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Supporting Information

To cyclopropanate or not to cyclopropanate? A look at cyclopropanation on the performance of biofuels

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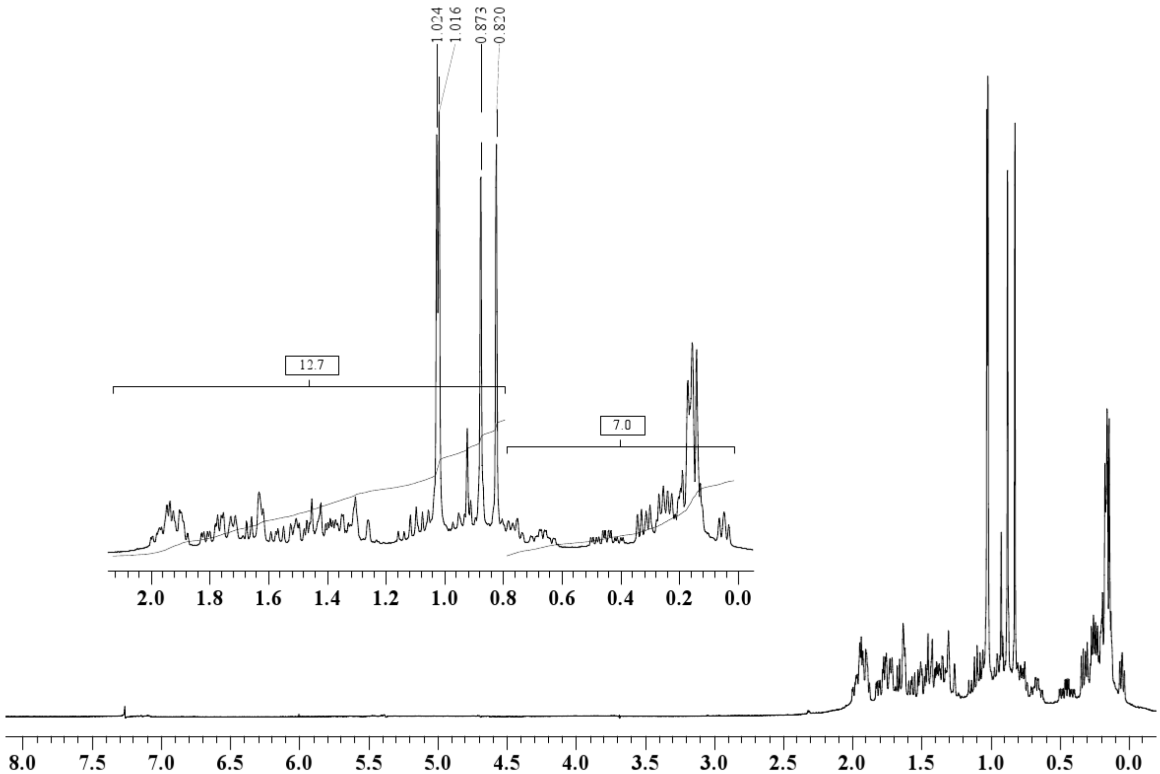
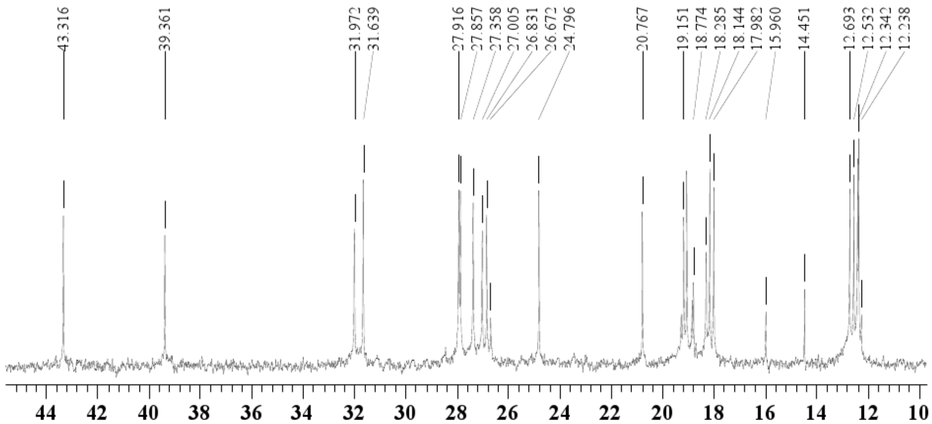
I. NMR Spectra of Compounds 1-3

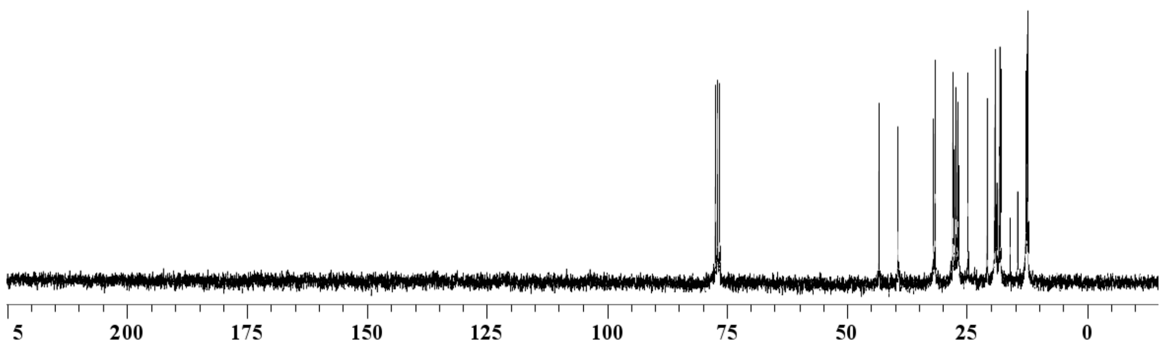
Compound 1:

^{1}H Spectrum:



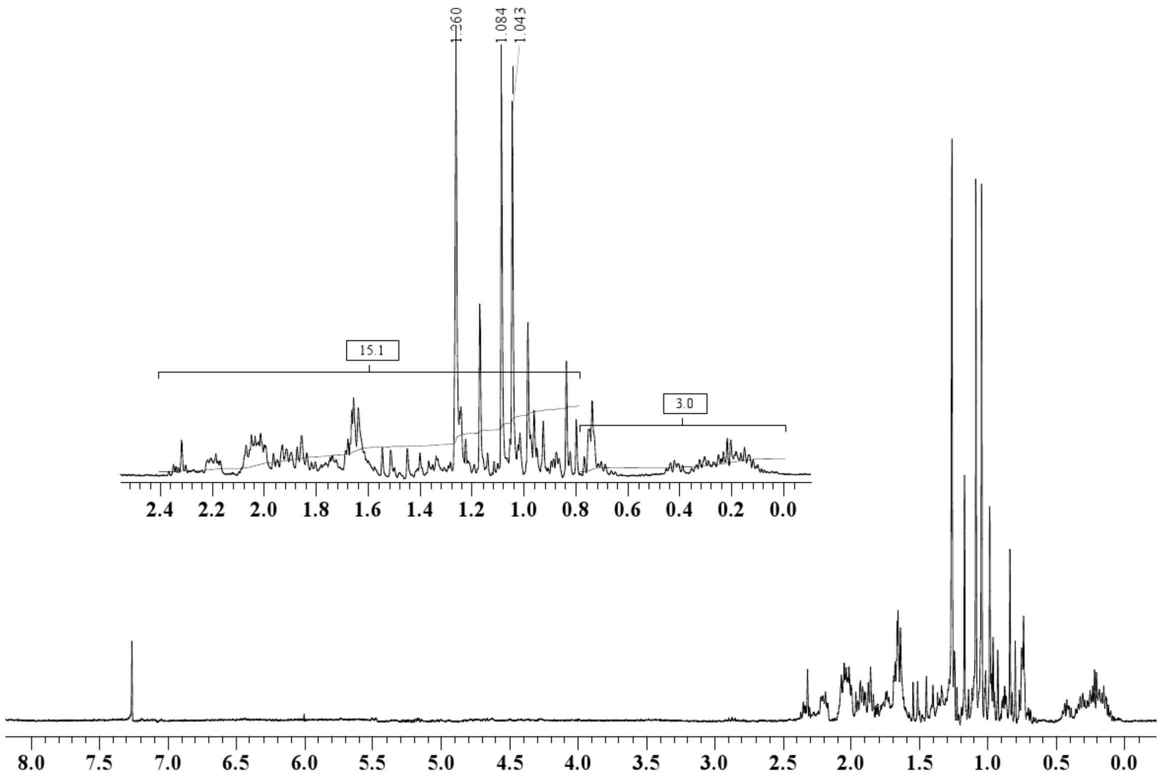
^{13}C Spectrum:



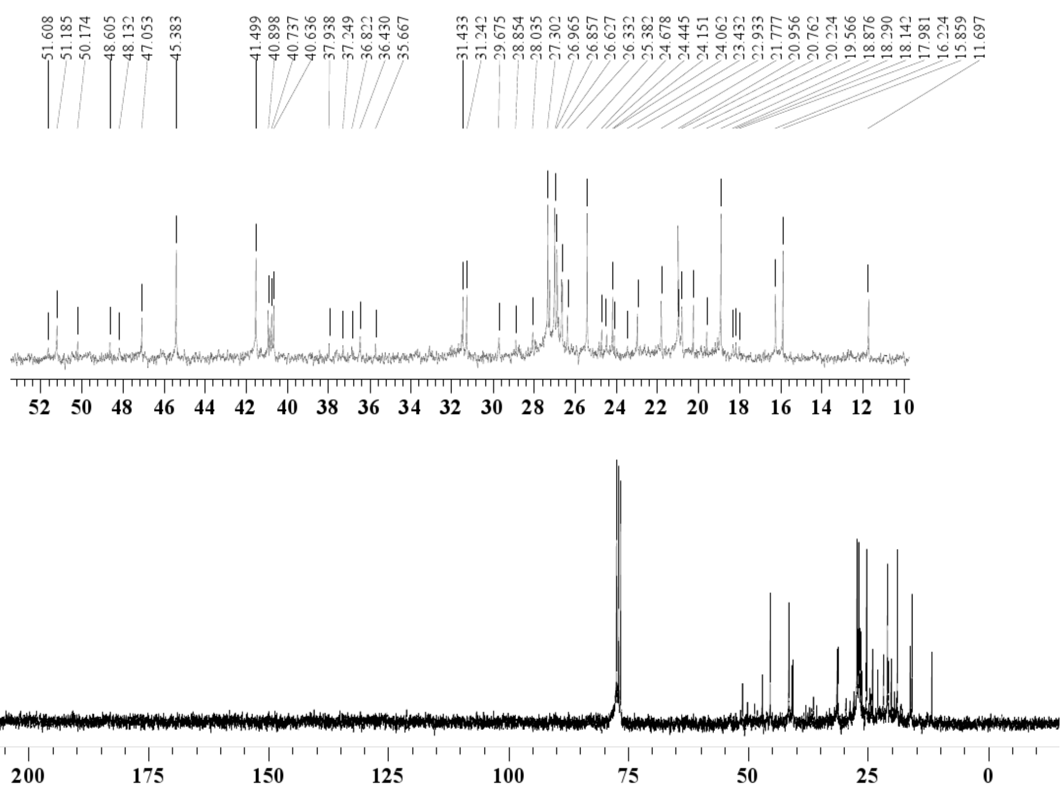


Compound 2:

^{1}H Spectrum:

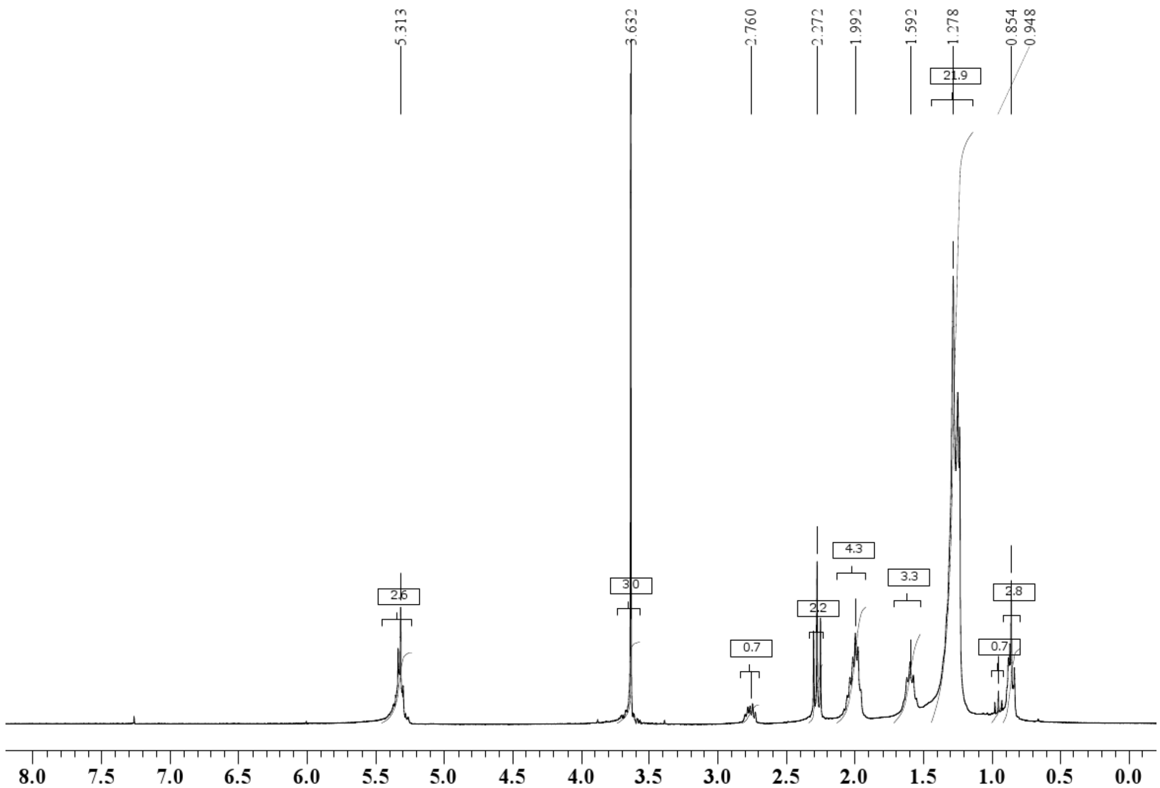


^{13}C Spectrum:



Canola Oil FAME:

^{1}H Spectrum:



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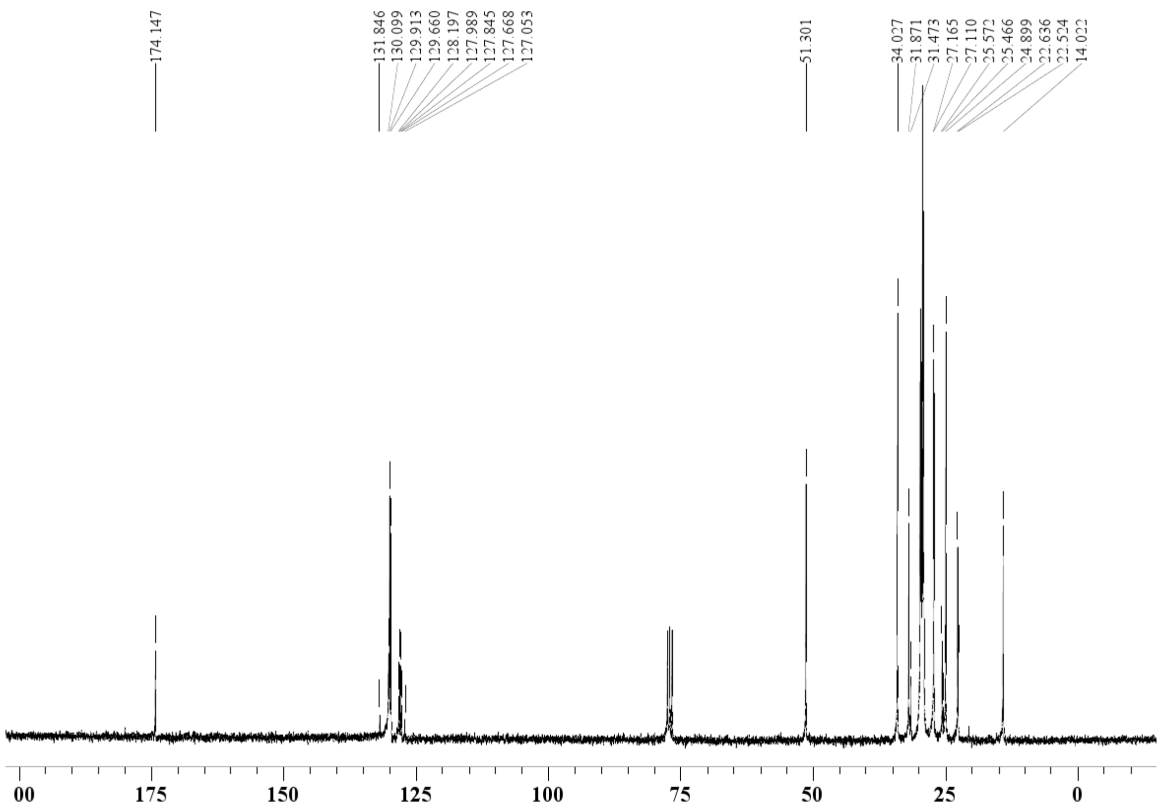
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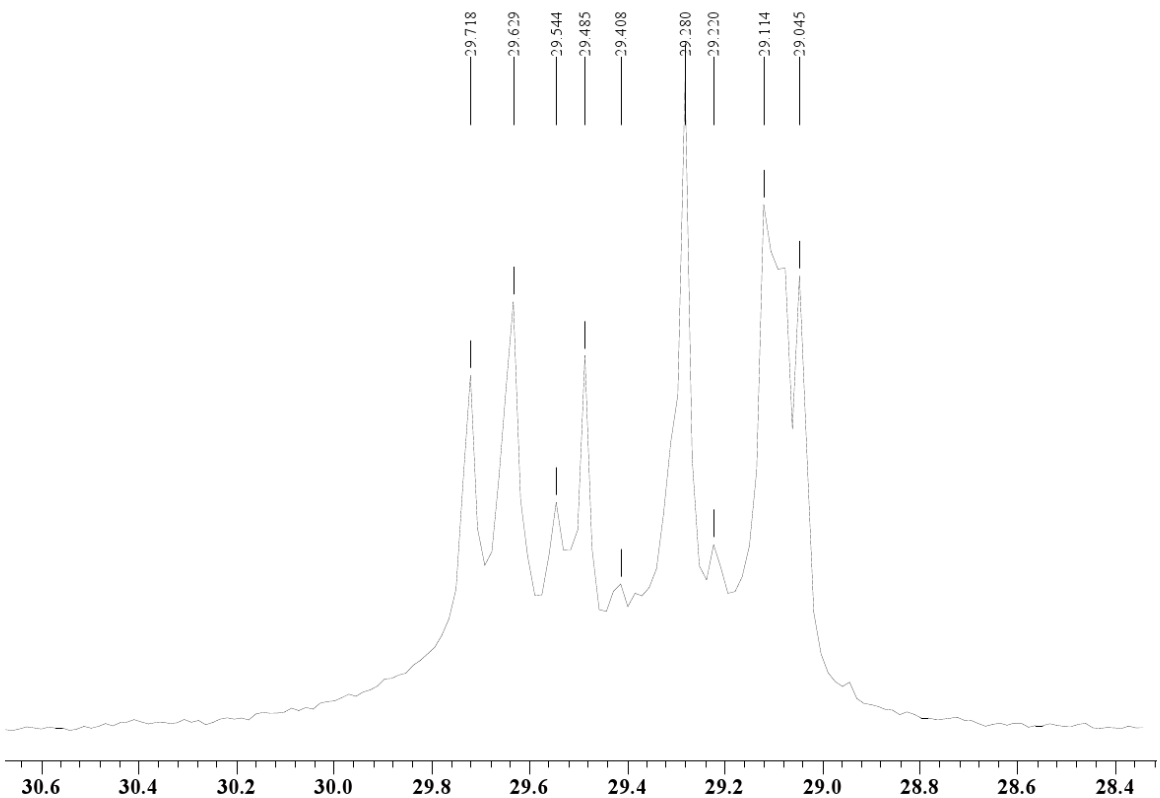
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29.6
29.4
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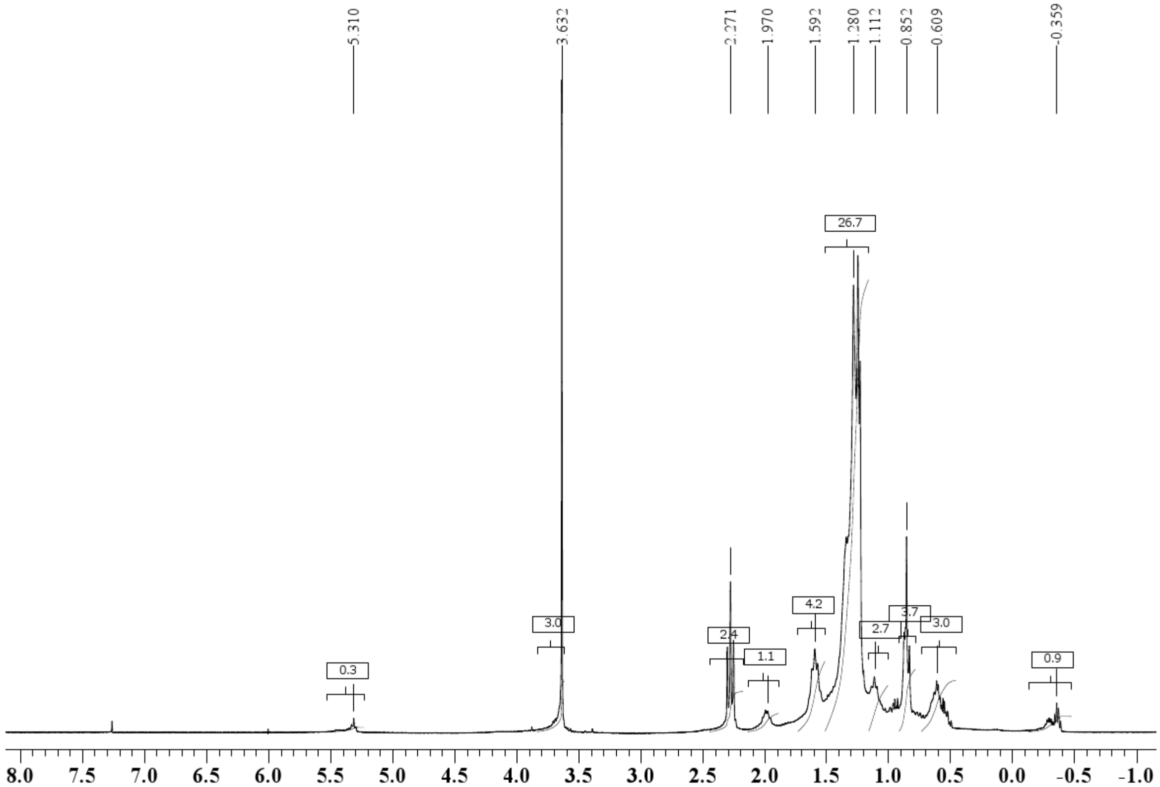
28.8
28.6
28.4

Compound 3:

^{1}H Spectrum:



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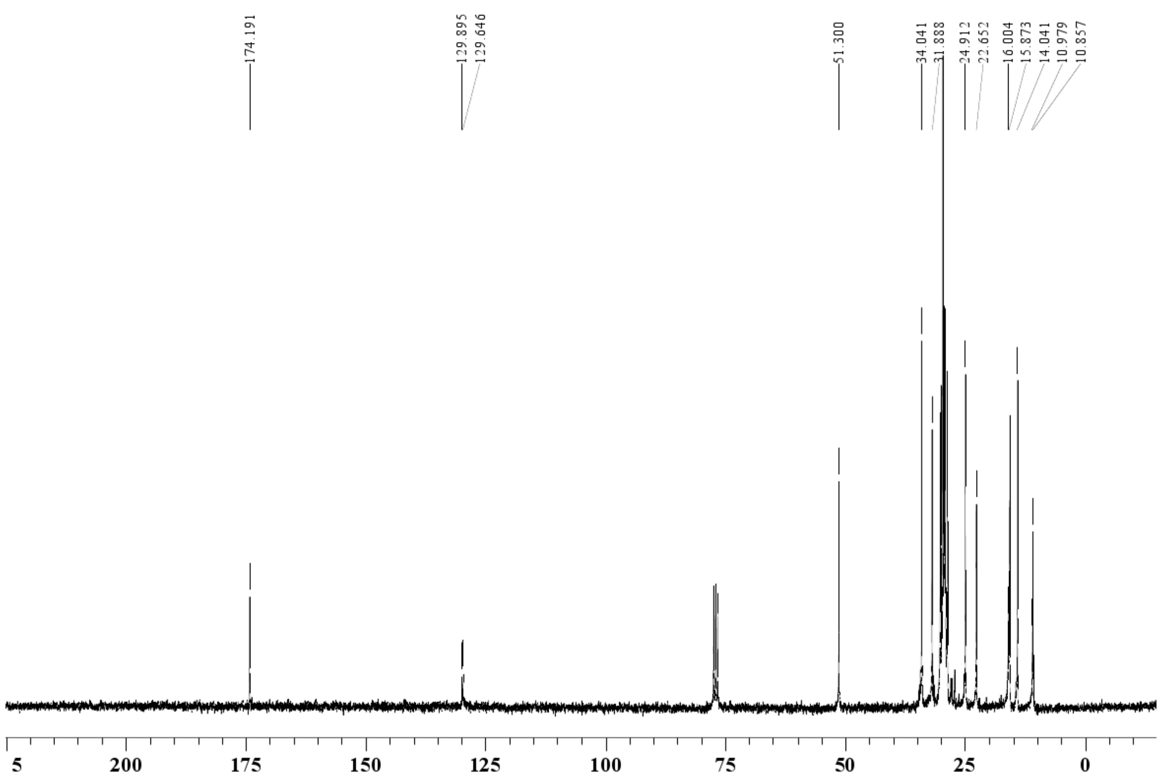
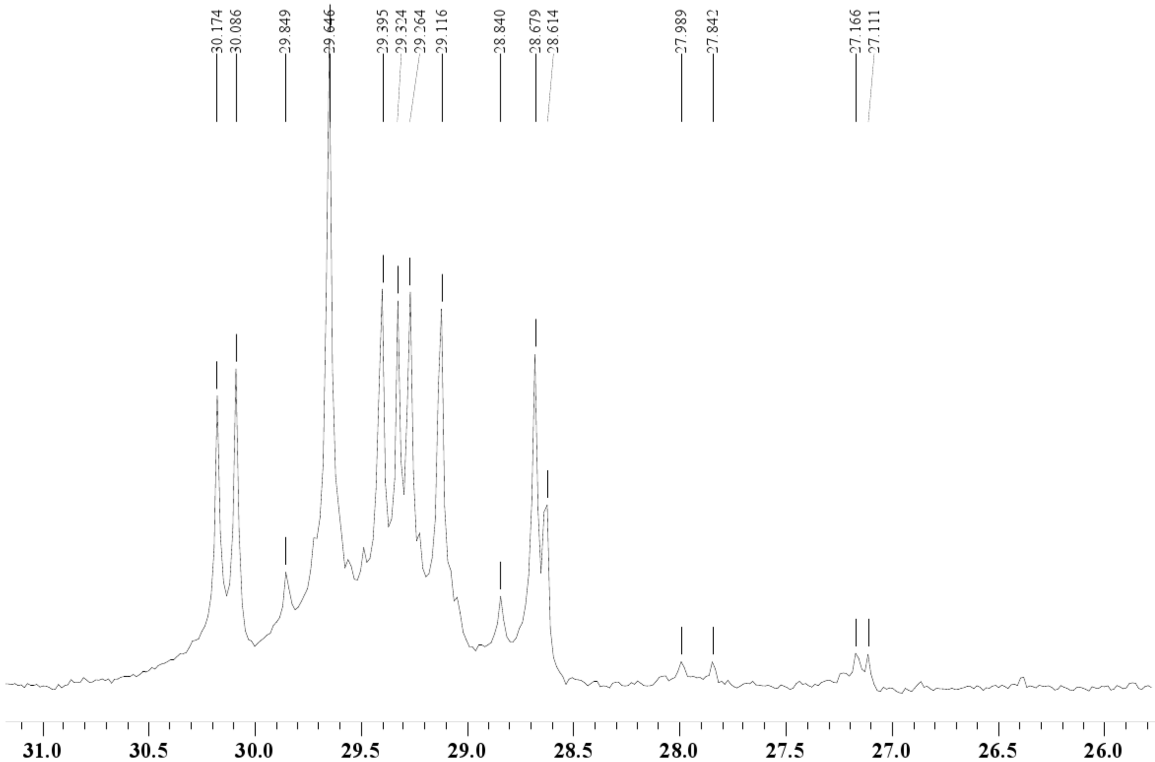
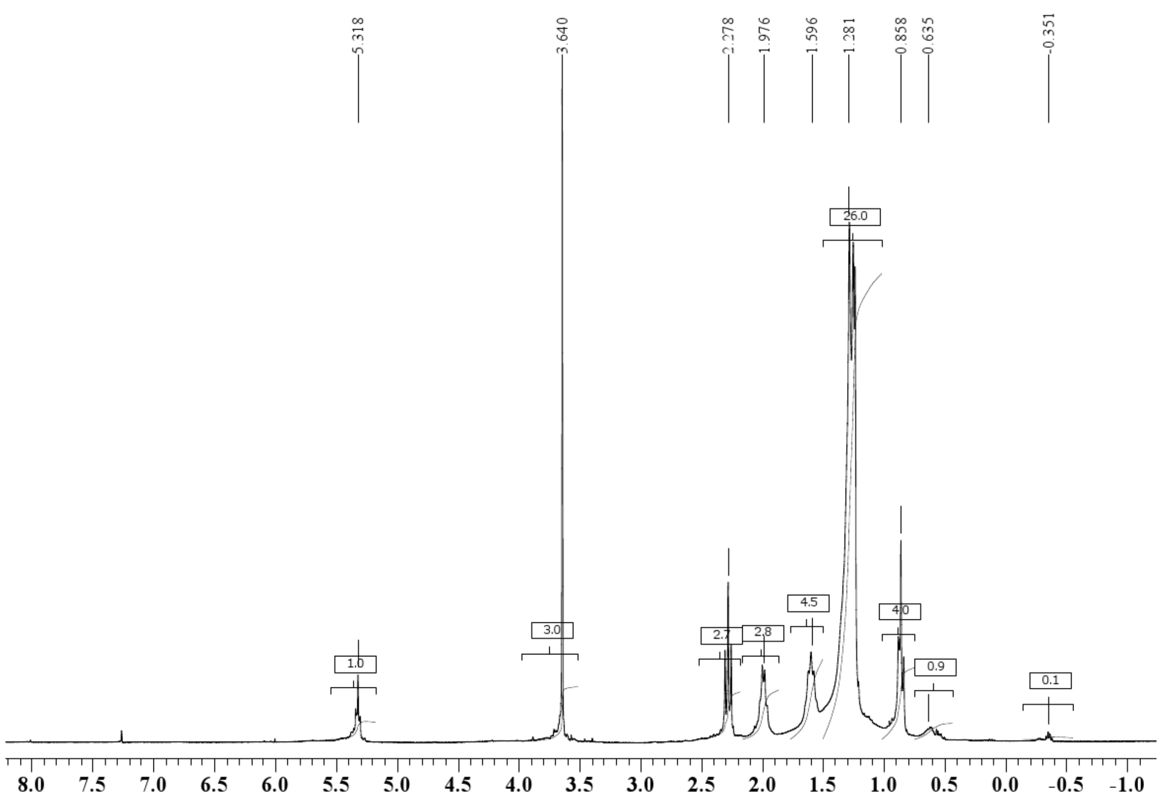
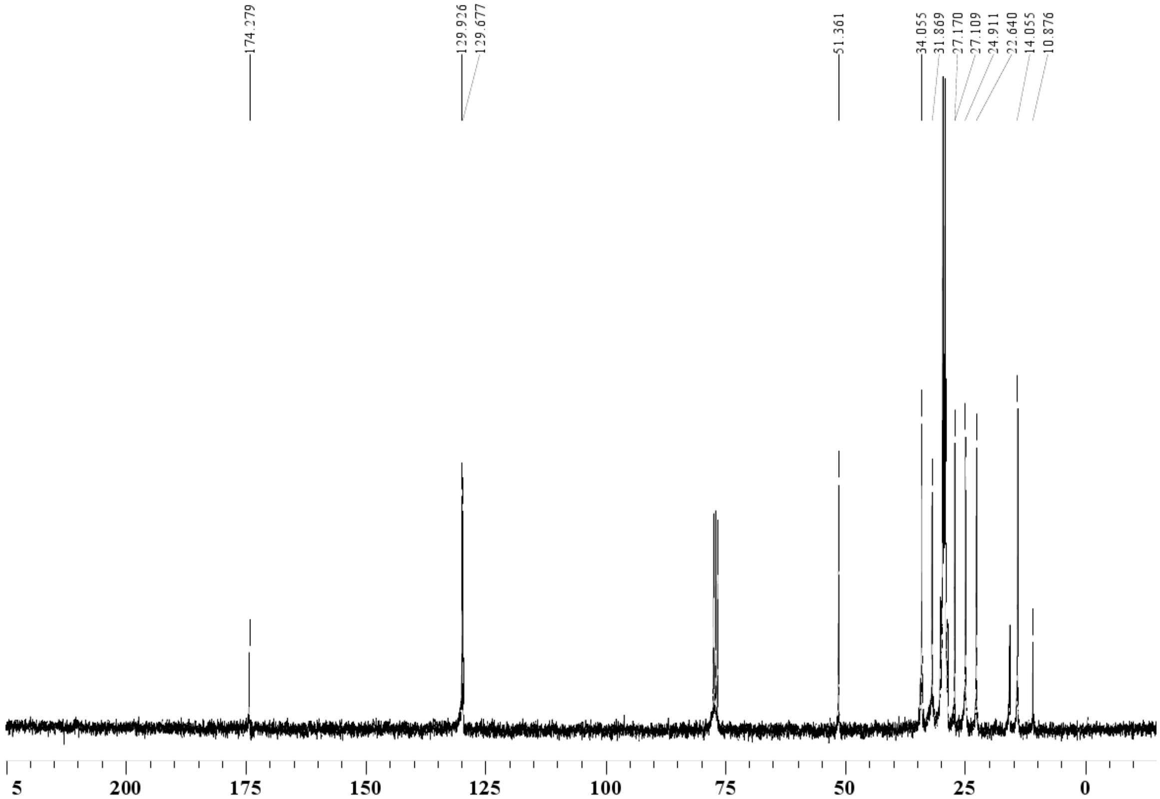


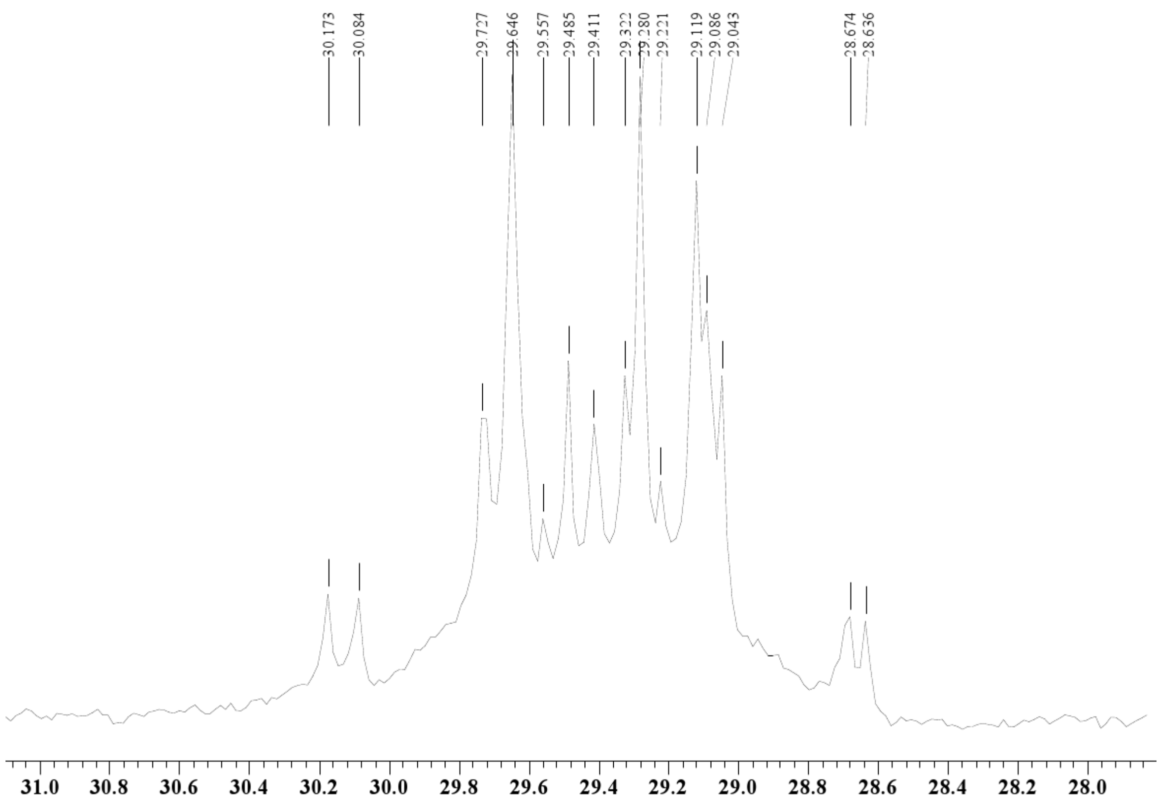


^{1}H Spectrum (after distillation):



^{13}C Spectrum (after distillation):





^{1}H Spectra After Accelerated Oxidation of Canola Oil FAME:

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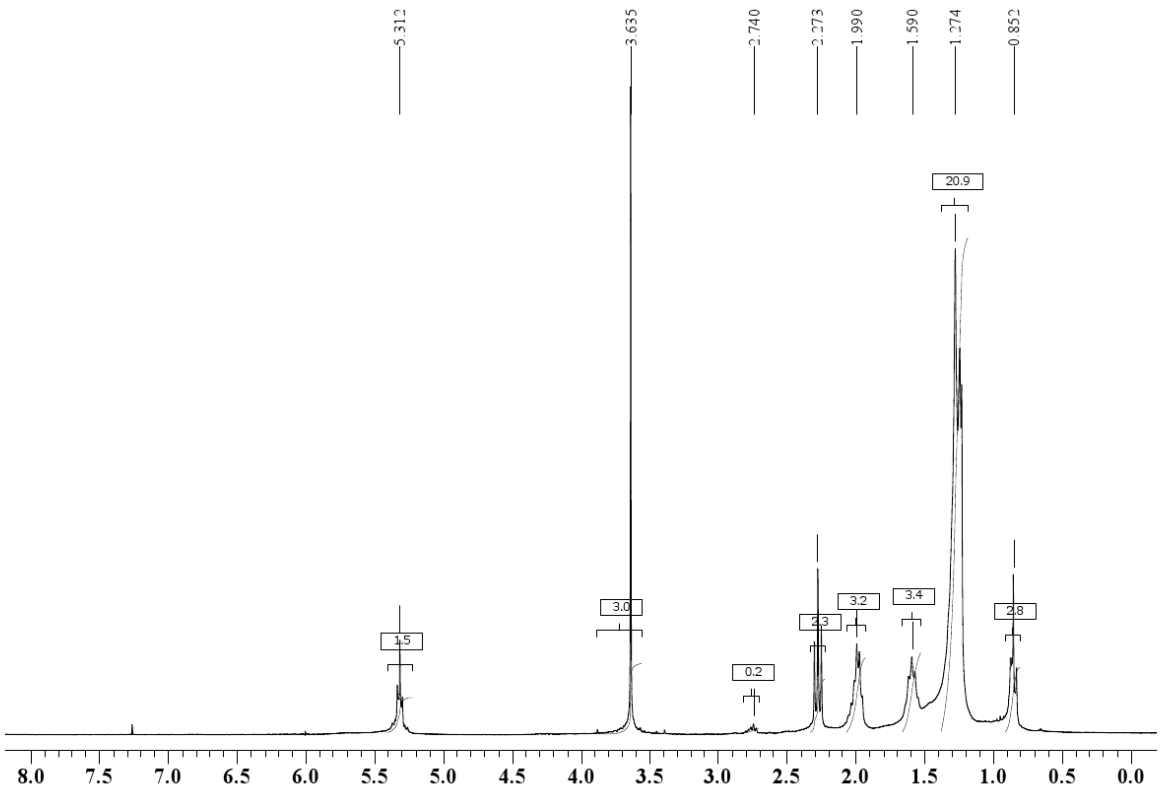

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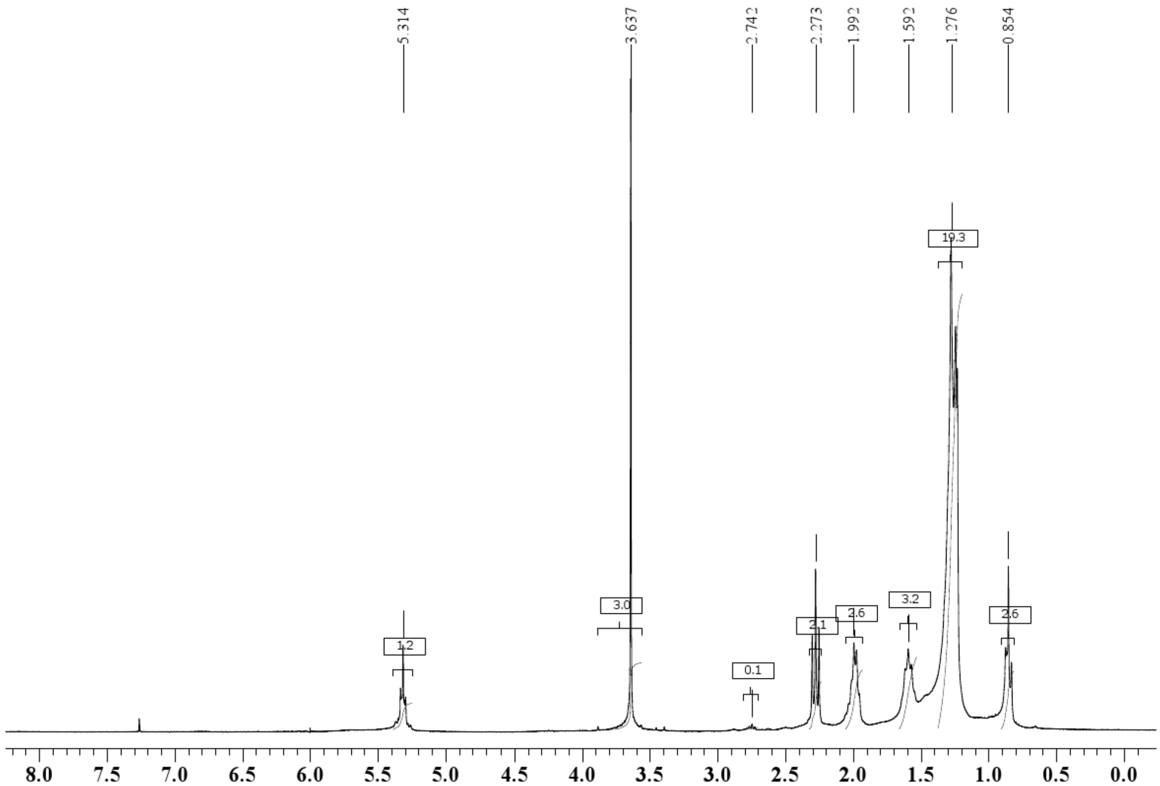

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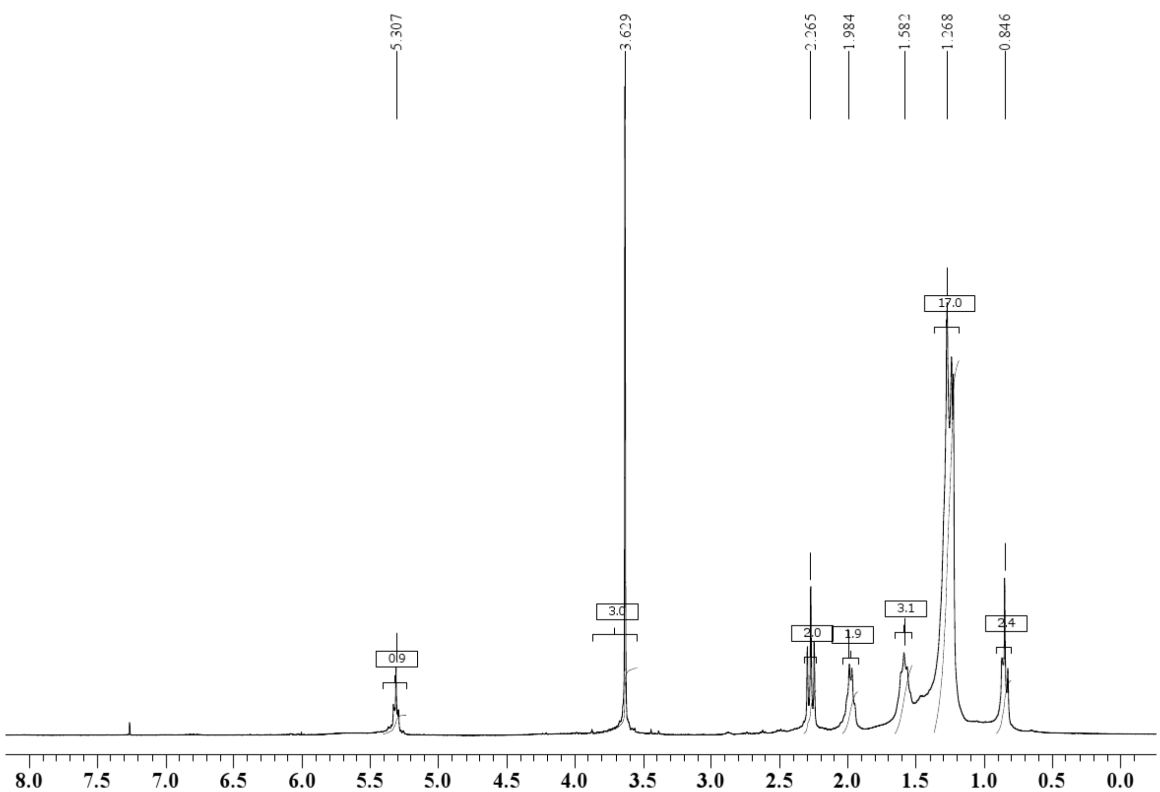

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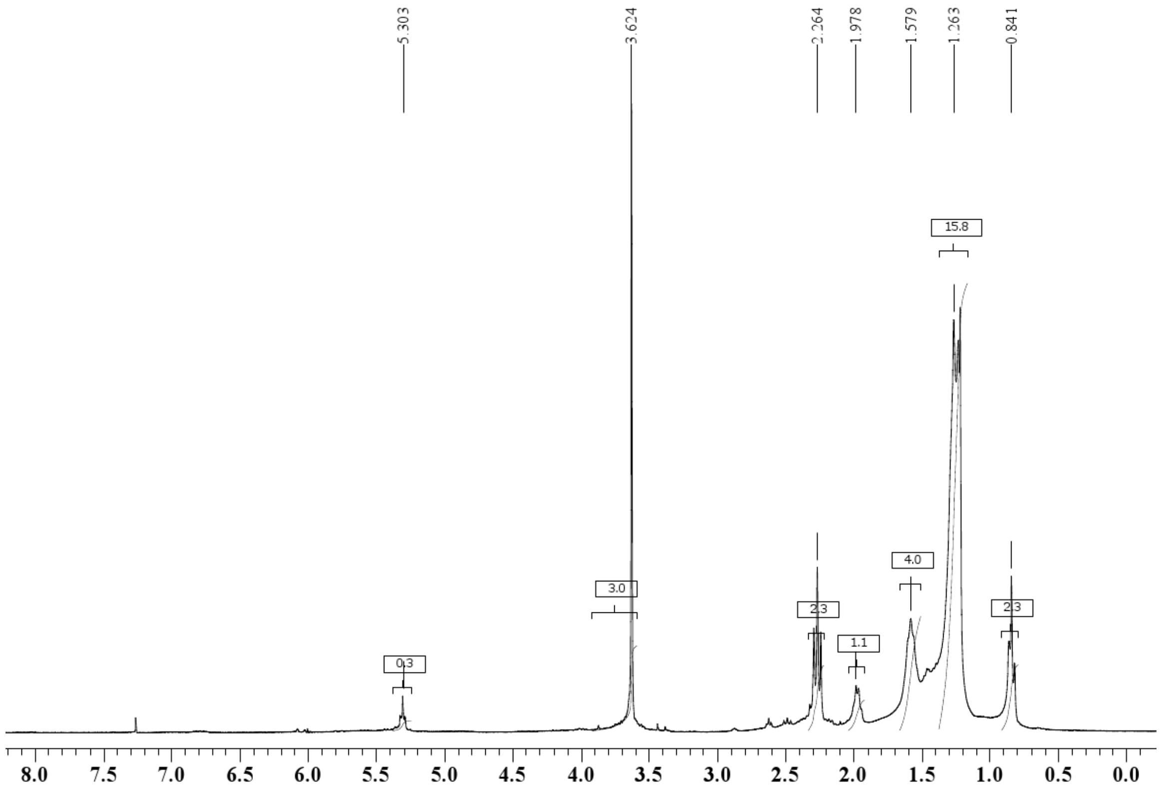

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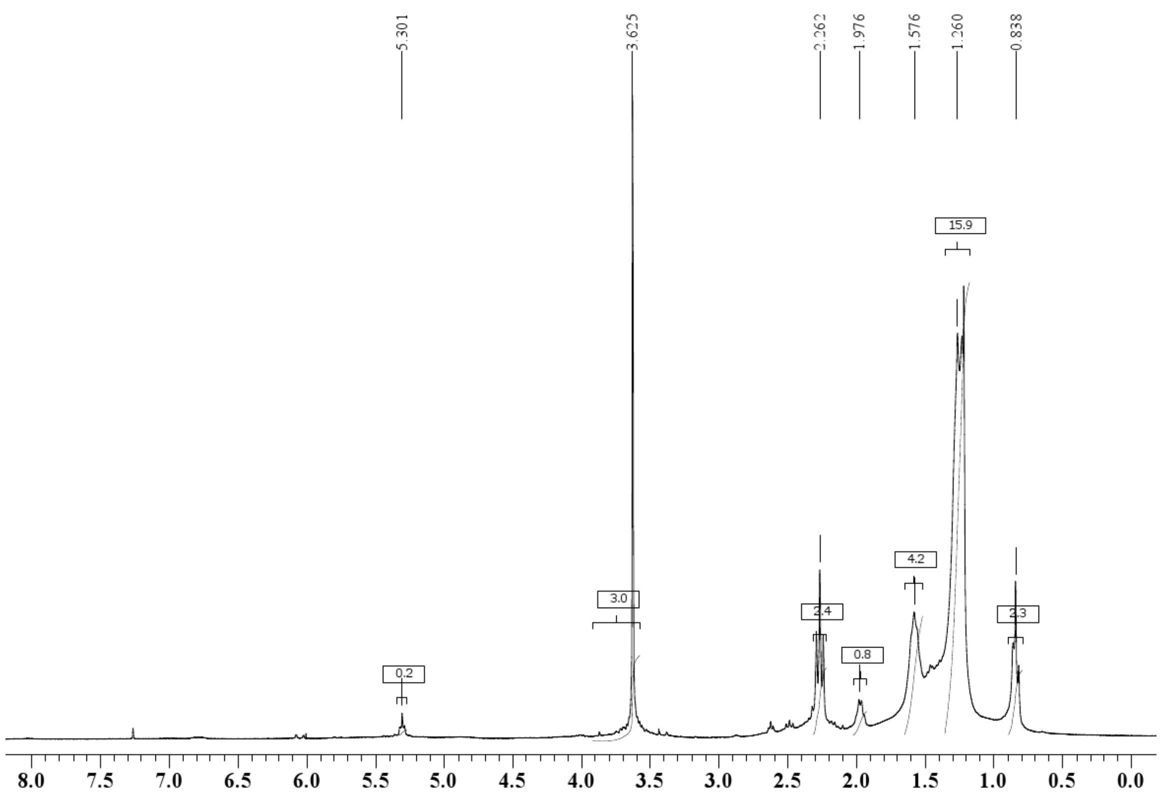

^{1}H Spectra After Accelerated Oxidation of Compound 3:

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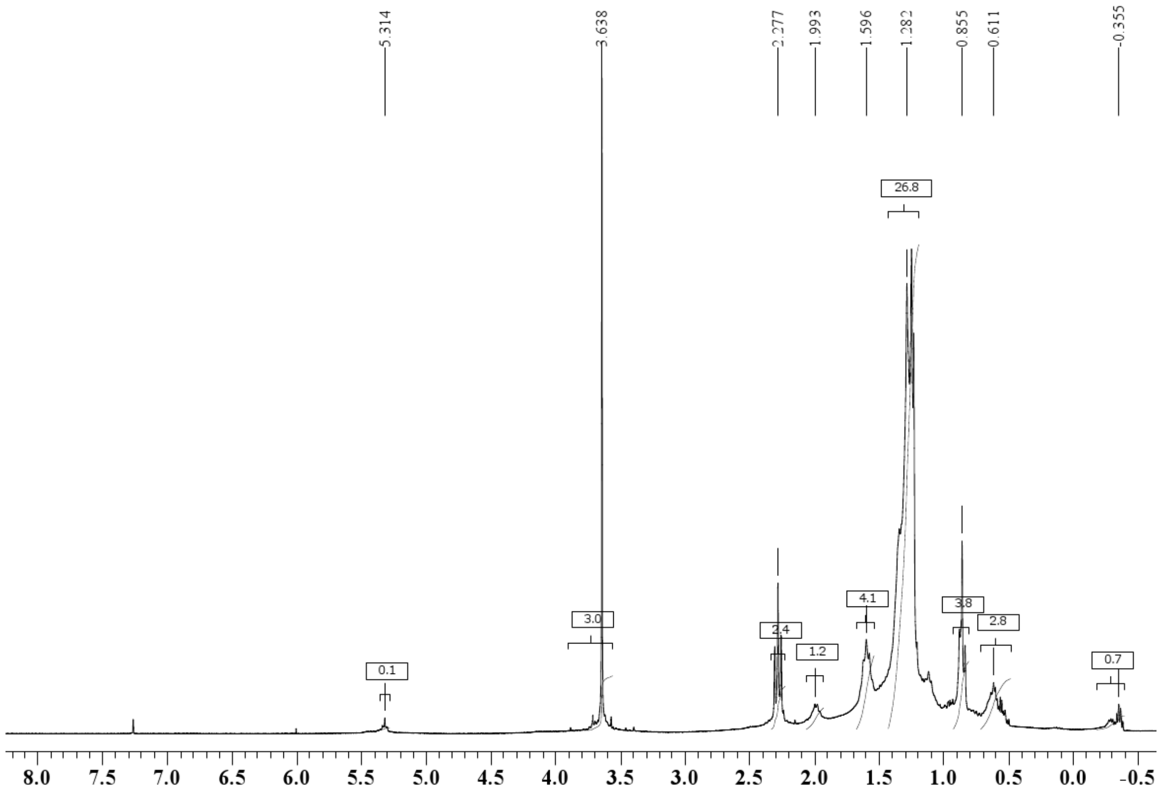

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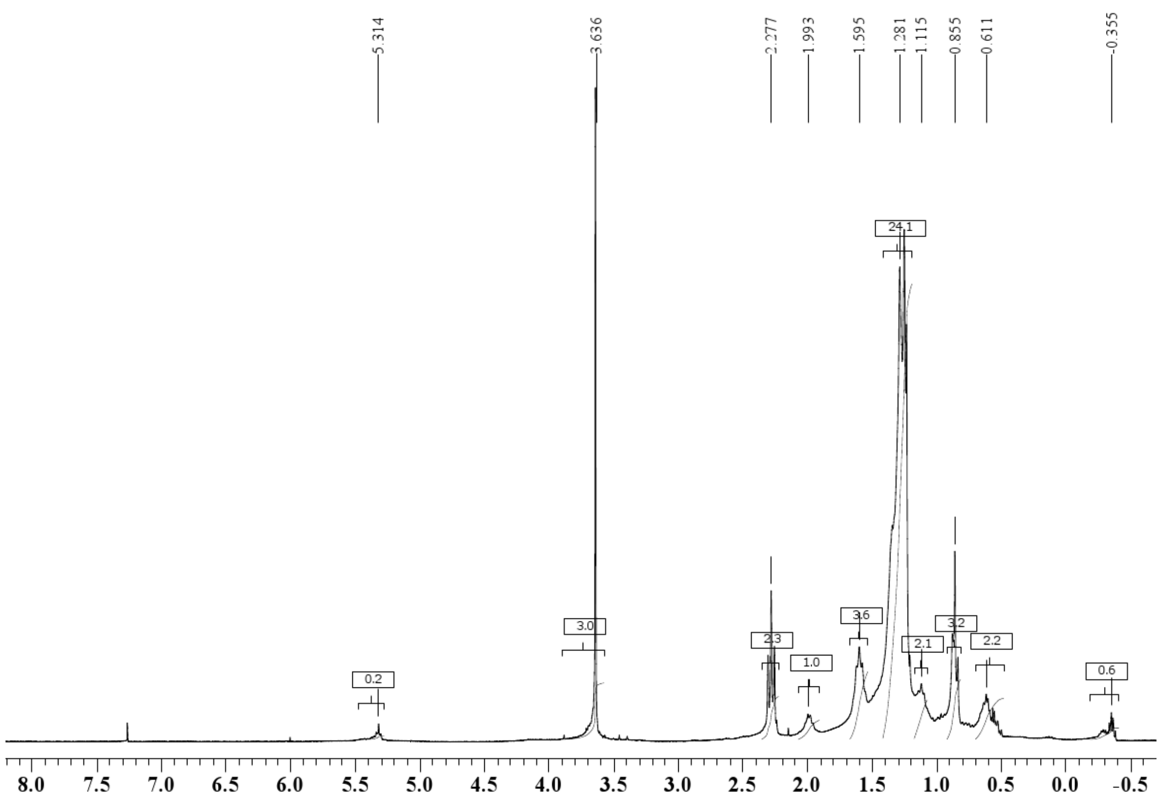

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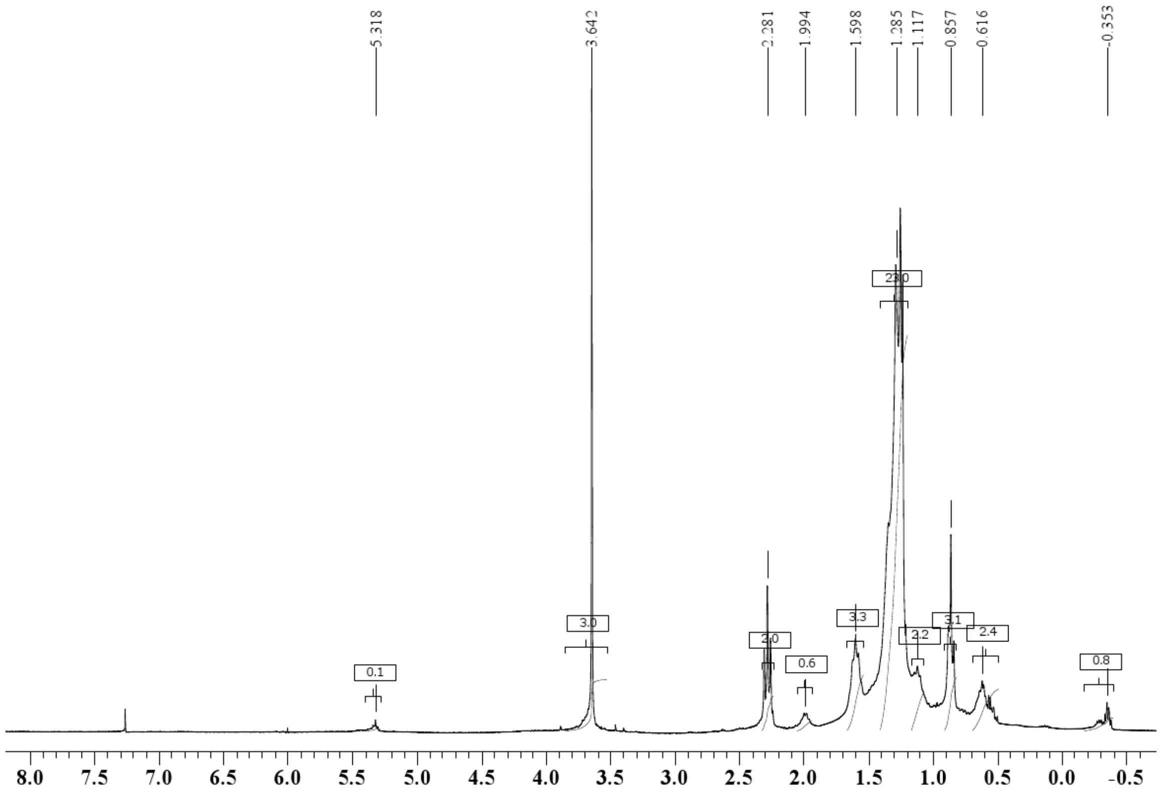

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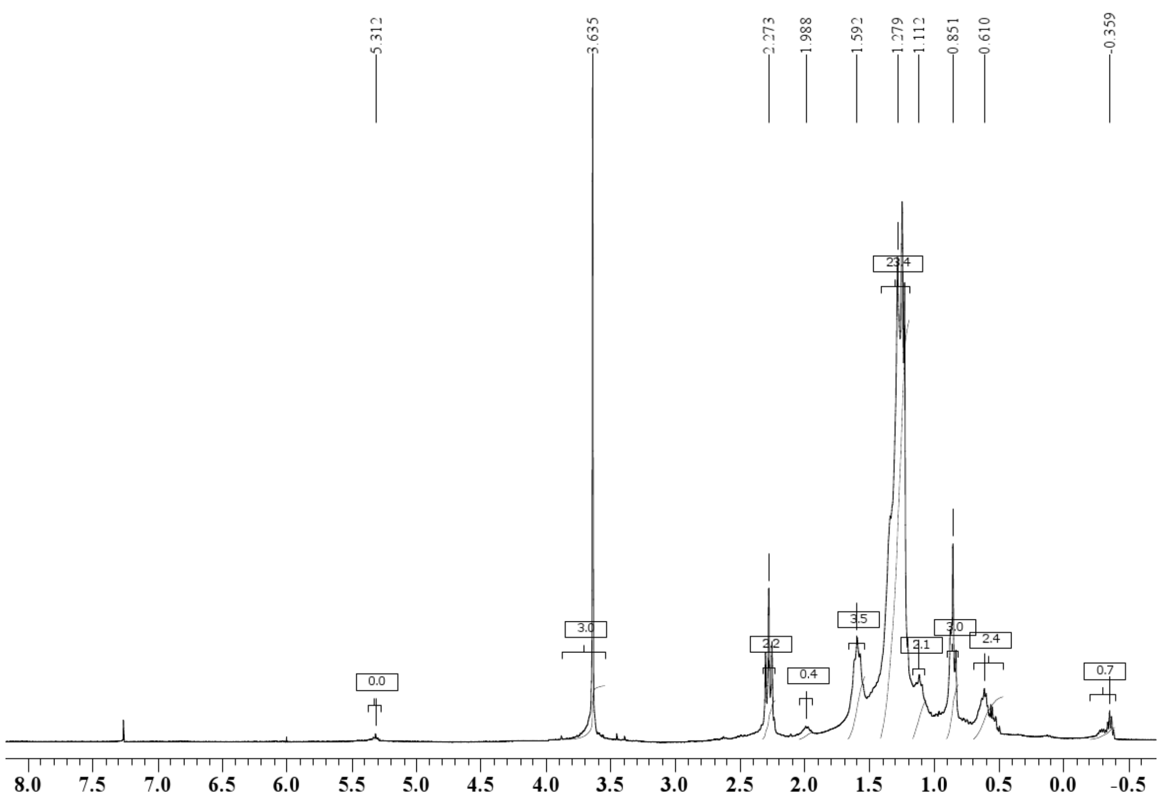

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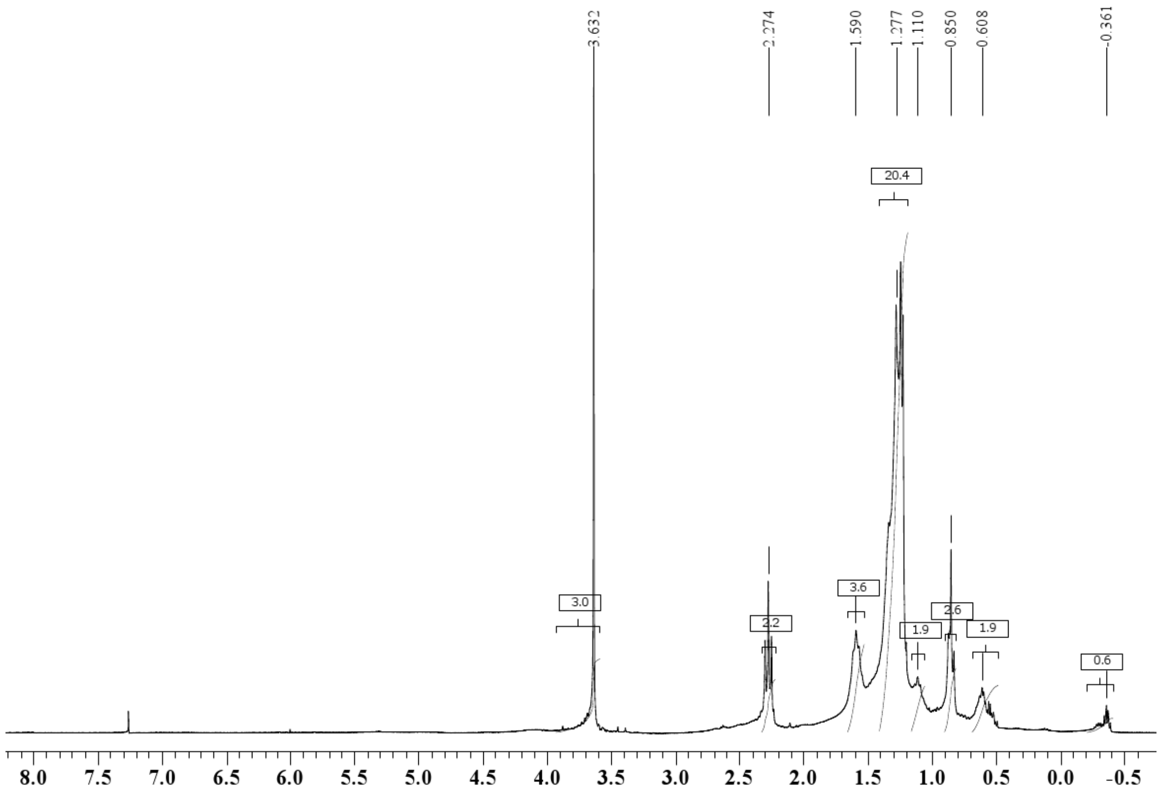

^{1}H Spectra After Accelerated Oxidation of Compound 3 Submitted to Vacuum Distillation:

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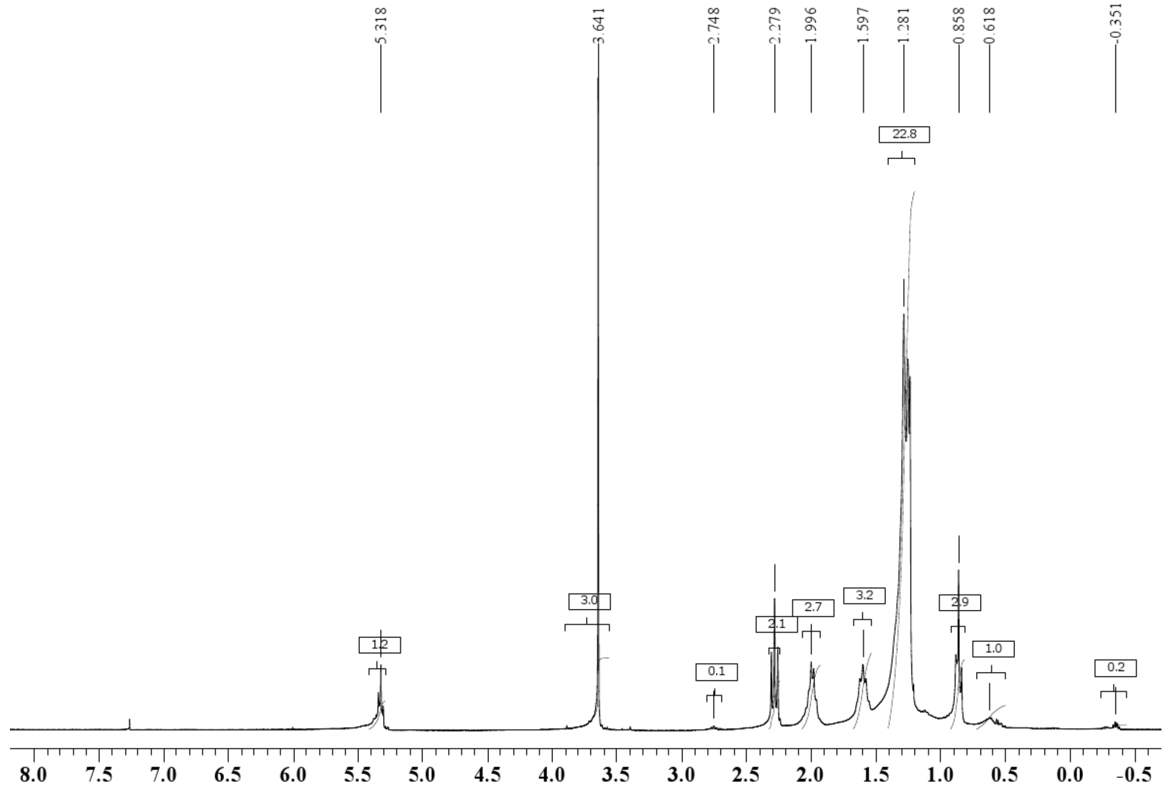

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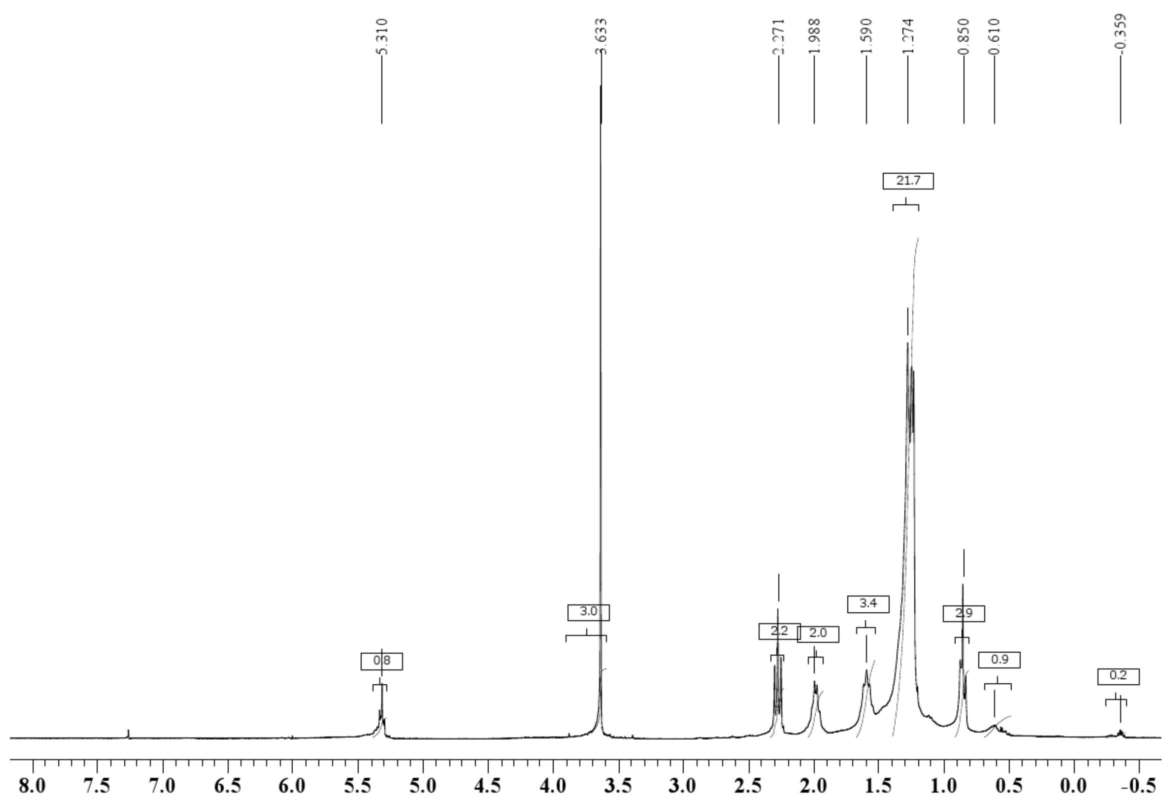

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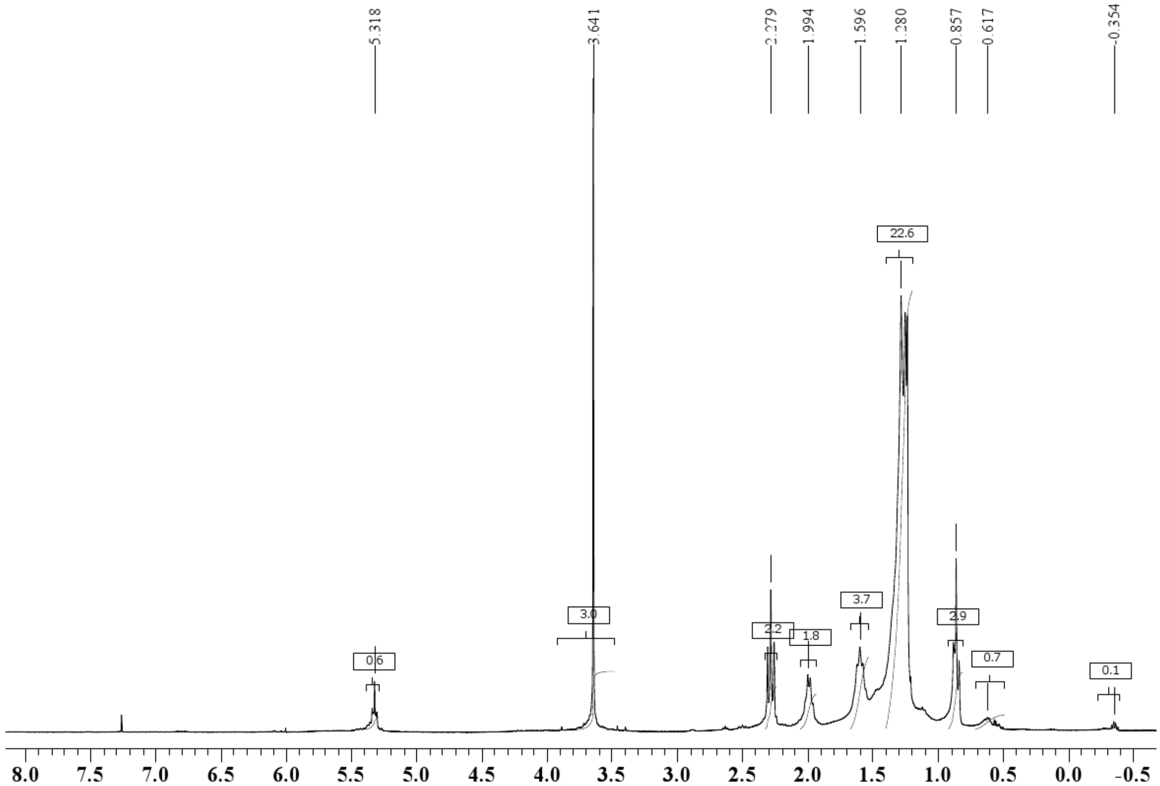

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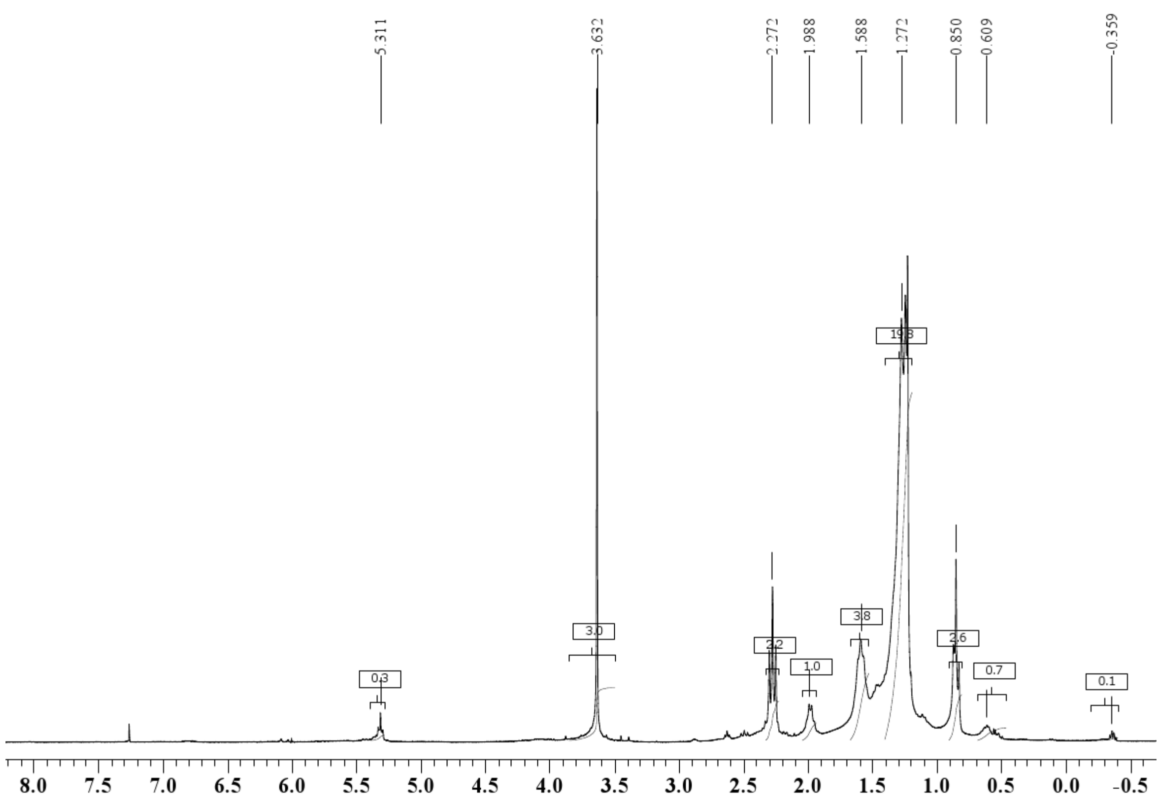

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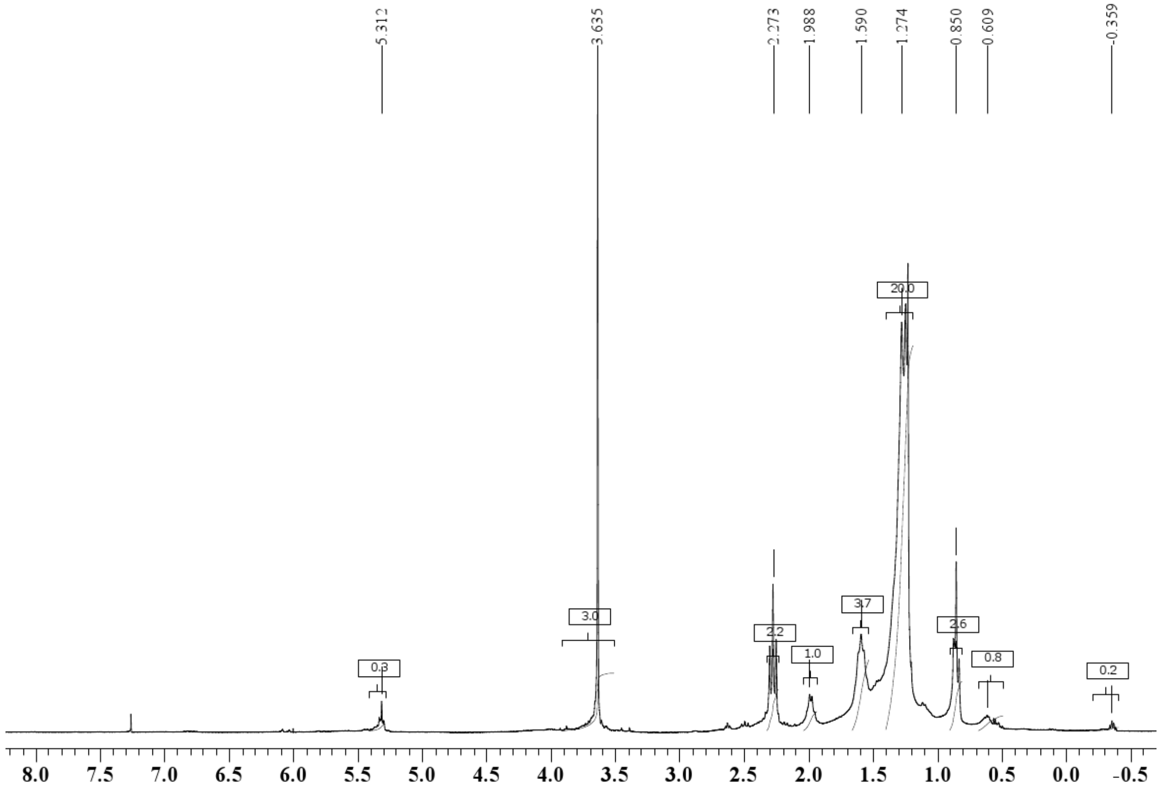
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-0.5

I. Specific gravity measurements

Standardisation

Table S1: Determination of real volume of the pycnometer by using water

	Weight mg
1	1895.06
2	1895.08
3	1895.85
4	1895.74
5	1896.07
6	1895.36
7	1895.11
8	1893.55
9	1894.20
10	1894.76
11	1895.16
12	1894.29
Mean	1895.02
Standard Deviation	0.73
Temperature (°C)	24.2
Litt. Density (g/mL)	0.9979073
Volume pycnometer (mL)	1.89105346

Samples

Table S21: Density of (+)-Limonene

	Weight mg
1	1588.08
2	1589.68
3	1590.18
4	1589.45
5	1590.04
6	1589.42
7	1589.53
8	1590.20
9	1589.27
10	1590.33
11	1590.00
12	1588.00
13	1589.50
14	1589.05
Mean	1589.48
Standard Deviation	0.72
Temperature (°C)	26.3

Density (g/mL)	0.84

Table S32: Density of (*R*)-4-(1-methylcyclopropyl)-1-methyl-bicyclo[4.1.0]heptane (**1**)

	Weight mg
1	1678.07
2	1678.33
3	1679.40
4	1679.38
5	1679.03
6	1680.77
7	1680.12
8	1678.61
9	1677.27
10	1678.72
11	1679.02
12	1680.55
13	1678.65
Mean	1679.07
Standard Deviation	0.99
Temperature (°C)	26.1
Density (g/mL)	0.89

Table S4: Density of Turpentine

	Weight mg
1	1633.59
2	1630.20
3	1630.60
4	1630.30
5	1631.22
6	1631.24
7	1631.81
8	1631.25
9	1630.89
10	1630.90
11	1630.15
12	1631.23
Mean	1631.12
Standard Deviation	0.93
Temperature (°C)	25.9
Density (g/mL)	0.86

Table S5: Density of Cyclopropanated Turpentine (**2**)

	Weight

	mg
1	1702.05
2	1699.42
3	1702.17
4	1703.20
5	1702.69
6	1701.78
7	1703.42
8	1703.64
9	1702.55
10	1702.36
11	1701.89
12	1702.17
13	1702.37
Mean	1702.29
Standard Deviation	1.04
Temperature (°C)	24.7
Density (g/mL)	0.90

Table S6: Density of Canola oil methyl ester

	Weight mg
1	1672.13
2	1672.32
3	1670.40
4	1671.12
5	1671.94
6	1670.57
7	1669.87
8	1669.98
9	1670.93
10	1670.09
11	1670.18
12	1668.93
13	1669.45
Mean	1670.61
Standard Deviation	1.04
Temperature (°C)	24.2
Density (g/mL)	0.88

Table 3: Density of Cyclopropanated Canola oil methyl ester

	Weight mg
1	1720.21
2	1719.76

3	1716.98
4	1719.68
5	1717.01
6	1717.03
7	1717.72
8	1715.71
9	1717.12
10	1716.59
11	1716.17
12	1717.55
13	1717.98
Mean	1717.65
Standard Deviation	1.41
Temperature (°C)	25.7
Density (g/mL)	0.91

II. Heat of Combustion Calculations

Table S8: References Values

Compound	ΔH_f (kJ/mol)
CO_2	-393.509
H_2O (l)	-285.83
H_2O (g)	-241.83

Heats of combustion were calculated from the heats of formation calculated by Spartan and the following equation:

$$C_xH_y + (x+y/4)\ O_2 \rightarrow x\ CO_2 + y/2\ H_2O$$

and $\Delta H_{comb} = \Delta H_f$ (products) - ΔH_f (reactants)

The low value for the heat of combustion was calculated with the heat of formation for gaseous H_2O, whereas the high value was calculated with the heat of formation for liquid H_2O.

Thus:
ΔH_{comb} (low) = -393.905x – 120.915y - ΔH_f (reactant)
ΔH_{comb} (high) = -393.905x – 142.915y - ΔH_f (reactant)

Table S9: Calculation of the heats of combustion from the heats of formation for the studied biofuels and their cyclopropanated derivatives calculated using the T1 thermochemical recipe of Spartan 06.

Compound	**ΔH_f (kJ/mol)**	**x**	**y**	**ΔH_{comb} (low) (kJ/mol)**	**ΔH_{comb} (high) (kJ/mol)**
Limonene	-0.91	10	16	-5869	-6262
1	36.07	12	20	-7176	-7665
α-pinene	28.03	10	16	-5898	-6290
β-pinene	39.09	10	16	-5909	-6302
Camphene	-24.1	10	16	-5846	-6238
Turpentine	-	-	-	-5894	-6287
2-Methanopinane	47.67	11	18	-6553	-6994
2-Ethylene-6,6-dimethylbicyclo[3.1.1]heptane	53.37	11	18	-6558	-6999
3-Ethylene-2,2-dimethylbicyclo[2.2.1]heptane	-11.65	11	18	-6493	-6934
2	-	-	-	-6581	-7025
Methyl stearate	-749.9	19	38	-11322	-12235
Methyl oleate	-633.84	19	36	-11196	-12065
Methyl linoleate	-515.07	19	34	-11073	-11898
Methyl linolenate	-402.29	19	32	-10944	-11725
Canola methyl ester	-	-	-	-11151	-12005
Methyl 9-methanooctadecanoate	-624.41	20	38	-11841	-12758
Methyl 9,12-dimethanooctadecanoate	-496.24	21	38	-12362	-13284
Methyl 9,12,15-trimethanoocta-decanoate	-372.58	22	38	-12879	-13805
3 (100% conversion)	-	-	-	-12028	-12947
3 (90% conversion)	-	-	-	-11940	-12853

Specific energies and energy densities were calculated from the heats of combustion shown above and the molecular weights or experimental densities of the respective compounds. For turpentine, canola oil methyl ester, and cyclopropanated derivatives **2** and **3**, the values were calculated from the values for individual components and the composition of the mixture (85% α-pinene, 5% β-pinene, 5% limonene and 5% camphene for turpentine; 61% methyl oleate, 21% methyl linoleate, 11% methyl linolenate and 7% methyl stearate for canola oil methyl ester).

III. Heat of Combustion Measurements

Table S10: References Values

ΔE Benzoic Acid	kJ/g	26.4438288
ΔE Fuse	kJ/mm	-0.00962964
Δformation HNO3	kJ/g	57.8

Table S11: Formula Weight of the Major Components of Compounds Measured

	Formula Weight g•mol^{-1}
(+)-Limonene	136.23
1	164.29
Turpentine	136.23
2	150.26
Canola FAME	296.49
3	310.51

Standardisation

Table S12: Energy Equivalent of the calorimeter by standardizing with Benzoic Acid

Test Number	Weight g	Titrant NaOH mL	Concentration NaOH mol•L^{-1}	Δ Fuse cm	Δ Temperature °C	Energy Equivalent kJ•°C^{-1}
1	1.0025	3.7	0.1002	-5.4	2.62	10.09
2	0.8580	3.0	0.1002	-7.3	2.22	10.18
3	1.1103	4.1	0.1002	-7.6	2.86	10.23
4	0.9759	6.8	0.1002	-7.9	2.54	10.13
5	0.9937	6.7	0.1002	-8.1	2.60	10.06
Mean						10.14
Standard Deviation						0.07

Samples

Table S13: Heat of combustion of (+)-Limonene

Test Number	Weight g	Titrant NaOH mL	Concentration NaOH mol•L^{-1}	Δ Fuse cm	Δ Temperature °C	Heat of Combustion kJ•g^{-1}
1	0.6015	7.5	0.1002	-7.1	2.63	44.15
2	0.6016	7.4	0.1002	-8.9	2.70	45.21
3	0.6081	7.5	0.1002	-9.4	2.65	43.88
4	0.6130	7.5	0.1002	-5.9	2.74	45.16
5	0.6128	7.1	0.1002	-5.8	2.74	45.18
Mean						44.72
Standard Deviation						0.65

Table S14: Heat of combustion of (*R*)-4-(1-methylcyclopropyl)-1-methyl-bicyclo[4.1.0]heptane (**1**)

Test Number	Weight g	Titrant NaOH mL	Concentration NaOH mol•L^{-1}	Δ Fuse cm	Δ Temperature °C	Heat of Combustion kJ•g^{-1}
1	0.5614	7.3	0.1002	-5.8	2.44	43.81
2	0.6088	8.1	0.1002	-8.4	2.65	43.84
3	0.6240	8.1	0.1002	-8.4	2.71	43.83
4	0.6011	7.7	0.1002	-7.2	2.58	43.33
5	0.6036	8.0	0.1002	-5.1	2.62	43.86
Mean						43.73
Standard Deviation						0.23

Table S15: Heat of combustion of Turpentine

Test Number	Weight g	Titrant NaOH mL	Concentration NaOH mol•L^{-1}	Δ Fuse cm	Δ Temperature °C	Heat of Combustion kJ•g^{-1}
1	0.6413	8.5	0.1002	-7.7	2.83	44.55
2	0.6110	7.9	0.1002	-9.0	2.71	44.76
3	0.6055	8.3	0.1002	-7.6	2.74	45.60
4	0.5990	8.1	0.1002	-7.5	2.66	44.83
5	0.6055	7.9	0.1002	-6.4	2.68	44.70
Mean						44.89
Standard Deviation						0.41

Table S16: Heat of combustion of Cyclopropanated Turpentine (**2**)

Test Number	Weight g	Titrant NaOH mL	Concentration NaOH mol•L^{-1}	Δ Fuse cm	Δ Temperature °C	Heat of Combustion kJ•g^{-1}
1	0.5533	6.7	0.0981	-5.9	2.42	44.18
2	0.5817	7.4	0.0981	-7.9	2.59	44.86
3	0.5789	7.6	0.0981	-8.5	2.58	44.89
4	0.5026	6.8	0.0981	-8.5	2.25	45.05
Mean						44.74
Standard Deviation						0.39

Table S17: Heat of combustion for Canola oil methyl ester

Test Number	Weight g	Titrant NaOH mL	Concentration NaOH mol•L^{-1}	Δ Fuse cm	Δ Temperature °C	Heat of Combustion kJ•g^{-1}
1	0.6457	6.4	0.1002	-7.5	2.54	39.72
2	0.6906	7.2	0.1002	-7.5	2.72	39.70
3	0.6946	5.8	0.1002	-7.8	2.66	38.67

4	0.6937	6.8	0.1002	-8.5	2.67	38.78
5	0.6955	8.3	0.1002	-7.6	2.73	39.63
Mean						39.30
Standard Deviation						0.52

Table S18: Heat of combustion for Cyclopropanated Canola methyl ester (**3**)

Test Number	Weight g	Titrant NaOH mL	Concentration NaOH mol•L^{-1}	Δ Fuse cm	Δ Temperature °C	Heat of Combustion kJ•g^{-1}
1	0.7250	9.4	0.1002	-8.3	2.79	38.84
2	0.6873	8.8	0.1002	-8.3	2.64	38.76
3	0.7278	8.7	0.1002	-7.8	2.86	39.67
4	0.6979	8.6	0.1002	-6.2	2.76	39.94
5	0.7185	9.2	0.1002	-8.7	2.79	39.18
6	0.7265	9.3	0.1002	-10.0	2.83	39.22
Mean						39.27
Standard Deviation						0.46

IV. Influence of Accelerated Oxidation on Kinematic Viscosity

Table S19: Kinematic Viscosity versus Accelerated Oxidation Time on Canola Biodiesel and its Derivatives

	Sample	Accelerated Oxidation Time h					
		0	8	16	24	48	72
Kinematic Viscosity $mm^2•s^{-1}$	Canola FAME	4.62	8.54	10.52	14.74	30.51	40.13
	3	10.01	14.95	17.65	21.19	26.58	45.19
	Distilled **3**	4.34	6.41	8.23	10.05	15.56	14.99

Standardisation

Table S20: Determination of the Capillary Constant of the Cannon-Fenske Viscometer

Temperature °C	Flow Times s	Mean s	Standard Deviation	Kinematic Energy Correction s	Reference Kinematic Viscosity $mm^2•s^{-1}$	Capillary Constant $mm^2•s^{-2}$
50	902.67	902.609	0.072	0.004	12.77	0.014148
	902.59					
	902.57					
	902.58					
	902.60					
	902.50					
	902.61					
	902.76					
	902.60					
80	405.84	405.698	0.073	0.020	5.724	0.014110
	405.71					
	405.74					
	405.66					
	405.63					
	405.61					
	405.68					
	405.65					
	405.76					
Mean						0.014129

Samples

Table S21: Kinematic Viscosity as a Function of Accelerated Oxidation Time for Canola oil methyl ester

Accelerated Oxidation Time	Flow Times	Mean	Standard Deviation	Kinematic Energy Correction	Kinematic Viscosity

h	s	s		s	mm^2•s^{-1}
0	326.70 326.74 326.76 326.74 326.70	326.728	0.027	0.030	4.62
8	606.97 607.33 607.24 607.28 607.64	607.292	0.239	3.000	8.54
16	743.68 743.78 743.97 747.26 744.24	744.586	1.510	0.006	10.52
24	1042.33 1043.06 1042.82 1043.40 1043.60	1043.042	0.499	0.003	14.74
48	2157.43 2157.92 2158.70 2159.33 2159.70 2159.99 2160.63 2160.88 2160.88	2159.496	1.266	0.001	30.51
72	2837.96 2838.70 2844.36 2839.67 2839.81 2841.79 2840.59 2840.99 2841.30	2840.574	1.879	0.000	40.13

Table S22: Kinematic Viscosity as a Function of Accelerated Oxidation Time for Cyclopropanated Canola oil methyl ester (**3**)

Accelerated Oxidation Time	Flow Times	Mean	Standard Deviation	Kinematic Energy Correction	Kinematic Viscosity

h	s	s		s	mm^2•s^{-1}
0	707.82 708.39 708.95 709.13 709.50	708.758	0.660	0.006	10.01
8	1057.58 1058.39 1057.71 1057.71 1057.80	1057.838	0.318	0.003	14.95
16	1248.64 1248.69 1248.77 1248.91 1249.04 1249.55 1249.76 1250.03 1250.25	1249.293	0.614	0.002	17.65
24	1499.31 1499.62 1499.68 1499.82 1499.90	1499.666	0.228	0.001	21.19
48	1881.31 1881.45 1881.52 1881.59 1881.70	1881.514	0.147	0.001	26.58
72	3204.36 3195.04 3197.89 3195.57 3199.44	3198.460	3.746	0.000	45.19

Table 4