

# **Expeditious Access to Spiro-fused 2,5-Cyclohexadienones via Thio(seleno)cyanative *ipso*-Cyclization**

Chada Raji Reddy,<sup>\*,a,b</sup> Uprety Ajaykumar<sup>a,b</sup> and Dattahari H. Kolgave<sup>a,b</sup>

<sup>a</sup>Department of Organic Synthesis & Process Chemistry

CSIR-Indian Institute of Chemical Technology (CSIR-IICT), Hyderabad 500007, India

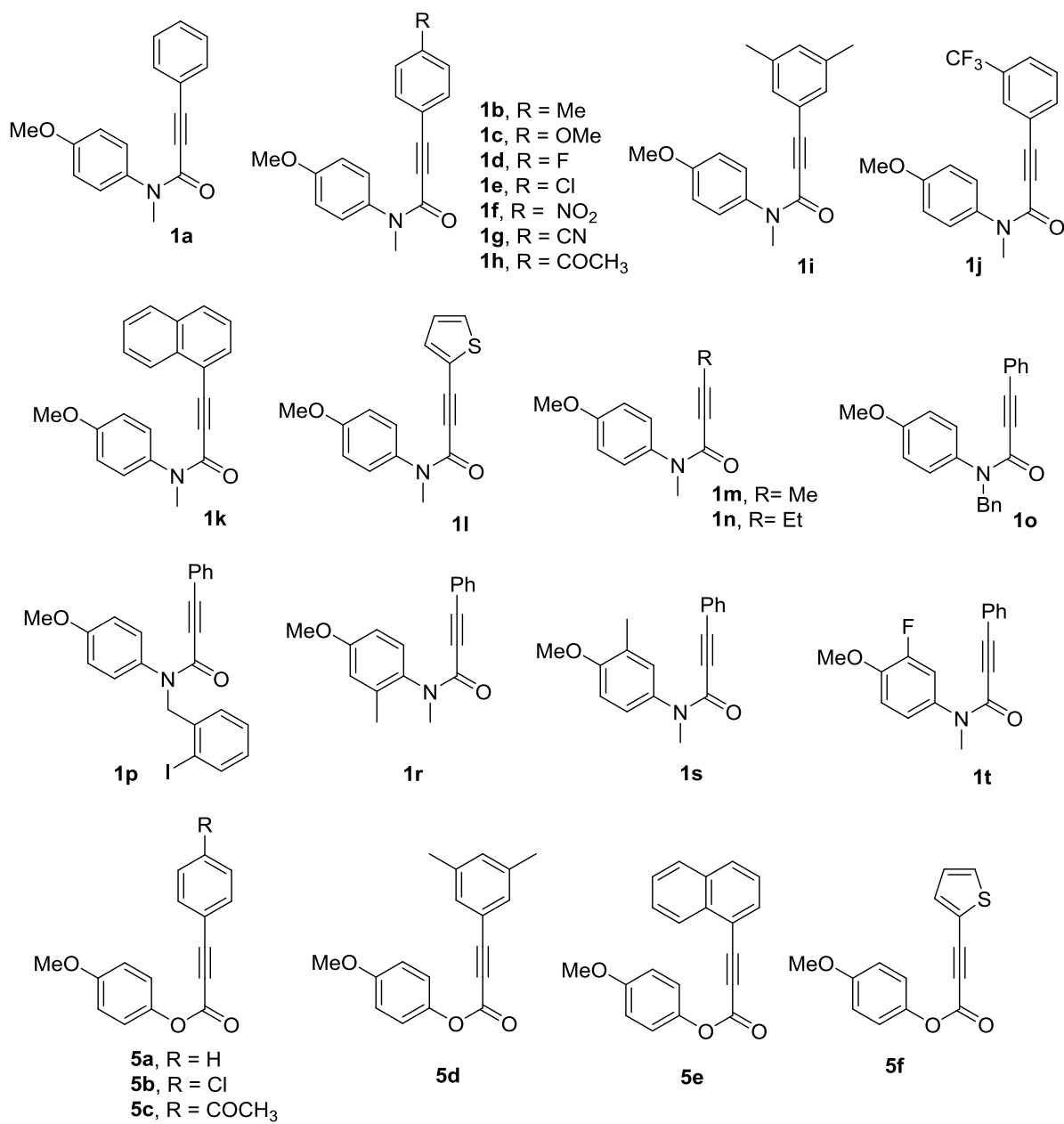
<sup>b</sup>Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India

E-mail: rajireddy@iict.res.in

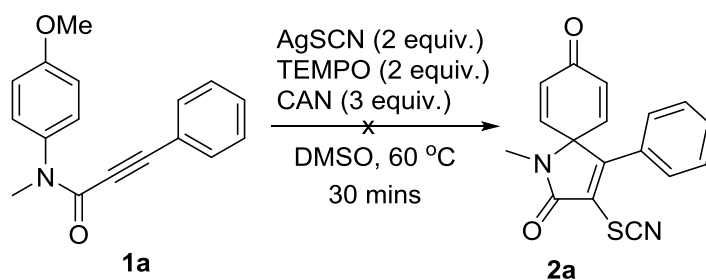
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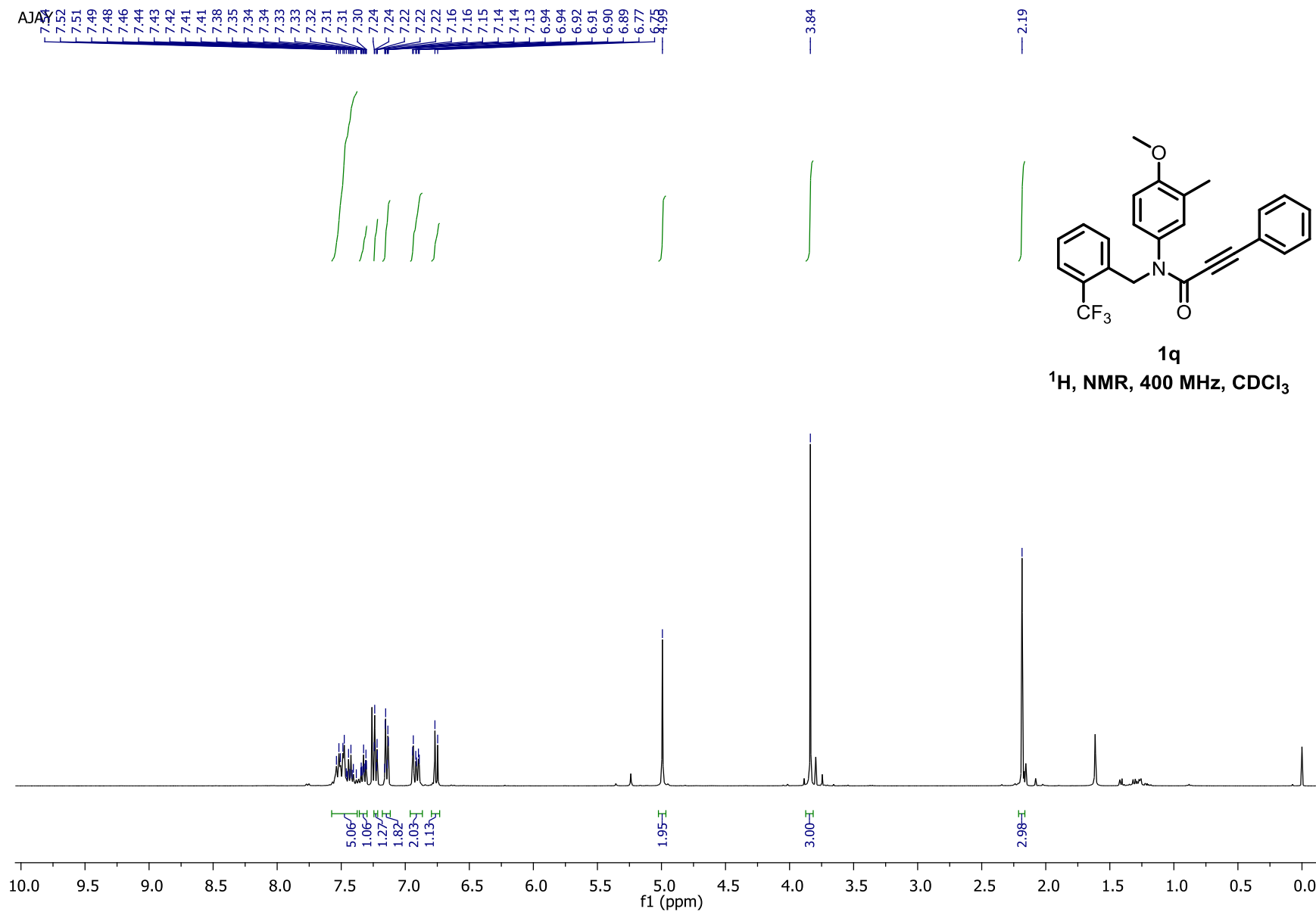
## Structures of Starting materials: *N*-Propiolamides and *N*-propiolates

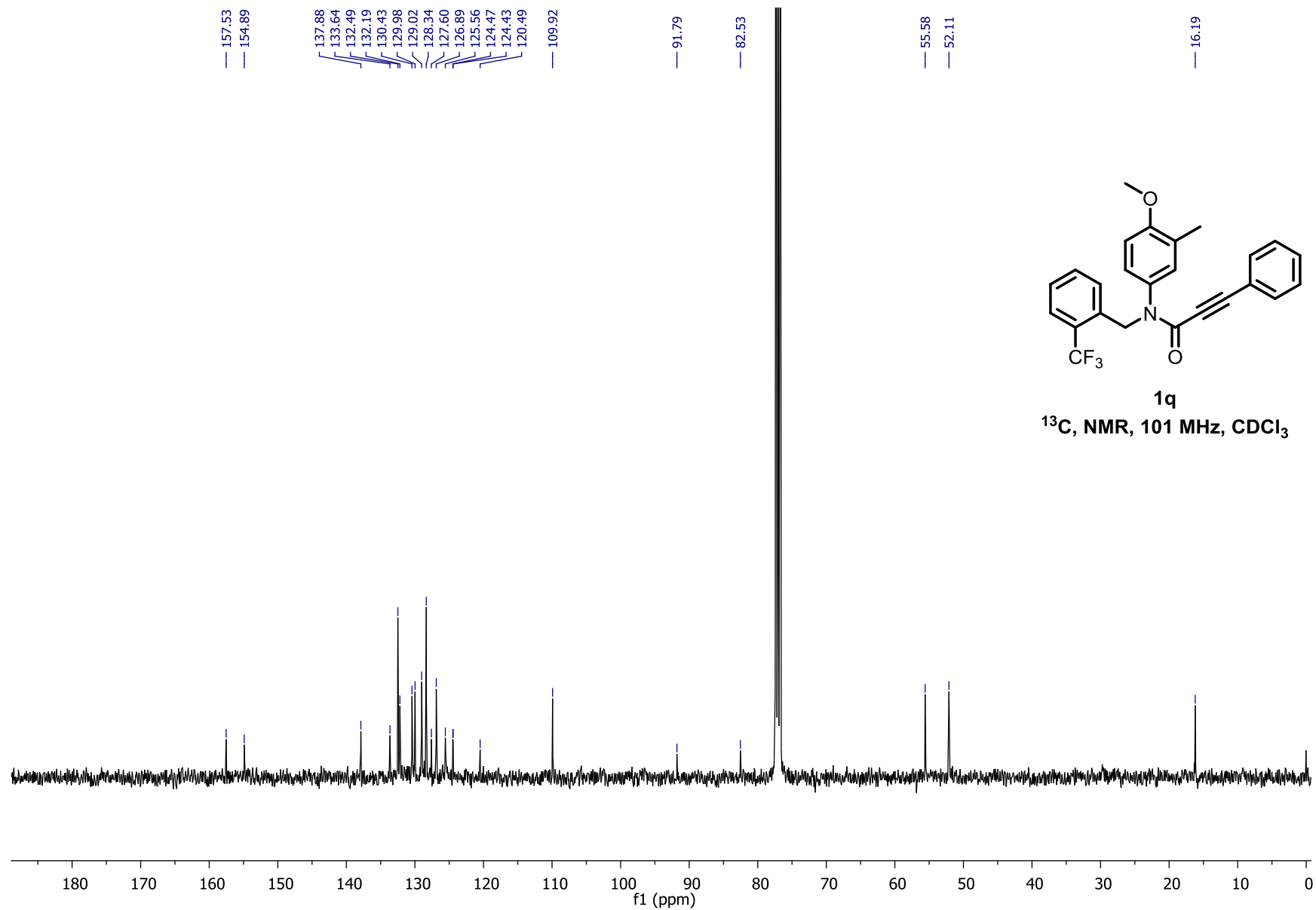


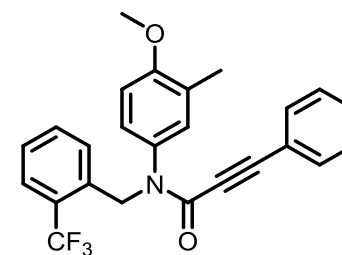
**Control Experiment with 2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO):**



*N*-(4-Methoxyaryl)-propionamide **1a** (50 mg, 0.19 mmol), Silver thiocyanate (64 mg, 0.38 mmol), 2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) (59 mg, 0.38 mmol) and Ceric Ammonium Nitrate (308 mg, 0.57 mmol) were taken in a reaction vial and 3 mL of DMSO was added. The reaction mixture was stirred at 60 °C (oil bath temperature) for 30 minutes and the progress of the reaction as monitored by TLC was found to be inhibited.

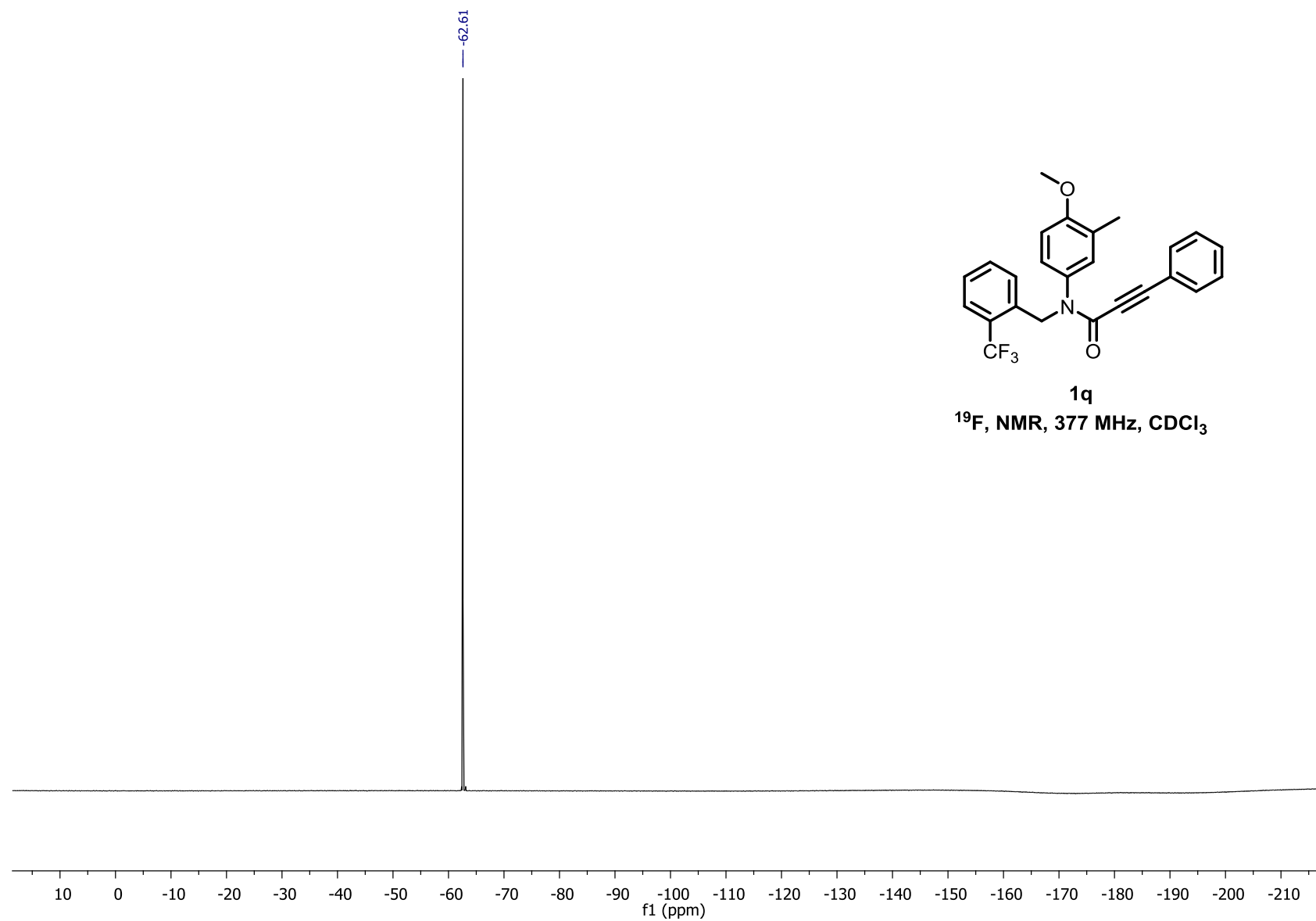


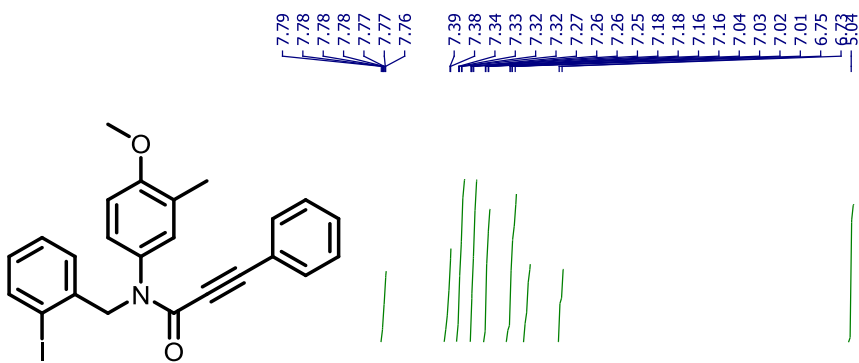




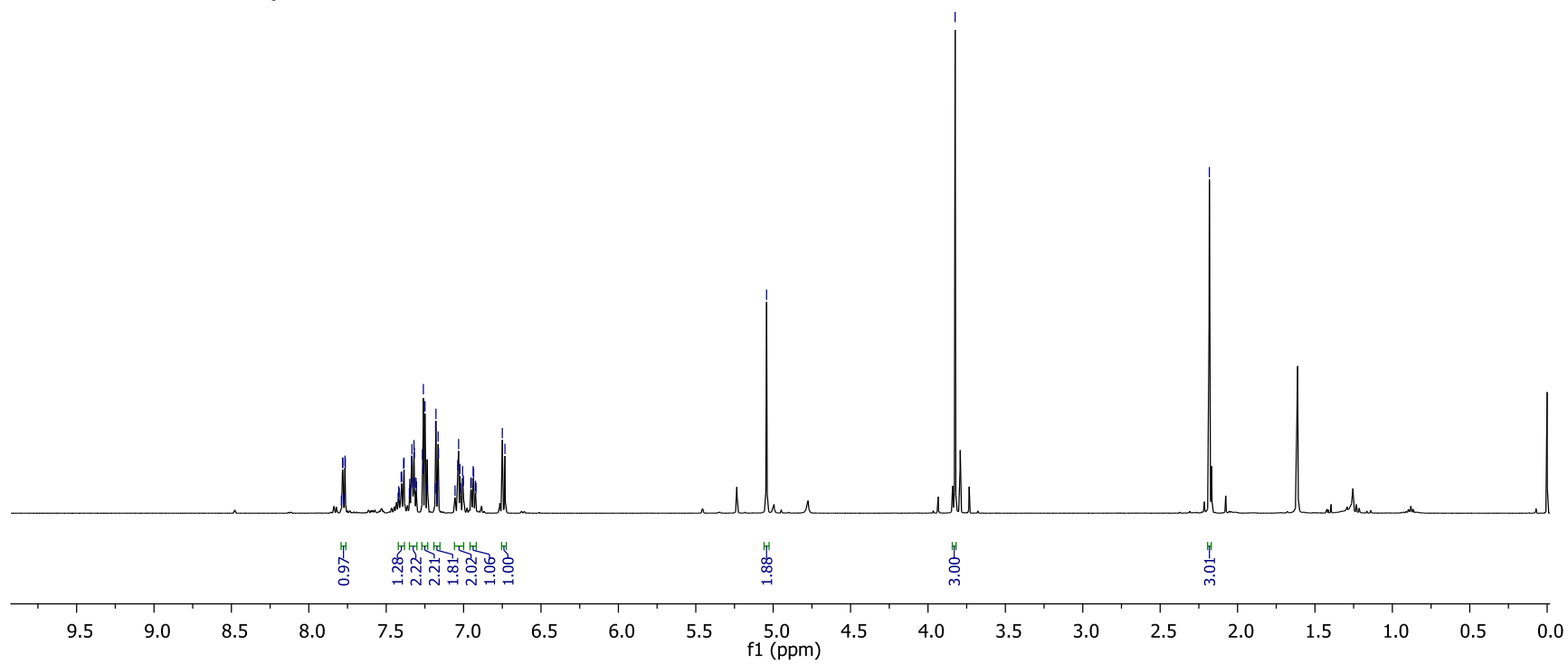
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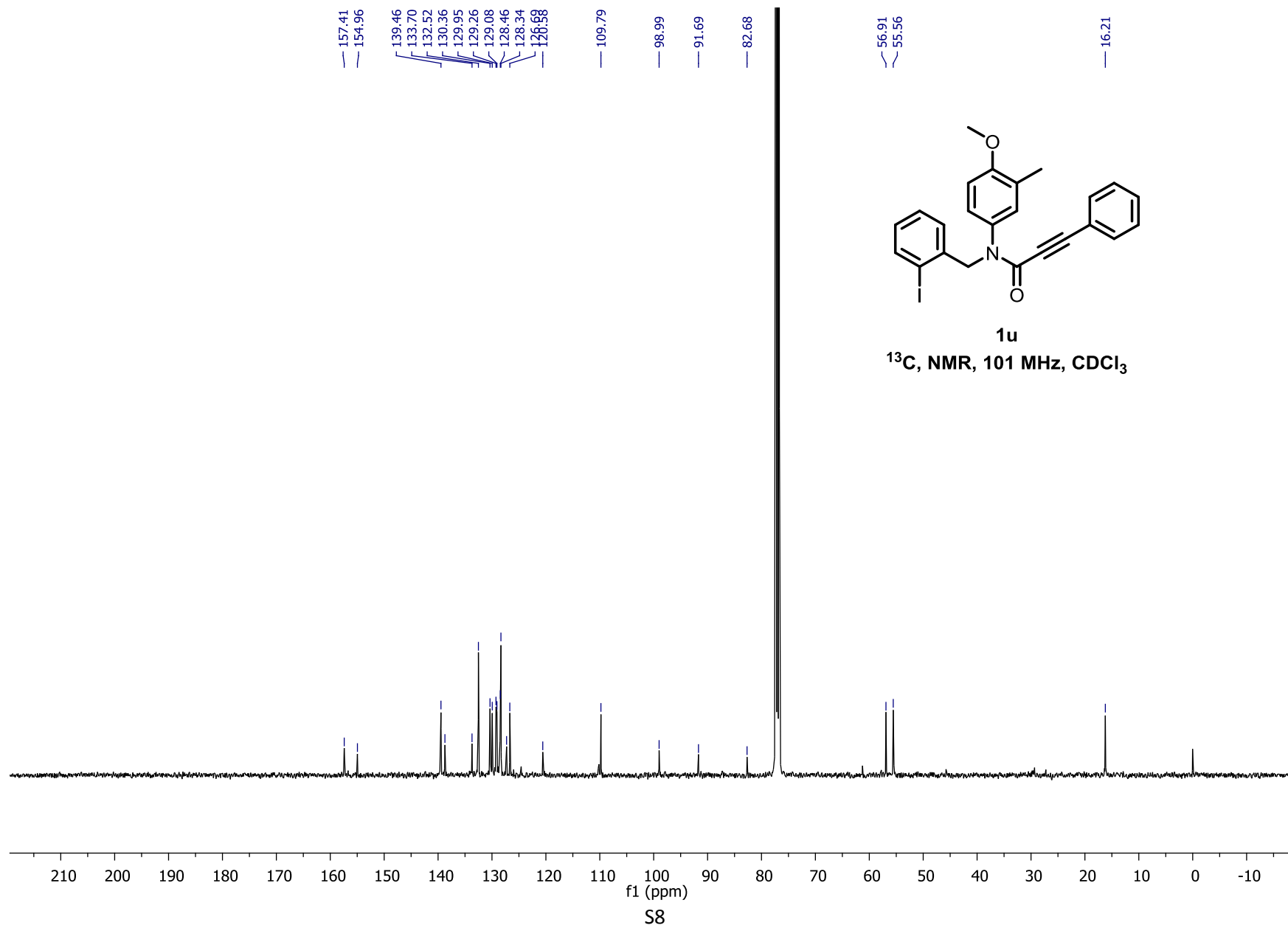
**$^{19}\text{F}$ , NMR, 377 MHz,  $\text{CDCl}_3$**



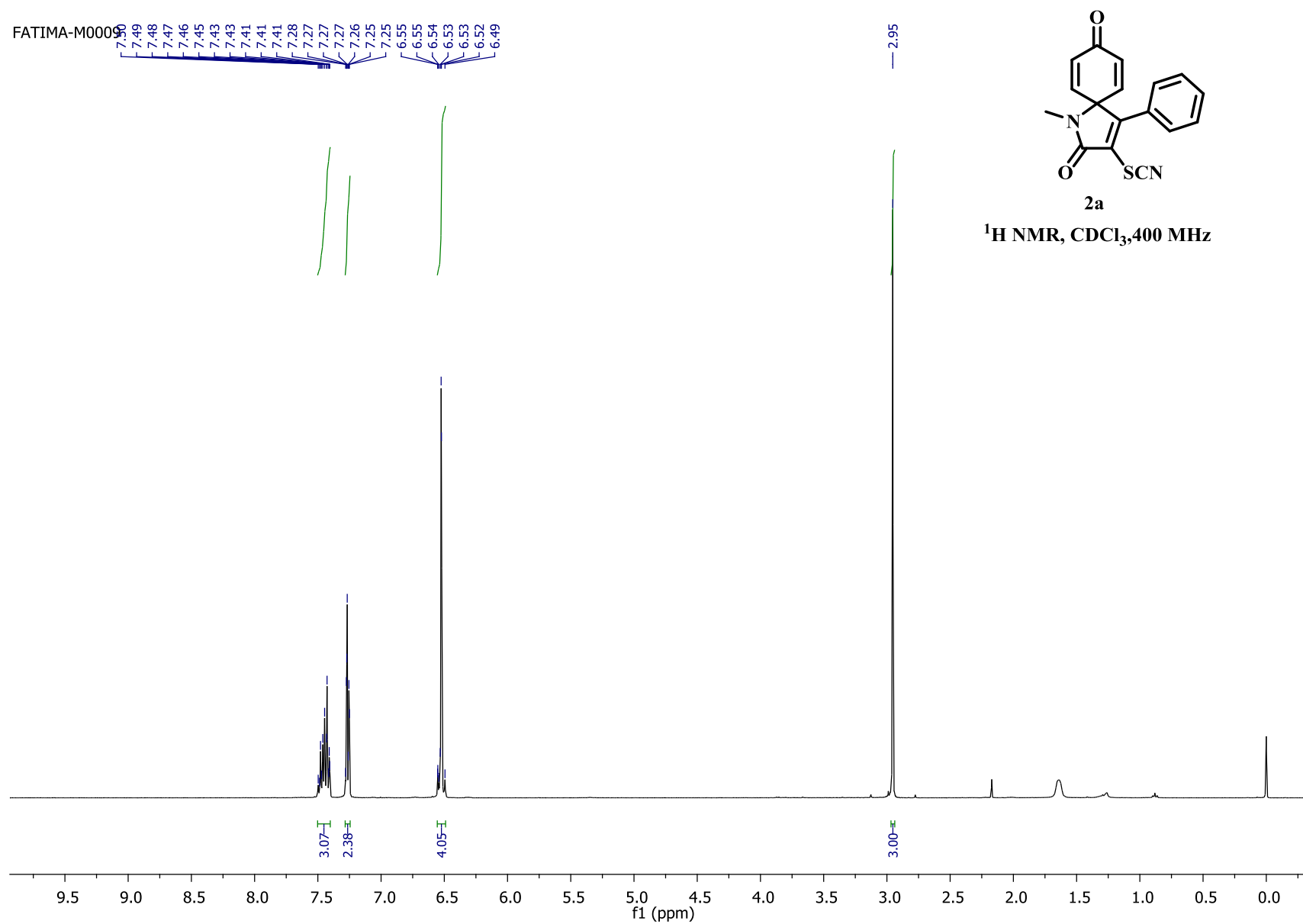


**1u**  
 $^1\text{H}$ , NMR, 500 MHz,  $\text{CDCl}_3$

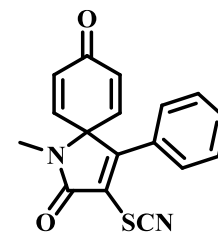
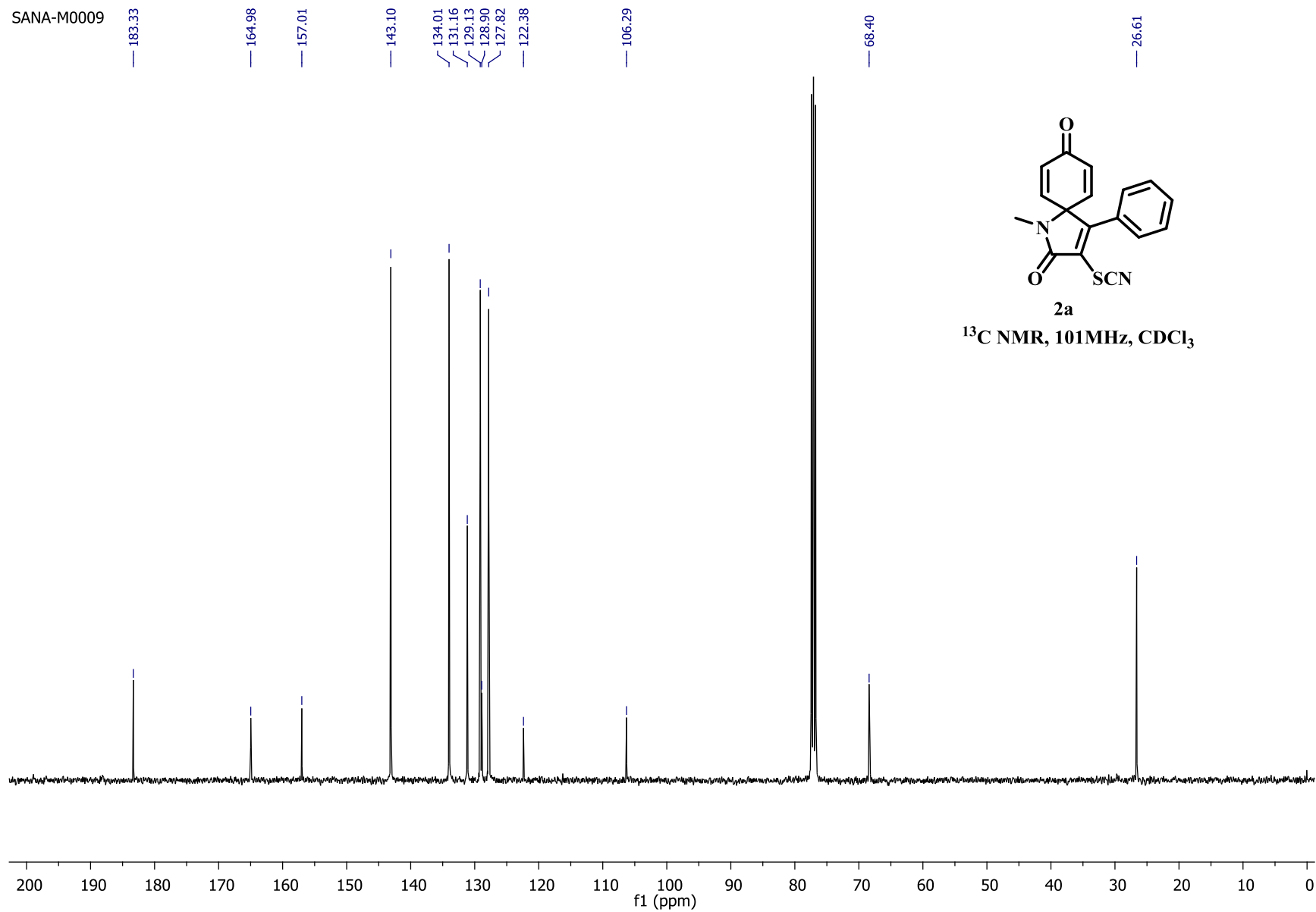








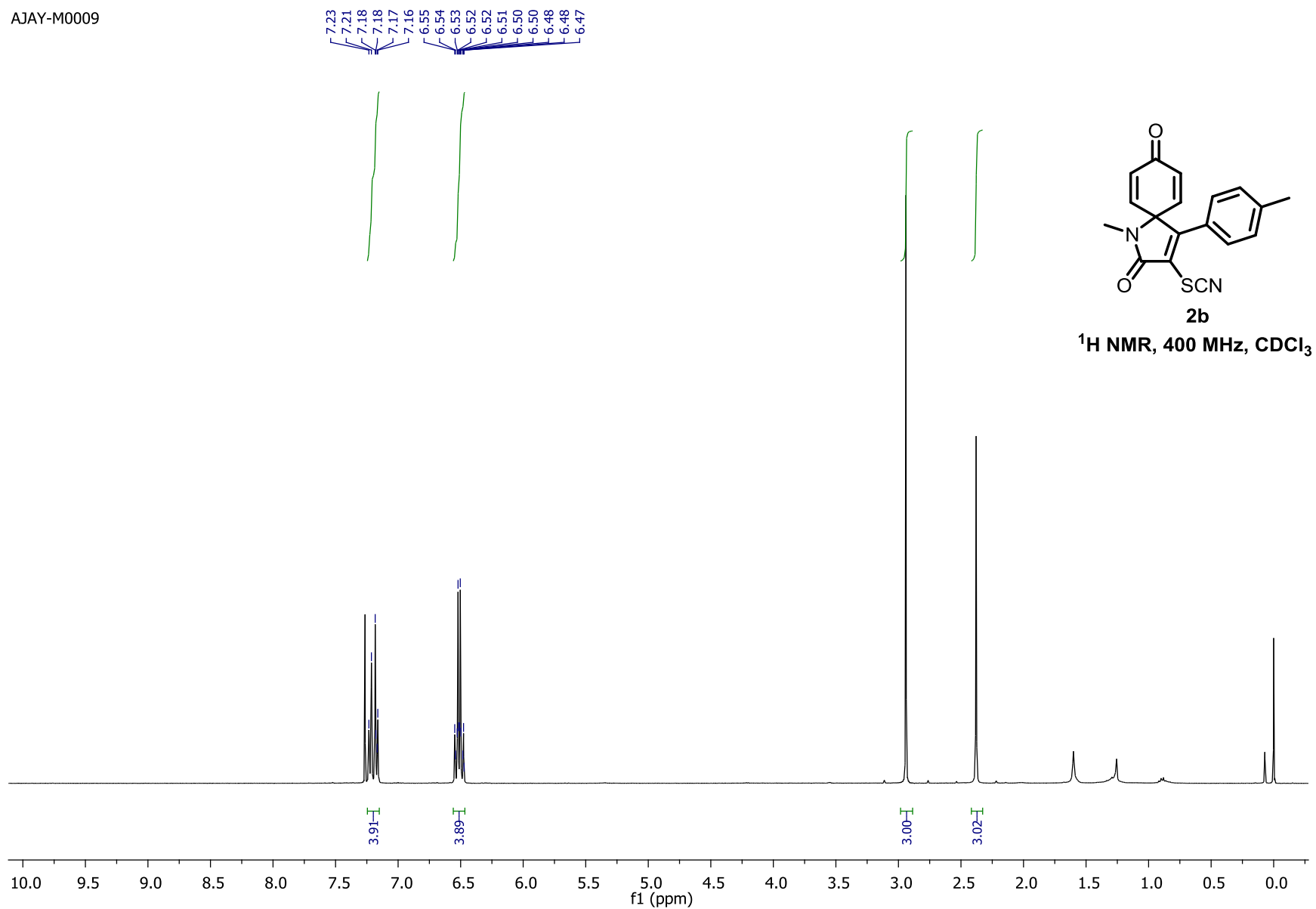
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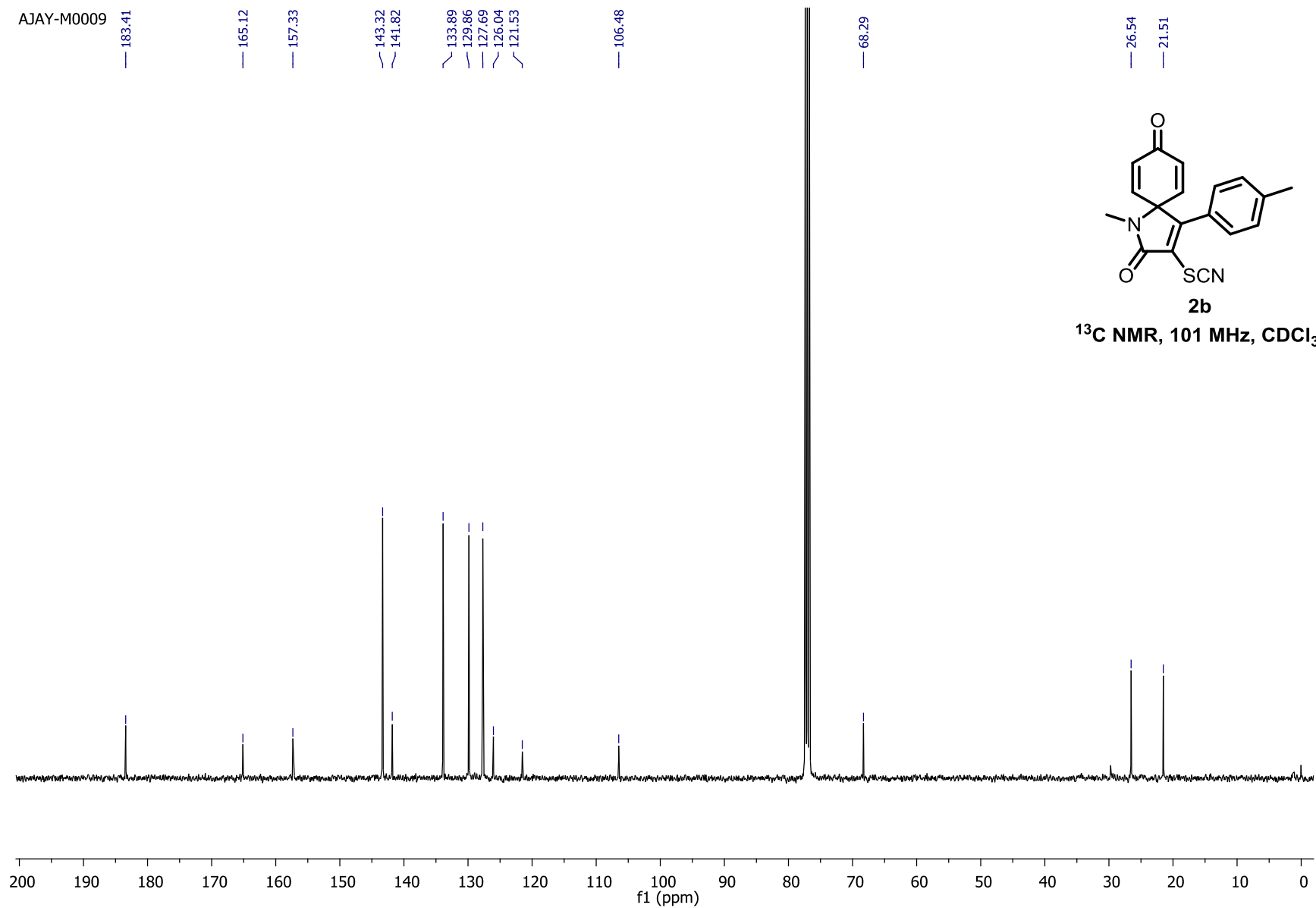
2a

<sup>13</sup>C NMR, 101MHz, CDCl<sub>3</sub>

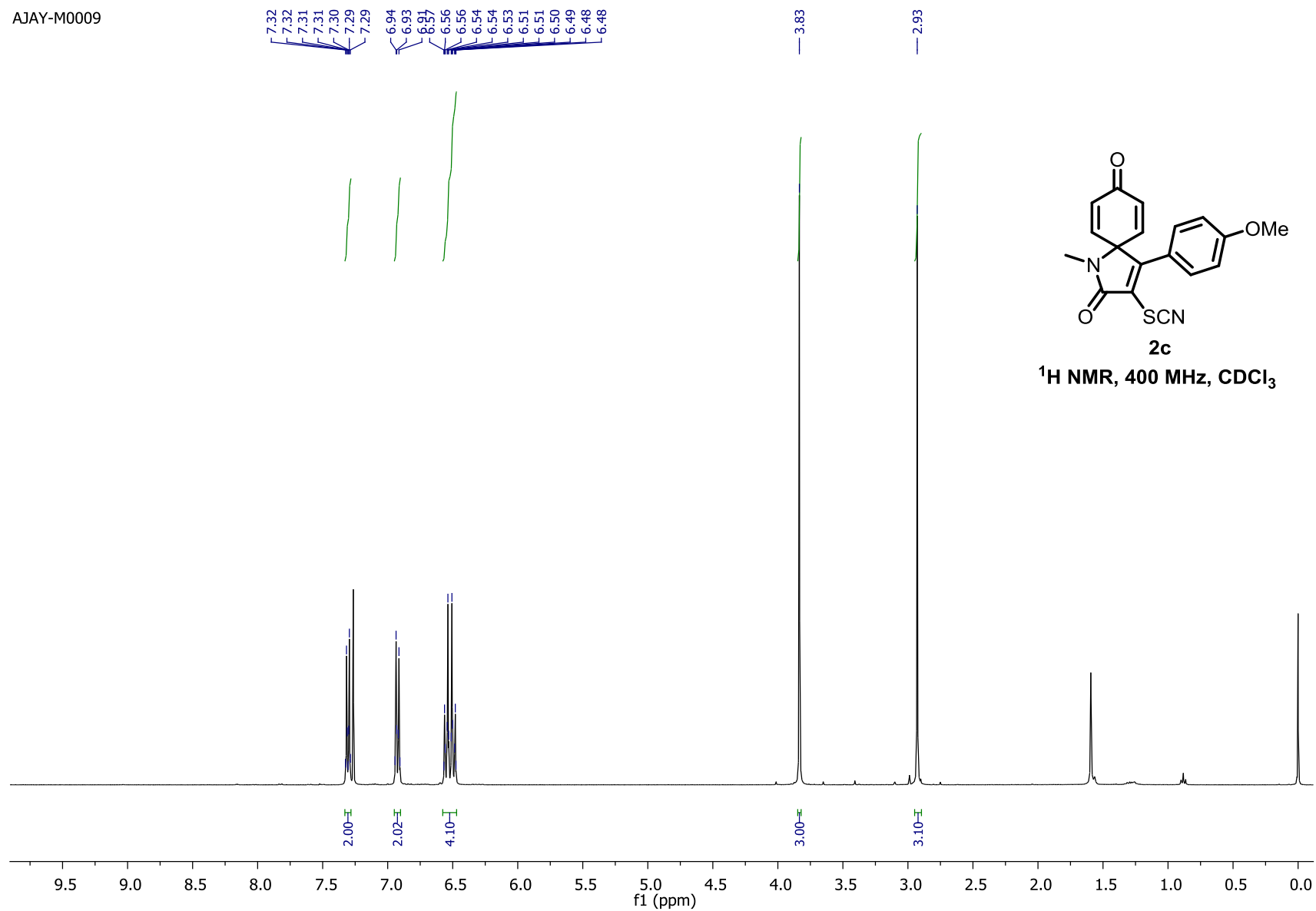
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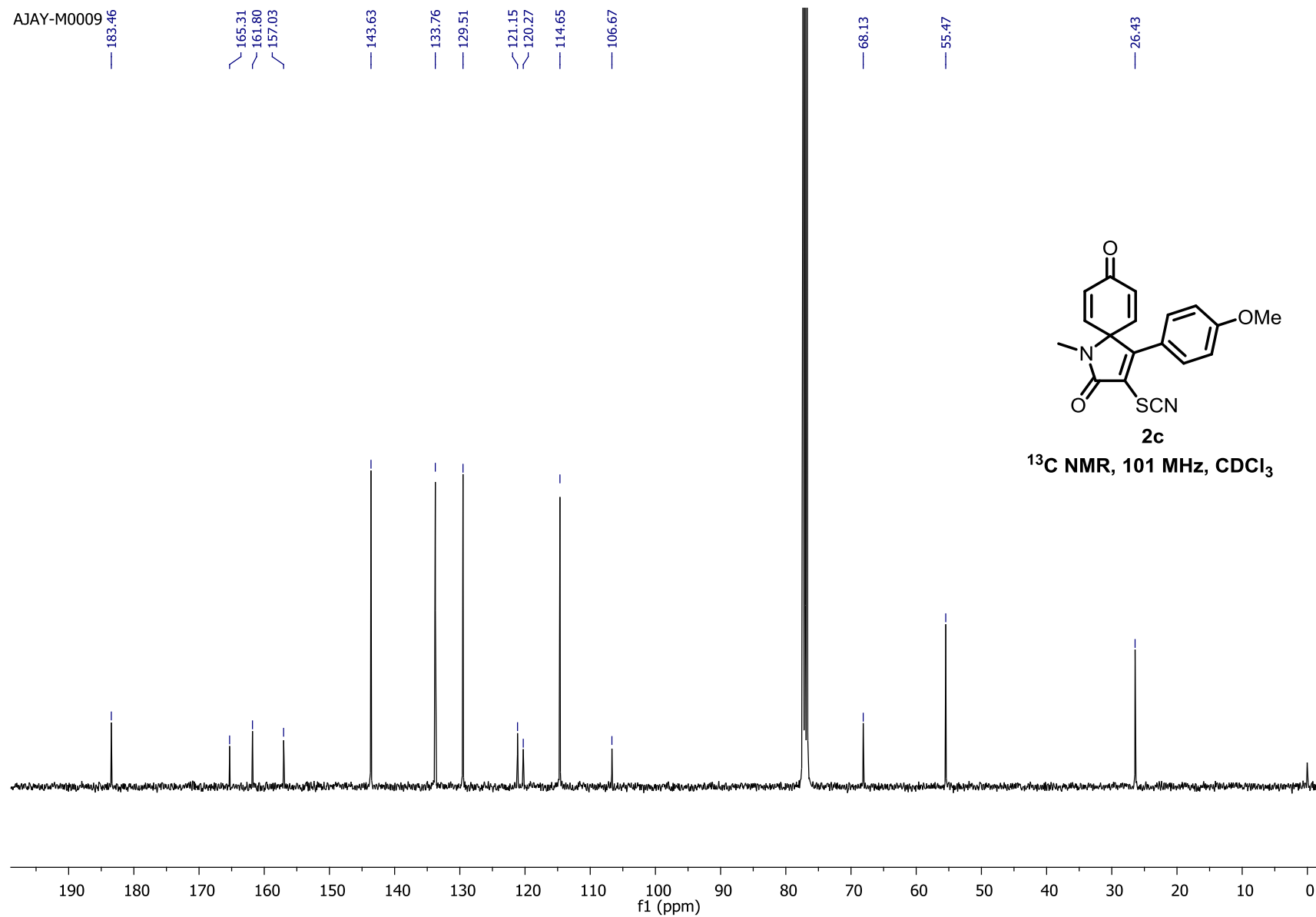
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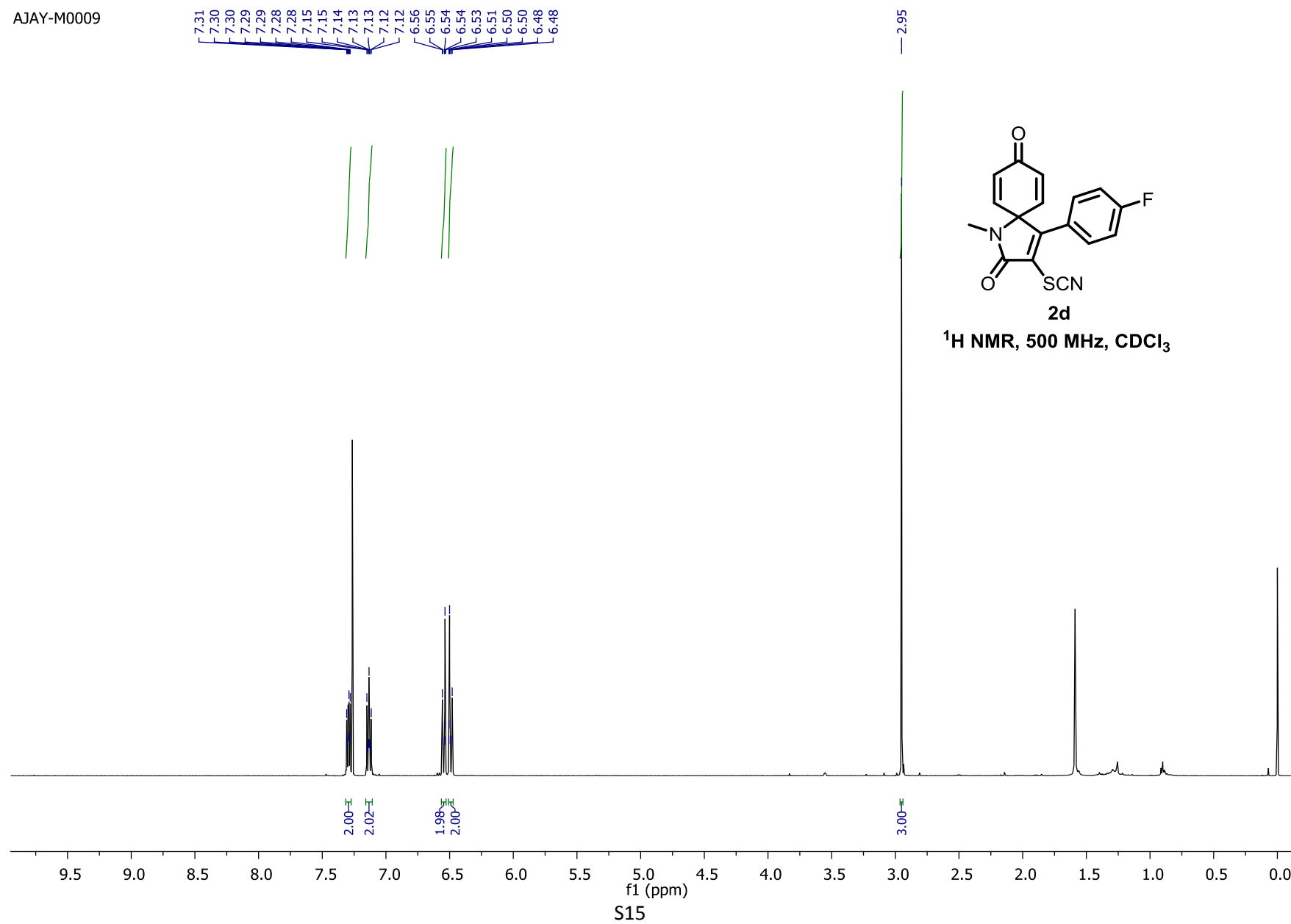
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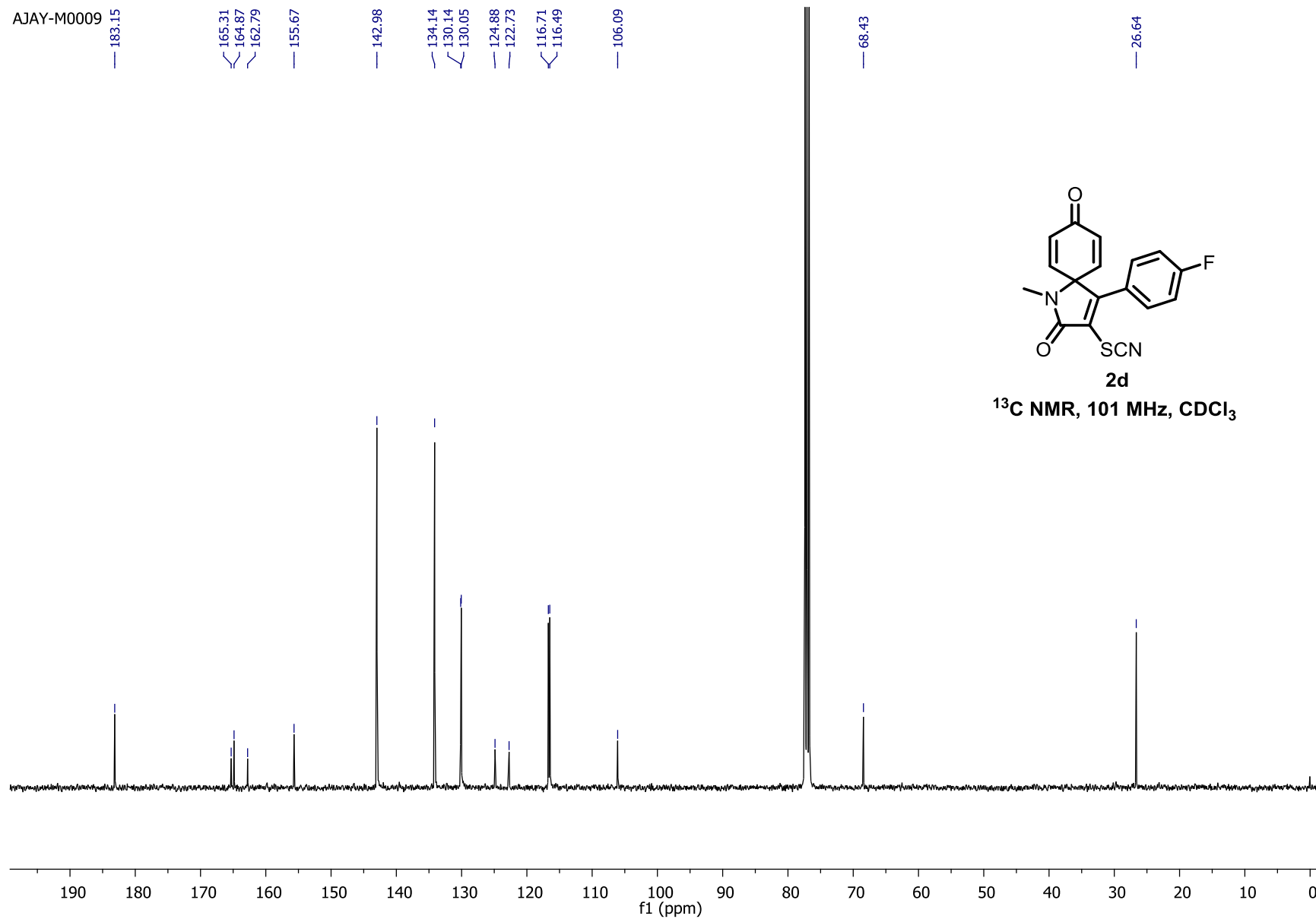


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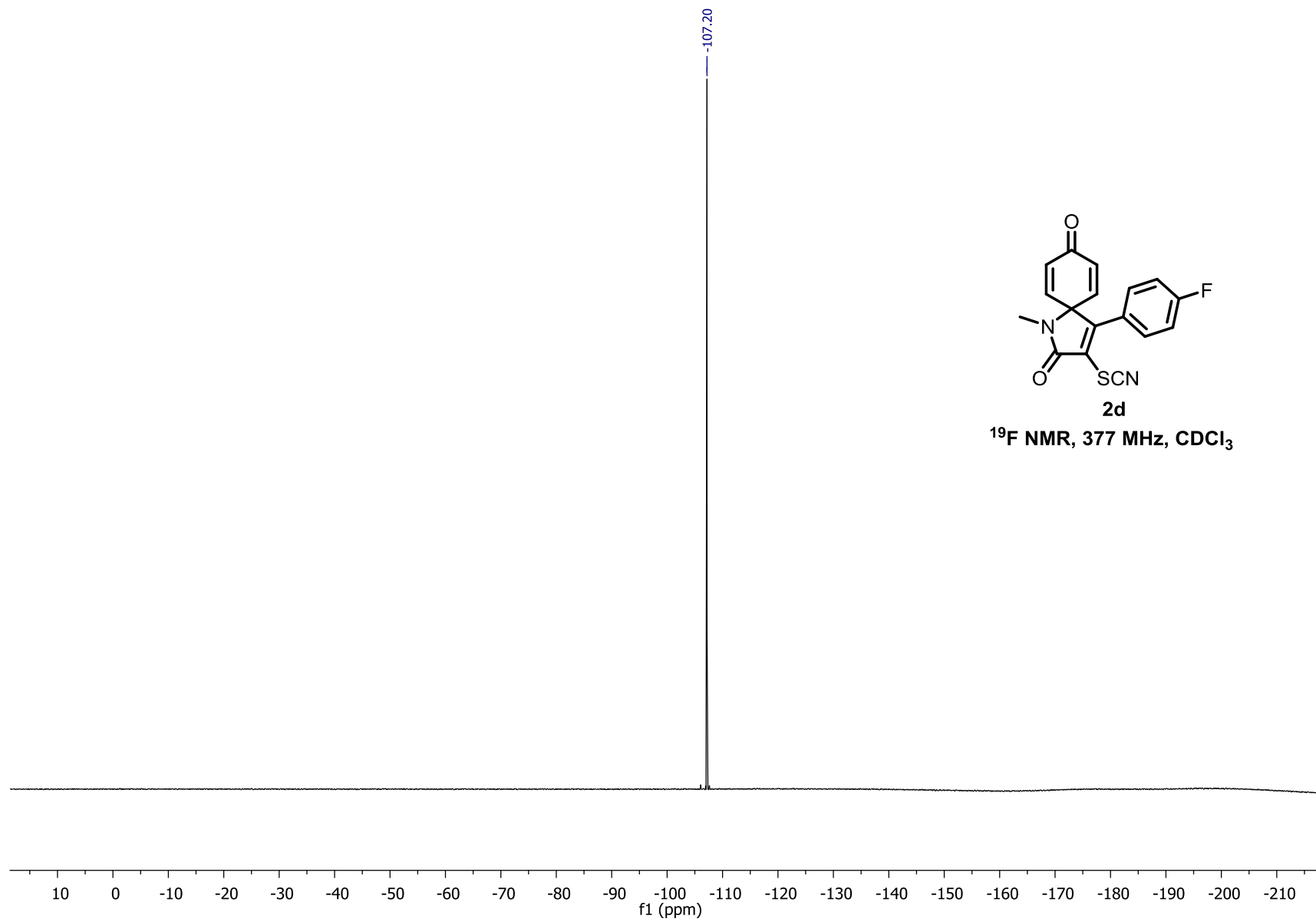


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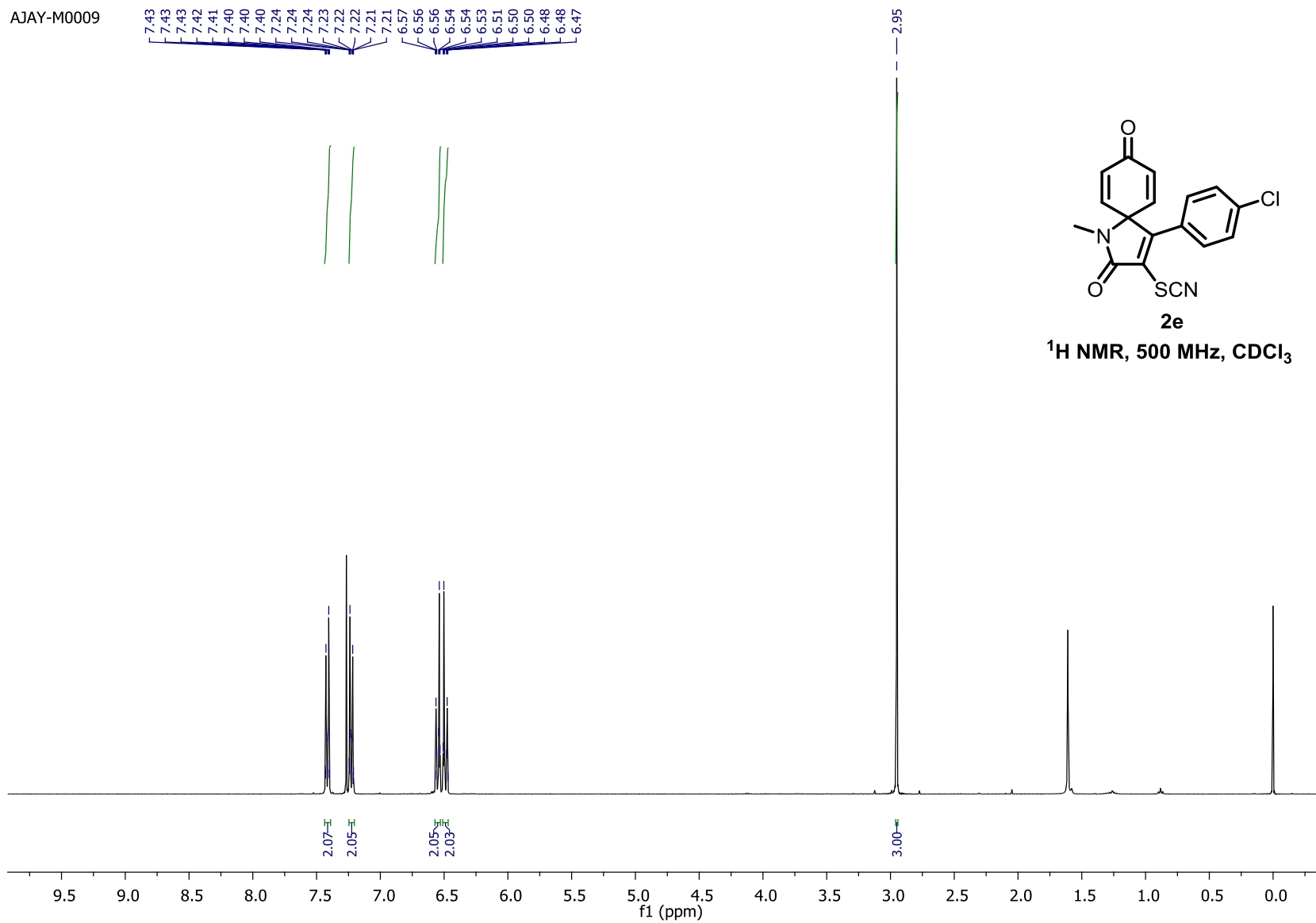




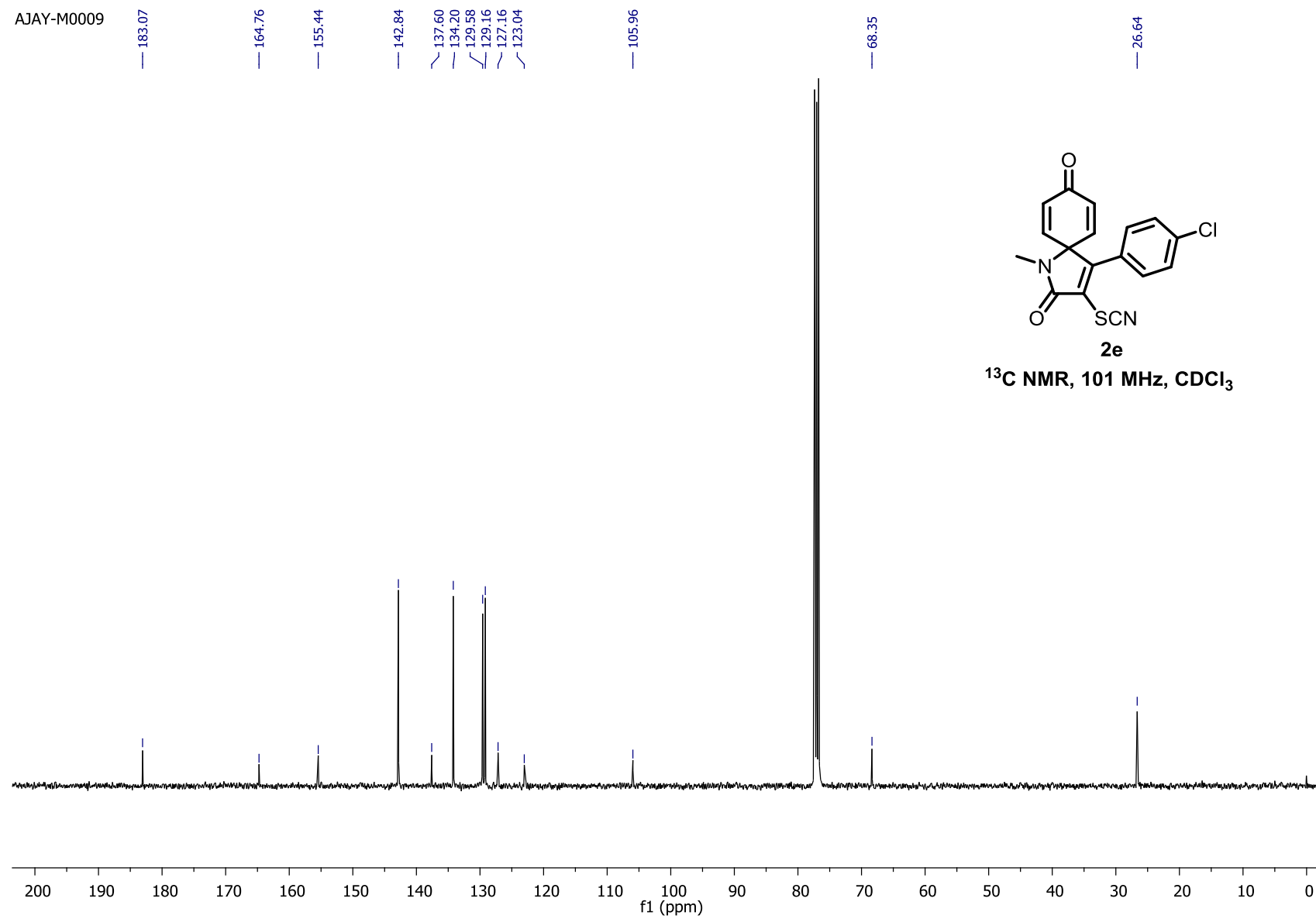




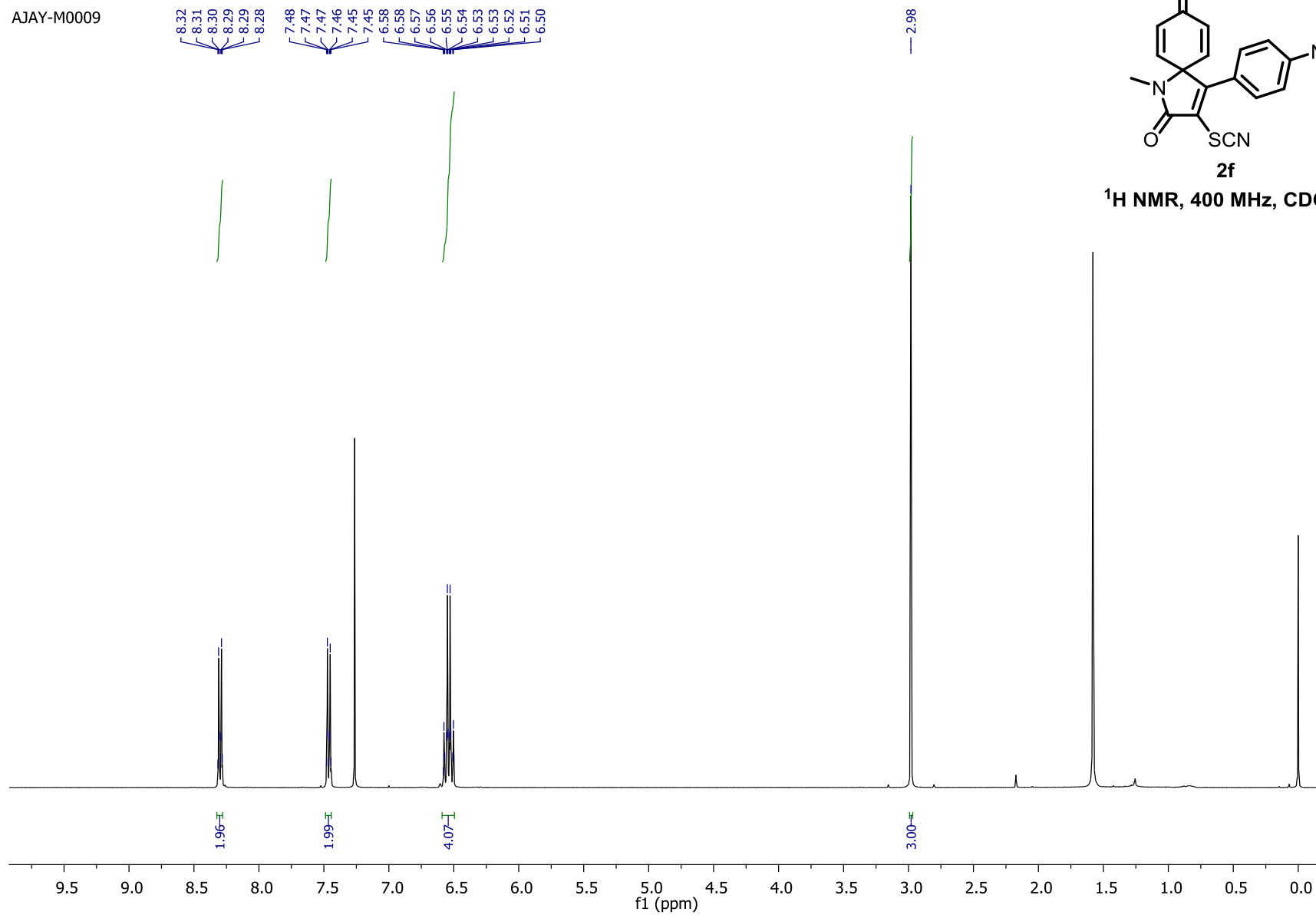
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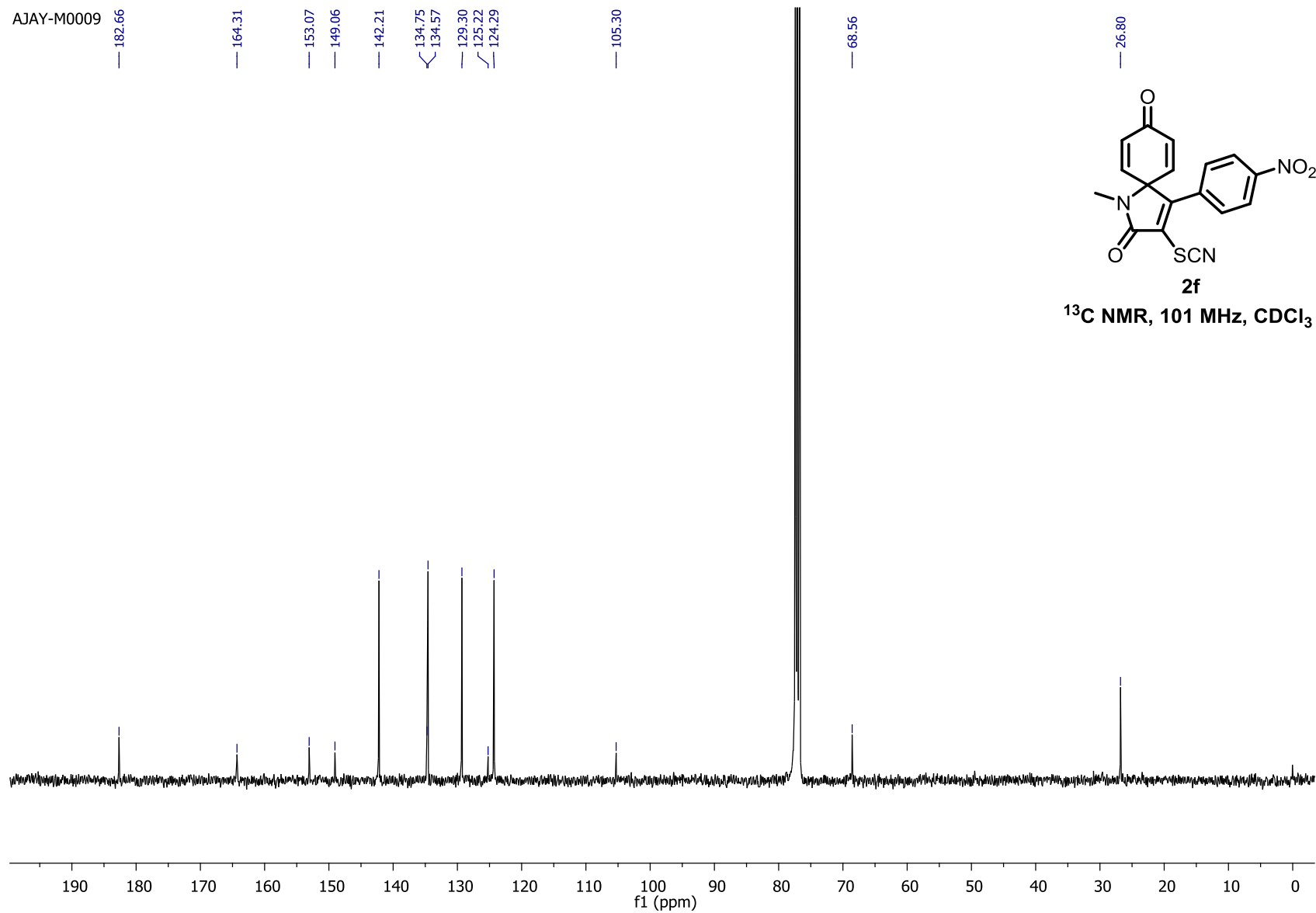


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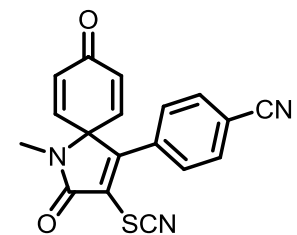




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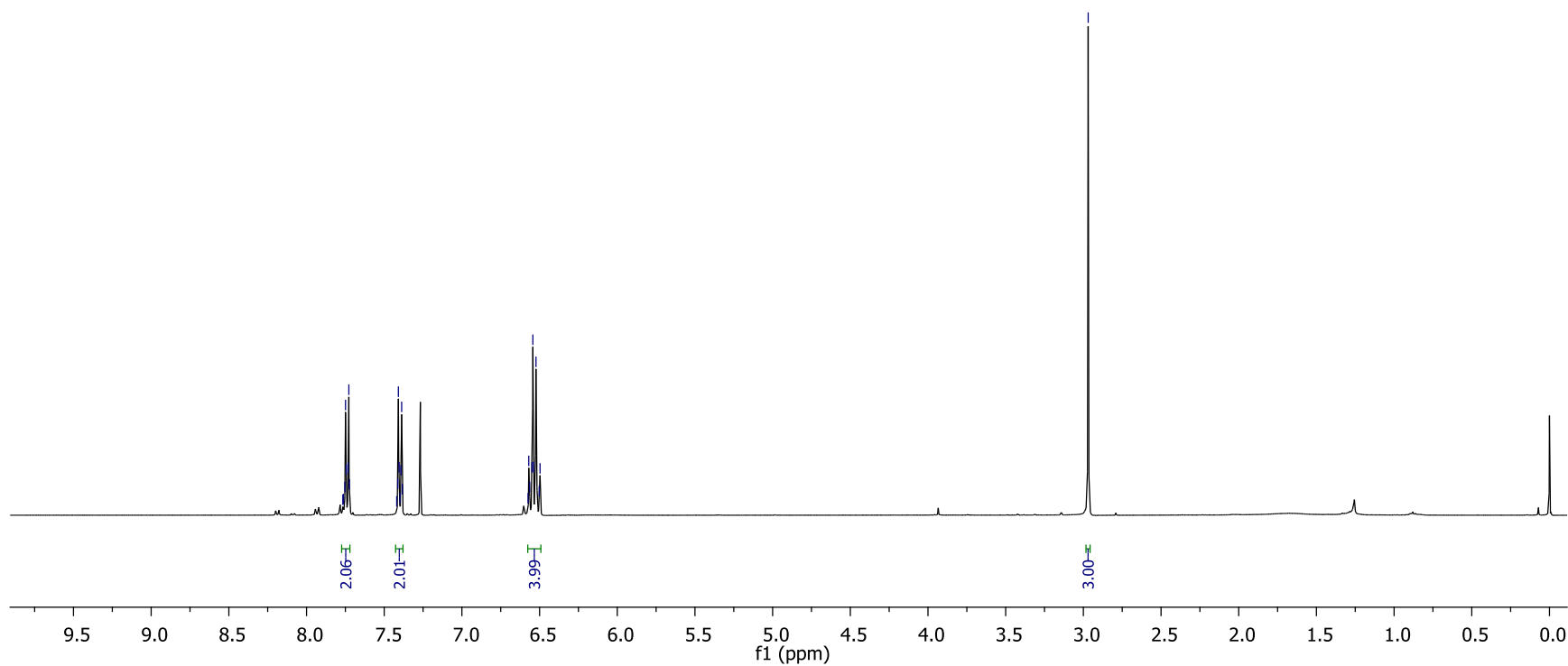
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7.76  
7.75  
7.74  
7.73  
7.72  
7.41  
7.40  
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6.57  
6.56  
6.55  
6.54  
6.52  
6.50

2.97

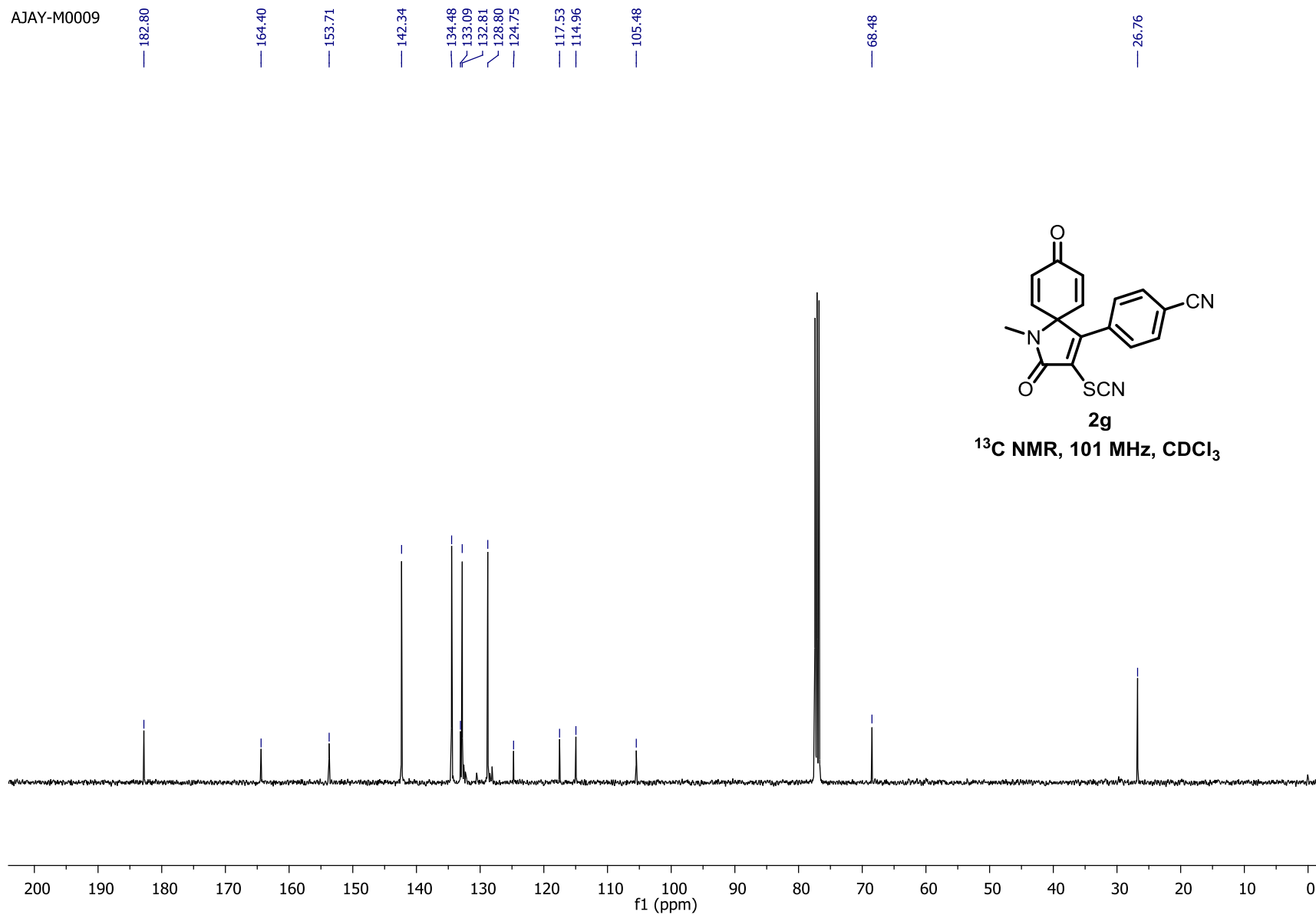


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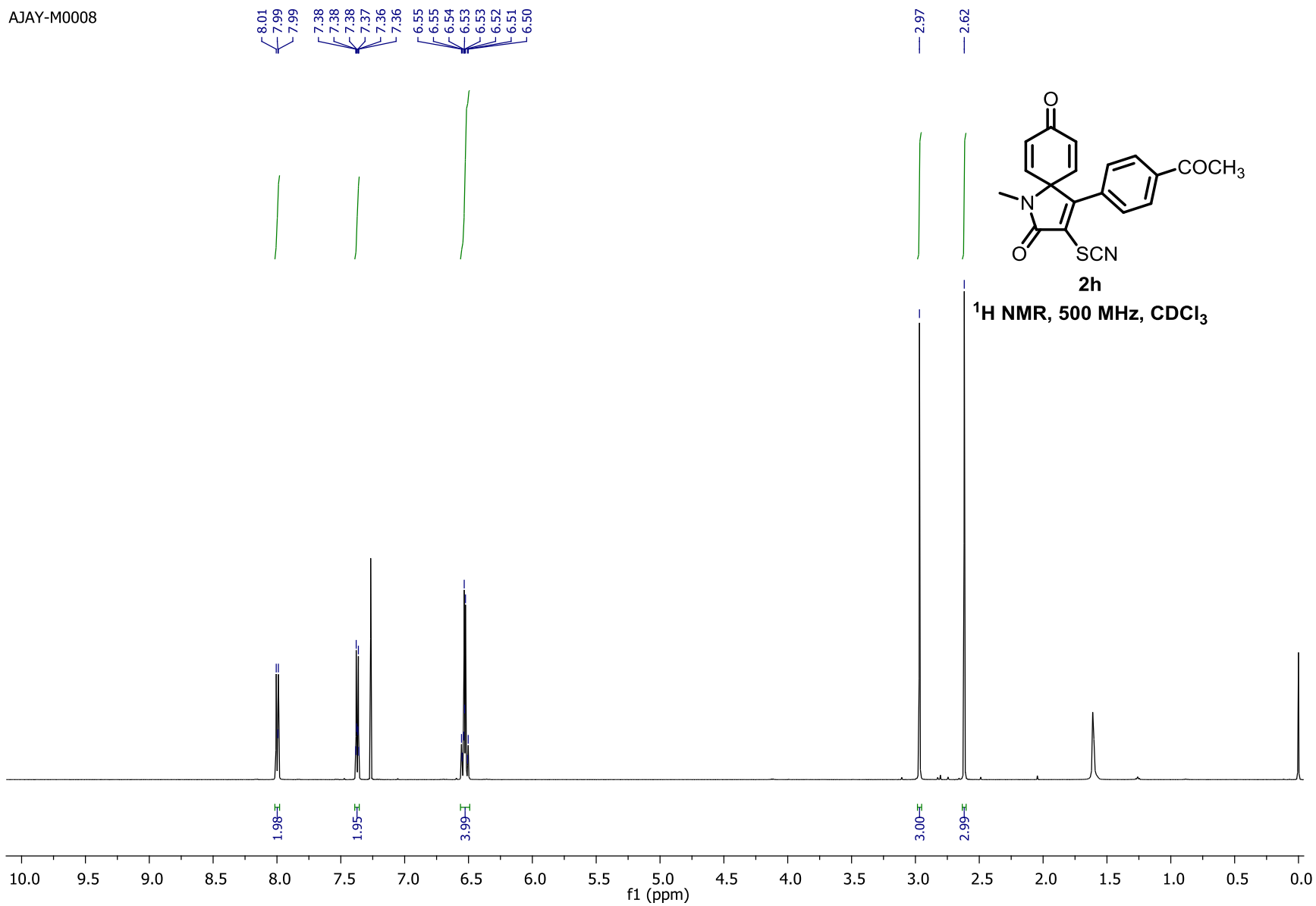
<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>



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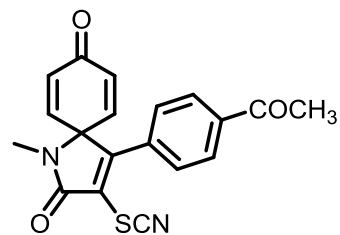


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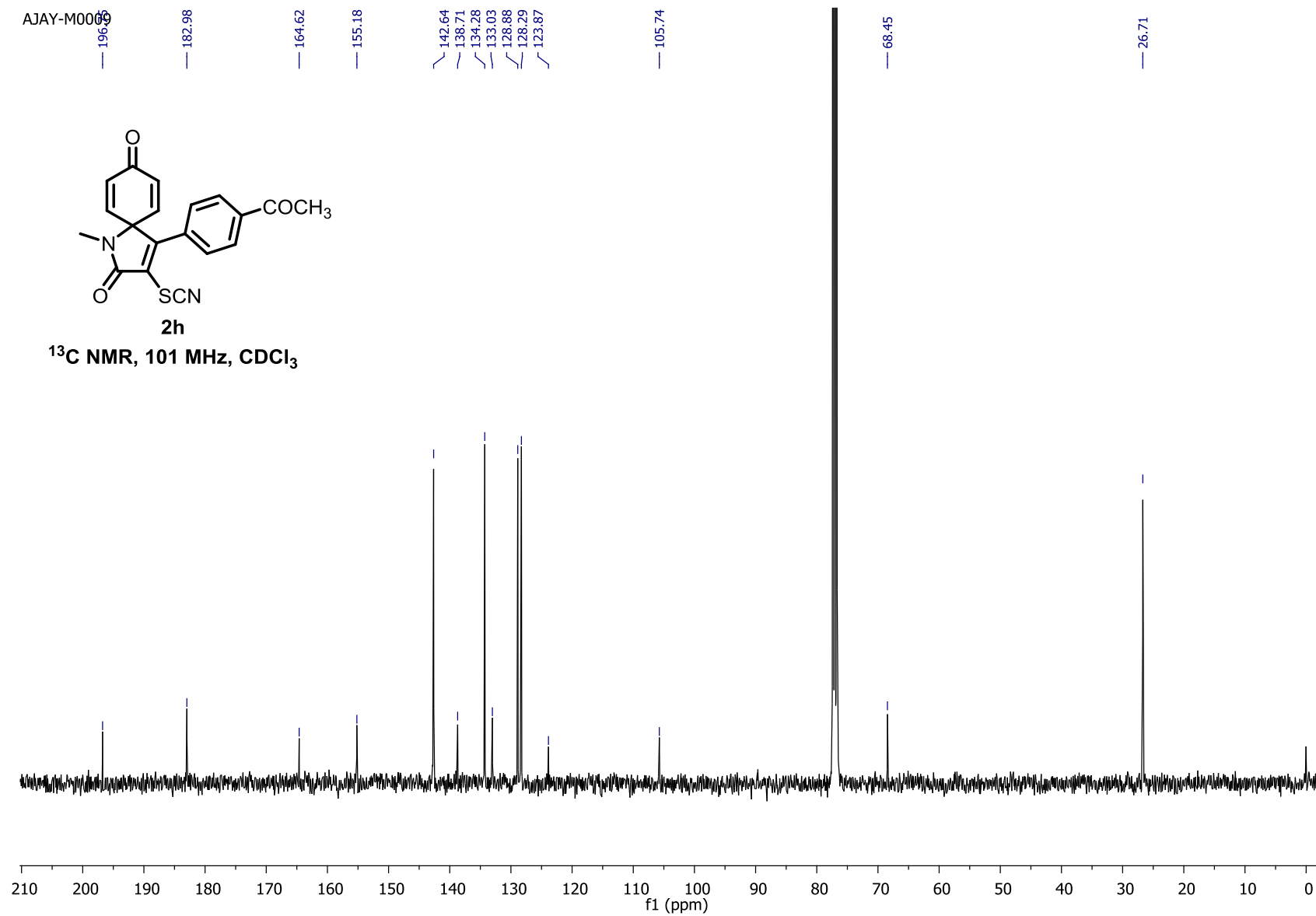


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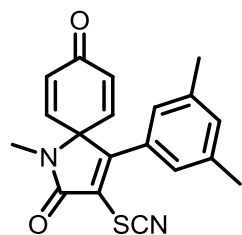


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$^{13}\text{C}$  NMR, 101 MHz,  $\text{CDCl}_3$

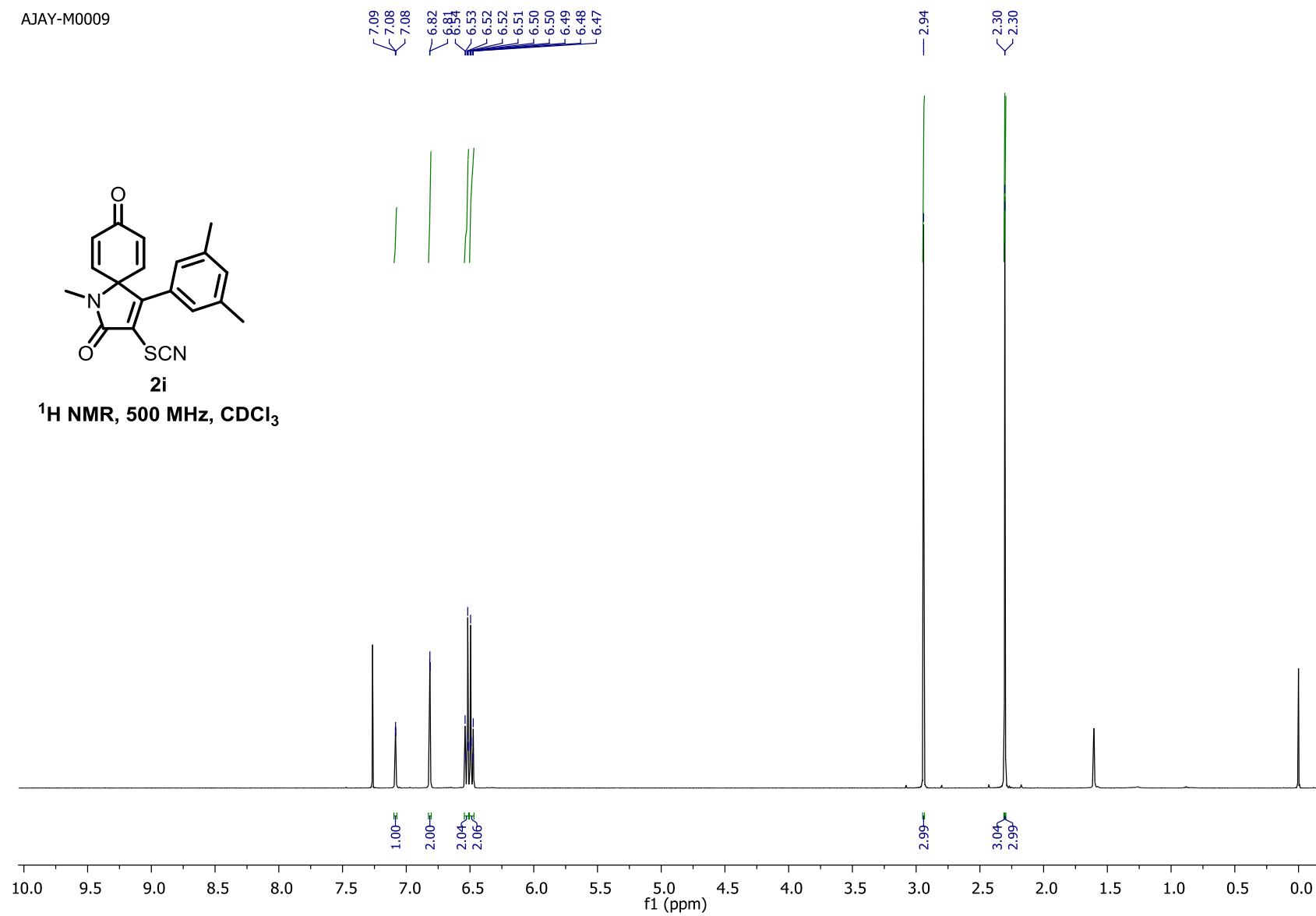


AJAY-M0009



2i

$^1\text{H}$  NMR, 500 MHz,  $\text{CDCl}_3$



AJAY-M0009

— 183.45

— 165.04

— 157.65

— 143.24

— 138.88

— 133.86

— 132.88

— 128.86

— 125.34

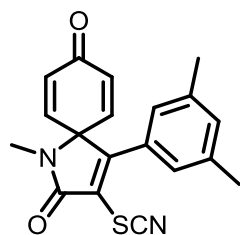
— 121.91

— 106.46

— 68.32

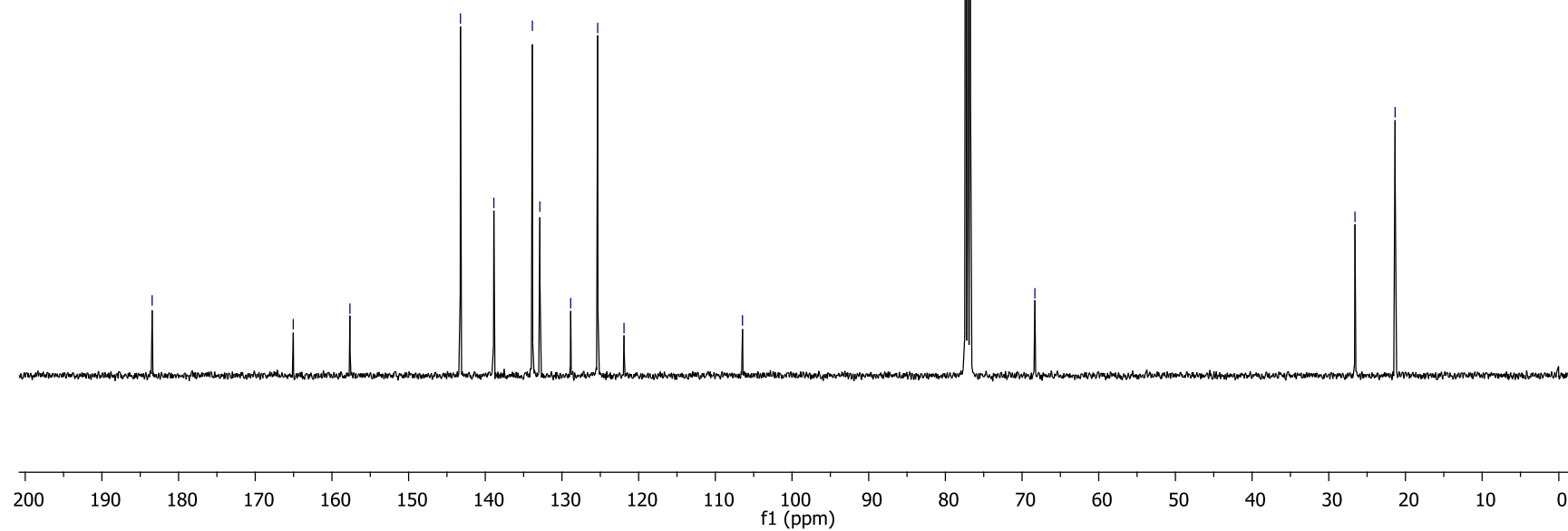
— 26.58

— 21.35

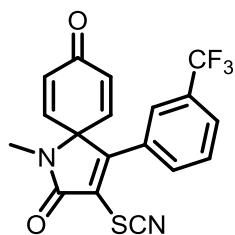


2i

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

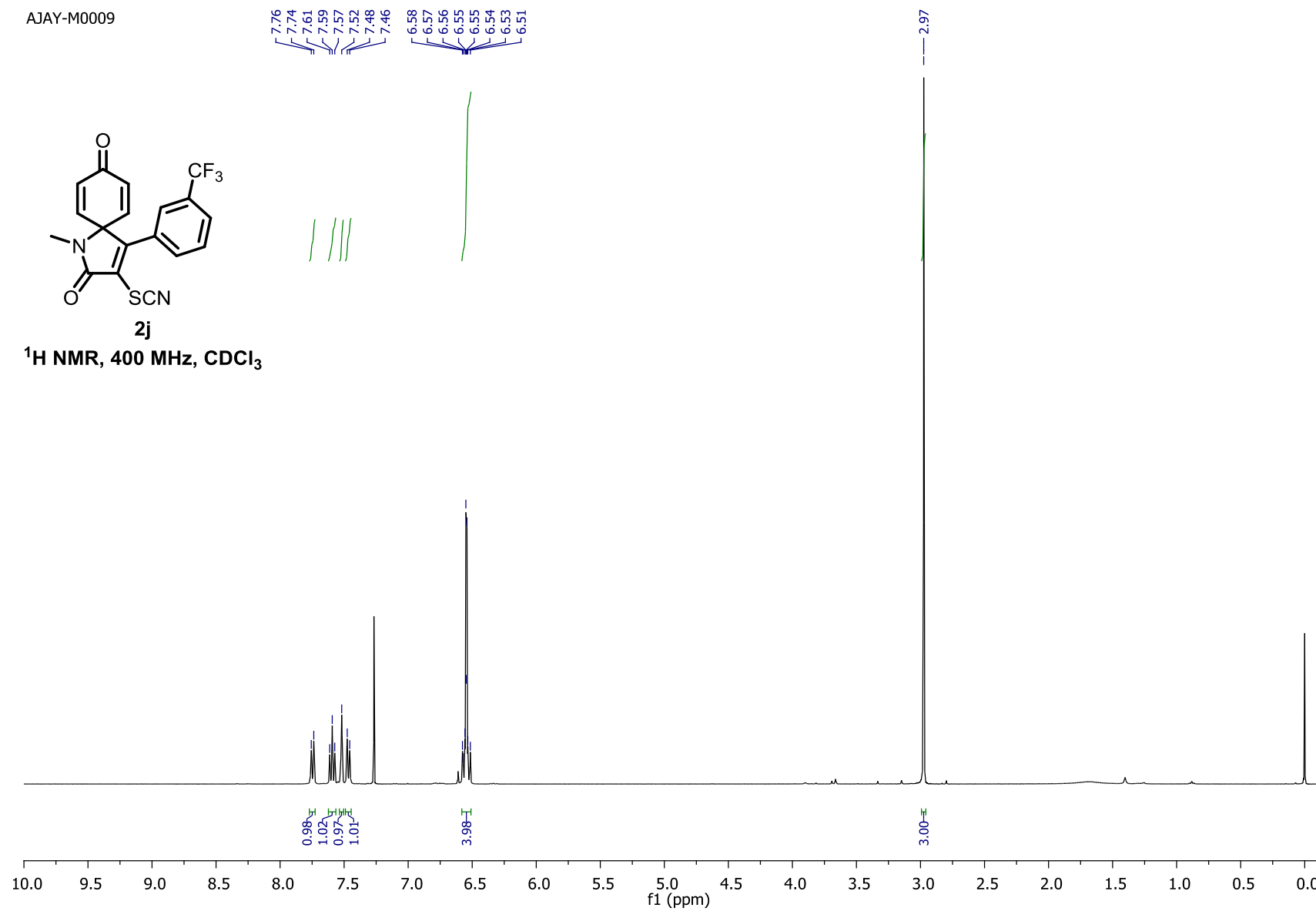


AJAY-M0009



2j

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



AJAY-M0009

— 182.90

— 164.55

— 154.49

— 142.57

134.37

131.81

131.48

131.17

129.86

129.57

127.78

124.88

124.84

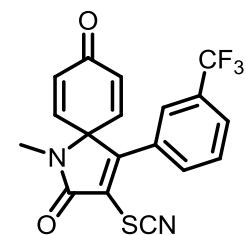
124.20

121.94

— 105.63

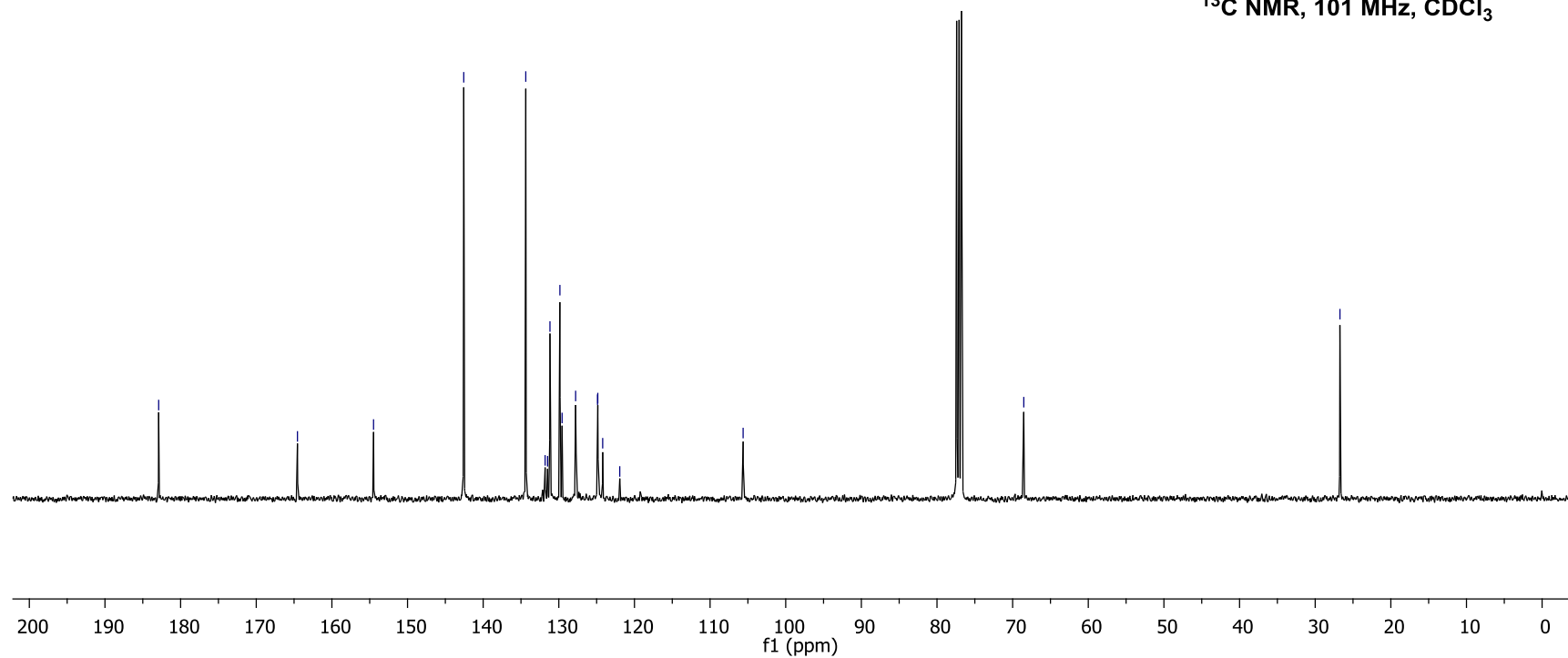
— 68.53

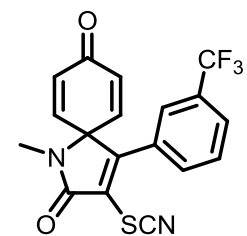
— 26.73



2j

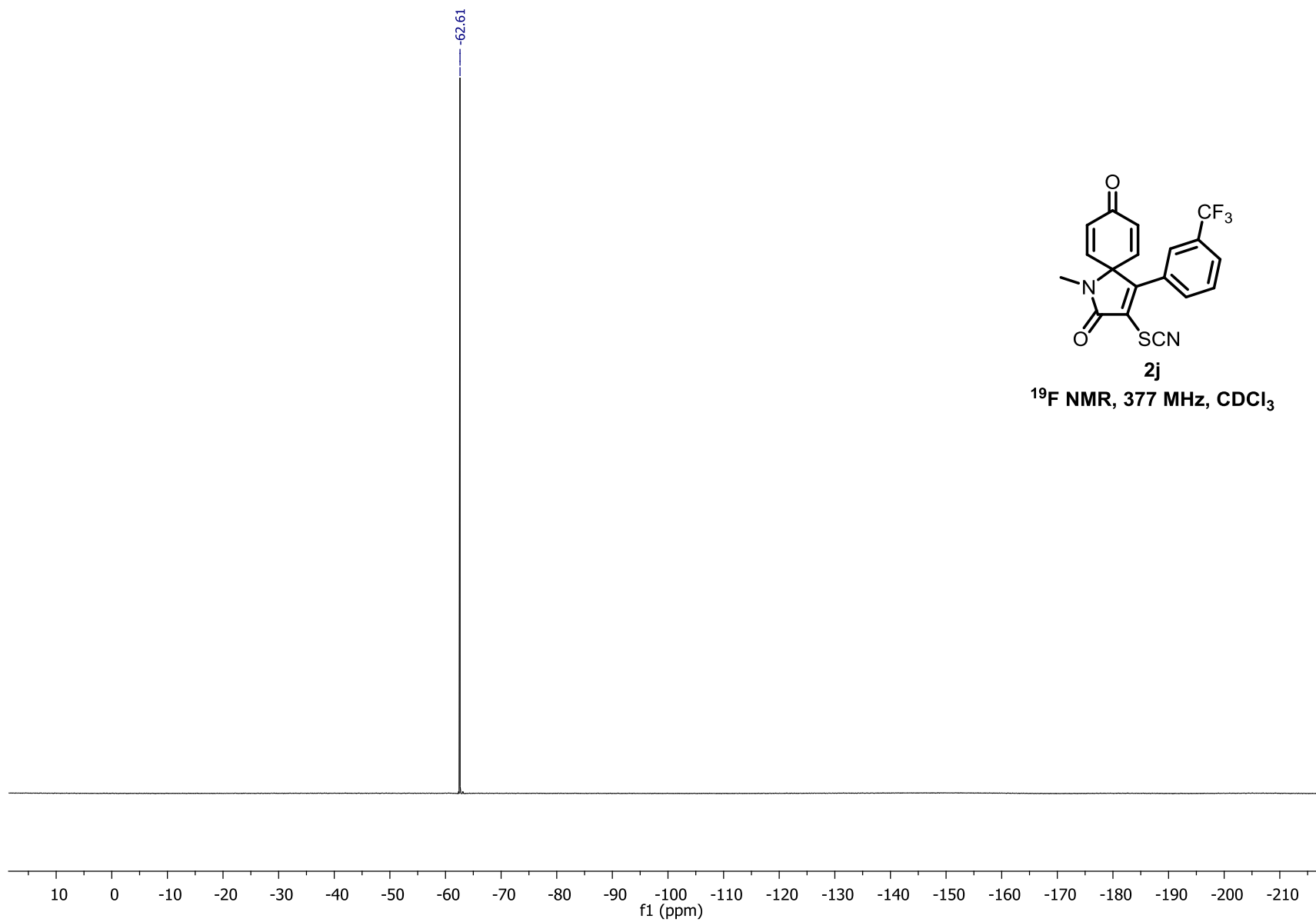
<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>





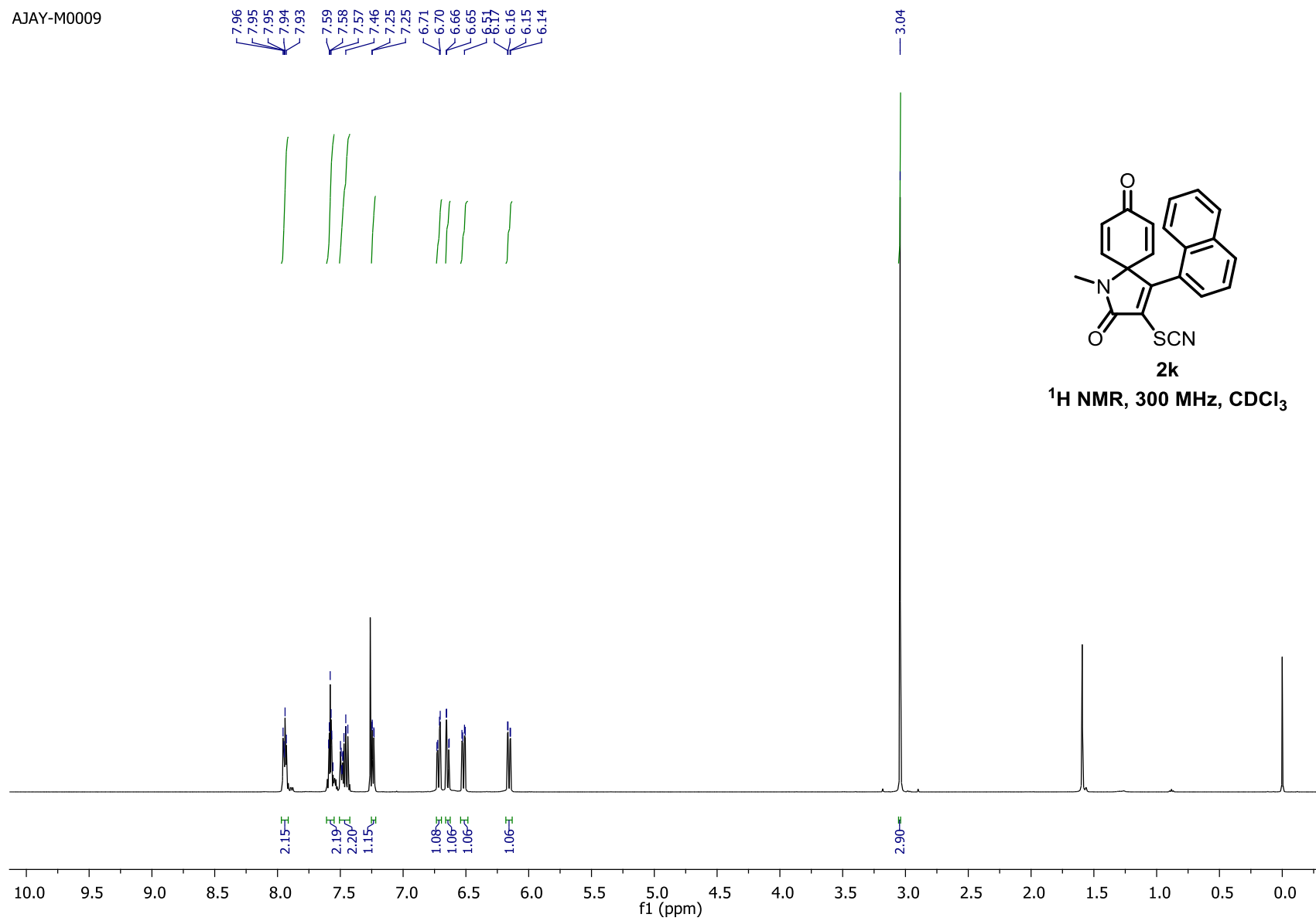
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$^{19}\text{F}$  NMR, 377 MHz,  $\text{CDCl}_3$

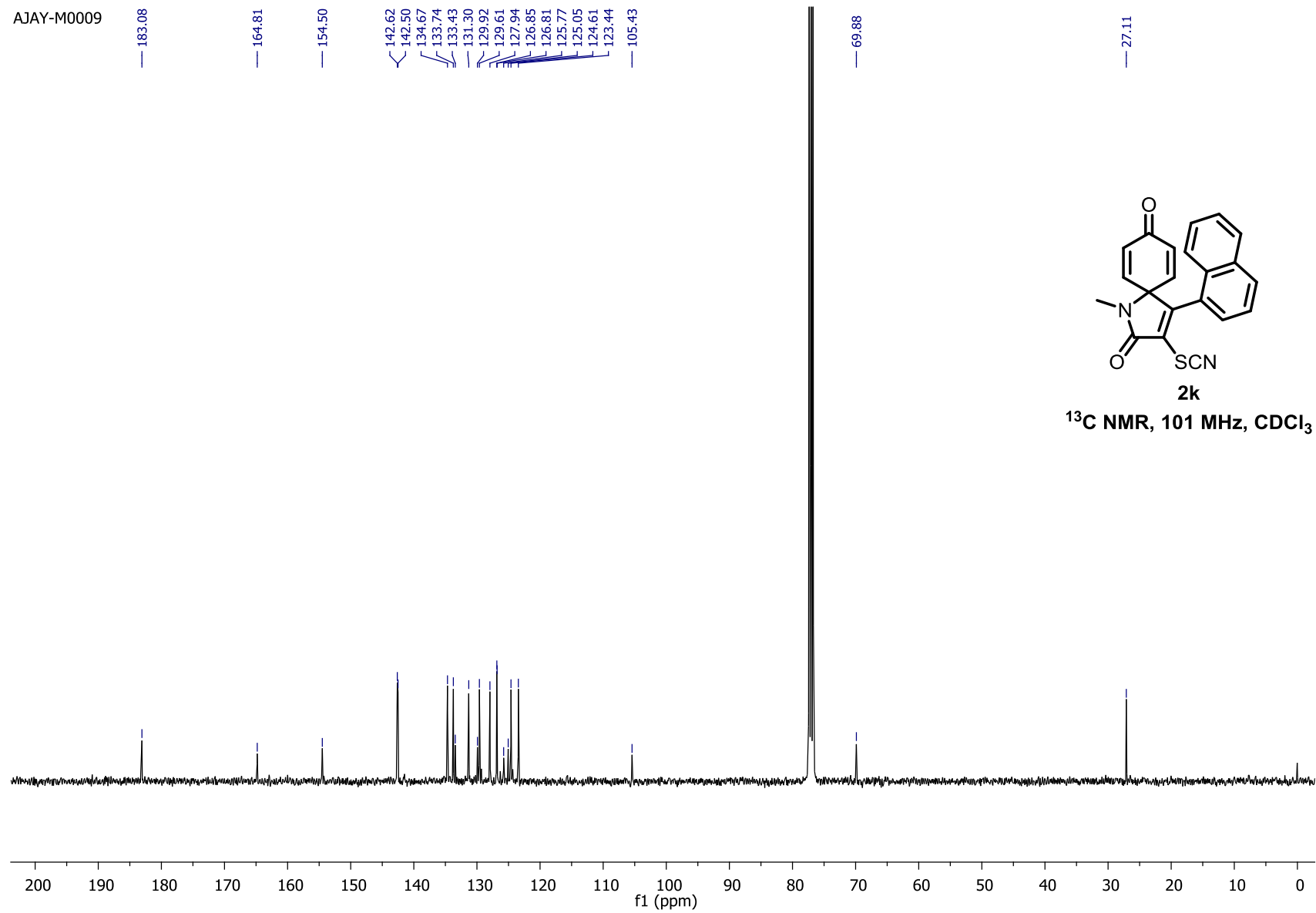


S30

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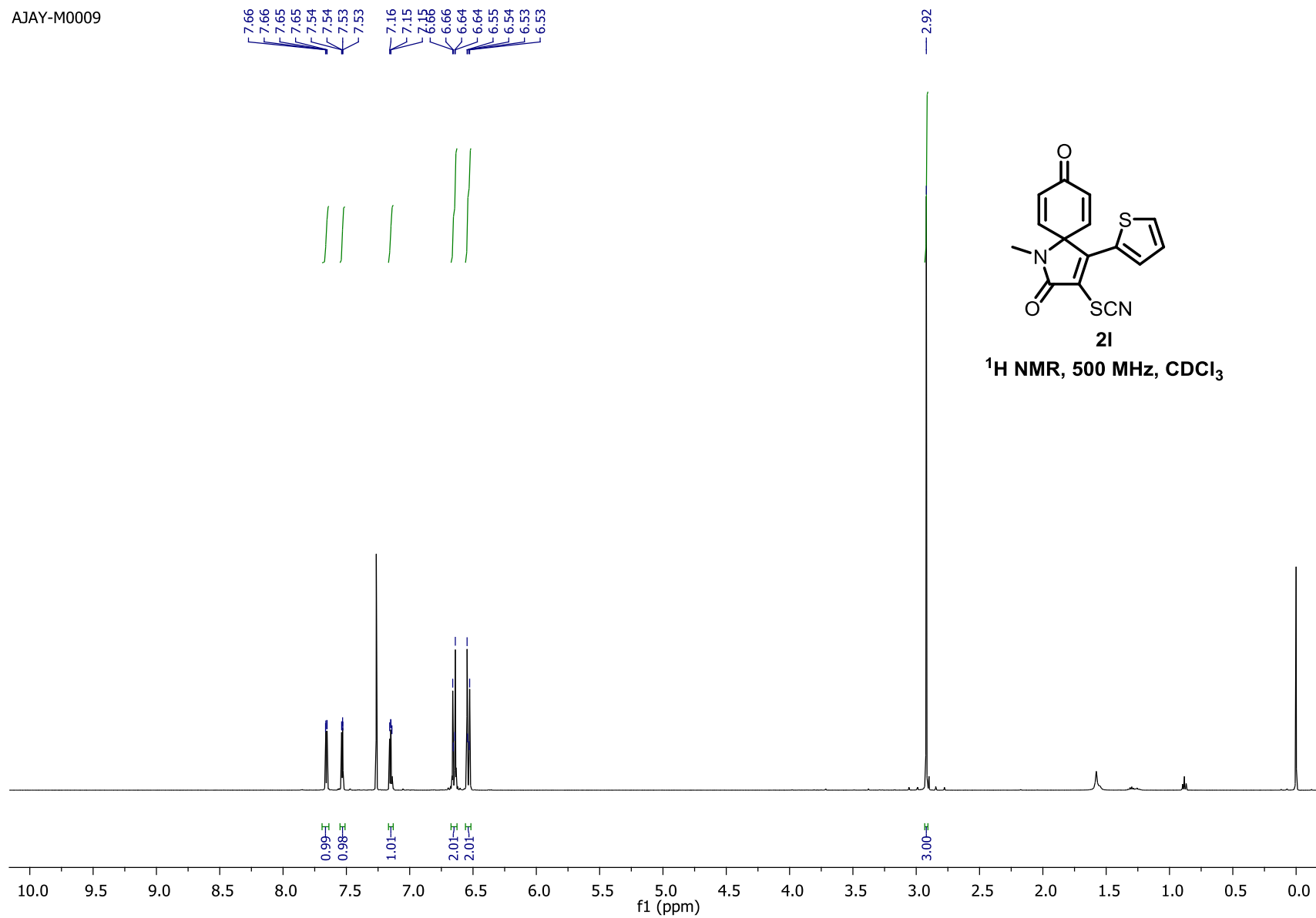


AJAY-M0009





AJAY-M0009



AJAY-M0009  
— 183.53

— 165.18

— 150.84

— 144.09

133.83

132.42

131.71

130.63

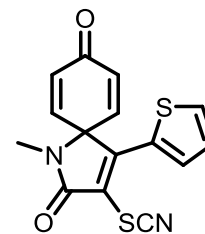
128.25

— 116.39

— 106.42

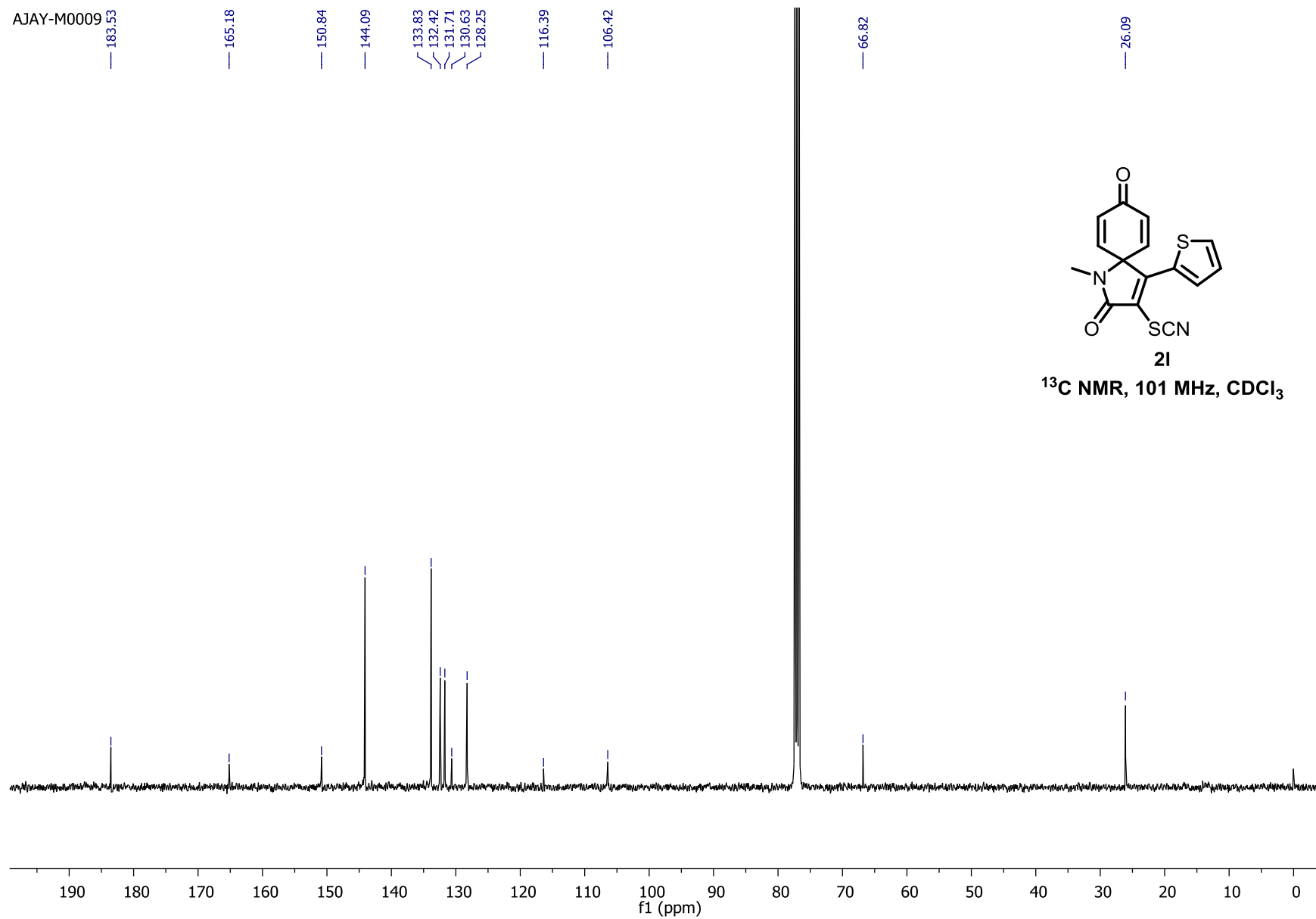
— 66.82

— 26.09



21

<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>



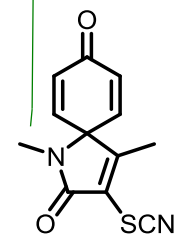
S34

AJAY

6.64  
6.63  
6.62  
6.61  
6.37  
6.37  
6.35  
6.35

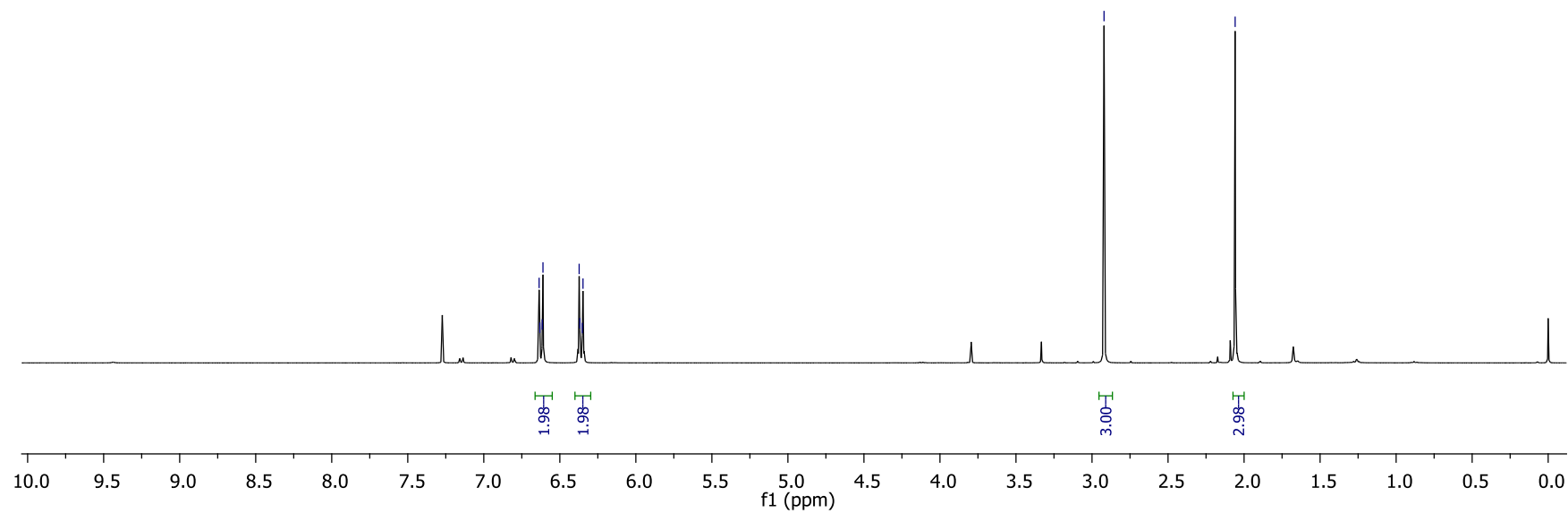
2.92

2.06



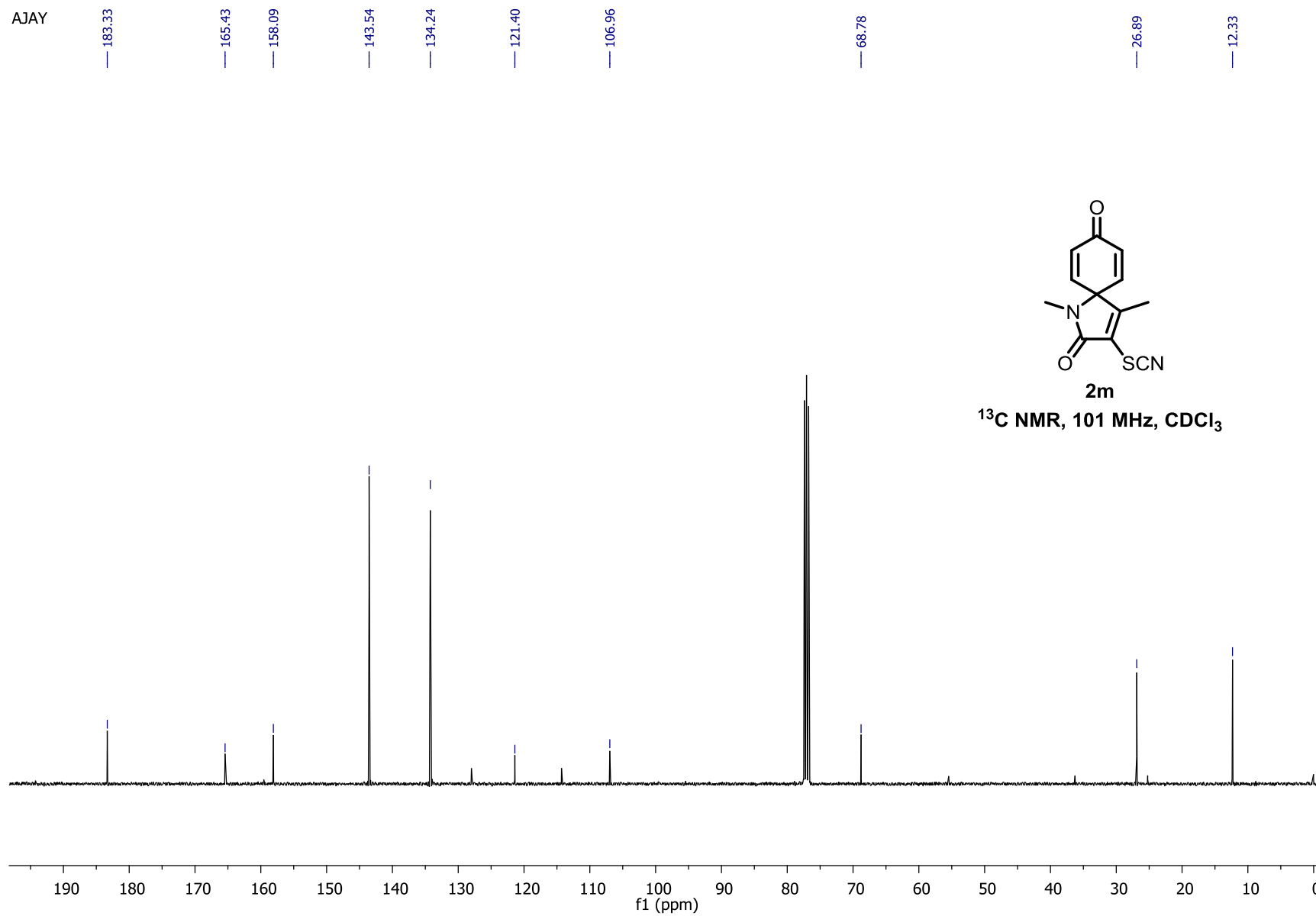
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$^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$

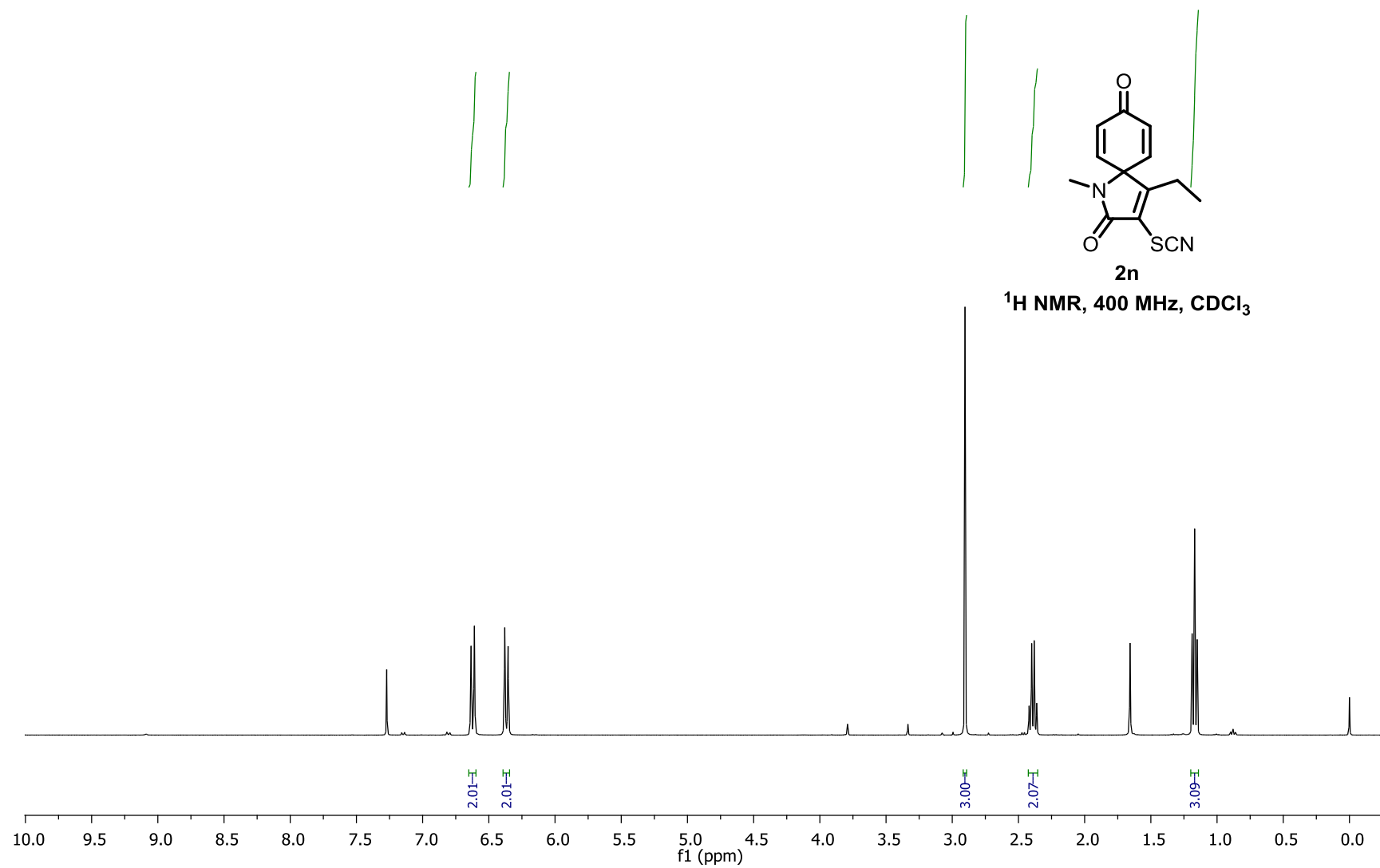


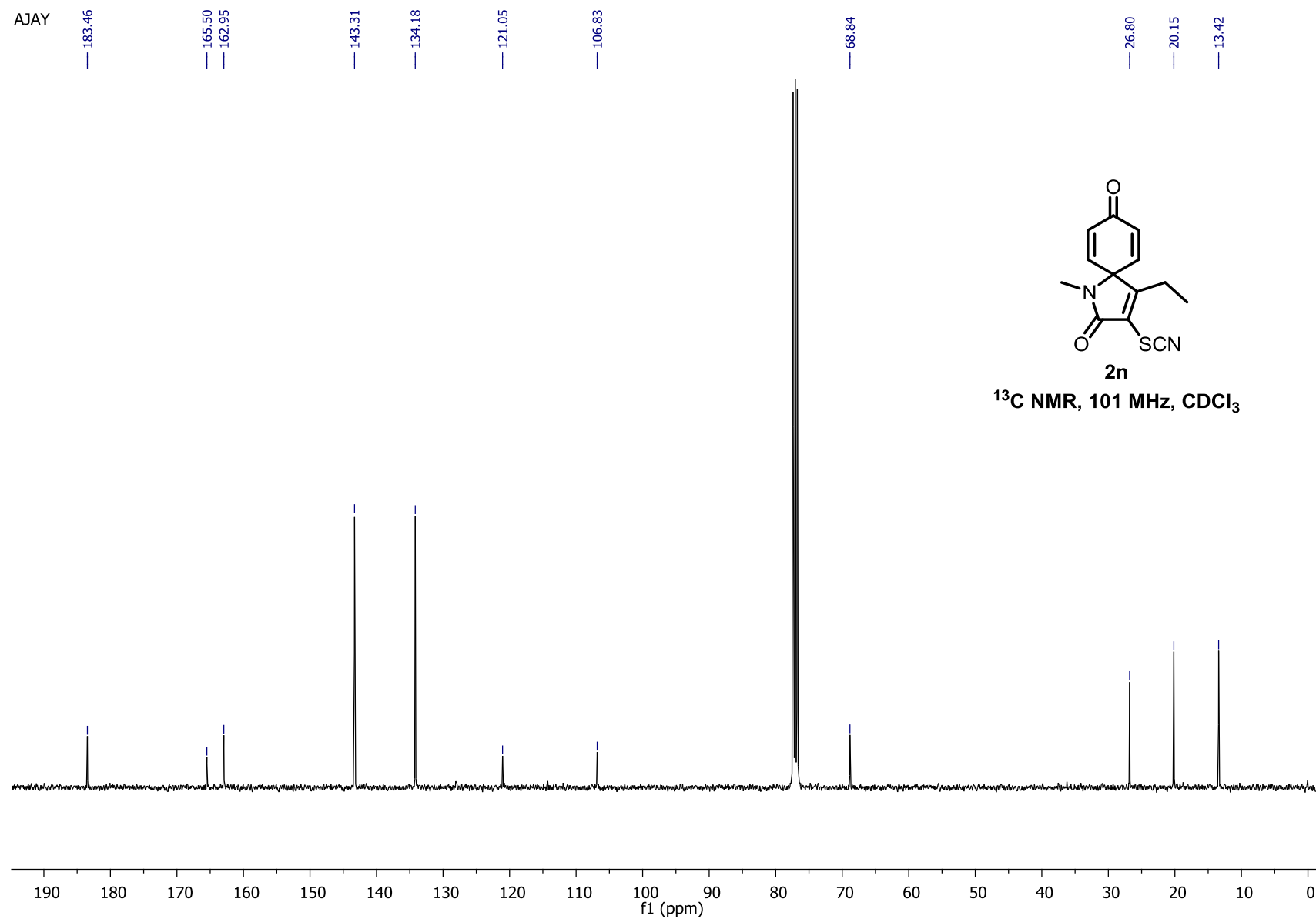
S35

AJAY



AJAY

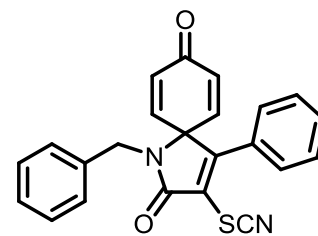




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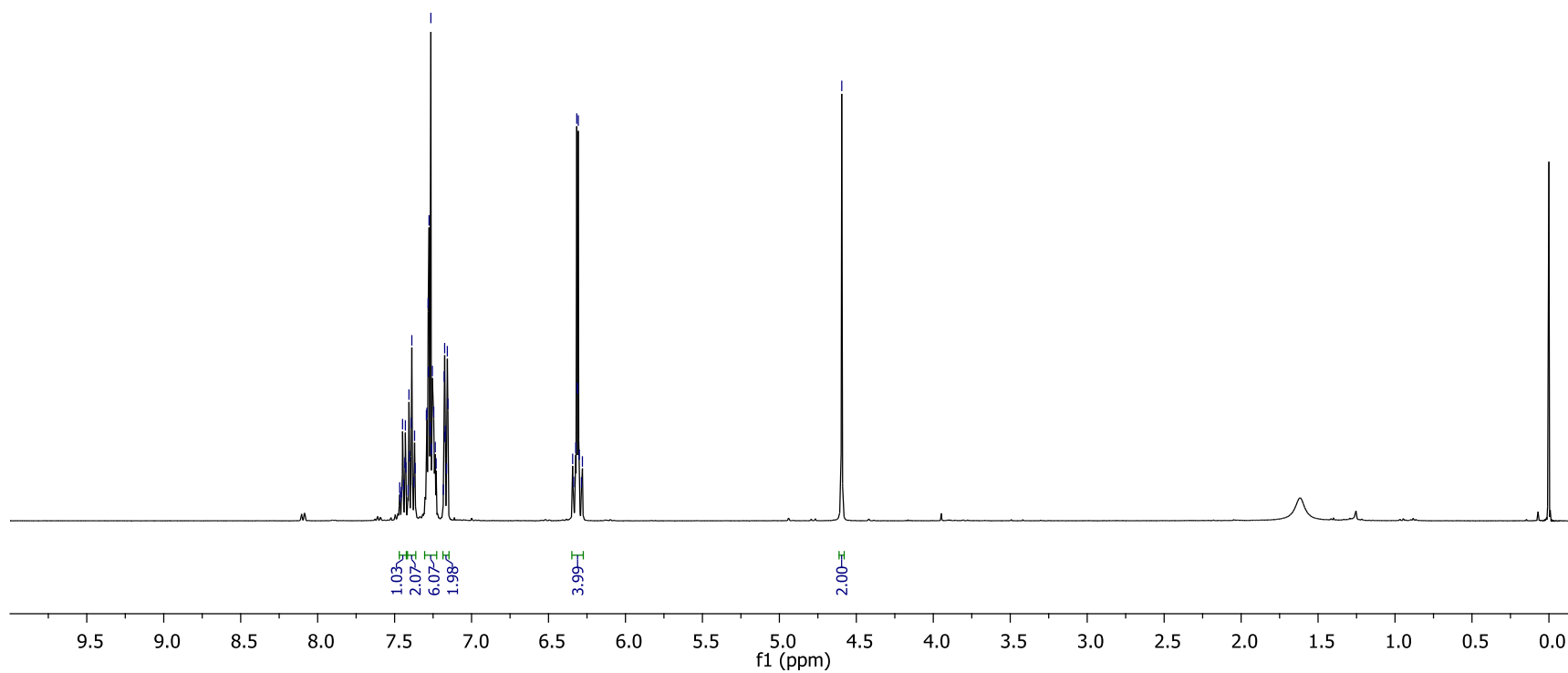
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4.59

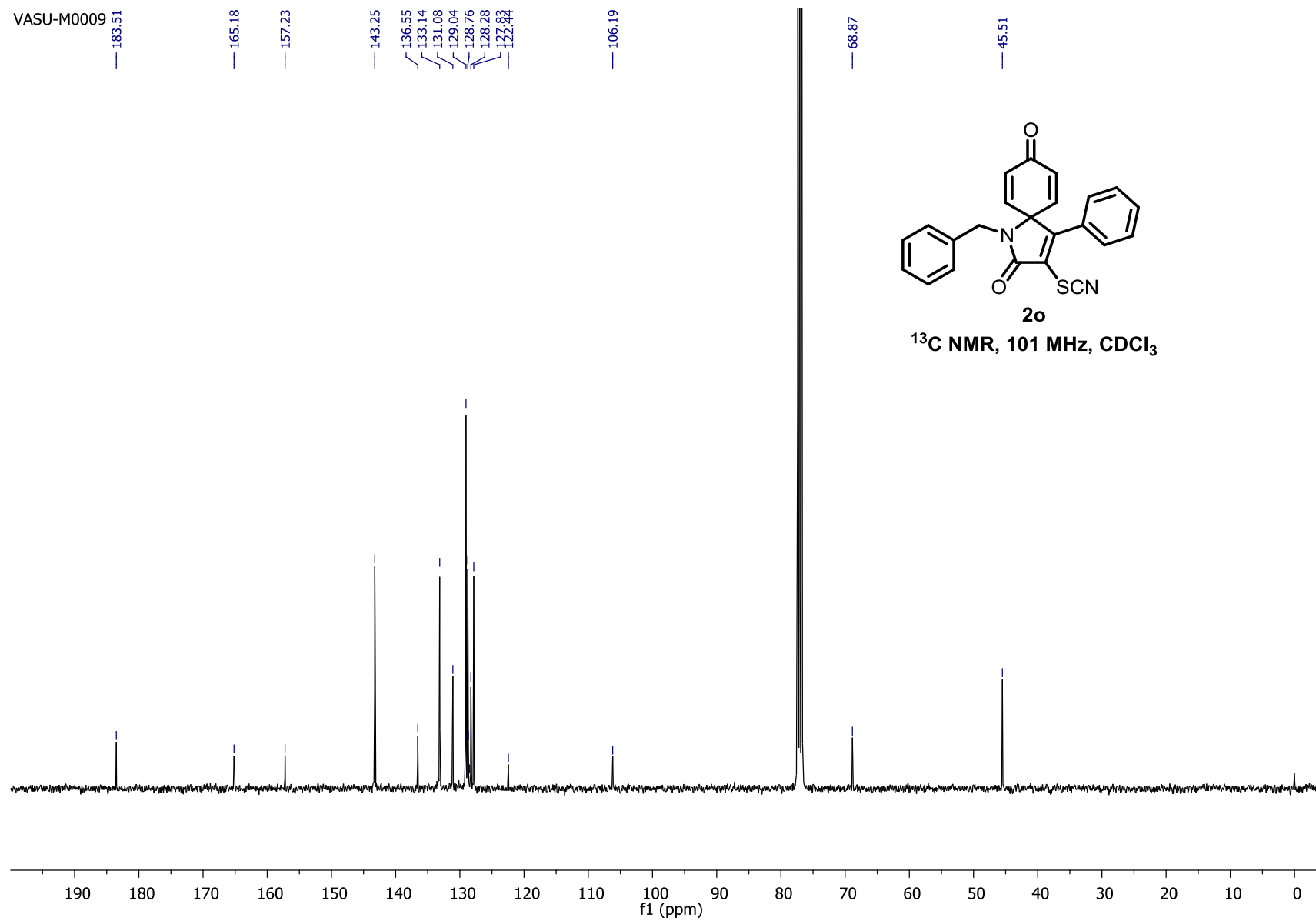


2o

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

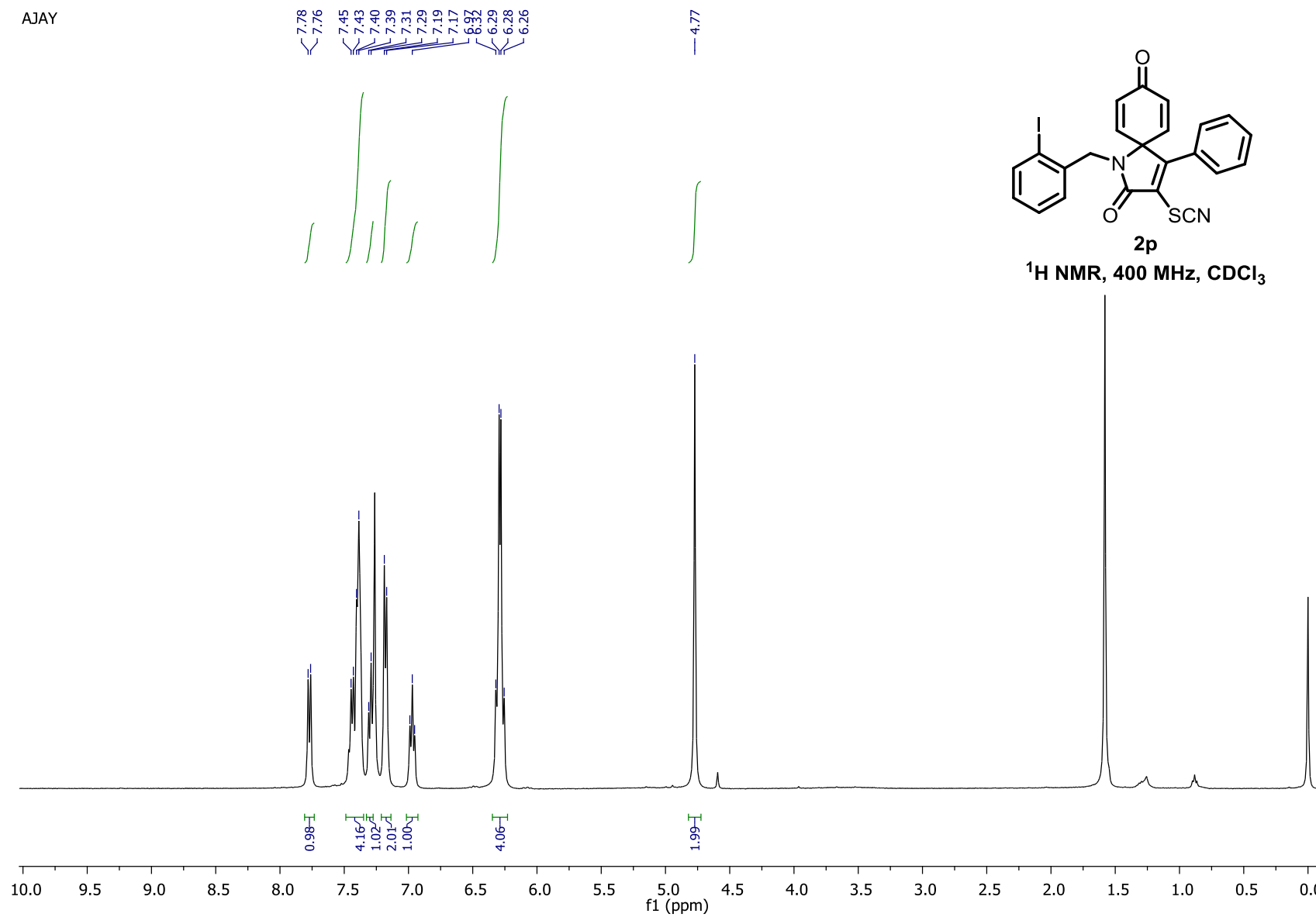


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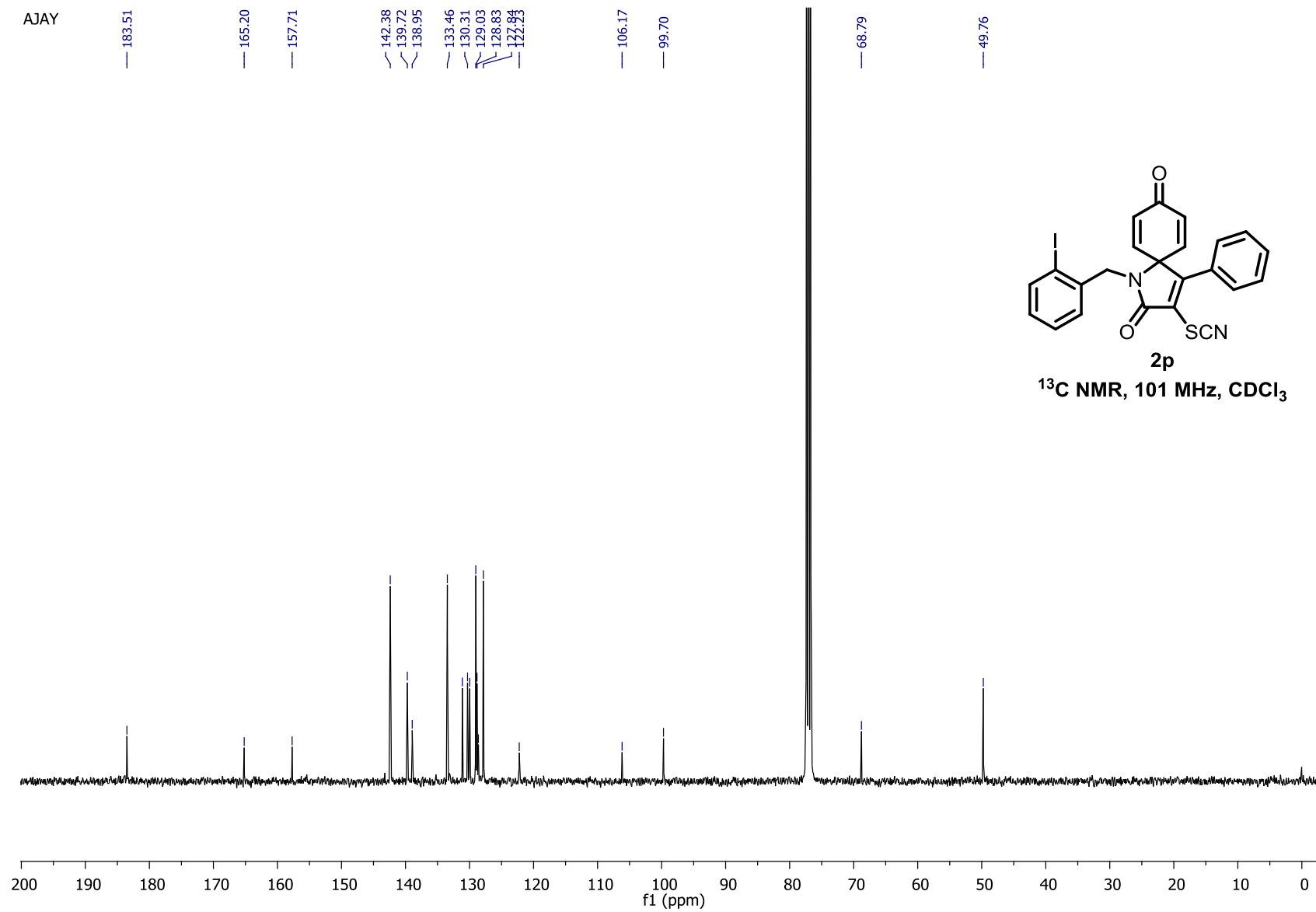


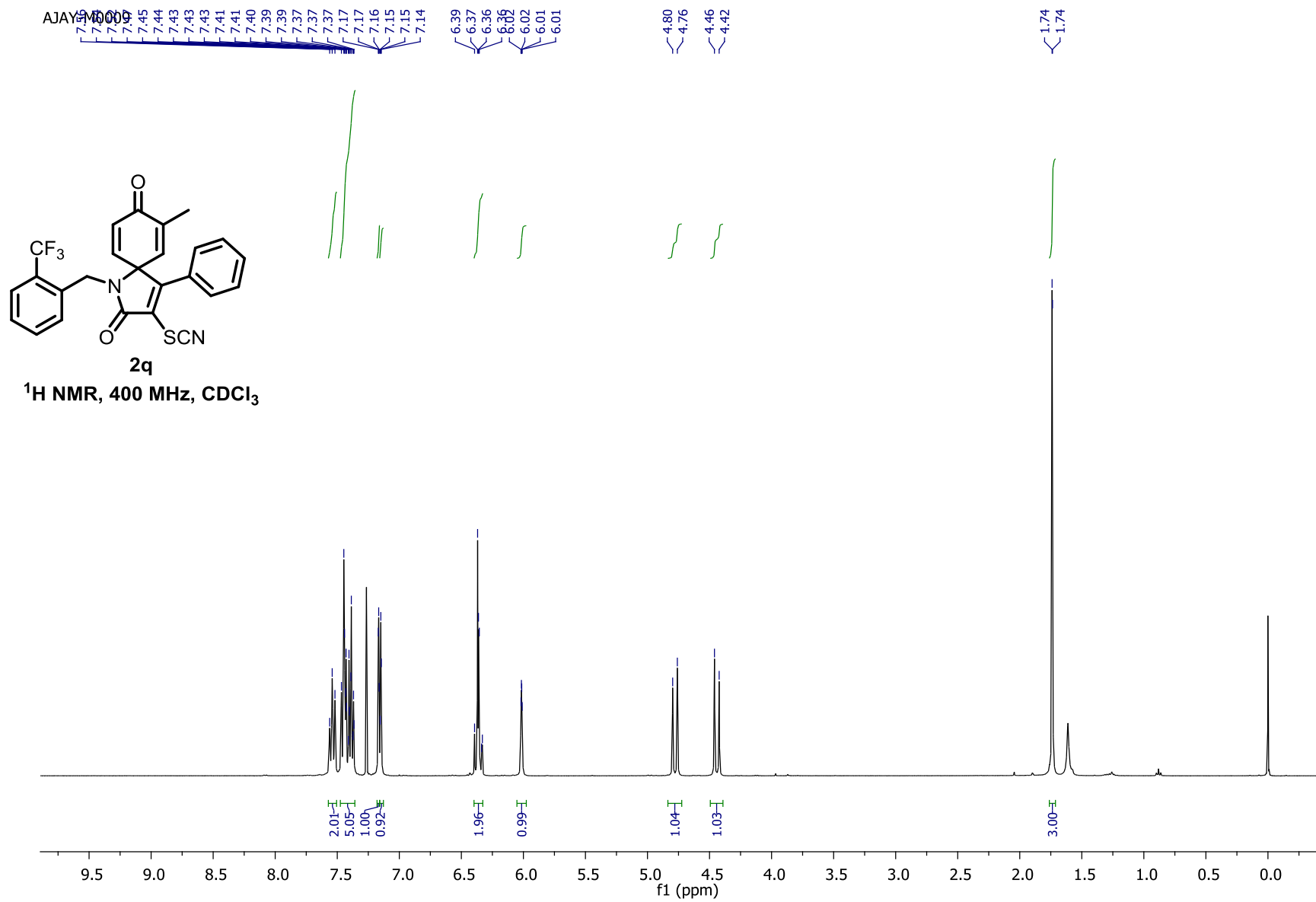


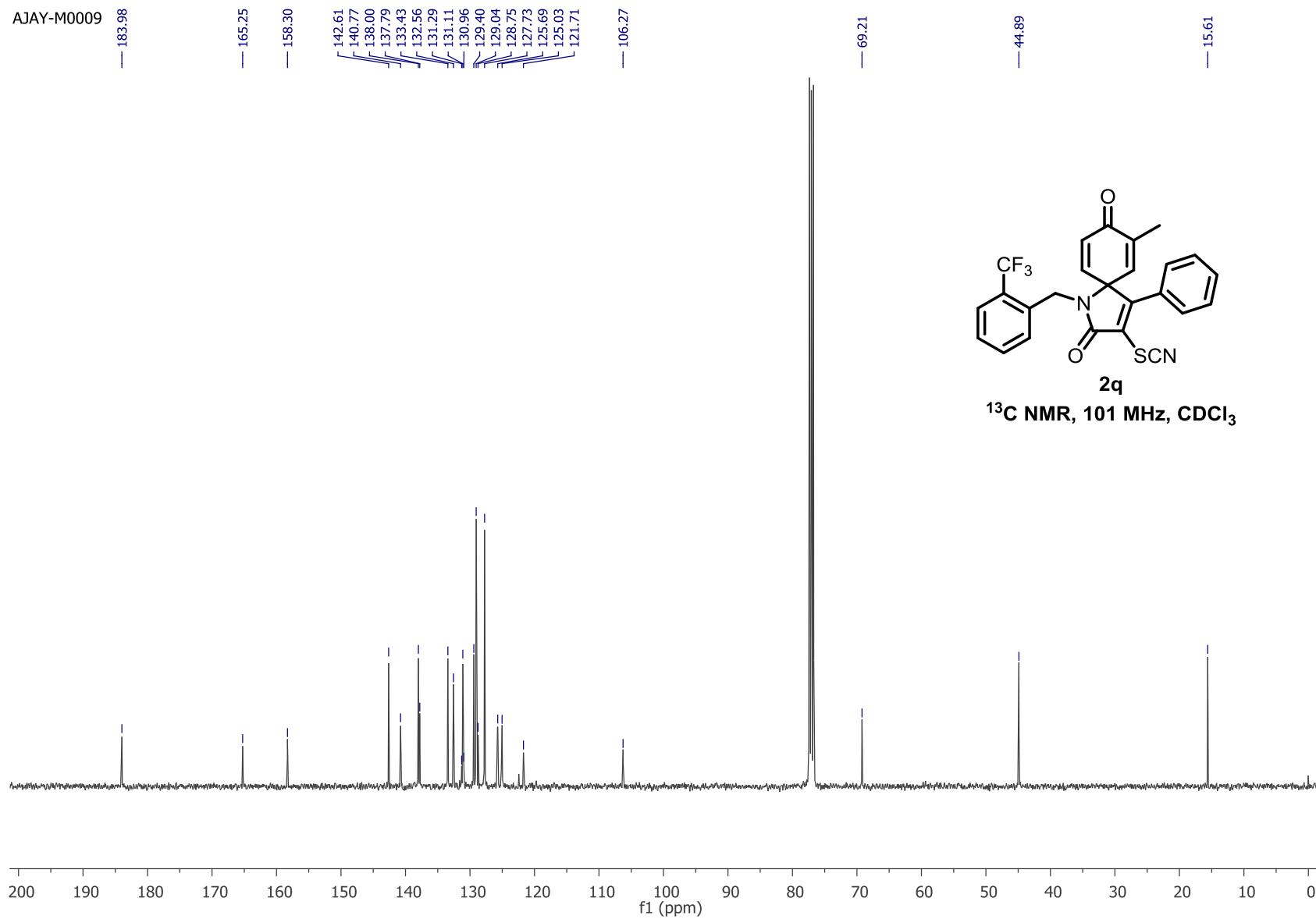
AJAY

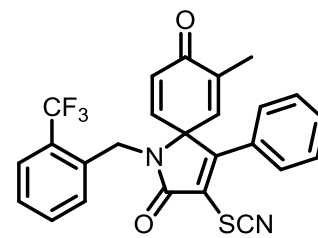


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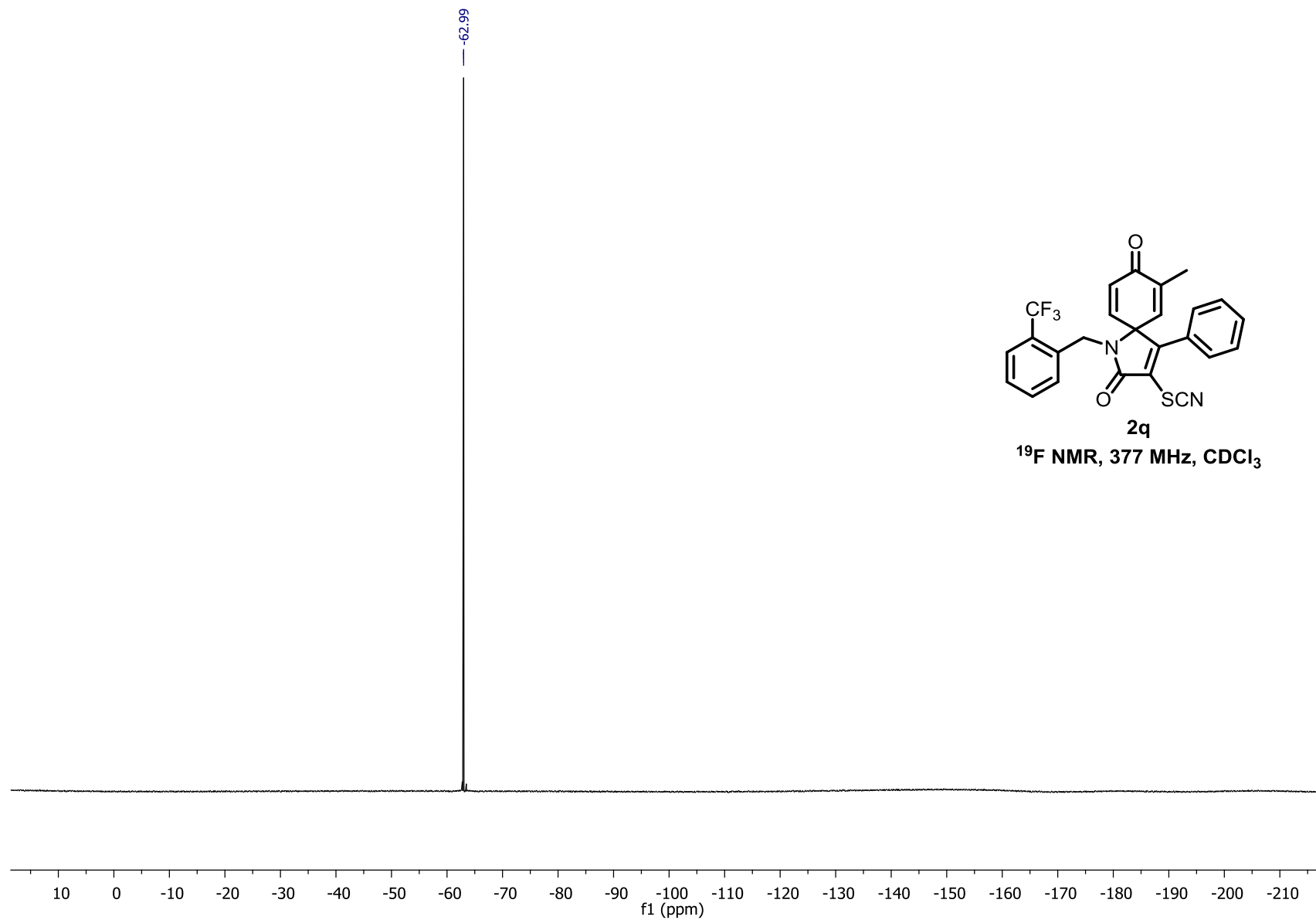


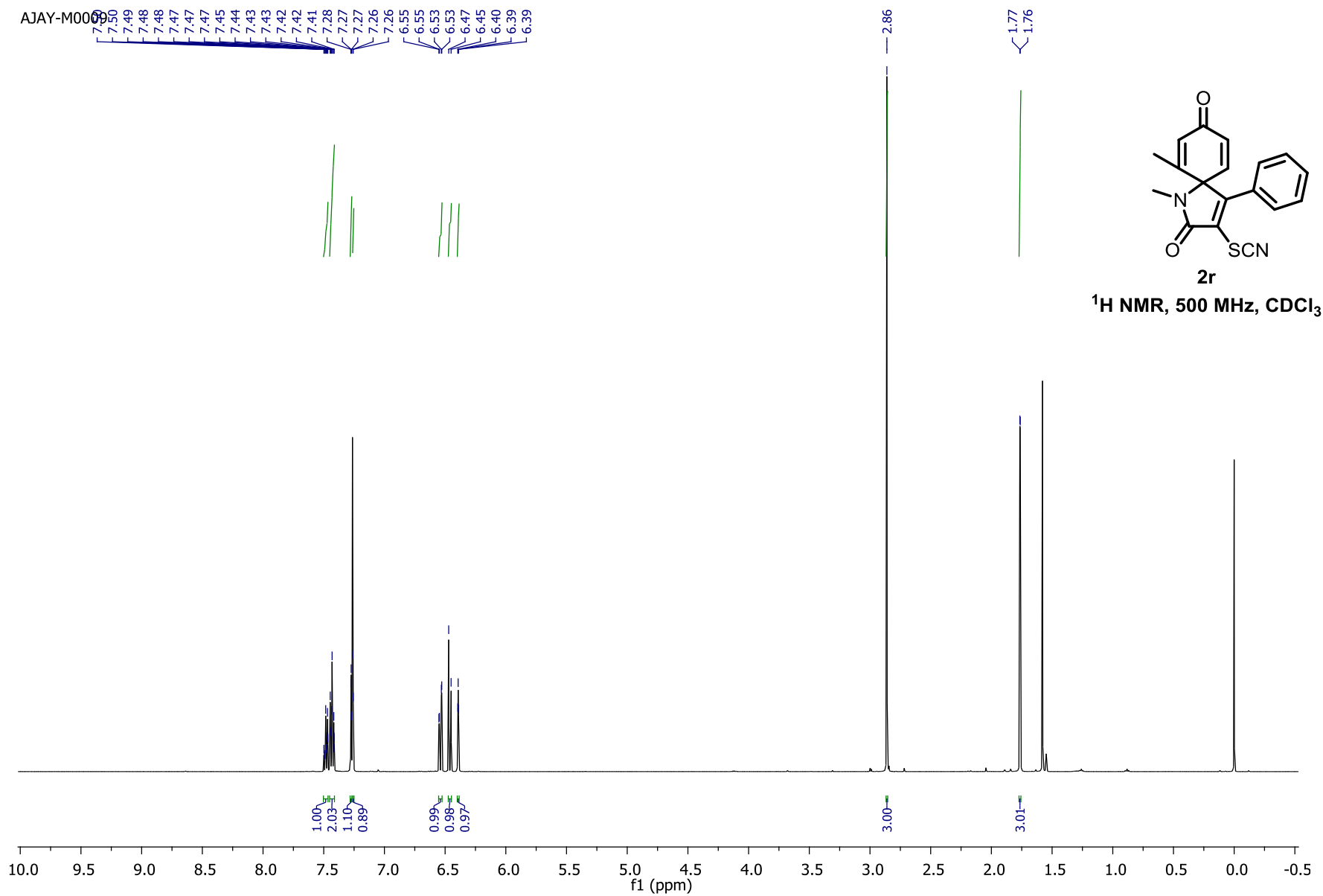




2q

<sup>19</sup>F NMR, 377 MHz, CDCl<sub>3</sub>





AJAY-M0009  
— 184.06

— 165.45

— 157.36

— 151.57

— 143.24

133.51

132.63

131.40

129.32

128.75

127.58

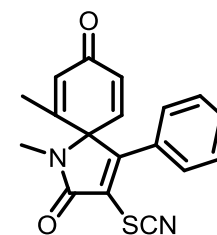
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— 106.30

— 70.53

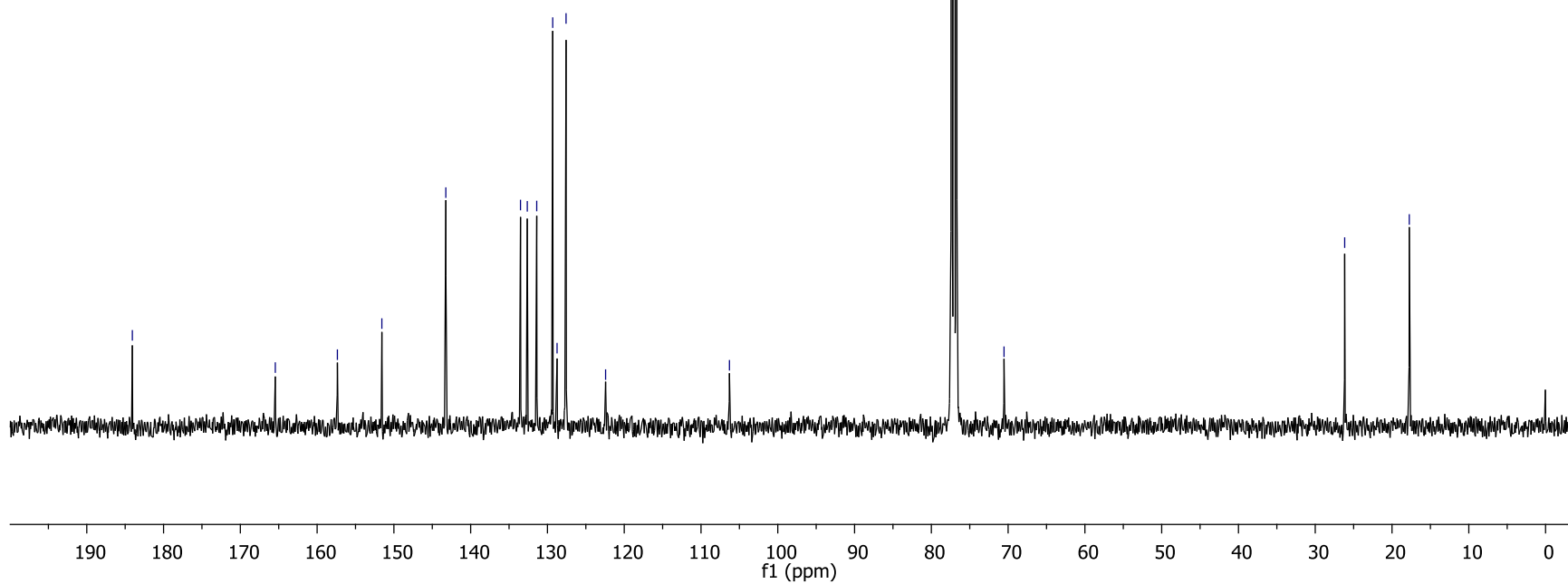
— 26.17

— 17.75

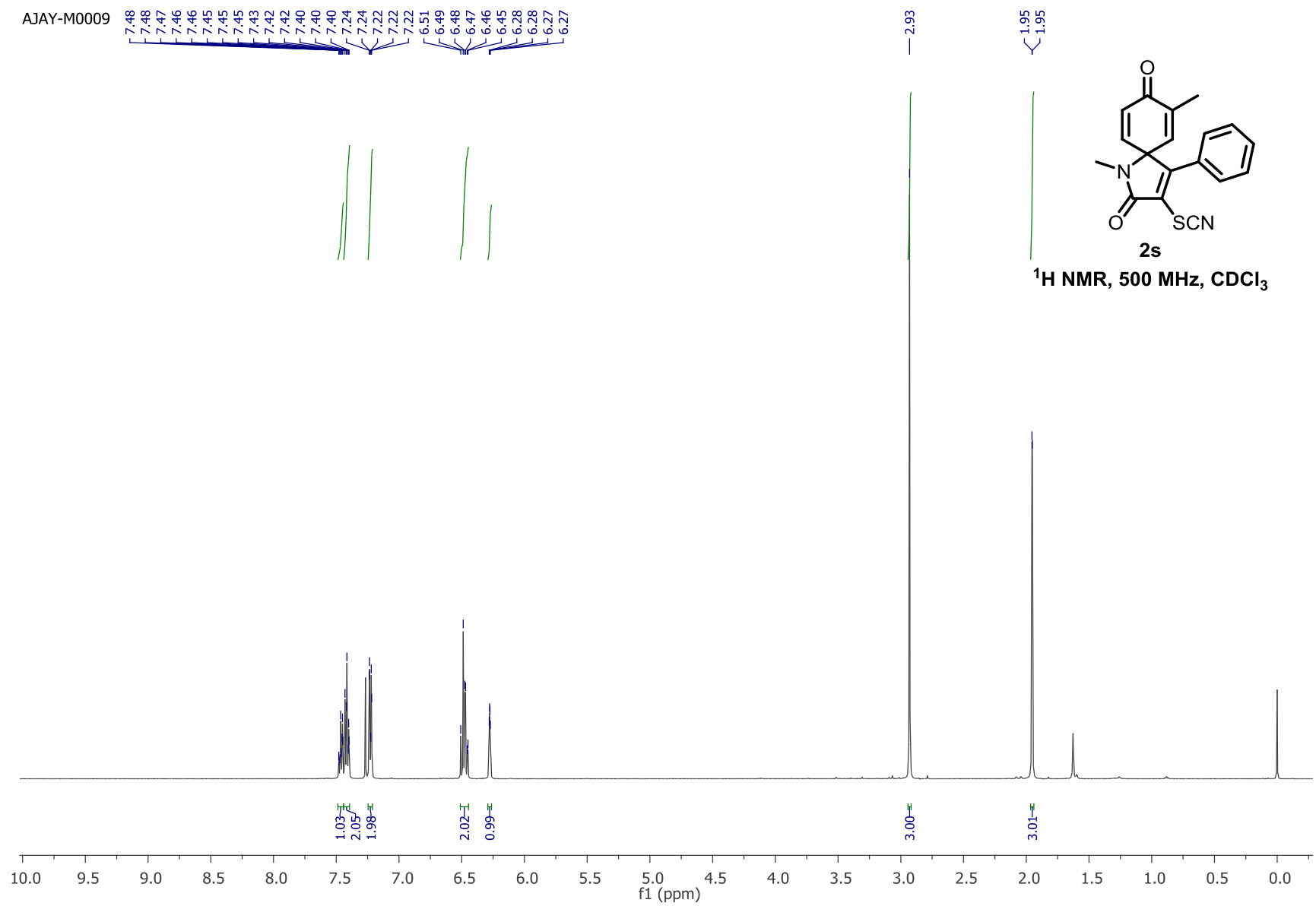


2r

<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>

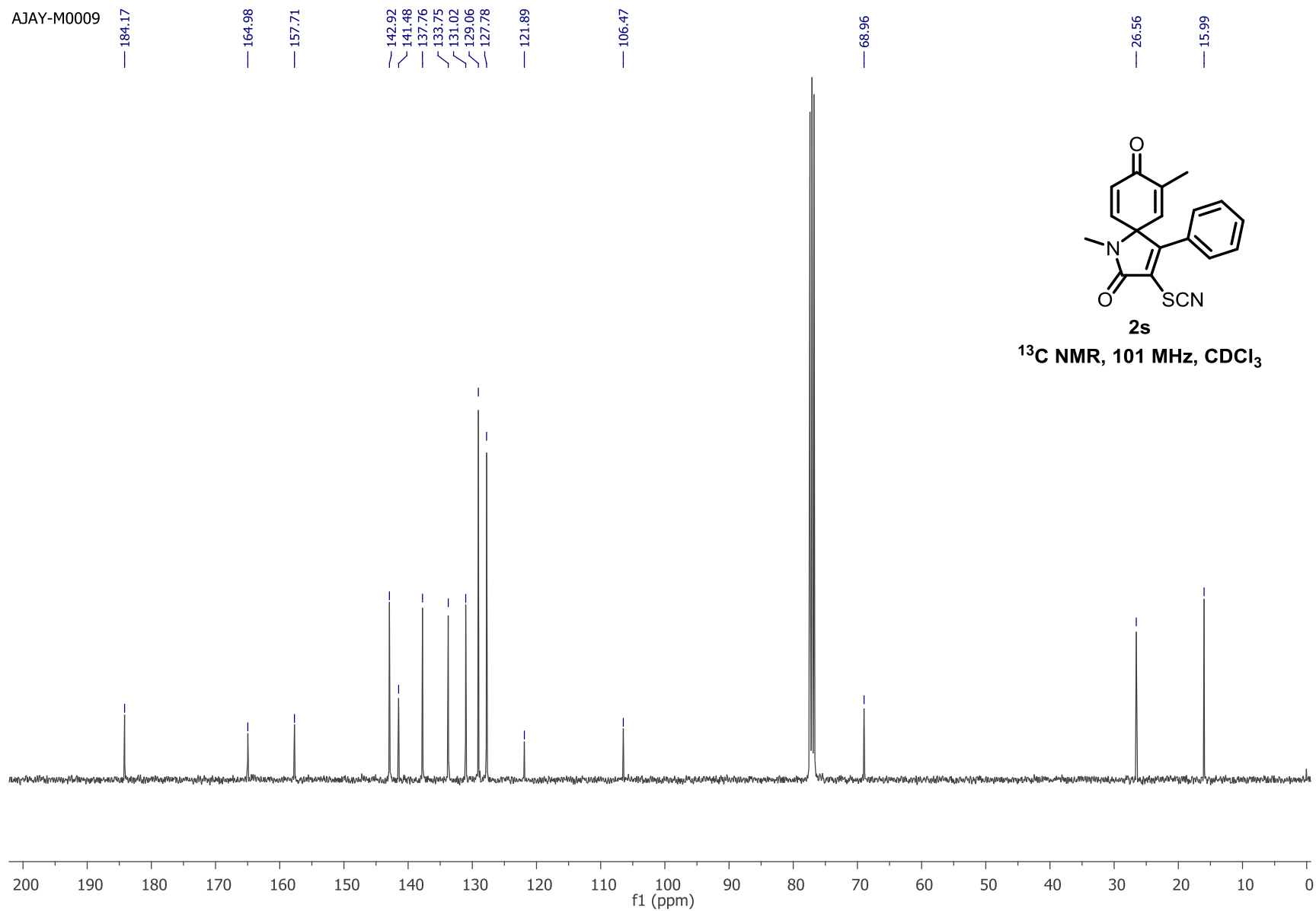


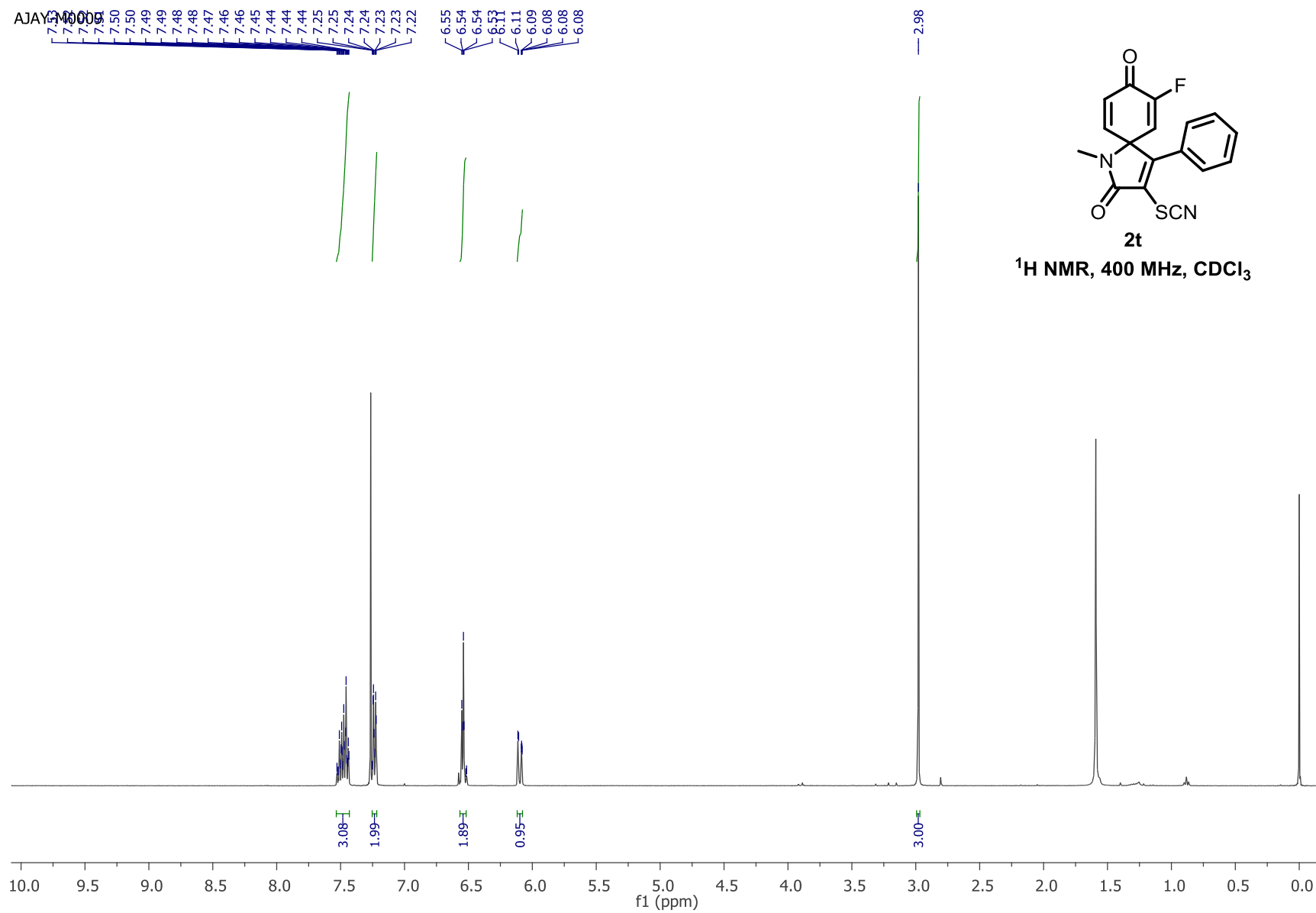
S47



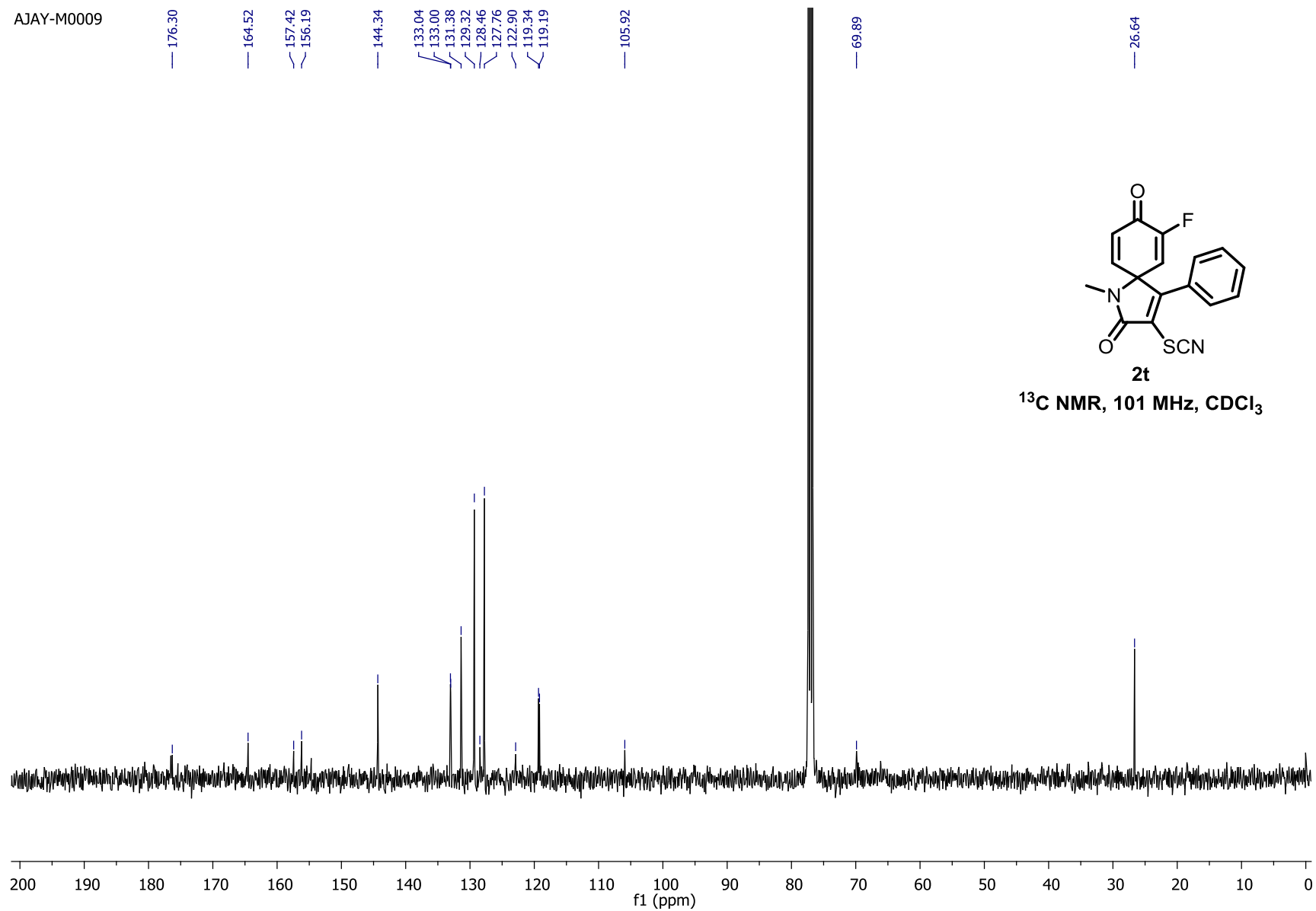


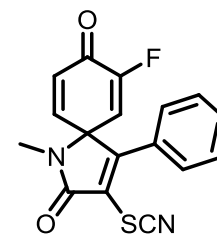
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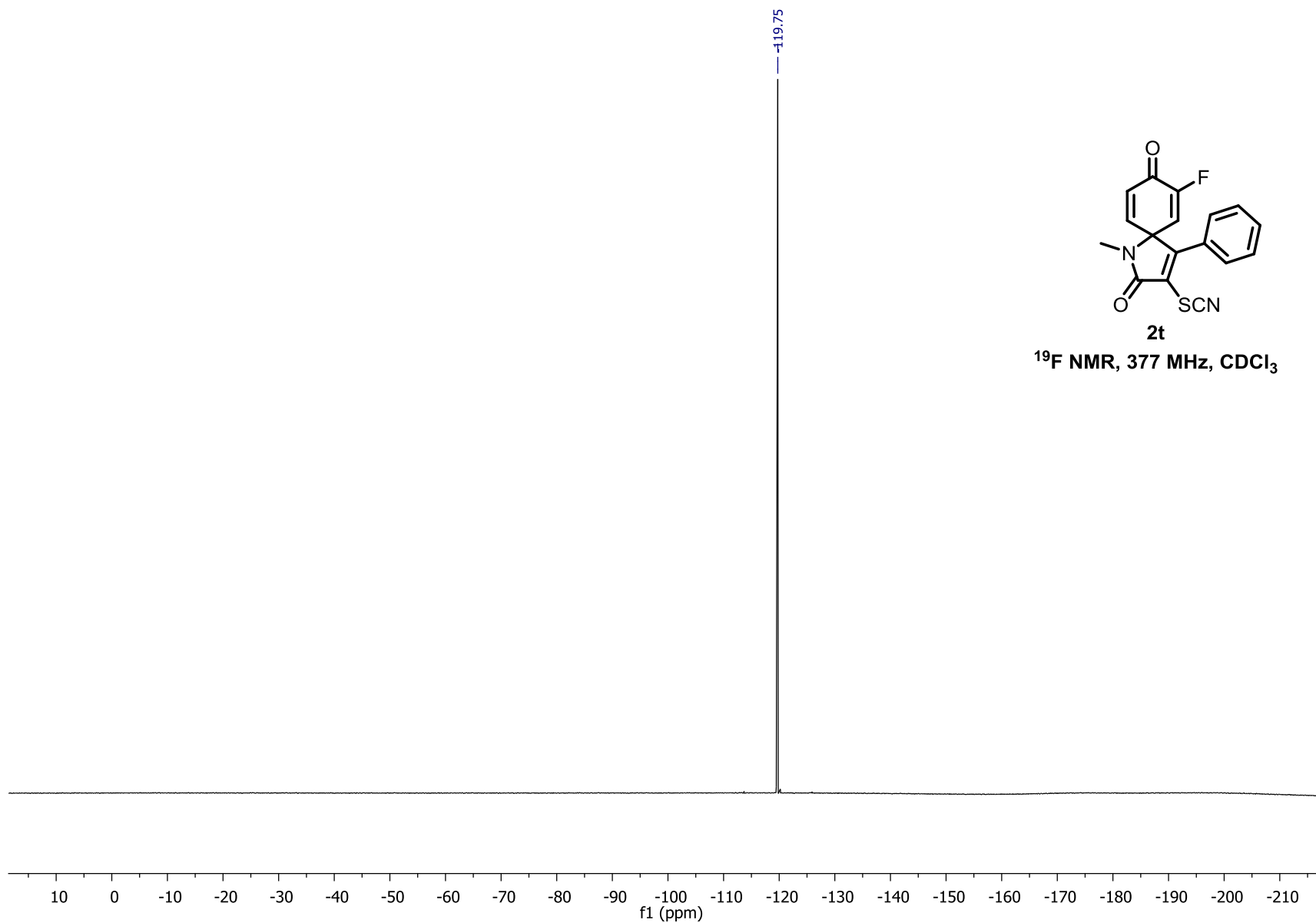
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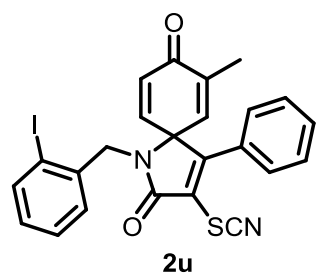


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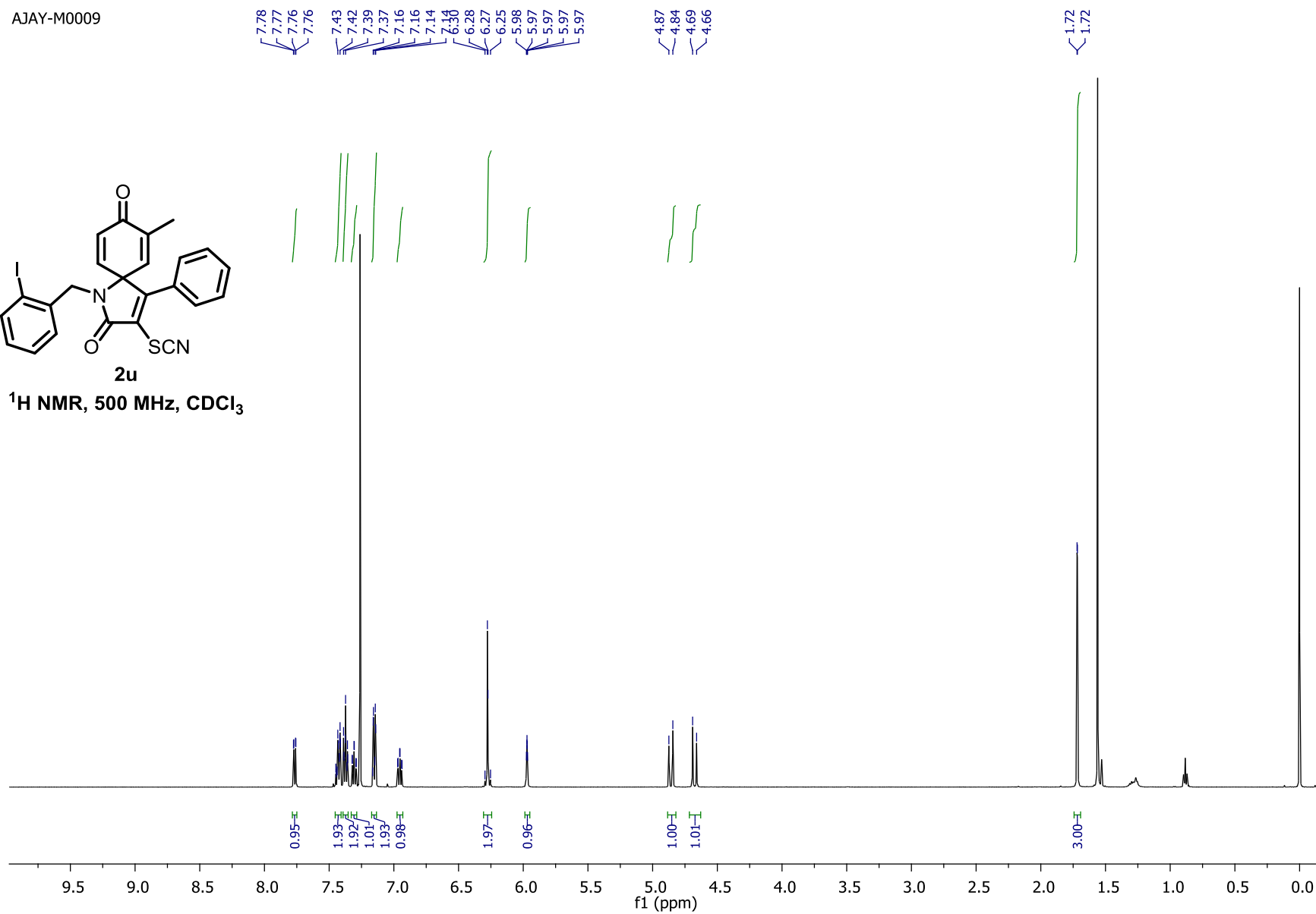
<sup>19</sup>F NMR, 377 MHz, CDCl<sub>3</sub>



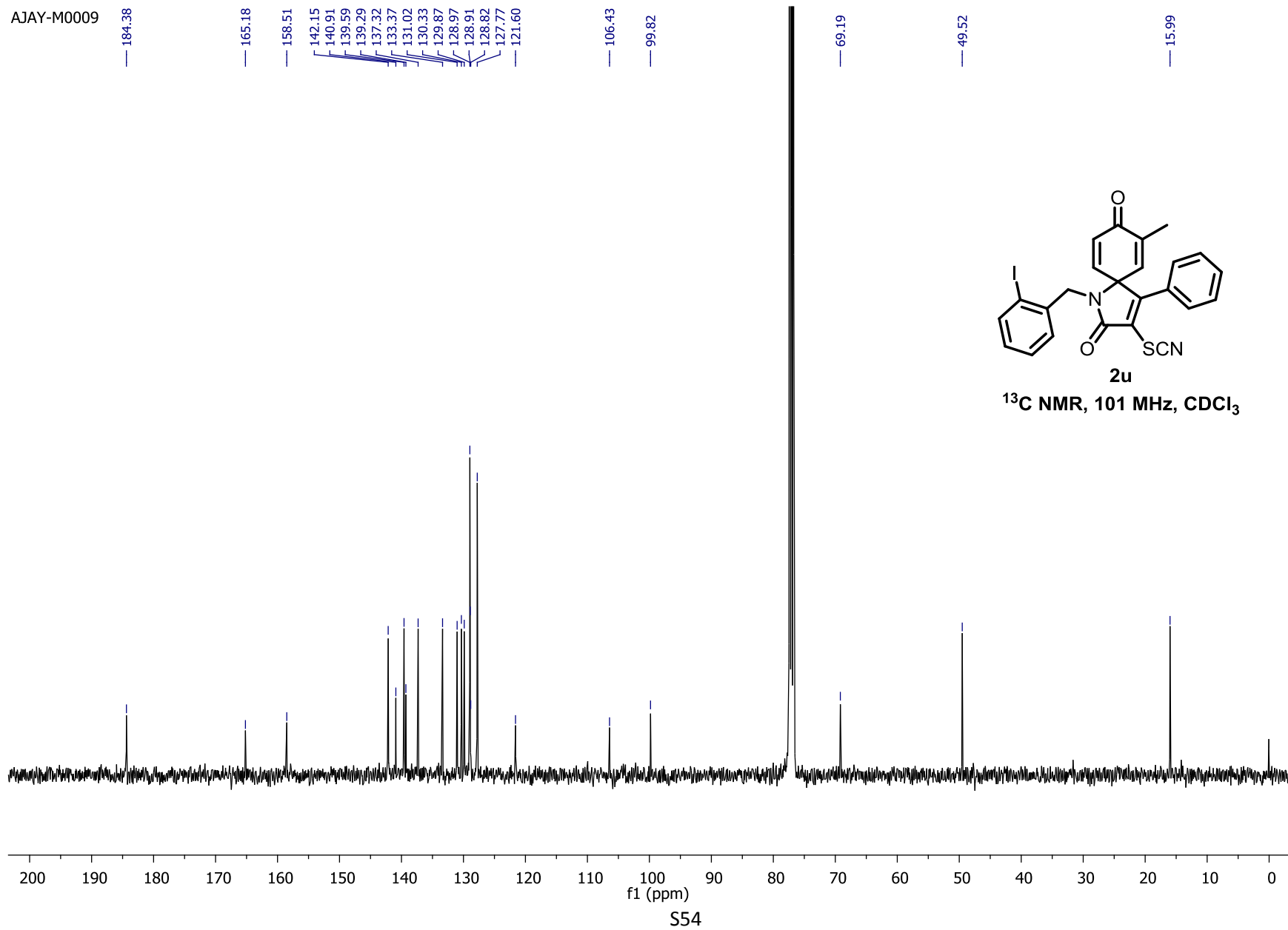
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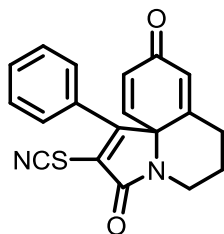
$^1\text{H}$  NMR, 500 MHz,  $\text{CDCl}_3$



AJAY-M0009

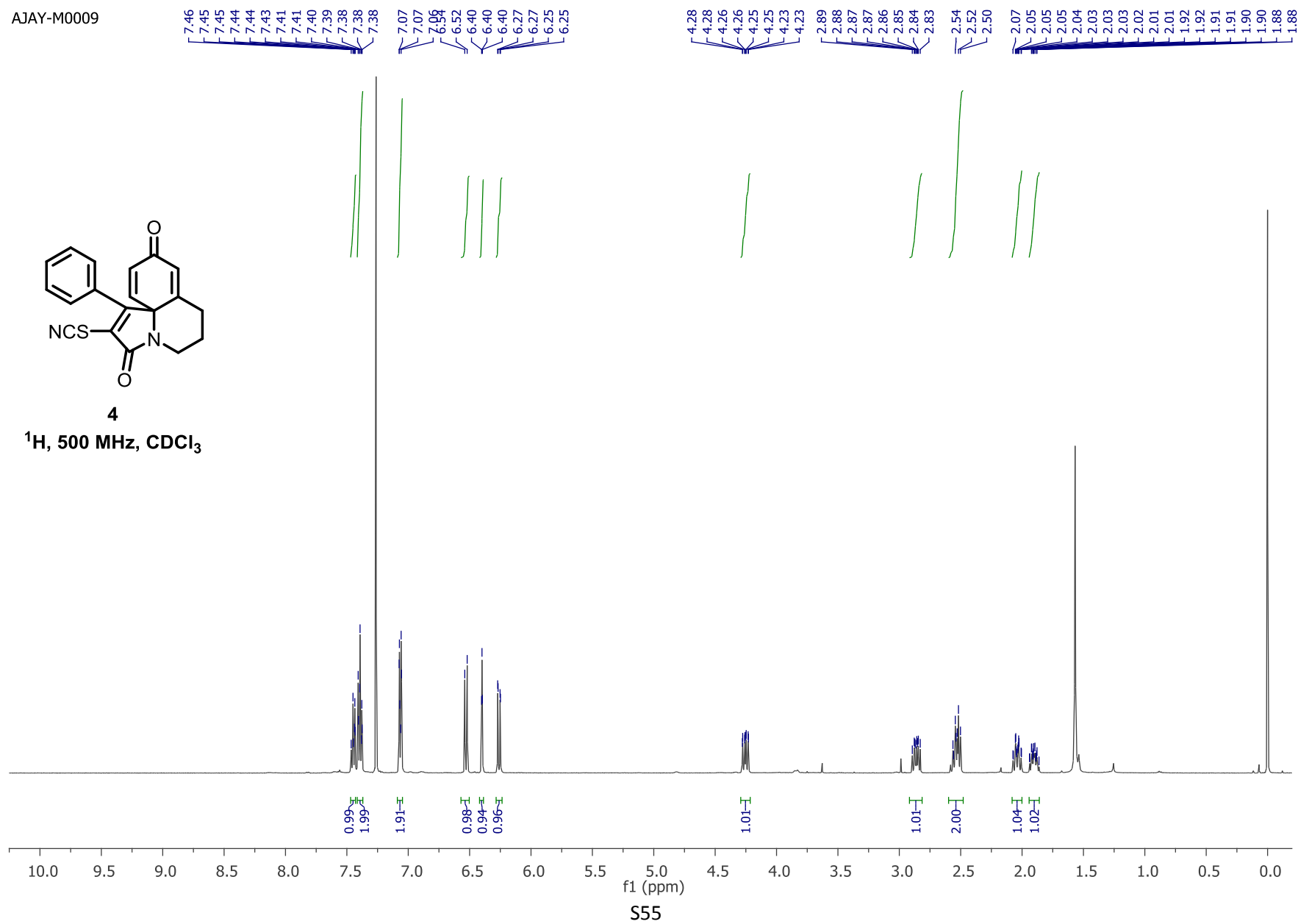


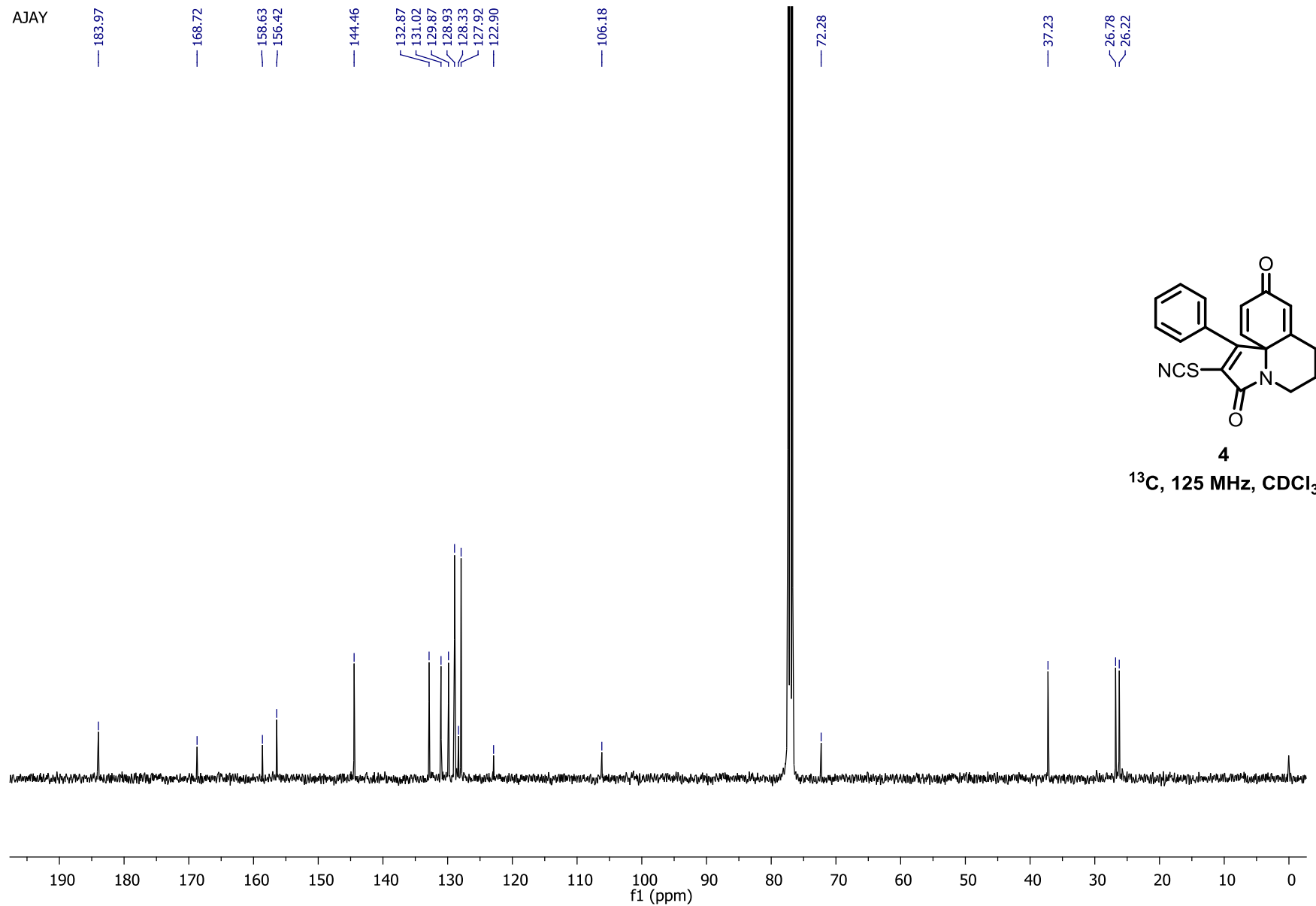
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4

$^1\text{H}$ , 500 MHz,  $\text{CDCl}_3$

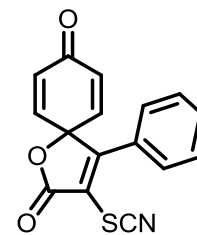






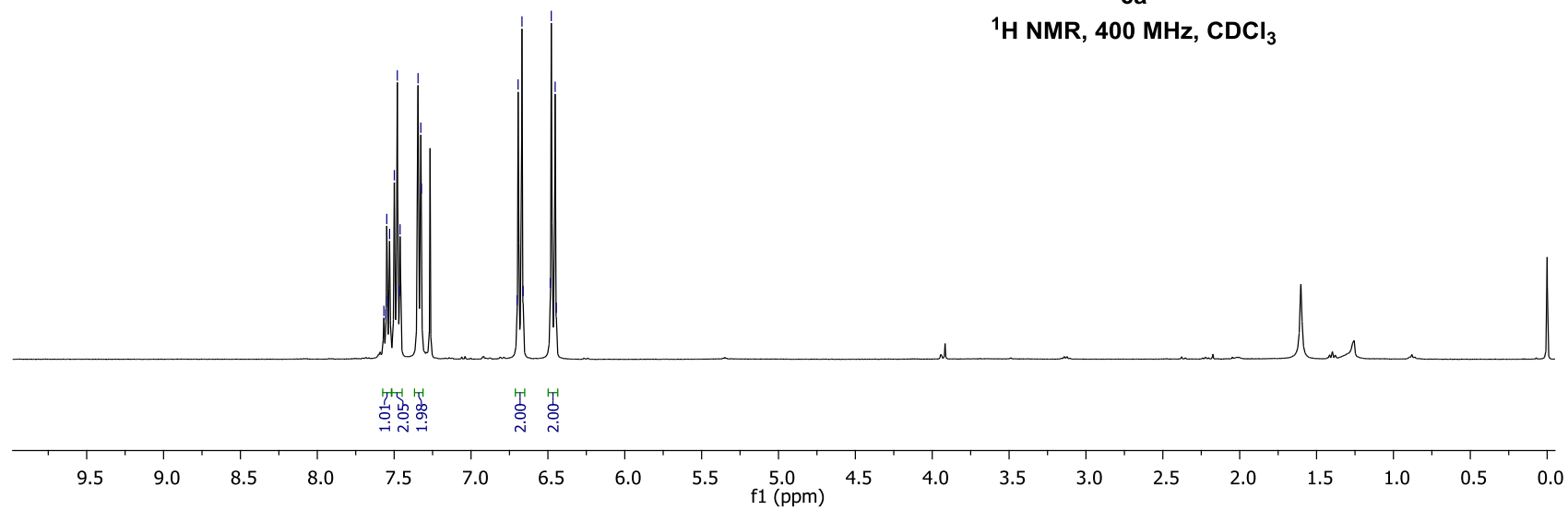
AJAY  
MLP0009  
OSPC1886

7.57  
7.55  
7.55  
7.54  
7.53  
7.50  
7.48  
7.47  
7.46  
7.34  
7.33  
7.32  
6.70  
6.69  
6.67  
6.66  
6.48  
6.45  
6.45



6a

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



AJAY  
MLP0009  
OSPC1886

— 183.10

165.97  
165.73

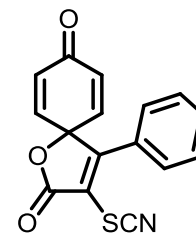
140.65  
139.72

132.75  
132.30  
129.47  
127.55

— 116.36

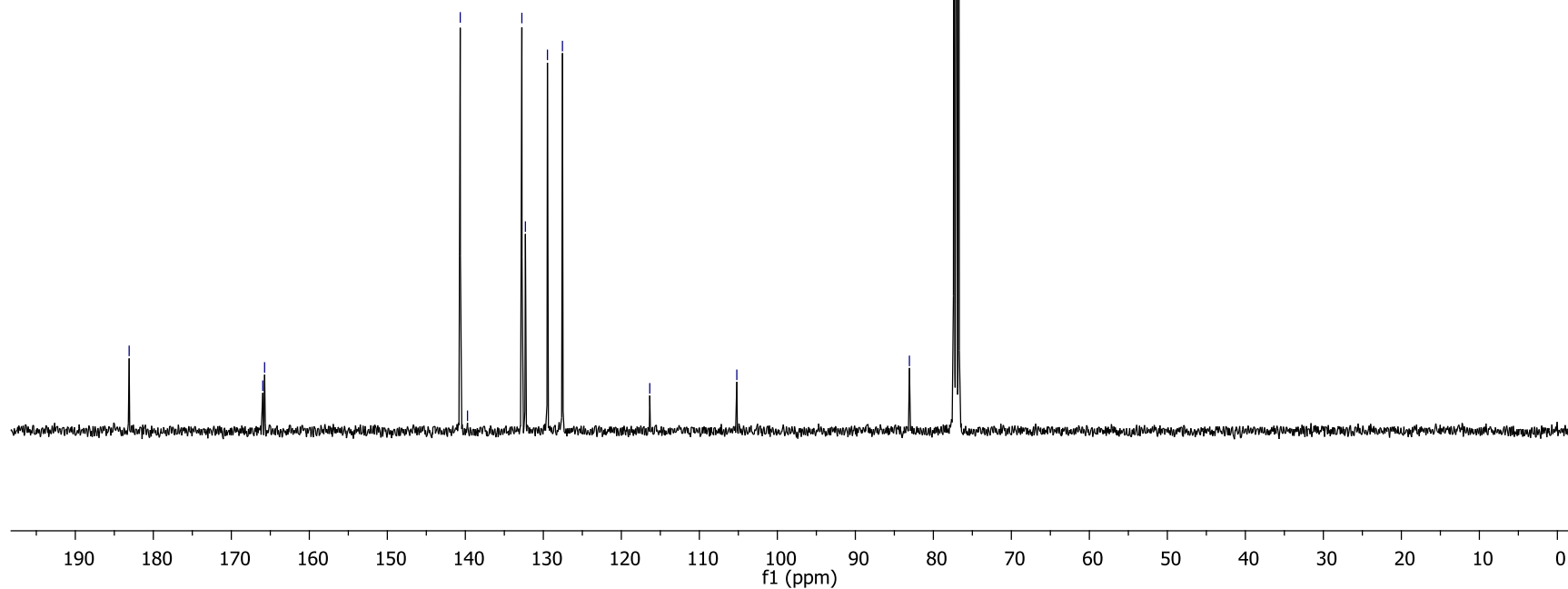
— 105.20

— 83.07



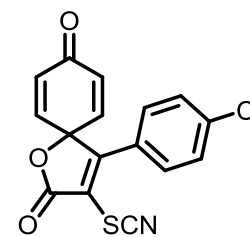
6a

<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>



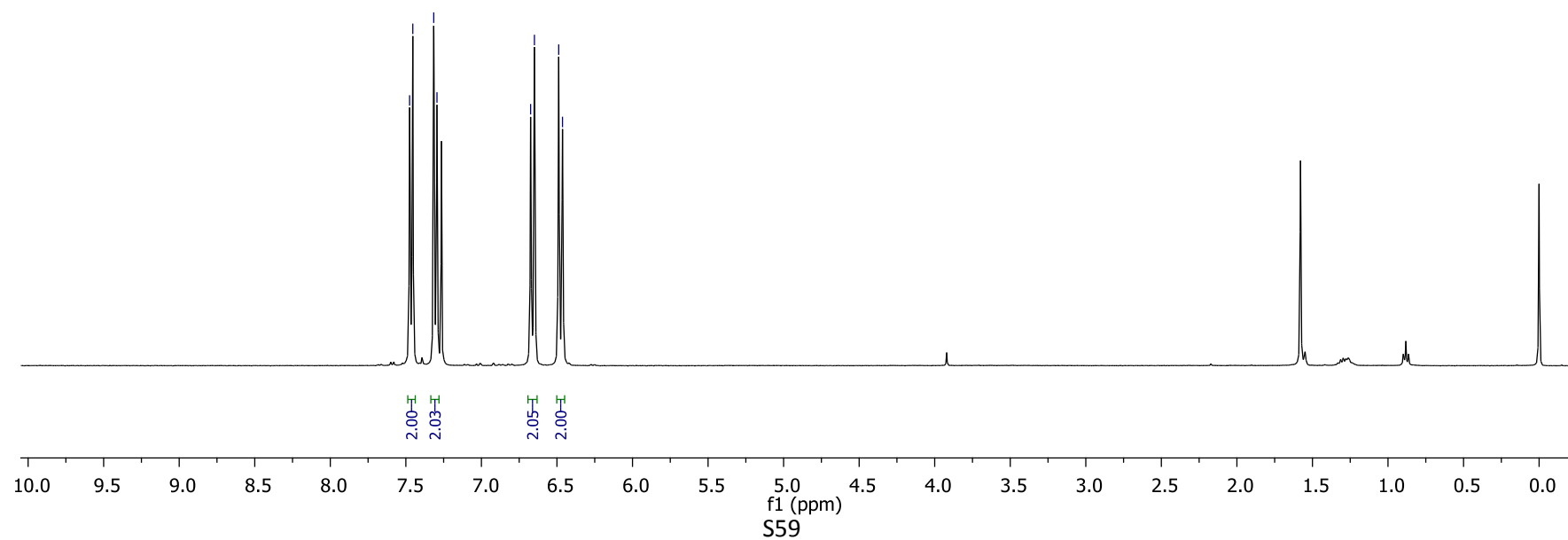
AJAY

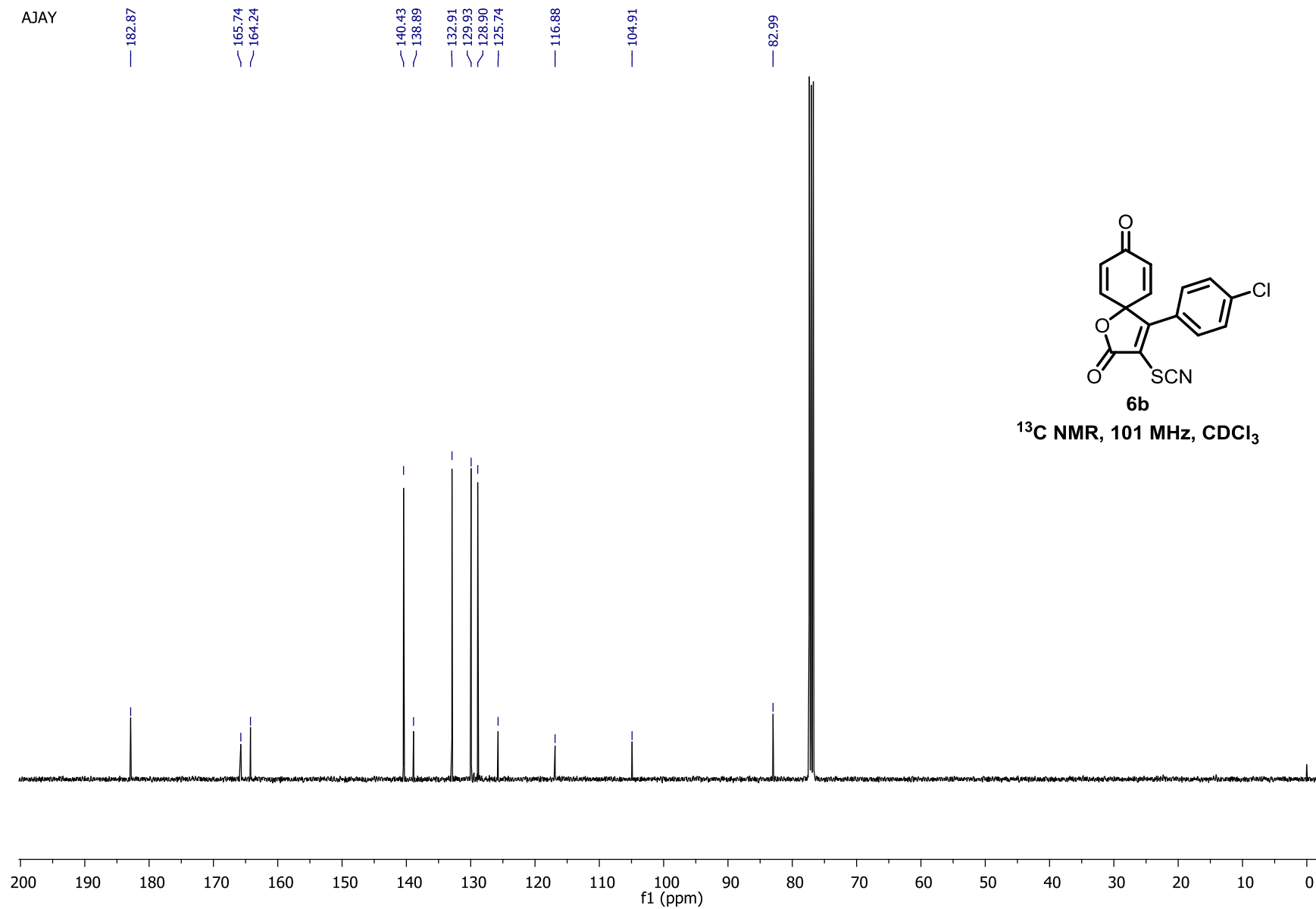
7.48  
7.45  
7.32  
7.29  
6.67  
6.65  
6.49  
6.46



6b

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





AJAY

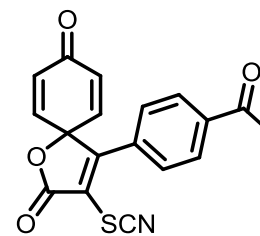
8.05  
8.02

7.43  
7.41

6.69  
6.66

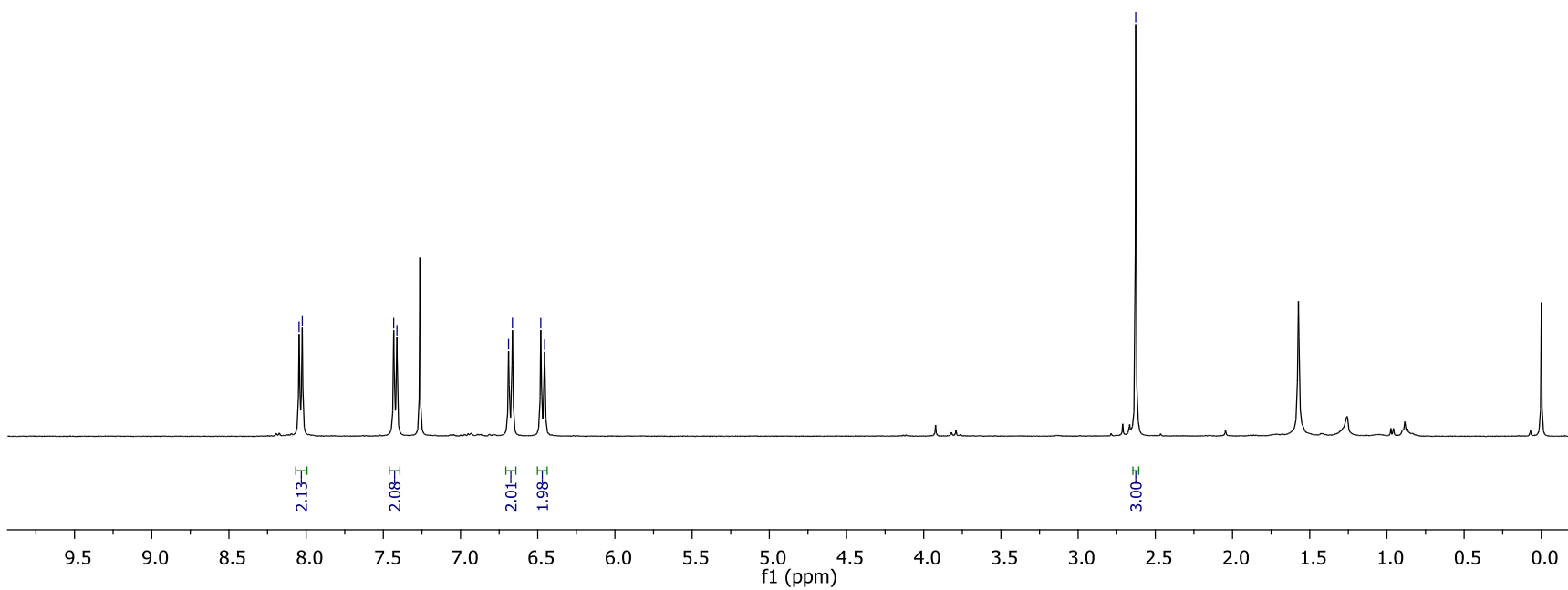
6.48  
6.46

2.63



6c

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



AJAY

— 196.49

— 182.76

— 165.61  
— 164.11

— 140.20  
— 139.44

— 132.99  
— 131.42

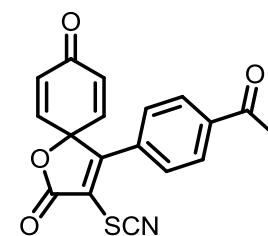
— 129.09  
— 127.97

— 117.99

— 104.63

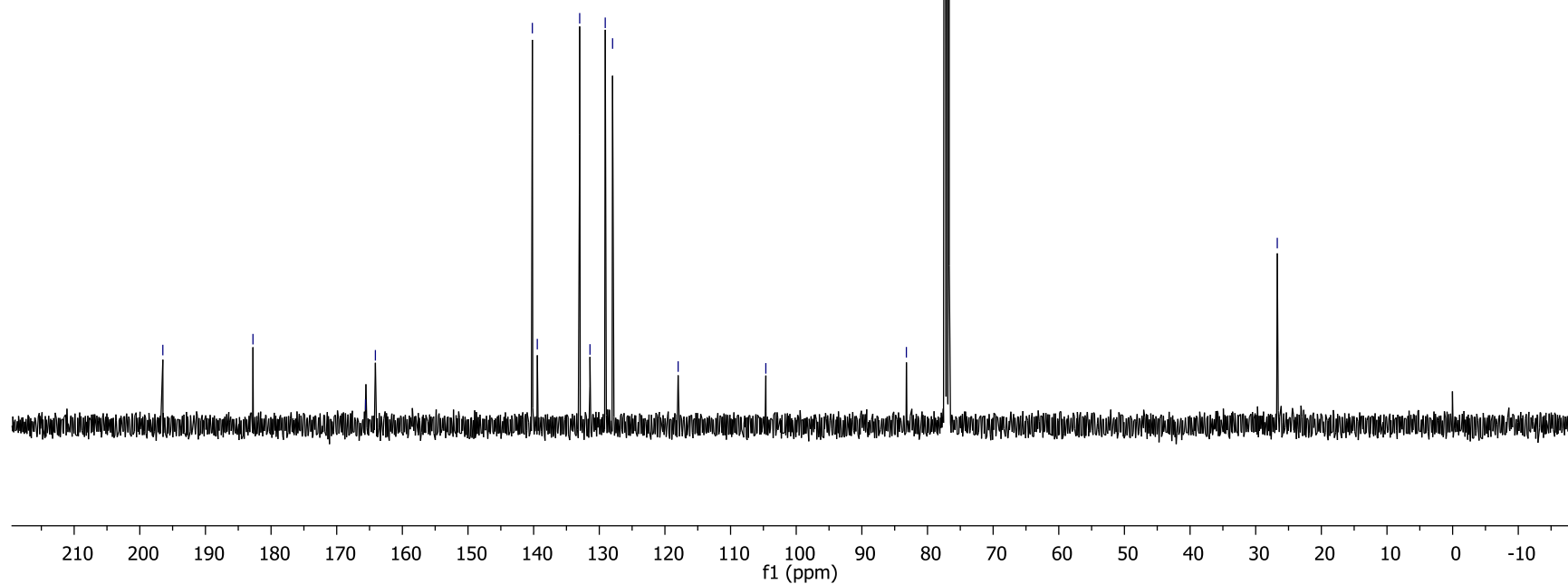
— 83.22

— 26.71

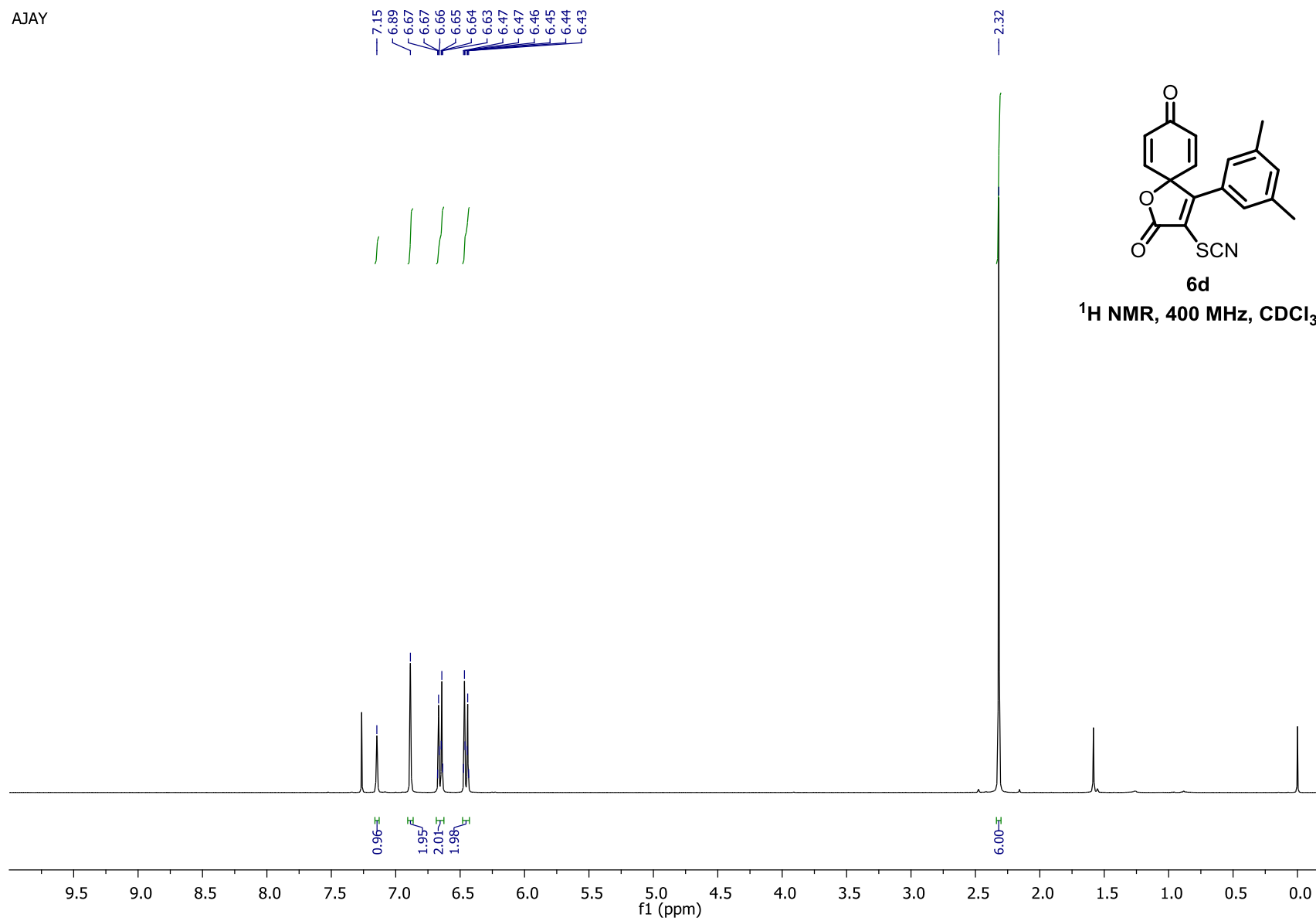


**6c**

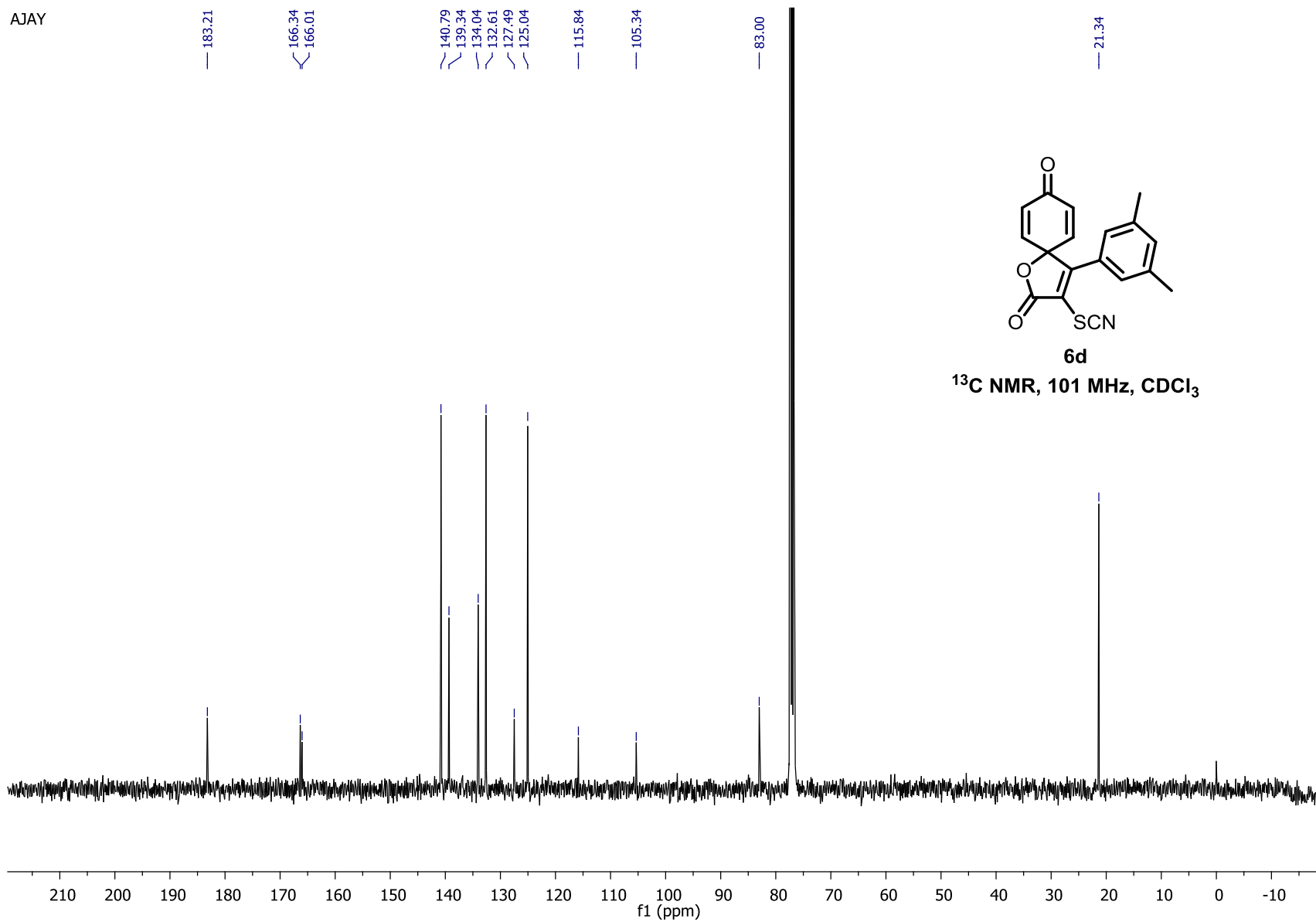
<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>



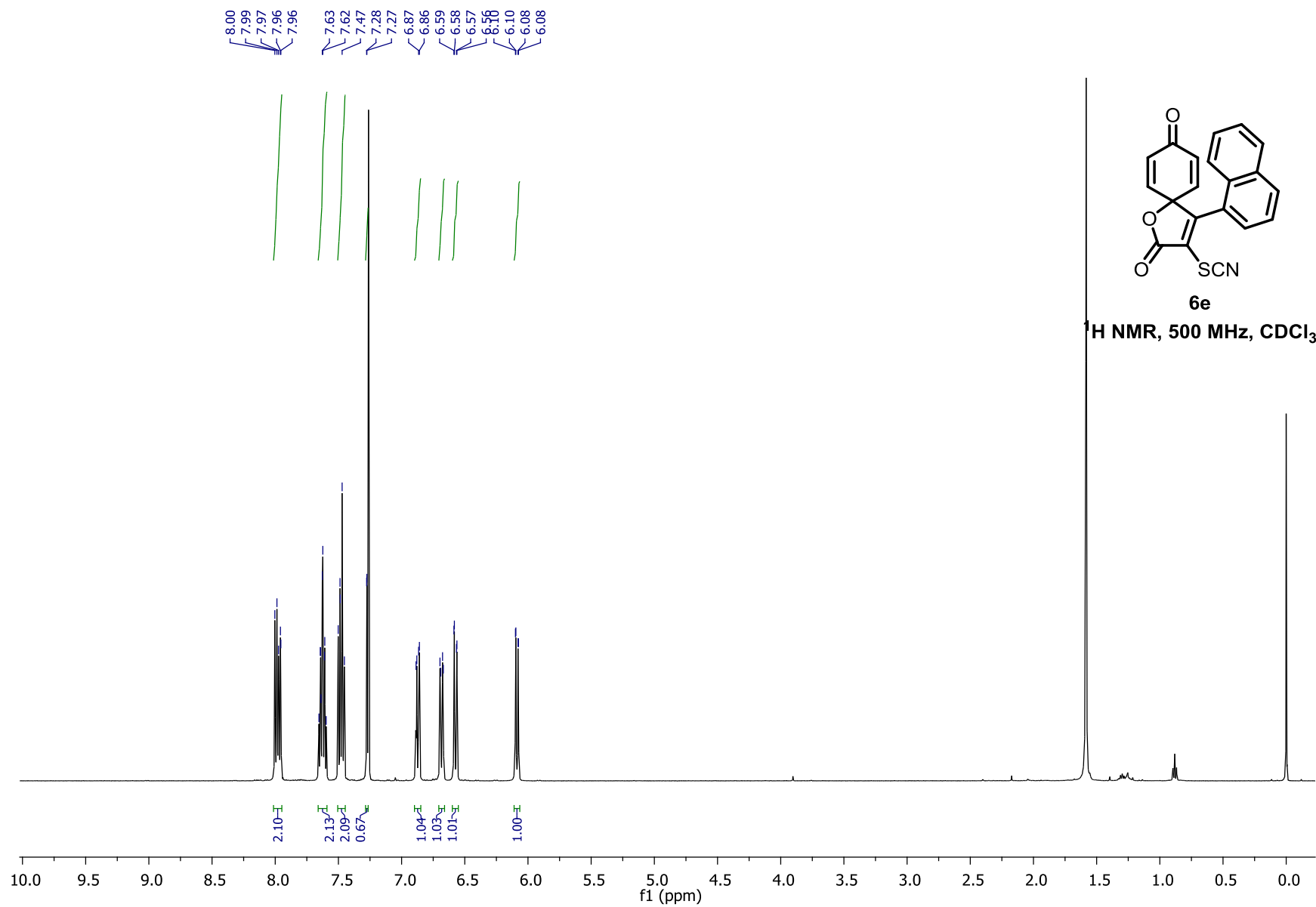
AJAY



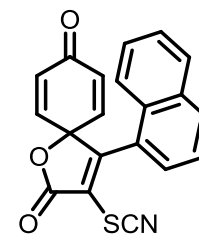
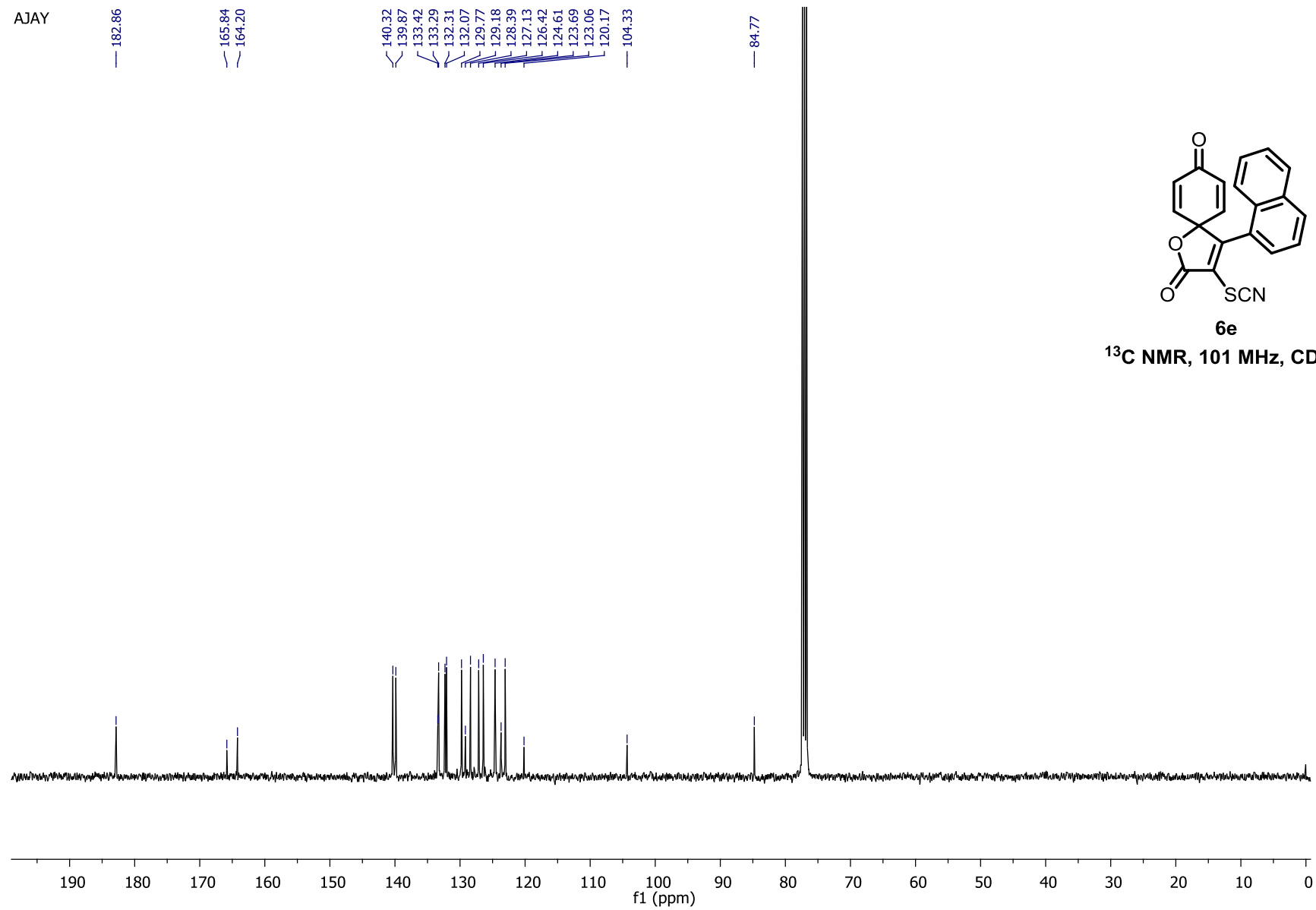
AJAY







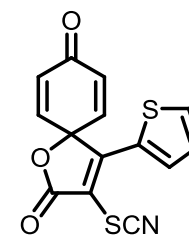
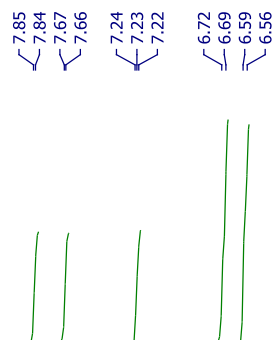
AJAY



**6e**

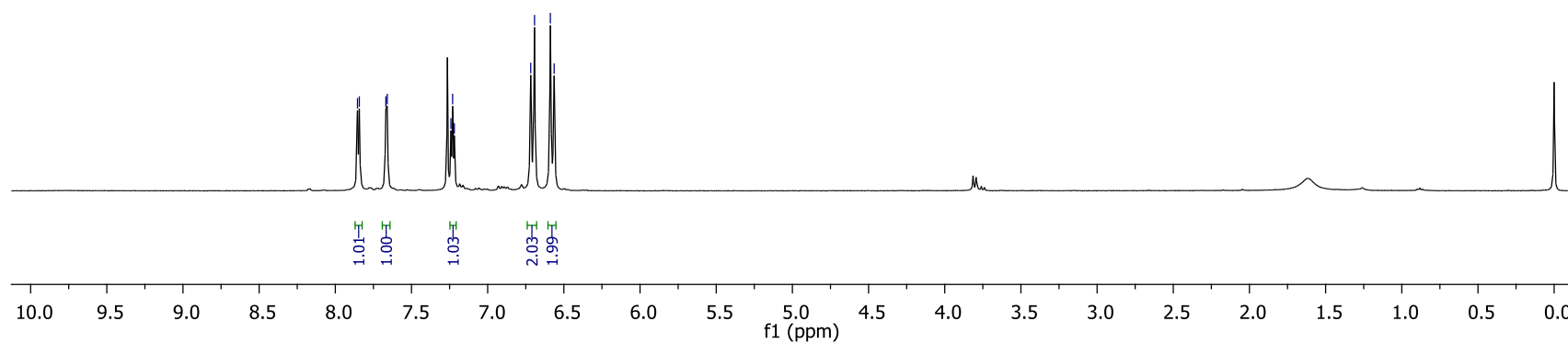
<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>

AJAY

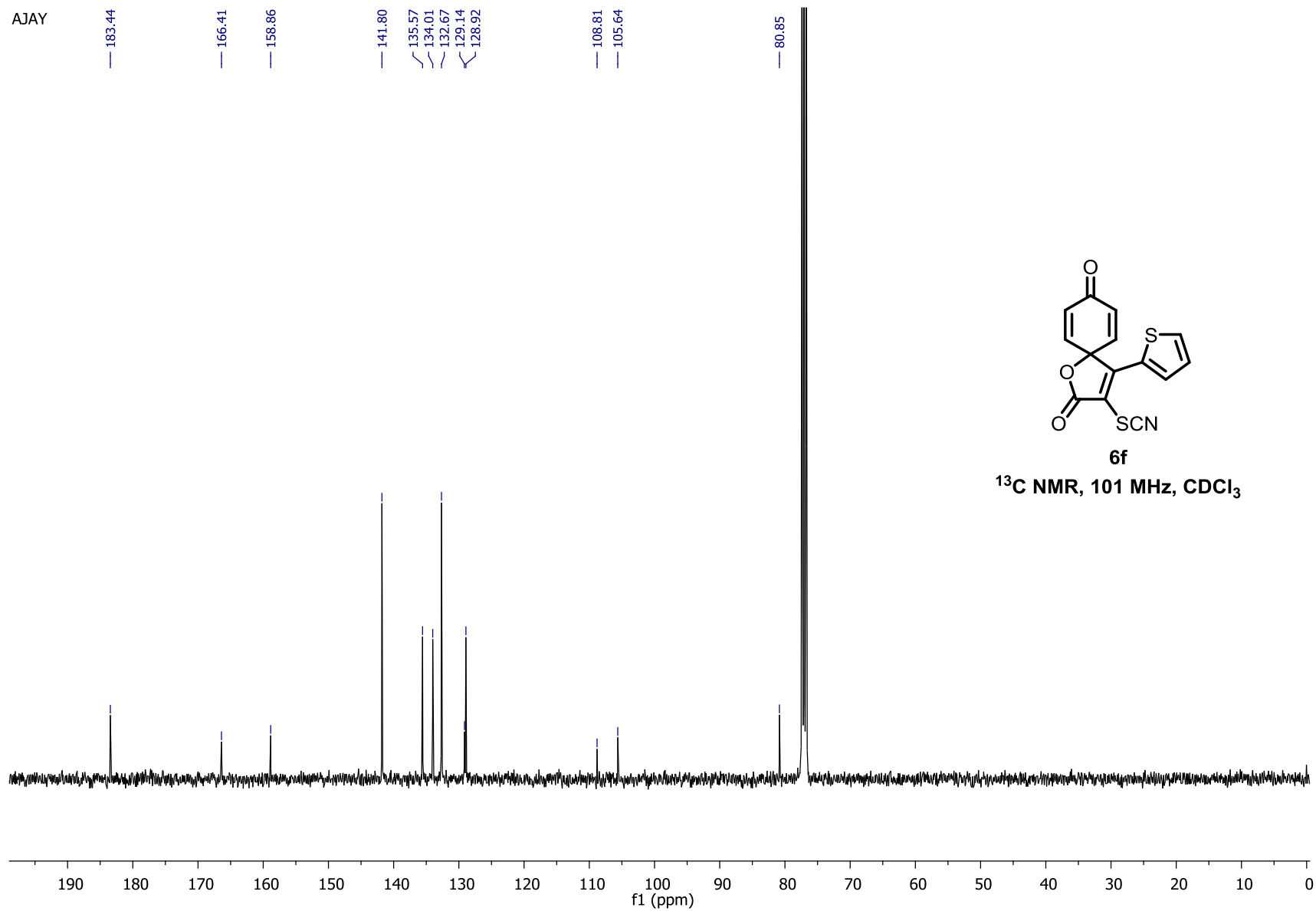


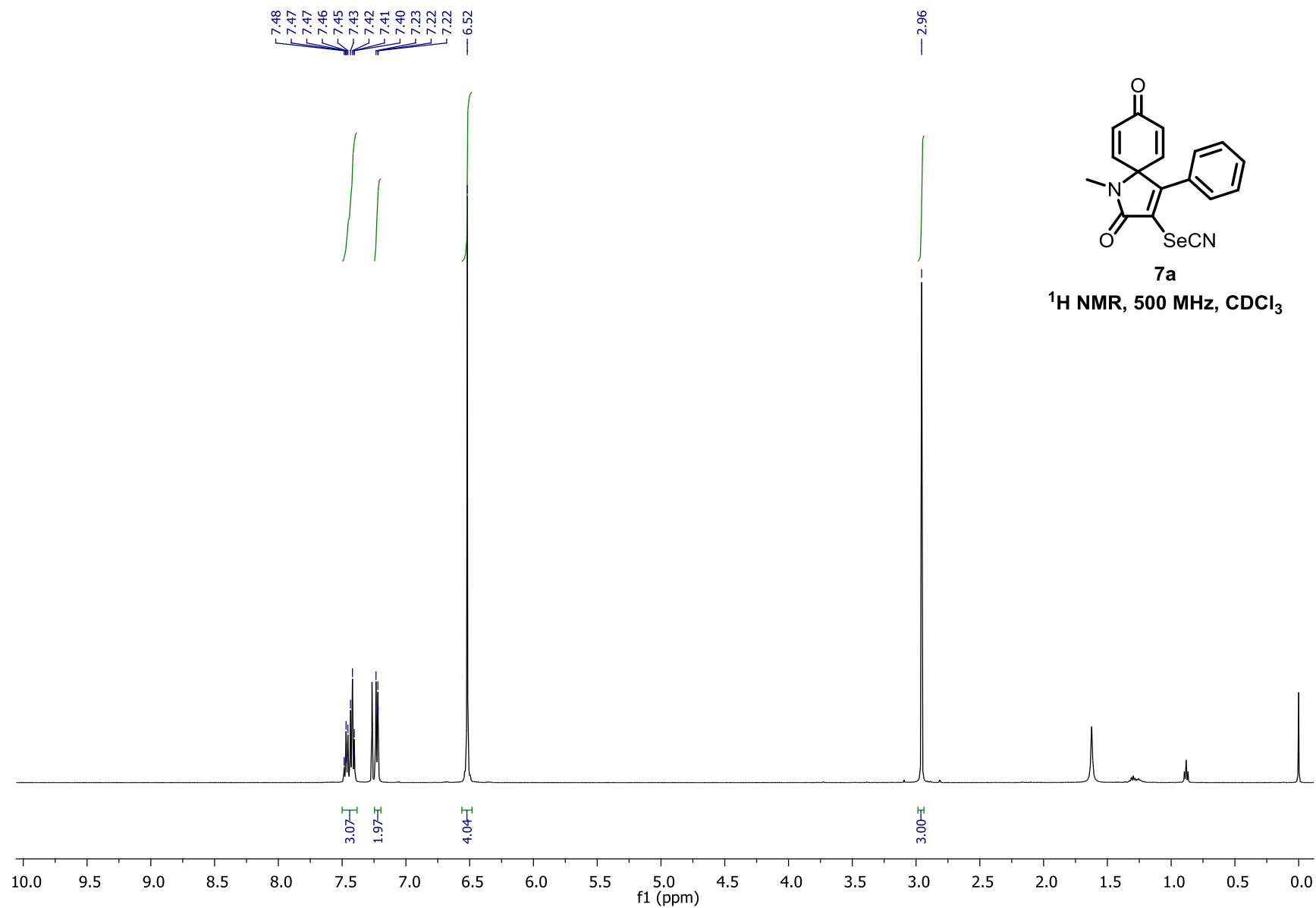
6f

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

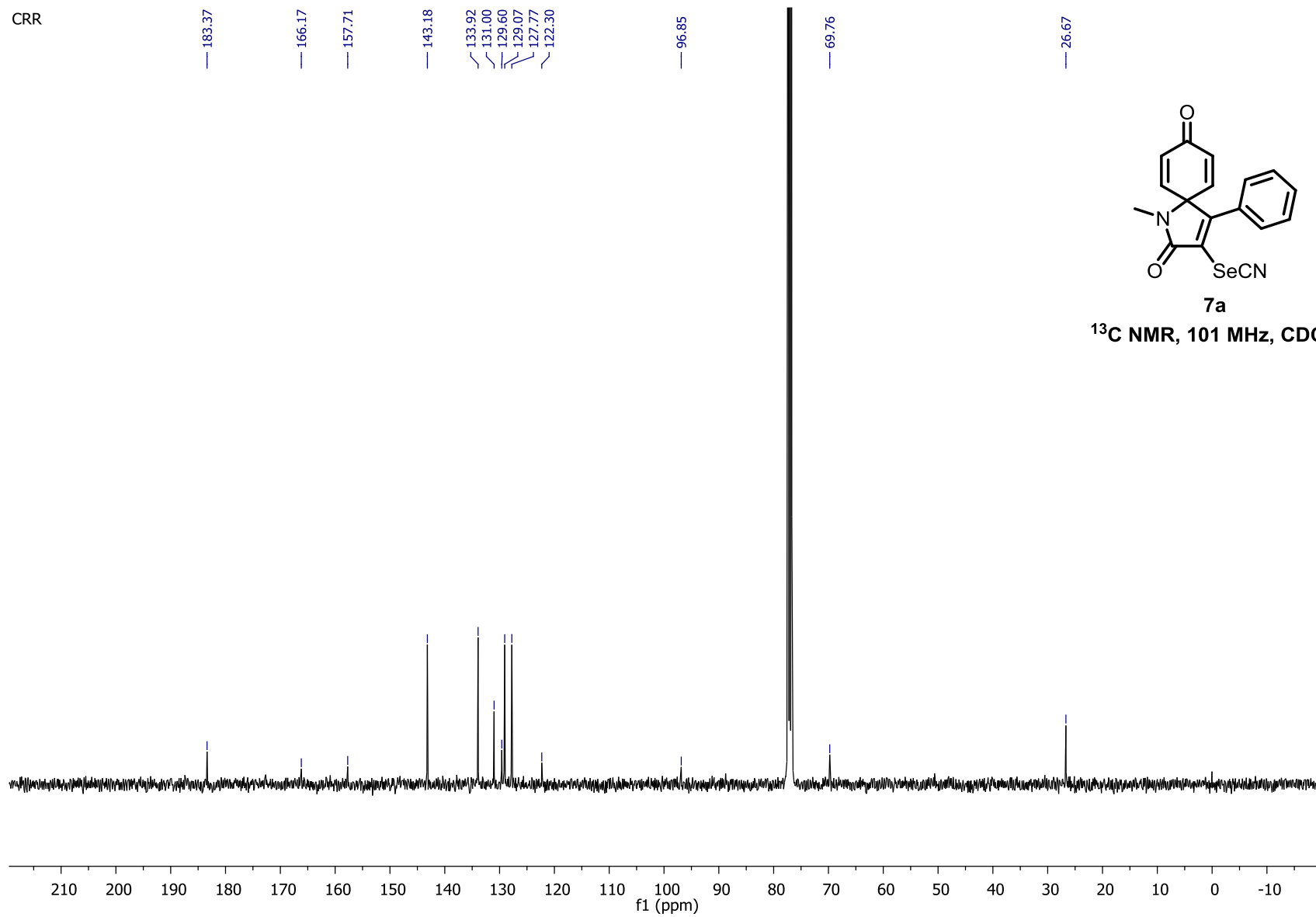


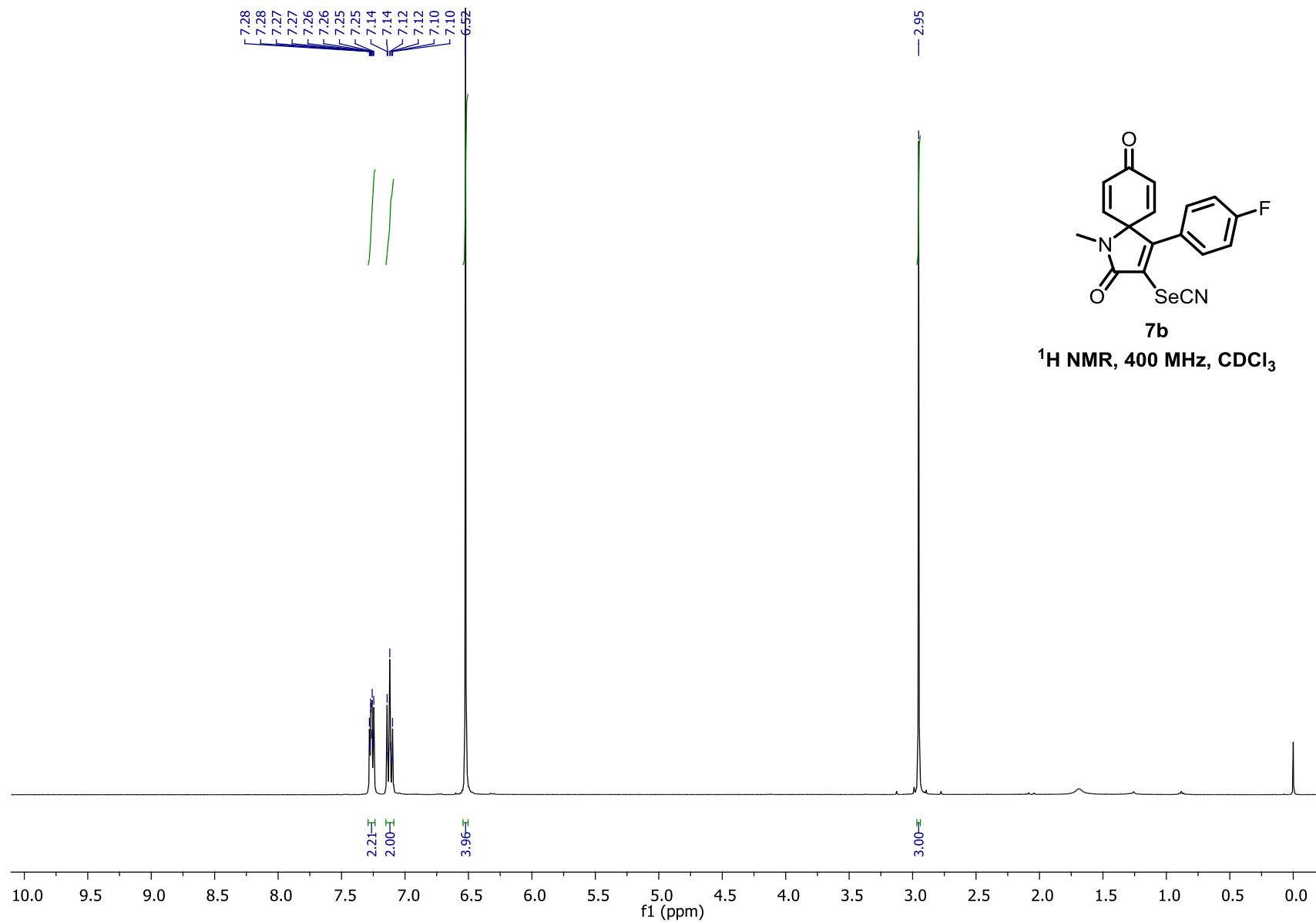
AJAY



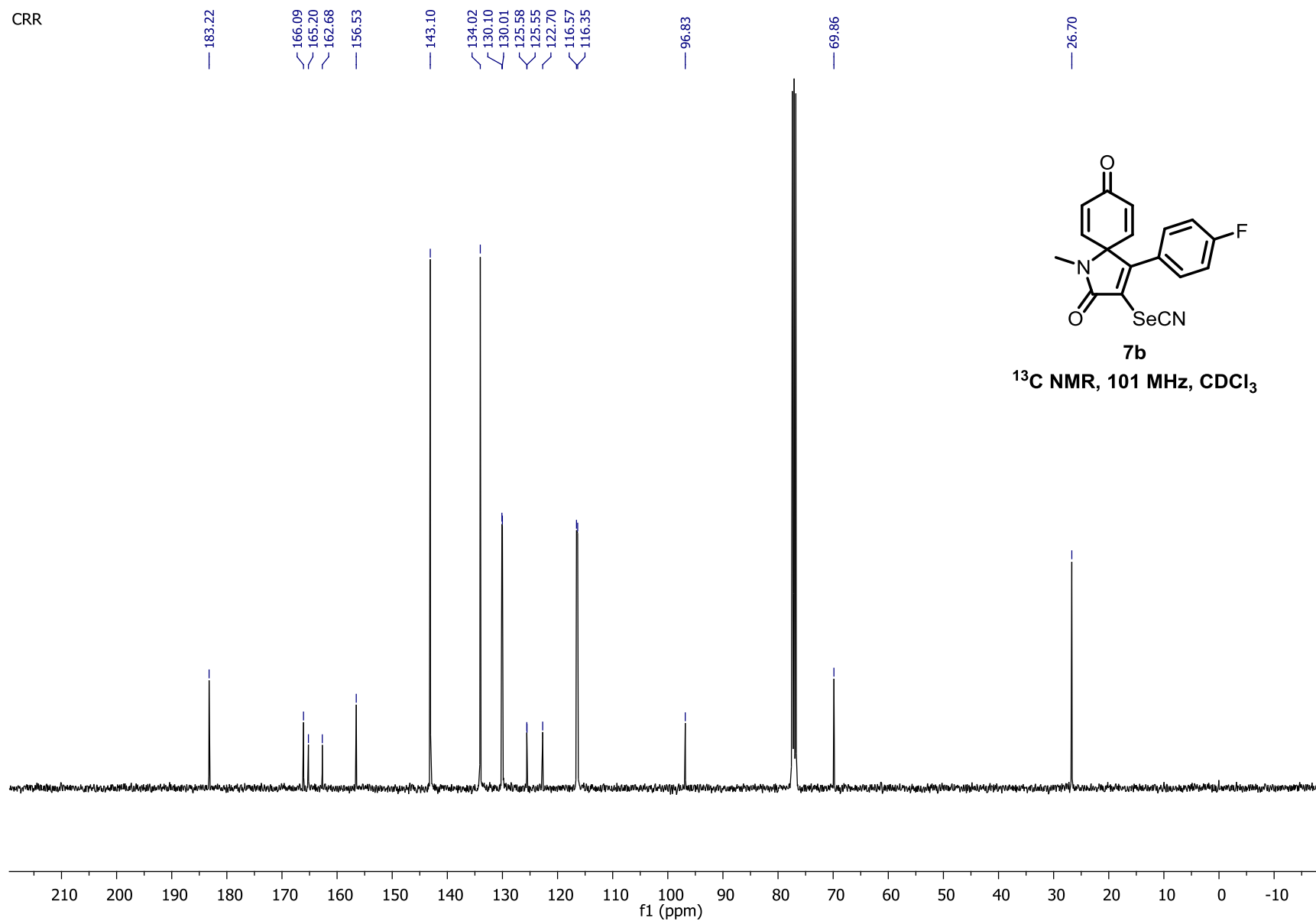


CRR

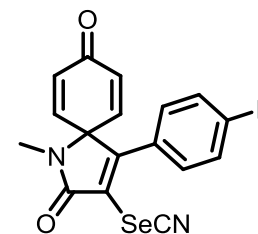




CRR

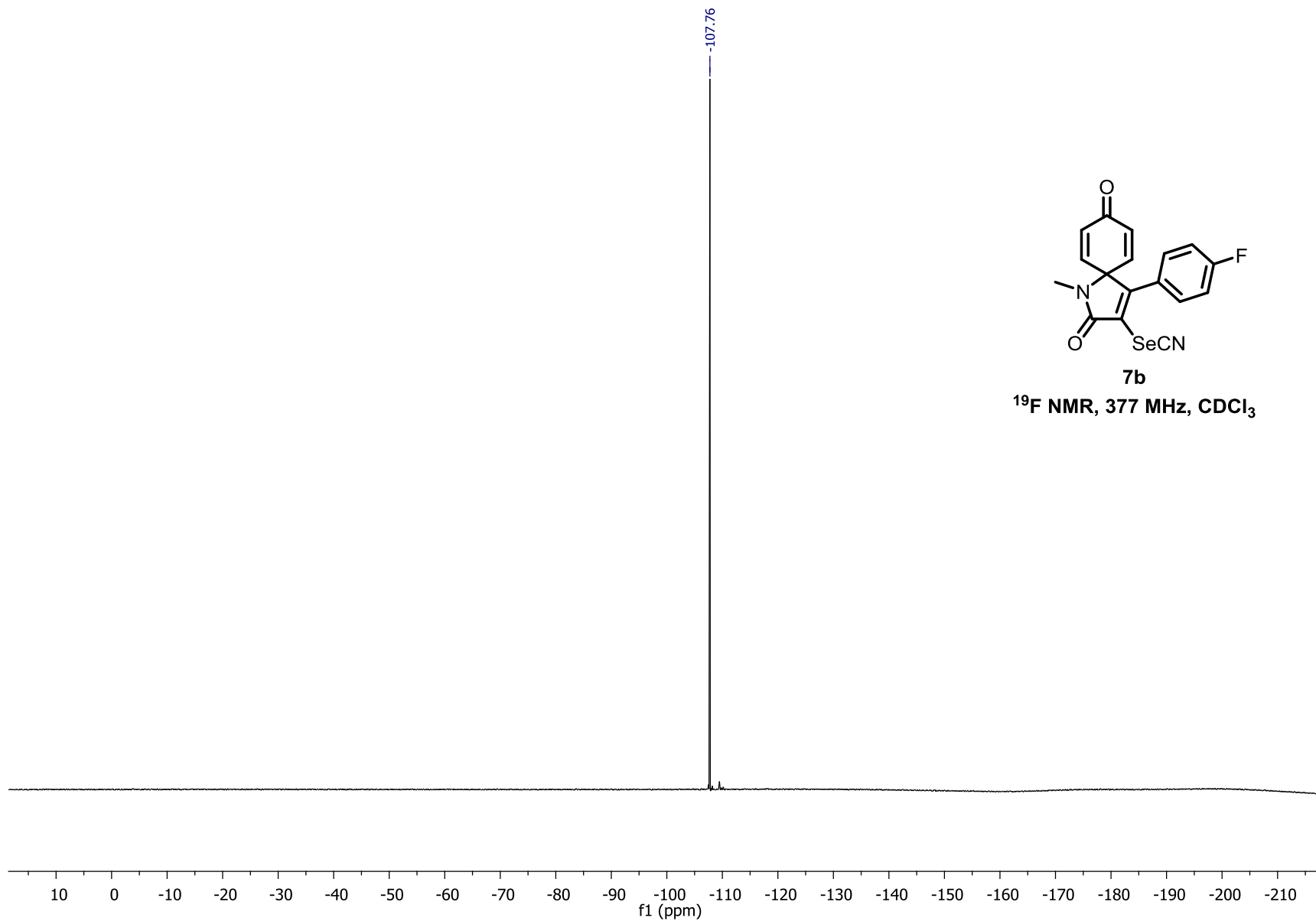


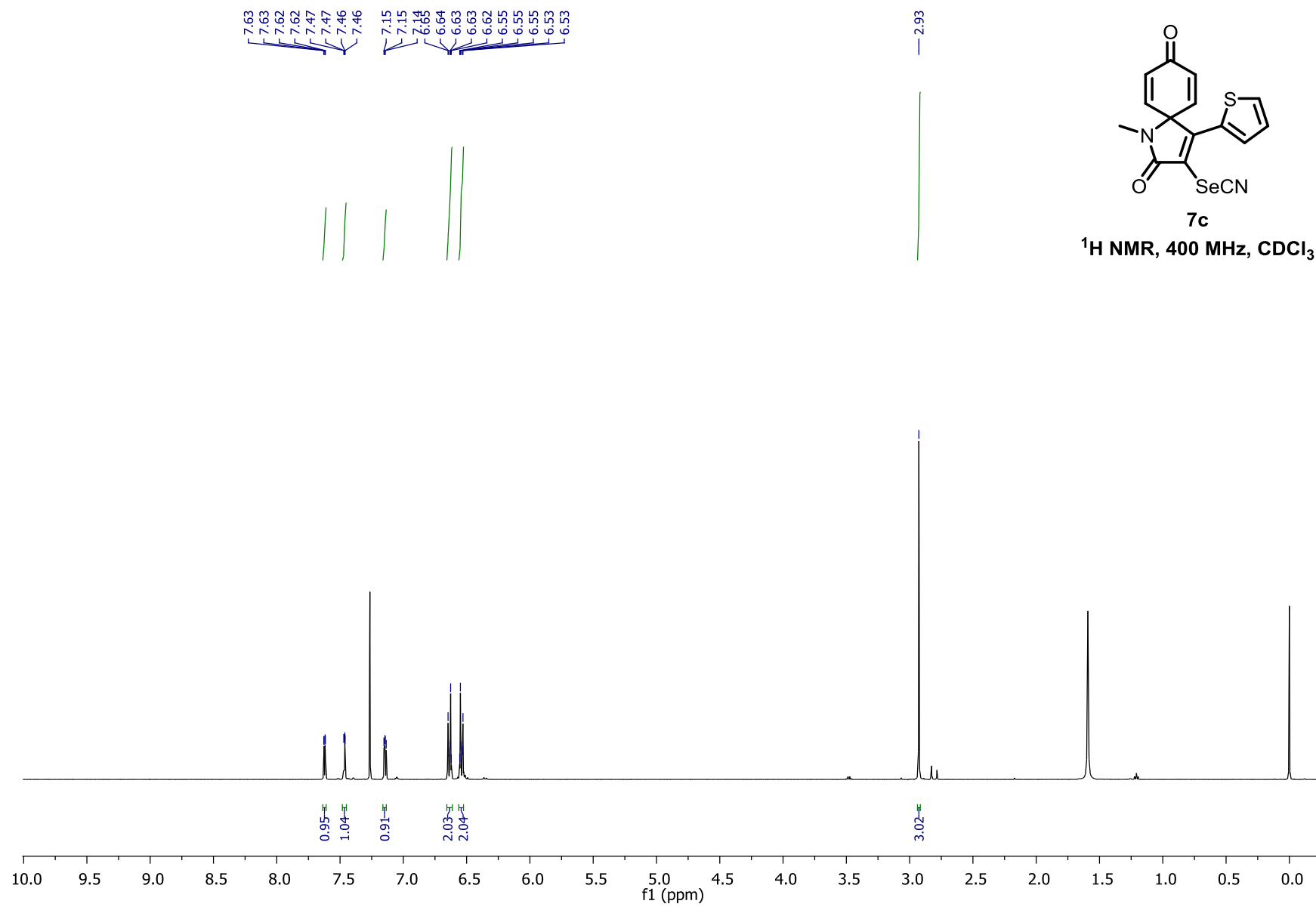


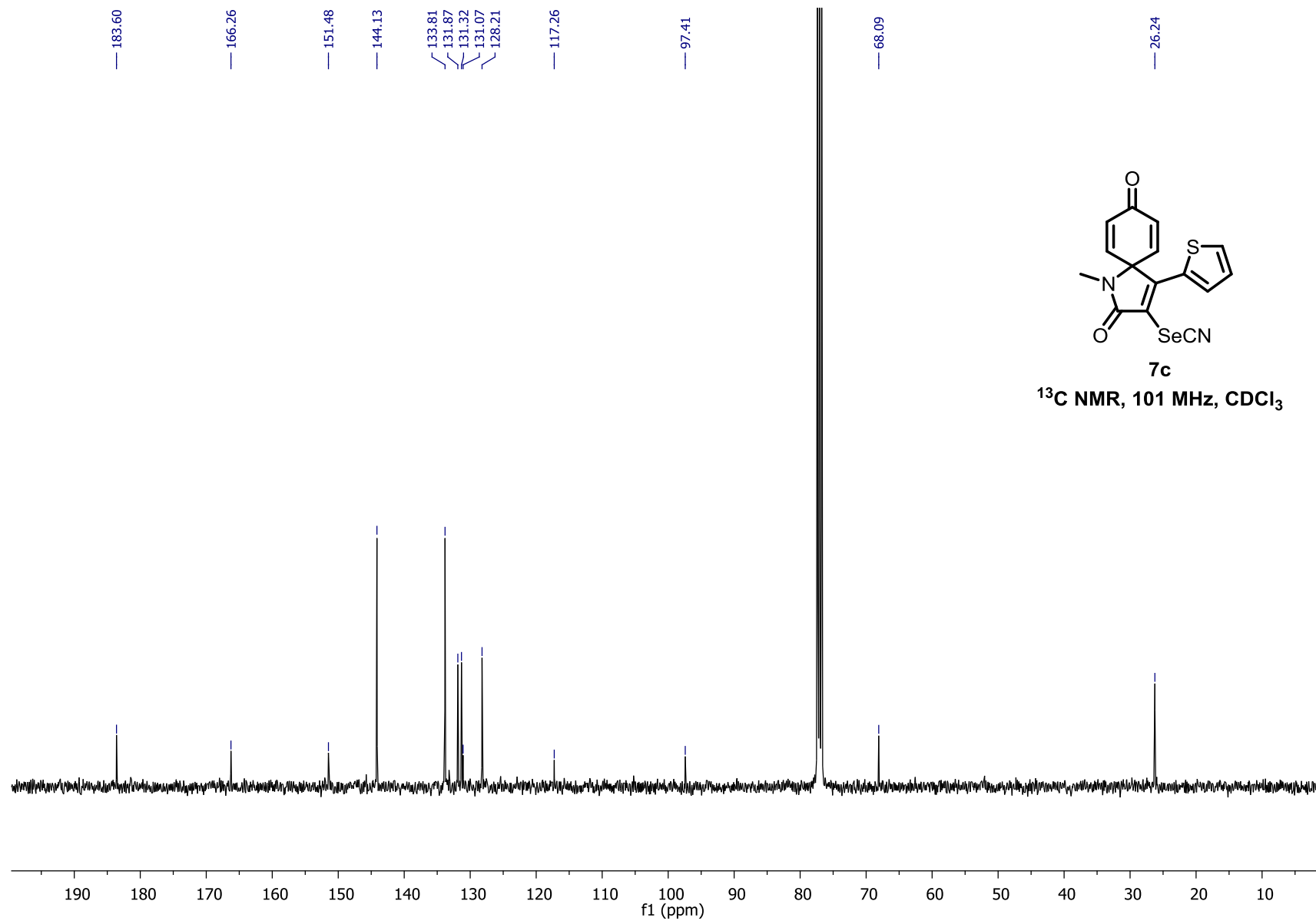


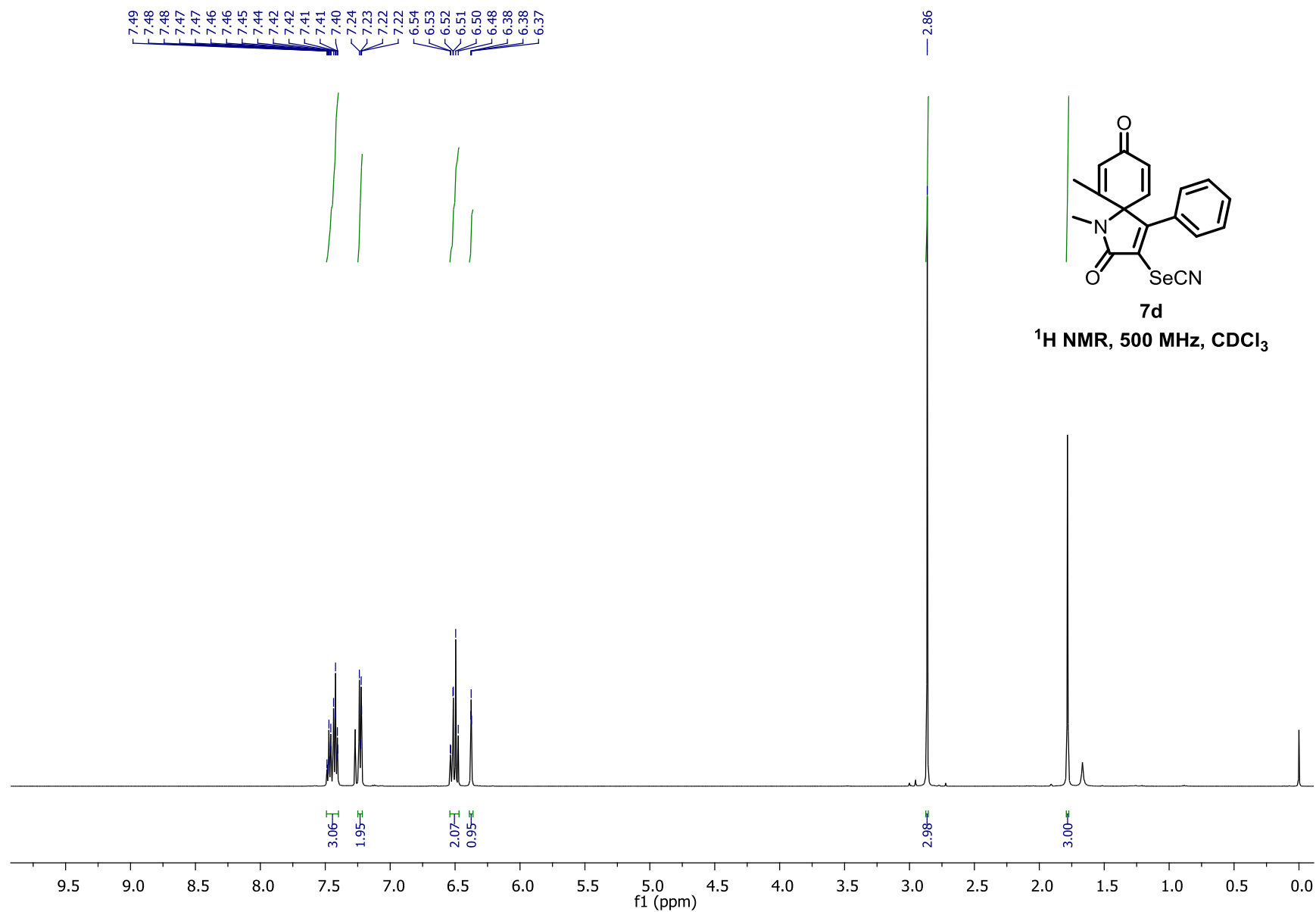
**7b**

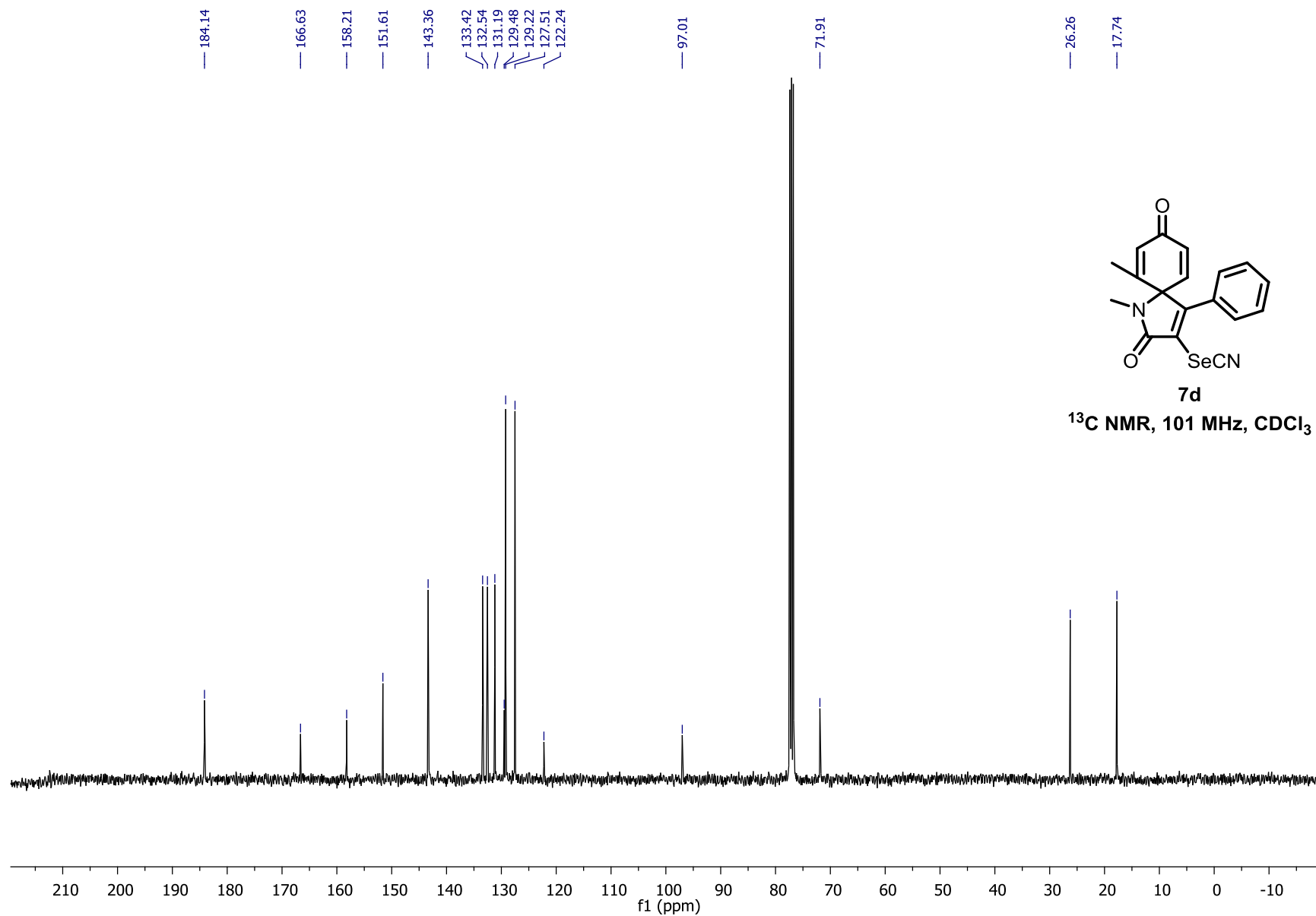
<sup>19</sup>F NMR, 377 MHz, CDCl<sub>3</sub>

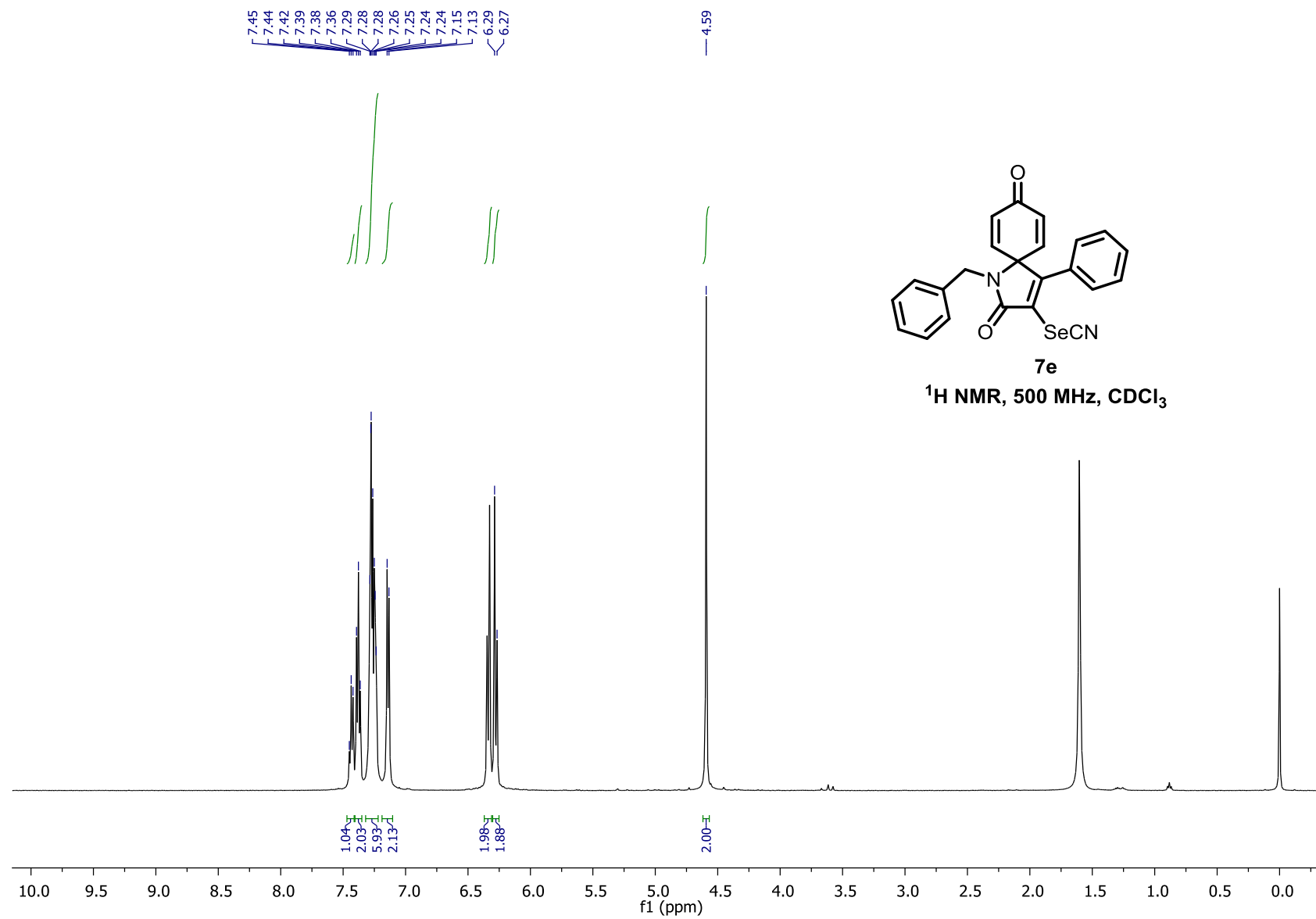


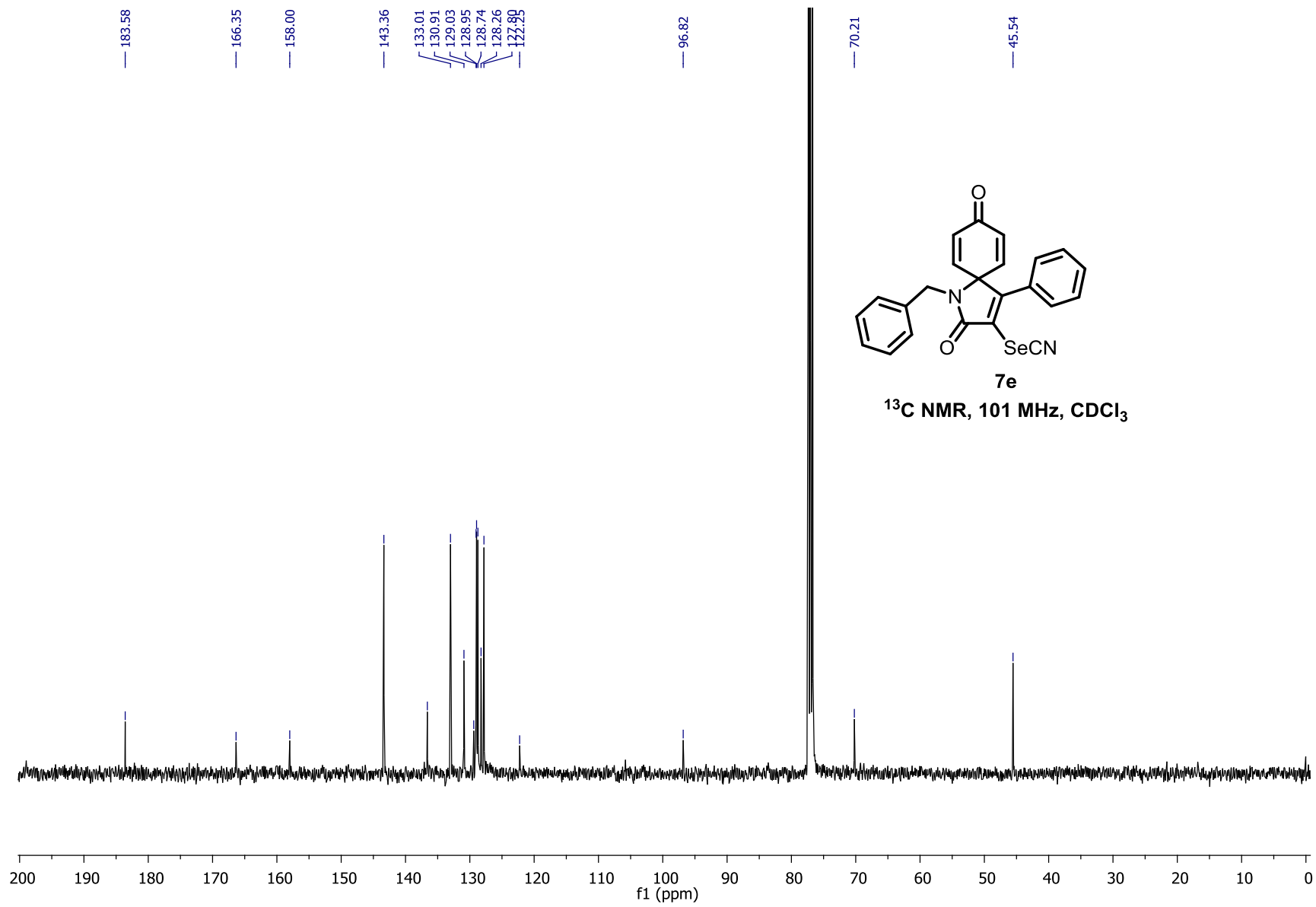




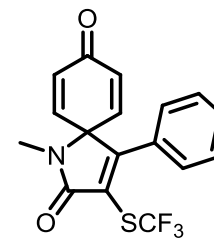
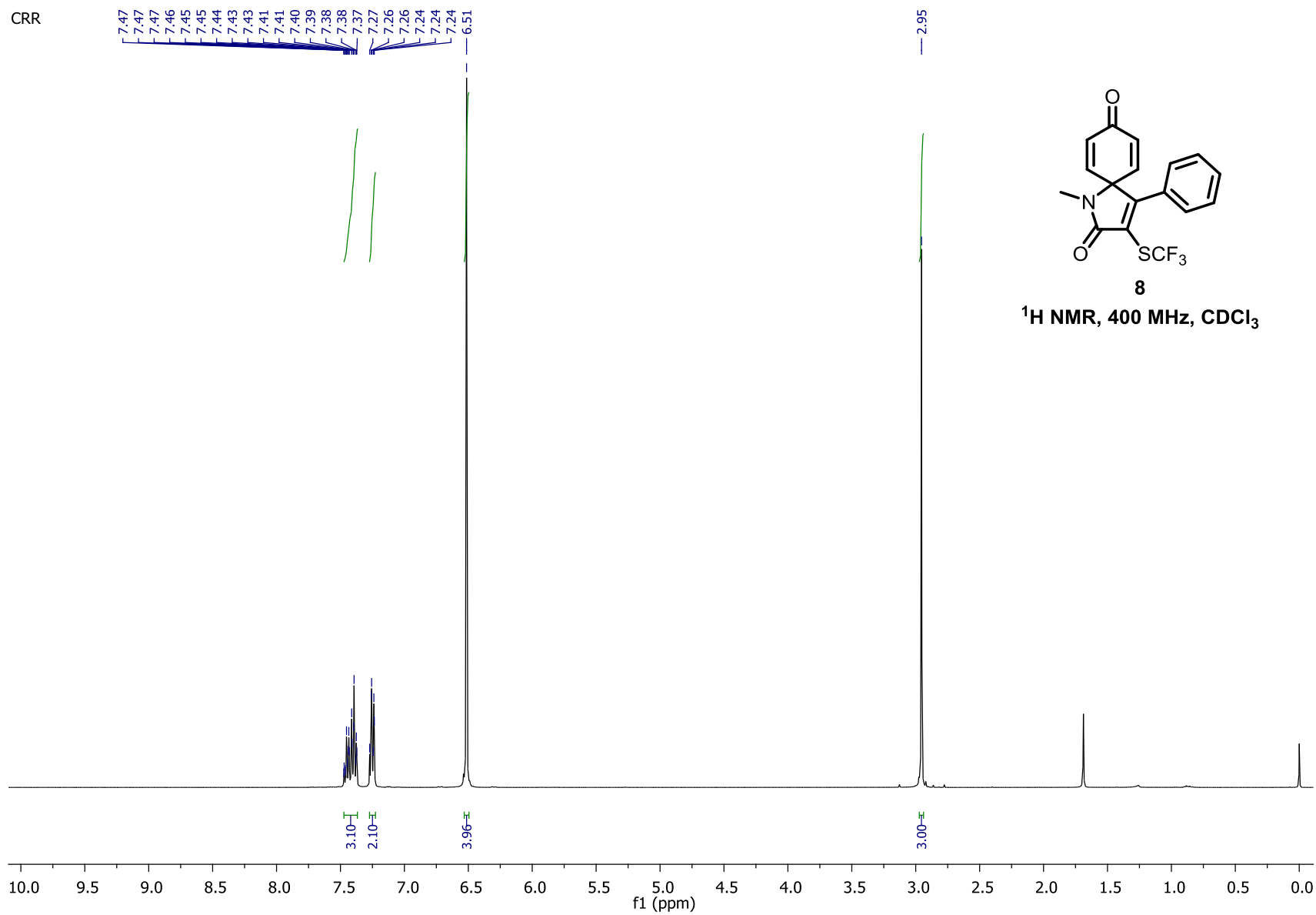








CRR



**8**

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



CRR

— 183.39

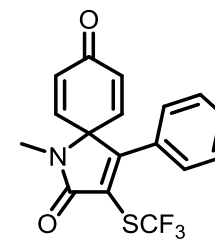
— 166.74  
— 165.12

— 143.35

— 133.86  
— 130.70  
— 129.86  
— 129.66  
— 128.68  
— 128.03  
— 126.77  
— 123.90

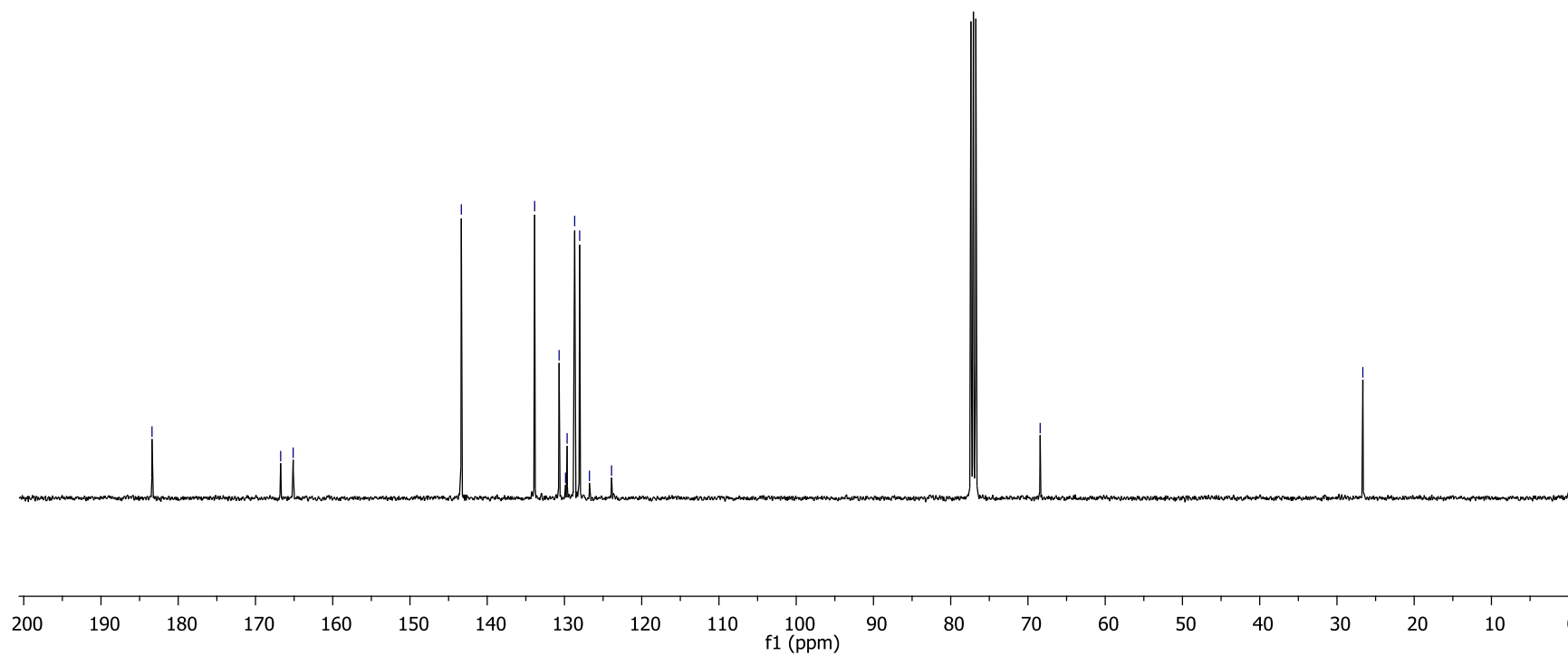
— 68.42

— 26.65

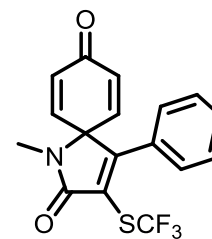


8

<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>

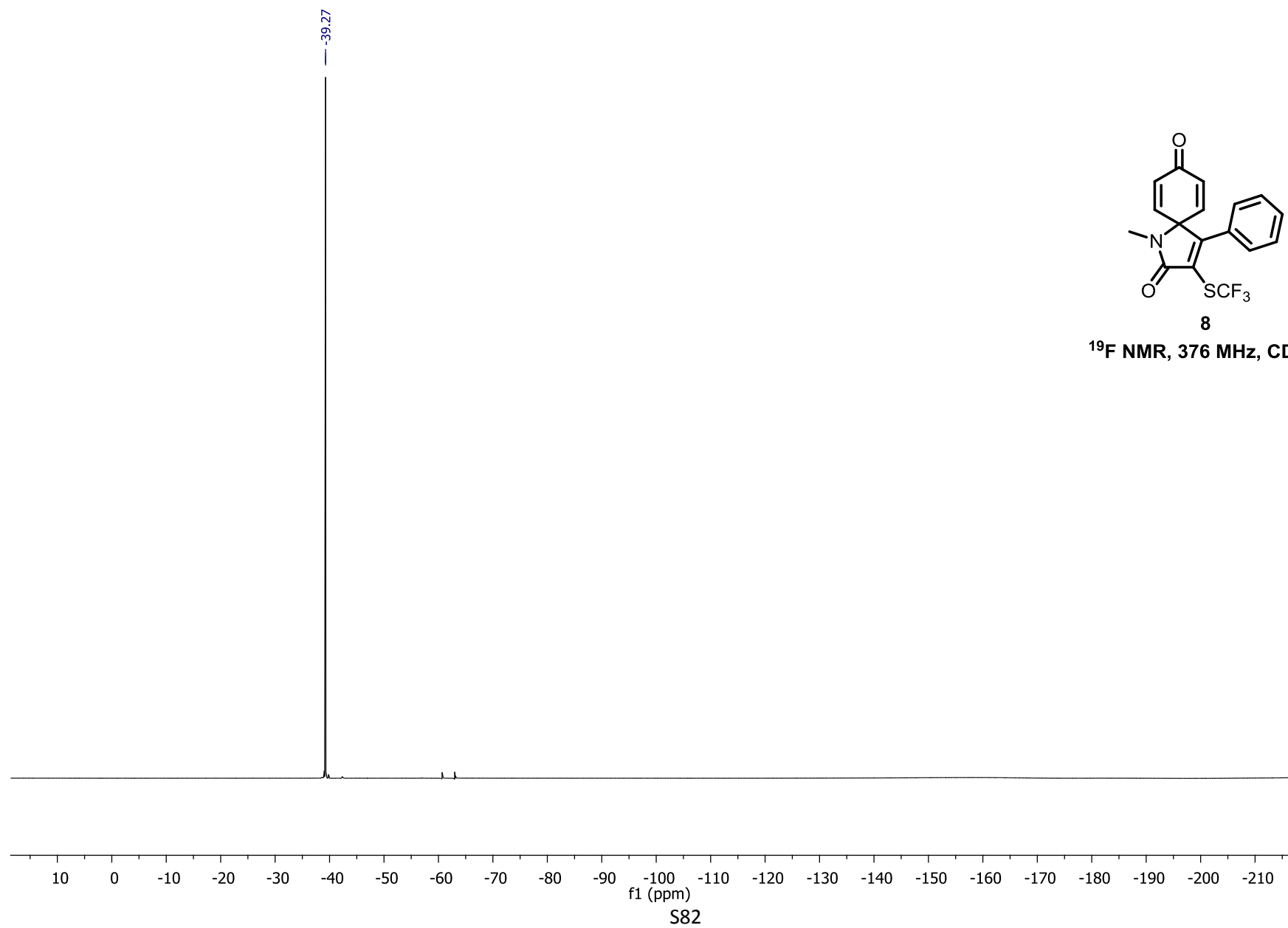


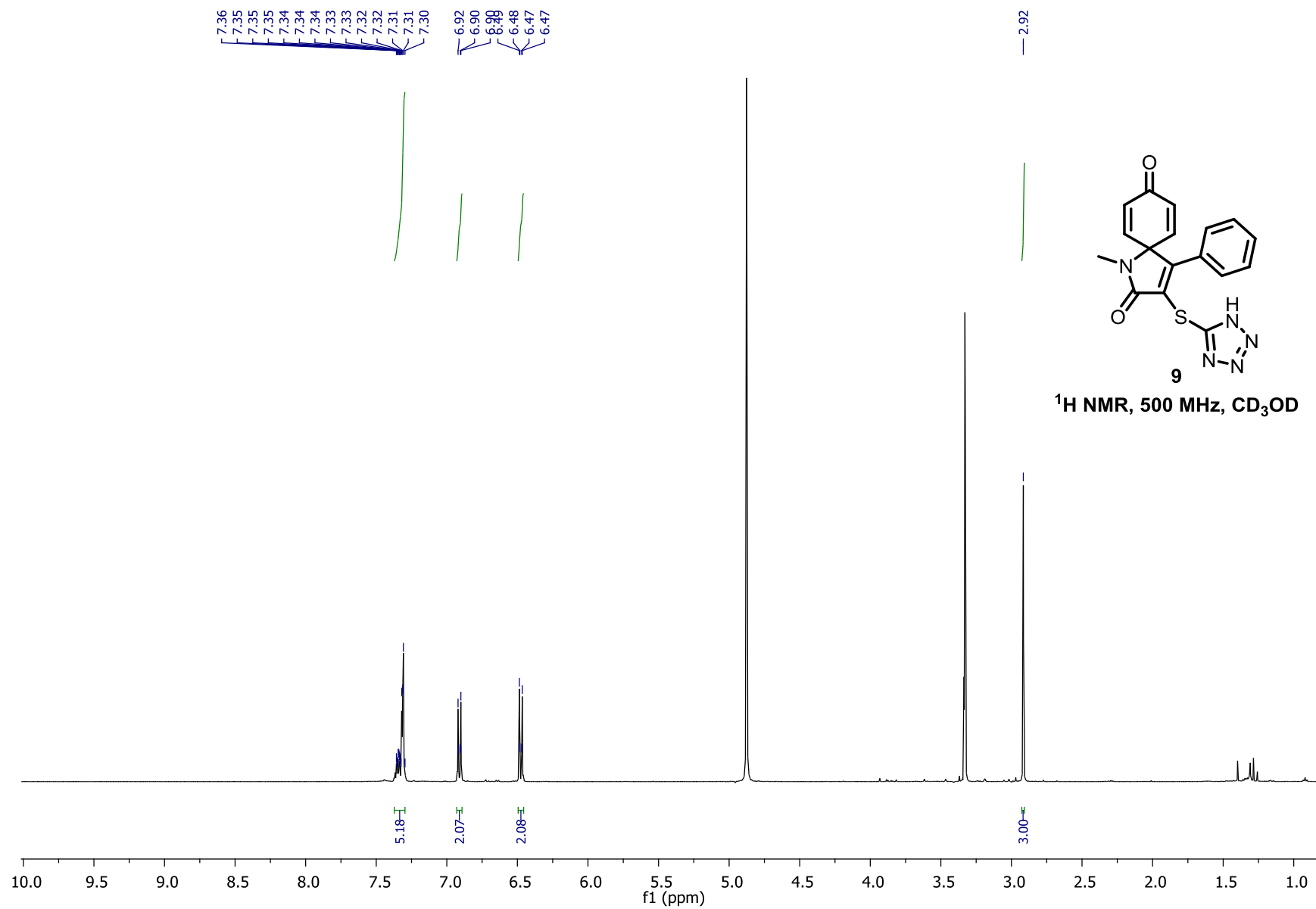
S81

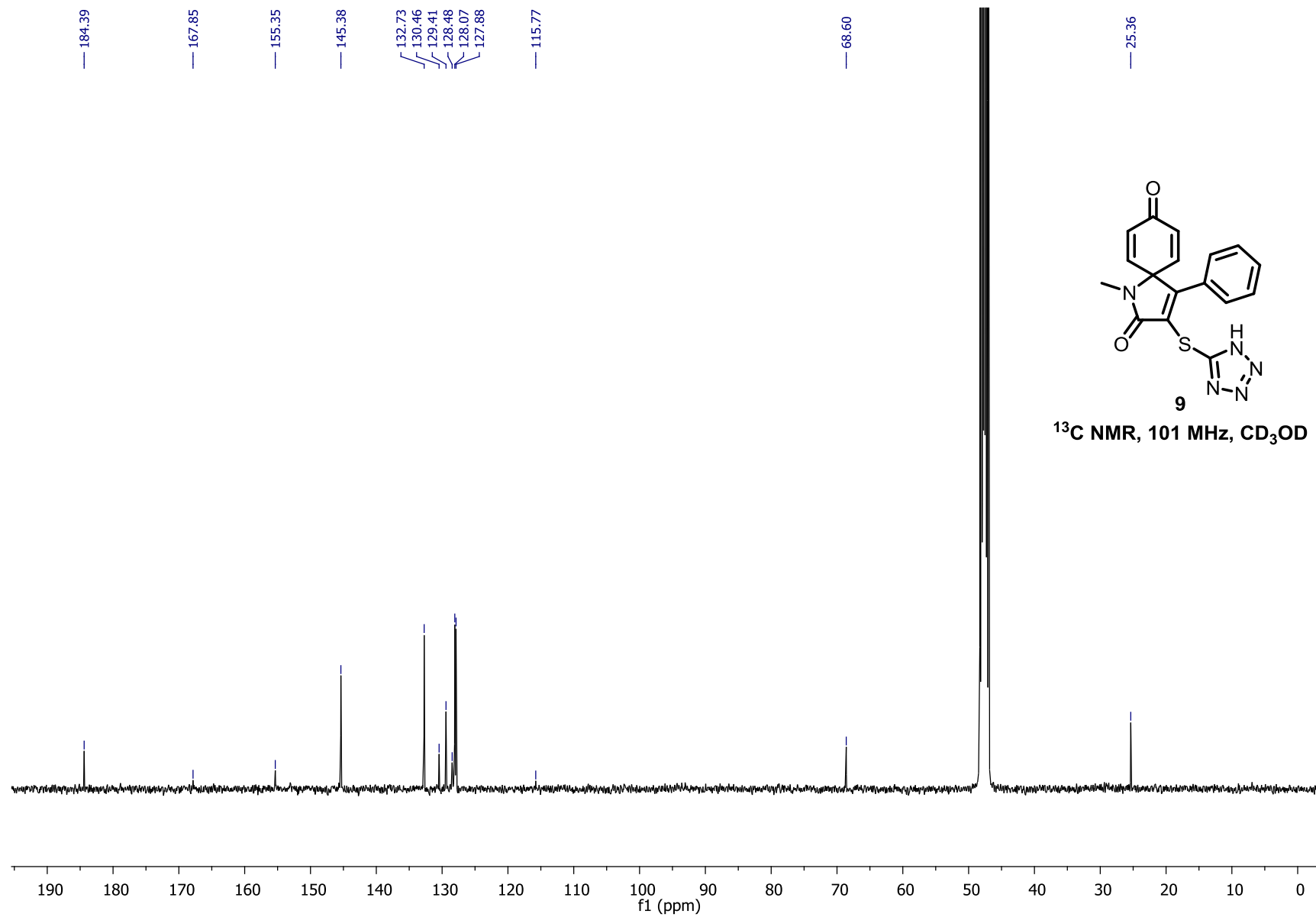


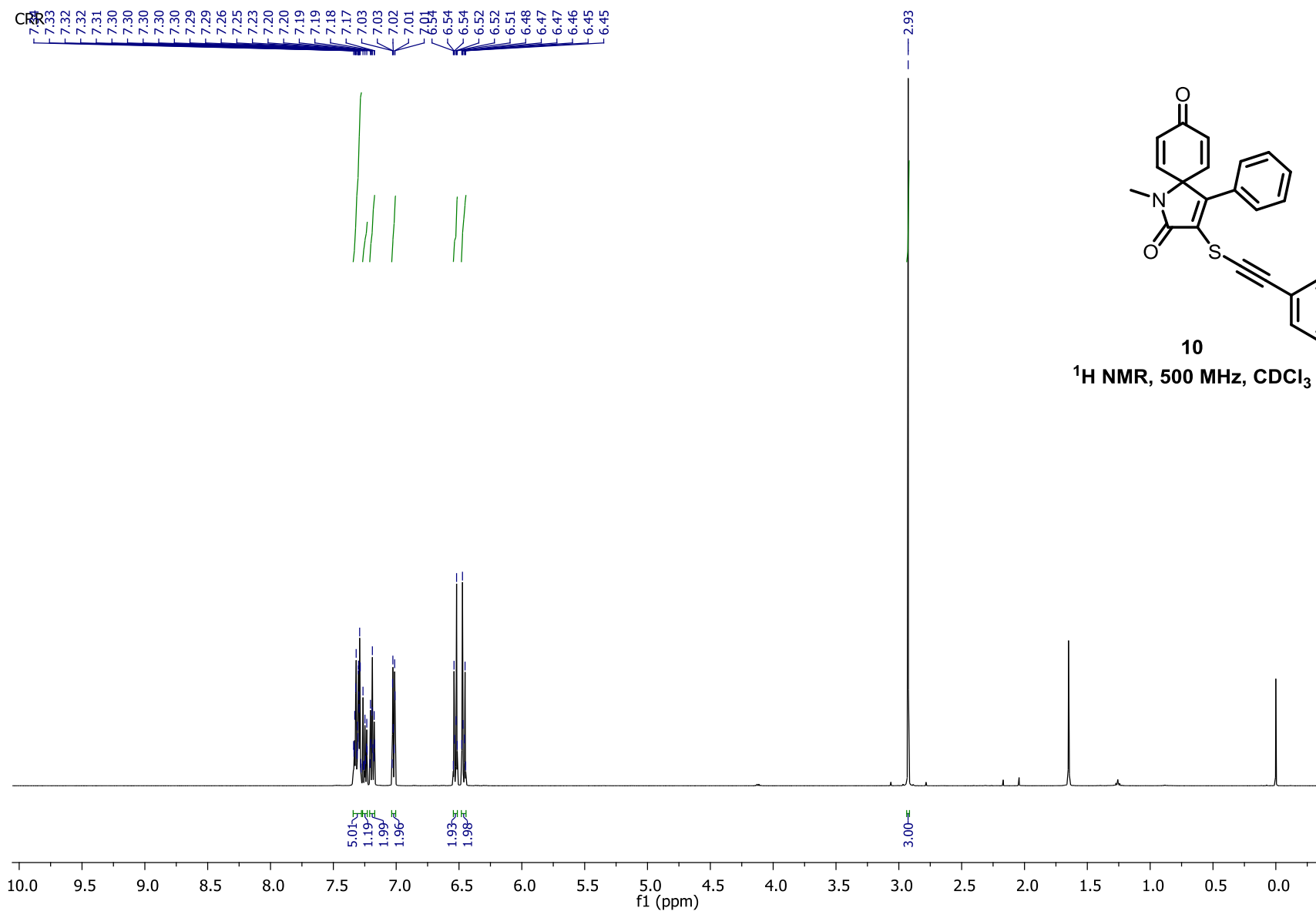
8

$^{19}\text{F}$  NMR, 376 MHz,  $\text{CDCl}_3$









**10**  
**<sup>1</sup>H NMR, 500 MHz, CDCl<sub>3</sub>**

4204

— 183.90

— 166.88

— 148.97

— 144.78

— 133.35

— 131.65

— 129.80

— 128.65

— 128.44

— 128.24

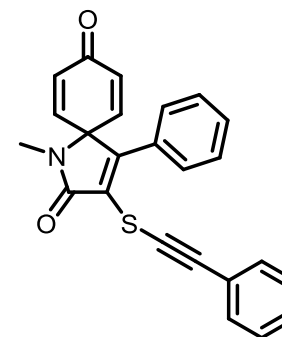
— 128.01

— 97.74

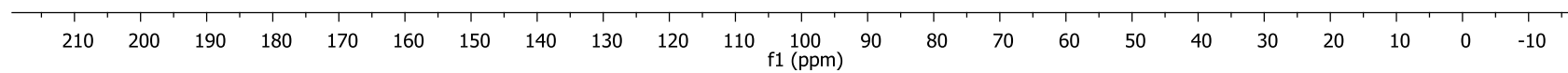
— 71.76

— 68.40

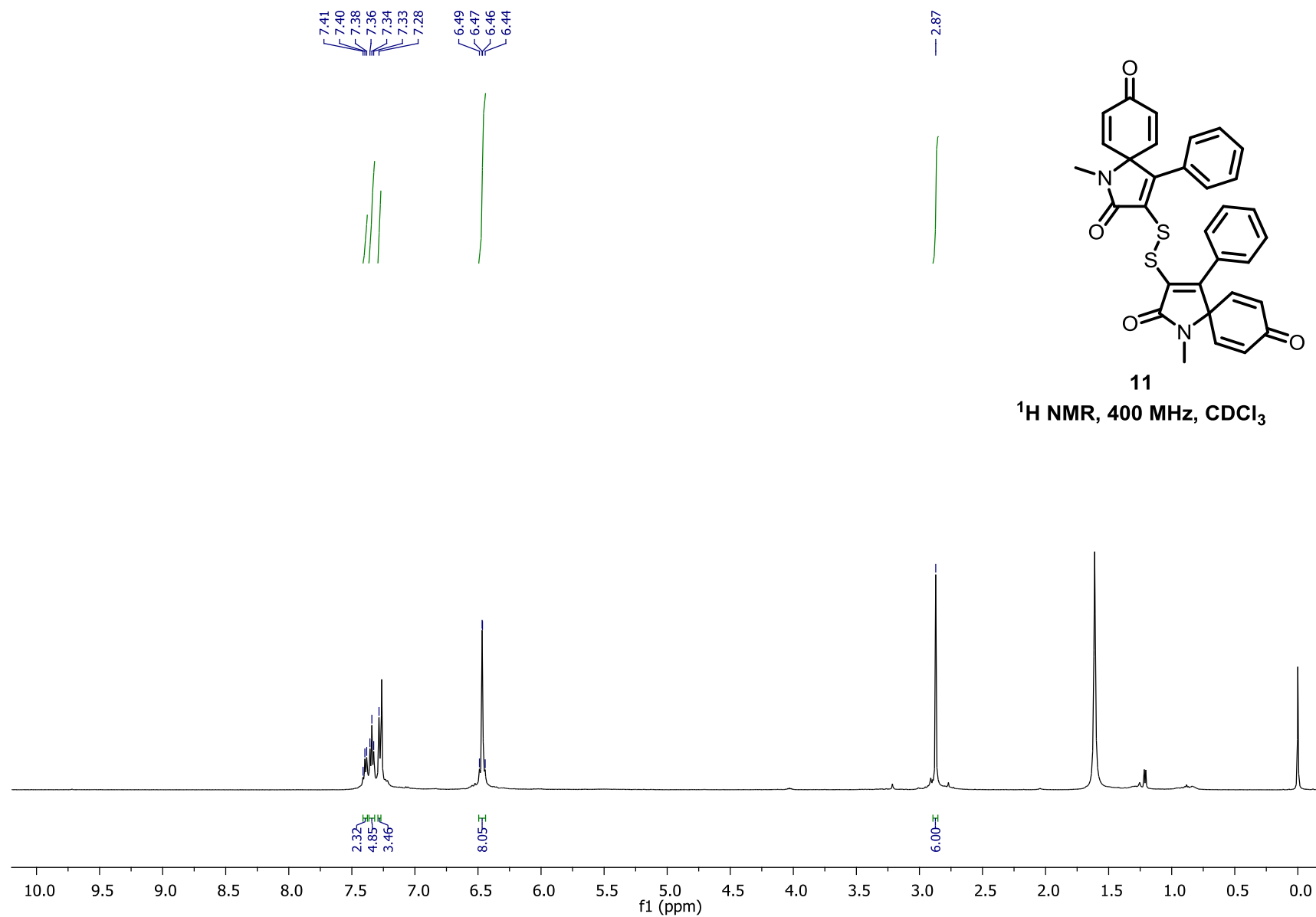
— 26.32



10

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

S86



4277

— 183.95

— 167.66

— 157.28

— 144.71

133.84

133.21

130.78

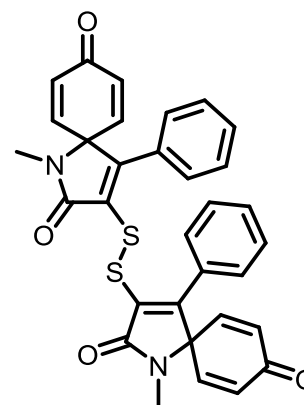
130.16

128.59

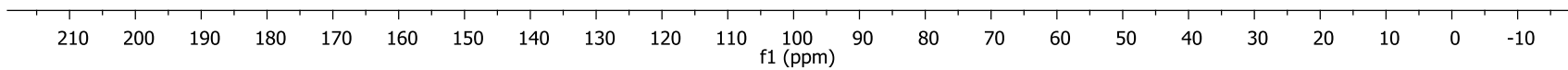
128.45

— 67.68

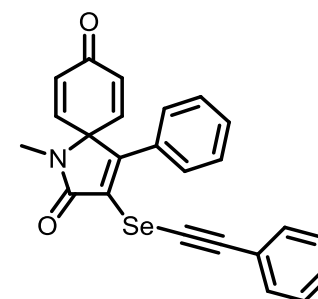
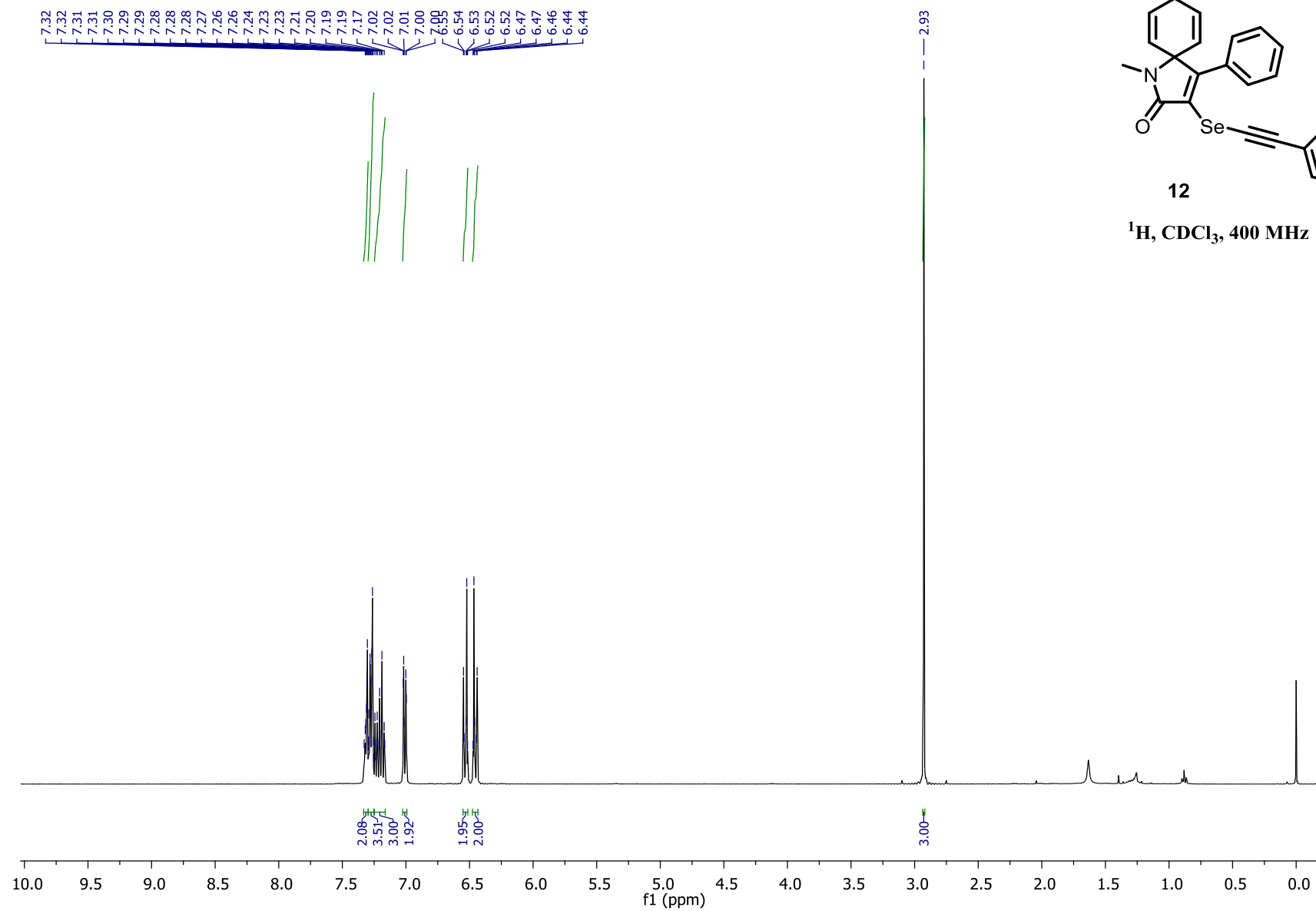
— 26.23



11

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





**12**

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

