# Supporting Information

# 1. Experimental

Chemicals were purchased from *Acros Organics* (Geel, Belgium), *Sigma-Aldrich* (Steinheim, Germany), *ABCR* (Karlsruhe, Germany) and *TCI* (Tokyo, Japan).

All chemicals were employed without drying or any further purification.

All compounds were directly weighed into the reaction vessel, which was afterwards closed and pressurized with argon (5 bars). The reactors were placed in an aluminium heating block and stirred magnetically. After 5 h the reaction was ended by cooling the reactors with an ice-bath.

# 2. Analytic Methods 2.1. GC-FID

The myrcene dimers were quantified via GC-FID using an *Agilent 7840B* gas chromatograph equipped with a *flame ionization detector* (*FID*). Injection volume was 1  $\mu$ L using a split ratio of 15:1 and HP-5 column with length of 30 m and a diameter 0f 0.320 mm. The temperature ramp was the following:

	<u>Heating Rate</u> [°C/min]	<u>Final Temperature</u> [°C]	<u>Hold [min]</u>
Start	-/-	40	3
Ramp 1	15	290	0
Ramp 2	40	320	10

## 2.2. HPLC-DAD

The desired products were quantified by high performance liquid chromatography using an *Elite LaChrom* device from *Hitachi*, consisting of a *Hitachi* L-2350 column oven (at 40 °C), a *Hitachi* L-2130 Pump and a *Hitachi* L-2200 auto-sampler. Quantification was accomplished with an *L-2450 diode array detector (DAD)* from *Hitachi*. The column used was an *Agilent* RP-C8 column (Eclipse XDB-C8). Retention was achieved by ion pair chromatography, using 1-octanesulfonic acid in water (0.005 mol/L) and water/acetonitrile (w/w = 1/9) with linear gradients between the following points:

time [min]	$\underline{ACN/H_2O} (w/w = 9/1)$	<u>H<sub>2</sub>O (OSA 5mM)</u>
0	0%	100%
3	0%	100%
6	70%	30%
25	78%	22%
30	100%	0%
39	100%	0%
45	0%	100%
60	0%	100%

The product was isolated and calibrated with 2-butanone as internal standard.



#### 2.1. Pendant Drop Experiments

The critical micelle concentration was determined by pendant drop experiments using a *contour analysis system OCA 15EC* from *DataPhysics* equipped with a video measuring system up to 311 frames/s from *DataPhysics*. The scientific exploitation was performed by *DataPhysics SCA 20* (v. 3.61.6).

#### **2.2. NMR**

<sup>1</sup>H-NMR spectra were recorded on a *Bruker DRX300* (300 MHz) spectrometer, using CD<sub>3</sub>OD from *Deutero* as solvent.

#### **2.3. HRMS**

High resolution mass spectra were recorded on a *TSQ* mass spectrometer from *ThermoQuest* coupled to an HPLC-system (HPLC column: *Hypersyl GOLD*, 50 mm  $\times$  1 mm, 1.9 µm) for HPLC-ESI-HRMS.

#### 2.4. Characterization of the Product

The product was isolated as a mixture of isomers. This means (E/Z)-configuration of internal double bonds as well as the linkage of the myrcene units (*tail-tail, tail-head, head-head* and *head-tail*).

OH OH. ÓH ÓH

Chemical Formula: C<sub>27</sub>H<sub>49</sub>NO<sub>5</sub> Exact Mass: 467.36107

NMR: <sup>1</sup>H-NMR (300 MHz, CD<sub>3</sub>OD): ppm (δ) = 5.62 - 5.41 (m, 1H), 5.22 (m, 1H), 5.07 (m, 2H), 5.00 (s, 1H), 4.96 (s, 1H), 3.95 - 3.81 (m, 1H), 3.81 - 3.62 (m, 3H), 3.62 - 3.48 (m, 2H), 3.31 (s, 1H), 3.29 - 3.21 (m, 2H), 3.19 - 2.99 (m, 1H), 2.57 (m, 2H), 2.28 (s, 3H), 2.14 - 1.77 (m, 11H), 1.64 (s, 6H), 1.56 (m, 3H), 1.56 - 1.40 (m, 5H), 1.40 - 1.14 (m, 3H).

<sup>13</sup>**C-NMR** (75 MHz, CD<sub>3</sub>OD) ppm (δ) = 145.05, 144.21, 132.71, 132.13, 125.69, 125.07, 121.81, 115.36, 73.28, 72.94, 72.85, 71.69, 64.90, 60.96, 56.44, 49.00, 44.78, 42.76, 36.33, 35.63, 34.63, 31.45, 27.95, 26.68, 25.94, 17.85, 17.80.

<u>ESI-HRMS</u> :	Calculated ([M+H] <sup>+</sup> ):	468.36835
	Measured ([M+H] <sup>+</sup> ):	468.36863

## 2.4.1. <sup>1</sup>H-NMR spectrum



2.4.2. <sup>13</sup>C-NMR spectrum



## **3. Isolation of the product**

The organic phase of a reaction was evaporated to dryness and further purified by silica gel chromatography. The column was packed with ethyl acetate and flushed with one volume equivalent of pure ethyl acetate to remove the non-polar compounds (myrcene, its isomers and dimers) the column was flushed with ethyl acetate. Afterwards the solvent is changed to methanol/ethyl acetate mixture (v/v = 1/1) to elute the desired products.