Supporting Information – Experimental

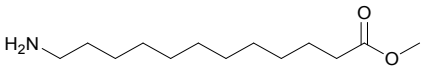
General

^{1}H-NMR and ^{13}C-NMR spectra were acquired in $CDCl_3$, on either Varian Unity Inova 600 (600 MHz) or Brucker Avance 600 (600 MHz) NMR spectrometers. Chemical shifts (δ) were reported as parts per million (ppm) with reference to tetramethylsilane (TMS) or solvent unless otherwise stated. The coupling constants (*J*) are reported in Hz. Mass spectra were obtained with Hewlett-Packard Esquire Ion Trap LC-MS (electrospray). GC analyses were performed with HP 5890 series II equipped with FID and an auto-sampler HP controller 7672A and Biodiesel TG column (5%diphenyl, 95% dimethyl polysiloxane, 15m, 0.33mm ID and 0.10µm dF) or MXT biodiesel TG (Siltek – treated stainless steel). Samples were analyzed with the following method: 60°C to 370°C at 10°C/min; 6min hold time.

Most reagents were purchased from commercial suppliers and used without further purification. Thin layer chromatography (TLC) was carried out on glass backed silica plates, purchased from Sorbent Technology. The plates were visualized under UV (254 nm) light, and by staining with either Potassium permanganate or Ninhydrin and gentle heating. Silica gel column chromatography was carried out using 20–60 micron dry silica purchased from Sorbent Technology.

All solvents were deoxygenated by passing through dry nitrogen gas for 20 min before being used.

Methyl 12-aminododecanoate (**5**)

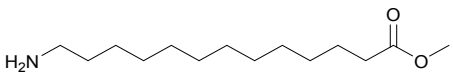


12-Cyano-9-dodecenoic acid methyl ester (19.9 mg, 0.08916 mmol) was dissolved in 2 mL of chlorobenzene, and transferred into a 2-dram vial containing *t*-BuOK (30 mol%, 2.9 mg, 0.02584 mmol). 2nd generation Grubbs catalyst (3 mol%, 2.2 mg, 0.002591 mmol) was dissolved in chlorobenzene (1mL) and transferred into the vial. The vial was placed in a Parr reactor which was purged 3 times with hydrogen gas before being pressurized at 20 bars and heated at 80 °C with stirring for 17hrs. Subsequently, the reaction mixture was purified by silica gel chromatography using a mixture of hexane/methanol/DCM (6:2:2) as eluent and concentrated under reduced pressure to give methyl 12-aminododecanoate (13.8 mg, 67.55% isolated yield). NMR data match with reported data.[1]

^{1}H-NMR ($CDCl_3$, 600 MHz) δ/ppm: 3.65 (s, 3H, $-OCH_3$), 2.67 (t, J=6.6Hz, 2H, $-CH_2-NH_2$), 2.28 (t, J=7.5Hz, 2H, $-CH_2-CO-$), 1.57 – 1.62 (m, 4H, $-CH_2-$,), 1.41 – 1.43 (m, 2H, $-NH_2$), 1.25 – 1.27 (m, 14H, $-CH_2-$).

^{13}C-NMR ($CDCl_3$, 600 MHz) δ/ppm: 174.5, 51.6, 42.3, 34.2, 33.8, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 27.0, 25.1.

Methyl 13-aminotridecanoate (**6**)



13-Cyano-9-tridecenoic acid methyl ester (20.1 mg, 0.08476 mmol) was dissolved in 2 mL of chlorobenzene, and transferred into a 2-dram vial containing *t*-BuOK (30 mol%, 2.9 mg, 0.02584 mmol). 2nd generation Grubbs catalyst (2 mol%, 1.4 mg, 0.001649 mmol) was dissolved in chlorobenzene (1mL) and transferred into the vial. The vial was placed in a Parr reactor which was purged 3 times with hydrogen gas before being pressurized at 20 bars and heated at 80 °C with stirring for 19hrs. Subsequently, the reaction mixture was purified by silica gel chromatography using a mixture of

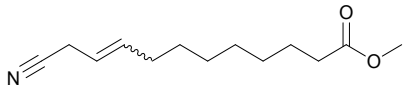
hexane/methanol/DCM (6:2:2) as eluent and concentrated under reduced pressure to give methyl 13-aminotridecanoate (13.7 mg, 66.5% as an uncorrected isolated yield).

^{1}H-NMR ($CDCl_3$, 600 MHz) δ/ppm: 3.66 (s, 3H, -OCH_3), 2.68 (t, J=6.6Hz, 2H, -CH_2-NH_2), 2.29 (t, J=7.5Hz, 2H, -CH_2-CO-), 1.58 – 1.63 (m, 4H, -CH_2-), 1.41 – 1.44 (m, 2H, -NH_2), 1.25 – 1.28 (m, 16H, -CH_2-).

^{13}C-NMR ($CDCl_3$, 600 MHz) δ/ppm: 174.5, 51.6, 42.3, 34.3, 33.9, 29.8, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 27.0, 25.1.

HRMS:$C_{14}H_{29}NO_2$ $[M+H]^+$ calc. 244.2271 found 244.2279

(*E/Z*)-11-Cyano-9-dodecenoic acid methyl ester (**9**)



a. Methyl oleate (0.538 mmol) was added into a dry three-necked round bottom flask. Chlorobenzene (5 mL) was then added into the flask with a syringe followed by allyl cyanide (0.220 mL, 2.735 mmol). 1,4-Benzoquinone (29.1 mg, 0.269 mmol, 50 mol%) was dissolved in chlorobenzene (2.5 mL) and transferred to the reaction mixture by a syringe. The flask containing the mixture was purged for 10 min with nitrogen, and then heated at 110 °C with stirring (400 rpm) for 20 min. The 2nd Generation Hoveyda-Grubbs catalyst (2 mol%, 7.5 mg, 0.01198 mmol) was dissolved in chlorobenzene (5 mL) and transferred into a syringe. The solution containing the catalyst was transferred to the reaction mixture drop wise over a period of 3h while keeping the reaction temperature at 110 °C with stirring (400 rpm). After the completion of the addition, the reaction mixture was kept at this temperature for additional 1 h before being cooled to room temperature.

The crude product was purified by column chromatography using hexane/ethylacetate (9/1) as eluent and concentrated under reduced pressure to provide the desired compound (*E/Z* mixtures) as brown oil (66.6 mg, 55.47 % isolated yield).

b. Methyl 9-decenoate (0.4388 mmol) was added into a dry three-necked round bottom flask. Chlorobenzene (4 mL) was then added into the flask with a syringe followed by allyl cyanide (0.176 mL, 2.188 mmol). 1,4-Benzoquinone (23.2 mg, 0.2146 mmol, 50 mol%) was dissolved in chlorobenzene (2 mL) and transferred to the reaction mixture by a syringe. The flask containing the mixture was purged for 10 min with nitrogen, and then heated at 110 °C with stirring (400 rpm) for 20 min. The 2nd Generation Hoveyda-Grubbs catalyst (2 mol%, 6.1 mg, 0.00974 mmol) was dissolved in chlorobenzene (4 mL) and transferred into a syringe. The solution containing the catalyst was transferred to the reaction mixture drop wise over a period of 3h while keeping the reaction temperature at 110 °C with stirring (400 rpm). After the completion of the addition, the reaction mixture was kept at this temperature for additional 1 h before being cooled to room temperature.

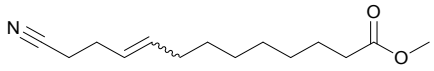
The crude product was purified by column chromatography using hexane/ethylacetate (8/2) as eluent and concentrated under reduced pressure to provide the desired compound (*E/Z* mixtures) as brown oil (35.4 mg, 36.16 % isolated yield). (Note: because of the difficult removal of impurities from the reaction mixture, only a part of the fractions containing the product was isolated).

^{1}H-NMR ($CDCl_3$, 600 MHz) δ/ppm: 5.65 – 5.83 (m, 1H, -CH=CH-), 5.30 – 5.40 (m, 1H, -CH=CH-), 3.66 (s, 3H, -OCH_3), 3.04 – 3.08 (m, 2H, -CH_2CN), 2.29 (t, J=7.5Hz, 2H, -CH_2CO-), 2.02 – 2.06 (m, 2H, -CH_2-), 1.58 – 1.63 (m, 2H, -CH_2-), 1.25 – 1.40 (m, 8H, -CH_2-).

^{13}C-NMR ($CDCl_3$, 600 MHz) δ/ppm: 174.4, 174.4, 136.4, 136.2, 118.4, 118.0, 118.4, 117.2, 116.9, 51.6, 34.2, 34.2, 32.2, 29.2, 29.1, 29.0, 29.0, 29.0, 28.9, 27.4, 25.0, 25.0, 25.0, 20.6, 15.7.

HRMS:$C_{13}H_{21}NO_2$ $[M+Na]^+$ calc. 246.1470 found 246.1462

(*E/Z*)-12-cyano-9-tridecenoic acid methyl ester (**10**)



a. Methyl oleate (0.543 mmol) was added into a dry three-necked round bottom flask. Chlorobenzene (5 mL) was then charged into the flask with a syringe followed by 4-pentenenitrile (0.130 mL, 1.346 mmol). 1,4-Benzoquinone (29.0 mg, 0.268 mmol, 50 mol%) was dissolved in chlorobenzene (2.5 mL) and transferred to the reaction mixture by a syringe. The flask containing the mixture was purged for 10 min with nitrogen, and then heated at 110 °C with stirring (400 rpm) for 20 min. The 2nd Generation Hoveyda-Grubbs catalyst (2 mol%, 7.5 mg, 0.01198 mmol) was dissolved in chlorobenzene (5 mL) and transferred into a syringe. The solution containing the catalyst was transferred to the reaction mixture drop wise over a period of 3h while keeping the reaction temperature at 110 °C. After the completion of the addition, the reaction was kept at this temperature for additional 1 h before being cooled to room temperature.

The crude product was purified by column chromatography using hexane/ethylacetate (9/1) as eluent and concentrated under reduced pressure to provide the desired compound (E/Z mixtures) as brown oil (55.2 mg, 42.86 % isolated yield).

b. Methyl 9-decenoate (0.4383 mmol) was added into a dry three-necked round bottom flask. Chlorobenzene (4 mL) was then charged into the flask with a syringe followed by 4-pentenenitrile (0.064 mL, 0.6627 mmol). 1,4-Benzoquinone (23.2 mg, 0.2146 mmol, 50 mol%) was dissolved in chlorobenzene (2) and transferred to the reaction mixture by a syringe. The flask containing the mixture was purged for 10 min with nitrogen, and then heated at 110 °C with stirring (400 rpm) for 20 min. The 2nd Generation Hoveyda-Grubbs catalyst (2 mol%, 6.1 mg, 0.00974 mmol) was dissolved in chlorobenzene (4 mL) and transferred into a syringe. The solution containing the catalyst was transferred to the reaction mixture drop wise over a period of 3h while keeping the reaction temperature at 110 °C. After the completion of the addition, the reaction was kept at this temperature for additional 1 h before being cooled to room temperature.

The crude product was purified by column chromatography using hexane/ethylacetate (8/2) as eluent and concentrated under reduced pressure to provide the desired compound (E/Z mixtures) as brown oil (46.9 mg, 45.06 % isolated yield).

^{1}H-NMR ($CDCl_3$, 600 MHz) δ/ppm: 5.54 – 5.59 (m, 1H, -CH=CH-), 5.34 – 5.42 (m, 1H, -CH=CH-), 3.65 (s, 3H, $-OCH_3$), 2.28 – 2.40 (m, 6H, $-CH_2$-), 1.98 – 2.05 (m, 2H, $-CH_2$-), 1.58 – 1.64 (m, 2H, $-CH_2$-), 1.26 – 1.37 (m, 8H, $-CH_2$-).

^{13}C-NMR ($CDCl_3$, 600 MHz) δ/ppm: 174.4, 174.4, 134.3, 133.7, 125.7, 125.1, 119.6, 117.2, 51.6, 34.2, 32.5, 29.5, 29.2, 29.2, 29.1, 29.0, 28.5, 27.4, 25.0, 23.4, 17.9, 17.7.

HRMS:$C_{14}H_{23}NO_2$ $[M+Na]^+$ calc. 260.1627 found 260.1623

Cross metathesis using algal lipid:

Microalgae: Freeze dried cultures of a Chlorella sp. strain SLA04 were used in this study. The alga, originally isolated from Soap Lake, WA, was grown in a medium that contained the following: $NaNO_3$ (2.94mM), KH_2PO_4 (1.43mM), Na_2CO_3 (2.35mM), NH_4Cl (0.93mM), $MgSO_4 \cdot 7H_2O$ (0.30mM), $CaCl_2 \cdot 2H_2O$ (0.17mM), NaCl (0.42mM), ferric ammonium citrate (10 mg/L)) and 1mL of trace metal solution which contains H_3BO_3 (0.6g/L), $MnCl_2 \cdot 4H_2O$ (0.25g/L), $ZnCl_2$ (0.02g/L), $CuC_{l2} \cdot 2H2O$ (0.015g/L), $Na_2MoO_4 \cdot 2H_2O$ (0.015g/L), $CoCl_2 \cdot 6H_2O$ (0.015g/L), NiCl2·6H2O (0.01g/L), V_2O_5 (0.002g/L), and KBr (0.01g/L). Cultures were grown phototrophically in 3L cytostir reactors illuminated by fluorescent lamps with an incident light intensity of 300μmoles/m^2.GC Analyses: GC conversion was calculated by integrating all the peaks in the chromatogram except the peaks that do not interfere the mass balance: by-products ((*E/Z*)-undec-2-enenitrile, dimer of acrylonitrile or allyl cyanide, 10-decene), unreactive substrates (C14:0, C15:0, C16:0 FAME), and impurities introduced from the starting material. This method is comparable to the method used to analyze the GC conversion of the reaction with pure oleic acid (**1**) used through out this manuscript.

(1) Cross-metathesis with acrylonitrile:

Using pure oleic acid (**1**) (control experiment):
Methyl oleate (**1**) (0.1 mmol), acrylonitrile (35 μL, 0.534 mmol) and 1 mL of dry toluene were placed in a round bottom flask. A 2nd-Generation Grubbs-Hoveyda catalyst (0.8 mg, 0.0013 mmol) was dissolved in dry toluene (1 mL) and transferred to a syringe. Additional 1 mL of toluene was used to rinse the vial. The catalyst solution was transferred to the reaction mixture using a syringe pump, over a period of 1 h under nitrogen atmosphere with magnetic stirring (400 rpm) at 95 ℃. At the end of the addition, the mixture was left to react for 1.5 h at 95 ℃. The reaction mixture was analyzed by gas chromatography, indicating the conversion being >99 % by area. GC analysis showed the four major peaks, methyl 10-cyano-9-decenoate and 2-undecenitrile (both as mixtures of *E* and *Z* isomers). The mixture was passed through a plug of silica gel (0.5cm in Pasteur pipette) with hexane/ethyl acetate (7/3) in order to remove the catalyst, concentrated, and the residue was purified by silica gel chromatography, yielding (*E*)-10-cyano-9-decenoate (4.69 mg, 0.022 mmol, 22%), (*Z*)-10- cyano-9-decenoate (12.3 mg, 0.059 mmol, 59%), (*E*)-2-undecenitrile (4.76 mg, 0.029 mmol), and (*Z*)-2- undecenitrile (11.5 mg, 0.070 mmol) all as clear oil.

Using allgal lipid:
Algal lipids, containing 55% methyl oleate (0.1119 mmol), obtained from microalgae (*Chlorella species*)by reactive extraction method,[2] was added into a dry three-necked round bottom flask. Toluene (1.5 mL) was then added into the flask with a syringe followed by acrylonitrile (0.034 mL, 0.519 mmol). The flask containing the mixture was purged for 10 min with nitrogen, and then heated at 95 °C with stirring (400 rpm) for 20 min. The 2nd Generation Hoveyda-Grubbs catalyst (1 mol%, 0.8 mg, 0.0013 mmol) was dissolved in toluene (1 mL) and transferred into a syringe. The solution containing the catalyst was transferred to the reaction mixture drop wise over a period of 1h while keeping the reaction temperature at 95 °C with stirring (400 rpm). After the completion of the addition, the reaction mixture was kept at this temperature for additional 1h before being cooled to room temperature.
The reaction mixture was passed through a pipette of silica using hexane/ethyl acetate (7/3) as eluent, and the crude product was analyzed by GC.

(2) Cross-metathesis with allyl cyanide:

Algal lipids, containing 55% methyl oleate (0.1119 mmol), obtained from microalgae (*Chlorella species*) by reactive extraction method,[2] was added into a dry three-necked round bottom flask. Chlorobenzene (1.5 mL) was then added into the flask with a syringe followed by allyl cyanide (0.044 mL, 0.5470 mmol). 1,4-Benzoquinone (6.3 mg, 0.0583 mmol, 50 mol%) was dissolved in chlorobenzene (0.5 mL) and transferred to the reaction mixture by a syringe. The flask containing the mixture was purged for 10 min with nitrogen, and then heated at 110 °C with stirring (400 rpm) for 20 min. The 2nd Generation Hoveyda-Grubbs catalyst (2 mol%, 1.4 mg, 0.0022 mmol) was dissolved in chlorobenzene (1 mL) and transferred into a syringe. The solution containing the catalyst was transferred to the reaction mixture drop wise over a period of 2h while keeping the reaction temperature at 110 °C with stirring (400 rpm). After the

completion of the addition, the reaction mixture was kept at this temperature for additional 2h before being cooled to room temperature.

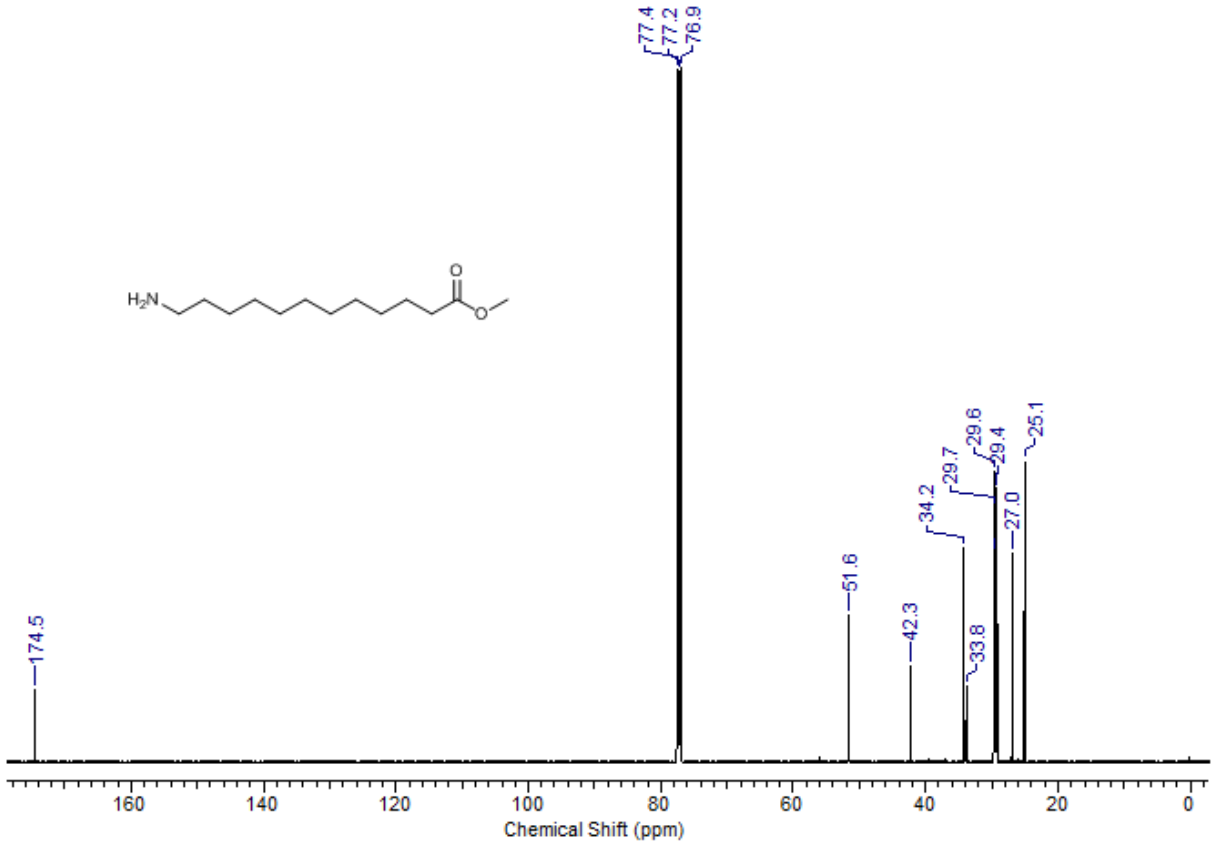
The reaction mixture was passed through a pipette filled with silica gel using hexane/ethyl acetate (7/3) as eluent, and the crude product was analyzed by GC.

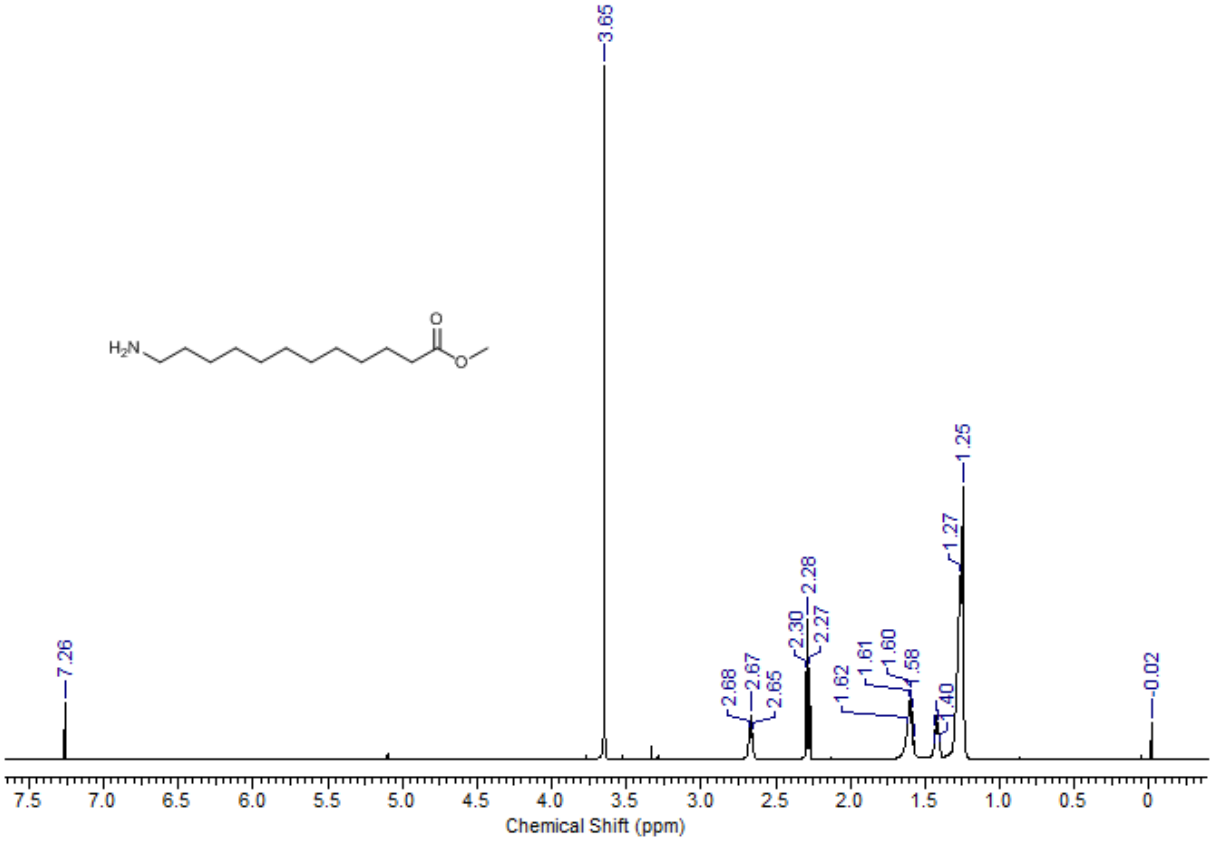
Reference:

1. X. Miao, C. Fischmeister, C. Bruneau, P. H. Dixneuf, J-L. Dubois, J-L. Couurier, ChemSusChem, 2012, **5**, 1410
2. S. Viamajala, D. Nelson, R. Sims, 2011-US24549

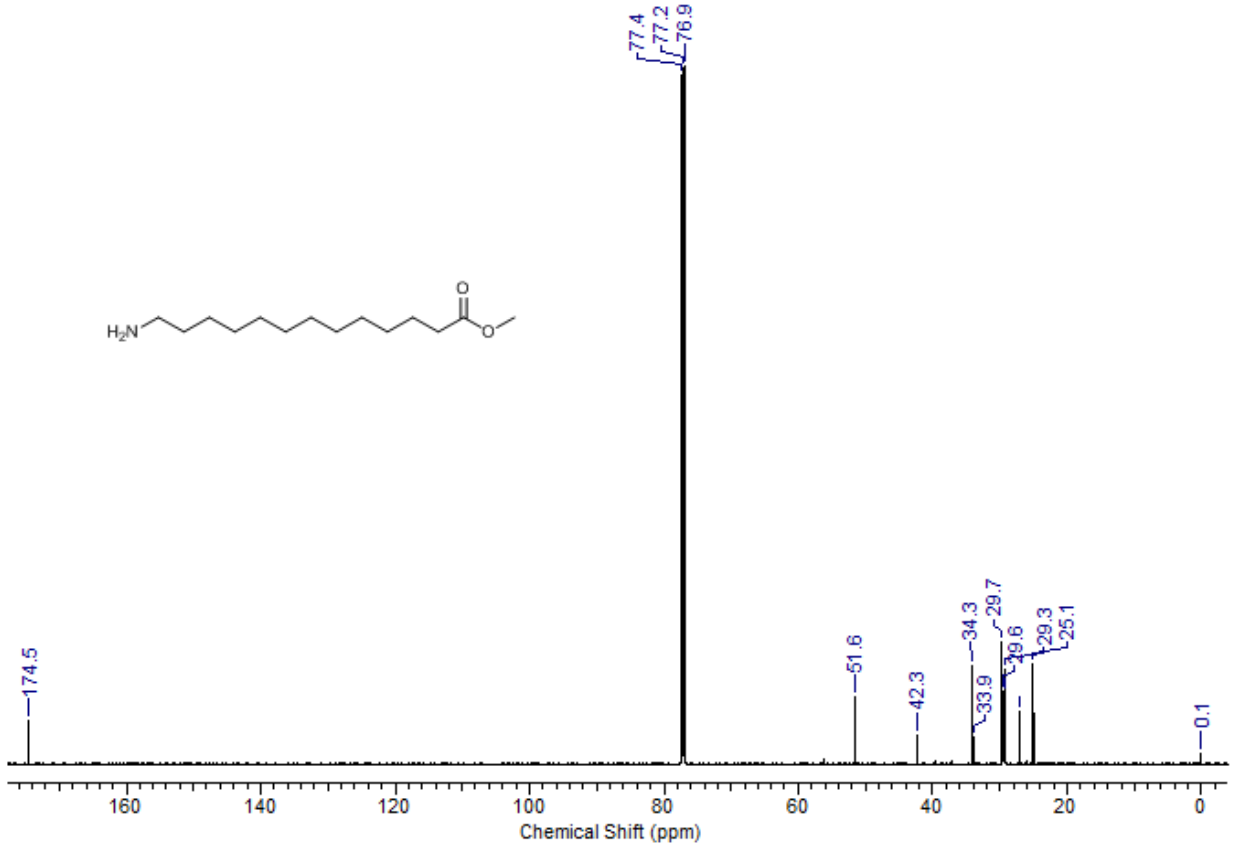
NMR spectral data:

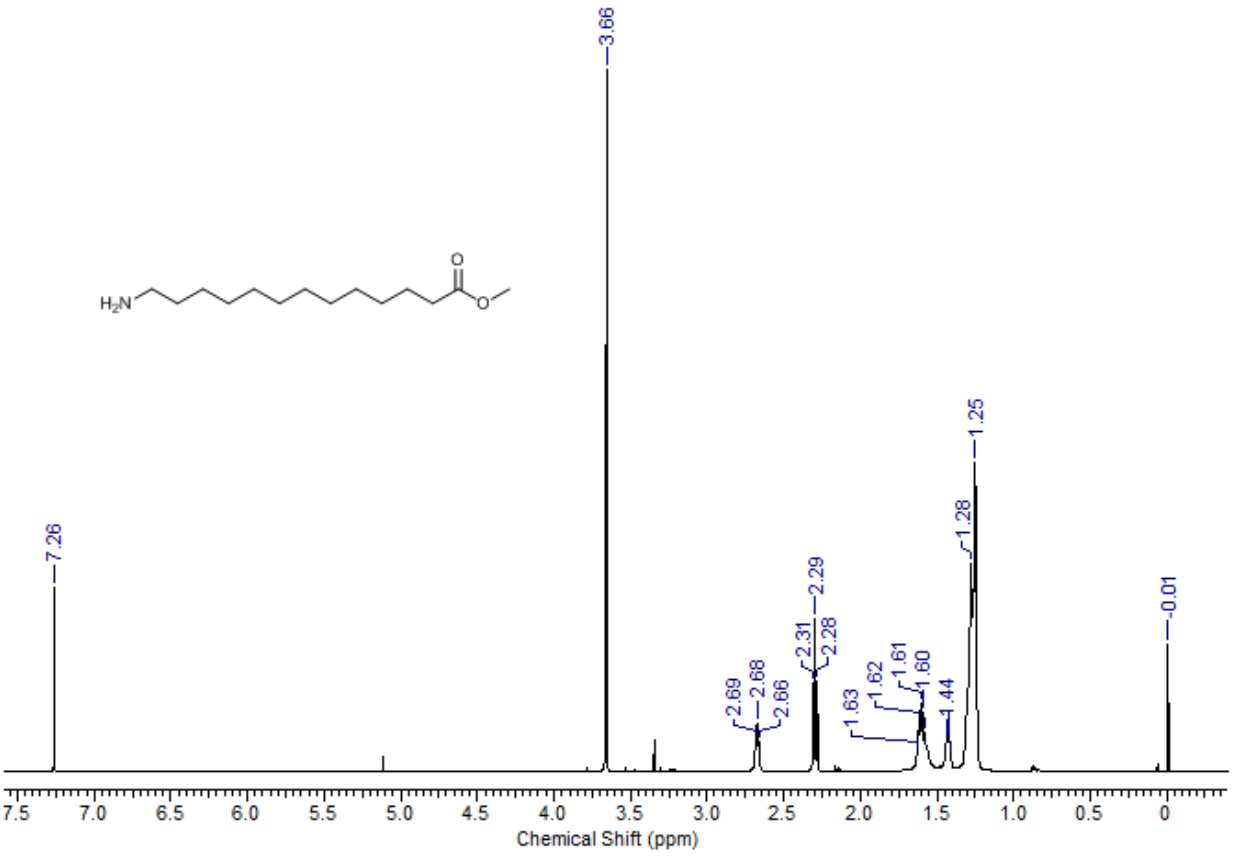
Methyl 12-aminododecanoate (**5**)



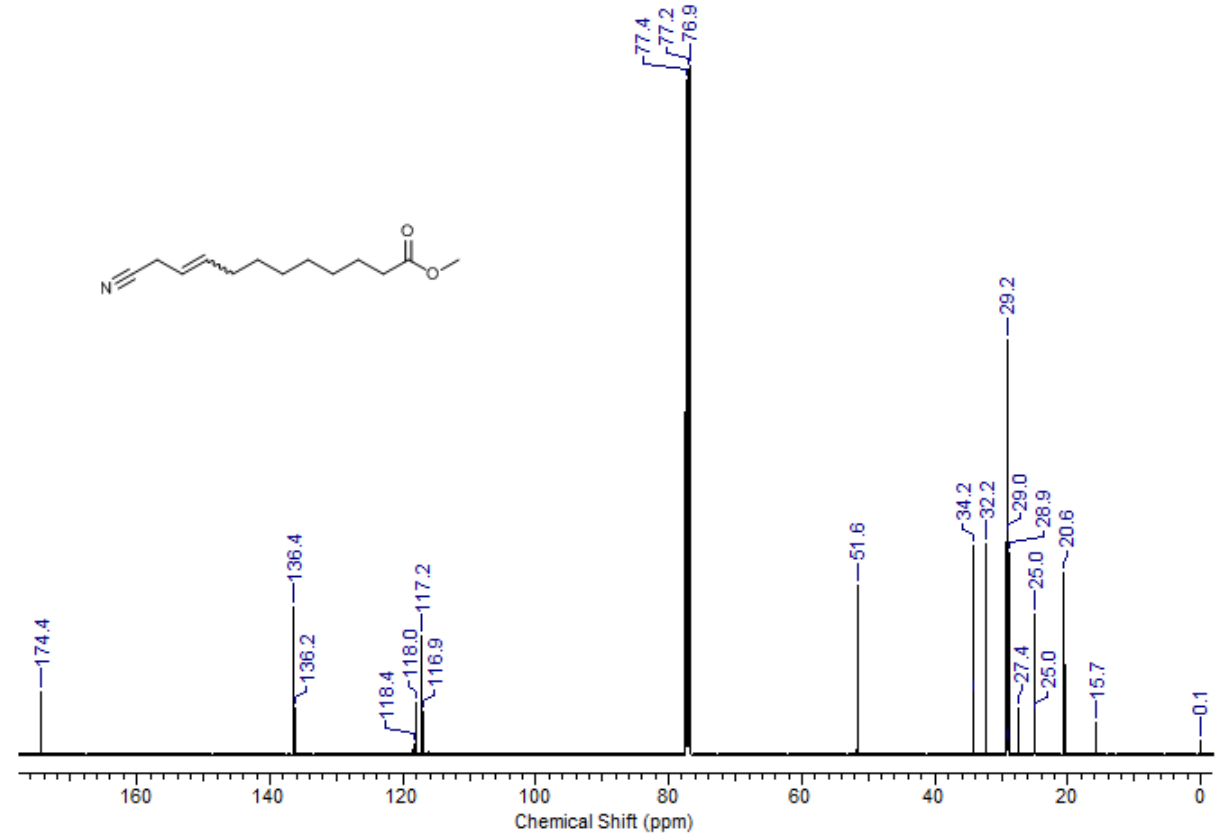


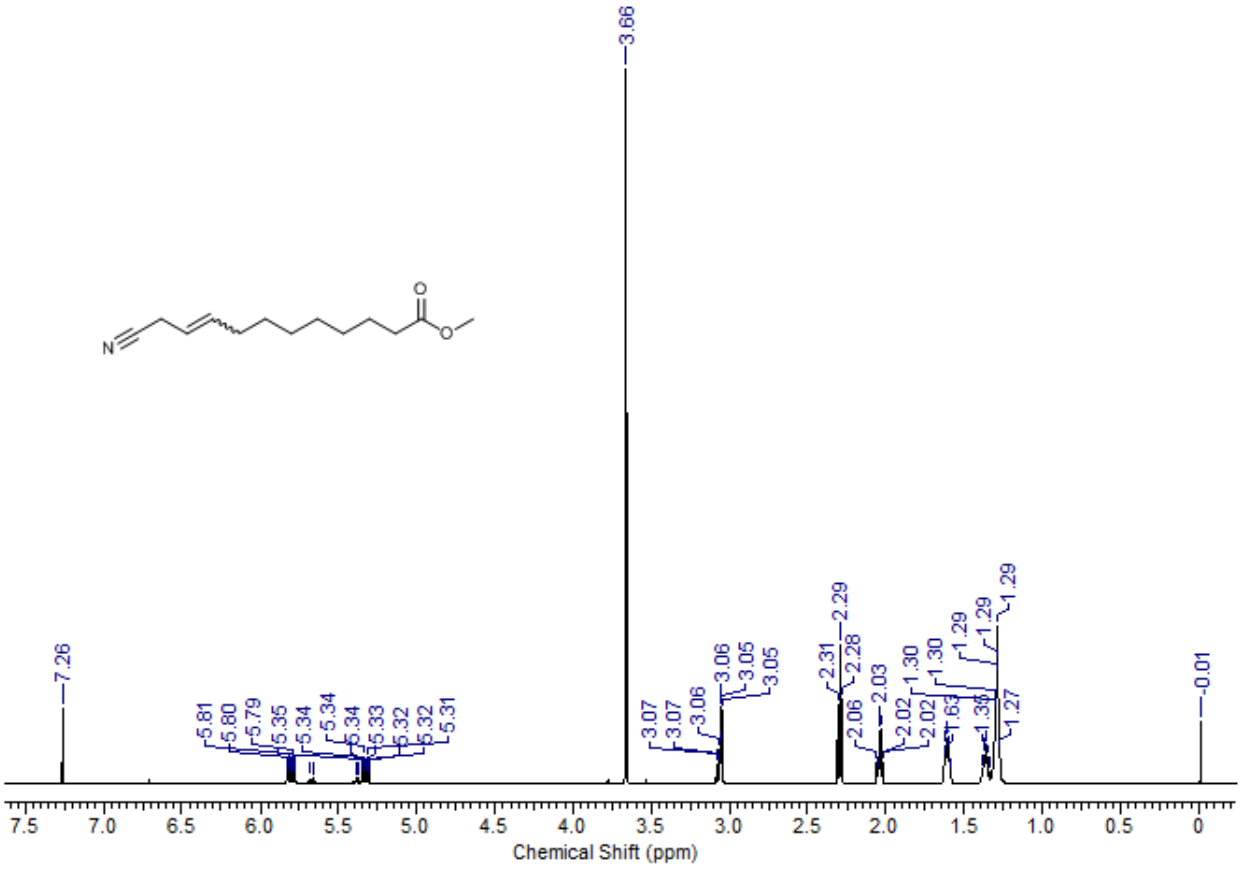
Methyl 13-aminotridecanoate (**6**)



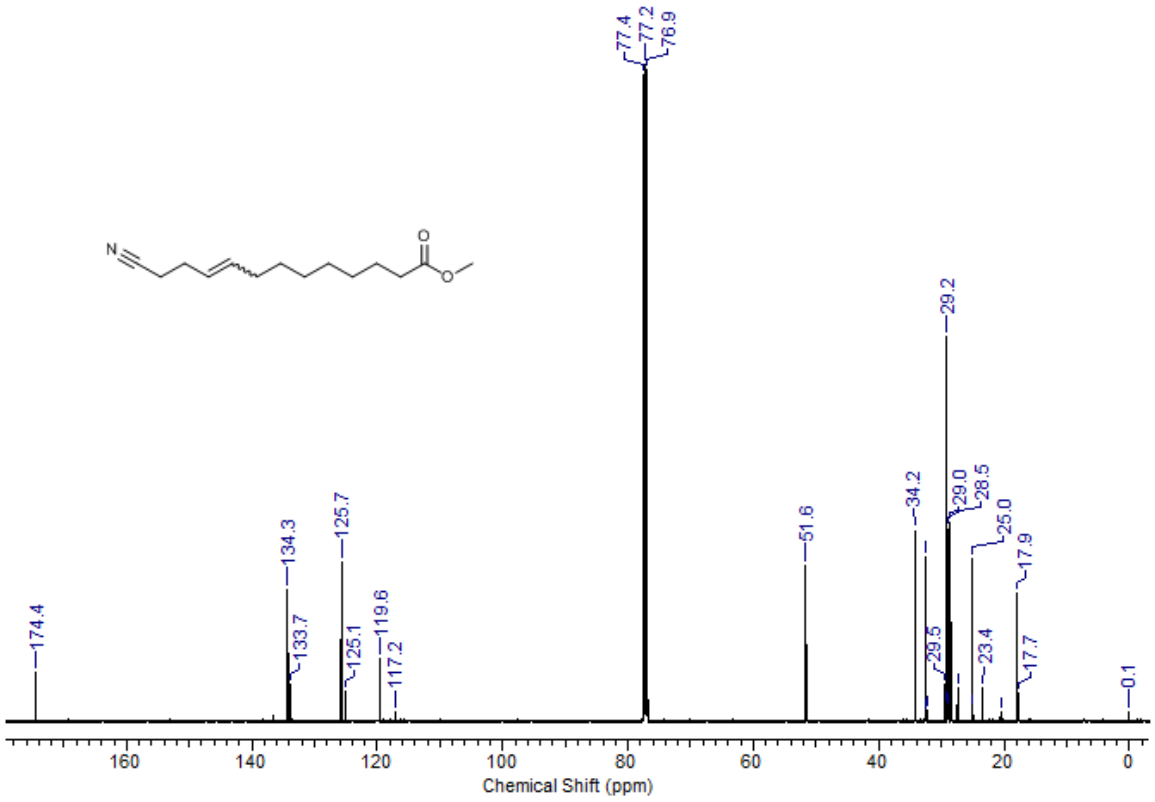


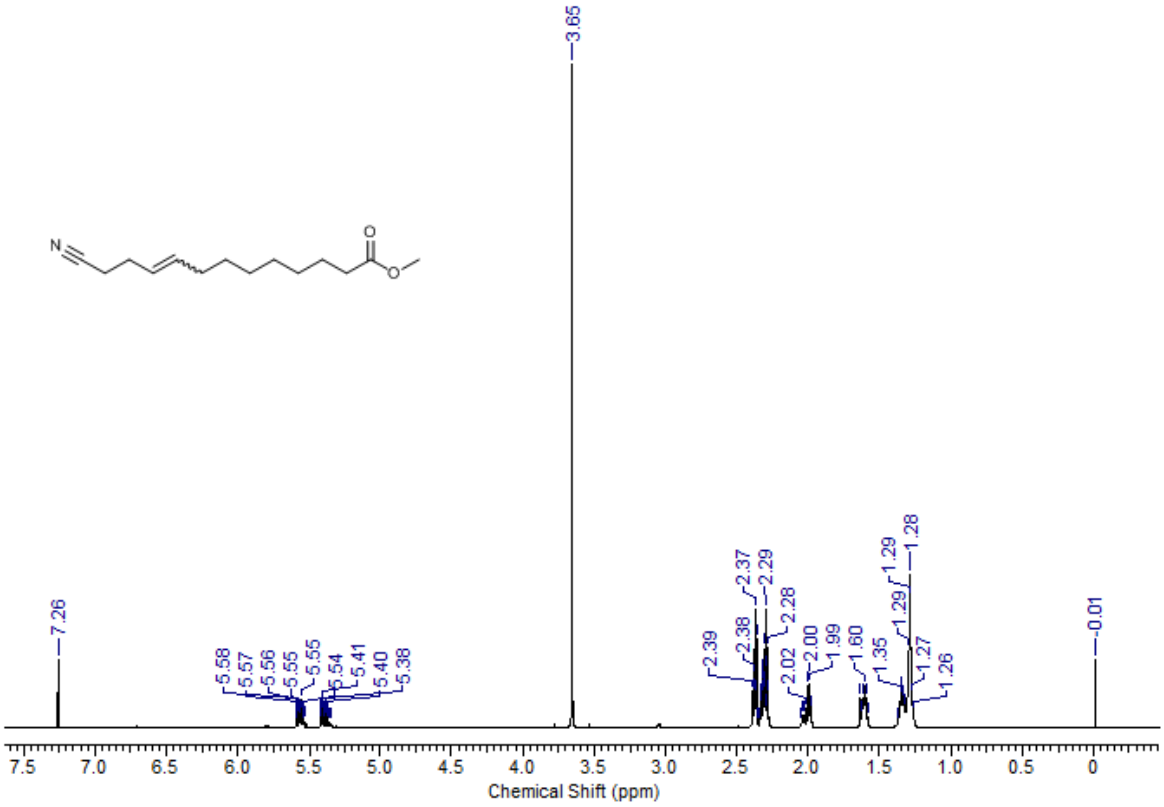
(E/Z) - 11-Cyano-9-dodecenoic acid methyl ester (**9**)





(E/Z) - 12-cyano-9-tridecenoic acid methyl ester (**10**)





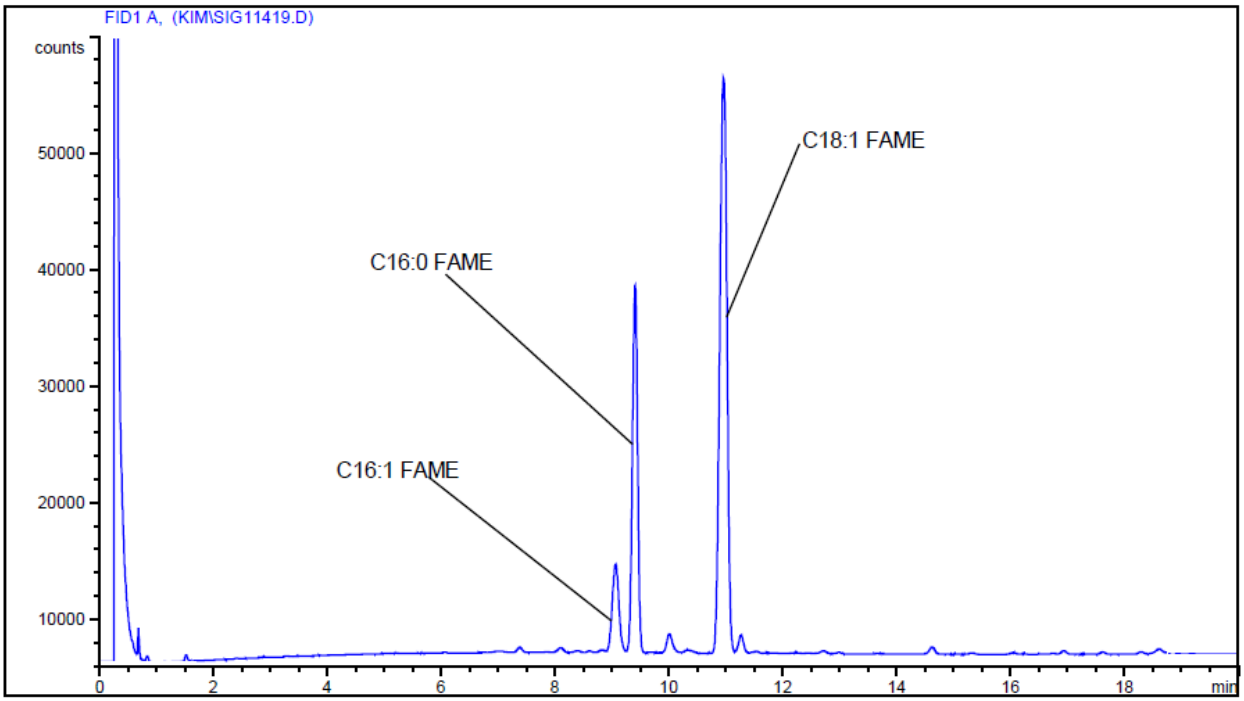


Figure S1. GC chromatogram of FAMEs after reactive extraction of Microalgae

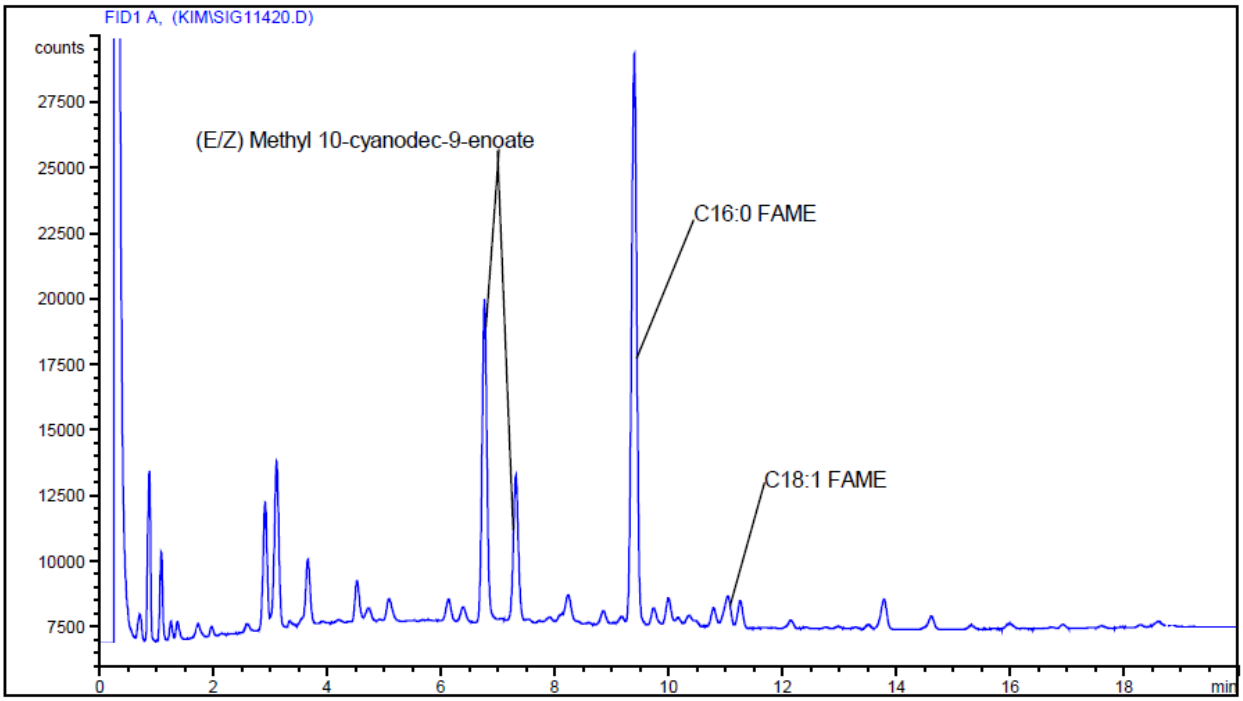


Figure S2. GC chromatogram of cross metathesis (algal lipids with acrylonitrile)

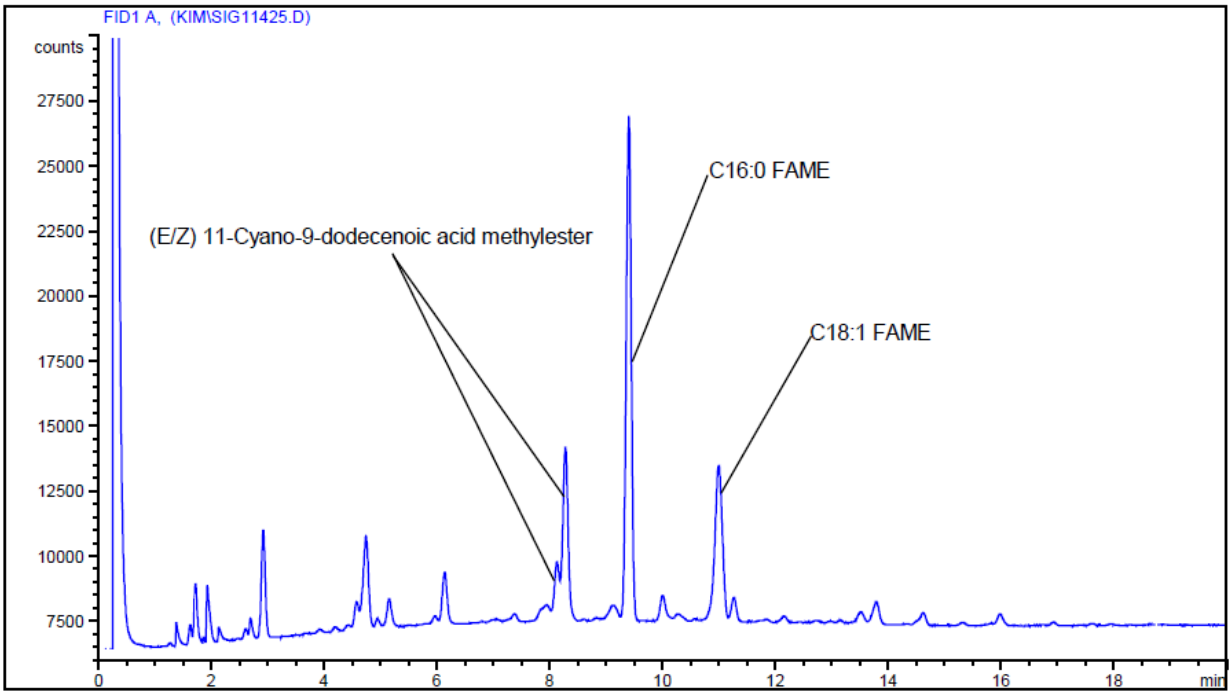


Figure S3. GC chromatogram of cross metathesis (algal lipids with allyl cyanide)