

Supplemental Material for

Alkenones as renewable phase change materials

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General: All reactions were carried out under N₂ in flame-dried glassware. The solvents used were dried by passing the solvent through a column of activated alumina under nitrogen immediately prior to use. Reagents were purchased and used as received unless otherwise mentioned. Silica gel: SilaCycle silica gel P60 (230-400 mesh).

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Microalgae and alkenone isolation. The marine microalgae *Isochrysis* was purchased from Reed Mariculture (San Jose, CA) and Necton S.A (Olhão, Portugal). Alkenones were isolated and purified from the *Isochrysis* biomass as previously described.¹ Briefly, Soxhlet extraction with hexanes produced a dark green near-black oily solid (mp. ~ 50-60 °C, yield = 15-20% w/w) that we refer to as hexane algal oil. This algal oil was then redissolved in methanol:dichloromethane (2:1, 10 x volume of algal oil) and treated with KOH (50% w/w, 60 °C, 3 h) resulting in saponification of the acylglycerols that could then be selectively partitioned into water. The remaining alkenone-containing neutral lipids were then filtered through silica with DCM followed by decolorization using Monmorillonite K10 (10% w/w neutral lipids, hexanes, 60 °C, 1h) [22], giving the alkenones as a white waxy solid (~20% w/w of the hexanes algal oil).

Alkenone crystallization. Select alkenone samples (100 mg) were further crystallized with hexanes, acetone, and ethanol. In a typical procedure, boiling solvent was added incrementally until all of the alkenones had dissolved. When using ethanol the alkenones appeared to oil out rather than dissolve. The flask was then covered and allowed to slowly cool to room temperature. For hexanes the solution was further cooled to 0 °C. The crystallized alkenones were then collected by filtration (cold hexanes or room temperature acetone and ethanol) using a Büchner funnel and cellulose filter paper. Mass recoveries were consistently >90 mg.

Analysis by nuclear magnetic resonance (NMR) spectroscopy. ¹H and ¹³C NMR spectra were recorded on a Bruker 500 MHz spectrometer under ambient conditions using CDCl₃ as solvent, which also served as an internal reference (shift value of residual CHCl₃ at 7.26 ppm).

Analysis by gas chromatography with flame ionization detection (GC-FID). Purified alkenones were analyzed on an Agilent 7890 GC-FID. Samples (1 µl) were injected cool-on-column and separated on a 100% dimethyl polysiloxane capillary column (Agilent HP-5, 30 m length, 0.32 mm I.D., 0.25 µm film thickness) with helium as the carrier gas at a constant flow of 6.5 mL min⁻¹. The GC oven was programmed from 75 °C (0.5 min hold) and ramped at 2 °C min⁻¹ to 320 °C (5 min hold). Alkenone samples were also spiked with tricosanoic acid (C₂₃) as an internal standard and treated with esterification conditions (1:1 MeOH:CHCl₃, cat. H₂SO₄, 90 °C, 40 min) followed by GC-FID analysis. Chromatograms were identical pre- and post-esterification aside from complete conversion of tricosanoic acid to methyl tricosanoate.

Analysis by gas chromatography-mass spectrometry (GC-MS). Alkenone samples were analyzed by GC-MS (full scan) on an Agilent 6890 GC-MS. Splitless 1 µL sample injections were separated on an Agilent HP-5MS (30 m x 0.25 mm x 0.25 µm film thickness) using helium as the carrier gas (Initial flow: 1.0 mL min⁻¹), and the following GC temperature program: 7 min at 70 °C and ramped to 325 at 6 °C min⁻¹.

Preparation and characterization of 18-3-18. This compound was prepared with a slight modification to the previously reported procedure:² To a solution of stearoyl chloride (1.0 g, 3.3

¹ O'Neil GW, Williams JR, Wilson-Peltier J, Knothe G, Reddy CM (2016) J Vis Exp 112:e54189.

² Floros MC, Narine SS. Mat Lett 2014;137:252-255.

mmol, 1.0 equiv) in DCM (16.5 mL) was added pyridine (0.53 mL, 6.6 mmol, 2.0 equiv) and 1,3-propanediol (0.126 g, 1.65 mmol, 0.5 equiv) and the resulting mixture was stirred for 15 h. The reaction was quenched with water (30 mL), the layers were separated, and the aqueous phase was re-extracted with DCM (30 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. Crystallization with 1:1 ethanol:acetone yielded 18-3-18 (620 mg, 67%) as a white solid.

Spectral data for the synthesized 18-3-18: ¹H NMR (500 MHz, CDCl₃) δ: ¹H NMR (500 MHz, CDCl₃) δ 4.15 (t, *J* = 6.3 Hz, 4H), 2.29 (t, *J* = 7.6 Hz, 4H), 1.96 (p, *J* = 6.3 Hz, 2H), 1.61 (p, *J* = 7.3 Hz, 4H) 1.35 – 1.20 (m, 56H) 0.88 (t, *J* = 6.9 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 173.80, 60.82, 34.26, 31.92, 29.69, 29.67, 29.65, 29.60, 29.46, 29.36, 29.26, 29.16, 28.01, 24.95, 22.68, 14.11.

Figure S1. Alkenones NMR data.

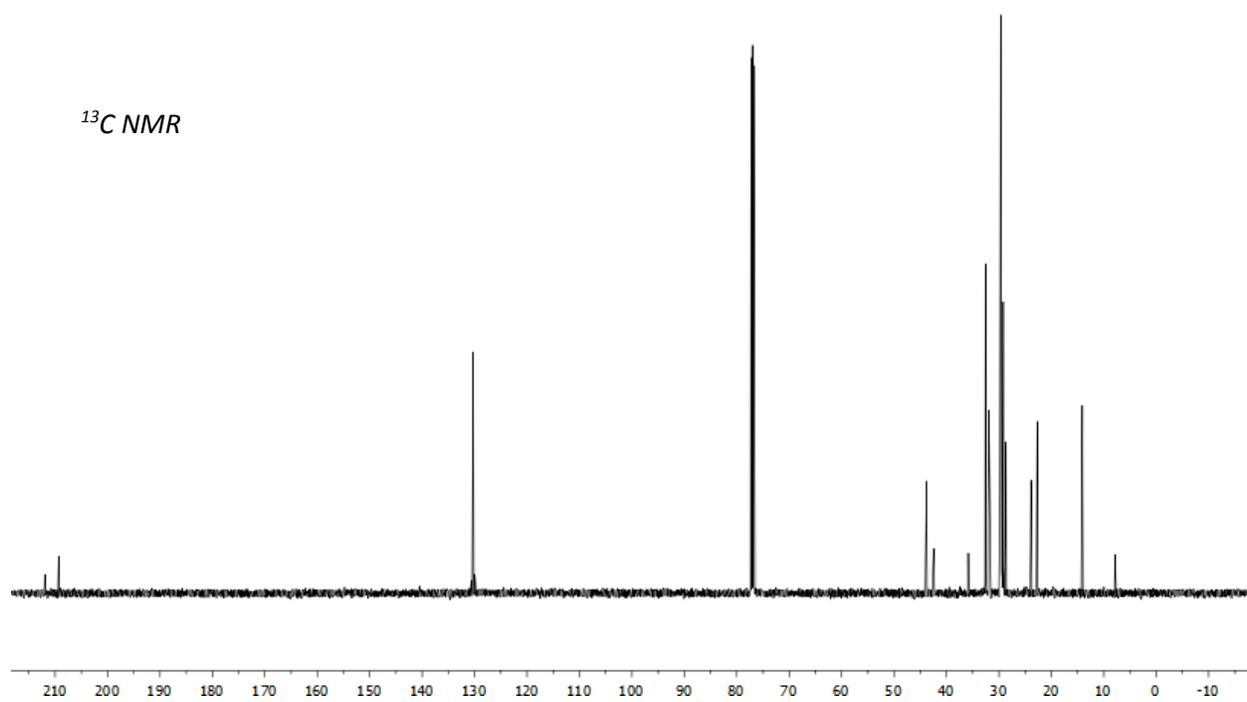
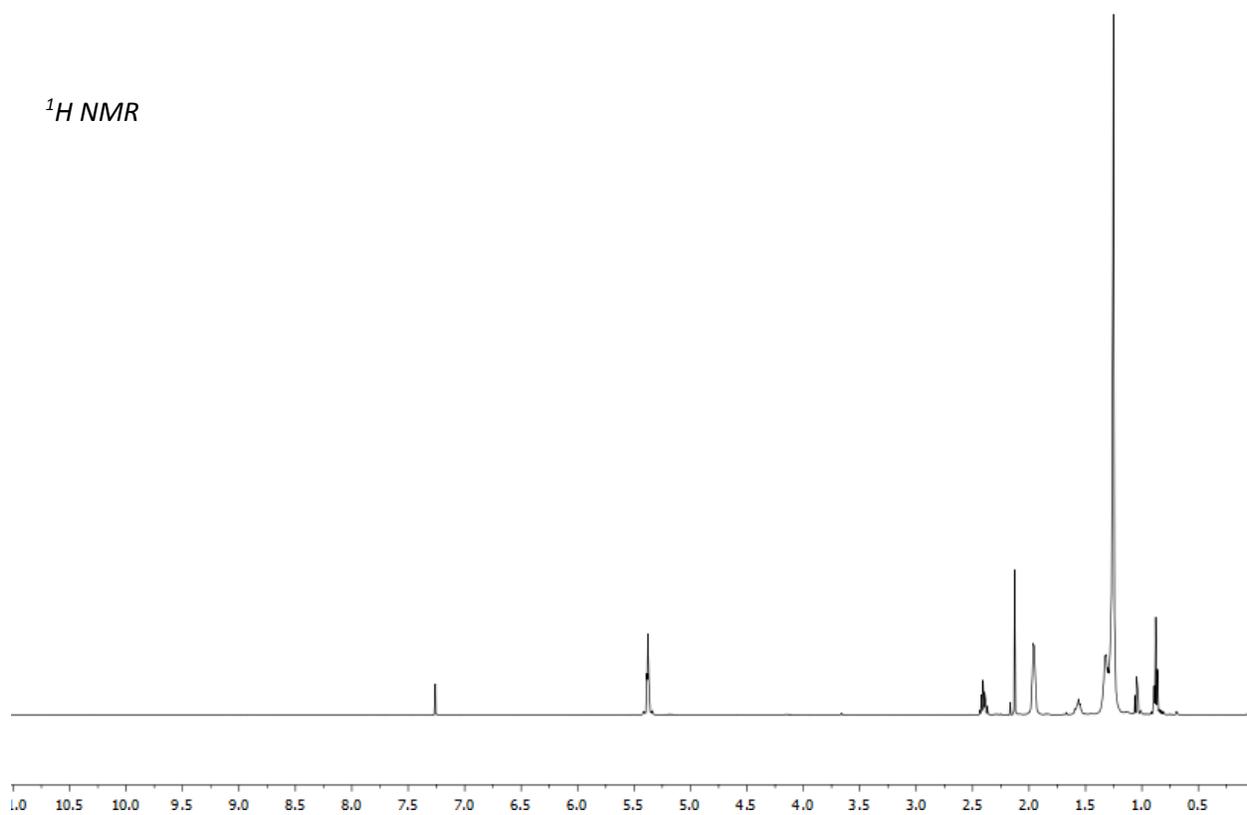


Figure S2. GC-FID chromatograms of alkenones pre- (top) and post treatment with acid-catalyzed esterification conditions (bottom). Alkenones were spiked with tricosanoic acid (C₂₃) as an internal standard prior to esterification which was then converted to methyl tricosanoate. No fatty acid methyl esters were detected after esterification indicating no contamination of the alkenones by these compounds.

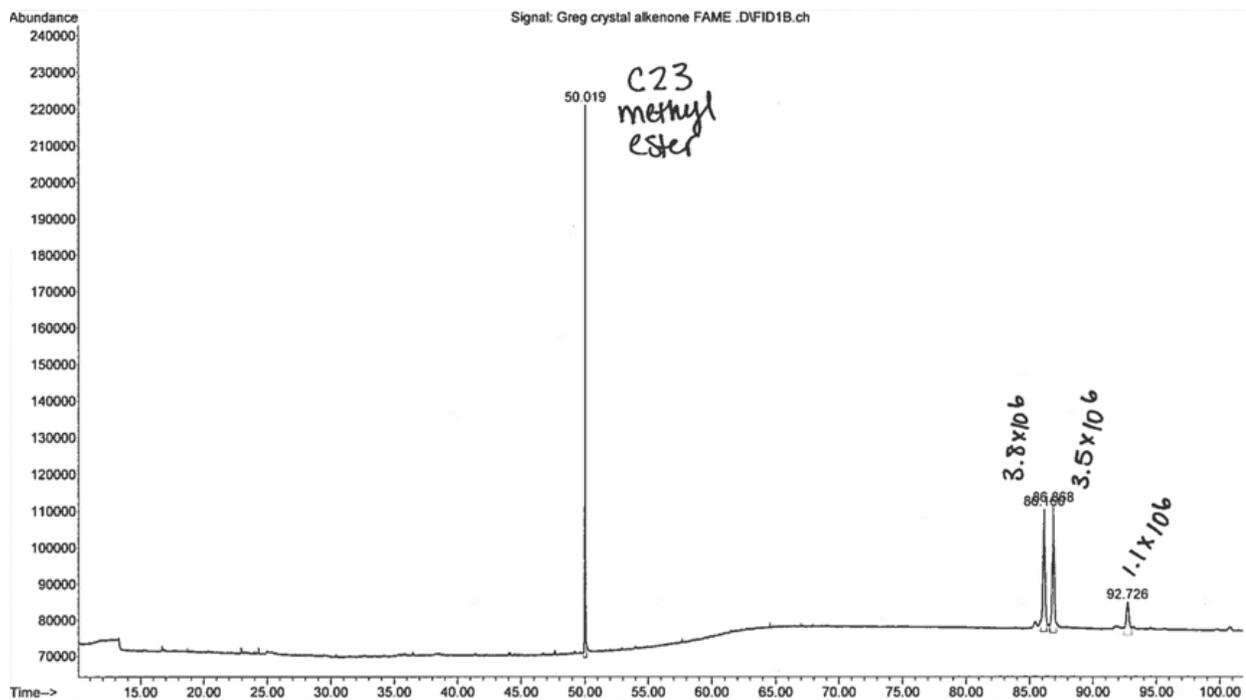
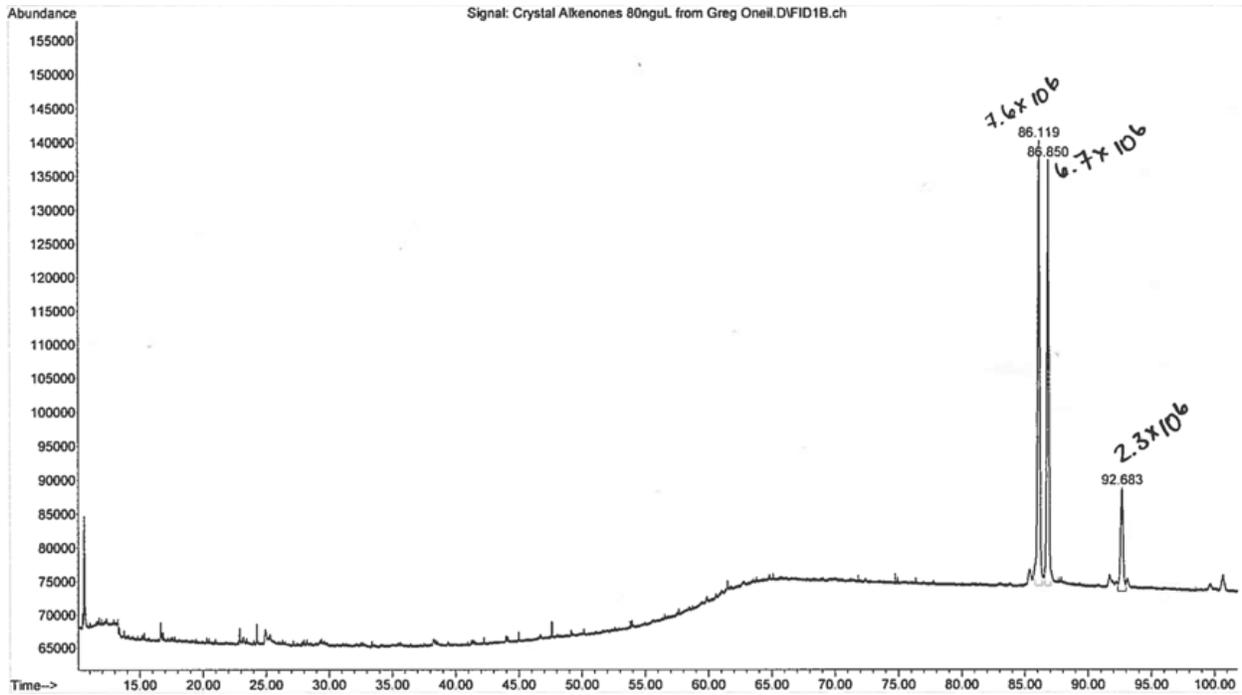
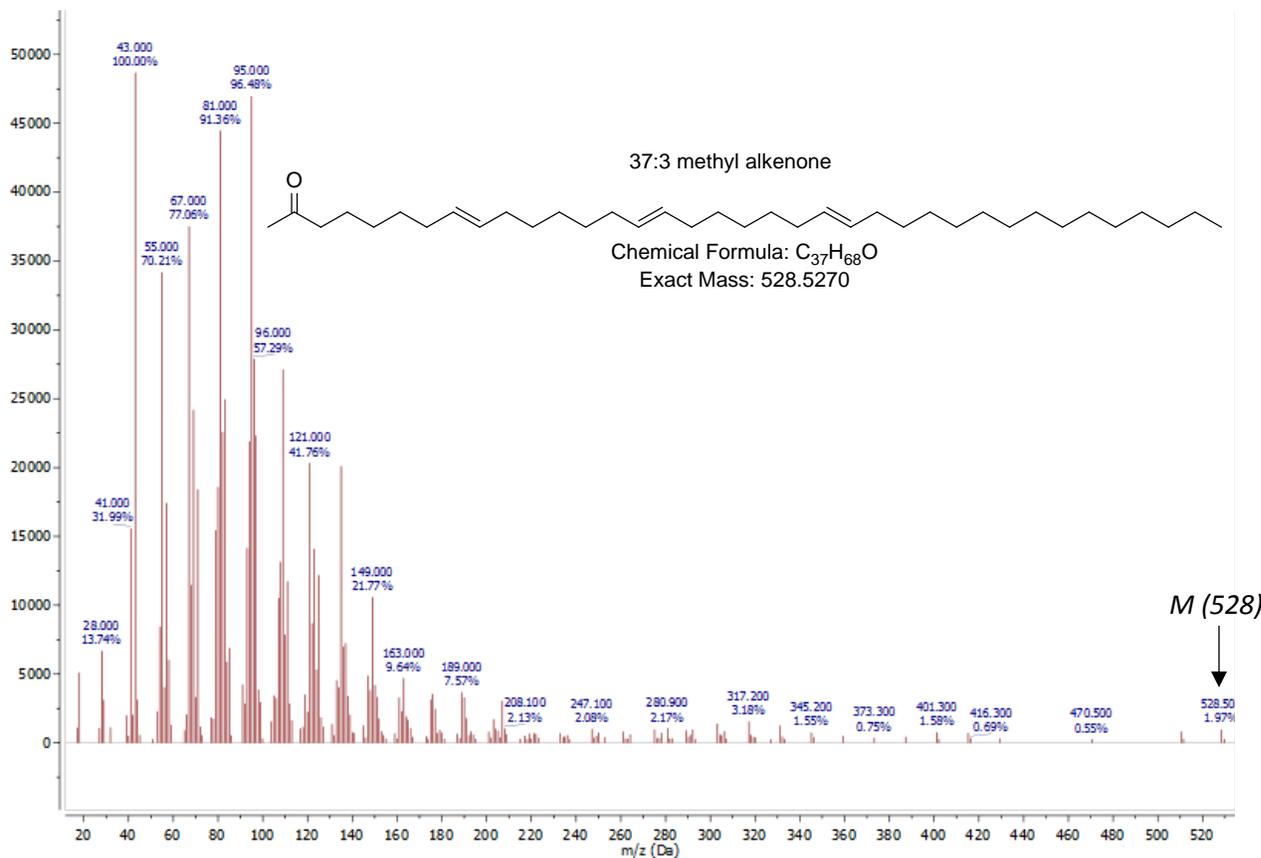
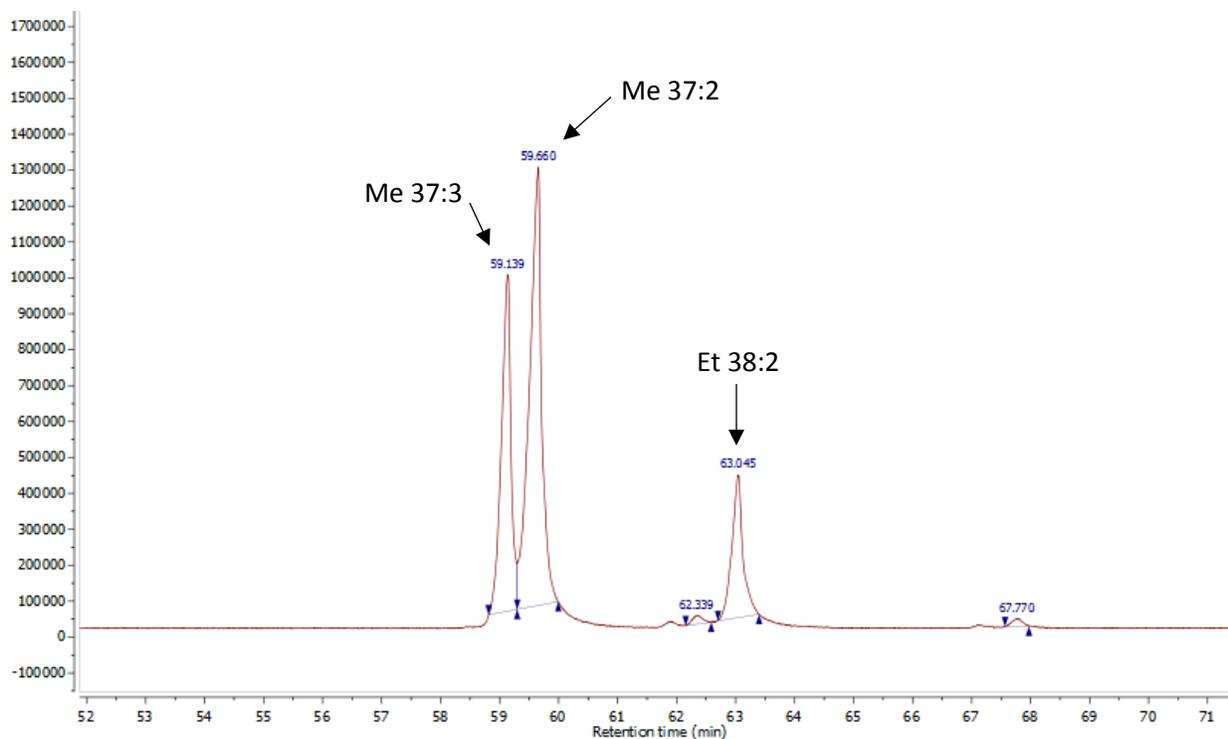


Figure S3. Alkenones GC-MS data.



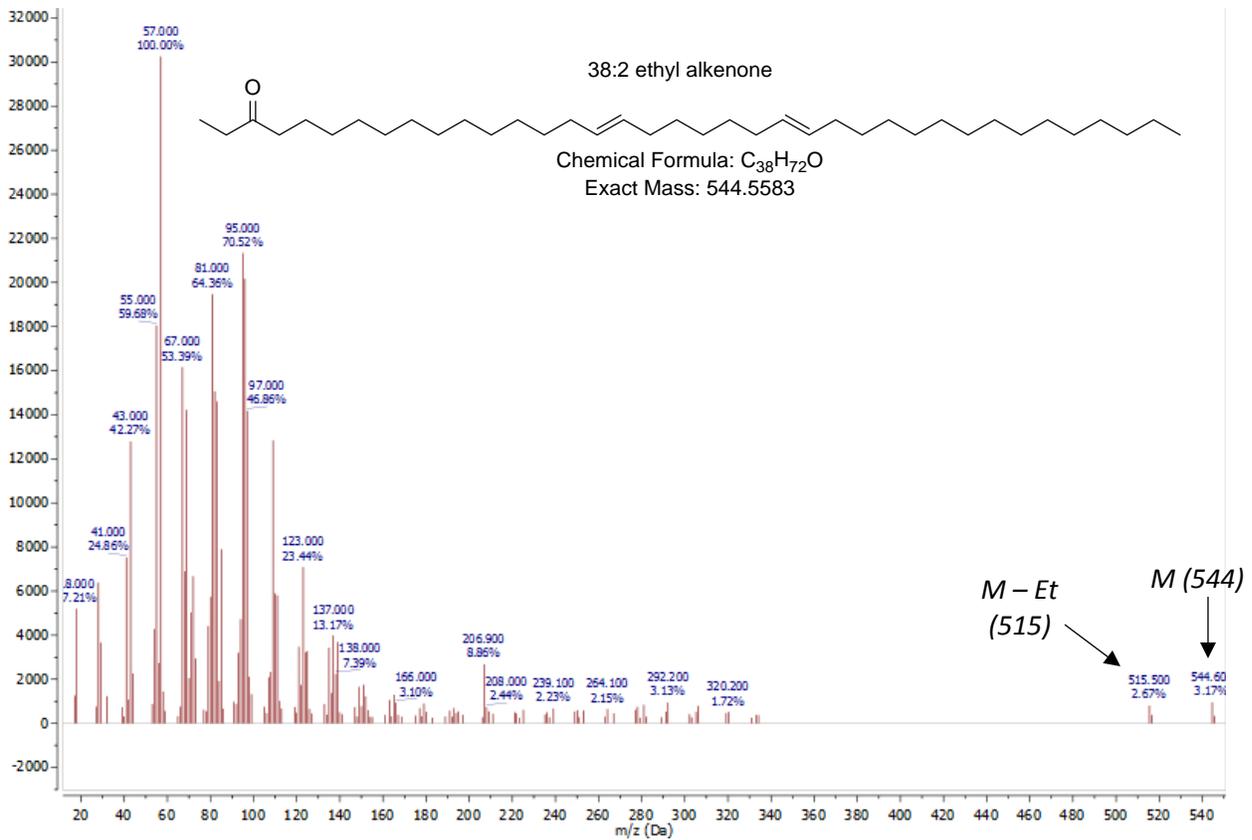
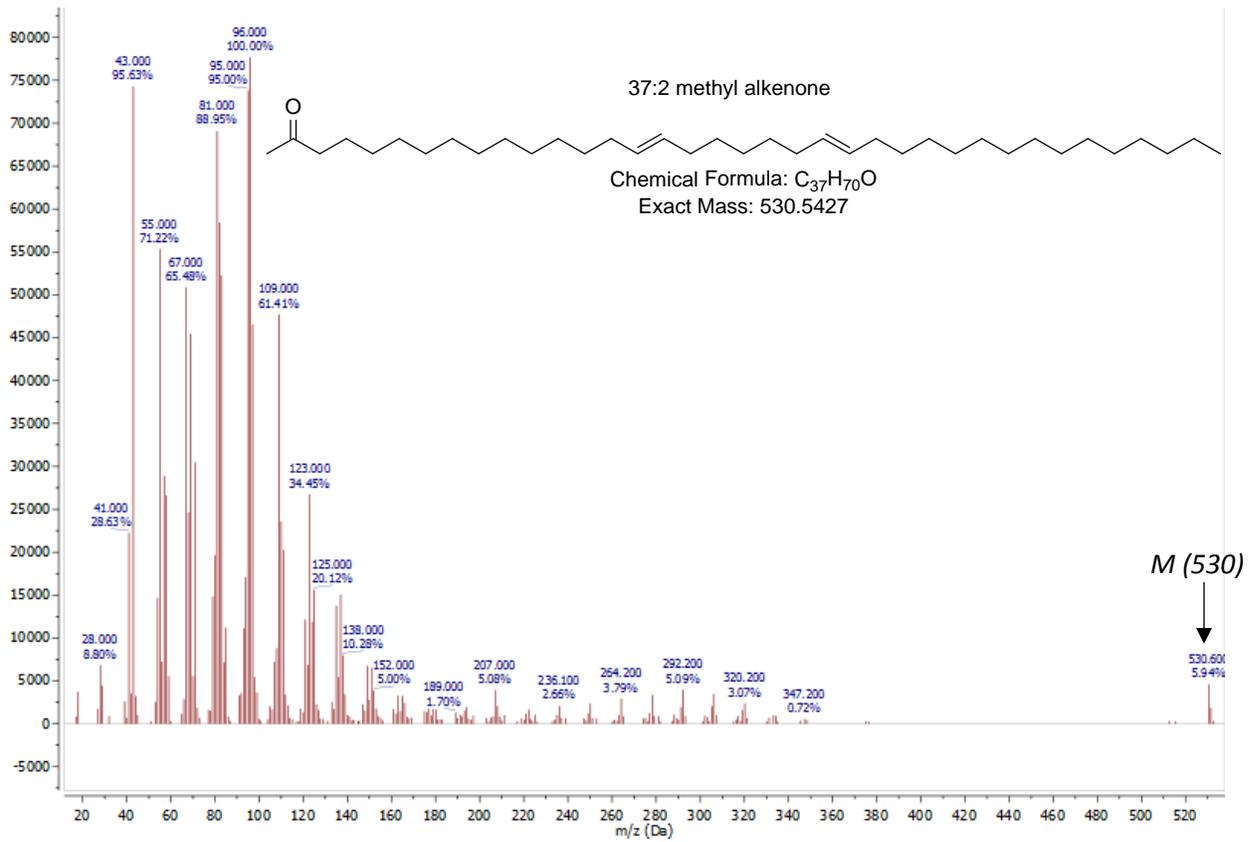


Figure S4. GC Chromatograms of alkenones crystallized from acetone (top), ethanol (middle) and hexanes (bottom) showing the same alkenone profile.

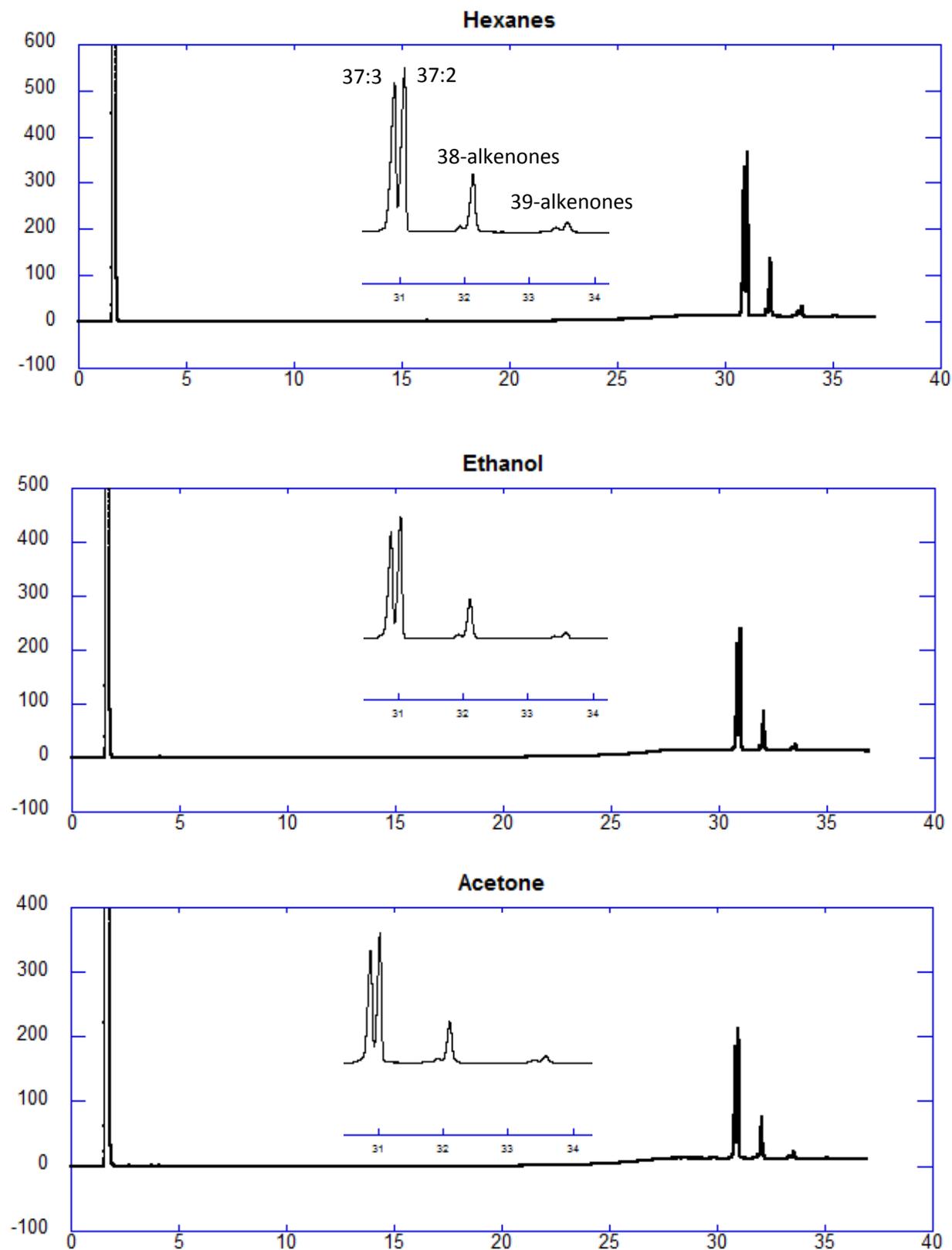
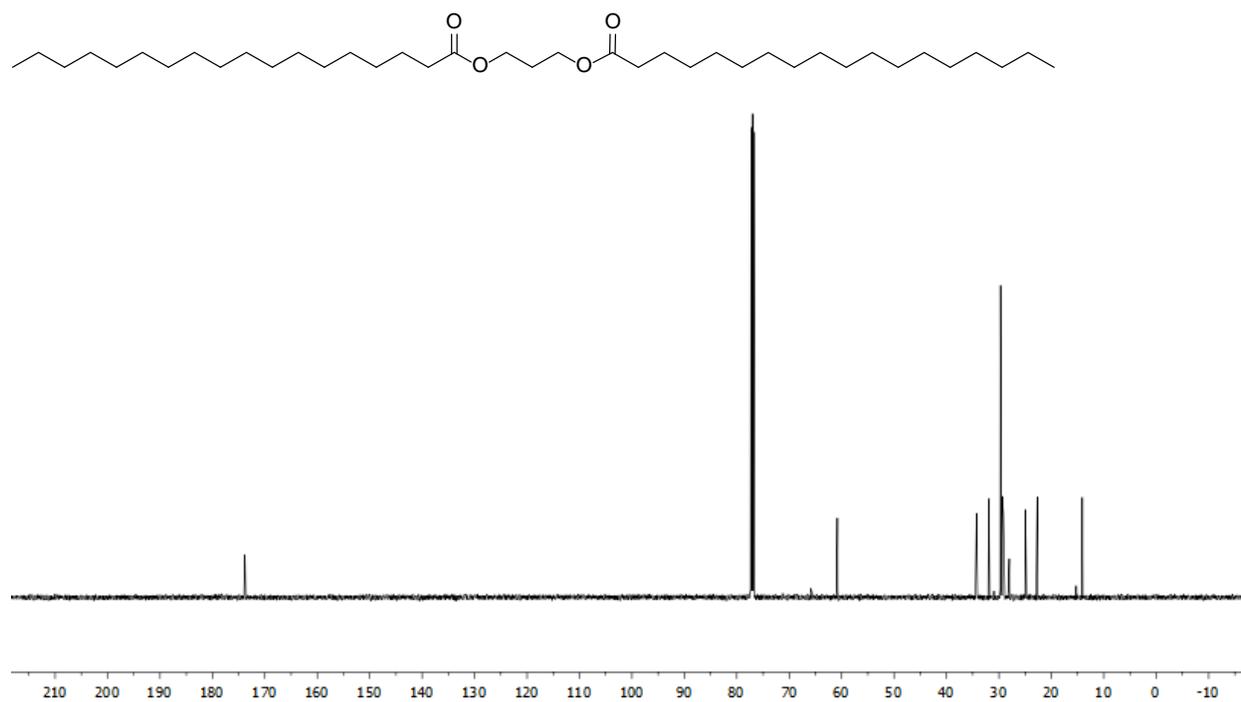
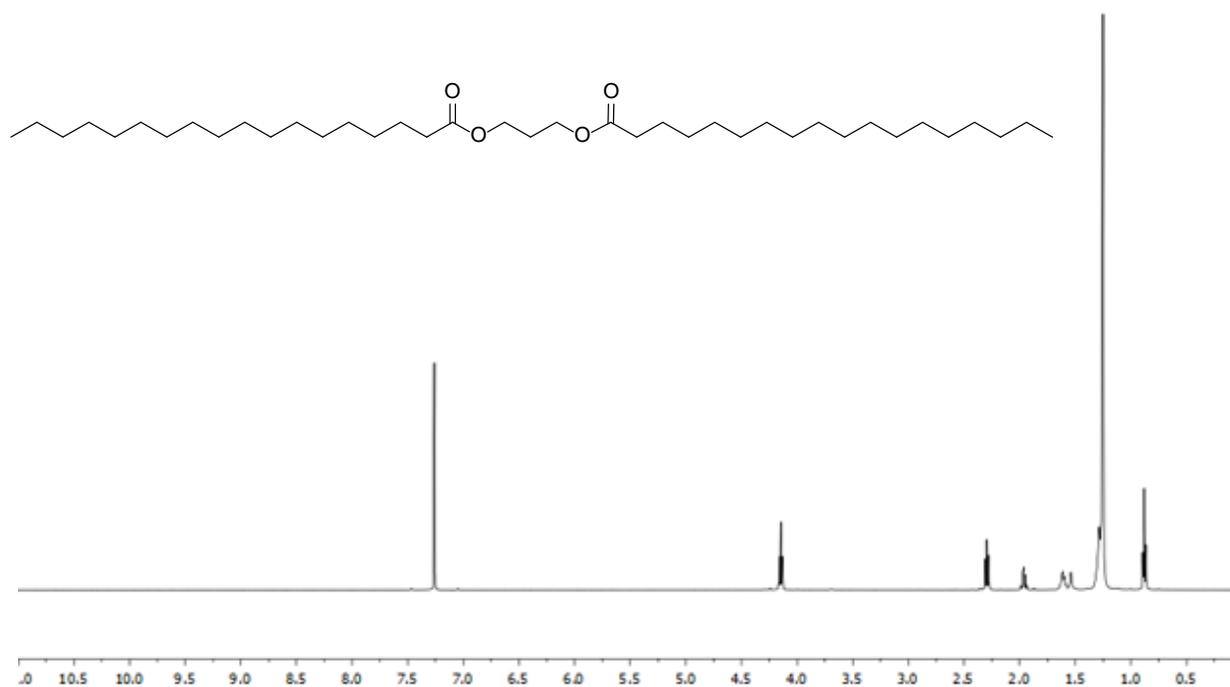


Figure S4. Synthetic 18-3-18 diester NMR data.



Alkenone Cost Analysis.

Calculated using data from:

JW Richardson, MD Johnson. "Financial Feasibility analysis of NAABB developed technologies", Algal Research 2015;10:16–24.

Using Data from Scenario #1:

Alkenone annual yield		
Data Table 2 For Scenario 1	Biomass output	119,900 tons/yr
Conversion of tons to grams	calculation	108×10^9 gm/yr
Dry weight assumption	Algae is 99.9% water	108×10^9 gm/yr
Total alkenones	4%	4.32×10^9 gm/yr
Data table 4 for Scenario # 1	Total OPEX year 5	$\$820 \times 10^6$
Per gram Cost of alkenones		$\$0.19/\text{gm}$
	Alkenone cost	$\$19/100\text{gm}$