das, B. Induvadana and C. V. Ramana, *Tetrahedron*, 2013, **16**, 1881-1896.
2. G. V. M. Sharma, B. Lavanya, A. K. Mahalingam and P. R. Krishna, *Tet. Lett.*, 2000, **41**, 10323-10326.
3. C. V. Ramana and S. B. Suryawanshi, *Tet. Lett.*, 2008, **49**, 445-448.



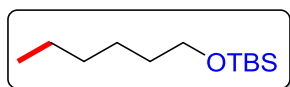
**Hexan-1-ol (1b):**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.78–0.96 (m, 3H), 1.18–1.42 (m, 6H), 1.44–1.64 (m, 2H), 2.16 (d,  $J$  = 3.0 Hz, 1H), 3.50–3.71 (m, 2H) ppm.



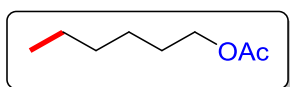
**((Hexyloxy)methyl)benzene (2b):**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.77–0.97 (m, 3H), 1.16–1.48 (m, 6H), 1.50–1.74 (m, 2H), 3.47 (t,  $J$  = 6.6 Hz, 2H), 4.51 (s, 2H), 7.14–7.41 (m, 5H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.1 (q), 22.7 (t), 25.9 (t), 29.8 (t), 31.8 (t), 70.6 (t), 72.9 (t), 127.5 (d), 127.6 (d, 2C), 128.4 (d, 2C), 138.8 (s) ppm.



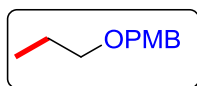
**1-((Hexyloxy)methyl)-4-methoxybenzene (3b):**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.77–0.96 (m, 3H), 1.29 (br. s., 6H), 1.50–1.66 (m, 2H), 3.43 (t,  $J$  = 6.6 Hz, 2H), 3.78 (s, 3H), 4.42 (s, 2H), 6.87 (m,  $J$  = 8.7 Hz, 2H), 7.26 (m,  $J$  = 8.7 Hz, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0 (q), 22.6 (t), 25.8 (t), 29.7 (t), 31.6 (t), 55.1 (q), 70.2 (t), 72.4 (t), 113.7 (d, 2C), 129.1 (d, 2C), 130.8 (s), 159.0 (s) ppm.



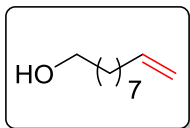
**tert-Butyl(hexyloxy)dimethylsilane (4b):**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.0 (m, 6H), 0.78–0.93 (m, 12H), 1.15–1.34 (m, 6H), 1.36–1.56 (m, 2H), 3.55 (t,  $J$  = 6.4 Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  -5.3 (q, 2C), 14.0 (q), 18.4 (s), 22.7 (t), 25.6 (t), 26.0 (q, 3C), 31.8 (t), 32.9 (t), 63.3 (t) ppm.



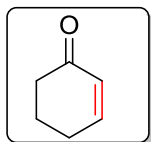
**Hexyl acetate (5b):**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.76–0.95 (m, 3H), 1.27 (s, 6H), 1.56 (d,  $J$  = 6.6 Hz, 2H), 2.00 (s, 3H), 4.01 (t,  $J$  = 6.6 Hz, 2H) ppm.



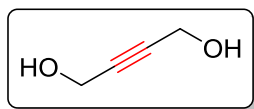
**1-Methoxy-4-(propoxymethyl)benzene (6b):**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.84–0.95 (m, 3H), 1.52–1.65 (m, 2H), 3.36 (t,  $J$  = 6.7 Hz, 2H), 3.76 (s, 3H), 4.40 (s, 2H), 6.80–6.89 (m, 2H), 7.19–7.26 (m, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.6 (q), 22.9 (t), 55.2 (q), 71.8 (t), 72.4 (t), 113.7 (d, 2C), 129.2 (d, 2C), 130.8 (s), 159.0 (s) ppm.



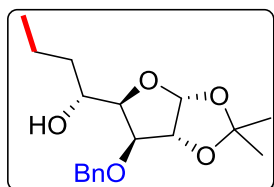
**Dec-9-en-1-ol (7b):**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.29–1.39 (m, 10H), 1.48–1.58 (m, 2H), 1.92 (br, 1H), 1.98–2.07 (m, 2H), 3.61 (t,  $J$  = 6.6 Hz, 1H), 4.88–5.03 (m, 2H), 5.70–5.90 (m, 1H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  25.7 (t), 28.8 (t), 29.0 (t), 29.3 (t), 29.4 (t), 32.6 (t), 33.7 (t), 62.7 (t), 114.0 (t), 139.0 (d) ppm.



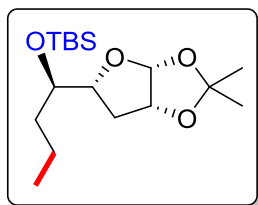
**Cyclohex-2-en-1-one (8b):**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.95–2.08 (m, 2H), 2.30–2.37 (m, 2H), 2.39–2.46 (m, 2H), 6.0 (td,  $J$  = 2.02, 10.11 Hz, 1H), 6.0 (td,  $J$  = 4.1, 10.11 Hz, 1H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.4 (t), 25.3 (t), 37.7 (t), 129.4 (d), 150.4 (d), 199.2 (s) ppm.



**But-2-yne-1,4-diol (9b):**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$  and MeOD):  $\delta$  3.3 (br, 2H), 4.2 (s, 4H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$  and MeOD):  $\delta$  50.0 (t), 83.2 (s) ppm.

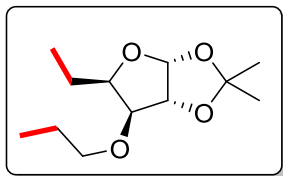


**(R)-1-((3aR,5R,6S,6aR)-6-(Benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)butan-1-ol (10b):**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.84–0.97 (m, 3H), 1.30–1.36 (m, 4H), 1.39 (d,  $J$  = 7.7 Hz, 1H), 1.49 (s, 3H), 1.54 (d,  $J$  = 5.4 Hz, 2H), 3.96 (d,  $J$  = 3.0 Hz, 2H), 4.08 (d,  $J$  = 2.9 Hz, 1H), 4.45–4.54 (m, 1H), 4.64 (d,  $J$  = 3.9 Hz, 1H), 4.70–4.80 (m, 1H), 5.98 (d,  $J$  = 3.9 Hz, 1H), 7.30–7.43 (m, 5H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0 (q), 18.7 (t), 26.2 (q), 26.7 (q), 36.6 (t), 69.3 (d), 71.8 (t), 81.9 (d), 82.2 (d), 105.1 (d), 111.6 (s), 128.1 (d, 2C), 128.4 (d), 128.8 (d, 2C), 136.9 (s) ppm.



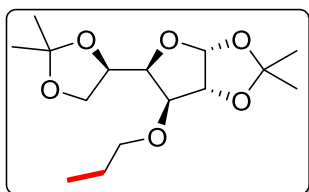
**tert-butyl((R)-1-((3aR,5R,6aR)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)butoxy)dimethylsilane (11b):**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.08 (s, 3H), 0.11 (s, 3H),

0.89 (m, 12H), 1.34 (s, 3H), 1.37–1.50 (m, 4H), 1.56 (s, 3H), 1.91 (ddd,  $J = 2.4, 5.96, 13.89$  Hz, 1H), 2.04–2.18 (m, 1H) 3.78–3.85 (m, 1H), 3.86–3.96 (m, 1H), 4.72 (ddd,  $J = 2.5, 4.2, 9.2$  Hz, 1H), 5.70 (d,  $J = 4.2$  Hz, 1H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  – 4.7 (q), – 4.0 (q), 14.3 (q), 18.2 (s), 18.3 (t), 26.0 (q, 3C), 26.7 (q), 27.6 (q), 33.6 (t), 35.7 (t), 74.0 (d), 81.0 (d), 83.1 (d), 105.9 (d), 112.9 (s) ppm.



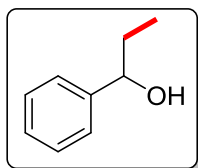
111.1 (s) ppm.

**(3aR,5R,6S,6aR)-5-ethyl-2,2-dimethyl-6-propoxytetrahydrofuro[2,3-d][1,3]dioxole (12b):**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.93 (t,  $J = 7.3$  Hz, 3H), 0.97 (t,  $J = 7.6$  Hz, 3H), 1.33 (s, 3H), 1.55 (s, 3H), 1.60–1.65 (m, 2H), 1.70–1.79 (m, 2H), 3.35 (dt,  $J = 6.7, 9.2$  Hz, 1H), 3.60 (dt,  $J = 6.4, 9.2$  Hz, 1H), 3.67 (d,  $J = 2.7$  Hz, 1H), 4.06 (ddd,  $J = 2.8, 7.0, 9.8$  Hz, 1H), 4.55 (d,  $J = 3.7$  Hz, 1H), 5.89 (d,  $J = 3.7$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.3(q), 10.6(q), 20.9 (t), 23.0 (t), 26.2 (q), 26.7 (q), 71.9 (t), 81.9 (d), 82.2 (d), 82.3 (d), 104.7 (d),

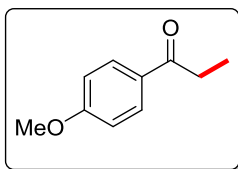


10.6(q), 23.0 (t), 25.4(q), 26.2 (q), 26.7 (q), 26.8 (q), 67.2 (t), 72.3 (t), 72.5 (d), 81.2(d), 82.1 (d), 82.5 (d), 105.3 (d), 108.9 (s), 111.7 (s) ppm.

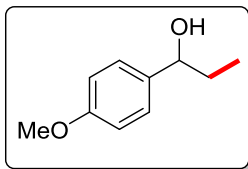
**(3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-propoxytetrahydrofuro[2,3-d][1,3]dioxole (13b):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.93 (t,  $J = 7.4$  Hz, 3H), 1.32 (s, 3H), 1.36 (s, 3H), 1.46 (s, 3H), 1.50 (s, 3H), 1.55–1.64 (m, 2H), 3.46–3.51 (m, 1H), 3.55–3.60 (m, 1H), 3.86 (d,  $J = 3.2$  Hz, 1H), 3.99 (dd,  $J = 5.9, 8.2$  Hz, 1H), 4.09(dd,  $J = 6.4, 8.7$  Hz, 1H), 4.14 (dd,  $J = 3.2, 7.3$ Hz, 1H), 4.30–4.35 (m, 1H), 4.53 (d,  $J = 3.7$  Hz, 1H), 5.88 (d,  $J = 3.7$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$



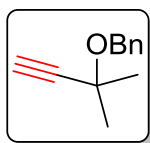
**1-Phenylpropan-1-ol (14b):**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.86–0.98 (m, 3H), 1.64–1.90 (m, 2H), 2.01 (br. s., 1H), 4.60 (t,  $J = 6.6$  Hz, 1H), 7.26–7.39 (m, 5H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.1 (q), 31.8 (t), 76.0 (d), 125.9 (d, 2C), 127.4(d), 128.4 (d, 2C), 144.6 (s) ppm.



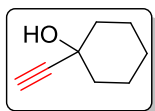
**1-(4-methoxyphenyl)propan-1-one (15b):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.19 (t,  $J = 7.1$  Hz, 3H), 2.93 (q,  $J = 7.3$  Hz, 2H), 3.84 (s, 3H), 6.90 (d,  $J = 9.2$  Hz, 2H), 7.90 (d,  $J = 9.2$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz):  $\delta$  8.4 (q), 31.3 (t), 55.4 (q), 113.6 (d, 2C), 129.9 (d, 2C), 130.1 (s), 163.2 (s), 199.5 (s) ppm.



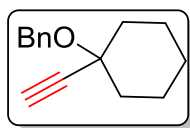
**1-(4-methoxyphenyl)propan-1-ol (16b):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  0.88 (t,  $J = 7.6$  Hz, 3H), 1.65–1.84 (m, 2H), 3.78 (s, 3H), 3.85 (s, 1H), 4.50 (t,  $J = 6.6$  Hz, 1H), 6.86 (d,  $J = 8.7$  Hz, 1H), 7.27 (d,  $J = 8.7$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz):  $\delta$  10.1 (q), 31.7 (t), 55.2 (q), 77.2 (d), 113.7 (d, 2C), 127.1 (d, 2C), 136.7 (s), 158.9 (s) ppm.



**((2-Methylbut-3-yn-2-yl)oxy)methylbenzene (17b):**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.55 (s, 6H), 2.56 (s, 1H), 4.62 (s, 2H), 7.22–7.39 (m, 5H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  28.8 (q, 2C), 66.5 (t), 70.5 (s), 72.2 (d), 86.1 (s), 127.3 (d), 127.7 (d, 2C), 128.3 (d, 2C), 138.9 (s) ppm.



**1-Ethynylcyclohexan-1-ol (18b):**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.25 (m, 1H), 1.50–1.73 (m, 7H), 1.90 (dd,  $J = 2.1, 1.2$  Hz, 2H), 2.36 (s, 1H), 2.47 (s, 1H) ppm.



**(((1-ethynylcyclohexyl)oxy)methyl)benzene (19b):**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.46–1.78 (m, 8H), 1.89–2.02 (m, 2H), 2.50 (s, 1H), 4.65 (s, 2H), 7.29–7.39 (m, 5H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.6 (t, 2C), 25.4 (t), 37.2 (t, 2C), 65.5 (t), 72.1 (s), 73.8 (d), 85.4 (s), 127.2 (d), 127.8 (d, 2C), 128.2 (d, 2C), 139.1 (s) ppm.

ESI-10. Copy of  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and DEPT spectra for the products of the hydrogenation reactions by using Pd-nanoparticles as catalyst:

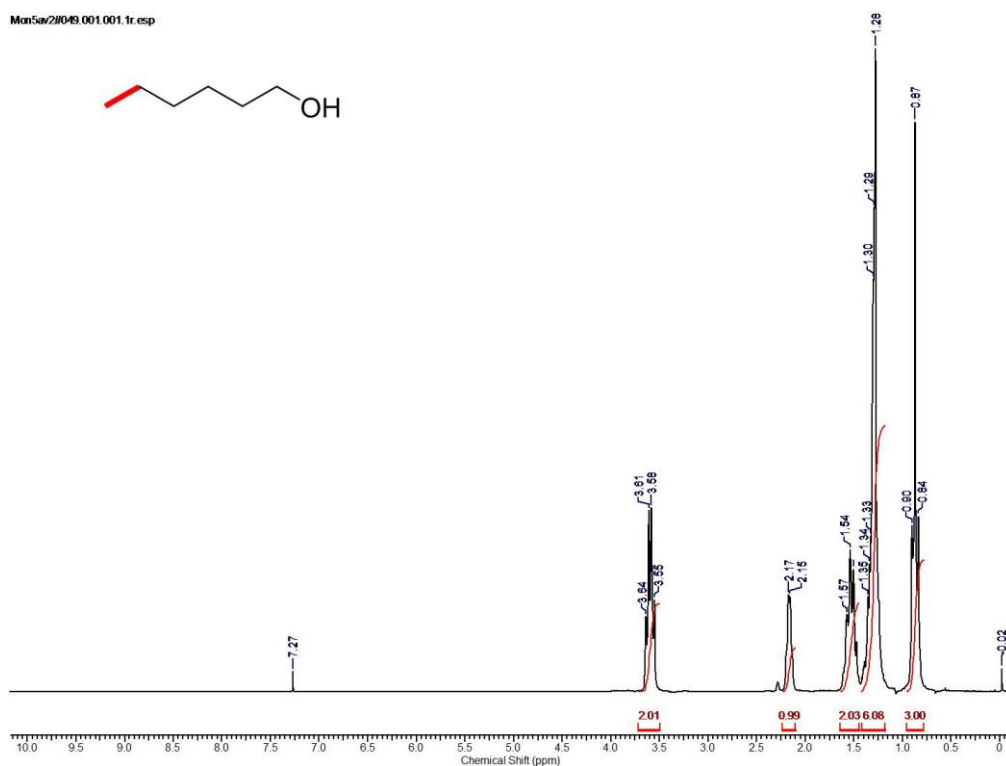


Figure ESI-10-1:  $^1\text{H}$  NMR of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-1, entry 1 (1b)

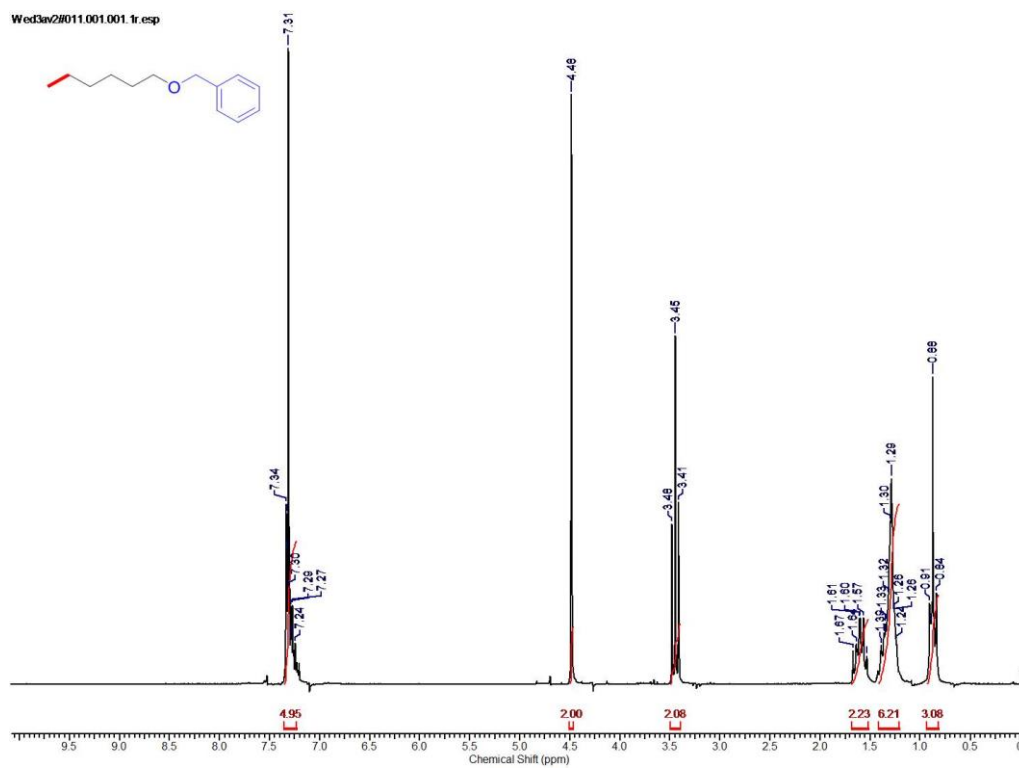


Figure ESI-10-2:  $^1\text{H}$  NMR of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-1, entry 2 (2b)

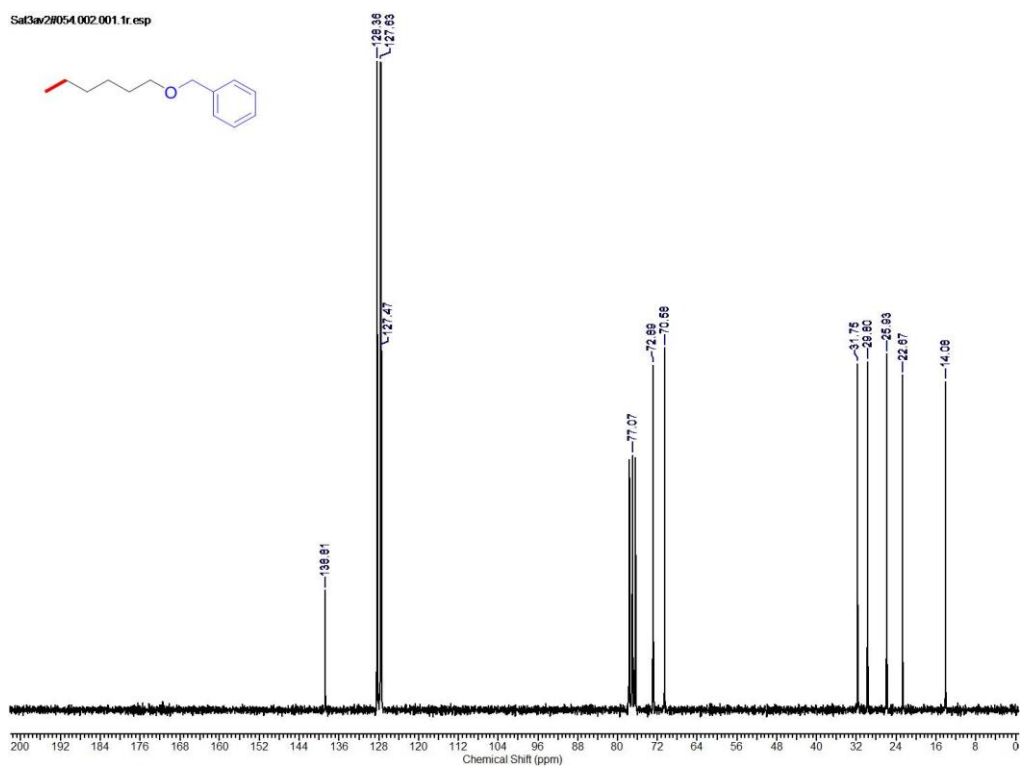


Figure ESI-10-3:  $^{13}\text{C}$  NMR of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-1, entry 2 (2b)

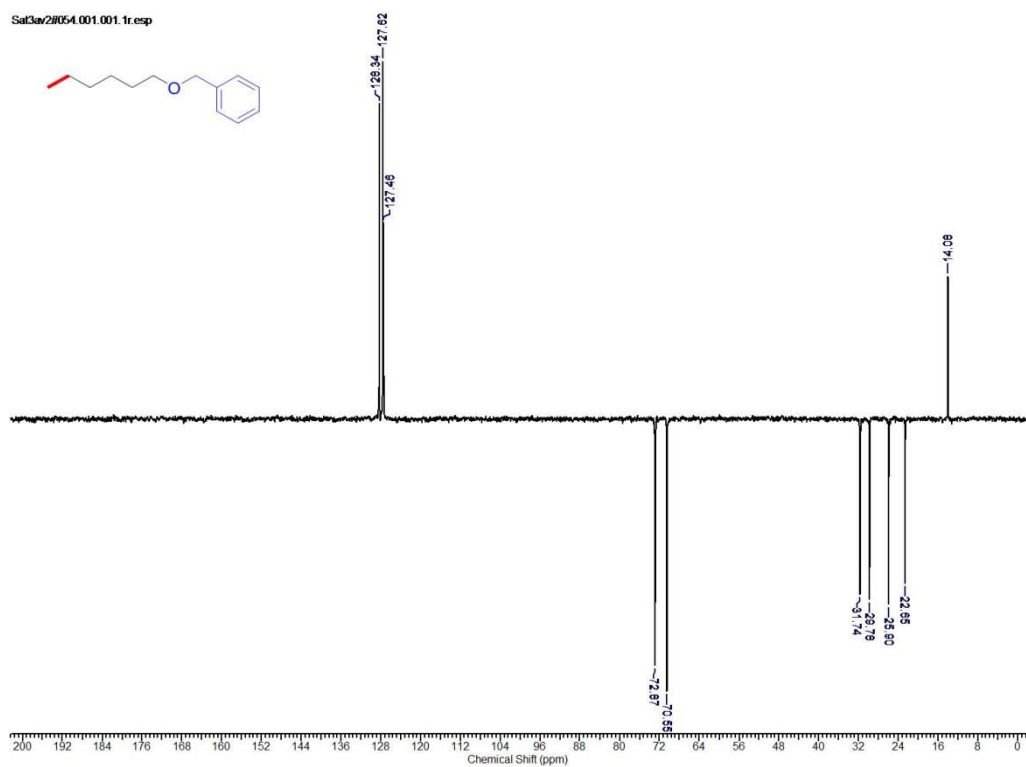


Figure ESI-10-4: DEPT spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-1, entry 2 (2b)

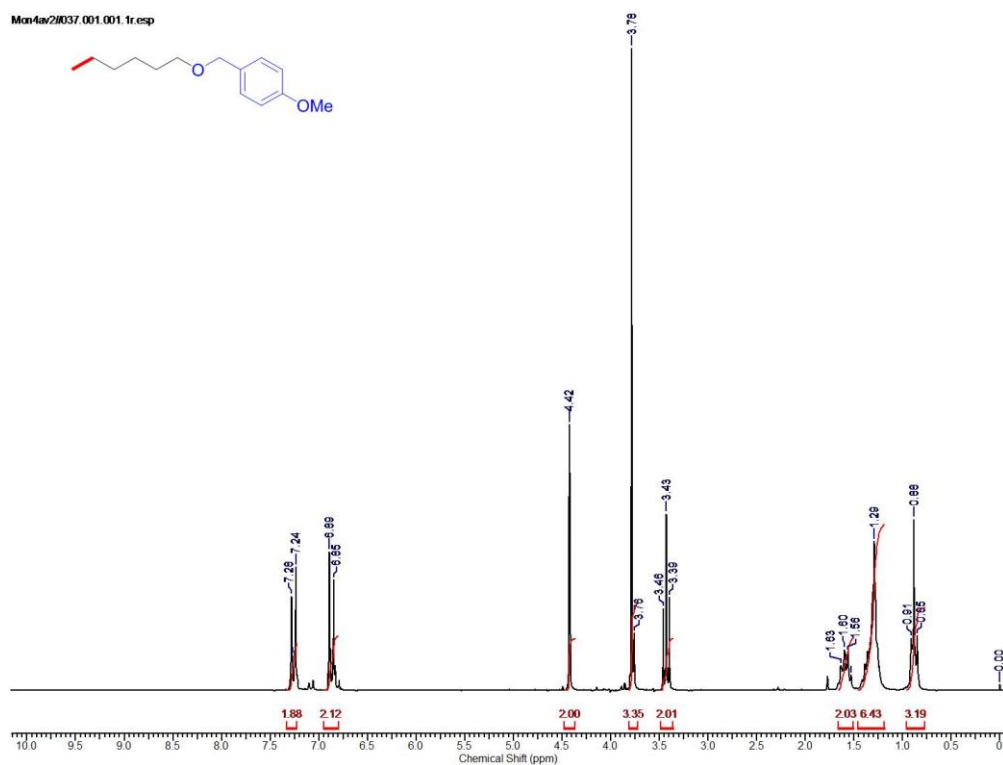


Figure ESI-10-5:  $^1\text{H}$  NMR of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-1, entry 3 (3b)

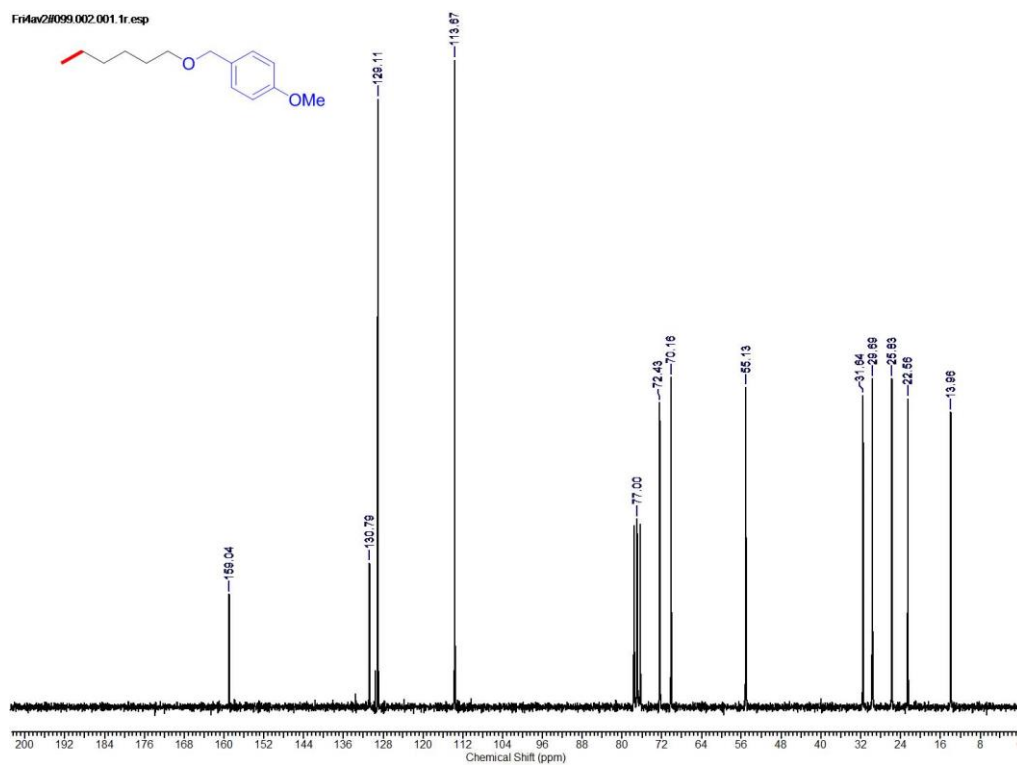


Figure ESI-10-6:  $^{13}\text{C}$  NMR of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-1, entry 3 (3b)



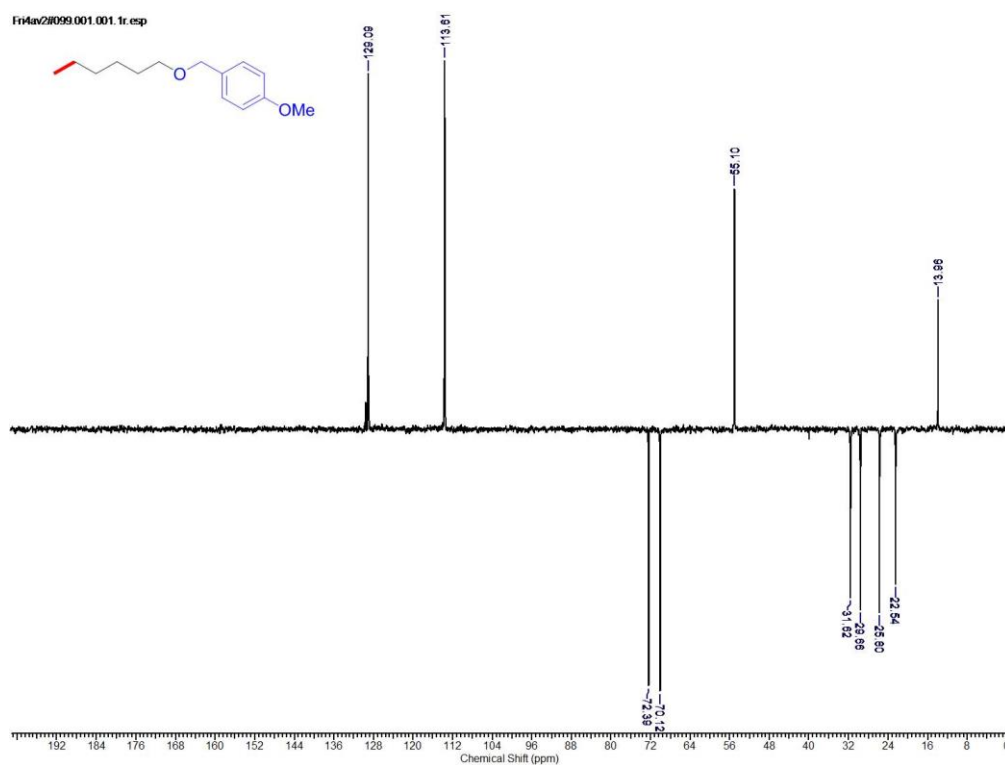


Figure ESI-10-7: DEPT spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-1, entry 3 (3b)

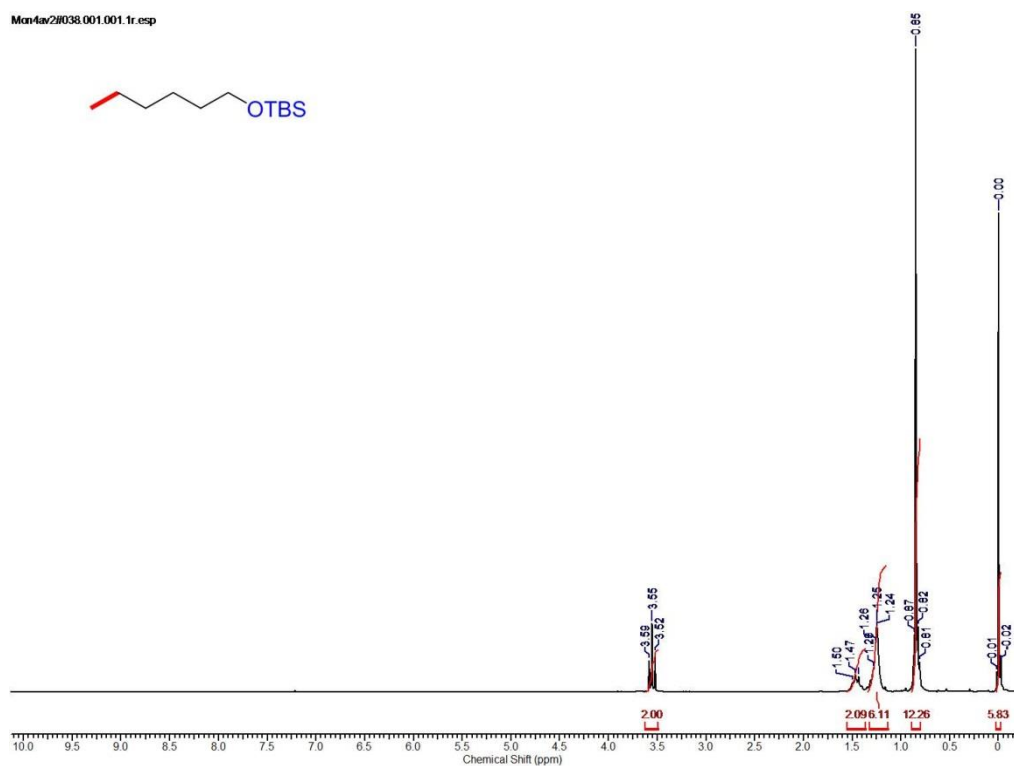


Figure ESI-10-8: <sup>1</sup>H NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-1, entry 4 (4b)

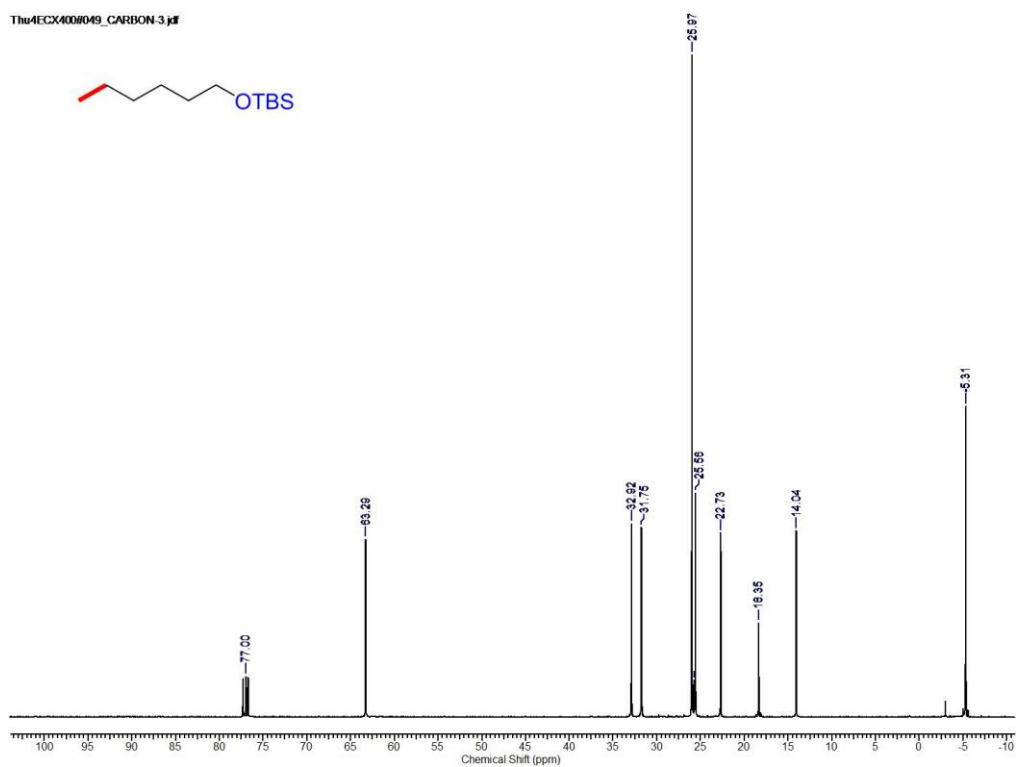


Figure ESI-10-9:  $^{13}\text{C}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-1, entry 4 (4b)

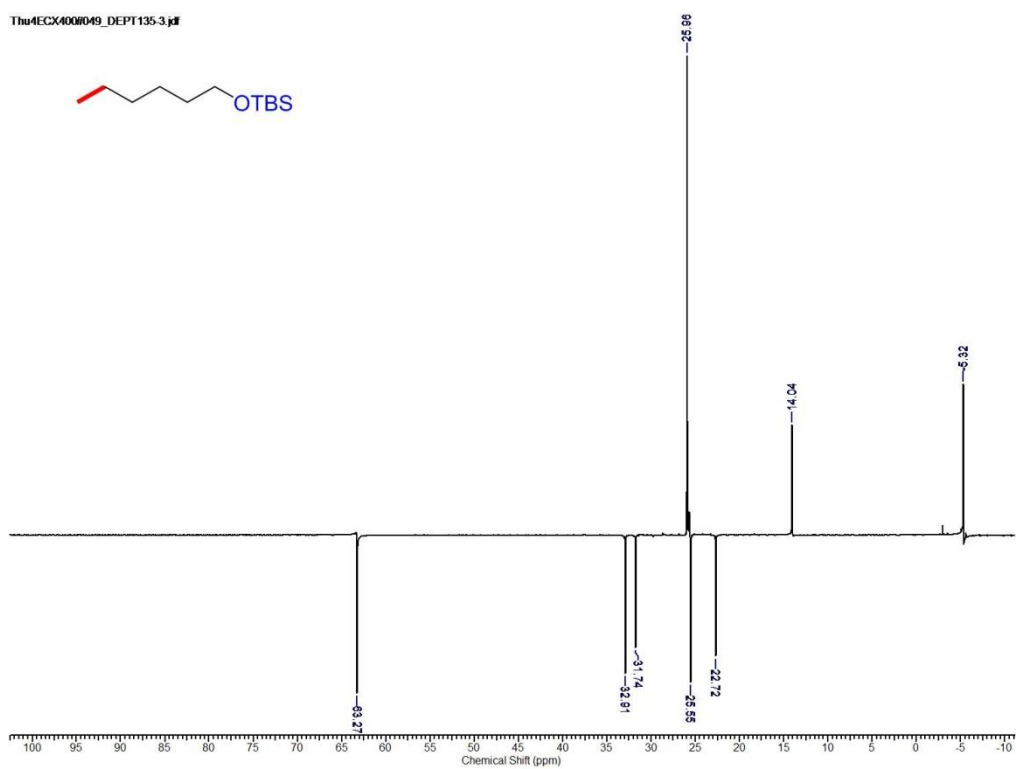


Figure ESI-10-10: DEPT spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-1, entry 4 (4b)

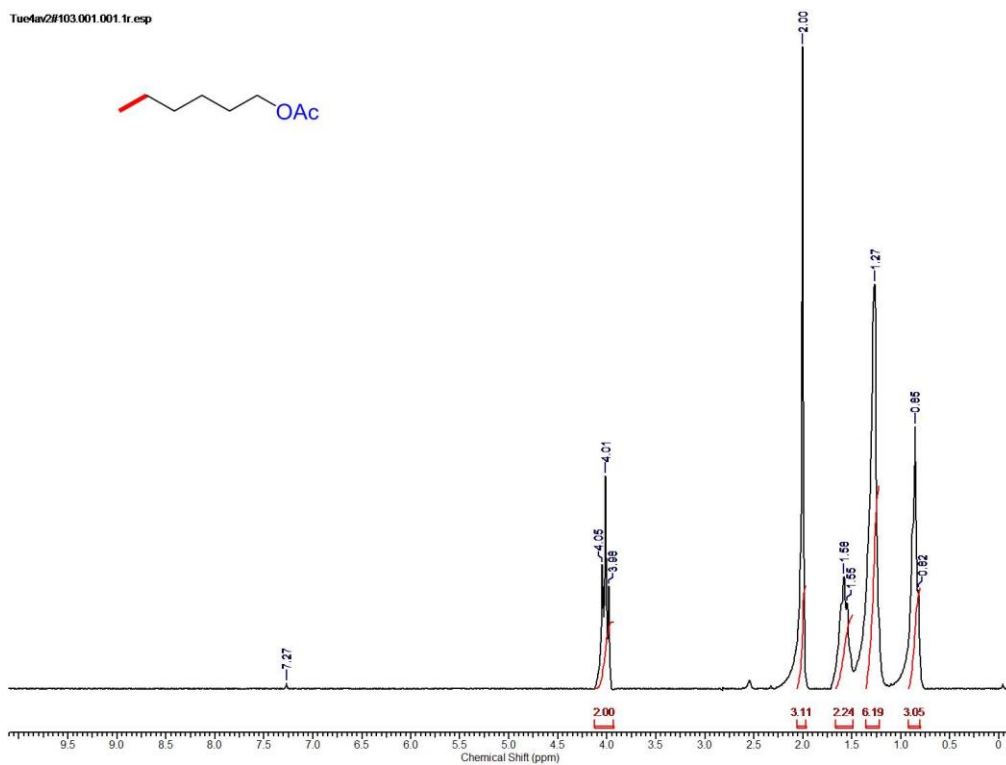


Figure ESI-10-11:  $^1\text{H}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-1, entry 5 (5b)

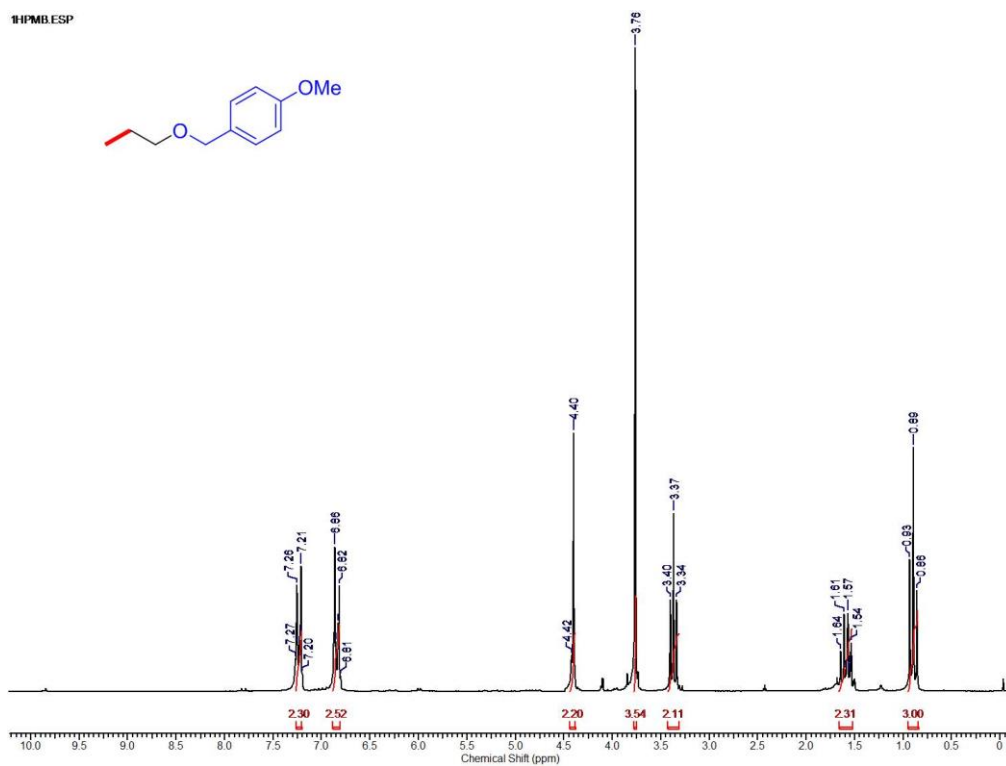


Figure ESI-10-12:  $^1\text{H}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-1, entry 6 (6b)

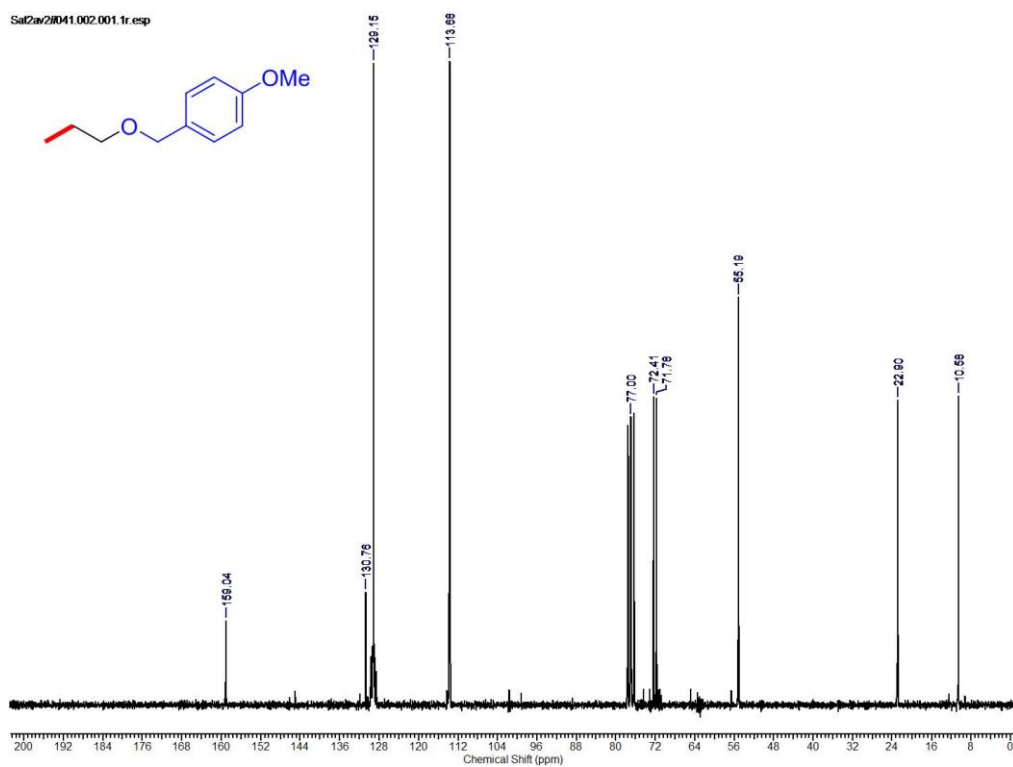


Figure ESI-10-13:  $^{13}\text{C}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-1, entry 6 (6b)

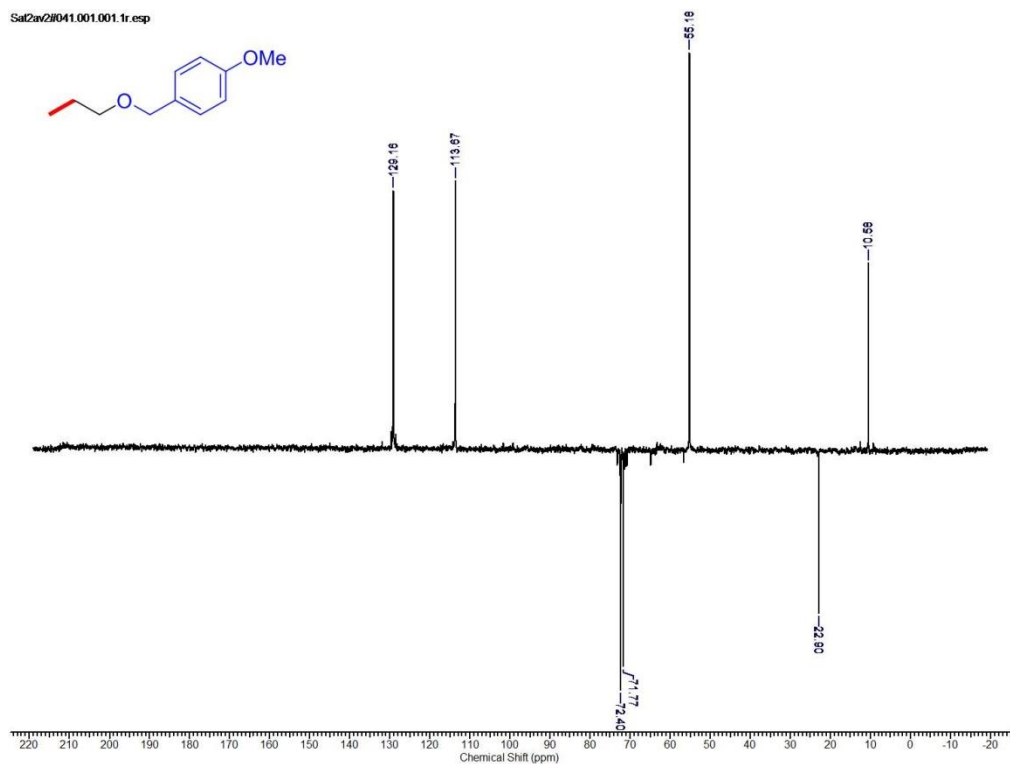


Figure ESI-10-14: DEPT NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-1, entry 6 (6b)

Mon4av2#091.001.001.1r-9-decand-H2-H.esp

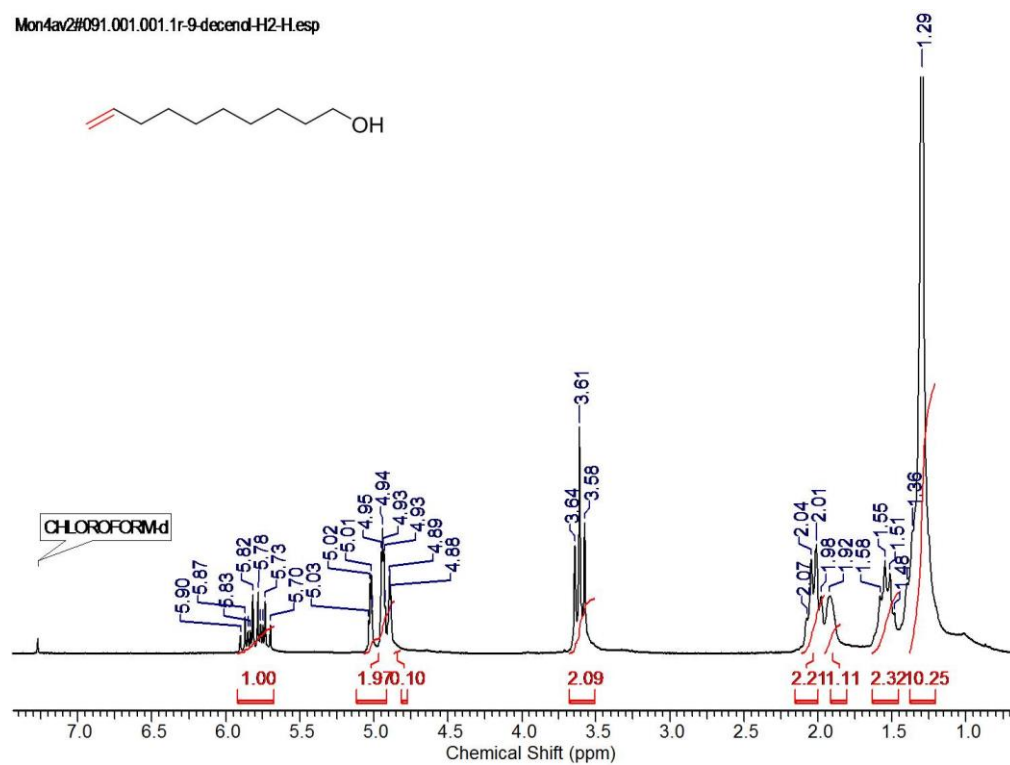


Figure ESI-10-15:  $^1\text{H}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-2, entry 7 (7b)

wed1av2#043.002.001.1r9-decand-H2-C.esp

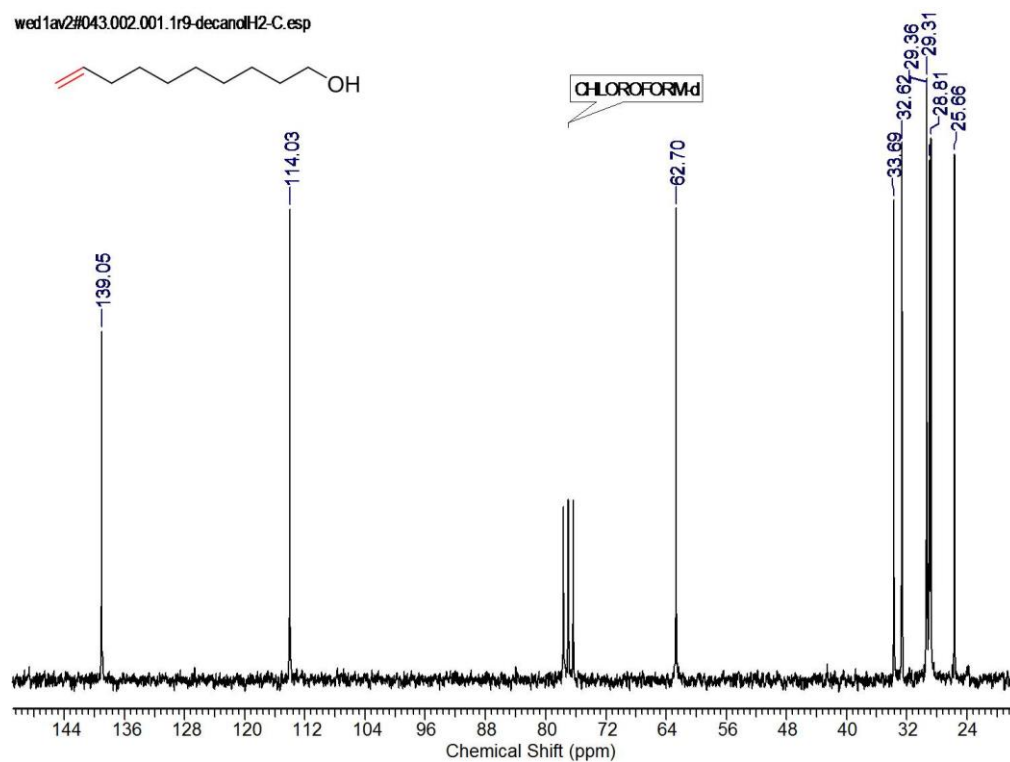


Figure ESI-10-16:  $^{13}\text{C}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-2, entry 78 (7b)

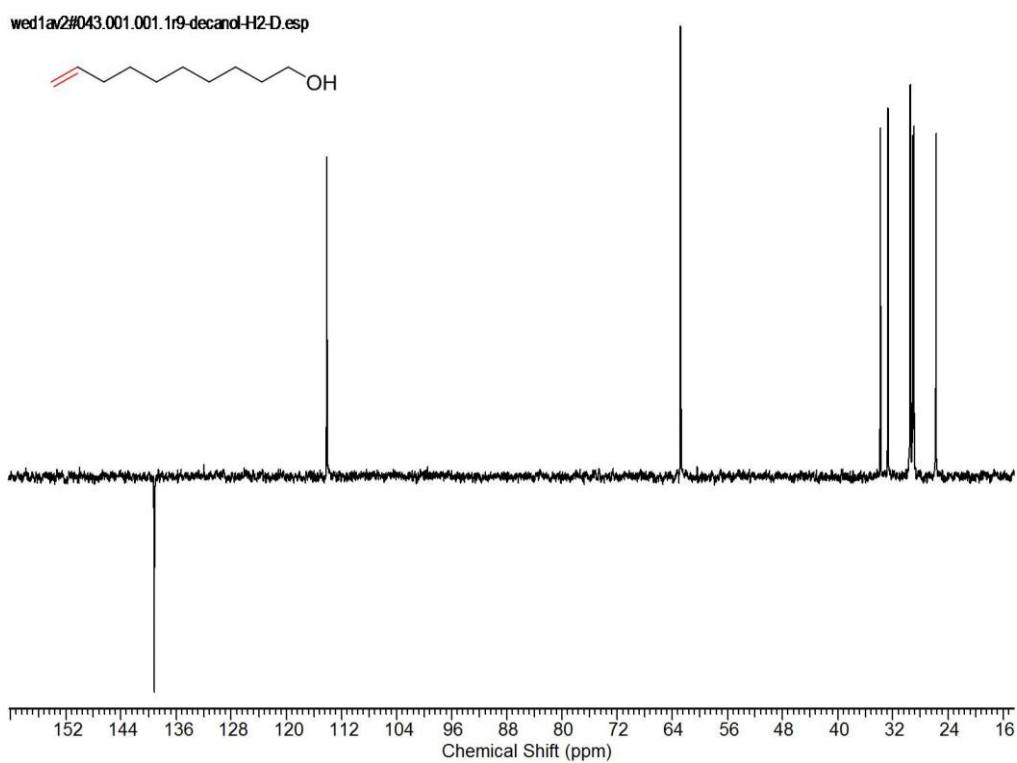


Figure ESI-10-17: DEPT spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-2, entry 7 (7b)

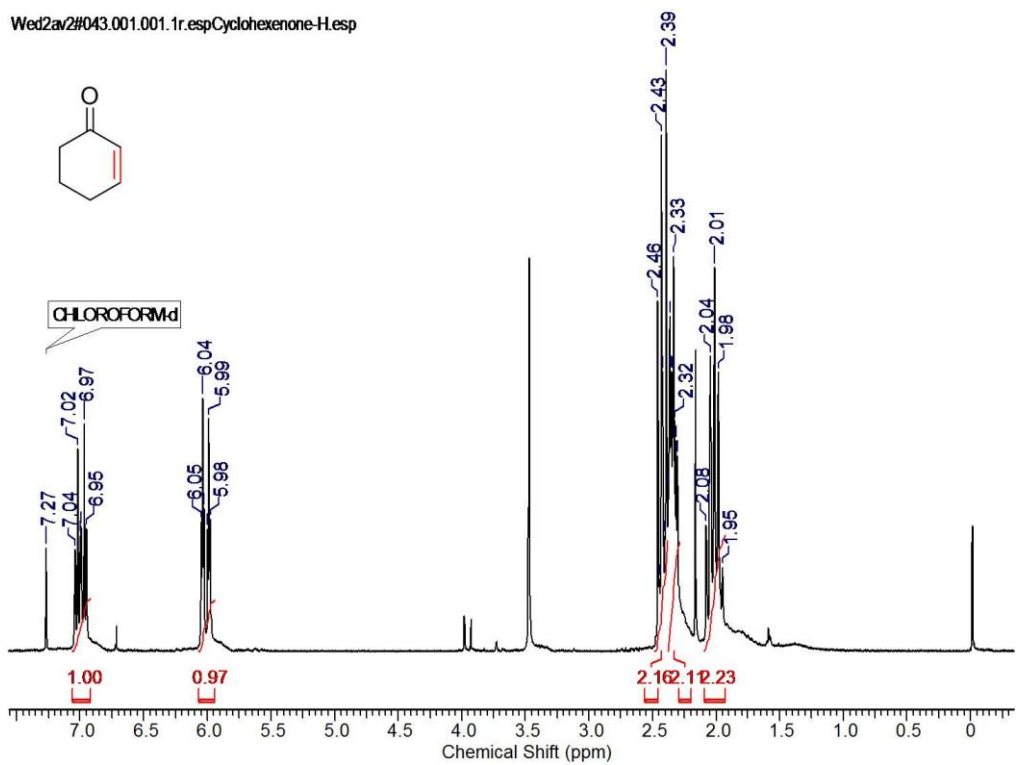


Figure ESI-10-18:  $^1\text{H}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-2, entry 8 (8b)

Wed2av2#124.002.001.1r.espCyclohexenone-C.esp

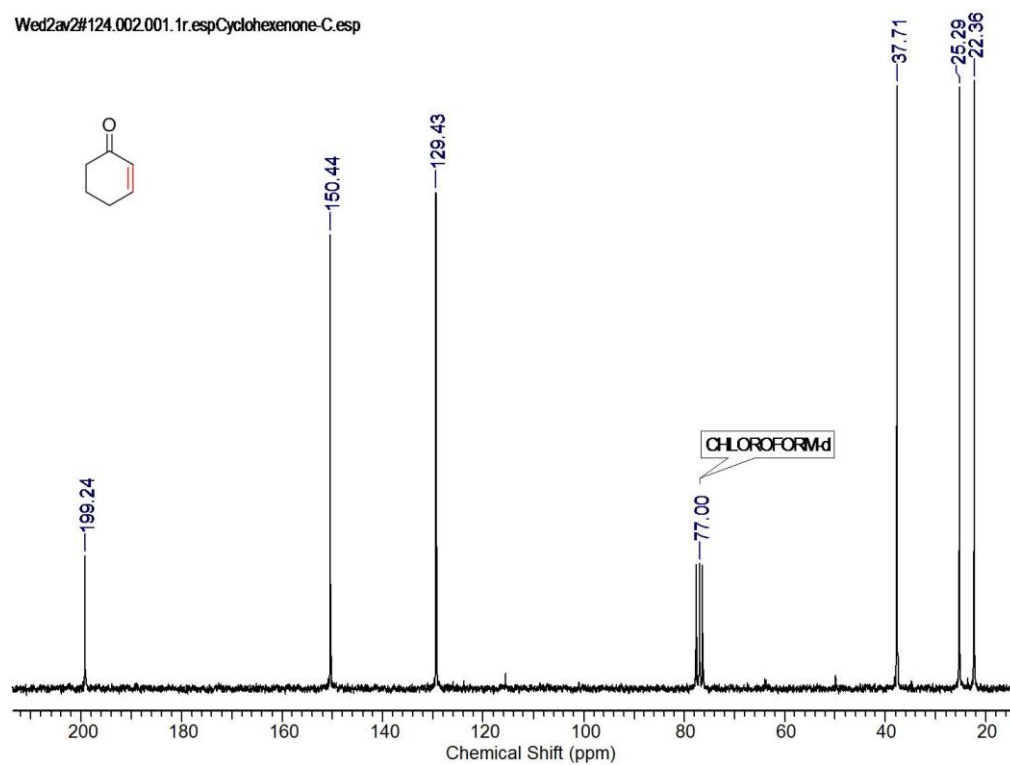


Figure ESI-10-19: <sup>13</sup>C NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles Table 2\_Set-2, entry 8 (8b)

Wed2av2#124.001.001.1r.espCyclohexenone-D.esp

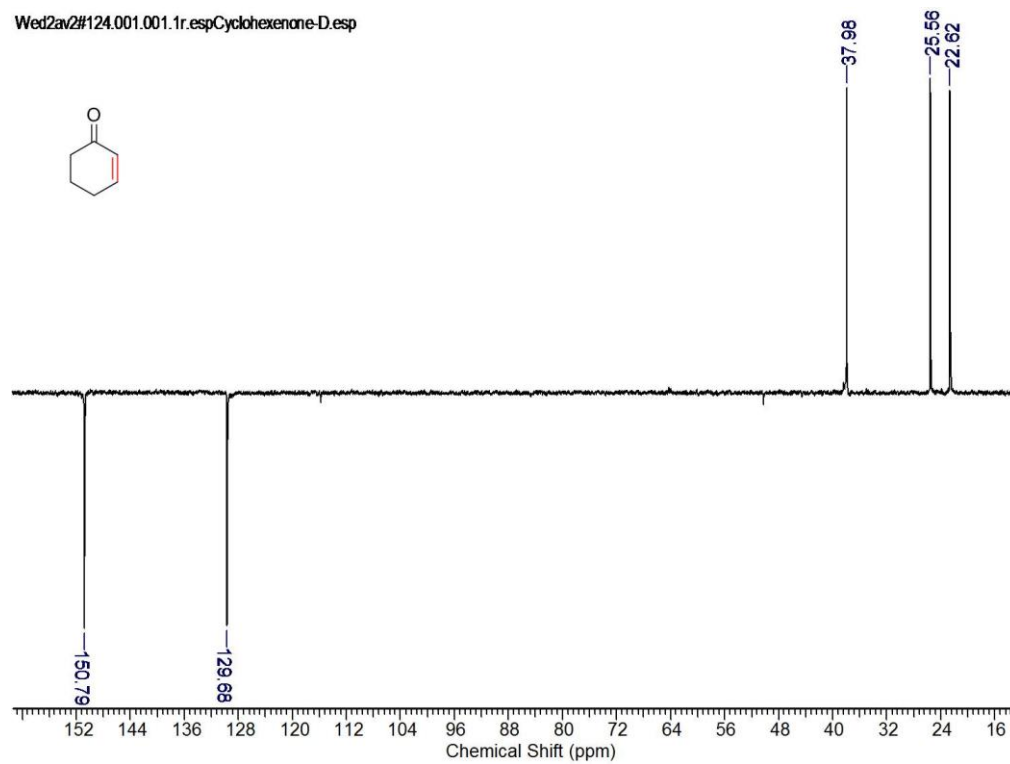


Figure ESI-10-20: DEPT spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-2, entry 8 (8b)

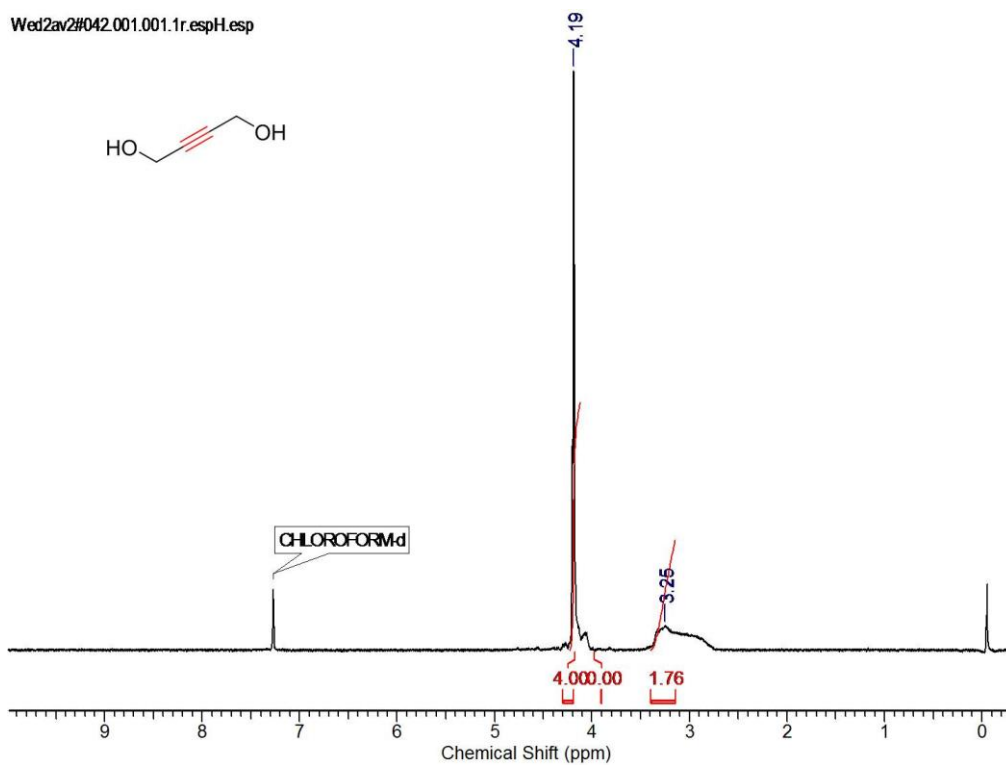


Figure ESI-10-21:  $^1\text{H}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-2, entry 9 (9b)

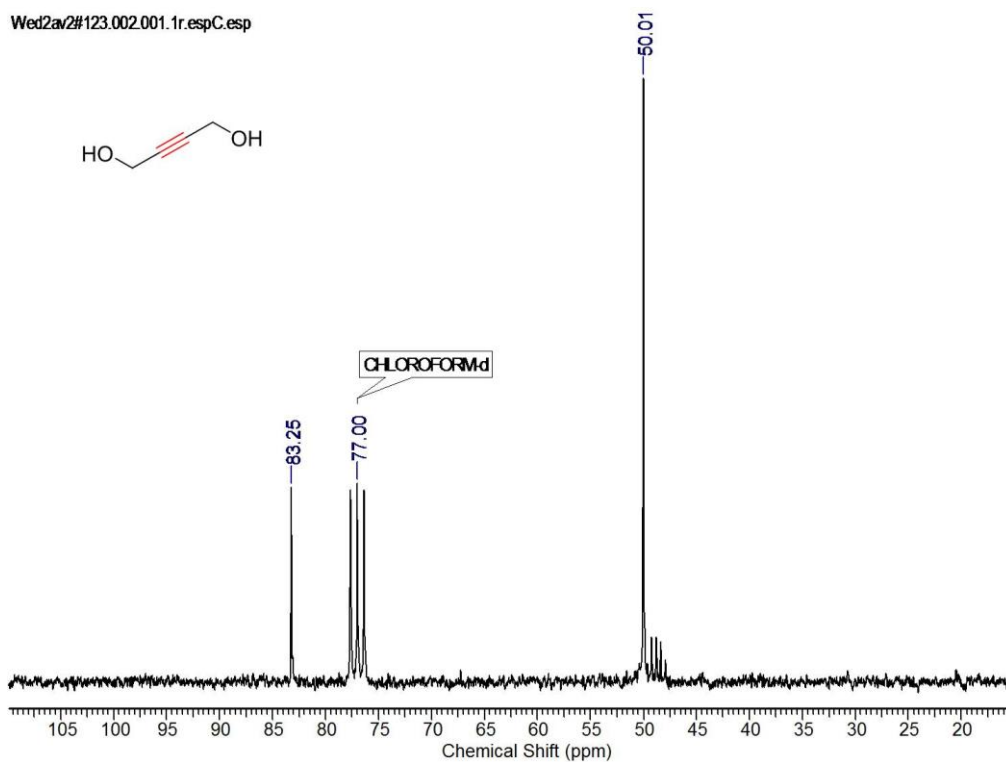


Figure ESI-10-22:  $^{13}\text{C}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-2, entry 9 (9b)



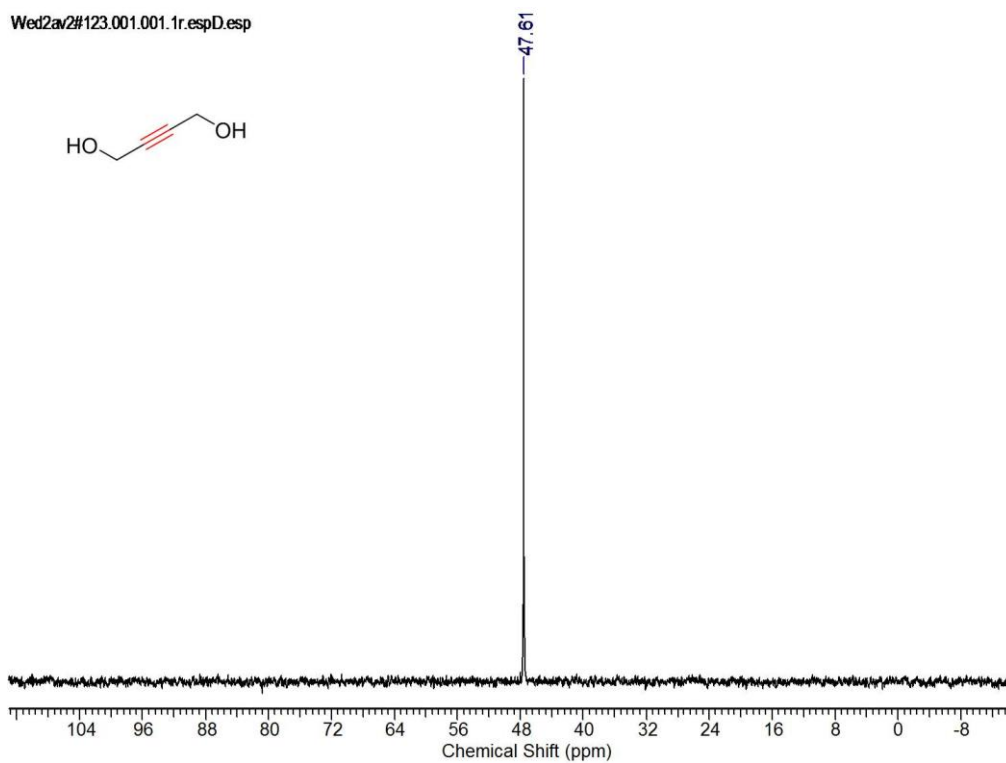


Figure ESI-10-23: DEPT spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-2, entry 9 (9b)

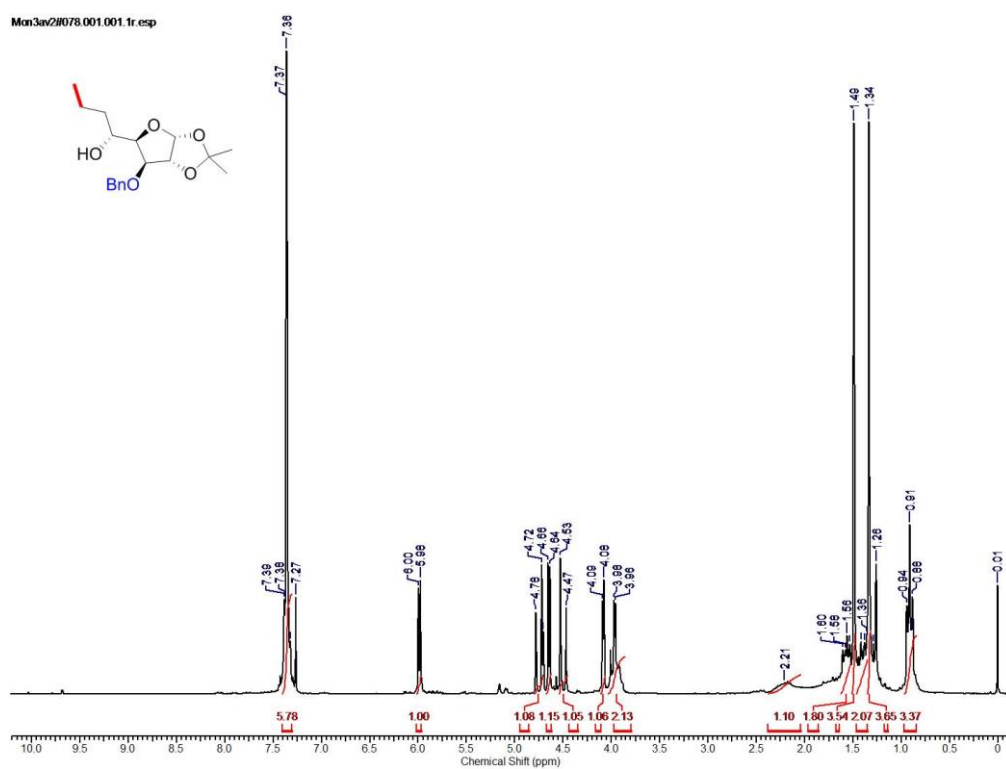


Figure ESI-10-24:  $^1\text{H}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-3, entry 10 (10b)

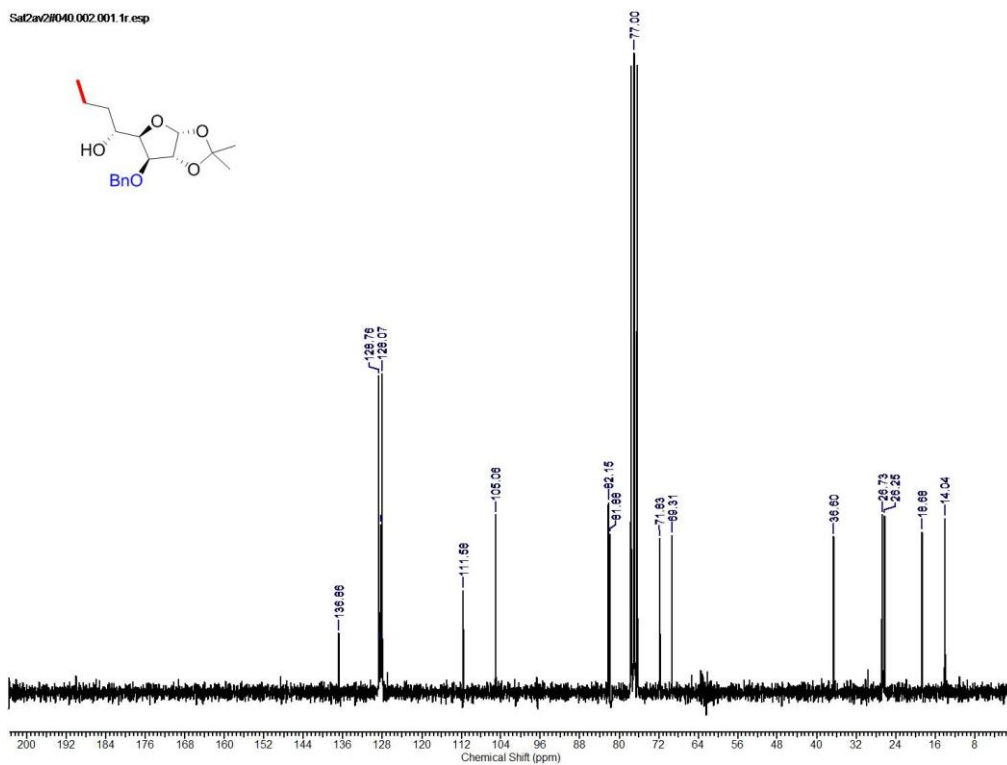


Figure ESI-10-25:  $^{13}\text{C}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_ Set-3, entry 10 (10b)

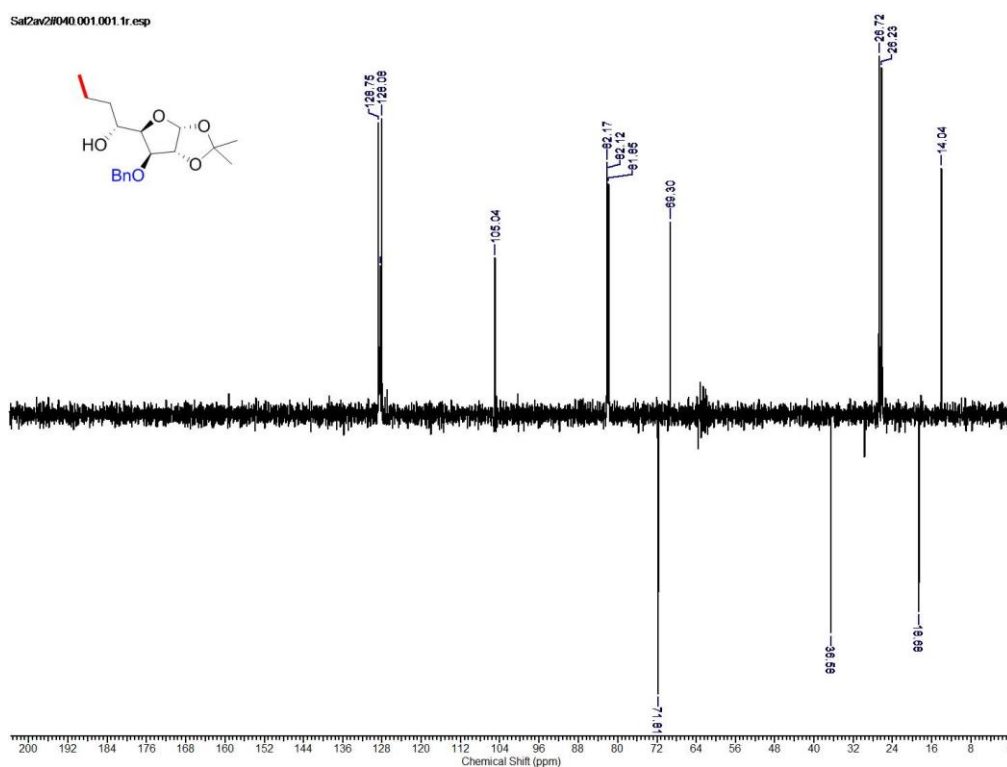


Figure ESI-10-26: DEPT spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_ Set-3, entry 10 (10b)

Wed2av2#019.001.001.1GDA-4inv-nor-otbs-H2-H.esp

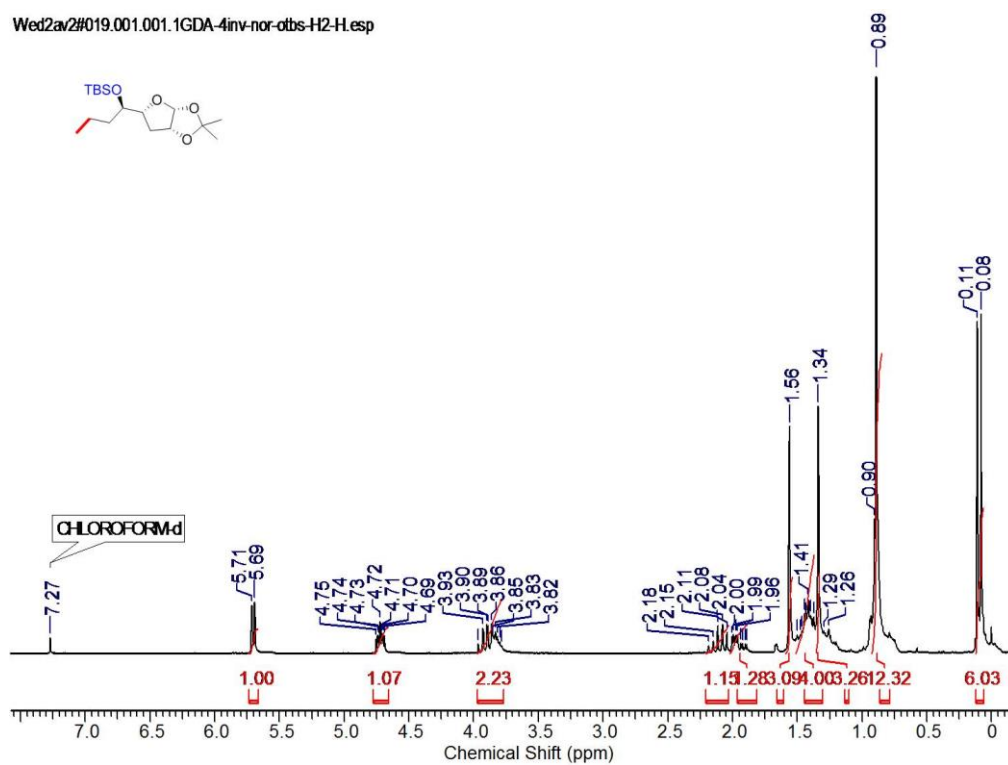


Figure ESI-10-27:  $^1\text{H}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-3, entry 11 (11b)

Wed2av2#021.001.001.1rGDA-nor-acetylene-OTBS-C.esp

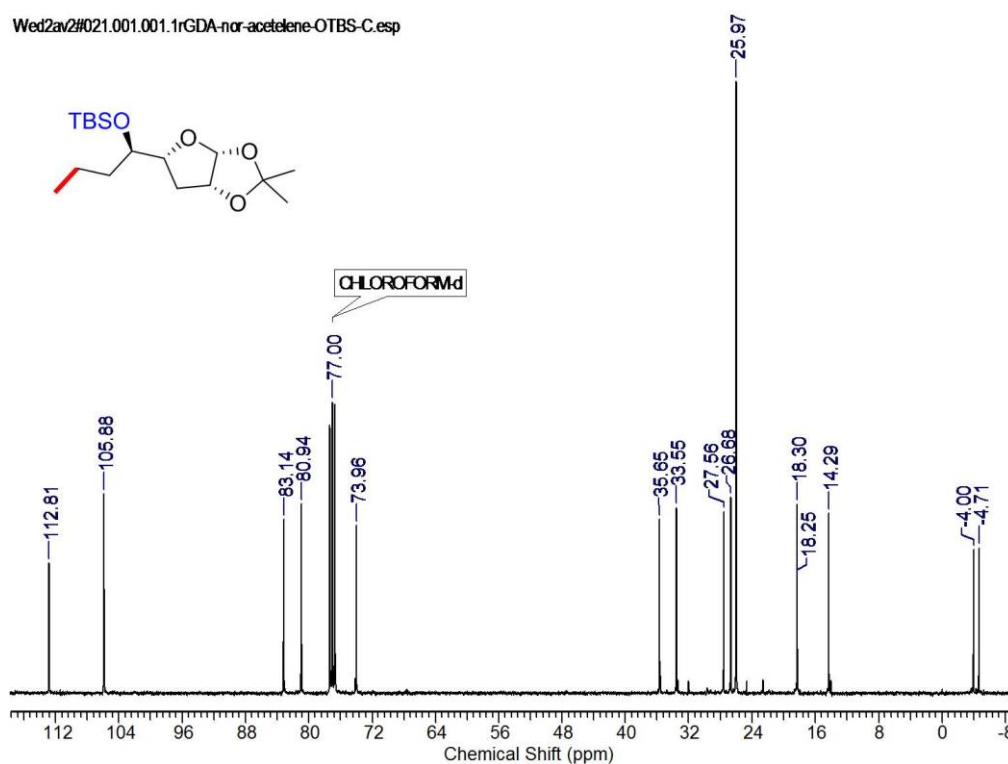


Figure ESI-10-28:  $^{13}\text{C}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-3, entry 11 (11b)

Sat2ECX400#023\_DEPT135-3.espGDA-nor-acetylene-OTBS-D.esp

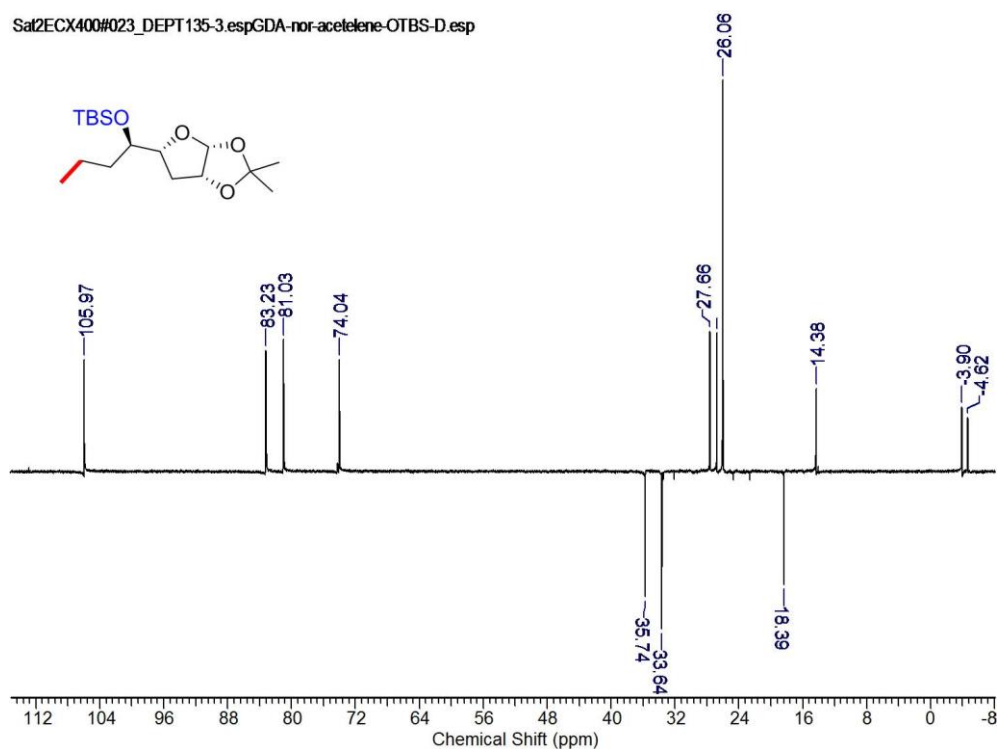


Figure ESI-10-29: DEPT spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-3, entry 11 (11b)

Fri2av500#001.001.001.1rGDA-diyne-H2-H.esp

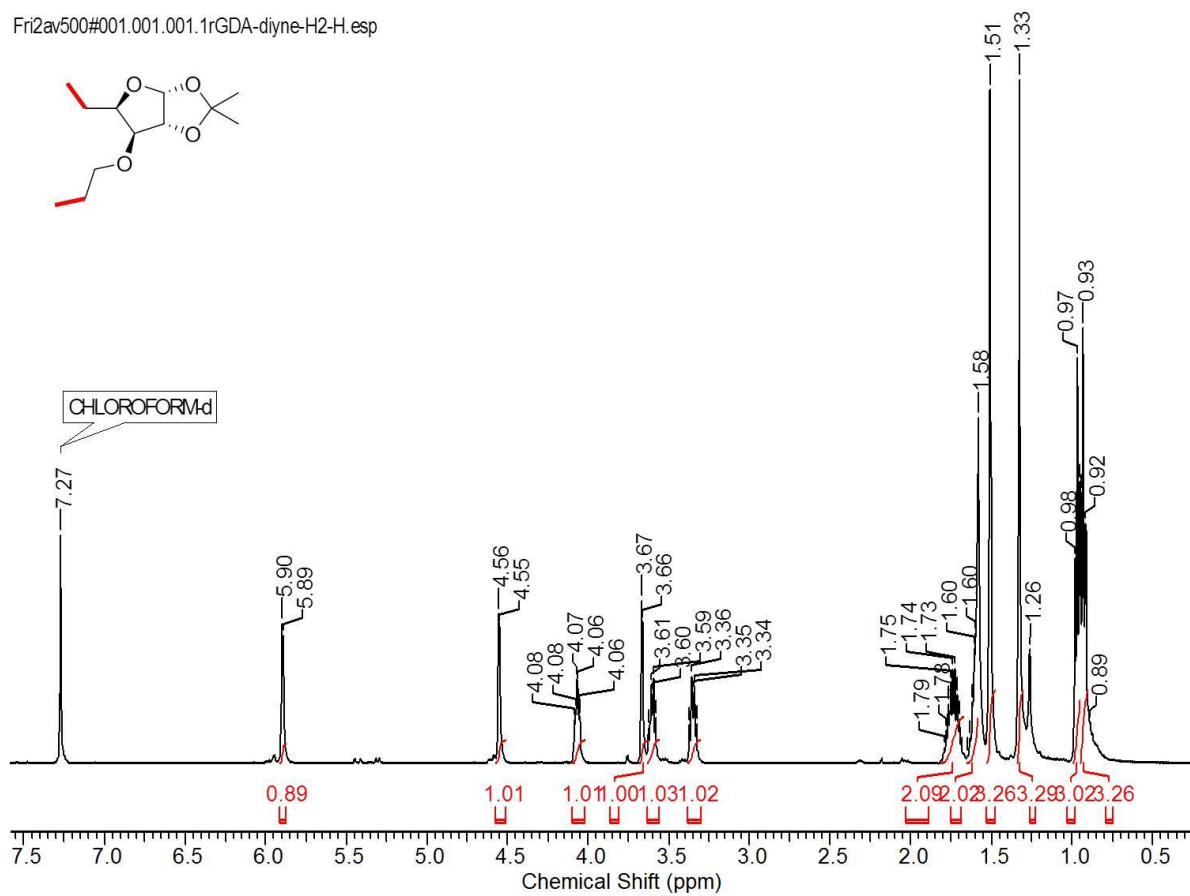


Figure ESI-10-30: <sup>1</sup>H spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-3, entry 12 (12b)

Fri2av500#001.003.001.1rGDA-diyne-H2-C.esp

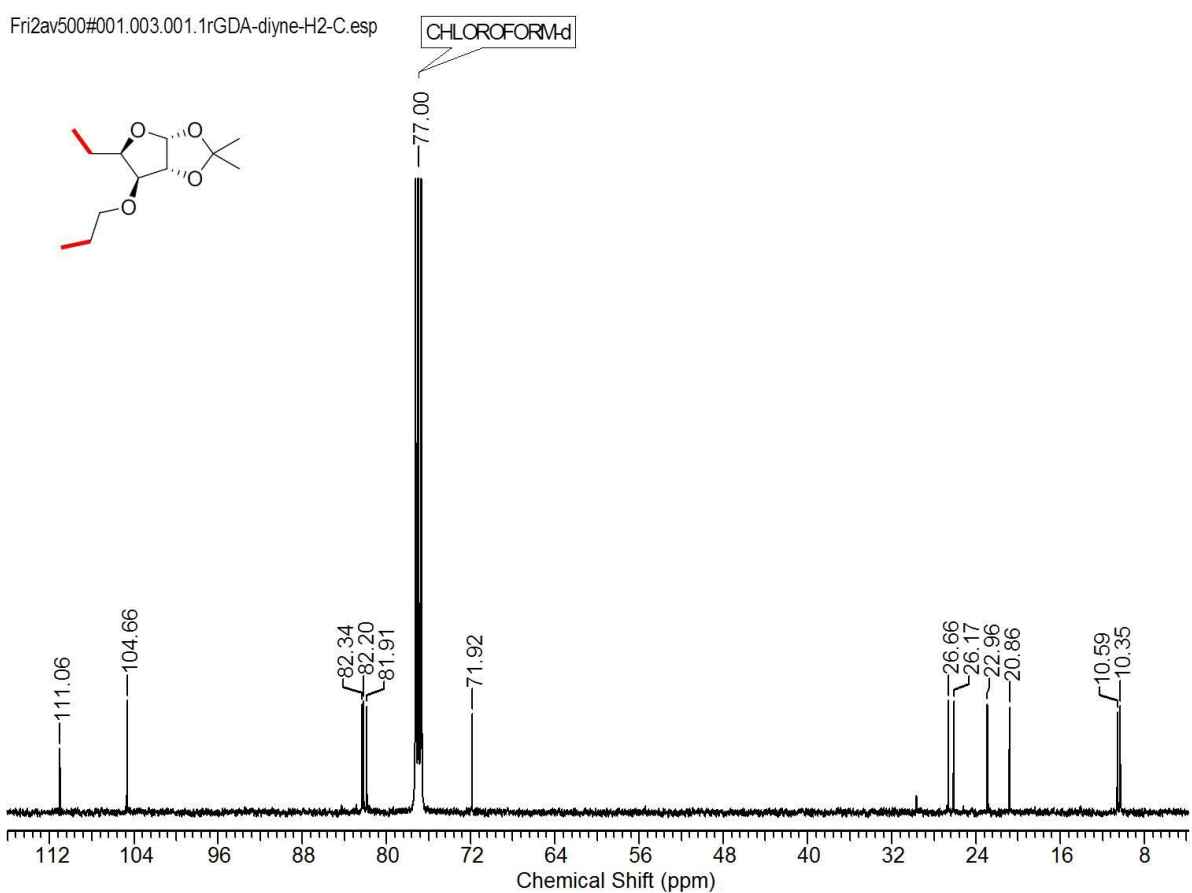


Figure ESI-10-31:  $^{13}\text{C}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-3, entry 12 (12b)

Fri2av500#001.002.001.1rGDA-diyne-H2-C.esp

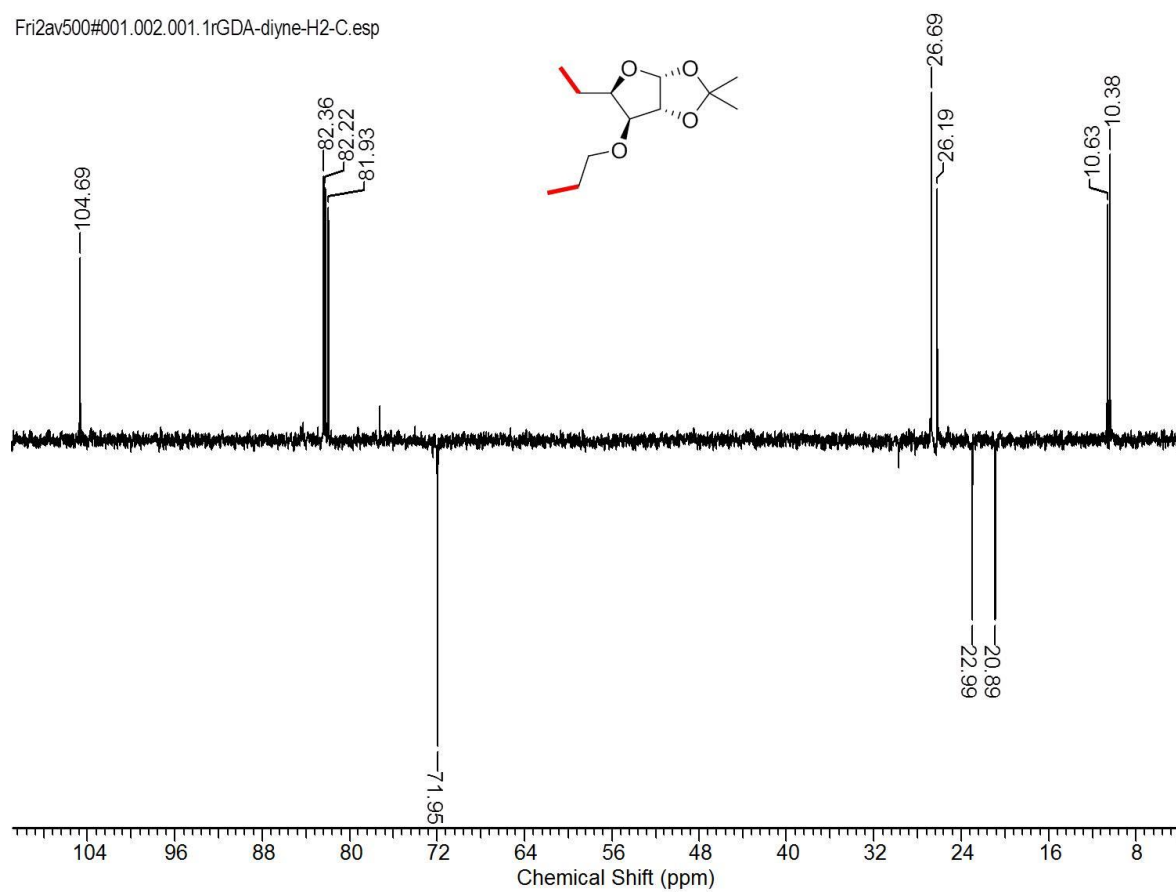


Figure ESI-10-32: DEPT spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-3, entry 12 (12b)

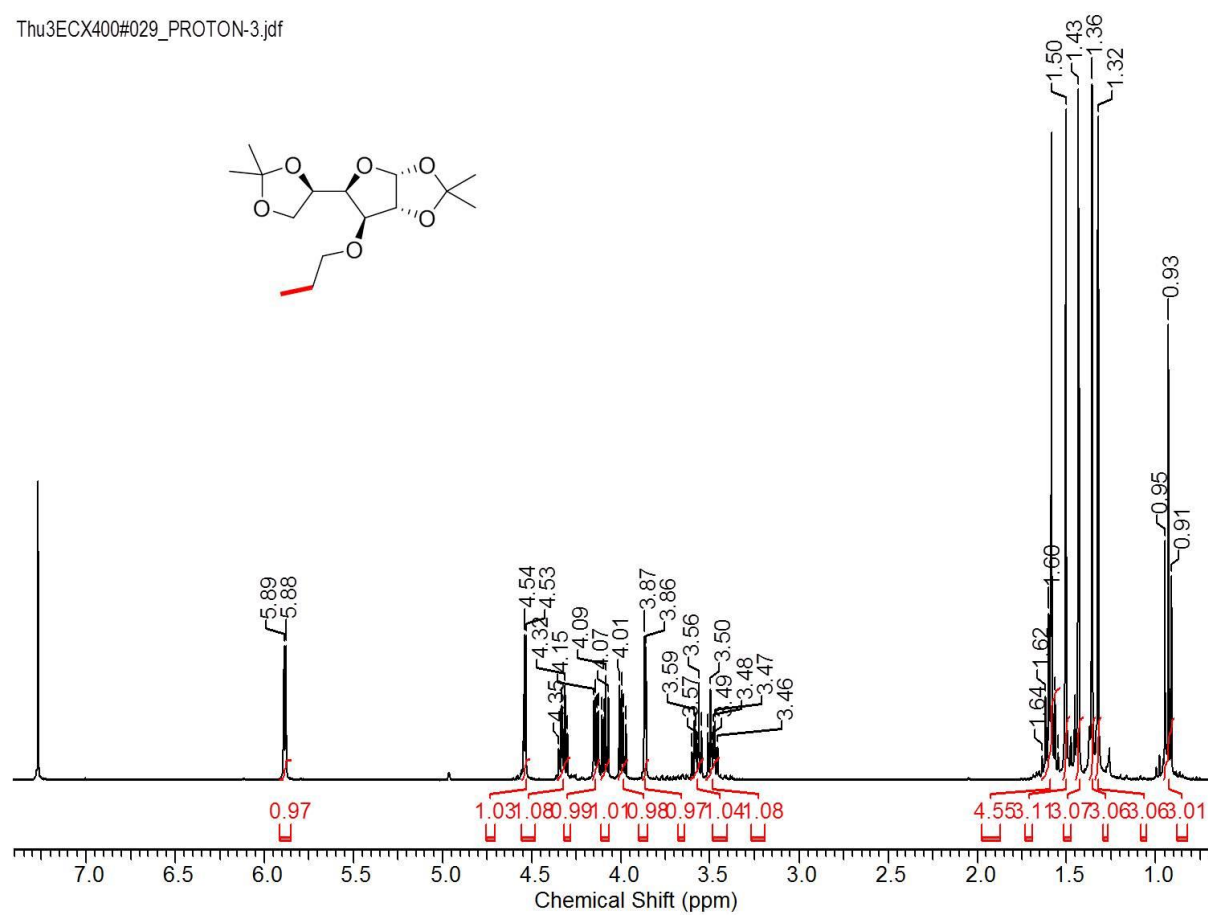


Figure ESI-10-33:  $^1\text{H}$  spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-3, entry 13 (13b)

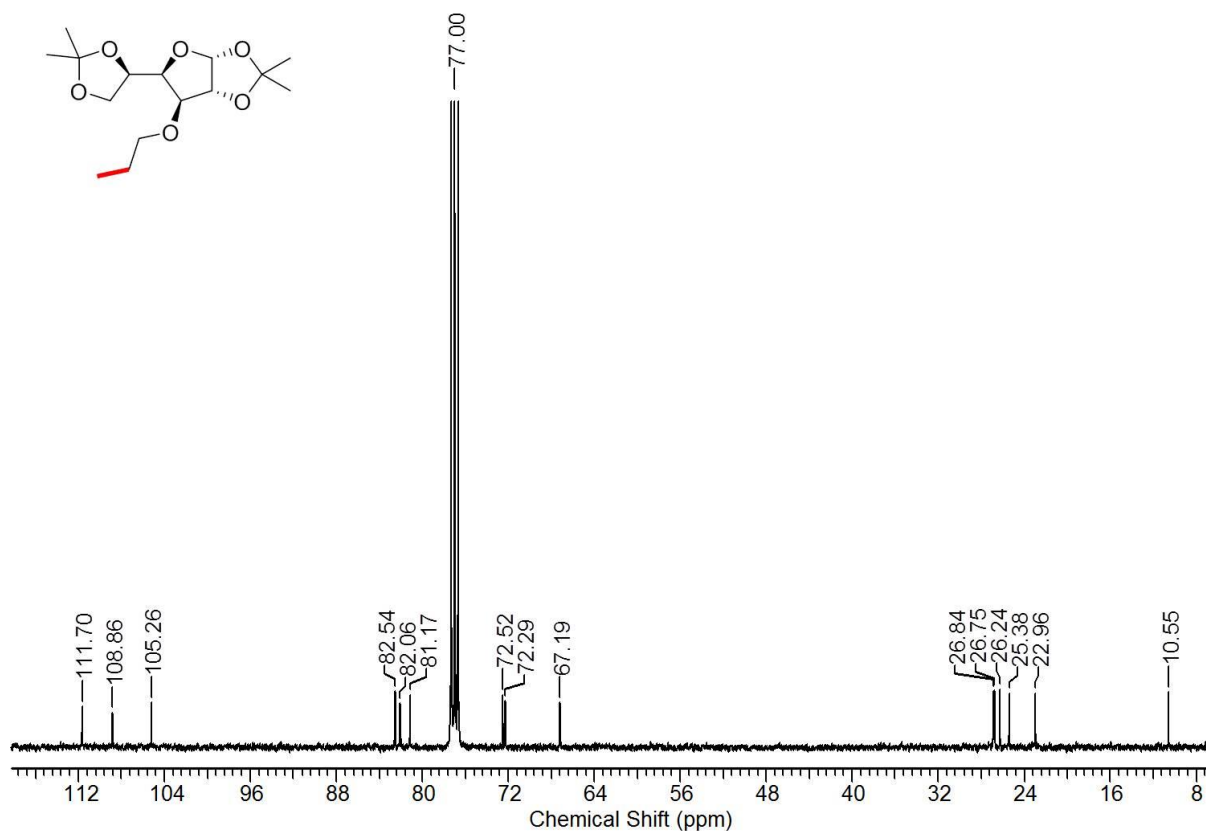
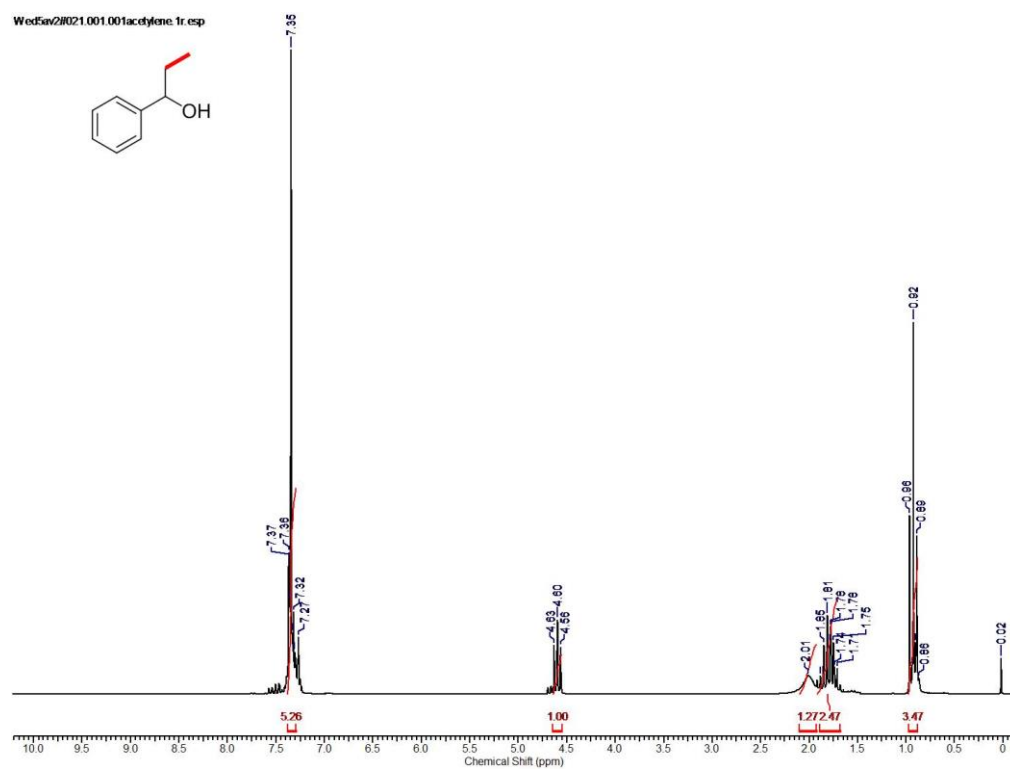
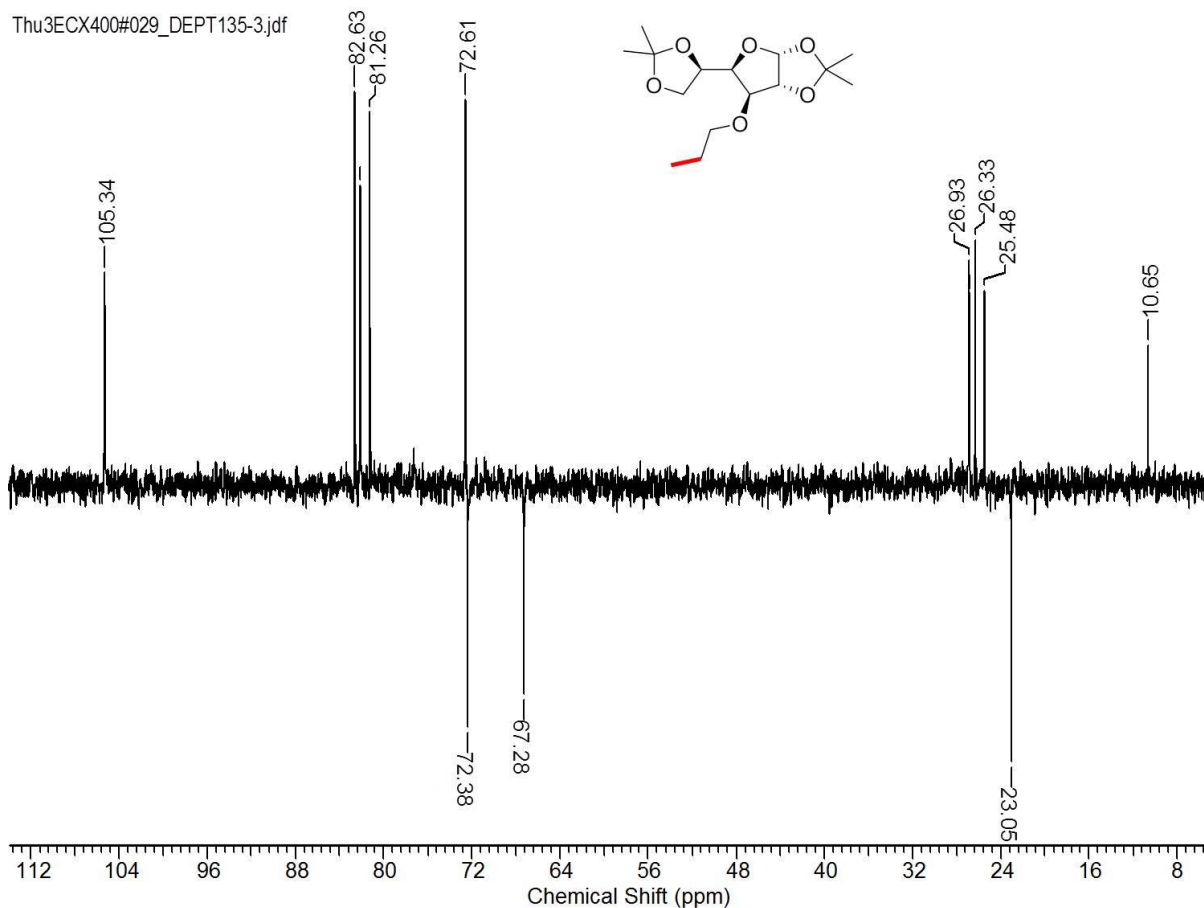


Figure ESI-10-34: <sup>13</sup>C NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Table 2\_Set-3, entry 13 (13b)





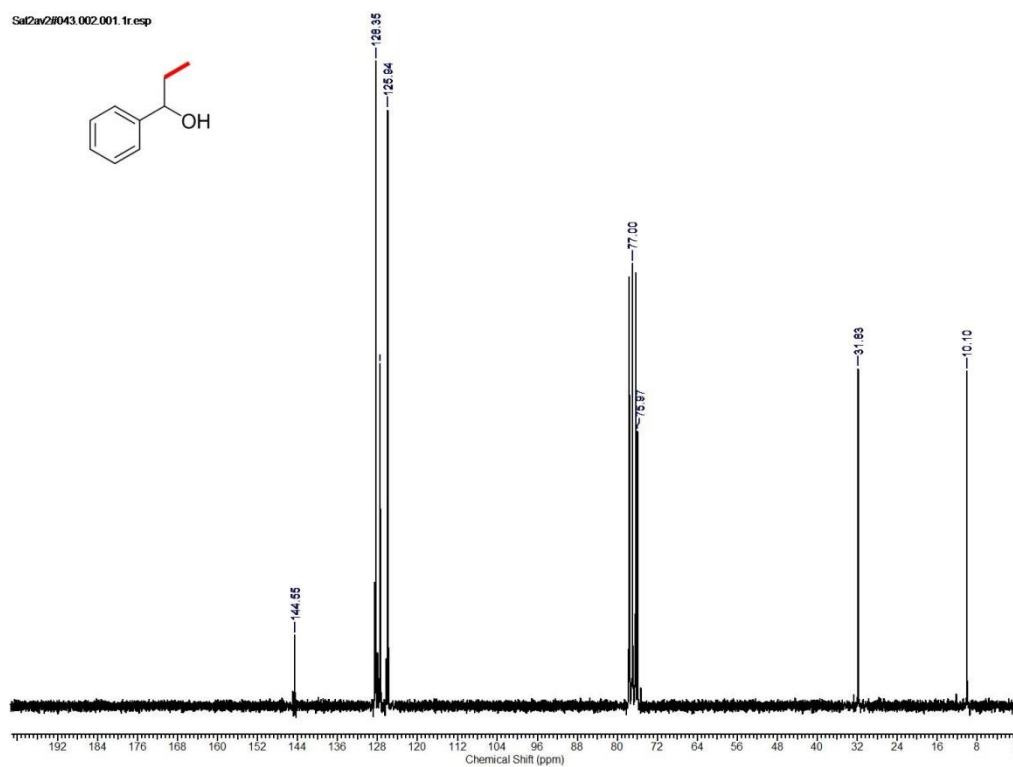


Figure ESI-10-37:  $^{13}\text{C}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-4, entry 14 (14b)

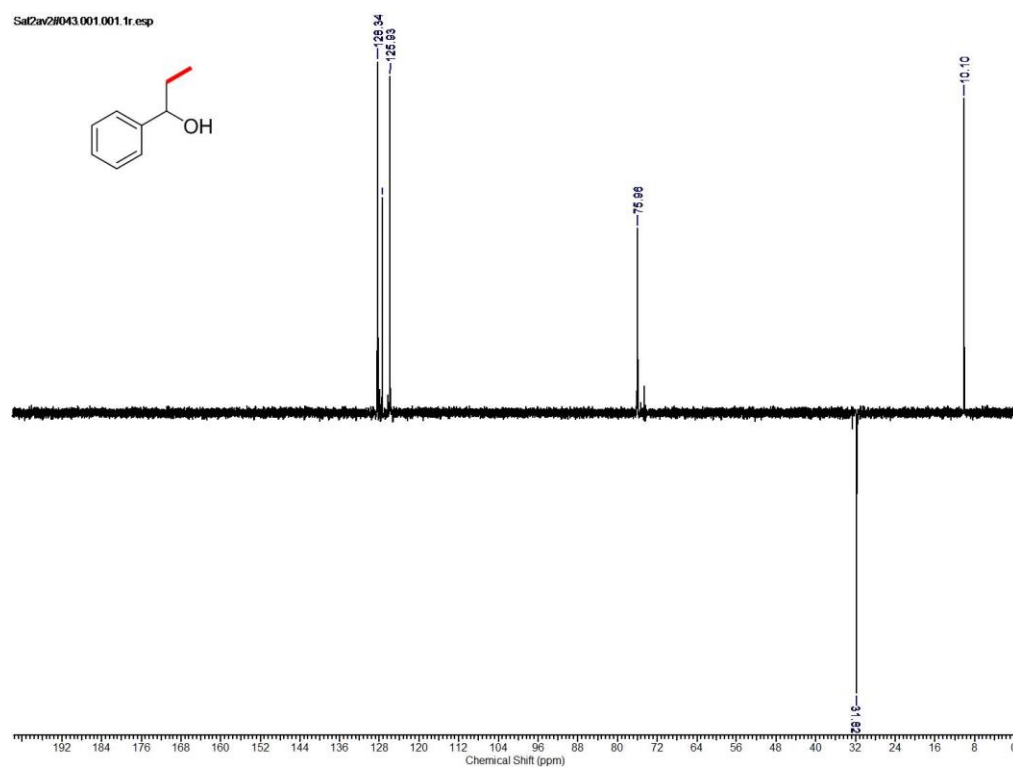


Figure ESI-10-38: DEPT spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-3, entry 14 (14b)

<b>Acquisition Time (sec)</b>	2.1838	<b>Comment</b>	KCB	<b>Date</b>	10 Sep 2014 18:10:56
<b>Date Stamp</b>	10 Sep 2014 08:32:54	<b>File Name</b>	\\aghi\nmr_data\JEOL_400\2014\Sep 2014\Tue2ECX400#036_PROTON-3.pdf		
<b>Frequency (MHz)</b>	399.78	<b>Nucleus</b>	<sup>1</sup> H	<b>Number of Transients</b>	16
				<b>Origin</b>	ECX 400

Tue2ECX400#036\_PROTON-3.esp

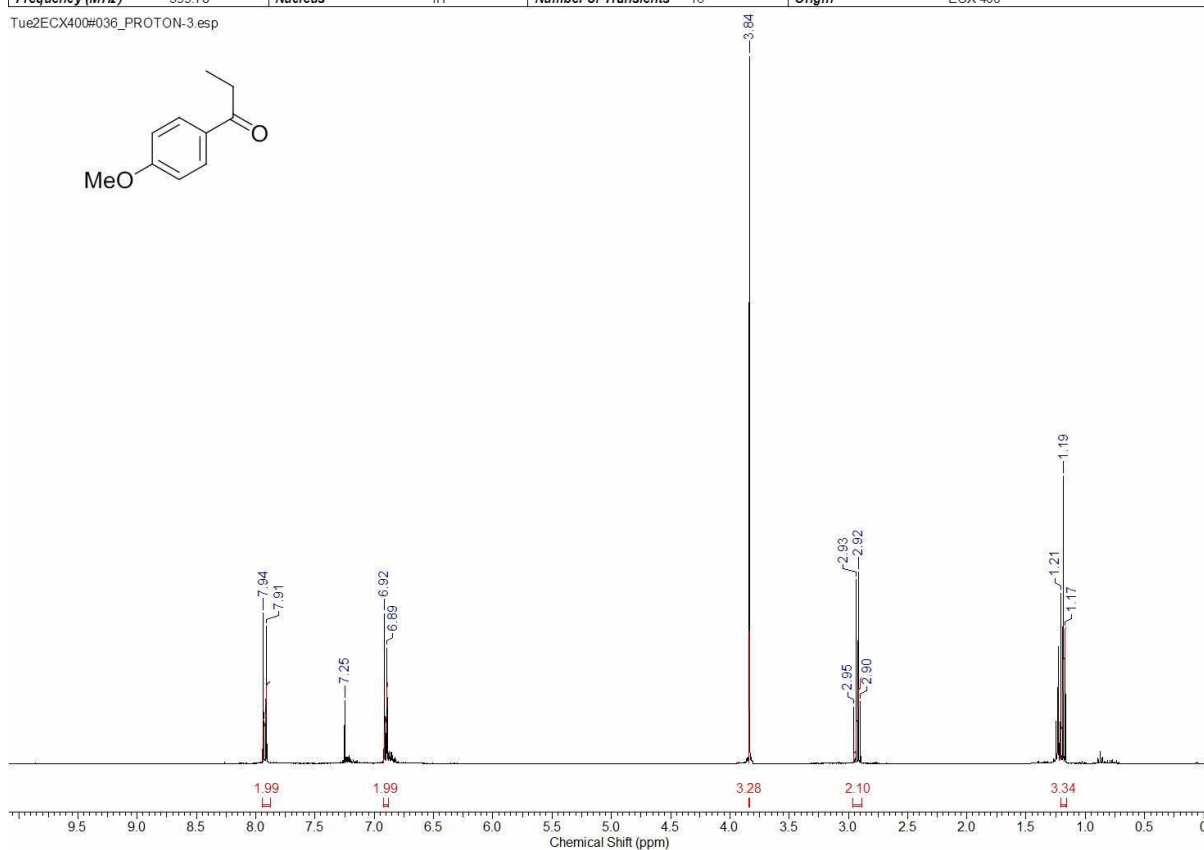


Figure ESI-10-39: <sup>1</sup>H NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-4, entry 15 (15b)

Acquisition Time (sec)	0.6832	Comment	KCB	Date	14 Sep 2014 18:20:56
Date Stamp	14 Sep 2014 18:20:56			Frequency (MHz)	50.32
Nucleus	<sup>13</sup> C	Number of Transients	600	Origin	av200
				Original Points Count	8192

Sat2av2#127.002.001.1r.esp

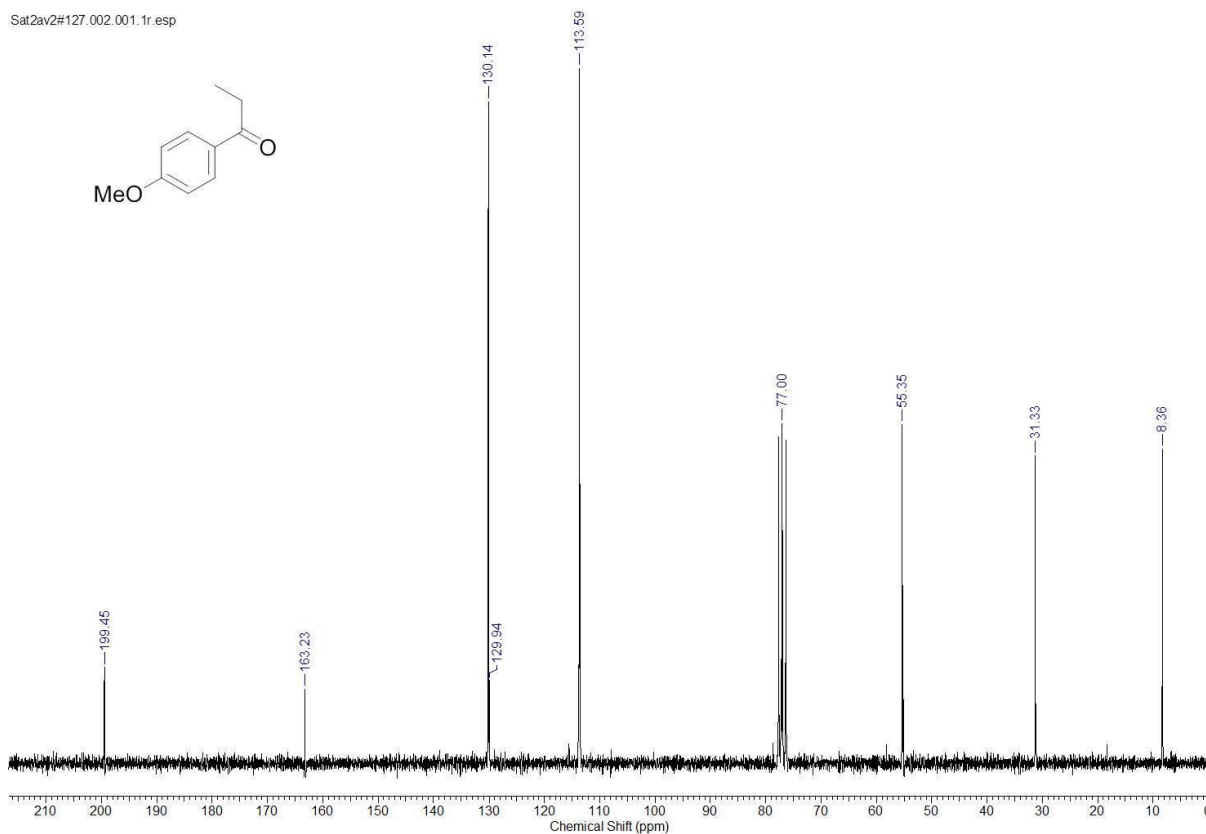


Figure ESI-10-40: <sup>13</sup>C NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-4, entry 15 (15b)

Acquisition Time (sec)	0.6832	Comment	KCB	Date	14 Sep 2014 17:51:04
Date Stamp	14 Sep 2014 17:51:04	Frequency (MHz)	50.32		
Nucleus	13C	Number of Transients	300	Origin	av200
				Original Points Count	8192

Sat2av2#127.001.001.1r.esp

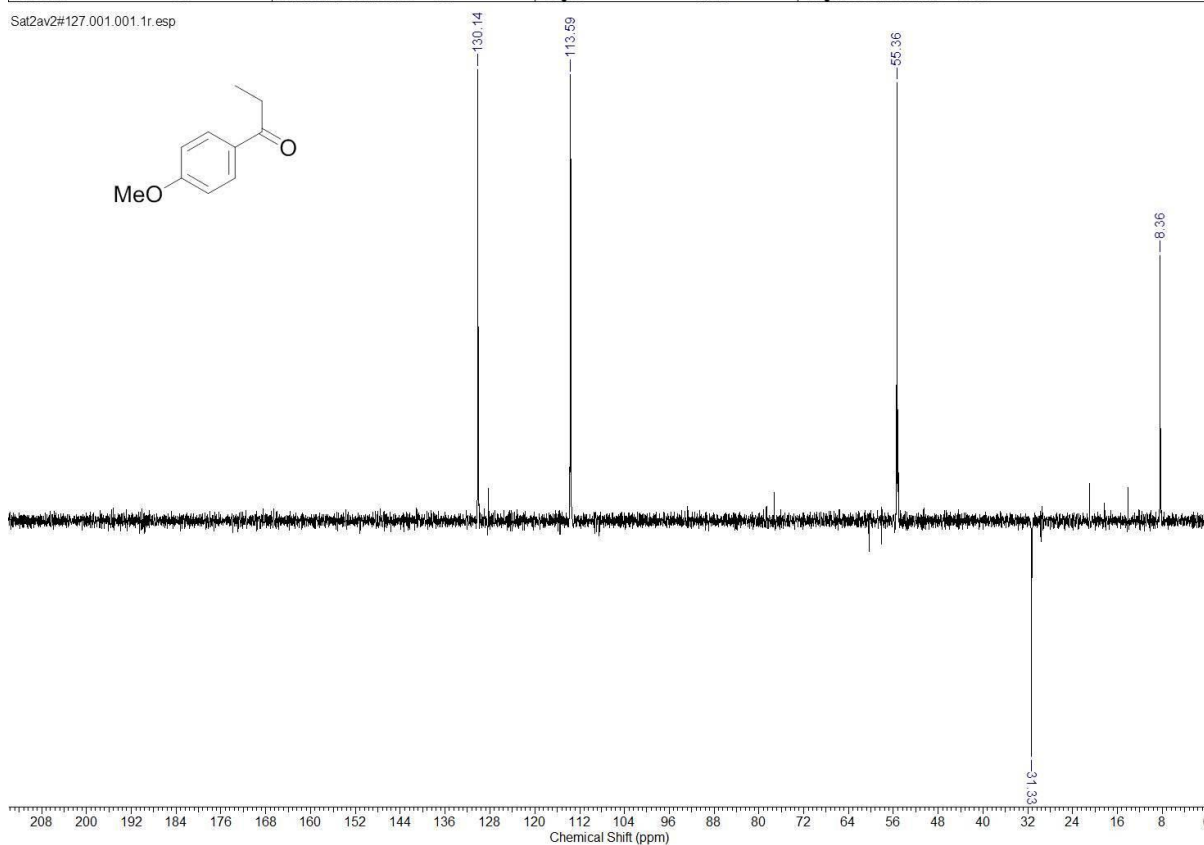


Figure ESI-10-41: DEPT spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-4, entry 15 (15b)

<b>Acquisition Time (sec)</b>	2 1838	<b>Comment</b>	KCB	<b>Date</b>	10 Sep 2014 18:04:03
<b>Date Stamp</b>	10 Sep 2014 08:26:01	<b>File Name</b>	\\aghi\inmr_data\JEOL_400\2014\Sep 2014\Tue2ECX400#035_PROTON-3.pdf		
<b>Frequency (MHz)</b>	399.78	<b>Nucleus</b>	<sup>1</sup> H	<b>Number of Transients</b>	16
				<b>Origin</b>	ECX 400

Tue2ECX400#035\_PROTON-3.esp

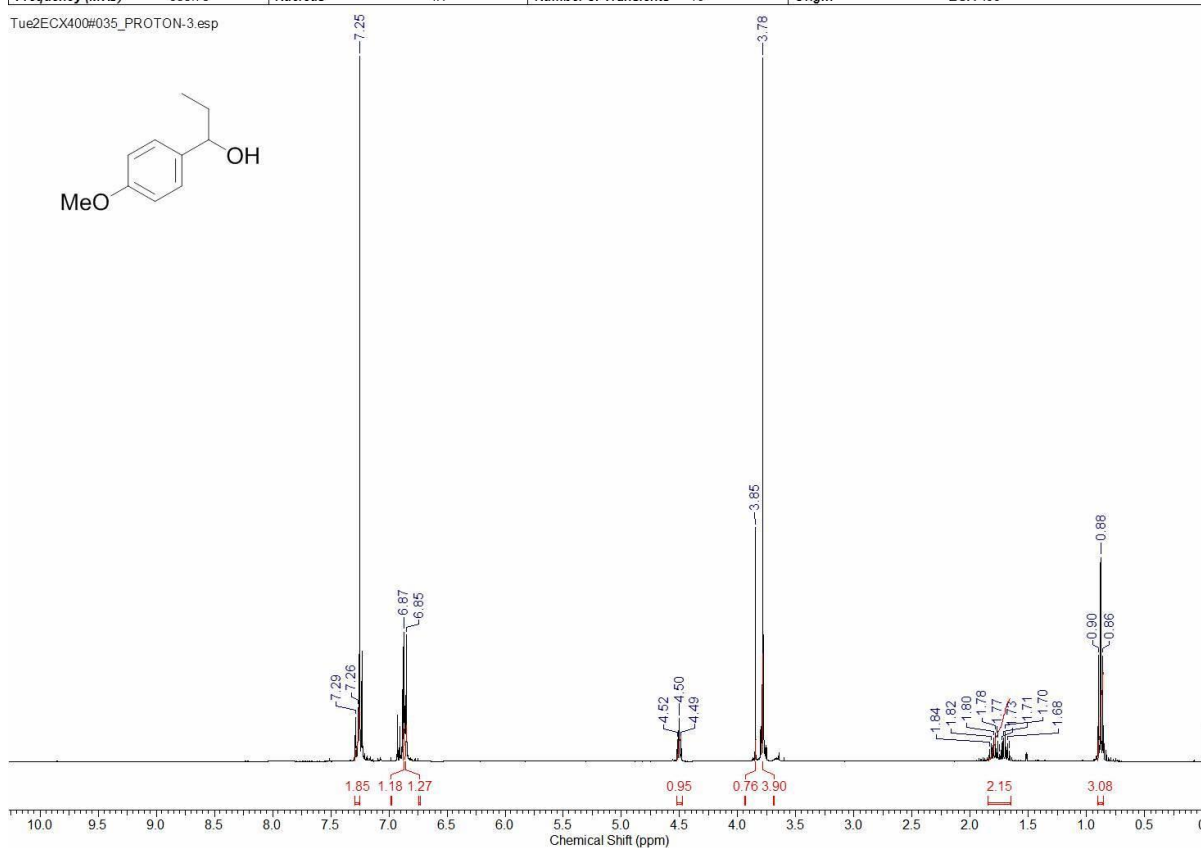


Figure ESI-10-42: <sup>1</sup>H NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-4, entry 16 (16b)

Acquisition Time (sec)	0.6832	Comment	KCB	Date	14 Sep 2014 19:10:00
Date Stamp	14 Sep 2014 19:10:00	Frequency (MHz)	50.32		
Nucleus	<sup>13</sup> C	Number of Transients	600	Origin	av200
				Original Points Count	8192

Sat2av2#128.002.001.1r.esp

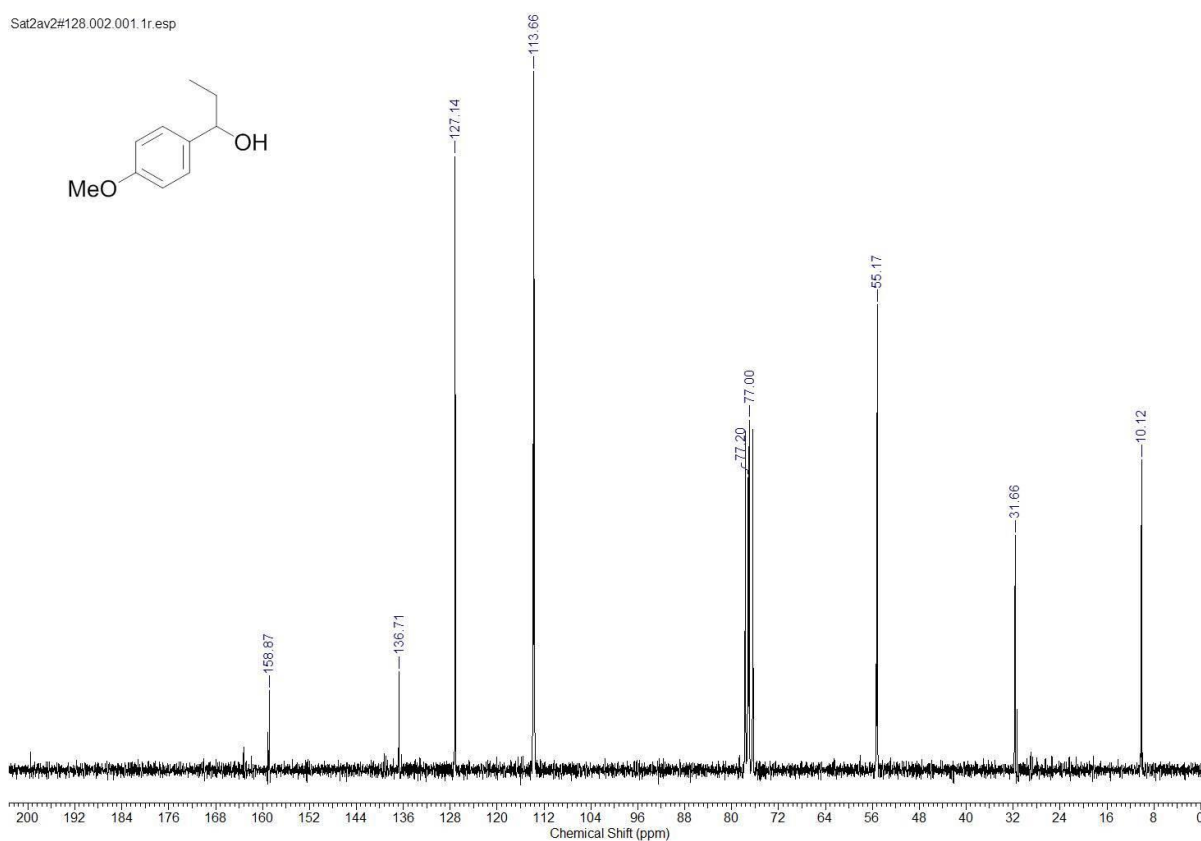


Figure ESI-10-43: <sup>13</sup>C NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-4, entry 16 (16b)

Acquisition Time (sec)	0.6832	Comment	KCB	Date	14 Sep 2014 18:42:16
Date Stamp	14 Sep 2014 18:42:16	Frequency (MHz)	50.32		
Nucleus	<sup>13</sup> C	Number of Transients	300	Origin	av200
				Original Points Count	8192

Sat2av2#128.001.001.1r.esp

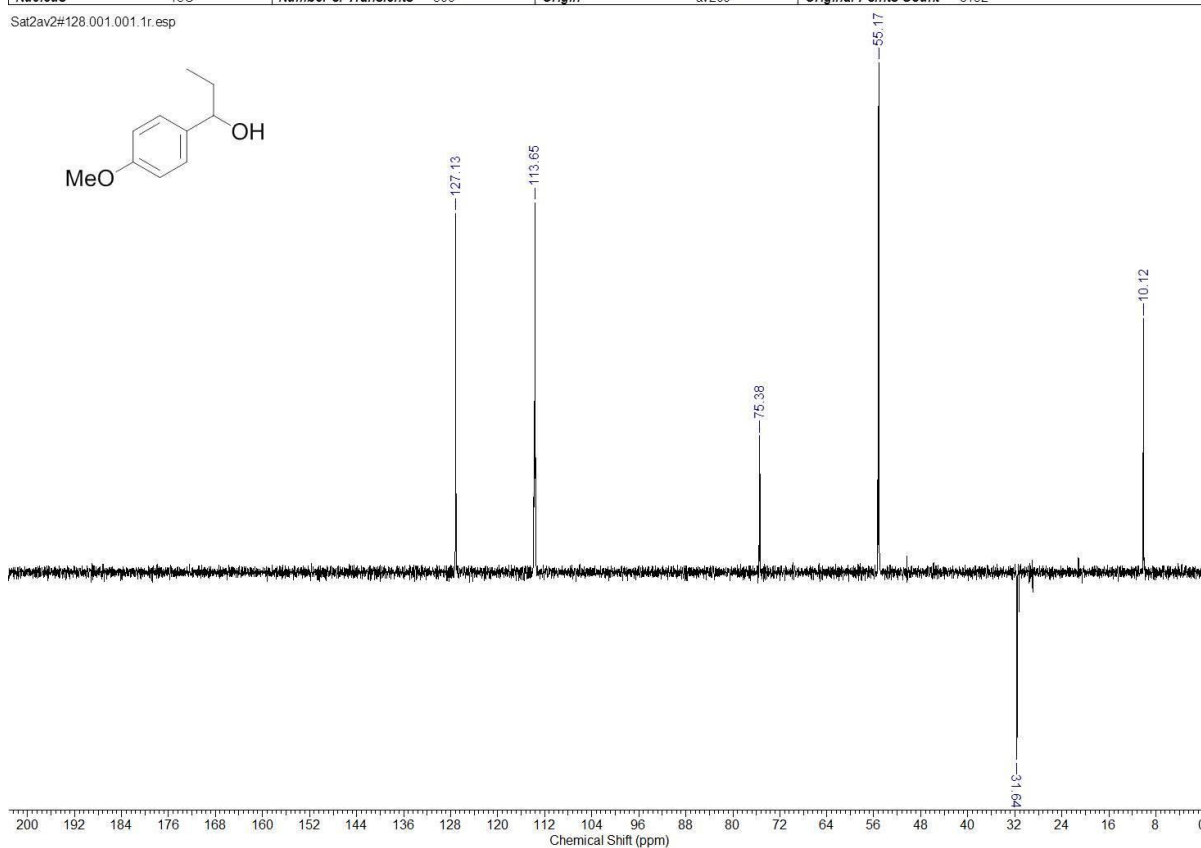


Figure ESI-10-44: DEPT spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-4, entry 16 (16b)



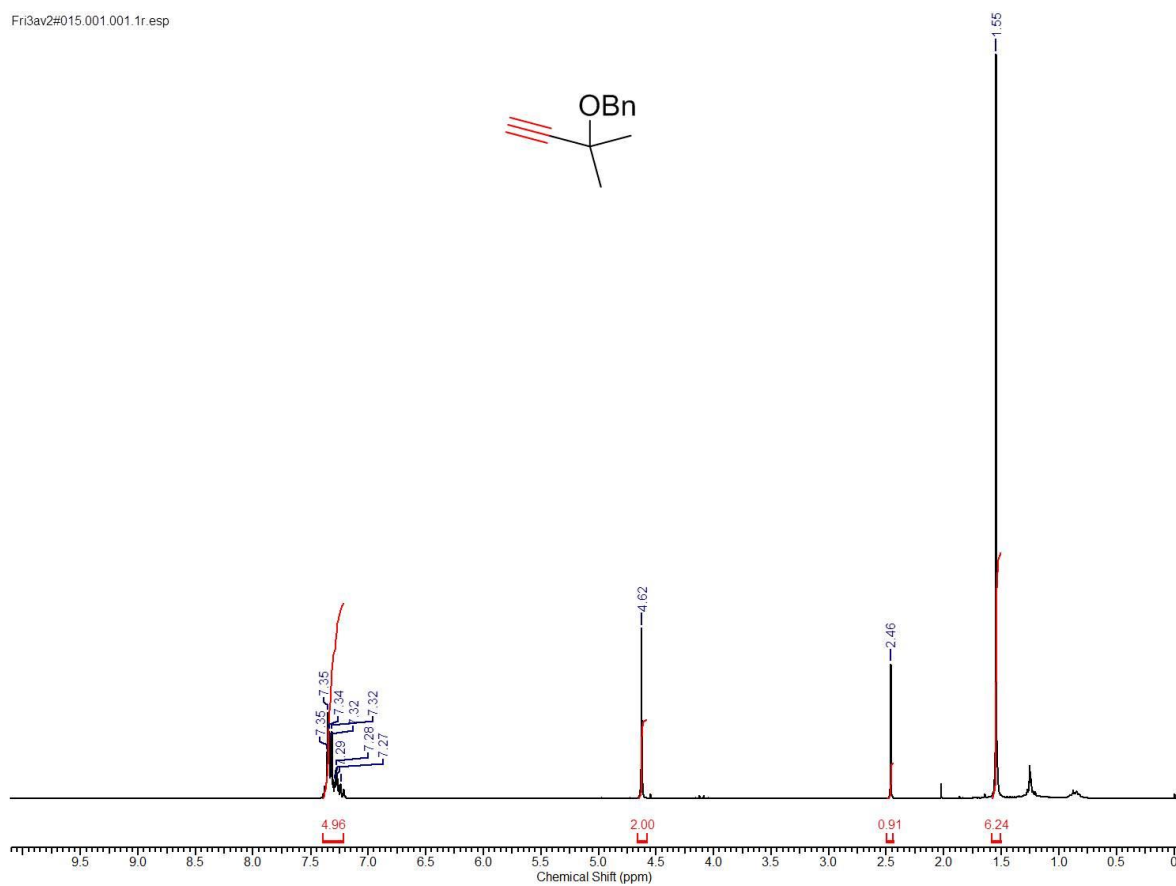


Figure ESI-10-45: <sup>1</sup>H NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-4, entry 17 (17b)

Fri4av2#083.002.001.1r.esp

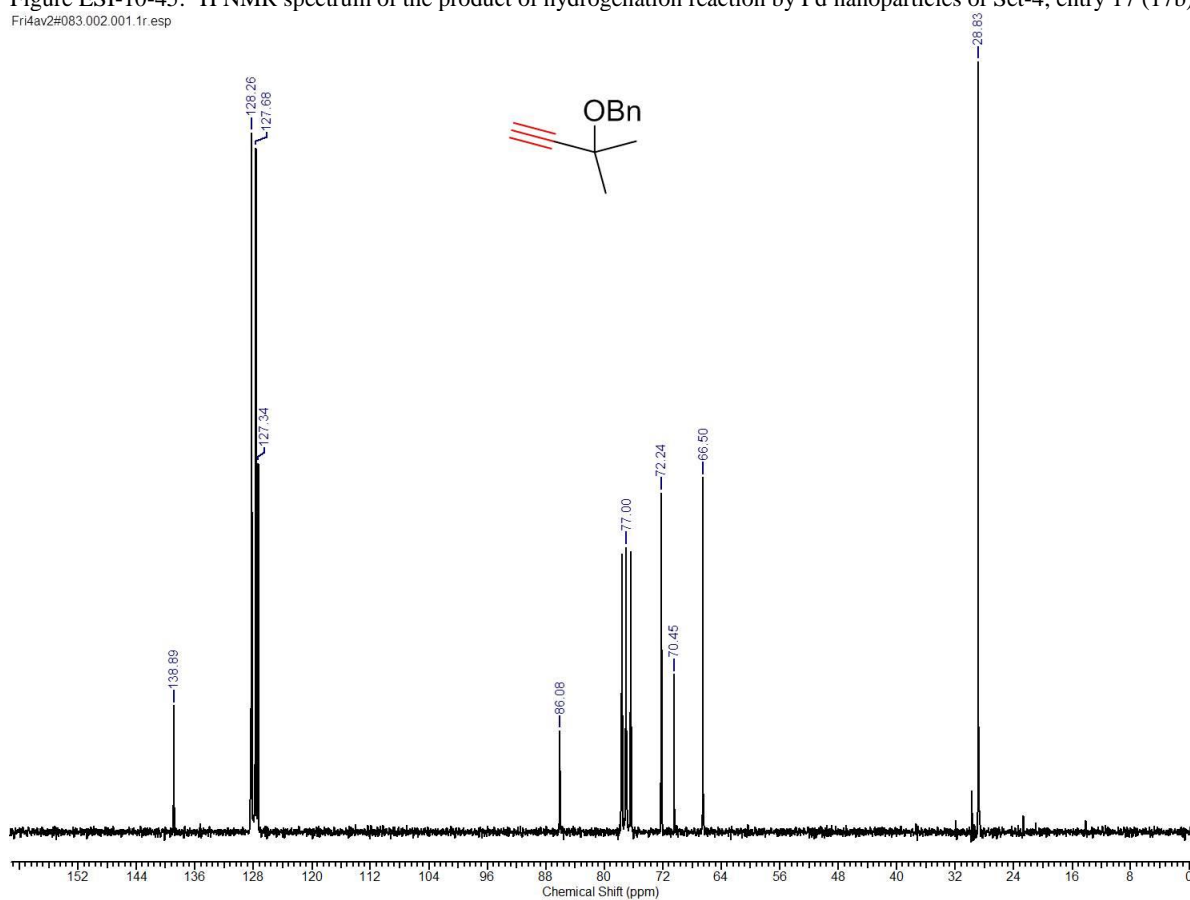


Figure ESI-10-46: <sup>13</sup>C NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-4, entry 17 (17b)

Fri4av2#083.001.001.1r.esp

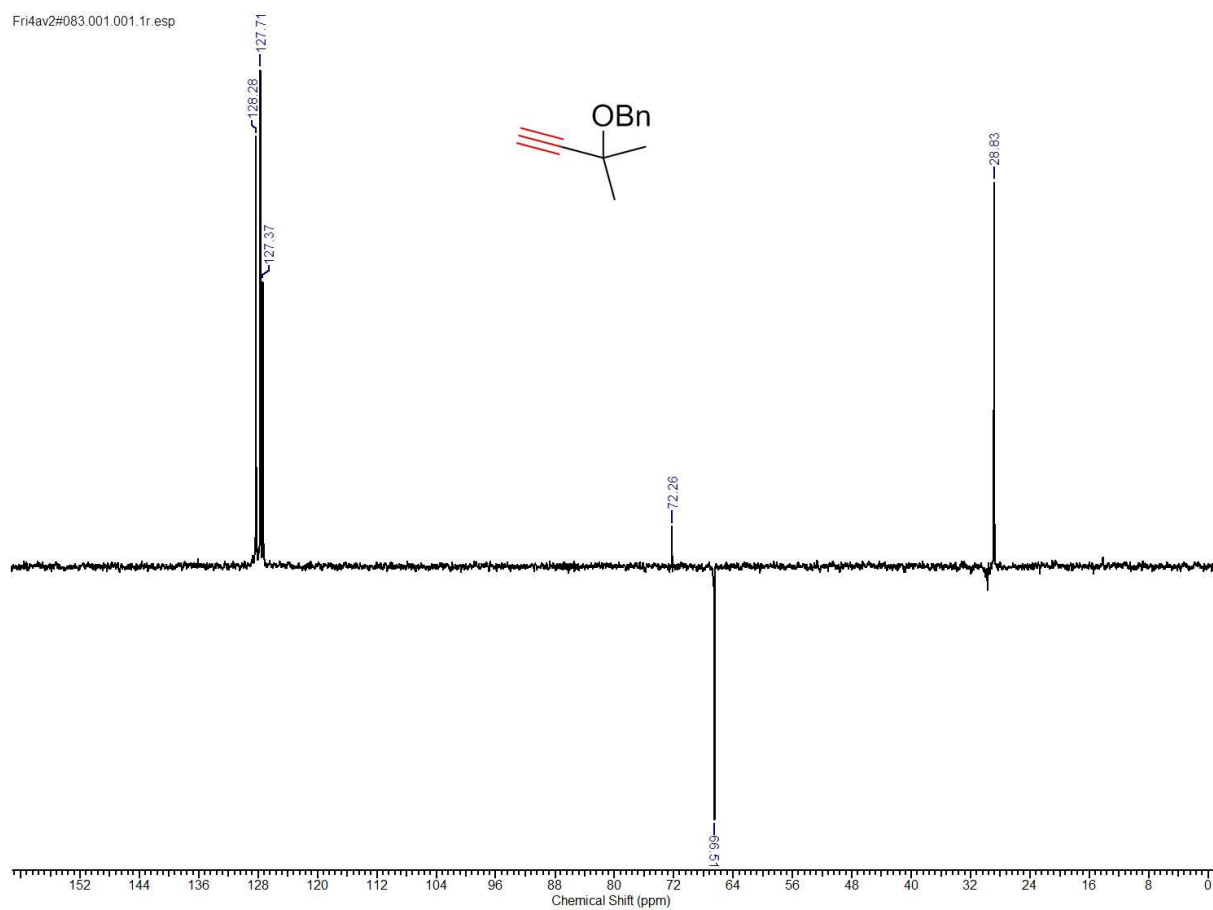


Figure ESI-10-47: DEPT spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-4, entry 17 (17b)

Fri3av2#016.001.001.1r.esp

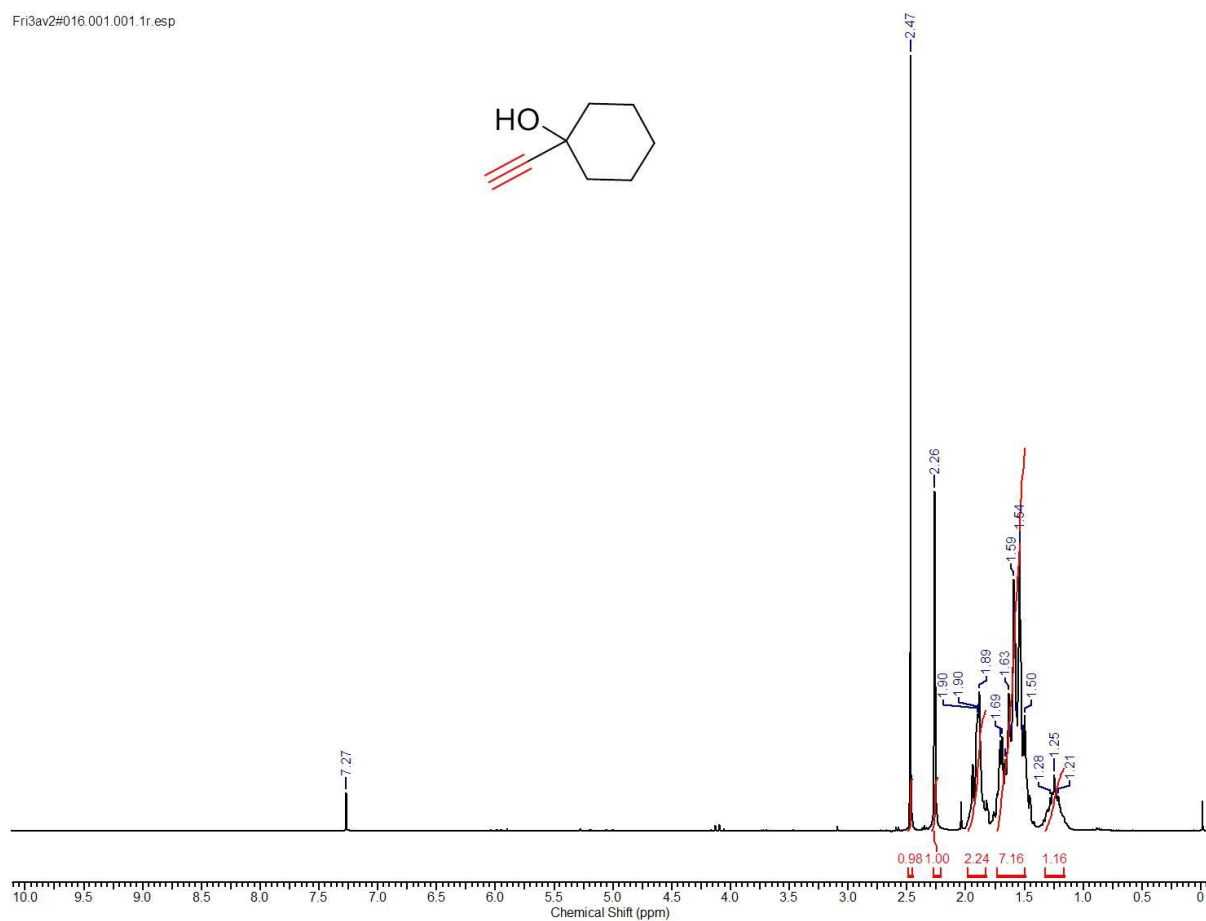


Figure ESI-10-48:  $^1\text{H}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-4, entry 18 (18b)

Fri3av2#014.001.001.1r.esp

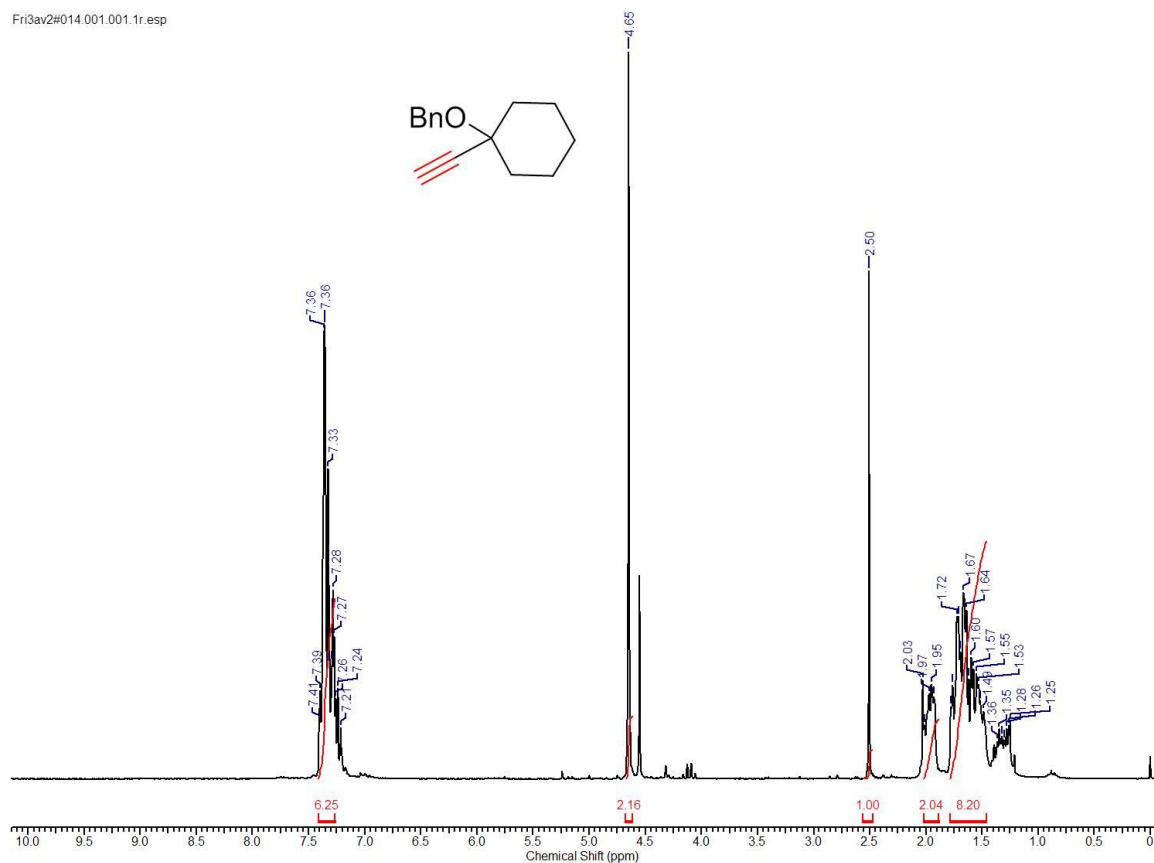


Figure ESI-10-49:  $^1\text{H}$  NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-4, entry 19 (19b)

Thu4av2#095.002.001.1r.esp

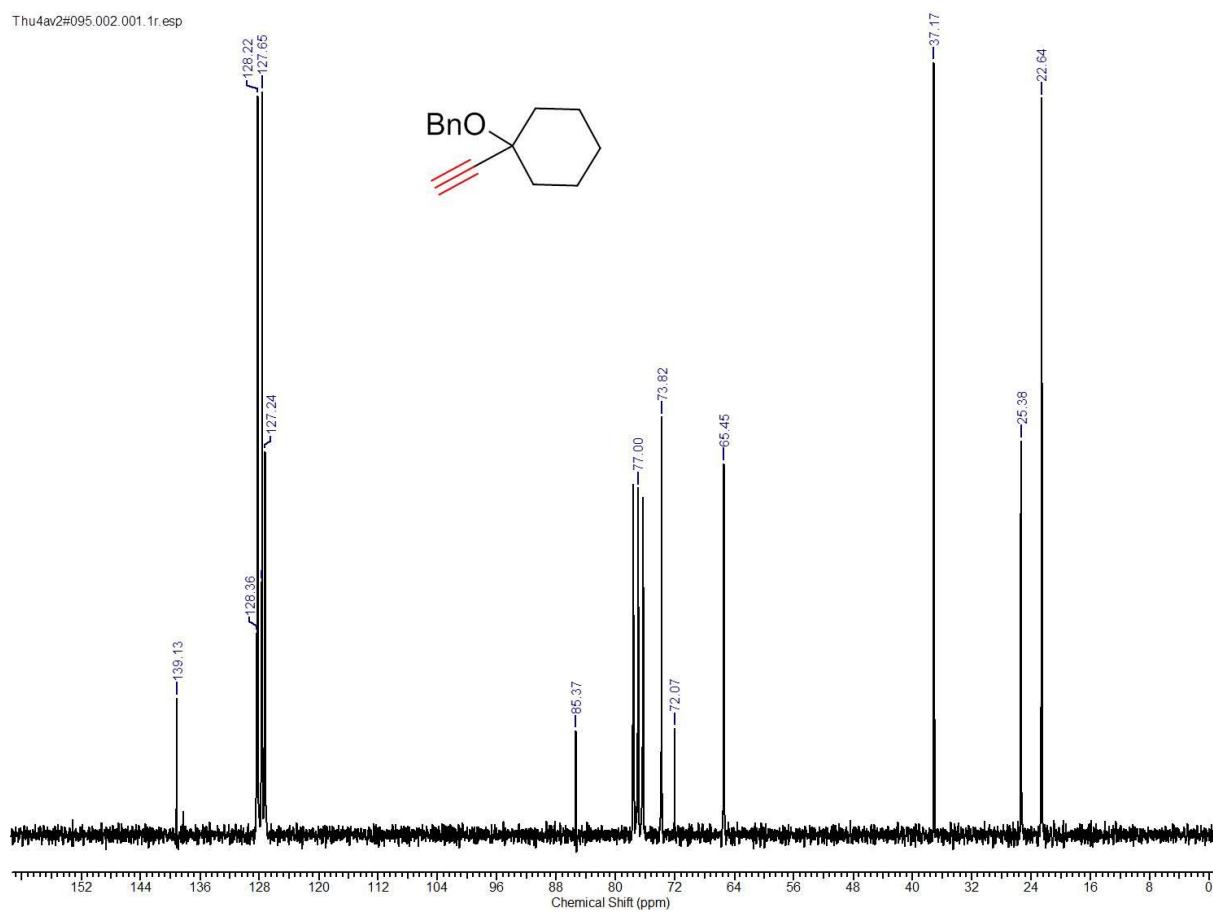


Figure ESI-10-50: <sup>13</sup>C NMR spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-4, entry 19 (19b)

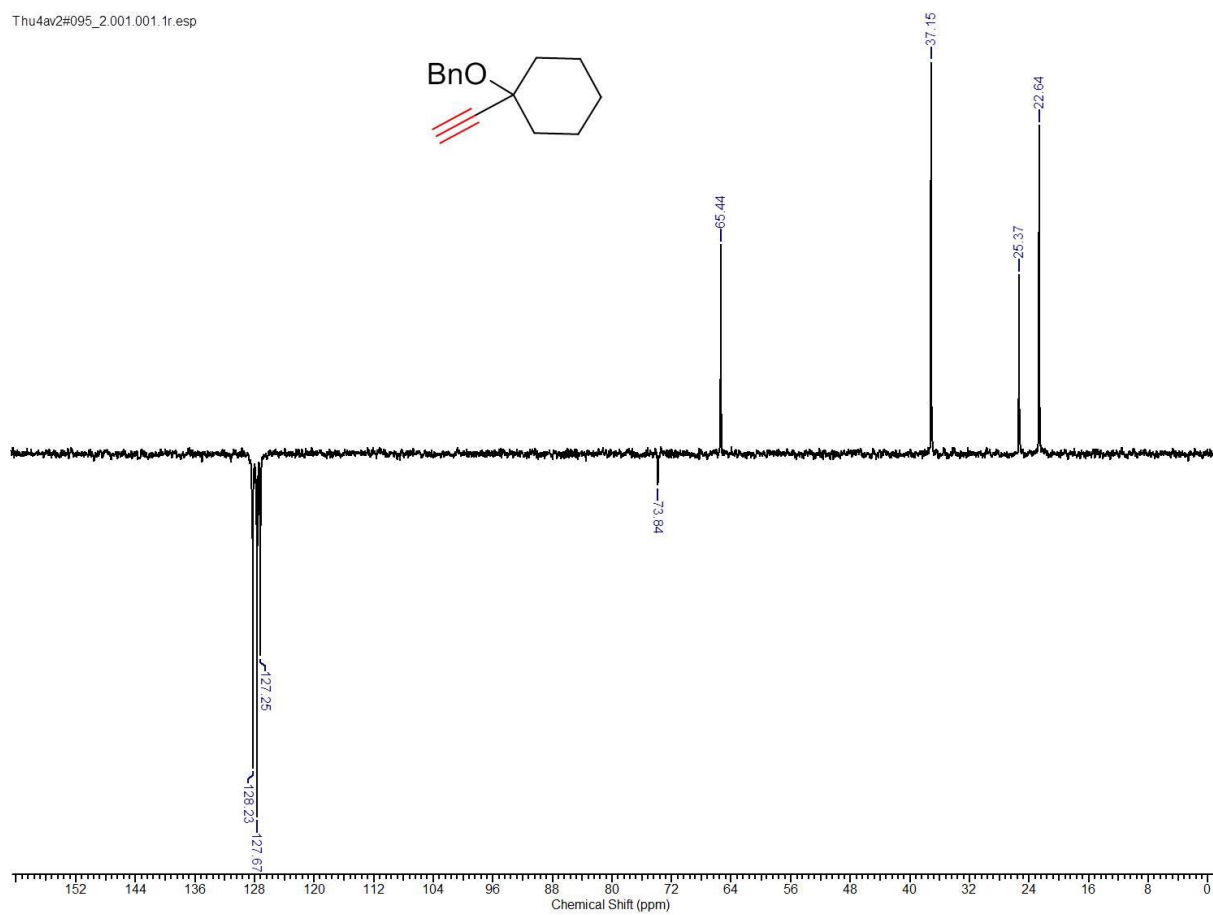


Figure ESI-10-51: DEPT spectrum of the product of hydrogenation reaction by Pd nanoparticles of Set-4, entry 19 (19b)