

# **SUPPORTING INFORMATION**

## ***Dendritic ZSM-5 Zeolites as Highly Active Catalysts for the Valorization of Monoterpene Epoxides***

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**Figure S5.** Initial reaction rate of limonene-1,2-epoxide as a function of catalyst mass over d-ZSM-5/7d. **Reaction conditions:**  $C_{\text{substrate},0} = 13 \text{ mmol L}^{-1}$ , 150 mL of total volume, anhydrous ethyl acetate as a solvent, 70 °C, 520-530 rpm,  $N_2$  atmosphere.

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**Figure S10.** Representative chromatogram of a reaction sample after 2 h in the isomerization of limonene-1,2-epoxide. **Reaction conditions:**  $C_{\text{substrate},0} = 13 \text{ mmol L}^{-1}$ , 75 mL of total volume, DMC as a solvent, 115 mg of d-ZSM-5/4d, 70 °C, 520-530 rpm,  $\text{N}_2$  atmosphere.

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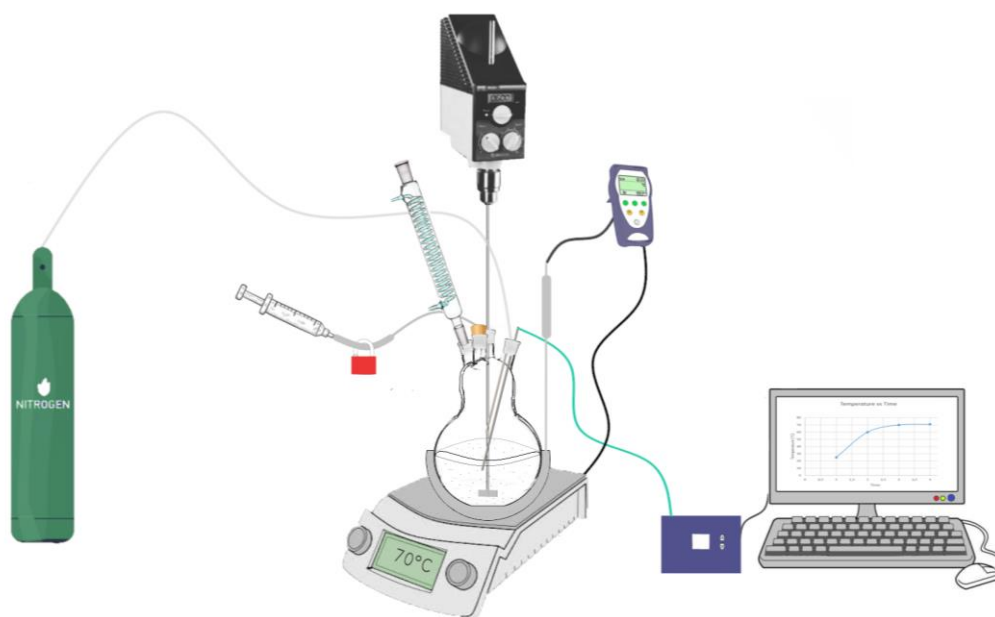
**Figure S17.** Representative chromatogram of a reaction sample after 60 min in the isomerization of  $\beta$ -pinene epoxide. **Reaction conditions:**  $C_{\text{substrate},0} = 13 \text{ mmol L}^{-1}$ , 75 mL of total volume, ethyl acetate as a solvent, 115 mg of d-ZSM-5/4d, 50 °C, 520-530 rpm,  $\text{N}_2$  atmosphere.

**Figure S18.** Mass spectrum of product 1.

**Figure S19.** Mass spectrum of product 2.

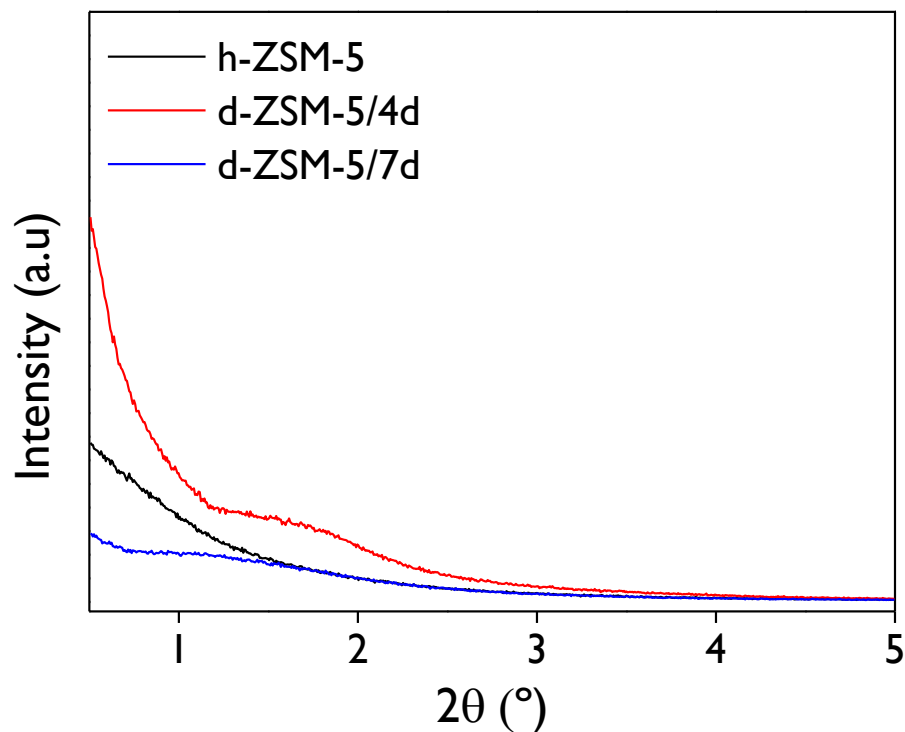
**Figure S20.** Mass spectrum of product 3.

## 1. Scheme of the reaction setup



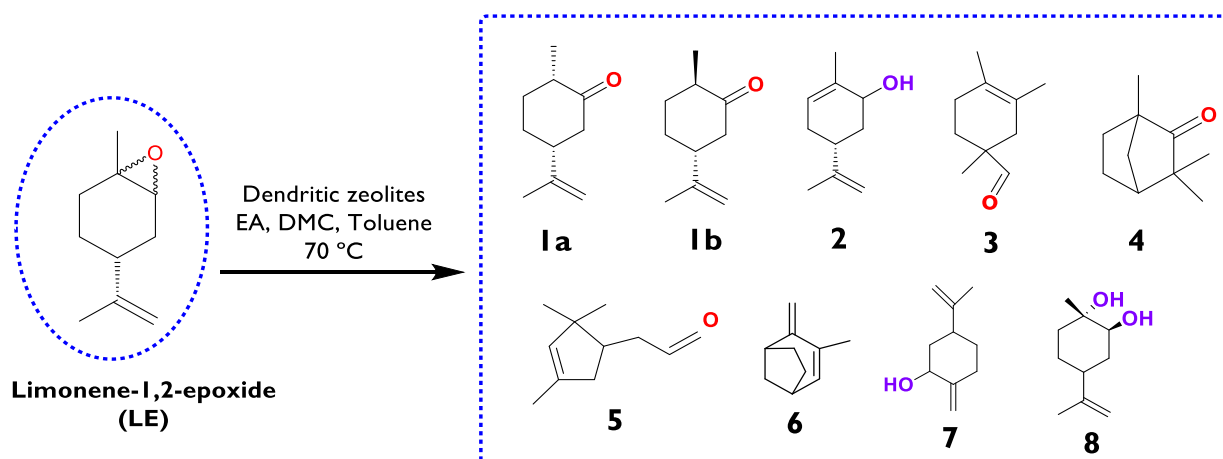
**Figure S1.** Reaction setup equipped with a mechanical stirrer, a condenser, a thermocouple, an N<sub>2</sub> feeding, and a sampling valve.

## 2. Low-angle XRD patterns



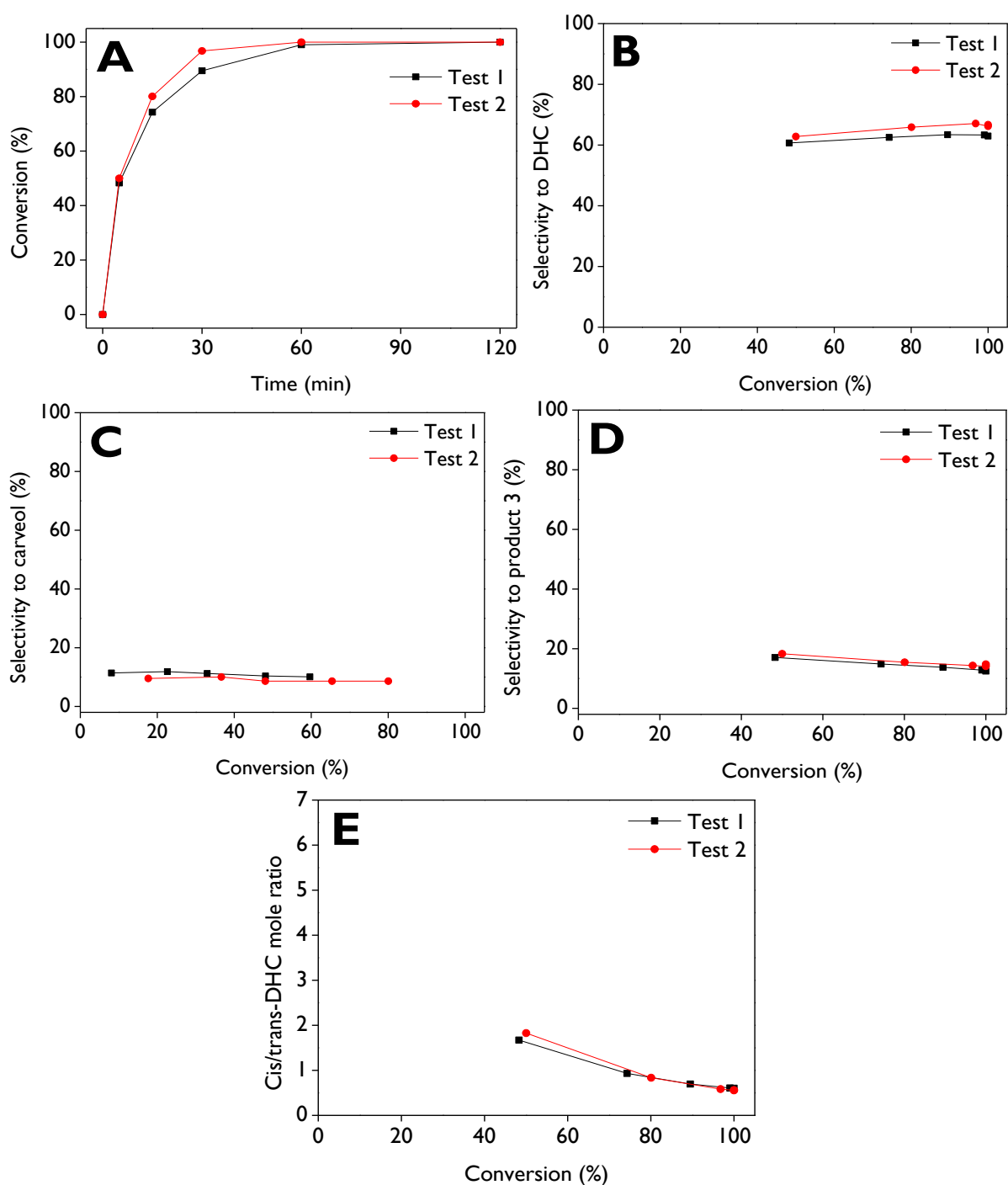
**Figure S2.** Low-angle XRD patterns of the zeolite samples.

### 3. Scheme of reaction products of limonene-1,2-epoxide isomerization



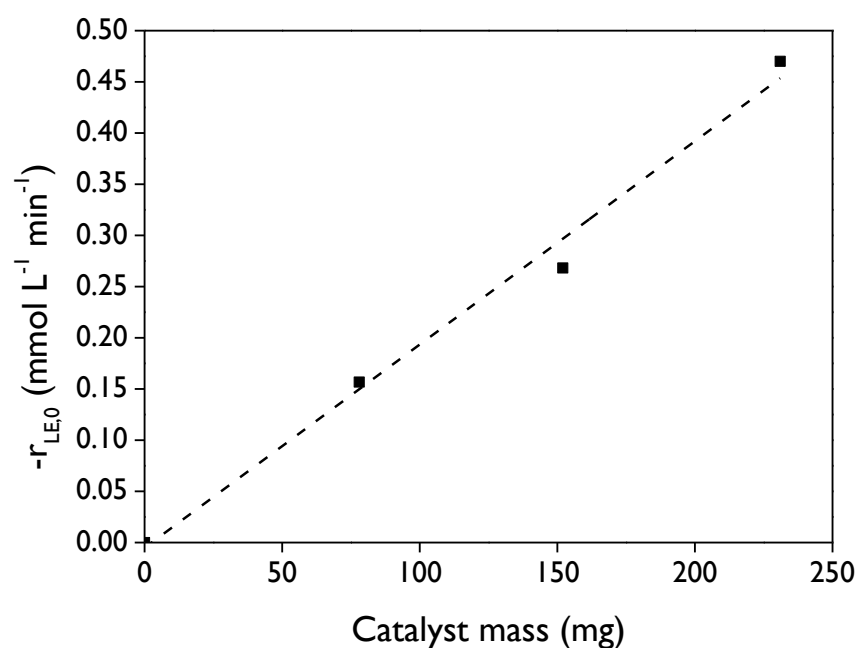
**Figure S3.** Reaction products of limonene-1,2-epoxide transformations over heterogeneous catalysts based on zeolite ZSM-5.

#### 4. Repeatability test



**Figure S4.** Repeatability test of d-ZSM-5/4d in the isomerization of LE. **(A)** LE conversion as a function of the reaction time, **(B)** selectivity to dihydrocarvone, **(C)** selectivity to carveol, **(D)** selectivity to product **3**, and **(E)** cis/trans dihydrocarvone mole ratio, as a function of the conversion. **Reaction conditions:**  $C_{LE,0} = 13 \text{ mmol L}^{-1}$ , 75 mL of total volume, anhydrous ethyl acetate as a solvent, 115 mg of catalyst, 70 °C, 520-530 rpm,  $N_2$  atmosphere.

## 5. Confirmation of catalytic route



**Figure S5.** Initial reaction rate of limonene-1,2-epoxide as a function of catalyst mass over d-ZSM-5/7d. **Reaction conditions:**  $C_{\text{substrate},0} = 13 \text{ mmol L}^{-1}$ , 150 mL of total volume, anhydrous ethyl acetate as a solvent, 70 °C, 520-530 rpm, N<sub>2</sub> atmosphere.

## 6. Turnover Frequency (TOF)

**Table S1.** Comparison of turnover of frequency (TOF) for various heterogeneous catalysts in the limonene-1,2-epoxide isomerization.

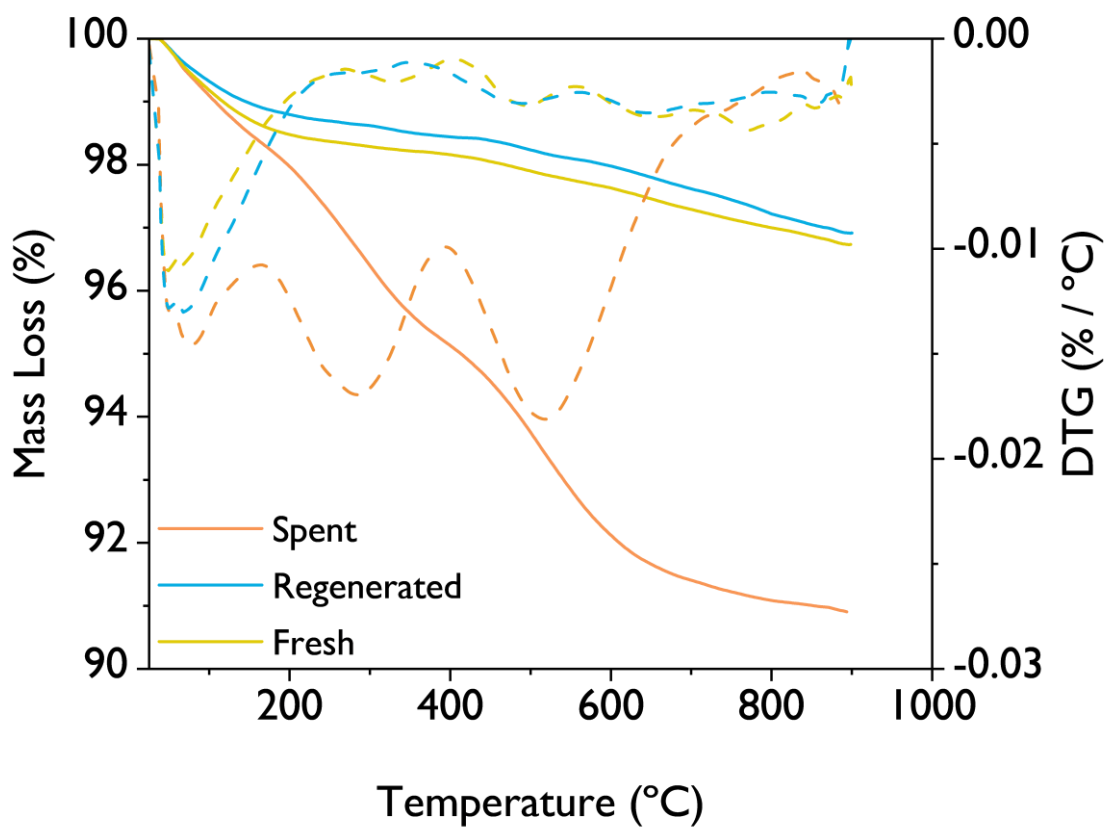
| Catalyst                   | Solvent       | Reaction conditions  | TOF <sup>b</sup> (min <sup>-1</sup> ) | Selectivity to target (%) <sup>d</sup> | Reference |
|----------------------------|---------------|--|---------------------------------------|--|-----------|
| ZSM-5                      | Ethyl acetate | 13 mmol L <sup>-1</sup> , 75 mL of total                                   | 0.6                                   | 42 (20)                                | This work |
| h-ZSM-5                    | Ethyl acetate | volume, 115 mg of catalyst, 70 °C,   | 1.6                                   | 43 (60)                                |           |
| d-ZSM-5/4d                 | Ethyl acetate | 520-530 rpm, N <sub>2</sub> atmosphere                                     | 4.4                                   | 62 (60)                                |           |
| d-ZSM-5/7d                 | Ethyl acetate |  | 2.3                                   | 55 (60)                                |           |
| 3.9Fe/SBA15 <sup>a</sup>   | Toluene       | 0.25 mmol of substrate, 1 mL of solvent, 70 °C, 750 rpm, 10 mg of catalyst | 0.46                                  | 42 (21)                                | [1]       |
|                            | Ethyl acetate |  | 0.29                                  | 44 (15)                                |           |
|                            | Acetonitrile  |  | 0.12                                  | 50 (5)                                 |           |
|                            | Acetone       |  | 0.35                                  | 0 (17)                                 |           |
|                            | THF           |  | 0.12                                  | 48 (5)                                 |           |
|                            | 1,4-Dioxane   |  | 0.17                                  | 0 (8)                                  |           |
|                            | Tert-butanol  |  | 0.12                                  | 13 (5)                                 |           |
|                            | Cyclohexane   |  | 0.23                                  | 7 (12)                                 |           |
| 8.6Fe/MCM41 <sup>a,c</sup> | Toluene       |  | 0.8                                   | 62 (100)                               | [1]       |
|                            | Ethyl acetate |  | 0.8                                   | 56 (100)                               |           |
|                            | tert-Butanol  |  | 0.8                                   | 56 (100)                               |           |
| 5.4Cu/MCM4 <sup>a,c</sup>  | Toluene       | 0.25 mmol of substrate, 1 mL of solvent, 70 °C, 750 rpm, 25 mg of catalyst | 0.2                                   | 69 (38)                                | [1]       |
|                            | Ethyl acetate |  | 0.01                                  | 96 (<1)                                |           |
|                            | tert-Butanol  |  | 0.00                                  | 0 (0)                                  |           |
| 9.2Fe/SBA15 <sup>a,c</sup> | Toluene       | 750 rpm, 25 mg of catalyst   | 0.2                                   | 65 (100)                               | [1]       |
|                            | Ethyl acetate |  | 0.2                                   | 56 (100)                               |           |
|                            | tert-Butanol  |  | 0.2                                   | 50 (100)                               |           |
| 7.2Cu/SBA15 <sup>a,c</sup> | Toluene       |  | 0.1                                   | 67 (41)                                | [1]       |
|                            | Ethyl acetate |  | 0.02                                  | 80 (6)                                 |           |
|                            | tert-Butanol  |  | 0.04                                  | 63 (11)                                |           |

<sup>a</sup> The values represent the metal loading (% wt.). <sup>b</sup> TOF was calculated with Eq. (5).

<sup>c</sup> Substrate corresponds to  $\alpha$ -pinene epoxide. <sup>d</sup> Values in parenthesis indicate the conversion and target corresponds to dihydrocarvone or campholenic aldehyde if the substrate is limonene-1,2-epoxide or  $\alpha$ -pinene epoxide, respectively.

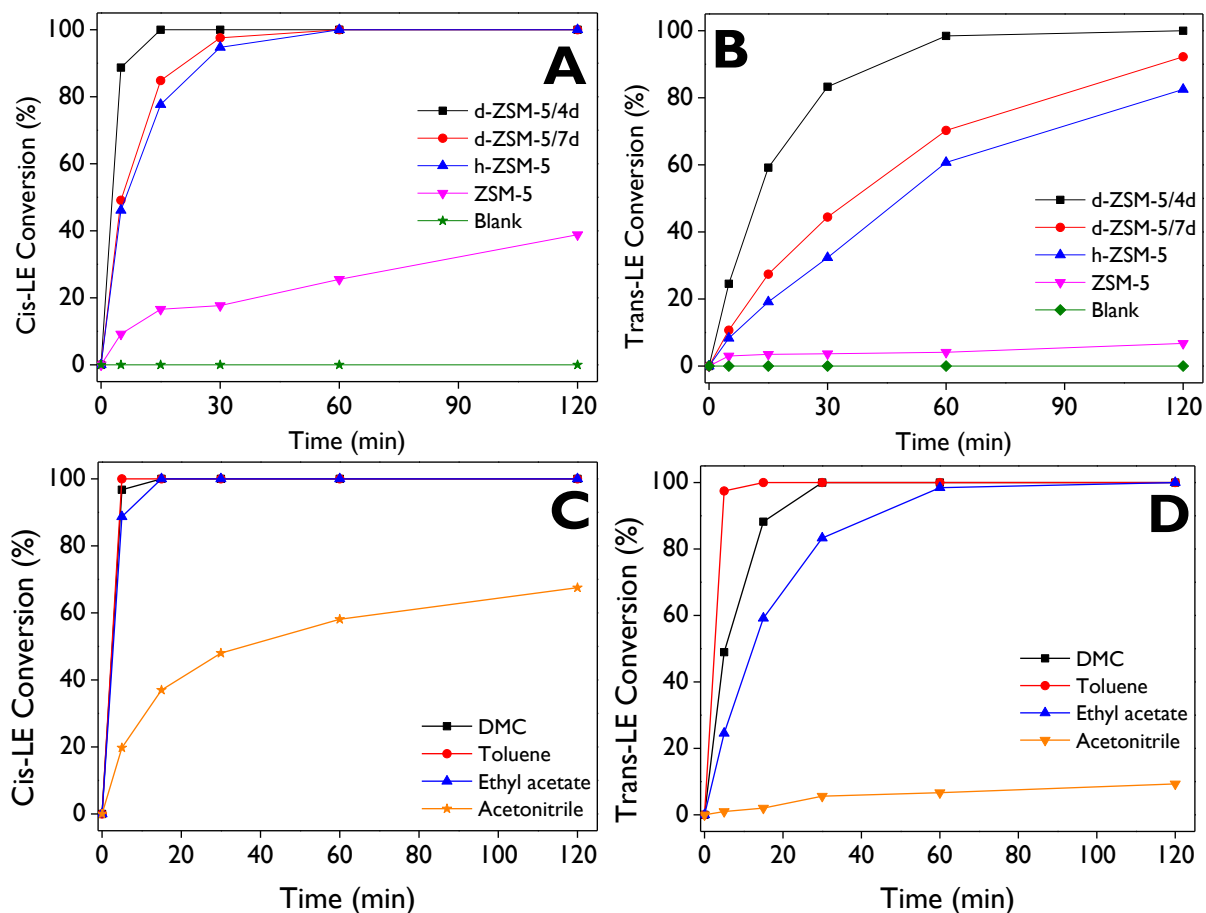


## 7. TG-Air Analyses



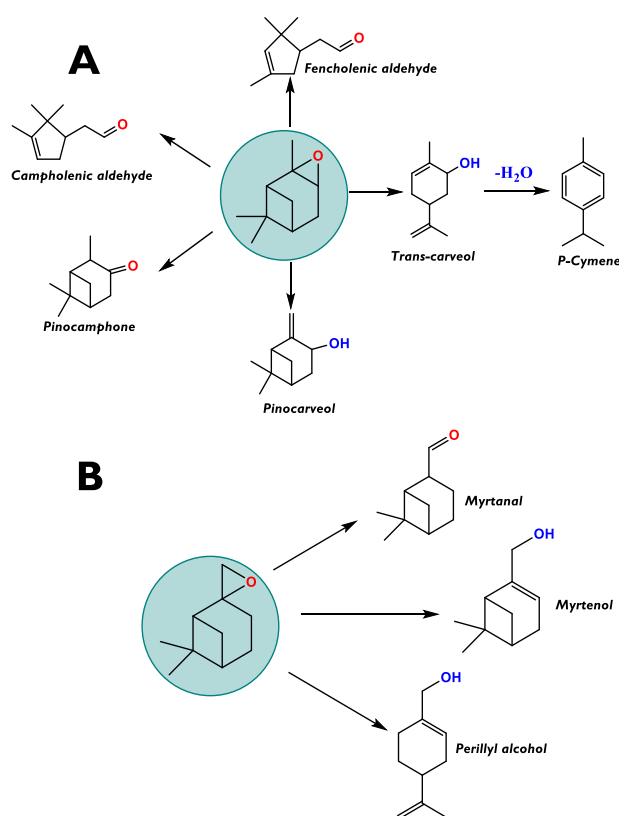
**Figure S6.** TG-DTG (air) analyses of the fresh, spent, and regenerated catalysts of sample d-ZSM-5/4d.

## 8. Conversion of limonene-1,2-epoxide isomers

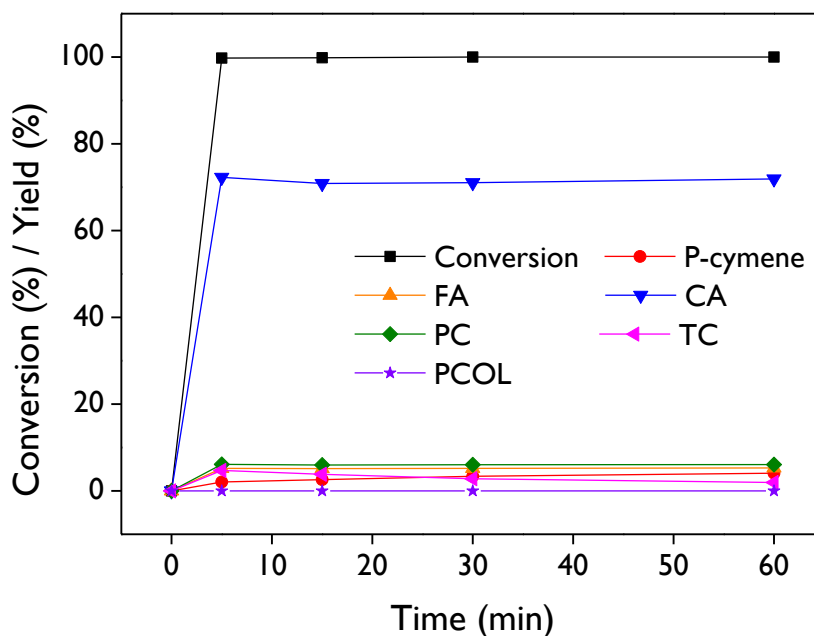


**Figure S7.** Conversion of cis-limonene-1,2-epoxide (**A**, **C**) and trans-limonene-1,2-epoxide (**B**, **D**) as a function of reaction time, evaluating the effect of the catalyst (**A**, **B**) and the solvent (**C**, **D**). Reaction conditions for Figures A and B are described in Figure 5, and those for Figures C and D are described in Figure 7.

## 9. Isomerization of pinene epoxides



**Figure S8.** Main products of **(A)**  $\alpha$ -pinene epoxide and **(B)**  $\beta$ -pinene epoxide rearrangement.



**Figure S9.** Conversion and product distribution of the isomerization of  $\alpha$ -pinene epoxide over d-ZSM-5/4d. FA: Fencholenic aldehyde, CA: Campholenic aldehyde, PC: Pinocamphone, TC: *Trans*-carveol, PCOL: Pinocarveol, PA: Perillyl alcohol. **Reaction conditions:**  $C_0 = 13 \text{ mmol L}^{-1}$ , 75 mL of total volume, dimethyl carbonate as a solvent, 115 mg of catalyst,  $70 \text{ }^\circ\text{C}$ , 520-530 rpm,  $\text{N}_2$  atmosphere.

## 10. Comparison of catalytic systems for the isomerization of pinene epoxides.

**Table S2.** Comparison of catalytic systems for the isomerization of  $\alpha$ - and  $\beta$ -pinene epoxides.

| Entry | Substrate   | Catalyst                                | Solvent   | Reaction conditions   | Conversion (%) | Selectivity (%) | Ref       |             |
|-------|---|---|---|---|----------------|-----------------|-----------|-------------|
| 1     | $\alpha$ -Pinene epoxide  | d-ZSM-5/4d                              | Ethyl acetate   | 13 mmol L <sup>-1</sup> , 115 mg catalyst, 60 °C, 15 min        | 100            | 62.5 CA         | This work |             |
|       |   |   |   |   |                | 8.1 TC          |           |             |
|       |   |   |   |   |                |                 | 5.7 FA    |             |
|       |   |   |   |   |                |                 | 5.6 PC    |             |
|       |   |   |   |   |                |                 | 2 PCY     |             |
| 2     |   |   | Dimethyl carbonate  | 13 mmol L <sup>-1</sup> , 115 mg catalyst, 70 °C, 5 min         | 100            | 72.4 CA         | 4.7 TC    | This work   |
|       |   |   |   |   |                |                 | 5.2 FA    |             |
|       |   |   |   |   |                |                 | 6.1 PC    |             |
|       |   |   |   |   |                |                 | 2.1 PCY   |             |
| 3     |   | ZrPa (2.4 M)                            | N, N-Dimethylacetamide  | 3.28 mmol substrate, 50 mg catalyst, 2 mL solvent, 160 °C, 5 h  | 100            | 19 CA           | 73 TC     | [2]         |
| 4     |   | Fe/MCM-41 (1.7 wt%)                     | Toluene   | 0.25 mmol substrate, 10 mg catalyst, 1 mL solvent, 70 °C, 2.5 h | 100            | 66 CA           | [1]       |             |
| 5     |   |   | Ethyl acetate   |   | 100            | 58 CA           |           |             |
| 6     |   |   | Toluene   |   | 20             | 82 CA           |           |             |
| 7     |   |   | Toluene   |   | 100            | 64 CA           |           |             |
| 8     |   |   | Ethyl acetate   |   | 100            | 58 CA           |           |             |
| 9     |   | Cu/SBA-15 (1.2 wt%)                     | Toluene   |   | 46             | 71 CA           |           |             |
| 10    |   | MZ-5 <sup>b</sup> (1.5)                 | N, N-Dimethylacetamide  | 2 mmol substrate, 75 mg catalyst, 100 mL solvent, 140 °C, 3 h   | 92             | 27 CA           | 45 TC     | [3]         |
| 11    |   | MoO <sub>3</sub> -Modified beta zeolite | Toluene   | 1.25 g substrate, 125 mg catalyst, 6 mL solvent, 70 °C, 3 h     | 100            | 34.2 CA         | 14.8 TC   | [4]         |
| 12    |   |   | Ethyl acetate   |   | 97             | 37.1 CA         | 15.8 TC   |             |
| 13    | Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> | Acetone                                 | 0.75 mmol substrate, 7.50 $\mu$ mol catalyst, 5 mL total, 40 °C, 5 min  | 100   | 17 CA          | 11 TS           | [5]       |             |
|       |   |   |   |   | 62 Pinol       |                 |           |             |
| 14    | Al-SiO <sub>2</sub> (12 wt%)  | Dichloroethane                          | 0.25 mmol substrate, 5 mg catalyst, 2 mL solvent, 30 °C, 30 min         | 80  | 72 CA          | 2 FA            | [6]       |             |
|       |   |   |   |   | 15 TC          | 8 TS            |           |             |
| 15    | Phosphonate/Carbon  | DMF                                     | 3.28 mmol substrate, 50 mg catalyst, 2 mL solvent, 140 °C, 1 h          | 100   | 22 CA          | 67 TC           | [7]       |             |
|       |   |   |   |   | 9 TPC          |                 |           |             |
| 16    | d-ZSM-5/4d  | Ethyl acetate                           | 13 mmol L <sup>-1</sup> , 115 mg catalyst, 50 °C, 5 min                 | 100   | 47.7 myrtanal  | 3.1 myrtenol    | This work |             |
|       |   |   |   |   | 18.5 PA        |                 |           |             |
| 17    | $\beta$ -Pinene epoxide   | Fe/MCM-41                               | 0.25 mmol substrate, 26% of catalyst, 1 mL solvent, 70 °C, 1 h          | 23  | 90 myrtanal    | 8 PA            | [8]       |             |
|       |   | Fe/SBA-15                               |   | Hexane  |                | 2 myrtenol      |           | 68 myrtanal |
| 18    |   |   |   |   |                | 27              |           | 26 PA       |
| 19    | Sn-Beta-300   | Toluene                                 | 0.012 mol L <sup>-1</sup> , 75 mg of catalyst, 150 mL total, 70 °C, 6 h | 72  | 66 myrtanal    | 10 PA           | [9]       |             |
|       |   |   |   |   | 2 myrtenol     |                 |           |             |

|    |                     |        |  |      |  |      |
|----|---------------------|--------|--|------|--|------|
| 20 | Zeolite beta 25     | DMSO   | 0.8 mL substrate, 25 wt% of catalyst (based on the substrate), volume ratio substrate: solvent = 1:5, 70 °C, 2 h | 100  | 19 myrtanal<br>36 PA<br>10 myrtenol<br>9 p-Menth-1-en-7,8-diol | [10] |
| 21 | Ti/SBA-15           | Hexane |  | > 99 | 20 myrtanal<br>45 PA   |      |
| 22 | Mo/SBA-15           | Hexane |  | > 99 | 63 PA  |      |
| 23 | Mo/MCM-41           | Hexane | 0.25 mmol substrate, 10 mg catalyst, 0.5 mL solvent, 80 °C, 1 h  | 98   | 2 myrtanal<br>20 PA<br>5 myrtenol                              | [11] |
| 24 | Mo/SiO <sub>2</sub> | Hexane |  | 99   | 12 myrtanal<br>32 PA<br>2 myrtenol                             |      |

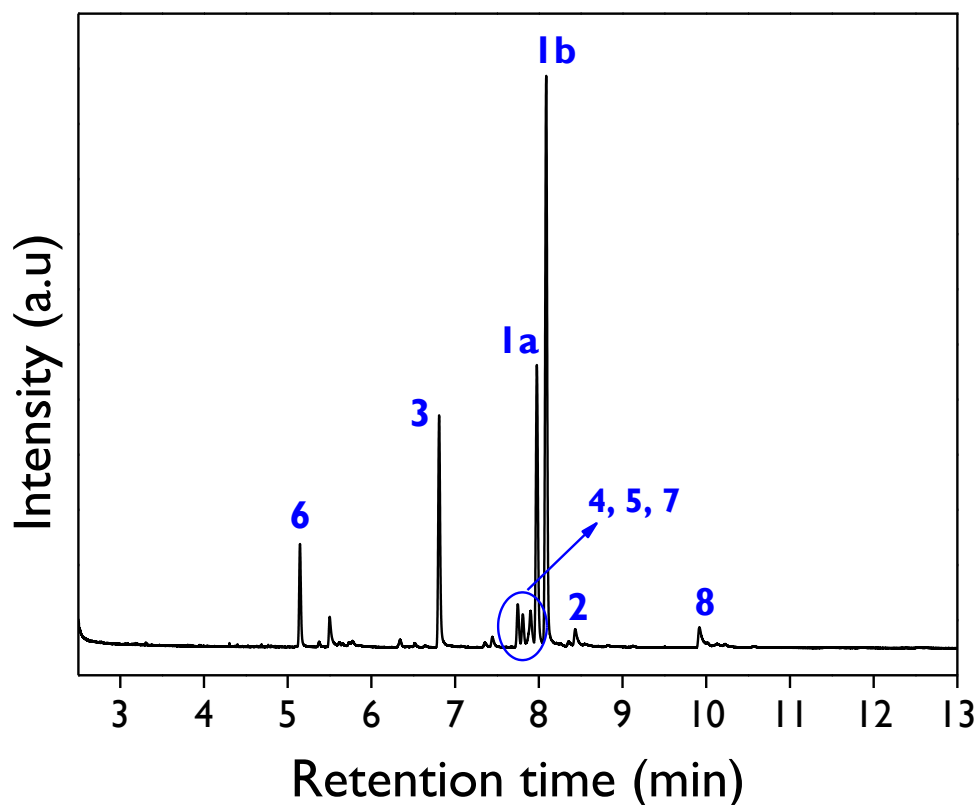
<sup>a</sup>Value in parenthesis refer to the concentration of H<sub>3</sub>PO<sub>4</sub> utilized in the synthesis of the catalyst. <sup>b</sup>Selectivities at 70 % conversion. **ZrP**: Zirconium phosphate. **MZ**: Mesoporous beta zeolite where the value in parenthesis denotes the Brønsted-to-Lewis acidity ratio. **CA**: Campholenic aldehyde. **TC**: *Trans*-Carveol. **FA**: Fencholenic aldehyde. **PC**: Pinocamphone. **PCY**: *p*-Cymene. **PMD**: *p*-Methadien-2-ol. **TS**: *trans*-Sobrerol. **TPC**: *Trans*-Pinocarveol. **PA**: Perillyl alcohol.

## 11. Characterization of substrate and reaction products

### 11.1. Isomerization of limonene-1,2-epoxide

**Table S3.** Retention times for the compounds involved in the isomerization of limonene-1,2-epoxide.

| Compound                          | Retention time (min) |
|-----------------------------------|----------------------|
| <i>Cis</i> limonene-1,2-epoxide   | 7.17                 |
| <i>Trans</i> limonene-1,2-epoxide | 7.22                 |
| <i>Cis</i> dihydrocarvone (1a)    | 7.99                 |
| <i>Trans</i> dihydrocarvone (1b)  | 8.10                 |
| Carveol (2)                       | 8.32 and 8.49        |
| Product 3                         | 6.81                 |
| Fenchone (4)                      | 7.75                 |
| Product 5                         | 7.82                 |
| Product 6                         | 5.15                 |
| Product 7                         | 7.91                 |
| Limonene glycol (8)               | 9.92                 |



**Figure S10.** Representative chromatogram of a reaction sample after 2 h in the isomerization of limonene-1,2-epoxide. **Reaction conditions:**  $C_{\text{substrate},0} = 13 \text{ mmol L}^{-1}$ , 75 mL of total volume, DMC as a solvent, 115 mg of d-ZSM-5/4d, 70 °C, 520-530 rpm,  $\text{N}_2$  atmosphere.

❖ Product 3

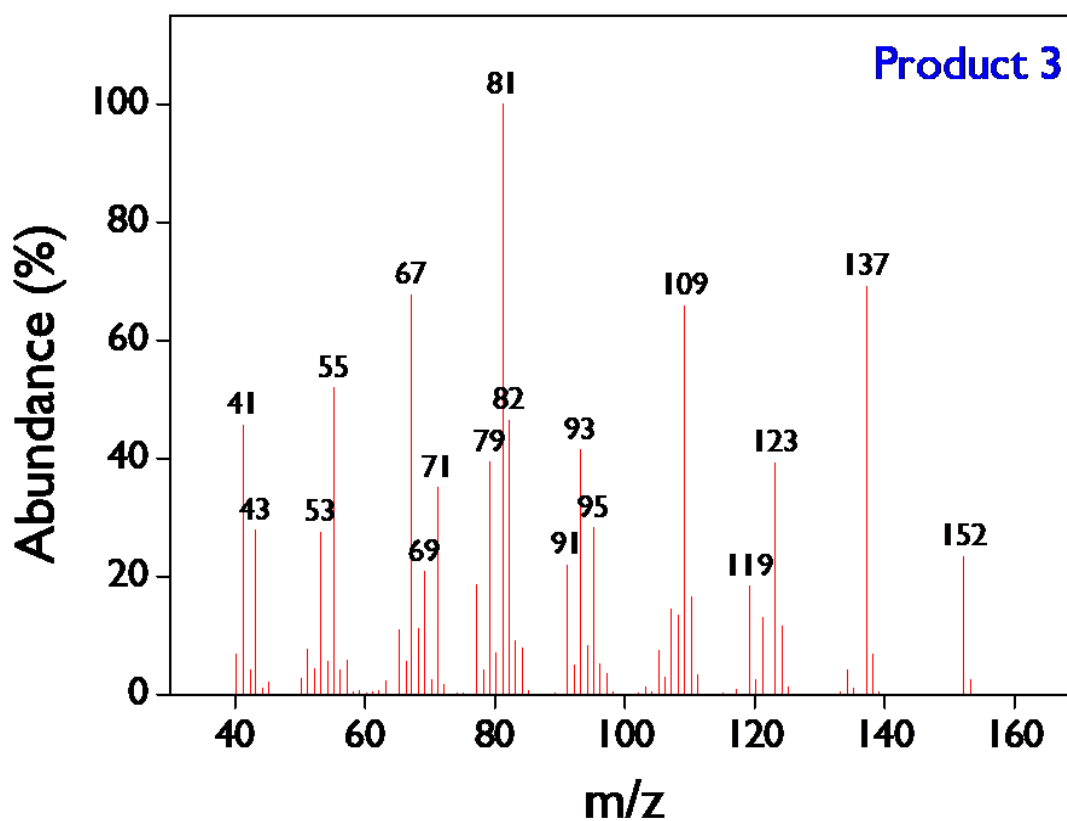


Figure S11. Mass spectrum of product 3.

❖ Product 5

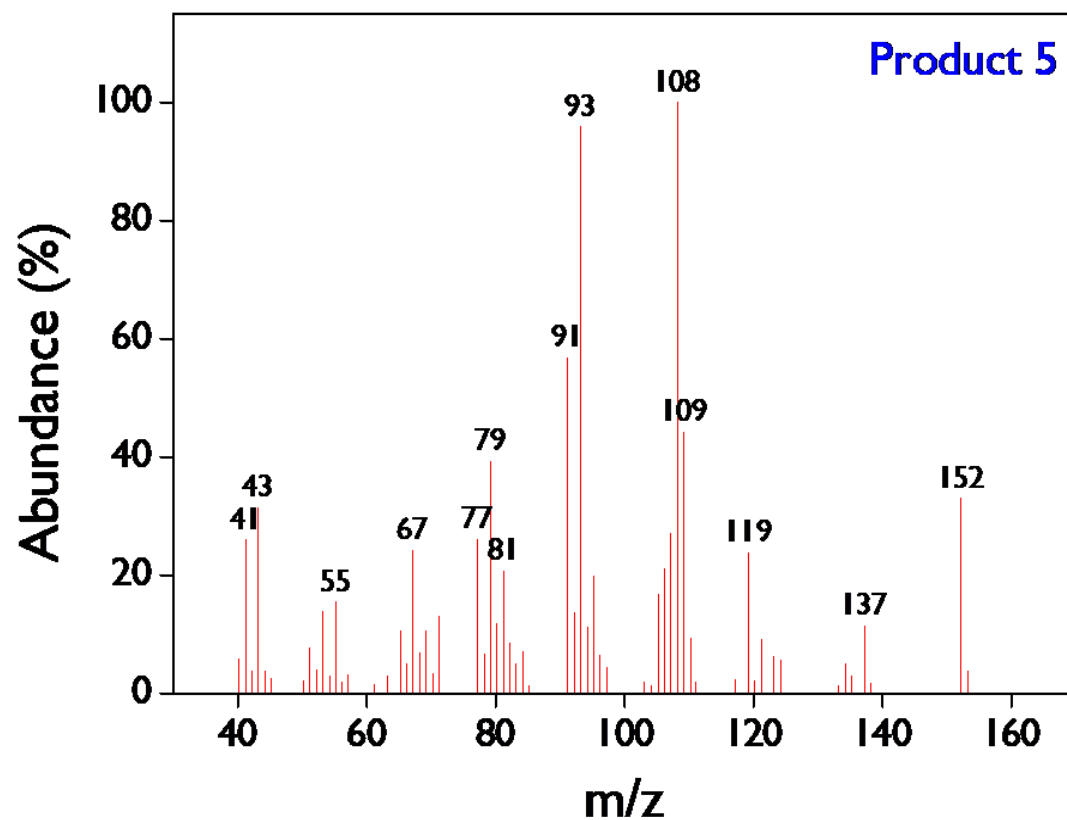


Figure S12. Mass spectrum of product 5.

❖ Product 6

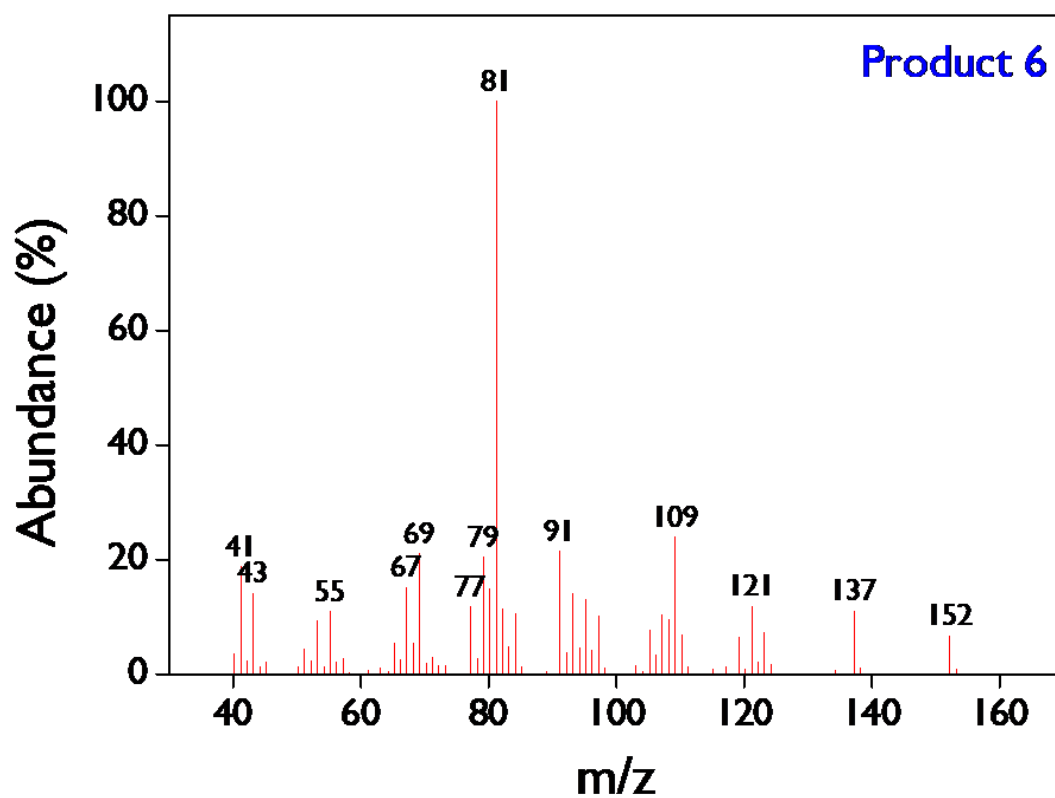


Figure S13. Mass spectrum of product 6.

❖ Product 7

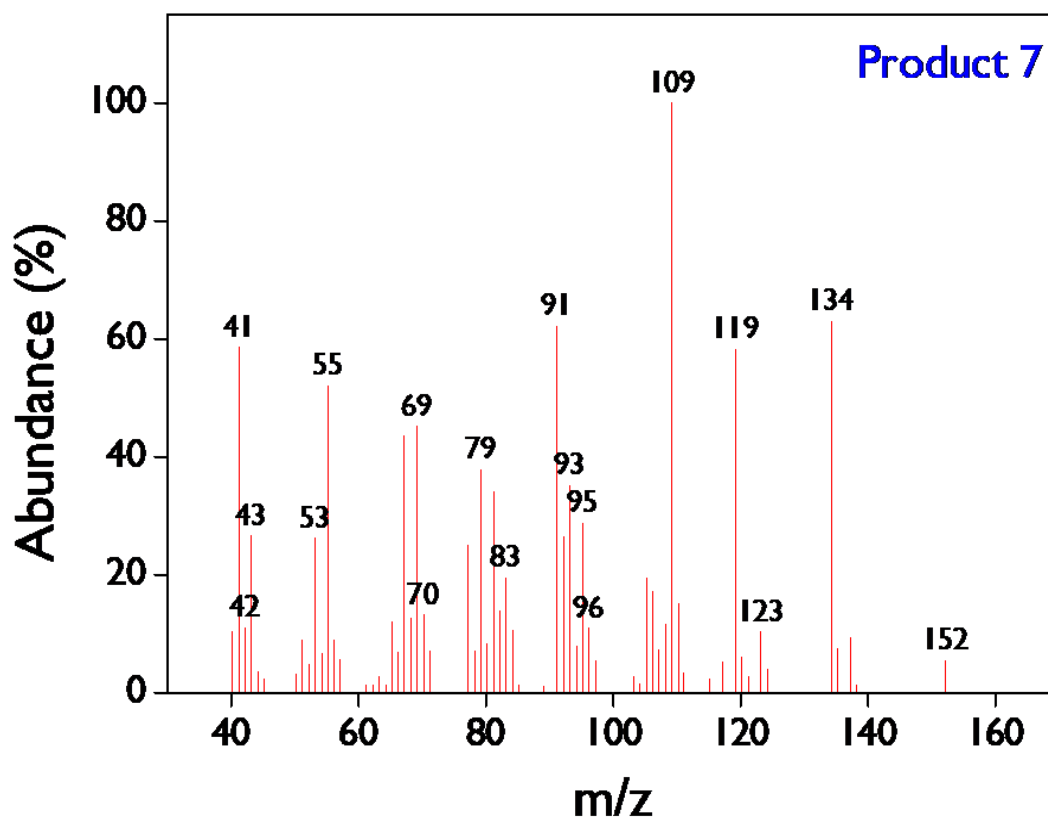


Figure S14. Mass spectrum of product 7.



❖ Product obtained with acetonitrile as solvent

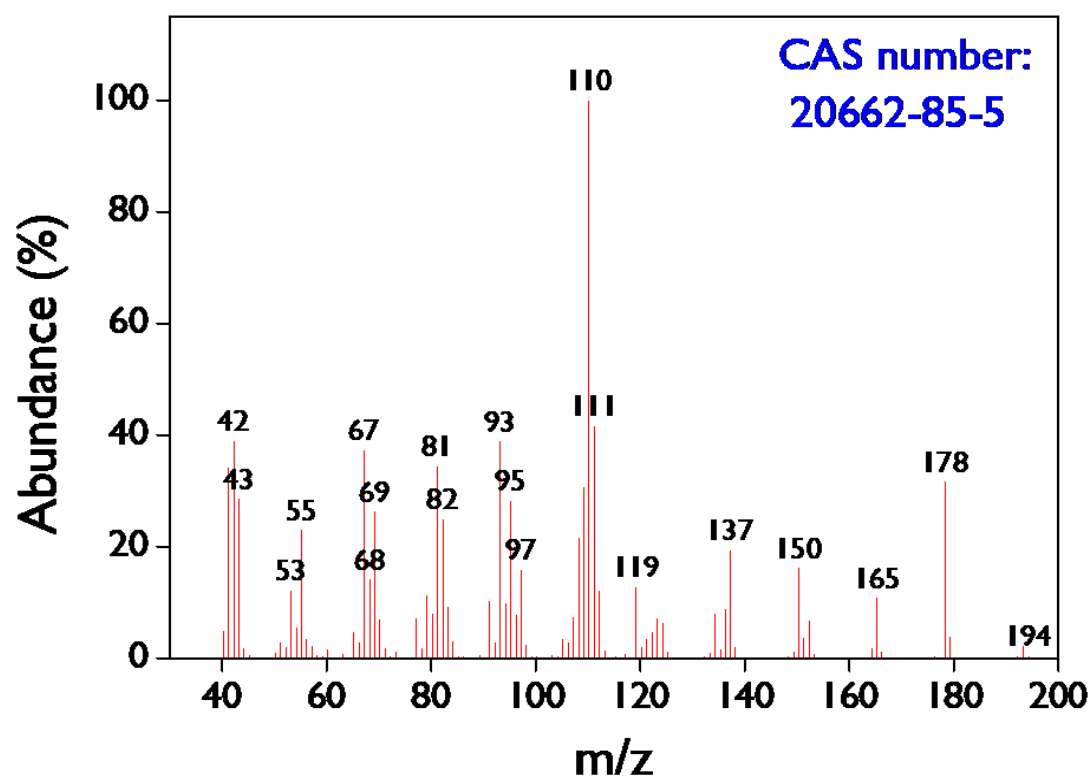
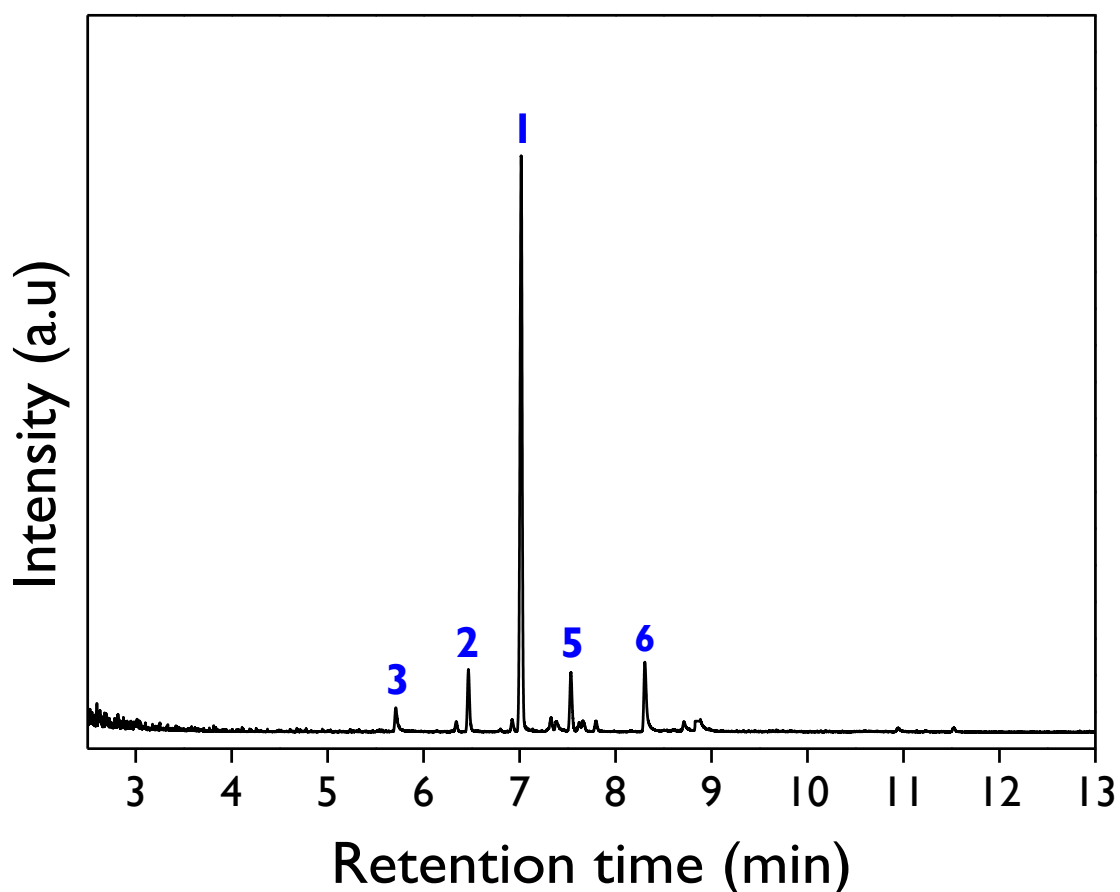


Figure S15. Mass spectrum of the main product obtained with acetonitrile as solvent.

## 11.2. Isomerization of $\alpha$ -pinene epoxide

**Table S4.** Retention times for the compounds involved in the isomerization of  $\alpha$ -pinene epoxide.

| Compound                      | Retention time (min) |
|-------------------------------|----------------------|
| $\alpha$ -Pinene epoxide      | 6.78                 |
| Campholenic aldehyde (1)      | 7.02                 |
| Fencholenic aldehyde (2)      | 6.47                 |
| <i>P</i> -Cymene (3)          | 5.72                 |
| <i>Trans</i> -pinocarveol (4) | 7.43                 |
| Pinocamphone (5)              | 7.54                 |
| <i>Trans</i> -Carveol (6)     | 8.32                 |

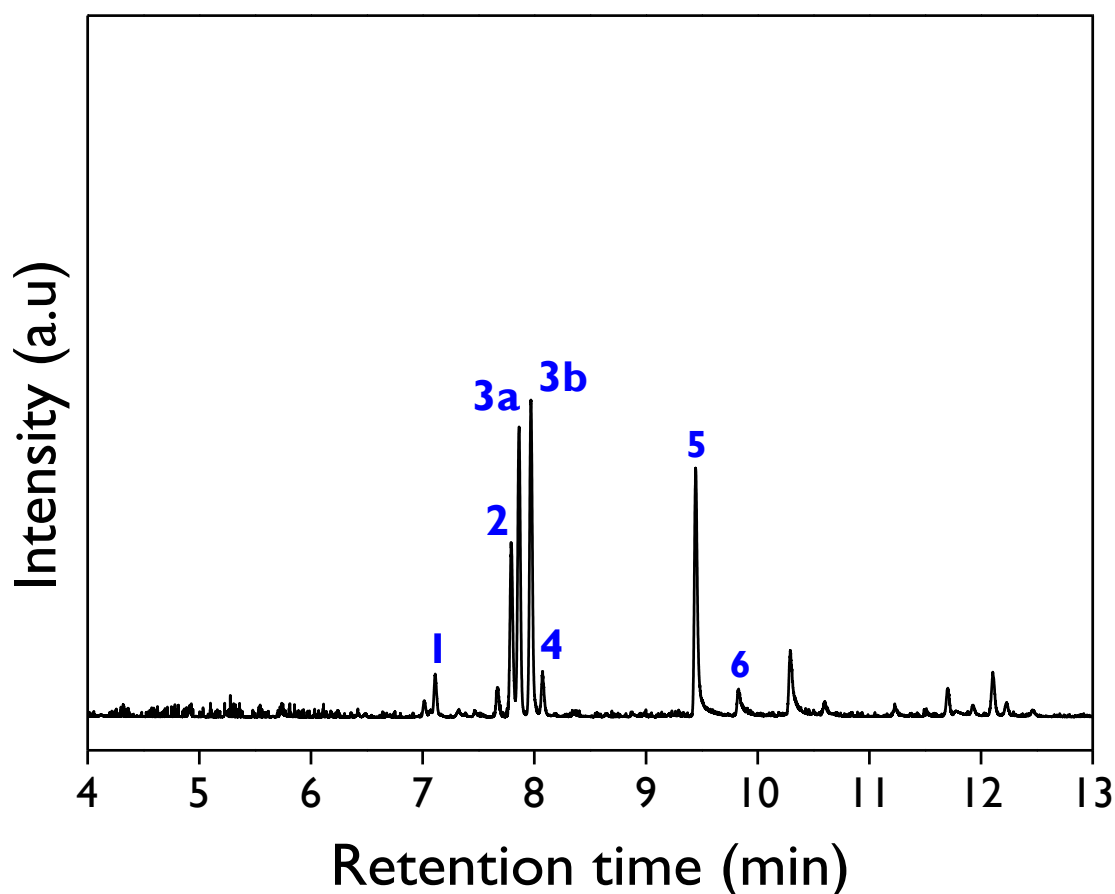


**Figure S16.** Representative chromatogram of a reaction sample after 60 min in the isomerization of  $\alpha$ -pinene epoxide. **Reaction conditions:**  $C_{\text{substrate},0} = 13 \text{ mmol L}^{-1}$ , 75 mL of total volume, ethyl acetate as a solvent, 115 mg of d-ZSM-5/4d, 60 °C, 520-530 rpm,  $\text{N}_2$  atmosphere.

### 11.3. Isomerization of $\beta$ -pinene epoxide

**Table S5.** Retention times for the compounds involved in the isomerization of  $\beta$ -pinene epoxide.

| Compound                    | Retention time (min) |
|-----------------------------|----------------------|
| $\beta$ -pinene epoxide     | 7.55                 |
| Product 1 (1)               | 7.11                 |
| Product 2 (2)               | 7.79                 |
| <i>Cis</i> -myrtanal (3a)   | 7.87                 |
| <i>Trans</i> -myrtanal (3b) | 7.96                 |
| Myrtenol (4)                | 8.08                 |
| Perillyl alcohol (5)        | 9.45                 |
| Product 3 (6)               | 9.84                 |



**Figure S17.** Representative chromatogram of a reaction sample after 60 min in the isomerization of  $\beta$ -pinene epoxide. **Reaction conditions:**  $C_{\text{substrate},0} = 13 \text{ mmol L}^{-1}$ , 75 mL of total volume, ethyl acetate as a solvent, 115 mg of d-ZSM-5/4d, 50 °C, 520-530 rpm,  $\text{N}_2$  atmosphere.

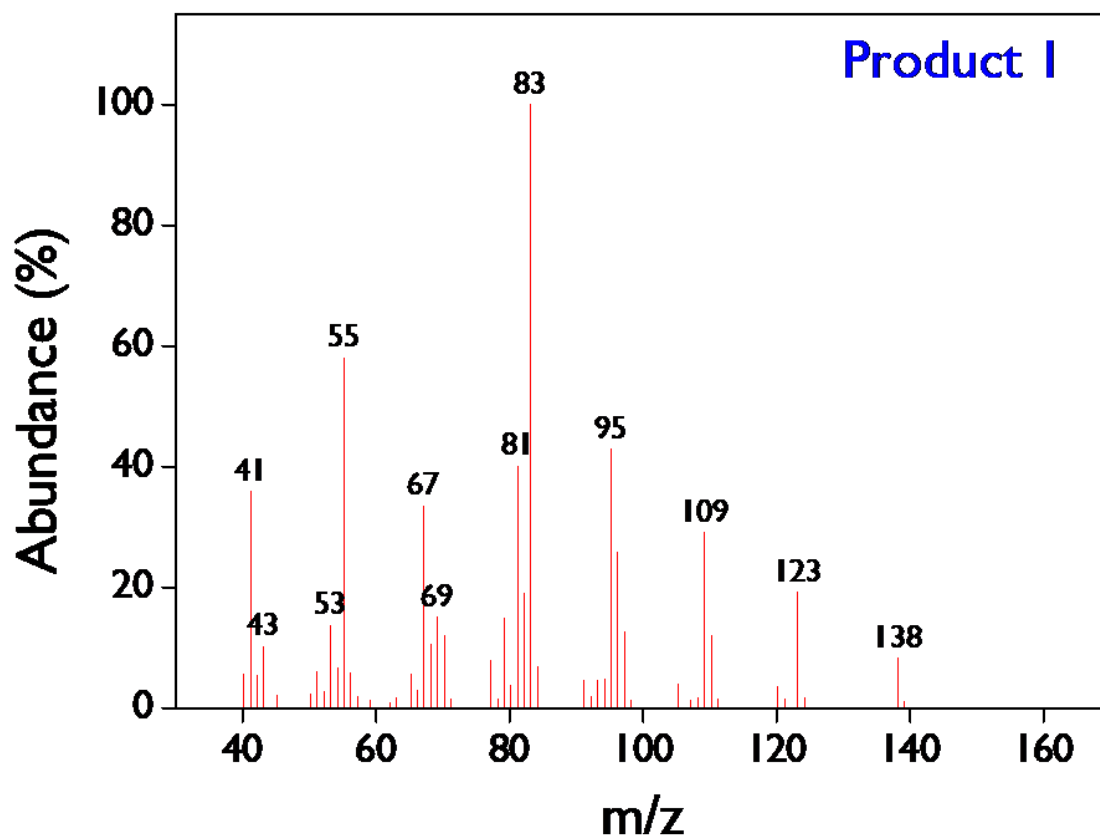


Figure S18. Mass spectrum of product 1.

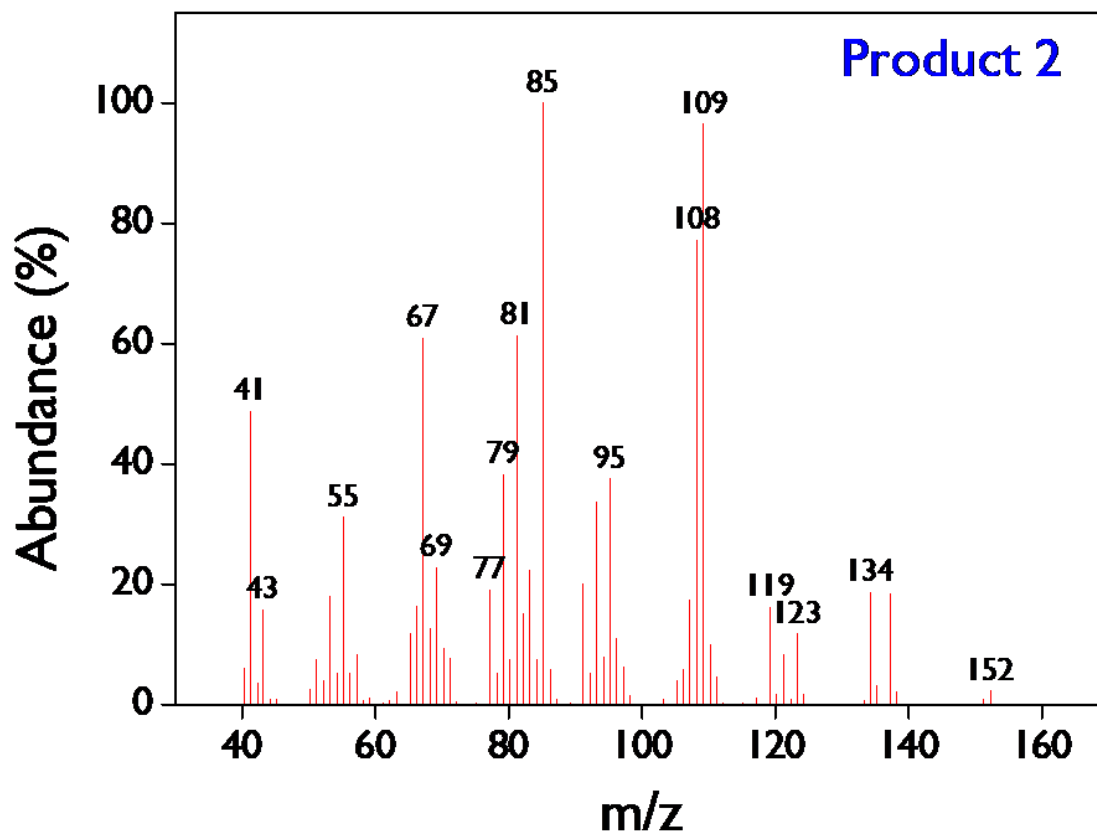


Figure S19. Mass spectrum of product 2.

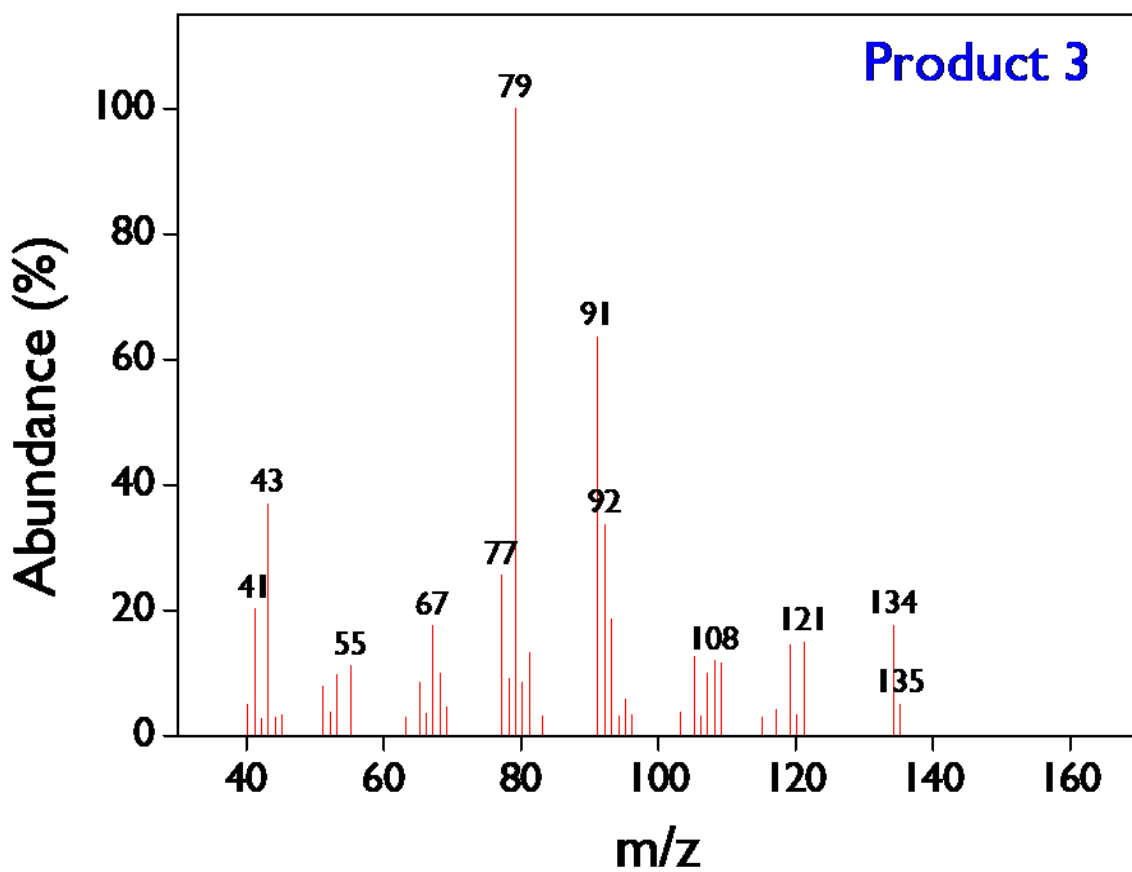


Figure S20. Mass spectrum of product 3.

## 12. References

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