

## Supporting Information

### Functionalized 10-Membered Aza- and Oxa-Enediynes through the Nicholas Reaction

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<sup>3</sup> Laboratory of chemo- and bioinformatics, I. M. Sechenov First Moscow State Medical  
University, 119991 Moscow, Russian Federation

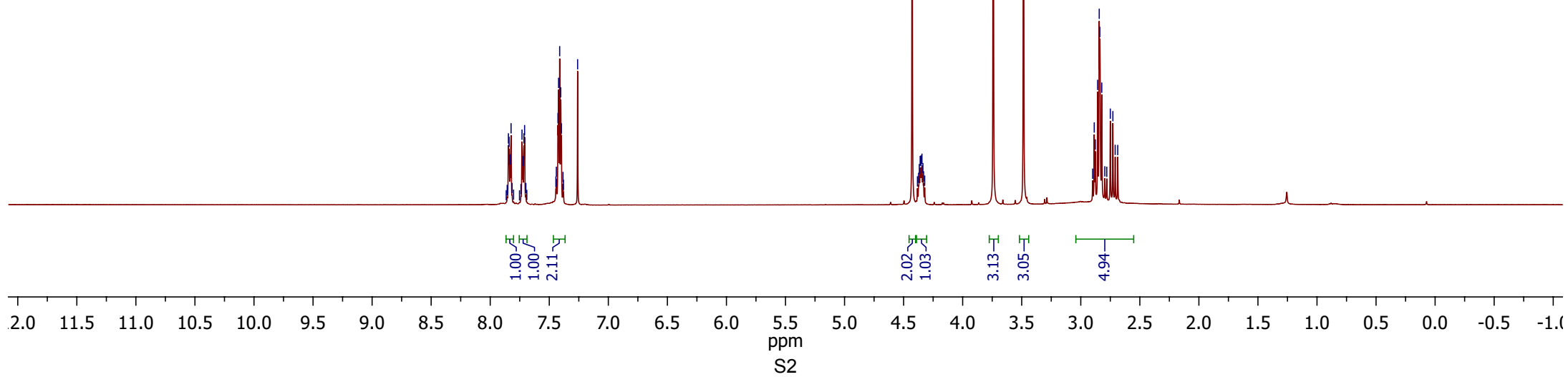
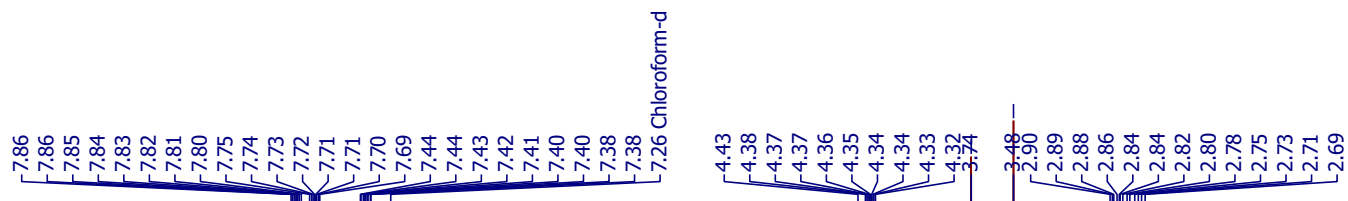
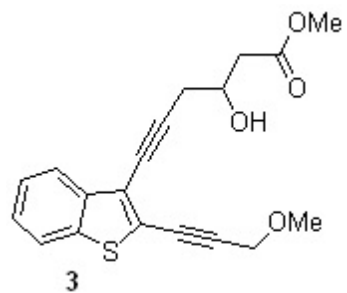
<sup>4</sup> Department of Computational Biology, Sirius University of Science and Technology,  
354349 Sochi, Russian Federation

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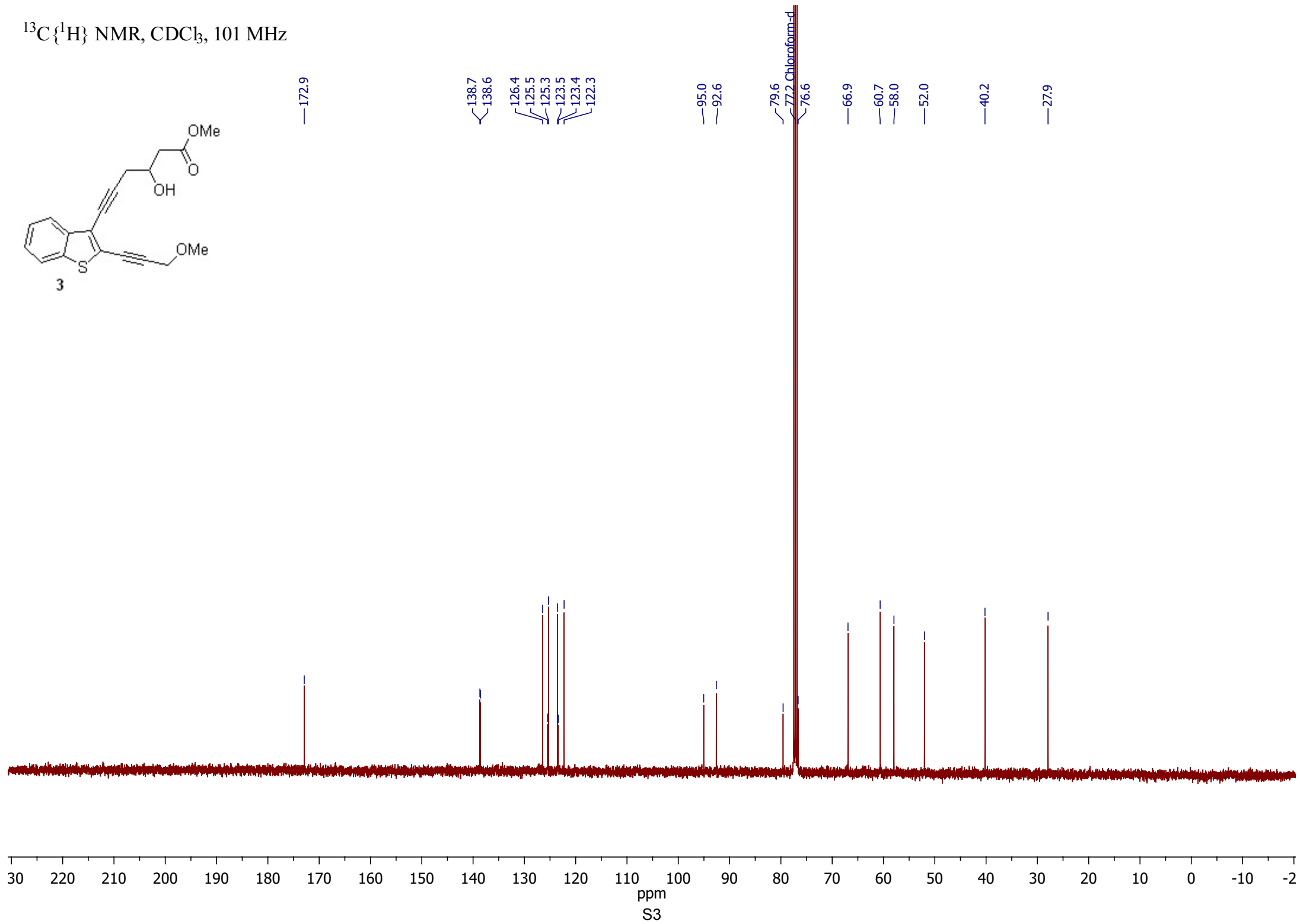
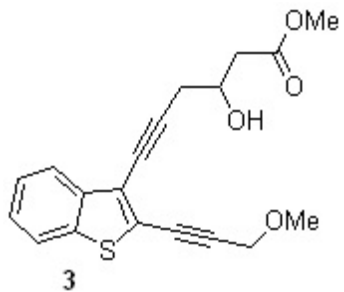
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Copies of ESI HRMS spectra for key compounds.....	S69

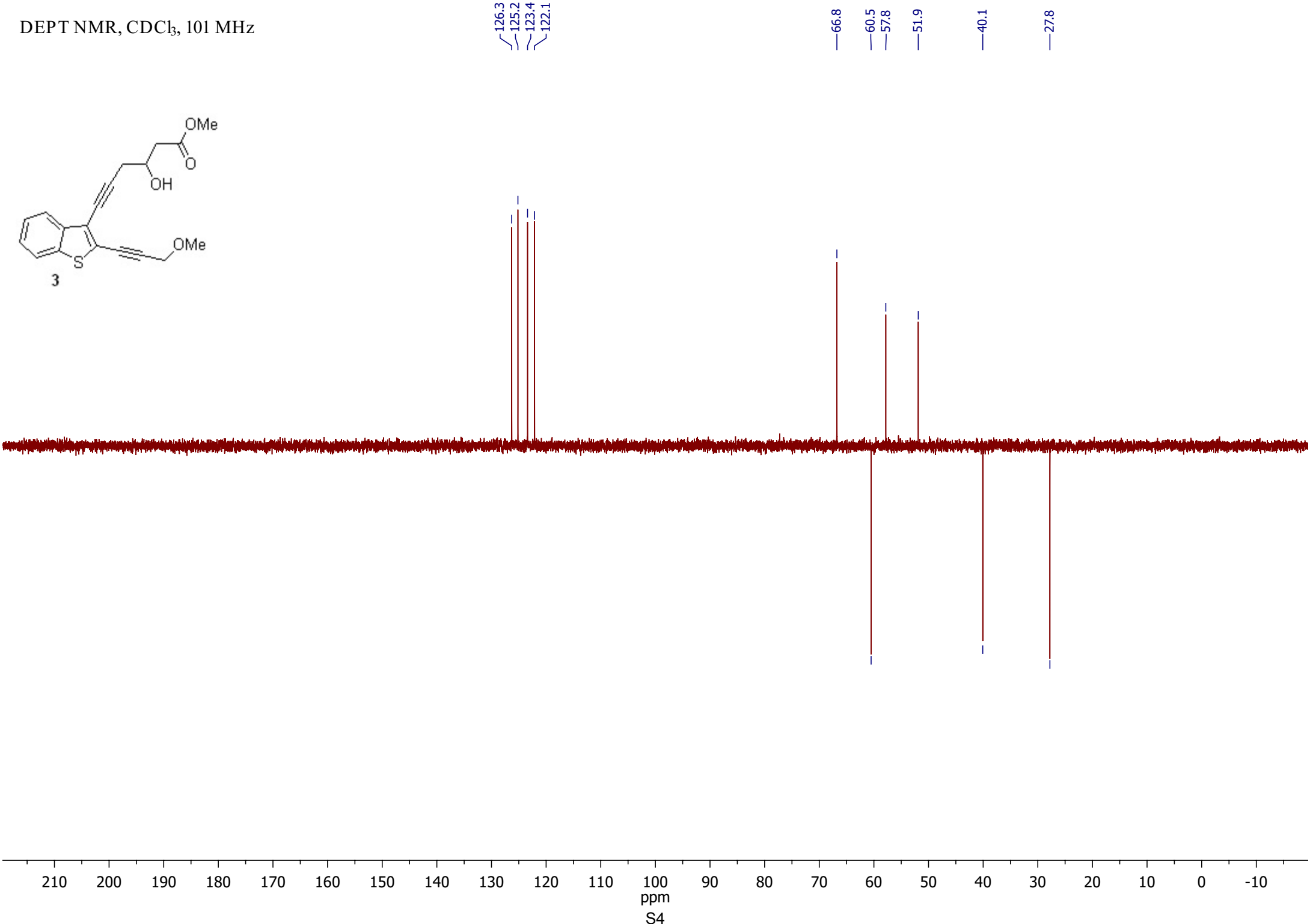
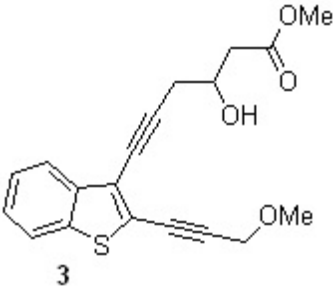
<sup>1</sup>H NMR, CDCl<sub>3</sub>, 400 MHz



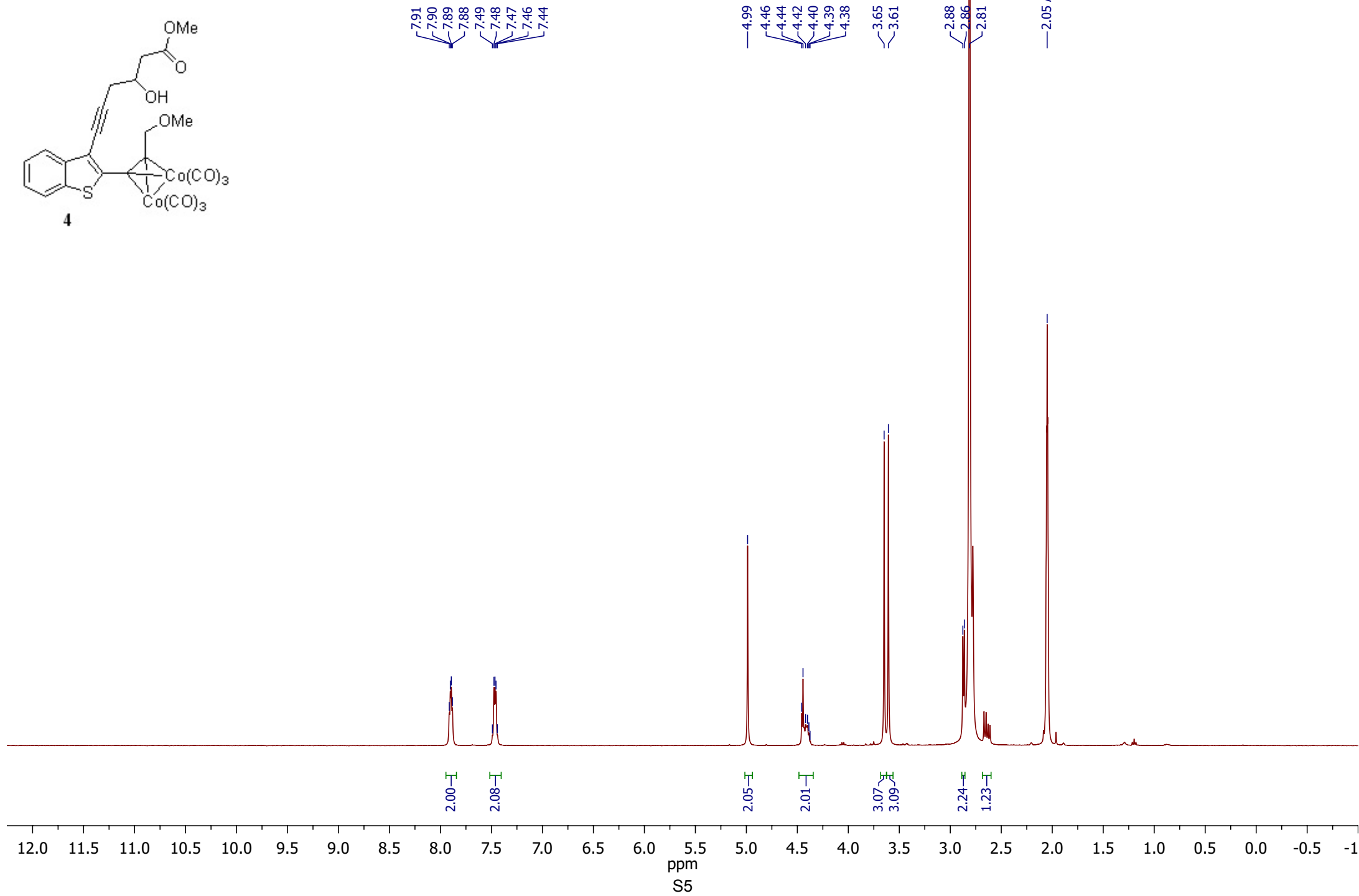
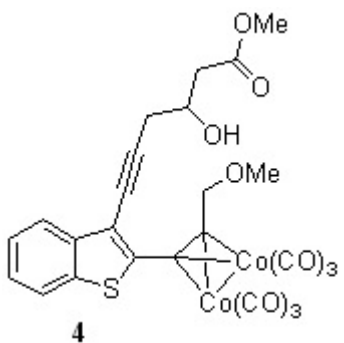
$^{13}\text{C}\{^1\text{H}\}$  NMR,  $\text{CDCl}_3$ , 101 MHz

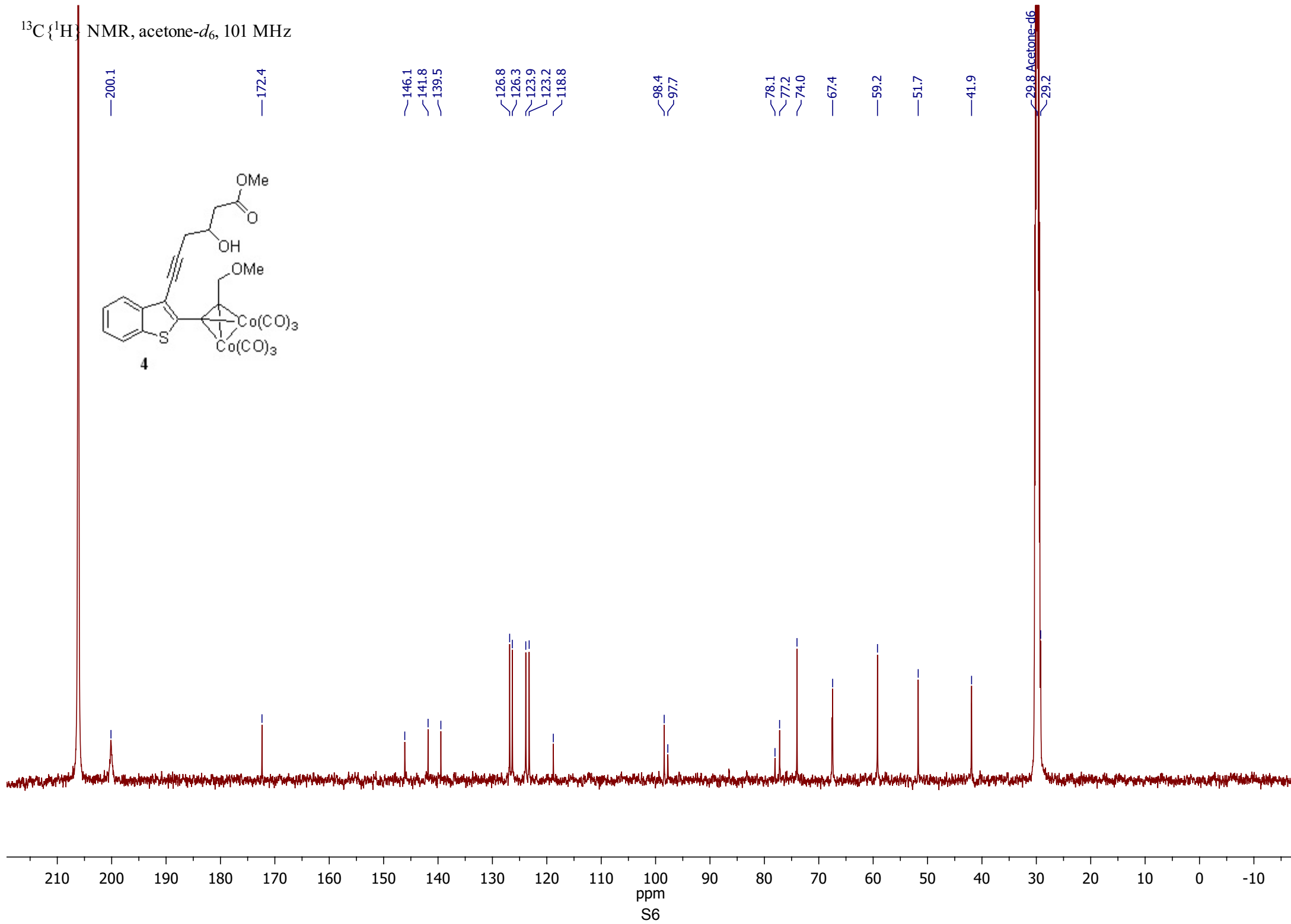
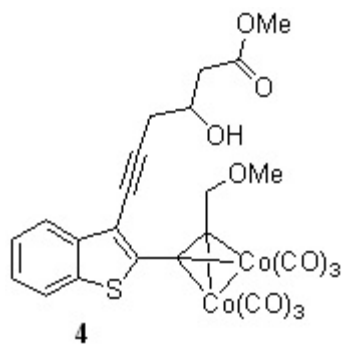


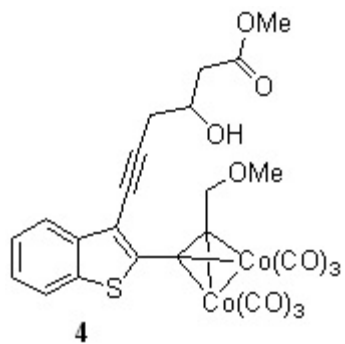
DEPT NMR, CDCl<sub>3</sub>, 101 MHz





<sup>1</sup>H NMR, acetone-*d*<sub>6</sub>, 400 MHz

$^{13}\text{C}\{^1\text{H}\}$  NMR, acetone- $d_6$ , 101 MHz

DEPT NMR, acetone-*d*<sub>6</sub>, 101 MHz

126.6  
126.1  
123.6  
123.0

—73.8

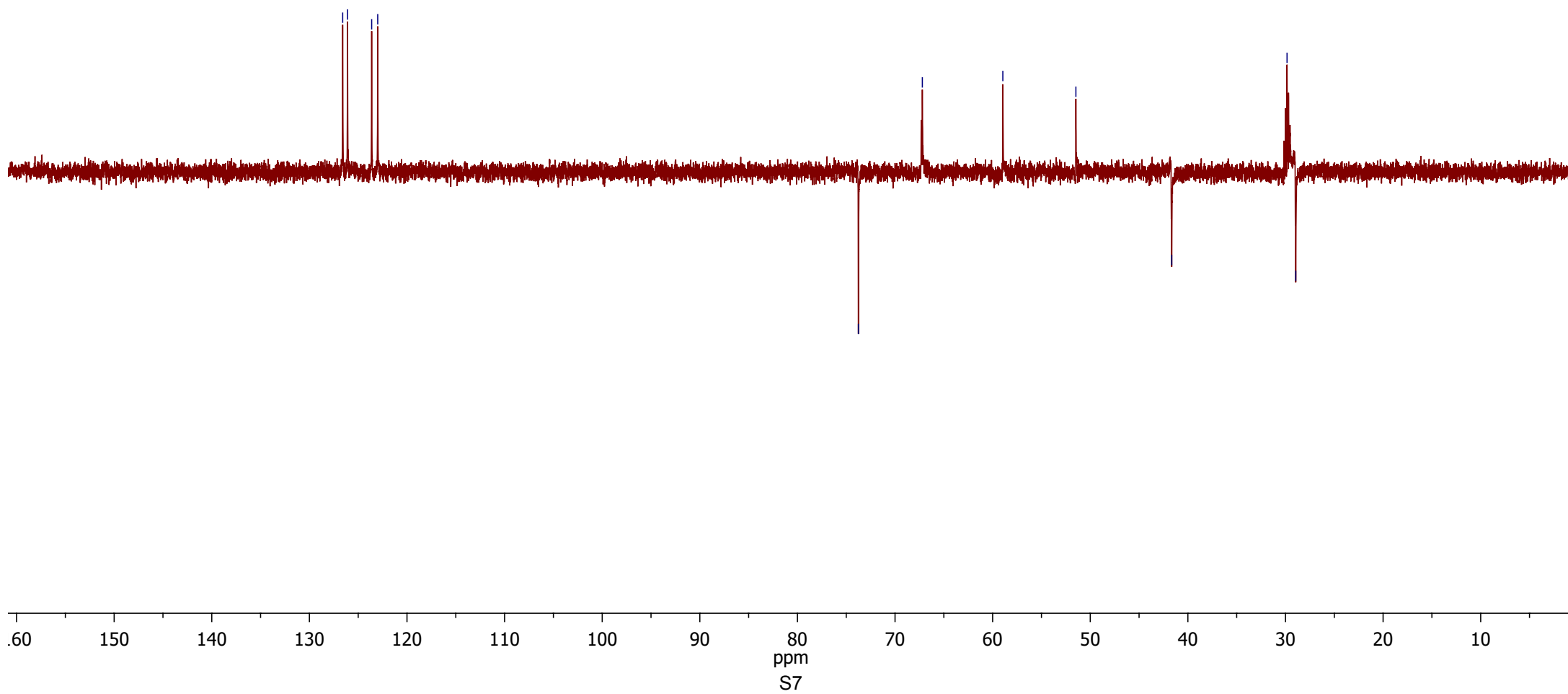
—67.2

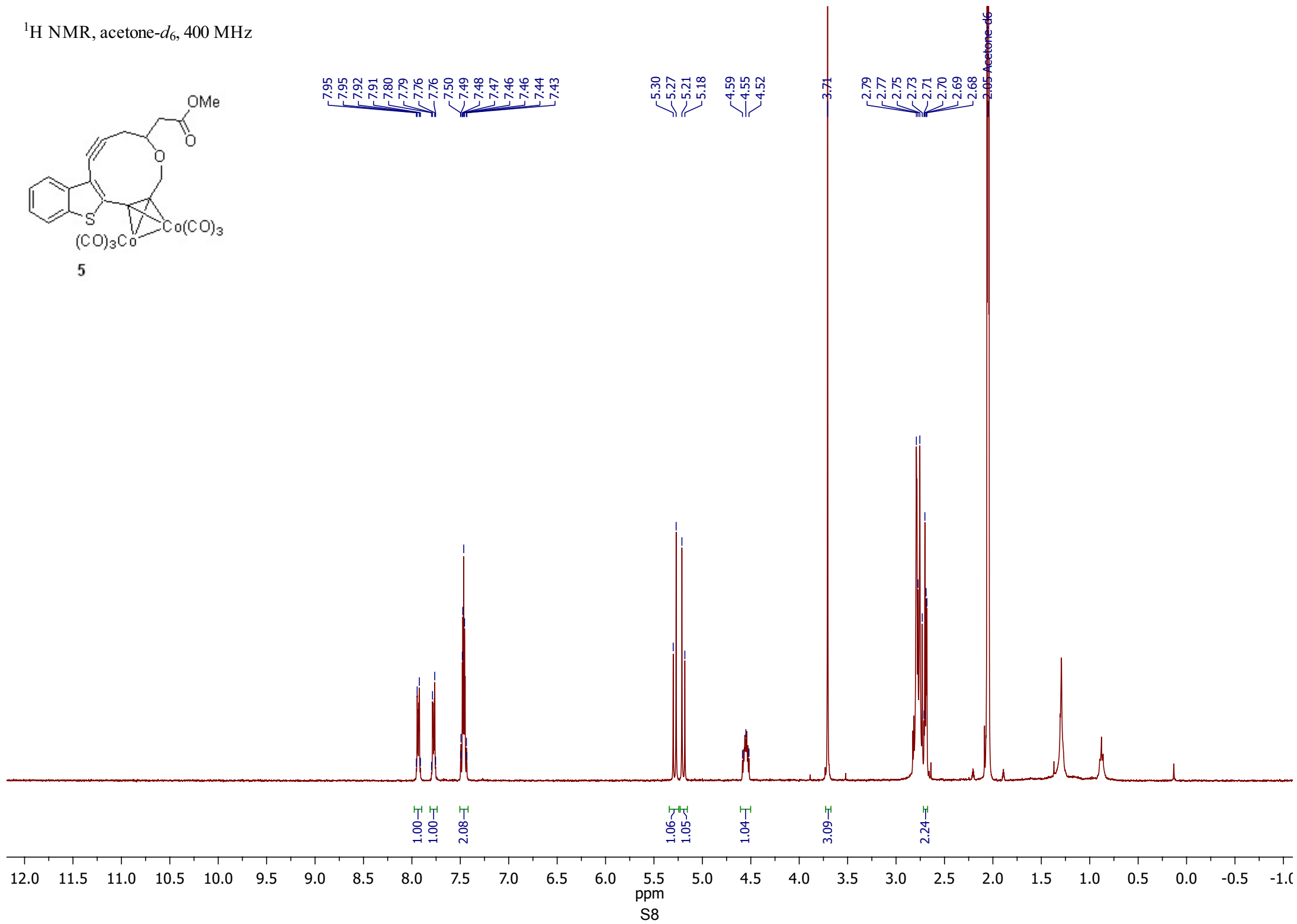
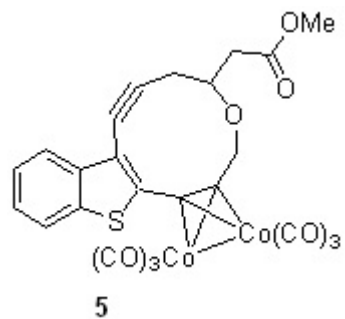
—59.0

—51.5

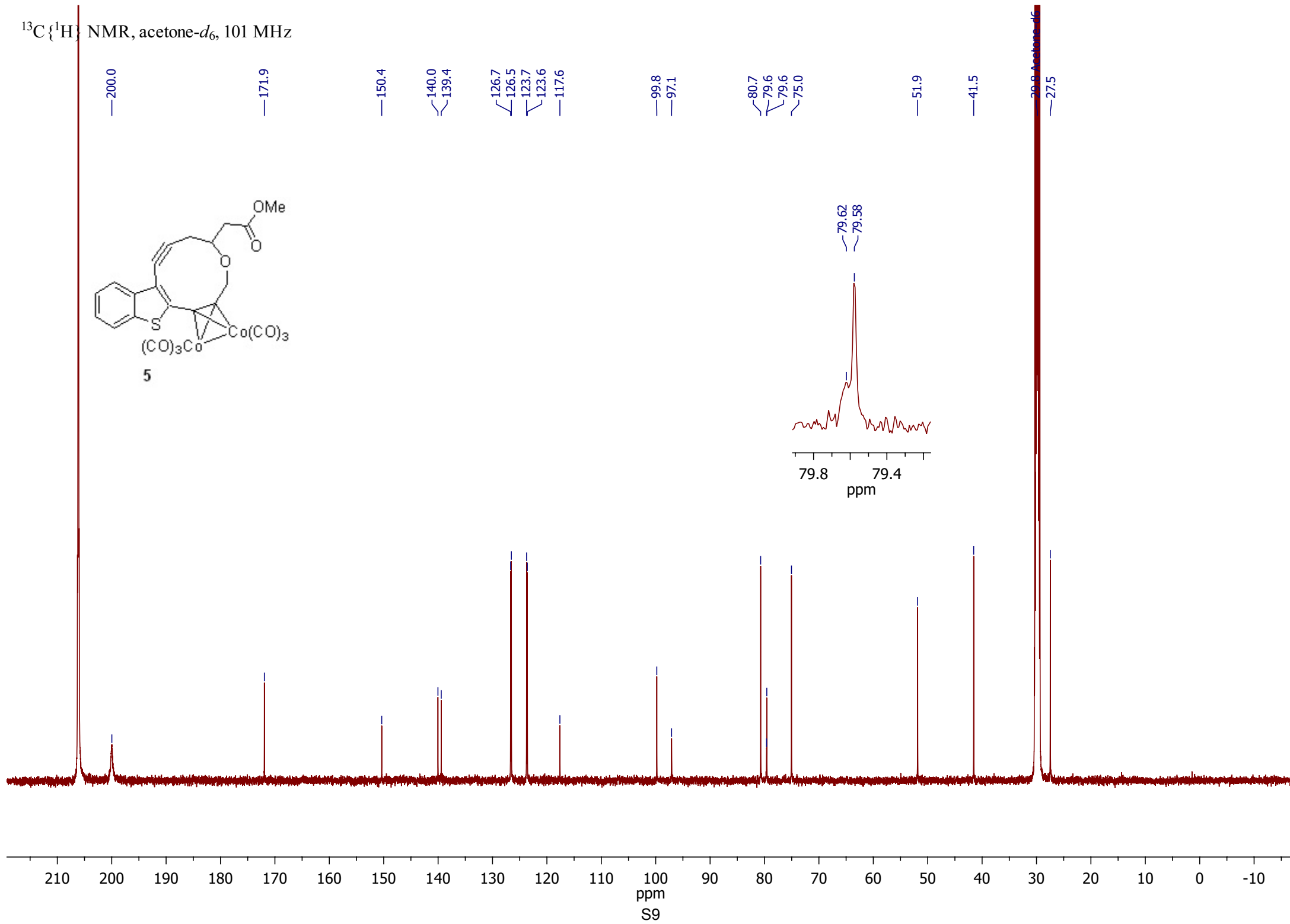
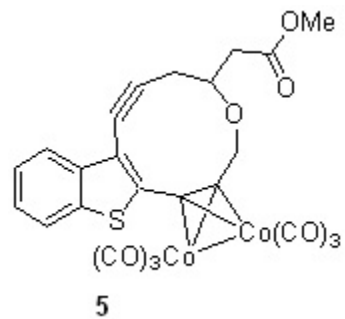
—41.7

— 29.8 Acetone-d6  
— 28.9

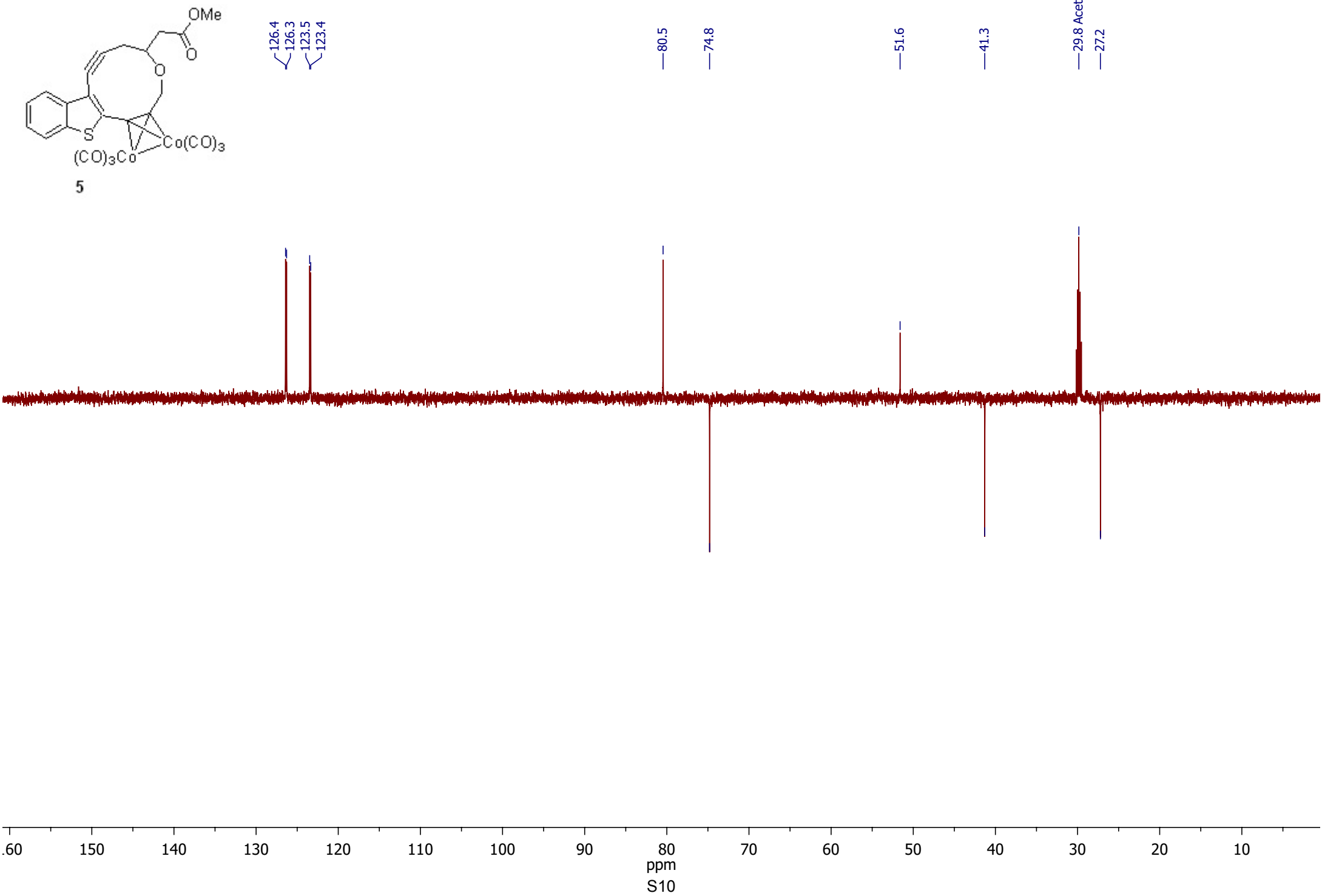


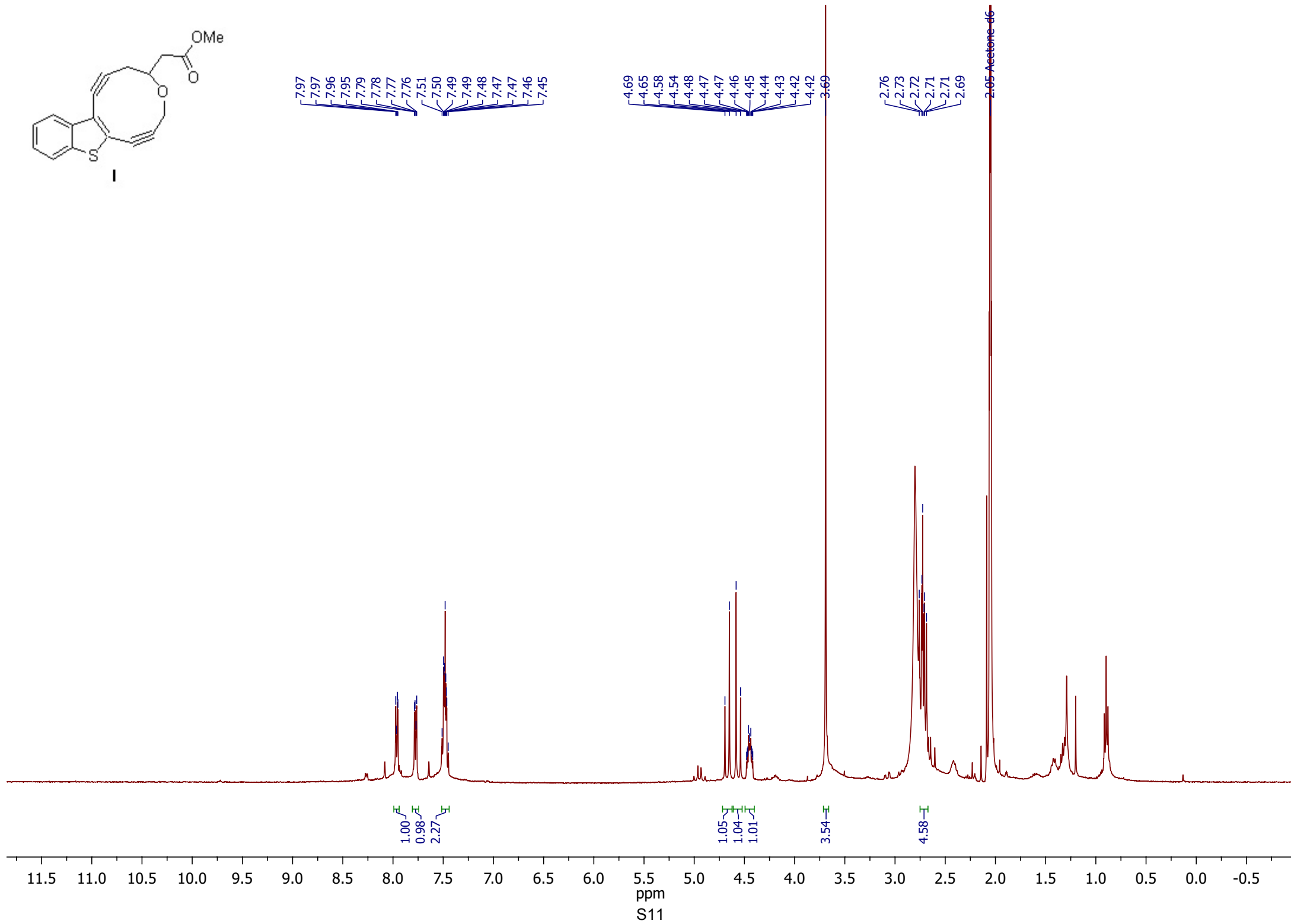
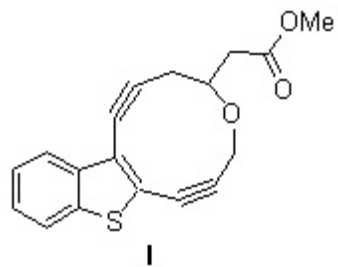
<sup>1</sup>H NMR, acetone-*d*<sub>6</sub>, 400 MHz

$^{13}\text{C}\{^1\text{H}\}$  NMR, acetone- $d_6$ , 101 MHz

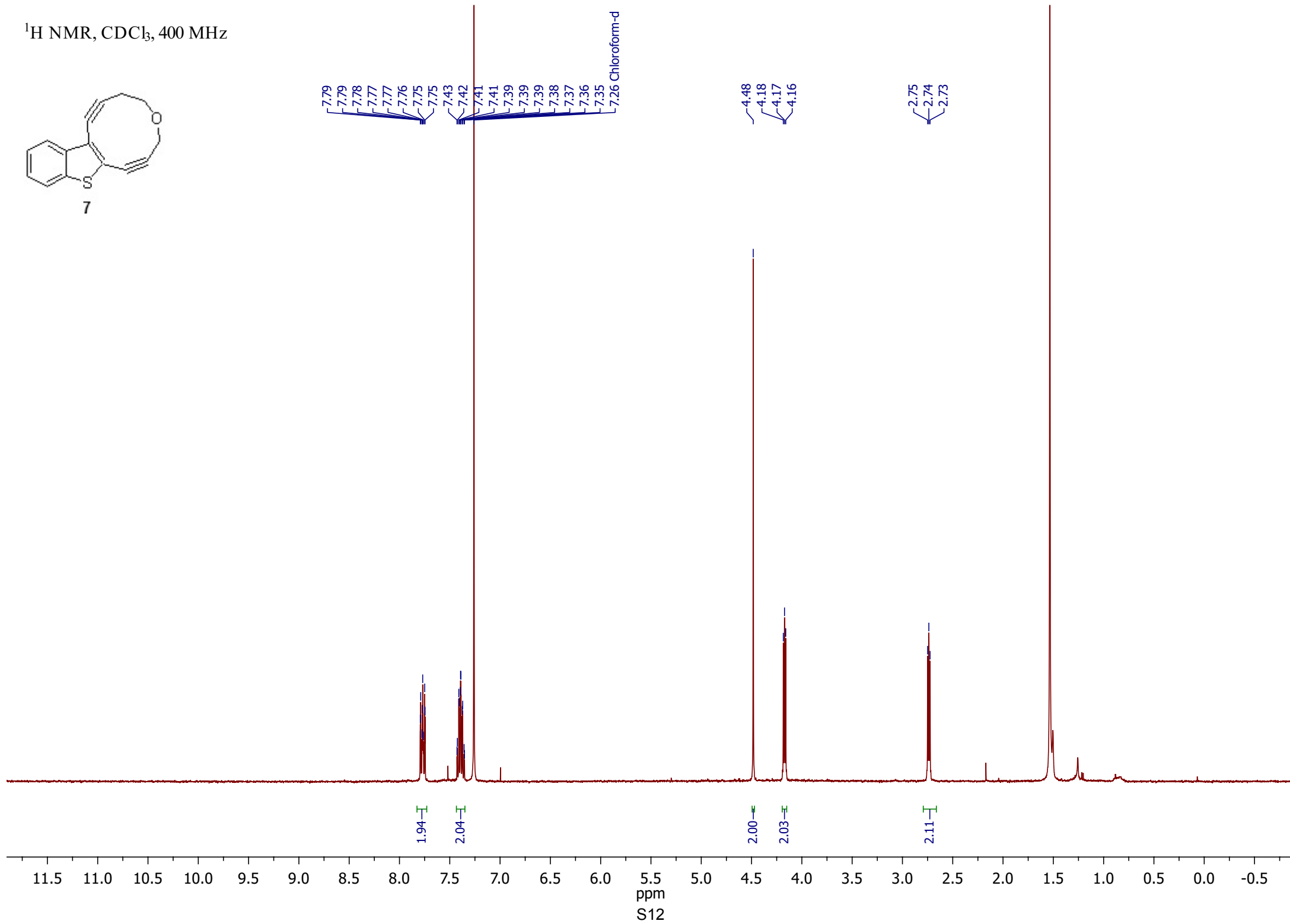
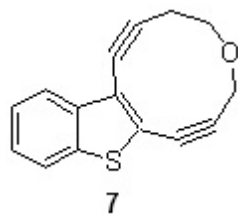


DEPT NMR, acetone-*d*<sub>6</sub>, 101 MHz



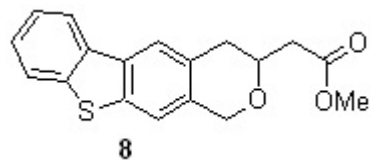


$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz





$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



8.10  
8.09  
8.09  
8.08  
8.07  
7.88  
7.84  
7.83  
7.82  
7.82  
7.81  
7.80  
7.49  
7.46  
7.45  
7.44  
7.43  
7.42  
7.41  
7.26 Chloroform-d

4.99  
4.28  
4.27  
4.25  
4.24  
4.24  
4.22  
4.21  
3.76  
3.05  
3.05  
3.02  
3.00  
2.98  
2.94  
2.81  
2.79  
2.77  
2.75  
2.69  
2.67  
2.65  
2.63

11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

ppm

S13

1.01  
0.98  
0.97

1.03  
1.98

2.01

0.98

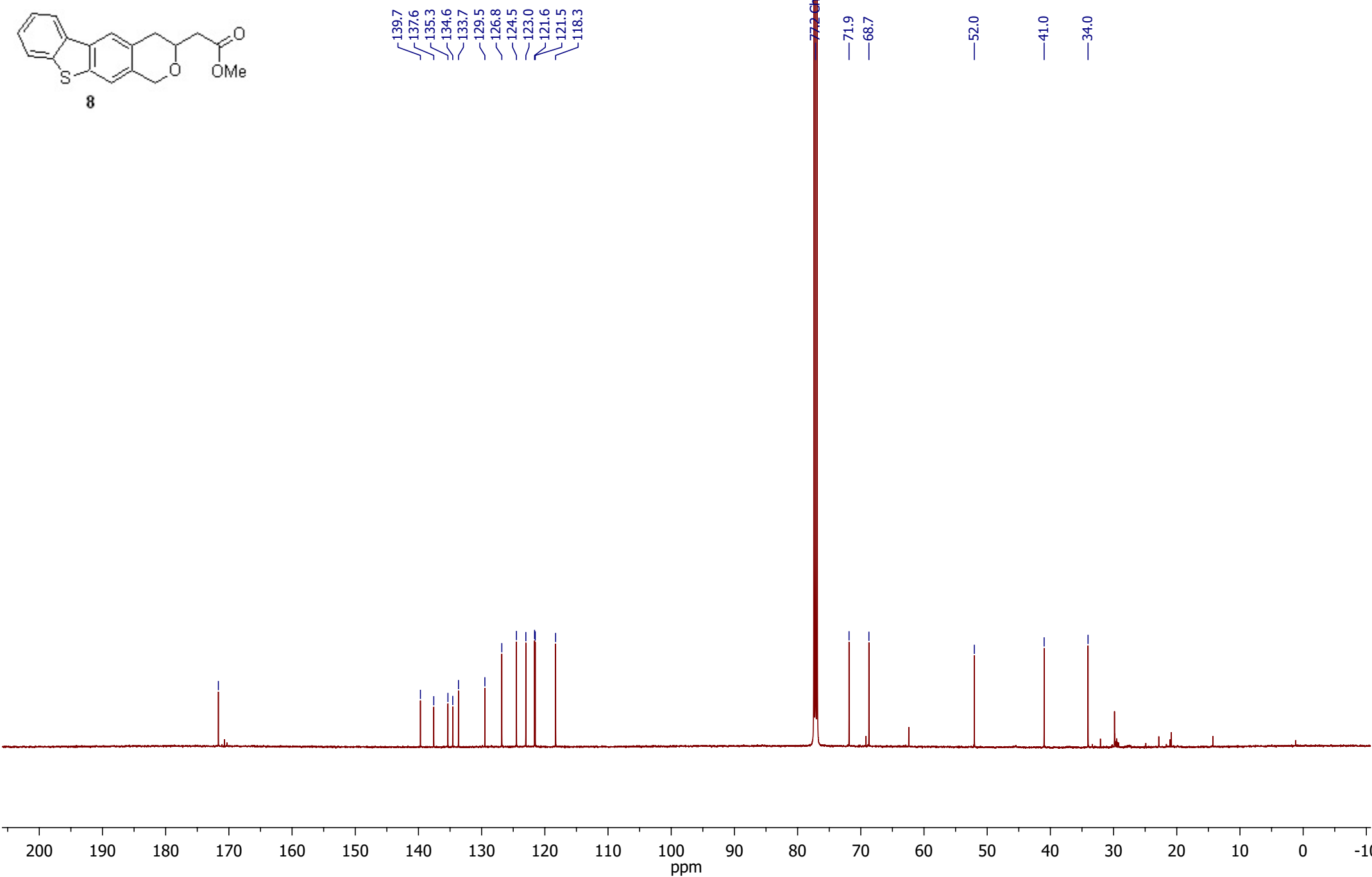
2.92

2.04

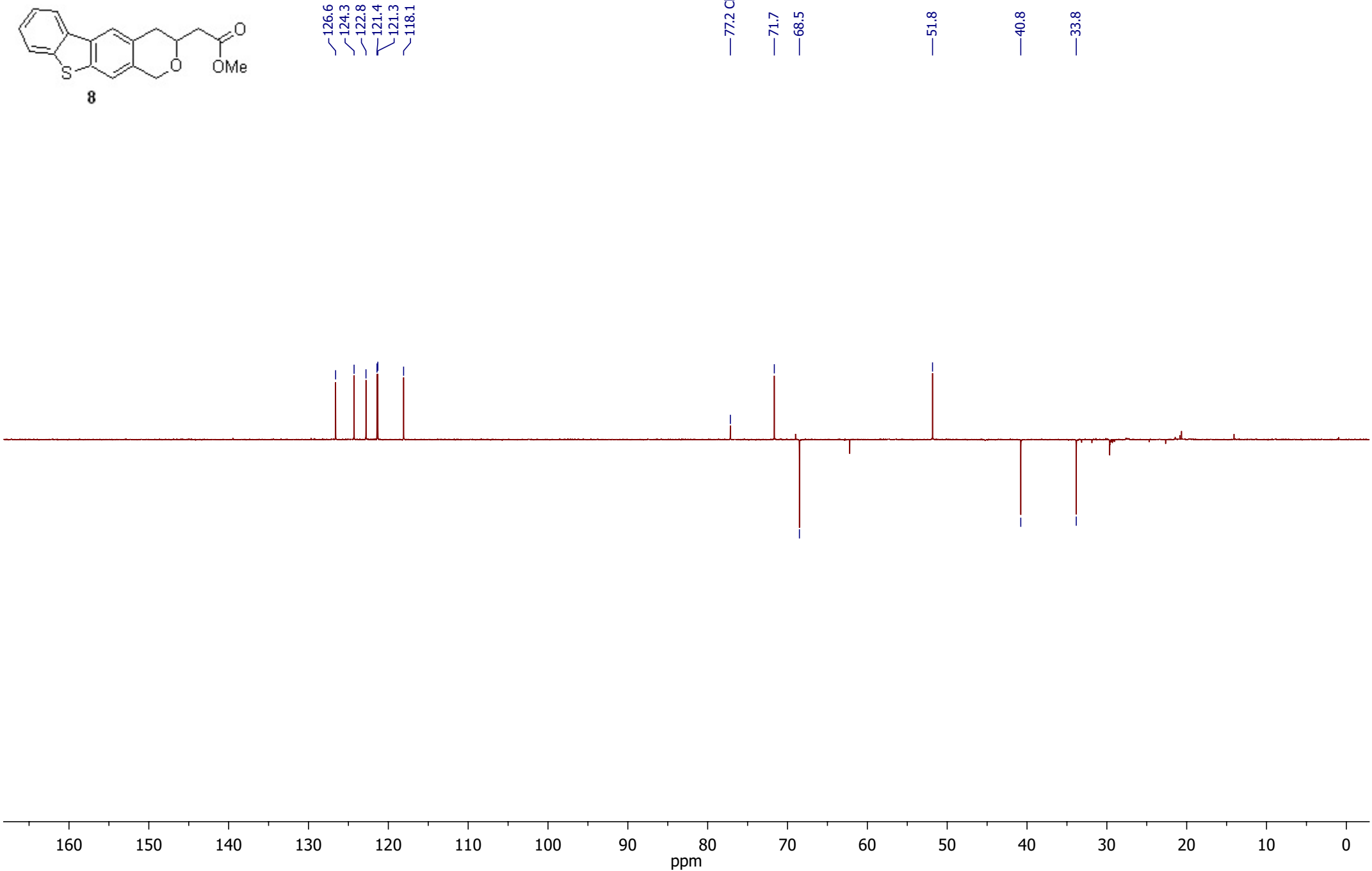
1.07

1.04

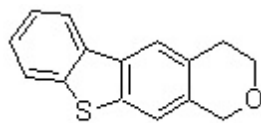
$^{13}\text{C}\{^1\text{H}\}$  NMR,  $\text{CDCl}_3$ , 101 MHz



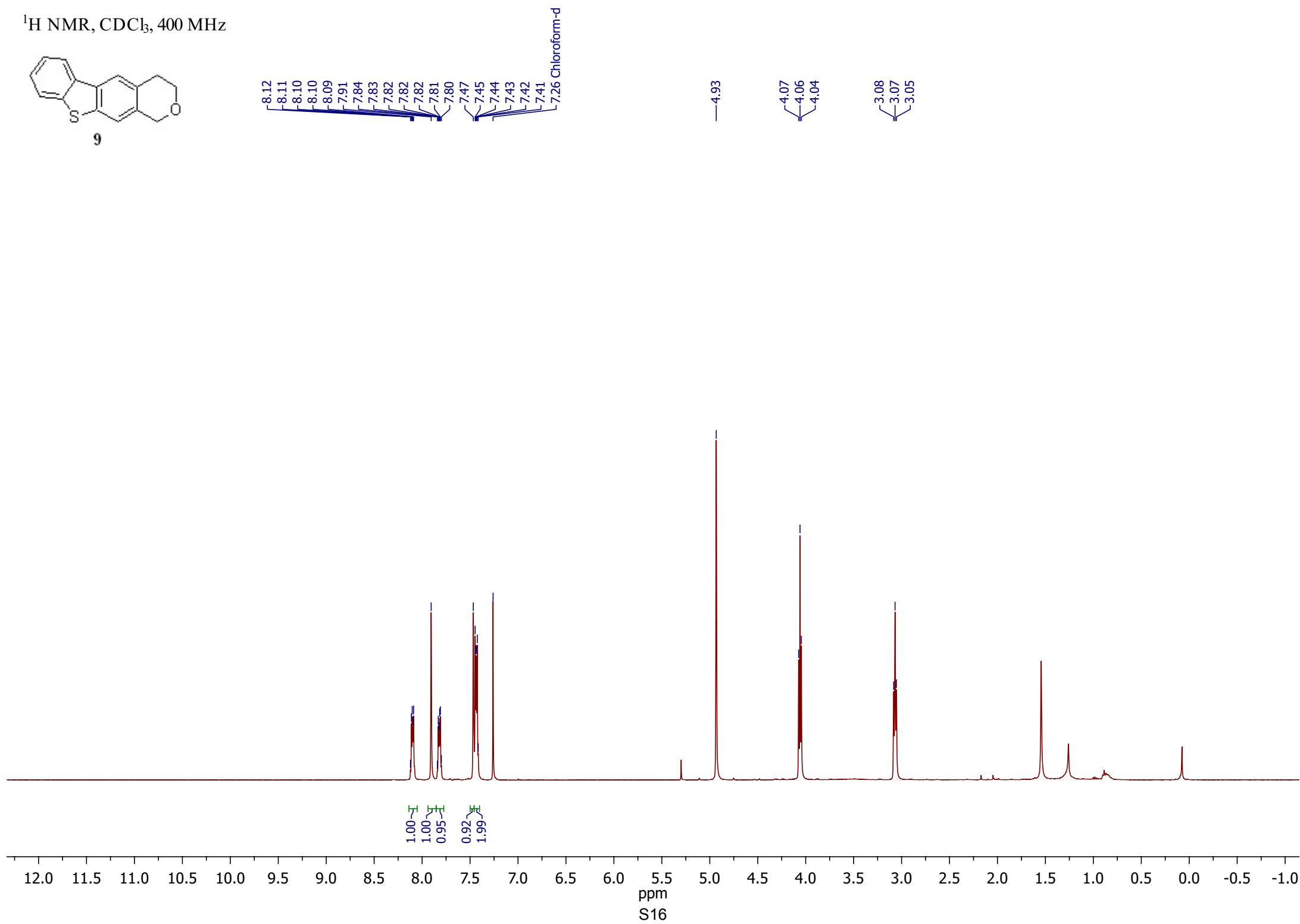
DEPT NMR, CDCl<sub>3</sub>, 101 MHz



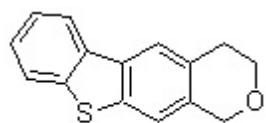
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



**9**



$^{13}\text{C}\{^1\text{H}\}$  NMR,  $\text{CDCl}_3$ , 101 MHz



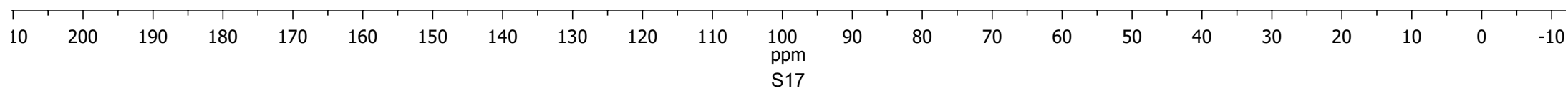
**9**

139.7  
137.4  
135.4  
134.5  
134.4  
130.1  
126.7  
124.5  
123.0  
121.7  
121.5  
118.4

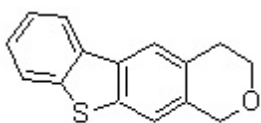
77.2 Chloroform-d

68.6  
65.8

28.8



DEPT NMR, CDCl<sub>3</sub>, 101 MHz

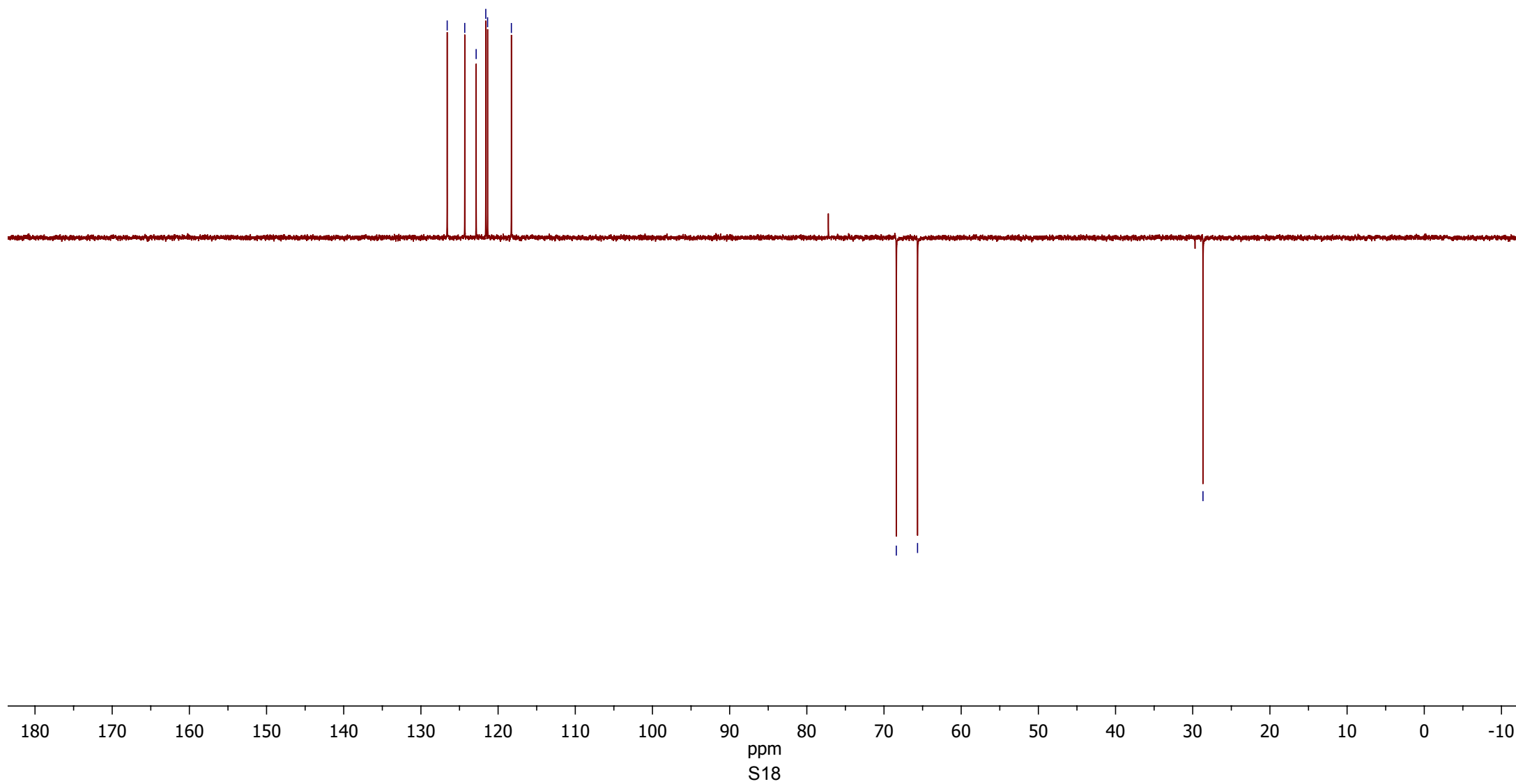


**9**

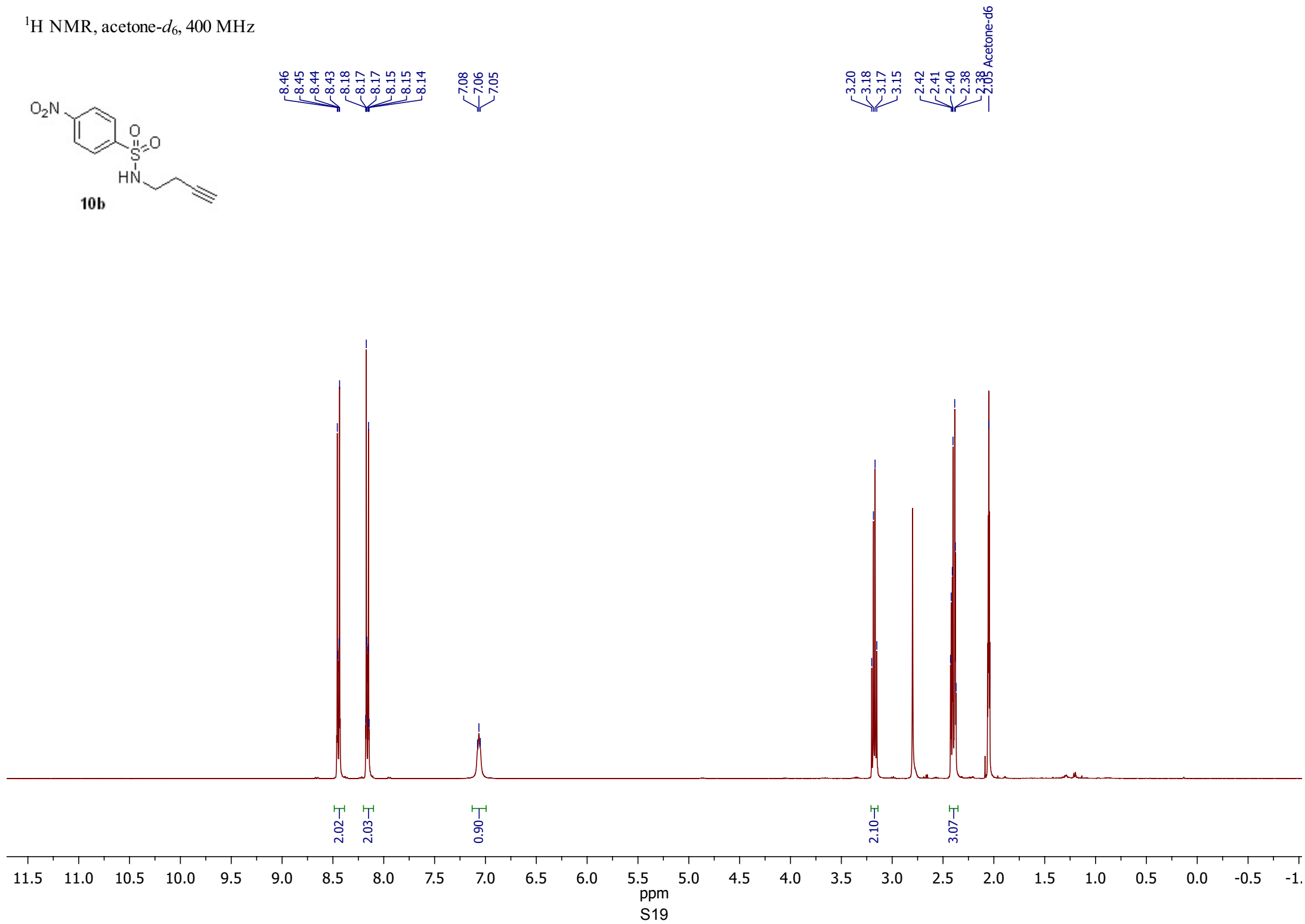
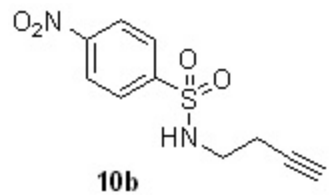
126.6  
124.3  
122.8  
121.6  
121.4  
118.3

68.4  
65.7

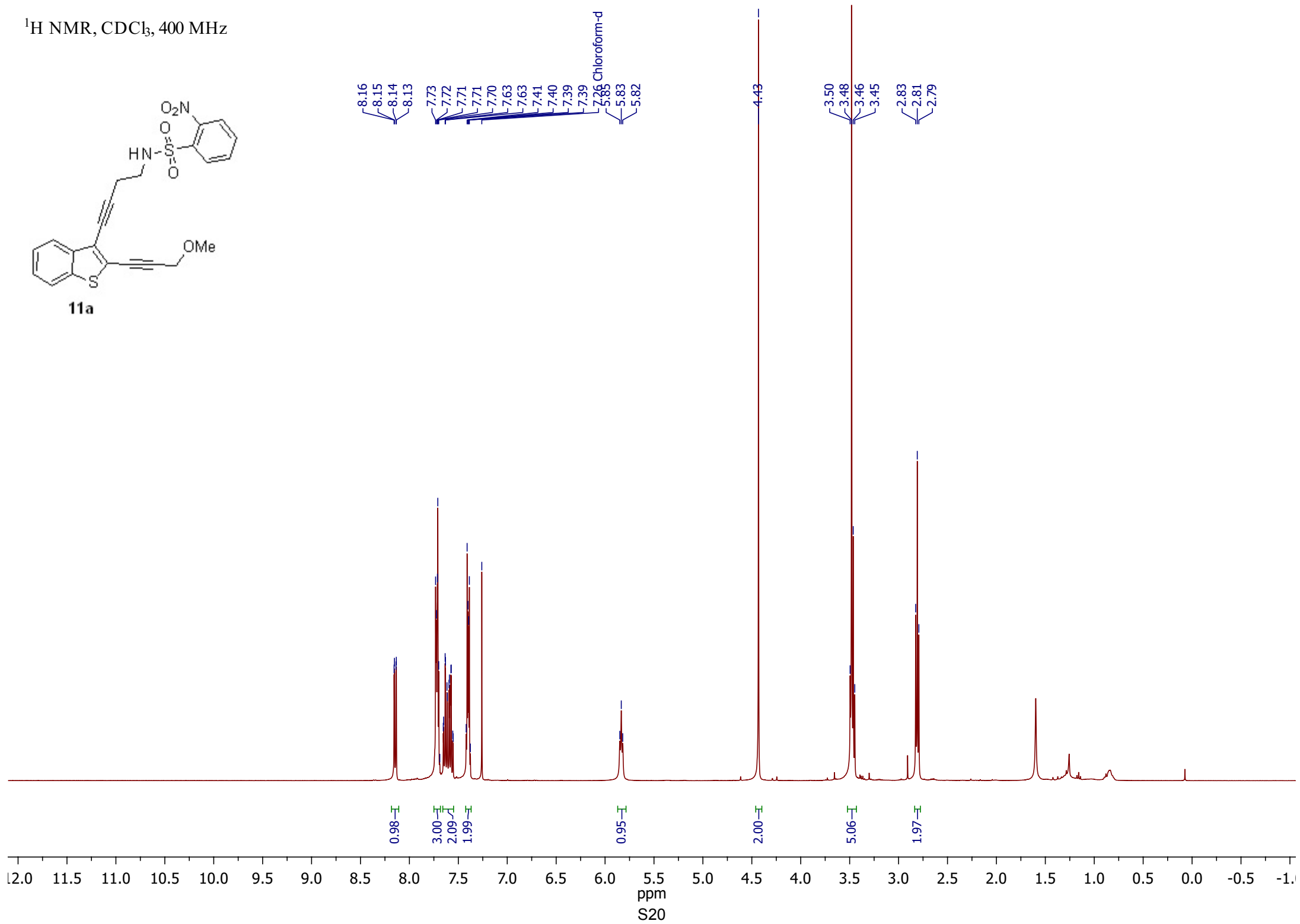
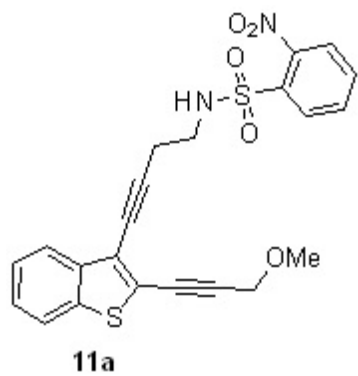
28.7



$^1\text{H}$  NMR, acetone- $d_6$ , 400 MHz

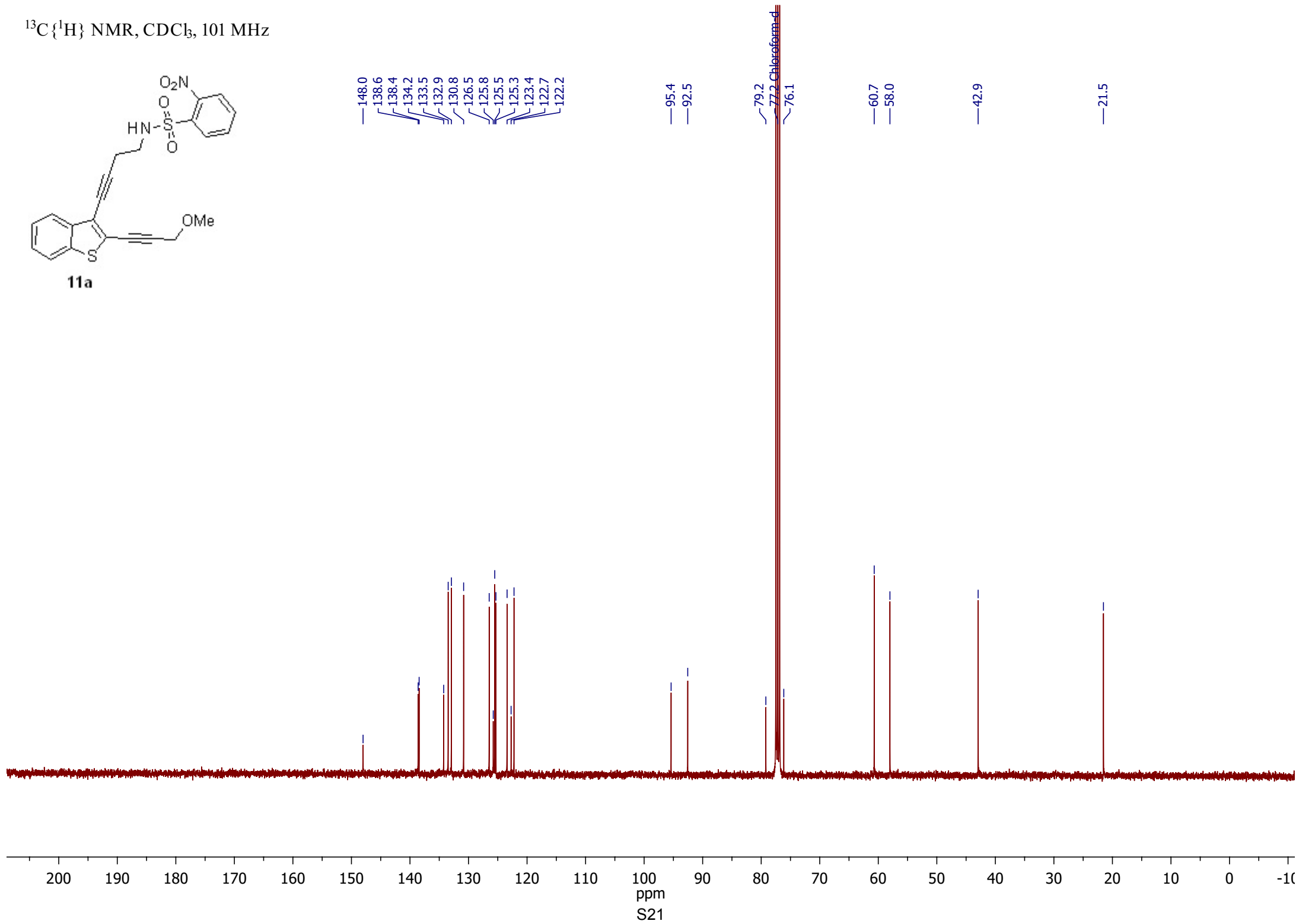
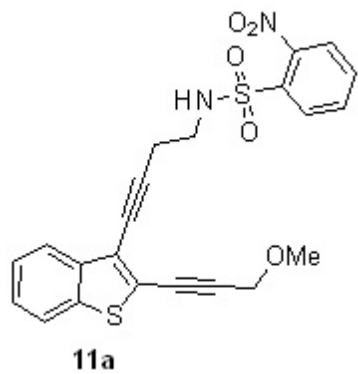


$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz

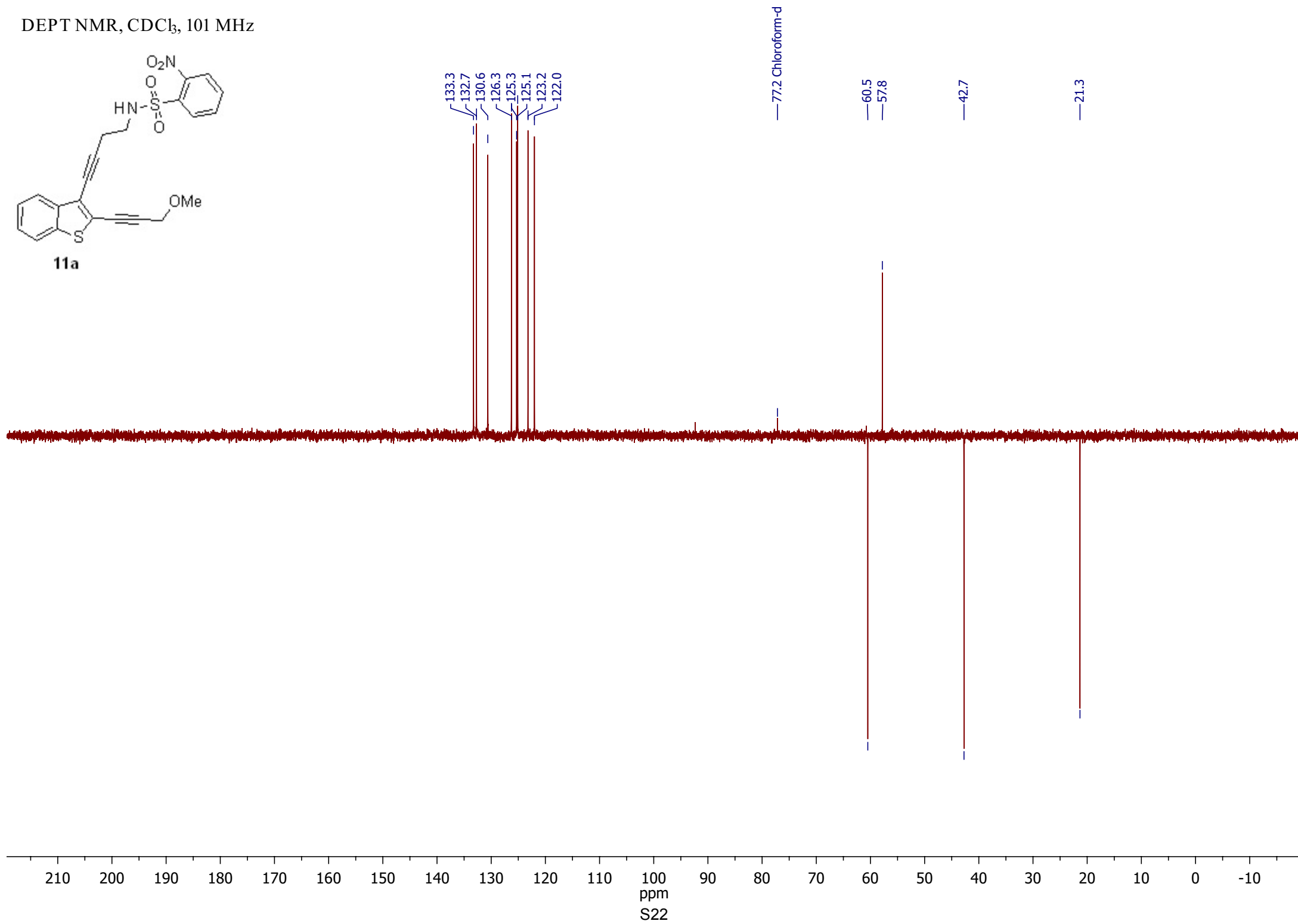
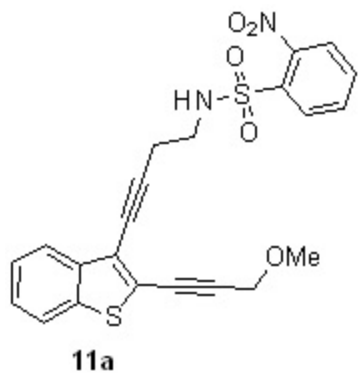




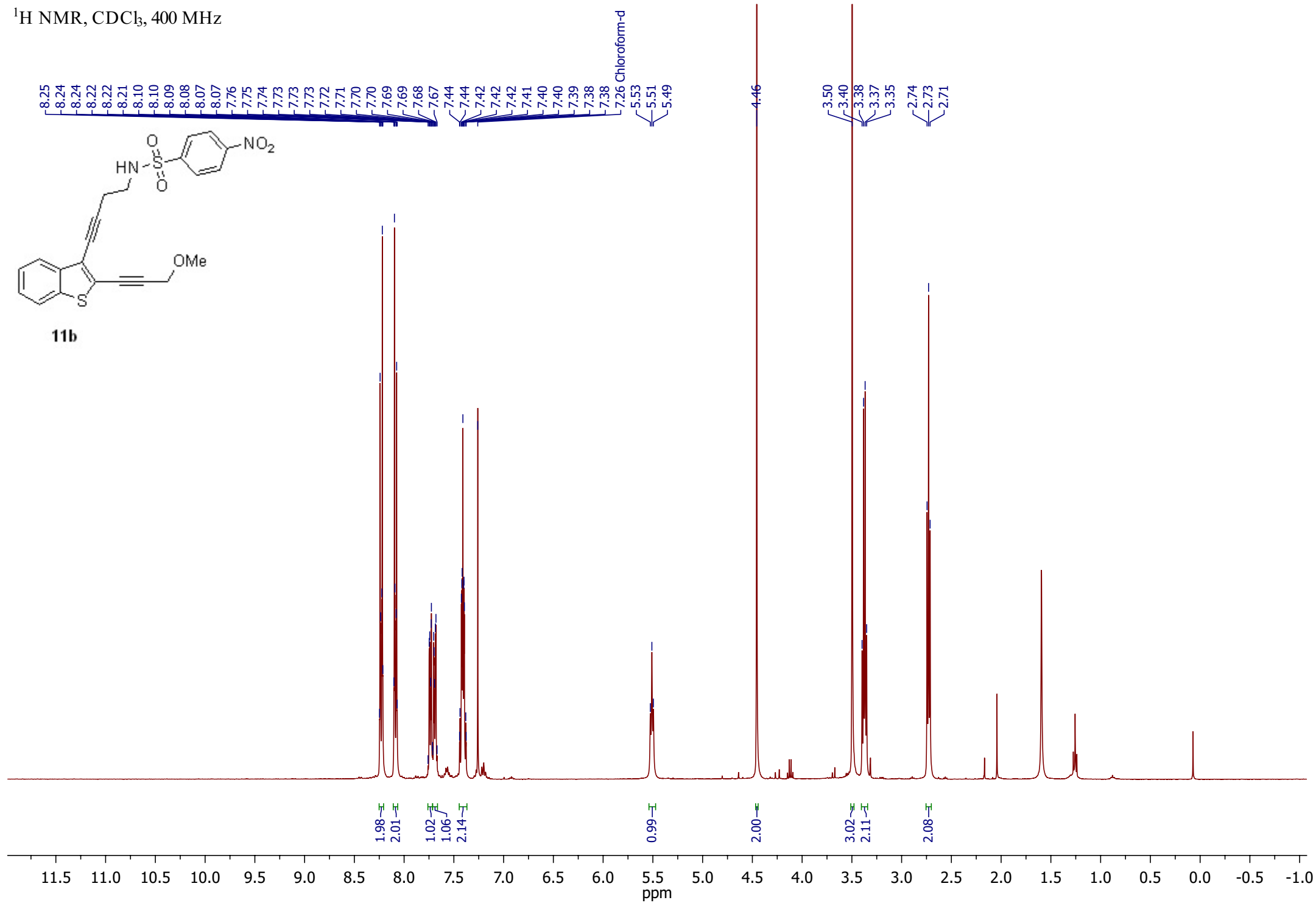
$^{13}\text{C}\{^1\text{H}\}$  NMR,  $\text{CDCl}_3$ , 101 MHz



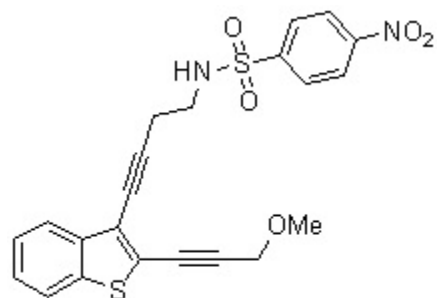
DEPT NMR, CDCl<sub>3</sub>, 101 MHz



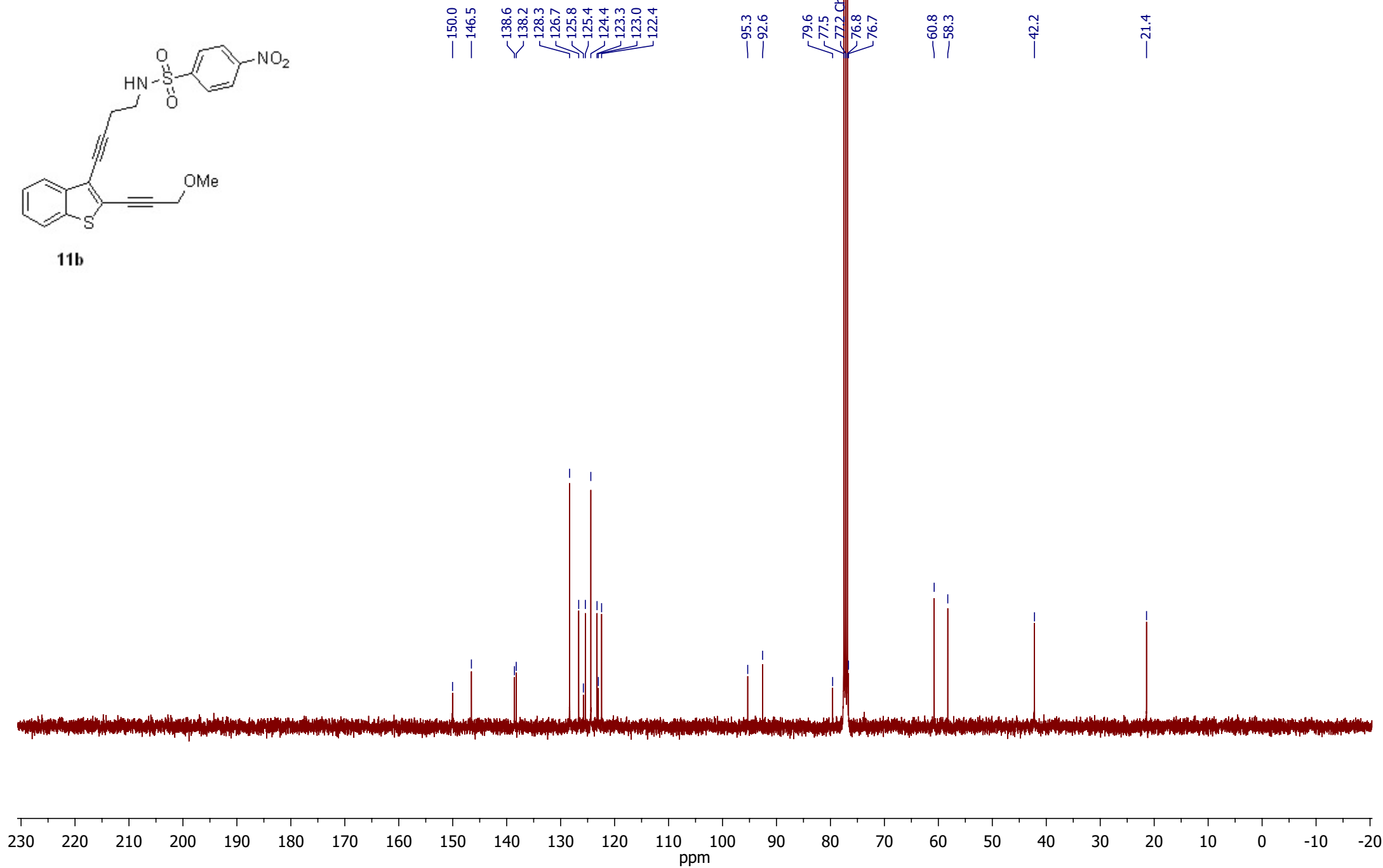
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



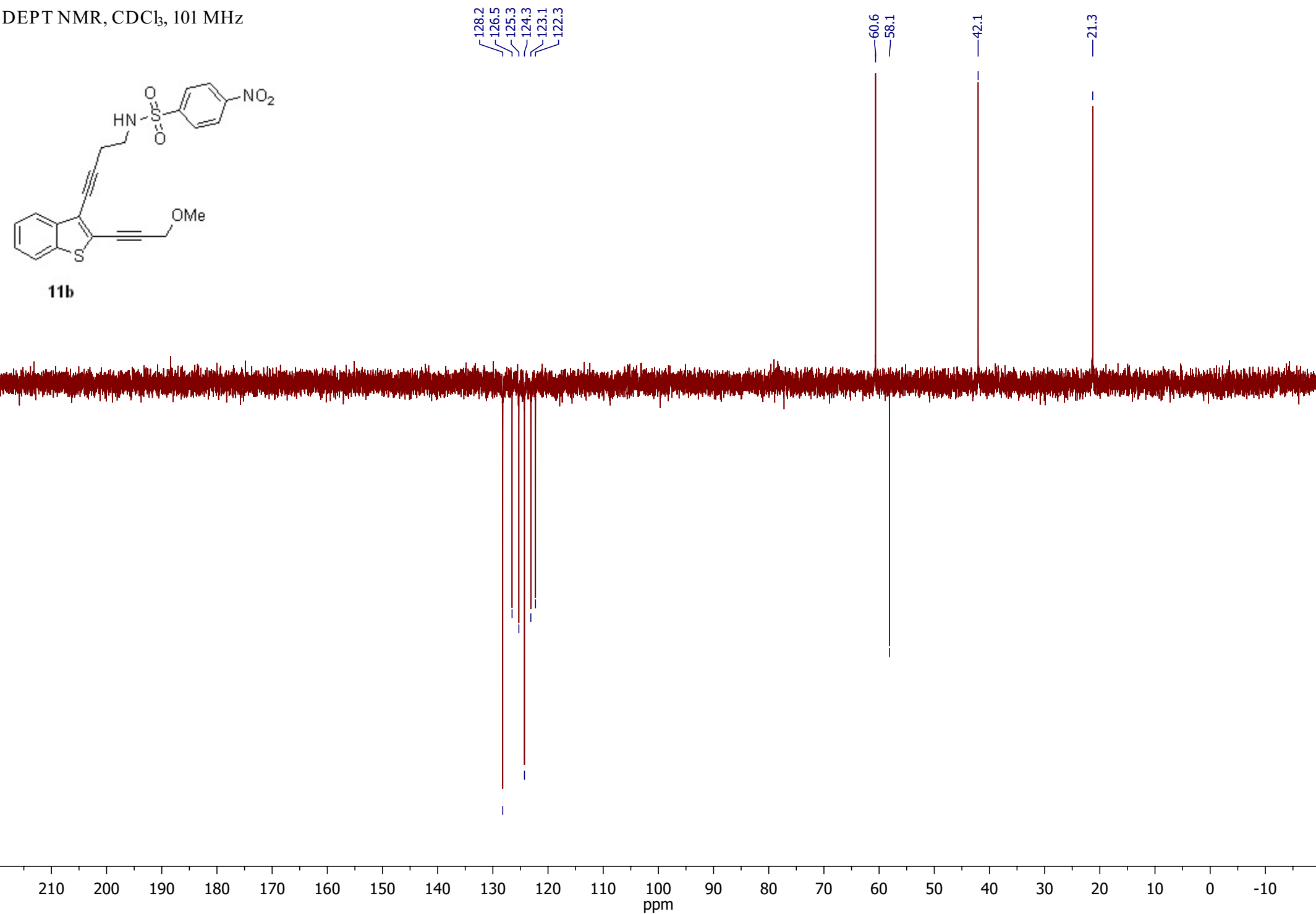
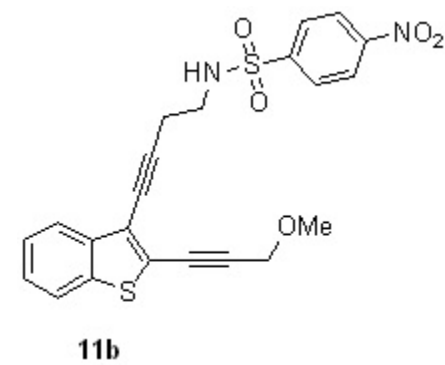
$^{13}\text{C}\{^1\text{H}\}$  NMR,  $\text{CDCl}_3$ , 101 MHz



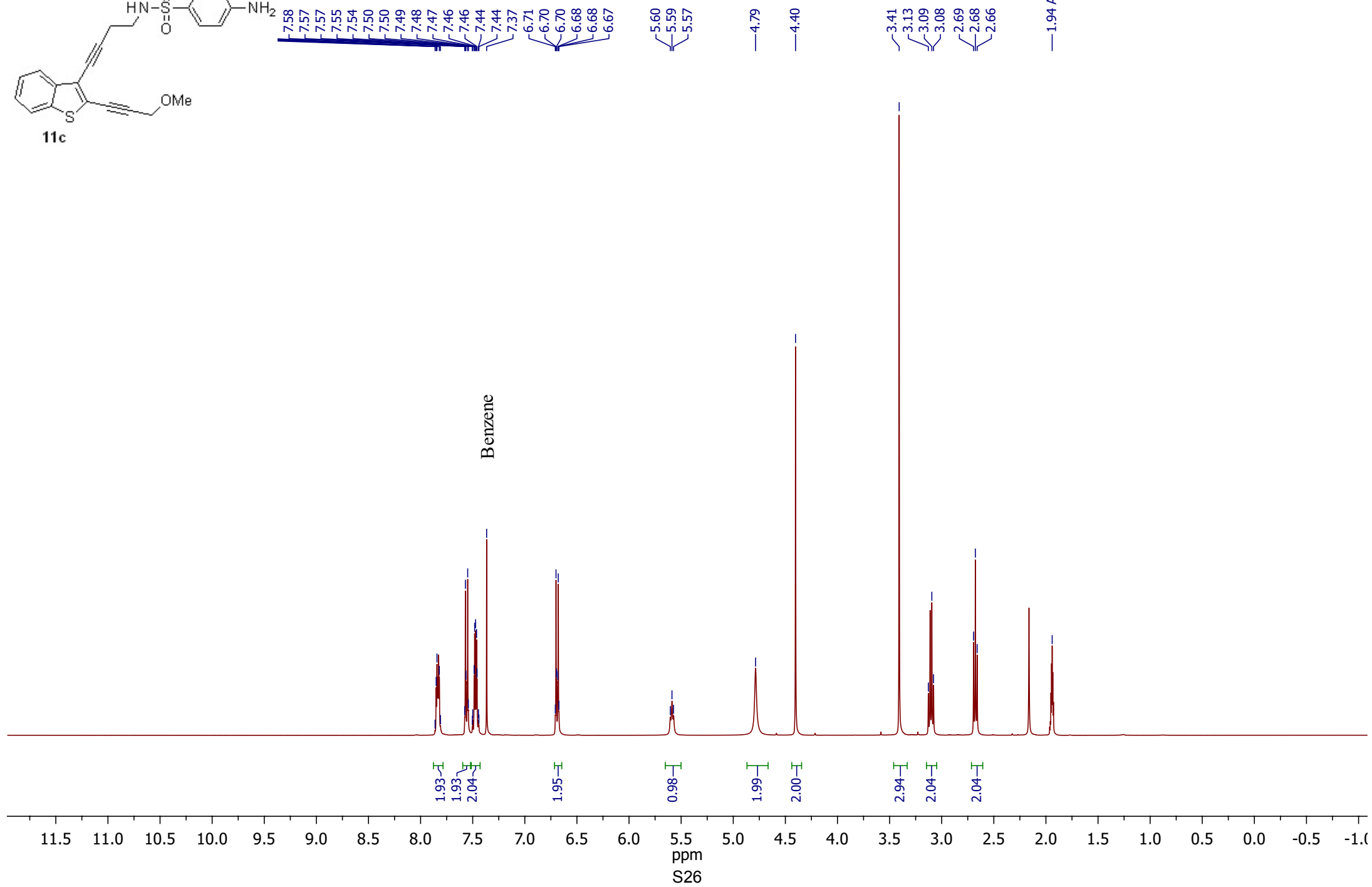
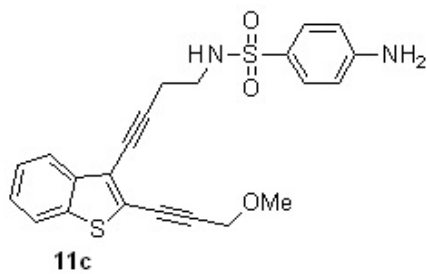
**11b**



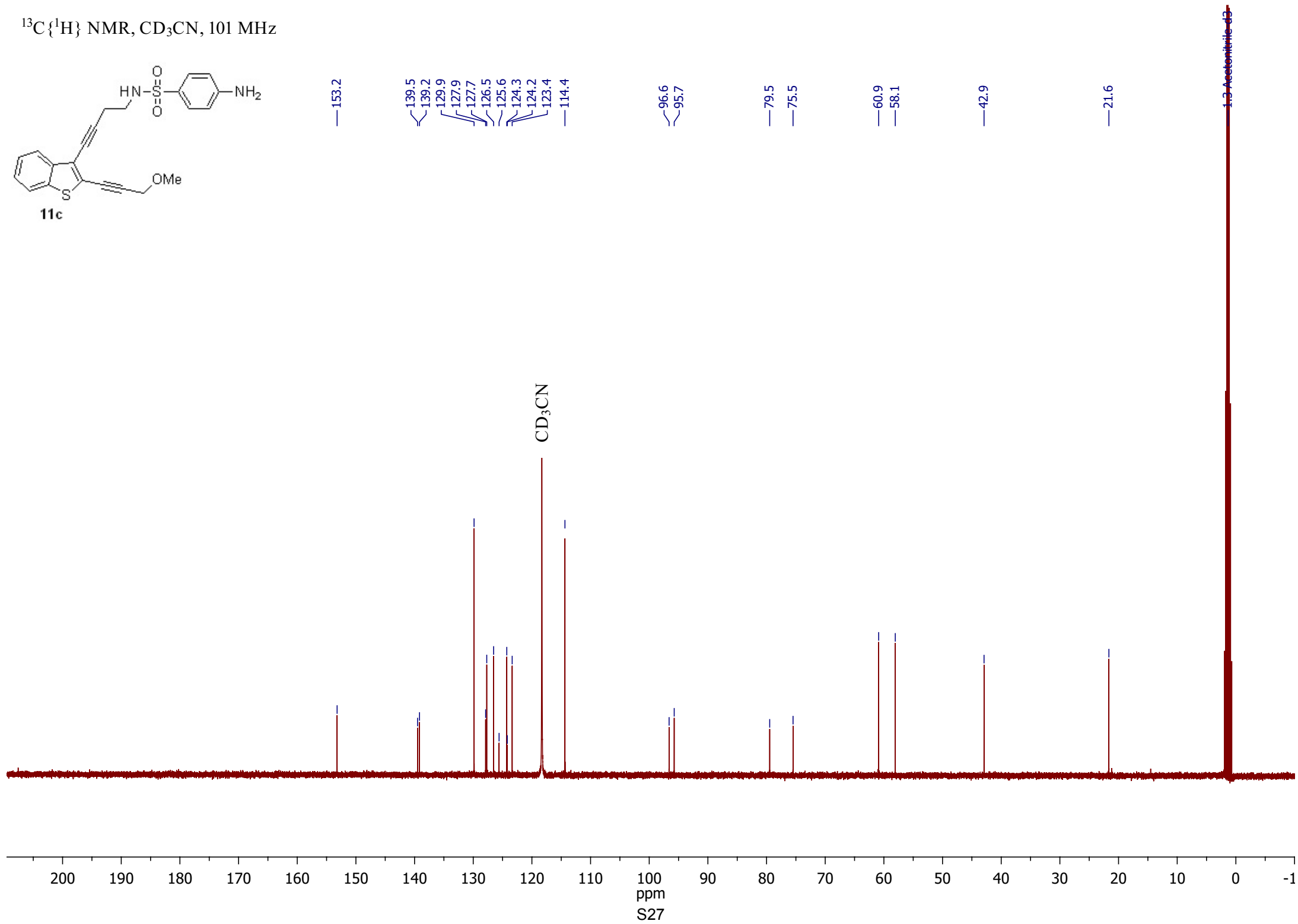
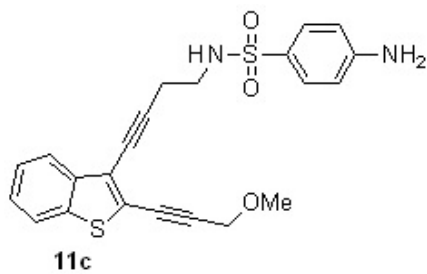
DEPT NMR, CDCl<sub>3</sub>, 101 MHz



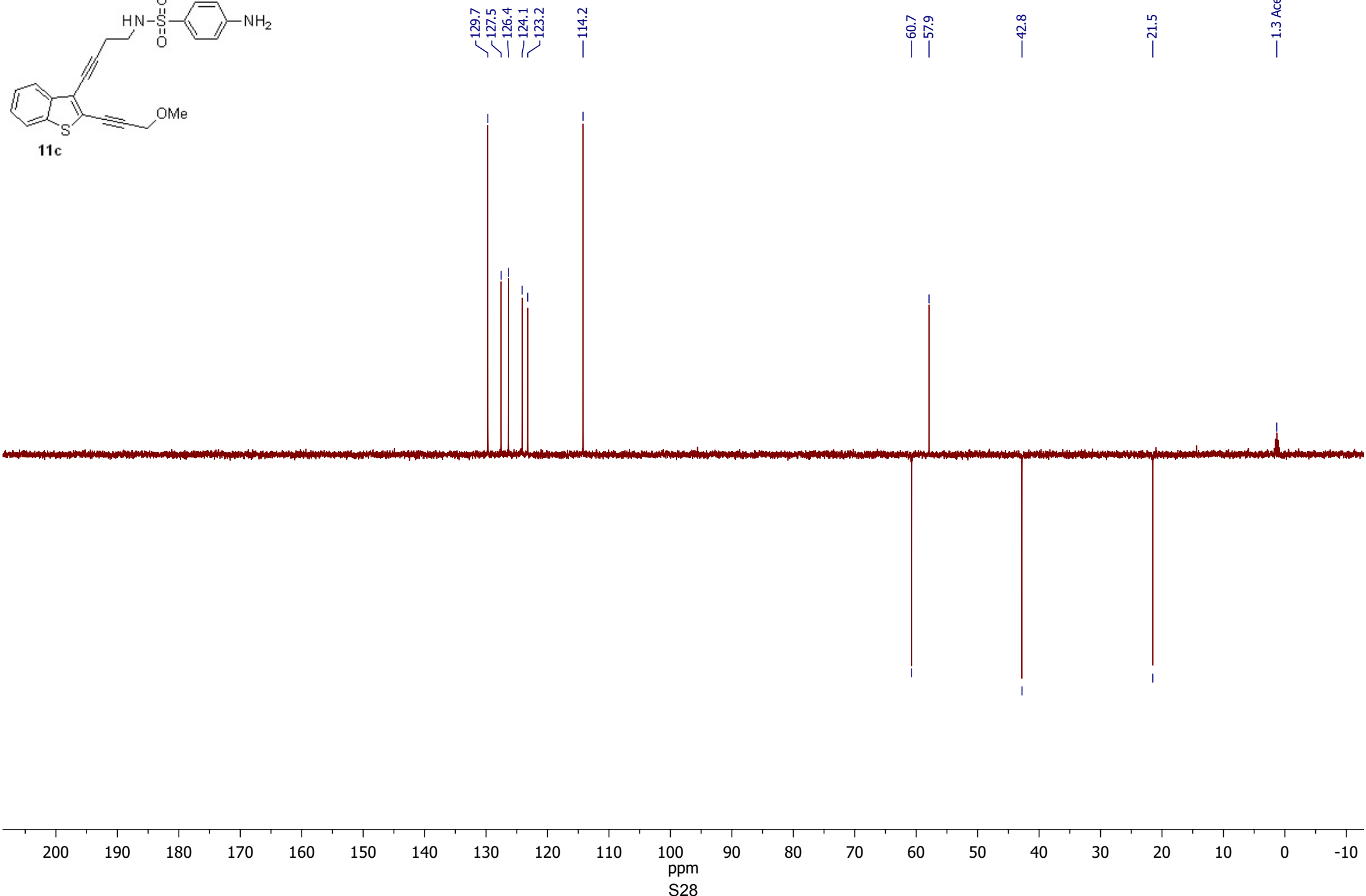
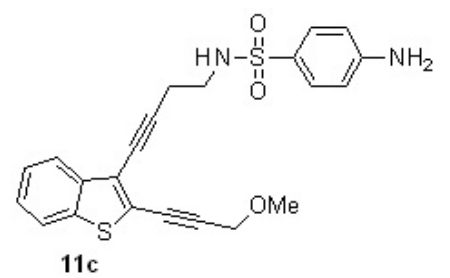
$^1\text{H}$  NMR,  $\text{CD}_3\text{CN}$ , 400 MHz



$^{13}\text{C}\{^1\text{H}\}$  NMR,  $\text{CD}_3\text{CN}$ , 101 MHz

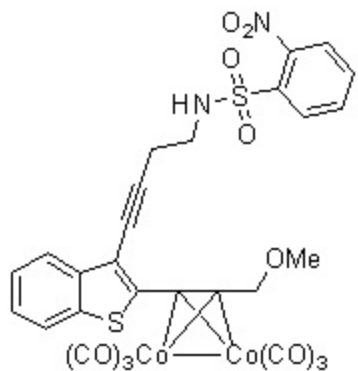


DEPT NMR, CD<sub>3</sub>CN, 101 MHz

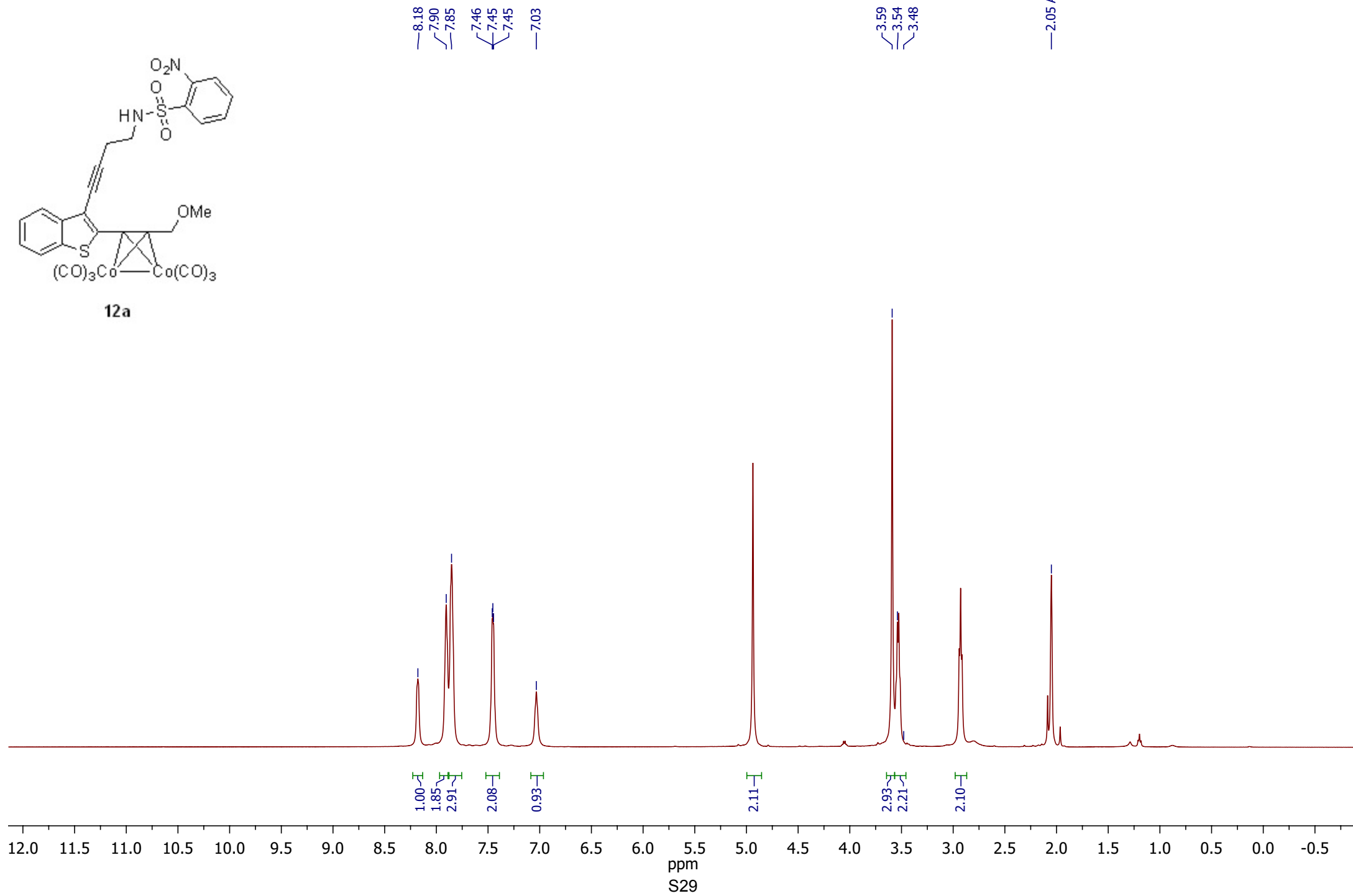




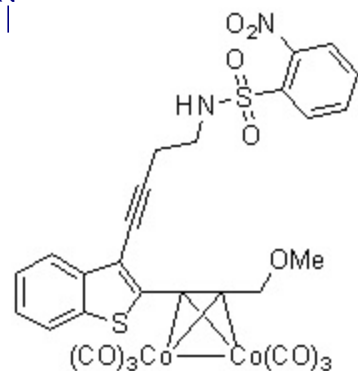
$^1\text{H}$  NMR, acetone- $d_6$ , 500 MHz



**12a**



$^{13}\text{C}\{^1\text{H}\}$  NMR, acetone- $d_6$ , 125 MHz



**12a**

200.1

149.1

146.3

141.7

139.4

134.9

134.5

133.6

131.3

126.8

126.3

125.8

123.9

123.2

118.6

98.0

97.5

77.8

76.9

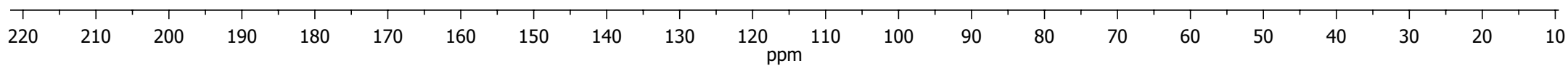
73.9

59.3

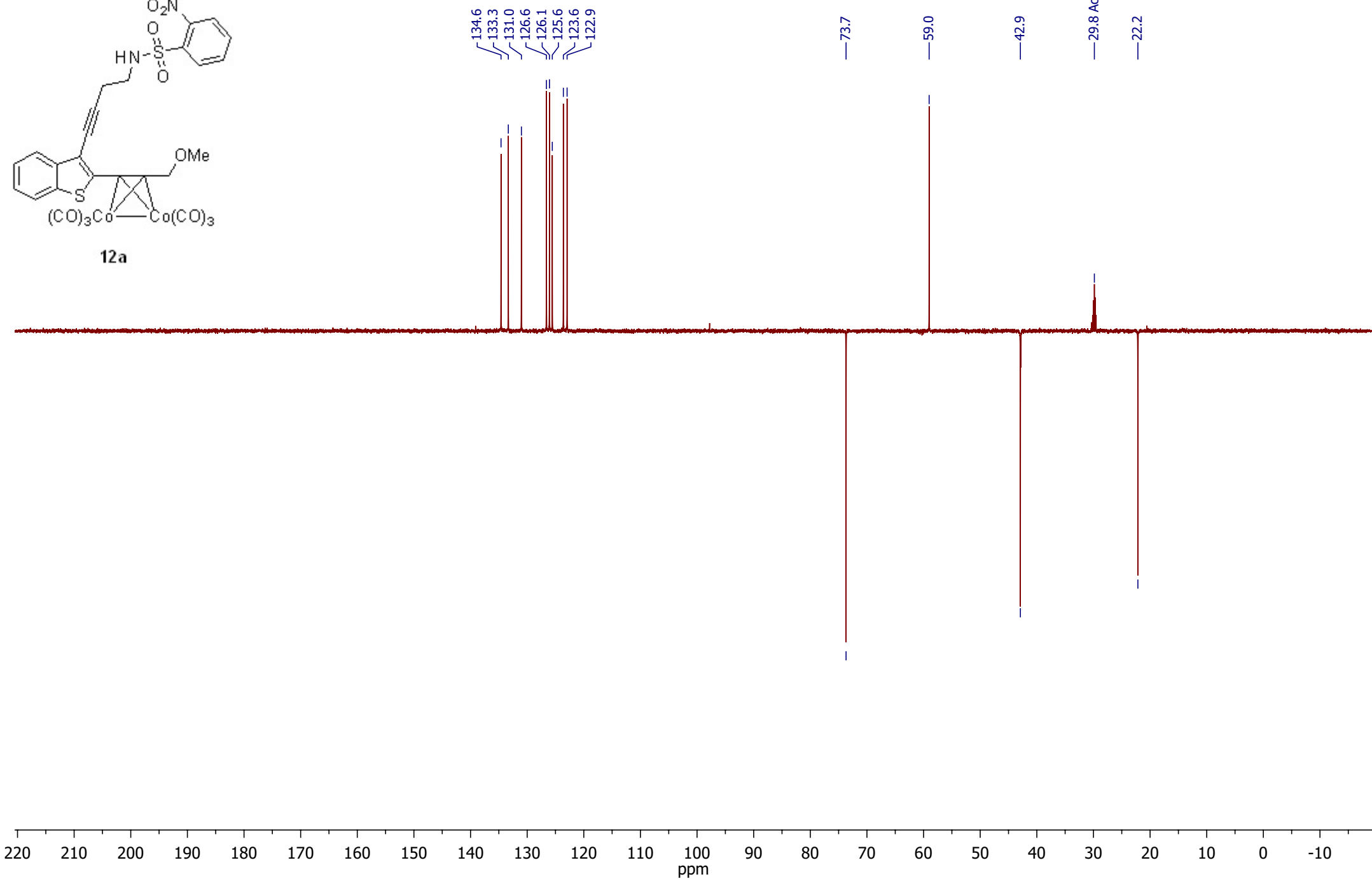
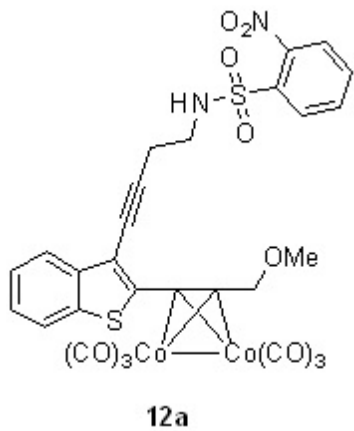
43.2

29.8 Acetone- $d_6$

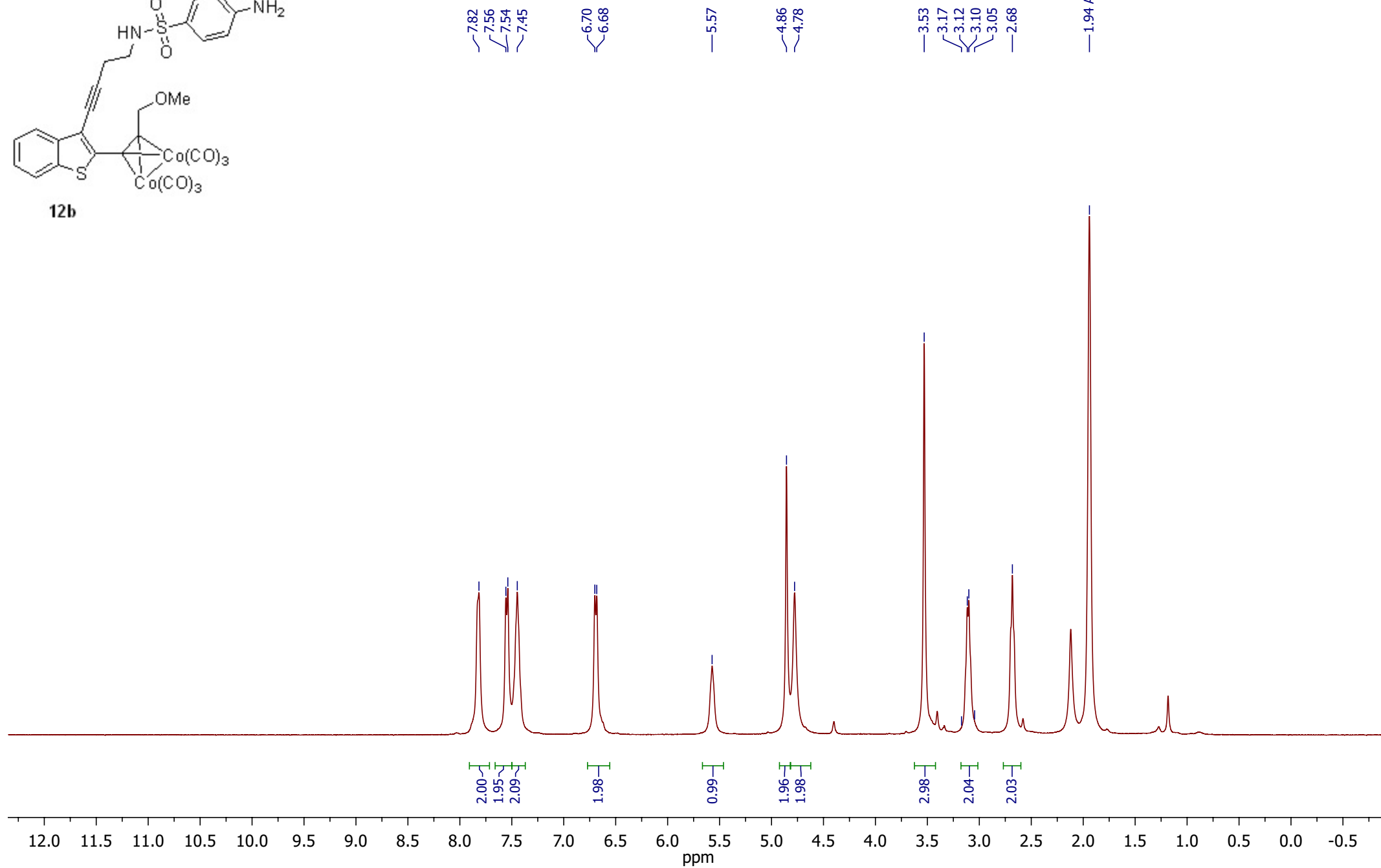
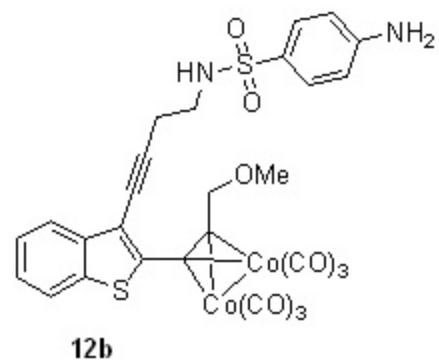
22.4



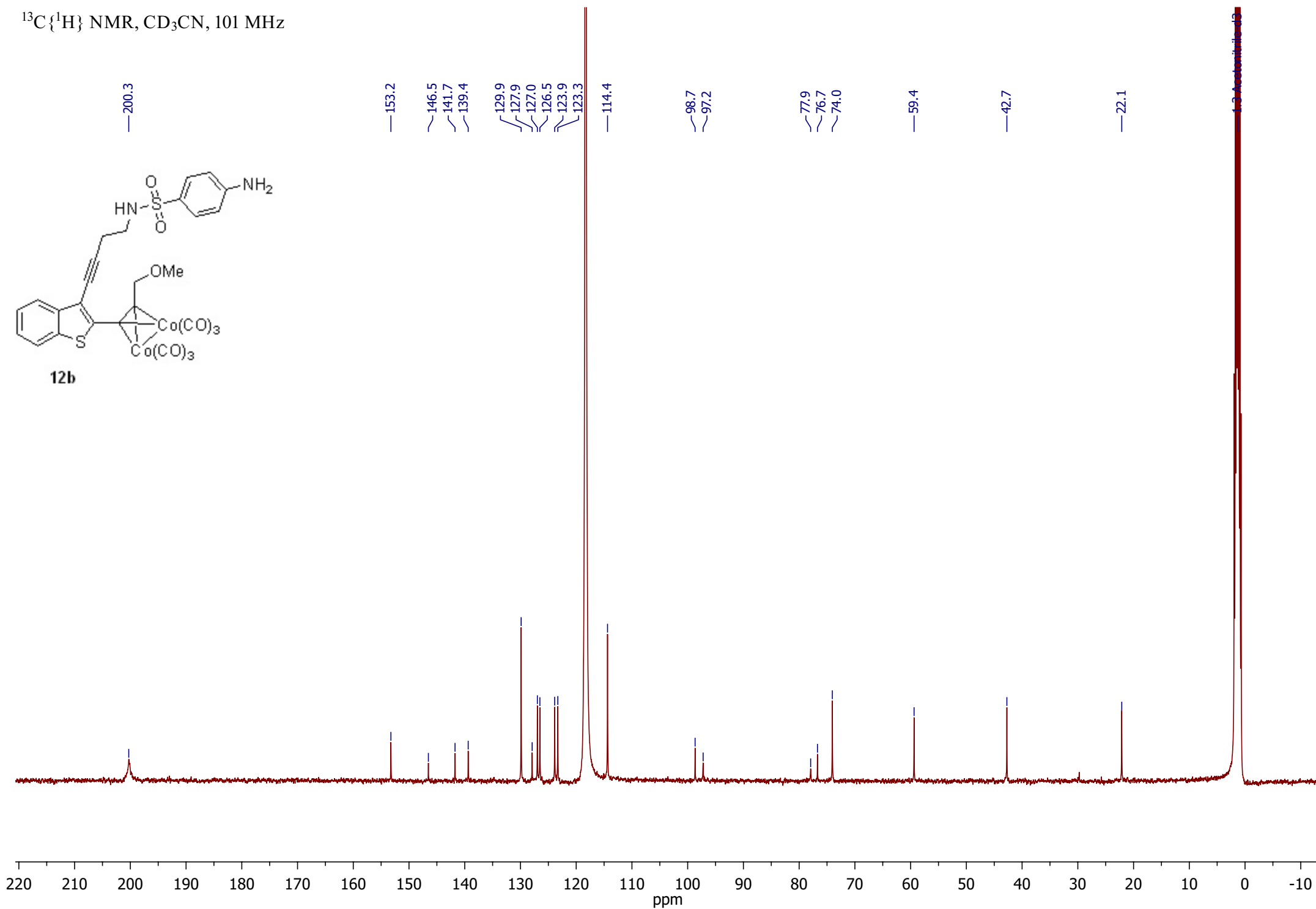
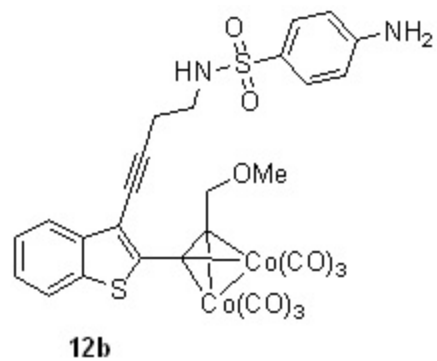
DEPT NMR, acetone-*d*<sub>6</sub>, 125 MHz



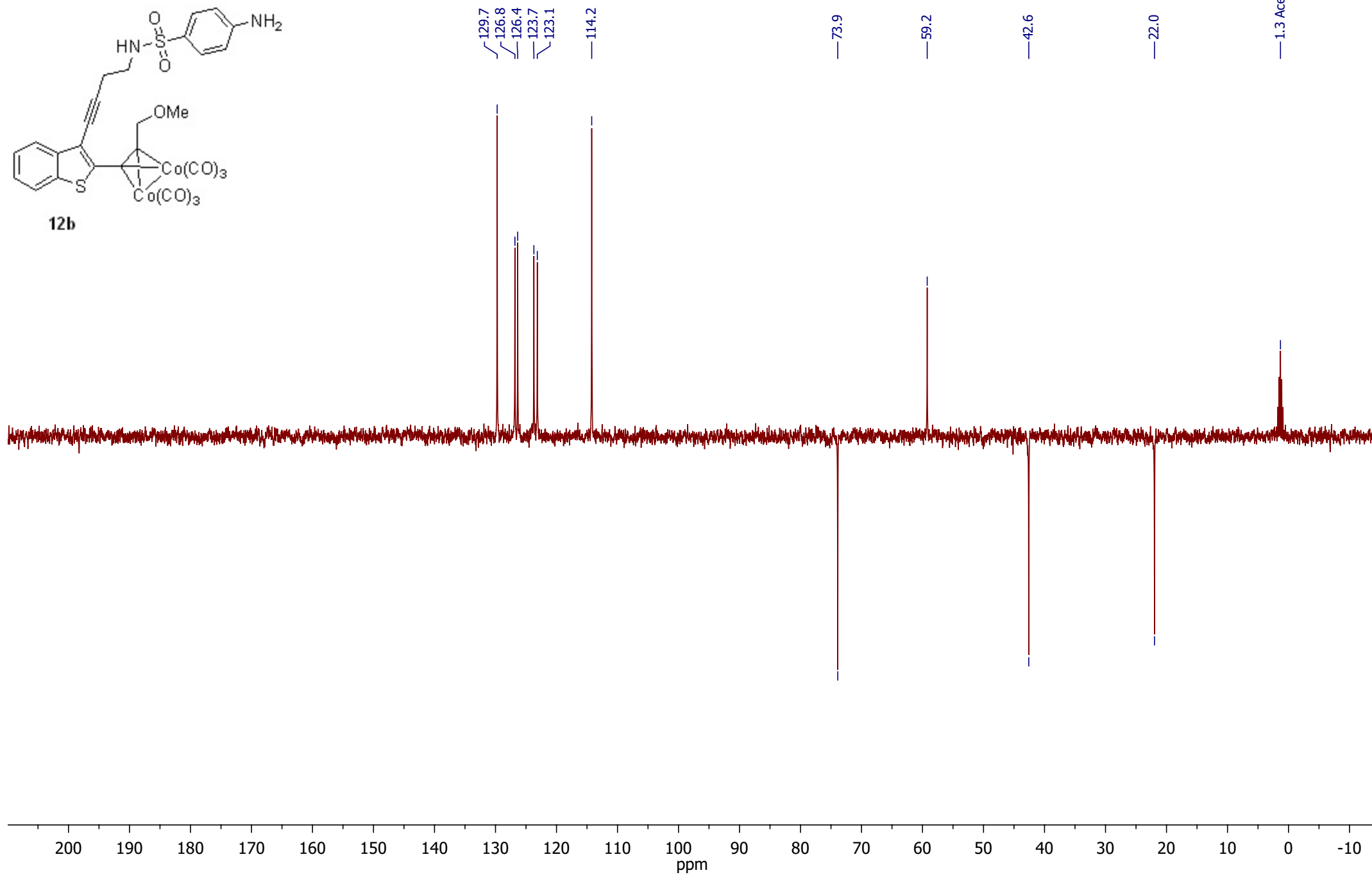
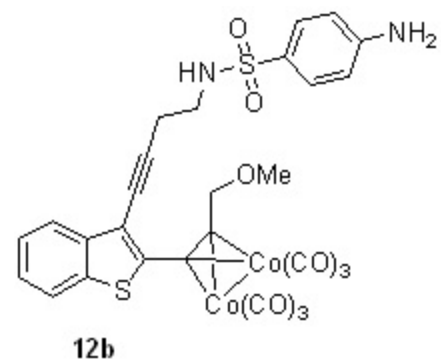
$^1\text{H}$  NMR,  $\text{CD}_3\text{CN}$ , 400 MHz



$^{13}\text{C}\{^1\text{H}\}$  NMR,  $\text{CD}_3\text{CN}$ , 101 MHz



DEPT NMR, CD<sub>3</sub>CN, 101 MHz



<sup>1</sup>H NMR, acetone-*d*<sub>6</sub>, 400 MHz

**12c**

Chemical structure of **12c** is shown above the spectrum. The structure includes a thienothiopyran core, a cobalt complex, a methoxy group, and a side chain containing a sulfonamide and an alkyne.

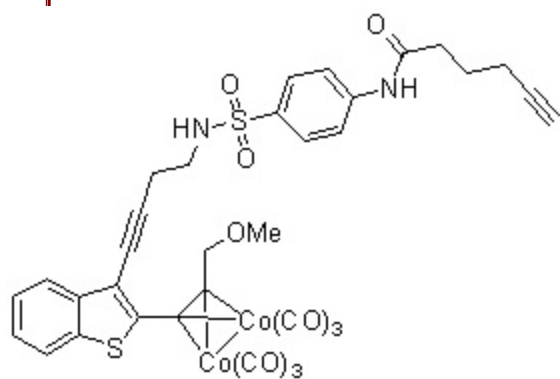
Chemical shifts (ppm) are labeled above the peaks:

- 7.90, 7.89, 7.88, 7.87, 7.85, 7.83, 7.81
- 7.47, 7.46, 7.45, 7.45, 6.77, 6.75, 6.74
- 4.93
- 3.58, 3.32, 3.30, 3.28, 3.27
- 2.84, 2.83, 2.81, 2.57, 2.55, 2.53
- 2.37, 2.36, 2.31, 2.30, 2.29, 2.27, 2.27
- 2.05 Acetone-*d*<sub>6</sub>, 1.92, 1.90, 1.88, 1.86, 1.85

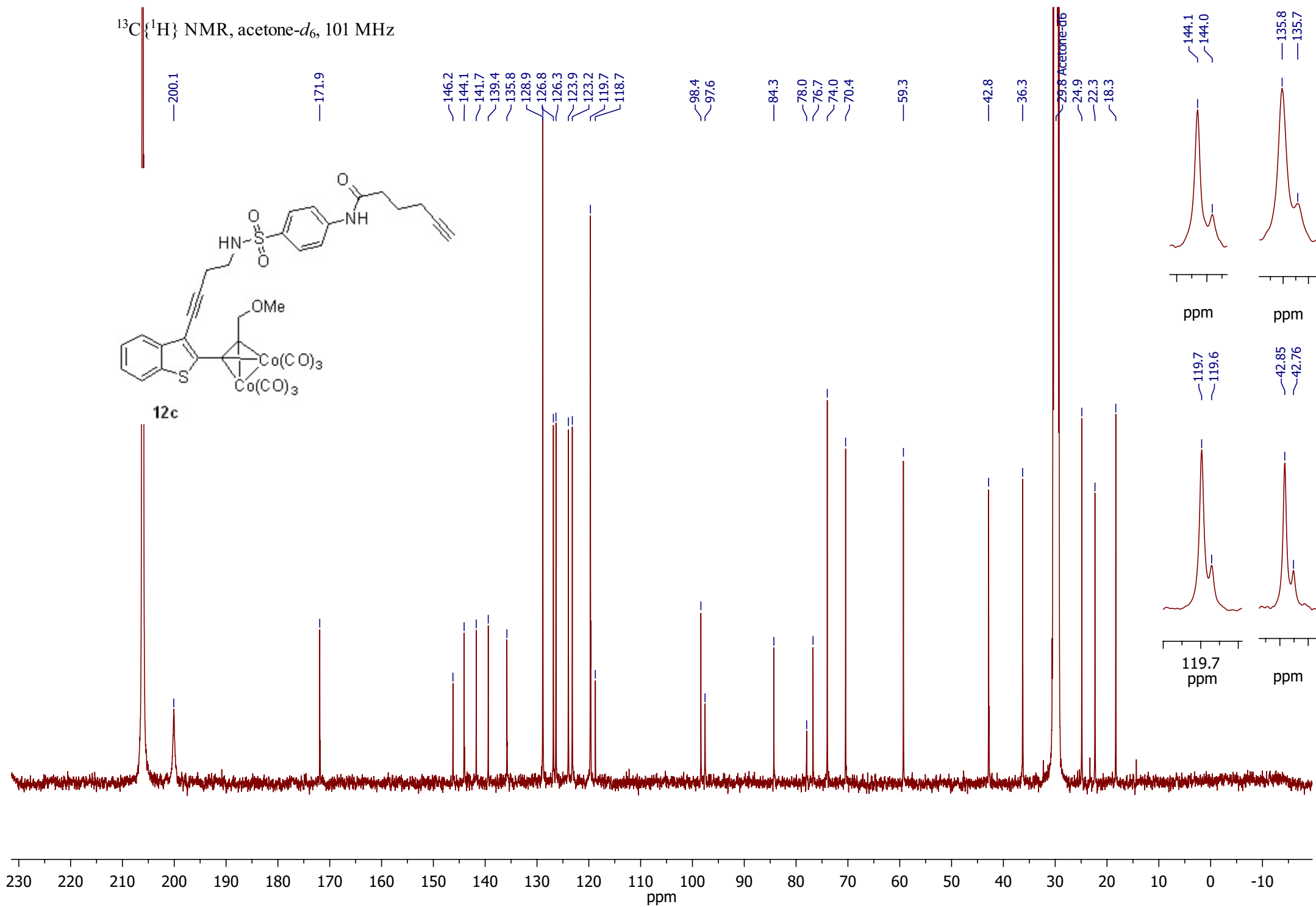
Integration values are shown below the baseline:

- 0.85
- 6.00
- 2.01
- 0.67
- 2.01
- 3.06
- 2.09
- 2.04
- 2.04
- 0.93
- 2.07
- 2.11

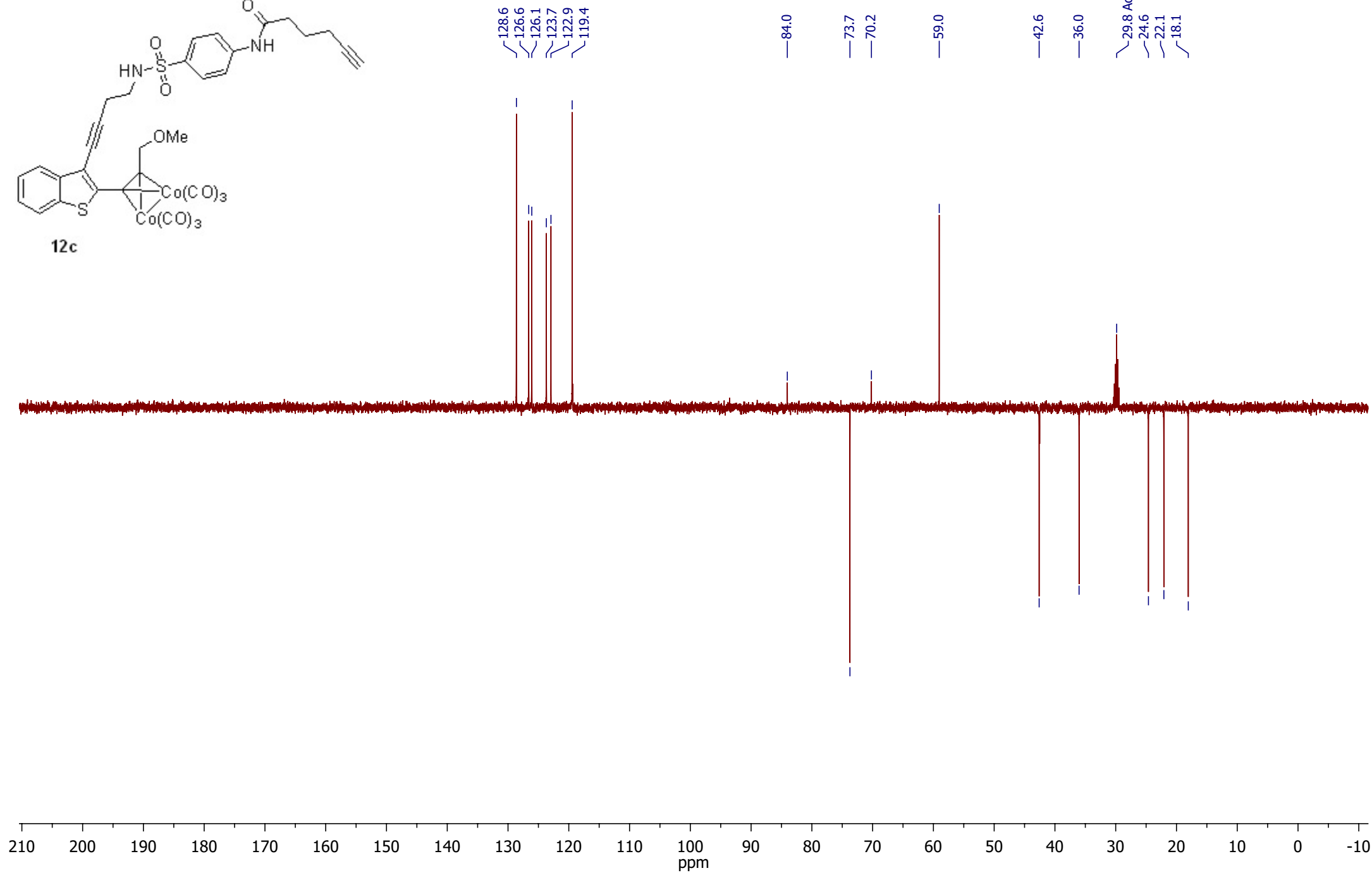
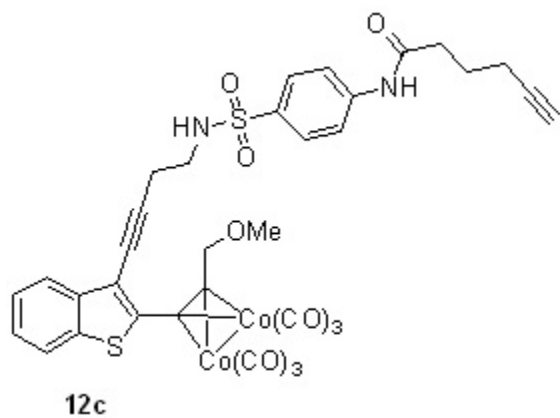
$^{13}\text{C}\{^1\text{H}\}$  NMR, acetone- $d_6$ , 101 MHz



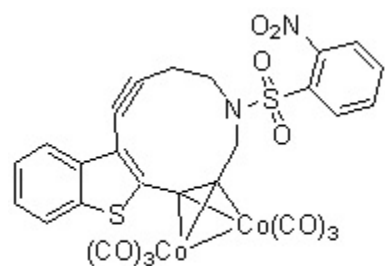
**12c**



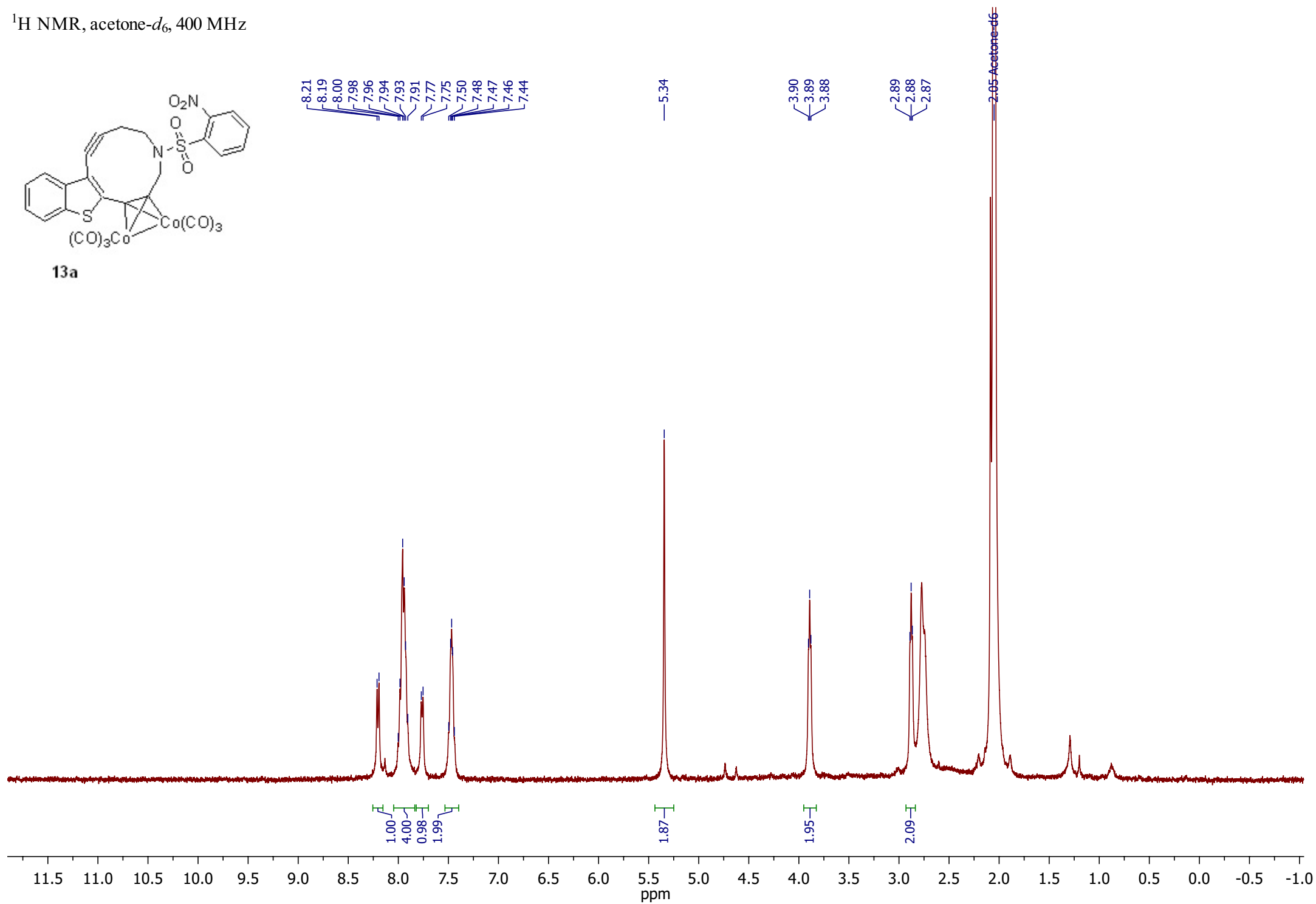


DEPT NMR, acetone- $d_6$ , 101 MHz

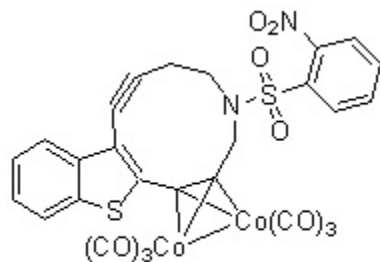
$^1\text{H}$  NMR, acetone- $d_6$ , 400 MHz



**13a**



$^{13}\text{C}\{^1\text{H}\}$  NMR, acetone- $d_6$ , 101 MHz



**13a**

199.8  
151.7  
150.1  
139.8  
139.4  
135.5  
133.1  
131.9  
131.1  
131.1  
126.6  
125.5  
123.6  
123.5  
116.8

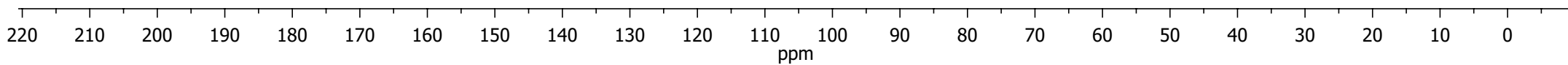
101.5  
98.6

80.7  
79.8

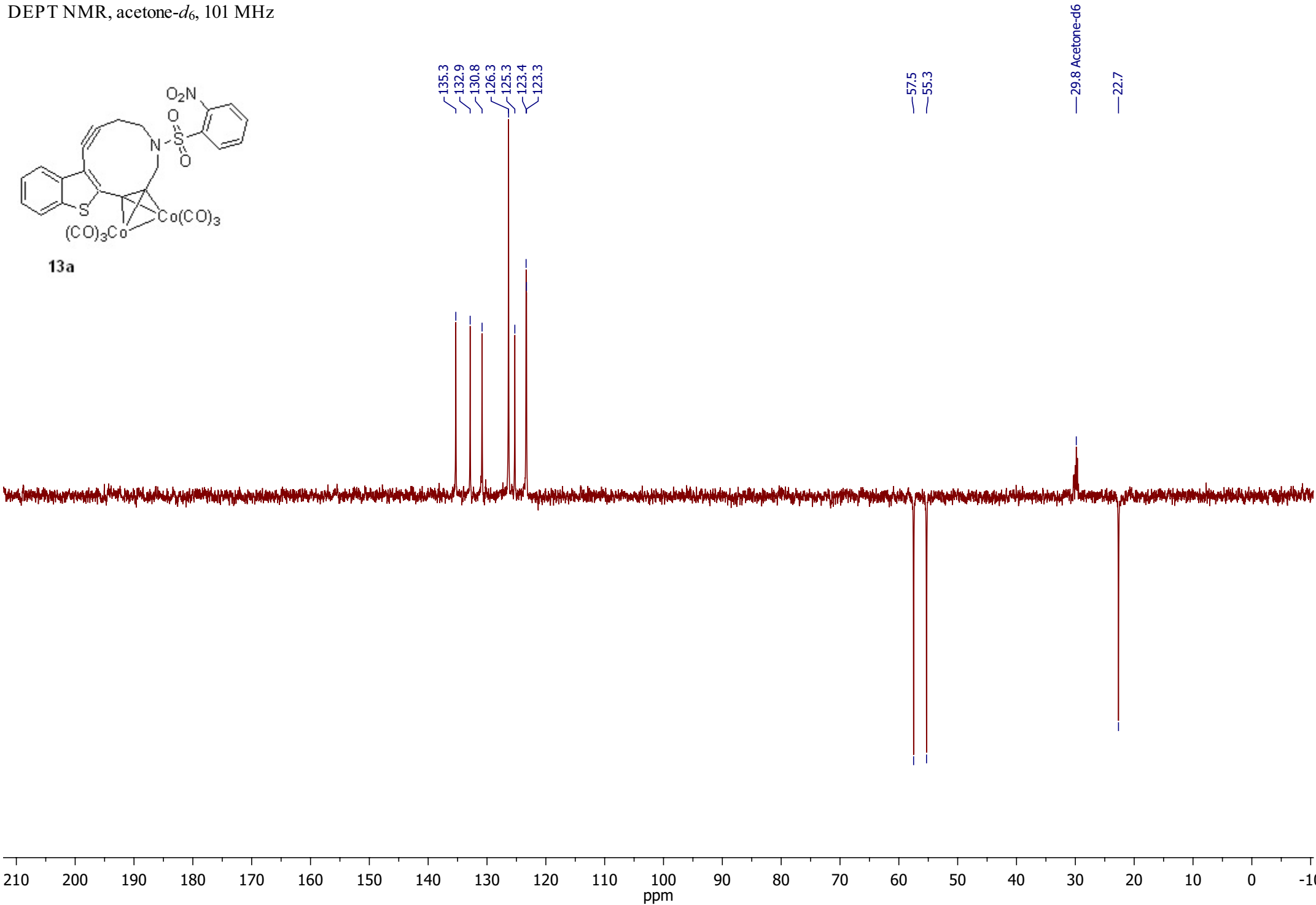
57.7  
55.5

26.8  
26.6  
26.4

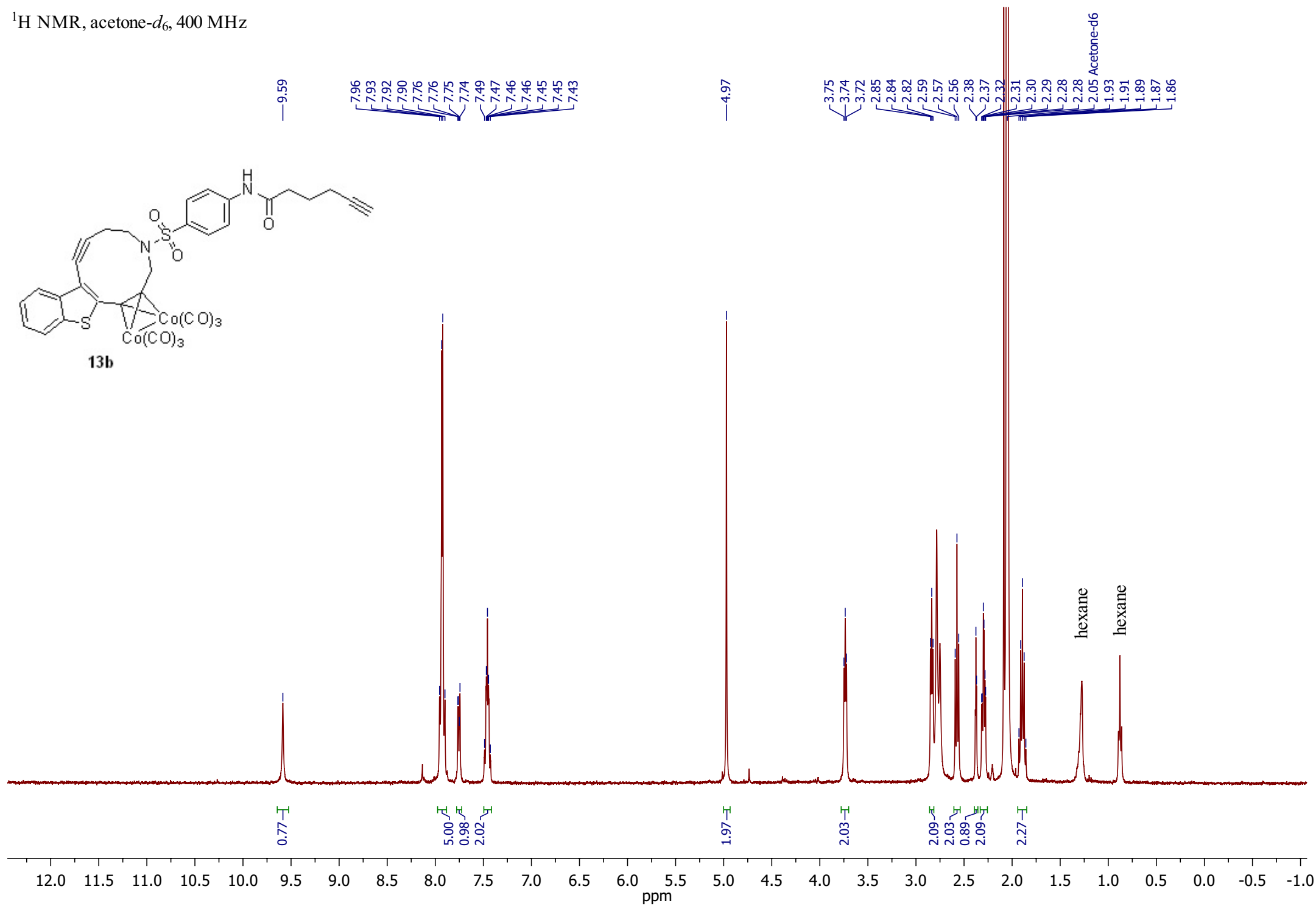
22.9

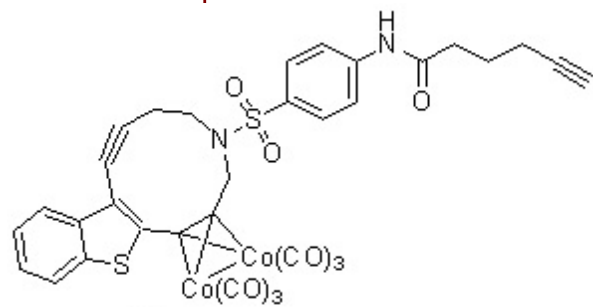


DEPT NMR, acetone-*d*<sub>6</sub>, 101 MHz

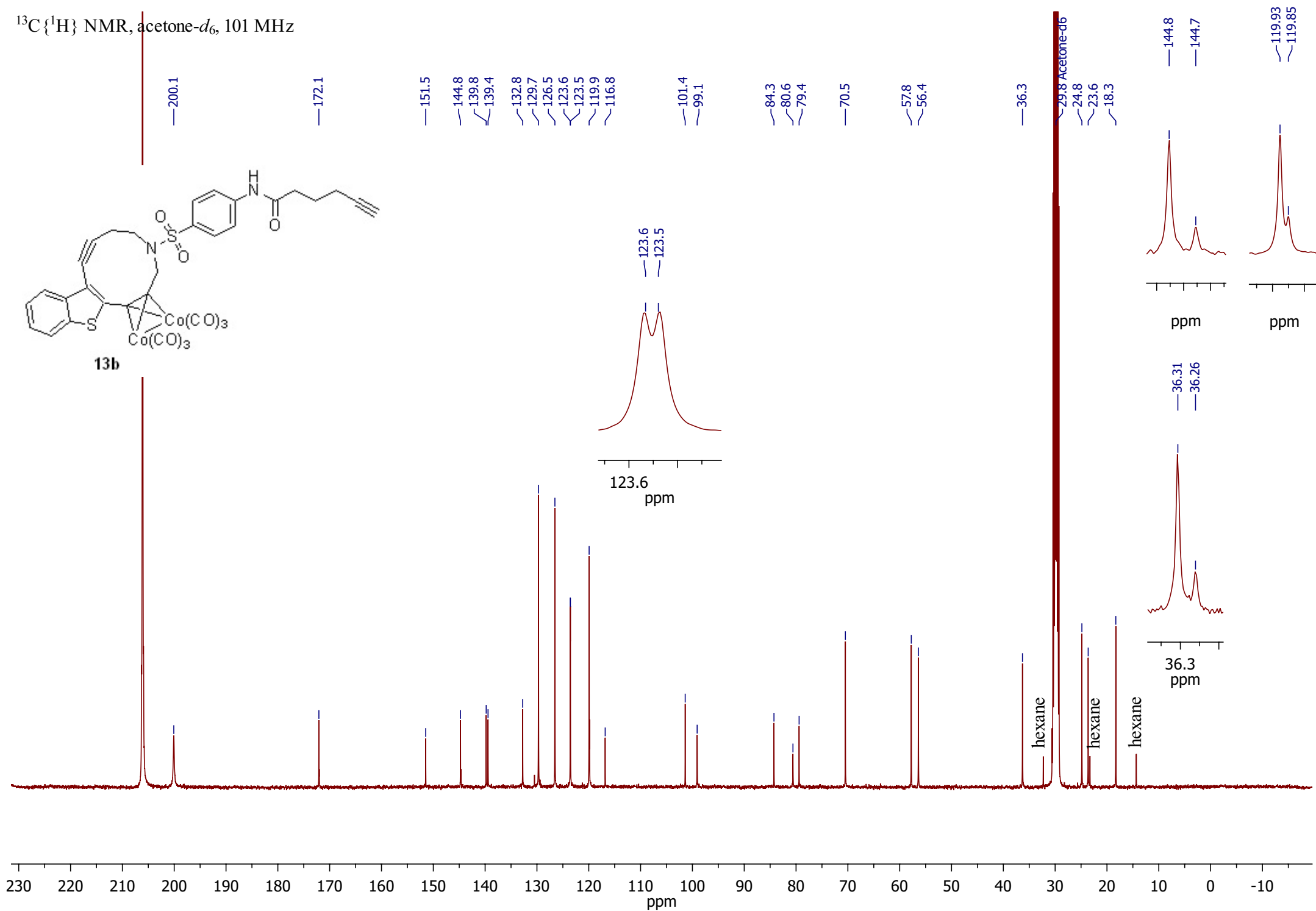


$^1\text{H}$  NMR, acetone- $d_6$ , 400 MHz

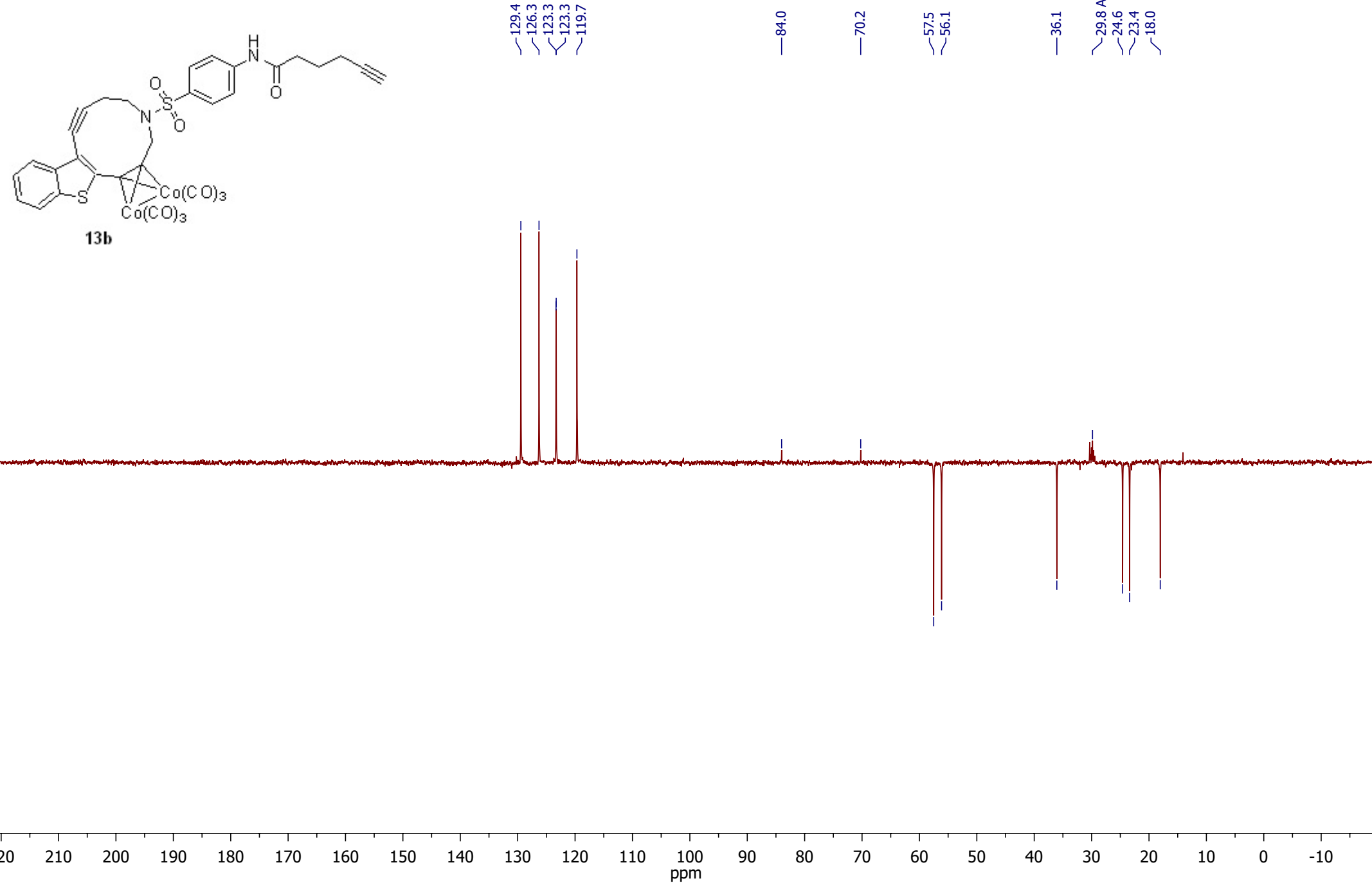


$^{13}\text{C}\{^1\text{H}\}$  NMR, acetone- $d_6$ , 101 MHz

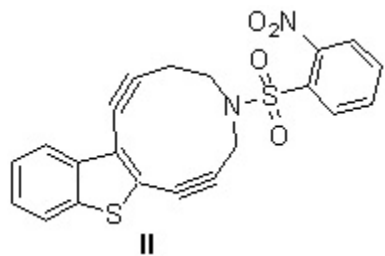
13b



DEPT NMR, acetone-*d*<sub>6</sub>, 101 MHz



$^1\text{H}$  NMR, acetone- $d_6$ , 400 MHz



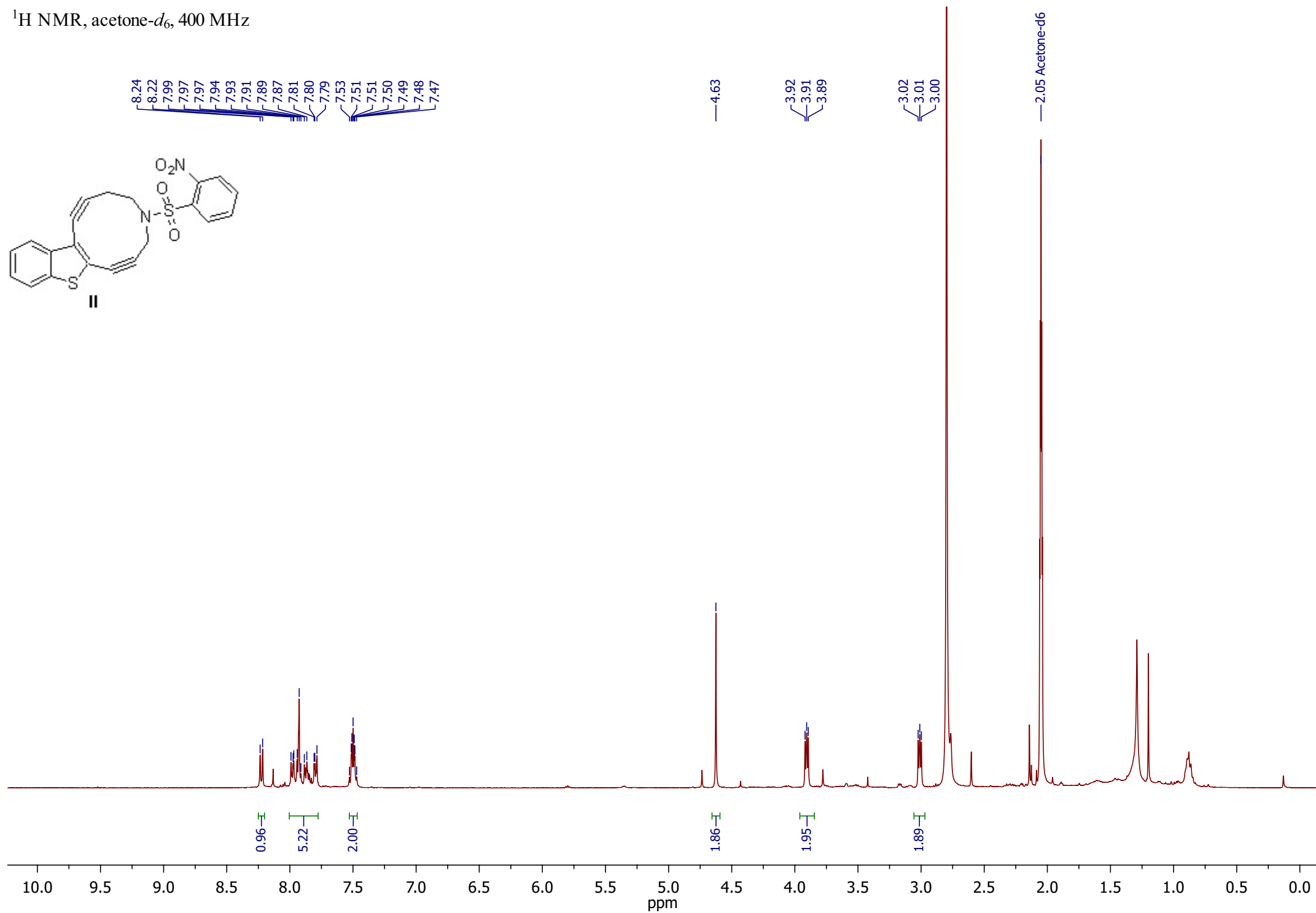
8.24  
8.22  
7.99  
7.97  
7.97  
7.94  
7.93  
7.91  
7.89  
7.87  
7.81  
7.80  
7.79  
7.53  
7.51  
7.51  
7.50  
7.49  
7.48  
7.47

4.63

3.92  
3.91  
3.89

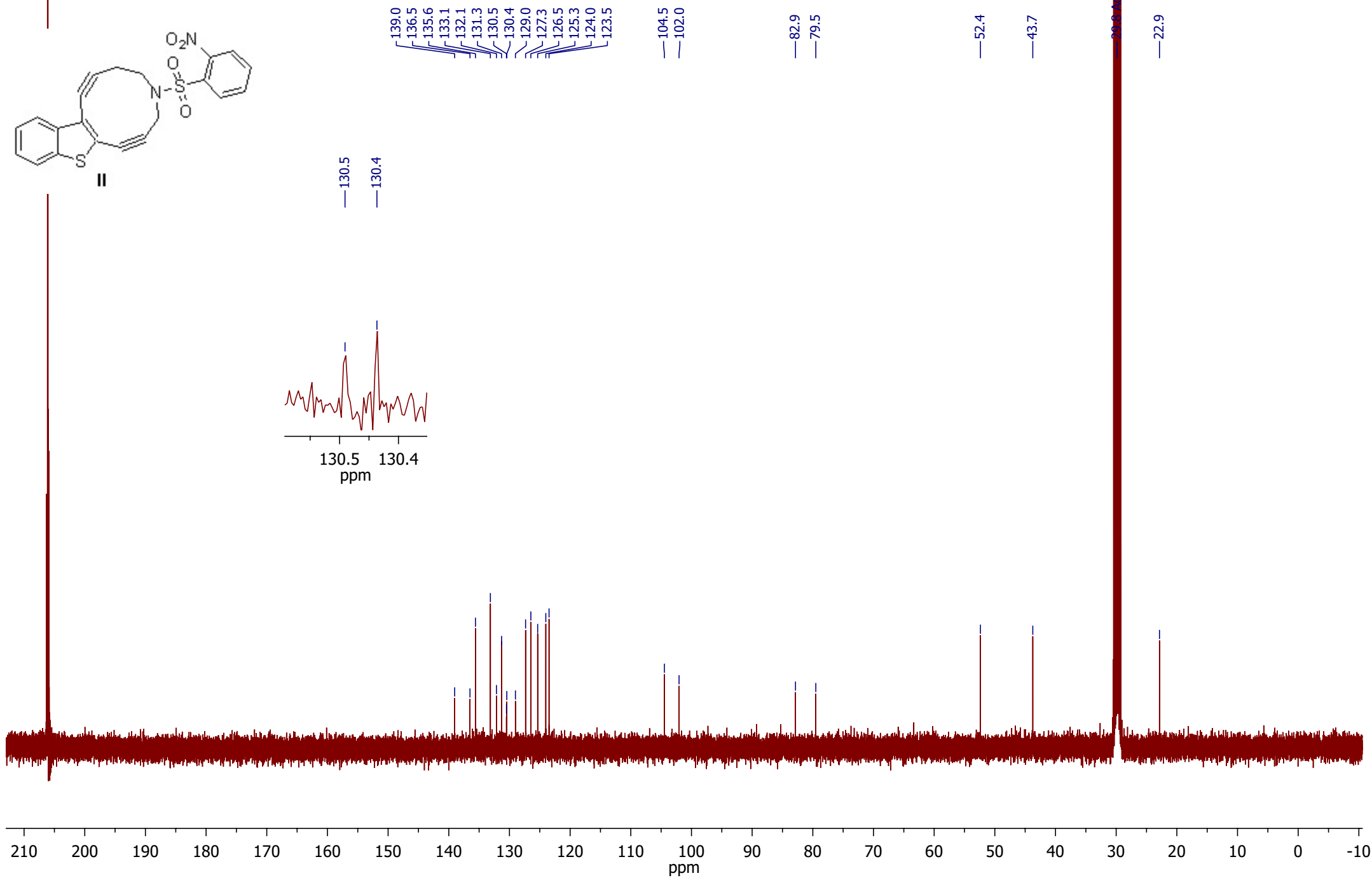
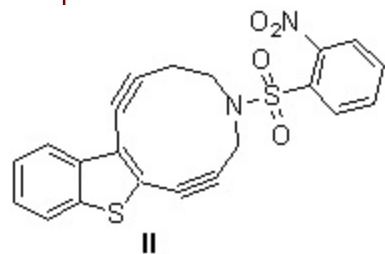
3.02  
3.01  
3.00

2.05 Acetone- $d_6$

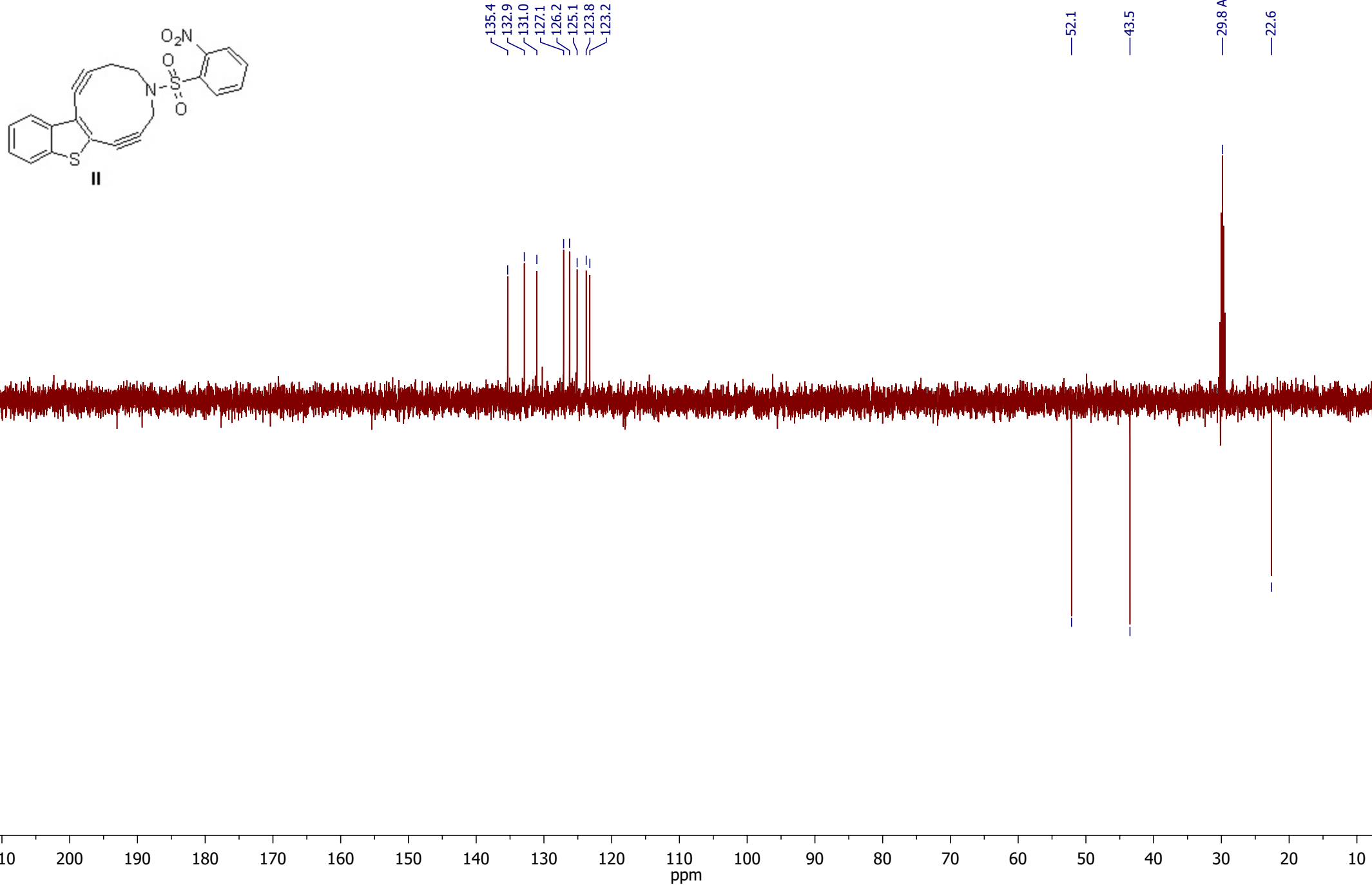




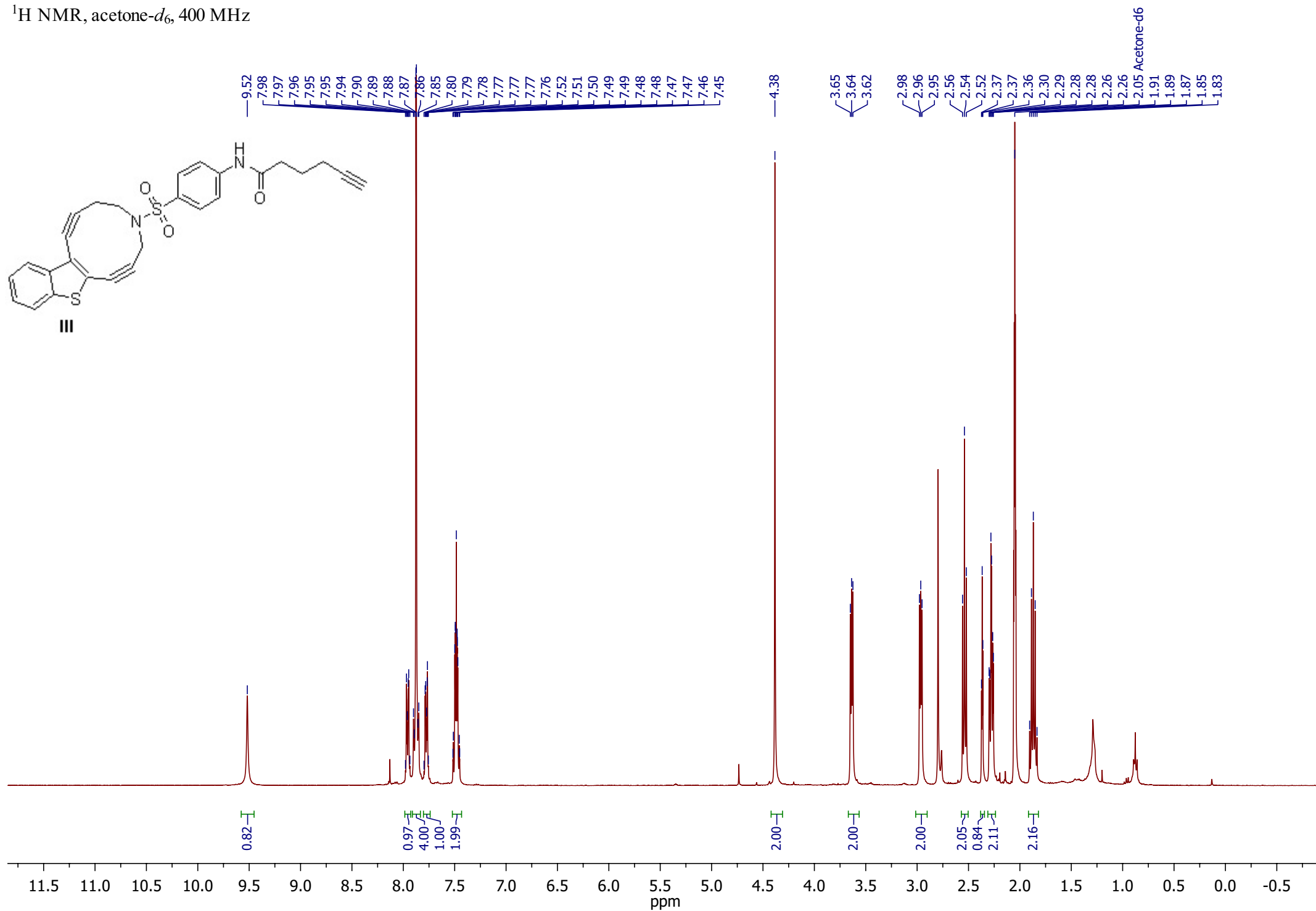
$^{13}\text{C}\{^1\text{H}\}$  NMR, acetone- $d_6$ , 101 MHz



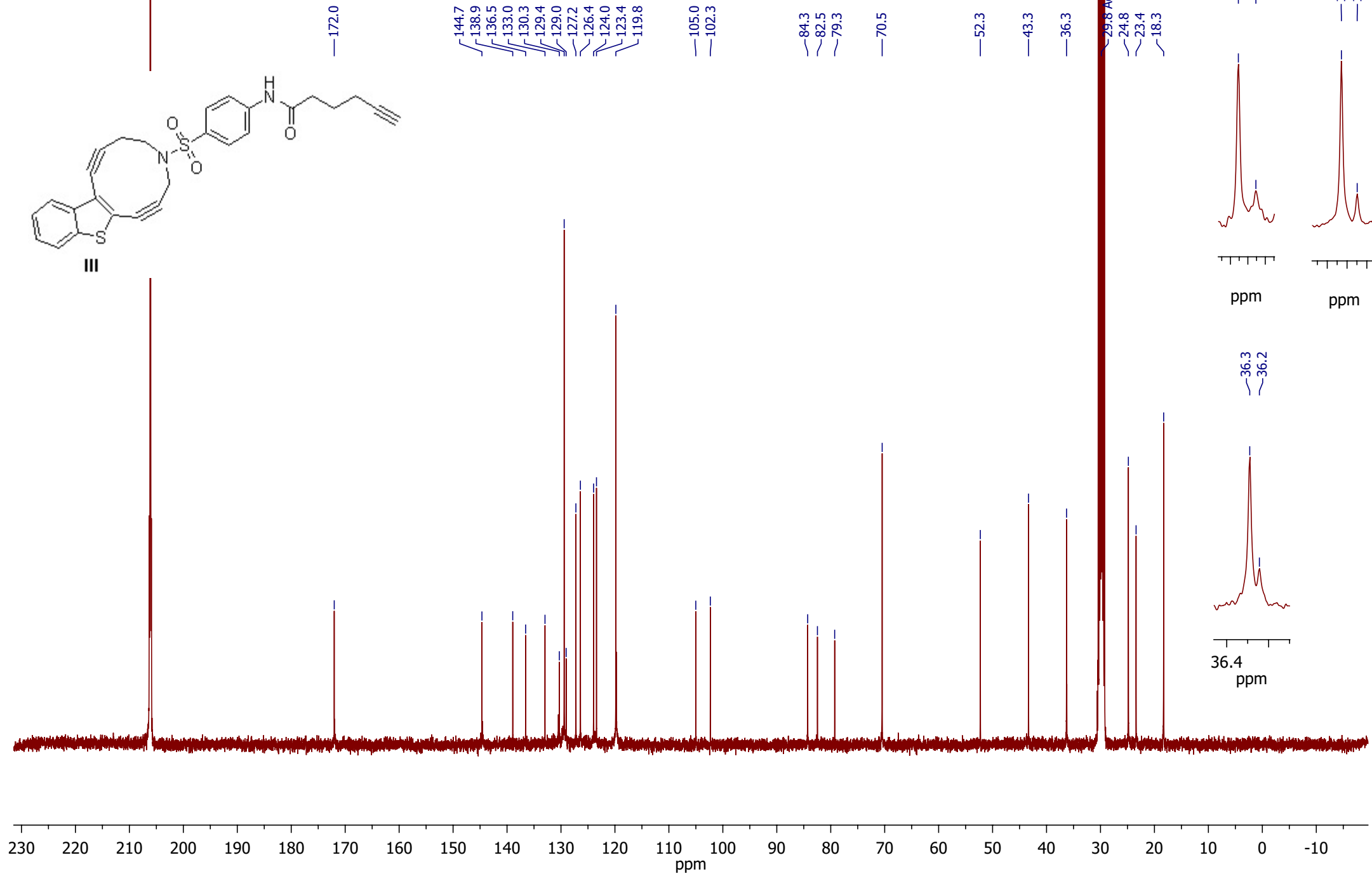
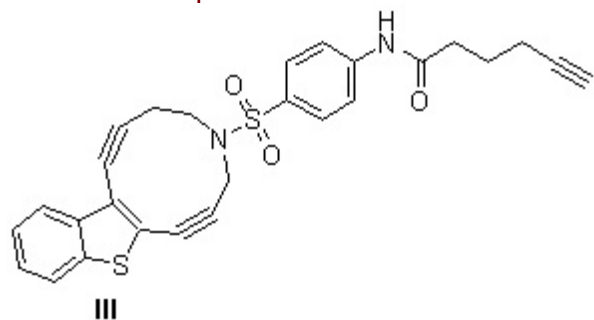
DEPT NMR, acetone-*d*<sub>6</sub>, 101 MHz



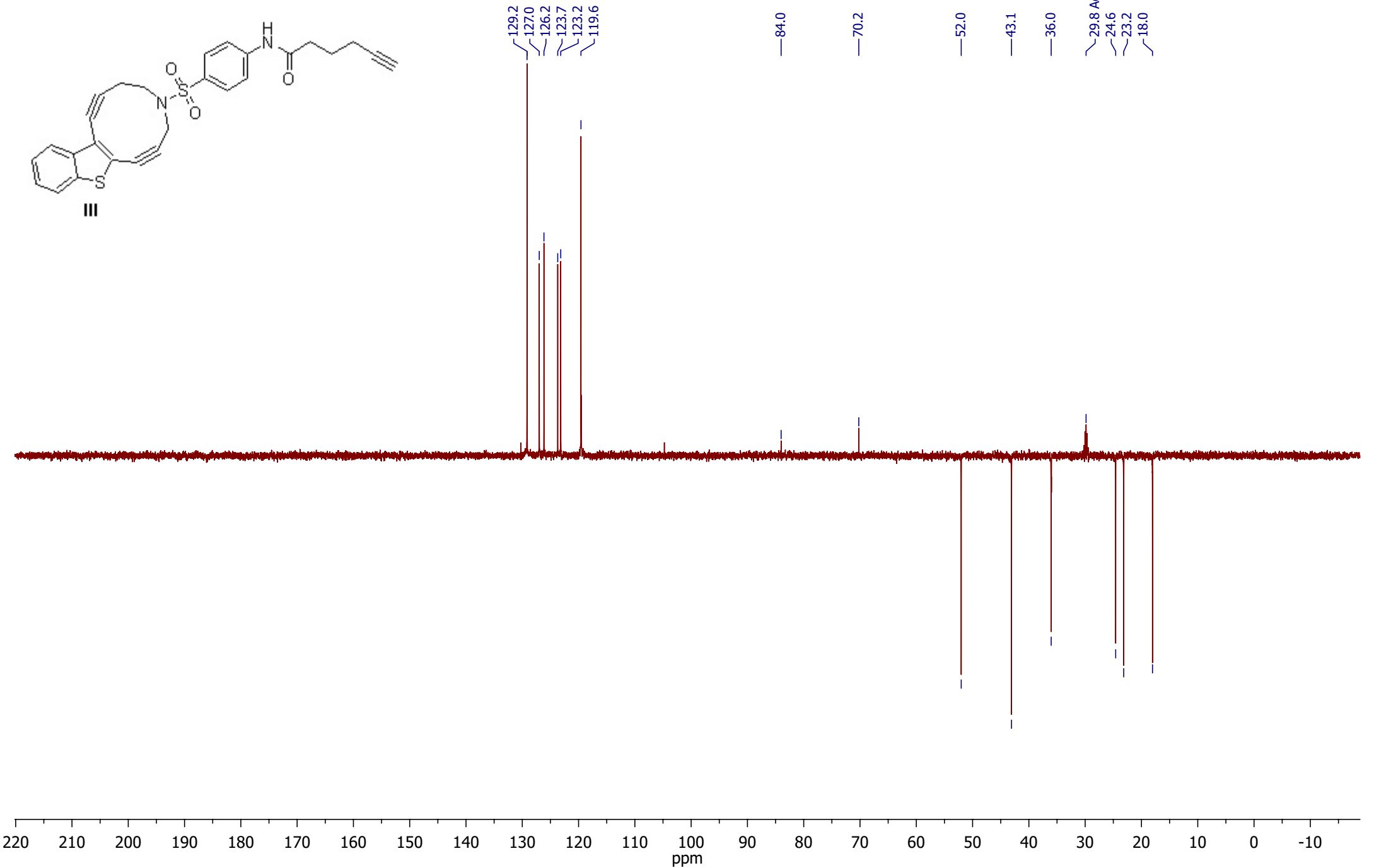
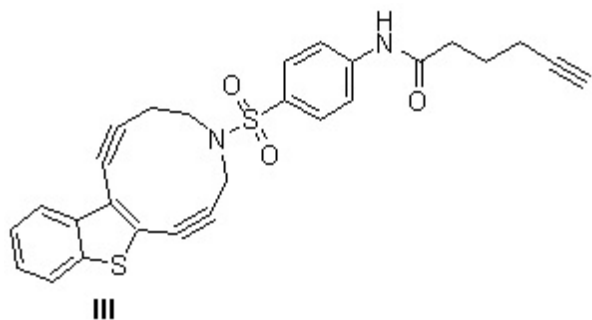
<sup>1</sup>H NMR, acetone-*d*<sub>6</sub>, 400 MHz



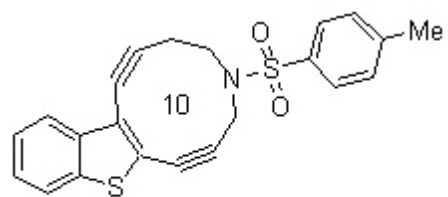
$^{13}\text{C}\{^1\text{H}\}$  NMR, acetone- $d_6$ , 101 MHz



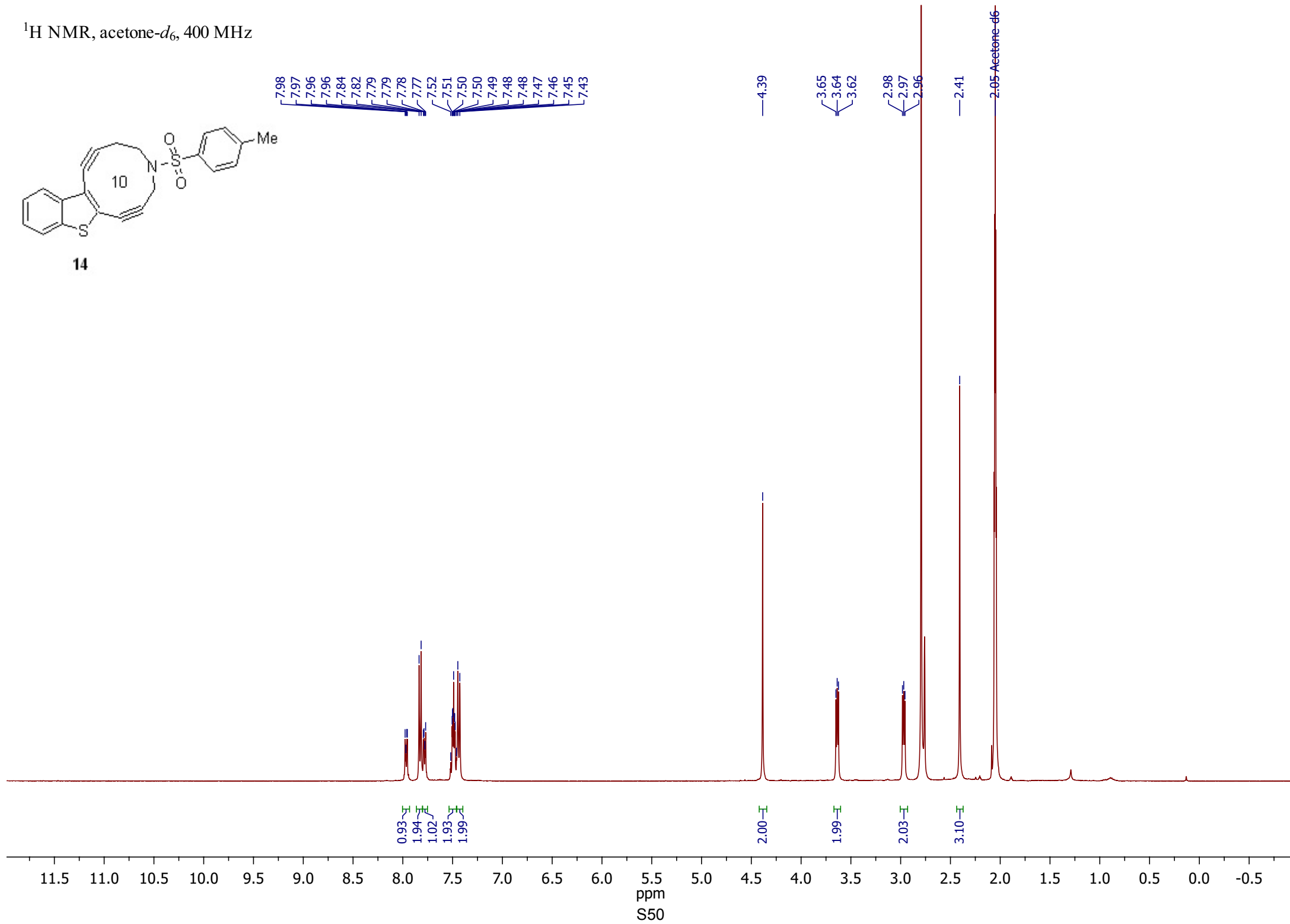
DEPT NMR, acetone-*d*<sub>6</sub>, 101 MHz

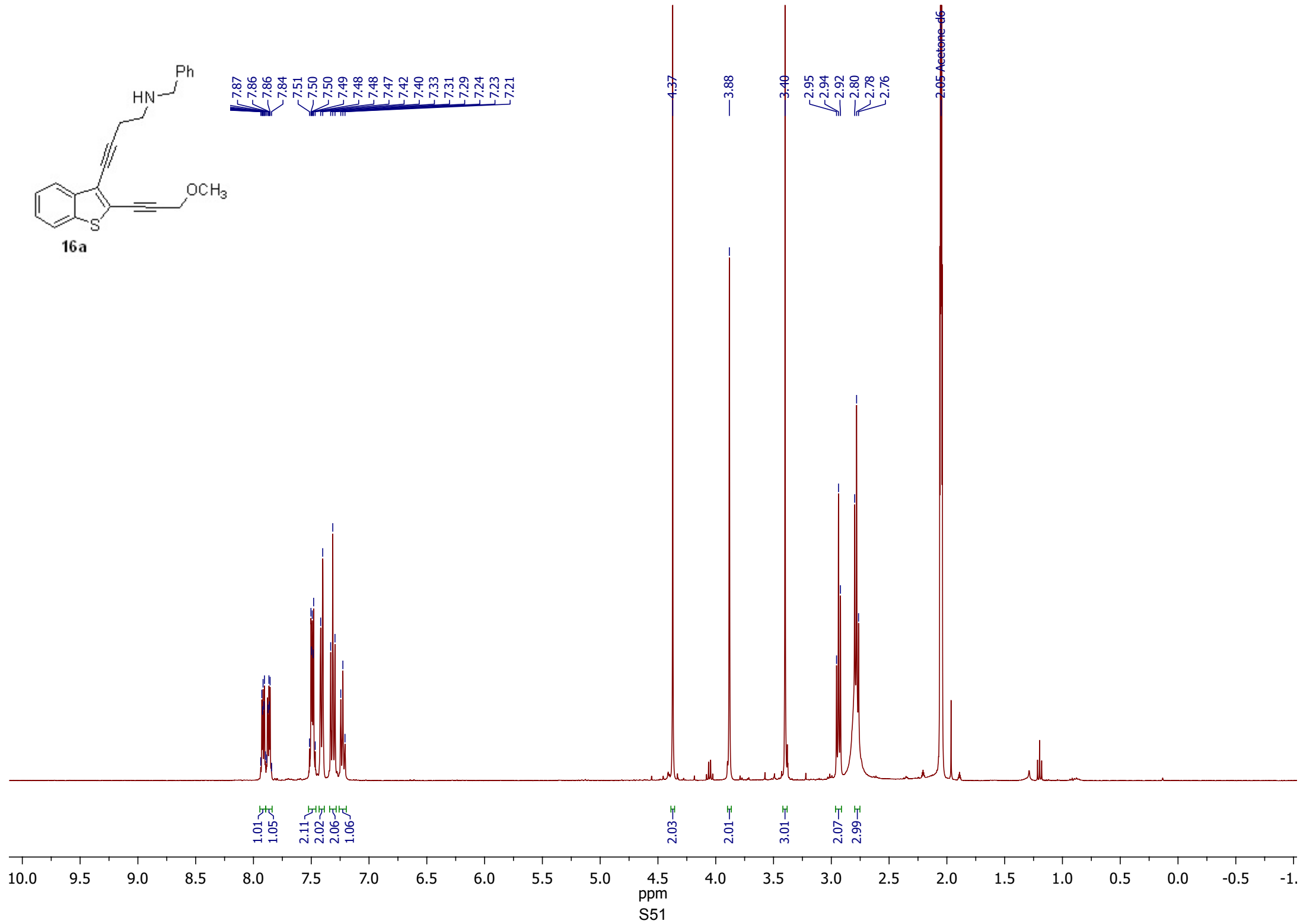
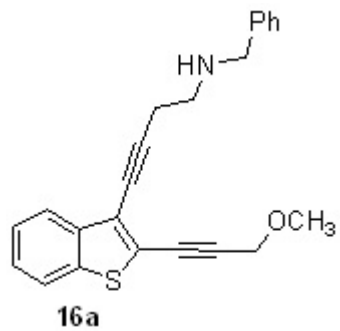


$^1\text{H}$  NMR, acetone- $d_6$ , 400 MHz

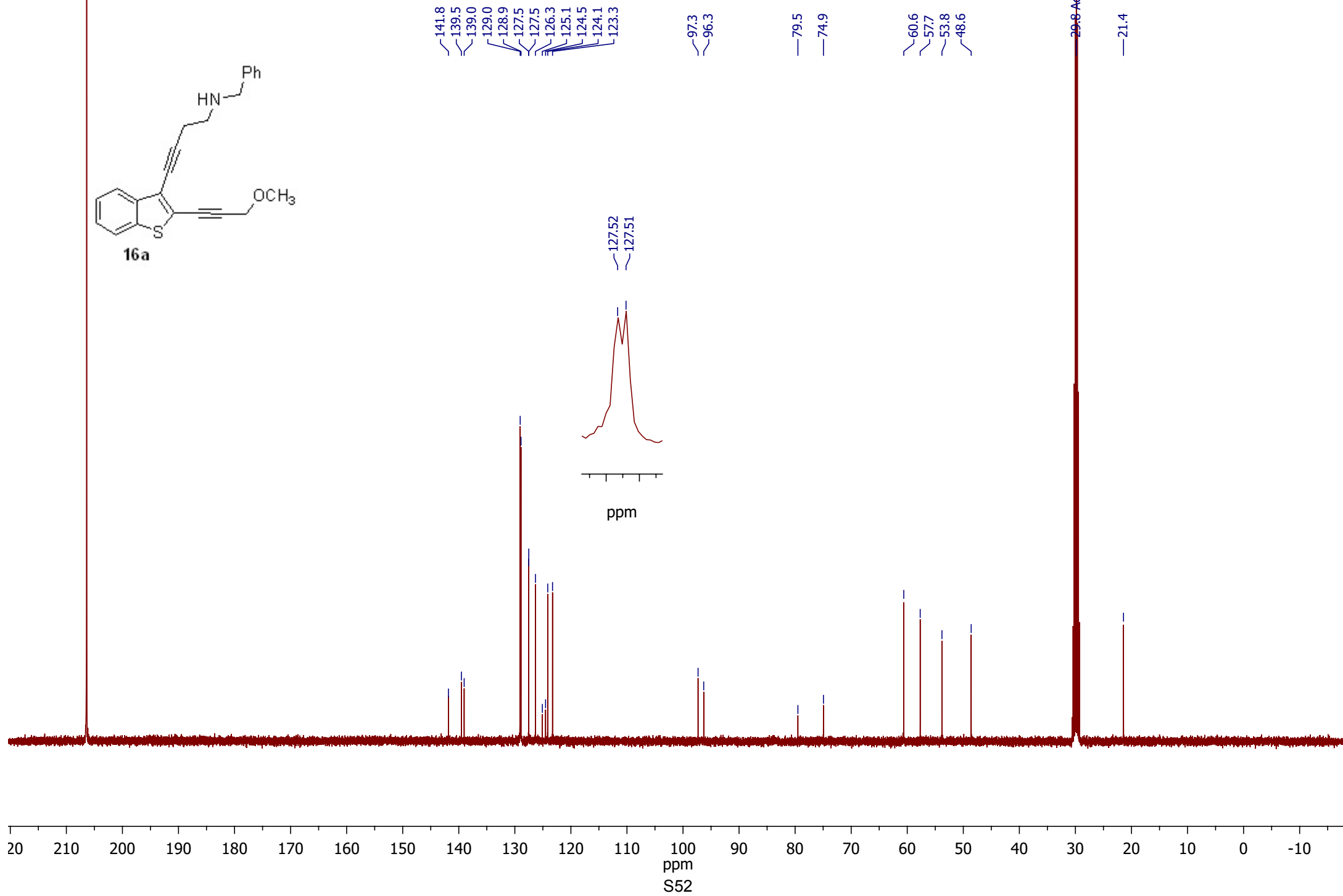
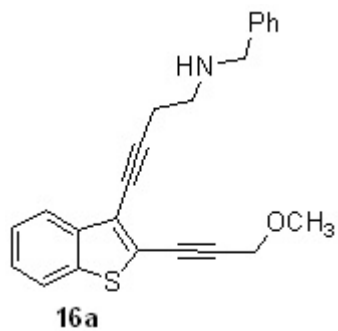


14



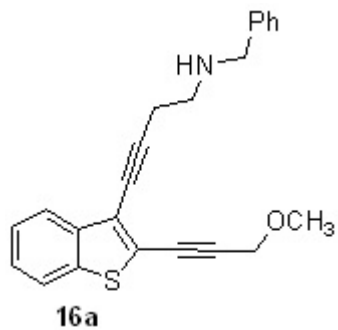


$^{13}\text{C}\{^1\text{H}\}$  NMR, acetone- $d_6$ , 101 MHz





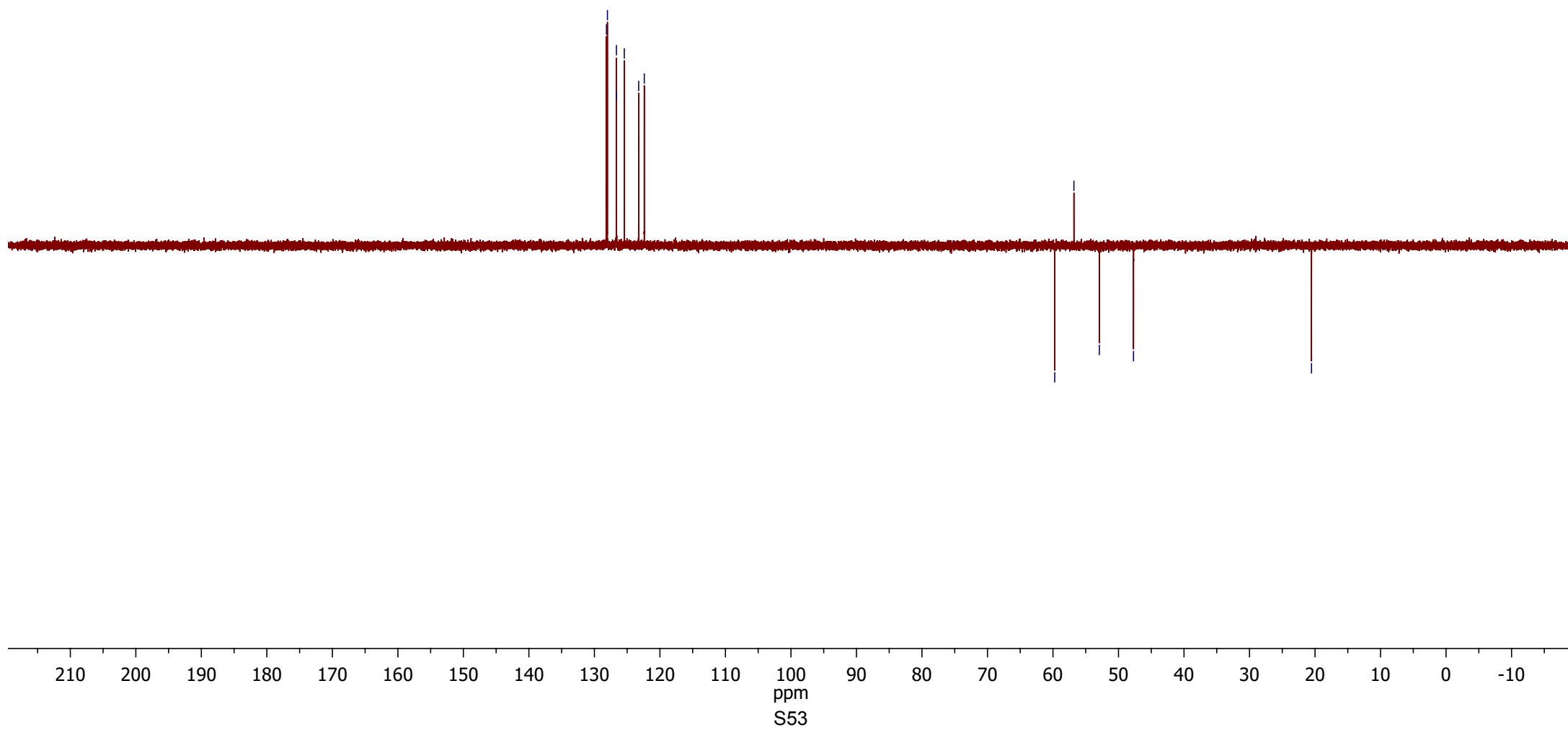
DEPT NMR, acetone-*d*<sub>6</sub>, 101 MHz



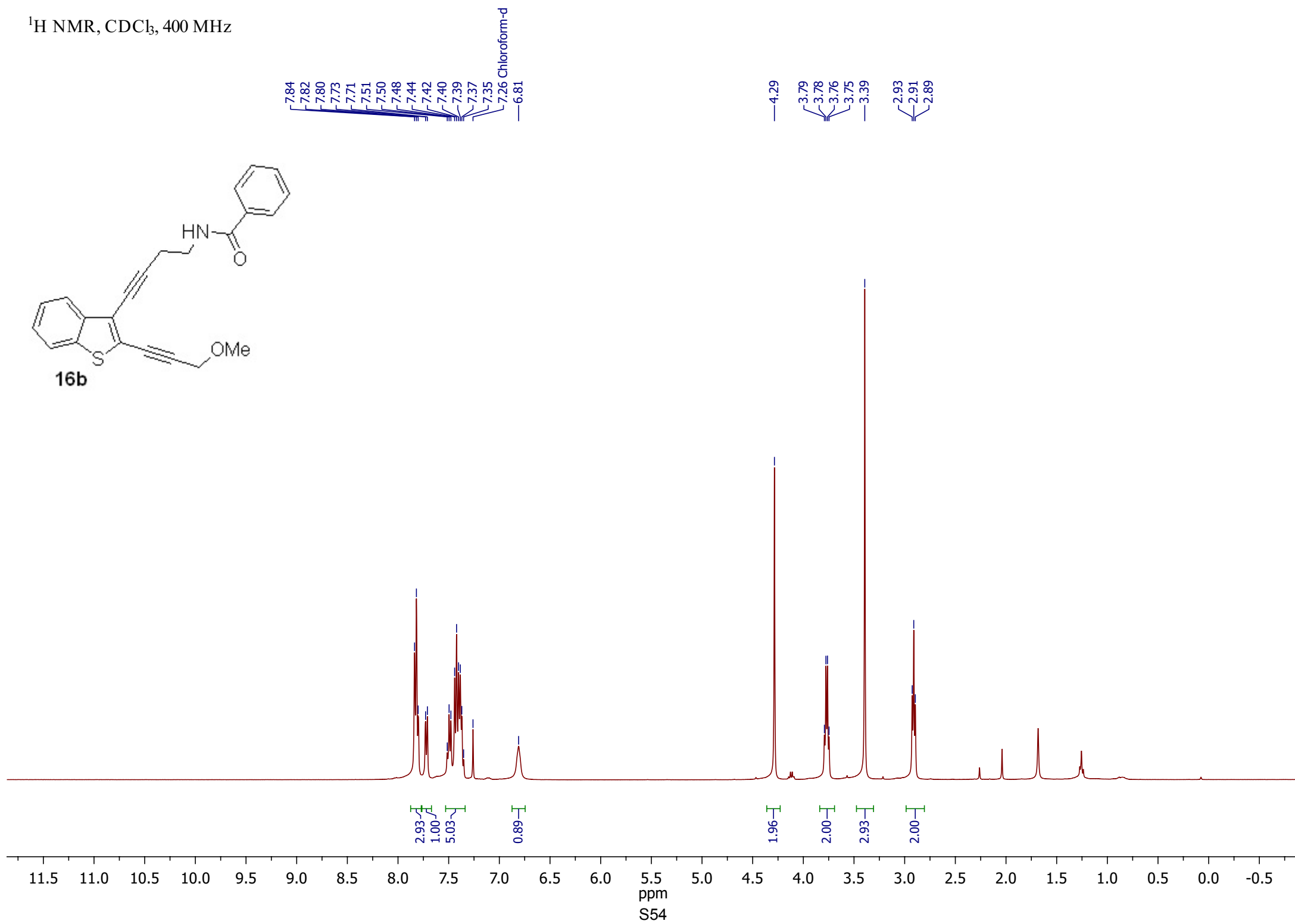
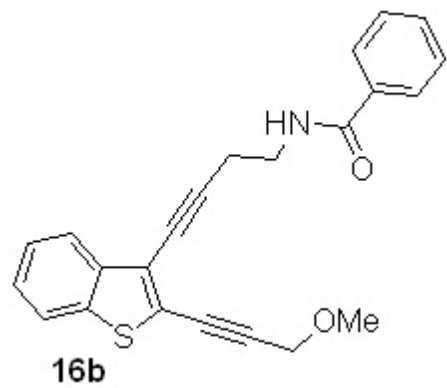
128.2  
128.0  
126.6  
126.6  
125.4  
123.2  
122.4

59.7  
56.8  
52.9  
47.7

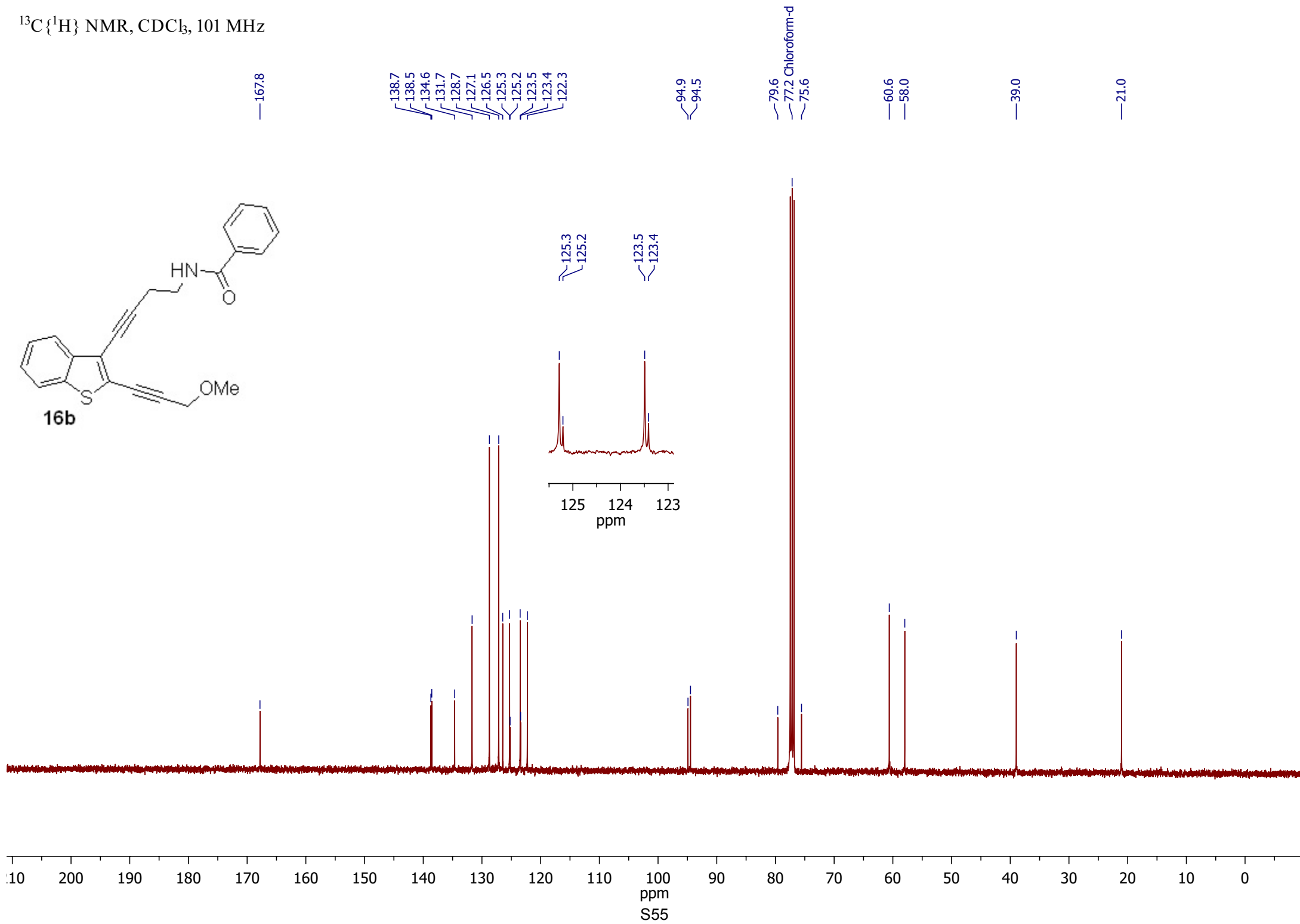
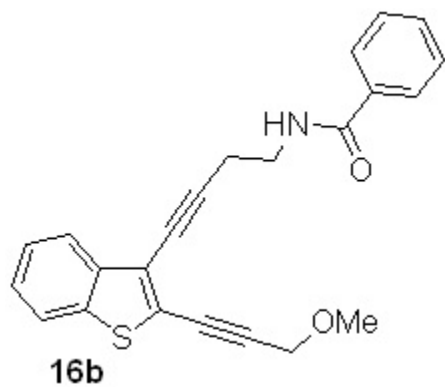
20.5



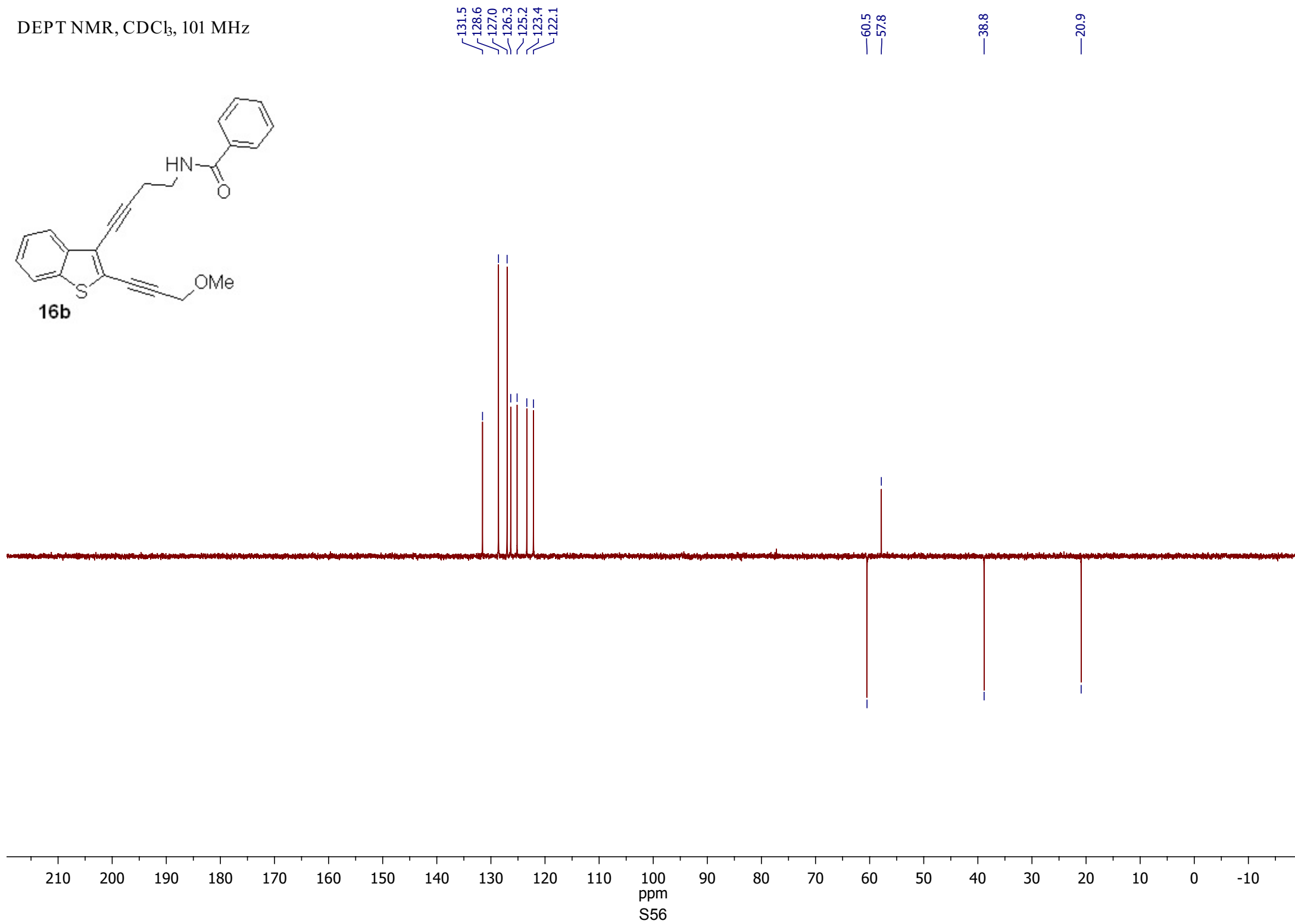
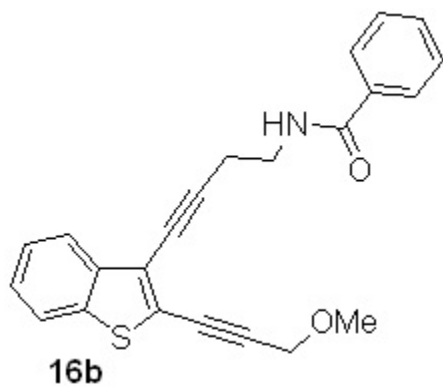
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



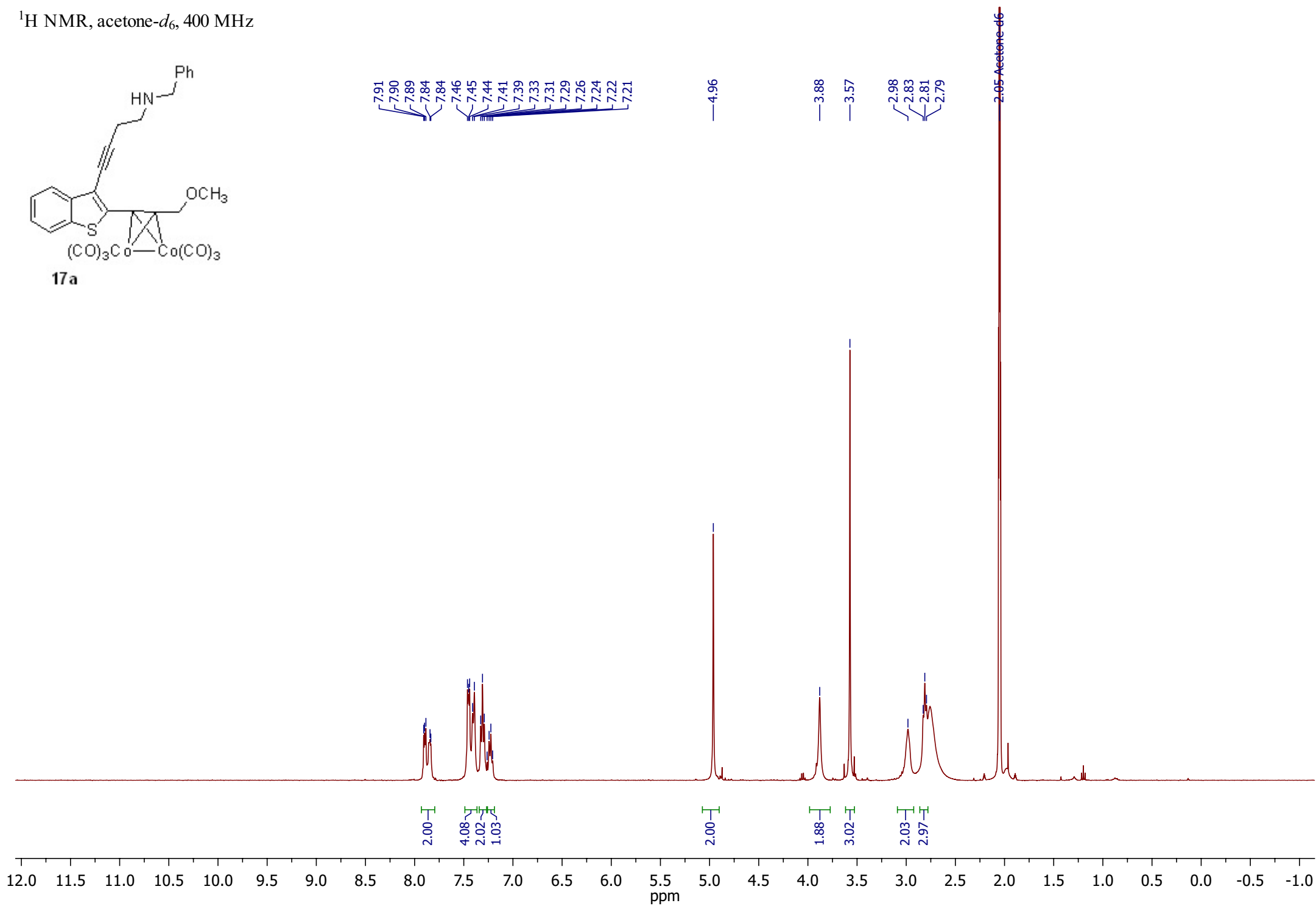
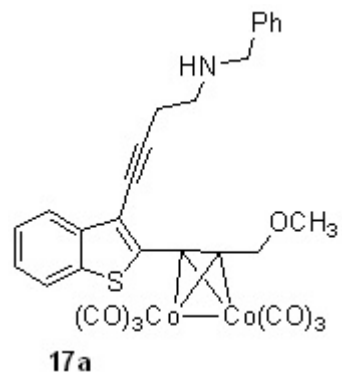
$^{13}\text{C}\{^1\text{H}\}$  NMR,  $\text{CDCl}_3$ , 101 MHz



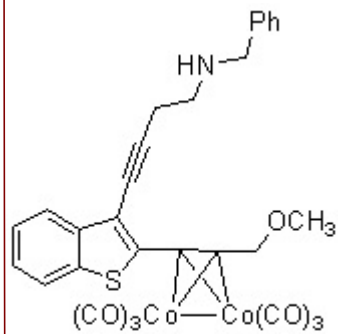
DEPT NMR, CDCl<sub>3</sub>, 101 MHz



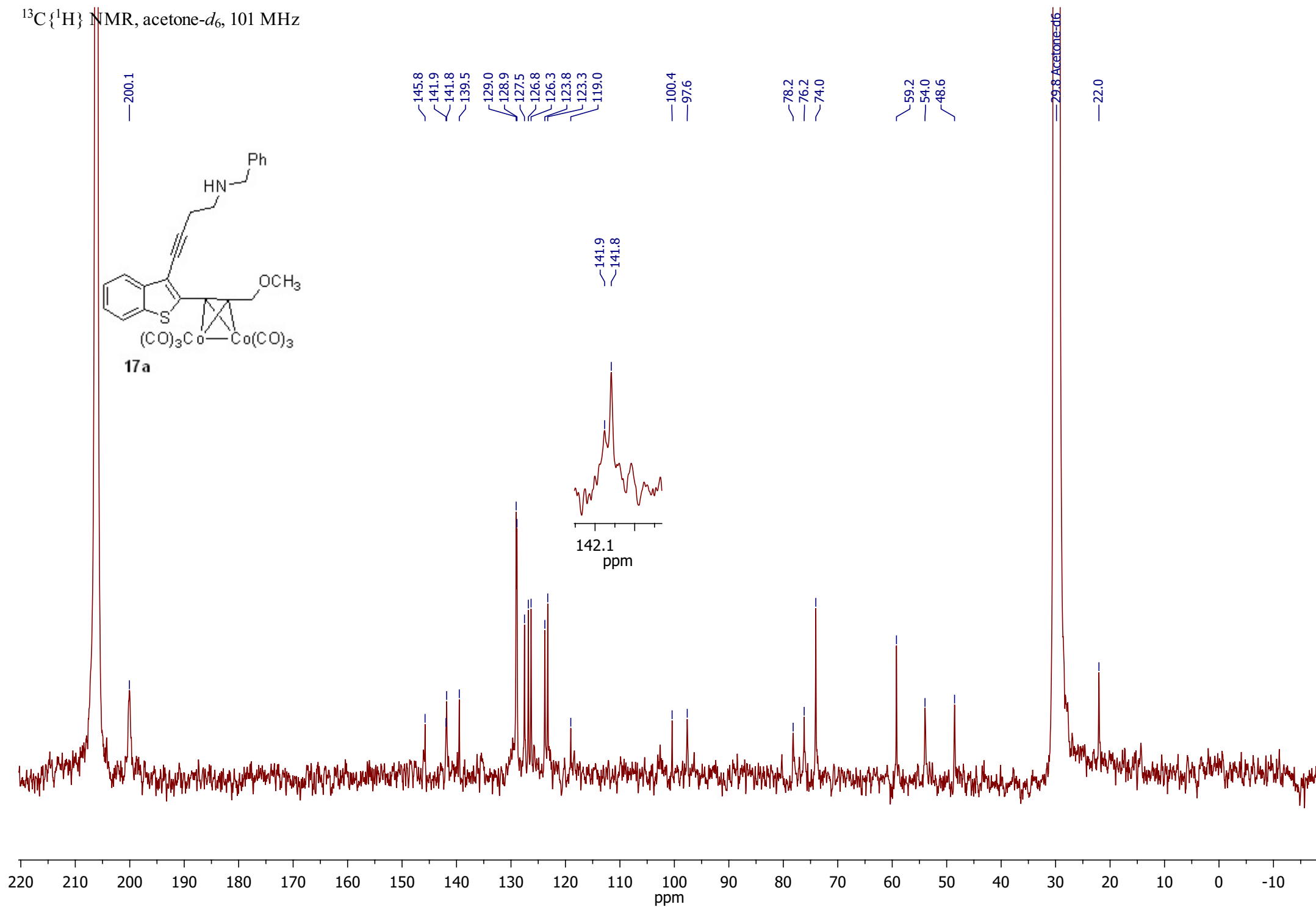
$^1\text{H}$  NMR, acetone- $d_6$ , 400 MHz



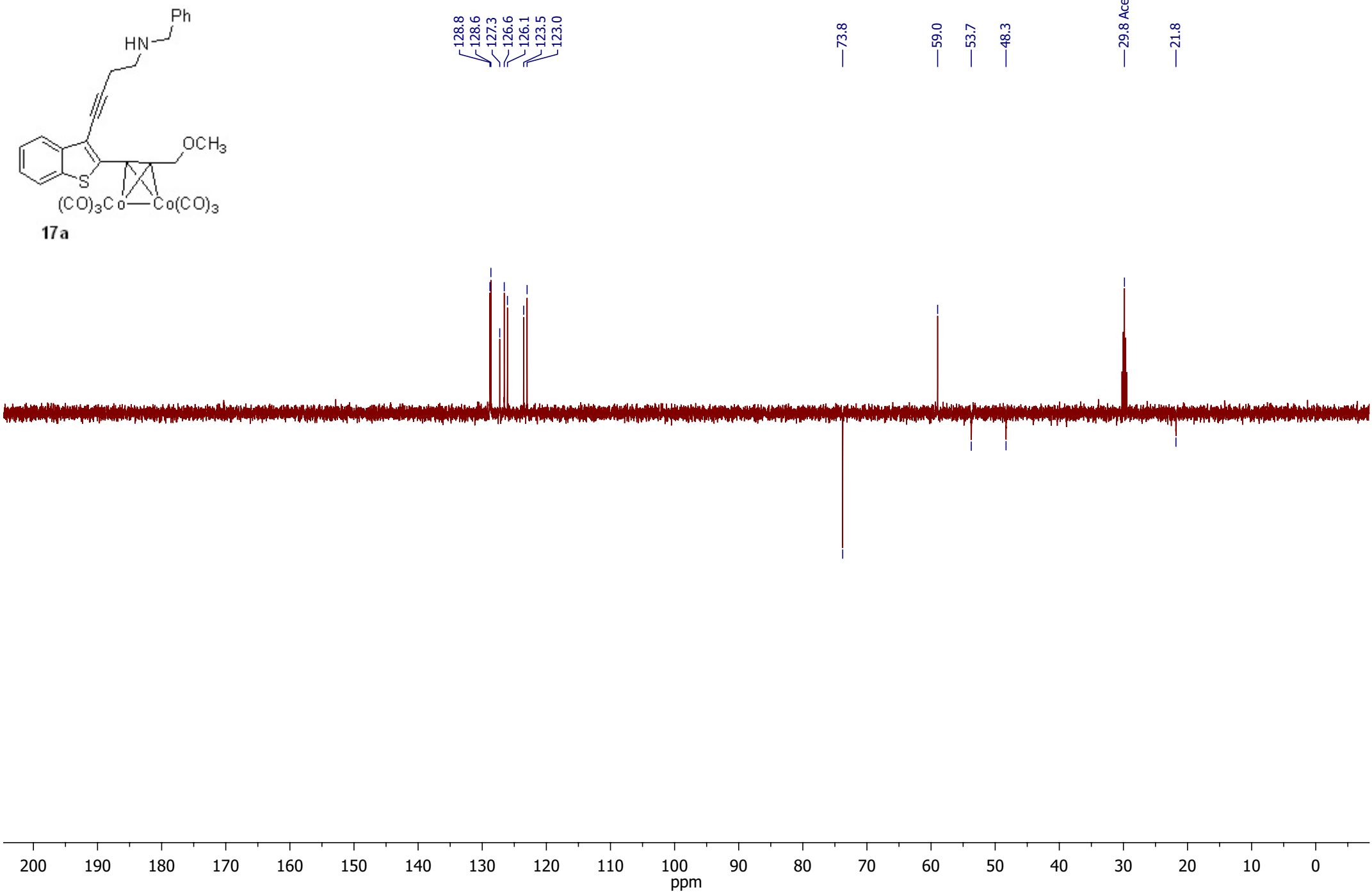
$^{13}\text{C}\{^1\text{H}\}$  NMR, acetone- $d_6$ , 101 MHz



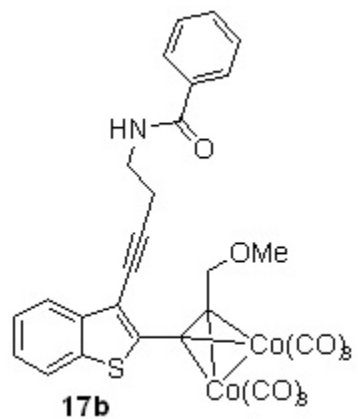
**17a**



DEPT NMR, acetone-*d*<sub>6</sub>, 101 MHz



$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz

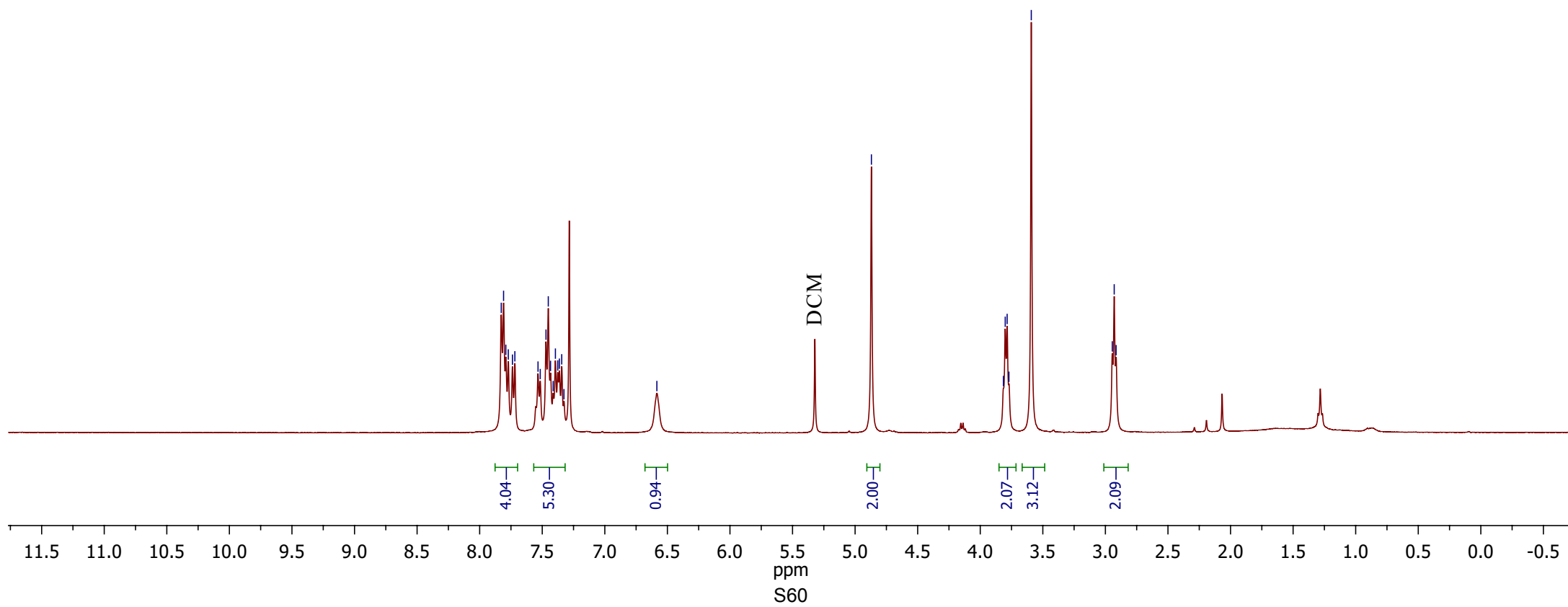


7.83  
7.81  
7.79  
7.77  
7.74  
7.72  
7.53  
7.52  
7.47  
7.45  
7.43  
7.41  
7.39  
7.38  
7.36  
7.34  
7.33  
6.58

4.87

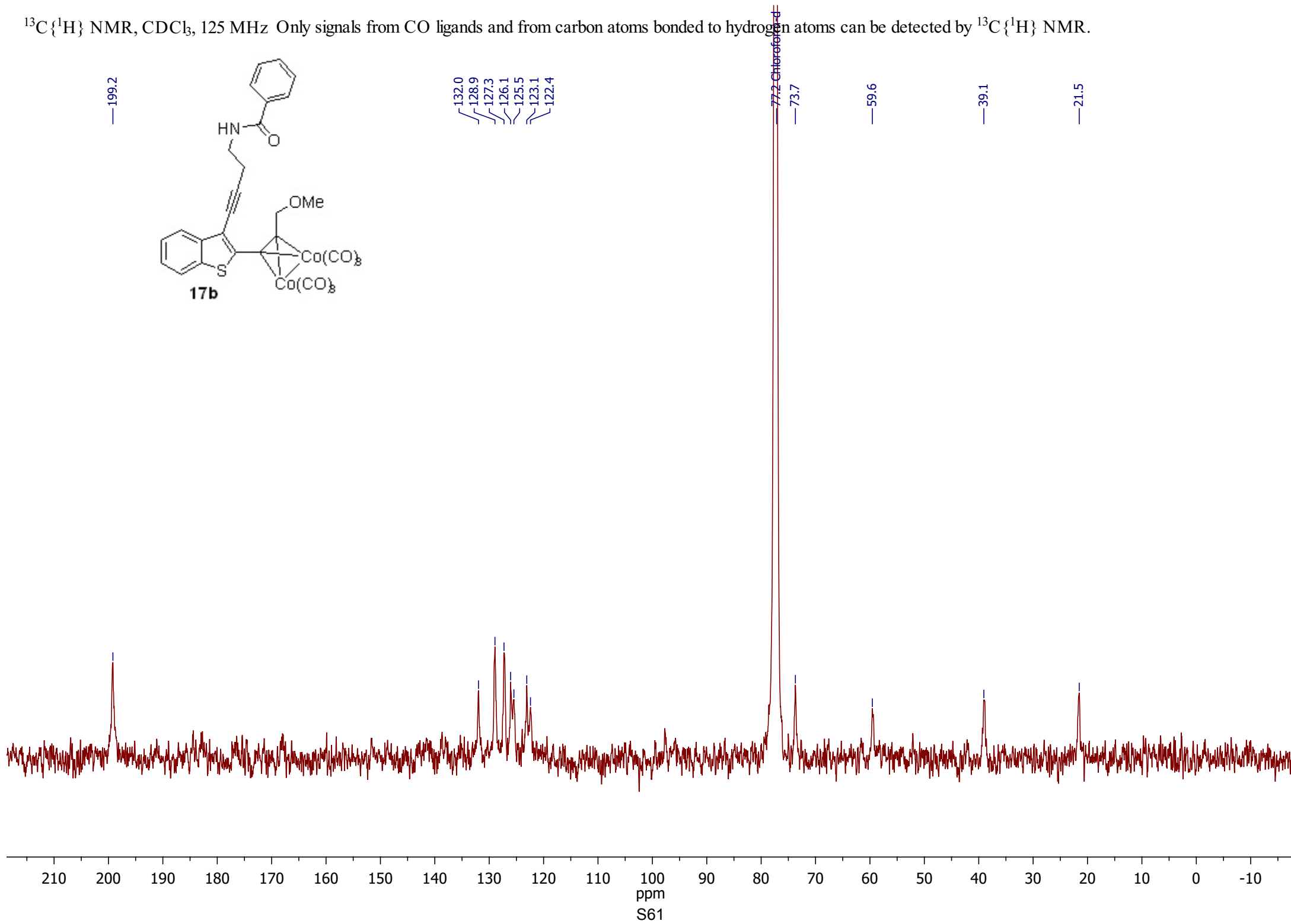
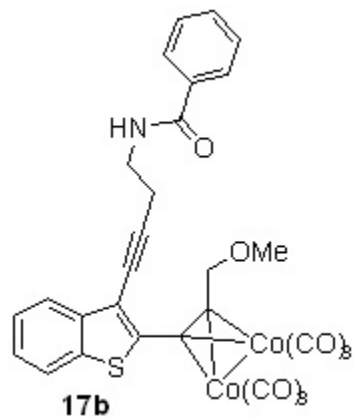
3.81  
3.80  
3.79  
3.77  
3.59

2.95  
2.93  
2.91

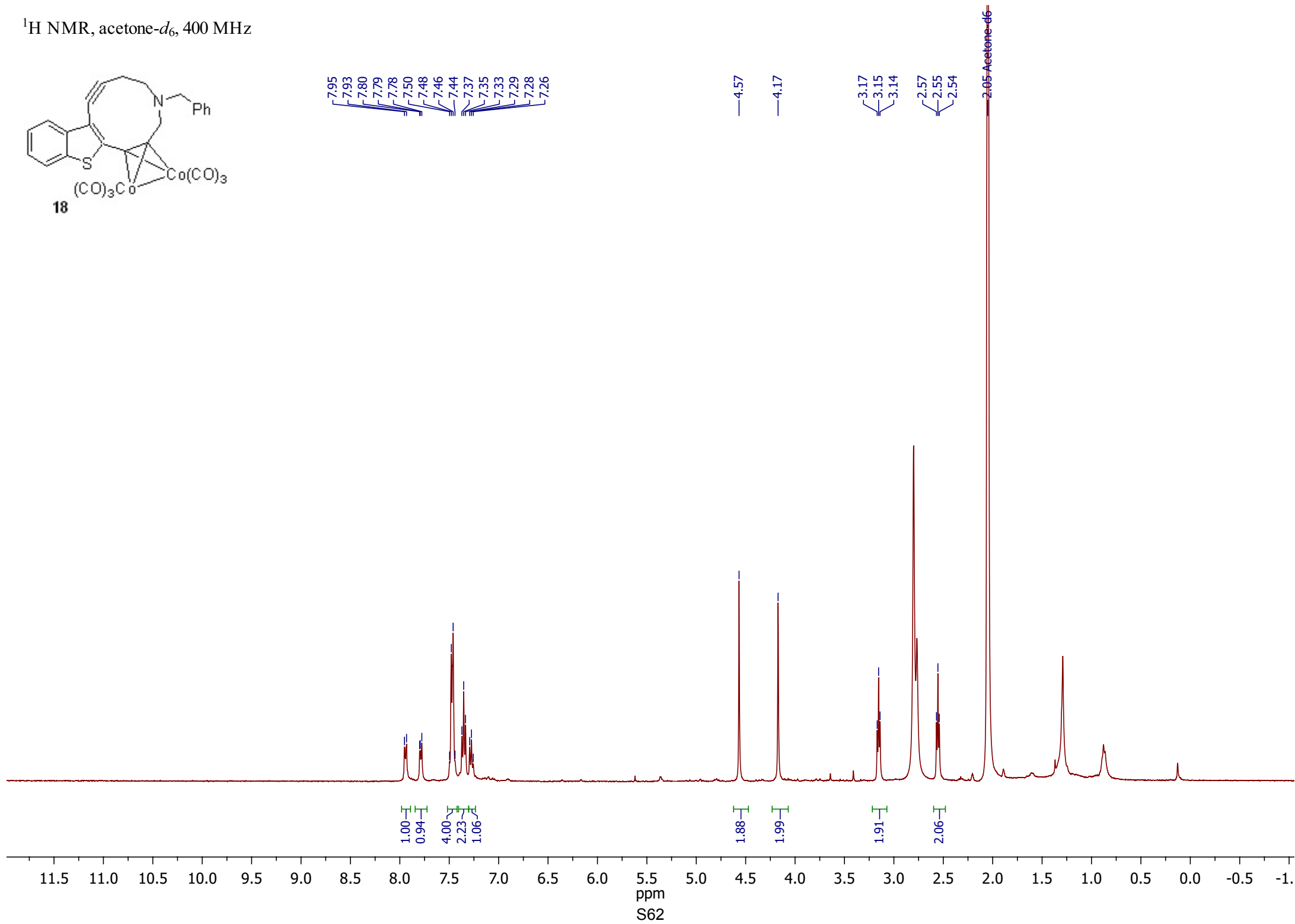
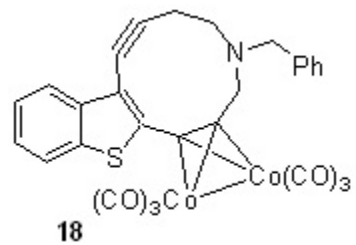


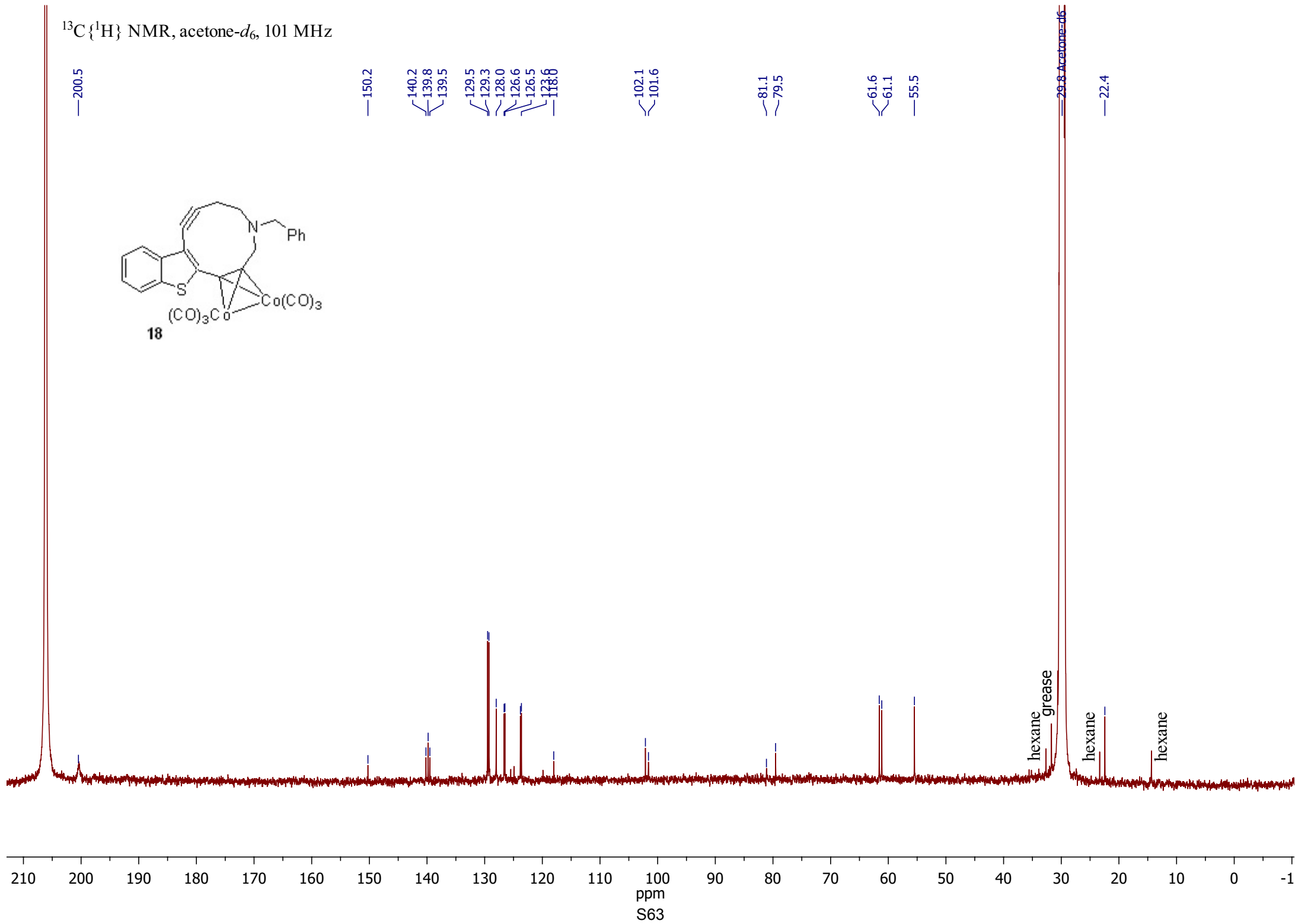
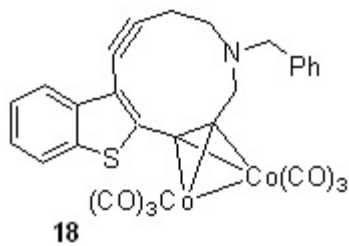


$^{13}\text{C}\{^1\text{H}\}$  NMR,  $\text{CDCl}_3$ , 125 MHz Only signals from CO ligands and from carbon atoms bonded to hydrogen atoms can be detected by  $^{13}\text{C}\{^1\text{H}\}$  NMR.

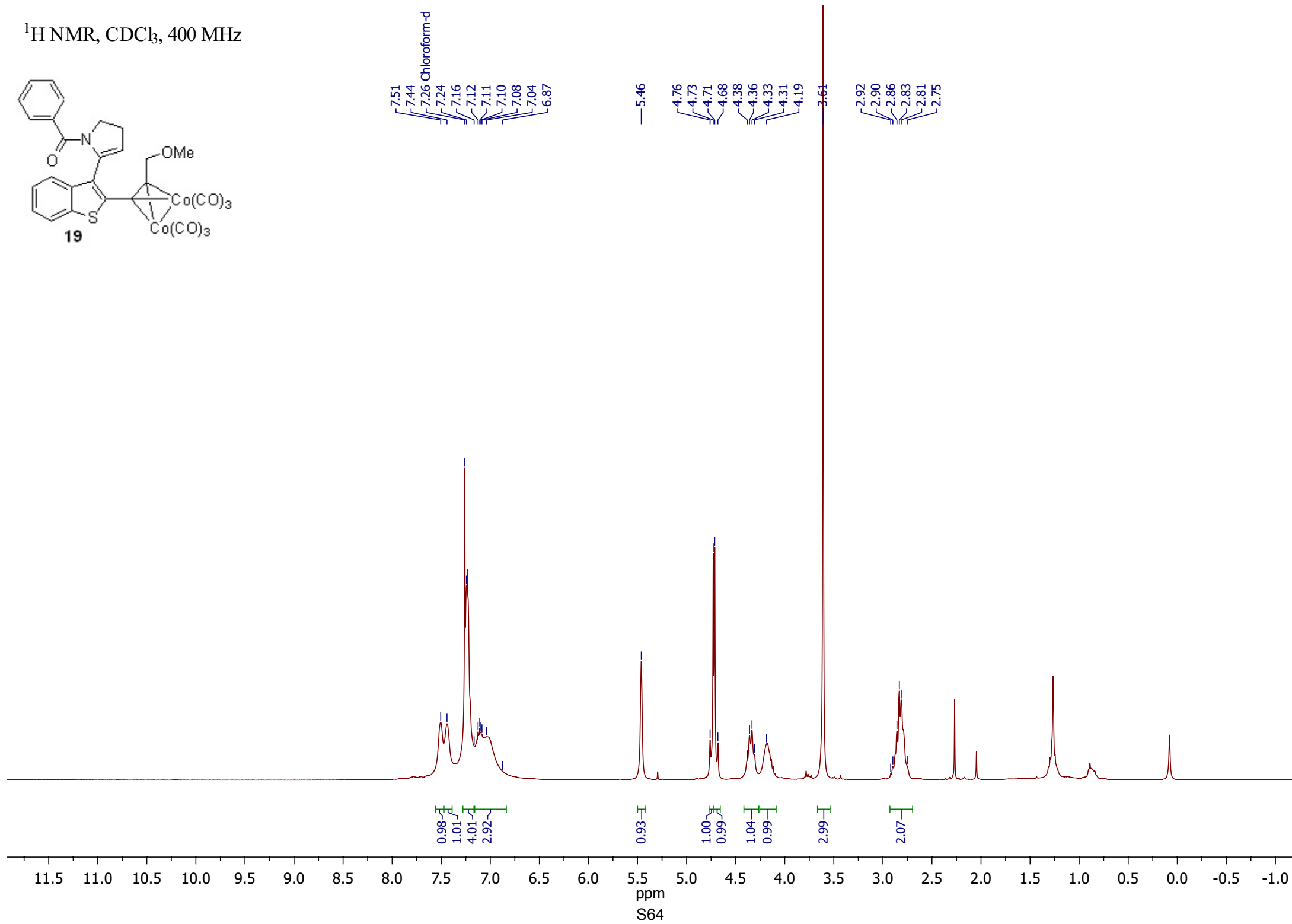
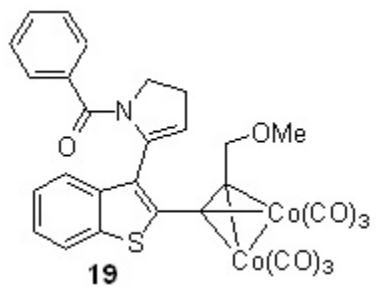


$^1\text{H}$  NMR, acetone- $d_6$ , 400 MHz

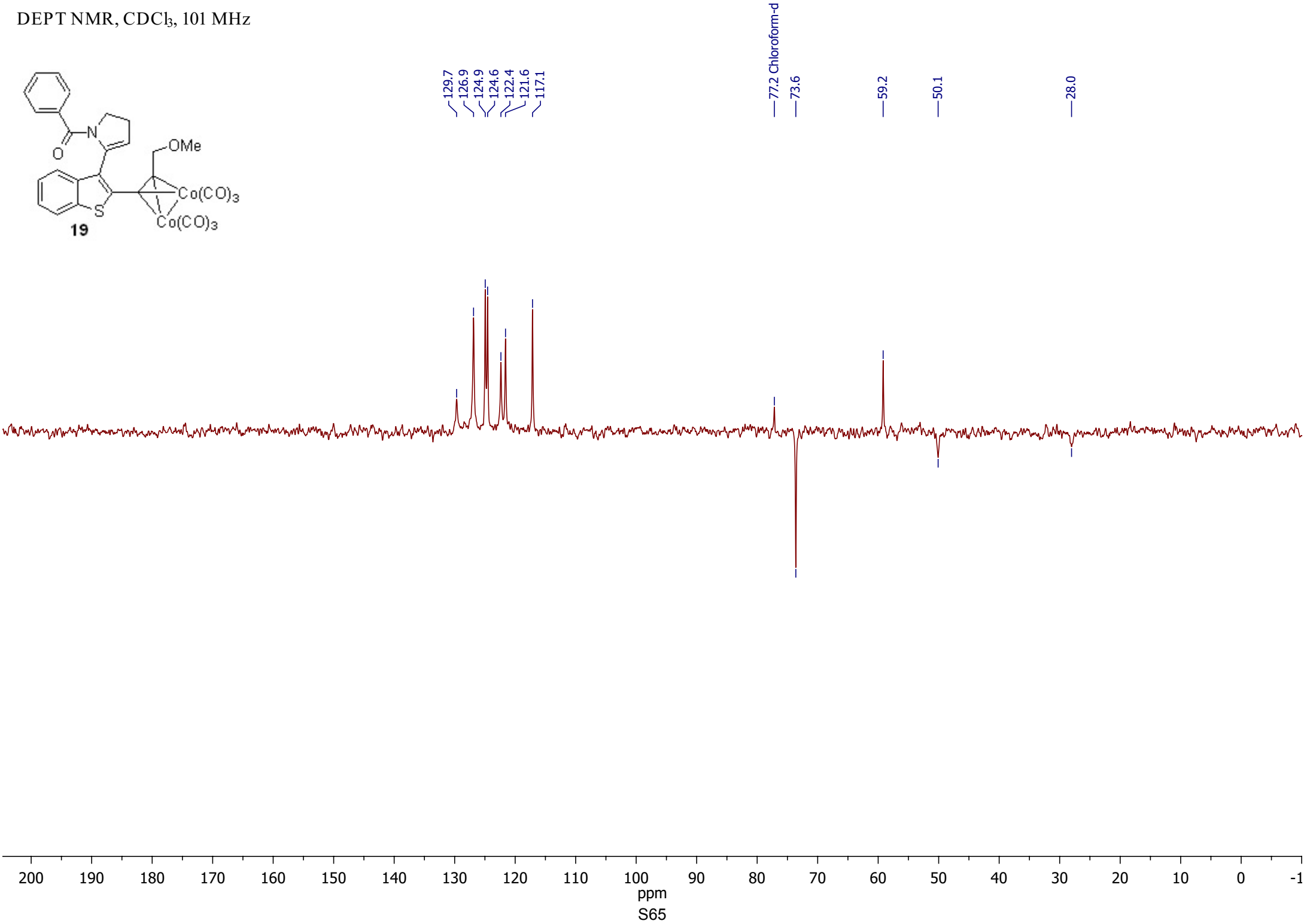


$^{13}\text{C}\{^1\text{H}\}$  NMR, acetone- $d_6$ , 101 MHz

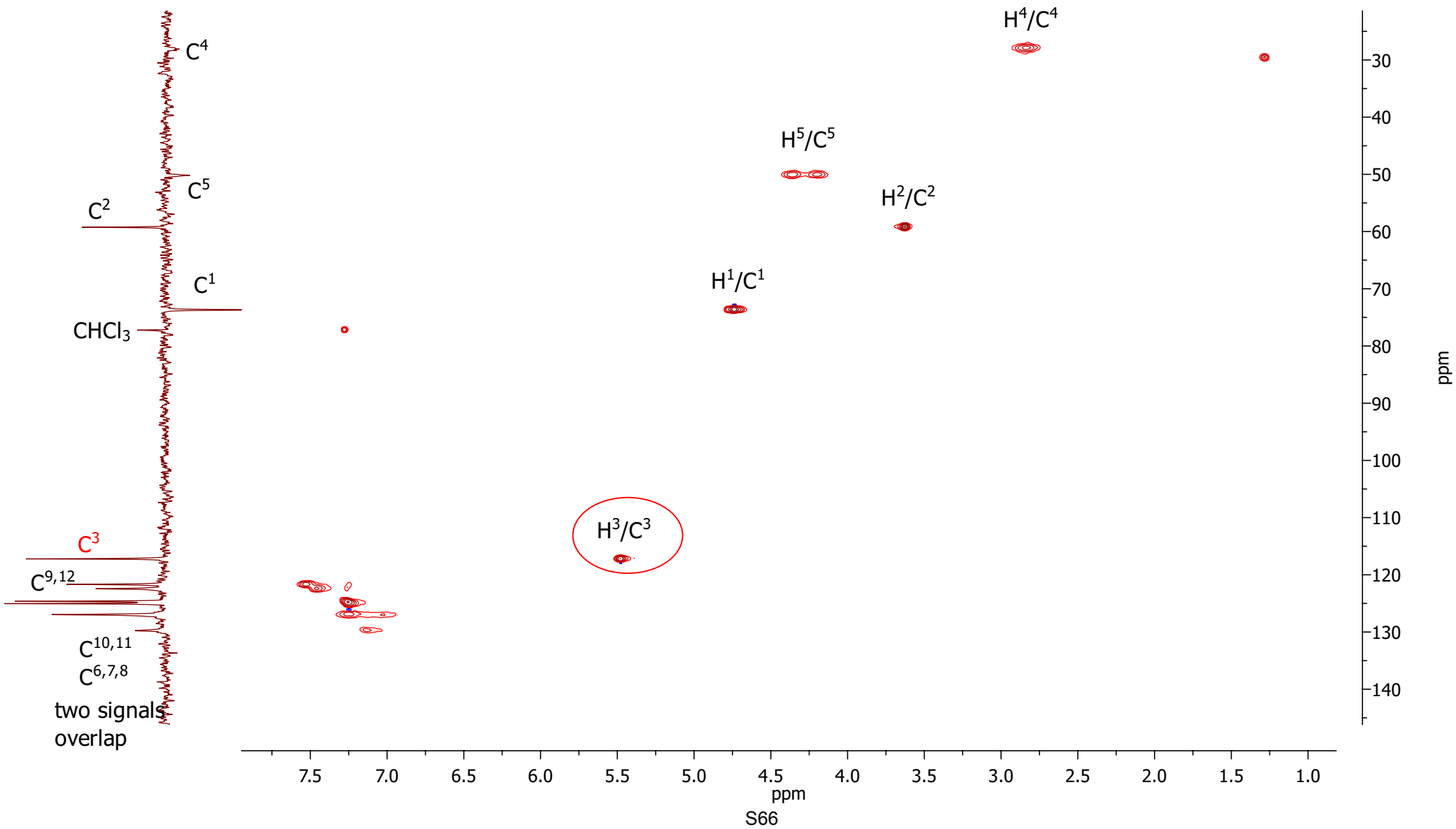
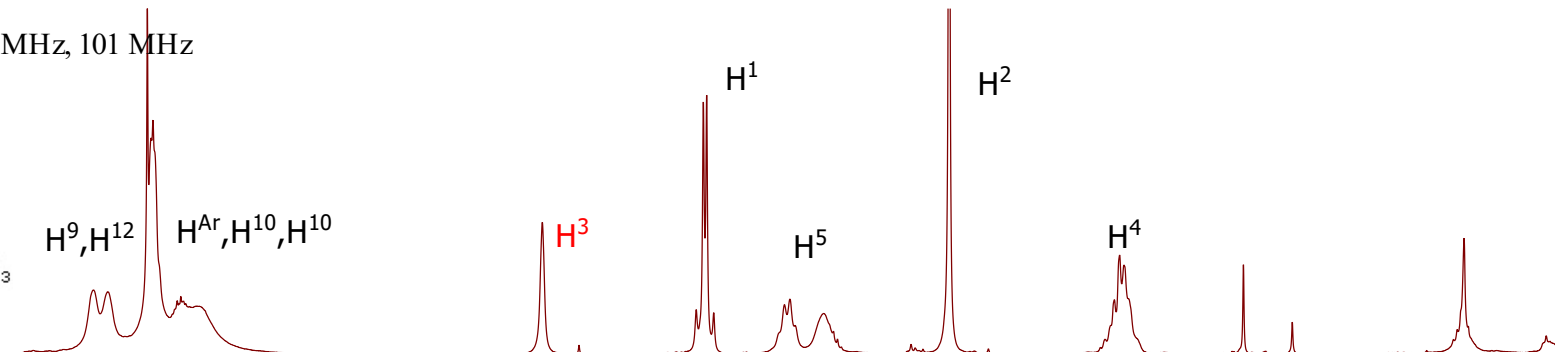
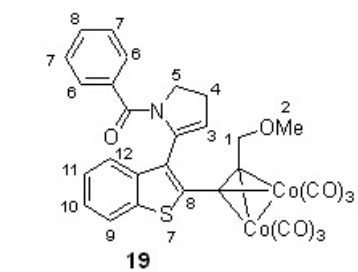
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



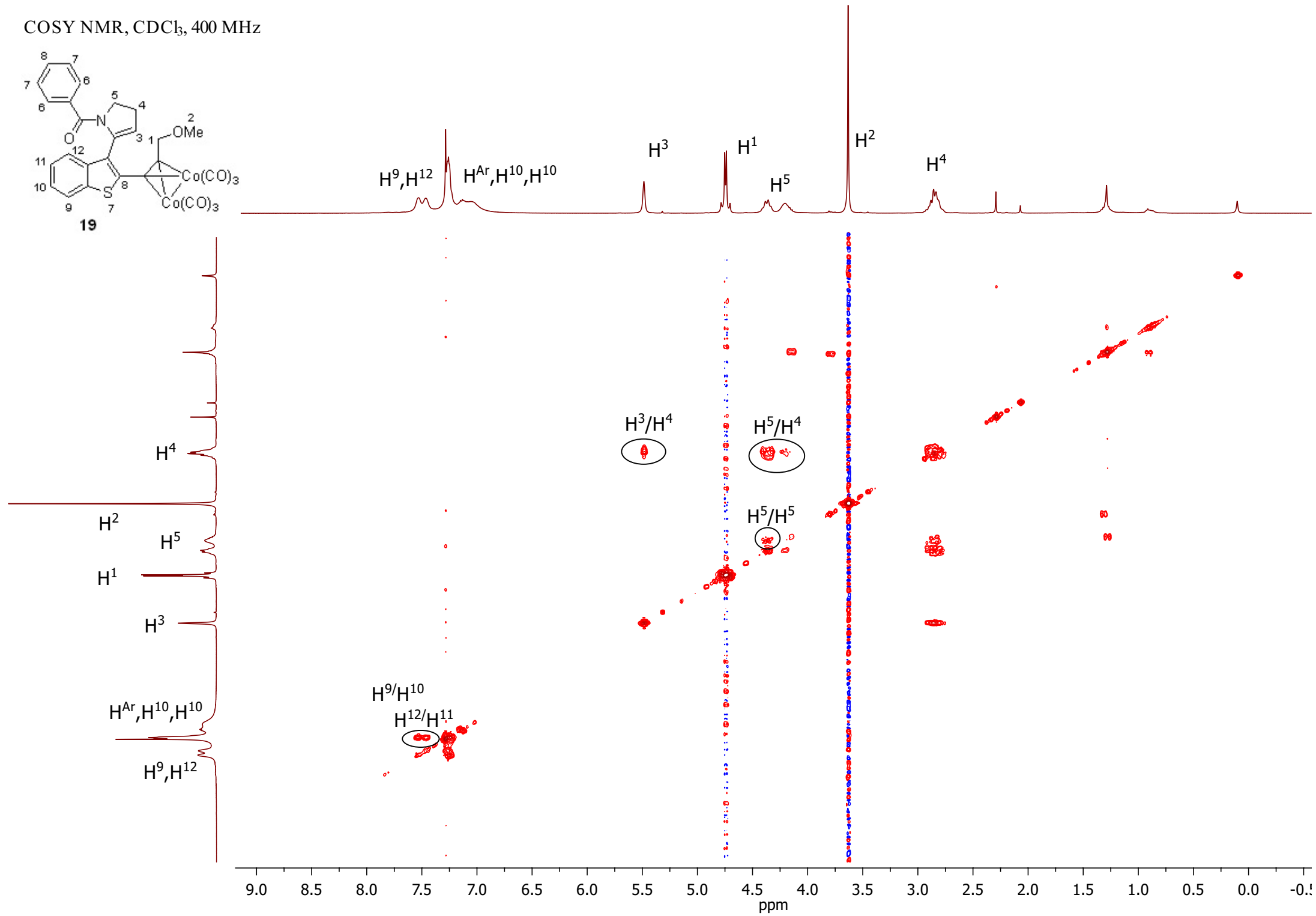
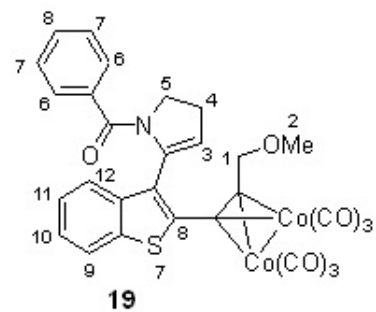
DEPT NMR, CDCl<sub>3</sub>, 101 MHz



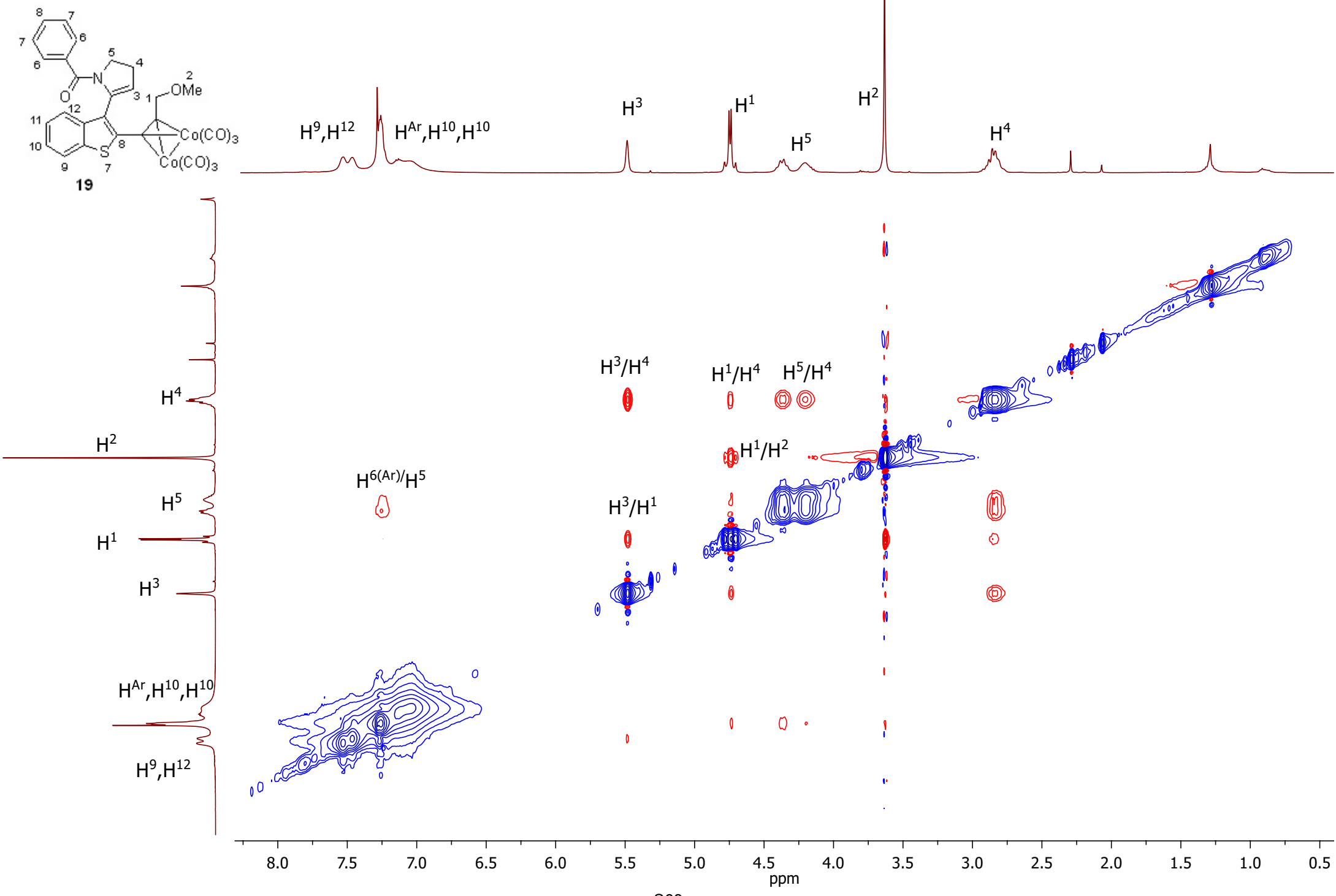
HSQC NMR, CDCl<sub>3</sub>, 400 MHz, 101 MHz



COSY NMR,  $\text{CDCl}_3$ , 400 MHz



NOESY NMR, CDCl<sub>3</sub>, 400 MHz





# Mass Spectrum Report

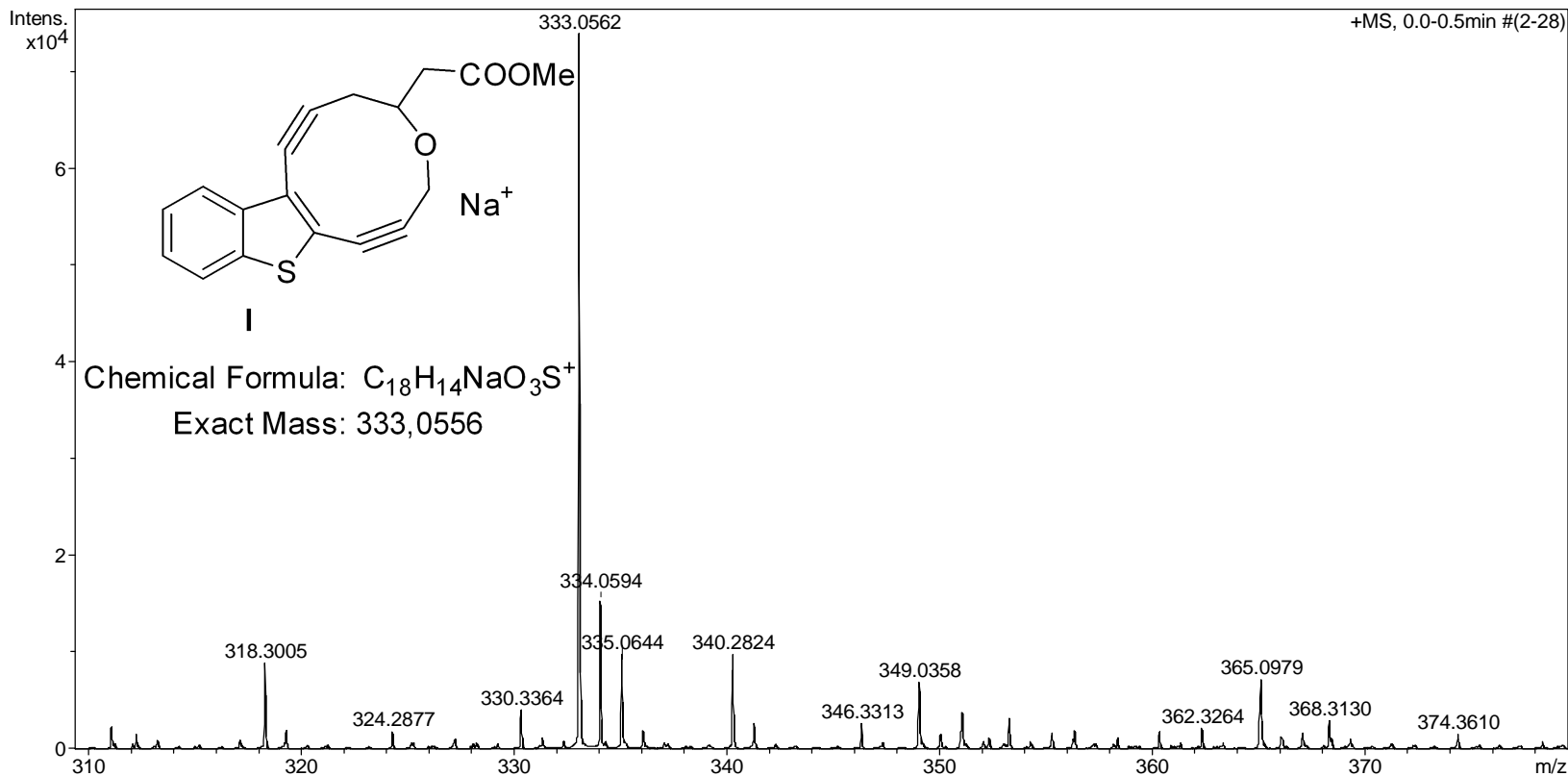
## Analysis Info

Analysis Name D:\Data\2018\may\17\DNA450.d  
Method tune\_low.m  
Sample Name DNA450  
Comment MeOH

Acquisition Date 17.05.2018 16:03:25  
Operator Bruker Customer  
Instrument / Ser# micrOTOF 10223

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



# MASS SPECTRUM REPORT

Instrument Name: Shimadzu Nexera X2 LCMS-9030

Sample Name: **EKh\_79**

Acquired: 30/05/2022

Interface: **ESI**

Nebulizing Gas Flow: 3,0 L/min

Heating Gas: On

Heating Gas Flow: 10,0 L/min

Interface heater: Off

Interface Temperature: 45 C

Drying Gas:

Drying Gas Flow: 10,0 L/min

DL Temperature: 120 C

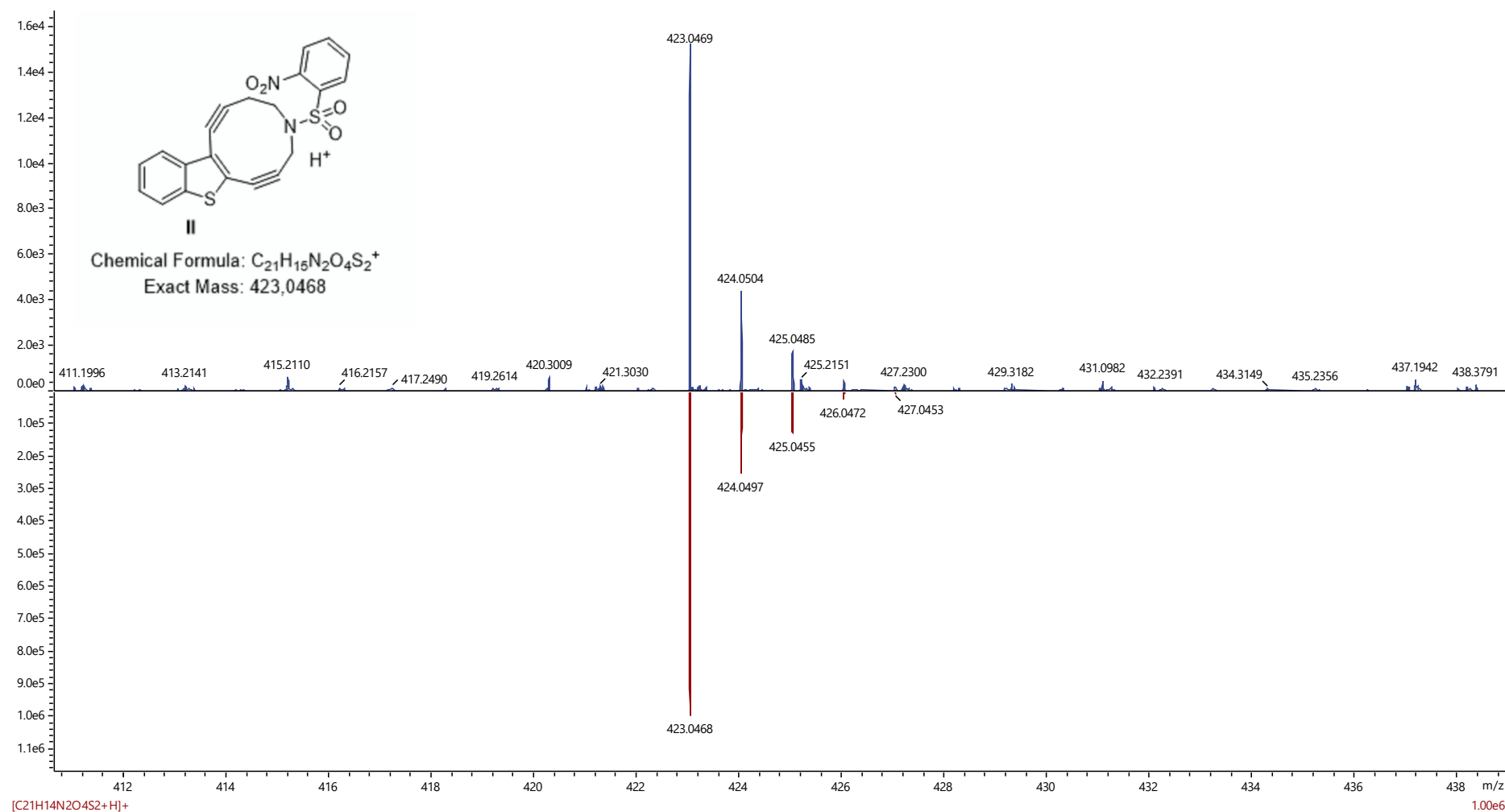
Heat Block: 120 C



Saint-Petersburg  
State  
University  
**Research Park**

1:MS(+) RT:[0.687-0.692]-[0.170-0.372]

1.52e4



# MASS SPECTRUM REPORT

Instrument Name: Shimadzu Nexera X2 LCMS-9030

Sample Name: **Ekh\_83**

Acquired: 12/05/2022

Interface: **ESI**

Nebulizing Gas Flow: 3,0 L/min

Heating Gas: On

Heating Gas Flow: 10,0 L/min

Interface heater: Off

Interface Temperature: 45 C

Drying Gas:

Drying Gas Flow: 10,0 L/min

DL Temperature: 120 C

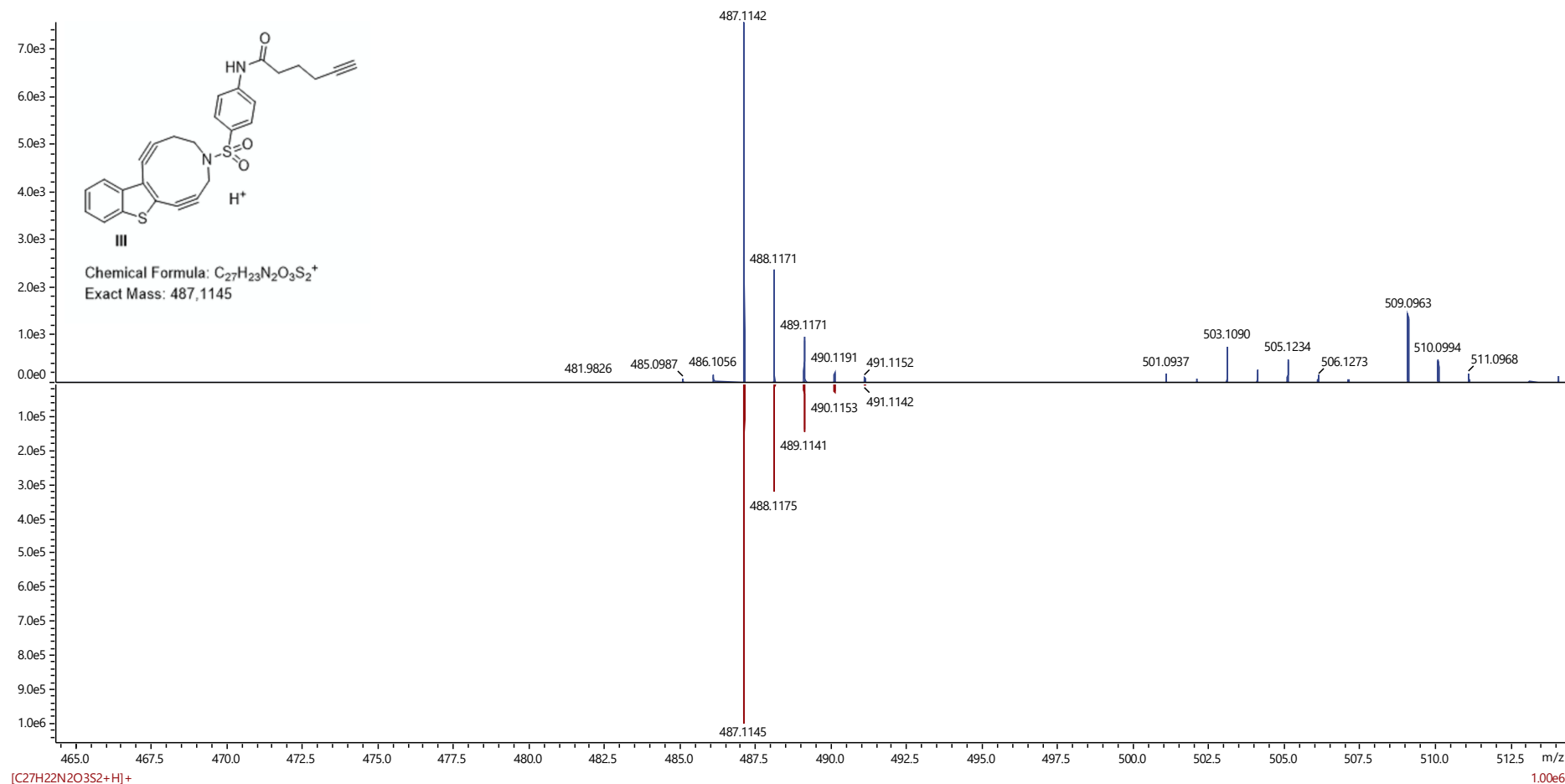
Heat Block: 120 C



Saint-Petersburg  
State  
University  
**Research Park**

1:MS(+) RT:[0.695-0.730]-[0.087-0.187]

7.56e3



# Display Report

## Analysis Info

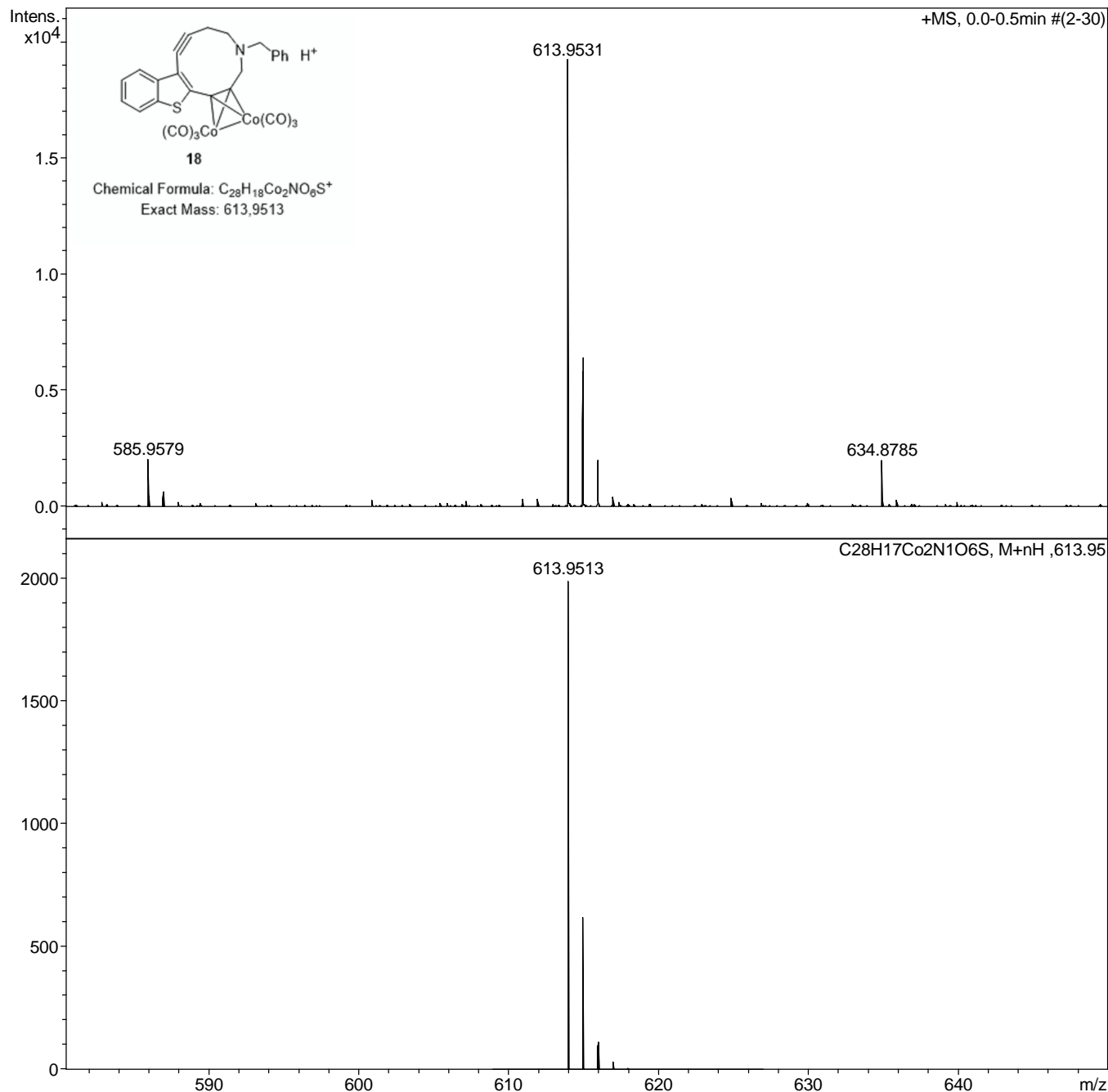
Analysis Name D:\Data\Work\2018\January\24\DNA58.d  
Method tune\_low\_pos.m  
Sample Name DNA58  
Comment MeOH

Acquisition Date 1/24/2018 1:29:20 PM

Operator BDAL@DE  
Instrument maXis 62

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Source



# Mass Spectrum Report

## Analysis Info

Analysis Name D:\Data\2020\february\21\R90.d  
Method tune\_wide.m  
Sample Name R90  
Comment MeOH

Acquisition Date 21.02.2020 12:28:31  
Operator  
Instrument / Ser# Bruker Customer  
microTOF 10223

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

