Electronic Supplementary Material (ESI) for Green Chemistry.

Scalable synthesis and polymerisation of an α-angelica lactone derived monomer

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Supporting Information

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Experimental Procedures

1. General information

Reagents: α-angelica lactone (98%, Sigma Aldrich) was used as received, triethylamine (99% Acros) was distilled over KOH and stored under argon atmosphere, aluminium triflate (98%, Sigma Aldrich) and zinc chloride (99%, abcr) were stored under argon in a glove box.

Cyclopentadiene (CPD) was prepared by thermal cracking of dicyclopentadiene (TCI) over iron(0) at 180°C.

NMR-Spectroscopy: ^{1}H-NMR and ^{13}C-NMR were recorded at ambient temperature on 300 MHz spectrometers (Avance 300 respectively Fourier 300) or a 400 MHz spectrometer (Avance 400) from Bruker. The chemical shifts δ are given in ppm and referenced to the residual proton signal of the deuterated solvent used.

Gel permeation chromatography (GPC): Gel permeation chromatograms were recorded with *1260 Infinity GPC/SEC System* from *Agilent Technologies*. The setup consisted of a *SECcurity Isocratic Pump*, SECcurity 2-Canal-Inline-Degaser*, SECcurity GPC-Column thermostat TCC6000, SECcurity Fraction Collector* and *SECcurity Differential Refractometer detector.* The measurements were performed at a constant temperature of 50 °C using three columns with a polyester co-polymer network as the stationary phase (PSS GRAM 30 Å, 10 µm particle size, 8.0 × 50 mm; PSS GRAM 30 Å, 10 µm particle size, 8.0 × 300 mm; PSS GRAM 1000 Å particle size, 8.0 × 300 mm). THF was applied as the mobile phase with a flow rate of 1 mL·min^{-1}. Polystyrene standards from *ReadyCal* (PSS-pskitr1l-10, M_p = 370–2520000 g·mol^{-1}) were used for calibration purposes.

Differential scanning calorimetry (DSC): Melting points and glass transition temperatures of polyesters were measured with a *Star-SW DSC* from *Mettler Toledo* using the following temperature program: -90.00 °C isothermal 5.00 min; Ramp 10.00 °C min^{-1} to 200.00 °C; Ramp 10.00 °C/min to -90.00 °C; -90.00 °C isothermal 5.00 min; Ramp 10.00 °C min to 200.00 °C; Ramp 10.00 °C/min to -90.00 °C.

2. Preparation of a mixture of angelica lactones with 90 mol-% content of the β-isomer

α-angelica lactone (98%, 120 g, 1.2 mol) was added to a 250 ml two neck flask equipped with a condenser and a magnetic stirrer followed by the addition of triethyl amine (5 mol-%, 8.5 ml). The mixture was heated to 100 °C under an argon atmosphere and monitored by ^{1}H-NMR. After 1.5 hours a ratio of β/α-angelica lactone of 90-95/10-5 was reached and the condenser exchanged with a distillation head. Subsequent vacuum distillation at 6 x10^{-2} mbar yielded two fractions: on at 38-42°C containing mainly the α-isomer (This fraction was reused for the next

isomerisation reaction.) and another one at 45-50°C contained a mixture of angelica lactones with 90 mol-% content of the β-isomer (106 g, 88% of theory).
^{1}H NMR (400 MHz, CD_2Cl_2, signals of β-isomer are reported) δ 7.46 (dd, *J* = 5.7, 1.5 Hz, 1H), 6.04 (dd, *J* = 5.7, 2.0 Hz, 1H), 5.11 (qt, *J* = 6.9, 2.0, 1.5 Hz, 1H), 1.41 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 173.3, 158.0, 121.3, 80.0, 19.0.

3. Screening procedure of the DA-reaction with β-Angelica lactone and CPD

In a dry and argon purged 10 ml reaction tube the angelica lactone mixture (β-AL=90%, 10 mmol, 900 µl) and the desired catalyst were mixed. Freshly prepared CPD (3.0-10 eq. 2.5-8.3 ml) was added, the tube was sealed and heated with a microwave oven to the desired reaction temperature where it is kept for the indicated time.

The 2 diasteroisomers of the product were separated by flash column chromatography (heptane/ethyl acetate 8:2), affording the *endo* and *exo* isomers (each of them is a racemic mixture of 2 diastereomers) adduct as colourless oils (*endo*: 949 mg, 5.9 mmol, 30%; *exo*: 119 mg, 0.7 mmol, 7%; *endo*/*exo* 89/11).
exo ^{1}H NMR (300 MHz, CD_2Cl_2) δ 6.21 – 6.04 (m, 2H), 4.17 (qd, *J* = 6.4, 3.2 Hz, 1H), 3.24 – 3.03 (m, 1H), 2.82 (dtq, *J* = 3.1, 1.5, 0.8 Hz, 1H), 2.59 (dt, *J* = 8.3, 1.3 Hz, 1H), 2.08 – 1.97 (m, 1H), 1.50 – 1.35 (m, 7H), 1.30 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 177.4, 136.4, 134.9, 78.9, 51.6, 48.5, 48.2, 46.0, 45.6, 22.8.
endo ^{1}H NMR (300 MHz, CD_2Cl_2) δ 6.22 – 6.09 (m, 2H), 3.95 (qd, *J* = 6.5, 3.1 Hz, 1H), 3.26 – 2.97 (m, 3H), 2.67 – 2.54 (m, 1H), 1.57 – 1.46 (m, 1H), 1.39 – 1.29 (m, 1H), 1.25 (d, *J* = 6.5 Hz, 3H). 13C NMR (75 MHz, $CDCl_3$) δ 177.3, 137.6, 137.5, 80.7, 50.0, 48.9, 47.6, 46.3, 43.1, 23.2.

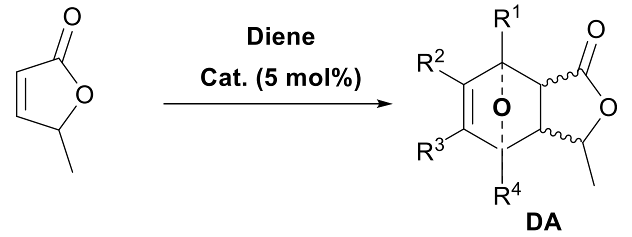
4. Semi continuous synthesis of the β-Angelica lactone CPD adduct

A 500 mL 2-neck round bottom flask was filled with dicyclopentadiene (100 mL) and iron(0) powder and equipped with a distillation setup. Cyclopentadiene was obtained by thermal cracking of its corresponding dimer at 180 °C and then condensed into a dropping funnel. 2 equivalents (84 mL, 67 g, 1.0 mol) were dropped over 10 hours into a 1 liter 3-necks round bottom flask containing the angelica lactone mixture (β-AL=90%; 50 g, 0.5 mol) and zinc(II) chloride (3.5 g, 0.03 mol, 0.05 eq) while heating up to 70 °C. Once the addition was complete, the reaction was stirred for another 10 hours and monitored by GC. After cooling down to room temperature, acetone (80-150 ml) was added to precipitate the Lewis acid catalyst. The remaining cyclopentadiene and α-Angelica lactone was removed by vacuum distillation (50 °C/0.06 mbar) and the remaining cyclopentadiene dimers were precipitated by addition of ice-cold methanol (100 ml) followed by filtration. Solvent removal afforded the product as an orange liquid (69 g, 0.4 mol, 82% yield, *endo*:*exo* 89/11).

5. Screening of the DA-reaction with other dienes

Microwave-assisted reactions. In an oven-dried 10 mL reaction tube the angelica lactones mixture (β-AL=90%; 98 mg, 1 mmol), the desired solvent (if used, 2 mL) and catalyst (5 mol%) were added under argon. The diene (10 eq) was added subsequently while stirring the mixture, then the tube was placed in a microwave oven and heated at the desired temperature for the indicated time (Table S1).

Table S1 Screening of the reaction conditions for the DA-reaction between β-AL and different dienes



Entry	Substrate	Lewis Acid	Solvent	Temperature [°C]	Time [min]	DA[a] [%]
1	2,5-DMF[b]	-	-	60	30	0
2	2,5-DMF	$ZnCl_2$	-	60	30	0
3	2,5-DMF	Et_3Al / $AlCl_3$	-	90	30	0
4	β-Farnesene	$ZnCl_2$	-	60	30	0
5	β-Farnesene	$AlCl_3$	-	60	30	0
6	β-Farnesene	Et_3Al / $AlCl_3$	-	90	30	0
7	β-Farnesene	Et_3Al / $AlCl_3$	Toluene	110	90	0
8	Myrcene	$ZnCl_2$	-	60	30	< 2%
9	Myrcene	Et_3Al / $AlCl_3$	-	90	30	< 2%
10	Myrcene	Et_3Al / $AlCl_3$	Toluene	110	90	0
11	Myrcene	$In(OTf)_3$	-	70	60	0
12	Myrcene	$Sm(OTf)_3$	-	70	60	0

13	Furan	$ZnCl_2$	-	60	30	0
14	Furan	Et_3Al / $AlCl_3$	-	90	30	0
15	Furan	Et_3Al / $AlCl_3$	Toluene	110	90	0
16	Furan	$Yb(OTf)_3$	-	70	30	0
17	Furan	$Yb(OTf)_3$	-	130	30	0
18	Furfuryl alcohol	$ZnCl_2$	-	70	30	0
19	Furfuryl alcohol	$ZnCl_2$	-	130	30	0
20	Furfuryl alcohol	$AlCl_3$	-	70	30	0
21	Furfuryl alcohol	$AlCl_3$	-	130	30	0
22	Isoprene	$ZnCl_2$	-	70	30	0
23	Isoprene	$ZnCl_2$	-	130	30	0
24	Isoprene	$AlCl_3$	-	70	30	0
25	Isoprene	$AlCl_3$	-	130	30	0

[a]GC conversion. [b]2,5-DMF = 2,5-dimethylfurane.

High temperature reactions. 4 mL glass vials equipped with magnetic stirring bar and PTFE septum were filled with the angelica lactones mixture (β-AL=90%; 98 mg, 1 mmol) and the diene (10 eq) under argon. The vials were then pierced with needles and placed in a 300 mL stainless steel autoclave, which was pressurised with 20 bar of nitrogen and heated up to 200 °C. The reaction was stirred for 16 hours, then cooled down to room temperature and the reaction mixture was filtered over a short path of silica and directly analysed by GC.

Isoprene/βAL. β-Angelica lactone (0.1 mL, 1.0 mmol, 1 eq) and isoprene (2.0 mL, 20 mmol, 20 eq) were added to a stainless steel autoclave and pressurized with 30 bar of nitrogen (to prevent isoprene evaporation). The reaction was stirred at 200 °C for 24 hours. The crude was purified by flash column chromatography (heptane/EtOAc 8:2). The desired product (as mixture of 2 regioisomers, each of them containing 2 diasteroisomers and 2 enantiomers) was obtained as a yellow oil (99.5 mg, 0.6 mmol, 60%).

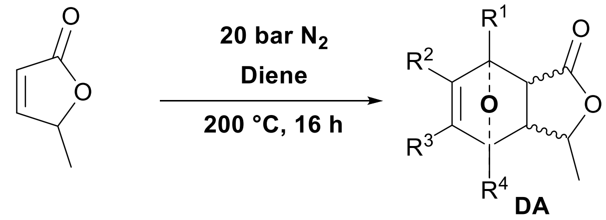
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.45 – 5.32 (m, 1H), 4.25 – 4.15 (m, 1H), 2.85 – 2.67 (m, 1H), 2.37 – 2.04 (m, 4H), 1.91 – 1.70 (m, 1H), 1.62 (dddt, J = 3.8, 2.4, 1.9, 0.9 Hz, 3H), 1.32 (dd, J = 6.4, 3.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.2, 179.1, 132.9, 132.4, 119.1, 118.8, 80.9, 80.9, 39.7, 38.6, 37.3, 36.3, 29.3, 26.9, 25.0, 23.7, 23.4, 22.6, 19.3, 19.2.

MS (EI): m/z calcd. for $[C_{10}H_{14}O_2]^+$: 166.1; found: 166.

Myrcene/βAL. β-Angelica lactone (0.1 mL, 1.0 mmol, 1 eq) and myrcene (1.7 mL, 20 mmol, 20 eq) were added to a SS autoclave and pressurized with 30 bar of nitrogen (to prevent isoprene evaporation). The reaction was stirred at 200 °C for 24 hours. The crude was purified by flash column chromatography (heptane/EtOAc 8:2). The desired product (as mixture of 2 regioisomers, each of them containing 2 diasteroisomers and 2 enantiomers) was obtained as a yellow oil (127 mg, 0.54 mmol, 54%).
MS (EI): m/z calcd. for $[C_{15}H_{22}O_2]^+$: 234.3; found: 234.

Farnesene/βAL. β-Angelica lactone (0.1 mL, 1.0 mmol, 1 eq) and β–farnesene (2.4 mL, 20 mmol, 20 eq) were added to a SS autoclave and pressurized with 30 bar of nitrogen (to prevent isoprene evaporation). The reaction was stirred at 200 °C for 24 hours. The crude was purified by flash-column chromatography (heptane/EtOAc 8:2). The desired product (as mixture of 2 regioisomers, each of them containing 2 diasteroisomers and 2 enantiomers) was obtained as a yellow oil (41.3 mg, 0.18 mmol, 18%).
MS (EI): m/z calcd. for $[C_{20}H_{30}O_2]^+$: 302.5; found: 302.

Table S2 Screening of the reaction conditions for the DA-reaction between β-AL and different dienes



Entry	**Diene**	**Conversion[a] [%]**
1	2,5-DMF	-
2	β-Farnesene	64 (18)[b]
3	Myrcene	> 99 (54)
4	Furane	-
5	Furfuryl alcohol	-
6	Isoprene	> 99 (60)

[a]GC Conversion. [b]Isolated yields after column chromatography (Heptane/Ethyl acetate 8:2) are reported in brackets.

6. Ring-opening metathesis polymerization (ROMP) of Cp/βAL adduct

Solvent screening. To a stirred solution of Grubbs II catalyst (4.7 mg, 0.006 mmol, 0.25 mol%) in the desired solvent (Table 3) the Cp/βAL adduct (0.2 mL, 2.2 mmol, 1 eq) was added under argon atmosphere. The reaction was stirred overnight. A few minutes after the addition, all the solutions turned opalescent and a white'ish precipitate appeared, except for the reaction in DCM. The reaction mixtures were then concentrated *in vacuo* and washed several times with methanol (using DCM to re-dissolve the polymer). All the reaction afforded a white'ish, gummy solid. A small portion of each sample was dissolved in a DMF/LiBr solution and analyzed by GPC.

- MTBE

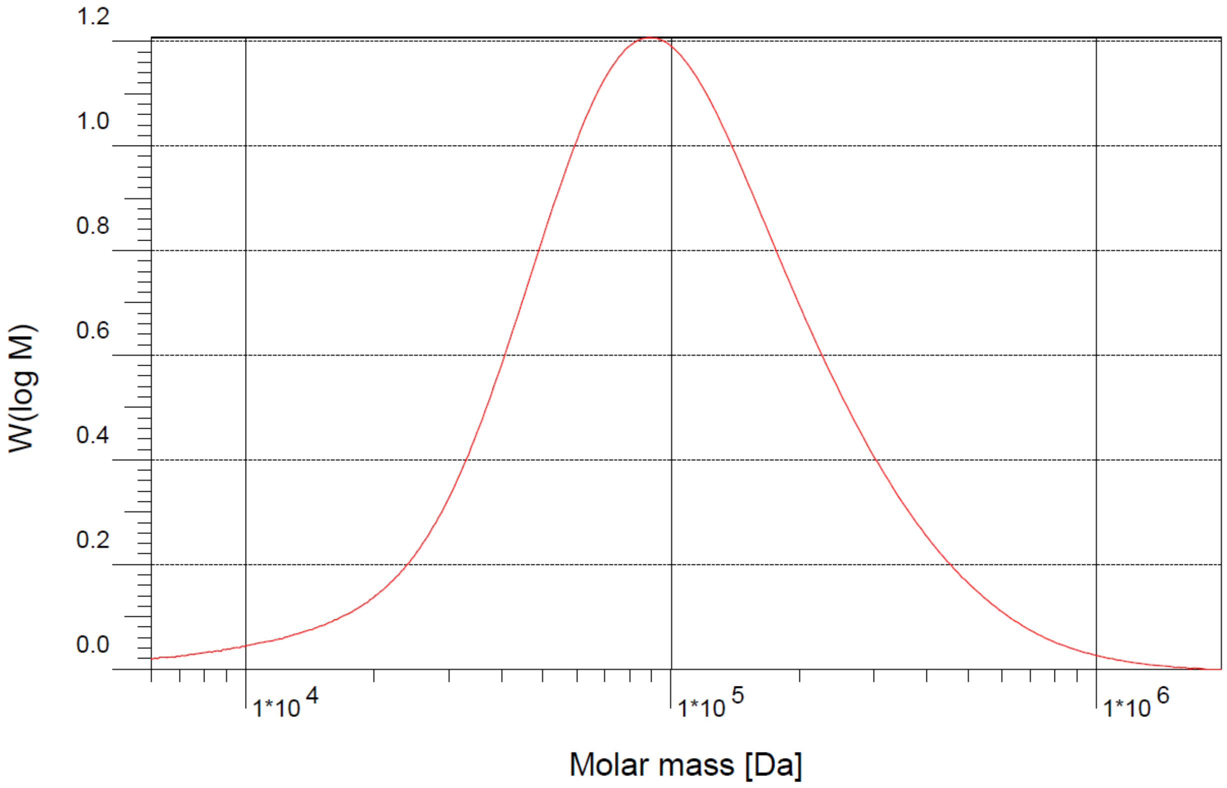


Figure S1. GPC chromatogram of *poly*-Cp/βAL; polymerization performed in MTBE.

$\overline{M}_n$ = 67.8 kDa; $\overline{M}_w$= 138 kDa; $Đ$ = 2.04

- 2-Methyl-THF

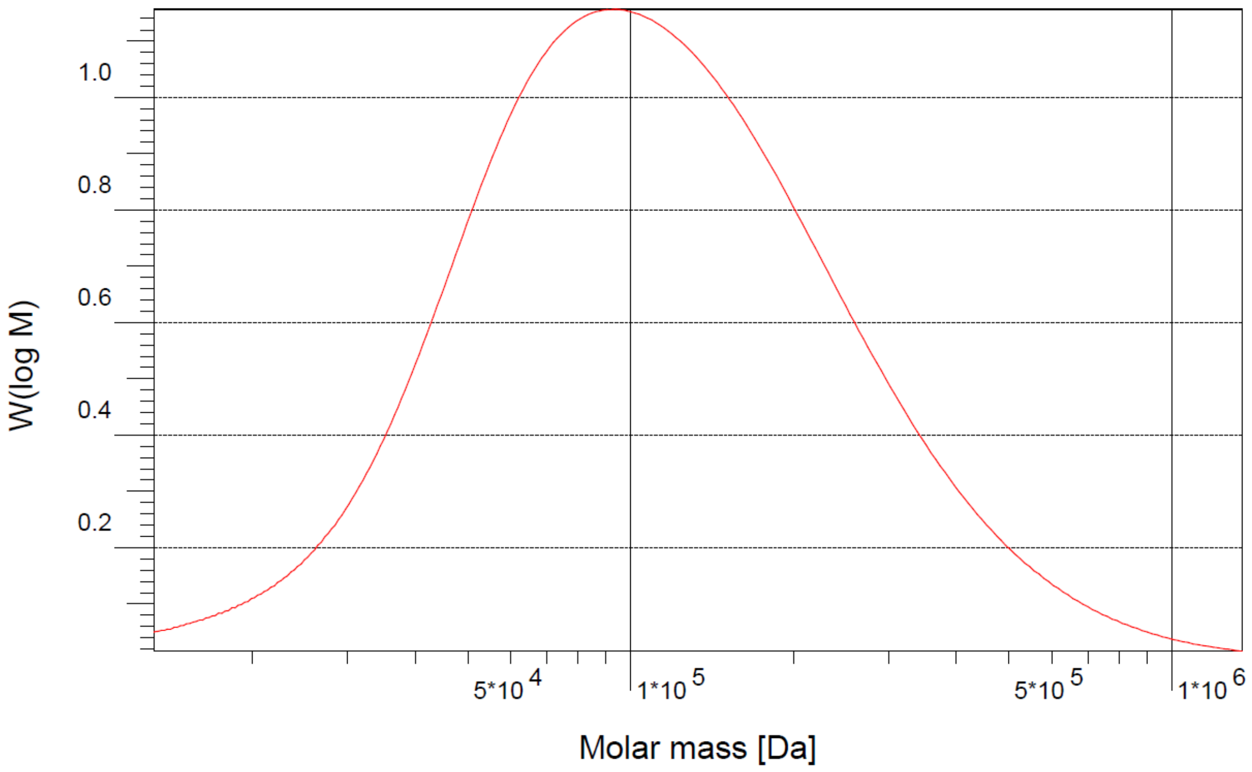


Figure S2. GPC chromatogram of *poly*-Cp/βAL; polymerization performed in 2-Me-THF.

$\overline{M}_n$ = 80.6 kDa; $\overline{M}_w$ = 154 kDa; $Đ$ = 1.91

- EtOAc

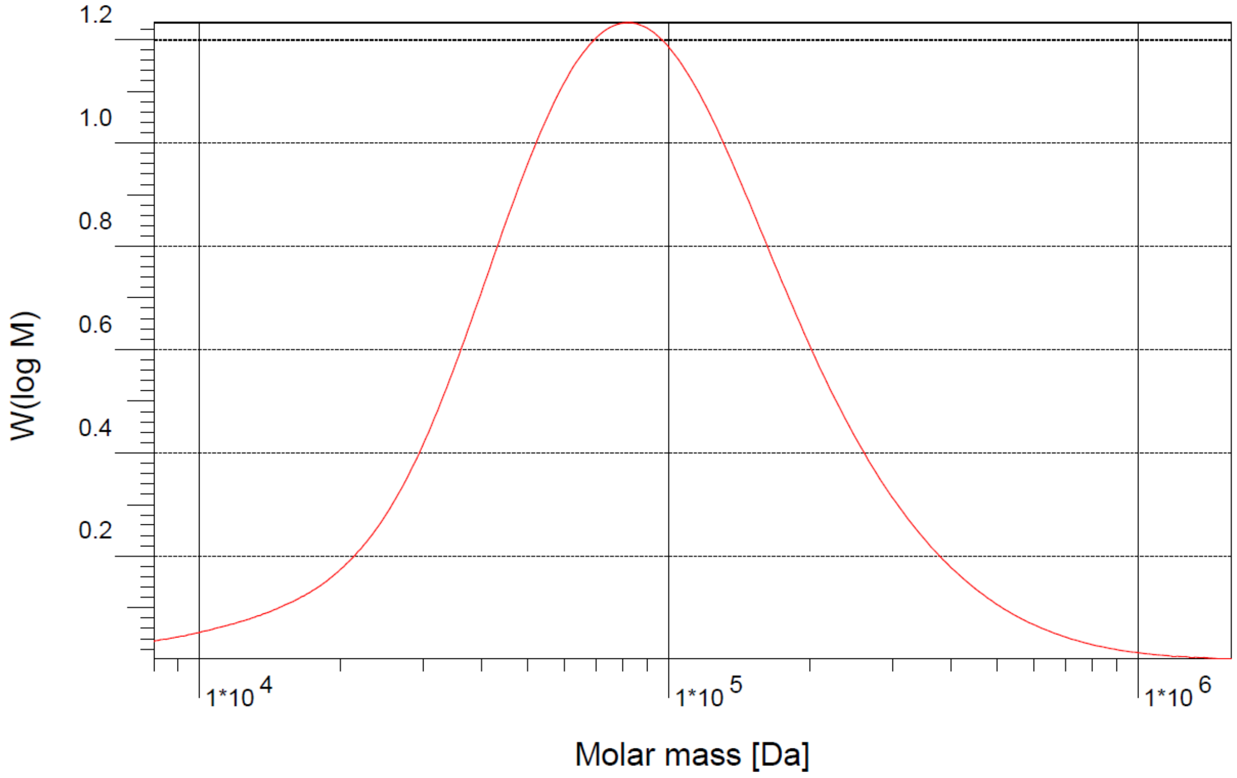


Figure S3. GPC chromatogram of *poly*-Cp/βAL; polymerization performed in EtOAc.

$\overline{M}_n$ = 64.1 kDa; $\overline{M}_w$ = 118 kDa; $Đ$ = 1.85

- MIBK

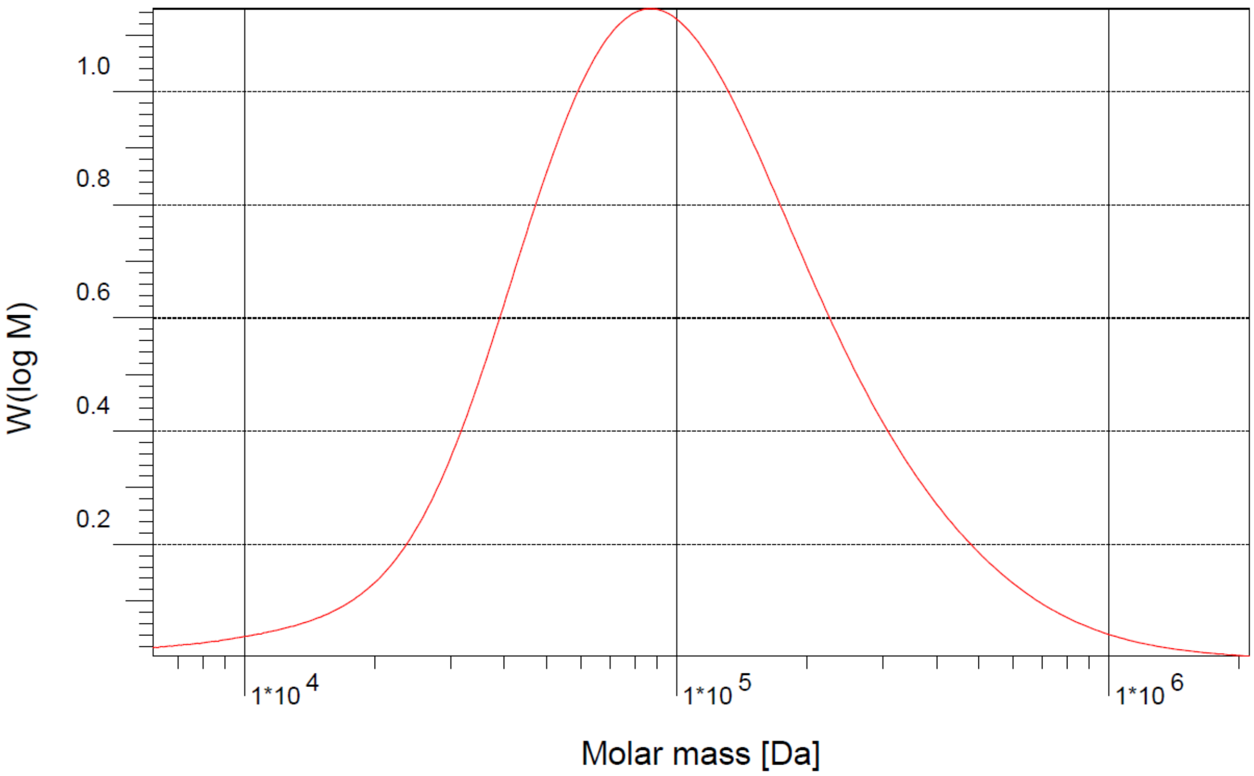


Figure S4. GPC chromatogram of *poly*-Cp/βAL; polymerization performed in MIBK.

$\overline{M}_n$ = 70.9 kDa; $\overline{M}_w$ = 146 kDa; $Đ$ = 2.06

- DCM

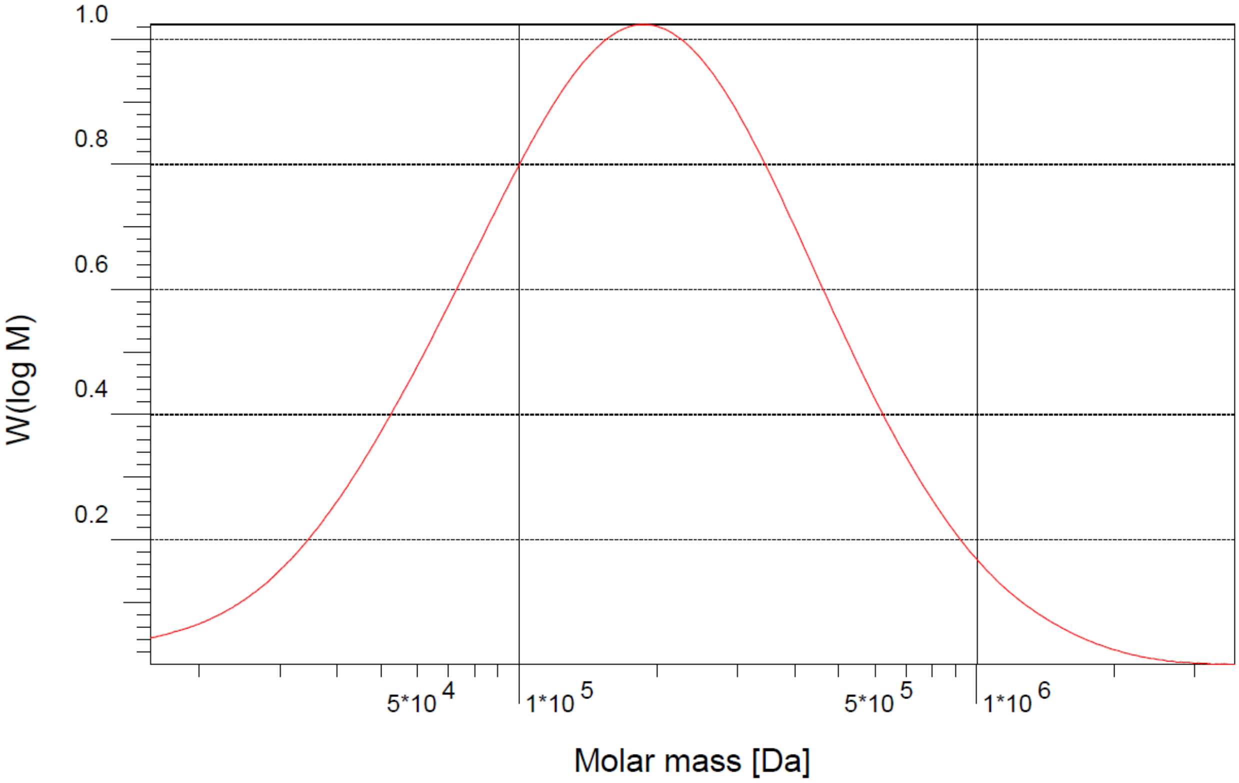


Figure S5. GPC chromatogram of *poly*-Cp/βAL; polymerization performed in DCM.

$\overline{M}_n$ = 122 kDa; $\overline{M}_w$ = 264 kDa; $Đ$ = 2.17

***Poly*-norbornene.** To a stirred solution of Grubbs II catalyst (4.7 mg, 0.006 mmol, 0.25 mol%) in 2 mL of dichloromethane, norbornene (207 mg, 2.2 mmol, 1 eq) was added under argon atmosphere. The reaction was stirred for 5 hours. The reaction mixtures were then concentrated *in vacuo* and washed several times with methanol (using DCM to re-dissolve the polymer). All the reaction afforded a white'ish, gummy solid. A small portion of each sample was dissolved in a THF and analyzed by GPC.

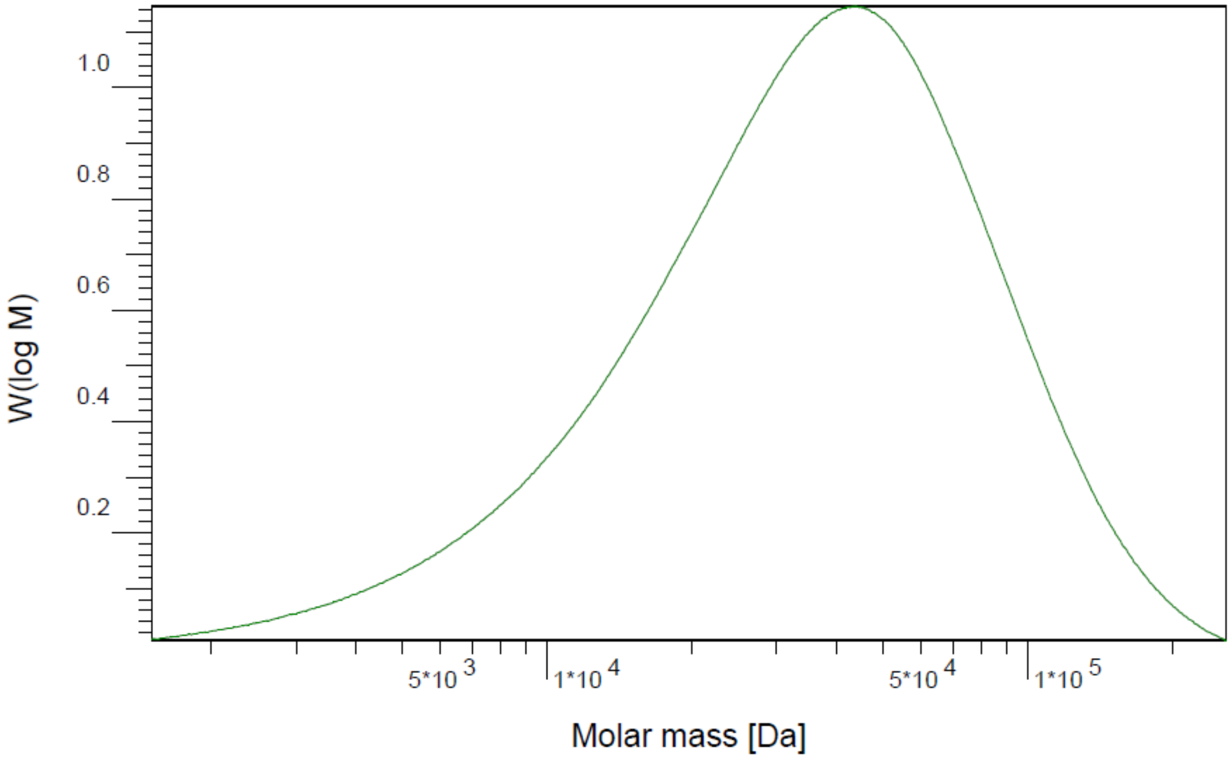


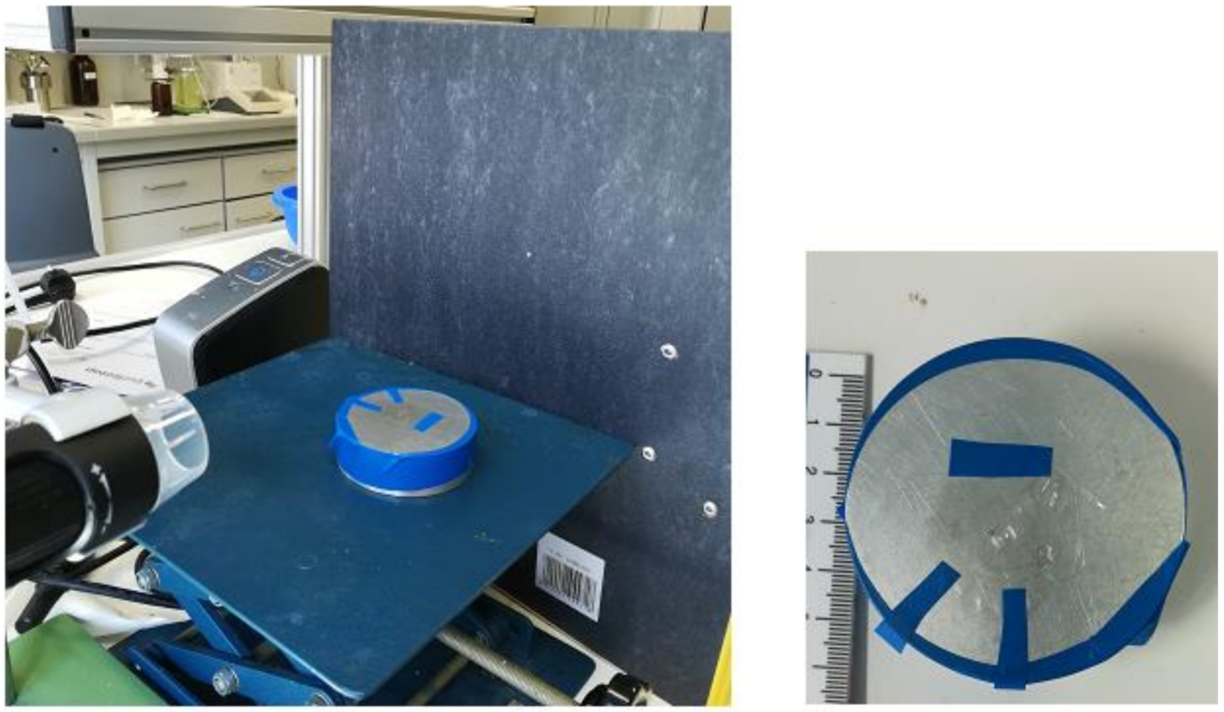
Figure S6. GPC chromatogram of *poly*-norbornene.

$\overline{M}_n$ = 21.8 kDa; $\overline{M}_w$ = 45.9 kDa; $Đ$ = 2.11

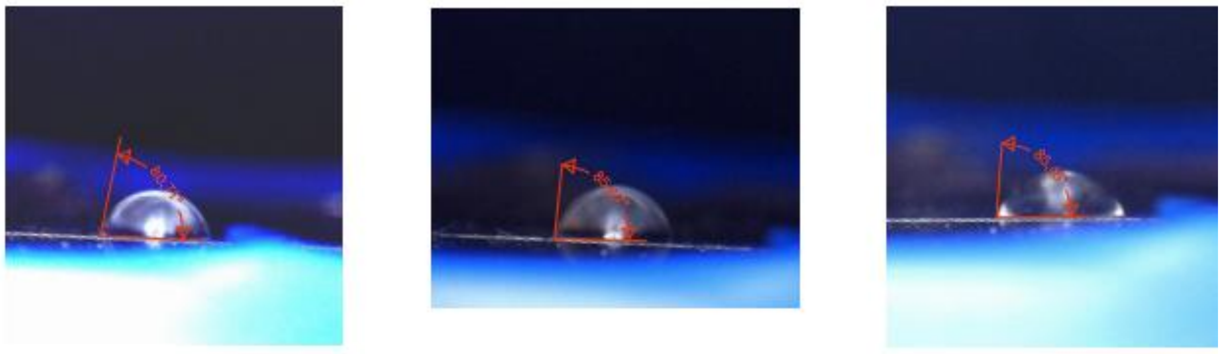
7. Contact angle measurements

A film of the desired polymer (obtained by casting a solution of the polymer in dichloromethane on a Teflon mold and letting the solvent evaporate over 4 hours) was anchored to a stainless-steel flat surface (Figure S7-a). 10 μL of distilled water were dropped on the polymer film using a Hamilton syringe. A picture of the drop was recorded using a DNT DigiMicro Profi digital microscope (Fig 7b. *poly*-norbornene, Fig. 7c. *poly*-Cp/βAL). Contact angles were determined by measuring the angle using CorrelDraw software. The reported values are the average between 3 different measurements.

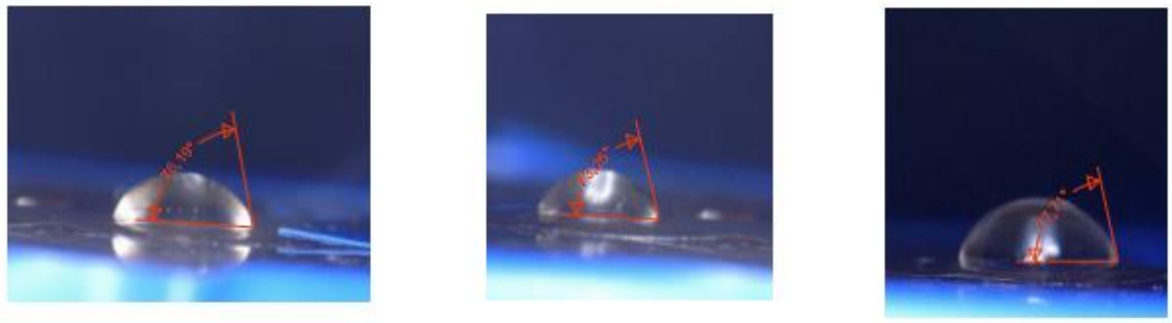
a)



b)



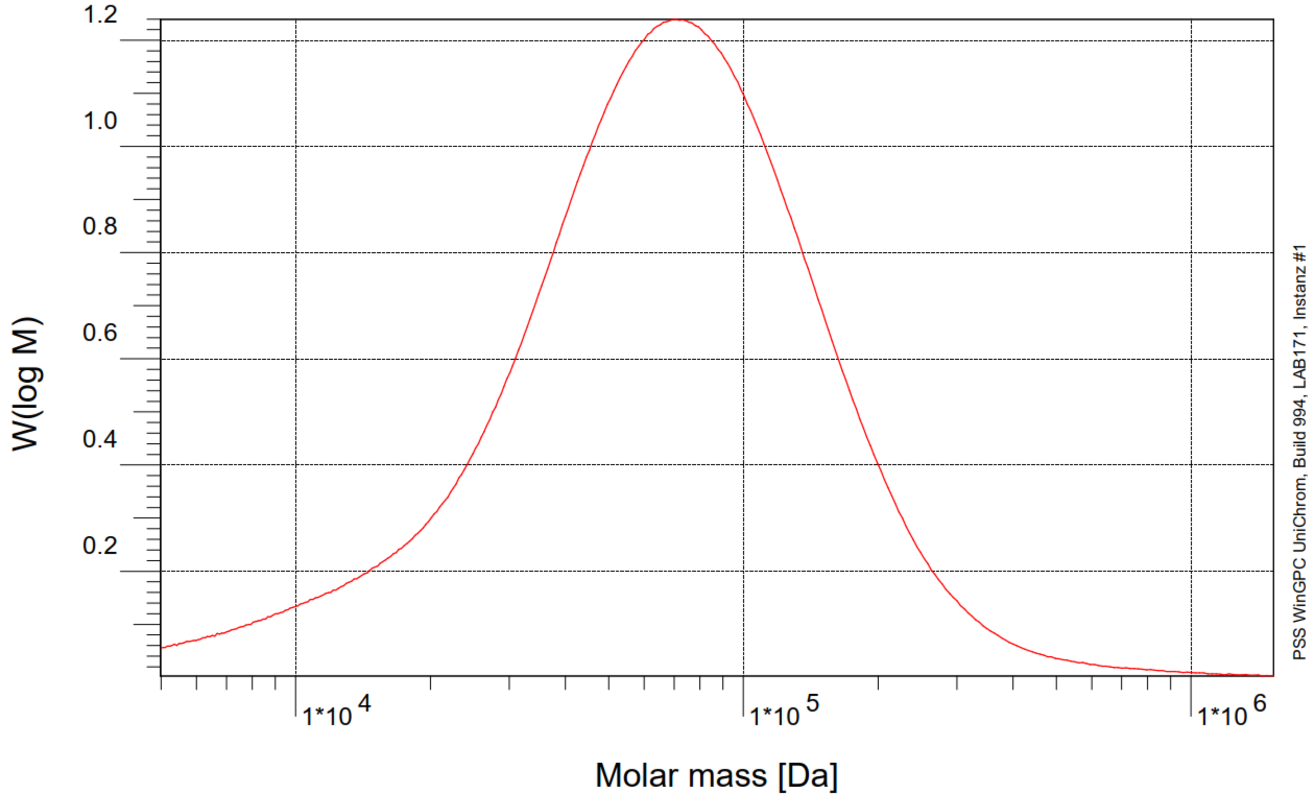
c)



Average contact angle: *poly*-Norbornene: θ = 83.9° *poly*-Cp/βAL: θ = 75.7°

8. Experiments at different monomer / initiator ratios.

100:1



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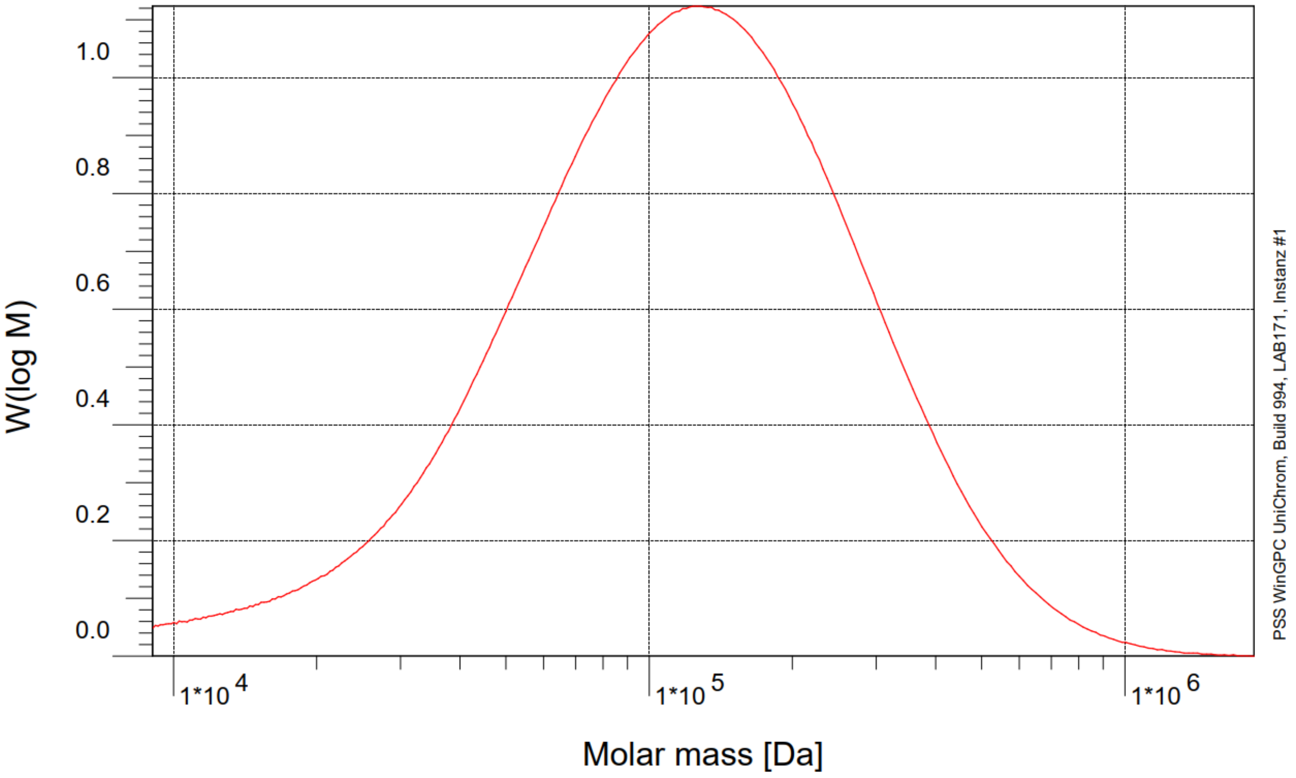

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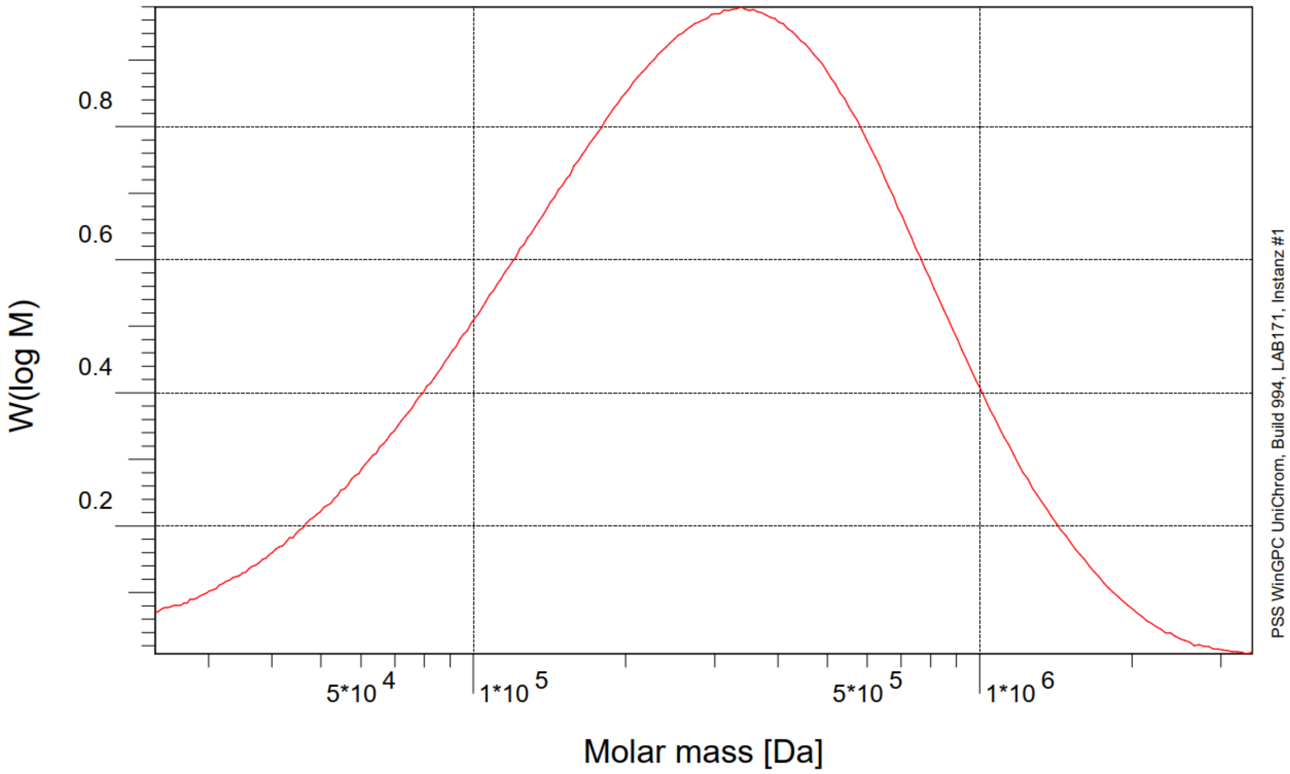

W(log M)
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0.4
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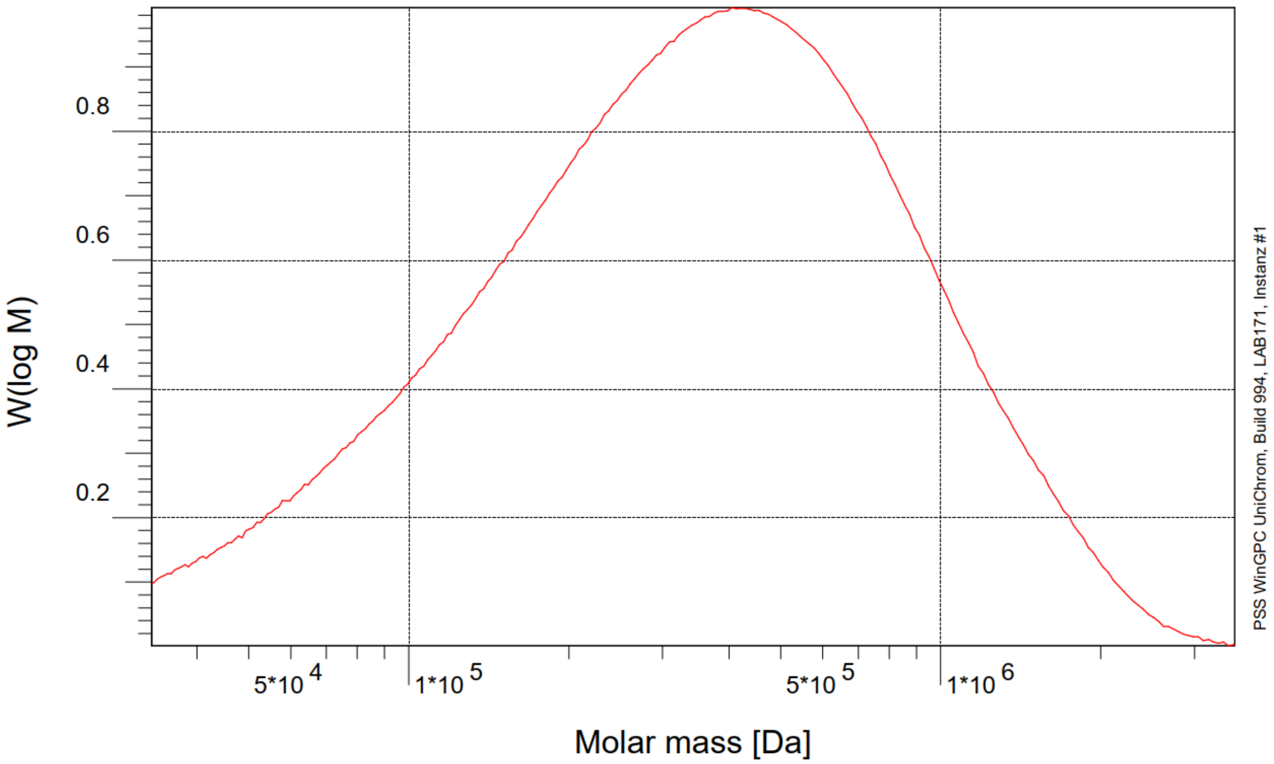

W(log M)
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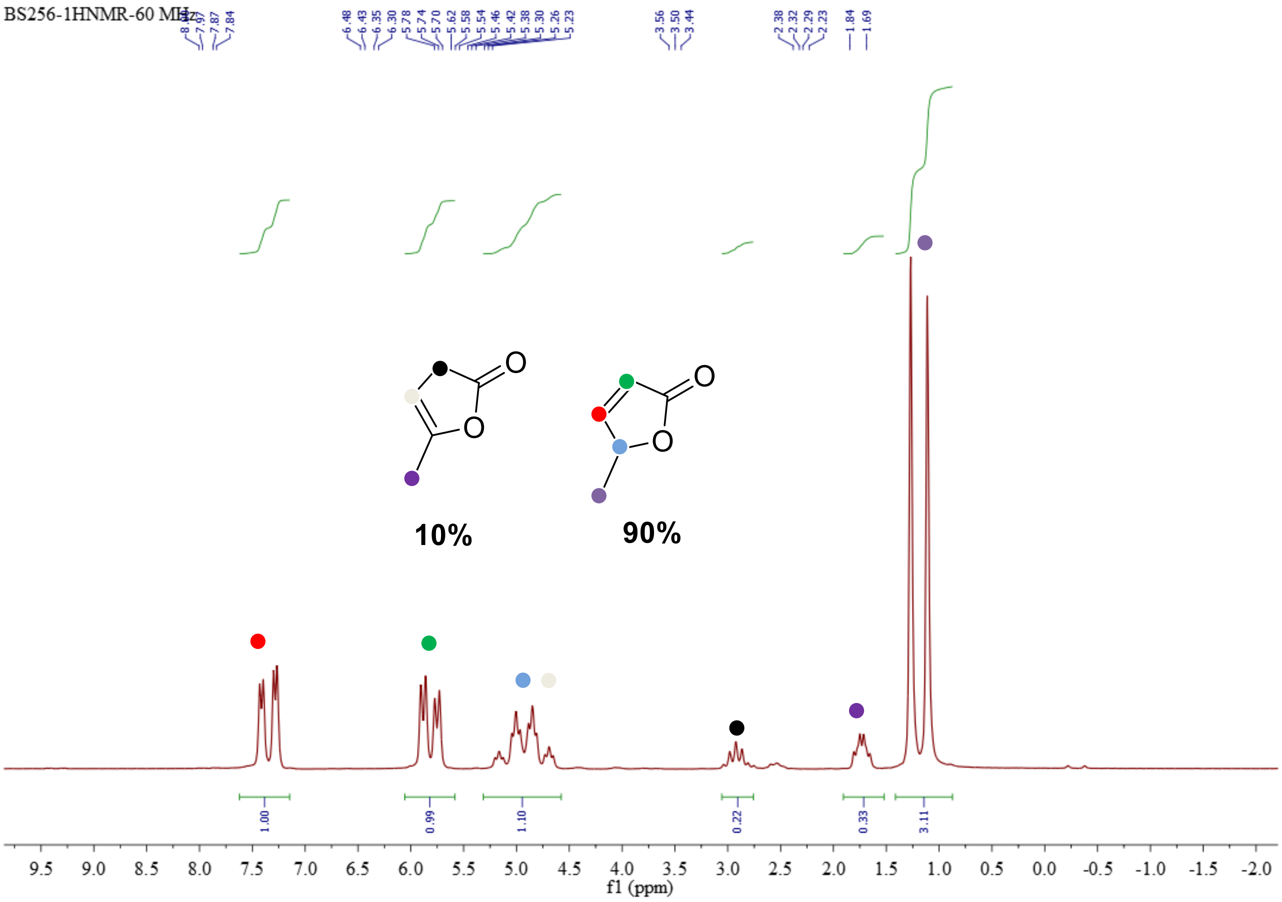
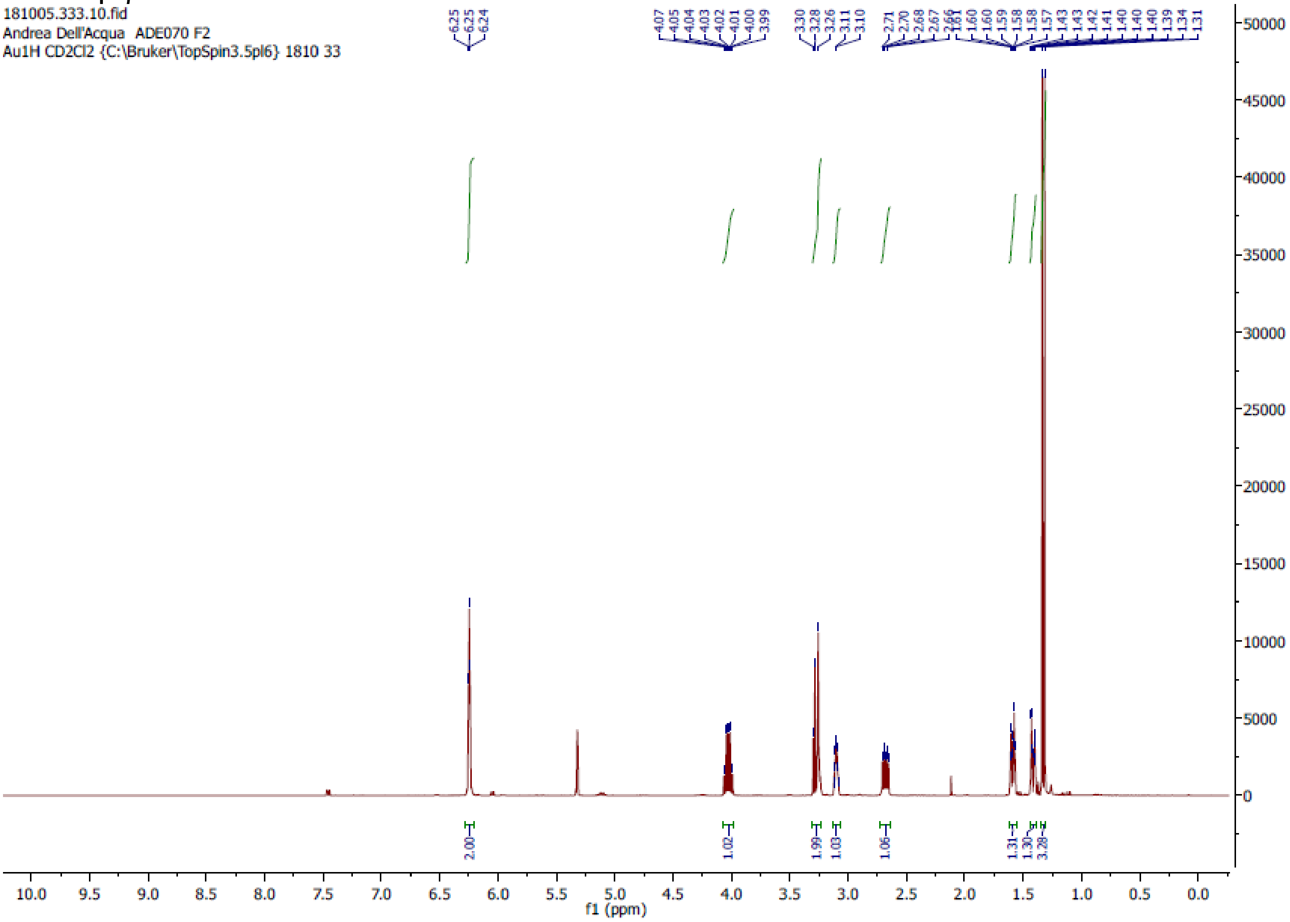
9. Spectral data

^{1}H-NMR of the angelica lactone product mixture



endo-Cp/βAL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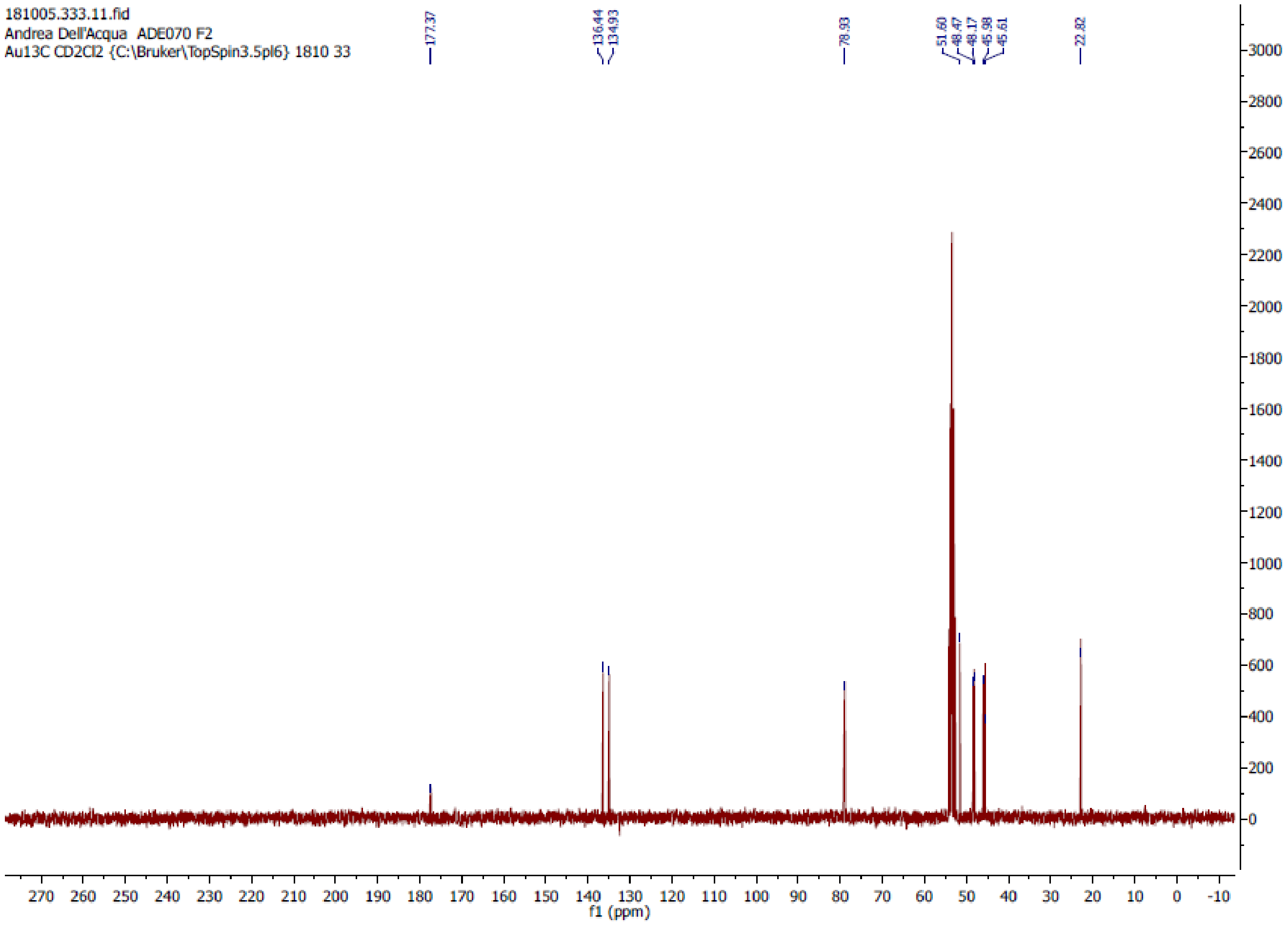
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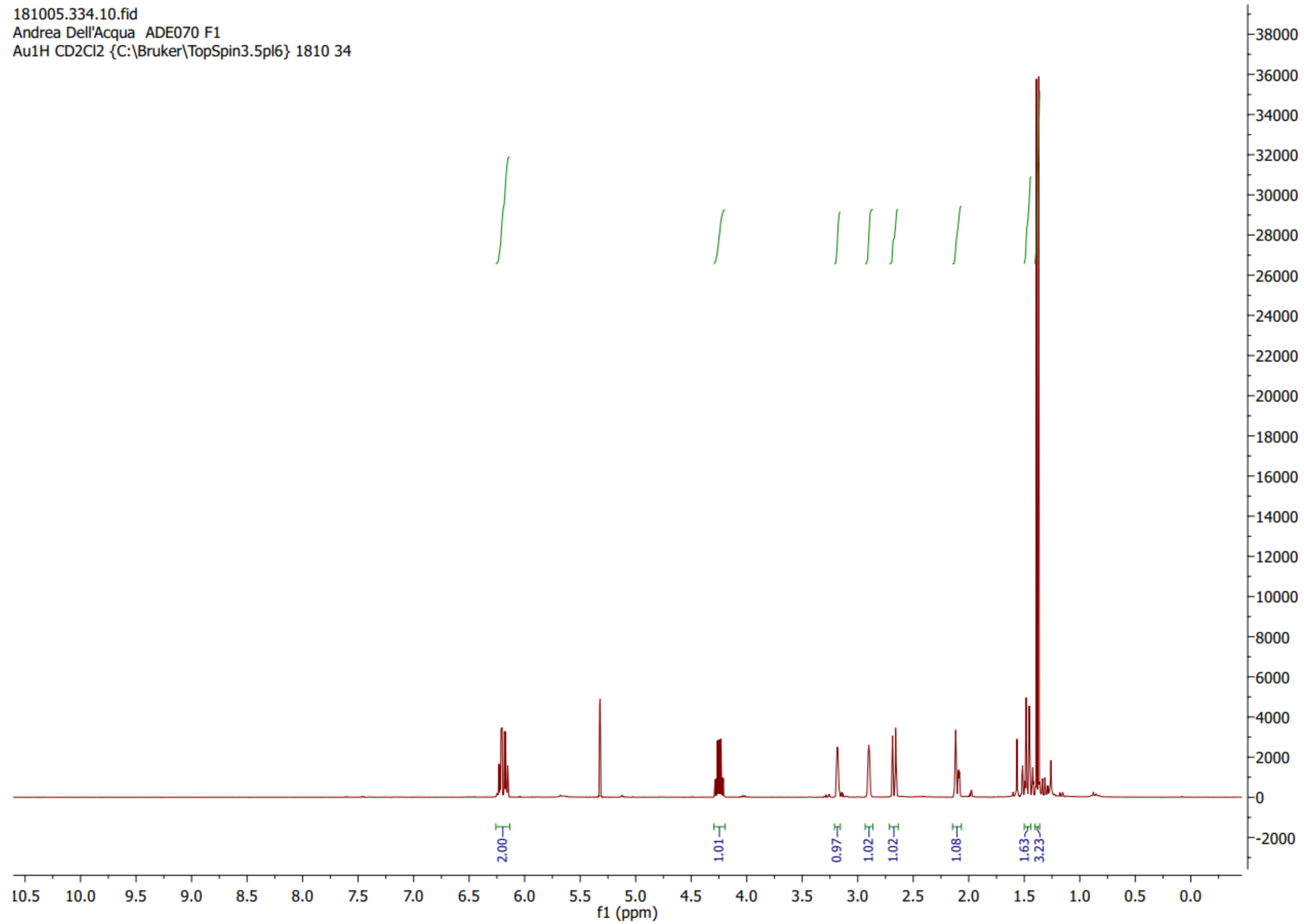
exo-Cp/βAL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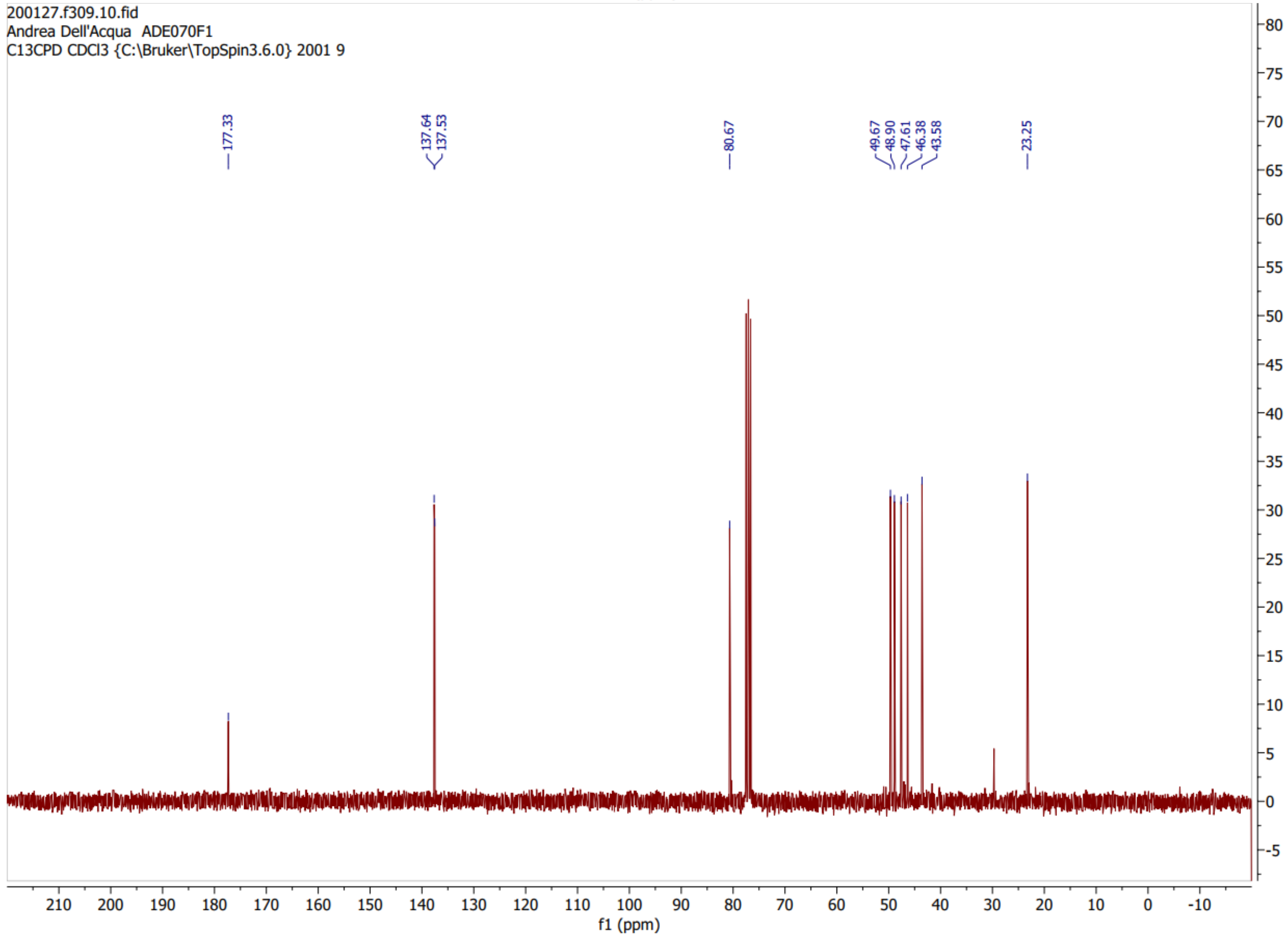
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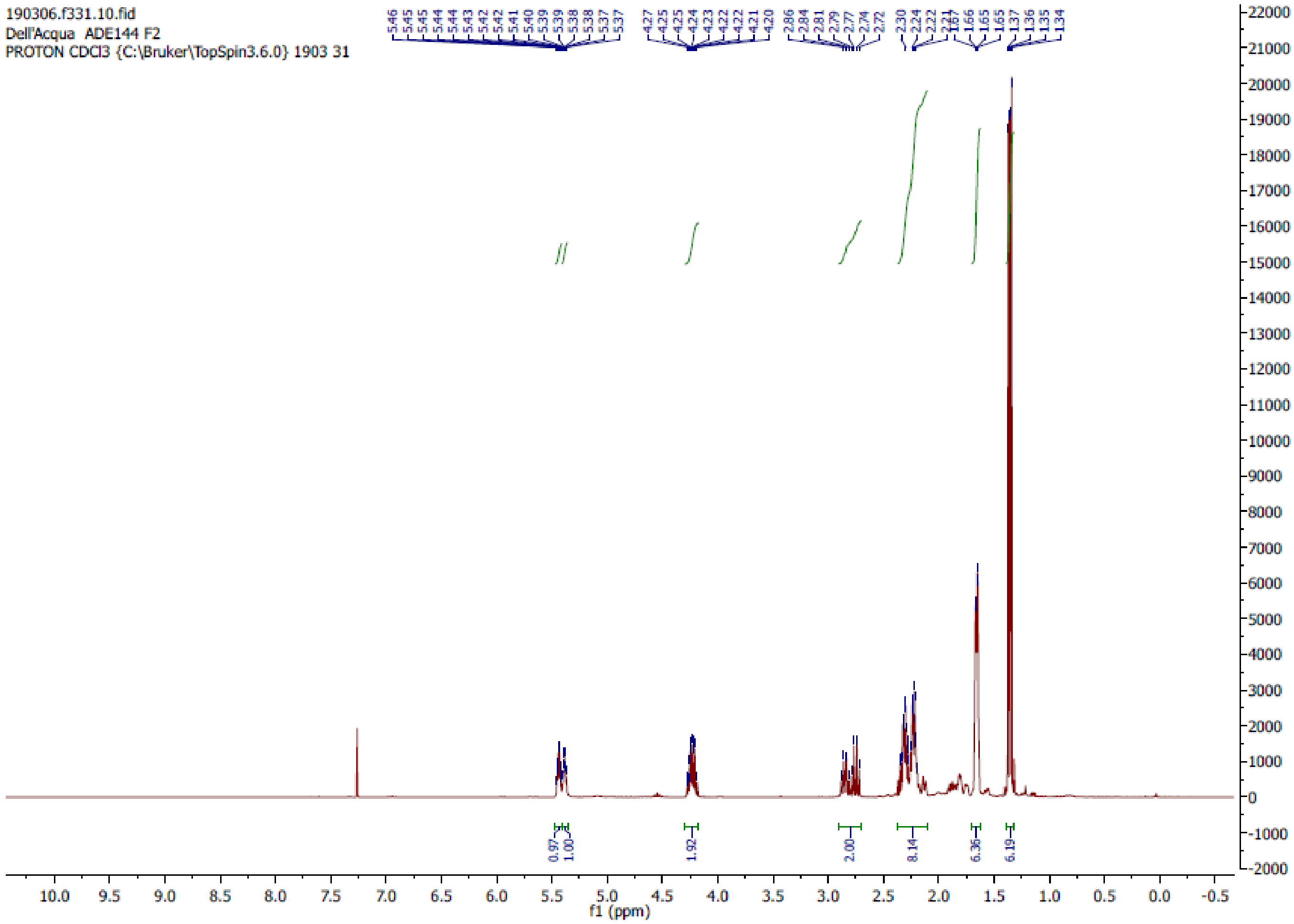
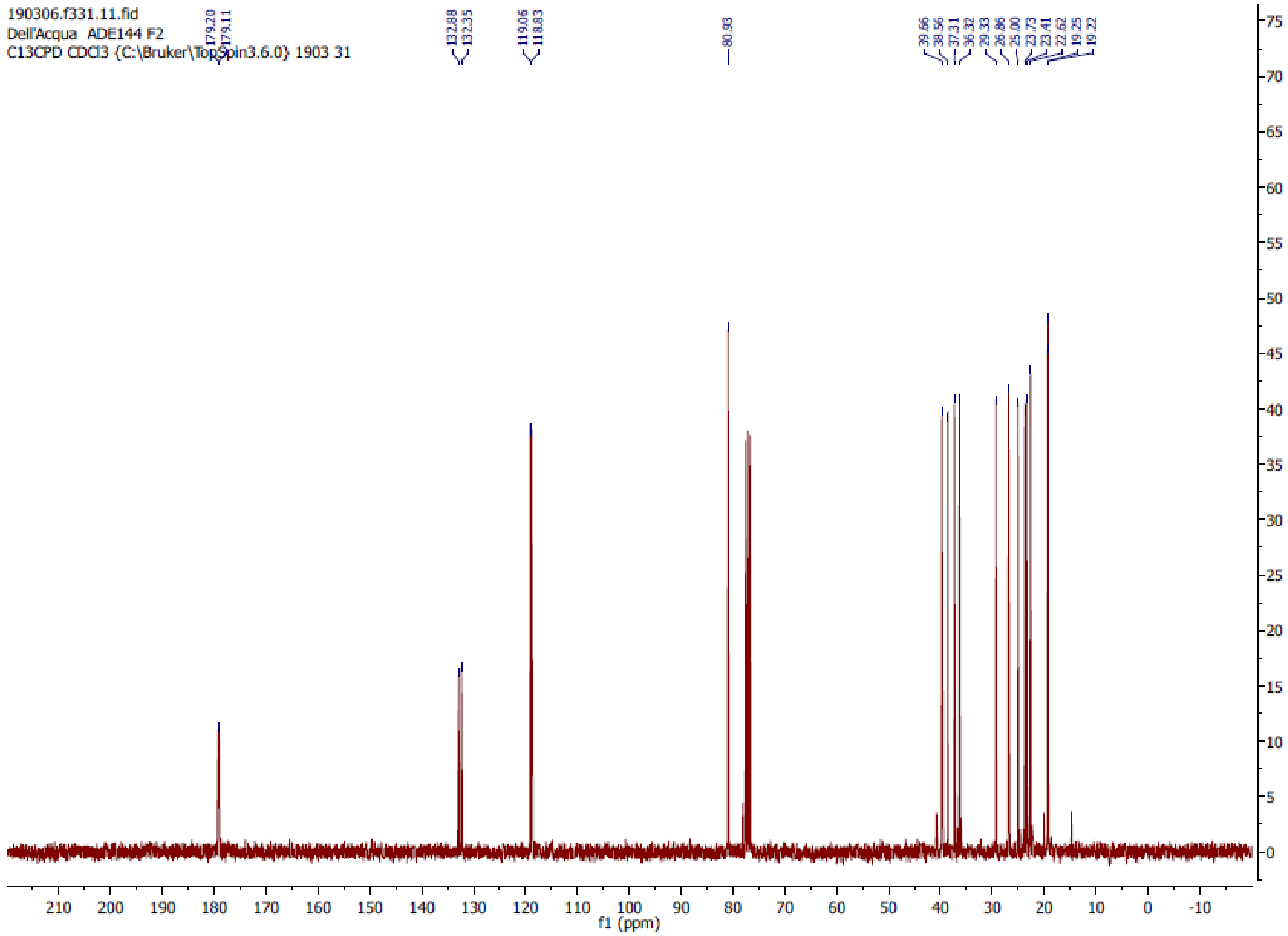
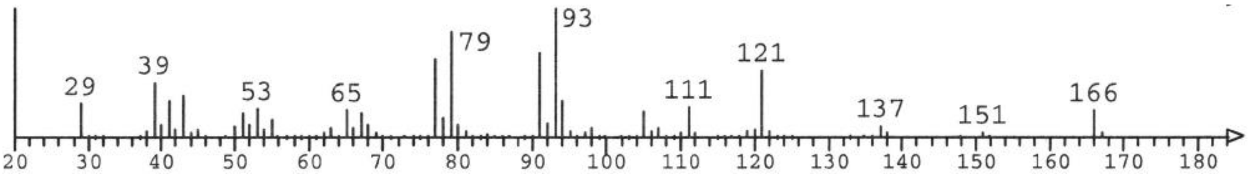
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5

Isoprene/βAL

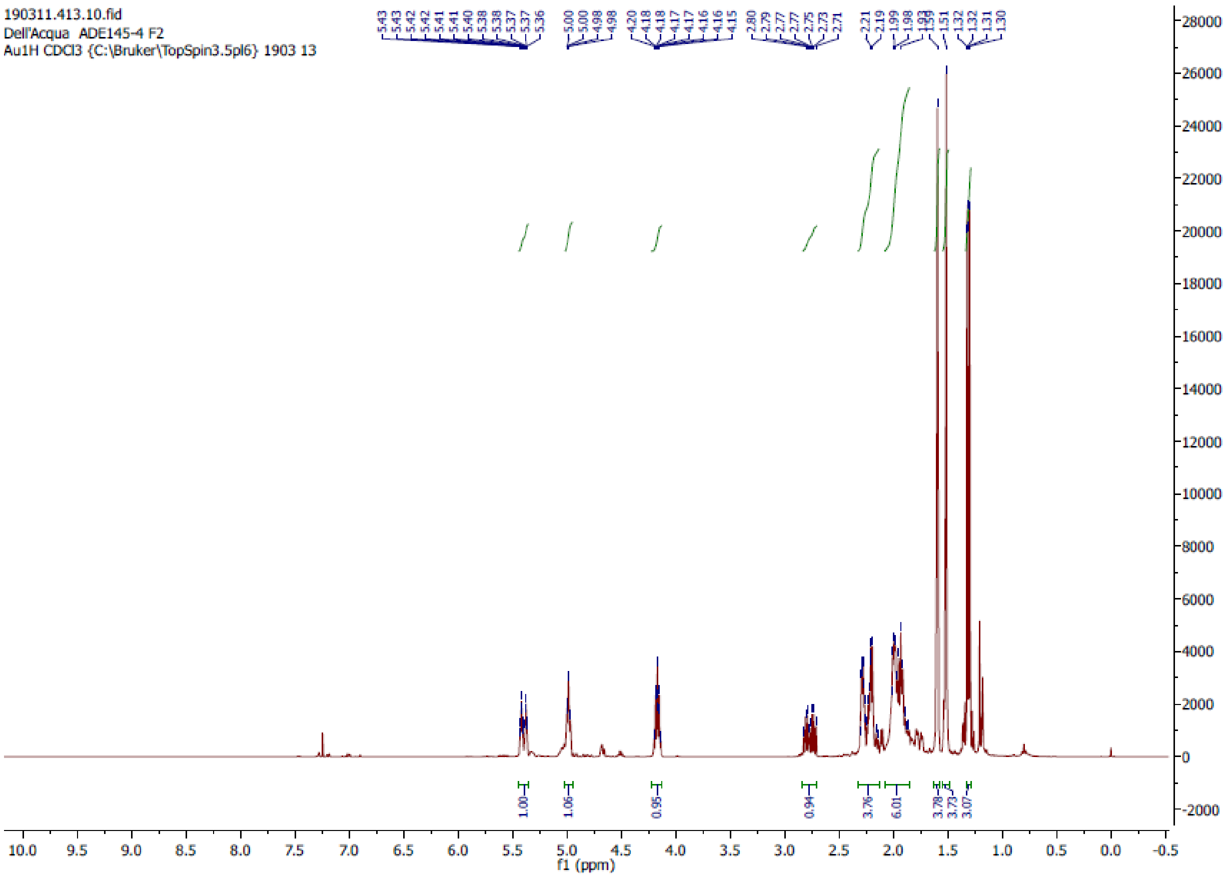
Due to the co-presence of different regio- and stereoisomers, NMR data for the other DA adducts are not easily intelligible. NMR was used mainly to confirm the absence of the βAL (C=C signal), while ESI to confirm the product structure.

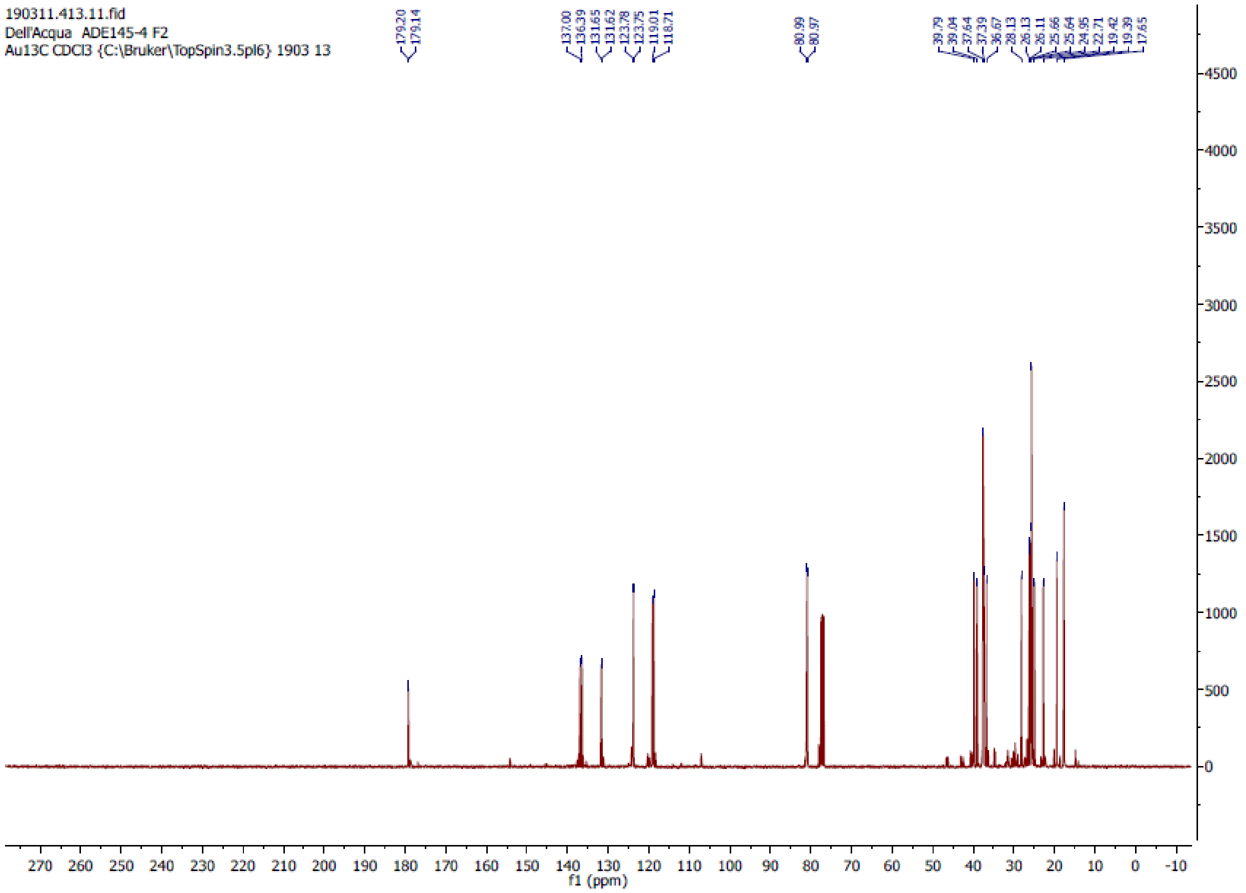


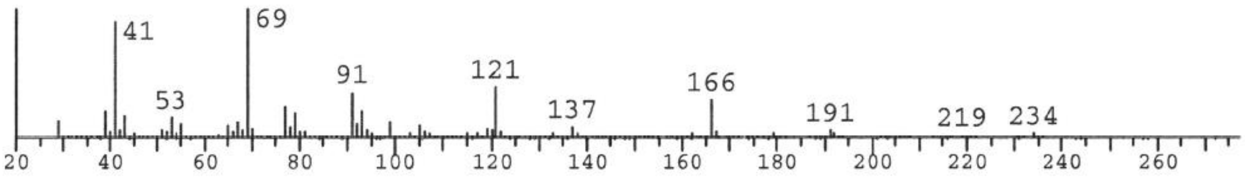

190306.f331.11.fid
Dell'Acqua ADE144 F2
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1903 31
179.20
179.11
132.88
132.35
119.06
118.83
80.93
39.66
38.56
37.31
36.32
29.33
26.86
25.00
23.73
23.41
22.62
19.25
19.22
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


29
39
53
65
79
93
111
121
137
151
166
20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180

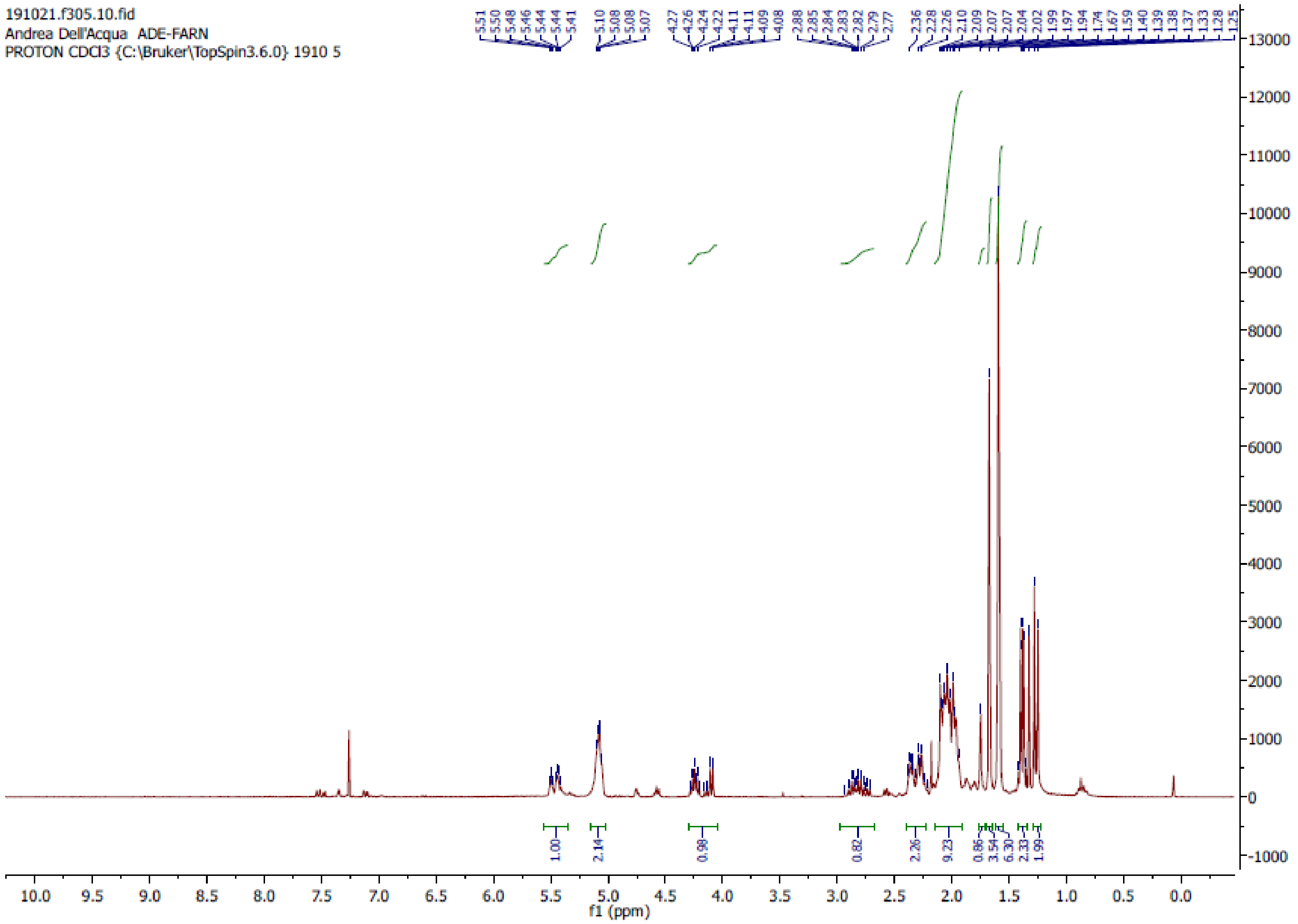
Myrcene/βAL

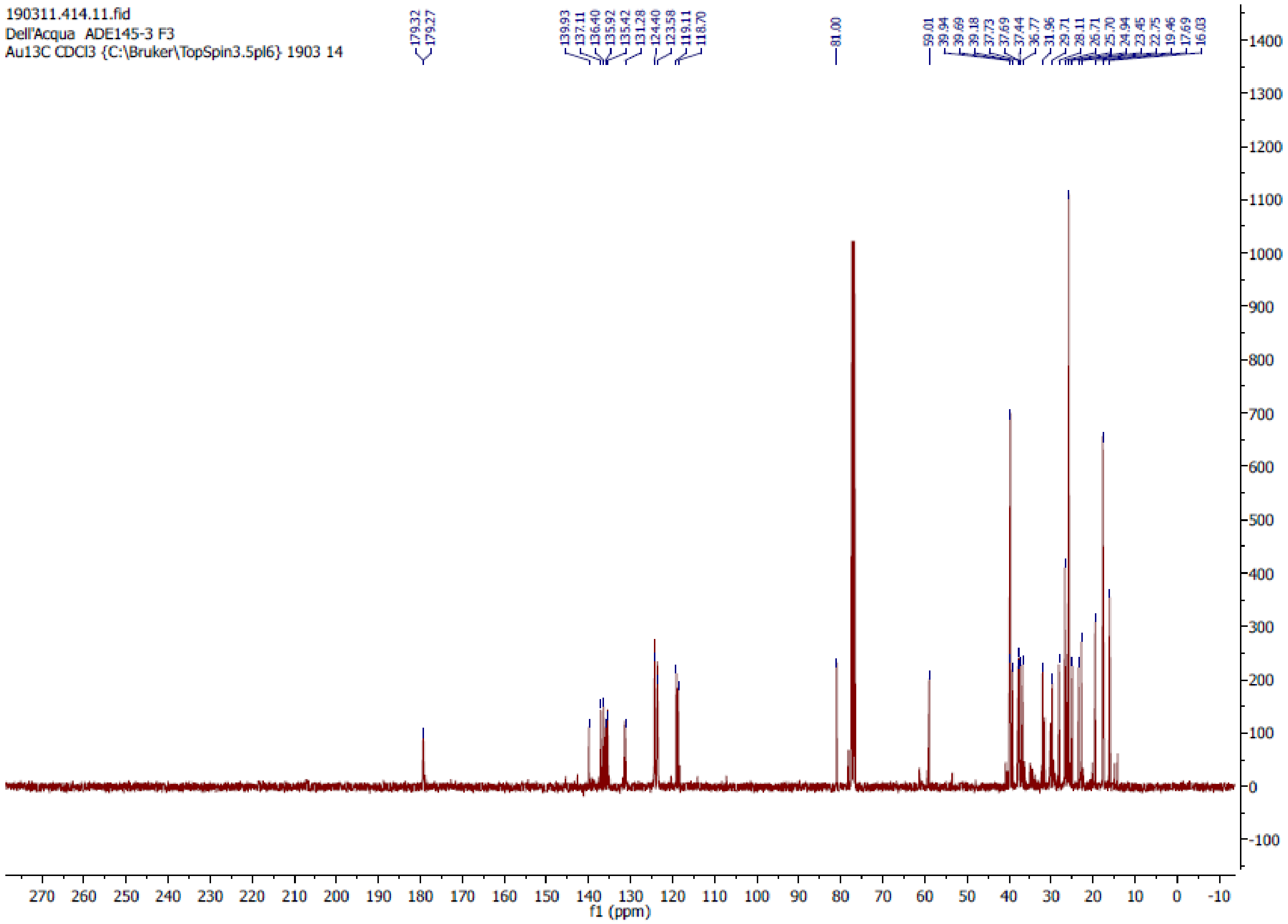

190311.413.10.fid
Dell'Acqua ADE145-4 F2
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1903 13
5.43
5.43
5.42
5.42
5.41
5.41
5.40
5.38
5.38
5.37
5.37
5.36
5.00
5.00
4.98
4.98
4.20
4.18
4.18
4.17
4.17
4.16
4.16
4.15
2.80
2.79
2.77
2.77
2.75
2.73
2.71
2.21
2.19
1.99
1.98
1.93
1.59
1.51
1.32
1.32
1.31
1.30
1.00
1.06
0.95
0.94
3.76
6.01
3.78
3.73
3.07
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

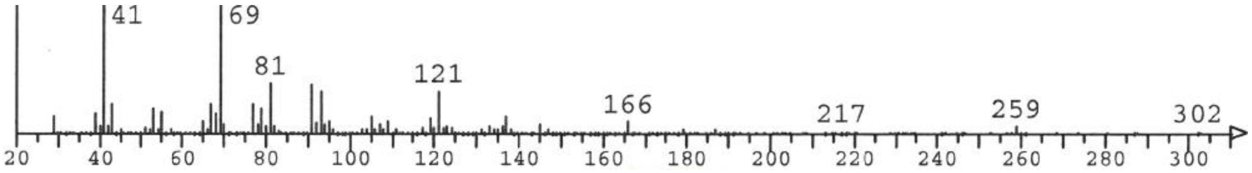

190311.413.11.fid
Dell'Acqua ADE145-4 F2
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1903 13
179.20
179.14
137.00
136.39
131.65
131.62
123.78
123.75
119.01
118.71
80.99
80.97
39.79
39.04
37.64
37.39
36.67
28.13
26.13
26.11
25.66
25.64
24.95
22.71
19.42
19.39
17.65
4500
4000
3500
3000
2500
2000
1500
1000
500
0
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



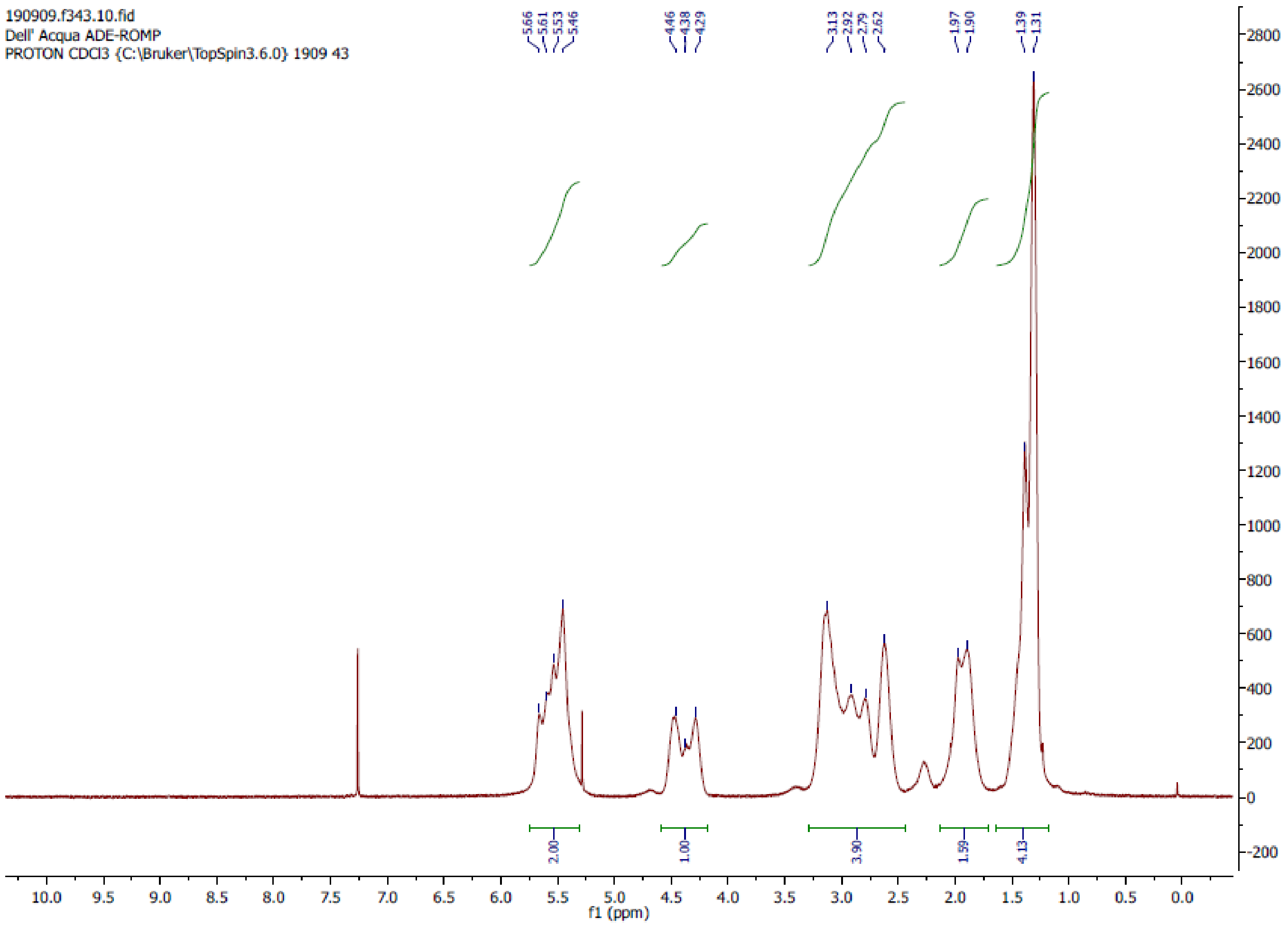
- Farnesene/βAL




190311.414.11.fid
Dell'Acqua ADE145-3 F3
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1903 14
179.32
179.27
139.93
137.11
136.40
135.92
135.42
131.28
124.40
123.58
119.11
118.70
81.00
59.01
39.94
39.69
39.18
37.73
37.69
37.44
36.77
31.96
29.71
28.11
26.71
25.70
24.94
23.45
22.75
19.46
17.69
16.03
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


41
69
81
121
166
217
259
302
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300

- *poly*-Cp/βAL


190909.f343.10.fid
Dell' Acqua ADE-ROMP
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1909 43
5.66
5.61
5.53
5.46
4.46
4.38
4.29
3.13
2.92
2.79
2.62
1.97
1.90
1.39
1.31
2.00
1.00
3.90
1.59
4.13
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

10. TGA/DSC analysis

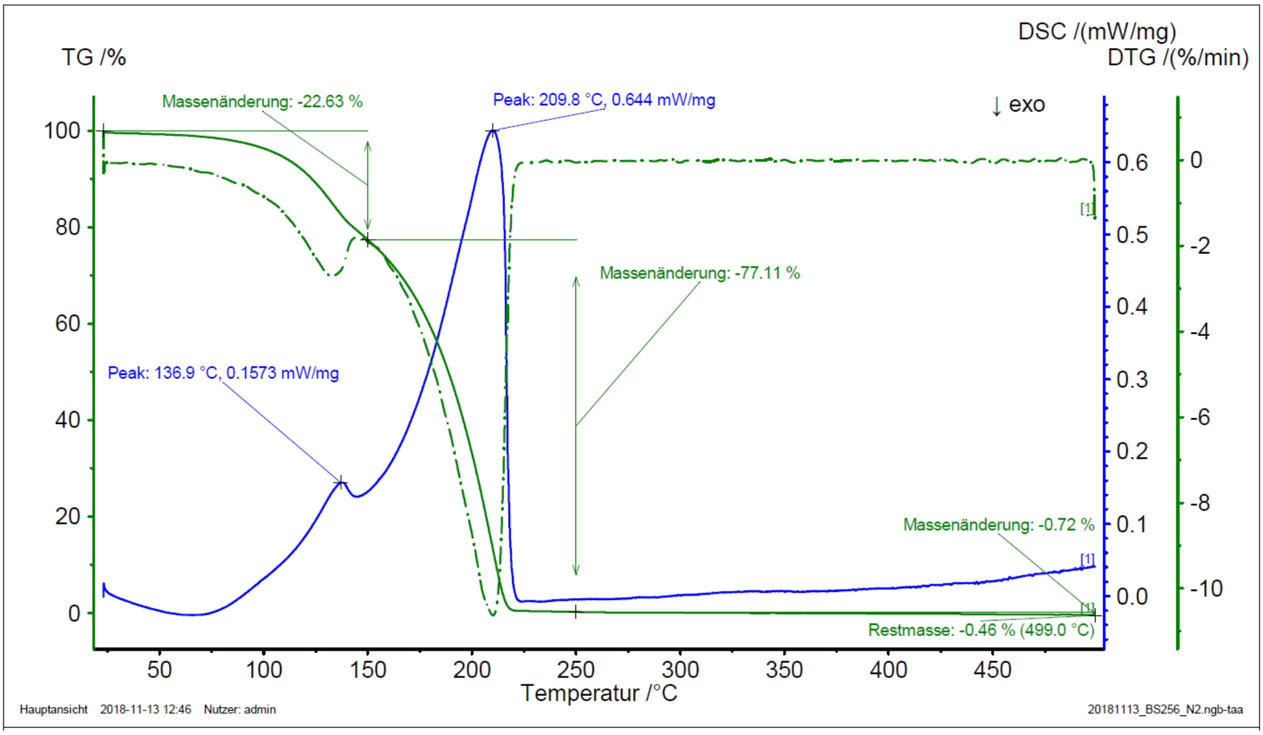


Figure S7 DSC-TG of the Cp/βAL Diels-Alder adduct.

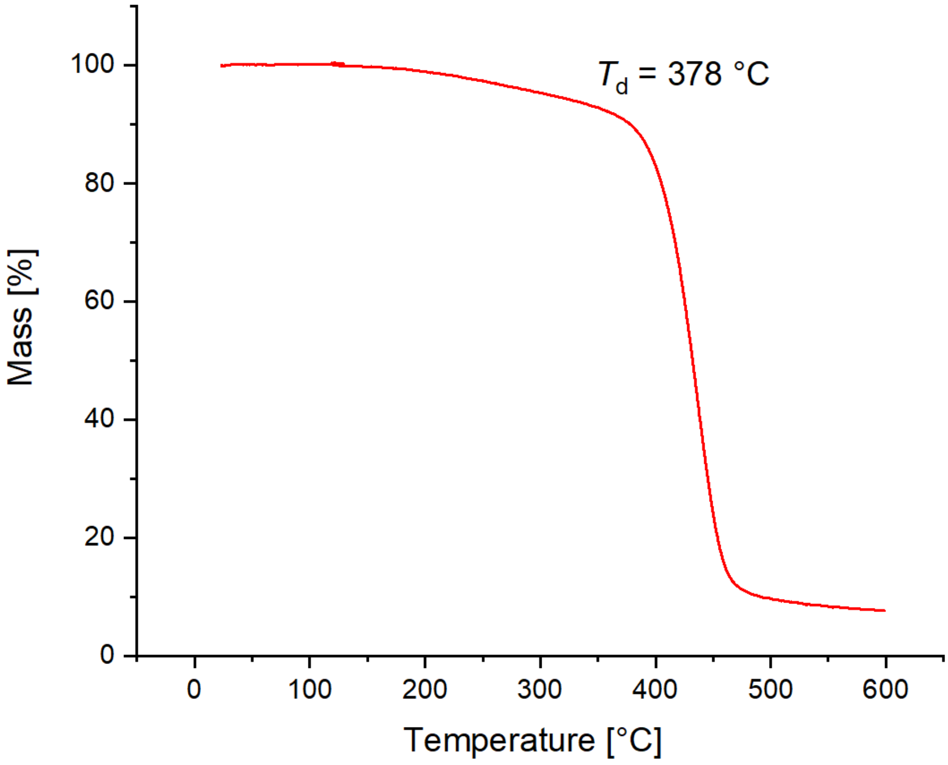


Figure S8 TGA of *poly*-Cp/βAL. The onset of decomposition (T_d) was taken at 10% of mass loss.

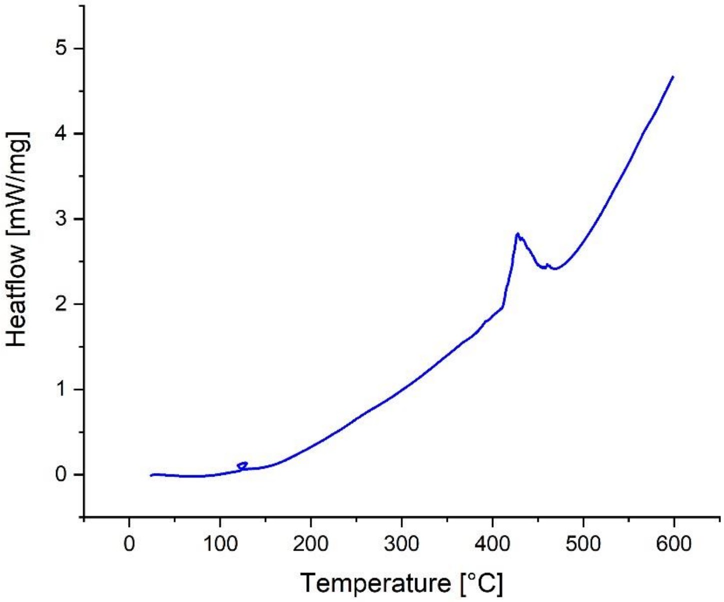


Figure S9 Corresponding DSC trace to Figure S8