

## New Bifunctional Monomers from Methyl Vinyl Glycolate.

Andrea Dell'Acqua,<sup>a</sup> Claas Schünemann,<sup>a</sup> Eszter Baráth,<sup>a</sup> Sergey Tin<sup>a</sup> and Johannes G. de Vries<sup>\*a</sup>

<sup>a</sup>Leibniz Institut für Katalyse e. V. an der Universität Rostock  
Albert-Einstein-Strasse 29a, 18055 Rostock  
E-mail: [johannes.devries@catalysis.de](mailto:johannes.devries@catalysis.de)

### Supporting Information

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## 1. General information

**Reagents:** Methyl vinylglycolate can be obtained from Sigma-Aldrich. For larger quantities it can be convenient to use a high yielding synthesis from (E)-4-iodobut-2-enoate,<sup>1</sup> which itself is easily prepared from the commercially available bromide. All the other reagents and solvents were obtained from commercial sources and used as received unless noted otherwise. Dry solvents were obtained from a solvent purification system or purchased water-free in a bottle with septum. All the reagents and solvents were handled in oven-dried glassware using standard Schlenk techniques, unless otherwise stated.

**NMR-Spectroscopy:** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were recorded at ambient temperature on 300 MHz spectrometers (Avance 300 or Fourier 300) or a 400 MHz spectrometer (Avance 400) from Bruker. The chemical shifts  $\delta$  are given in ppm and referenced to the residual proton signal of the deuterated solvent used.

**Gas Chromatography (GC):** GC analysis was carried out on an Agilent 7890B GC system with a HP-5 normal-phase silica column, using He as a carrier gas and dodecane as internal standard.

**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  $\mu$ m particle size, 8.0  $\times$  50 mm; PSS GRAM 30 Å, 10  $\mu$ m particle size, 8.0  $\times$  300 mm; PSS GRAM 1000 Å particle size, 8.0  $\times$  300 mm). THF was applied as the mobile phase with a flow rate of 1 mL $\cdot$ min<sup>-1</sup>. Polystyrene standards from *ReadyCal* (PSS-pskitr1I-10,  $M_p = 370\text{--}2520000$  g $\cdot$ mol<sup>-1</sup>) 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<sup>-1</sup> to 150.00 °C; Ramp 10.00 °C/min to -90.00 °C; -90.00 °C isothermal 5.00 min; Ramp 10.00 °C min to 150.00 °C; Ramp 10.00 °C/min to -90.00 °C.

**Infrared Spectroscopy:** ATR-IR measurements were recorded on a Nicolet iS5 FT-IR (ThermoFisher) device calibrated on 1.5 mil polystyrene and equipped with a GladiATR 210 accessory from PIKE technologies.

**Mass spectroscopy (ESI-MS):** measurements were recorded on an Agilent 6210 time-of-flight LC/MS (ESI) or on a Thermo Electron MAT 95-XP (EI, 70 eV). Peaks as listed correspond to the highest abundant peak and are of the expected isotope pattern.

## 2. Experimental procedures

**Hydroformylation of MVG:** In a glovebox, dicarbonyl(acetylacetonato)rhodium(I) (1.2 mg, 0.005 mmol, 0.5 mol%) and the desired ligand (0.095 mmol, 0.1 eq) were weighted into a vial. The vial was sealed, equipped with a magnetic stirrer and transferred out of the glovebox. The desired solvent (toluene or THF, 1.35 mL, 0.7 mol/L with respect to MVG) and MVG (110 mg, 0.95 mmol, 1 eq) were added under argon atmosphere. The vials were placed into a 300 mL Parr stainless steel autoclave and pierced with a needle. The autoclave was flushed three times with nitrogen, then pressurized with 10 bar of syngas and heated to 80 °C. After stirring overnight, the reaction was cooled down to room temperature, the crude mixtures filtered over celite, and volatiles evaporated under reduced pressure. The crude residue was dissolved in CDCl<sub>3</sub> and analysed by <sup>1</sup>H NMR and GC-MS. Linear product (**1**) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.77 (t, *J* = 1.2 Hz, 1H), 4.23 (dd, *J* = 7.8, 4.2 Hz, 1H), 3.77 (s, 3H), 2.65 – 2.55 (m, 2H), 2.48 – 2.36 (m, 2H). Branched product (**2**), mixture of 2 diastereoisomers: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.73 (d, *J* = 0.7 Hz, 1H), 9.65 (s, 1H), 4.76 (d, *J* = 3.0 Hz, 1H), 4.42 (d, *J* = 3.9 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 2.54 – 2.37 (m, 1H), 2.37 – 2.12 (m, 1H), 1.26 (d, *J* = 7.3 Hz, 3H), 1.12 (d, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 201.9, 201.7, 174.9, 70.9, 69.6, 53.1, 53.0, 49.8, 49.6, 9.9, 7.6. Hydroxyacetal (**3**), mixture of 2 diastereoisomers: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 5.75 – 5.71 (m, 1H), 5.60 (t, *J* = 3.2 Hz, 1H), 4.71 (dd, *J* = 8.6, 4.2 Hz, 1H), 4.55 (dd, *J* = 8.2, 7.1 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 2.11 – 1.82 (m, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 174.8, 173.2, 100.2, 99.7, 77.2, 76.3, 52.5, 52.3, 33.7, 32.2, 28.1, 28.0.

**Methylation of MVG:** In a 250 mL Schlenk flask Ag<sub>2</sub>O (19.6 g, 84.4 mmol, 2 eq) was suspended in 60 mL of diethyl ether (0.7 mol/L with respect to MVG). MVG (4.90 g, 42.2 mmol, 1 eq) was added under argon atmosphere. To the stirred suspension, methyl iodide (13.0 g, 84.4 mmol, 2 eq) was slowly added via syringe. The reaction was stirred at room temperature while monitoring the conversion by GC. After 60 hours, MVG was fully converted. The reaction was filtered to remove the solids, then the solvent and the excess of methylating agent removed by carefully distilling under vacuum, affording a colourless liquid (5.51 g, quantitative yield). The analytical data corresponds to the known literature.<sup>2</sup>

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.85 (ddd,  $J = 17.2, 10.4, 6.4$  Hz, 1H), 5.46 (dt,  $J = 17.2, 1.3$  Hz, 1H), 5.34 (dt,  $J = 10.4, 1.3$  Hz, 1H), 4.26 (dt,  $J = 6.4, 1.3$  Hz, 1H), 3.76 (s, 3H), 3.40 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  171.1, 132.7, 119.6, 81.7, 57.5, 52.4.

**Acetylation of MVG:** In a 50 mL Schlenk flask, MVG (550 mg, 4.74 mmol, 1 eq) and pyridine (750 mg, 9.47 mmol, 2 eq) were dissolved in dichloromethane (16 mL, 0.3 mol/L with respect to MVG). To the stirred mixture, acetic anhydride (967 mg, 9.47 mmol, 2 eq) was slowly added via syringe. The reaction was stirred at room temperature overnight, then poured into ice-cold water and extracted three times with DCM. The organic phase was washed with 1M HCl, water and brine, then dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuum, affording 746 mg of colourless liquid (quantitative yield). The analytical data corresponds to the known literature.<sup>3</sup>

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.87 – 5.77 (m, 1H), 5.41 – 5.31 (m, 2H), 5.24 (ddd,  $J = 10.5, 1.4, 0.9$  Hz, 1H), 3.63 (s, 3H), 2.04 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.7, 168.7, 129.9, 119.5, 72.8, 52.3, 20.3.

**Methoxycarbonylation reactions:** In a glovebox, palladium(II) diacetate (1.7 mg, 0.01 mmol, 1.0 mol%) and the desired ligand (0.02 mmol, 2.0 mol%) were weighted into a vial. The vial was sealed, equipped with a magnetic stirrer, and transferred out of the glovebox. Methanol (1.5 mL, 0.5 mol/L with respect to the substrate), methanesulfonic acid (2.2 mg, 0.02 mmol, 2 mol%) and the desired MVG derivative (see Table 2 main text; 0.80 mmol, 1 eq) were added under argon atmosphere. The vials were placed into a 300 mL Parr stainless steel autoclave and pierced with a needle. The autoclave was flushed three times with nitrogen, then pressurized with the desired pressure of carbon monoxide and heated to the required temperature. After stirring for the desired time, the reaction was cooled down to room temperature, the crude mixtures filtered over celite, and volatiles evaporated under reduced pressure. The crude was purified by flash column chromatography (gradient elution, from 100% *n*-hexane to 100% ethyl acetate), affording the diester as a yellowish liquid.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.82 (dd,  $J = 7.8, 4.7$  Hz, 1H), 3.75 (s, 3H), 3.67 (s, 3H), 3.38 (s, 3H), 2.44 (ddd,  $J = 7.7, 7.0, 3.6$  Hz, 2H), 2.18 – 1.92 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 172.7, 79.3, 58.4, 52.1, 51.8, 29.6, 27.9. ESI-MS ( $\text{ES}^+$ ): calculated for  $\text{C}_8\text{H}_{14}\text{O}_5$ : 190.1932; found: 213.0737  $[\text{M}-\text{Na}]^+$ .

**Polycondensation reactions:** A 5 mL vial equipped with stirring bar was charged with the desired diol (2.0 mmol, 1 eq) and **8** (380 mg, 2.0 mmol, 1 eq). The starting materials were extensively dried via vacuum-argon cycles, then titanium(IV) isopropoxide (3.2 mg, 0.01 mmol, 1 mol%) was added via syringe and the reaction heated up to 150 °C. After stirring under argon

atmosphere for 6 hours, vacuum was applied for 1 hour. Viscosity visibly increased up to the point that the mixture wasn't stirred. Temperature was then increased to 190 °C and the reaction kept in vacuum another hour. After cooling down to room temperature, the solid products were analysed by NMR and GPC.

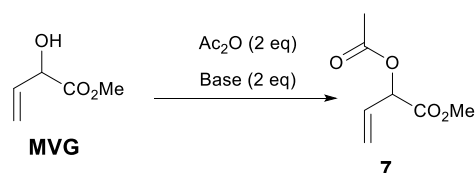
### 3. Screening of reaction conditions for the protection of the OH group of MVG

#### Methylation



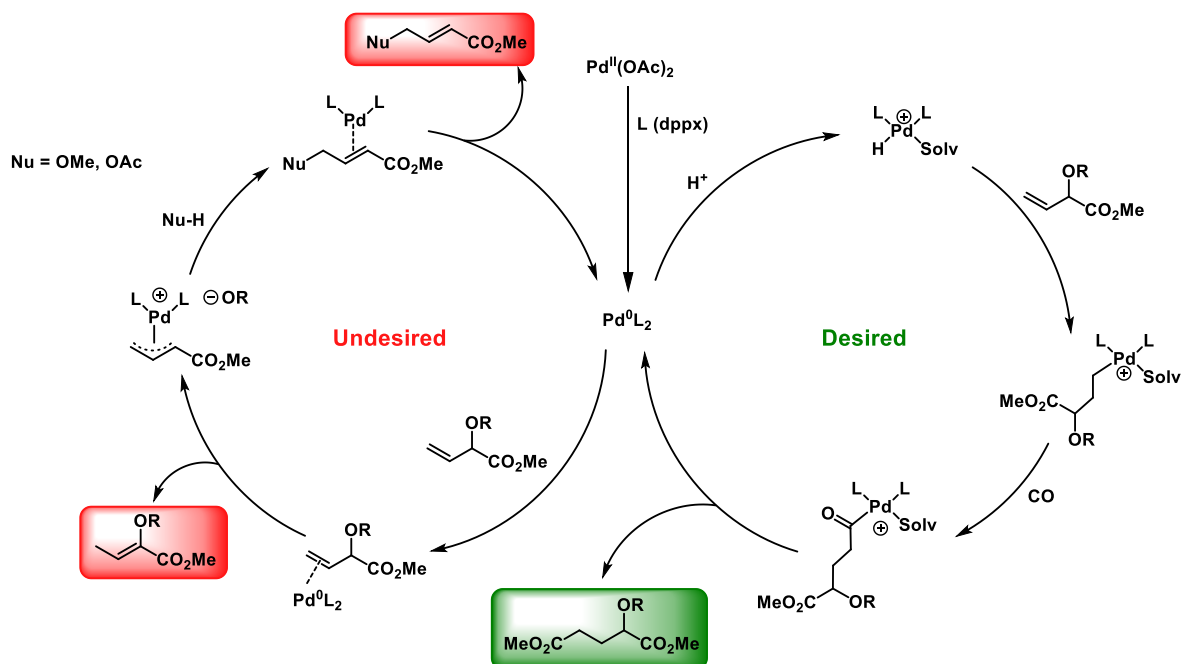
Entry	Conditions	Outcome
1	NaH, THF, 0 °C – r.t., 16 h	C=C isomerization
2	Ag <sub>2</sub> O, Et <sub>2</sub> O, r.t., 24 h	<b>6</b> (49 % after FCC)
3	K <sub>2</sub> CO <sub>3</sub> , THF, 80 °C, 1 h	-
4	K <sub>2</sub> CO <sub>3</sub> , MeOH, 80 °C, 1 h	MeOMVG dimerization
5	K <sub>2</sub> CO <sub>3</sub> , neat, 80 °C, 1 h	-
6	K <sub>2</sub> CO <sub>3</sub> , acetone, 80 °C, 1 h	-
7	NaOMe, MeOH, 80 °C, 1 h	C=C isomerization
8	DIPEA, Et <sub>2</sub> O, r.t., 48 h	C=C isomerization

#### Acetylation



Entry	Conditions	Outcome
1	Et <sub>3</sub> N, DCM, r.t., 24 h	C=C isomerization
2	iPr <sub>2</sub> EtN, DCM, r.t., 24 h	C=C isomerization
3	Pyridine, r.t., 16 h	<b>7</b> (>99%)

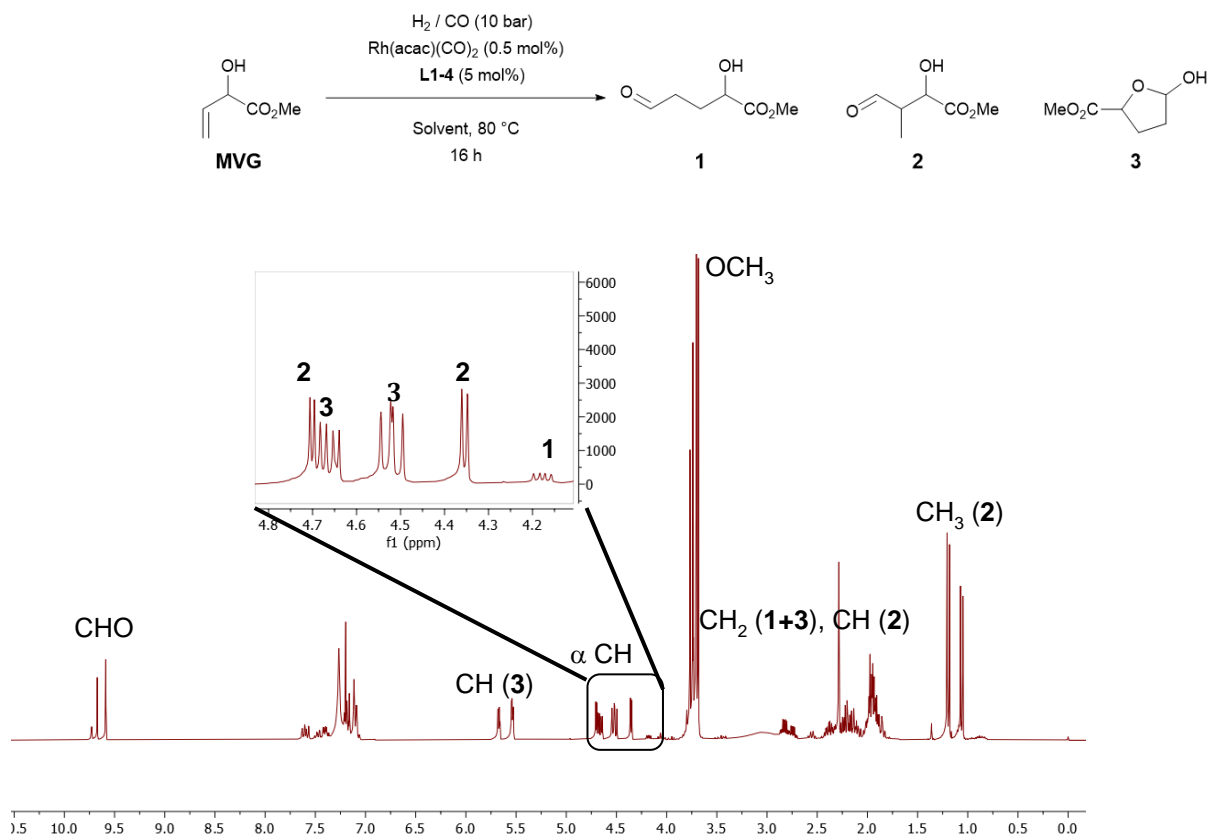
#### 4. Mechanisms involved in the Pd-catalysed methoxycarbonylation



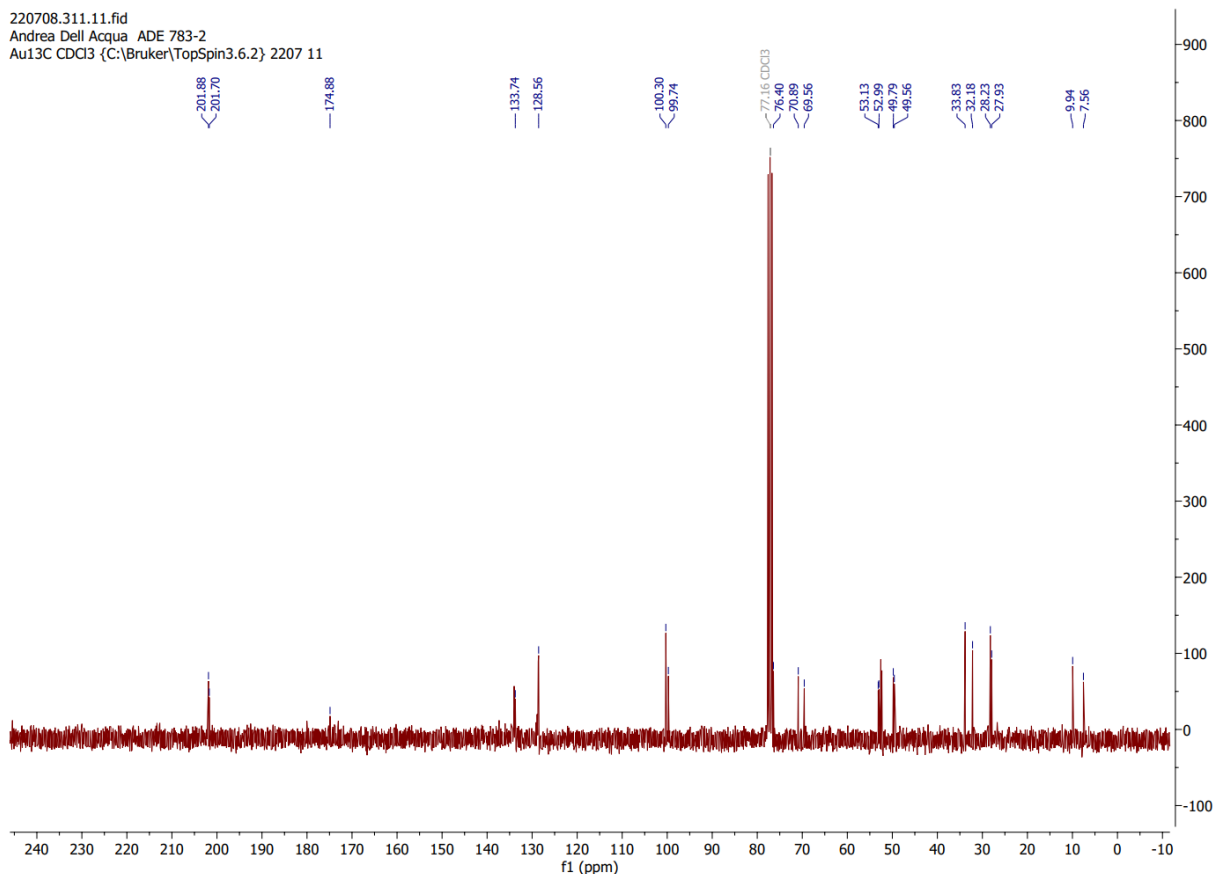
## 5. Characterization of products

### NMR Spectra

- Representative spectra in CDCl<sub>3</sub> of the crude mixture after hydroformylation of MVG using PPh<sub>3</sub> as ligand (Table 1 main text, entry 1 and 2):

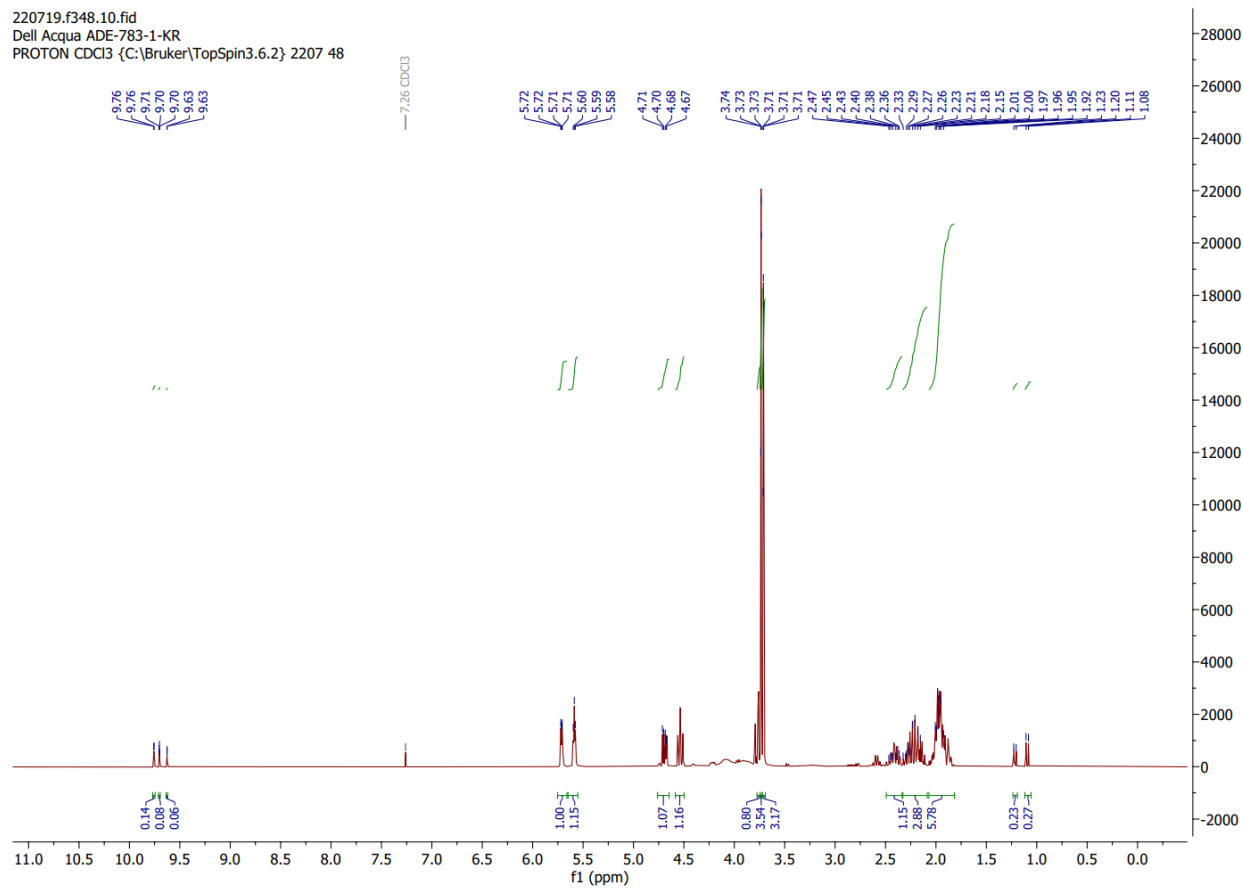


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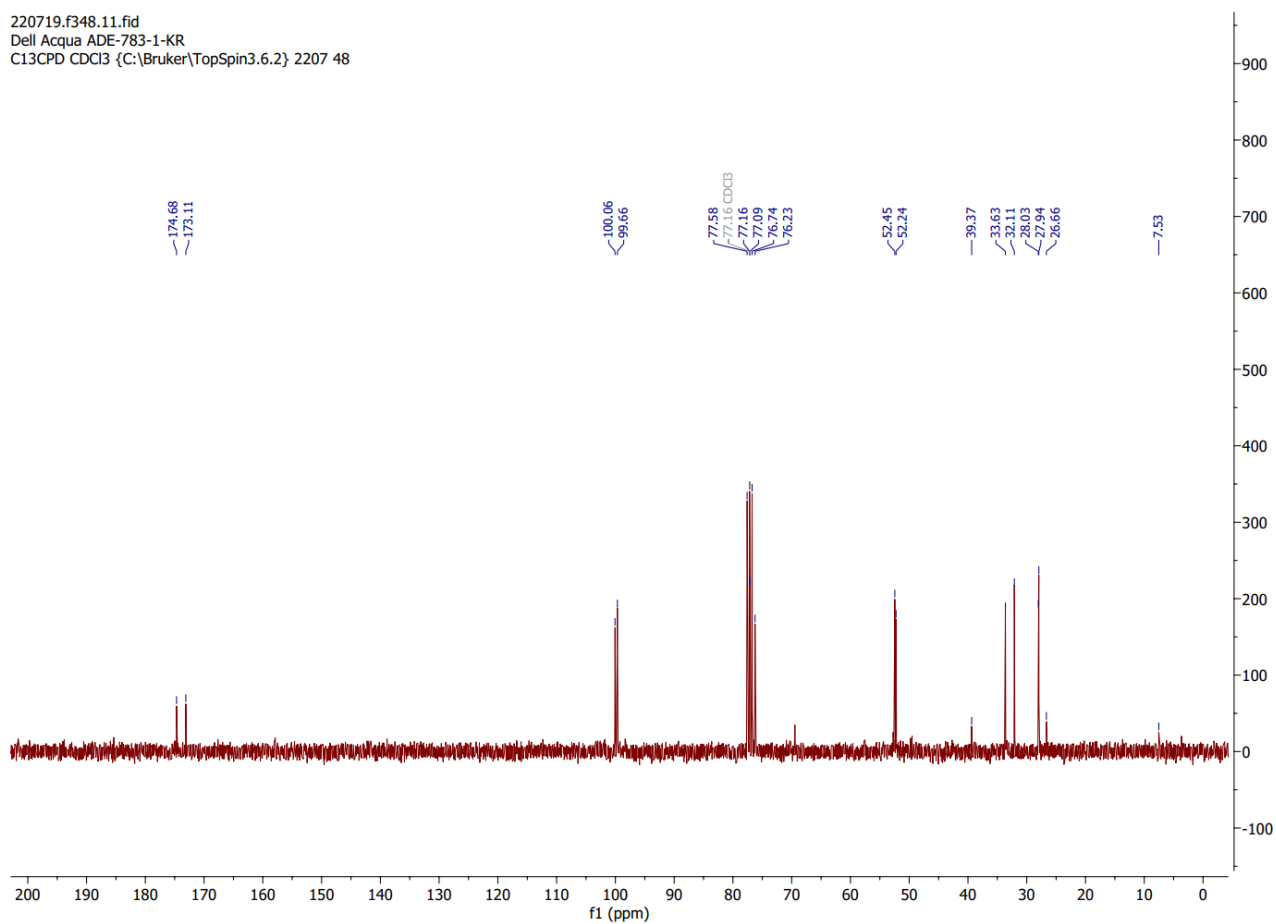
- Representative spectra in CDCl<sub>3</sub> of the high linear containing mixture after hydroformylation of MVG using Xantphos as ligand (Table 1 main text, entry 3 and 4):

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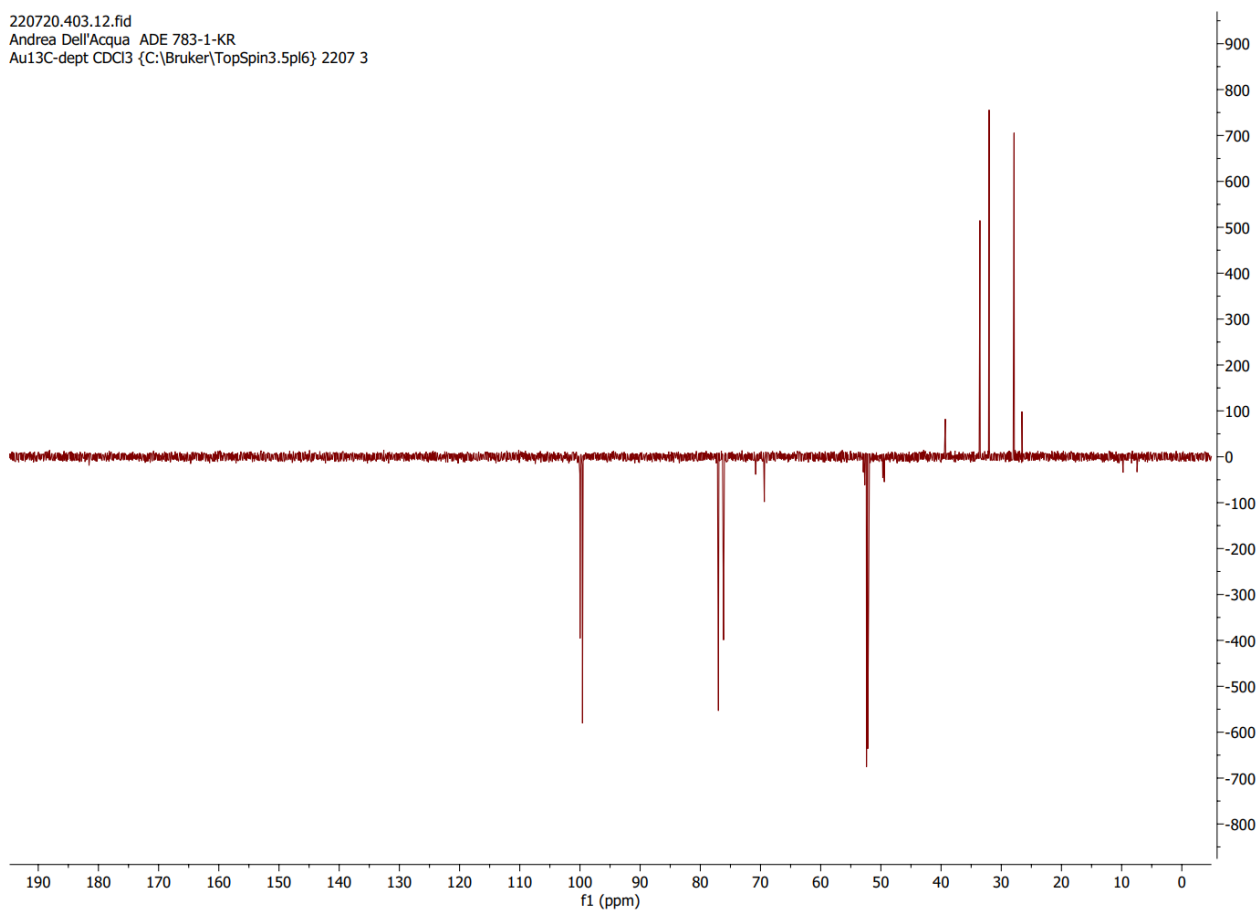


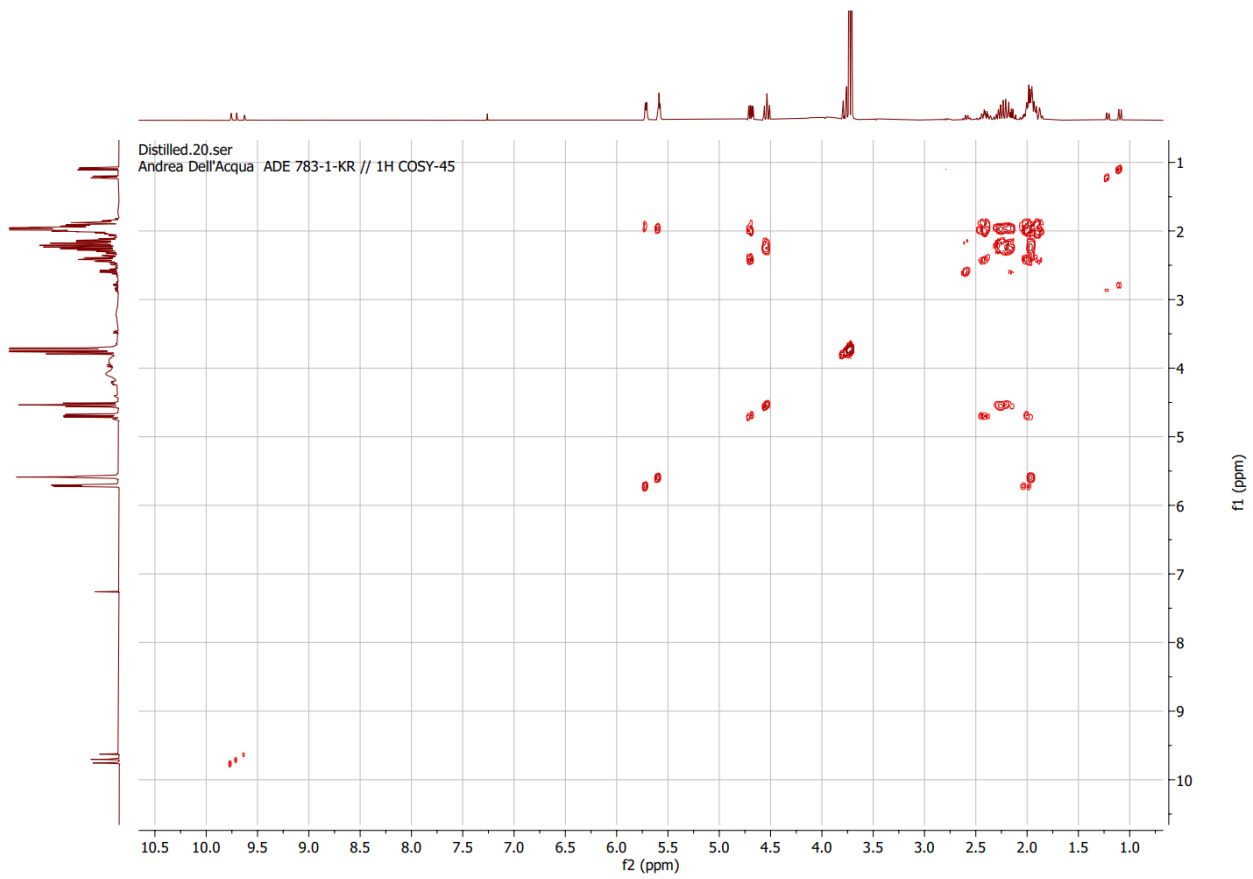


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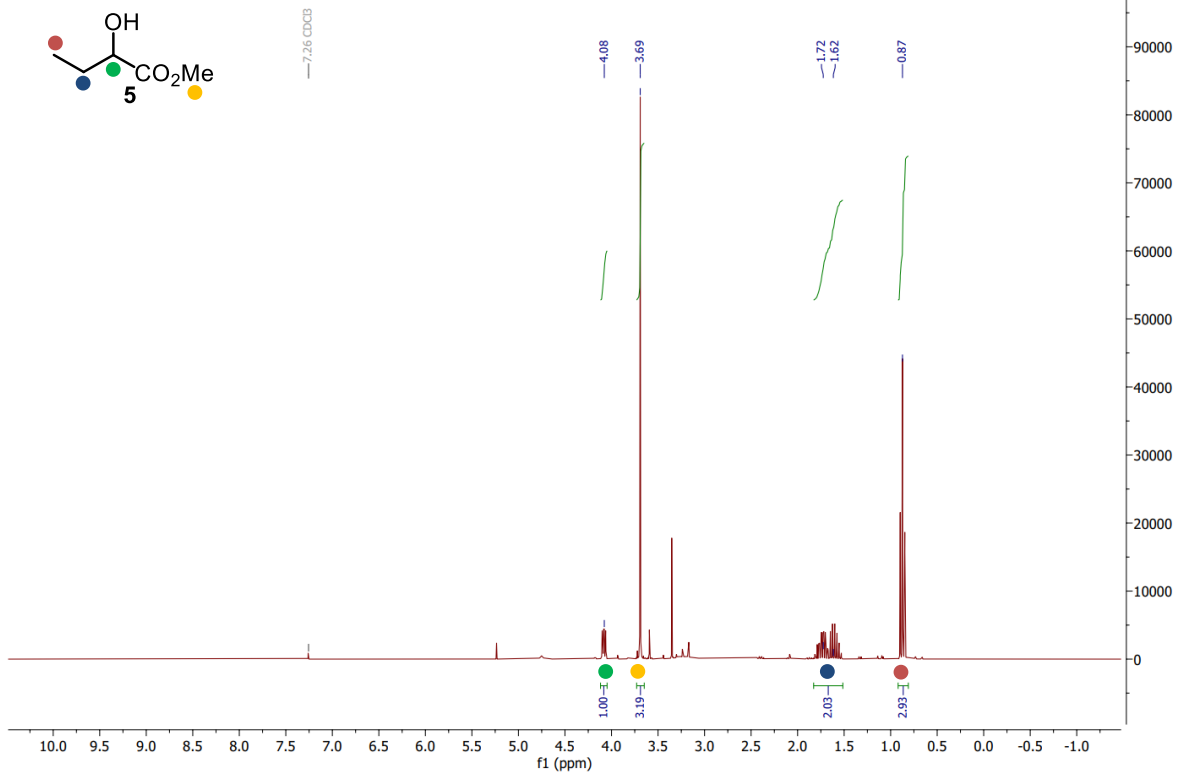
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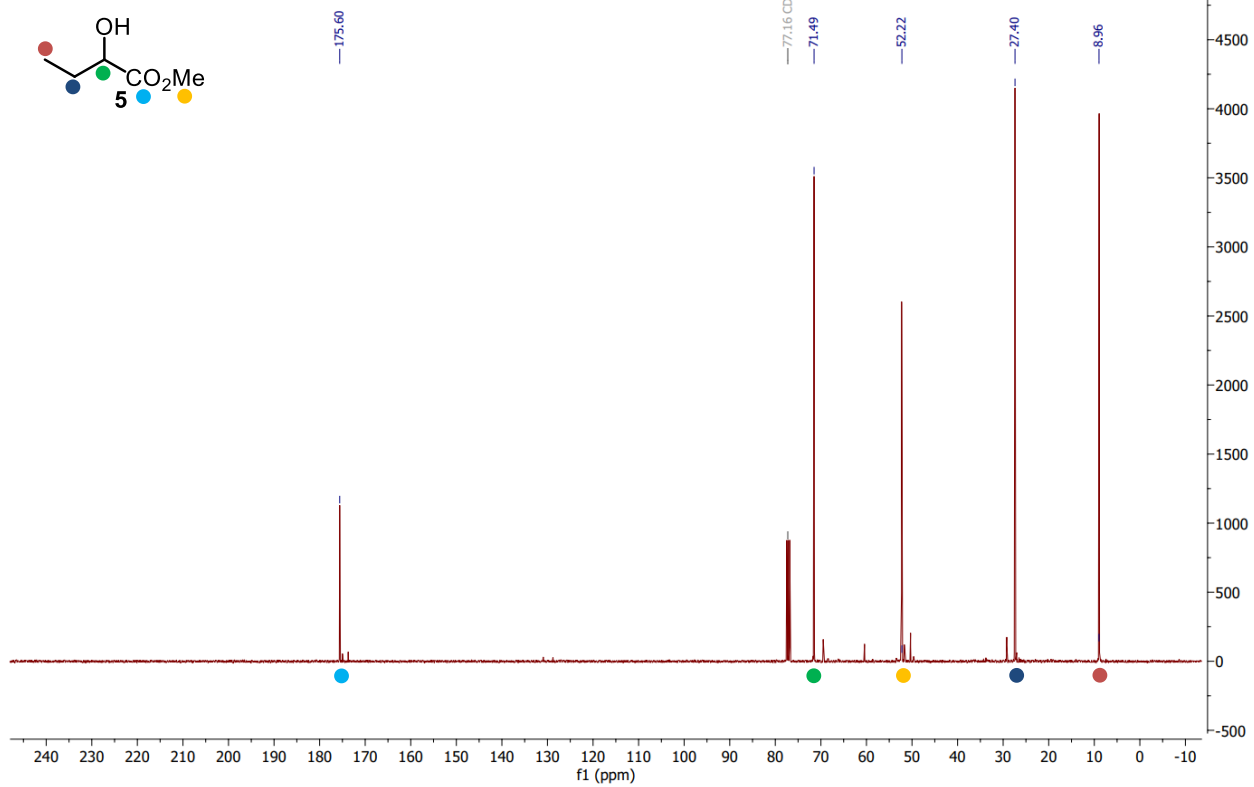


- NMR spectra of isolated products:

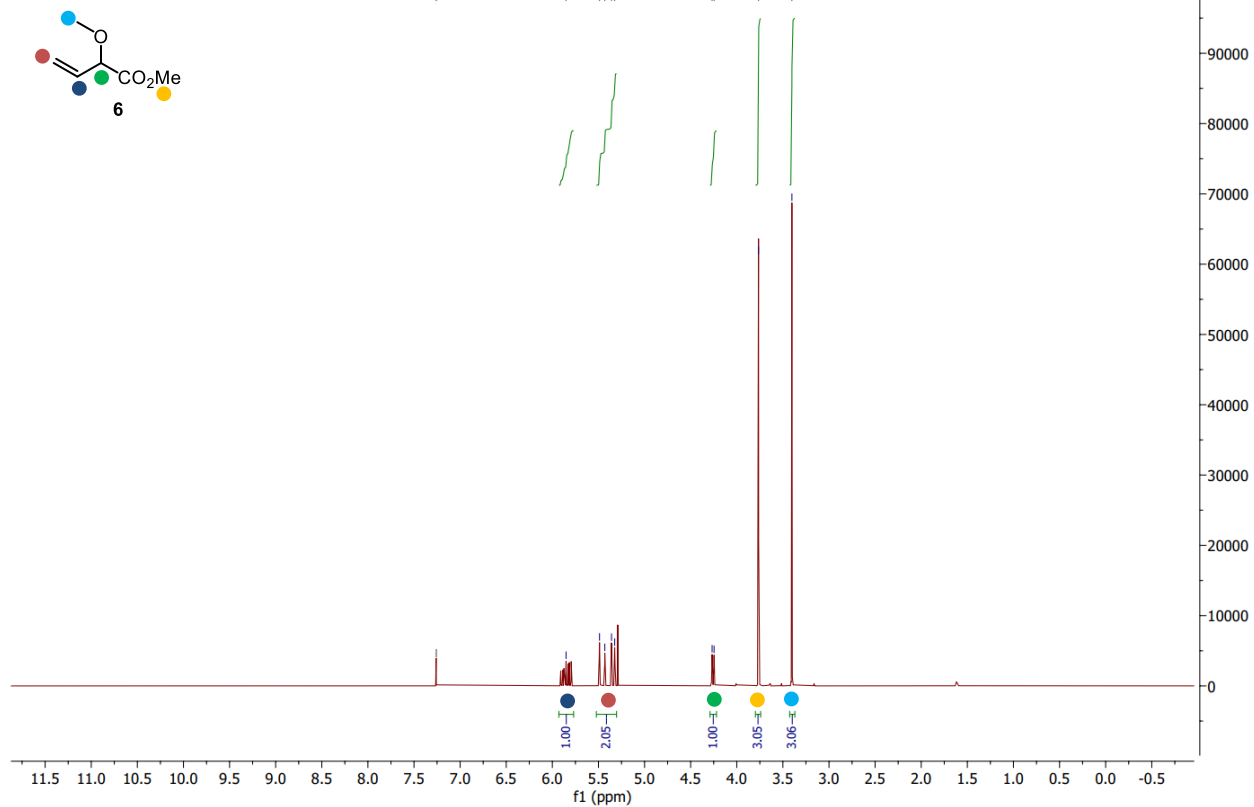
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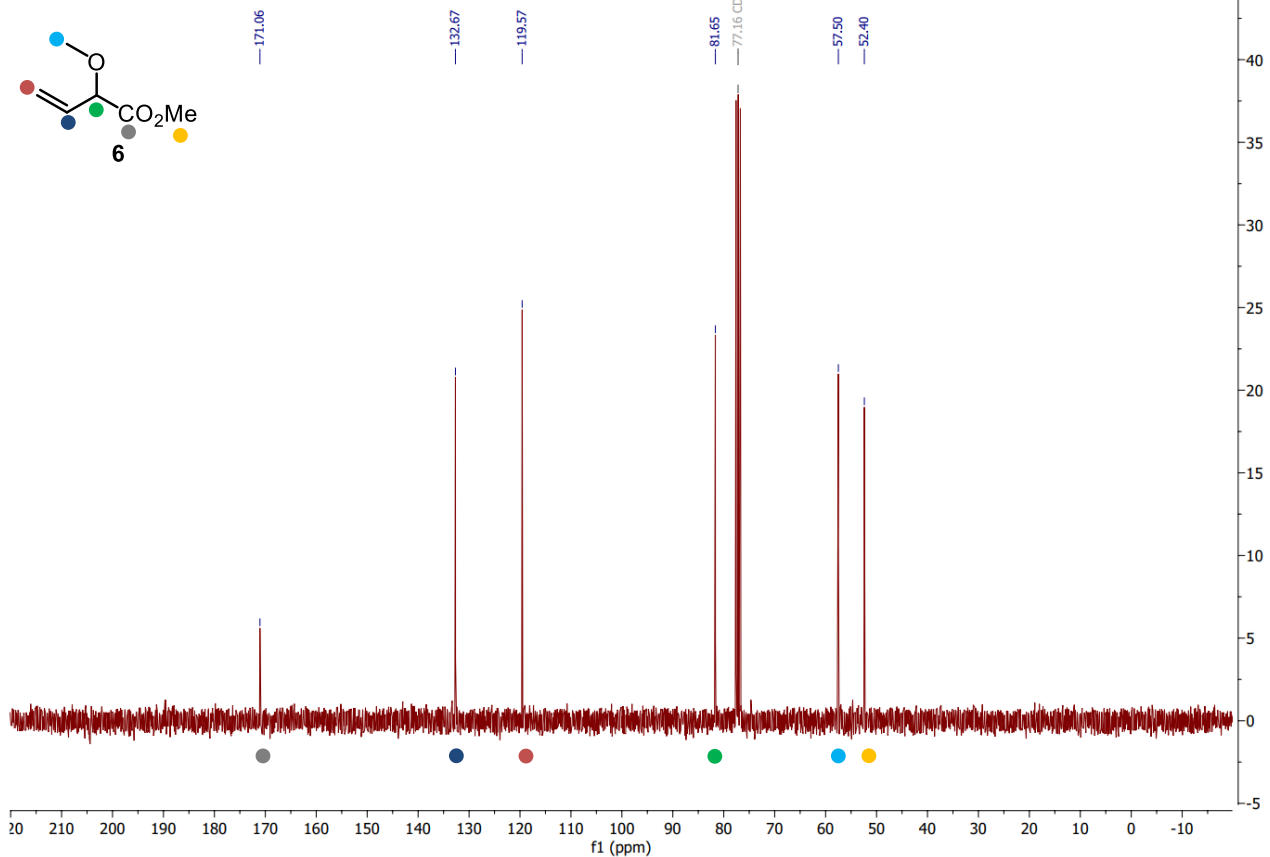
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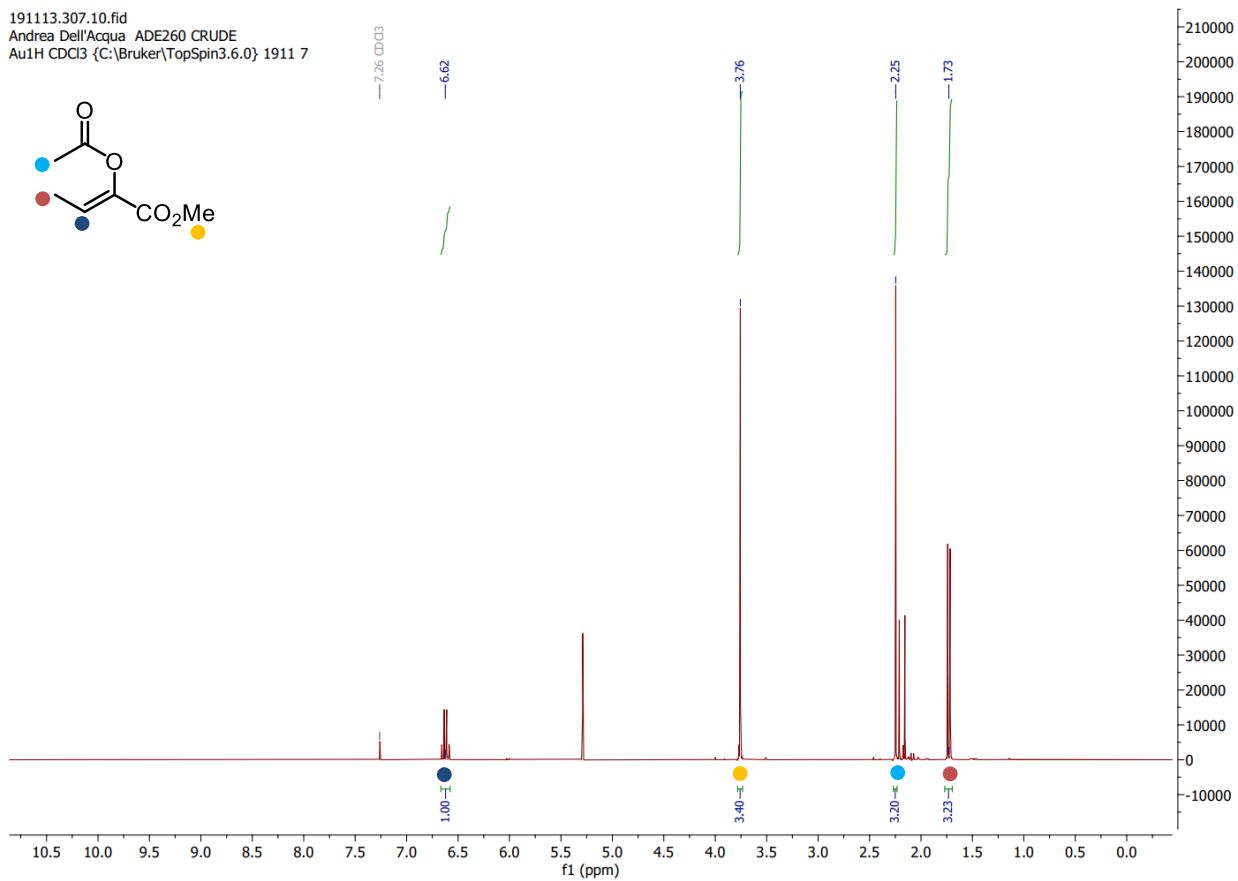
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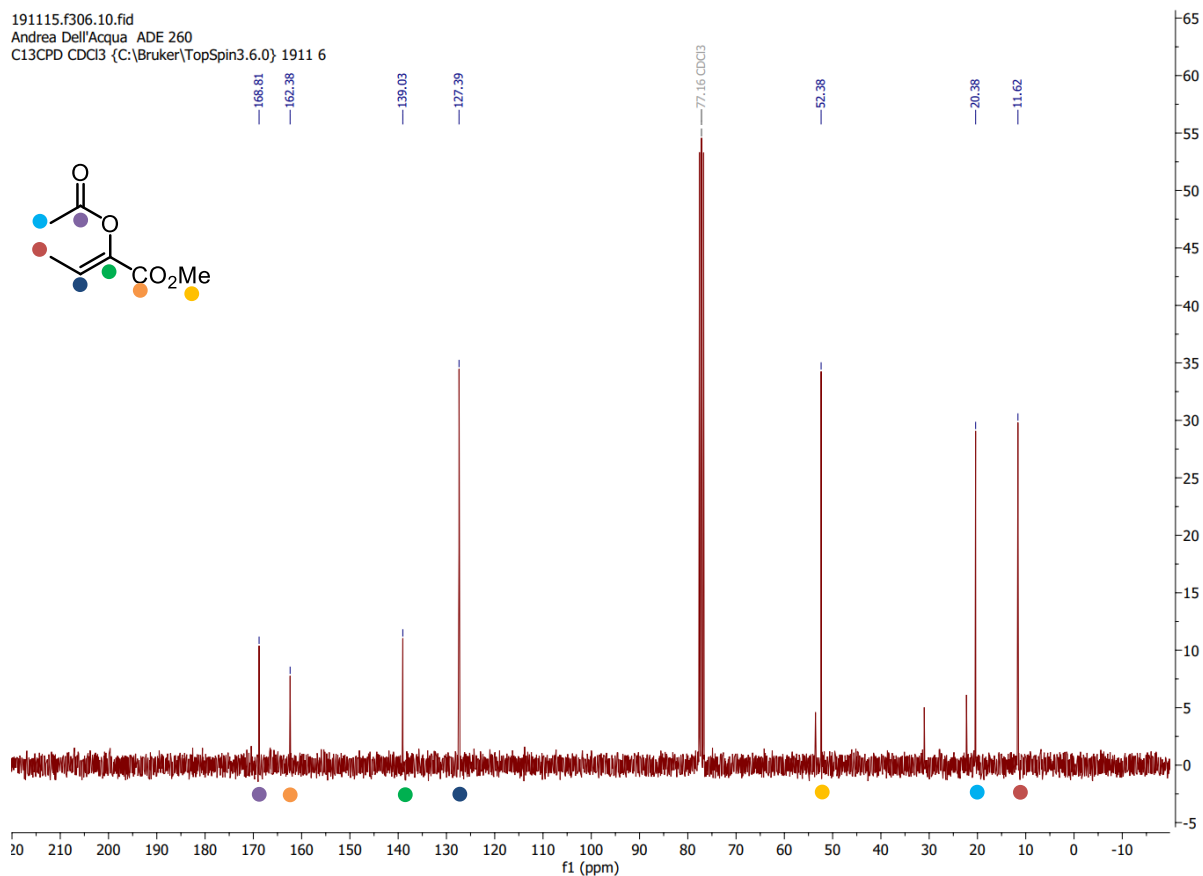
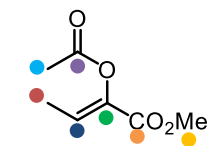
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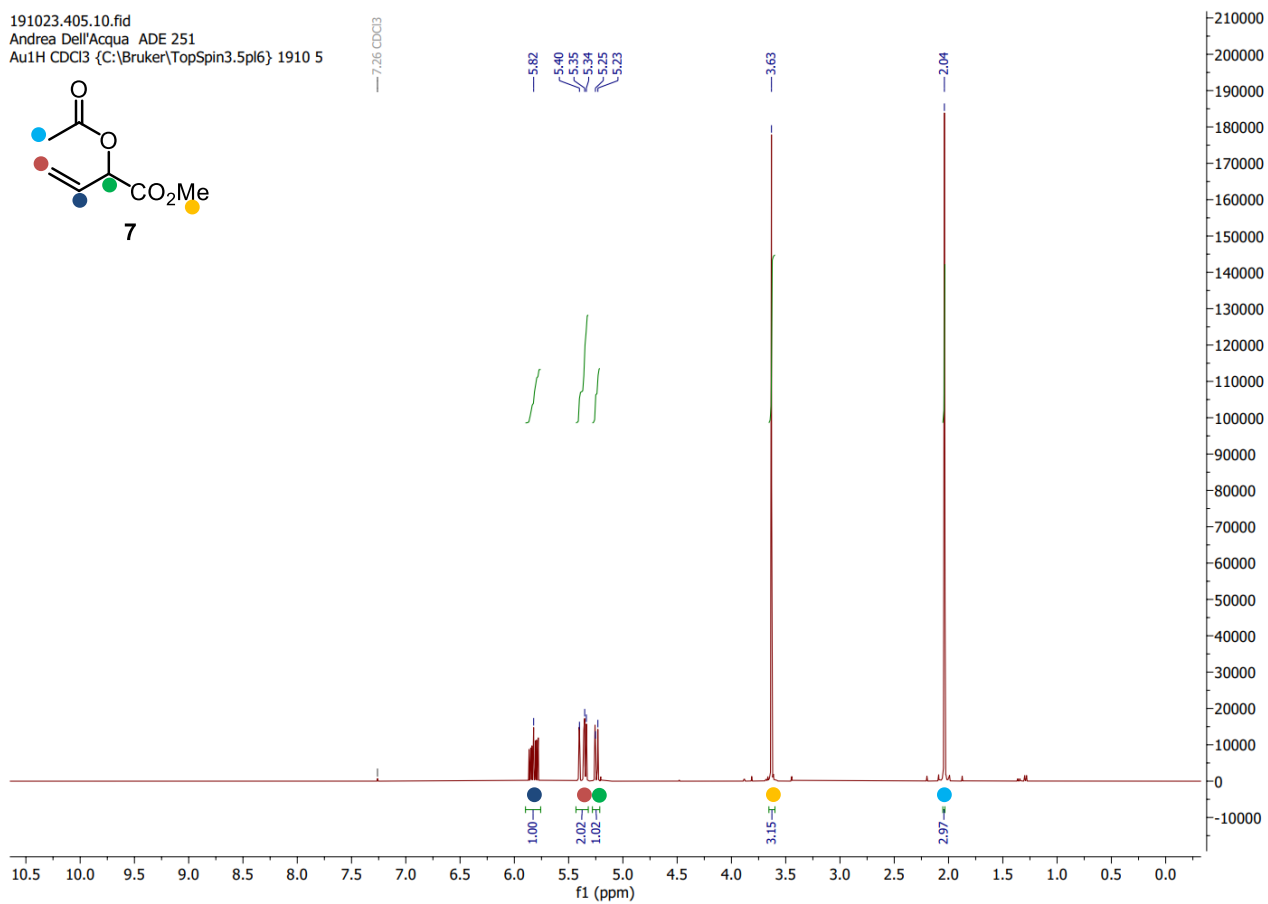
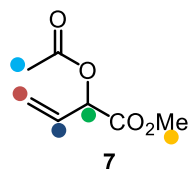
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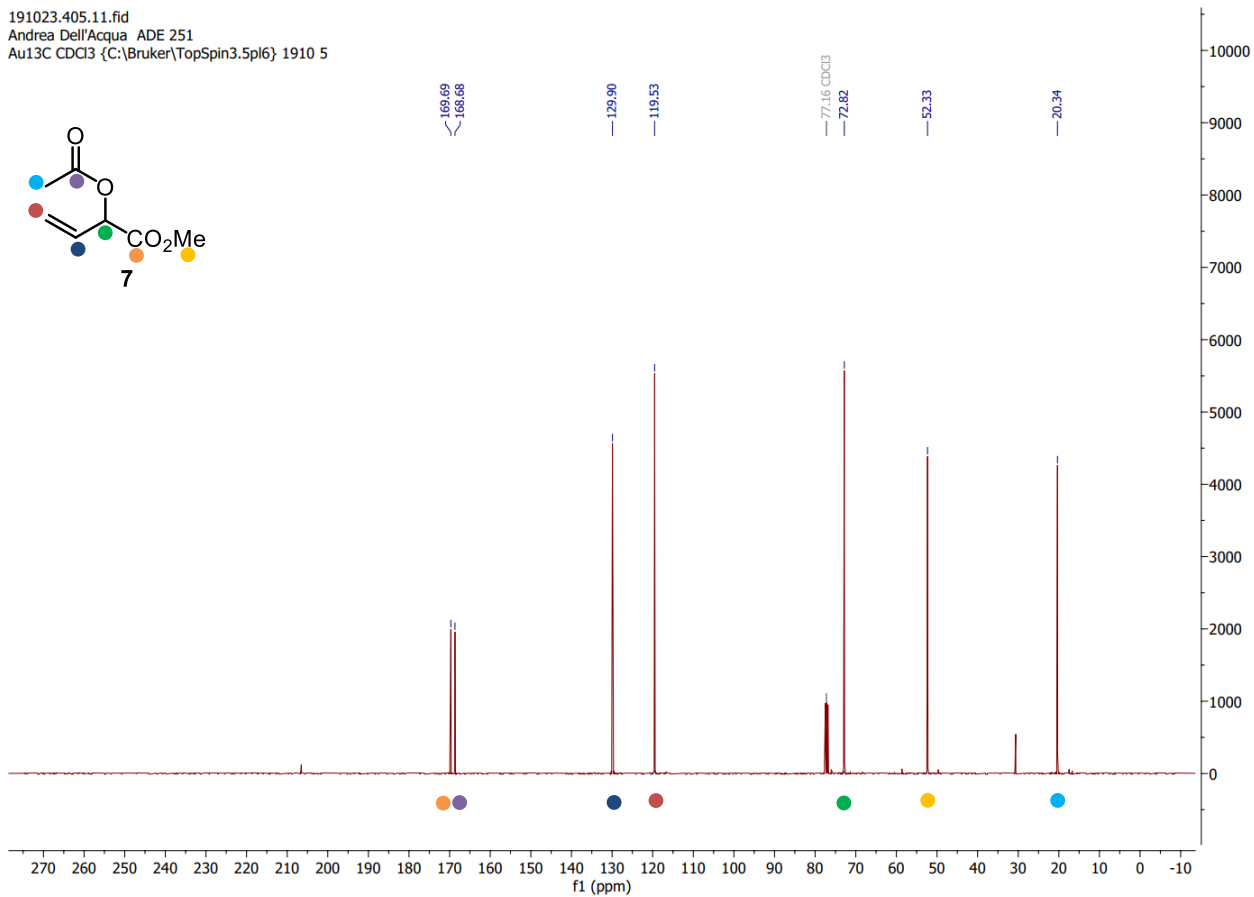
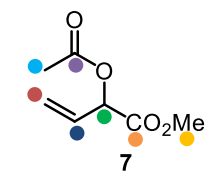
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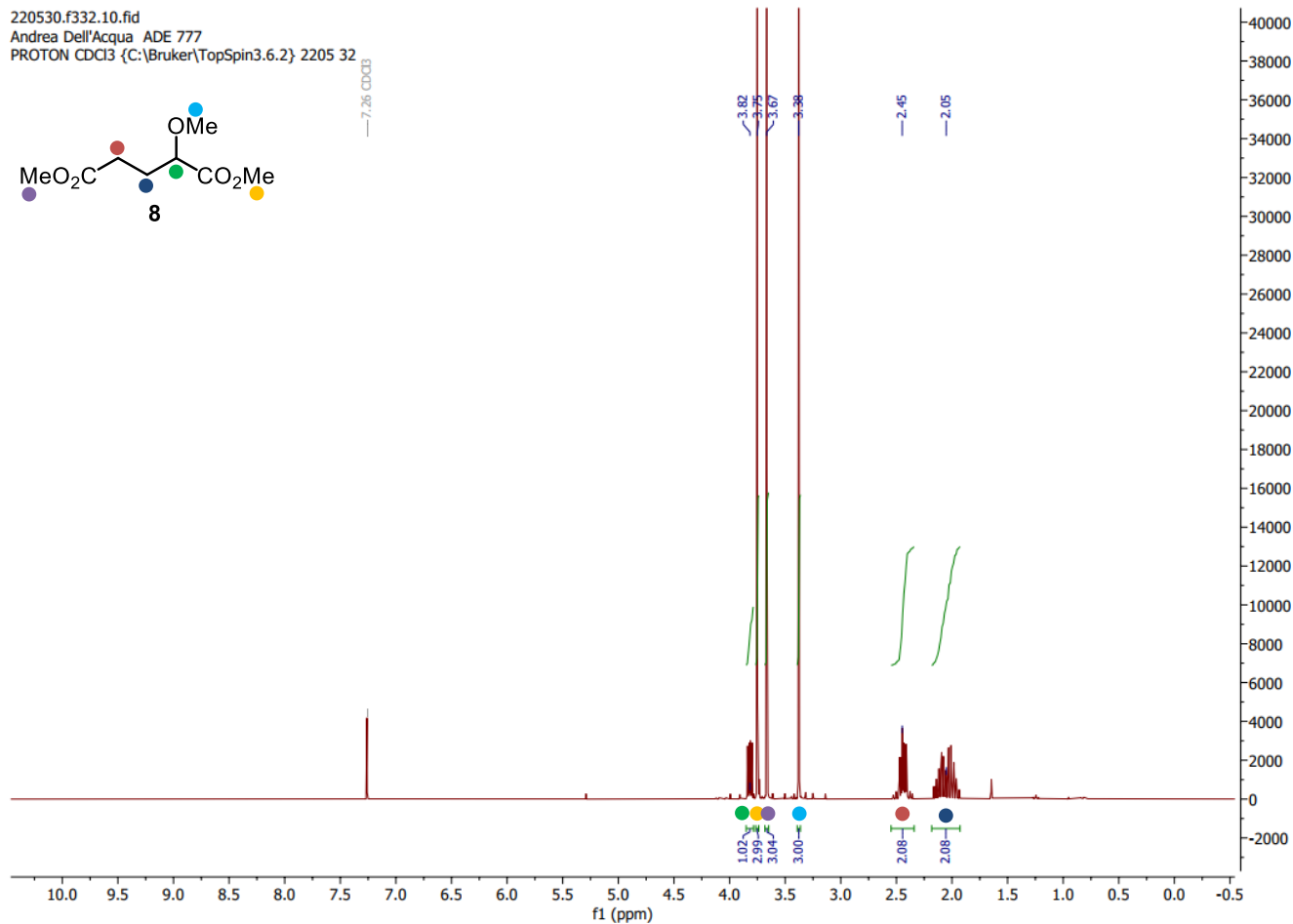
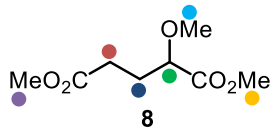
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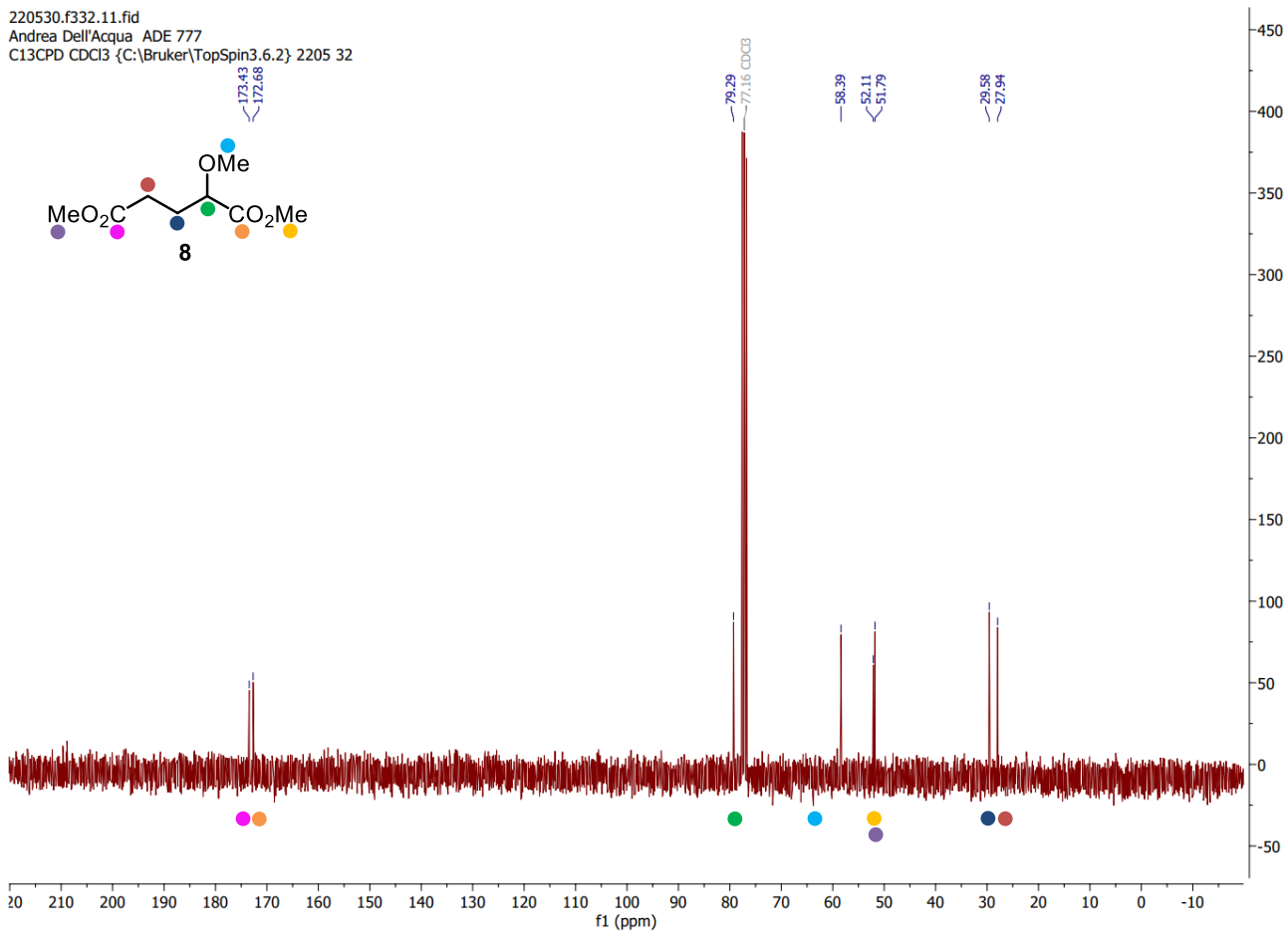
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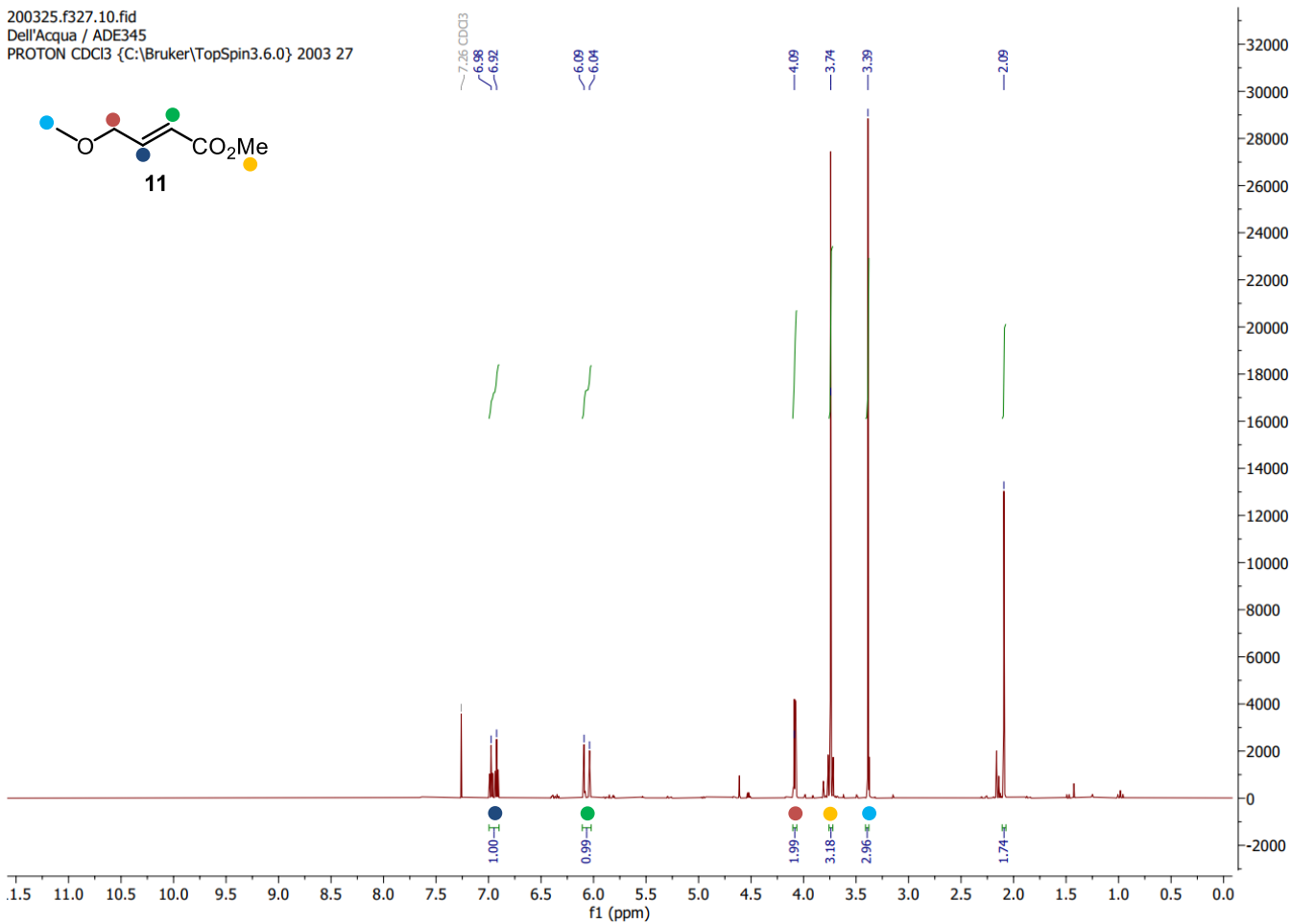
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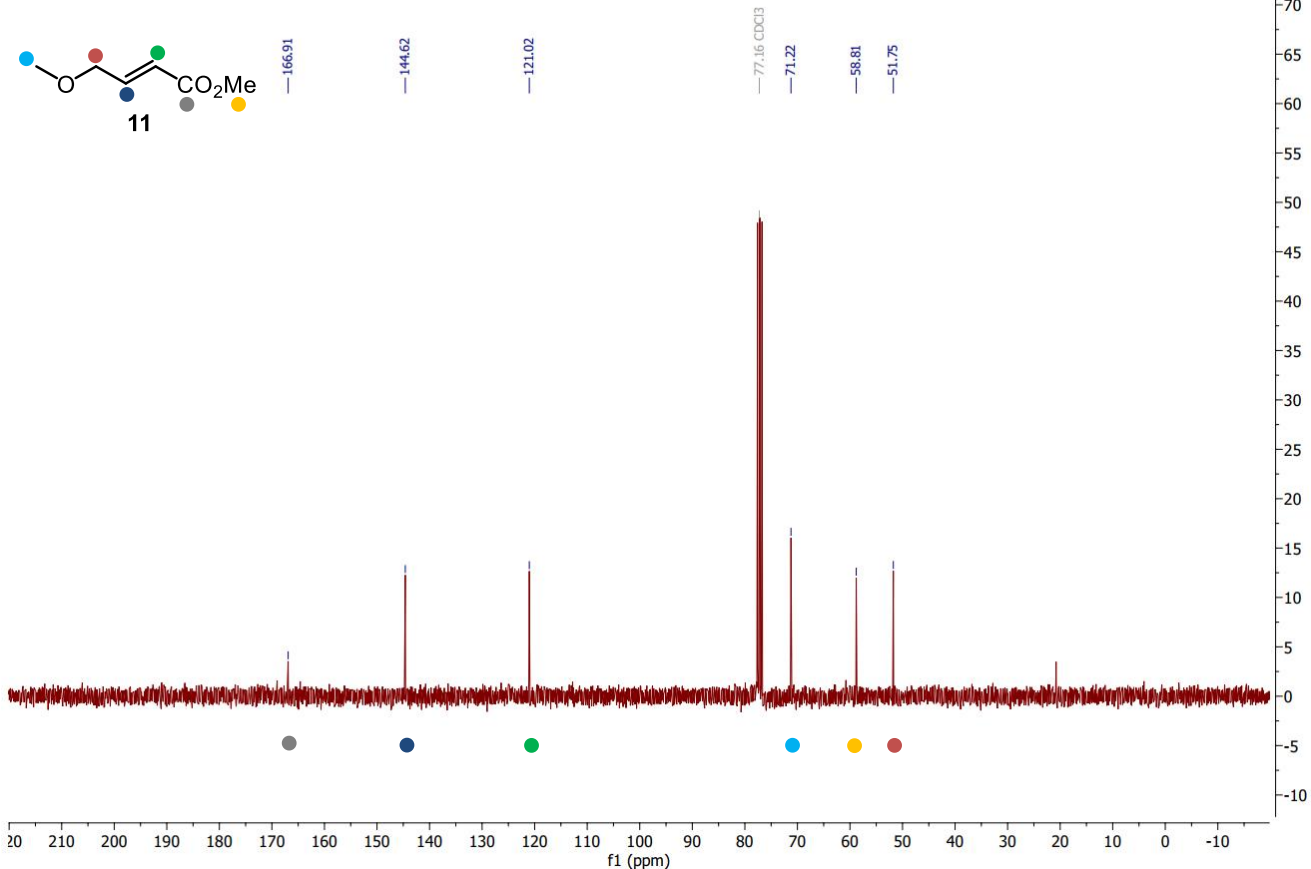
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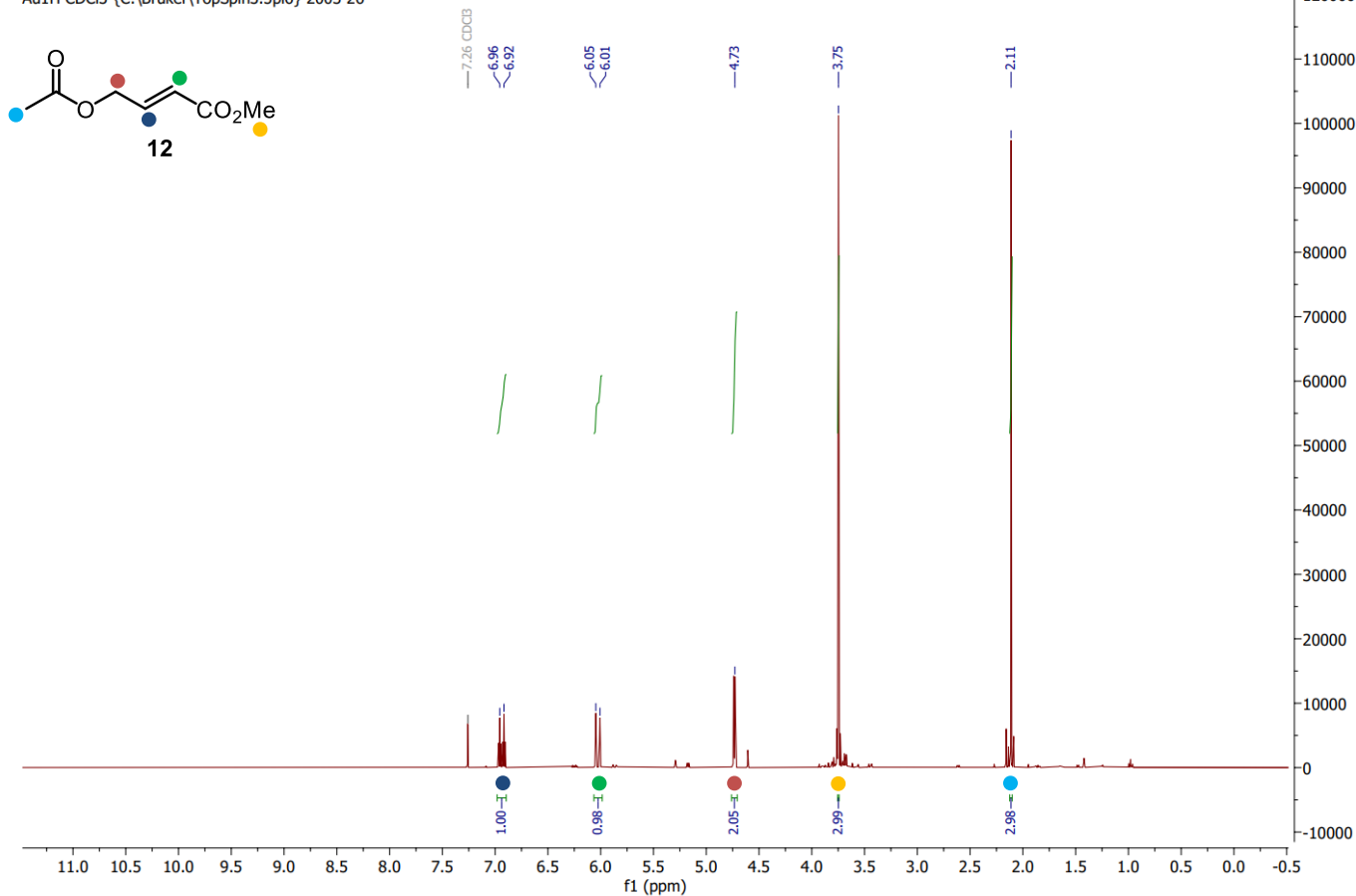
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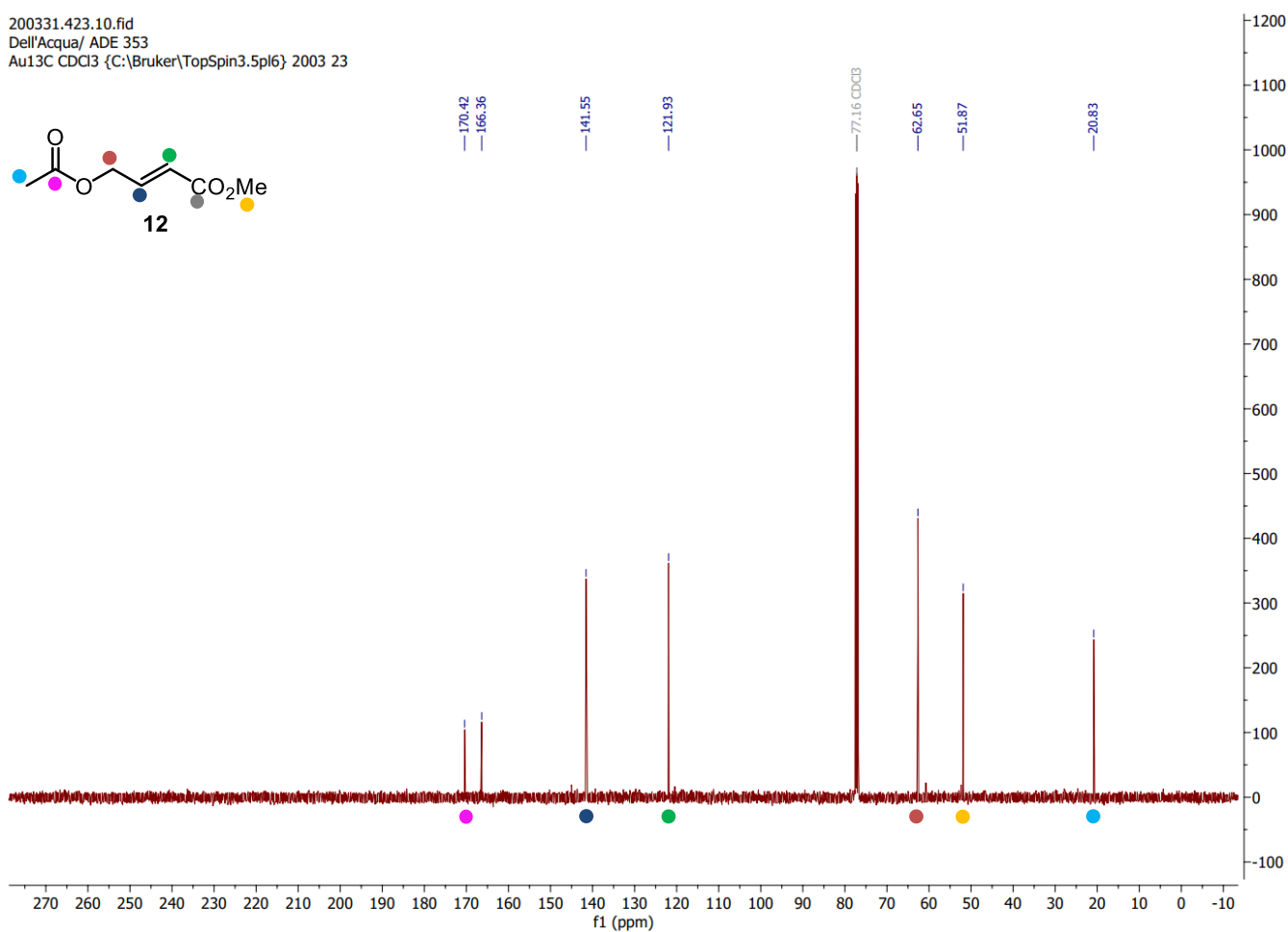


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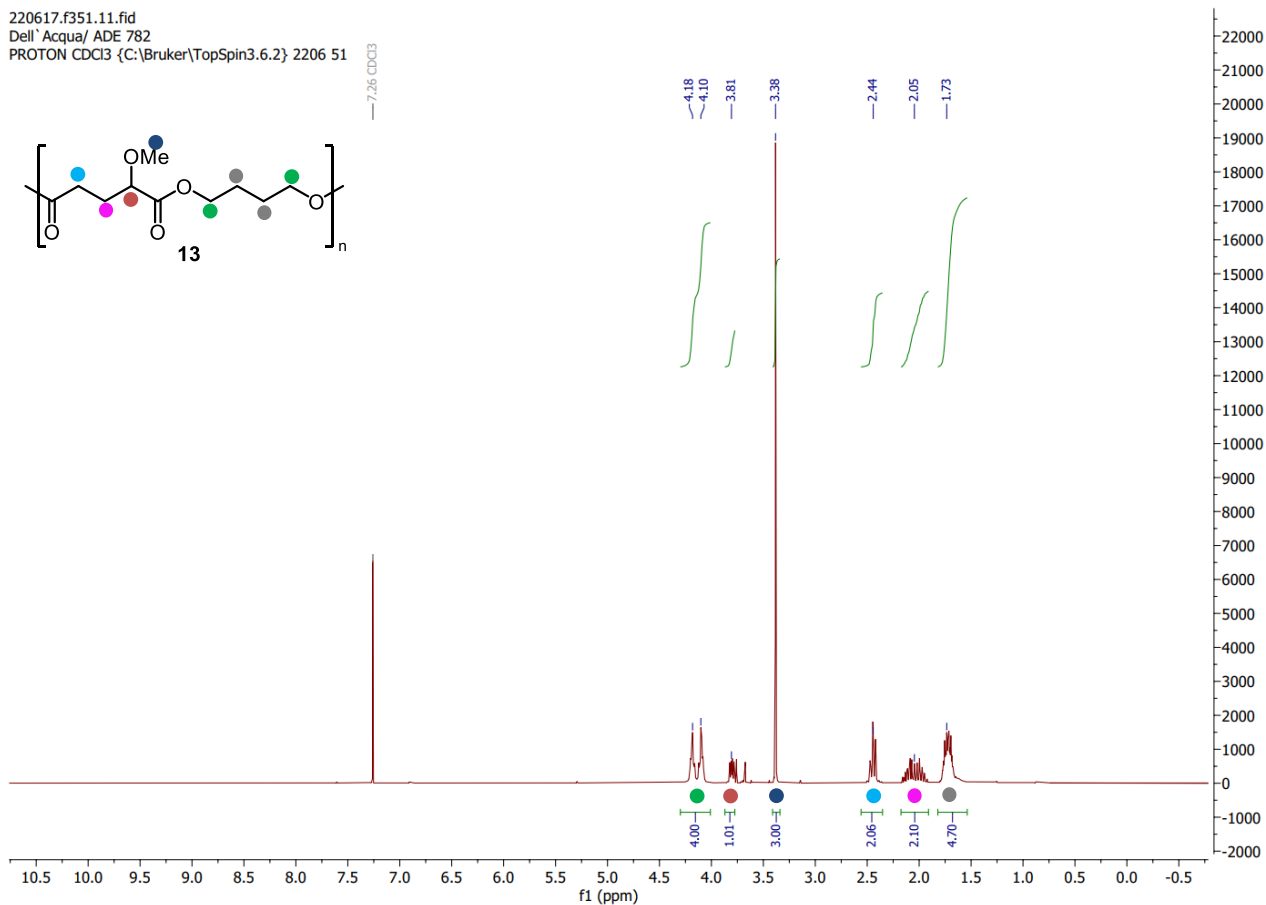
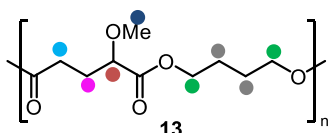




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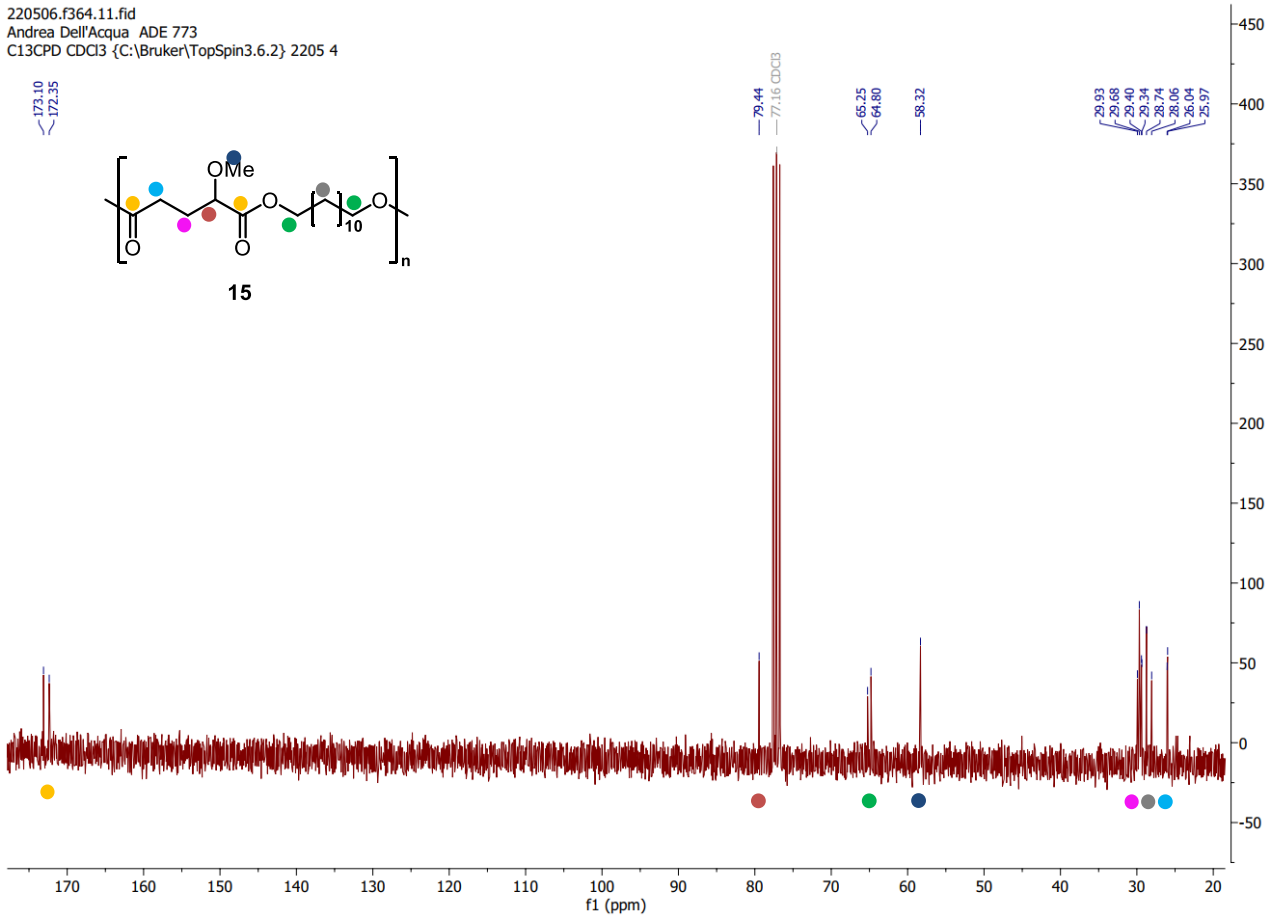
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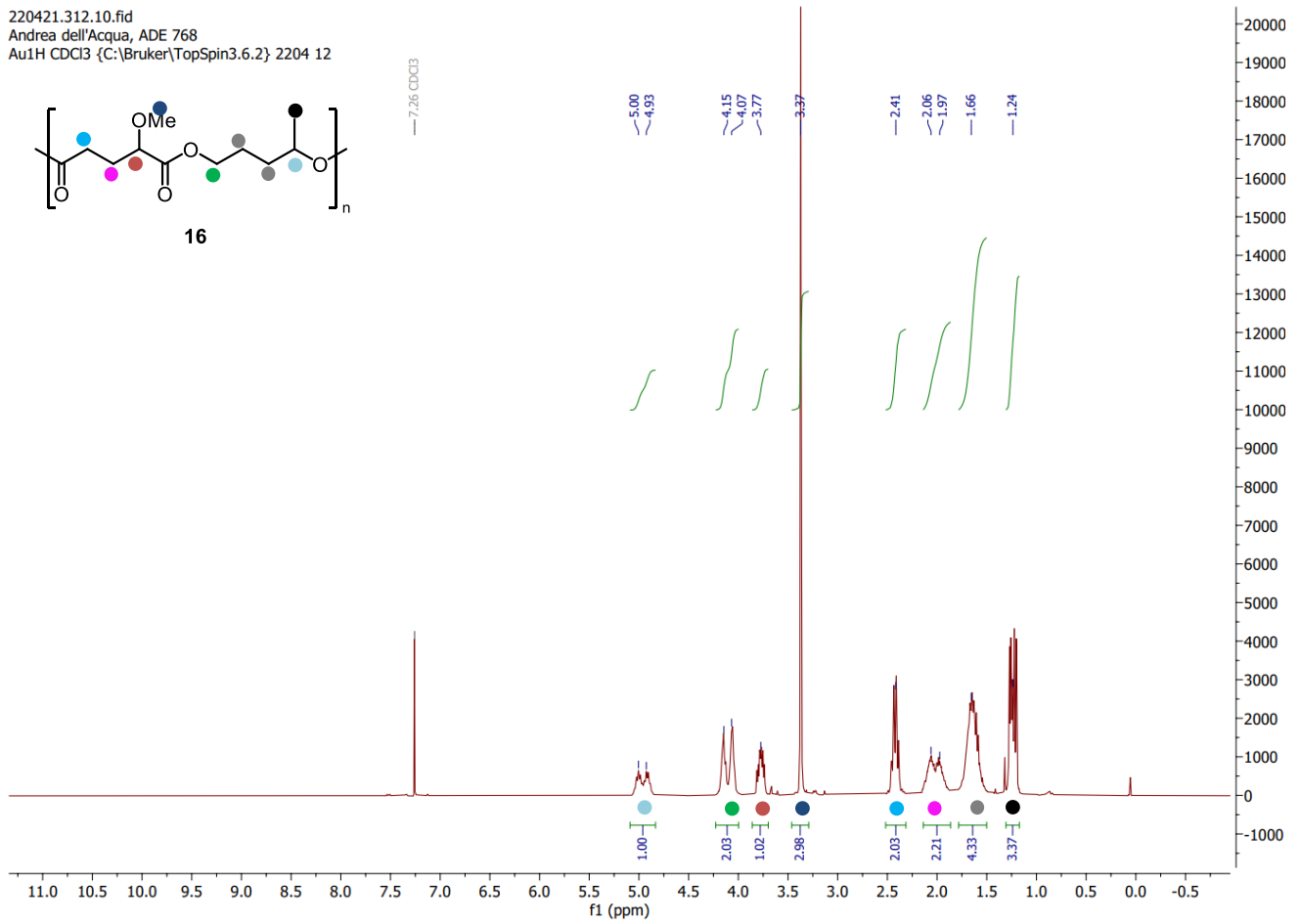




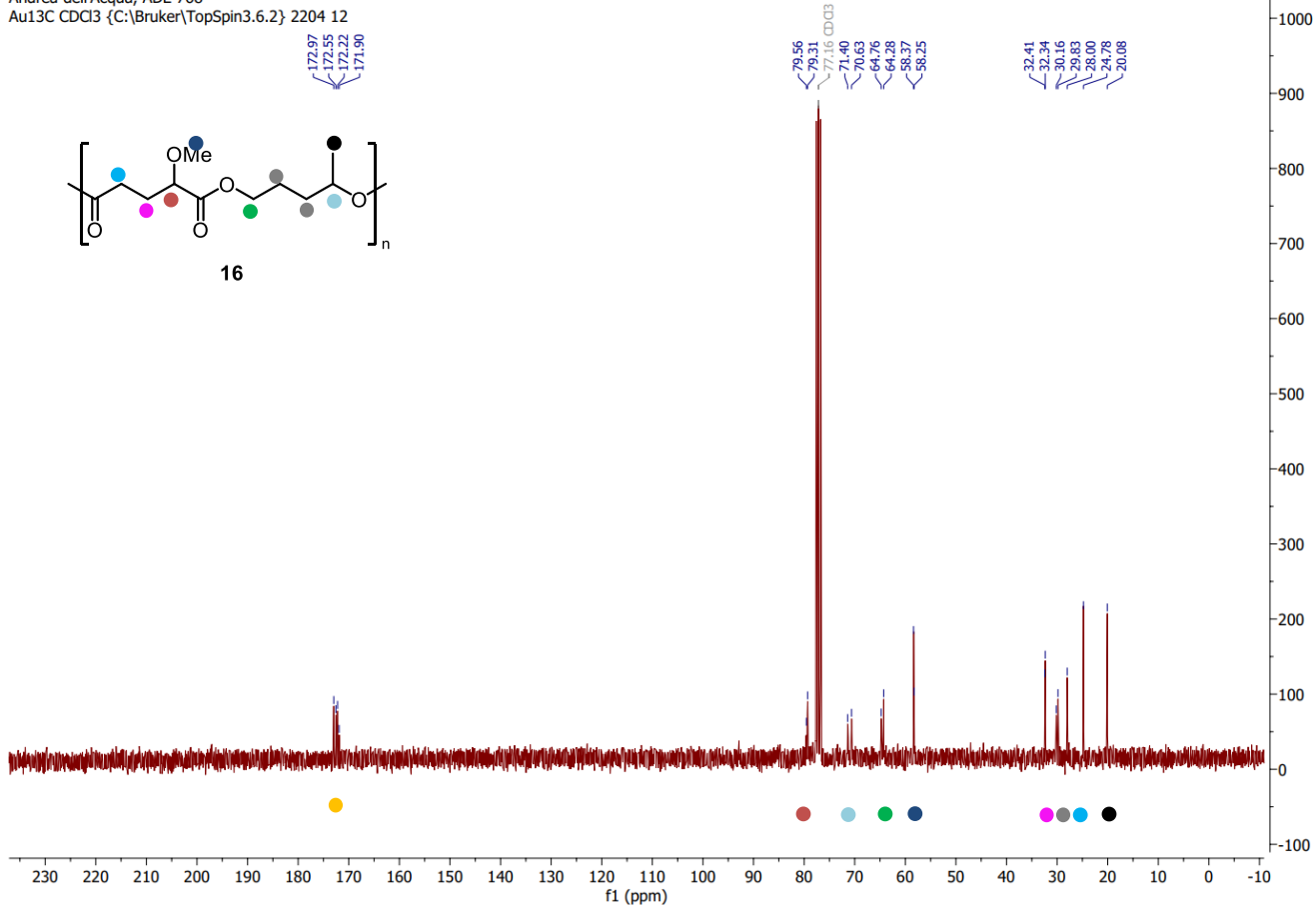
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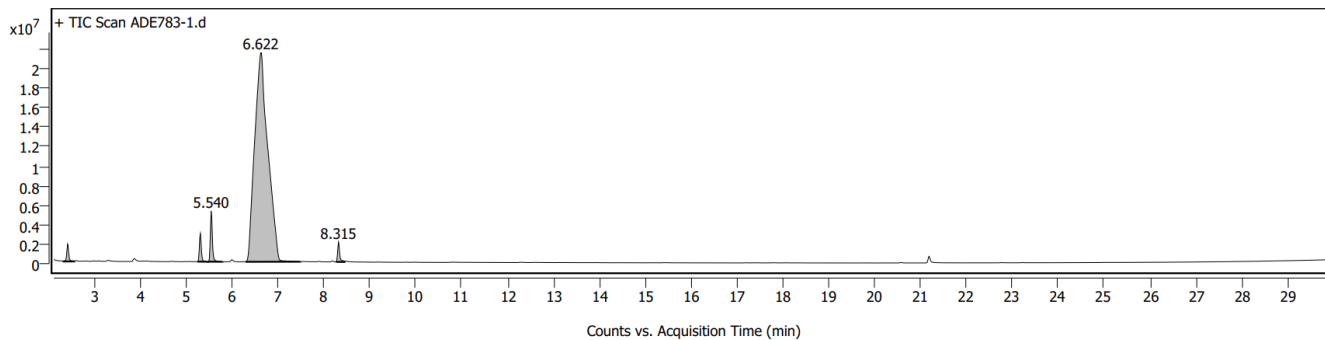
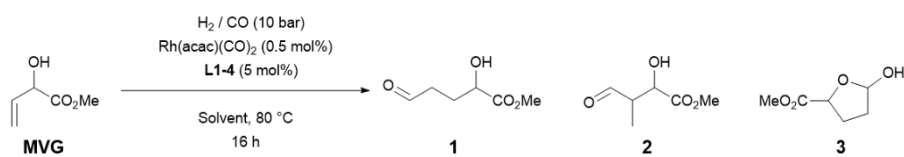
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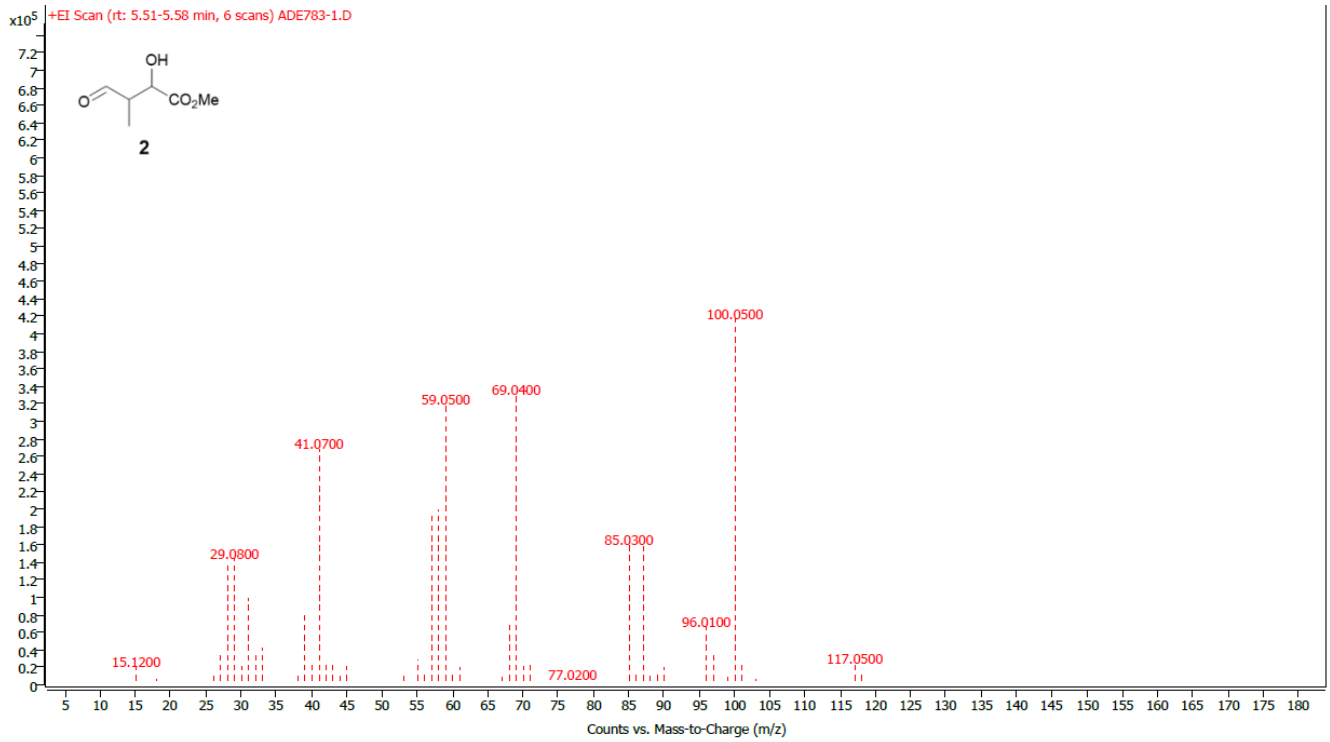
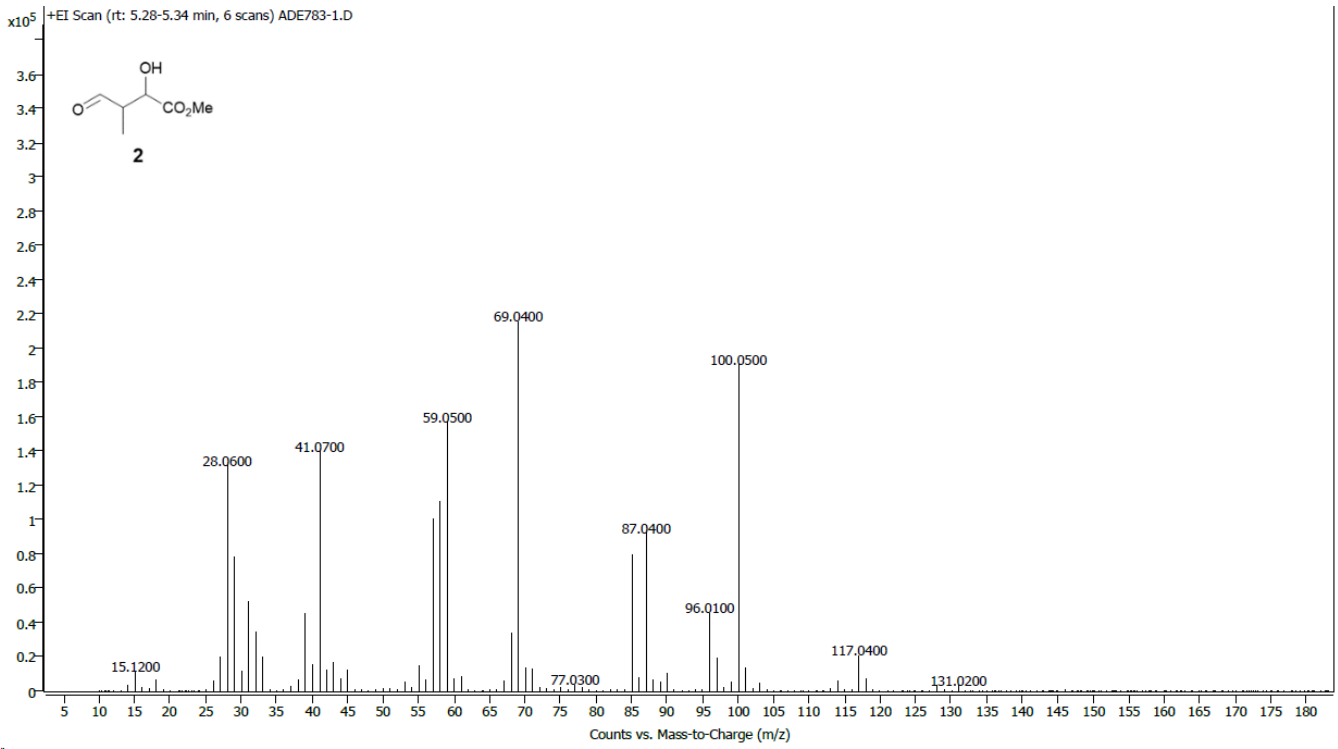


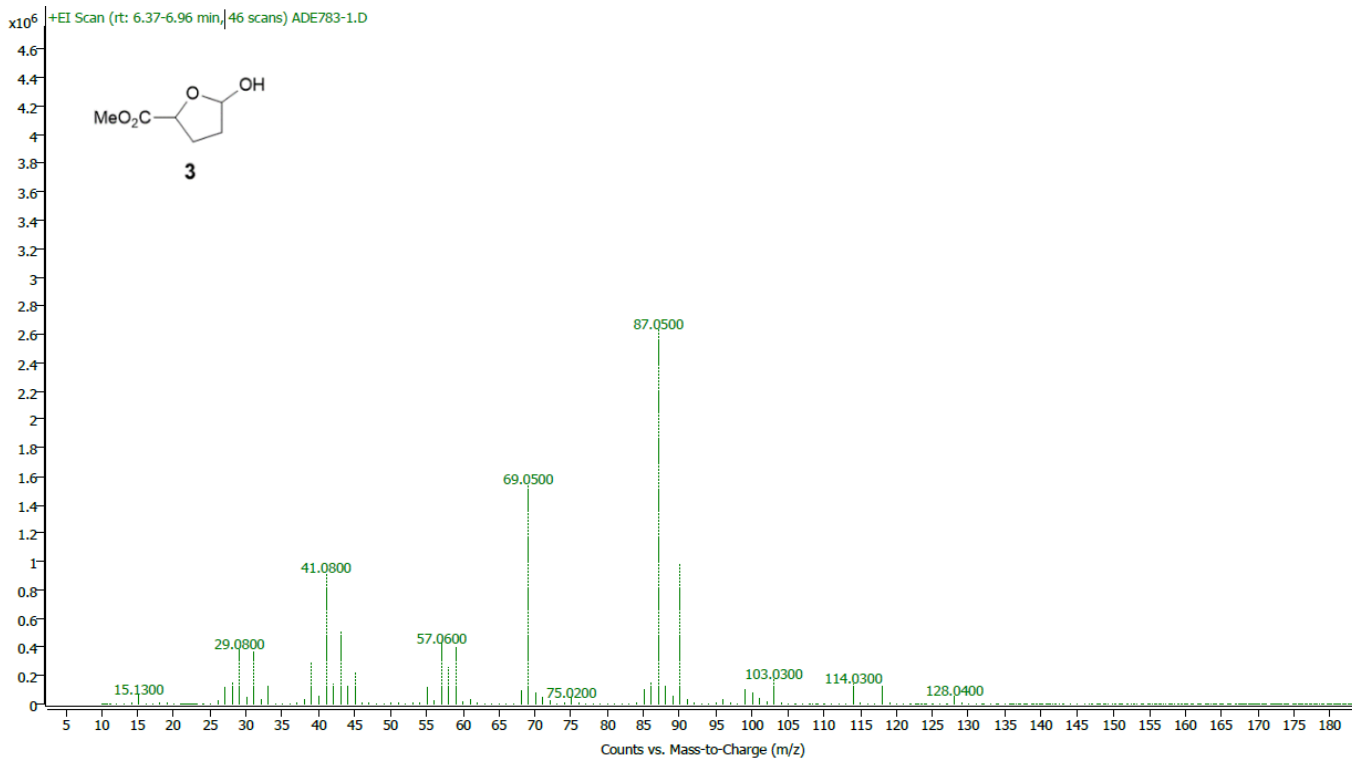
## GC-MS



Chromatogram Peaks

Peak	Start	RT	End	Height	Area	Area %	SNR
1	2.322	2.413	2.556	1757307	5428561	1.27	
2	5.245	5.306	5.462	2868752	8368390	1.95	
3	5.462	5.540	5.788	5207776	16126777	3.76	
4	6.293	6.622	7.482	21451469	428881013	100.00	
5	8.263	8.315	8.446	2018584	6272950	1.46	





## ESI-MS Chromatograms

### ESI-TOF Accurate Mass Report

File:22062015  
 Vial:1:F.4  
 Description:MeOH/0,1%HCOOH in H2O 90:10

Sample Name:ADE777  
 Date:20-Jun-2022

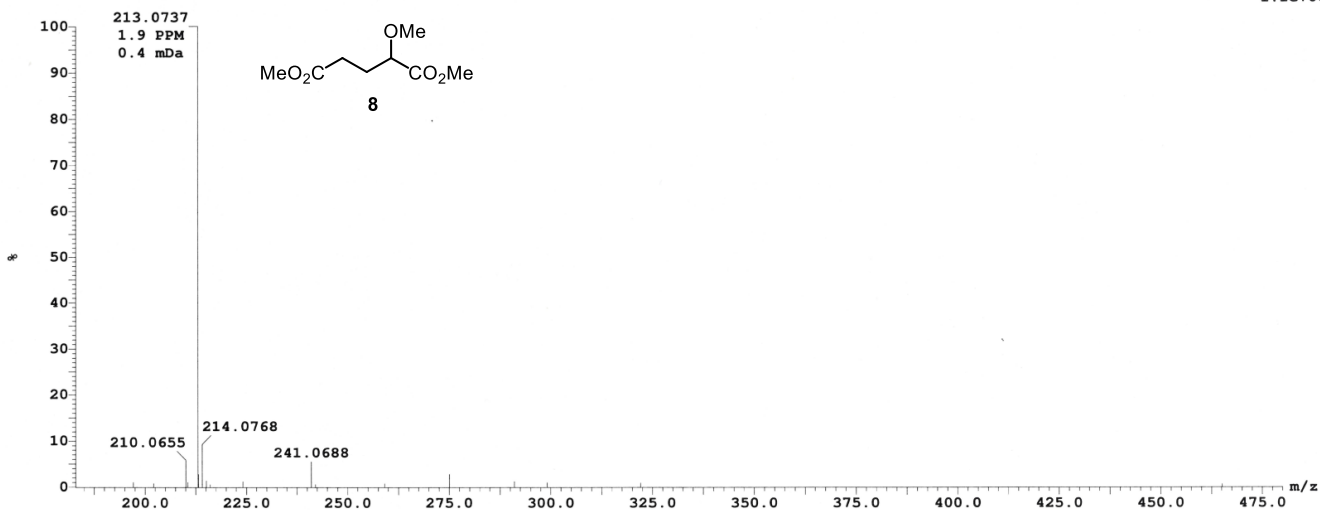
UserName:Dell'Acqua  
 Time:16:03:20

Page 2

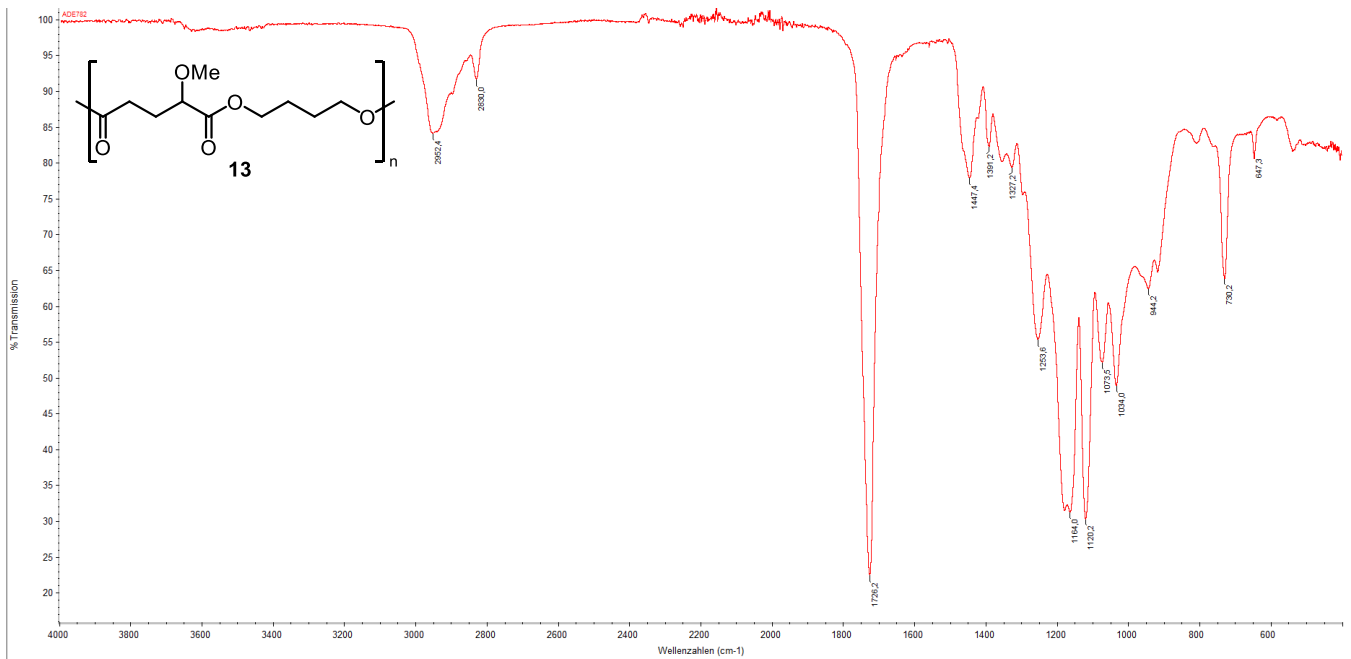
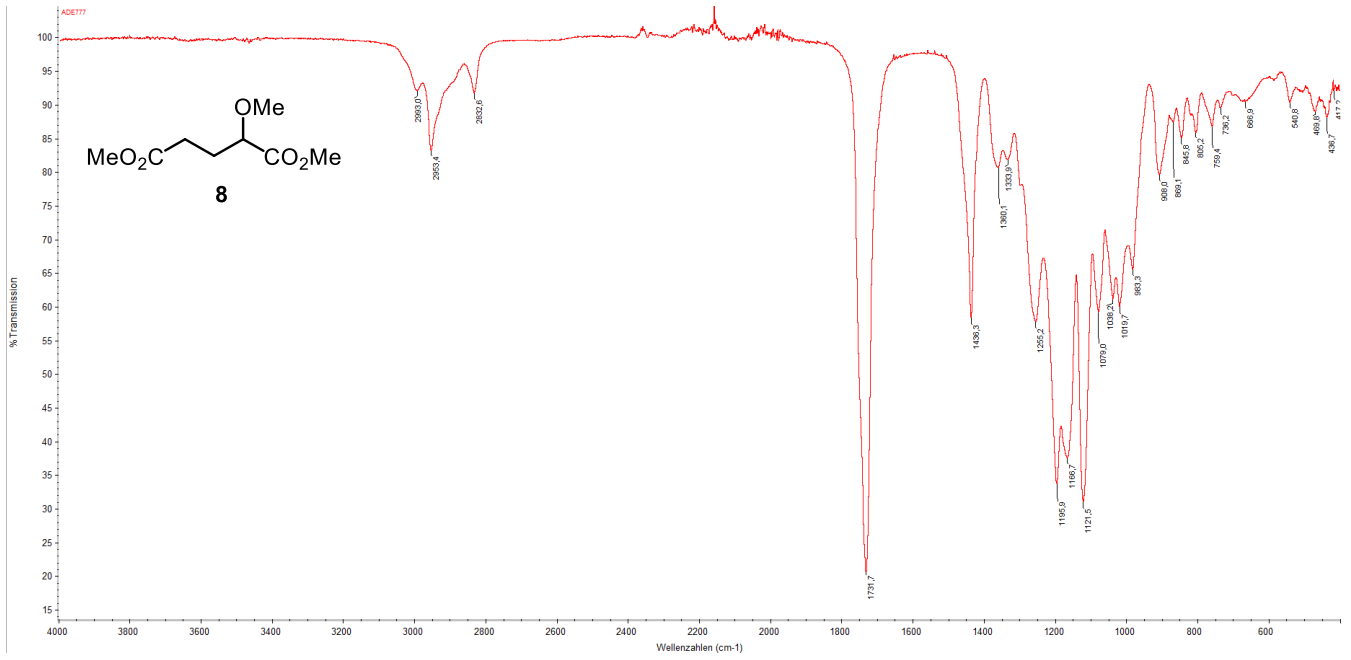
### Sample Report:

(Time: 0.31) Combine ((23:26+31)-112:117) - Dead time test passed

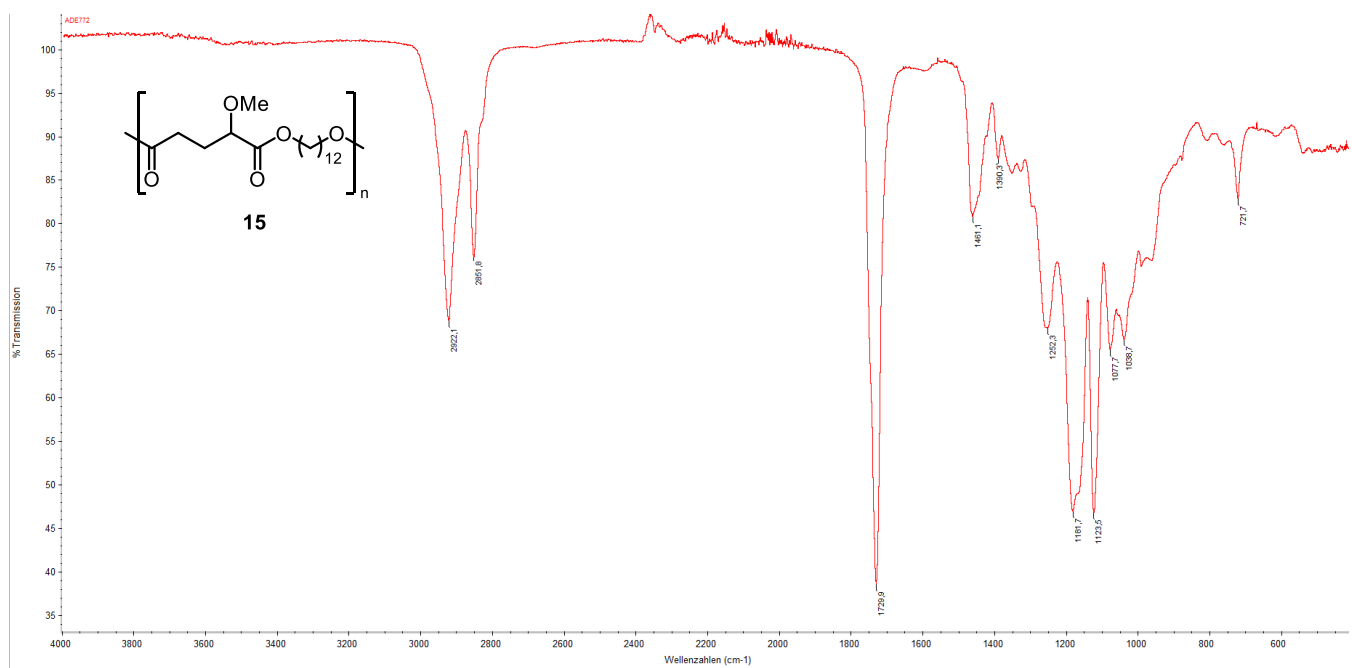
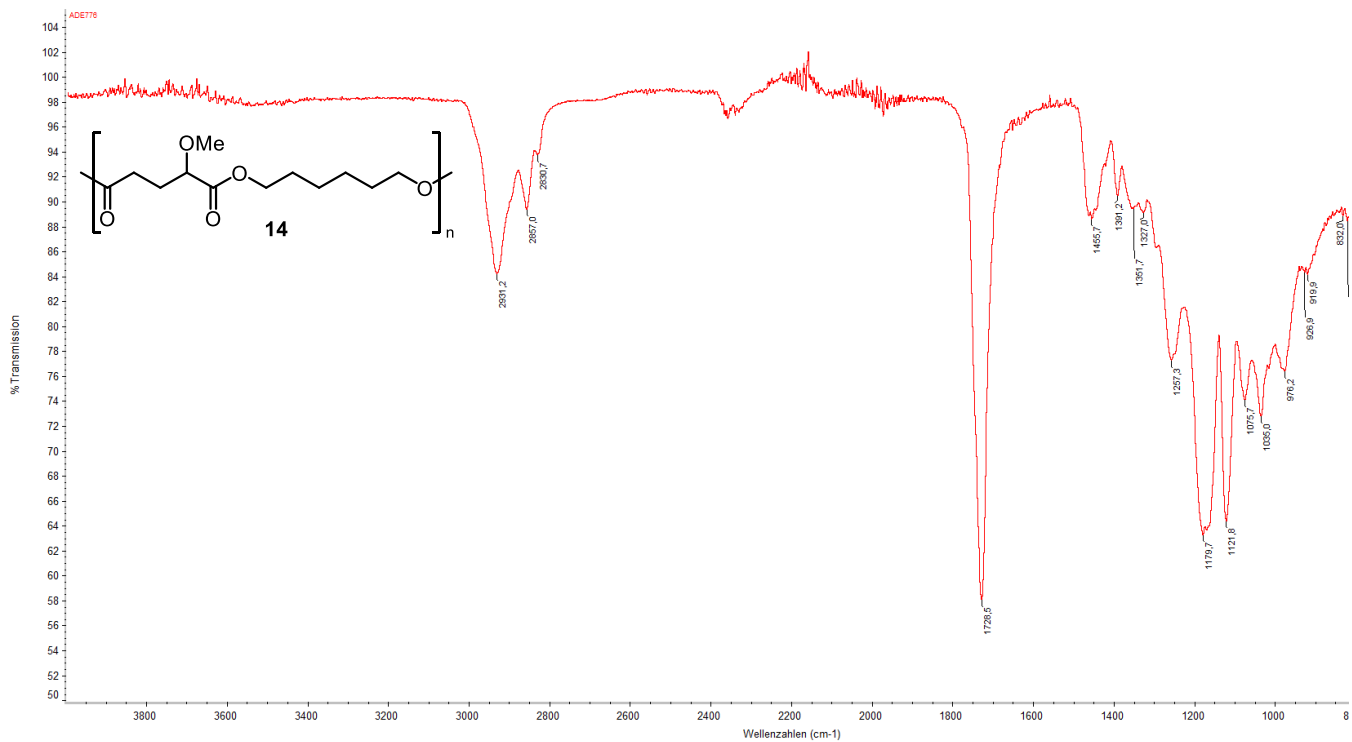
1:TOF MS ES+  
 1.1e+008

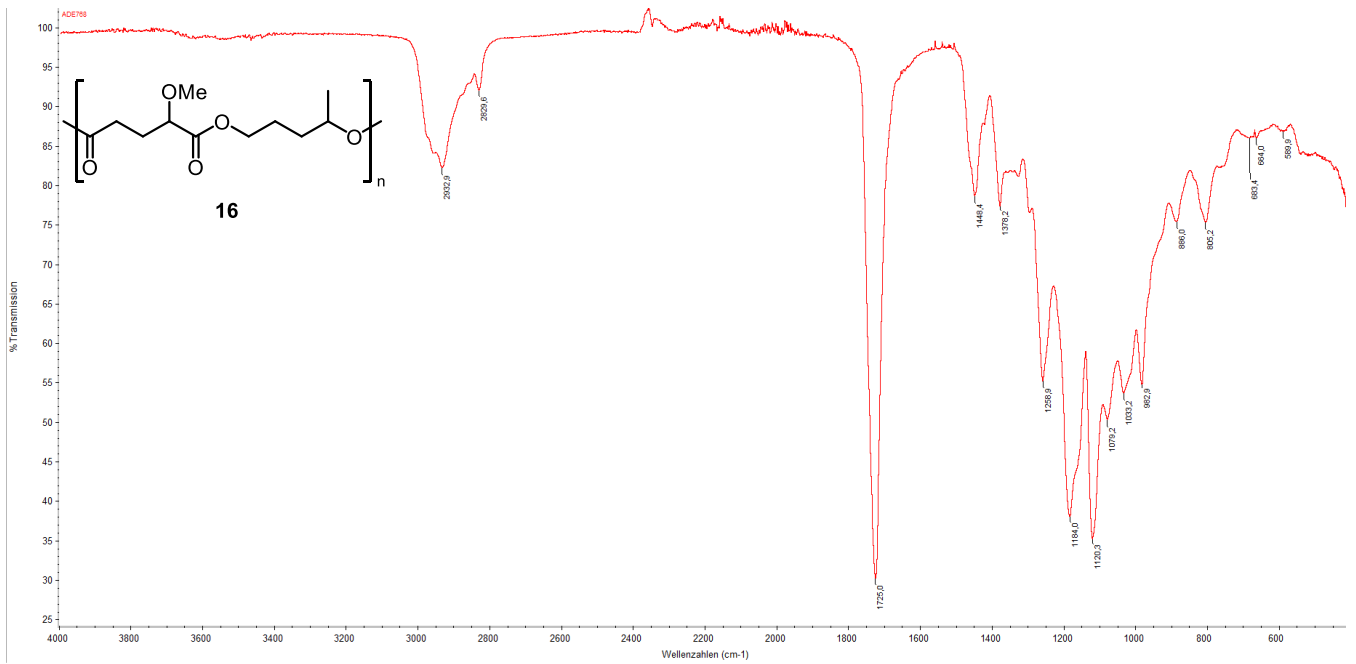


# ATR-IR

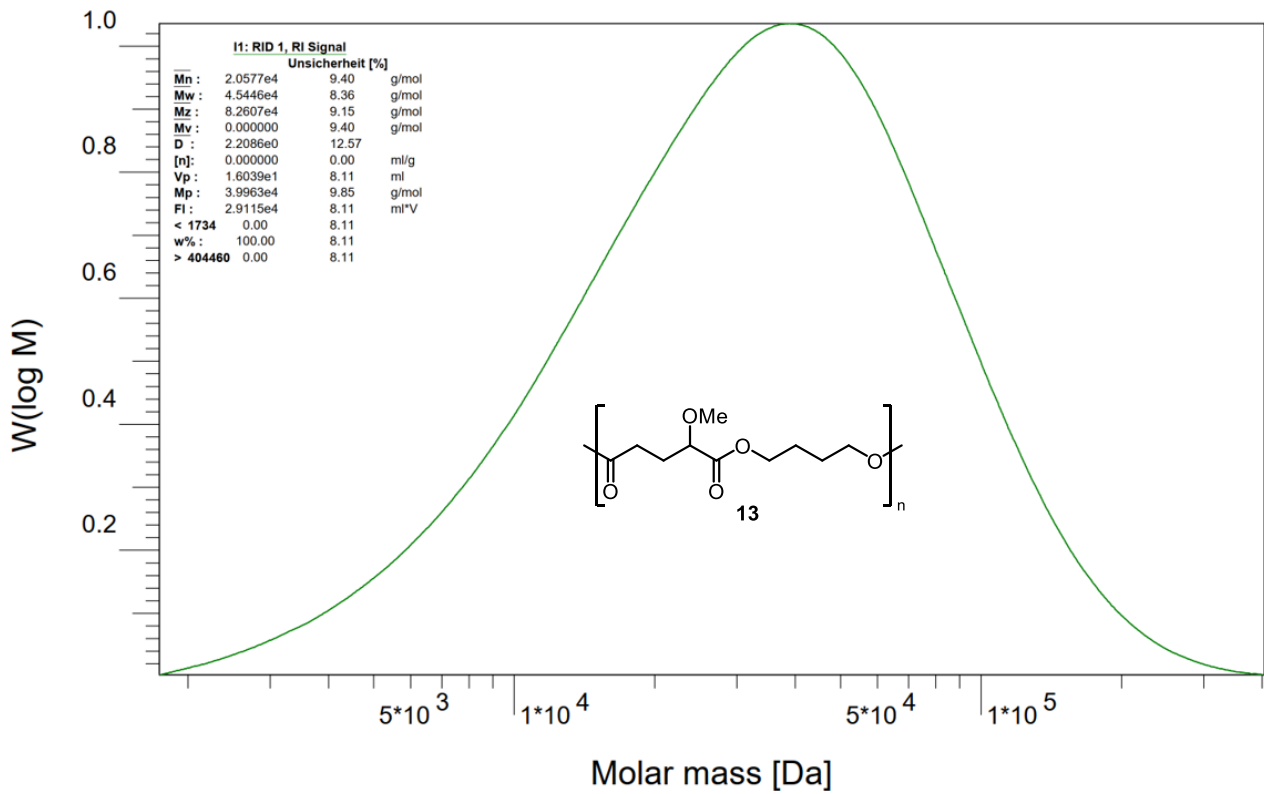




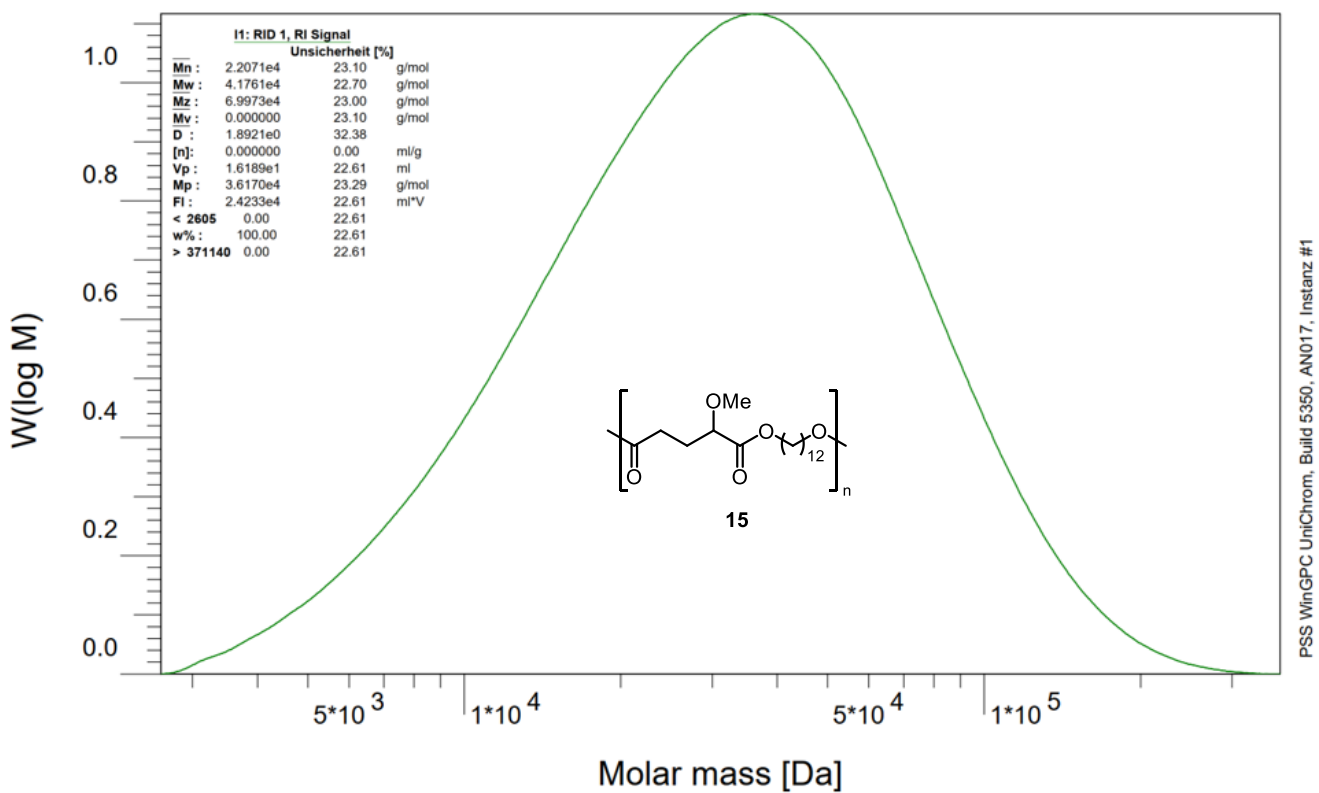
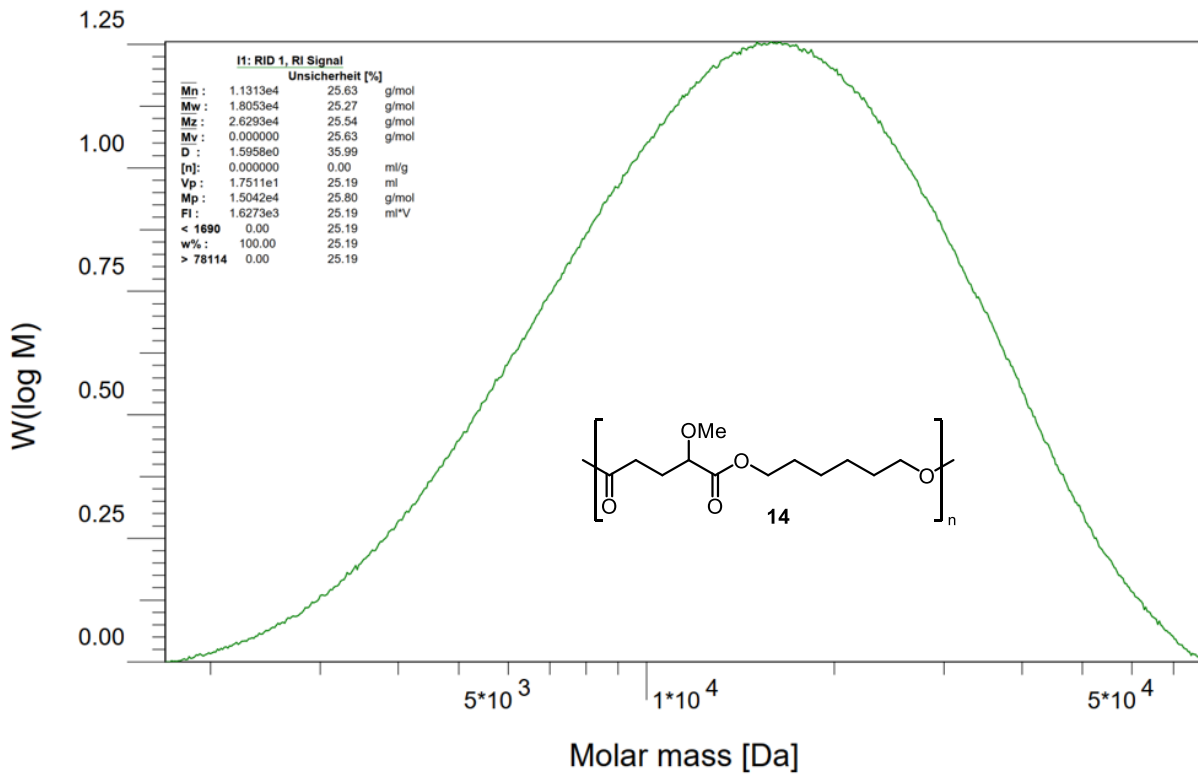


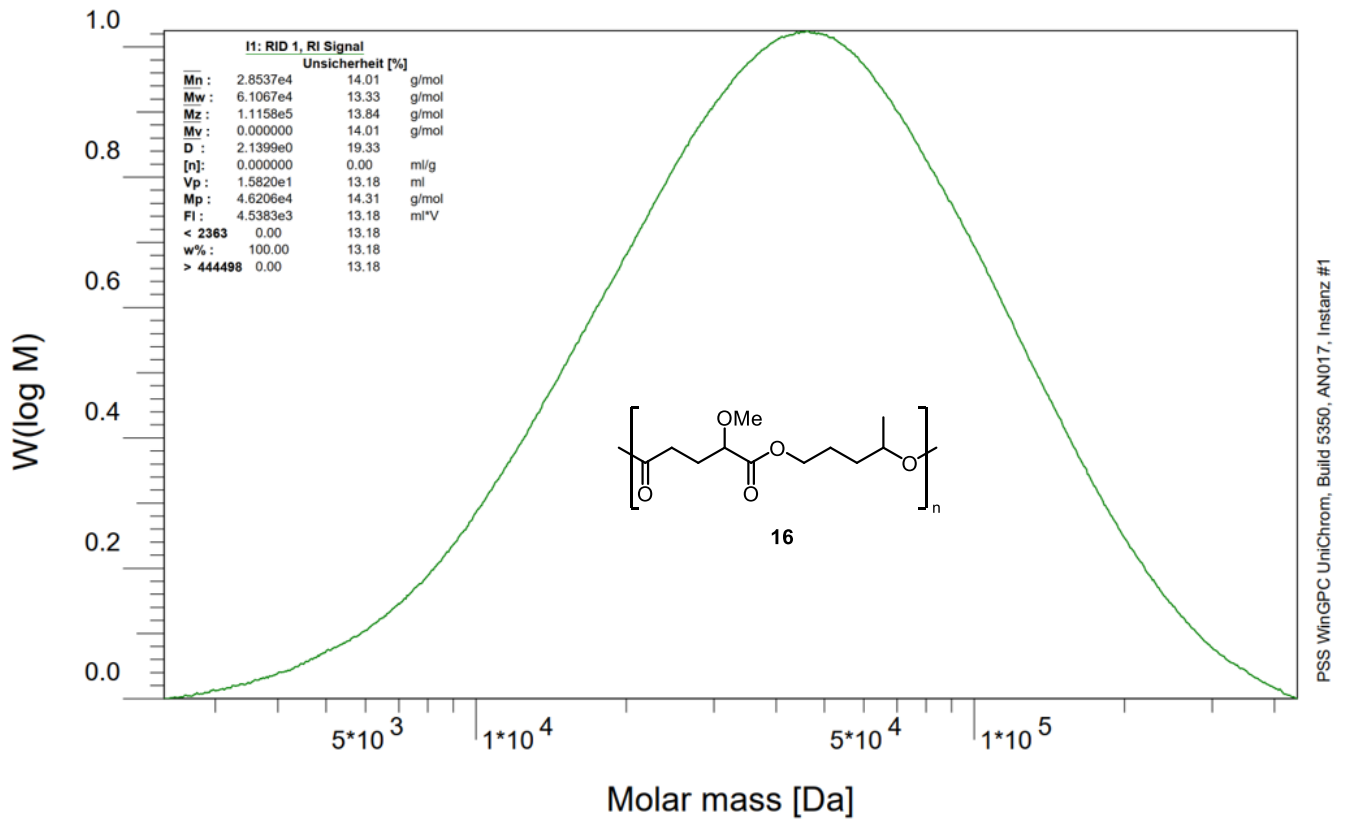


## GPC Chromatograms

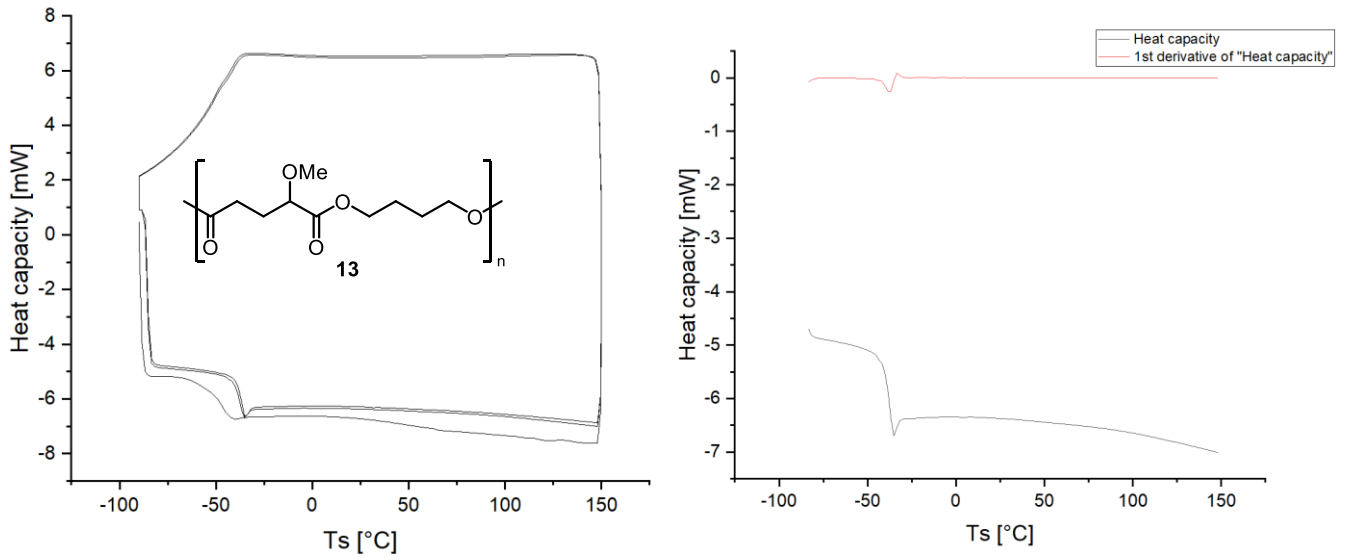


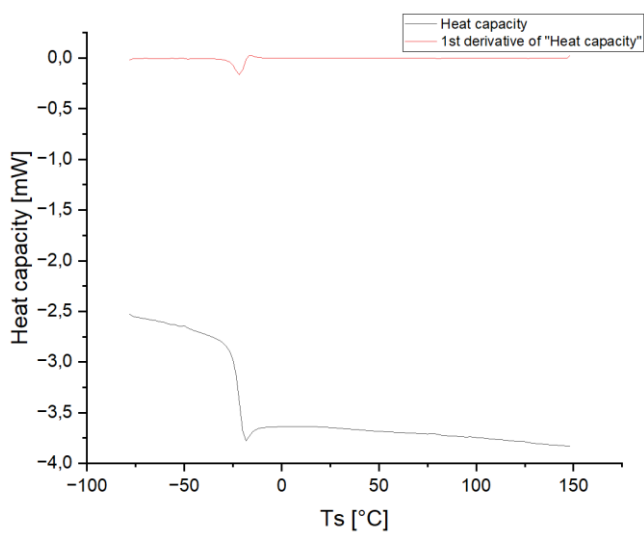
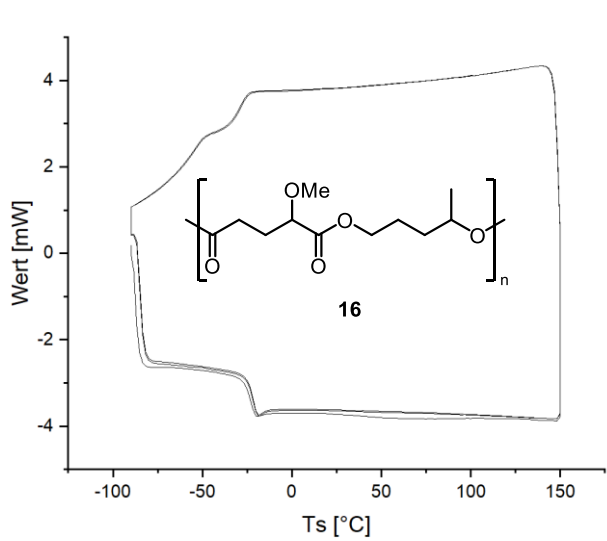
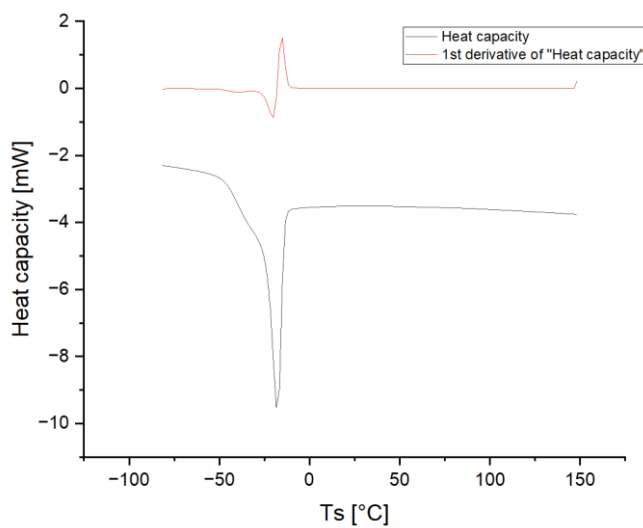
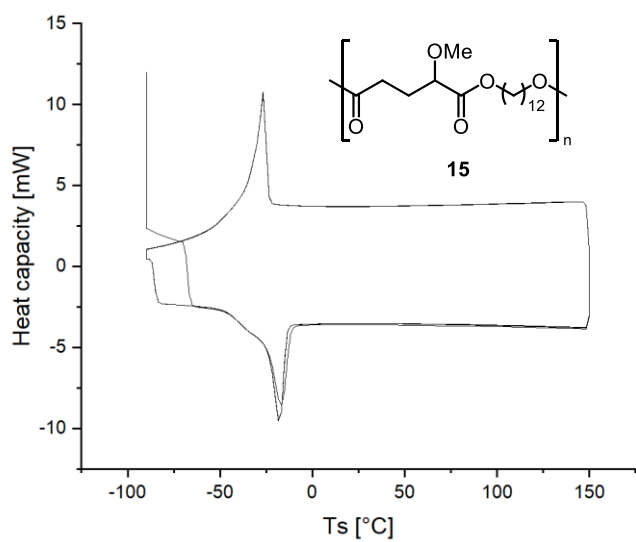
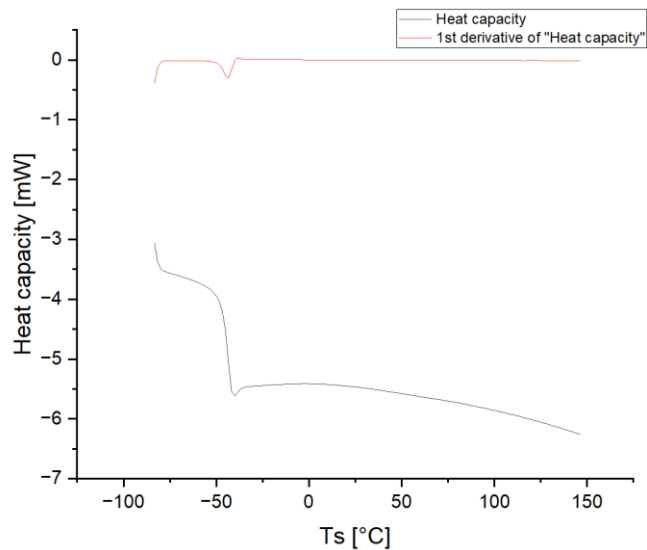
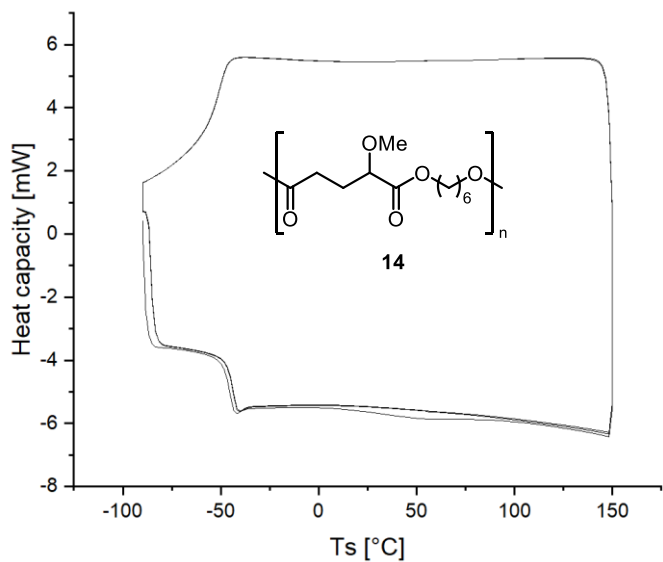
PSS WinGPC UniChrom, Build 5350, AN017, Instanz #1



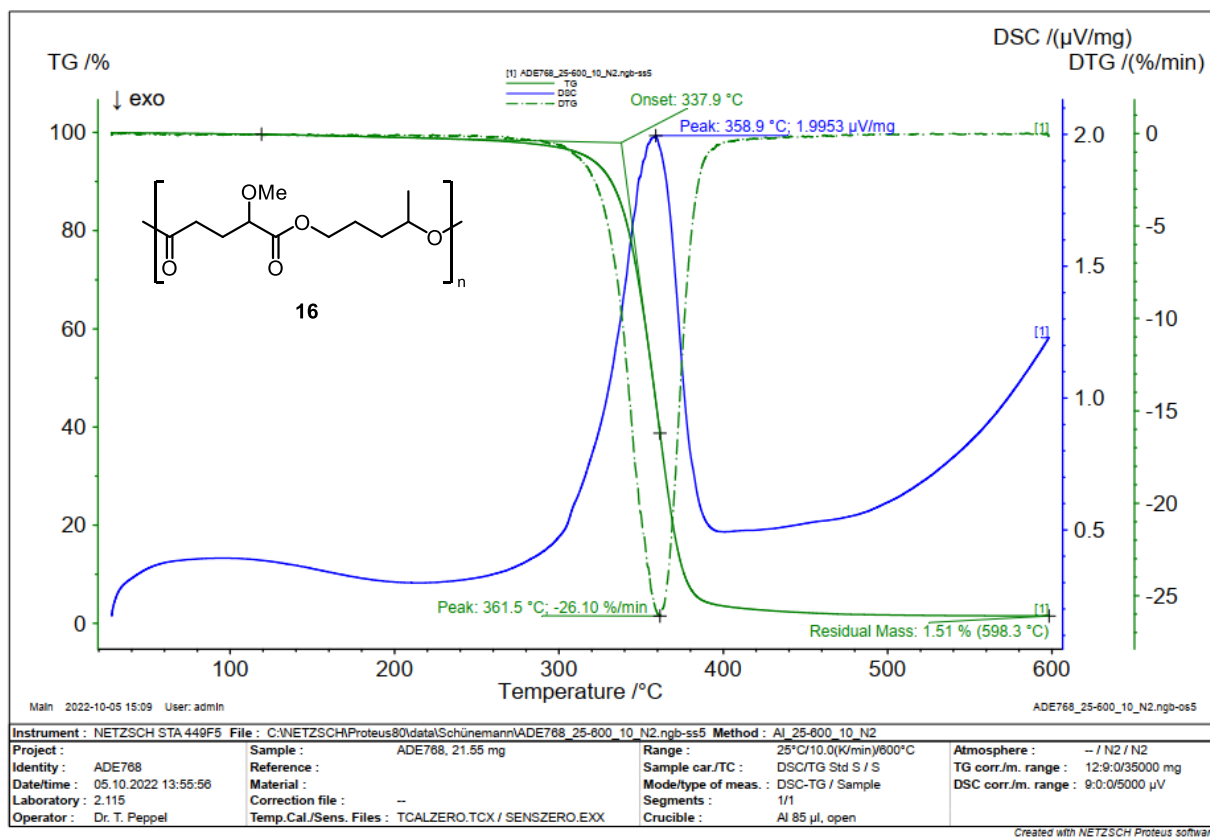
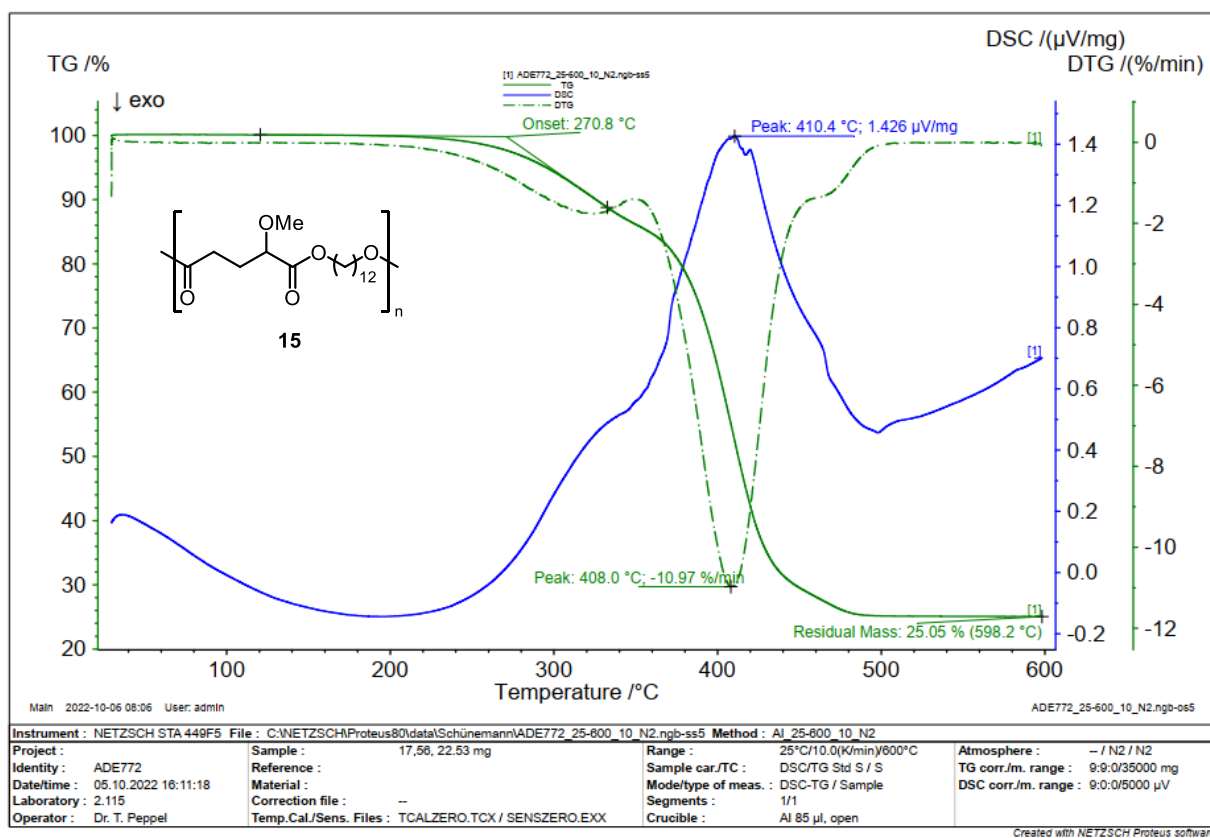


### DSC









## 6. References

1. S. Yamamoto, H. Itani, T. Tsuji and W. Nagata, *J. Am. Chem. Soc.*, 1983, **105**, 2908-2909.
2. J. Savard and P. Brassard, *Tetrahedron*, 1984, **40**, 3455-3464.
3. B. M. Jessen, J. M. Onozabal, C. M. Pedersen, A. Sølvhøj, E. Taarning and R. Madsen, *ChemistrySelect*, 2020, **5**, 2559-2563.

