Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

A General and Efficient Method for the Palladium Catalysed Conversion of Allylic Alcohols into their Corresponding Dienes

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Supplementary Information

Table of content

1 General Experimental Methods

All solvents and substrates were purchased from Acros, Sigma-Aldrich, Fisher-Scientific and TCI. All phosphorus ligands were purchased from ABCR. $Pd(acac)_2$ was donated by UMICORE AG & Co. KG. Xantphos was purchased from Strem. All reagents were used without further purification. For column chromatography technical quality solvents were used. Thin-layer chromatography (SiO_2, TLC) was performed on Merck TLC silica gel 60 F254. Column chromatography was performed on Merck silica gel 60 (0.040 - 0.063 nm). NMR spectra were recorded on Bruker DRX500 (500 MHz) spectrometers with TMS as internal standard. $CDCl_3$ was used as solvent and purchased from DEUTERO. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet, dt = doublet of triplet), coupling constant, and integration. Gas chromatography was performed on a HP 6890 (Hewlett-Packard, Waldbronn, Germany) using a flame ionization detector at 325°C and a HP-5 column (30 m, diameter 0.32 mm, film thickness 25 µm) in connection with an auto sampler. The carrier gas was nitrogen (v = 1.2 mL/min, 30 cm/s). The injection volume was 1 µL and the split ratio 1:30. This HP 6890 (Hewlett-Packard, Waldbronn, Germany) was equipped with a 70 eV detection unit was used for LCMS (EI). High resolution mass spectra were recorded on a TSQ mass spectrometer from ThermoQuest coupled to an HPLC-System (HPLC column: Hypersyl GOLD, 50 mm × 1 mm, 1.9 µm) for HPLC-ESI-HRMS.

2 General procedure for the quantitative analysis of the conversion of an allylic alcohol into a diene

$Pd(acac)_2$ (0.02 mmol), Xantphos (0.022 mmol), 2,7-octadienol (**1a**) (2 mmol) were dissolved in a 20 mL custom made stainless steel autoclaves in 2.5 mL toluene. After adding TFA (0.2 mmol) the autoclave was pressurised with 40 bar carbon monoxide and the mixture was stirred at 105°C for 18 h magnetically with 500 rpm. After cooling to room temperature the autoclave was vented and flushed with argon. For the quantitative analysis a sample of the mixture (0.4750 g) was taken and analysed by GC with dodecane (0.0250 g) as internal standard and isopropyl alcohol (0.5000 g) as additional solvent.

3 General procedure for the qualitative analysis of the conversion of an allylic alcohol into a diene

$Pd(acac)_2$ (0.02 mmol), Xantphos (0.022 mmol), 2,7-octadienol (**1a**) (2 mmol) were dissolved in a 20 mL custom made stainless steel autoclaves in 2.5 mL dioctyl ether. After adding TFA (0.2 mmol) the autoclave was pressurised with 40 bar carbon monoxide and the mixture was stirred at 105°C for 18 h magnetically with 500 rpm. After cooling to room temperature the autoclave was vented and flushed with argon. The reaction mixture was purified by coloumn chromatography (pentane as solvent) yielding compound **3**.

4 Full Process of elimination

Table 1S. Process of elimination for determining the reqired conditions

Nr.	$Pd(acac)_2$	Xantphos	TFA	MeOH	CO	Y_3	3a/3[g]
1.1S	+	+	+	+	+	>99	99
1.2S	+	+	+	+	-	---[f]	---
1.3S	+	+	+	-	+	>99	95
1.4S	+	+	-	+	+	---	---
1.5S	+	+	+	-	-	---[f]	---
1.6S	+	+	-	+	-	29	83
1.7S	+	+	-	-	+	---	---
1.8S	+	+	-	-	-	---	---
1.9S	+	-	-	-	-	---	---
1.10S	-	-	+	-	-	---	---
1.11S	+	+	+	-	+[a]	>99	95
1.12S	+	+	+	-	+[b]	77[f]	45
1.13S[c]	+	+	+	-	-	47[f]	11
1.14S	+	-	+	-	+	---	---
1.15S[d]	+	+	+	-	-	83	80
1.16S[d]	-	+	+	-	-	---	---
1.17S	+	+[e]	+	-	+	64	13

Conditions: 2 mmol **1a**, 10 mol% TFA, 1 mol% $Pd(acac)_2$, 1.1 mol% Xantphos, 1,2 eq MeOH, 40 bar CO, 2.5 ml toluene, T = 105 °C, t = 18 h, 500 rpm, results determined with GC in % with dibutylether as internal standard; [a] 10 bar CO, [b] 5 times flushed with CO, reaction under CO atmosphere; [c] under argon; [d] with 1 mol% Ru_3CO_{12} as co-catalyst and CO-source; [e] with 2.2 mol% triphenylphosphie as ligand; [f] 100% conversion, missing yield can be found as oligomers; [g] share of major isomer **3a** in **3**, E/Z-isomers have not been separated.

5 Reaction Progress

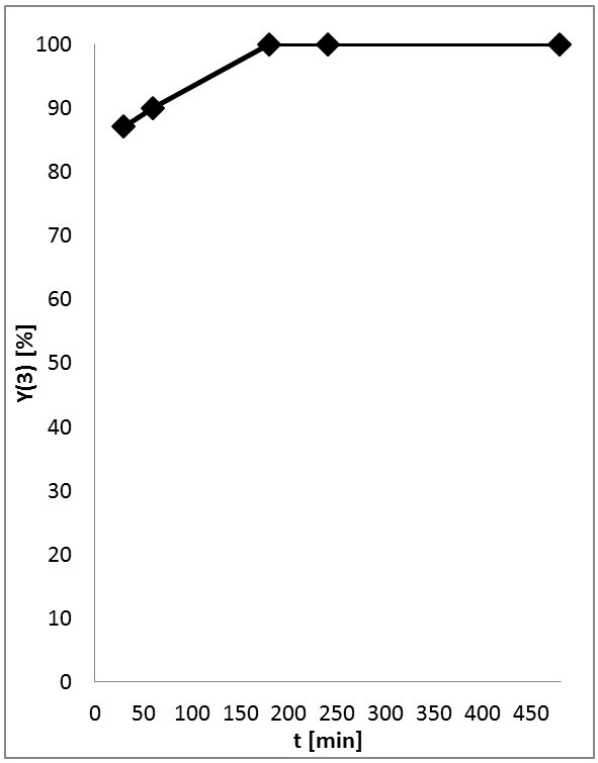
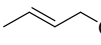
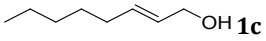
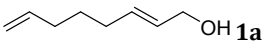
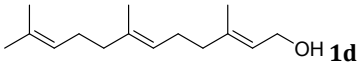
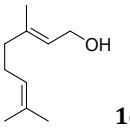
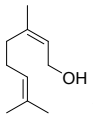
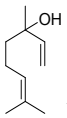
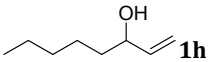
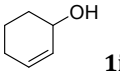
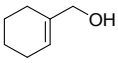
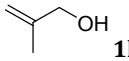
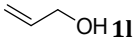
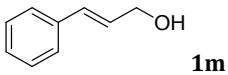
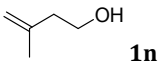
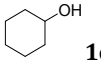
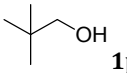
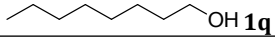


Figure 1S: Investigation oft he reaction progress

Conditions: 2 mmol substrate **1a**, 10 mol% TFA, 1 mol% $Pd(acac)_2$**,** 1.1 mol% Xantphos, 40 bar CO, 2.5 ml toluene, T = 105 °C, 500 rpm, results determined with GC in % with dibutylether as internal standard,

6 Full Substrate Scope

Table 2S. **Substrate scope**

Nr.	substrate	X	$Y_{product}$	Share of major isomer
2.1S	 **1b**	85	85[a]	n.a.
2.2S	 **1c**	100	>99	78
2.3S	 **1a**	100	>99	95
2.4S	 **1d**	99	96	n.a.; substrate was applied as isomeric mixture
2.5S	 **1e**	100	>99	n.a.; Please see SI for further details
2.6S	 **1f**	100	>99	n.a.; Please see SI for further details
2.7S	 **1g**	100	>99	n.a.; Please see SI for further details
2.8S	 **1h**	100	>99	78
2.9S	 **1i**	100	98	n.a.
2.10S	 **1j**	---	---	---
2.11S	 **1k**	---	---	---
2.12S	 **1l**	---	---	---
2.13S	 **1m**	---	---	---
2.14S	 **1n**	---	---	---
2.15S	 **1o**	---	---	---
2.61S	 **1p**	---	---	---
2.17S	 **1q**	---	---	---

Conditions: 2 mmol substrate, 10 mol% TFA, 1 mol% $Pd(acac)_2$, 1.1 mol% Xantphos, 40 bar CO, 2.5 ml toluene, T = 105 °C, t = 18 h, 500 rpm, results determined with GC in % with dibutylether as internal standard; n.a. = not applicable; [a] yield of the product butadiene was determined via the conversion of **1b**.

7 Characterisation data of products

The following products were observed depending on the applied substrates (Figure 2S):

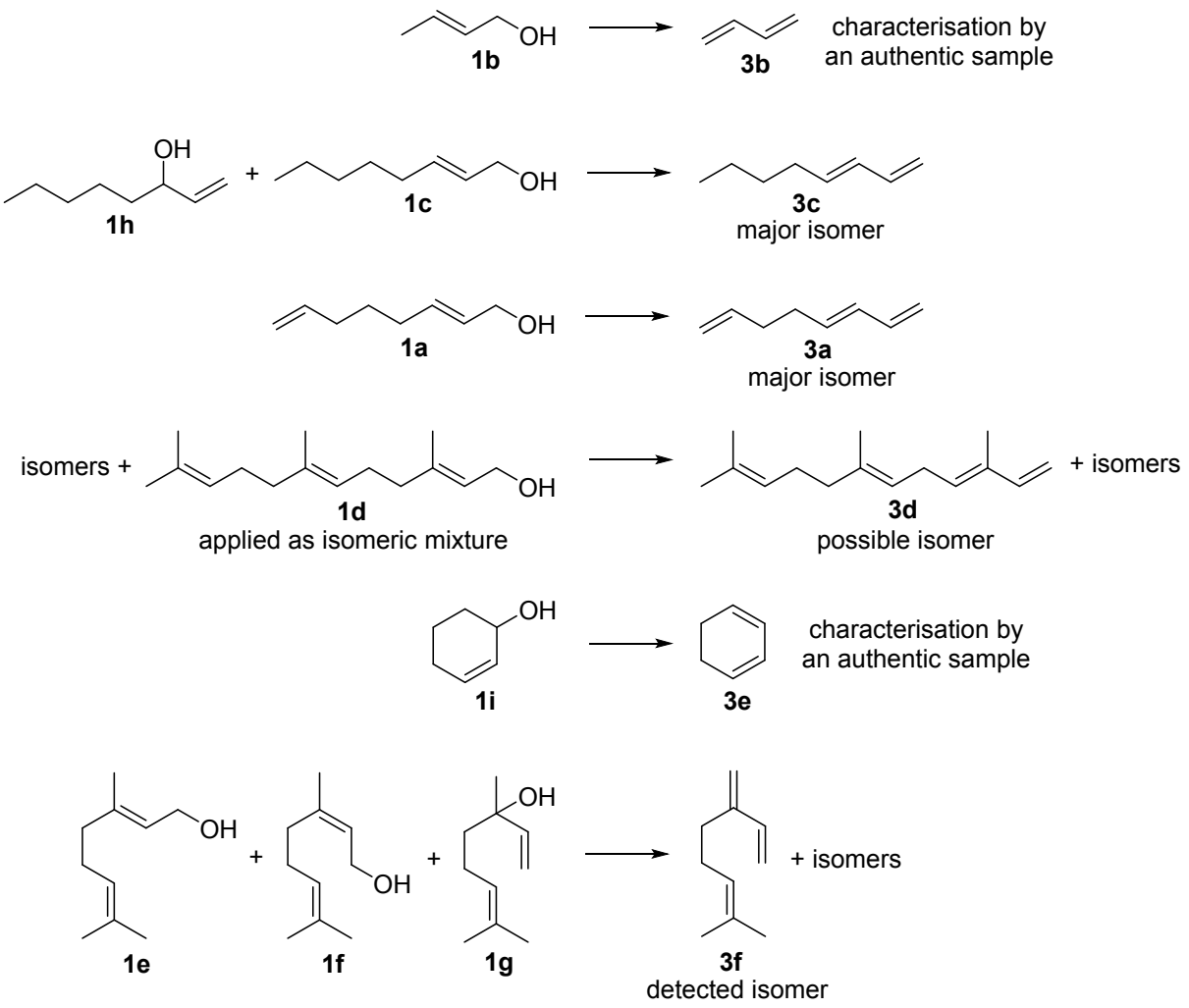
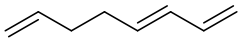


Figure 2S: substrates and their corresponding products

The compounds **3b** and **3e** were determined by authentic samples of butadiene (**3b**) and 1,3-cyclohexadiene (**3d**).

The procedure of purifying the compounds **3a** (major isomer), **3c** (major isomer), **3d** (as possible isomer + further isomers) and **3f** (as detected isomer + further isomers) is attached in the following.

7.1 1,3,7-octatriene (3a)



3a
major isomer

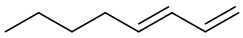
$Pd(acac)_2$ (0.02 mmol), Xantphos (0.022 mmol), 2,7-octadienol (**1a**) (2 mmol) were dissolved in a 20 mL custom made stainless steel autoclaves in 2.5 mL dioctyl ether. After adding TFA (0.2 mmol) the autoclave was pressurised with 40 bar carbon monoxide and the mixture was stirred at 105°C for 18 h magnetically with 500 rpm. After cooling to room temperature the autoclave was vented and flushed with argon. The reaction mixture was purified by coloumn chromatography (pentane as solvent) yielding **3a** as major isomer and further double bond isomers

^{1}H NMR (500 MHz, $CDCl_3$) (major isomer) δ: 2.19 (m, 4H), 4.99 (m, 4H), 5.71 (m, 1H), 5.82 (m, 1H), 6.06 (m, 1H), 6.30 (m, 1H); signals from further isomers are visible;

^{13}C NMR (100 MHz, $CDCl_3$) (major isomer) δ: 31.9, 33.3, 114.8 x 2, 131.3, 134.4, 137.2, 138.1; signals from further isomers are visible;

HRMS (ESI) was already determined in the literature[1].

7.2 1,3-octadiene (3c)



3c
major isomer

$Pd(acac)_2$ (0.02 mmol), Xantphos (0.022 mmol), 2-octenol (**1c**) (2 mmol) were dissolved in a 20 mL custom made stainless steel autoclaves in 2.5 mL dioctyl ether. After adding TFA (0.2 mmol) the autoclave was pressurised with 40 bar carbon monoxide and the mixture was stirred at 105°C for 18 h magnetically with 500 rpm. After cooling to room temperature the autoclave was vented and flushed with argon. The reaction mixture was purified by coloumn chromatography (pentane as solvent) yielding **3c** as major isomer and further double bond isomers

^{1}H NMR (500 MHz, $CDCl_3$) (major isomer) δ: 0.93 (m, 3H), 1.34 (m, 4H), 2.10 (m, 2H), 4.96 (m, 1H), 5.09 (m, 1H), 5.74 (m, 1H), 6.05 (m, 1H), 6.32 (m, 1H); signals from further isomers are visible;

^{13}C NMR (100 MHz, $CDCl_3$) (major isomer) δ: 13.9, 22.3, 31.3, 32.3, 114.5, 130.9, 135.5, 137.3; signals from further isomers are visible;

MS (EI): calcd. For C_8H_{14} [M] 110.10955, found (Figure 3):

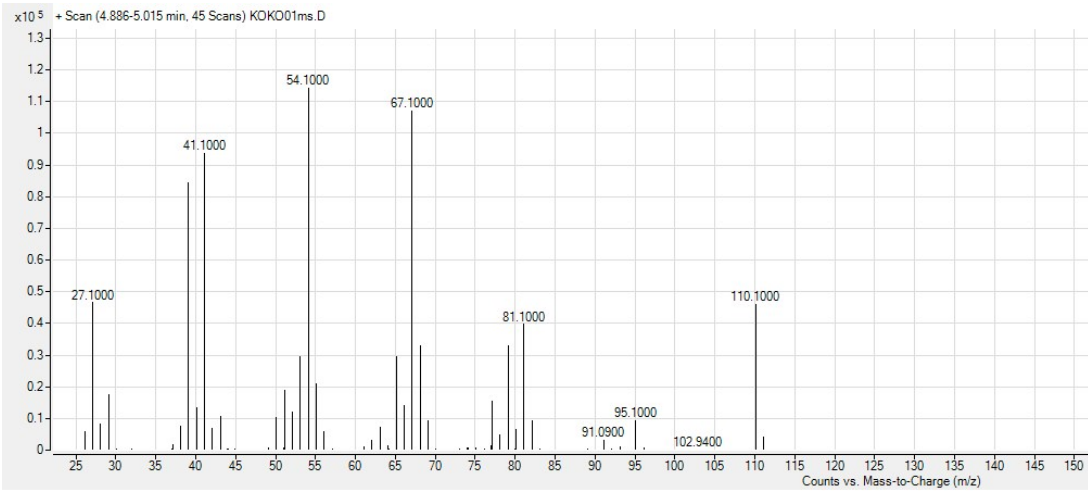
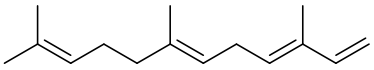


Figure 3S: LR-MS of **3c**

7.3 Isomeric mixture of 3d



3d
possible isomer

$Pd(acac)_2$ (0.02 mmol), Xantphos (0.022 mmol), farnesol as isomeric mixture (**1d**) (2 mmol) were dissolved in a 20 mL custom made stainless steel autoclaves in 2.5 mL dioctyl ether. After adding TFA (0.2 mmol) the autoclave was pressurised with 40 bar carbon monoxide and the mixture was stirred at 105°C for 18 h magnetically with 500 rpm. After cooling to room temperature the autoclave was vented and flushed with argon. The reaction mixture was purified by coloumn chromatography (pentane as solvent) yielding an isomeric mixture of **3d** and further double bond isomers.

^{1}H NMR and ^{13}C NMR of the isomeric mixture is attached. An exact assignment is not possible.

MS (EI): calcd. For $C_{15}H_{24}$ [M] 204.18780, found (Figure 4):

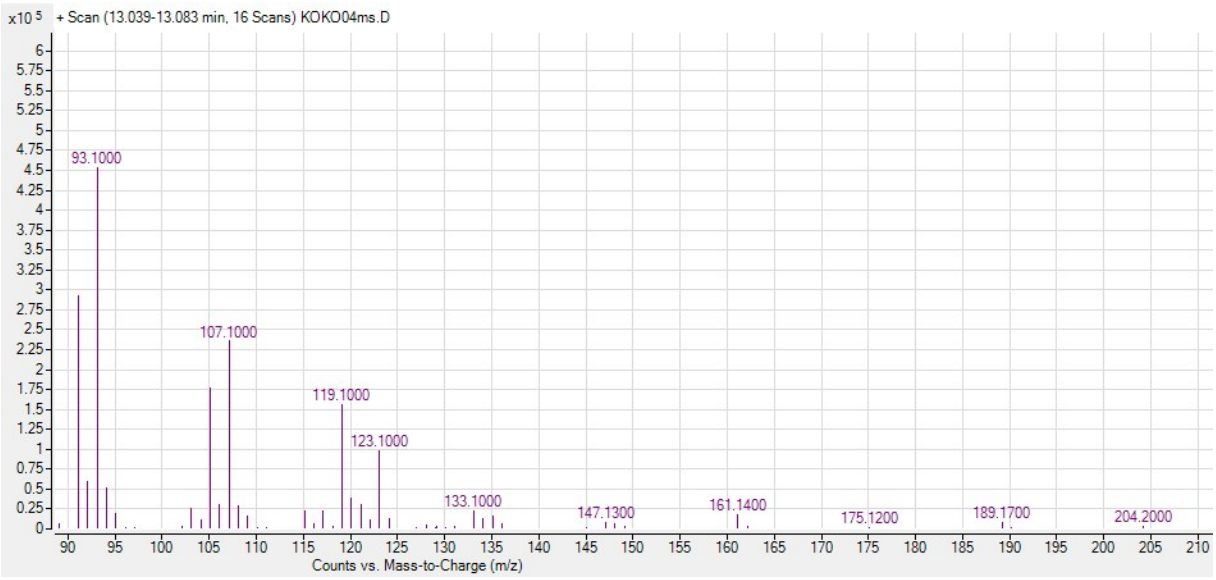


Figure 4S: LR-MS of **3d;** area <90 m/z was cut out

GC of the isomeric substrate (farnesol) mixture and GC after the reaction of the product (farnesene) isomeric mixture is displayed in the following (Figure 5).

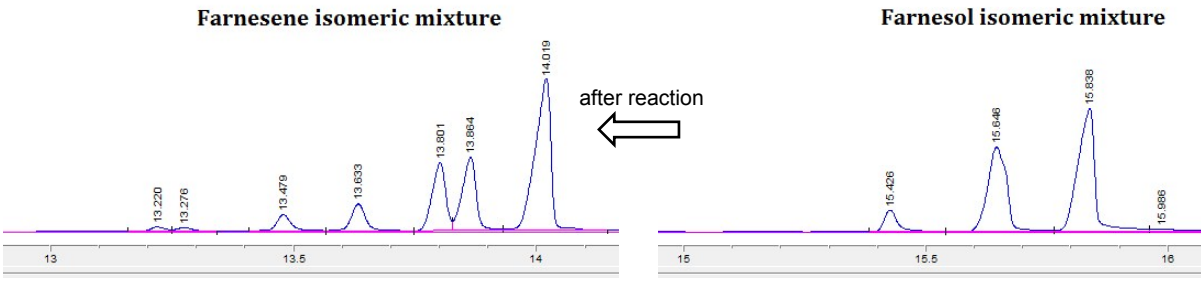
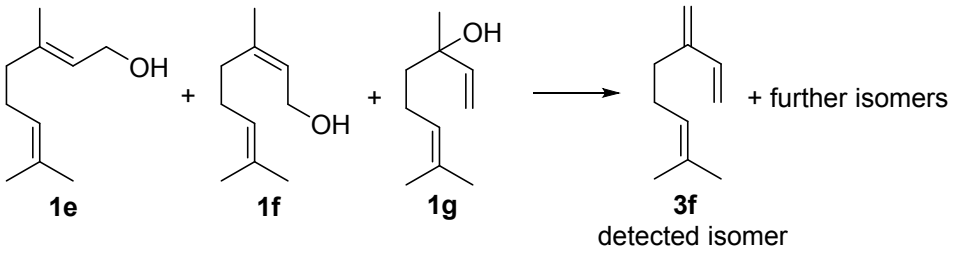


Figure 5S: GC-FID of the isomers before (right) and after (left) the reaction

7.4 Isomeric mixture of 3f



$Pd(acac)_2$ (0.02 mmol), Xantphos (0.022 mmol), geraniol (**1e**) or nerol (**1f**) or linalool (**1g**) (2 mmol) were dissolved in a 20 mL custom made stainless steel autoclaves in 2.5 mL toluene. After adding TFA (0.2 mmol) the autoclave was pressurised with 40 bar carbon monoxide and the mixture was stirred at 105°C for 18 h magnetically with 500 rpm. After cooling to room temperature the autoclave was vented and flushed with argon. The reaction mixture was purified by coloumn chromatography (pentane as solvent) yielding an isomeric mixture of **3d** and further double bond isomers.

The following signals for Myrcen were detected: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.66 (s, 3H), 1.71 (s, 3H), 2.23 (m, 4H), 5.03 (m, 3H), 5.17 (m, 1H), 5.24 (m, 1H), 6.39 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 17.7, 25.7, 26.7, 31.4, 113.5, 115.7, 124.1, 131.8, 139.0, 146.1.

^{1}H NMR and ^{13}C NMR of the isomeric mixture is attached. An exact assignment of other isomers is not possible.

MS (EI): calcd. For $C_{10}H_{16}$ [M] 136.12520, found (Figure 6):

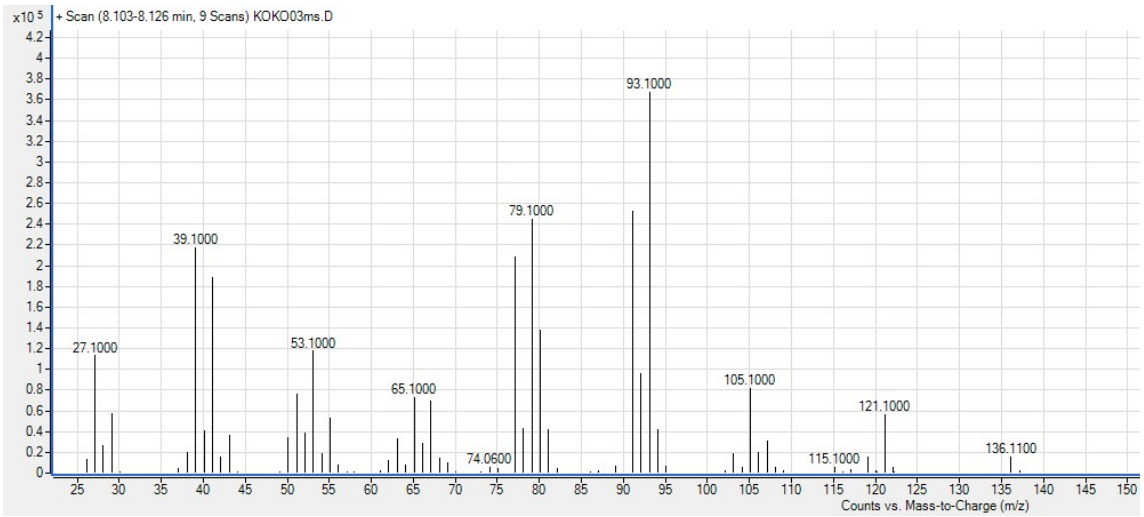


Figure 6S: LR-MS of **3f**

The following product distribution was obderved in the GC-FID for each applied substrate (geraniol (**1e**) or nerol (**1f**) or linalool (**1g**)) (Figure 7).

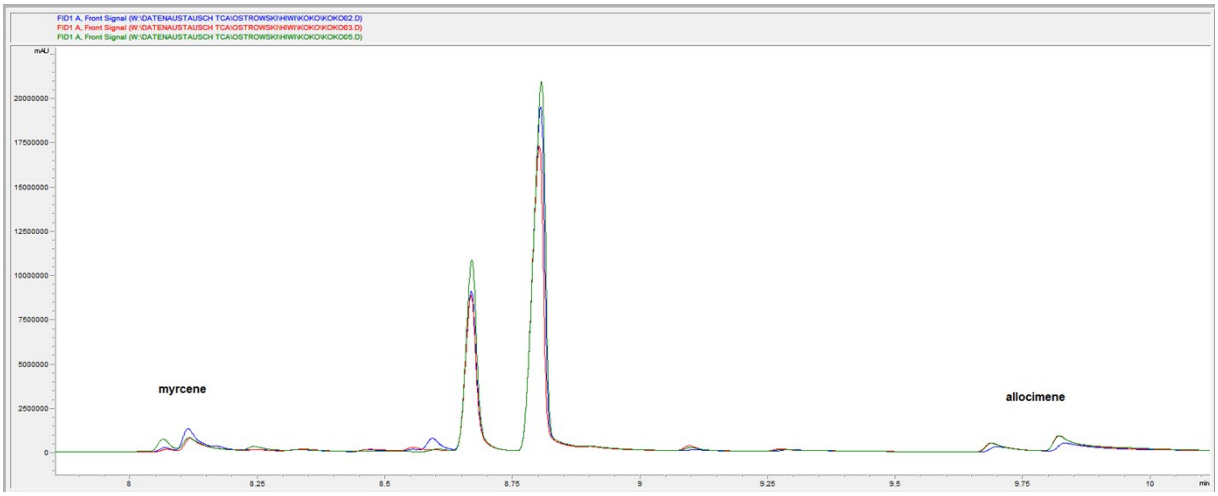


Figure 7S: Product distribution of the applied substrates **1e**, **1f** and **1g** in the GC-FID; Blue: product distribution of geraniol; Red: product distribution of nerol; Green: product distribution of linalool; retention time of myrcen : 8.15 min; retention time of alloocimene : 8.85

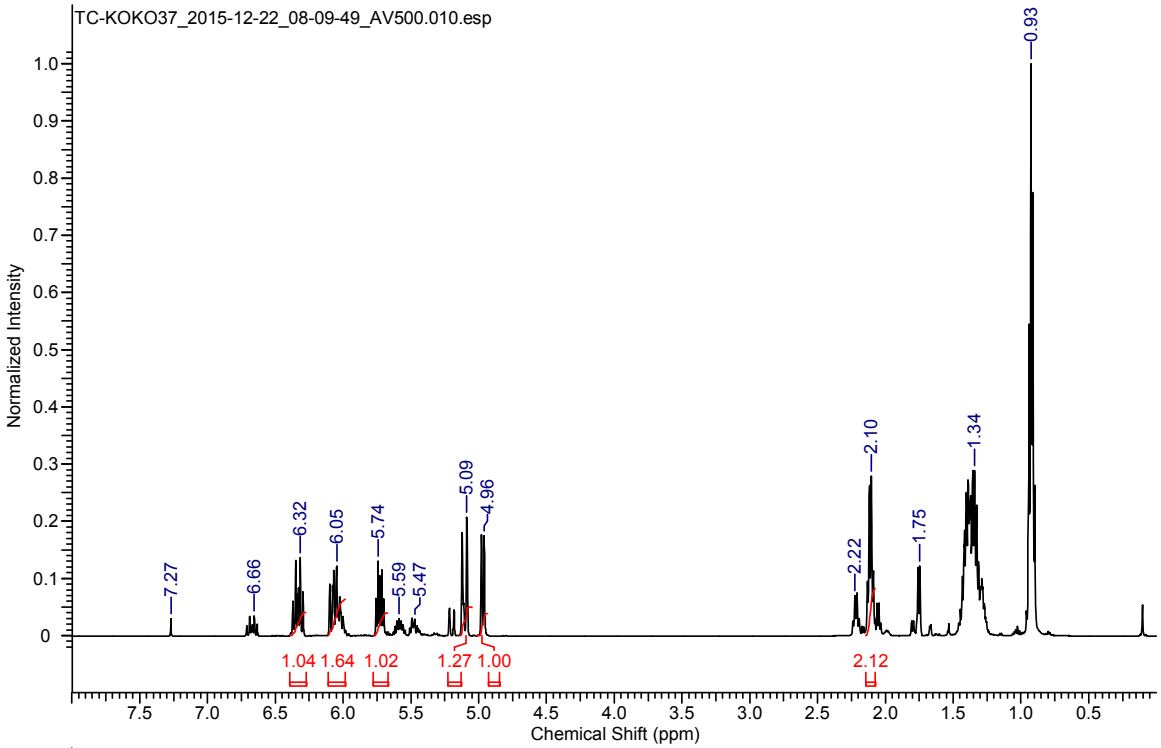
8 References

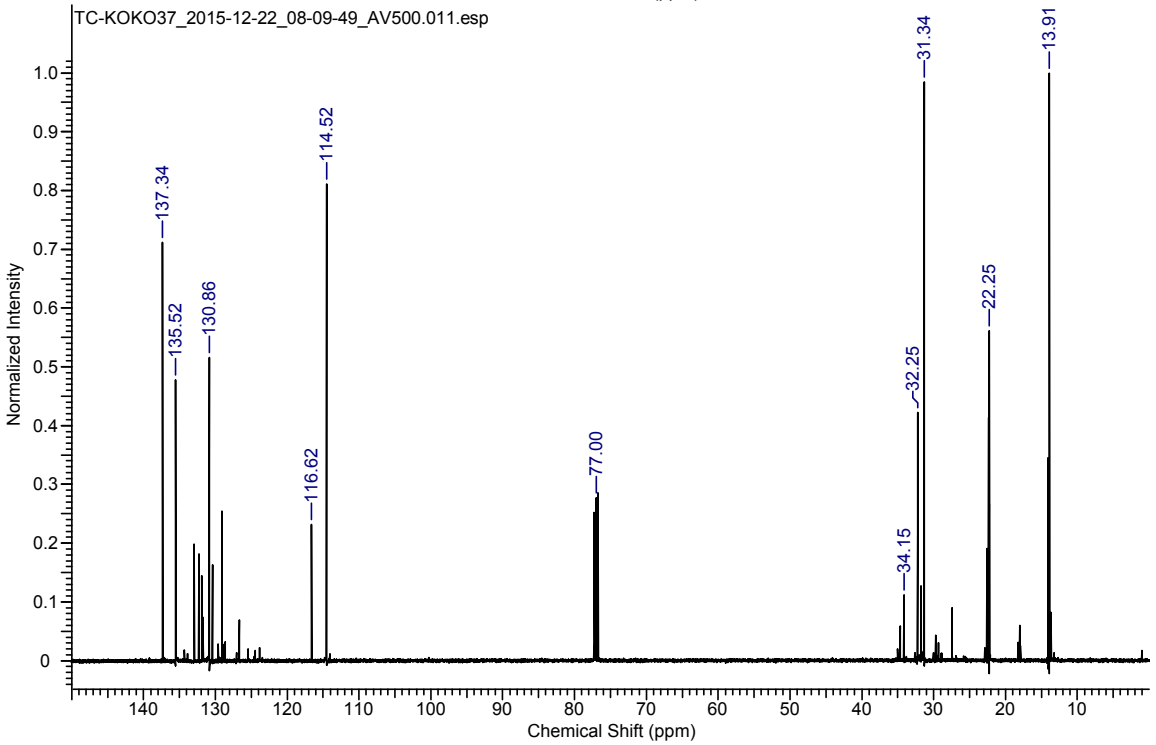
[1] K. A. Ostrowski, D. Vogelsang, A. J. Vorholt, *Chem. Eur. J.*, accepted, DOI: 10.1002/chem.201503785.

9 NMR-spectra

9.1 Compound 3c

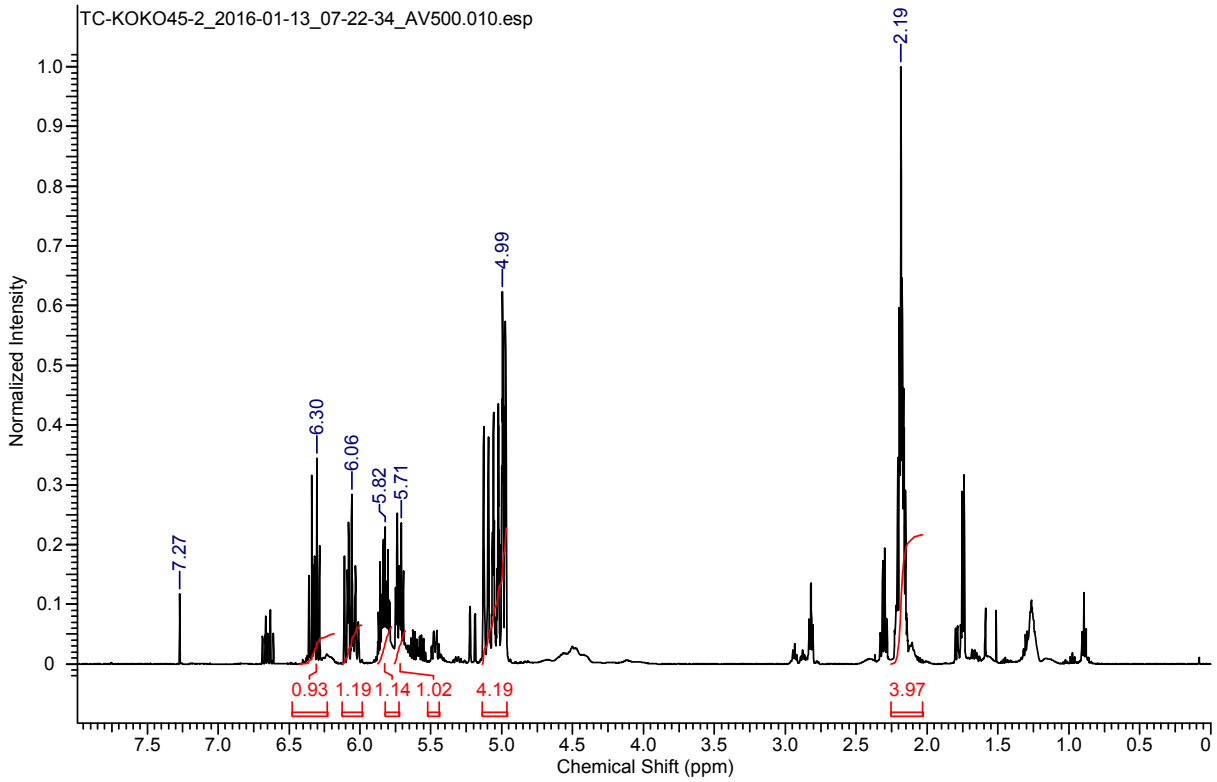
Signals of further isomers are visible

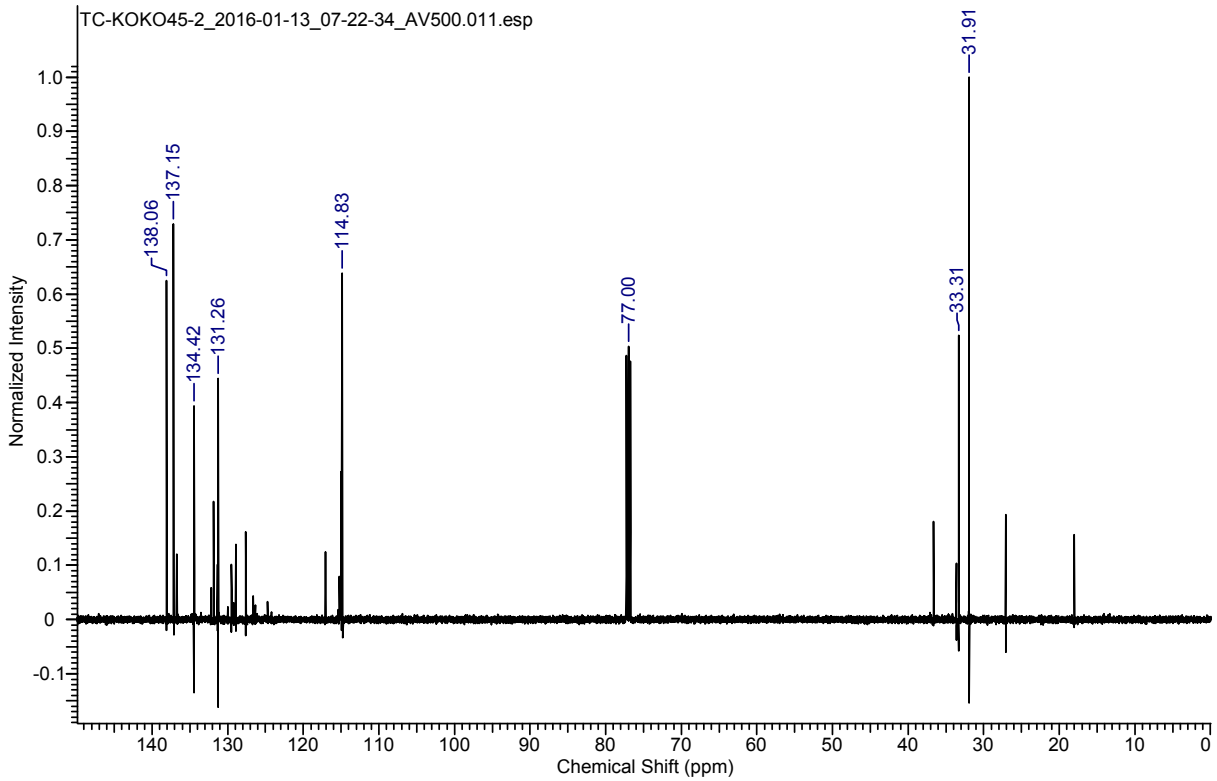




9.2 Compound 3a

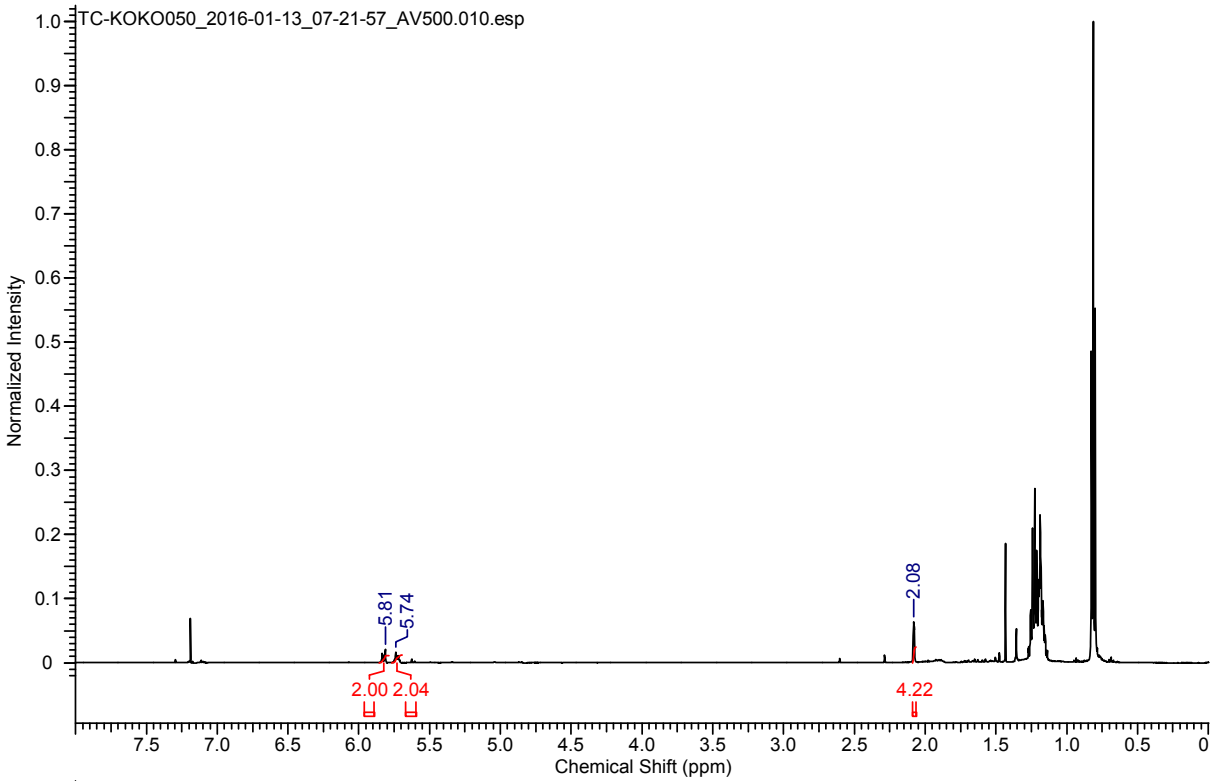
Signals of further isomers are visible

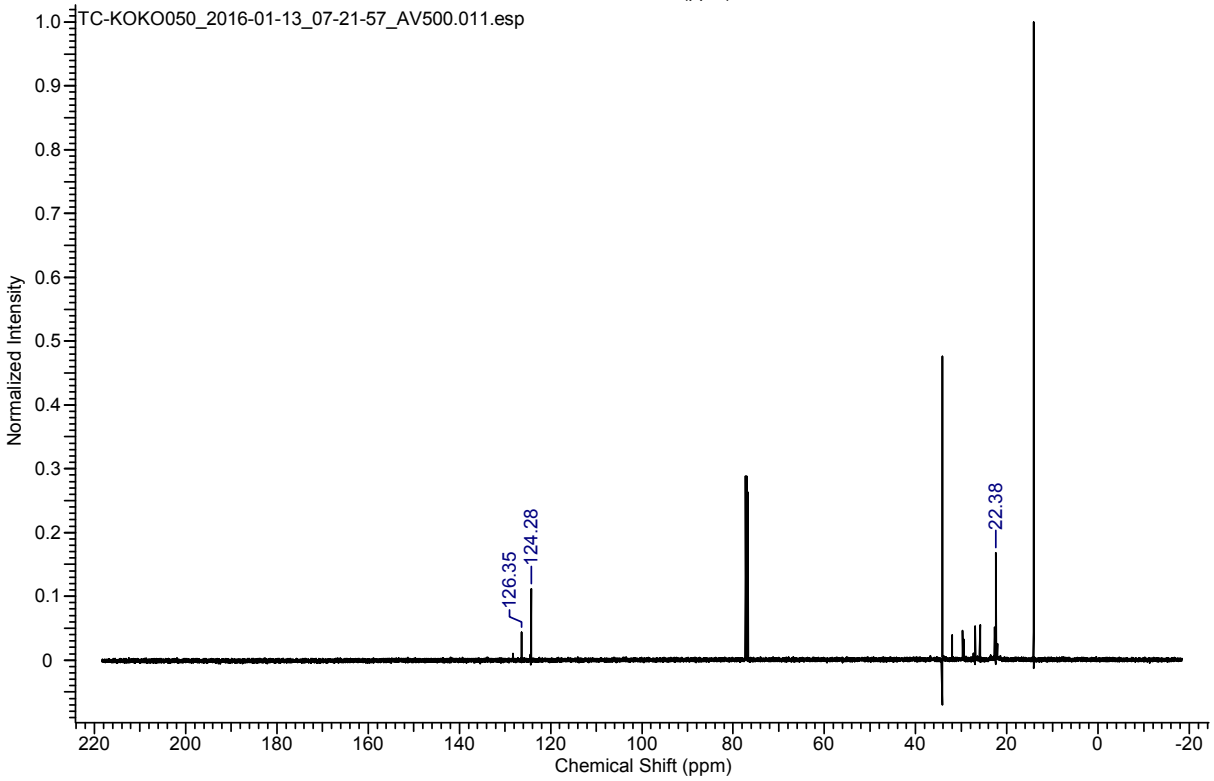




9.3 Compound 3e

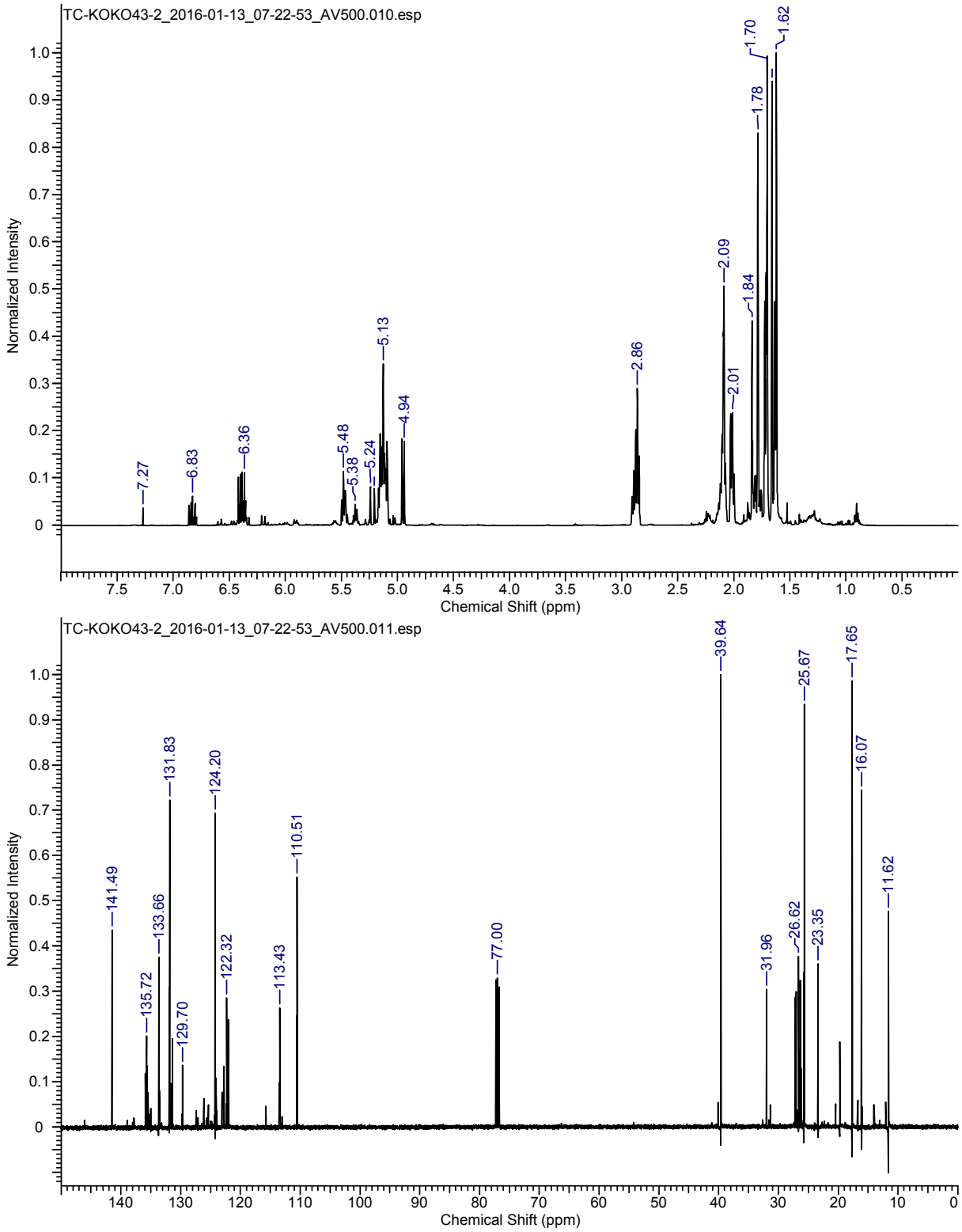
Signals for pentane are visible in ^{1}H at δ 0.88, 1.27 and in ^{13}C at δ 14.1, 22.4, 34.2.





9.4 Compound 3d

Signals of further isomers are visible



9.5 Compound 3f

Signals for pentane are visible in ^{1}H at δ 0.88, 1.27 and in ^{13}C at δ 14.1, 22.4, 34.2; Signals of further isomers are visible