Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

β-Methyl-δ-valerolactone-containing Thermoplastic Poly(ester-amide)s: Synthesis, Mechanical Properties, and Degradation Behavior

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I. General Experimental Information

Materials

Solvents: All solvents were used as received from the manufacturer. Acetone (Certified ACS) for recrystallizations was purchased from Fisher. Absolute ethanol was purchased from Pharmco-AAPR; for use with sodium ethoxide and diethyl malonate, the ethanol was treated with sodium and distilled directly into the flask used for the reaction. Chloroform was purchased from Fisher. Chloroform used for polymerization reactions was washed several times with H_2O, dried over $MgSO_4$ and filtered, and further dried by distillation from CaH_2 before use (chloroform purified in this manner was stored under a N_2 atmosphere in a glovebox). Pyridine used for polymerization reactions was dried by distillation from CaH_2 before use (pyridine purified in this manner was stored in a Schlenk flask over 4Å molecular sieves).

Reagents for monomer synthesis: β-Methyl-δ-valerolactone (MVL) was prepared according to a previously reported procedure.[1] Ethylenediamine, 1,4-diaminobutane, and 1,6-diaminohexane were purchased from Sigma-Aldrich and used as received. Aliphatic acid chlorides were prepared from the corresponding acids by heating with 3 equivalents of thionyl chloride (Aldrich); the crude acid chlorides were purified by two sequential distillations and stored in a Schlenk flask under N_2. HBr in acetic acid (33% w/w) was purchase from Aldrich and used as received. Sulfuric acid was purchased from Macron Chemicals and used as received. Diethyl malonate (99%) was purchased from Lancaster and used as received. Sodium (in kerosene) was purchased from Aldrich and cut into appropriately sized pieces before use. Hydrochloric acid (37%) was purchased from Aldrich and used as received.

Reagents for polymer synthesis: *N*,*N*-Dimethylaminopyridine (DMAP) was purchased from Aldrich and used as received.

Instrumental Methods

Nuclear magnetic resonance spectroscopy (NMR): Spectra were collected on a Bruker Avance III or Avance II 500 (500 MHz) or a Bruker Avance III 400 (400 MHz) spectrometer. Chemical shifts for ^1H NMR in $CDCl_3$ and d_6-DMSO are referenced to $CHCl_3$ (7.27 ppm) and $CHD_2(S{=}O)CD_3$ (2.50 ppm), respectively. Chemical shifts for ^{13}C NMR in $CDCl_3$ and d_6-DMSO are referenced to $\mathit{C}DCl_3$ (77.00 ppm) and $\mathit{C}D_3(S{=}O)\mathit{C}D_3$ (39.52 ppm), respectively. Resonances are reported in the following format: chemical shift in ppm [multiplicity, coupling constant(s) in Hz, integral, and assignment]. ^1H NMR assignments are indicated by the environment in which the proton resides (e.g., $C\mathit{H}_aH_b$).

The poly(ester-amide)s were soluble in DMSO upon warming. The samples were dissolved and allowed to cool before then collecting the NMR spectra.

IR spectroscopy (IR): IR spectra were recorded with a Bruker Alpha Platinum ATR-FTIR instrument that uses a diamond single bounce crystal. The data are reported as the average of 32 scans.

Thermogravimetric analysis (TGA): Performed on a TA instruments Q-500, under an atmosphere of nitrogen, using a heating rate of 10 °C/min. Sample sizes were between 8 and 15 mg.

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(1) Zhang, J.; Li, T.; Mannion, A. M.; Schneiderman, D. K.; Hillmyer, M. A.; Bates, F. S. *ACS Macro Lett.* **2016**, *5*, 407−412.

Differential scanning calorimetry (DSC): Differential scanning calorimetry data were collected on a TA instruments Q-1000 under nitrogen. Samples were prepared in hermetically sealed, aluminum pans. Data were collected from two heating cycles from –70 to 200 °C at a heating rate of 10 °C /min and cooling at a rate of 5 °C/min in between. The reported T_gs and T_ms were those observed during a second heating cycle.

Size exclusion chromatography (SEC): $CHCl_3$ SEC data were obtained by passing the sample (50 □L, ca. 2 mg/mL) through three successive PLgel Mixed C columns (7.5 mm id, 25 cm length) at a rate of 1 mL/min. The eluant was detected using a refractive index detector (HP1047A). The values are reported relative to poly(styrene) standards.

The relative molecular weights of the PEAs were estimated using size exclusion chromatography with a DMF mobile phase (doped with 0.1 M LiBr). A flow rate of 1 mL/min and sample concentrations of ca. 2 mg/mL was used. These samples (20 □L injection volume) were passed through a pair of Styragel HT4 columns (7.8 mm id, 30 cm length). Again, the values are reported relative to poly(styrene) standards.

HFIP SEC data were collected at 0.35 mL/ min at 40 °C using an eluant containing potassium trifluoroacetate (0.025 M). Two Tosoh TSKgel SuperAWM–H columns were used. Molecular masses were determined by calibration vs. polymethyl methacrylate (PMMA) standards. Prior to analysis, samples were filtered through a 0.2 µm filter (Whatman).

Tensile testing: A Shimadzu Autograph AGS-X Series tensile tester (Columbia, MD) was used to collect uniaxial extension data. Samples were observed at a constant crosshead velocity of 10 mm min^{-1} until failure. Data from these experiments are reported as the average from 5–7 separate specimens prepared from the same batch of polymer film.

Films for all PEAs were prepared by compression molding. The precipitated polymer samples were first heated above their melting point in a PTFE dish and compressed by hand with another slightly smaller PTFE dish. The films so produced (> 1 mm thickness) were then pressed into films (0.3 to 0.5 mm) by compression molding between two PTFE sheets at 150 °C. The films were allowed to cool to room temperature and aged for at least 24 hours before the tensile testing.

Tensile bars were cut from each of the above films using a dogbone-shaped dye. The final dogbone bars were ca. 3.0 mm wide and had a gauge length of ca. 11.5 mm.

II. Synthesis Procedures and Characterization Data for "Small" Molecules

Synthesis of Diamidodiols 2a-2c

Diamidodiols **2a-2c** were prepared according to our previously reported procedure.[2]

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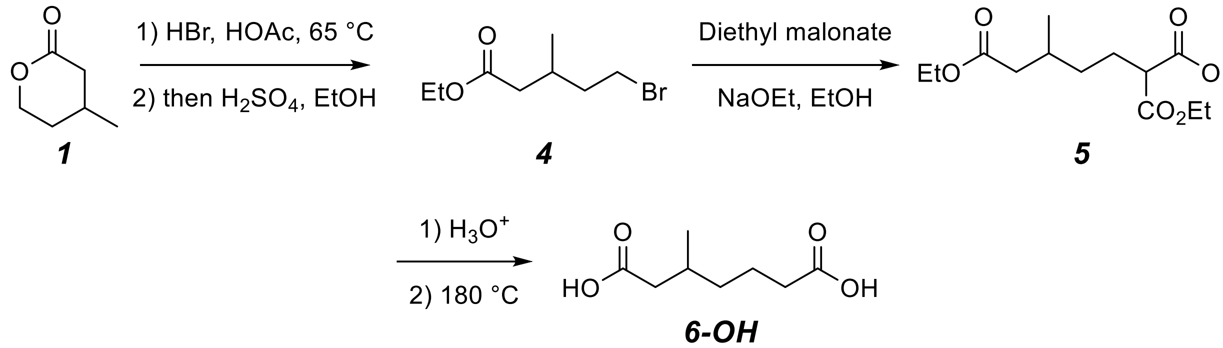
(2) Guptill, D. M.; Brutman, J. P.; Hoye, T. R *Polymer*, **2017**, *111*, 252–257.

Synthesis of Diacid 6-OH



Ethyl 5-bromo-3-methylpentanoate (4): β-Methyl-δ-valerolactone (**1**, MVL, 50 g, 0.44 mol) was dissolved in 230 mL of HBr solution (33% in AcOH). The mixture was heated to 65 °C in an oil bath until the reaction was complete (>97% conversion after ca. 5 hours; monitored by ^{1}H NMR analysis of aliquots). The remaining HBr/AcOH was removed by distillation (under a mild vacuum; water aspirator). The reaction flask (which contained ca. 15 mol% residual AcOH) was then dissolved in ethanol (250 mL) and concentrated sulfuric acid (several drops from a pipet) was added. The mixture was heated at reflux for 3 hours and then allowed to stand at room temperature overnight. Most of the ethanol was removed by rotary evaporation and the residue was diluted with Et_2O (300 mL). The mixture was washed several times with water (100 mL) and brine (100 mL) and dried over $MgSO_4$. The ether was removed by rotary evaporation and the crude product purified by vacuum distillation. The product was isolated as a colorless oil (79 g, 81% yield), which contained several wt percent of MVL.

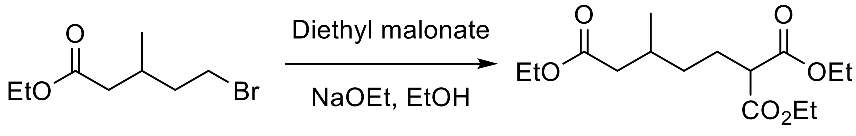
Characterization Data:

^{1}H NMR: (500 MHz, $CDCl_3$) δ 4.13 (q, 2H, J = 7.1 Hz, $\mathrm{COOC}H_2\mathrm{CH_3}$), 3.45 (ddd, 1H, J = 10.0, 7.8, 6.0 Hz, $\mathrm{BrC}H_a\mathrm{H_b}$), 3.39 (ddd, 1H, J = 10.0, 7.5, 7.5 Hz, $\mathrm{BrCH_a}H_b$), 2.30 [nfom, 1H, $\mathrm{C}H_a\mathrm{H_b(C{=}O)O}$], 2.18 [m, 2H, $\mathrm{CH_a}H_b\mathrm{(C{=}O)O}$ and $\mathrm{CH_2C}H\mathrm{(CH_3)CH_2}$], 1.92 (dddd, 1H, J = 14.8, 7.6, 7.6, 5.2 Hz, $\mathrm{BrCH_2C}H_a\mathrm{H_b}$), 1.76 (dddd, 1H, J = 14.8, 7.5, 7.5, 6.0 Hz, $\mathrm{BrCH_2CH_a}H_b$), 1.25 (t, 3H, J = 7.1 Hz, $\mathrm{COOCH_2C}H_3$), and 0.98 [d, 3H, J = 6.3 Hz, $\mathrm{CH_2CH(C}H_3\mathrm{)CH_2}$].

^{13}C NMR: (125 MHz, $CDCl_3$) δ 172.4, 60.3, 41.1, 39.3, 31.0, 29.1, 19.0, and 14.2.

IR (neat): 2964, 2934, 2875, and 1729 cm^{-1}

HRMS: (ESI) *m/z*: $[M+Na]^+$ calcd for $C_8H_{15}O_2BrNa$ 245.0148, found 245.0160.



4 **5**

Triethyl 4-methylpentane-1,1,5-tricarboxylate (5): *The ethanol used for this reaction was treated with a small amount of sodium (ca. 1-2% by weight) and stirred until it had dissolved. The ethanol was then distilled directly into an oven-dried flask, which was used for the reaction.* To this flask containing the distilled ethanol and a PTFE magnetic stir bar was affixed an oven-dried reflux condenser. To the ethanol in the flask (ca. 250 mL) was added clean cut pieces of sodium metal (5.16 g, 0.224 gat, 1 equiv) in portions. The mixture was heated to reflux to facilitate complete reaction of the sodium. Once the sodium had reacted, the turbid mixture was removed from the heat source and diethyl malonate (41.2 g, 0.258 mol, 1.15 equiv) was added to the stirred mixture at ambient temperature. Ethyl 5-bromo-3-methylpentanoate (**4**, 50.0 g, 0.224 mol, 1 equiv) was then added slowly by pipet. After the addition was complete, the reaction mixture was brought to reflux. After 2 hours, ^{1}H NMR analysis indicated that the reaction was mostly complete. However, to ensure complete conversion, it was allowed to stir at reflux for an additional 15 hours. The mixture was cooled to room temperature, diluted with Et_2O (500 mL), washed with H_2O (3 x 300 mL) and brine (200 mL), and dried over $MgSO_4$. The residue was purified by fractional distillation under high vacuum (0.1 to 0.05 torr). A low temperature forerun was collected (ca. 10 g), which consisted of excess diethyl malonate and side products. The final (and major) fraction distilled from a 140–160 °C oil bath at 0.1 to 0.05 torr. The pure product was isolated as a colorless oil (51 g, 75% yield).

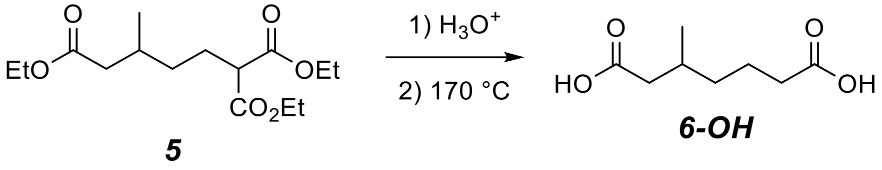
Characterization Data:

^{1}H NMR: (500 MHz, $CDCl_3$) δ 4.19 (m, 4H, $[\mathrm{CH_3C}H_2\mathrm{O(O{=}C)}]_2\mathrm{CH}$), 4.11 (q, 2H, *J* = 7.2 Hz, $\mathrm{CH_2(C{=}O)OC}H_2\mathrm{CH_3}$), 3.27 (t, 1H, 7.5 Hz, $[\mathrm{EtO(O{=}C)}]_2\mathrm{C}H$), 2.29 (dd, 1H, *J* = 14.8, 6.1 Hz, $\mathrm{C}H_a\mathrm{H_b(C{=}O)OEt}$), 2.11 (dd, 1H, *J* = 14.8, 8.1 Hz), 1.98 (app octet, *J* = 7 Hz, RR'C*H*Me), 1.98-1.83 (m, 2H, $\mathrm{C}H_2\mathrm{CH(CO_2Et)_2}$], 1.35 (dddd, 1H, *J* = 13.1, 11.0, 5.3, 5.3 Hz, $\mathrm{CH_2C}H_a\mathrm{H_bCH(CH_3)CH_2}$), 1.25 [m, 10H, $\mathrm{CO_2CH_2C}H_3$ (3x) and $\mathrm{CH_2CH_a}H_b\mathrm{CH(CH_3)CH_2}$], and 0.95 (d, 3H, *J* = 6.7 Hz, $\mathrm{RR'CHC}H_3$).

^{13}C NMR: (125 MHz, $CDCl_3$) δ 172.8, 169.33, 169.29, 61.27, 61.26, 60.1, 52.1, 41.5, 34.1, 30.1, 26.2, 19.5, 14.2, and 14.0 (2x).

IR (neat): 2980, 2937, 2875, 1728, and 1150 cm^{-1}.

HRMS: (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{26}O_6Na$ 325.1622, found 325.1617.



3-Methylheptanedioic acid (6-OH): A 1 L round-bottomed flask containing a PTFE-coated magnetic stir bar was charged with the triester **5** (50 g, 0.165 mol) and 6M HCl (600 mL). This stirred solution was placed in a heated oil bath at an appropriate temperature such that the reaction mixture maintained a consistent temperature of ca. 95-98 °C. After 1.5 hours, the mixture had become homogenous. The solution was stirred for another 1.5 hours at the same temperature. A short path distillation apparatus was attached to the flask and the temperature of the oil bath was slowly increased until the aqueous HCl began to distill from the reaction vessel. During the distillation, the oil bath temperature reached ca. 160 °C. After ca. 500 mL of the aqueous HCl had been removed, a light vacuum (> 200 torr) was applied to facilitate removal of the remaining water. Once the water was essentially gone, the vacuum was removed, and the internal temperature monitored. The temperature of the oil bath was increased to 180 °C, at which point bubbling from the loss of CO_2 was observed; the internal temperature was ca. 170 °C. The mixture was stirred at this temperature for 30-40 minutes, after which time bubbling had ceased. The flask was removed from the oil bath and allowed to cool to room temperature. The residue of **6-OH** was used for NMR characterization. To further dry the material, it was dissolved in dichloromethane and dried with $MgSO_4$. The dichloromethane was then removed by rotary evaporation. After removing residual dichloromethane under high vacuum, the thick yellow oil solidified. The final product was a slightly yellow, waxy solid (28 g, 97% yield).

Characterization Data:

^{1}H NMR: (500 MHz, $CDCl_3$) δ 11.34 (bs, 2H, COO*H*), 2.37 (br t, 2H, *J* = 5 Hz, $HOOCCH_2CH_2$), 2.31 (dd, 1H, *J* = 15.3, 7.6 Hz, $CHCH_aH_bCOOH$), 2.24 (dd, 1H, *J* = 15.3, 7.0 Hz, $CHCH_aH_bCOOH$), 2.01 [app oct, 1H, *J* = 7 Hz, $CH_2CH(CH_3)$], 1.72 (m, 1H, $HOOCCH_2CH_aH_b$), 1.63 (m, 1H, $HOOCCH_2CH_aH_b$), 1.44 (m, 1H, $CHCH_2CH_aCH_b$), 1.25 (m, 1H, $CHCH_2CH_aCH_b$), and 0.99 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ 180.2, 179.7, 41.5, 35.3, 33.9, 29.7, 21.8, and 19.5.

IR (neat): 3050, 2938, 2903, 2628, 1686, and 1205 cm^{-1}.

melting point: 40–45 °C (lit. 42–44 °C)[3]

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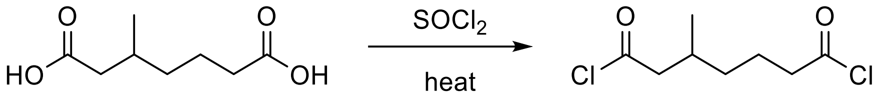
(3) Blomquist, A. T.; Wolinsky, J *J. Org. Chem.*, **1956**, *21*, 1371–1373.



6-OH **6-Cl**

3-Methylheptanedioyl dichloride(6-Cl):[4] The diacid from the previous step (28 g, 0.161 mol) was treated with 35 mL (3 equiv) of thionyl chloride. The solution was heated at reflux for 1 hour. ^{1}H NMR analysis of an aliquot of the reaction mixture was assayed to determine that the reaction was complete. The excess thionyl chloride was removed under vacuum to give the crude acid chloride. This distilled three times under vacuum to give the purified acid chloride (ca. 15 g) as a colorless oil.

Characterization Data:

^{1}H NMR: (400 MHz, CDCl$_3$) δ 2.91 (br t, J = 7 Hz, CH$_2$CH_2COCl), 2.88 [dd, 1H, J = 16.4, 6.1 Hz, Cl(C=O)CH_aH$_b$CH(CH$_3$)], 2.74 [dd, 1H, J = 16.4, 7.6 Hz, Cl(C=O)CH$_a$$H_b$CH(CH$_3$)], 2.09 [app oct, 1H, J = 6.7 Hz, CH(CH$_3$)], 1.79 (ddddd, J = 13.7, 10.9, 7.2, 7.2, 5.4 Hz, 1H, CH$_2$CH_aH$_b$CH$_2$COCl) 1.71 (ddddd, J = 13.7, 10.8, 7.2, 7.2, 5.4 Hz, 1H, CH$_2$CH$_a$$H_bCH_2$COCl), 1.44 [dddd, 1H, J = 13.5, 10.9, 5.5, 5.5 Hz, CH$_2$CH_aH$_b$CH(CH$_3$)], 1.30 [dddd, 1H, J = 13.5, 10.8, 8.1, 5.4 Hz, CH$_2$CH$_a$$H_b$CH(CH$_3$)], and 1.03 (d, 3H, J = 6.7 Hz).

^{13}C NMR: (100 MHz, CDCl$_3$) δ 173.5, 172.9, 53.8, 46.8, 34.6, 30.3, 22.4, and 18.9.

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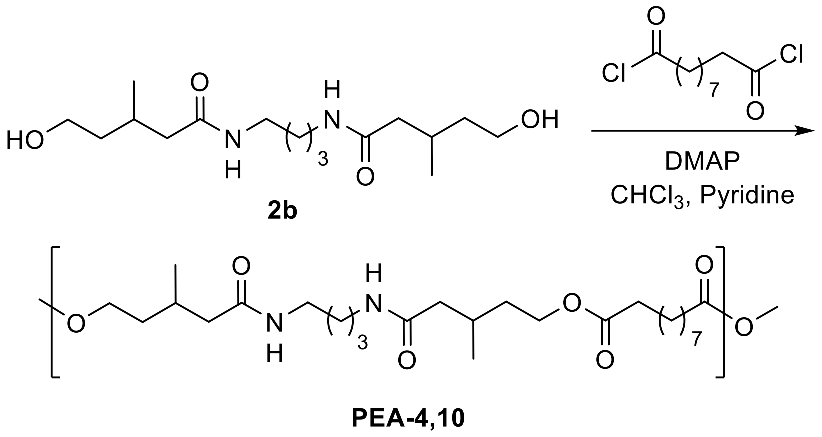
(4) Mousseron, M.; Granger, R.; Bourrel, H.; Cellier, M.; Jullien, J.; Canals, E.; Cabanes, J. *Bull. Soc. Chim. Fr.* **1947**, 605–615.

III. Synthesis Procedures and Characterization Data for Poly(ester-amide)s

Representative Procedure for PEA Synthesis:

PEA-4,10



Procedure: Inside of a dry-box, the amido-diol **2b** (3.16 g, 10 mmol) was added to a round-bottomed flask (previously oven-dried) containing a PTFE-coated magnetic stir bar. To a separate oven-dried flask was added sebacoyl chloride (2.39 g, 10 mmol). A third flask was filled with dried, EtOH-free chloroform. The flasks were capped with rubber septa and removed from the box. To the flask containing the diol was added, successively, *N*,*N*-dimethyl-4-aminopyridine (122 mg, 1 mmol), 4 mL of dry pyridine, and 6 mL of dry chloroform. The flask was sealed with a rubber septum and a nitrogen balloon was attached. This apparatus was gently agitated and warmed with a heat gun until the diol had fully dissolved. The acid chloride was dissolved in 10 mL of dry chloroform, and the solution was taken into a 20 mL syringe and added by syringe pump to the reaction mixture at a rate of ca. 12 mL•hour^{-1}. After complete addition, the flask that had contained the acid chloride was rinsed with 1 mL chloroform and this added to the reaction mixture. The solution had become more viscous and was stirred overnight. The contents of the flask were slowly poured into 400 mL of stirred acetone to precipitate the polymer. The white solid so produced was collected by vacuum filtration and washed several times each with acetone, water, and then acetone again before it was dried under vacuum (4.2 g, 88%)

Characterization Data:

^{1}H NMR: (500 MHz, DMSO-d_6) See annotated spectrum on page S60

^{13}C NMR: (125 MHz, DMSO-d_6) See spectrum on page S61

IR (neat): 3295, 2927, 2854, 1727, 1633, 1543, and 1168 cm^{-1}

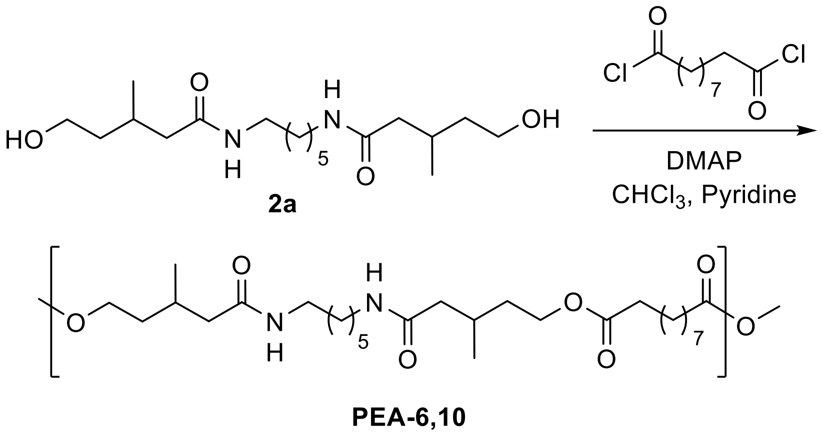
T_g (measured by DSC): –10 °C

T_m (measured by DSC): 120 °C

M_n (SEC, DMF): 122,000

Đ (SEC): 1.42

PEA-6,10



Procedure: The representative procedure above was followed using amido-diol **2a** (3.44 g, 10 mmol) and sebacoyl chloride (2.39 g, 10 mmol). The resulting polymer was a white, stringy solid (4.3 g, 84%).

Characterization Data:

^{1}H NMR: (500 MHz, DMSO-d_6) See annotated spectrum on page S58

^{13}C NMR: (125 MHz, DMSO-d_6) See spectrum on page S59

IR (neat): 3297, 2927, 2854, 1729, 1632, 1542, and 1168 cm^{-1}

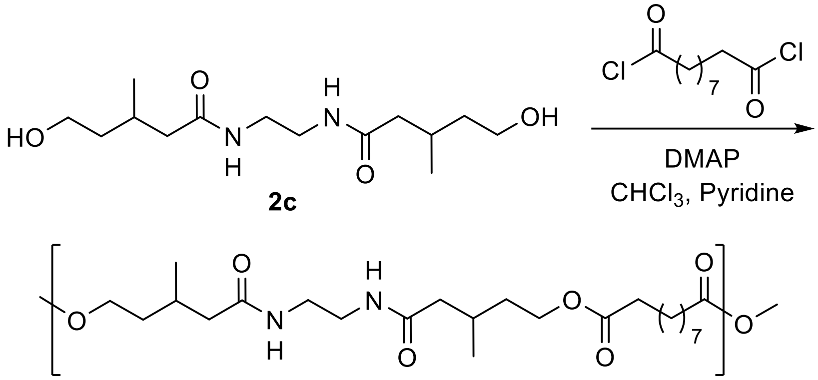
***T_g* (measured by DSC):** –13 °C

***T_m* (measured by DSC):** 106 °C

***M_n* (SEC):** 142,000

***Đ* (SEC):** 1.35

PEA-2,10



PEA-2,10

Procedure: The representative procedure above was followed using amido-diol **2c** (2.88 g, 10 mmol) and sebacoyl chloride (2.39 g, 10 mmol). The resulting polymer was a white, stringy solid. (4.0 g, 89%)

Characterization Data:

^{1}H NMR: (500 MHz, DMSO-*d*$_6$) See annotated spectrum on page S62

^{13}C NMR: (125 MHz, DMSO-*d*$_6$) See spectrum on page S63

IR (neat): 3295, 2924, 2852, 1727, 1637, 1550, and 1168 cm^{-1}

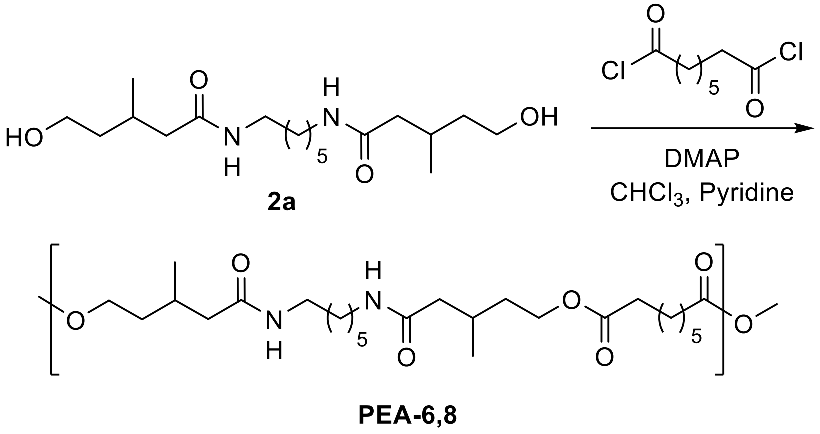
T_g (measured by DSC): –2 °C

T_m (measured by DSC): 119 °C

M_n (SEC): 152,000

Đ (SEC): 1.51

PEA-6,8



Procedure: The representative procedure above was followed using amido-diol **2a** (3.44 g, 10 mmol) and suberoyl chloride (2.11 g, 10 mmol). The resulting polymer was a hard white solid (4.2 g, 88%).

Characterization Data:

^{1}H NMR: (500 MHz, DMSO-*d*$_6$) See annotated spectrum on page S64

^{13}C NMR: (125 MHz, DMSO-*d*$_6$) See spectrum on page S65

IR (neat): 3296, 2926, 2855, 1729, 1633, 1543, and 1168 cm^{-1}

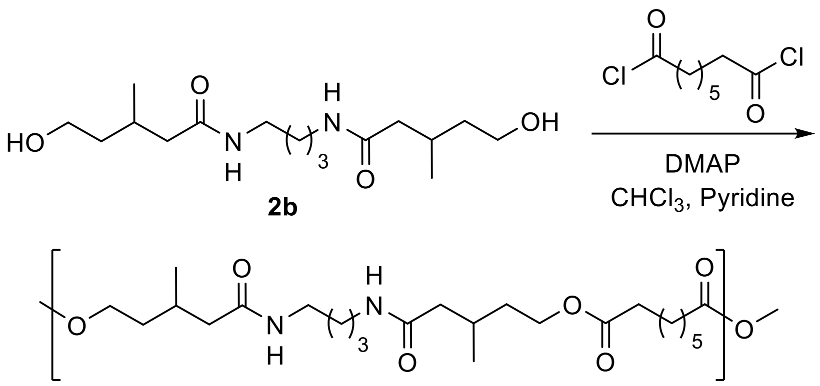
T_g (measured by DSC): –11 °C

T_m (measured by DSC): 95 °C

M_n (SEC): 121,000

Đ (SEC): 1.43

PEA-4,8



PEA-4,8

Procedure: The representative procedure above was followed using amido-diol **2b** (3.16 g, 10 mmol) and suberoyl chloride (2.11 g, 10 mmol). The resulting polymer was a white, stringy solid (3.9 g, 87%).

Characterization Data:

^{1}H NMR: (500 MHz, DMSO-*d*$_6$) See annotated spectrum on page S66

^{13}C NMR: (125 MHz, DMSO-*d*$_6$) See spectrum on page S67

IR (neat): 3294, 2929, 2864, 1727, 1633, 1543, and 1168 cm^{-1}

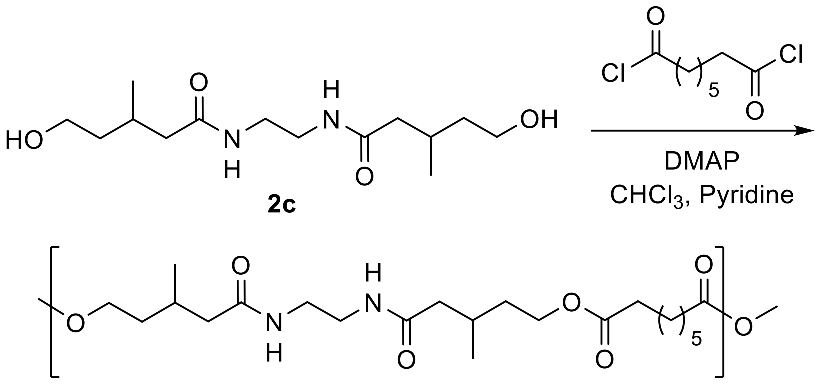
T_g (measured by DSC): –8 °C

T_m (measured by DSC): 119 °C

M_n (SEC): 165,000

$Đ$ (SEC): 1.46

PEA-2,8



2c

PEA-2,8

Procedure: The representative procedure above was followed using amido-diol **2c** (2.88 g, 10 mmol) and suberoyl chloride (2.11 g, 10 mmol). The resulting polymer was a hard, off-white solid (3.5 g, 81%).

Characterization Data:

^{1}H NMR: (500 MHz, DMSO-*d_6*) See annotated spectrum on page S68

^{13}C NMR: (125 MHz, DMSO-*d_6*) See spectrum on page S69

IR (neat): 3291, 2927, 2855, 1730, 1637, 1549, and 1168 cm^{-1}

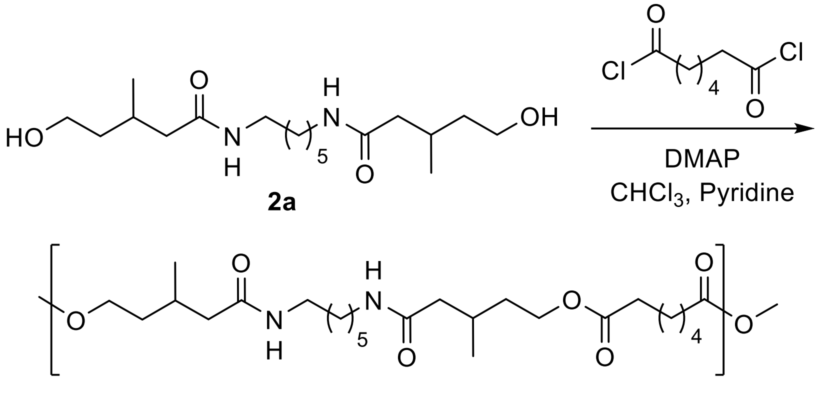
T_g (measured by DSC): –3 °C

T_m (measured by DSC): 113 °C

M_n (SEC): 128,000

Đ (SEC): 1.43

PEA-6,7



PEA-6,7

Procedure: The representative procedure above was followed using amido-diol **2a** (3.44 g, 10 mmol) and pimeloyl chloride (1.97 g, 10 mmol). The resulting polymer was a white, hard solid (4.0 g, 85%).

Characterization Data:

^{1}H NMR: (500 MHz, DMSO-*d$_6$*) See annotated spectrum on page S70

^{13}C NMR: (125 MHz, DMSO-*d$_6$*) See spectrum on page S71

IR (neat): 3294, 2928, 1730, 1634, 1544, and 1169 cm^{-1}

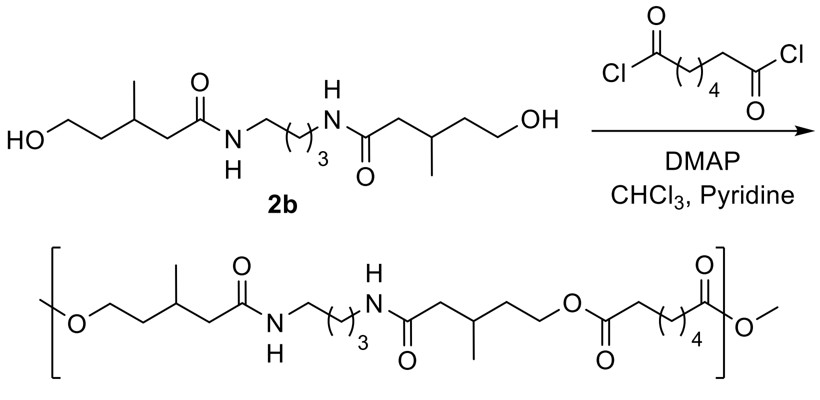
T_g (measured by DSC): –10 °C

T_m (measured by DSC): 99 °C

M_n (SEC): 204,000

Đ (SEC): 1.36

PEA-4,7



PEA-4,7

Procedure: The representative procedure above was followed using amido-diol **2b** (3.16 g, 10 mmol) and pimeloyl chloride (1.97 g, 10 mmol). The resulting polymer was a white, powdery solid (3.0 g, 68%).

Characterization Data:

^{1}H NMR: (500 MHz, DMSO-*d*$_6$) See annotated spectrum on page S72

^{13}C NMR: (125 MHz, DMSO-*d*$_6$) See spectrum on page S73

IR (neat): 3293, 2927, 2868, 1730, 1632, 1543, and 1169 cm^{-1}

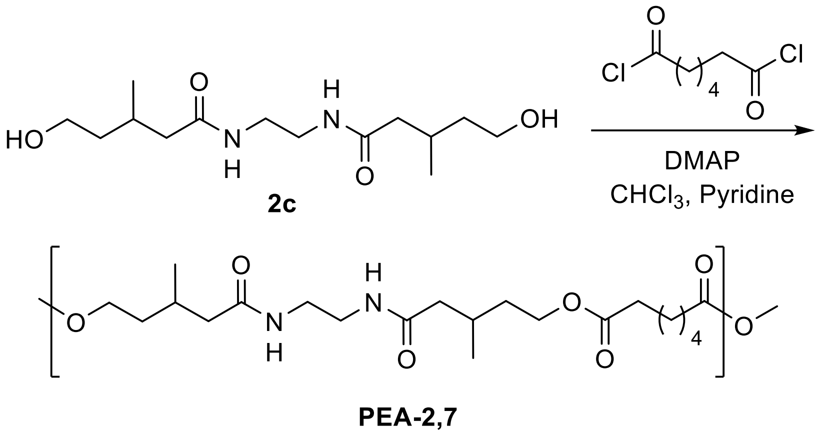
T_g (measured by DSC): –7 °C

T_m (measured by DSC): 115 °C

M_n (SEC): 108,000

Đ (SEC): 1.52

PEA-2,7



Procedure: The representative procedure above was followed using amido-diol **2c** (2.88 g, 10 mmol) and pimeloyl chloride (1.97 g, 10 mmol). The resulting polymer was a white, crumbly solid (2.9 g, 70%).

Characterization Data:

^{1}H NMR: (500 MHz, DMSO-*d*$_6$) See annotated spectrum on page S74

^{13}C NMR: (125 MHz, DMSO-*d*$_6$) See spectrum on page S75

IR (neat): 3292, 2927, 2870, 1729, 1635, 1551, and 1167 cm^{-1}

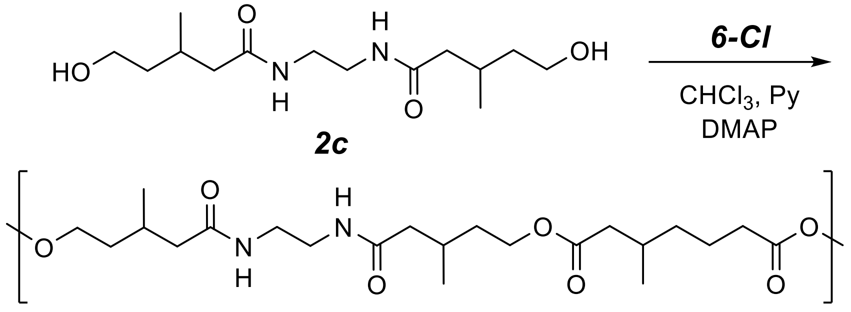
T_g (measured by DSC): –2 °C

T_m (measured by DSC): 116 °C

M_n (SEC): 126,000

Đ (SEC): 1.37

PEA-2,7-Me



PEA-2,7-Me

Procedure: The representative procedure above was followed using amido-diol **2c** (2.88 g, 10 mmol) and 3-methylheptanedioyl chloride (2.11 g, 10 mmol). The resulting polymer was a crumbly white solid (3.1 g, 73%).

Characterization Data:

^{1}H NMR: (500 MHz, DMSO-d_6) See annotated spectrum on page S76

^{13}C NMR: (125 MHz, DMSO-d_6) See spectrum on page S77

IR (neat): cm^{-1}

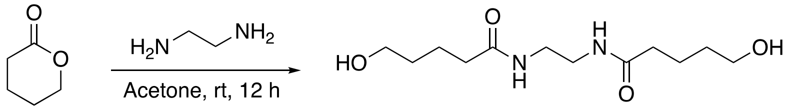
***T_g* (measured by DSC):** –2 °C

***T_m* (measured by DSC):** 98 °C

***M_n* (SEC):** 129,000

***Đ* (SEC):** 1.28

norMe-PEA-2,10 (from diamidodiol 2d)



2d

***N,N′*-(Ethane-1,2-diyl)bis(5-hydroxypentanamide) (2d).** By a procedure similar to one reported for an earlier preparation of this compound,[5] ethylenediamine (3.0 g, 50 mmol) was taken into a round-bottomed flask (previously oven-dried) containing a PTFE-coated magnetic stir bar, and acetone (20 mL) was added to that flask. Tetrahydro-2H-pyran-2-one (valerolactone, 10 g, 100 mmol) was then added dropwise to the reaction mixture at 0 °C, which turned turbid after ca. 15 min and grew thicker over time. The mixture was allowed to warm to ambient temperature and then to stand overnight. Acetone was removed on a rotary evaporator and the crude solid product was recrystallized in acetonitrile (~500 mL). The white crystals of **2d** so produced were collected by vacuum filtration and dried under vacuum (8.6 g, 66%).

^{1}H NMR: (400 MHz, DMSO-d_6) δ 7.77 (br t, J = 5.3 Hz, 2H, *NH*), 4.35 (t, J = 5.2 Hz, 2H, CH_2-O*H*), 3.37 (dt, J = 5.2, 6.5 Hz, 4H, *CH_2*-OH), 3.06 (nfom, 4H, *CH_2*-NH), 2.04 (t, J = 7.3 Hz, 4H, *CH_2*-CO), 1.50 (br pent, J ~ 7.4 Hz, 4H, *CH_2*CH_2OH), and 1.37 (br pent, J ~ 7.0 Hz, 4H, *CH_2*CH_2CH_2OH).

^{13}C NMR: (100 MHz, DMSO-d_6) δ 172.3, 60.4, 38.3, 35.3, 32.1, and 21.8.

IR (neat): 3374 3297, 2947, 2932, 2900, 2861, 1638, 1537, 1425, 1264, 1241, 1062, 1040, 991, 945, 709, 647, and 586 cm^{-1}.[6]

mp: 137–139 °C (lit.[6] 134.6 °C).

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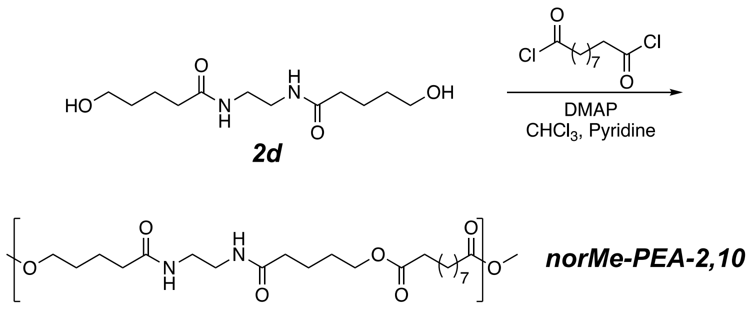
[5] Bera, S.; Jedlinski, Z. Block/segmented polymers. A new method of synthesis of copoly(amide-ester)-ester polymer. *J. Polym. Sci. A* **1993**, *31*, 731–739.

[6] Sudha, J. D. Synthesis and characterization of hydrogen-bonded thermotropic liquid crystalline aromatic-aliphatic poly(esteramide)s from amidodiol. *J. Polym. Sci. A* **2000**, *38*, 2469–2486.



norMe-PEA-2,10. The amidodiol **2d** (2.60 g, 10.0 mmol) was taken into a round-bottomed flask (previously oven-dried) containing a PTFE-coated magnetic stir bar. Dry $CHCl_3$ (40 mL, ethanol-free (amylene inhibited)), dry pyridine (10 mL), and, *N*,*N*-dimethyl-4-aminopyridine (231 mg, 0.2 mmol) were added. The resulting mixture was heterogeneous. The flask was sealed with a rubber septum and a nitrogen balloon was attached. Sebacoyl chloride (2.42 g, 10.1 mmol) was dissolved in the same source of chloroform (20 mL), and this solution was slowly added (ca. 15 min) to the reaction mixture at ambient temperature. After complete addition, the flask that had contained the acid chloride was rinsed with a small portion of additional chloroform (ca. 2 mL) and added to the reaction mixture. The mixture became homogenous in a few min after addition had been completed. The solution, which had become somewhat viscous, was stirred overnight. The viscosity of this mixture had increased further, but it was still able to be slowly stirred magnetically. The solution was gently warmed so that the contents could be slowly poured into of stirred acetone (400 mL) at ambient temperature to precipitate the polymer. The white solid so produced was collected by vacuum filtration and washed with acetone, water, and acetone again. Finally, it was dried under vacuum to give the polymer as a white powder (3.4 g, 79 %).

Characterization Data:

NMR sample preparation: Polymer **norMe-PEA-2,10** (~10 mg) was slurried in $CDCl_3$ (0.5 mL). Hexafluoroisopropanol (4 drops) was added at room temperature and the mixture quickly became homogeneous.

^{1}H NMR: (400 MHz, $CDCl_3$, ca. 10% HFIP) δ 6.68 (br s, 2H, *NH*), 4.05 (t, *J* = 5.3 Hz, 4H, CH_2-O), 3.66 (t, *J* = 6.6 Hz, CH_2OH end group), 3.30 (s, 4H, CH_2-NH), 2.32 (t, J = 7,2 Hz, CH_2-CO_2H end group), 2.28 (t, *J* = 7.4 Hz, 4H, CH_2-$COOCH_2$), 2.21 (br t, *J* = 7.2 Hz, 4H, CH_2-CONH), 1.54–1.70 (m, 12H), and 1.25–1.32 (m, 8H).

^{13}C NMR: (100 MHz, $CDCl_3$) 175.5, 175.2, 64.0, 40.0, 35.9, 34.4, 29.1, 28.1, 24.9, and 22.1.

IR (neat): 3299, 2926, 2854, 1723, 1639, 1549, 1419, 1380, 1218, 1173, 1050, 947, 724, 695, 586, and 434 cm^{-1}.

T_g (measured by DSC): 5 °C.

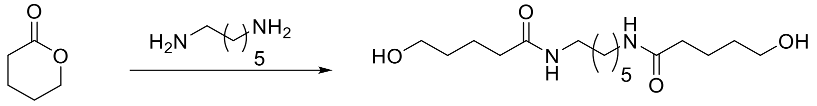
T_m (measured by DSC): 130, 138 °C.

M_n (SEC, HFIP): 8,100 Da (from analysis of the principal high molar mass peak); 1800 Da (from analysis of the entire array of non-solvent peaks).

Đ (SEC, HFIP): 2.2 (from analysis of the principal high molar mass peak); 6.0 (from analysis of the entire array of non-solvent peaks).

This polymerization to prepare **norMe-PEA-2,10** was not well-controlled. The SEC (HFIP) shows a relatively large amount of low molecular weight oligomeric material compared to that for **norMe-PEA-6,10**. We presume that this poor behavior arises from the considerably lower solubility of the monomer **2d** (vs. **2e**) in the reaction solvent ($CHCl_3$/pyridine).

norMe-PEA-6,10 (from diamidodiol 2e)



2e

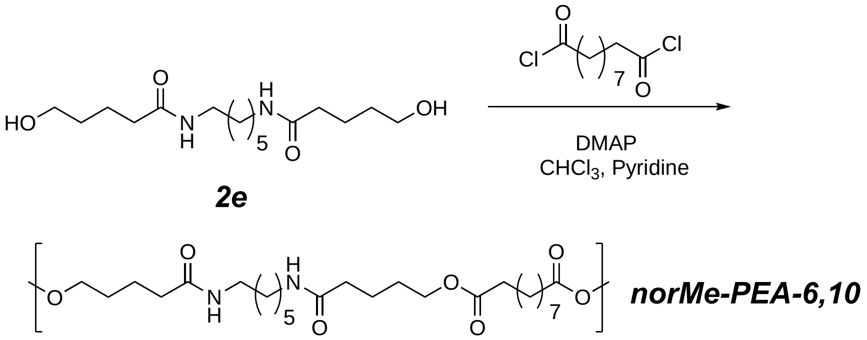
***N,N′*-(Hexane-1,6-diyl)bis(5-hydroxypentanamide) (2e).** By a procedure similar to one reported for an earlier preparation of this compound,[5] hexane-1,6-diamine **(**5.8 g, 50 mmol) was taken into a round-bottomed flask (previously oven-dried) containing a PTFE-coated magnetic stir bar. Tetrahydro-2H-pyran-2-one (valerolactone, 10 g, 100 mmol, 9.3 mL) was added dropwise to the reaction mixture at 0 °C, and the resulting mixture was allowed to slowly warm to ambient temperature and then to stand overnight. The resulting crude mixture, a solid mass, was recrystallized in $CHCl_3$:MeOH (10:1). The white crystals of **2e** so produced were collected by vacuum filtration and dried under vacuum (9.7 g, 61%).

^{1}H NMR: (400 MHz, DMSO-d_6) δ 7.72 (br t, J = 5.6 Hz, 2H, *NH*), 4.36 (br s, 2H, O*H*), 3.37 (t, J = 6.3 Hz, 4H, CH_2-OH), 3.00 (dt, J = 5.8, 7.0 Hz, 4H, CH_2-NH), 2.04 (t, J = 7.1 Hz, 4H, CH_2-CO), 1.50 (quin, J = 7.1 Hz, 4H, CH_2CH_2OH), 1.41–1.33 (m, 8H, $CH_2CH_2CH_2OH$ and CH_2CH_2NH), and 1.24 (nfom, 4H, $CH_2CH_2CH_2NH$).

^{13}C NMR: (100 MHz, DMSO-d_6) δ 171.9, 60.5, 38.3, 35.3, 32.1, 29.2, 26.1, and 22.0.

IR (neat): 3389, 3298, 2943, 2859, 1631, 1530, 1474, 1373, 1343, 1226, 1059, 1024, 990, 731, and 578 cm^{-1}.[6]

mp: 146–148 °C (lit.[6] 126 °C).



norMe-PEA-6,10. The amidodiol **2e** (3.0 g, 9.49 mmol) was taken into a round-bottomed flask (previously oven-dried) containing a PTFE-coated magnetic stir bar. Dry $CHCl_3$ (25 mL, ethanol-free (amylene inhibited)), 15 mL of dry pyridine, and *N*,*N*-dimethyl-4-aminopyridine (231 mg, 0.2 mmol) were added. The resulting mixture was heterogeneous. The flask was sealed with a rubber septum and a nitrogen balloon was attached. Sebacoyl chloride (2.26 g, 9.49 mmol) was dissolved in 5 mL of the same chloroform, and this solution was slowly added to the stirred reaction mixture at ambient temperature. The mixture became homogenous and in 2-3 min. This solution became viscous after a few hours to the point where it was no longer able to be stirred. The mixture was allowed to stand overnight. It was then warmed to ca. 50–70 °C so that the contents could be slowly poured into 400 mL of stirred acetone at ambient temperature to precipitate the polymer. The white solid so produced was collected by vacuum filtration, washed with saturated $NaHCO_3$ and several times with acetone, and dried under vacuum (4.8 g, 100%).

Characterization Data:

^{1}H NMR: (500 MHz, $CDCl_3$) δ 6.00 (br s, 2H, *NH*), 4.07 (t, *J* = 6.2 Hz, 4H, CH_2-O), 3.64 (t, *J* = 6.6 Hz, CH_2OH end group), 3.23 (m, 4H, CH_2-NH), 2.29 (t, *J* = 7.5 Hz, 4H, CH_2-COO), 2.19 (br t, *J* = 7.1 Hz, 4H, CH_2-CONH), 1.64–1.74 (m, 8H), 1.59 (m, ca. 4H, superimposed on a resonance for H_2O), 1.49 (m, 4H), and 1.27–1.36 (m, 12H). [repeat unit : end group integrals = ca. 18; a more accurate assessment of MW by NMR analysis was carried out following derivatization with TFAA.]

IR (neat): 3303, 2929, 2857, 1727, 1633, 1536, 1421, 1293, 1216, 1168, 1098, 969, 685, and 540 cm^{-1}.

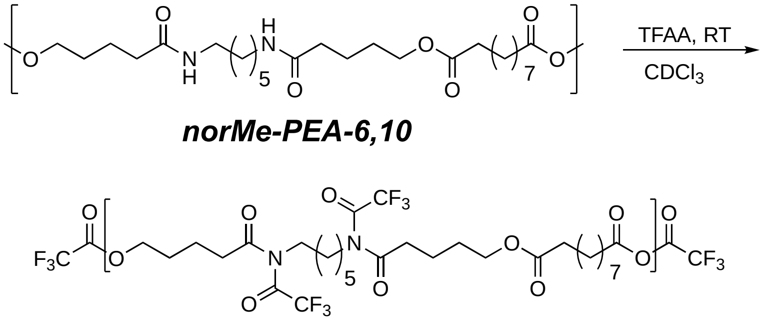
T_g (measured by DSC): 4 °C.

T_m (measured by DSC): 140 °C.

M_n (SEC, HFIP): 15,300 Da

Đ (SEC, HFIP): 6.0.

TFAA derivatization of norMe-PEA-6,10



norMe-PEA-6,10

perTFA-norMe-PEA-6,10

Per-trifluoroacetylation of all OH and NH functionality in norMe-PEA-6,10. Polymer **norMe-PEA-6,10** (10 mg) was slurried in $CDCl_3$ (0.5 mL). Trifluoroacetic anhydride (4 drops) was added at room temperature, and the mixture quickly became homogeneous. The ^{1}H NMR spectrum indicated efficient conversion to cleanly derivatized TFA ester of the OH end group, mixed anhydride of the acid end group, and imides from the backbone secondary amides present in the polymer.

Characterization of **perTFA-norMe-PEA-6,10**:

^{1}H NMR: (500 MHz, $CDCl_3$) δ 4.37 (t, J = 6.0 Hz, CH_2OCOCF_3 end group, 0.092H), 4.14 (t, J = 5.8 Hz, 4H, CH_2OCO), 3.69 (t, J = 8.2 Hz, 4H, $CH_2N(COCF_3)CO$), 2.84 (t, J = 6.6 Hz, 4H, $CH_2CON(COCF_3)$), 2.60 (t, J = 7.3 Hz, $CH_2CO_2COCF_3$ end group, 0.087H), 2.36 (t, J = 7.7 Hz, 4H, CH_2COO), 1.70-1.78 (m, 8H), 1.55-1.66 (m, 8H), 1.36 (m, 4H), and 1.29-1.32 (m, 8H). [integrated ratio of the backbone to the sum or the CH_2OTFA and CH_2CO_2TFA end group methylene resonances: 22:1]

^{13}C NMR: (125 MHz, $CDCl_3$) δ 176.2, 176.0, 159.7 (q, J_{CF} = 38.4 Hz), 116.0 (q, J_{CF} = 288 Hz), 67.9 (minor, CH_2OTFA end group), 64.7, 44.7, 38.3, 34.6, 29.22, 29.19, 29.15, 28.0, 26.3, 25.1, and 21.4.

IR (neat): 2928, 1718, 1445, 1391, 1152, 1086, 844, 803, and 725 cm^{-1}.

M_n (^{1}H NMR integration): 15,500 Da.

IV. Additional Polymer Characterization Data

Tensile Testing Data

Table S1. Tabulated tensile testing data for PEAs

PEA[a]	$M_{n,\text{ rel}}$ (kg/mol)[b]	E (MPa)[c]	σ_y (MPa)[c]	σ_b (MPa)[c]	ε_b (%)[c]
PEA-6,10	142	255 ± 25	16 ± 2	42 ± 5	600 ± 50
PEA-4,10	122	350 ± 10	16 ± 1	43 ± 5	530 ± 39
PEA-6,8	121	205 ± 11	9 ± 0.2	44 ± 7	612 ± 89
PEA-4,8	165	323 ± 12	15 ± 0.3	53 ± 6	598 ± 66
PEA-2,8	128	436 ± 22	18 ± 1	47 ± 3	642 ± 44
PEA-6,7	204	192 ± 15	9 ± 1	47 ± 8	603 ± 40
PEA-4,7	108	304 ± 28	13 ± 0.5	41 ± 6	537 ± 79
PEA-2,7	126	462 ± 38	18 ± 1	41 ± 5	595 ± 73
PEA-2,7-Me	129	651 ± 28	21 ± 1	43 ± 2	697 ± 42

[a]Nomenclature for the polyesteramides (**PEA**s): **PEA-x,y**, where x = # of carbon atoms between the amides of the diol and y = # of carbon atoms in the acid chloride. [b]Measured by size exclusion chromatography (DMF eluent, PS standards). [c]Tensile strength (σ_b) and maximum elongation (ε_b) are the stress and elongation at break, respectively. The yield point (σ_y) is the stress at yield (the maximum stress as the material transitions from elastic to plastic deformation, see Figure S1 below). These values, as well as the elastic modulus (E), were determined by uniaxial extension tests at a constant crosshead velocity of 10 mm/min. See Figures S2–S10 for the raw data.

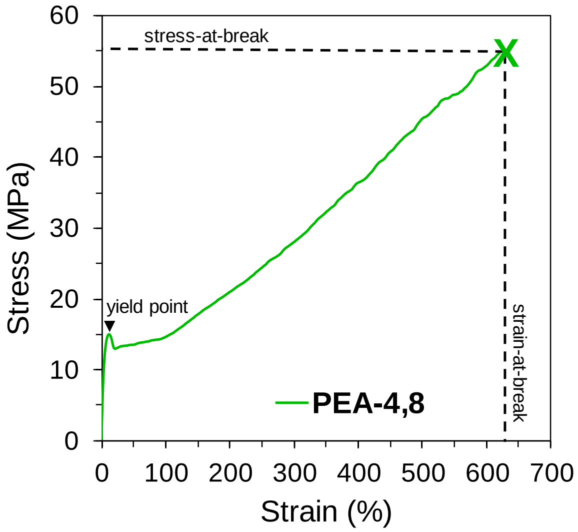


Figure S1. A representative stress-strain curve for a sample of **PEA-4,8**, showing the origin of several of the tabulated values in Table S1.

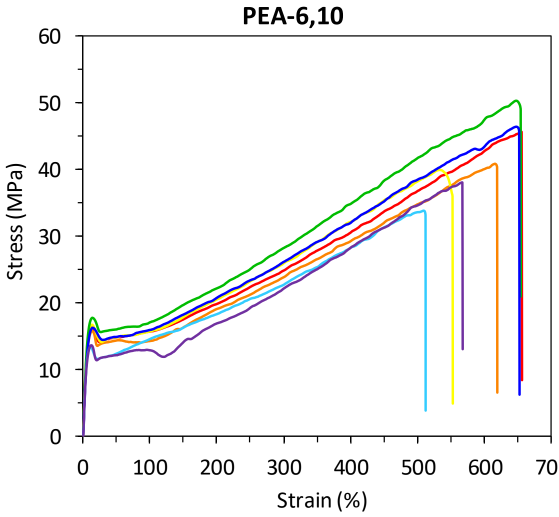


Figure S2. Stress vs. strain curves for seven **PEA-6,10** sample bars, each cut from the same stock sample of polymer.

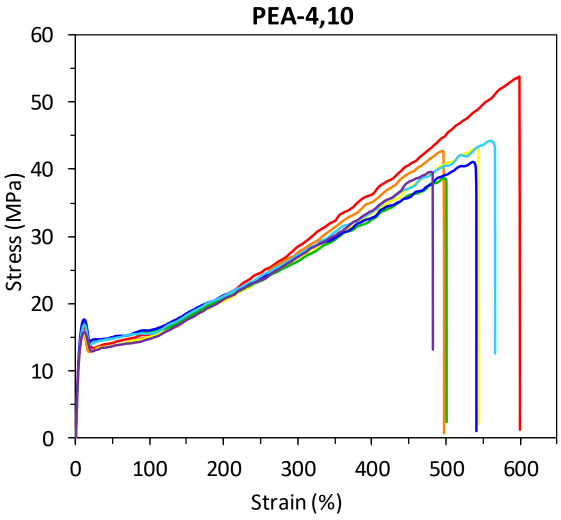


Figure S3. Stress vs. strain curves for seven **PEA-4,10** sample bars, each cut from the same stock sample of polymer.

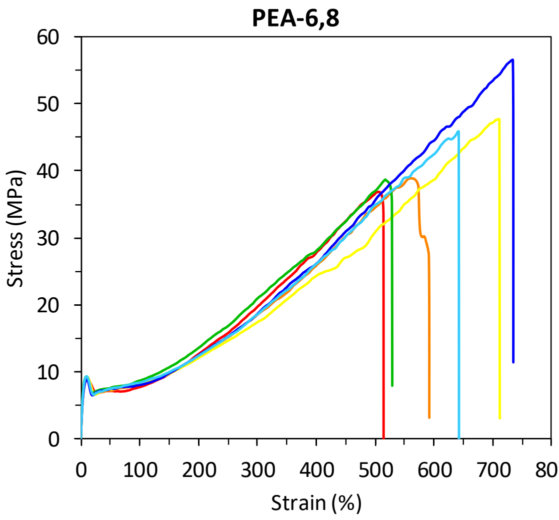


Figure S4. Stress vs. strain curves for six **PEA-6,8** sample bars cut from the same stock sample of polymer.

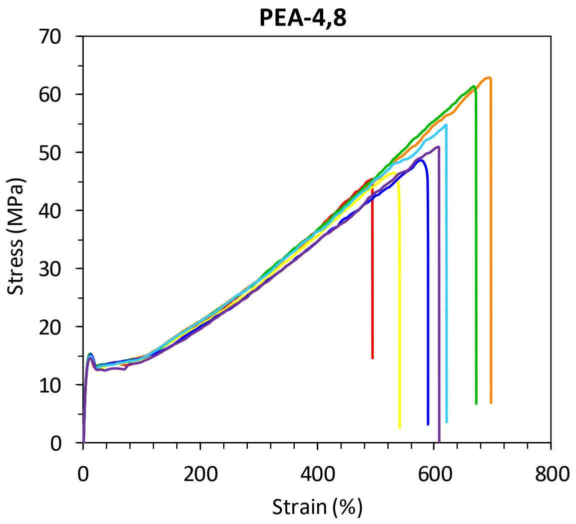


Figure S5. Stress vs. strain curves for seven **PEA-4,8** sample bars cut from the same stock sample of polymer.

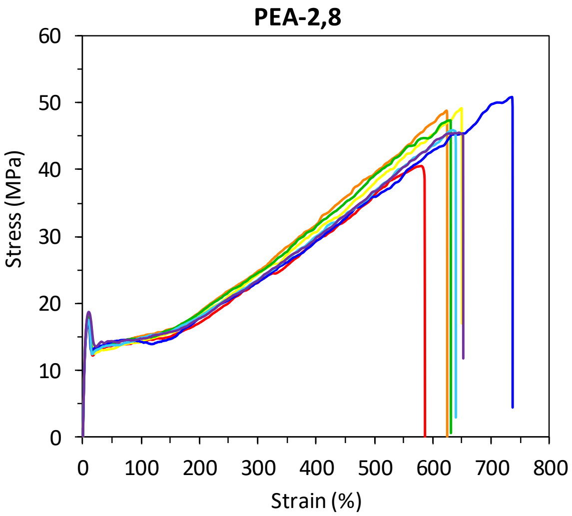


Figure S6. Stress vs. strain curves for seven **PEA-2,8** sample bars, each cut from the same stock sample of polymer.

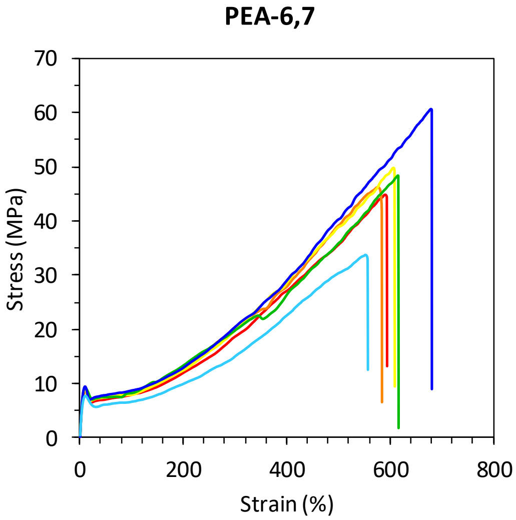


Figure S7. Stress vs. strain curves for six **PEA-6,7** sample bars, each cut from these same stock sample of polymer.

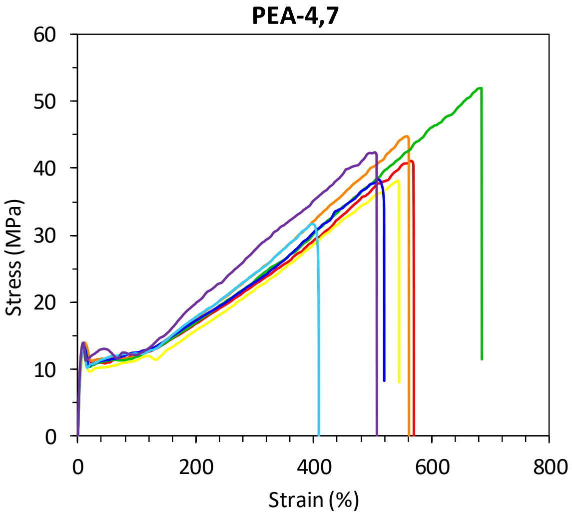


Figure S8. Stress vs. strain curves for seven **PEA-4,7** sample bars cut from the same stock sample of polymer.

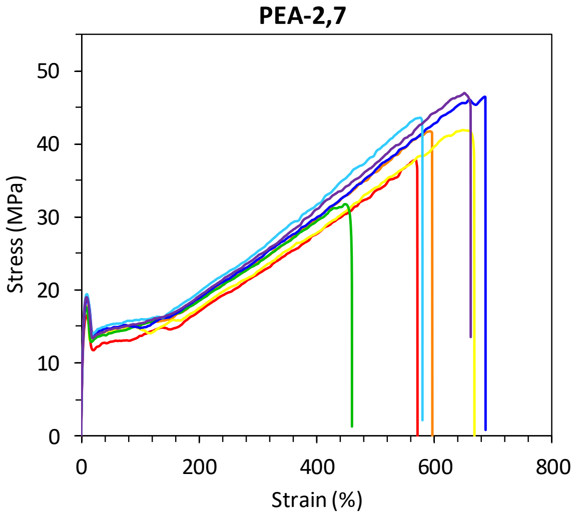


Figure S9. Stress vs. strain curves for seven **PEA-2,7** sample bars cut from the same stock sample of polymer.

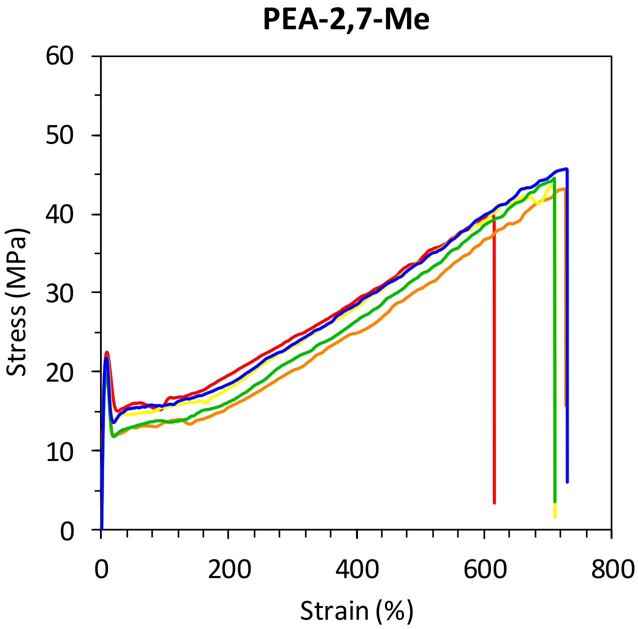


Figure S10. Stress vs. strain curves for five **PEA-2,7-Me** sample bars cut from the same stock sample of polymer.

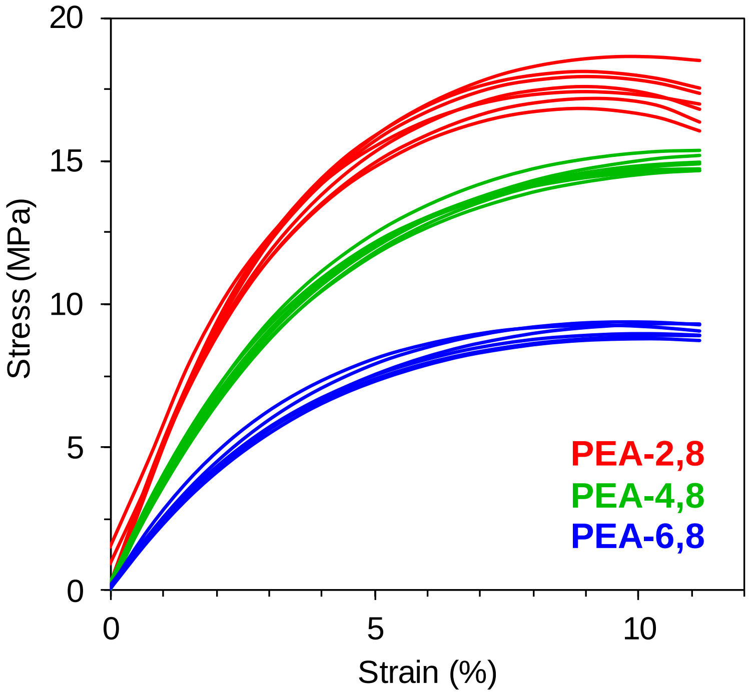


Figure S11. Expansion showing the elastic region of the stress vs. strain curves (0–11% strain) for all sample bars of **PEA-2,8**, **PEA-4,8**, and **PEA-6,8.** The reproducibility of the behavior clearly suggests that there is a structural correlation.

Size exclusion chromatograms for the PEA and norMe-PEA polymers

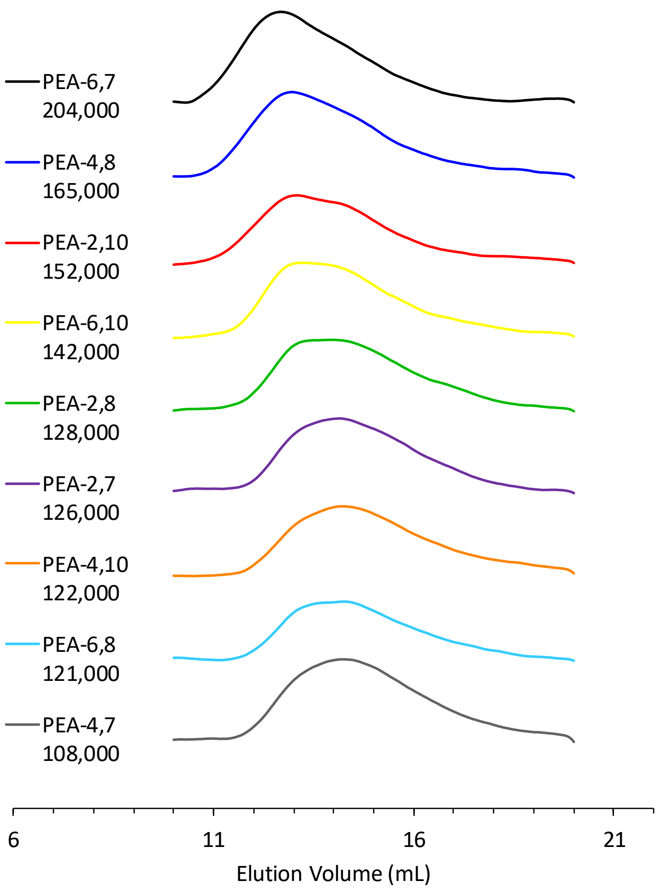


Figure S12. Overlay of DMF size exclusion chromatograms (offset vertically for clarity). Chromatograms are organized by decreasing molecular weight from top to bottom.

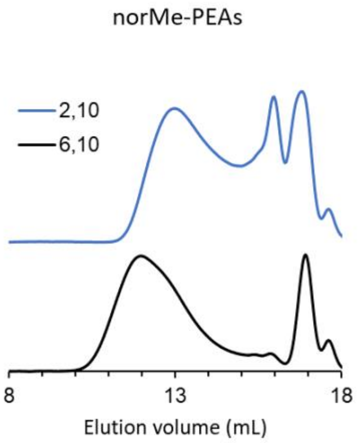


Figure S13. Overlay of HFIP size exclusion chromatograms (offset vertically for clarity) of **norMe-PEAs**

Thermogravimetric analysis data for PEA and norMe-PEA Polymers

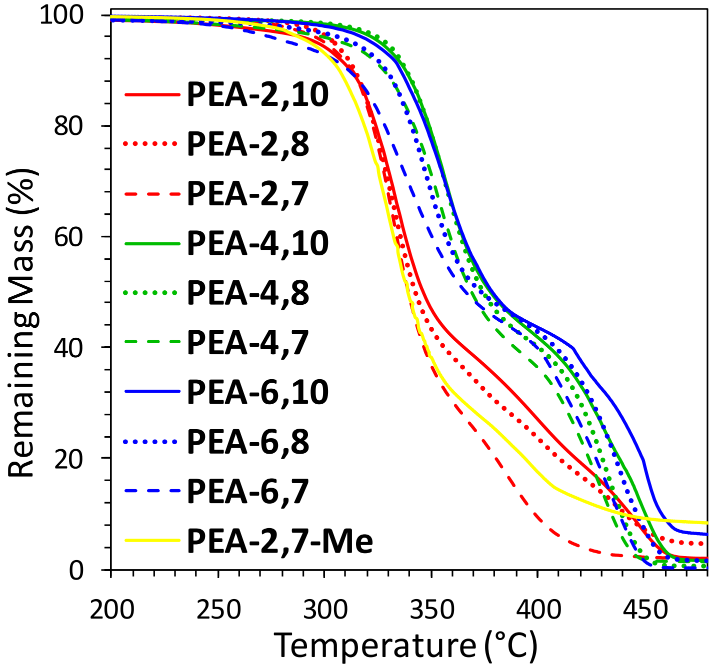


Figure S14. Thermogravimetric analysis curves for all **PE**As.

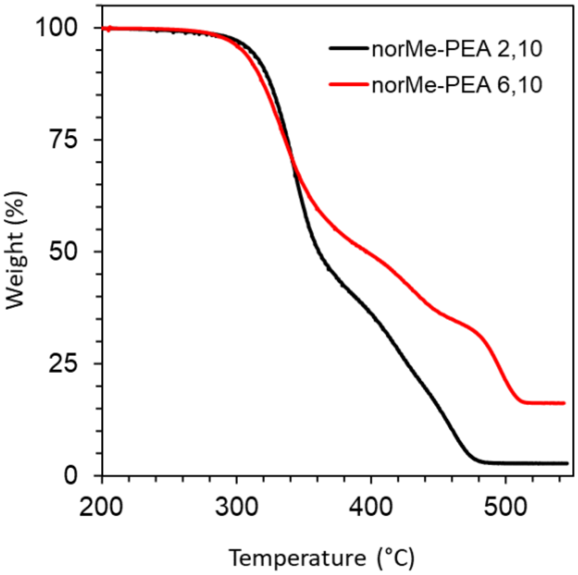
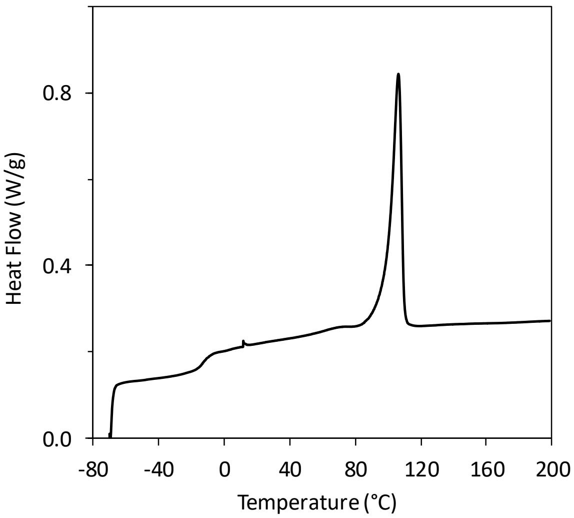
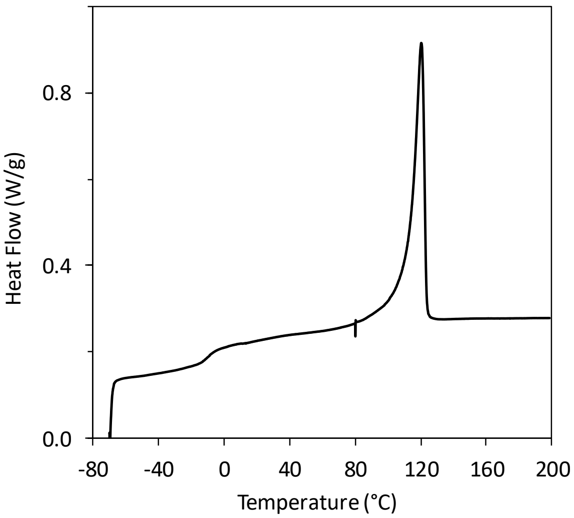


Figure S15. Thermogravimetric analysis curves for the two **norMe-PEA**s.

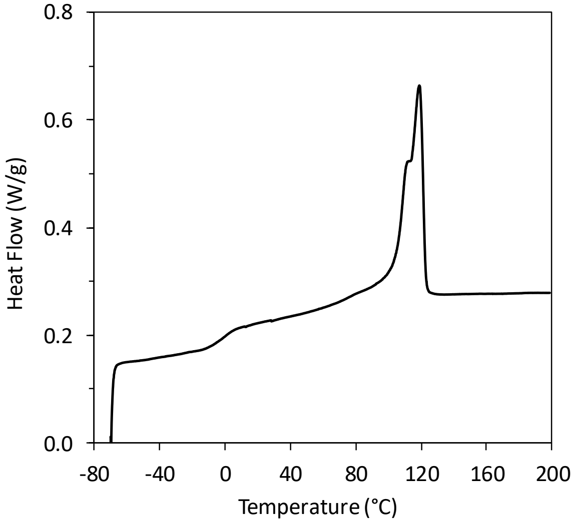
Differential Scanning Calorimetry Data (from second heating curve; see “Instrumental Methods”) for PEA and norMe-PEA Polymers



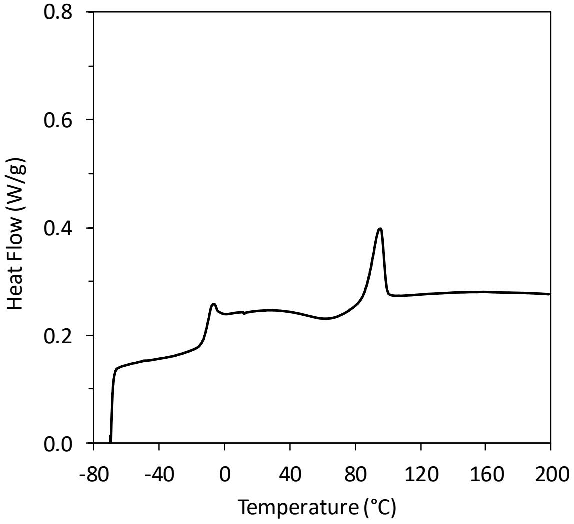
PEA-6,10



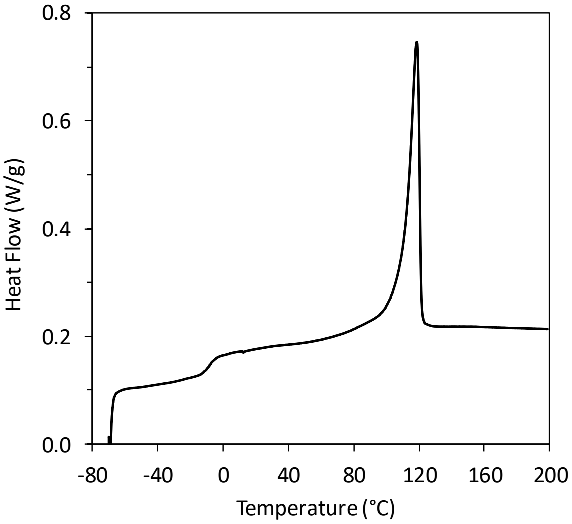
PEA-4,10



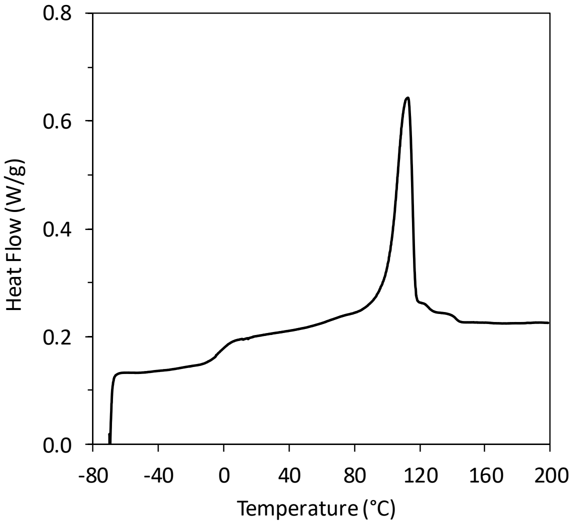
PEA-2,10



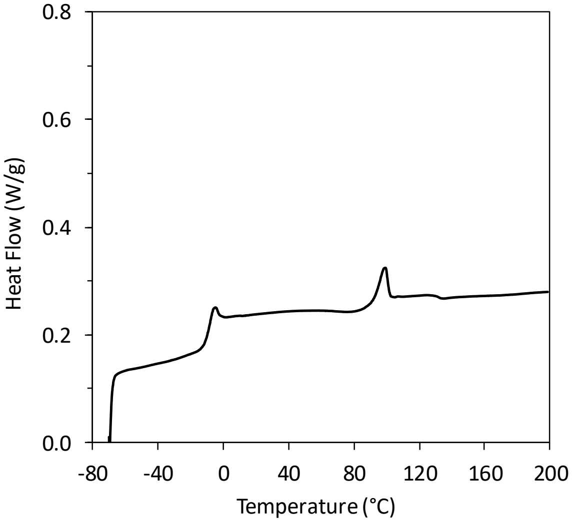
PEA-6,8



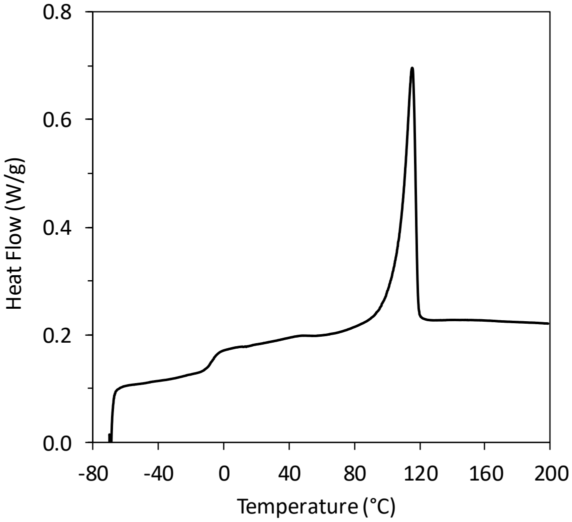
PEA-4,8



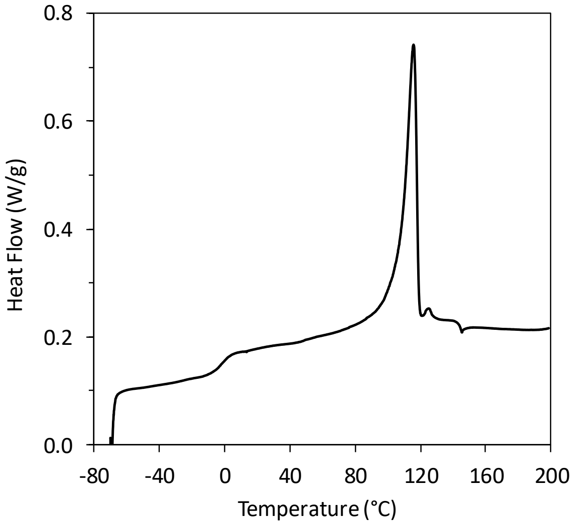
PEA-2,8



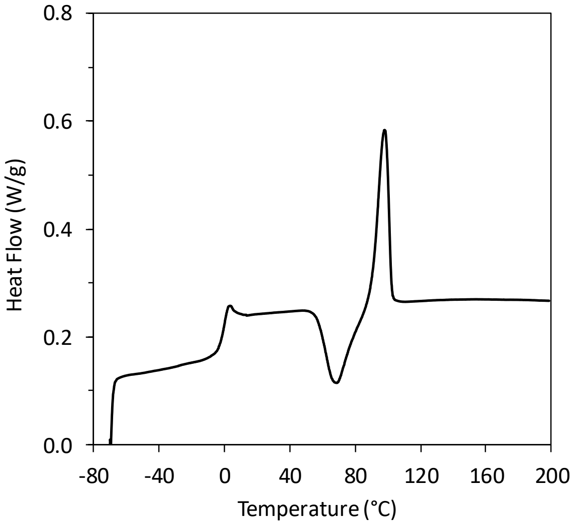
PEA-6,7



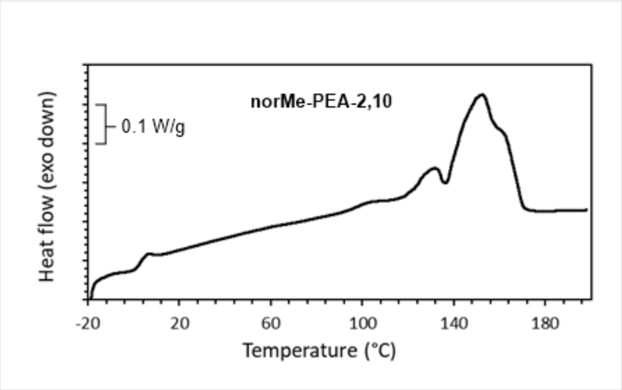
PEA-4,7



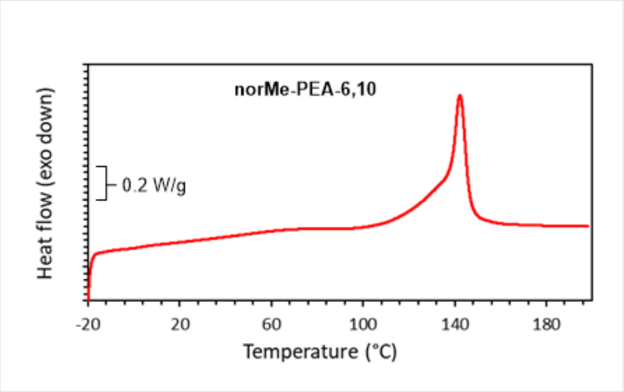
PEA-2,7



PEA-2,7-Me



norMe-PEA-2,10



norMe-PEA-6,10

V. Hydrolytic Degradation Studies of PEAs

Polymer films used for these degradation studies were (for **PEA-2,8**, **PEA-6,8**, **PEA-4,10**, **PEA-4,8**, and **PEA-4,7**) of the same source as that used for preparation of the tensile testing samples (described above under "Instrumental Methods"). These films were 0.3–0.4 mm thick. Rectangular pieces weighing 50–60 mg each were cut from the bulk film. Each was examined in each of the following aqueous media: 1M NaOH, 1M HCl, and deionized H_2O. Each piece was submerged in ca. 10 mL of the reaction medium inside a glass vial. Each polymer sample was periodically removed from the solution, dabbed dry with a Kimwipe®, weighed, and returned to the same solution. The degradation products from **PEA-2,8** were tentatively identified to include those shown in Figure S17 by performing the reaction in D_2O/NaOH and analyzing the spectra by analogy to what is described in the manuscript text for **norMe-PEA-6,10** (Figure 4).

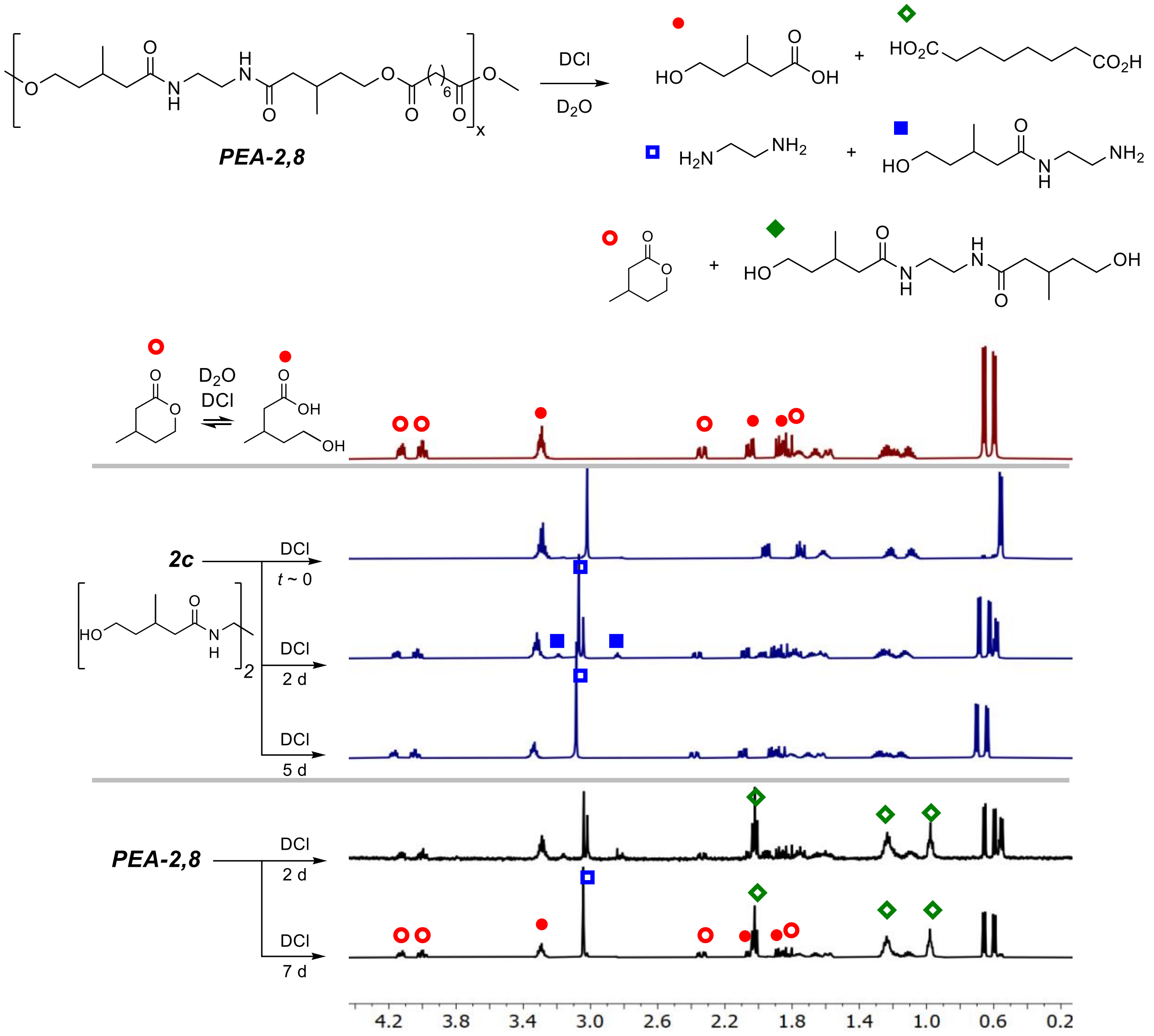


Figure S16. Hydrolysis of **PEA-2,8** under DCl/D_2O over time.

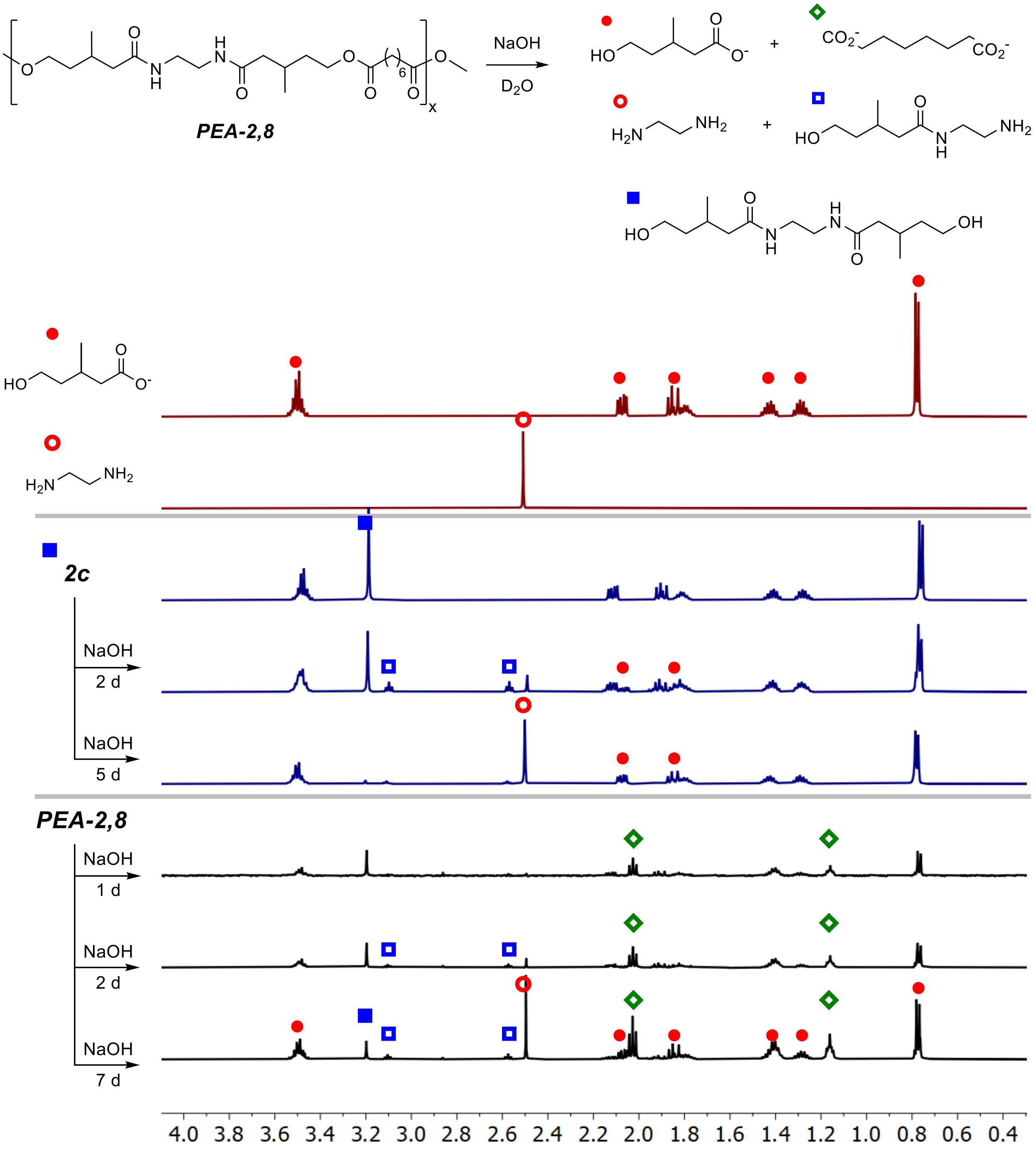


Figure S17. Hydrolysis of **PEA-2,8** under NaOH/D_2O over time.

For **norMe-PEA-6,10** a film of similar size and thickness was used. It was observed that this polymer became brittle and easily fractured, so mass loss over time was not measured. The degradation products from **norMe-PEA-6,10** were identified to include those shown in Figure S18 by performing the reaction in D_2O/NaOH and examining the proton NMR spectrum of the compounds present in the homogenous supernatant liquid.

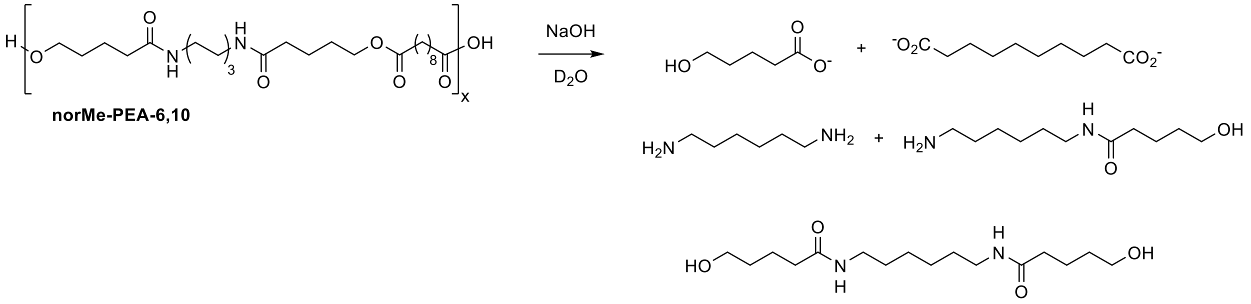
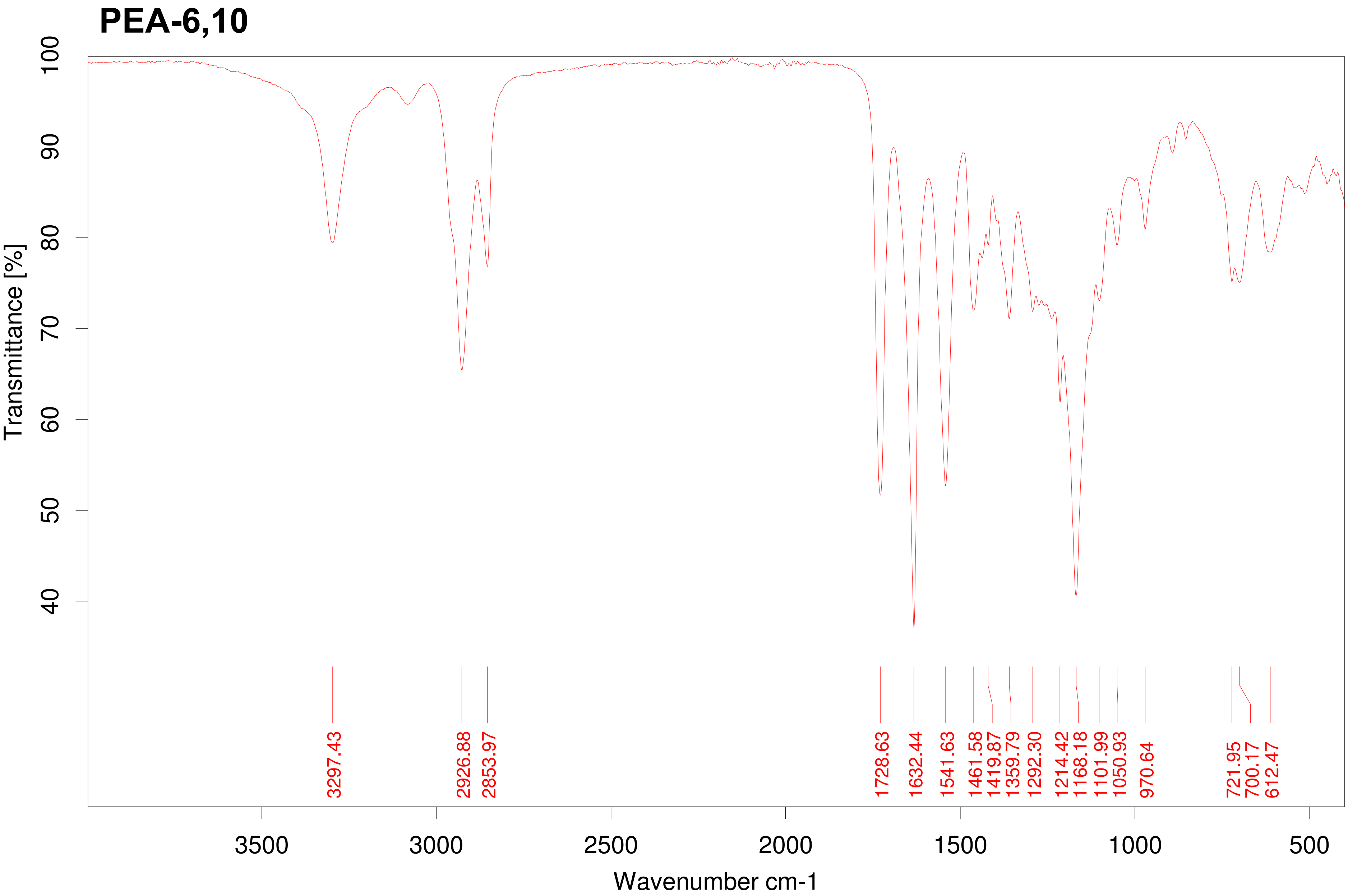
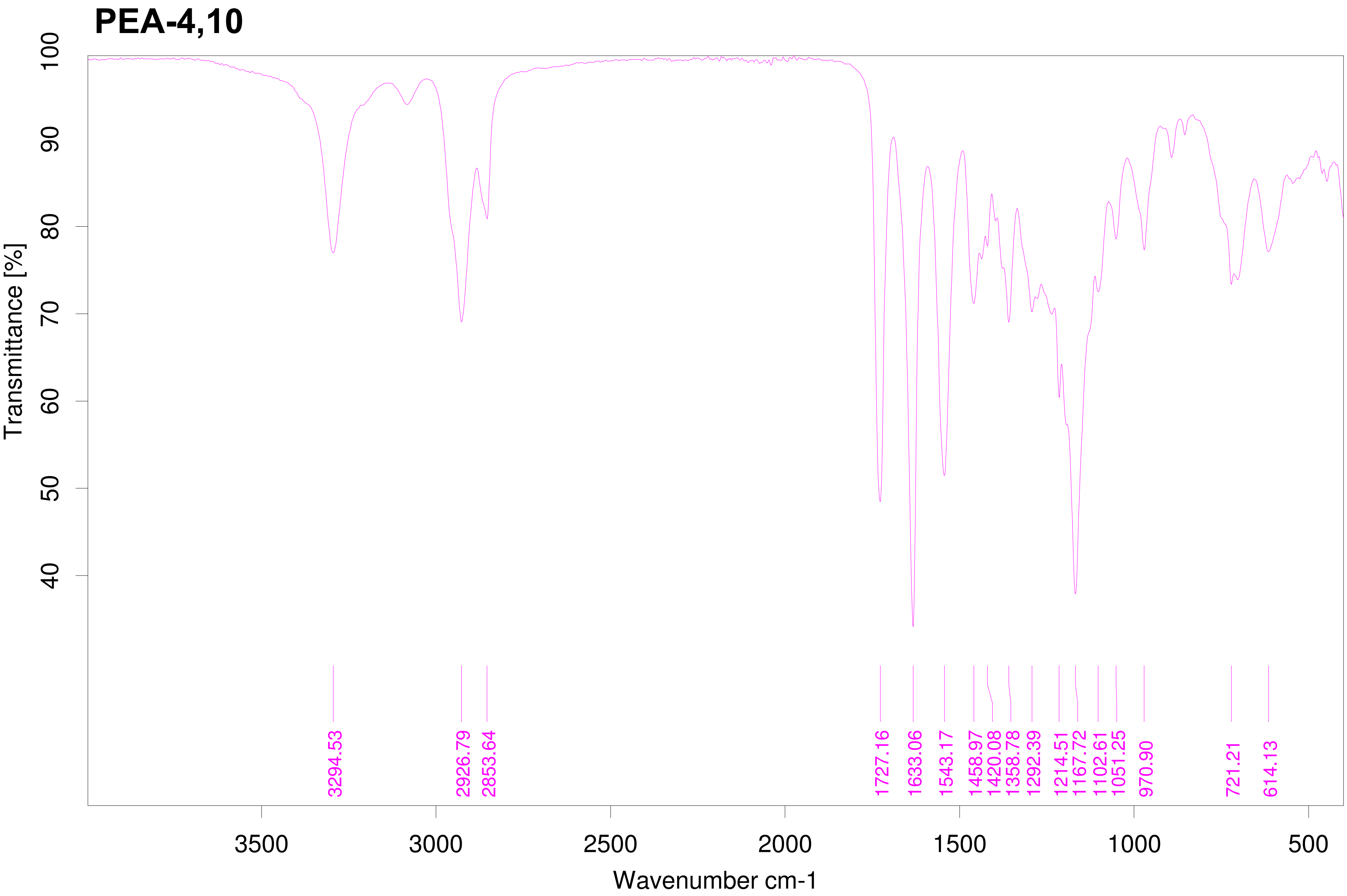


Figure S18. Hydrolysis of **norMe-PEA-6,10** under NaOH/D_2O over time.

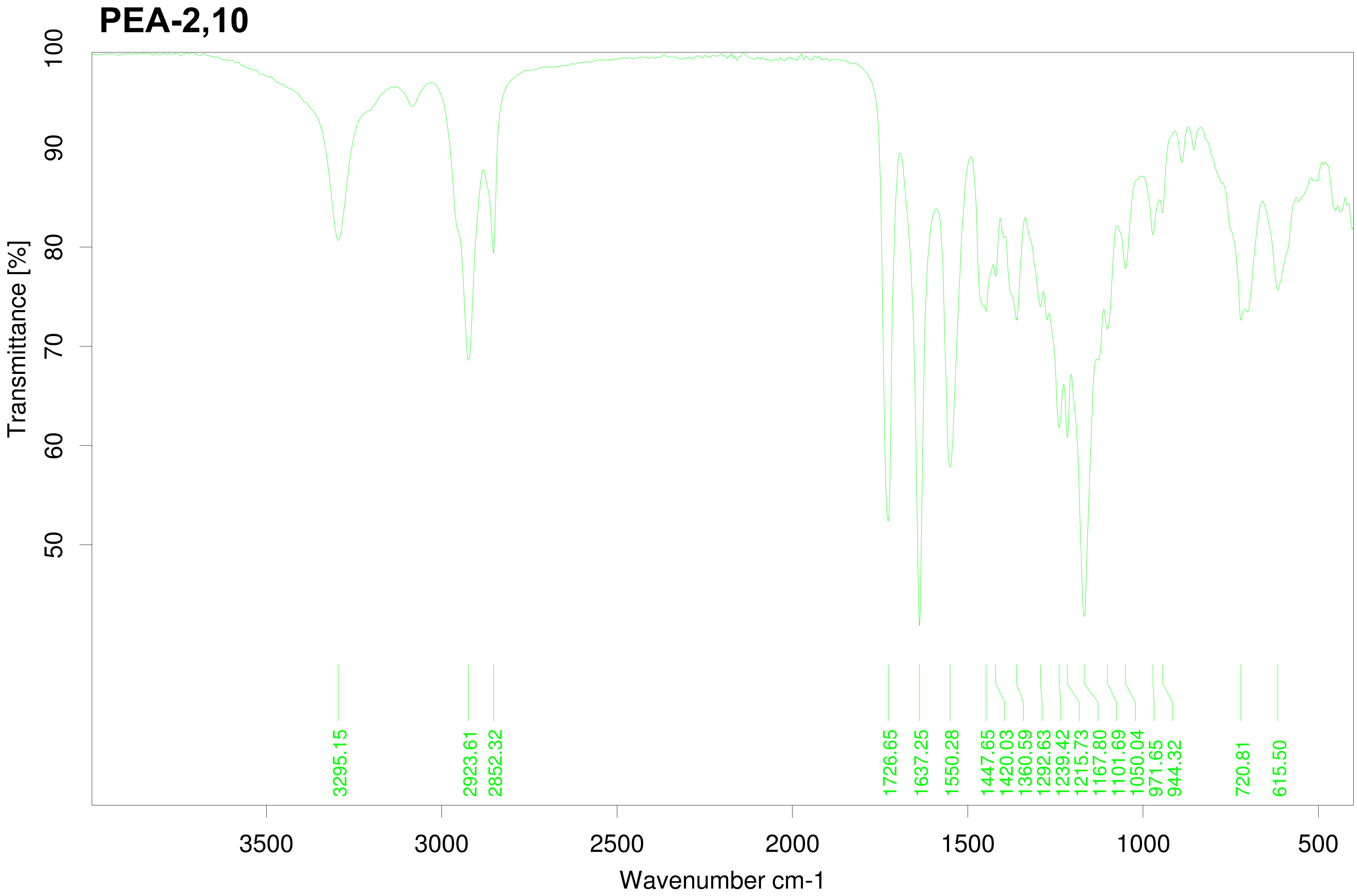
VI. Infrared Spectra of PEAs



FTIR Spectrum of **PEA-6,10**

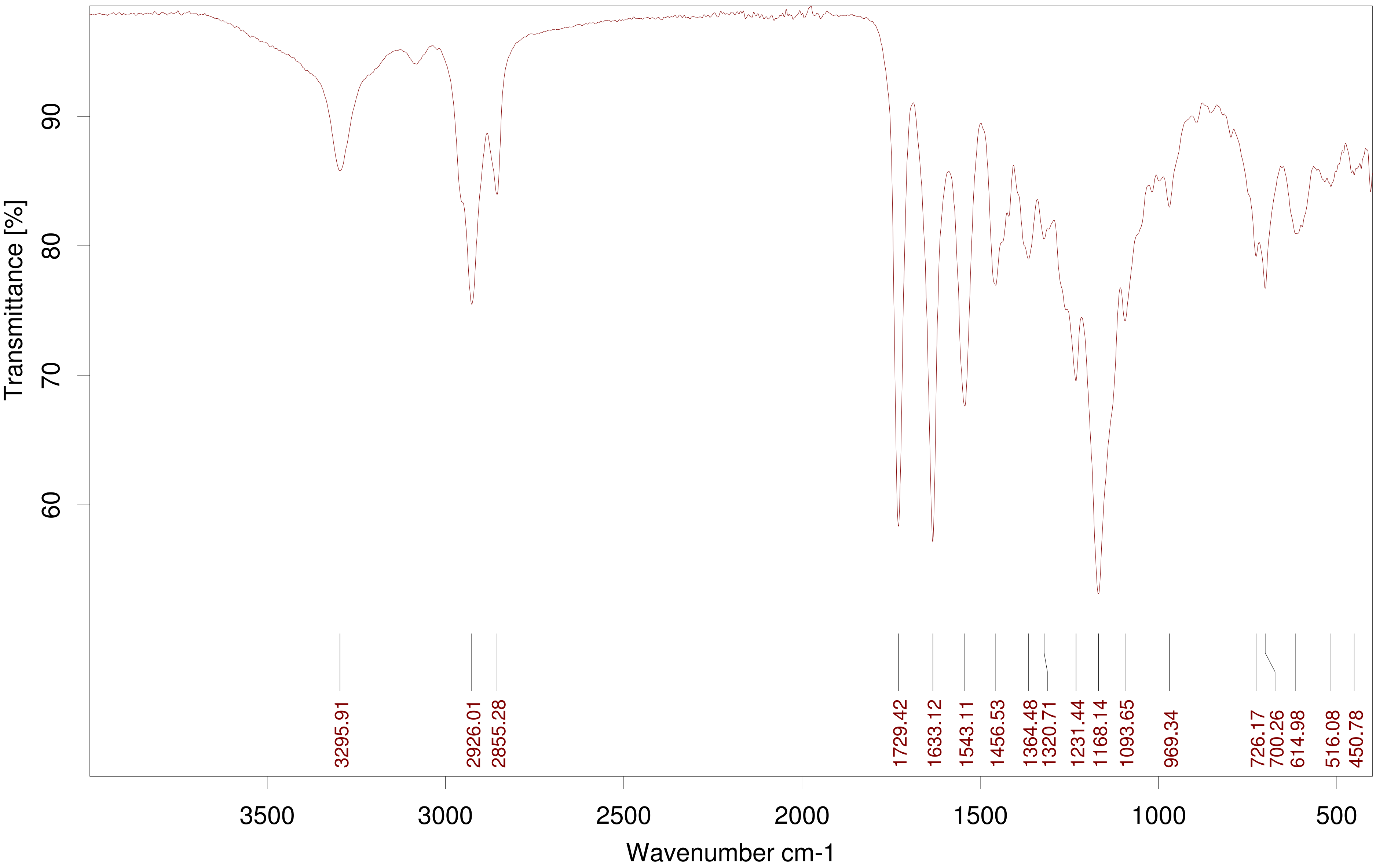


FTIR Spectrum of **PEA-4,10**



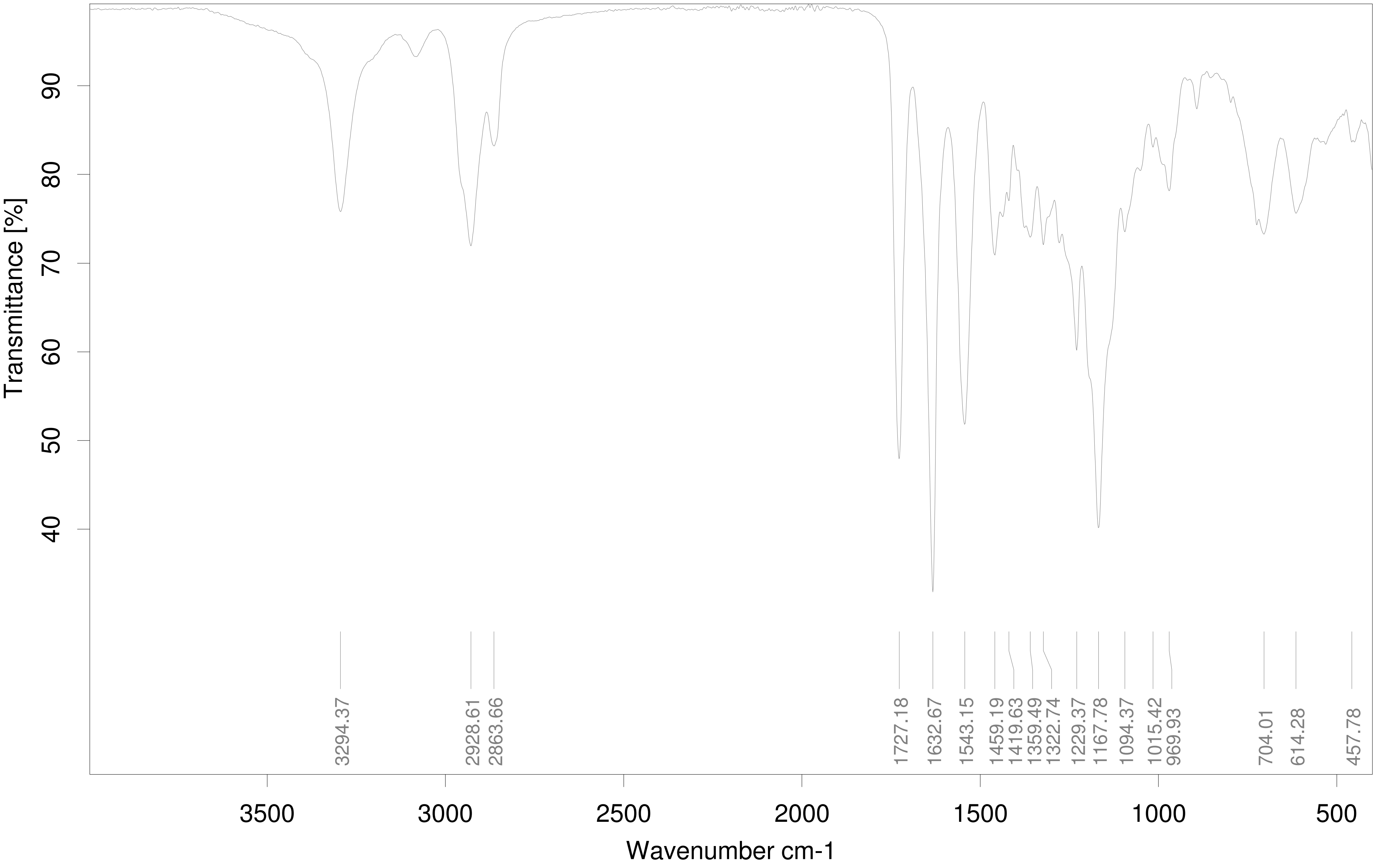
FTIR Spectrum of **PEA-2,10**

PEA-6,8

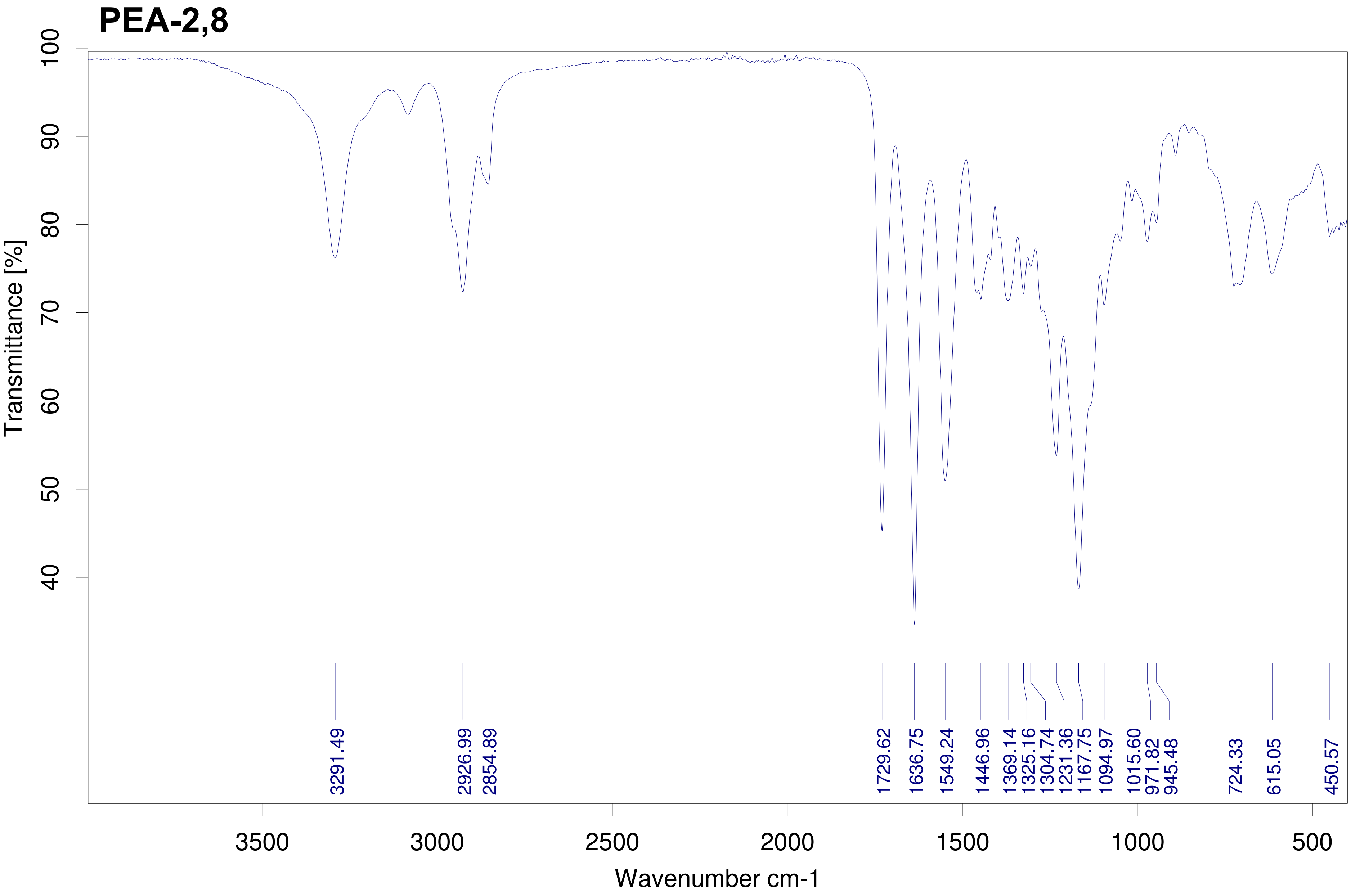


FTIR Spectrum of **PEA-6,8**

PEA-4,8

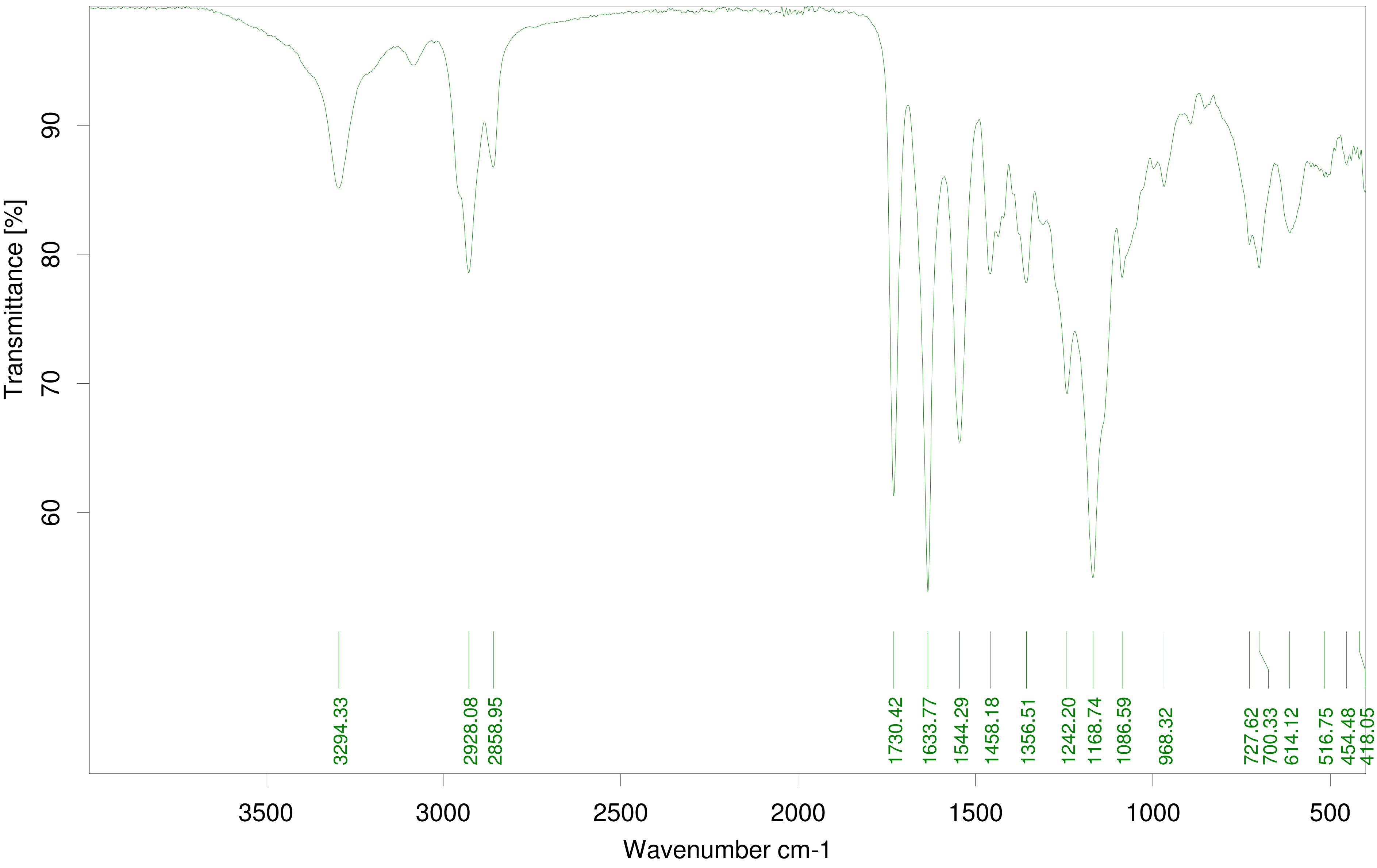


FTIR Spectrum of **PEA-4,8**



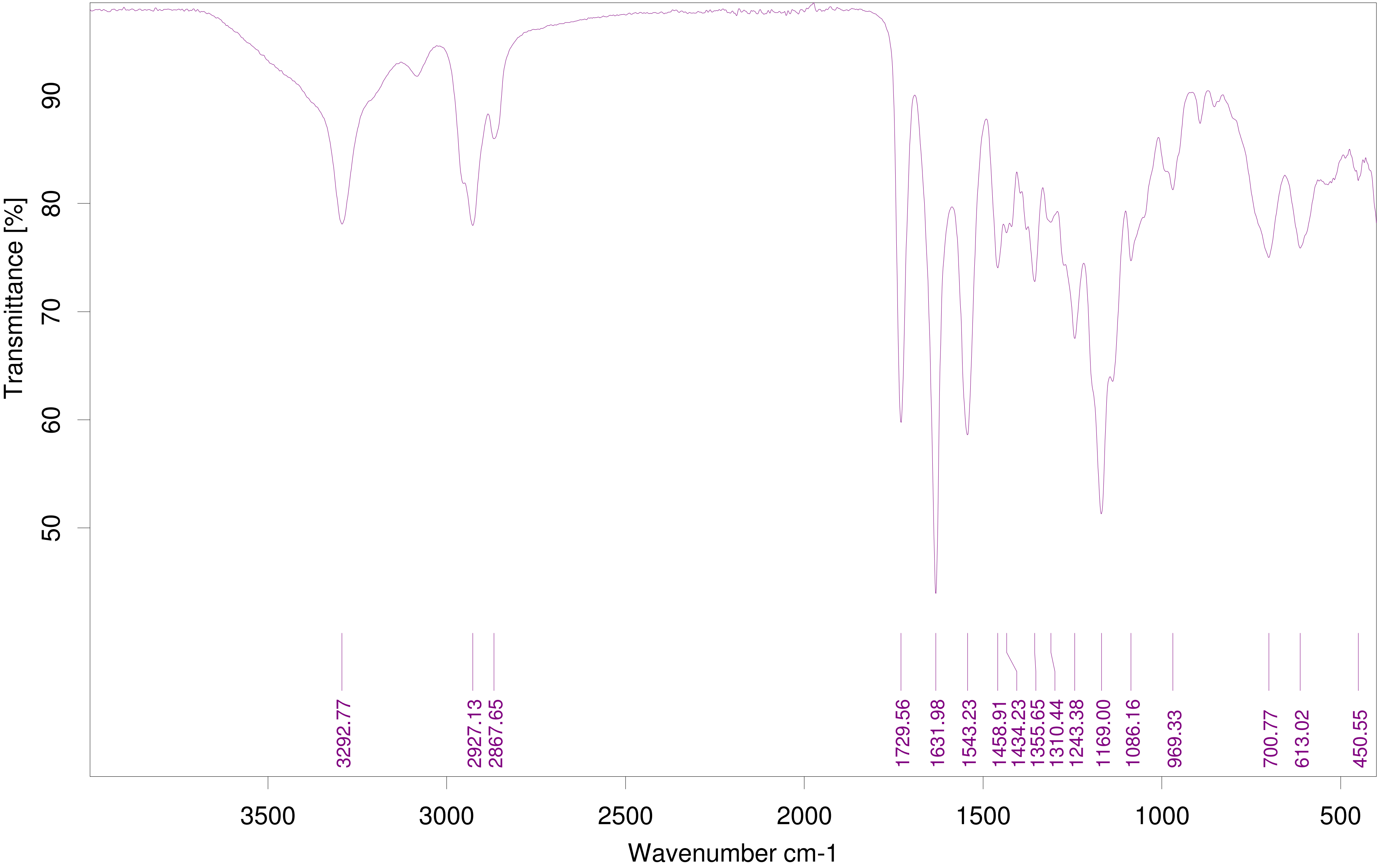
FTIR Spectrum of **PEA-2,8**

PEA-6,7



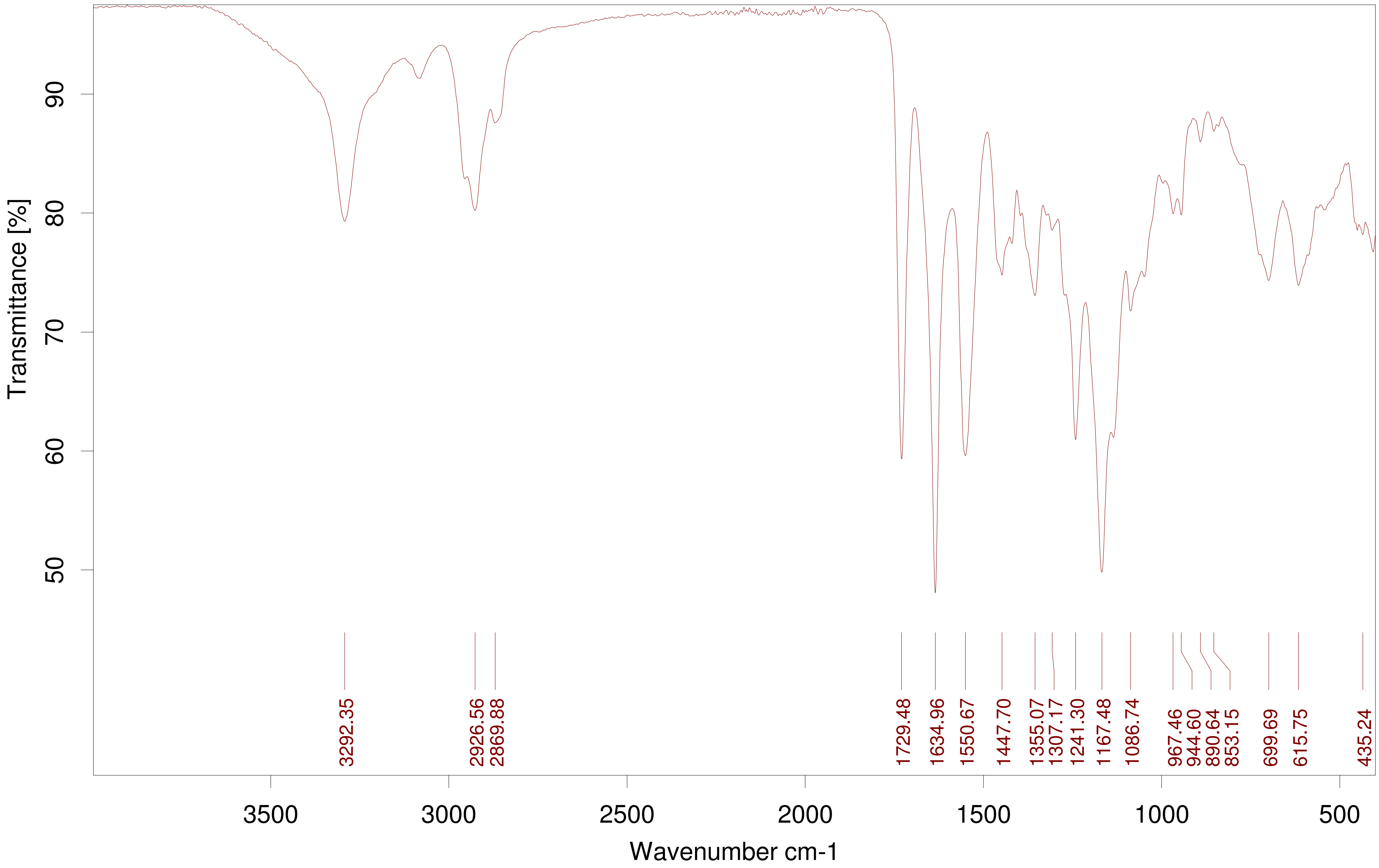
FTIR Spectrum of **PEA-6,7**

PEA-4,7

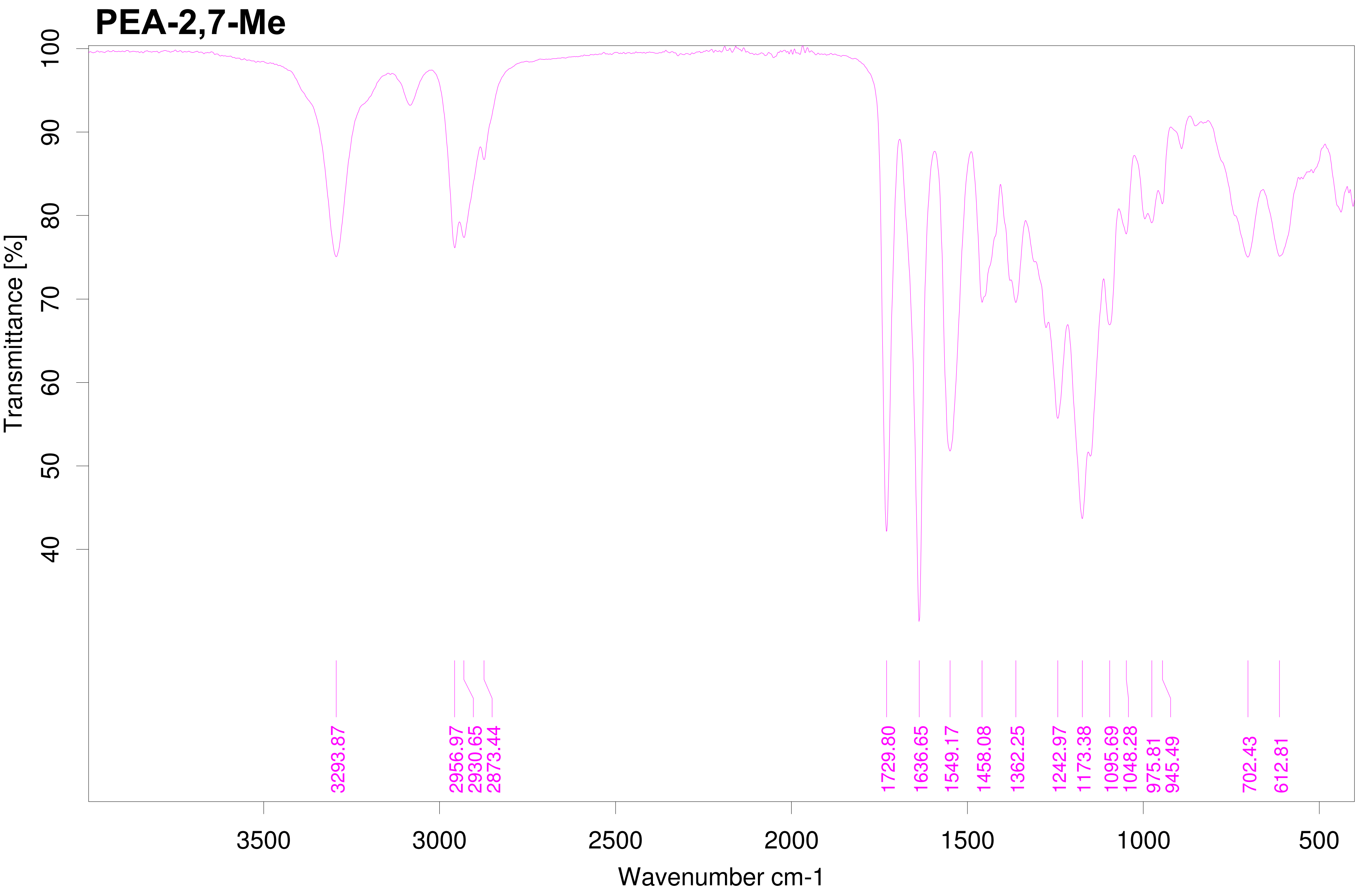


FTIR Spectrum of **PEA-4,7**

PEA-2,7



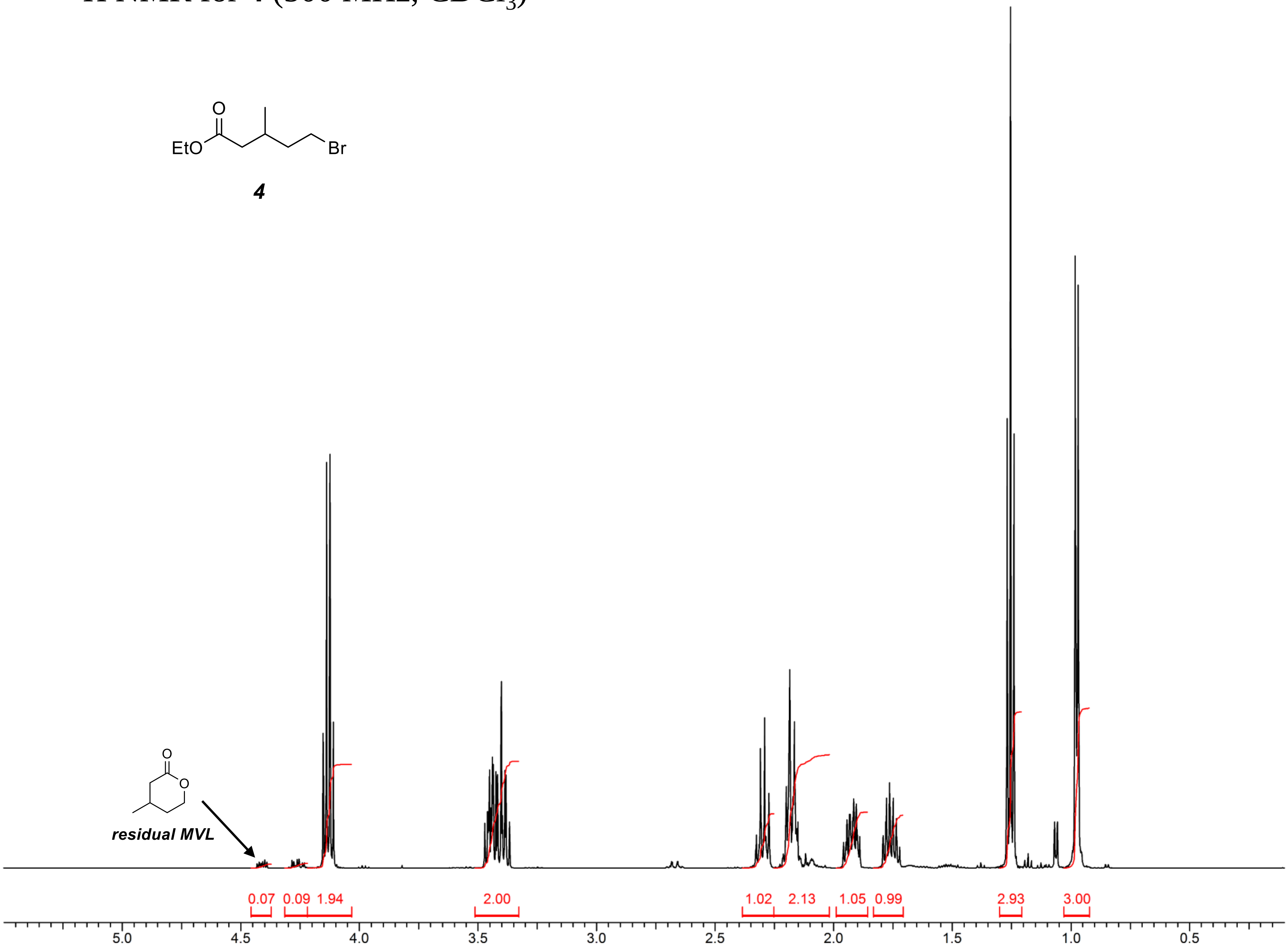
FTIR Spectrum of **PEA-2,7**



FTIR Spectrum of **PEA-2,7-Me**

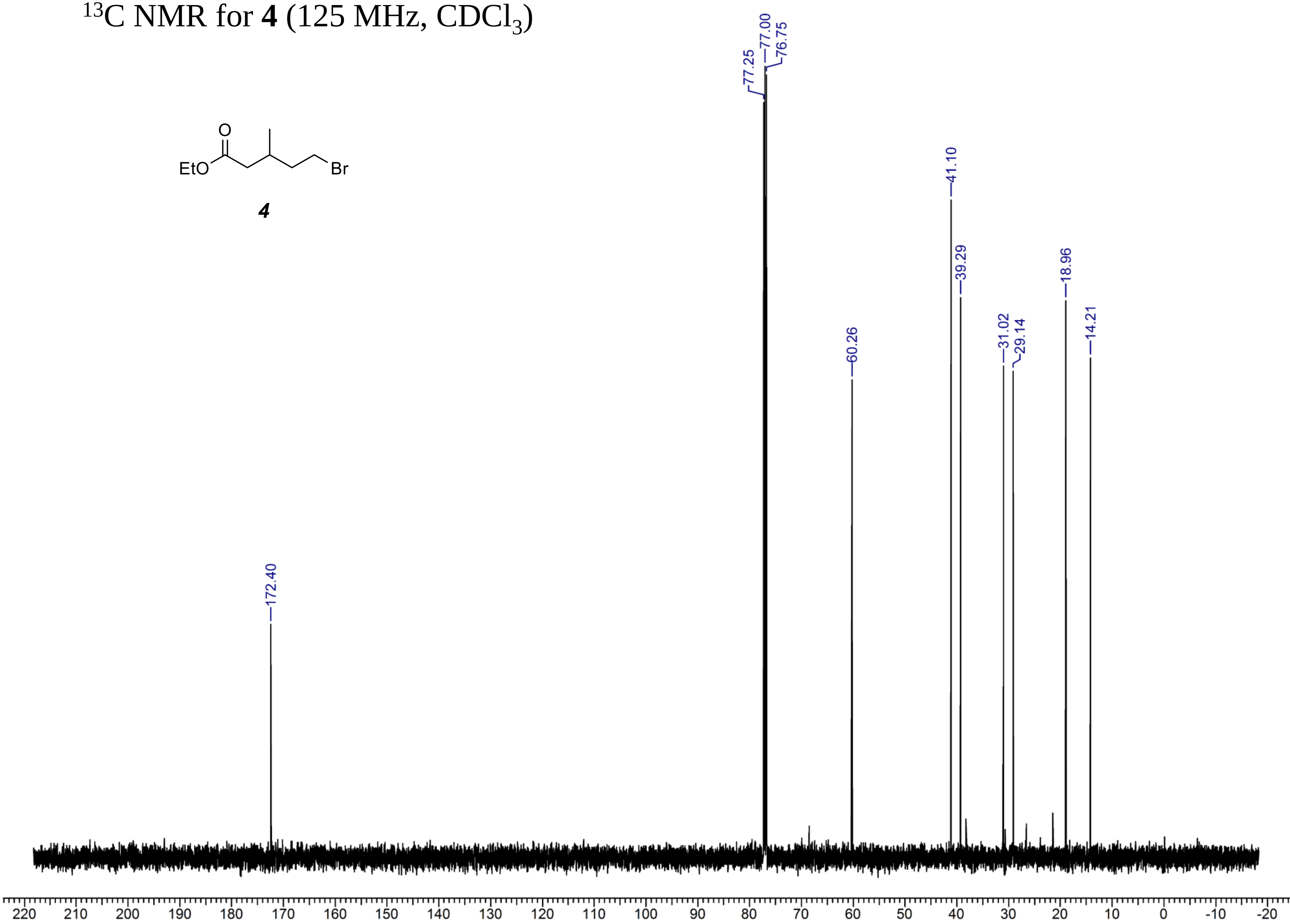
VII. Copies of ^{1}H and ^{13}C NMR Spectra for all New Compounds and Polymers

^{1}H NMR for **4** (500 MHz, $CDCl_3$)

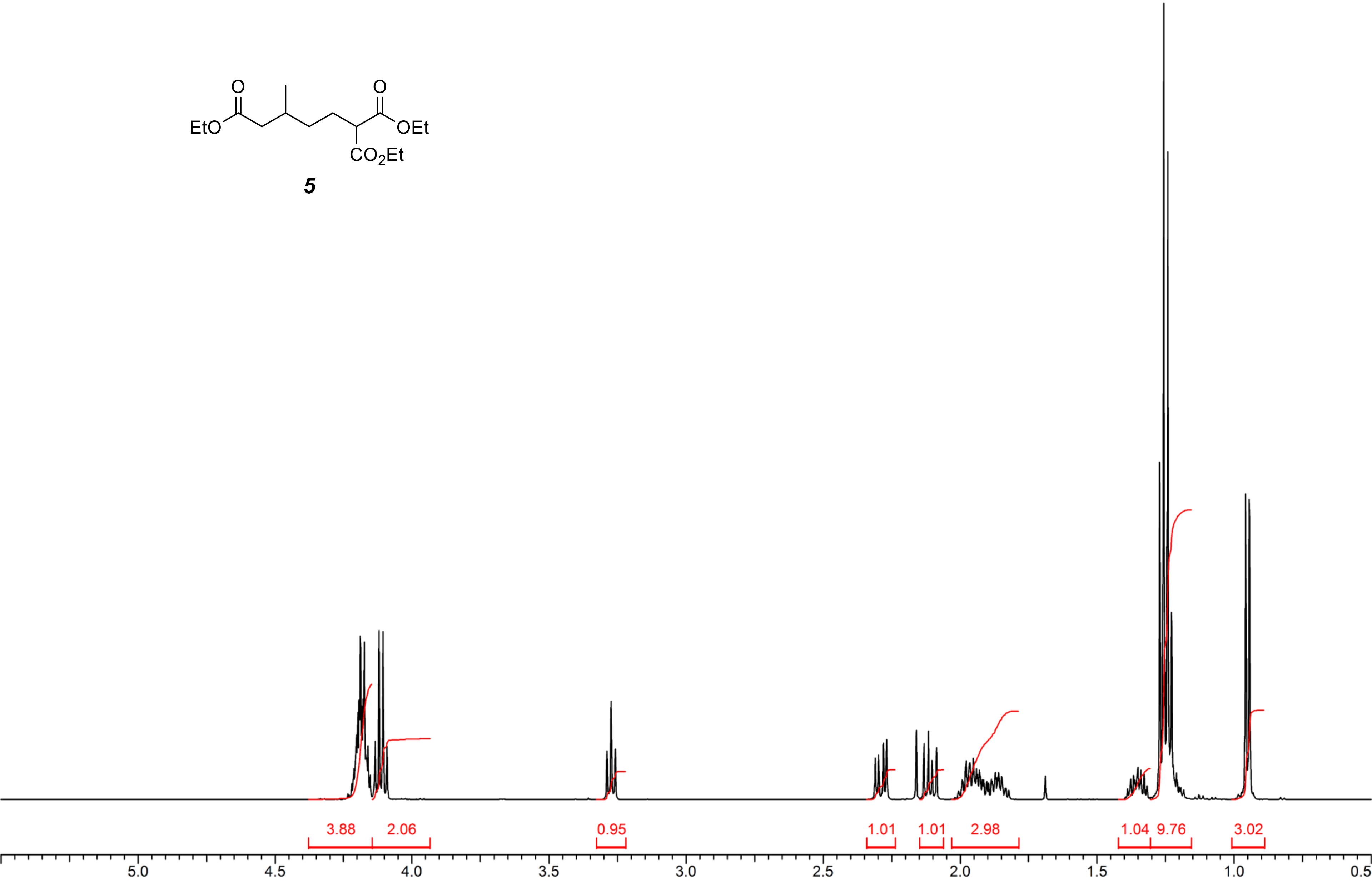


^{13}C NMR for **4** (125 MHz, $CDCl_3$)

4



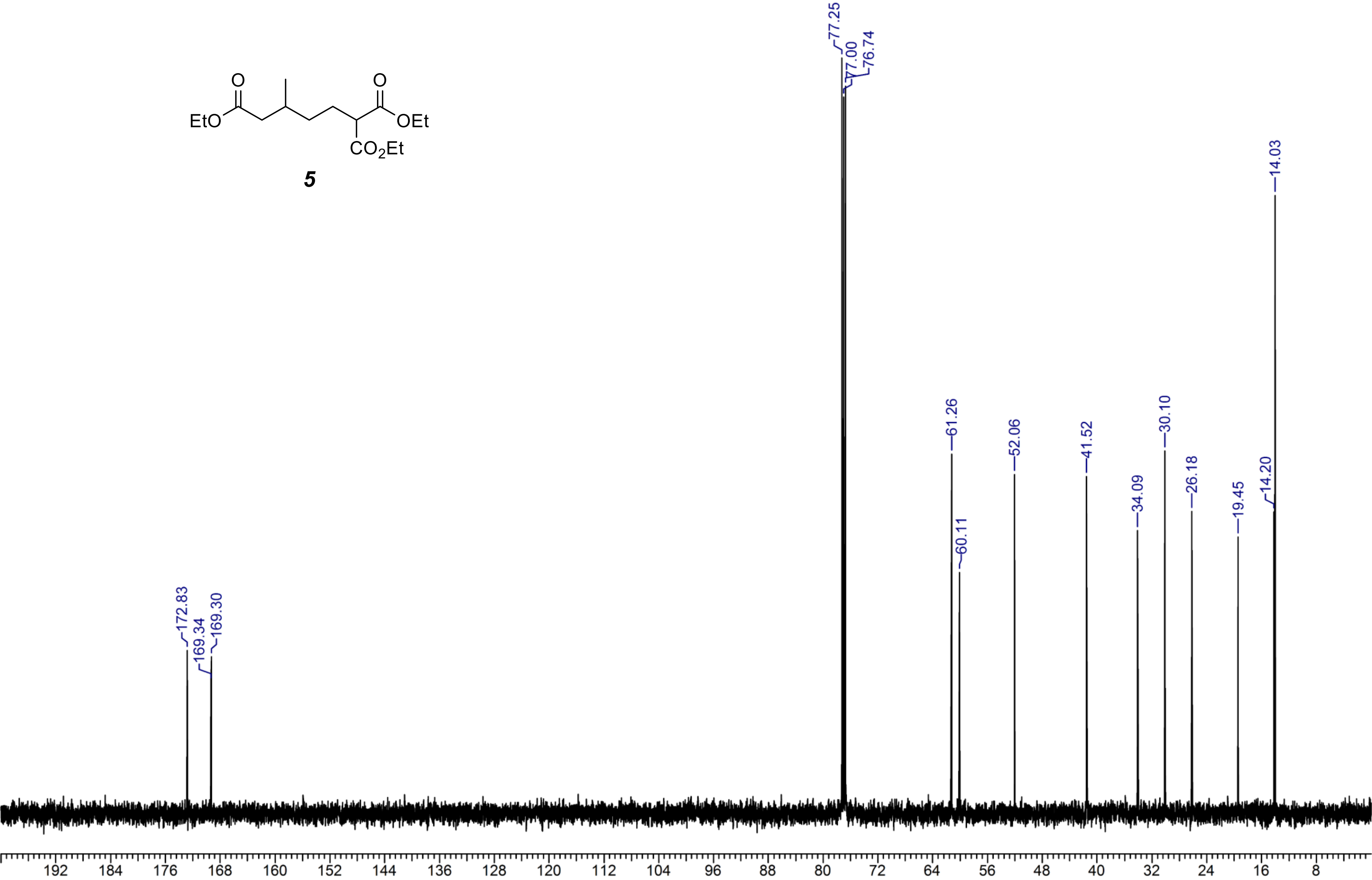
^{1}H NMR for **5** (500 MHz, $CDCl_3$)



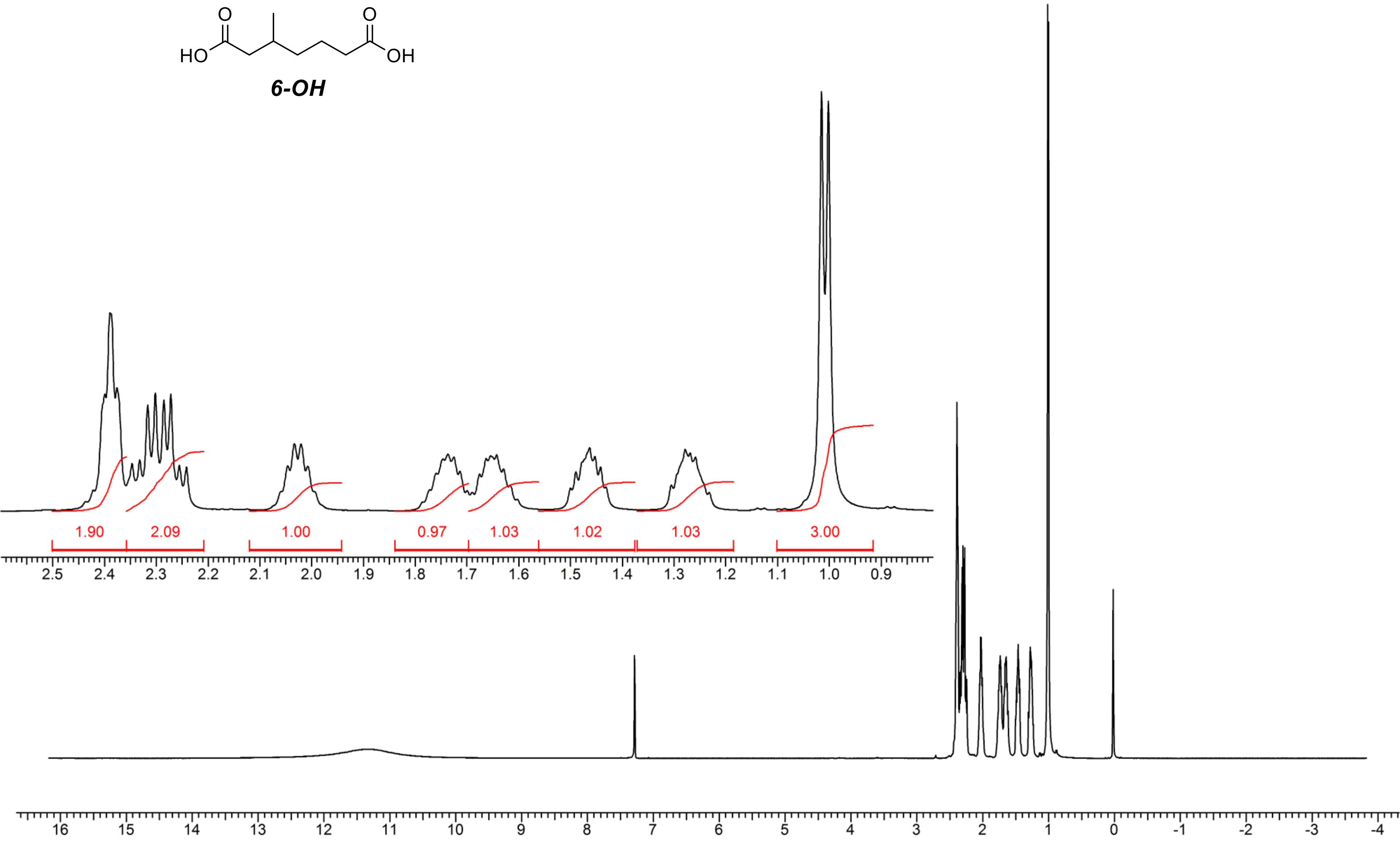
5

^{13}C NMR for **5** (125 MHz, $CDCl_3$)

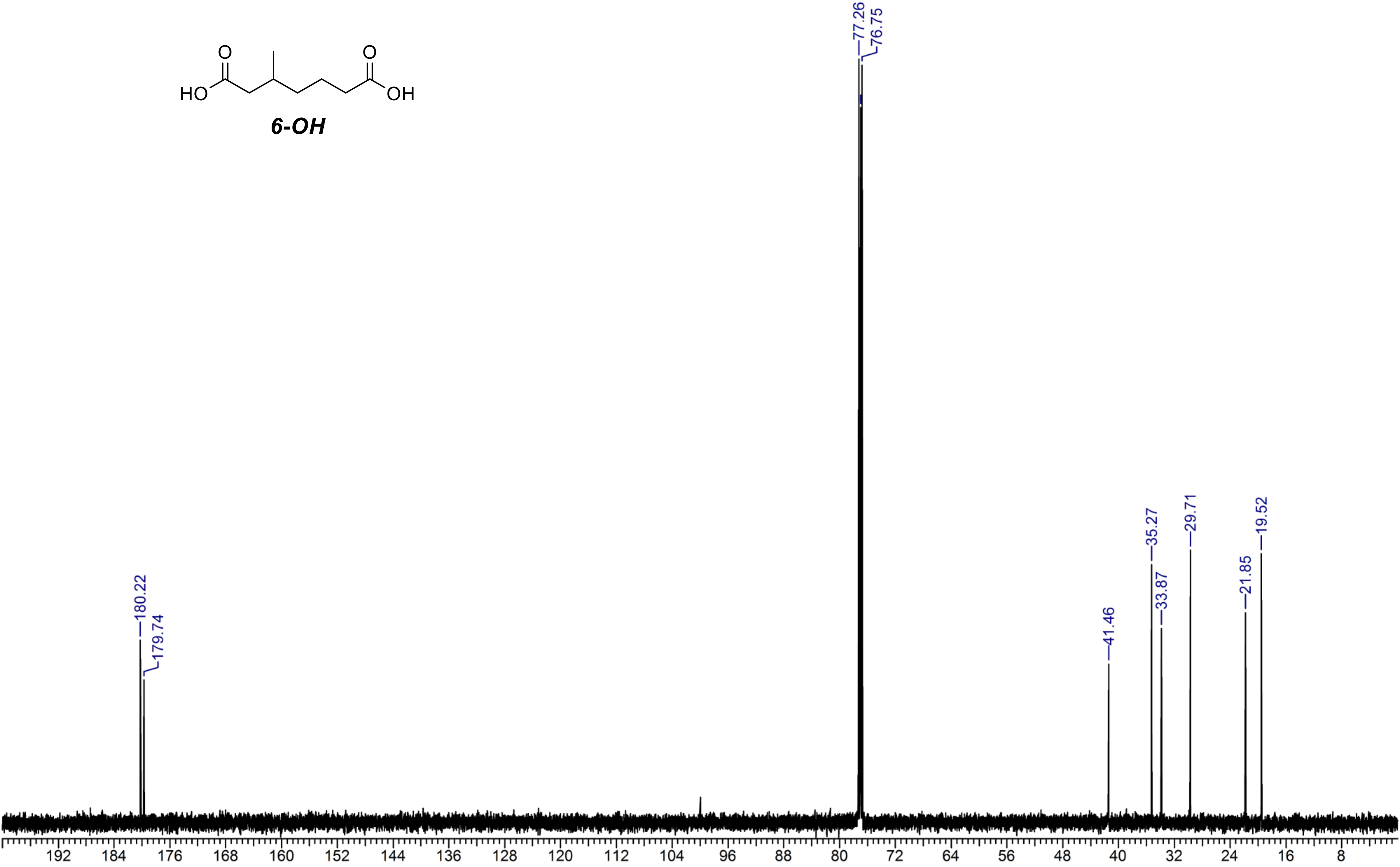
5



^{1}H NMR for **6-OH** (500 MHz, $CDCl_3$)

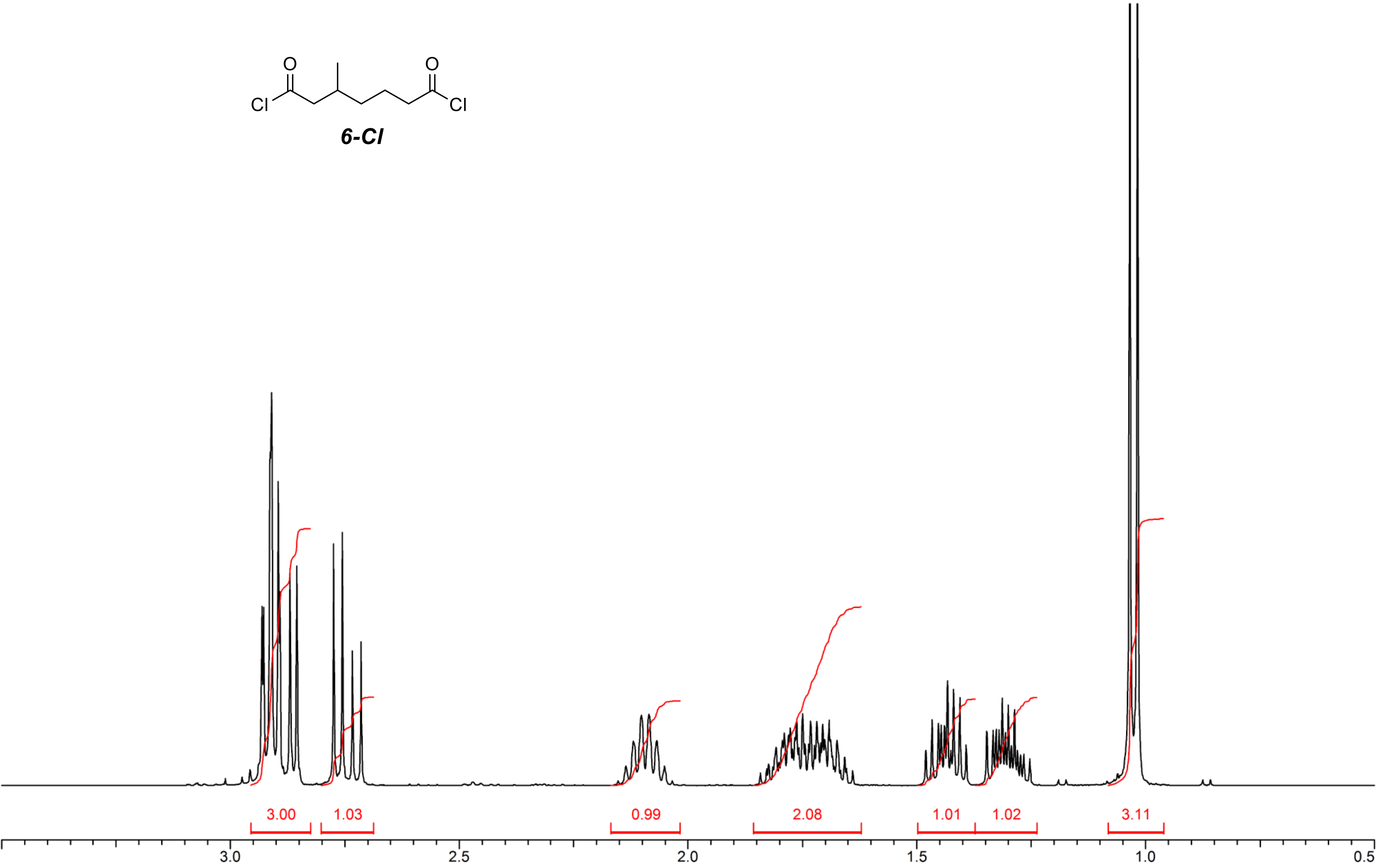


^{13}C NMR for **6-OH** (125 MHz, $CDCl_3$)

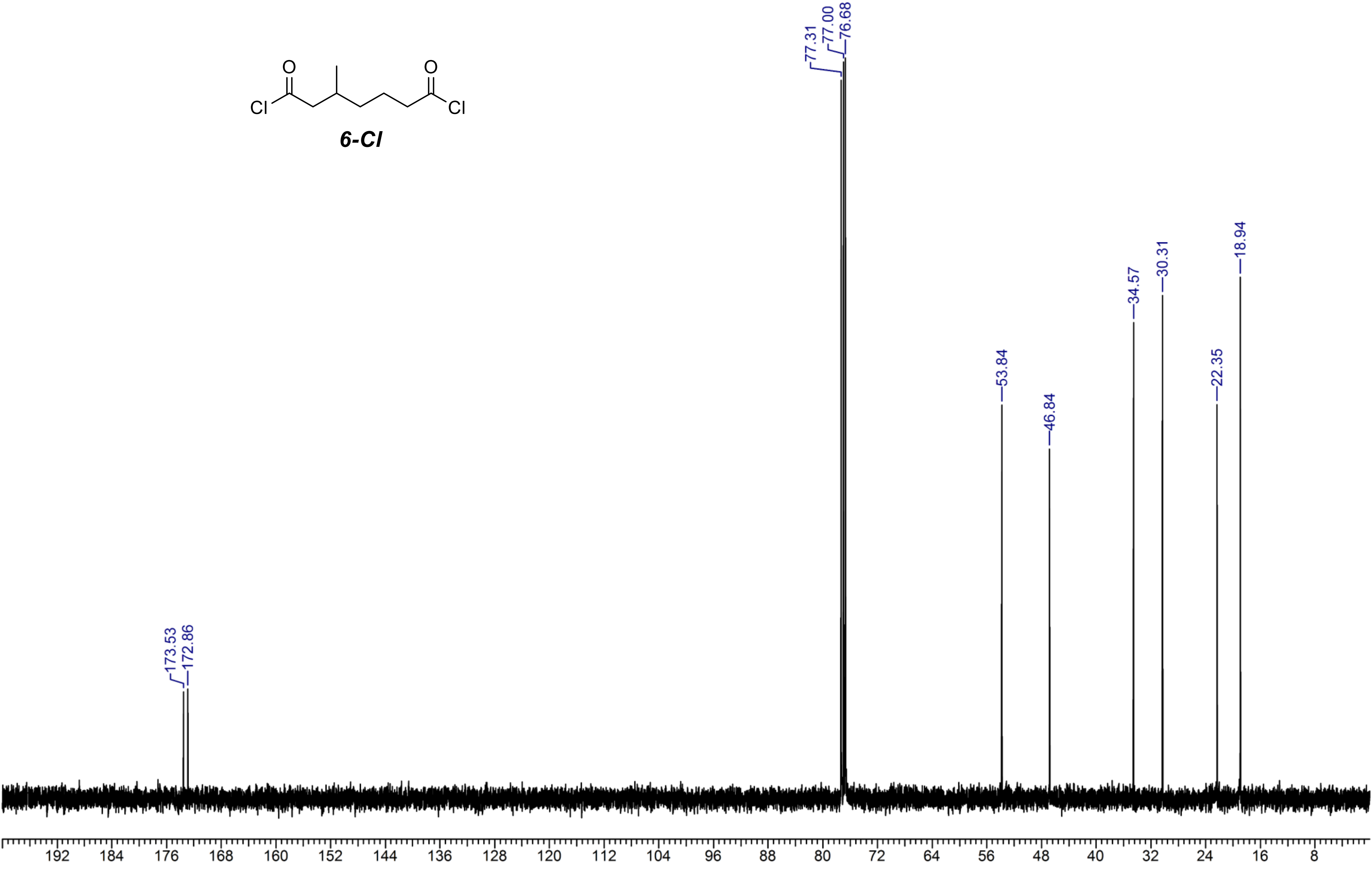


^{1}H NMR for **6-Cl** (400 MHz, $CDCl_3$)

6-Cl

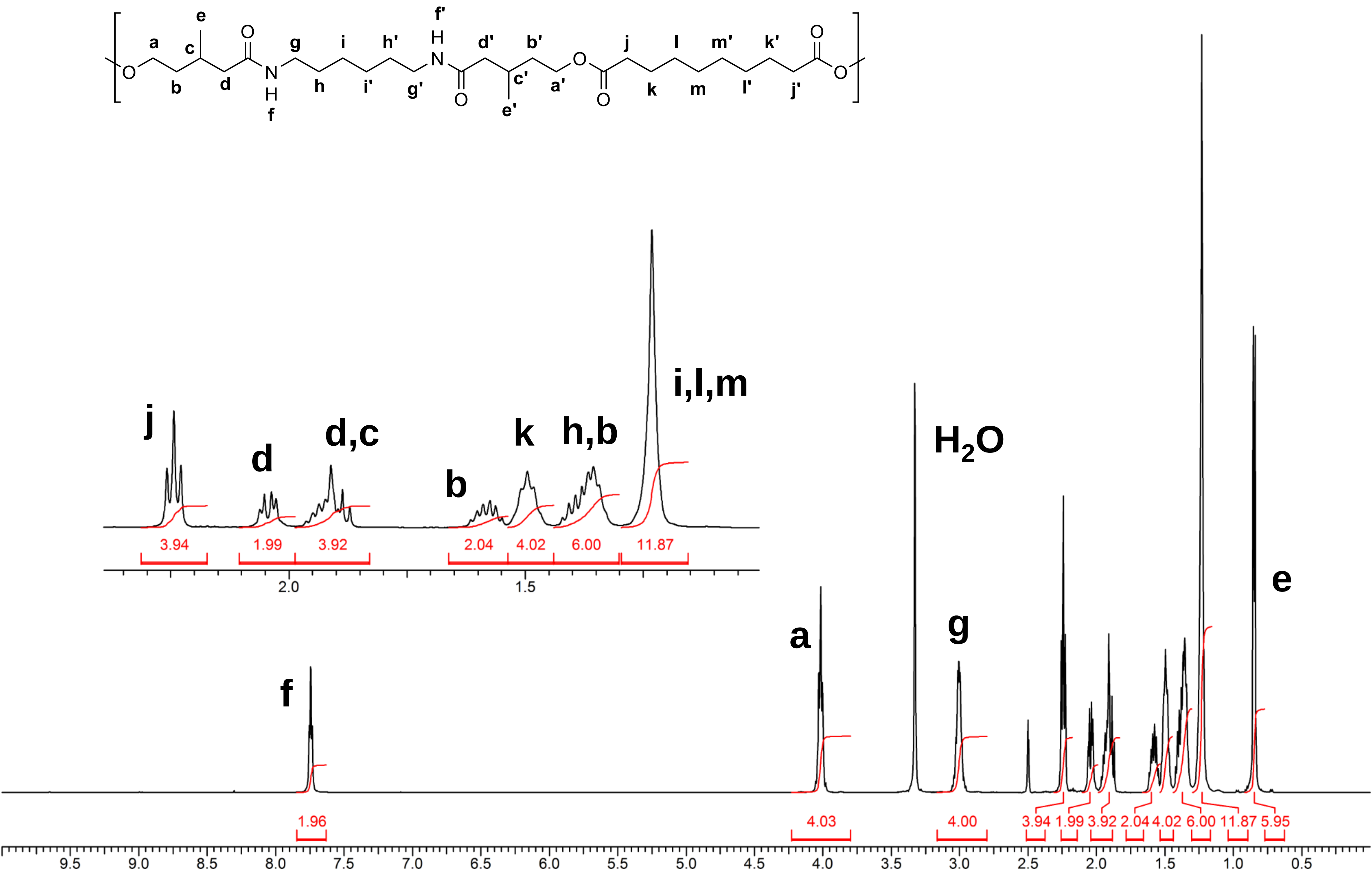


^{13}C NMR for **6-Cl** (100 MHz, $CDCl_3$)

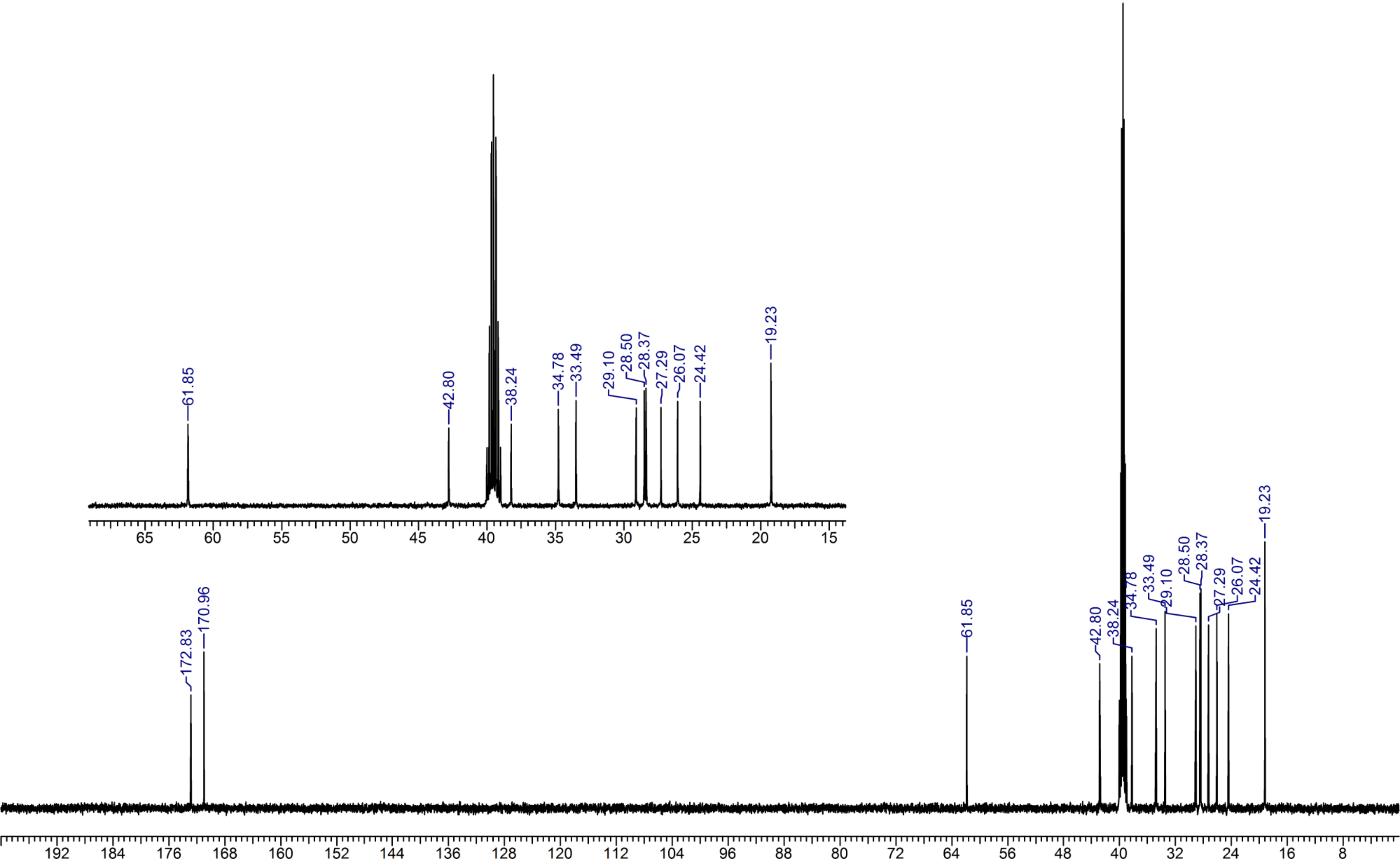


6-Cl

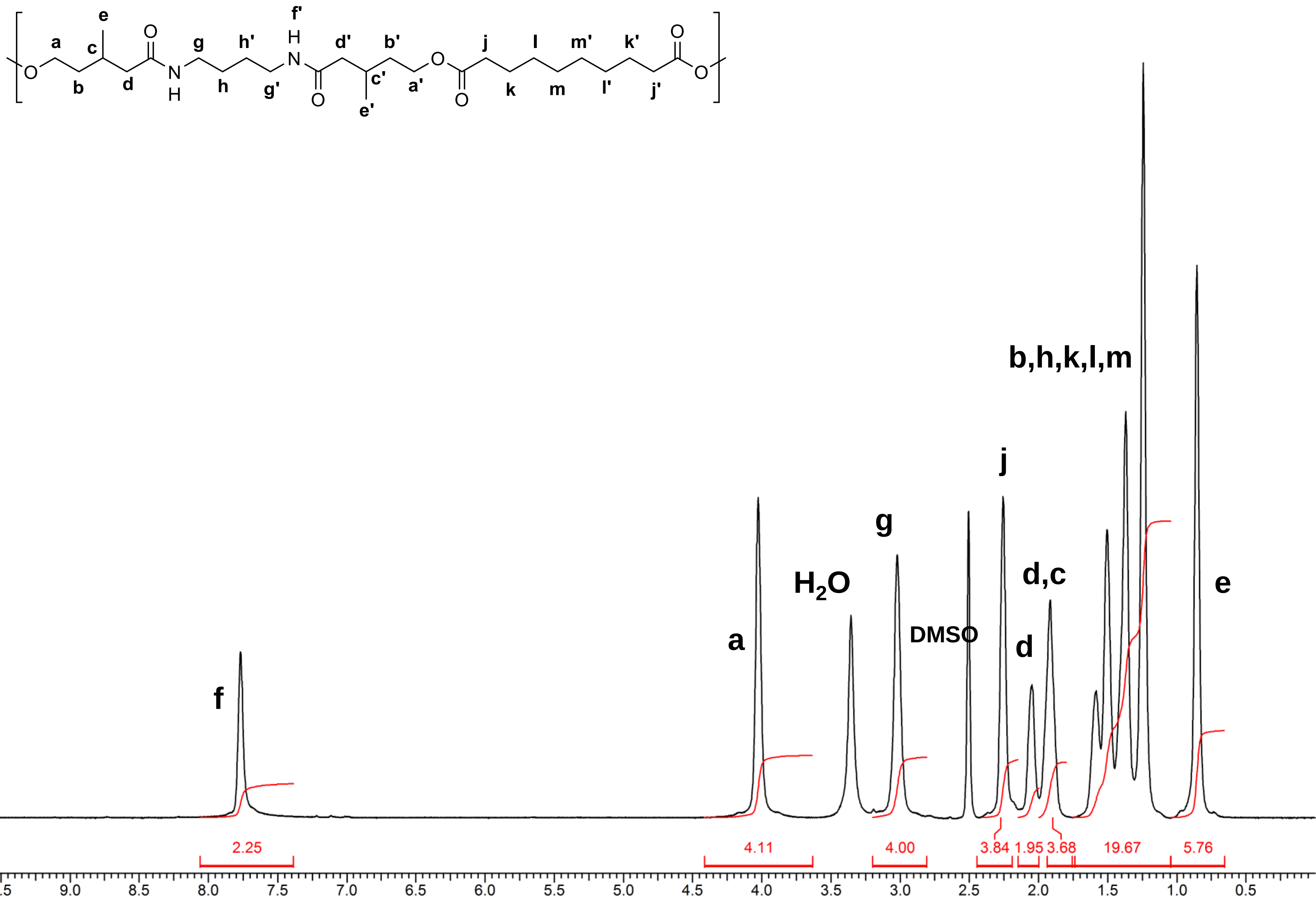
^{1}H NMR for **PEA-6,10** (500 MHz, DMSO-d_6)



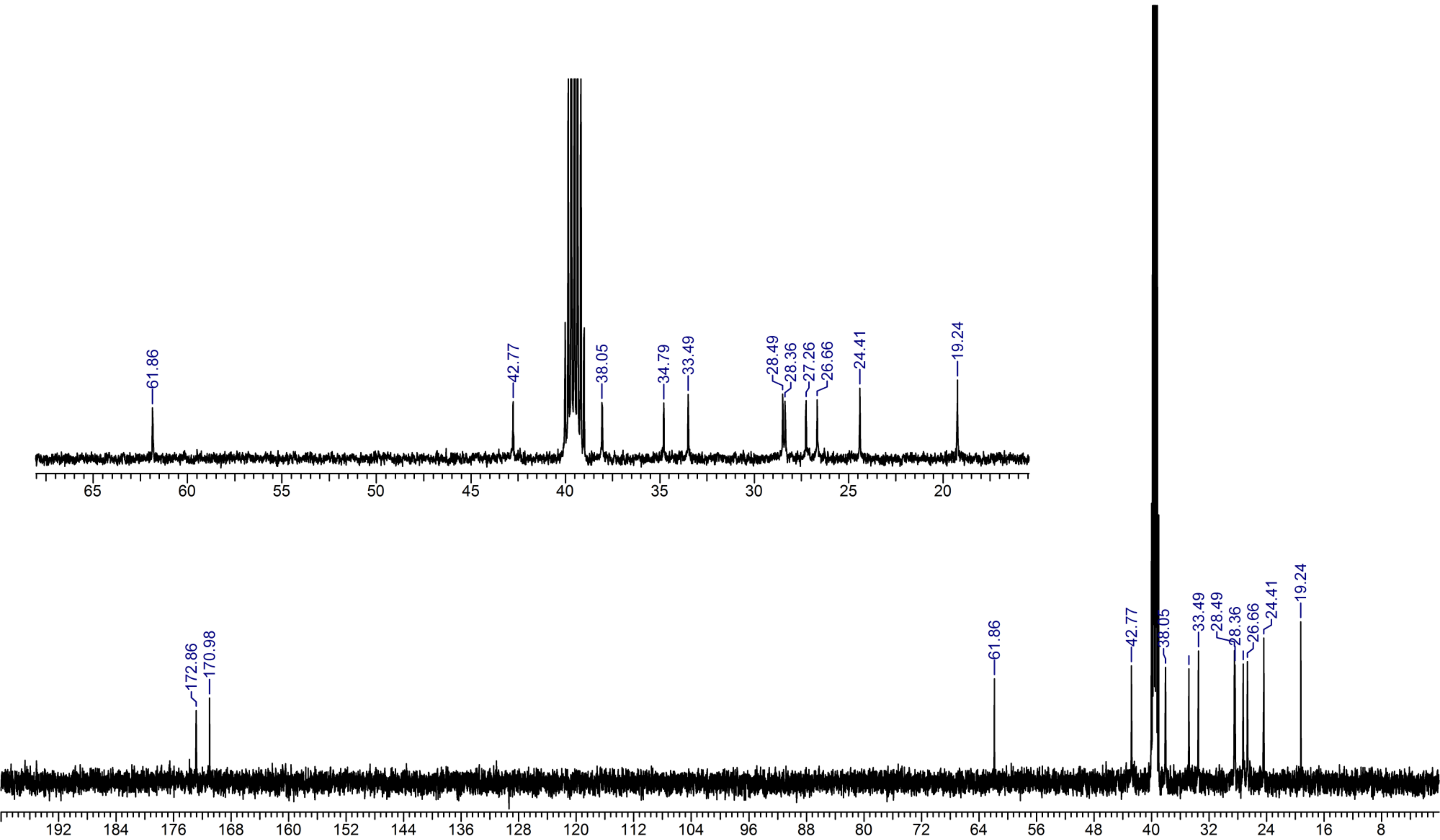
^{13}C NMR for **PEA-6,10** (125 MHz, DMSO-d_6)



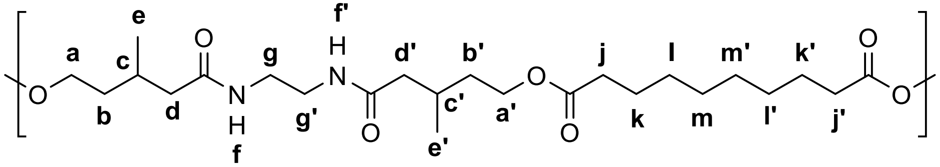
^{1}H NMR for **PEA-4,10** (500 MHz, DMSO-d_6)

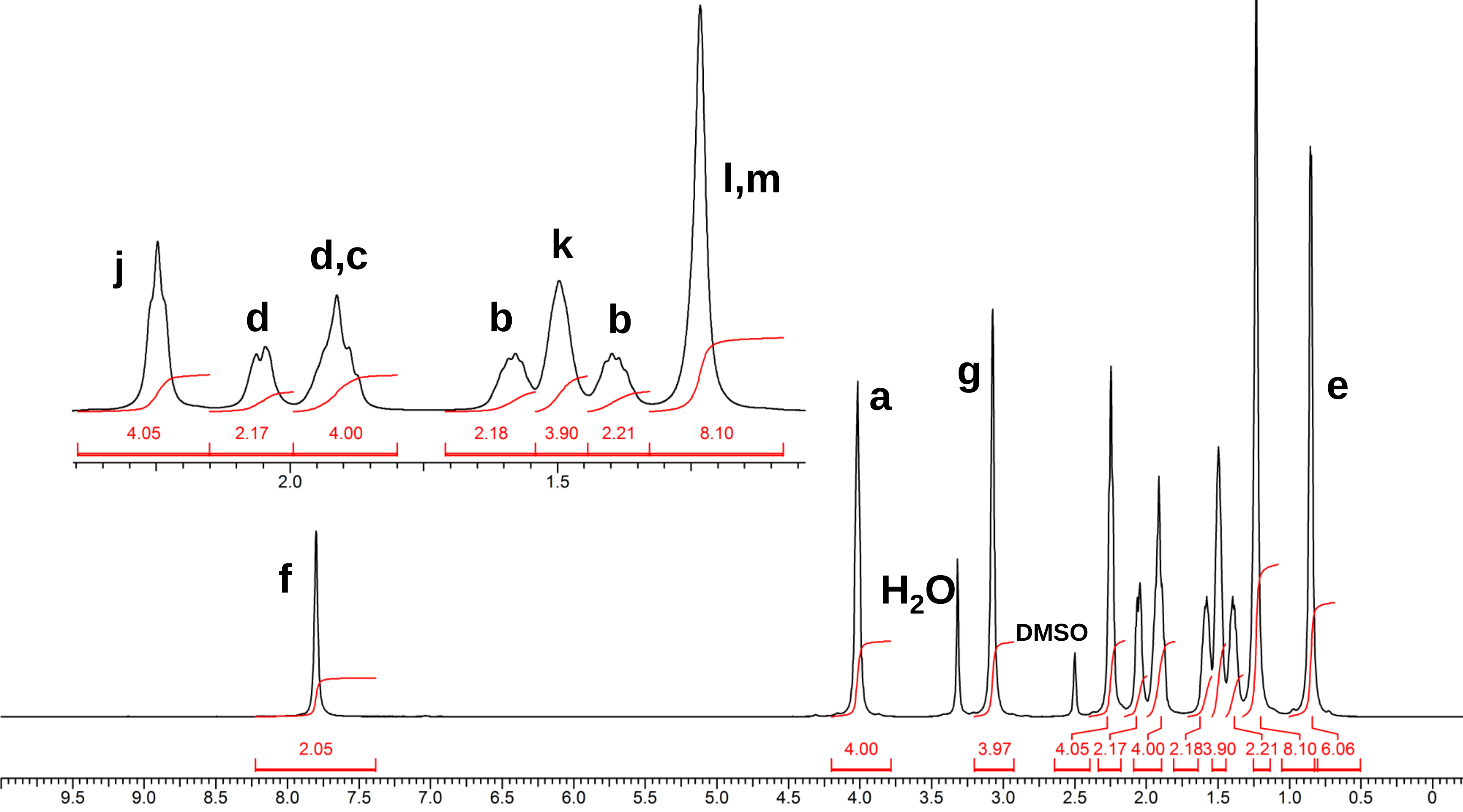


^{13}C NMR for **PEA-4,10** (125 MHz, DMSO-d_6)

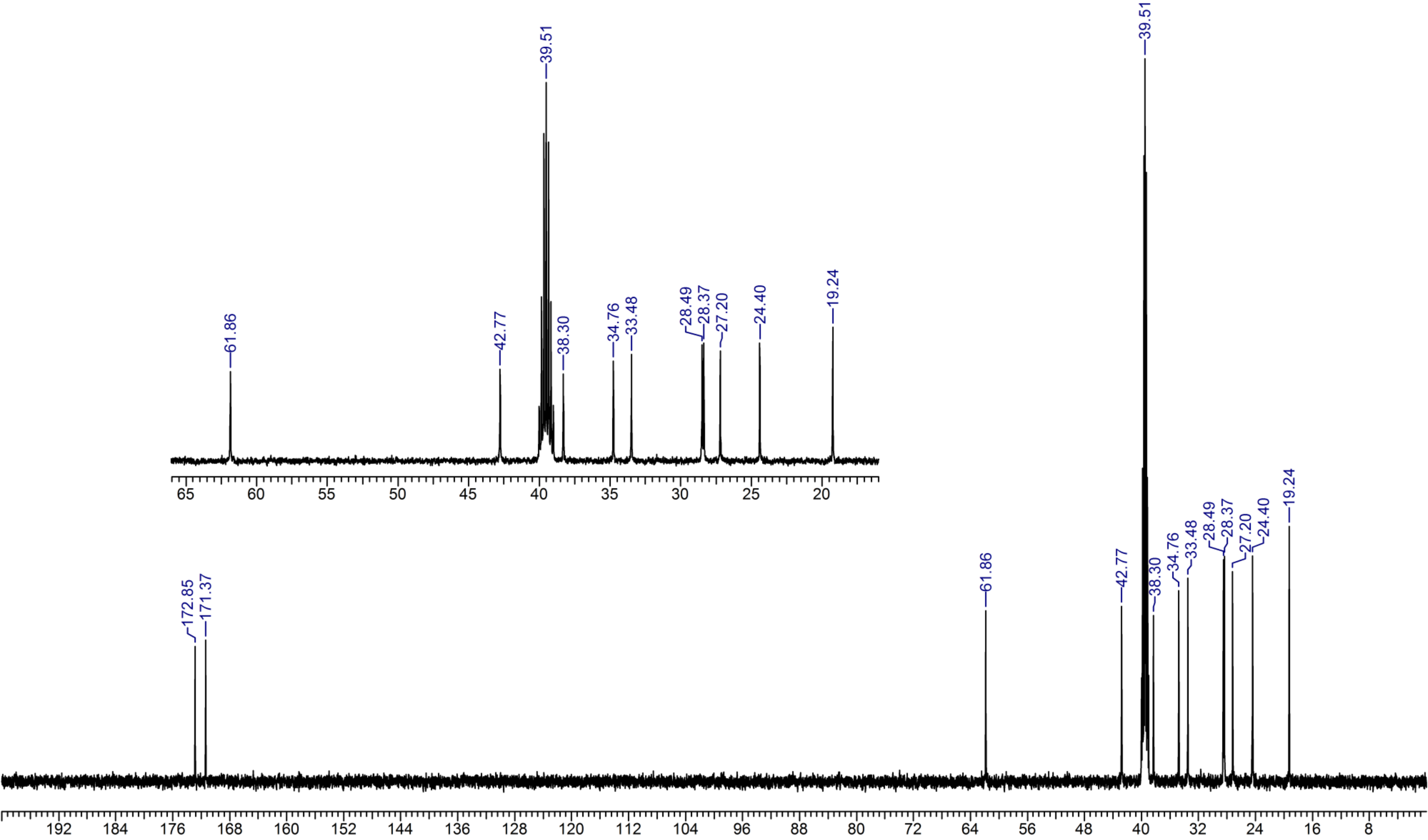


^{1}H NMR for **PEA-2,10** (500 MHz, DMSO-d_6)

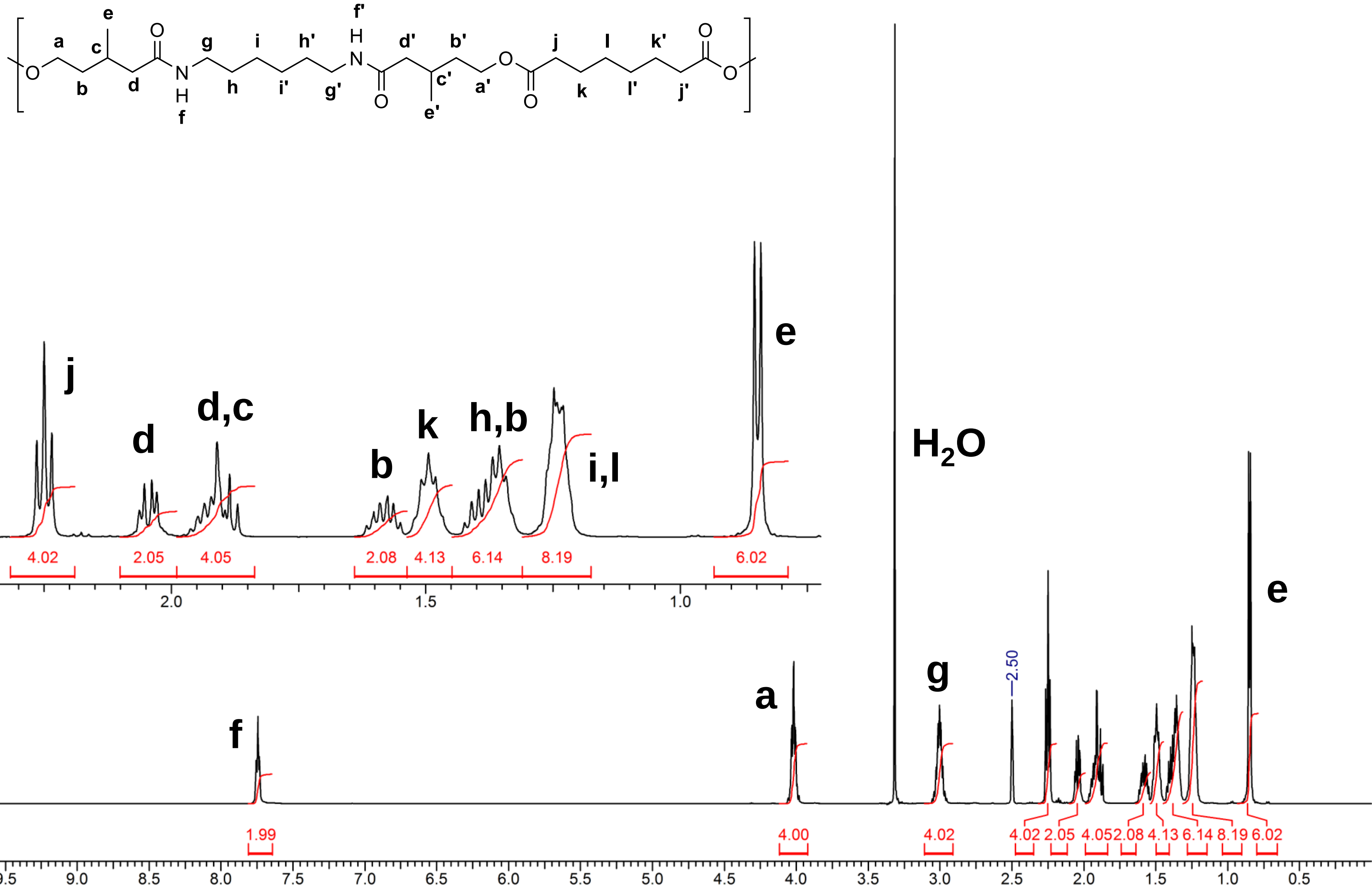




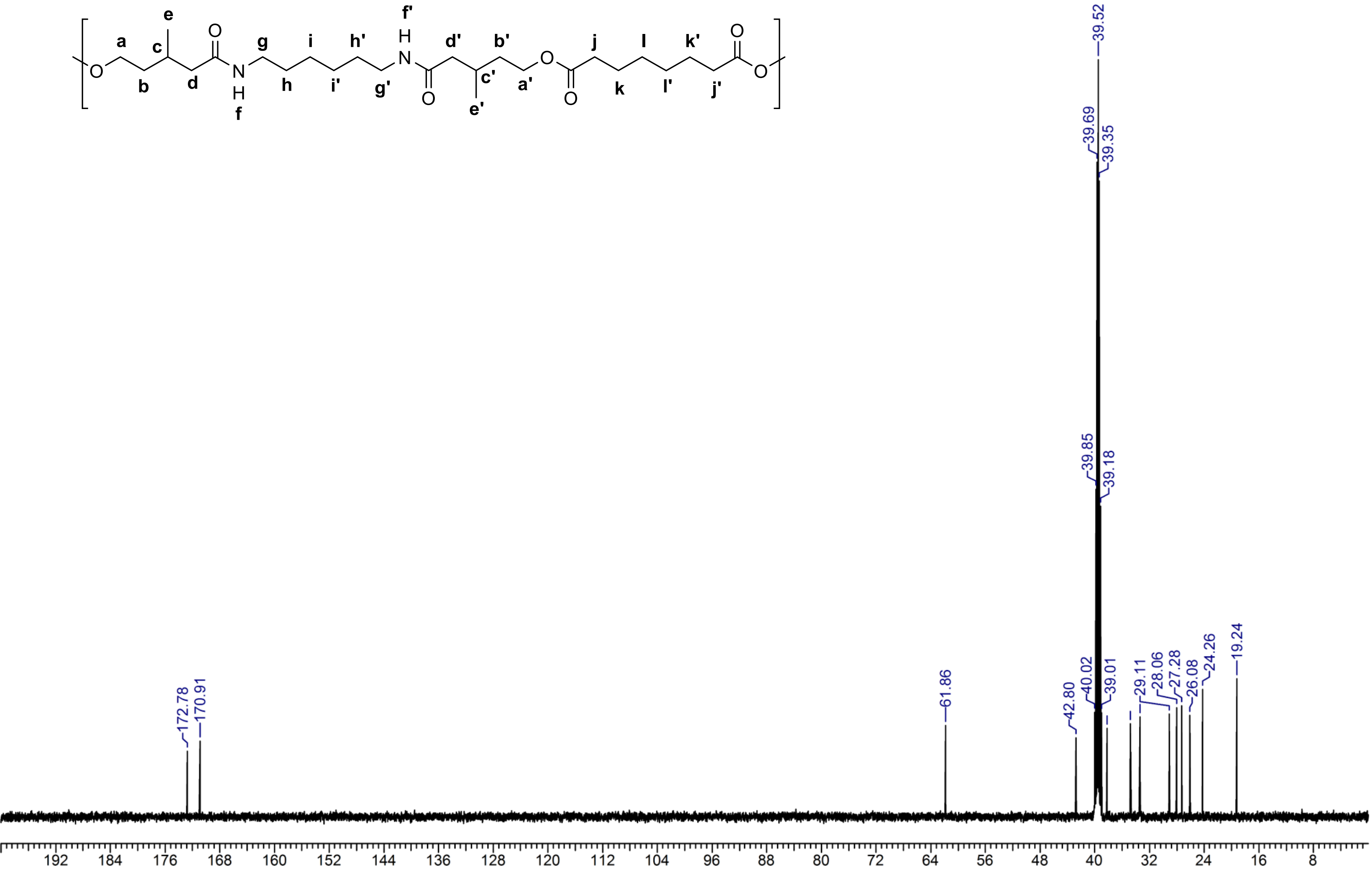
^{13}C NMR for **PEA-2,10** (125 MHz, DMSO-d_6)



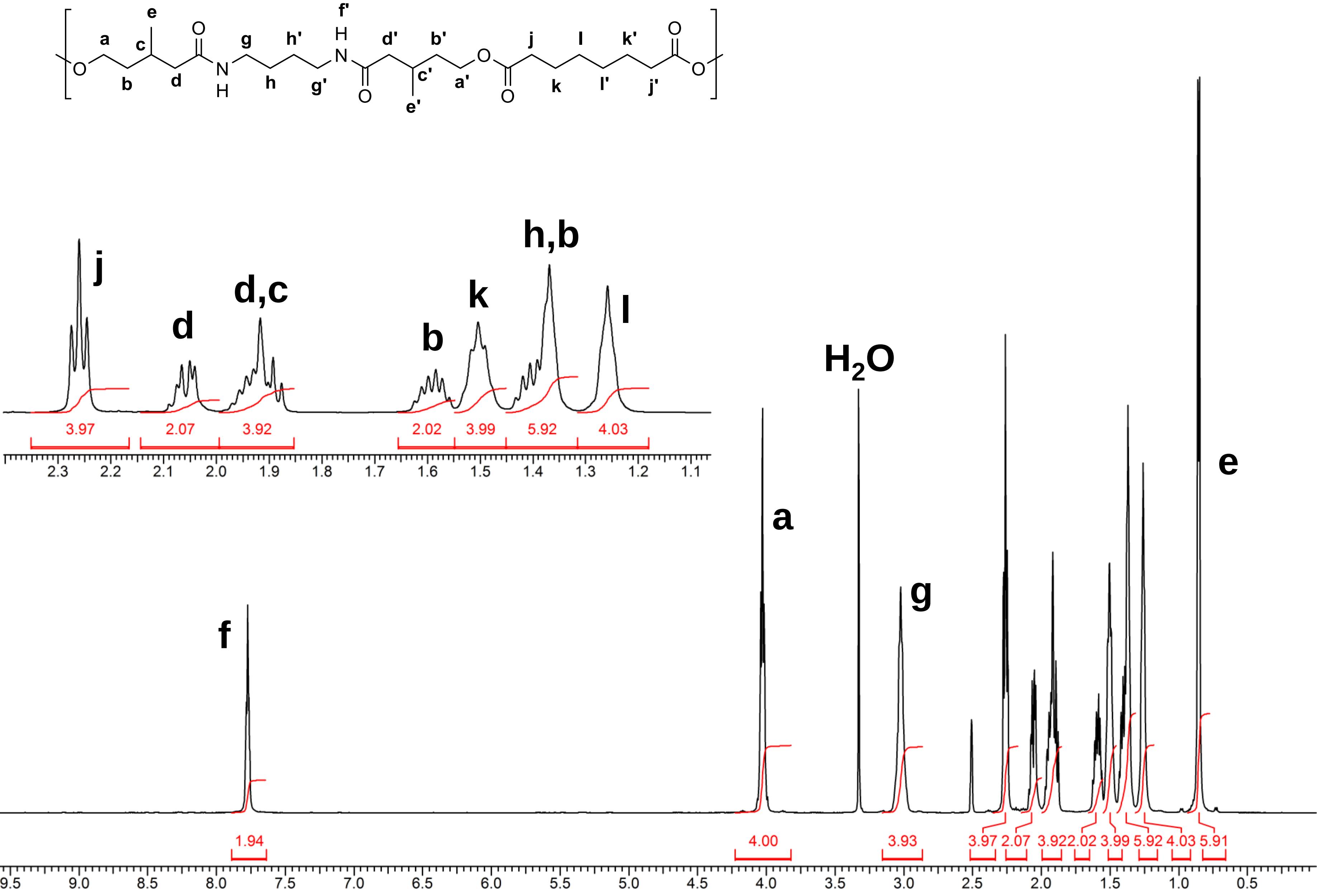
^{1}H NMR for **PEA-6,8** (500 MHz, DMSO-d_6)



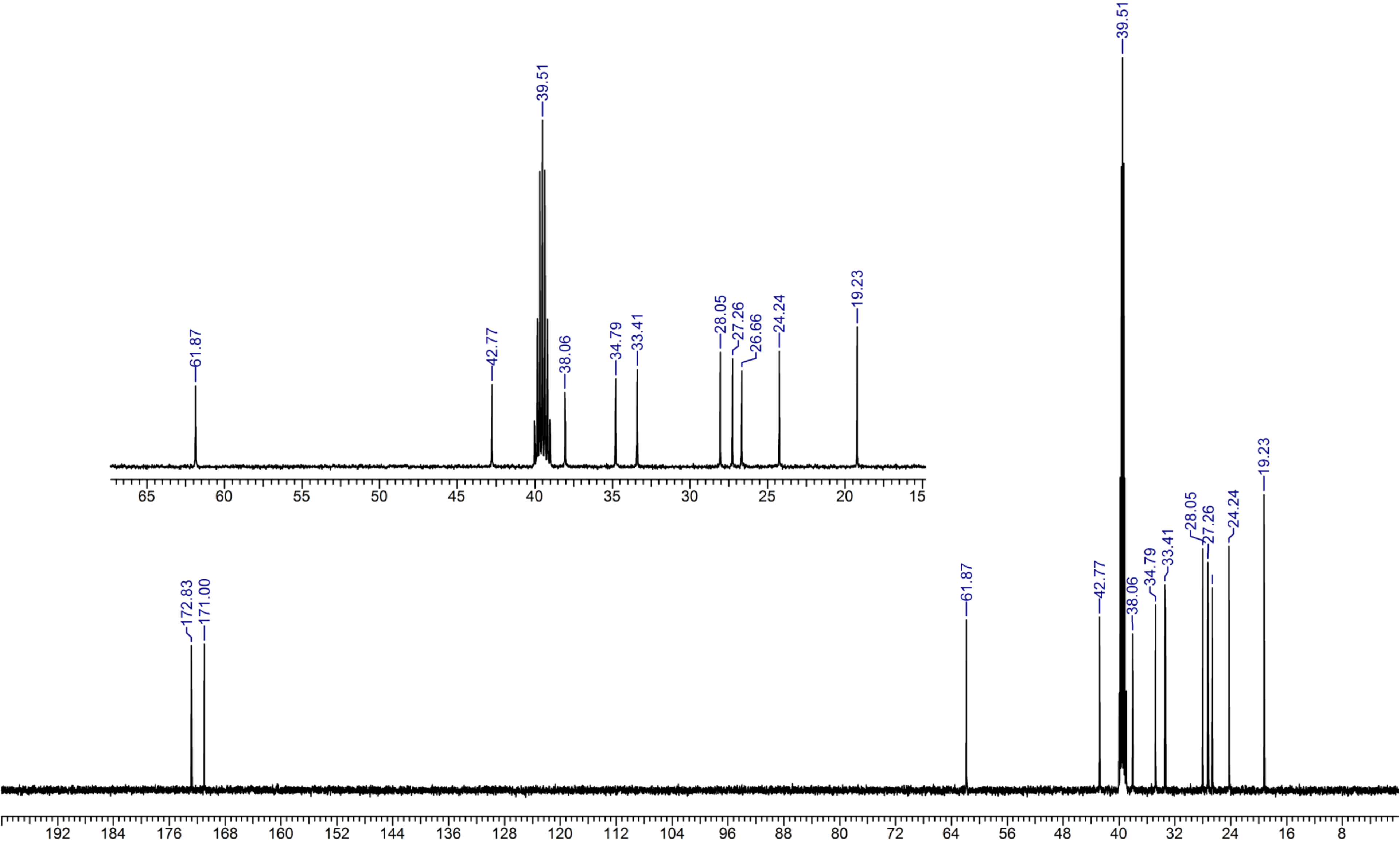
^{13}C NMR for **PEA-6,8** (125 MHz, DMSO-d_6)



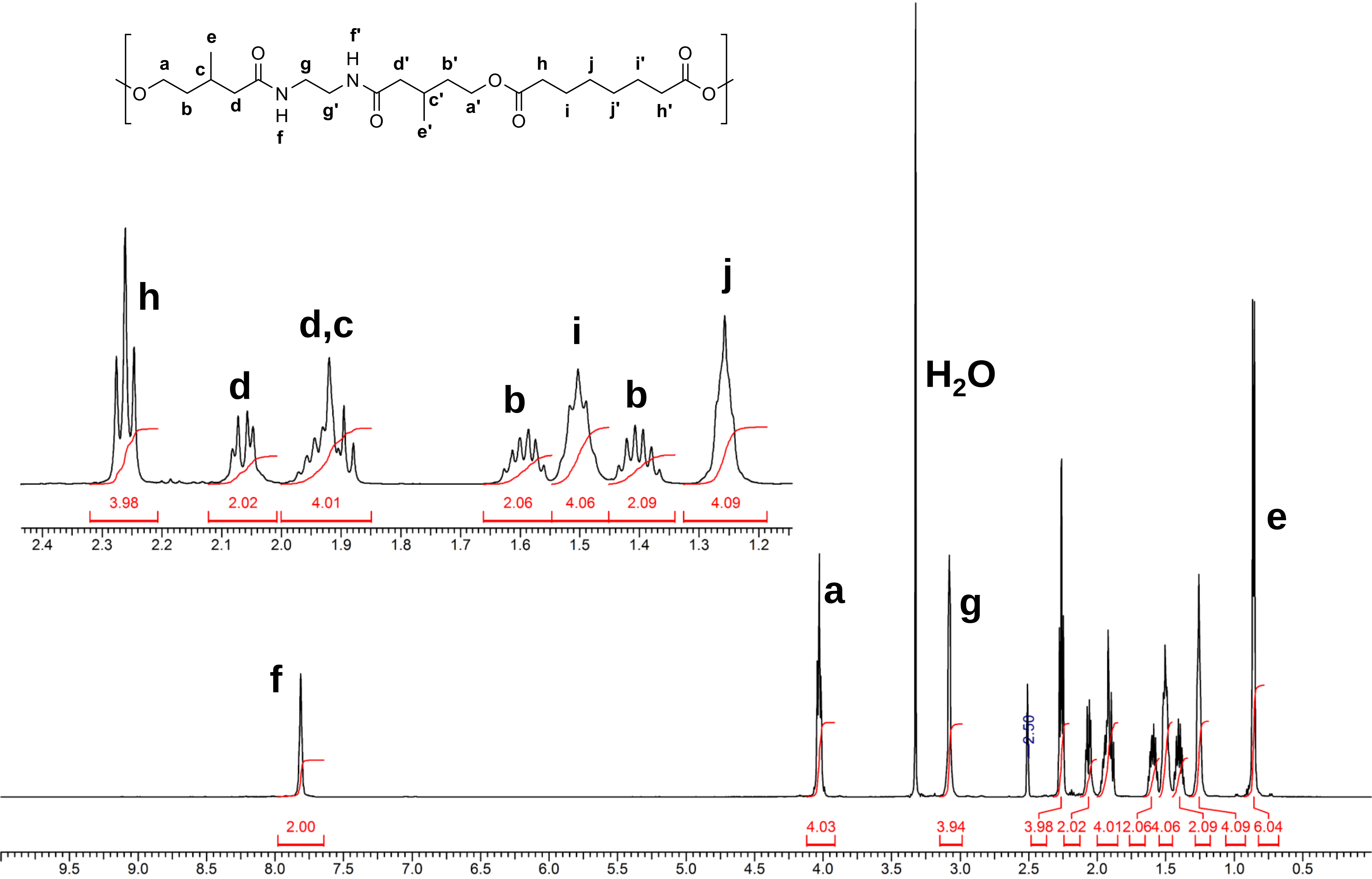
^{1}H NMR for **PEA-4,8** (500 MHz, DMSO-d_6)



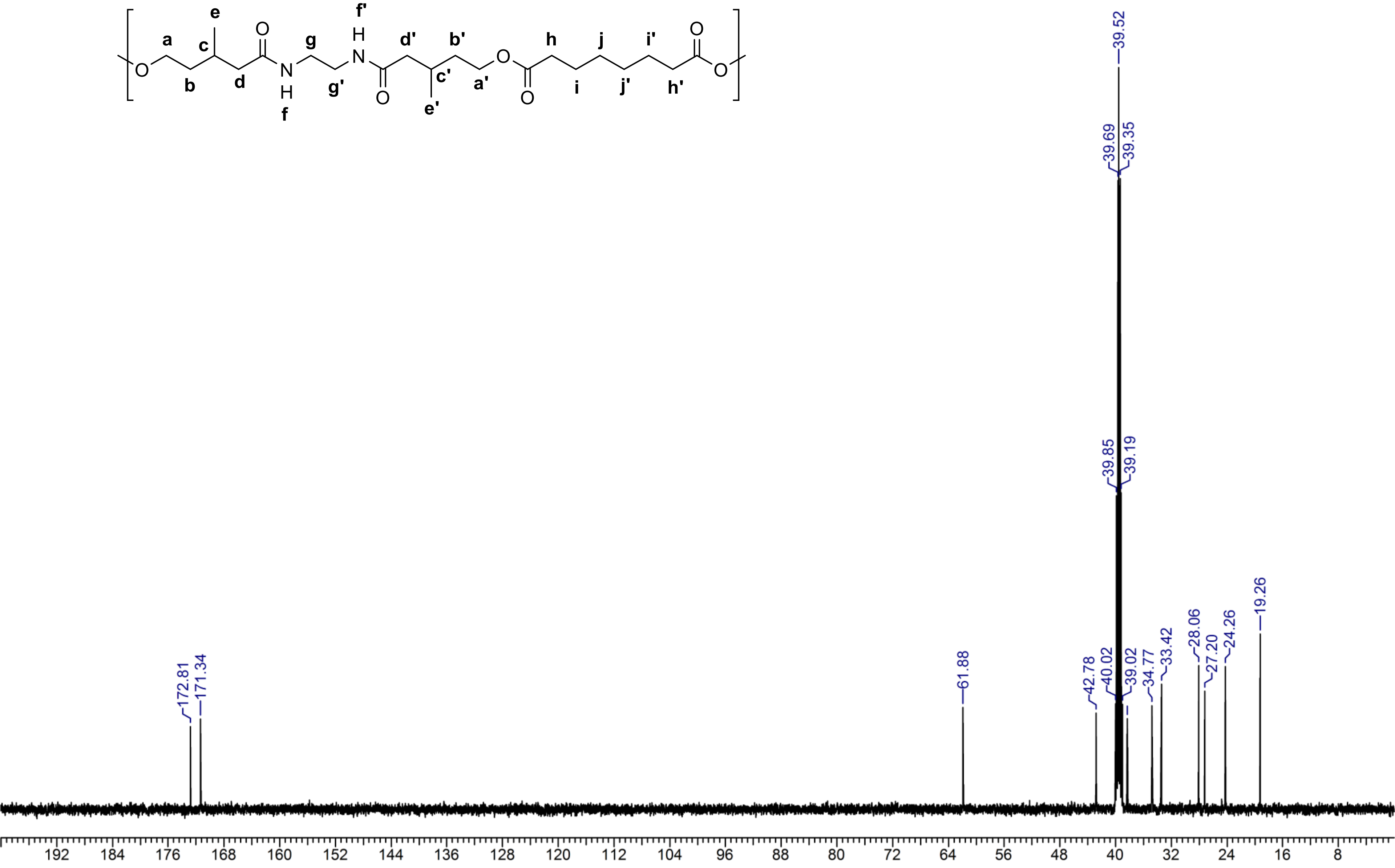
^{13}C NMR for **PEA-4,8** (125 MHz, DMSO-d_6)



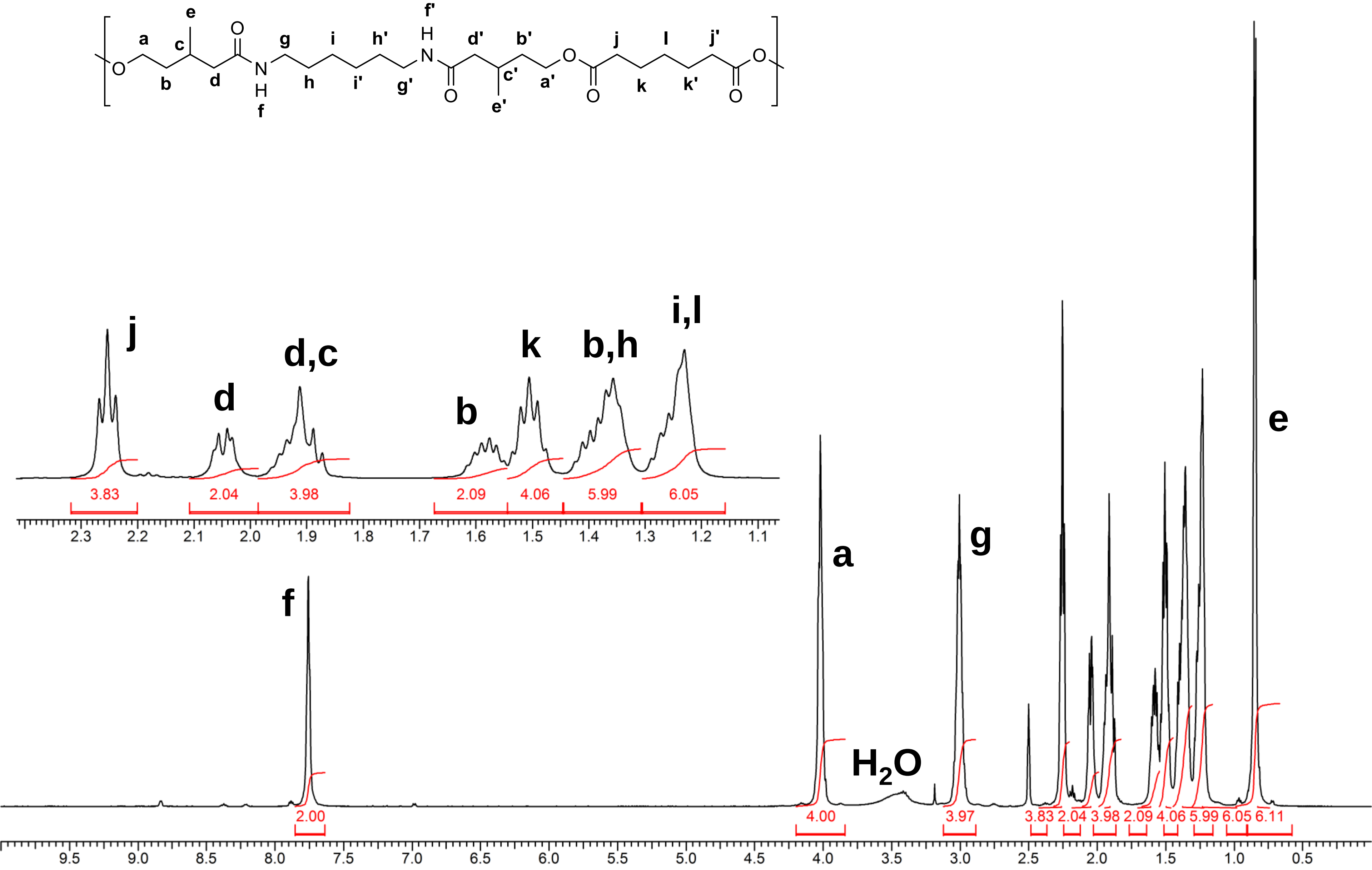
^{1}H NMR for **PEA-2,8** (500 MHz, DMSO-d_6)



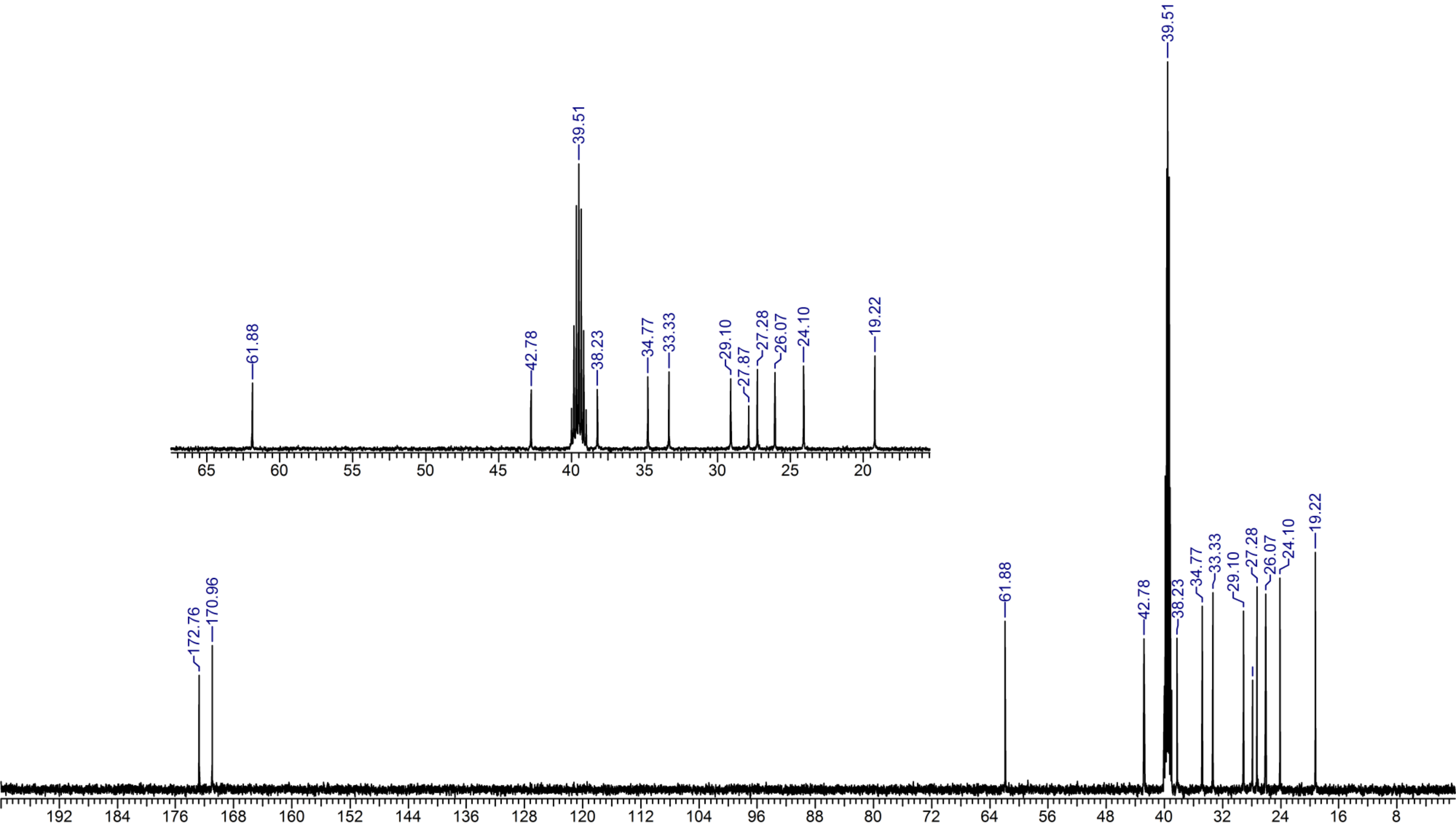
^{13}C NMR for **PEA-2,8** (125 MHz, DMSO-d_6)



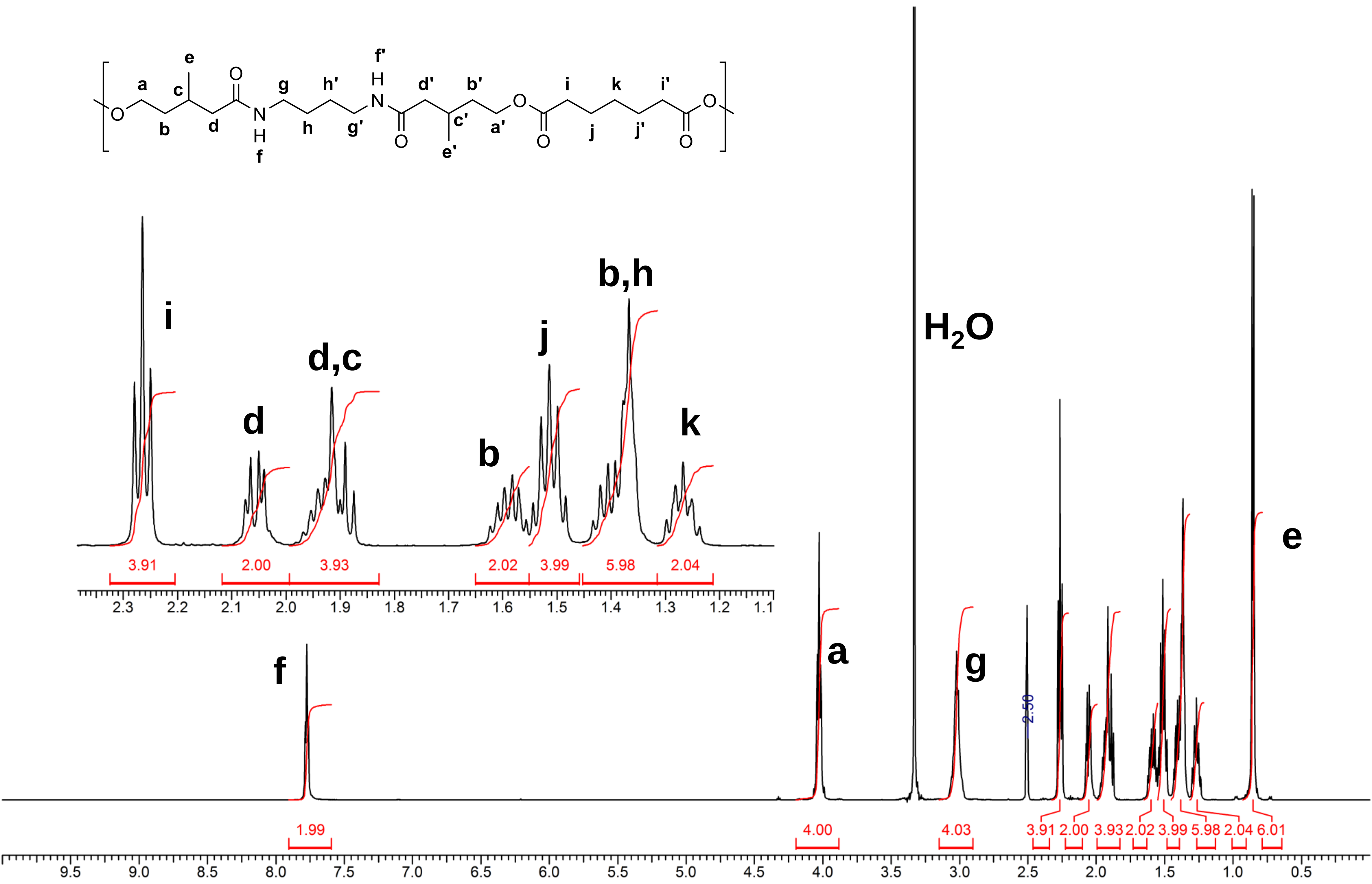
^{1}H NMR for **PEA-6,7** (500 MHz, DMSO-d_6)



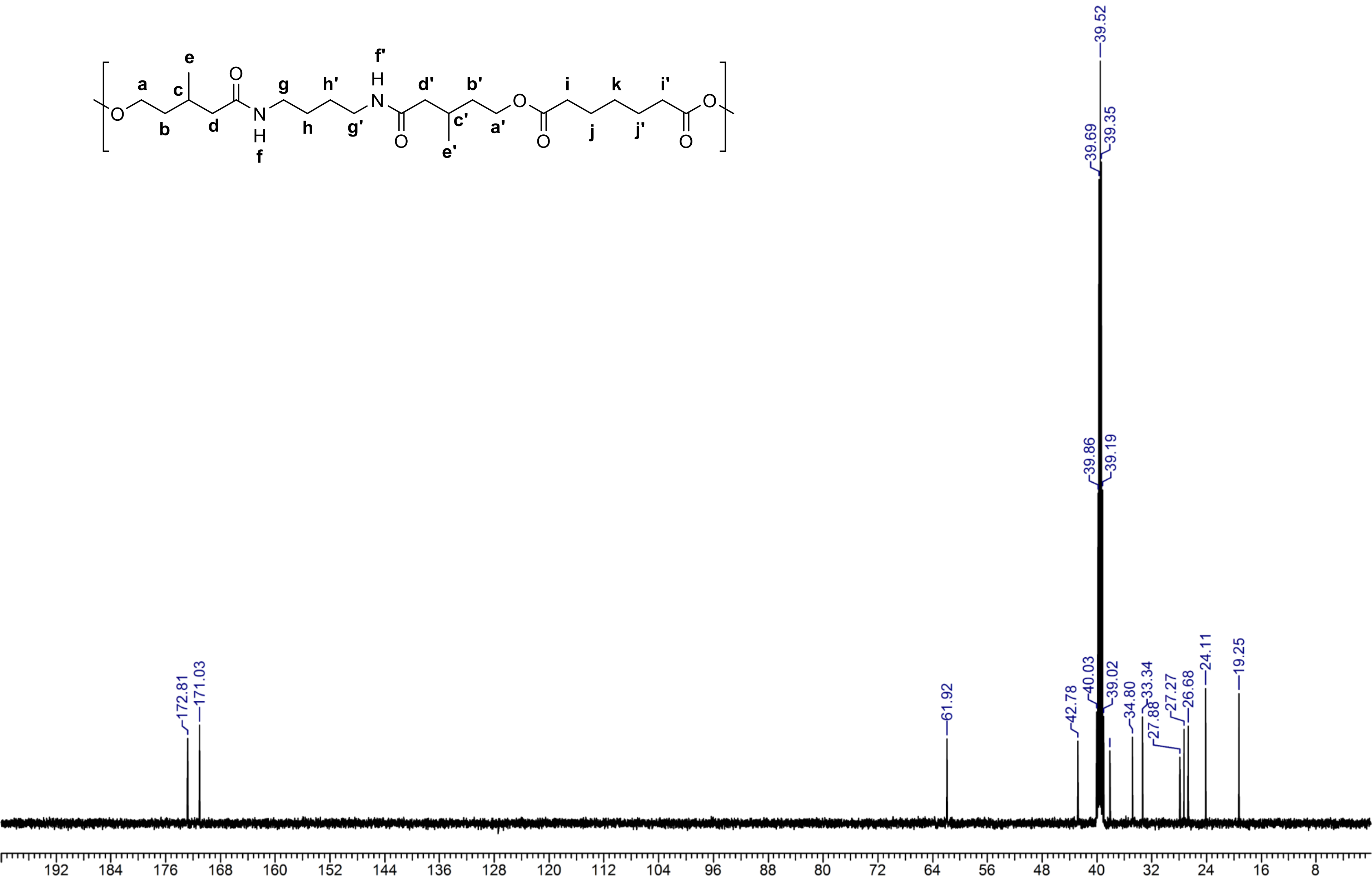
^{13}C NMR for **PEA-6,7** (125 MHz, DMSO-d_6)



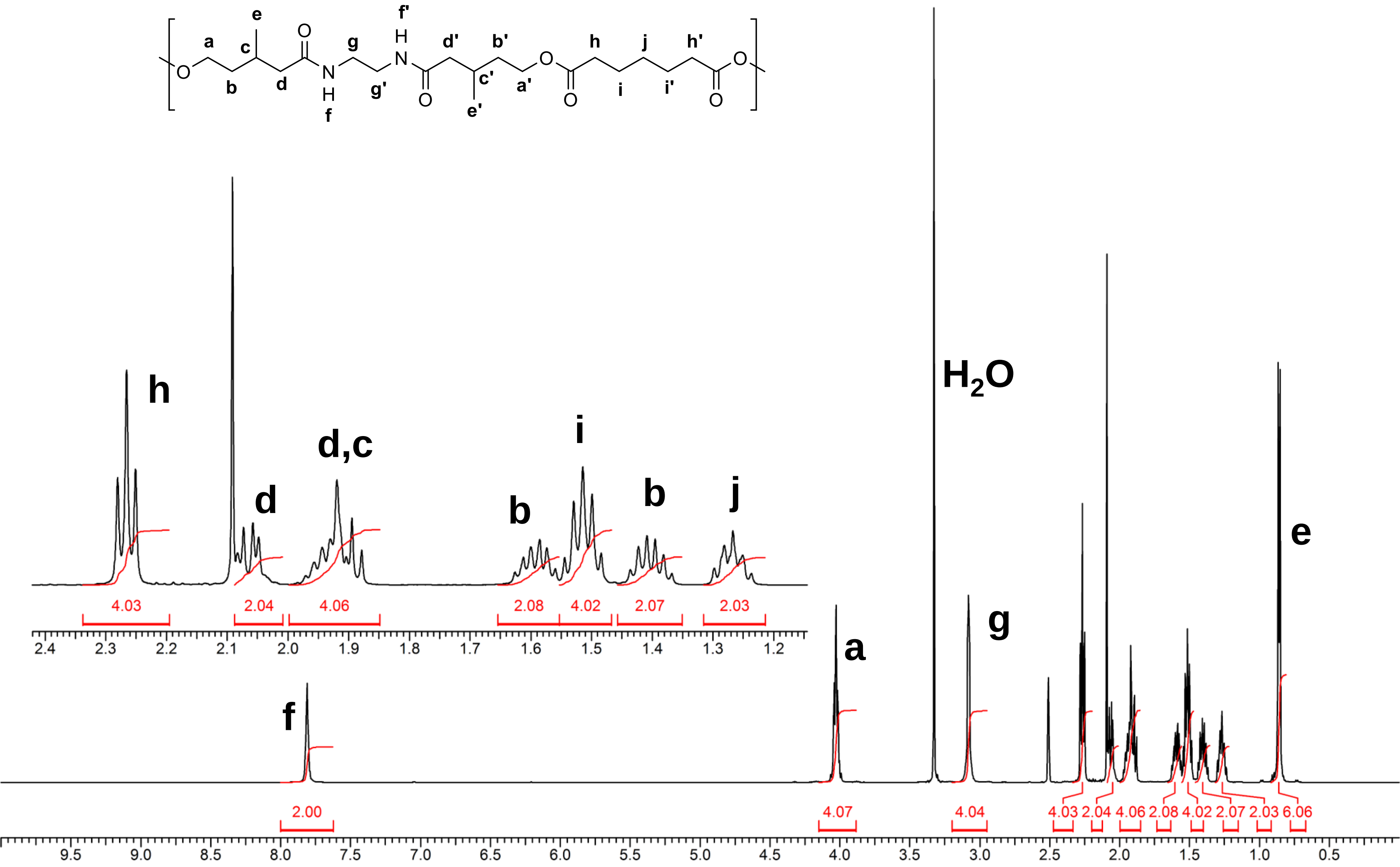
^{1}H NMR for **PEA-4,7** (500 MHz, DMSO-d_6)



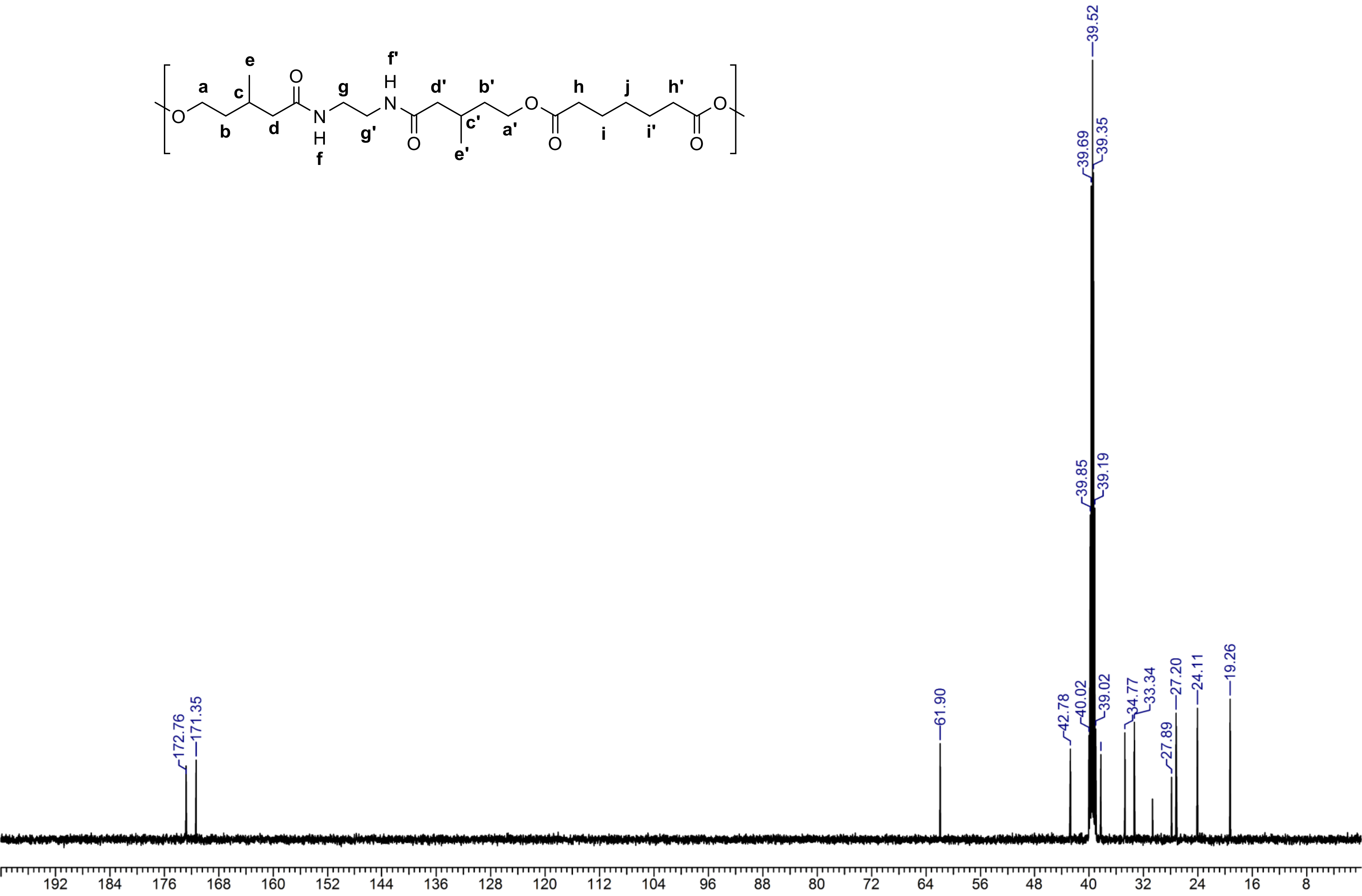
^{13}C NMR for **PEA-4,7** (125 MHz, DMSO-d_6)



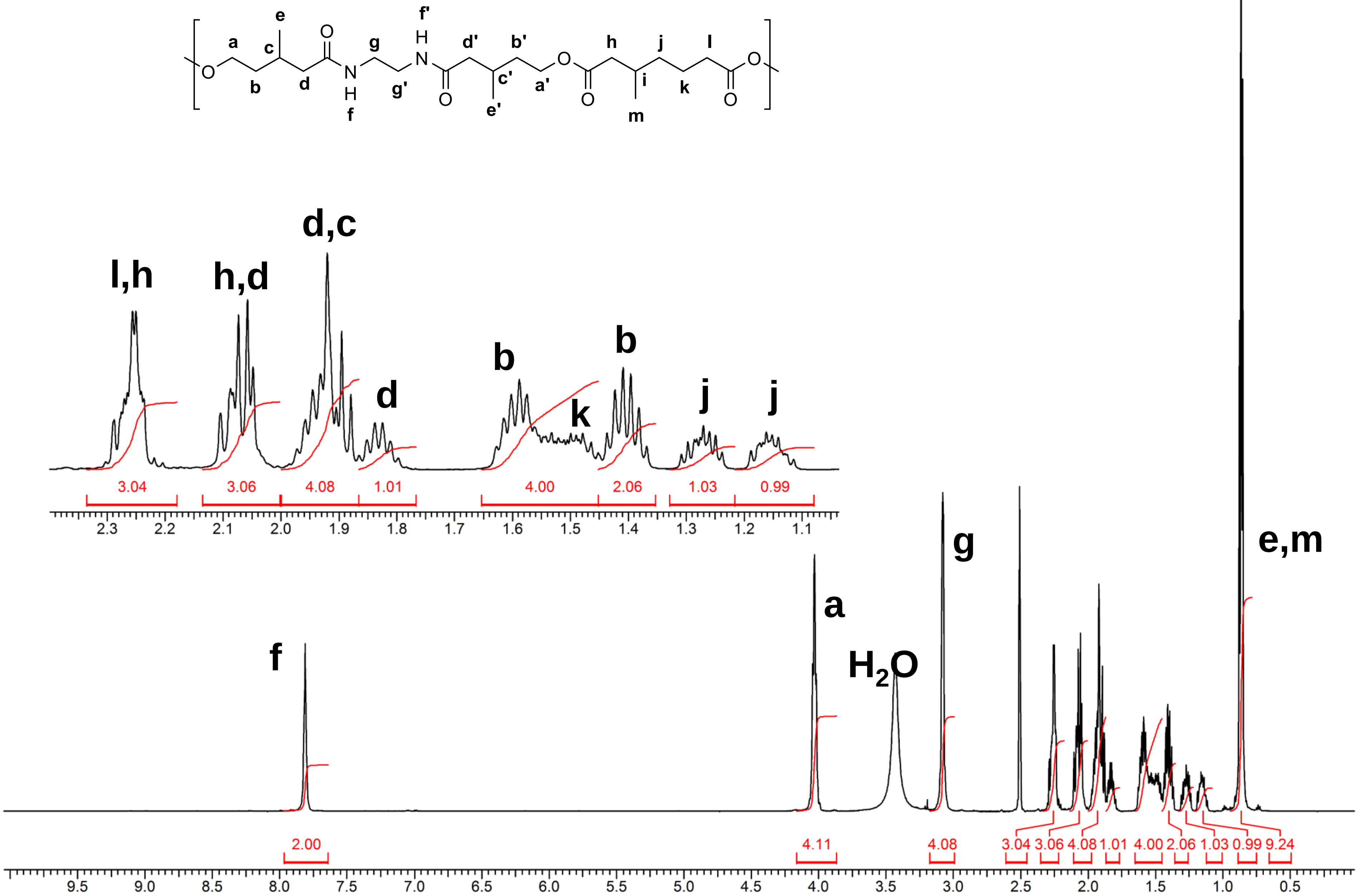
^{1}H NMR for **PEA-2,7** (500 MHz, DMSO-d_6)



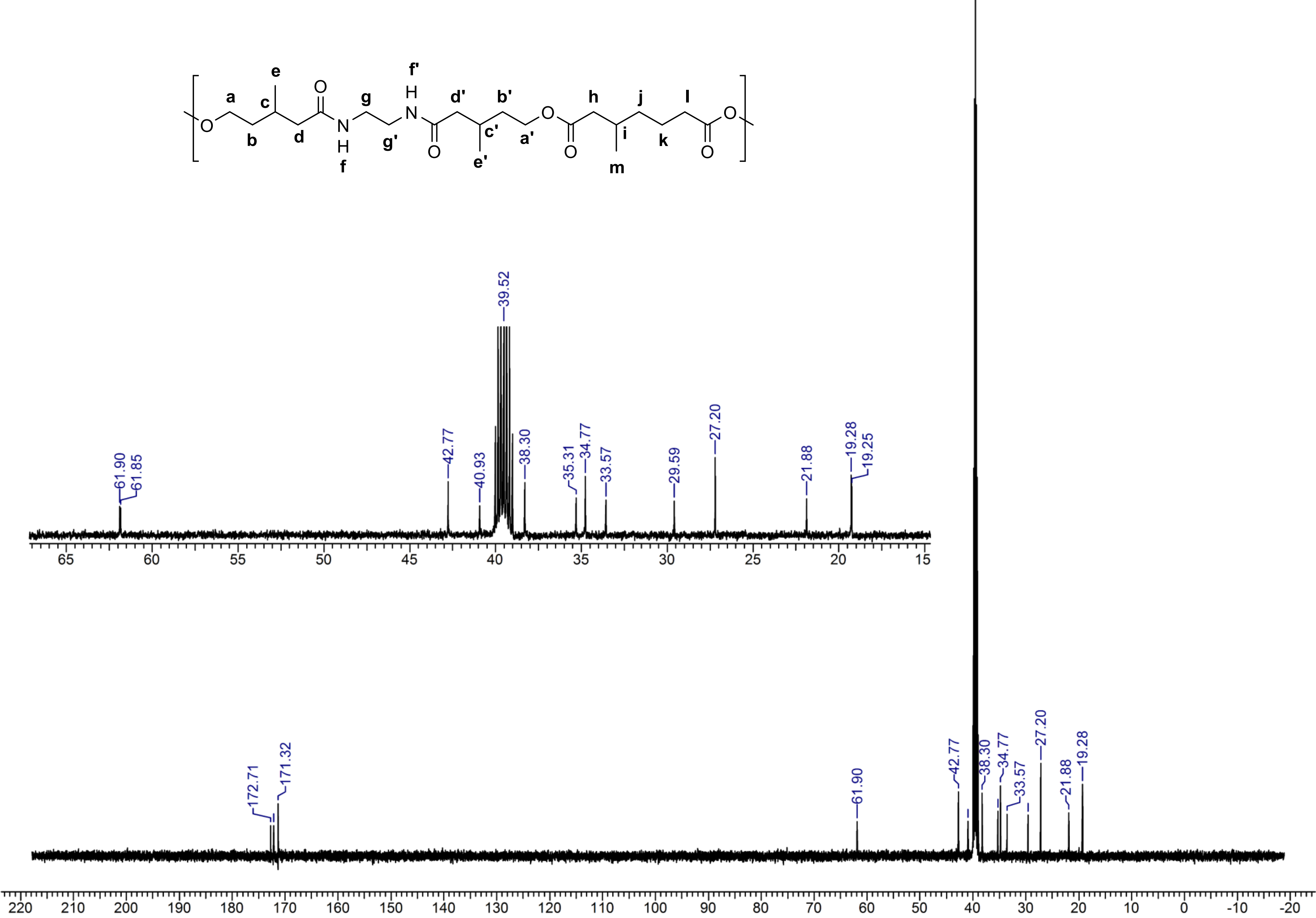
^{13}C NMR for **PEA-2,7** (125 MHz, DMSO-d_6)



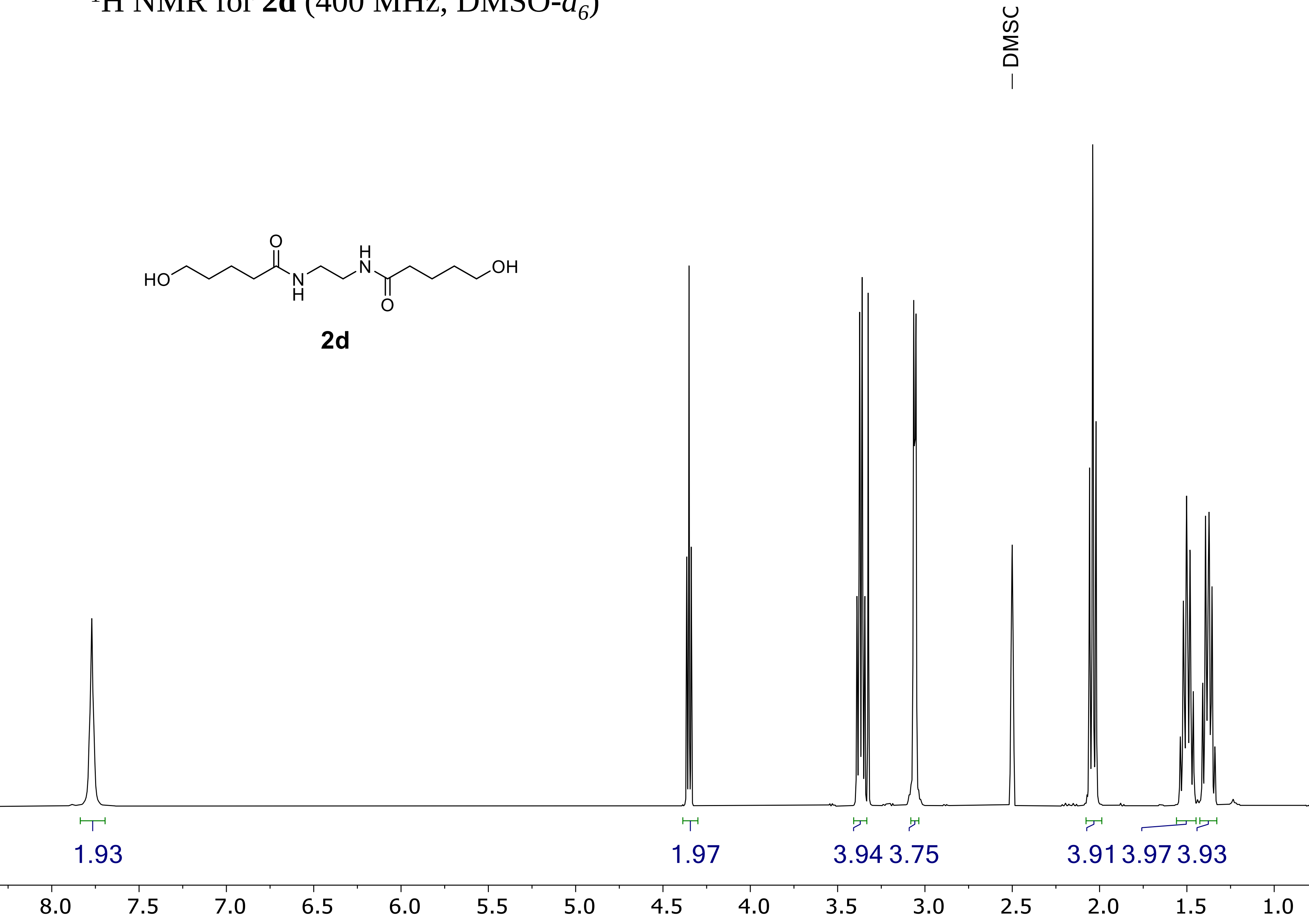
^{1}H NMR for **PEA-2,7-Me** (500 MHz, DMSO-d_6)



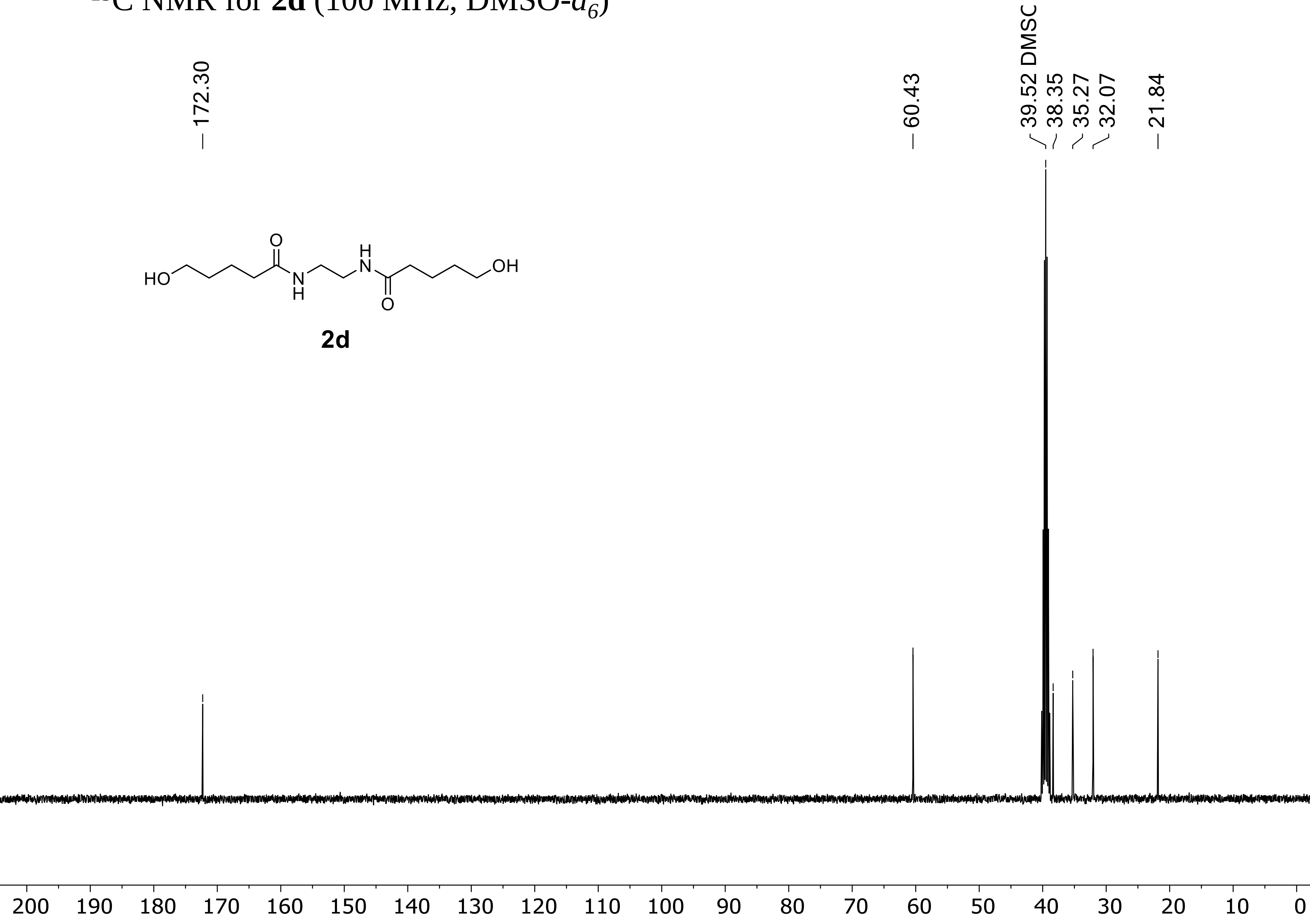
^{13}C NMR for **PEA-2,7-Me** (125 MHz, DMSO-d_6)



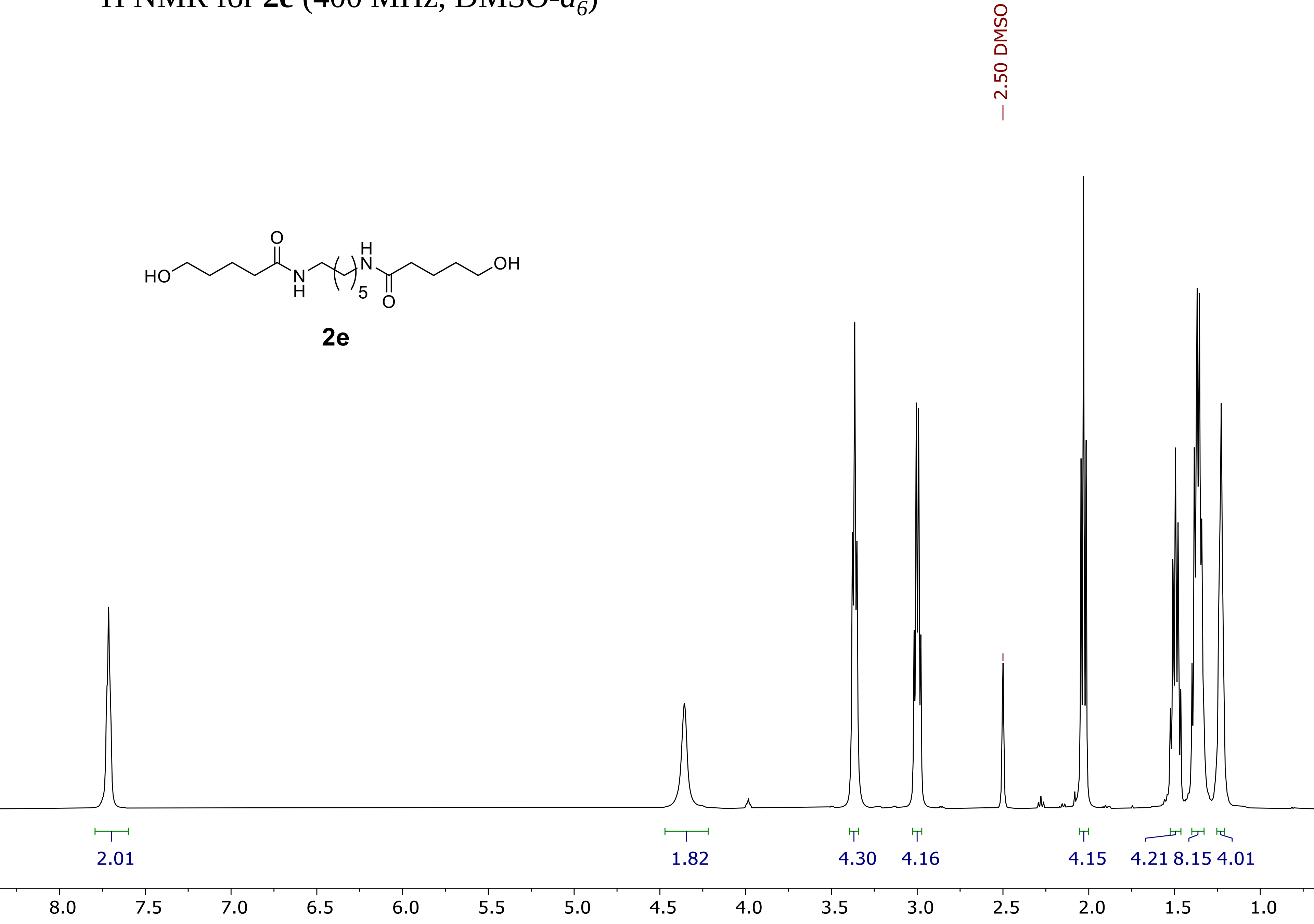
^{1}H NMR for **2d** (400 MHz, DMSO-d_6)



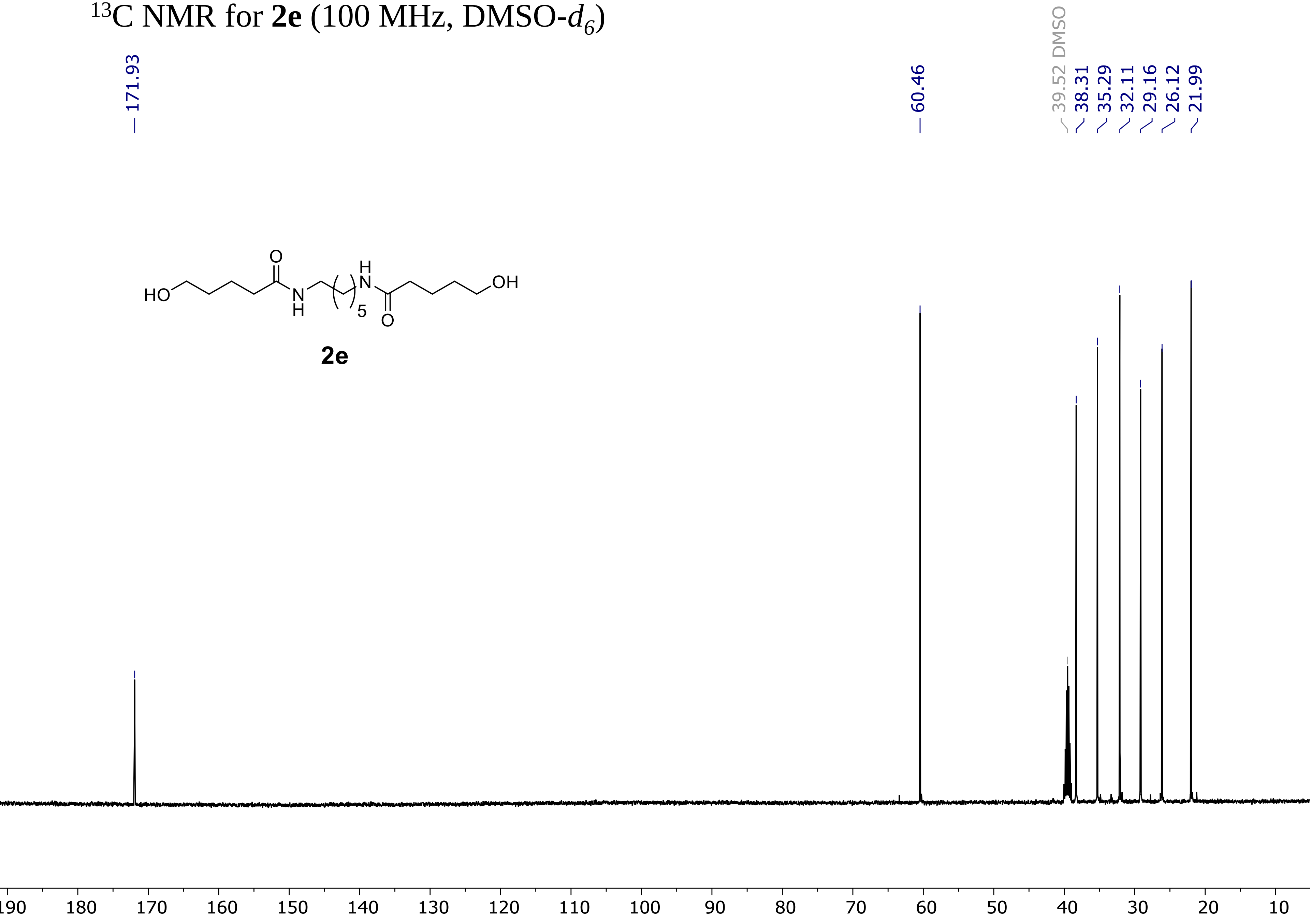
^{13}C NMR for **2d** (100 MHz, DMSO-d_6)



^{1}H NMR for **2e** (400 MHz, DMSO-d_6)

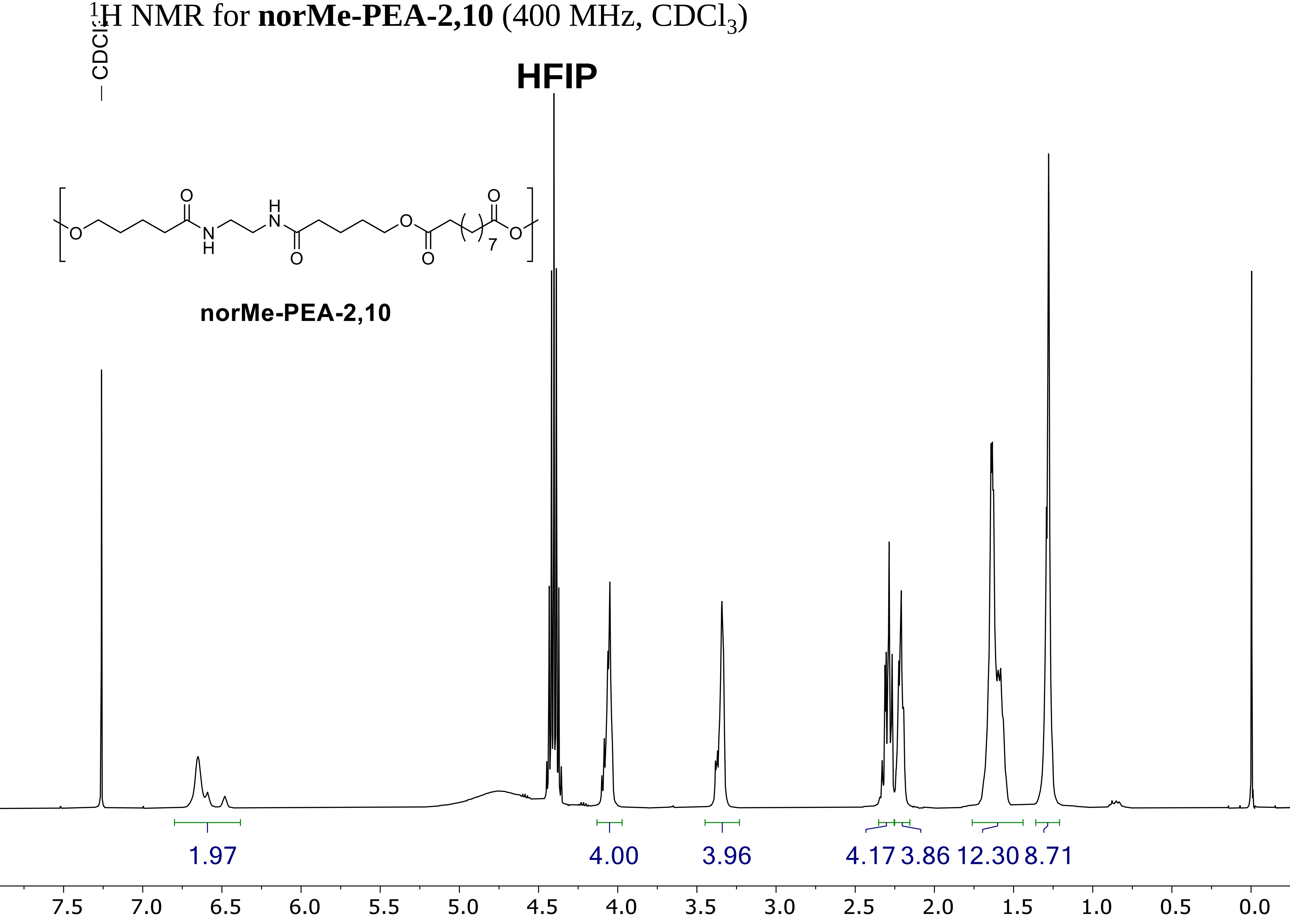


^{13}C NMR for **2e** (100 MHz, DMSO-d_6)

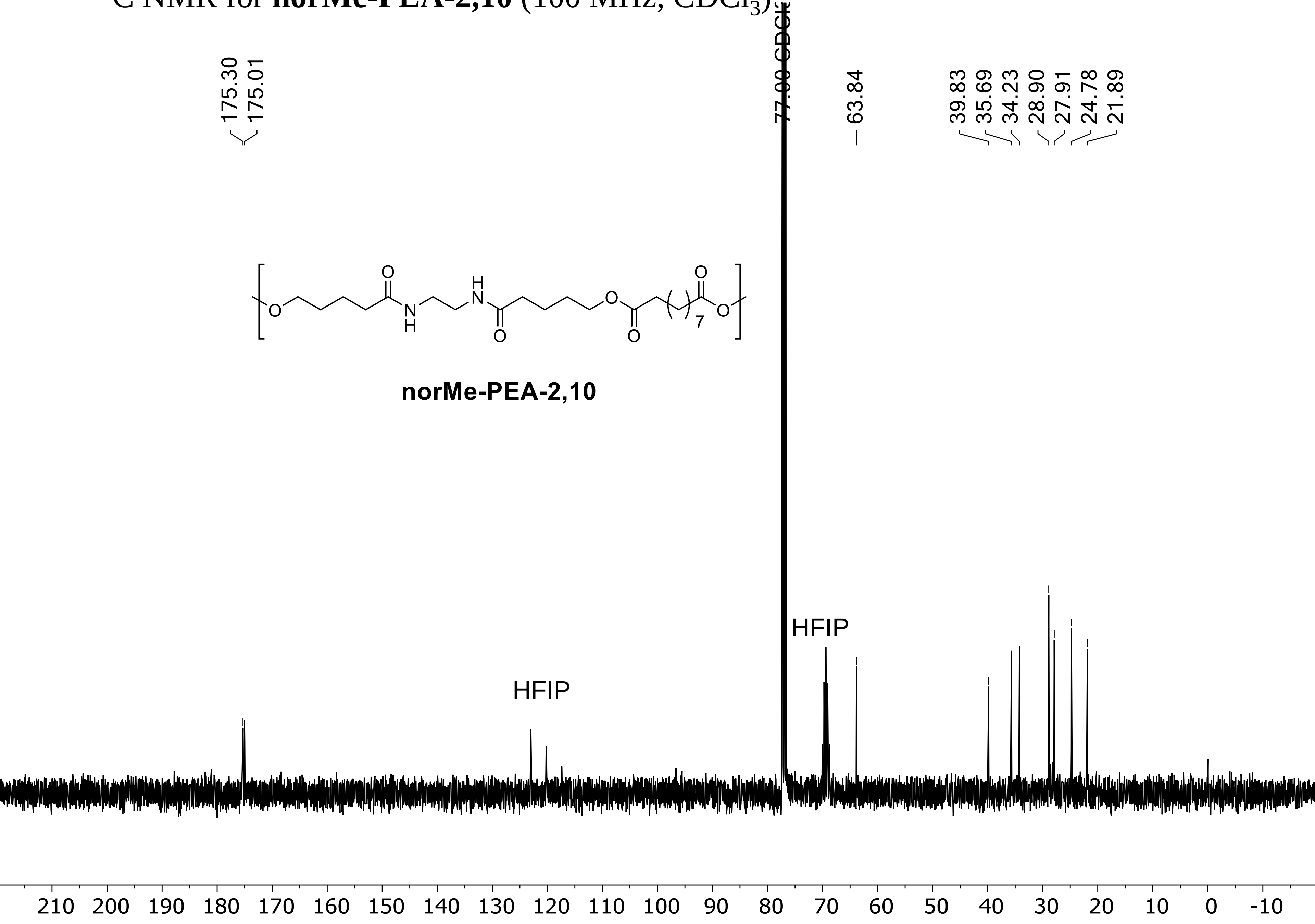


2e

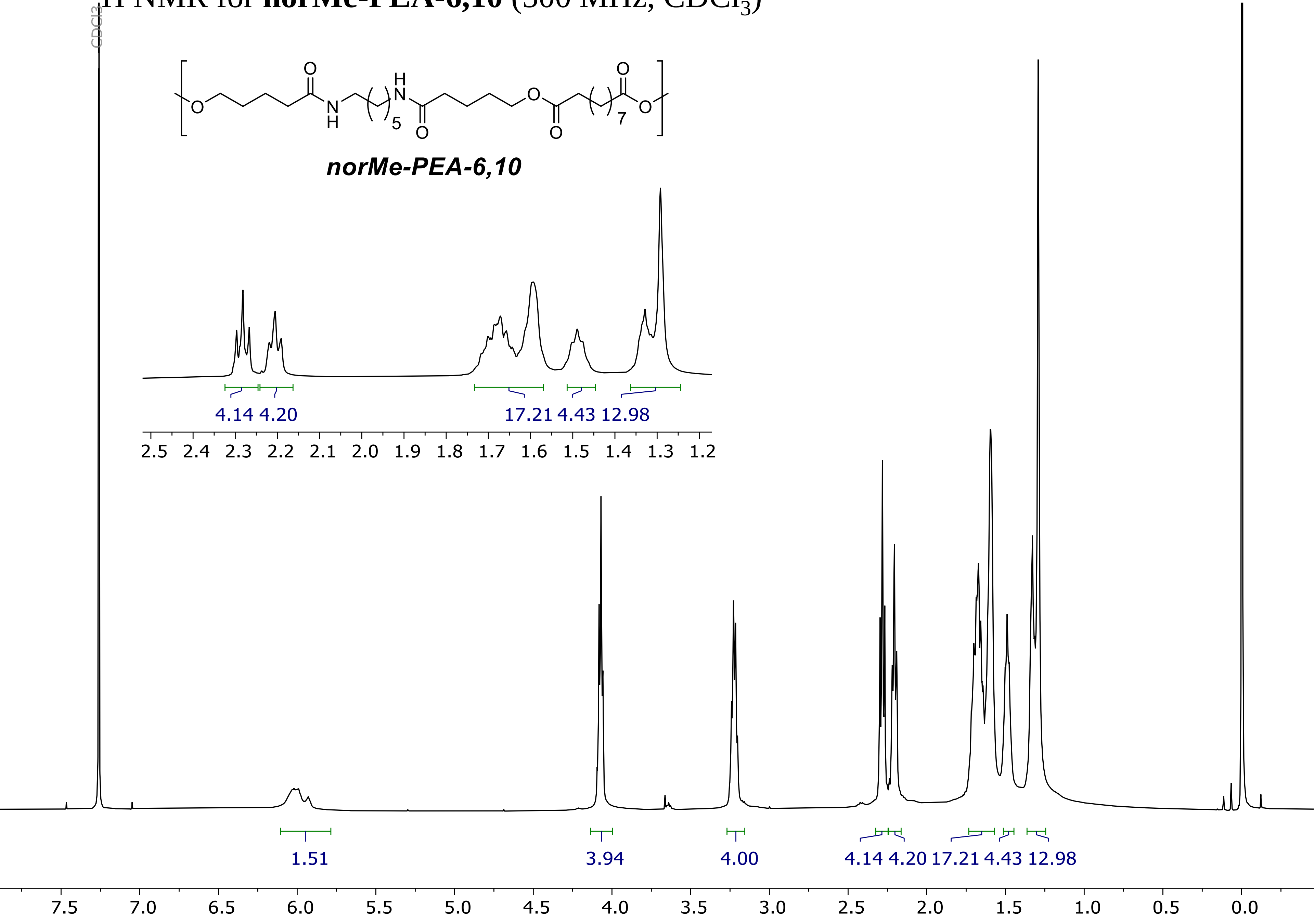
^{1}H NMR for **norMe-PEA-2,10** (400 MHz, $CDCl_3$)



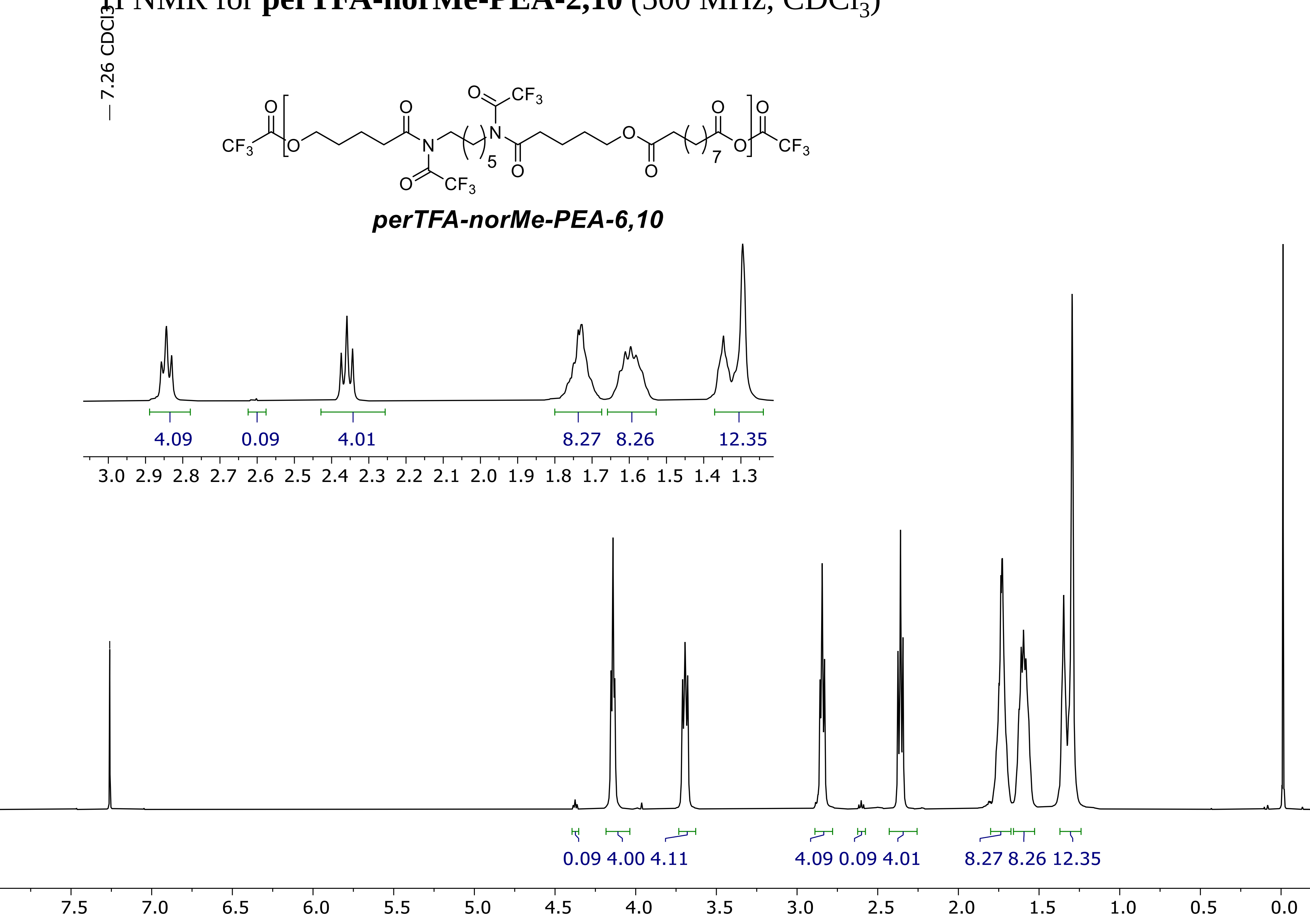
^{13}C NMR for **norMe-PEA-2,10** (100 MHz, CDCl$_3$)



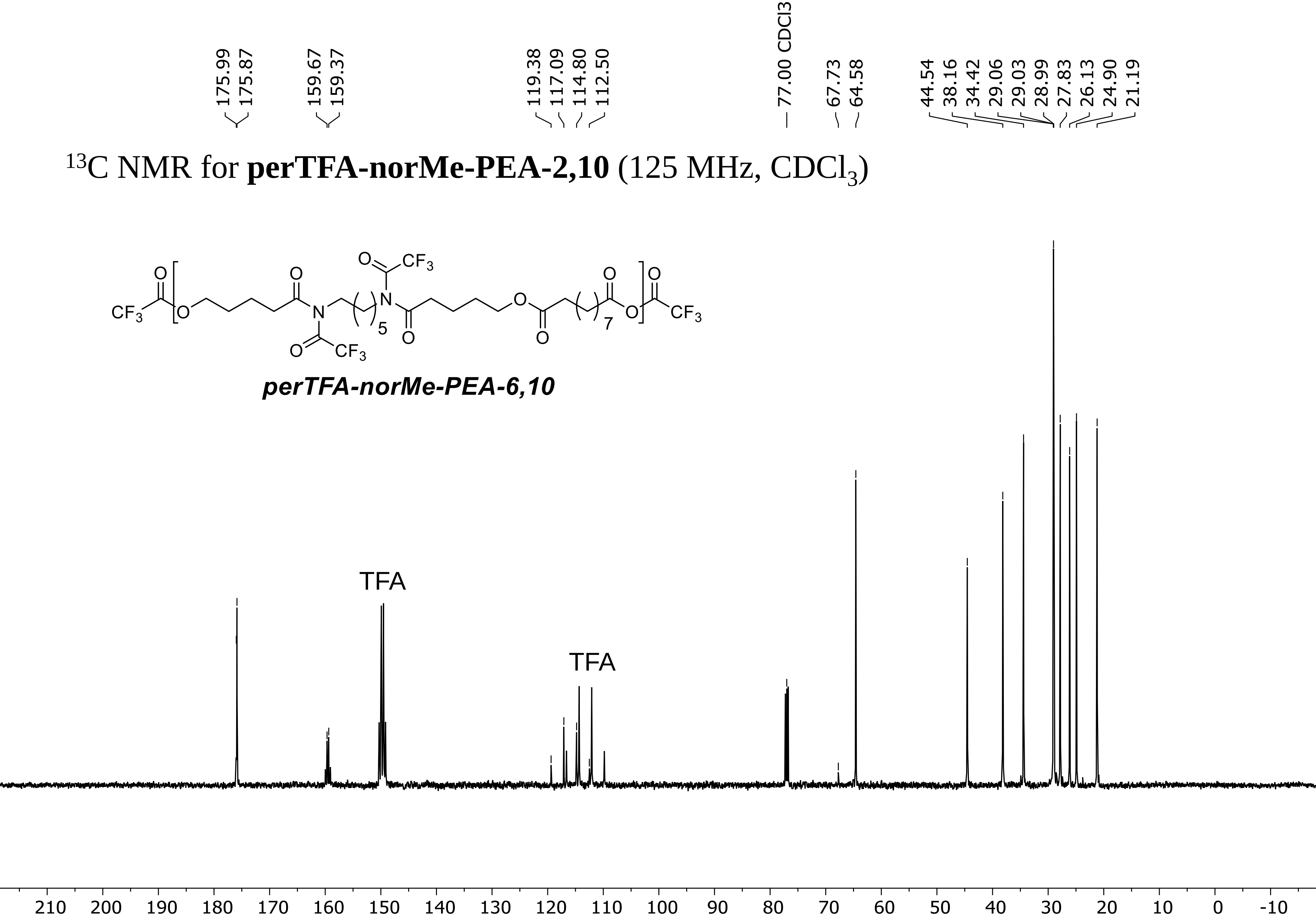
^{1}H NMR for **norMe-PEA-6,10** (500 MHz, $CDCl_3$)



^{1}H NMR for **perTFA-norMe-PEA-2,10** (500 MHz, $CDCl_3$)



^{13}C NMR for **perTFA-norMe-PEA-2,10** (125 MHz, $CDCl_3$)



perTFA-norMe-PEA-6,10