SUPPORTING INFORMATION

Incorporation of renewable carbons via formamide reactivity for the production of novel biobased polymers

Bianca C. Rocha, Isabela L. A. Dourado, Marialy N. Sanabria, Noemi S. P. Kimura, Priscila H. Cordeiro, Luiz H. Catalani and Leandro H. Andrade*

Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo, Av. Professor Lineu Prestes, 748, SP 05508-900, São Paulo, Brazil.

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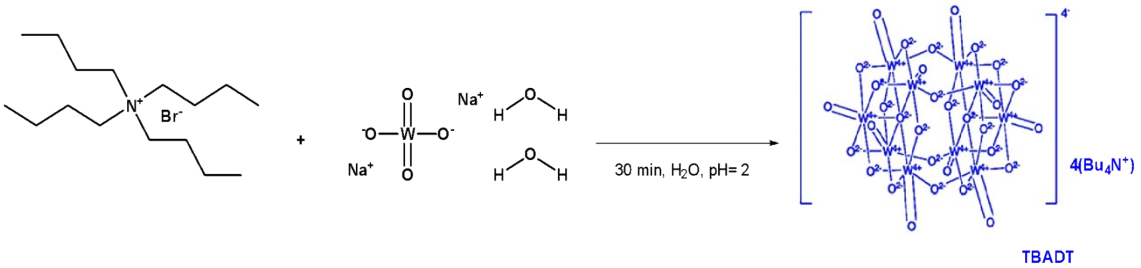
1. General information

The reagents were purchased from Sigma-Aldrich. Formamide (Cod = 295876, Sigma-Aldrich) was used without purification. Solvents were purified by standard procedures.[1] Reactions were monitored using GCM-QP2010SE (Shimadzu) with low-resolution electron impact (EI, 70 eV) equipped with a RTX-5MS capillary column. GC/MS conditions: injector 280 °C; detector: 110 °C; pressure: 100 kPa; column temperature: 3 min at 80 °C, 15 °C/min up to 280 °C, kept 8 min at 280 °C. Thin-layer chromatography (TLC) was conducted with Merck silica gel 60 F254 precoated plates and visualized with UV light, vanillin, or ninhydrin solutions. Flash column chromatography was performed on silica gel (200−300 mesh). ^{1}H NMR spectra were recorded on a Varian Inova-300 (300 MHz) or Bruker Avance III (500 MHz) spectrometer. The chemical shifts (δ) are reported in ppm using TMS as an internal standard. ^{13}C NMR spectra were recorded on a Varian-300 (75 MHz) or Bruker Avance III (125 MHz) spectrometer. The chemical shifts (δ) are reported in ppm relative to the solvent residual peak ($CDCl_3$ at δ 77.0). High-resolution mass spectra were recorded using MicroToF Bruker Daltonics, ESI-TOF techniques. Gel Permeation Chromatography (GPC) was conducted on a Malvern Instruments, Viscotel 305 TDA Chromatograph, triple detection (refraction, light scattering, and viscometer), loop of 200 μL, pump VE 2001. The mobile phase was THF at a flow rate of 1 mL/min. The system was set up with a pre-column and three Viscotek columns set up in series: T600 M (General Mixed Org, 300 × 8 mm, exclusion limit of 20,000,000 g/mol), I-MBMMW 3078 (300 × 8 mm, exclusion limit of 200,000 g/mol), and l-Oligo 3078 (300 × 8 mm, exclusion limit of 10,000 g/mol). The GPC system was calibrated with polystyrene standards (Aldrich/Waters, 820, 1200, 2460, 4300, 13200, 29300, 47500, 216000 and 1210000 g/mol). Toluene was employed to identify the exclusion limit. Matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analysis were performed on the MALDI Ultraflextreme Bruker Daltonics apparatus, TOF analyzer and TOF-MS data acquisition (reflector mode). The samples were prepared in solutions of 1 mg/mL concentration in THF, using 2,5-dihydrobenzoic acid (DHB) 10 mg/mL as matrix and NaCl (10 mg/mL) as cationizing salt. The UV-Vis analyses were carried out in a Varian UV-Vis-NIR Cary 60 equipment. The solutions were prepared in acetonitrile. FT-IR analyses were carried out in Agilent Cary 63 apparatus. The solutions were prepared in chloroform. The melting points were determined with a Gehaka PF 1500

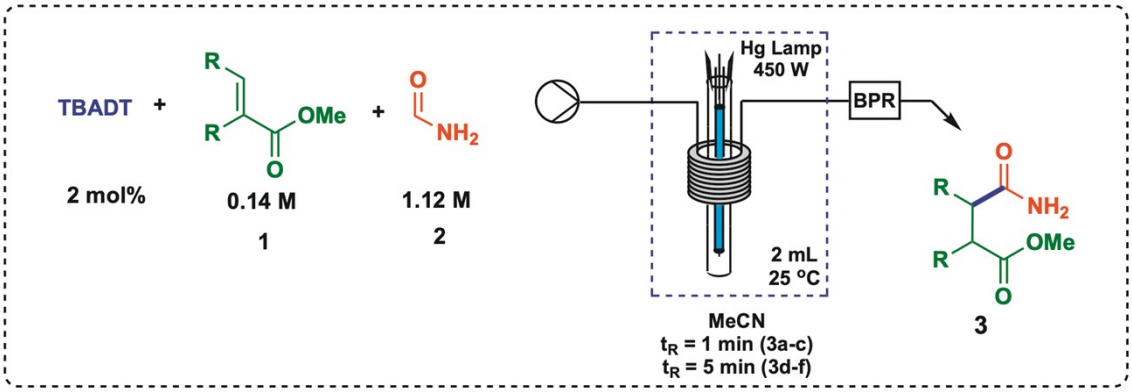
FARMA apparatus. Thermogravimetric (TGA) analysis were carried out in a TA Q500 instrument with nitrogen gas and a heating ramp of 10 °C/min. Differential scanning calorimetry (DSC) curves were obtained in a TA Q20 calorimeter, with the heating ramp of 10 °C/min in the temperature range of -20 °C to 200 °C.

2. Synthesis of tetrabutylammonium decatungstate (TBADT)[2]



Tetrabutylammonium bromide (2.4 g, 7.4 mmol) and sodium tungstate dihydrate (5.0 g, 15 mmol) were dissolved separately in deionized water (150 mL for each solution) at 90 °C. The pH of both solutions was adjusted to pH = 2 by adding concentrated hydrochloric acid (37%). Subsequently, they were mixed and kept under magnetic stirring at 90 °C for 30 min. The formation of a white suspension of TBADT was observed. After this reaction time, it was filtered through a Buchner funnel containing 80 g of silica gel. The solid was washed with 180 mL of deionized water and the aqueous phase was discharged, then the silica was washed with 200 mL of acetonitrile to solubilize the TBADT. Acetonitrile was removed under reduced pressure. The solid was recrystallized in a mixture of water:acetone (1:1) at room temperature overnight, filtered and dried. A white crystalline solid was obtained, and the final mass was 4.1 g (W Yield = 82%). UV-vis $\lambda_{máx}$ = 321 nm, ε_{321} = 1,50 x 10^4 dm^3 mol^{-1} cm^{-1}.

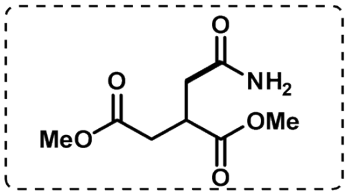
3. General procedure for photocatalytic carbamoylation of acrylate derivatives under continuous flow conditions



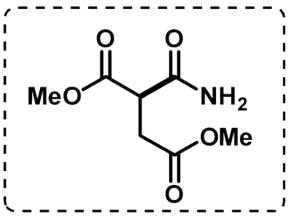
Flow system setup: A photoreactor consisting of a medium-pressure mercury vapour lamp (450 W), a high-purity perfluoroalkoxy alkane (HPFA) tube reactor (volume = 2 mL, 1/16" OD x 0.030" x 14.50 ft) from IDEX Health & Science wrapped around a medium-pressure Hg lamp (450 W) from Ace Glass INC. A syringe pump (Harvard Apparatus; PHD ULTRA™ Syringe Pump) was used to inject the chemicals. The reactions were maintained at 25°C with the aid of a refrigeration system.

Preparing chemical solutions: acrylate ester **1** (0.14 mol/L, 7.0 mmol) and formamide (Sigma-Aldrich, cod = 295876, 1.12 mol/L, 56.0 mmol) were dissolved in 20 mL of acetonitrile (Solution 1). TBADT (2 mol%; 465 mg) was dissolved in 25 mL of acetonitrile (Solution 2). Nitrogen gas was bubbled through the solutions for 40 min. Both solutions were mixed in a volumetric flask (50 mL), and deoxygenated acetonitrile was used to filled up to the mark (50 mL).

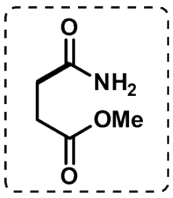
Continuous flow operation: A stainless-steel syringe (8 mL) was loaded with the solution and inject with a flow rate of 2 mL/min to produce monomers **3a-c** (residence time = 1 min; reactor volume = 2 mL) or a flow rate of 400 μL/min for **3d-f** (residence time = 5 min; reactor volume = 2 mL). The mercury-medium vapor lamp was turned on and let the system stabilize for 15 min. The reaction effluent was collected in a single flask for a 3-fold the desired residence time, and then it was discharged. After the reactor equilibration, the reaction effluent was collected in a separate flask for 25 to 120 min. Reaction solvent (acetonitrile) was removed under reduced pressure in a rotary evaporator. The crude material was purified by flash column chromatography using a mixture of chloroform/methanol (9:1) as eluent.



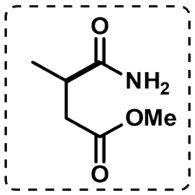
3a: Light-yellow solid, yield = 89%, 1.2 g; **mp** (°C) = 75.4-76.9; $\mathbf{R_f}$ = 0.46 (9:1 $CHCl_3$/MeOH). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 5.83 (s, 2H), 3.71 (s, 3H), 3.69 (s, 3H), 3.34-3.25 (m, 1H), 2.78-2.67 (m, 3H), 2.50 (dd, J_1= 15.0 Hz, J_2 = 6.0 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 174.1, 172.8, 172.0, 52.3, 51.9, 37.4, 36.2, 35.0 ppm. **MS-EI**: *m/z* (%) 186 (M+, 15) 59 (100). **HRMS (ESI-TOF)** calcd for $C_8H_{13}NO_5$ [M+ Na]+ 226.0691, found 226.0688.



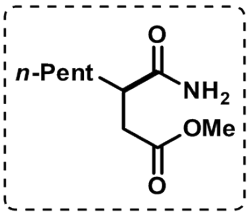
3b: White solid, yield = 81%, 0.9 g; **mp** (°C) = 96.4-97.5; $\mathbf{R_f}$ = 0.46 (9:1 $CHCl_3$/MeOH). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 6.63 (s, 1H), 6.02 (s, 1H), 3.78 (s, 3H), 3.75 (d, *J* = 6.0 Hz, 1H), 3.70 (s, 3H), 3.00 (d, *J* = 6.0 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 172.0, 169.9, 168.9, 52.9, 52.0, 47.6, 32.3 ppm. **MS-EI**: *m/z* (%) 172 (M+, 0) 55 (100). **HRMS (ESI-TOF)** calcd for $C_7H_{11}NO_5$ [M+ Na]+ 212.0535, found 212.0532.



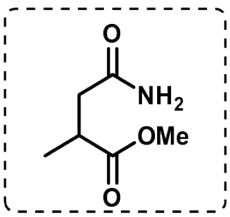
3c: White solid, yield = 84%, 0.7 g; **mp** (°C) = 78.1-78.6; $\mathbf{R_f}$ = 0.43 (9:1 $CHCl_3$/MeOH). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 5.84 (s, 2H), 3.70 (s, 3H), 2.68 (t, *J* = 6.0 Hz, 2H), 2.54 (t, *J* = 6.0 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 173.9, 173.4, 51.8, 30.1, 29.0 ppm. **MS-EI**: *m/z* (%) 131 (M+, 0) 88 (100).



3d: Light-orange solid, yield = 98%, 0.8 g; **mp** (°C) = 68.8-69.4; $\mathbf{R_f}$ = 0.43 (9:1 $CHCl_3$/MeOH). **^{1}H NMR H** ($CDCl_3$, 300 MHz) δ 5.83 (s, 1H), 5.63 (s, 1H), 3.69 (s, 3H), 2.88-2.68 (m, 1H), 2.48-2.35 (m, 1H), 1.22 (d, J = 6.0 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 177.5, 173.0, 51.8, 37.7, 36.3, 17.8 ppm. **MS-EI**: *m/z* (%) 182 (M+, 10) 87 (100).



3e: White solid, yield = 64%, 0.7 g; **mp** (°C) = 49.6-50.1; $\mathbf{R_f}$ = 0.43 (9:1 $CHCl_3$/MeOH). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 5.82 (s, 1H), 5.66 (s, 1H), 3.68 (s, 3H), 2.81-2.54 (m, 2H), 2.42 (dd, J_1 = 15.0, J_2 = 3.0 Hz, 1H), 1.65 (s, 1H), 1.29 (s, 6H), 0.88 (t, J = 6.0 Hz, J = 6.0 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 177.2, 173.1, 51.8, 42.2, 36.4, 32.4, 31.6, 26.8, 22.4, 14.0 ppm. **MS-EI**: *m/z* (%) 185 (M+, 0) 99 (100).



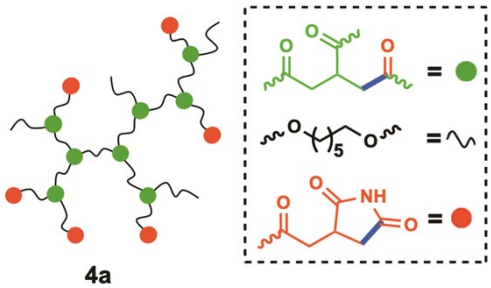
3f: White solid, yield = 84%, 0.7 g; **mp** (°C) = 62.2-63.0; $\mathbf{R_f}$ = 0.40. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 5.80 (s, 2H), 3.69 (s, 3H), 3.01-2.92 (m, 1H), 2.63 (dd, J_1 = 15.0, J_2 = 6.0, 1H), 2.30 (dd, J_1 = 15.0, J_2 = 6.0, 1H), 1.23 (d, J = 6.0 Hz, 3H). **^{13}C NMR**($CDCl_3$, 75 MHz) δ 176.4, 173.5, 51.9, 38.9, 35.9, 17.2 ppm. **MS-EI:** *m/z* (%) 128 (M+, 10) 59 (100).

4. General procedure for the polycondensation[3]

A classical two-step procedure was applied for the bulk polycondensation. The reaction was carried out in a EYELA Process Station PPS-5510 reactor. The flask was charged with the monomer **3** (0.74 mmol), diol (1.11 mmol), $ZnCl_2$ (5 mg, 0.04 mmol) and a magnetic stirrer bar.

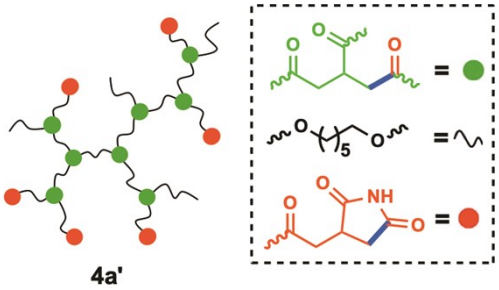
- To produce **4a** and **5**, the reaction was maintained under magnetic stirring for 2 h at 130 °C, 2 h at 160 °C and 4 h at 190 °C under N_2. Then, reduced pressure (50 mmHg) was applied, and the reaction was maintained at 190 °C for 20 h.
- To produce **4a'**, **4b** and **4c**, the reaction was maintained under magnetic stirring for 2 h at 130 °C and 6 h at 160 °C under N_2. Then, reduced pressure (50 mmHg) was applied, and the reaction was maintained at 160 °C for 20 h.

After cooling down to room temperature, the remaining material (oil or solid) was washed with a 0.4 M HCl solution, solubilized in 2 mL of chloroform, and precipitated in 25 mL of diethyl ether to yield the polymers.

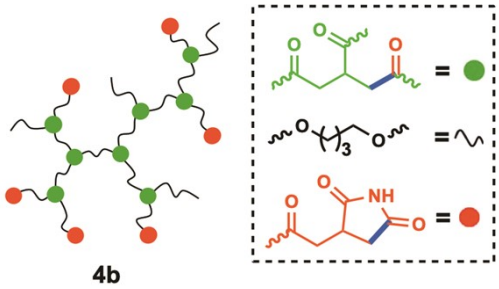


4a

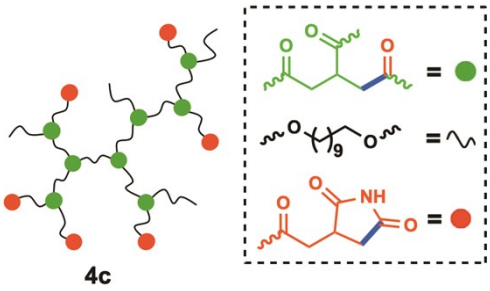
4a: Dark-brown solid, yield = 62%, **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.90 (s), 4.10 (t), 3.74-3.71 (m), 3.26–3.15 (m), 3.00-2.91 (m), 2.84-2.70 (m), 2.61-2.55 (m), 1.63-1.37 (m). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 171.5, 65.1, 64.8, 64.7, 37.5, 35.3, 34.1, 29.7, 28.4, 25.4. **GPC** M_n = 3.3 kDa, M_w = 7.2 kDa, PDI = 2.2. **CHN** N(%) = 7.48.



4a': Dark-brown solid, yield = 61%, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 9.18 (s), 4.15– 4.04 (m), 3.71 (s), 3.44–3.35 (m), 3.25 (s), 3.16 (s), 2.98-2.93 (m), 2.87–2.70 (m), 2.65–2.49 (m), 1.63 (s), 1.37 (s). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 179.6, 177.0, 173.2, 171.5, 170.9, 70.64, 65.09, 64.7, 64.6, 35.4, 35.2, 34.0, 29.5, 28.3, 25.4. **GPC** M_n = 1.0 kDa, M_w = 1.7 kDa, PDI = 1.7.

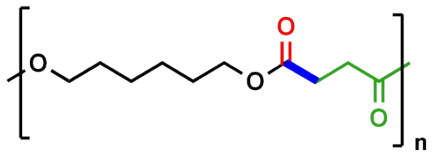


4b: Light-brown solid, yield =17%, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.97 (d), 4.14–4.11 (m), 3.72-3.69 (m), 3.16–3.13 (m), 3.00-2.93 (m), 2.85-2.81 (m), 2.79-2.74 (m), 2.60-2.58 (m), 2.57–2.55 (m), 1.69 (s), 1.67-1.64 (m). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 179.6, 176.7, 176.3, 170.3, 170.2, 64.7, 37.4, 35.3, 35.1, 34.1, 33.7, 25.1. **GPC** M_n = 0.5 kDa, M_w = 0.5 kDa, PDI = 1.2.



4c: Brown solid, yield = 25%, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 4.12– 4.05 (m), 3.39 (t), 3.17–3.14 (m), 2.99-2.93 (m), 2.84-2.75 (m), 2.61-2.55 (m), 2.57–2.55 (m), 1.59 (s), 1.28 (s). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 178.5, 177.2, 173.3, 171.5, 170.2, 71.0, 65.4,

65.0, 63.0, 37.5, 35.4, 34.1, 29.5, 29.3, 29.2, 28.5, 26.2, 25.8. **GPC** M_n = 1.4 kDa, M_w = 6.7 kDa, PDI = 4.7.

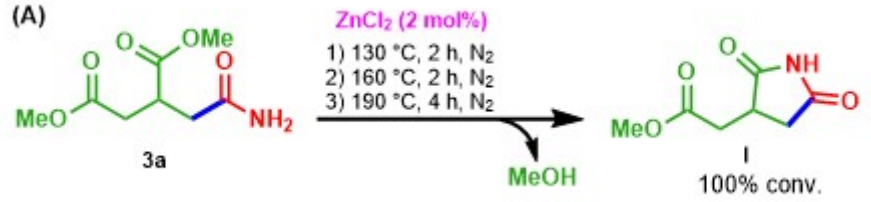


5

5: Brown solid, yield = 51%, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 4.29–3.96 (m), 3.72 (d, J = 7.0 Hz), 3.40 (d, J = 6.6 Hz), 2.62 (s), 1.73–1.54 (m), 1.54–1.23 (m). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 172.4, 64.6, 29.1, 28.5, 25.5. **GPC** M_n = 1.9 kDa, M_w = 1.9 kDa, PDI = 1.0.

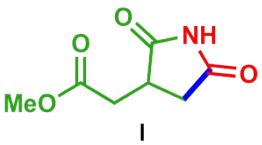
5. Control experiments

5.1 Control experiment (A): Evaluation of succinimide formation at 190 °C



Monomer **3a** (42 mg, 0.2 mmol) and $ZnCl_2$ (3 mg, 10 mol%) were added to a 5 mL vial, equipped with a stirring bar. The reaction was maintained under magnetic stirring for 2 h at 130 °C, 2 h at 160 °C and 4 h at 190 °C under N_2. After cooling down to room temperature, the oil was solubilized in 2 mL of chloroform and washed with 2 mL of deionized water. The organic layer was analyzed by GC-MS.

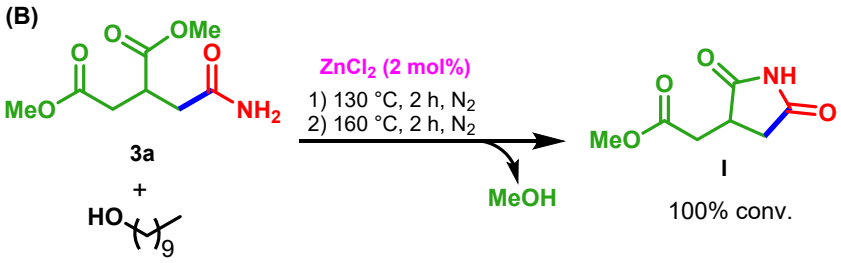
Result: GC-MS analysis revealed the full consumption of the monomer **3a** with succinimide **I** as the sole product.



I

I: White solid, yield = 75%; $\mathbf{R_f}$ = 0.57 (9:1 $CHCl_3$/MeOH). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.21 (s, 1H), 3.72 (s, 3H), 3.21-3.13 (m, 1H), 2.97 (dd, J_1 = 18.0 Hz, J_2= 9.0 Hz, 1H), 2.85 (d, J= 6.0 Hz, 2H), 2.57 (dd, J_1 = 18.0, J_2= 6.0 Hz, 1H) **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 178.6, 175.8, 171.2, 52.2, 37.5, 35.4, 33.9. **MS-EI**: *m/z* (%) 171 (M+, 5) 100 (100). **HRMS (ESI-TOF)** calcd for $C_7H_9NO_4$ [M+ Na]+ 194.0429, found 194.0429. **IR ($CHCl_3$)** 2961.4, 2919.4, 2849.5, 1706.2, 1440.6, 1375.4, 1375.4, 1363.3, 1177.8, 1044.6, 969.6, 801.4, 762.2 cm^{-1}.

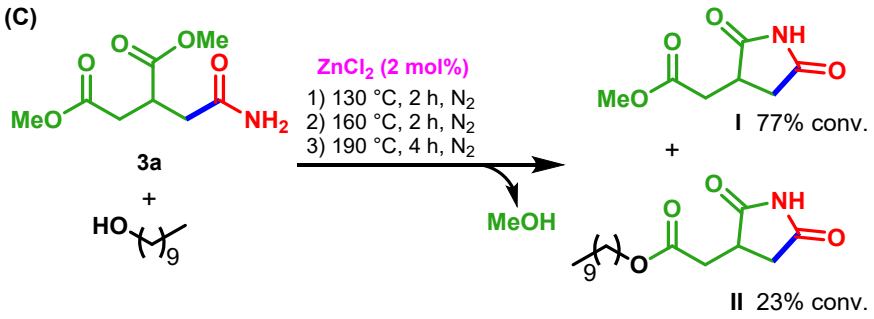
5.2 Control experiment (B): Evaluation of succinimide formation and transesterification reaction in the presence of 1-decanol at 160 °C



Amide-ester **3a** (101.5 mg, 0.5 mmol), 1-decanol (97.0 μL , 0.75 mmol) and $ZnCl_2$ (1.4 mg, 2 mol%) were added to a 5 mL vial, equipped with a stirring bar. The reaction was maintained under magnetic stirring for 2 h at 130 °C and for 2 h at 160 °C under N_2. After cooling down to room temperature, the oil was solubilized in 2 mL of chloroform and washed with 2 mL of deionized water. The organic layer was analyzed by GC-MS.

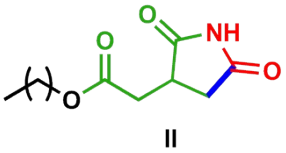
Result: GC-MS analysis revealed the full consumption of the monomer **3a** with succinimide **I** as the sole product. None transesterification product was observed.

5.3 Control experiment (C): Evaluation of succinimide formation and transesterification reaction in the presence of 1-decanol at 190 °C



Amide-ester **3a** (101.5 mg, 0.5 mmol), 1-decanol (97.0 μL , 0.75 mmol) and $ZnCl_2$ (1.4 mg, 2 mol%) were added to a 5 mL vial, equipped with a stirring bar. The reaction was maintained under magnetic stirring for 2 h at 130 °C, 2 h at 160 °C and 4 h at 190 °C under N_2. After cooling down to room temperature, the oil was solubilized in 2 mL of chloroform and washed with 2 mL of deionized water. The organic layer was analyzed by GC-MS. The crude material was purified by flash column chromatography using a mixture of *n*-hexane/ethyl acetate (4:1) as eluent.

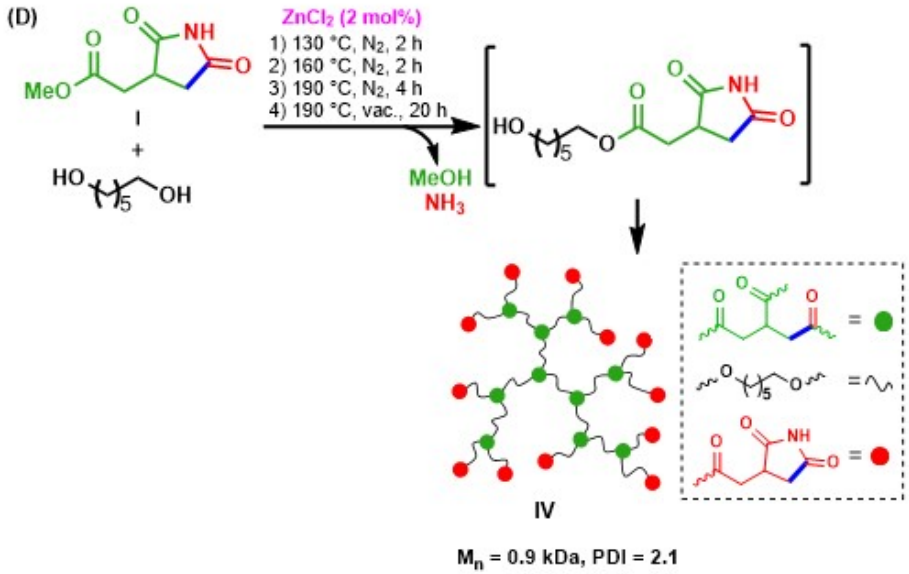
Results: GC-MS analysis revealed the presence of the succinimide **I** (77% conversion) and its transesterification product **II** (23% conversion).



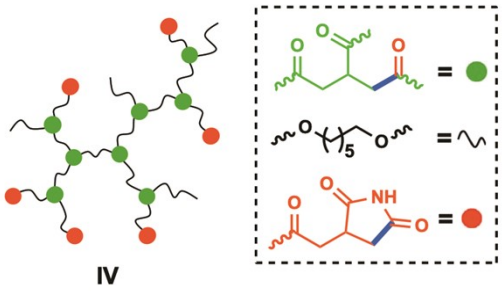
II

II': Orange solid; $\mathbf{R_f}$ = 0.37 (4:1 n-Hex/AcOEt). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.96 (s, 1H), 4.10 (t, *J*= 6.0 Hz, 2H), 3.19-3.12 (m, 1H), 2.97 (dd, J_1 = 18.0 Hz, J_2= 9.0 Hz, 1H), 2.84 (d, *J*= 3.0 Hz, 2H), 2.57 (dd, J_1 = 18.0, J_2= 6.0 Hz, 1H), 1.64-1.59 (m, 2H), 1.27 (s, 14H), 0.88 (t, *J*= 6.0 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 178.5, 175.7, 170.7, 65.5, 37.5, 35.4, 31.9, 29.5, 29.3, 29.2, 28.5, 25.8, 22.7, 14.1. **MS-EI**: *m/z* (%) 297 (M+, 0) 140 (100). **HRMS (ESI-TOF)** calcd for $C_{16}H_{27}NO_4$ [M+ Na]+ 320.1838, found 320.1839. **IR ($CHCl_3$)** 2951.1, 2922.2, 2850.5, 1714.6, 1558.0, 1506.7, 1455.5, 1374.4, 1185.3, 803.2 cm^{-1}.

5.4 Control experiment (D): Evaluation of the polycondensation of the succinimide I with 1,6-hexanediol

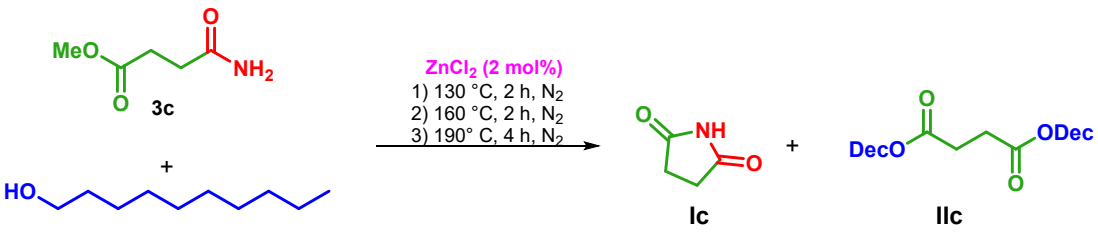


The reaction was carried out in a EYELA Process Station PPS-5510 reactor. The flask was charged with the succinimide **I** (0.74 mmol), 1,6-hexanediol (130.85 mg, 1.11 mmol), $ZnCl_2$ (5 mg, 0.04 mmol) and a magnetic stirrer bar. The reaction was maintained under magnetic stirring for 2 h at 130 °C, 2 h at 160 °C and 4 h at 190 °C under N_2. Then, reduced pressure (50 mmHg) was applied, and the reaction was maintained at 190 °C for 20 h. After cooling down to room temperature, the remaining oil was washed with a 0.4 M HCl solution, solubilized in 2 mL of chloroform, and precipitated in 25 mL of diethyl ether to yield the polymer **IV**.



IV: Dark-brown solid, yield = 31%; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.84 (s), 4.14– 4.07 (m), 3.65 (s), 3.16-3.13 (m), 2.99–2.95 (m), 2.85-2.76 (m), 2.62-2.56 (m), 1.64 (s), 1.37 (s). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 179.2, 171.5, 129.5, 65.2, 37.4, 35.2, 34.0, 28.3, 28.3, 25.4, 25.4. **GPC** M_n = 0.9 kDa, M_w = 1.9 kDa, PDI = 2.1.

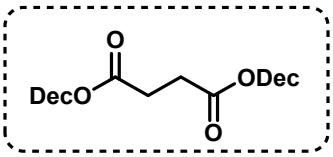
5.5 Transesterification of the monomer 3c with 1-decanol



Amide-ester **3c** (65.5 mg, 0.5 mmol), 1-decanol (97.0 μL, 0.75 mmol) and $ZnCl_2$ (1.4 mg, 2 mol%) were added to a 5 mL vial, equipped with a stirring bar. The reaction was maintained under magnetic stirring for 2 h at 130 °C, 2 h at 160 °C and 4 h at 190 °C under N_2. After cooling down to room temperature, the oil was solubilized in 2 mL of chloroform and washed with 2 mL of deionized water. The organic layer was analyzed by GC-MS.

Results: GC-MS analysis revealed the presence of the succinimide **Ic** (34% conversion) and di-ester **IIc** (39% conversion).

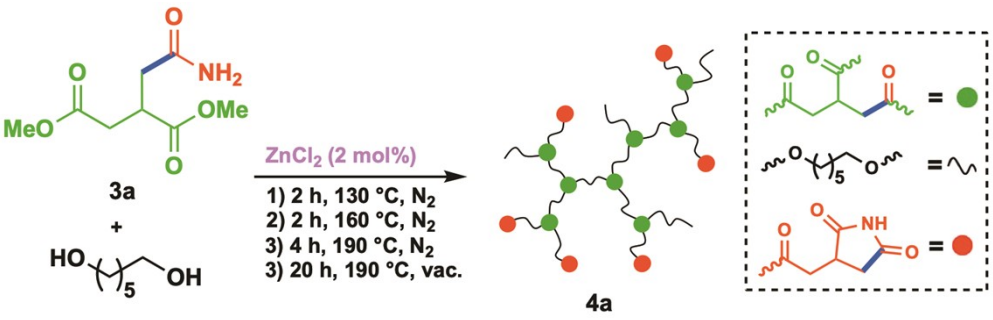
The succinimide **Ic** was compared against an external standard, using a commercial sample of the succinimide (CAS 123-56-8) in the same GC-MS method. The compound **IIc** was isolated after flash column chromatography.



IIc: Orange oil. Yield = 27%. $\mathbf{R_f}$ = 0.69 (4:1 n-Hex/AcOEt). **RMN-^{1}H** ($CDCl_3$, 300 MHz) δ 4.08 (t, J = 6.0 Hz, 4H); 2.62 (s, 4H); 1.64-1.57 (m, 4H); 1.27 (s, 28H); 0.88 (t, J = 6.0 Hz, 6H). **RMN-^{13}C** ($CDCl_3$, 75 MHz) δ 172,4; 64,9; 31,9; 29,5; 29,3; 29,2; 29,1; 28,6; 25,9; 22,7; 14,1 ppm. **MS-EI**: *m/z* (%) 280 (M+, 0) 101 (100).

6. Characterization of the polyester 4a

Different techniques (^{1}H NMR, CHN and MALDI-TOF-MS analyses) were used to elucidate the structure of the polyester **4a** (Scheme 1).



Scheme **1**: Synthesis of the polyester **4a**.

Initially, a close look to the ^{1}H NMR spectrum (Figure 1) of the monomer **3a** revealed that at δ = 5.83 ppm, we have a broad singlet with an integral of 2, which is attributed to the hydrogens of the primary amide H_e. At δ = 3.71 ppm and δ = 3.69 ppm we have two singlets, both with an integral of 3, which are attributed to the methyl hydrogens H_a, due to their proximity to the oxygen atom. In the region of δ = 3.34-3.25 ppm, we have a multiplet with an integral of 1, which is attributed to the hydrogen H_c, which couples with both H_b and H_d hydrogens. We have another multiplet in the region of δ = 2.76-2.68 ppm with an integral of 3, which is originated by the overlap of the signals of the methylene hydrogens H_b with the signal of one of the diastereotopic hydrogens H_d. Finally, we have a doublet of doublets at δ = 2.50 ppm, with an integral of 1, which is attributed to one of the diastereotopic hydrogens H_d and shows coupling constants J = 6.0 Hz and J = 15.0 Hz, corroborating the geminal coupling between the two methylene hydrogens H_d.

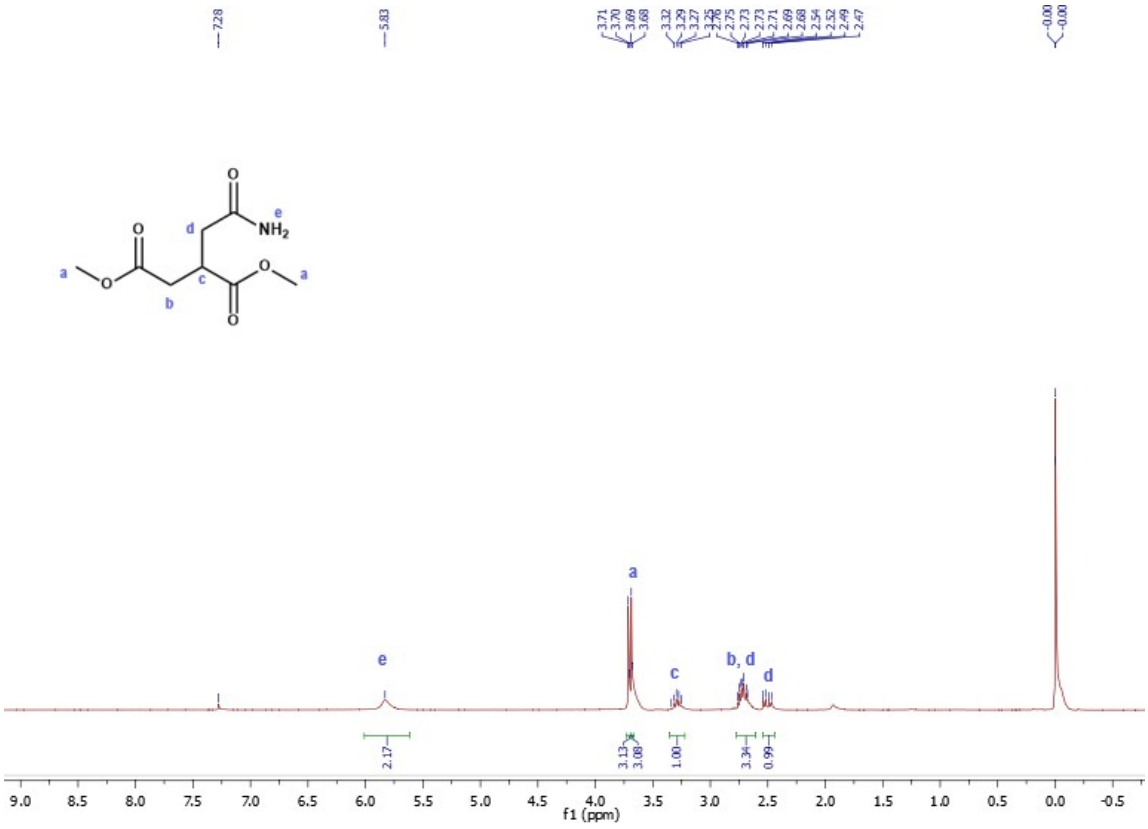
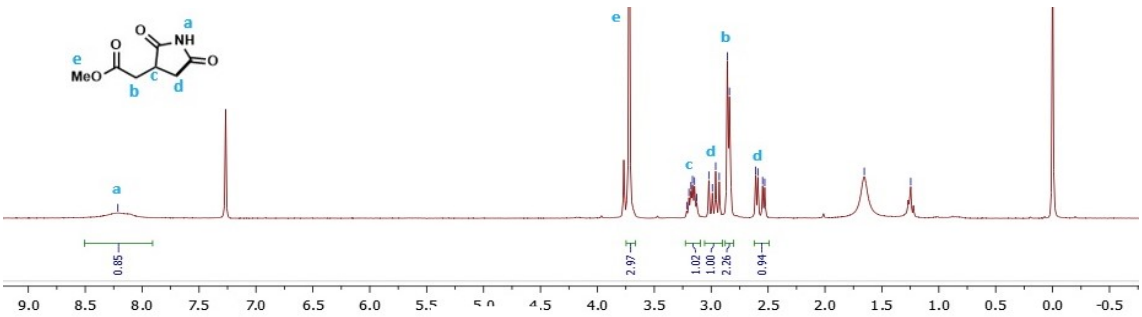


Figure **1**: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of the monomer **3a**.

A comparison of the ^{1}H NMR spectra of the monomer **3a** (Figure 1 and Figure 2A), a succinimide derivative (Figure 2B) and polyester **4a** (Figure 2C) provided important information about the structure of the polyester (Figure 2).

(A)

(B)



(C)

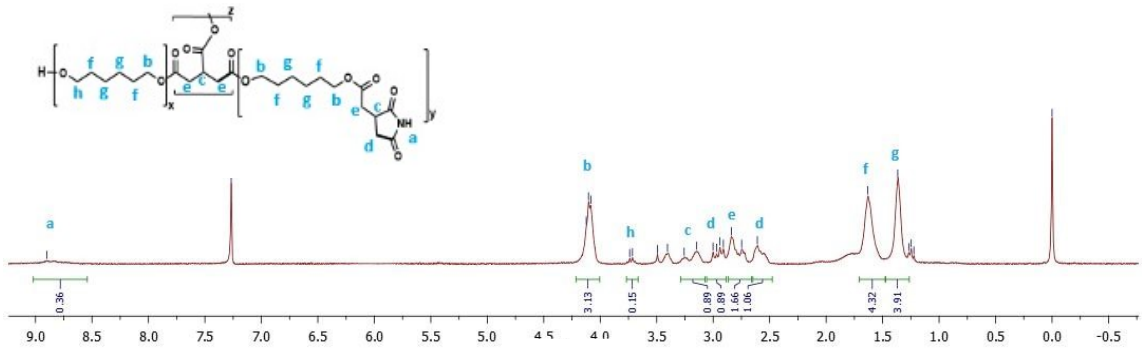


Figure **2**: Comparison of ^{1}H NMR spectra. (A) Spectrum of the monomer **3a**; (B) Spectrum of the succinimide derivative; (C) Spectrum of the polyester **4a**.

As we can see in the ^{1}H NMR spectrum of the polyester **4a** (Figure 2C), there is no primary amide (wide singlet at δ= 5.83 ppm for compound **3a**, Figure 2A). However, a new singlet at δ= 8.90 ppm is attributed to the NH_a group of a succinimide unit, which also can be seen in Figure 2B. The absence of the singlets at δ = 3.71 ppm and δ = 3.69 ppm indicates that the monomer was fully consumed, and a new triplet at 4.10 ppm is attributed to the methylene hydrogens H_b. We have a multiplet in the region of δ = 3.26-3.15 ppm, which is attributed to the hydrogen H_c, and a multiplet in the region 2.84-2.70 attributed to the methylene hydrogens H_e. Two multiplets in δ = 3.00-2.91 ppm and δ = 2.61-2.55 ppm are attributed to the diasterotopic hydrogens H_d at the succinimide. There is also two multiplets (broad signal) in δ = 1.63-1.37 ppm, which can be attributed to the methylene hydrogens H_f and H_g. Finally, the multiplet in δ = 3.74-3.71 ppm can be attributed to the methylene hydrogens H_h of ending group ($-CH_2OH$).

To corroborate the proposed polymer structure and the repeating unit (Figure 3), a MALDI-TOF-MS analysis of polyester **4a** was performed. The MS data was processed with the Polytool software, which revealed the repeating unit as 497.237 Da.

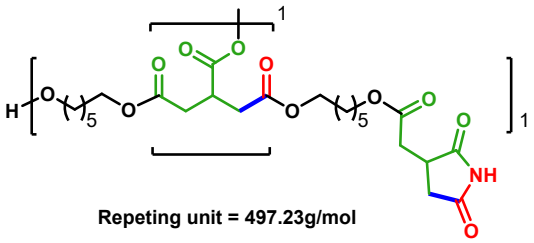
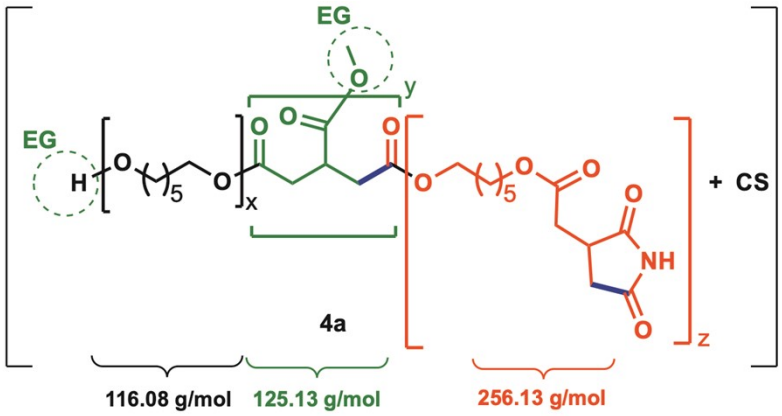


Figure **3**: Repeating unit observed for the polymer **4a**.

The interpretation of MALD-TOF-MS spectra of hyperbranched polymers can be difficult due to the complexity of polymer distribution. Also, the amide-ester polymer **4**, which certainly will have high affinity to protons and alkali metal ions, can generate protonated ions, sodium and potassium adducts. We have used 2,5-dihydrobenzoic acid (DHB) as matrix and NaCl as cationizing salt, then, it was proposed mainly protonated ions $(M + H)^+$ and sodium adducts $(M + Na)^+$. Based on the repeating unit suggested by the Polytool software, we have proposed an equation to help us on the identification of protonated ions and sodium adducts m/z (Scheme 2).[4]



Adduct m/z = 116.08*x* + 125.13*y* + 256.13*z* + **Σ***EG* + *CS* **(Equation 1)**

Scheme **2**: Molecular fragments considered for the adduct m/z equation and MALDI-TOF-MS interpretation.

The values of *x, y* and *z* correspond to the molar fractions of the residues of diol (1,6-hexanediol), monomer **3a** and the cyclization product (succinimide) (Scheme 2). EG corresponds to the ending group, and CS to the charged specimen. Considering a hyperbranched polymer, it is possible to have multiples and different ending groups (EG) per adduct. The value of the EG can also be zero, which means that ion has ended with succinimide unit, since the proposed mechanism demonstrates that ring opening of the succinimide unit is necessary to increase the polymer size. It was considered as EG: -H (value = 1), -OH (value = 17), -Na (value = 23) or -ONa (value = 39). CS can assume a value of 23 for Na^+ or a value of 1 for H^+.

It is worth mentioning that we have a hyperbranched polymer, then the protonated ion or sodium adduct proposed by us from MALDI-TOF Mass spectra can have different structures than those suggested by the equation. However, the calculated *m/z* values were important to elucidate the structures for the protonated ions or sodium adducts. A good correlation between experimental and calculated *m/z* data was observed for several cases. For example, the experimental *m/z* values for the polyester **4a** were obtained by MALDI-TOF-MS analyses (Figure 4) and the calculated *m/z* values for sodium adduct $(M + Na)^+$ by applying the Equation 1. The proposed adducts for the polyester **4a** are depicted in Figure 5.

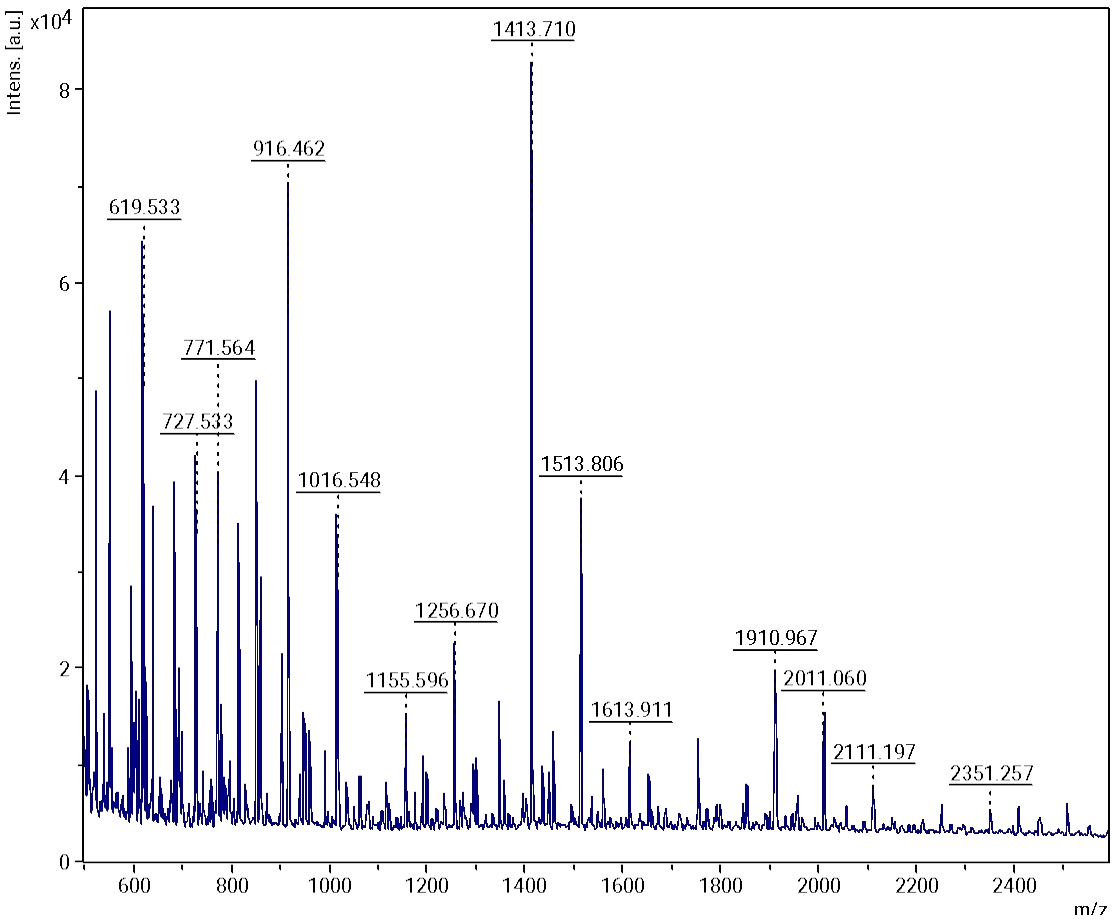


Figure **4**: MALDI-TOF-MS spectrum of the compound **4a** obtained with DHB as matrix.

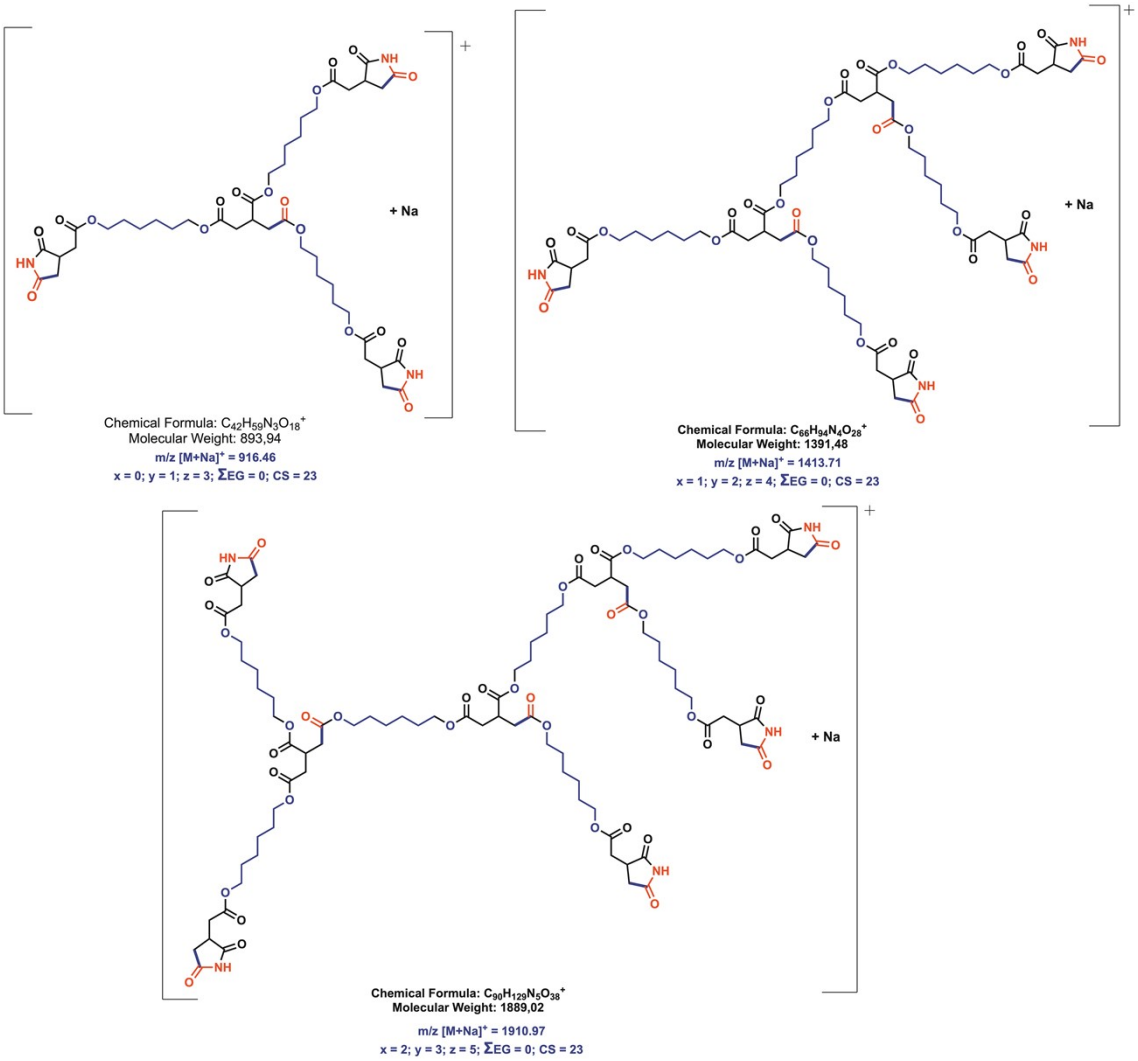


Figure **5**: Sodium adducts assigned for the polyester **4a** in the MALDI-TOF Mass spectrum. Equation for Adduct m/z = 116.08x + 125.13y + 256.13z + **Σ***EG* + *CS*. (see Scheme 2, page 19, for an explanation of this equation).

A CHN elemental analysis of the polyester **4a** was also very useful to confirm the presence of nitrogen in the polyester structure (Table 1).

Table 1: *CHN analysis of the polyester* ***4a****.*

Sample	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Polyester 4a	51.08	6.31	7.48

7. E-factor calculations for the monomers 3

Table 2. *Calculation of E-factor for the monomer* ***3a***

	n(x) [mmol]	Mw [g/mol]	V(x) [mL]	d [g/mL]	m(x) [g]	m(recovered) [g]
Reactant 1a	7.00	158.15			**1.10**	
Formamide	56.00	45.05	2.23	1.13	**2.52**	
TBADT	0.14	3320.24			**0.46**	**0.32***
Acetonitrile	907.68	41.05	47.77	0.78	**37.26**	**37.26****
Product 3a					**1.20**	

*Approximately 70% of TBADT was recovered after purification by column chromatography.
** Acetonitrile was recovered by distillation.

$$\text{E-factor} = \frac{1.10 + 2.25 + 0.46 + 37.26 - 0.32 - 37.26}{1.20}$$

$$\text{E-factor} = 3.1$$

Table 3. *Calculation of E-factor for the monomer* ***3b***

	n(x) [mmol]	Mw [g/mol]	V(x) [mL]	d [g/mL]	m(x) [g]	m(recovered) [g]
Reactant 1b	7.00	144.13			**1.01**	
Formamide	56.00	45.05	2.23	1.13	**2.52**	
TBADT	0.14	3320.24			**0.46**	**0.32***
Acetonitrile	907.68	41.05	47.77	0.78	**37.26**	**37.26****
Product 3b					**0.90**	

*Approximately 70% of TBADT was recovered after purification by column chromatography.
** Acetonitrile was recovered by distillation.

$$\text{E-factor} = \frac{1.01 + 2.25 + 0.46 + 37.26 - 0.32 - 37.26}{0.90}$$

$$\text{E-factor} = 4.0$$

Table 4. *Calculation of E-factor for the monomer* ***3c***

	n(x) [mmol]	Mw [g/mol]	V(x) [mL]	d [g/mL]	m(x) [g]	m(recovered) [g]
Reactant 1c	7.00	86.09	0.63	0.95	**0.60**	
Formamide	56.00	45.05	2.23	1.13	**2.52**	
TBADT	0.14	3320.24			**0.46**	**0.32***
Acetonitrile	907.68	41.05	47.77	0.78	**37.26**	**37.26****
Product 3c					**0.70**	

*Approximately 70% of TBADT was recovered after purification by column chromatography.
** Acetonitrile was recovered by distillation.

$$\text{E-factor} = \frac{0.60 + 2.25 + 0.46 + 37.26 - 0.32 - 37.26}{0.70}$$

$$\text{E-factor} = 4.6$$

Table 5. *Calculation of E-factor for the monomer* ***3d***

	n(x) [mmol]	Mw [g/mol]	V(x) [mL]	d [g/mL]	m(x) [g]	m(recovered) [g]
Reactant 1d	7.00	100.12	0.74	0.94	**0.70**	
Formamide	56.00	45.05	2.23	1.13	**2.52**	
TBADT	0.14	3320.24			**0.46**	**0.32***
Acetonitrile	907.68	41.05	47.77	0.78	**37.26**	**37.26****
Product 3d					**0.80**	

*Approximately 70% of TBADT was recovered after purification by column chromatography.
** Acetonitrile was recovered by distillation.

$$\text{E-factor} = \frac{0.70 + 2.25 + 0.46 + 37.26 - 0.32 - 37.26}{0.80}$$

$$\text{E-factor} = 4.2$$

Table 6. *Calculation of E-factor for the monomer* ***3e***

	n(x) [mmol]	Mw [g/mol]	V(x) [mL]	d [g/mL]	m(x) [g]	m(recovered) [g]
Reactant 1e	7.00	158.24			**1.10**	
Formamide	56.00	45.05	2.23	1.13	**2.52**	
TBADT	0.14	3320.24			**0.46**	**0.32***
Acetonitrile	907.68	41.05	47.77	0.78	**37.26**	**37.26****
Product 3e					**0.70**	

*Approximately 70% of TBADT was recovered after purification by column chromatography.
** Acetonitrile was recovered by distillation.

$$\text{E-factor} = \frac{1.10 + 2.25 + 0.46 + 37.26 - 0.32 - 37.26}{0.70}$$

$$\text{E-factor} = 5.3$$

Table 7. *Calculation of E-factor for the monomer* ***3f***

	n(x) [mmol]	Mw [g/mol]	V(x) [mL]	d [g/mL]	m(x) [g]	m(recovered) [g]
Reactant 1f	7.00	100.12	0.74	0.94	**0.70**	
Formamide	56.00	45.05	2.23	1.13	**2.52**	
TBADT	0.14	3320.24			**0.46**	**0.32***
Acetonitrile	907.68	41.05	47.77	0.78	**37.26**	**37.26****
Product 3f					**0.70**	

*Approximately 70% of TBADT was recovered after purification by column chromatography.
** Acetonitrile was recovered by distillation.

$$\text{E-factor} = \frac{0.70 + 2.25 + 0.46 + 37.26 - 0.32 - 37.26}{0.70}$$

$$\text{E-factor} = 4.8$$

8. ^{1}H NMR and ^{13}C NMR spectra of the compounds

Figure **6**: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of the compound **3a**.

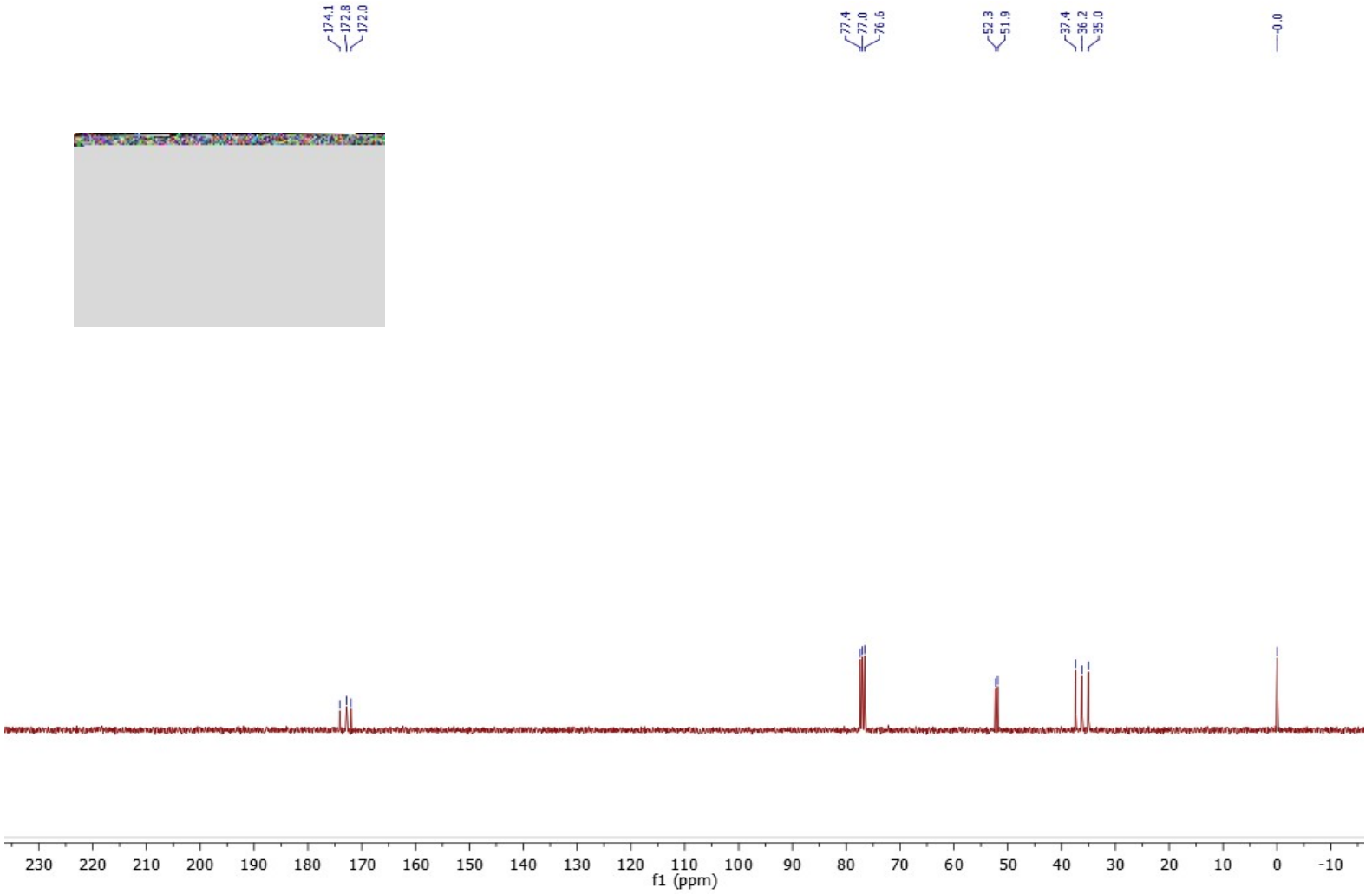


Figure **7**: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of the compound **3a**.

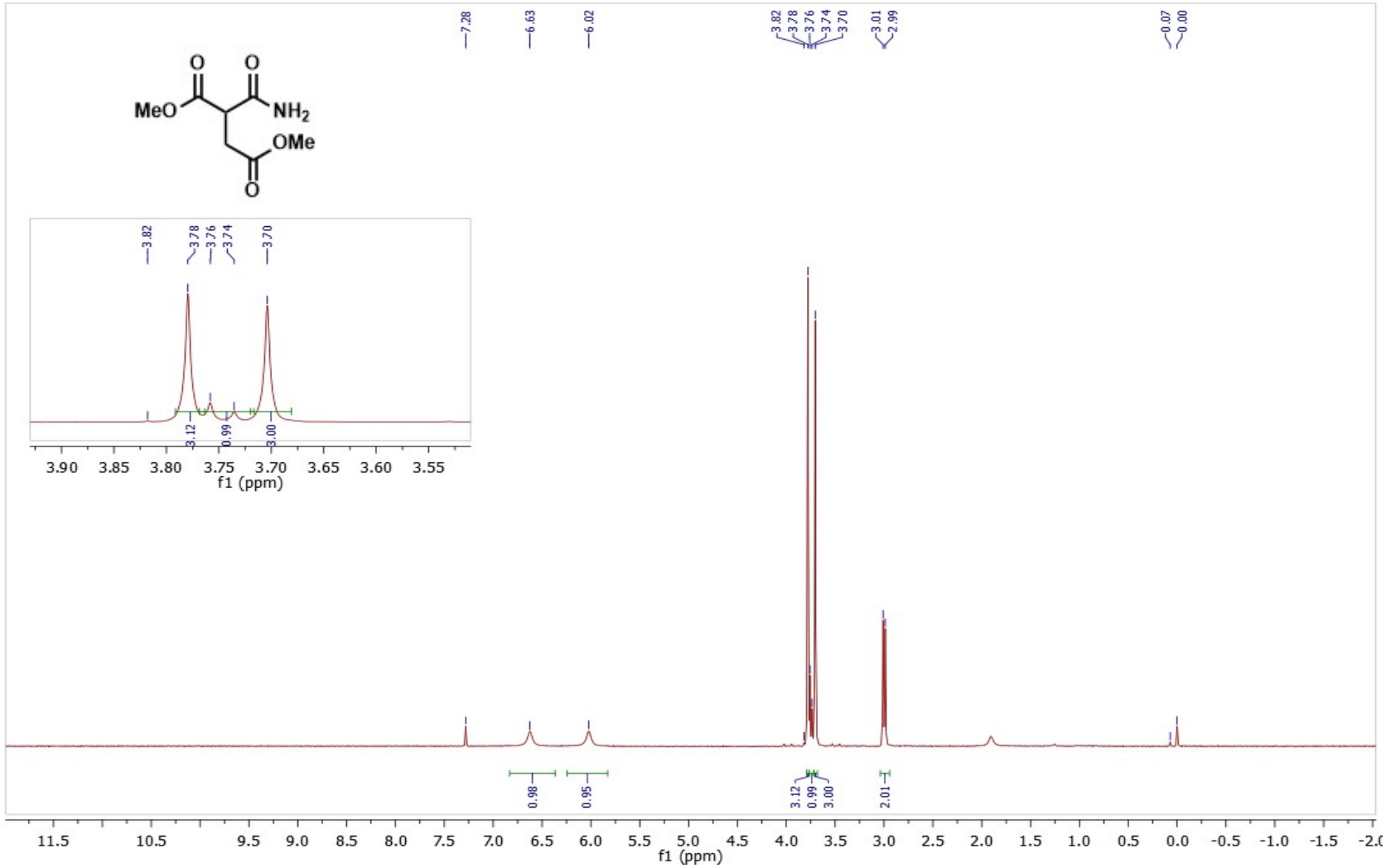


Figure **8**: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of the compound **3b**.

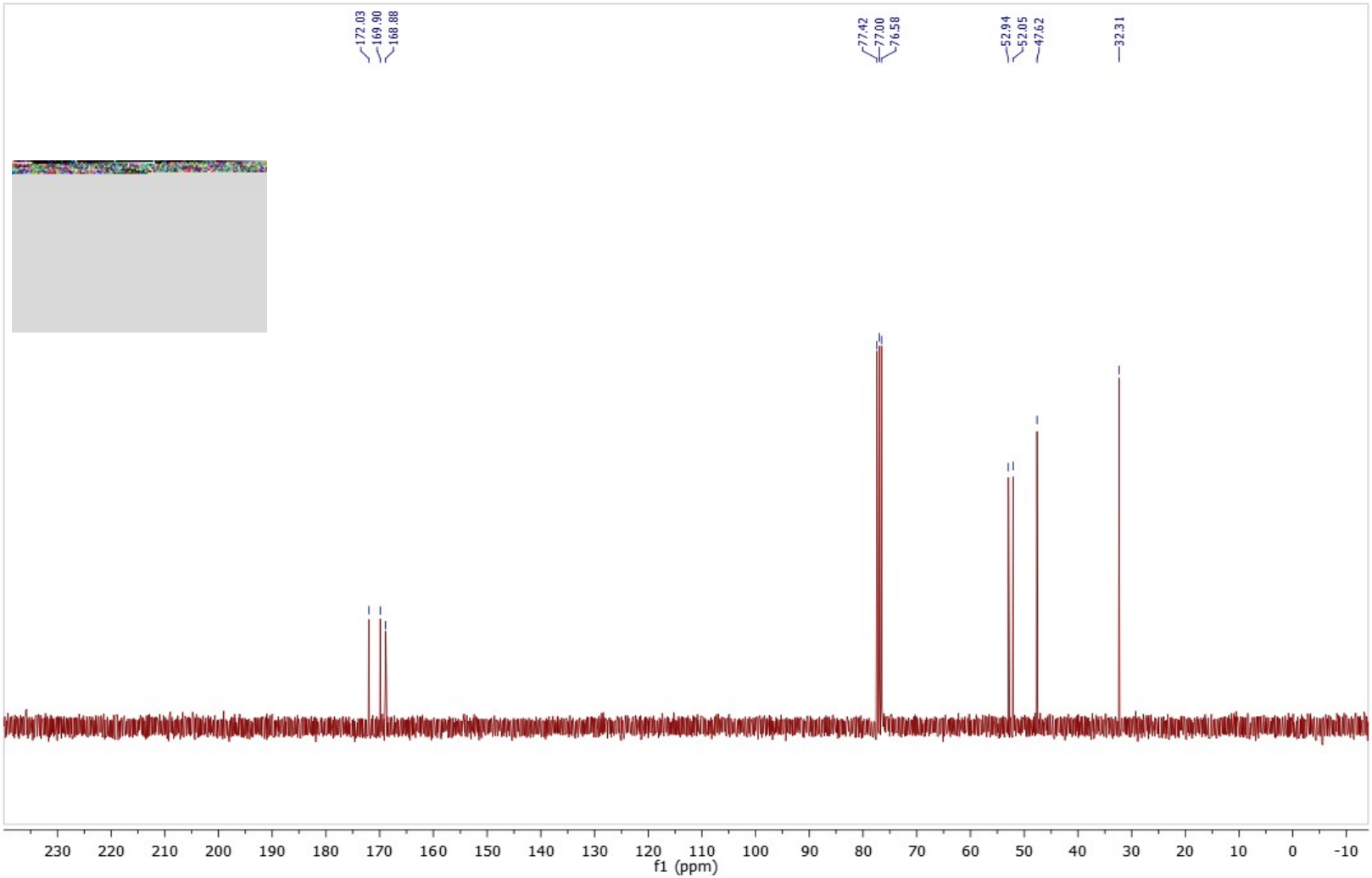


Figure **9**: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of the compound **3b**.

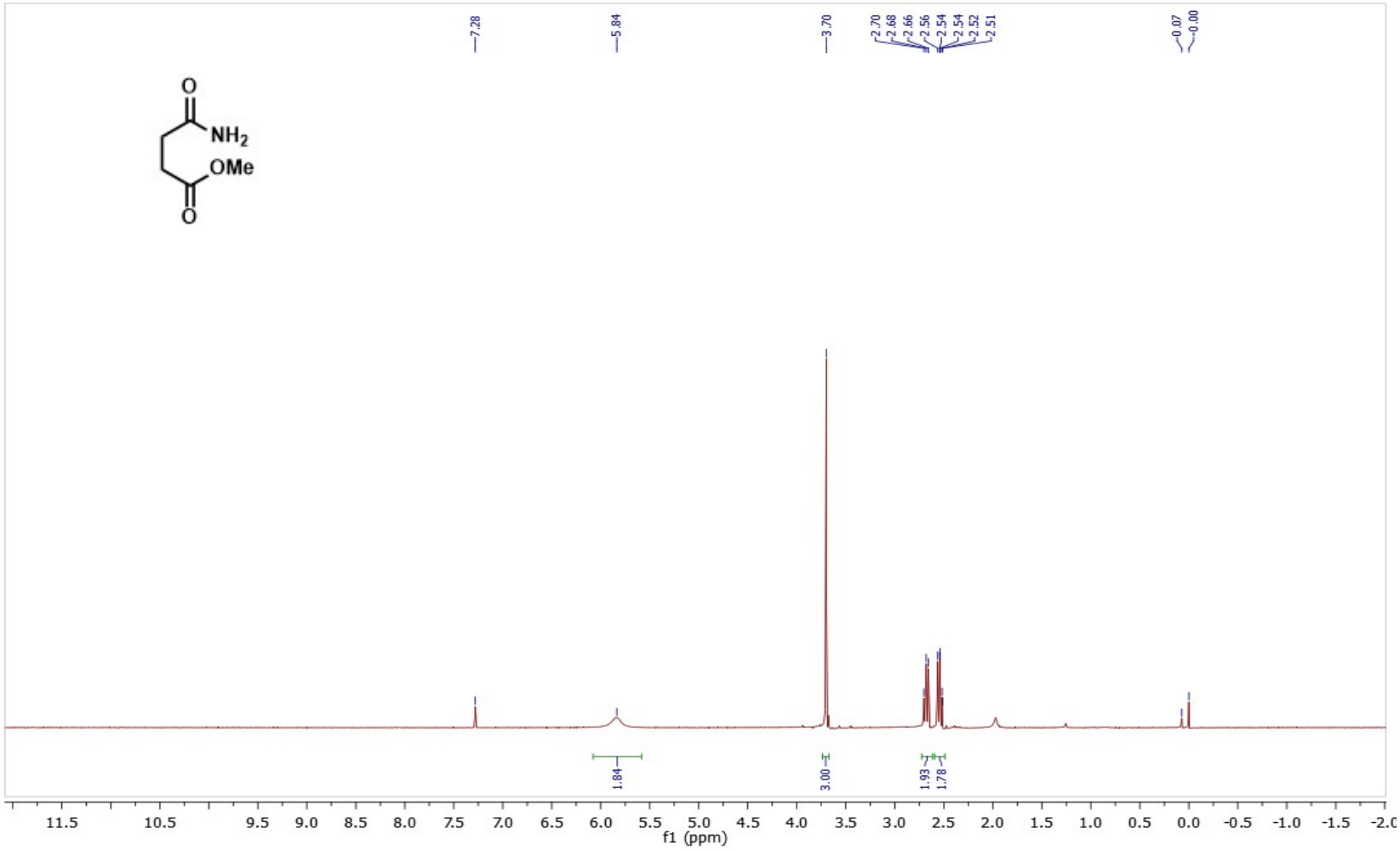


Figure **10**: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of the compound **3c**.

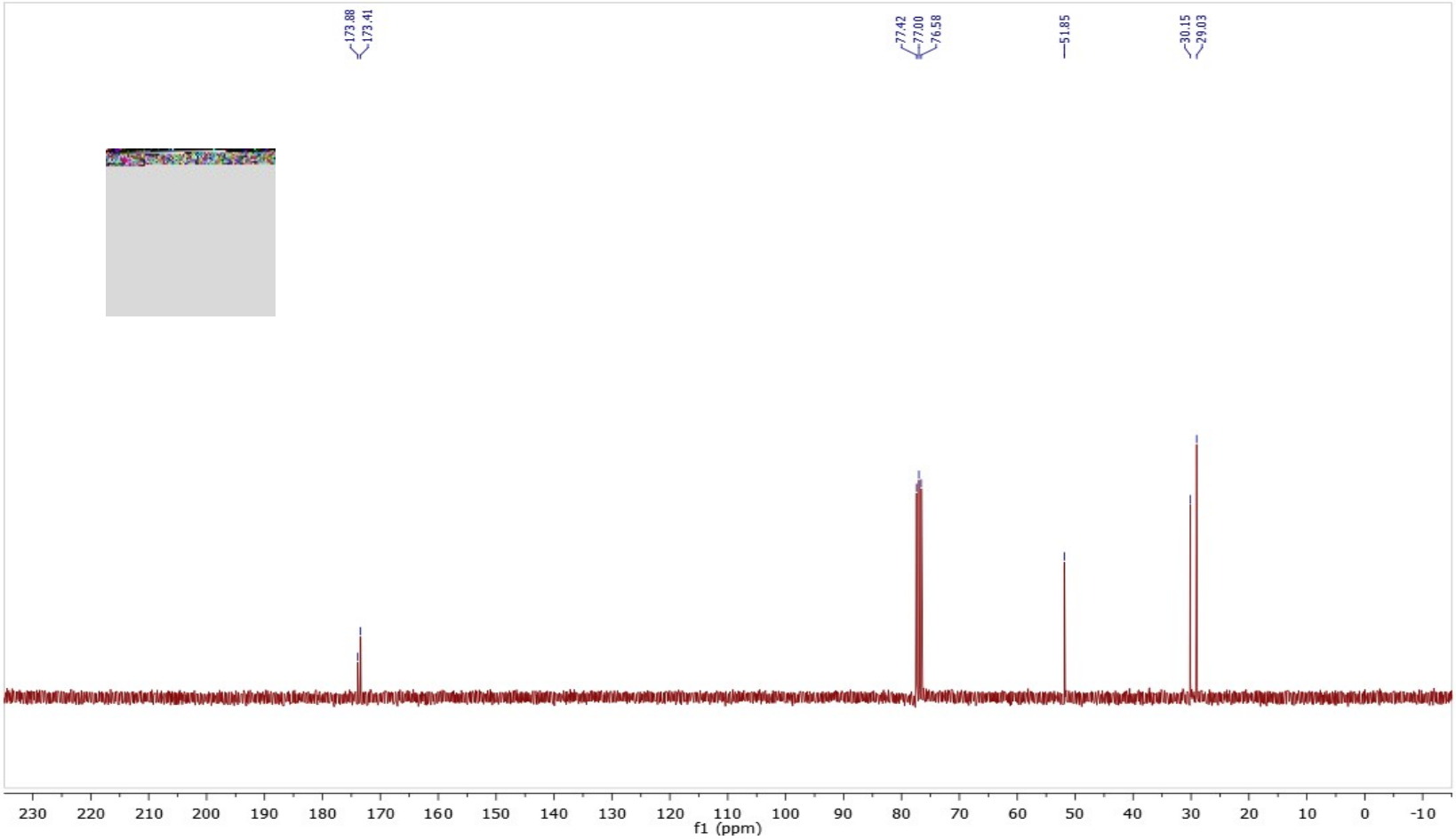


Figure **11**: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of the compound **3c**.

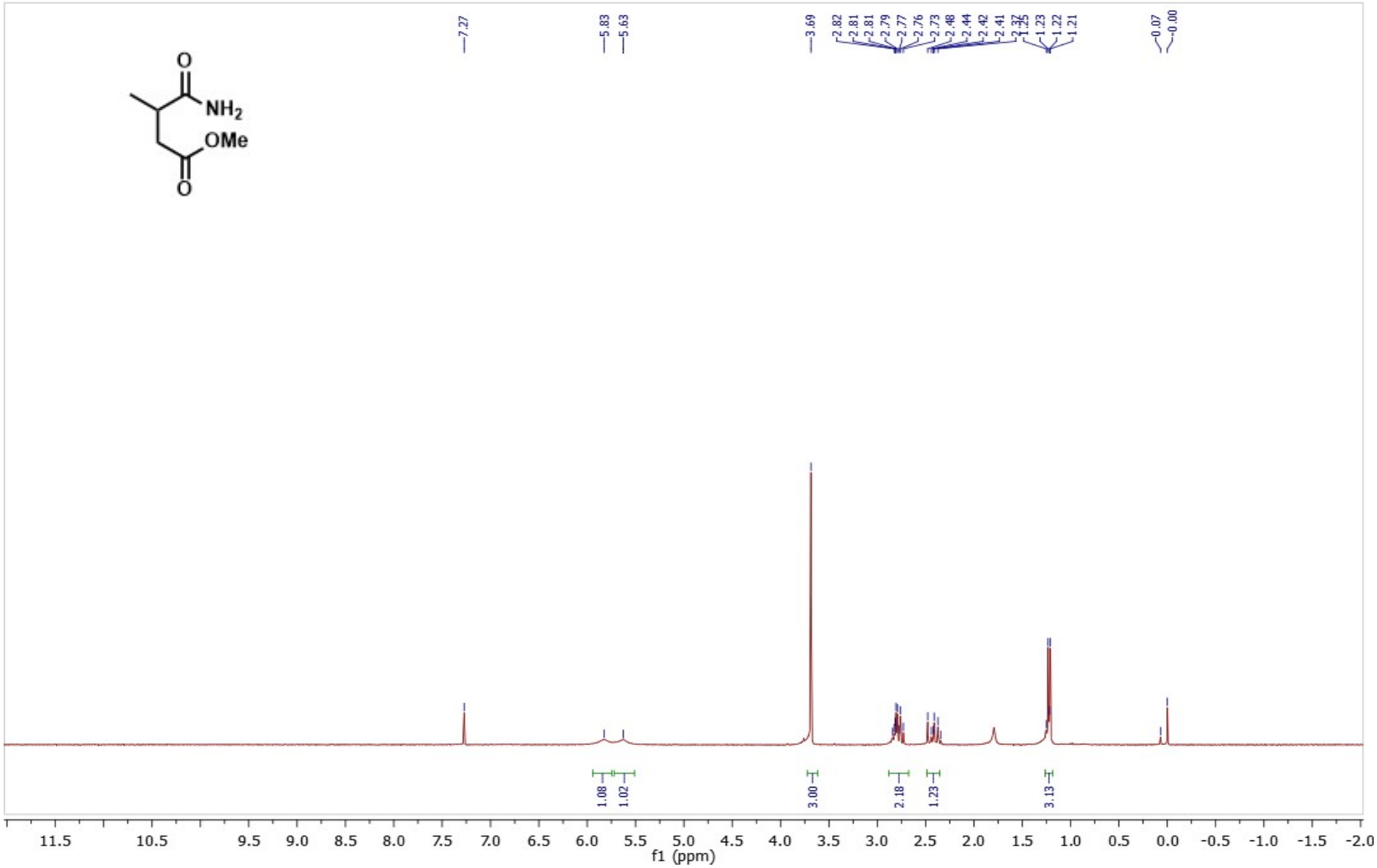


Figure **12**: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of the compound **3d**.

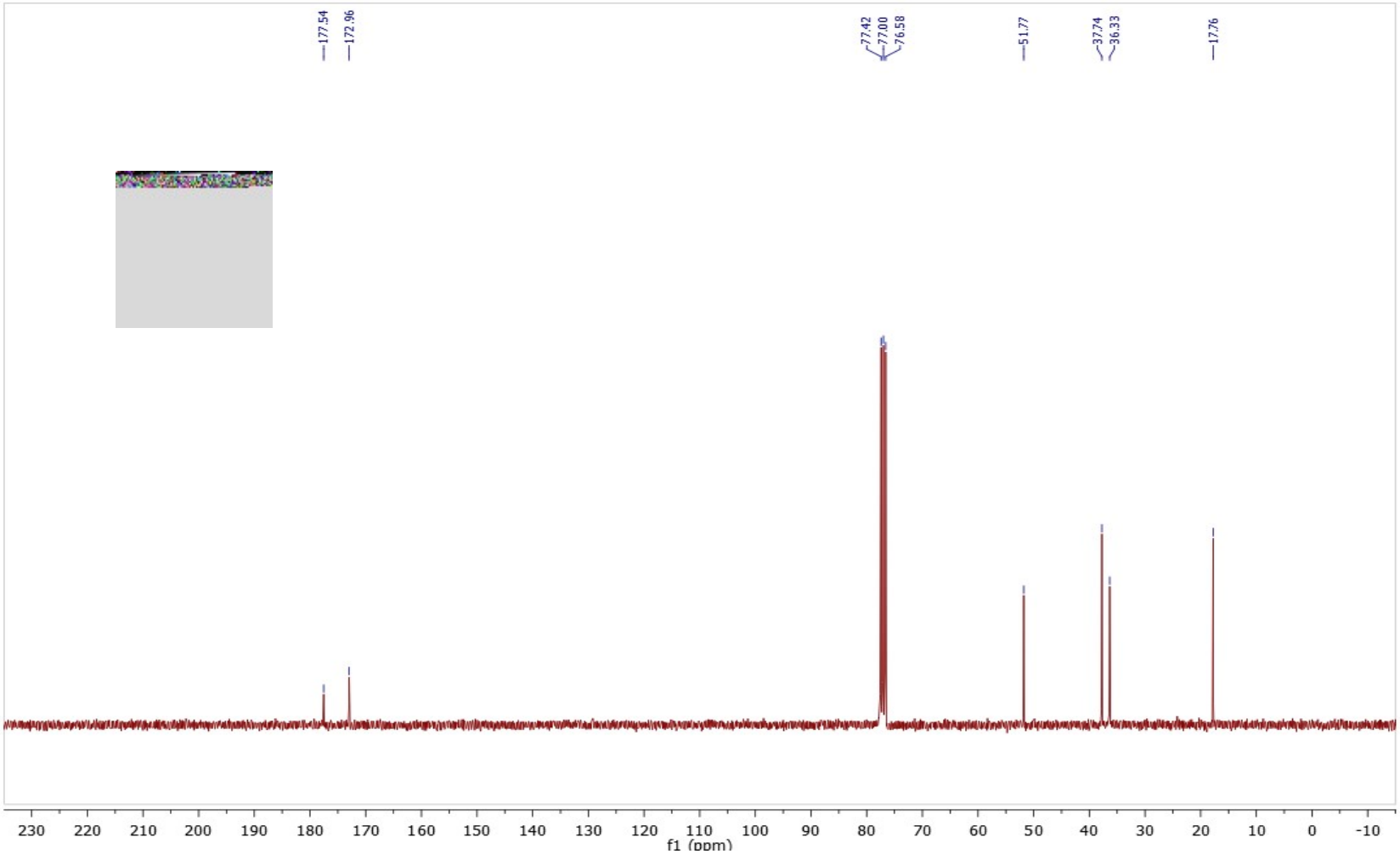


Figure **13**: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of the compound **3d**.

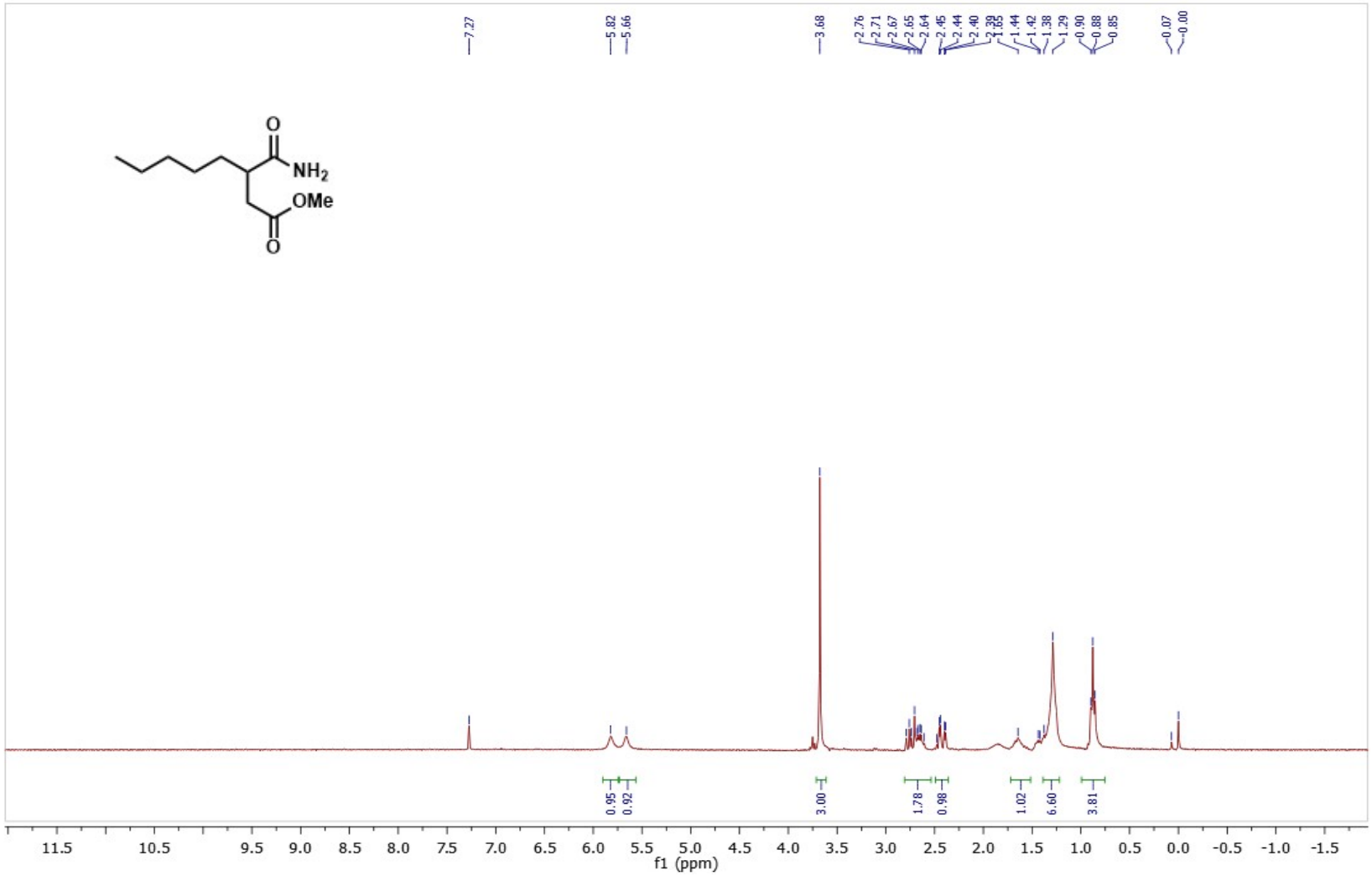


Figure **14**: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of the compound **3e**.

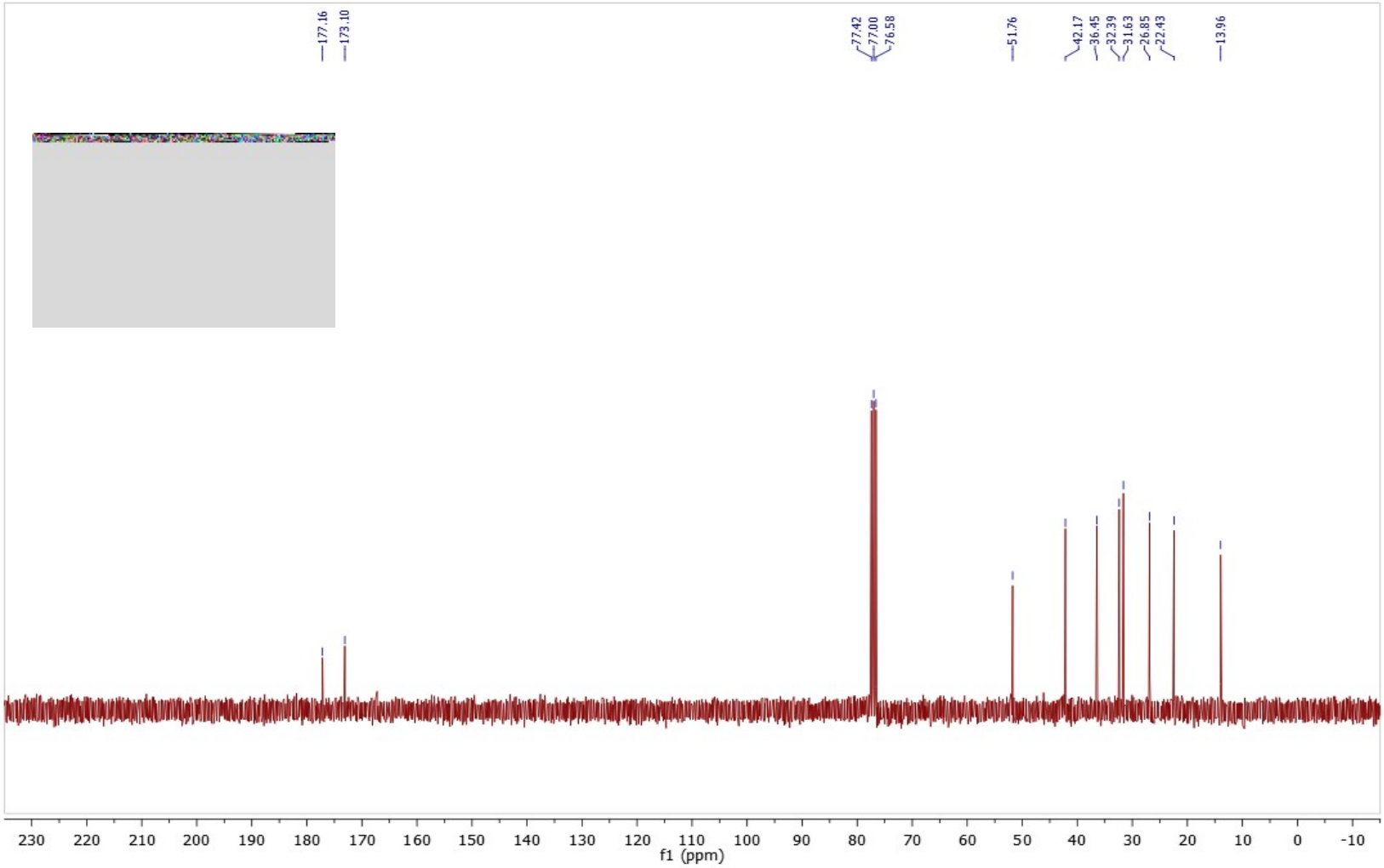


Figure **15**: ^{13}C NMR($CDCl_3$, 75 MHz) spectrum of the compound **3e**.

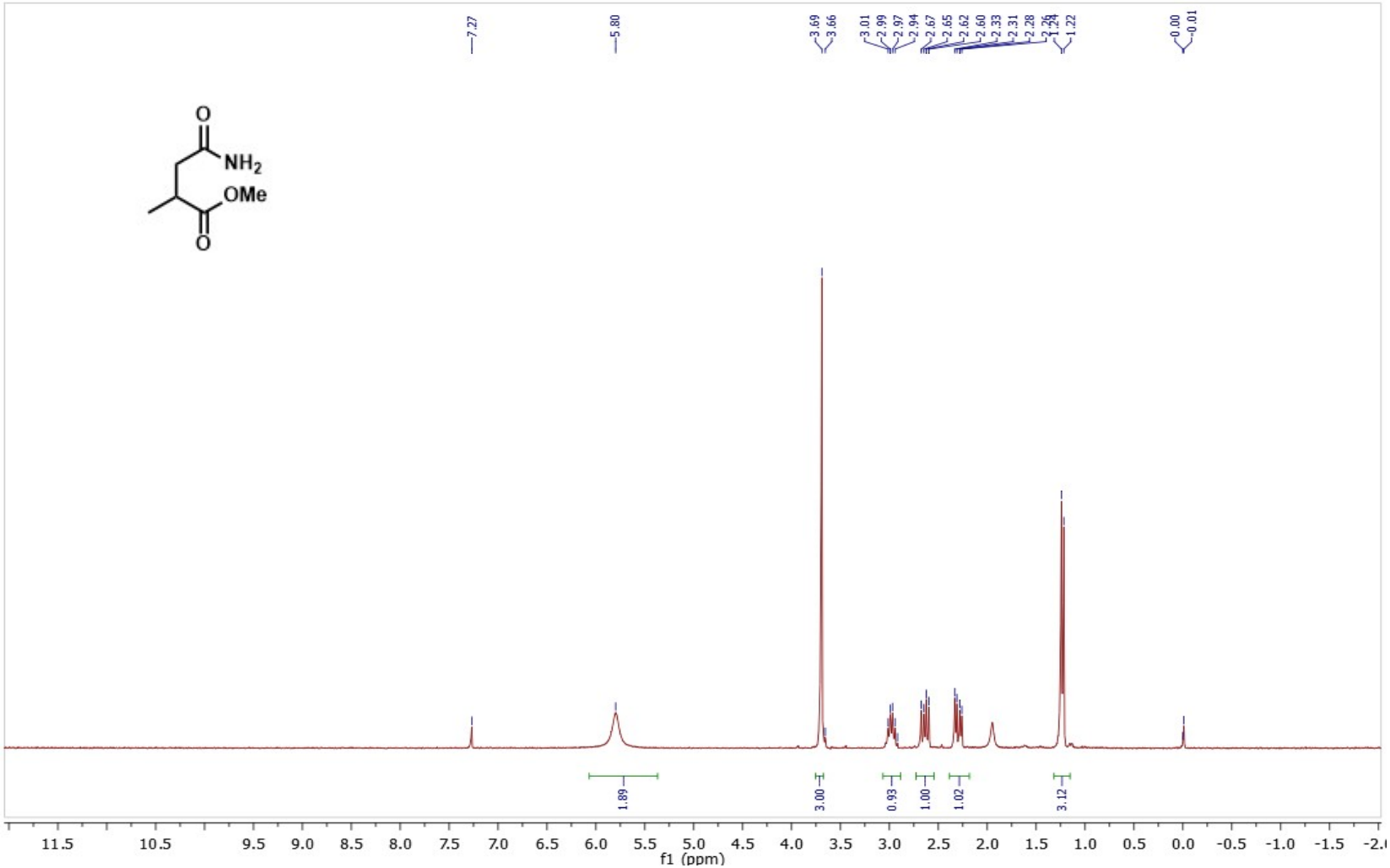


Figure **16**: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of the compound **3f**.

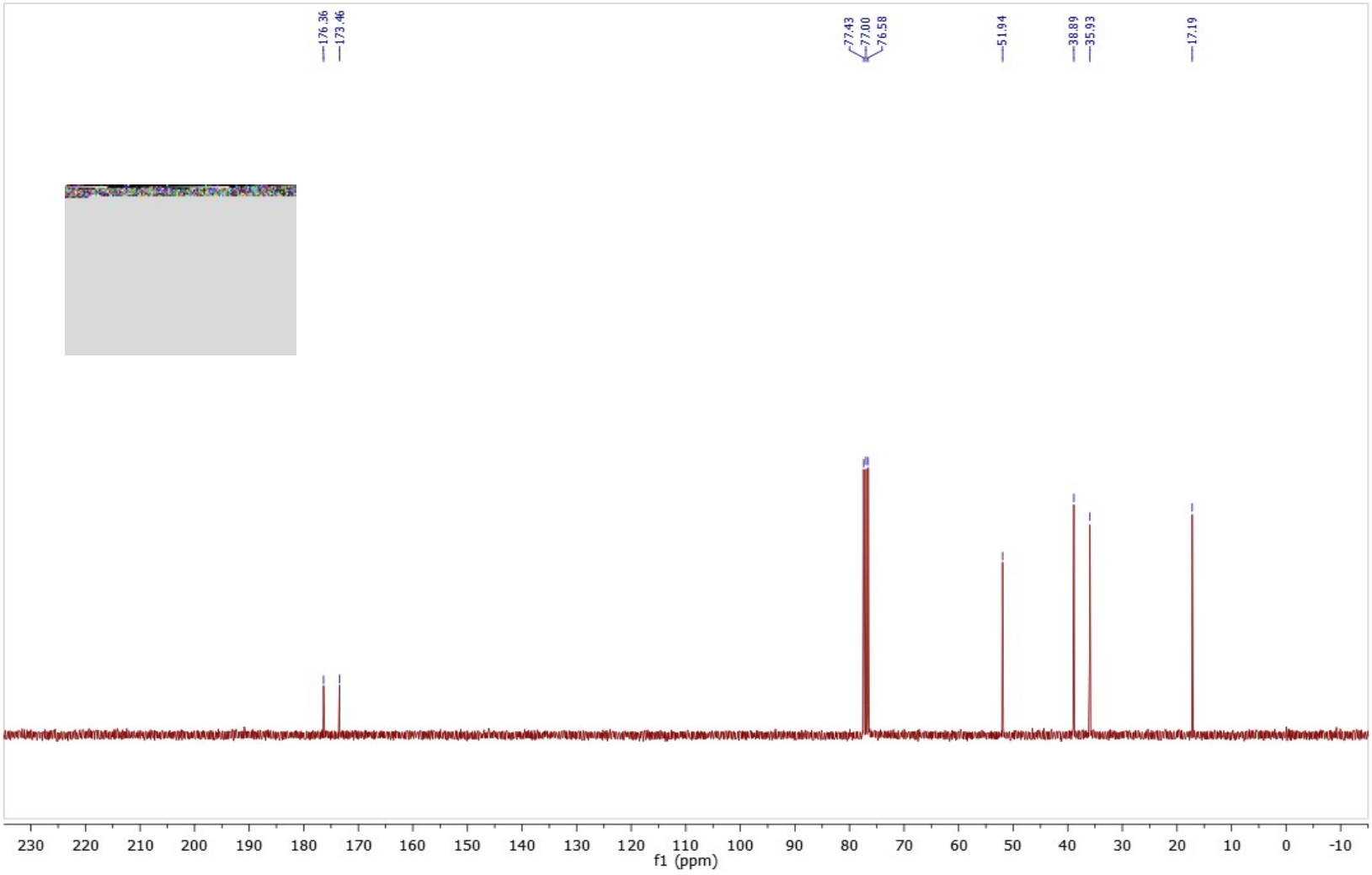


Figure **17**: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of the compound **3f.**

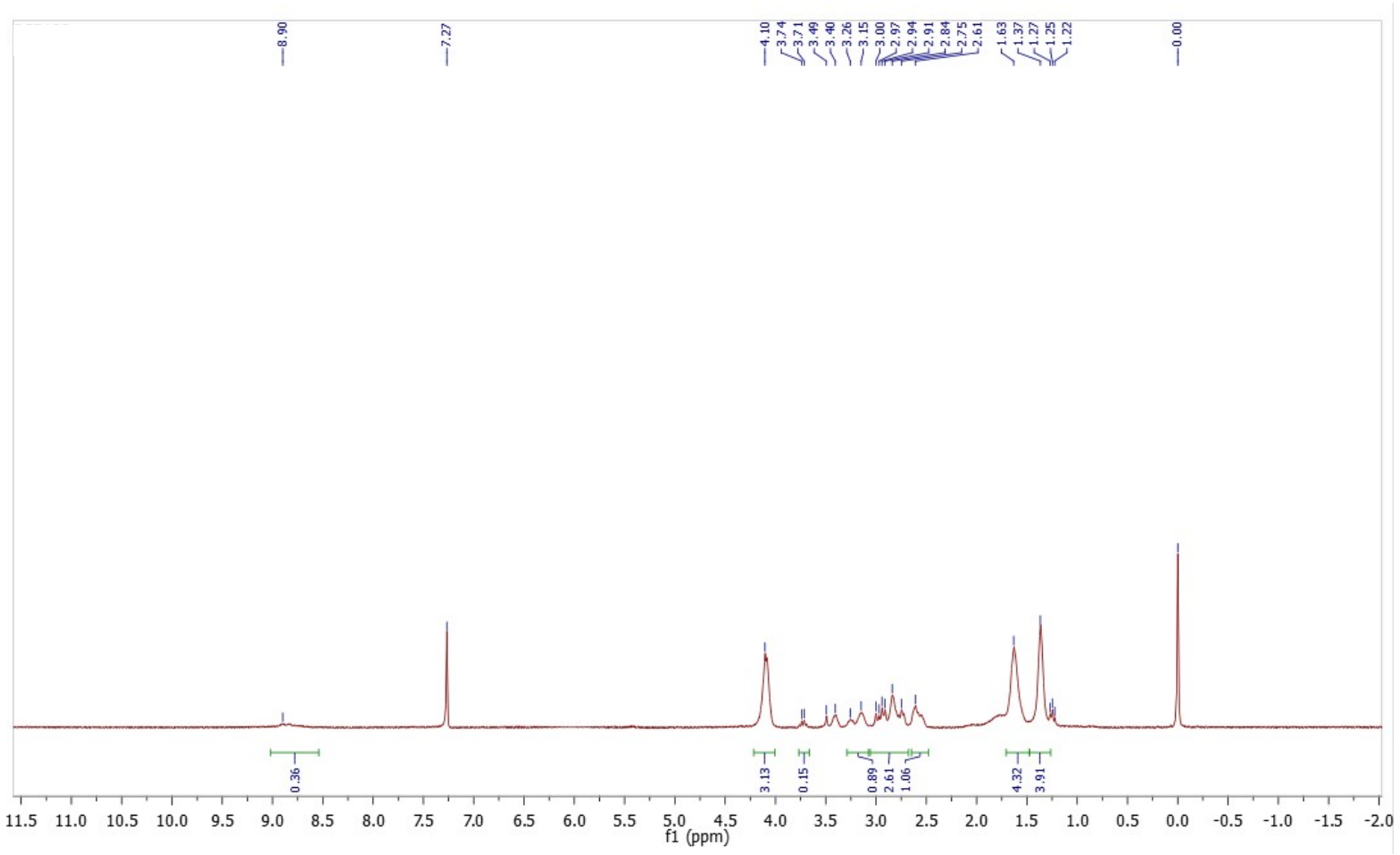


Figure **18**: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of the compound **4a**.

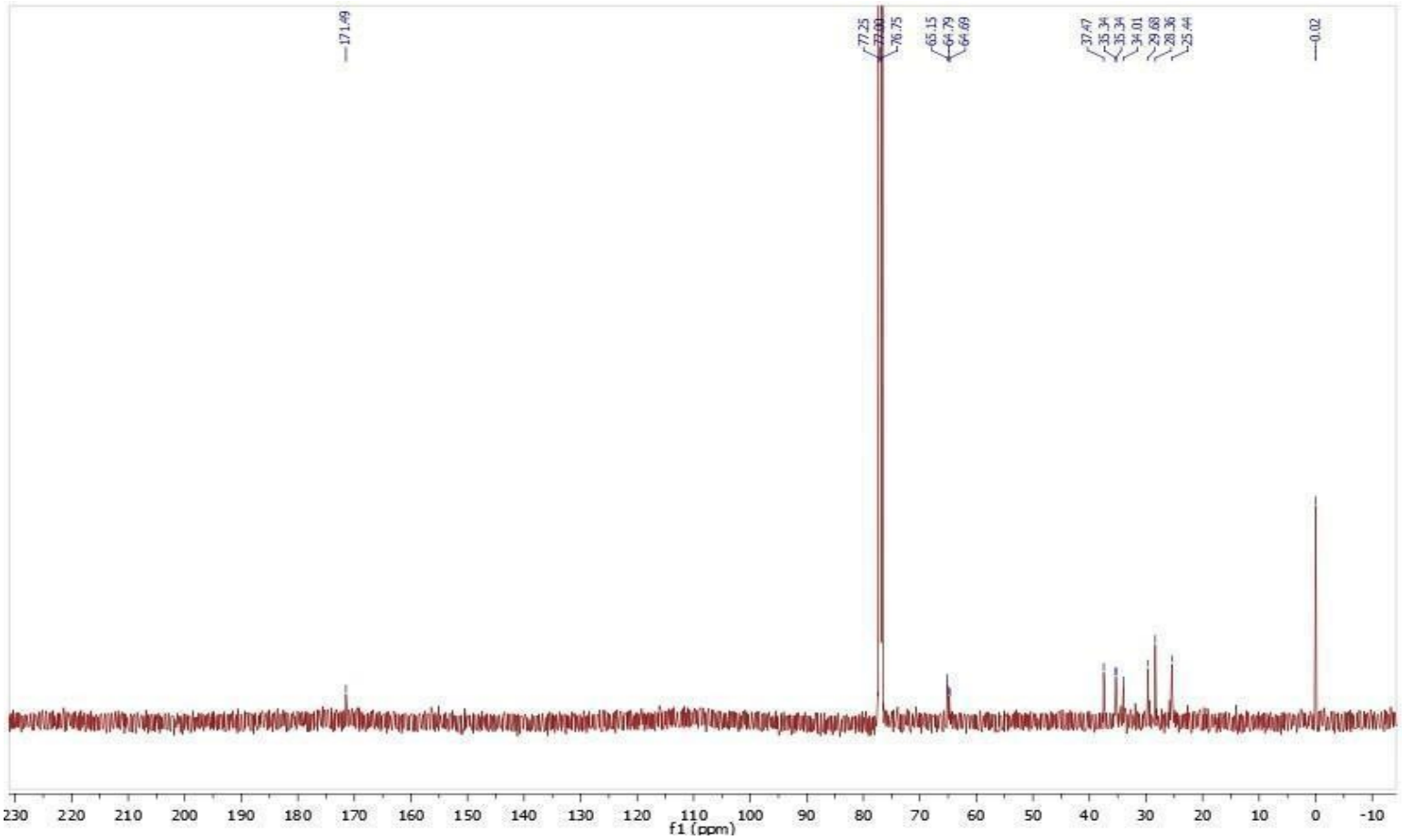


Figure **19**: ^{13}C NMR ($CDCl_3$, 75 MHz, *NS= 71345*) spectrum of the compound **4a.**

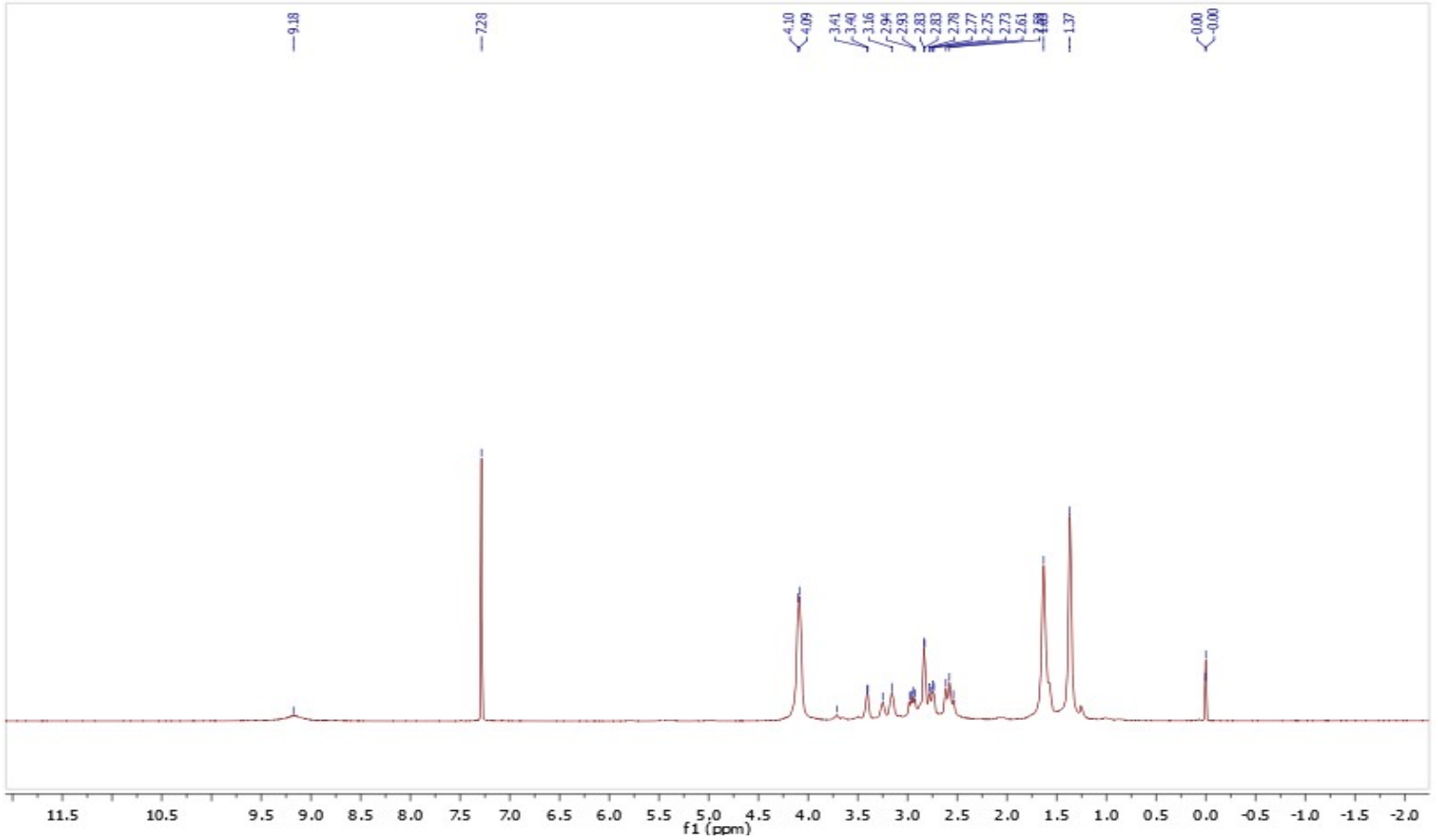


Figure **20**: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of the polyester **4a'**.

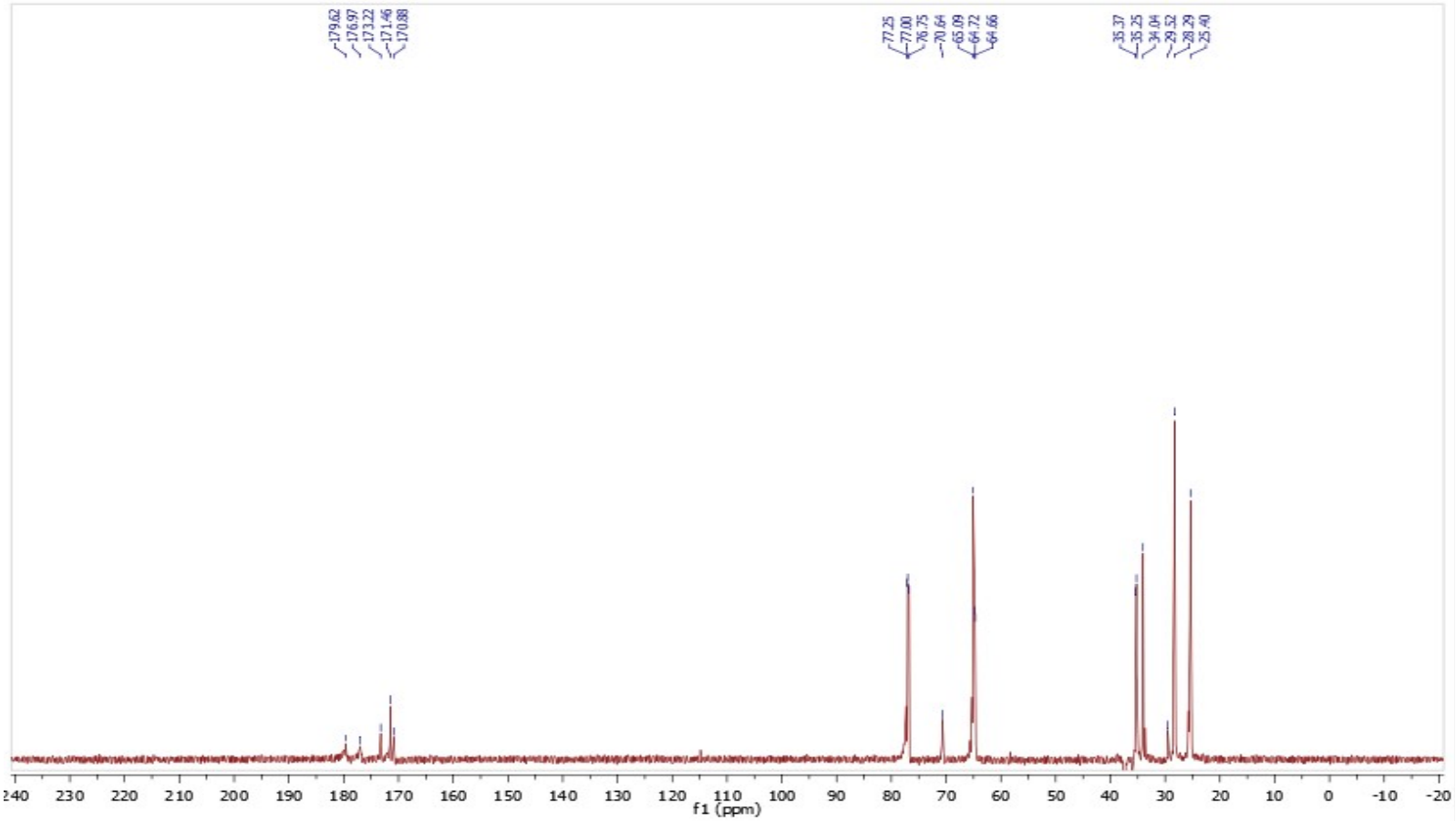


Figure **21**: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of the polyester **4a'**.

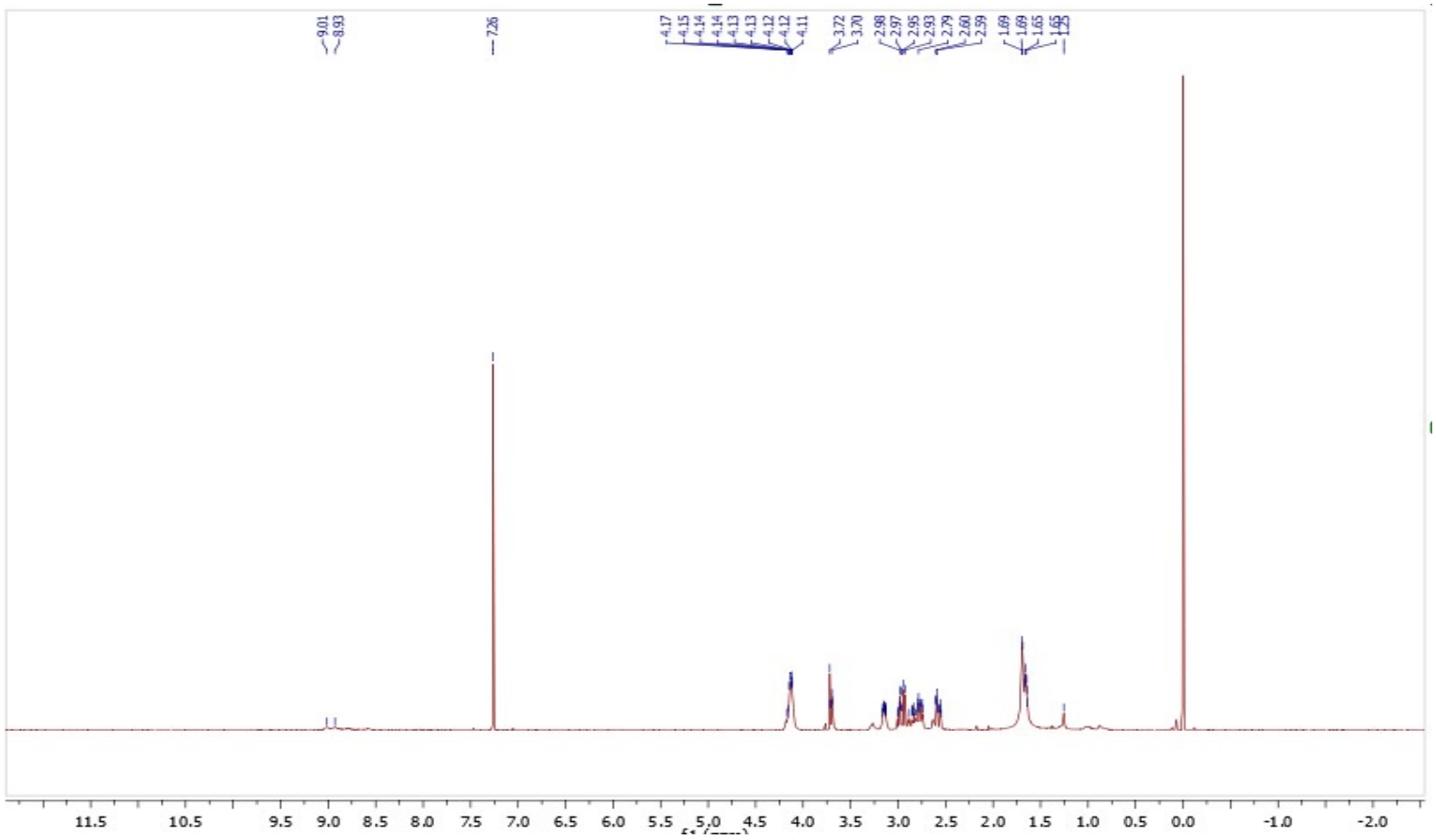


Figure **22**: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of the polyester **4b**.

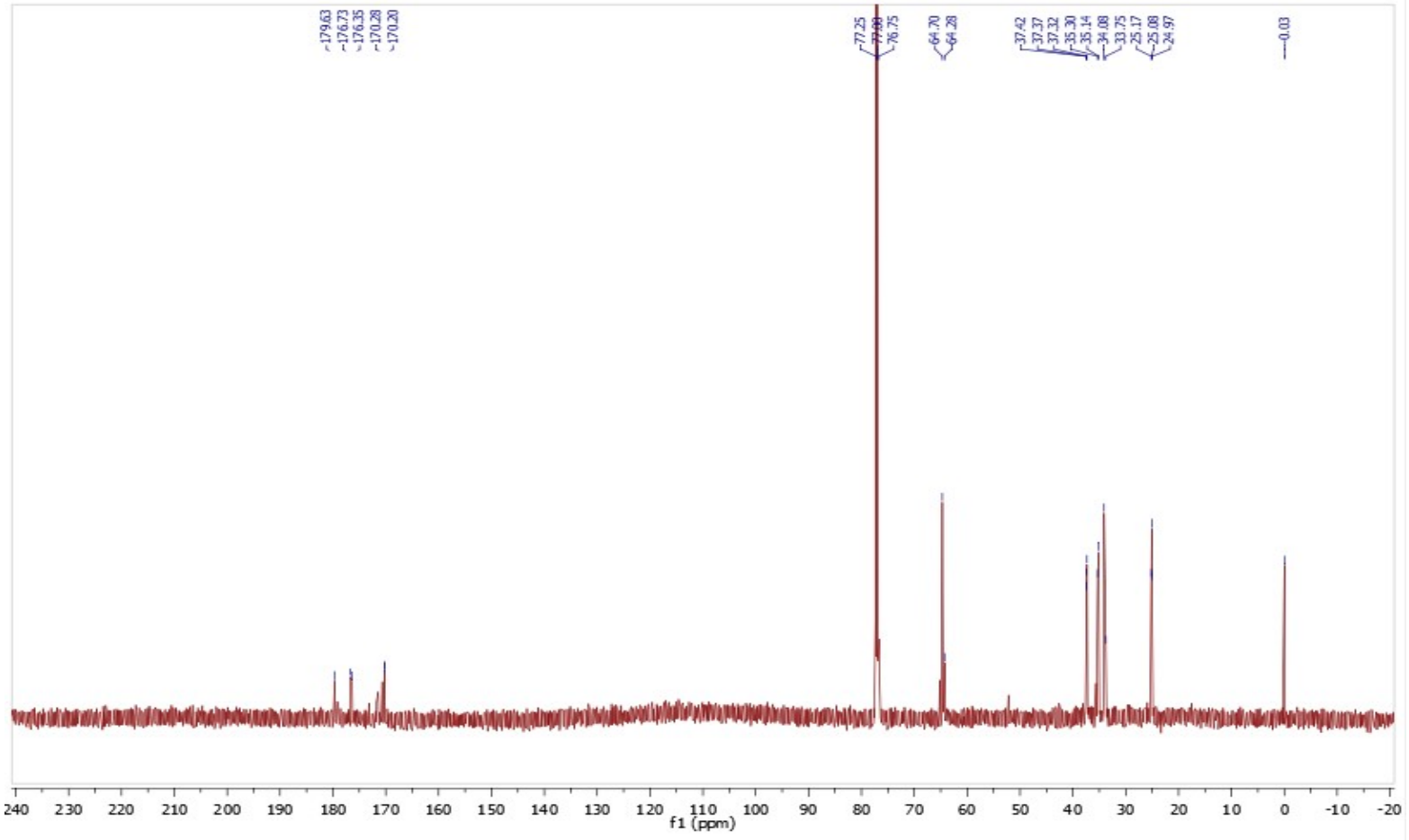


Figure **23**: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of the polyester **4b**.

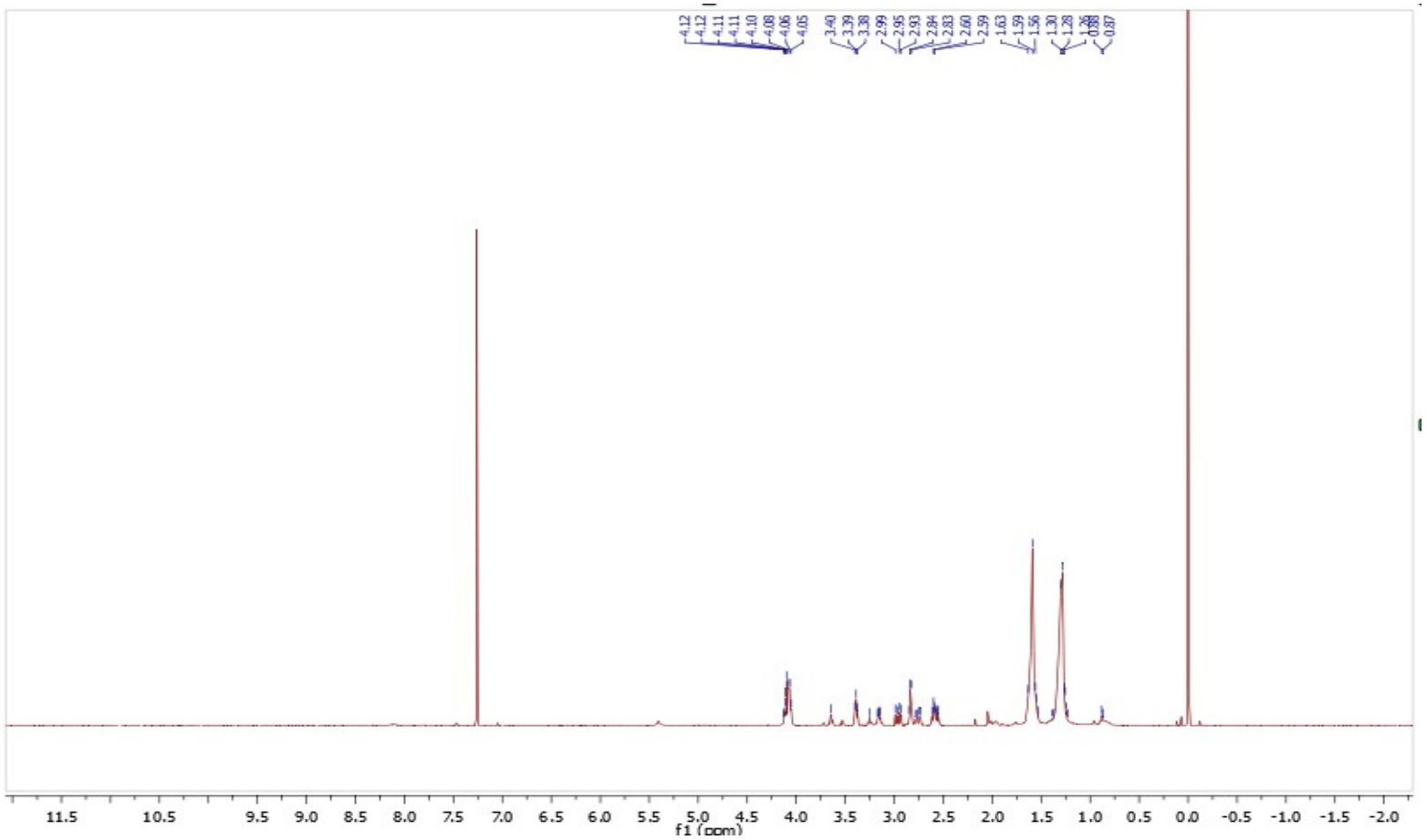


Figure **24**: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of the polyester **4c**.

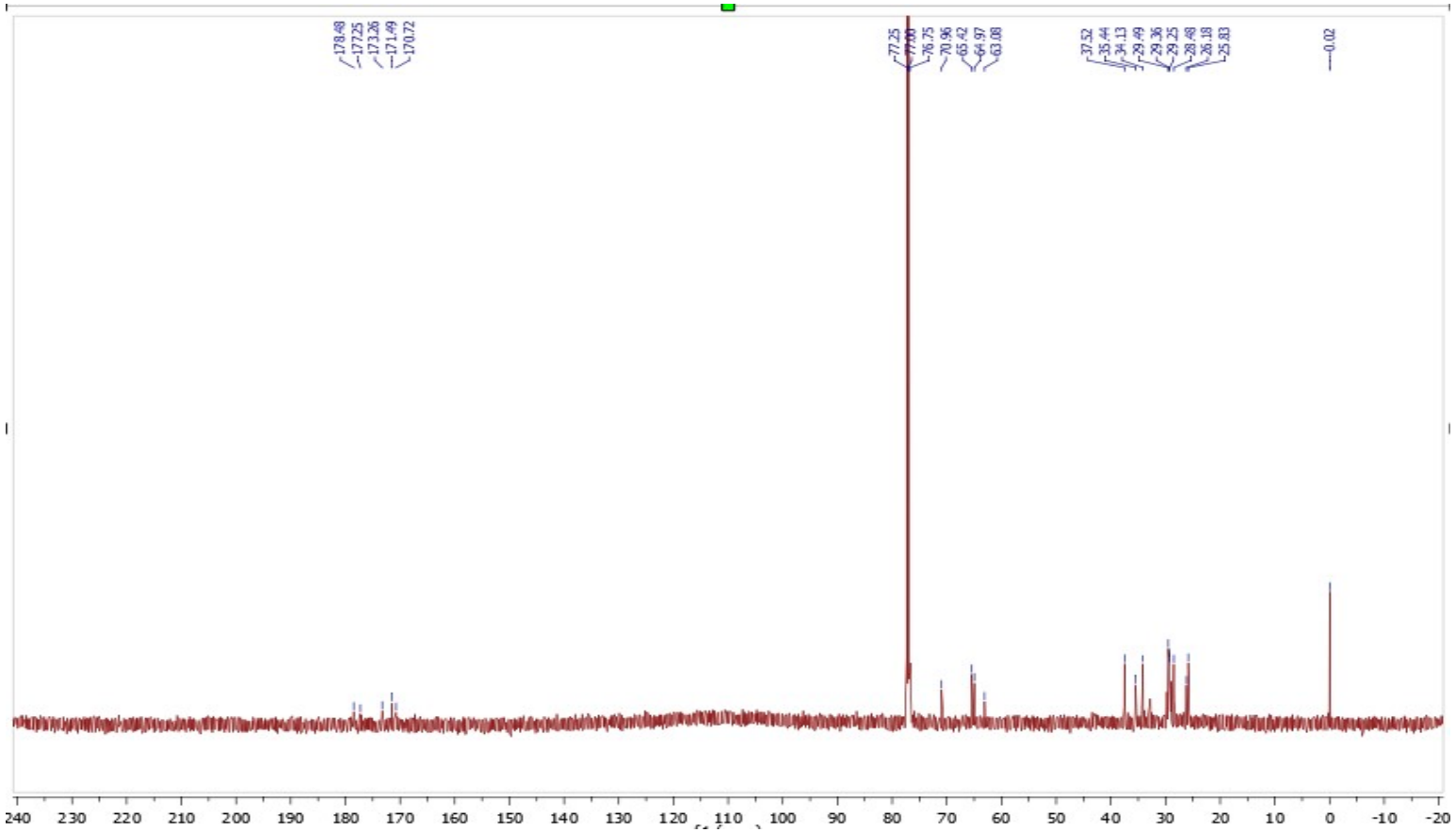


Figure **25**: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of the polyester **4c**.

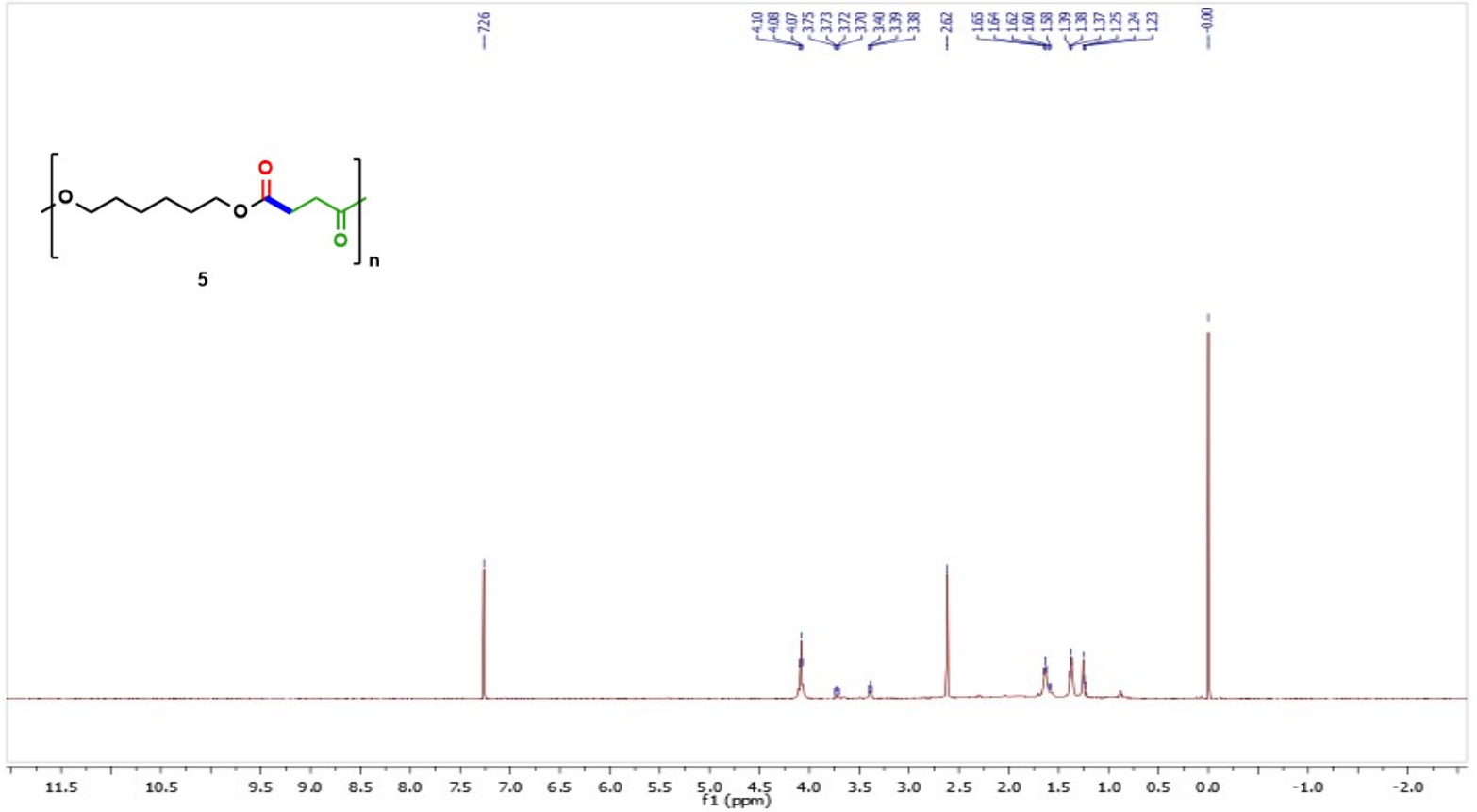


Figure **26**: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of the polyester **5**.

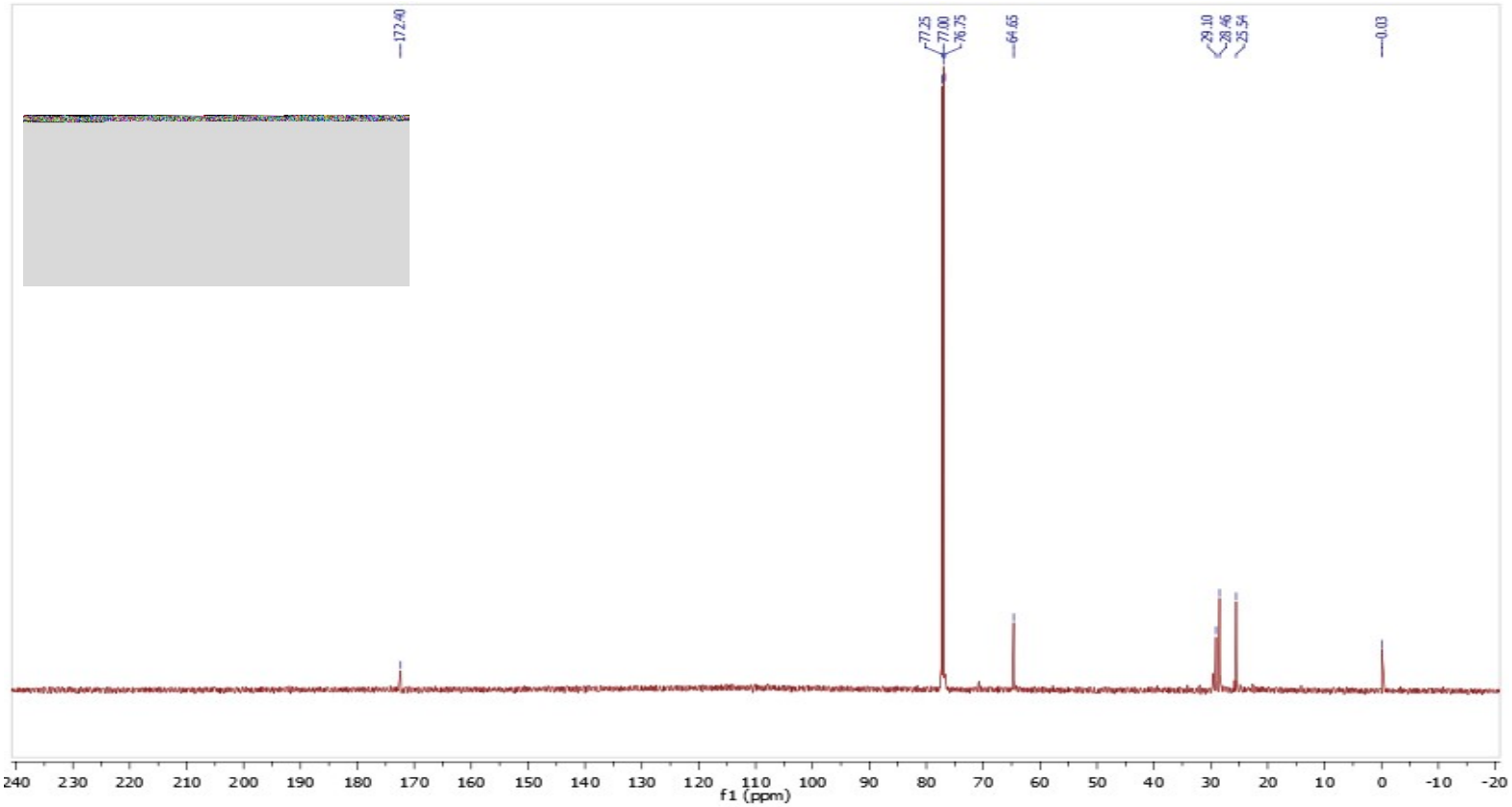


Figure **27**: ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of the polyester **5.**

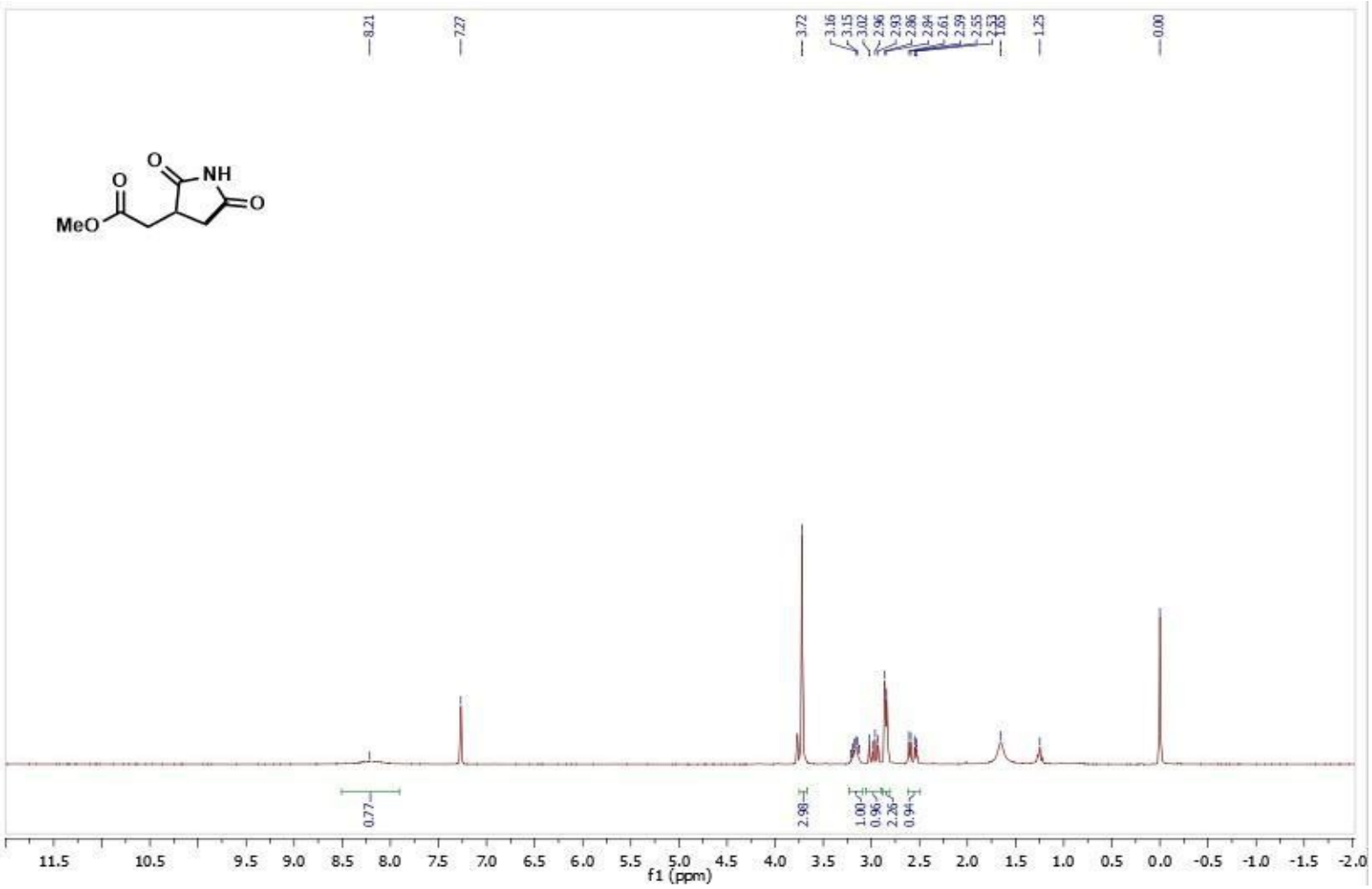


Figure **28**: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of the compound **I**.

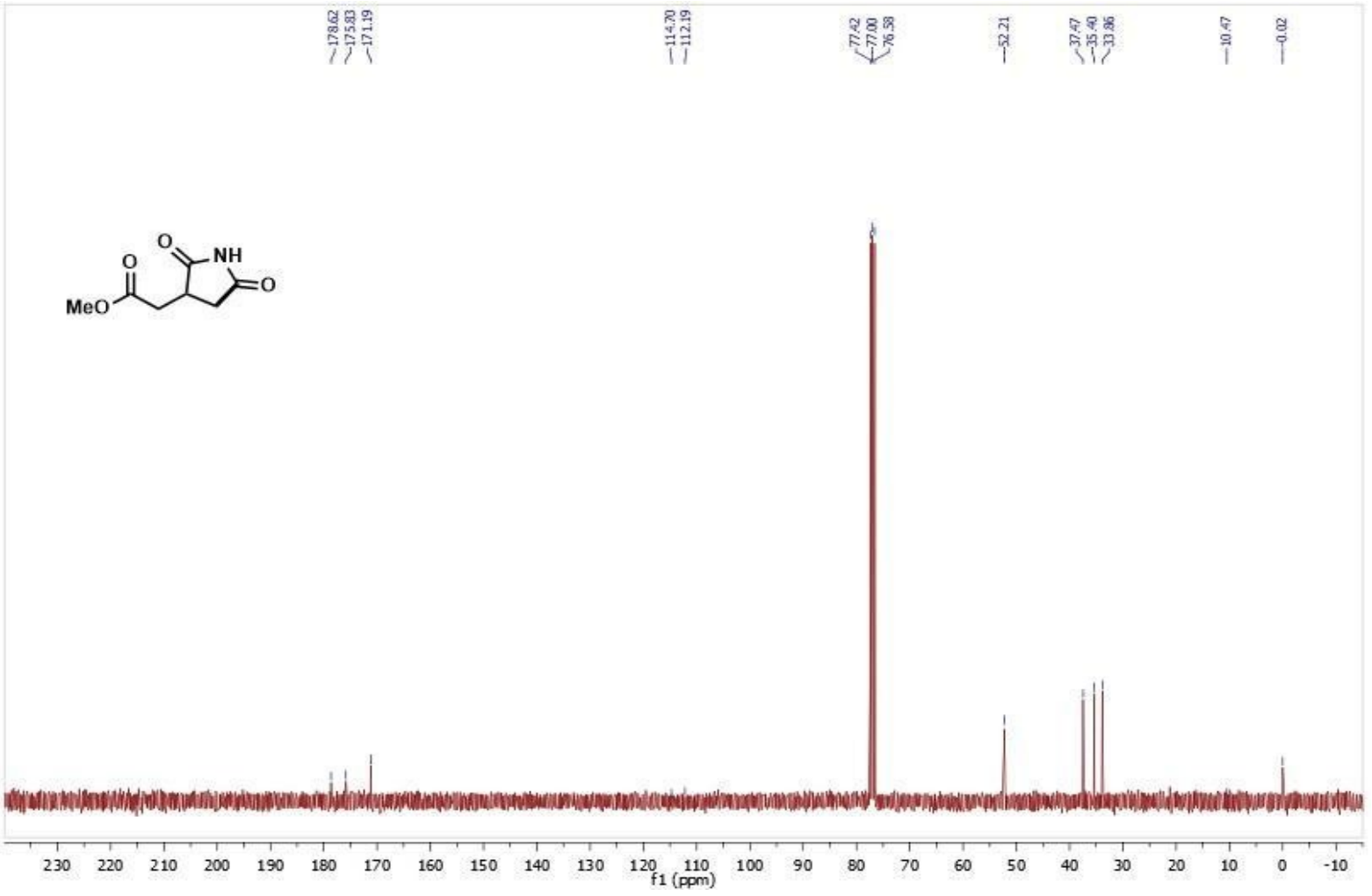


Figure **29**: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of the compound **I**.

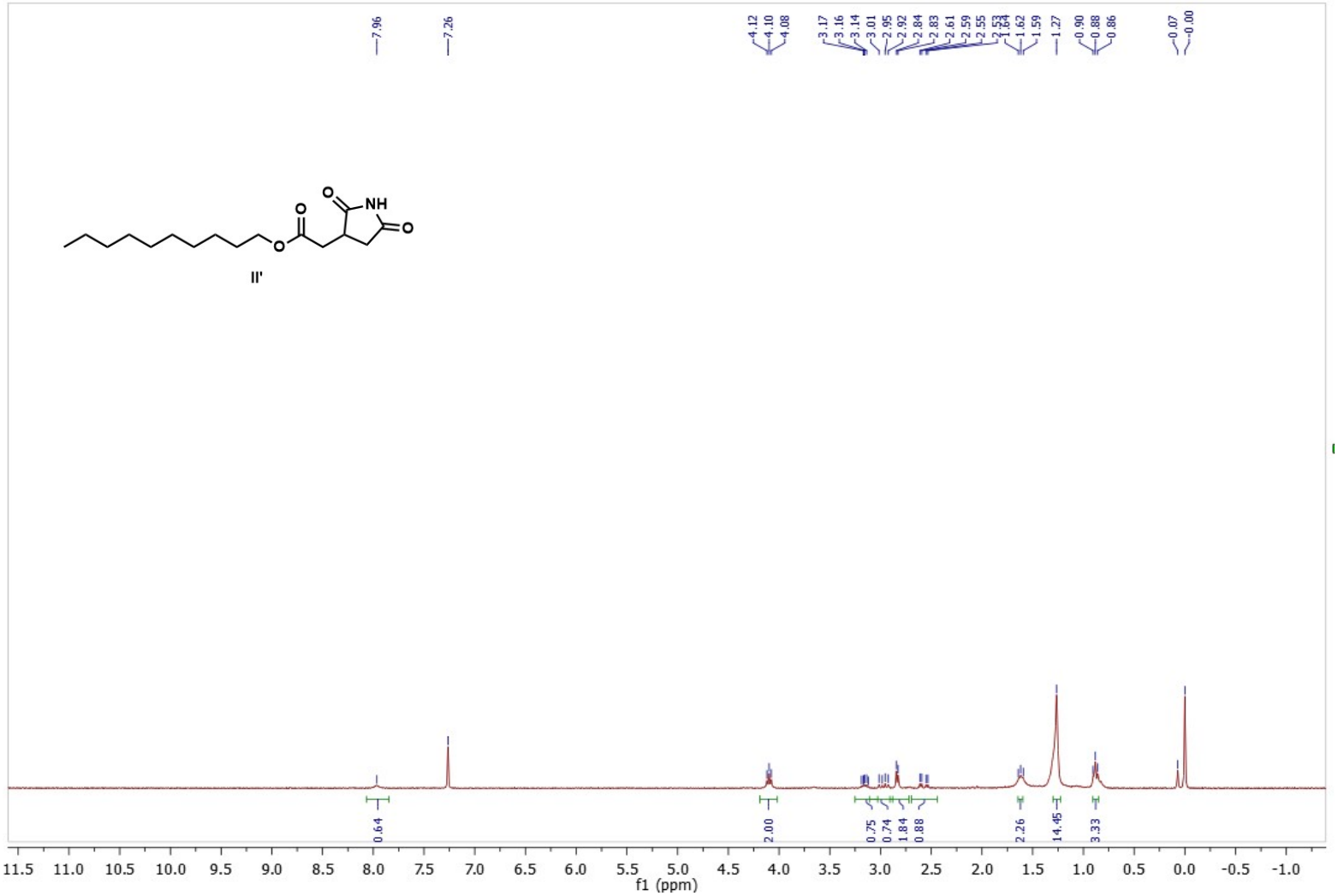


Figure **30**: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of the compound **II'**.

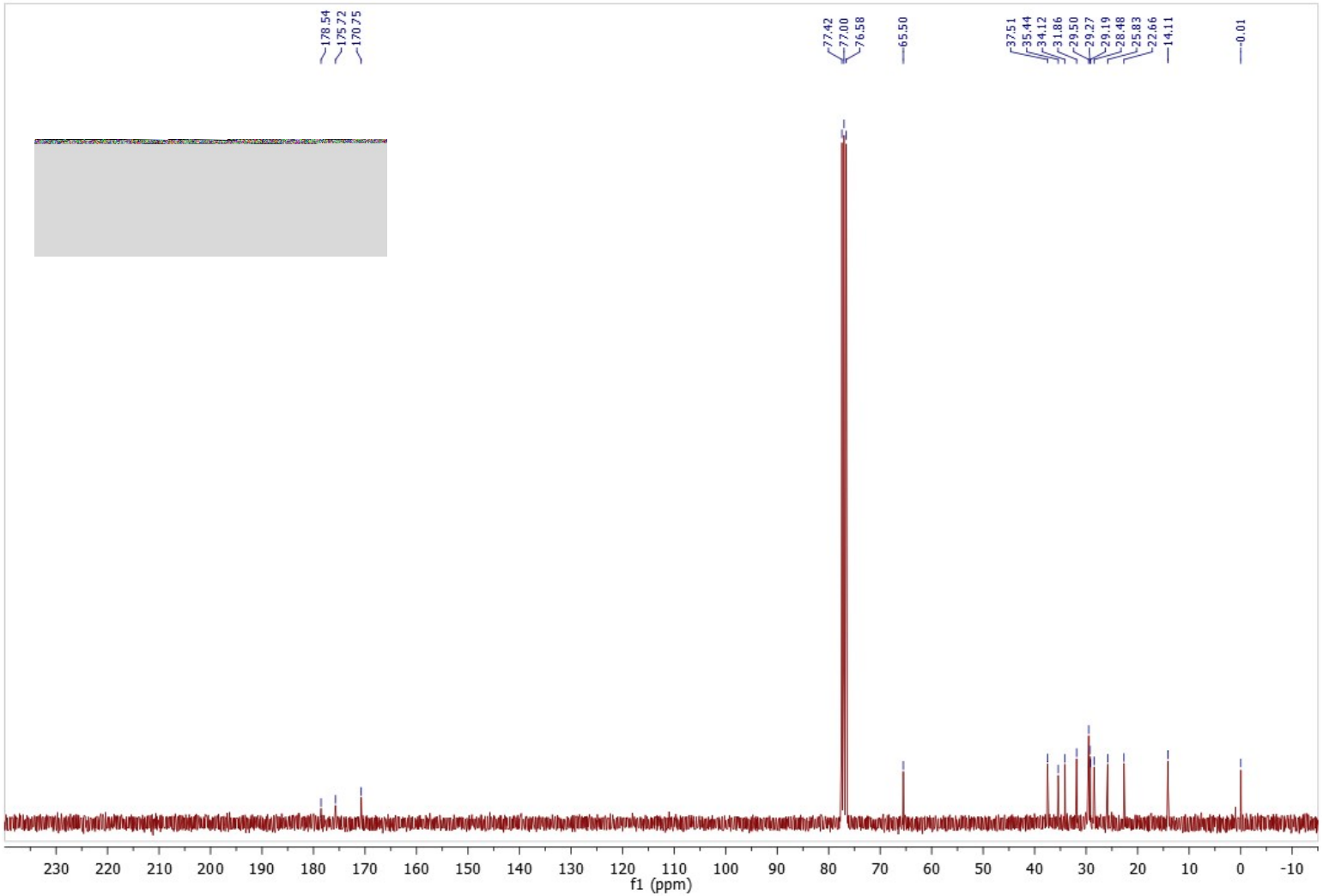


Figure **31**: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of the compound **II'**.

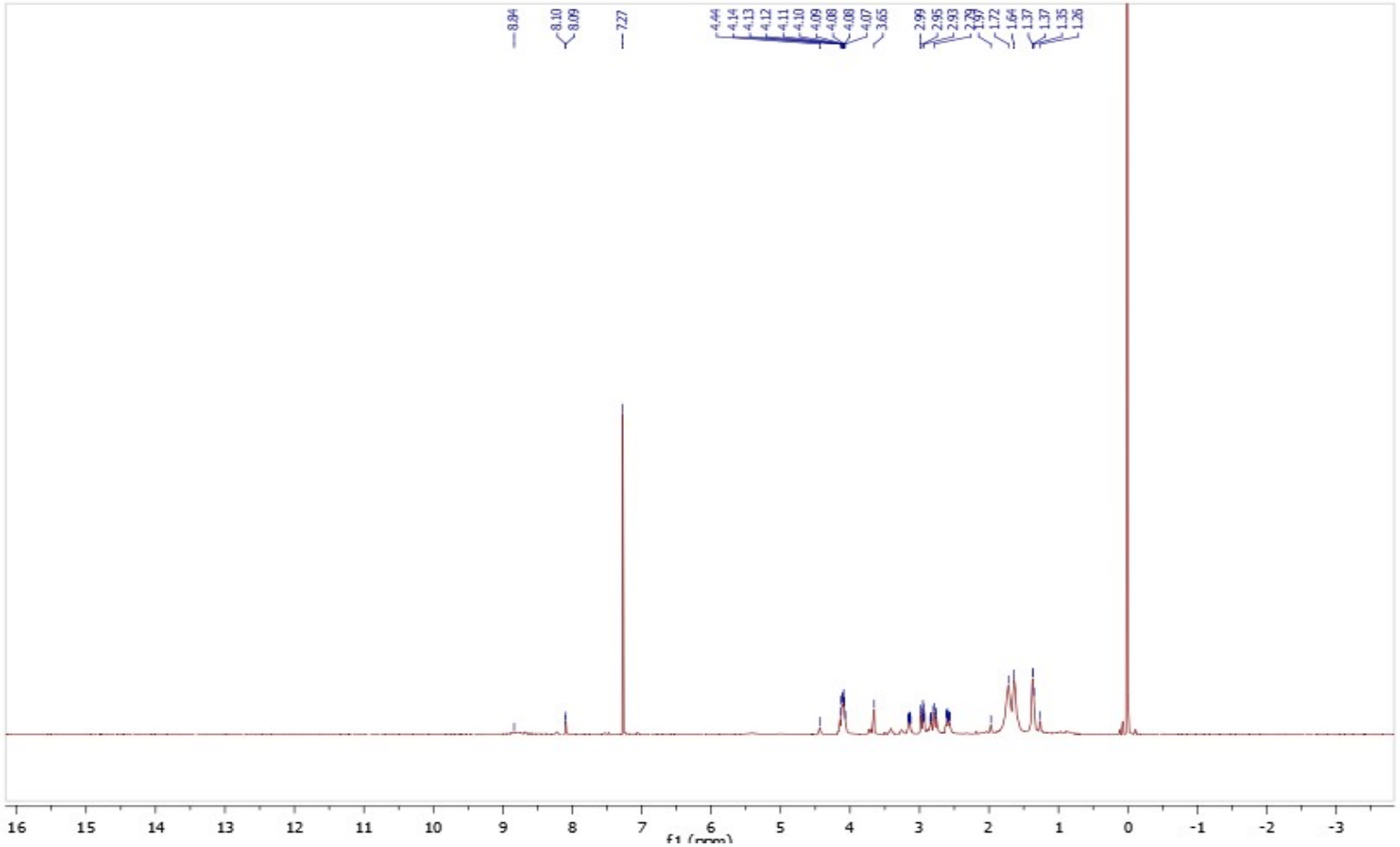


Figure **32**: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of the compound **IV**.

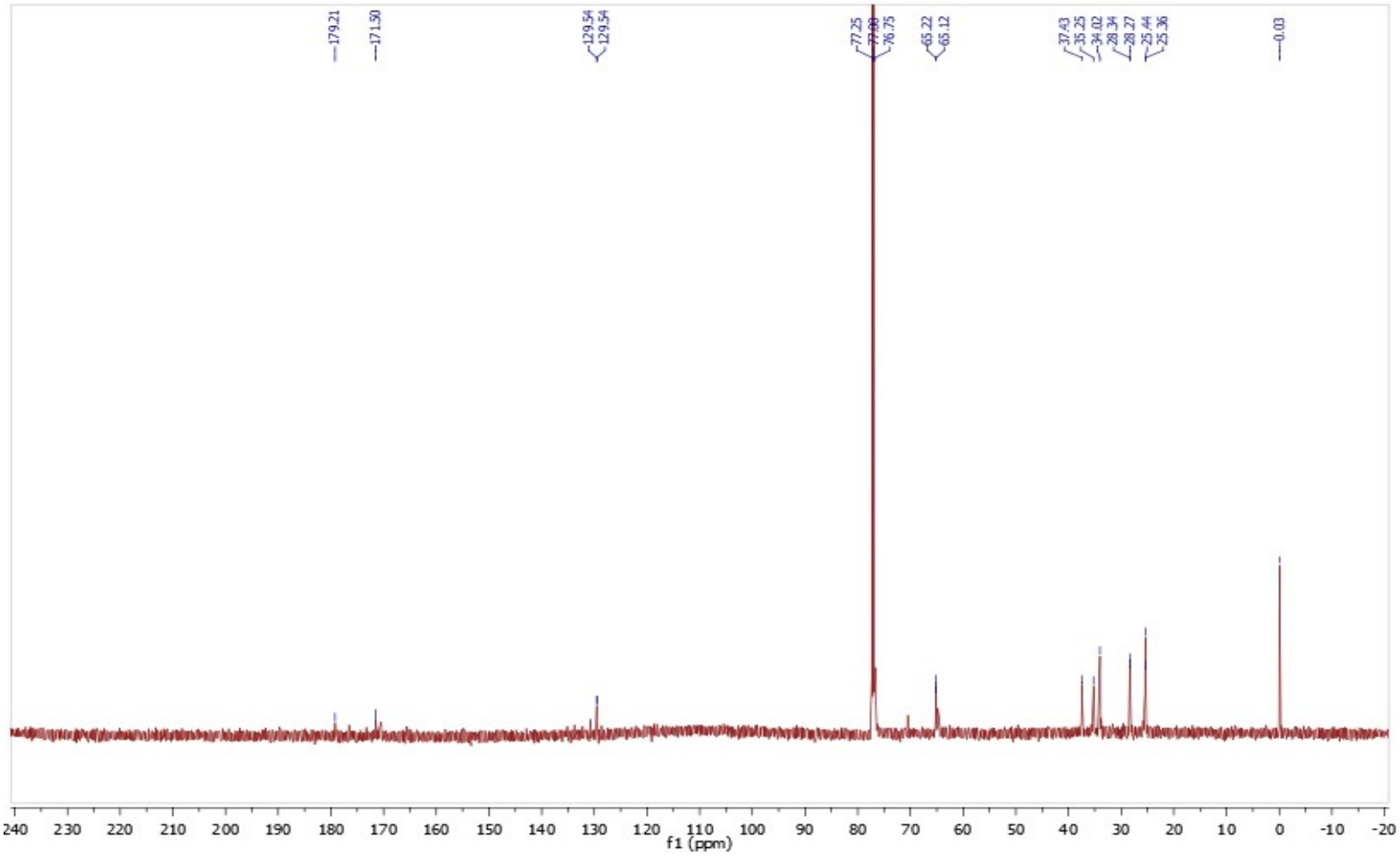


Figure **33**: ^{13} C NMR ($CDCCl_3$, 125 MHz) spectrum of the compound **IV**.

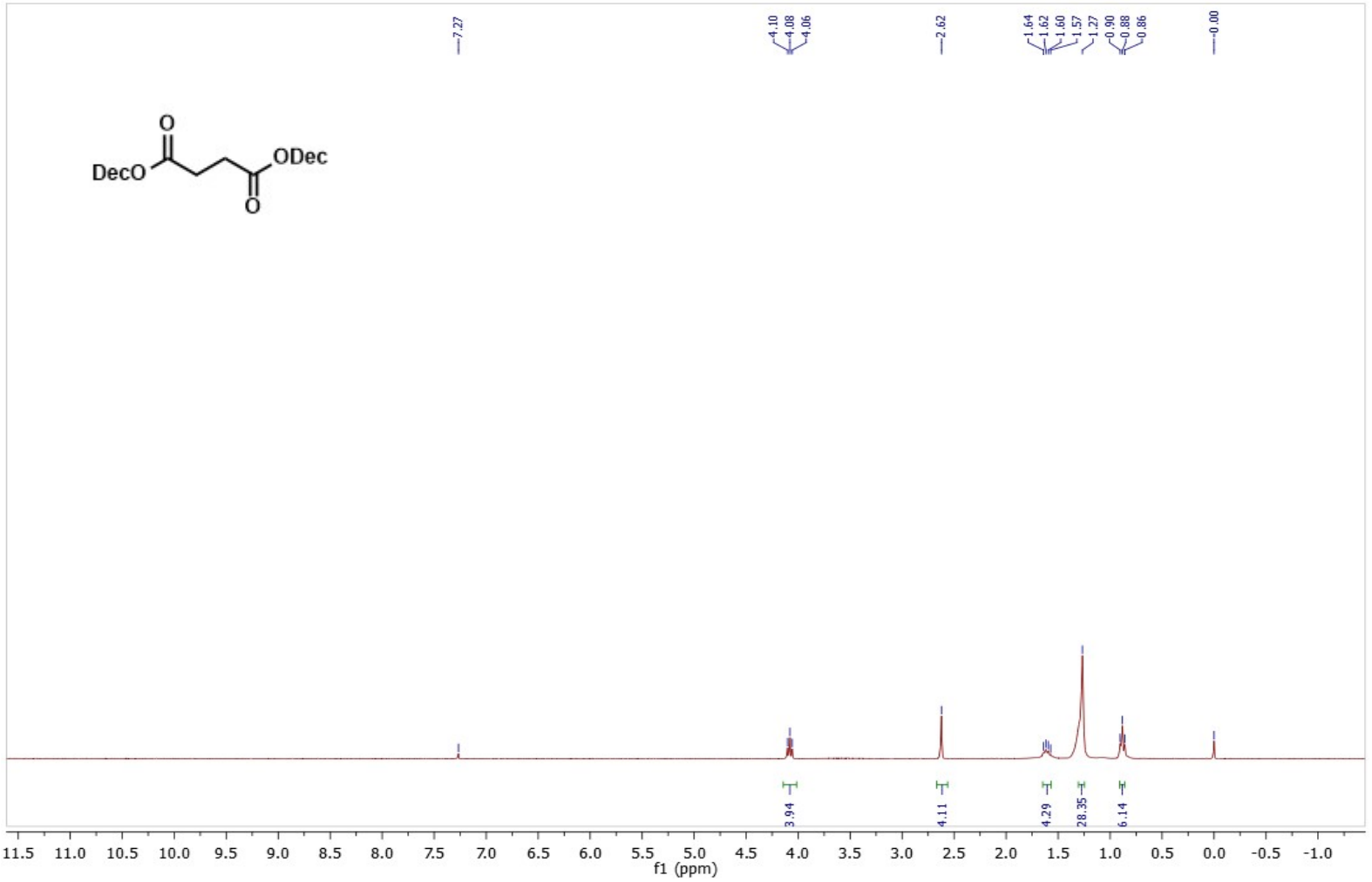


Figure **34**: ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of the compound **IIc**.

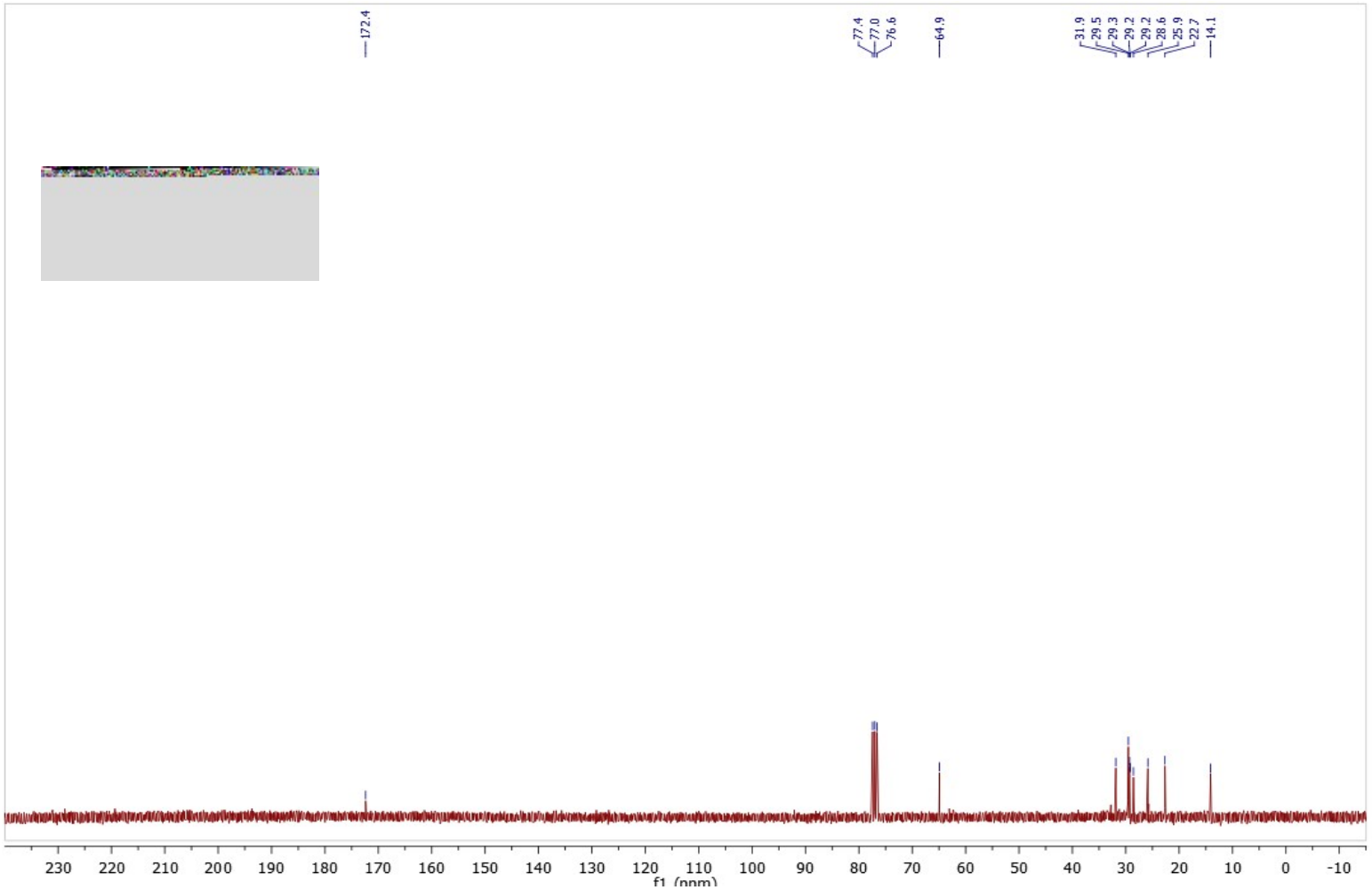


Figure **35**: ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of the compound **IIc**.

9. Absorbance spectra of the compounds

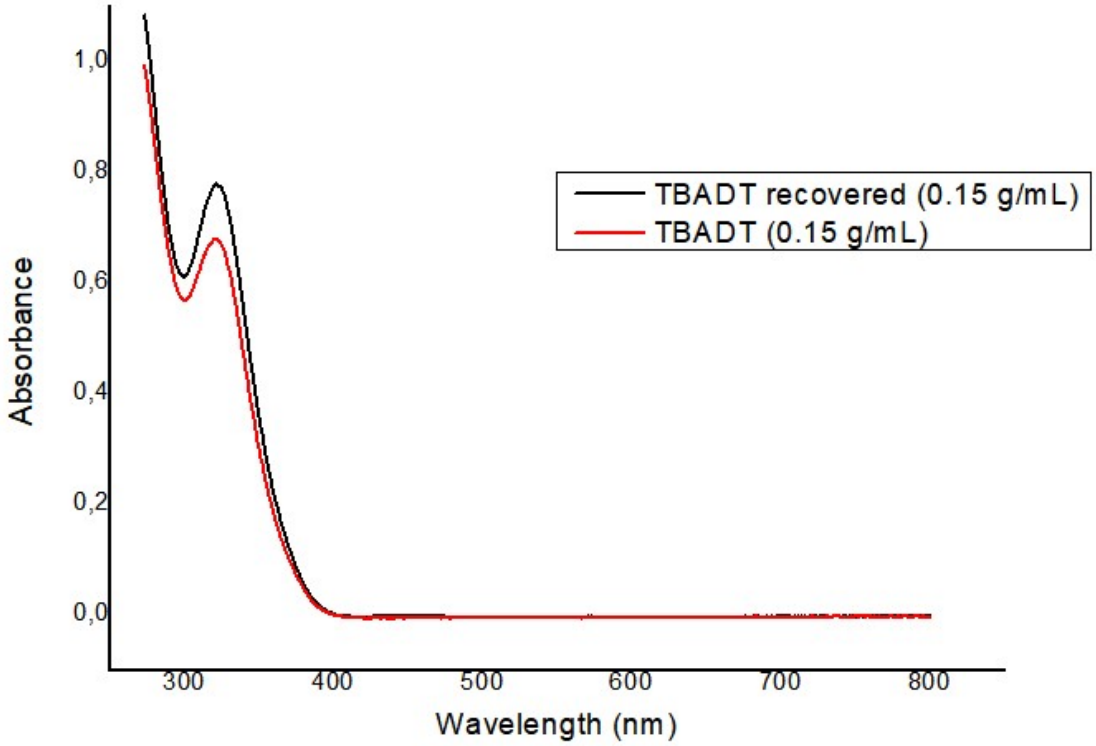


Figure **36**: Absorbance spectra of TBADT and the recovered TBADT (after the photocatalytic reaction) in acetonitrile.

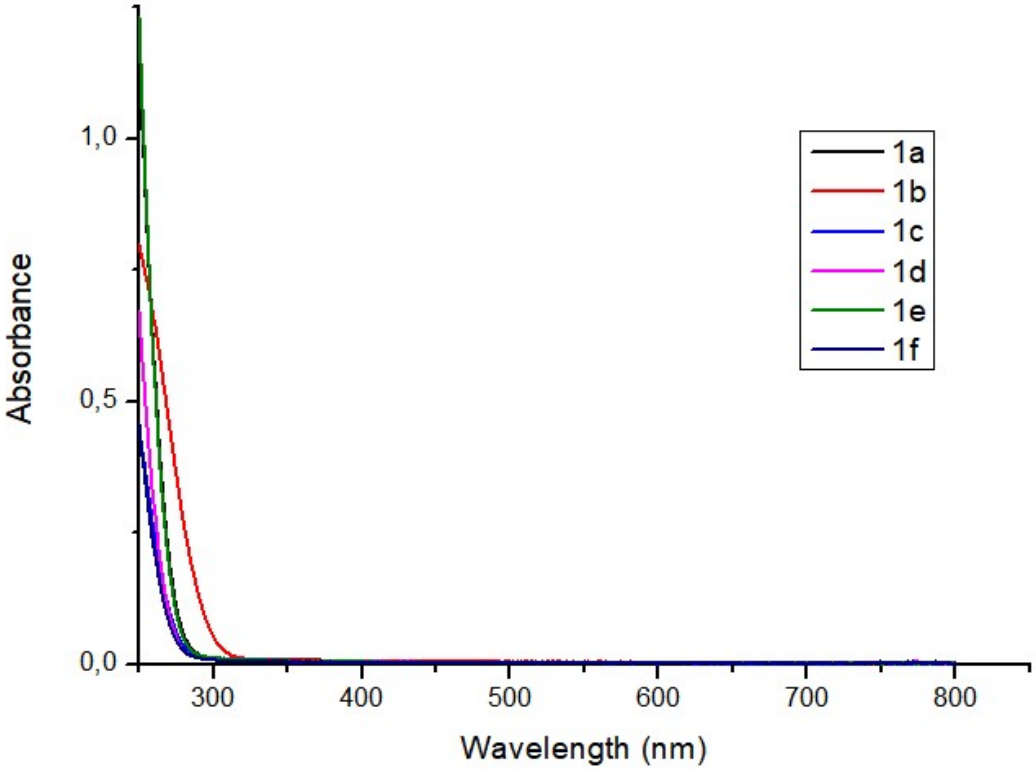


Figure **37**: Absorbance spectra of the acrylate ester **1** in acetonitrile.

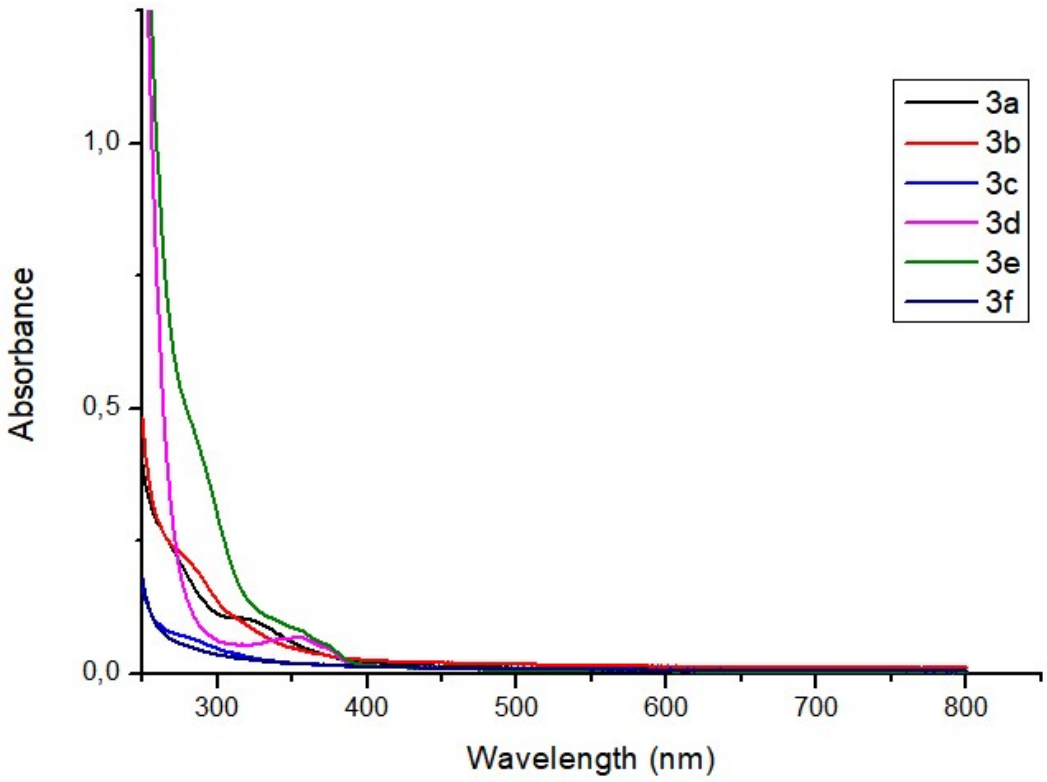


Figure **38**: Absorbance spectra of the monomers **3** in acetonitrile.

10. Thermal analysis of the polyesters

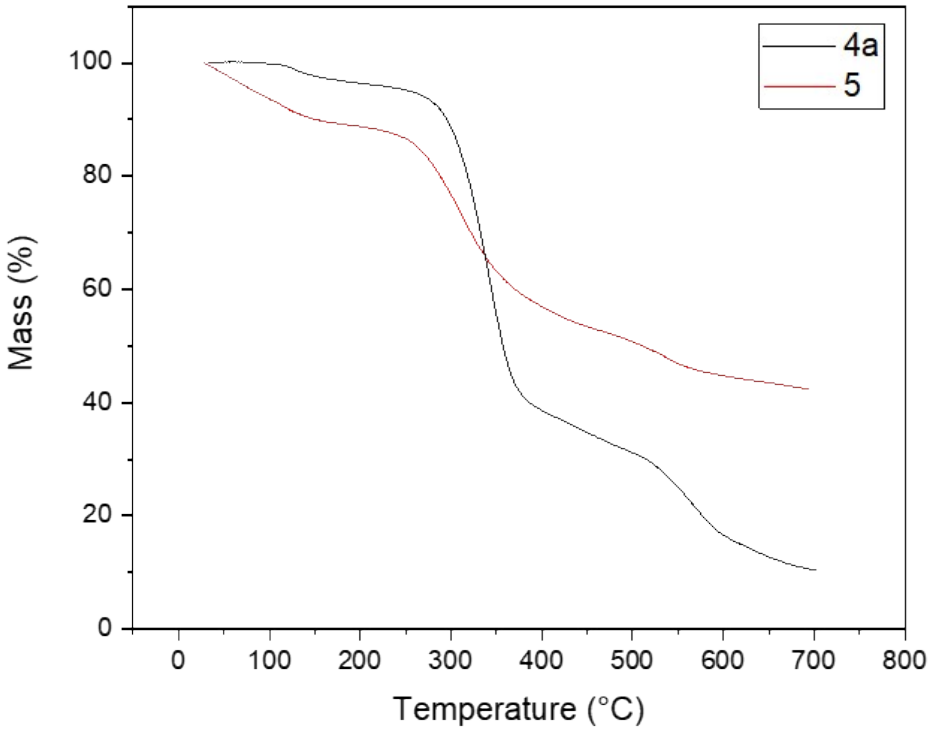


Figure **39**: Thermogram of the polyester **4a** and **5**.

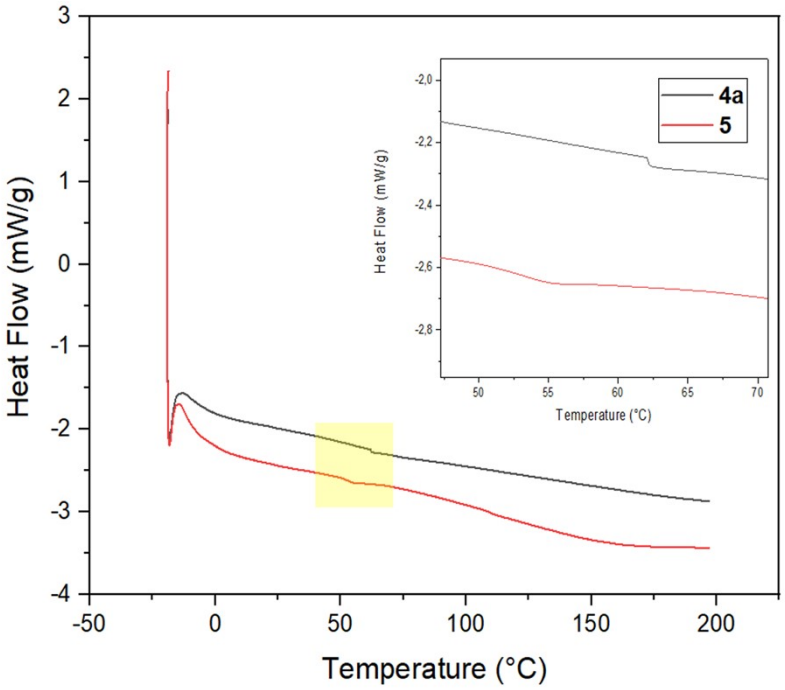


Figure 40: DSC thermogram of the polyesters **4a** and **5**. A zoom illustrates the region in which it is possible to identify the glass transition temperatures.

11. MALDI-TOF-MS spectra of the polyesters 4a'-5

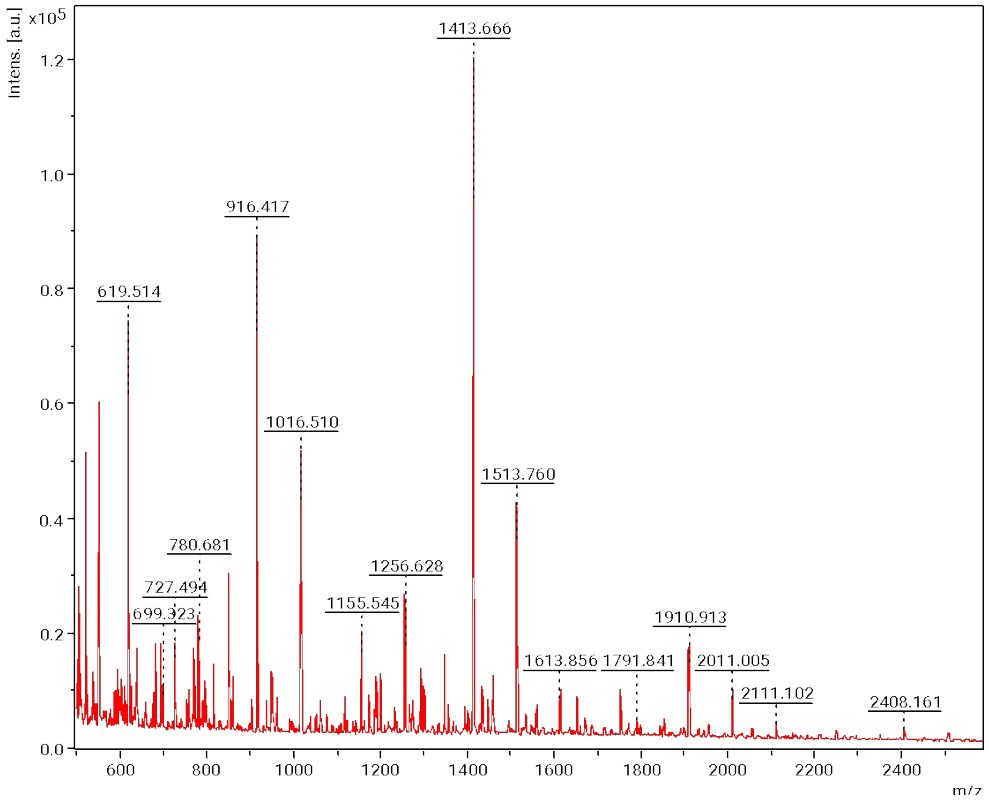
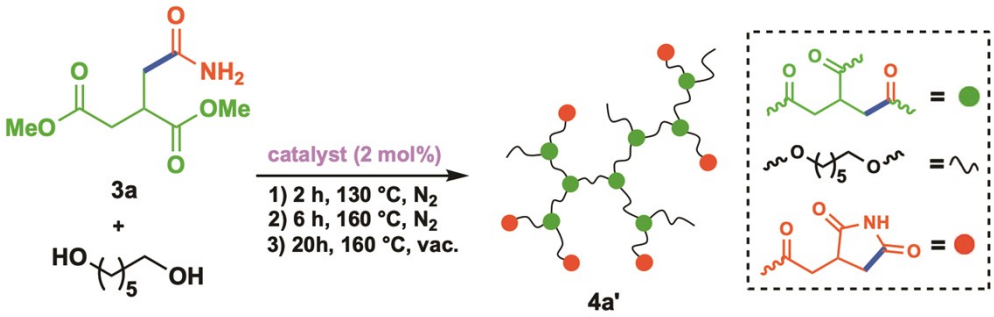


Figure **41**: MALDI-TOF-MS spectrum of the polyester **4a'** which was synthesized according to the equation below.



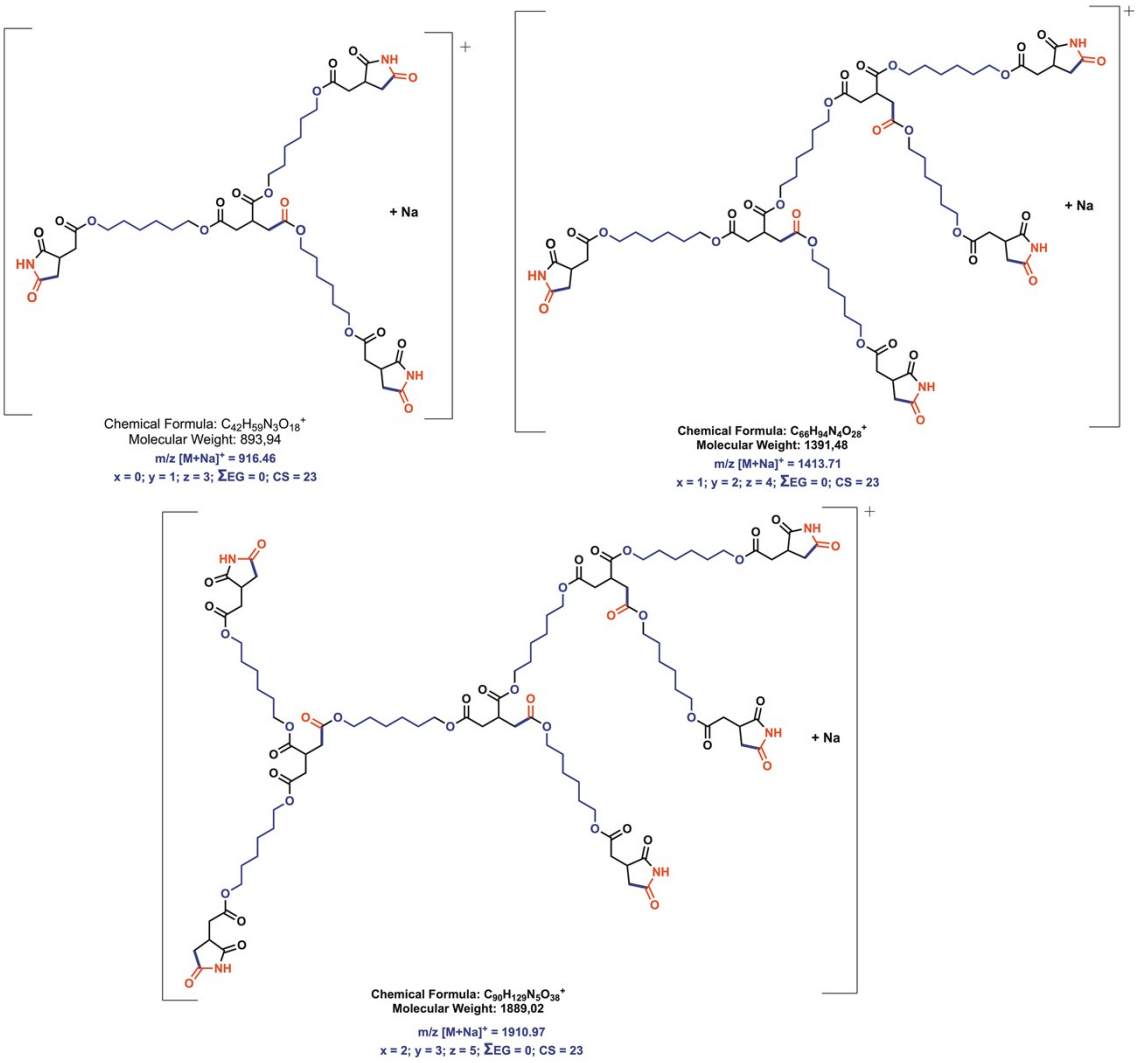


Figure **42**: Sodium adducts assigned for the polyester **4a'** in the MALDI-TOF Mass spectrum. Equation for Adduct m/z = 116.08*x* + 125.13*y* + 256.13*z* + **Σ***EG* + *CS*. (see Scheme 2, page 19, for an explanation of this equation)

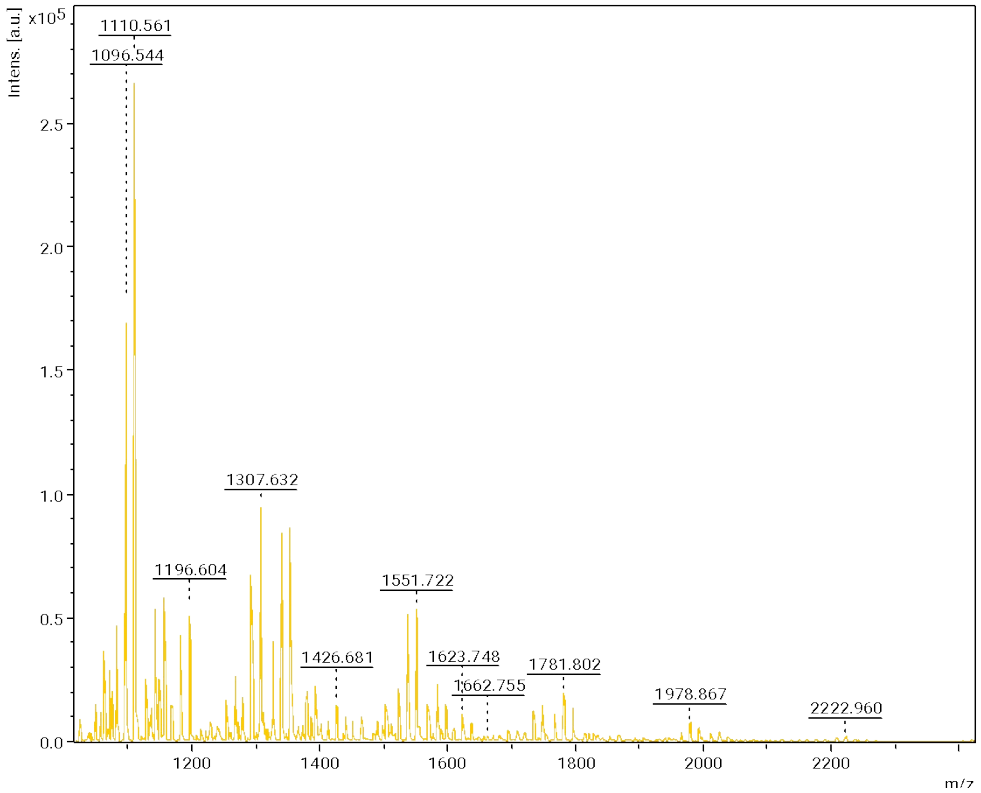
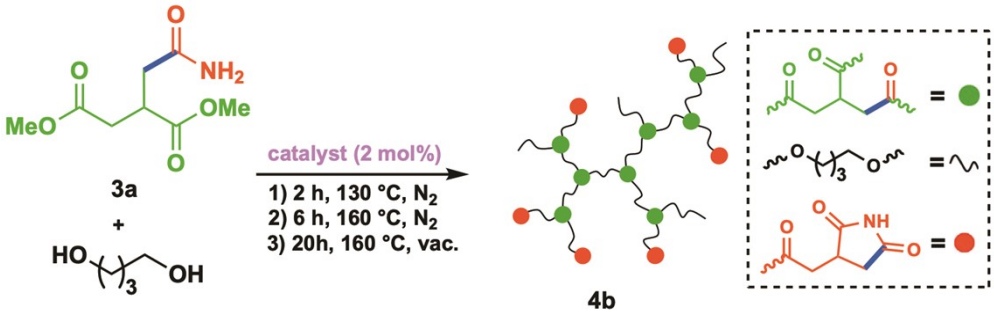


Figure **43**: MALDI-TOF-MS spectrum of the polyester **4b** which was synthesized according to the equation below.



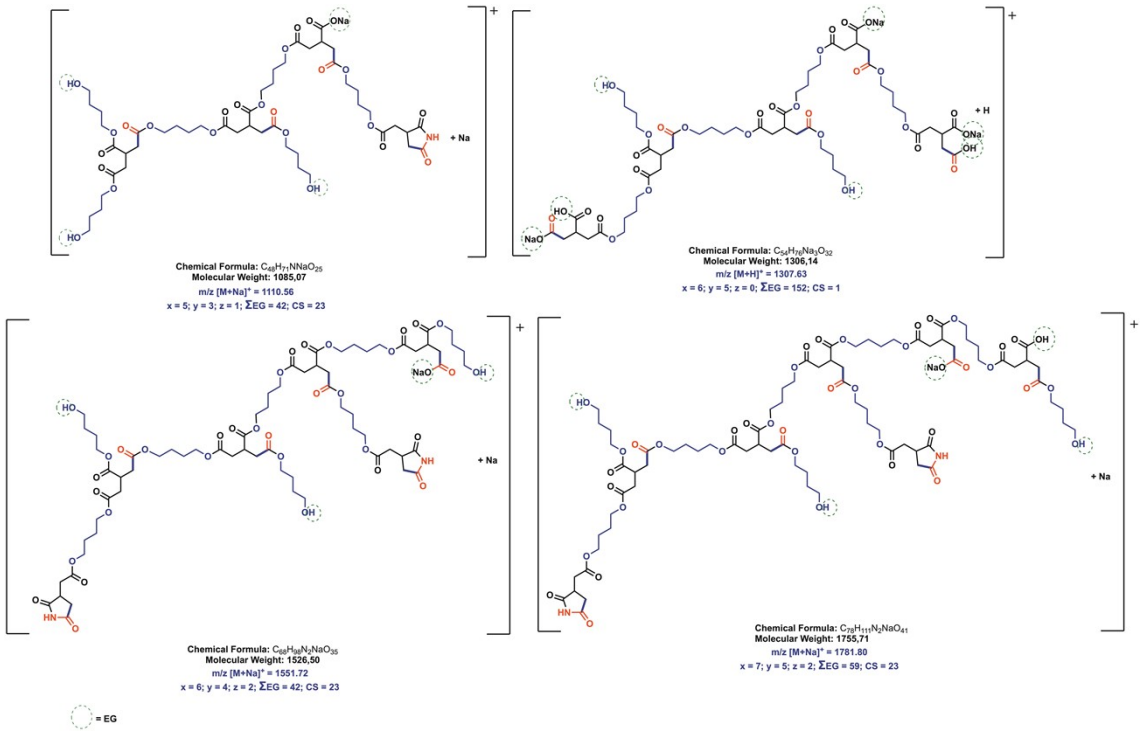


Figure **44**: Sodium adducts and protonated ion assigned for the polyester **4b** in the MALDI-TOF Mass spectrum. Equation for Adduct m/z = 88.11x + 125.13y + 228.22z + **Σ***EG* + *CS* (see Scheme 2, page 19, for an explanation of this equation).

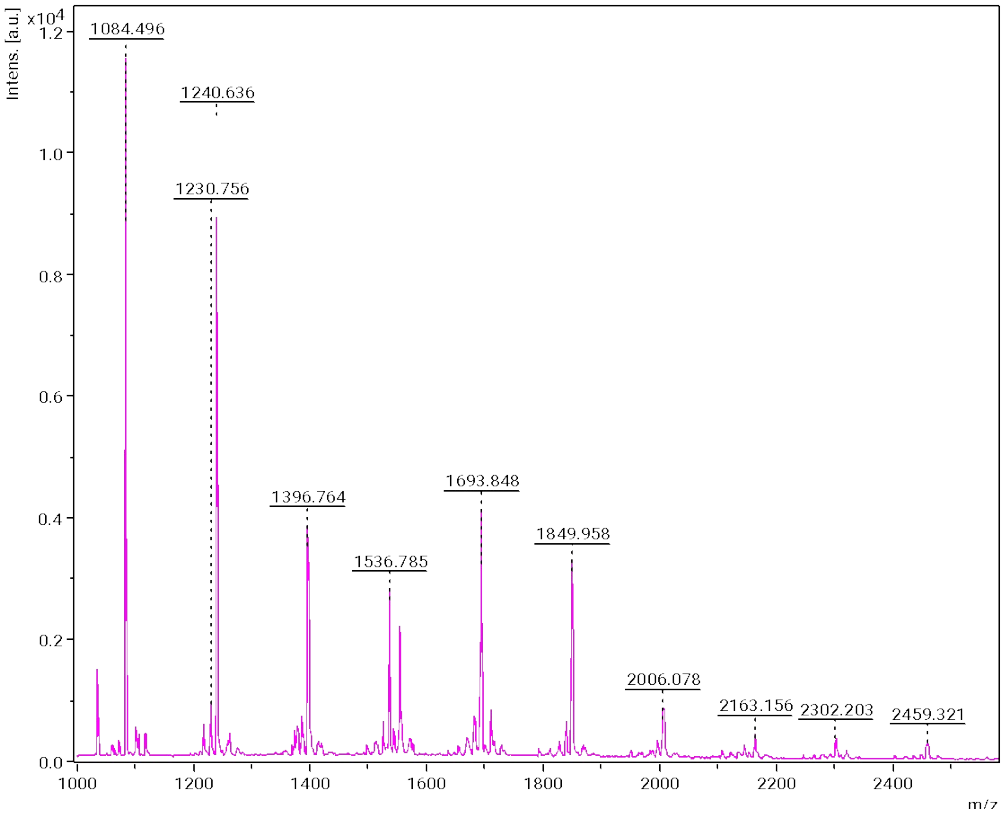
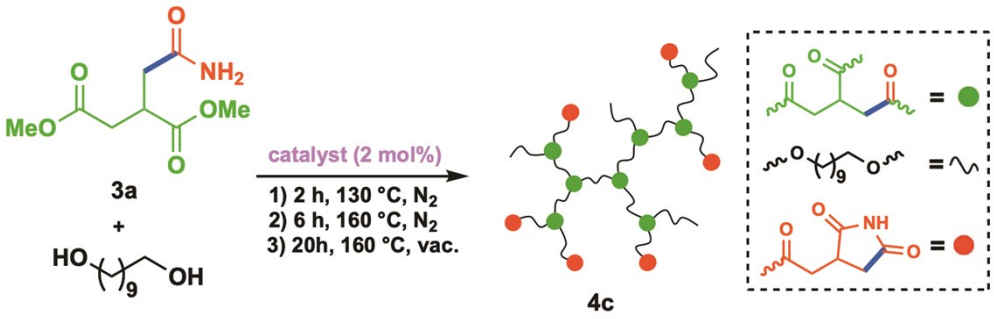


Figure **45**: MALDI-TOF-MS spectrum of the polyester **4c** which was synthesized according to the equation below.



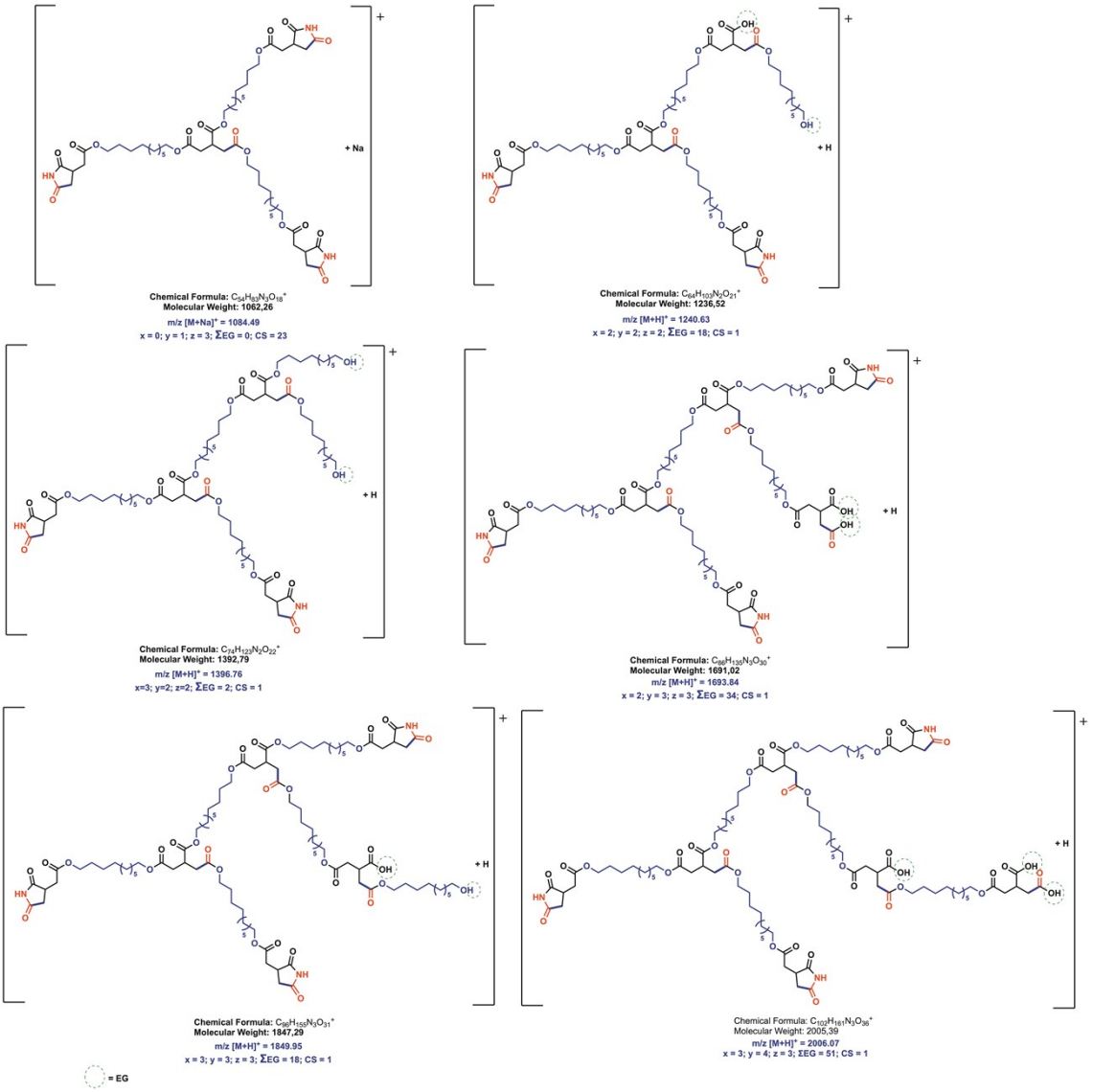


Figure 4**6**: Sodium adduct and protonated ions assigned for the polyester **4c** in the MALDI-TOF Mass spectrum. Equation for Adduct m/z = 172.27x + 125.13y + 312.39z + **Σ***EG* + *CS* (see Scheme 2, page 19, for an explanation of this equation).

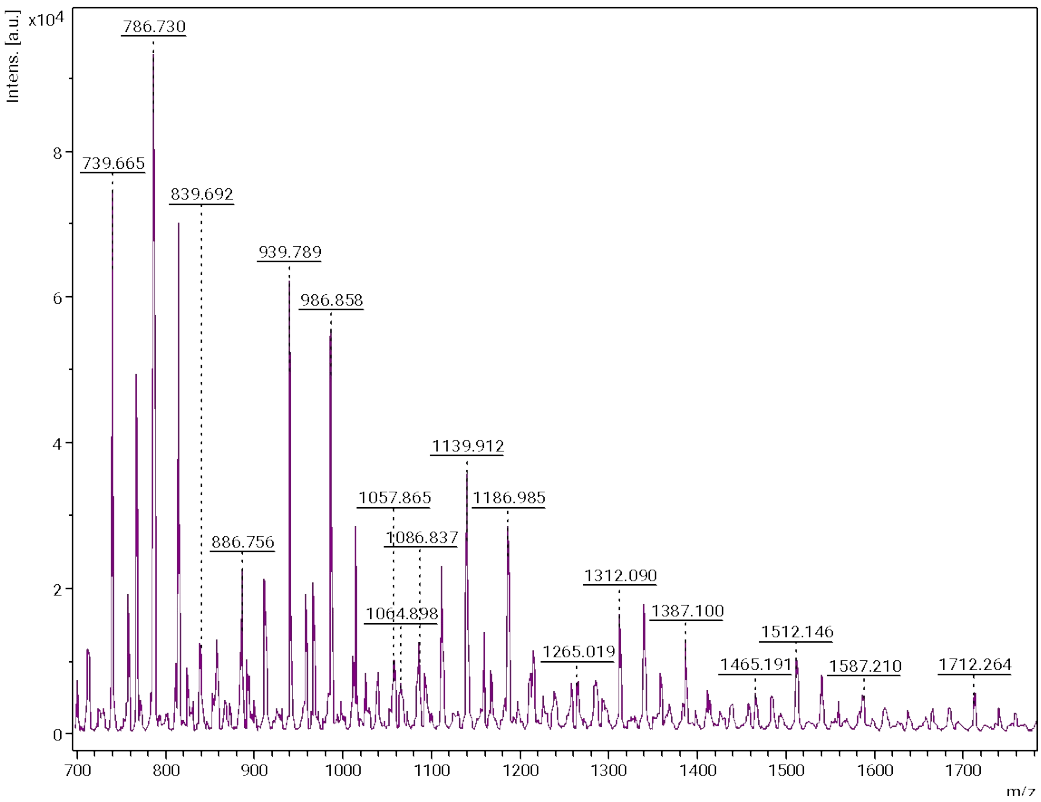
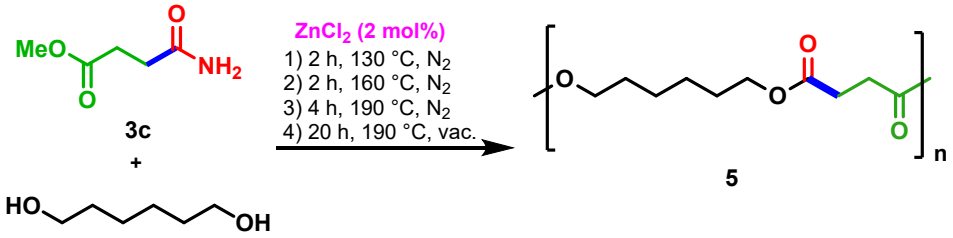


Figure **47**: MALDI-TOF-MS spectrum of the polyester **5** which was synthesized according to the equation below.



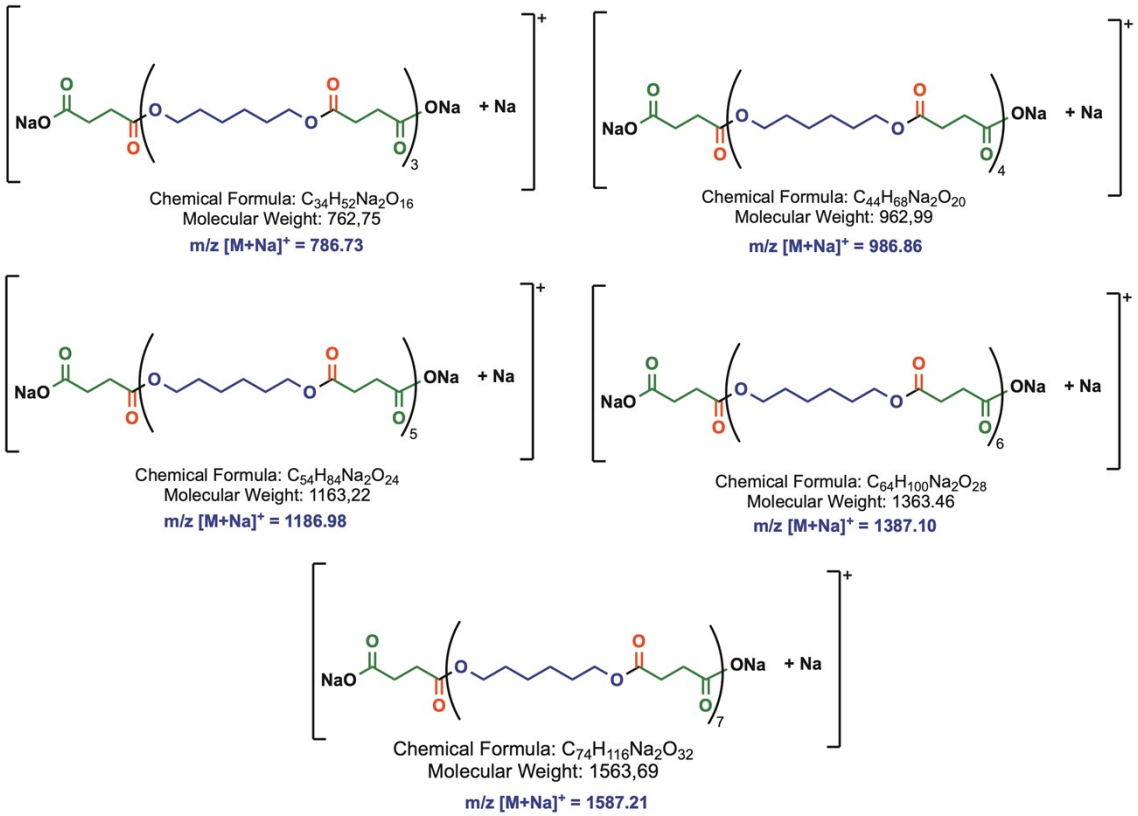


Figure **48**: Sodium adducts assigned for the polyester **5** in the MALDI-TOF Mass spectrum.

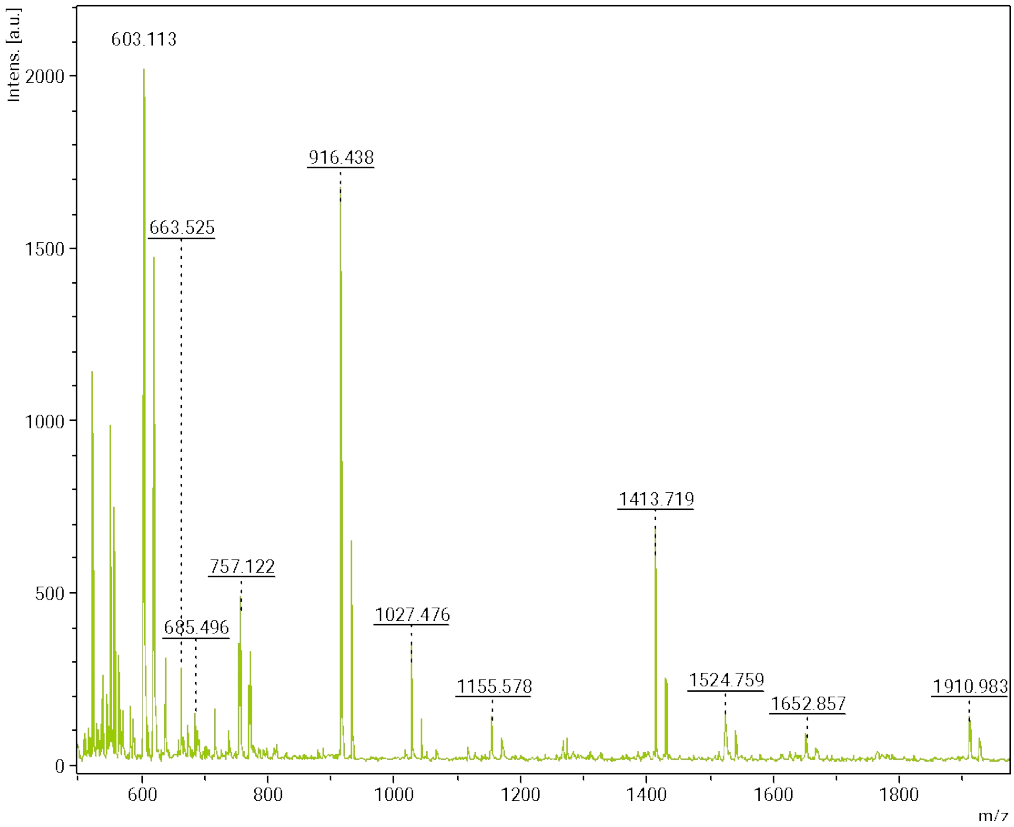


Figure **49**: MALDI-TOF-MS spectrum of the polyester **IV** which was synthesized according to the equation below.

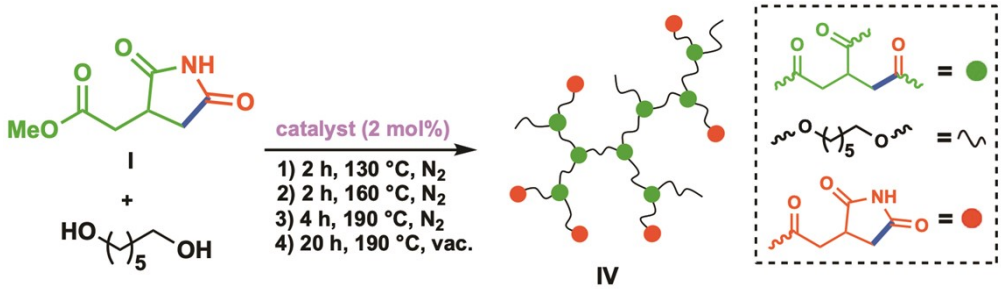


Figure **50**: Sodium adducts assigned for the polyester **IV** in the MALDI-TOF Mass spectrum. Equation for Adduct m/z = 116.08*x* + 125.13*y* + 256.13*z* + **Σ***EG* + *CS* (see Scheme 2, page 19, for an explanation of this equation).

12. GPC chromatograms of the polyesters

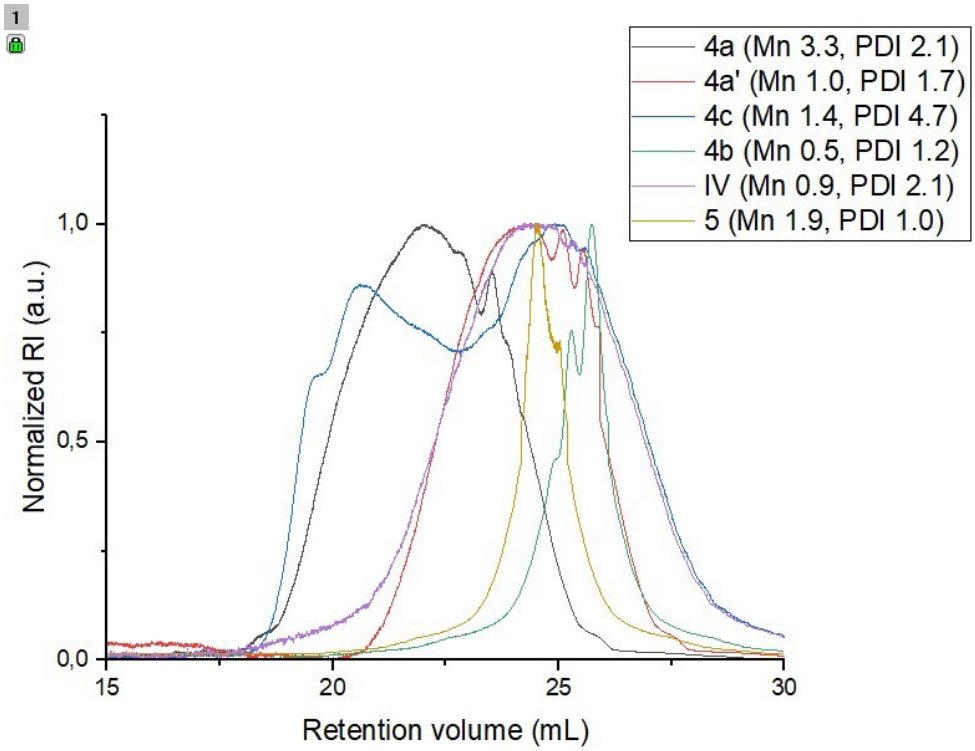


Figure 51: GPC chromatograms illustrating the profile of molar mass distribution for different polymers.

13. References

[1] D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, 2nd ed. Oxford: Pergamon Press; **1989**.

[2] D. Dondi, M. Fagnoni and A. Albini, *Chem. Eur. J.* 2006, **12**, 4153 – 4163.

[3] Y. Bernhard, S. Pellegrini, T. Bousquet, A. Favrelle, L. Pelinski, F. Cazaux, V. Gaucher, P. Gerbaux and P. Zinck, *ChemSusChem*, 2019, **12**, 3370-3376.

[4] R. Casarano, D. F. S. Petri, M. Jaffe and L. H. Catalani, *J. Braz. Chem. Soc.,* 2009, **20**, 1414-1424.