

## ESI

### **Multi-functional Palladium-Ruthenium Nanocomposites: Approach towards Semi-Hydrogenation Catalysis and Hydrogen Sorption**

Chirasmitta Bhattacharya, Kamla D Netam, Balaji R Jagirdar\*

#### **Table of contents**

- A.** Calculation of Turn Over Frequency (TOF) based on dispersion degree from TEM images
- B.** Comparison of the relative performance of our catalyst with other Pd-Ru bimetallic catalysts for semi-hydrogenation of phenyl acetylene
- C.** Supporting Figures and Data

Figure S1. Characterization of Pd-THF nanoparticles: (a) PXRD pattern, (b) BFTEM image, (c) HRTEM image, (d) SAED pattern.

Figure S2. Characterization of Ru nanoparticles: (a) PXRD pattern, (b) BFTEM image, (c) HRTEM image, (d) SAED pattern.

Figure S3. Powder X-ray diffraction pattern corresponding to Ru nanoparticles annealed at 150 °C and 300 °C.

Figure S4. Enlarged STEM EDS area map images of bimetallic Pd-Ru nanocomposites with stoichiometric ratio between Pd and Ru as Pd<sub>0.5</sub>Ru<sub>0.5</sub> (Reference to Figure 4)

Figure S5. Elemental area mapping analysis of bimetallic Pd-Ru nanocomposites with stoichiometric ratio between Pd and Ru as: (a) Pd<sub>0.8</sub>Ru<sub>0.2</sub>, (b) Pd<sub>0.6</sub>Ru<sub>0.4</sub>, (c) Pd<sub>0.4</sub>Ru<sub>0.6</sub>, (d) Pd<sub>0.2</sub>Ru<sub>0.8</sub>.

Figure S6. (a) Bright-field, (b) high-resolution TEM images of Pd nanoparticles obtained upon digestive ripening process.

Figure S7. Pressure-composition isotherms corresponding to: (a) Pd, (b) Pd<sub>0.5</sub>Ru<sub>0.5</sub> nanoparticles measured at 1 atm H<sub>2</sub> pressure and different temperatures, i.e., 25 °C, 100 °C, and 150 °C.

Figure S8. <sup>1</sup>H NMR spectral stack plot showing gradual conversion of styrene to ethyl benzene at 5 bar H<sub>2</sub> pressure and 25 °C.

Figure S9. NMR spectral and GC-MS analysis corresponding to hydrogenation reactions carried out on various olefinic substrates in their neat form using Pd<sub>0.5</sub>Ru<sub>0.5</sub> bimetallic catalyst. Reaction conditions: catalyst to substrate ratio of 1:500; H<sub>2</sub> gas pressure of 5 bar; room temperature condition. [Table 3]

Figure S10. NMR spectral analysis corresponding to hydrogenation of Benzene in neat form using Pd<sub>0.5</sub>Ru<sub>0.5</sub> bimetallic catalyst. Reaction conditions: catalyst to substrate ratio of 1:500; H<sub>2</sub> gas pressure of 5 bar; room temperature condition.

Figure S11. GC-MS analysis corresponding to sequential hydrogenation of phenyl acetylene (with THF as a solvent) using Pd<sub>0.5</sub>Ru<sub>0.5</sub> bimetallic catalyst. Reaction conditions: catalyst to substrate ratio of 1:500; H<sub>2</sub> gas pressure of 5 bar; room temperature condition.

Figure S12. NMR spectral and GC-MS analysis corresponding to hydrogenation reactions carried out on styrene in neat form using Pd<sub>0.5</sub>Ru<sub>0.5</sub> bimetallic catalyst [Table 4]

Figure S13. Enlarged STEM EDS area map images corresponding to catalyst recycling for neat styrene hydrogenation by Pd-Ru nanocomposite for 7 cycles using Pd<sub>0.5</sub>Ru<sub>0.5</sub> bimetallic catalysts. Reaction Conditions: 5 bar, 298 K, 1:500 catalyst to substrate ratio (Reference to Figure 7)

Figure S14. NMR spectral and GC-MS analysis corresponding to catalyst recycling for neat styrene hydrogenation by Pd-Ru nanocomposite for 7 cycles using Pd<sub>0.5</sub>Ru<sub>0.5</sub> bimetallic catalysts. Reaction Conditions: 5 bar, 298 K, 1:500 catalyst to substrate ratio

Figure S15. NMR spectral analysis corresponding to catalyst poisoning study using neat styrene as substrate and tricyclohexylphosphine (PCy<sub>3</sub>) as catalyst poison. Reaction Conditions: 5 bar, 298 K, 1:500 catalyst to substrate ratio

Figure S16. NMR spectral analysis corresponding to catalyst poisoning study using neat styrene as substrate and quinoline as catalyst poison. Reaction Conditions: 5 bar, 298 K, 1:500 catalyst to substrate ratio

#### **A. Calculation of Turn Over Frequency (TOF) based on dispersion degree from TEM images:**

In order to estimate the Turnover frequency (TOF), following assumptions were made:

1. The shape of all the bimetallic Pd<sub>0.5</sub>Ru<sub>0.5</sub> nanoparticles have been considered to be spherical. Based on analysis of HR-TEM images, the average particle size was estimated to be 5.04 nm.
2. The calculation of catalyst dispersity was done by considering Pd nanoparticles as active sites for catalysis.

Turnover frequency (TOF) has been calculated as the amount of a reacted substrate (in moles) per mole of Pd<sub>0.5</sub>Ru<sub>0.5</sub> catalyst per unit of time with the account of catalyst dispersity, D<sub>M</sub> according to the formula:

$$\text{TOF}^* = \text{Moles of substrate transformed per mole of catalyst per hour} \times \frac{1}{D}$$

where, D is catalyst dispersity and defined as the ratio of surface atoms to those in the particle volume and were calculated according to the formula:  $D=0.885/d$ , where d is mean particle diameter, expressed in nanometers and 0.885 is a Pd reduced factor, corresponding to the ratio of the atomic phase volume to the average atomic effective area on the particle surface.

According to this formula:

$$D=0.885/5.04 = 0.1755$$

Therefore, Turnover frequency (TOF) (Considering dispersed active catalyst sites) = Turnover frequency (TOF) (Total metal sites) x 5.6980

Where, Turnover frequency (TOF) (Total metal sites) = moles of substrate transformed per mole of catalyst per hour

In parenthesis, Turnover frequency (TOF) (Considering dispersed active catalyst sites) = moles of substrate transformed per mole of exposed catalyst per hour (for dispersed catalyst sites) x 5.6980

[\*Reference: E.A. Karakhanov et. al., Selective semi-hydrogenation of phenyl acetylene by Pd nanocatalysts encapsulated into dendrimer networks; Molecular Catalysis 469 (2019) 98–110 <https://doi.org/10.1016/j.mcat.2019.03.005>].

#### B. Comparison of the relative performance of our catalyst with other Pd-Ru bimetallic catalysts for semi-hydrogenation of phenyl acetylene

| S. No. | Catalyst   | Temperature (K) | Pressure (Bar) | Time (h) | % conversion | % Selectivity | TOF (h <sup>-1</sup> ) | Reference |
|--------|--|-----------------|----------------|----------|--------------|---------------|------------------------|-----------|
| 1      | Pd <sub>0.5</sub> Ru <sub>0.5</sub> NPs                              | 298             | 5              | 0.5      | 64.8         | >99.9         | 650* (3704)            | This work |
| 2      | Pd-Ru@ZIF-8  | 373             | 1              | 2        | 98           | 96            | 2188                   | [14]      |
| 3      | Pd <sub>5</sub> Ru <sub>95</sub> -ZPO (zirconium hydrogen phosphate) | 333             | 20             | 2        | 97           | 91            | -                      | [15]      |
| 4      | Ru <sub>2</sub> Pd <sub>3</sub> nanoporous alloy                     | 308-313         | 2.75           | 4        | 100          | 85            | -                      | [18]      |

\*Turnover frequency = mol(substrate)/mol(Pd<sub>0.5</sub>Ru<sub>0.5</sub> catalyst) h. In parenthesis: Turnover frequency (TOF) (Considering dispersed active catalyst sites)- Refer ESI - Part A for detailed calculation

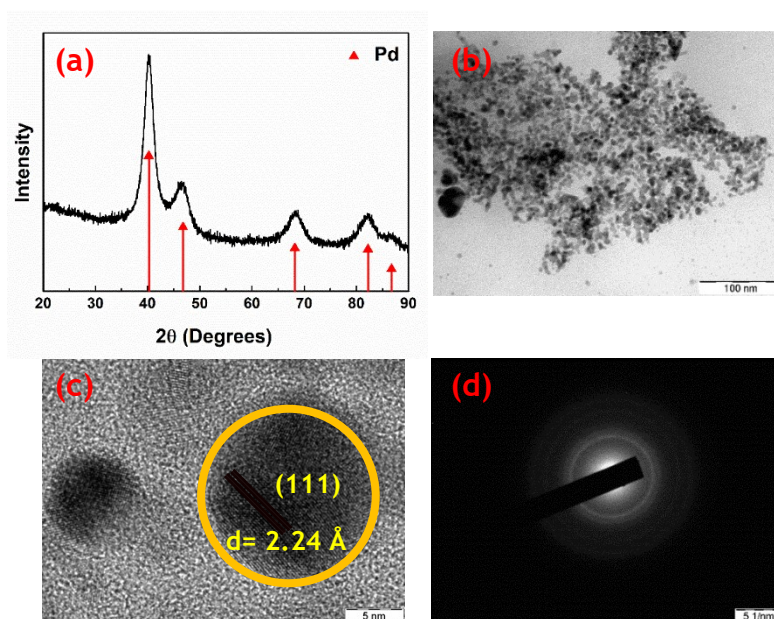


Figure S1. Characterization of Pd-THF nanoparticles: (a) PXRD pattern, (b) BFTEM image, (c) HRTEM image, (d) SAED pattern.

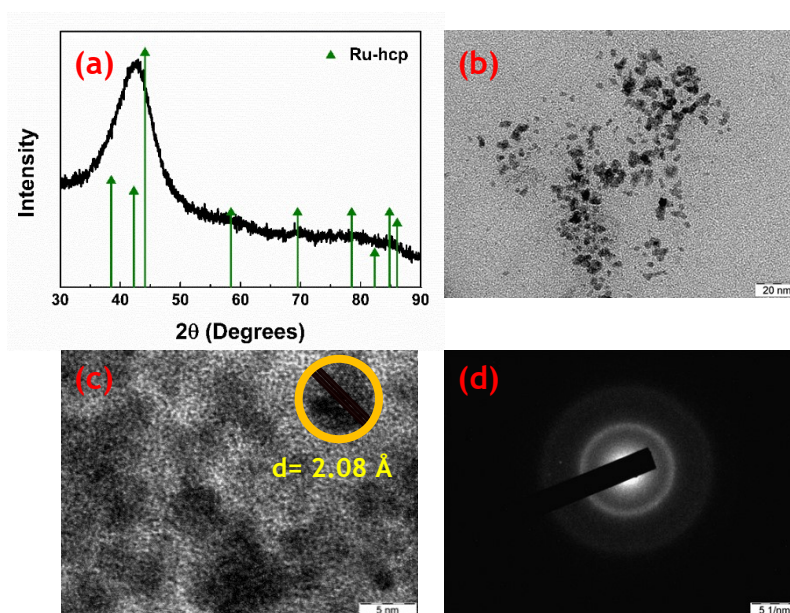


Figure S2. Characterization of Ru nanoparticles: (a) PXRD pattern, (b) BFTEM image, (c) HRTEM image, (d) SAED pattern.

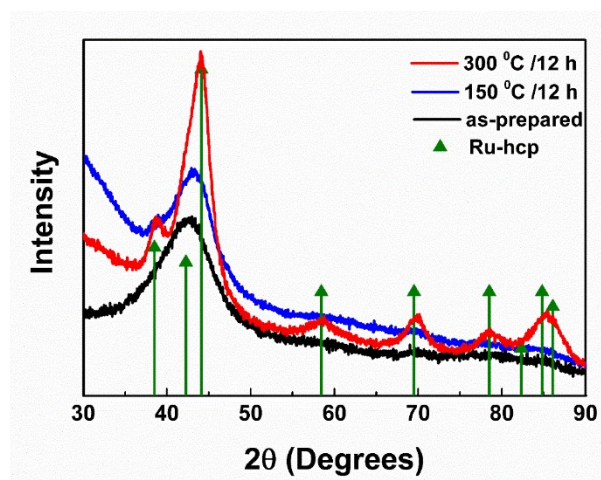


Figure S3. Powder X-ray diffraction pattern corresponding to Ru nanoparticles annealed at 150 °C and 300 °C.

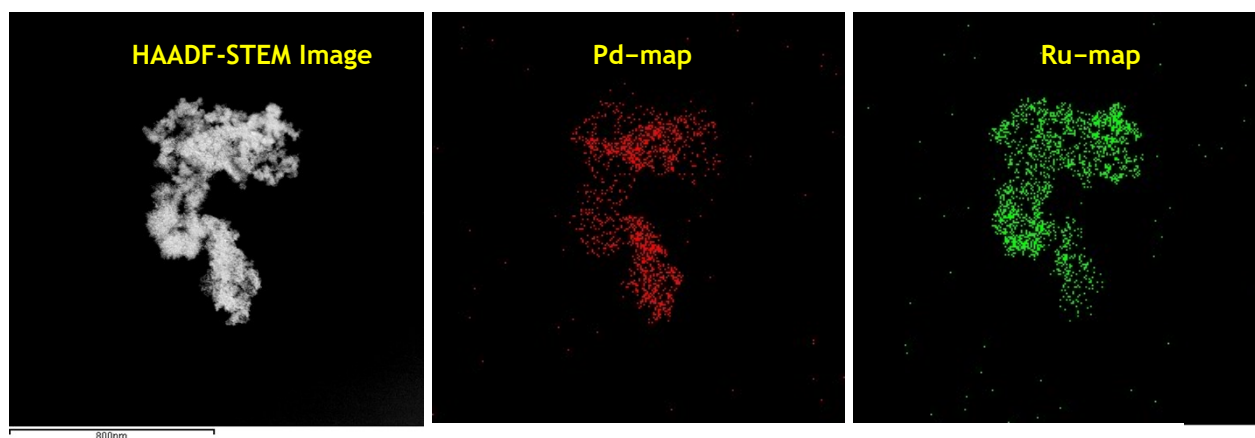


Figure S4. Elemental area mapping analysis of bimetallic Pd-Ru nanocomposites with stoichiometric ratio between Pd and Ru as  $\text{Pd}_{0.5}\text{Ru}_{0.5}$  (Reference to Figure 4)



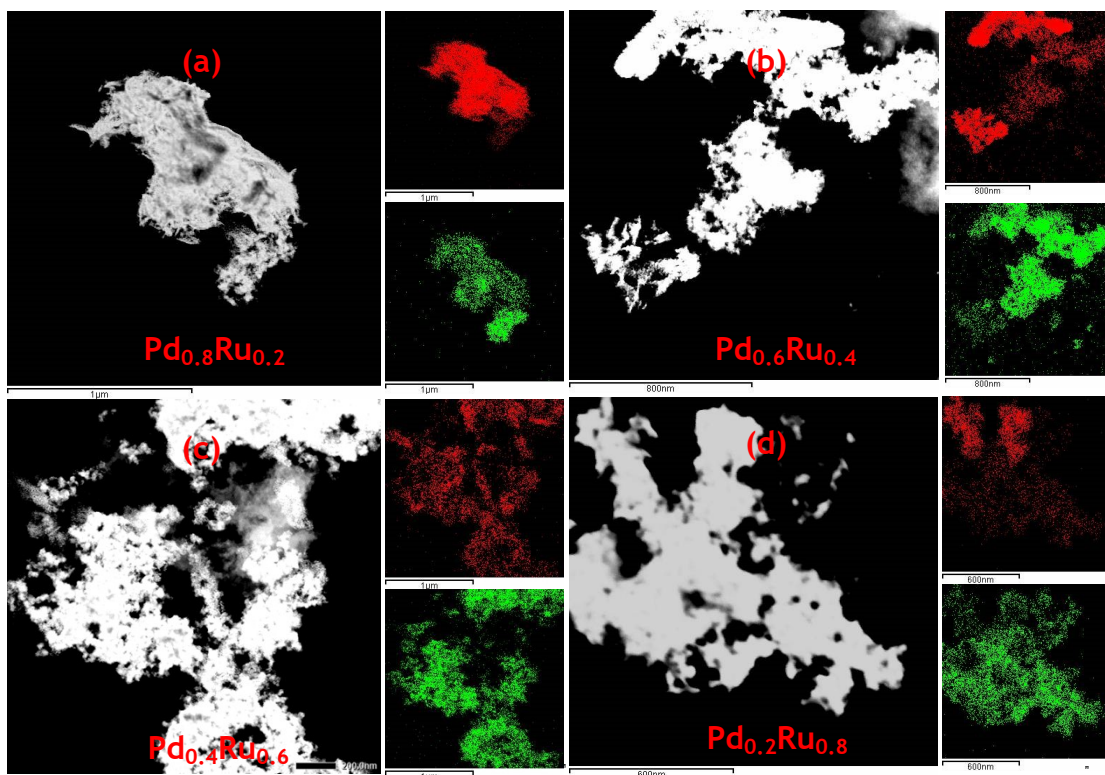


Figure S5. Elemental area mapping analysis of bimetallic Pd-Ru nanocomposites with stoichiometric ratio between Pd and Ru as: (a)  $\text{Pd}_{0.8}\text{Ru}_{0.2}$ , (b)  $\text{Pd}_{0.6}\text{Ru}_{0.4}$ , (c)  $\text{Pd}_{0.4}\text{Ru}_{0.6}$ , (d)  $\text{Pd}_{0.2}\text{Ru}_{0.8}$ .

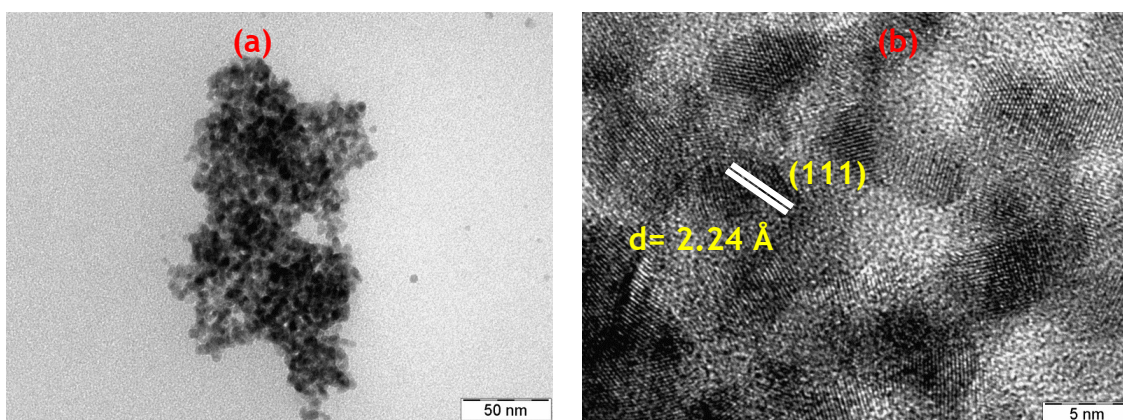


Figure S6. (a) Bright-field, (b) high-resolution TEM images of Pd nanoparticles obtained upon digestive ripening process.

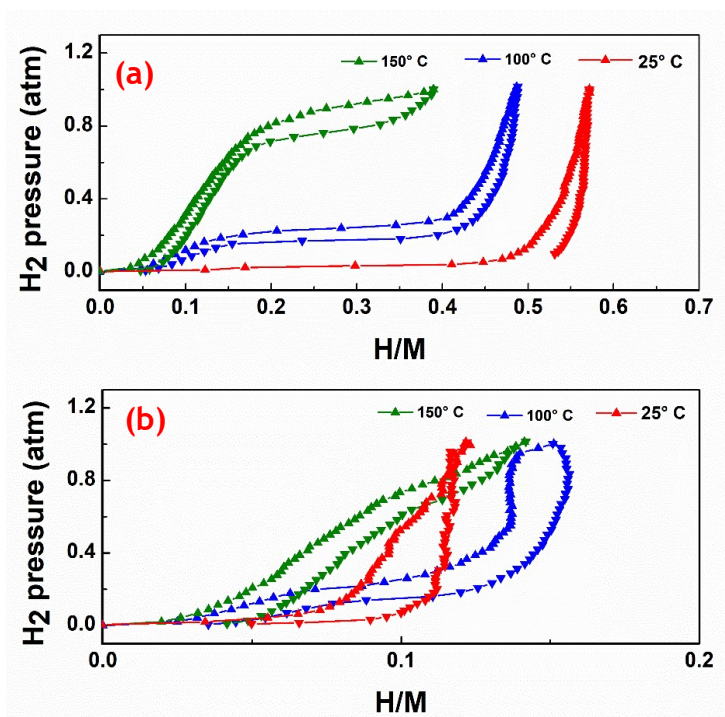


Figure S7. Pressure-composition isotherms corresponding to: (a) Pd, (b) Pd<sub>0.5</sub>Ru<sub>0.5</sub> nanoparticles measured at 1 atm H<sub>2</sub> pressure and different temperatures, i.e., 25 °C, 100 °C, and 150 °C.

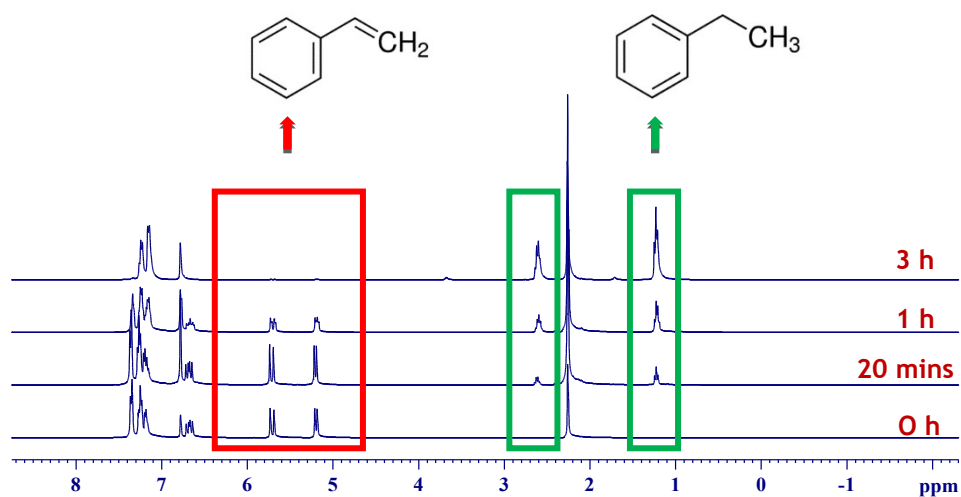
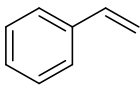
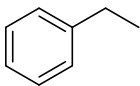


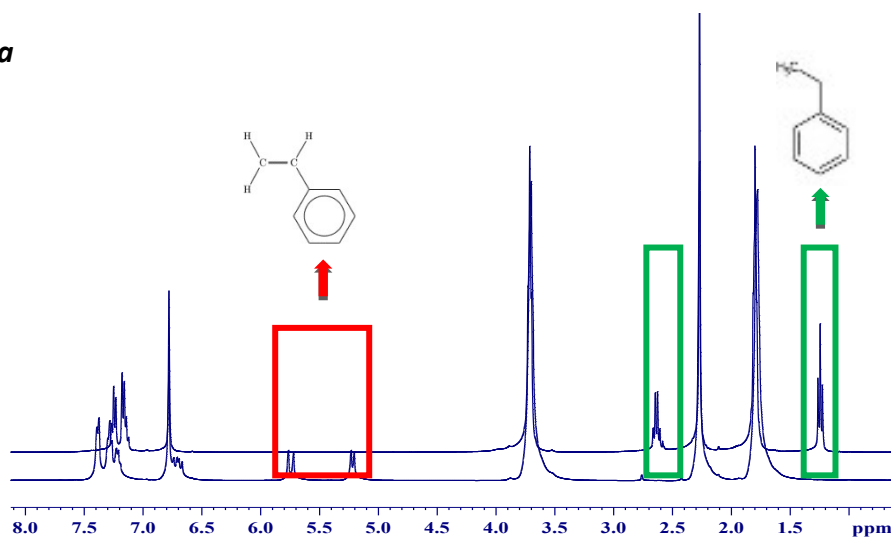
Figure S8. <sup>1</sup>H NMR spectral stack plot showing gradual conversion of styrene to ethyl benzene at 5 bar H<sub>2</sub> pressure and 25 °C.

Figure S9. NMR spectral and GC-MS analysis corresponding to hydrogenation reactions carried out on various olefinic substrates in their neat form using Pd<sub>0.5</sub>Ru<sub>0.5</sub> bimetallic catalyst. Reaction conditions: catalyst to substrate ratio of 1:500; H<sub>2</sub> gas pressure of 5 bar; room temperature condition. [Table 3]

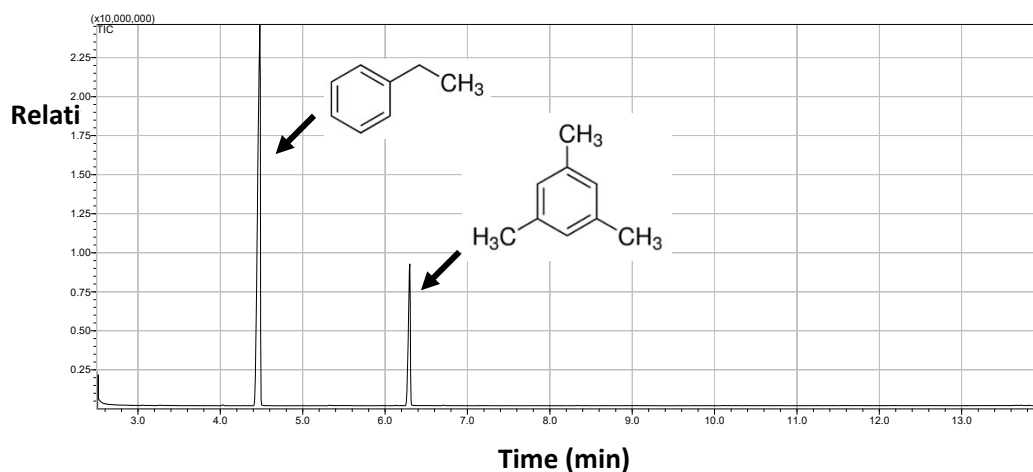
1. Hydrogenation of styrene

| Entry | Substrate   | Product   | Time (h) | Conversion(%) | TOF (h <sup>-1</sup> ) |
|-------|---|---|----------|---------------|------------------------|
| 1     |  |  | 0.3      | >99.9         | 1666                   |

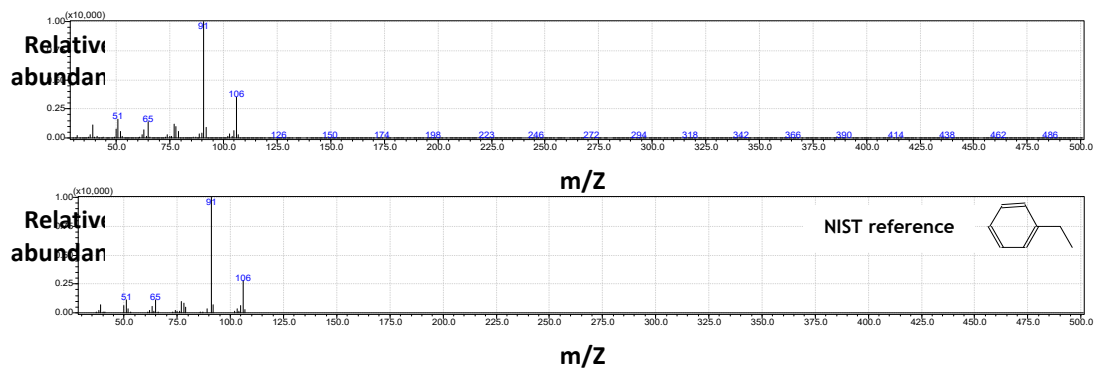
**NMR spectra**



**GC-MS spectrum**



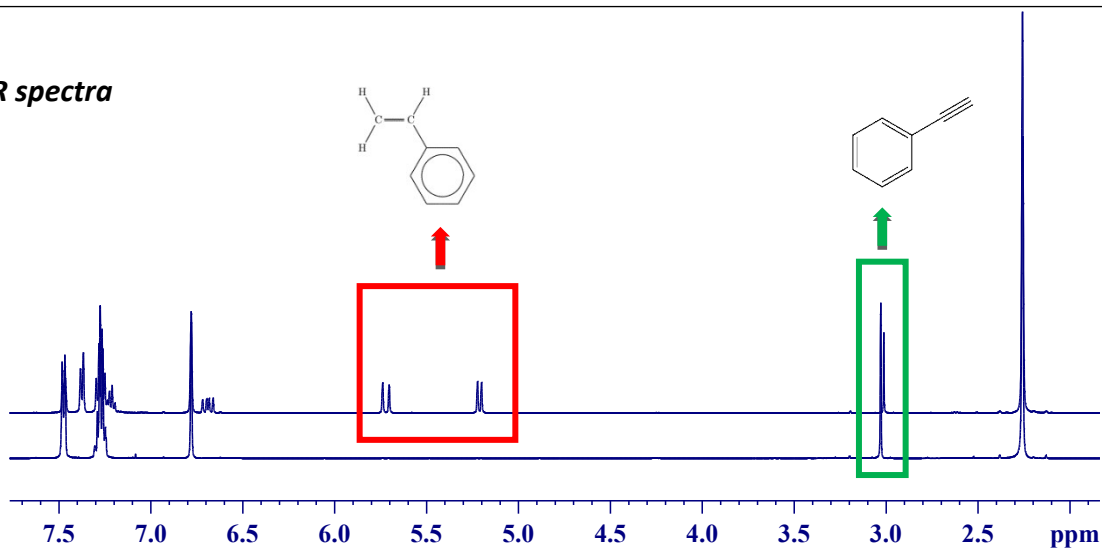




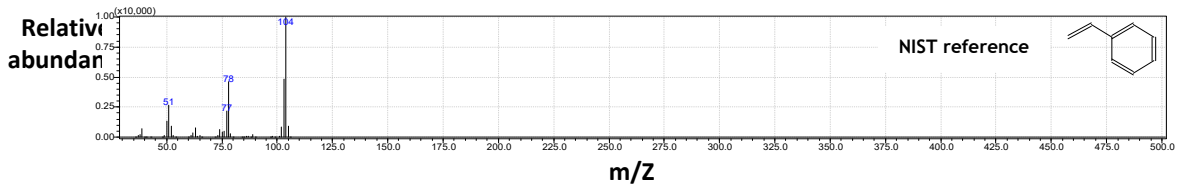
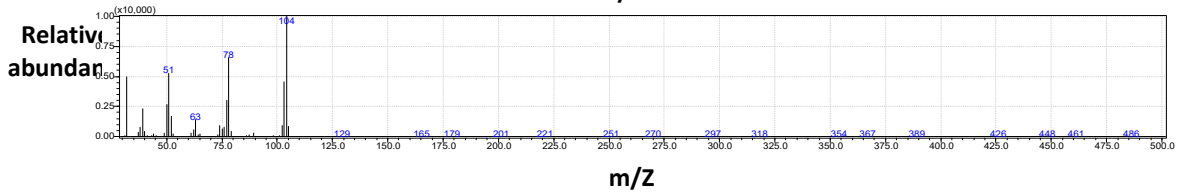
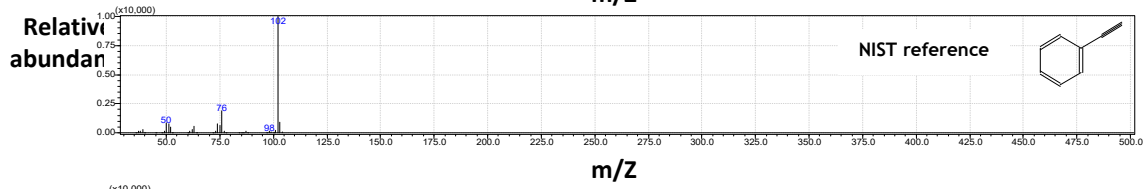
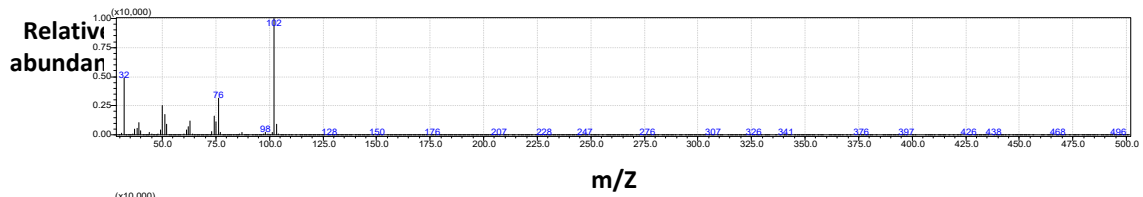
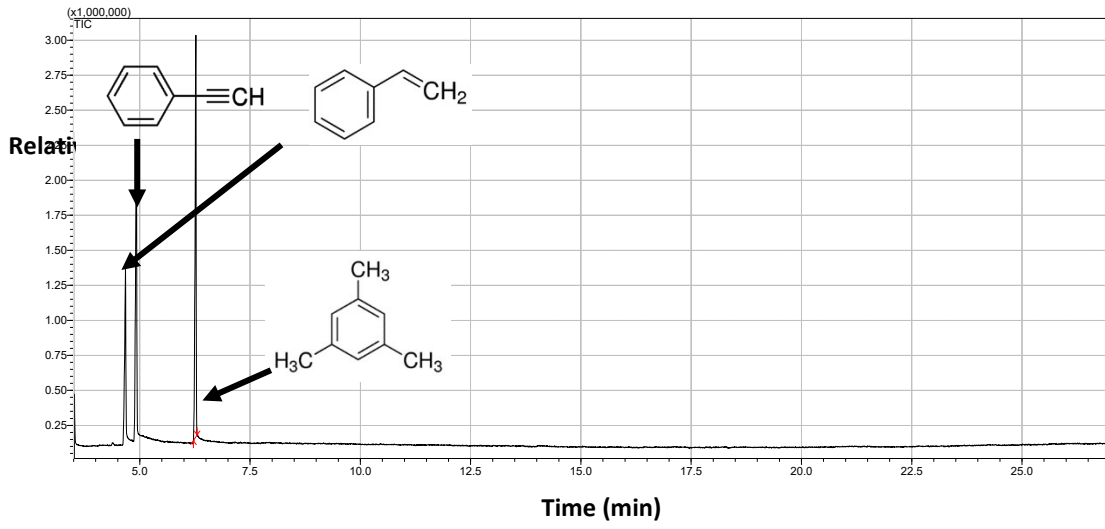
## 2. Hydrogenation of phenyl acetylene

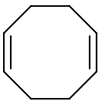
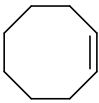
| Entry | Substrate | Product | Time (h) | Conversion (%) | TOF ( $\text{h}^{-1}$ ) |
|-------|-----------|---------|----------|----------------|-------------------------|
| 2     |           |         | 0.5      | 64.8           | 650                     |

### NMR spectra

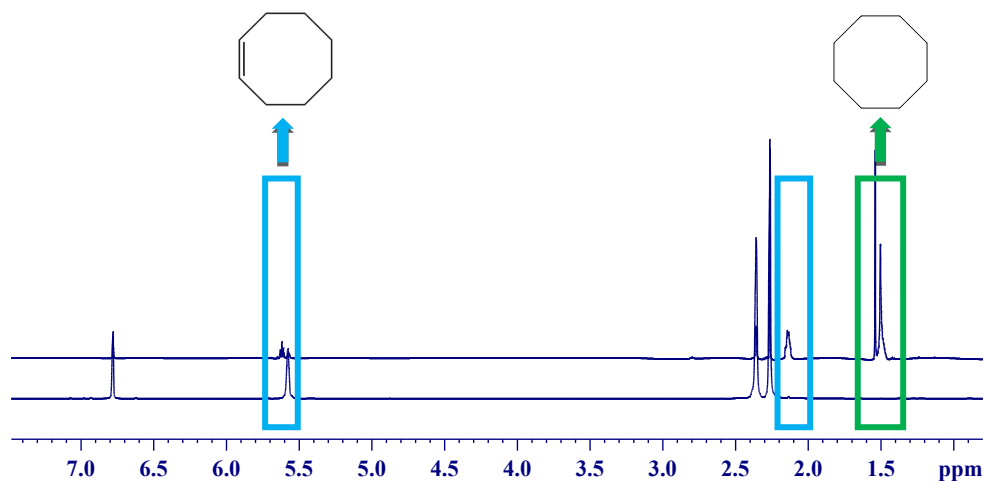


# GC-MS spectrum



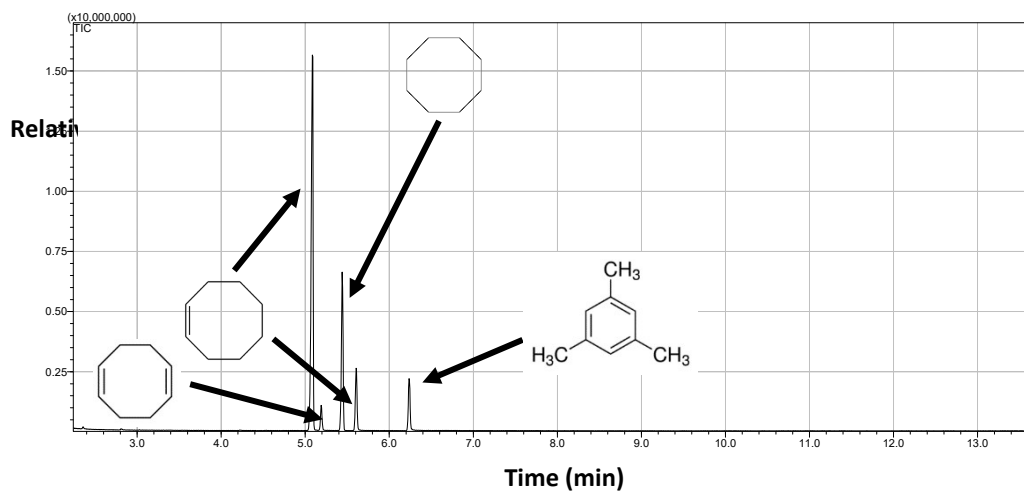
| Entry | Substrate   | Product   | Time (h) | Conversion (%) | TOF (h-1) |
|-------|---|---|----------|----------------|-----------|
| 3     |  |  | 0.8      | 85.5           | 567       |

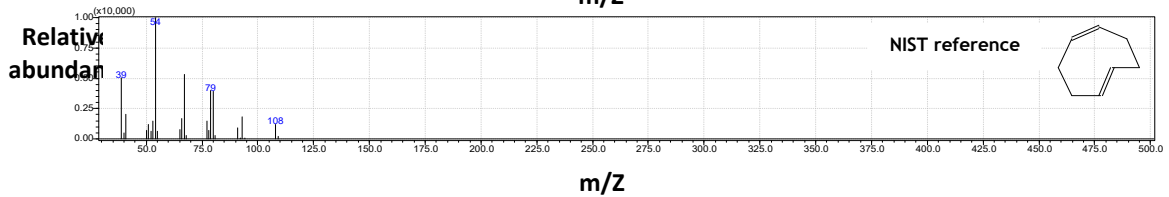
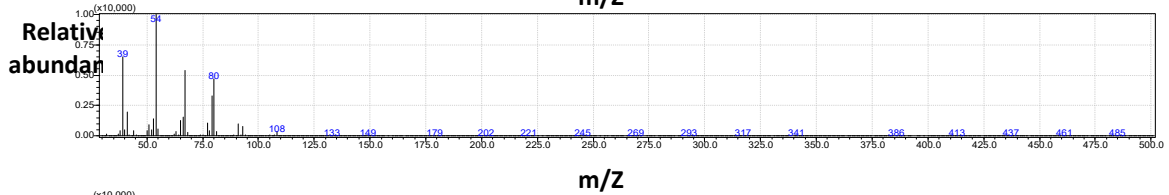
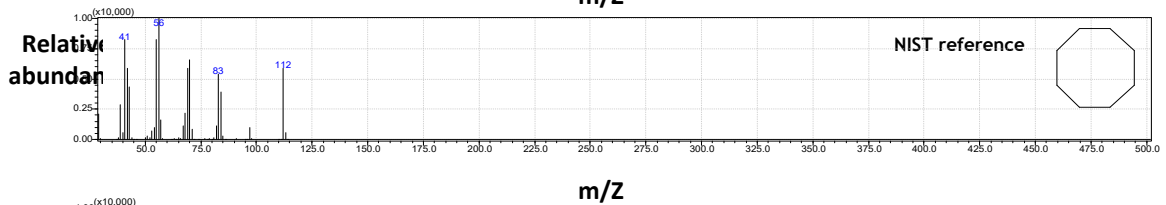
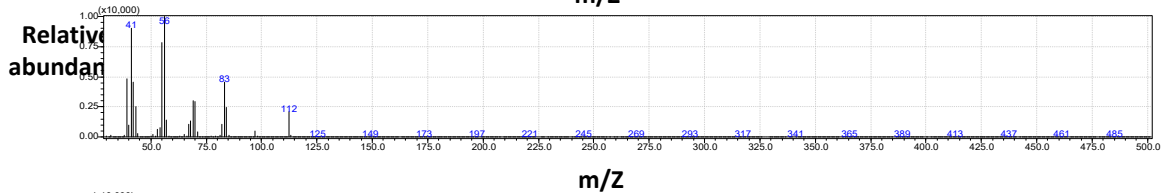
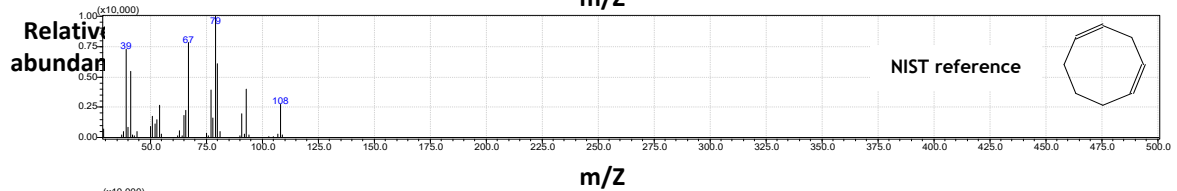
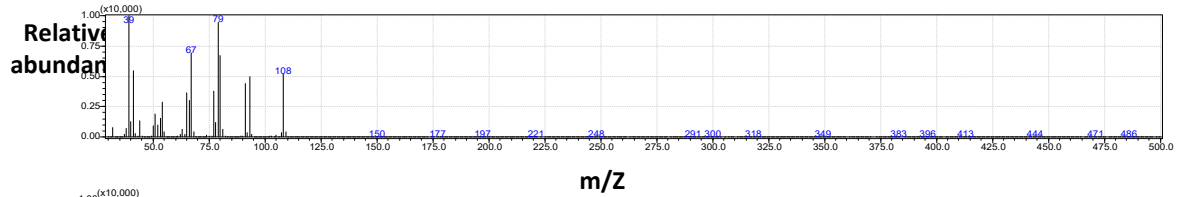
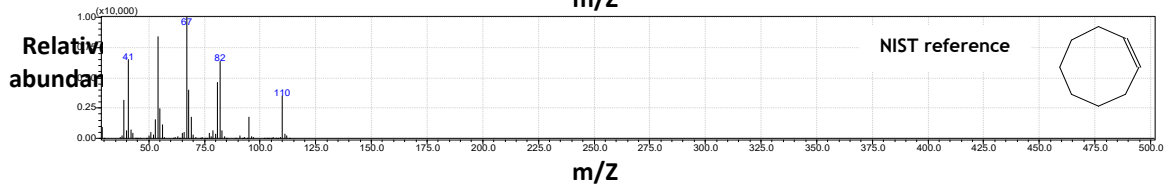
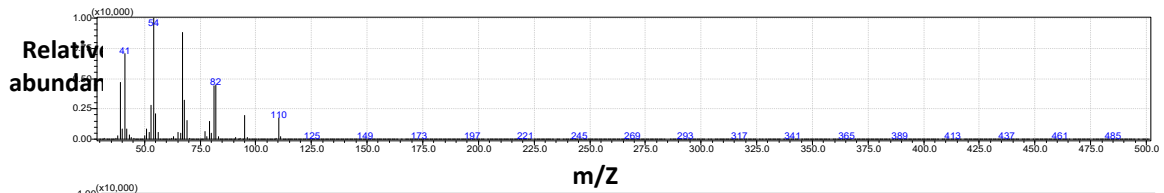
### 3. Hydrogenation of 1,5-cyclooctadiene



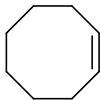
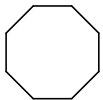
**NMR spectra**

**GC-MS spectrum**

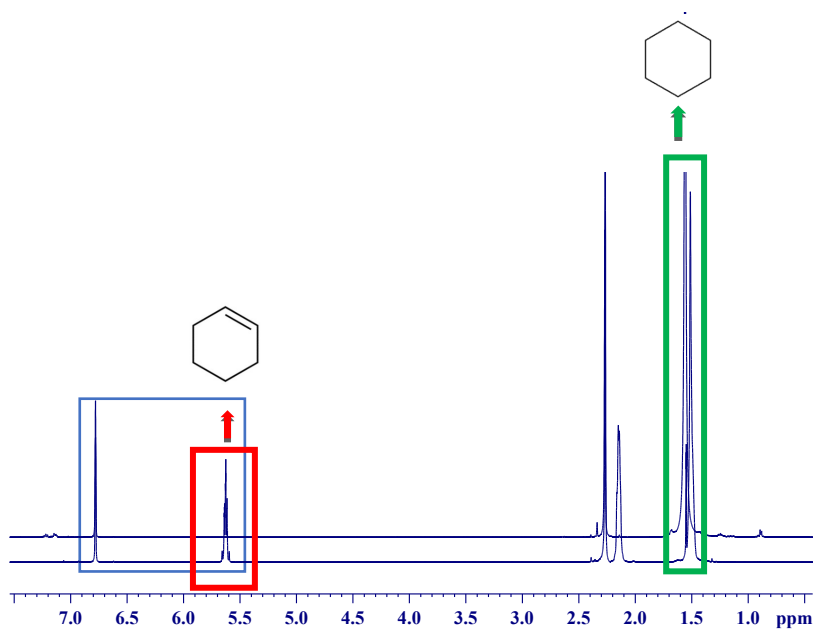




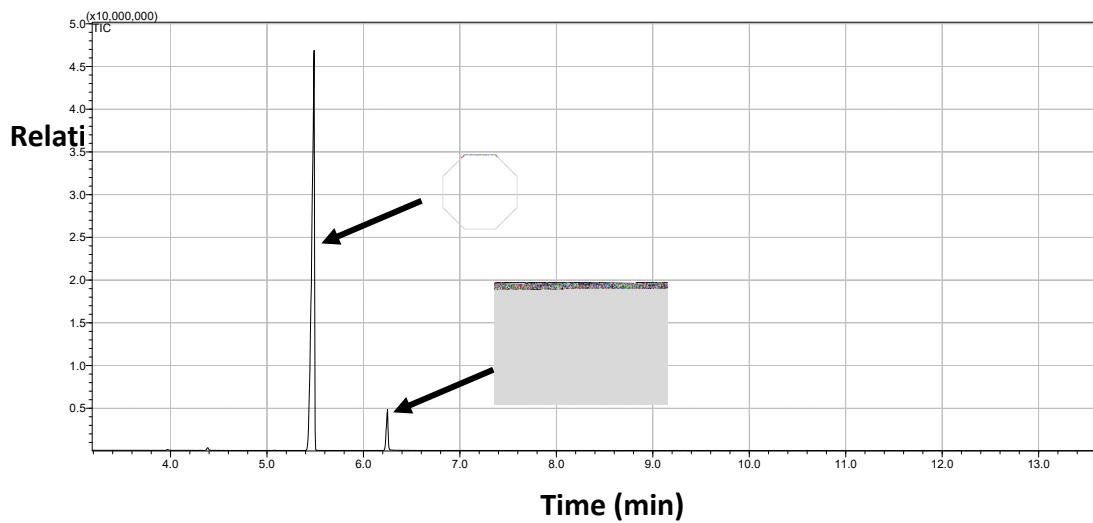
#### 4. Hydrogenation of Cyclooctene

| Entry | Substrate   | Product   | Time (h) | Conversion (%) | TOF (h-1) |
|-------|---|---|----------|----------------|-----------|
| 4     |  |  | 0.8      | 98.1           | 653       |

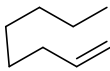
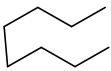
#### NMR spectra



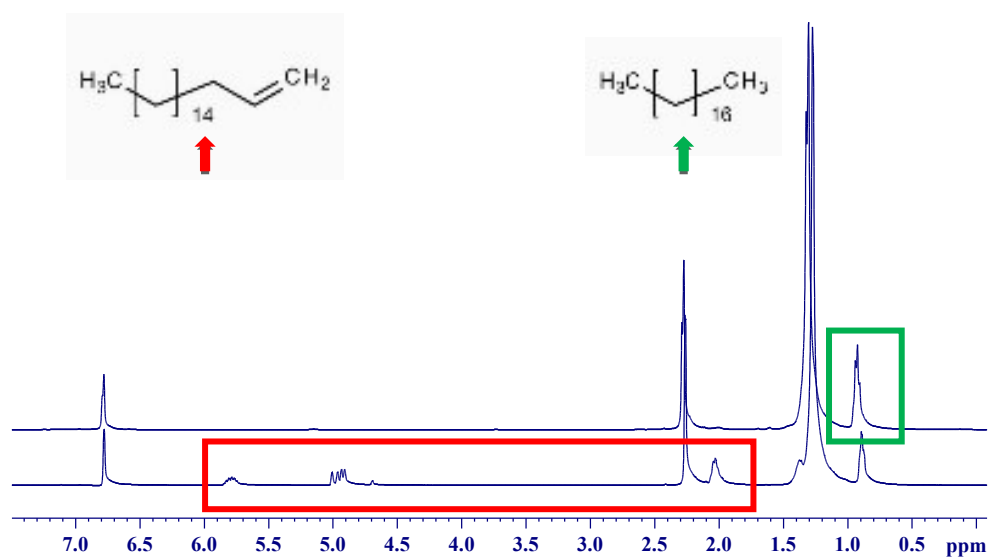
#### GC-MS spectrum



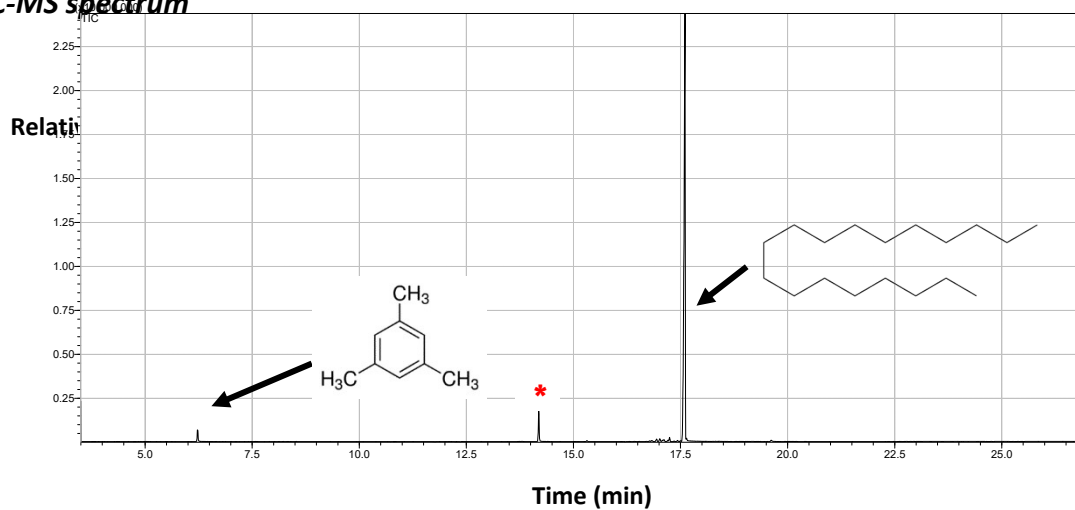
## 5. Hydrogenation of 1-octadecene

| Entry | Substrate   | Product   | Time (h) | Conversion (%) | TOF (h-1) |
|-------|---|---|----------|----------------|-----------|
| 5     |  |  | 9        | >99            | 55.5      |

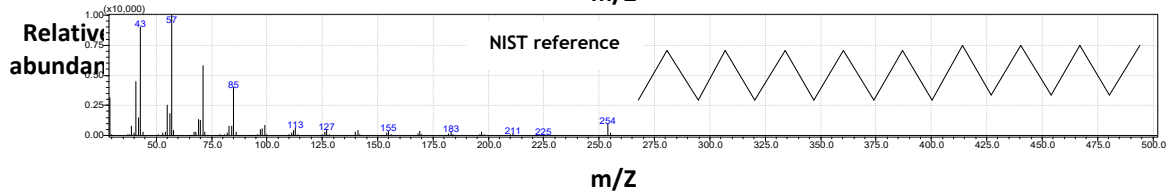
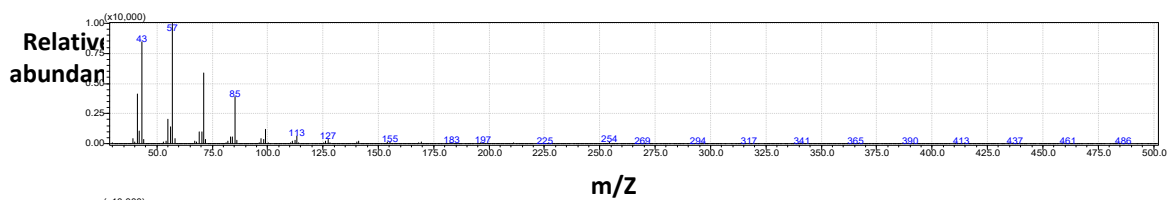
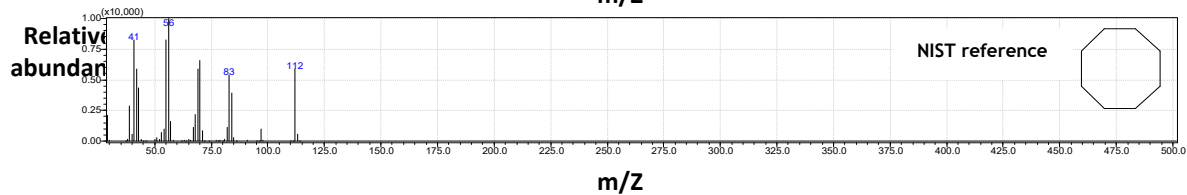
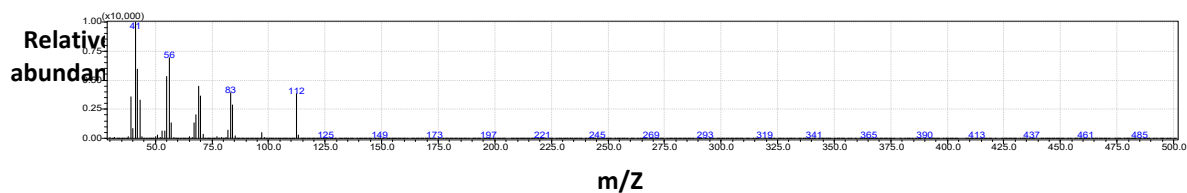
### NMR spectra



### GC-MS spectrum

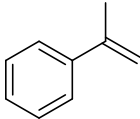
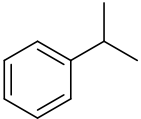




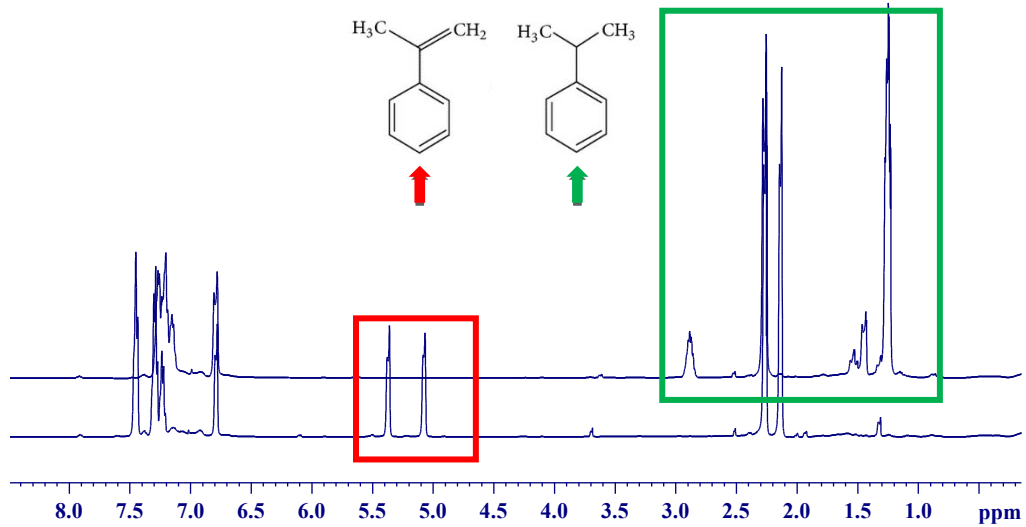


\* Butylated hydroxytoluene (BHT) present as stabilizer in THF used for sample dilution.

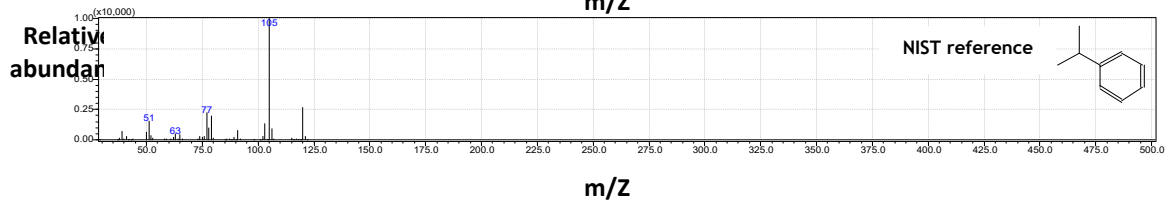
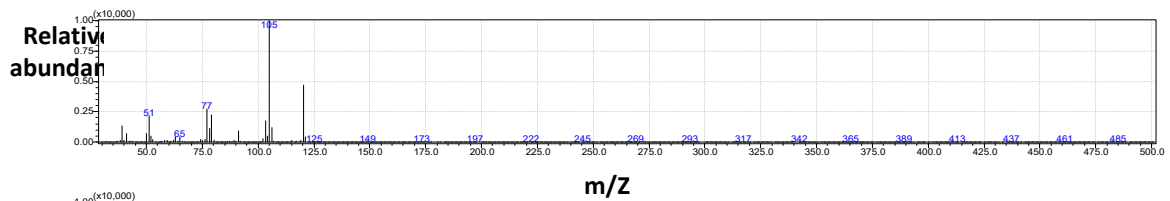
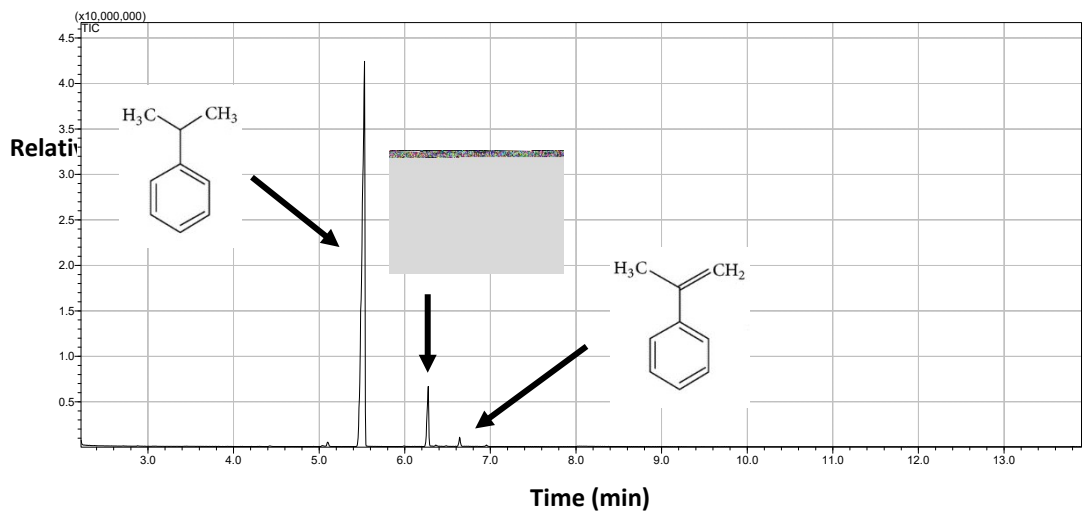
## 6. Hydrogenation of $\alpha$ -methyl styrene

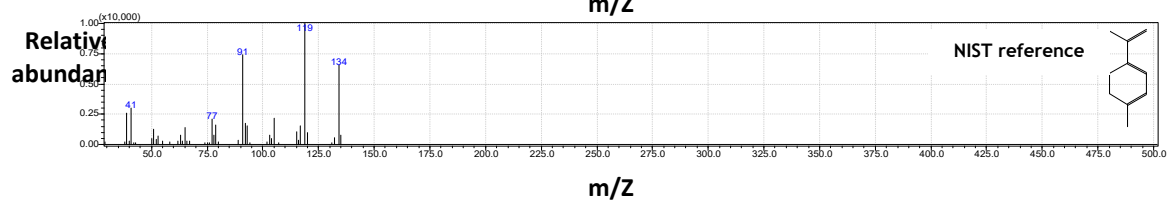
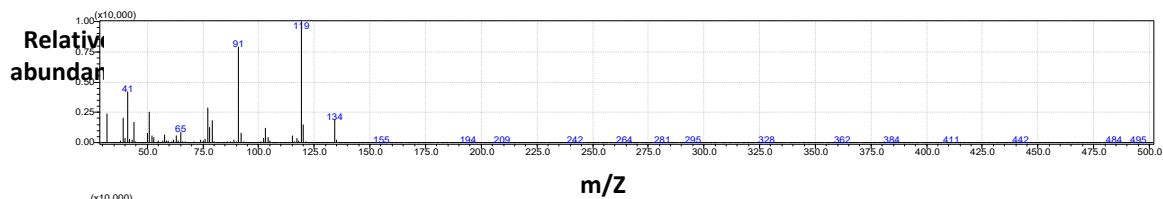
| Entry | Substrate   | Product   | Time (h) | Conversion (%) | TOF ( $\text{h}^{-1}$ ) |
|-------|---|---|----------|----------------|-------------------------|
| 6     |  |  | 1.2      | 97.5           | 420                     |

## NMR spectra



## GC-MS spectrum

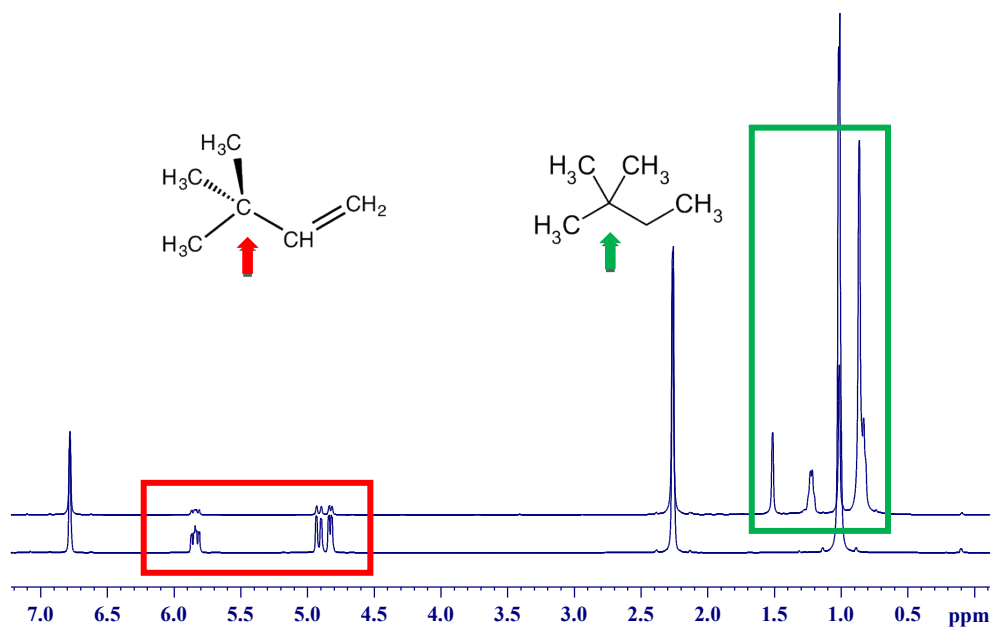




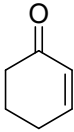
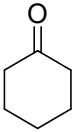
### 7. Hydrogenation of neohexene

| Entry | Substrate | Product | Time (h) | Conversion (%) | TOF ( $\text{h}^{-1}$ ) |
|-------|-----------|---------|----------|----------------|-------------------------|
| 7     |           |         | 9        | 57.0           | 37.6                    |

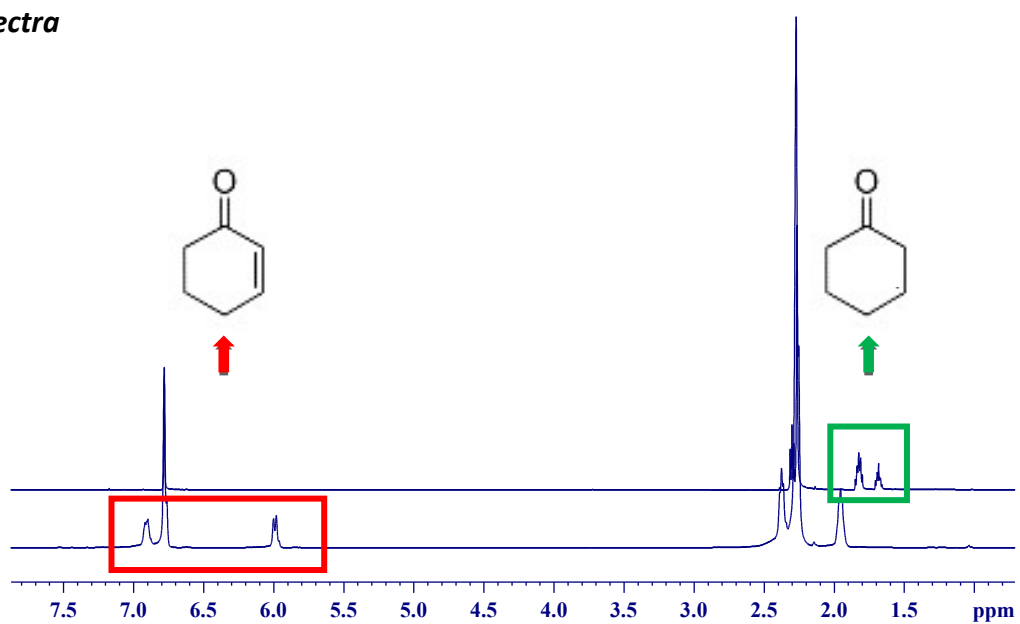
### NMR spectra



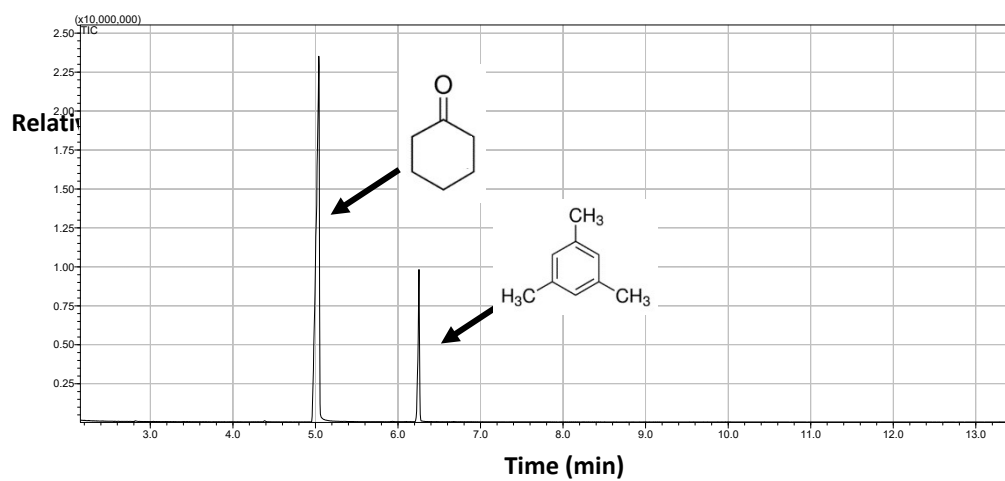
## 8. Hydrogenation of Cyclohexenone

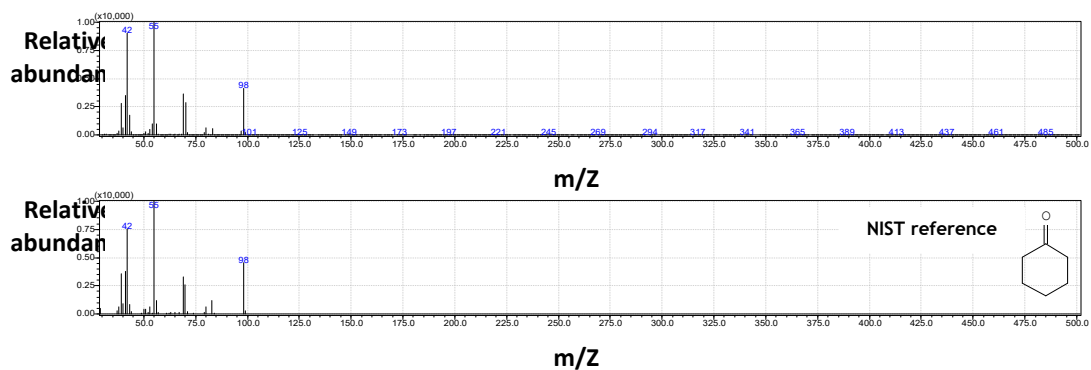
| Entry | Substrate   | Product   | Time (h) | Conversion (%) | TOF (h-1) |
|-------|---|---|----------|----------------|-----------|
| 8     |  |  | 5        | >99            | 100       |

### NMR spectra



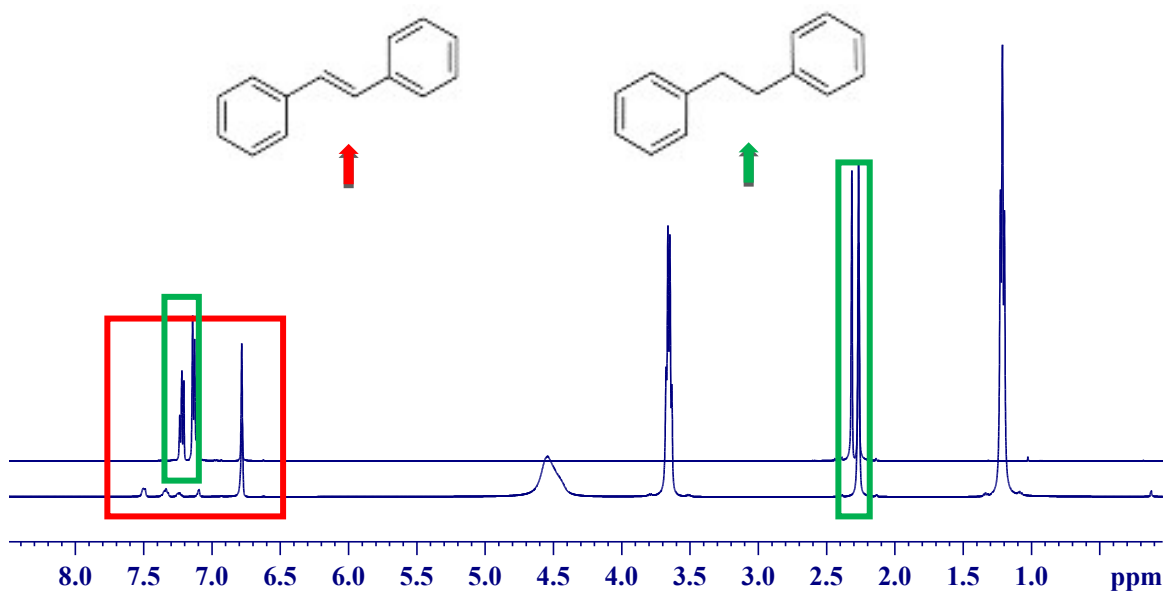
### GC-MS spectra



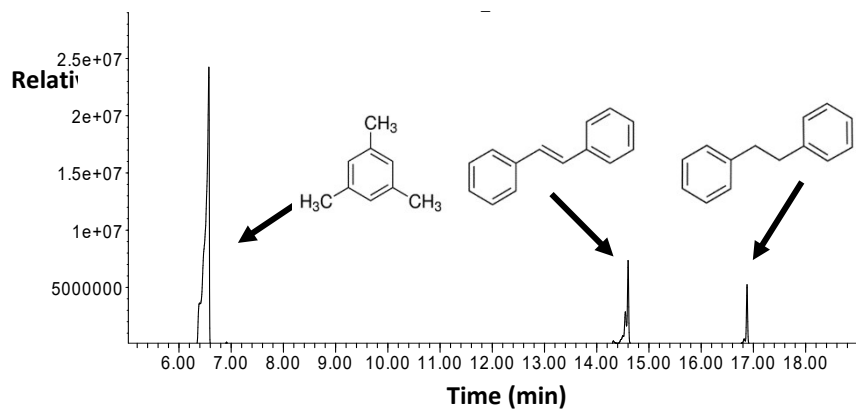


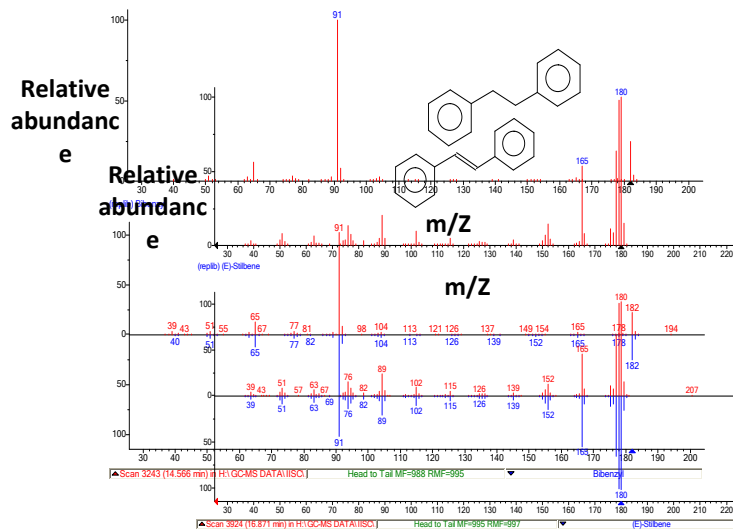
9. Hydrogenation of trans-stilbene

**NMR spectra**



**GC-MS spectrum**

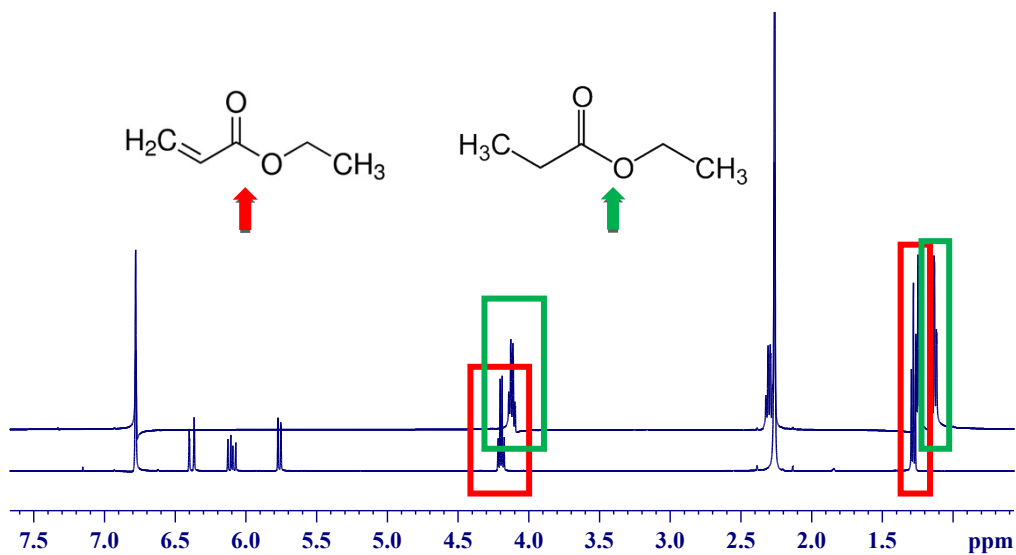




## 10. Hydrogenation of ethyl acrylate

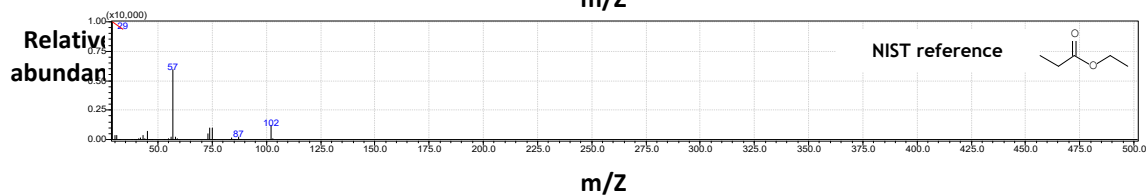
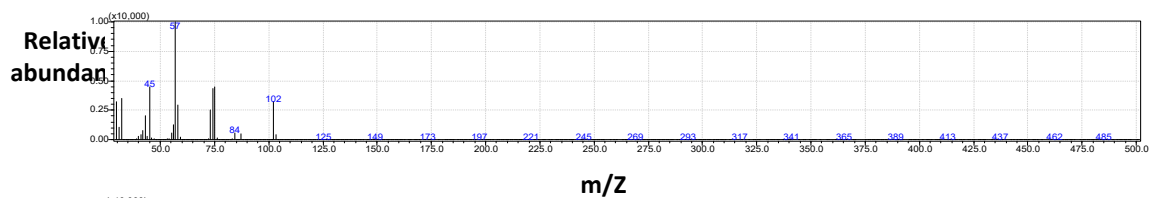
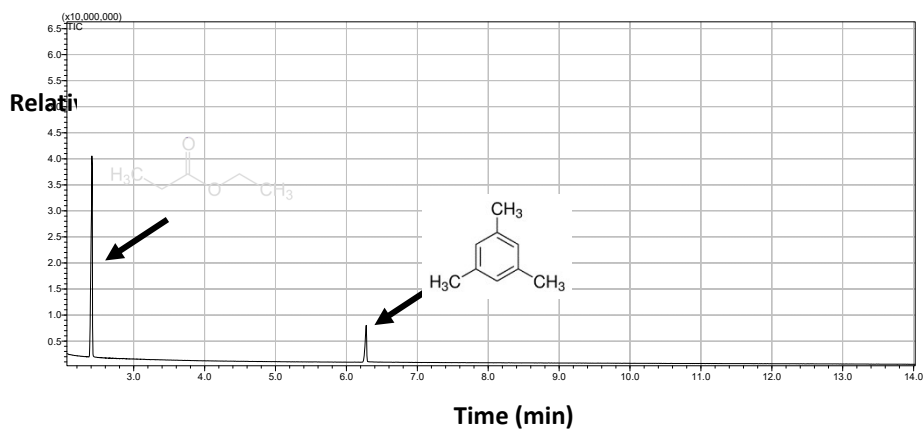
| Entry | Substrate              | Product                | Time (h) | Conversion (%) | TOF (h-1) |
|-------|------------------------|------------------------|----------|----------------|-----------|
| 10    | <chem>CCOC=CC=O</chem> | <chem>CCOC=CC=O</chem> | 0.3      | 97.0           | 1511      |

## NMR spectra





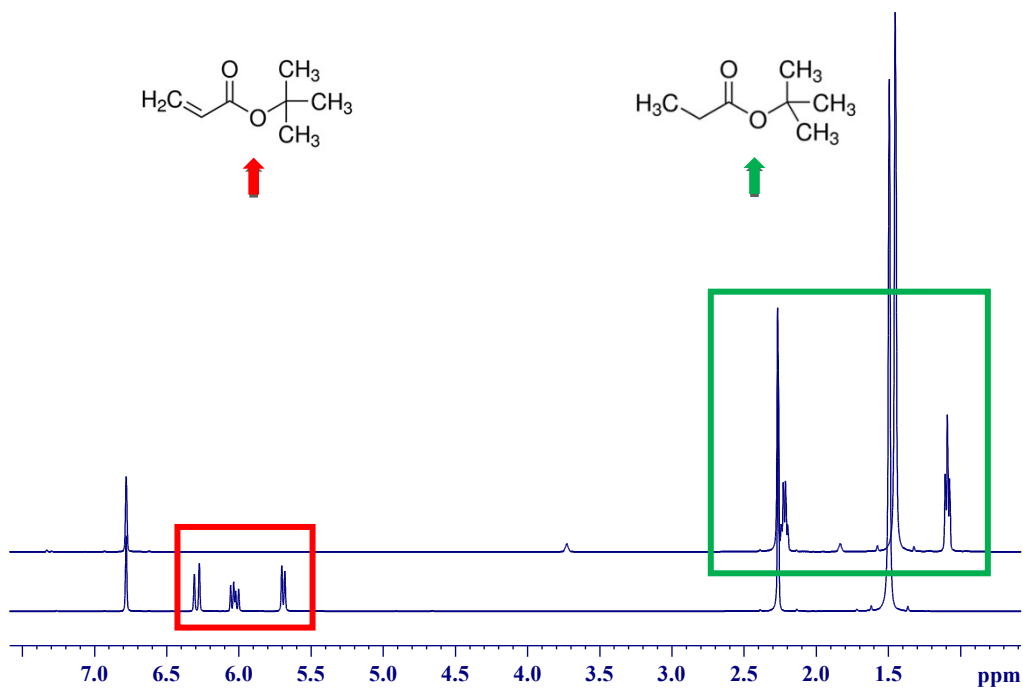
## GC-MS spectrum



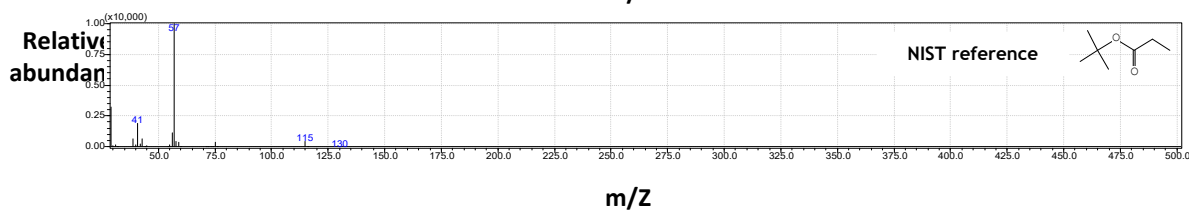
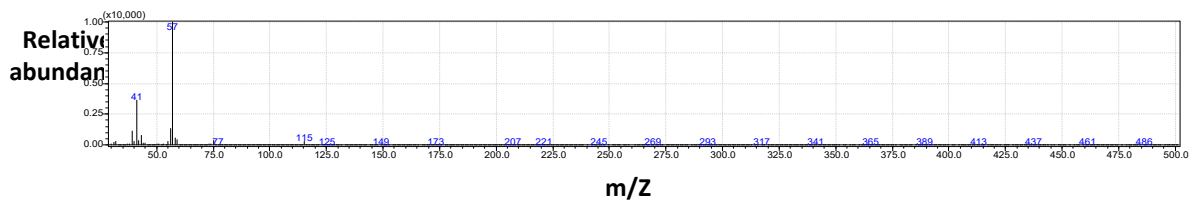
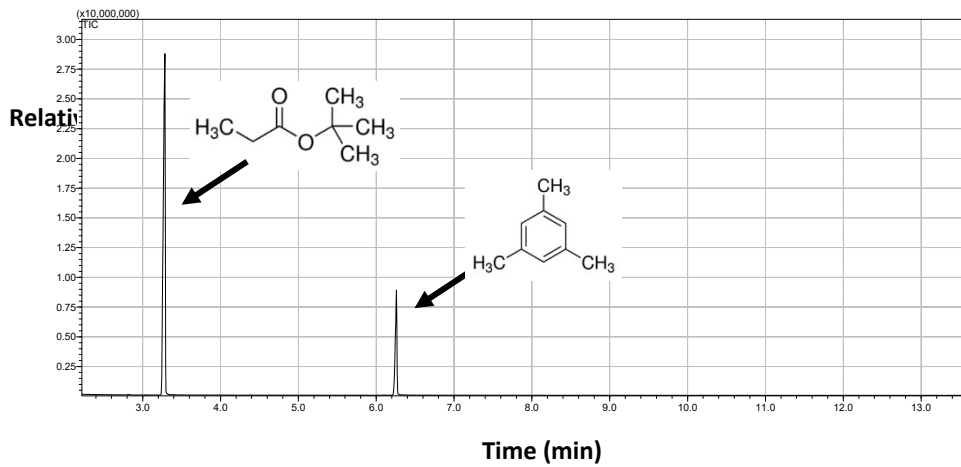
## 11. Hydrogenation of tertiary butyl acrylate

| Entry | Substrate                      | Product                       | Time (h) | Conversion (%) | TOF (h <sup>-1</sup> ) |
|-------|--------------------------------|-------------------------------|----------|----------------|------------------------|
| 11    | <chem>CC(C)(C)OC(=O)C=C</chem> | <chem>CC(C)(C)OC(=O)CC</chem> | 0.4      | >99            | 1388                   |

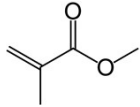
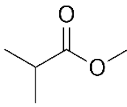
### NMR spectra



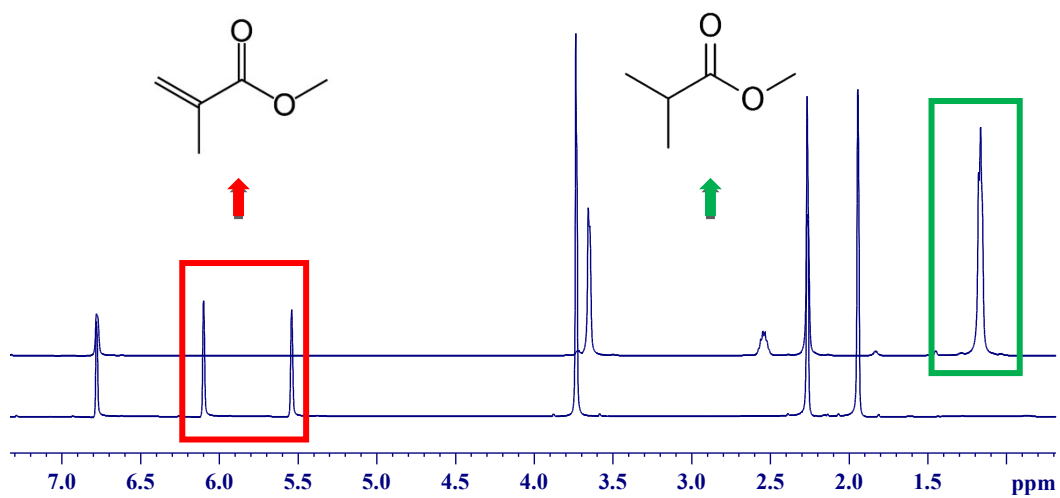
### GC-MS spectrum



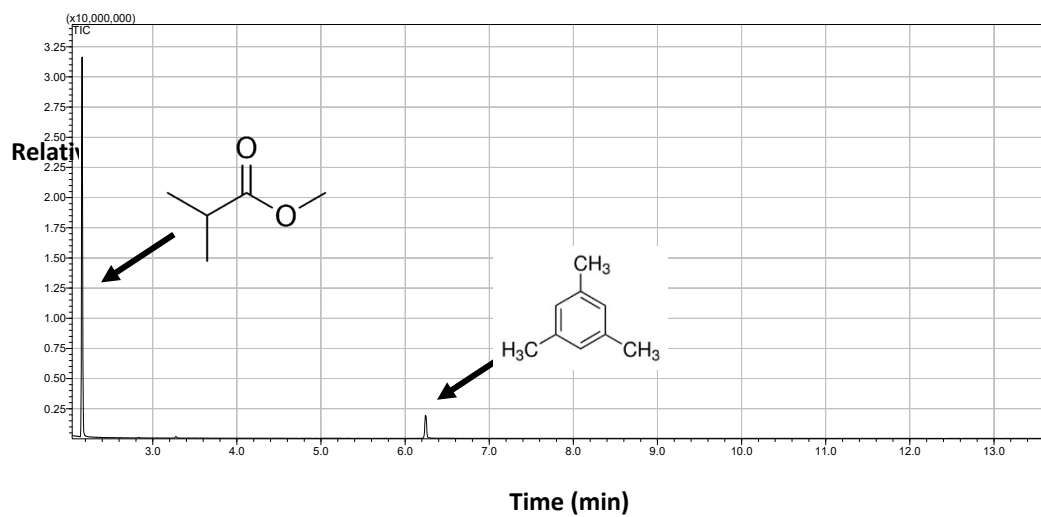
## 12. Hydrogenation of methyl methacrylate

| Entry | Substrate   | Product   | Time (h) | Conversion (%) | TOF (h <sup>-1</sup> ) |
|-------|---|---|----------|----------------|------------------------|
| 12    |  |  | 0.7      | >99            | 758                    |

### NMR spectra



### GC-MS spectrum



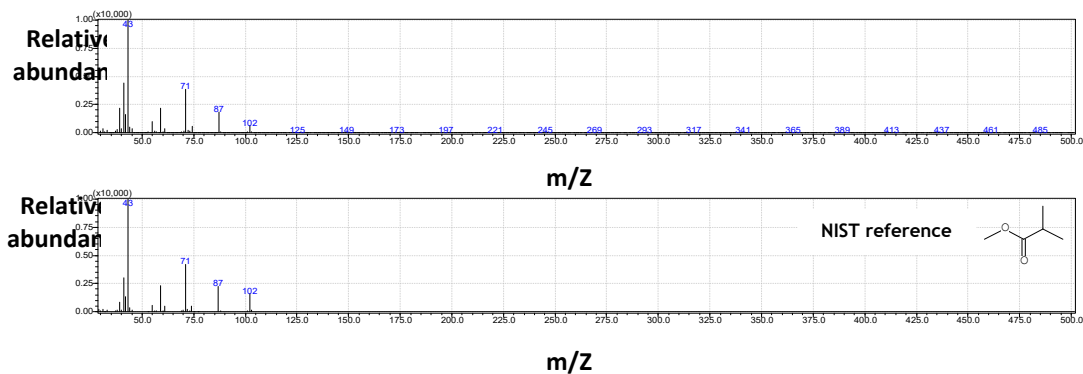


Figure S10. NMR spectral analysis corresponding to hydrogenation of Benzene in neat form using Pd<sub>0.5</sub>Ru<sub>0.5</sub> bimetallic catalyst. Reaction conditions: catalyst to substrate ratio of 1:500; H<sub>2</sub> gas pressure of 5 bar; room temperature condition.

### NMR spectra

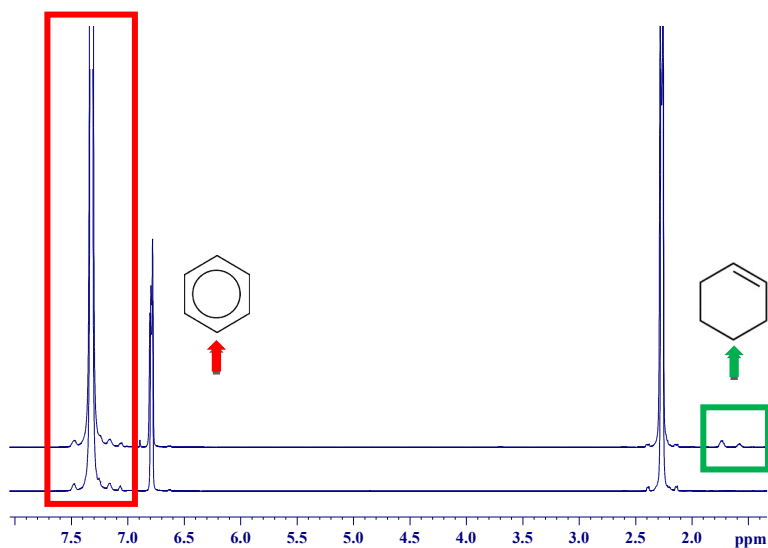
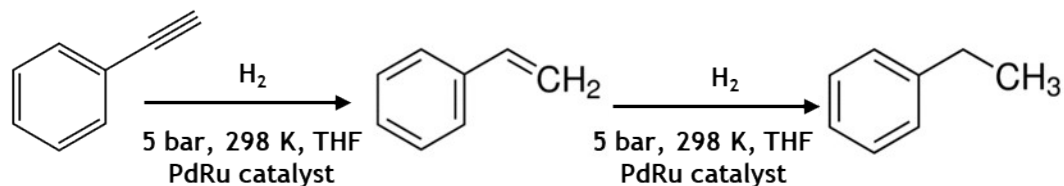
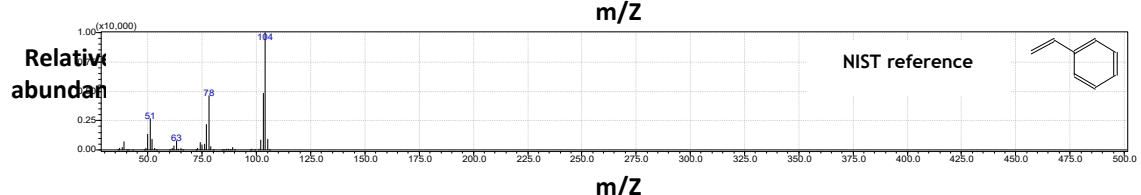
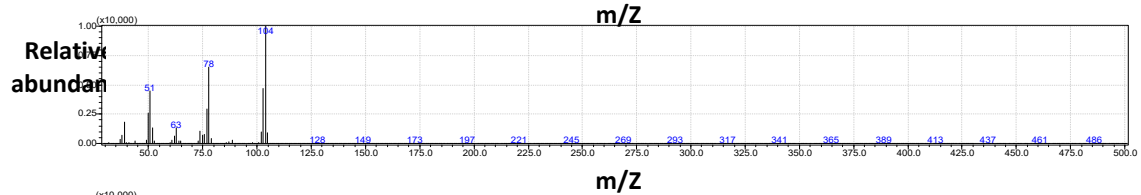
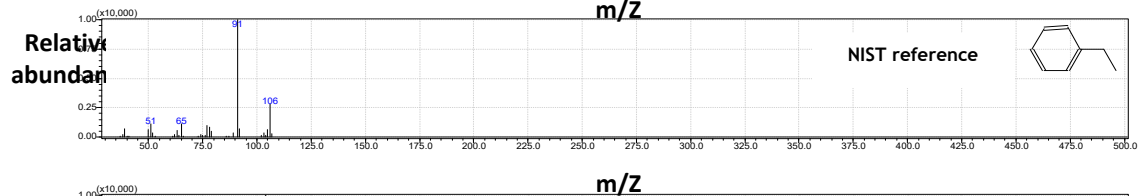
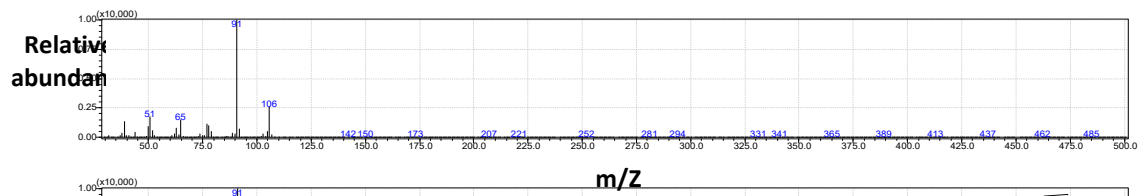
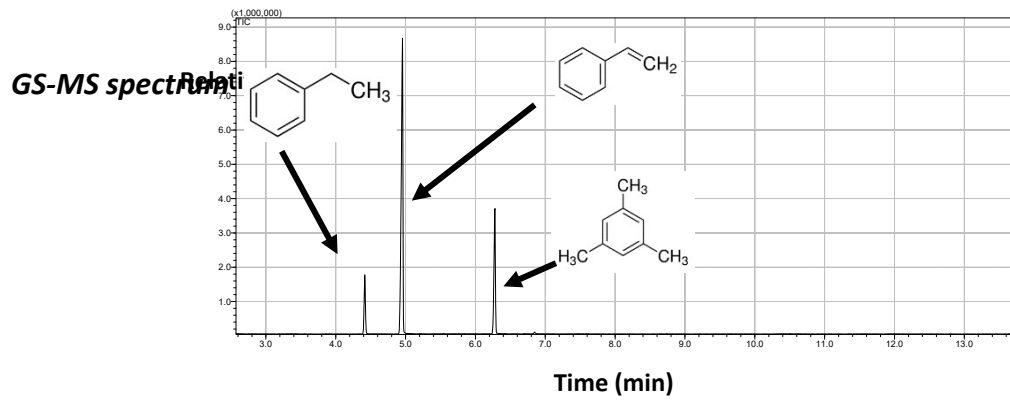


Figure S11. GC-MS analysis corresponding to sequential hydrogenation of phenyl acetylene (with THF as a solvent) using Pd<sub>0.5</sub>Ru<sub>0.5</sub> bimetallic catalyst. Reaction conditions: catalyst to substrate ratio of 1:500; H<sub>2</sub> gas pressure of 5 bar; room temperature condition.





## General Information

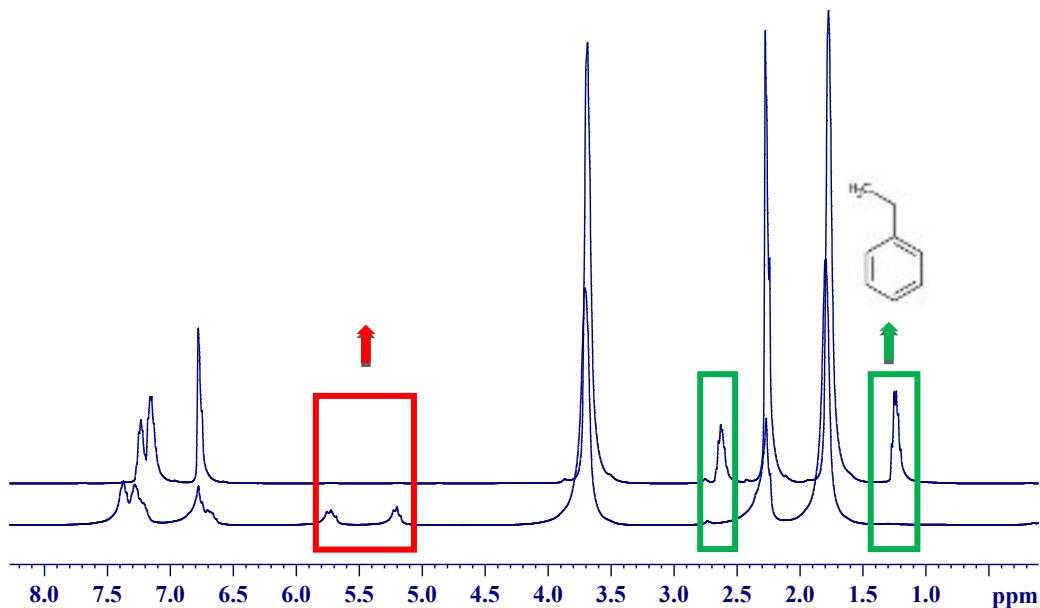
For evaluation of the performance of catalyst under different reaction conditions (Table 5.5) and recyclability study, styrene was used as a model substrate and the product obtained was ethyl benzene. The percentage conversion and turnover frequency ( $\text{h}^{-1}$ ) was calculated based on GC-MS studies. The retention time for ethyl benzene is 4.437 and that of styrene is 4.918 s. Only the gas-chromatogram and NMR spectra is provided for the reactions involving styrene and ethyl benzene.

Figure S12. NMR spectral and GC-MS analysis corresponding to hydrogenation reactions carried out on styrene in

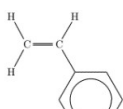
| Entry | Catalyst:<br>substrate<br>ratio | Pressure (bar) | Temperature<br>(K) | Time (h) | Conversion <sup>a</sup><br>(%) | TOF <sup>b</sup><br>( $\text{h}^{-1}$ ) |
|-------|---------------------------------|----------------|--------------------|----------|--------------------------------|---|
| 1     | 1:500                           | 3              | 323                | 8.6      | >99                            | 58.1                                    |

neat form using  $\text{Pd}_{0.5}\text{Ru}_{0.5}$  bimetallic catalyst [Table 4]

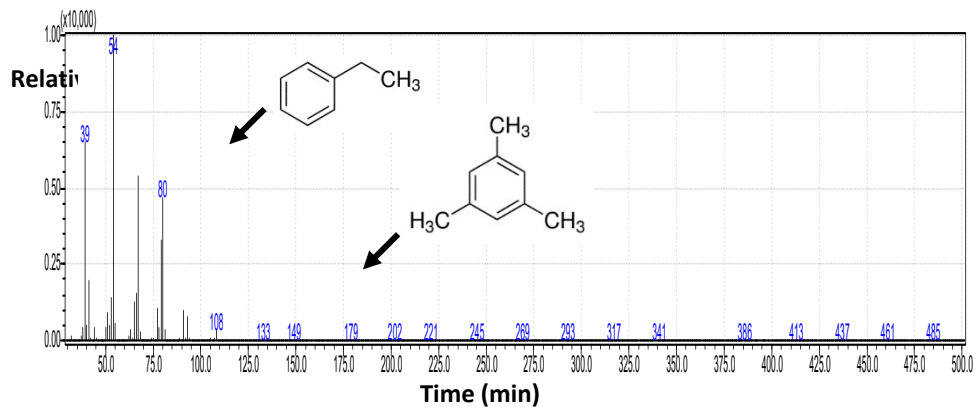
### 1. Hydrogenation of Styrene



### NMR spectra





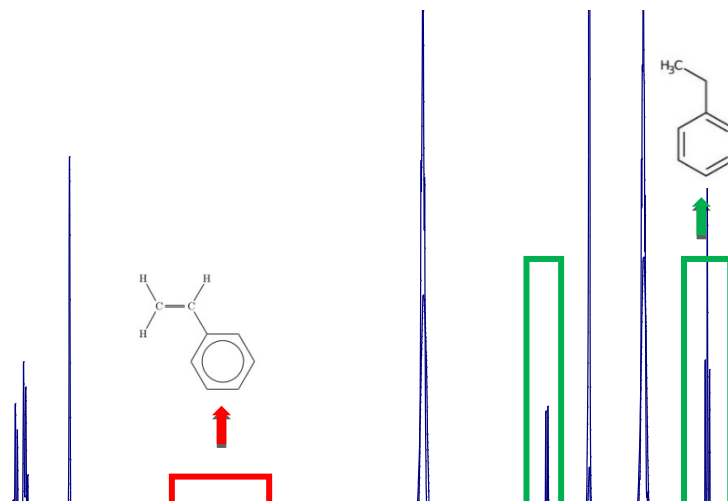


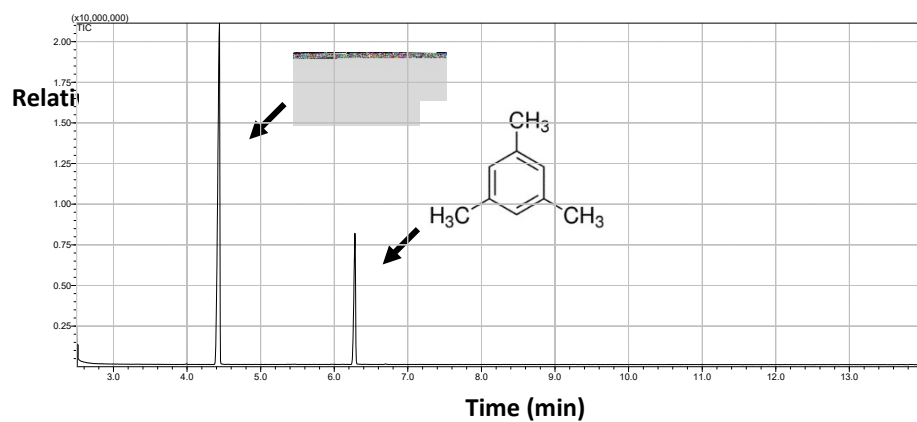
| Entry | Catalyst:<br>substrate<br>ratio | Pressure<br>(bar) | Temperature<br>(K) | Time (h) | Conversion <sup>a</sup><br>(%) | TOF <sup>b</sup><br>(h <sup>-1</sup> ) |
|-------|---------------------------------|-------------------|--------------------|----------|--------------------------------|--|
| 2     | 1:500                           | 5                 | 298                | 15       | >99                            | 33.3                                   |

### Gas-chromatogram

2. Hydrogenation of Styrene

### NMR spectra



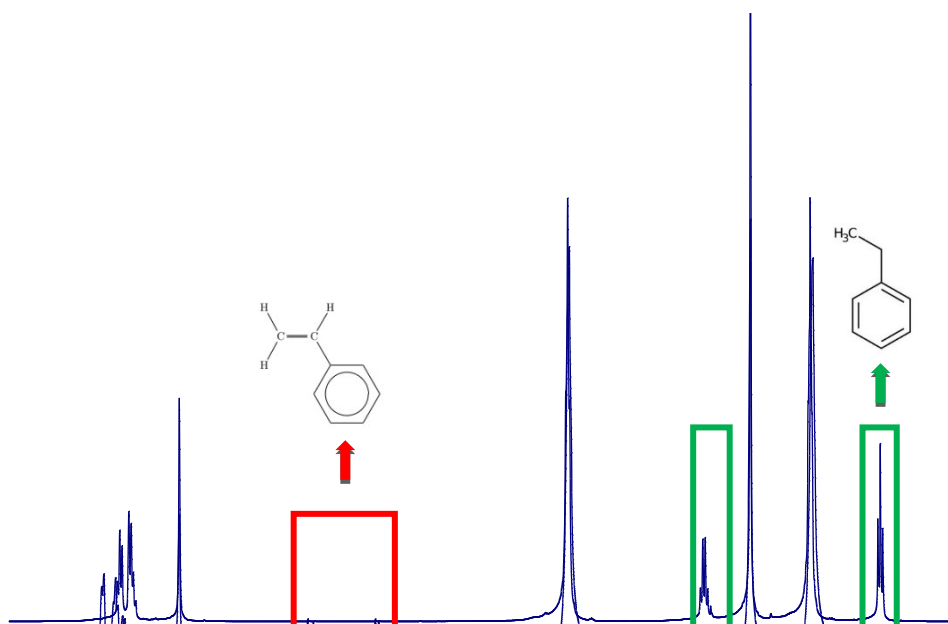


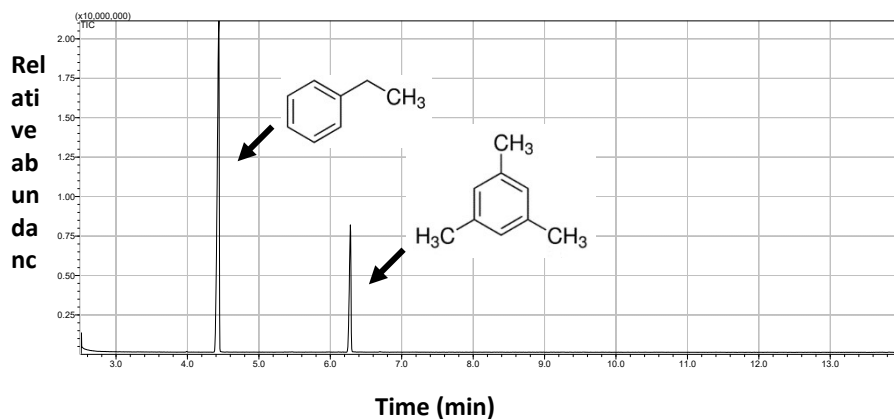
| Entry | Catalyst:<br>substrate ratio | Pressure (bar) | Temperature<br>(K) | Time (h) | Conversion <sup>a</sup><br>(%) | TOF <sup>b</sup><br>(h <sup>-1</sup> ) |
|-------|------------------------------|----------------|--------------------|----------|--------------------------------|--|
| 3     | 1:500                        | 5              | 323                | 5        | >99                            | 100                                    |

### Gas-chromatogram

### 3. Hydrogenation of Styrene

### NMR spectra



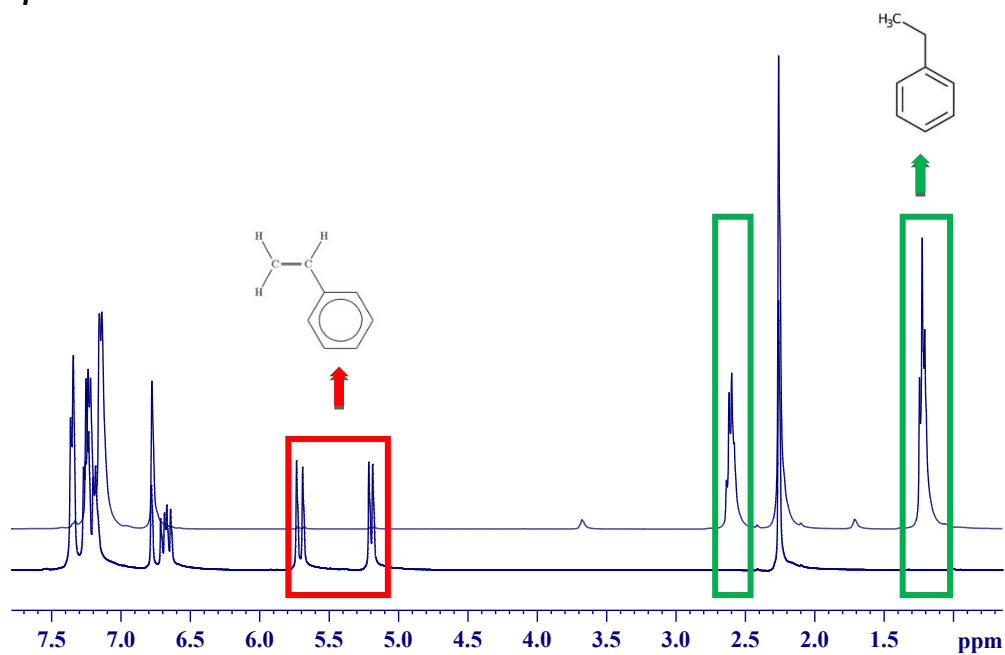


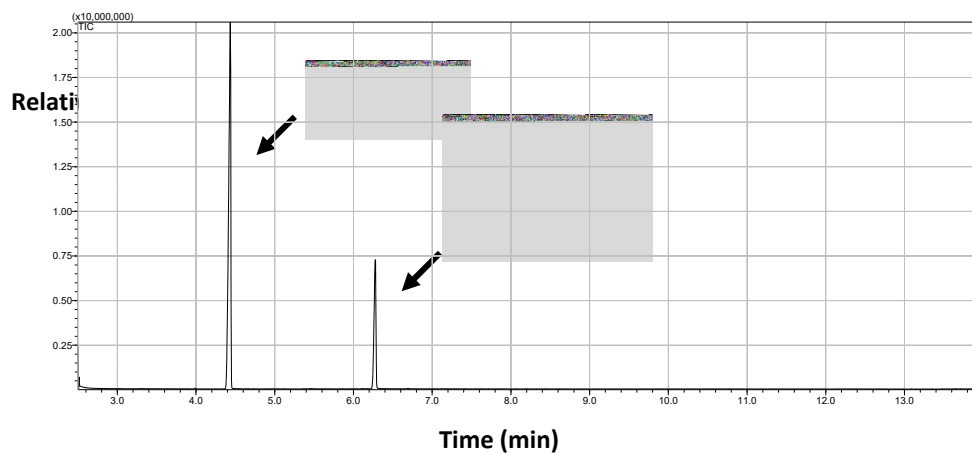
| Entry | Catalyst:<br>substrate<br>ratio | Pressure (bar) | Temperature<br>(K) | Time (h) | Conversion <sup>a</sup><br>(%) | TOF <sup>b</sup><br>(h <sup>-1</sup> ) |
|-------|---------------------------------|----------------|--------------------|----------|--------------------------------|--|
| 4     | 1:1000                          | 5              | 323                | 6.5      | >99                            | 153.8                                  |

### Gas-chromatogram

4. Hydrogenation of Styrene

### NMR spectra



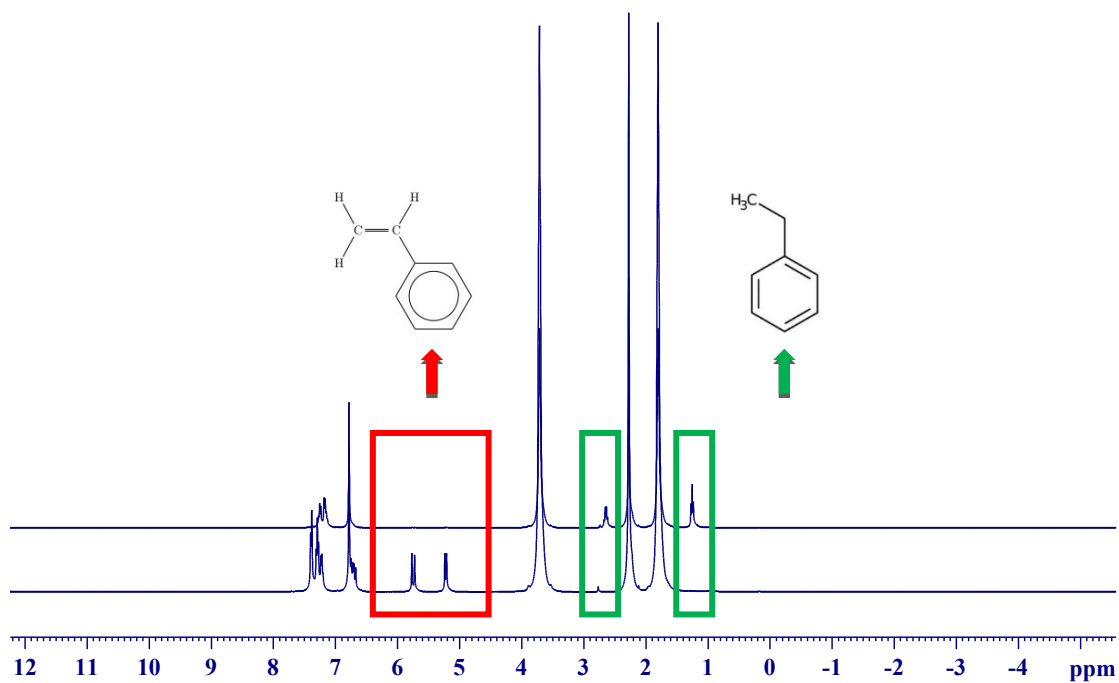


| Entry | Catalyst:<br>substrate<br>ratio | Pressure (bar) | Temperature<br>(K) | Time (h) | Conversion <sup>a</sup><br>(%) | TOF <sup>b</sup><br>(h <sup>-1</sup> ) |
|-------|---------------------------------|----------------|--------------------|----------|--------------------------------|--|
| 5     | 1:2000                          | 5              | 323                | 8        | >99                            | 250                                    |

### Gas-chromatogram

#### 5. Hydrogenation of Styrene

### NMR spectra



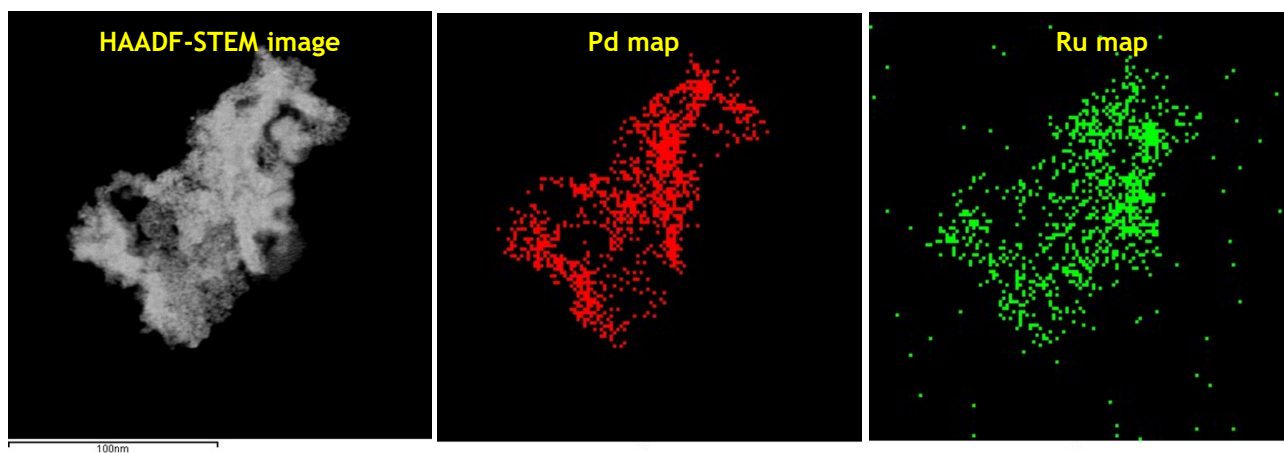
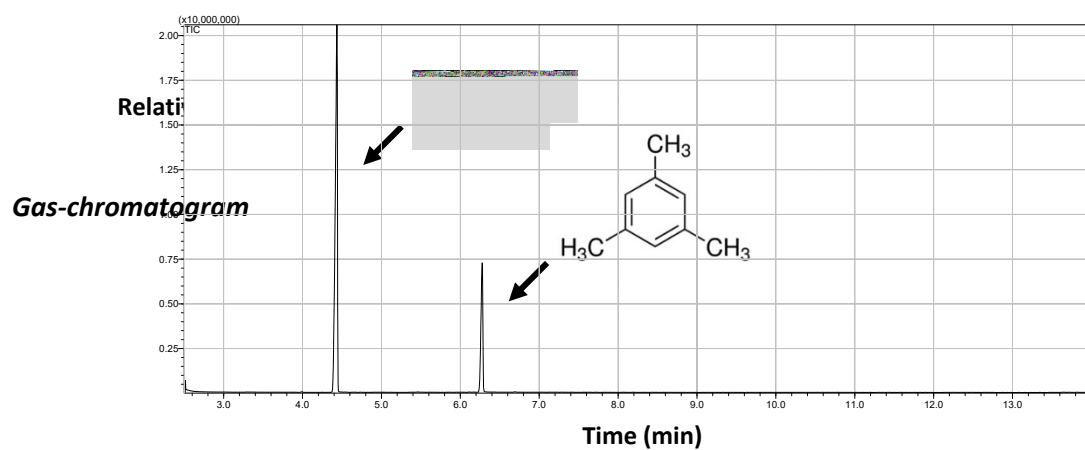
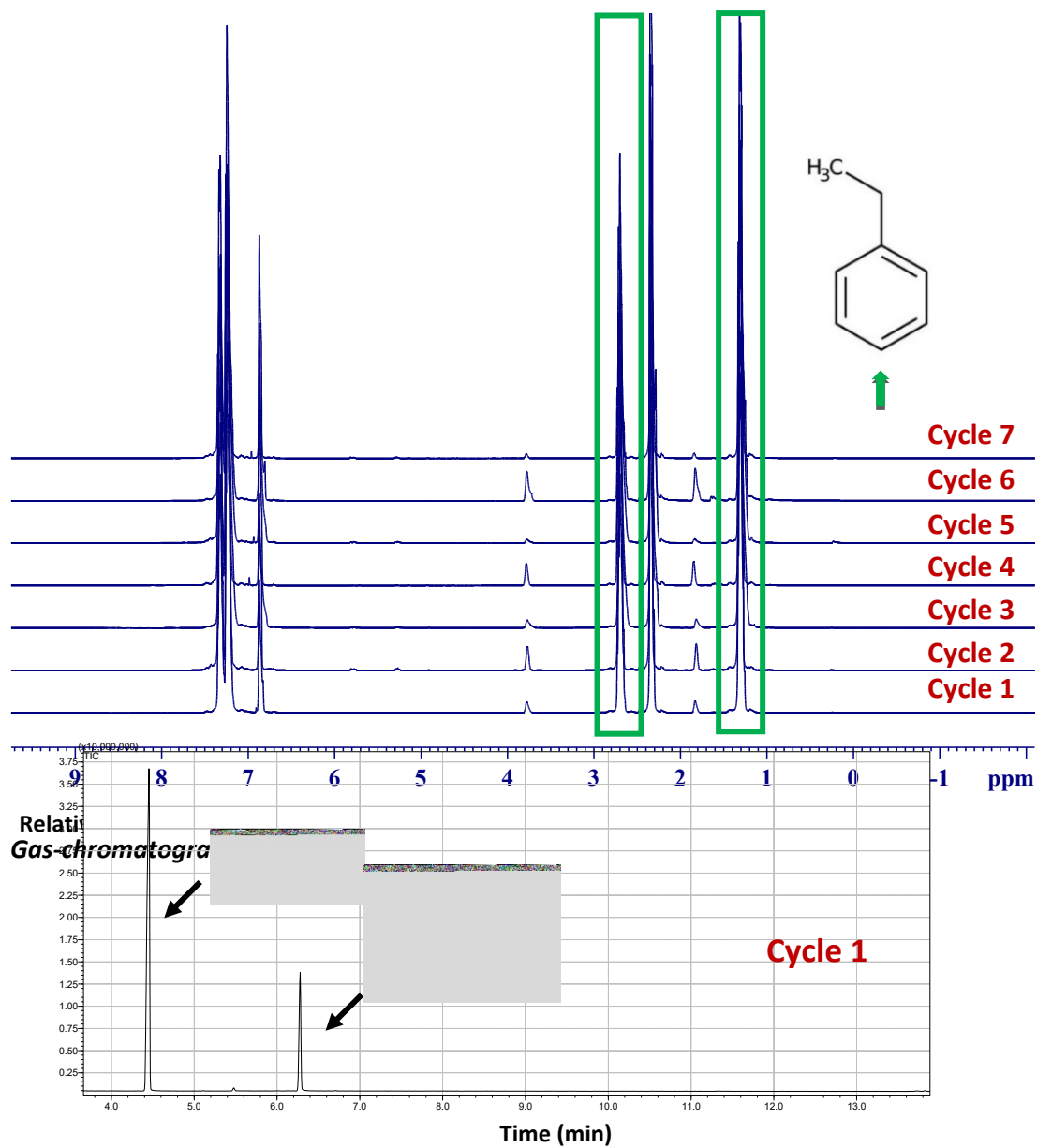
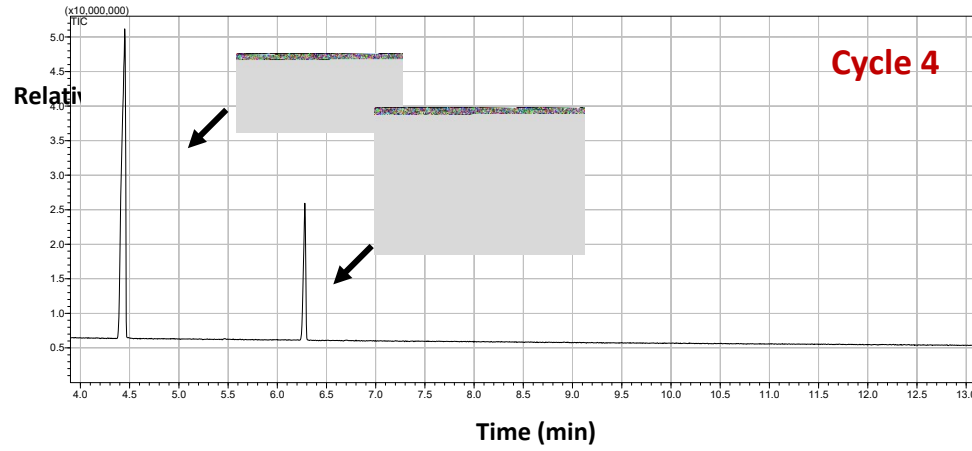
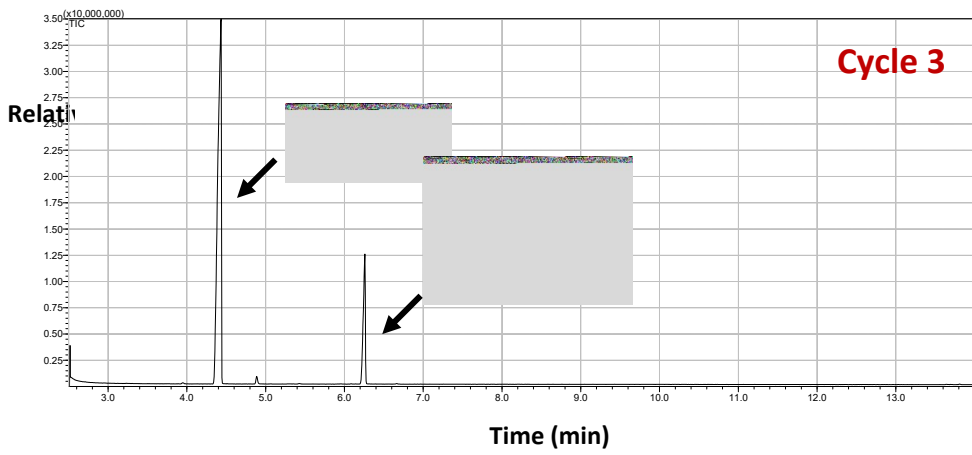
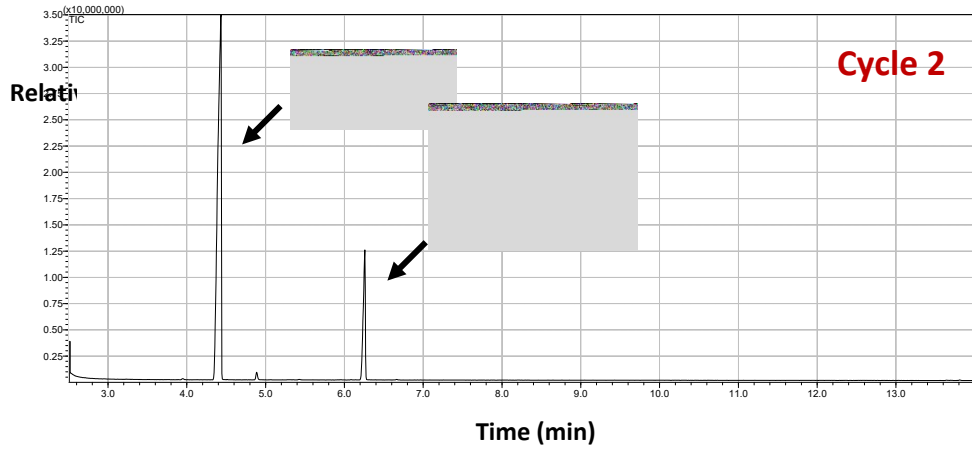


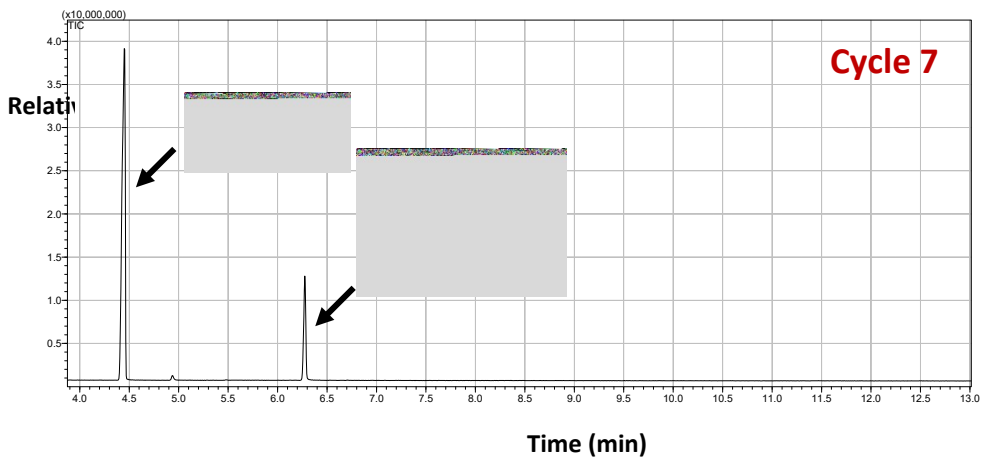
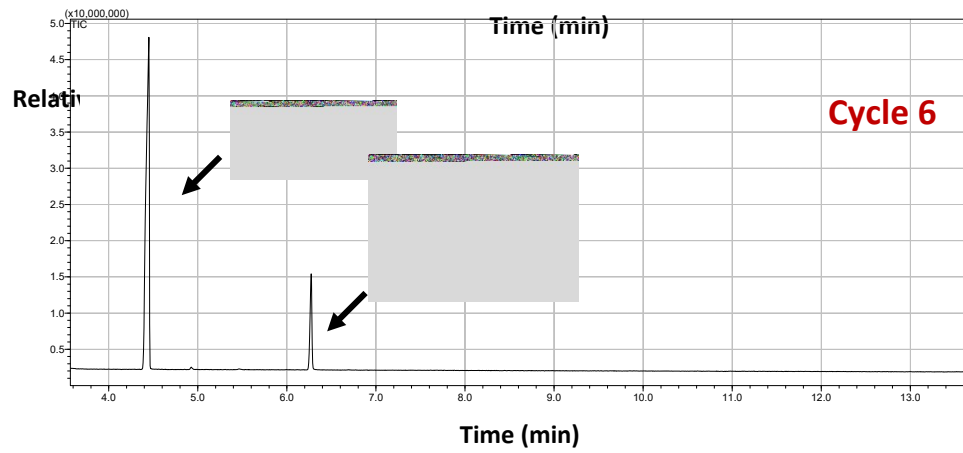
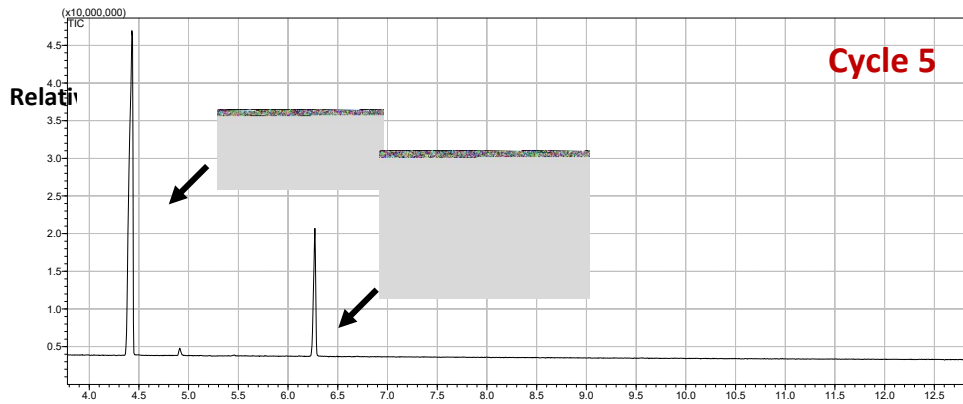
Figure S13. Enlarged STEM EDS area map images corresponding to catalyst recycling for neat styrene hydrogenation by Pd-Ru nanocomposite for 7 cycles using Pd<sub>0.5</sub>Ru<sub>0.5</sub> bimetallic catalysts. Reaction Conditions: 5 bar, 298 K, 1:500 catalyst to substrate ratio (Reference to Figure 7)

Figure S14. NMR spectral and GC-MS analysis corresponding to catalyst recycling for neat styrene hydrogenation by Pd-Ru nanocomposite for 7 cycles using Pd<sub>0.5</sub>Ru<sub>0.5</sub> bimetallic catalysts. Reaction Conditions: 5 bar, 298 K, 1:500 catalyst to substrate ratio

**NMR spectra**









**NMR spectra**

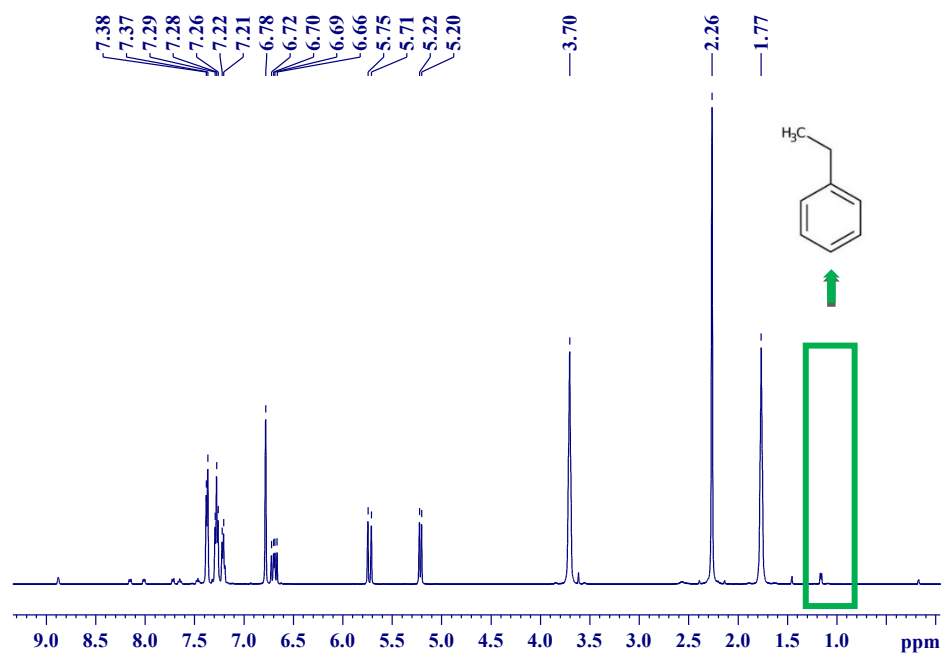


Figure S15. NMR spectral analysis corresponding to catalyst poisoning study using neat styrene as substrate and tricyclohexylphosphine (PCy<sub>3</sub>) as catalyst poison. Reaction Conditions: 5 bar, 298 K, 1:500 catalyst to substrate ratio

**NMR spectra**

Figure S16. NMR spectral analysis corresponding to catalyst poisoning study using neat styrene as substrate and quinoline as catalyst poison. Reaction Conditions: 5 bar, 298 K, 1:500 catalyst to substrate ratio

