SUPPORTING INFORMATION

Amino Acid-Bearing ROMP Polymers with a Stereoregular Backbone

Jae Chul Lee, Kathlyn A. Parker*, and Nicole S. Sampson*

Department of Chemistry, Stony Brook University, Stony Brook, NY 11794-3400

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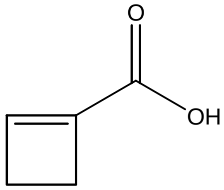
Spectrum list

General Information

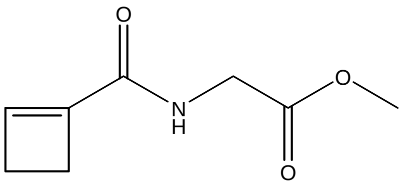
All reactions were performed under an N_2 or Ar atmosphere. CH_2Cl_2 was dried over CaH_2 and distilled prior to use. CD_2Cl_2 was degassed before use for reactions. Second generation Grubbs' catalyst $[(H_2IMes)(Pcy_3)(Cl)_2Ru{=}CHPh]$ and ethyl 1-bromocyclobutanecarboxylate were purchased from Aldrich (Cat # 56974-7 and 19729-7). The synthesis of precatalyst **2** was performed using the procedure published by Love, J.A. et al.[1] Neutral alumina and Mallinckrodt silica gel 60 (230-400 mesh) were used for column chromatography. Aluminum TLC (thin layer chromatography) plates were silica gel 60 (F_{254}). ^1H NMR spectra were reported as chemical shift in ppm (multiplicity, coupling constant in Hz, and integration). ^{13}C NMR spectra were reported as chemical shift in ppm. The solvent peak was used as an internal reference. High resolution mass spectra (ESI) were acquired at the University of Illinois at Urbana-Champaign mass spectrometry facility supported by a grant from the National Science Foundation, Division of Biological Infrastructure (DBI-010085).



Cyclobut-1-enecarboxylic acid[2]

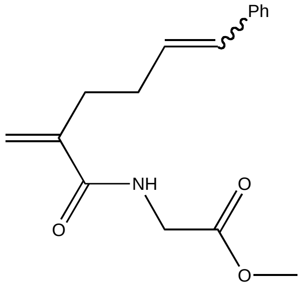
Cyclobut-1-enecarboxylic acid was prepared according to the procedure for preparation of 3,3-dimethylcylobutene carboxylic acid[3] as described by Campbell et al. with minor modifications. KOH (6.00 g, 107 mmol) and toluene (90 mL) were mixed and then heated to reflux until the KOH dissolved. Ethyl 1-bromocyclobutanecarboxylate (4.90 g, 23.7 mmol) was added dropwise without heating.

The reaction mixture was heated at reflux for 1 h, then cooled to RT. Cold water (60 mL) was added, the aqueous layer was washed with pentane (2 x 40 mL) and the pH was adjusted to 2.5 with 30% aq H_2SO_4. The product was then extracted from the aqueous layer with Et_2O (4 x 40 mL) and dried over anhydrous Na_2SO_4. The Et_2O was evaporated to give a yellow oil. The oil was dissolved in pentane (50 mL) and the upper layer was separated from the lower layer. The upper layer was cooled in an acetone-dry ice bath and stirred for 20 min. The resulting precipitate was filtered and dried under vacuum (1.14 g, 49% yield). The dried solid was stored at -20 °C to prevent decomposition. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.23 (bs, 1H), 6.94 (t, J=1.2 Hz,1H), 2.76 (t, J=3.2 Hz, 2H), 2.51 (td, J=3.2 Hz, 1.2 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.5, 150.1, 138.4, 29.1, 27.5.



[(Cyclobut-1-enecarbonyl)-amino]-acetic acid methyl ester, (1).

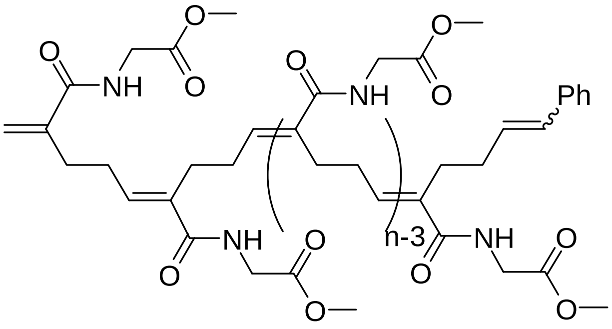
Cyclobut-1-enecarboxylic acid (300 mg, 3.06 mmol), glycine methyl ester hydrochloride (423 mg, 3.37 mmol), and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (704 mg, 3.67 mmol) were added to a round-bottomed flask. After addition of CH_2Cl_2 (6 mL) and N,N-diisopropylethylamine (1.07 mL, 6.12 mmol), the reaction mixture was stirred for 12 h at 24 °C. When the reaction was complete, EtOAc (60 mL) was added and the resulting solution was washed with 1N aq HCl (3 x 20 mL) and 5% aq $NaHCO_3$ (3 x 20 mL). The combined aqueous HCl wash (60 mL) was re-extracted with ethyl acetate (2 x 30 mL). The combined organic solution was washed with the separated aqueous $NaHCO_3$ solution. The combined organic solution was dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by neutral aluminum oxide column chromatography with 40% EtOAc/CH_2Cl_2 (216 mg, 42% yield). The purified fractions were concentrated and diluted with dry CH_2Cl_2 (3 mL) (complete concentration by vacuum should be avoided to prevent radical or ionic polymerization). In the solution state, monomer **1** is stable. For long term storage, the solution was kept at -80 °C to prevent possible decomposition. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.67 (t, J=1.2 Hz, 1H), 6.09 (br s, 1H), 4.11 (d, J=5.2 Hz, 2H), 3.78 (s, 3H), 2.73 (t, J=3.2 Hz, 2H), 2. 49 (td, J=3.2 Hz, 1.2 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.6, 162.7, 141.5, 140.9, 52.5, 40.9, 28.6, 26.5; HRMS (ESI) calcd for $C_8H_{12}NO_3$ $[M+H]^+$ 170.0817, found 170.0809.



ROM (Ring Opening Metathesis) One-mer, (3).

Precatalyst **2** (70.8 mg, 0.0798 mmol) was dissolved in CH_2Cl_2 (200 μL) under an Ar atmosphere. A solution of **1** (13.5 mg, 0.0798 mmol) in CH_2Cl_2 (200 μL) was added to the catalyst solution. After 1 h, the reaction was quenched with ethyl vinyl ether (382 μL, 3.99 mmol). After evaporation of solvent, the residue was purified by silica gel column chromatography with 40% EtOAc/CH_2Cl_2 to obtain the ROM One-mer (mixture of *E* and

Z isomers, 3 mg, 15% yield). ^{1}H-NMR (500 MHz, CD_3OD) *Z-isomer* δ 7.31-7.17 (m, 5H), 6.44 (d, J=11.5 Hz, 1H), 5.70 (s, 1H), 5.66 (dt, J=11.5 Hz, 7.0 Hz, 1H) 5.38 (s, 1H), 3.93 (s, 2H), 3.70 (s, 3H), 2.50 (m, 4H); *E-isomer* δ 7.36-7.14 (m, 5H), 6.42 (d, J=15.5 Hz, 1H), 6.24 (dt, J=15.5 Hz, 7.0 Hz, 1H), 5.73 (s, 1H) 5.43 (s, 1H), 3.95 (s, 2H), 3.72 (s, 3H), 2.49 (t, J=7.5 Hz, 2H), 2.38 (q, J=7.0 Hz, 2H); ^{13}C-NMR (100 MHz, CD_3OD) *Z-isomer* δ 172.0, 145.5, 139.0, 132.4, 130.9, 129.9, 129.6, 129.3, 119.9, 52.7, 42.2, 33.7, 28.4 ; *E-isomer* δ 172.0, 145.6, 139.3, 132.2, 130.5, 128.1, 127.8, 127.2, 120.1, 52.7, 42.2, 33.5, 32.9; HRMS (ESI) calcd for $C_{16}H_{20}NO_3$ $[M+H]^+$ 274.1443, found 274.1436.



General procedure for ROMP of 1

7: 10-mer

Under an N_2 atmosphere, precatalyst **2** (27.0 mg, 0.0302 mmol) was dissolved in CH_2Cl_2 (1.8 mL). A solution of 51 mg of **1** in CH_2Cl_2 (600 μL) was added to the catalyst solution. The reaction mixture was stirred for 2 h at 24 °C and then the reaction was quenched with ethyl vinyl ether (300 μL, 3.13 mmol). After evaporation of solvent, 0.5 mL of CH_2Cl_2 was added to dissolve the residue and 2 ml of Et_2O was added while stirring. The resulting sticky precipitate (48 mg, 89% yield) was further purified by silica gel column chromatography with 10% MeOH/CH_2Cl_2. The pure fractions were combined and dried under vacuum to yield 31 mg of the polymer (57% final yield).

8: 18-mer, 9: 35-mer and 10: 50-mer

For polymers longer than the 10-mer, **7**, the polymerization procedure was slightly modified. Polymerizations were performed in an NMR tube and CD_2Cl_2 was used in order to monitor the reactions. For **9** and **10**, the reaction mixtures were warmed to 40 °C after 5 min to increase the reaction rate. A summary of the reaction conditions is presented in Table S1.

Table S1. Reaction Summary

Product	Rxn solvent	Rxn temp (°C)	Rxn time (h)	% yield after precipitation (MC/diethyl ether)	% yield after silica column purification
3, ROM One-mer	CH_2Cl_2	24	1.5	------------	15
7, 10-mer	CH_2Cl_2	24	2	90	57
8, 18-mer	CD_2Cl_2	24	20	80	59
9, 35-mer	CD_2Cl_2	24-40	4	71	59
10, 50-mer	CD_2Cl_2	24-40	4	76	64

Characterization of the polymers

The polymers were characterized by ^1H NMR, ^{13}C NMR, gHMQC, and ^{13}C-APT spectroscopy.

Polymer 7: ^{1}H-NMR (500 MHz, CD_2Cl_2:CD_3OD/2:1) δ 7.90~7.60 (bm, NH), 7.36~7.15 (m, 5H), 6.35~6.10 (bs, 11H), 5.56 (bs, 1H), 5.39 (bs, 1H), 4.03~3.84 (bs, 20H), 3.75~3.58 (bs, 30H) 2.55~2.10 (bm, 40H); ^{13}C-NMR (100 MHz, CD_2Cl_2:CD_3OD/2:1) δ 171.7, 171.6, 136.4, 136.3, 133.0–128.5 (styrenyl carbons), 119.8, 52.6, 42.0, 28.4, 26.9. The gHMQC data is summarized in Table S2.

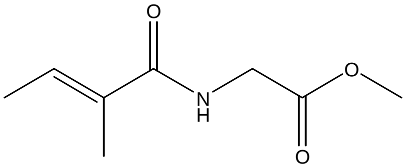
Table S2. ^{1}H-NMR and ^{13}C-NMR correlation of **7** using gHMQC spectroscopy.

^{1}H-NMR (δ)	7.29	6.22	3.91	3.65	2.39	2.25
^{13}C-NMR (δ)	129.3	136.4	42.0	52.6	26.9	28.4

Polymers 8, 9 and 10: The ^{1}H-NMR and ^{13}C-NMR spectra were the same as in polymer **7** except the relative integrations of peaks changed. The integration of the alkene peak at 6.22 ppm relative to the phenyl proton peak at 7.36-7.15 ppm increases as expected with the increasing length of the polymers. The integrations of the glycine (methylene and methyl protons) and backbone (methylene protons) protons also increase in the same way (Figure S1).[7]

Polymer 8, ^{13}C-APT: A ^{13}C-APT spectrum of polymer **8** was acquired. (100 MHz, CD_2Cl_2:CD_3OD/2:1) δ 171.7 (quaternary C, carbonyl), 171.6 (quaternary C, carbonyl), 136.4 (CH, alkene), 136.3 (quaternary C, alkene), 133.0–128.5 (CH, styrenyl carbons), 119.7 (CH_2, terminal alkene), 52.6 (CH_3, methyl ester of glycine), 42.0 (CH_2, methylene of glycine), 28.4 (CH_2, methylene of backbone), 26.9 (CH_2, methylene of backbone).

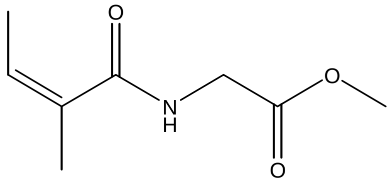
In order to elucidate the geometry of the conjugated double bond(s), we prepared two trisubstituted unsaturated amides as model compounds for the (*E*) or (*Z*) units of the polymers; [(*E*)-2-methyl-but-2-enoylamino]-acetic acid methyl ester (**11**) and [(*Z*)-2-methyl-but-2-enoylamino]-acetic acid methyl ester (**12**). The chemical shift of the proton on carbon 3 in reference compound **11** is 6.47 ppm and in reference compound **12** is 5.65 ppm. Furthermore, the chemical shift of the proton on carbon 3 of (*E*)-N,2-dimethyl-2-butenamide is 6.29 ppm.[6] The observed chemical shift of the alkene proton in polymers **7-10** is 6.22 ppm, and thus, these polymers are stereoregular with *E* stereochemistry.



[(*E*)-2-methyl-but-2-enoylamino]-acetic acid methyl ester, 11.

(*E*)-2-methyl-2-butenoic acid (300 mg, 3.00 mmol) was dissolved in CH_2Cl_2 (6 mL) and N-methyl morpholine (396 µL, 3.60 mmol) was added to the solution. The reaction mixture was cooled to -15 °C. Isobutyl chloroformate (389 µL, 3.00 mmol) was added and stirred at -15 °C for 15 min. Glycine methyl ester hydrochloride (377 mg, 3.00 mmol), CH_2Cl_2 (4 mL), and N-methyl morpholine (330 µL, 3.00 mmol) were added to the solution. After stirring at -15 °C for 15 min, the reaction mixture was warmed to 24 °C and stirred for 16 h. CH_2Cl_2 (60 mL) was added to the reaction mixture and the organic layer was washed with 1 N aq HCl (3 x 20 mL) and 5% aq $NaHCO_3$ (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The crude product was purified by silica gel column chromatography using 30% and 40%

EtOAc/CH_2Cl_2 to give **11** (219 mg, 43% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.47 (m, 1H), 6.37 (bs, 1H), 4.05 (d, J=4.8 Hz, 2H), 3.73 (s, 3H), 1.83 (m, 3H), 1.73 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.8, 169.4, 131.8, 131.2, 52.4, 41.6, 14.0, 12.3; HRMS (ESI) calcd for $C_8H_{14}NO_3$ $[M+H]^+$ 172.0974, found 172.0974.



[(*Z*)-2-methyl-but-2-enoylamino]-acetic acid methyl ester, 12.

[(*Z*)-2-methyl-but-2-enoylamino]-acetic acid methyl ester was prepared by coupling procedure above with (*Z*)-2-methyl-2-butenoic acid (300 mg, 3.00 mmol). Amide **12** was obtained after chromatography (219 mg, 45% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.21 (bs, 1H), 5.65 (m, 1H), 4.07 (d, J=5.2 Hz, 1H), 4.06 (d, J=5.6 Hz, 1H), 3.73 (s, 3H), 1.86 (m, 3H), 1.81 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.6, 170.2, 132.0, 129.3, 52.4, 41.1, 20.8, 15.2; HRMS (ESI) calcd for $C_8H_{14}NO_3$ $[M+H]^+$ 172.0974, found 172.0967.

PDI (Poly Dispersity Index) determination

Purified polymers were dissolved in 10% MeOH/CH_2Cl_2 (0.25 mg/mL). An aliquot (50 μL) of the polymer solution was injected and analyzed by gel permeation chromatography using a Phenogel column (300 x 4.60 mm, 5 μm, linear mixed bed, 100-10^7 MW range). Elution was performed at 0.35 mL/min with CH_2Cl_2:MeOH (9:1) and detection at 240 nm at 24 °C. Narrowly dispersed polystyrene standards from Aldrich were used as molecular weight calibrants. The number average and weighted average molecular weights were calculated from the chromatogram. The results are shown in Table 1 of the manuscript. A plot of molecular weight versus [Monomer]/[Catalyst] is linear (Figure S3).

MALDI-TOF Mass Analysis

The 10-mer, **7,** was analyzed by MALDI-TOF on an Autoflex TOF/TOF (Bruker Daltonics) and spectra were recorded in the linear mode without matrix suppression. 5-Chloro-2-mercaptobenzothiazole (CMBT) was used as the matrix, and a three point calibration was performed using angiotensin II (human, monoisotopic $[M+H]^+$: 1046.5423), ACTH fragment 18-39 (human, monoisotopic $[M+H]^+$: 2465.1989), and insulin (bovine, average $[M+H]^+$: 5734.51). The polymer was dissolved in 10% MeOH/CH_2Cl_2 at a concentration of 1 mg/mL. The matrix solution was prepared at a concentration of 4 mg/mL in 50% MeOH/ CH_2Cl_2. The polymer was mixed in a ratio of 1/10 (v/v) with the matrix solution and 1 µL of the mixture was applied to the target surface and dried. Fig S4 shows the spectrum with centroided mass/charge values. Only the $[M+Na]^+$ ions were observed. The mass of the residual end group was 104.6 which is consistent with the expected structure of **7**. The number average molecular weight ($\overline{M}_n$) is 1935.29, the weight average molecular weight ($\overline{M}_w$) is 2230.44, the degree of polymerization is 11.45, and the PDI is 1.15 (calculated by PolyTools, Bruker) The calculated monoisotopic molecular weight for the 11-mer was 1986.82 $[M+Na]^+$ and the observed monoisotopic peak was 1986.75 $[M+Na]^+$ (Figure S4, inset).

References:

1. Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H., *Angew. Chem. Int. Ed*. **2002**, 41, 4035-4037.
2. This compound has been prepared previously by the method of Campbell et al.[3] However, no spectroscopic data appeared in these reports.[4, 5]
3. Campbell, A.; Rydon, H. N., *J. Chem. Soc.* **1953**, 3002-3008.
4. Griffin, R. J.; Arris, C. E.; Bleasdale, C.; Boyle, F. T.; Calvert, A. H.; Curtin, N. J.; Dalby, C.; Kanugula, S.; Lembicz, N. K.; Newell, D. R.; Pegg, A. E.; Golding, B. T. *J. Med. Chem.* **2000**, *43*, 4071-4083.
5. Lange, G. L.; Otulakowski, J. A. *J. Org. Chem.* **1982**, *47*, 5093-5096.
6. Beak, P.; Kempf, D. J.; Wilson, K. D., *J. Am. Chem. Soc*. **1985**, 107, 4745-4756.
7. A small doublet appears at δ 5.66 in the ^{1}H NMR spectrum of **7**. The multiplicity of this peak is inconsistent with assignment to the *Z*-isomer. Moreover, the relative integration of this peak decreases as the polymer becomes longer. It appears to be an impurity arising from the catalyst. This impurity also appears in the ^{13}C NMR spectra at 137.4 ppm and 134.9 ppm. Again, the peak intensity decreases with increasing polymer length, consistent with it originating from catalyst.

Figure S1. ^{1}H-NMR spectra of ROMP polymers.

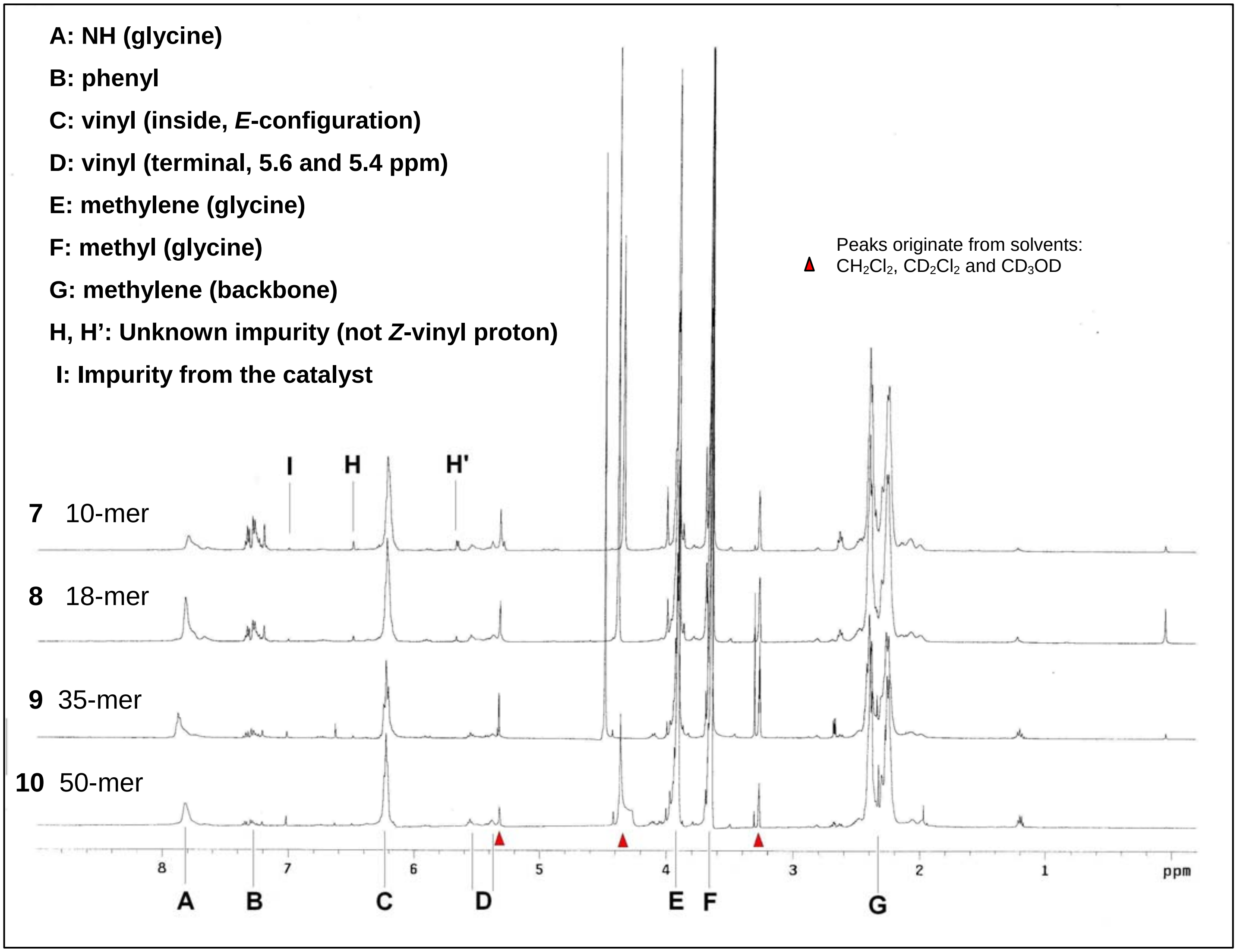


Figure S2. ^{13}C-NMR and ^{13}C-APT-NMR spectra of **8**.

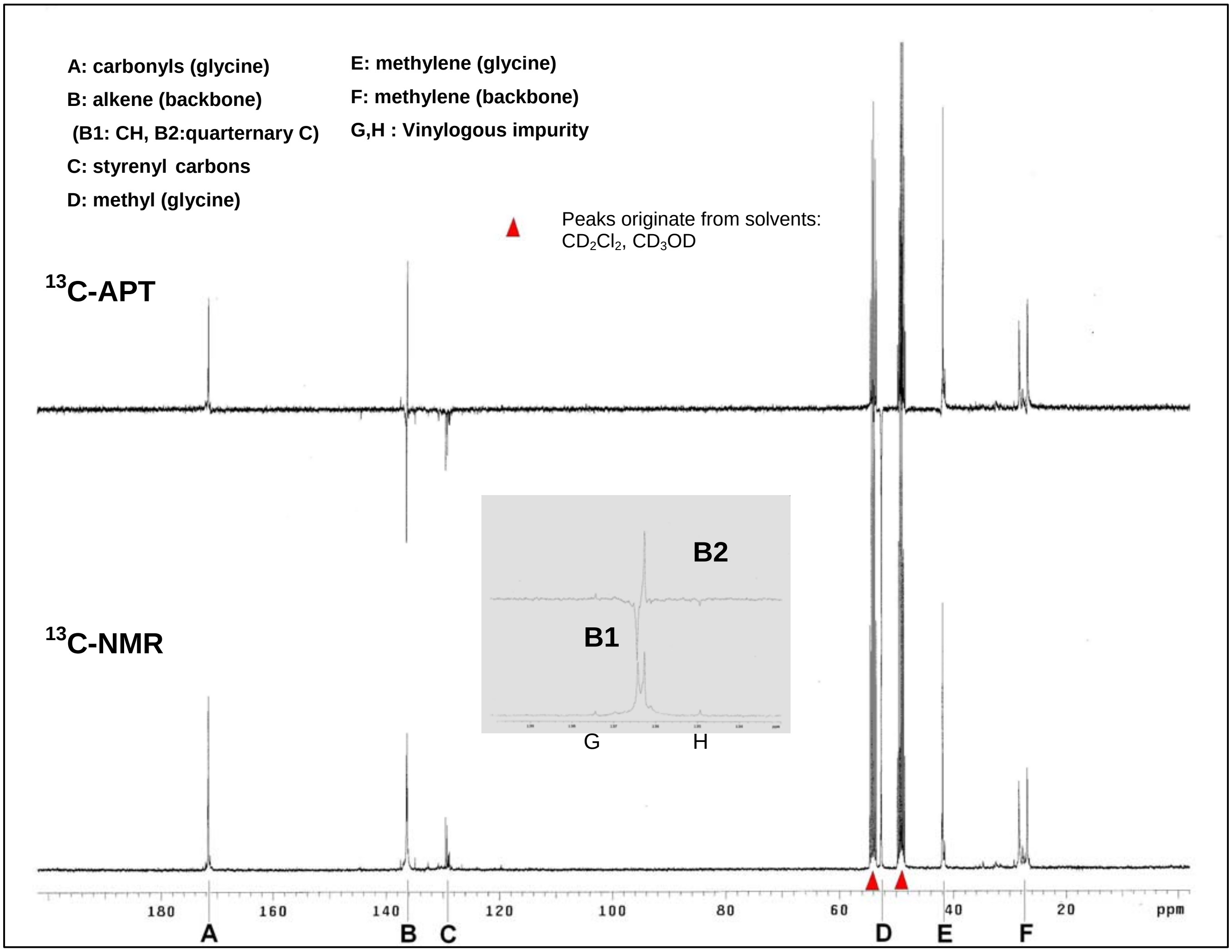


Figure S3. Plot of molecular weight versus [Monomer]/[Catalyst] for polymers **7-10**.

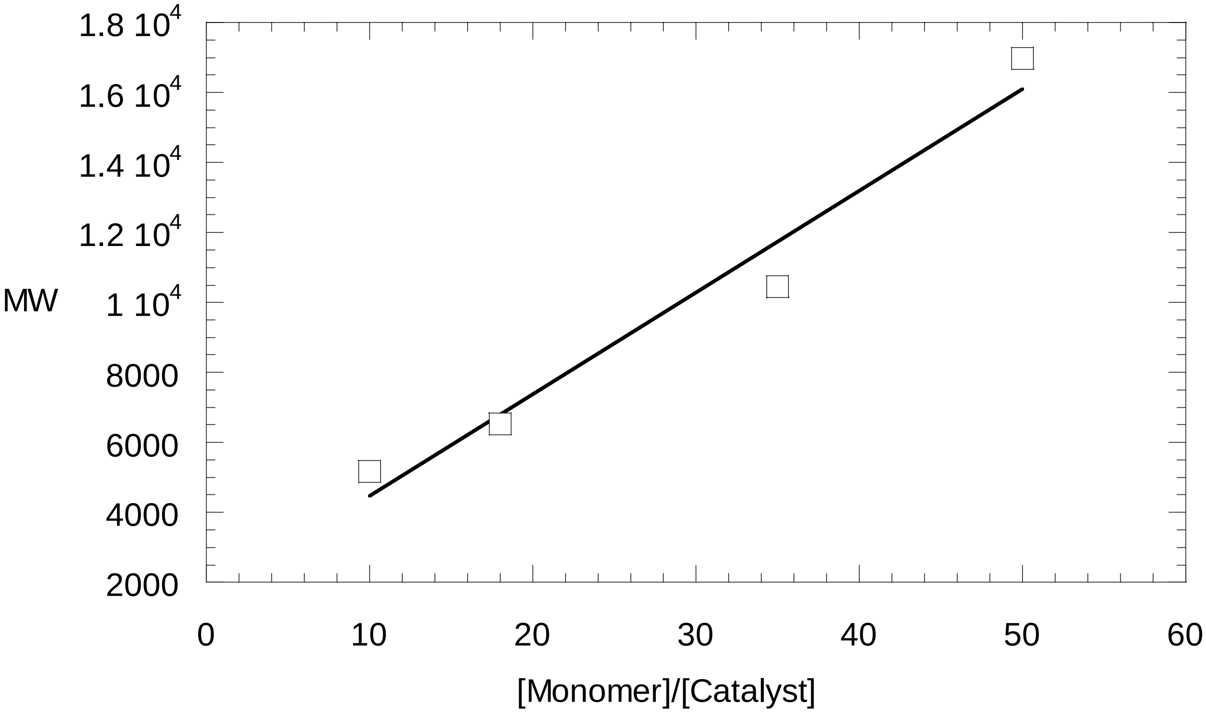
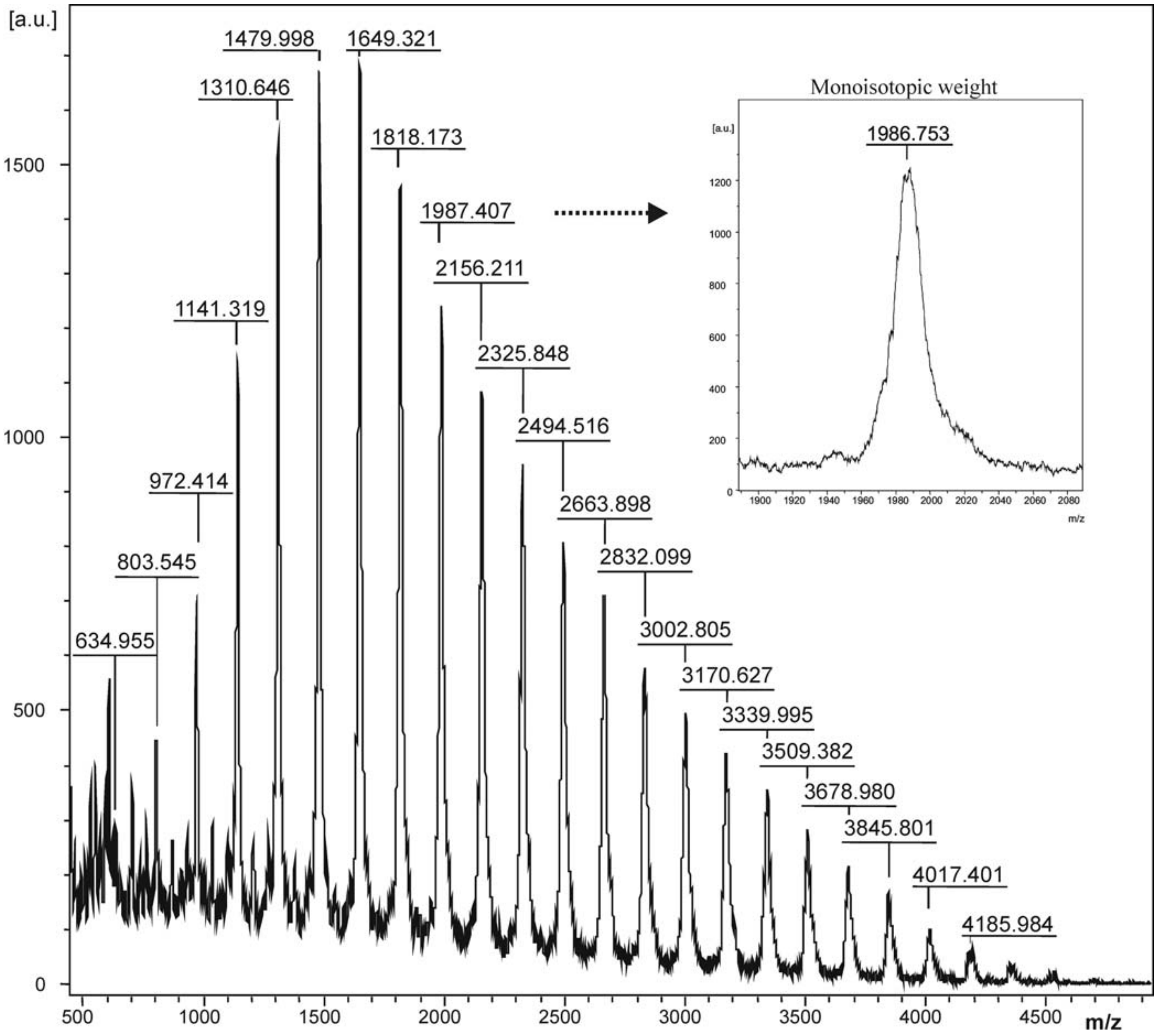
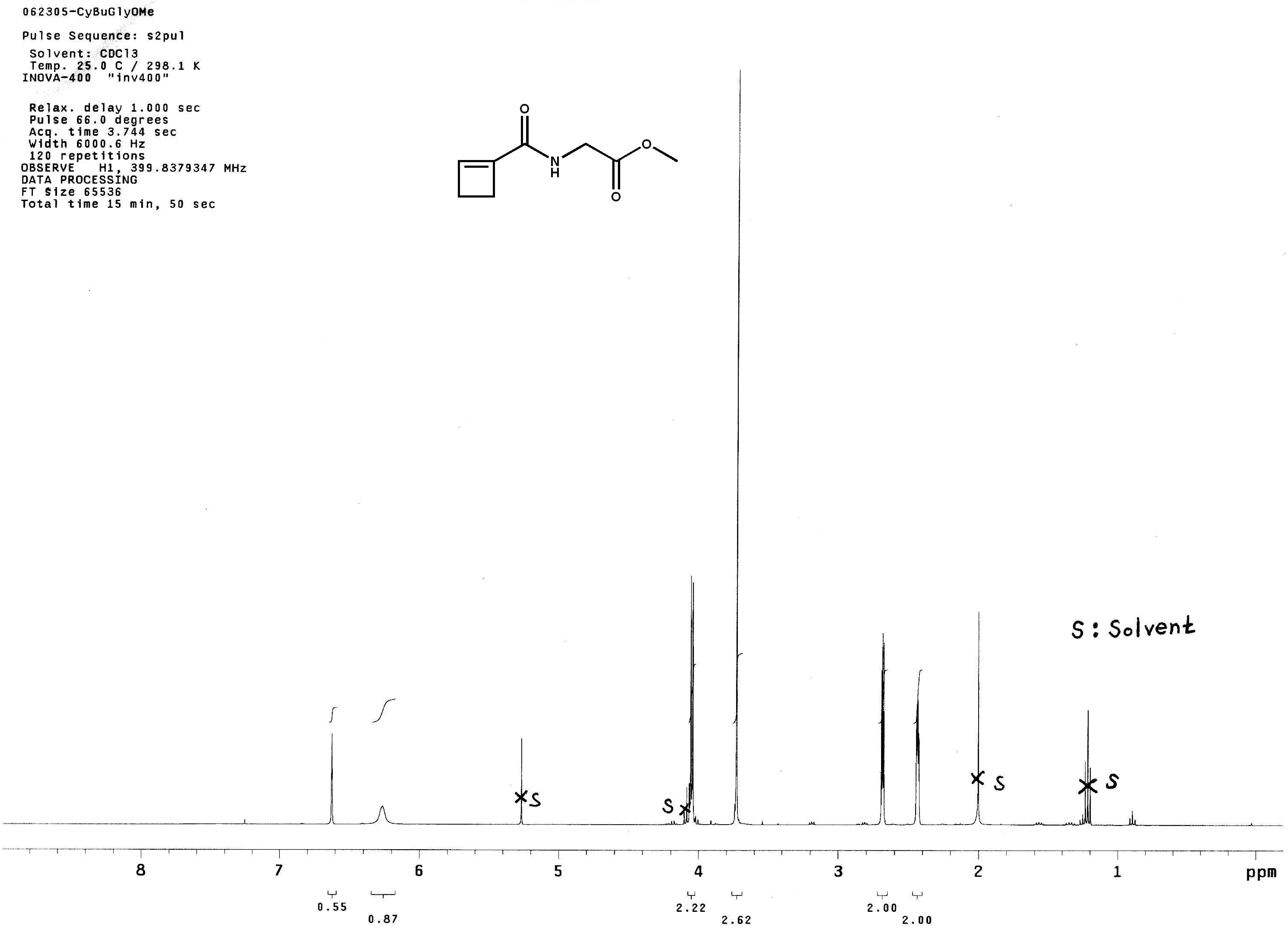


Figure S4. MALDI-TOF mass spectrum of polymer **7**. (The inset shows the peaks corresponding to n=11, labeled with the monoisotopic mass/charge ratio.)



1H-NMR



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13C-NMR

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 Acq. time 1.199 sec
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 5000 repetitions
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DECOUPLE  H1, 399.8399342 MHz
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DATA PROCESSING
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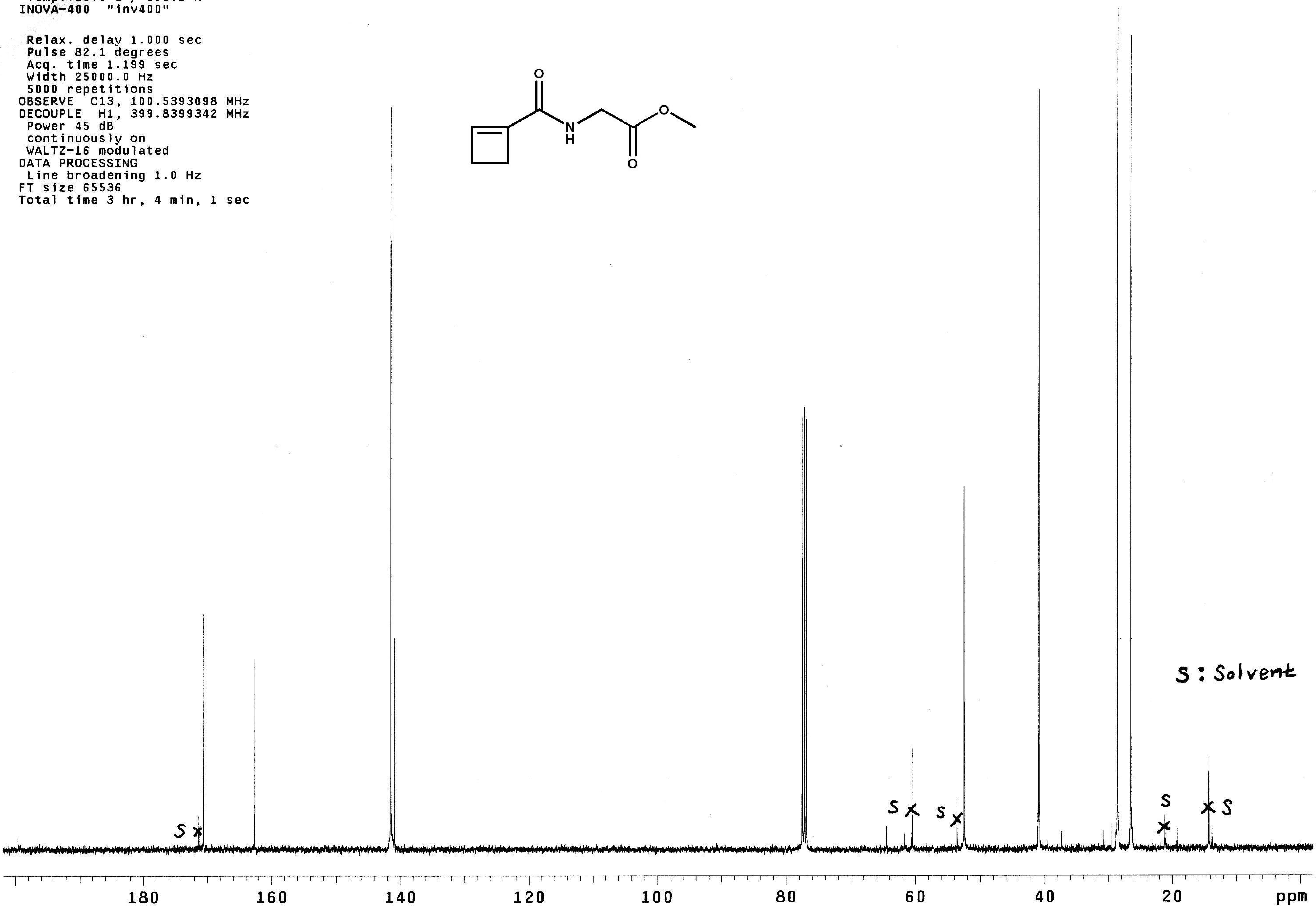
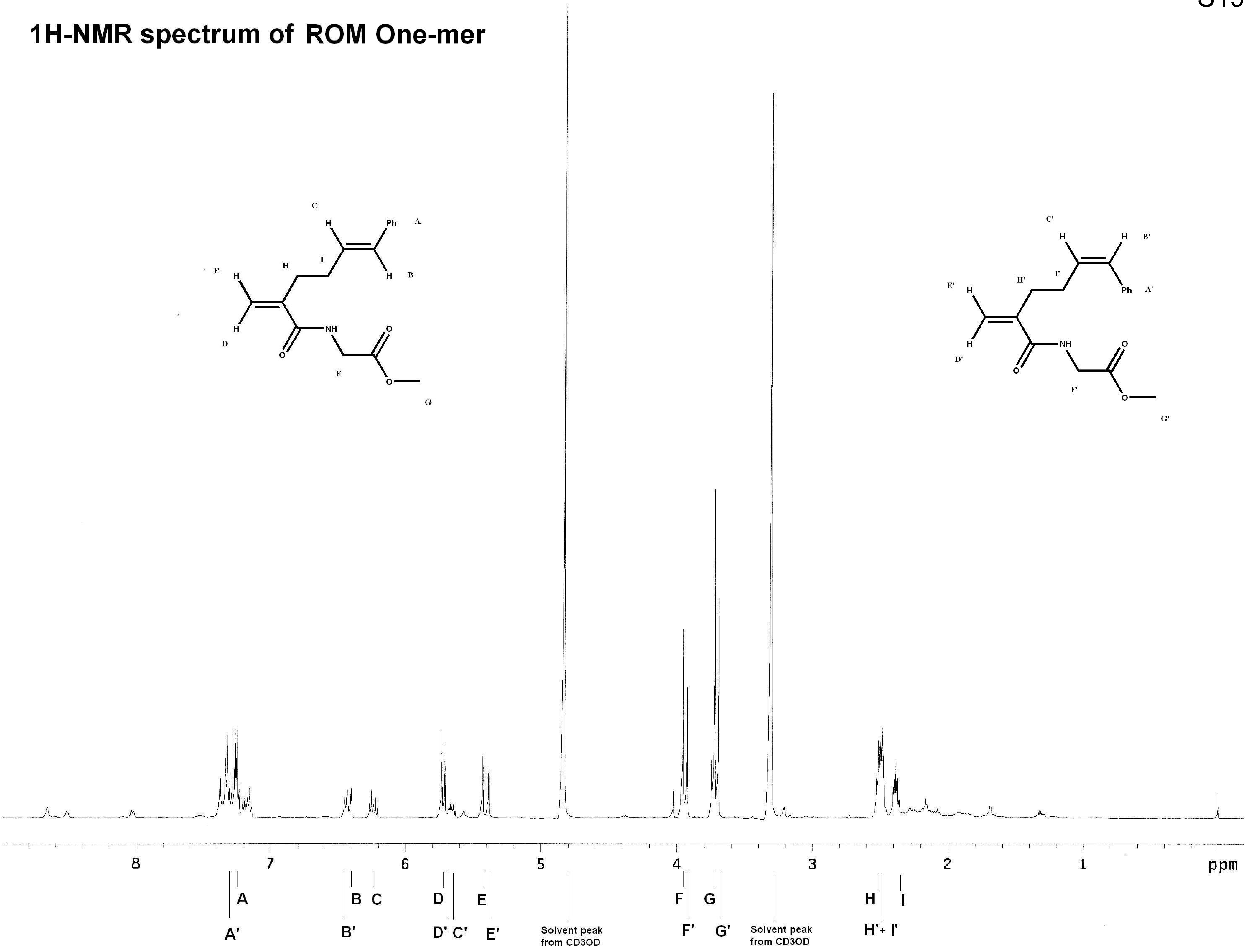
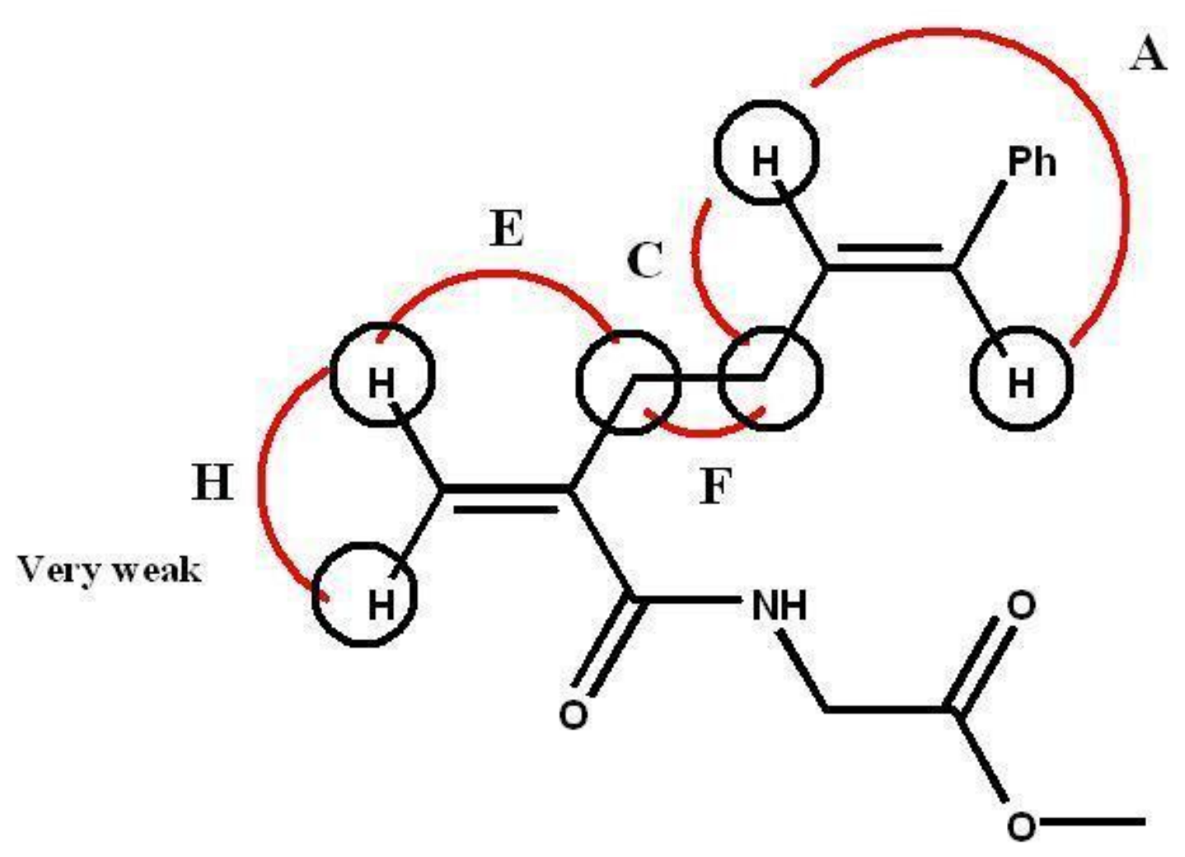
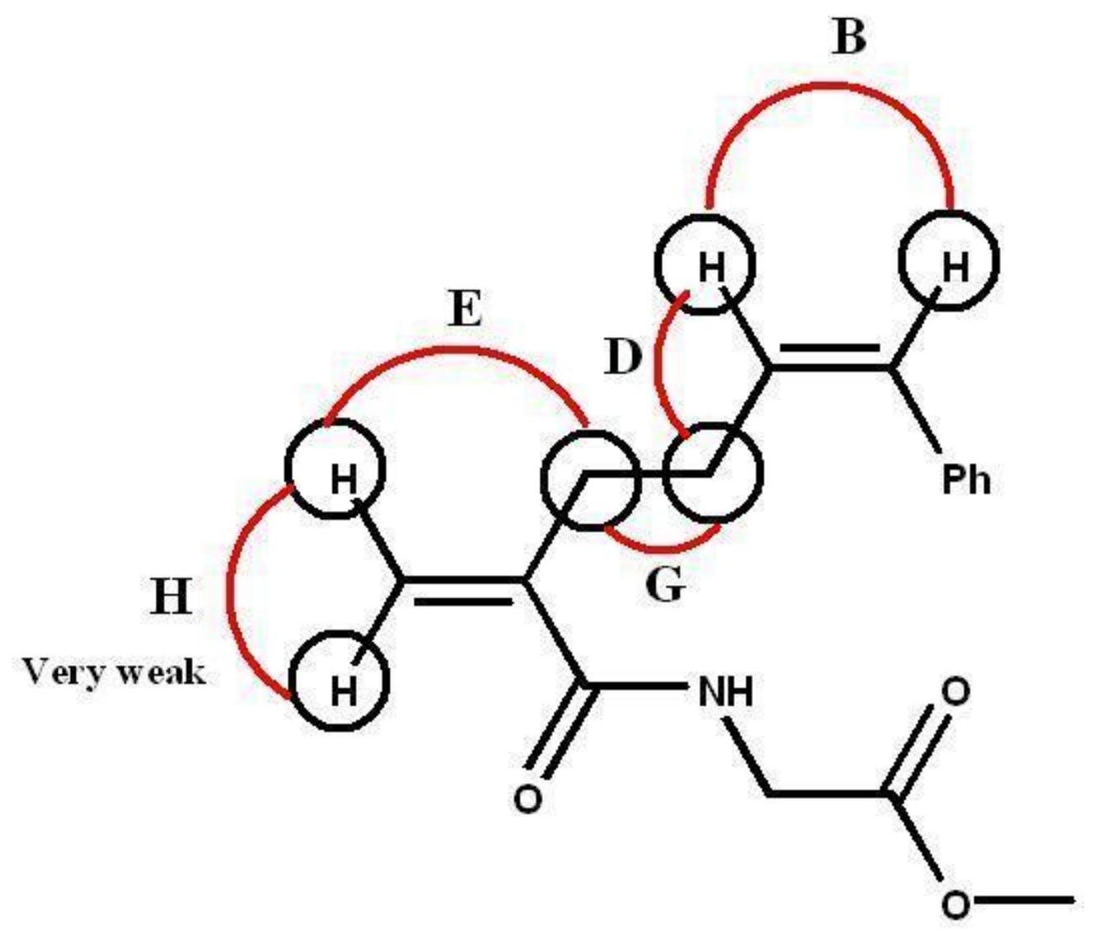


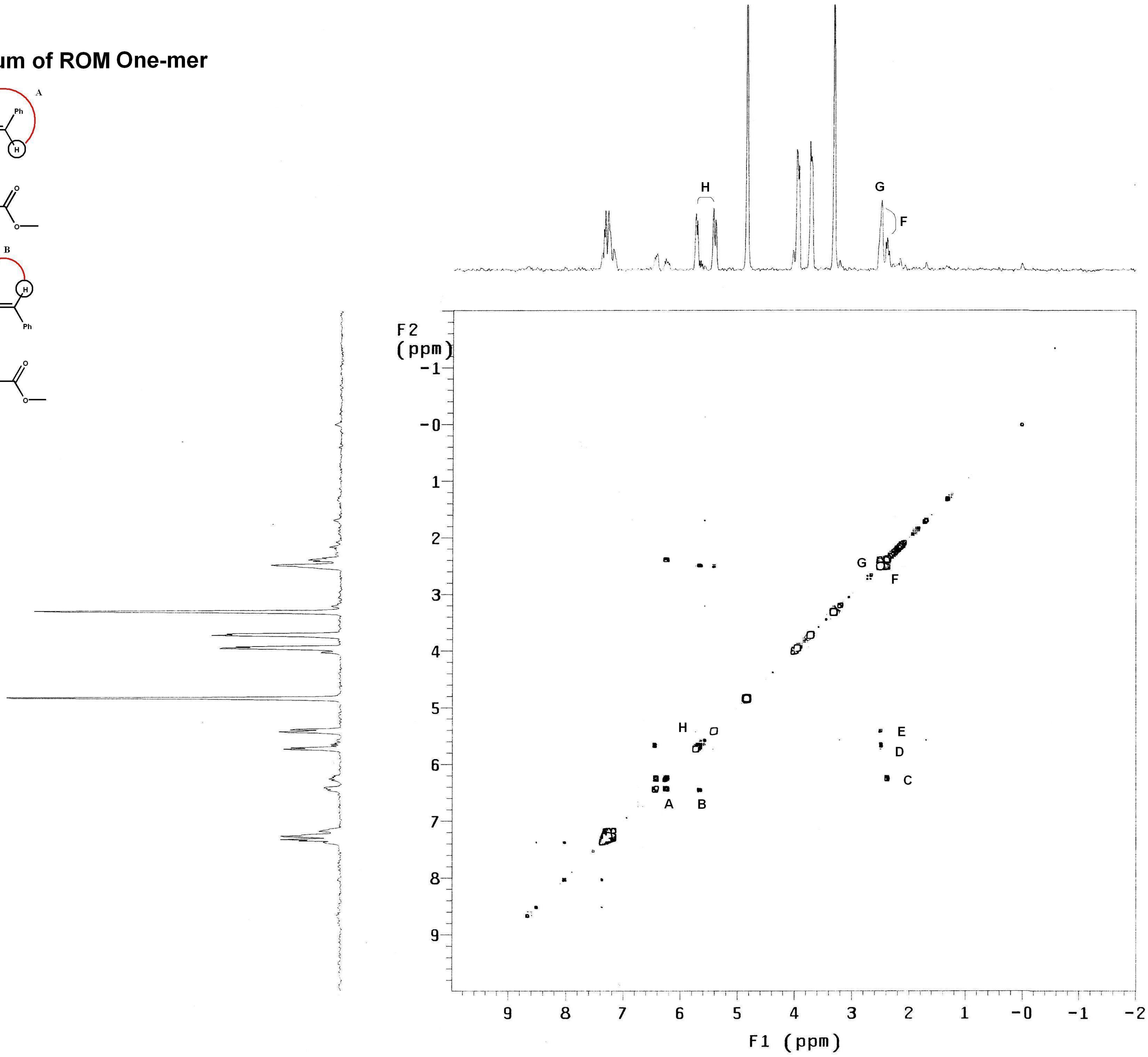
1H-NMR spectrum of ROM One-mer



gCOSY spectrum of ROM One-mer







CyBuGlyOMe-ROM-One-mer-combined

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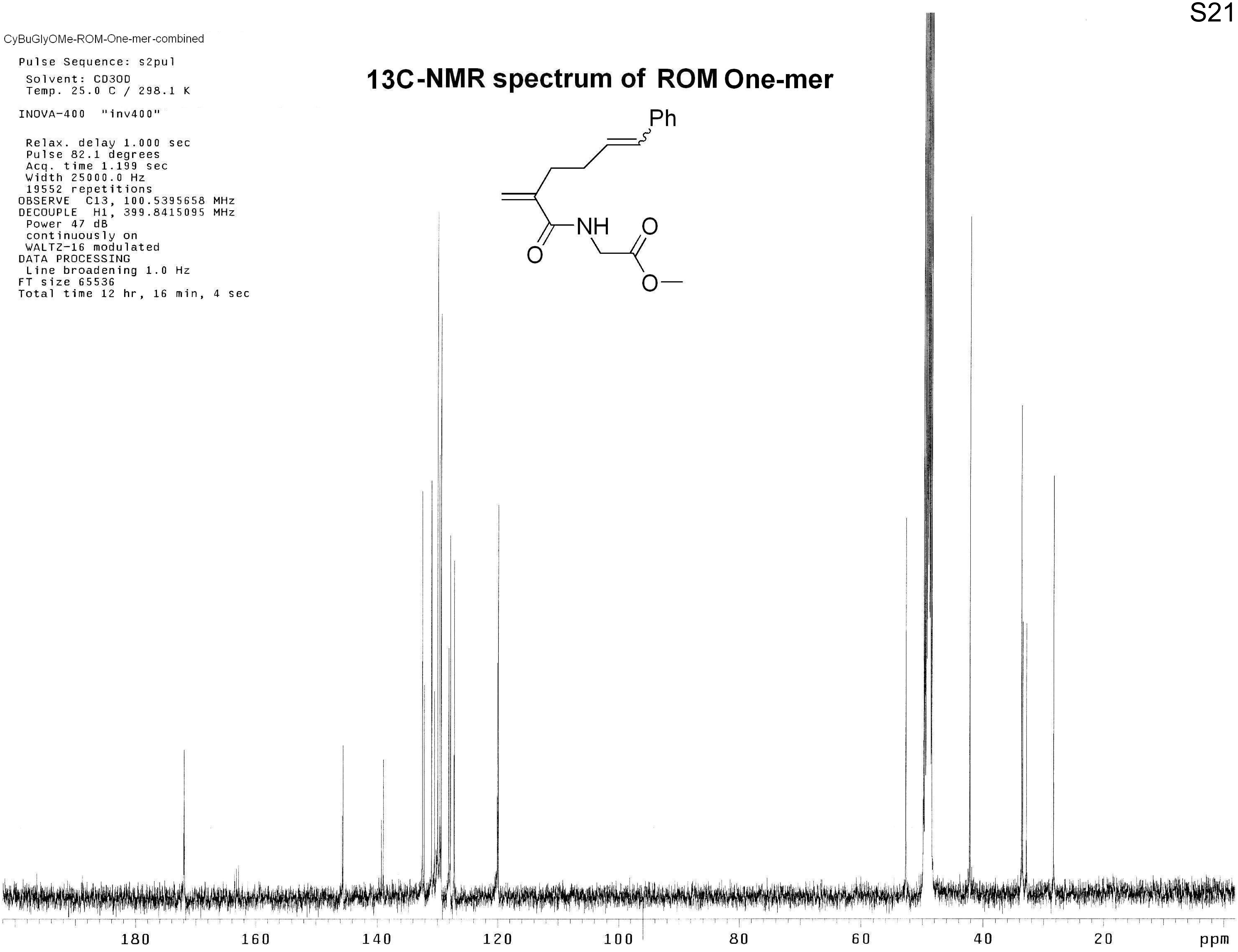
13C-NMR spectrum of ROM One-mer



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DATA PROCESSING
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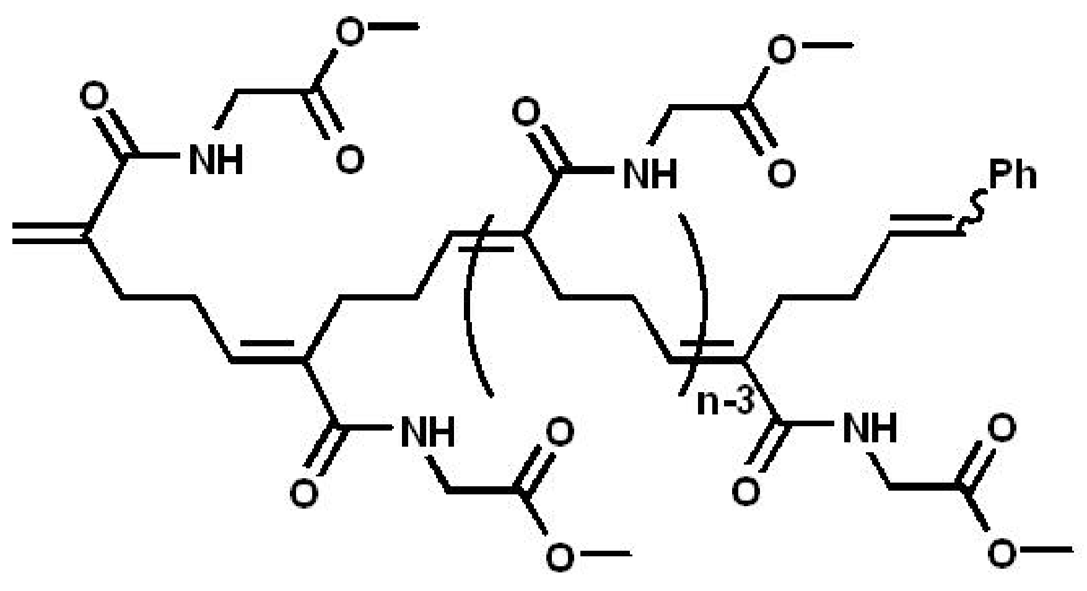
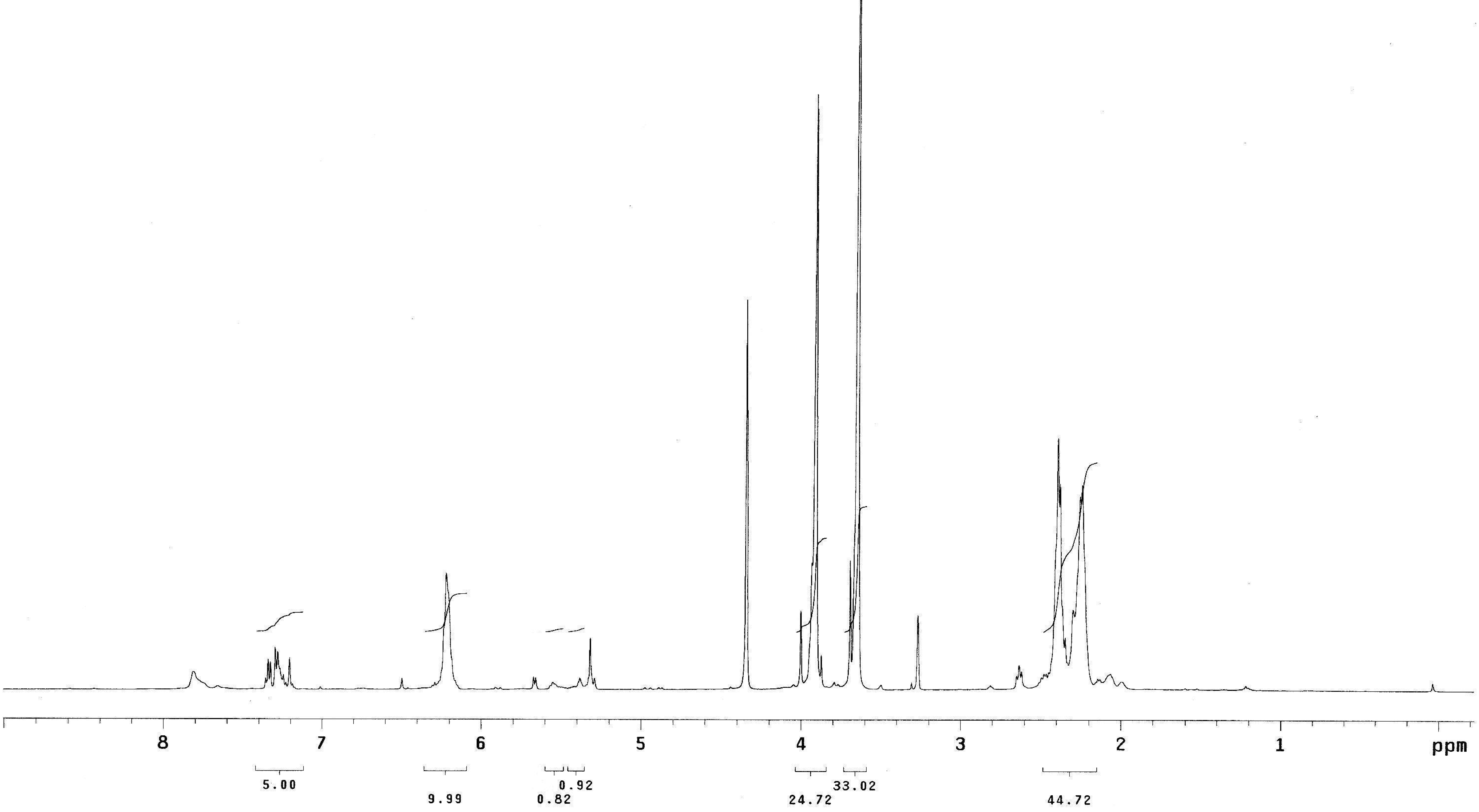
1H-NMR



10-mer, n=10



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INOVA-500  "inv500"

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Total time 9 min, 40 sec
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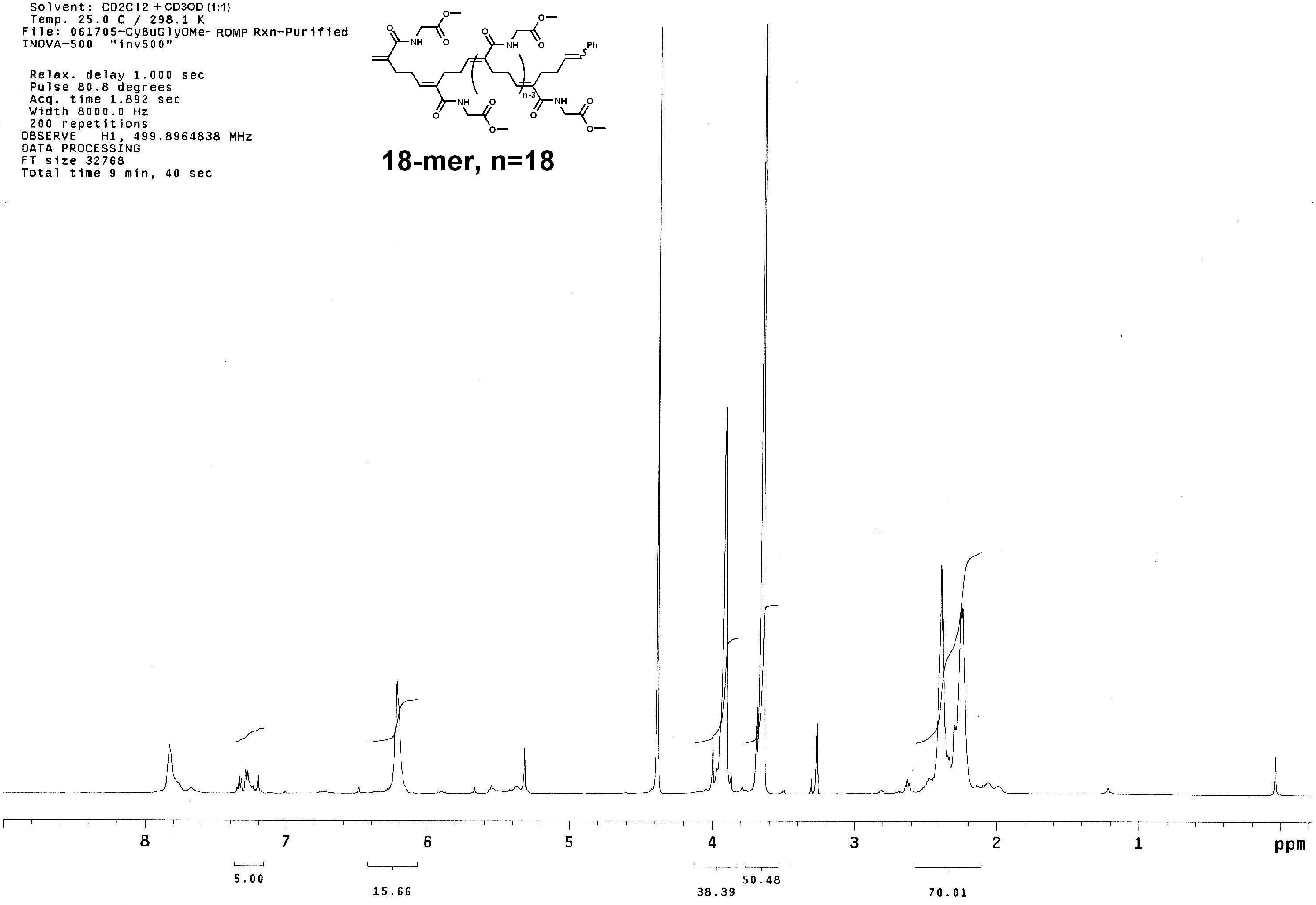
1H-NMR



18-mer, n=18

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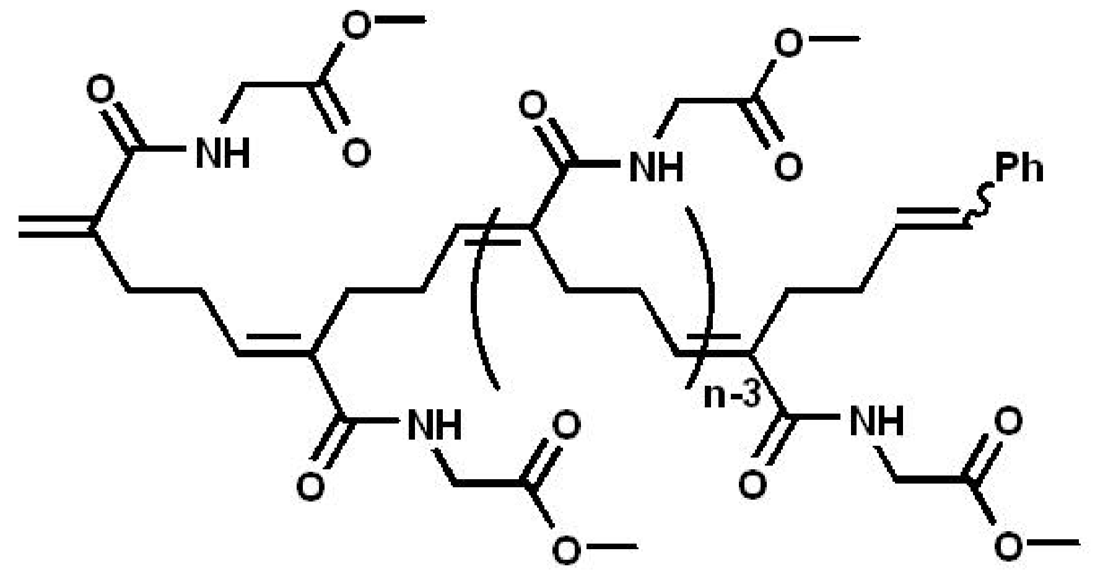
072905-Purified-1

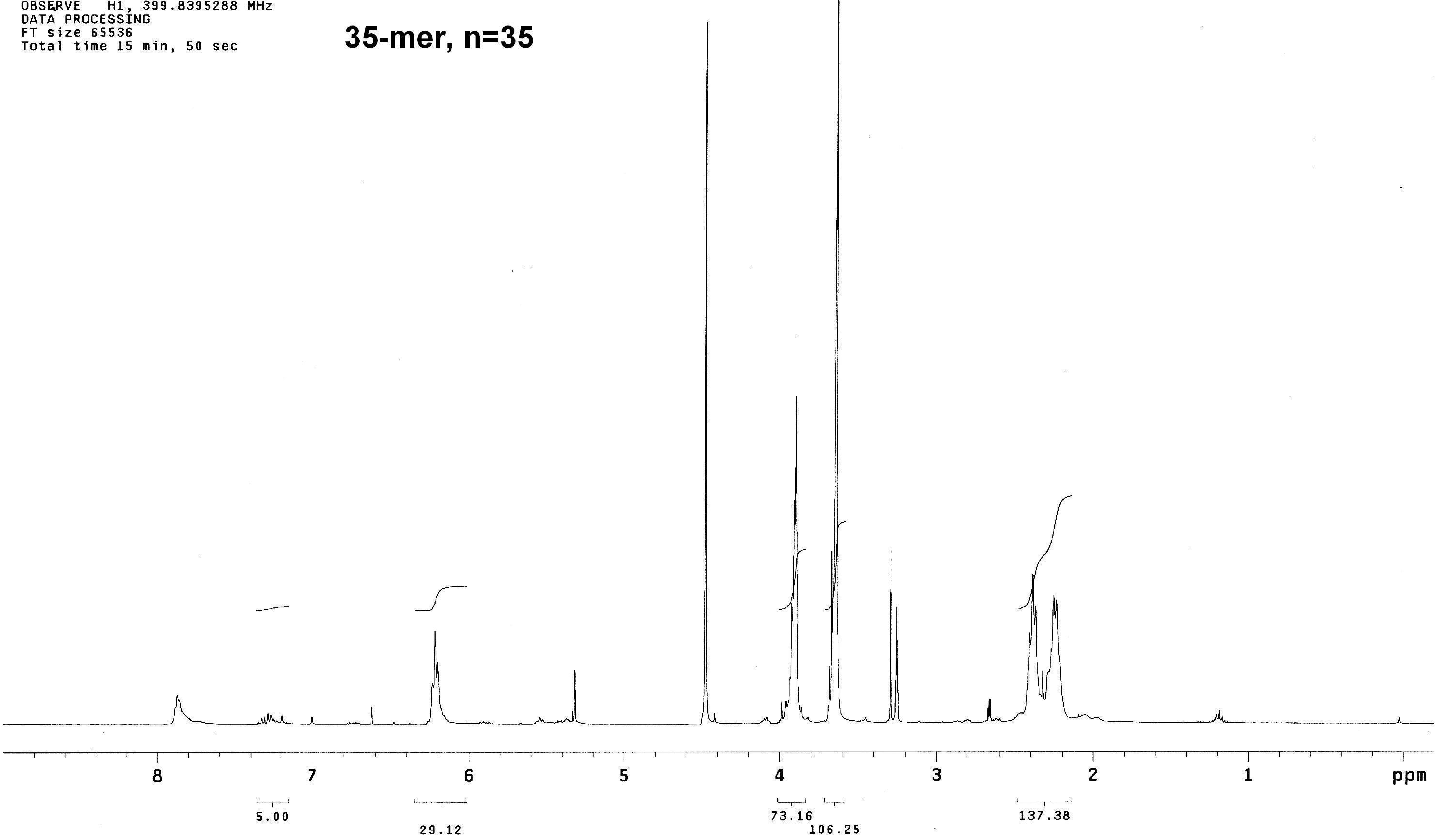
Pulse Sequence: s2pul
 Solvent: CD2Cl2+CD3OD (2:1)
 Temp. 25.0 C / 298.1 K
File: 072905-Purified-1
INOVA-400  "inv400"

 Relax. delay 1.000 sec
 Pulse 66.0 degrees
 Acq. time 3.744 sec
 Width 6000.6 Hz
 200 repetitions
OBSERVE   H1, 399.8395288 MHz
DATA PROCESSING
FT size 65536
Total time 15 min, 50 sec
```

1H-NMR



35-mer, n=35

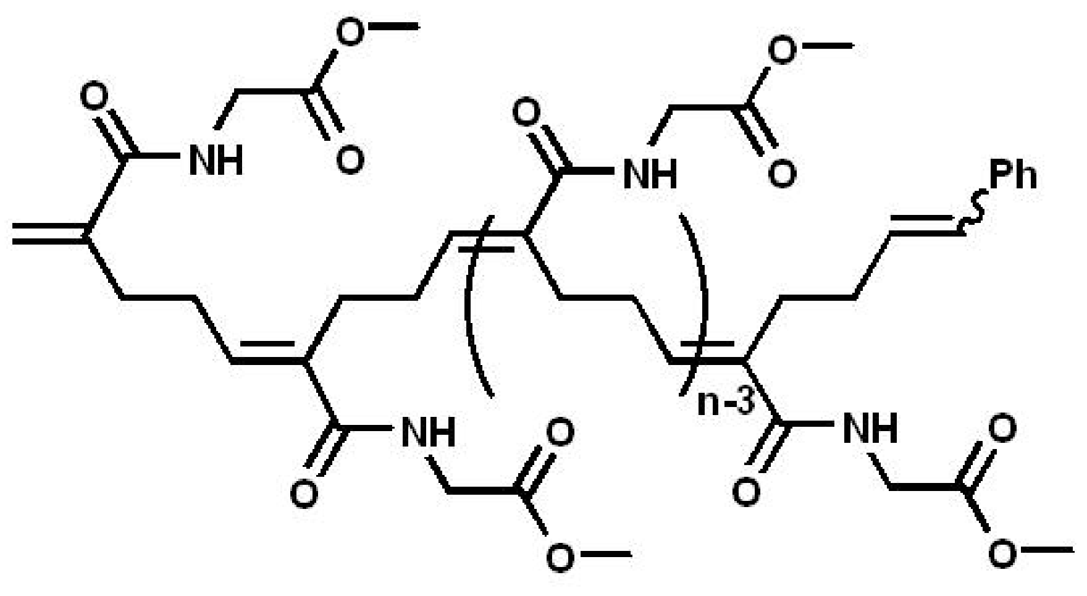


```
080505-Purified-Polymer

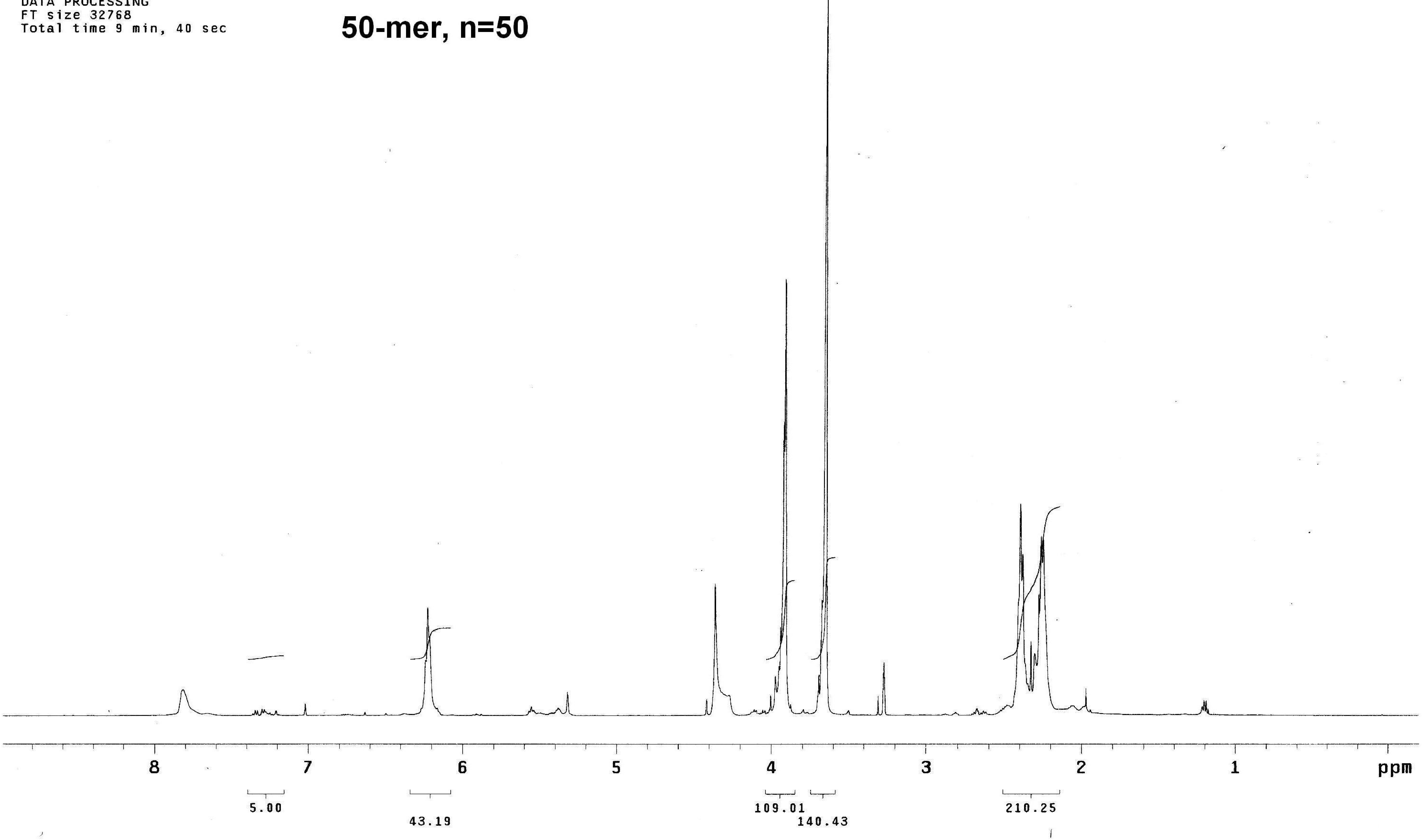
Pulse Sequence: s2pul
 Solvent: CD2Cl2+CD3OD (2:1)
 Temp. 25.0 C / 298.1 K
INOVA-500  "inv500"

 Relax. delay 1.000 sec
 Pulse 80.8 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 200 repetitions
OBSERVE   H1, 499.8964799 MHz
DATA PROCESSING
FT size 32768
Total time 9 min, 40 sec
```

1H-NMR



50-mer, n=50



10-mer, g-HMQC

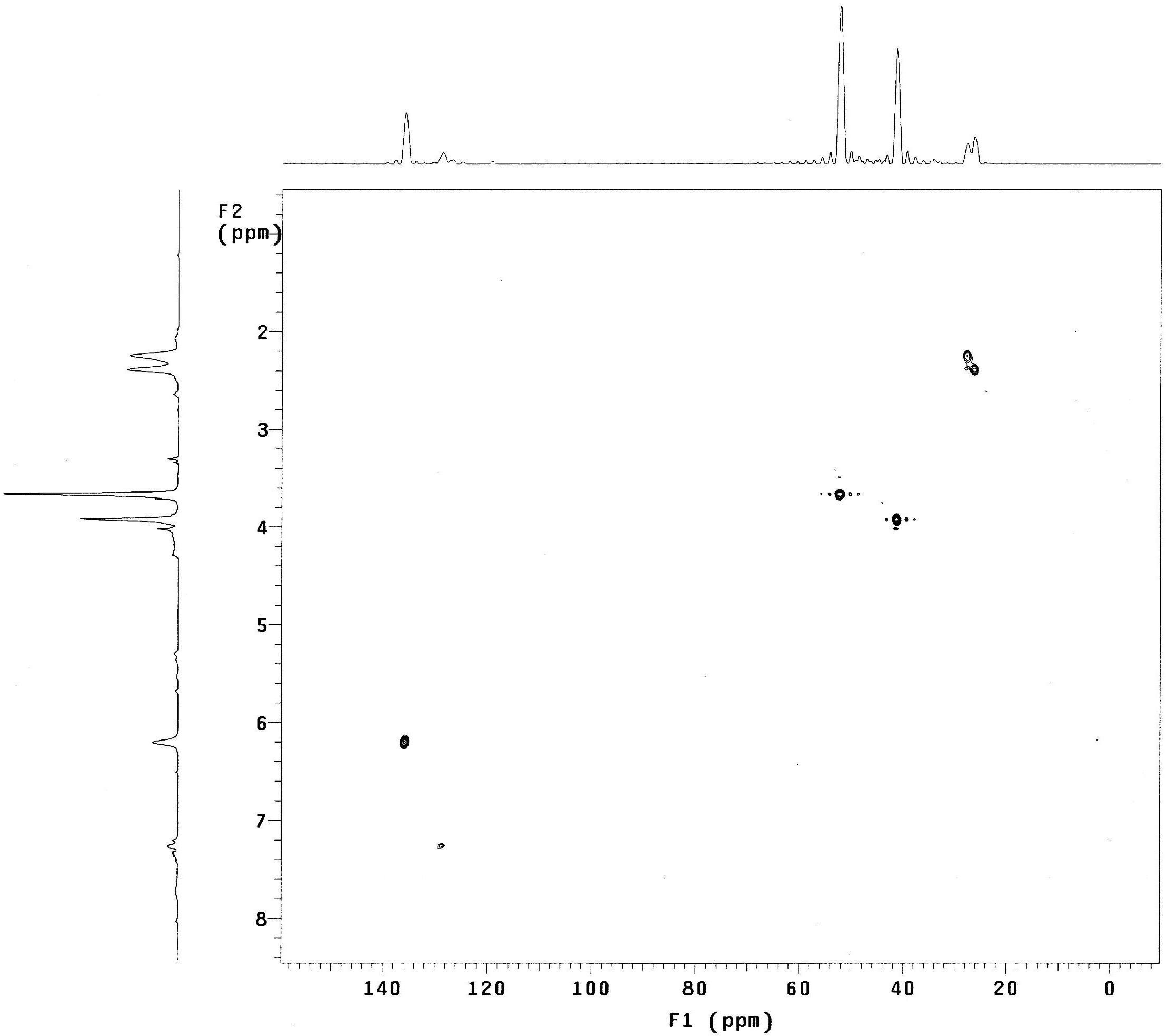
```
6-20-05 10mer gHMQC

 Archive directory: /export/home/jclee/vnmrsys/data
 Sample directory: jclee_20Jun2005

Pulse Sequence: gHMQC

 Solvent: CD3OD + CDCl3 (1:3)
 Temp. 25.0 C / 298.1 K
File: gHMQC
INOVA-400  "inv400"

 Relax. delay 1.000 sec
 Acq. time 0.160 sec
 Width    3198.7 Hz
 2D Width 20105.6 Hz
 32 repetitions
 2 x 128 increments
OBSERVE   H1, 399.8395100 MHz
DECOUPLE C13, 100.5487493 MHz
 Power 31 dB
 on during acquisition
 off during delay
 W40_asw5133 modulated
DATA PROCESSING
 Gauss apodization 0.074 sec
F1 DATA PROCESSING
 Gauss apodization 0.012 sec
FT size 1024 x 2048
Total time 2 hr, 46 min, 27 sec
```

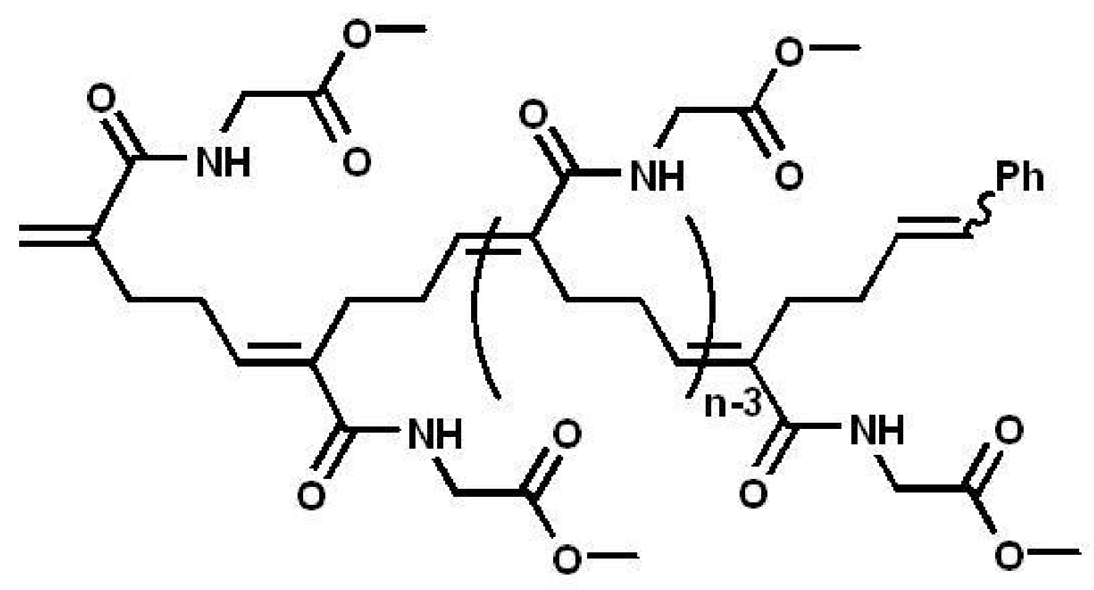


13C-NMR

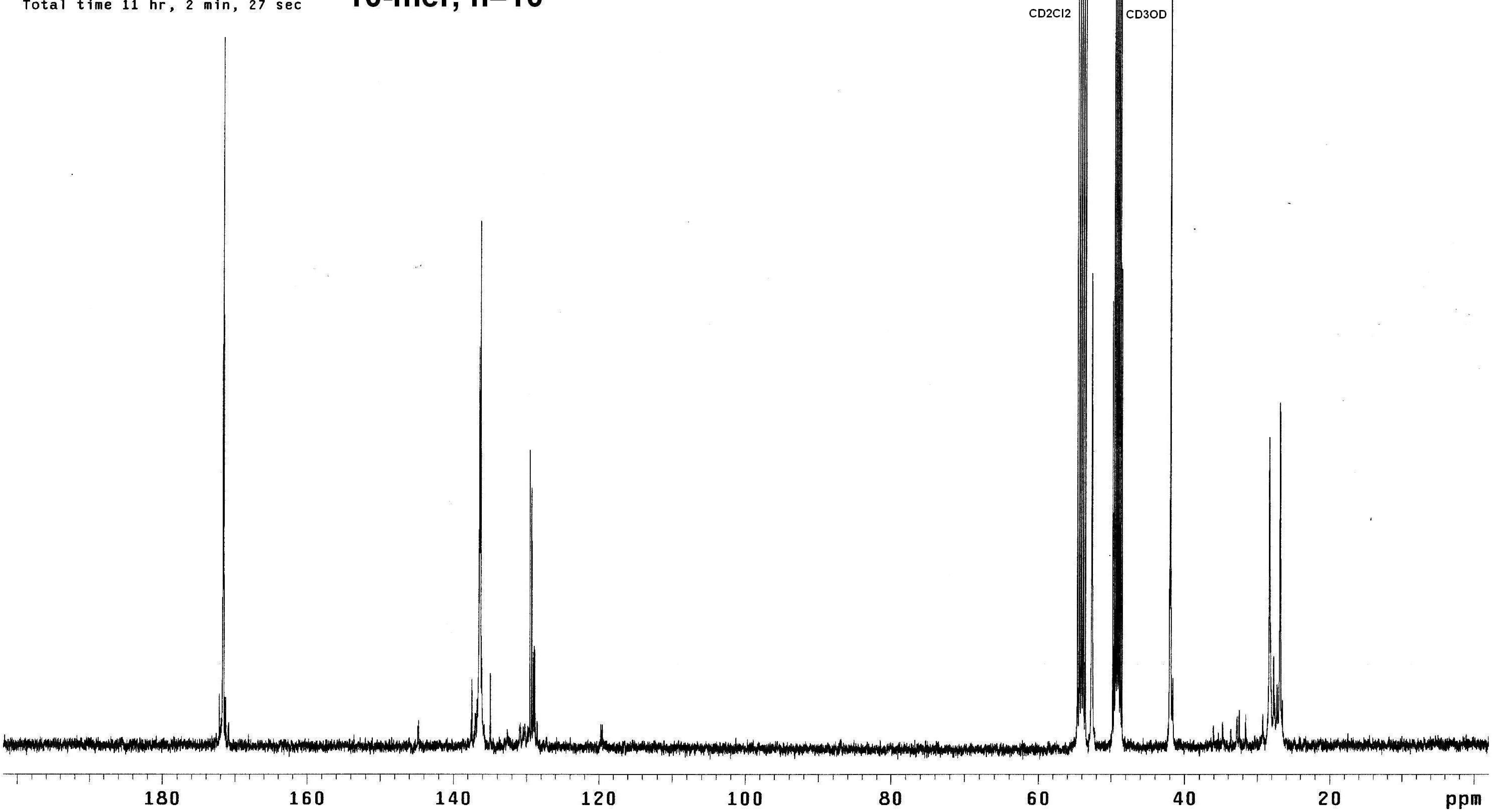
```
062005-CyBuGlyOMe-10mer-C13

Pulse Sequence: s2pul
 Solvent: CD2Cl2 + CD3OD (2:1)
 Temp. 25.0 C / 298.1 K
INOVA-400  "inv400"

 Relax. delay 1.000 sec
 Pulse 82.1 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 17144 repetitions
OBSERVE  C13, 100.5396359 MHz
DECOUPLE  H1, 399.8407019 MHz
 Power 45 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 11 hr, 2 min, 27 sec
```



10-mer, n=10

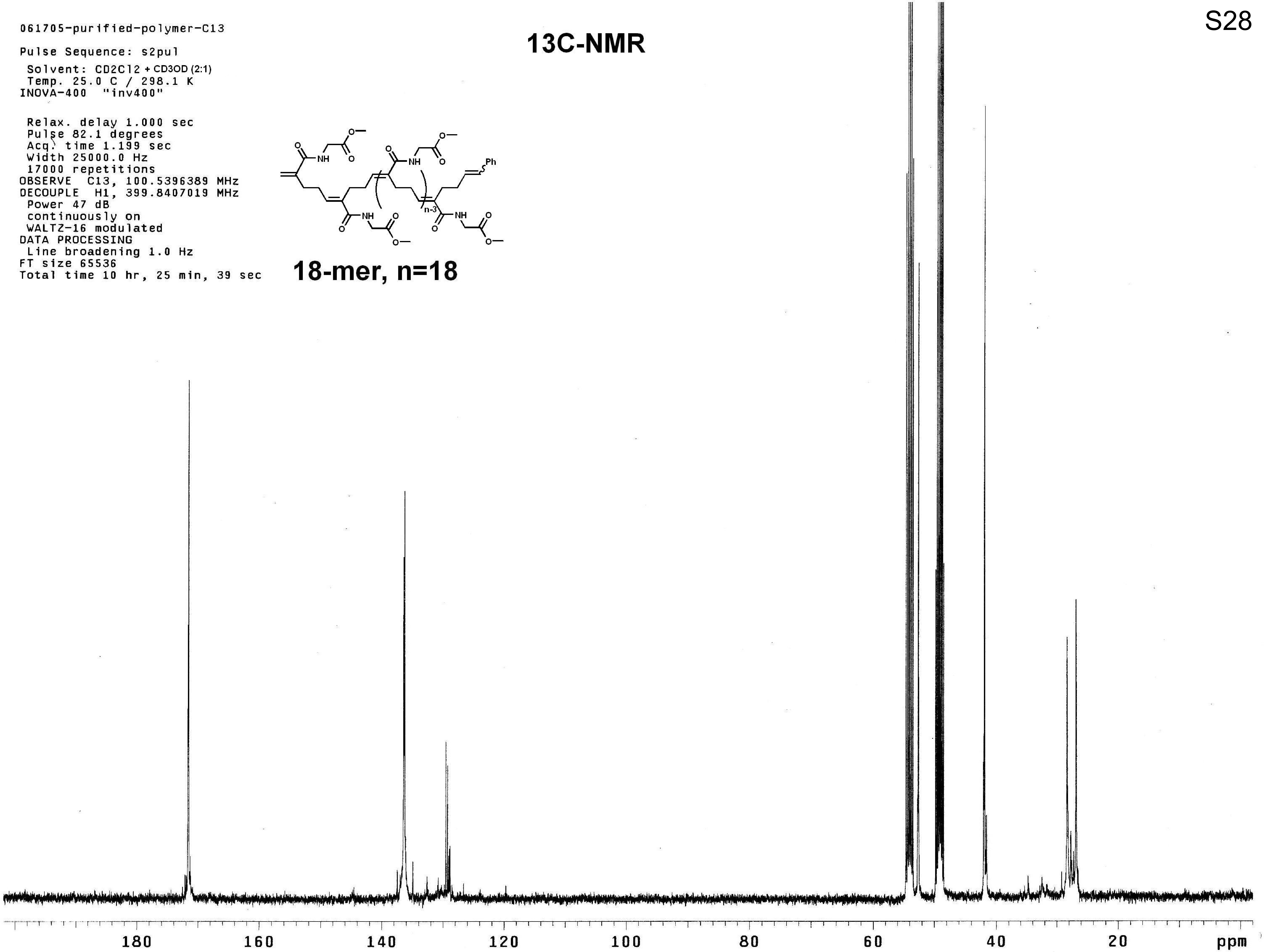


13C-NMR

```
061705-purified-polymer-C13

Pulse Sequence: s2pul
 Solvent: CD2Cl2 + CD3OD (2:1)
 Temp. 25.0 C / 298.1 K
INOVA-400  "inv400"

 Relax. delay 1.000 sec
 Pulse 82.1 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 17000 repetitions
OBSERVE  C13, 100.5396389 MHz
DECOUPLE  H1, 399.8407019 MHz
 Power 47 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 10 hr, 25 min, 39 sec
```



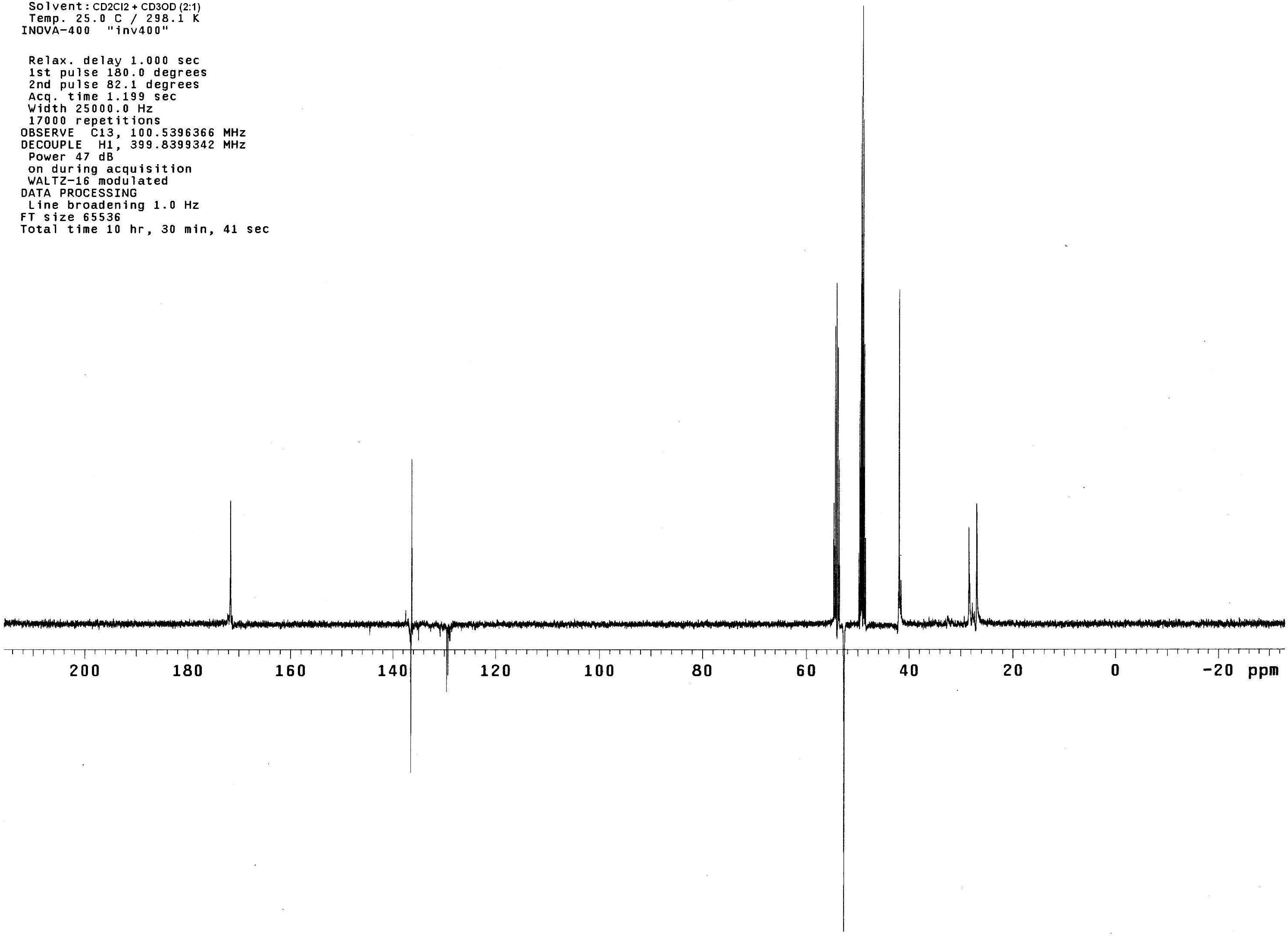
18-mer, n=18

18-mer, 13C-APT spectrum

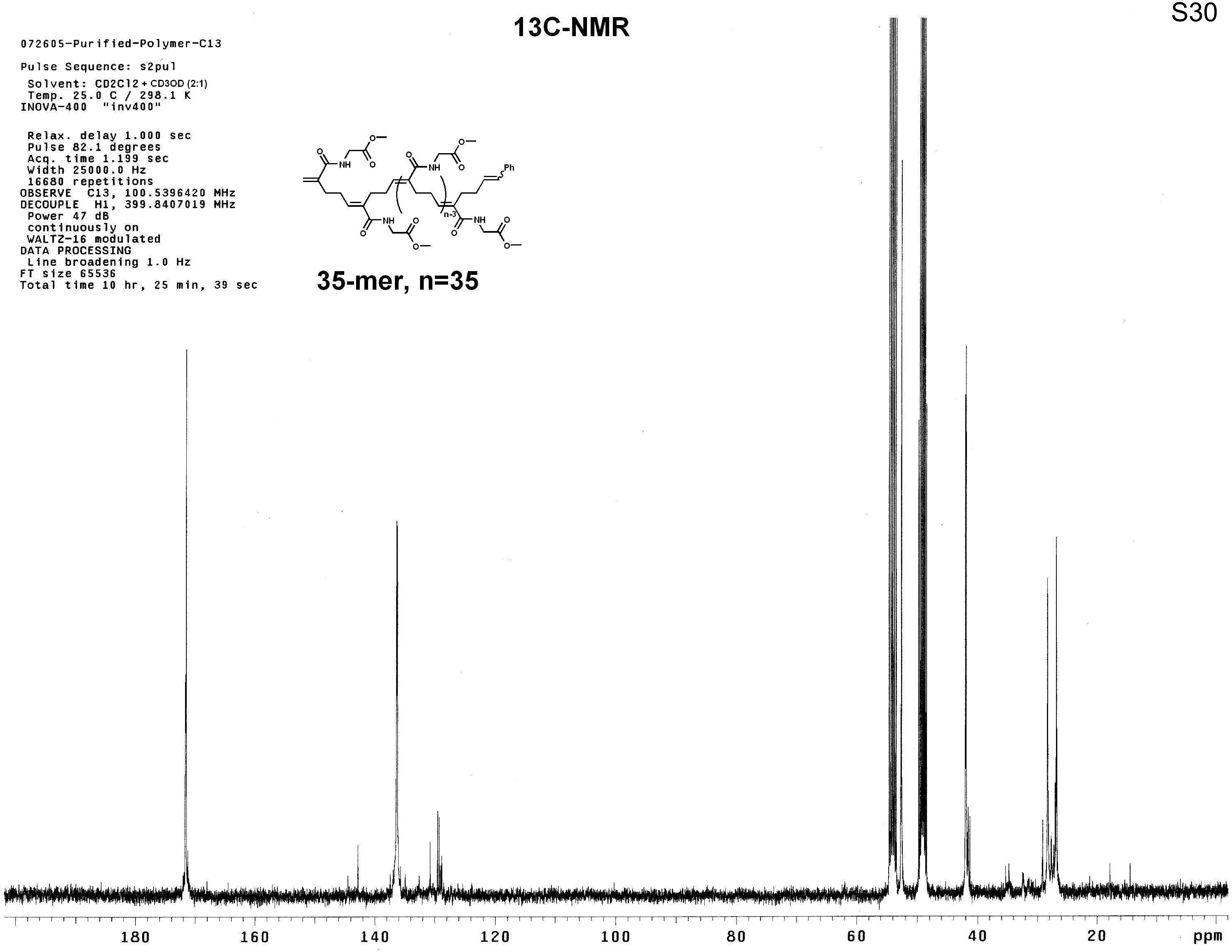
```
061705-purified-polymer-C13-APT

Pulse Sequence: apt
 Solvent: CD2Cl2 + CD3OD (2:1)
 Temp. 25.0 C / 298.1 K
INOVA-400  "inv400"

 Relax. delay 1.000 sec
 1st pulse 180.0 degrees
 2nd pulse 82.1 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 17000 repetitions
OBSERVE  C13, 100.5396366 MHz
DECOUPLE  H1, 399.8399342 MHz
 Power 47 dB
 on during acquisition
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 10 hr, 30 min, 41 sec
```



13C-NMR



```
072605-Purified-Polymer-C13

Pulse Sequence: s2pul
 Solvent: CD2Cl2 + CD3OD (2:1)
 Temp. 25.0 C / 298.1 K
INOVA-400  "inv400"

 Relax. delay 1.000 sec
 Pulse 82.1 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 16680 repetitions
OBSERVE  C13, 100.5396420 MHz
DECOUPLE  H1, 399.8407019 MHz
 Power 47 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 10 hr, 25 min, 39 sec
```

35-mer, n=35

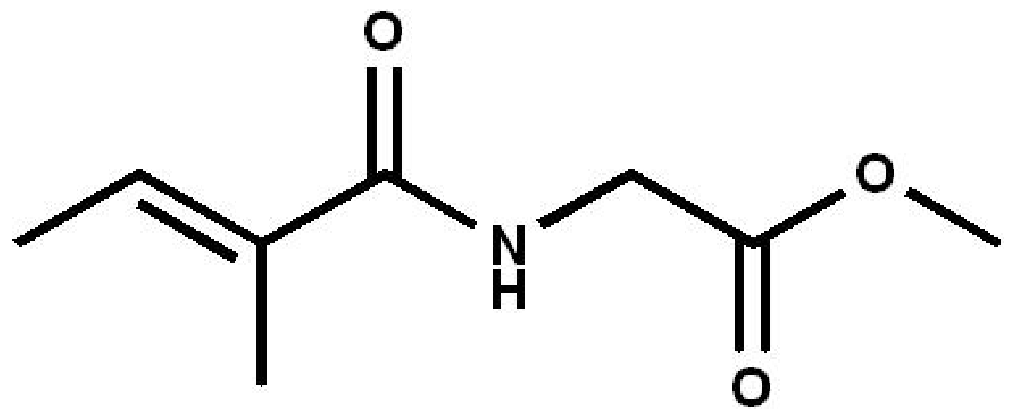
1H-NMR

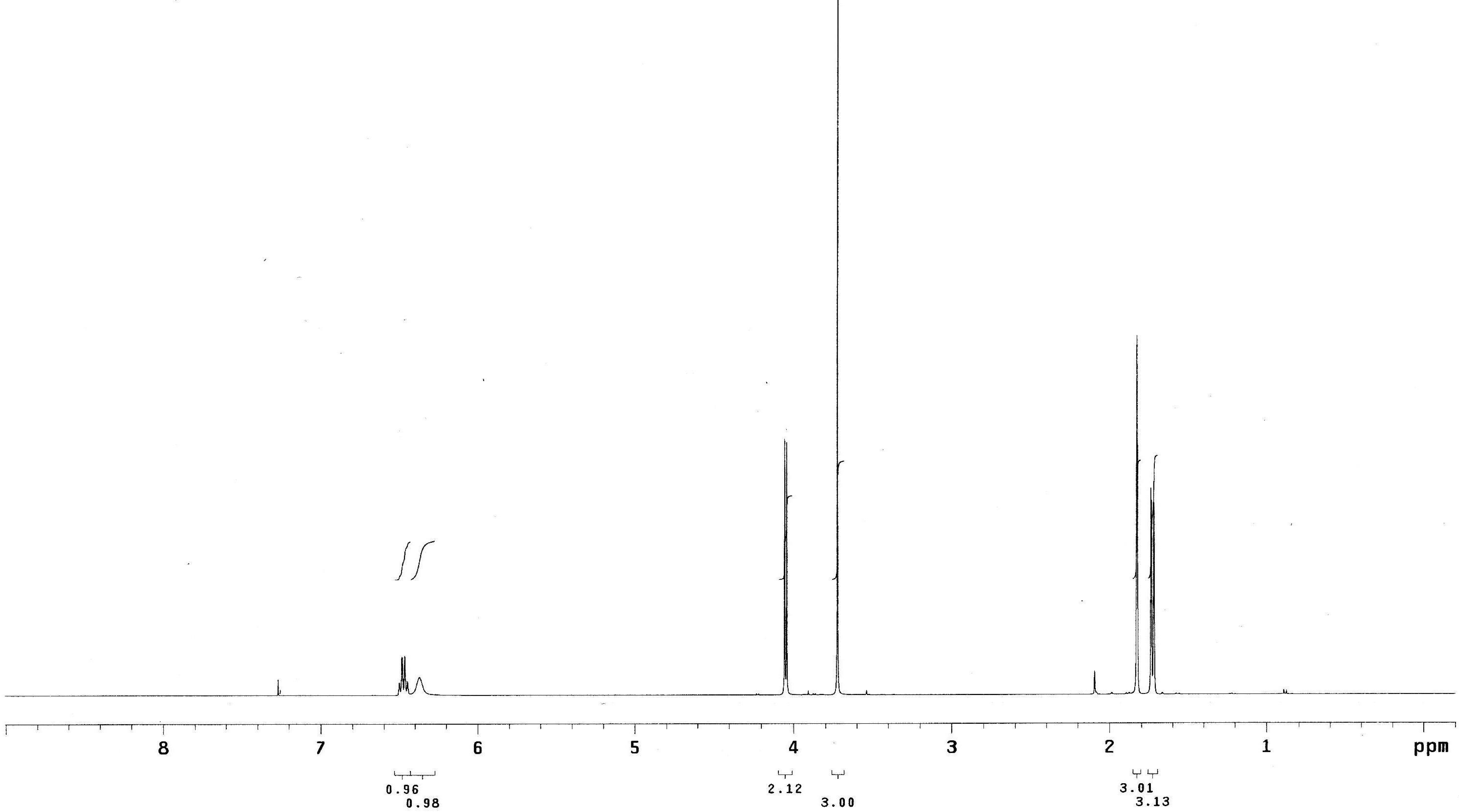
071905-Sep-B-tiglicAcidGlyOMe

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
INOVA-400 "inv400"

Relax. delay 1.000 sec
Pulse 66.0 degrees
Acq. time 3.744 sec
Width 6000.6 Hz
144 repetitions
OBSERVE H1, 399.8379287 MHz
DATA PROCESSING
FT size 65536
Total time 15 min, 50 sec



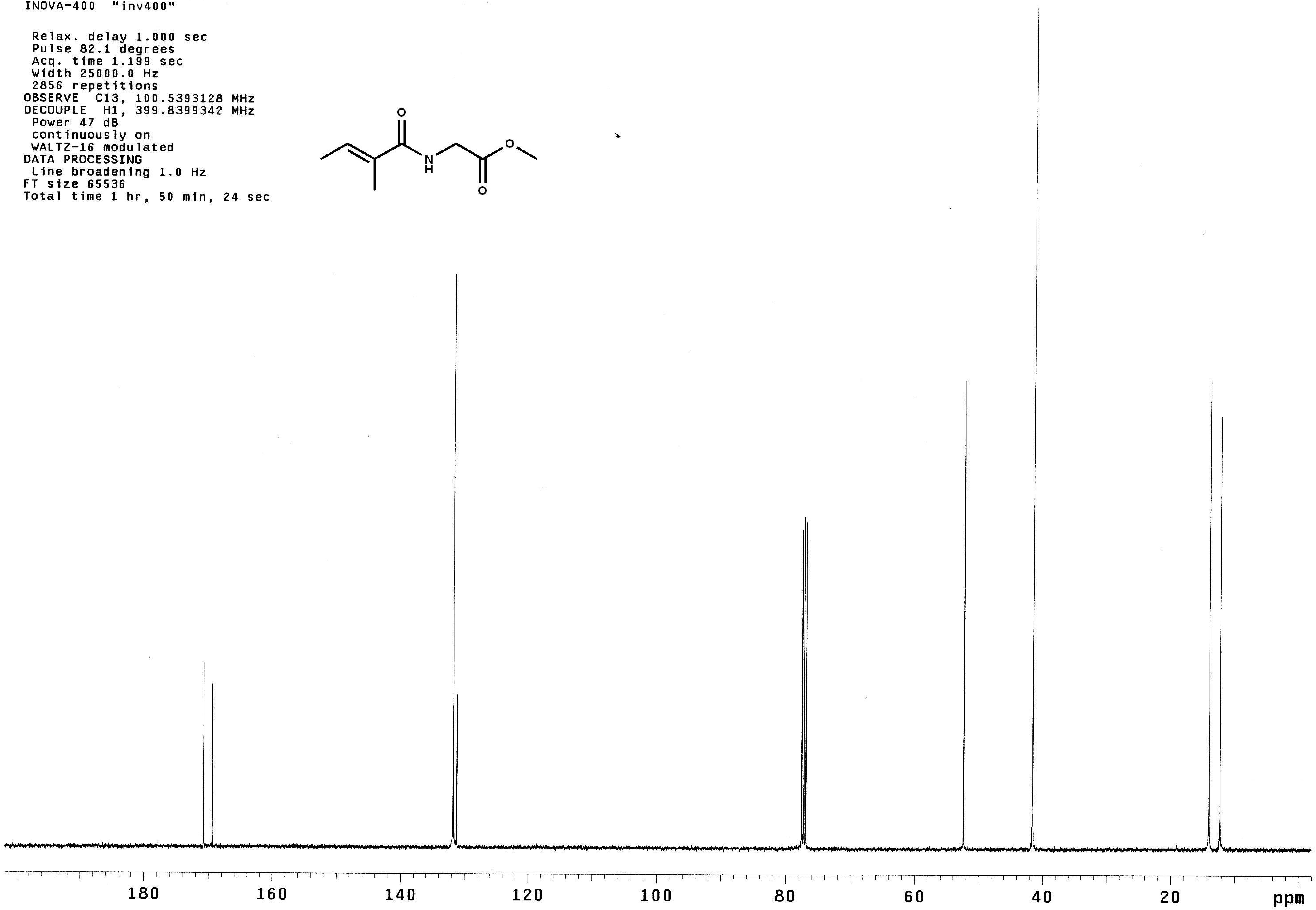


13C-NMR

```
071905-Sep-B-TiglicAcidGlyOMe-C13

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
INOVA-400  "inv400"

 Relax. delay 1.000 sec
 Pulse 82.1 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 2856 repetitions
OBSERVE  C13, 100.5393128 MHz
DECOUPLE  H1, 399.8399342 MHz
 Power 47 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 50 min, 24 sec
```



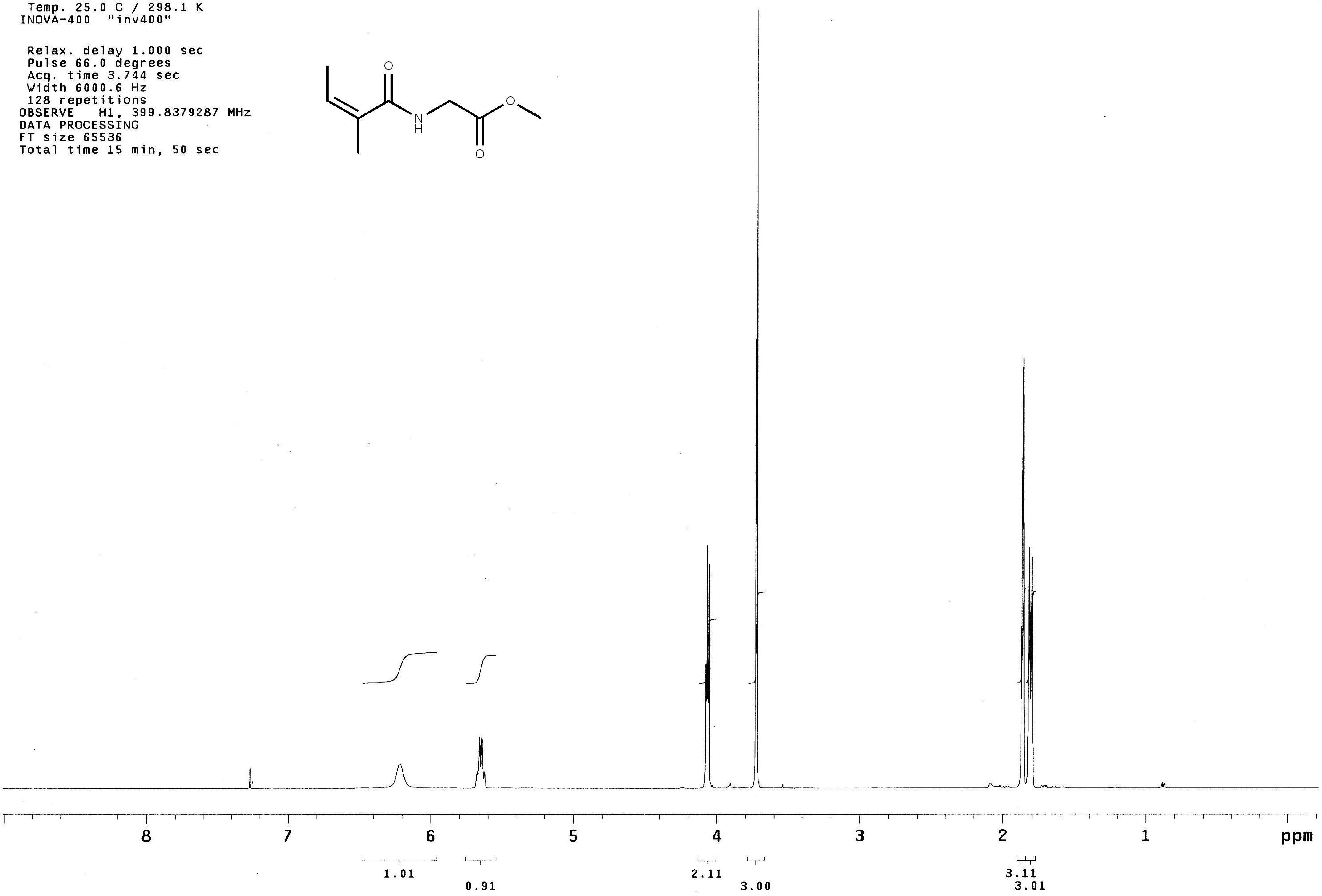
1H-NMR

072105-Sep-B-AngelicAcidGlyOMe

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
INOVA-400 "inv400"

Relax. delay 1.000 sec
Pulse 66.0 degrees
Acq. time 3.744 sec
Width 6000.6 Hz
128 repetitions
OBSERVE H1, 399.8379287 MHz
DATA PROCESSING
FT size 65536
Total time 15 min, 50 sec



13C-NMR

```
072105-Sep-B-AngelicAcidGlyOMe-C13

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
INOVA-400  "inv400"

 Relax. delay 1.000 sec
 Pulse 82.1 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 2352 repetitions
OBSERVE  C13, 100.5393128 MHz
DECOUPLE  H1, 399.8399342 MHz
 Power 47 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 32 min, 0 sec
```