Supporting information to the manuscript:

Palladium-catalysed carboxytelomerisation of β-myrcene to highly branched C_{21}-esters

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Table of contents

1 General procedures

All solvents, reagents and substrates were purchased from Acros, Sigma-Aldrich, Fisher-Scientific and TCI. All phosphorus ligands were purchased from ABCR. $Pd(OAc)_2$ and the other tested palladium precursors were donated by UMICORE AG & Co. KG. Solvents were purified *via* distiallation and molecular sieves. For column chromatography technical quality solvents were used. Column chromatography was performed on Merck silica gel 60 (0.040 – 0.063 nm). NMR spectra were recorded on Bruker DRX400 (300-500 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. High resolution mass spectra were measured 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.

1.1 General procedure for the carboxytelomerisation of β-myrcene with alcohols

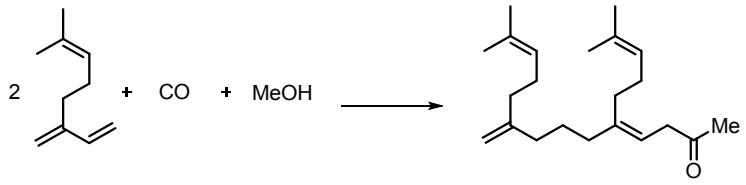
The alcohol (1 eq.) was added to a mixture of $Pd(OAc)_2$ (1 mol%) and dicyclohexylphenyl phosphine as ligand (5 mol%) dissolved in fresh distilled β-myrcene (5 eq.) under argon in a stainless steel autoclave. Afterwards, the reactor was pressurised with 3 bar carbon monoxide and stirred for 6 h at 80 °C reaction temperature. After conduction of the experiments, the reactor was cooled down by an ice-bath, degassed, flashed with argon and the yields of the products were determined *via* GC-FID-analysis. For detailed characterisation, the products were isolated through column chromatography over silica with cyclohexane/ethyl acetate (100:1→5:1) as eluents and characterized by *NMR*- and MS-analysis.

2 DoE

2.1 Settings in the DoE

Ranges of the investigated parameters by MODDE® based on initial studies:

- T: 20-110 °C
- P:Pd-ratio: 1-10
- β-myrcene:methanol-ratio: 1-20
- p_{CO}: 1-50 bar
- palladium catalyst concentration cat: 0.1-2 mol%



Scheme S1: Model substrates applied in the carboxytelomerisation in the design of experiments

Table S1: Setting in the DoE

experiment	T [°C]	p [bar]	β-myrcen/MeOH	cat [mol%]	P/Pd	X_{MeOH} [%]	Y_2 [%]	Y_3 [%]
1	40	40	1	0.1	1	0	0	0
2	110	10	10	0.1	5	54	7	47
3	20	1	1	0.1	10	0	0	0
4	110	50	1	0.1	10	20	0	20
5	80	20	5	0.1	10	88	0	88
6	20	50	20	0.1	10	0	0	0
7	110	1	1	0.5	1	80	6	74
8	20	50	5	0.5	1	0	0	0
9	80	40	20	0.5	5	88	0	88
10	40	15	20	0.5	10	0	0	0
11	20	15	1	1	2	0	0	0
12	80	50	1	1	7	60	4	56
13	40	1	5	1	7	0	0	0
14	110	40	10	1	10	82	0	82
15	110	50	1	1	2	90	30	60
16	80	1	10	1	2	94	0	94
17	110	40	5	2	5	80	0	80
18	110	15	20	2	7	96	5	91
19	110	1	1	2	10	80	10	70
20	80	50	20	2	10	90	0	90
21	60	5	1	1	2	30	0	30
22	60	5	1	1	2	33	0	33
23	40	40	1	0.1	1	0	0	0

24	110	10	10	0.1	5	46	4	42
25	20	1	1	0.1	10	0	0	0
26	110	50	1	0.1	10	25	0	25
27	80	20	5	0.1	10	85	0	85
28	20	50	20	0.1	10	0	0	0
29	110	1	1	0.5	1	78	5	73
30	20	50	5	0.1	5	0	0	0
31	80	40	20	0.5	5	75	0	75
32	40	15	20	0.5	10	0	0	0
33	20	15	1	1	1	0	0	0
34	80	50	1	1	7	60	8	52
35	40	1	5	1	7	0	0	0
36	110	40	10	1	10	84	0	84
37	110	50	2	2	1	78	20	58
38	80	1	10	2	1	94	0	94
39	110	40	5	2	5	88	10	78
40	110	15	20	2	7	96	5	91
41	110	1	2	2	10	79	11	68
42	80	50	20	2	10	85	0	85
43	60	10	2	0.5	7	32	0	32
44	60	10	2	0.5	7	36	0	36

Conditions: 3.7 mmol β-myrcene, $Pd(OAc)_2$, ligand = PCy_2Ph, t = 6 h, 500 rpm.

2.2 Results of the DoE

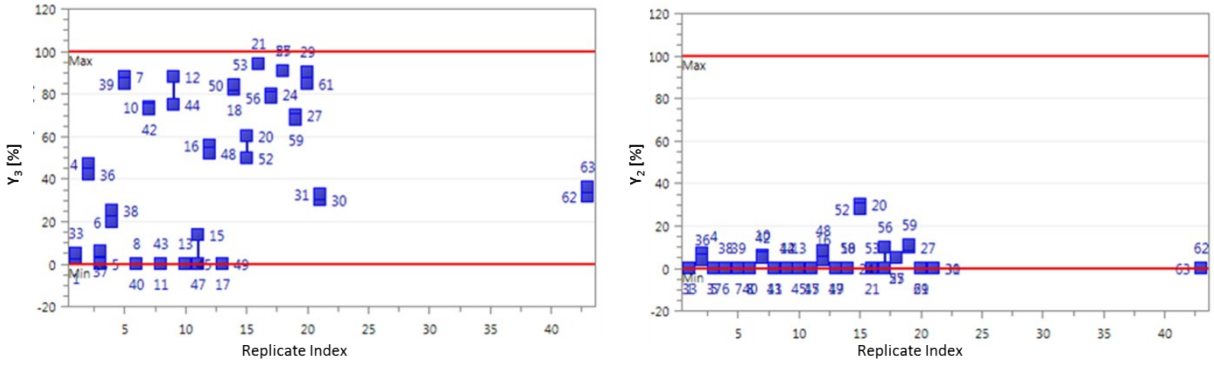


Figure S1: Results oft the DoE

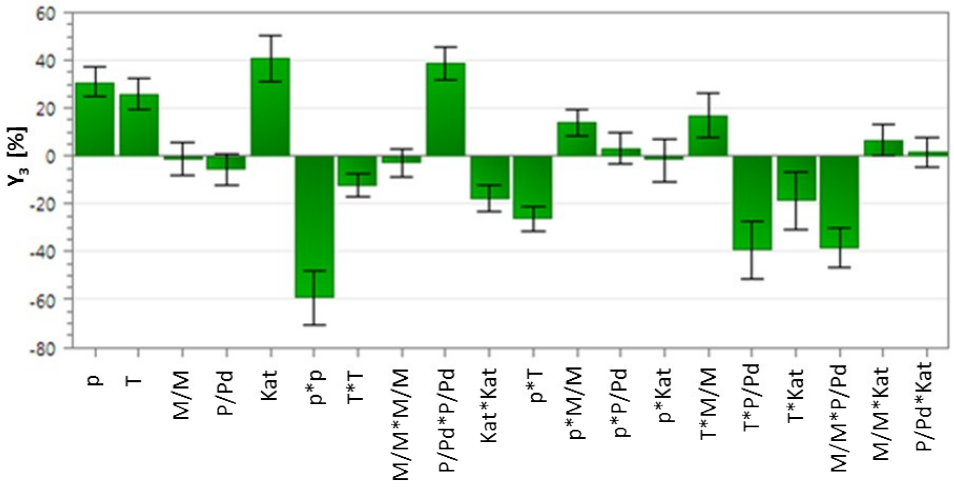


Figure S2. Sensitive plot of each parameter in case of the desired C_{21}-ester **3** formation

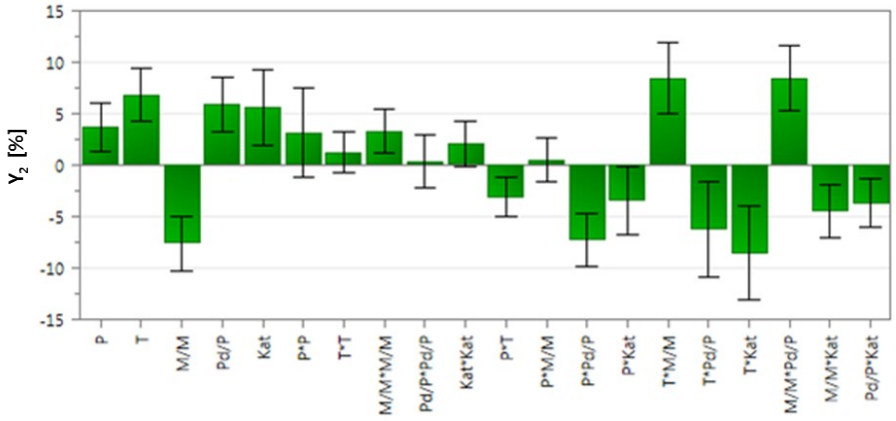


Figure S3. Sensitive plot of each parameter in case of the C_{11}-ester **2** formation

3 Applied 1,3-dienes

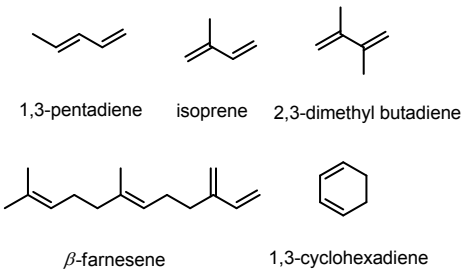
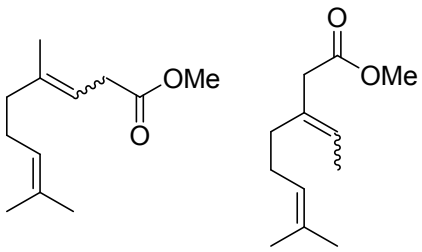


Figure S4: Applied 1,3-dienes under optimised carboxytelomerisation conditions without any formation of the target products; conditions: 7.3 mmol 1,3-diene, 1.5 mmol MeOH, 1 mol% $Pd(OAc)_2$, 5 mol% Cy_2Ph, 80 °C, 3 bar CO, 6 h, 500 rpm

4 Characterisation data of products

4.1.1 Methyl 4,8-dimethylnona-3,7-dienoate + isomers – 2a

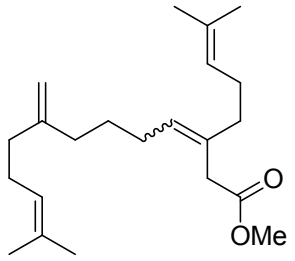


^{1}H-NMR: ($CDCl_3$, 600 MHz), δ 1.59 (s, 3H), 1.63 (s, 3H), 1.67 (s, 3H, isomer), 1.74 (s, 3H, Isomer), 2.04 (m, 4H), 3.05 (d, 2H, Isomer), 3.67 (s, 3H), 5.08 (m, 1H), 5.32 (m, 1H).

^{13}C-NMR: ($CDCl_3$, 150 MHz), δ 16,47, 17.81, 25.82, 26.44, 30.07, 33.53, 39.69, 42.66, 51.83, 115.78, 124.13, 131.74, 139.20, 173.03

HR-MS: $C_{12}H_{21}O_2$ $[M+H]^+$ calculated: 197.15361; measured: 197.15361

4.1.2 Methyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – 3a

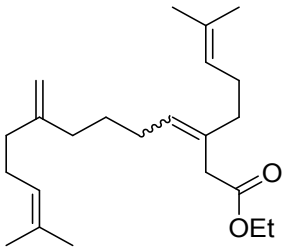


^{1}H-NMR: ($CDCl_3$), 600 MHz), δ 1.59 (s, 3H), 1.61 (s, 3H, isomer), 1.62 (s, 3H, isomer), 1.68 (s, 3H, isomer), 2.04 (m, 4H), 2.09 (m, 4H, isomer), 3.00 (m, 2H, tail-head/tail-tail-isomers), 3.67 (s, 3H), 3.68 (s, 3H, isomer), 4.73, (s, 1H), 4.99 (m, 2H), 5.11 (m, 2H), 5.34 (m, 1H, isomer), 5.51 (m, 1H)

^{13}C-NMR: ($CDCl_3$, 150 MHz), δ 16.3, 17.5, 17.6, 26.3, 26.9, 33.4, 37.5, 39.5, 42.5, 51.7, 115.6, 116.3, 123.8, 124.0, 131.6, 131.9, 133.0, 139.1, 139.6, 172.8

HR-MS: $C_{22}H_{37}O_2$ $[M+H]^+$ calculated: 333.27881; measured: 333.27893

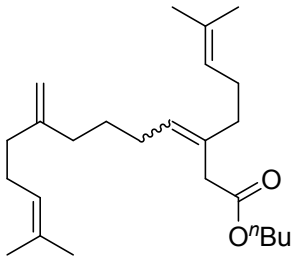
4.1.3 Ethyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – 3b



^{1}H-NMR: ($CDCl_3$), 400 MHz), δ 1.26 (t, 3 H), 1.5 (m, 2H), 1.56 (s, 3H), 1.62 (s, 3H), 1.69 (s, 2H), 2.08 (m, 4H), 3.00 (s, 2H), 4.15 (q, 2H), 4.50 (s, 1H,), 4.73 (s, 1H), 5.12 (m, 2H), 5.31 (m, 1H)

GC-MS (EI, 70 eV): m/z [%] = 346.20 (1.37), 303.20 (0.87), 258.20 (1.64), 215.2 (1.86), 189.20 (7.97), 161.2 (6.37), 135.1 (5.47), 107.1 (17.44), 69.10 (100)

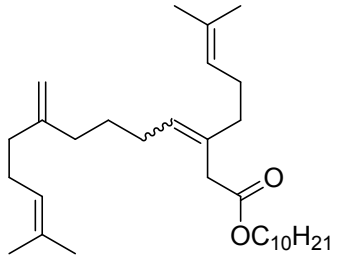
4.1.4 Butyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – 3c



^{1}H-NMR: ($CDCl_3$), 500 MHz), δ 0.93 (t, 3H), 1.37 (m, 2H), 1.49 (m, 4H), 1.62 (s, 6H), 1.69 (s, 6H), 2.04 (m, 10H), 3.00 (s, 2H), 3.05 (t, 1H, isomer), 4.07 (q, 2H), 4.72 (s, 1H, isomer), 4.91 (s, 1H), 4.97 (s, 1H), 5.12 (m, 2H), 5.30 (m, 1H)

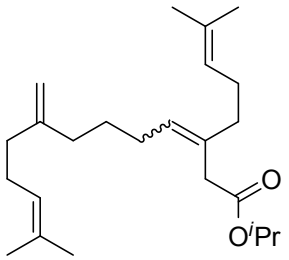
HR-MS: $C_{25}H_{43}O_2$ $[M+H]^+$ calculated: 375.32576; measured: 375.32621

4.1.5 Decyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – 3d



GC-MS (EI, 70 eV): m/z [%] = 458.46 (2.07), 389.370 (1.6), 258.26 (2.83), 215.19 (2.91), 189.18 (11.33), 107.1 (12.64), 69.1 (100)

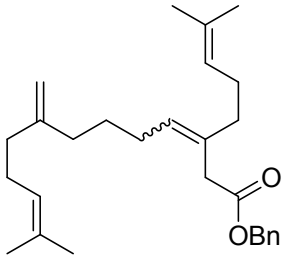
4.1.6 Isopropyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – 3e



^{1}H-NMR: ($CDCl_3$), 500 MHz), δ 1.24 (m, 2H,), 1,34 (s, 3H, Isomer), 1.44 (s, 3H, Isomer), 1.50 (m, 2H), 1.56 (s, 2H), 1.69 (s, 2H), 2.06 (m, 10H), 2.97 (s, 2H, Isomer), 3.02 (t, 1H), 4.50 (s, 1H), 4.73 (s, 1H), 5.00 (m, 2H), 5.11 (s, 3H), 5.30 (m, 1H)

GC-MS (EI, 70 eV): m/z [%] = 360.4 (1.61), 317.10 (1.82), 275.1 (1.78), 249.10 (2.38), 215.10 (1.77), 189.20 (8.08), 135.00 (10.34), 107.10 (15.96), 69.1 (100)

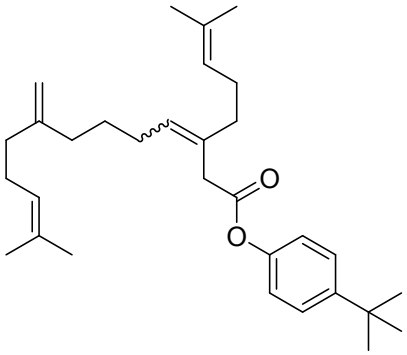
4.1.7 Benzyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – 3g



^{1}H-NMR: ($CDCl_3$), 400 MHz), δ 1.27 (m, 2H), 1.49 (m, 2H, isomer), 1.62 (s, 1H), 1.70 (s, 1H) 2.05 (m, 10H), 3.07 (s, 2H), 3.11 (t, 1H), 4.72 (s, 2H), 5.13 (s, 2H), 5.34 (m, 1H), 7.35 (s, 5H)

HR-MS: $C_{28}H_{41}O_2$ $[M+H]^+$ calculated: 409.31011; measured: 409.31023

4.1.8 4-(tert-butyl)phenyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – 3h



GC-MS (EI, 70 eV): m/z [%] = 450.5 (0.94), 301.34 (5.69), 257.28 (2.55) 215.21 (3.05), 189.19 (4.76), 163.17 (6.99), 150.2 (23.4), 135.10 (100), 121.1 (12.84), 107.1 (27.52), 69.1 (89.51)

5 NMR-spectra

5.1.1 Methyl 4,8-dimethylnona-3,7-dienoate + isomers – 2a

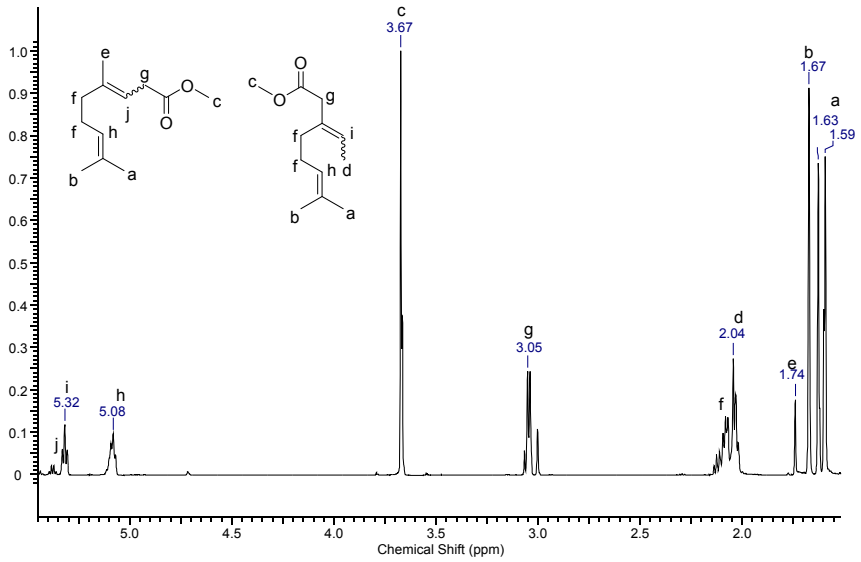


Figure S5: ^{1}H-NMR spectrum in d-$CDCl_3$ of methyl 4,8-dimethylnona-3,7-dienoate - **2a**

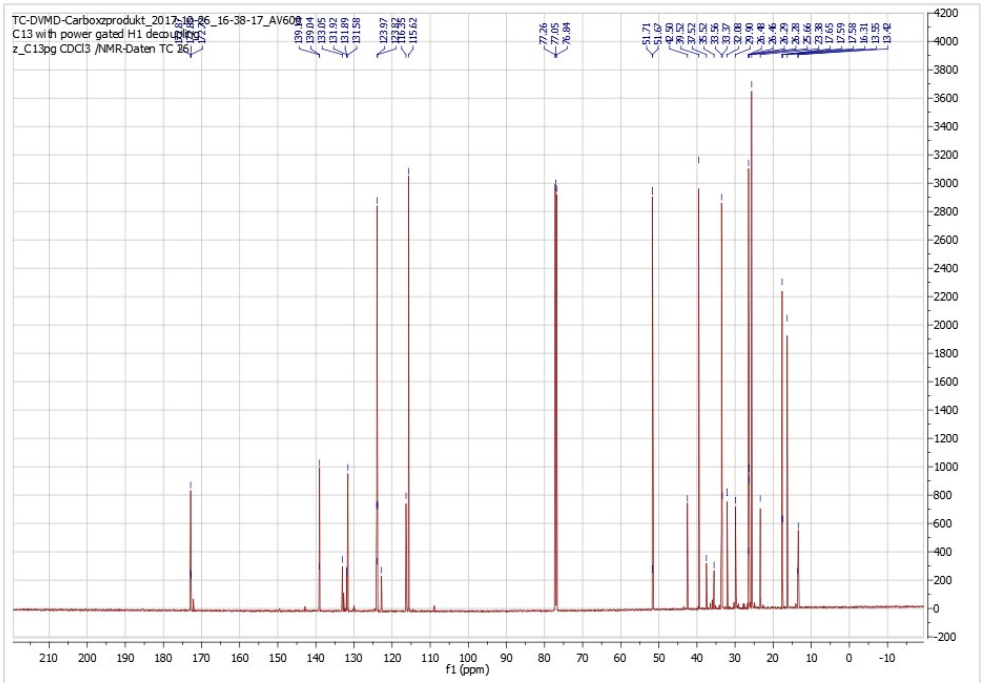


Figure S6: ^{13}C-NMR spectrum in d-$CDCl_3$ of methyl 4,8-dimethylnona-3,7-dienoate - **2a**

5.1.2 Methyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – 3a

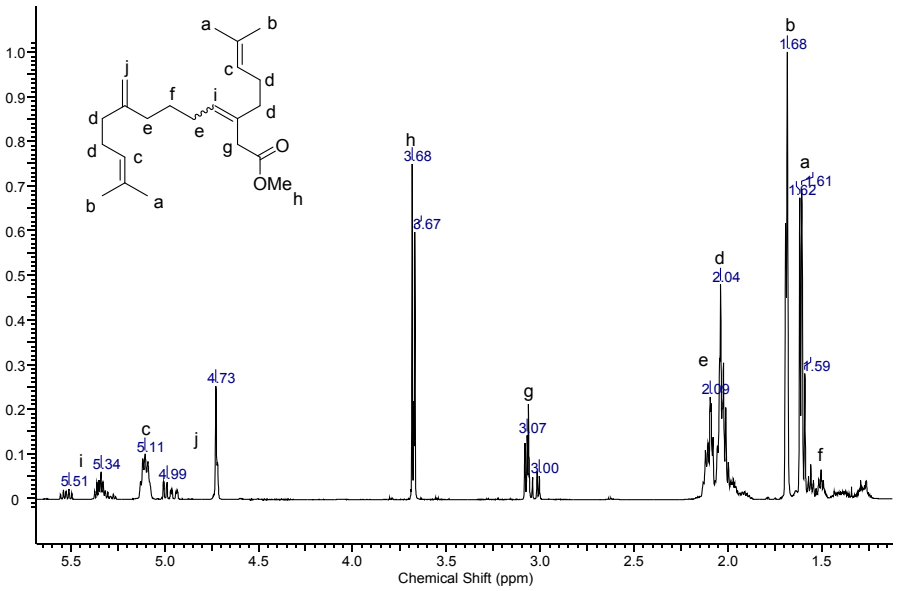


Figure S7: ^{1}H-NMR spectrum in d-$CDCl_3$ of Methyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate - **3a**

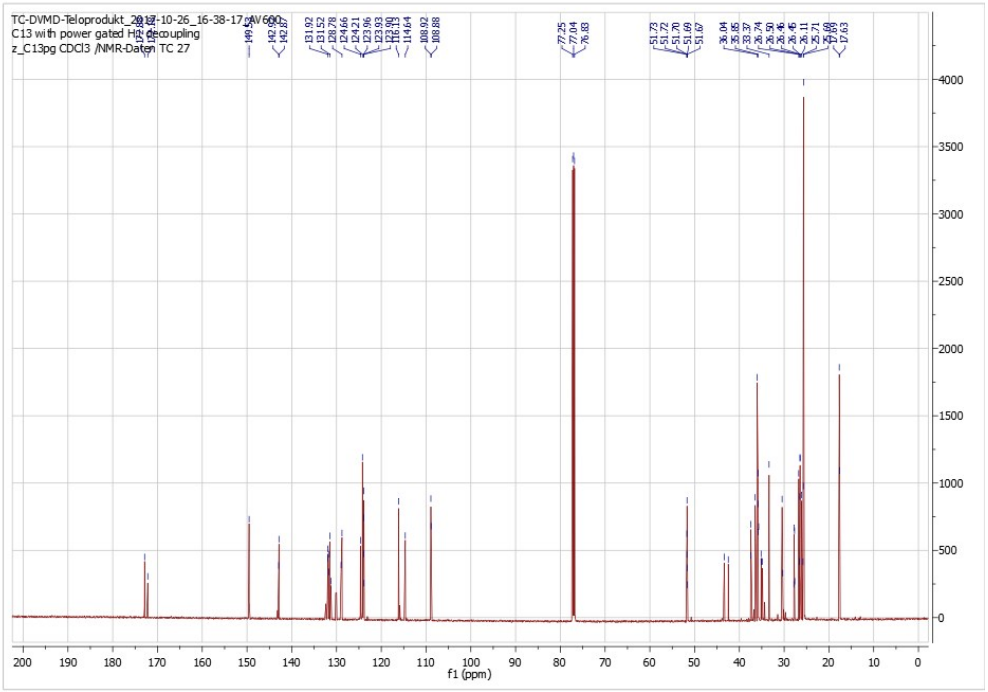


Figure S8: ^{13}C-NMR spectrum in d-$CDCl_3$ of Methyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate - **3a**

5.1.3 Ethyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – 3b

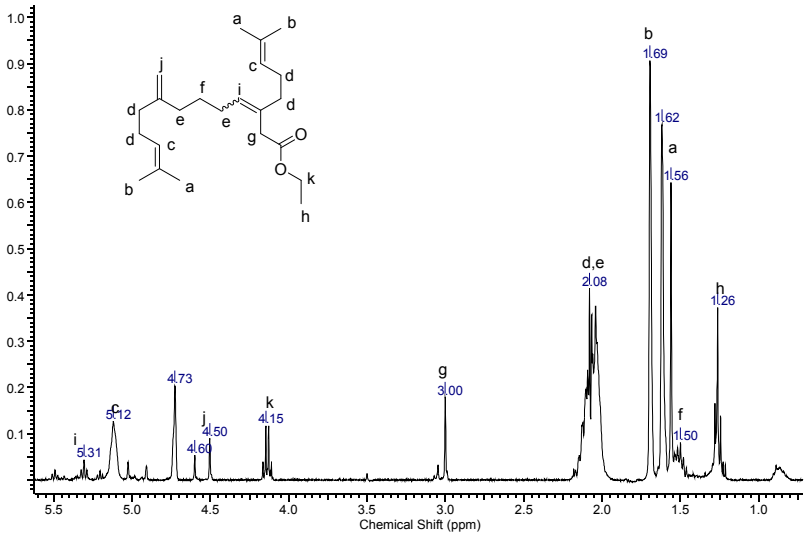


Figure S9: ^{1}H-NMR spectrum in d-$CDCl_3$ of Ethyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – **3b**

5.1.4 Butyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – 3c

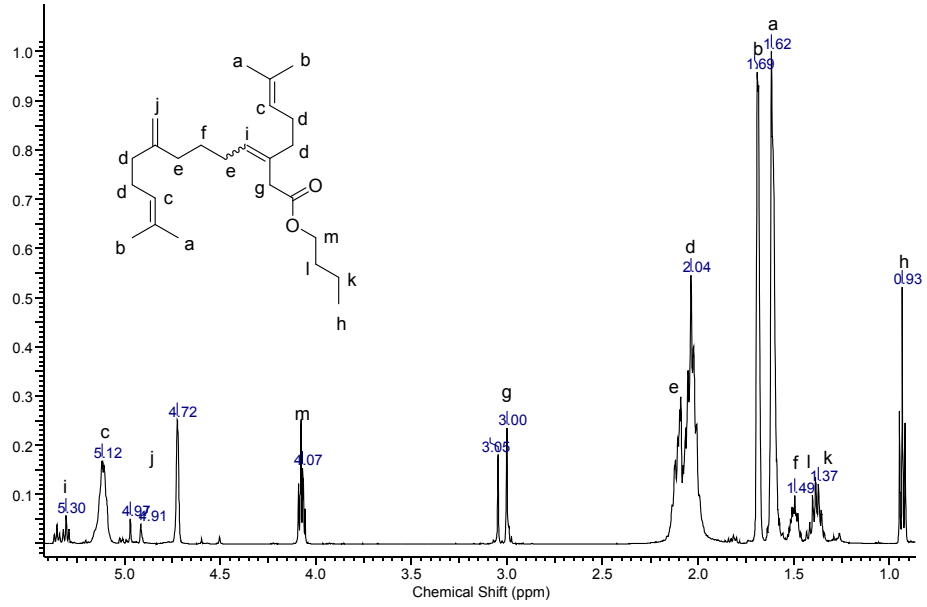


Figure S10: ^{1}H-NMR spectrum in d-$CDCl_3$ of Butyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – **3c**

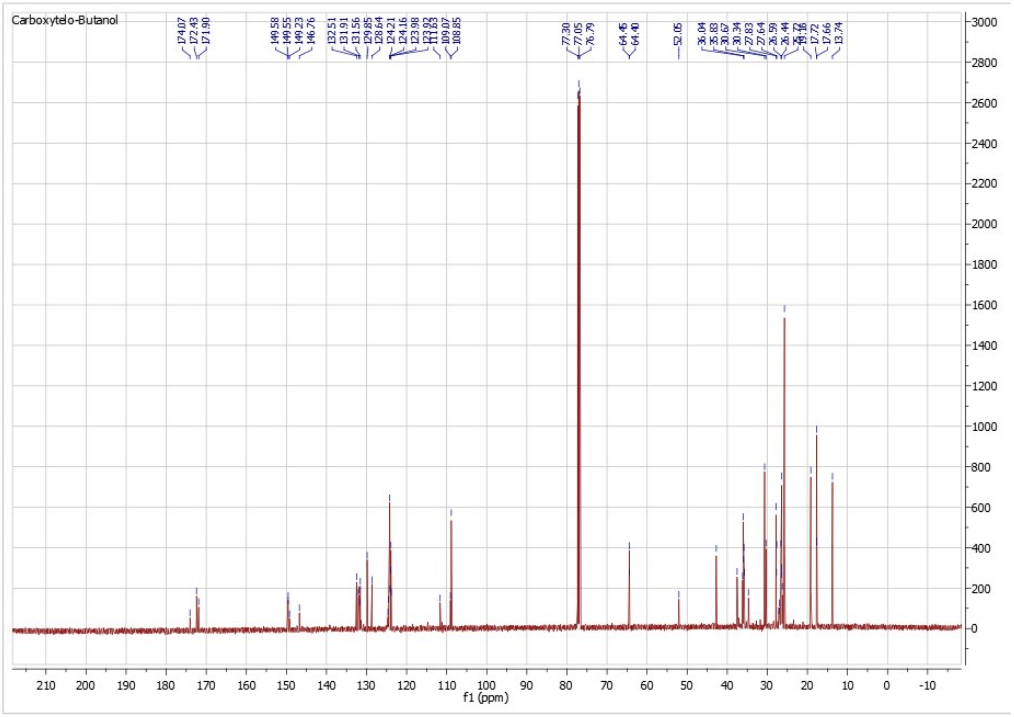


Figure S11: ^{13}C-NMR spectrum in d-$CDCl_3$ of Butyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – **3c**

5.1.5 Decyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – 3d

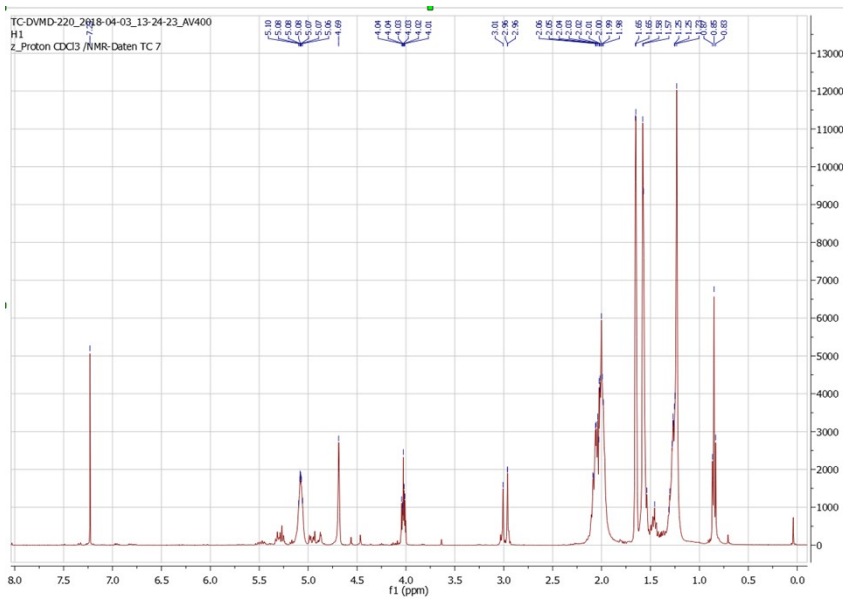


Figure S12: ^{1}H-NMR spectrum in d-$CDCl_3$ of Decyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – **3d**

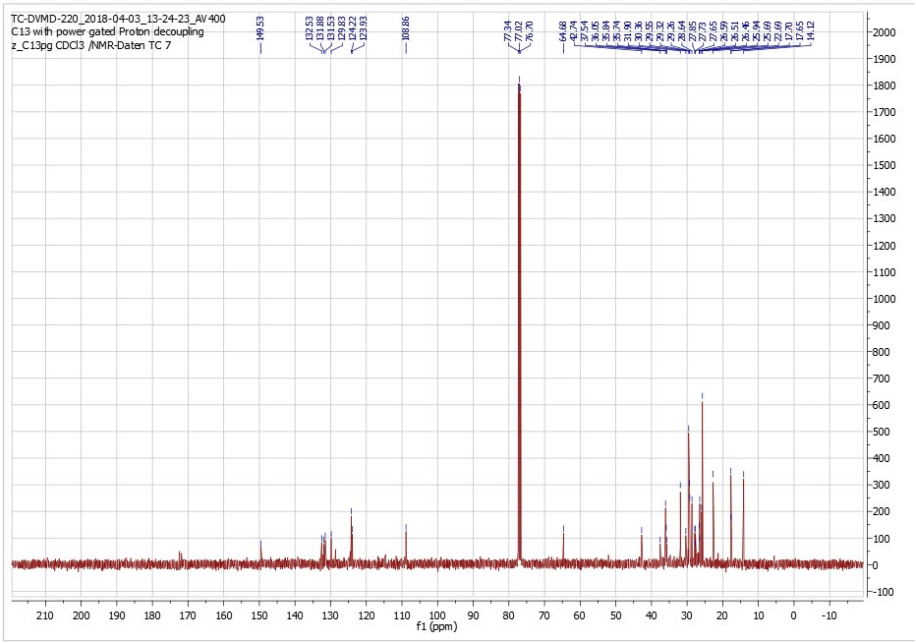


Figure S13: ^{13}C-NMR spectrum in d-$CDCl_3$ of Decyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – **3d**

5.1.6 Isopropyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – 3e

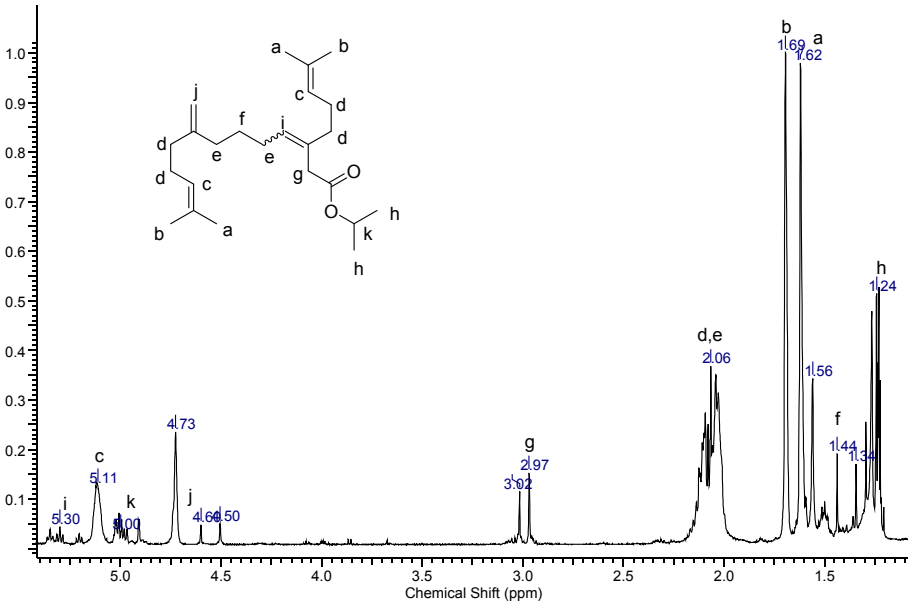


Figure S14: ^{1}H-NMR spectrum in d-$CDCl_3$ of Isopropyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – **3e**

5.1.7 Benzyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – 3g

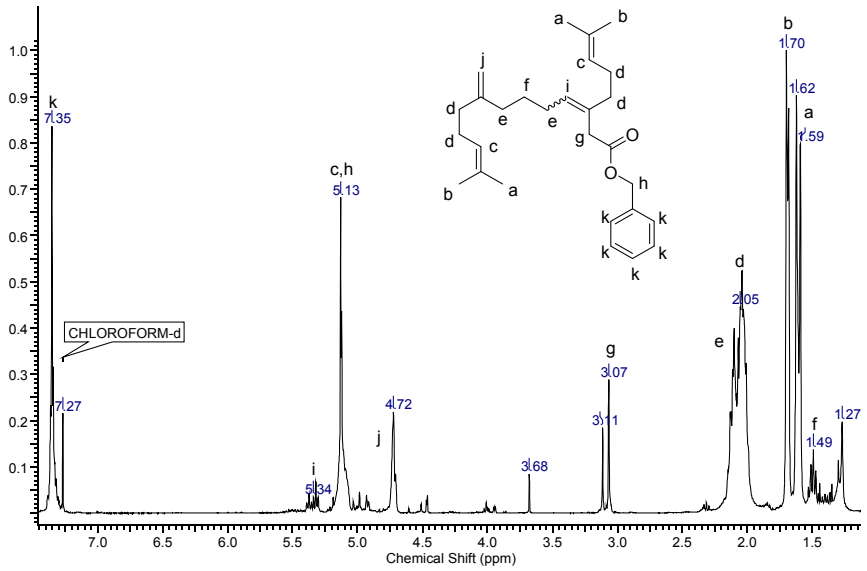


Figure S15: ^{1}H-NMR spectrum in d-$CDCl_3$ of Benzyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – **3g**

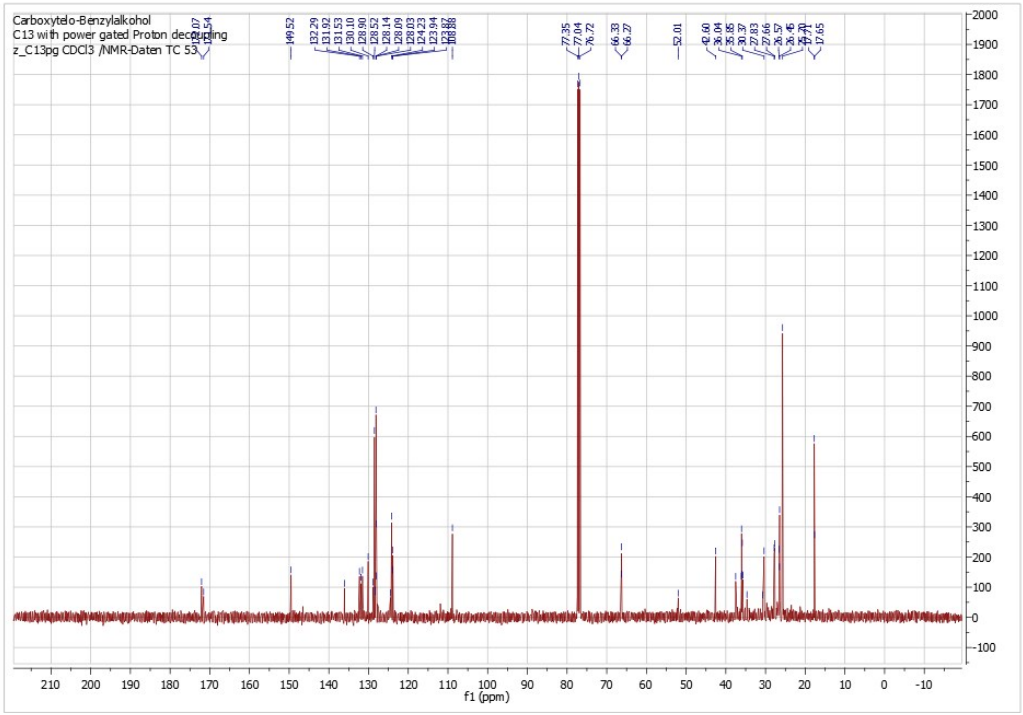


Figure S16: ^{13}C-NMR spectrum in d-$CDCl_3$ of Benzyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – **3g**

5.1.8 4-(tert-butyl)phenyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – 3h

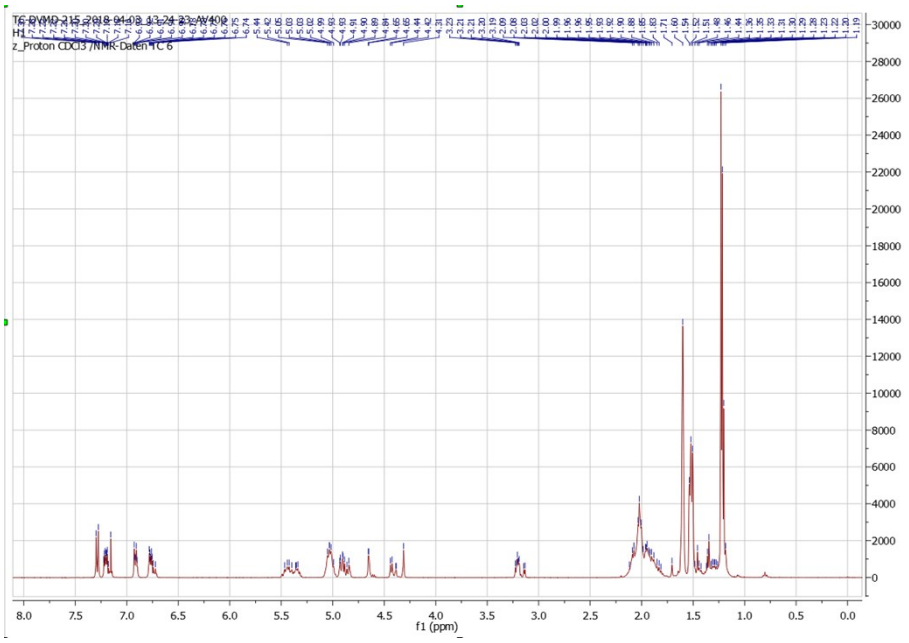


Figure S17: ^{1}H-NMR spectrum in d-$CDCl_3$ of 4-(tert-butyl)phenyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – **3h**

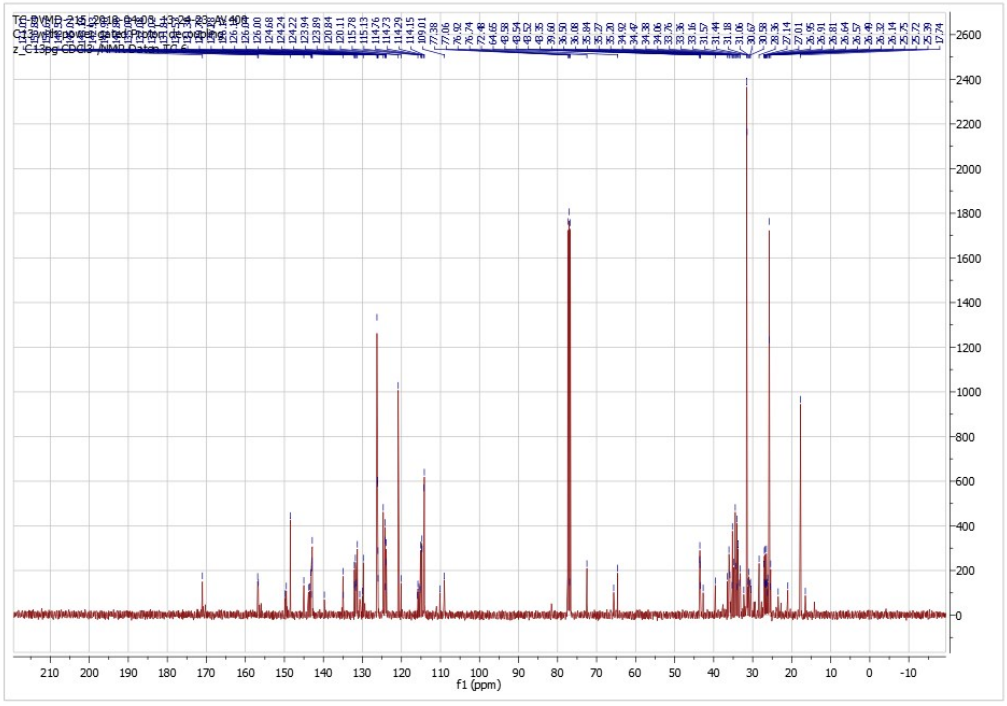


Figure S18: ^{13}C-NMR spectrum in d-$CDCl_3$ of 4-(tert-butyl)phenyl 12-methyl-8-methylene-3-(4-methylpent-3-en-1-yl)trideca-3,11-dienoate + isomers – **3h**