Stable Bio-oil Production from Proteinaceous Cyanobacteria: Tail Gas Reactive Pyrolysis of Spirulina

Supporting Information

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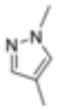
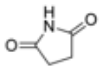
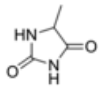
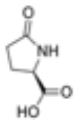
Table S1
Characterization of Spirulina used in this study.

Ultimate analysis (wt.%, daf)		Proximate analysis (wt.%)	
C	48.05	Moisture	5.60
H	7.04	Ash	7.94
N	10.74	Volatile matter	79.38
S	0.72	Fixed Carbon	5.28
O[a]	33.45	HHV (MJ/kg)	22.56

Table S2
Identified nitrogen containing compounds in regular and TGRP pyrolysis of spirulina (% area)

Compounds	% Area		Functional group/structure
	Regular[e]	TGRP[f]	
Nitriles[a]	5.8	9.5 - 11.4	
Pyrroles[b]	4.0	4.2 - 4.3	
Amides[c]	13.0	9.7 – 11.0	
Indoles[d]	8.2	10.3- 11.9	
2,5-dimethylpiperazine	8.5	Nd	
2-Aminopyridine	0.4	1.0	
1,4-dimethylpyrazole	0.7	nd	
2,2,6,6 - Tetramethyl-4-piperidone	3.9	nd	
2,5-Pyrrolidinedione	2.3	nd	
5-(2-methylpropyl)-2,4-imidazoledinedione	0.8	nd	
5-oxoproline	2.5	nd	

[a] 4-methyl-pentanitrile, 3-methyl-butanitrile, benzonitrile, benzyl nitrile, benzenepropanenitrile, hexadecanenitrile
[b] pyrrole, 3-methyl-1H-Pyrrole, hexahydropyrrolo[1,2-α]pyrazine-1,4-dione
[c] acetamide, propanamide, hexanamide, hexadecanamide, 3-methyl-butanamide
[d] Indole, 3-methyl-1H-indole
[e] Results from a single experiment
[f] Experiments conducted in duplicate

NMR Analysis of ESP Oils and Condensers' Organic Fraction

Carbon 13 (^{13}C) Nuclear Magnetic Resonance Spectroscopy (NMR) and Proton (^{1}H) NMR were conducted on the ESP oils from the regular and tail-gas reactive pyrolysis of Spirulina as well as the condensers' organic fraction from the TGRP of Spirulina. Solution-state NMR spectra were recorded at 9.4 T on a Varian Inova NMR spectrometer (Palo Alto, CA) using a 5 mm dual broad-band probe equipped with z-axis pulsed field gradients or on a 14 T Agilent VNMRS NMR spectrometer (Santa Clara, CA) using a 5 mm One NMR probe with z-axis pulsed field gradients. All spectra were acquired at 40 °C in CD_3OD. The ^{1}H NMR spectra, at 400 MHz, had a spectral width of 13 ppm and were acquired with a 45° pulse angle with a 6 s relaxation delay and were referenced to the sodium salt of 3-(trimethylsilyl)propionic acid-d_4 (TSP). All ^{13}C NMR spectra had a sprectral width of 250 ppm, were acquired using a 45° pulse angle, inverse-gating, and were referenced to the solvent ^{13}C peak. Reasonable signal-to-noise was achieved with 15,000−70,000 transients, utilizing a 4 or 6 s relaxation delay to provide adequate recovery of the signal for integration purposes. All data processing was performed using Spinworks4 (Version 4.1.0.0) (Copyright 2015, Kirk Marat, University of Manitoba (ftp://davinci.chem.umanitoba.ca/pub/marat/SpinWorks/).

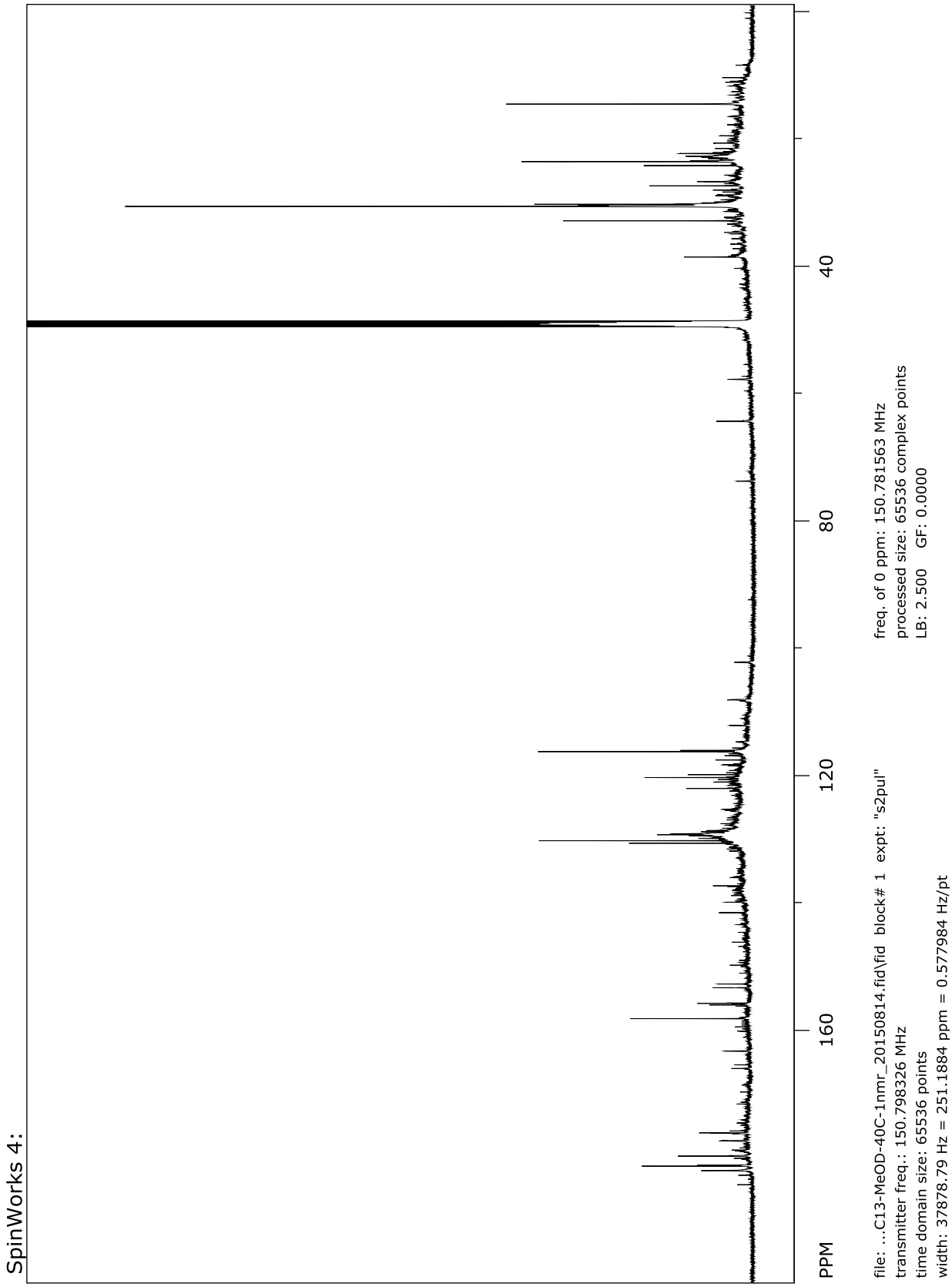


Figure S1. ^{13}C NMR of ESP oil from the Regular Pyrolysis of Spirulina recorded at a frequency of 150 MHz in Deuterated Methanol

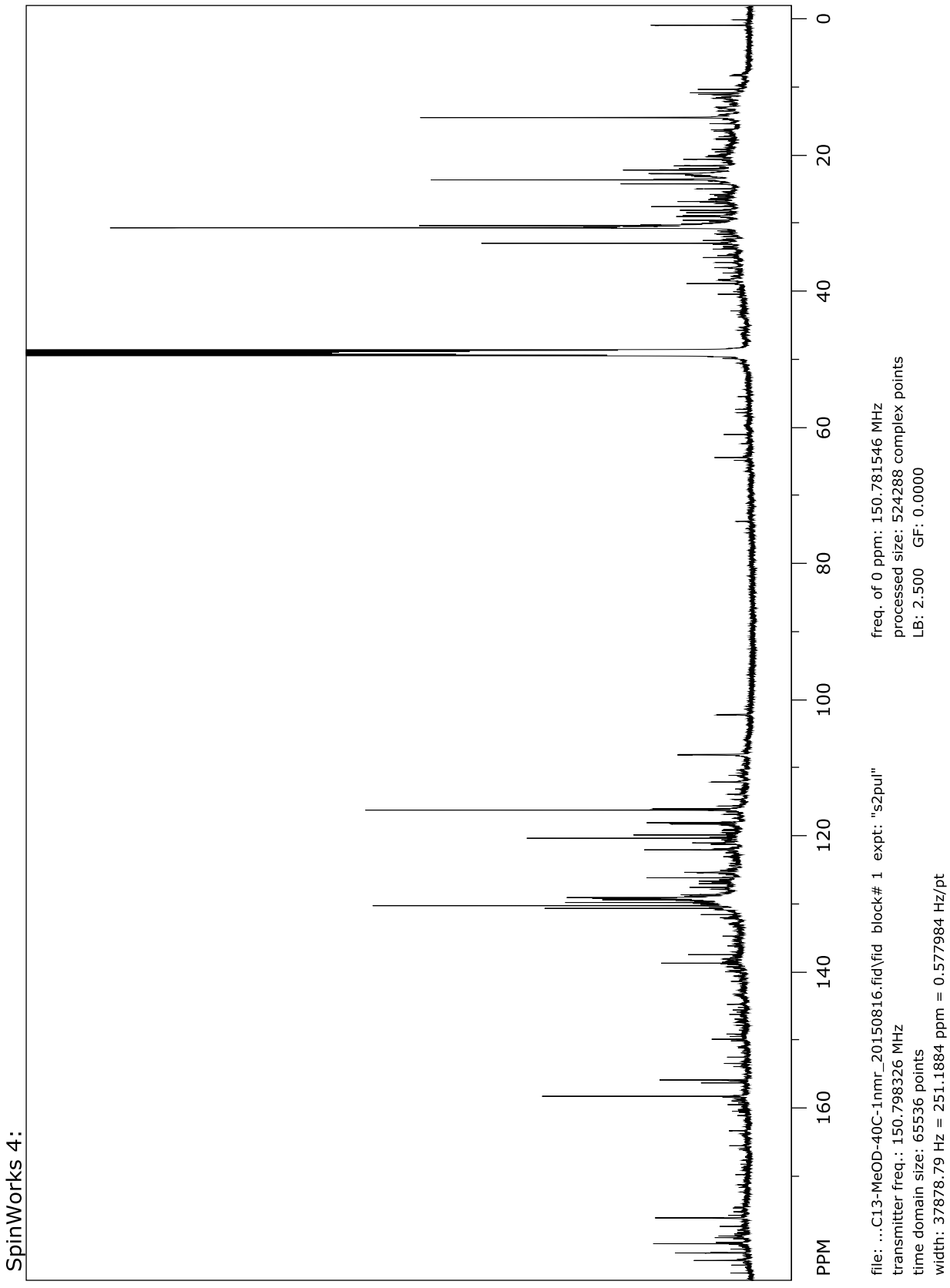


Figure S2. ^{13}C NMR of ESP oil from the TGRP of Spirulina recorded at a frequency of 150 MHz in Deuterated Methanol

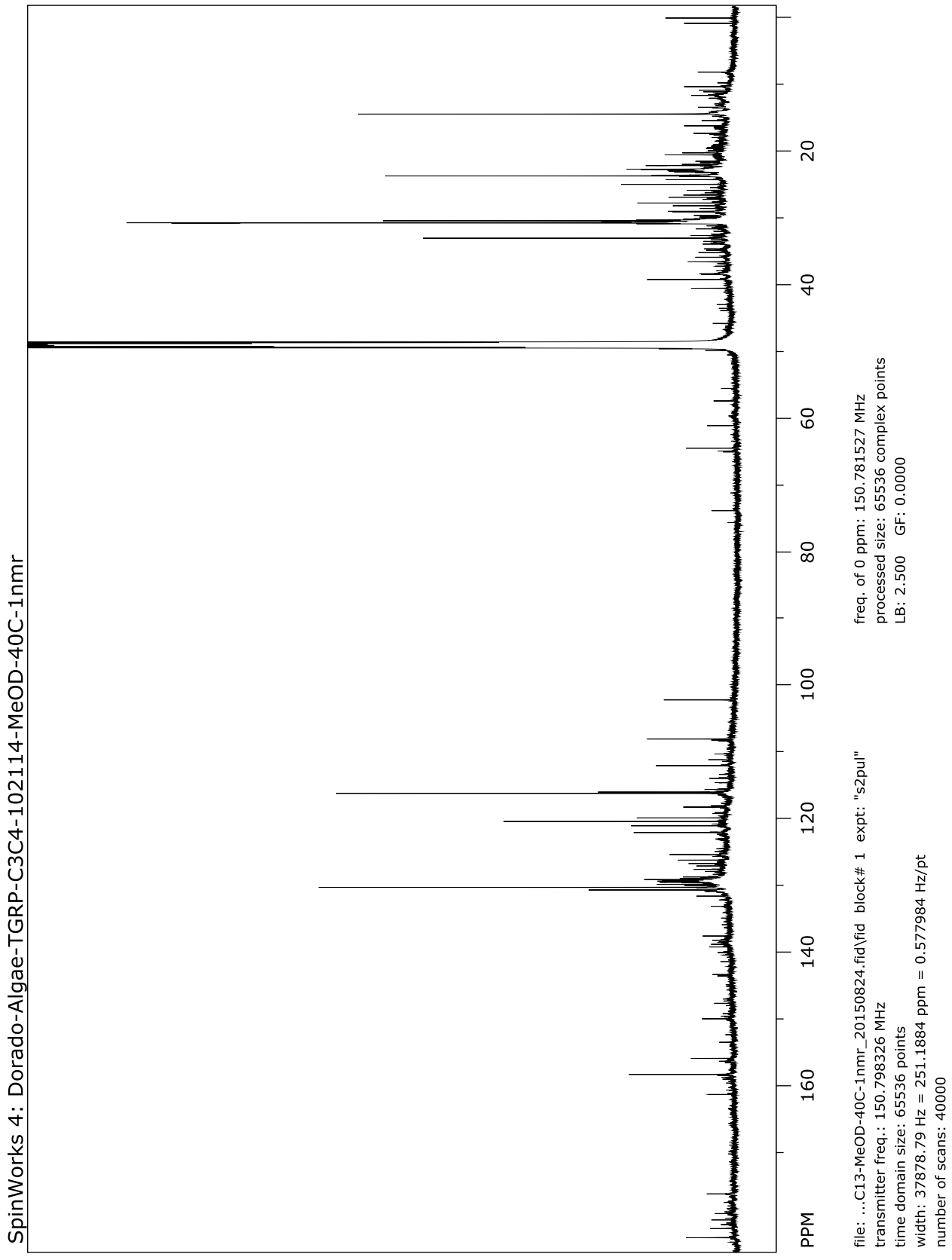


Figure S3. ^{13}C NMR of the Condensers' Organic Fraction from the TGRP of Spirulina recorded at a frequency of 150 Mz in Deuterated Methanol

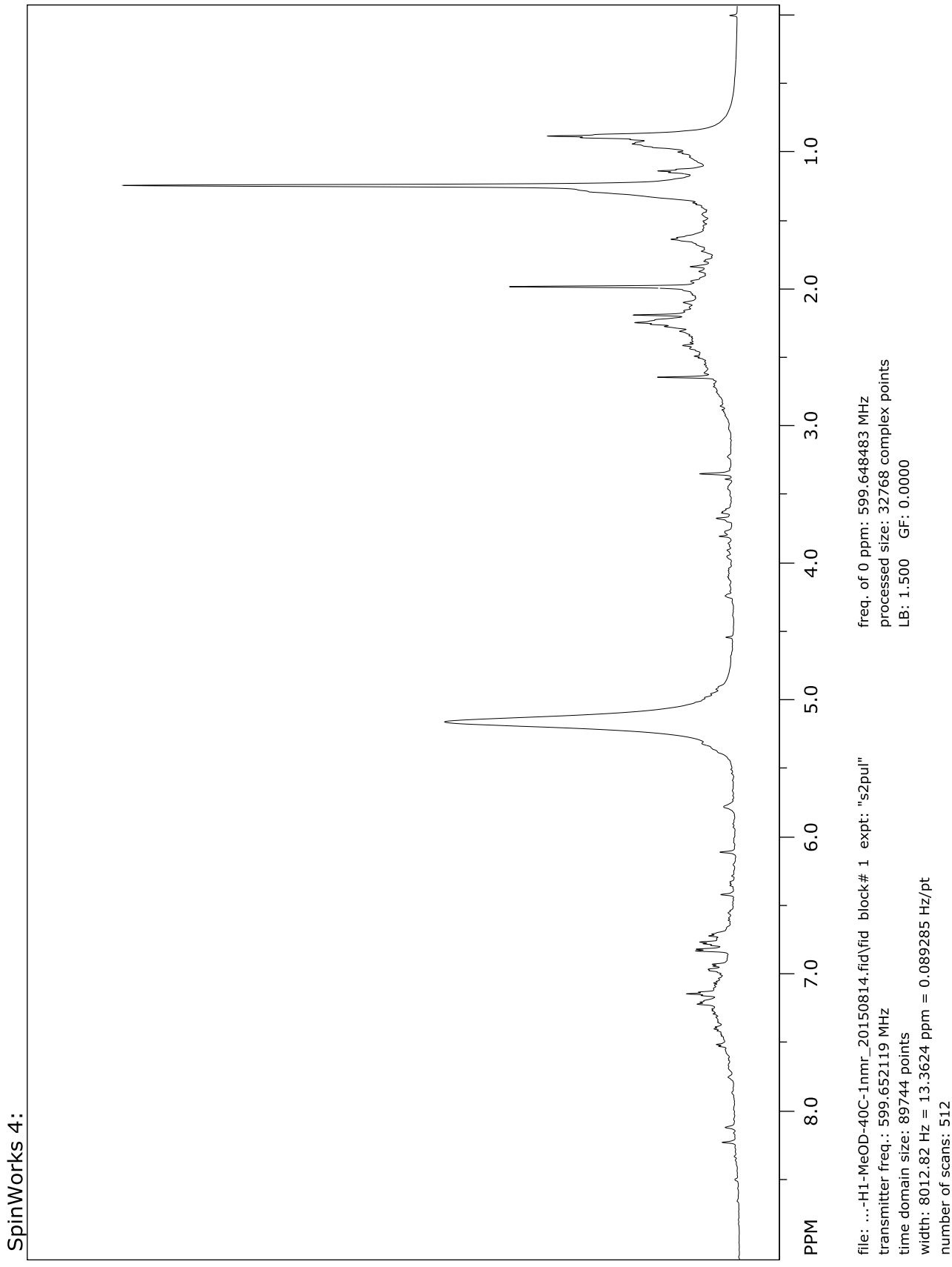


Figure S4. ^{1}H NMR of the ESP oil from the Regular Pyrolysis of Spirulina recorded at a frequency of 600 MHz in Deuterated Methanol

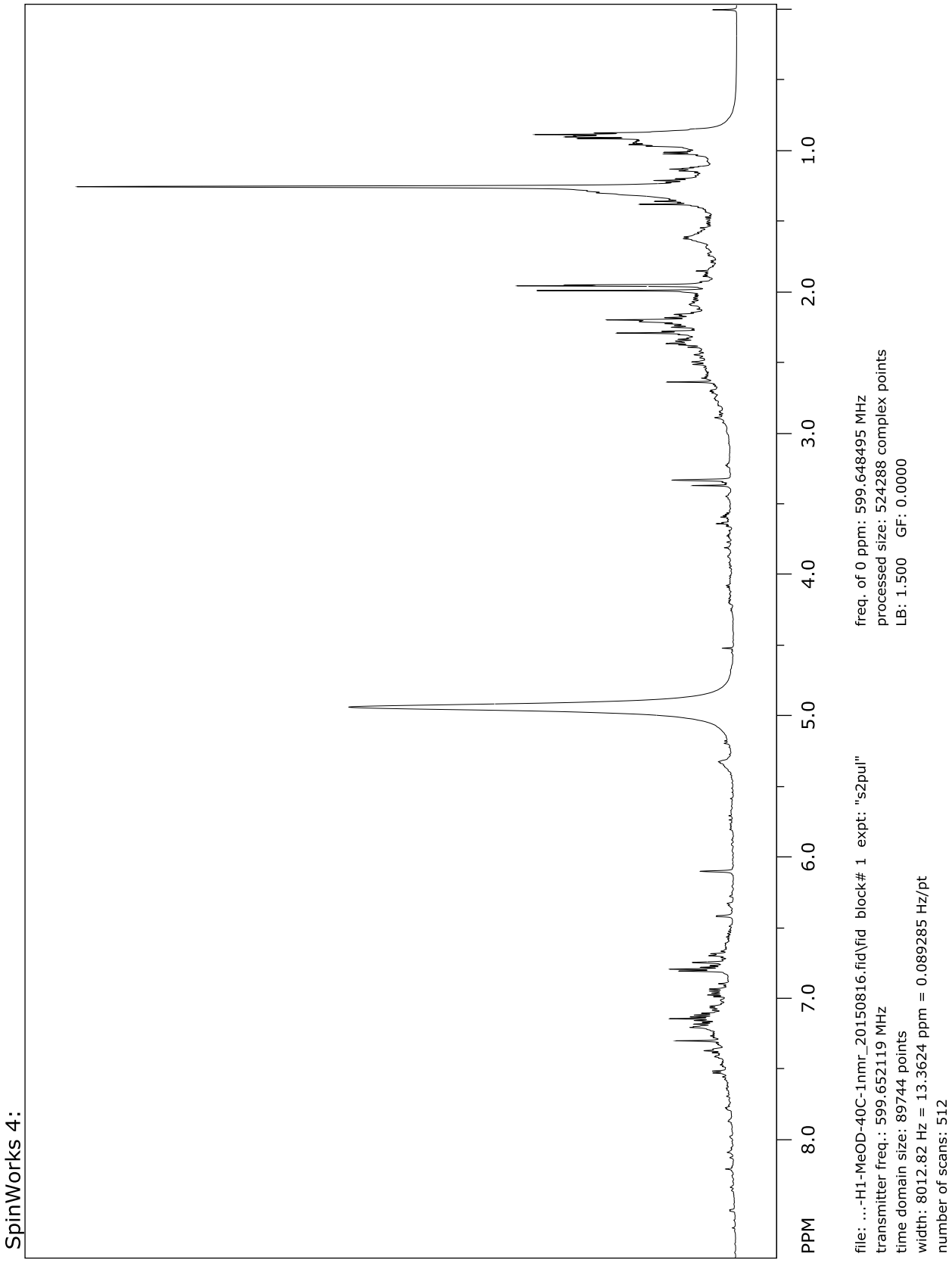


Figure S5. ^{1}H NMR of the ESP oil from the TGRP of Spirulina recorded at a frequency of 600 MHz in Deuterated Methanol

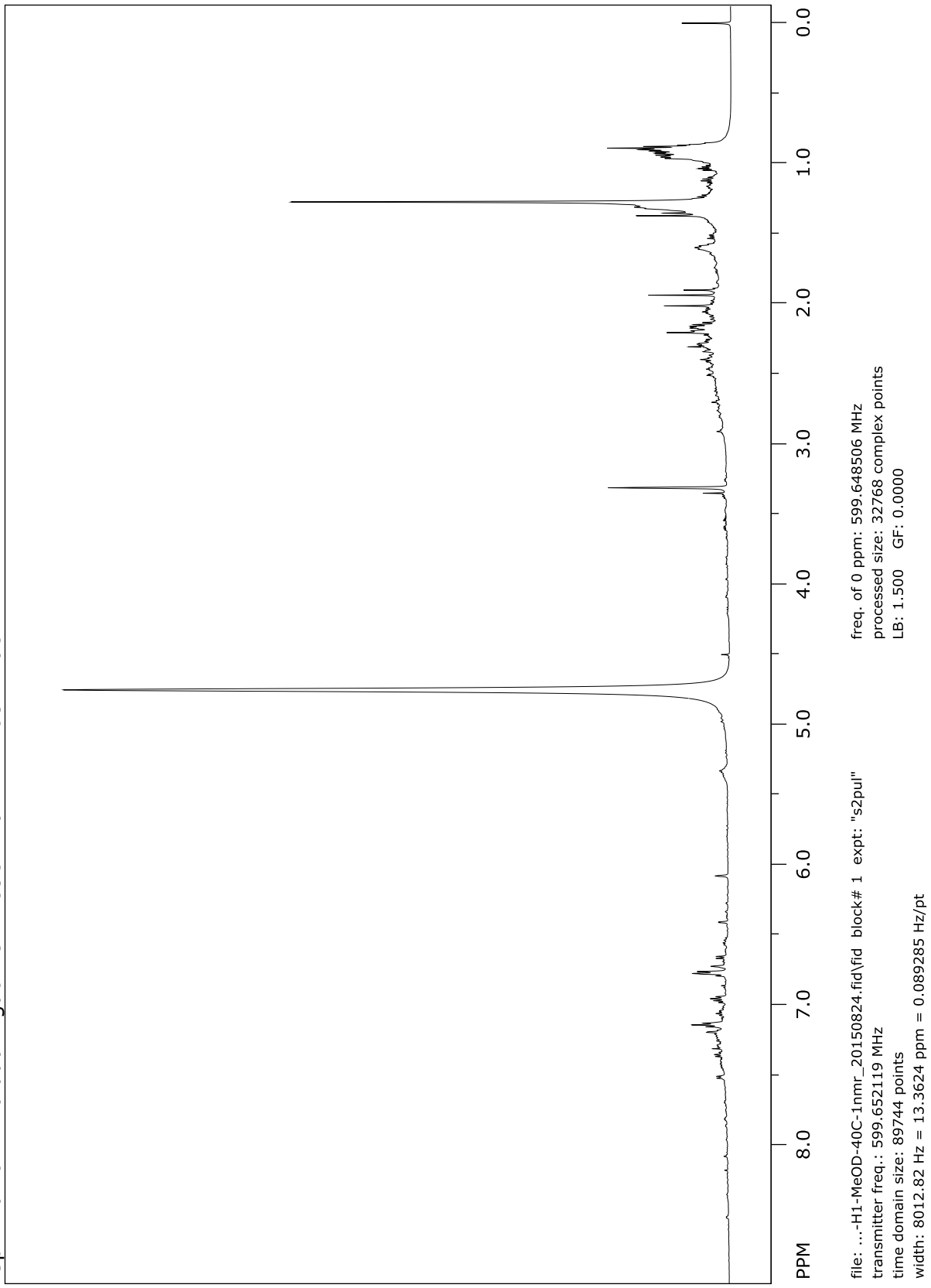
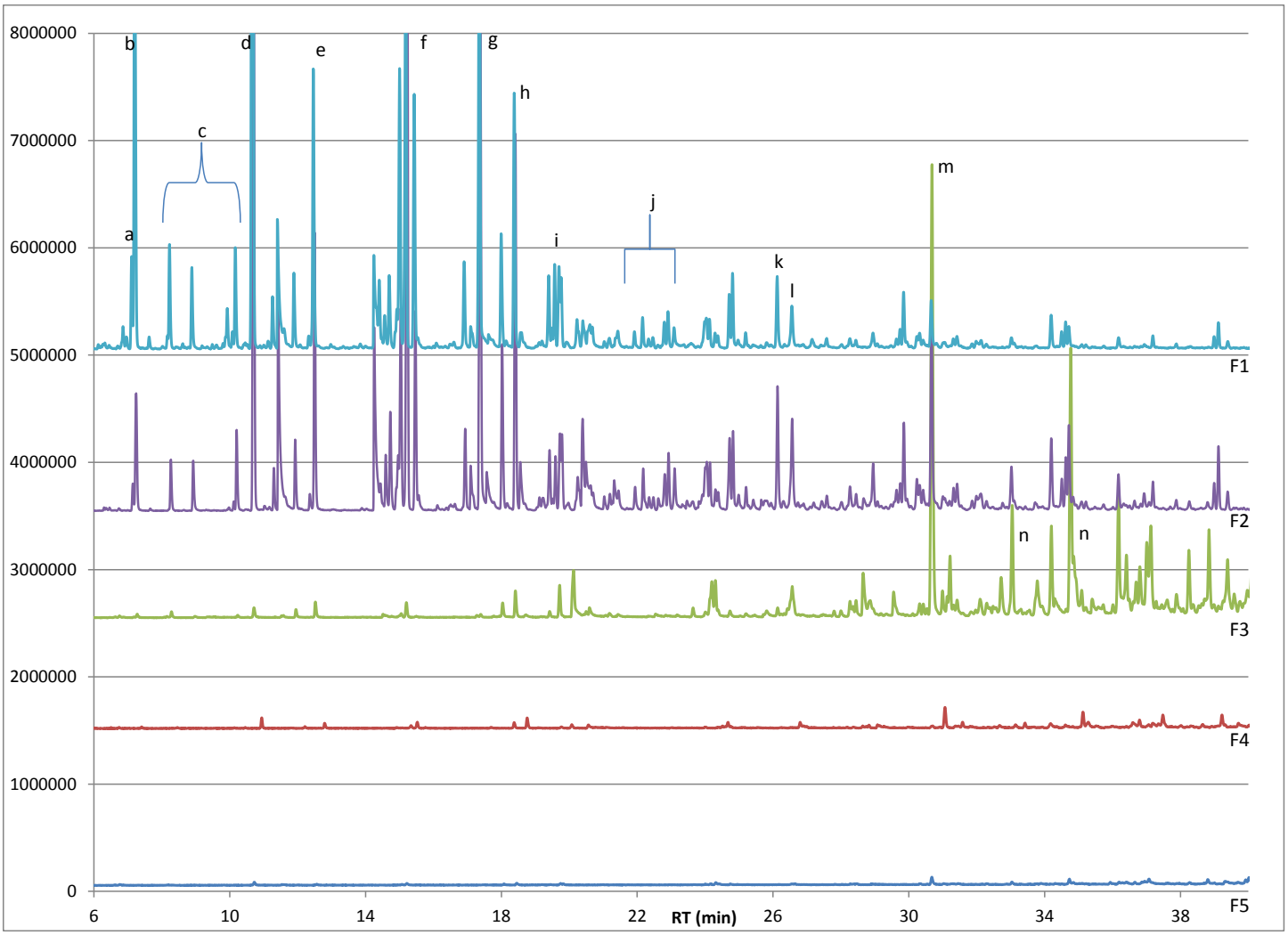


Figure S6. ^{1}H NMR of the Condensers' Organic Fraction from the TGRP of Spirulina recorded at a frequency of 600 MHz in Deuterated Methanol

A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6
10
14
18
22
26
30
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a
b
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n
n
F1
F2
F3
F4
F5

B

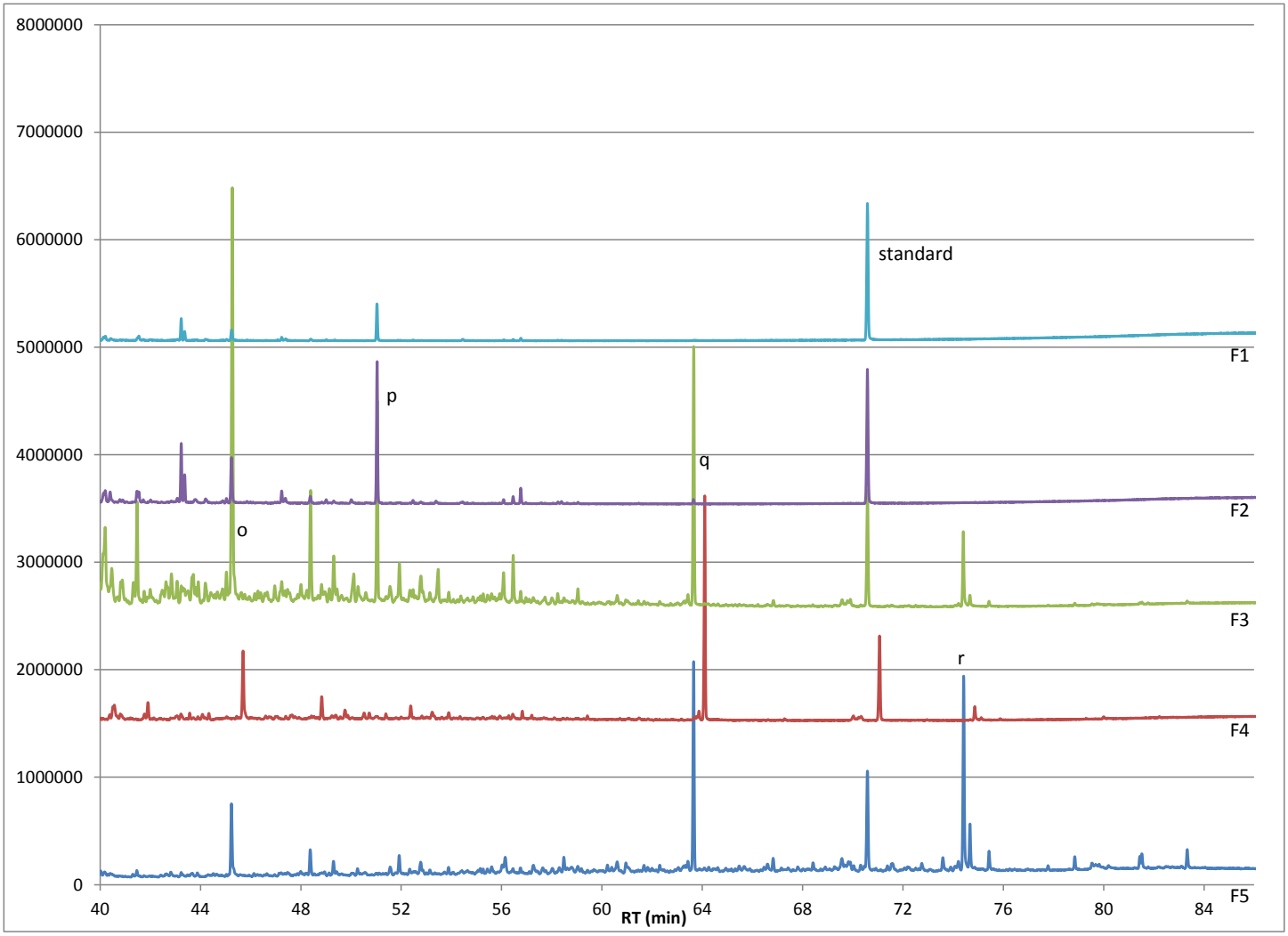

Figure S7. GC/MS Chromatograms of distillate fractions from Spirulina TGRP bio-oil. a. propenitrile b. benzene c. C4-nitriles d. toluene e. *p*-xylene f. pyrrole g. styrene h. pentenitrile i. dimethyl pyridines j. C3-alkyl benzenes k. indene l. benzonitrile m. phenol n. cresols o. indole p. hexadecane q. hexadecane nitrile r. hexdecanamide (A)Retention time 6-40 min (B) Retention time 40-85 min

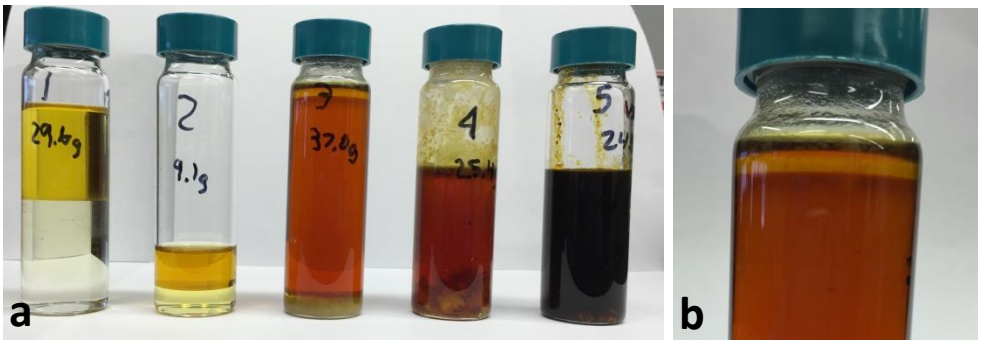

Figure S8 – (a) Spirulina TGRP bio-oil distillation fractions, with fraction 3 (b) exhibiting triphasic behavior. The top organic phase consisted primarily of hexadecane