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## Supporting Information

# Synthesis of biobased amines *via* Pd-catalysed telomerisation of the renewable $\beta$ -myrcene in a water/ethanol multiphase system: catalyst recycling enabled by a self-separating product phase

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# 1. Autoclaves and setups

The used autoclaves are shown in Figure S1.

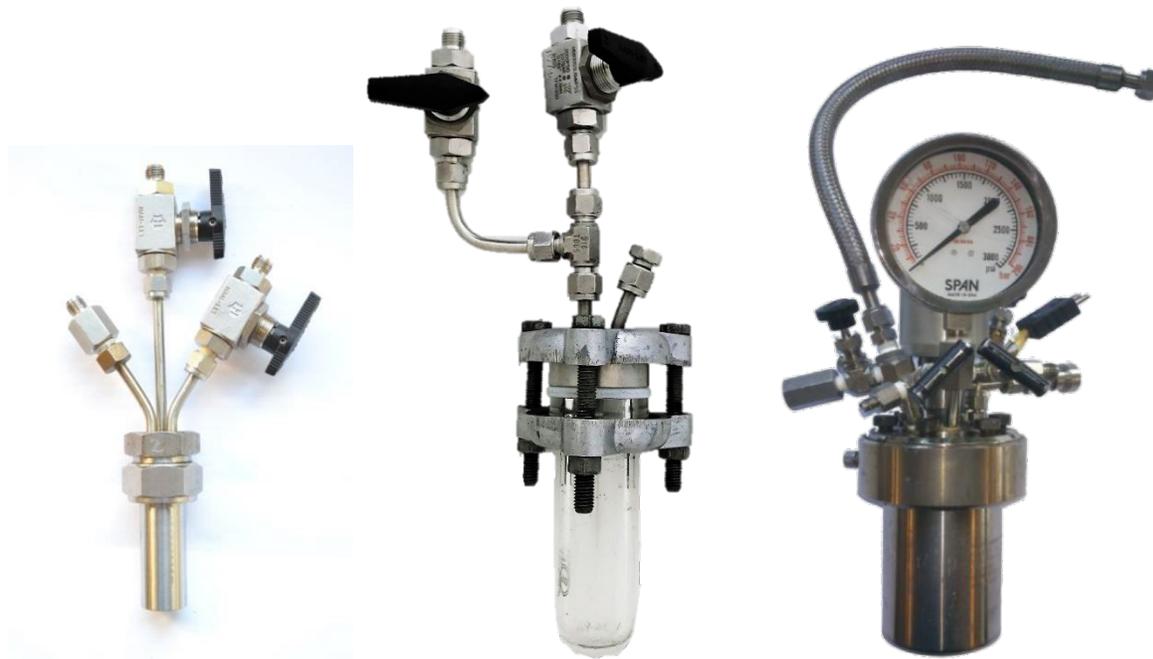


Figure S1: 25 mL stainless steel autoclave for screening experiments (left), glass autoclave for recycling experiments (middle), and 300 mL stainless steel autoclave from PARR for scale-up experiment (right)

## Setup for recycling experiments

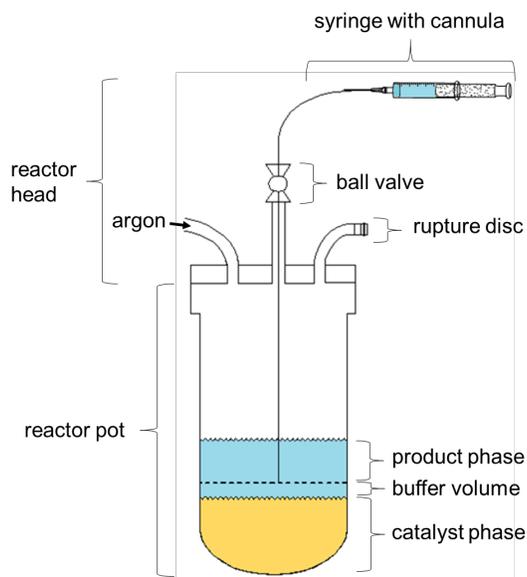


Figure S2: Scheme of the setup for the recycling experiments in the 40 mL glass autoclave.

## 2. Chemicals used

All chemicals used are listed in the table below.

Table S1: list of chemicals.

<b>name</b>	<b>purity</b>	<b>company</b>
<b><math>\beta</math>-myrcene</b>	90 %	ACROS ORGANICS
<b><i>n</i>-diethylamine</b>	99 %	FISCHER SCIENTIFIC
<b>dimethylamine</b>	40 w% in water	
<b>ethylamine</b>	30% in methanol	TCI
<b><i>n</i>-butylamine</b>	>99 %	ACROS ORGANICS
<b>di-<i>n</i>-butylamine</b>	98 %	ABCR
<b>aniline</b>	99.8 %	ACROS ORGANICS
<b>piperidine</b>	99 %	MERCK
<b>morpholine</b>	>99 %	MERCK
<b>di-<i>iso</i>-propylamine</b>	>99 %	ACROS ORGANICS
<b>sarcosine</b>	98 %	ABCR
<b>ammonia</b>	99.98 vol.-%	MESSER INDUSTRIEGASE GMBH
<b>argon</b>	99.996 %	MESSER INDUSTRIEGASE GMBH
<b><i>n</i>-dodecane</b>	99 %	ACROS ORGANICS
<b>ethanol</b>	>99.9%	VWR
<b>isopropanol</b>	>99.7 %	VWR
<b>Pd[acac]<sub>2</sub></b>		UMICORE AG & Co. KG
<b>TPPTS</b>		OQ CHEMICALS

### 3. Analytics

**NMR-Spectroscopy:**  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR-spectra were recorded with the spectrometer from BRUKER (Bruker Avance III HD NanoBay - 400 MHz) with the frequency and solvent noted. Chemical shifts  $\delta$  are given in ppm relative to tetramethylsilane. The  $^{31}\text{P}$ -NMR-spectra were recorded with the spectrometer SPINSOLVE PHOSPHORUS 60 MHz ULTRA ( $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$ ) portable benchtop NMR device.

**Gaschromatography:** Conversion and yield of the reactions were determined via GC on an AGILENT TECHNOLOGIES INC. gas chromatograph of the model Intuvo 9000 with a flame ionization detector (FID). A HP-5 column was used (30 m long, 0.32 mm diameter, 0.25  $\mu\text{m}$  thickness of the layer, 3 minutes at 40  $^\circ\text{C}$ , heating rate 30  $^\circ\text{C}/\text{min}$  to 100  $^\circ\text{C}$ , heating rate 20  $^\circ\text{C}/\text{min}$  to 150, heating rate 35  $^\circ\text{C}/\text{min}$  to 320  $^\circ\text{C}$ , holding for 5 minutes). The split was set to 1:100 and the inlet temperature was 350  $^\circ\text{C}$ . *n*-Dodecane was chosen as internal standard and response factors of the substrates and products were obtained experimentally by analyzing known quantities of the substances. For a sample, a certain amount of substrate or product, 25 mg *n*-dodecane was used and diluted to 1 g total mass with isopropanol.

**High-Resolution Mass Spectrometry (HR-MS):** Samples for HRMS were diluted in methanol to a concentration of 100  $\mu\text{g}\cdot\text{mL}^{-1}$  and measured with an LTQ-Orbitrap (THERMO SCIENTIFIC).

**ICP-OES-Analytics:** The ICP-OES analysis (Optical Emission Spectrometry with Inductively Coupled Plasma) of the palladium and phosphorus leaching into the organic product phase was performed on a Plasma Quant PQ 9000 spectrometer.

### 4. Determination of Mixing Temperatures

The telomers **3a** for the determination of the mixing temperatures (MT) were synthesized with the optimized reaction conditions. The telomers were isolated via kugelrohr distillation of the crude mixture.

The investigation was carried out in pressure tubes of the brand ACE GLASS (Figure S3).



Figure S3: pressure tubes for investigations on mixing temperatures.

The tubes were filled with the solvent mixture of ethanol and water in the ratio to be tested. For the pre-reaction mixture the substrates  $\beta$ -myrcene **1** and diethylamine **2** and for the post-reaction mixtures the telomer products **3a** were added. The tubes were sealed and the mixtures were heated and stirred. If two phases were present, the mixture looked milky. When the mixing temperature was reached, the mixture became clear. The temperature at which a change was evident was determined several times by cooling and reheating to obtain a representative result.

Table S2: Mixing temperatures of reaction mixtures with different ethanol/water ratios with  $\beta$ -myrcene and diethylamine as pre-reaction mixtures and with telomers (with regard to a 100% selective telomerization reaction towards the telomers) as post-reaction mixtures (total volume ~ 4 mL)

#	pre-reaction			post-reaction (100% conversion of myrcene to telomers)		
	ethanol/water ratio [w/w]	Myrcene/ (ethanol+water) [w/w]	MT [°C]	ethanol/water ratio [w/w]	Telomers/ (ethanol+water) [w/w]	MT [°C]
2.1	40/60	1/1	>140	40/60	1.16/1	>140
2.2	50/50	1/1	>140	50/50	1.16/1	>140
2.3	60/40	1/1	105	60/40	1.16/1	140.5
2.4	70/30	1/1	83	70/30	1.16/1	115
2.5	80/20	1/1	25	80/20	1.16/1	80

## 5. Product identification: Isolation, identification, and calibration

All telomer products are a mixture of isomers. In the following, the head-tail isomer is used as an example for the nomenclature. Due to the formation of 12 possible isomers in the telomerization, the assignments of individual H atoms are not always possible, since these usually represent only a part of the different isomers. Furthermore, these mixtures can also produce fractional integrals/protons. However, with the help of selected protons, the ratio of myrcene to amine can be checked, which must be 2:1 for telomer products. Particularly suitable for this purpose are the protons at positions 10 and 17, which in the case of a telomer must thus give two protons. For the amine, the protons at the C-atoms, which are directly attached to the nitrogen, are suitable. As a comparison, the already published NMR spectrum of **3b** can also be used.<sup>[1]</sup> The NMR spectra for the telomerization of  $\beta$ -farnesene published by the group of Vorholt in 2018 can also be used as a comparison, since  $\beta$ -myrcene and  $\beta$ -farnesene only have a different residual group.<sup>[2]</sup> In addition, the total proton number must also match the desired telomer.

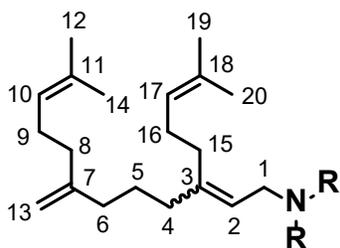
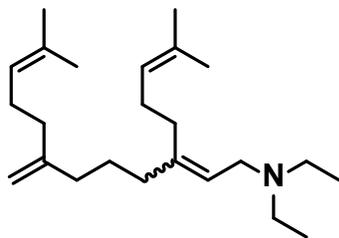


Figure S4: Product of telomerization of  $\beta$ -myrcene with an amine (head-tail isomer).

***N,N*-diethyl-11-methyl-7-methylene-3-(4-methylpent-3-en-1-yl)dodeca-2,10-dien-1-amine  
(3a)**

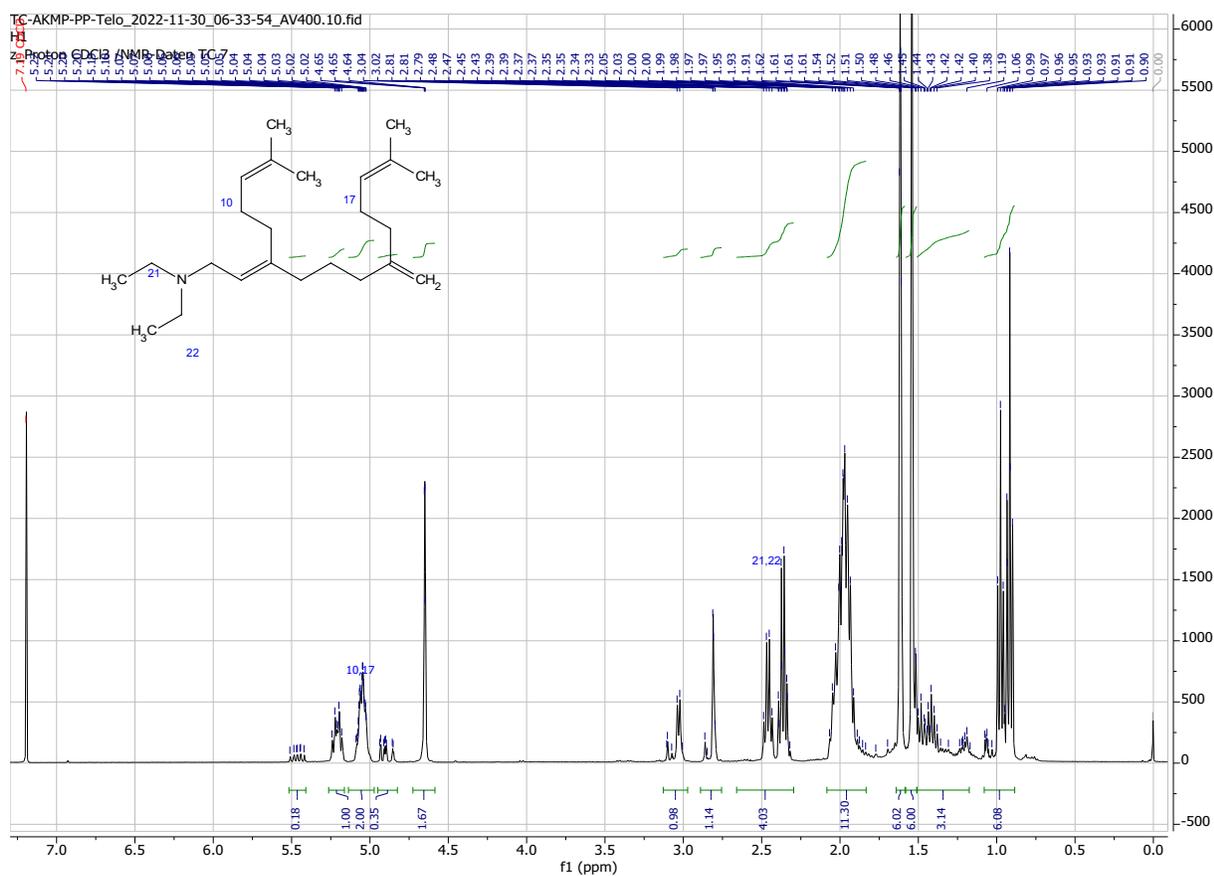


**Isolation:**

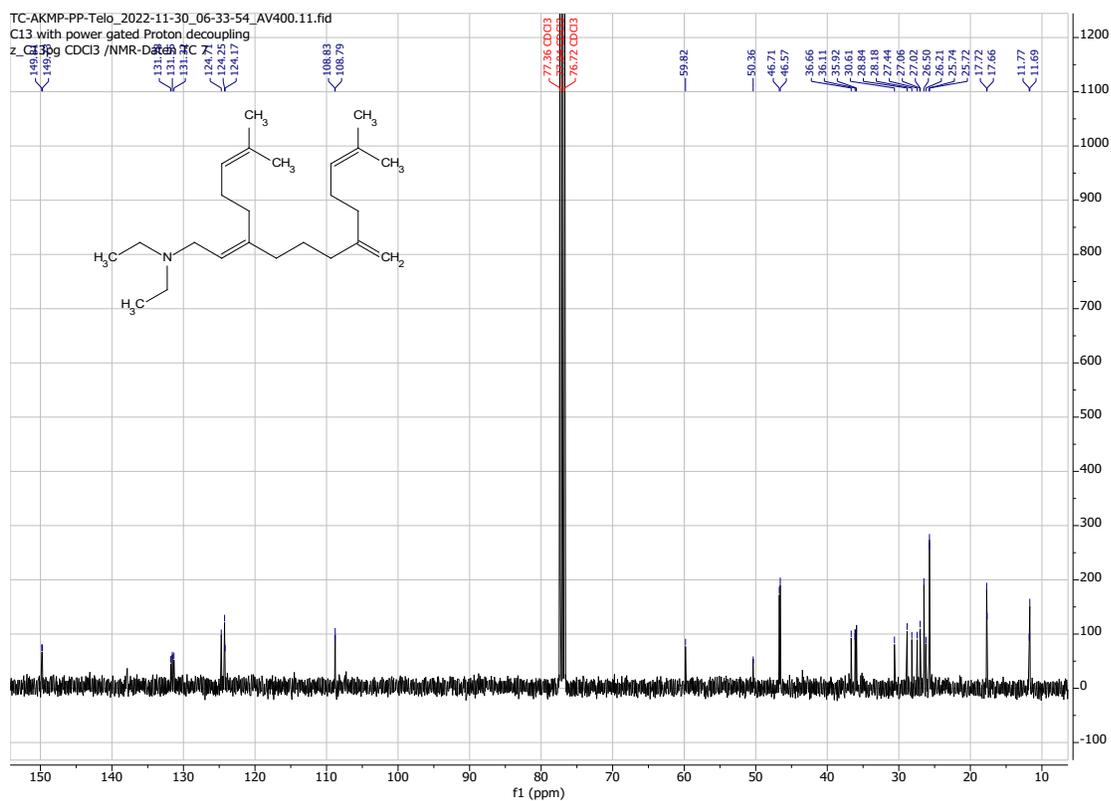
A syringe filter was used to remove the catalyst from the crude reaction mixture. Afterwards product phase was distilled with a kugelrohr distillation under vacuum ( $T = 105\text{ }^{\circ}\text{C}$ ,  $p = 0.036\text{ mbar}$ ) to give **3a** as a yellowish liquid.

**NMR Spectroscopy:** The spectroscopic data correspond to those previously reported in the literature.<sup>[3]</sup> The ratio of myrcene to amine is the desired 2:1, since there are 2 protons (10, 17) of the myrcene parts and 4 protons (21, 22) from the  $\text{N}(\text{CH}_2\text{R})_2$  group of the amine.

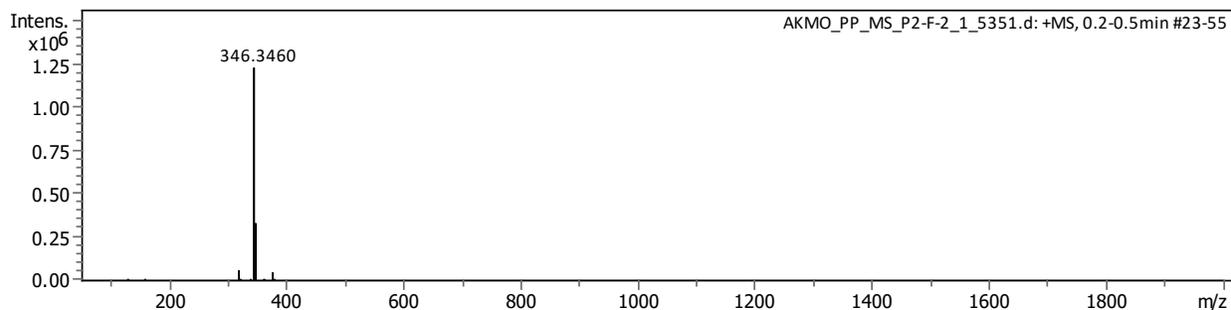
**$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm)**



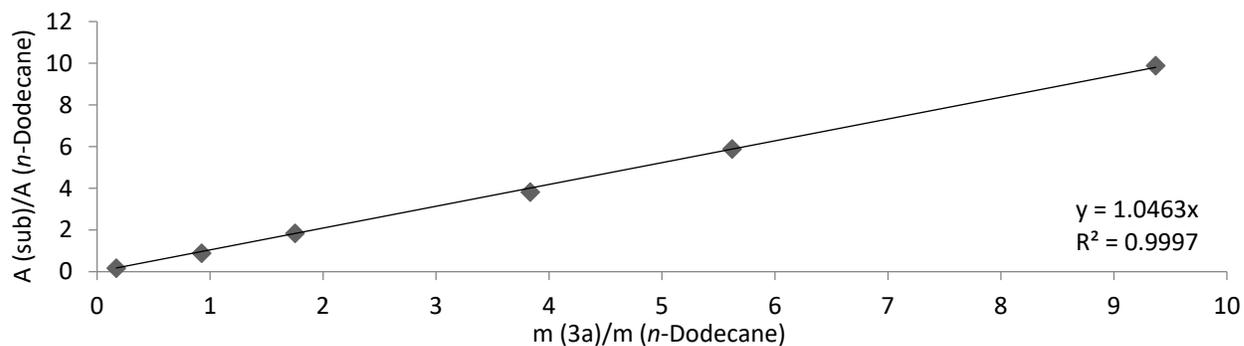
### $^{13}\text{C-NMR}$ (100 MHz, $\text{CDCl}_3$ ) $\delta$ (ppm)



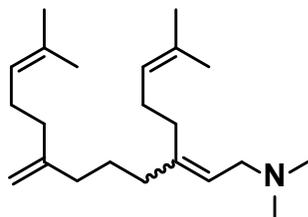
HR-MS (ESI): calcd.  $[\text{M}+\text{H}]^+ = 346.3469$ , found  $[\text{M}+\text{H}]^+ = 346,3460$ .



### GC-Calibration:



***N,N*-dimethyl-11-methyl-7-methylene-3-(4-methylpent-3-en-1-yl)dodeca-2,10-dien-1-amine (3b)**

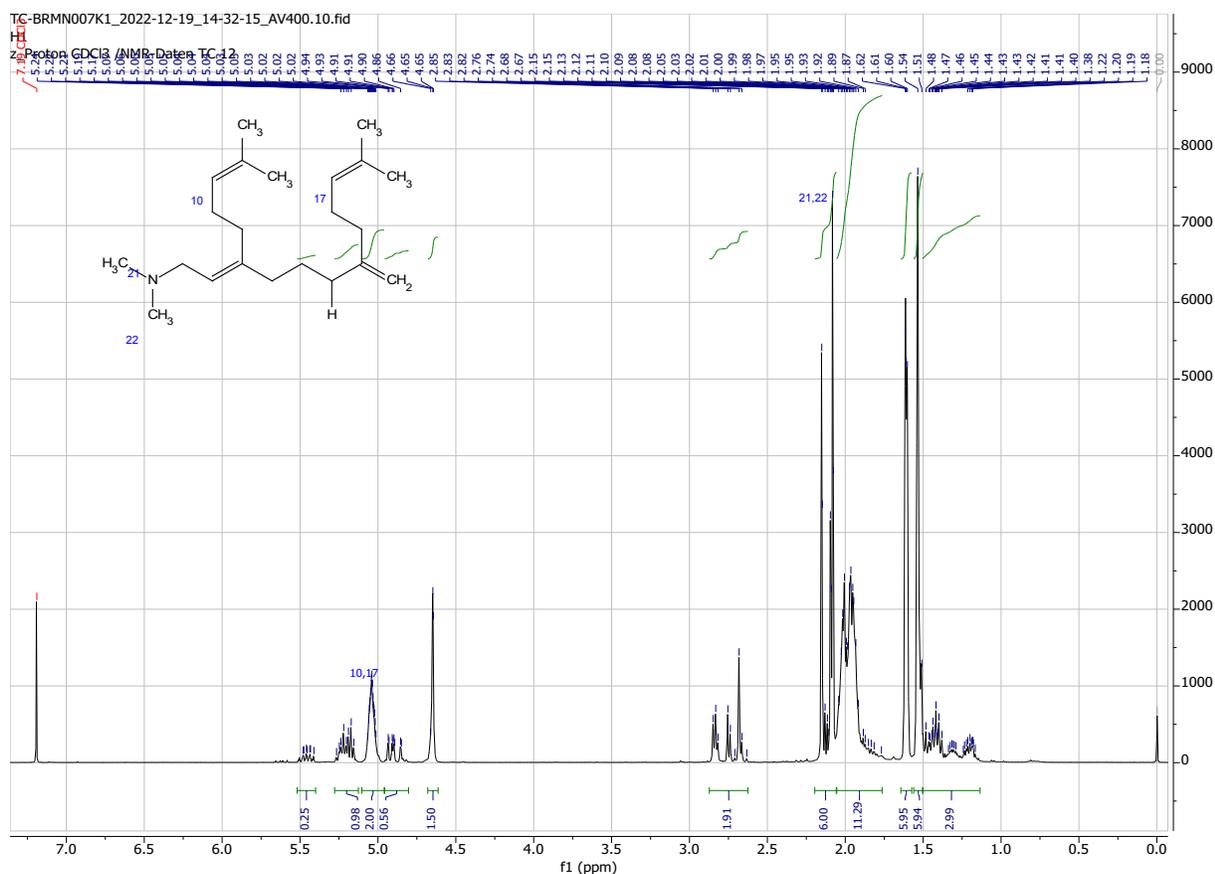


**Isolation:**

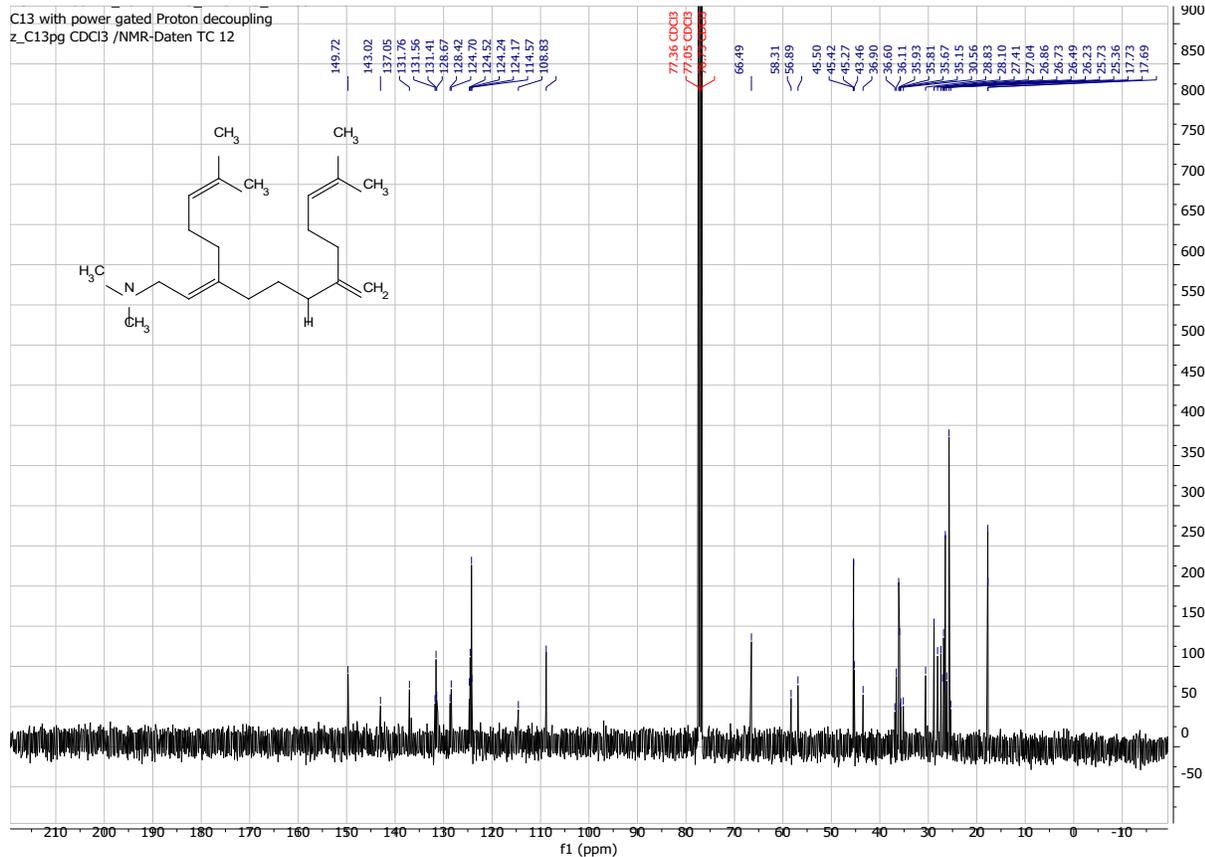
A syringe filter was used to remove the catalyst from the crude reaction mixture. Afterwards, product phase was distilled with a kugelrohr distillation under vacuum ( $T = 105\text{ }^{\circ}\text{C}$ ,  $p = 0.031\text{ mbar}$ ) to give **3b** as a yellowish liquid.

**NMR Spectroscopy:** The spectroscopic data correspond to those previously reported in the literature. The ratio of myrcene to amine is the desired 2:1, since there are 2 protons (10, 17) of the myrcene parts and 6 protons (21, 22) from the  $\text{CH}_3$  group of the amine.

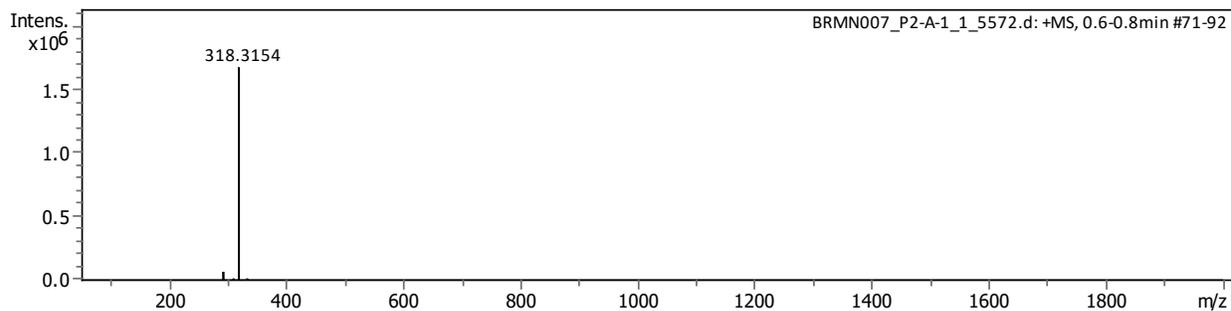
**$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm)**



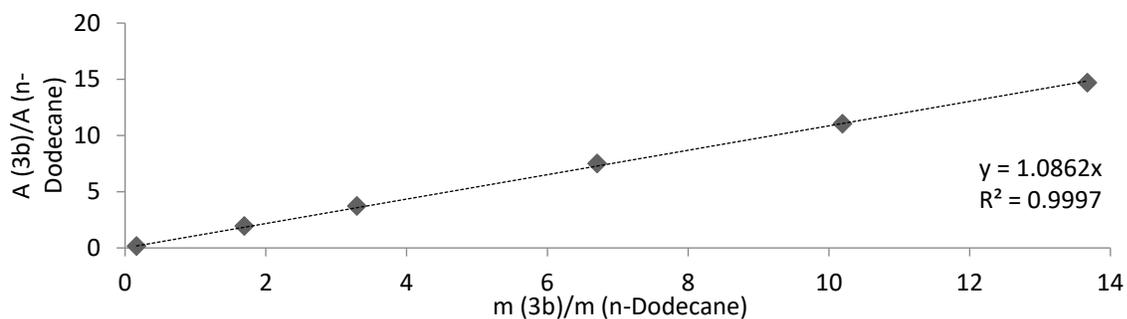
### <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm)



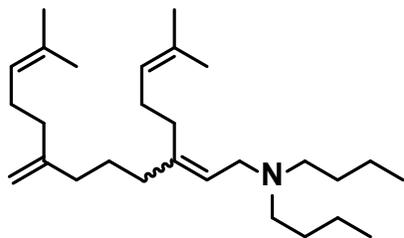
**HR-MS (ESI):** calcd. [M+H]<sup>+</sup> = 318.3155, found [M+H]<sup>+</sup> = 318.3154



### GC-Calibration:



***N,N*-dibutyl-11-methyl-7-methylene-3-(4-methylpent-3-en-1-yl)dodeca-2,10-dien-1-amine  
(3c)**

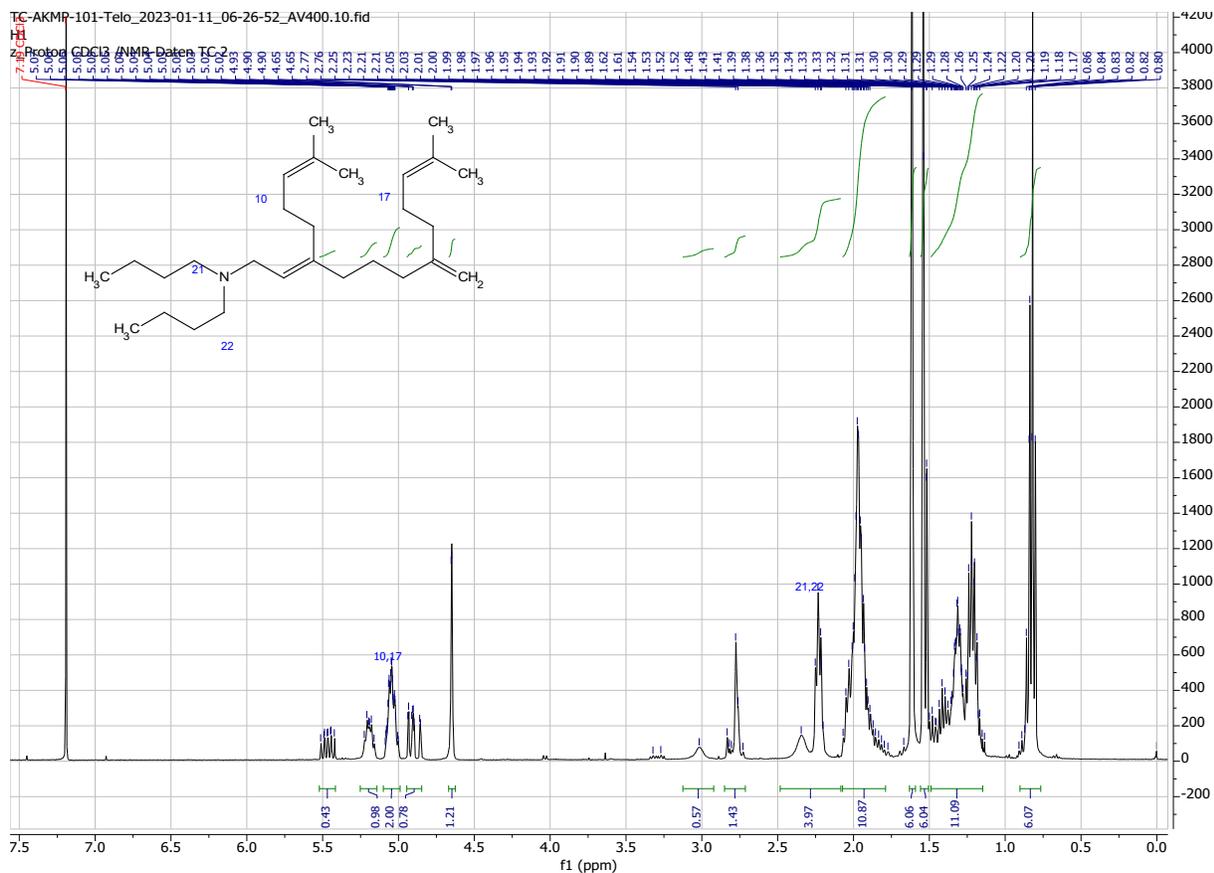


**Isolation:**

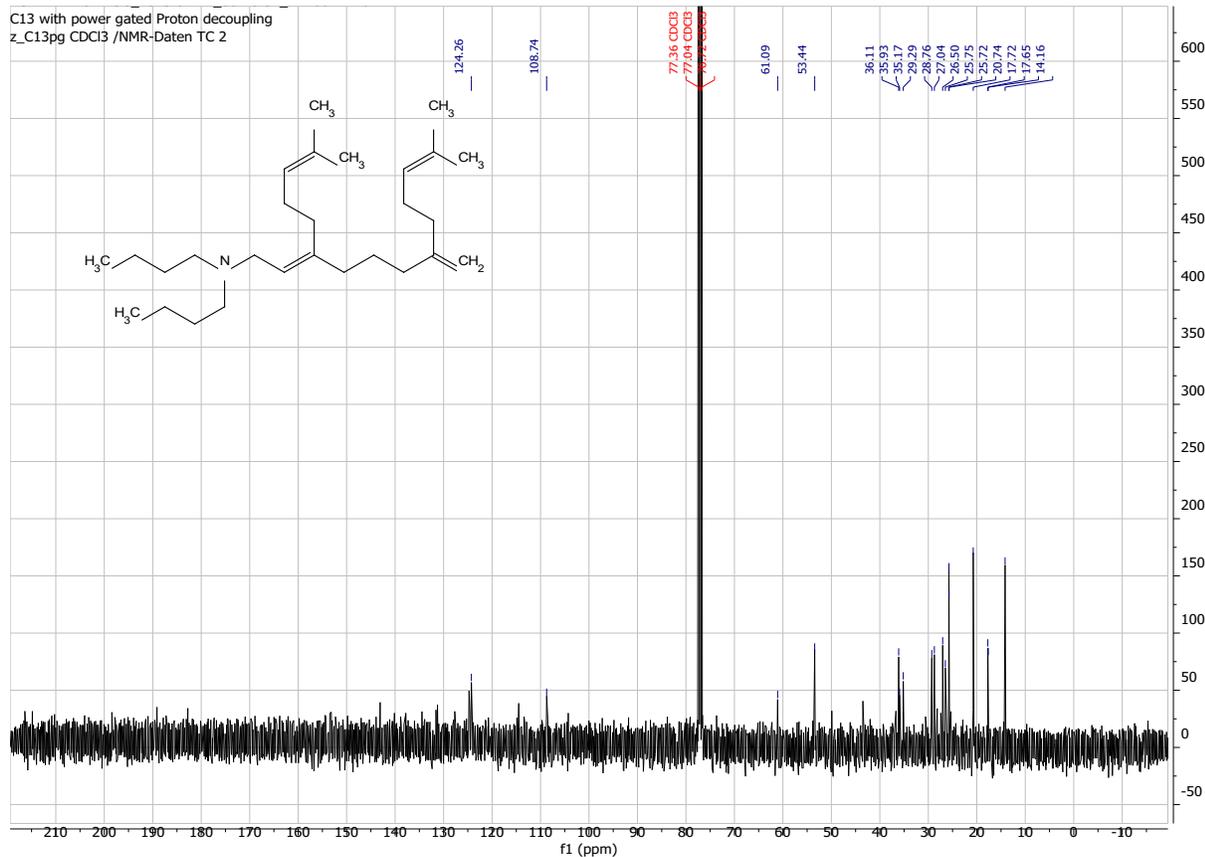
A syringe filter was used to remove the catalyst from the crude reaction mixture. Afterwards, product phase was distilled with a kugelrohr distillation under vacuum ( $T = 140\text{ }^{\circ}\text{C}$ ,  $p = 0.02\text{ mbar}$ ) to give **3c** as a yellowish liquid.

**NMR Spectroscopy:** The ratio of myrcene to amine is the desired 2:1, since there are 2 protons (10, 17) of the myrcene parts and 4 protons (21, 22) from the  $\text{N}(\text{CH}_2\text{R})_2$  group of the amine.

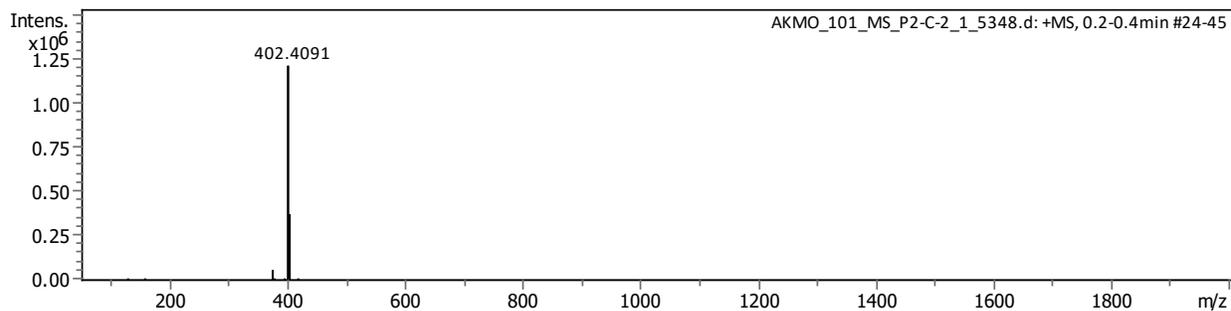
**$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm)**



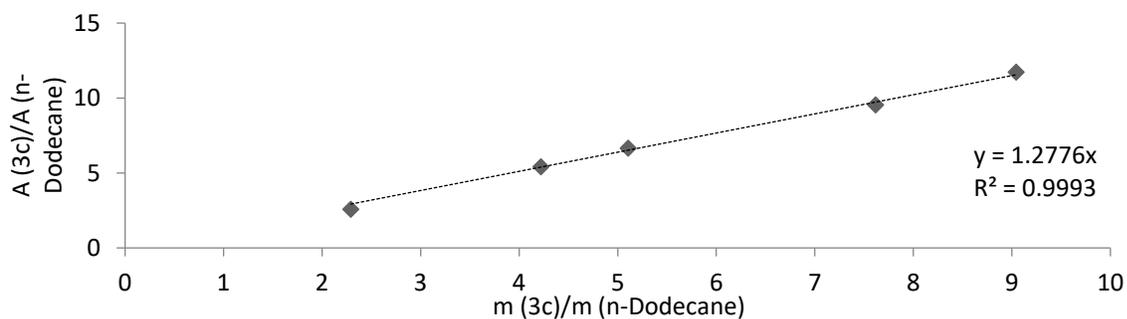
### <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm)



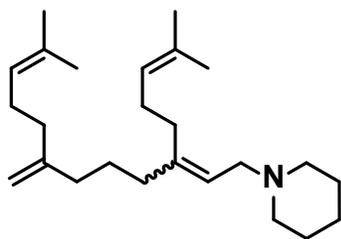
**HR-MS (ESI):** calcd. [M+H]<sup>+</sup> = 402.4095, found [M+H]<sup>+</sup> = 402.4091.



### GC-Calibration:



### 1-(11-methyl-7-methylene-3-(4-methylpent-3-en-1-yl)dodeca-2,10-dien-1-yl)piperidine (3d)

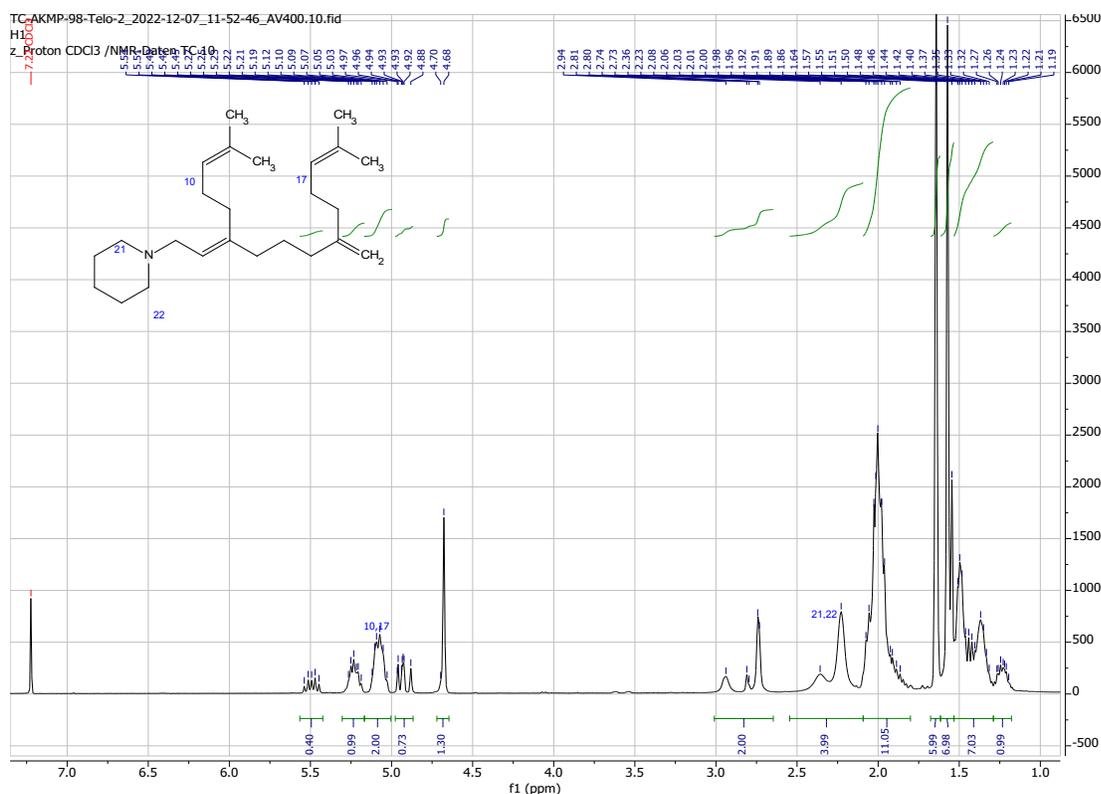


#### Isolation:

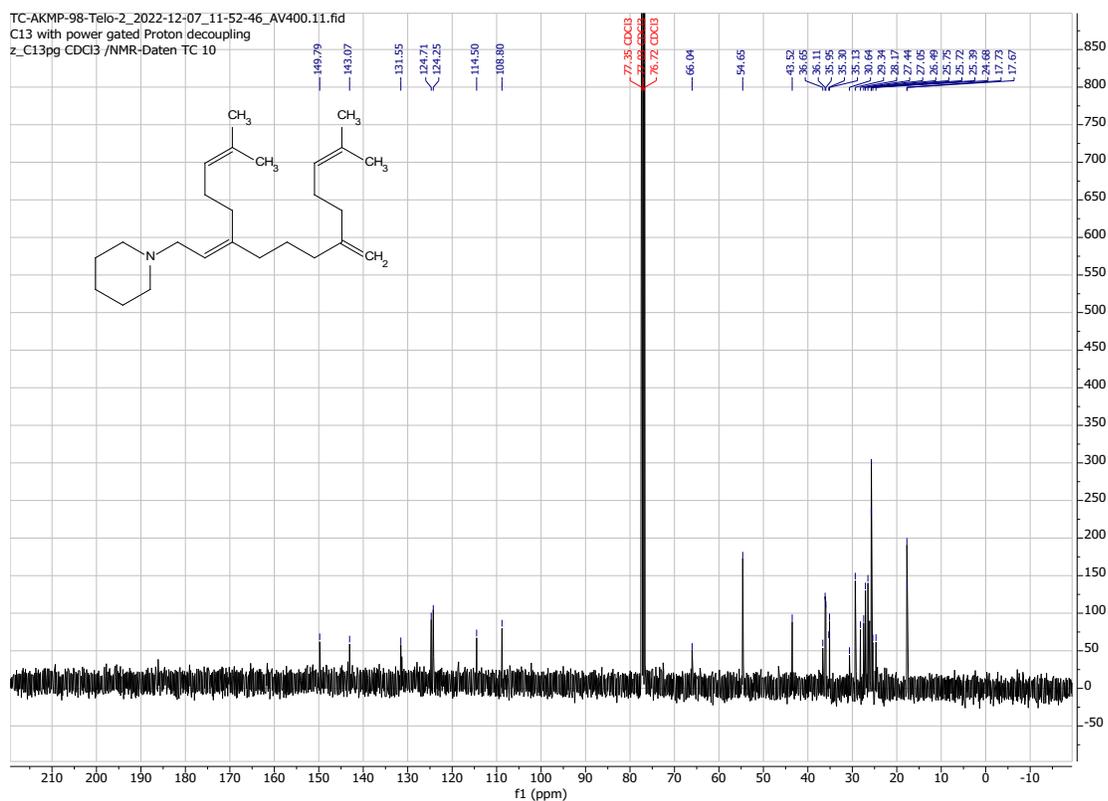
A syringe filter was used to remove the catalyst from the crude reaction mixture. Afterwards, product phase was distilled with a kugelrohr distillation under vacuum ( $T = 134\text{ }^{\circ}\text{C}$ ,  $p = 0.018\text{ mbar}$ ) to give **3d** as a yellowish liquid.

**NMR Spectroscopy:** The ratio of myrcene to amine is the desired 2:1, since there are 2 protons (10, 17) of the myrcene parts and 4 protons (21, 22) from the  $\text{N}(\text{CH}_2\text{R})_2$  group of the amine.

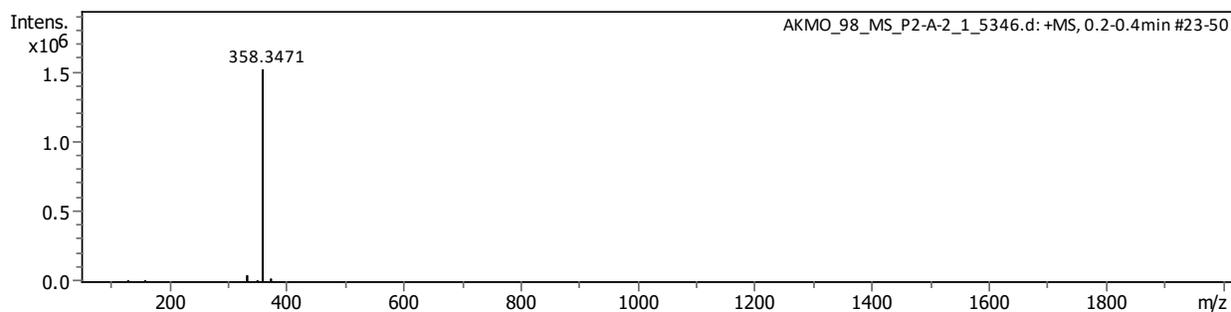
#### $^1\text{H-NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ (ppm)



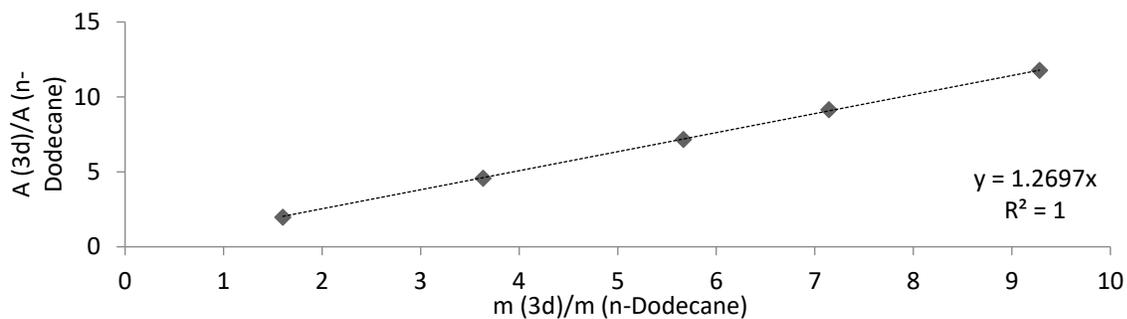
### $^{13}\text{C-NMR}$ (100 MHz, $\text{CDCl}_3$ ) $\delta$ (ppm)



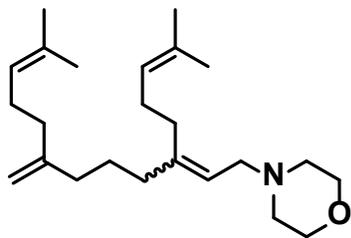
HR-MS (ESI): calcd.  $[\text{M}+\text{H}]^+ = 358.3469$ , found  $[\text{M}+\text{H}]^+ = 358.3471$ .



### GC-Calibration:



**4-(11-methyl-7-methylene-3-(4-methylpent-3-en-1-yl)dodeca-2,10-dien-1-yl)morpholine  
(3e)**

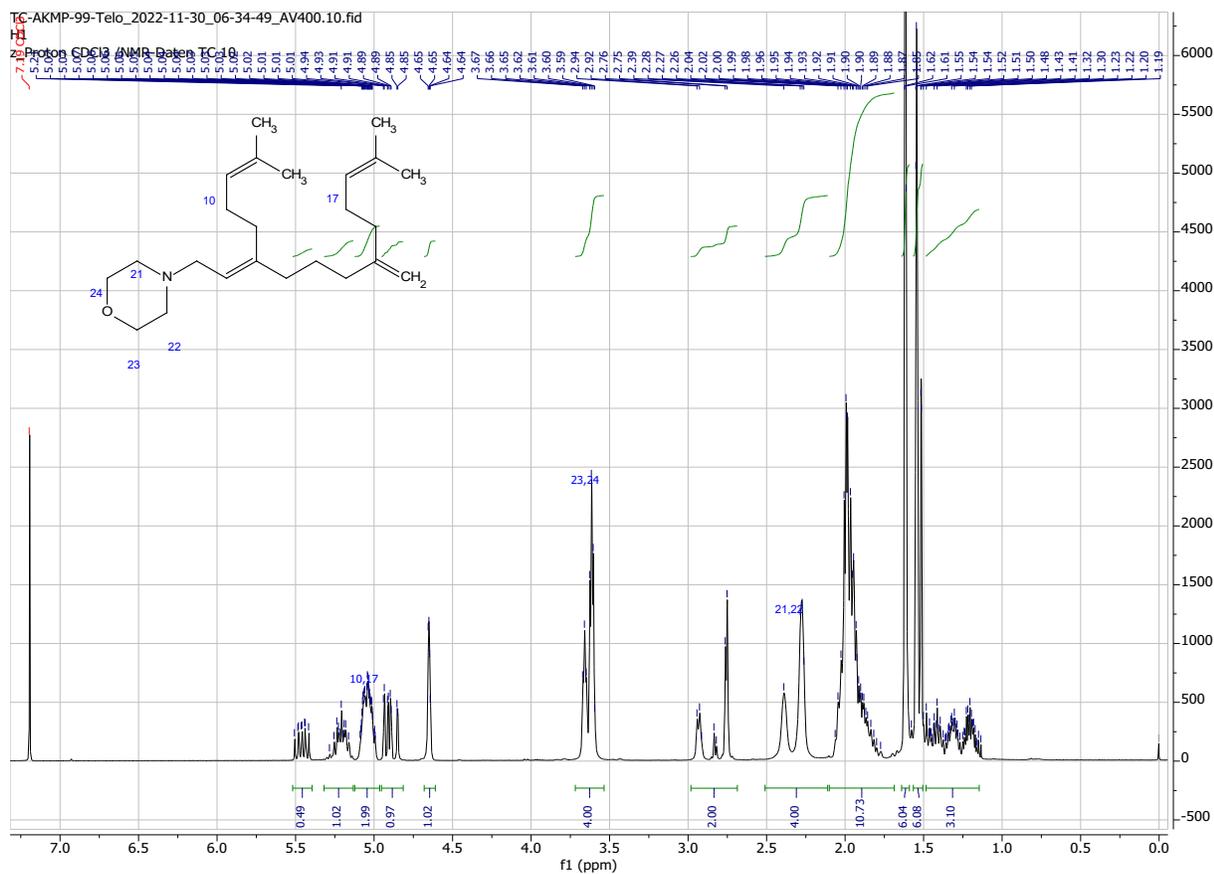


**Isolation:**

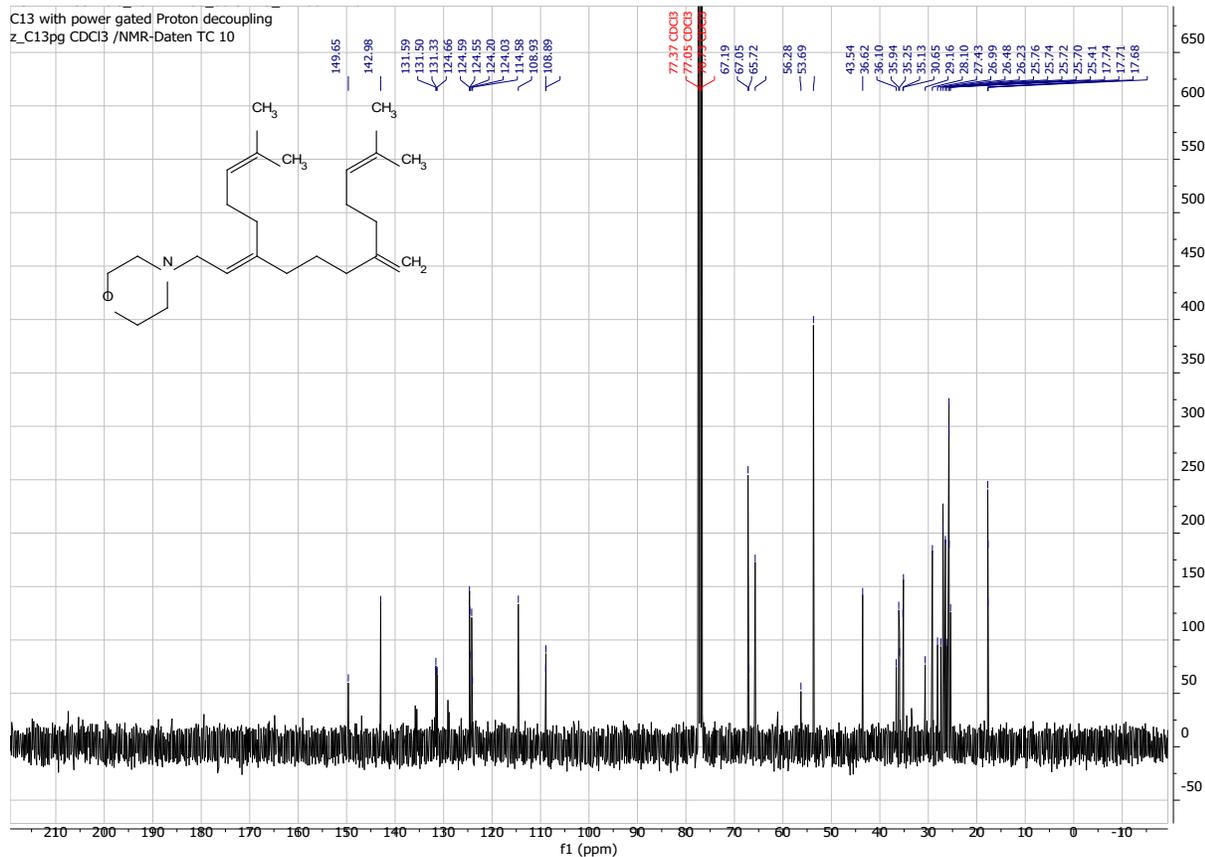
A syringe filter was used to remove the catalyst from the crude reaction mixture. Afterwards, product phase was distilled with a kugelrohr distillation under vacuum ( $T = 144\text{ }^{\circ}\text{C}$ ,  $p = 0.015\text{ mbar}$ ) to give **3e** as a yellowish liquid.

**NMR Spectroscopy:** The ratio of myrcene to amine is the desired 2:1, since there are 2 protons (10, 17) of the myrcene parts and 4 protons (21, 22) from the  $\text{N}(\text{CH}_2\text{R})_2$  group as well as 4 protons (23, 24) from the  $(\text{RCH}_2)_2\text{O}(\text{CH}_2\text{R})_2$  group of the amine.

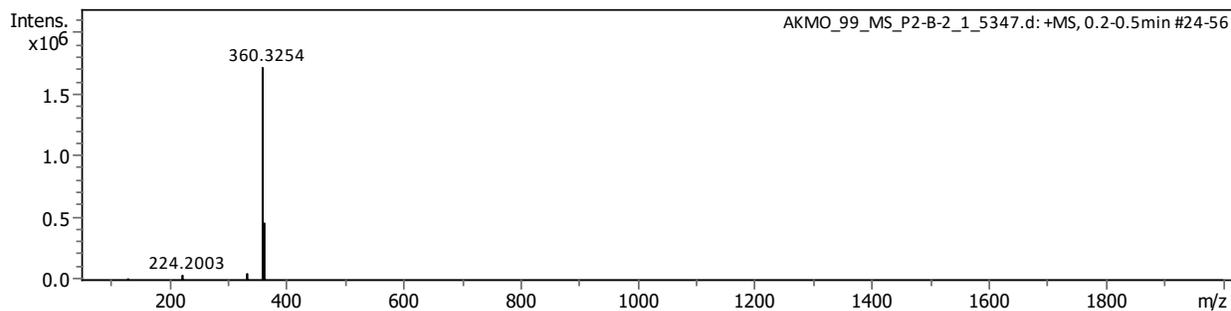
**$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm)**



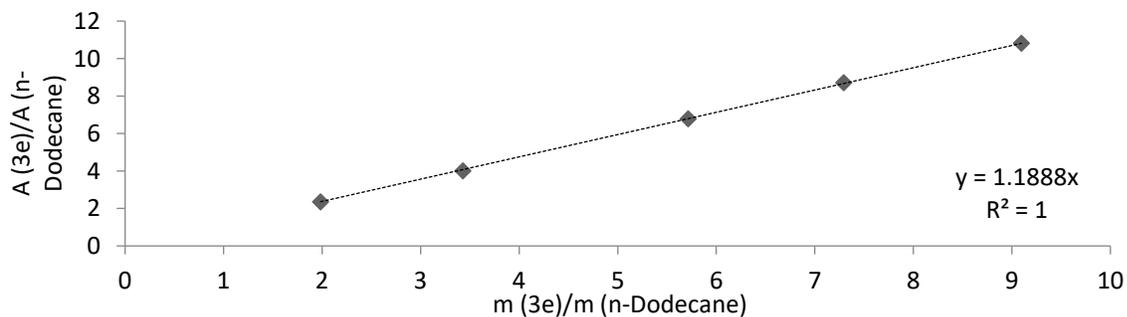
### <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm)



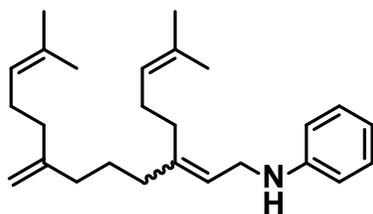
**HR-MS (ESI):** calcd. [M+H]<sup>+</sup> = 360.3261, found [M+H]<sup>+</sup> = 360.3254.



### GC-Calibration:



## ***N*-(11-methyl-7-methylene-3-(4-methylpent-3-en-1-yl)dodeca-2,10-dien-1-yl)aniline (3f)**

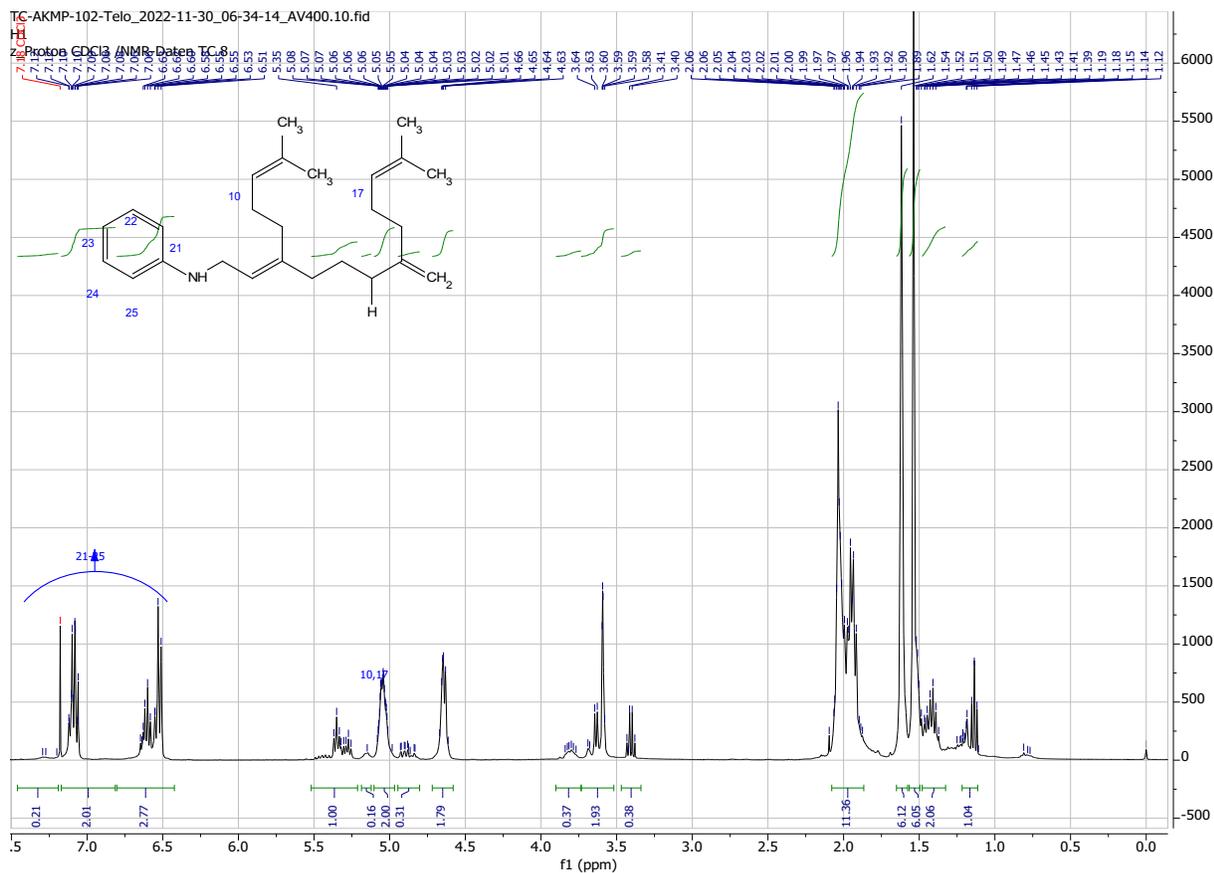


### Isolation:

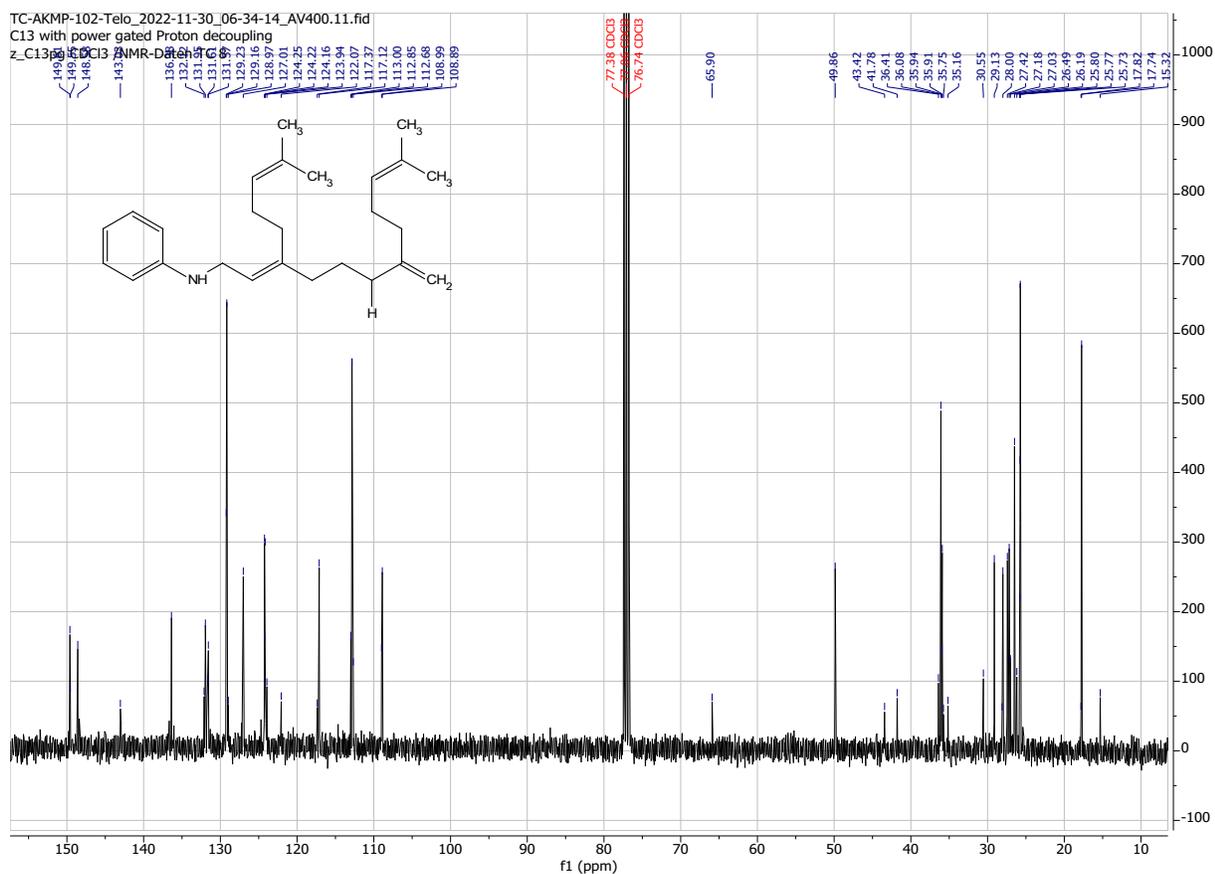
A syringe filter was used to remove the catalyst from the crude reaction mixture. Afterwards, product phase was distilled with a kugelrohr distillation under vacuum ( $T = 160\text{ }^{\circ}\text{C}$ ,  $p = 0.02\text{ mbar}$ ) to give **3f** as a yellowish liquid.

NMR Spectroscopy: The ratio of myrcene to amine is the desired 2:1, since there are 2 protons (10, 17) of the myrcene parts and 5 protons (21-25) from the phenyl group of the amine.

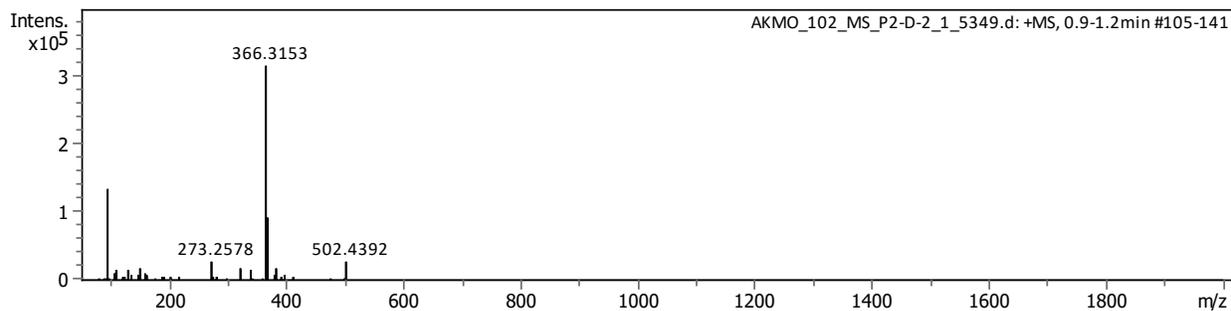
### **$^1\text{H-NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ (ppm)**



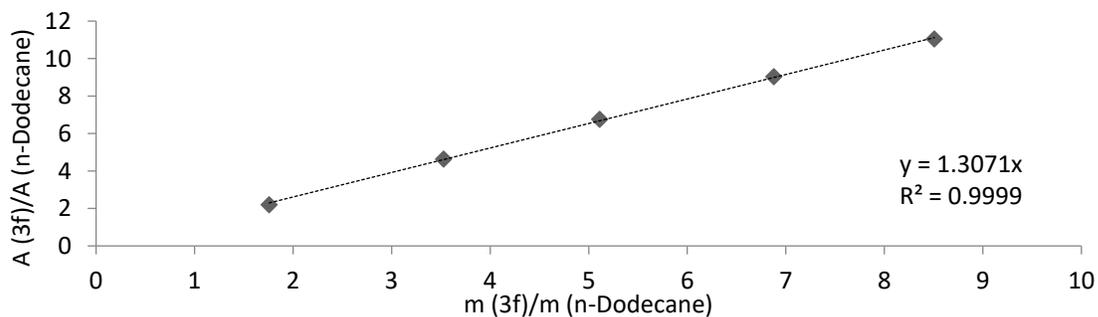
**$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm)**



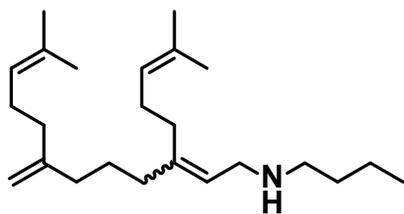
**HR-MS (ESI):** calcd.  $[\text{M}+\text{H}]^+ = 366.3155$ , found  $[\text{M}+\text{H}]^+ = 366.3153$ .



**GC-Calibration:**



## N-butyl-11-methyl-7-methylene-3-(4-methylpent-3-en-1-yl)dodeca-2,10-dien-1-amine (3g)

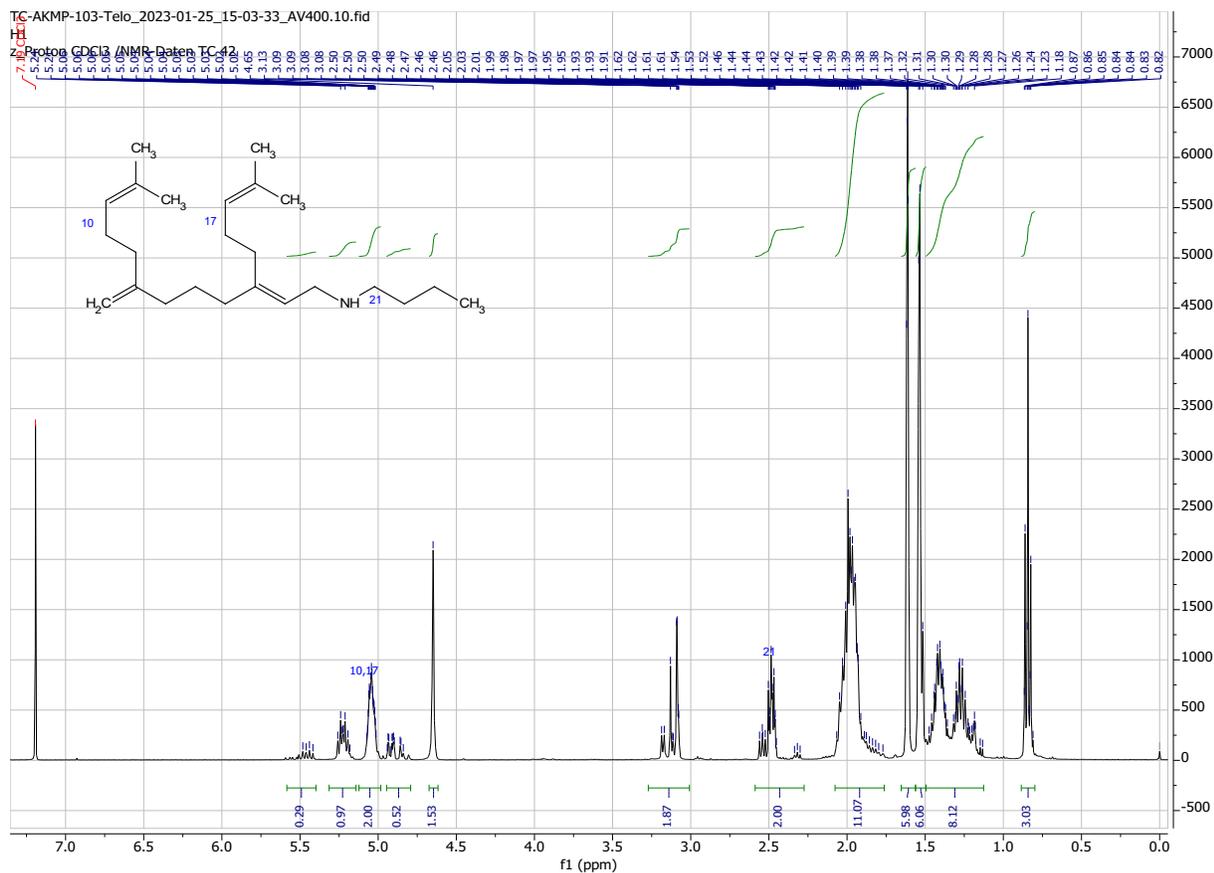


### Isolation:

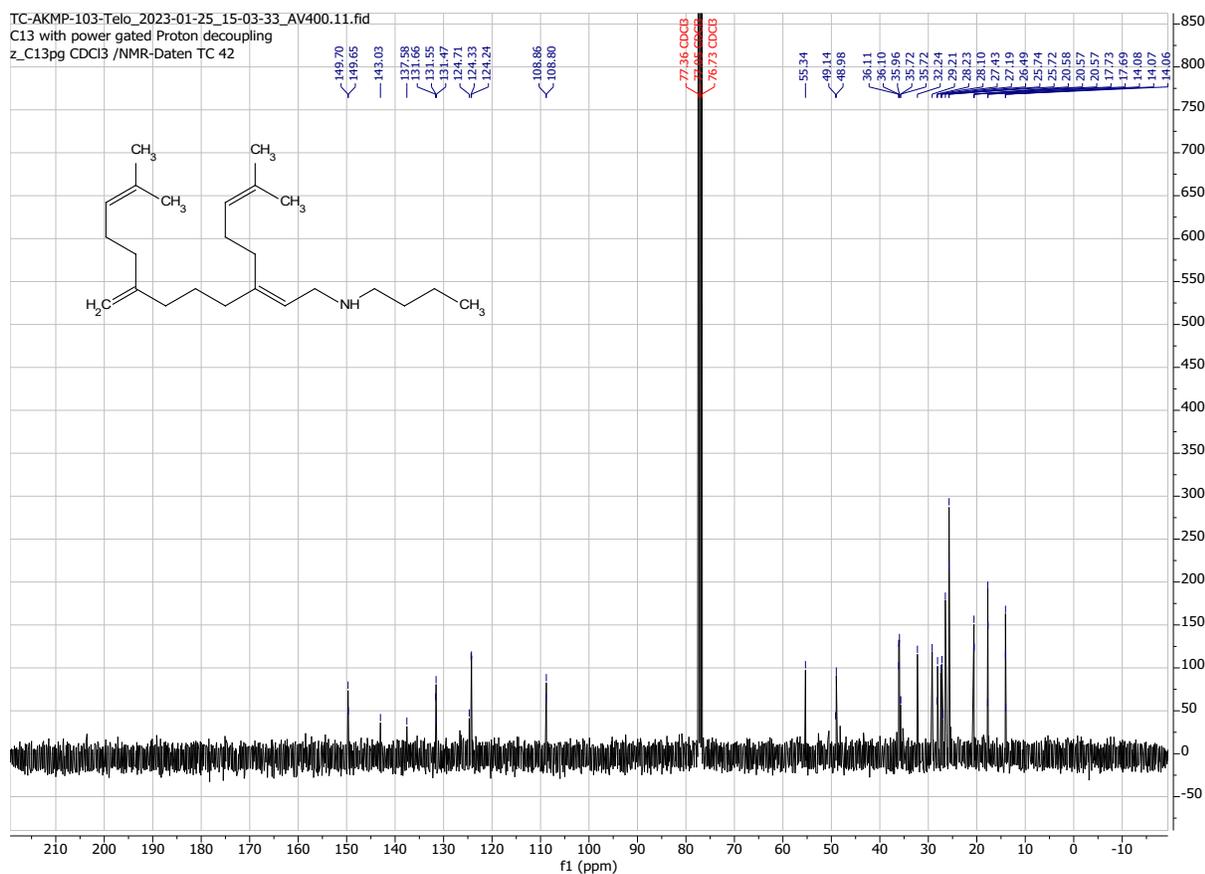
A syringe filter was used to remove the catalyst from the crude reaction mixture. Afterwards, product phase was distilled with a kugelrohr distillation under vacuum ( $T = 132\text{ }^{\circ}\text{C}$ ,  $p = 0.02\text{ mbar}$ ) to give **3g** as a yellowish liquid.

**NMR Spectroscopy:** The ratio of myrcene to amine is the desired 2:1, since there are 2 protons (10, 17) of the myrcene parts and 2 protons (21) from the  $\text{N}(\text{CH}_2\text{R})$  group of the amine.

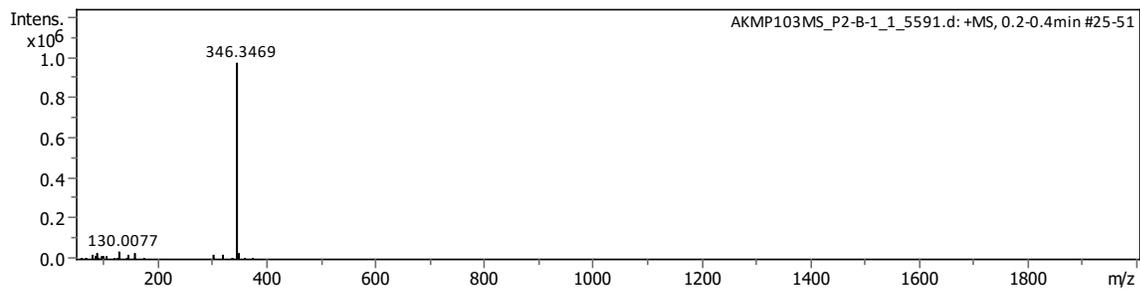
### $^1\text{H-NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ (ppm)



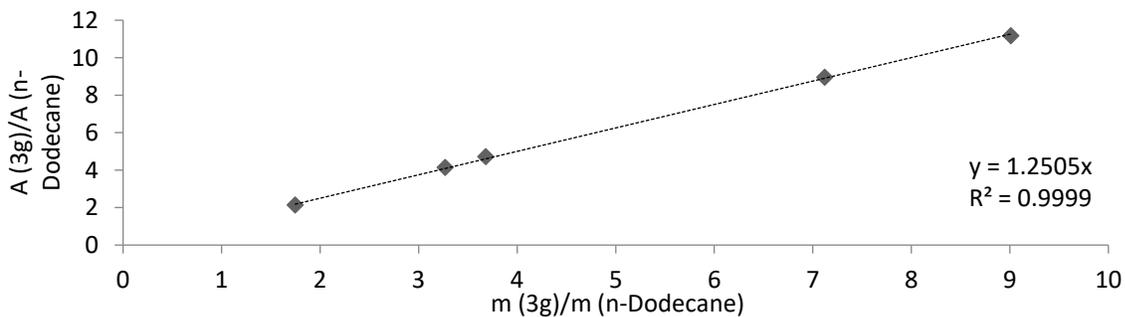
### $^{13}\text{C-NMR}$ (100 MHz, $\text{CDCl}_3$ ) $\delta$ (ppm)



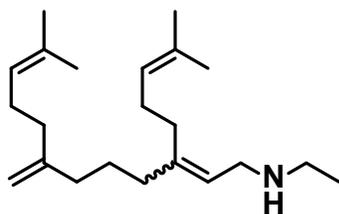
**HR-MS (ESI):** calcd.  $[\text{M}+\text{H}]^+ = 346.3468$ , found  $[\text{M}+\text{H}]^+ = 346.3469$ .



### GC-Calibration:



## N-ethyl-11-methyl-7-methylene-3-(4-methylpent-3-en-1-yl)dodeca-2,10-dien-1-amine (3h)

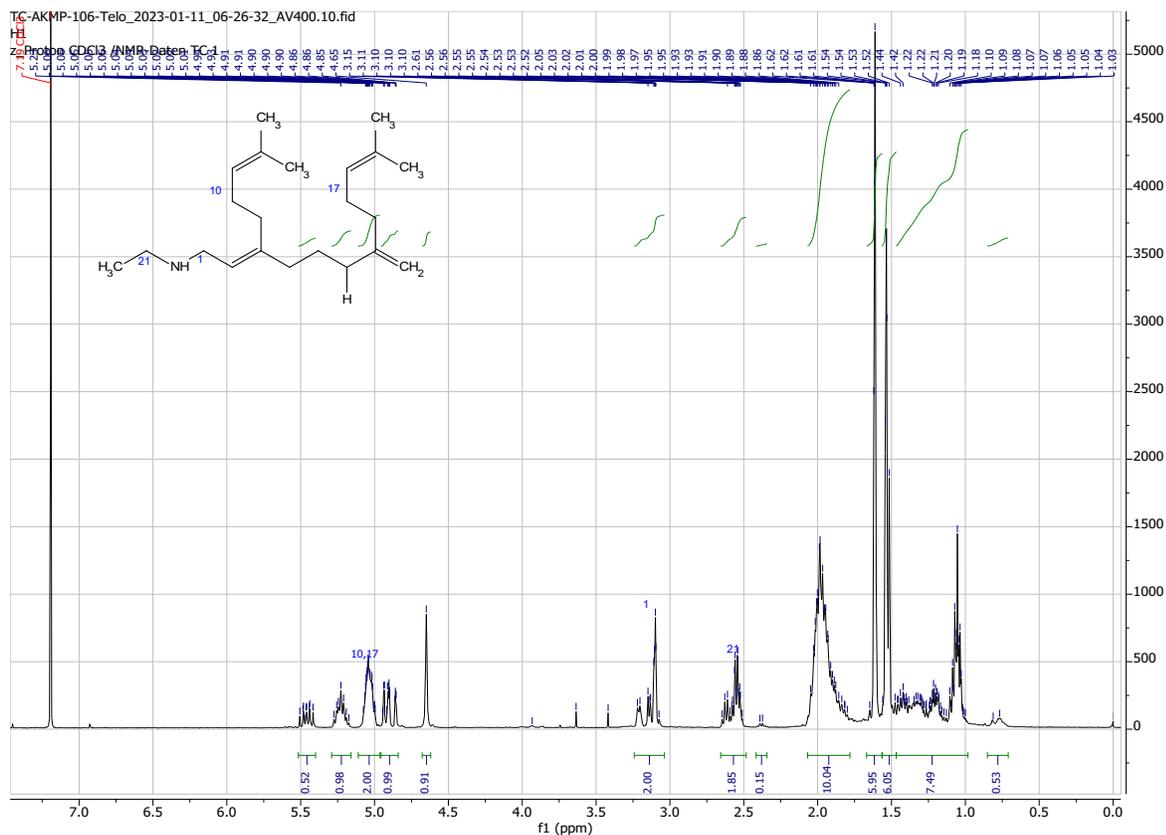


### Isolation:

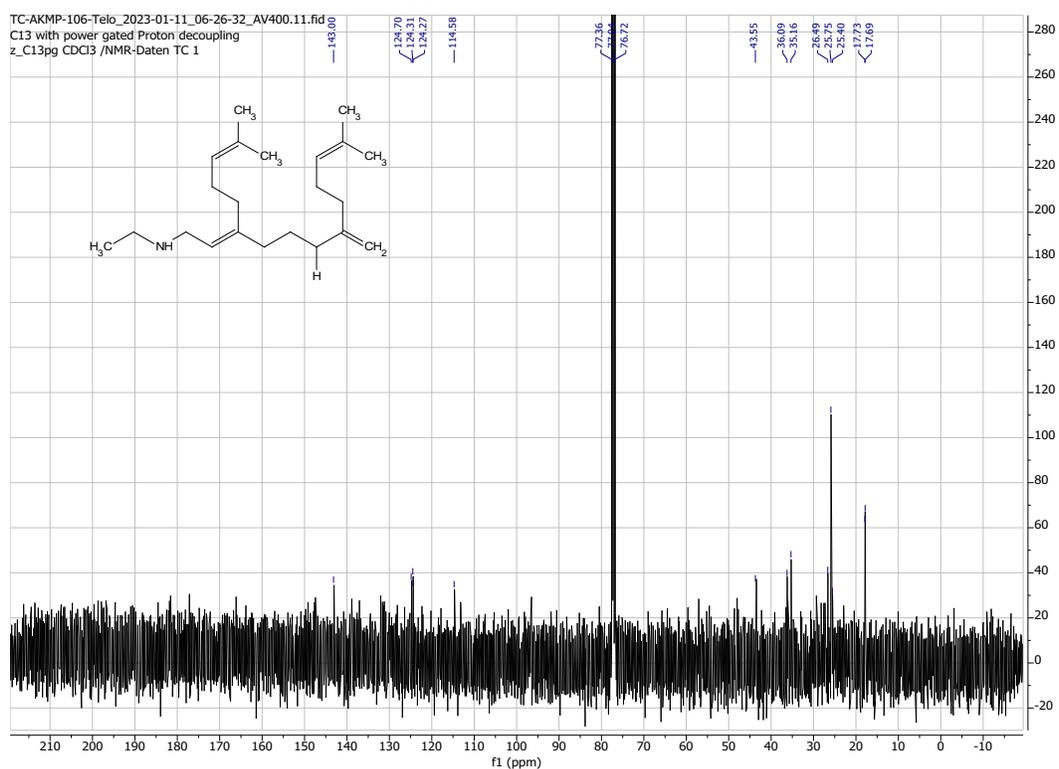
A syringe filter was used to remove the catalyst from the crude reaction mixture. Afterwards, product phase was distilled with a kugelrohr distillation under vacuum ( $T = 115\text{ }^{\circ}\text{C}$ ,  $p = 0.02\text{ mbar}$ ) to give **3h** as a yellowish liquid.

**NMR Spectroscopy:** The ratio of myrcene to amine is the desired 2:1, since there are 2 protons (10, 17) of the myrcene parts and 2 protons (21) from the  $\text{N}(\text{CH}_2\text{R})$  group of the amine.

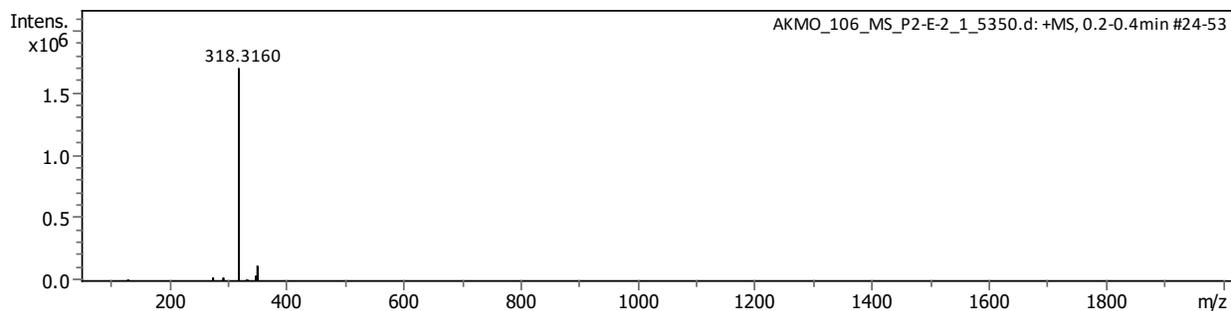
### $^1\text{H-NMR}$ (400 MHz, $\text{CDCl}_3$ ) $\delta$ (ppm)



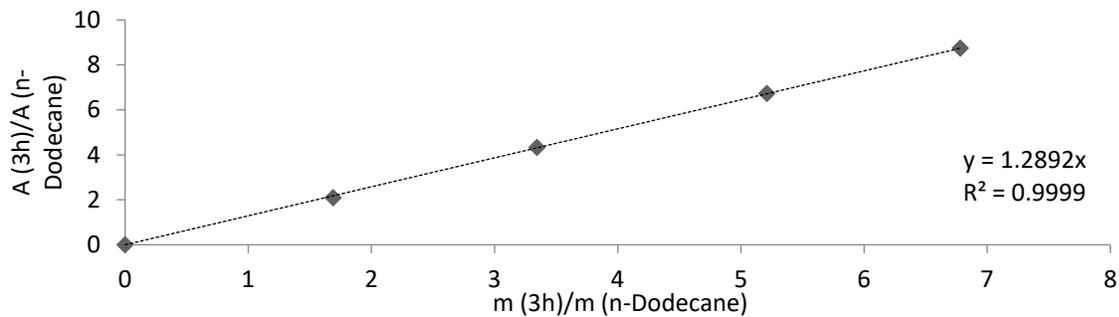
### $^{13}\text{C-NMR}$ (100 MHz, $\text{CDCl}_3$ ) $\delta$ (ppm)



HR-MS (ESI): calcd.  $[\text{M}+\text{H}]^+ = 318.3155$ , found  $[\text{M}+\text{H}]^+ = 318.3160$ .



### GC-Calibration:



## 6. Further reaction experiments

### Recycling experiment with lower P:Pd ratio of 3:1

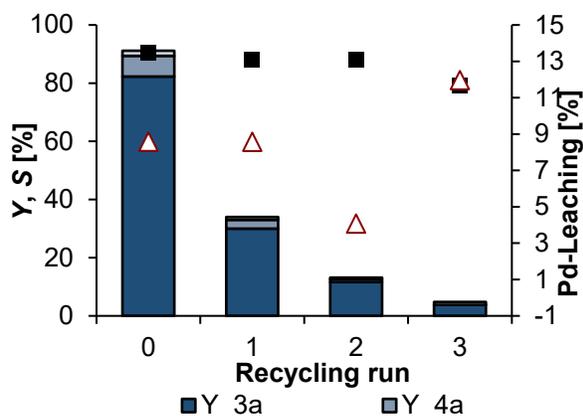


Figure S5: Recycling experiments with an increased P:Pd ratio of 5:1 in the telomerization of  $\beta$ -myrcene (1) with diethylamine (2a).

**Conditions:** 35 mmol  $\beta$ -myrcene (1), 0.7 eq HNEt<sub>2</sub>, 0.035 mol% Pd(acac)<sub>2</sub>, 0.105 mol% TPPTS, P:Pd 3:1, EtOH:H<sub>2</sub>O (w/w) 70:30, 1:solvent (w/w) 1:1, 1 bar Ar, 100 °C, 4 h, 500 rpm. After phase separation overnight, addition of 30 mmol 1, 21 mmol of HNEt<sub>2</sub>; yield (Y), and selectivity (S) determined by GC-FID with *n*-dodecane as internal standard related to the product phase removed, Leaching determined by ICP-OES and calculated as the amount lost with respect to the initial amount of palladium.

### Telomerization in vodka

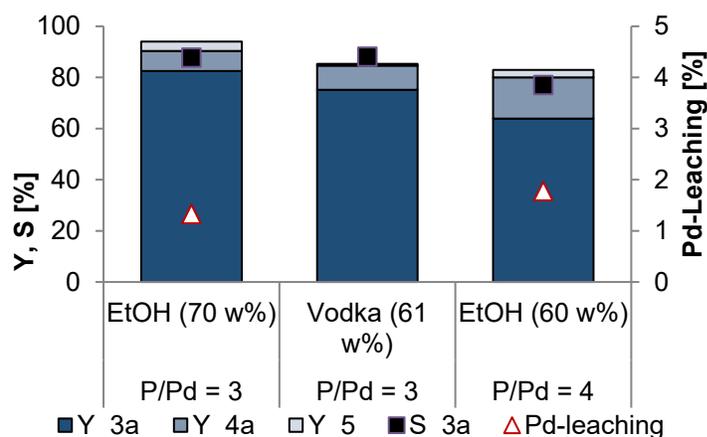
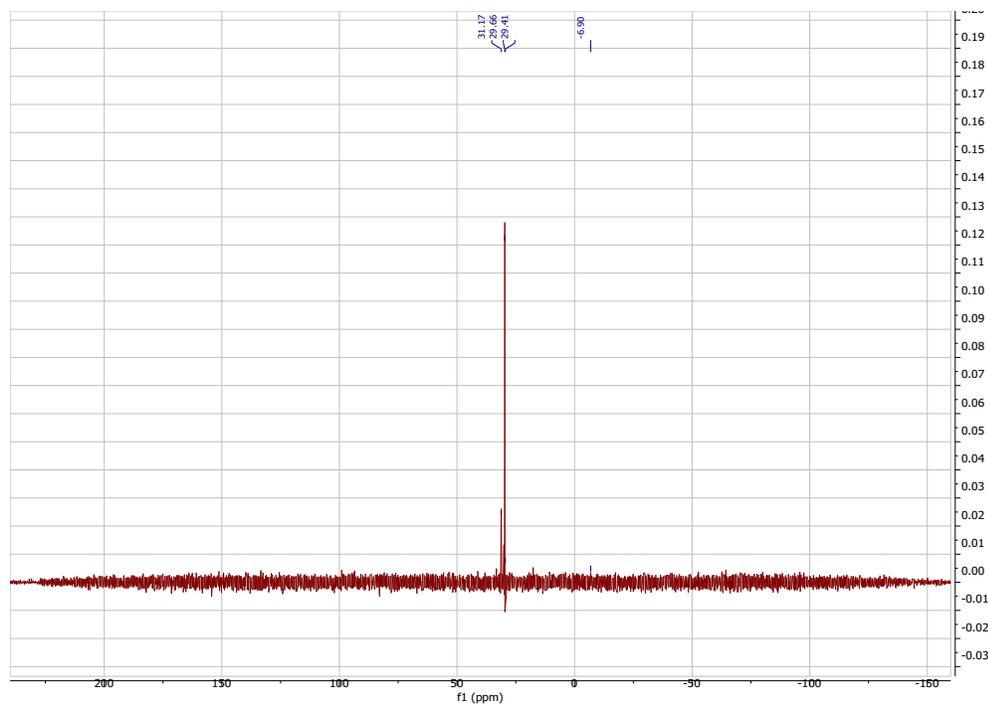


Figure S6: Testing Vodka as solvent - comparison of different solvent mixture origins in the telomerization of  $\beta$ -myrcene with diethylamine.

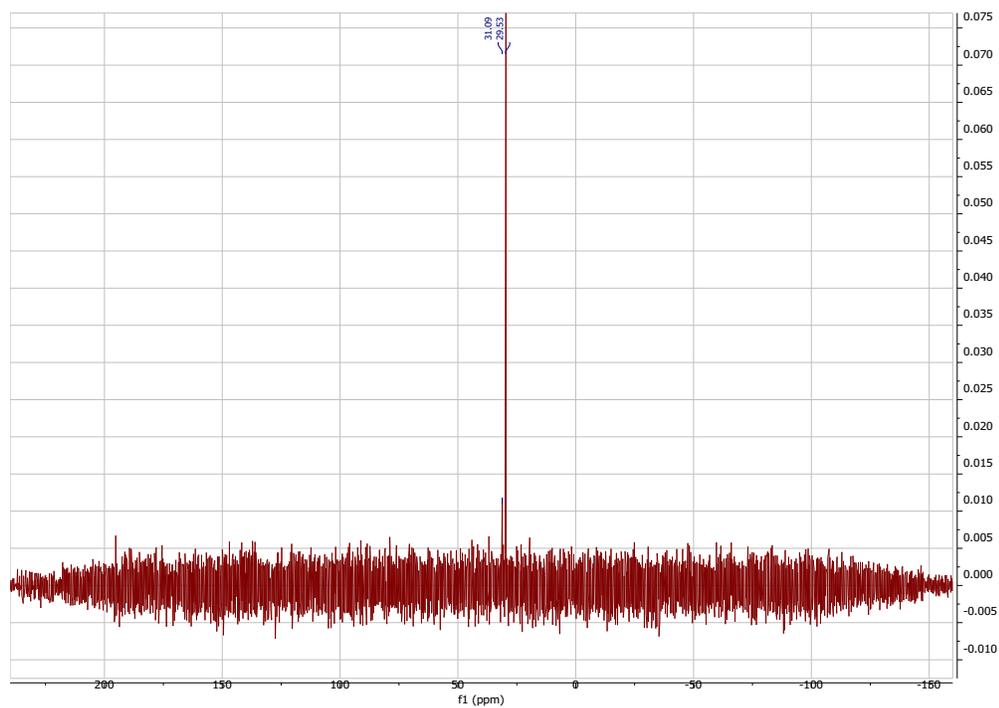
**Conditions:** 20 mmol  $\beta$ -myrcene, 0.7 eq HNEt<sub>2</sub>, 0.035 mol% Pd(acac)<sub>2</sub>, 0.105 mol% TPPTS, P:Pd 3:, EtOH:H<sub>2</sub>O,  $\beta$ -myrcene:solvent (w/w) 1:1, 1 bar Ar, 100 °C, 4 h, 500 rpm. Yield (Y), and selectivity (S) determined by GC-FID with *n*-dodecane as internal standard, Leaching determined by ICP-OES and calculated as the amount lost with respect to the initial amount of palladium.

## 7. $^{31}\text{P}$ -NMR Measurements

### $^{31}\text{P}$ -NMR Measurements of catalyst phase before recycling



### $^{31}\text{P}$ -NMR Measurements of catalyst phase after recycling



## 8. Additional Literature

- [1] M. Terhorst, A. Kampwerth, A. Marschand, D. Vogt, A. Vorholt, T. Seidensticker, "Facile Catalyst Recycling by Thermomorphic Behaviour Avoiding Organic Solvents – A Reactive Ionic Liquid in the Homogeneously Pd-Catalysed Telomerisation of the Renewable  $\beta$ -Myrcene", *Catal. Sci. Technol.* **2020**.
- [2] D. Vogelsang, T. A. Faßbach, P. P. Kossmann, A. J. Vorholt, "Terpene-Derived Highly Branched C<sub>30</sub>-Amines via Palladium-Catalysed Telomerisation of  $\beta$ -Farnesene", *Adv. Synth. Catal.* **2018**, *360*, 1984–1991.
- [3] A. Behr, L. Johnen, A. J. Vorholt, "Telomerization of myrcene and catalyst separation by thermomorphic solvent systems", *ChemCatChem* **2010**, *2*, 1271–1277.