Supplementary material

Microwave Assisted Esterification of Aryl/Alkyl Acids Catalyzed by *N*-Fluorobenzenesulfonimide

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Table S1. The central composite design and experimental results.

	X_1	X_2	X_3	Y
Space Type	Temperature (°C)	Time (min)	Amount of Catalyst (%)	Conversion
Center	120	15	7	71
Center	120	15	7	72
Center	120	15	7	73
Center	120	15	7	72
Center	120	15	7	71
Axial	120	30	7	100
Axial	70	15	7	1
Axial	120	15	10	81
Axial	120	15	3	38
Axial	120	0	7	0
Axial	150	15	7	100
Factorial	150	30	4	100
Factorial	90	0	4	0
Factorial	90	30	10	11
Factorial	150	0	10	0
Center	120	15	7	71

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Table S2. Coefficients for quadratic equation.

	Intercept	X_1	X_2	X_3	$X_1 X_2$	$X_1 X_3$	$X_2 X_3$	X_1^2	X_2^2	X_3^2
Conversion	73.4907	31.7281	50	14.8122	37.0622	22.25	9.4781	-7.5670	-26.6217	-9.9866
p-values		< 0.0001	< 0.0001	0.0014	< 0.0001	0.0009	0.0238	0.0046	< 0.0001	0.0026

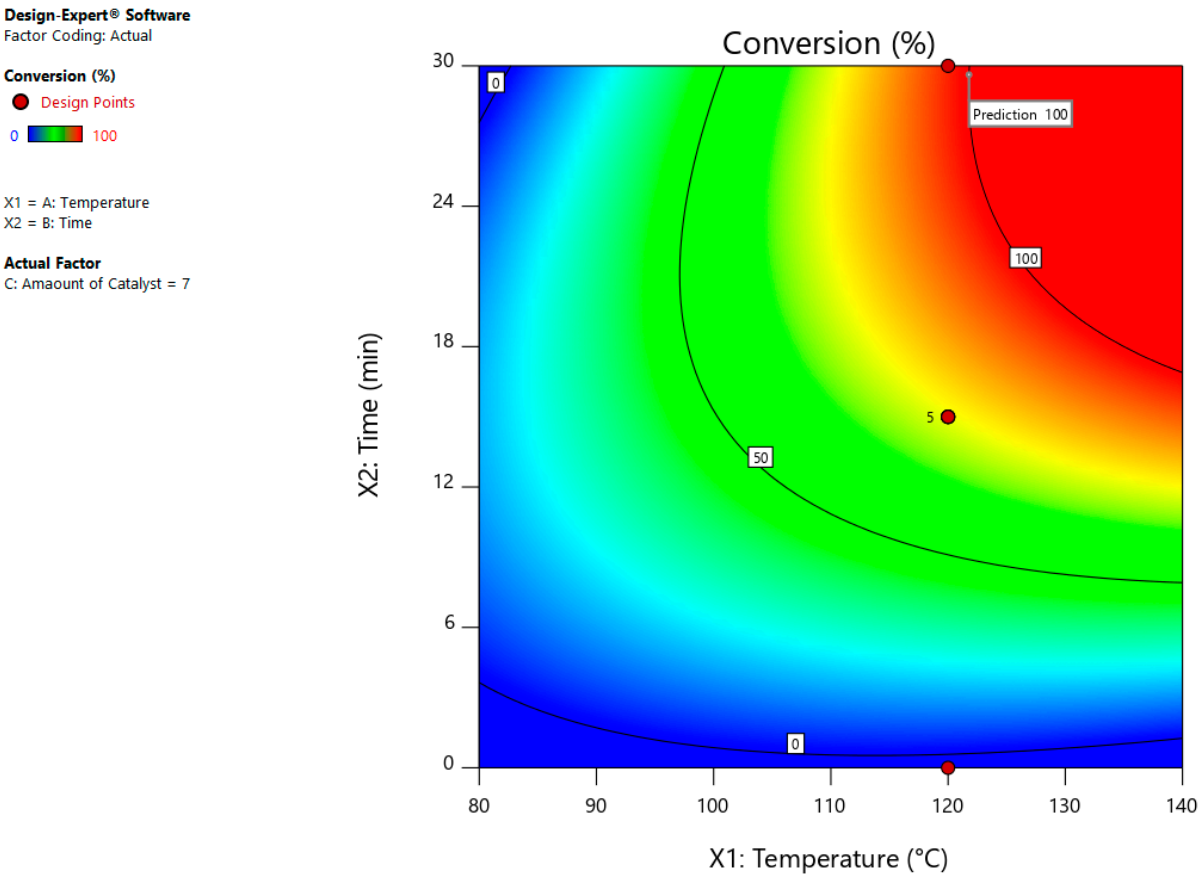

Figure S1. 2D plot obtained after RSM analysis and numerical optimization.

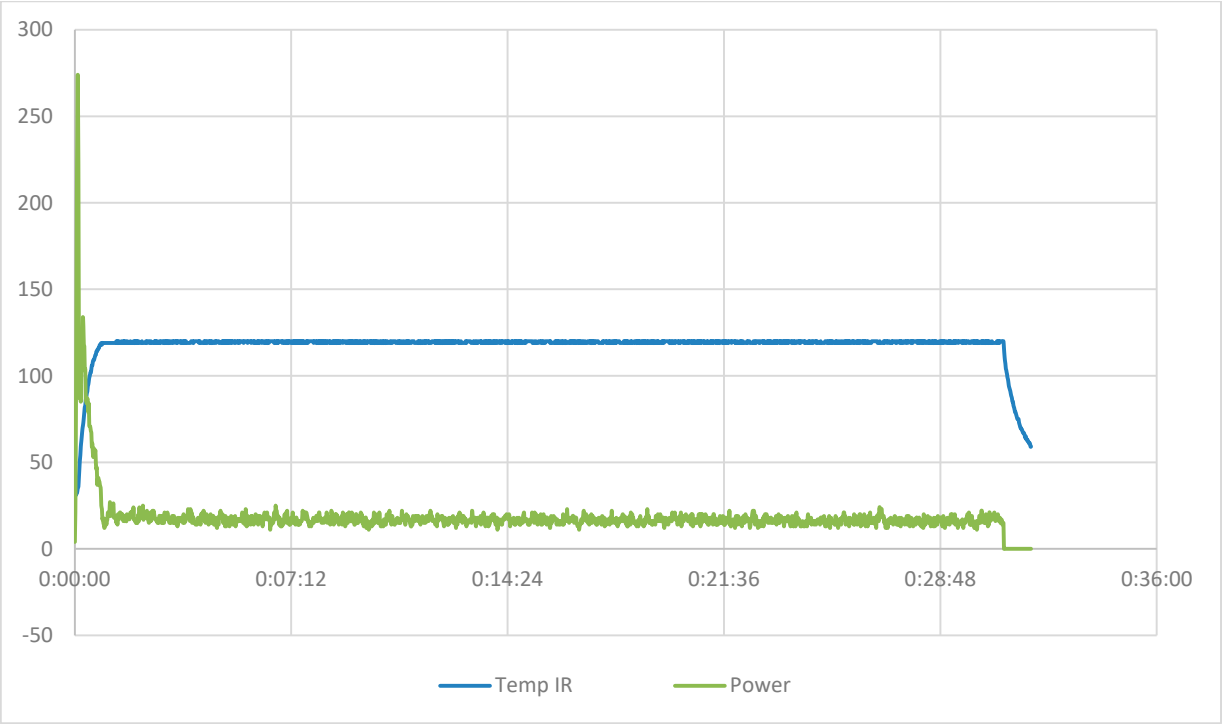

Figure S2. Energy input (gray line – power [W]) and temperature (blue line – in °C) for esterification under optimal reaction conditions and MW irradiation.

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List S1. NMR spectral data of synthesized esters.

Methyl benzoate - 1a [1]

^{1}H NMR (400 MHz, CDCl3) δ 8.05 – 8.03 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 3.91 (s, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 167.1, 132.9, 130.2, 129.6, 128.3, 52.1.

Ethyl benzoate – 1b [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.04 (m, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 132.8, 130.6, 129.6, 128.3, 60.9, 14.3.

Butyl benzoate – 1c [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.03 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 1.81 – 1.73 (m, 2H), 1.47 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 132.8, 130.6, 129.5, 128.3, 64.8, 30.8, 19.3, 13.8.

Methyl stearate – 2a [3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.62 (dd, *J* = 14.3, 7.1 Hz, 2H), 1.28-1.26 (m, 28H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 51.4, 34.1, 31.9, 29.7, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 25.0, 22.7, 14.1.

Ethyl stearate – 2b [4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (q, *J* = 7.1 Hz, 2H), 2.28 (t, *J* = 7.6 Hz, 2H), 1.63 – 1.60 (m, 2H), 1.29 – 1.26 (m, 30H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 60.2, 34.4, 32.0, 29.8, 29.7, 29.7, 29.5, 29.4, 29.3, 29.2, 25.0, 22.7, 14.3, 14.1.

Butyl stearate – 2c [5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (t, *J* = 6.7 Hz, 2H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.64 – 1.59 (m, 4H), 1.44 – 1.34 (m, 2H), 1.28-1.26 (m, 28H), 0.91 (dt, *J* = 13.6, 7.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 64.1, 34.4, 31.9, 30.7, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 25.1, 22.7, 19.2, 14.1, 13.7.

Isopropyl stearate – 2d [6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.00 (dt, *J* = 12.5, 6.2 Hz, 1H), 2.25 (t, *J* = 7.5 Hz, 2H), 1.62 – 1.59 (m, 2H), 1.26 – 1.23 (m, 34H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 67.3, 34.7, 31.9, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 25.1, 22.7, 21.9, 14.1.

Methyl 4-hidroxybenzoate – 3a [7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.25 (s, 1H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 160.1, 131.9, 122.5, 115.3, 52.0.

Methyl 3-hidroxybenzoate – 4a [8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.0, 5.1 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.10 – 7.07 (m, 1H), 6.35 (s, 1H), 3.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 156.0, 131.2, 129.8, 121.8, 120.4, 116.4, 52.4.

Methyl 3-methoxybenzoate – 5a [9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.56 – 7.55 (m, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.11 – 7.08 (m, 1H), 3.91 (s, 3H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 159.6, 131.5, 129.4, 122.0, 119.5, 114.0, 55.4, 52.1.

Methyl 4-methylbenzoate – 6a [10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 143.5, 129.6, 129.1, 127.5, 51.9, 21.6.

Methyl 4-chlorobenzoate – 7a [11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 139.4, 131.0, 128.7, 52.2.

Methyl 4-formylbenzoate – 8a [12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.19 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 3.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 166.1, 139.2, 130.2, 129.5, 52.6.

Methyl 4-nitrobenzoate – 9a [1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.9 Hz, 2H), 8.22 (d, *J* = 8.9 Hz, 2H), 3.98 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 150.6, 130.7, 123.6, 52.8.

Methyl 2-nitrobenzoate – 10a [13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.76 – 7.74 (m, 1H), 7.70 – 7.62 (m, 2H), 3.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 132.9, 131.8, 129.9, 127.6, 123.9, 53.2.

Dimethyl phthalate – 11a [14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 5.7, 3.3 Hz, 2H), 7.54 (dd, *J* = 5.7, 3.3 Hz, 2H), 3.91 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 131.9, 131.1, 128.9, 52.7.

Methyl oleate – 12a [3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (dt, *J* = 8.5, 5.9 Hz, 2H), 3.66 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.06 – 1.99 (m, 4H), 1.64 – 1.60 (m, 2H), 1.31 – 1.26 (m, 20H), 0.88 (dd, *J* = 8.7, 4.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 130.0, 129.8, 51.4, 34.1, 31.9, 29.8, 29.7, 29.7, 29.6, 29.4, 29.3, 29.2, 29.2, 29.1, 27.3, 27.2, 25.0, 22.7, 14.1.

Methyl 4-methoxyphenylacetate – 13a [15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.7 Hz, 2H), 6.84 (d, *J* = 7.3 Hz, 2H), 3.75 (s, 3H), 3.65 (s, 3H), 3.54 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 158.7, 130.3, 126.1, 114.0, 55.2, 51.9, 40.2.

Methyl 4-chlorophenylacetate – 14a [16]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 3.68 (s, 3H), 3.58 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 133.1, 132.5, 130.7, 128.7, 52.1, 40.4.

Methyl 4-nitrophenylacetate – 15a [17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 2H), 3.72 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 147.2, 141.4, 130.4, 123.7, 52.4, 40.7.

2-(4-Isobutyl-phenyl)-propionic acid methyl ester (Ibuprofen methyl ester) – 16a [18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.68 (q, *J* = 7.2 Hz, 1H), 3.62 (s, 3H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.84 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.47 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 140.5, 137.8, 129.3, 127.1, 51.9, 45.1, 45.0, 30.2, 22.4, 18.6.

Methyl cinnamate – 17a [19]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.51 – 7.49 (m, 2H), 7.36 – 7.35 (m, 3H), 6.43 (d, *J* = 16.0 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 144.8, 134.4, 130.3, 128.9, 128.1, 117.8, 51.6.

Methyl 1H-indol-2-carboxylate – 18a [20]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.44 – 7.42 (m, 1H), 7.34 – 7.30 (m, 1H), 7.23 (d, *J* = 1.1 Hz, 1H), 7.17 – 7.13 (m, 1H), 3.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 136.9, 127.5, 127.1, 125.4, 122.6, 120.8, 111.9, 108.8, 52.0.

Methyl cyclohexylcarboxylate – 19a [21]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.30 (ddd, *J* = 14.9, 7.5, 3.6 Hz, 1H), 1.89 (d, *J* = 13.3 Hz, 2H), 1.75 (dd, *J* = 9.3, 6.1 Hz, 2H), 1.64 (dd, *J* = 9.7, 4.0 Hz, 1H), 1.48 – 1.39 (m, 2H), 1.26 – 1.20 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 51.4, 43.2, 29.1, 25.8, 25.5.

Dimethyl succinate – 21a [18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (d, *J* = 1.4 Hz, 6H), 2.64 (d, *J* = 1.3 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 51.9, 28.9.

Dimethyl phenylsuccinate – 22a [22]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 15.5, 6.4 Hz, 5H), 4.09 (dd, *J* = 10.0, 5.2 Hz, 1H), 3.67 (s, 6H), 3.21 (dd, *J* = 16.9, 10.1 Hz, 1H), 2.67 (dd, *J* = 17.0, 5.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 171.9, 137.7, 128.9, 127.7, 52.3, 51.8, 47.1, 37.6.

Dimethyl itaconate – 23a [23]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (s, 1H), 5.73 (d, *J* = 0.9 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.35 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 166.7, 133.7, 128.6, 52.2, 52.1, 37.5.

Dimethyl malate – 24a [24]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.54 – 4.51 (m, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 3.06 (s, 1H), 2.84 (qd, *J* = 16.4, 5.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 171.0, 67.3, 52.9, 52.1, 38.5.

Dimethyl tartarate – 25a [25]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57 (s, 2H), 3.86 (s, 6H), 2.79 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 72.1, 53.1.

Dimethyl fumarate – 26a [18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 2H), 3.82 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 133.4, 52.3.

Dimethyl maleate – 27a [18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.28 – 6.27 (m, 2H), 3.80 (dd, *J* = 3.5, 1.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 129.8, 52.2.

Trimethyl citrate – 28a [26]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (s, 1H), 3.83 (s, 3H), 3.69 (s, 6H), 2.86 (dd, *J* = 40.4, 15.6 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 170.3, 73.3, 53.2, 52.0, 43.1.

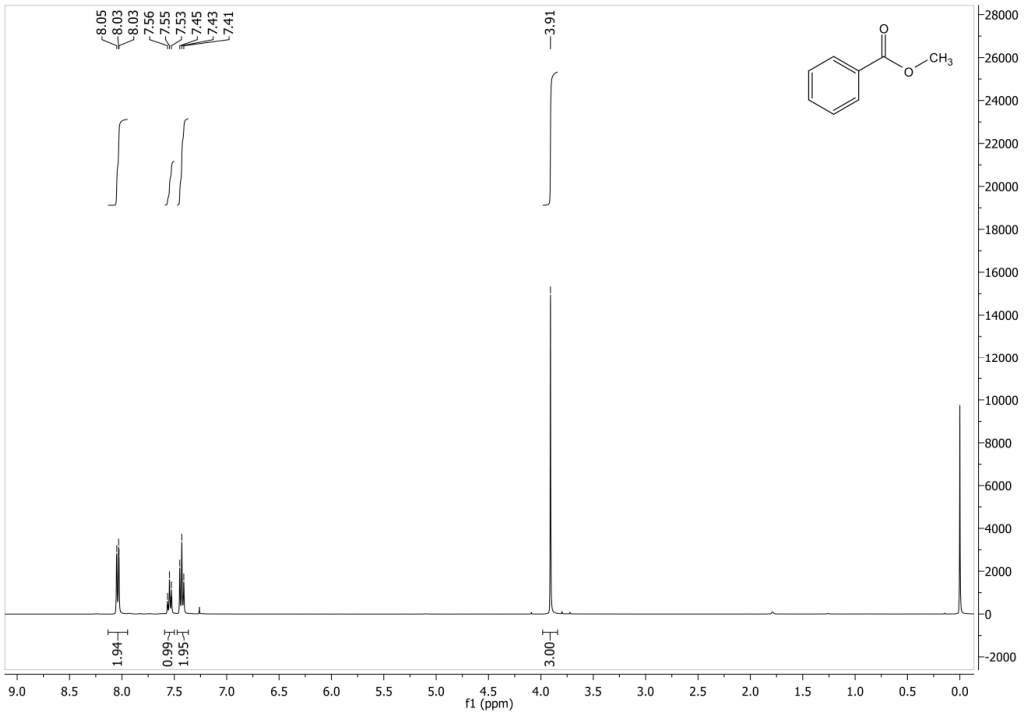
Methyl palmitate – 30a [3]

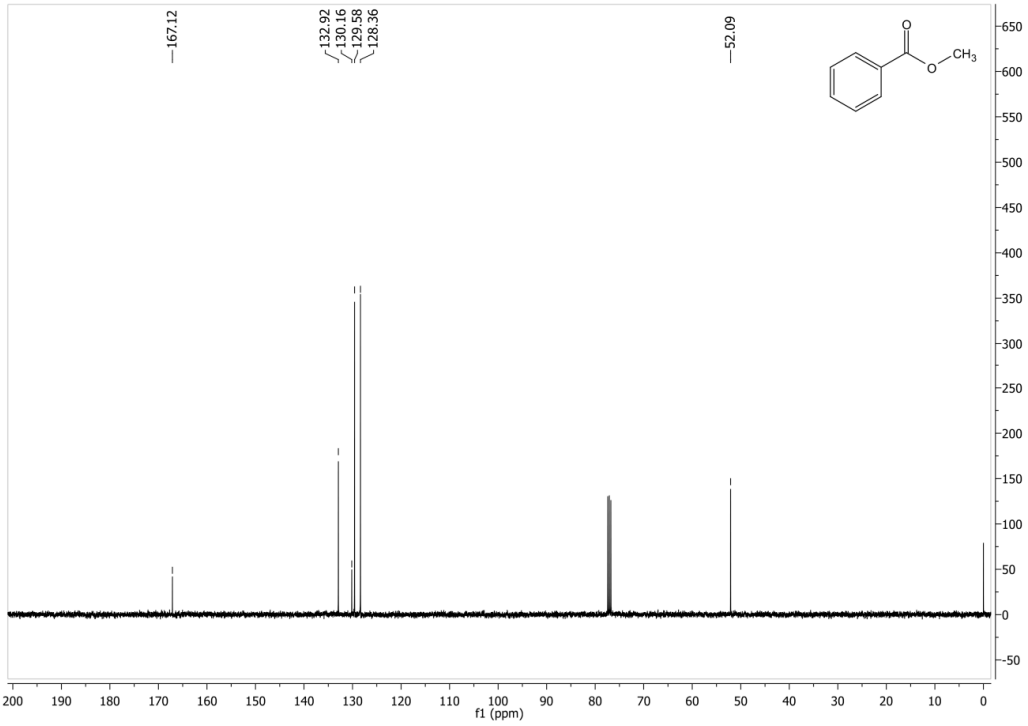
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.63 – 1.60 (m, 2H), 1.26 (s, 24H), 0.88 (t, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 51.4, 34.1, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 25.0, 22.7, 14.1.

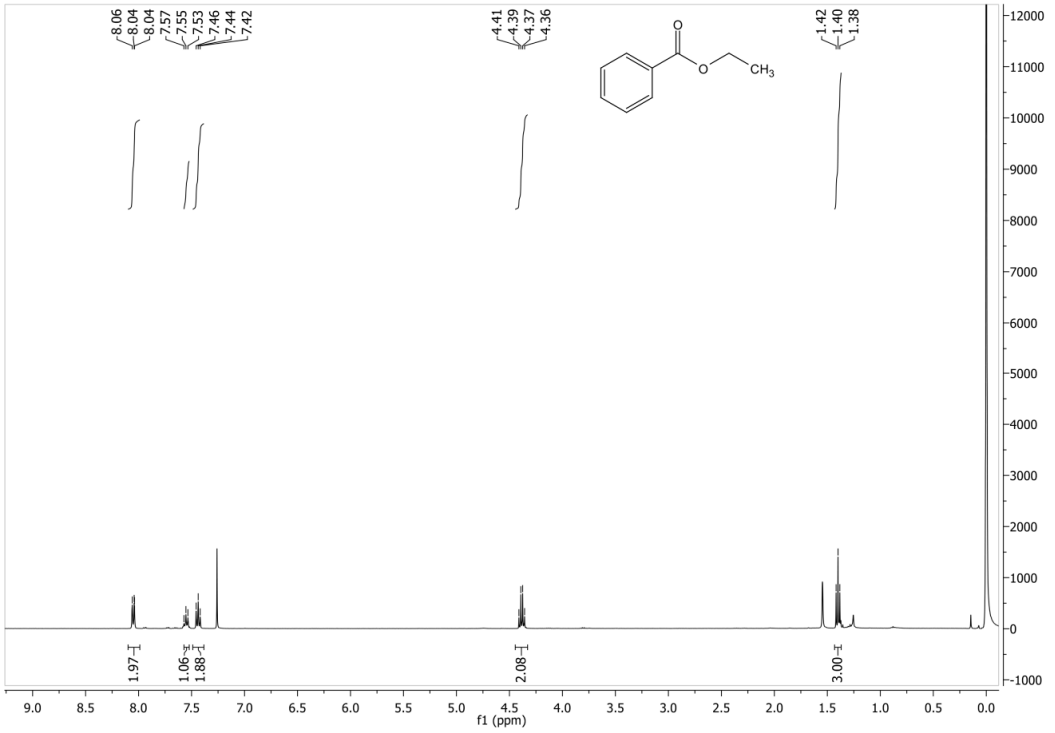
List S2. ^{1}H and ^{13}C NMR spectra of synthesized esters.

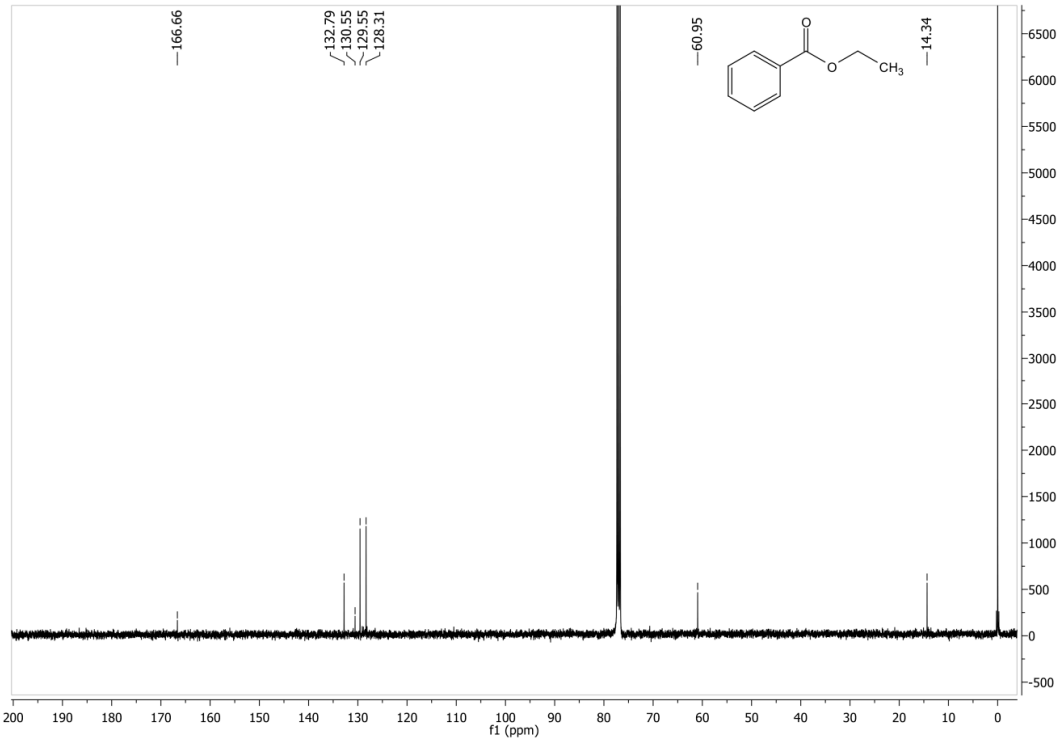
Methyl benzoate – 1a



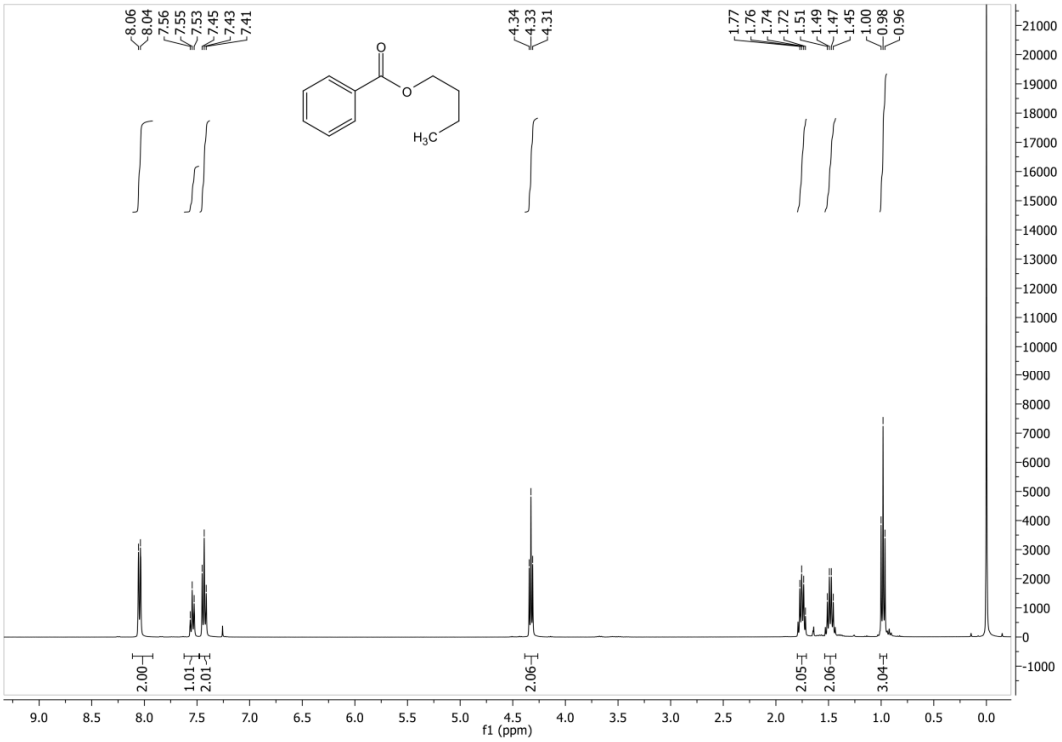


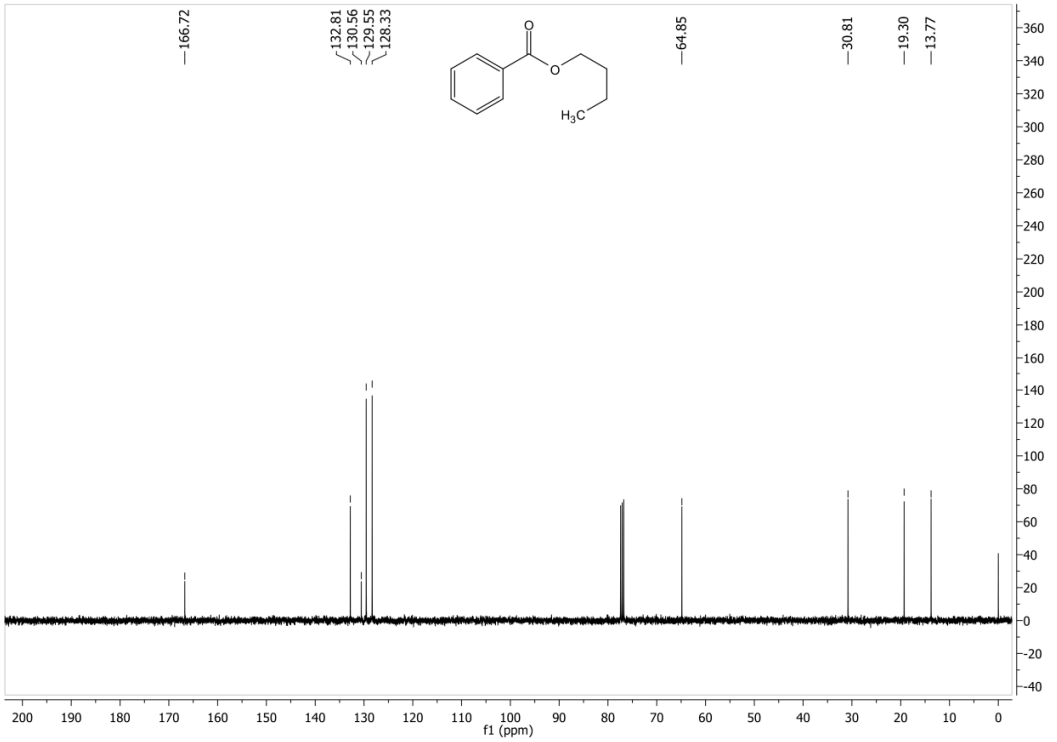
Ethyl benzoate – 1b



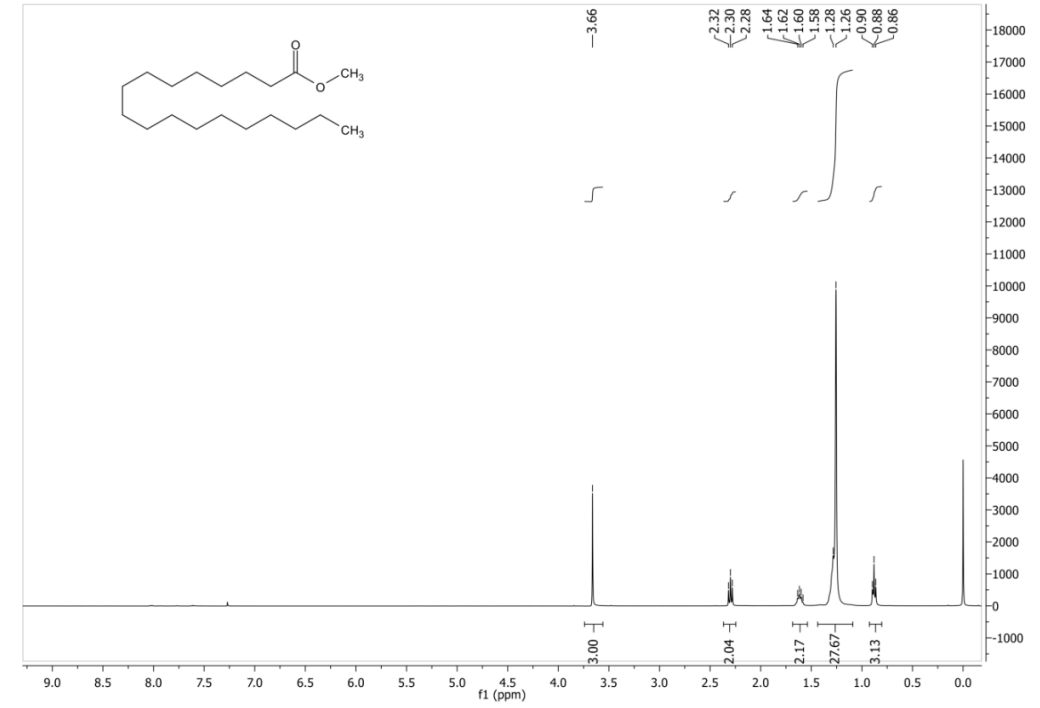


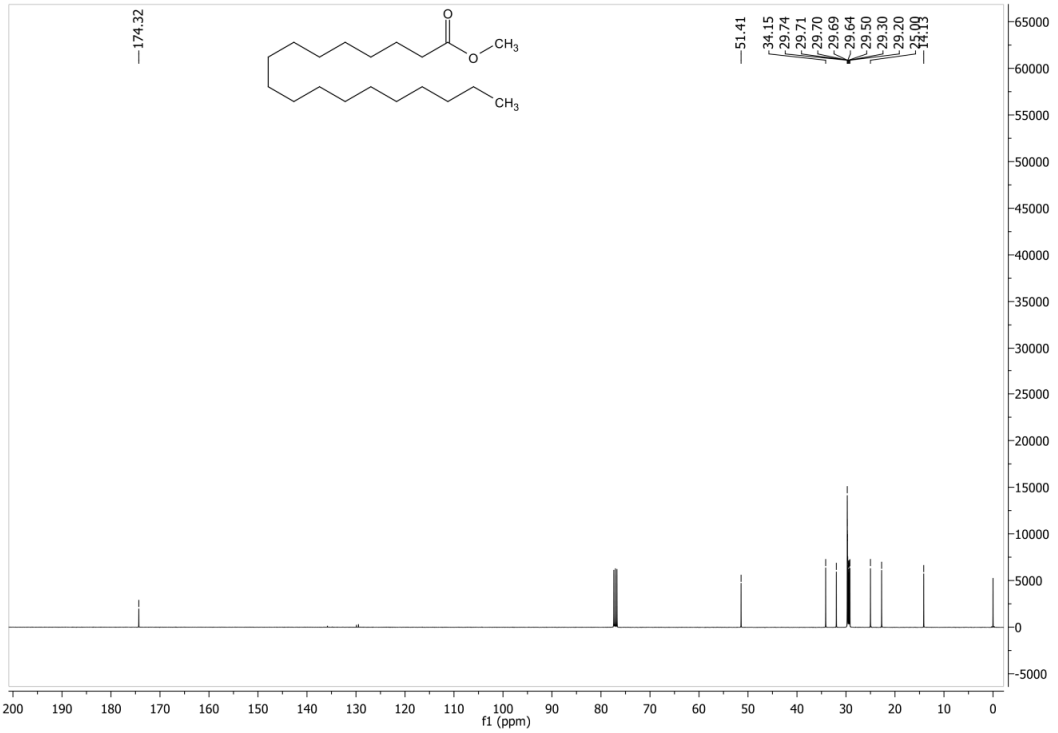
Butyl benzoate – 1c



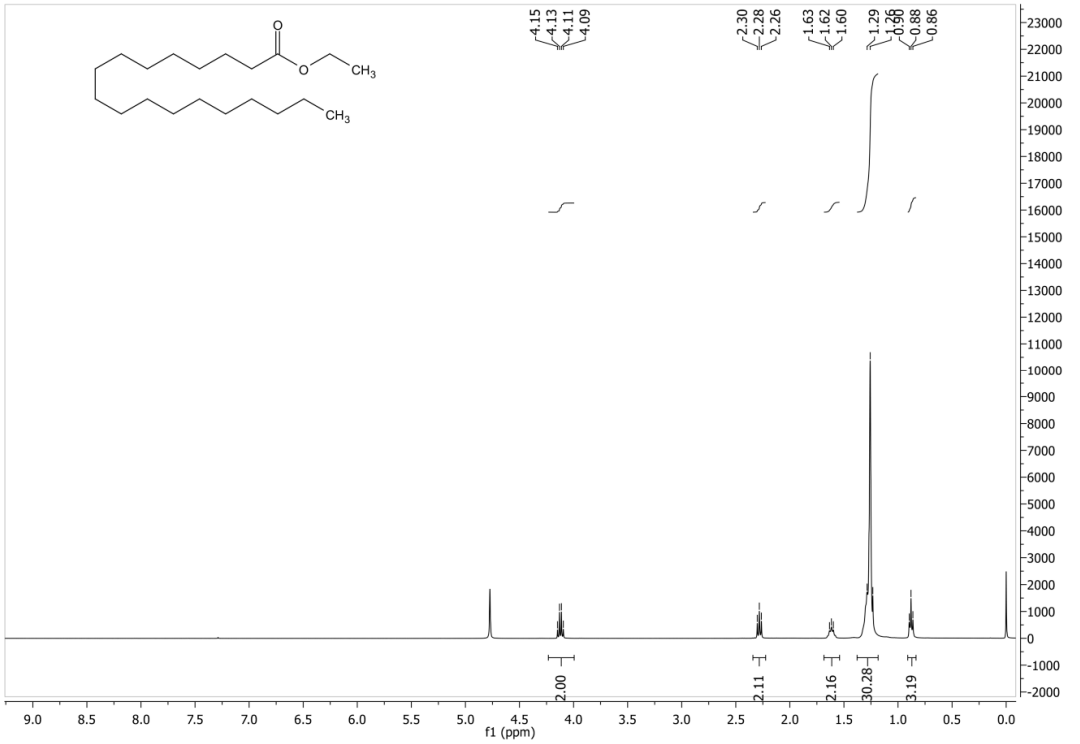


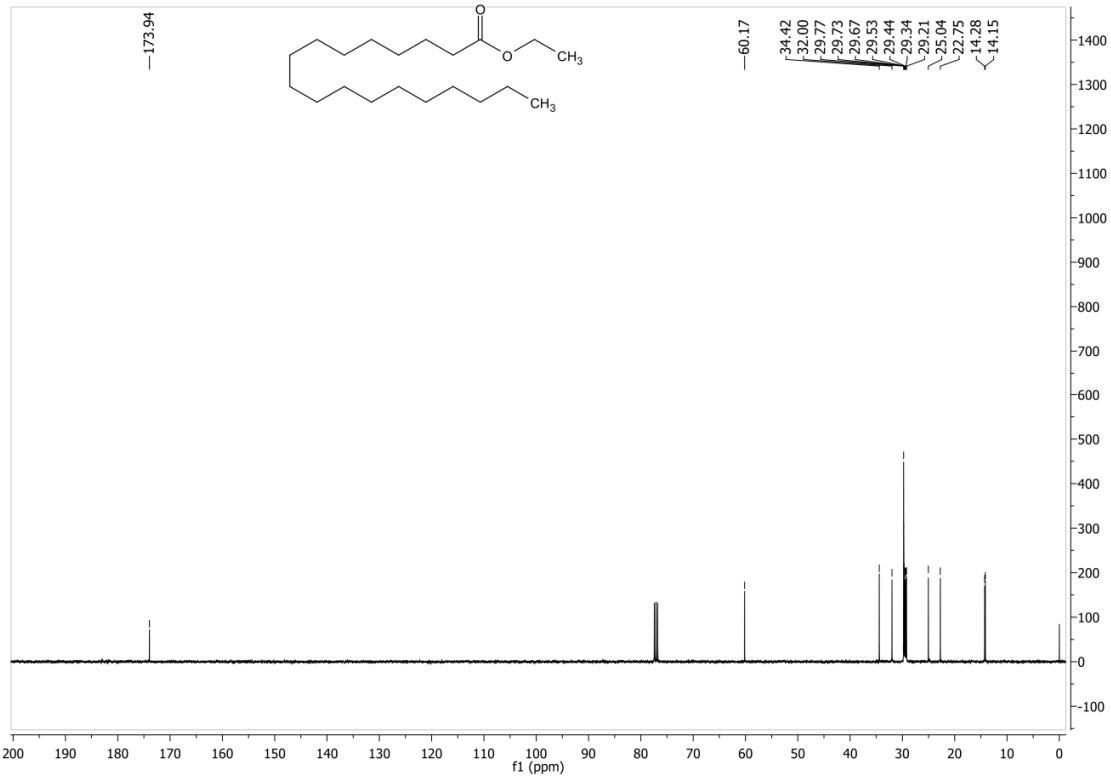
Methyl stearate – 2a



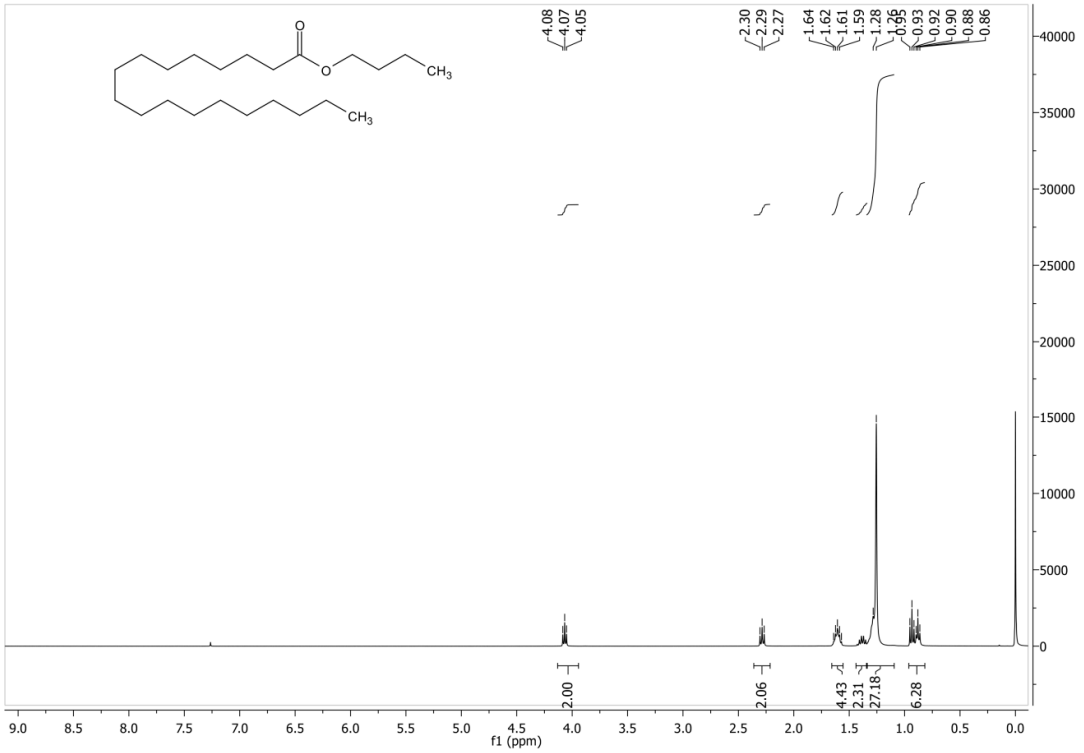


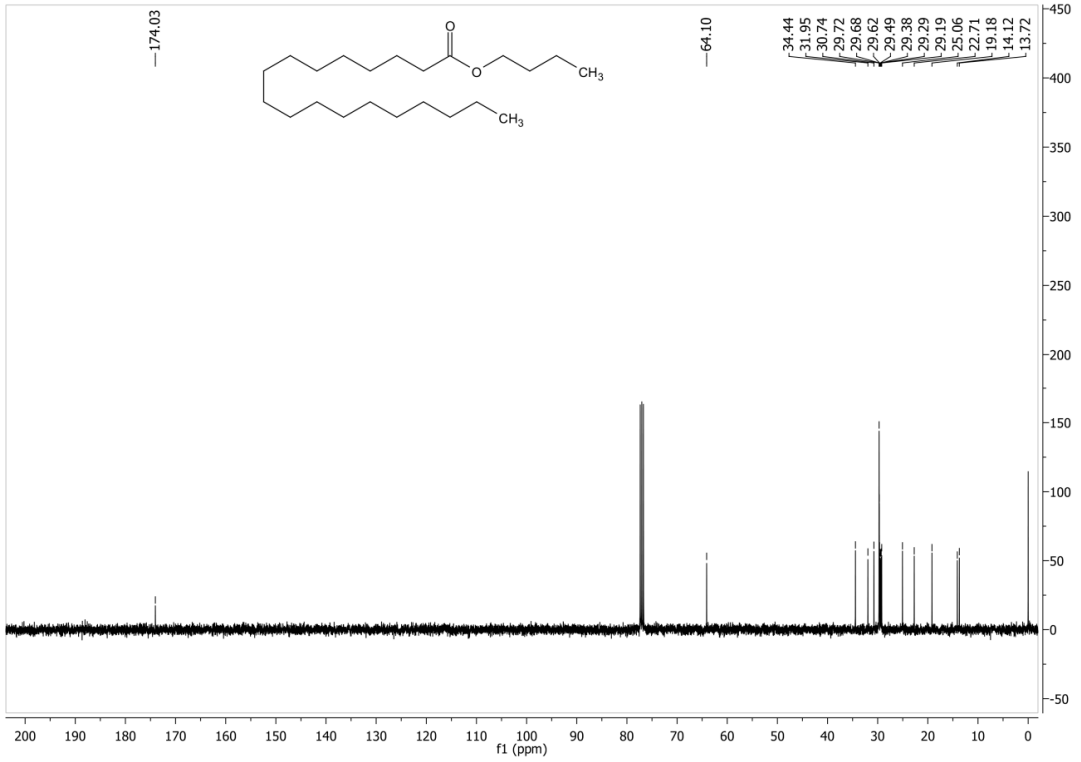
Ethyl stearate – 2b



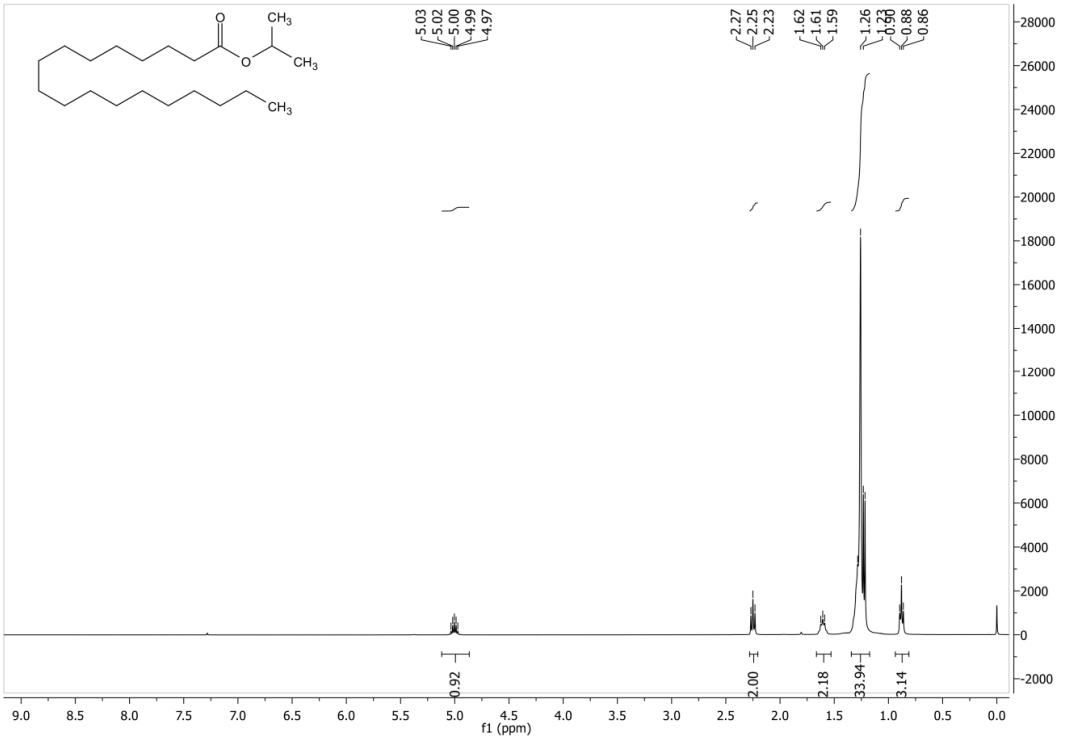


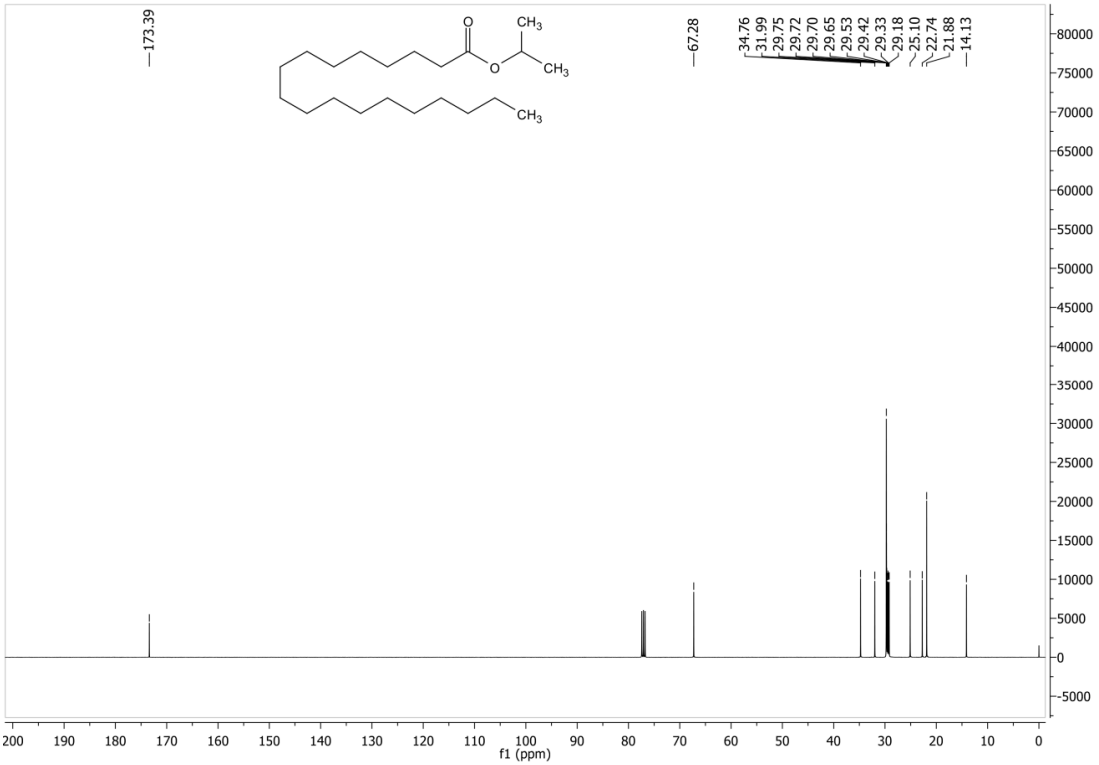
Butyl stearate – 2c



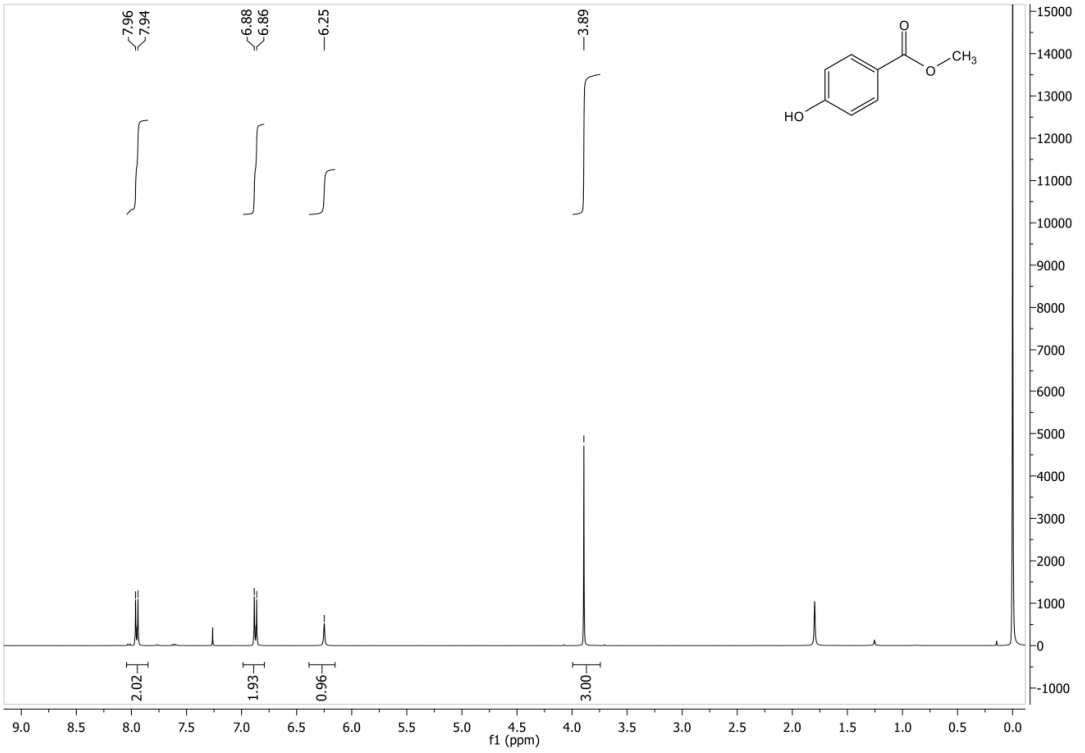


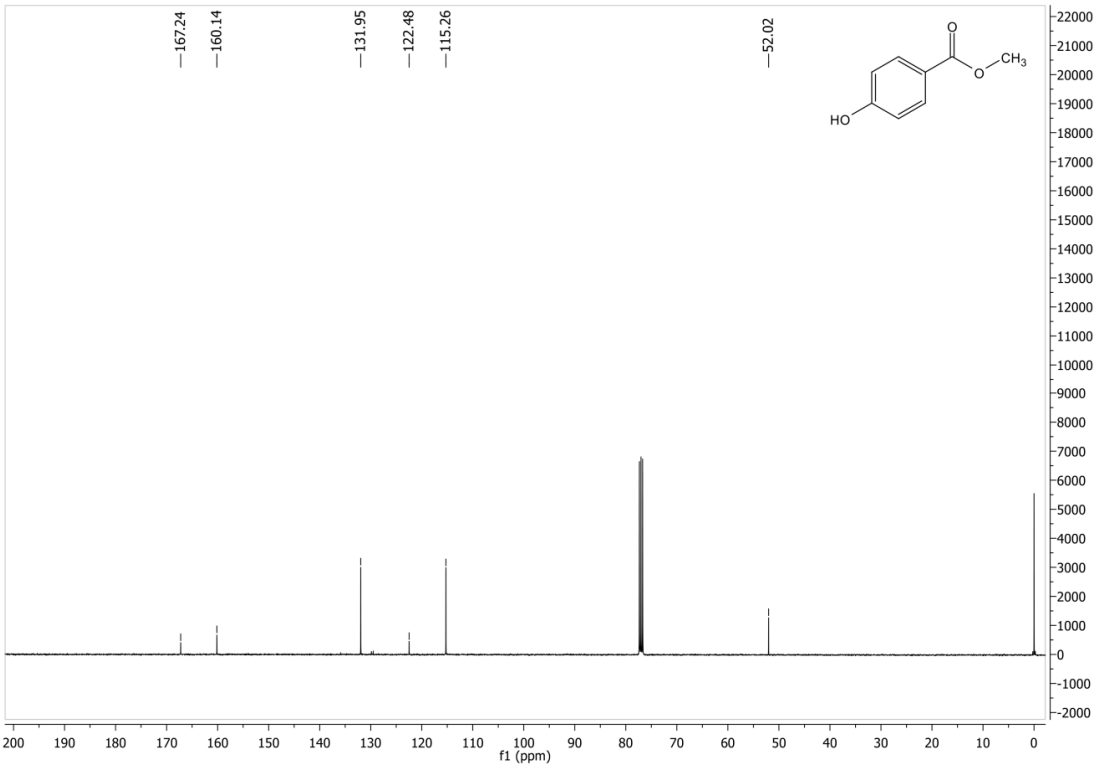
Isopropyl stearate – 2d



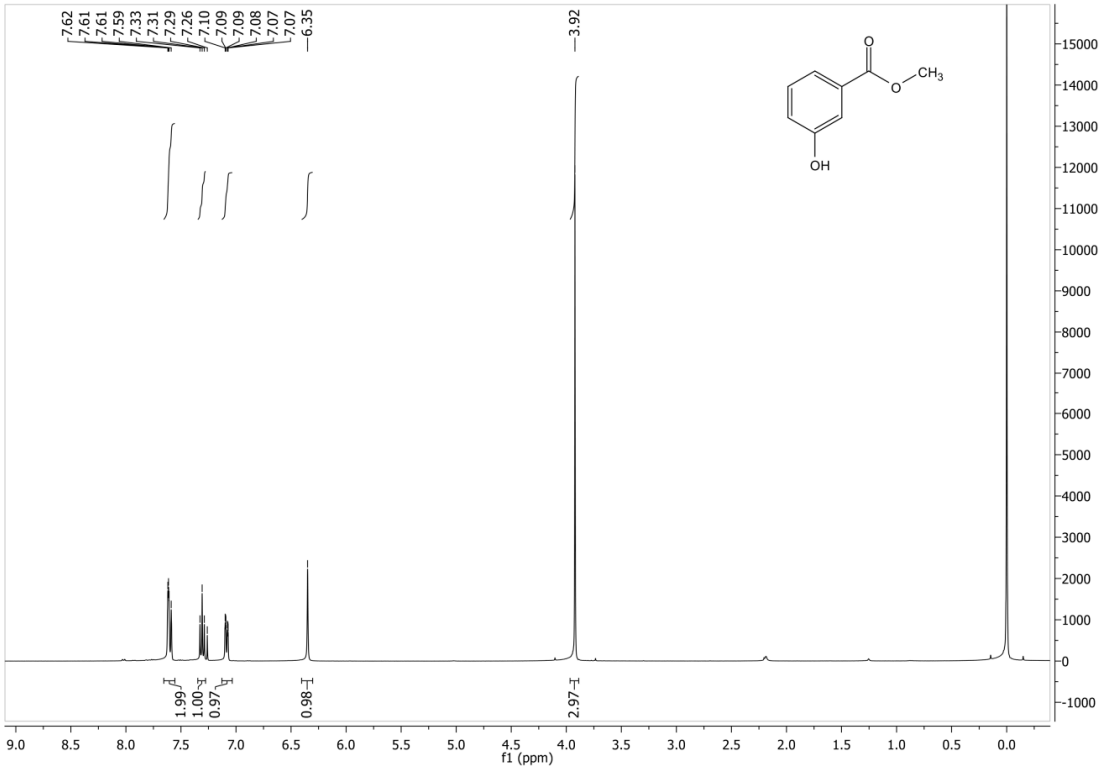


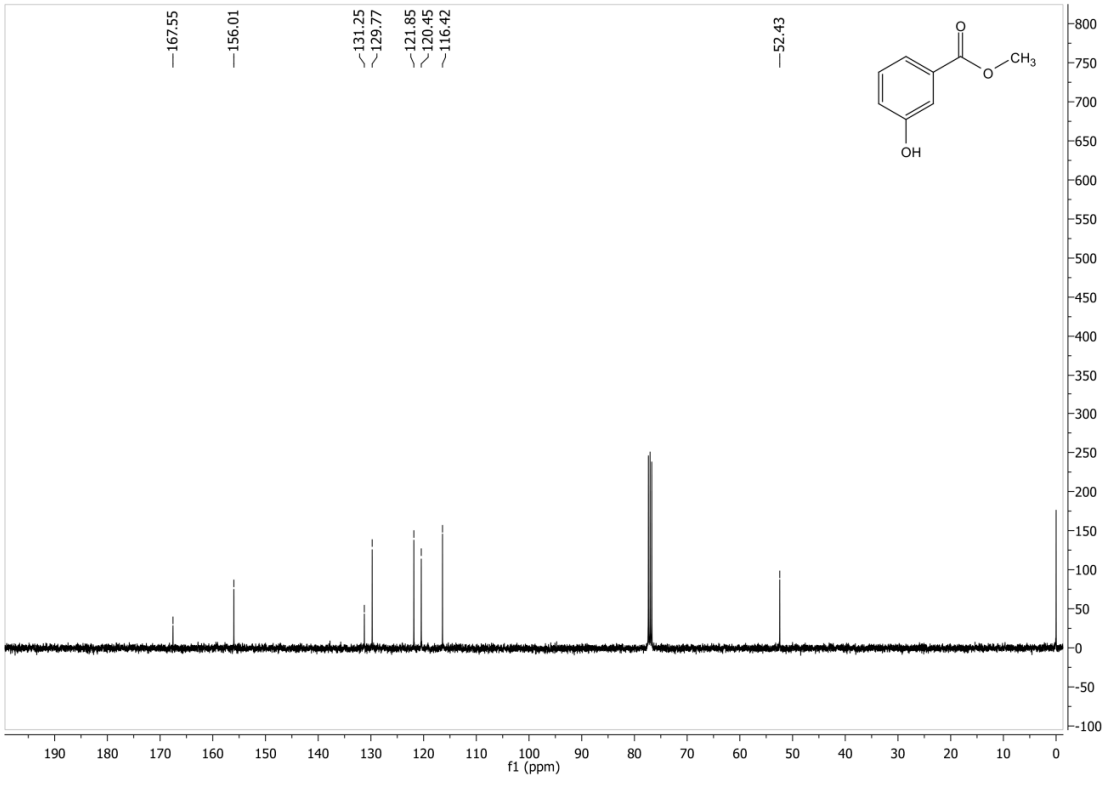
Methyl 4-hidroxybenzoate – 3a



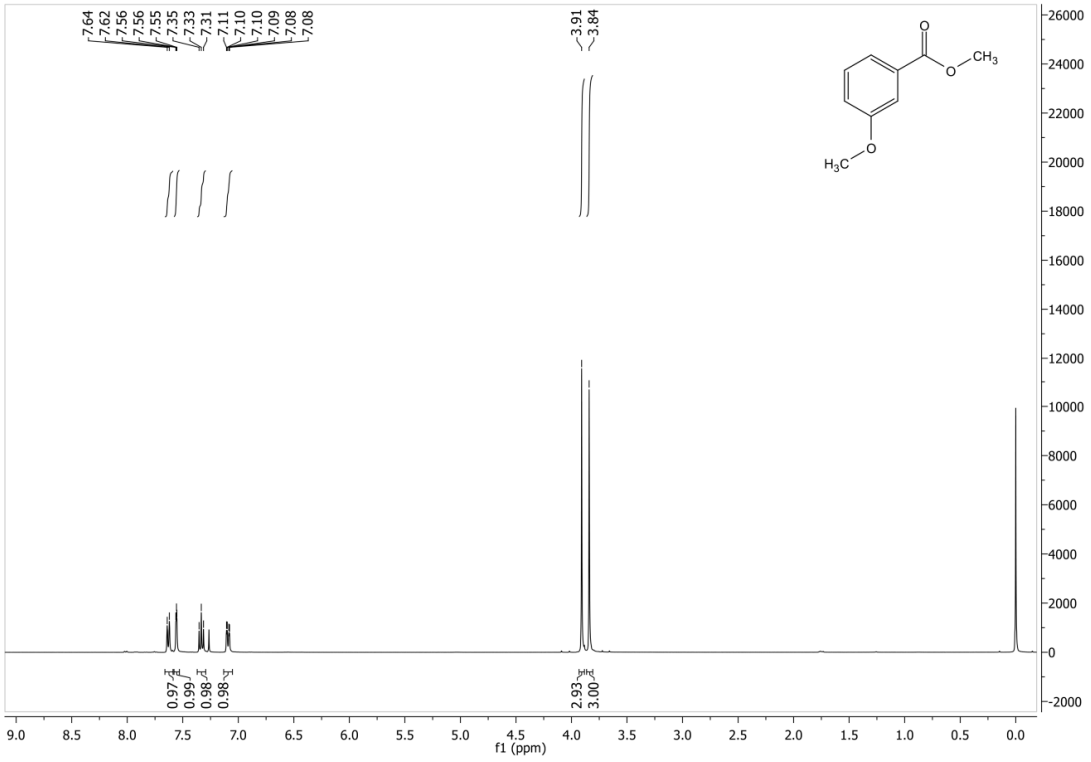


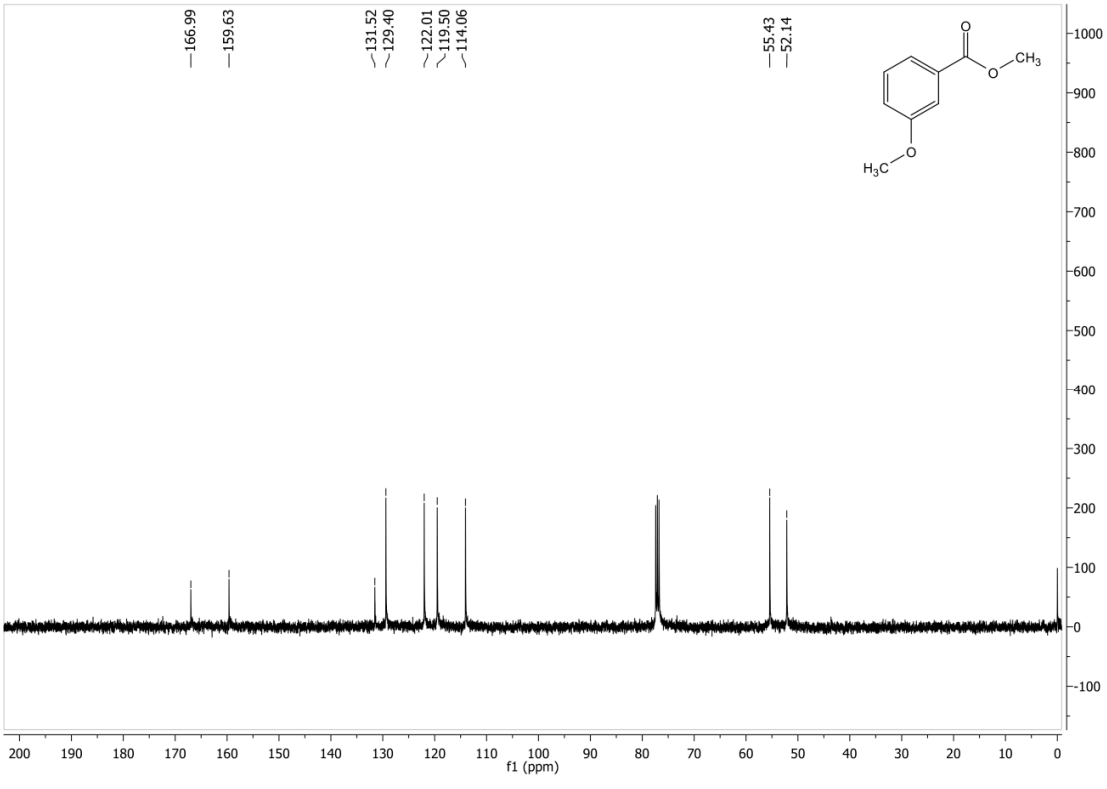
Methyl 3-hidroxybenzoate – 4a



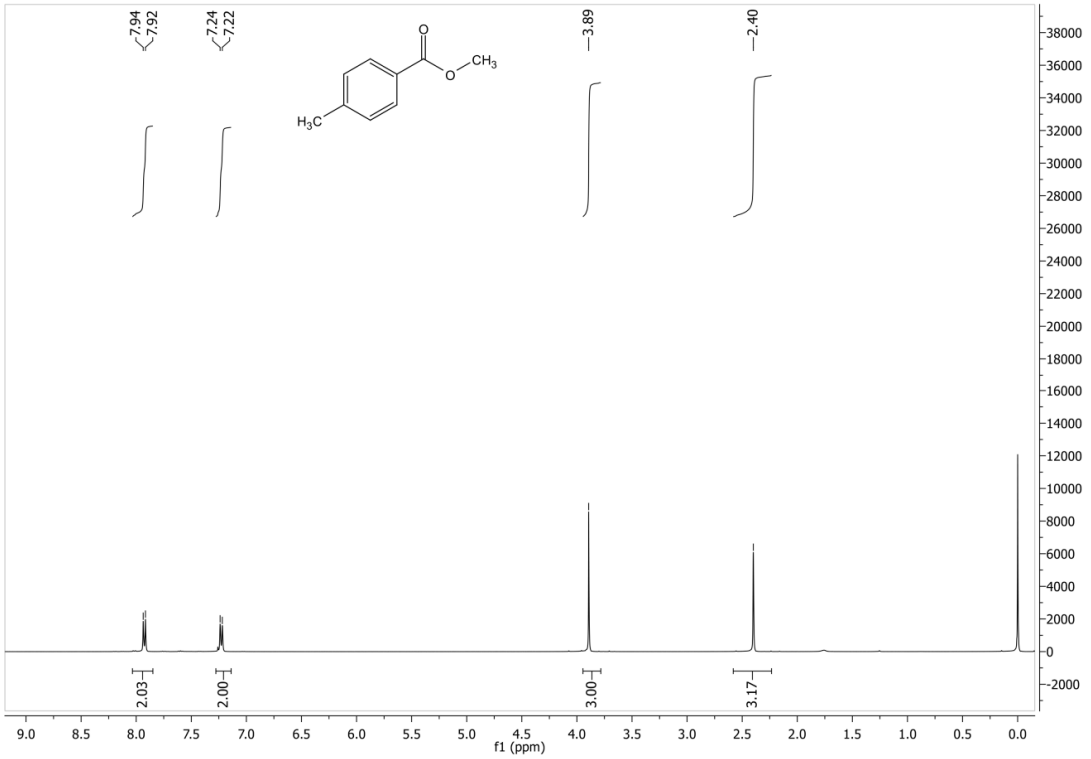


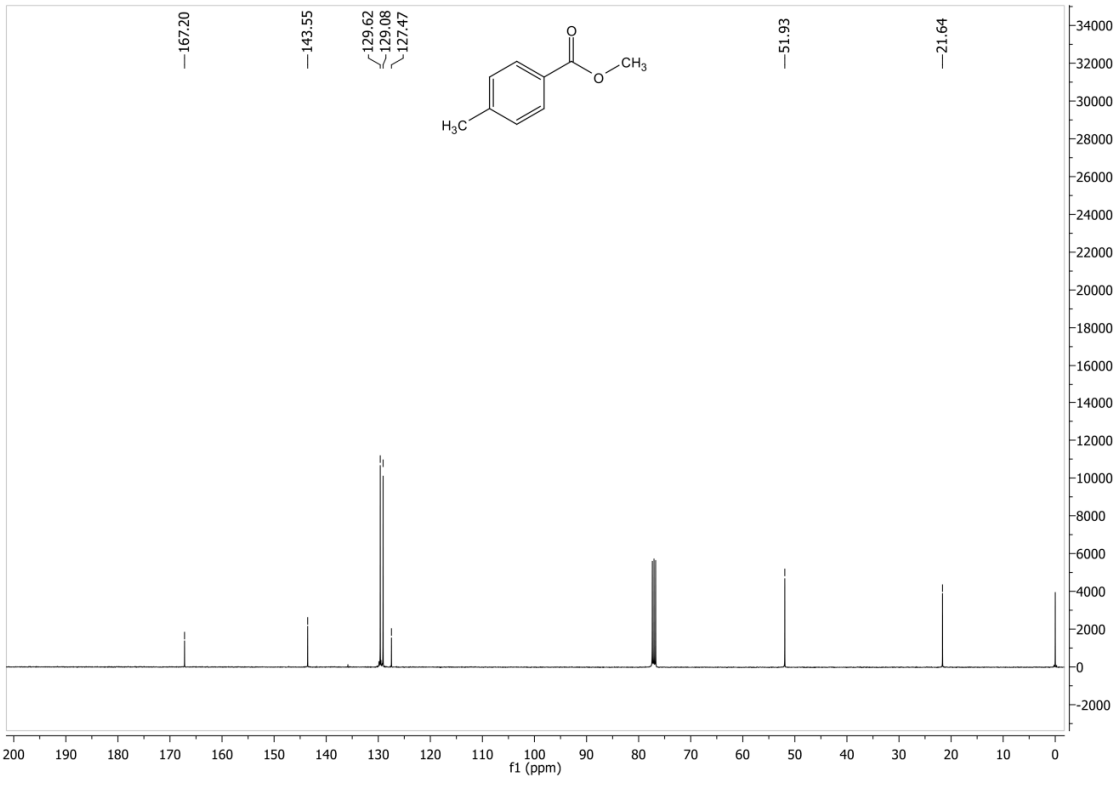
Methyl 3-methoxybenzoate – 5a



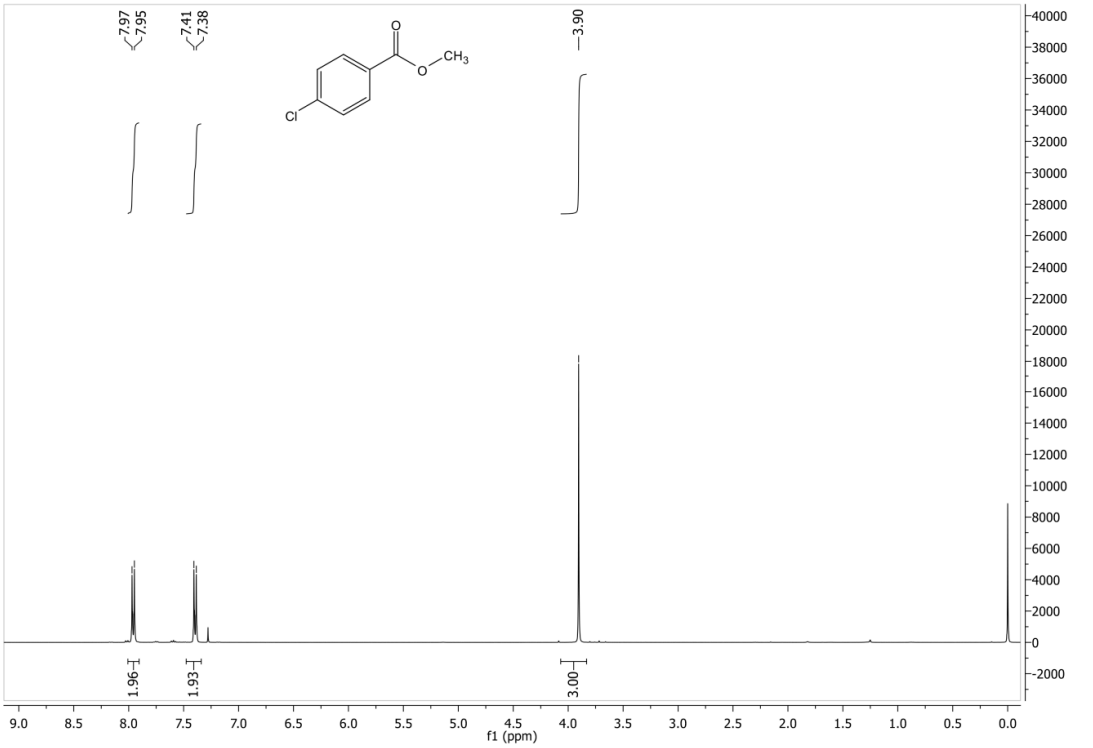


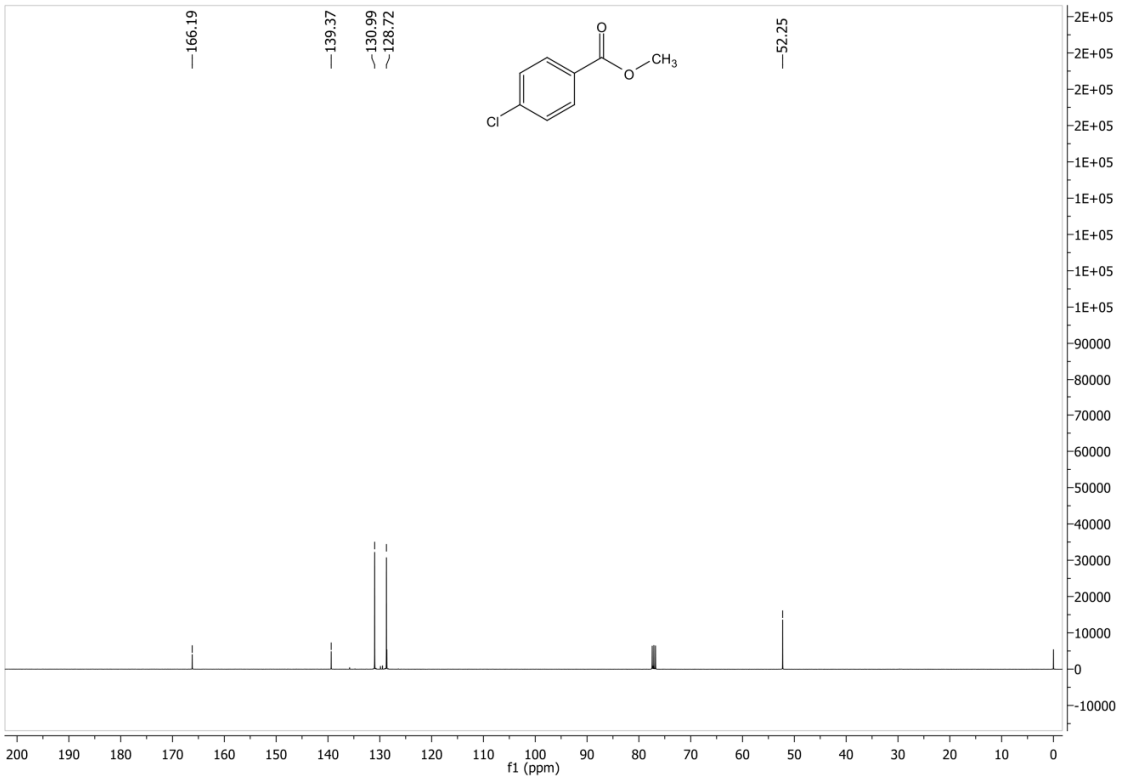
Methyl 4-methylbenzoate – 6a



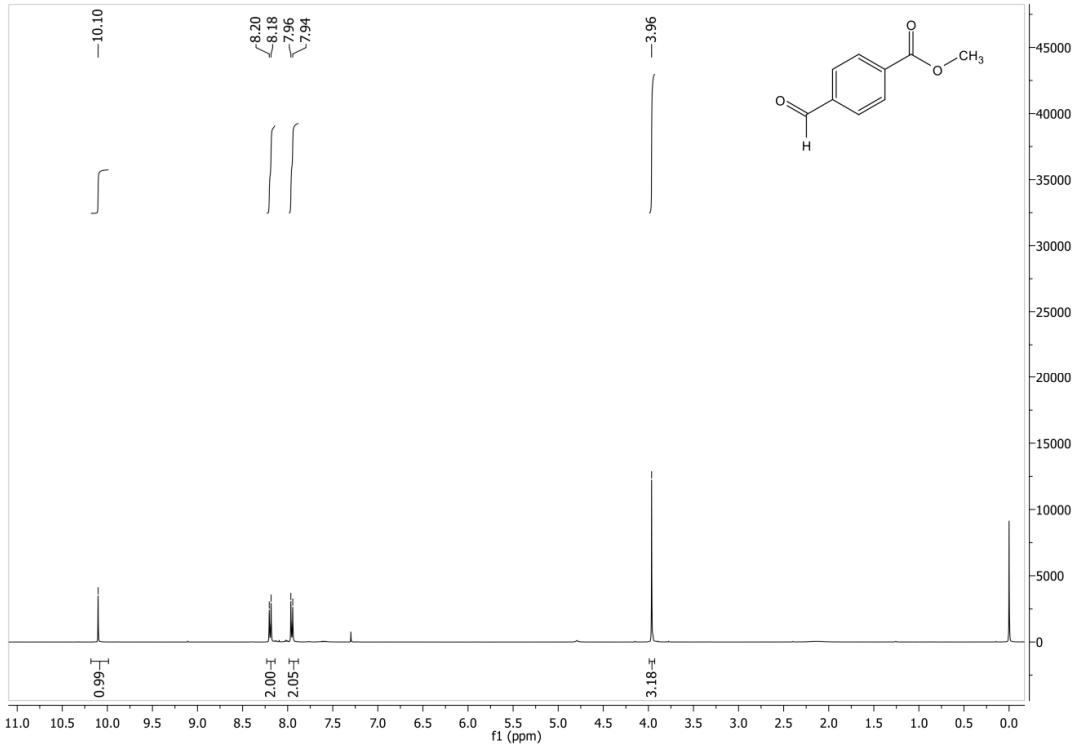


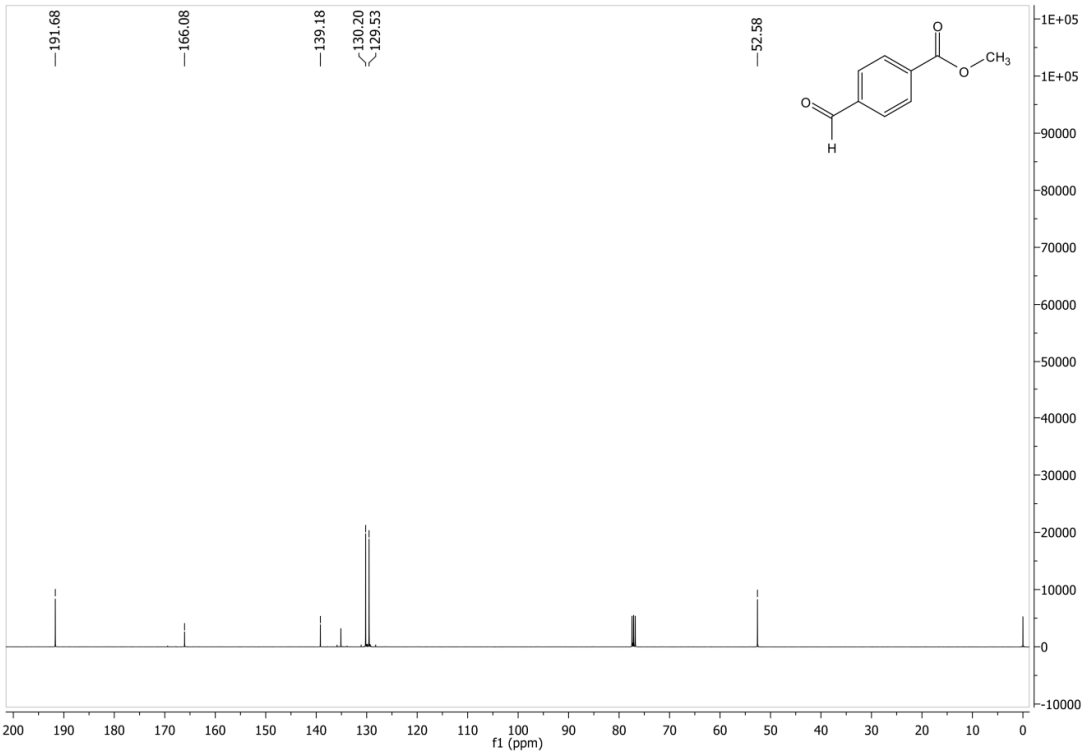
Methyl 4-chlorobenzoate – 7a



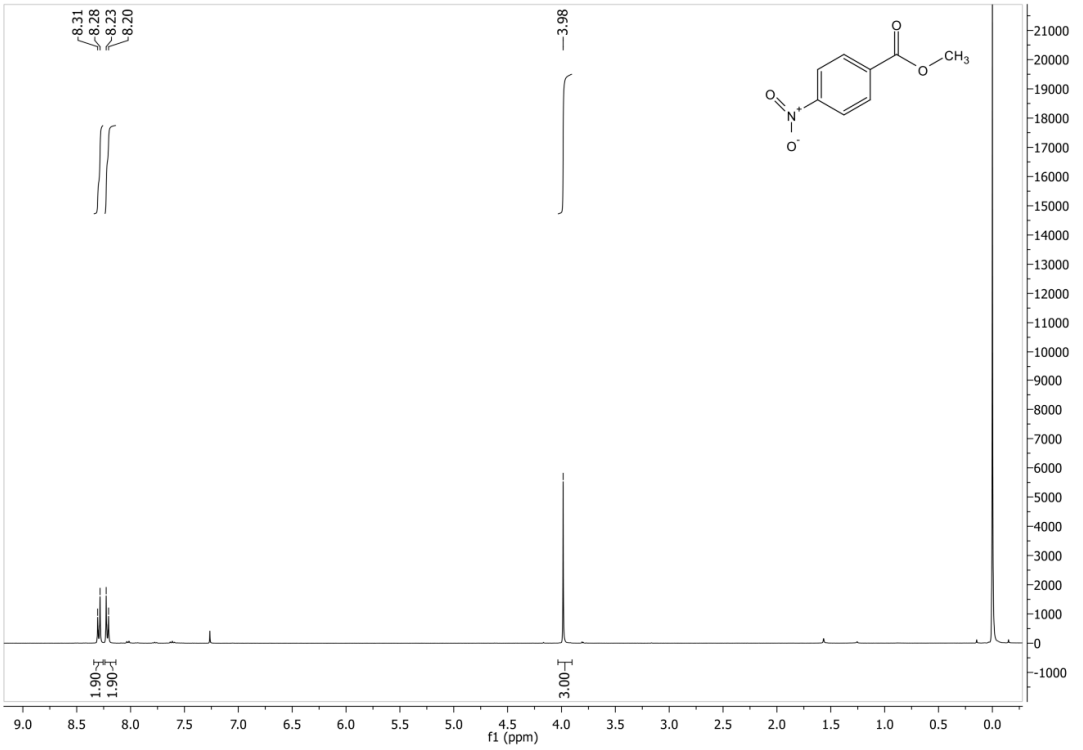


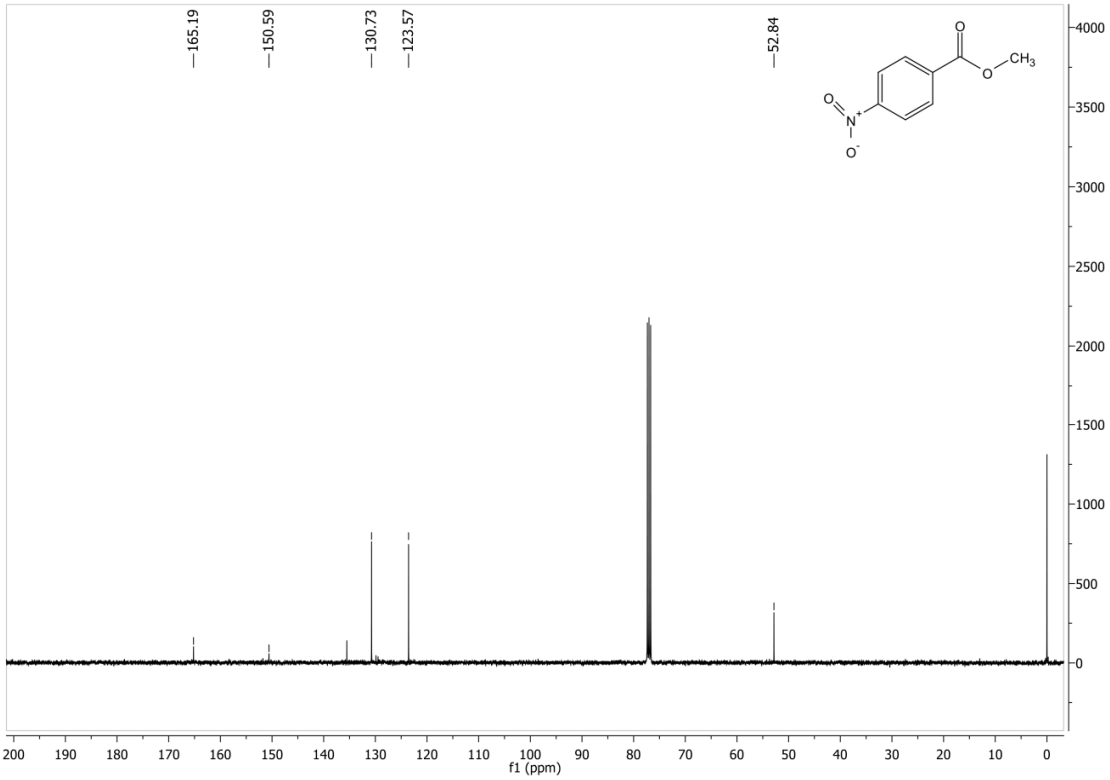
Methyl 4-formylbenzoate – 8a



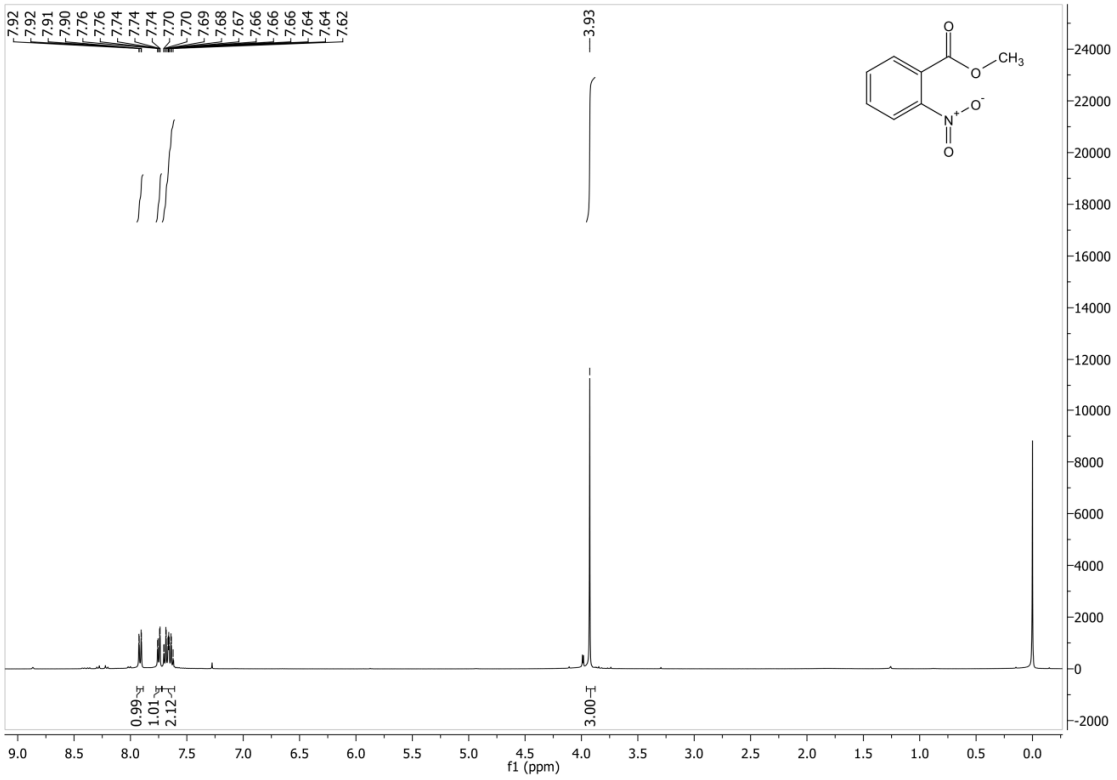


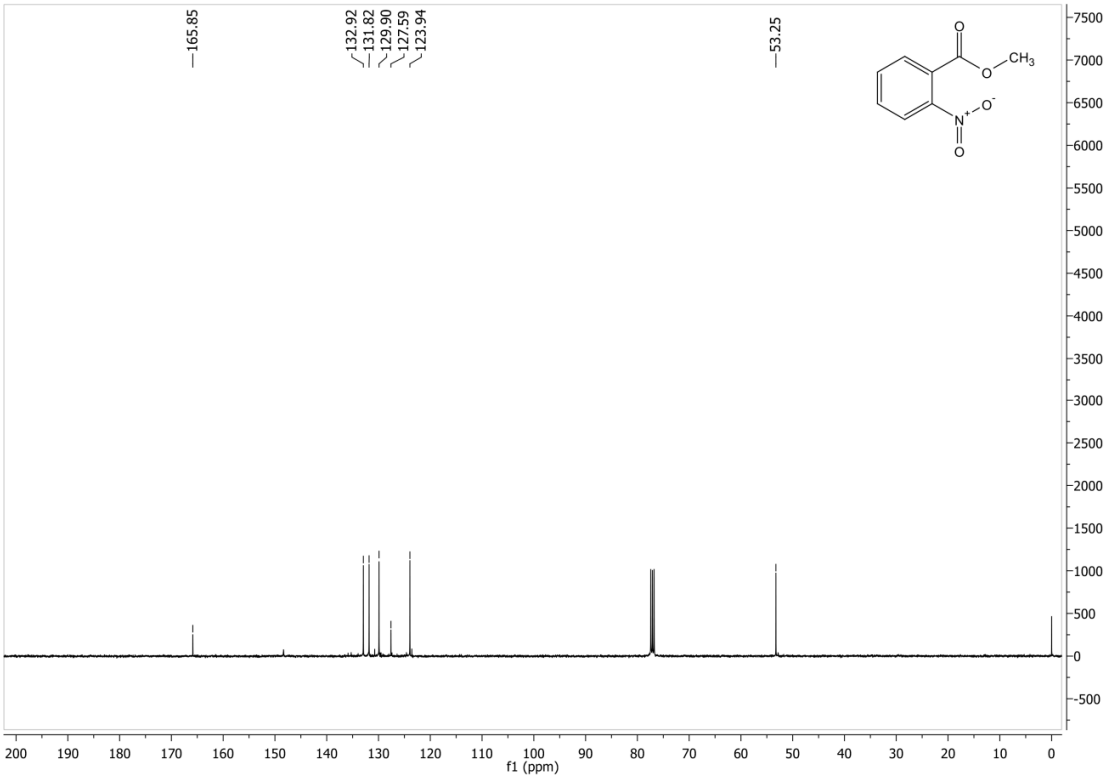
Methyl 4-nitrobenzoate – 9a



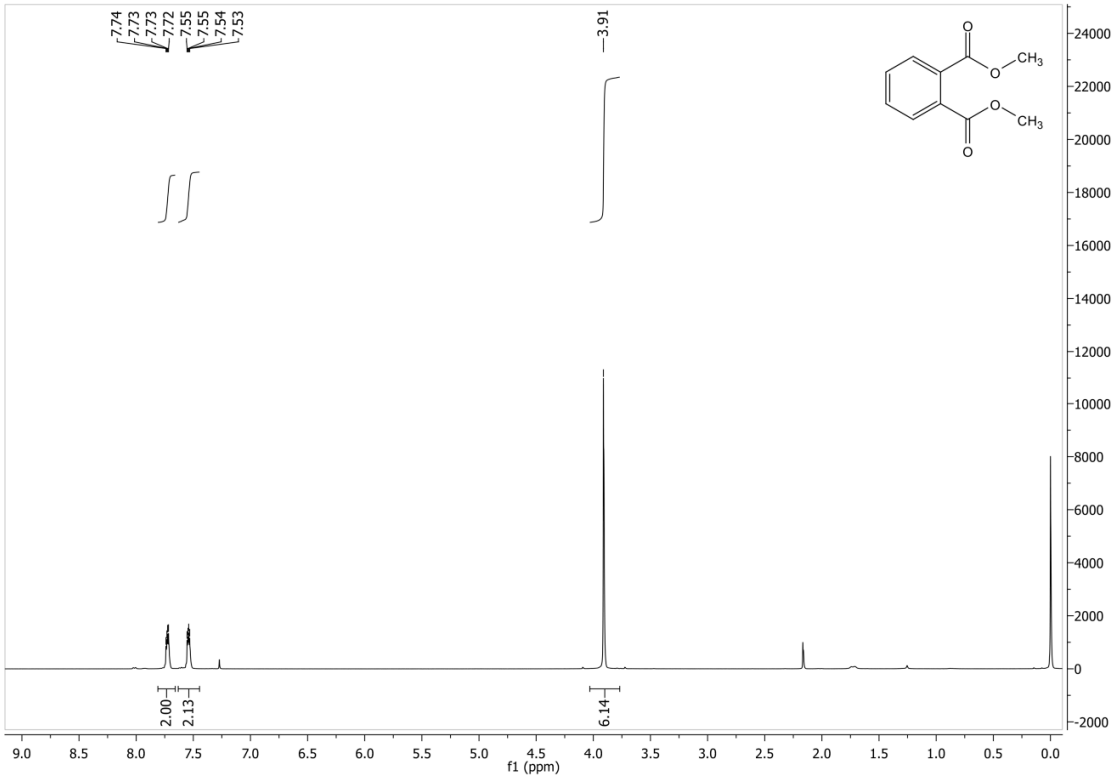


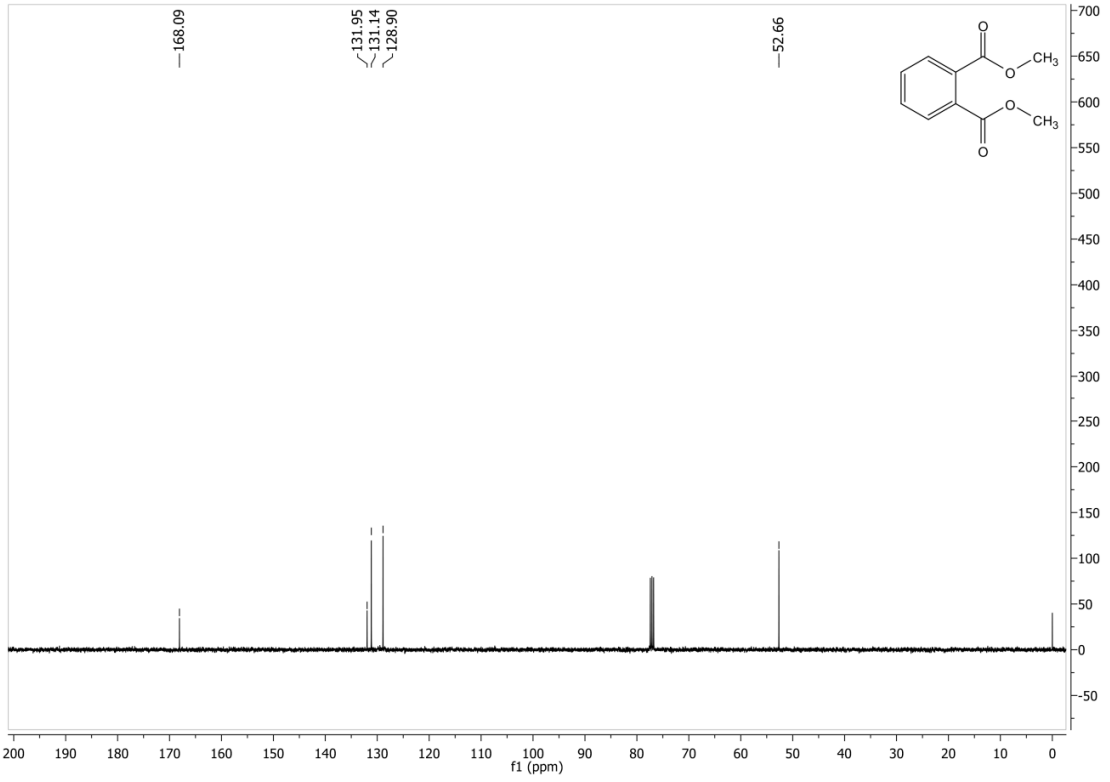
Methyl 2-nitrobenzoate – 10a



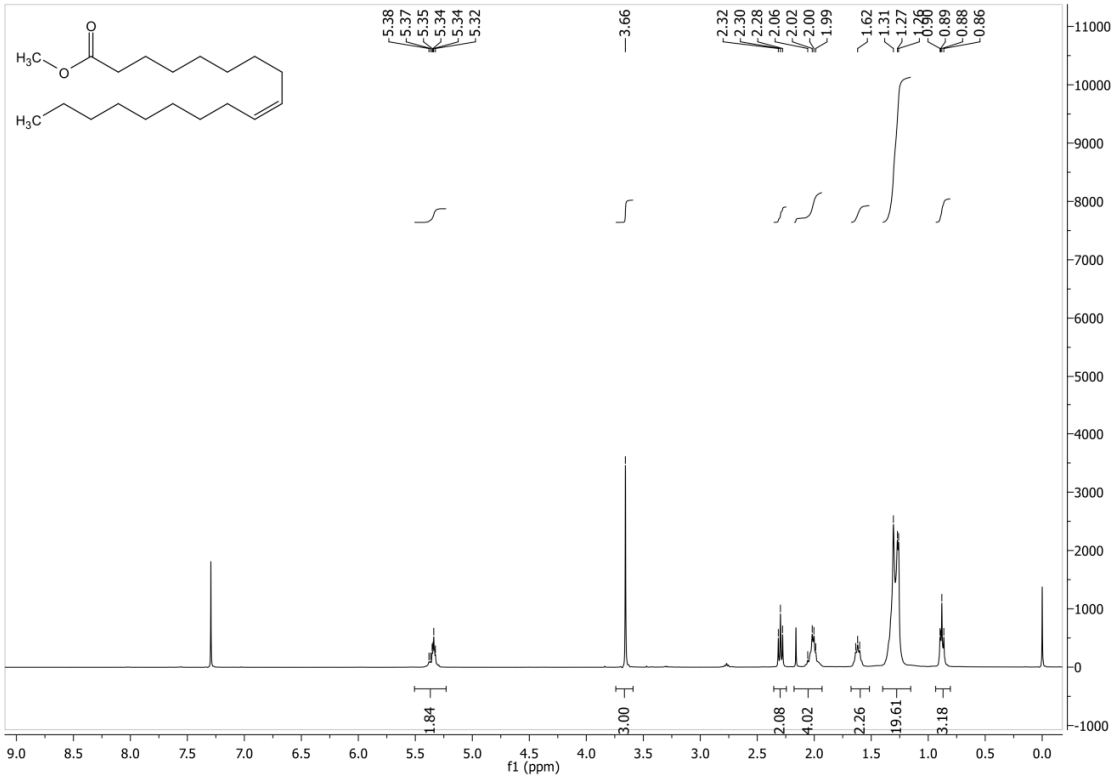


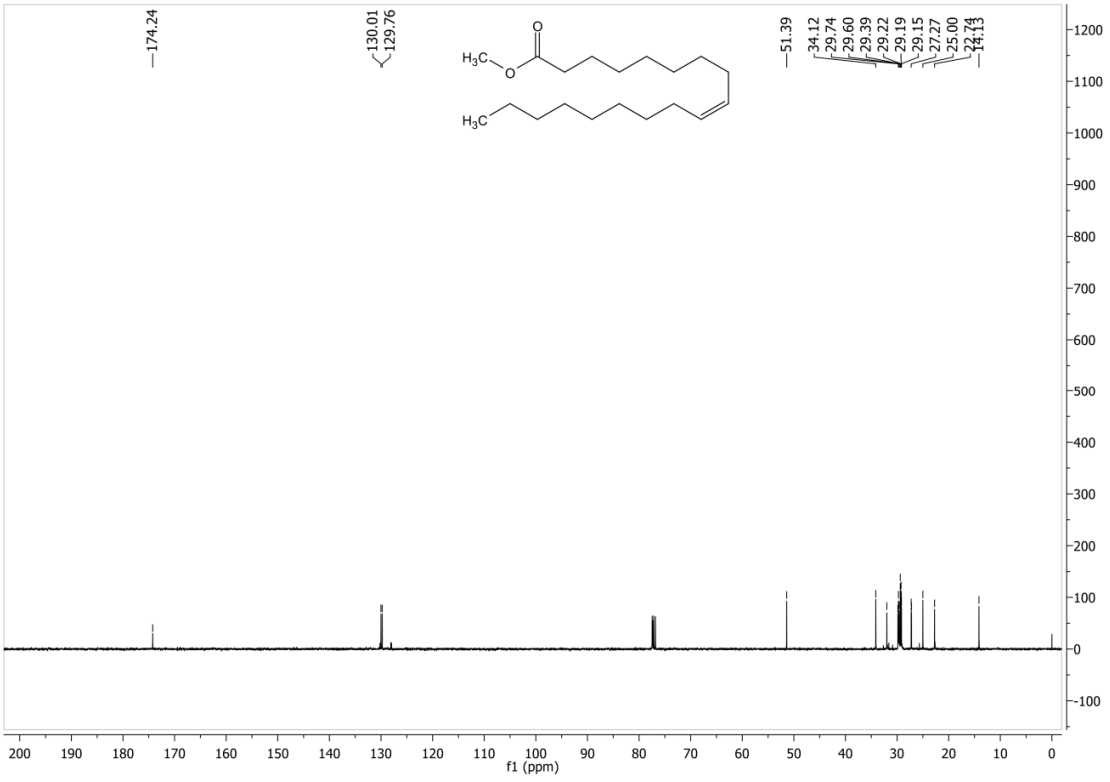
Dimethyl phthalate – 11a



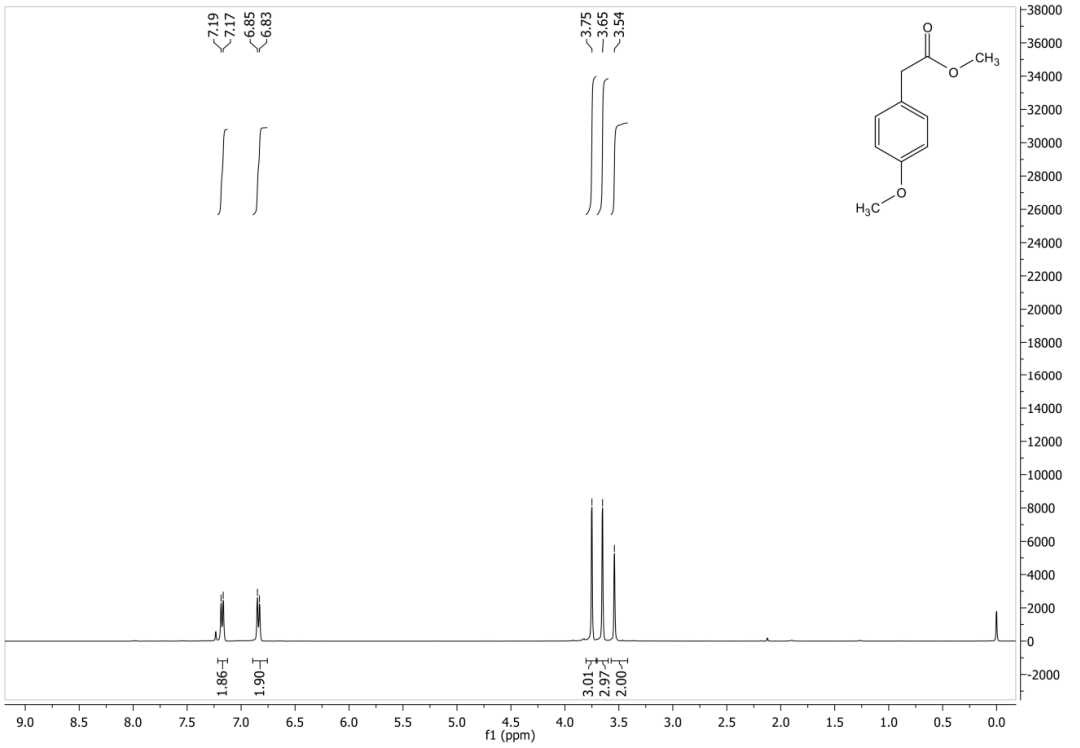


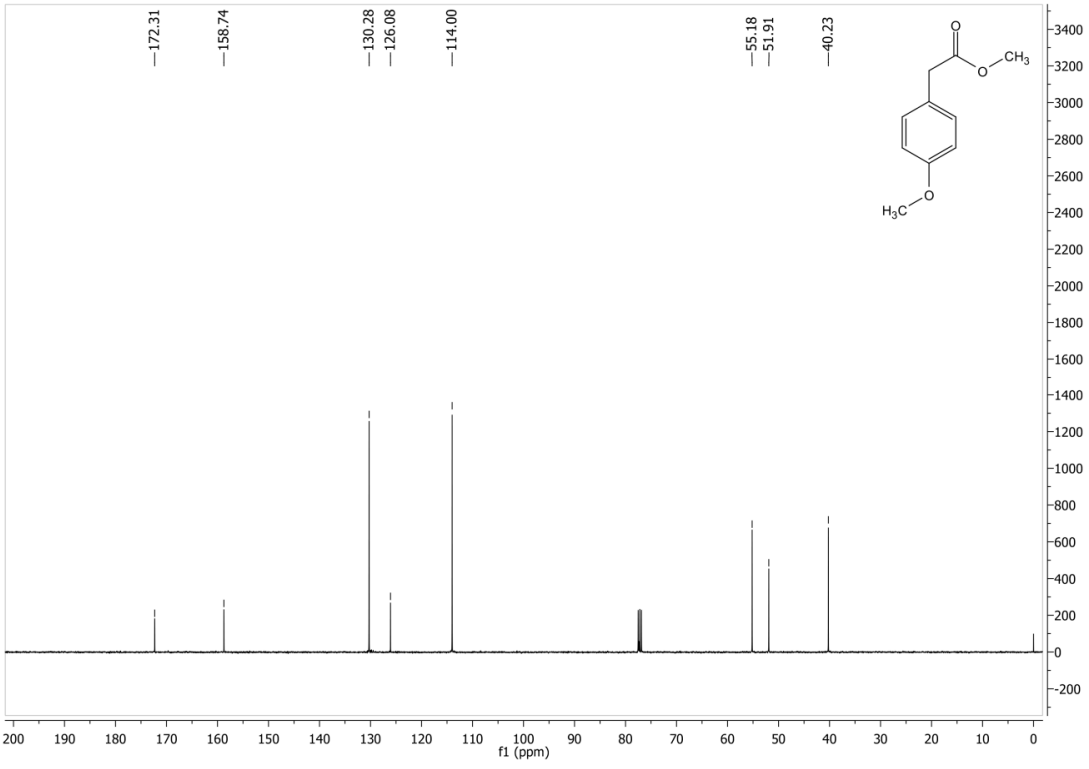
Methyl oleate – 12a



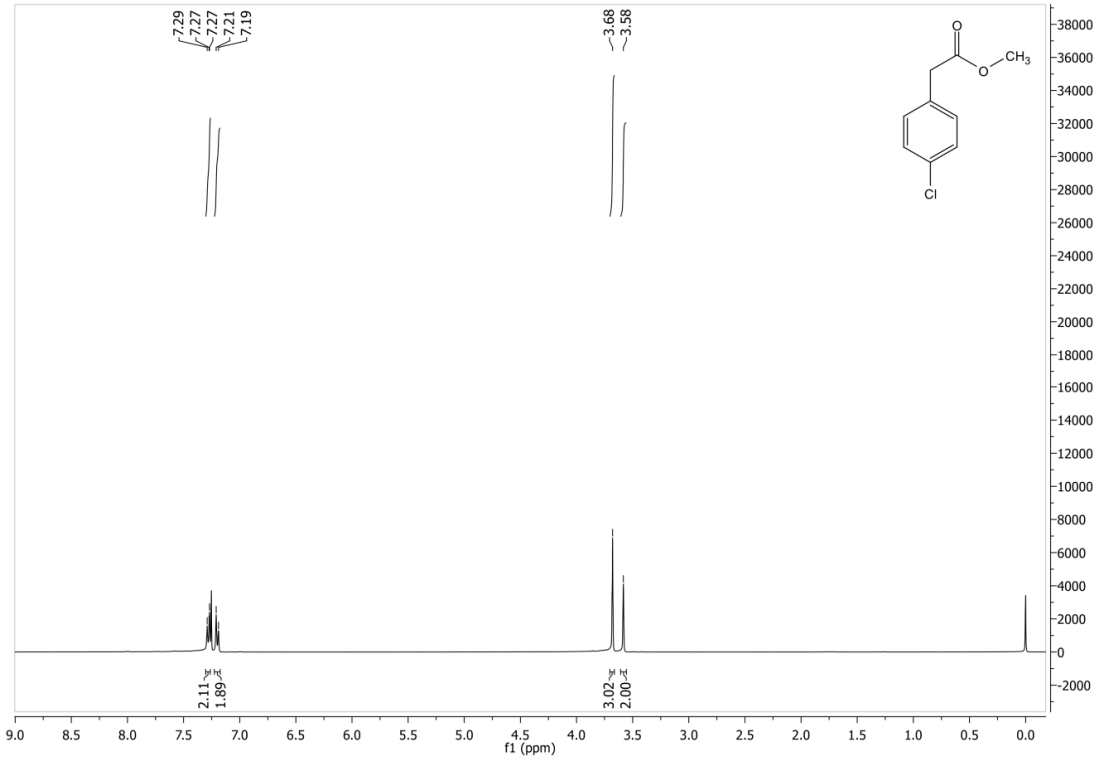


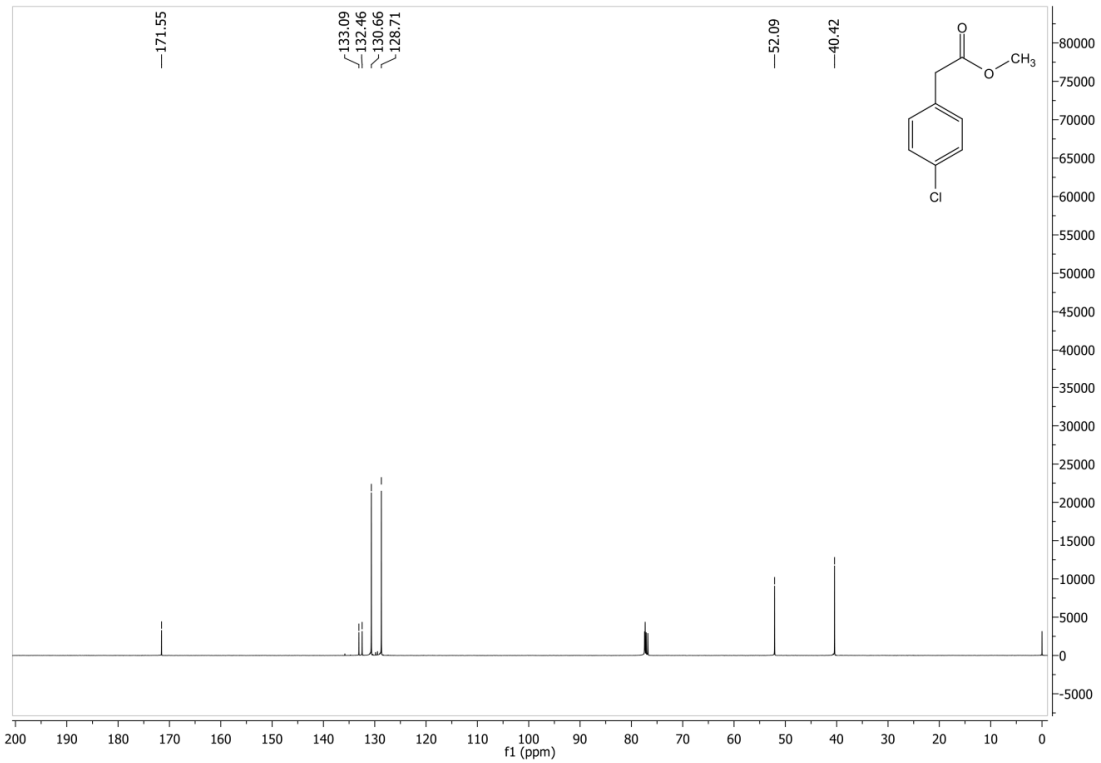
Methyl 4-methoxyphenylacetate – 13a



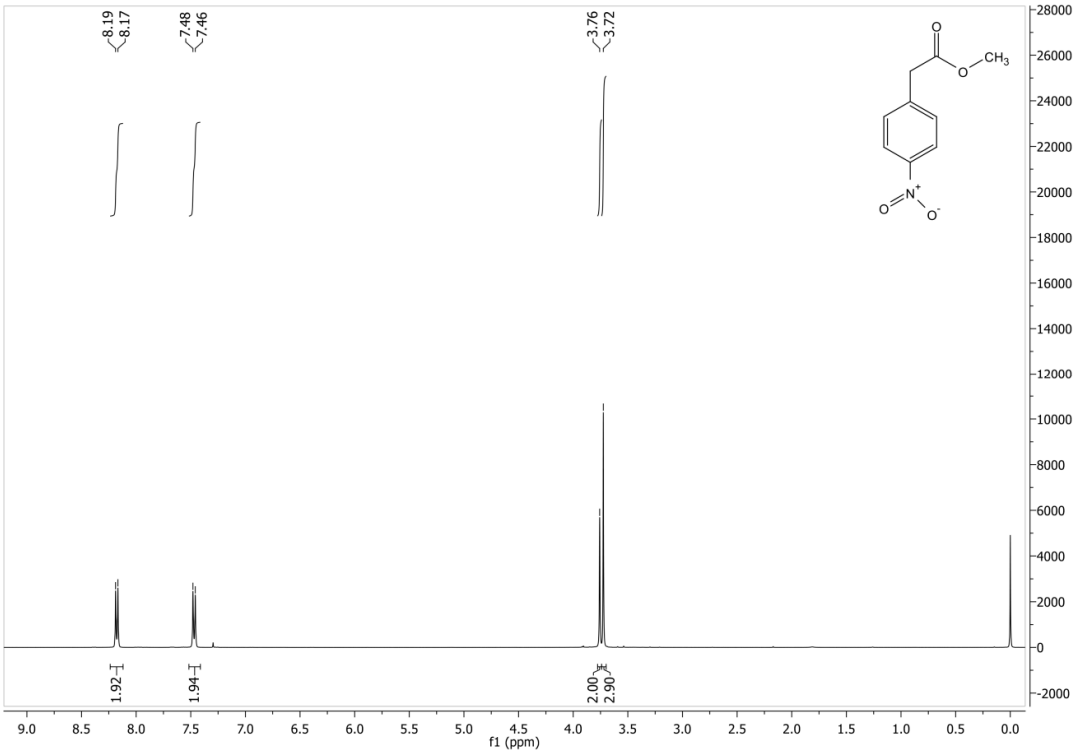


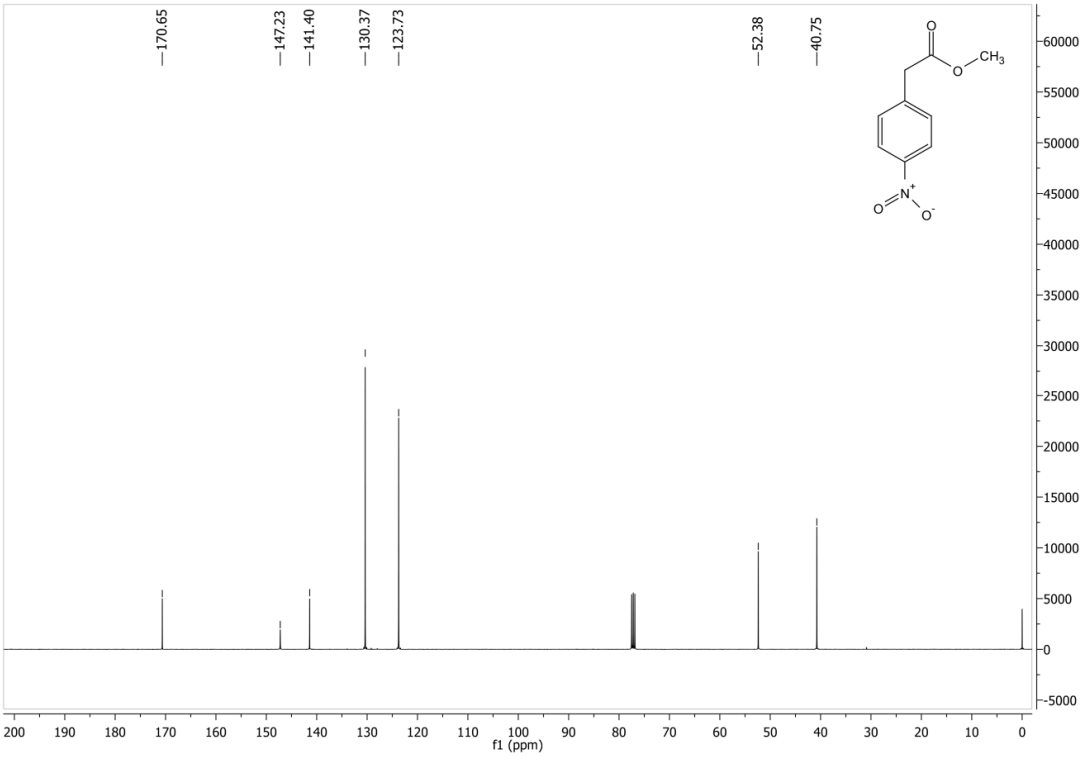
Methyl 4-chlorophenylacetate – 14a



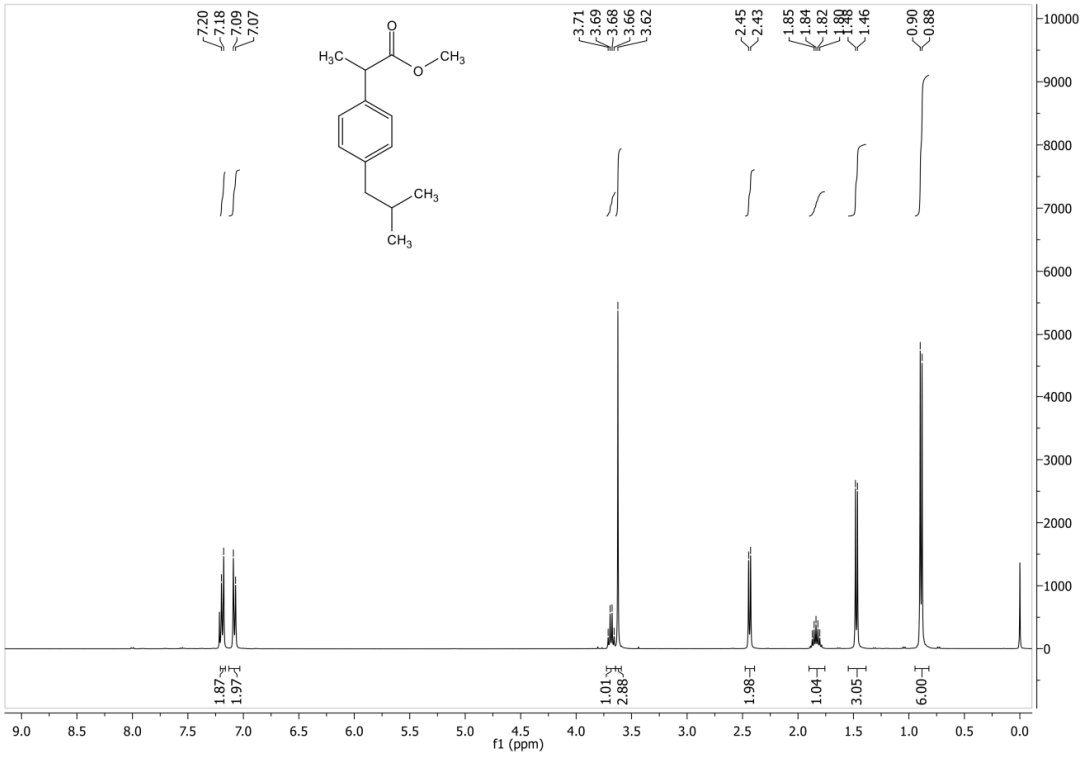


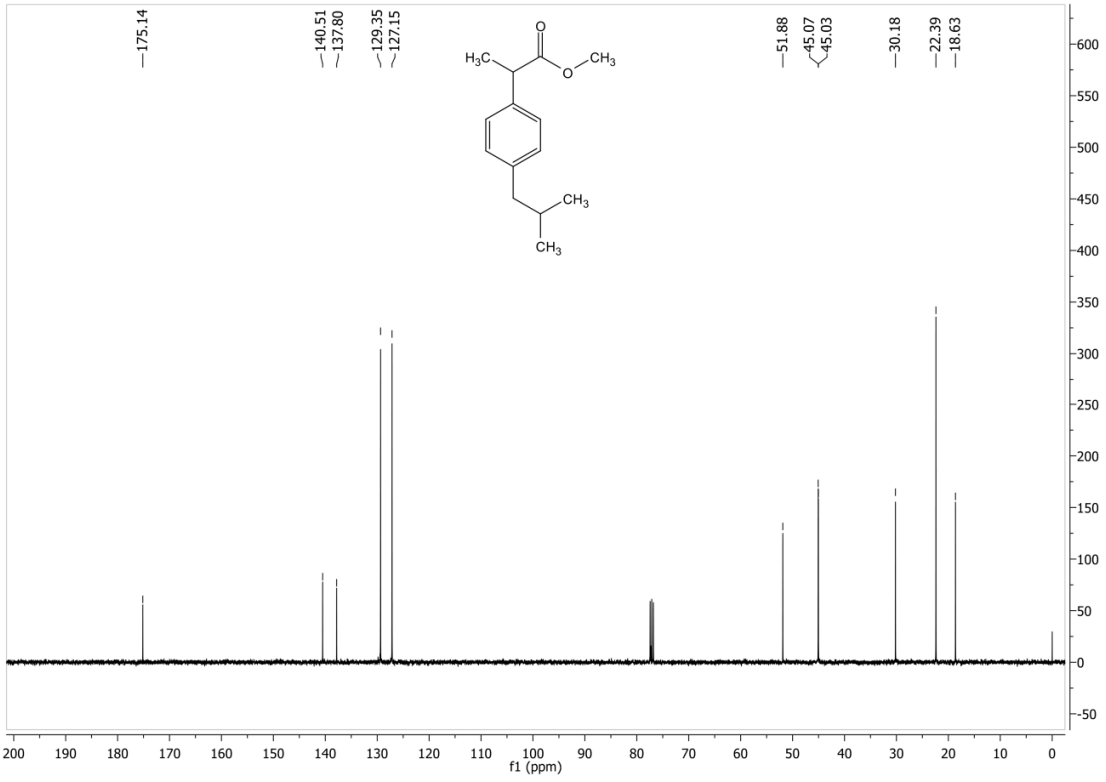
Methyl 4-nitrophenylacetate – 15a



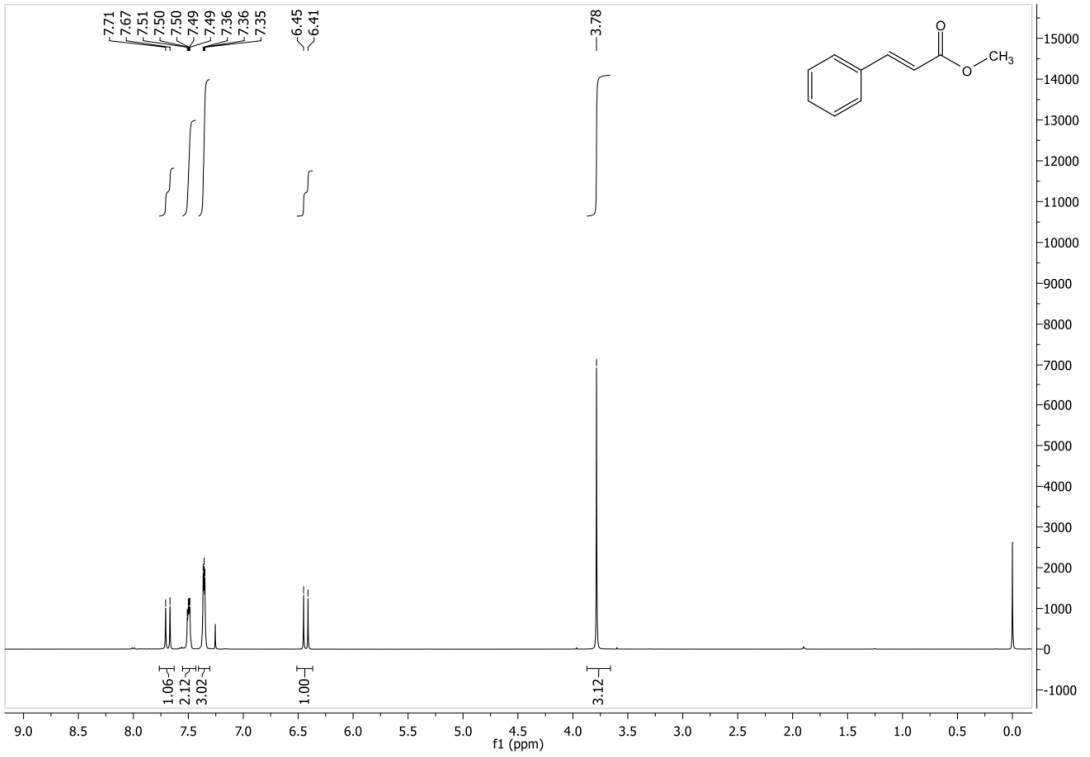


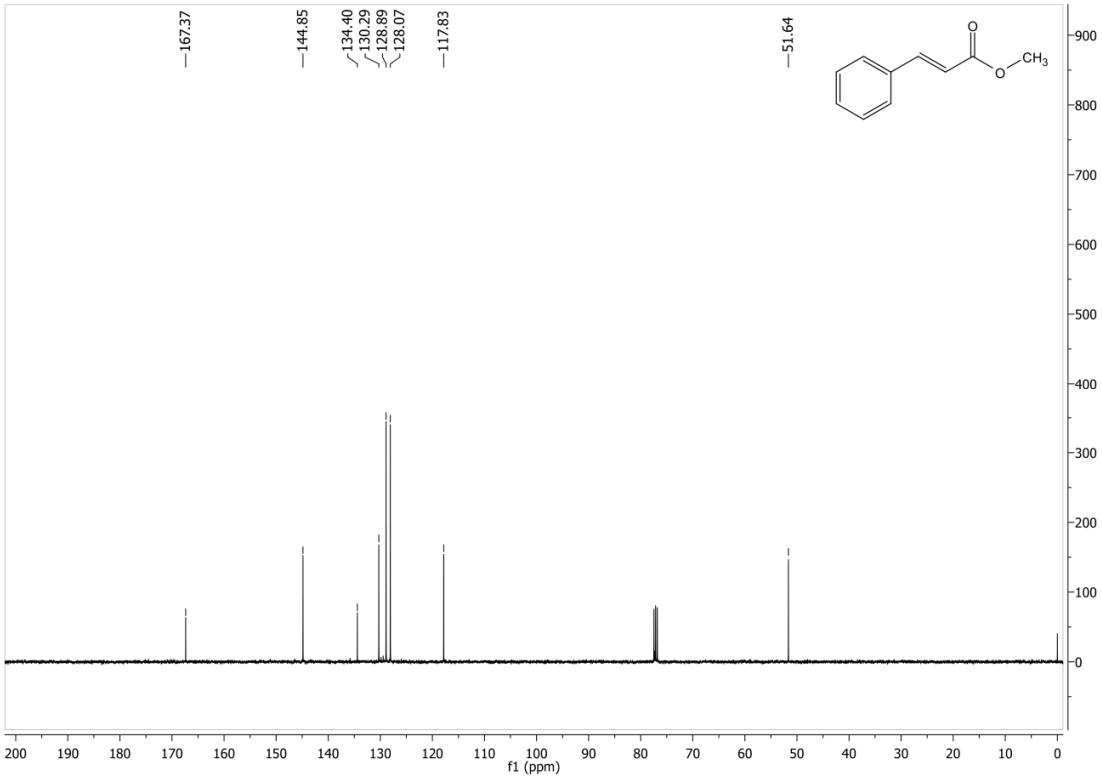
Ibuprofen methyl ester – 16a



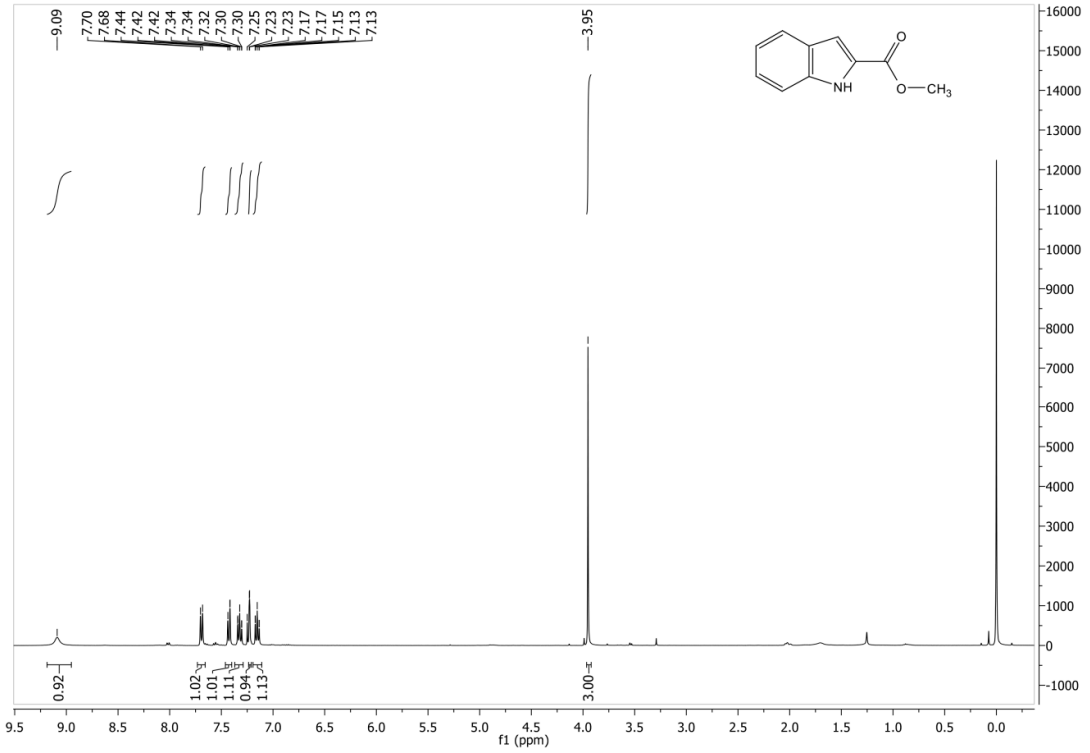


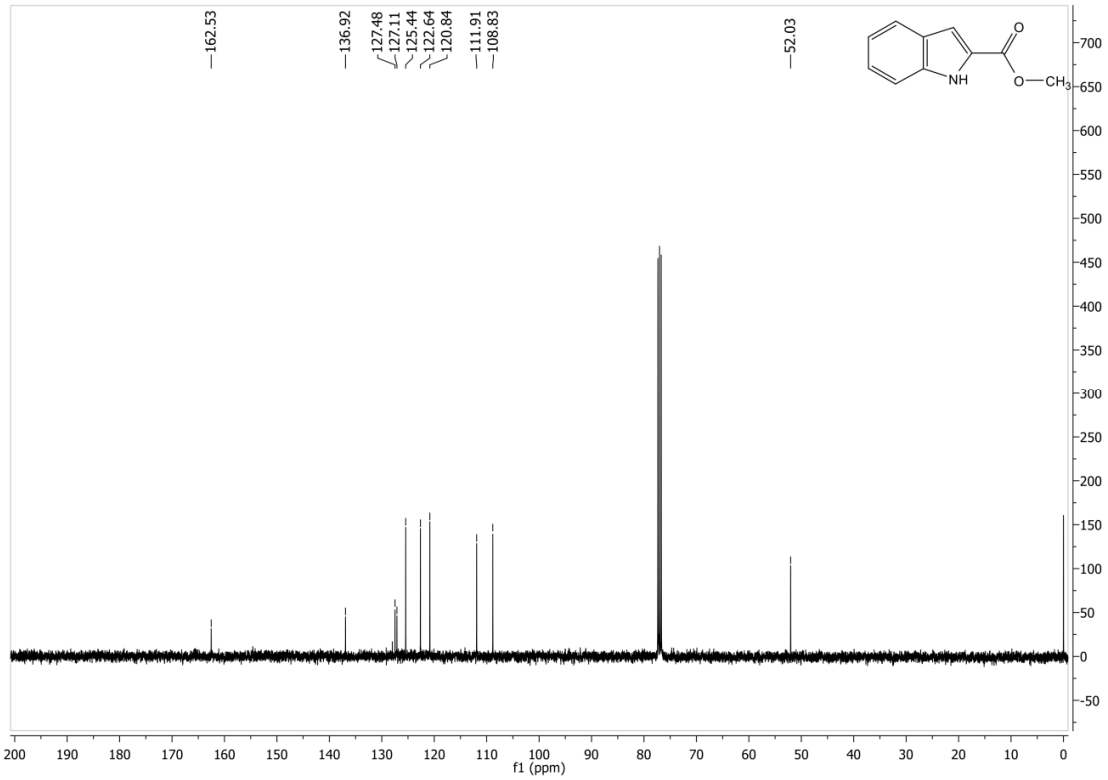
Methyl cinnamate – 17a



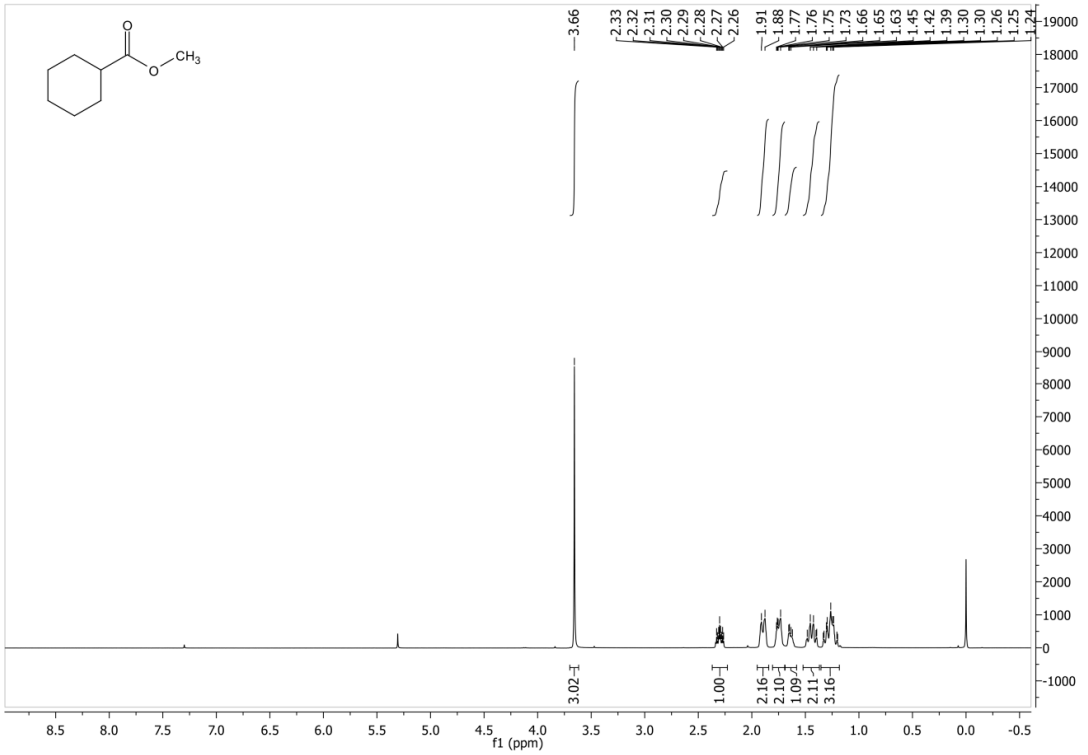


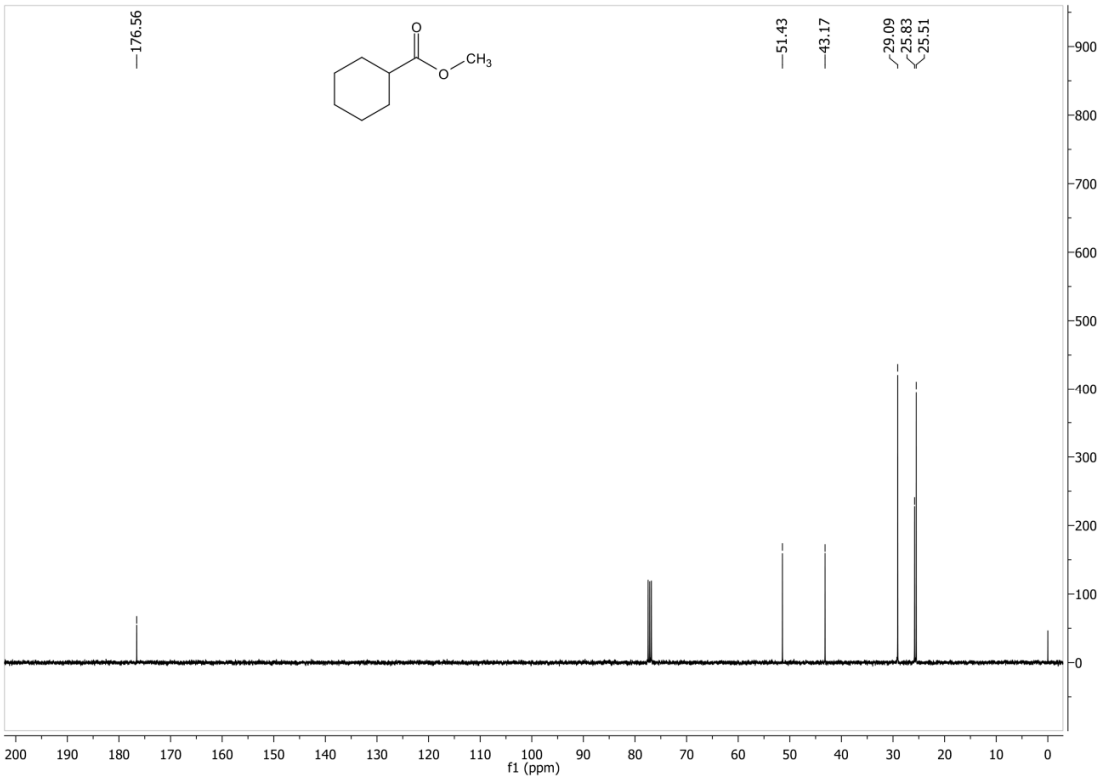
Methyl indol-2-carboxylate – 18a



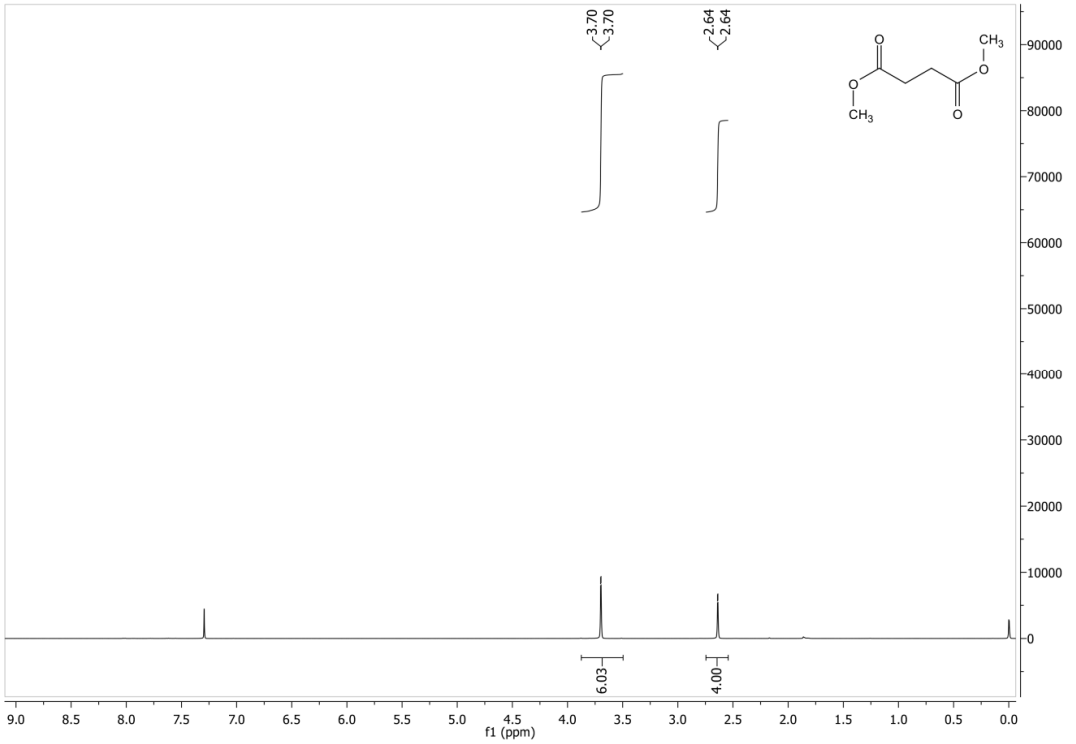


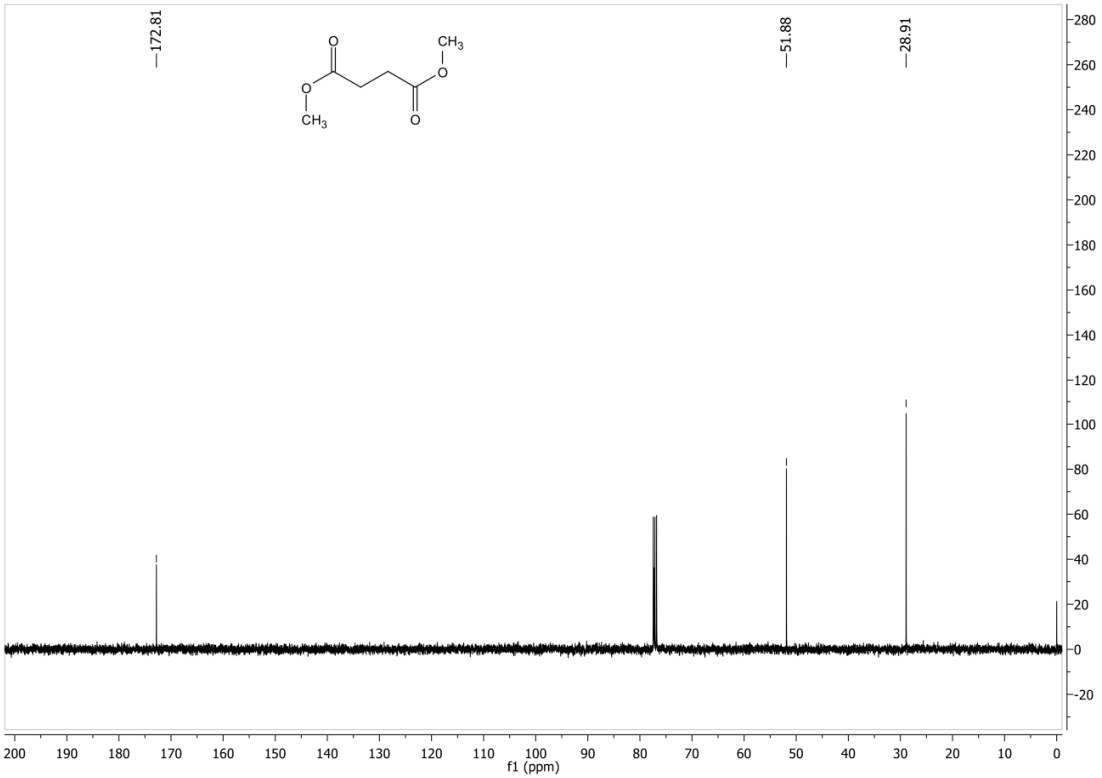
Methyl cyclohexylcarboxylate – 19a



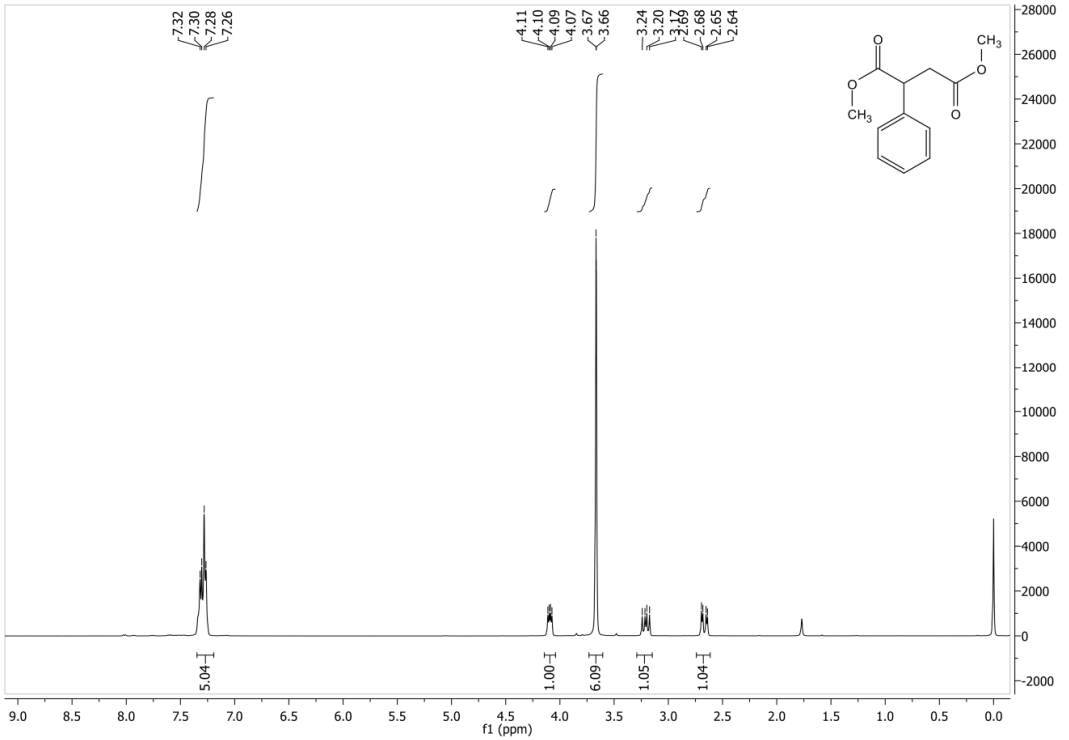


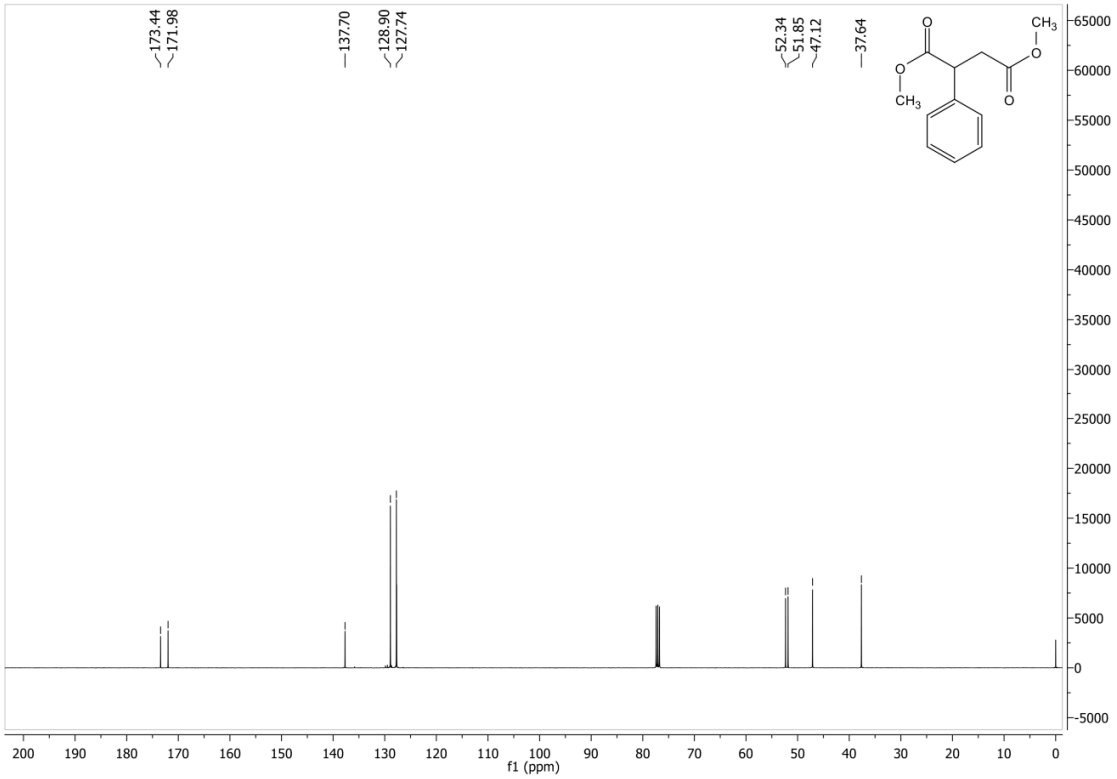
Dimethyl succinate – 21a



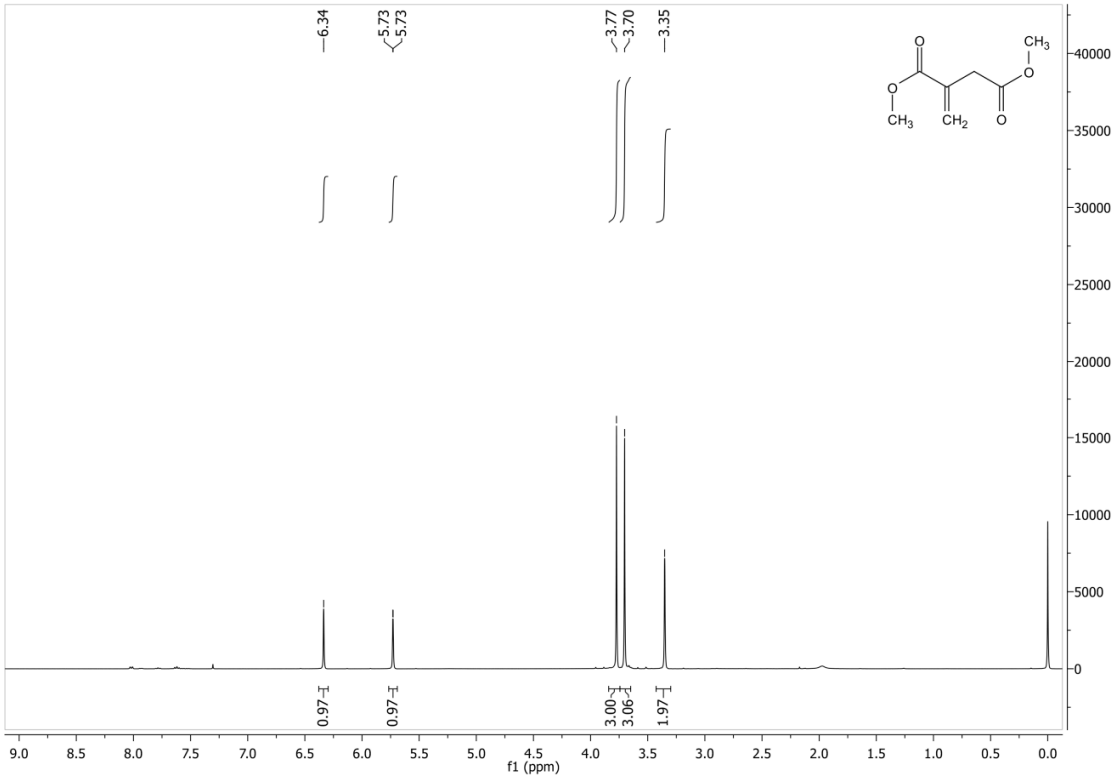


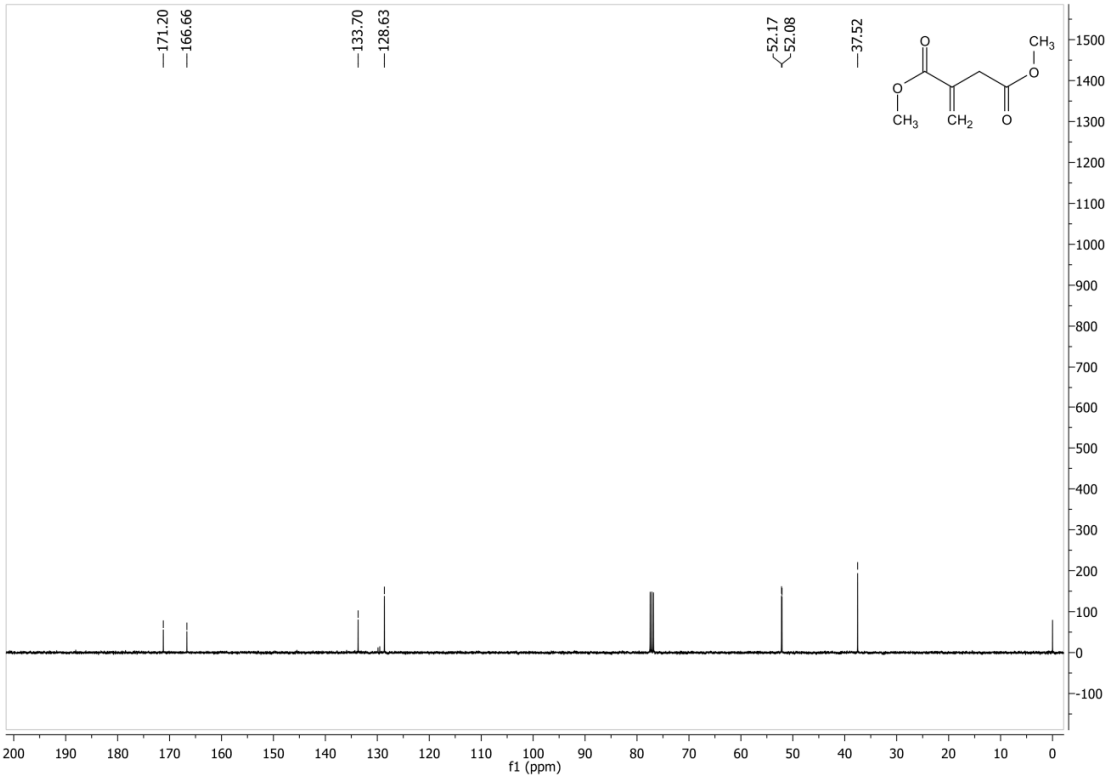
Dimethyl phenylsuccinate – 22a



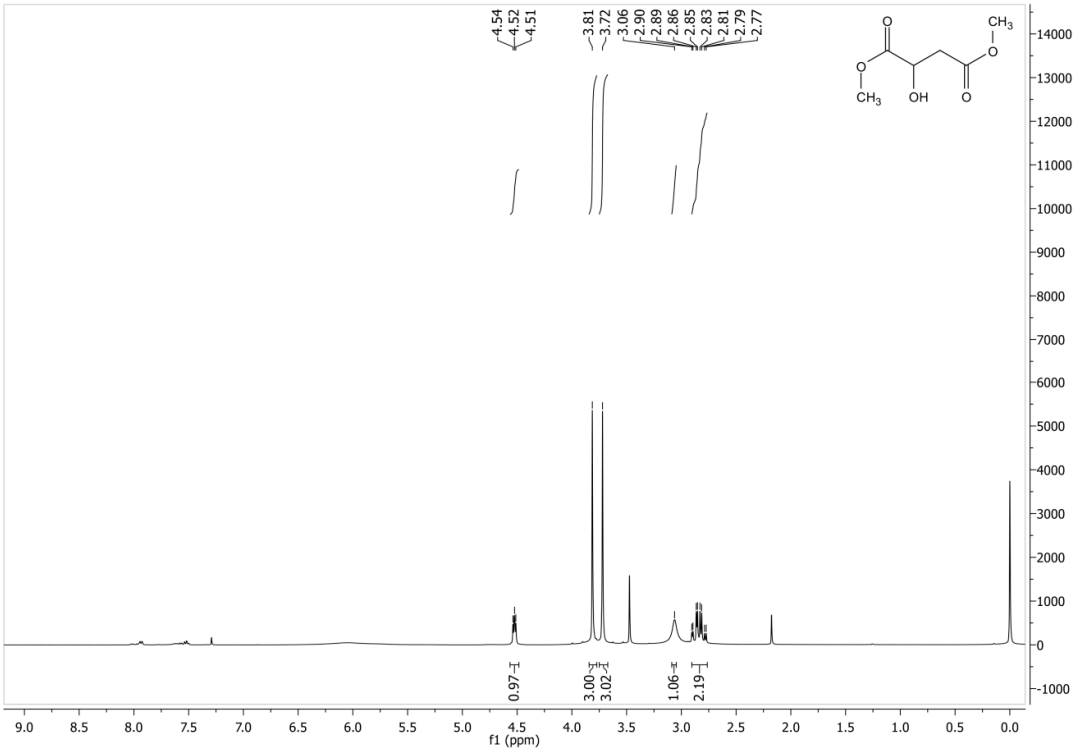


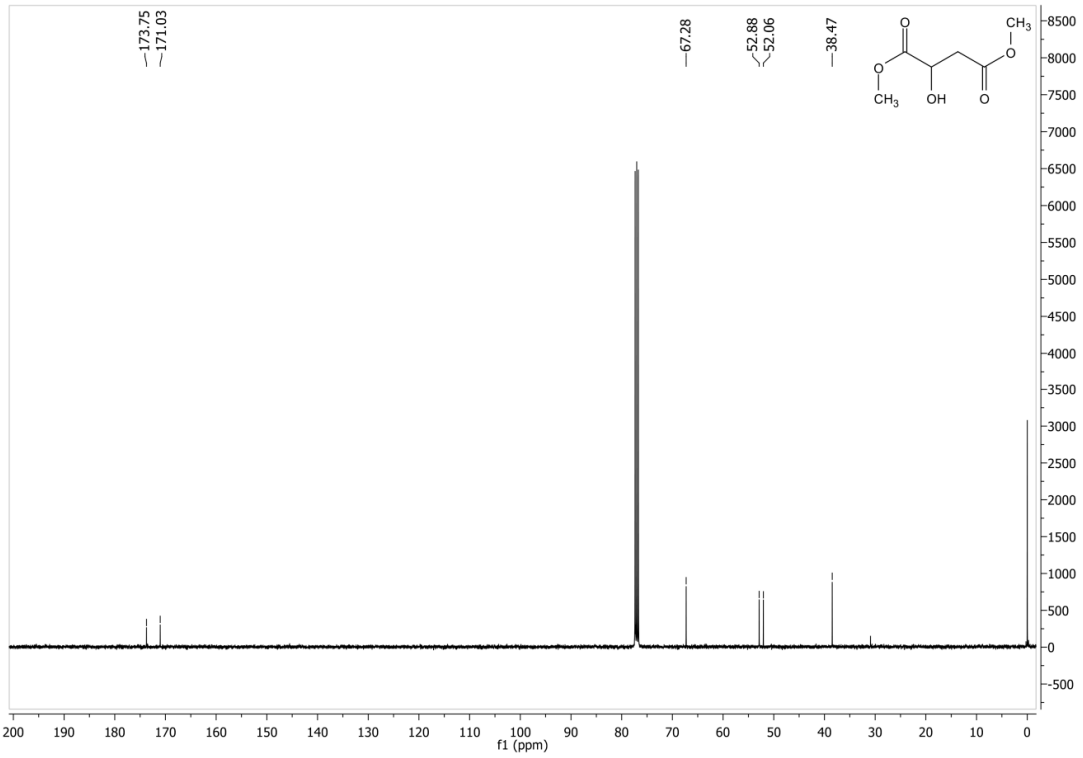
Dimethyl itaconate – 23a



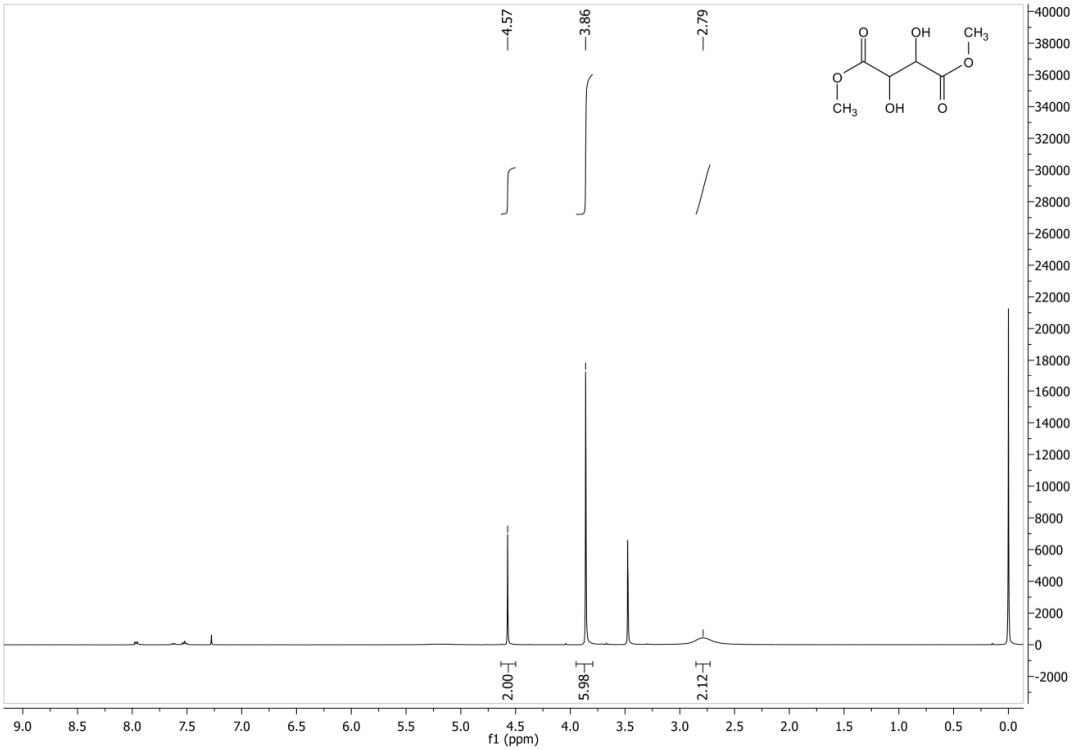


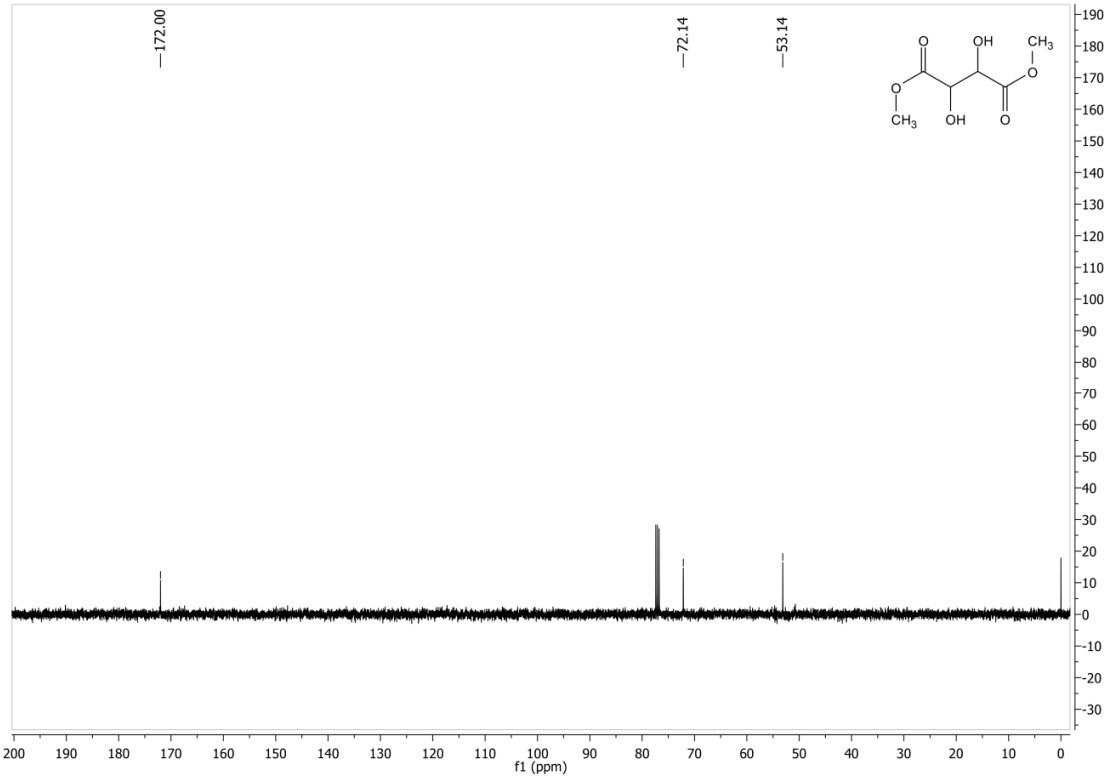
Dimethyl malate – 24a



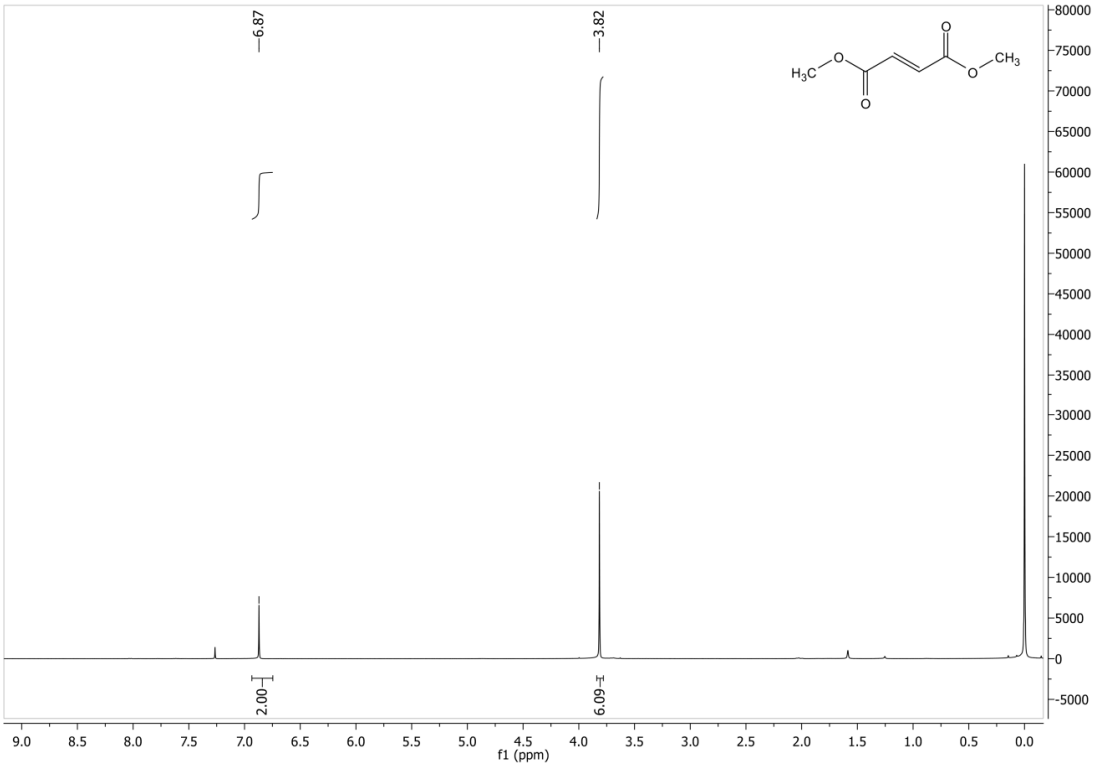


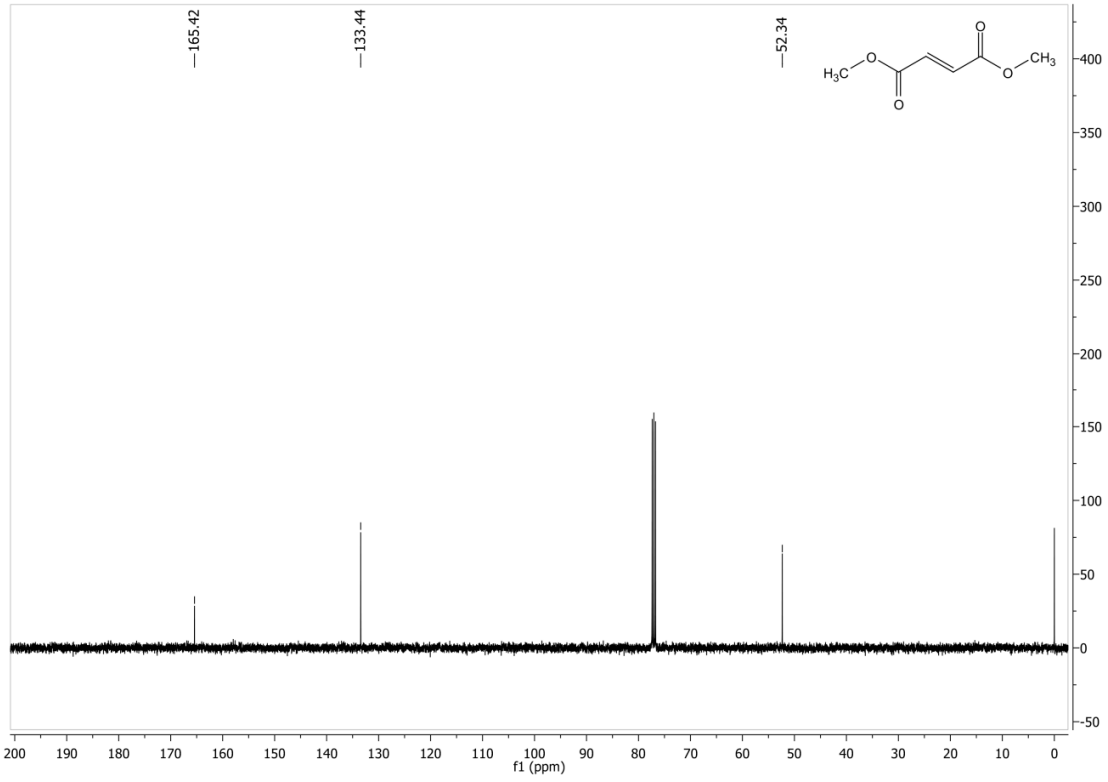
Dimethyl tartarate – 25a



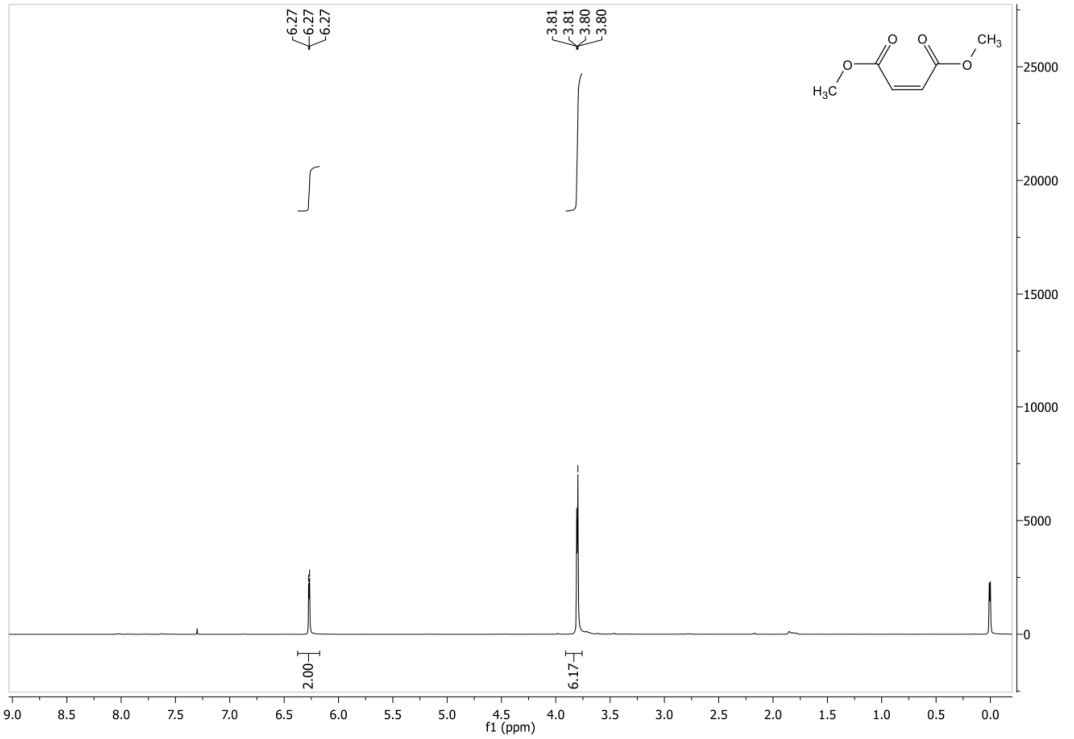


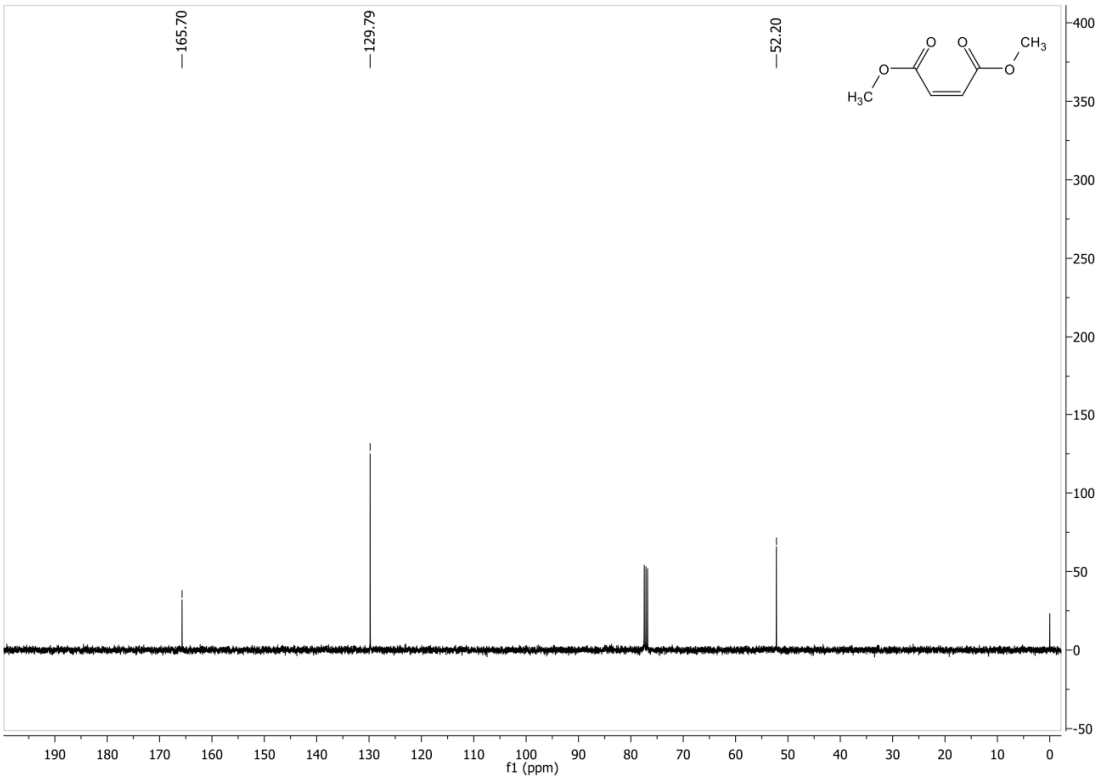
Dimethyl fumarate – 26a



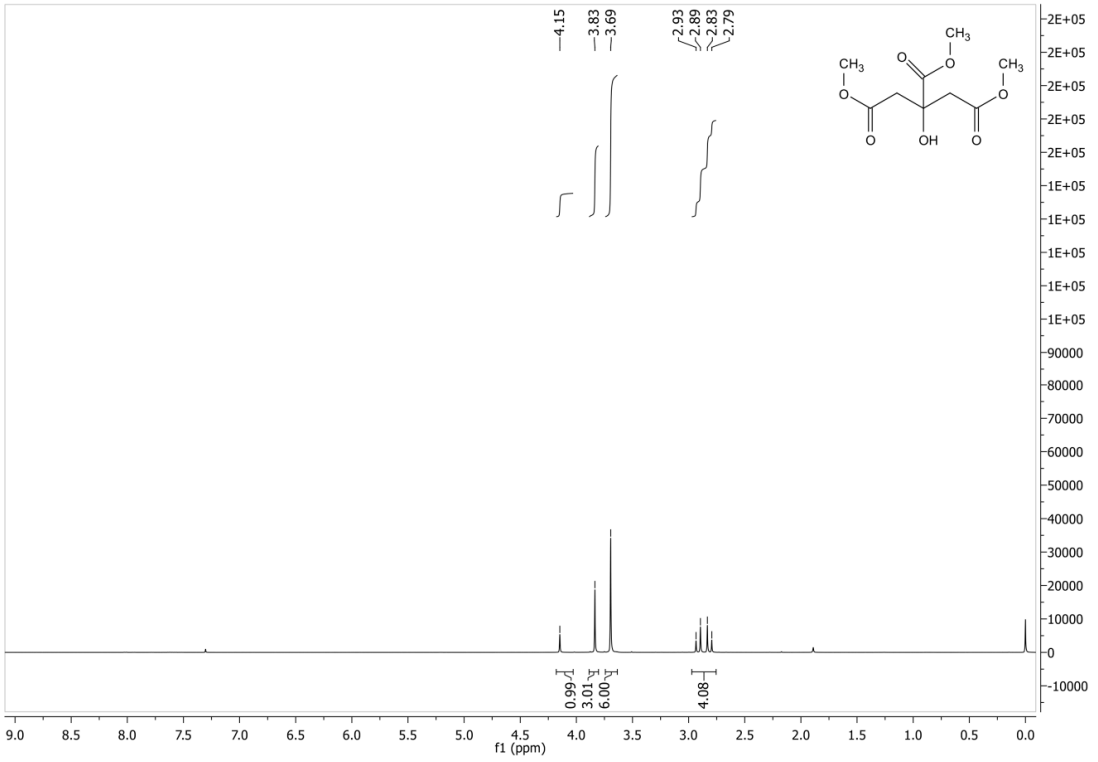


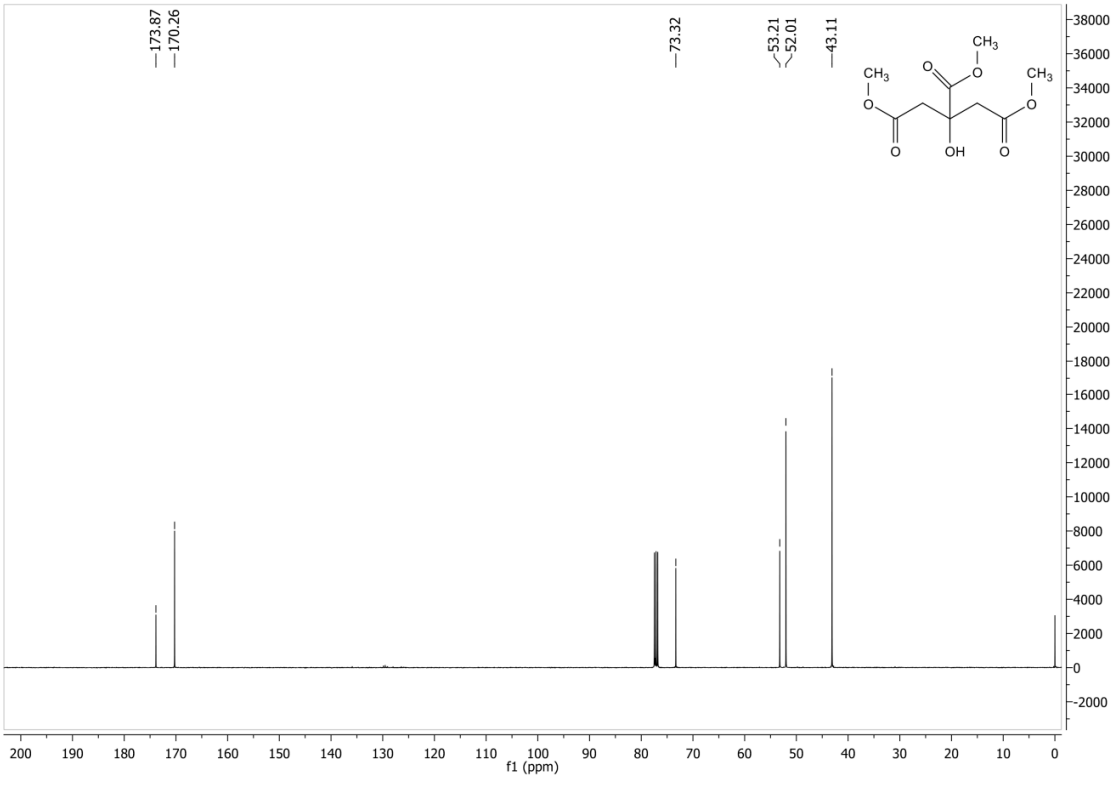
Dimethyl maleate – 27a



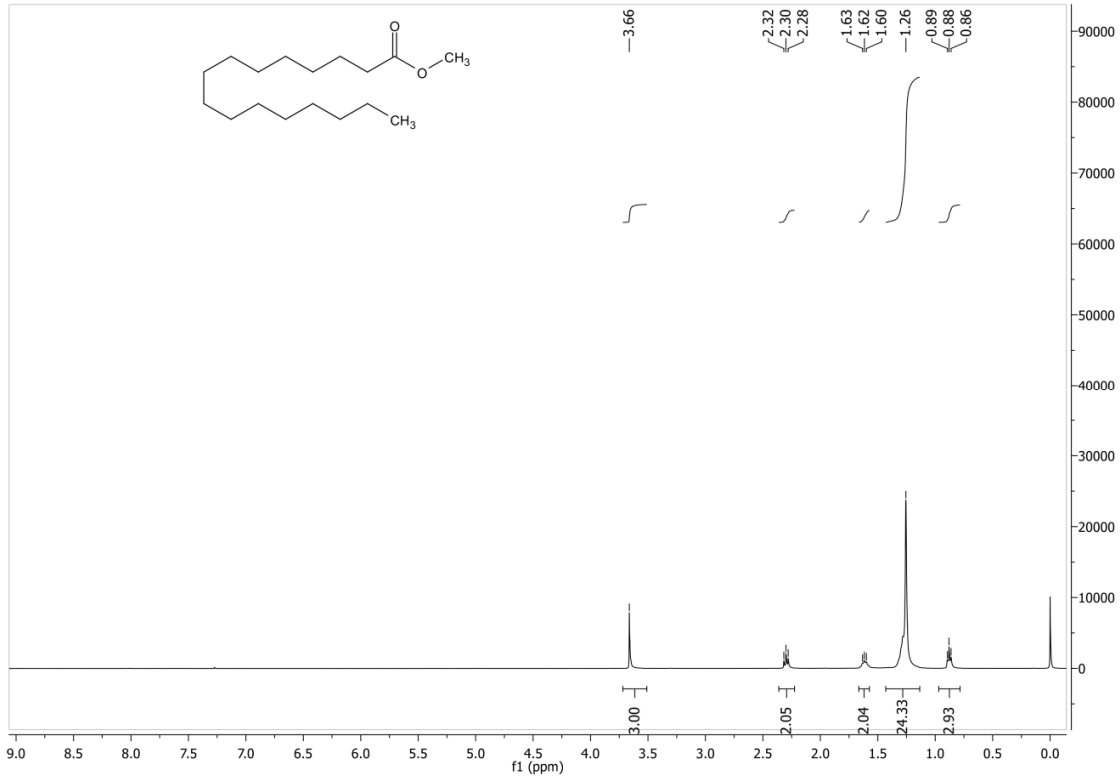


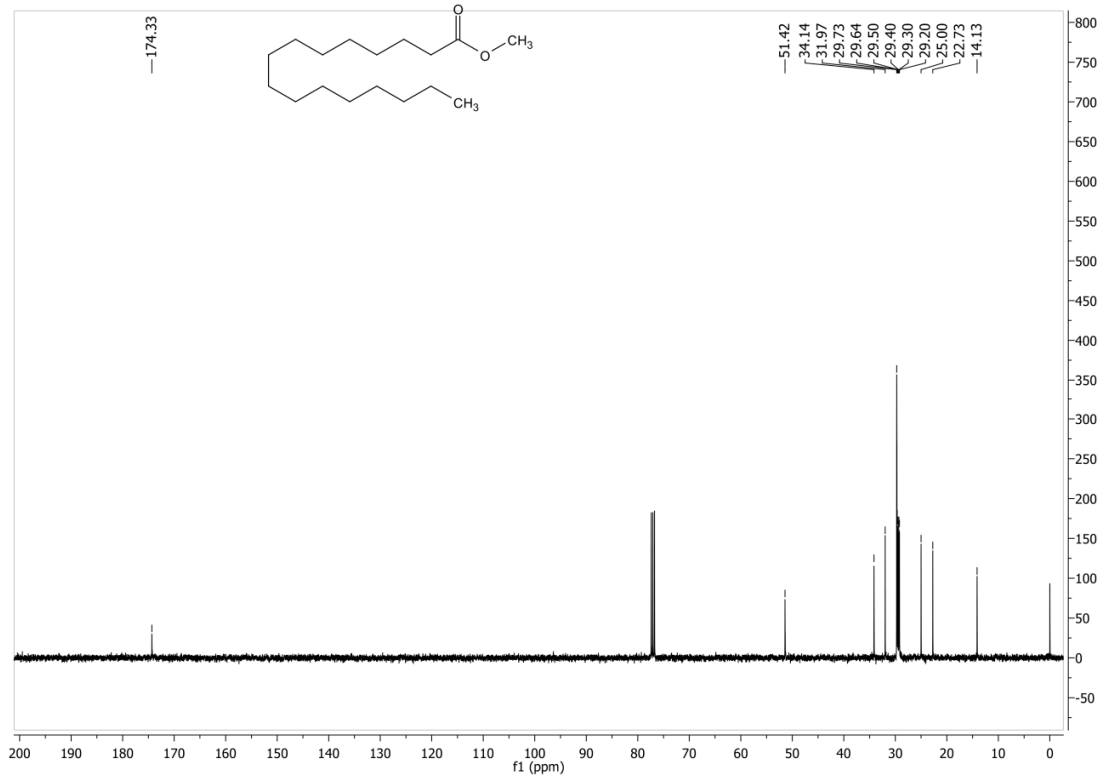
Trimethyl citrate – 28a



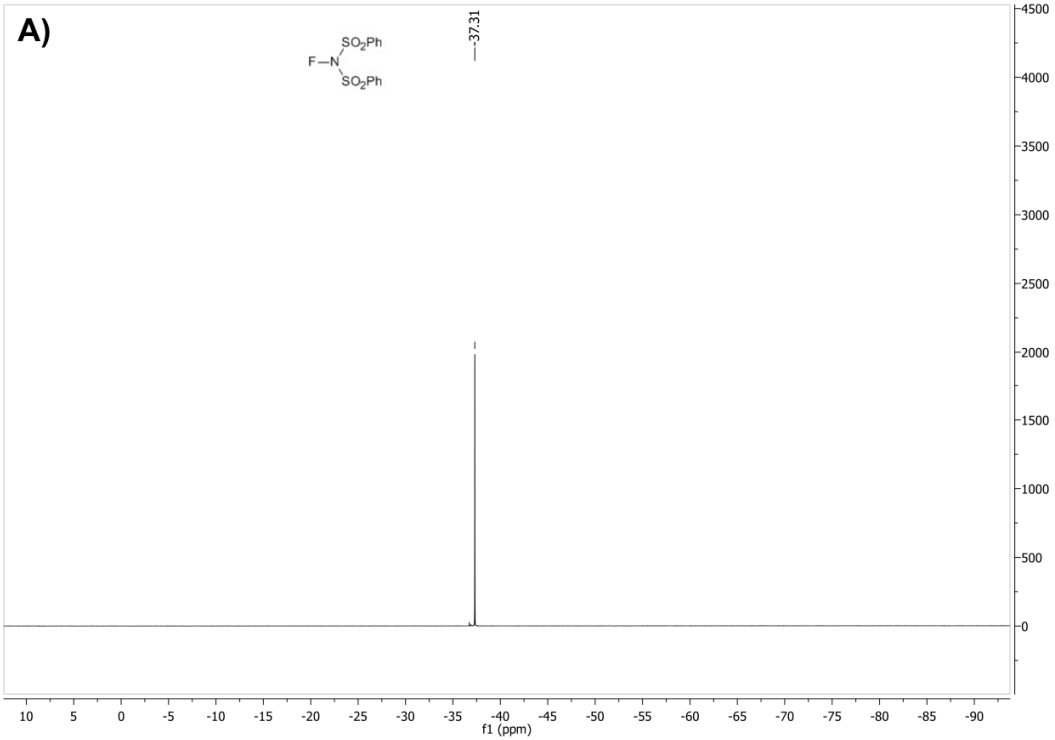


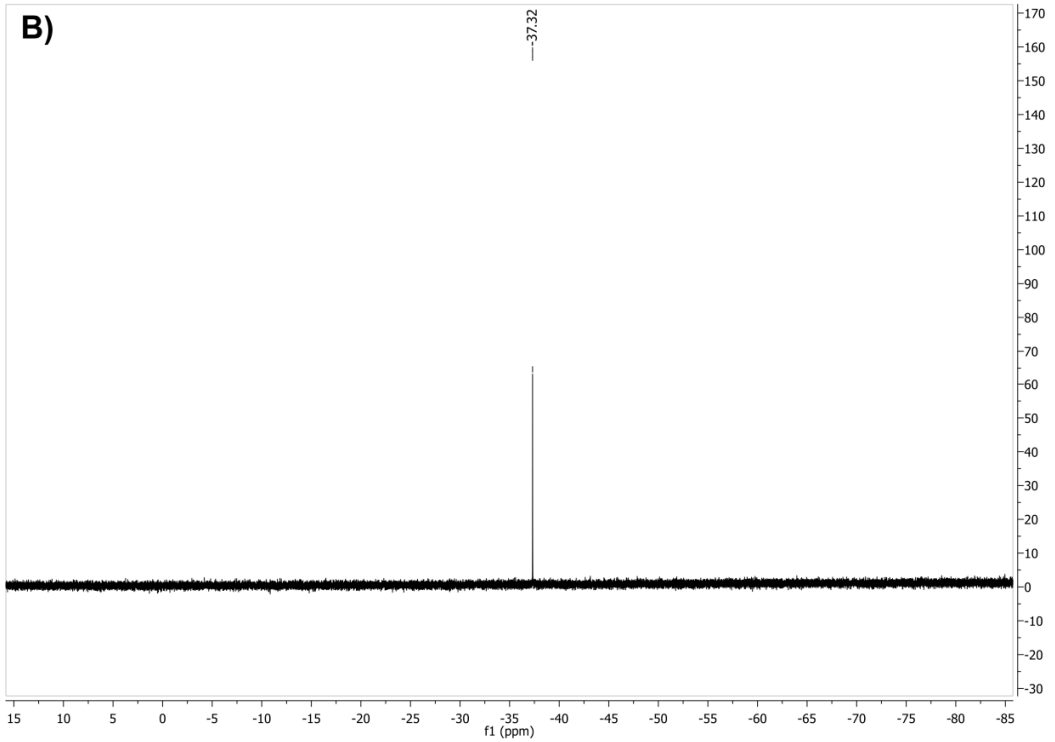
Methyl palmitate – 30a





List S3. ^{19}F NMR spectra of NFSi (**A**) and crude reaction mixture of cinnamic acid, MeOH and NFSi (**B**).





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