

Microalgae Lipids as a Feedstock for Production of Benzene

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Supporting Information

Additional Experimental Procedures and Results	S2
Gas Chromatography	S6
NMR spectra	S21
References	S22

Additional Experimental Procedures and Results

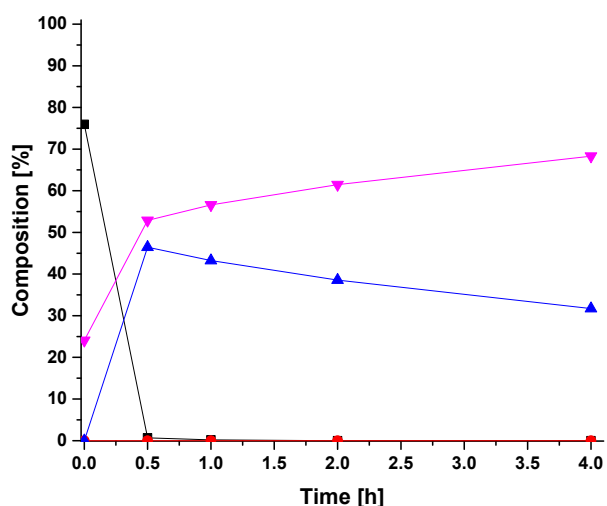
Procedure for the hydrogenation of a model metathesis mixture

A mixture of 4-octene (2.5 mmol), oleic acid (5 mmol) and 1,18-octadecenedioic acid (2.5 mmol) was prepared. This resembles the metathesis of EPA mixture without 1,4-cyclohexadiene present. The mixture was dissolved in degassed toluene. In a glass inlet for autoclaves, Pd/C (53.2 mg, 10% w/w) and a stirring bar were placed. The glass inlet was placed in the autoclave with was subsequently closed. The autoclave was purged with nitrogen. The solution of the model metathesis mixture was transferred to the autoclave. After pressurization with H₂ (5 bar) the autoclave was placed into a preheated aluminium block and allowed to stir for 8 hours at 110°C. Samples were taken at t=0, 15, 30, 60, 120, 240, 360, 480 minutes. All samples were measured by GC and were esterified using methanol prior to the measurement.

Table S1: Results in the subsequent one-pot metathesis and dehydrogenation of eicosapentaenoic acid.

Entry	Dehydrogenation cat. (loading)	Temp. (°C)	Notes	Time (h)	Conversion of 1,4-cyclohexadiene (%) ^{a,b}	Benzene Selectivity (%) ^{a,b}
1 ^{c,d}	Pd/C (5 mol%)	110	1 equiv. fumarate, 1,4-cyclohexadiene isolated from EPA metathesis	20	100	66
2	Pd/Al ₂ O ₃ (0.1 mol%)	70	Isolated conjugated EPA	6	0	0
3	Pd/Al ₂ O ₃ (0.1 mol%)	70		20	0	0
4	Pd/Al ₂ O ₃ (0.1 mol%)	90	Mixture of entry 3	20	0	0
5	Pd/Al ₂ O ₃ (0.1 mol%)	110	Mixture of entry 4	20	100	33
6	--	45→110	No Pd cat	0.25+20	100	0

Conditions: HGII (0.005 mmol, 0.1 mol%), 10 mL toluene, 45°C, 15 min. after this, Pd, was added a) Analysed by GC, the conversion of the metathesis was determined with respect to the consumption of EPA. 1,4-Cyclohexadiene selectivity is determined with respect to EPA. b) The benzene conversion and selectivity was based on EPA. c) 0.2 equiv. AMS added as hydrogen accepted. d) Chlorobenzene instead of toluene as a solvent.



Graph S1: Reaction profile of the dehydrogenation of 1,4-cyclohexadiene over 0.1 mol% Pd/Al₂O₃ (5%w/w) at 110°C. Conditions: 1,4-cyclohexadiene (10 mmol), Pd/Al₂O₃(5%) (0.01 mmol, 0.1 mol%), toluene (10 mL), 110°C, 4h. ■= 1,4-cyclohexadiene, ●= 1,3-cyclohexadiene, ▲= cyclohexene, ▼= benzene.

The selectivity to 1,4-cyclohexadiene was determined over the conversion of EPA, that is a ratio of benzene formed to EPA consumed of 2:1 corresponds to 100% selectivity.

Additionally, the dehydrogenation of neat 1,4-cyclohexadiene was investigated to determine the conditions required for the subsequent dehydrogenation of the metathesis reaction mixture.^[1,2] Upon dehydrogenation of 1,4-cyclohexadiene, hydrogen is liberated from the molecule, therefore it is possible that a hydrogen acceptor is required to prevent that the hydrogen can hydrogenate 1,4-cyclohexadiene in the mixture.^[3] A procedure reported for the dehydrogenation of cyclohexene was adopted initially, where various Pd sources and AMS (Anthraquinone-2-sulfonic acid sodium salt) as hydrogen transfer agent are used. Generally the dehydrogenation of cyclohexene or cyclohexadienes to benzene proceeds at high temperatures, and the use of a hydrogen acceptor and transfer agent may allow to work at lower temperatures. A known procedure employing these conditions is actually used in the aerobic oxidation of cyclohexene to benzene, where oxygen is the hydrogen acceptor and facilitates the reaction due to water formation.^[4,5] An olefin was chosen here as hydrogen acceptor to investigate if the remaining olefins of the EPA metathesis can be used as hydrogen acceptor later in a one-pot reaction. The results of the dehydrogenation screening are listed in Figure S1.

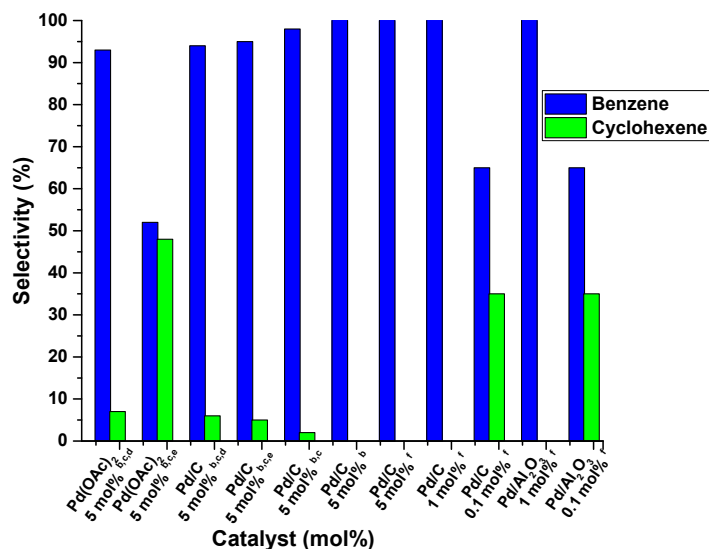
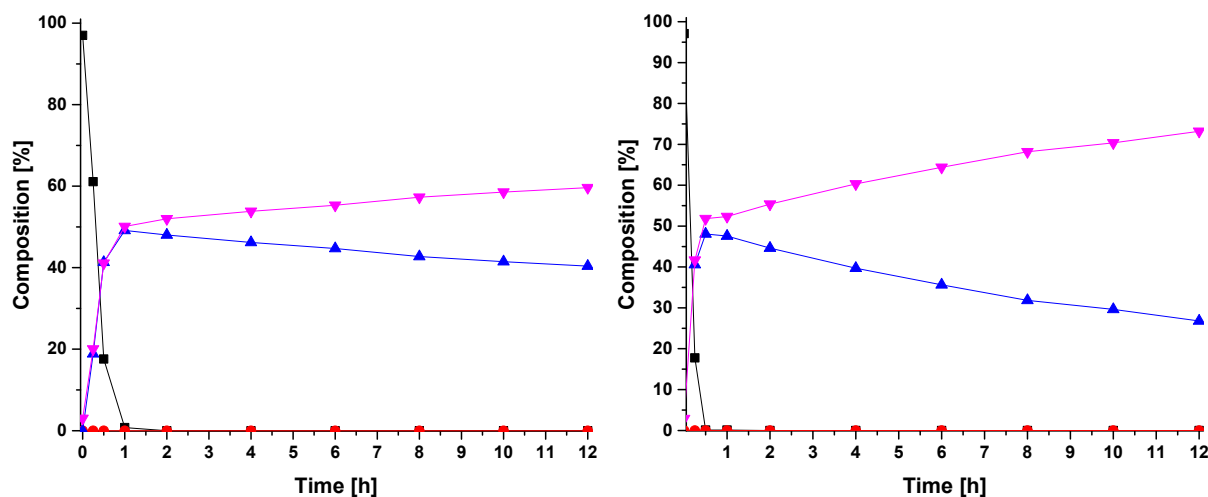


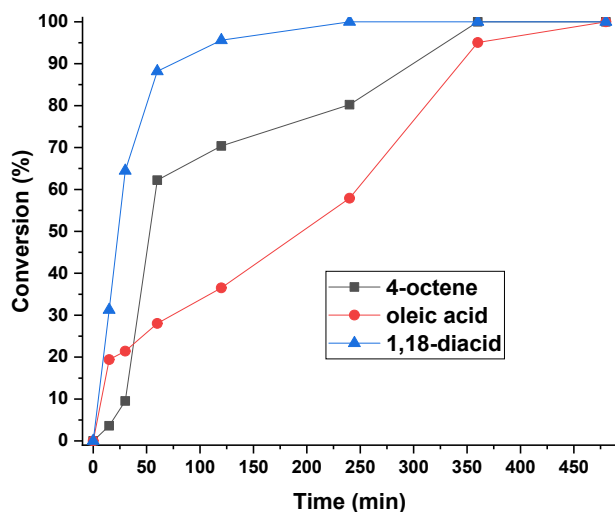
Figure S1: Results of the dehydrogenation of 1,4-cyclohexadiene employing different Pd catalysts under different conditions. Conditions: 1,4-cyclohexadiene (10 mmol), Pd catalyst (0.5 mmol (5 mol%) or 0.001 mmol (0.1 mol%), solvent (10 mL), 20h, 110°C. a) Analysed by GC., conversion was complete in all cases. b) In chlorobenzene as a solvent (10mL) c) 0.2 equivalents AMS were added. d) 1 equivalent dimethyl fumarate was added. e) 0.25 equivalent dimethyl fumarate was added. f) In toluene as a solvent.

Under the reaction conditions as described for aerobic cyclohexene oxidation, the 1,4-cyclohexadiene readily reacts to benzene over Pd(OAc)₂ as a catalyst with a small amount of by-product, which was identified as cyclohexene (Figure S1, column 1). Most remarkably, only about 25% of the dimethyl fumarate was hydrogenated to dimethyl succinate. For this reason, the amount of dimethyl fumarate was reduced to only 25%. Notable, the selectivity towards benzene was now only 50%, giving a strong indication that the fumarate still does have a function (Figure S1, column 2). Cyclohexene was present in much higher amount now (1:1 ratio), which is the result of 1,4-cyclohexadiene hydrogenation. The catalyst range was expanded to supported Pd catalysts for further optimization. With both Pd/Al₂O₃ and Pd/C full conversion was achieved.^[6] The same conditions were employed and benzene was formed in 95% selectivity, only slightly higher compared to Pd(OAc)₂. Surprisingly, in the case where dimethyl fumarate was employed as a hydrogen acceptor, the amount of hydrogenated dimethyl succinate was minimal (column 4 and 5, Figure S1), and therefore any hydrogen acceptor and AMS were further omitted. Notably, full conversion was achieved, without the presence of a hydrogen acceptor in employing supported Pd catalysts. The selectivity towards benzene was in both cases 100% (column 6 and 7, Figure S1). The catalyst loading was reduced to 1 mol% and to 0.1 mol%. With both loadings, full conversion is achieved, though with 1 mol% also full selectivity to benzene was achieved, whereas only 65% selectivity was reached with 0.1 mol% catalyst loading (column 8-11, Figure S1). Cyclohexene was again observed as a side product (column 11, Figure S1). To learn more about the reaction and all the intermediates, reaction profiles were recorded by taking samples at specified time-intervals. The system using Pd/Al₂O₃ as a catalyst was chosen as this gave a good conversion, but still showed the side products in sufficient amount for analysis. A loading of 0.1 mol% was chosen to observe intermediates and possible side products optimally (Graph S2) Graph S1.



Graph S2: Reaction profile of the dehydrogenation of 1,4-cyclohexadiene over 0.1 mol% Pd/Al₂O₃ (5%w/w) at 70°C. Conditions: 1,4-cyclohexadiene (10 mmol), Pd/Al₂O₃(5%) (0.01 mmol, 0.1 mol%), toluene (10 mL left, 1 mL right), 70°C, 12h. ■ = 1,4-cyclohexadiene, ● = 1,3-cyclohexadiene, ▲ = cyclohexene, ▼ = benzene.

The reaction was first performed at 110°C which already showed 25% conversion during heating up ($t = 0$ in Graph S1Graph S2). For better observation of intermediates, the temperature was reduced to 70°C. It can be seen that complete conversion is achieved in about 1 hour (Graph S2). Here it becomes obvious that the 1,4-cyclohexadiene is indeed converted into benzene, though via an intermediate. First cyclohexene is formed, with at the same time one equivalent of benzene.^[7] The hydrogen from the dehydrogenated 1,4-cyclohexadiene is first transferred to a second 1,4-cyclohexadiene molecule. Over time, the cyclohexene is further converted to benzene, which must proceed over a loss of two hydrogen equivalents. The latter reaction appeared to be much slower, though still viable under these conditions, and therefore the concentration of the compounds in the reaction mixture was increased, by reduction of the solvent volume (Graph S2, right). The dehydrogenation of both 1,4-cyclohexadiene and cyclohexene is now indeed slightly increased.



Graph S3: Reaction profile of the hydrogenation of a model metathesis-mixture of 4-octene, oleic acid and 1,18-octadecenedioic acid. Conditions: 4-octene (2.5 mmol, 392 μ L), oleic acid (5 mmol, 1.6 mL), 1,18-octadecenedioic acid (2.5 mmol, 781 mg), toluene (10 mL), Pd/C (53.2 mg), 110°C, 8 h.

From the above graph (Graph S3), it can be seen that oleic acid hydrogenation reaches full conversion slower than 4-octene or the diacid. As this is a model for the metathesis mixture, it can be expected that the same occurs in the hydrogenation of the post-metathesis mixture. As was observed in this,

the equilibrium seemed to have shifted towards the diacid. This is now supported by the difference in hydrogenation rate of all components.

Gas Chromatography

Gas chromatography was measured on a Perkin-Elmer GC Clarus 500 equipped with an elite-5 column (Length = 30 m, Inner Diameter = 0.25 mm, Thickness = 25 μ) and a FID-detector via the following programs: 1 min at 90°C, 30°C/min to 280°C, 280°C for 8 minutes (method 1), or 3 min at 50°C, 20°C/min to 280°C, 280°C for 5 minutes (method 2), both with an injector temperature of 300°C and a detector temperature of 280°C.

Table S2: Retention times of the compounds detected from the metathesis of EPA and the dehydrogenation reactions. Response factors were measured with respect to dodecane.

Component	Method 1	Method 2	Molar Response factor
1,3-cyclohexadiene	--	2.32	0.49
Cyclohexane	1.66	2.42	0.51
Benzene	1.67	2.46	0.50
Cyclohexene	1.69	2.61	0.49
1,4-cyclohexadiene	1.77	2.92	0.49
Methyl 5-octenoate	3.42	7.67-7.76	*
dodecadiene	3.85	8.31	*
Methyl 5,8-undecadienoate	4.82	9.78	*
Dimethyl decenedioate	5.70	10.93-11.11	0.91
Methyl tetradecatrienoate	6.00	11.54	*
Octadecapentaene	6.25	--	*
EPA	7.86	14.31	1.70

* Estimated using comparable compounds

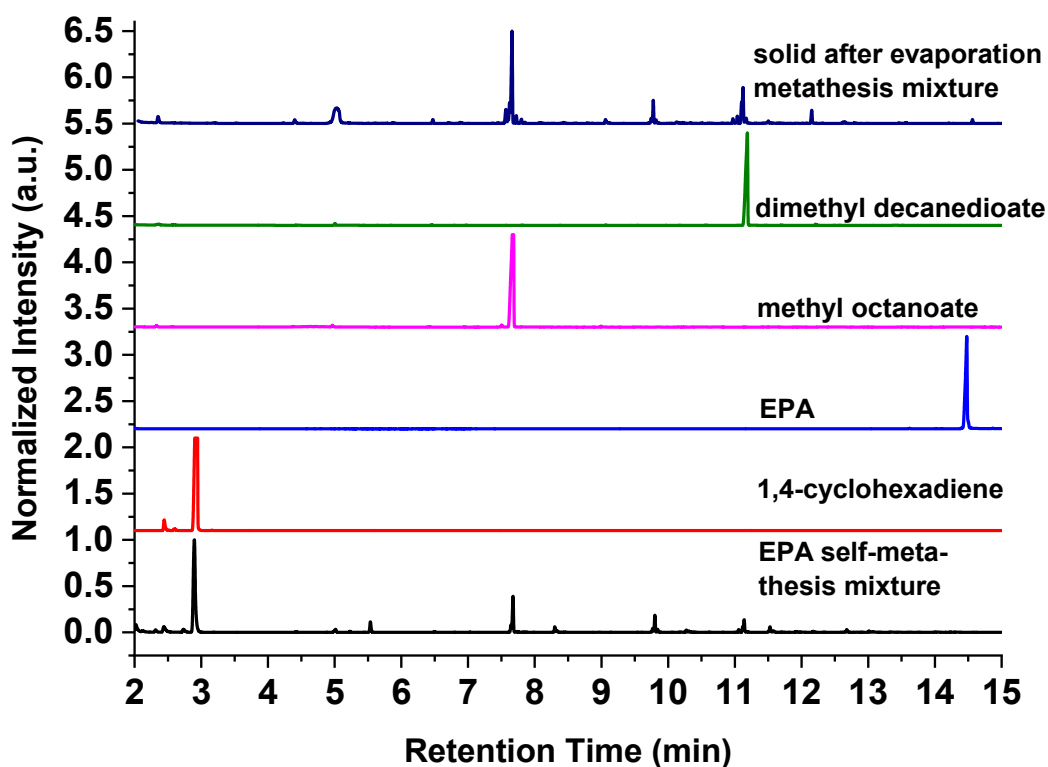


Figure S2: GC traces (method 2) of the metathesis of EPA with pure compounds for comparison. Methyl octanoate was used for comparison to methyl octanoate. Dimethyl decanedioate was used for comparison of dimethyl decanedioate because of the very similar retention times (Vide Intra, Figure S4).

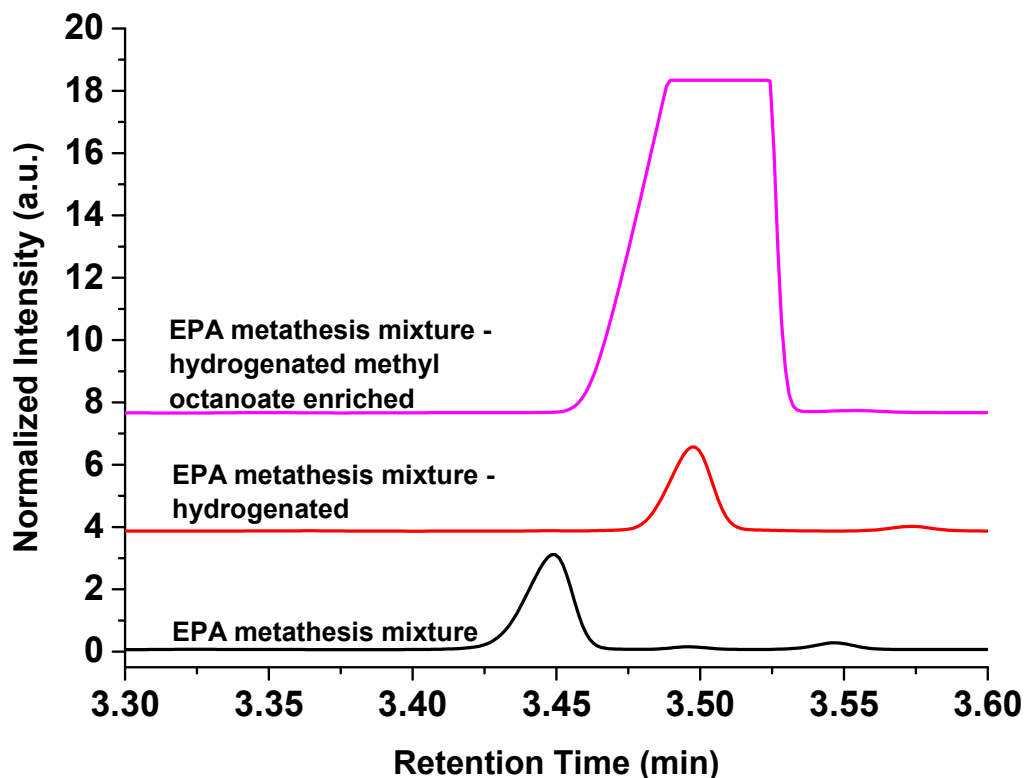


Figure S3: GC traces (method 1) of the reaction mixture from incomplete EPA metathesis, which was subsequently hydrogenated and enriched with methyl octanoate (8:0 ester). The retention time of the saturated and unsaturated compound are very similar, though these differ sufficiently to distinguish both components.

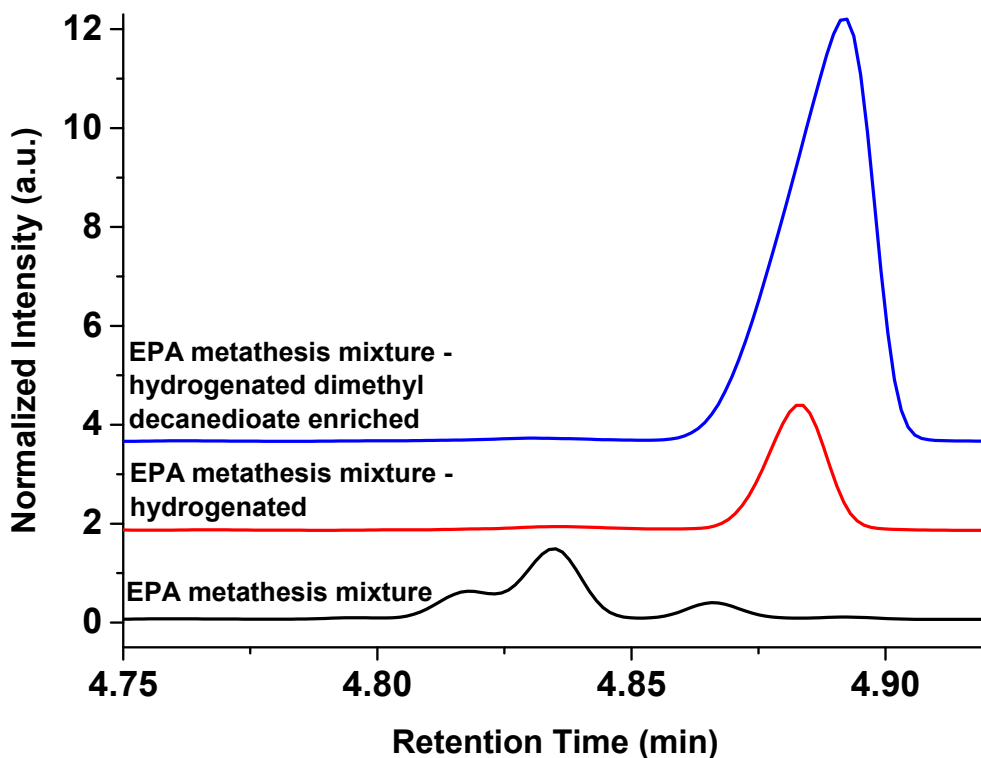


Figure S4: GC traces (method 1) of the reaction mixture from incomplete EPA metathesis mixture, which was subsequently hydrogenated and enriched with dimethyl decanedioate (1:10 diester). The retention time of the saturated and unsaturated compound are very similar, though these differ sufficiently to distinguish both components.

Table S3: Areas of the remaining by-products from a dried metathesis sample measured by GC using method 2.

Signal	Compound	Area (%) ^a
7.67-7.76	Methyl 5-octenoate	60
10.93-11.11	Dimethyl decenedioate	11
9.78	Methyl 5,8-undecadienoate	29

a) The ratio between methyl 5-octenoate and dimethyl 5-decenedioate is as expected; 2:1.

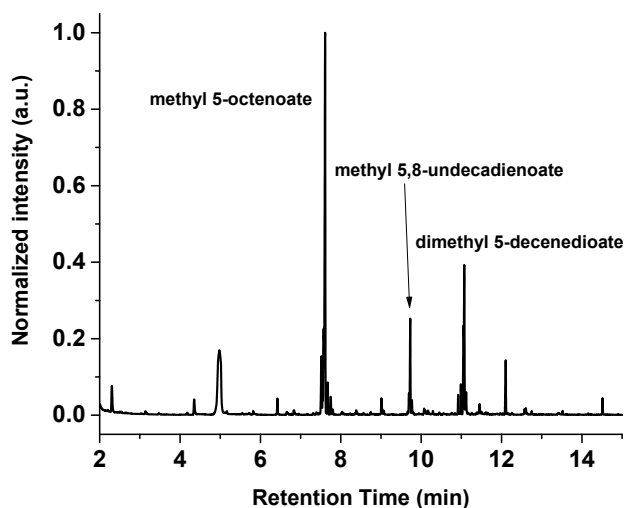


Figure S5: GC-trace (method 2) of a post-metathesis mixture of EPA after evaporation of all volatile

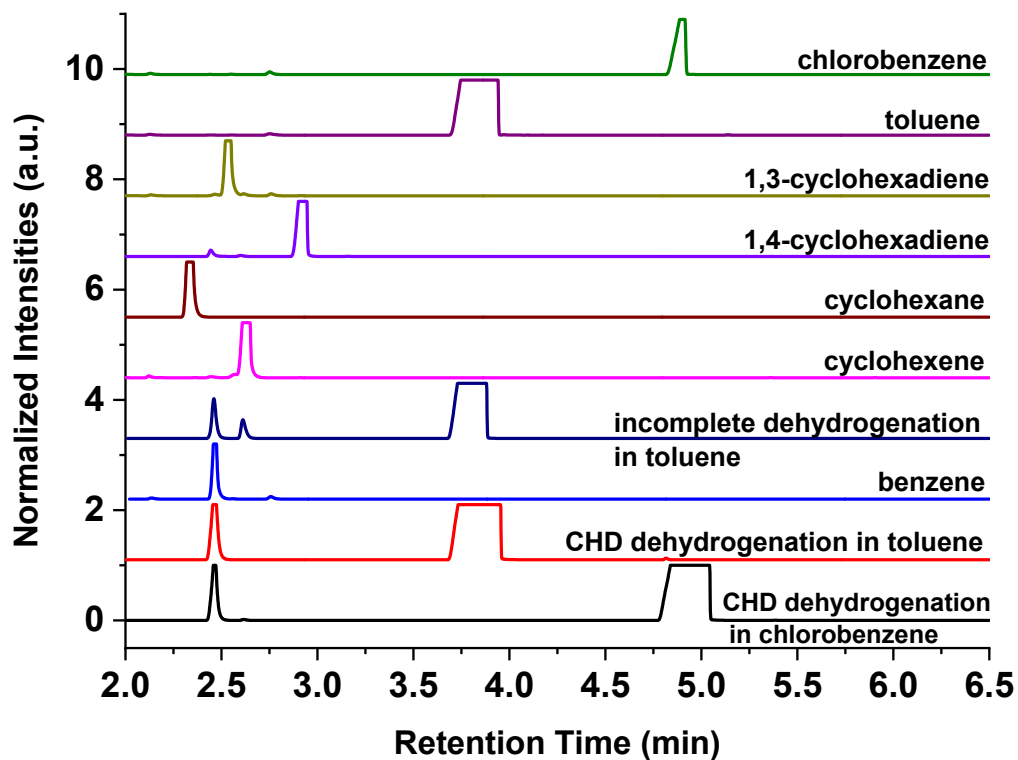


Figure S6: GC traces (method 2) of dehydrogenation reactions in chlorobenzene and toluene and the pure compounds for comparison.

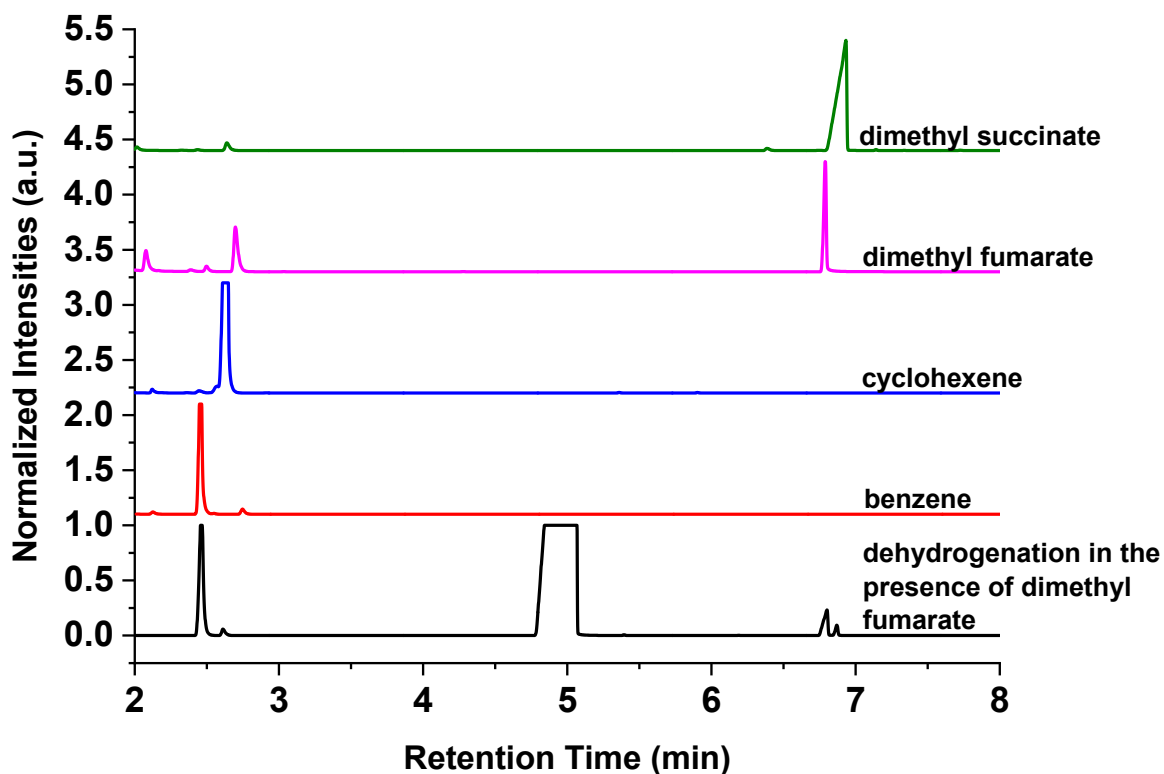


Figure S7: GC traces (method 2) of a 1,4-cyclohexadiene dehydrogenation reaction mixture in the presence of dimethyl fumarate. The GC traces of pure compounds have been added for comparison.

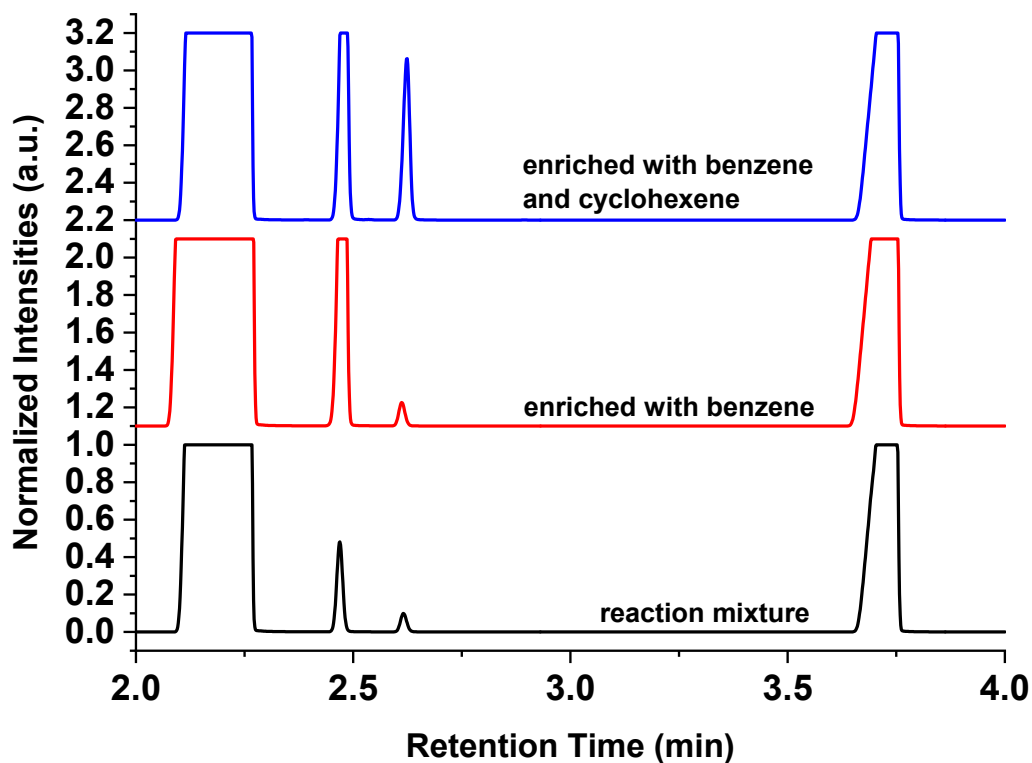


Figure S8: GC traces (method 2) of a representative reaction mixture of the dehydrogenation of 1,4-cyclohexadiene (bottom) enriched with benzene (centre) and cyclohexene (top).

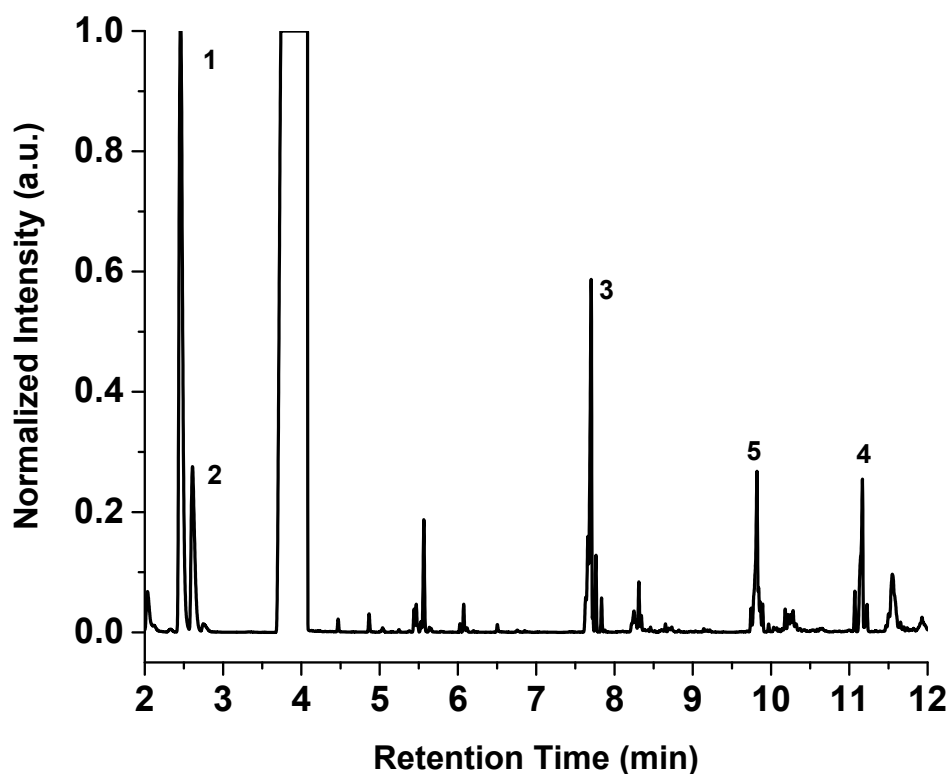


Figure S9: Exemplary GC trace (method 2) of a the metathesis reaction mixture of EPA followed directly by the dehydrogenation of 1,4-cyclohexadiene. In this case also incomplete conversion is shown, with cyclohexene as by-product. Compounds: 1: benzene, 2: cyclohexene, 3: methyl 5-octenoate, 4: dimethyl 5-decenedioate, 5: methyl 5,8-undeceneoate.

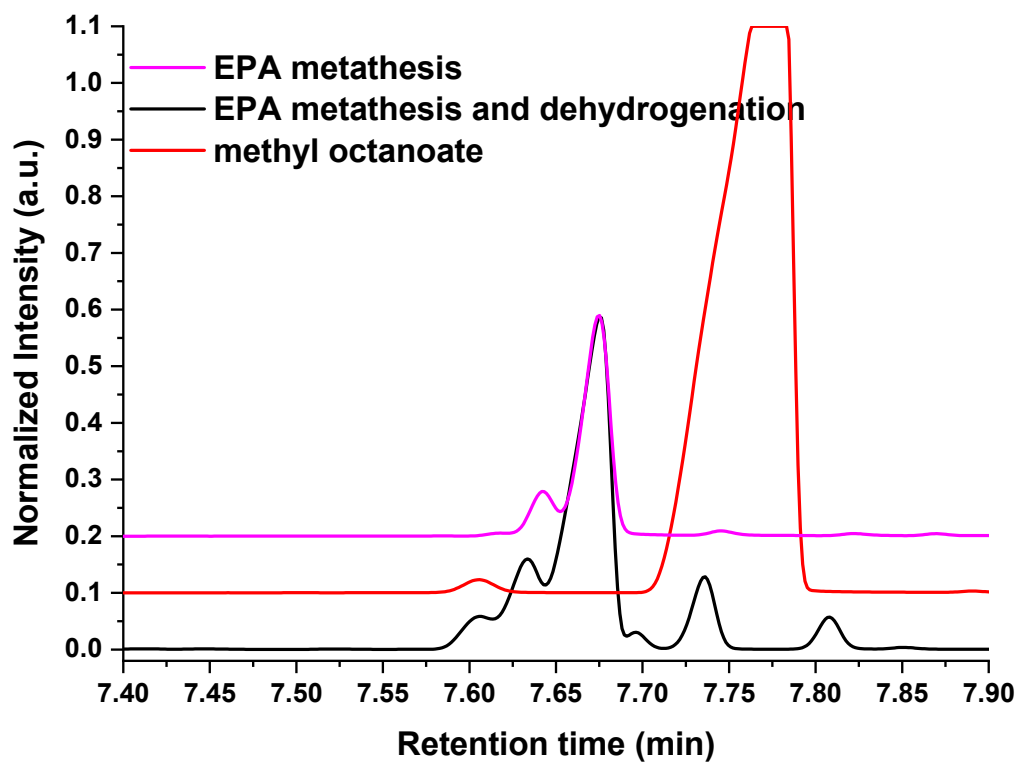


Figure S10: Detail of Figure S9 in the methyl 5-octenoate region, with a comparison to pure methyl octanoate to emphasize that no hydrogenation occurs (method 2).

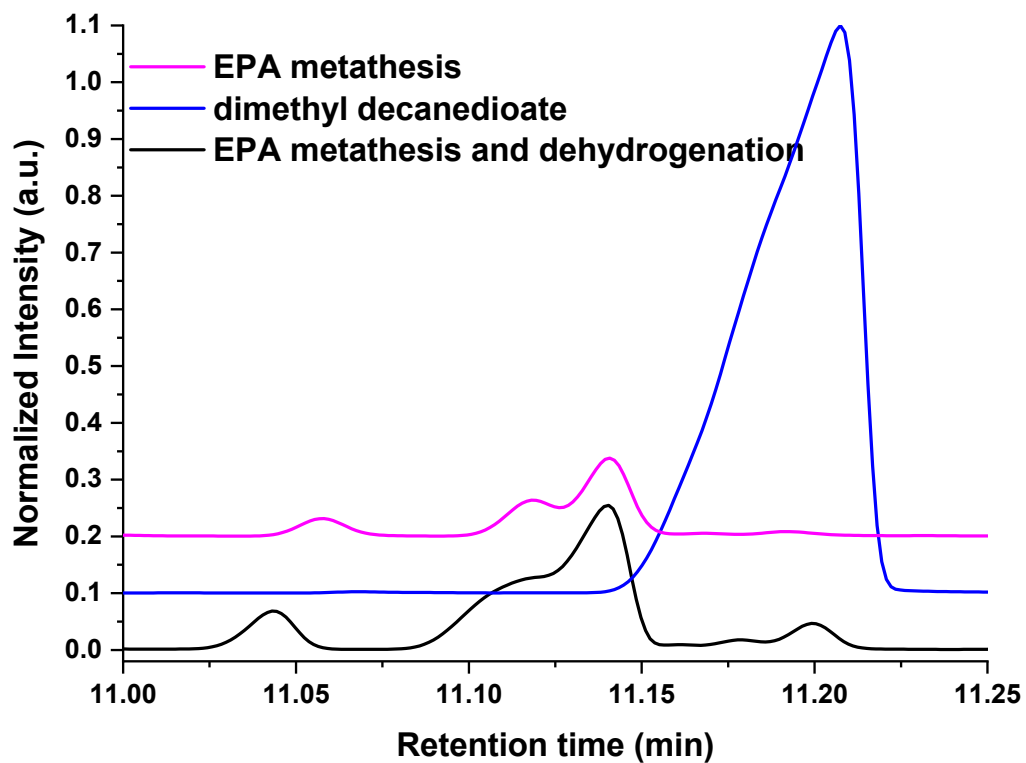


Figure S11: Detail of Figure S9 in the dimethyl decanedioate region, with a comparison to pure dimethyl decanedioate to emphasize that no hydrogenation occurs.

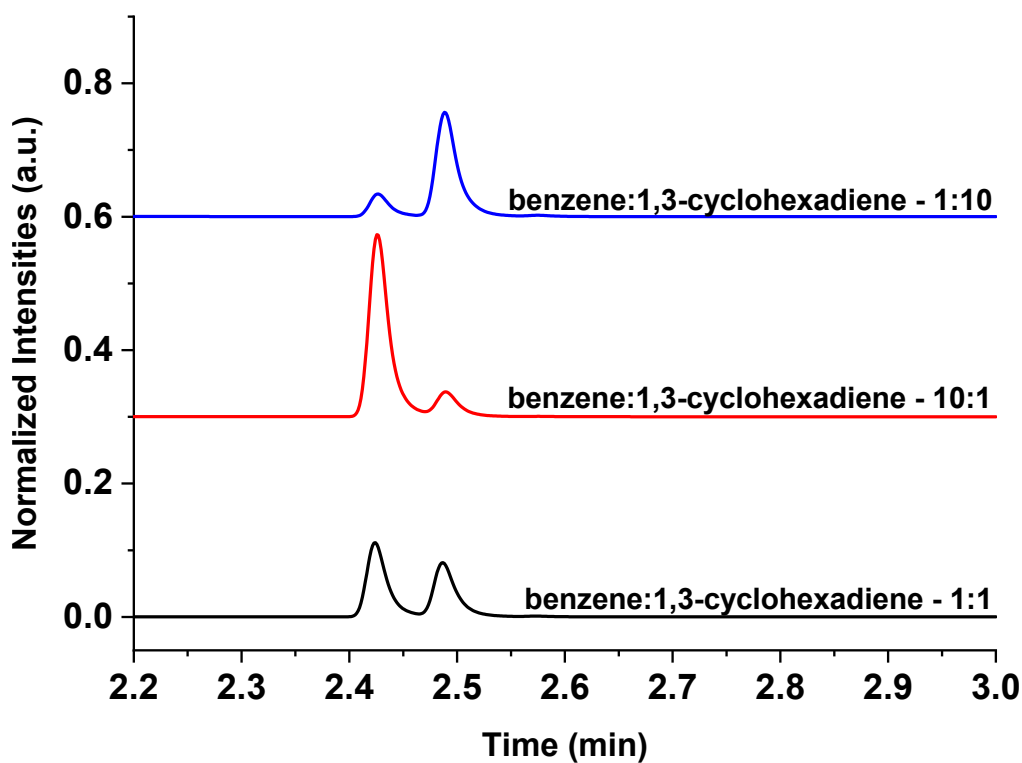


Figure S12: GC traces (method 2) of 3 combinations of benzene and 1,3-cyclohexadiene to emphasize the observable difference between the two different compounds for confirmation and comparison of the presence of benzene.

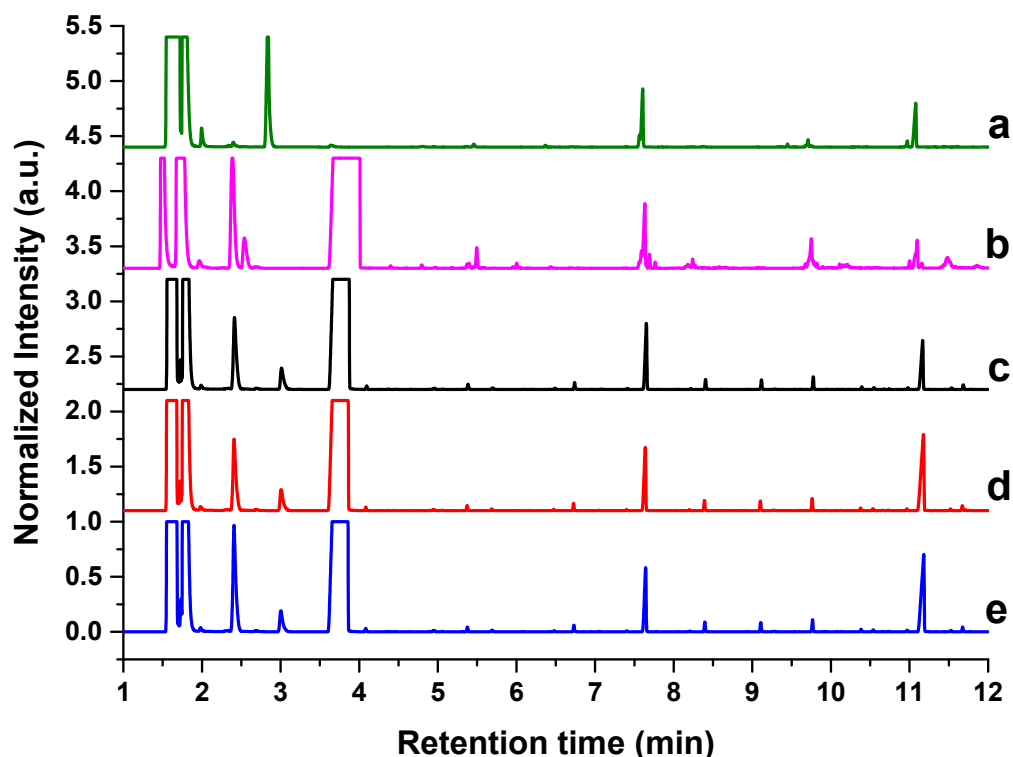


Figure S13: GC traces of a mixture of full conversion metathesis (a), the mixture after dehydrogenation to benzene (b), subsequently hydrogenated (at 10 bar H₂) mixture (c), enriched with dimethyl decanedioate (d), and additionally enriched with benzene (e).

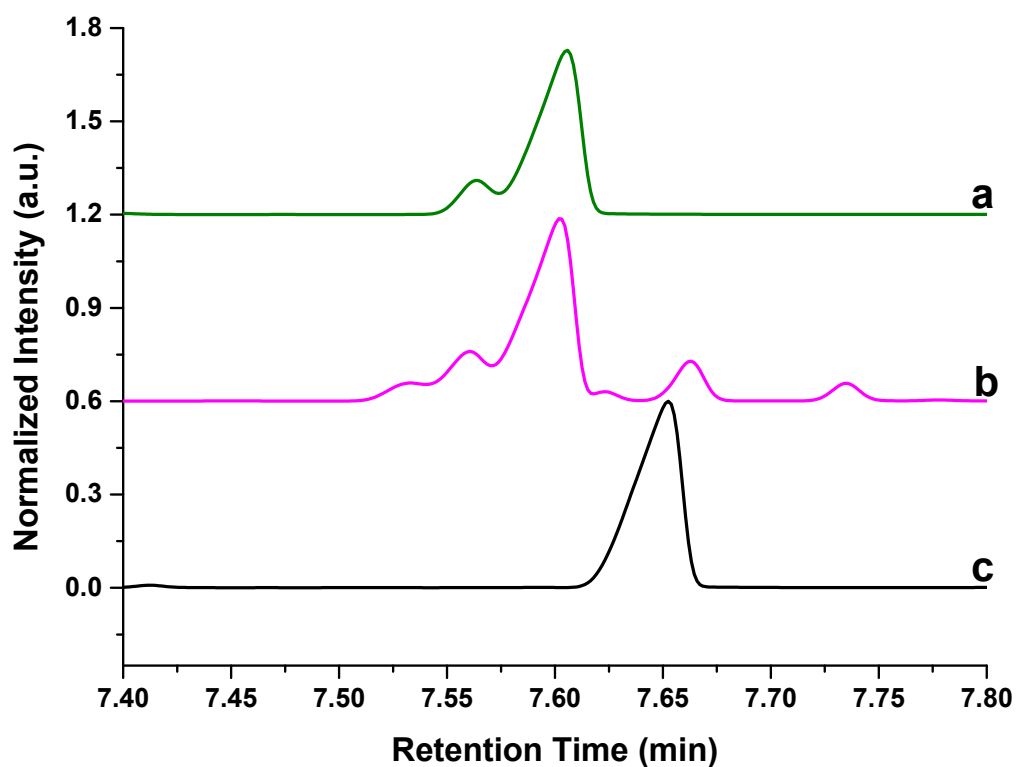


Figure S14: GC traces of a mixture of full conversion metathesis (a), the mixture after dehydrogenation to benzene (b), the subsequently hydrogenated (at 10 bar H_2) mixture (c). Detail of the C_8 region.

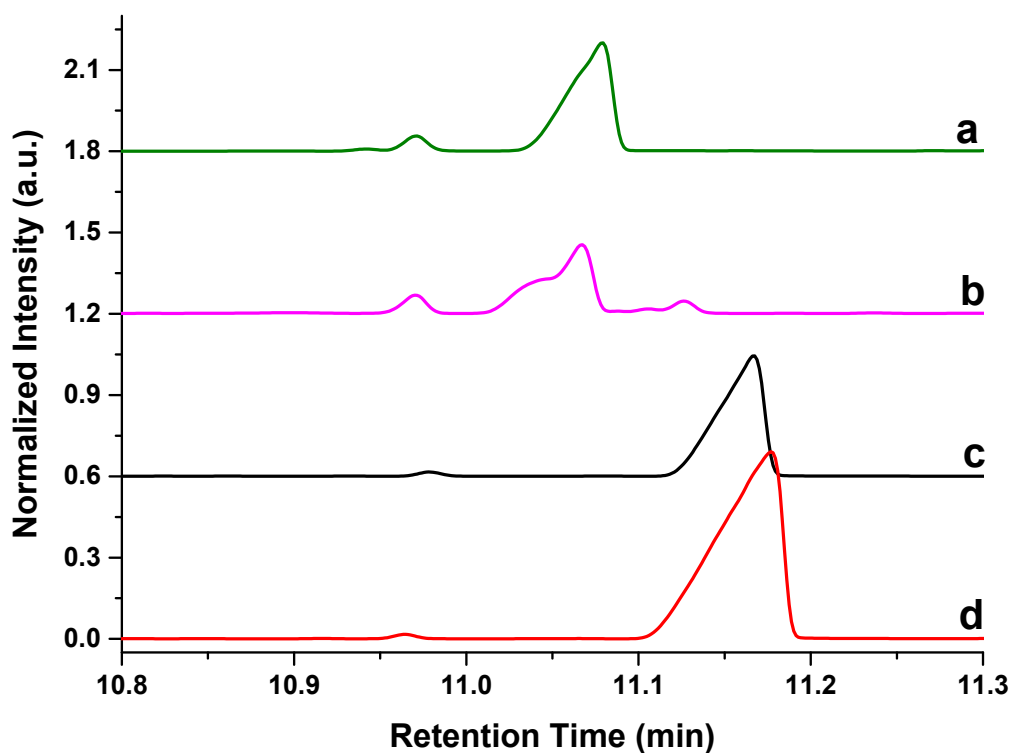


Figure S15: GC traces of a mixture of full conversion metathesis (a), the mixture after dehydrogenation to benzene (b), the subsequently hydrogenated (at 10 bar H_2) mixture (c), enriched with dimethyl decanedioate (d). Detail of the C_{10} region.

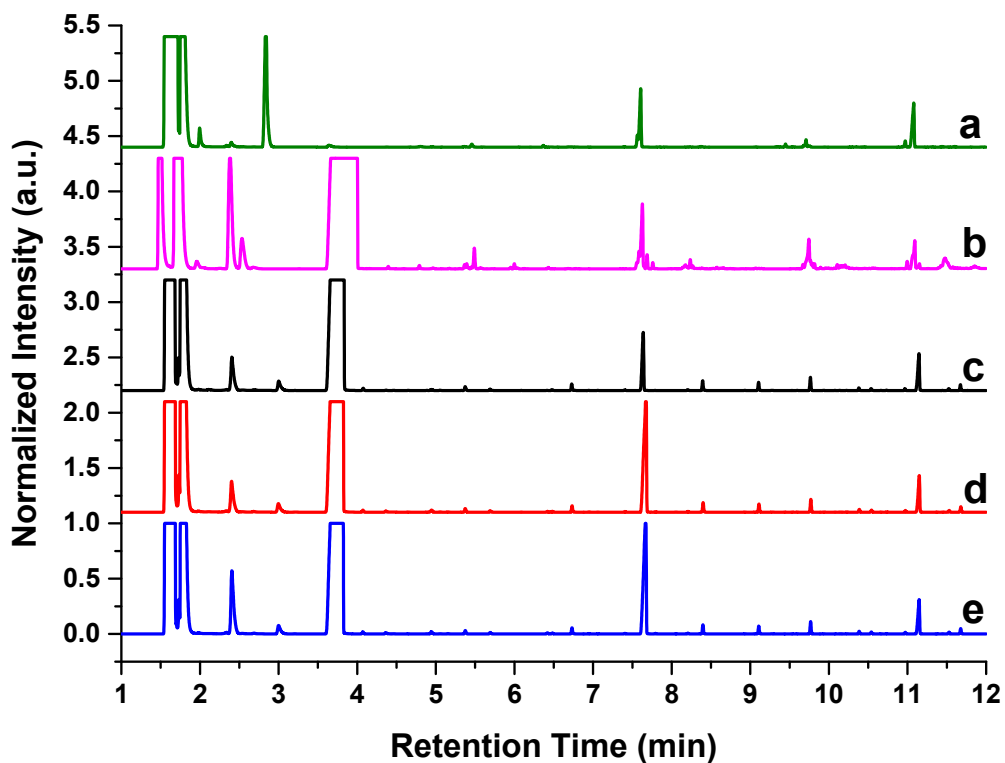


Figure S16: GC traces of a mixture of full conversion metathesis (a), the mixture after dehydrogenation to benzene (b), subsequently hydrogenated (at 5 bar H_2) mixture (c), enriched with methyl octanoate (d), and additionally enriched with benzene (e).

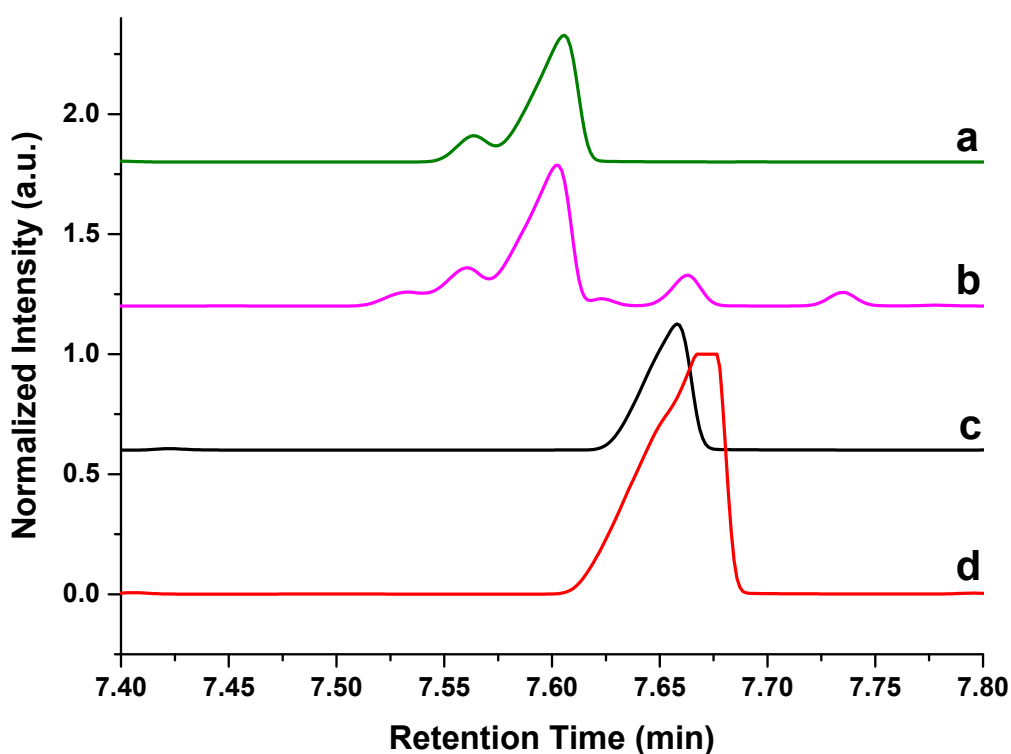


Figure S17: GC traces of a mixture of full conversion metathesis (a), the mixture after dehydrogenation to benzene (b), subsequently hydrogenated (at 5 bar H_2) mixture (c), enriched with methyl octanoate (d). Detail of the C_8 region.

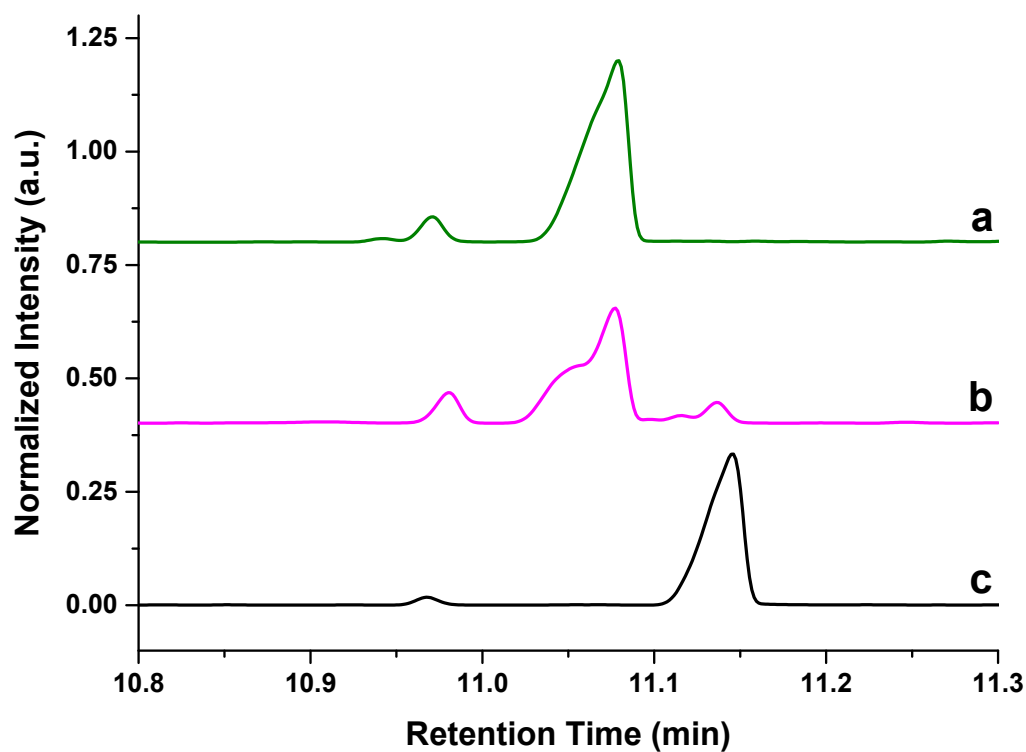


Figure S18: GC traces of a mixture of full conversion metathesis (a), the mixture after dehydrogenation to benzene (b), subsequently hydrogenated (at 5 bar H_2) mixture (c). Detail of the C_{10} region.

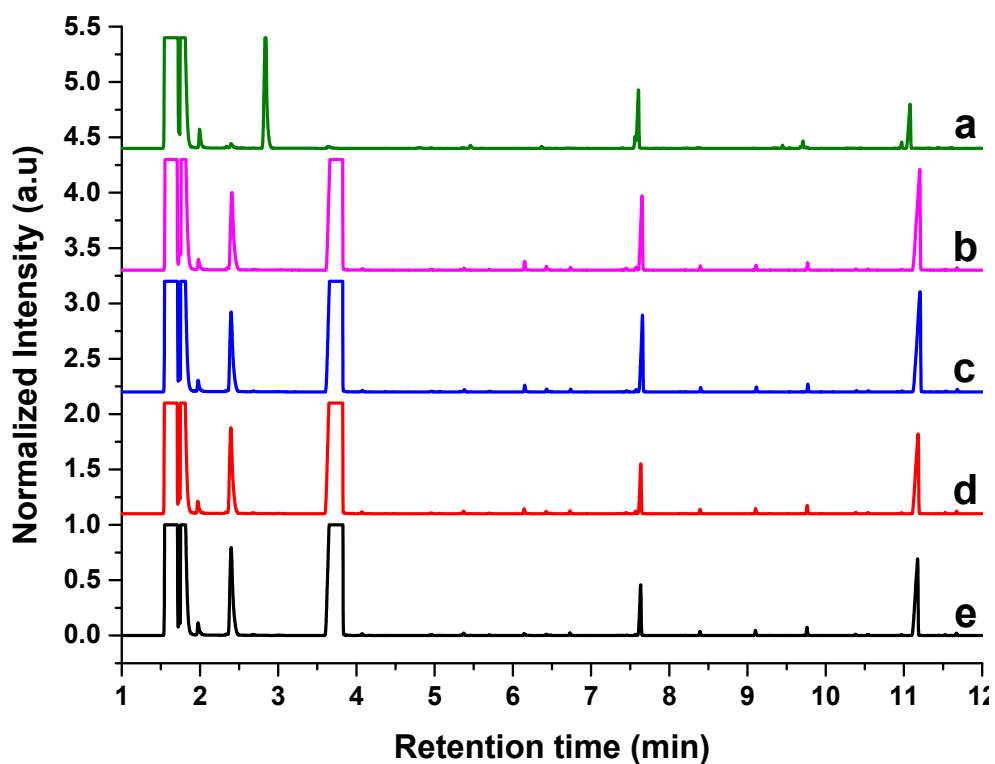


Figure S19: GC traces of the starting metathesis mixture (a), the mixture of (a) enriched with benzene and methyl octanoate and dimethyl decanedioate (b), enriched with methyl octanoate and dimethyl decanedioate (c) enriched with only dimethyl decanedioate (d), simultaneous dehydrogenation and hydrogenation (at 10 bar H_2) of a metathesis mixture (e).

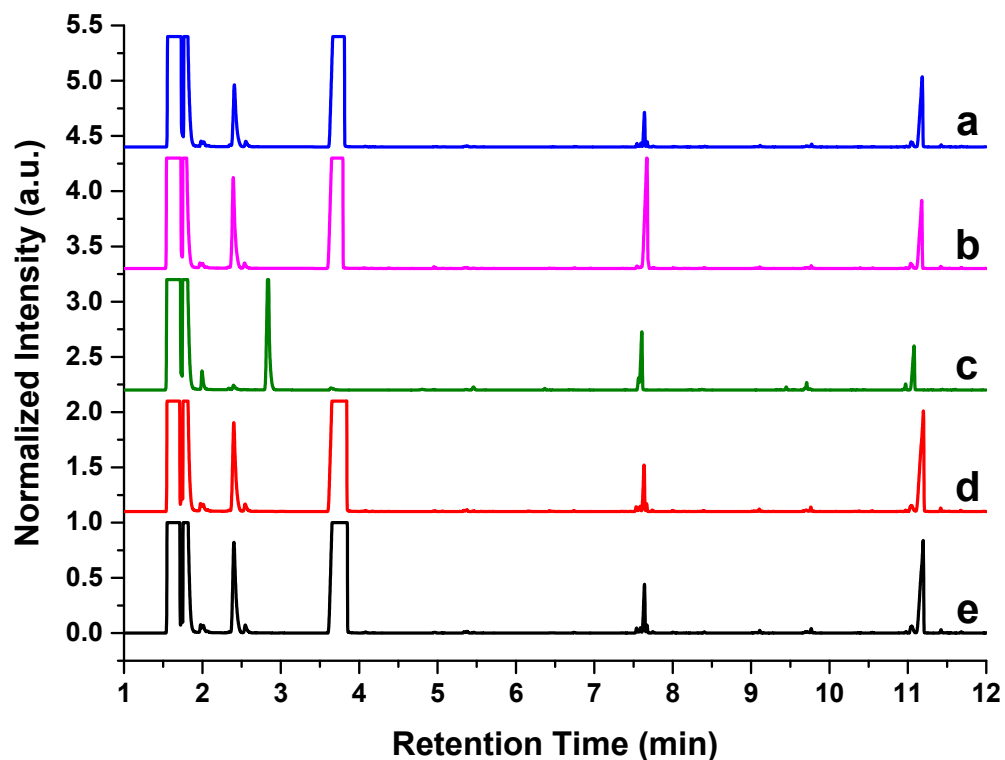


Figure S20: GC traces of simultaneous dehydrogenation to aromatics and hydrogenation of alkenes at 5 bar H_2 of a metathesis mixture (a), the mixture of (a) enriched with benzene and methyl octanoate (b), the starting metathesis mixture (c) simultaneous dehydrogenation and hydrogenation (at 5 bar H_2) of a metathesis mixture (d), the mixture of (d) enriched with dimethyl decanedioate (e).

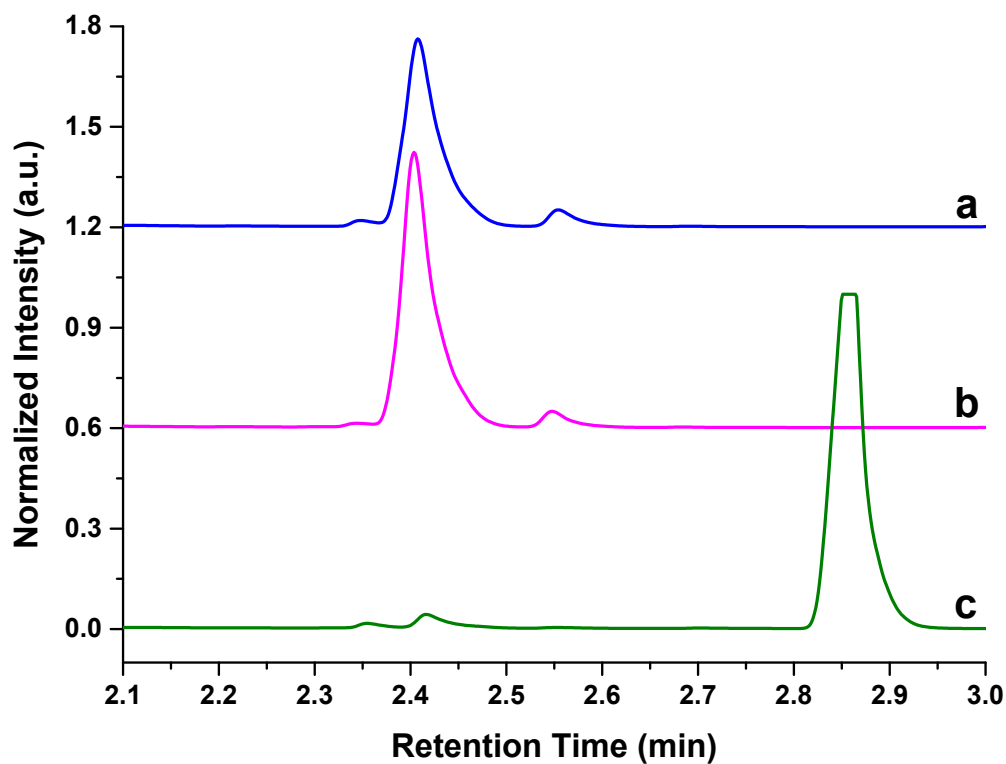


Figure S21: GC traces of simultaneous dehydrogenation to aromatics and hydrogenation of alkenes at 5 bar H_2 of a metathesis mixture (a), the mixture of (a) enriched with benzene and methyl octanoate (b), the starting metathesis mixture (c). Detail of the cyclic C_6 region.

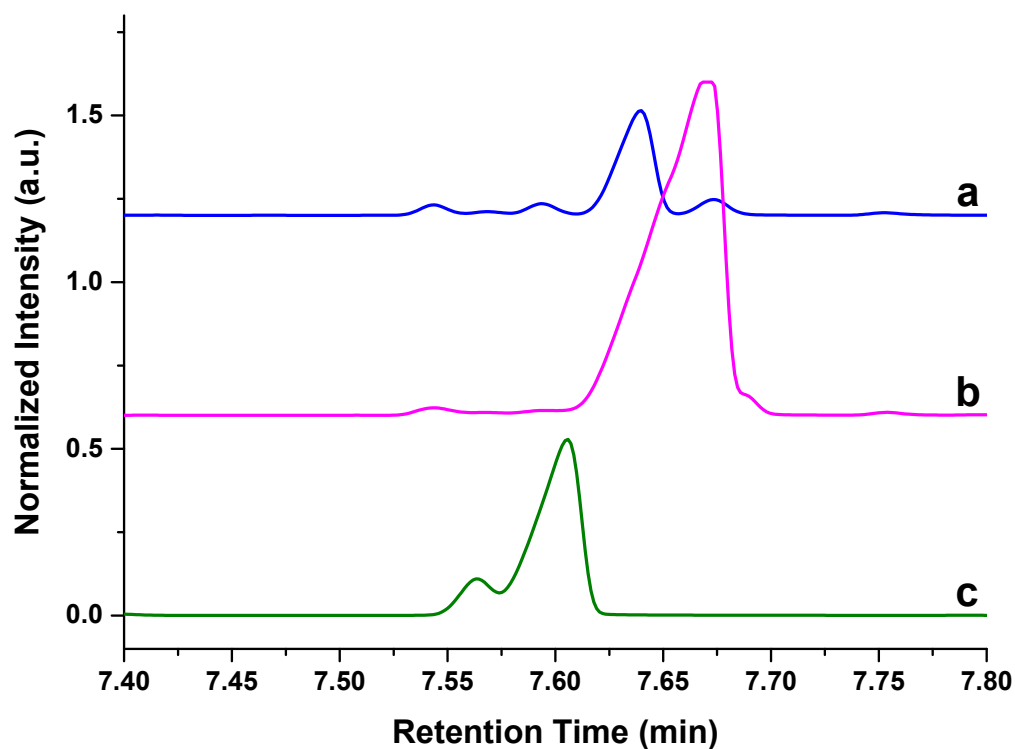


Figure S22: GC traces of simultaneous dehydrogenation to aromatics and hydrogenation of alkenes at 5 bar H_2 of a metathesis mixture (a), the mixture of (a) enriched with benzene and methyl octanoate (b), the starting metathesis mixture (c). Detail of the C_8 region

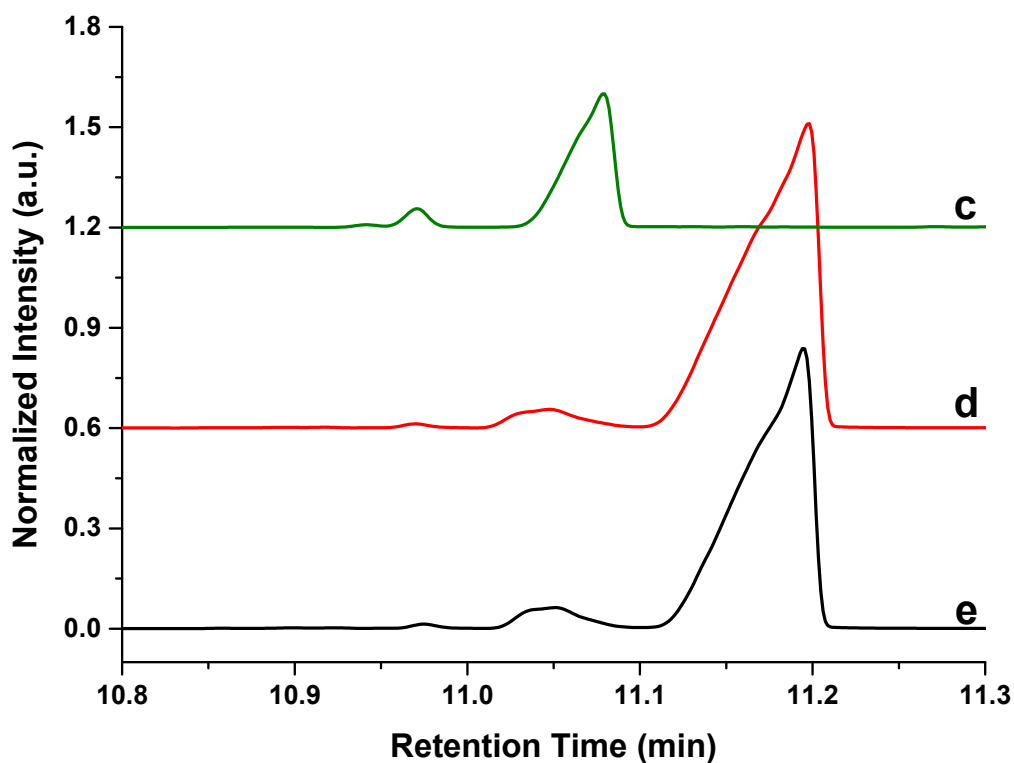


Figure S23: GC traces of the starting metathesis mixture (c) simultaneous dehydrogenation to aromatics and hydrogenation of alkenes at 5 bar H_2 of a metathesis mixture (d), the mixture of (d) enriched with dimethyl decanedioate (e). Detail of the C_{10} region.

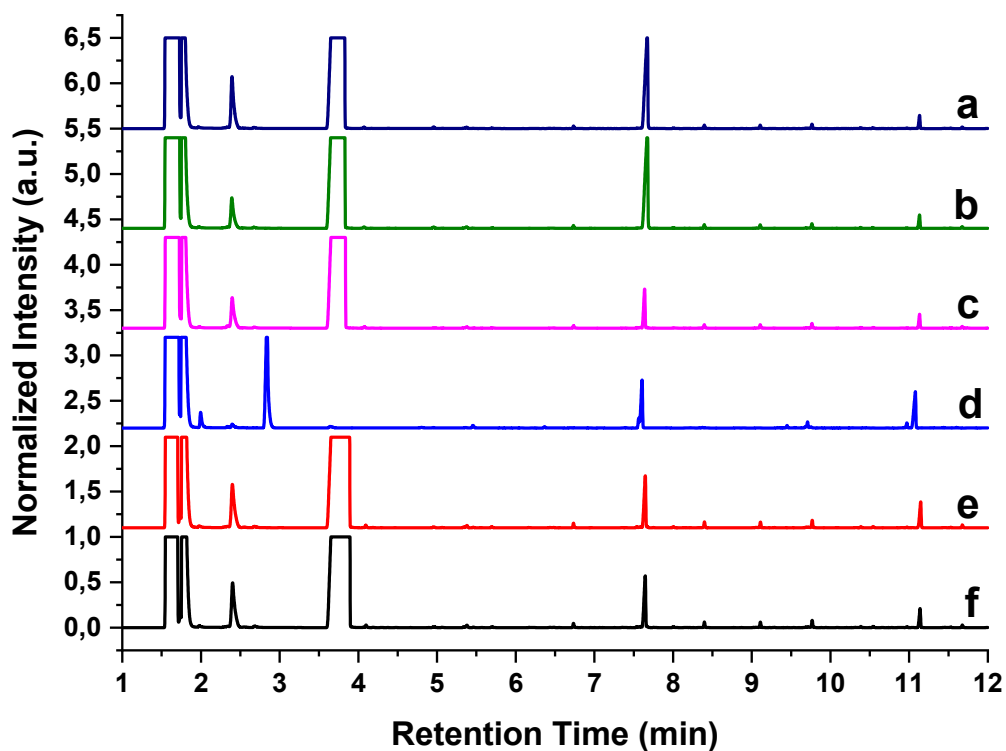


Figure S24: GC traces of the mixture of (c) enriched with benzene and methyl octanoate (a), the mixture of (c) enriched with methyl octanoate (b), simultaneous dehydrogenation and hydrogenation at 1 bar H_2 of a metathesis mixture (c), the starting metathesis mixture (d), the mixture of (f) enriched with dimethyl decanedioate (e) simultaneous dehydrogenation and hydrogenation at 1 bar H_2 of a metathesis mixture enriched with methyl octanoate and benzene(f).

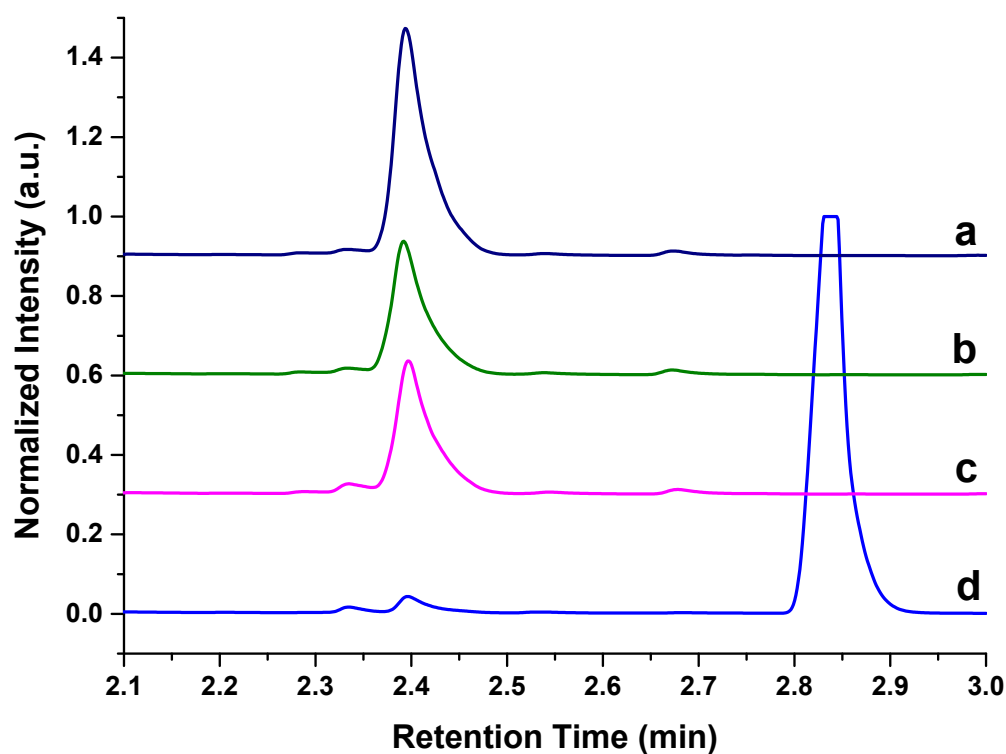


Figure S25: GC traces of mixtures the mixture of (c) enriched with benzene and methyl octanoate (a), the mixture of (c) enriched with methyl octanoate (b), simultaneous dehydrogenation and hydrogenation at 1 bar H_2 of a metathesis mixture (c), the starting metathesis mixture (d). Detail of the cyclic C_6 region.

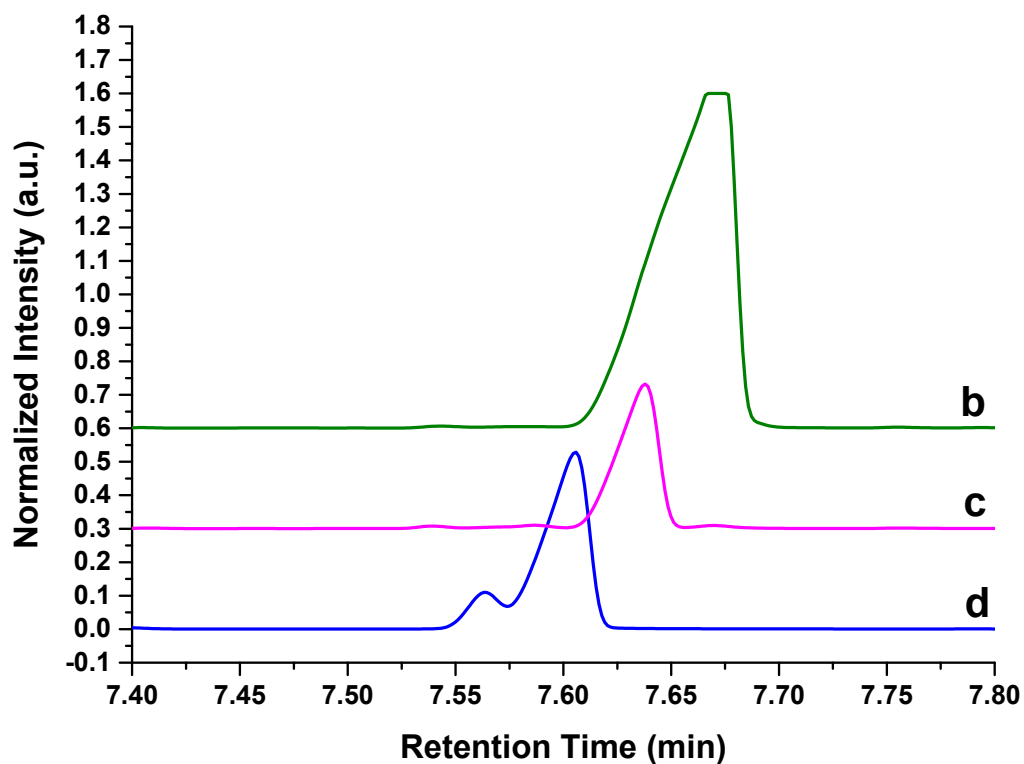


Figure S26: GC traces of the mixture of (c) enriched with methyl octanoate (b), simultaneous dehydrogenation to aromatics and hydrogenation of alkenes at 1 bar H_2 of a metathesis mixture (c), the starting metathesis mixture (d). Detail of the cyclic C_6 region.

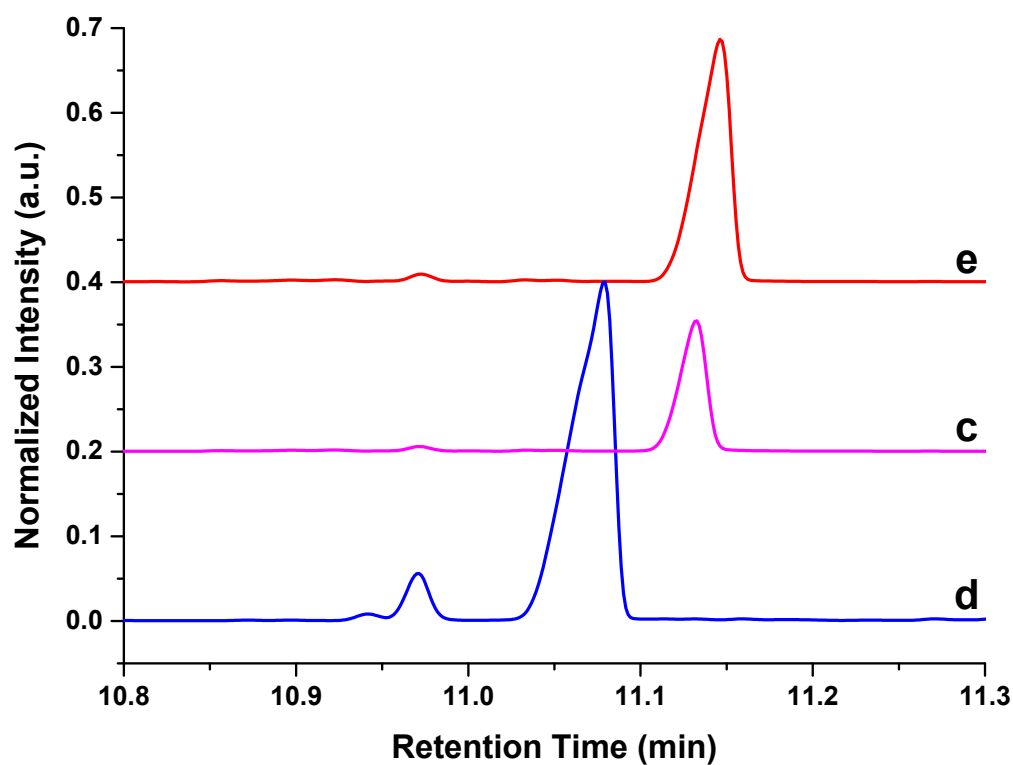


Figure S27: GC traces of the simultaneous dehydrogenation to aromatics and hydrogenation of alkenes at 1 bar H_2 of a metathesis mixture (c), the starting metathesis mixture (d), the mixture of (f) enriched with dimethyl decanedioate (e).

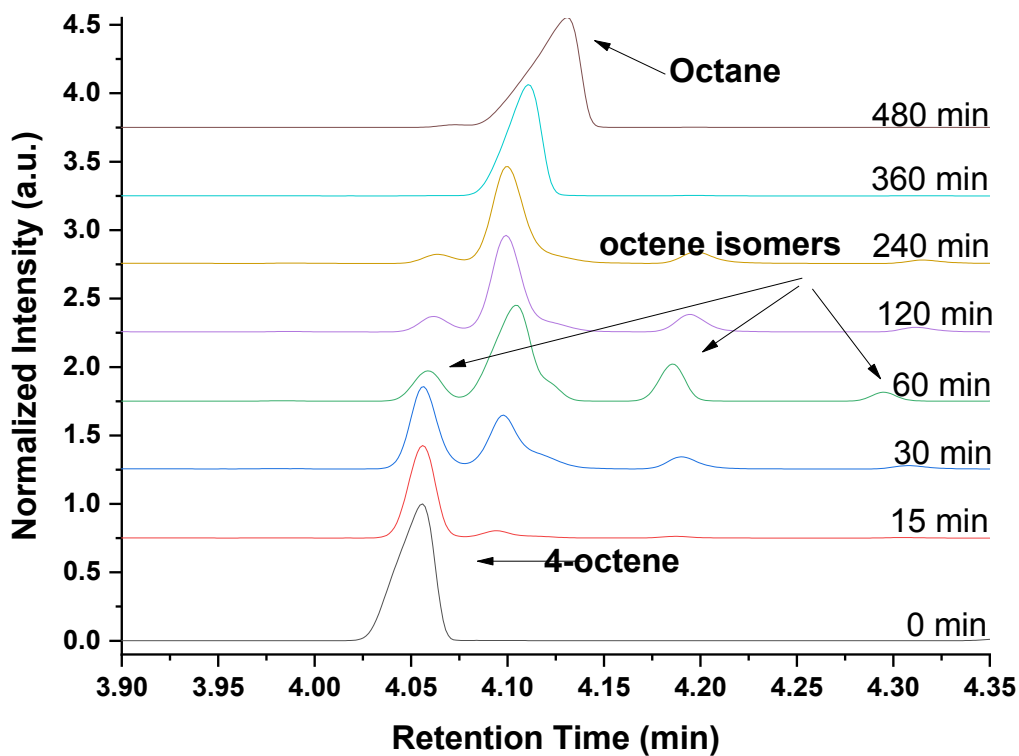


Figure S28: GC-traces of the samples taken at different time intervals during the hydrogenation of the model metathesis mixture, detail of the octene region (conditions see Graph S3).

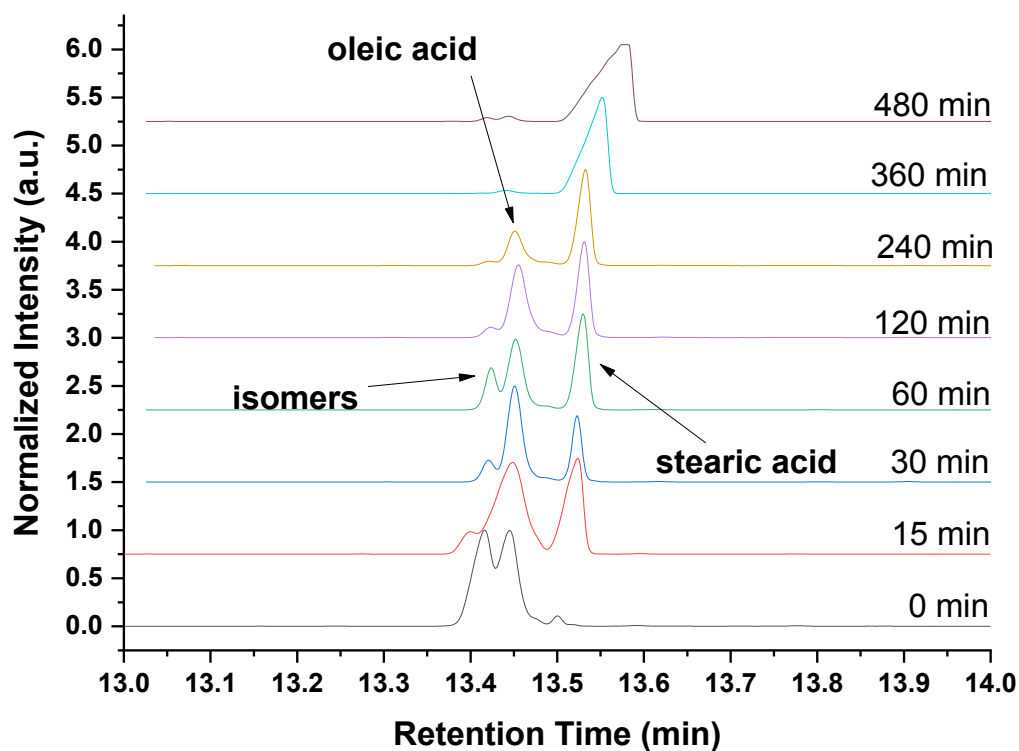


Figure S29: GC-traces of the samples taken at different time intervals during the hydrogenation of the model metathesis mixture, detail of the oleic acid region (conditions see Graph S3).

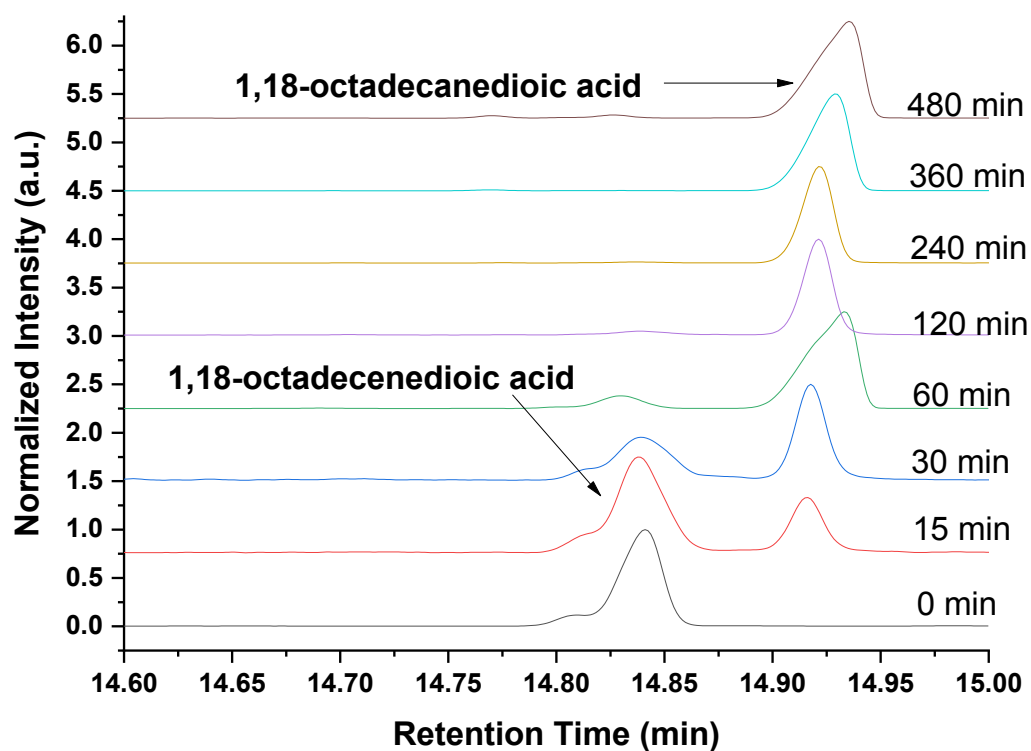


Figure S30: GC-traces of the samples taken at different time intervals during the hydrogenation of the model metathesis mixture, detail of the oleic acid region (conditions see Graph S3).

NMR spectra

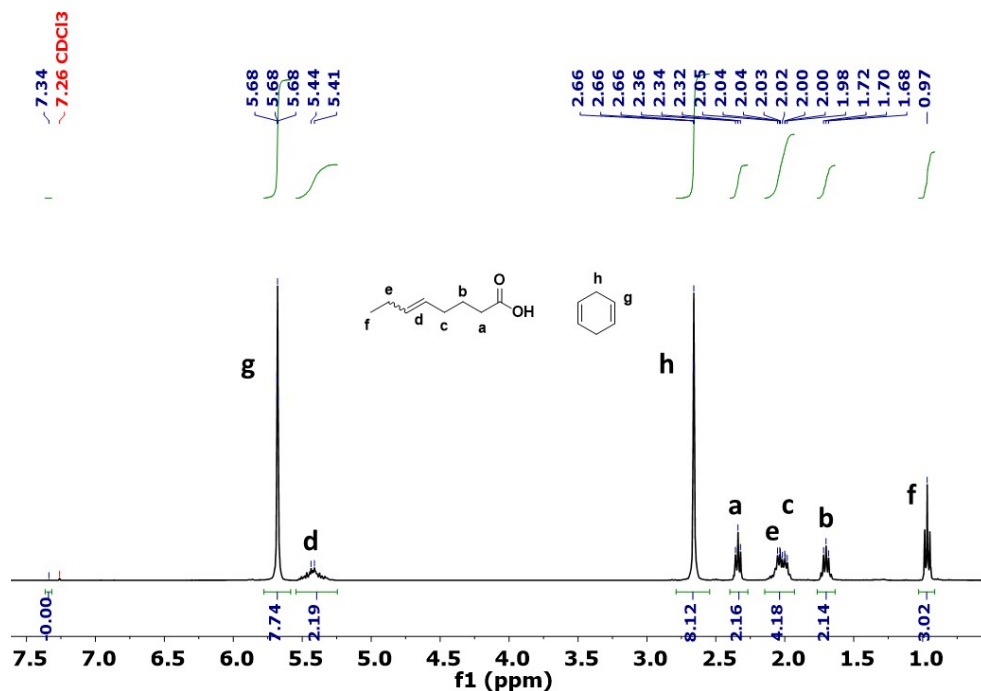


Figure S31: representative ^1H NMR spectrum (400 MHz, CDCl_3 , 302K) of metathesis of EPA with Hoveyda-Grubs 2nd generation metathesis catalyst. The final ratio of 2:1 in 1,4-cyclohexadiene to octenoic acid is clearly seen from the integral values.

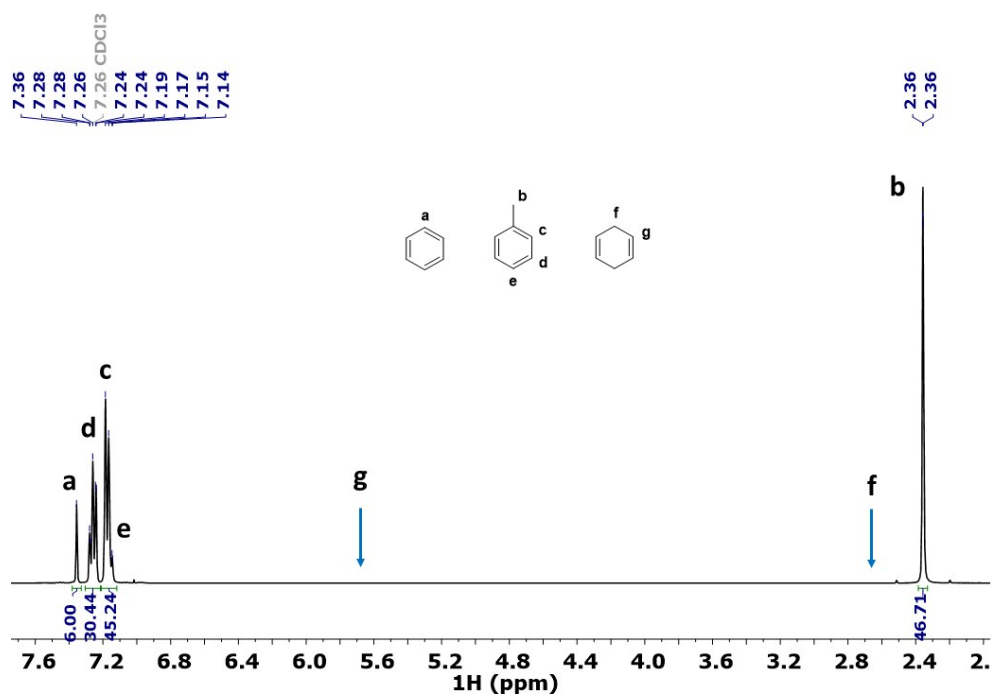


Figure S32: representative ^1H NMR spectrum (400 MHz, CDCl_3 , 302K) of dehydrogenation of 1,4-cyclohexadiene with Pd/C. Toluene is still present as it was used as solvent and not removed for measuring a ^1H NMR spectrum.

References

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