Electronic Supplementary Material (ESI) for Polymer Chemistry.

Wholly biomass derivable sustainable polymers by ring-opening metathesis polymerisation of monomers obtained from furfuryl alcohol and itaconic anhydride

Supplementary Information

Yinjuan Bai, James H. Clark, Thomas J. Farmer, Ian D. V. Ingram and Michael North

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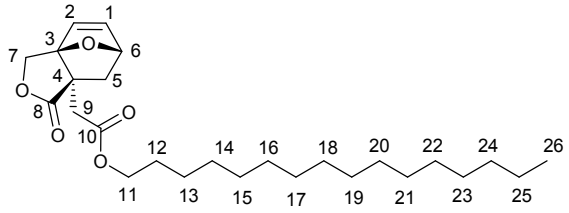
The original data associated with this research is available at:
DOI: 10.15124/f4cf9761-ba74-4de4-9903-16261b5baa7c

Cetyl ester 8b



Not all ^{13}C peaks within the cetyl chain are resolved or have been assigned.

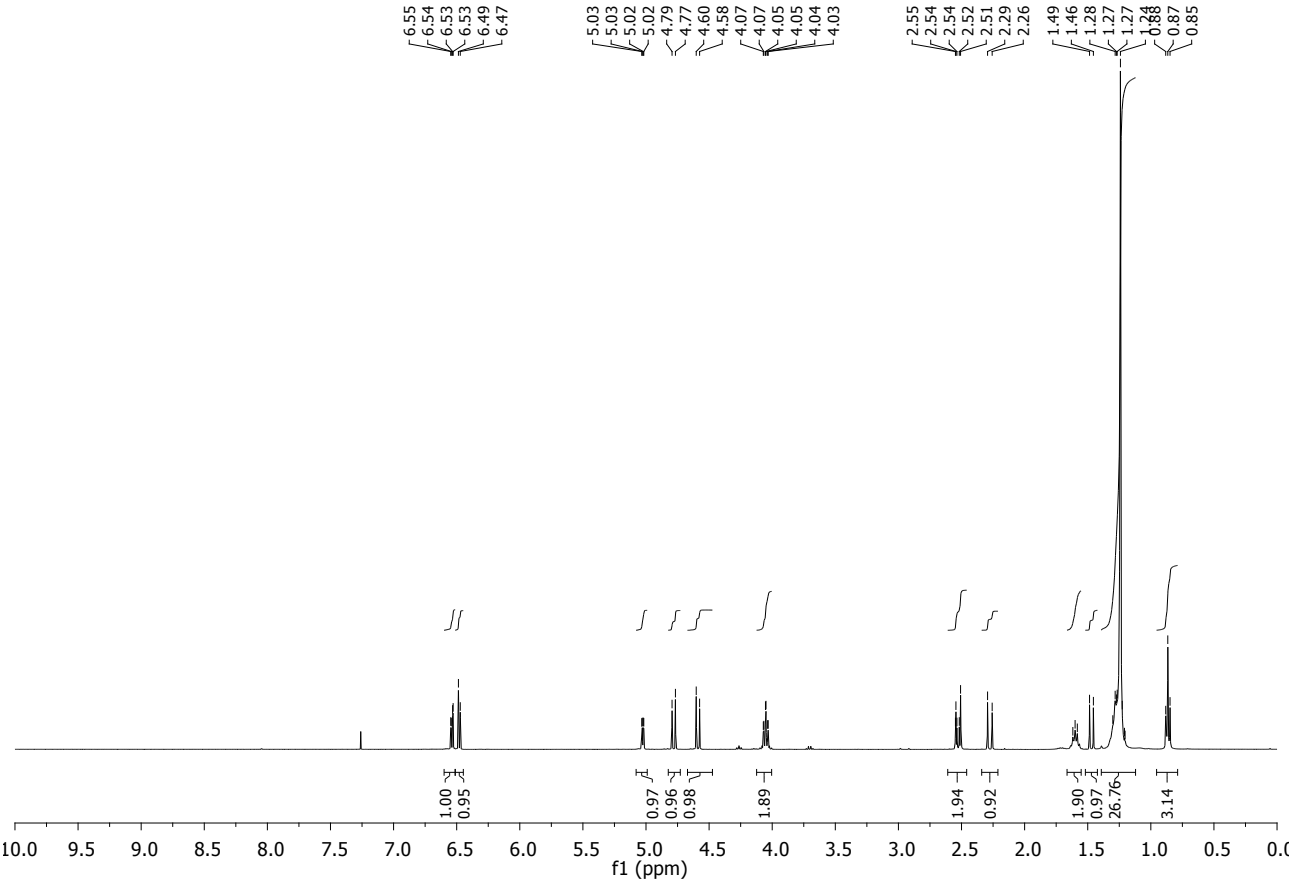
^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 6.54 (1H, dd, *J* 5.8, 1.7 Hz, H1), 6.48 (1H, d, *J* 5.8 Hz, H2), 5.03 (1H, dd, *J* 4.7, 1.6 Hz, H6), 4.78 (1 H, d, *J* 10.7 Hz, H7), 4.59 (1H, d, *J* 10.7 Hz, H7), 4.05 (2H, td, *J* 6.8, 1.7 Hz, H11), 2.6–2.4 (2H, m, H5+H9), 2.28 (1H, d, *J* 14.6 Hz, H9), 1.7– 1.5 (2H, m, H12), 1.47 (1H, d, *J* 12.2 Hz, H5), 1.4–1.1 (26H, m, H13-25), 0.87 (3H, t, *J* 6.8 Hz, H26).

^{13}C NMR ($CDCl_3$, 101 MHz) δ_C 177.2 (C8), 169.7 (C10), 138.1 (C1), 130.8 (C2), 94.2 (C3), 78.8 (C6), 68.9 (C7), 65.7 (C11), 53.6 (C12), 52.2 (C4), 40.3 (C9), 36.8 (C5), 32.1, 29.8, 29.7, 29.6, 29.5, 29.3, 28.5, 26.0, 22.8, 14.3 (C26).

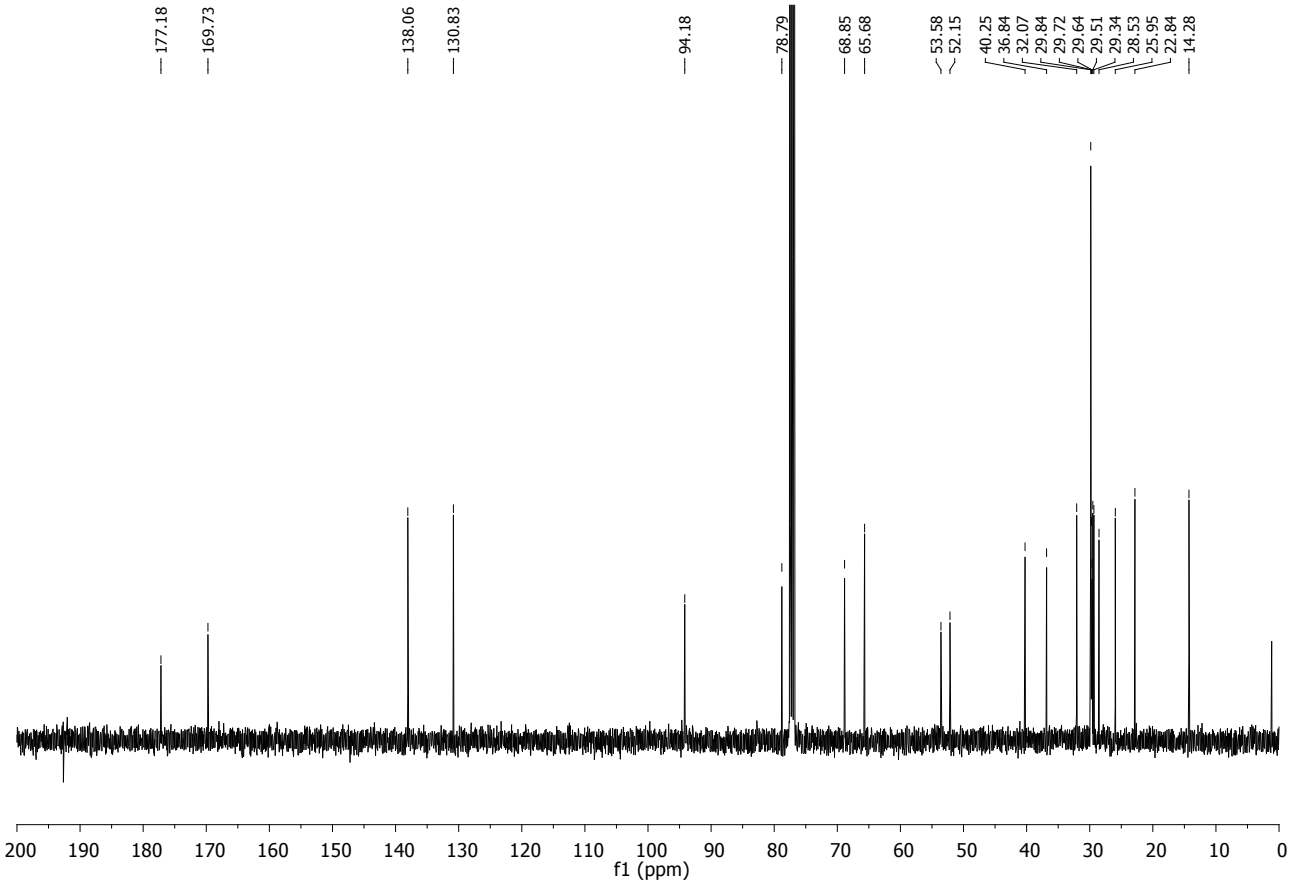
FTIR (neat, ATR) ν_{max} 3013, 2952, 2913, 2850, 1768 and 1739 cm^{-1}

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{26}H_{42}NaO_5$ 457.2924, Found 457.2929

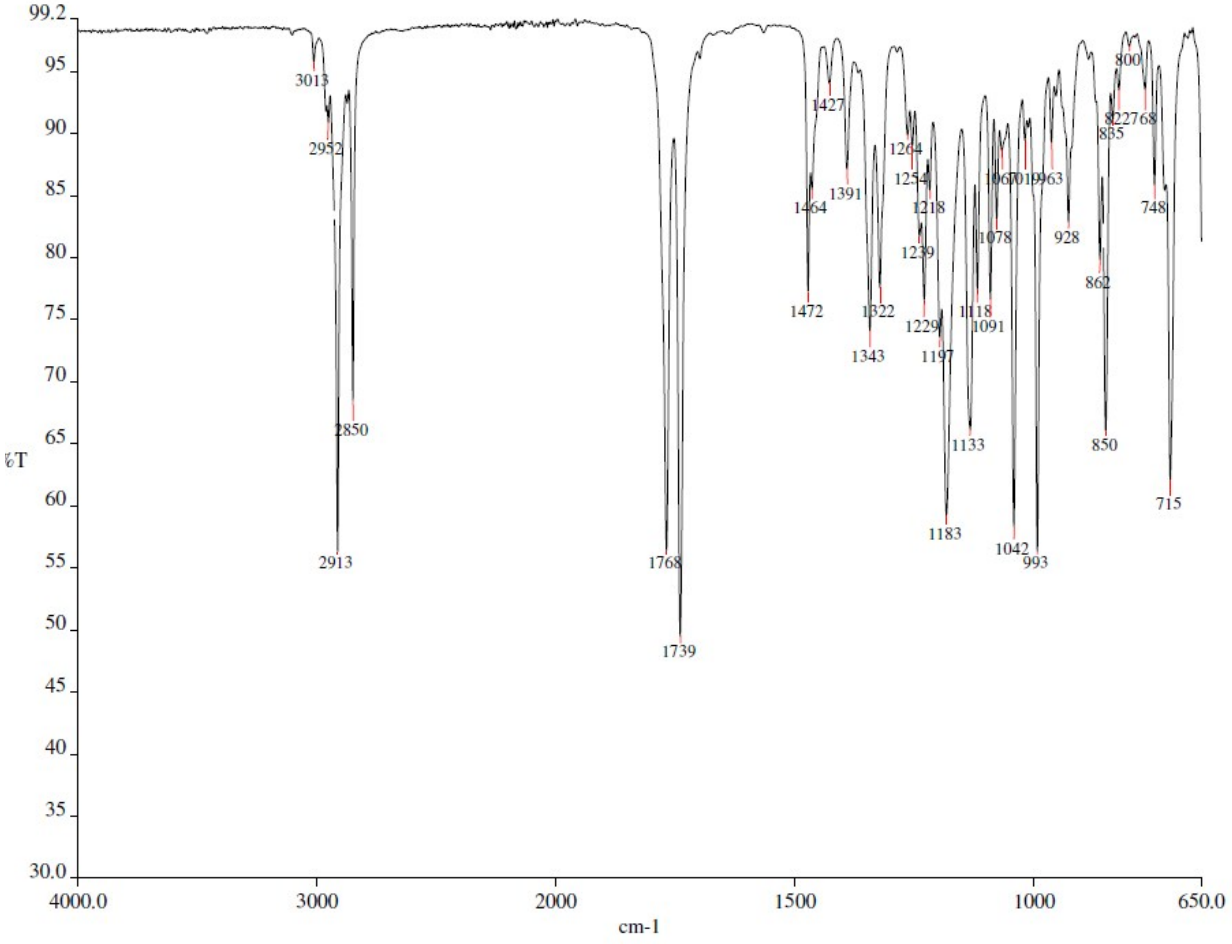
<u>^{1}H NMR spectrum</u>



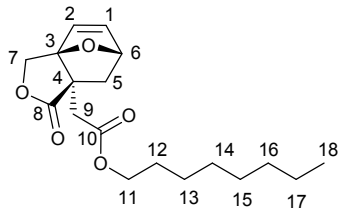
^{13}C NMR spectrum



IR Spectrum



Octyl ester 8c



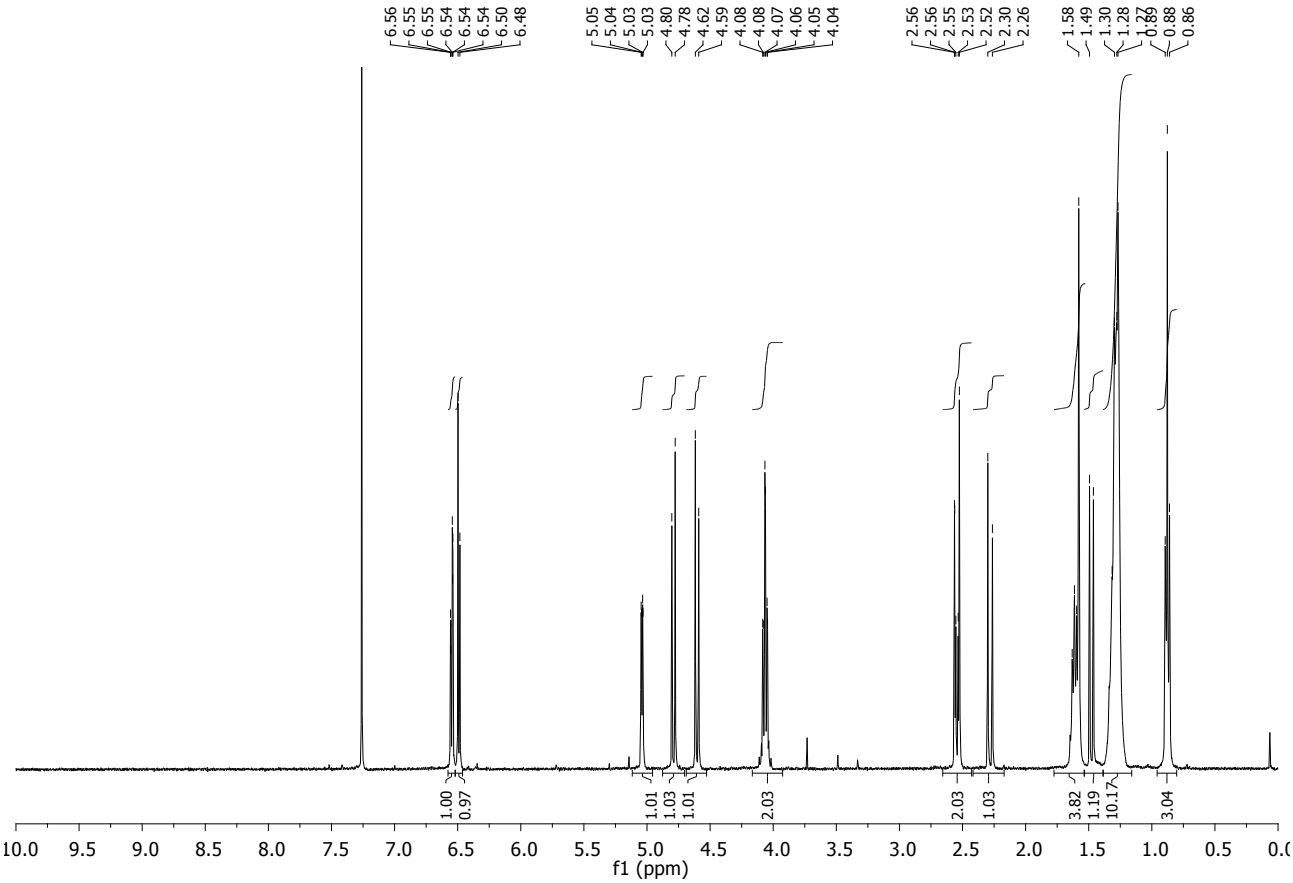
^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 6.6–6.5 (1H, m, H1), 6.49 (1H, d, *J* 5.8 Hz, H2), 5.04 (1H, dd, *J* 4.7, 1.3 Hz, H6), 4.79 (1H, d, *J* 10.7 Hz, H7), 4.60 (1H, d, *J* 10.7 Hz, H7), 4.06 (2H, td, *J* 6.9, 1.6 Hz, H11), 2.6–2.4 (2H, m, H5+H9), 2.28 (1H, d, *J* 14.6 Hz, H9), 1.7– 1.5 (2H, m, H12), 1.48 (1H, d, *J* 12.2 Hz, H5), 1.4-1.2 (10H, m, H13-H17), 0.88 (3H, t, *J* 6.8 Hz, H18).

^{13}C NMR ($CDCl_3$, 101 MHz) δ_C 177.1 (C8), 169.6 (C10), 138.0 (C1), 130.7 (C2), 94.1 (C3), 78.7 (C6), 68.7 (C7), 65.5 (C11), 52.0 (C4), 40.1 (C9), 36.7 (C5), 31.8 (C12), 29.2 (C13+C14), 28.4 (C15), 25.8 (C16), 22.6 (C17), 14.1 (C18).

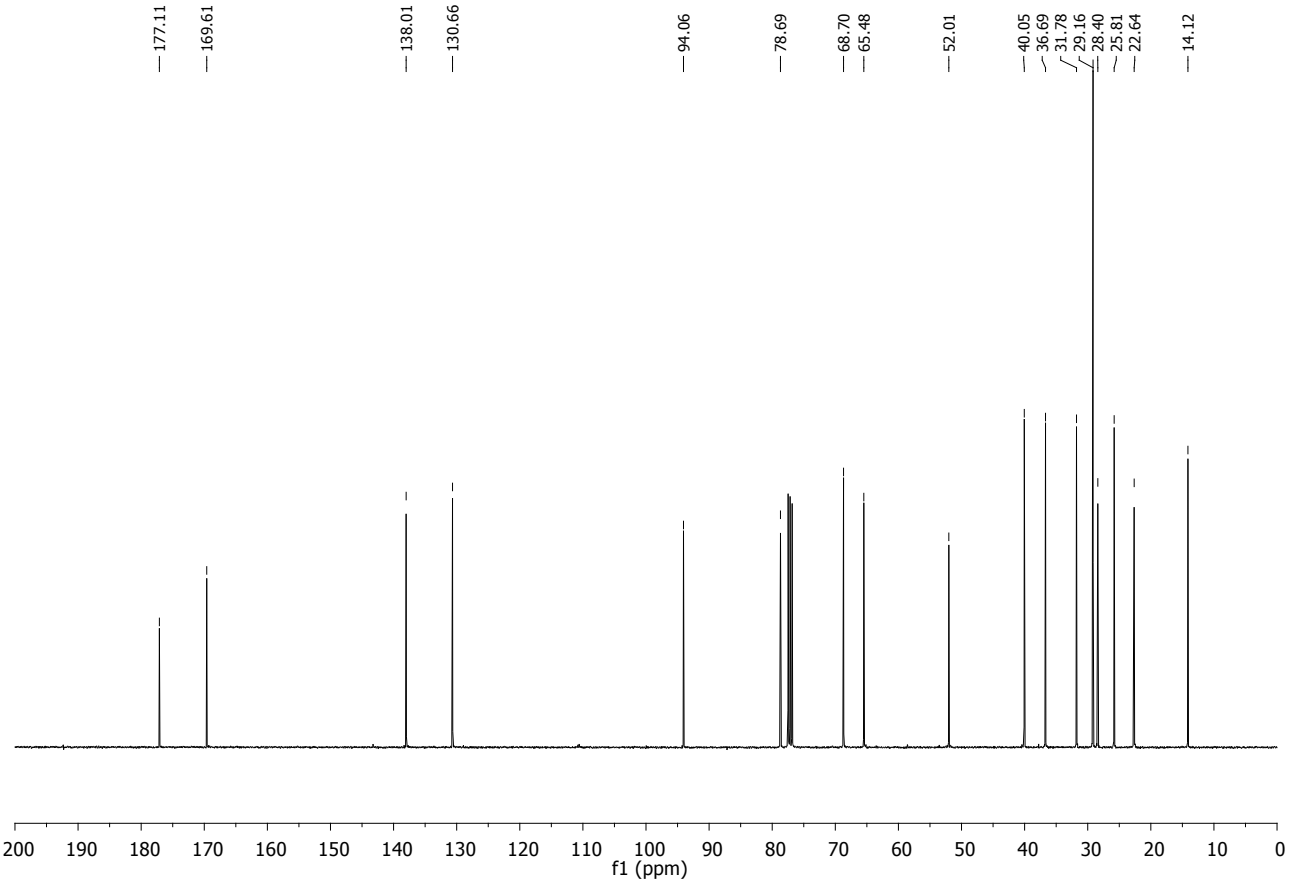
FTIR (neat, ATR) ν_{max} 2955, 2926, 2856, 1774 and 1730 cm^{-1}

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{18}H_{26}NaO_5$ 345.1672, Found 345.1663

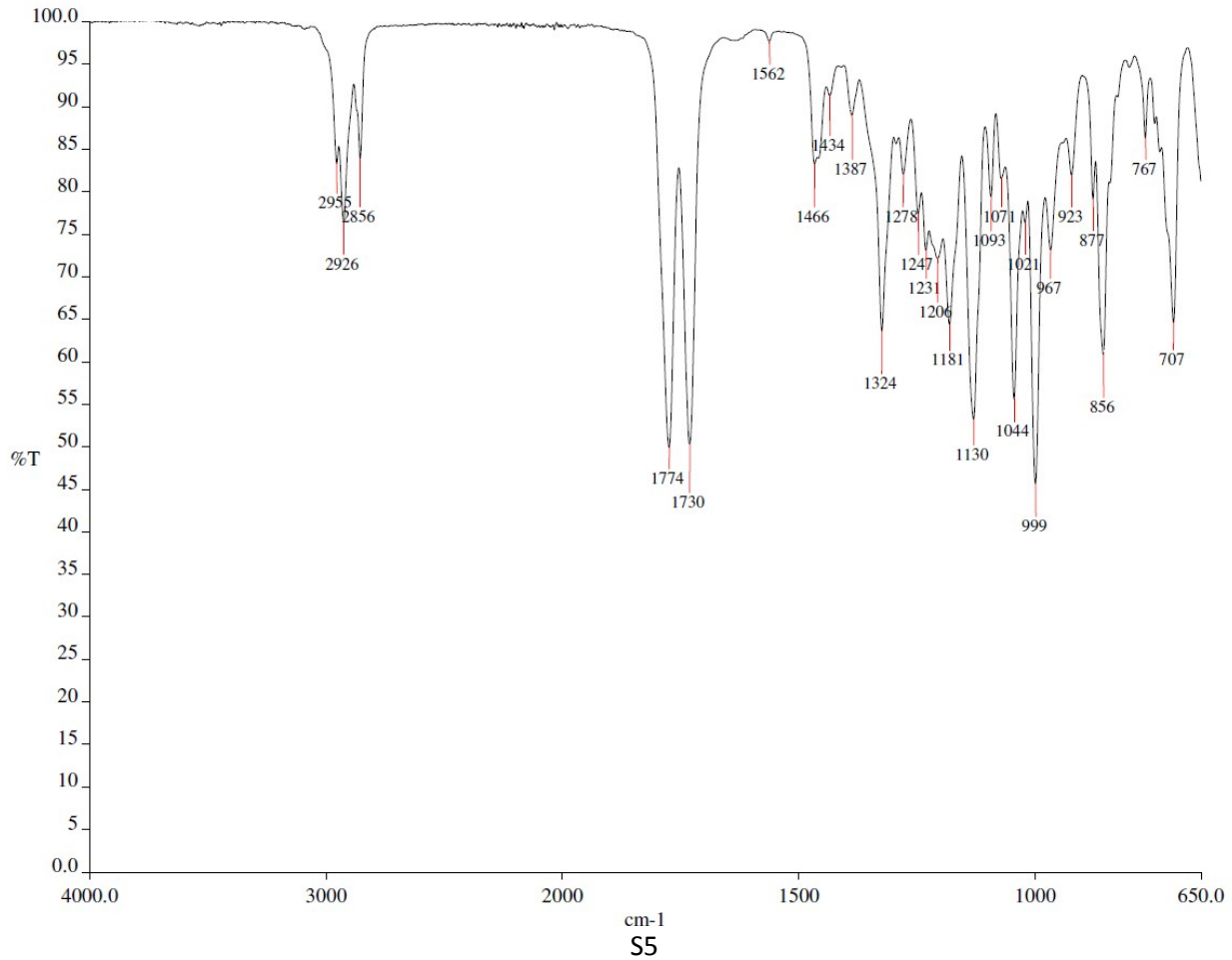
<u>^{1}H NMR spectrum</u>



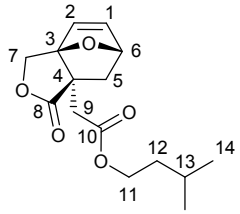
^{13}C NMR spectrum



IR Spectrum



Isoamyl ester 8d



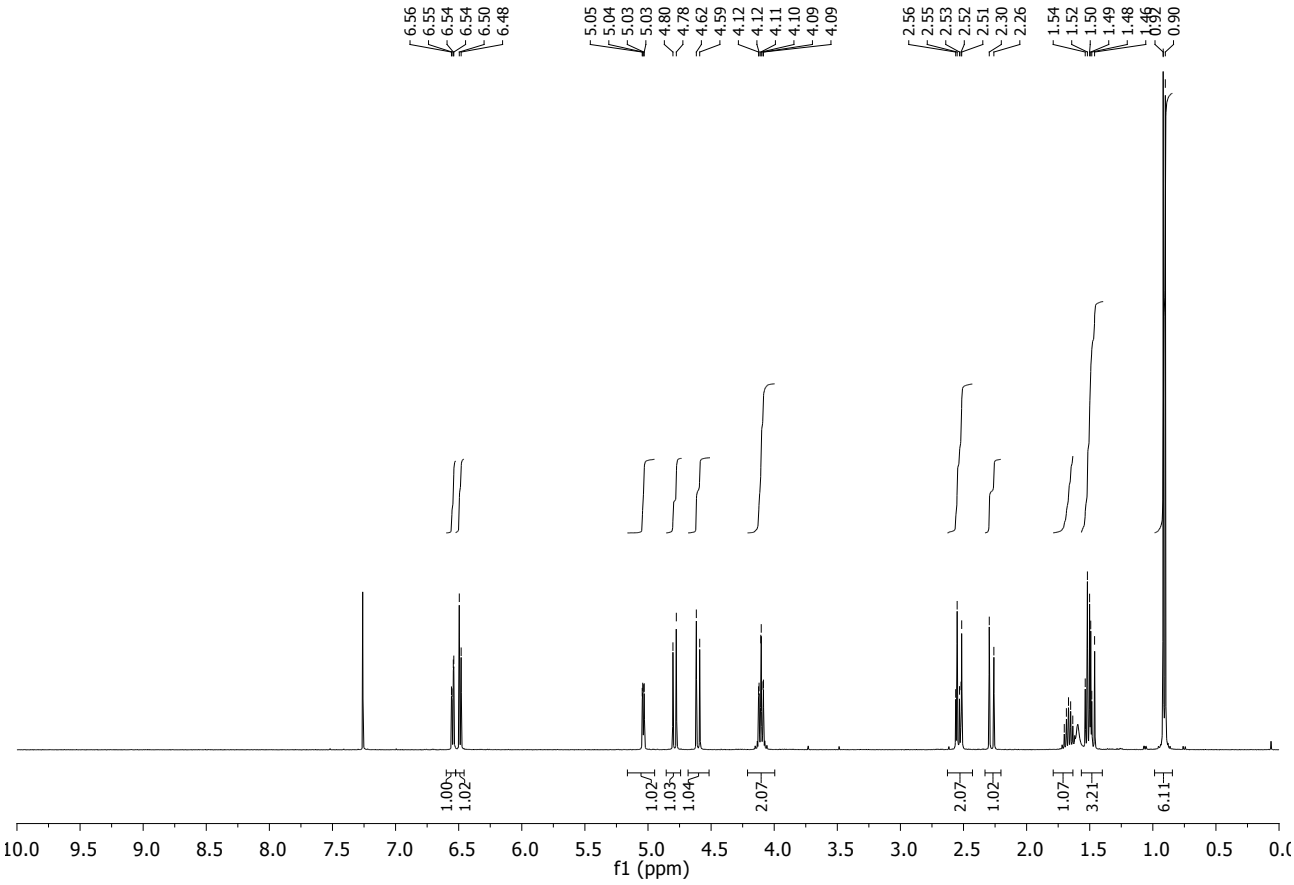
^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 6.55 (1H, dd, *J* 5.8, 1.6 Hz, H1), 6.49 (1H, d, *J* 5.9 Hz, H2), 5.04 (1H, dd, *J* 4.7, 1.5 Hz, H6), 4.79 (1H, d, *J* 10.7 Hz, H7), 4.60 (1H, d, *J* 10.7 Hz, H7), 4.10 (2H, td, *J* 7.0, 1.4 Hz, H11), 2.6–2.4 (2H, m, H5+H9), 2.28 (1H, d, *J* 14.6 Hz, H9), 1.7-1.6 (1H, m, H13), 1.6–1.4 (3H, m, H5+H12), 0.91 (6H, d, *J* 6.7, H14).

^{13}C NMR ($CDCl_3$, 101 MHz) δ_C 177.1 (C8), 169.5 (C10), 138.0 (C1), 130.6 (C2), 94.0 (C3), 78.7 (C6), 68.6 (C7), 63.9 (C11), 52.0 (C4), 40.0 (C9), 37.0 (C5), 36.6 (C13), 24.9 (C12), 22.4 (C14), 22.3 (C14).

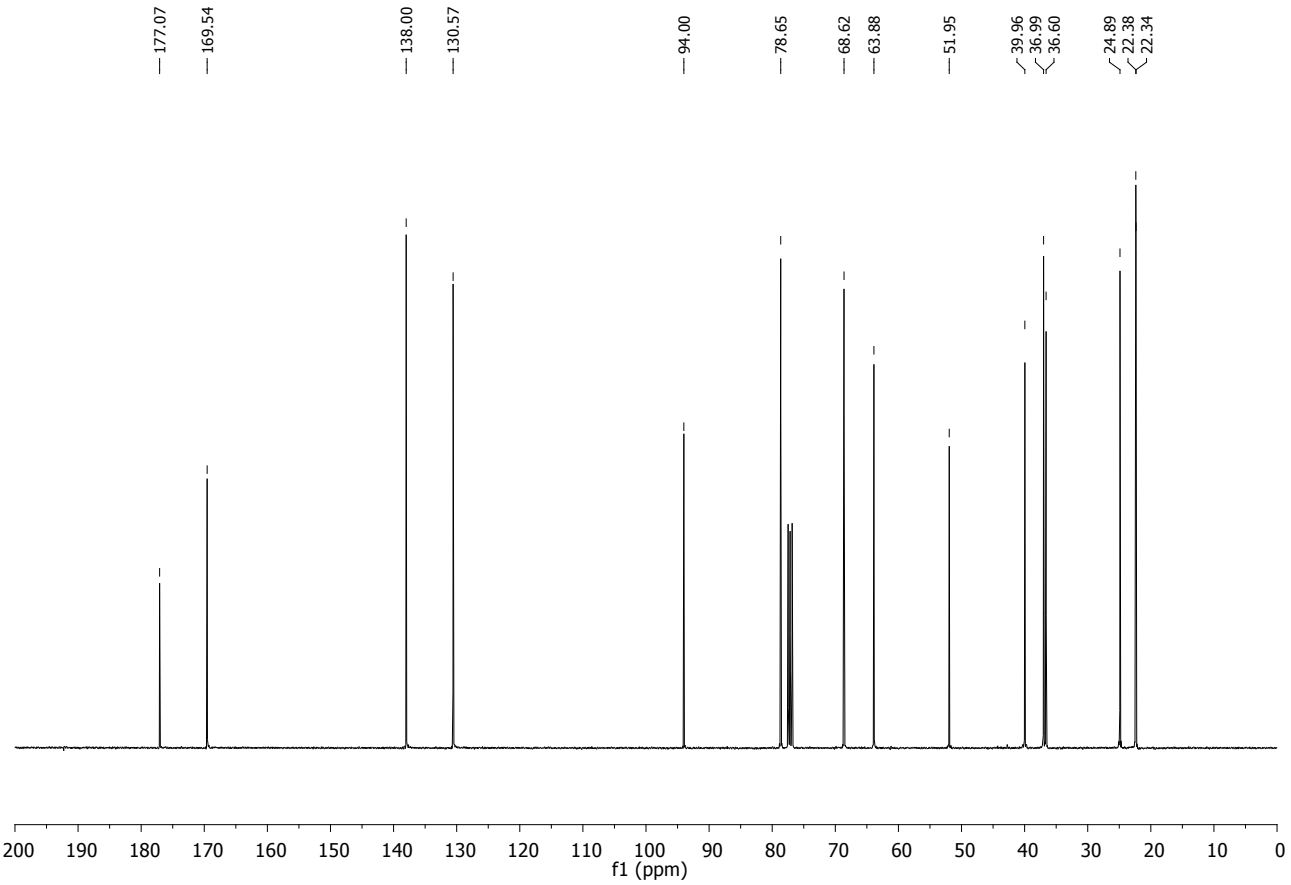
FTIR (neat, ATR) v_{max} 2958, 2872, 1772 and 1729 cm^{-1}

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{15}H_{20}NaO_5$ 303.1203, Found 303.1197

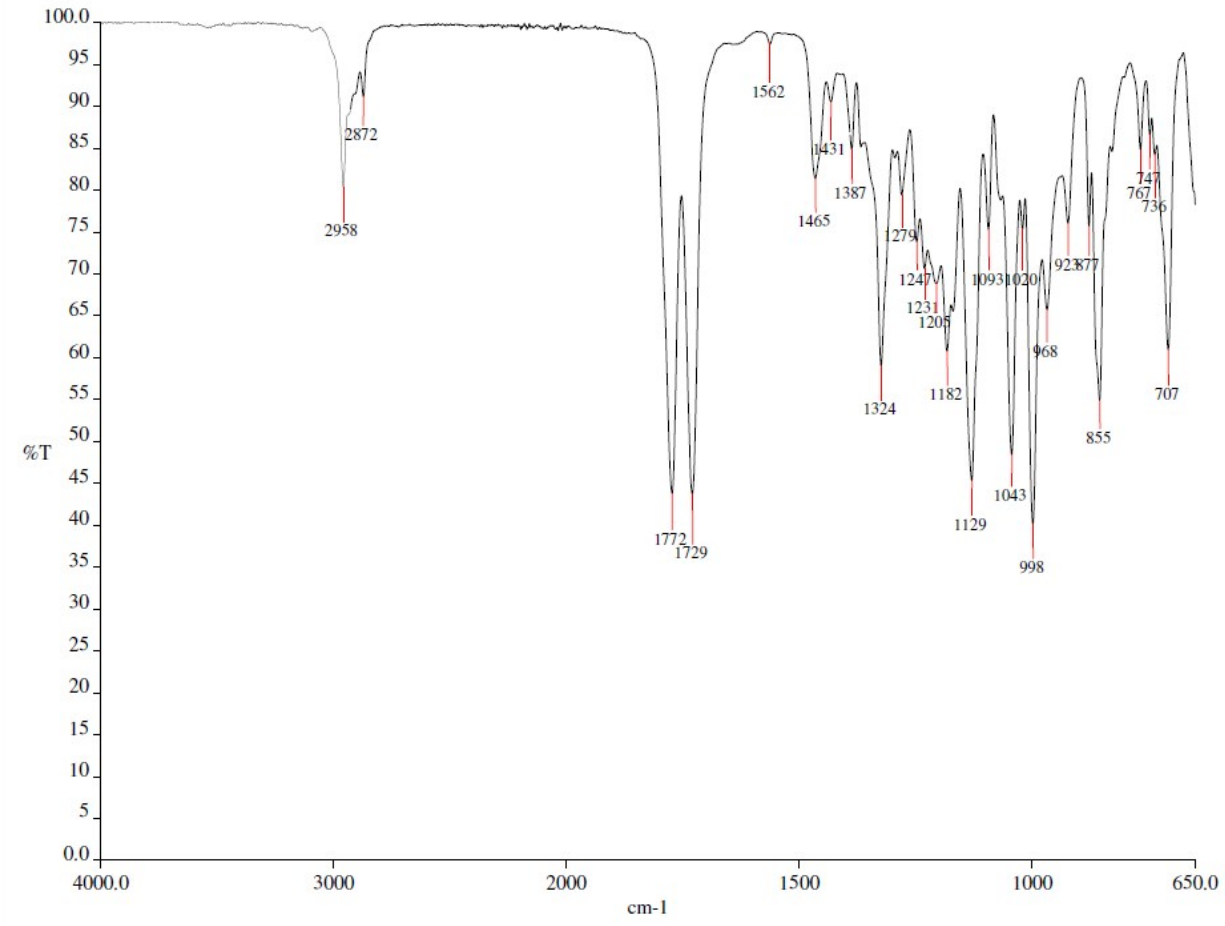
<u>^{1}H NMR spectrum</u>



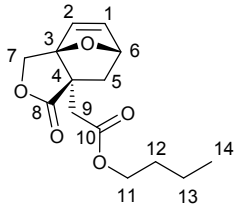
^{13}C NMR spectrum



IR Spectrum



Butyl ester 8e



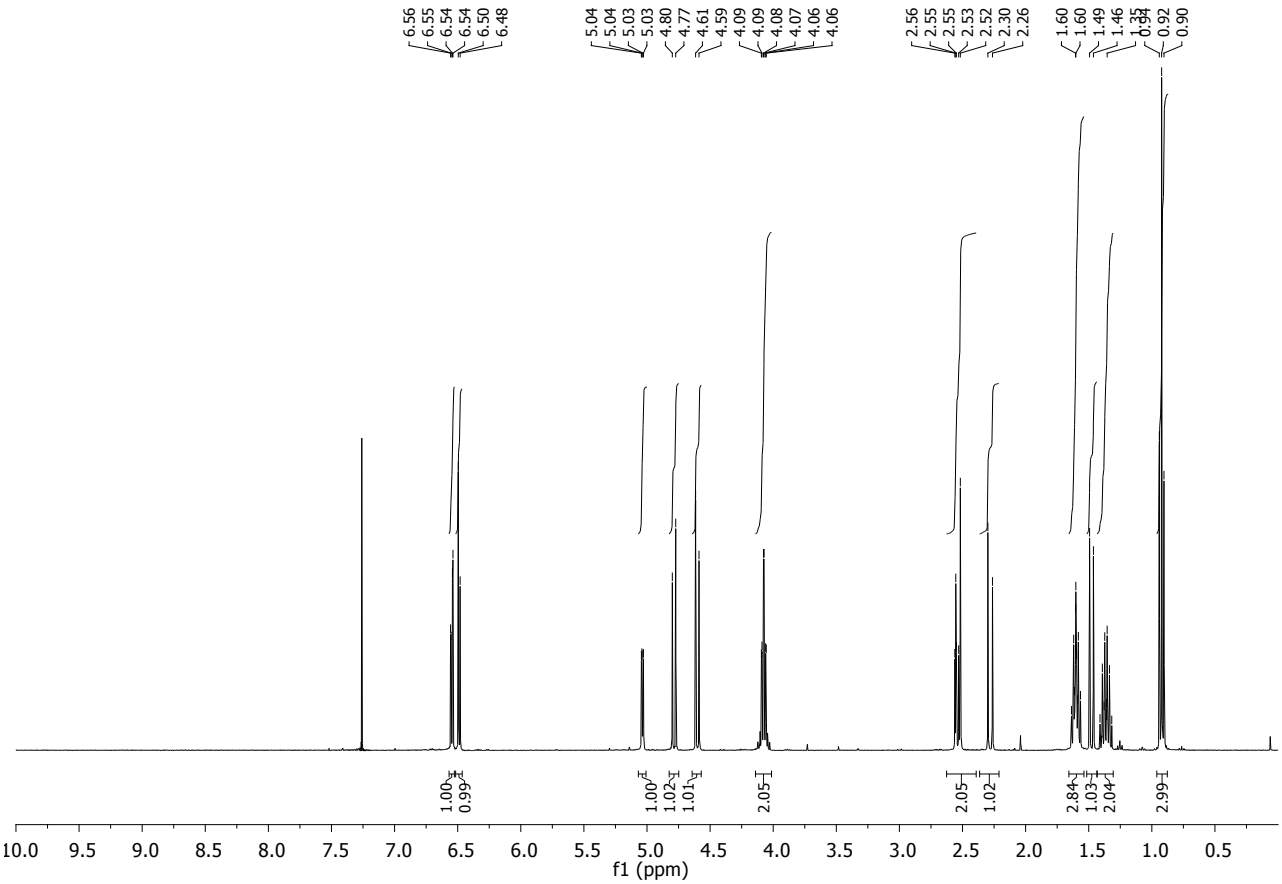
^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 6.55 (1H, dd, *J* 5.8, 1.7 Hz, H1), 6.49 (1 H, d, *J* 5.8 Hz, H2), 5.04 (1H, dd, *J* 4.7, 1.7 Hz, H6), 4.79 (1H, d, *J* 10.8 Hz, H7), 4.60 (1H, d, *J* 10.7 Hz, H7), 4.07 (2H, td, *J* 6.7, 1.9 Hz, H11), 2.6–2.4 (2H, m, H5+H9), 2.28 (1H, d, *J* 14.5 Hz, H9), 1.7–1.5 (2H, m, H12), 1.48 (1H, d, *J* 12.2 Hz, H5), 1.4–1.3 (2 H, m, H13), 0.92 (3H, t, *J* 7.4 Hz, H14).

^{13}C NMR ($CDCl_3$, 101 MHz) δ_C 177.1 (C8), 169.6 (C10), 138.0 (C1), 130.6 (C2), 94.0 (C3), 78.6 (C6), 68.6 (C7), 65.1 (C11), 52.0 (C4), 40.0 (C9), 36.6 (C5), 30.4 (C12), 19.0 (C13), 13.6 (C14).

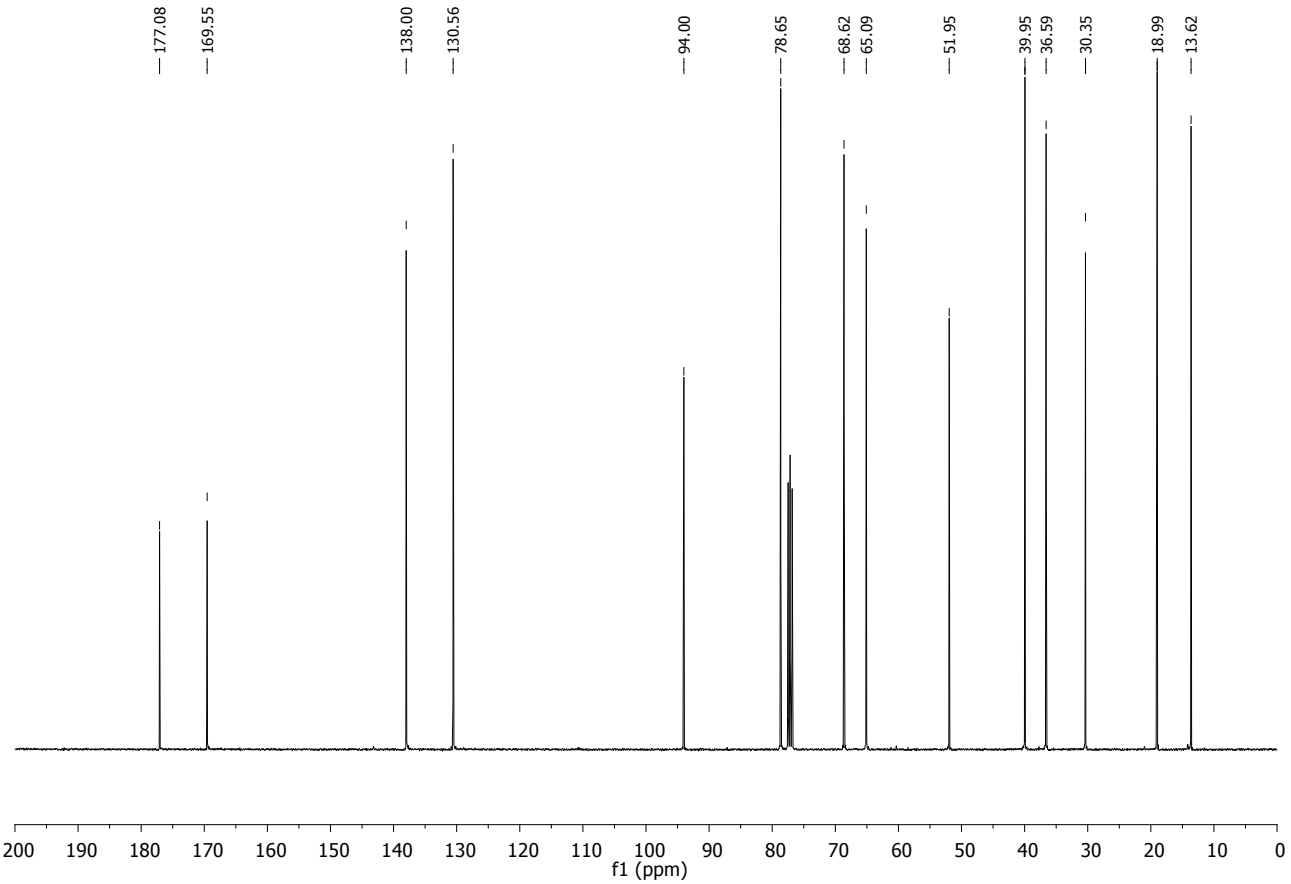
FTIR (neat, ATR) v_{max} 2960, 2785, 1772 and 1728 cm^{-1}

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{14}H_{18}NaO_5$ 289.1046, Found 289.1048

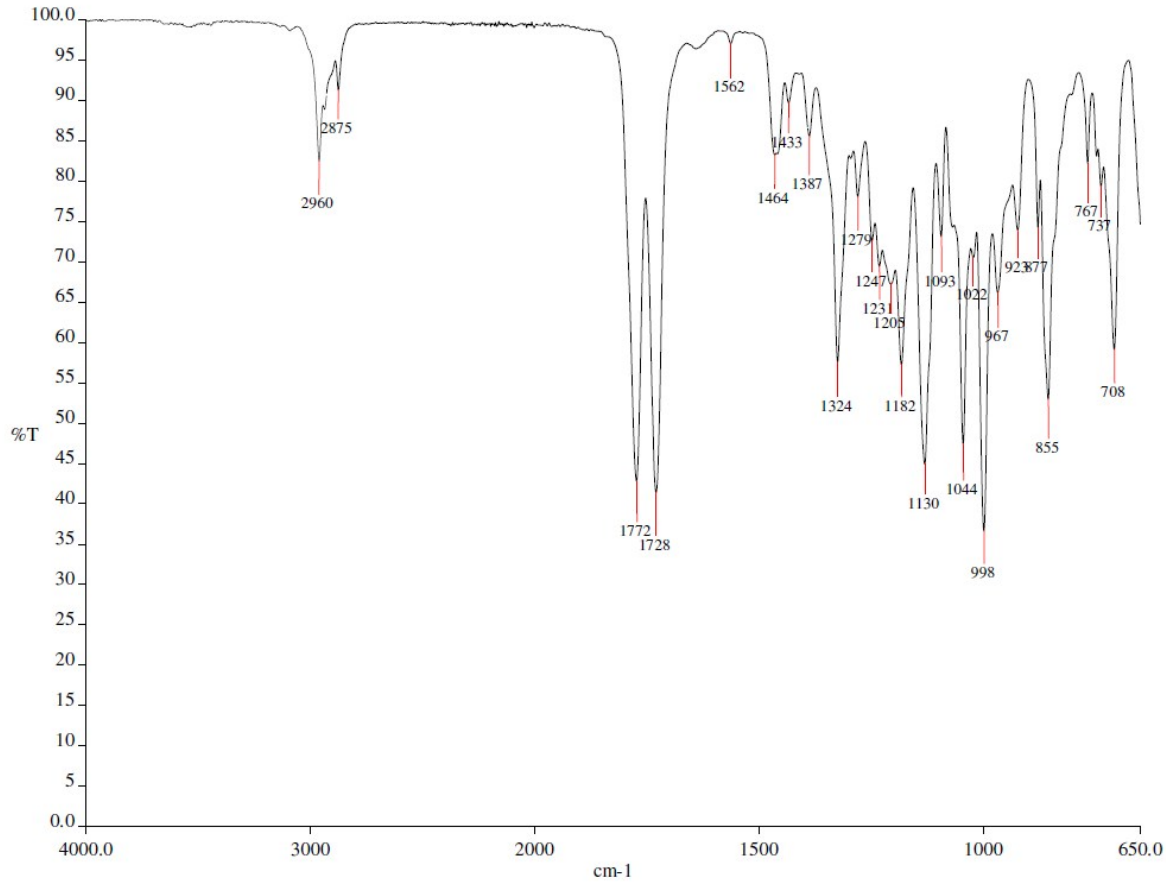
<u>^{1}H NMR spectrum</u>



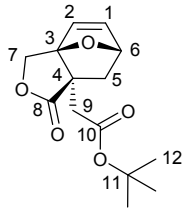
^{13}C NMR spectrum



IR Spectrum



tert-Butyl ester 8f



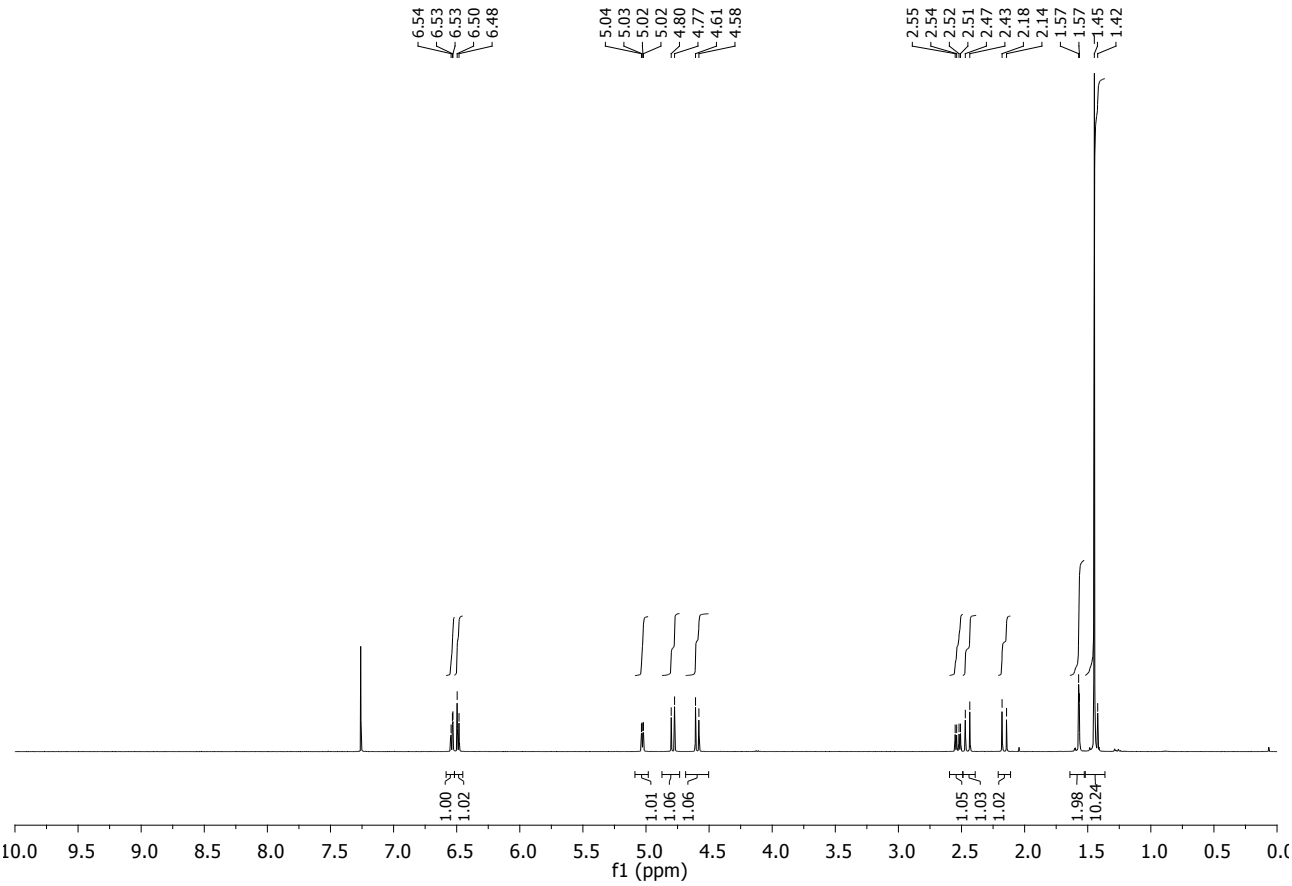
^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 6.54 (1H, dd, *J* 5.8, 1.7 Hz, H1), 6.49 (1H, d, *J* 5.8 Hz, H2), 5.03 (1H, dd, *J* 4.7, 1.6 Hz, H6), 4.79 (1H, d, *J* 10.7 Hz, H7), 4.59 (1H, d, *J* 10.7 Hz, H7), 2.53 (1H, dd, *J* 12.2, 4.8 Hz, H5), 2.45 (1H, d, *J* 14.2 Hz, H9), 2.16 (1H, d, *J* 14.2 Hz, H9), 1.57 (2H, d, *J* 2.5 Hz, H5), 1.45 (9H, s, H12).

^{13}C NMR ($CDCl_3$, 101 MHz) δ_C 177.2 (C8), 168.9 (C10), 138.0 (C1), 130.9 (C2), 94.2 (C3), 82.2 (C11), 78.8 (C6), 68.7 (C7), 52.2 (C4), 41.5 (C9), 36.7 (C5), 28.0 (C12).

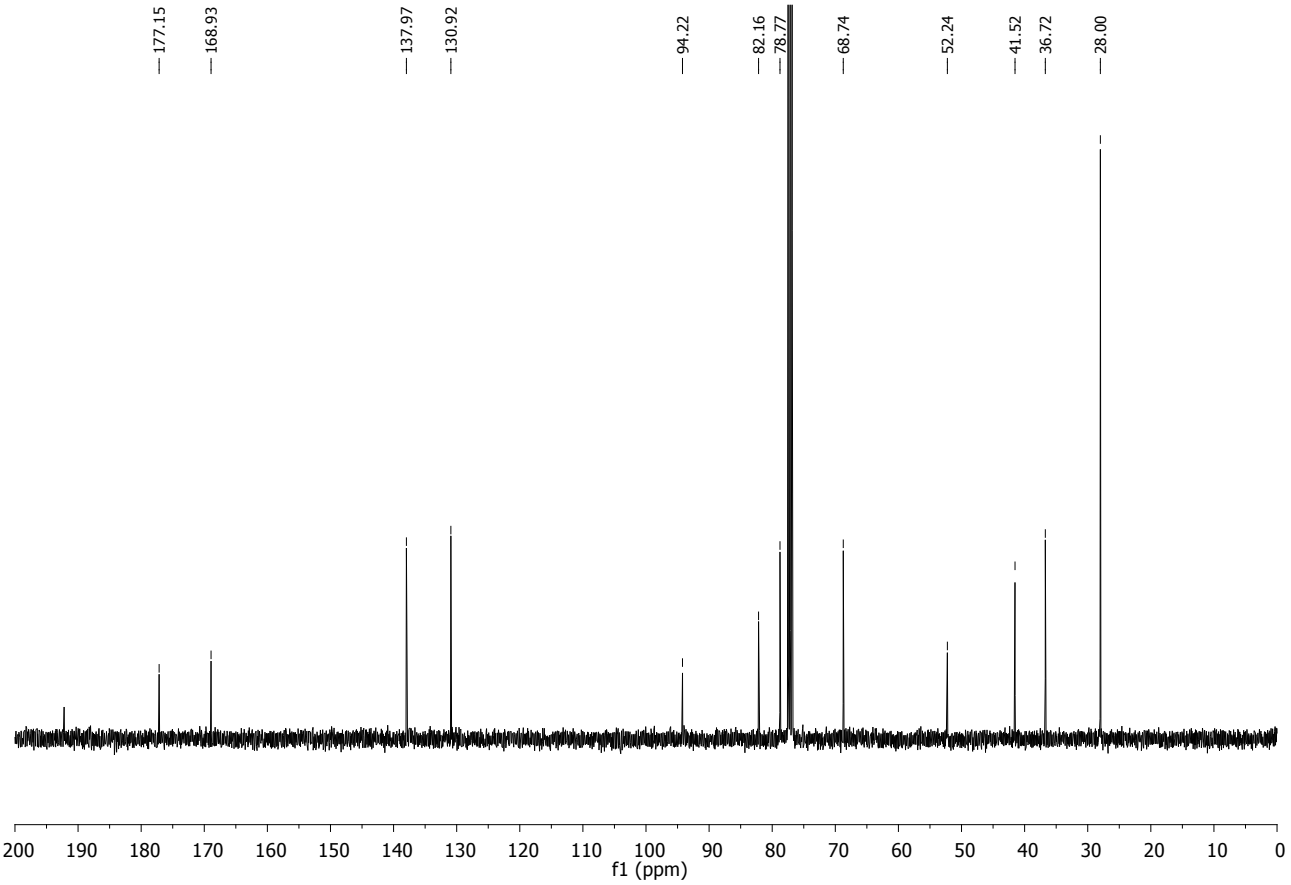
FTIR (neat, ATR) v_{max} 3070, 2980, 2938, 1774 and 1716 cm^{-1}

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{14}H_{18}NaO_5$ 289.1046, Found 289.1043

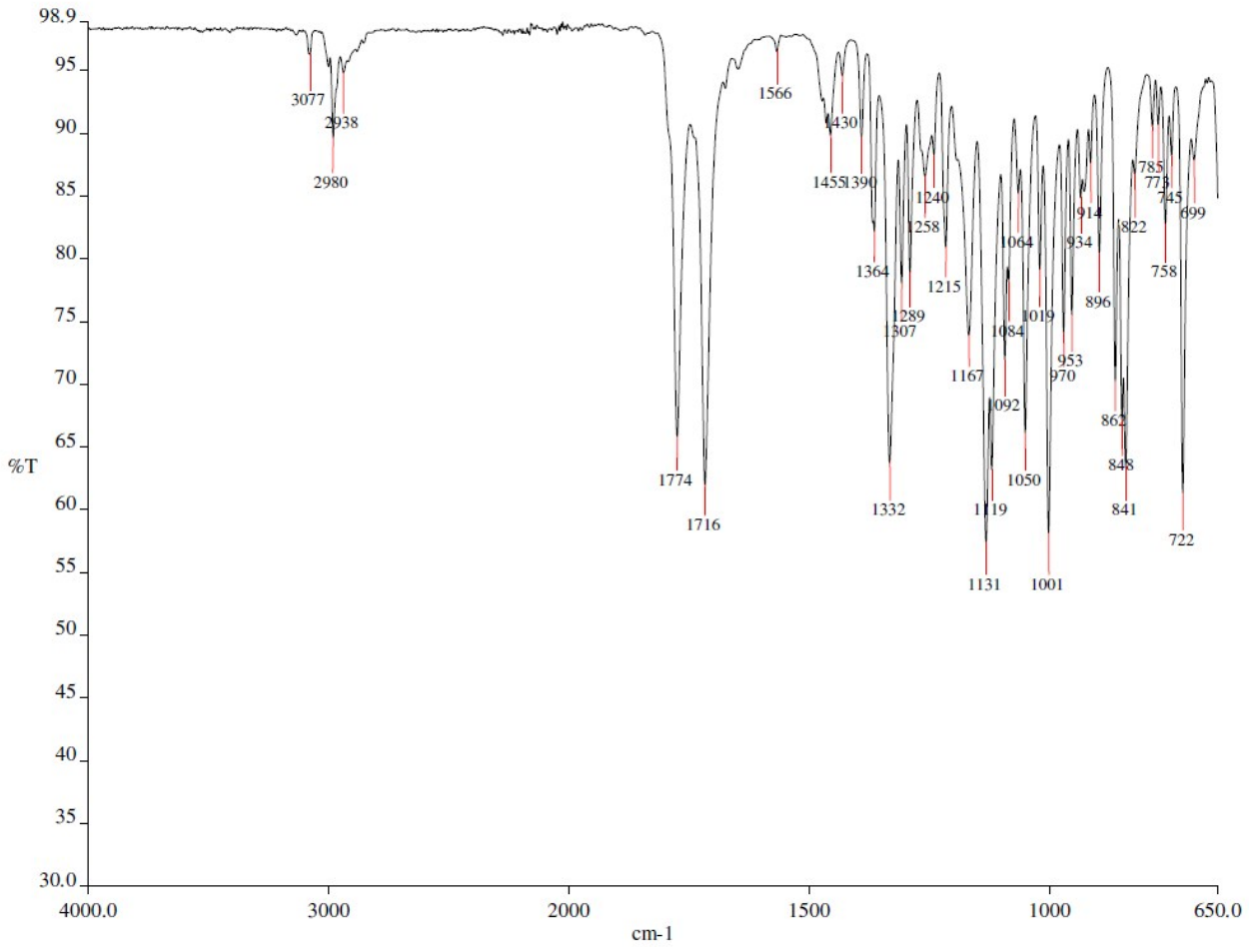
<u>^{1}H NMR spectrum</u>



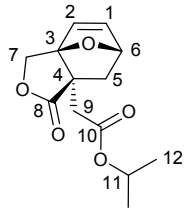
^{13}C NMR spectrum



IR spectrum



Isopropyl ester 8g



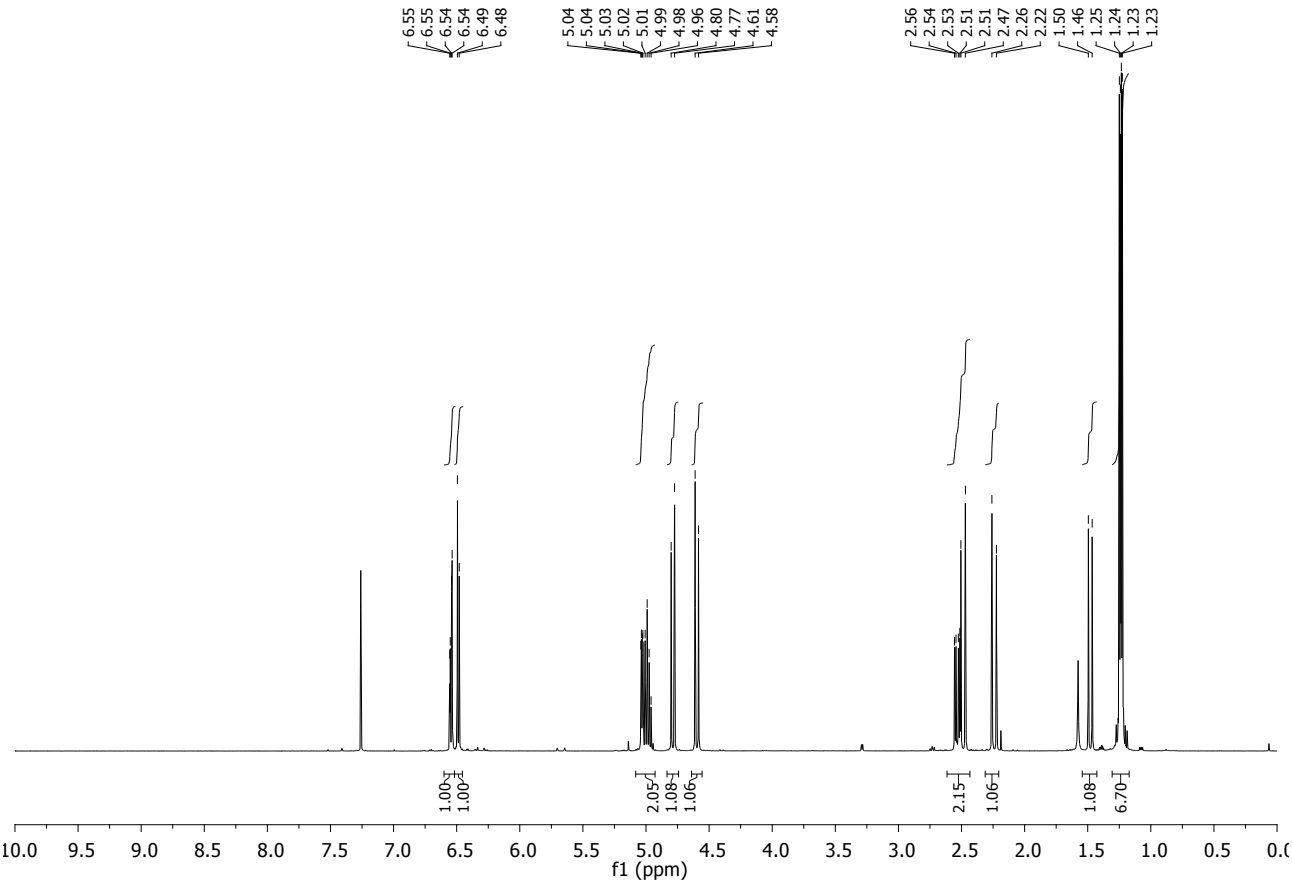
^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 6.55 (1H, dd, *J* 5.8, 1.6 Hz, H1), 6.49 (1H, d, *J* 5.8 Hz, H2), 5.1-4.8 (2H, m, H11+H6), 4.79 (1H, d, *J* 10.8 Hz, H7), 4.60 (1H, d, *J* 10.7 Hz, H7), 2.6-2.5 (1H, m, H5), 2.49 (1H, d, *J* 14.3 Hz, H9), 2.24 (1H, d, *J* 14.3 Hz, H9), 1.48 (1H, d, *J* 12.1 Hz, H5), 1.24 (3H, d, *J* 6.3 Hz, H12), 1.23 (3H, d, *J* 6.3 Hz, H12).

^{13}C NMR ($CDCl_3$, 101 MHz) δ_C 177.1 (C8), 169.0 (C10), 138.0 (C1), 130.6 (C2), 94.0 (C3), 78.7 (C6), 69.0 (C7), 68.6 (C11), 52.0 (C4), 40.2 (C9), 36.6 (C5), 21.7 (C12), 21.6 (C12).

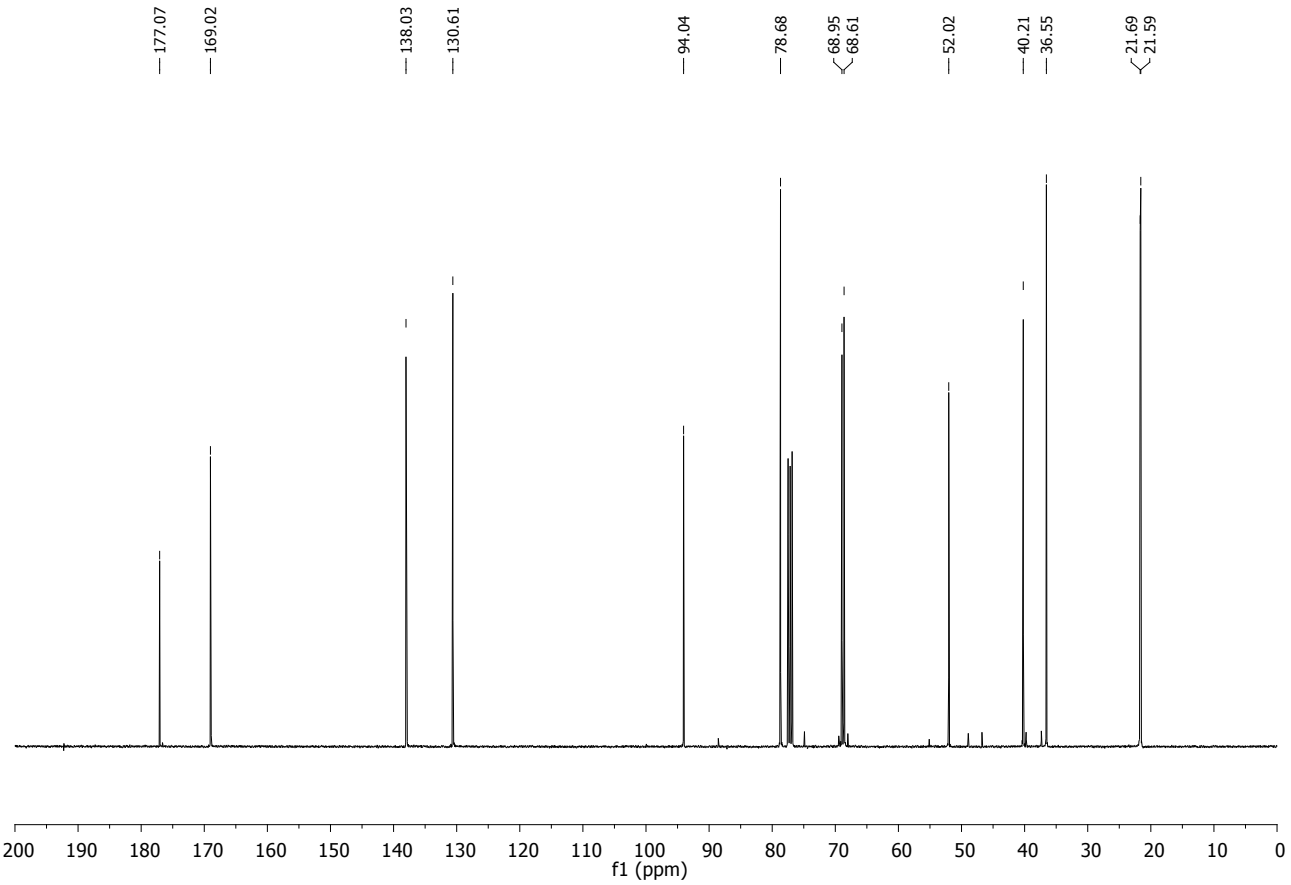
FTIR (neat, ATR) ν_{max} 2982, 1772 and 1723 cm^{-1}

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{13}H_{16}NaO_5$ 275.0890, Found 275.0888

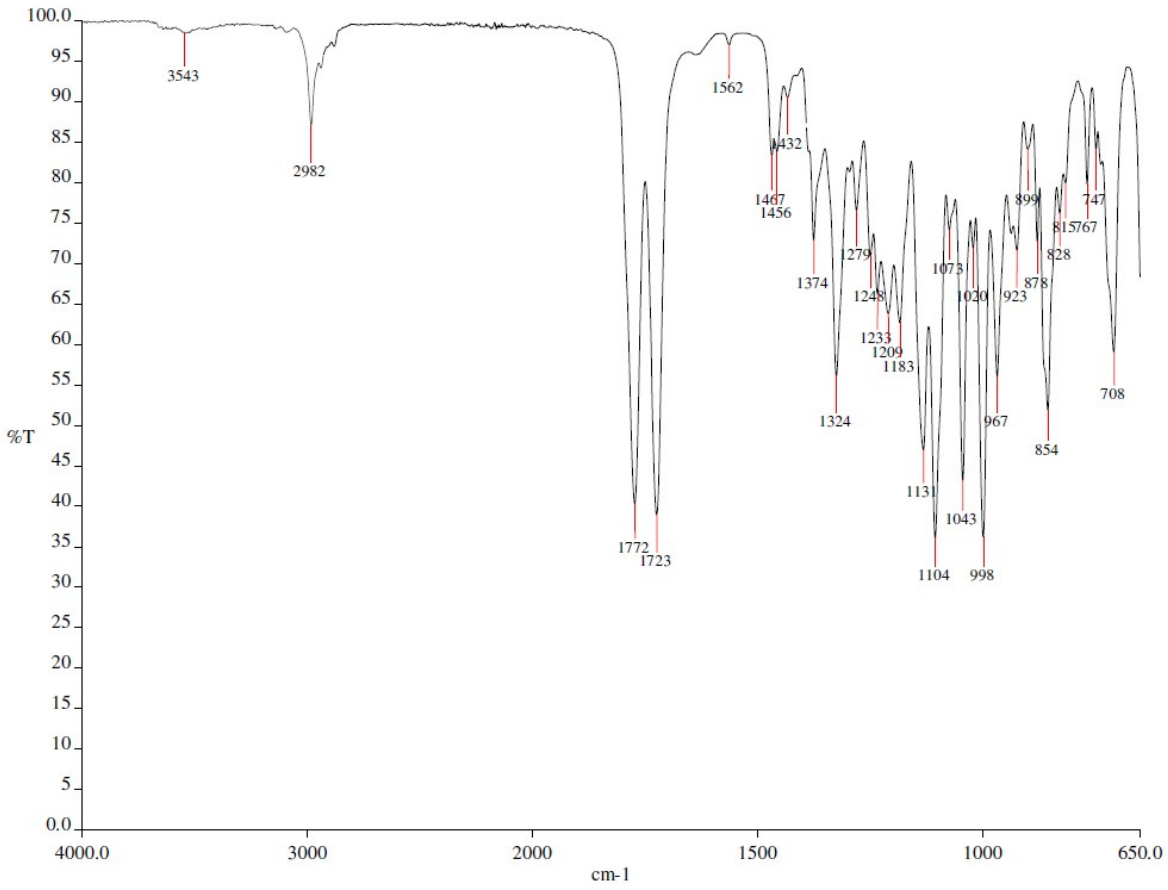
<u>^{1}H NMR spectrum</u>



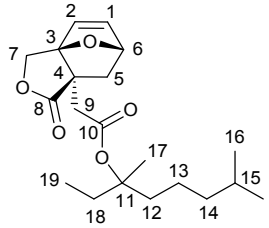
^{13}C NMR spectrum



IR spectrum



4H-Linalooyl ester 8h



This compound was formed as a 1:1 mixture of two diastereomers.

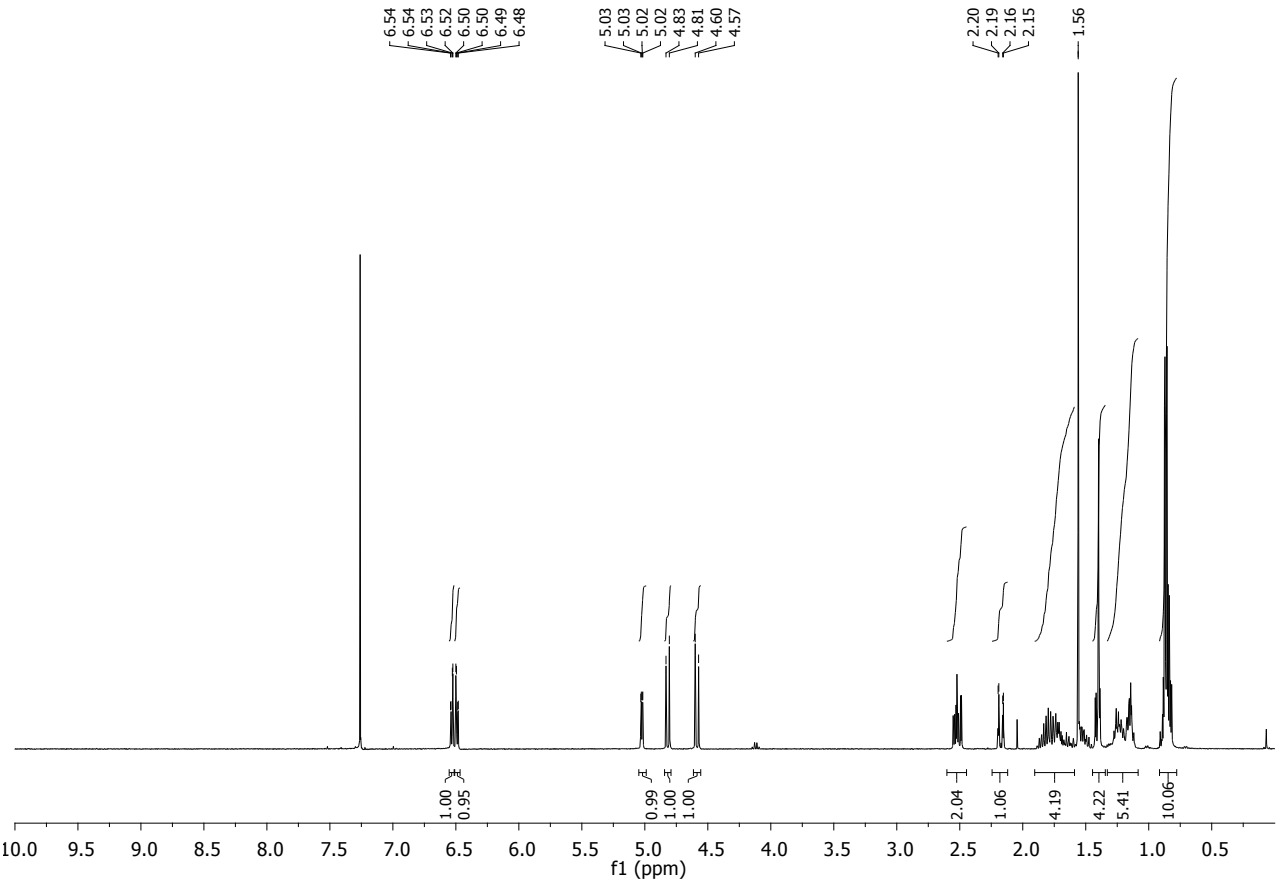
^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 6.53 (1H, dd, *J* 5.8, 1.6 Hz, H1), 6.49 (1H, dd, *J* 5.8, 1.9 Hz, H2), 5.02 (1H, dd, *J* 4.7, 1.6 Hz, H6), 4.82 (1H, d, *J* 10.6 Hz, H7), 4.59 (1H, d, *J* 10.6 Hz, H7), 2.6–2.4 (2H, m, H5+H9), 2.17 (1H, dd, *J* 14.6, 2.2 Hz, H9), 1.9–1.6 (4H, m, H12+H18), 1.6–1.4 (1H, m, H5), 1.36 (3H, s, H17), 1.3–1.0 (5H, m, H13+H14+H15), 0.9–0.8 (9H, m, H16+H19).

^{13}C NMR ($CDCl_3$, 101 MHz) δ_C (101 MHz) 177.2 (C8), 168.86 and 168.85 (C10), 137.86 and 137.83 (C1), 130.99 and 130.97 (C2), 94.3 (C3), 87.4 (C11), 78.69 and 78.68 (C6), 68.85 and 68.83 (C7), 52.09 and 52.08 (C4), 41.60 and 41.57 (C9), 39.33 and 39.31 (C14), 37.90 and 37.88 (C12), 36.88 and 36.86 (C5), 30.84 and 30.81 (C18), 27.93 and 27.92 (C15), 23.20 and 23.16 (C17), 22.73, 22.71, 22.69 and 22.68 (C16), 21.45 and 21.43 (C13), 8.15 and 8.12 (C19).

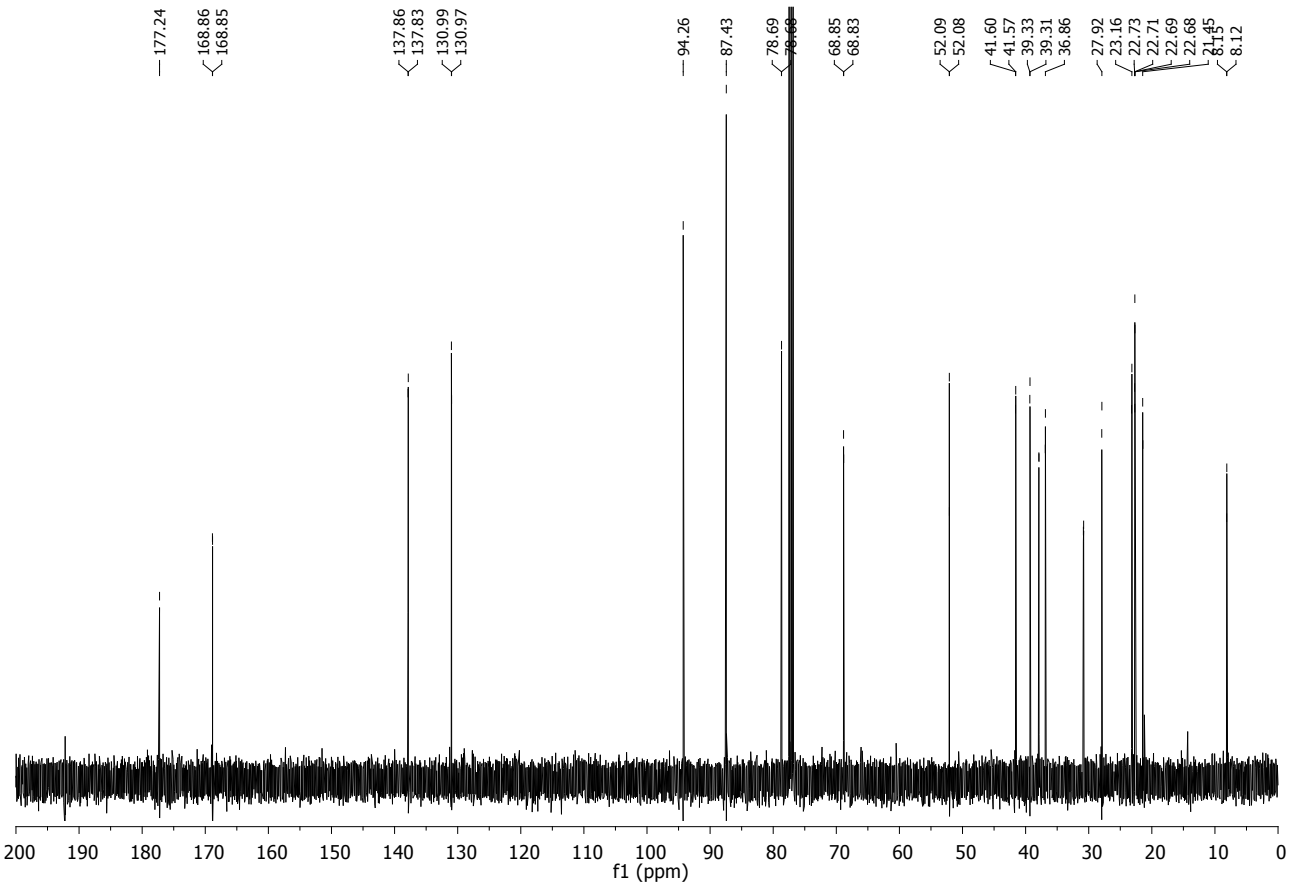
FTIR (neat, ATR) ν_{max} 2953, 2870, 1775 and 1721 cm^{-1}

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{20}H_{30}NaO_5$ 373.1985, Found 373.1985.

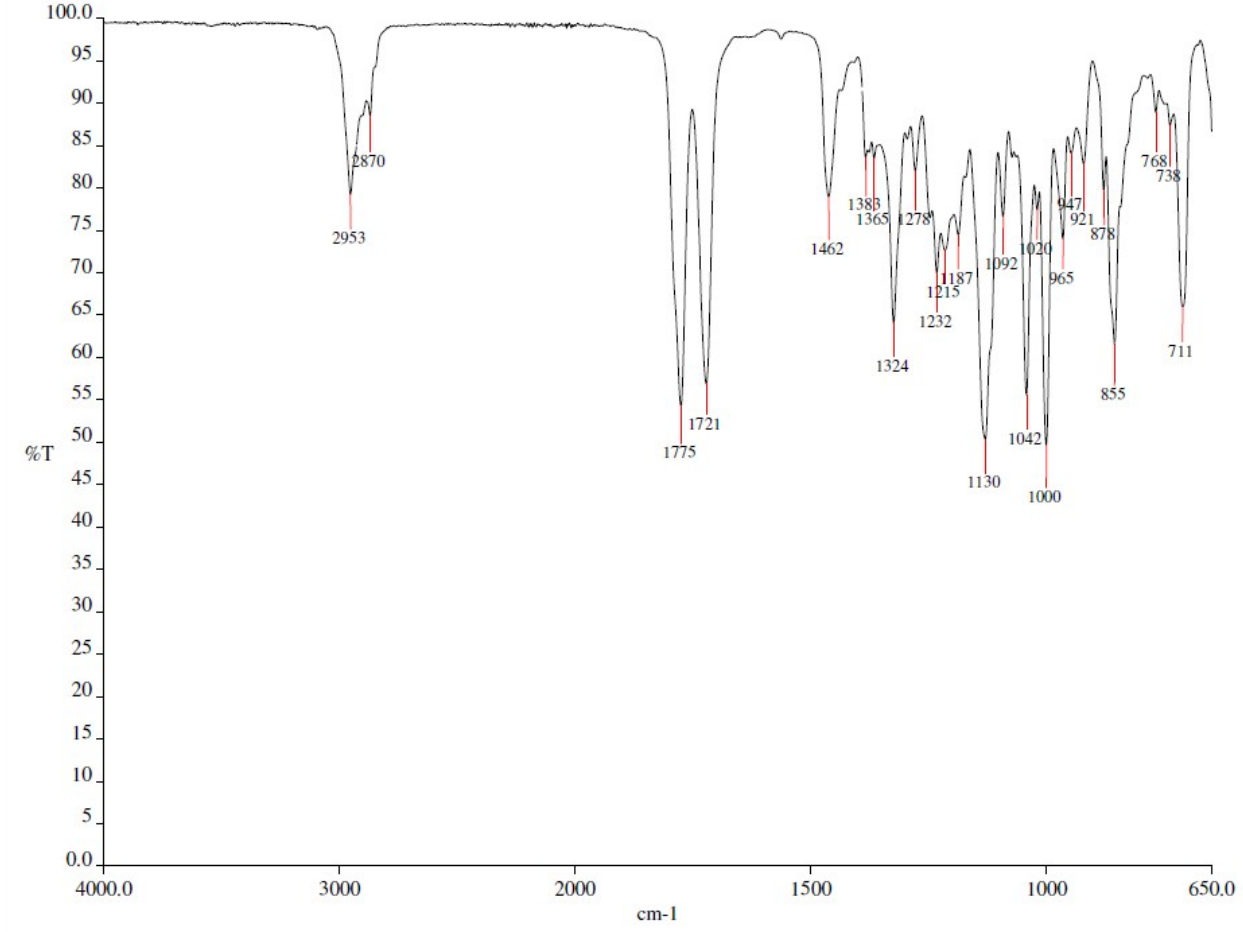
<u>^{1}H NMR spectrum</u>



^{13}C NMR spectrum

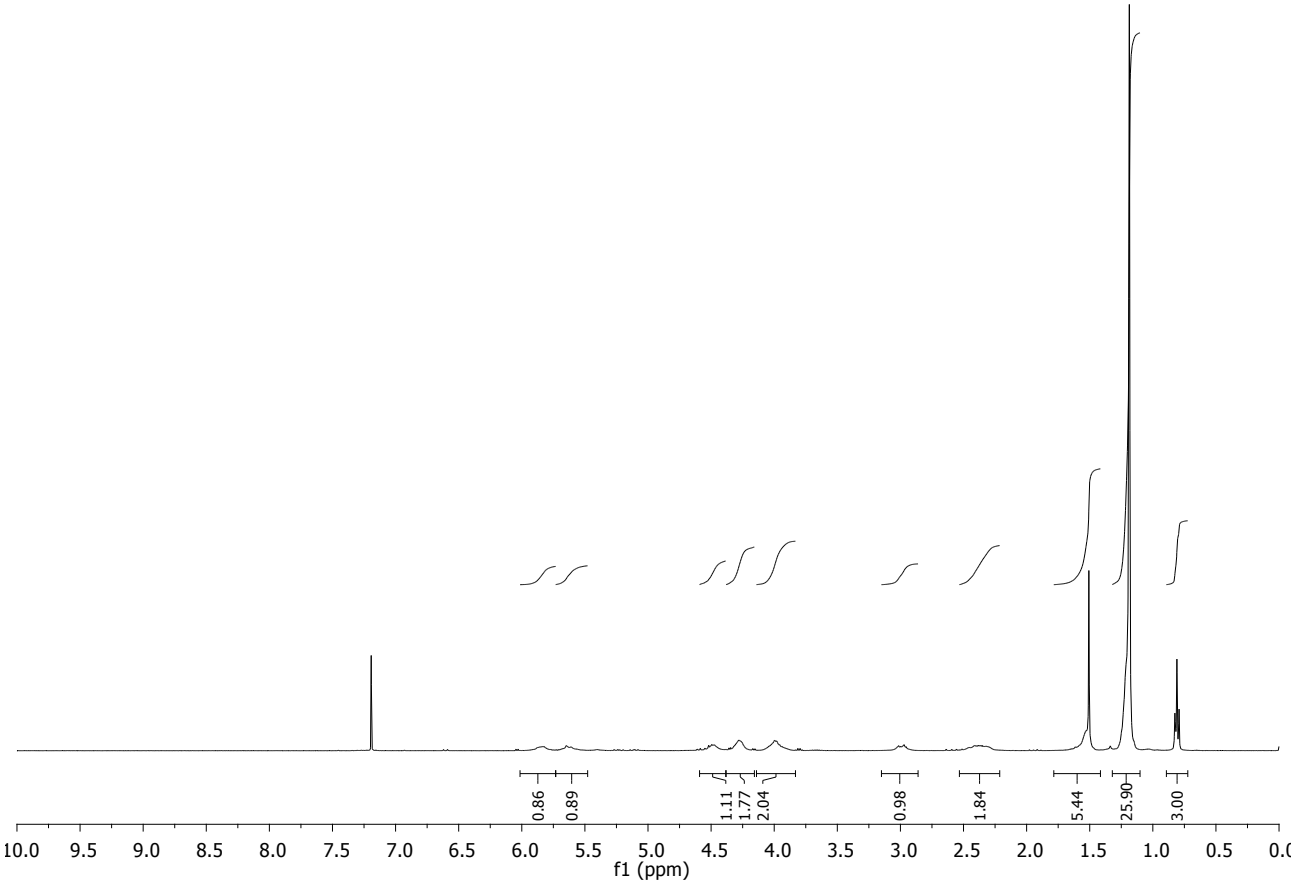


IR Spectrum



Polymerised cetyl ester 9b (100:1 homopolymer)

^{1}H NMR Spectrum



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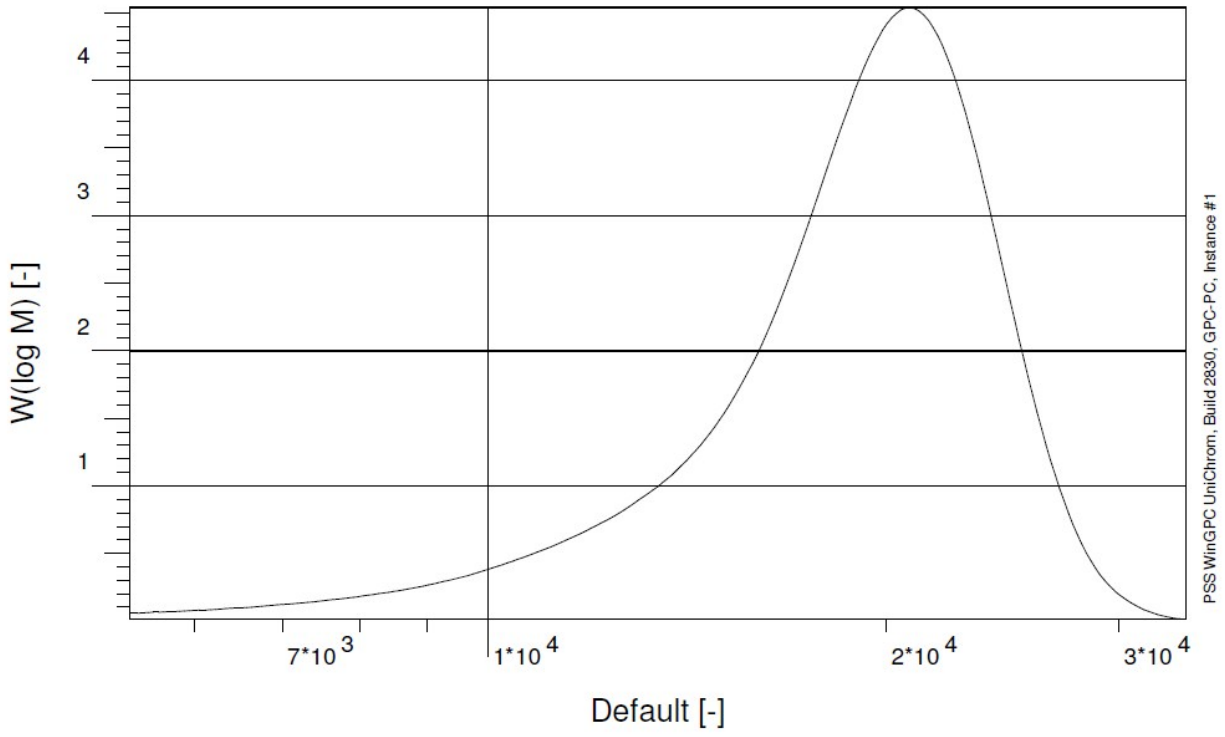
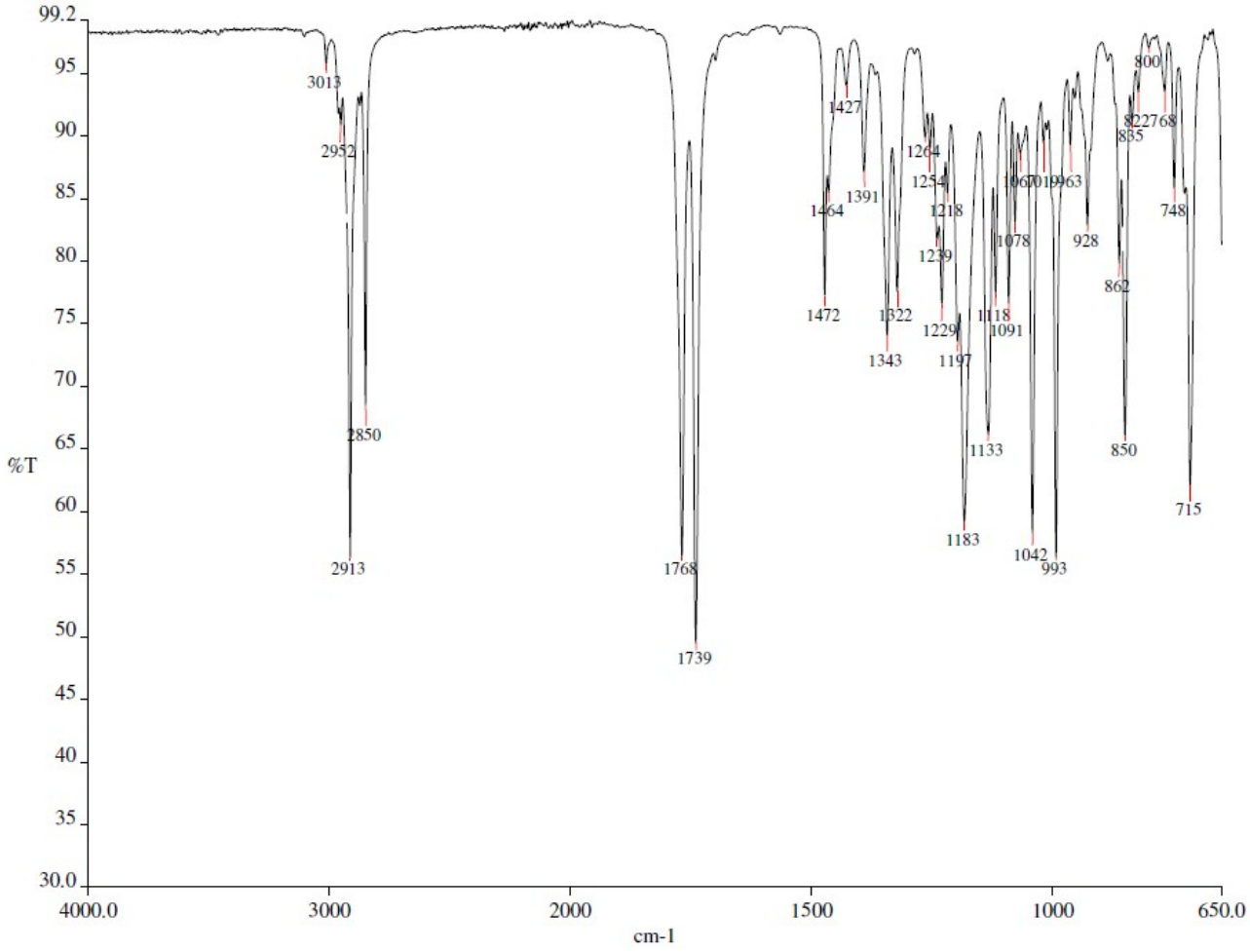


IR Spectrum



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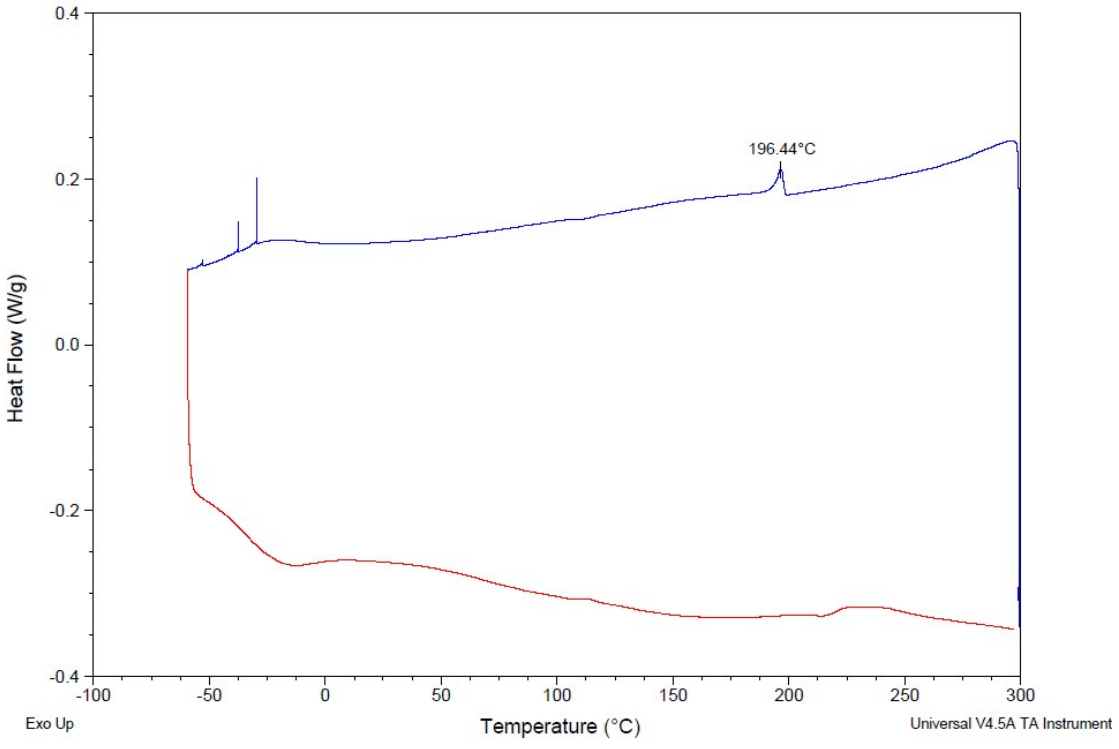
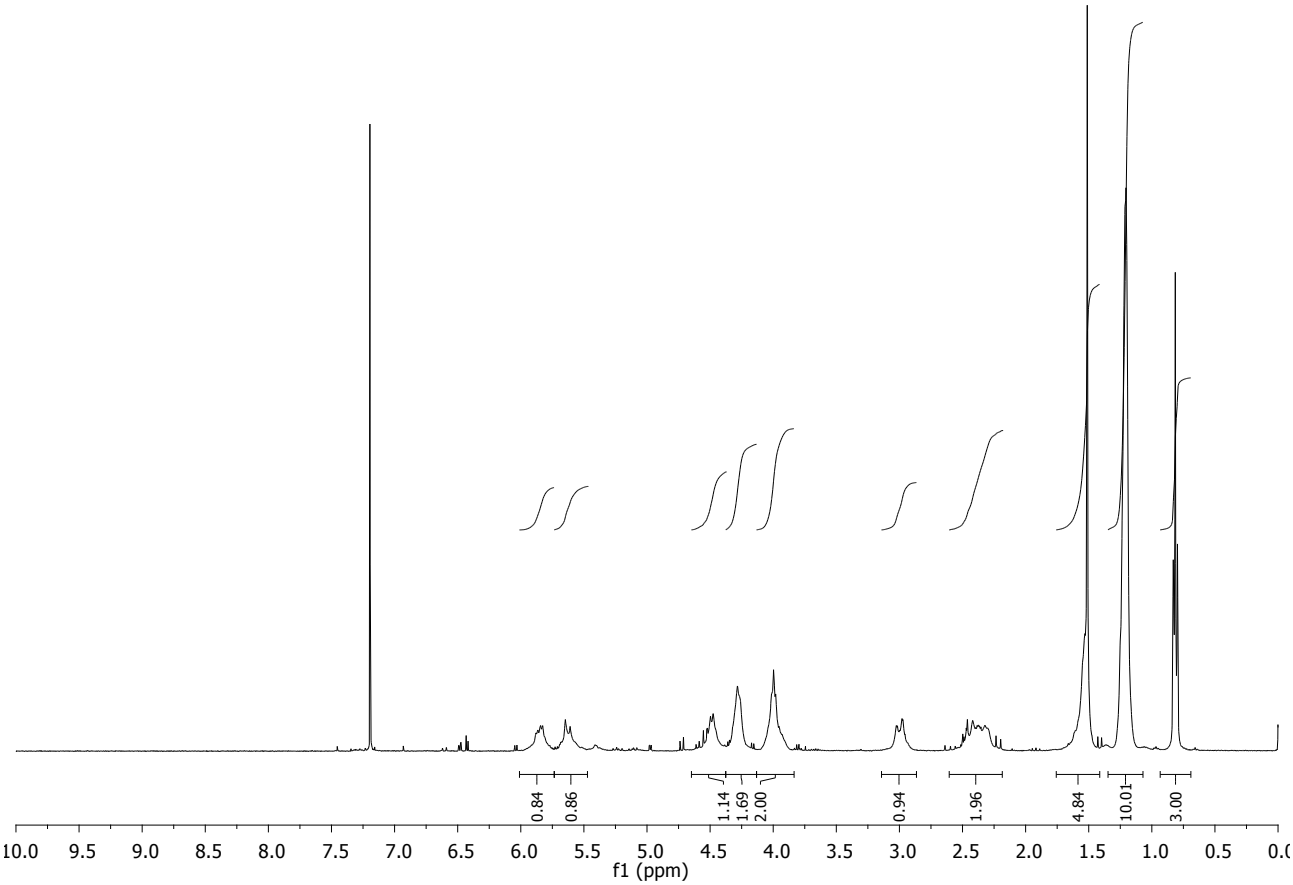
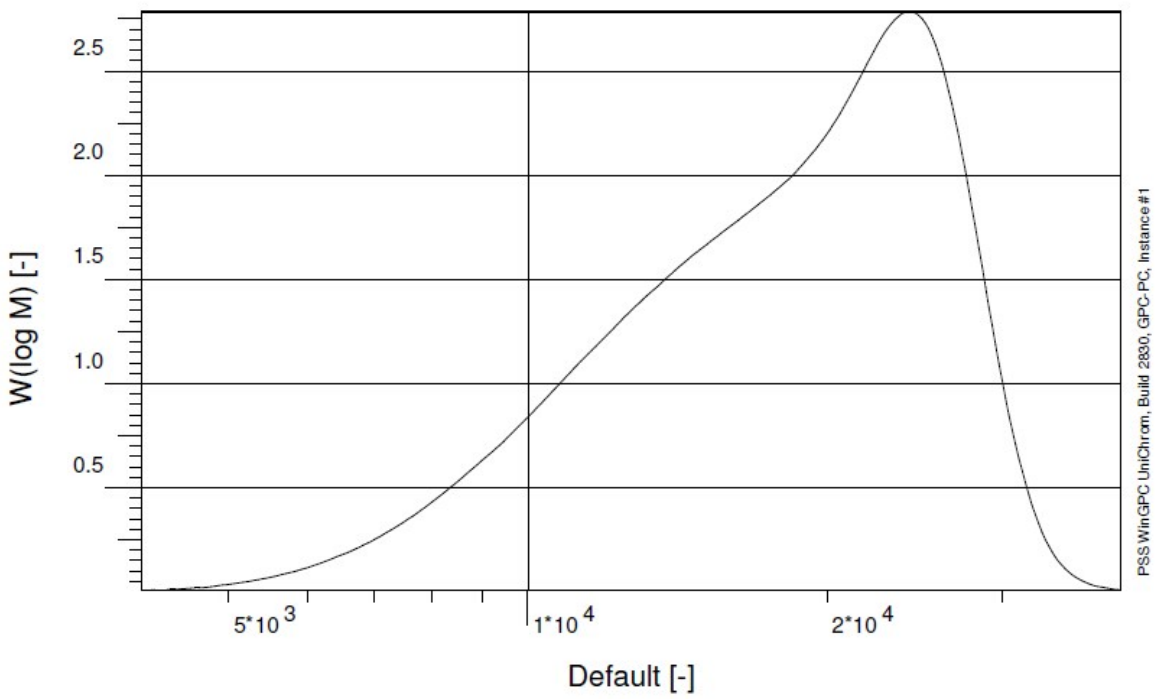


Polymerised octyl ester 9c (100:1 homopolymer)

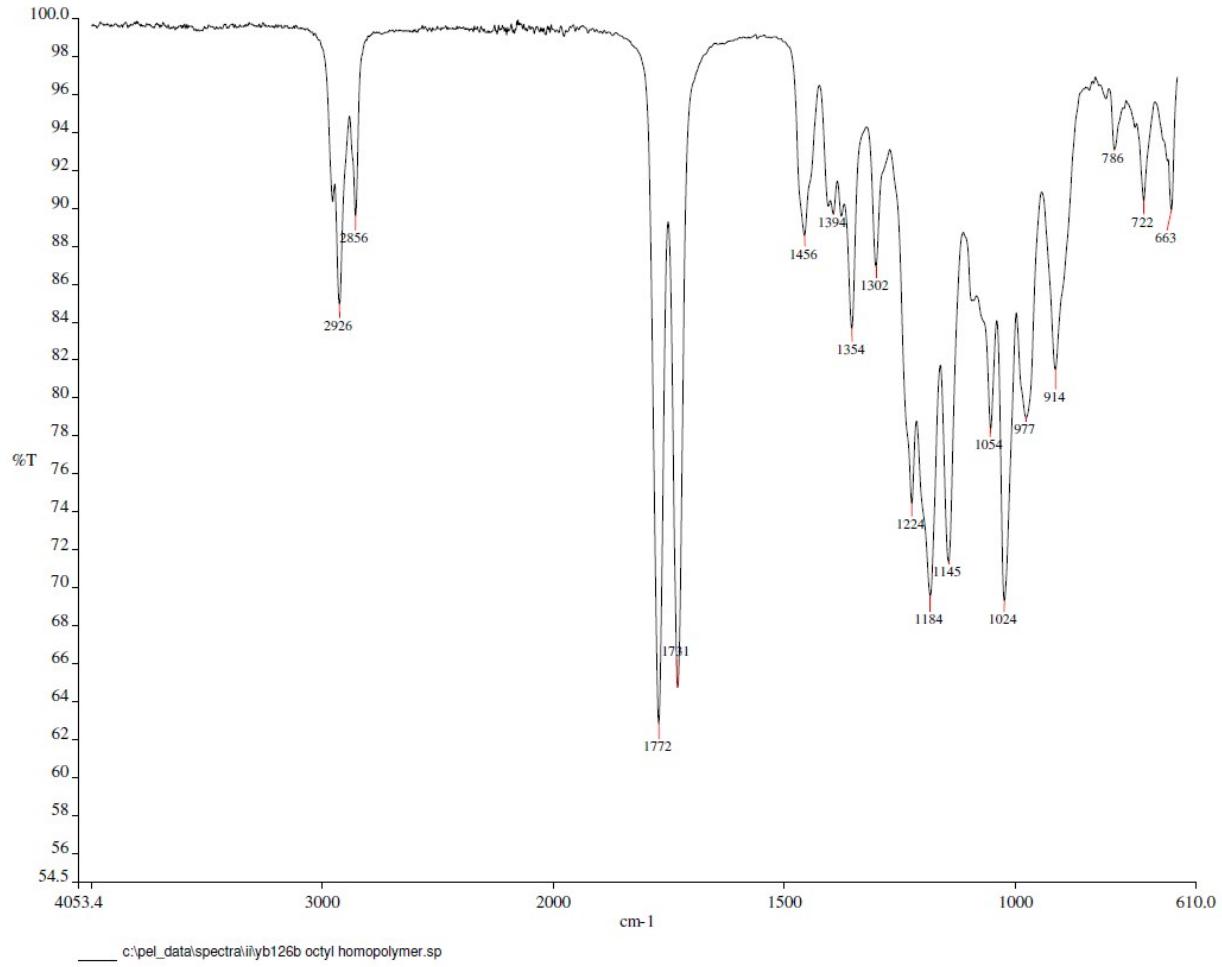
^{1}H NMR Spectrum



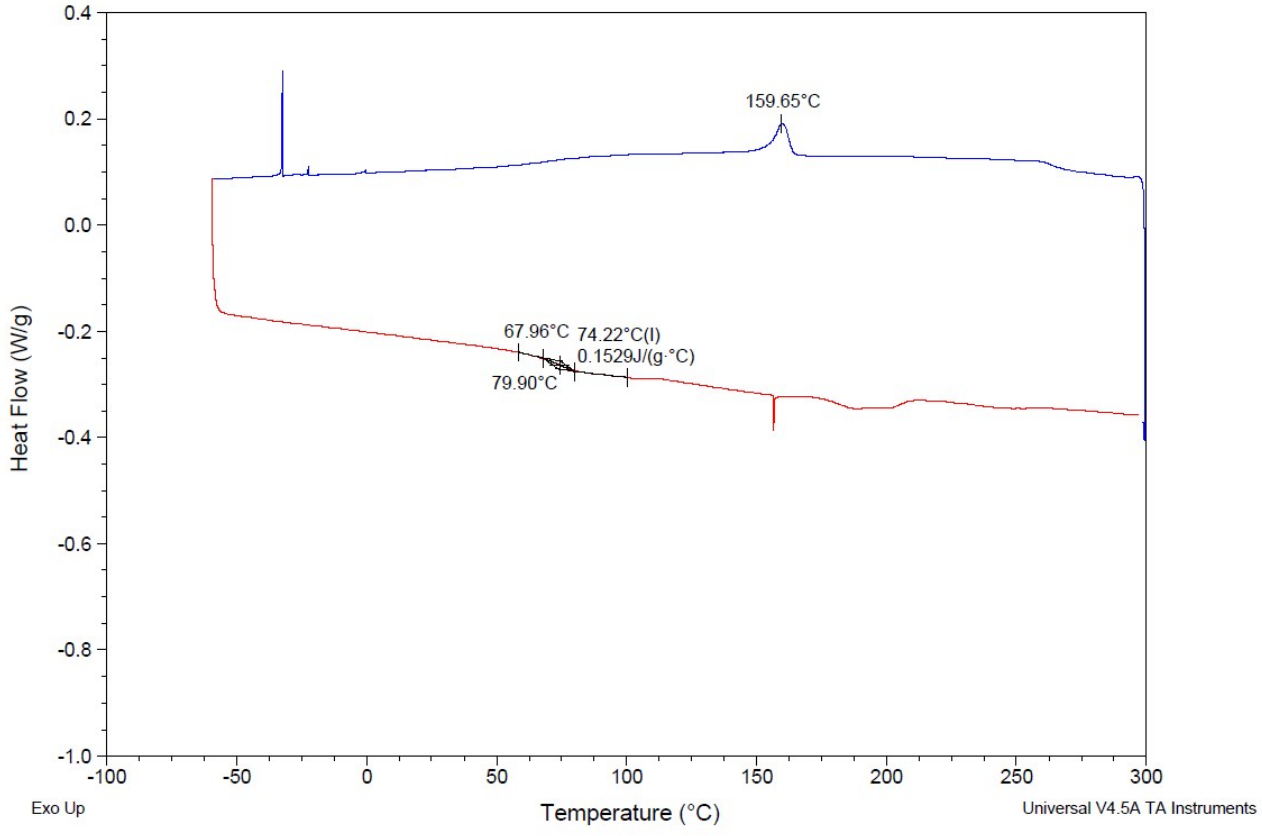
SEC



IR Spectrum

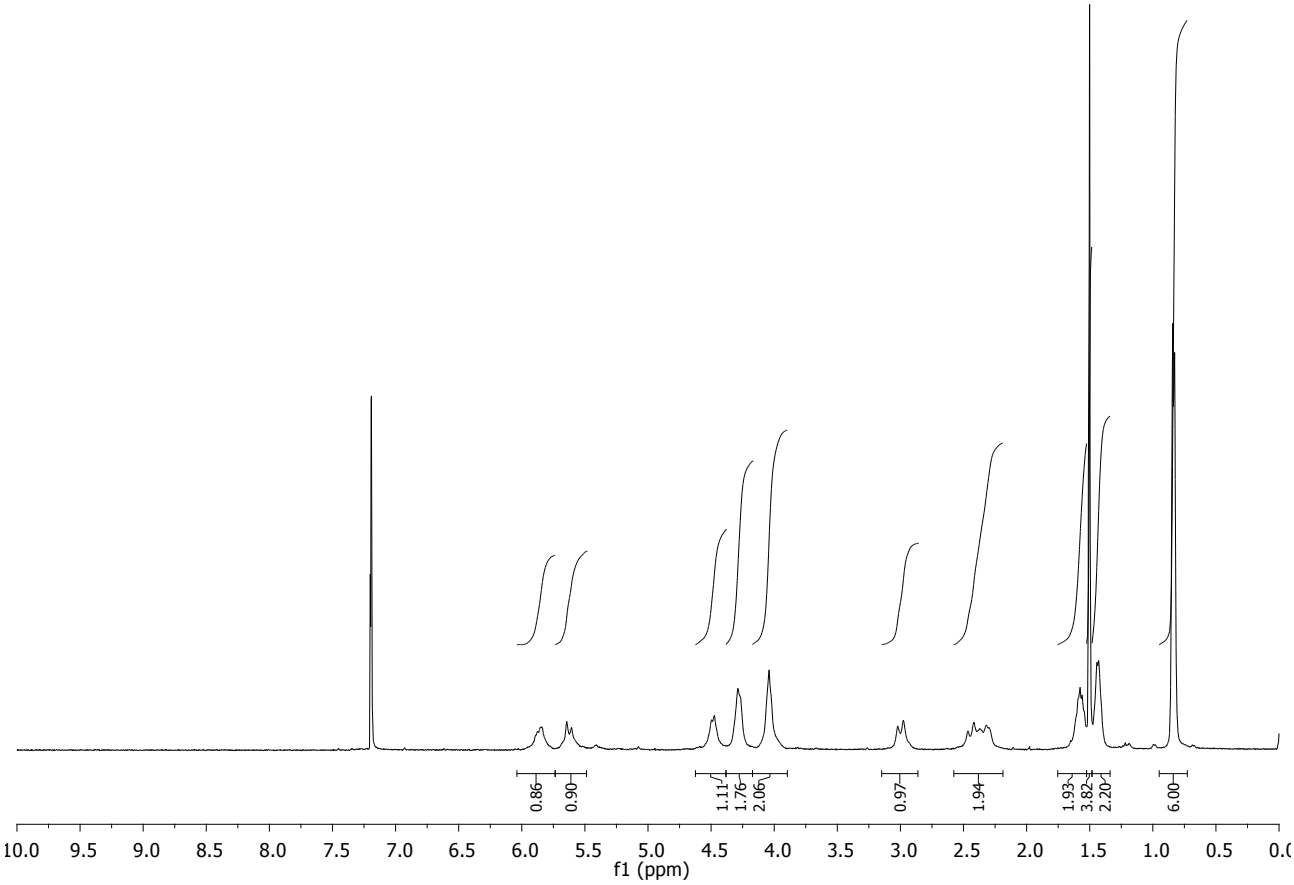


DSC

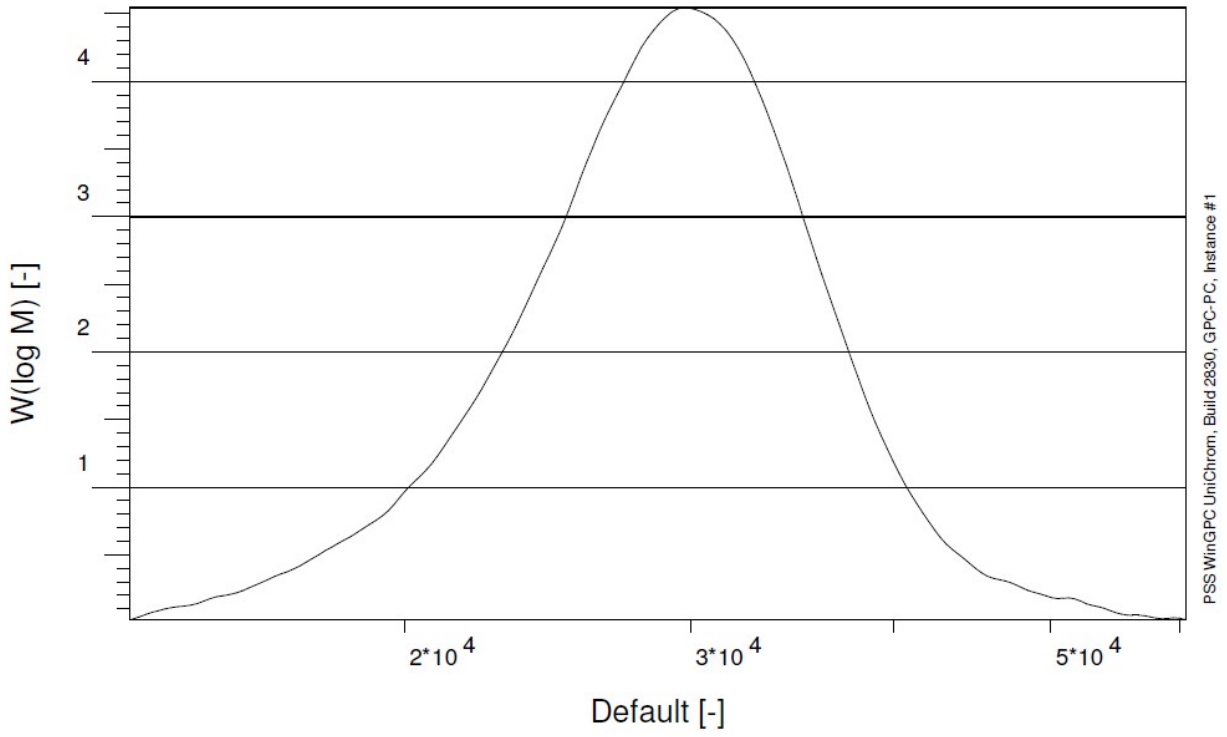


Polymerised isoamyl ester 9d (100:1 homopolymer)

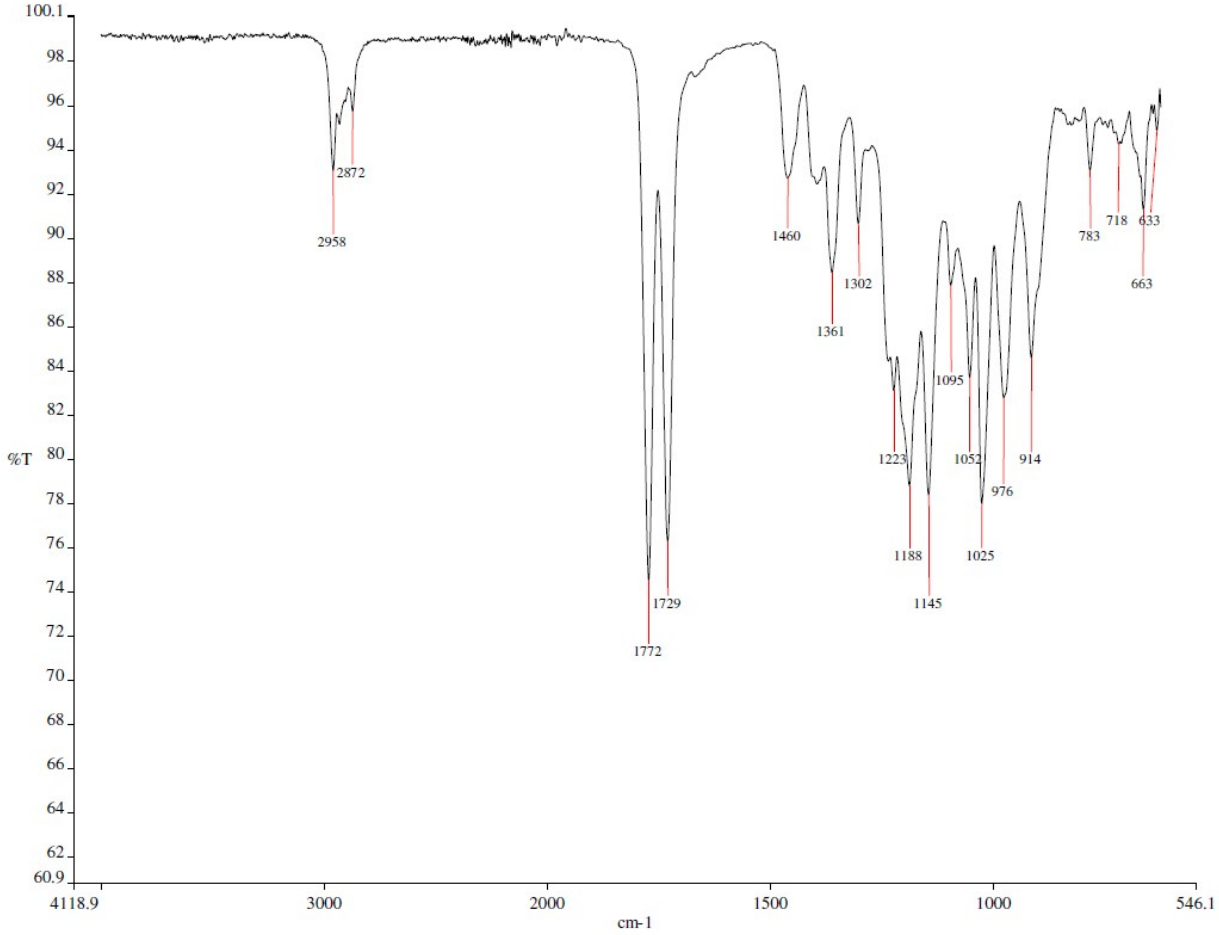
^{1}H NMR Spectrum



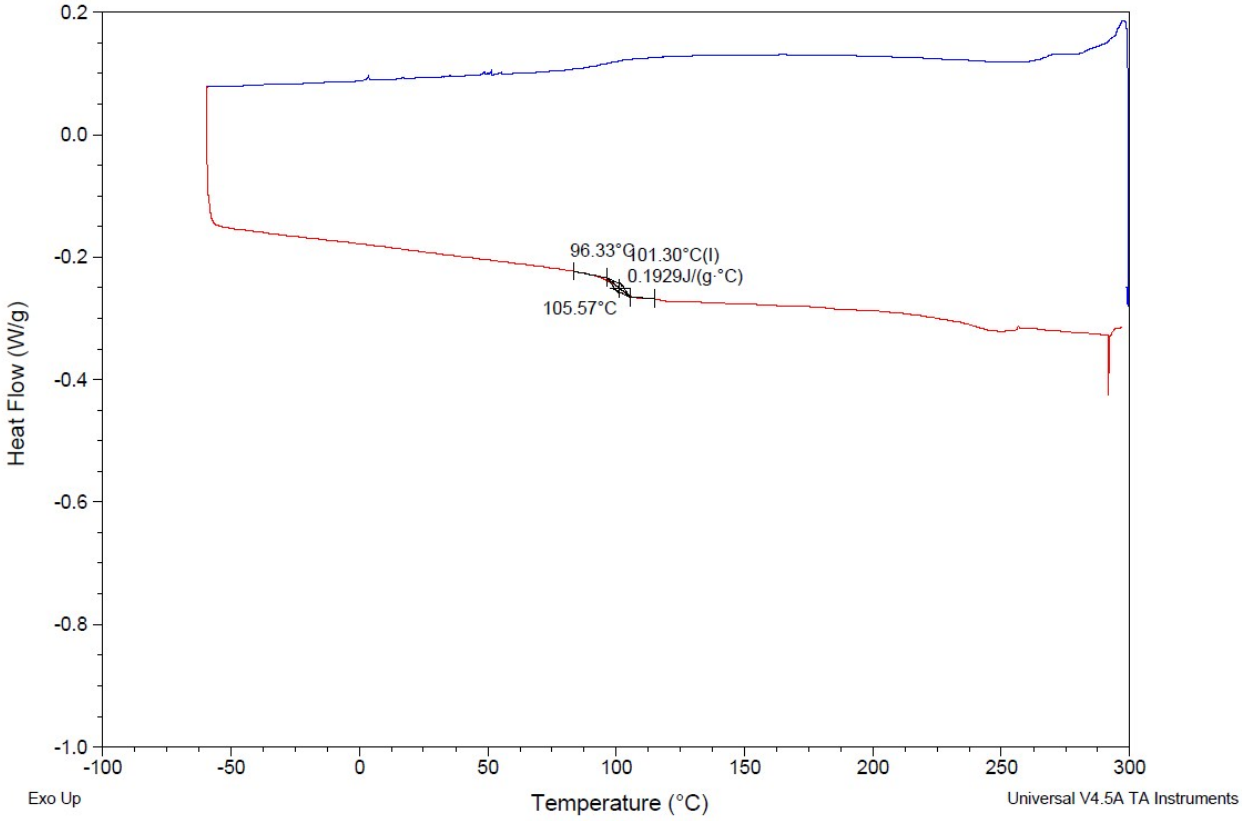
SEC



IR Spectrum

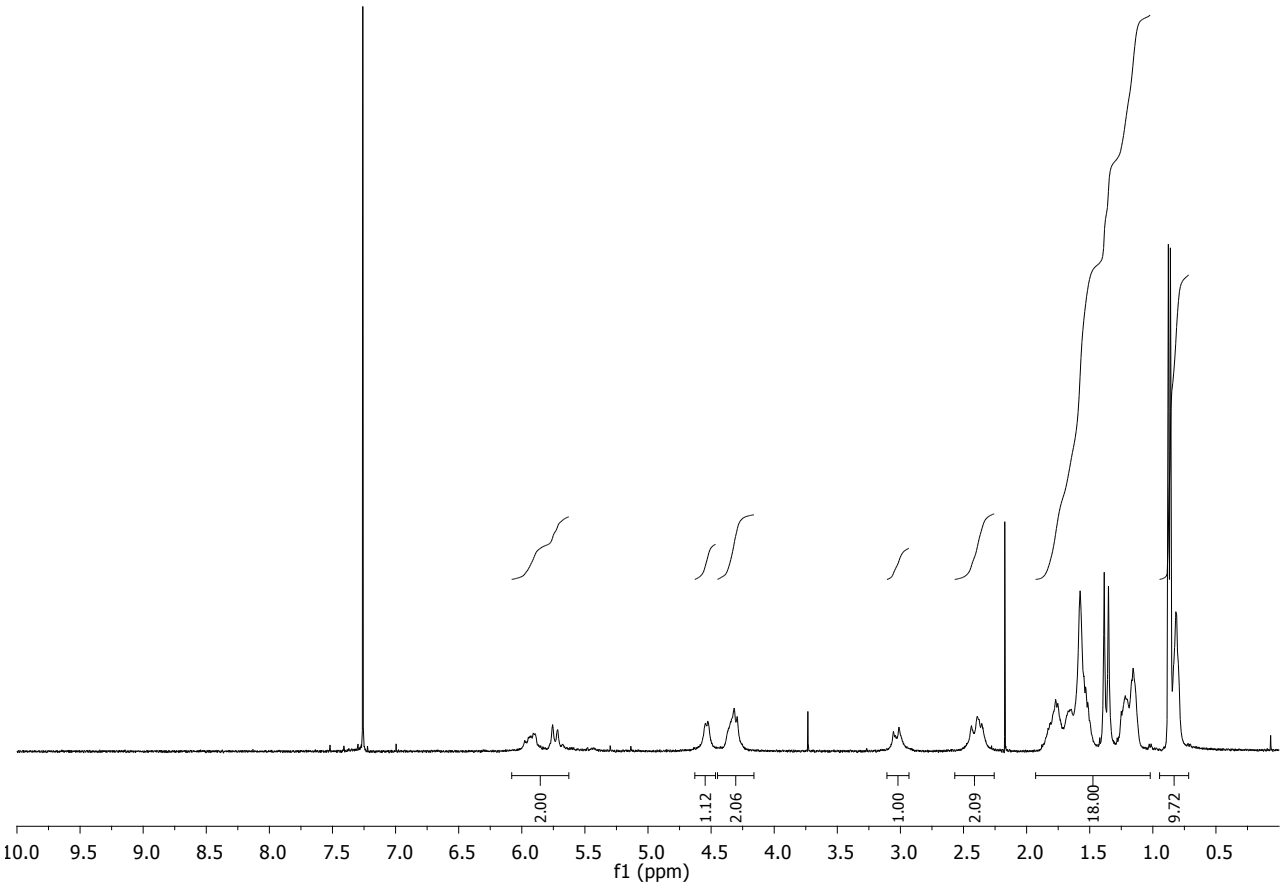


DSC

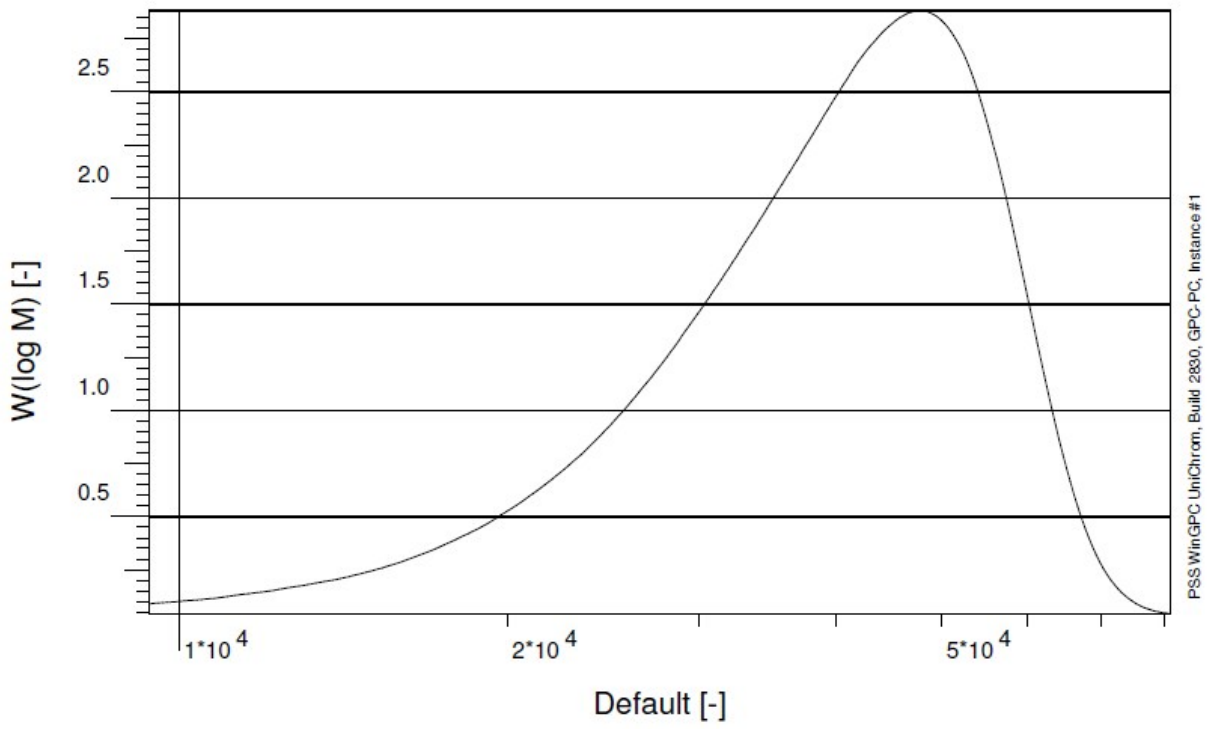


Polymerised linalooyl ester 9h (100:1 homopolymer)

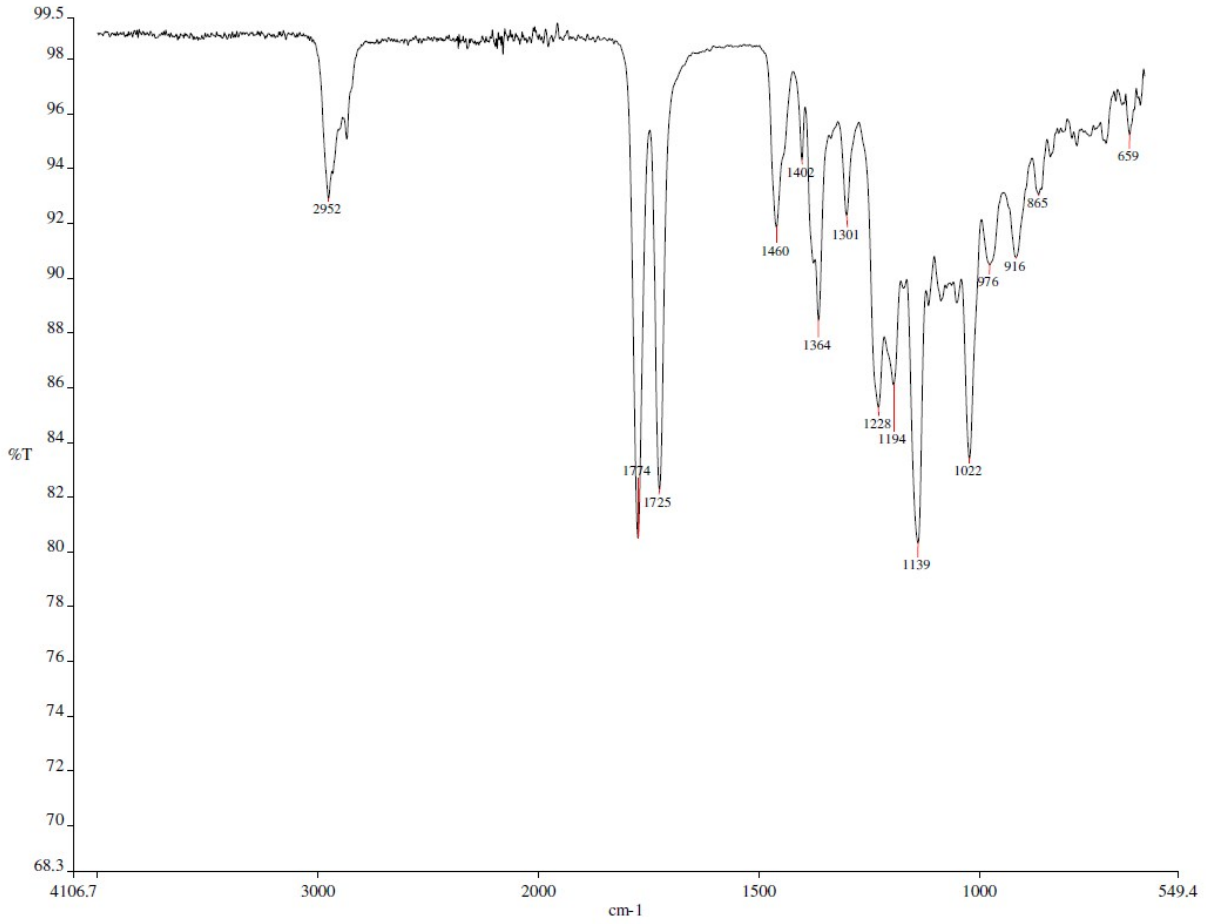
^{1}H NMR Spectrum



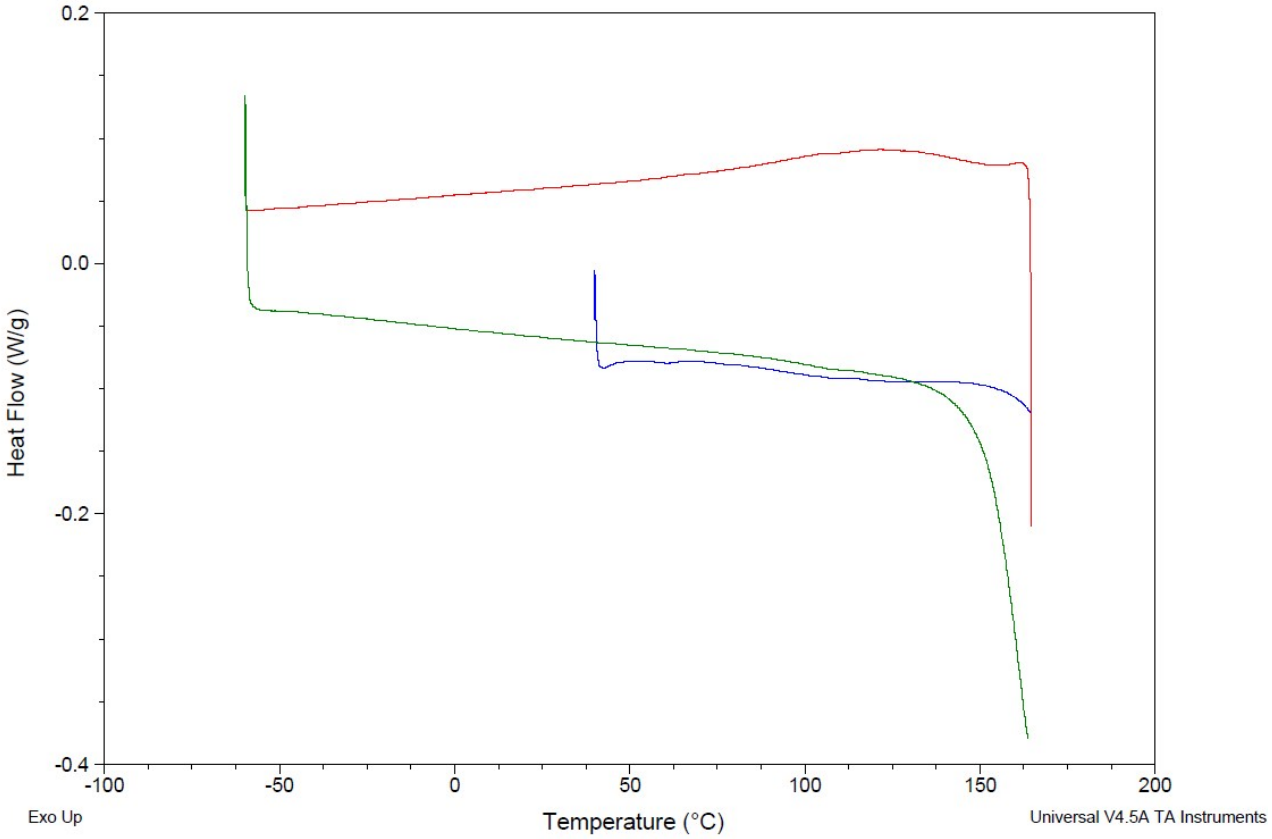
SEC



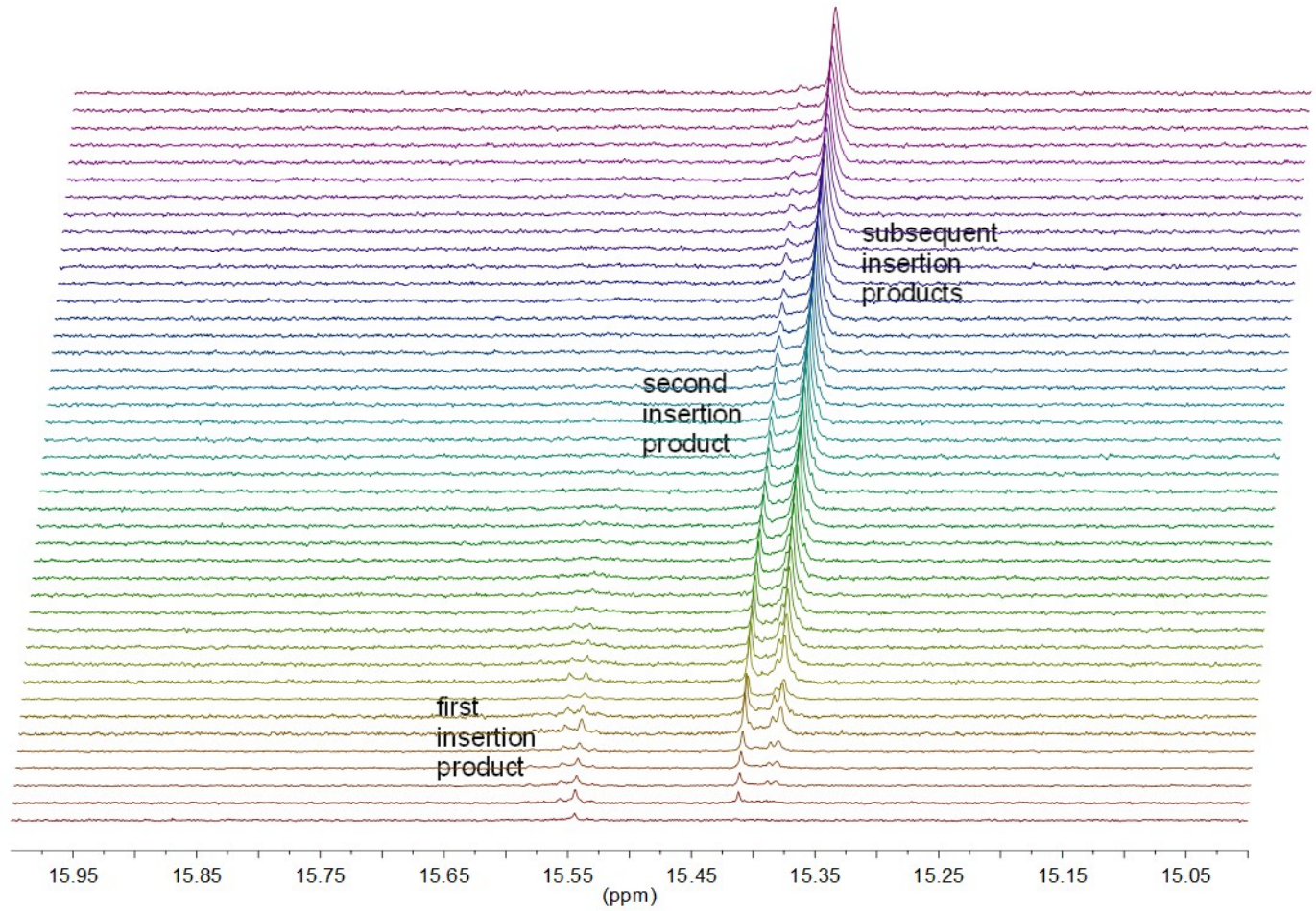
IR Spectrum



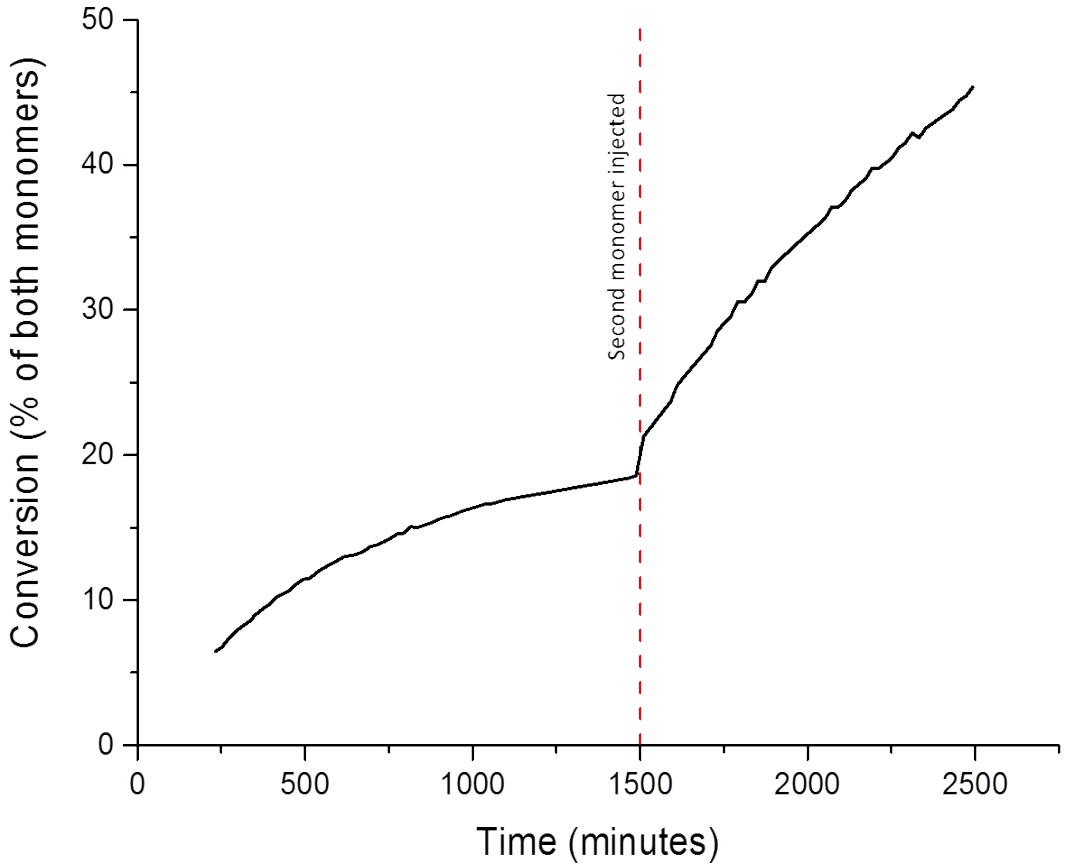
DSC



NMR monitoring of the block copolymerisation of monomers 8a and 8b

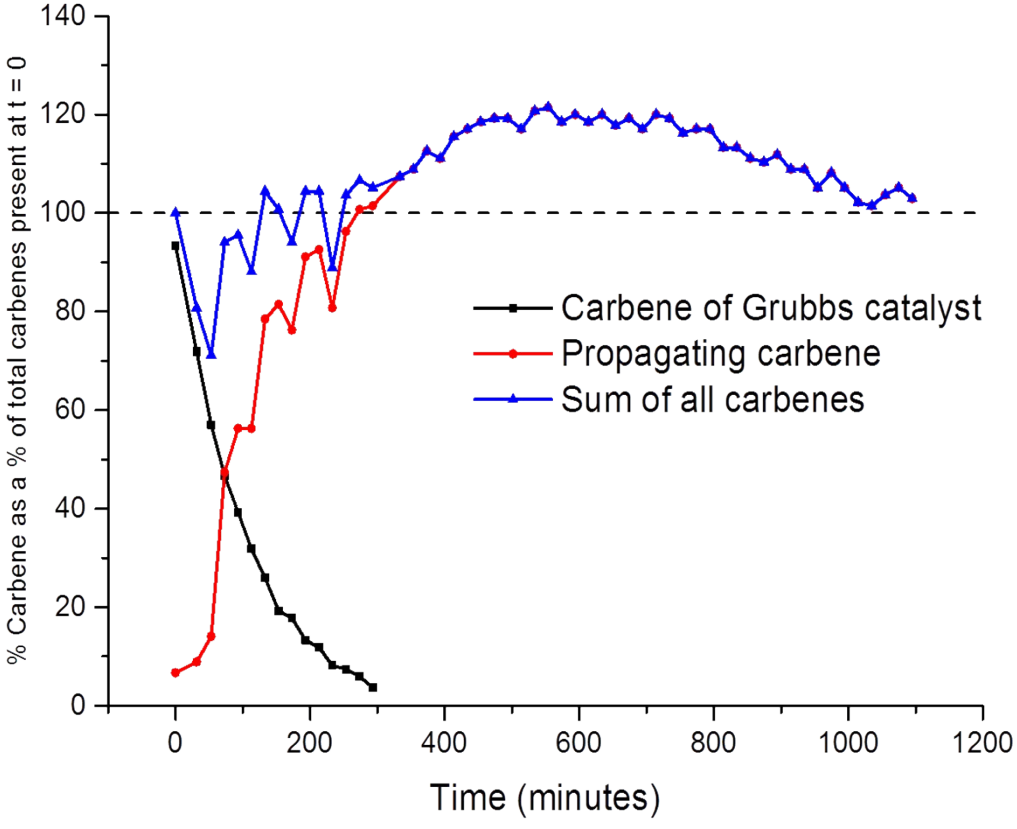


Additional stacked ^{1}H NMR plot showing more detail of the alkylidene region during the initial stages of polymerisation of **8a**. The change in alkylidene signal reflecting monomer, dimer, and then oligomer bound to ruthenium, is apparent.

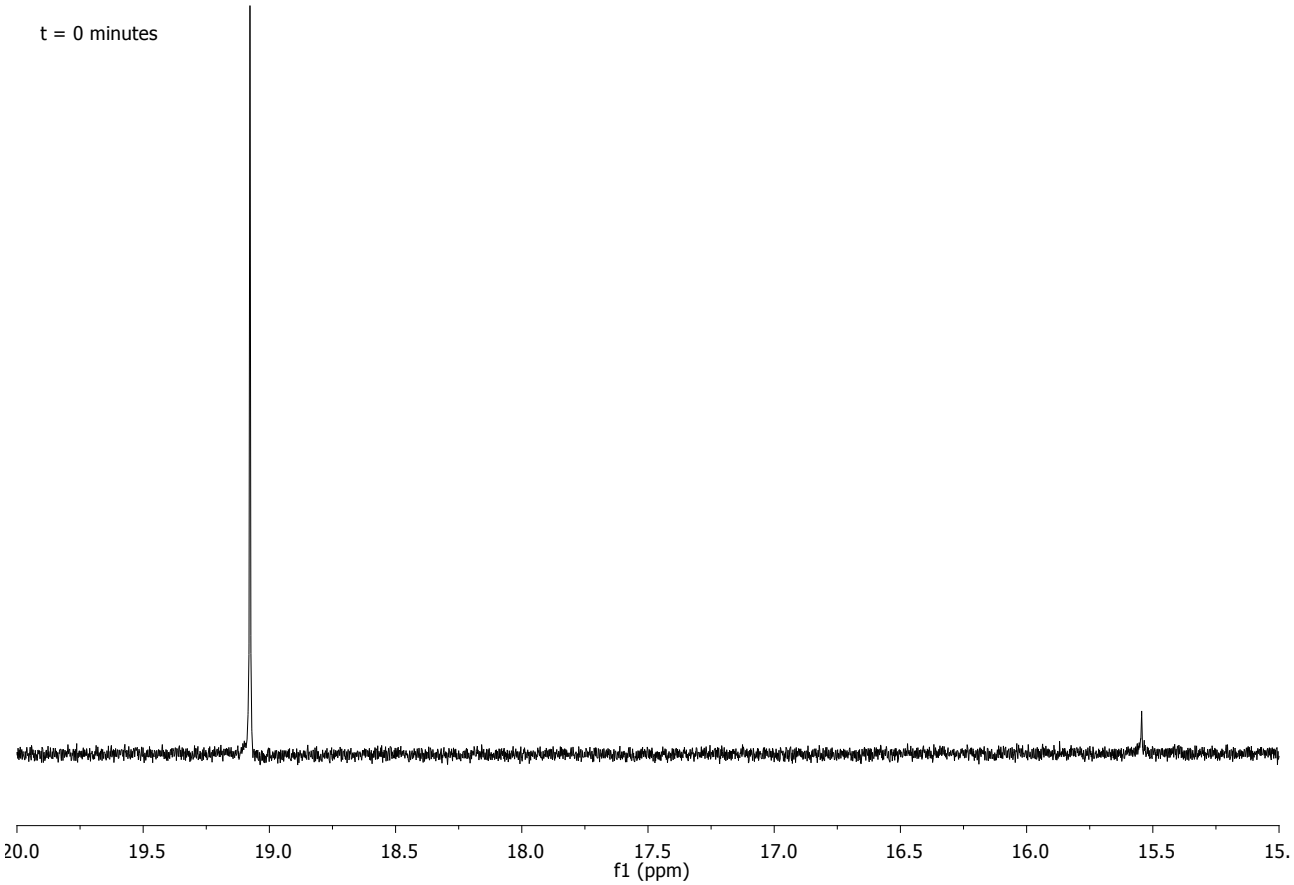


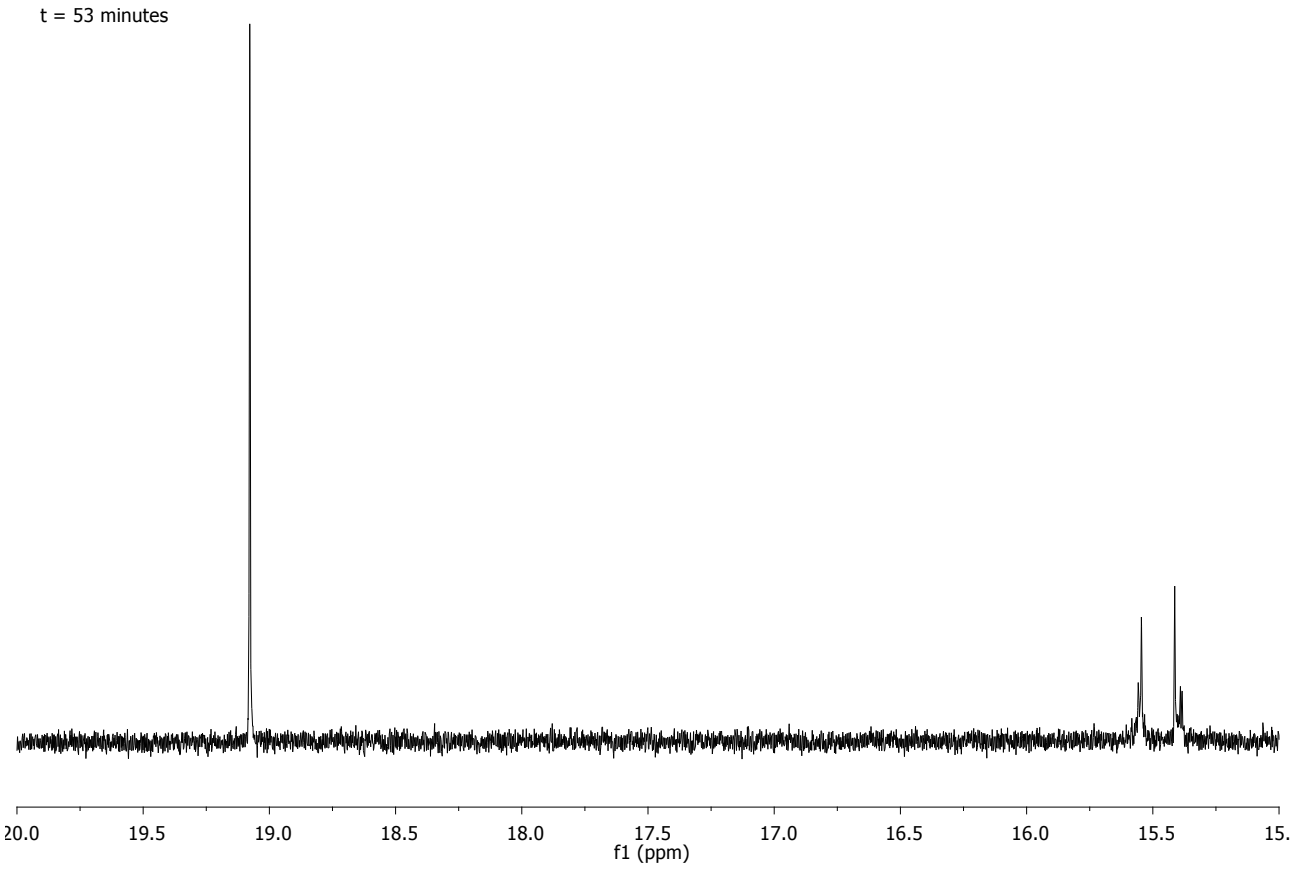
Graph showing total monomer conversion throughout the experiment as a function of time.

Plot of carbene integral versus time

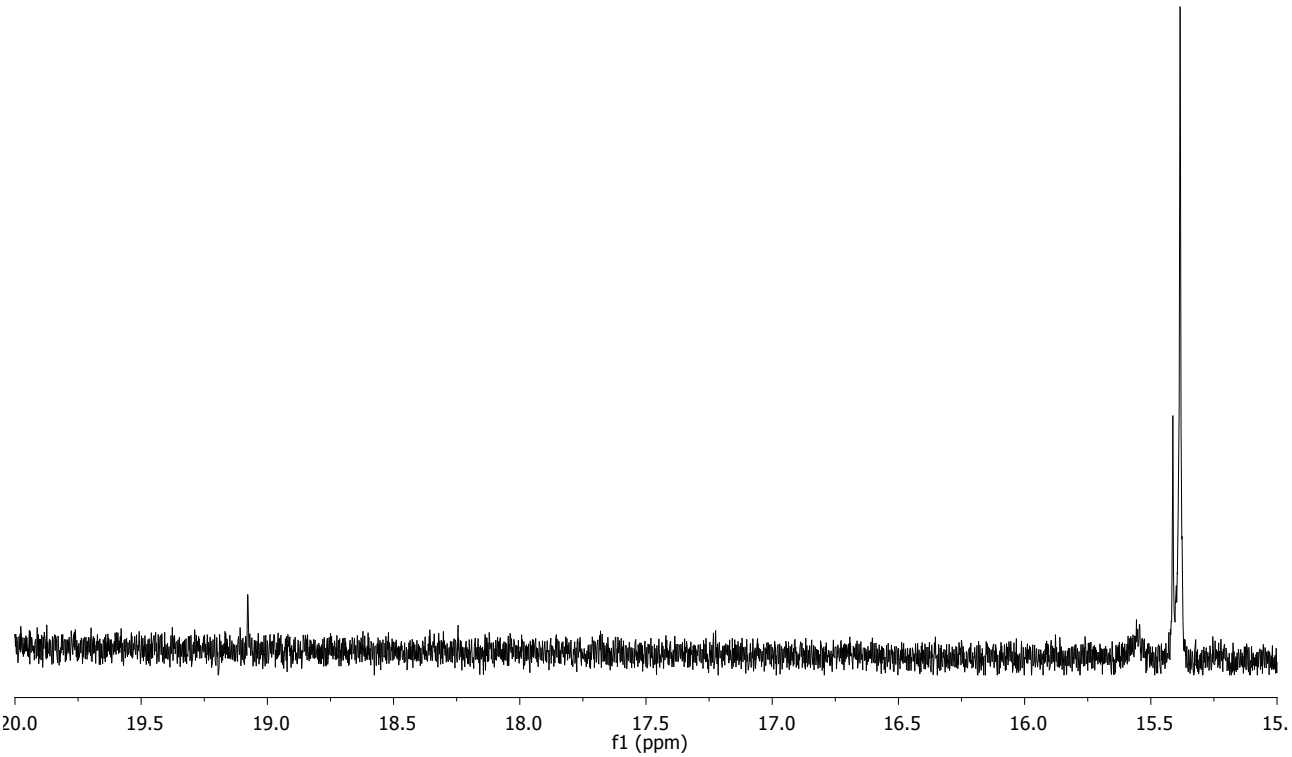


Individual spectra from Figure 7

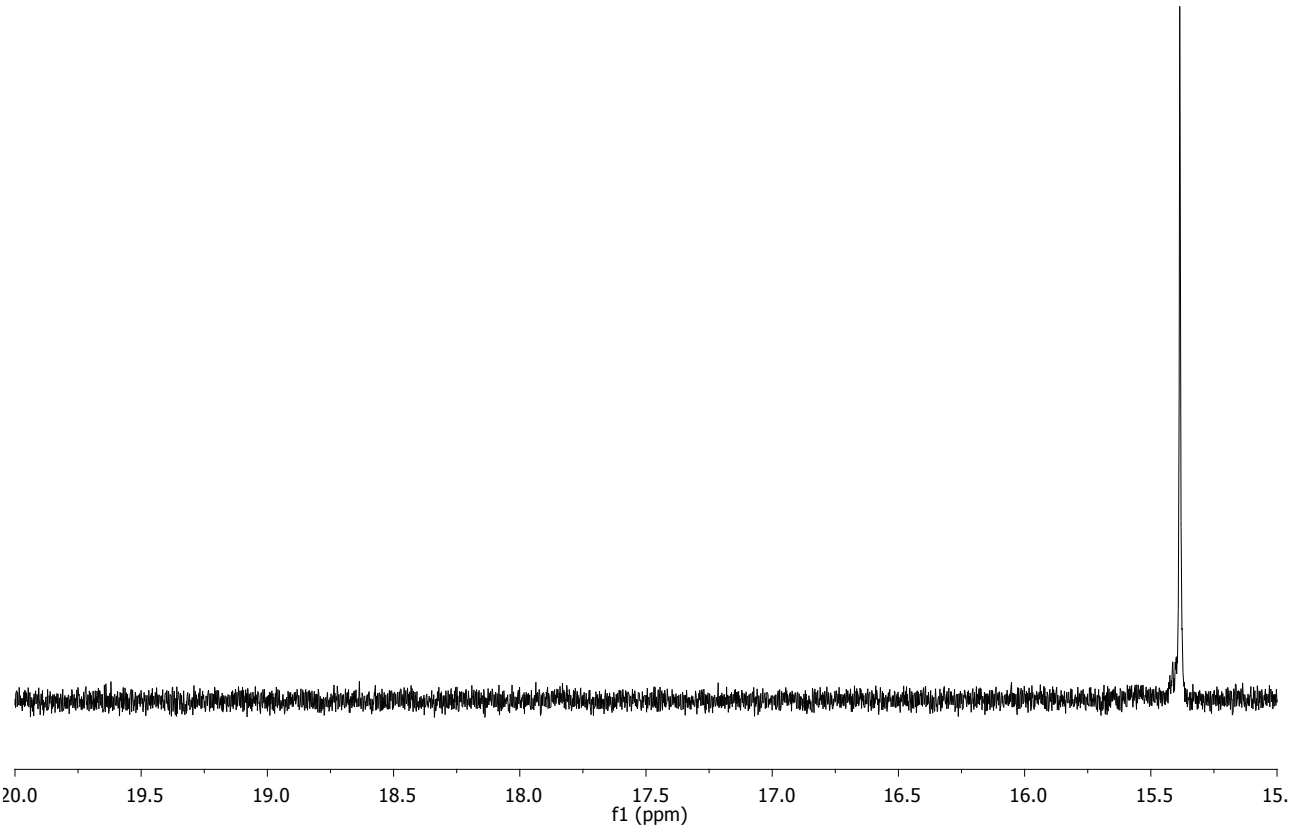


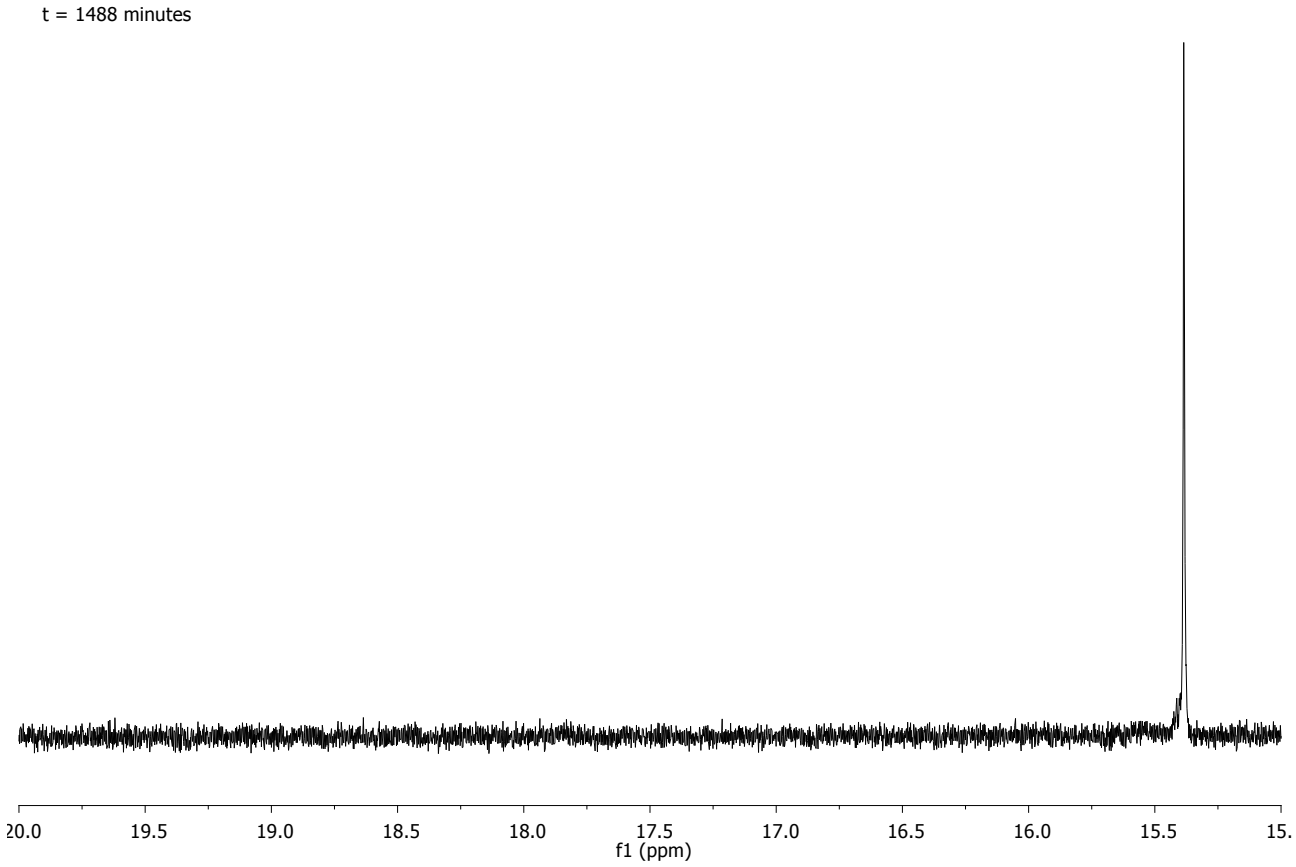


t = 333 minutes



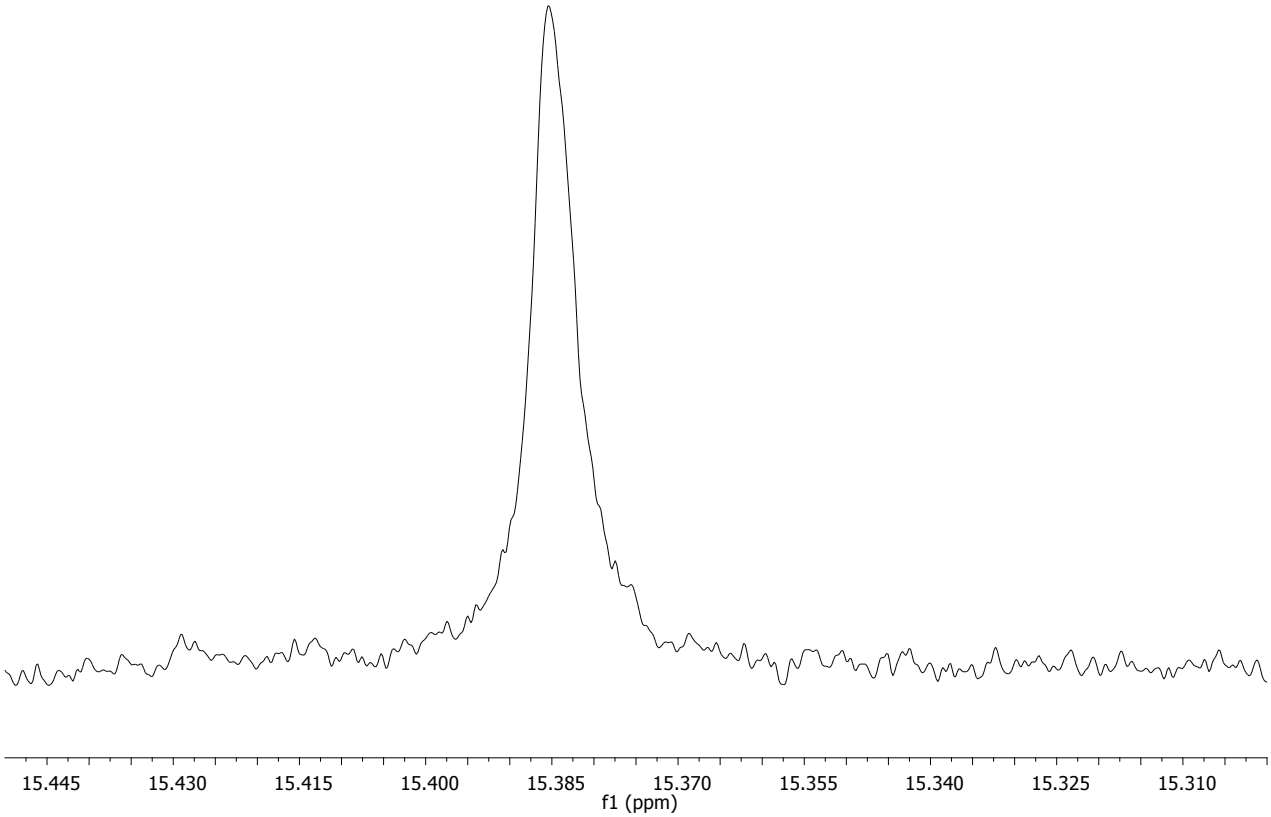
t = 534 minutes



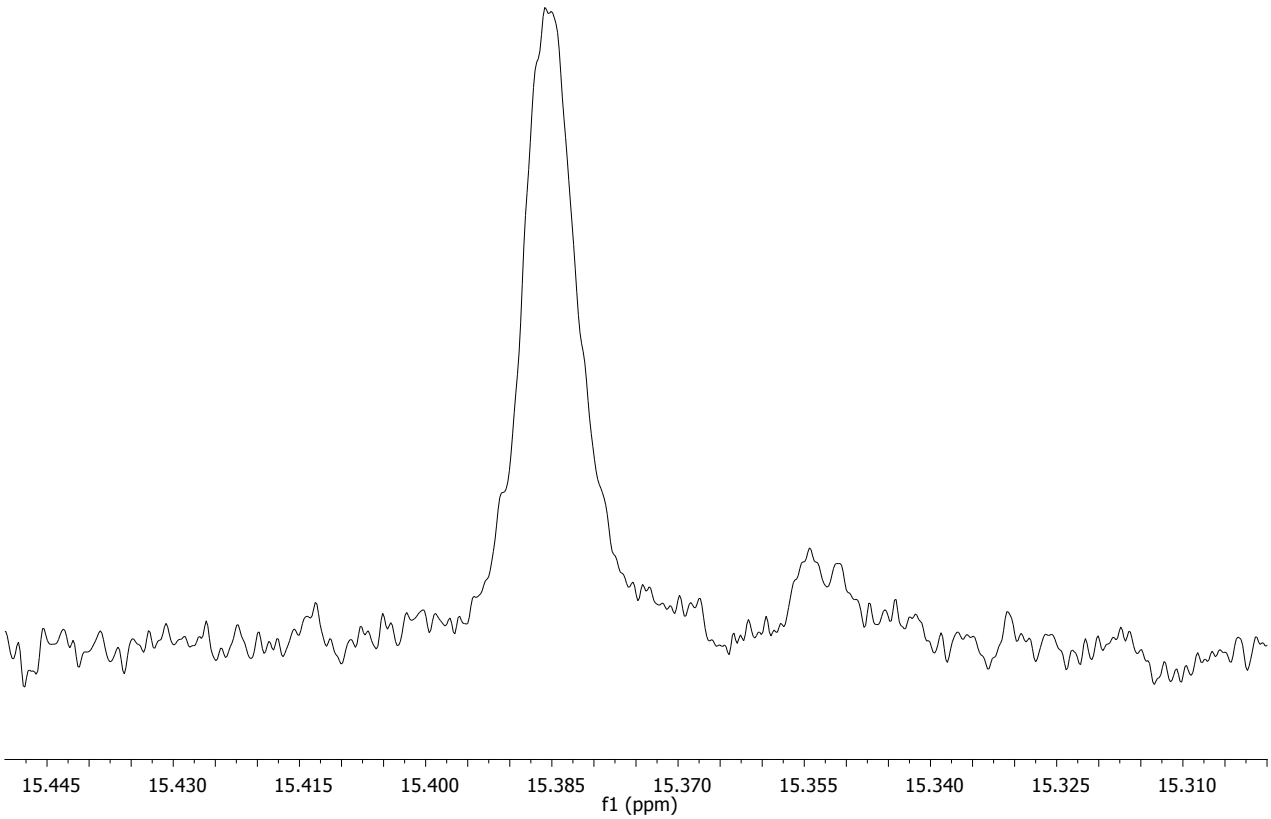

t = 1488 minutes
20.0
19.5
19.0
18.5
18.0
17.5
17.0
16.5
16.0
15.5
15.
f1 (ppm)

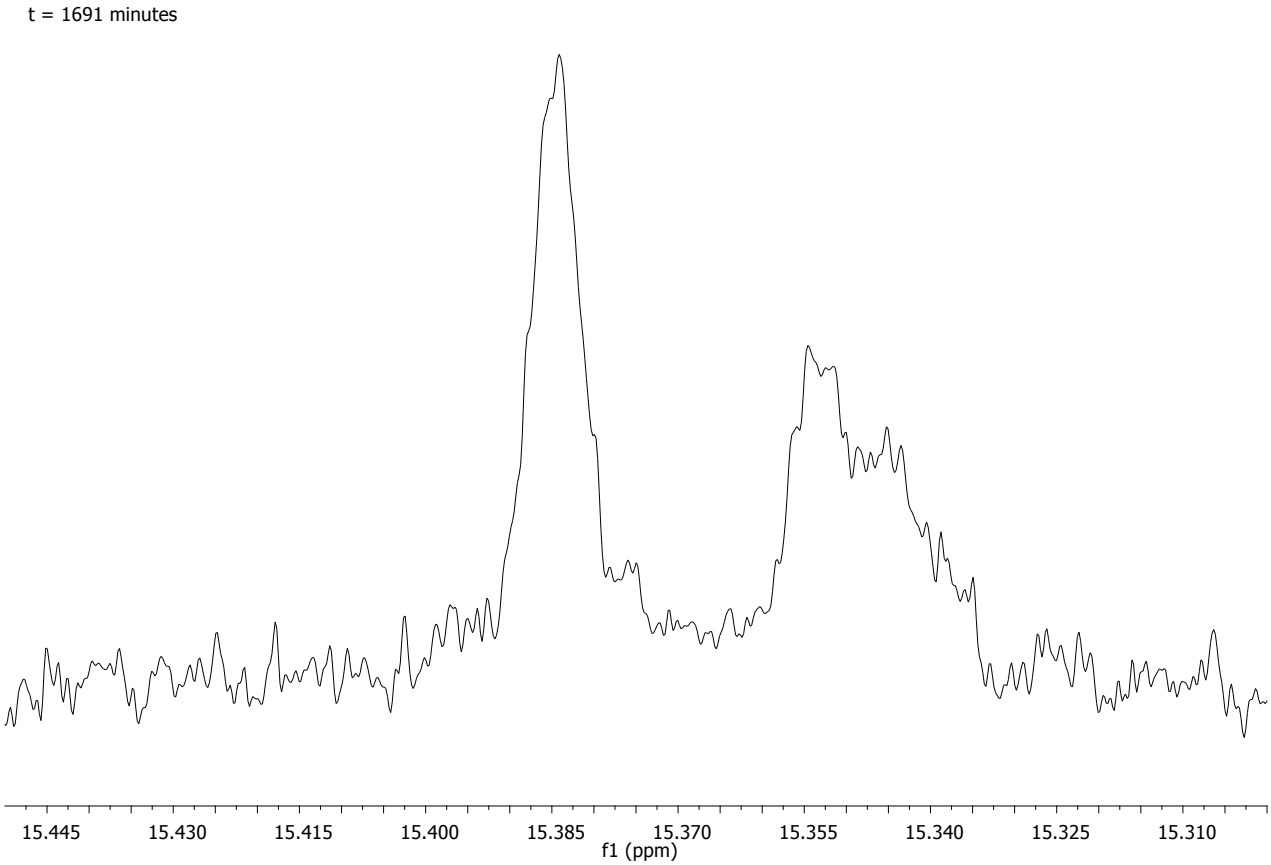
Individual spectra from Figure 8

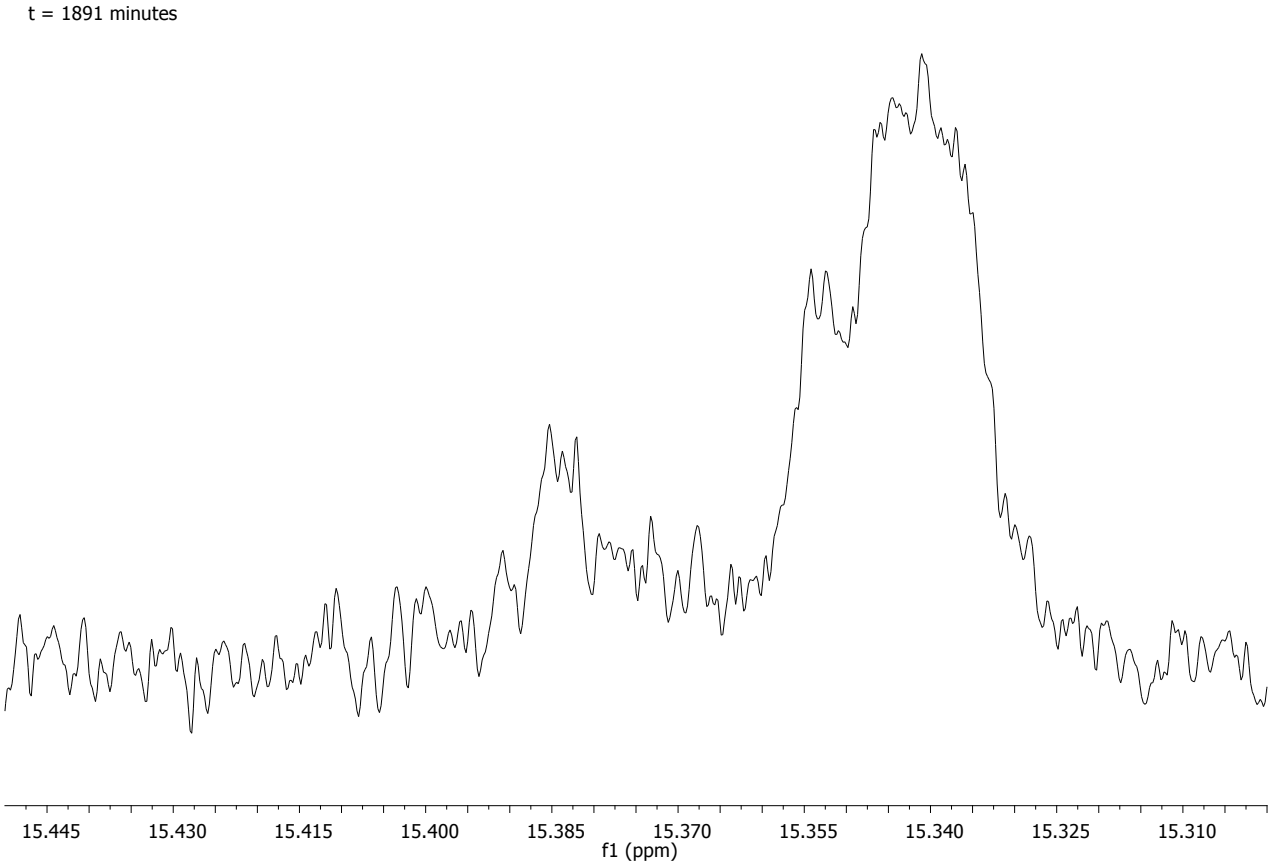
t = 1510 minutes

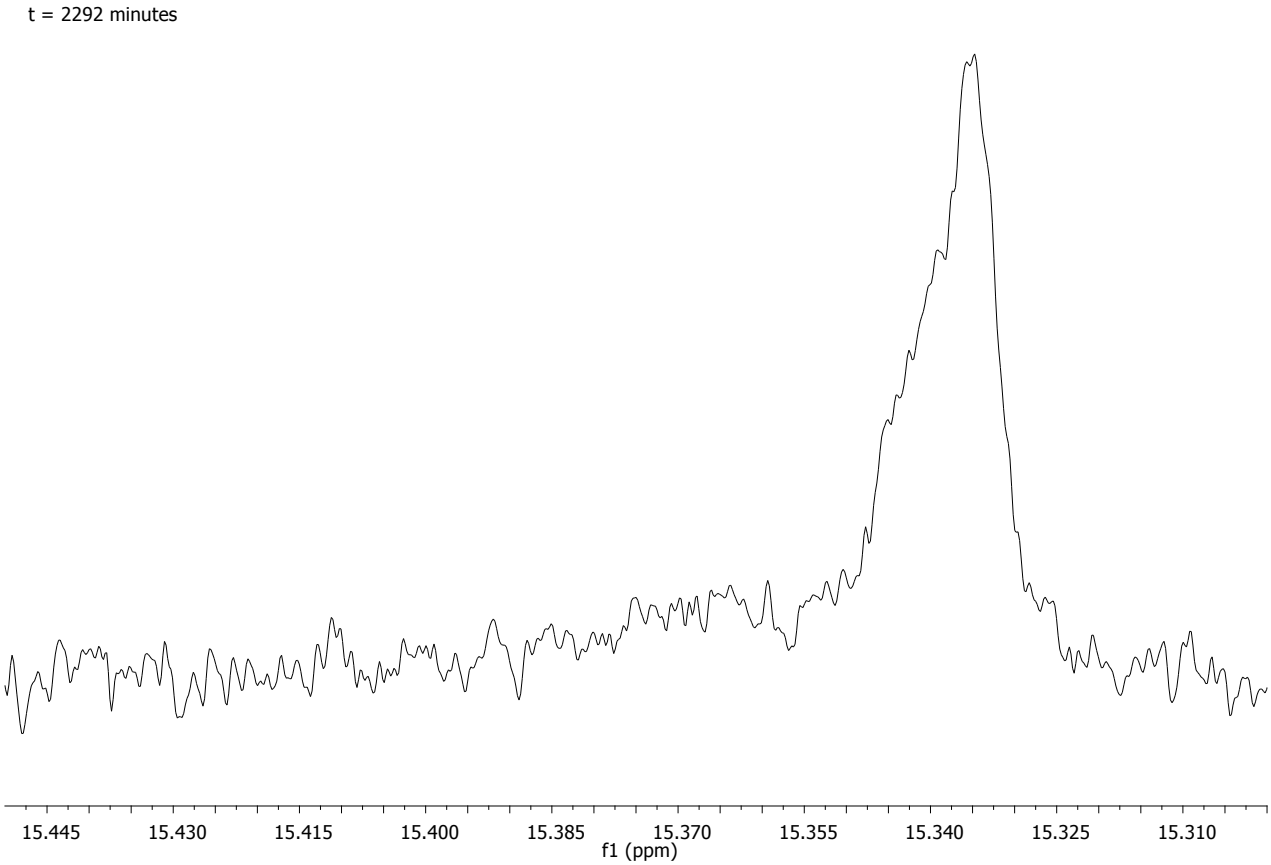


t = 1590 minutes



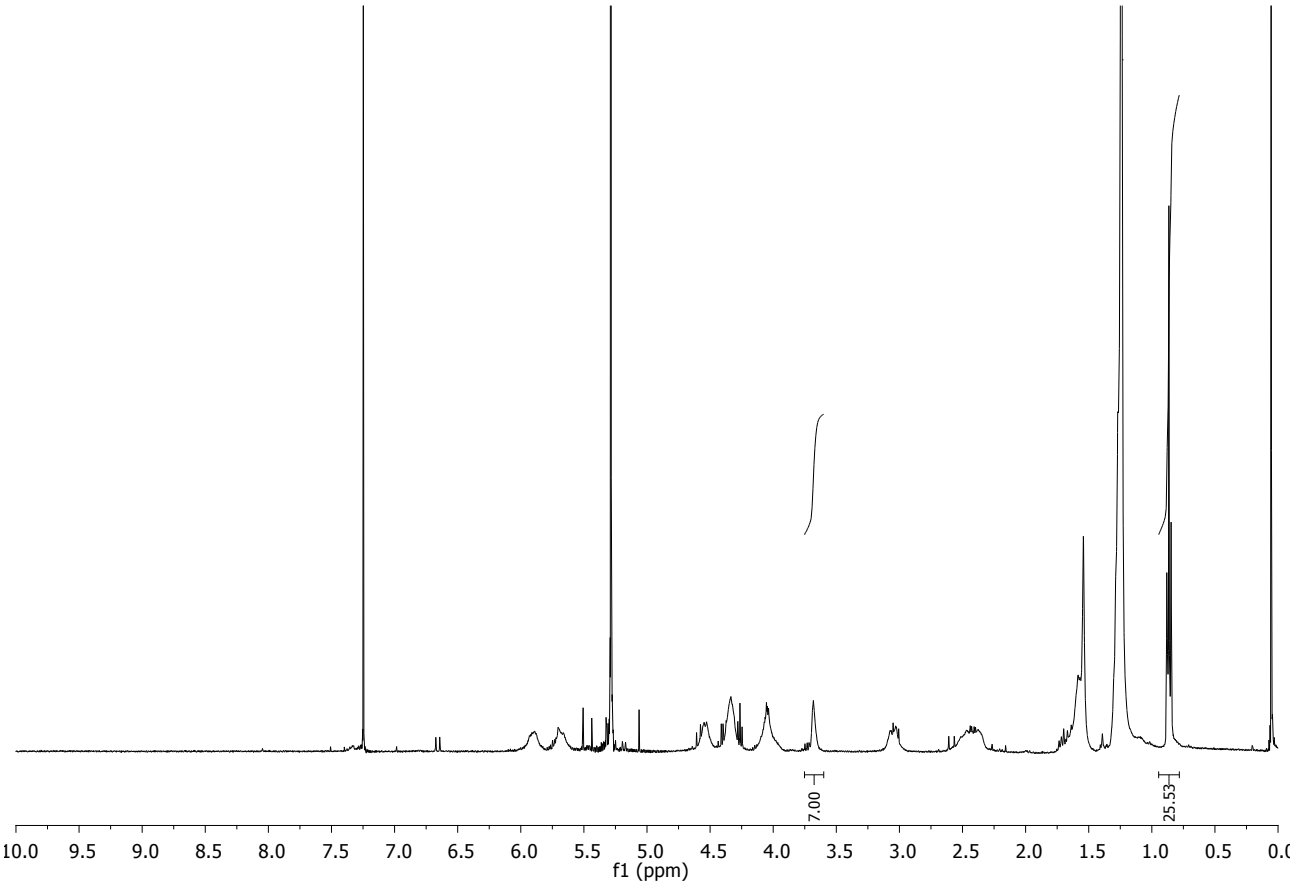

t = 1691 minutes
15.445
15.430
15.415
15.400
15.385
15.370
15.355
15.340
15.325
15.310
f1 (ppm)


t = 1891 minutes
15.445
15.430
15.415
15.400
15.385
15.370
15.355
15.340
15.325
15.310
f1 (ppm)

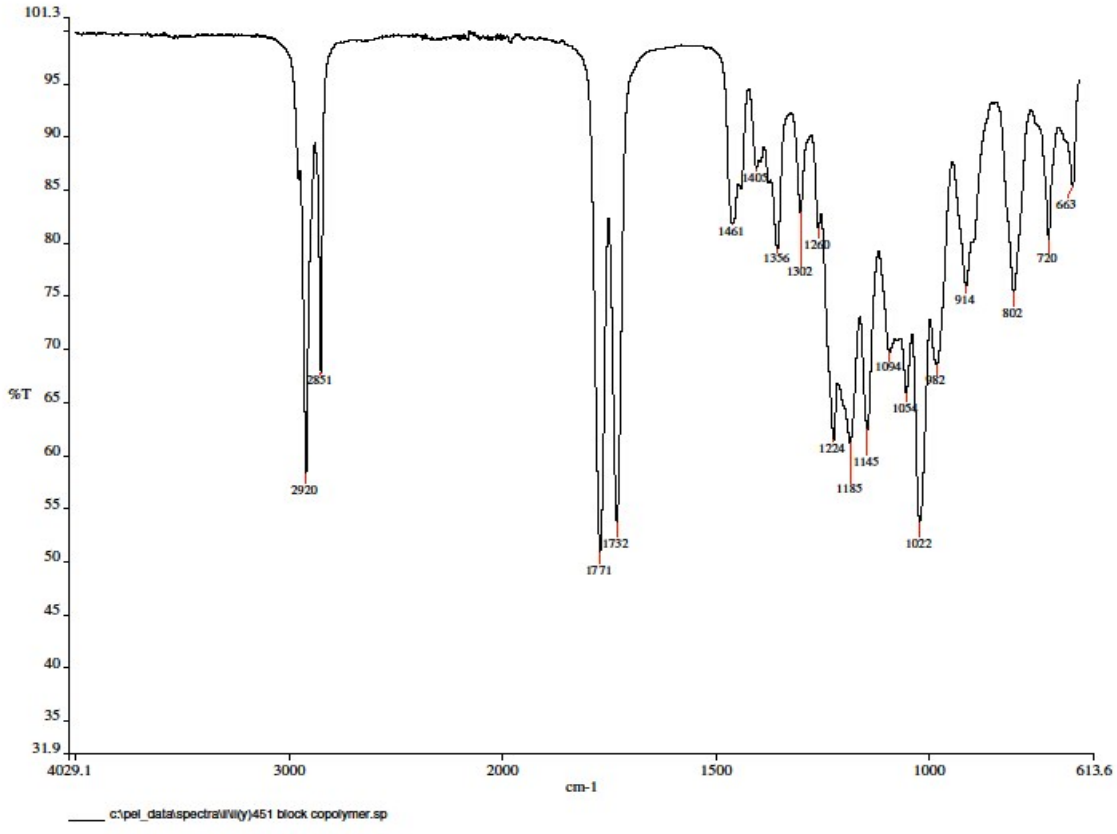

t = 2292 minutes
15.445
15.430
15.415
15.400
15.385
15.370
15.355
15.340
15.325
15.310
f1 (ppm)

Block copolymer of monomers 8a and 8b

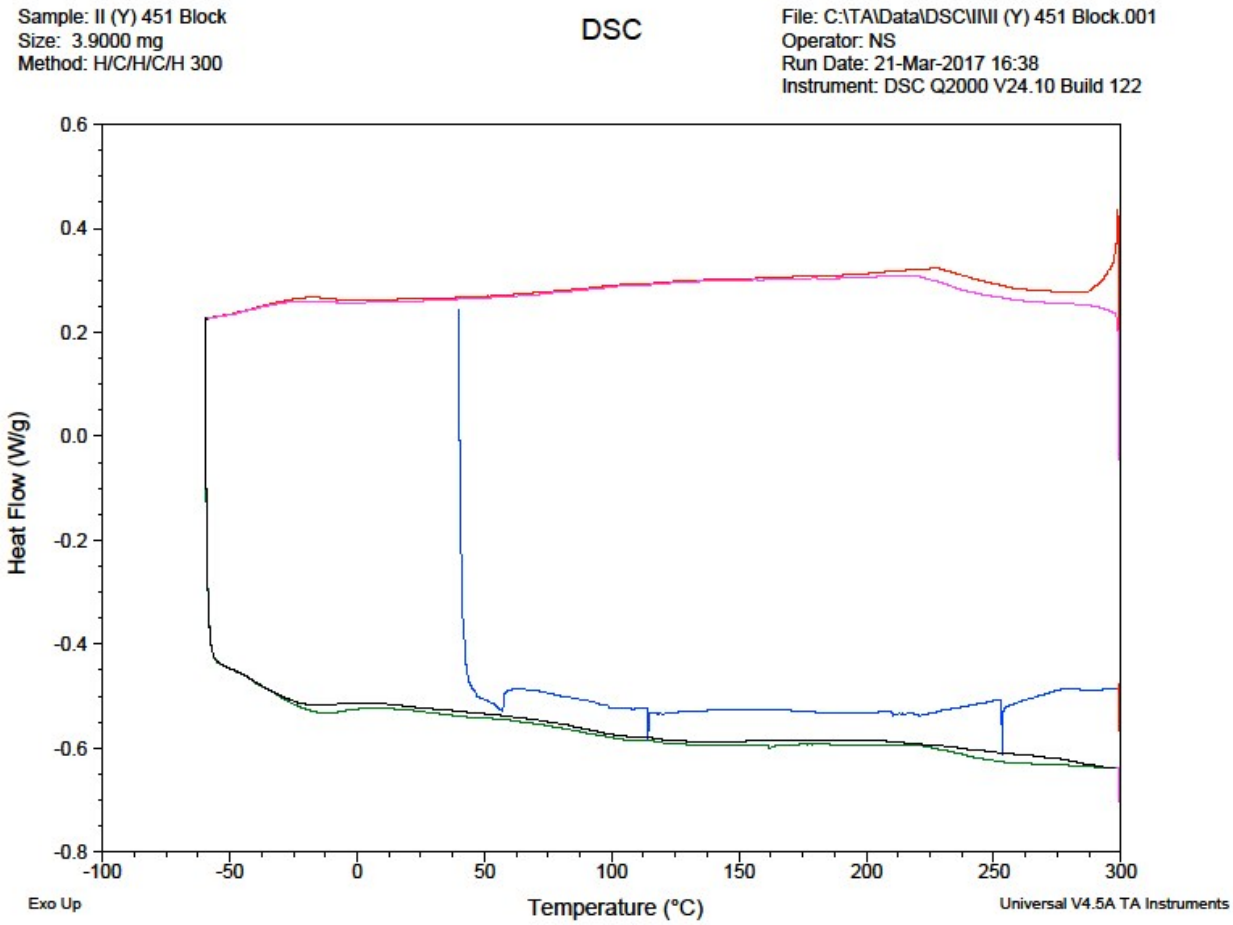
^{1}H NMR spectrum



IR spectrum

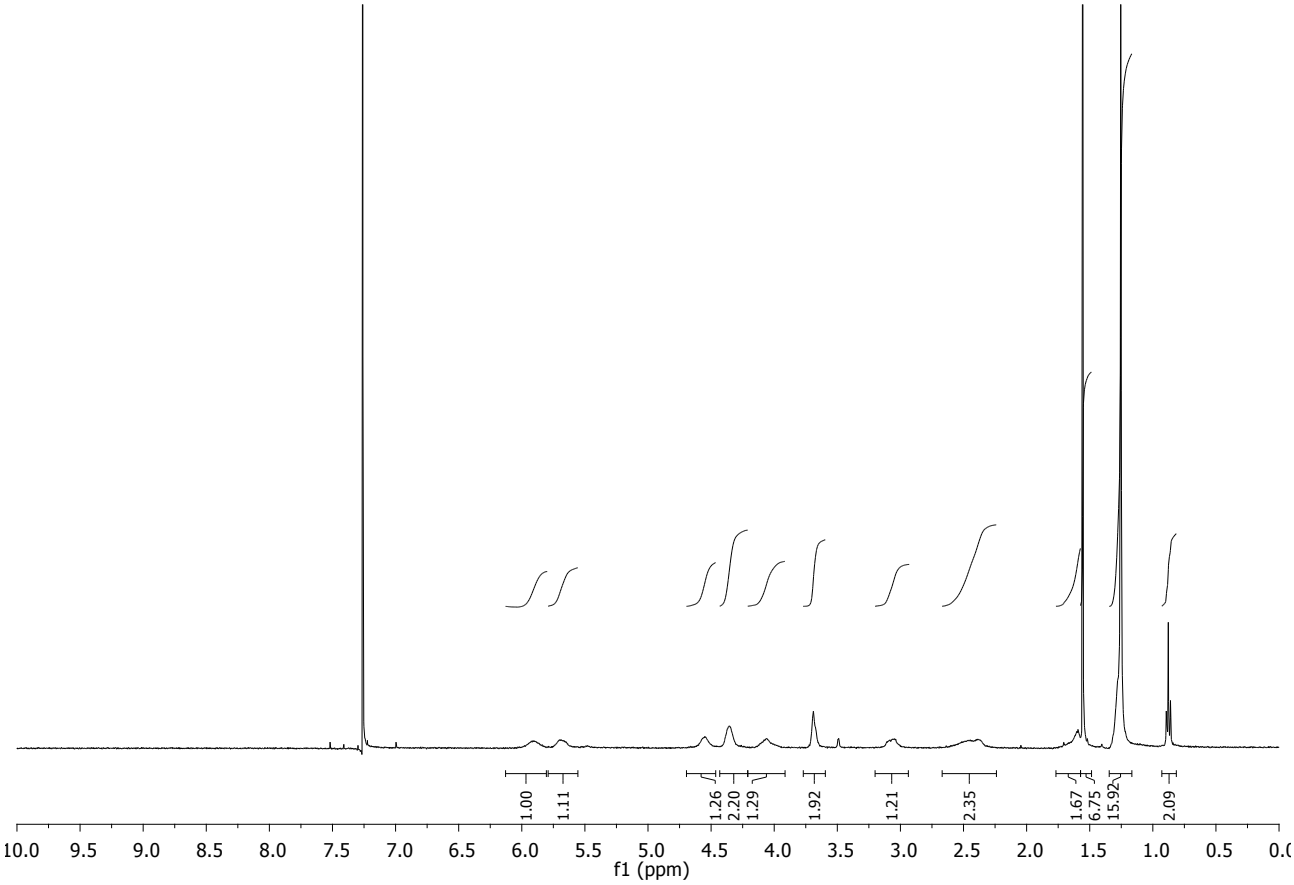


DSC

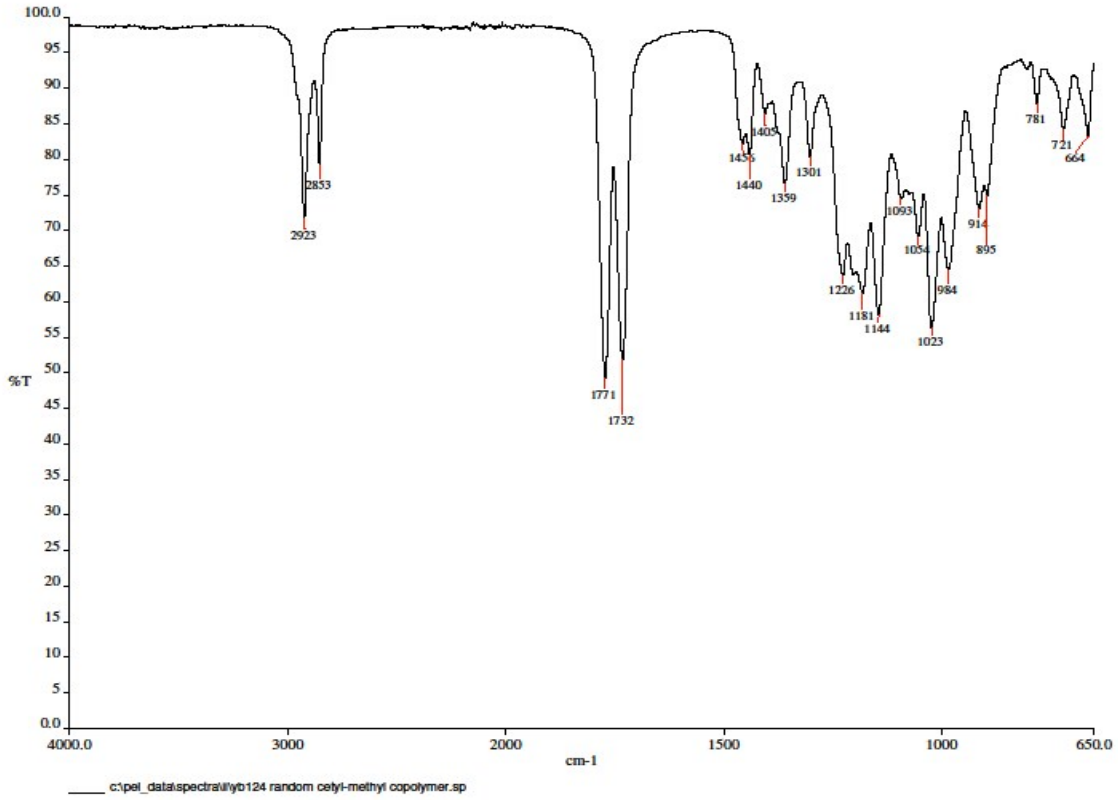

Sample: II (Y) 451 Block
Size: 3.9000 mg
Method: H/C/H/C/H 300
DSC
File: C:\TA\Data\DSC\II\II (Y) 451 Block.001
Operator: NS
Run Date: 21-Mar-2017 16:38
Instrument: DSC Q2000 V24.10 Build 122
Heat Flow (W/g)
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-100
-50
0
50
100
150
200
250
300
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

Random copolymer of monomers 8a and 8b

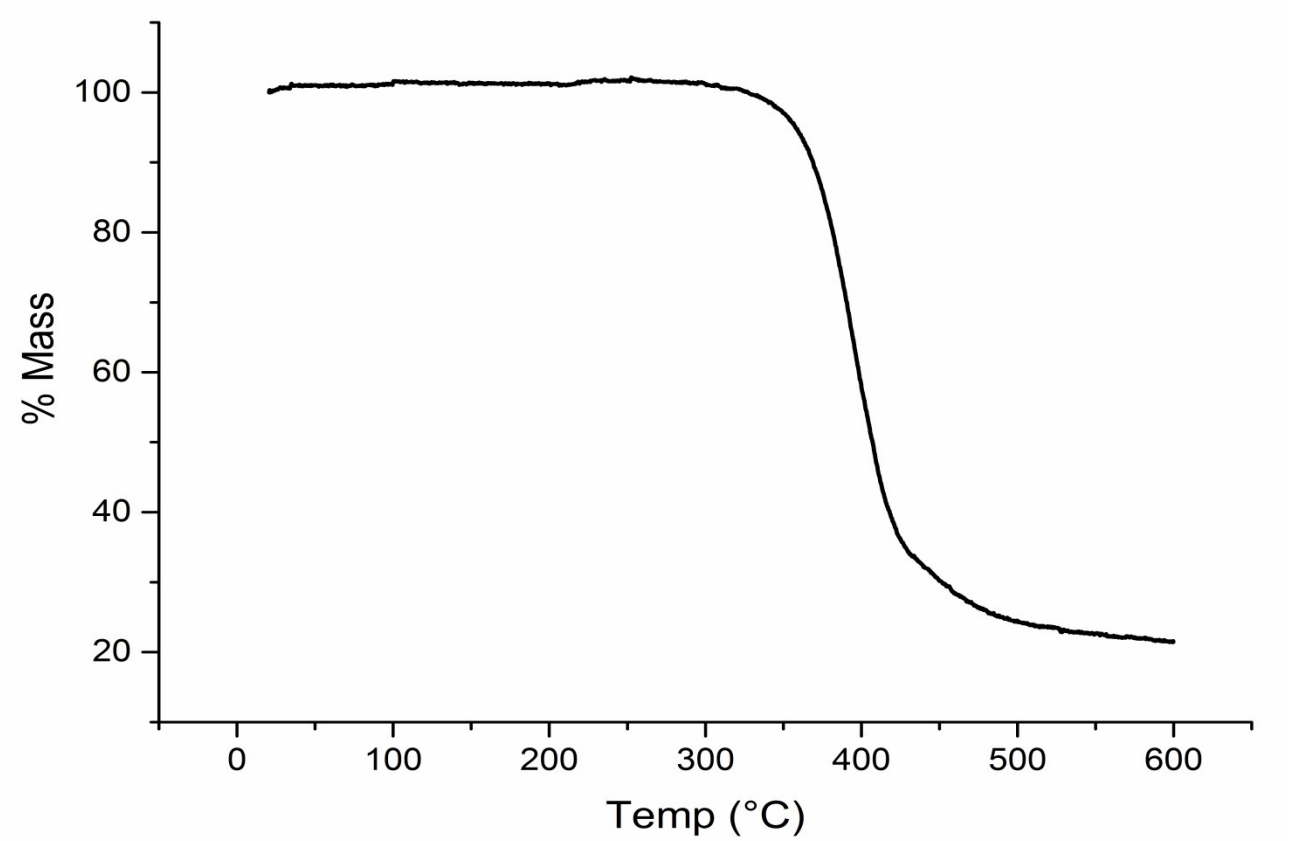
^{1}H NMR spectrum



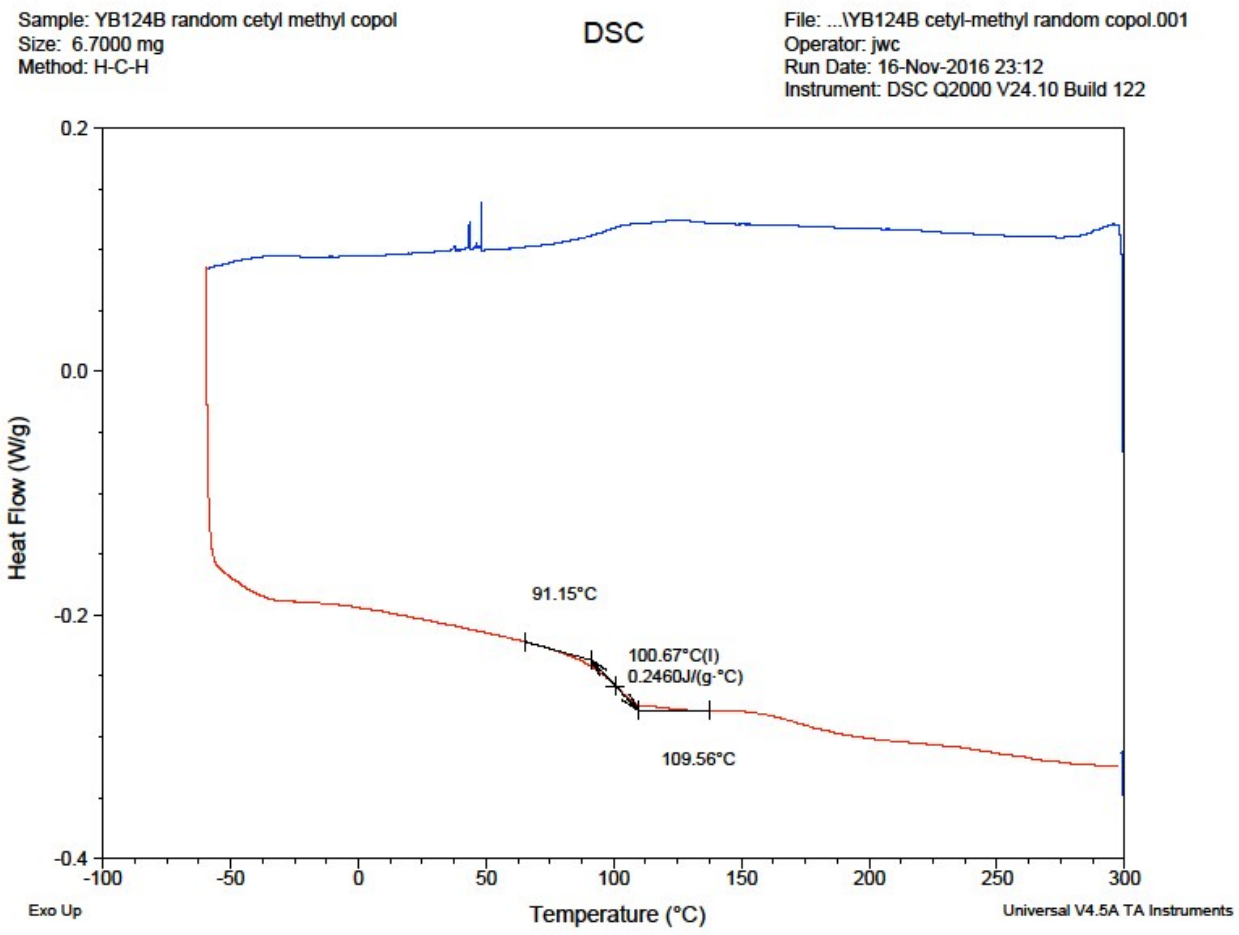
IR spectrum



TGA


100
80
60
40
20
% Mass
0
100
200
300
400
500
600
Temp (°C)

DSC


Sample: YB124B random cetyl methyl copol
Size: 6.7000 mg
Method: H-C-H
DSC
File: ...\YB124B cetyl-methyl random copol.001
Operator: jwc
Run Date: 16-Nov-2016 23:12
Instrument: DSC Q2000 V24.10 Build 122
0.2
0.0
-0.2
-0.4
Heat Flow (W/g)
91.15°C
100.67°C(I)
0.2460J/(g·°C)
109.56°C
-100
-50
0
50
100
150
200
250
300
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments