Supplementary Information

Catalyzed Chain Growth Polymerisation of Ethylene using lanthanidocenes/dialkylmagnesium: Further developments and one pot synthesis of narrow dispersed high molecular weight fatty alcohols

T. Chenal, M. Drelon, B. Marsh, F. F. Silva, M. Visseaux and A. Mortreux

Overview[1]

S1 Shapes of the reactors used in the study.

Pages 2 – 3

S2 Detailed results of each experiment presented in **Table 1**: CCG polymerisation of ethylene on various $Cp^RH/Nd(BH_4)_3(THF)_3/MgR_2$ (2/1/50), 1.1 bar ethylene.

Pages 4 – 22

S3 Detailed conditions and results of each experiment presented in **Table 2**: improvement of the reaction rate upon using different ether additives on the CCG of ethylene on butyl-ethyl-magnesium using $Cp^*_2NdCl_2Li(OEt_2)_2$ as catalytic precursor.

Pages 23 – 25

S4 Detailed conditions and results (GC, ^{13}C and ^1H NMR) of each experiment presented in **Tables 3** and **4**: one pot synthesis of narrow dispersed high molecular weight fatty alcohols.

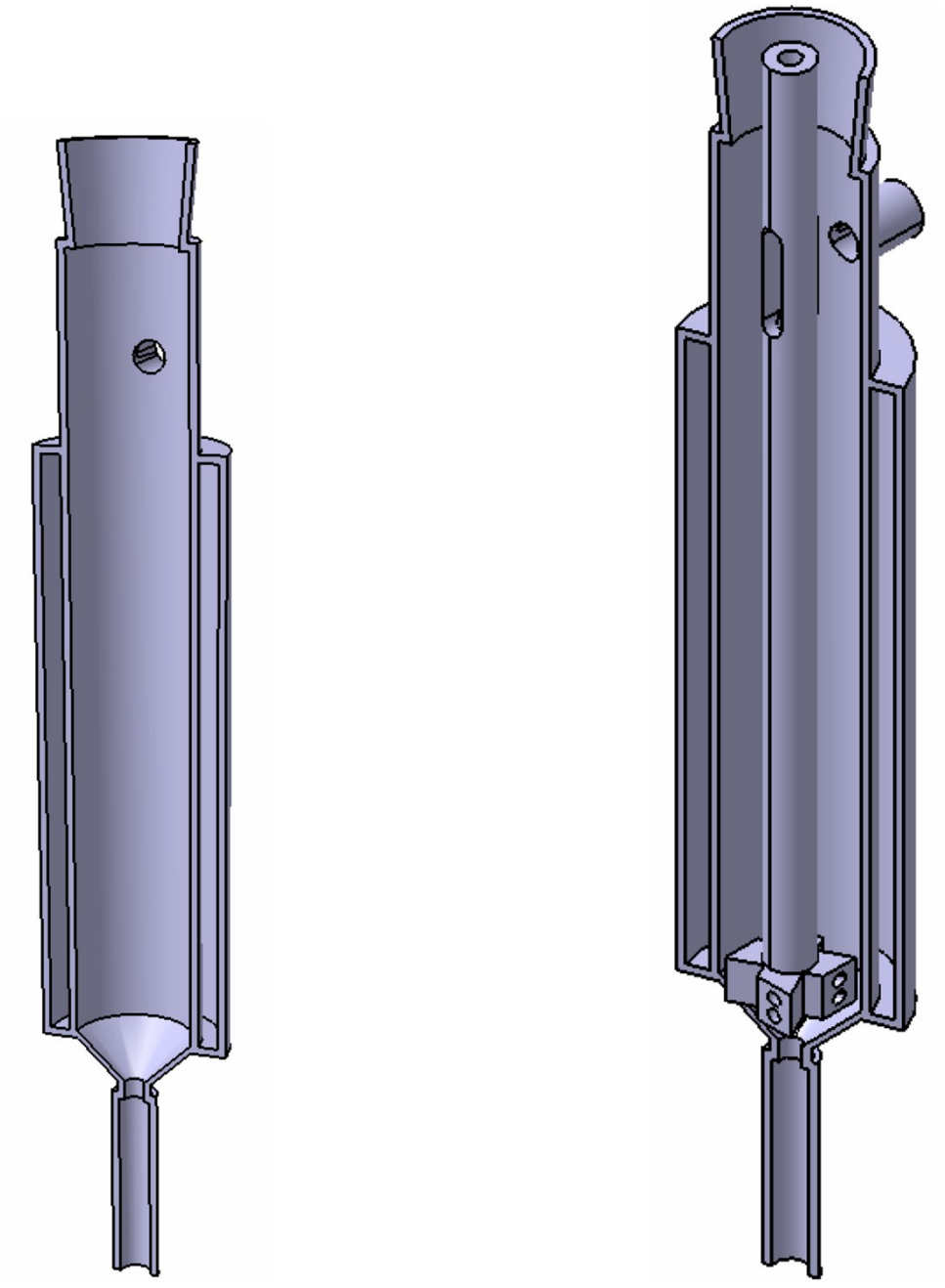
Pages 26 – 68

S5 GC-MS and IR analyses for aldehyde determination in fatty alcohols.

Pages 69 – 77

[1] The reader must be aware that all experiments are not systematically duplicated due to the fact that their implementation requires significant preparation. Nevertheless, the validity of the results is considered to be correct insofar as experiments carried out with structurally similar ligands give similar (and thus reproducible) results (entries 1-3, Table 1 for example). In general, the large number of experiments carried out and the overall consistency of the results is to some extent a guarantee of the reliability of the experimental procedure used.

S1 Shapes of the reactors used in the study.



Cut view of naked glass main part

With stainless steel stirring impeller

Figure S1-1 Shape drawing of the small reactor (20 mL) homemade by the glass blower of the laboratory.

Scale: Inner diameter is 30 mm, stirring blade is 25 mm diameter and 10 mm height.

S1 continuing

Figure S1-2 Shape photography of the batch reactor (total volume 600 mL) purchased from the Parr Company

Scale: Inner diameter is 50 mm, stirring blade is 27 mm diameter and 13 mm height.

S2 Results details of experiments in **Table 1**: CCG polymerisation of ethylene on various $Cp^RH/Nd(BH_4)_3(THF)_3/MgR_2$ (2/1/50), 1.1 bar ethylene, small reactor.

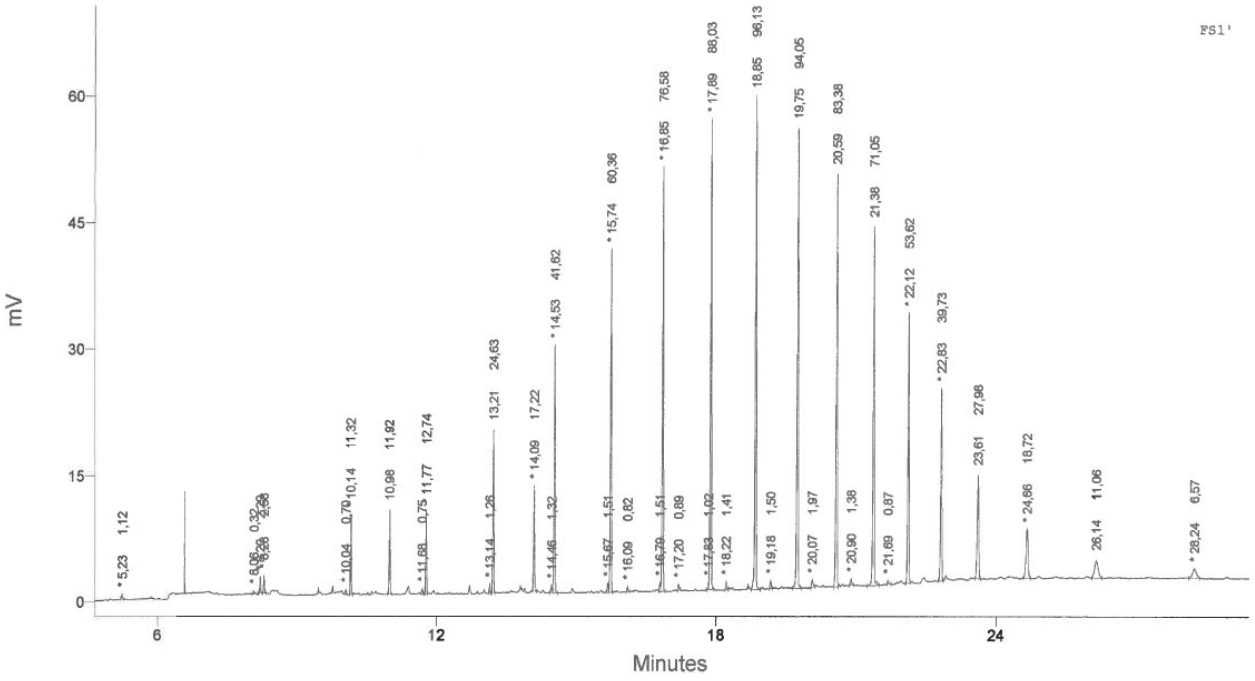


Figure S2-1a Raw signal Gas Chromatography analysis Entry 1 Table 1.

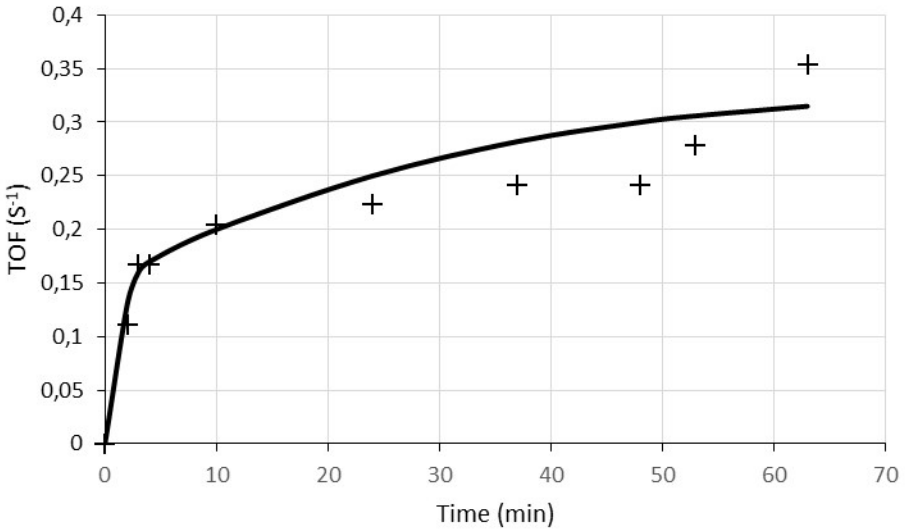


Figure S2-1b Kinetic measurement of ethylene consumption Entry 1 Table 1.

S2 continuing

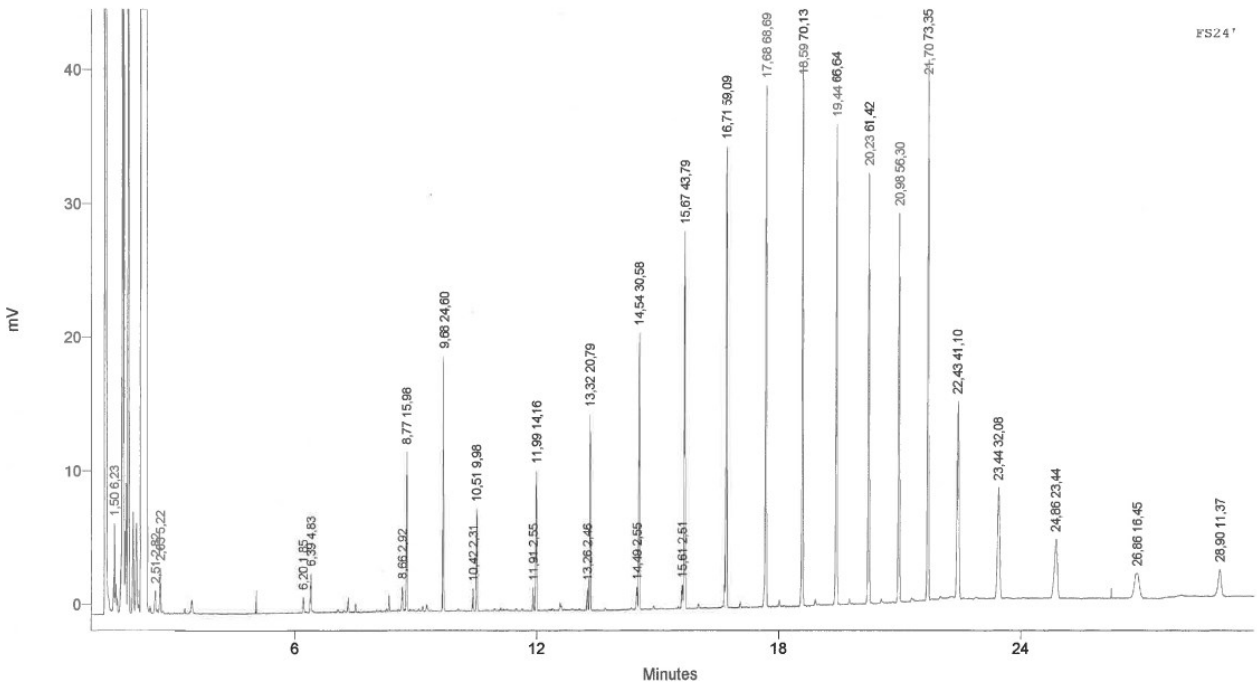


Figure S2-2a Raw signal Gas Chromatography analysis Entry 2 Table 1.

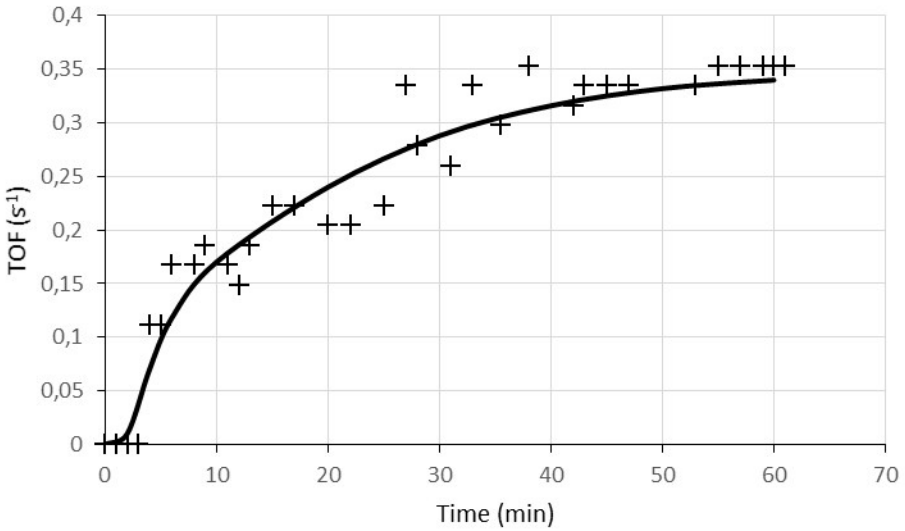


Figure S2-2b Kinetic measurement of ethylene consumption Entry 2 Table 1.

S2 continuing

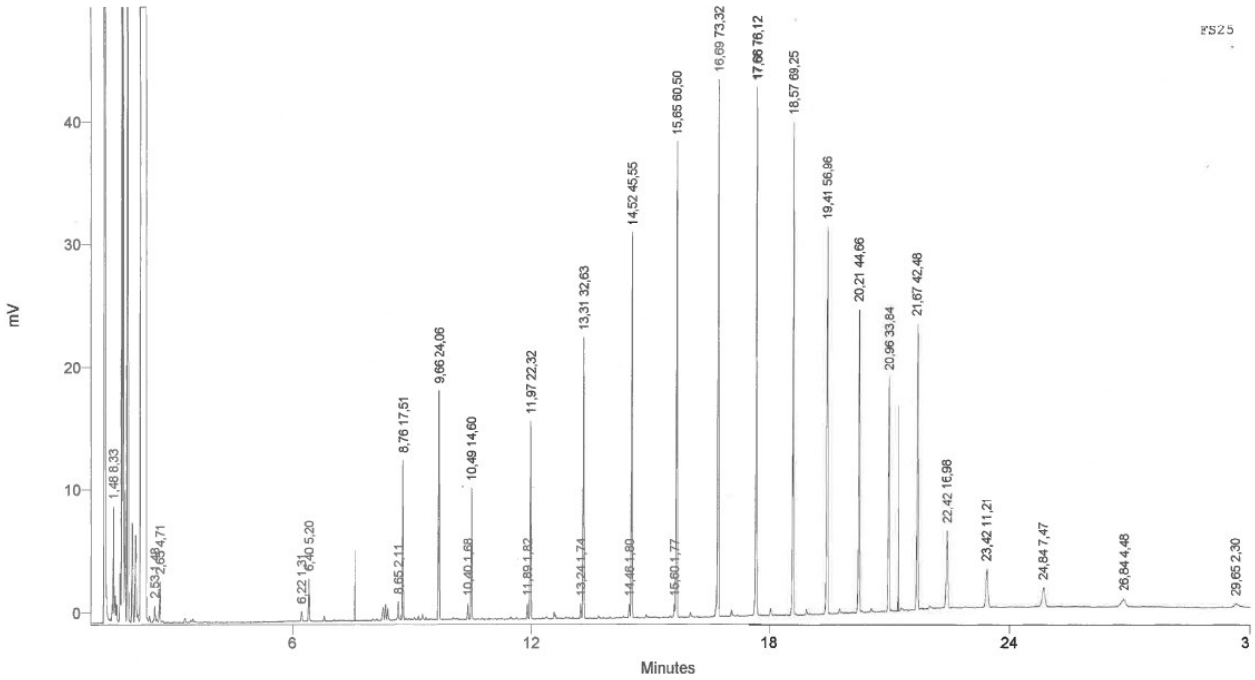


Figure S2-3a Raw signal Gas Chromatography analysis Entry 3 Table 1.

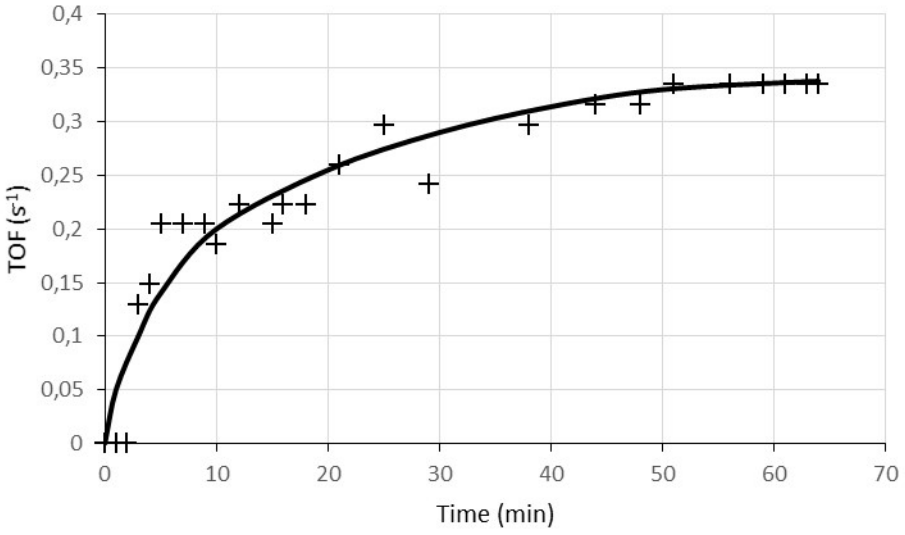


Figure S2-3b Kinetic measurement of ethylene consumption Entry 3 Table 1.

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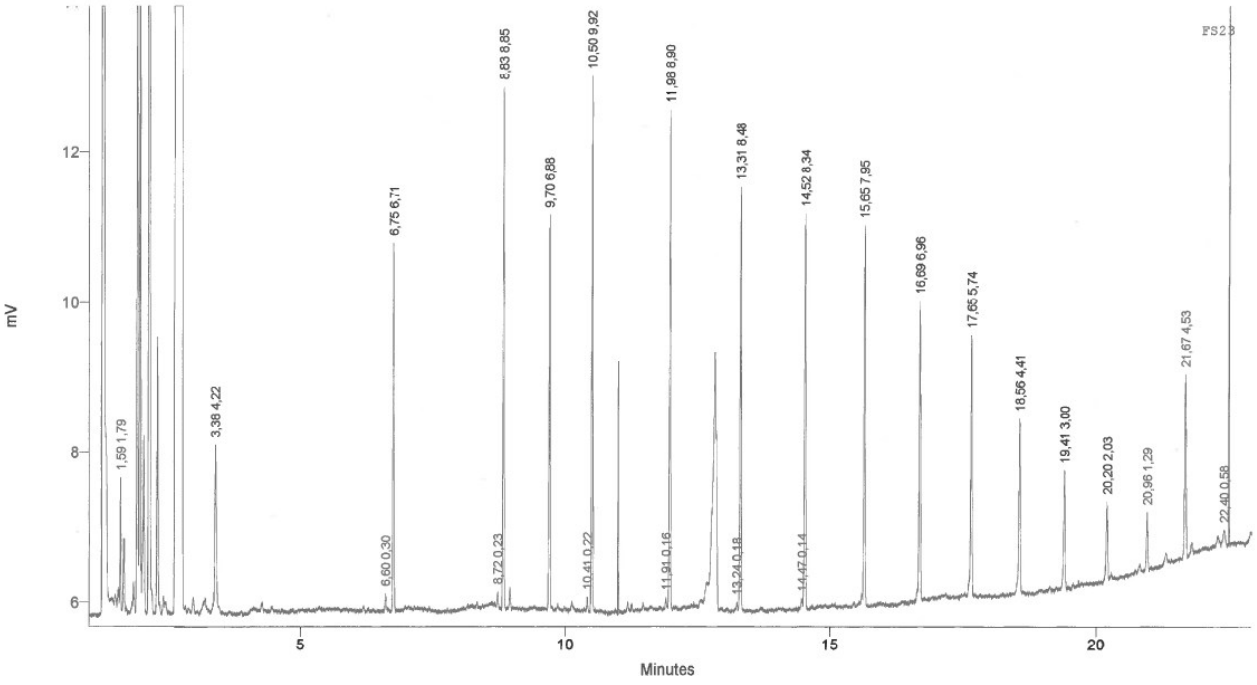


Figure S2-4a Raw signal Gas Chromatography analysis Entry 4 Table 1.

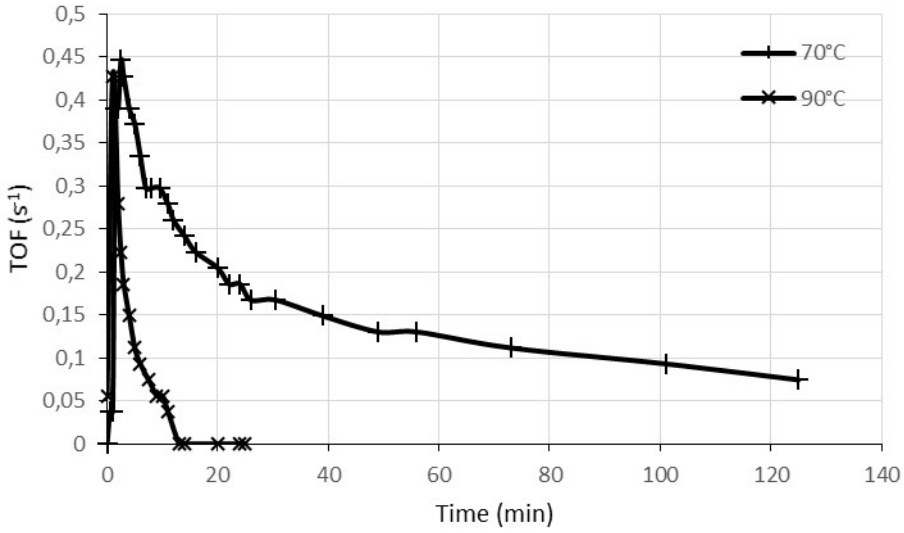


Figure S2-4b Kinetic measurement of ethylene consumption Entry 4 Table 1.

S2 continuing

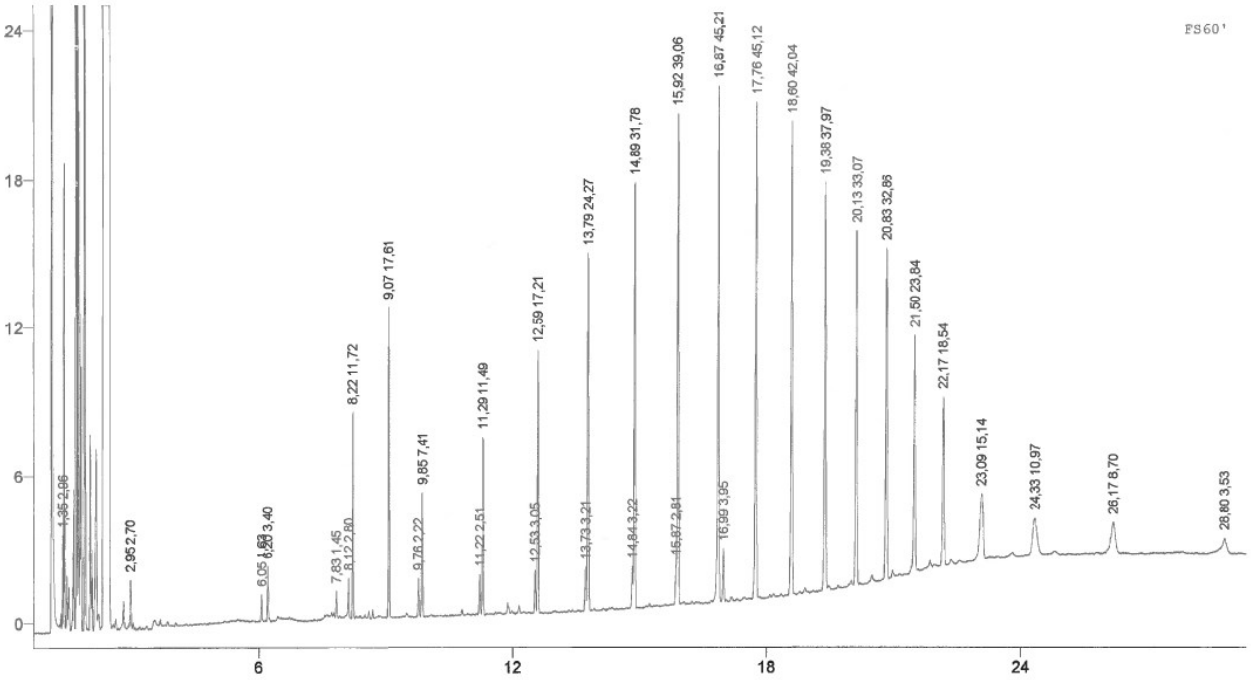


Figure S2-5a Raw signal Gas Chromatography analysis Entry 5 Table 1.

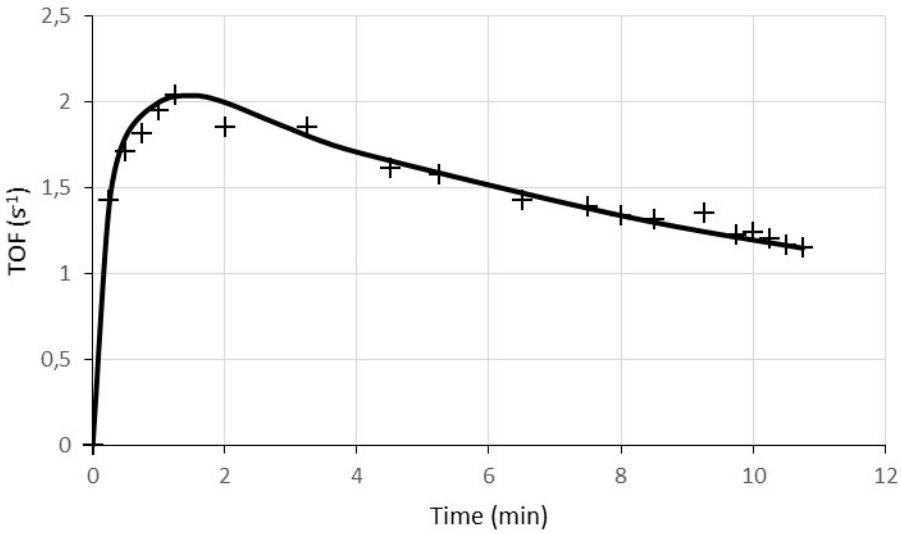


Figure S2-5b Kinetic measurement of ethylene consumption Entry 5 Table 1.

S2 continuing

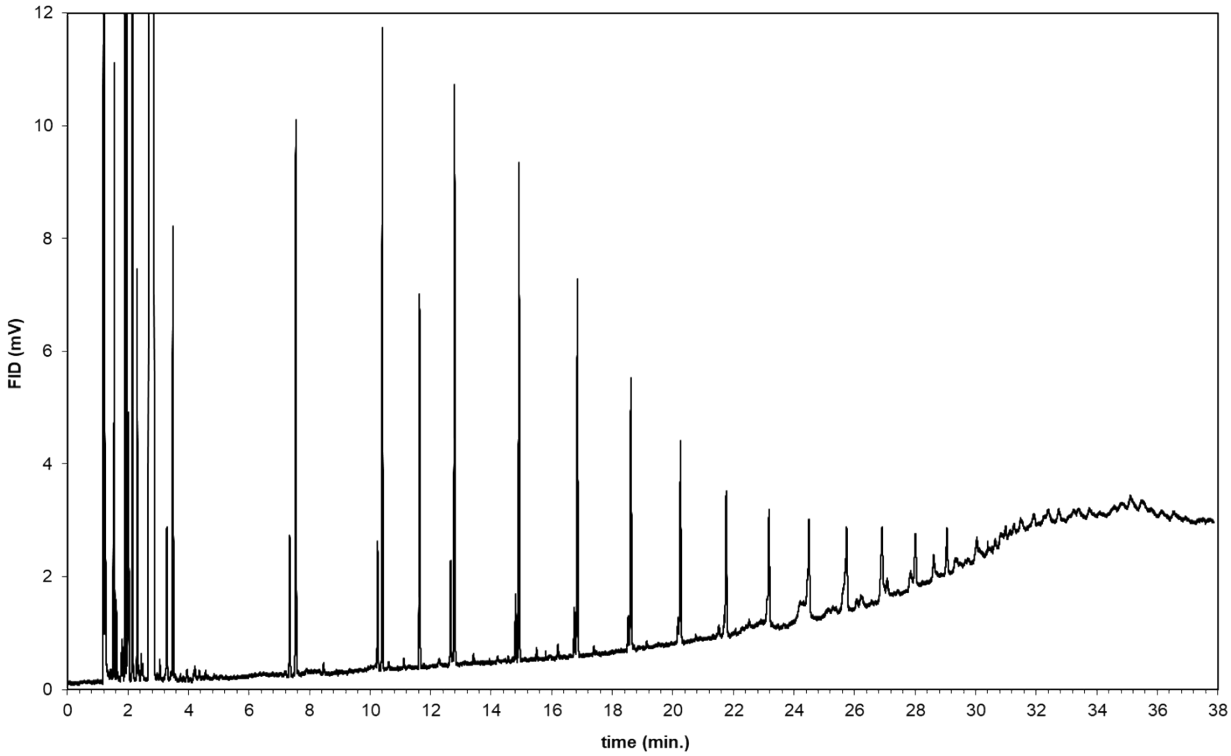


Figure S2-6a Raw signal Gas Chromatography analysis Entry 6 Table 1.

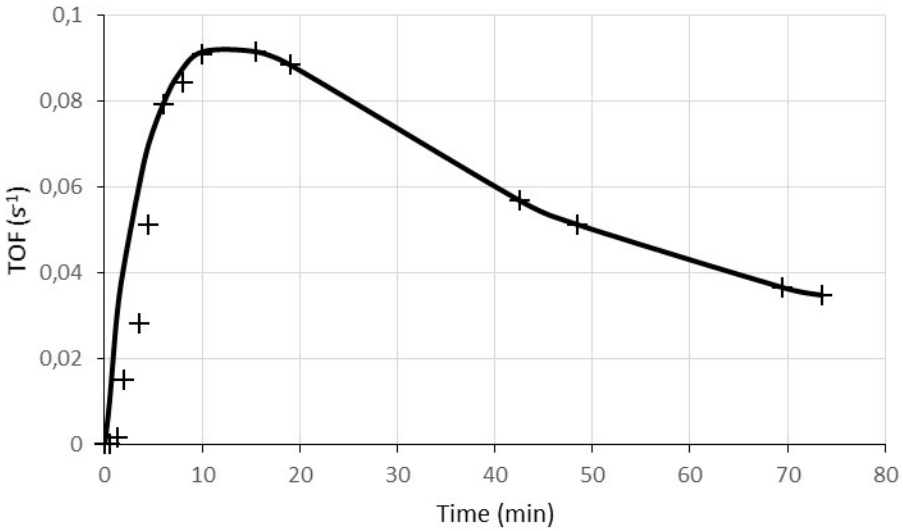


Figure S2-6b Kinetic measurement of ethylene consumption Entry 6 Table 1.

S2 continuing

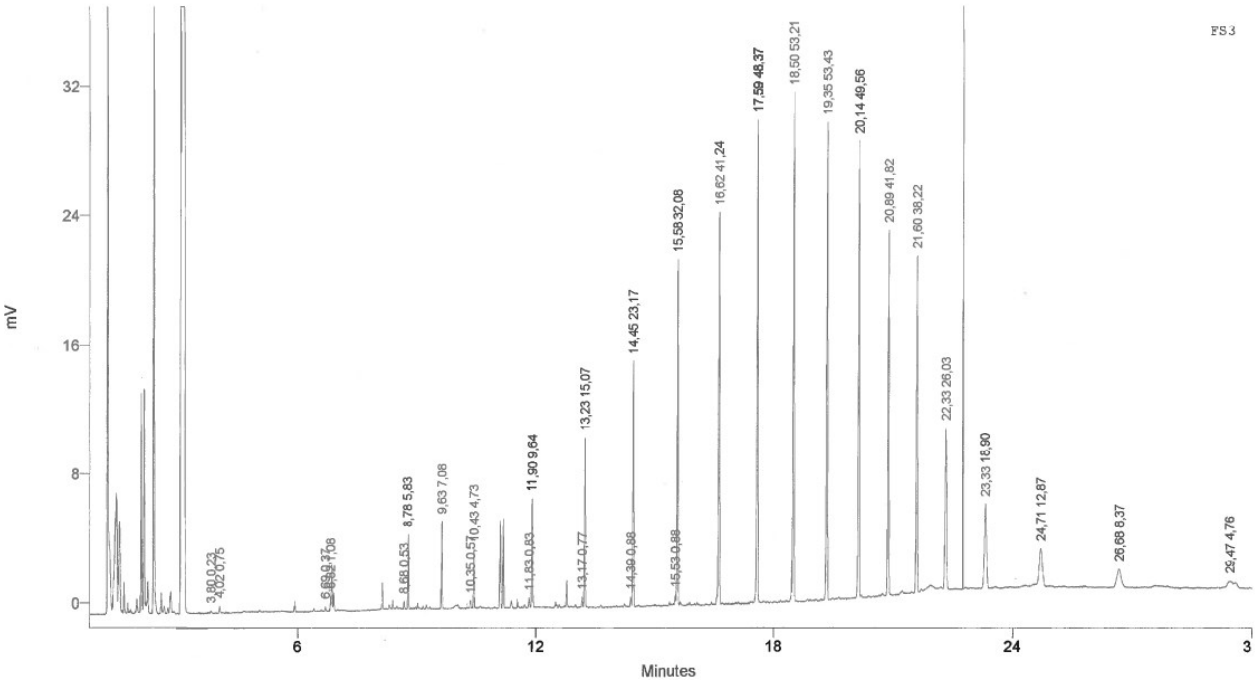


Figure S2-7a Raw signal Gas Chromatography analysis Entry 7 Table 1.

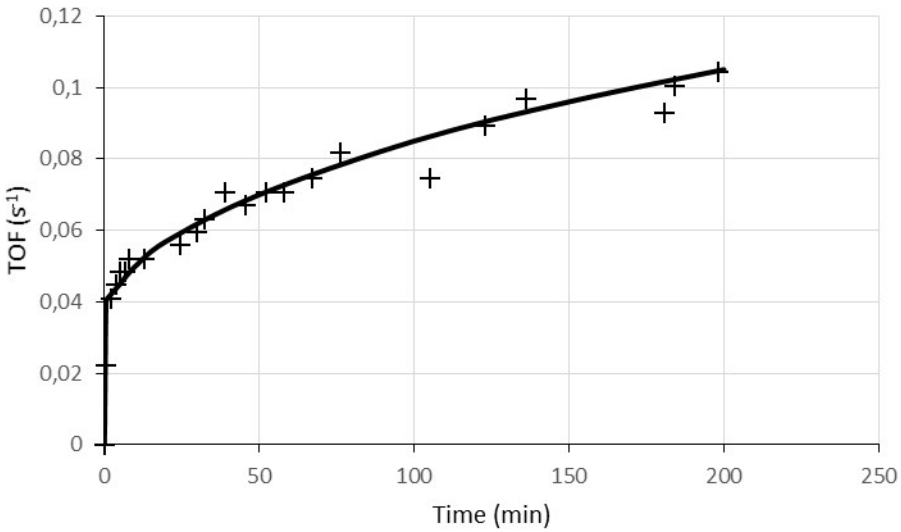


Figure S2-7b Kinetic measurement of ethylene consumption Entry 7 Table 1.

S2 continuing

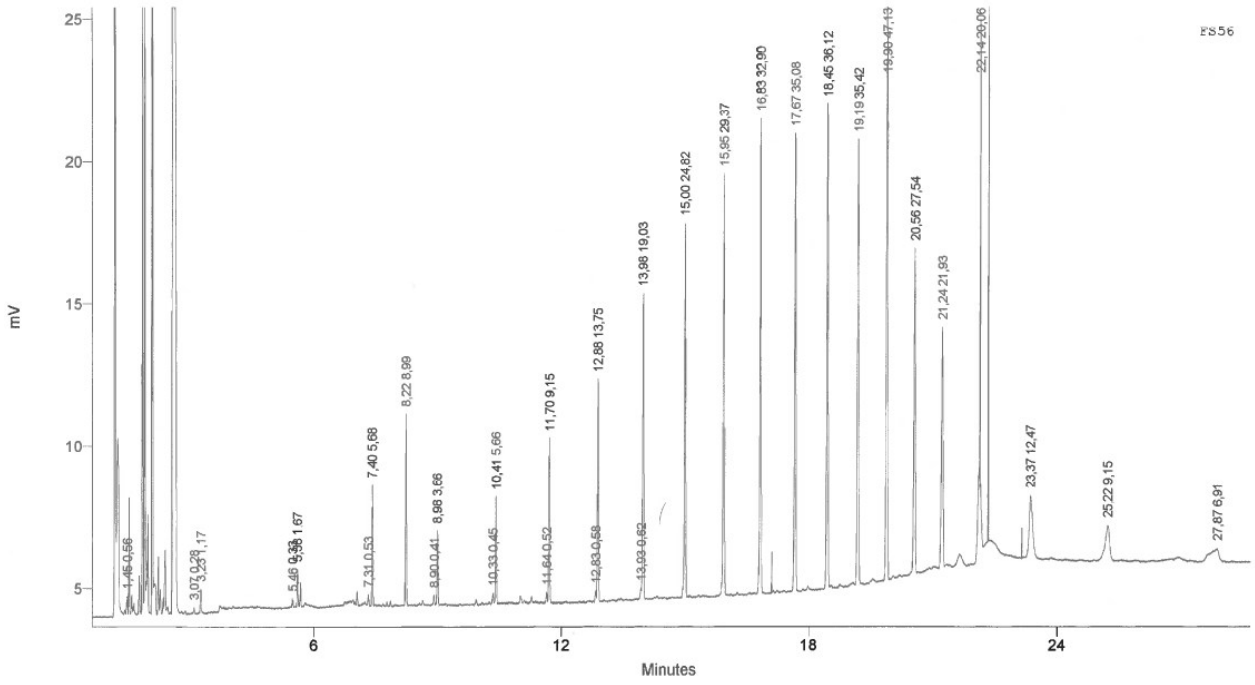


Figure S2-8a Raw signal Gas Chromatography analysis Entry 8 Table 1.

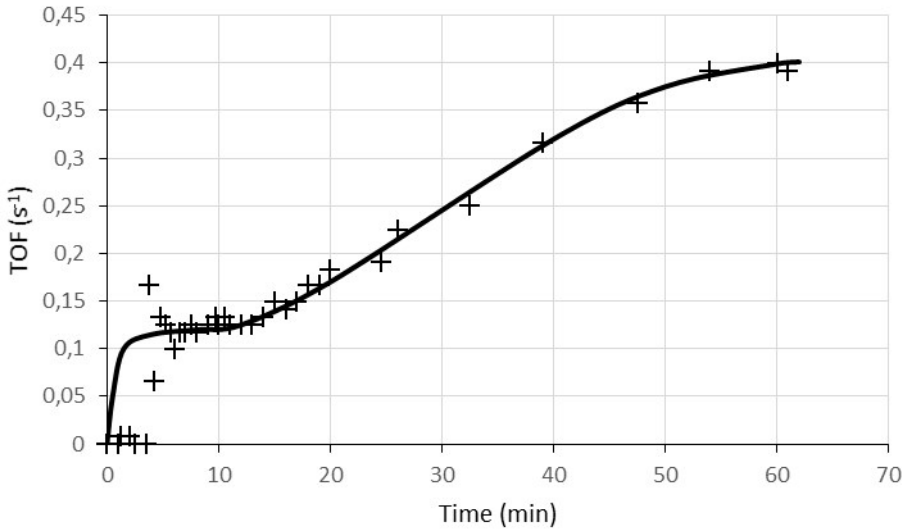


Figure S2-8b Kinetic measurement of ethylene consumption Entry 8 Table 1.

S2 continuing

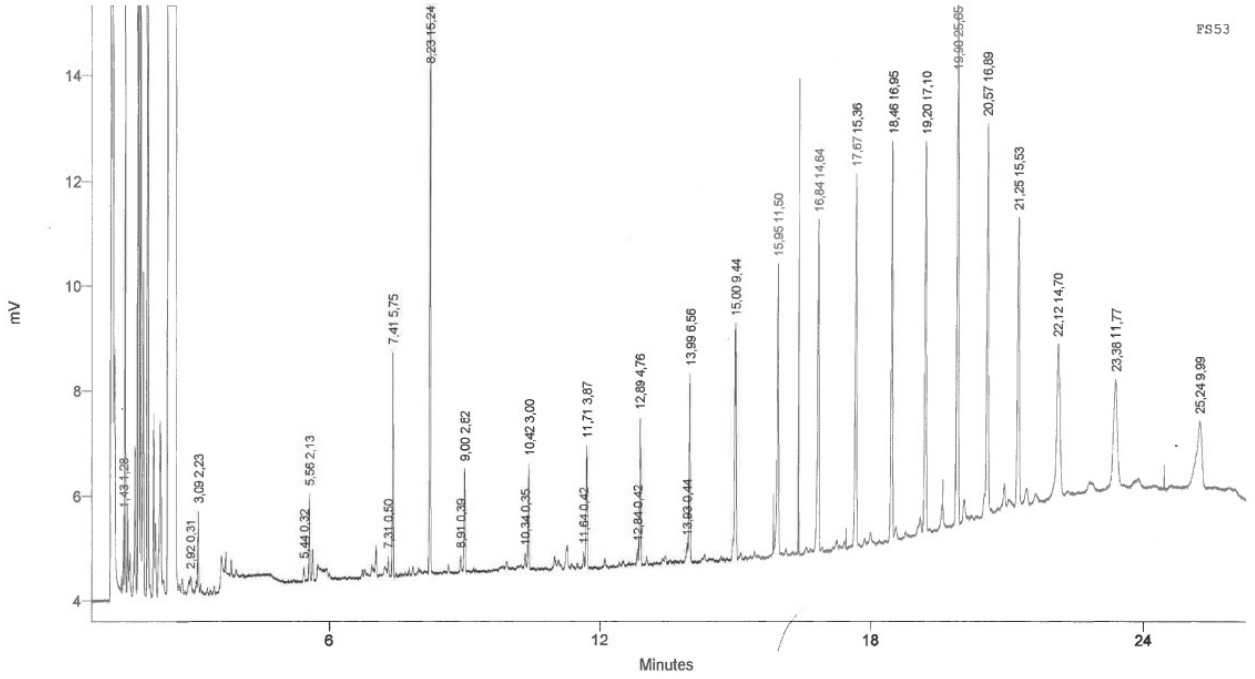


Figure S2-9a Raw signal Gas Chromatography analysis Entry 9 Table 1.

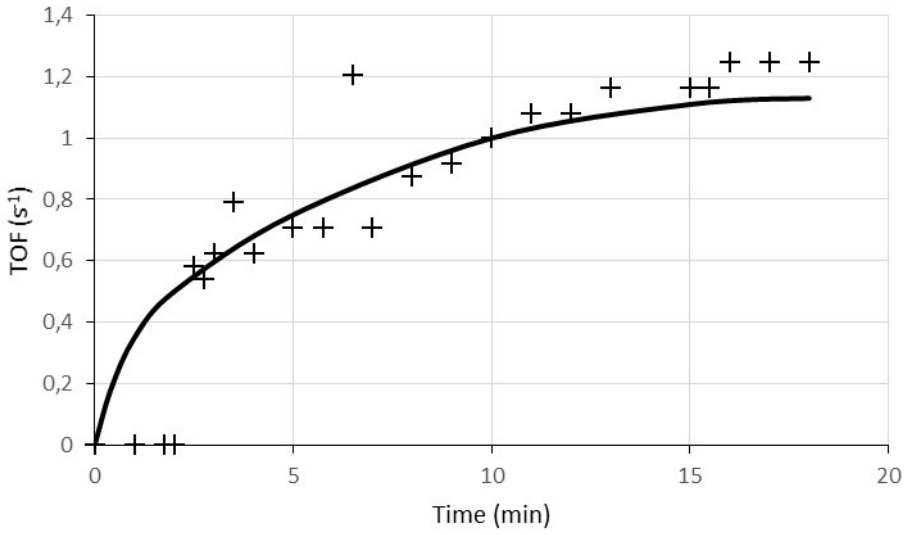


Figure S2-9b Kinetic measurement of ethylene consumption Entry 9 Table 1.

S2 continuing

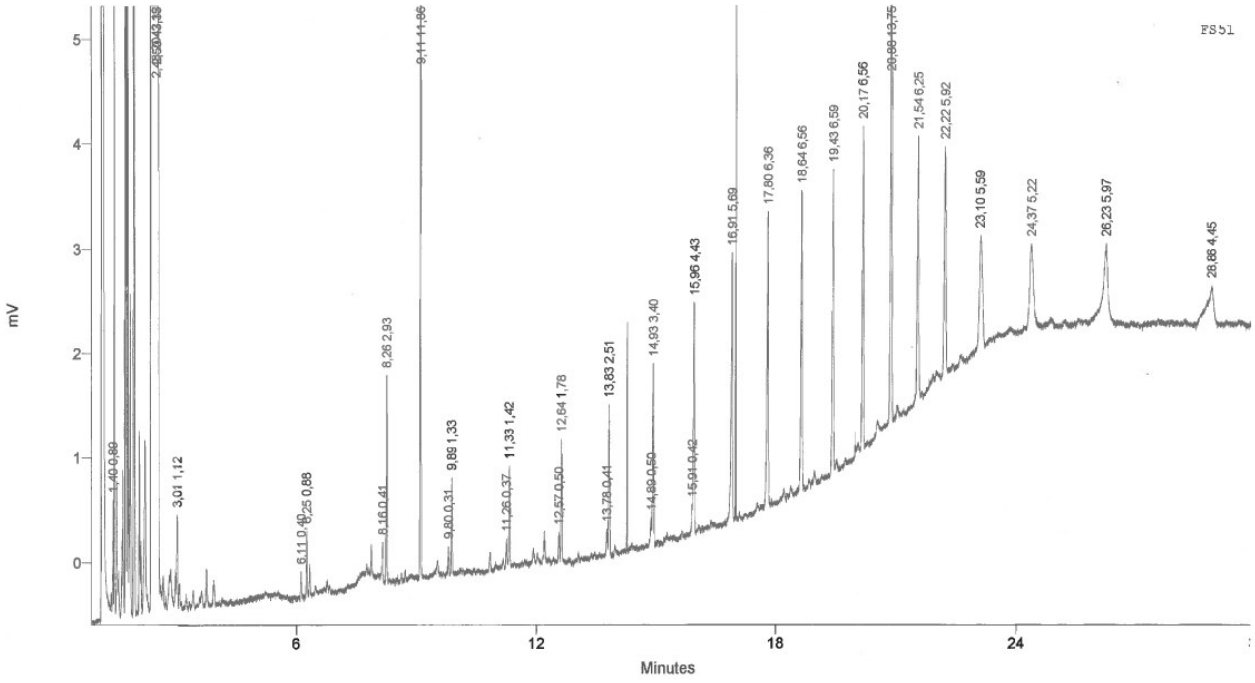


Figure S2-10a Raw signal Gas Chromatography analysis Entry 10 Table 1.

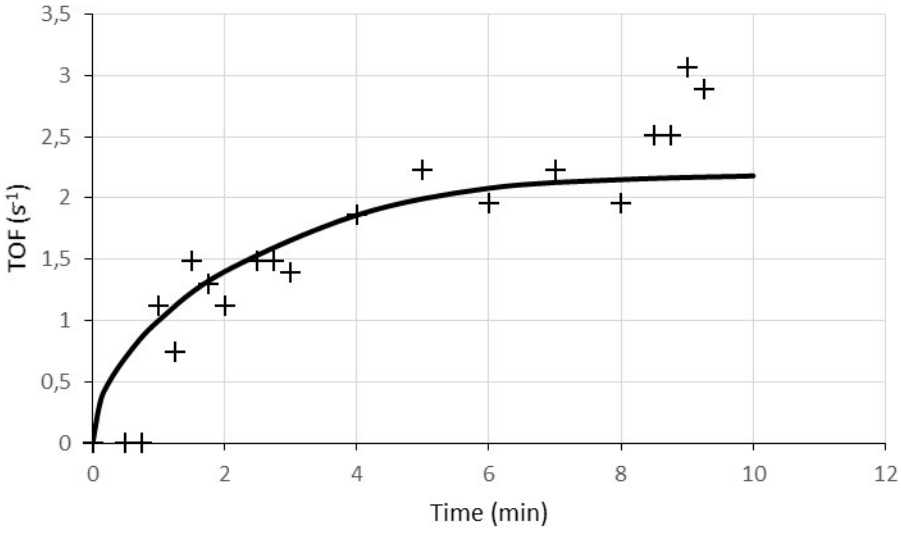


Figure S2-10b Kinetic measurement of ethylene consumption Entry 10 Table 1.

S2 continuing

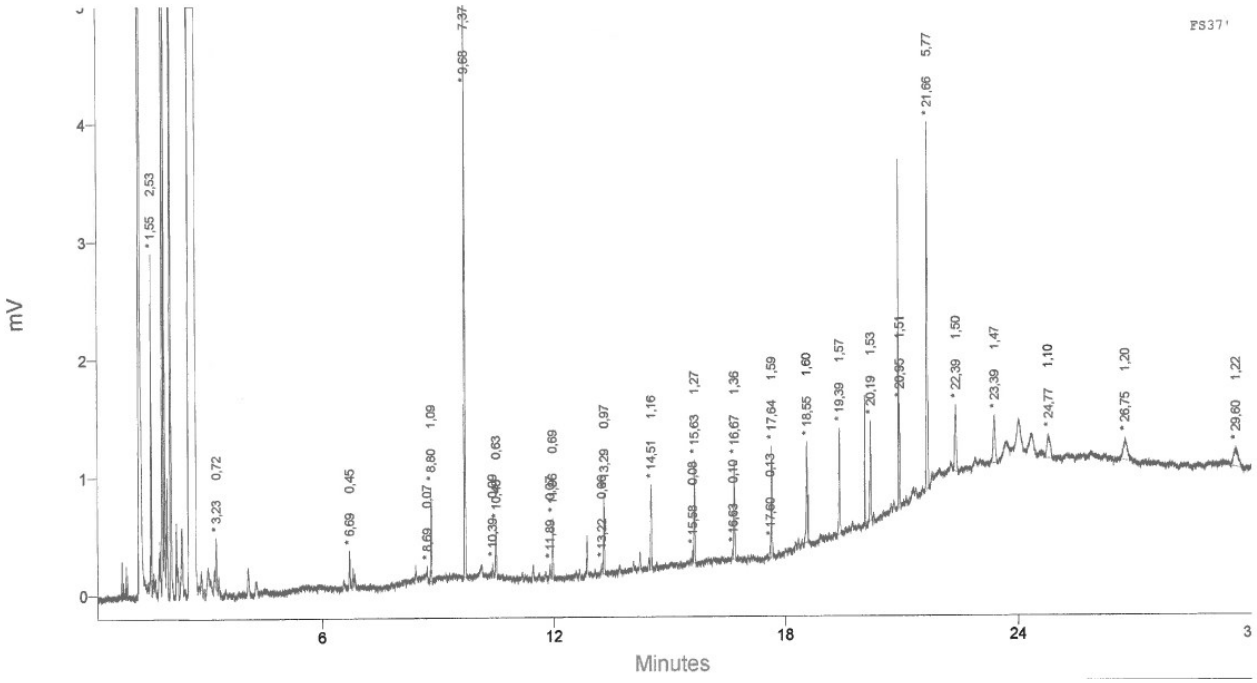


Figure S2-11a Raw signal Gas Chromatography analysis Entry 11 Table 1.

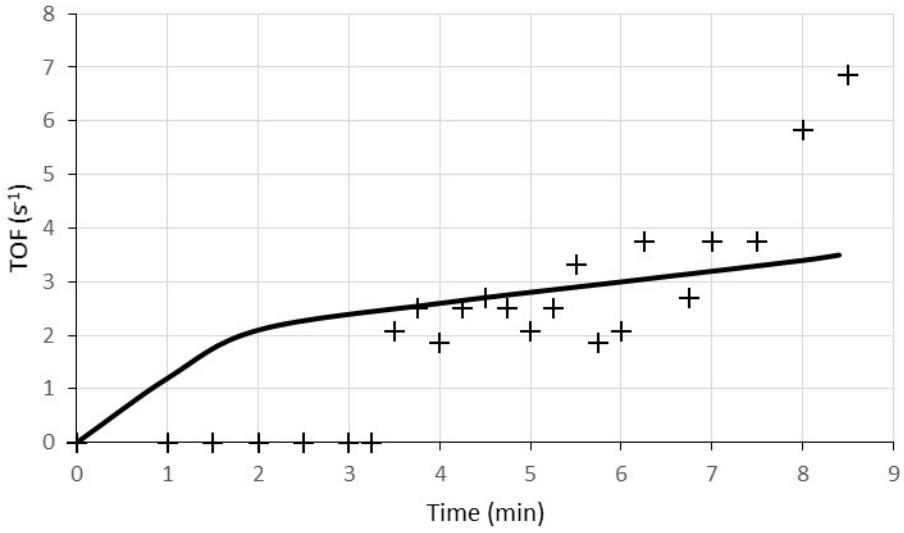


Figure S2-11b Kinetic measurement of ethylene consumption Entry 11 Table 1.

S2 continuing

Too low amounts of polymer

Figure S2-12a Raw signal Gas Chromatography analysis Entry 12 Table 1.

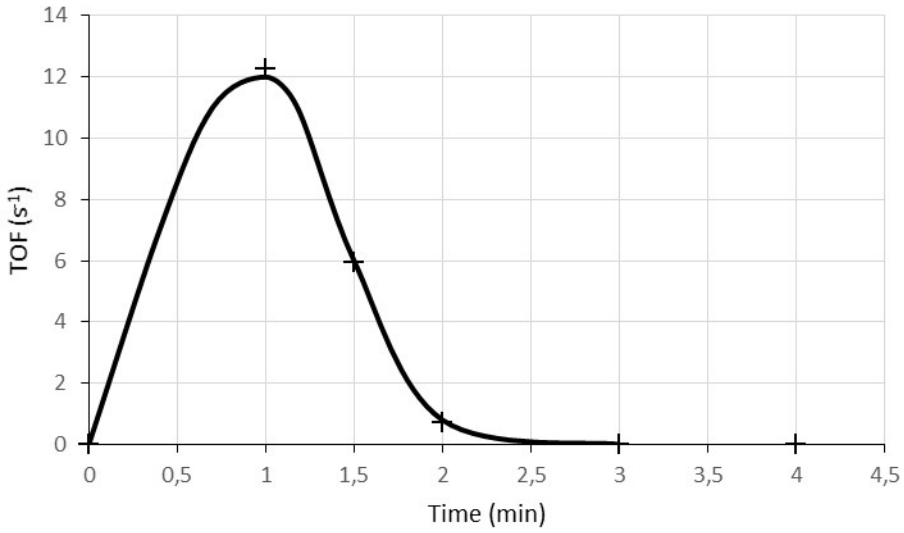


Figure S2-12b Kinetic measurement of ethylene consumption Entry 12 Table 1.

S2 continuing

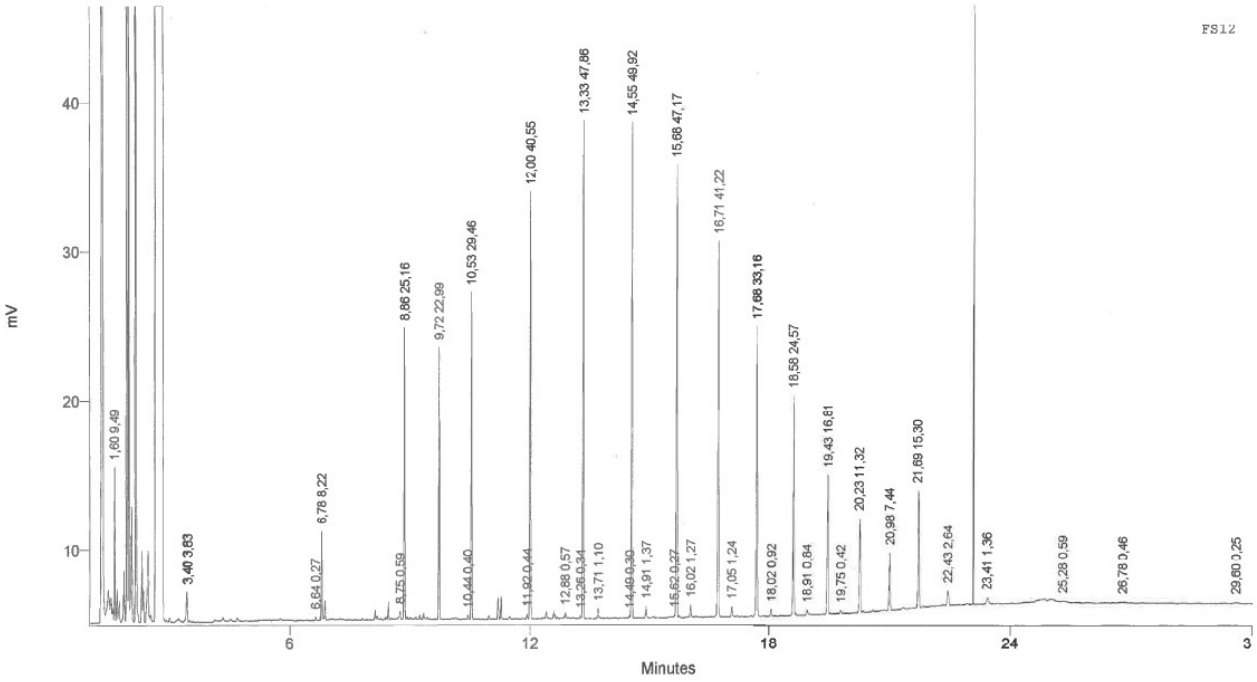


Figure S2-13a Raw signal Gas Chromatography analysis Entry 13 Table 1.

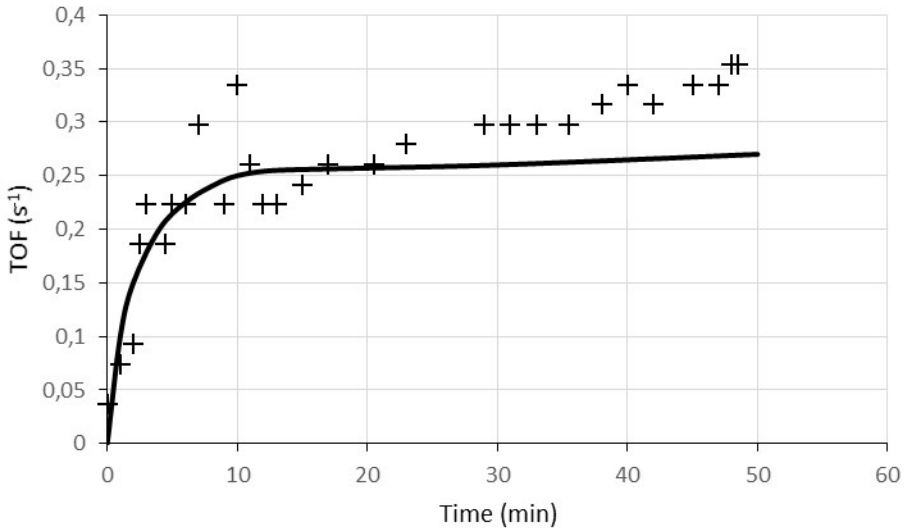


Figure S2-13b Kinetic measurement of ethylene consumption Entry 13 Table 1.

S2 continuing

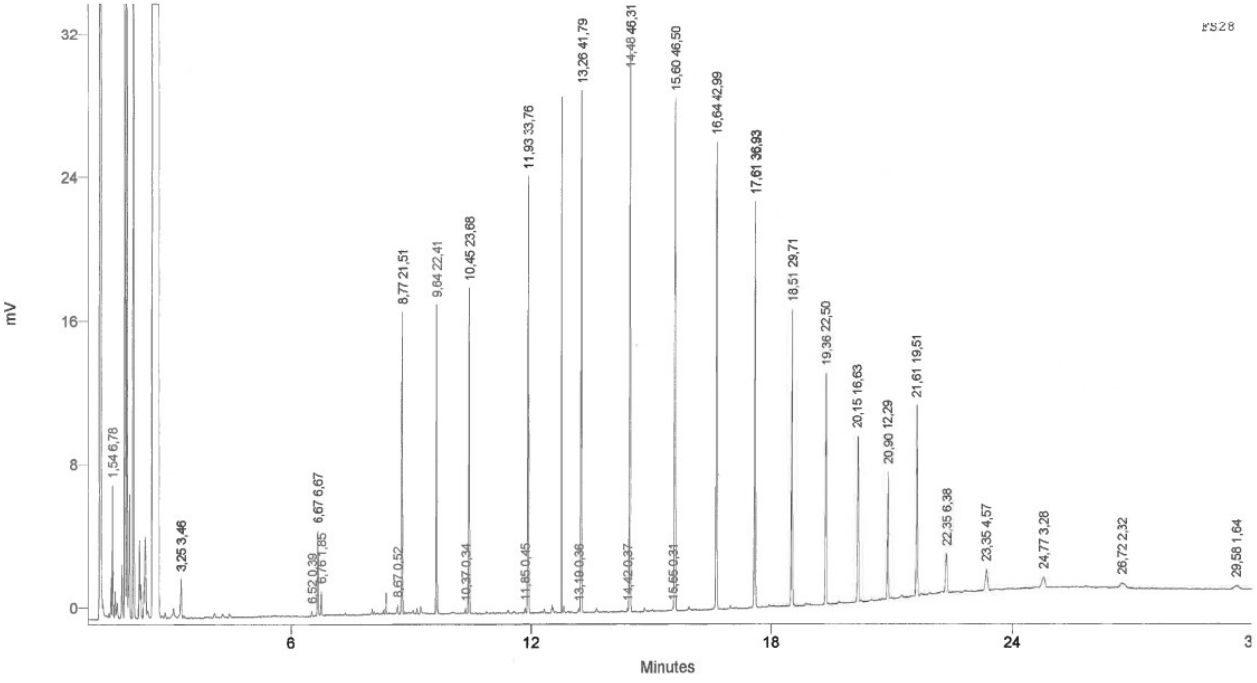


Figure S2-14a Raw signal Gas Chromatography analysis Entry 14 Table 1.

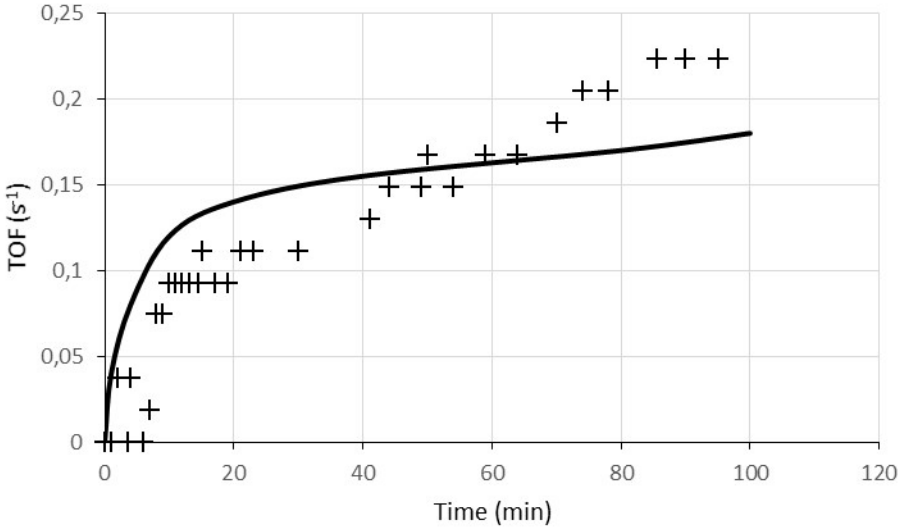


Figure S2-14b Kinetic measurement of ethylene consumption Entry 14 Table 1.

S2 continuing

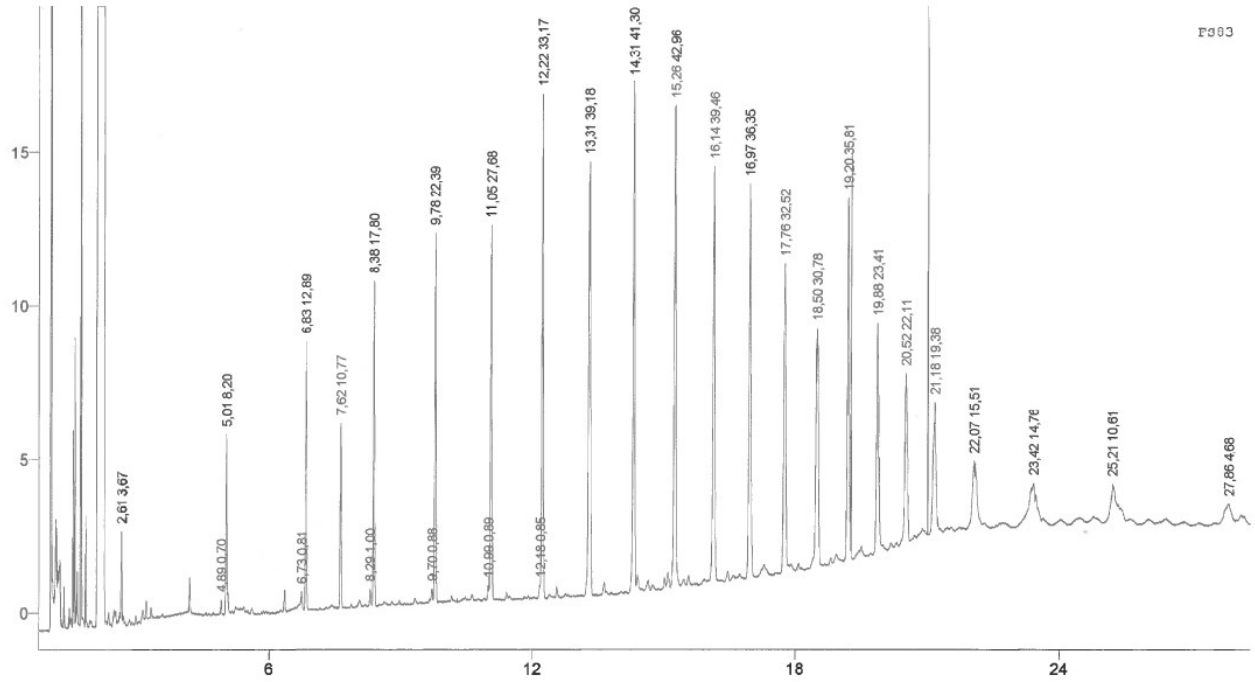


Figure S2-15a Raw signal Gas Chromatography analysis Entry 15 Table 1.

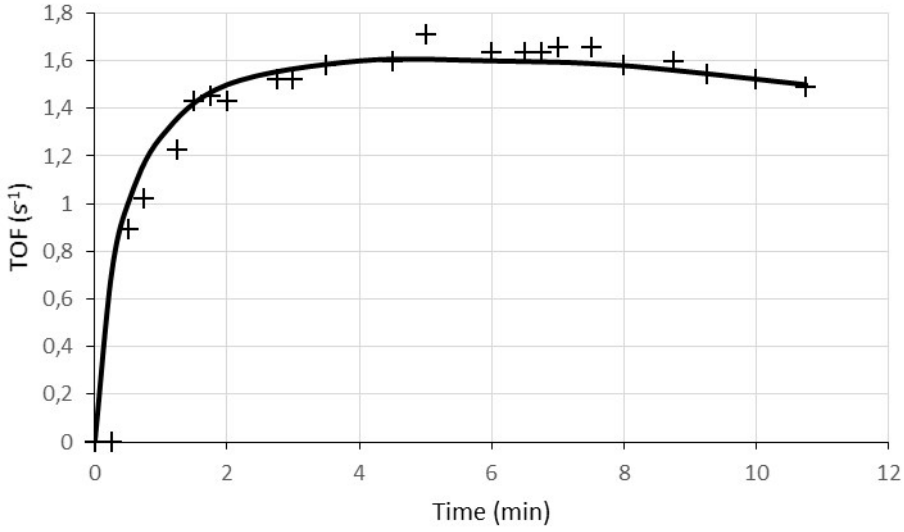


Figure S2-15b Kinetic measurement of ethylene consumption Entry 15 Table 1.

S2 continuing

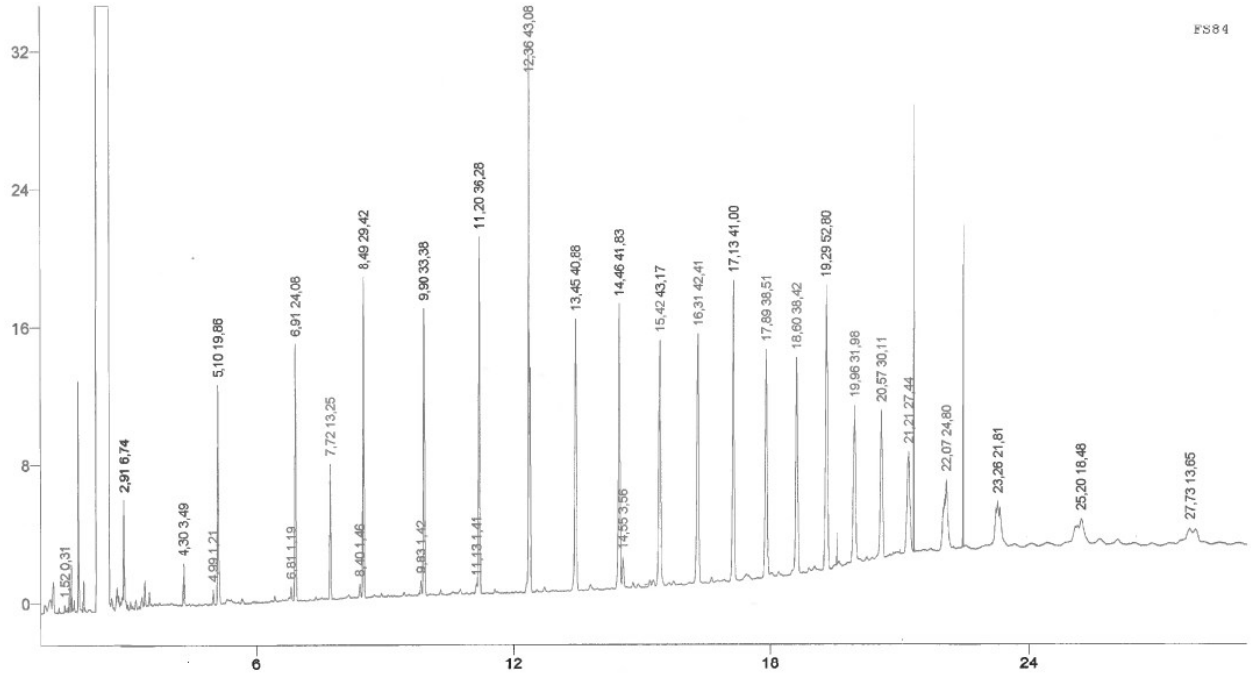


Figure S2-16a Raw signal Gas Chromatography analysis Entry 16 Table 1.

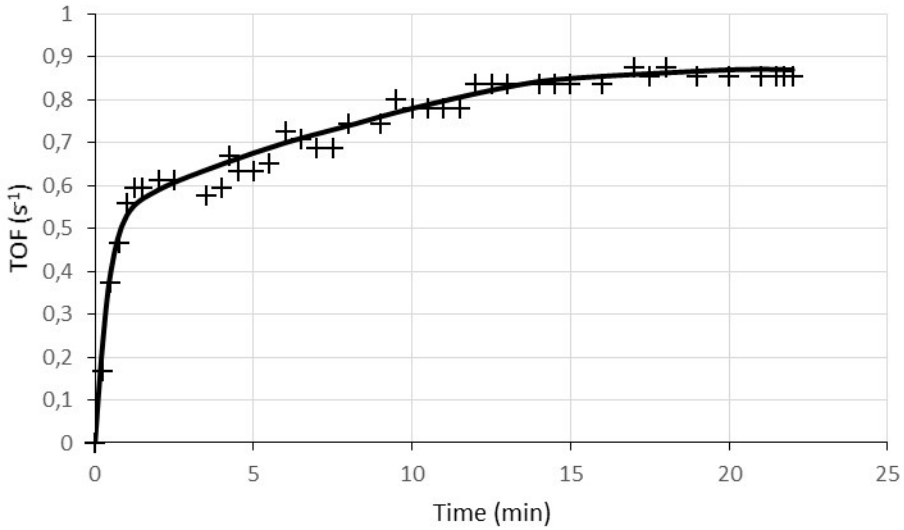


Figure S2-16b Kinetic measurement of ethylene consumption Entry 16 Table 1.

S2 continuing

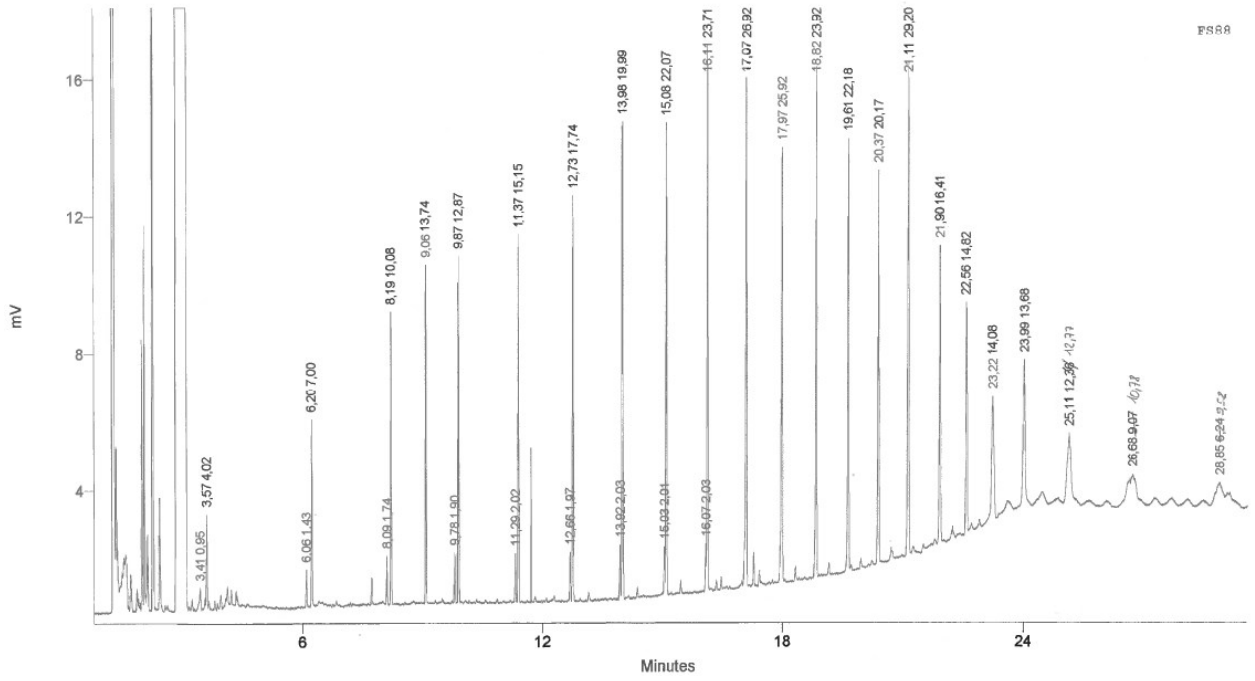


Figure S2-17a Raw signal Gas Chromatography analysis Entry 17 Table 1.

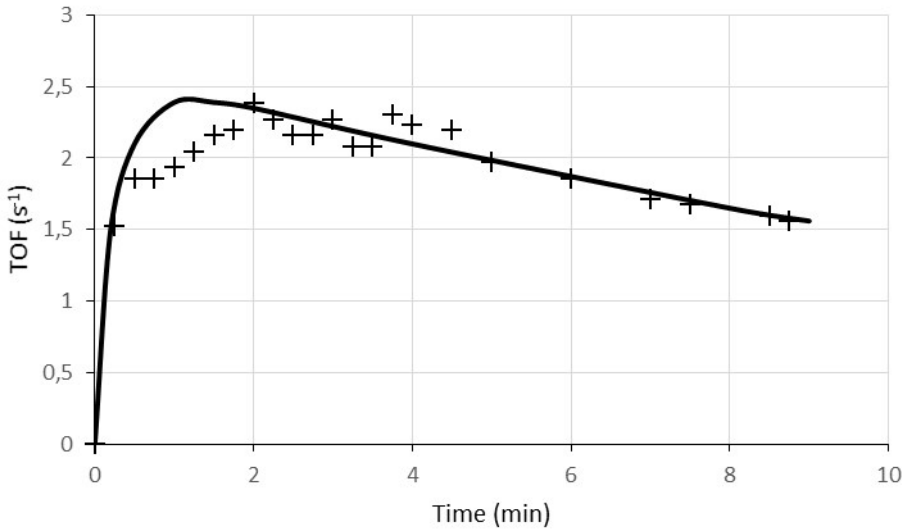


Figure S2-17b Kinetic measurement of ethylene consumption Entry 17 Table 1.

S2 continuing

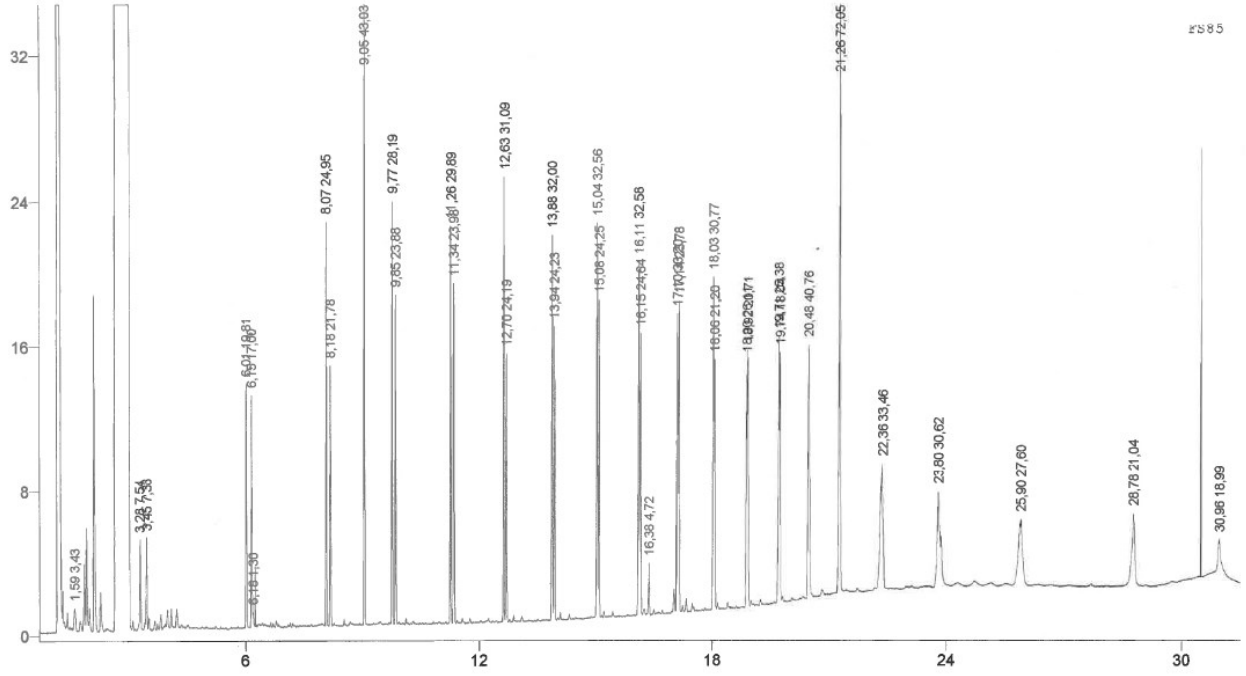


Figure S2-18a Raw signal Gas Chromatography analysis Entry 18 Table 1.

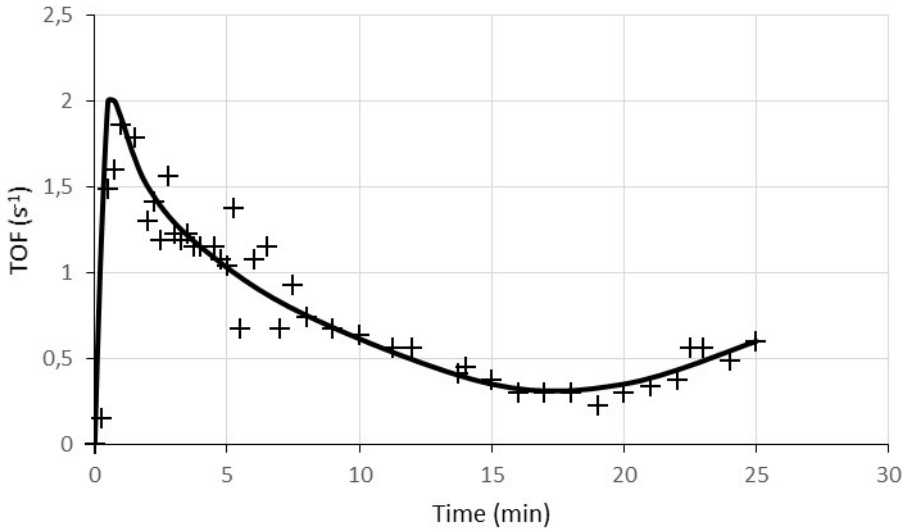


Figure S2-18b Kinetic measurement of ethylene consumption Entry 18 Table 1.

S2 continuing

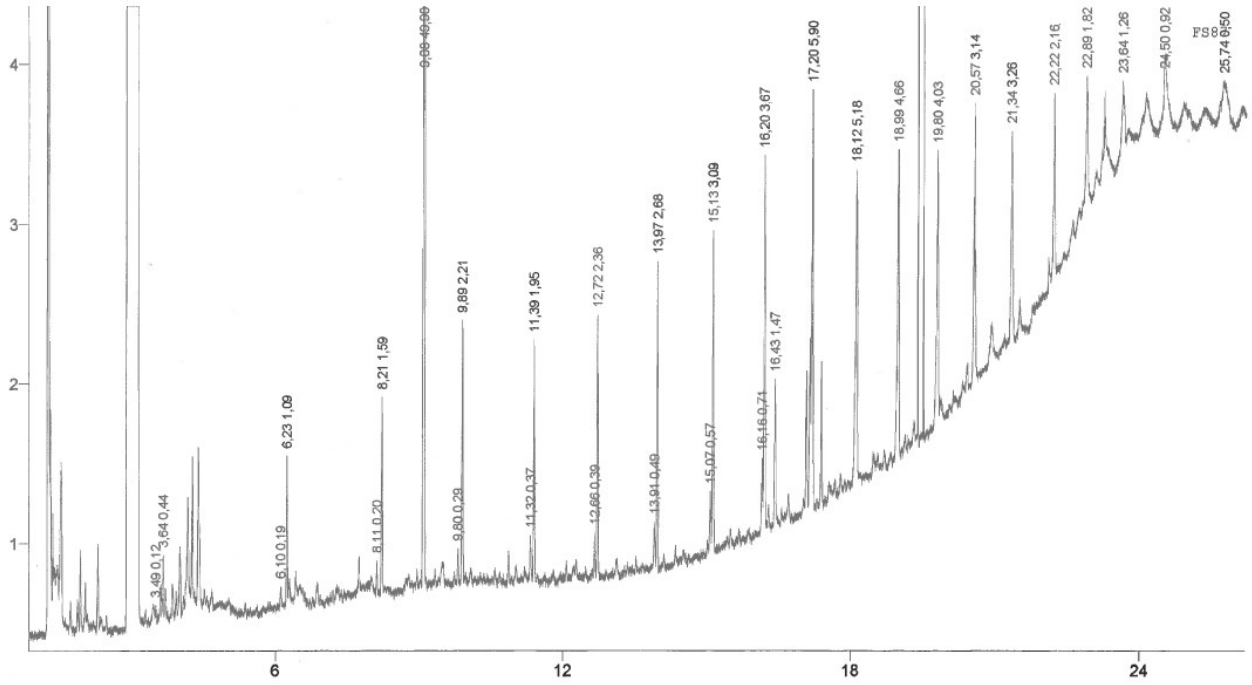


Figure S2-19a Raw signal Gas Chromatography analysis Entry 19 Table 1.

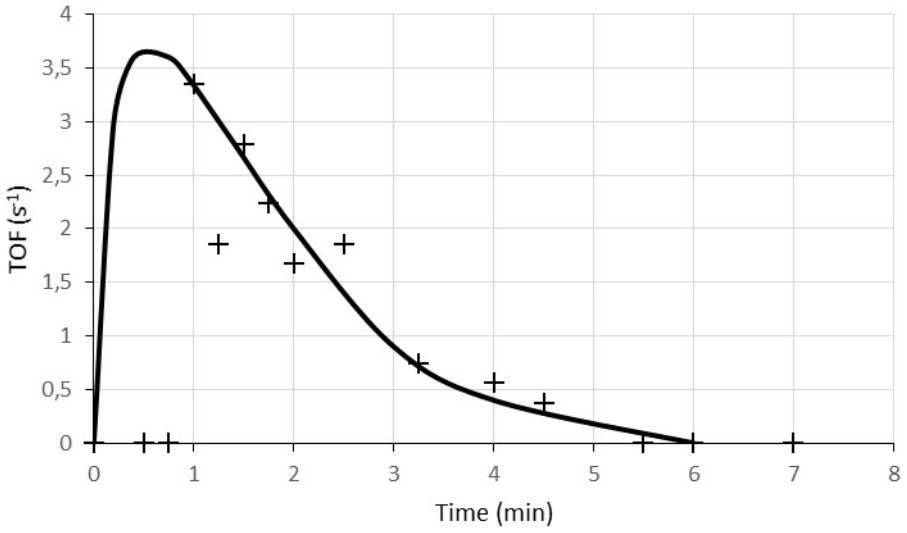


Figure S2-19b Kinetic measurement of ethylene consumption Entry 19 Table 1.

S3 Detailed conditions and results of each experiment presented in **Table 2**: Improvement of the reaction rate upon using different ether additives on the CCG of ethylene on butyl-ethyl-magnesium using $Cp^*_2NdCl_2Li(OEt_2)_2$ as catalytic precursor.

Common conditions: solvent, toluene 250 mL; batch reactor, total volume 600 mL (entry 23: small reactor, 20 mL); regulated temperature by circulating water in the calandria; stirring at 1000 rpm with a gas impeller; start by casting the Nd + ether solution from an upper isobar cylinder; initial pressure of ethylene monomer 4.8 bar abs.; free consumption until atmospheric pressure, then stop by opening the reactor to air and immediate precipitation by quench in 1 L acidified methanol, cooling 1 h, filtration and drying; mass of polymerised ethylene 4.65 g (166 mmol).

Table S3

Entry	Ether	Nd (µmol)	Mg (mmol)	Ether (mmol)	Initial Temperature (°C)	Maximum Temperature (°C)	Note
20	12-crown-4	6.27	4.99	5.76	70.7	89.0	
21	15-crown-5	6.31	4.98	4.99	71.6	73.2	
22	Tetraglyme	6.31	4.98	4.99	69.3	93.1	Yellow colour
23	Dimethoxyethane	6.20	4.98	9.76	69.8	73.7	

Nota Bene:

Temperature was recorded from an internal probe in an assembly having some inertia, the values must therefore be compared with each other in relative mode, and they are not representative of the exact local temperature at a given moment, when the evolution is rapid.

The catalytic activities expressed in the following figures are Turnover Frequencies (moles of ethylene consumed by moles of neodymium catalyst and by time) and they have been calculated from the recorded pressure drop as a function of time, assuming that mass is proportional to pressure.

S3 continuing.

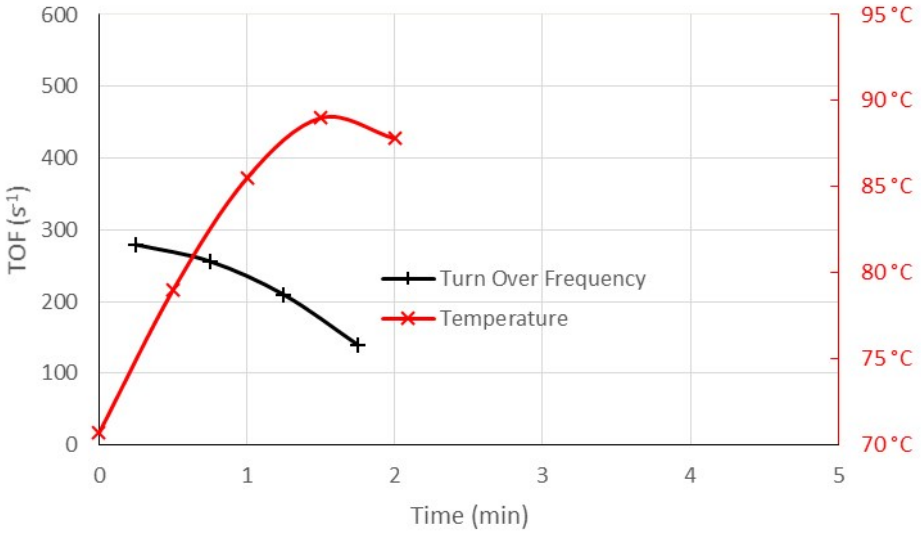


Figure S3-1 Activity and Temperature effect of the exothermic reaction, Entry 20 Table 2. (12-crown-4)

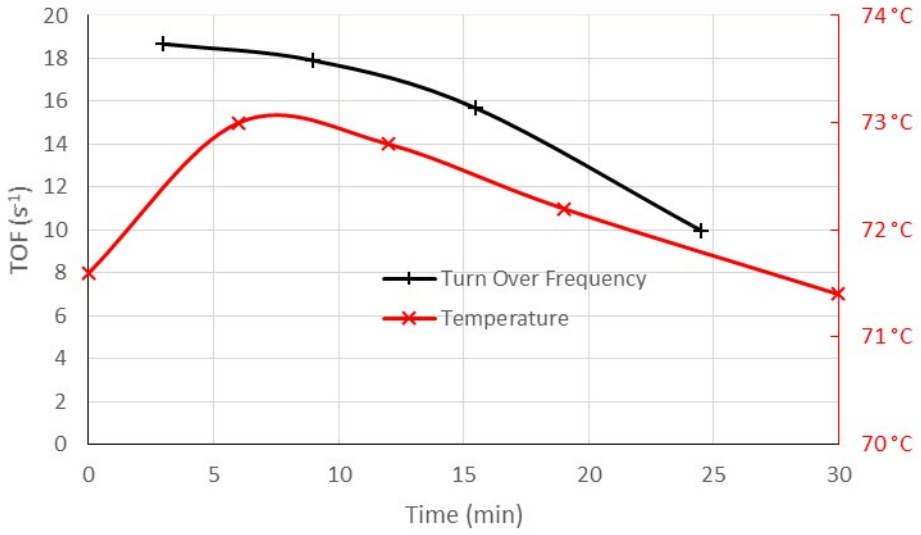


Figure S3-2 Activity and Temperature effect of the exothermic reaction, Entry 21 Table 2. (15-crown-5)

S3 continuing.

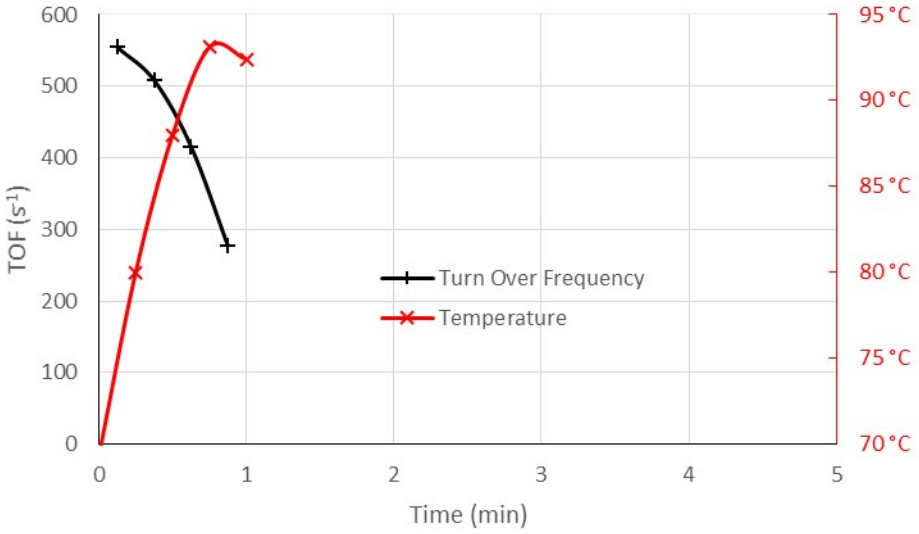


Figure S3-3 Activity and Temperature effect of the exothermic reaction, Entry 22 Table 2. (tetraglyme)

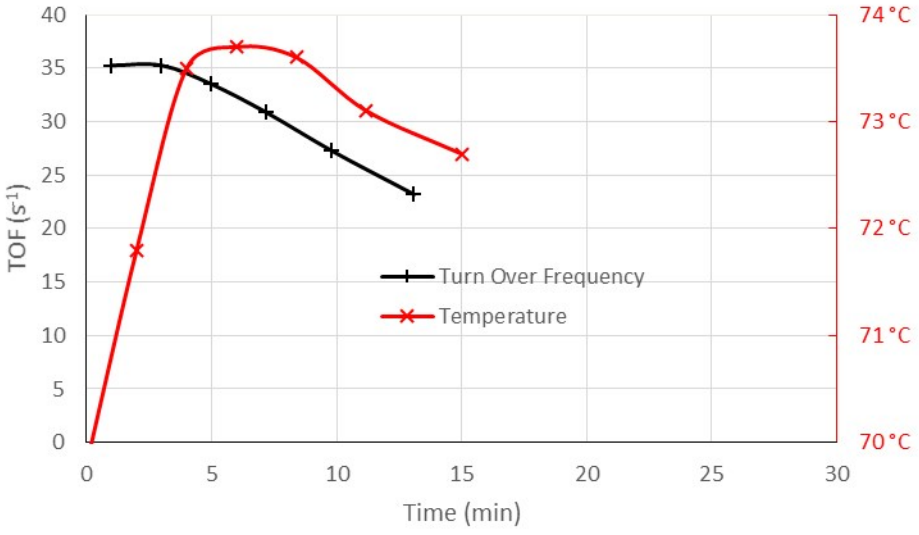


Figure S3-4 Activity and Temperature effect of the exothermic reaction, Entry 23 Table 2. (dimethoxyethane)

S4 Detailed conditions and results of each experiment presented in **Tables 3** and **4**: one pot synthesis of narrow dispersed high molecular weight fatty alcohols.

Table S4 – 1 Detailed conditions of the first step: polymerisation.

Entry	Volume [a] (mL)	Pressure [b] (bar abs.)	Temperature [c] (°C)	Nd [d] (µmol)	Mg [e] (mmol)	DME [f] (mmol)	Time (min)	Ethylene uptake (g)
1	250	3.8 – 0.5	70 – 72.9	6.25	4.99	10.0	15	3.91
2	20	1.15	50	1.56	0.405	0.410	4	0.29
3	20	1.4	50	1.41	1.00	0.99	15	1.00
4	20	1.4	50	1.88	1.016	1.08 [g]	15	1.13
5	250	6 – 1	50 – 61	8.70	5.01	5.62	15	6.08
6	250	6 – 1	70 – 85 [h]	5.91	4.97	8.98	15	6.01
7	250	4.8 – 0.5	70 – 76 [h]	3.42	4.99	9.12	30	5.38
8	250	4.8 – 0.5	70 – 87 [h]	8.27	5.10	9.62	15	5.32
9	250	5 – 1	72 – 80	6.09	5.01	9.25	15	4.96
10	250	3.8 – 1	70 – 72	6.09	5.03	9.25	15	3.29

[a] Toluene as solvent. For 20 mL, use of the small reactor with continuous ethylene intake on demand at constant pressure. For 250 mL, use of a batch reactor. [b] For the batch reactor, initial and final pressures are given. [c] For the batch reactor, real temperature of the solution is given (ΔT is due to the exothermic reaction), while for the small reactor (no probe inside) only the temperature of the water, circulating in the calandria, is given. [d] $Cp^*_2NdCl_2Li(OEt_2)_2$. [e] BEM Butyl-Ethyl-Magnesium. [f] DME dimethoxyethane. [g] 12-crown-4 instead of DME. [h] No decrease of temperature at the end of the polymerisation step because the next steps needed higher temperature, so the water of the calandria was evacuated in order to heat the reactor with hot air of a heat gun.

S4 continuing

Table S4 – 2 Detailed conditions of the next steps: oxidation and hydrolysis.

Entry	Oxidation Temperature (°C)	Oxidation Pressure (bar abs)	Oxidation Time (min)	Hydrolysis and work-up [a]
1-1	70	2	30	Air
1-2				Water
1-3				Conc. HCl
1-4				H_2SO_4
1-5				Butanol
1-6				Standard
2	50	1	30	Standard
3	50	1	30	Standard
4	50	1	30	Standard
5	50	1	30	Standard
6	120	2-2.5	10	Standard
7	130	2-3.3	15	Standard
8	150	2-3.6	15	Standard
9 [b]	70	1-2	30	Standard
10 [c]	70	1-2	30	Standard

[a] See Experimental part for details. [b] 2 mol% $Fe(acac)_3$ *vs* Mg. [c] 2 mol% $Ti(OiPr)_4$ *vs* Mg.

S4 continuing, Entry 1-1 Table 3.

Nota Bene: GC analyses of Entries 1-1 to 1-6 were performed with a 30 m column, injector and detector at 350 °C and oven temperature limited to 300 °C. The standard at 10 min was tetradecane.

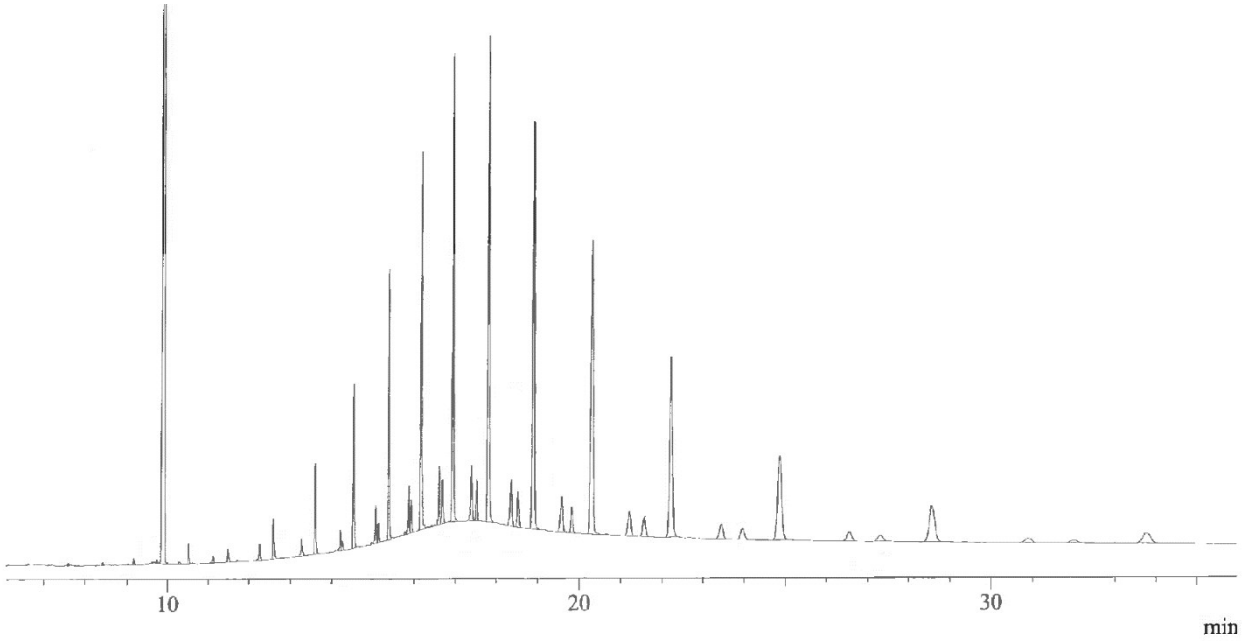


Figure S4-1-1a Raw signal Gas Chromatography analysis Entry 1-1 Table 3.

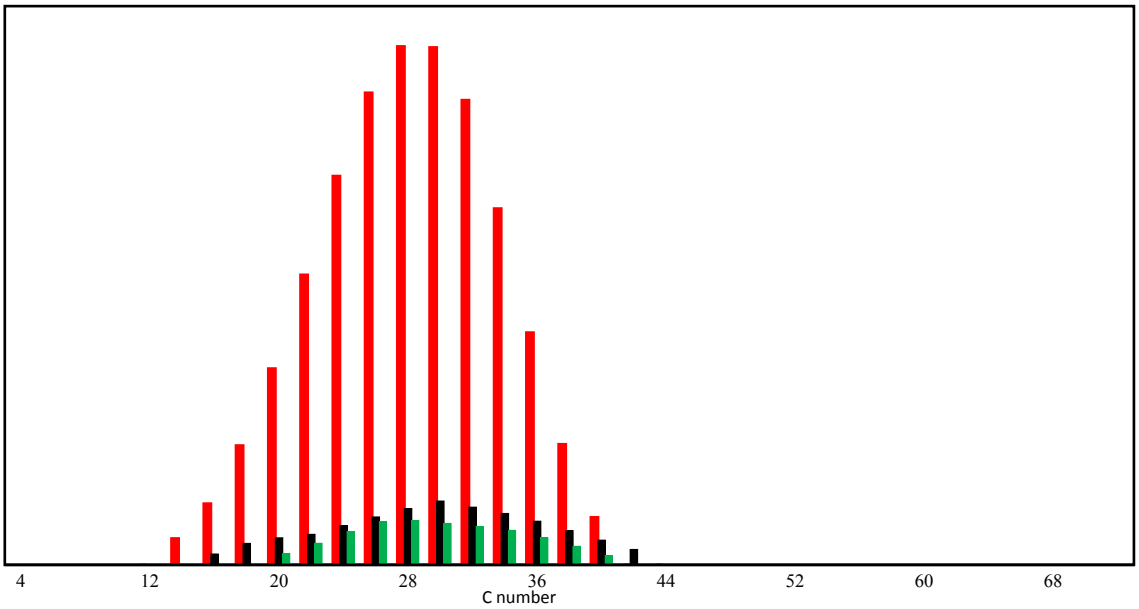


Figure S4-1-1b Distributions of alcohols ROH (red), hydrocarbons RH (black) and aldehydes RCHO (green). Molar amounts calculated from the GC analysis of Entry 1-1 Table 3.

S4 continuing, Entry 1-1 Table 3.

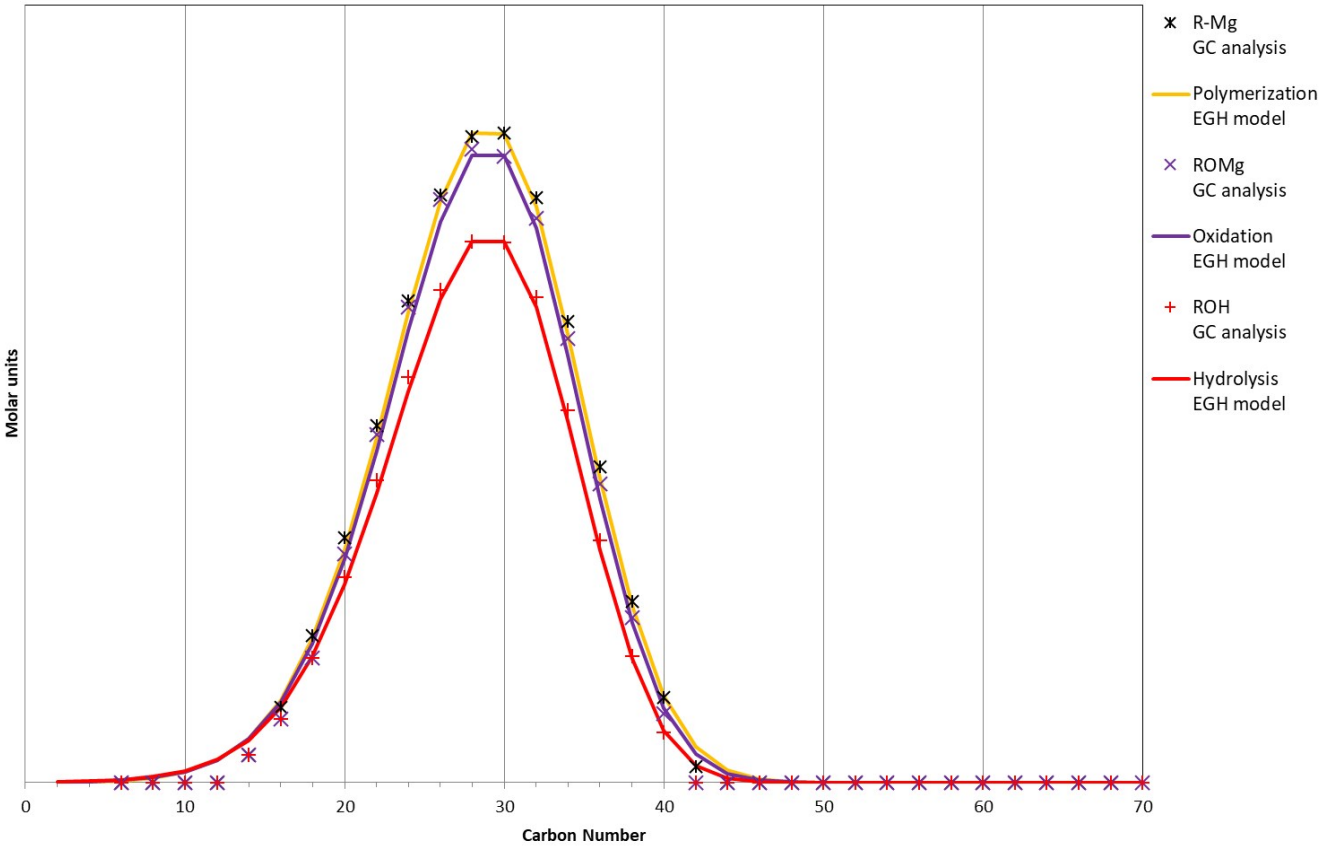


Figure S4-1-1c Distributions (graphics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 1-1 Table 3.

Table S4-1-1 Distributions (numerics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 1-1 Table 3.

Step	Polymerisation	Oxidation	Hydrolysis
Distribution sum of GC peaks	***R***-Mg ROH + RCHO + RH	R-***O***-Mg ROH + 2 RCHO	R-O-***H*** ROH
Step efficiency relative area of EGH fitting		**95.6%**	**85.7%**
R^2 of EGH fitting	0.9986	0.9969	0.9981
Mn (Carbon number) of EGH fitting	**28.32**	28.21	27.95
Dispersity of EGH fitting	**1.04**	1.04	1.04
Dispersity awaited for a Poisson distribution of same Mn	1.063	1.063	1.064
Skewness of EGH fitting	-0.225	-0.265	-0.352
Skewness awaited for a Poisson distribution of same Mn	0.281	0.282	0.283

S4 continuing, Entry 1-2 Table 3.

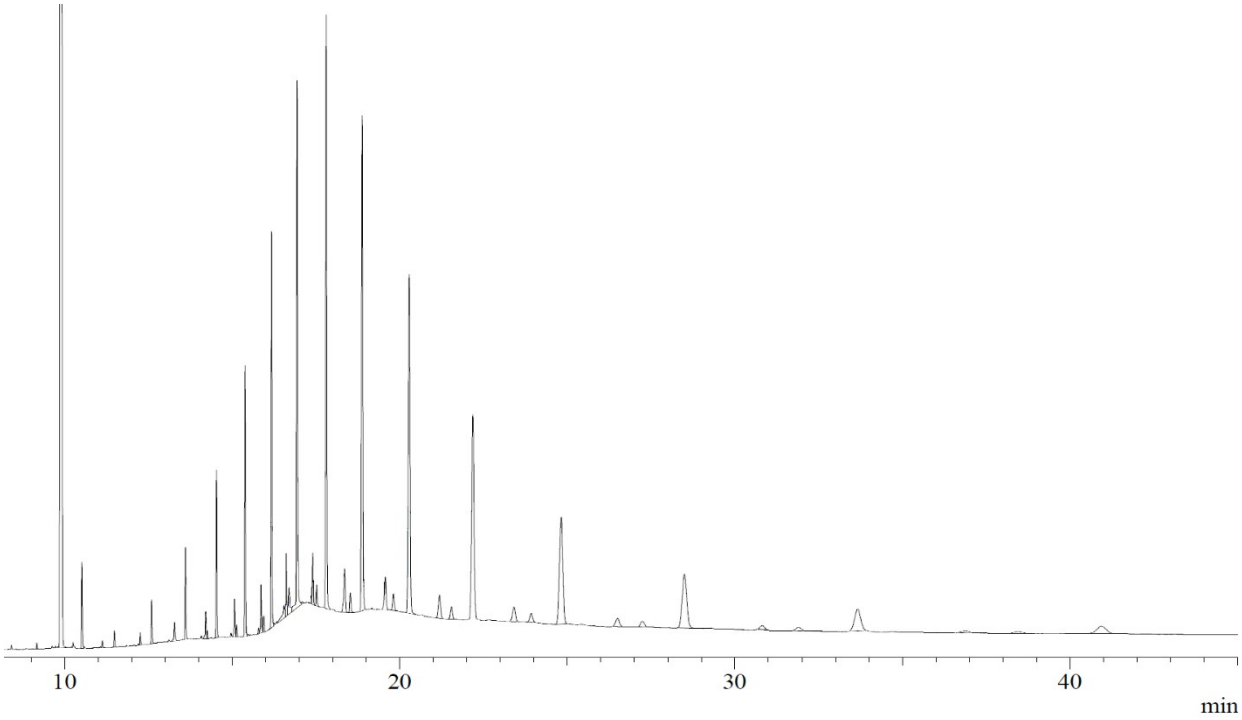


Figure S4-1-2a Raw signal Gas Chromatography analysis Entry 1-2 Table 3.

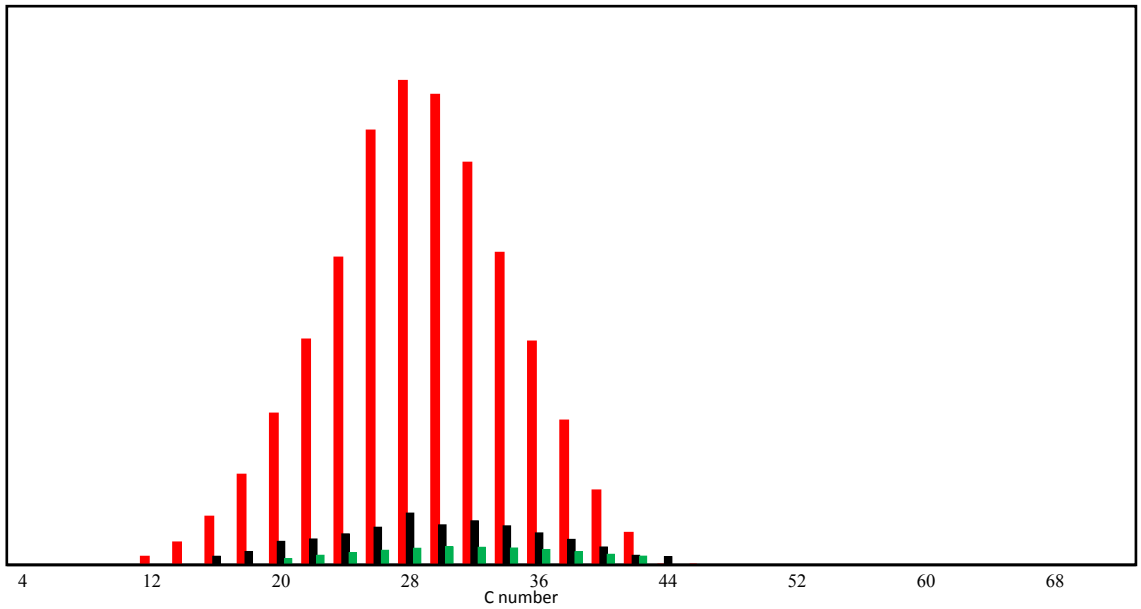


Figure S4-1-2b Distributions of alcohols ROH (red), hydrocarbons RH (black) and aldehydes RCHO (green). Molar amounts calculated from the GC analysis of Entry 1-2 Table 3.

S4 continuing, Entry 1-2 Table 3.

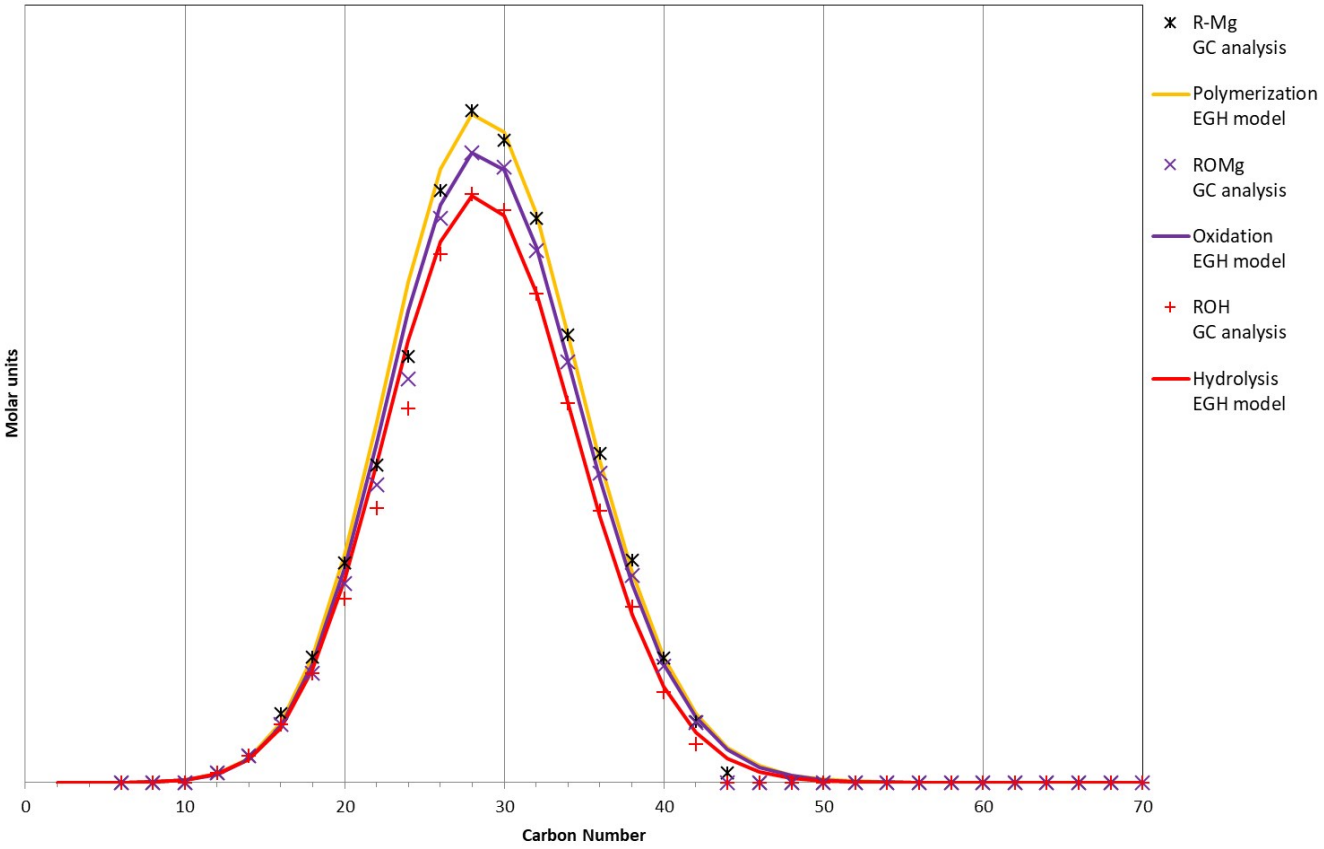


Figure S4-1-2c Distributions (graphics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 1-2 Table 3.

Table S4-1-2 Distributions (numerics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 1-2 Table 3.

Step	Polymerisation	Oxidation	Hydrolysis
Distribution sum of GC peaks	***R***-Mg ROH + RCHO + RH	R-***O***-Mg ROH + 2 RCHO	R-O-***H*** ROH
Step efficiency relative area of EGH fitting		**94.2%**	**91.5%**
R^2 of EGH fitting	0.9918	0.9914	0.9892
Mn (Carbon number) of EGH fitting	**28.95**	28.95	28.70
Dispersity of EGH fitting	**1.04**	1.04	1.04
Dispersity awaited for a Poisson distribution of same Mn	1.062	1.062	1.062
Skewness of EGH fitting	0.150	0.150	0.102
Skewness awaited for a Poisson distribution of same Mn	0.278	0.278	0.279

S4 continuing, Entry 1-3 Table 3.

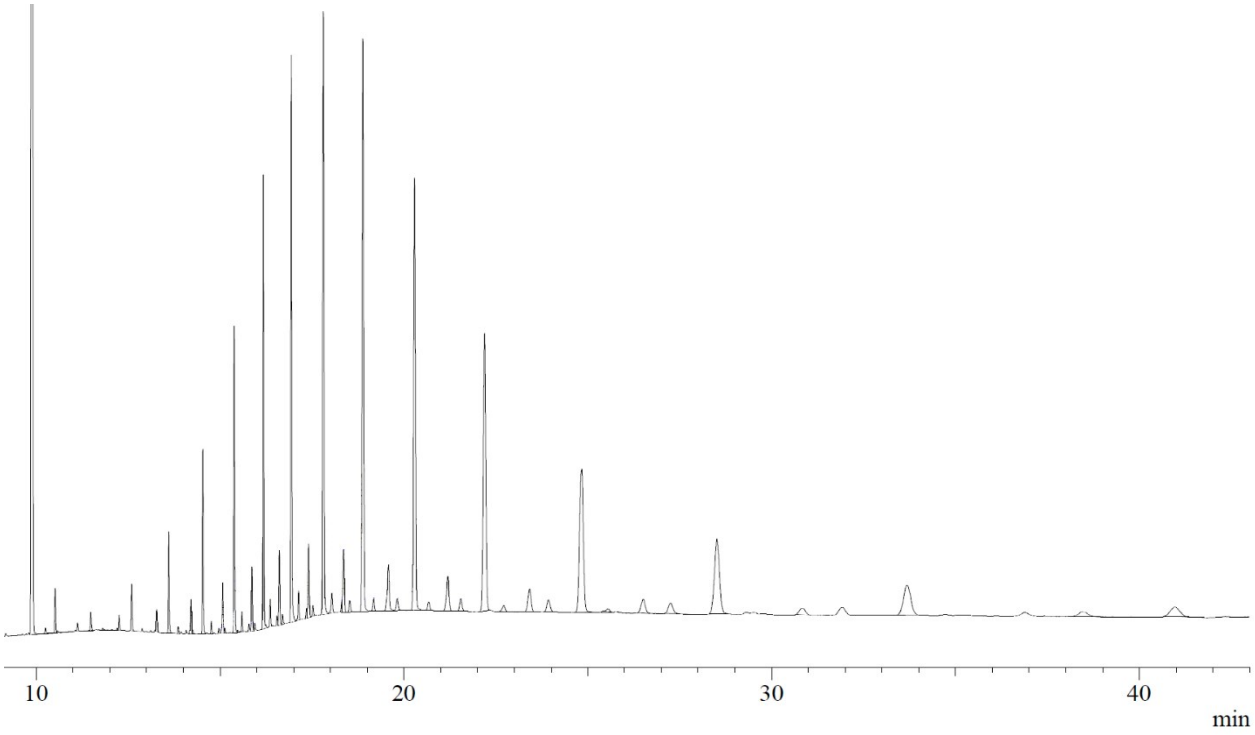


Figure S4-1-3a Raw signal Gas Chromatography analysis Entry 1-3 Table 3.

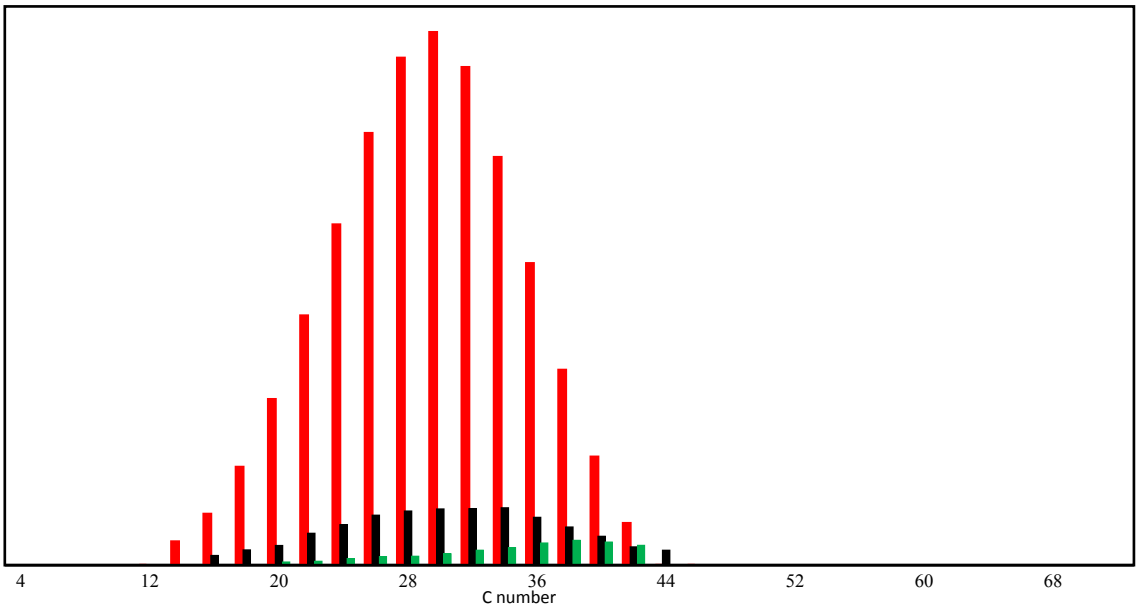


Figure S4-1-3b Distributions of alcohols ROH (red), hydrocarbons RH (black) and aldehydes RCHO (green). Molar amounts calculated from the GC analysis of Entry 1-3 Table 3.

S4 continuing, Entry 1-3 Table 3.

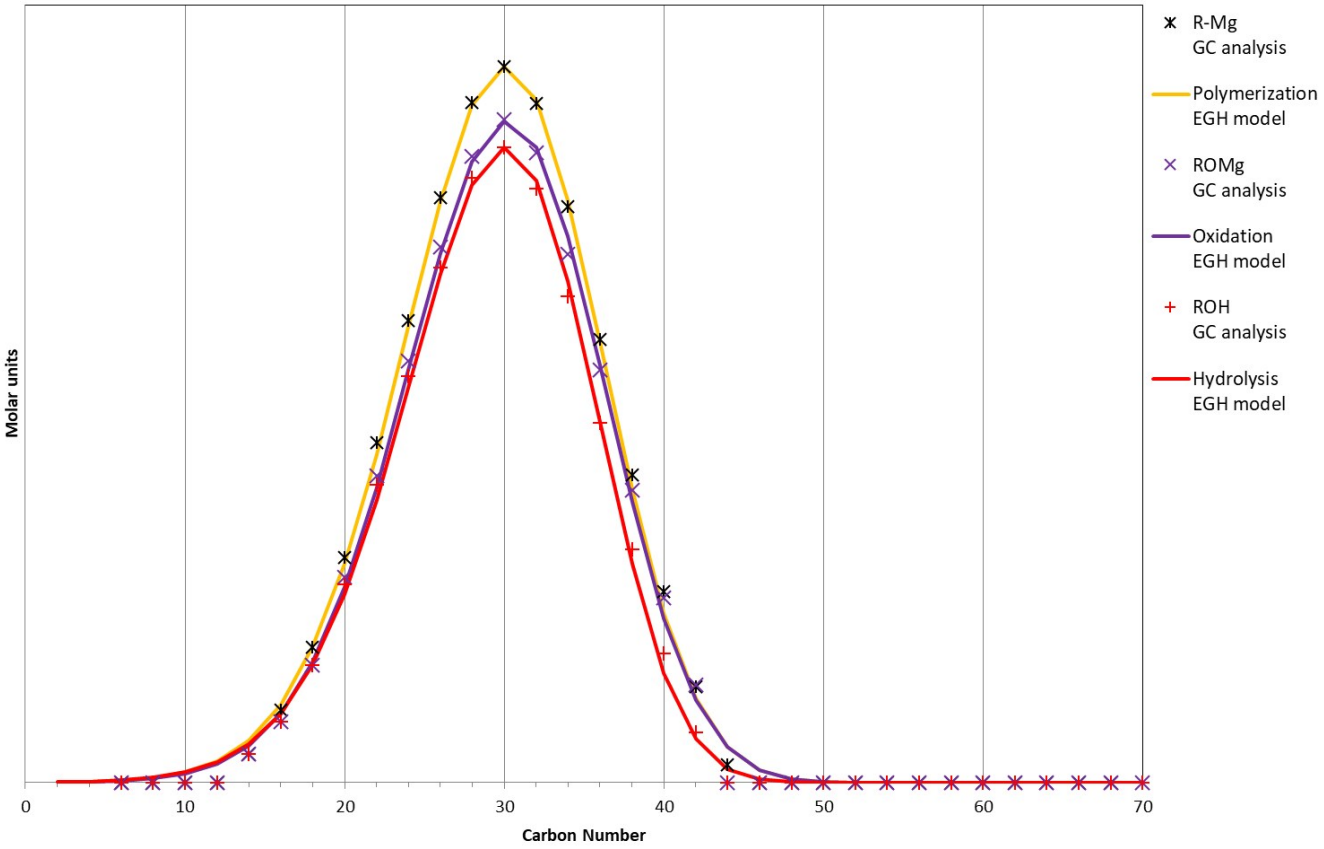


Figure S4-1-3c Distributions (graphics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 1-3 Table 3.

Table S4-1-3 Distributions (numerics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 1-3 Table 3.

Step	Polymerisation	Oxidation	Hydrolysis
Distribution sum of GC peaks	***R***-Mg ROH + RCHO + RH	R-***O***-Mg ROH + 2 RCHO	R-O-***H*** ROH
Step efficiency relative area of EGH fitting		**92.4%**	**91.6%**
R^2 of EGH fitting	0.9987	0.9980	0.9979
Mn (Carbon number) of EGH fitting	**29.43**	29.58	29.05
Dispersity of EGH fitting	**1.05**	1.05	1.04
Dispersity awaited for a Poisson distribution of same Mn	1.061	1.061	1.062
Skewness of EGH fitting	-0.214	-0.214	-0.346
Skewness awaited for a Poisson distribution of same Mn	0.275	0.274	0.277

S4 continuing, Entry 1-4 Table 3.

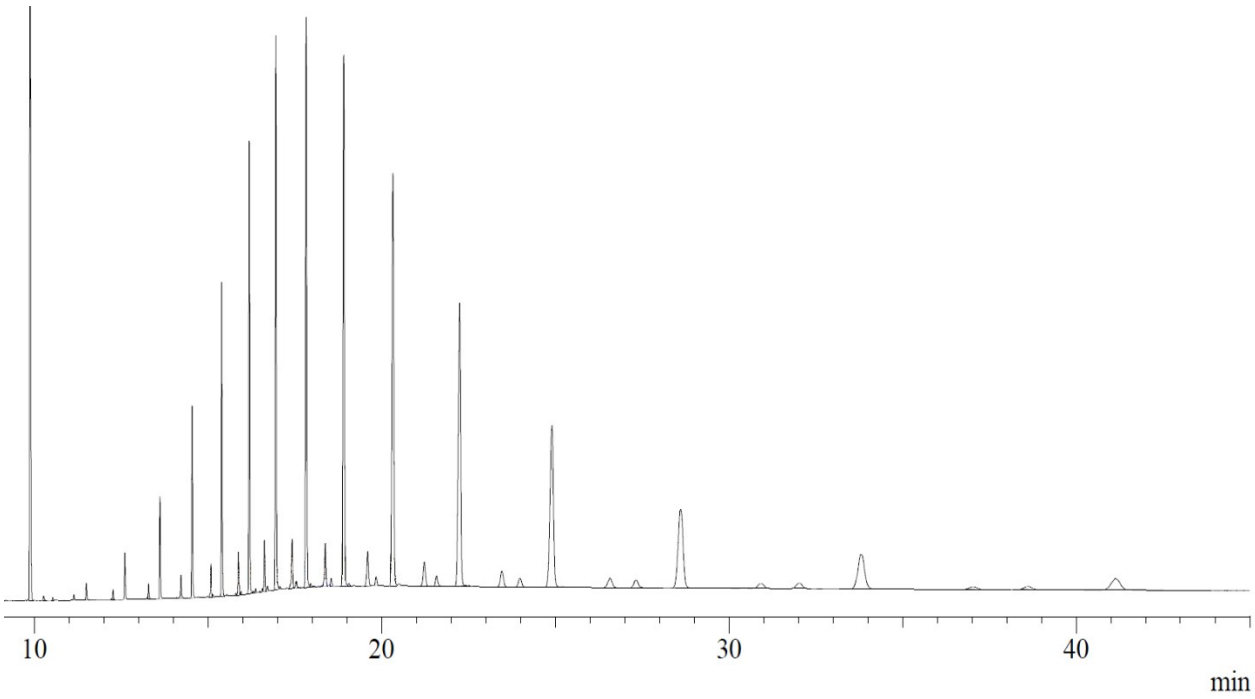


Figure S4-1-4a Raw signal Gas Chromatography analysis Entry 1-4 Table 3.

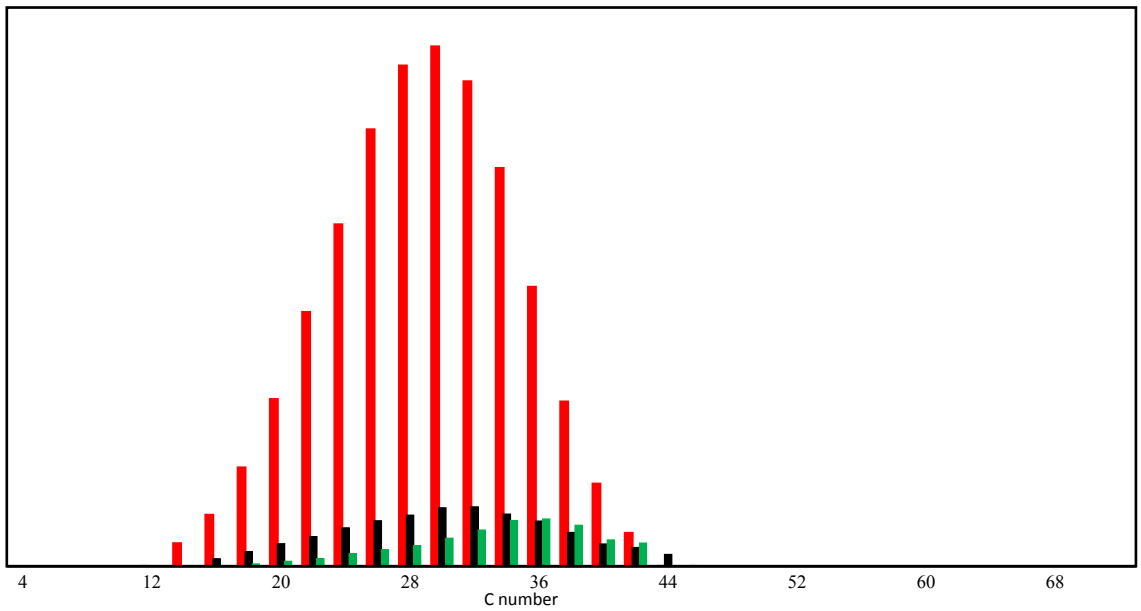


Figure S4-1-4b Distributions of alcohols ROH (red), hydrocarbons RH (black) and aldehydes RCHO (green). Molar amounts calculated from the GC analysis of Entry 1-4 Table 3.

S4 continuing, Entry 1-4 Table 3.

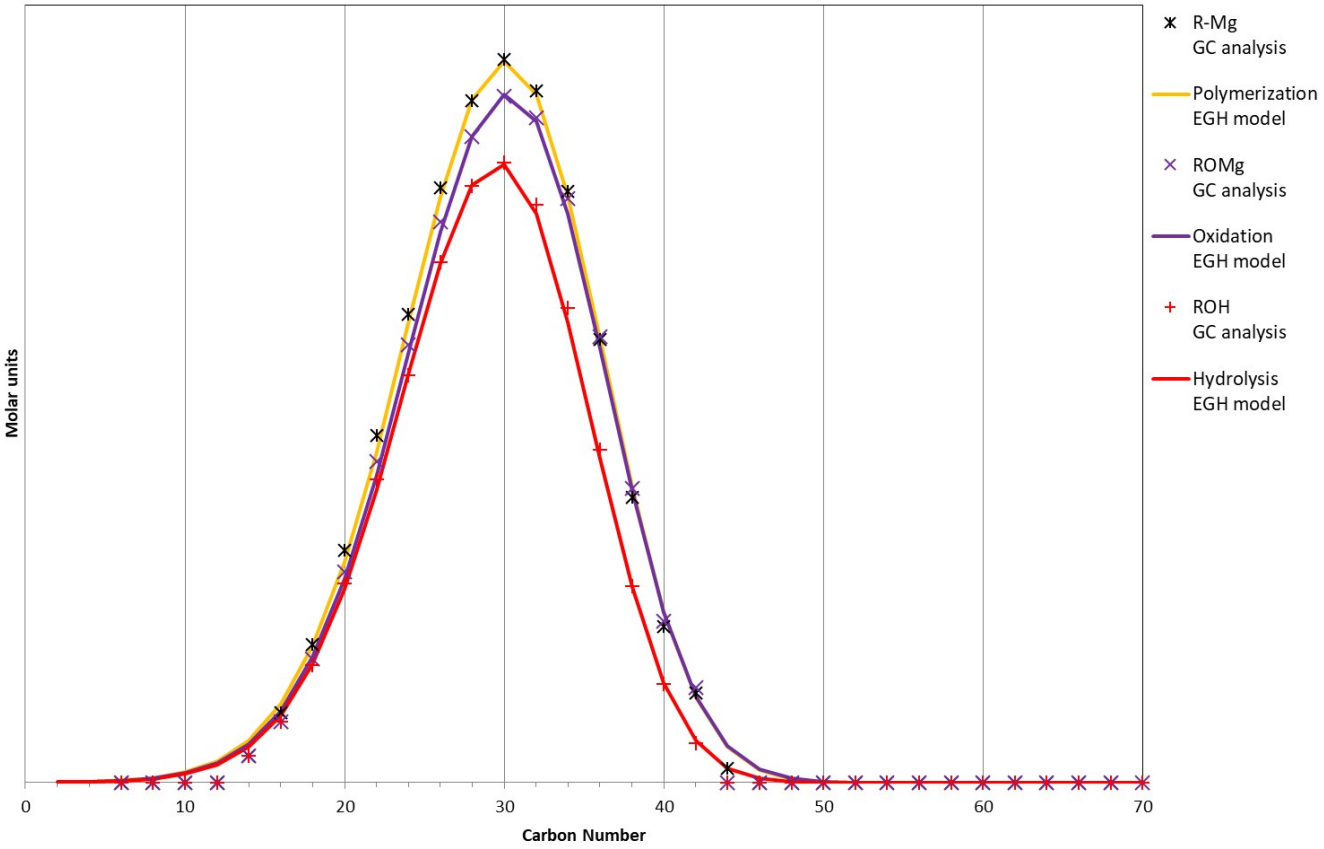


Figure S4-1-4c Distributions (graphics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 1-4 Table 3.

Table S4-1-4 Distributions (numerics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 1-4 Table 3.

Step	Polymerisation	Oxidation	Hydrolysis
Distribution sum of GC peaks	***R***-Mg ROH + RCHO + RH	R-***O***-Mg ROH + 2 RCHO	R-O-***H*** ROH
Step efficiency relative area of EGH fitting		**95.4%**	**85.6%**
R^2 of EGH fitting	0.9987	0.9988	0.9992
Mn (Carbon number) of EGH fitting	**29.43**	29.58	28.85
Dispersity of EGH fitting	**1.05**	1.05	1.04
Dispersity awaited for a Poisson distribution of same Mn	1.061	1.061	1.062
Skewness of EGH fitting	-0.214	-0.214	-0.250
Skewness awaited for a Poisson distribution of same Mn	0.275	0.274	0.278

S4 continuing, Entry 1-5 Table 3.

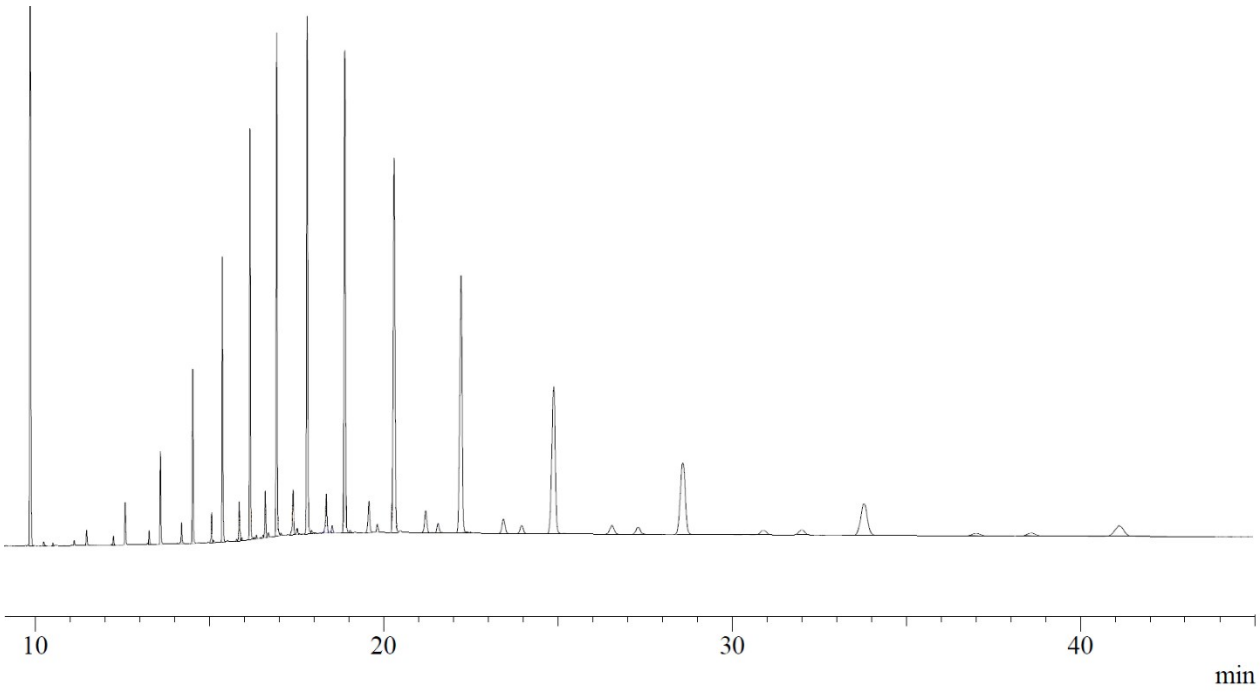


Figure S4-1-5a Raw signal Gas Chromatography analysis Entry 1-5 Table 3.

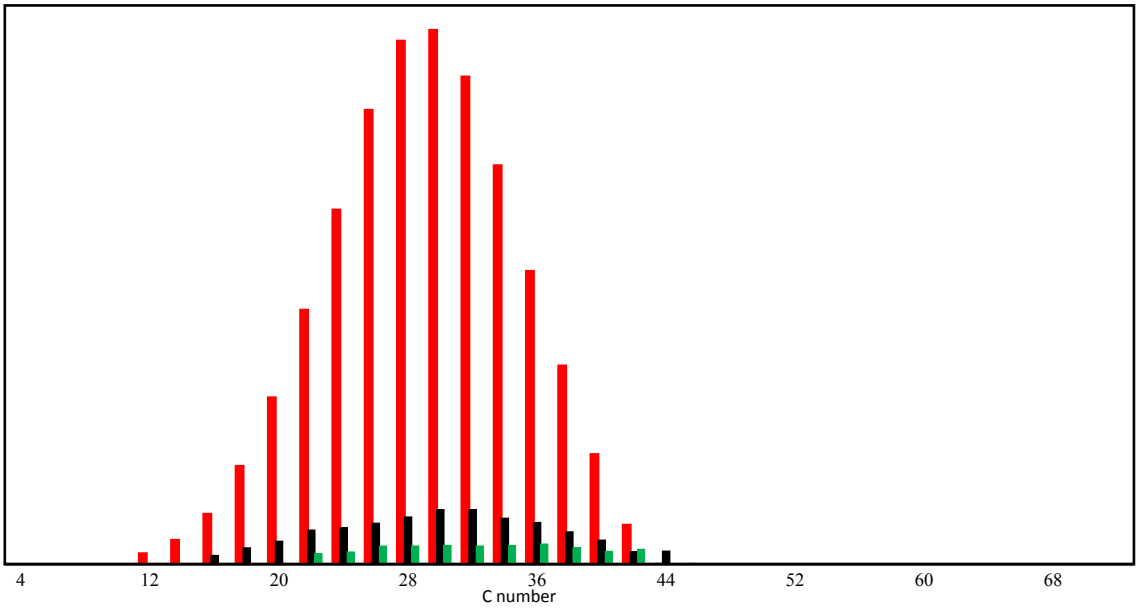


Figure S4-1-5b Distributions of alcohols ROH (red), hydrocarbons RH (black) and aldehydes RCHO (green). Molar amounts calculated from the GC analysis of Entry 1-5 Table 3.

S4 continuing, Entry 1-5 Table 3.

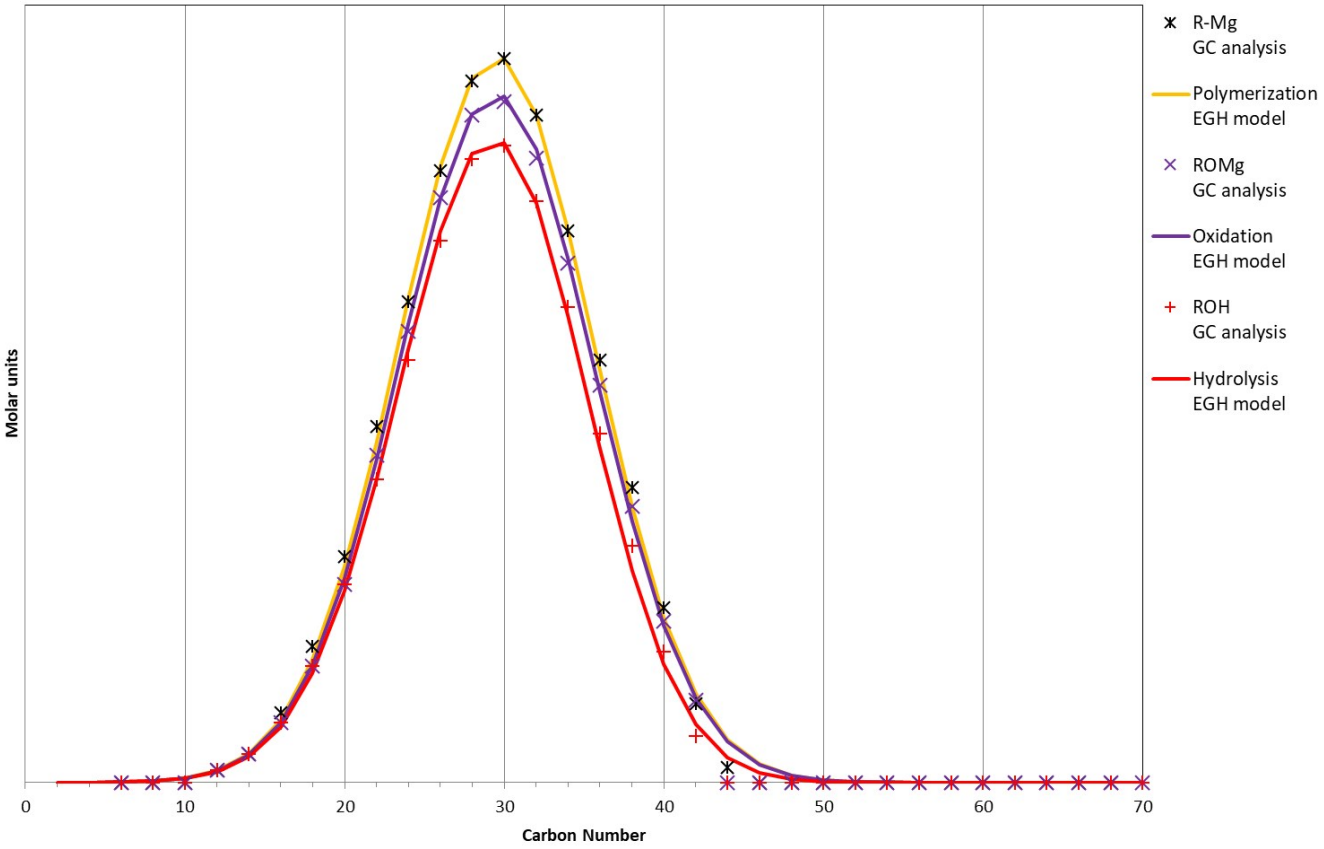


Figure S4-1-5c Distributions (graphics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 1-5 Table 3.

Table S4-1-5 Distributions (numerics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 1-5 Table 3.

Step	Polymerisation	Oxidation	Hydrolysis
Distribution sum of GC peaks	***R***-Mg ROH + RCHO + RH	R-***O***-Mg ROH + 2 RCHO	R-O-***H*** ROH
Step efficiency relative area of EGH fitting		**94.8%**	**90.5%**
R^2 of EGH fitting	0.9985	0.9995	0.9981
Mn (Carbon number) of EGH fitting	**29.50**	29.50	29.15
Dispersity of EGH fitting	**1.04**	1.04	1.04
Dispersity awaited for a Poisson distribution of same Mn	1.061	1.061	1.062
Skewness of EGH fitting	0.000	0.000	-0.051
Skewness awaited for a Poisson distribution of same Mn	0.275	0.275	0.277

S4 continuing, Entry 1-5 Table 3.

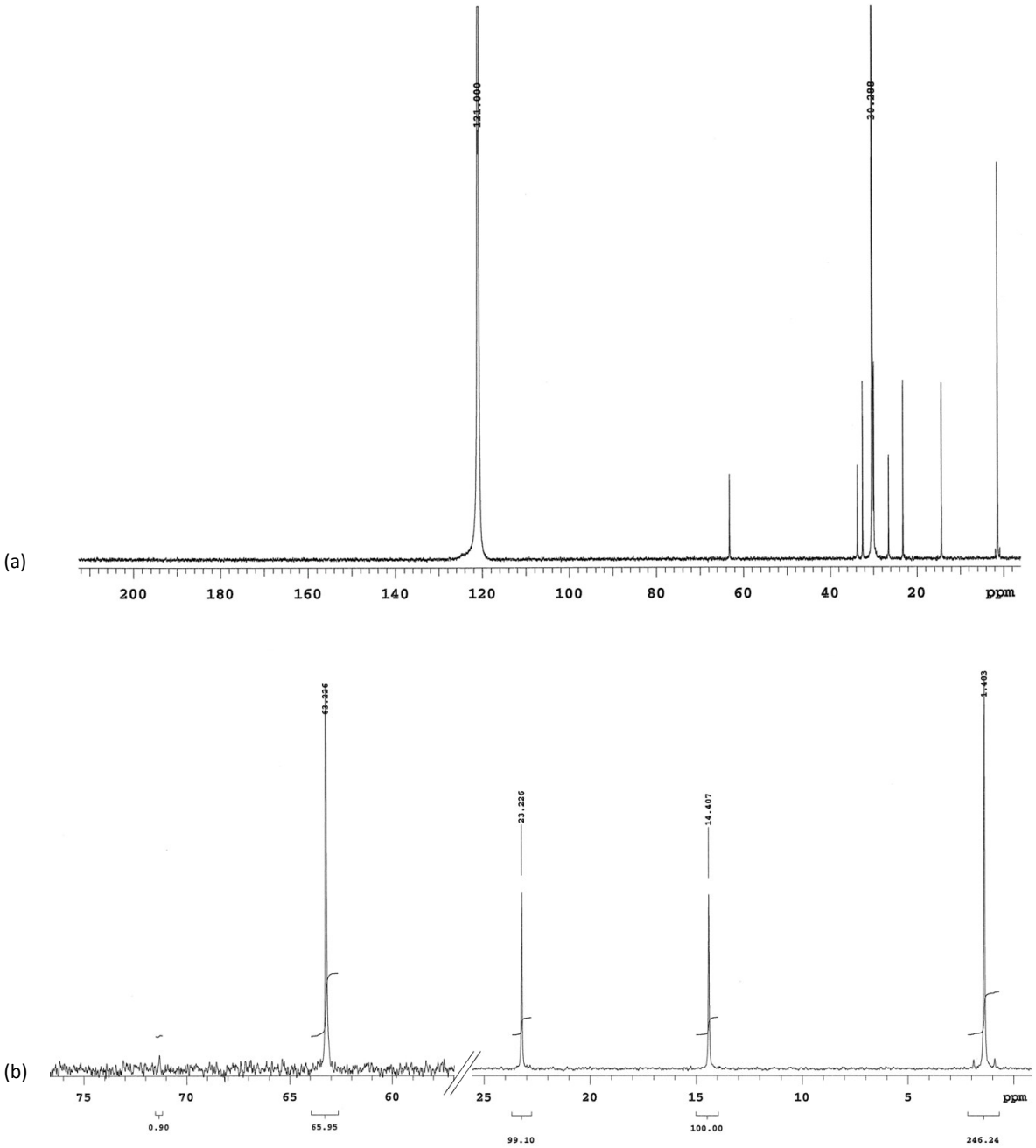


Figure S4-1-5d ^{13}C NMR spectrum (solvent $Cl_2C{=}CCl_2$, in the presence of $Cr(acac)_3$, D_2O capillary lock, 368 K) of Entry 1-5 Table 3. Full range (a) and selected zone for integration (b). ROH % = 80.0 %

S4 continuing, Entry 1-6 Table 3.

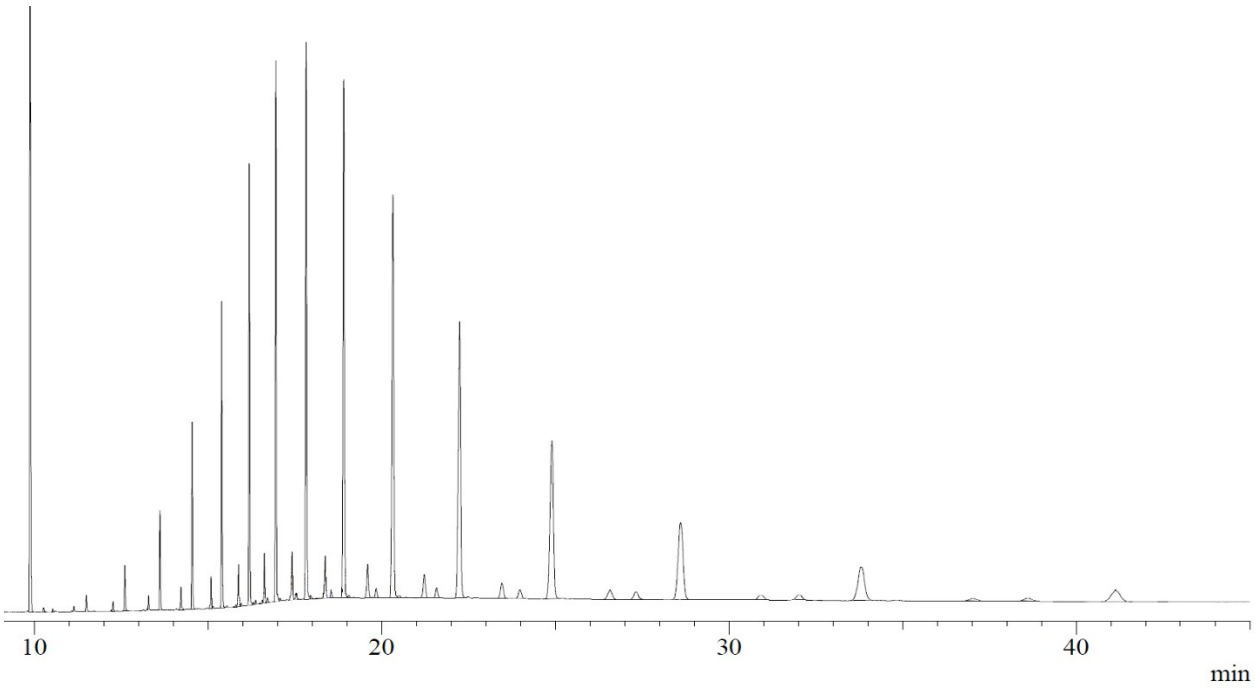


Figure S4-1-6a Raw signal Gas Chromatography analysis Entry 1-6 Table 3.

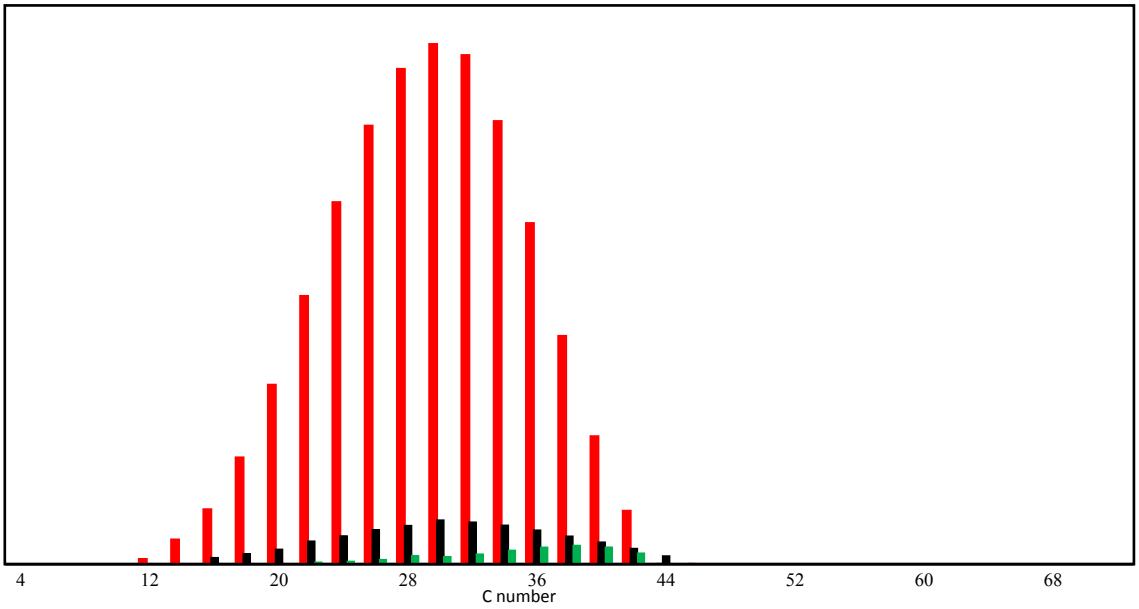


Figure S4-1-6b Distributions of alcohols ROH (red), hydrocarbons RH (black) and aldehydes RCHO (green). Molar amounts calculated from the GC analysis of Entry 1-6 Table 3.

S4 continuing, Entry 1-6 Table 3.

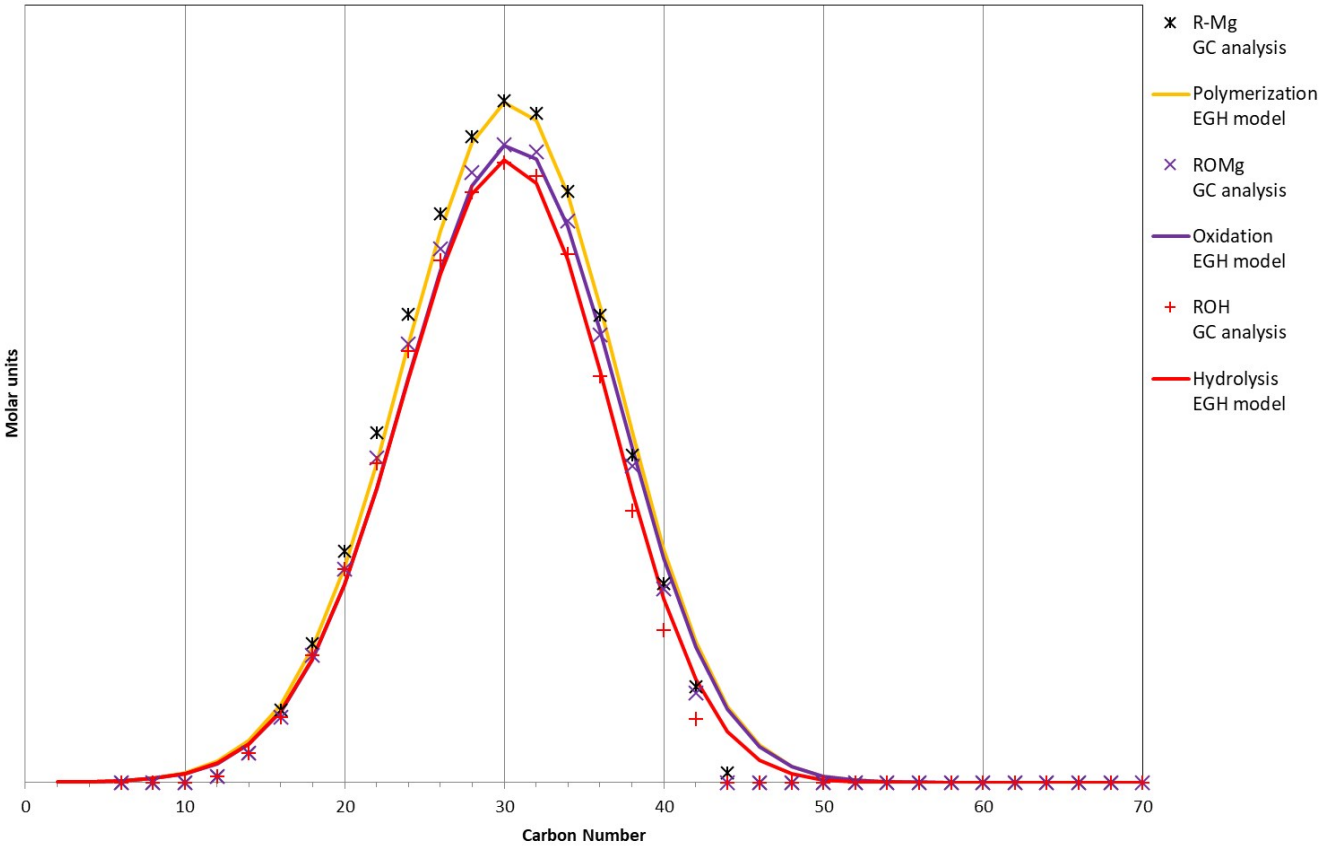


Figure S4-1-6c Distributions (graphics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 1-6 Table 3.

Table S4-1-6 Distributions (numerics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 1-6 Table 3.

Step	Polymerisation	Oxidation	Hydrolysis
Distribution sum of GC peaks	***R***-Mg ROH + RCHO + RH	R-***O***-Mg ROH + 2 RCHO	R-O-***H*** ROH
Step efficiency relative area of EGH fitting		**93.8%**	**94.6%**
R^2 of EGH fitting	0.9912	0.9927	0.9937
Mn (Carbon number) of EGH fitting	**30.10**	30.20	29.75
Dispersity of EGH fitting	**1.05**	1.05	1.05
Dispersity awaited for a Poisson distribution of same Mn	1.060	1.060	1.060
Skewness of EGH fitting	-0.088	-0.088	-0.136
Skewness awaited for a Poisson distribution of same Mn	0.272	0.271	0.273

S4 continuing, Entry 1-6 Table 3.

(a)

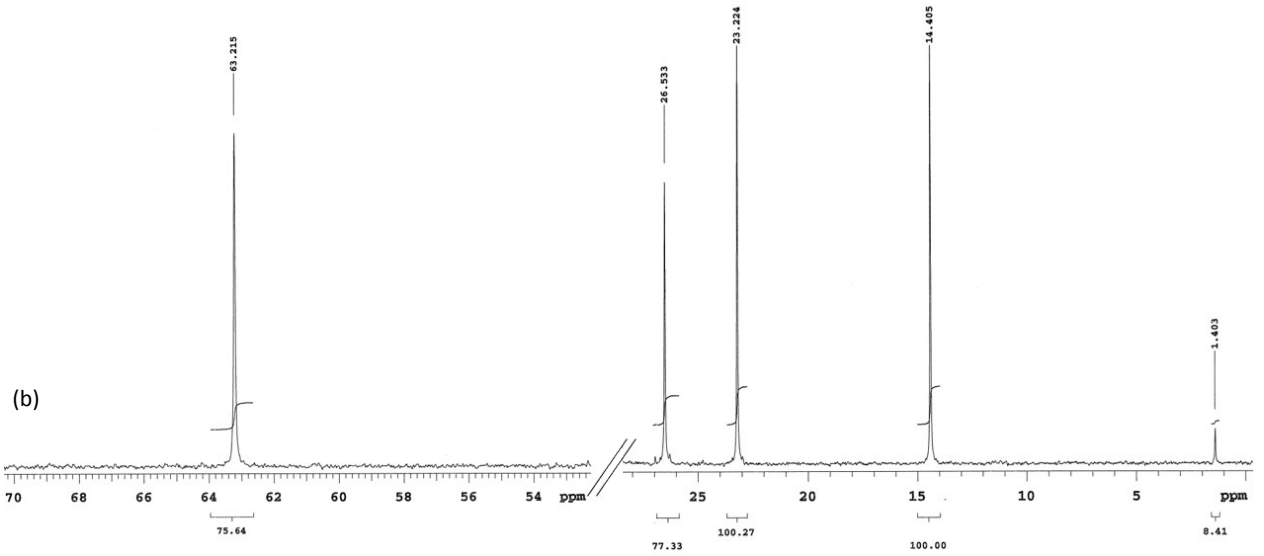


Figure S4-1-6d ^{13}C NMR spectrum (solvent $Cl_2C{=}CCl_2$, in the presence of $Cr(acac)_3$, D_2O capillary lock, 368 K) of Entry 1-6 Table 3. Full range (a) and selected zone for integration (b). ROH % = 86.0 %

S4 continuing, Entry 2 Table 3.

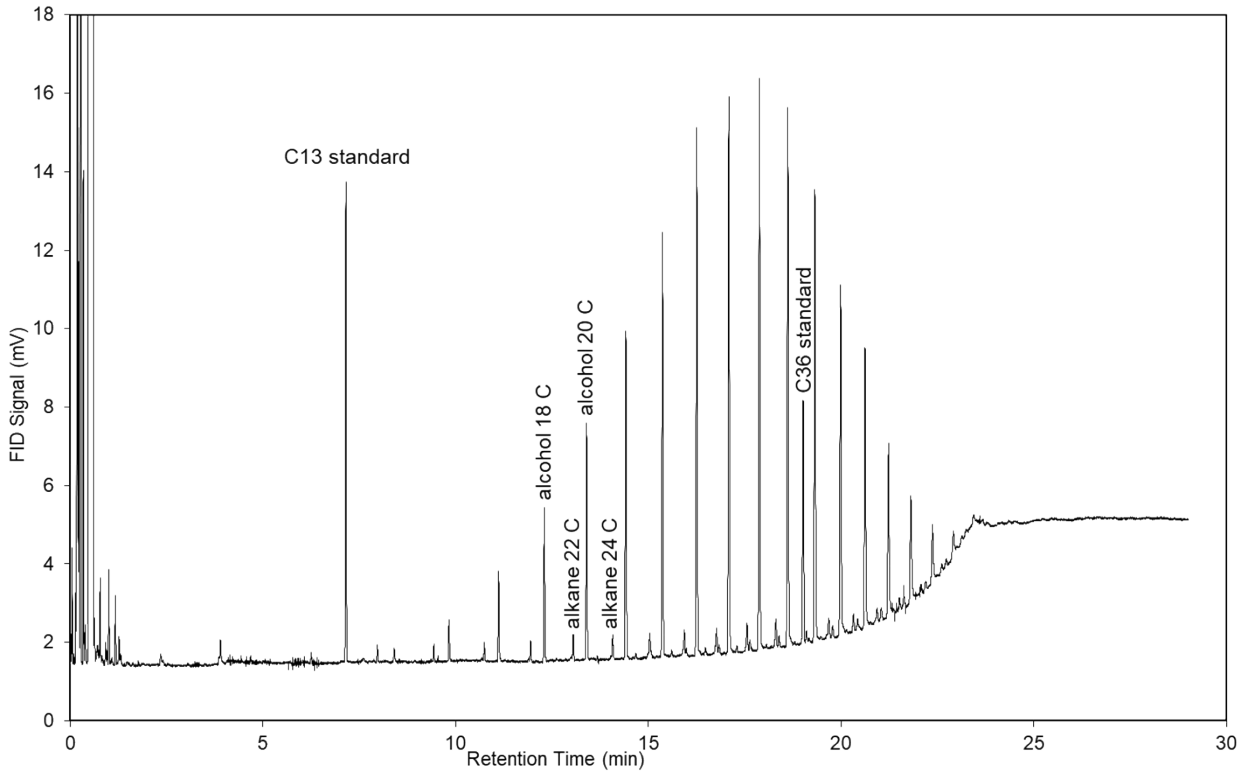


Figure S4-2a Raw signal Gas Chromatography analysis Entry 2 Table 3.

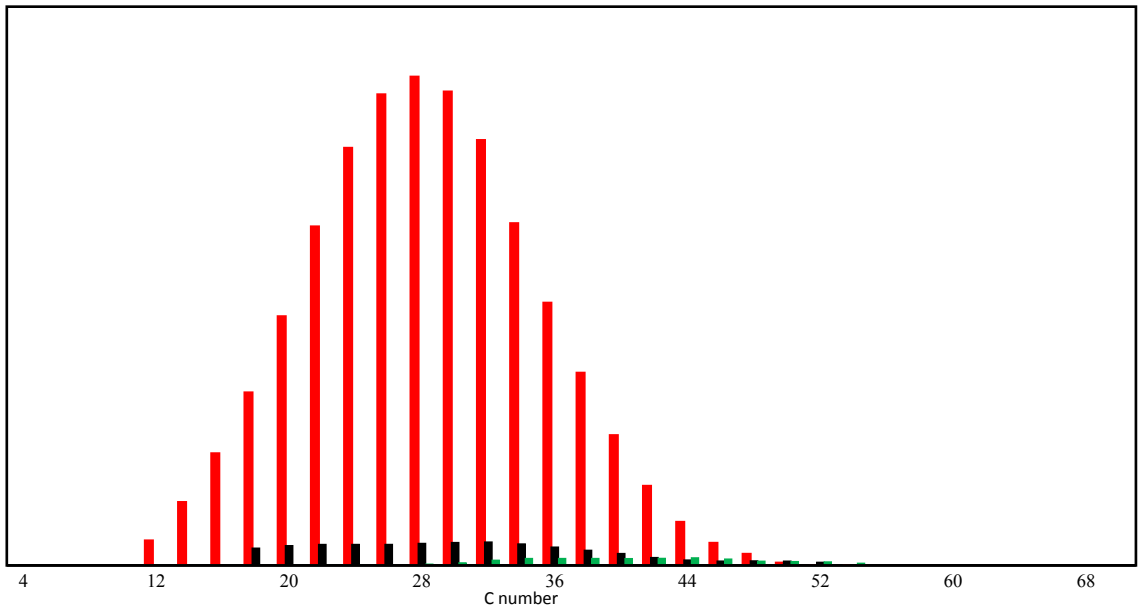


Figure S4-2b Distributions of alcohols ROH (red), hydrocarbons RH (black) and aldehydes RCHO (green). Molar amounts calculated from the GC analysis of Entry 2 Table 3.

S4 continuing, Entry 2 Table 3.

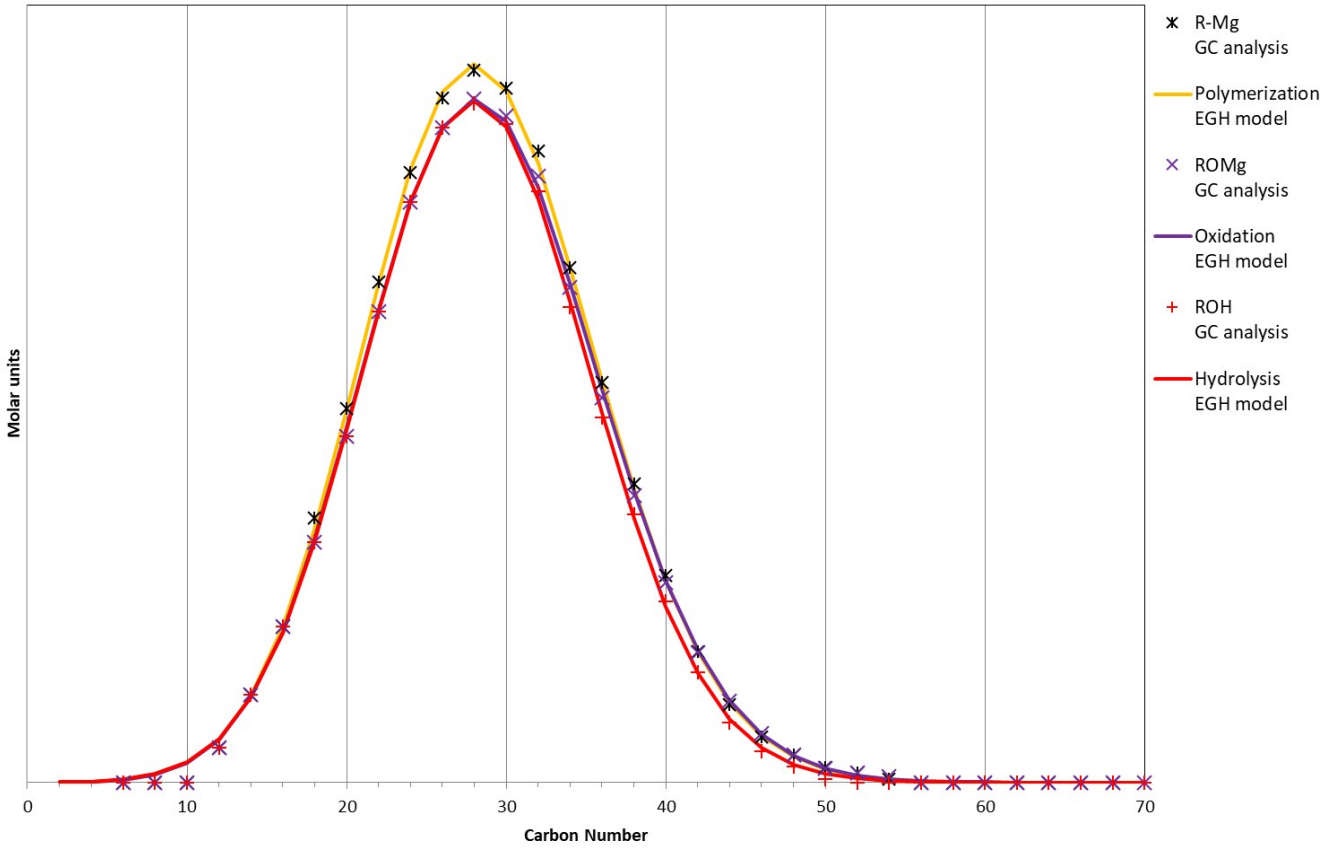


Figure S4-2c Distributions (graphics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 2 Table 3.

Table S4-2 Distributions (numerics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 2 Table 3.

Step	Polymerisation	Oxidation	Hydrolysis
Distribution sum of GC peaks	***R***-Mg ROH + RCHO + RH	R-***O***-Mg ROH + 2 RCHO	R-O-***H*** ROH
Step efficiency relative area of EGH fitting		**96.4%**	**96.9%**
R^2 of EGH fitting	0.9996	0.9996	0.9997
Mn (Carbon number) of EGH fitting	**28.60**	28.70	28.35
Dispersity of EGH fitting	**1.06**	1.07	1.06
Dispersity awaited for a Poisson distribution of same Mn	1.063	1.062	1.063
Skewness of EGH fitting	0.167	0.165	0.100
Skewness awaited for a Poisson distribution of same Mn	0.280	0.279	0.281

S4 continuing, Entry 3 Table 3.

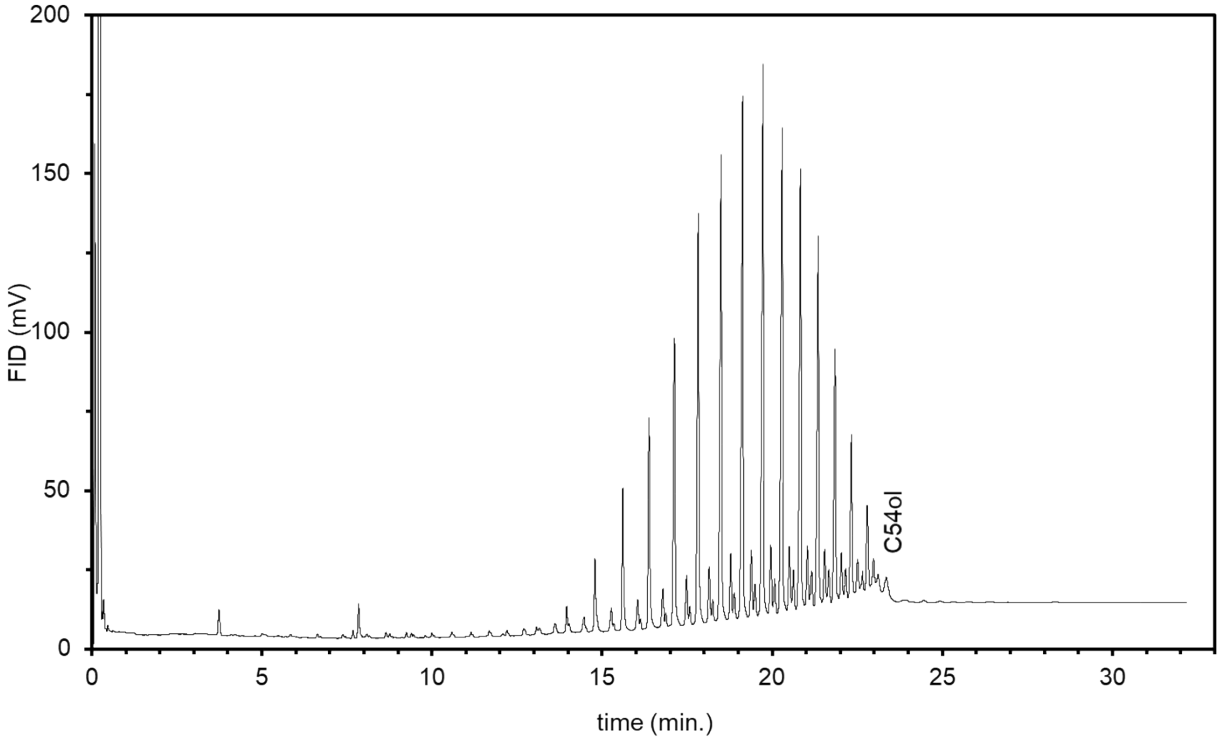


Figure S4-3a Raw signal Gas Chromatography analysis Entry 3 Table 3.

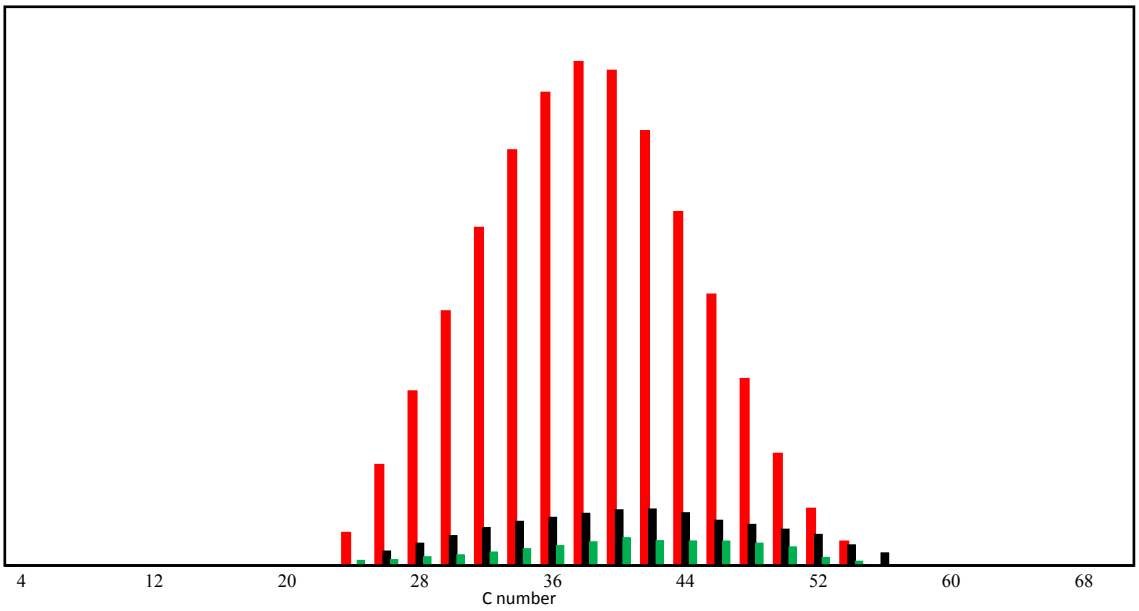


Figure S4-3b Distributions of alcohols ROH (red), hydrocarbons RH (black) and aldehydes RCHO (green). Molar amounts calculated from the GC analysis of Entry 3 Table 3.

S4 continuing, Entry 3 Table 3.

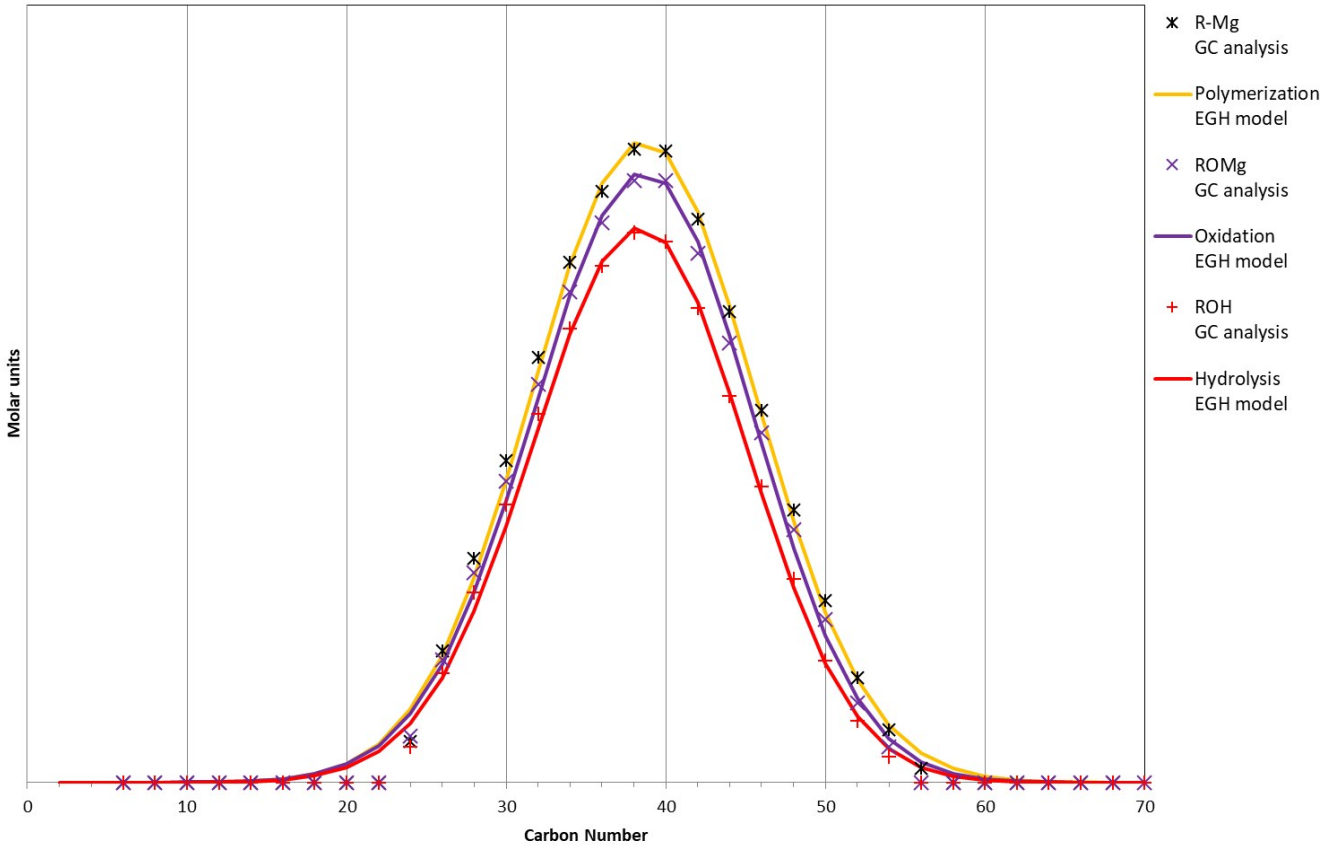


Figure S4-3c Distributions (graphics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 3 Table 3.

Table S4-3 Distributions (numerics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 3 Table 3.

Step	Polymerisation	Oxidation	Hydrolysis
Distribution sum of GC peaks	***R*-Mg** ROH + RCHO + RH	R-***O*-Mg** ROH + 2 RCHO	R-O-***H*** ROH
Step efficiency relative area of EGH fitting		**93.1%**	**88.9%**
R^2 of EGH fitting	0.9969	0.9960	0.9964
Mn (Carbon number) of EGH fitting	**38.60**	38.42	38.25
Dispersity of EGH fitting	**1.03**	1.03	1.03
Dispersity awaited for a Poisson distribution of same Mn	1.048	1.048	1.048
Skewness of EGH fitting	0.000	-0.066	-0.045
Skewness awaited for a Poisson distribution of same Mn	0.237	0.238	0.238

S4 continuing, Entry 3 Table 3.

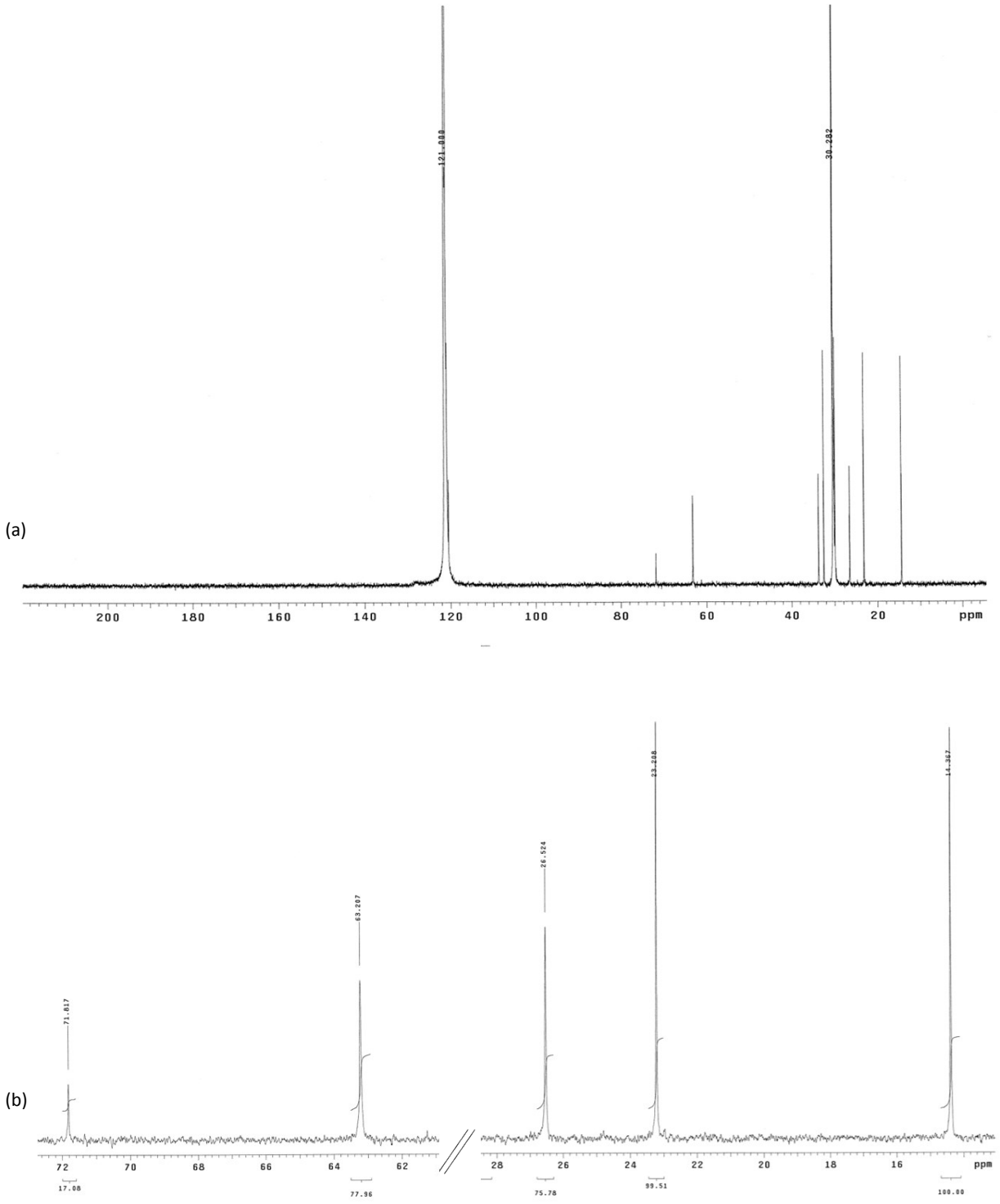


Figure S4-3d ^{13}C NMR spectrum (solvent $Cl_2C{=}CCl_2$, in the presence of $Cr(acac)_3$, D_2O capillary lock, 376 K, ether residue at *ca*. 70 ppm) of Entry 3 Table 3. Full range (a) and selected zone for integration (b). ROH % = 87.9 %

S4 continuing, Entry 4 Table 3.

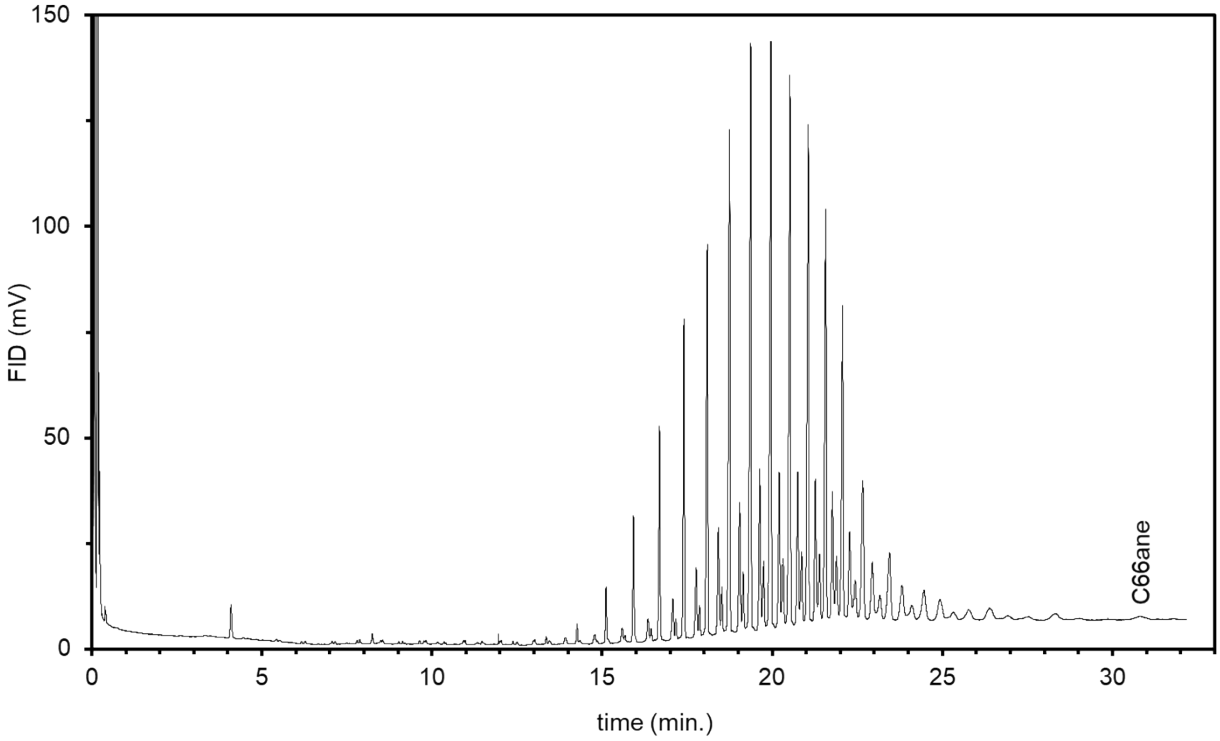


Figure S4-4a Raw signal Gas Chromatography analysis Entry 4 Table 3.

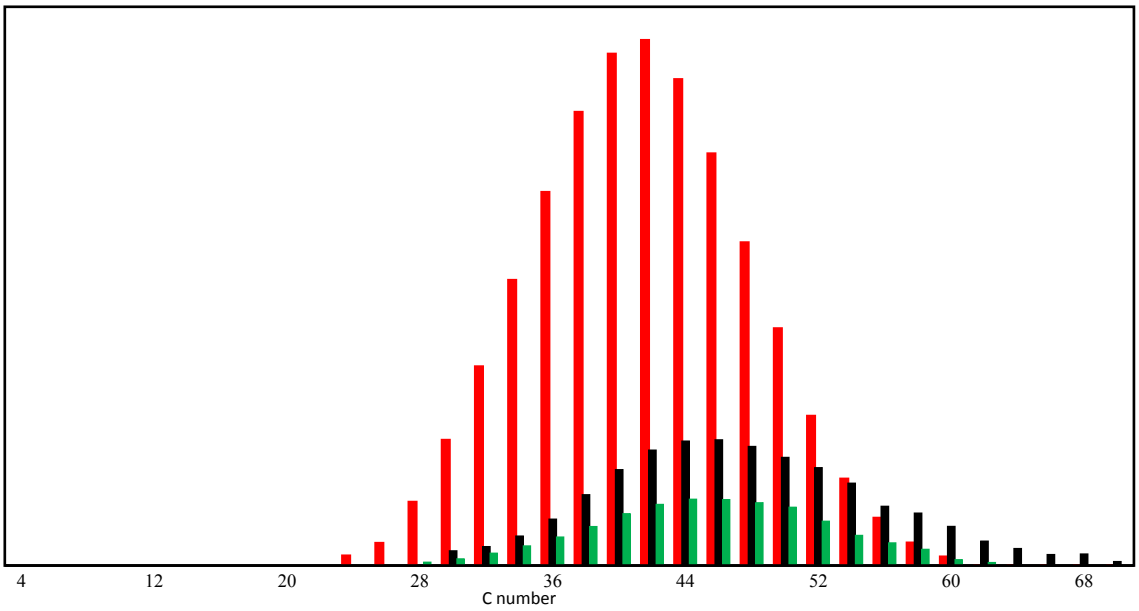


Figure S4-4b Distributions of alcohols ROH (red), hydrocarbons RH (black) and aldehydes RCHO (green). Molar amounts calculated from the GC analysis of Entry 4 Table 3.

S4 continuing, Entry 4 Table 3.

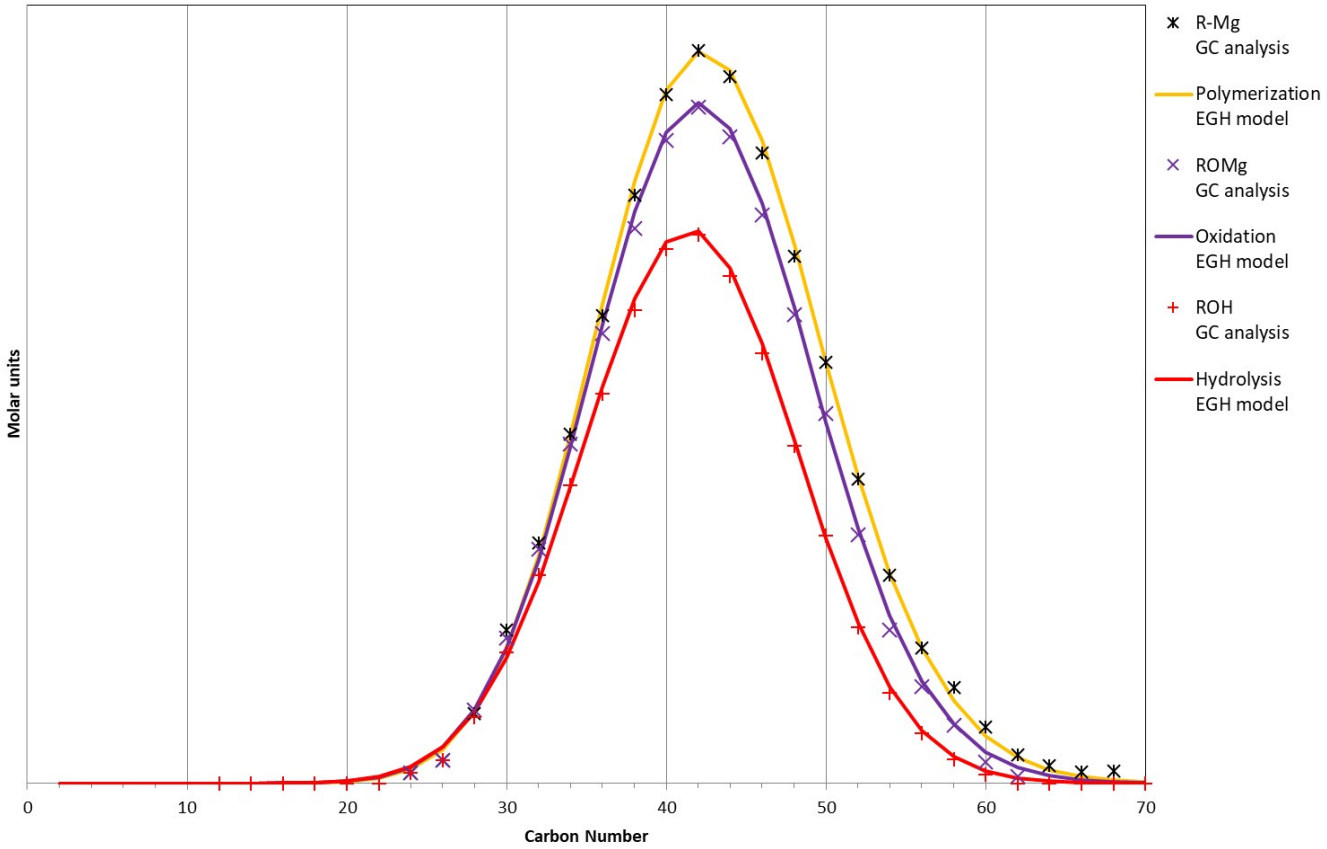


Figure S4-4c Distributions (graphics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 4 Table 3.

Table S4-4 Distributions (numerics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 4 Table 3.

Step	Polymerisation	Oxidation	Hydrolysis
Distribution sum of GC peaks	***R*-Mg** ROH + RCHO + RH	R-***O*-Mg** ROH + 2 RCHO	R-O-***H*** ROH
Step efficiency relative area of EGH fitting		**91.0%**	**78.4%**
R^2 of EGH fitting	0.9989	0.9985	0.9988
Mn (Carbon number) of EGH fitting	**42.93**	42.43	41.51
Dispersity of EGH fitting	**1.03**	1.03	1.03
Dispersity awaited for a Poisson distribution of same Mn	1.043	1.044	1.045
Skewness of EGH fitting	0.168	0.108	0.018
Skewness awaited for a Poisson distribution of same Mn	0.224	0.225	0.228

S4 continuing, Entry 4 Table 3.

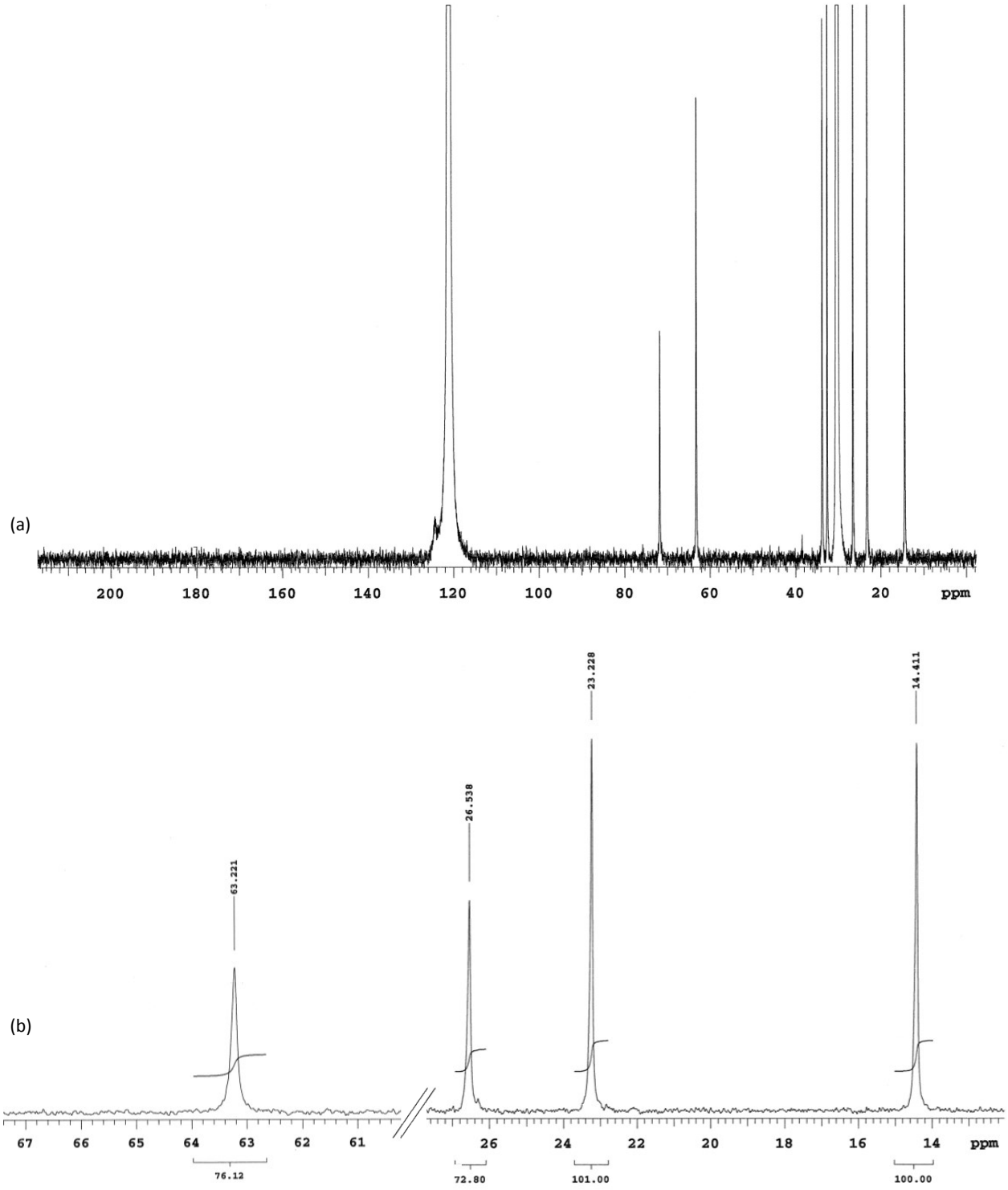


Figure S4-4d ^{13}C NMR spectrum (solvent $Cl_2C{=}CCl_2$, in the presence of $Cr(acac)_3$, D_2O capillary lock, 368 K, ether residue at *ca*. 70 ppm) of Entry 4 Table 3. Full range (a) and selected zone for integration (b). ROH % = 86.0 %

S4 continuing, Entry 5 Table 3.

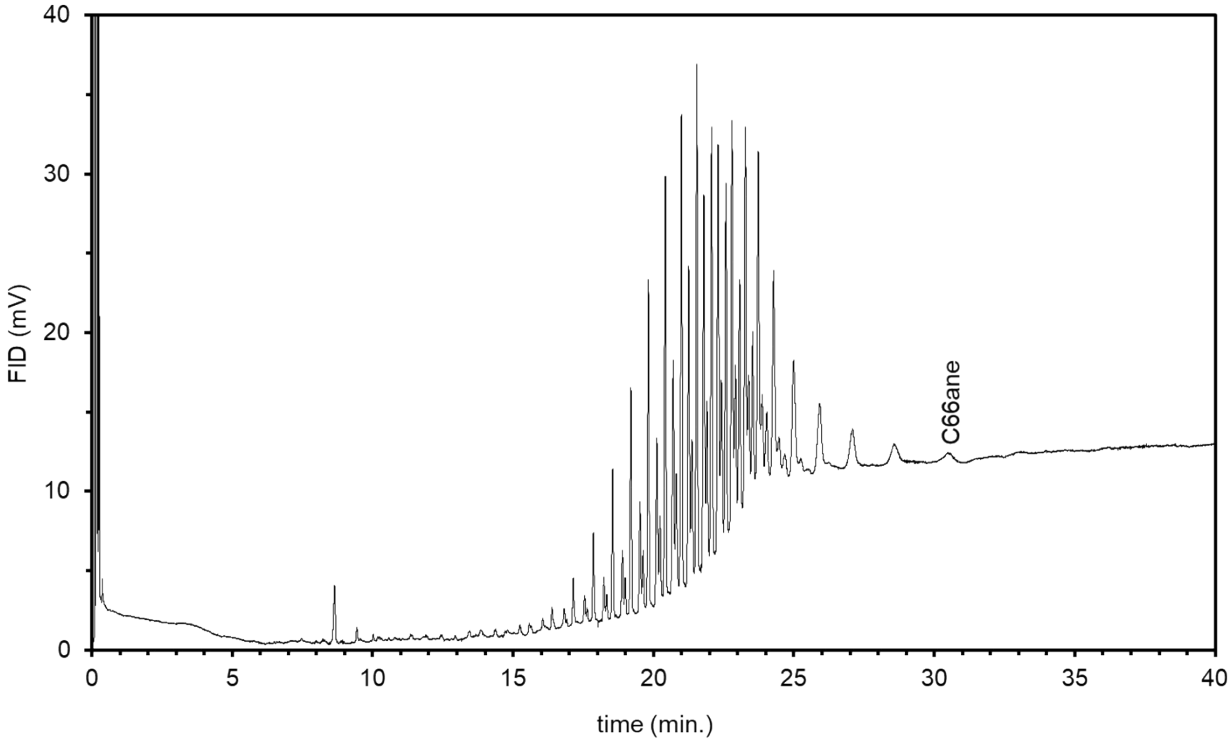


Figure S4-5a Raw signal Gas Chromatography analysis Entry 5 Table 3.

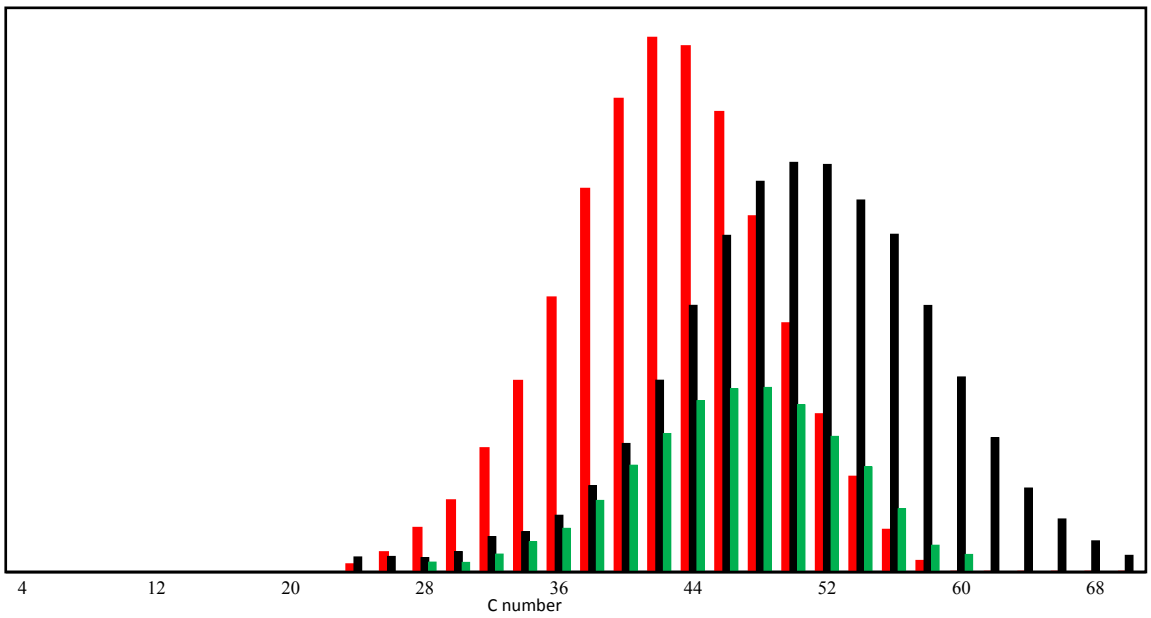


Figure S4-5b Distributions of alcohols ROH (red), hydrocarbons RH (black) and aldehydes RCHO (green). Molar amounts calculated from the GC analysis of Entry 5 Table 3.

S5 continuing, Entry 5 Table 3.

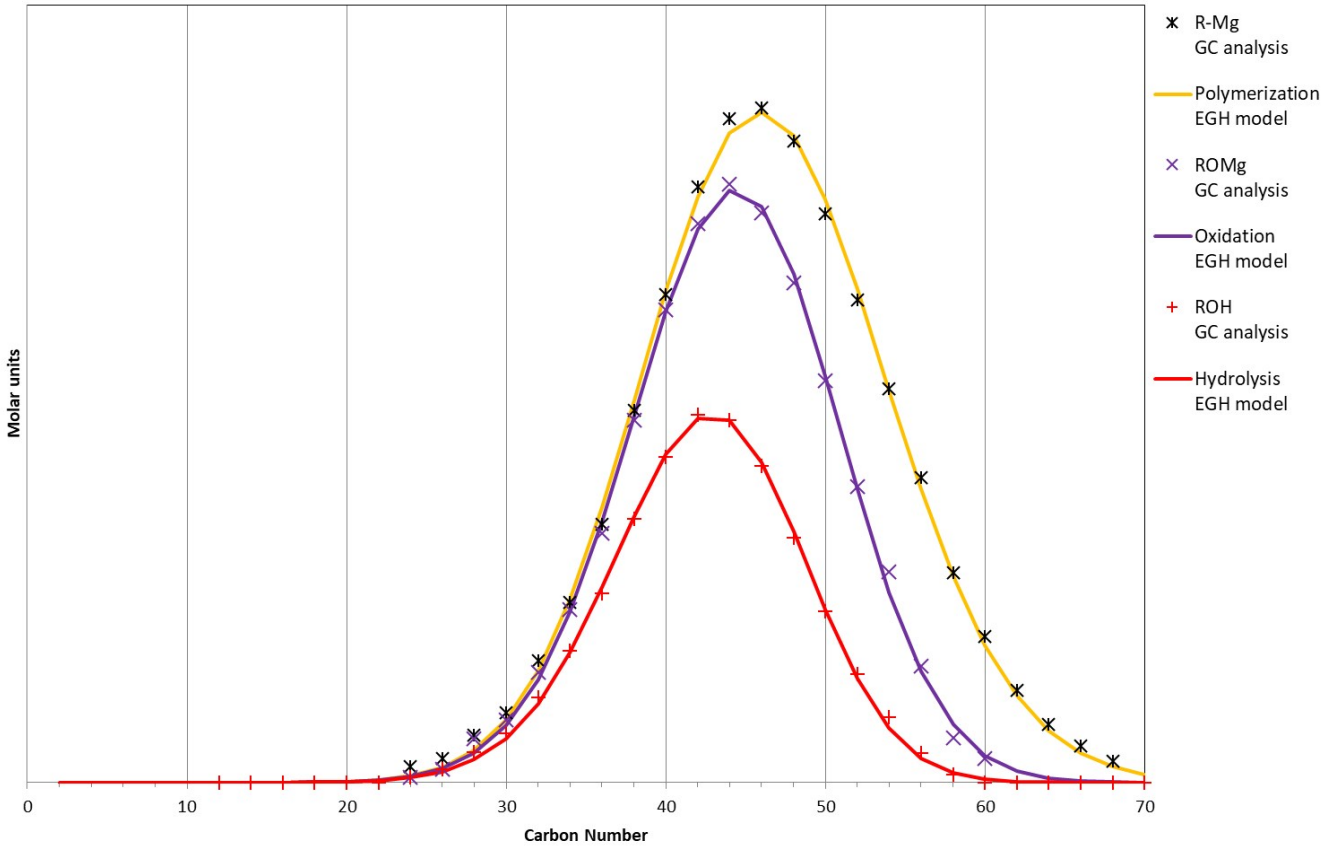


Figure S4-5c Distributions (graphics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 5 Table 3.

Table S4-5 Distributions (numerics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 5 Table 3.

Step	Polymerisation	Oxidation	Hydrolysis
Distribution sum of GC peaks	***R***-Mg ROH + RCHO + RH	R-***O***-Mg ROH + 2 RCHO	R-O-***H*** ROH
Step efficiency relative area of EGH fitting		**75.0%**	**57.1%**
R^2 of EGH fitting	0.9984	0.9982	0.9986
Mn (Carbon number) of EGH fitting	**46.37**	44.17	42.46
Dispersity of EGH fitting	**1.03**	1.02	1.02
Dispersity awaited for a Poisson distribution of same Mn	1.040	1.042	1.044
Skewness of EGH fitting	0.116	-0.083	-0.148
Skewness awaited for a Poisson distribution of same Mn	0.215	0.220	0.225

S4 continuing, Entry 6 Table 4.

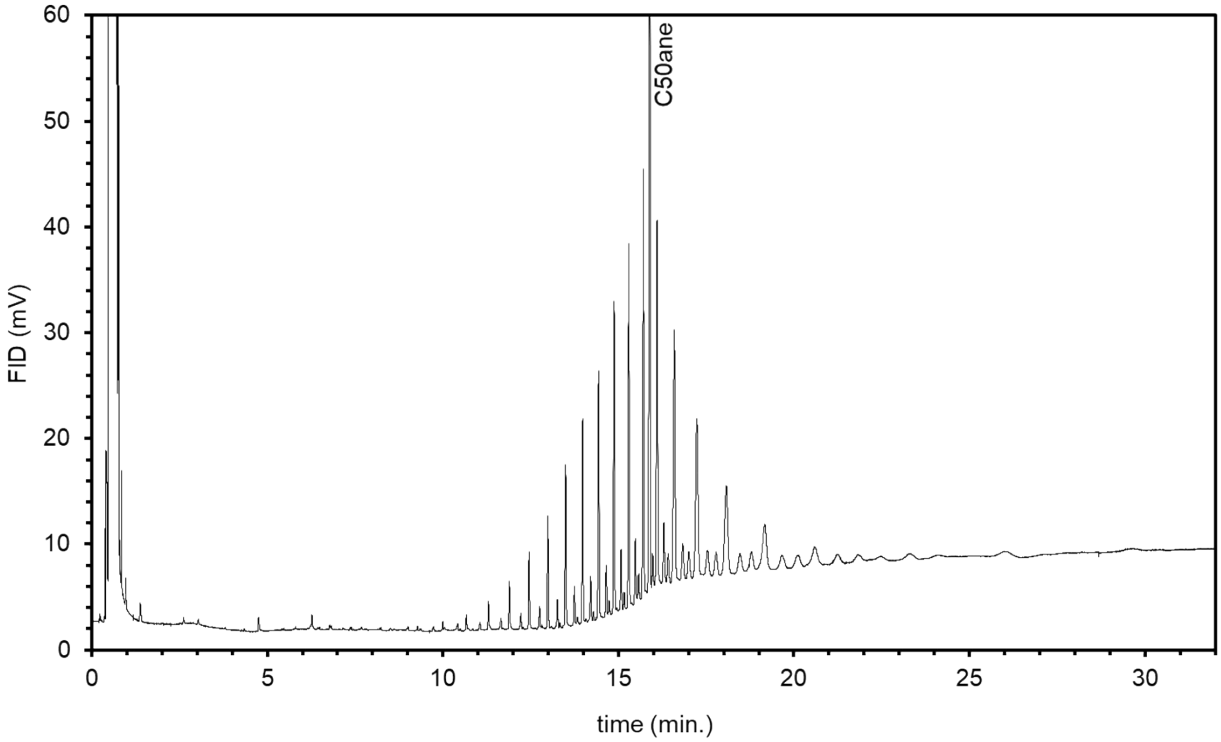


Figure S4-6a Raw signal Gas Chromatography analysis Entry 6 Table 4.

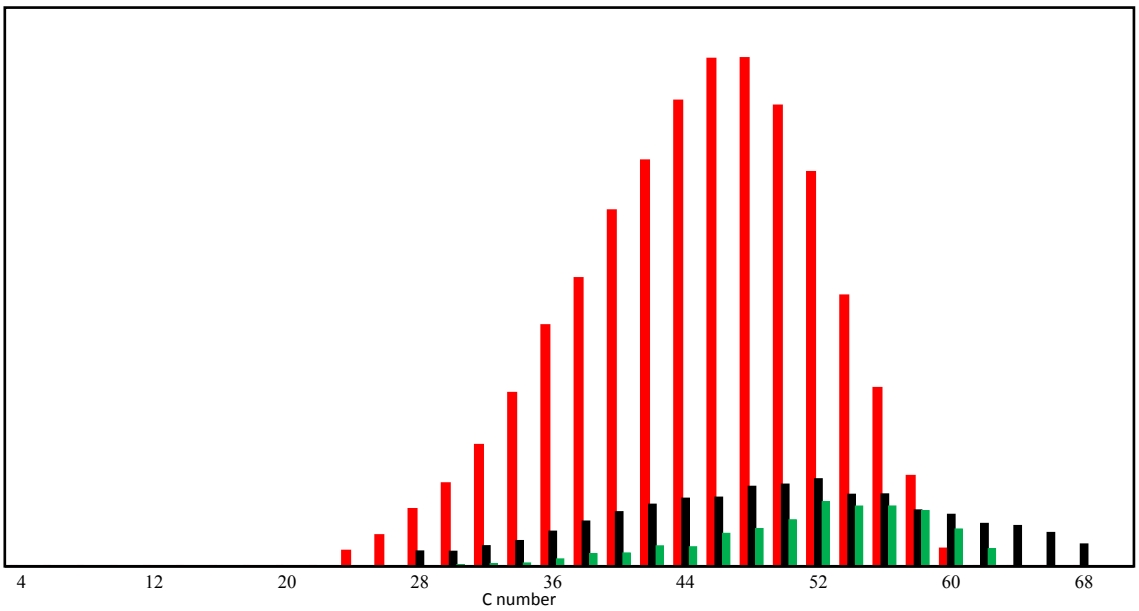


Figure S4-6b Distributions of alcohols ROH (red), hydrocarbons RH (black) and aldehydes RCHO (green). Molar amounts calculated from the GC analysis of Entry 6 Table 4.

S4 continuing, Entry 6 Table 4.

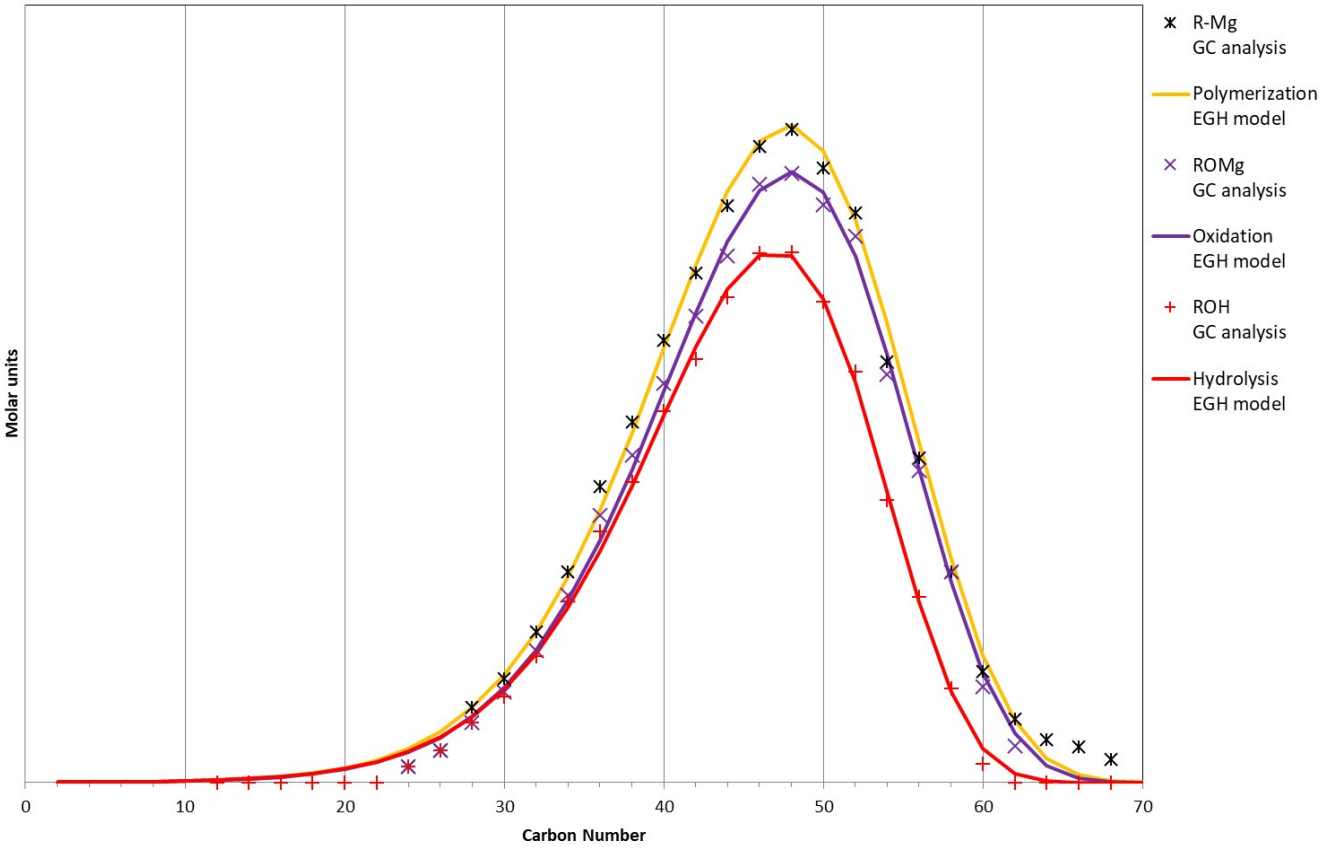


Figure S4-6c Distributions (graphics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 6 Table 4.

Table S4-6 Distributions (numerics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 6 Table 4.

Step	Polymerisation	Oxidation	Hydrolysis
Distribution sum of GC peaks	***R***-Mg ROH + RCHO + RH	R-***O***-Mg ROH + 2 RCHO	R-O-***H*** ROH
Step efficiency relative area of EGH fitting		**90.6%**	**82.7%**
R^2 of EGH fitting	0.9952	0.9965	0.9972
Mn (Carbon number) of EGH fitting	**45.69**	45.73	44.36
Dispersity of EGH fitting	**1.03**	1.03	1.03
Dispersity awaited for a Poisson distribution of same Mn	1.041	1.041	1.042
Skewness of EGH fitting	-0.517	-0.564	-0.672
Skewness awaited for a Poisson distribution of same Mn	0.216	0.216	0.220

S4 continuing, Entry 6 Table 4.

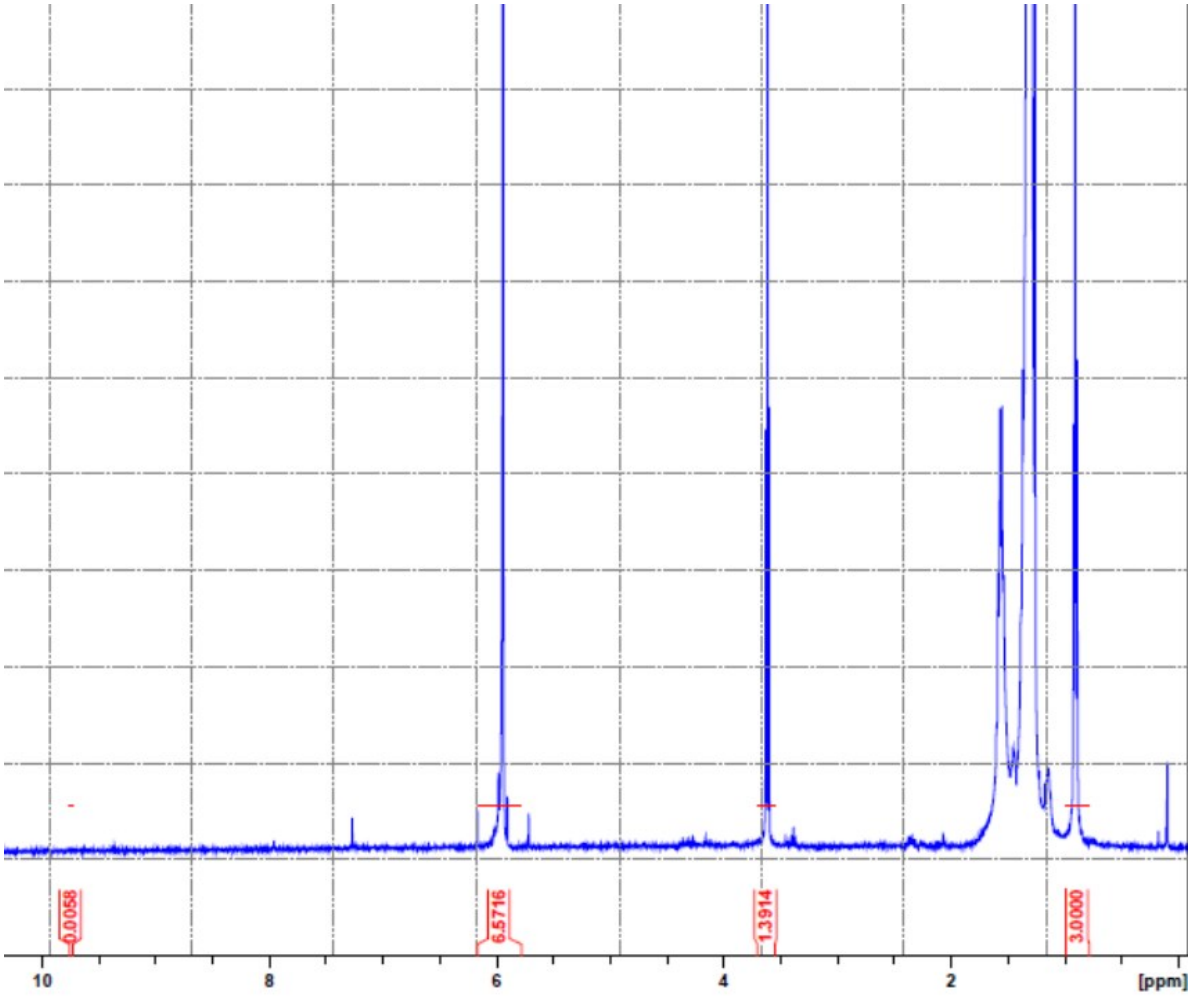


Figure S4-6d ^{1}H NMR spectrum (solvent $C_2D_2Cl_4$, T = 383 K) of Entry 6 Table 4. ROH % = 82.1 %

S4 continuing, Entry 7 Table 4.

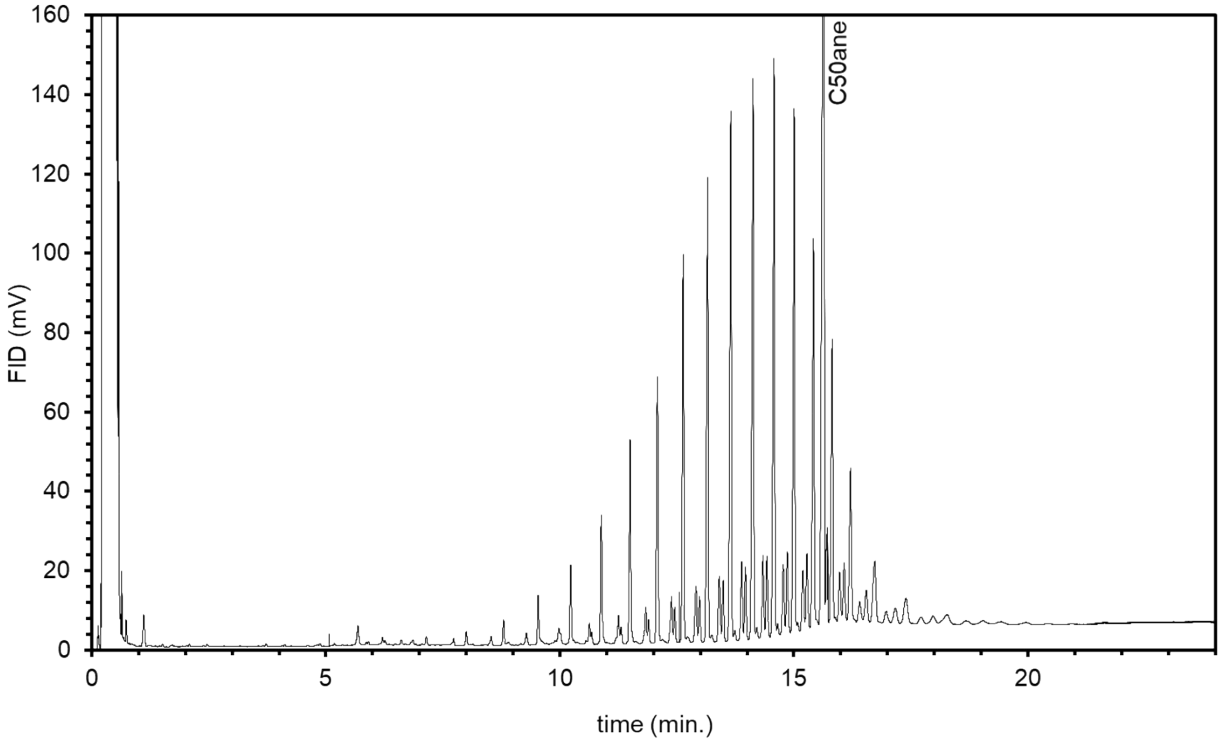


Figure S4-7a Raw signal Gas Chromatography analysis Entry 7 Table 4.

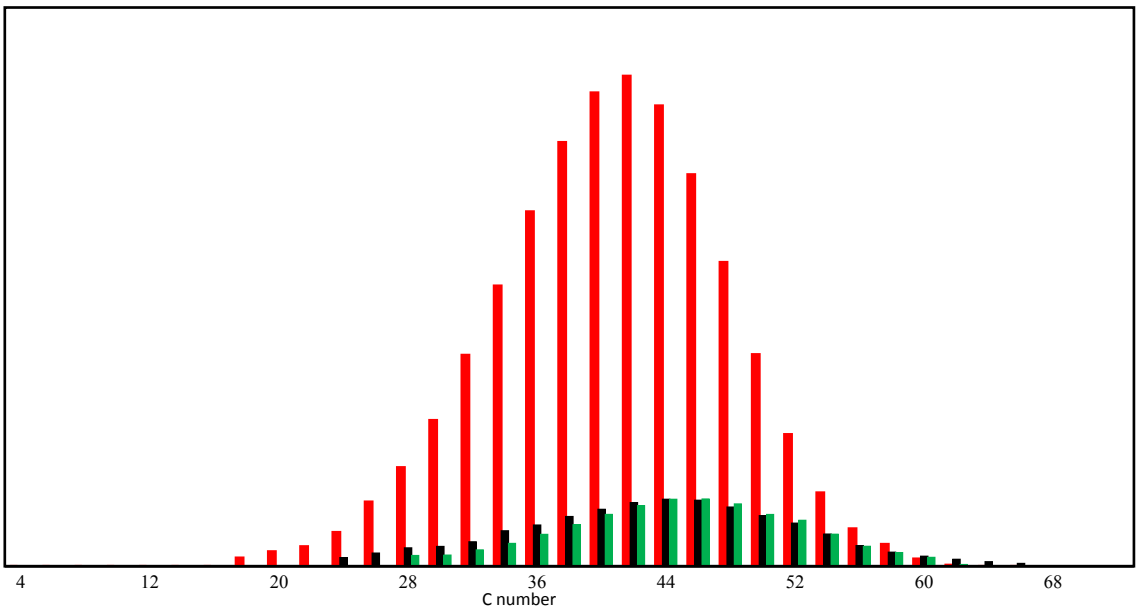


Figure S4-7b Distributions of alcohols ROH (red), hydrocarbons RH (black) and aldehydes RCHO (green). Molar amounts calculated from the GC analysis of Entry 7 Table 4.

S4 continuing, Entry 7 Table 4.

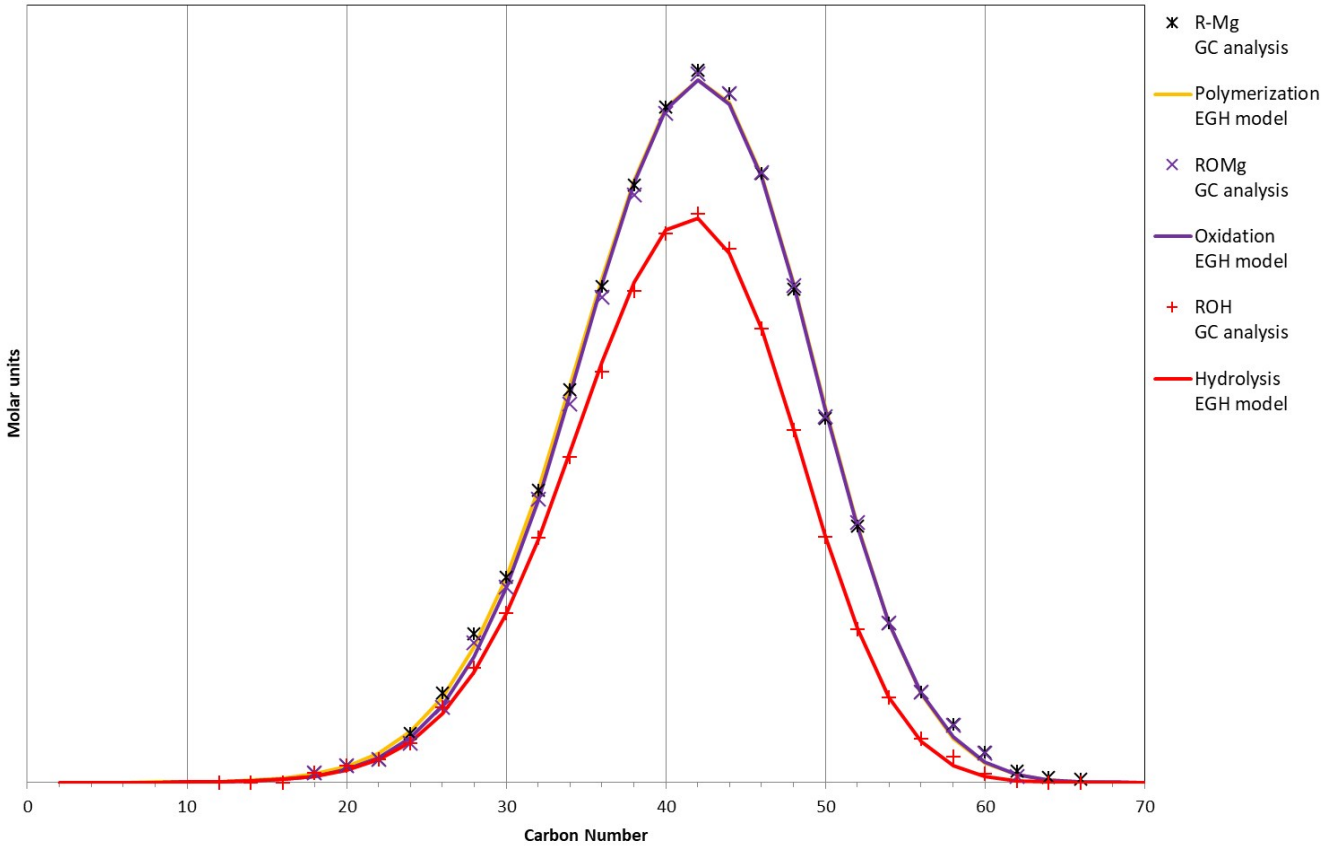


Figure S4-7c Distributions (graphics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 7 Table 4.

Table S4-7 Distributions (numerics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 7 Table 4.

Step	Polymerisation	Oxidation	Hydrolysis
Distribution sum of GC peaks	***R***-Mg ROH + RCHO + RH	R-***O***-Mg ROH + 2 RCHO	R-O-***H*** ROH
Step efficiency relative area of EGH fitting		**98.8%**	**77.5%**
R^2 of EGH fitting	0.9993	0.9992	0.9995
Mn (Carbon number) of EGH fitting	**41.37**	41.52	40.66
Dispersity of EGH fitting	**1.03**	1.03	1.03
Dispersity awaited for a Poisson distribution of same Mn	1.045	1.045	1.046
Skewness of EGH fitting	-0.205	-0.166	-0.243
Skewness awaited for a Poisson distribution of same Mn	0.228	0.228	0.230

S4 continuing, Entry 7 Table 4.

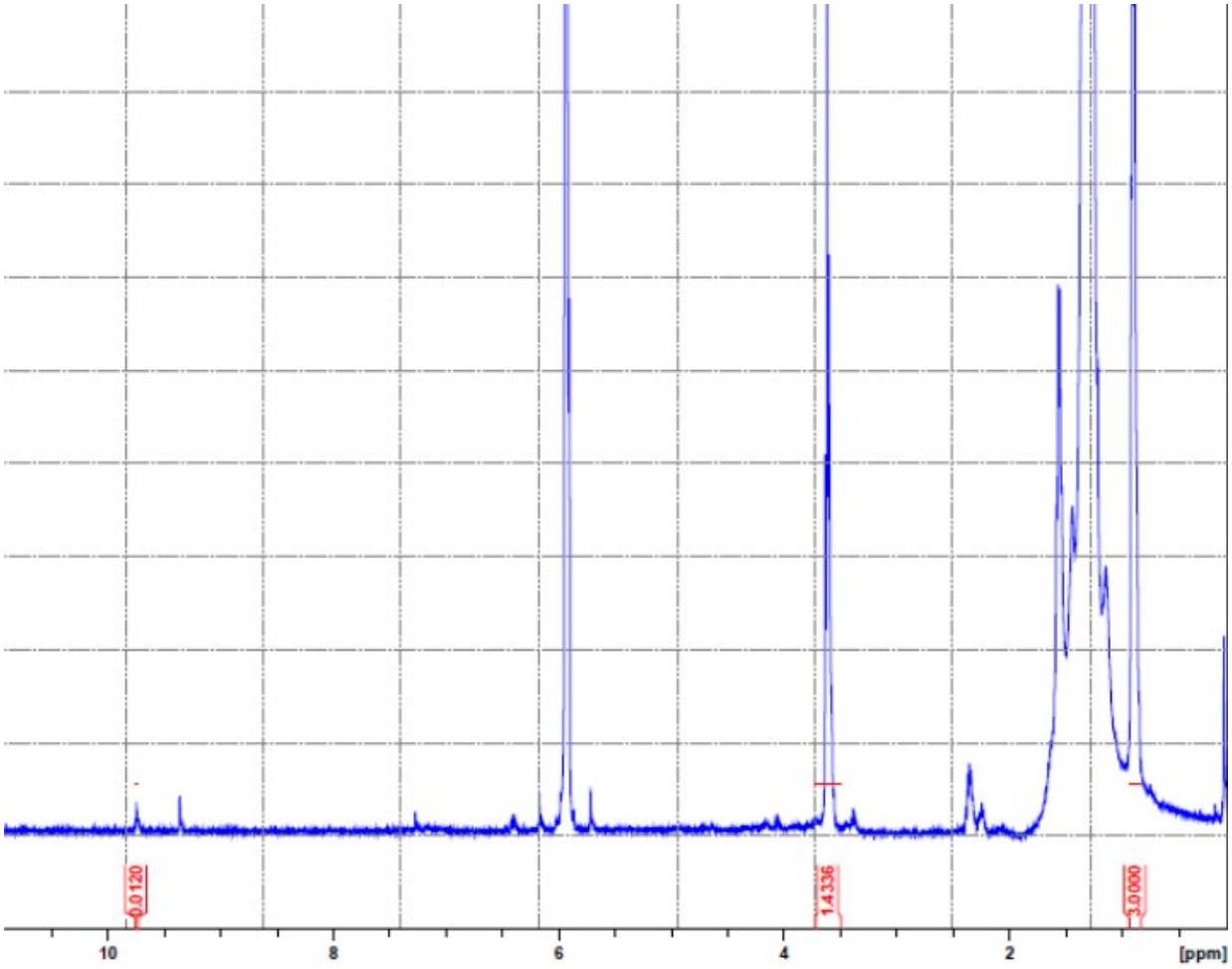


Figure S4-7d ^{1}H NMR spectrum (solvent $C_2D_2Cl_4$, T = 383 K) of Entry 7 Table 4. ROH % = 83.5 %

S4 continuing, Entry 8 Table 4.

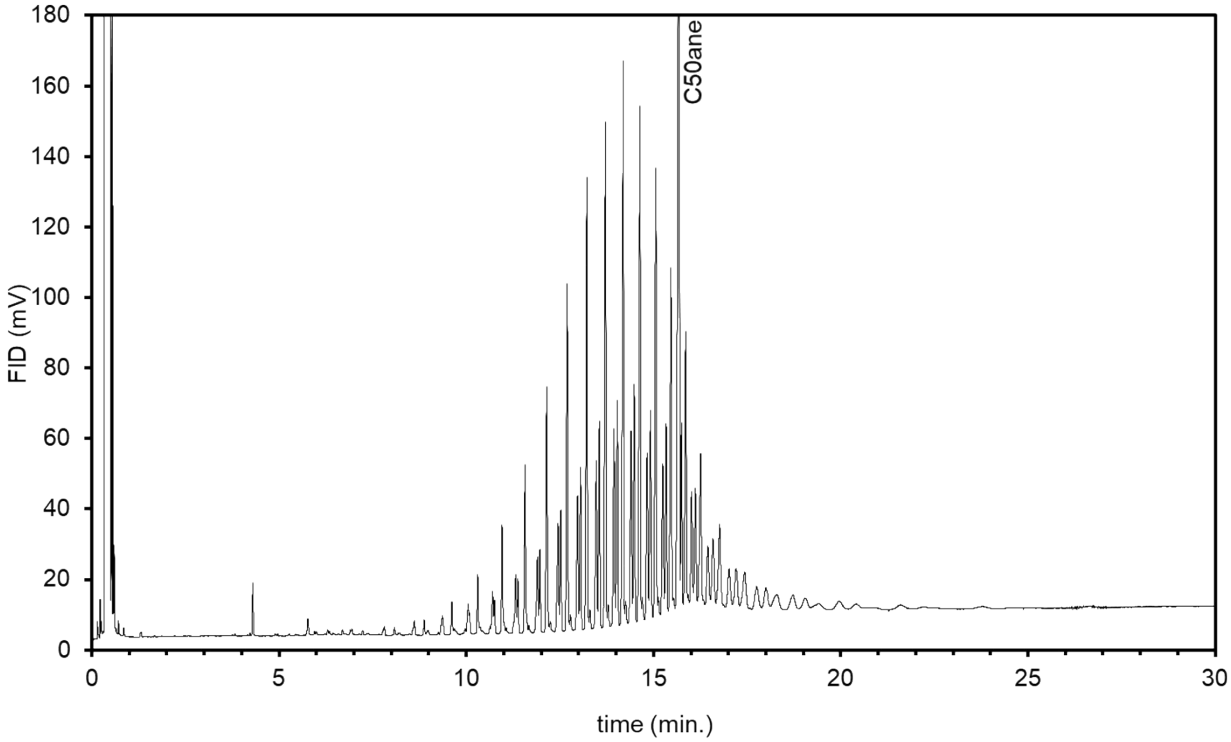


Figure S4-8a Raw signal Gas Chromatography analysis Entry 8 Table 4.

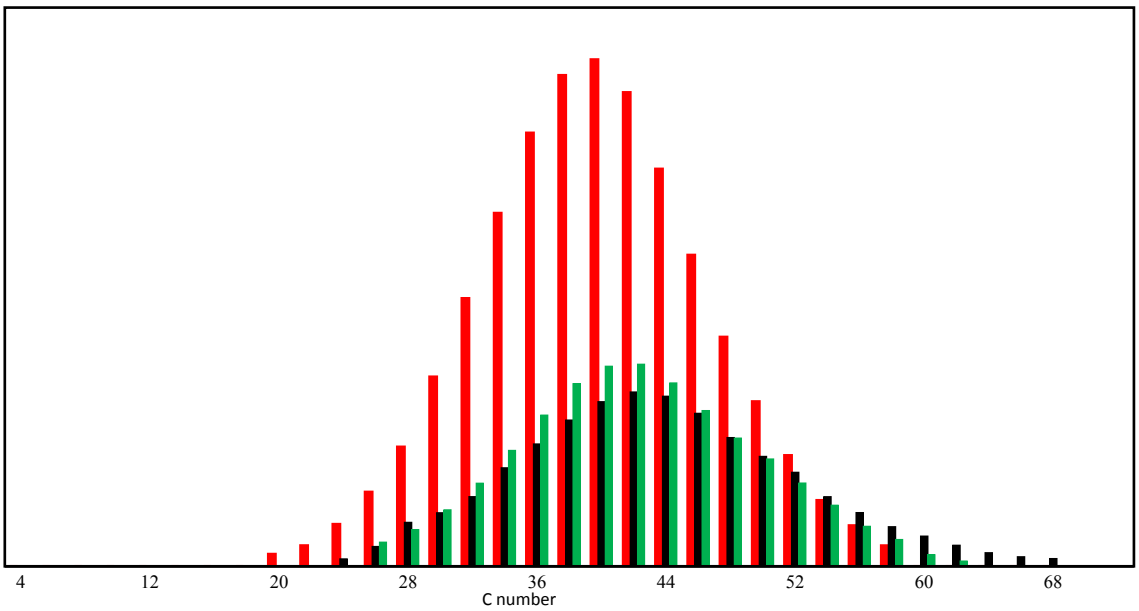


Figure S4-8b Distributions of alcohols ROH (red), hydrocarbons RH (black) and aldehydes RCHO (green). Molar amounts calculated from the GC analysis of Entry 8 Table 4.

S4 continuing, Entry 8 Table 4.

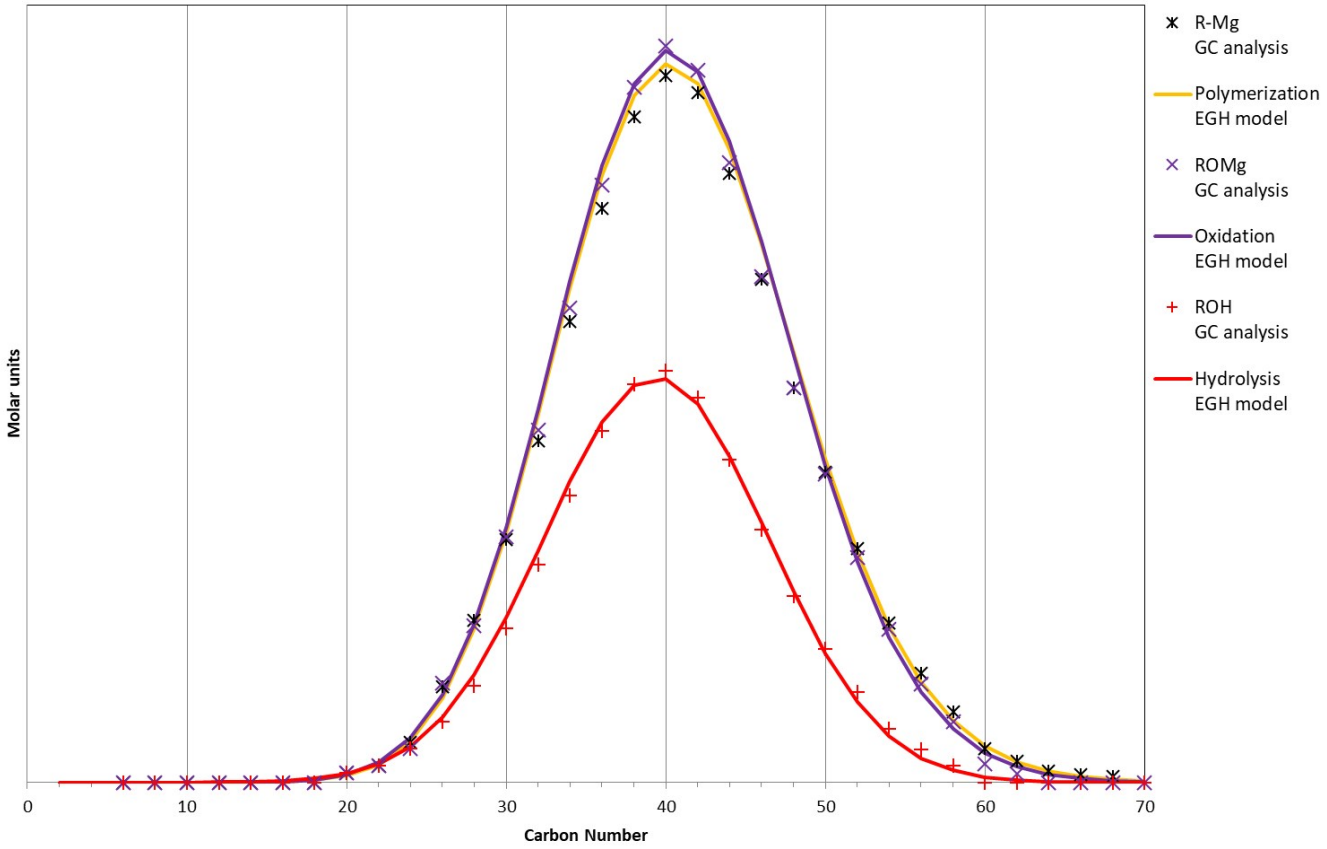


Figure S4-8c Distributions (graphics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 8 Table 4.

Table S4-8 Distributions (numerics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 8 Table 4.

Step	Polymerisation	Oxidation	Hydrolysis
Distribution sum of GC peaks	***R***-Mg ROH + RCHO + RH	R-***O***-Mg ROH + 2 RCHO	R-O-***H*** ROH
Step efficiency relative area of EGH fitting		**100.3%**	**53.0%**
R^2 of EGH fitting	0.9950	0.9964	0.9969
Mn (Carbon number) of EGH fitting	**41.03**	40.80	39.40
Dispersity of EGH fitting	**1.03**	1.03	1.03
Dispersity awaited for a Poisson distribution of same Mn	1.045	1.045	1.047
Skewness of EGH fitting	0.222	0.164	0.000
Skewness awaited for a Poisson distribution of same Mn	0.229	0.230	0.234

S4 continuing, Entry 8 Table 4.

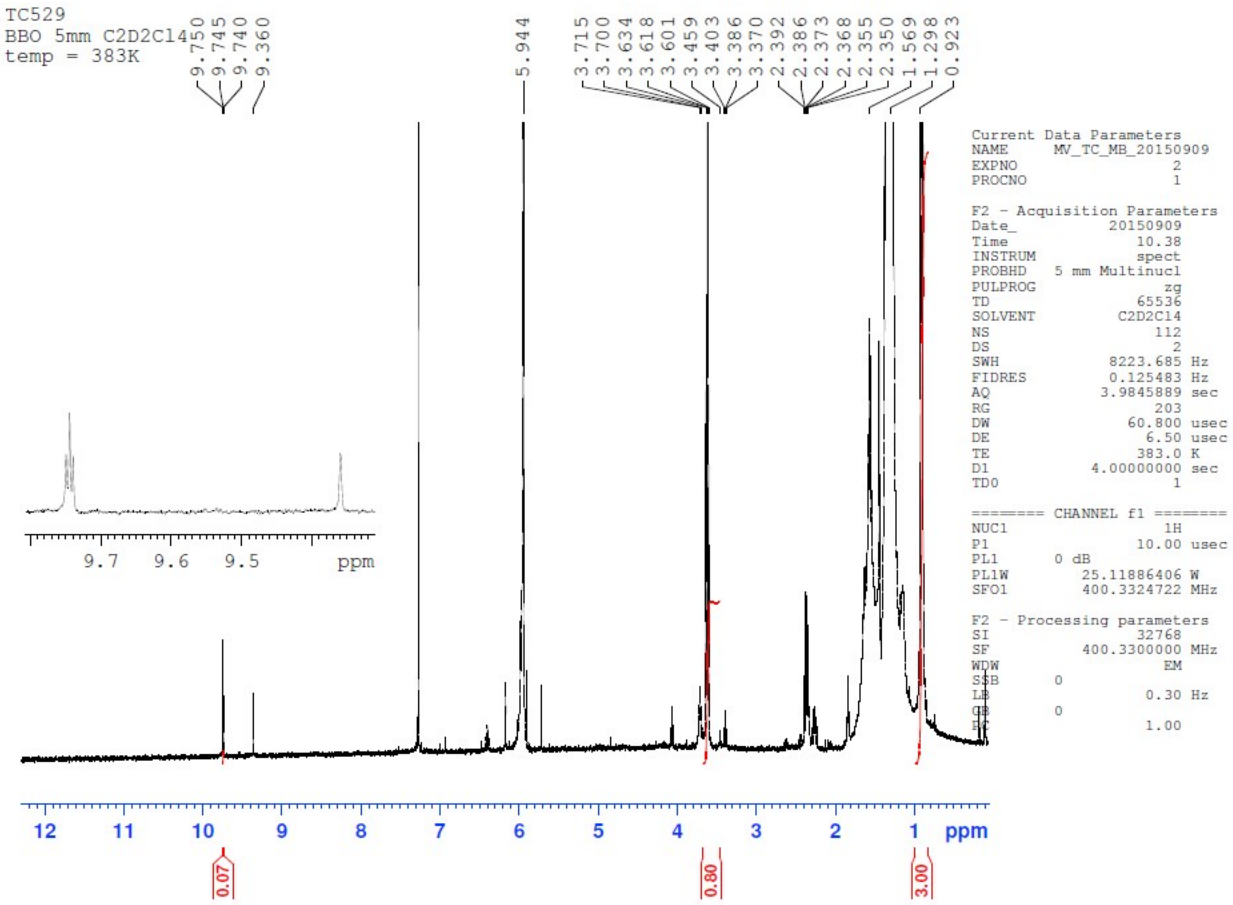


Figure S4-8d ^{1}H NMR spectrum (solvent $C_2D_2Cl_4$, T = 383 K) of Entry 8 Table 4. ROH % = 57.1 %

S4 continuing, Entry 9 Table 4.

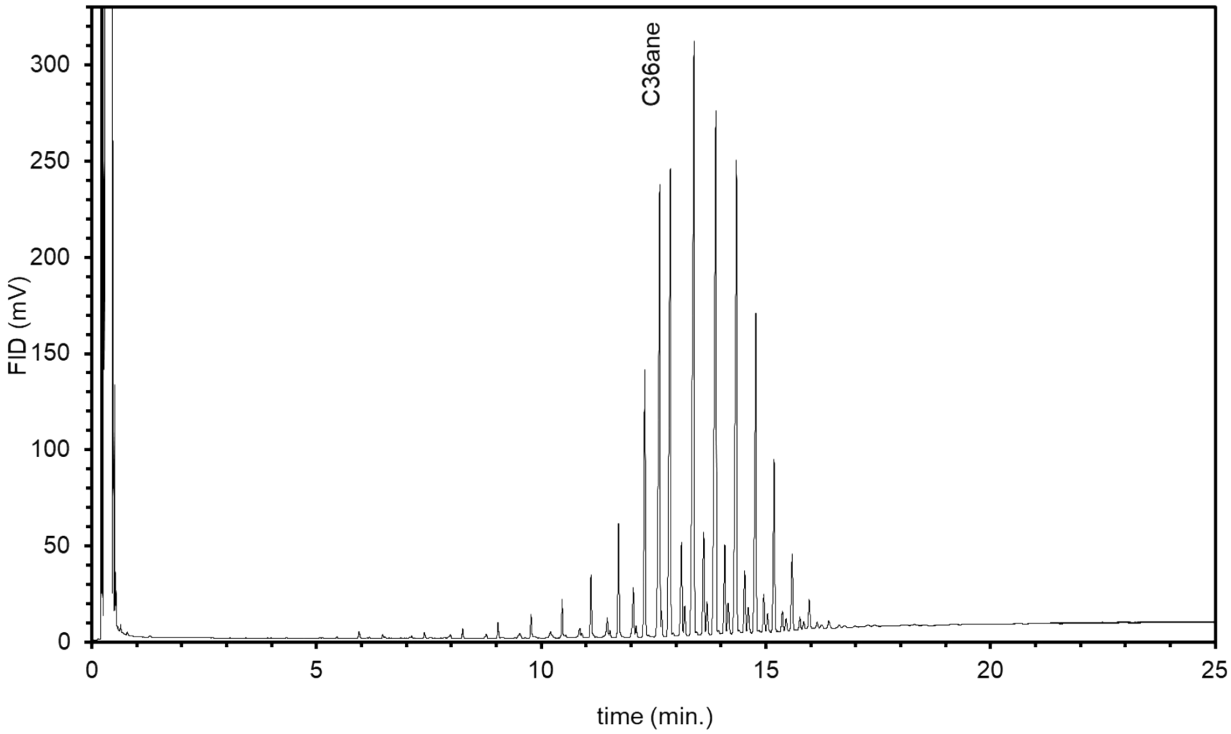


Figure S4-9a Raw signal Gas Chromatography analysis Entry 9 Table 4.

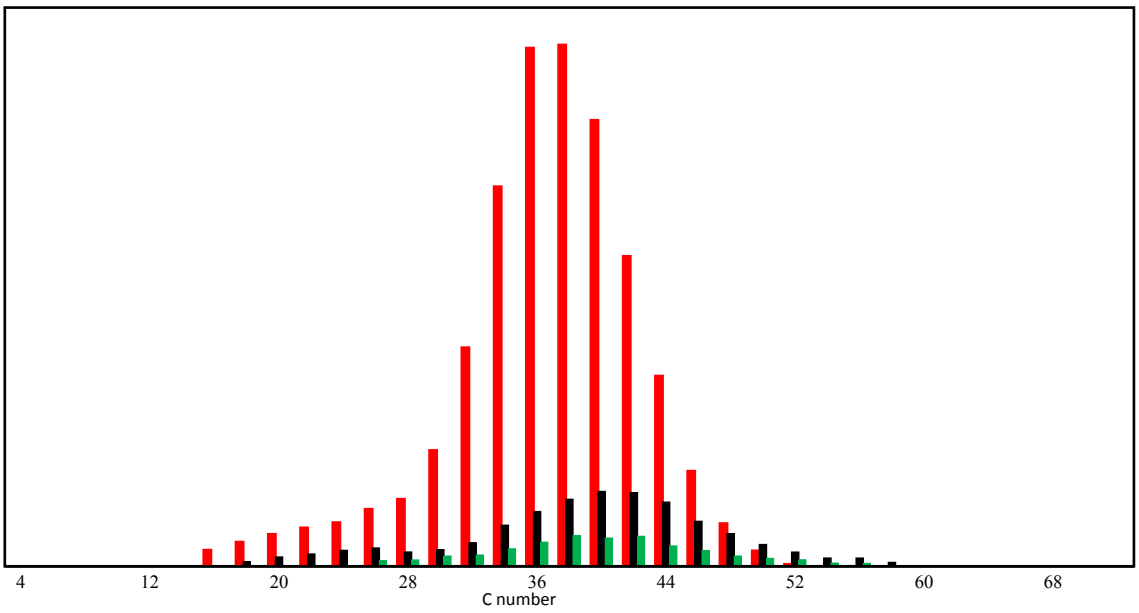


Figure S4-9b Distributions of alcohols ROH (red), hydrocarbons RH (black) and aldehydes RCHO (green). Molar amounts calculated from the GC analysis of Entry 9 Table 3.

S4 continuing, Entry 9 Table 4.

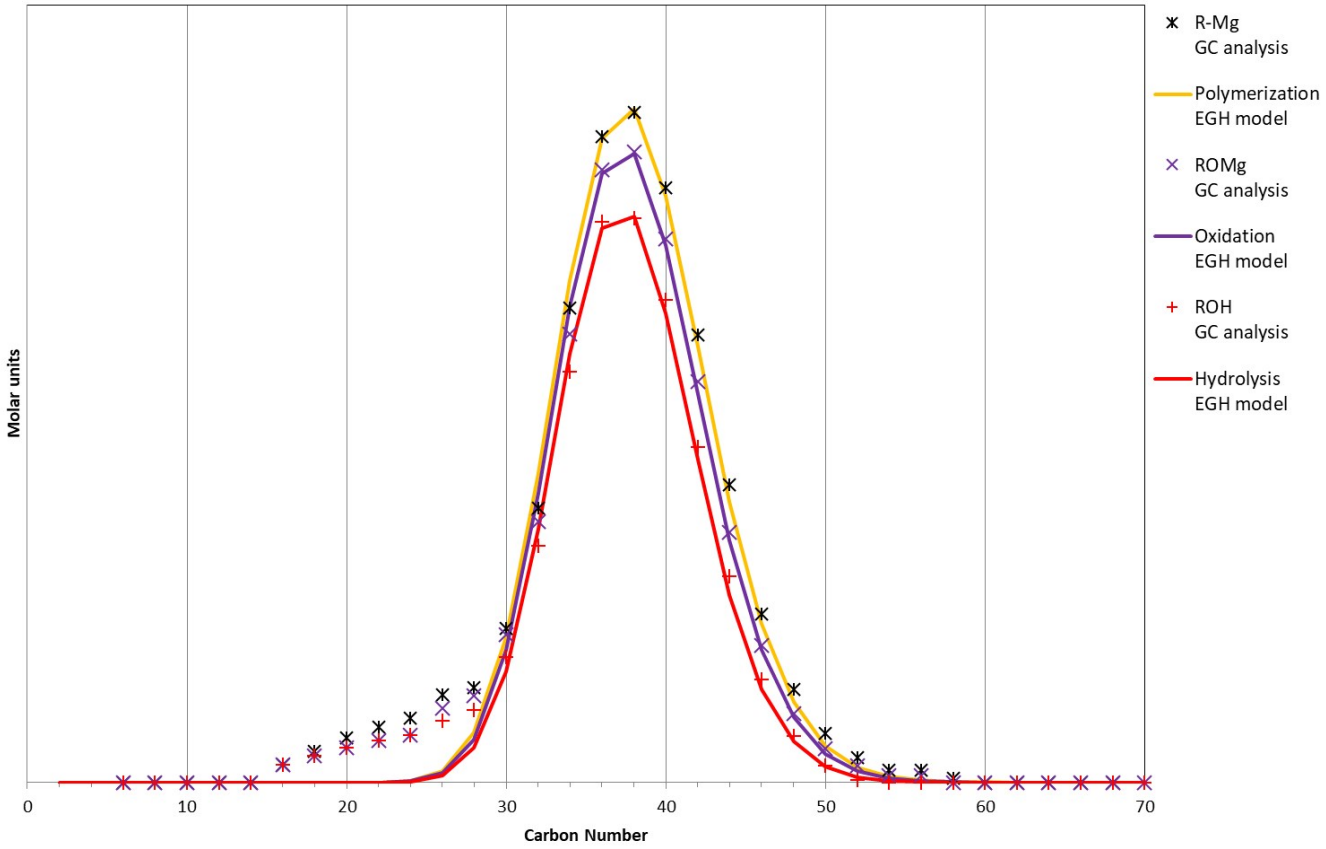


Figure S4-9c Distributions (graphics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 9 Table 4.

Table S4-9 Distributions (numerics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 9 Table 4.

Step	Polymerisation	Oxidation	Hydrolysis
Distribution sum of GC peaks	***R*-Mg** ROH + RCHO + RH	R-***O*-Mg** ROH + 2 RCHO	R-O-***H*** ROH
Step efficiency relative area of EGH fitting		**91.4%**	**85.9%**
R^2 of EGH fitting	0.9800	0.9842	0.9822
Mn (Carbon number) of EGH fitting	**38.13**	37.98	37.72
Dispersity of EGH fitting	**1.02**	1.01	1.01
Dispersity awaited for a Poisson distribution of same Mn	1.048	1.049	1.049
Skewness of EGH fitting	0.291	0.298	0.245
Skewness awaited for a Poisson distribution of same Mn	0.239	0.239	0.240

S4 continuing, Entry 9 Table 4.

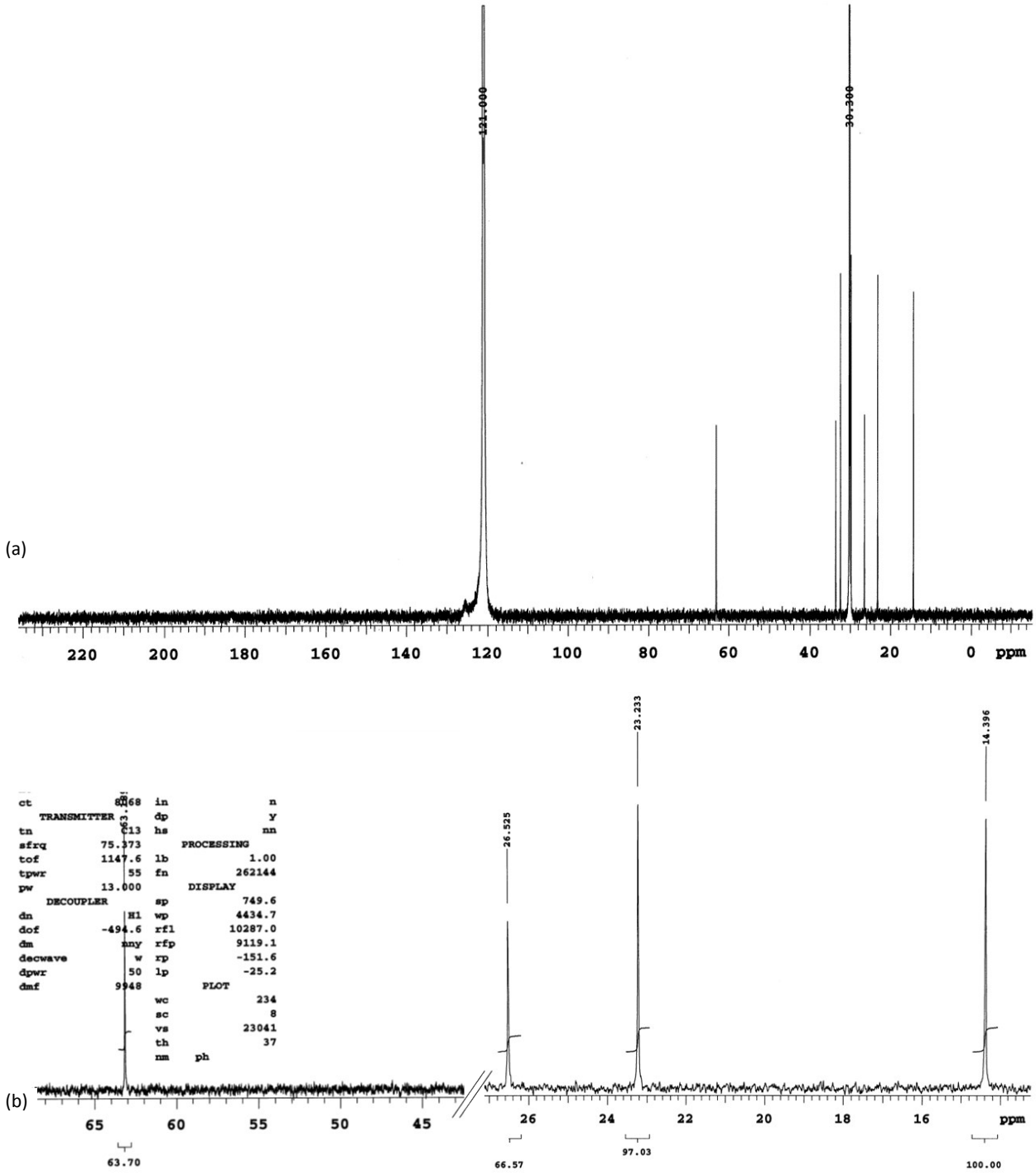


Figure S4-9d ^{13}C NMR spectrum (solvent $Cl_2C{=}CCl_2$, in the presence of $Cr(acac)_3$, D_2O capillary lock, T = 368 K) of Entry 9 Table 4. Full range (a) and selected zone for integration (b). ROH % = 79.3 %

S4 continuing, Entry 9 Table 4.

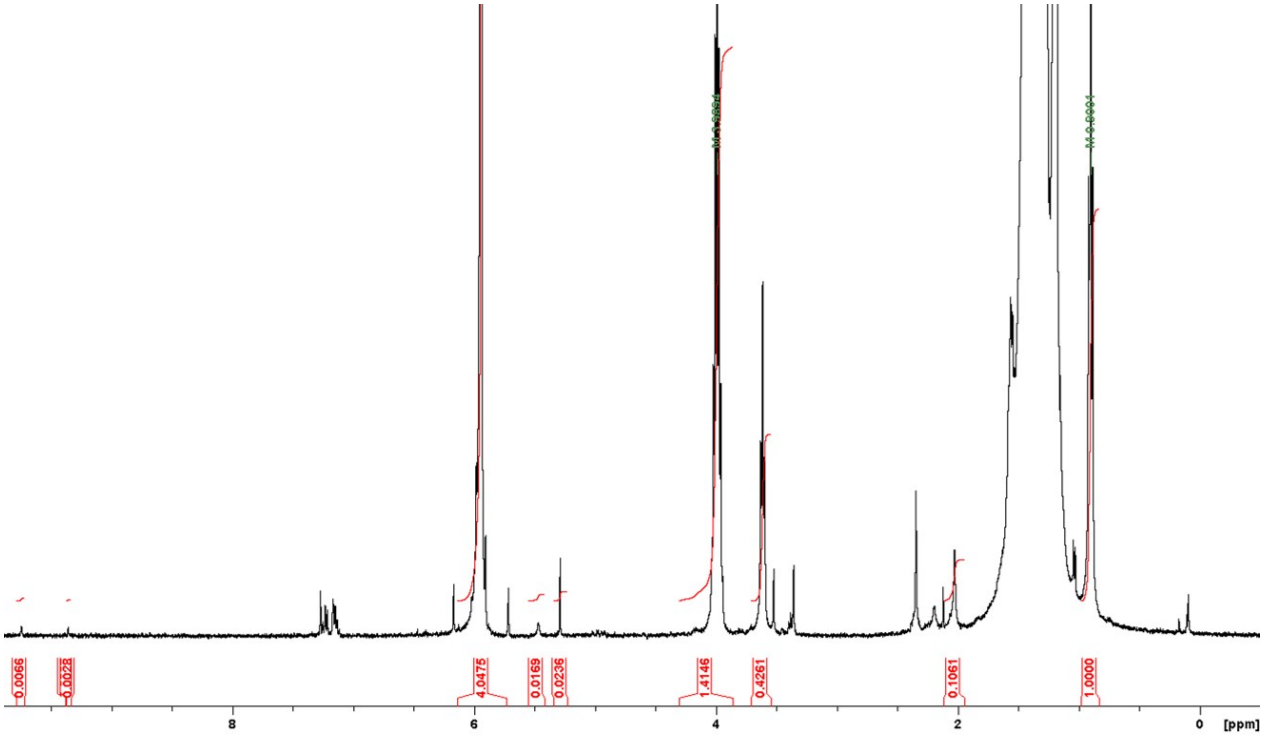


Figure S4-9e ^{1}H NMR spectrum (solvent $C_2D_2Cl_4$, T = 383 K) of Entry 9 Table 4. ROH % = 78 %.

S4 continuing, Entry 10 Table 4.

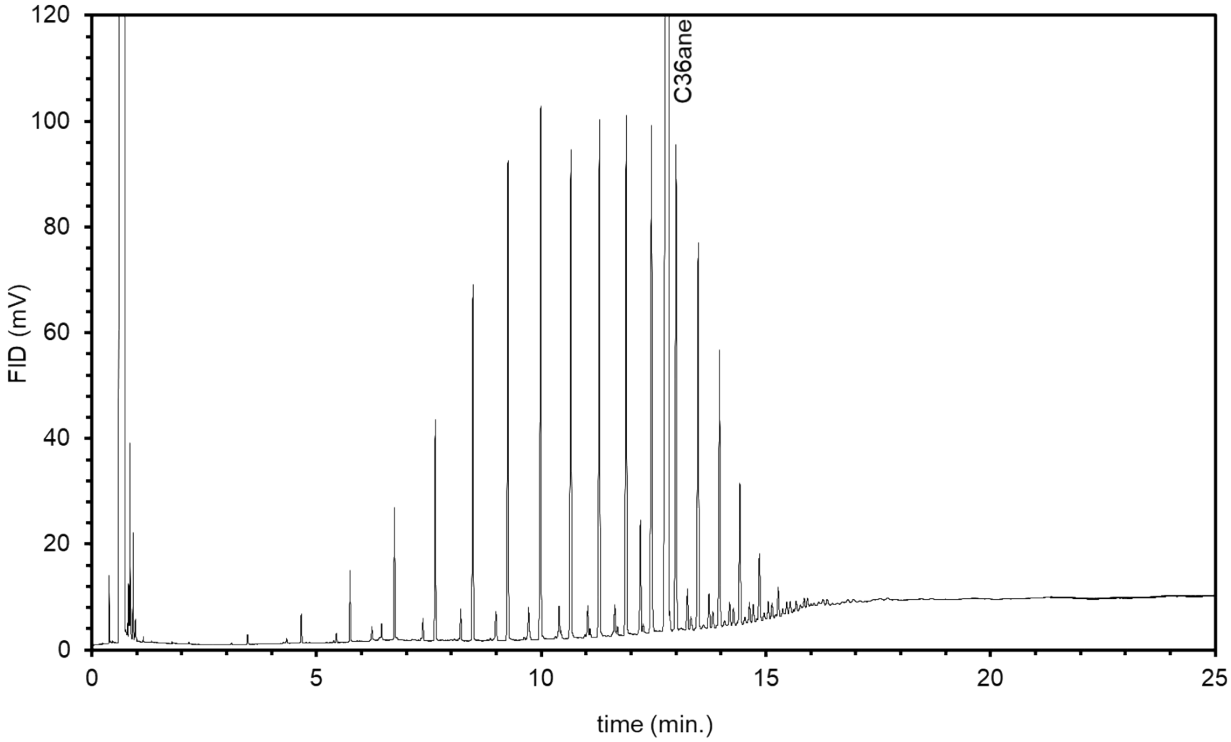


Figure S4-10a Raw signal Gas Chromatography analysis Entry 10 Table 4.

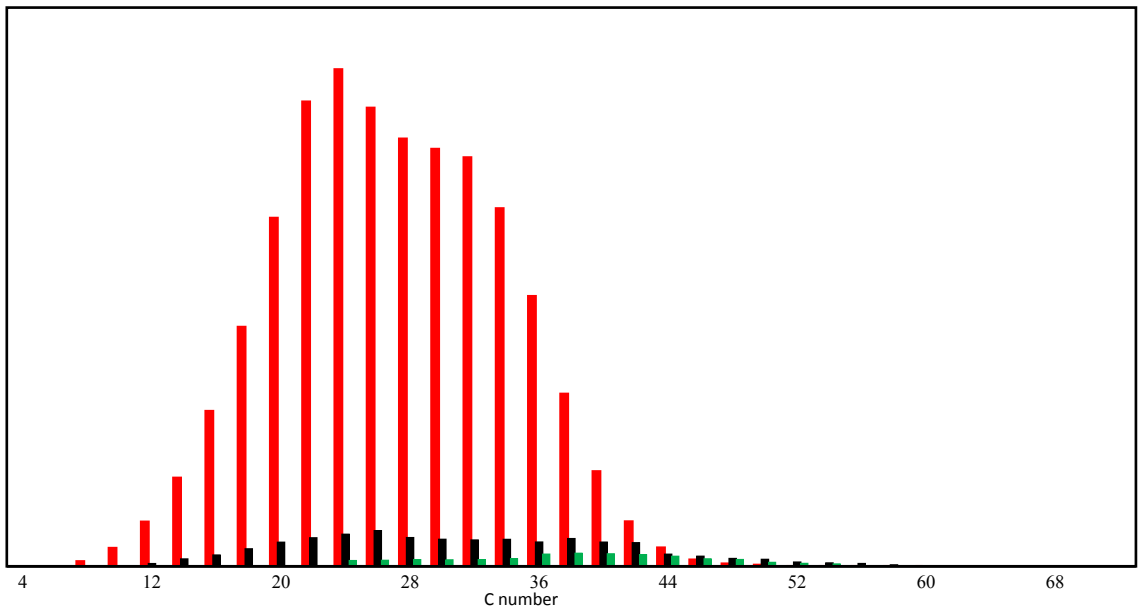


Figure S4-10b Distributions of alcohols ROH (red), hydrocarbons RH (black) and aldehydes RCHO (green). Molar amounts calculated from the GC analysis of Entry 10 Table 4.

S4 continuing, Entry 10 Table 4.

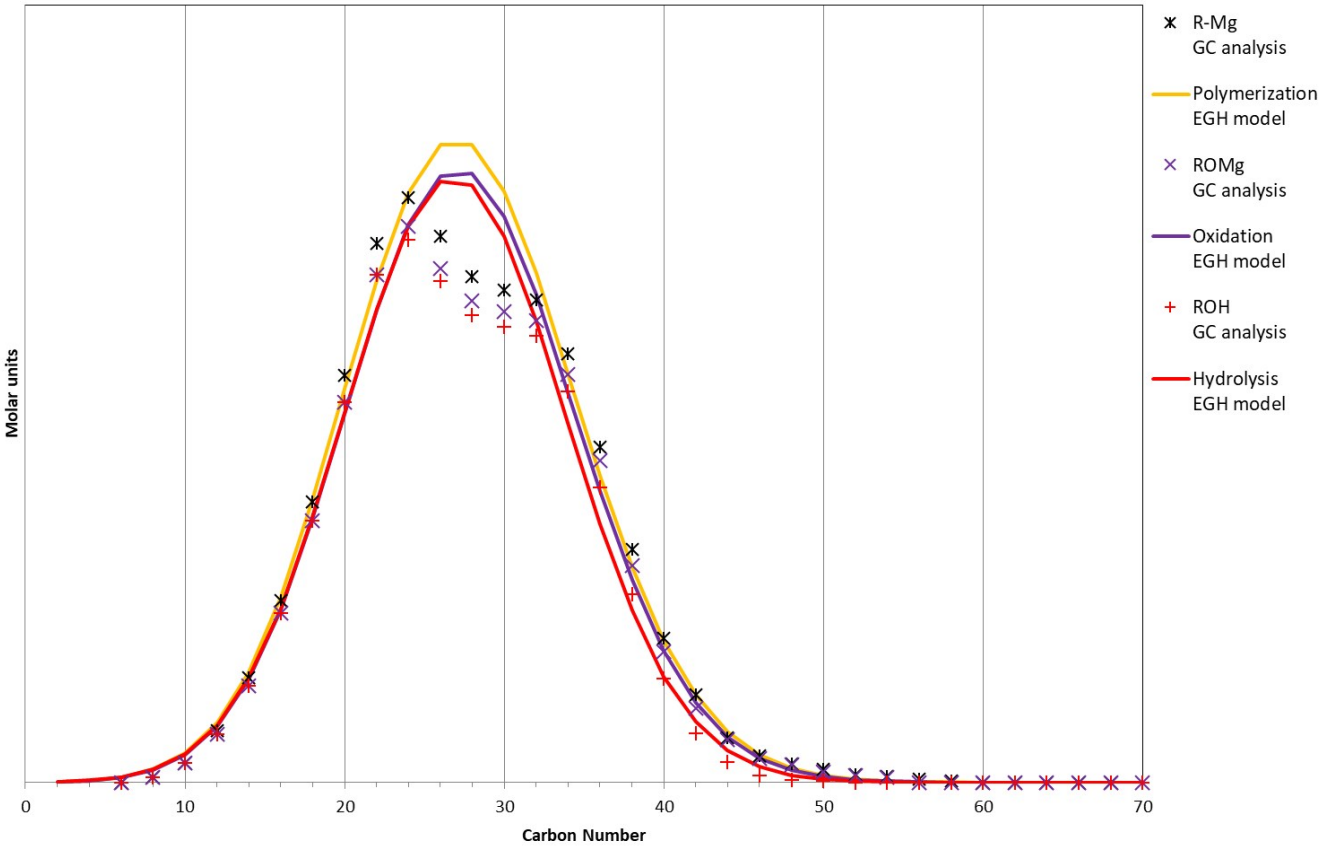


Figure S4-10c Distributions (graphics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 10 Table 4.

Table S4-10 Distributions (numerics) resulting from polymerisation, oxidation and hydrolysis steps, and fitting using the Exponential-Gaussian-Hybrid model, based on the GC analysis of Entry 10 Table 4.

Step	Polymerisation	Oxidation	Hydrolysis
Distribution sum of GC peaks	***R***-Mg ROH + RCHO + RH	R-***O***-Mg ROH + 2 RCHO	R-O-***H*** ROH
Step efficiency relative area of EGH fitting		**94.6%**	**95.9%**
R^2 of EGH fitting	0.9673	0.9612	0.9545
Mn (Carbon number) of EGH fitting	**27.45**	27.44	27.00
Dispersity of EGH fitting	**1.07**	1.07	1.07
Dispersity awaited for a Poisson distribution of same Mn	1.065	1.065	1.066
Skewness of EGH fitting	0.127	0.097	0.046
Skewness awaited for a Poisson distribution of same Mn	0.286	0.286	0.289

S4 continuing, Entry 10 Table 4.

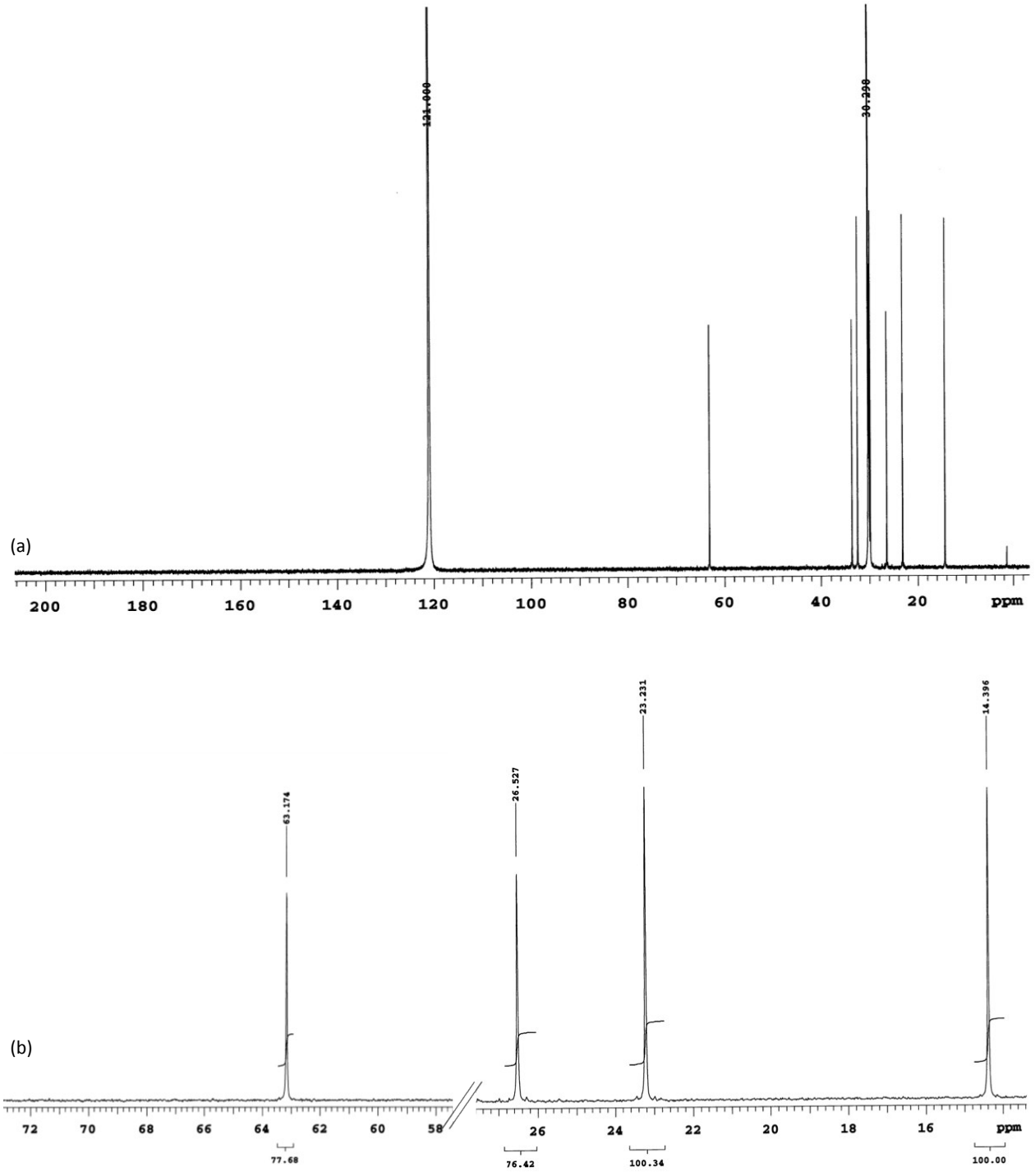


Figure S4-10d ^{13}C NMR spectrum (solvent $Cl_2C{=}CCl_2$, in the presence of $Cr(acac)_3$, D_2O capillary lock, T = 373 K) of Entry 10 Table 4. Full range (a) and selected zone for integration (b). ROH % = 87.3 %

S4 continuing, Entry 10 Table 4.

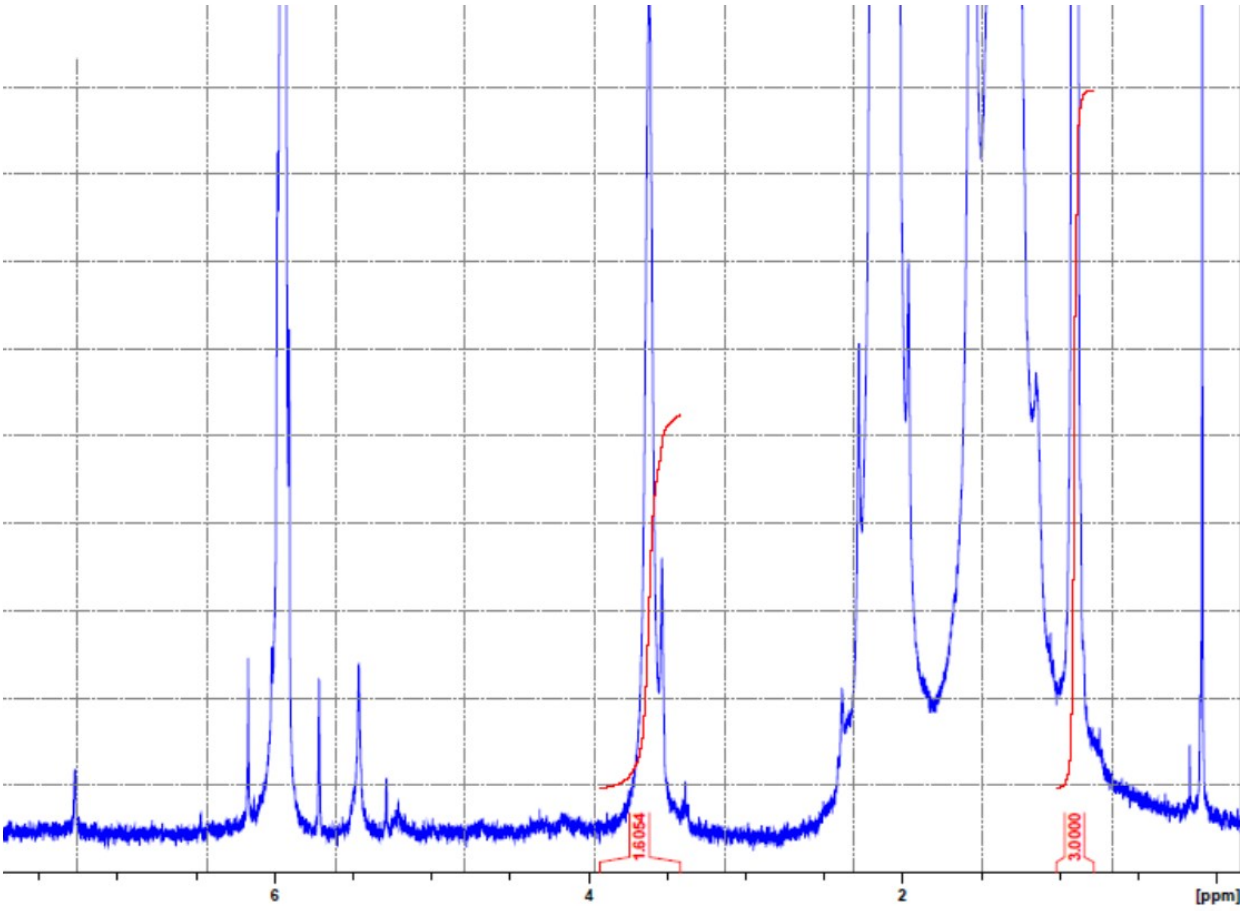
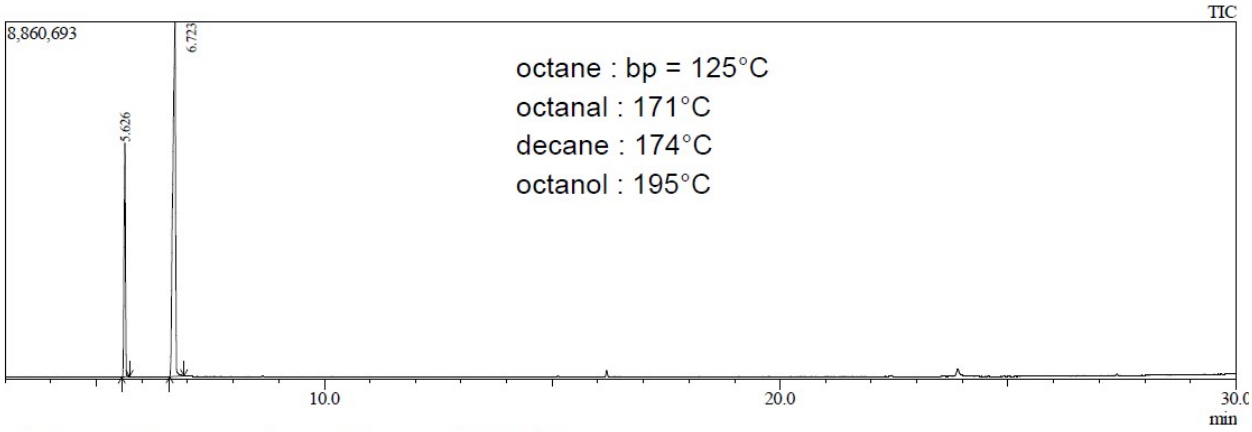


Figure S4-10e ^{1}H NMR spectrum (solvent $C_2D_2Cl_4$, in the presence of $Cr(acac)_3$, T = 383 K) of Entry 10 Table 4. ROH % = 89.0 %.

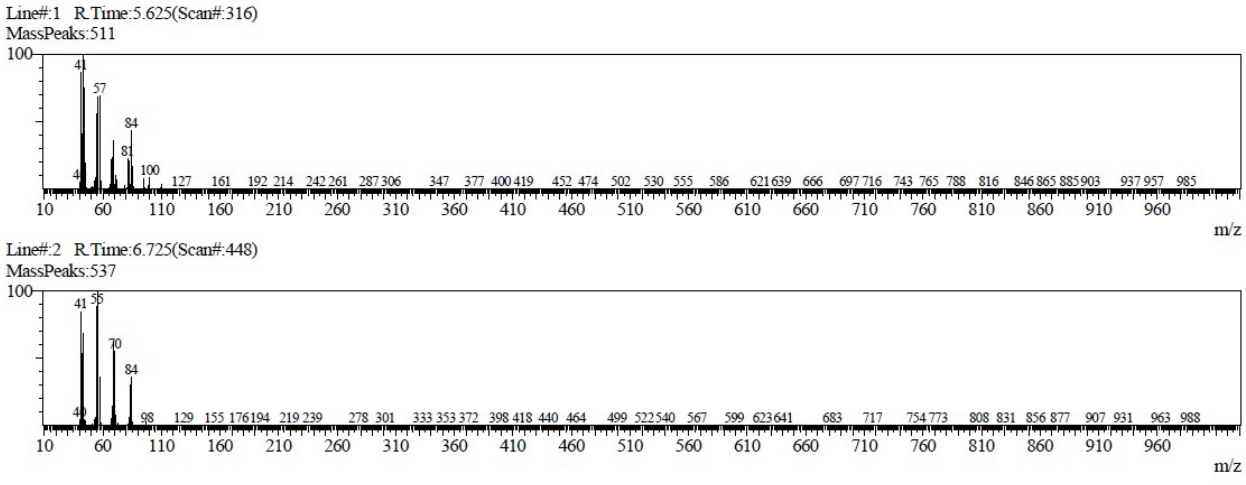
S5 GC/MS, IR and ^{1}H NMR analyses for aldehyde determination in fatty alcohols.

S5-1 GC/MS analysis of a mixture of octanal and 1-octanol standards.

Analyzed : 18/06/2014 19:21:05
Sample Name : 1-octanal+1-octanol
Data File : F:\1-octanal+1-octanol.qgd
Org Data File : C:\GCMSsolution\Data\EI\CD\1-octanal+1-octanol.qgd
Method File : C:\GCMSsolution\Data\EI\CD\methode 25032014-thomas.qgm



Peak#	R.Time	Area	Area%	Height	Height%
1	5.626	12397263	25.28	5805112	39.76
2	6.723	36649686	74.72	8794760	60.24
		49046949	100.00	14599872	100.00



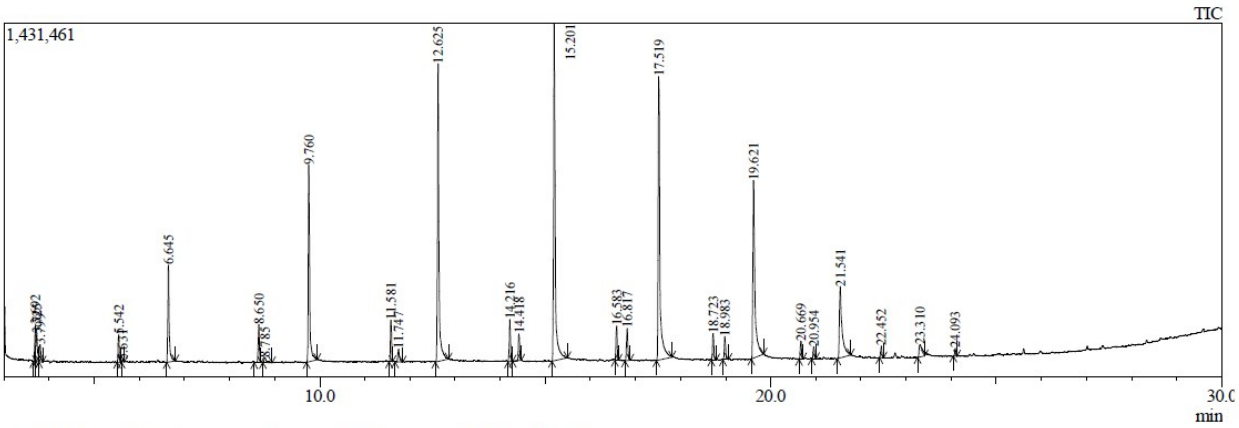
Note that:

These reference mass spectra are indicative of chemical function of homologous chains.

Relative order of retention times in GC column of low polarity depends on chemical function and carbon number of chains: the $C_{(n+2)}$-alkane is near the C_n-aldehyde which is between the $C_{(n-2)}$- and C_n-alcohols.

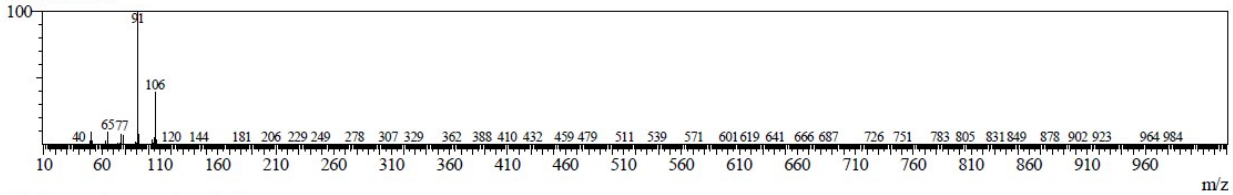
S5-2 GC/MS analysis of fatty alcohols.

Analyzed : 18/06/2014 21:35:54
Sample Name : TC517
Data File : F:\TC517.qgd
Org Data File : C:\GCMSsolution\Data\EI\CD\TC517.qgd
Method File : C:\GCMSsolution\Data\EI\CD\methode 25032014-thomas.qgm

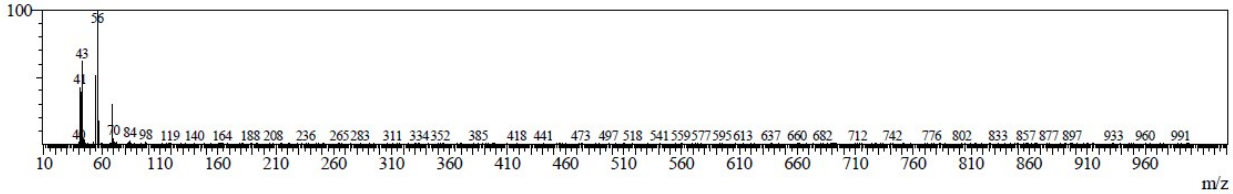


Peak#	R.Time	Area	Area%	Height	Height%
1	3.692	230393	1.21	148022	1.91
2	3.725	220901	1.16	113467	1.46
3	3.799	163532	0.86	70680	0.91
4	5.542	181760	0.96	109743	1.41
5	5.631	14862	0.08	8566	0.11
6	6.645	858119	4.51	391606	5.05
7	8.650	280083	1.47	154703	1.99
8	8.785	69295	0.36	19476	0.25
9	9.760	1748920	9.19	797867	10.28
10	11.581	303098	1.59	169515	2.19
11	11.747	125786	0.66	51882	0.67
12	12.625	2790687	14.67	1206221	15.55
13	14.216	307551	1.62	170240	2.19
14	14.418	205150	1.08	106642	1.37
15	15.201	3341729	17.56	1365980	17.61
16	16.583	251950	1.32	139232	1.79
17	16.817	260421	1.37	129737	1.67
18	17.519	3191857	16.77	1148159	14.80
19	18.723	212923	1.12	107072	1.38
20	18.983	191482	1.01	94267	1.22
21	19.621	2240504	11.77	719483	9.27
22	20.669	137190	0.72	72143	0.93
23	20.954	98777	0.52	46940	0.61
24	21.541	1195687	6.28	288818	3.72
25	22.452	92173	0.48	47270	0.61
26	23.310	257652	1.35	49936	0.64
27	24.093	55780	0.29	29976	0.39
		19028262	100.00	7757643	100.00

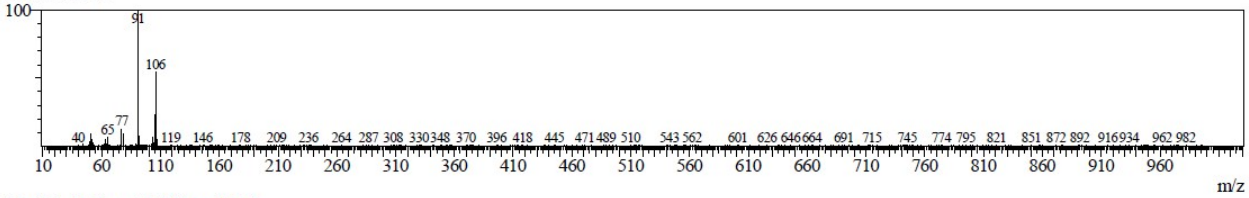
Line#:1 R.Time:3.692(Scan#:84)
MassPeaks:477



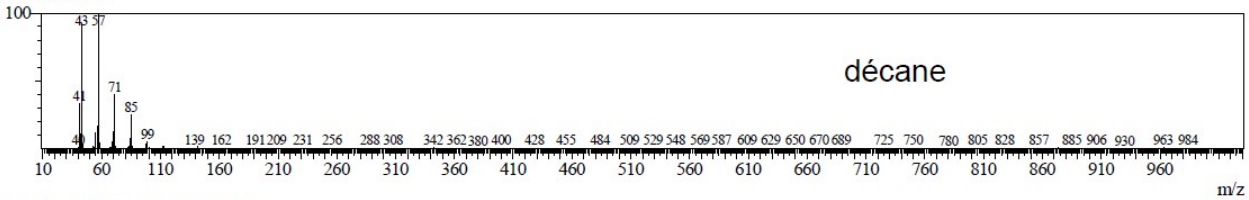
Line#:2 R.Time:3.725(Scan#:88)
MassPeaks:471



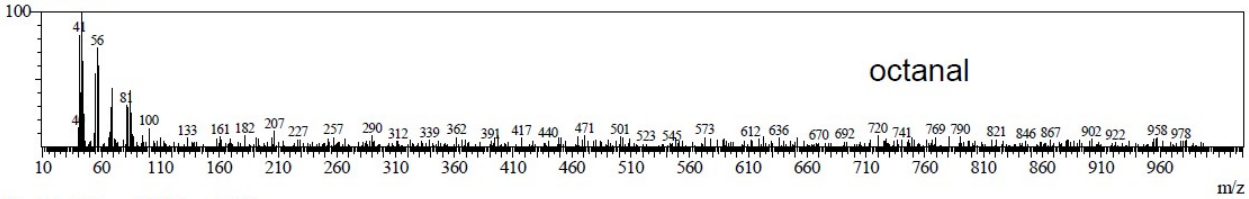
Line#:3 R.Time:3.800(Scan#:97)
MassPeaks:530



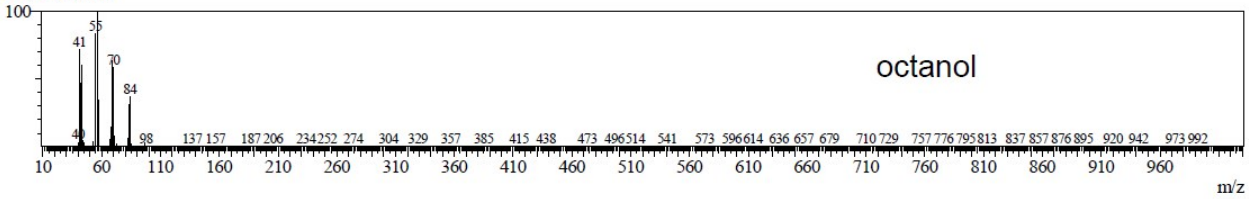
Line#:4 R.Time:5.542(Scan#:306)
MassPeaks:482



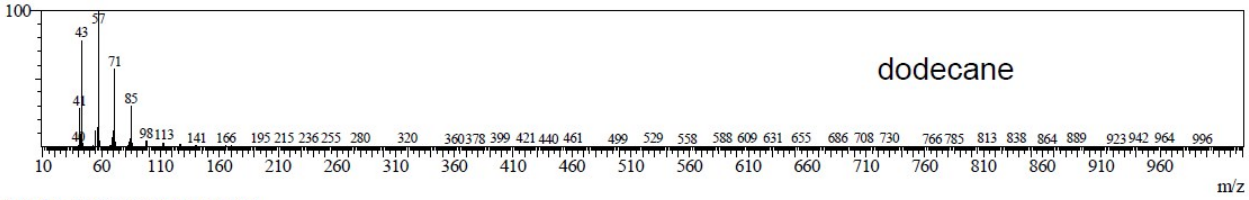
Line#:5 R.Time:5.633(Scan#:317)
MassPeaks:472



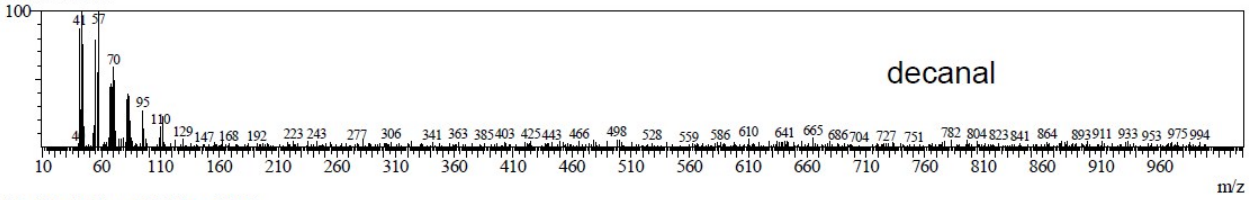
Line#:6 R.Time:6.642(Scan#:438)
MassPeaks:507



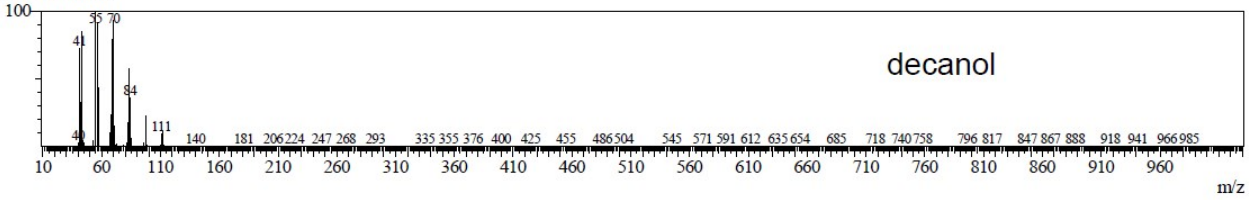
Line#:7 R.Time:8.650(Scan#:679)
MassPeaks:486



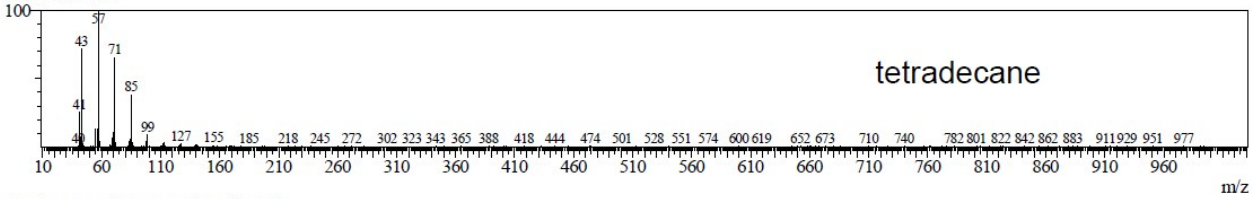
Line#:8 R.Time:8.783(Scan#:695)
MassPeaks:499



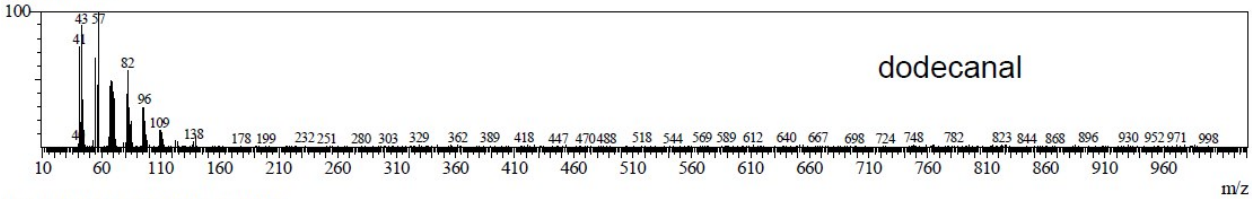
Line#:9 R.Time:9.758(Scan#:812)
MassPeaks:497



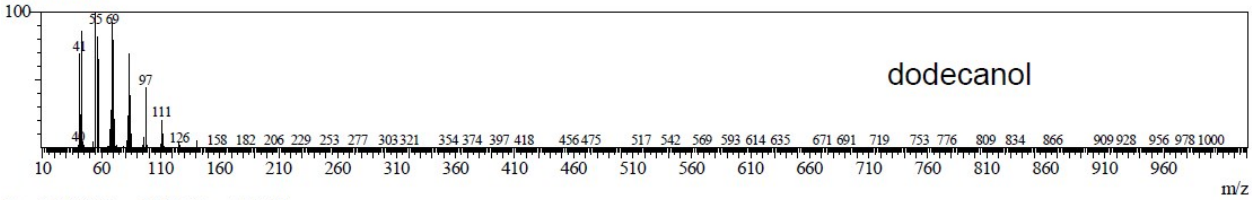
Line#:10 R.Time:11.583(Scan#:1031)
MassPeaks:491



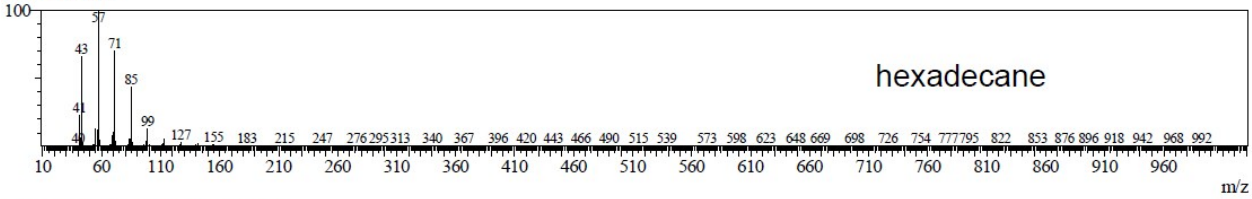
Line#:11 R.Time:11.750(Scan#:1051)
MassPeaks:469



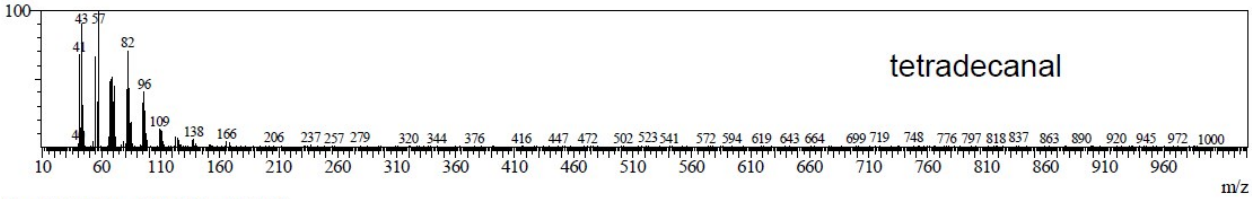
Line#:12 R.Time:12.625(Scan#:1156)
MassPeaks:515



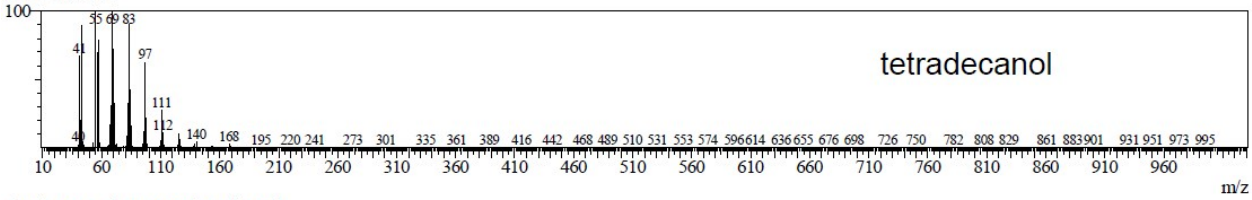
Line#:13 R.Time:14.217(Scan#:1347)
MassPeaks:488



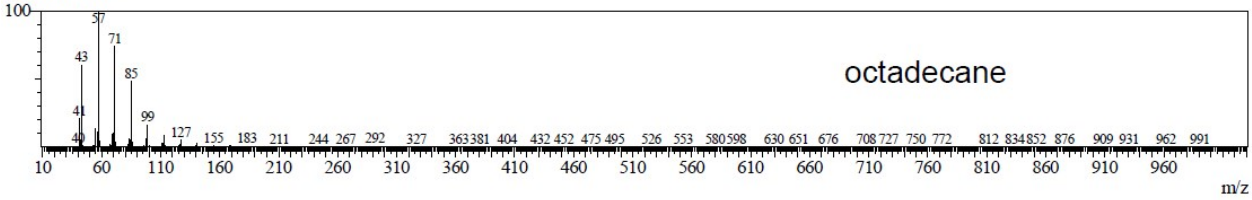
Line#:14 R.Time:14.417(Scan#:1371)
MassPeaks:510



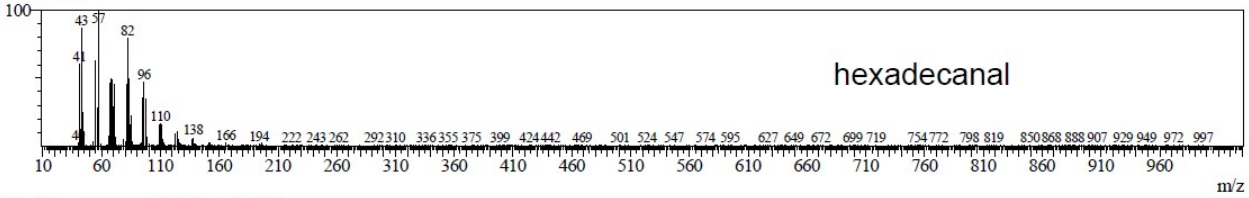
Line#:15 R.Time:15.200(Scan#:1465)
MassPeaks:511



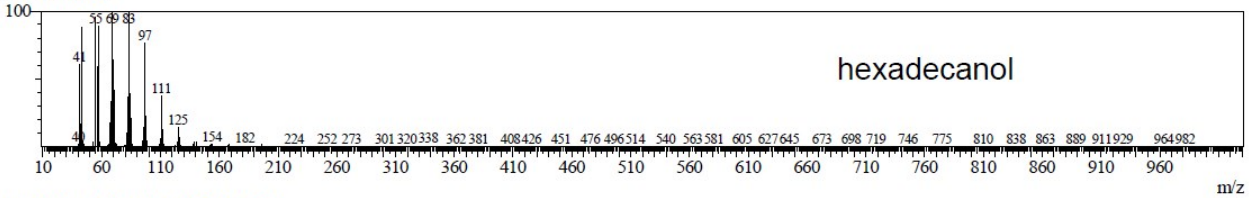
Line#:16 R.Time:16.583(Scan#:1631)
MassPeaks:489



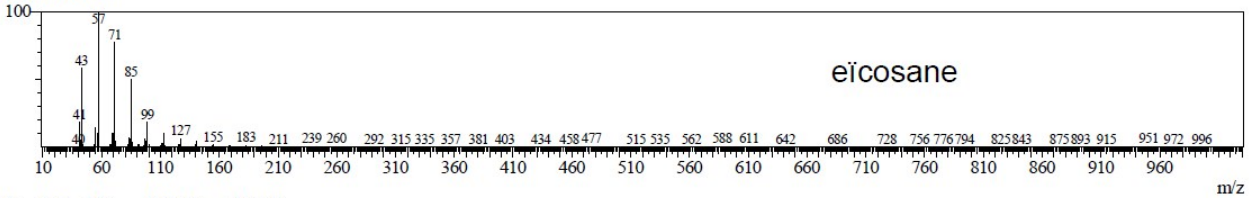
Line#:17 R.Time:16.817(Scan#:1659)
MassPeaks:519



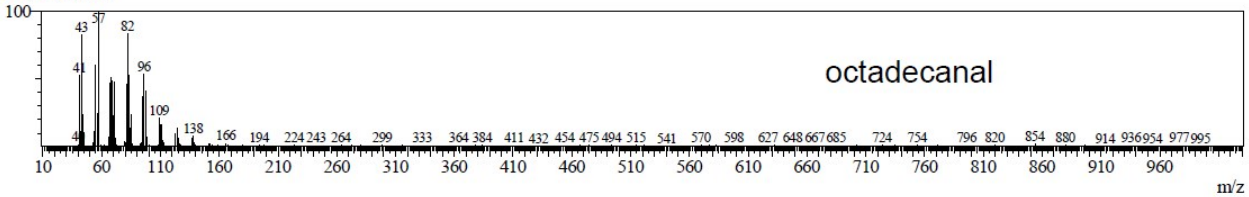
Line#:18 R.Time:17.517(Scan#:1743)
MassPeaks:514



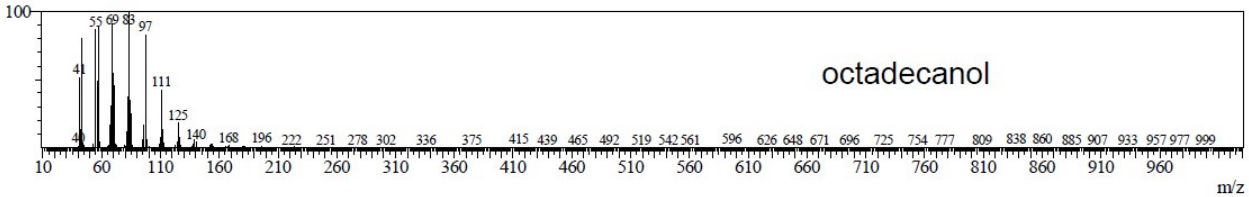
Line#:19 R.Time:18.725(Scan#:1888)
MassPeaks:514



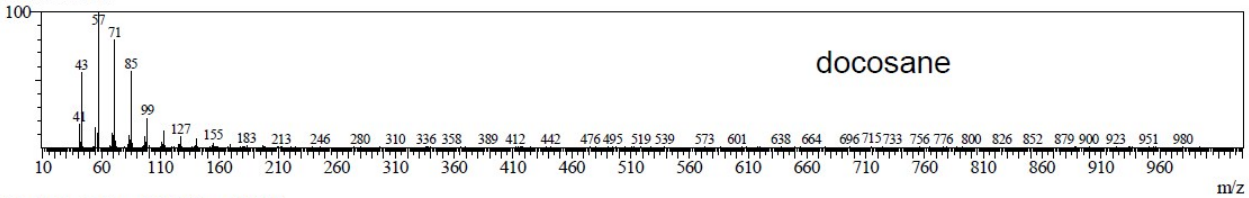
Line#:20 R.Time:18.983(Scan#:1919)
MassPeaks:517



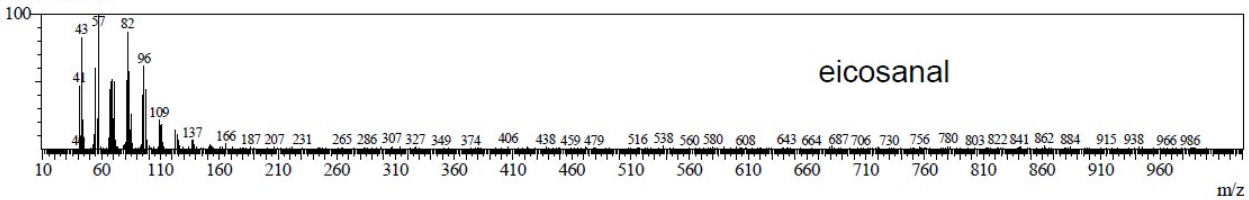
Line#:21 R.Time:19.617(Scan#:1995)
MassPeaks:527



Line#:22 R.Time:20.667(Scan#:2121)
MassPeaks:523



Line#:23 R.Time:20.958(Scan#:2156)
MassPeaks:494



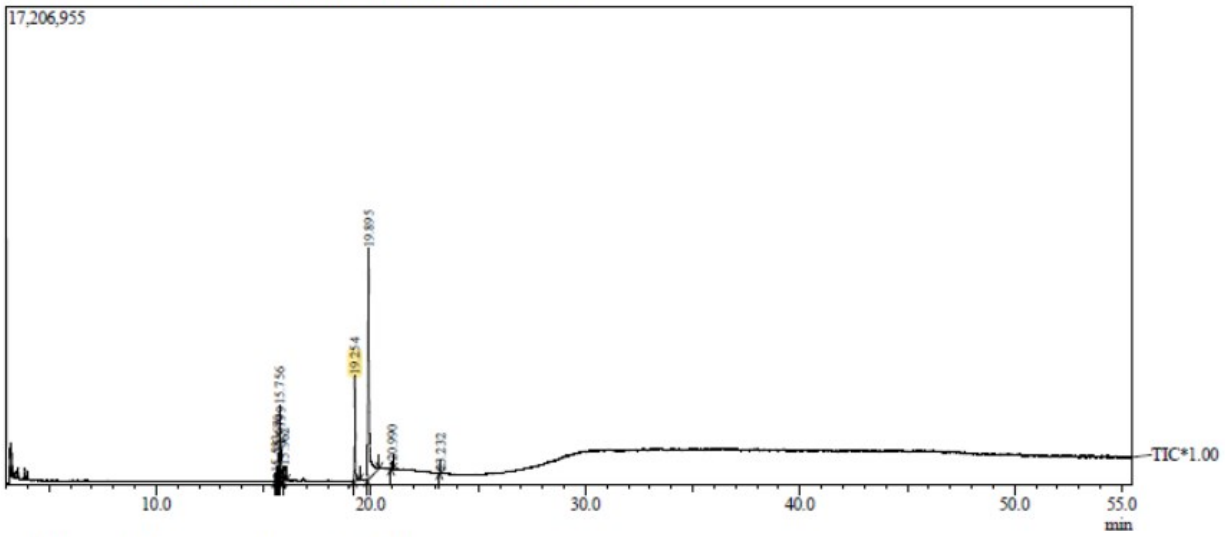
Note that:

To protect the sensitive parts of the GC/MS device, the analysis presented here was performed with a sample from a dedicated experiment with a low Mn targeted at C14.

S5-3 GC/MS analysis of *in situ* prepared $(n\text{-}C_{18}H_{37}O)_2Mg$.

Sample Information

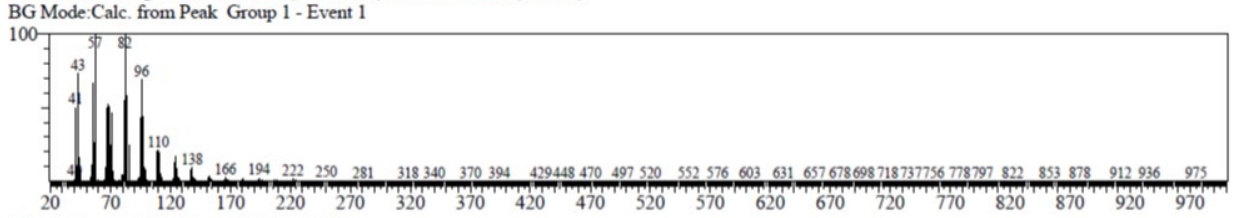
Analyzed : 21/05/2019 14:40:34
Sample Name : MV80- 21052019 dilué 2
Injection Volume : 1
Method File : C:\GCMSsolution\Data\EI\CD\methode 25032014-thomas.qgm
Date File : C:\GCMSsolution\Data\EI\CD\MV80 21052019 dilué-2.qgd



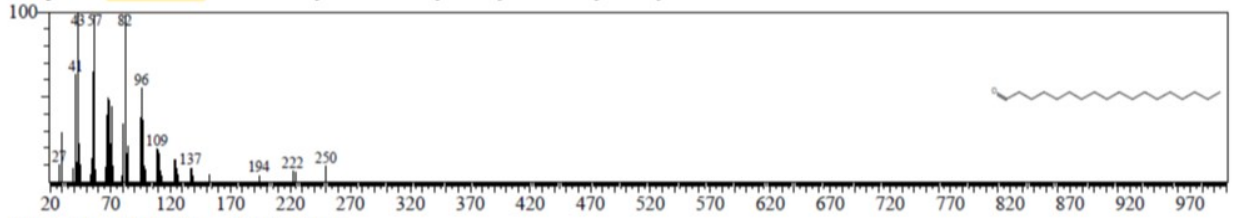
Peak#	R.Time	Area	Area%	Name
1	15.583	835480	1.41	
2	15.670	4361937	7.37	
3	15.756	6247059	10.56	
4	15.799	2964702	5.01	
5	15.962	1367496	2.31	
6	19.254	9398130	15.88	
7	19.895	33343544	56.36	
8	20.990	509754	0.86	
9	23.232	135917	0.23	
		59164019	100.00	

S5-3 (continuing) GC/MS analysis of *in situ* prepared $(n\text{-}C_{18}H_{37}O)_2Mg$.

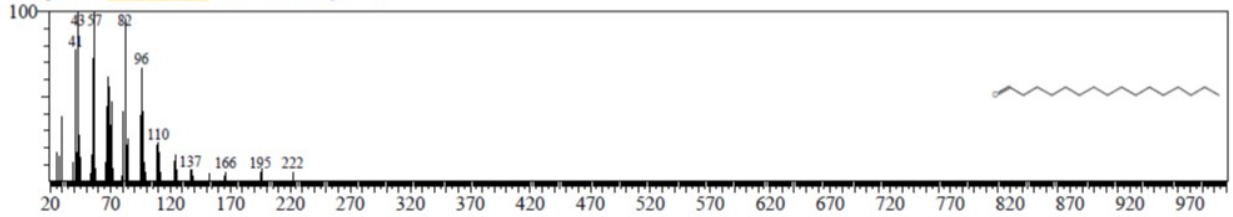
<< Target >>
Line#:6 R.Time:19.250(Scan#:1951) MassPeaks:543
RawMode:Averaged 19.242-19.258(1950-1952) BasePeak:82.10(278919)
BG Mode:Calc. from Peak Group 1 - Event 1



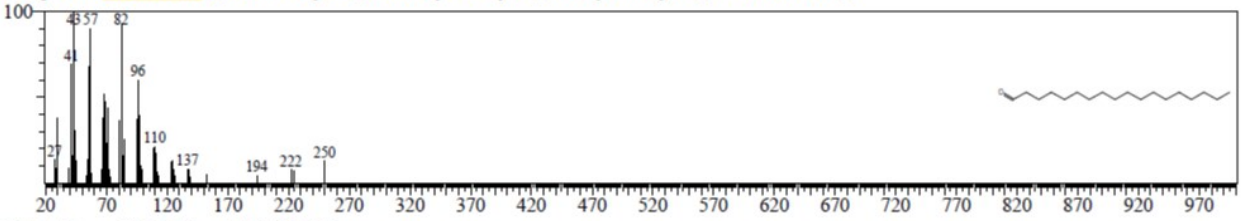
Hit#:1 Entry:22614 Library:NIST08s.LIB
SI:95 Formula:C18H36O CAS:638-66-4 MolWeight:268 RetIndex:1999
CompName:Octadecanal $$ Stearaldehyde $$ Octadecyl aldehyde $$ Stearyl aldehyde $$ n-Octadecanal $$



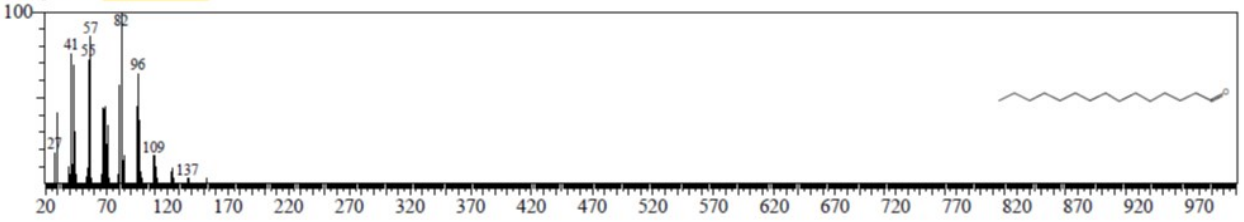
Hit#:2 Entry:20690 Library:NIST08s.LIB
SI:95 Formula:C16H32O CAS:629-80-1 MolWeight:240 RetIndex:1800
CompName:Hexadecanal $$ Palmitaldehyde $$



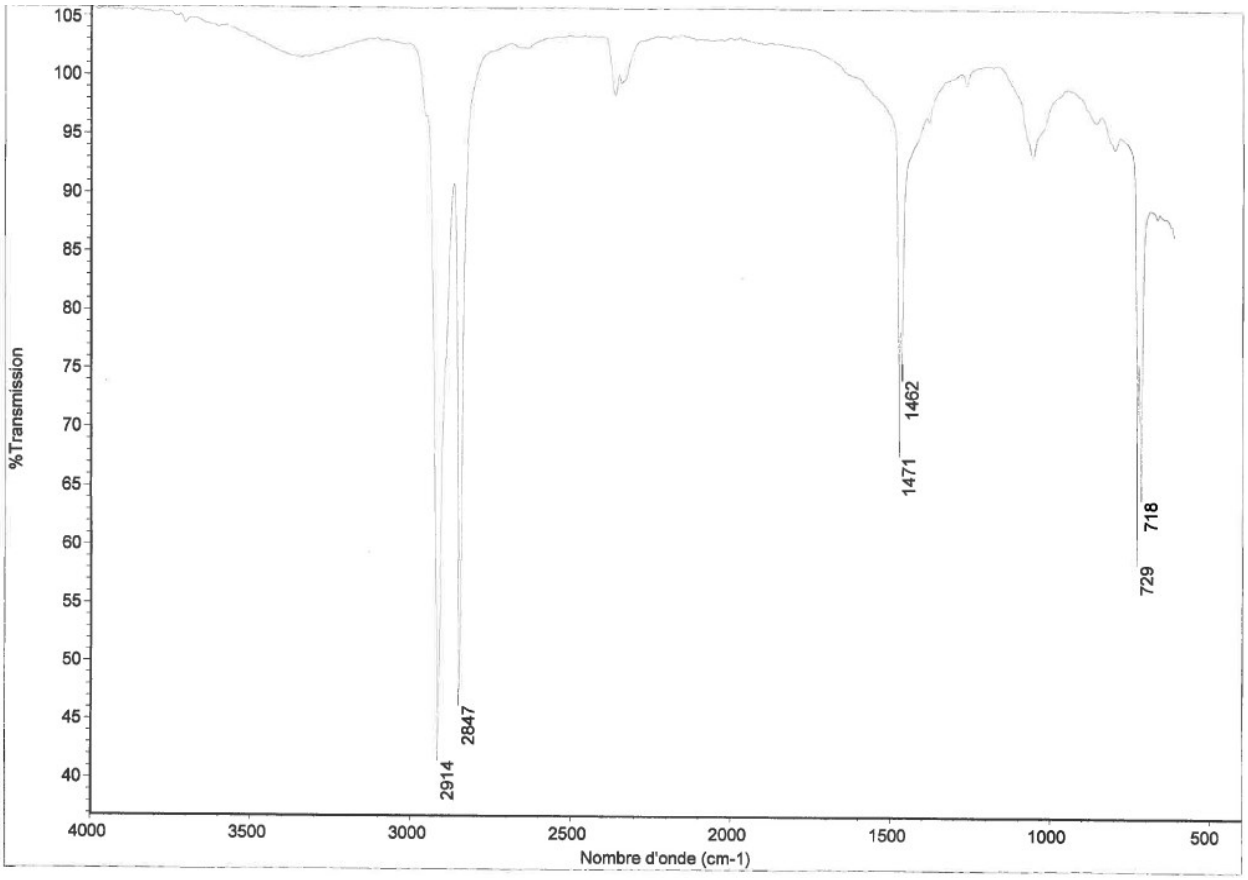
Hit#:3 Entry:22613 Library:NIST08s.LIB
SI:94 Formula:C18H36O CAS:638-66-4 MolWeight:268 RetIndex:1999
CompName:Octadecanal $$ Stearaldehyde $$ Octadecyl aldehyde $$ Stearyl aldehyde $$ n-Octadecanal $$



Hit#:4 Entry:60326 Library:NIST08.LIB
SI:94 Formula:C15H30O CAS:2765-11-9 MolWeight:226 RetIndex:1701
CompName:Pentadecanal-



S5-4 I-R spectra of fatty alcohols: Entry 5, Table 3



Note that:

No signal is recorded around 1700 cm^{-1}.