



## Supporting Information

for

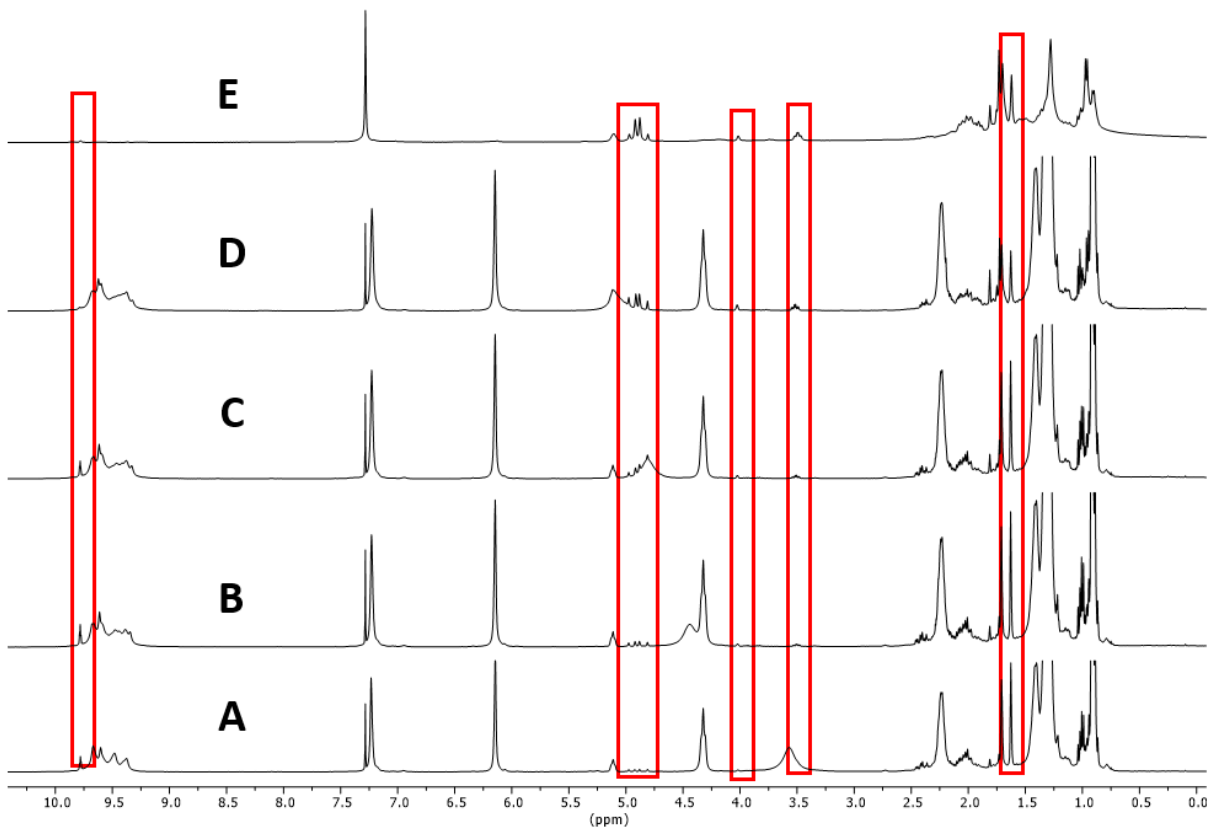
### **A resorcin[4]arene hexameric capsule as a supramolecular catalyst in elimination and isomerization reactions**

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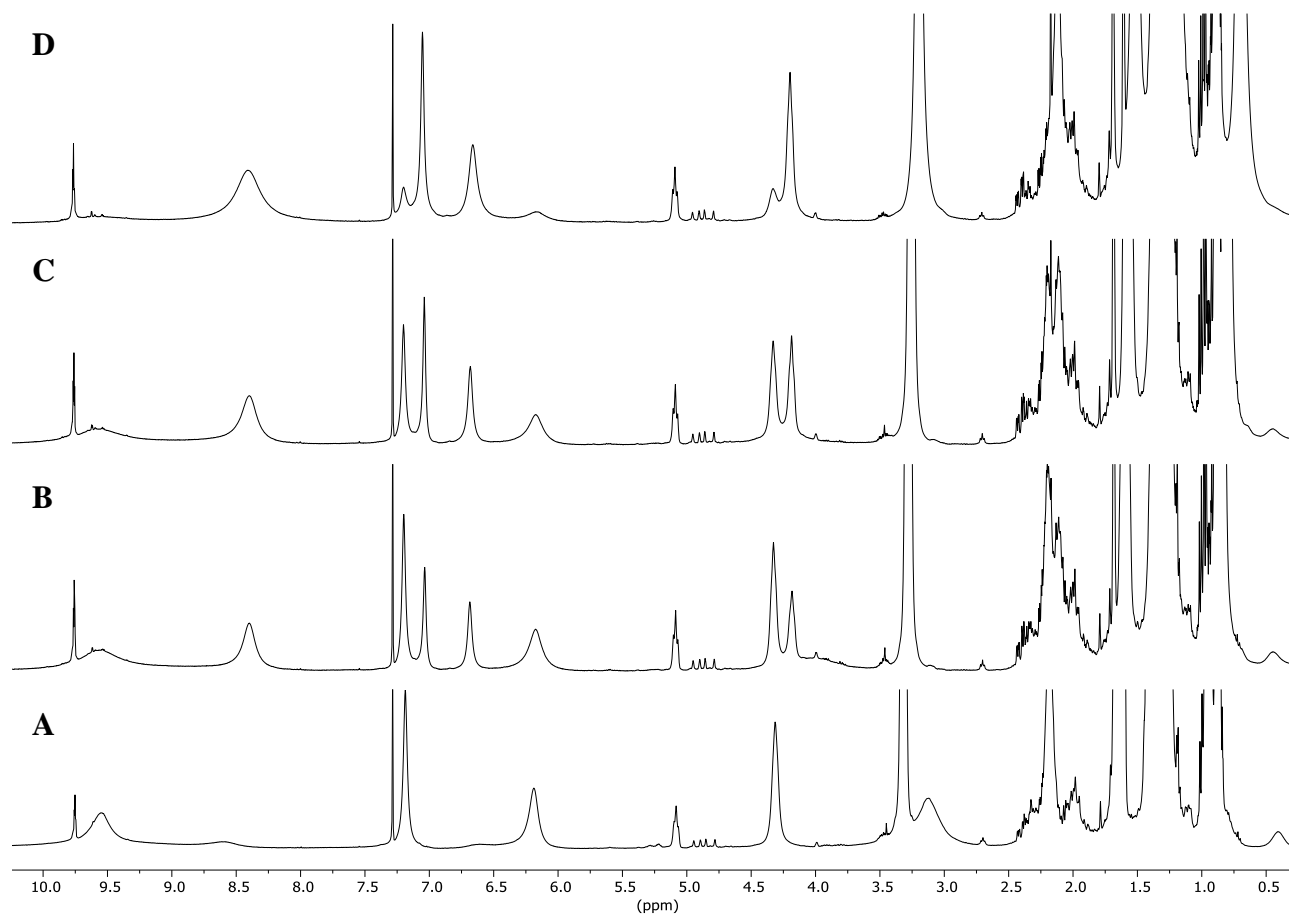
### **Details on experimental procedures and $^1\text{H}$ NMR spectra for the catalytic tests**

**Citronellal isomerization: experiment with capsule **[1<sub>6</sub>]****



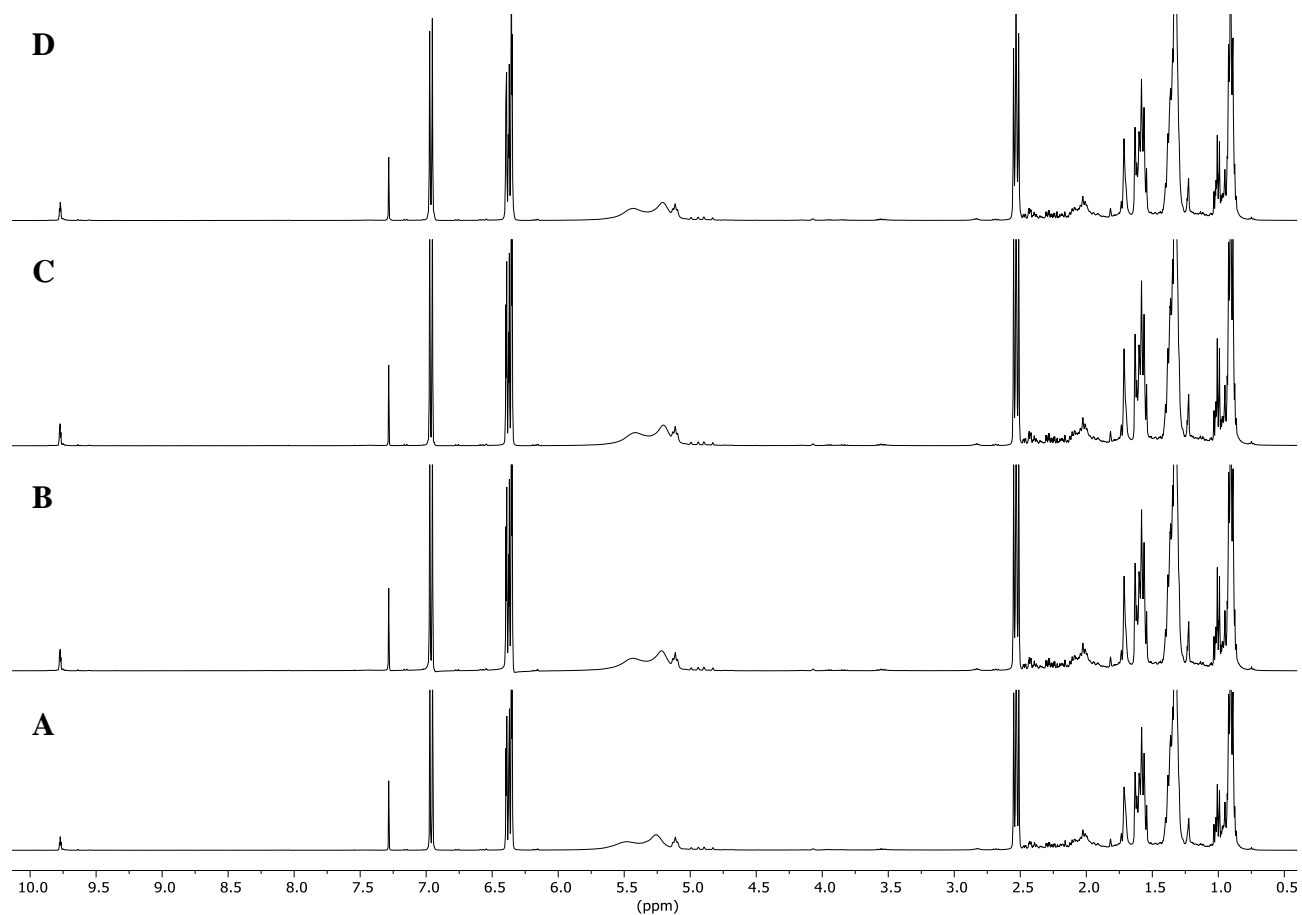
**Figure S1:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub> of a solution of citronellal (75 mM), **[1<sub>6</sub>]** (7.5 mM), recorded after preparation (A), after 1.5 h (B), 3 h (C), 24 h (D), 72 h (E) at 60 °C.

**Citronellal isomerization: control experiments with capsule **[1<sub>6</sub>]** and competitive ammonium guests **3****



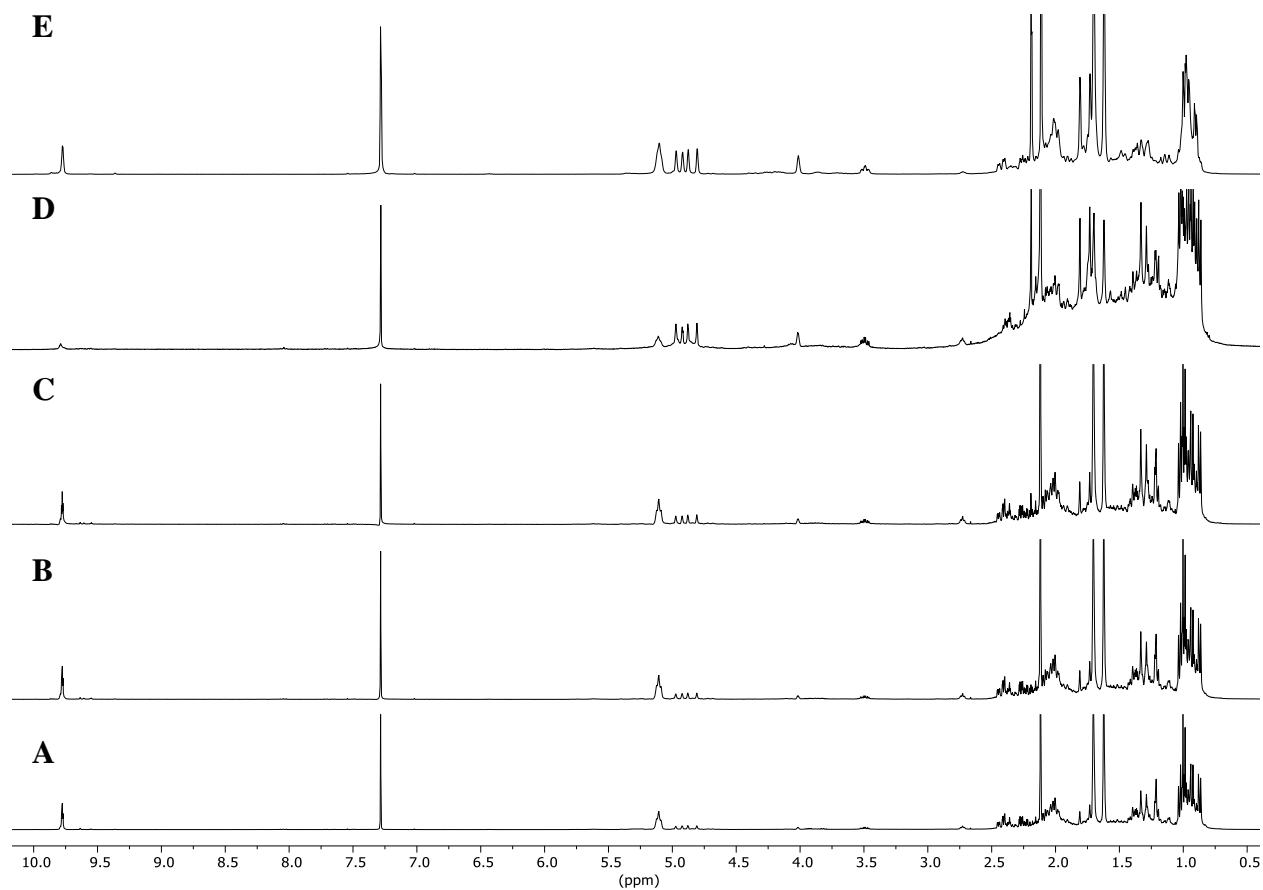
**Figure S2:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub> of a solution of citronellal (75 mM), **[1<sub>6</sub>]** (7.5 mM), Bu<sub>4</sub>NBr **3** (78 mM) recorded after preparation (A), after 1.5 h (B), 3 h (C), 24 h (D) at 60 °C.

**Citronellal isomerization: control experiments with 4-*n*-hexyl-resorcinol **2****



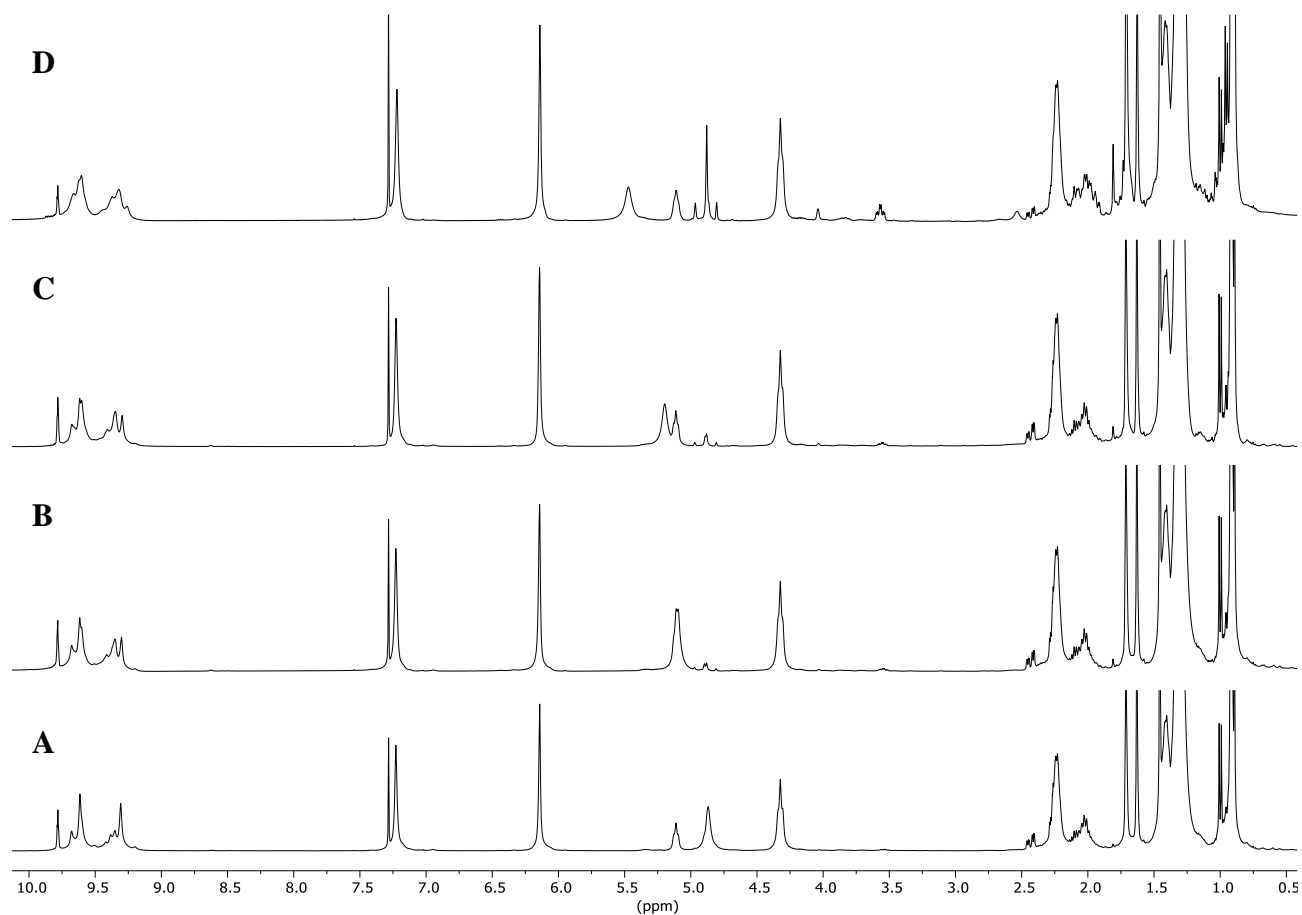
**Figure S3:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub> of a solution of citronellal (75 mM), *n*-hexylresorcinol **2** (30 mM) recorded after preparation (A), after 1.5 h (B), 3 h (C), 24 h (D) at 60 °C.

**Citronellal isomerization: control experiments with acetic acid**



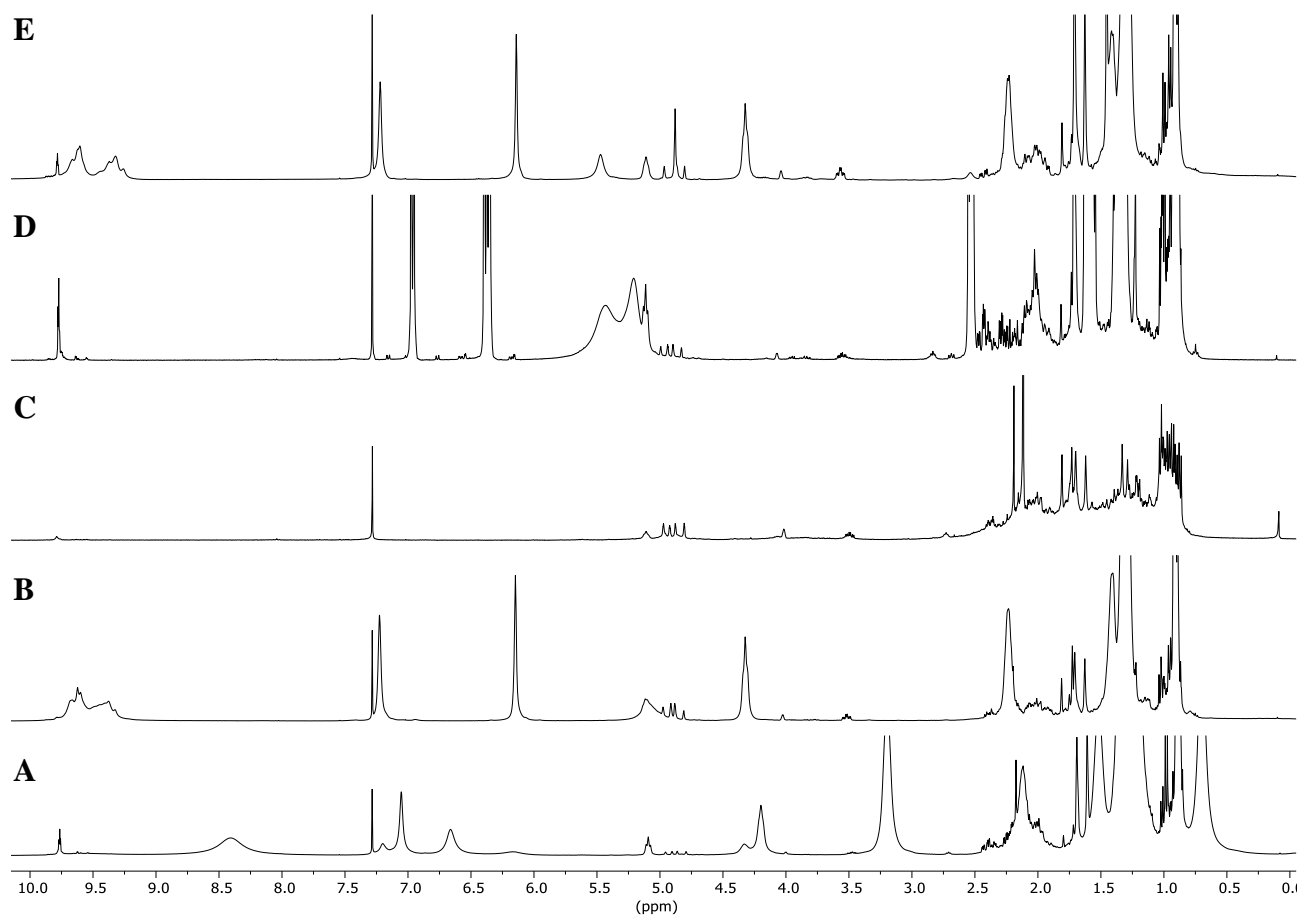
**Figure S4:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub> of a solution of citronellal (75 mM), acetic acid (29 mM) recorded after preparation (A), after 1.5 h (B), 3 h (C), 24 h (D), 72 h (E) at 60 °C.

**Citronellal isomerization: experiment with capsule  $[1_6 \cdot (H_2O)_8]$**



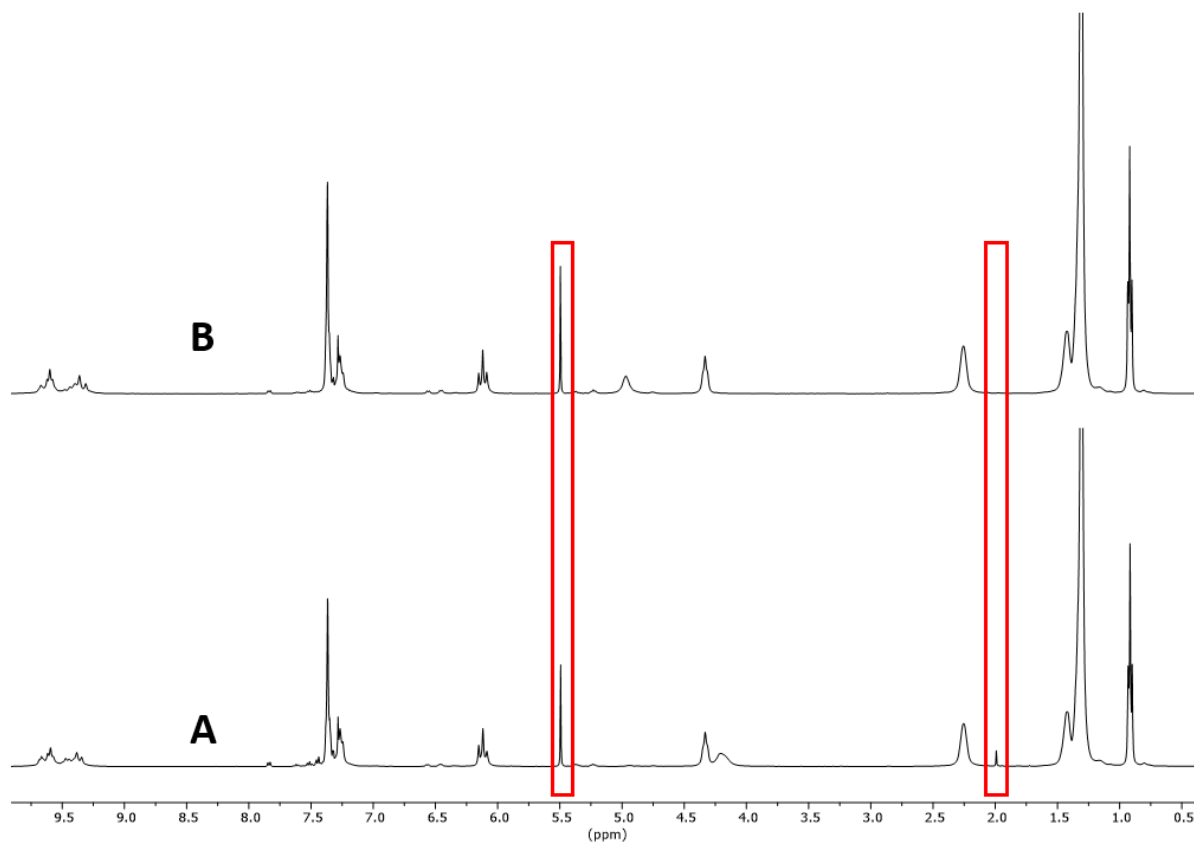
**Figure S5:**  $^1\text{H}$  NMR spectra in water-saturated  $\text{CDCl}_3$  of a solution of citronellal (75 mM),  $[1_6 \cdot (H_2O)_8]$  (7.5 mM), recorded after preparation (A), after 1.5 h (B), 3 h (C), 24 h (D) at 60 °C.

**Citronellal isomerization: overview after 24 h**



**Figure S6:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub>. A: citronellal (75 mM), [1<sub>6</sub>(H<sub>2</sub>O)<sub>8</sub>] (7.5 mM), Bu<sub>4</sub>NBr **3** (78 mM); B: citronellal (75 mM), [1<sub>6</sub>(H<sub>2</sub>O)<sub>8</sub>] (7.5 mM); C: citronellal (75 mM), acetic acid (29 mM); D: citronellal (75 mM), *n*-hexylresorcinol **2** (30 mM); E: citronellal (75 mM), [1<sub>6</sub>(H<sub>2</sub>O)<sub>8</sub>] (7.5 mM). Spectra recorded after 24 h at 60 °C.

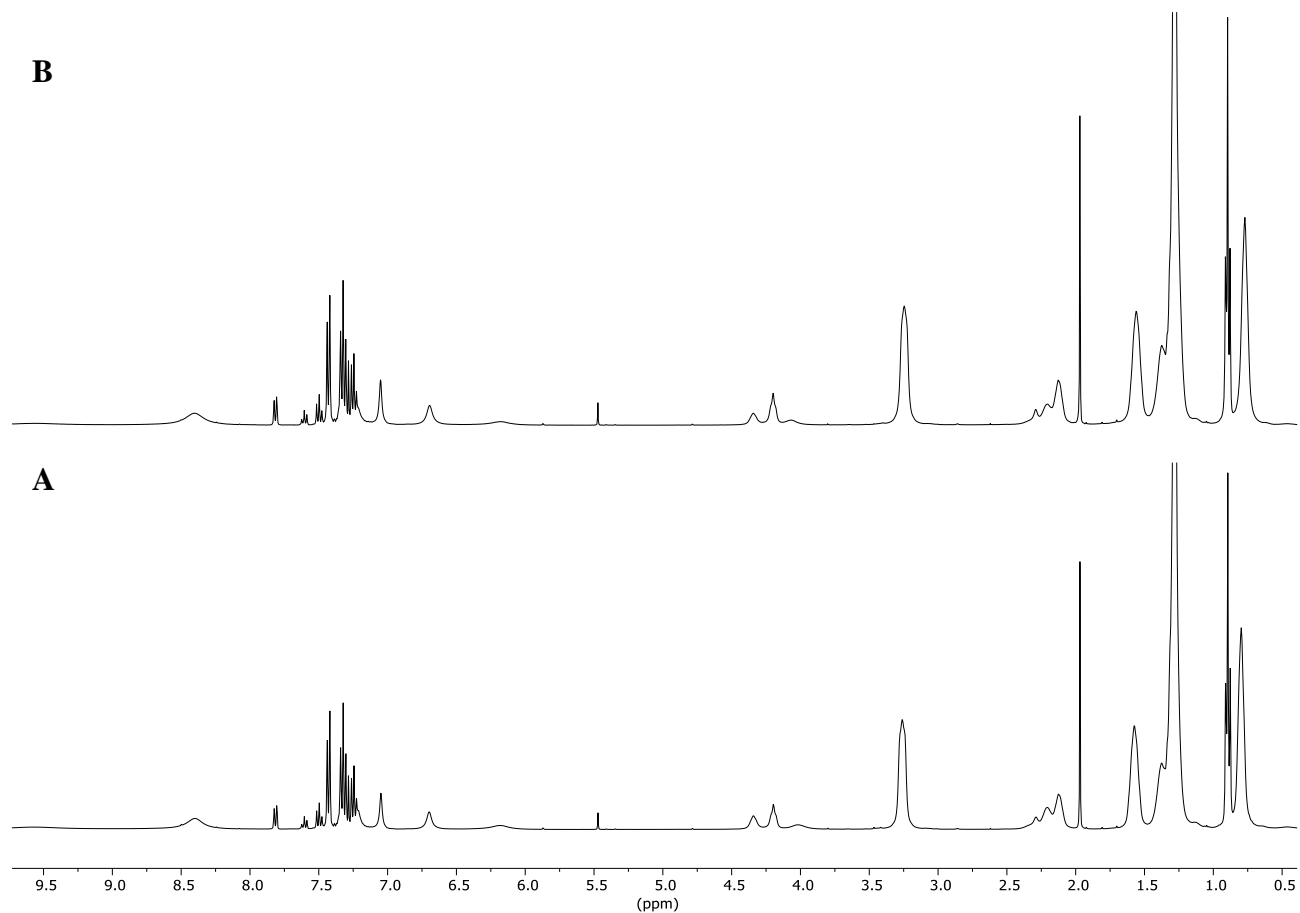
**Dehydration of 1,1-diphenylethanol: experiment with capsule [1<sub>6</sub>]**



**Figure S7:**  $^1\text{H}$  NMR spectra in water-saturated  $\text{CDCl}_3$  of a solution of 1,1-diphenylethanol (75 mM), [1<sub>6</sub>] (7.5 mM) recorded after 3 h (A) and 20 h (B) at 60 °C.

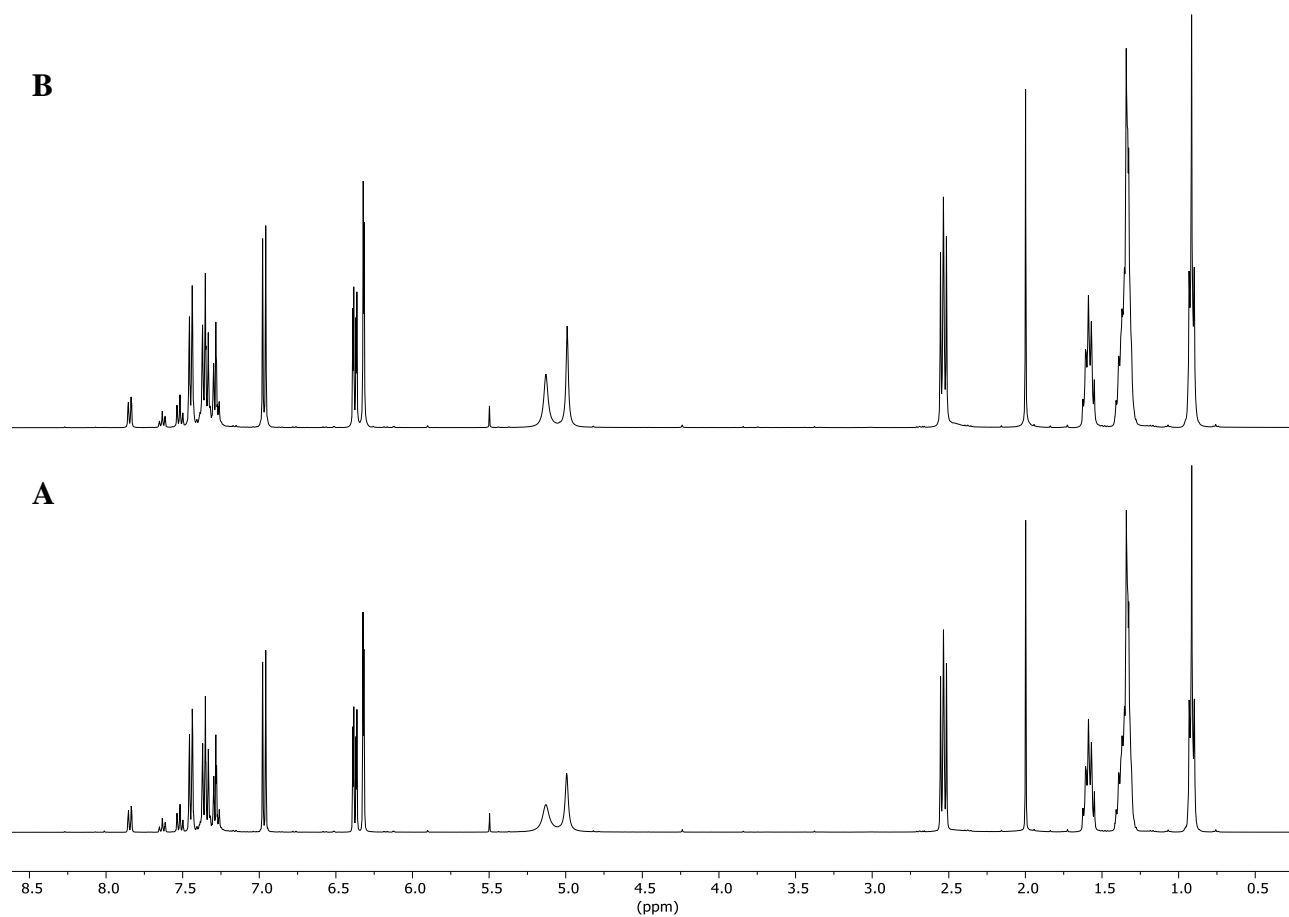


**Dehydration of 1,1-diphenylethanol: control experiments with capsule [1<sub>6</sub>] and competitive ammonium guests 3**



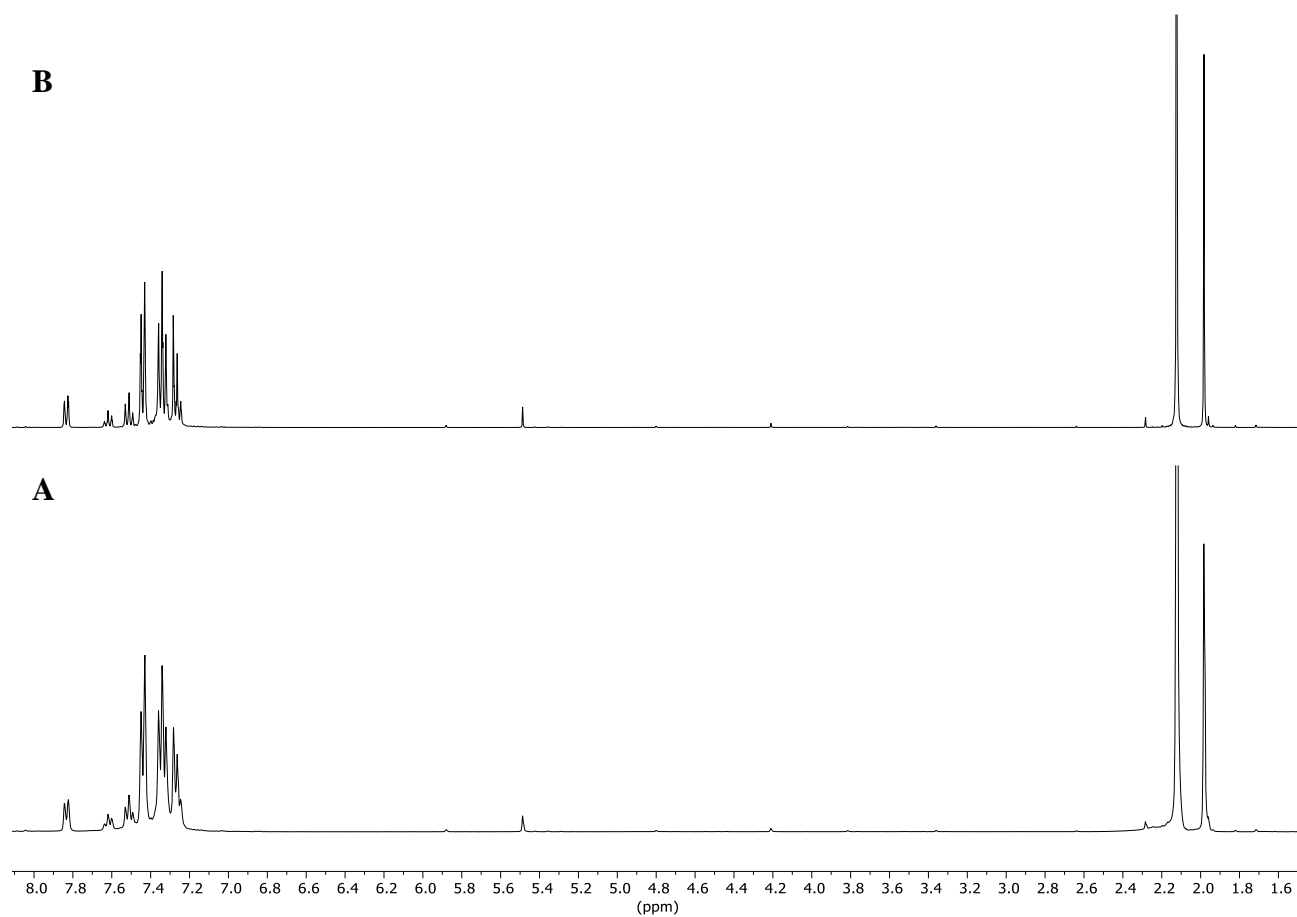
**Figure S8:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub> of a solution of 1,1-diphenylethanol (75 mM), [1<sub>6</sub>] (7.5 mM), Bu<sub>4</sub>NBr 3 (78 mM) recorded after 3 h (A) and 20 h (B) at 60 °C.

**Dehydration of 1,1-diphenylethanol: control experiments with 4-*n*-hexylresorcinol (**2**)**



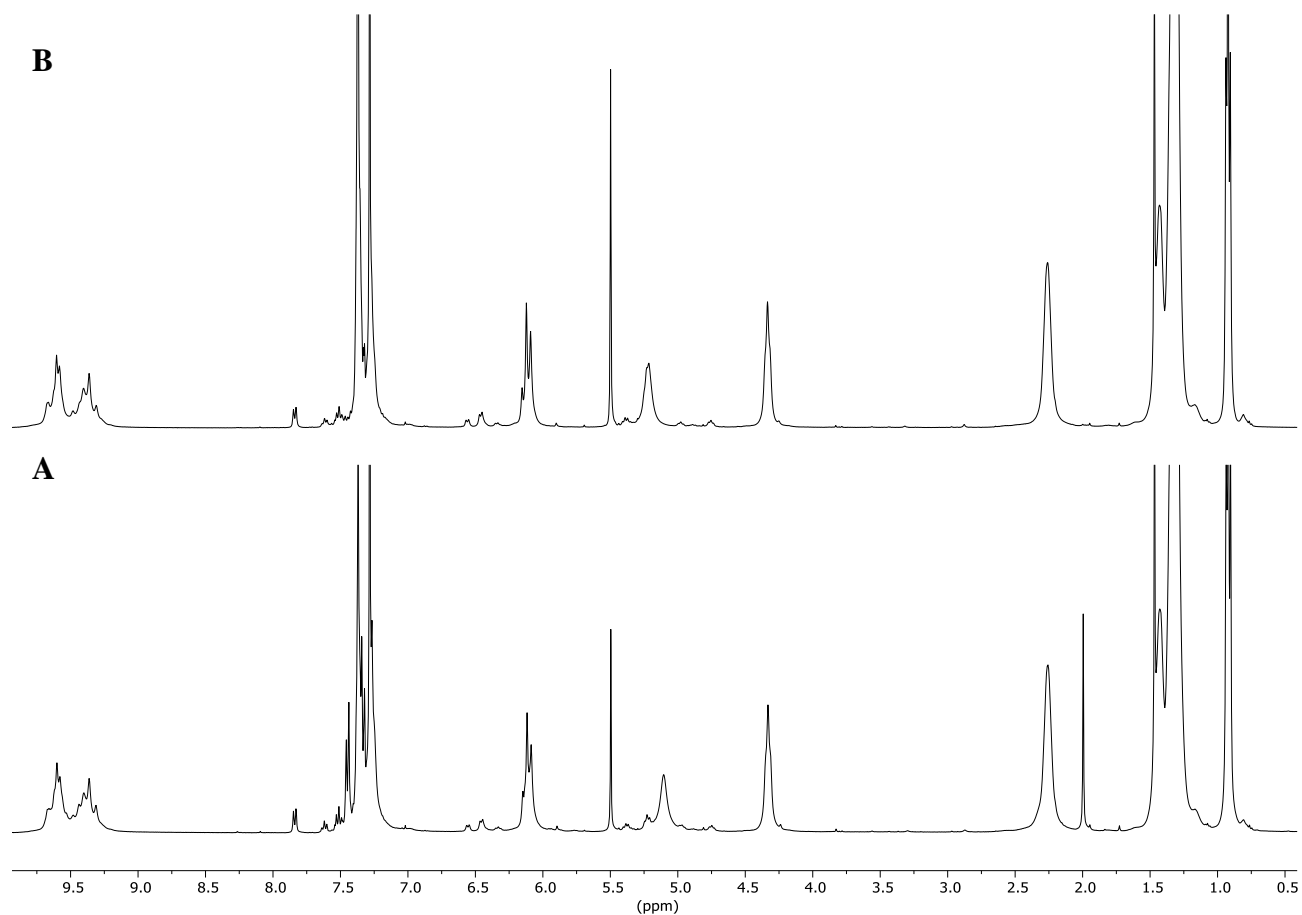
**Figure S9:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub> of a solution of 1,1-diphenylethanol (75 mM), n-hexylresorcinol **2** (30 mM) recorded after 3 h (A) and 20 h (B) at 60 °C.

**Dehydration of 1,1-diphenylethanol: control experiments with acetic acid**



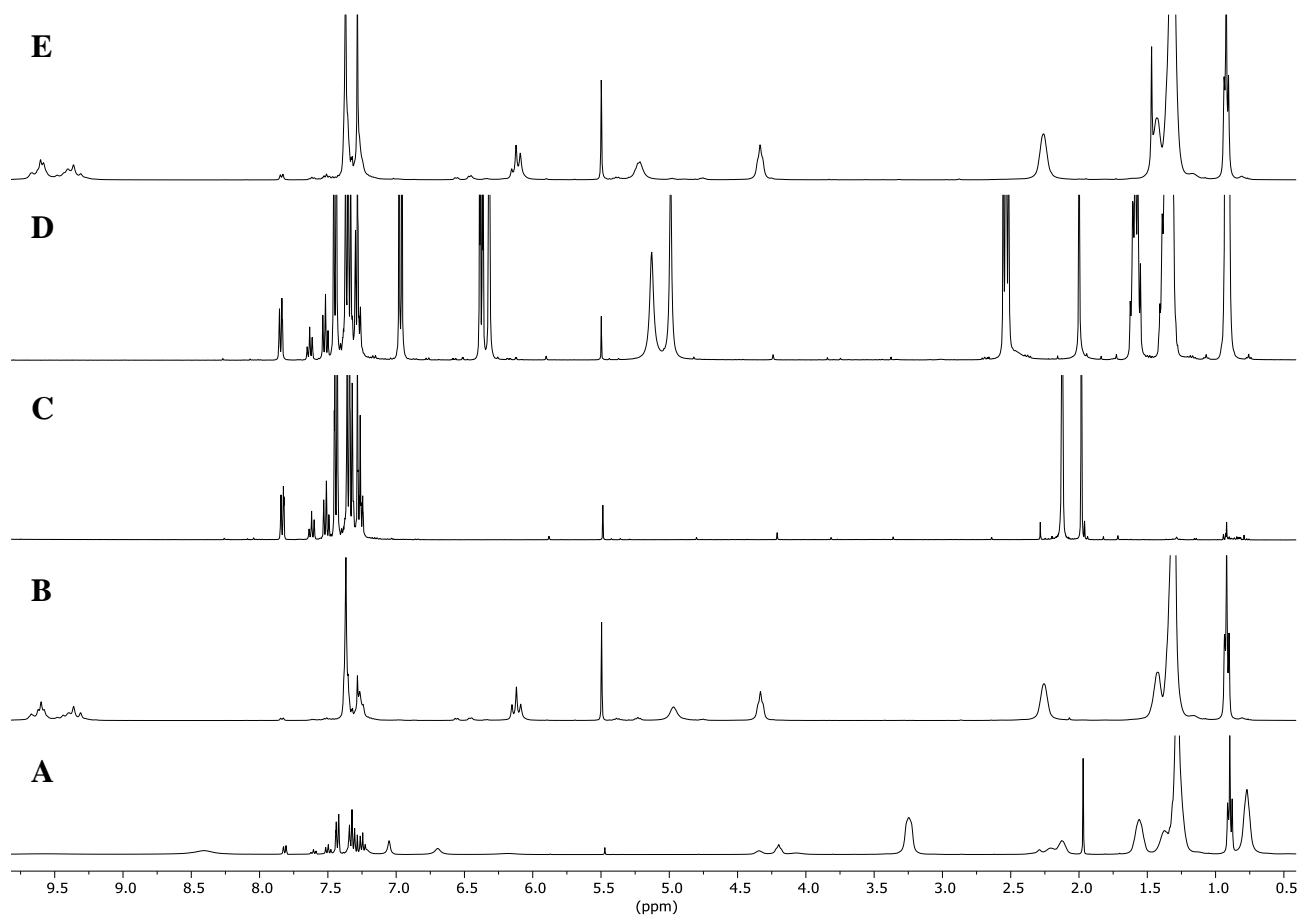
**Figure S10:**  $^1\text{H}$  NMR spectra in water-saturated  $\text{CDCl}_3$  of a solution of 1,1-diphenylethanol (75 mM), acetic acid (29 mM) recorded after 3 h (A) and 20 h (B) at 60 °C.

**Dehydration of 1,1-diphenylethanol: experiment with  $[1_6 \cdot (H_2O)_8]$**



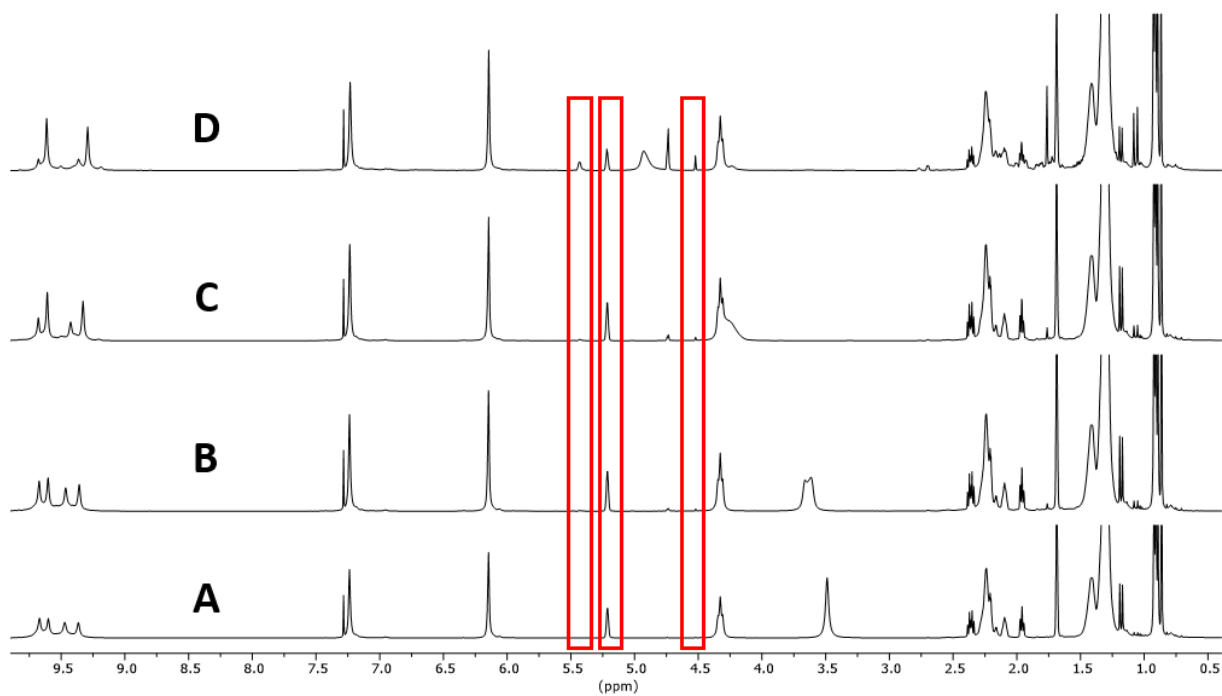
**Figure S11:**  $^1\text{H}$  NMR spectra in water-saturated  $\text{CDCl}_3$  of a solution of 1,1-diphenylethanol (75 mM),  $[1_6 \cdot (H_2O)_8]$  (7.5 mM) recorded after 3 h (A) and 20 h (B) at 60 °C.

**Dehydration of 1,1-diphenylethanol: overview after 20 h**



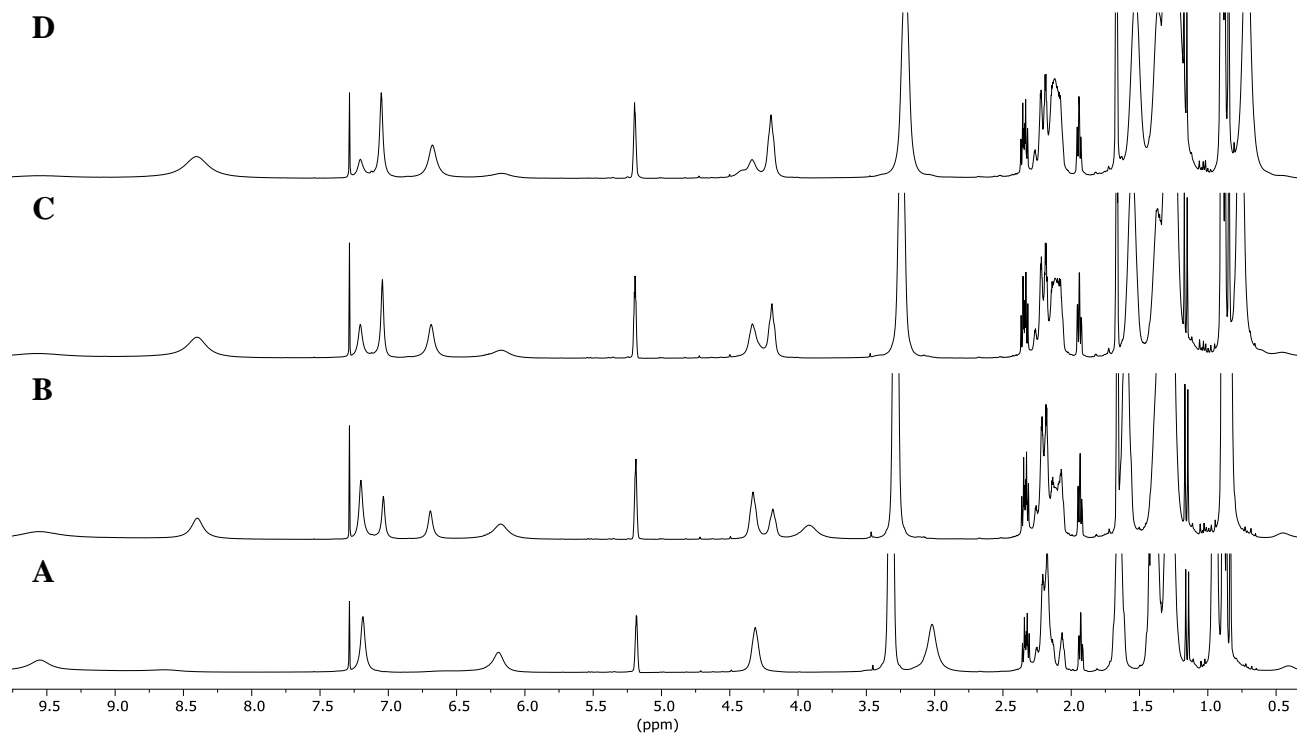
**Figure S12:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub>. A: 1,1-diphenylethanol (75 mM), [1]<sub>6</sub> (7.5 mM), Bu<sub>4</sub>NBr 3 (78 mM); B: 1,1-diphenylethanol (75 mM), [1]<sub>6</sub> (7.5 mM); C: 1,1-diphenylethanol (75 mM), acetic acid (29 mM); D: 1,1-diphenylethanol (75 mM), *n*-hexylresorcinol 2 (30 mM); E: 1,1-diphenylethanol (75 mM), [1]<sub>6</sub>(H<sub>2</sub>O)<sub>8</sub> (7.5 mM). Spectra recorded after 20 h at 60 °C.

**$\alpha$ -Pinene isomerization: experiment with capsule [1<sub>6</sub>]**



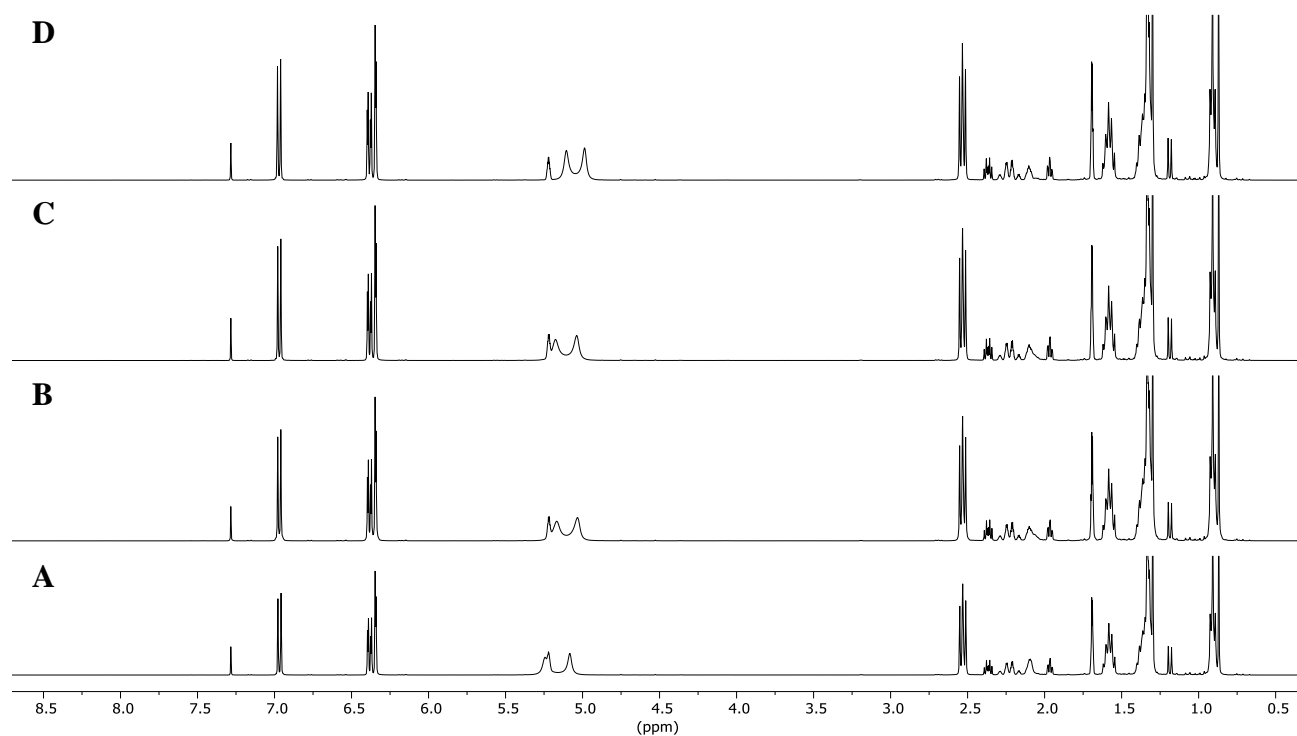
**Figure S13:**  $^1\text{H}$  NMR spectra in water-saturated  $\text{CDCl}_3$  of a solution of  $\alpha$ -pinene (75 mM), [1<sub>6</sub>] (7.5 mM), recorded after preparation (A), after 1.5 h (B), 3 h (C), 24 h (D) at 60 °C.

**$\alpha$ -Pinene isomerization: control experiments with capsule [1<sub>6</sub>] and competitive ammonium guests 3**



**Figure S14:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub> of a solution of  $\alpha$ -pinene (75 mM), [1<sub>6</sub>] (7.5 mM), Bu<sub>4</sub>NBr 3 (78 mM) recorded after preparation (A), after 1.5 h (B), 3 h (C), 24 h (D) at 60 °C.

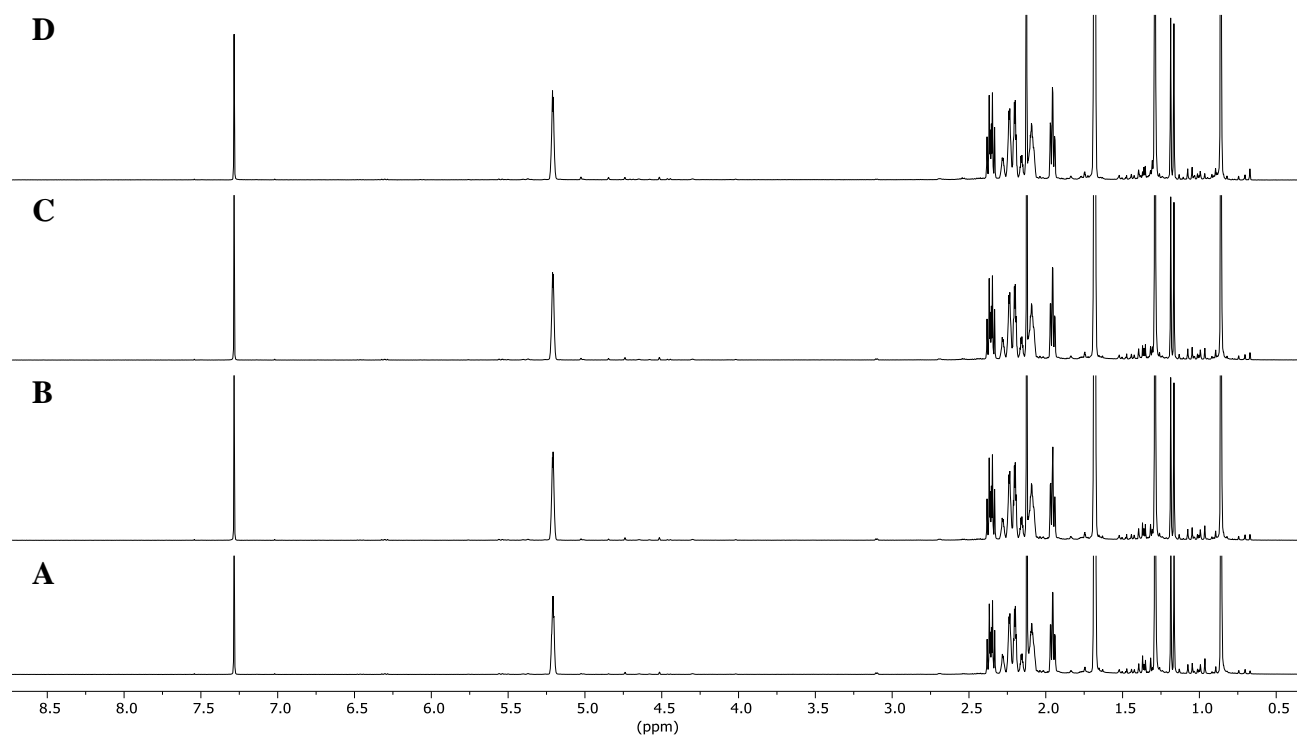
**$\alpha$ -Pinene isomerization: control experiments with 4-*n*-hexyl-resorcinol **2****



**Figure S15:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub> of a solution of  $\alpha$ -pinene (75 mM), n-hexylresorcinol **2** (30 mM), recorded after preparation (A), after 1.5 h (B), 3 h (C), 24 h (D) at 60 °C.

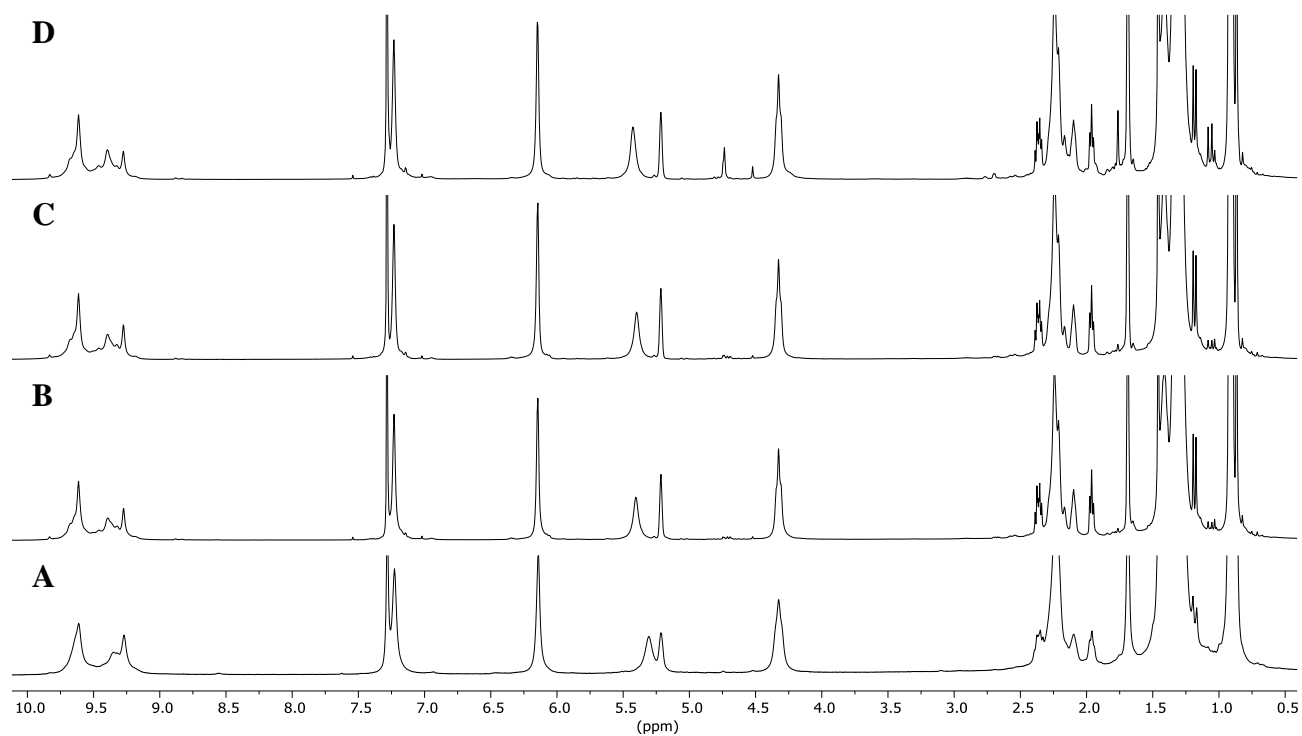


**$\alpha$ -Pinene isomerization: control experiments with acetic acid**



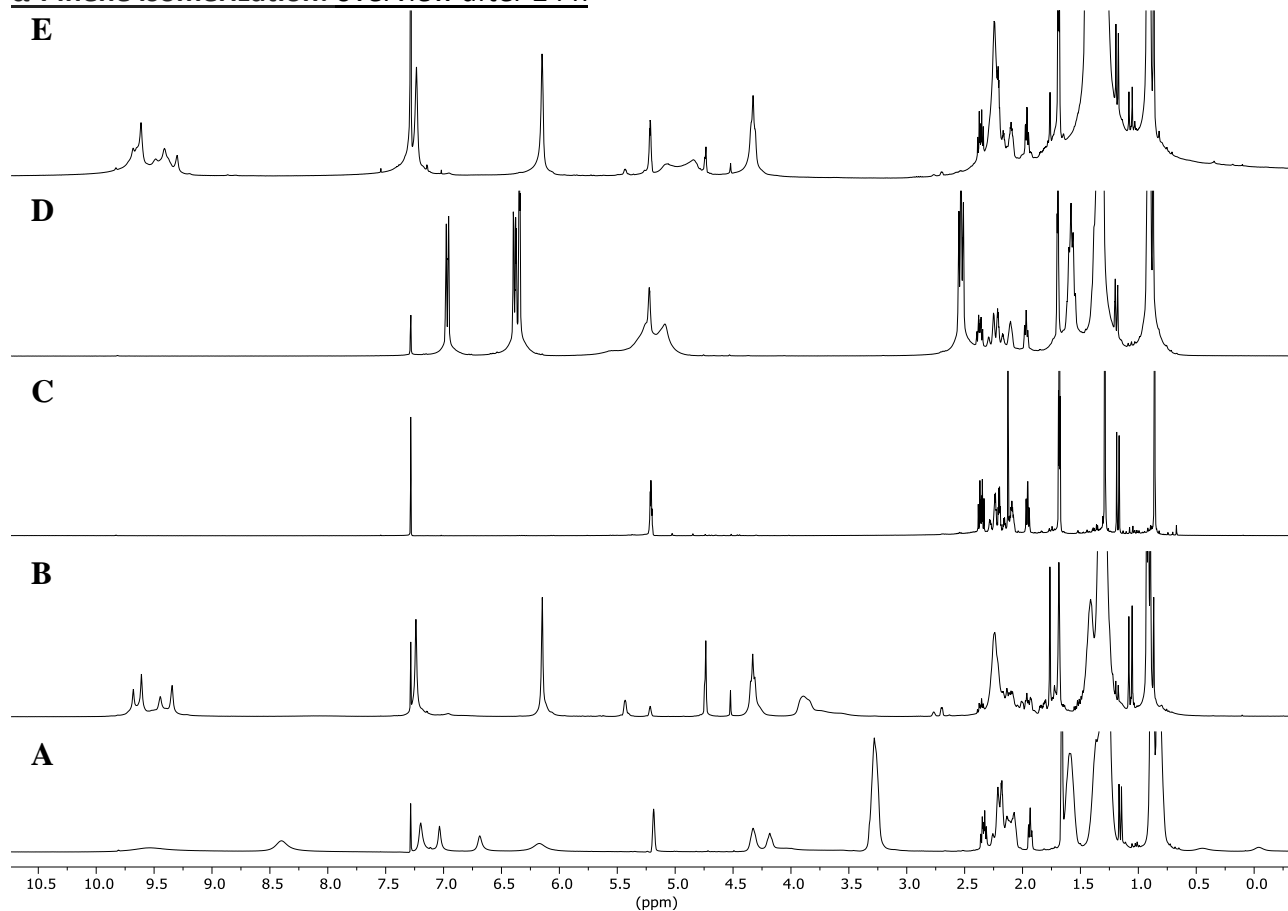
**Figure S16:**  $^1\text{H}$  NMR spectra in water-saturated  $\text{CDCl}_3$  of a solution of  $\alpha$ -pinene (75 mM), acetic acid (29 mM), recorded after preparation (A), after 1.5 h (B), 3 h (C), 24 h (D) at 60 °C.

**$\alpha$ -Pinene isomerization: experiment with capsule  $[\mathbf{1}_6 \cdot (\text{H}_2\text{O})_8]$**



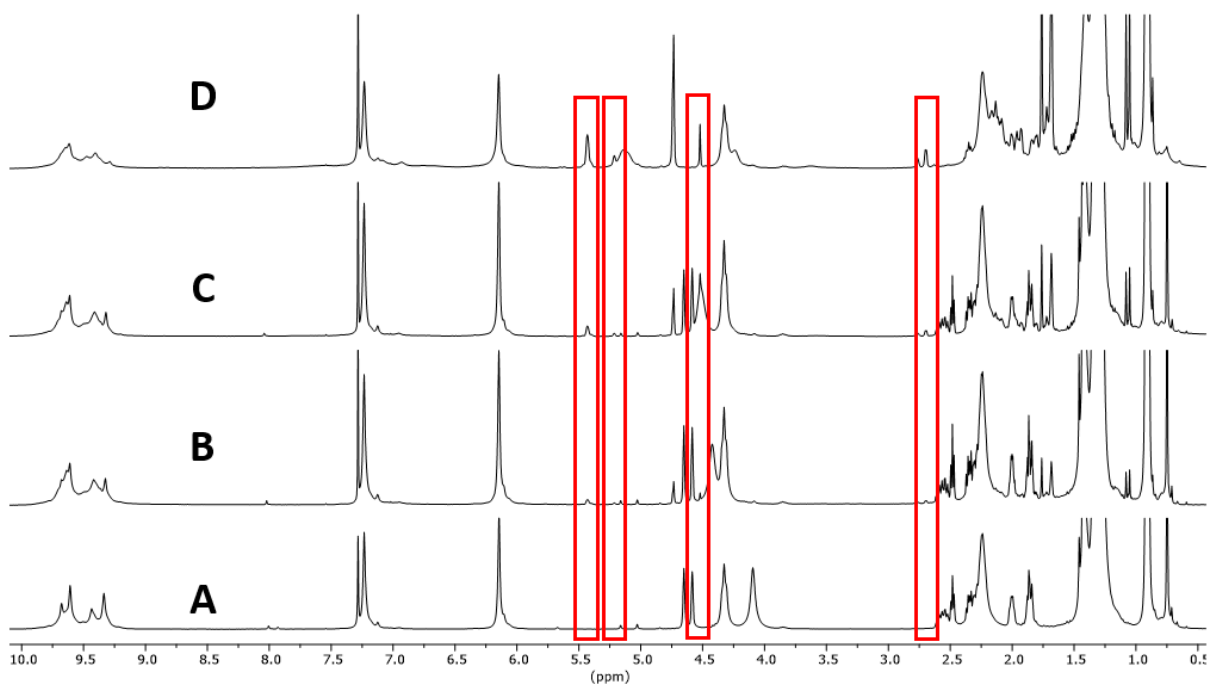
**Figure S17:**  $^1\text{H}$  NMR spectra in water-saturated  $\text{CDCl}_3$  of a solution of  $\alpha$ -pinene (75 mM),  $[\mathbf{1}_6 \cdot (\text{H}_2\text{O})_8]$  (7.5 mM), recorded after preparation (A), after 1.5 h (B), 3 h (C), 24 h (D) at 60 °C.

**$\alpha$ -Pinene isomerization: overview after 24 h**



**Figure S18:**  $^1\text{H}$  NMR spectra in water-saturated  $\text{CDCl}_3$ . A:  $\alpha$ -pinene (75 mM),  $[\mathbf{1}_6(\text{H}_2\text{O})_8]$  (7.5 mM),  $\text{Bu}_4\text{NBr}$  **3** (78 mM); B:  $\alpha$ -pinene (75 mM),  $[\mathbf{1}_6(\text{H}_2\text{O})_8]$  (7.5 mM); C:  $\alpha$ -pinene (75 mM), acetic acid (29 mM); D:  $\alpha$ -pinene (75 mM), *n*-hexylresorcinol **2** (30 mM); E:  $\alpha$ -pinene (75 mM),  $[\mathbf{1}_6(\text{H}_2\text{O})_8]$  (7.5 mM). Spectra recorded after 24 h at  $60^\circ\text{C}$ .

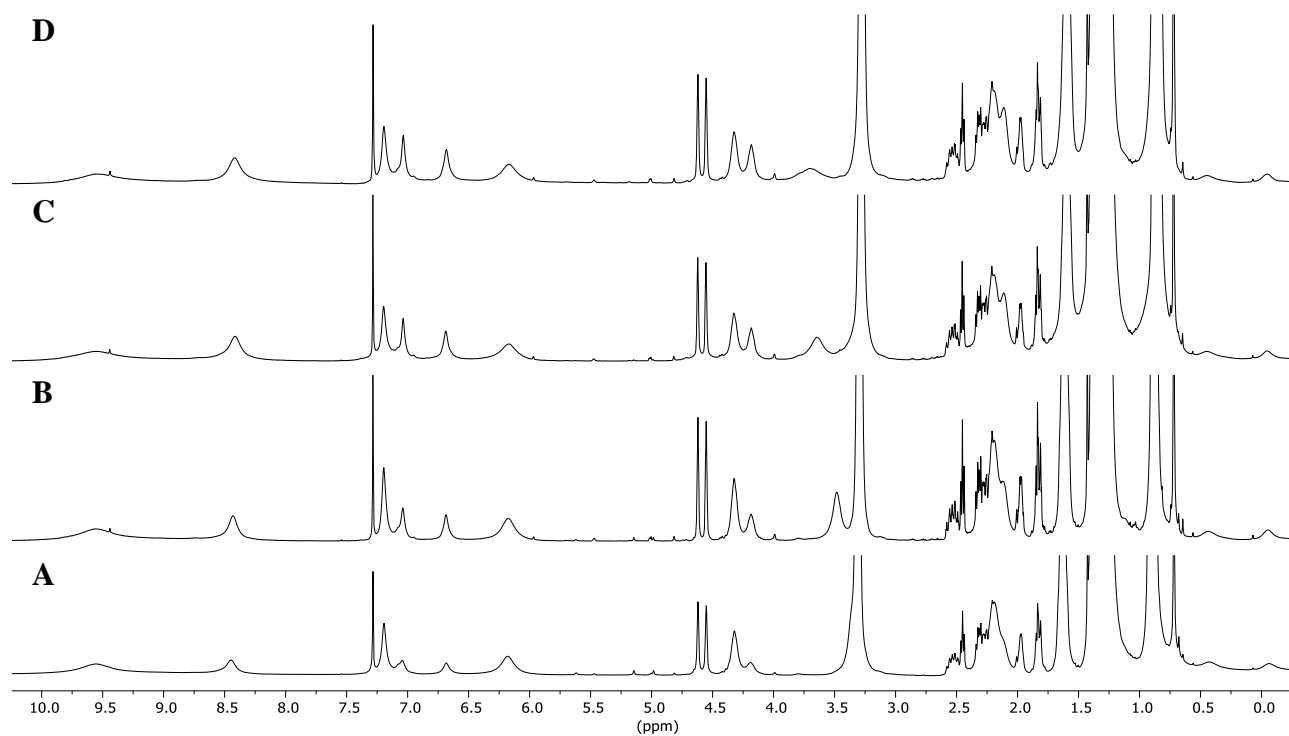
**$\beta$ -Pinene isomerization: Experiment with capsule **[1<sub>6</sub>]****



**Figure S19:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub> of a solution of  $\beta$ -pinene (75 mM), **[1<sub>6</sub>]** (7.5 mM), recorded after preparation (A), after 1.5 h (B), 3 h (C), 24 h (D) at 60 °C.

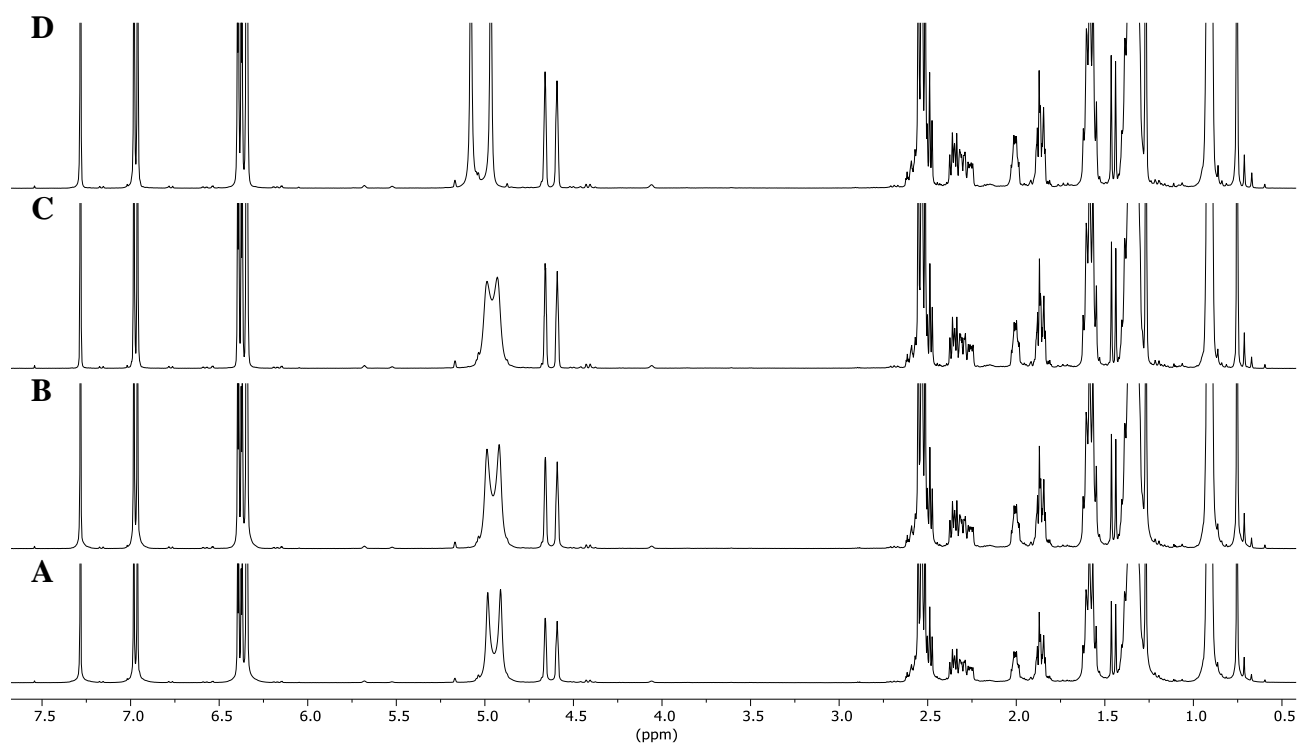
**$\beta$ -Pinene isomerization: control experiments with capsule **[1<sub>6</sub>]** and competitive ammonium**

**guests 3**



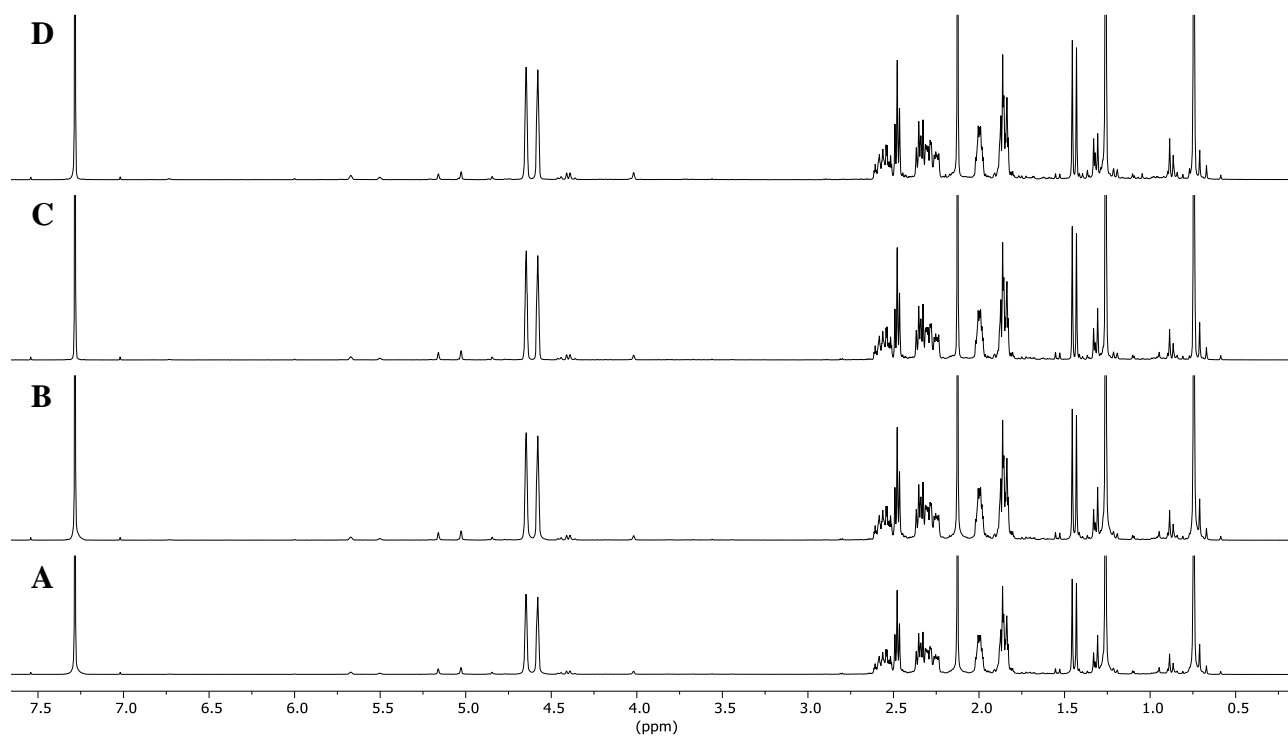
**Figure S20:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub> of a solution of  $\beta$ -pinene (75 mM), **[1<sub>6</sub>]** (7.5 mM), Bu<sub>4</sub>NBr **3** (78 mM) recorded after preparation (A), after 1.5 h (B), 3 h (C), 24 h (D) at 60 °C.

**$\beta$ -Pinene isomerization: control experiments with 4-*n*-hexyl-resorcinol **2****



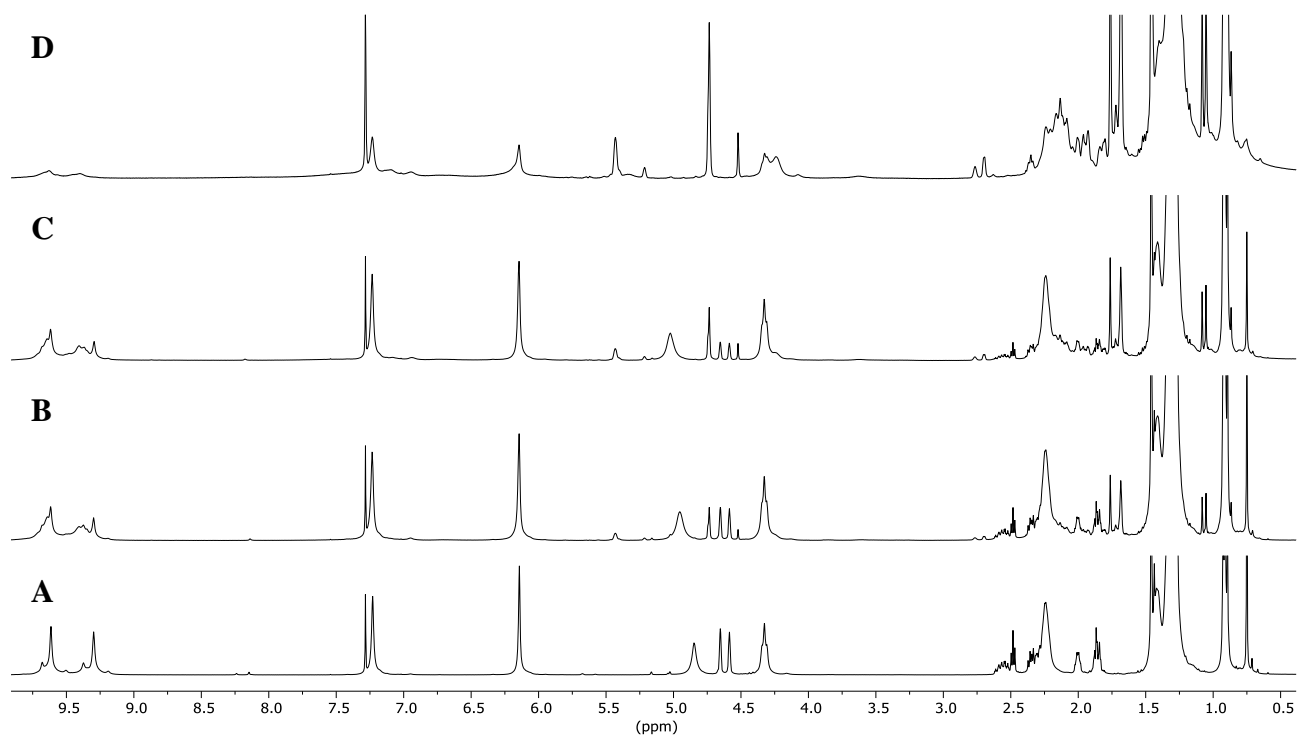
**Figure S21:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub> of a solution of  $\beta$ -pinene (75 mM), n-hexylresorcinol **2** (30 mM), recorded after preparation (A), after 1.5 h (B), 3 h (C), 24 h (D) at 60 °C.

**β-Pinene isomerization: control experiments with acetic acid**



**Figure S22:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub> of a solution of β-pinene (75 mM), acetic acid (29 mM), recorded after preparation (A), after 1.5 h (B), 3 h (C), 24 h (D) at 60 °C.

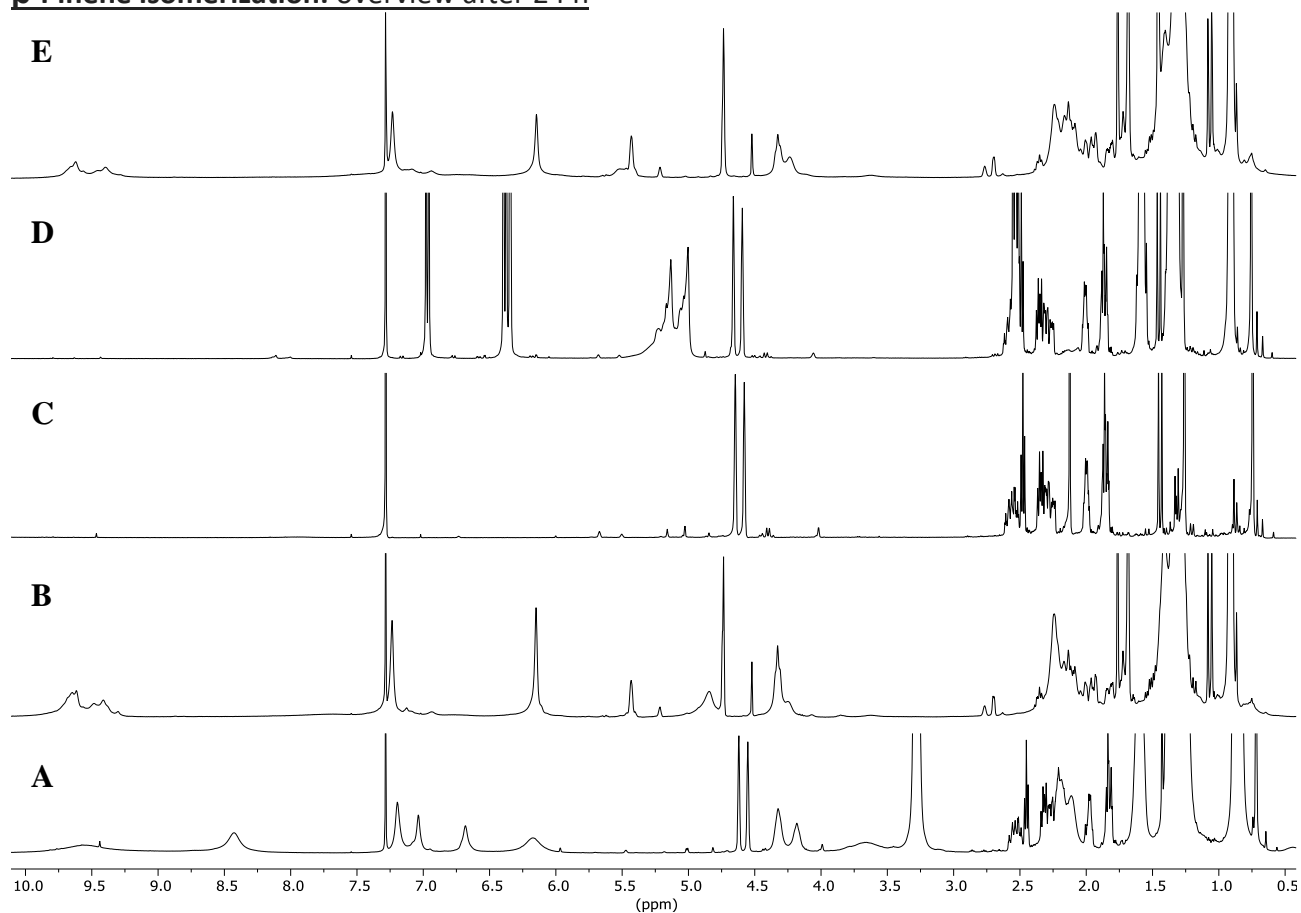
**$\beta$ -Pinene isomerization: experiment with capsule  $[\mathbf{1}_6(\text{H}_2\text{O})_8]$**



**Figure S23:**  $^1\text{H}$  NMR spectra in water-saturated  $\text{CDCl}_3$  of a solution of  $\beta$ -pinene (75 mM),  $[\mathbf{1}_6(\text{H}_2\text{O})_8]$  (7.5 mM), recorded after preparation (A), after 1.5 h (B), 3 h (C), 24 h (D) at 60 °C.

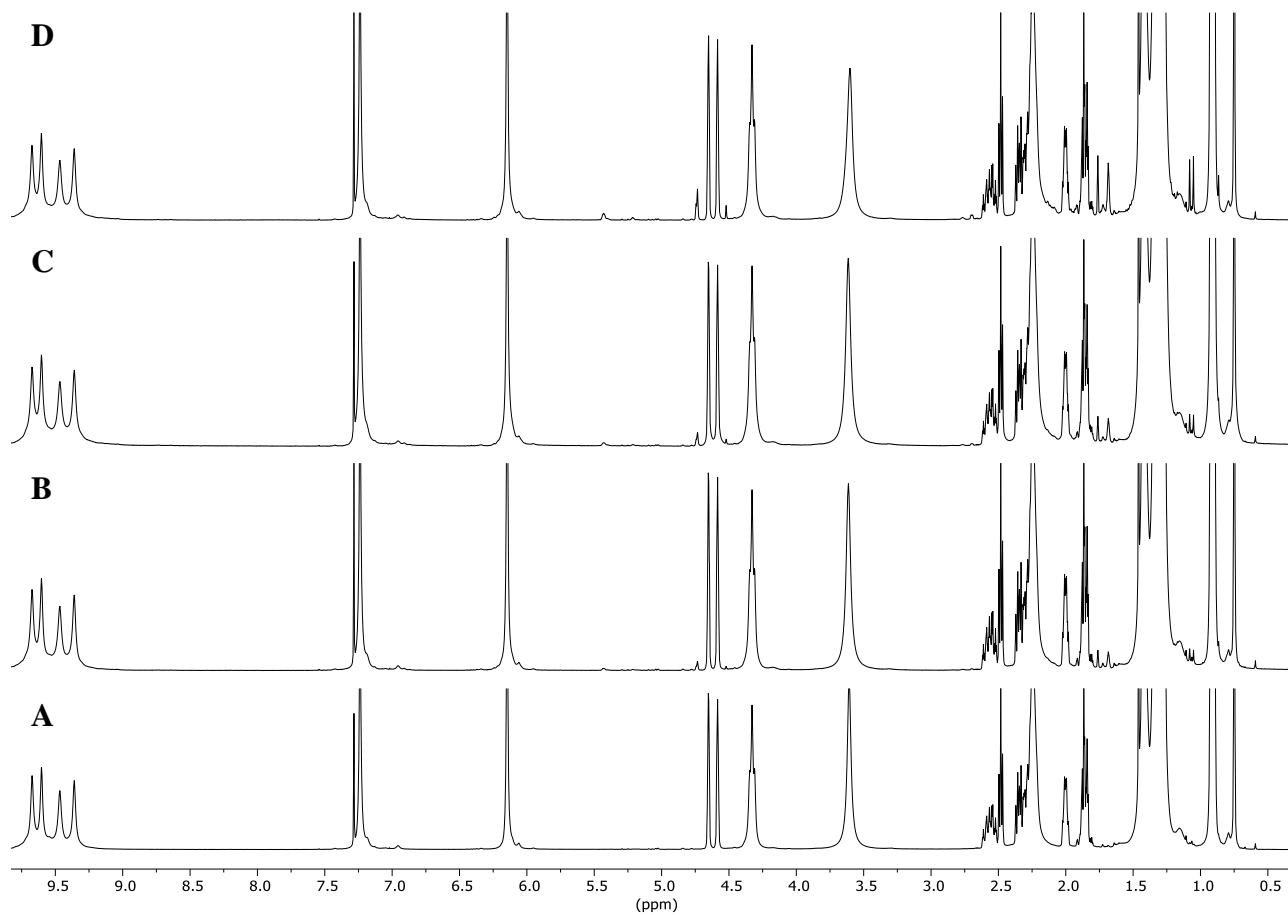


**$\beta$ -Pinene isomerization: overview after 24 h**



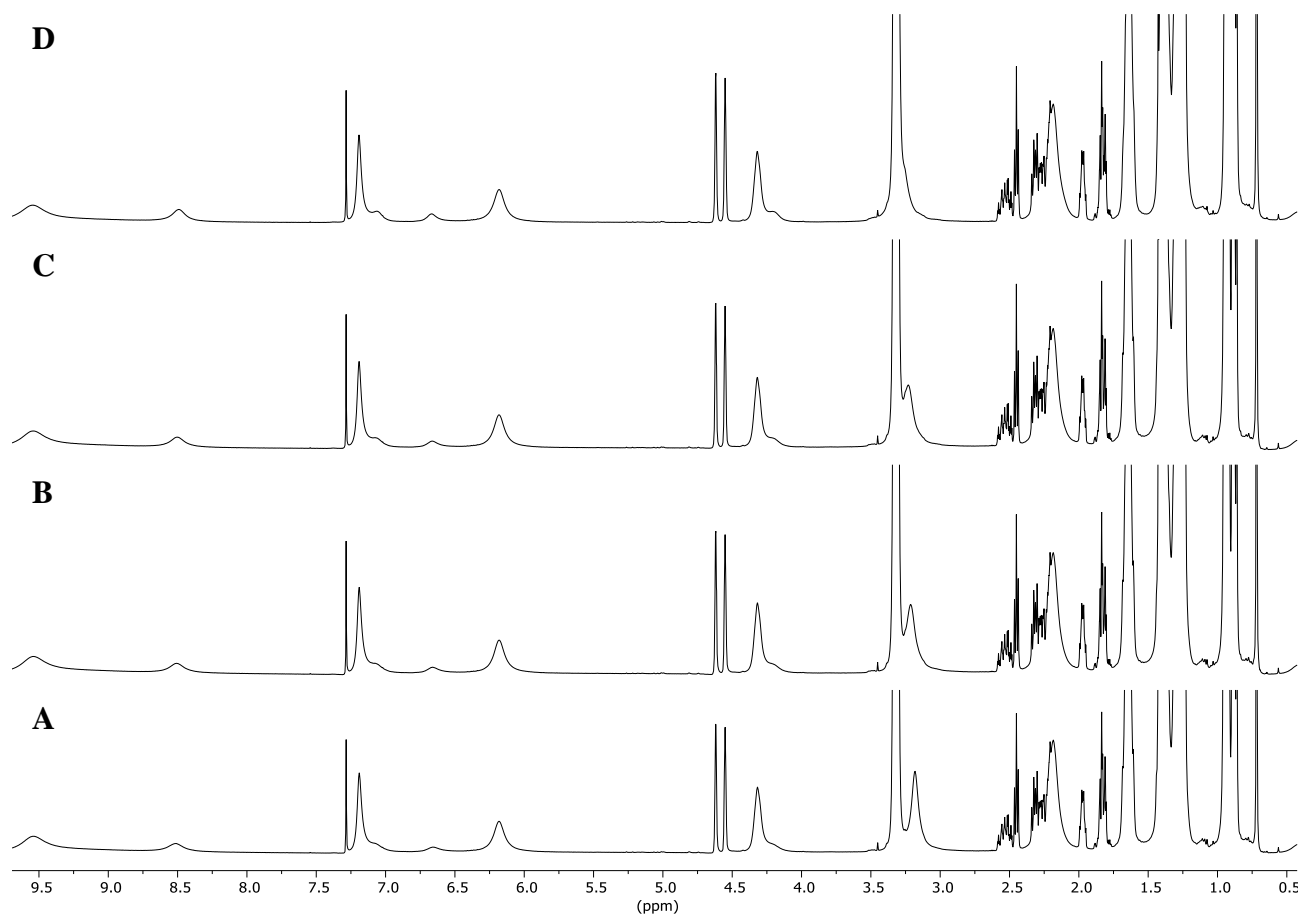
**Figure S24:**  $^1\text{H}$  NMR spectra in water-saturated  $\text{CDCl}_3$ . A:  $\beta$ -pinene (75 mM),  $[\mathbf{1}_6]$  (7.5 mM),  $\text{Bu}_4\text{NBr}$   $\mathbf{3}$  (78 mM); B:  $\beta$ -pinene (75 mM),  $[\mathbf{1}_6]$  (7.5 mM); C:  $\beta$ -pinene (75 mM), acetic acid (29 mM); D:  $\beta$ -pinene (75 mM), *n*-hexylresorcinol  $\mathbf{2}$  (30 mM); E:  $\beta$ -pinene (75 mM),  $[\mathbf{1}_6 \cdot (\text{H}_2\text{O})_8]$  (7.5 mM). Spectra recorded after 24 h at 60 °C.

**$\beta$ -Pinene isomerization at room temperature: experiment with capsule [1<sub>6</sub>]**



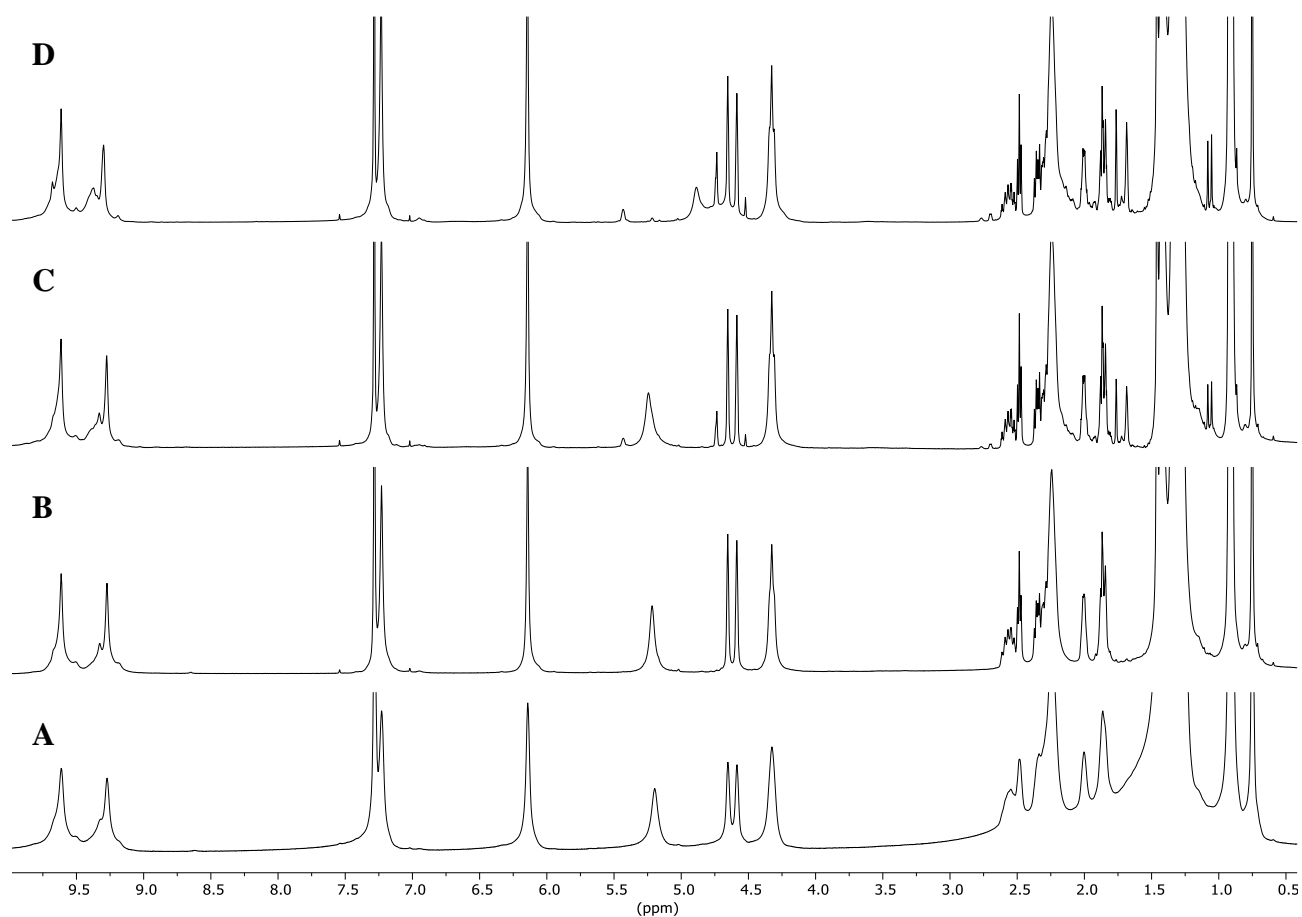
**Figure S25:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub> of a solution of  $\beta$ -pinene (75 mM), [1<sub>6</sub>] (7.5 mM) recorded after 1 h (A), 23 h (B), 35 h (C), 64 h (D) at room temperature.

**$\beta$ -Pinene isomerization at room temperature: control experiments with capsule [1<sub>6</sub>] and competitive ammonium guests 3**



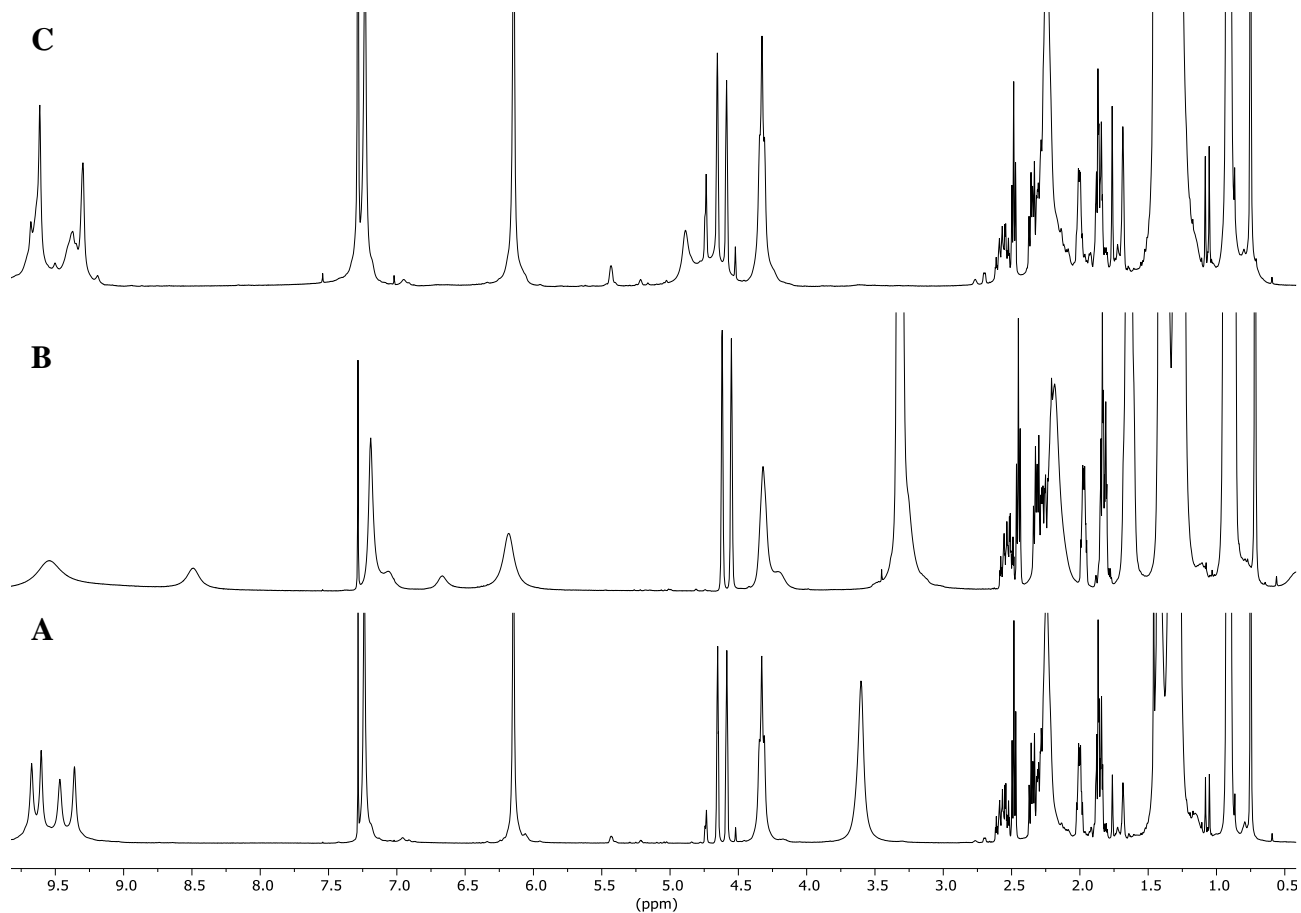
**Figure S26:** <sup>1</sup>H NMR spectra in water-saturated CDCl<sub>3</sub> of a solution of β-pinene (75 mM), [1<sub>6</sub>] (7.5 mM), Bu<sub>4</sub>NBr **3** (78 mM) recorded after 1 h (A), 23 h (B), 35 h (C), 64 h (D) at room temperature.

**$\beta$ -Pinene isomerization at room temperature: experiment with capsule  $[\mathbf{1}_6 \cdot (\text{H}_2\text{O})_8]$**



**Figure S27:**  $^1\text{H}$  NMR spectra in water-saturated  $\text{CDCl}_3$  of a solution of  $\beta$ -pinene (75 mM),  $[\mathbf{1}_6 \cdot (\text{H}_2\text{O})_8]$  (7.5 mM) recorded after 1 h (A), 23 h (B), 35 h (C), 64 h (D) room temperature.

**$\beta$ -Pinene isomerization at room temperature: overview after 64 h**



**Figure S28:**  $^1\text{H}$  NMR spectra in water-saturated  $\text{CDCl}_3$ . A:  $\beta$ -pinene (75 mM),  $[\mathbf{1}_6]$  (7.5 mM); B:  $\beta$ -pinene (75 mM),  $[\mathbf{1}_6]$  (7.5 mM),  $\text{Bu}_4\text{NBr}$   $\mathbf{3}$  (78 mM); C:  $\beta$ -pinene (75 mM),  $[\mathbf{1}_6(\text{H}_2\text{O})_8]$  (7.5 mM). Spectra recorded after 64 h at room temperature.

PlacidoB-bPineneCapsula60C\_100415 #458 RT: 7.34 AV: 1 SB: 2 7.28, 7.41 NL: 4.97E4  
T: (0;0) + c El det=350.00 Full ms [ 35.00-500.00]

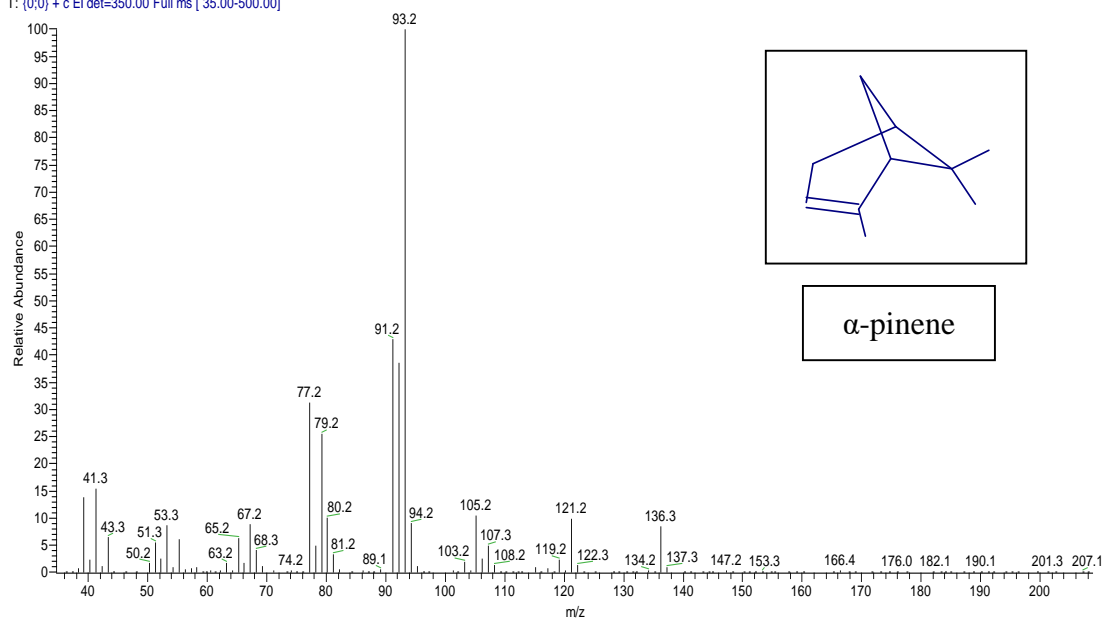


Figure S29: EIMS spectrum of  $\alpha$ -pinene.

PlacidoB-bPineneCapsula60C\_100415 #492 RT: 7.59 AV: 1 SB: 2 7.28, 7.41 NL: 8.02E4  
T: (0;0) + c El det=350.00 Full ms [ 35.00-500.00]

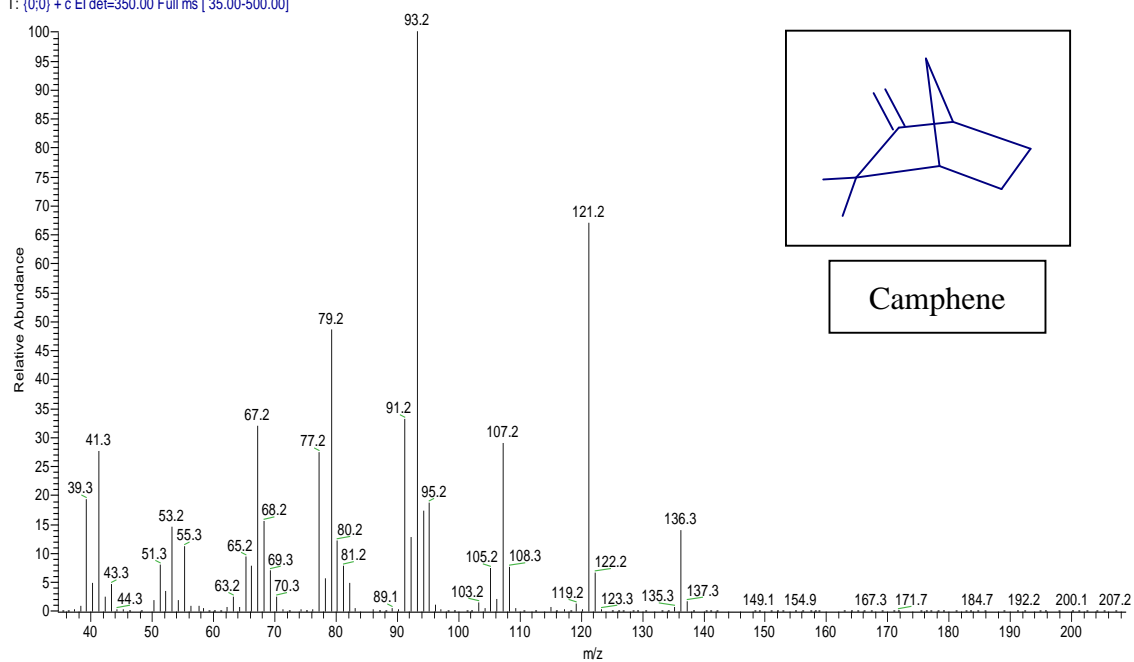


Figure S30: EIMS spectrum of camphene.

PlacidoB-bPineneCapsula60C\_100415 #549 RT: 8.01 AV: 1 SB: 2 7.28, 7.41 NL: 2.74E4  
T: (0;0) + c El det=350.00 Full ms [ 35.00-500.00]

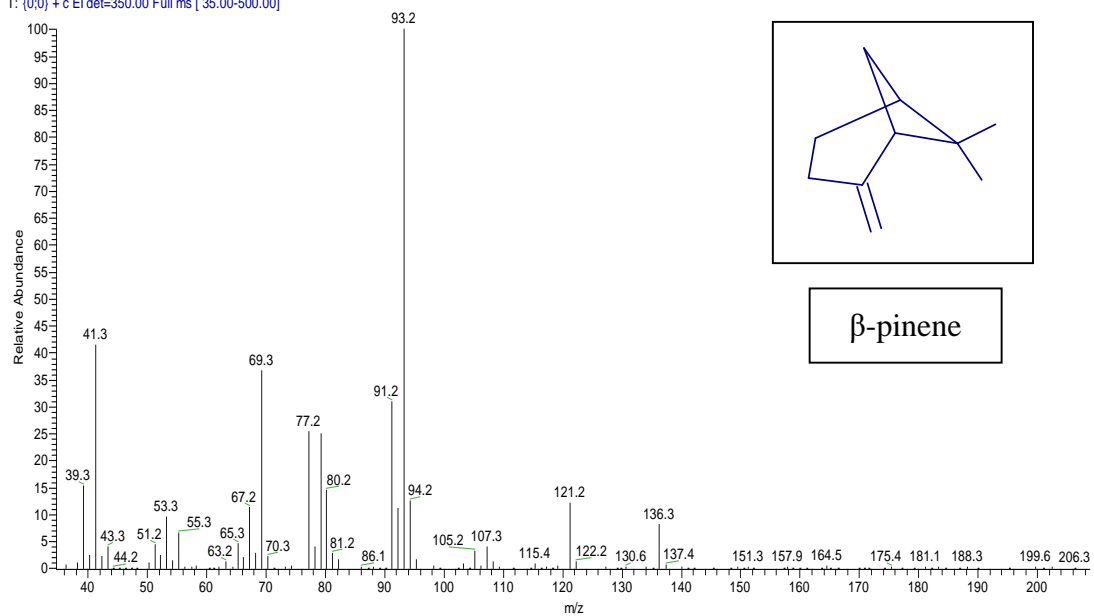


Figure S31: EIMS spectrum of  $\beta$ -pinene.

PlacidoB-bPineneCapsula60C\_100415 #620 RT: 8.53 AV: 1 SB: 2 7.28, 7.41 NL: 1.13E4  
T: (0;0) + c El det=350.00 Full ms [ 35.00-500.00]

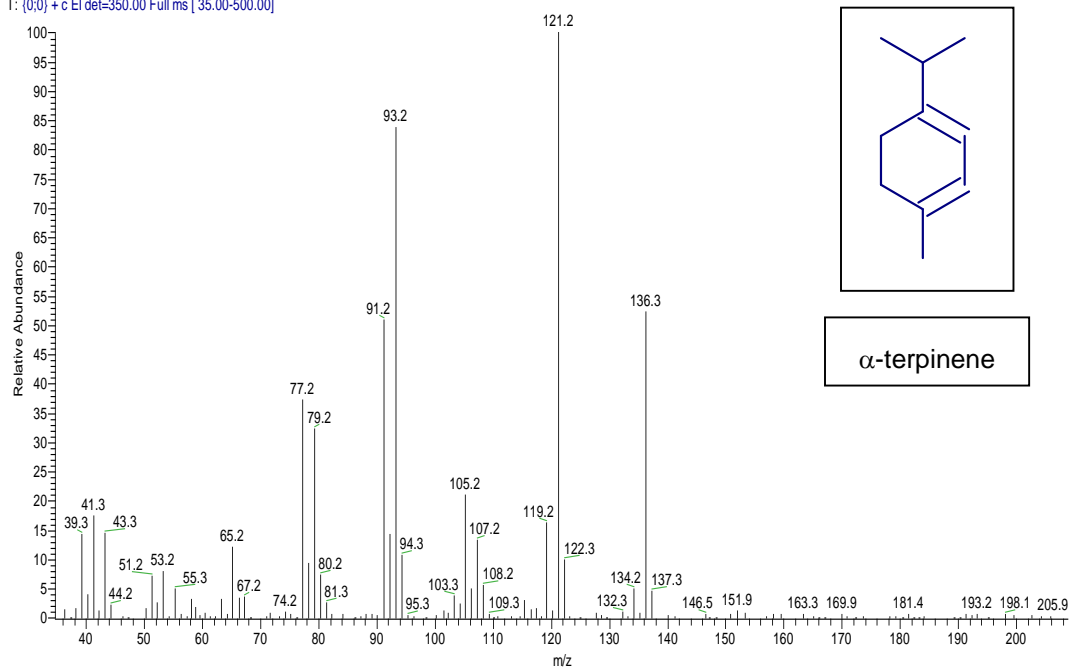


Figure S32: EIMS spectrum of  $\alpha$ -terpinene

PlacidoB-bPineneCapsula60C\_100415 #640 RT: 8.67 AV: 1 SB: 2 7.28, 7.41 NL: 1.82E5  
T: (0;0) + c El det=350.00 Full ms [ 35.00-500.00]

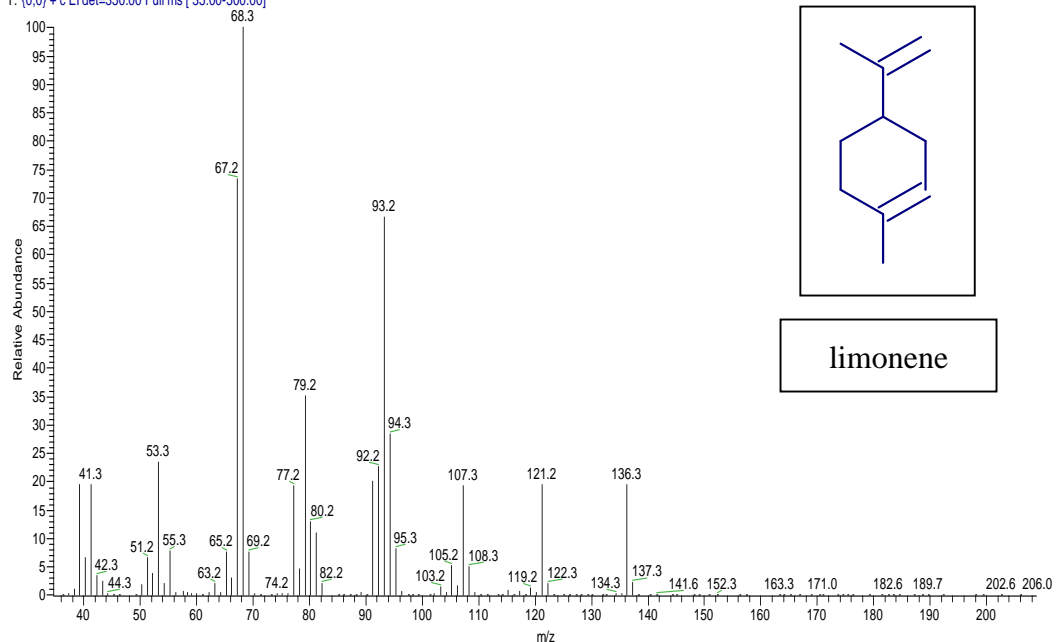


Figure S33: EIMS spectrum of limonene.

PlacidoB-bPineneCapsula60C\_100415 #689 RT: 9.03 AV: 1 SB: 2 7.28, 7.41 NL: 1.25E4  
T: (0;0) + c El det=350.00 Full ms [ 35.00-500.00]

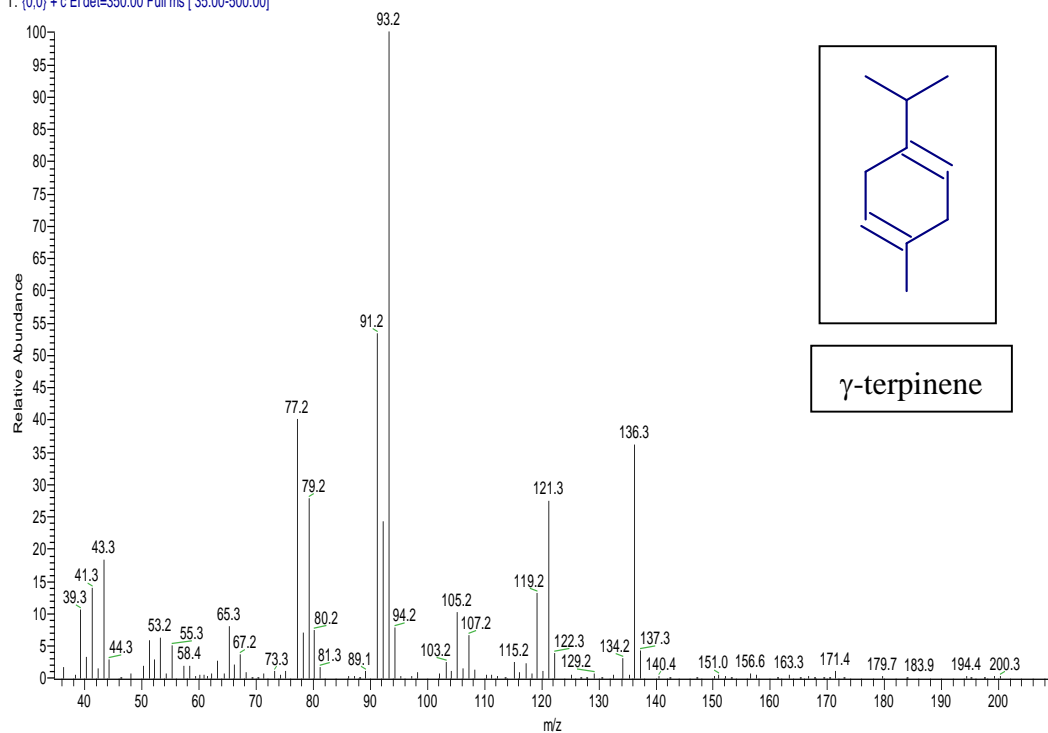


Figure S34: EIMS spectrum of  $\gamma$ -terpinene



PlacidoB-bPineneCapsula60C\_100415 #735 RT: 9.37 AV: 1 SB: 2 7.28, 7.41 NL: 3.10E4  
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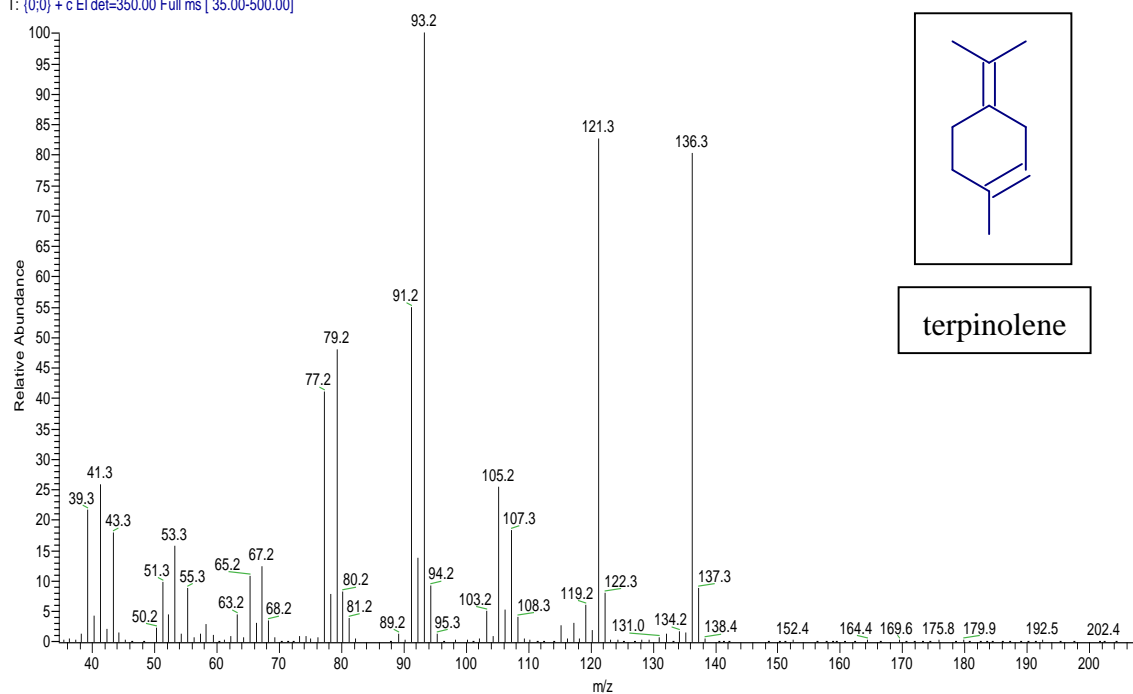


Figure S35: EIMS spectrum of terpinolene.

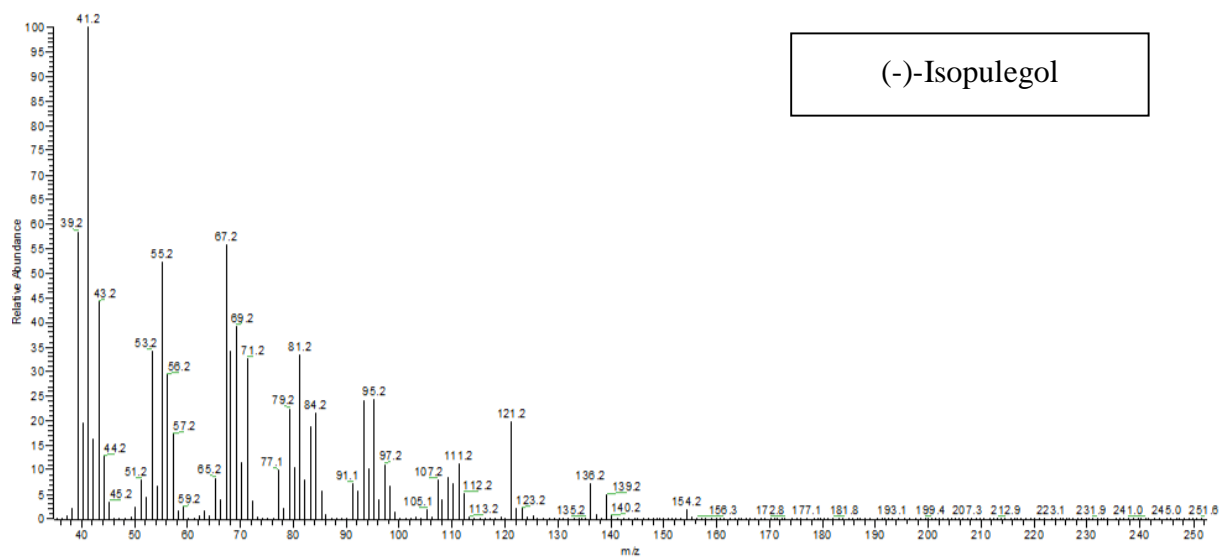


Figure S36: MSEI spectrum for (-)-isopulegol M.W. = 154

Placido-CitronellaCaps-18h\_170415 #912 RT: 10.16 AV: 1 NL: 3.30E4  
T: (0;0) + c EI det=350.00 Full ms [ 35.00-500.00]

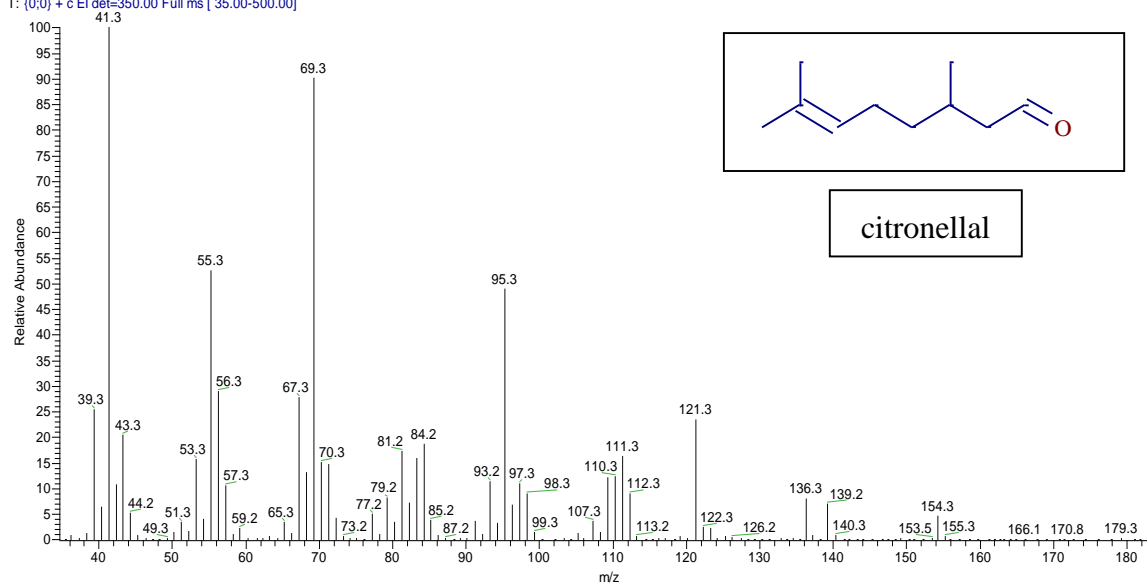


Figure S37: EIMS spectrum of citronellal.

Placido-CitronellaCaps-18h\_170415 #963 RT: 10.53 AV: 1 NL: 3.04E3  
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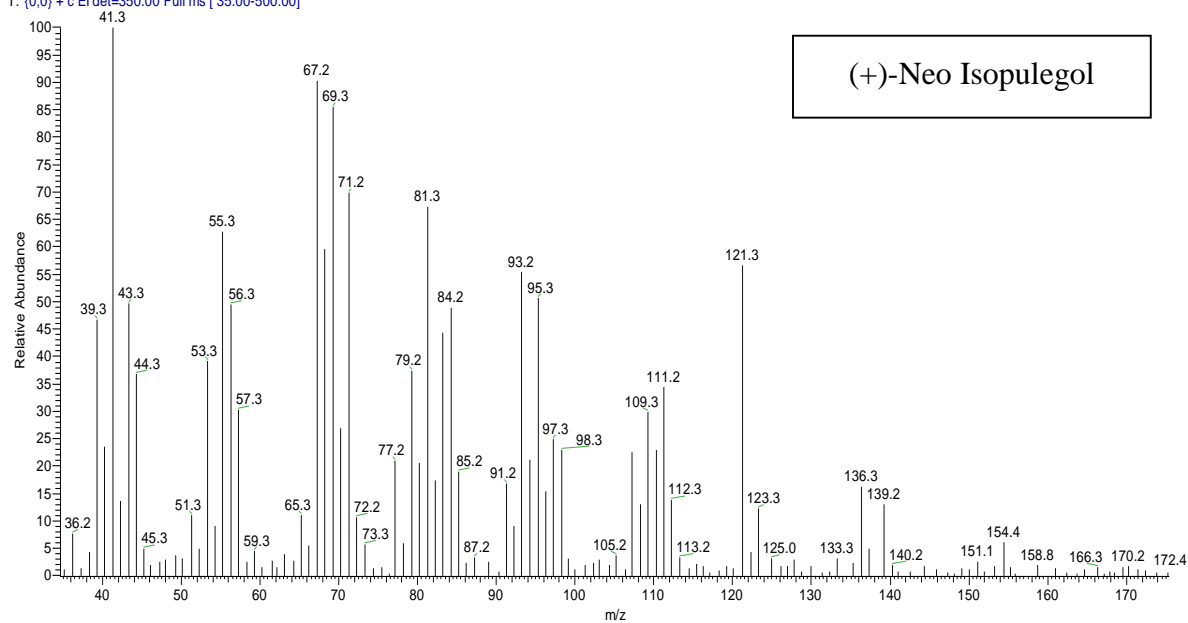


Figure S38: EIMS spectrum of neo-isopulegol.