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Supporting Information

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Topochemical Polymerization in Supramolecular Polymers of Oligopeptide Functionalized Diacetylenes

Eike Jahnke,[1] Ingo Lieberwirth,[2] Nikolai Severin,[3] Jürgen P. Rabe,[3] Holger Frauenrath[1]*

[1] *ETH Zürich, Departement Materialien,*
ETH Hönggerberg, HCI H515, CH-8093 Zürich, Switzerland
Tel: +41 44 633 6474; Fax: (+41) 44 633 1390; E-mail: frauenrath@mat.ethz.ch

[2] *Max-Planck-Institut für Polymerforschung*
Ackermannweg 10, 55128 Mainz, Germany

[3] *Humboldt-Universität zu Berlin, Institut für Physik*
Newtonstr. 15, 12489 Berlin, Germany

Supporting Information

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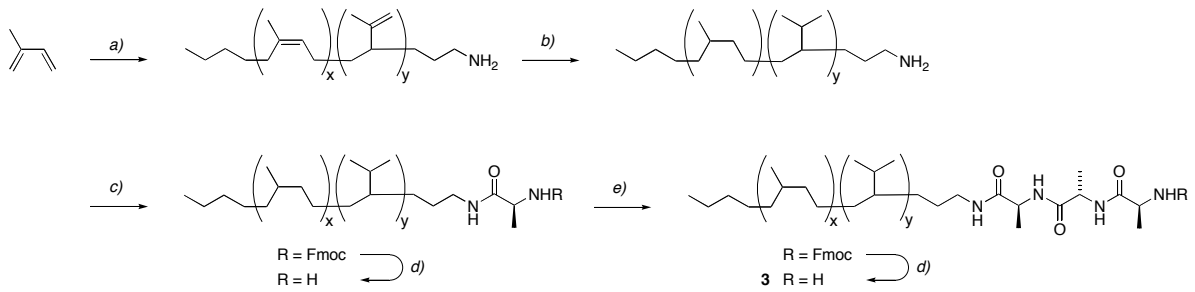
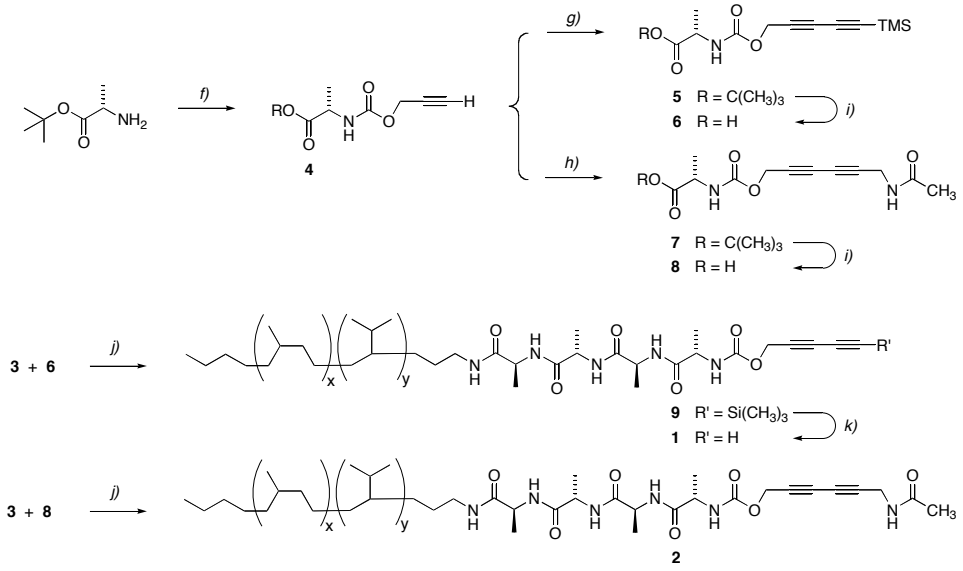
1. Summary of the Synthetic Approach

The intermediate **3** was synthesized as published previously (Scheme S-1).[1] Thus, amine terminated poly(isoprene) was prepared by a living anionic polymerization in THF. The olefin functions were subsequently removed by high pressure hydrogenation. The oligopeptide segment was then built up by solution phase peptide coupling to Fmoc-Ala-OH followed by deprotection. This sequence was repeated with Fmoc-Ala-Ala-OH to yield the intermediate **3**. The oligopeptide substituted diacetylenes **9** and **2** were then synthesized via an EDCI/HOBt promoted peptide coupling to the intermediate **3** instead, starting from the prefabricated building blocks **6** and **8** (Scheme S-2).



Scheme S-1. Synthesis of the intermediate **3**; reaction conditions: *a) n*-BuLi, THF, -78°C→0°C; 1-(3-bromopropyl)-2,2,5,5-tetramethyl-11-aza-2,5-disilacyclopentane; THF/HCl; *b)* H_2, Pd/C, toluene, 80°C, 3 d; *c)* Fmoc-Ala-OH, EDCI/HOBt, TEA, DCM, -40°C→r.t.; *d)* piperidine, DCM; *e)* Fmoc-Ala-Ala-OH, PyBOP, DIEA, DCM, 0°C.



Scheme S-2. Synthesis of the macromonomers **1** and **2**; reaction conditions: *f)* propargyl chloroformate; TEA, DCM, -78°C→0°C; *g)* 2-iodoethynyl trimethylsilane, $PdCl_2(PPh_3)_2$, CuI, DIPA, N_2/H_2; *h) N*-(3-iodoprop-2-ynyl)acetamide, $PdCl_2(PPh_3)_2$, CuI, DIPA, N_2/H_2; *i)* TFA; DCM, r.t.; *j)* EDCI/HOBt, TEA, DCM, -40°C→r.t.; *k)* TBAF, DCM/THF, 0°C, 15 min.

2. Experimental Procedures

Transmission Electron Microscopy. Samples for transmission electron microscopy were prepared by spraying a 0.05 mg mL^{-1} solution of **2** in DCM onto a carbon-coated TEM grid. Some samples were carbon-shadowed at an angle of 70° (relative to the surface normal) in order to determine the height of the fibrillar features. Electron diffraction was performed on samples obtained by drop casting a 1 mg mL^{-1} solution in DCM onto a carbon coated TEM grid, using gold as an internal standard for calibration. The investigations were performed on a FEI Tecnai F20 transmission electron microscope operated at an acceleration voltage of 200 kV. Images were recorded either on a CCD camera for bright field imaging or on imaging plates for electron diffraction.

Scanning Force Microscopy. Scanning force microscopy (SFM) was performed in tapping mode™ using a Multimode Microscope™ (Digital Instruments Inc., Santa Barbara, CA, USA). Olympus Micro Cantilevers were used with a typical resonance frequency of 300 and 70 kHz and a spring constant of 42 N m^{-1} and 2 N m^{-1}, respectively. Samples were prepared by spin-coating from dilute solutions in $CHCl_3$. The correction of the observed fibrils' apparent width was calculated assuming a 9 nm tip radius, consistent with the manufacturer's specifiactions. As the apparent height of the fibrils appeared to have a slight dependence on the scanning conditions, all images for height analysis were taken under 'soft' scanning conditions, with an amplitude damping of 10-20%. The apparent height was determined at the maxima of the fibrils' helical fine structure, and the height profiles were measured along the SFM fast scan direction to minimize the influence of thermal drift.

General Synthesis Procedures. Unless otherwise noted, all reactions were carried out in dried Schlenk glassware in an inert N_2 atmosphere. All reagents were purchased as reagent grade and used without further purification. Solvents were purchased as reagent grade and distilled prior to use. Ether, toluene and THF were dried over sodium/benzophenone, DCM over CaH_2, and acetone was dried using P_2O_5. The solvents were freshly distilled and stored over molecular sieves prior to use. *N*-Fmoc-L-alanine (Fomc-Ala-OH), L-Alanine *tert*.-butyl ester hydrochloride, propargyl amine, and (2-iodoethynyl)trimethylsilane were commercially obtained and used without further purification. *N*-(3-iodoprop-2-ynyl)acetamide and hPI-Ala_3-H **3** were synthesized as published elsewhere.[1]

***N*-Propargyloxycarbonyl-L-alanine *tert*.-butyl ester 4.** L-Alanine *tert*.-butyl ester hydrochloride (3.30 g, 18.15 mmol) was dissolved in 50 ml dry DCM. TEA (3.86 g, 38.12 mmol) was added which led to the precipitation of the hydrochloride. The mixture was cooled to -78°C, and propargyl chloroformate (2.15 g, 18.15 mmol) was added dropwise. The solution was stirred for 1 h at -78°C, heated to 0°C, and stirred for 2 h before it was allowed to warm up to r.t. The organic phase was washed three times with water and once with brine. It was dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was carfully dried in HV. 3.87 g (93%) of **4** were obtained as a colorless oil, and no further purification was necessary.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (d, J = 8 Hz, 3H, CHCH_3), 1.41 (s, 9H, C(CH_3)$_3$), 2.44 (t, J = 2.5 Hz, 1H, C≡C*H*), 4.18 (m, 1H, C*H*), 4.63 (m, 2H, $NHCO_2CH_2$), 5.6 (d, J = 8 Hz, 1 H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.6 (CH*C*H$_3$), 27.9 (C(*C*H$_3$)$_3$), 50.2 (*C*HCH$_3$), 52.4 ($NHCO_2CH_2$), 74.7 (C≡*C*H), 78.2 (*C*≡CH), 81.8 (*C*(CH$_3$)$_3$), 154.6 (carbamate *C*=O), 171.9 (ester *C*=O). Anal. calcd for $C_{11}H_{17}NO_4$: C, 58.14%; H, 7.54%; N, 6.16%; found: C, 57.85%; H, 7.50%; N, 6.14%. MS (ESI): calcd for $C_{11}H_{18}NO_4$: ([M-H]$^+$) 228.3; found: 228.3. R_f: 0.7 (DCM/MeOH 10:1).

***N*-[5-(Trimethylsilyl)penta-2,4-diynyl]oxycarbonyl-L-alanine *tert*.-butyl ester 5.** **4** (0.98 g, 4.41 mmol), (2-iodoethynyl)trimethylsilane (1.22 g, 5.3 mmol) and diisopropylamine (1.78 g, 17.64 mmol) were dissolved in 50 ml dry THF. The solution was degassed with three pump-freeze-thaw cycles. After covering the flask with aluminum foil and cooling to 0°C, $PdCl_2(PPh_3)_2$ (64 mg, 2.0 mol%) and CuI (80 mg, 10 mol%) were added. The brown solution was stirred

over night. The solvent was reomoved, and the crude material was taken up in 150 ml DCM, followed by an aqueous workup. The organic phase was dried over $MgSO_4$, filtered and concentrated in vacuo. Purification was carried out by column chromatography (silica gel, DCM). 0.85 g (59%) of **5** were obtained as an orange oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.17 (s, 9H, Si(CH_3)$_3$), 1.35 (d, J = 7.7 Hz, 3H, CHCH_3), 1.44 (s, 9H, C(CH_3)$_3$), 4.21 (m, 1H, CHCH$_3$), 4.71 (m, 2H, NHCO$_2$CH_2); 5.43 (d, J = 8 Hz, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = -0.6 (Si(CH$_3$)$_3$), 18.7 (CHCH$_3$), 27.9 (C(CH$_3$)$_3$), 50.3 (CHCH$_3$), 52.8 (NHCO$_2$$CH_2$), 71.1, 72.1, 87.1, 87.8 (acetylenic C), 82.0 (C(CH$_3$)$_3$), 154.5 (carbamate C=O), 171.9 (ester C=O). Anal. calcd for $C_{16}H_{25}N_2O_4Si$: C, 59.41%; H, 7.79%; N, 4.33%; found: C, 59.40%; H, 8.04%; N, 4.31%. R_f: 0.3 (DCM).

***N*-[5-(Trimethylsilyl)penta-2,4-diynyl]oxycarbonyl-L-alanine 6. 5** (0.85 g, 2.6 mmol) was dissolved in 10 ml dry DCM. TFA (3.90 g, 34.24 mmol) was added, and the solution was stirred over night. TLC indicated a complete conversion. The solvent was removed in vacuo, and the crude product was dried in HV. 0.70 g (100%) of **6** were obtained as a brown amorphous material, and no further purification was carried out before the next step.

^{1}H NMR (300 MHz, DMSO-D$_6$): δ = 0.19 (s, 9H, Si(CH_3)$_3$), 1.27 (d, J = 8 Hz, 3H, CHCH_3), 4.01 (m, 1H, CHCH$_3$), 4.76 (m, 2H, NHCO$_2$CH_2); 7.74 (d, J = 8 Hz, 1H, NH). ^{13}C NMR (DMSO-D$_6$): δ = -0.3 (Si(CH$_3$)$_3$), 17.5 (CHCH$_3$), 49.7 (CHCH$_3$), 52.3 (NHCO$_2$$CH_2$), 70.3, 74.8, 87.6, 88.3 (acetylenic C), 155.3 (carbamate C=O), 174.6 (ester C=O). R_f: 0.15 (DCM/MeOH 10:1).

***N*-(6-*N*-Acetylaminohexa-2,4-diynyl)oxycarbonyl-L-alanine *tert.*-butyl ester 7. 4** (1.5 g, 6.63 mmol), *N*-(3-iodoprop-2-ynyl)acetamide (1.78 g, 7.98 mmol) and diisopropylamine (2.68 g, 26.5 mmol) were dissolved in 70 ml dry THF. The solution was degassed The solution was degassed with three pump-freeze-thaw cycles. After covering the flask with aluminum foil and cooling to 0°C, $PdCl_2(PPh_3)_2$ (93 mg, 2.0 mol%) and CuI (120 mg, 10 mol%) were added. The brown solution was stirred over night. The solvent was removed, and the crude material was taken up in 150 ml DCM, followed by an aqueous workup. The organic phase was dried over $MgSO_4$, filtered and concentrated in vacuo. Purification was carried out by column chromatography (silica gel, DCM/MeOH 50:1 to 20:1). 1.02 g (49%) of **7** were obtained as a brownish, amorphous solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (d, J = 8 Hz, 3H, CHCH_3), 1.41 (s, 9H, C(CH_3)$_3$), 1.96 (s, 3H, C(O)CH_3), 4.05 (d, J = 7.5 Hz, 2 H, CH_2NHAc), 4.15 (m, 1H, CHCH$_3$), 4.67 (m, 2H, NHCO$_2$CH_2); 5.63 (d, J = 8 Hz, 1H, NH), 6.76 (m, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.4 (CHCH$_3$), 22.7 (C(O)CH$_3$), 27.8 (C(CH$_3$)$_3$), 29.5 (CH$_2$NHAc), 50.2 (CHCH$_3$), 52.4 (NHCO$_2$$CH_2$), 66.8, 70.4, 72.3, 76.0 (acetylenic C), 82.0 (C(CH$_3$)$_3$), 154.6 (carbamate C=O), 170.2 (amide C=O), 171.9 (ester C=O). Anal. calcd for $C_{16}H_{22}N_2O_5$: C, 59.62%; H, 6.88%; N, 8.96%; found: C, 58.74%; H, 6.87%; N, 8.17%. R_f: 0.5 (DCM/MeOH 10:1).

***N*-(6-*N*-Acetylaminohexa-2,4-diynyl)oxycarbonyl-L-alanine 8. 7** (0.86 g, 2.67 mmol) was dissolved in 10 ml dry DCM. TFA (3.95 g, 34.68 mmol) was added, and the solution was stirred over night. TLC indicated a complete conversion. All solvents were removed in vacuo. The crude product was dried in HV. 0.71 g (100%) of **8** were obtained as a brown amorphous material, and no further purification was carried out before the next step.

^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 1.26 (d, J = 8 Hz, 3H, CH-CH_3), 1.83 (s, 3H, C(O)CH_3), 3.9-4.1 (m, 3 H, CH_2NHAc, CHCH$_3$), 4.73 (s, 2H, NHCO$_2$CH_2); 7.25 (d, J = 8 Hz, 1H, NH), 8.37 (m, 1H, NH), 9.75 (s, 1H, COOH). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 17.4 (CH-CH$_3$), 22.6 (C(O)CH$_3$), 28.9 (CH$_2$NHAc), 49.7 (CHCH$_3$), 52.4 (NHCO$_2$$CH_2$), 65.6, 70.0, 74.2, 78.7 (acetylenic C), 155.3 (carbamate C=O), 169.7 (acid C=O), 174.6 (amide C=O). R_f: 0.15 (DCM/MeOH 10:1).

hPI-Ala$_4$-C(O)O-CH$_2$-C≡C-C≡C-TMS 9. HOBt (0.10 g, 0.74 mmol) was added to a solution of **6** (0.18 g, 0.67 mmol) in a mixture of 10 ml dry DMF and 20 ml dry DCM. The reaction mixture was cooled to -20°C, and EDCI (0.16 g, 0.83 mmol) was added. The mixture was stirred for 1 h at -20°C and then allowed to reach r. t. over a period of 1 h while the formation of the active ester intermediate was monitored by TLC. Both the reaction mixture and a solution of hPI-Ala$_3$-H **3** (0.4 g, 0.39 mmol) in 150 ml dry DCM and TEA (0.22 g, 2.17 mmol) were cooled to -40°C and combined. The reaction mixture was stirred for 90 min, during which time it slowly warmed up to 15°C. The solution was diluted with 100 mL $CHCl_3$ and washed with $NaHCO_3$ solution and brine. The combined organic phases were dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, DCM/MeOH 25:1). 0.40 g (81%) of **9** were obtained as a colorless and amorphous solid.

^{1}H NMR (300 MHz, $CDCl_3$/TFA 50:1): δ = 0.2 (s, 9H, Si(C*H*$_3$)$_3$, 0.8-1.8 (m, 160 H, aliphatic), 3.2-3.4 (m, 2 H, C*H*$_2$NHR), 4.2-4.4 (m, 1H, C*H*CH$_3$), 4.5-4.9 (m, 5H, C*H*CH$_3$, NHCO$_2$C*H*$_2$); 5.8 (m, 1H, N*H*), 6.8-6.9 (m, 1H, N*H*), 7.4-7.5 (m, 2H, N*H*), 7.7-7.8 (m, 1H, N*H*). Anal. calcd for $C_{78}H_{147}N_5O_6Si$: C, 73.24%; H, 11.58%; N, 5.48%; found: C, 72.80%; H, 11.57%; N, 5.17%. MS (ESI): calcd for $C_{73}H_{137}N_5O_6SiNa$: ([M-Na]$^+$) 1231.0; found: 1231.4. R_f: 0.5 (DCM/MeOH 10:1).

hPI-Ala$_4$-NHC(O)O-CH$_2$-C≡C-C≡C-H 1. 9 (210 mg, 0.16 mmol) was dissolved in a mixture of 50 ml DCM and 50 ml THF. The solution was cooled to 0°C, and tetrabutylammonium fluoride trihydrate (55.5 mg, 0.176 mmol) was added. The reaction mixture was stirred for 15 min and then quenched with water. After an aqueous workup, drying of the organic phase and removal of the solvent, an amorphous solid remained. The crude product was purified by column chromatography (silica gel, $CHCl_3$/MeOH 25:1). 0.18 g (93%) of **2** were obtained as a colorless and amorphous solid.

^{1}H NMR (300 MHz, $CDCl_3$/TFA 50:1): δ = 0.8-1.8 (m, 168 H, aliphatic), 2.23 (s, 1H, C≡C*H*), 3.2-3.4 (m, 2 H, C*H*$_2$NHR), 4.2-4.3 (m, 1H, C*H*CH$_3$), 4.4-4.9 (m, 3H, C*H*CH$_3$, 2H, NHCO$_2$C*H*$_2$); 5.8 (m, 1H, N*H*), 6.8-6.9 (m, 1H, N*H*), 7.4-7.5 (m, 2H, N*H*), 7.7-7.9 (m, 1H, N*H*). Anal. calcd for $C_{75}H_{139}N_5O_6$: C, 74.64%; H, 11.61%; N, 5.80%; found: C, 73.53%; H, 11.28%; N, 5.36%. MS (ESI): calcd for $C_{70}H_{129}N_5O_6Na$: ([M-Na]$^+$) 1159.0; found: 1159.2. R_f: 0.5 (DCM/MeOH 10:1).

hPI-Ala$_4$-NHC(O)O-CH$_2$-C≡C-C≡C-NHAc 2. HOBt (0.14 g, 1.03 mmol) was added to a solution of **8** (0.27 g, 1.00 mmol) in a mixture of 5 ml dry DMF and 5 ml dry DCM. The reaction mixture was cooled to -20°C, and EDCI (0.20 g, 1.04 mmol) was added. The mixture was stirred for 1 h at -20°C and then allowed to reach room temperature over a period of 1 h while the formation of the active ester intermediate was monitored by TLC. Both the reaction mixture and a solution of hPI-Ala$_3$-H **3** (0.75 g, 0.68 mmol) in 15 ml dry DCM and TEA (1.45 g, 14.4 mmol) were cooled to -40°C and combined. The reaction mixture was stirred over night, during which time it slowly warmed up to 15°C. The solution was diluted with 100 ml $CHCl_3$ and washed with aqueous HCl and brine. The combined organic phases were dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, $CHCl_3$/MeOH 15:2). 0.35 g (42%) of **1** were obtained as a light sensitive, sligthly pink and amorphous solid.

^{1}H NMR (300 MHz, $CDCl_3$/TFA 50:1): δ = 0.8-1.8 (m, 148 H, aliphatic), 2.1 (s, 3H, C(O)C*H*$_3$), 3.2-3.4 (m, 2 H, C*H*$_2$NHR), 4.0-4.3 (m, 3H, C*H*CH$_3$, C*H*$_2$NHAc), 4.4-4.6 (m, 3H, C*H*CH$_3$), 4.6-4.8 (m, 2H, NHCO$_2$C*H*$_2$); 6.3 (m, 1H, N*H*), 6.6 (m, 1H, N*H*), 7.1-7.3 (m, 2H, N*H*), 7.5 (m, 2H, N*H*). Anal. calcd for $C_{78}H_{144}N_6O_7$: C, 73.30%; H, 11.36%; N, 6.58%; found: C, 72.67%; H, 11.30%; N, 6.17%. MS (ESI): calcd for $C_{78}H_{145}N_6O_7$: ([M-H]$^+$) 1208.0; found: 1208.0. R_f: 0.3 ($CHCl_3$/MeOH 10:1).

3. Gelation Properties and ^{1}H NMR Spectroscopy of Macromonomers 1 and 2

The macromonomers **1** and **2** exhibited no tendency toward gelation. Thus, solutions in DCM, $CHCl_3$ or $C_2H_2Cl_4$ showed an increased viscosity but remained fluid even at concentrations of up to 30 mg mL^{-1}. Nevertheless, ^{1}H NMR spectra of both **1** and **2** gave a clear indication of strong aggregation, even when they were recorded at temperatures of 60°C in $CDCl_3$, or at 120°C in $C_2D_2Cl_4$. Only ^{1}H NMR spectra of very dilute samples (5 mg mL^{-1}) in $CDCl_3$/TFA 50:1 were well-resolved, and all peaks had the expected multiplicity and integration.

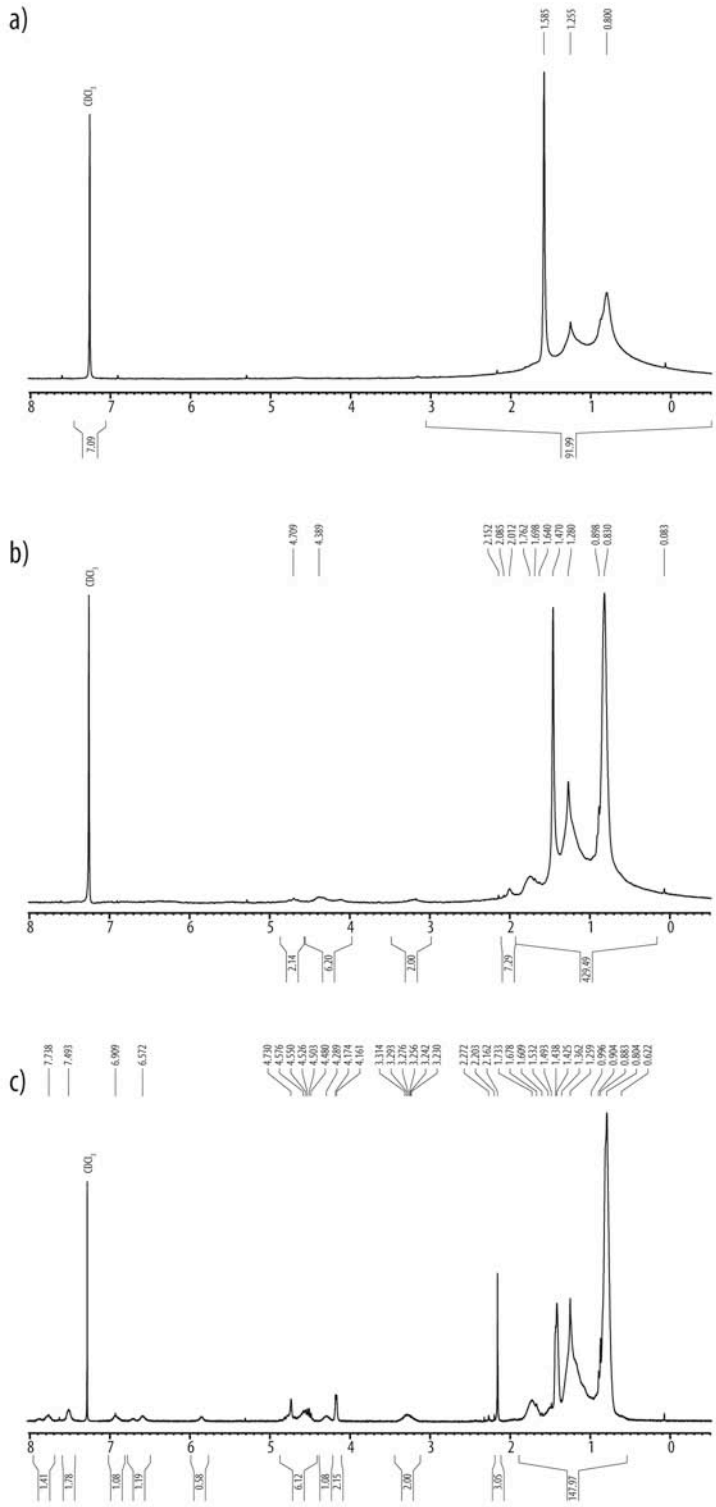


Figure S-1. ^{1}H NMR spectra of **2**; 5 mg mL^{-1} in (a) $CDCl_3$ at 25°C; (b) $CDCl_3$ at 60°C; (c) $CDCl_3$/TFA at 25°C.

4. Discussion of the Infrared Spectra of 1 and 2

Infrared spectra of **1** and **2** were recorded in DCM or $CHCl_3$ solutions (IR spectra of the same compound in either solvent were found to be virtually identical). Peakfitting of the amide I regions was performed with Gaussian peak functions, starting with the same number and positions of peaks for **1** and **2**. The peak fitting was fairly sensitive to the starting parameters, and the results are, therefore, just to be regarded as a qualitative support rather than a means of quantitative determination of the secondary structures of **1** and **2**.

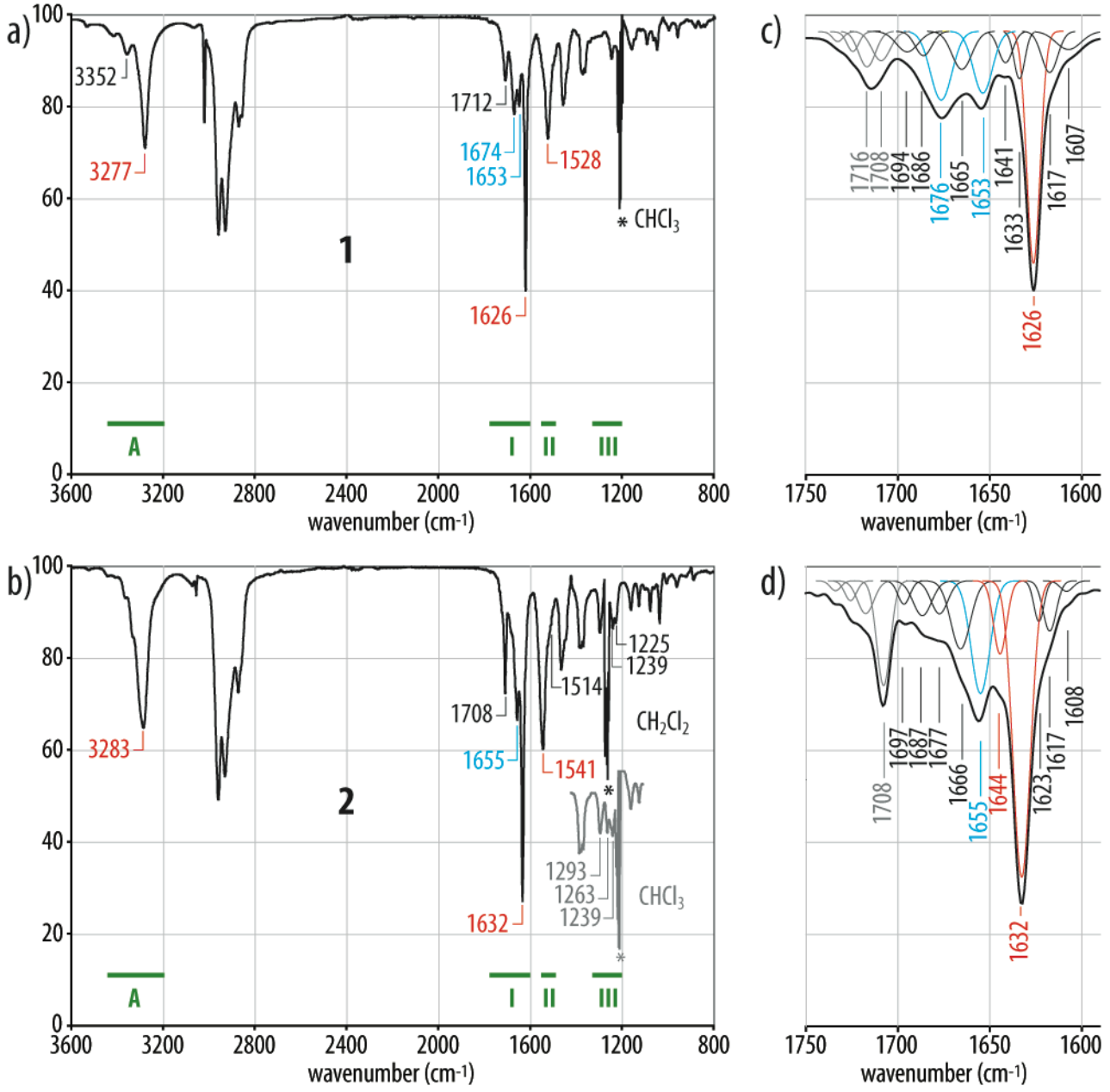


Figure S-2. (a,b) IR spectra of **1** and **2**; (c,d) peakfitting of the respective amide I absorptions (envelope curves are plotted with a vertical offset for the sake of clarity).

In the IR spectra of **2**, the amide A (ν_{NH}) band at 3283 cm^{-1} was consistent with β-sheet type hydrogen bonding. The amide I (ν_{CO}) region was dominated by a strong absorption at 1632 cm^{-1} which was, likewise, in agreement with a β-sheet structure and exactly the same value as found in β-poly(L-alanine).[2] The band at 1655 cm^{-1} was assigned to

unordered conformations. Only a shoulder was observed at 1677 cm^{-1} which is also often found in β-sheet type structures according to the literature. The fact that it did not occur at higher values of 1685-1695 cm^{-1} may be interpreted as an indication for a parallel orientation of the β-strands.[3] Finally, the bands above 1700 cm^{-1} were assigned to the non-peptidic carbonyl functions. The peakfitting of the amide I region supported this analysis and, additionally, clearly revealed a shoulder originating from a band at 1645 cm^{-1} which has been discussed as an evidence for parallel β-strand orientation.[4] In the amide II region, the main band was observed at 1541 cm^{-1} (with a shoulder at 1514 cm^{-1})′, i.e., distinctly different from the value of 1524 cm^{-1} found in β-poly(L-alanine).[2] Finally, the amide III region in IR spectra of **2** was supportive of a mixture of β-sheet (1225 cm^{-1}, 1239 cm^{-1}) and unordered structures (1263 cm^{-1}, 1293 cm^{-1}). Unfortunately, the presence of artefacts from the subtraction of solvent peaks in this usually informative region prevented a more thorough investigation.

Taking into account the structural similarity of **1** and **2**, it was surprising to find that the IR spectrum of **1** was similar, but exhibited some distinct differences. The amide A region of **1** showed a main absorption at 3277 cm^{-1}, and a second band at 3352 cm^{-1}, indicating the presence of other secondary structures along with the expected β-sheet structures. Likewise, the three strong amide I bands at 1626 cm^{-1}, 1653 cm^{-1}, 1674 cm^{-1}, and 1626 cm^{-1}, were consistent with mixtures of β-sheets with unordered structures. Again, the peakfitting of the amide I region further confirmed this analysis. In the case of **1**, the observed amide II band at 1528 cm^{-1} was very similar to the experimental value found for β-poly(L-alanine).[5] The amide III region in the IR spectra of **2** in $CHCl_3$ was unfortunately obscured by artefacts from the subtraction of solvent peaks.

Of course, conclusions from the above results will have to be drawn with care because of the conflicting assignments of IR bands in the amide I region to protein secondary structures in the literature.[6] Furthermore, **1** and **2** are short, synthetic peptides in a hydrophobic environment, i.e., in an organic solvent, as opposed to proteins in aqueous solution. Nevertheless, our results were well in line with examples of synthetic polymers containing β-sheet forming oligopeptide sequences reported in the literature. For example, Sogah et al. reported bands at 1632 cm^{-1} and a weak band at 1645 cm^{-1} as an evidence for parallel-chain β-sheets in GAGA containing polymers, and bands at 1630 cm^{-1}, 1663 cm^{-1}, 1655 cm^{-1}, and 1692 cm^{-1} for supposedly antiparallel-chain β-sheets in AAAA containing polymers.[4] Similar results were reported by Shao et al.[7]

The combination of the observed amide I, II, and III bands observed in the IR spectra of **2** were in much better agreement with calculated IR absorptions of parallel-chain single-sheet β-poly(L-alanine) reported by Krimm et al.[8] than with experimentally determined values for antiparallel-chain β-poly(L-alanine).[3,5] A twisting and bending of β-sheets would exert a substantial influence on their IR spectra.[8] We, therefore, investigated the literature for examples and found the IR spectra of membrane proteins with β-barrel or related twisted β-sheet type conformations to be remarkably similar to the spectra of macromonomer **2**.[9] By contrast, the amide I, II, and III bands observed in IR spectra of **1** were found to be very similar to experimentally determined values in antiparallel-chain β-poly(L-alanine) and, thus, more consistent with a predominantly antiparallel-chain β-sheet structure. In conclusion, the different end groups in **1** and **2** (H vs. CH_2NHAc) appear to exert a decisive influence on the mode of aggregation. As a predominantly anti-parallel alignment of the molecules would be detrimental to the molecules' reactivity in terms of a topochemical polymerization, we would tentatively attribute the experimentally observed differences in their polymerizability to the role of the end groups, as well.

5. Electron and X-Ray Diffraction of Macromonomer 2

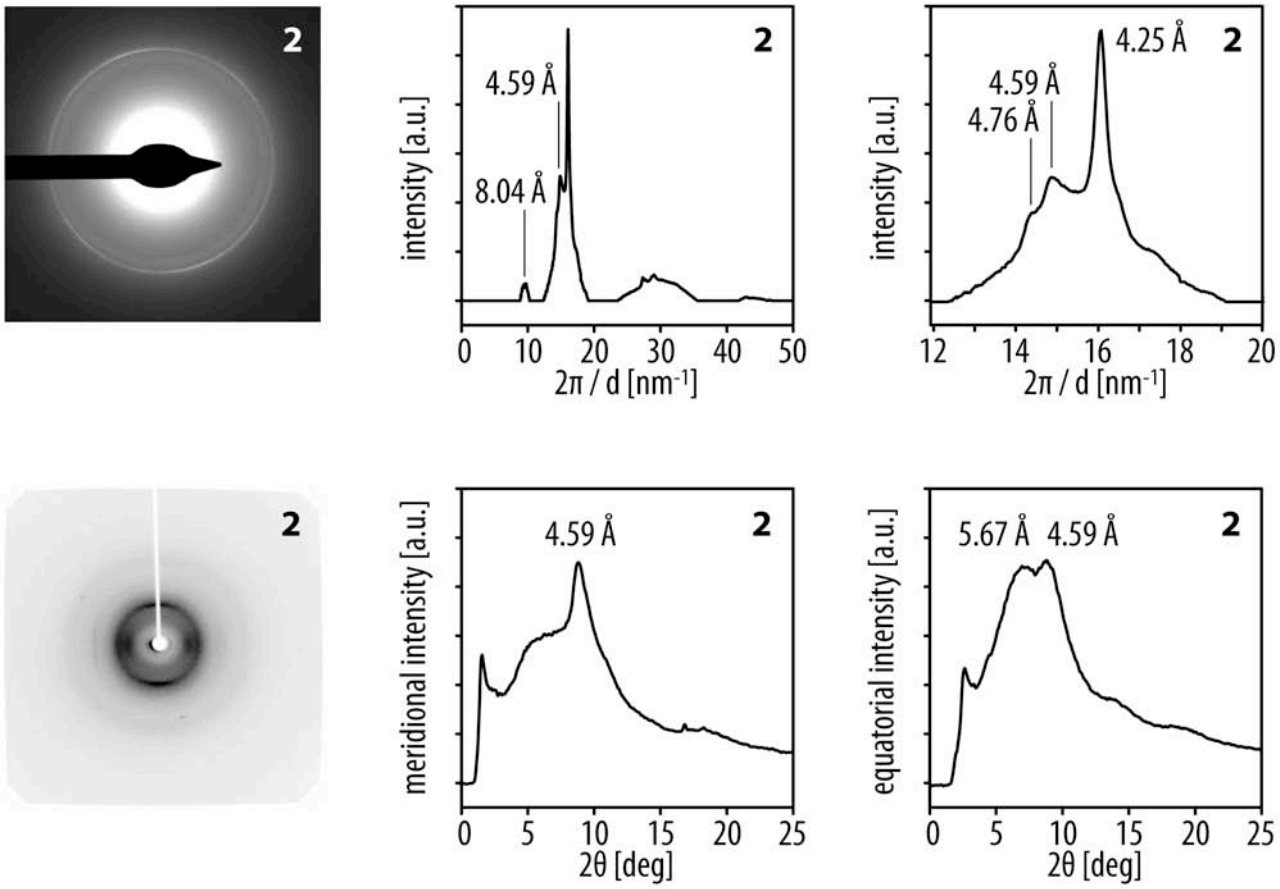


Figure S-3. Electron diffraction of multi-layer films (top) and X-ray diffraction of solid samples (bottom) of **2**.

6. Additional TEM and SFM Images

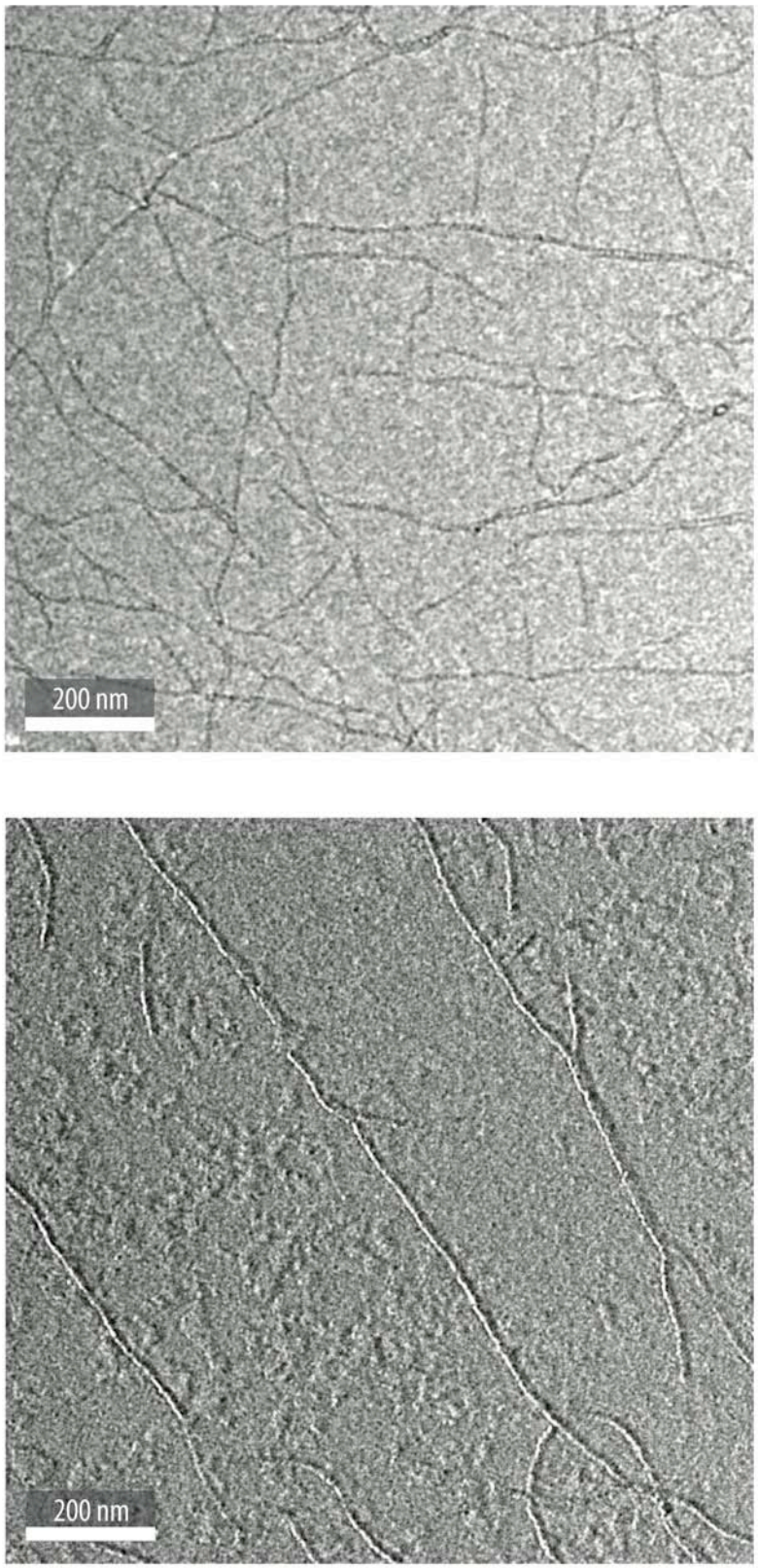


Figure S-4. Transmission electron microscopy images of **2**; unstained sample (top); after carbon shadowing (bottom).

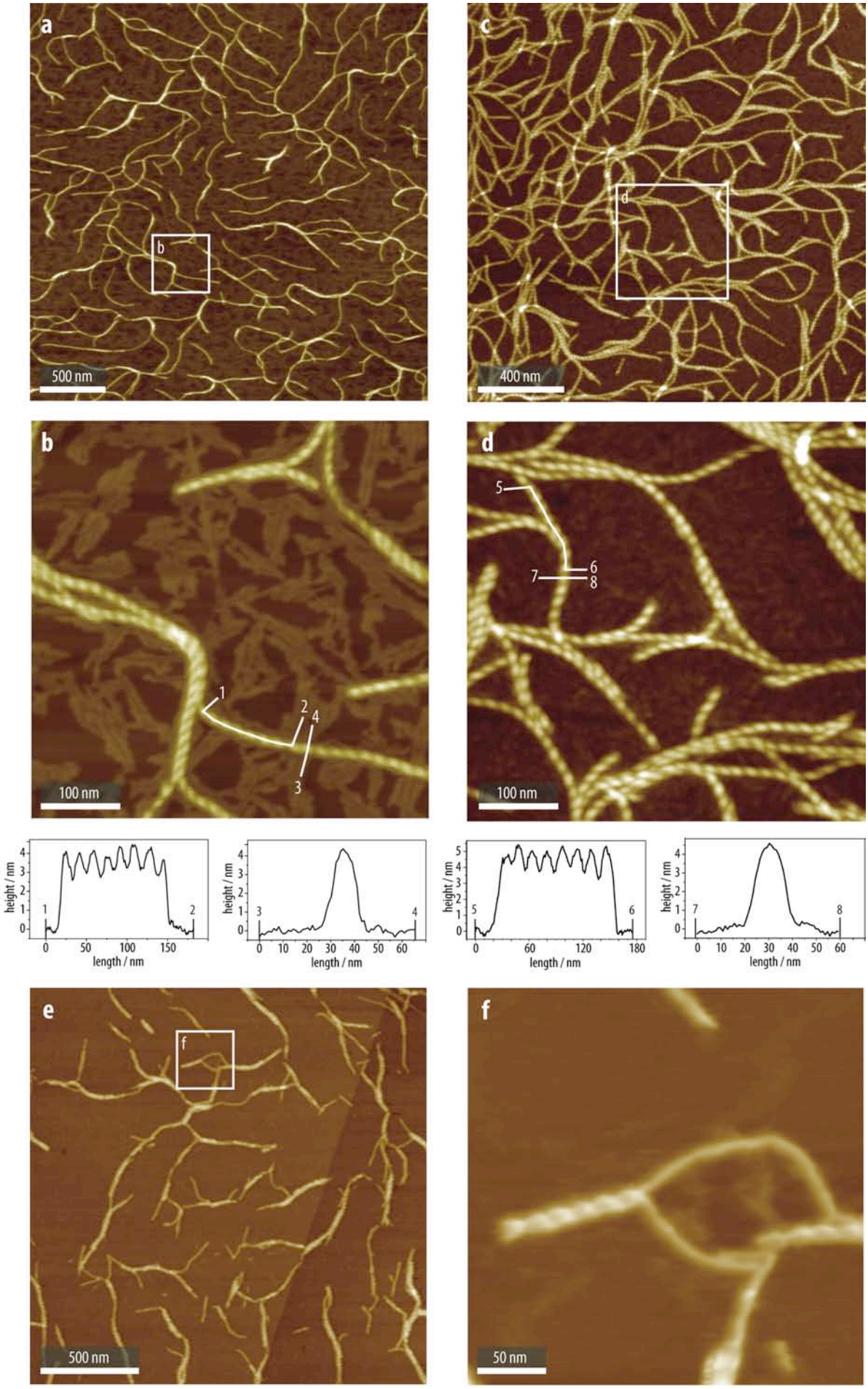


Figure S-5. Scanning force microscopy images of **2**, and height profiles along and across the fibrils.

7. UV Spectra of the Polymerization Experiments

Only UV irradiation of solutions of **2** show the formation of the poly(diacetylene) backbone. In the case of **1**, UV spectra reveal the disappearance of the diacetylene absorption and an increase of absorption between 300 and 400 nm.

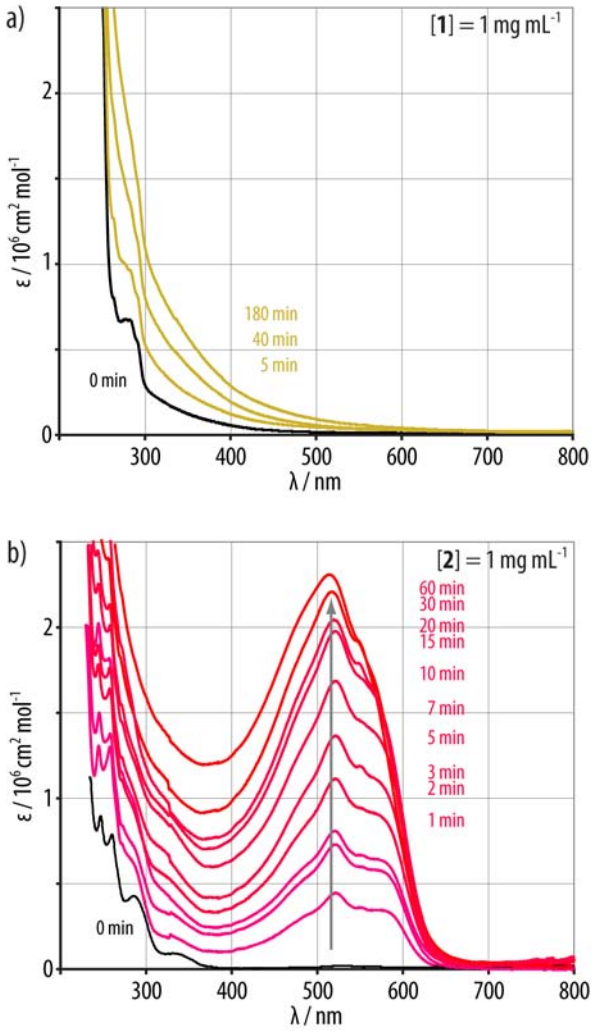


Figure S-6. UV spectra of **1** and **2** in DCM solutions after different periods of UV irradiation.

8. Raman and Solid State ^{13}C NMR Spectroscopy of 2 and P2

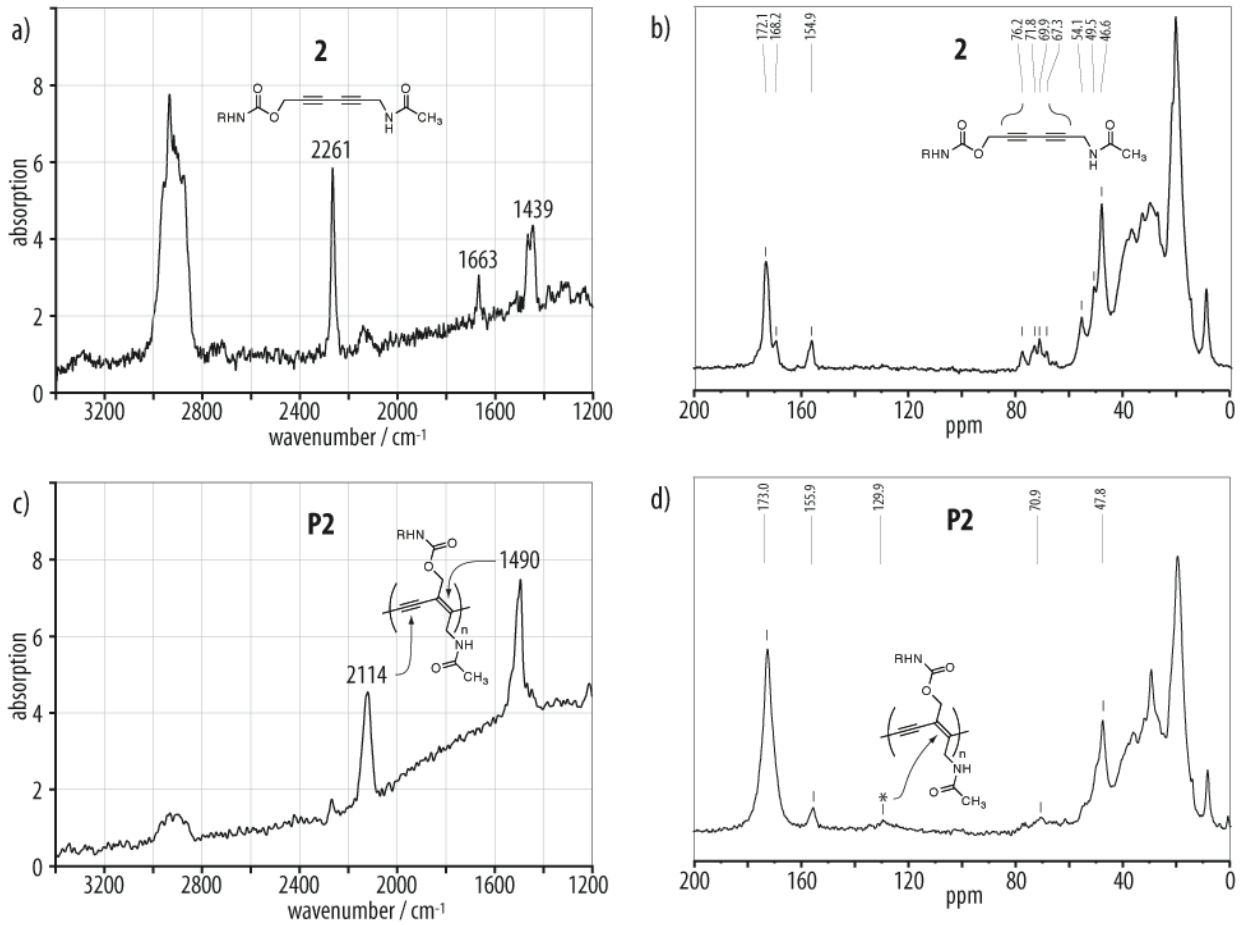


Figure S-7. (a,b) Raman spectra and (c,d) solid state ^{13}C NMR spectra of macromonomer **2** and the corresponding poly(diacetylene) **P2** obtained after UV irradiation.

9. References

[1] E. Jahnke, Holger Frauenrath, submitted.

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[4] (a) M. J. Winningham, D. Y. Sogah, *Macromolecules* **1997**, *30*, 862; (b) O. Rathore, M. J. Winningham, D. Y. Sogah, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 352; (c) O. Rathore, D. Y. Sogah, *J. Am. Chem. Soc.* **2001**, *123*, 5231.

[5] (a) W. H. Moore, S. Krimm, *Biopolymers* **1976**, *15*, 2465; (b) A. M. Dwivedi, S. Krimm, *Macromolecules* **1982**, *15*, 186; (c) J. Bandekar, S. Krimm, *Biopolymers* **1988**, *27*, 885.

[6] For good reviews of this issue, see (a) B. R. Singh in *Infrared Analysis of Peptides and Proteins*, B. R. Singh (ed.), ACS Symposium Series, *750*, **2000**, 2-37; (b) S. Krimm, ibd. 38-53; (c) P. I. Haris, ibd., 54-95.

[7] J. Yao, D. Xiao, X. Chen, P. Zhou, T. Yu, Z. Shao, *Macromolecules* **2003**, *36*, 7508.

[8] (a) J. Bandekar, S. Krimm, *Biopolymers* **1988**, *27*, 909; (b) W. Qian, J. Bandekar, S. Krimm, *Biopolymers* **1991**, *31*, 193.

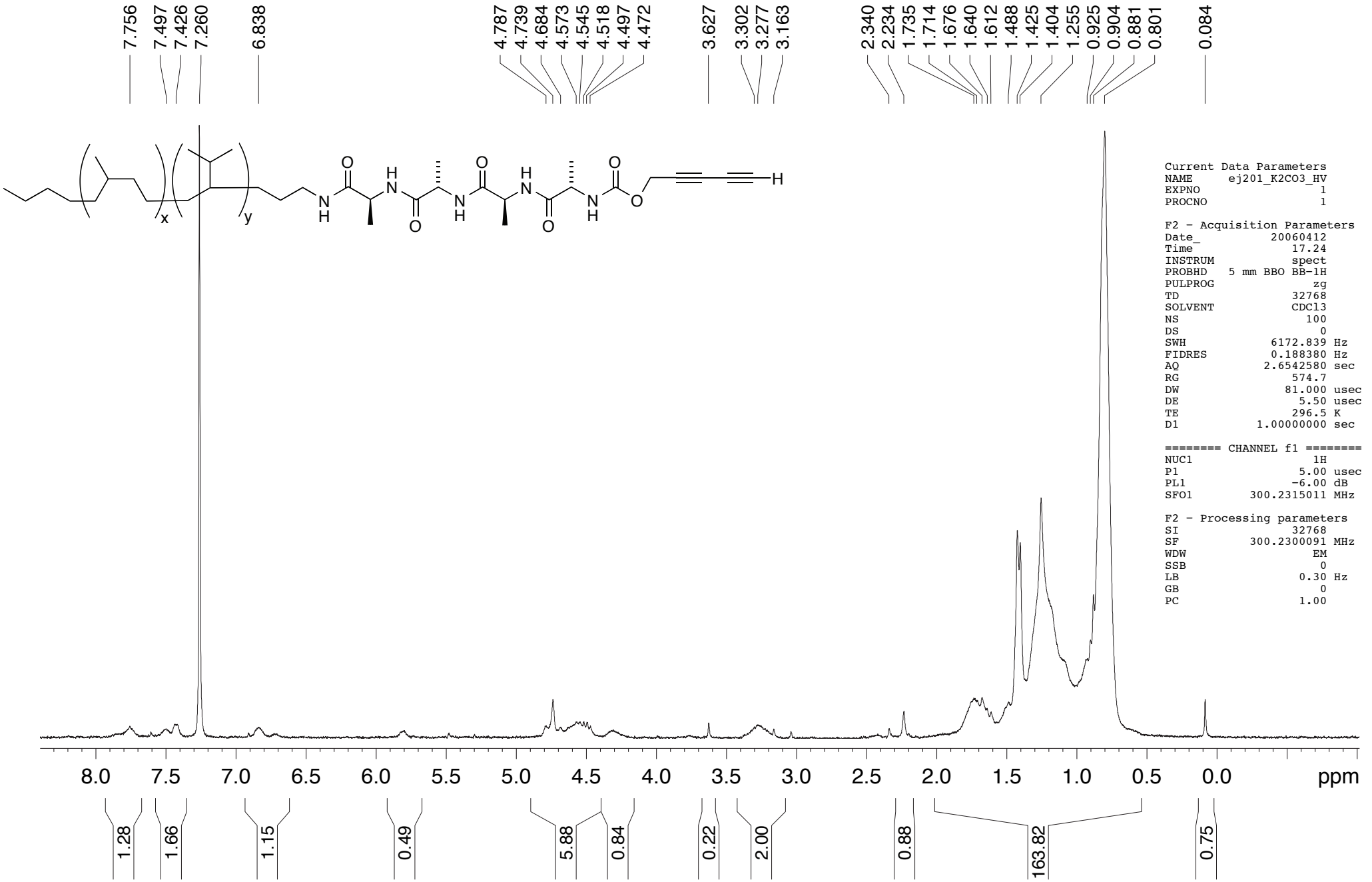
[9] H. Susi, D. M. Byler, *Arch. Biochem. Biophys.* **1987**, *258*, 465.

Appendix

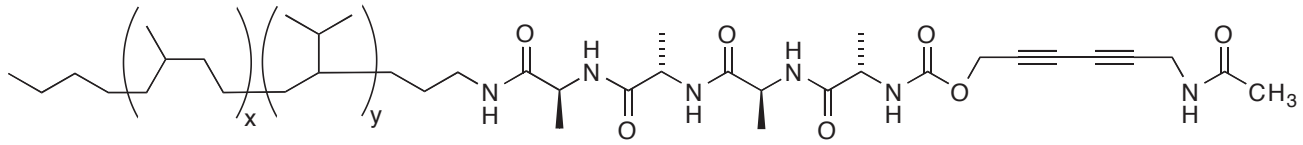
NMR Spectra

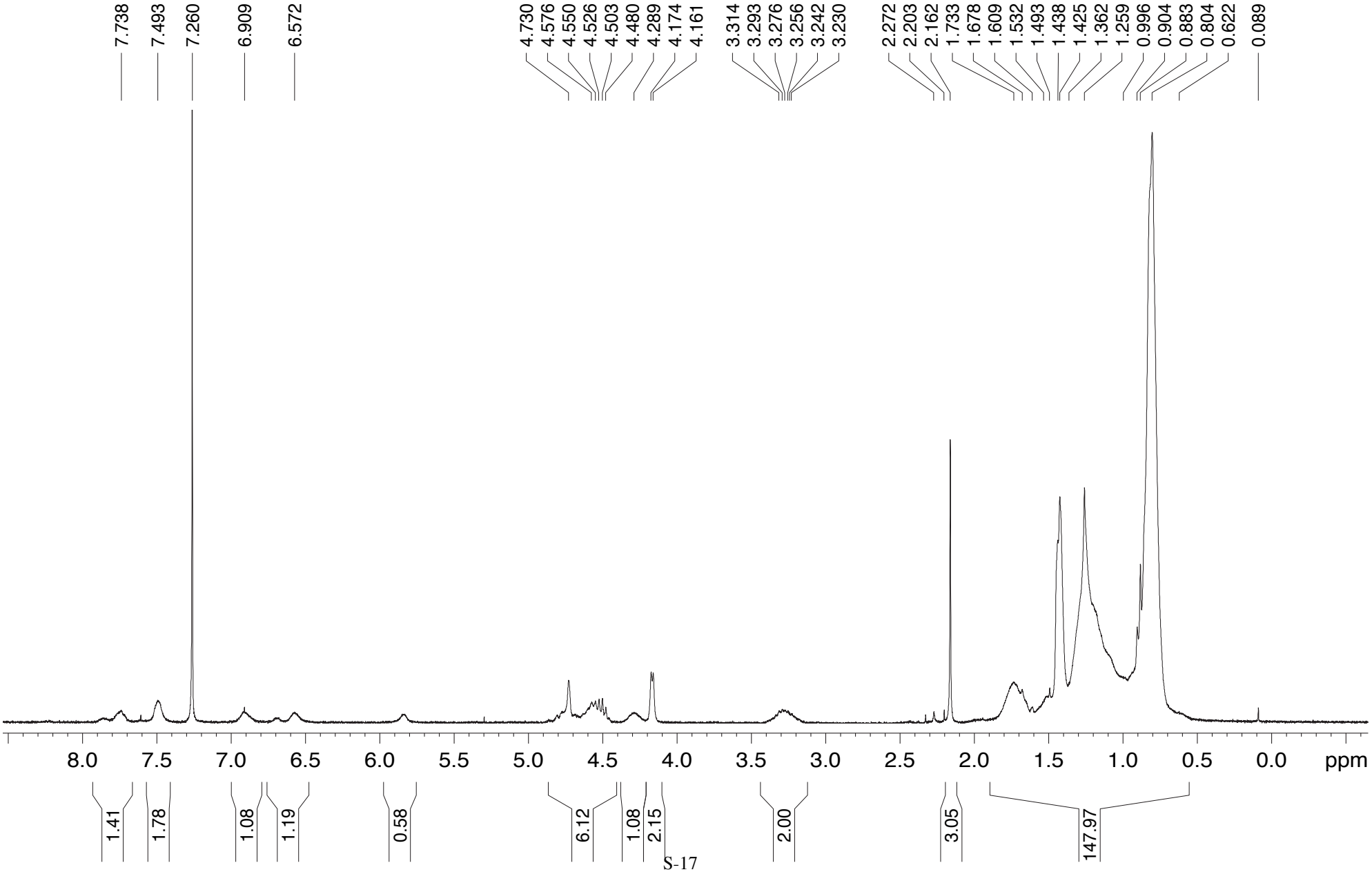
ESI Mass Spectra

^{1}H NMR spectrum of **1**

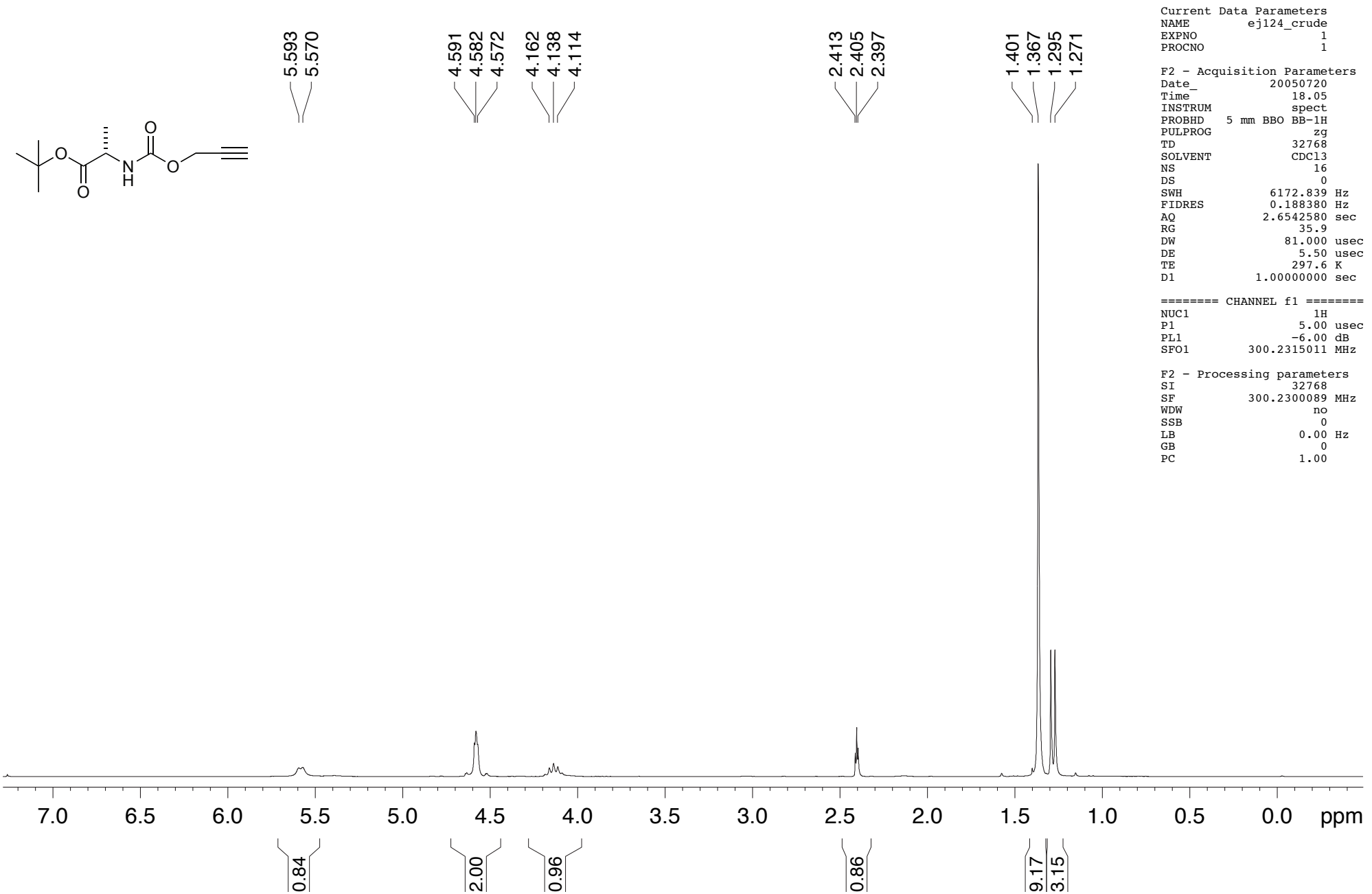


^{1}H NMR spectrum of **2**





^{1}H NMR spectrum of **4**

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PROCNO                 1

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PULPROG              zg
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            6172.839 Hz
FIDRES         0.188380 Hz
AQ             2.6542580 sec
RG                35.9
DW               81.000 usec
DE                5.50 usec
TE                297.6 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 5.00 usec
PL1               -6.00 dB
SFO1         300.2315011 MHz

F2 - Processing parameters
SI                32768
SF           300.2300089 MHz
WDW                  no
SSB                   0
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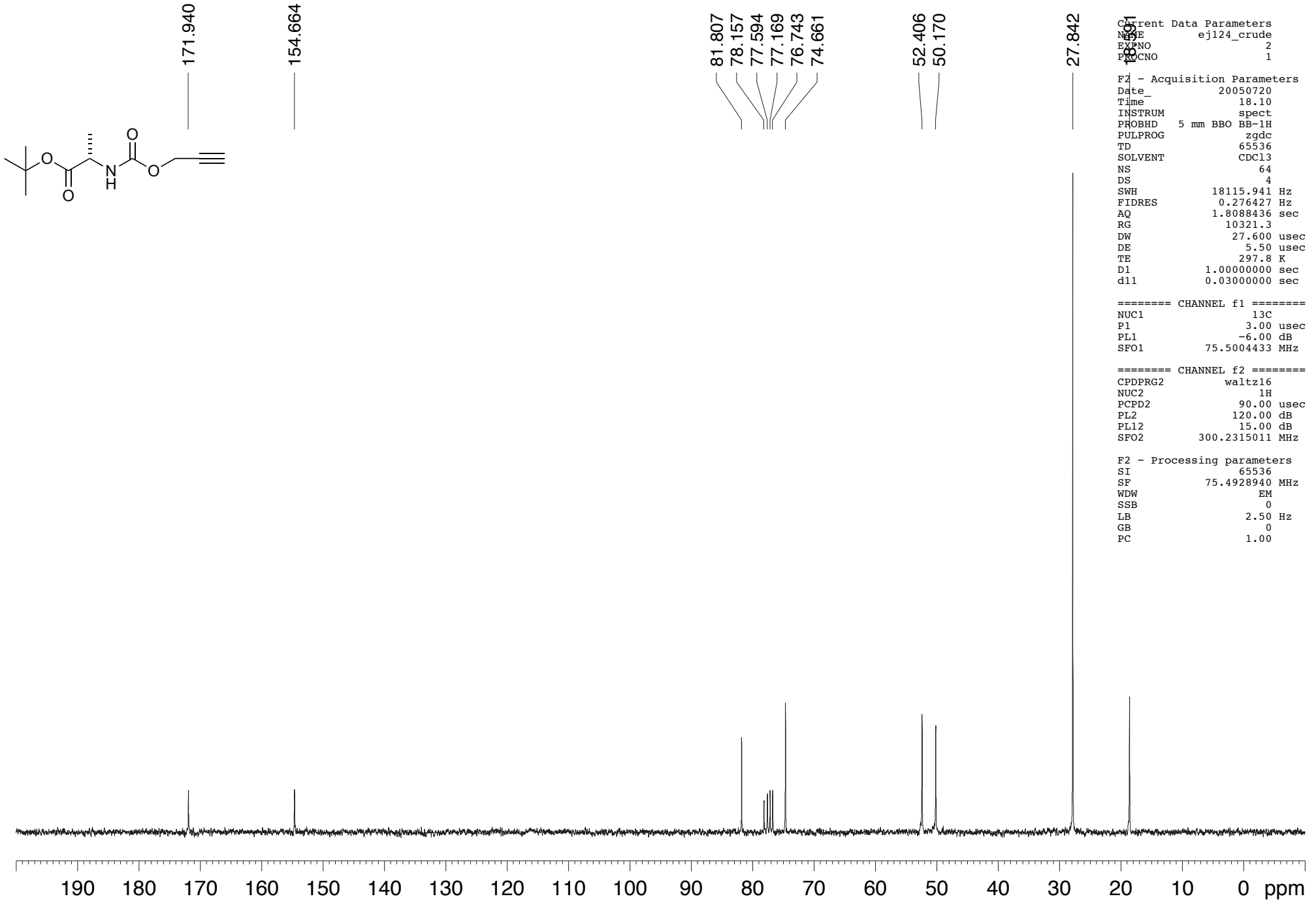
^{13}C NMR spectrum of **4**

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SWH           18115.941 Hz
FIDRES         0.276427 Hz
AQ            1.8088436 sec
RG              10321.3
DW               27.600 usec
DE                5.50 usec
TE               297.8 K
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d11         0.03000000 sec

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PL1              -6.00 dB
SFO1        75.5004433 MHz

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NUC2               1H
PCPD2             90.00 usec
PL2              120.00 dB
PL12              15.00 dB
SFO2       300.2315011 MHz

F2 - Processing parameters
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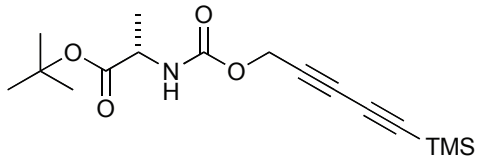
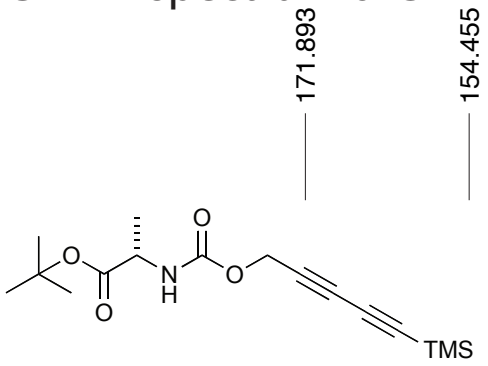
^{1}H NMR spectrum of ***5***



^{13}C NMR spectrum of ***5***

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TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      4
SWH             18115.941 Hz
FIDRES          0.276427 Hz
AQ              1.8088436 sec
RG                11585.2
DW                27.600 usec
DE                39.43 usec
TE                296.7 K
D1             1.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   3.00 usec
PL1                 -6.00 dB
SFO1          75.5004433 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2               90.00 usec
PL2                120.00 dB
PL12                15.00 dB
SFO2         300.2315011 MHz

F2 - Processing parameters
SI                  65536
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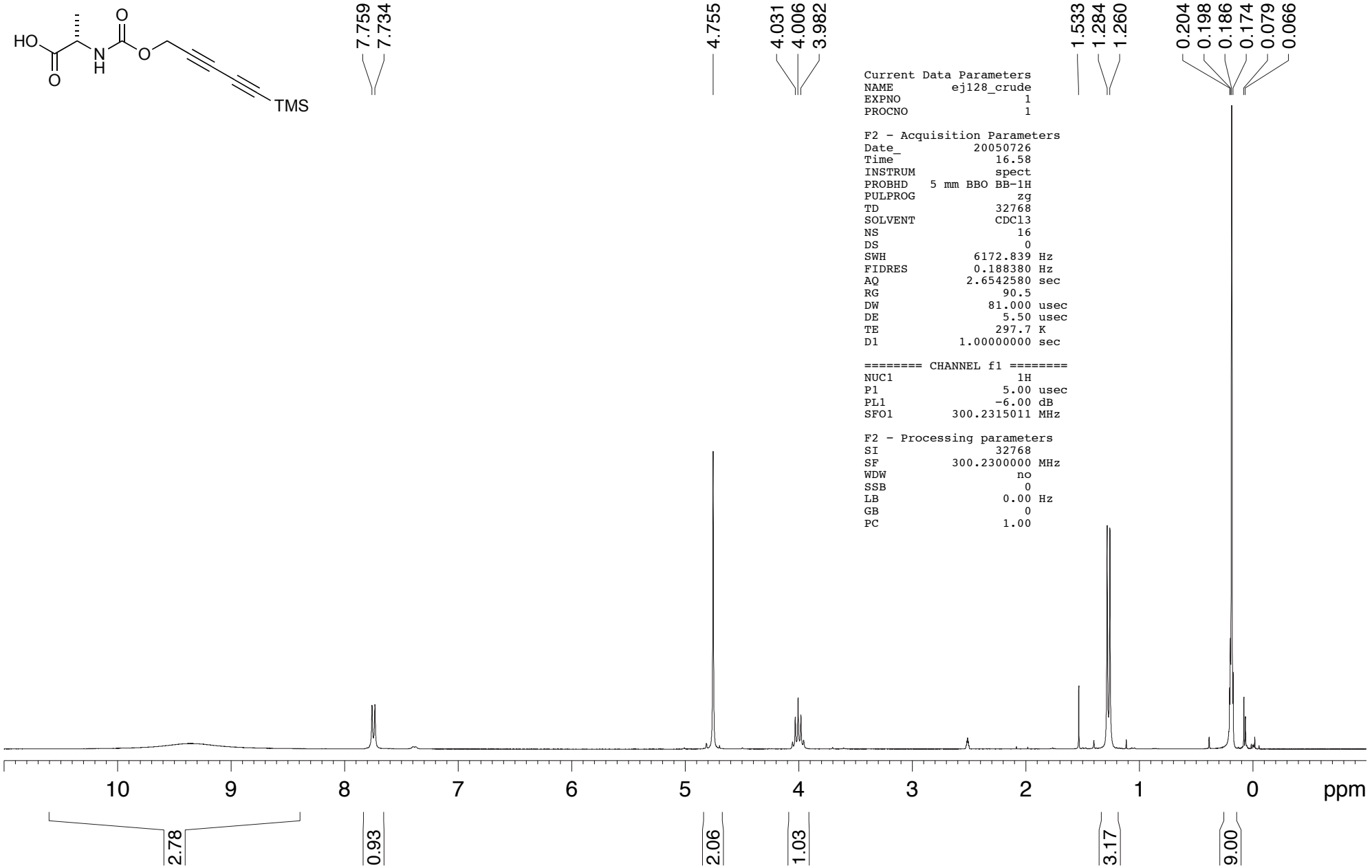
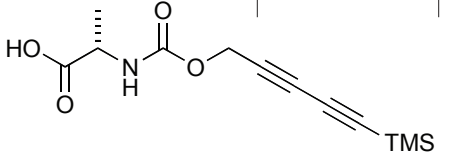
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of **6**



^{13}C NMR spectrum of **6**

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PROCNO                 1

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PULPROG             zgdc
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     4
SWH           18115.941 Hz
FIDRES         0.276427 Hz
AQ            1.8088436 sec
RG              11585.2
DW               27.600 usec
DE                5.50 usec
TE               297.9 K
D1           1.00000000 sec
d11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 3.00 usec
PL1               -6.00 dB
SFO1         75.5004433 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL2             120.00 dB
PL12             15.00 dB
SFO2        300.2315011 MHz

F2 - Processing parameters
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PC                  1.00
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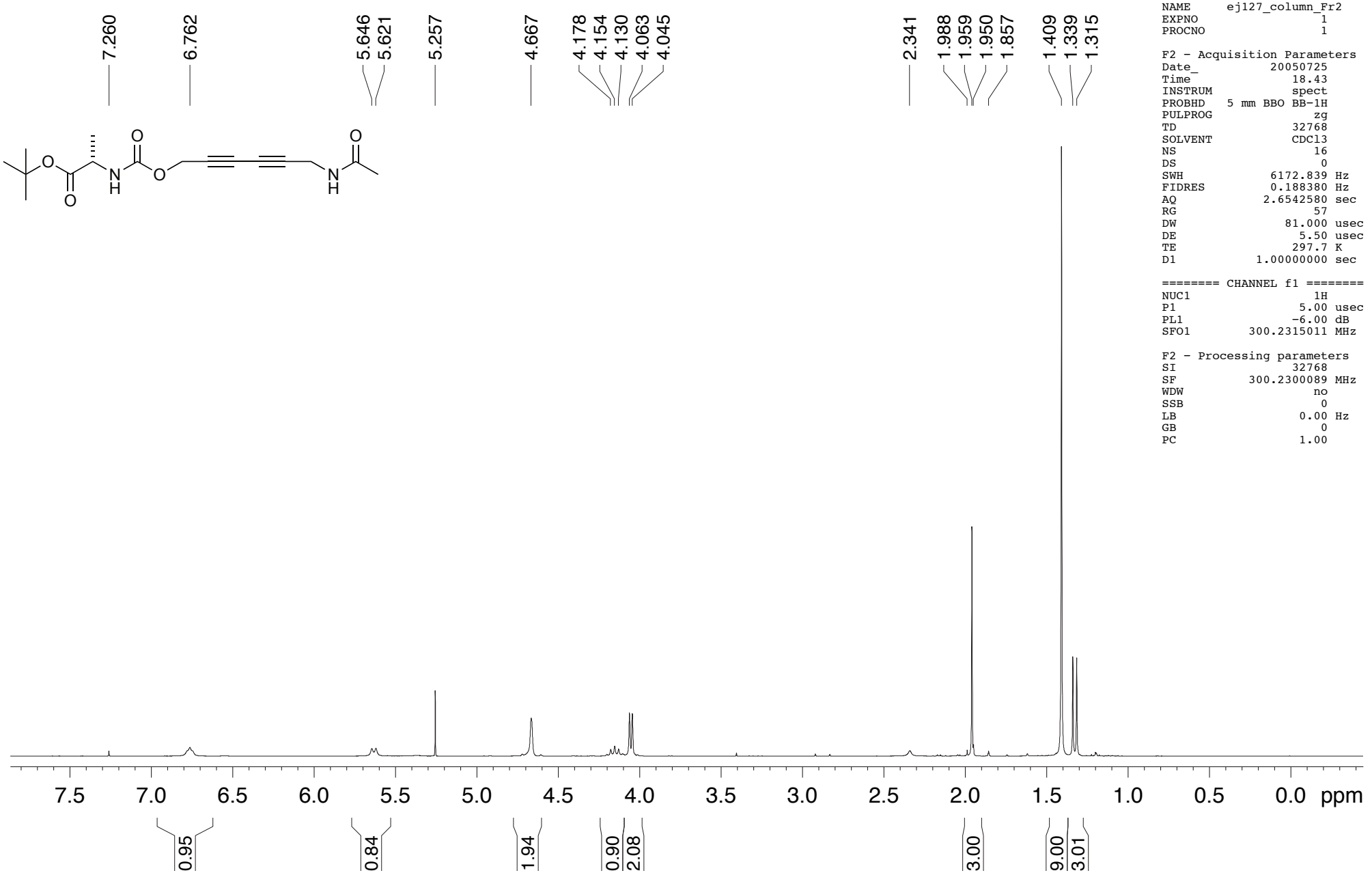
^{1}H NMR spectrum of **7**

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SOLVENT              CDCl3
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DS                       0
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FIDRES            0.188380 Hz
AQ                2.6542580 sec
RG                      57
DW                 81.000 usec
DE                  5.50 usec
TE                  297.7 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   5.00 usec
PL1                 -6.00 dB
SFO1          300.2315011 MHz

F2 - Processing parameters
SI                   32768
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WDW                     no
SSB                      0
LB                  0.00 Hz
GB                       0
PC                    1.00
```
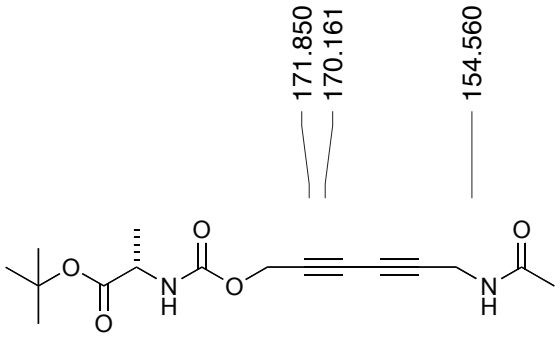
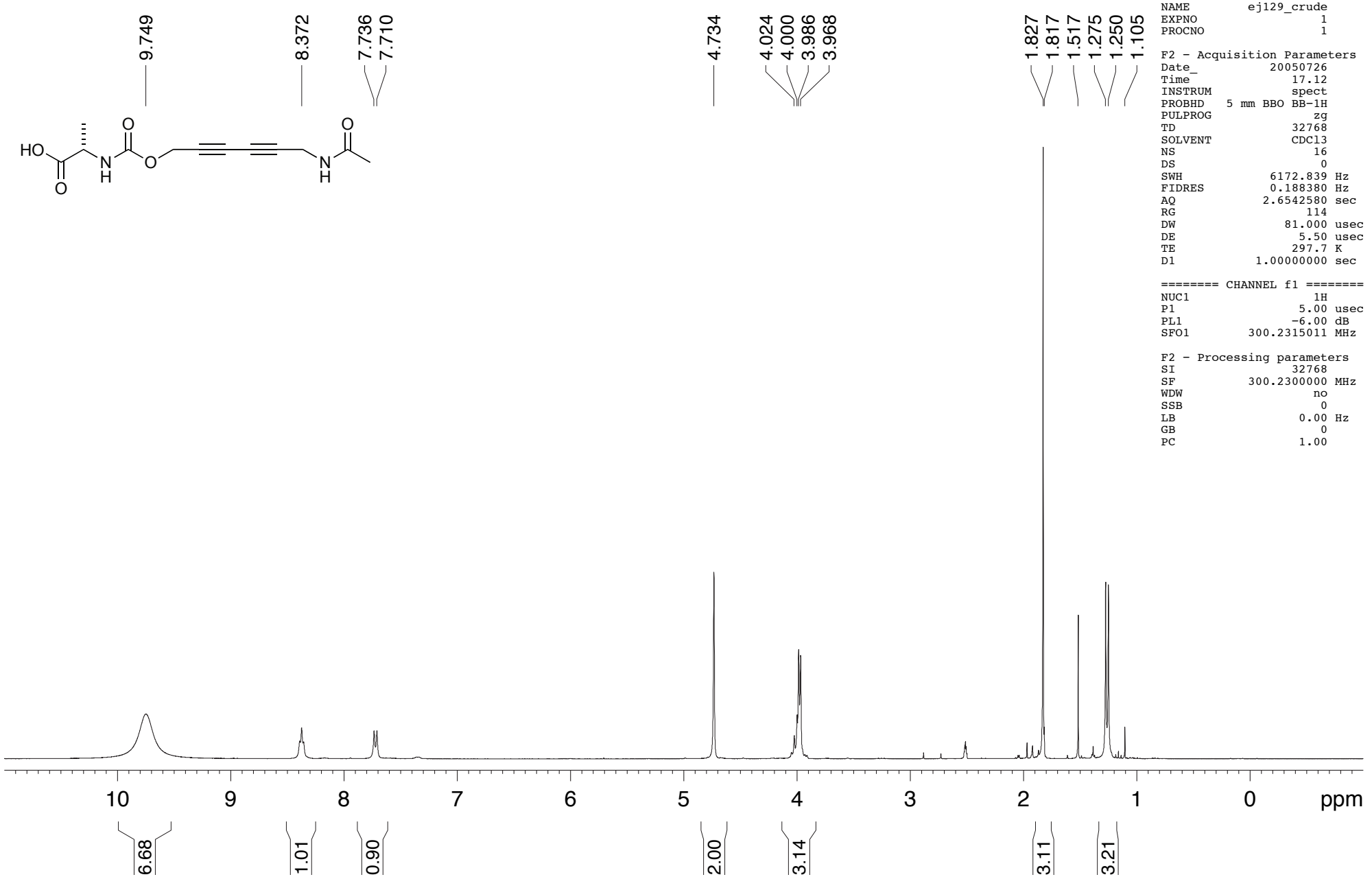
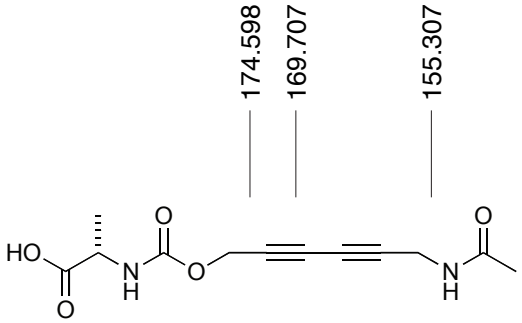

^{13}C NMR spectrum of **7**



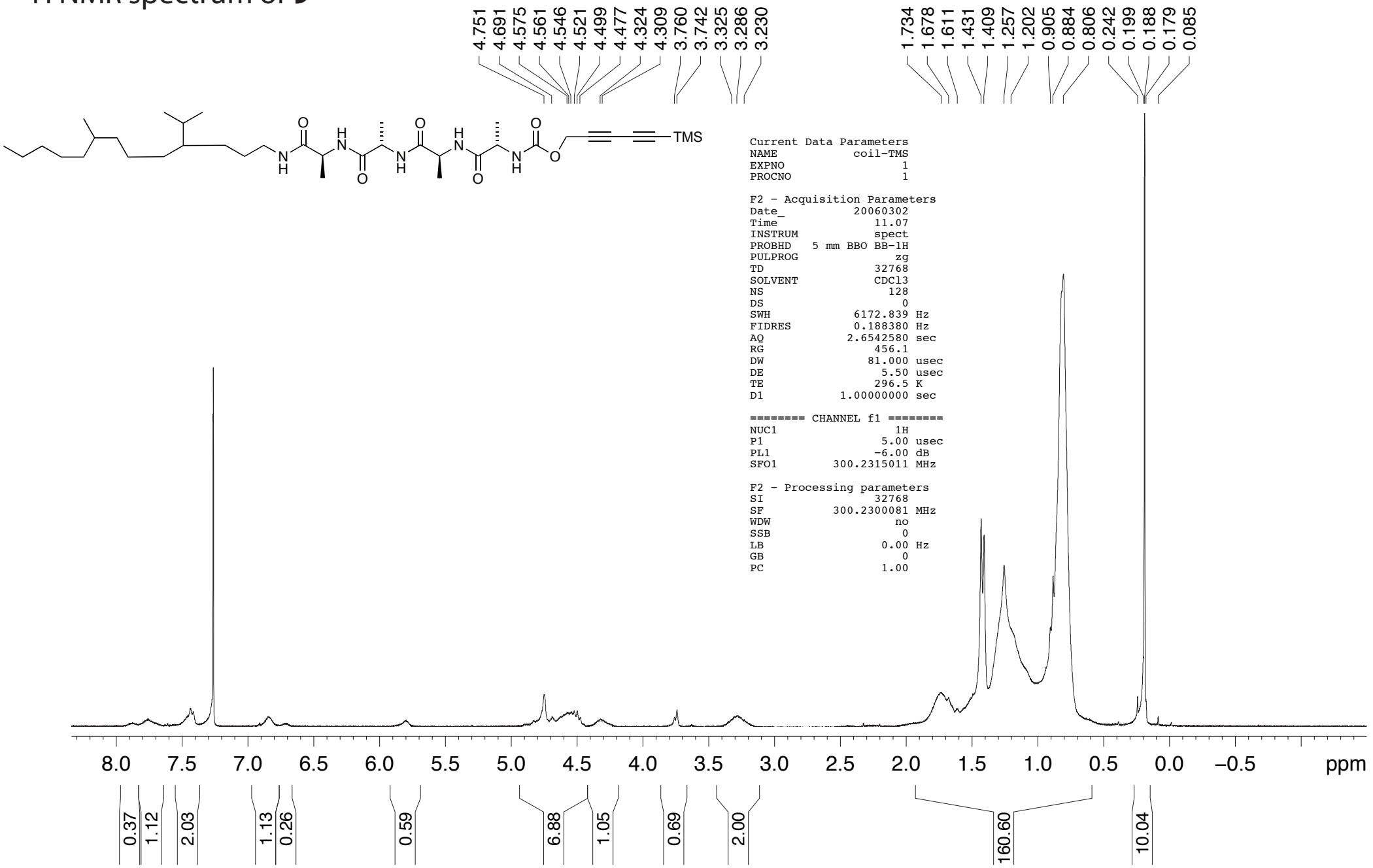
^{1}H NMR spectrum of **8**



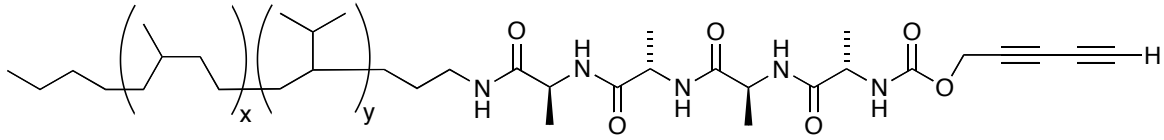
^{13}C NMR spectrum of **8**



^{1}H NMR spectrum of **9**



ESI MS of **1**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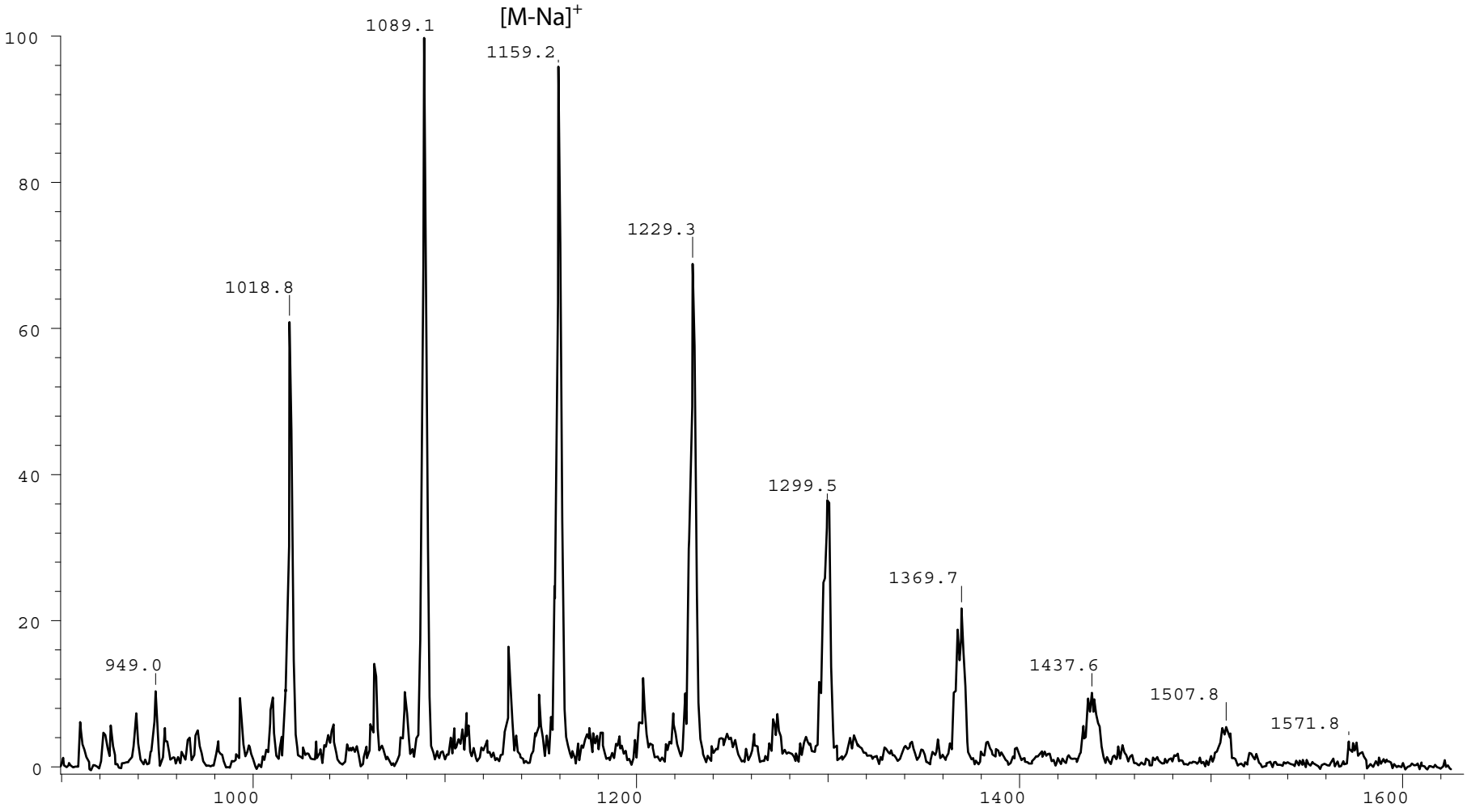
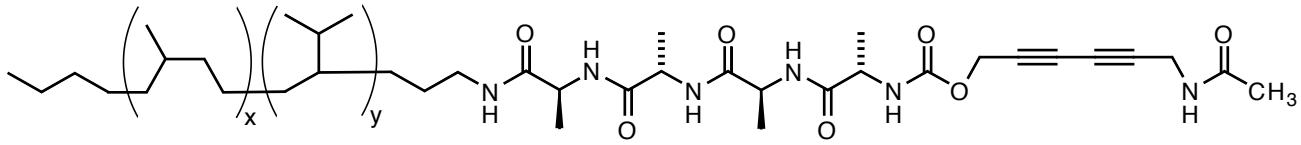
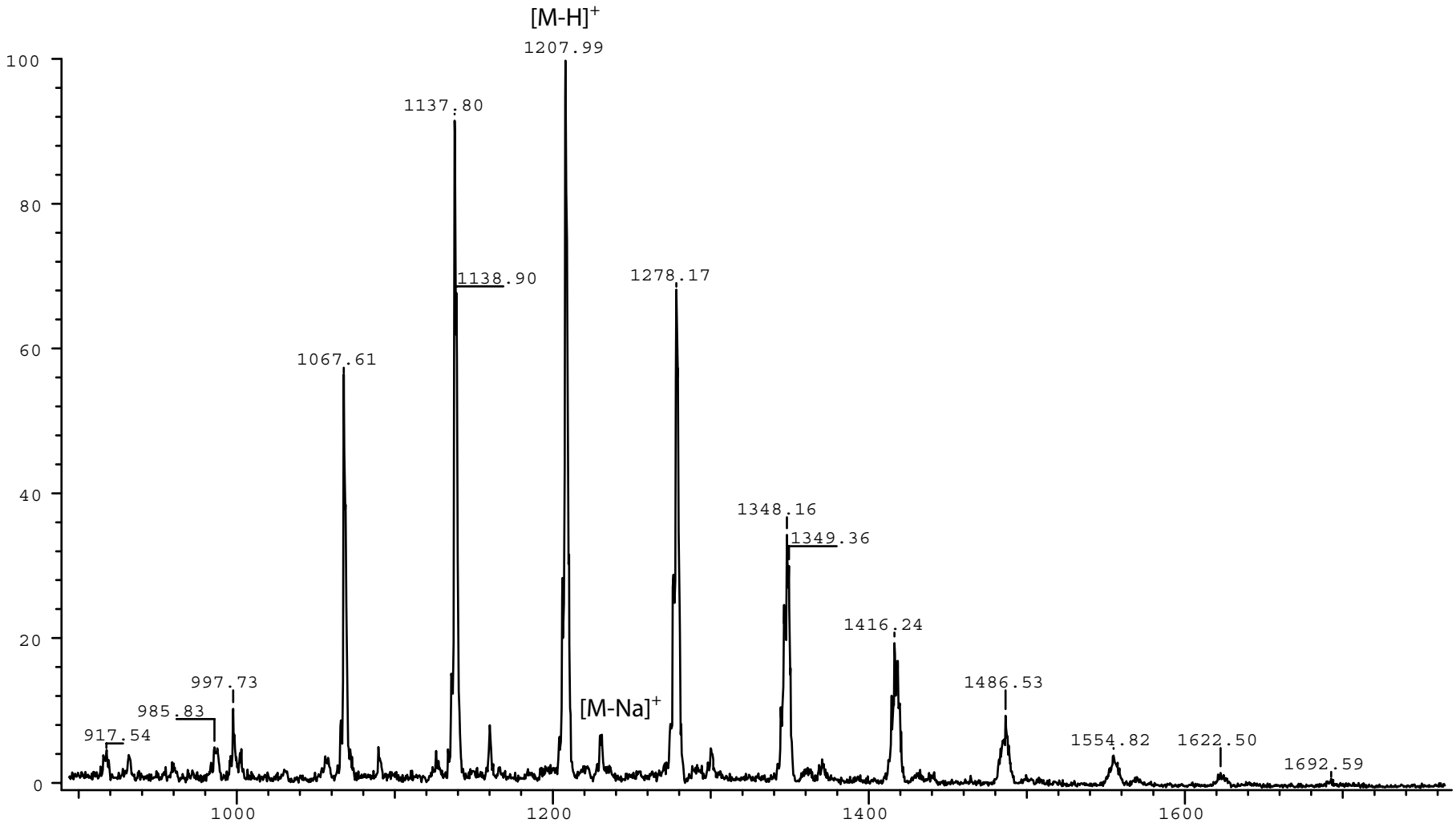
y
O
H
N
O
H
N
O
H
N
O
N
H
O
O
H


[M-Na]+
1089.1
1159.2
1018.8
1229.3
1299.5
1369.7
949.0
1437.6
1507.8
1571.8
100
80
60
40
20
0
1000
1200
1400
1600

ESI MS of **2**

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1067.61
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1416.24
997.73
985.83
917.54
[M-Na]+
1486.53
1554.82
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1692.59
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80
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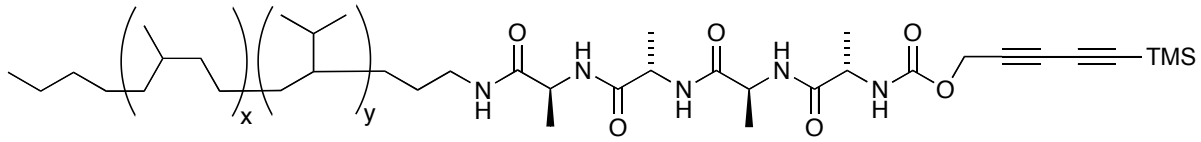
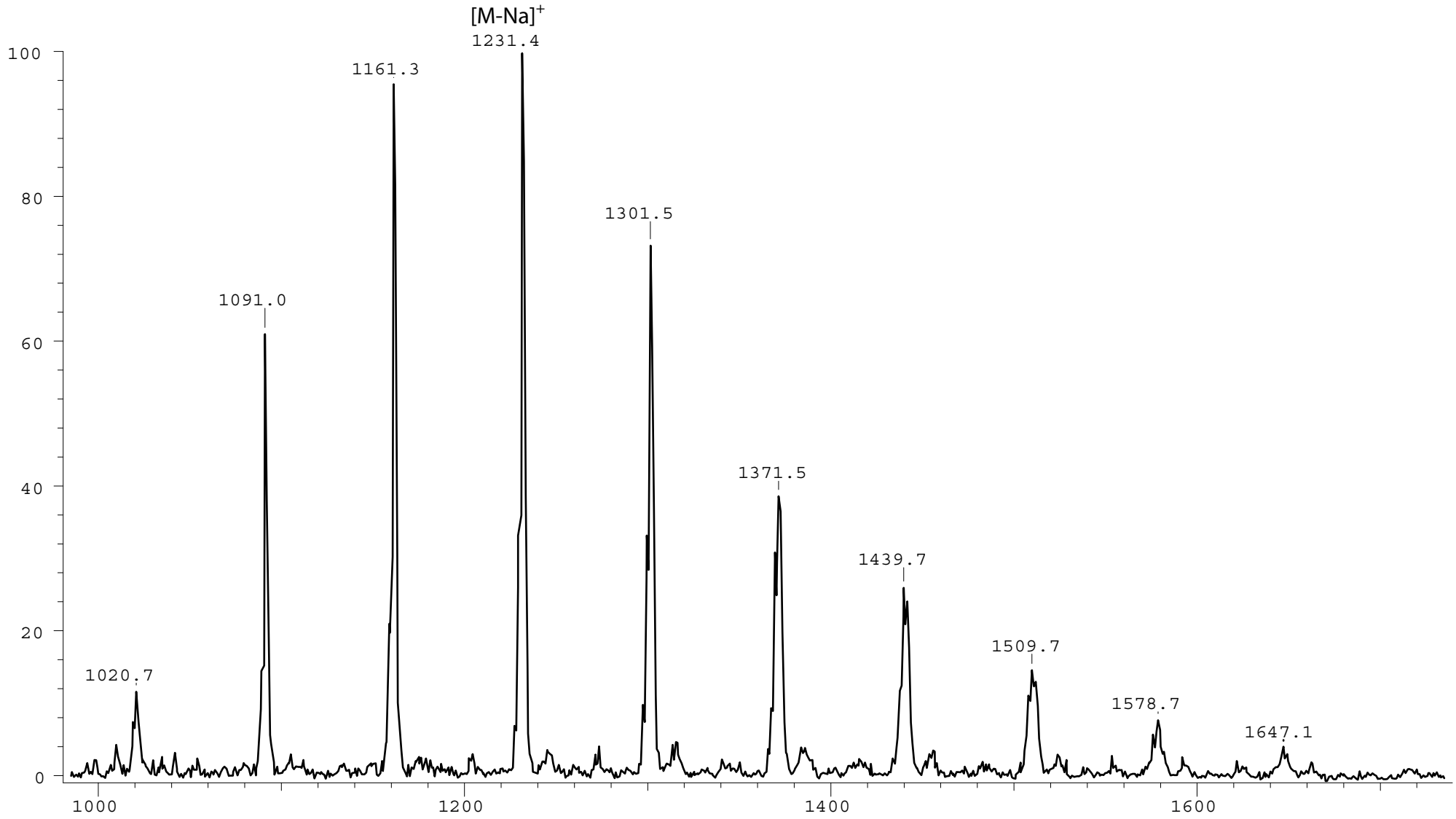
40
20
0
1000
1200
1400
1600

ESI MS of **9**


x
y
TMS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1647.1
1020.7
100
80
60
40
20
0
1000
1200
1400
1600