Supporting information

Jojoba Oil Olefin Metathesis: A Valuable Source for Bio-renewable Materials

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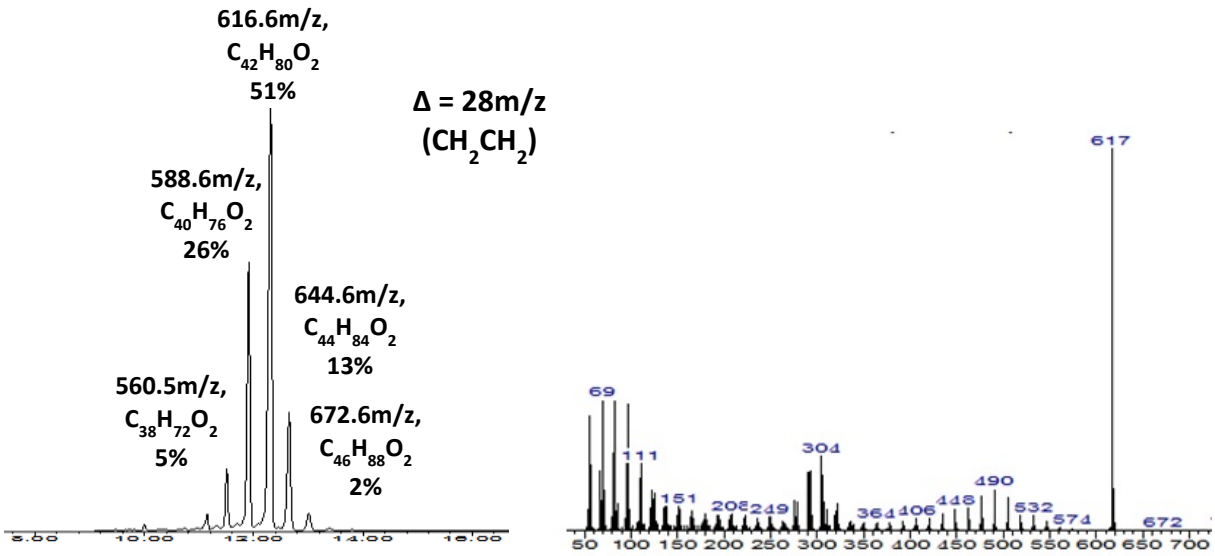
Jojoba oil analysis

The jojoba oil is a mixture of hydrocarbon chains; the most abundant one contains 42 carbons (51%). Each chain differs in the number of pairs of methylene groups present between the ester group and the double bond (the molecular weight difference between chains being 28 Daltons).[1]

(a) **(b)**



(c)

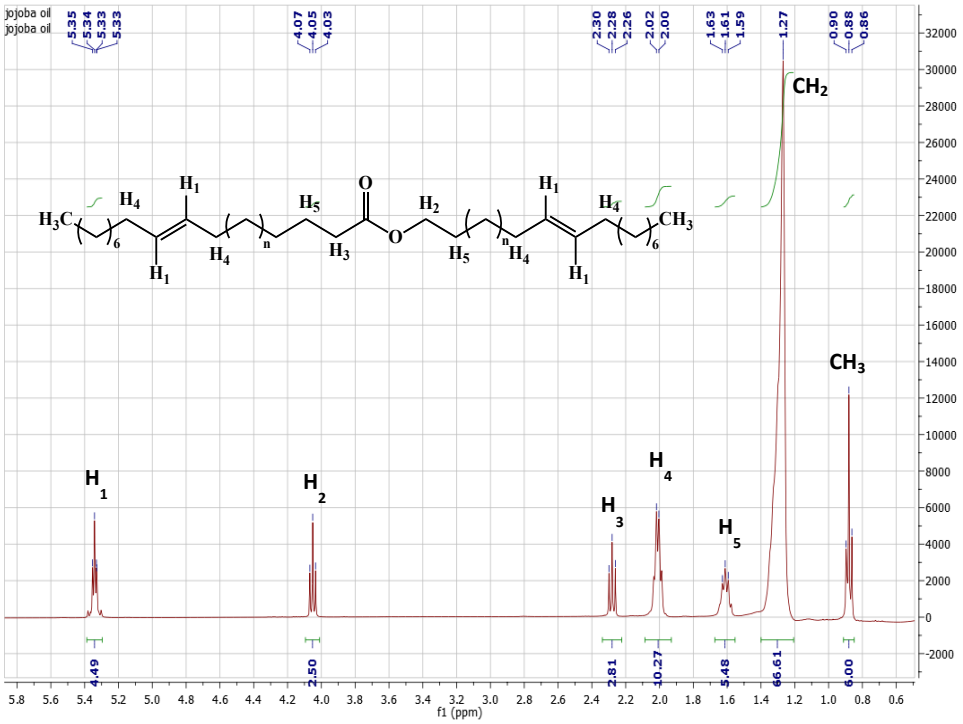


Figure S1. Jojoba oil analysis. (a) SMB-cold EI GC-MS. (b) MS spectrum of the main peak. (c) ^{1}H-NMR (400MHz, $CDCl_3$).

Experimental

General Procedures. Pure jojoba oil was obtained from Kibbutz Hatzerim, Israel and was degassed by applying high vacuum before use. All other commercial reagents were of reagent grade quality, purchased from Sigma-Aldrich and Alfa-Aesar and used without further purification. NMR spectra were recorded on Bruker DPX400 or DMX500 instruments; chemical shifts, given in ppm, are relative to the residual solvent peak. A thermoscientific LTQU XL Orbitrap was used for high resolution mass spectrometry analyses. Gas chromatography data were obtained using an Agilent 6850 GC equipped with an Agilent 5973 MSD working under standard conditions and an Agilent HP5-MS column. All reactions were carried out either under vacuum (as noted) or under an inert nitrogen atmosphere.

General procedure for precatalyst screening experiments. After degassing the Jojoba oil under high vacuum, precatalyst was added (0.14% mol) dissolved in minimum amount of DCM. The mixture was heated to 200^{o}C and distilled under high vacuum (0.1-0.3 torr).

G1. Jojoba oil (5.28 g, 8.56 mmol), precatalyst (10.2 mg, 0.012 mmol). Distillate (0.16 g), Wax (5.12 g).^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.84-0.91 (m, 6H), 1.20-1.38 (bs, aliphatic, 64H), 1.54-1.66 (m, aliphatic, 5H), 1.89-2.06 (m, allylic, 10H), 2.28 (t, J = 7.6, 4H, $CH_2(C=O)O$), δ 4.05(t, J = 6.8, 2H, $(C=O)OCH_2$), 5.29-5.44 (m, vinylic, 4H).

G2. Jojoba oil (5.98 g, 9.70 mmol), precatalyst (12.1 mg, 0.014 mmol). Distillate (0.98 g), Wax (5.04 g). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.85-0.91 (m, 6H), 1.20-1.39 (bs, aliphatic, 91H), 1.54-1.66 (m, aliphatic, 10H), 1.90-2.05 (m, allylic, 14H), 2.25-2.30 (m, 4H, $CH_2(C=O)O$), 4.05 (t, J = 6.8 Hz, 4H, $(C=O)OCH_2$), 5.30-5.44 (m, vinylic, 6H).

G3. Jojoba oil (4.90 g, 7.94 mmol), precatalyst (10 mg, 0.011 mmol). Distillate (0.50 g), Wax (4.22 g). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.84-0.91 (m, 6H), 1.20-1.40 (bs, aliphatic, 97H), 1.54-1.70 (m, aliphatic, 9H), 1.90-2.06 (m, allylic, 14H), 2.25 (t, J = 7.6, 4H, $CH_2(C=O)O$), 4.05 (t, J = 6.8 Hz, 4H, $(C=O)OCH_2$), 5.30-5.45 (m, vinylic, 6H).

HG1. Jojoba oil (5.24 g, 8.50 mmol), precatalyst (7.3 mg, 0.012 mmol). Distillate (0.22 g), Wax (5.02 g). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.85-0.92 (m, 6H), 1.20-1.40 (bs, aliphatic, 72H), 1.55-1.66 (m, aliphatic, 6H), 1.91-2.07 (m, allylic, 11H), 2.25 (t, J = 7.6, 3H, $CH_2(C=O)O$), 4.05 (t, J = 6.8 Hz, 3H, $(C=O)OCH_2$), 5.30-5.44 (m, vinylic, 5H).

HG2. Jojoba oil (5.48 g, 8.88 mmol), precatalyst (8.8 mg, 0.013 mmol). Distillate (0.46 g), Wax (4.86 g). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.85-0.92 (m, 6H), 1.20-1.40 (bs, aliphatic, 96H), 1.55-1.66 (m, aliphatic, 9H), 1.90-2.05 (m, allylic, 13H), 2.25 (t, J = 7.6, 4H, $CH_2(C=O)O$), 4.05 (t, J = 6.8 Hz, 4H, $(C=O)OCH_2$), 5.30-5.45 (m, vinylic, 6H).

PSHG2. Jojoba oil (5.08 g, 8.23 mmol), precatalyst (8.0 mg, 0.012 mmol). Distillate (1.10 g), Wax (3.94 g). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.84-0.91 (m, 6H), 1.21-1.39 (bs, aliphatic, 122H), 1.55-1.70 (m, aliphatic, 3H), 1.90-2.05 (m, allylic,

17H), 2.25 (t, *J* = 7.6, 7H, $CH_2(C=O)O$), 4.02-4.08 (m, 6H, $(C=O)OCH_2$), 5.30-5.45 (m, vinylic, 7H).

Hydride scavenger (Table 2, entry 2). To jojoba oil (5.50 g, 8.91 mmol), pinacol phenylboronic acid (91 mg, 0.45 mmol) was added. The solution was heated to 50°C and **HG2** was added (11.2 mg, 0.018 mmol). The mixture was stirred for 5 minutes and vacuum was applied. The mixture was heated to 150°C and unsaturated hydrocarbon chains were distilled (0.23 g). Distillate flask was cooled to -78°C. Wax (5.19 g). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.83-0.91 (m, 6H), 1.21-1.39 (bs, aliphatic, 72H), 1.56-1.70 (m, aliphatic, 5H), 1.90-2.04 (m, allylic, 10H), 2.25-2.31 (m, 3H, $CH_2(C=O)O$), 4.02-4.08 (m, 3H, $(C=O)OCH_2$), 5.30-5.44 (m, vinylic, 4H).

Portion-wise addition of precatalyst (Table 2, entry 3). To neat Jojoba oil (5.48 g, 8.89 mmol) **HG2** was added (11.1 mg, 0.02 mmol) while stirring the oil. Vacuum was applied and the mixture was then heated for distillation at 150°C. The receiving flask was cooled to 0°C. After no more distillate was collected, the heating was discontinued and nitrogen was introduced into the system. The distillate head was removed and a second portion of precatalyst was added and the distillation continued, under the same conditions. The procedure was repeated for the third portion of precatalyst. Distillate (total of 589.5 mg) was collected and analysed by GC-MS. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.86-0.89 (m, 6H), 1.20-1.38 (bs, aliphatic, 103H), 1.54-1.70 (m, aliphatic, 11H), 1.90-2.05 (m, allylic, 13H), 2.28 (t, *J* = 7.6 Hz, 4H, $CH_2(C=O)O$), 4.05 (t, *J* = 6.4 Hz, 4H, $(C=O)OCH_2$), 5.30-5.44 (m, vinylic, 5H).

Steam distillation (Table 2, entry 4). Jojoba oil (5.50 g, 8.92 mmol) was heated to 40°C and **HG2** was added (11.2 mg, 0.018 mmol). Then water was added in excess and the unsaturated hydrocarbon chains were distilled at 150°C. After no more distillate was collected, the heating was discontinued and another portion of precatalyst was added (11.2 mg, 0.018 mmol). The procedure was repeated twice more with equal amounts of catalyst. The system was cooled to room temperature and the collected distillate was extracted with diethyl ether, dried over $MgSO_4$, filtered and the solvent was gently removed by reduced pressure to give colourless liquid (51.3 mg). The wax residue was dissolved in chloroform, separated from the aqueous phase, dried over $MgSO_4$, filtered and the solvent removed by reduced pressure (4.97 g). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.84-0.92 (m, 6H), 1.20-1.38 (bs, aliphatic, 75H), 1.52-1.70 (m, aliphatic, 7H), 1.90-2.06 (m, allylic, 10H), 2.28 (t, *J* = 7.6 Hz, 3H, $CH_2(C=O)O$), 4.05 (t, *J* = 6.8 Hz, 2H, $(C=O)OCH_2$), 5.30-5.46 (m, vinylic, 4H).

Butenolysis (Table 2, entry 5). 2-Butene gas (mixture of *cis* and *trans*) was bubbled into jojoba oil (8.72 g, 14.12 mmol) at 0°C until 1.65 g were absorbed (29.44 mmol). **HG2** was added (17.7 mg, 0.03 mmol) at room temperature and the mixture was stirred for an hour at 55°C. Vacuum was applied (0.16-0.14 torr) and the mixture was heated to 150°C. Unsaturated hydrocarbon chains were distilled (2.04 g) to afford a polyester wax residue (6.72 g). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.85-0.91 (m, 6H), 1.20-1.45 (bs, aliphatic, 104H), 1.57-1.66 (m, aliphatic, 13H), 1.90-2.05 (m, allylic, 14H), 2.28 (t, *J* = 7.6, 5H, $CH_2(C=O)O$), 4.05 (t, *J* = 6.8, 5H, $(C=O)OCH_2$), 5.31-5.44 (m, vinylic, 6H).

Hexenolysis (Table 2, entry 6). To neat jojoba oil (4.23 g, 6.85 mmol) (E)-3-hexene

(1.70 mL, 13.70 mmol) and **HG2** were added (8.6 mg, 0.01 mmol) and the mixture was stirred for 5 minutes at room temperature. Vacuum was applied (0.18-0.12 torr) and the mixture was then heated to 140°C. Unsaturated hydrocarbon chains were distilled (1.19 g) to afford a polyester wax residue (3.08 g). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.81-0.91 (m, 6H), 1.22-1.38 (bs, aliphatic, 75H), 1.54-1.67 (m, aliphatic, 10H), 1.89-2.04 (m, allylic, 11H), 2.28 (t, J = 7.6, 4H, $CH_2(C=O)O$), 4.05 (t, J = 6.8, 4H, $(C=O)OCH_2$), 5.33-5.43 (m, vinylic, 4H).

Dilution in THF (Table 2, entry 7). Jojoba oil (3.00 g, 4.86 mmol) was diluted in THF (10 mL). **HG2** was added (6.1 mg, 9.7 μmol) and the mixture was stirred over night at room temperature. A white polymer precipitated (254 mg). After filtration the solvent was removed by reduced pressure to give a wax (2.3175 g). Polymer- ^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.84-0.91 (m, 6H), 1.20-1.40 (bs, aliphatic, 148H), 1.56-1.64 (m, aliphatic, 21H), 1.90-2.05 (m, allylic, 21H), 2.28 (t, J = 7.6 Hz, 8H, $CH_2(C=O)O$), 4.05 (t, J = 6.8 Hz, 8H, $(C=O)OCH_2$), 5.32-5.44 (m, vinylic, 8H). wax- ^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.84-0.91 (m, 6H), 1.20-1.38 (bs, aliphatic, 59H), 1.57-1.66 (m, aliphatic, 4H), 1.91-2.05 (m, allylic, 9H), 2.28 (t, J = 7.6 Hz, 2H, $CH_2(C=O)O$), 4.02-4.06 (m, 2H, $(C=O)OCH_2$), 5.32-5.44 (m, vinylic, 3H).

Low temperature (Table 2, entry 8). To neat jojoba oil (5.36 g, 8.70 mmol) at 70°C **HG2** (10.9 mg, 0.02 mmol) was added and the mixture was stirred for 2 hours and then cooled to room temperature to afford a waxy solid. The wax obtained was heated to 140°C and vacuum was applied for distillation (0.18-0.12 torr). The receiving flask was cooled to 0°C. After no more distillate was collected, the heating was discontinued. 770 mg of distillate and 4.58g of polyester wax residue were obtained. Wax (before distillation) ^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.84-0.92 (m, 6H), 1.20-1.40 (bs, aliphatic, 63H), 1.52-1.68 (m, aliphatic, 10H), 1.90-2.06 (m, allylic, 10H), 2.28 (t, J = 7.6, 3H, $CH_2(C=O)O$), 4.05 (t, J = 6.8, 2H, $(C=O)OCH_2$), 5.31-5.44 (m, vinylic, 4H). Wax (after distillation) ^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.86-0.89 (m, 6H), 1.19-1.40 (bs, aliphatic, 80H), 1.54-1.66 (m, aliphatic, 10H), 1.89-2.05 (m, allylic, 12H), 2.28 (t, J = 7.6, 4H, $CH_2(C=O)O$), 4.05 (t, J = 6.8, 4H, $(C=O)OCH_2$), 5.29-5.43 (m, vinylic, 5H).

Low loading of precatalyst (Table 2, entry 9). To neat jojoba oil (5.68 g, 9.20 mmol) at room temperature **HG2** (1.2 mg, 1.8 μmol) was added and the mixture was stirred for 5 minutes and then heated to 155°C. Vacuum was applied for distillation (0.15 torr). The receiving flask was cooled to 0°C. After no more distillate was collected, the heating was discontinued. After no more distillate was collected, the heating was discontinued. 723 mg of hydrocarbon chains distillate and 4.87g of polyester wax residue were obtained. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm)- δ 0.85-0.90 (m, 6H), 1.22-1.37 (bs, aliphatic, 78H), 1.58-1.65 (m, aliphatic, 7H), 1.91-2.05 (m, allylic, 11H), 2.28 (t, J = 7.5, 3H, $CH_2(C=O)O$), 4.04-4.07 (m, 3H, $(C=O)OCH_2$), 5.32-5.43 (m, vinylic, 5H).

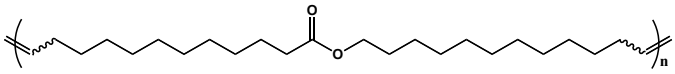
Basic hydrolysis. In a pressure flask, polyester wax (191.4 mg) (obtained from the metathesis reaction of Jojoba oil with **HG2**) was dissolved in THF (5 mL). Then KOH 2M (4 mL) was added. The pressure flask was sealed and heated to reflux overnight. The flask was cooled to room temperature and HCl 1M was added until

slightly acidic pH. The organic phase was separated and aqueous phase was extracted with ether. The organic phases were combined and dried over $MgSO_4$, filtered and the solvent was removed by reduced pressure to give a white wax (160 mg). ^{1}H-NMR (500 MHz, $CDCl_3$, ppm)- δ 0.85-0.95 (t, *J* = 7 Hz, 2H), 1.23-1.38 (bs, aliphatic, 30H), 1.52-1.60 (m, 2H, CH_2CH_2OH), 1.60-1.68 (m, 2H, $CH_2CH_2(C{=}O)OH$), δ 1.91-2.05 (m, allylic, 4H), 2.31-2.38 (m, 2H, $CH_2(C{=}O)OH$), 3.64 (t, *J* = 6.5 Hz, 2H, CH_2OH), 5.30-5.44 (m, vinylic, 2H).

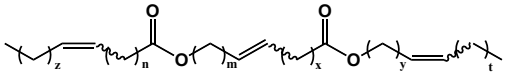
Thiol-ene oligomerisation. Into a flame dried Schlenk flask, Jojoba oil (200 mg, 0.324 mmol) was added under N_2 atmosphere. Then, 1,2-ethanedithiol (27 µL, 0.324 mmol) and 1,1'-diazene-1,2-diyldicyclohexanecarbonitrile (4 mg, 2.0 µmol) were added and the mixture was stirred for 5 min. at room temperature. Then the mixture was heated to 80^{o}C for 2h. After cooling to room temperature the reaction mixture was dissolved in THF and precipitated into methanol. The precipitate was dissolved completely in chloroform. ^{1}H-NMR spectrum in $CDCl_3$ showed a reduction of 50% of double bonds in the material compared to the starting compound. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm)- δ 0.86-0.89 (m, 6H), 1.23-1.26 (bs, aliphatic, 68H), 1.48-1.56 (m, aliphatic, 3H), 1.58-1.64 (m, aliphatic, 5H), 1.94-2.03 (m, allylic, 6H), 2.28 (t, *J* = 8, 2H, $CH_2(C{=}O)O$) 2.54-2.90 (m, 4H), 4.05 (t, *J* = 8 Hz, 2H, $(C{=}O)OCH_2$), 5.33-5.39 (m, vinylic, 2H).

ESI-MS analysis of wax - Catalyst screening

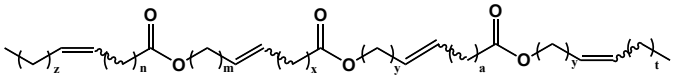
Monomer average size - 364 m/z



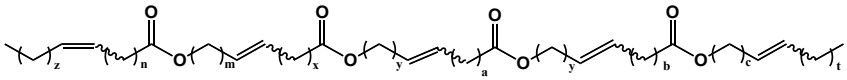
Dimer MWs range between 800-1050 m/z:



Trimer MWs range between 1200-1500 m/z:



Tetramer MWs range between 1500-1800 m/z:



Pentamer MWs range between 1900-2200 m/z and so on…

In some of the ESI-MS spectra a molecular weight distribution centered at 1234 m/z (617 X 2) can be observed. This is most likely due to the interaction of two whole Jojoba molecules; it is a common phenomenon in MALDI where two molecules are

bound by non-covalent interactions (probably at the ester site where the acidic proton which gives the charge resides). This is not a metathesis dimerization (or trimerization) and it is just an artifact of the MS method.

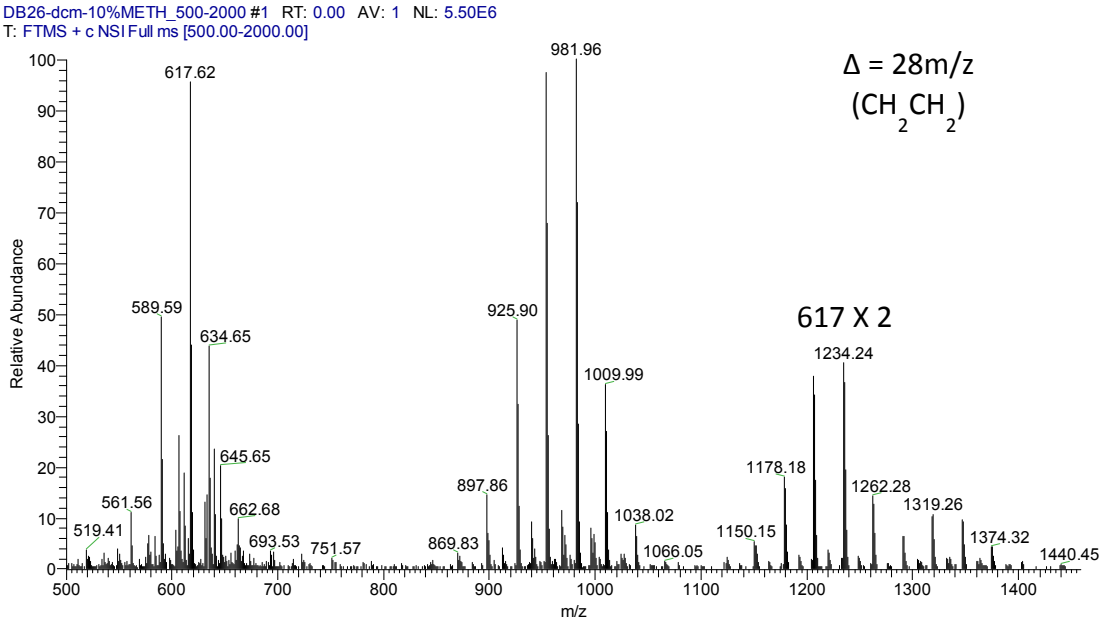


Figure S2. ESI-MS analysis of wax, experiment catalysed by **G1**.

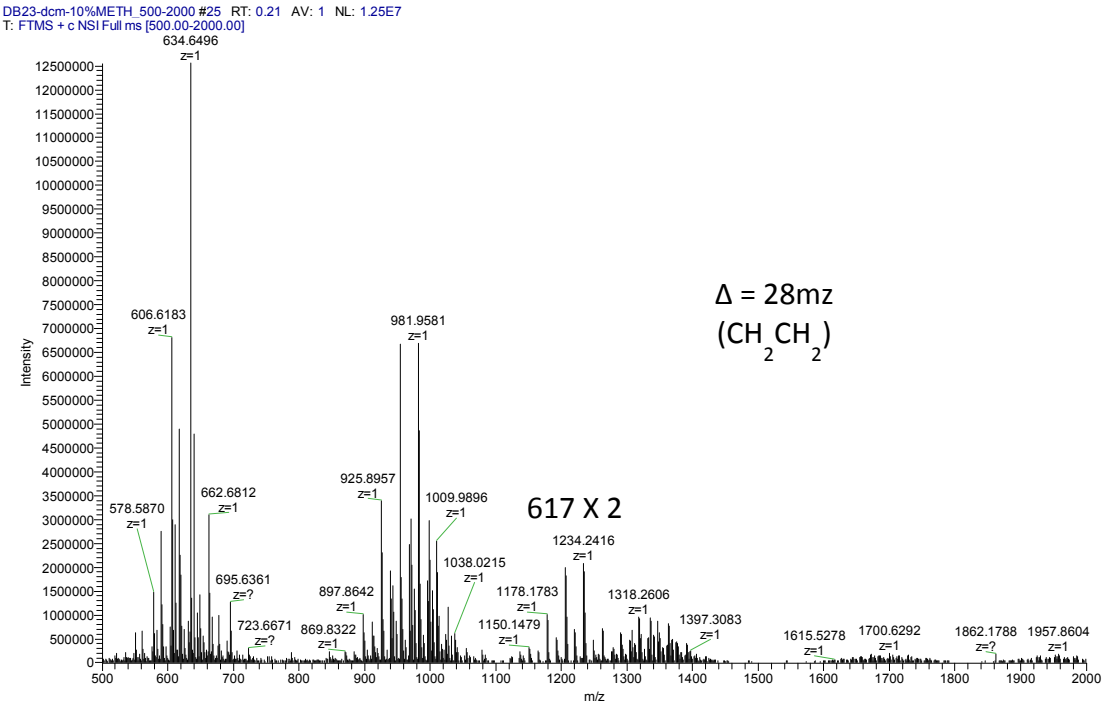


Figure S3. ESI-MS analysis of wax, experiment catalysed by **HG1**.

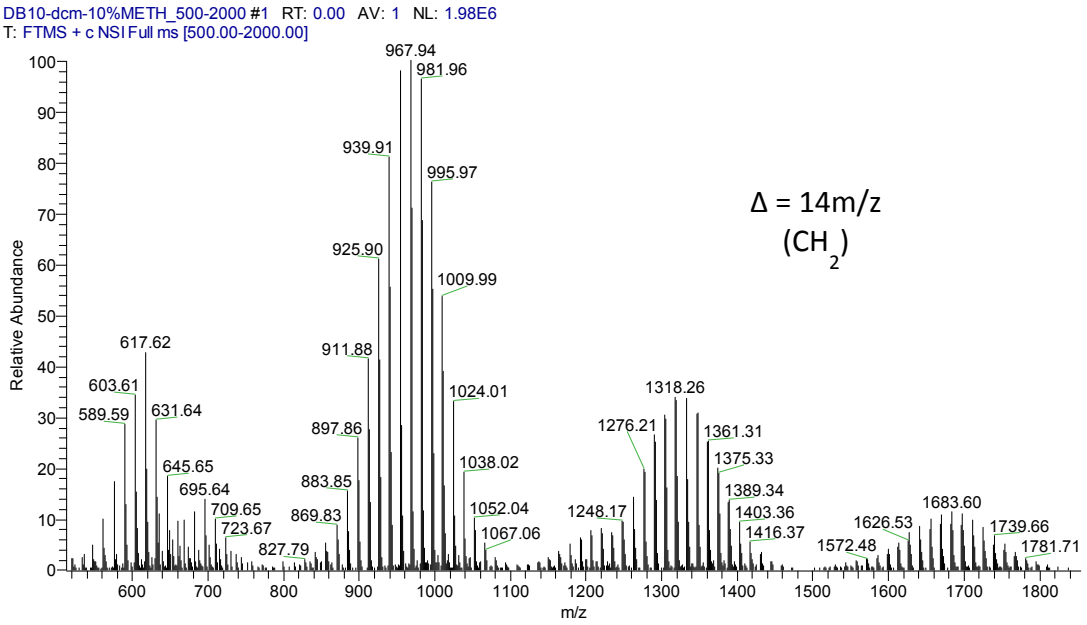


Figure S4 (a). ESI-MS analysis of wax, experiment catalysed by **G2**.

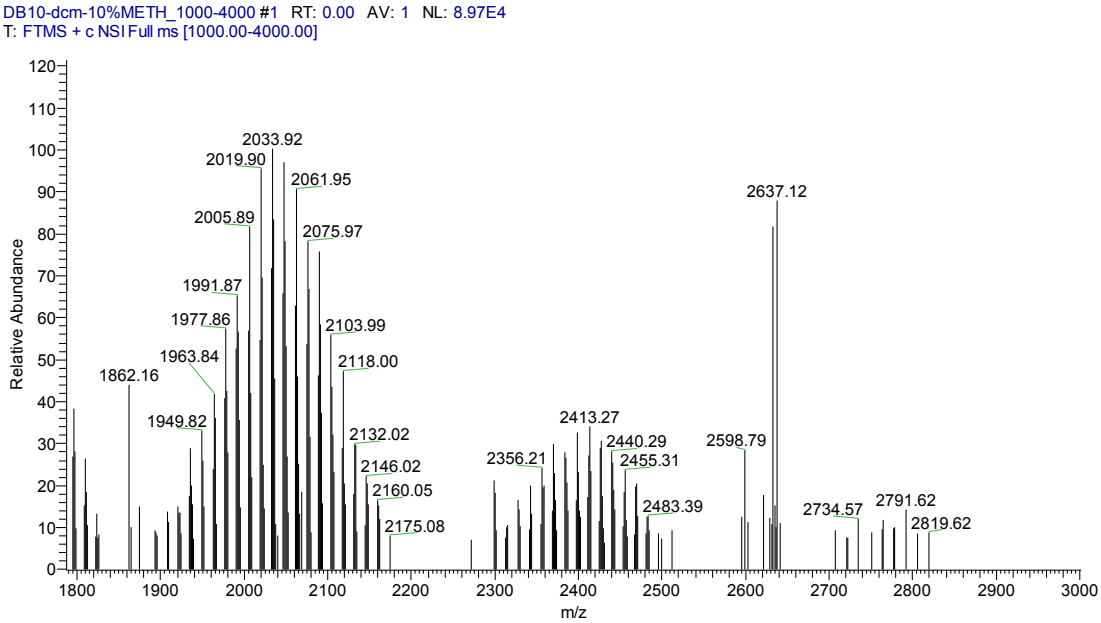


Figure S4 (b). ESI-MS analysis of wax, experiment catalysed by **G2**, higher molecular weights.

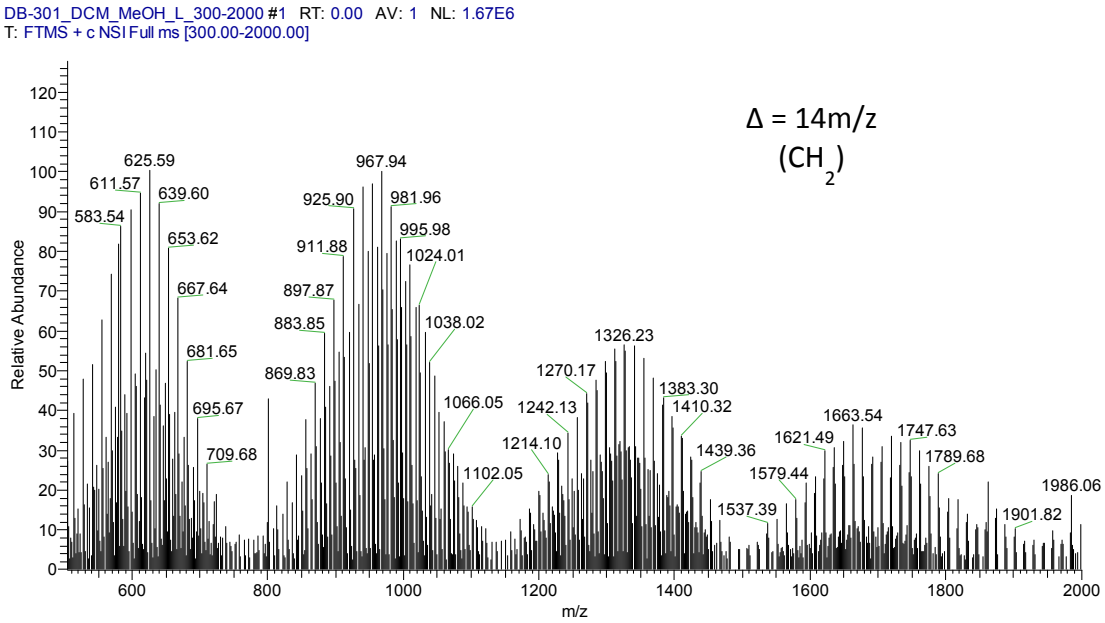


Figure S5 (a). ESI-MS analysis of wax, experiment catalysed by **HG2**.

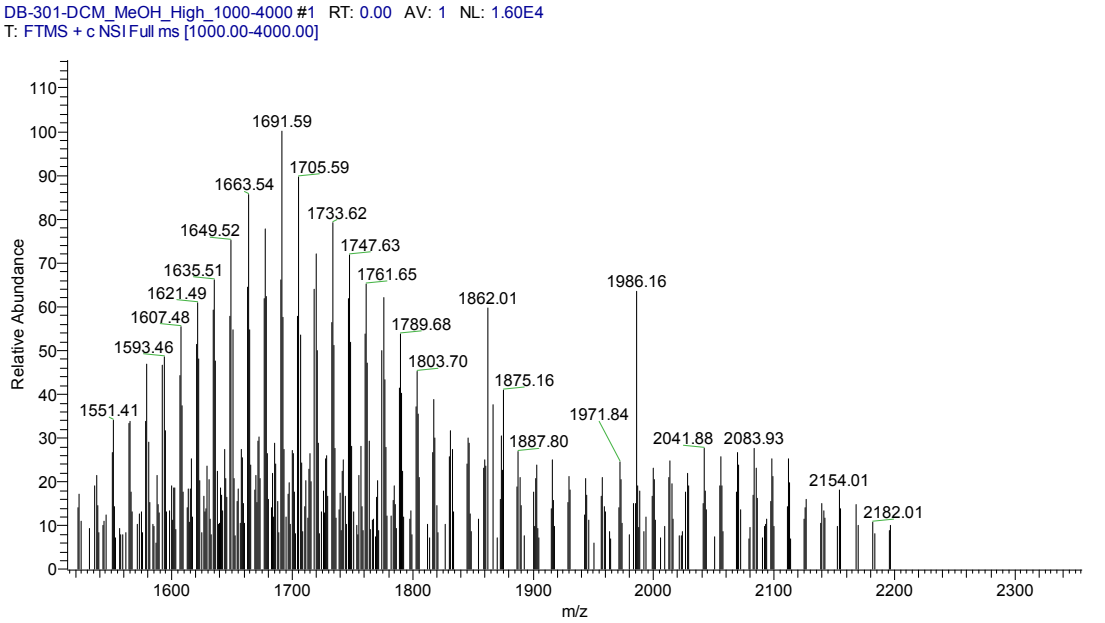


Figure S5 (b). ESI analysis of wax, experiment catalysed by **HG2**, higher molecular weights.

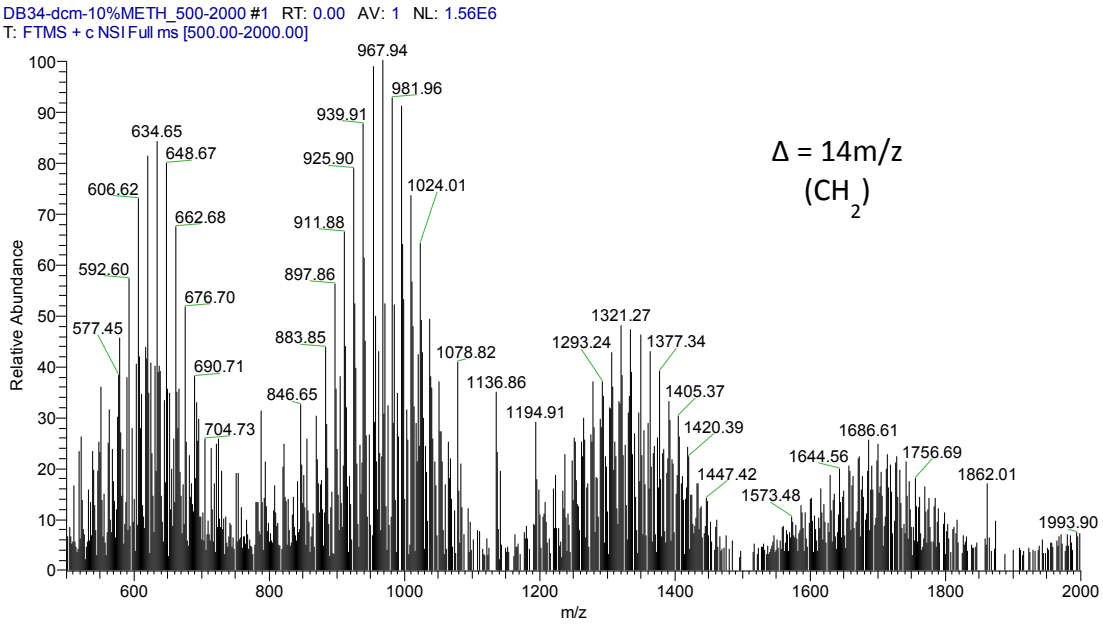


Figure S6 (a). ESI-MS analysis of wax, experiment catalysed by **PSHG2**.

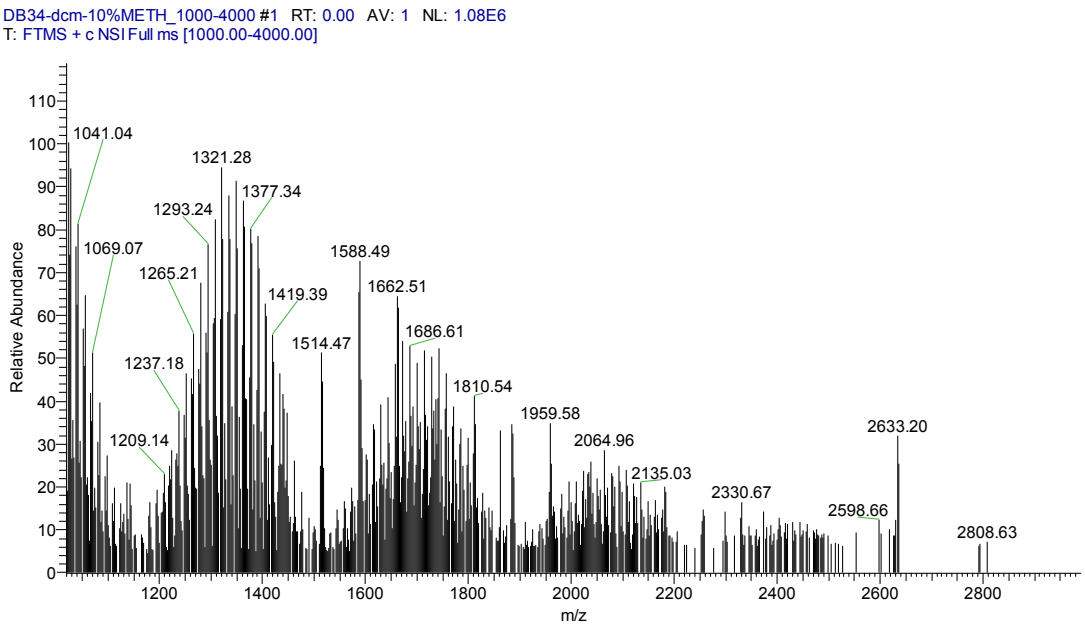


Figure S6 (b). ESI-MS analysis of wax, experiment catalysed by **PSHG2**, higher molecular weights.

Reaction optimization with Hoveyda-Grubbs second generation (HG2)

GC-MS and ESI-MS analyses of distillate and wax-

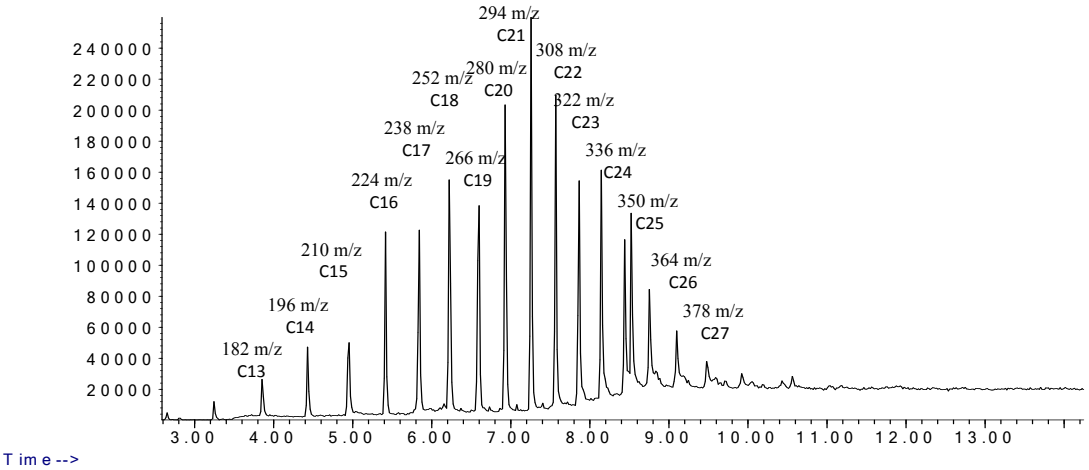


Figure S7. GC-MS analysis of distillate, experiment catalysed by **HG2** with isomerisation reagent $[Pd(\mu\text{-}Br)t\text{-}Bu_3P]_2$.

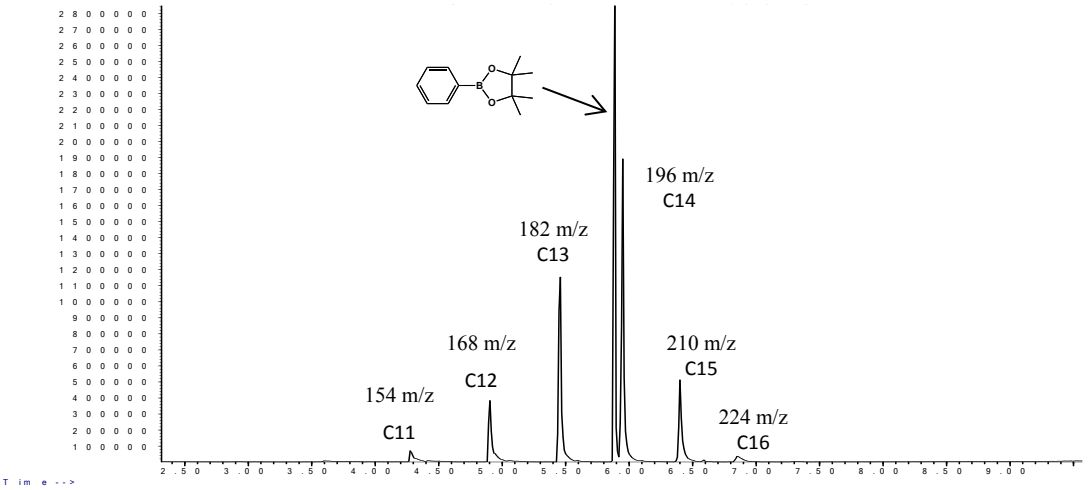


Figure S8. GC-MS analysis of distillate, experiment catalysed by **HG2** with pinacol phenyl borate.

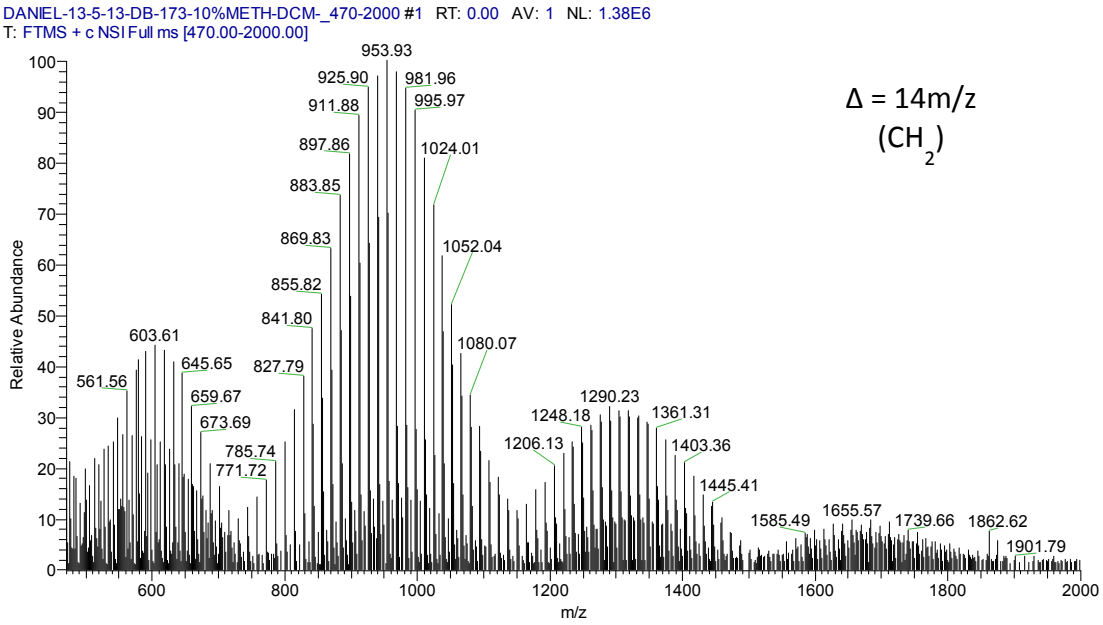


Figure S9. ESI-MS analysis of wax, experiment catalysed by **HG2** with hydride scavenger.

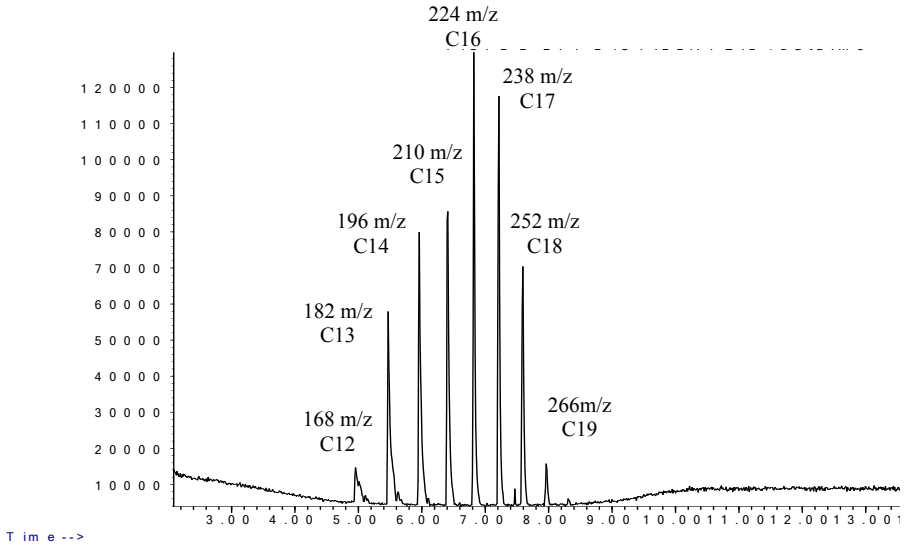


Figure S10. GC-MS analysis of distillate, experiment catalysed by **HG2** under steam distillation.

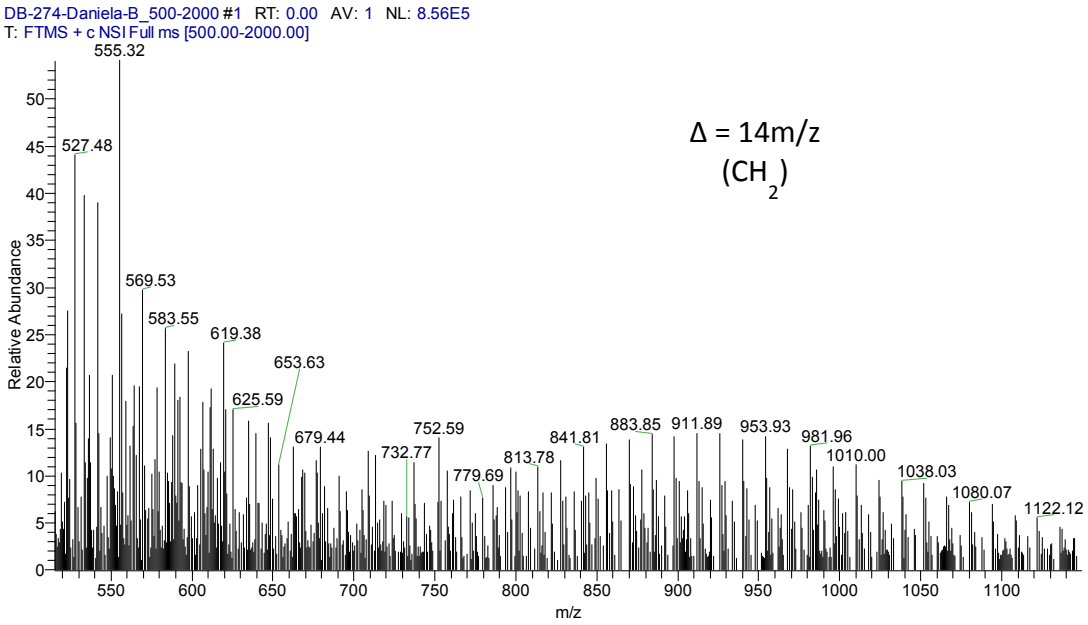


Figure S11. ESI-MS analysis of wax, experiment catalysed by **HG2** under steam distillation.

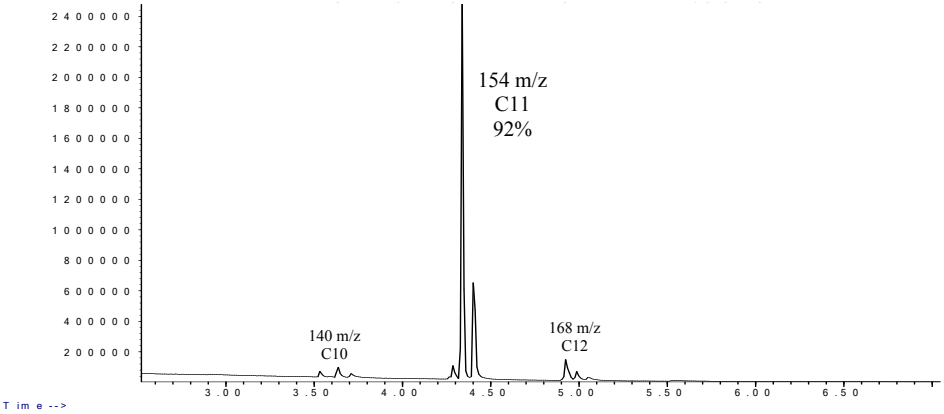


Figure S12. GC-MS analysis of distillate, experiment catalysed by **HG2** with butenolysis reaction (2 eq.).

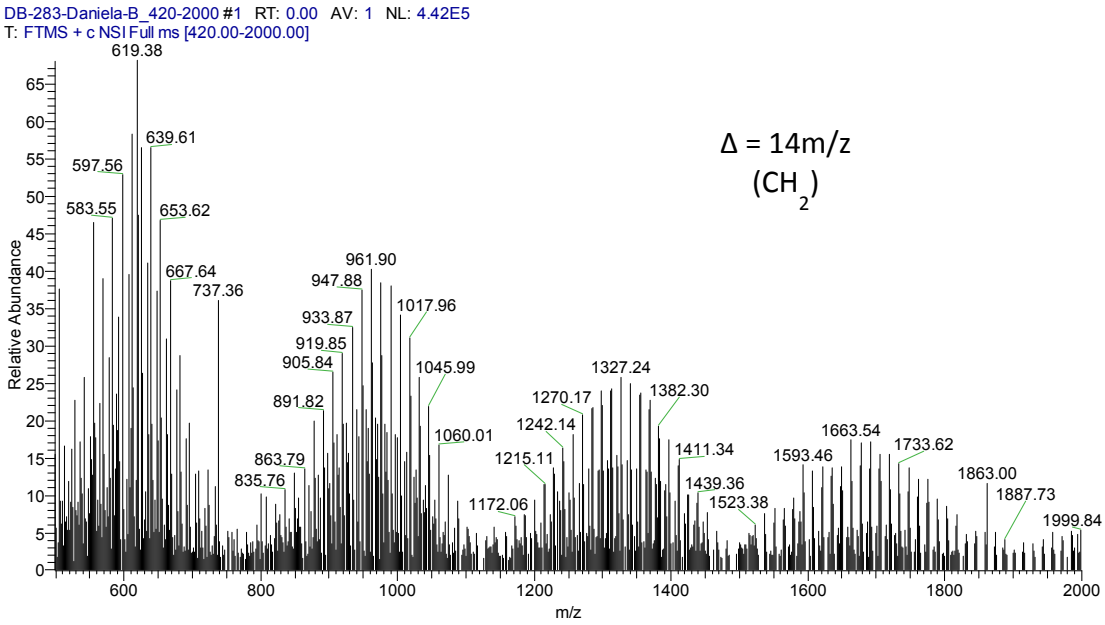


Figure S13. ESI-MS analysis of wax, experiment catalysed by **HG2** with butenolysis reaction (2 eq.).

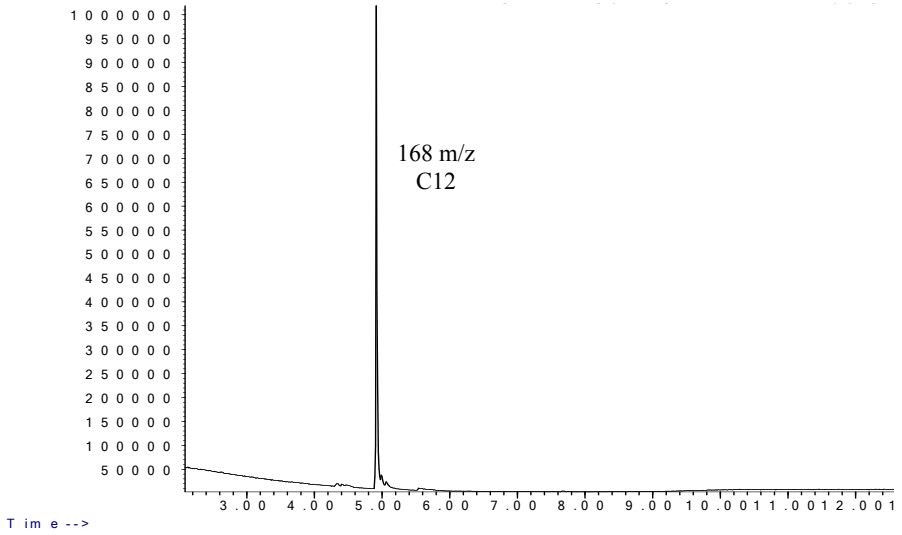


Figure S14. GC-MS analysis of distillate, experiment catalysed with hexenolysis reaction.

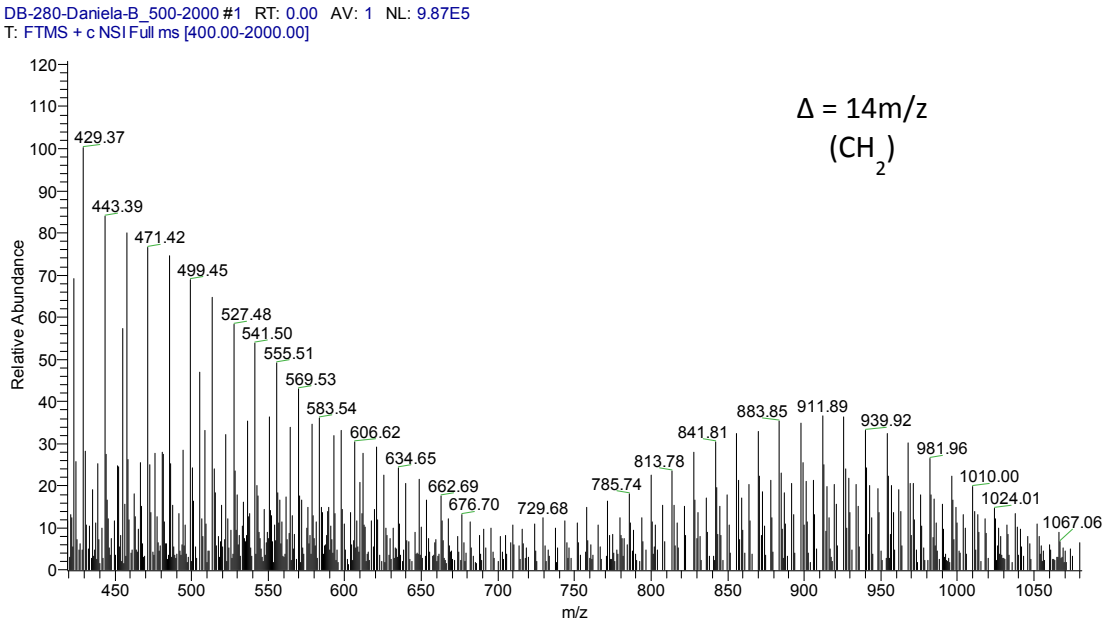


Figure S15 (a). ESI-MS analysis of wax, experiment catalysed by **HG2** with hexenolysis reaction.

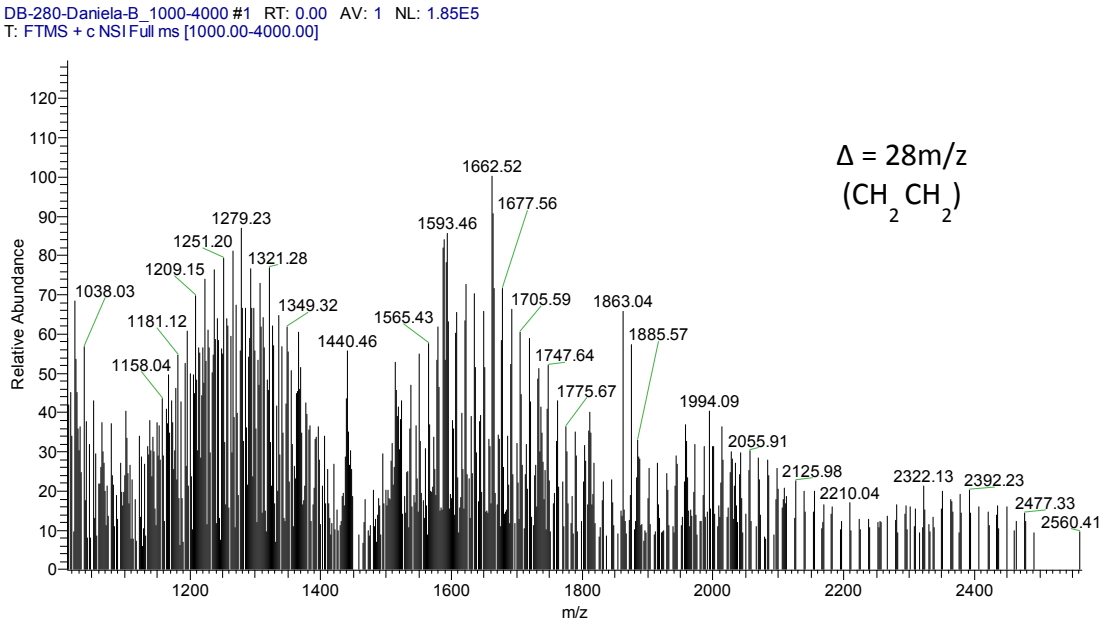


Figure S15 (b). ESI-MS analysis of wax, experiment catalysed by **HG2** with hexenolysis reaction, higher molecular weights.

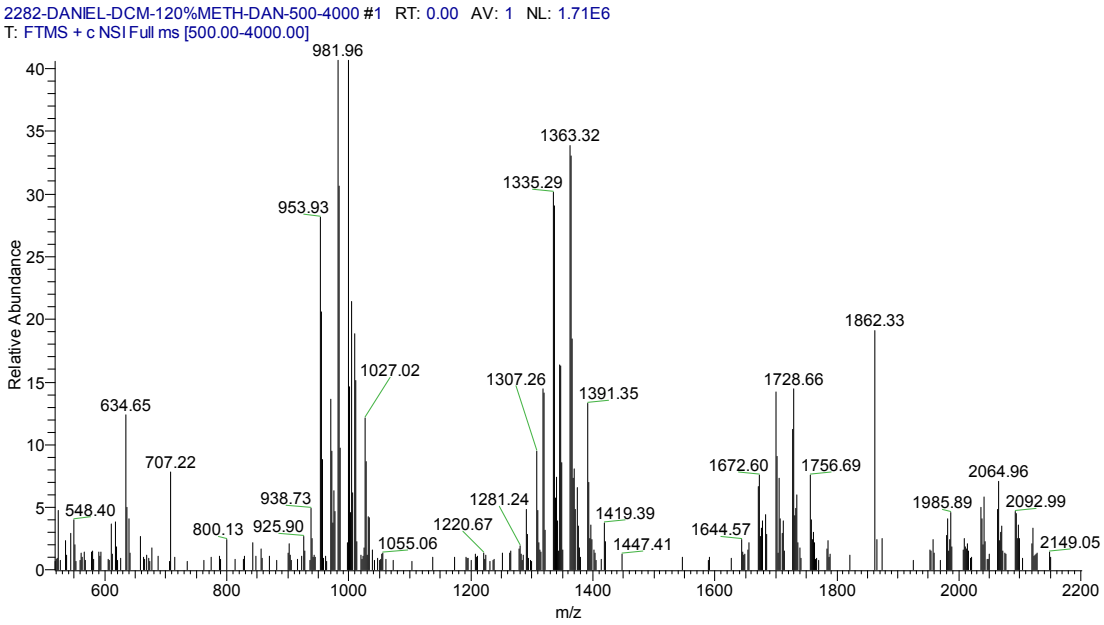


Figure S16 (a). ESI-MS analysis of precipitate, experiment catalysed by **HG2**, dilution with THF.

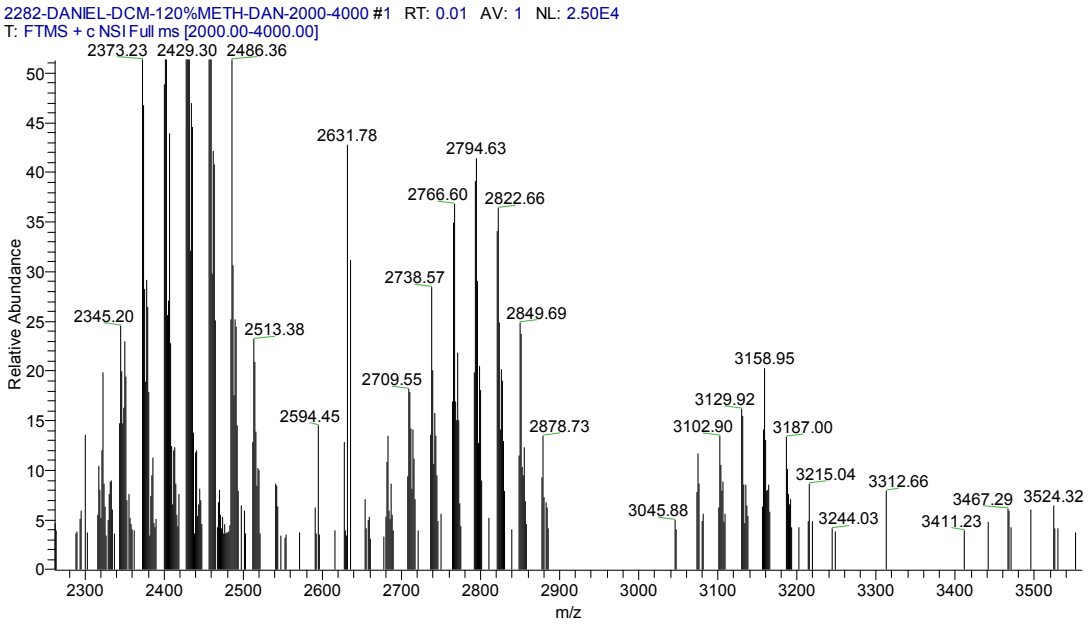


Figure S16 (b). ESI-MS analysis of precipitate, experiment catalysed by **HG2**, dilution with THF, higher molecular weights.

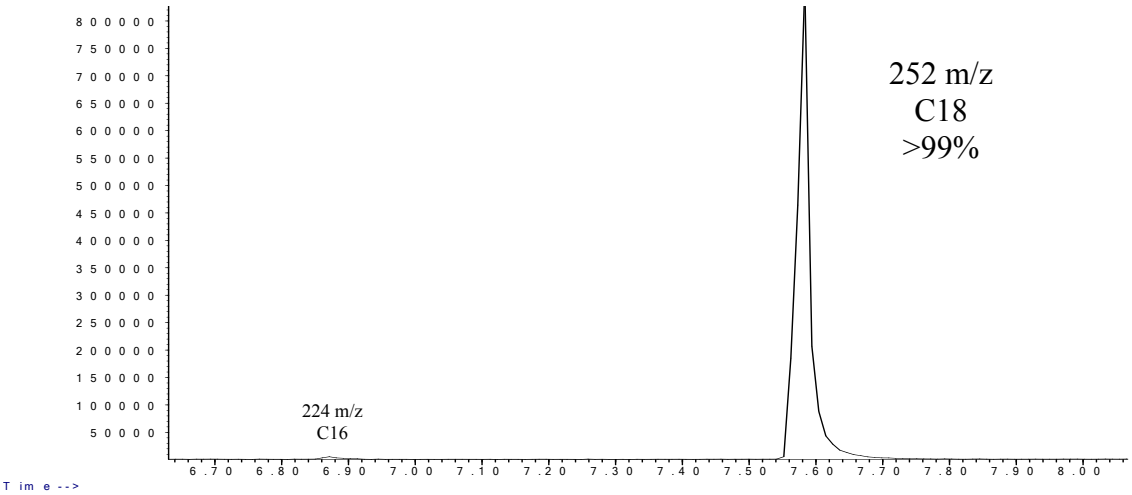


Figure S17. GC-MS analysis of distillate, experiment catalysed by **HG2**, dilution with THF.

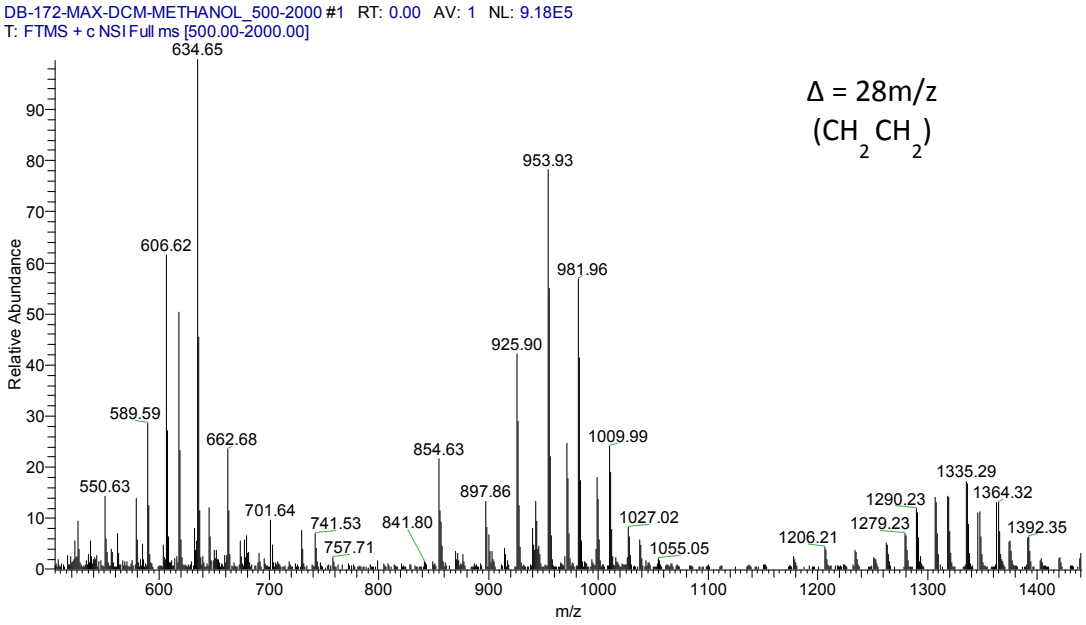


Figure S18 (a). ESI-MS analysis of filtrate, experiment catalysed by **HG2**, dilution with THF.

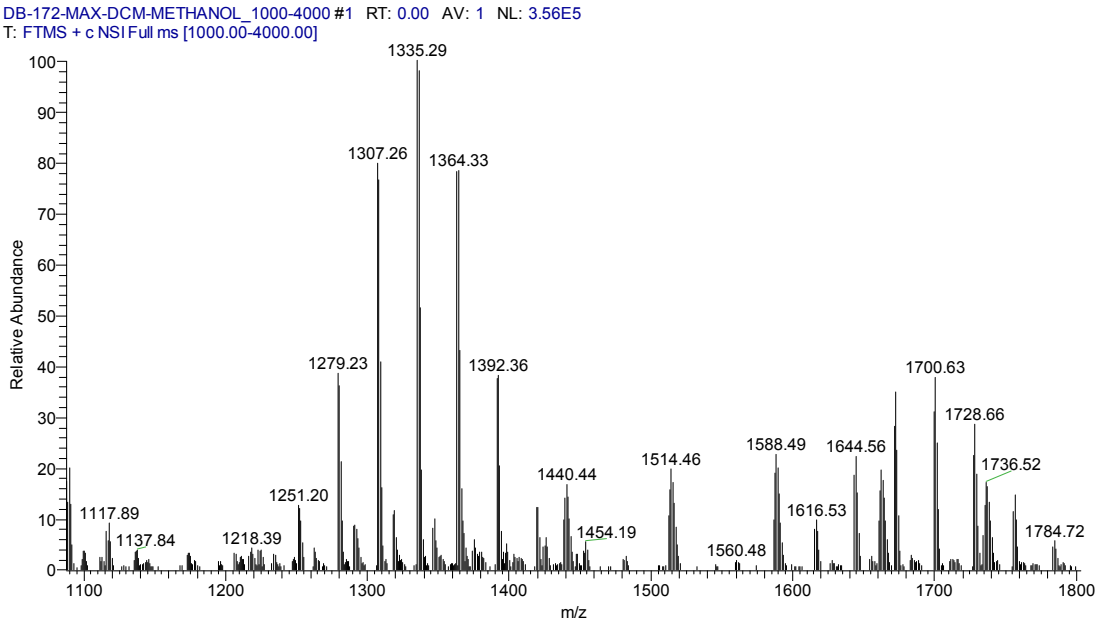


Figure S18 (b). ESI-MS analysis of filtrate, experiment catalysed by **HG2**, dilution with THF, higher molecular weights.

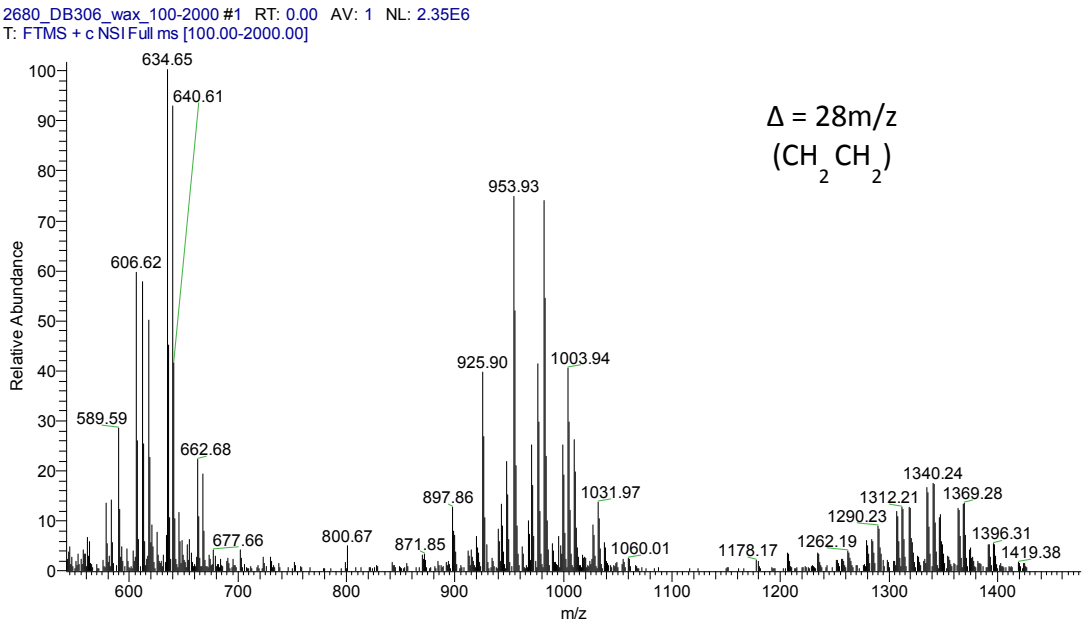


Figure S19 (a). ESI-MS analysis of filtrate, experiment catalysed by **HG2** at low temperature, before distillation.

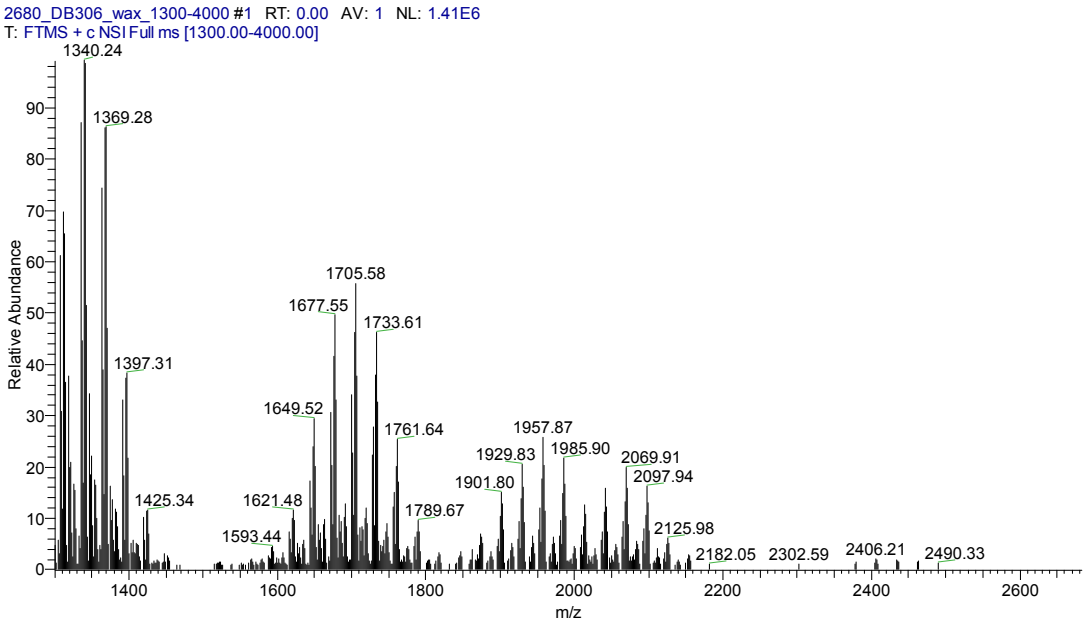


Figure S19 (b). ESI-MS analysis of wax, experiment catalysed by **HG2** at low temperature, before distillation, higher molecular weights.

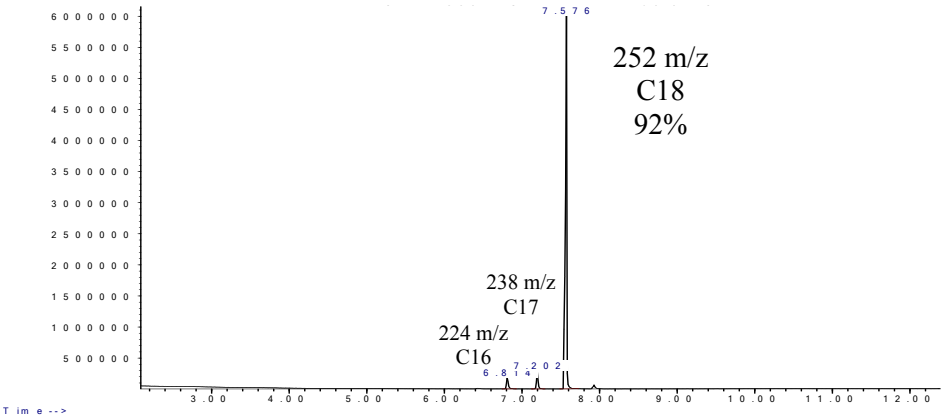


Figure S20. GC-MS analysis of distillate, experiment catalysed by **HG2** at low temperature.

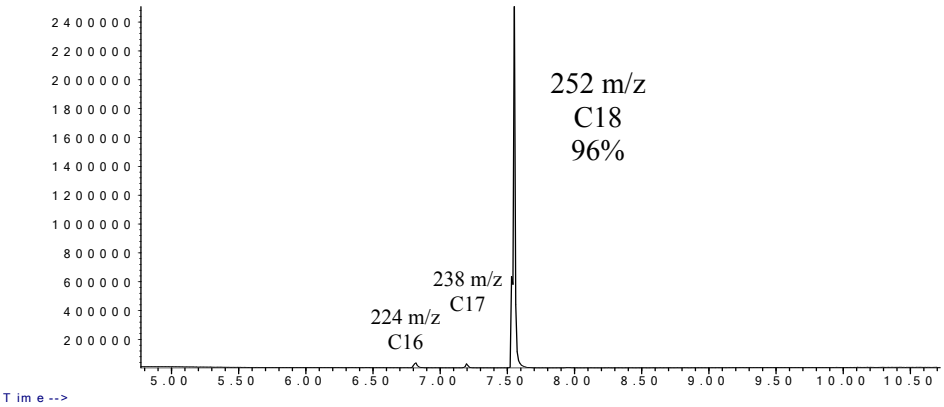


Figure S21. GC-MS analysis of distillate, experiment catalysed by low loading of **HG2**.

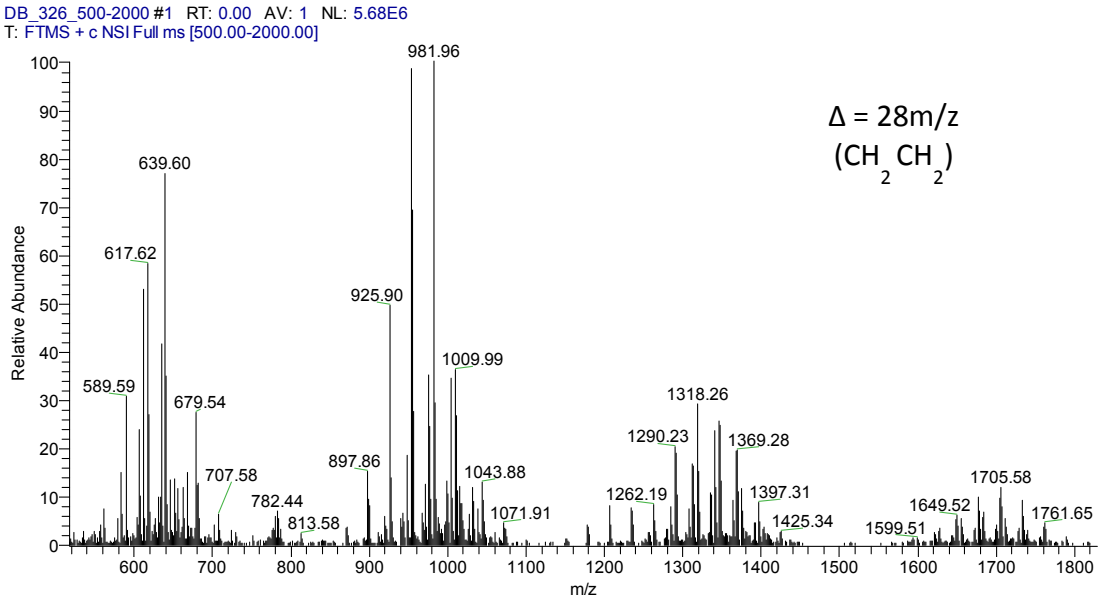


Figure S22. ESI-MS analysis of wax, experiment catalysed by low loadings of **HG2**.

ESI-MS analysis of product - Thiol-ene reaction

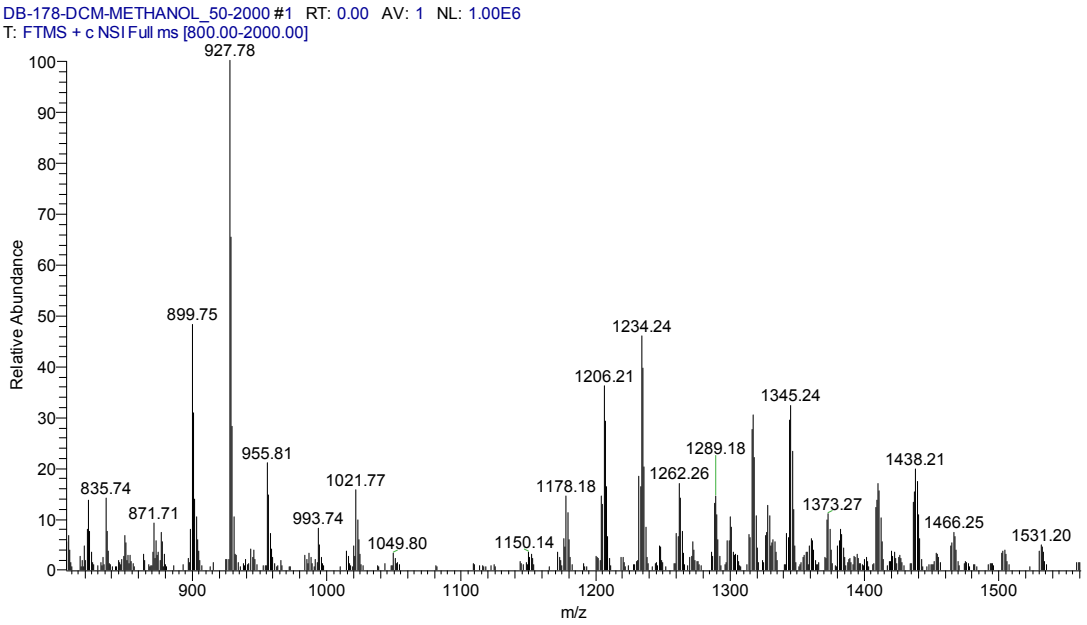


Figure S23 (a). ESI-MS analysis of wax. Oligomerisation with 1,2-ethanedithiol through thiol-ene 'click' reaction.

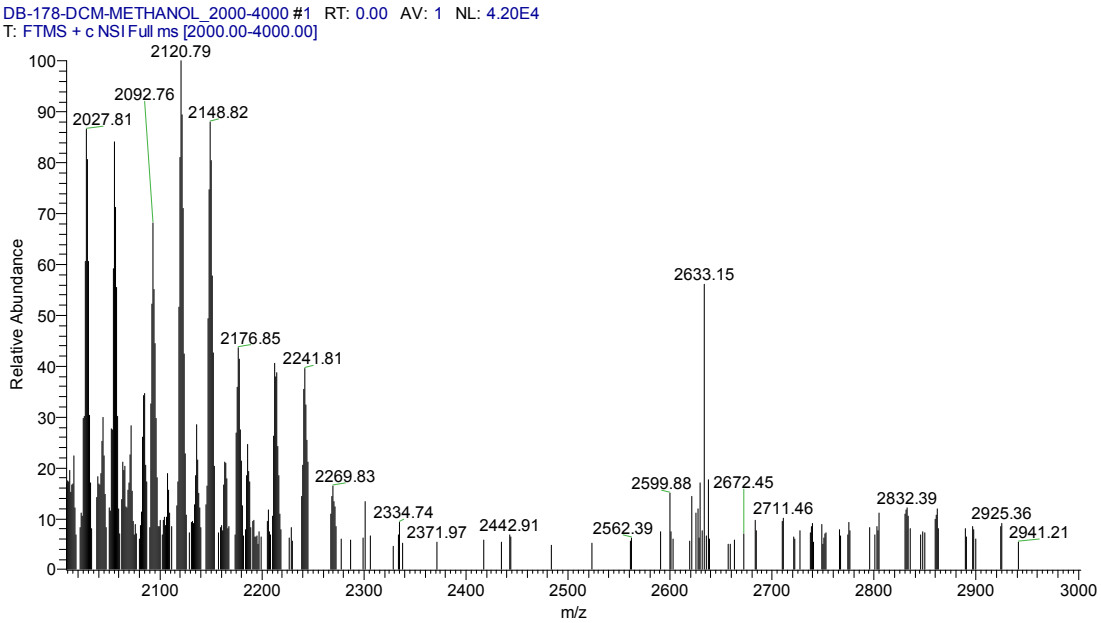


Figure S23 (b). ESI-MS analysis of wax. Oligomerisation with 1,2-ethanedithiol through thiol-ene 'click' reaction, higher molecular weights.

ESI-MS analysis of product - Hydrolytic degradation

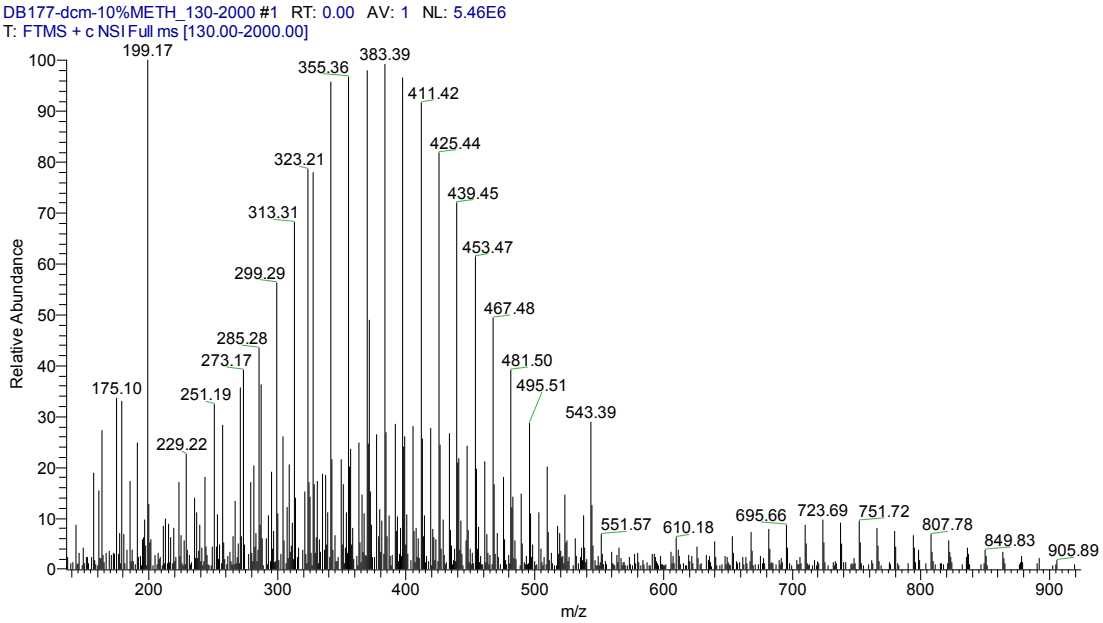


Figure S24. ESI-MS analysis of wax under basic hydrolysis.

References

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