

## Supporting information

### Regio- and Diastereoselective Access to Densely Functionalized Ketones via Boekelheide Rearrangement of Isoxazoline *N*-oxides

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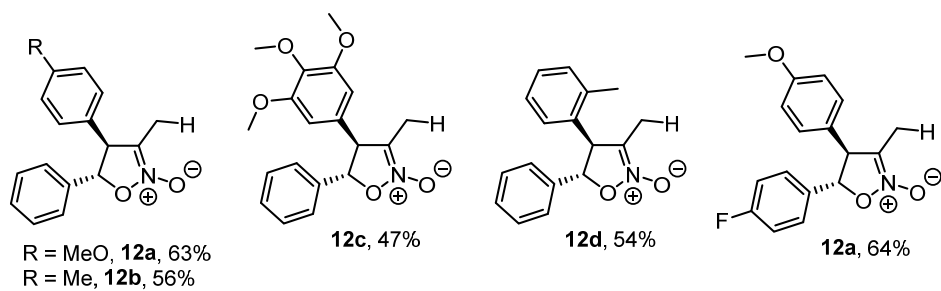
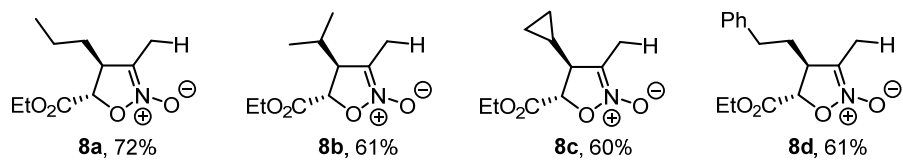
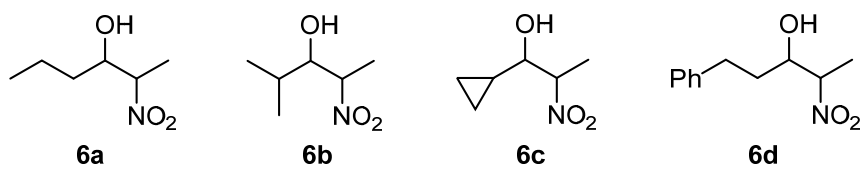
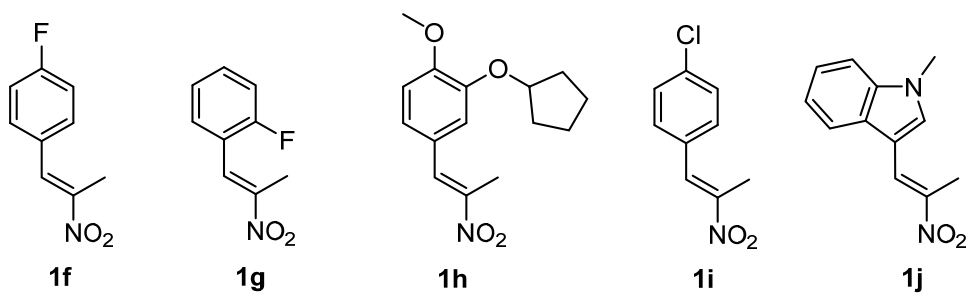
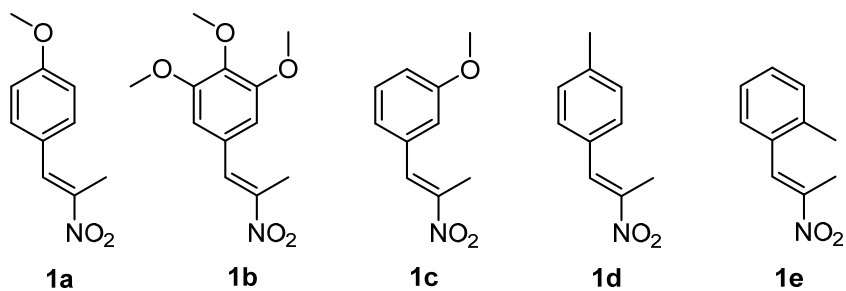
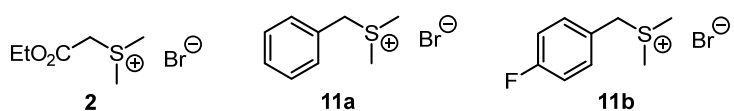
N. D. Zelinsky Institute of Organic Chemistry, 119991, Leninsky prospect, 47, Moscow, Russian Federation

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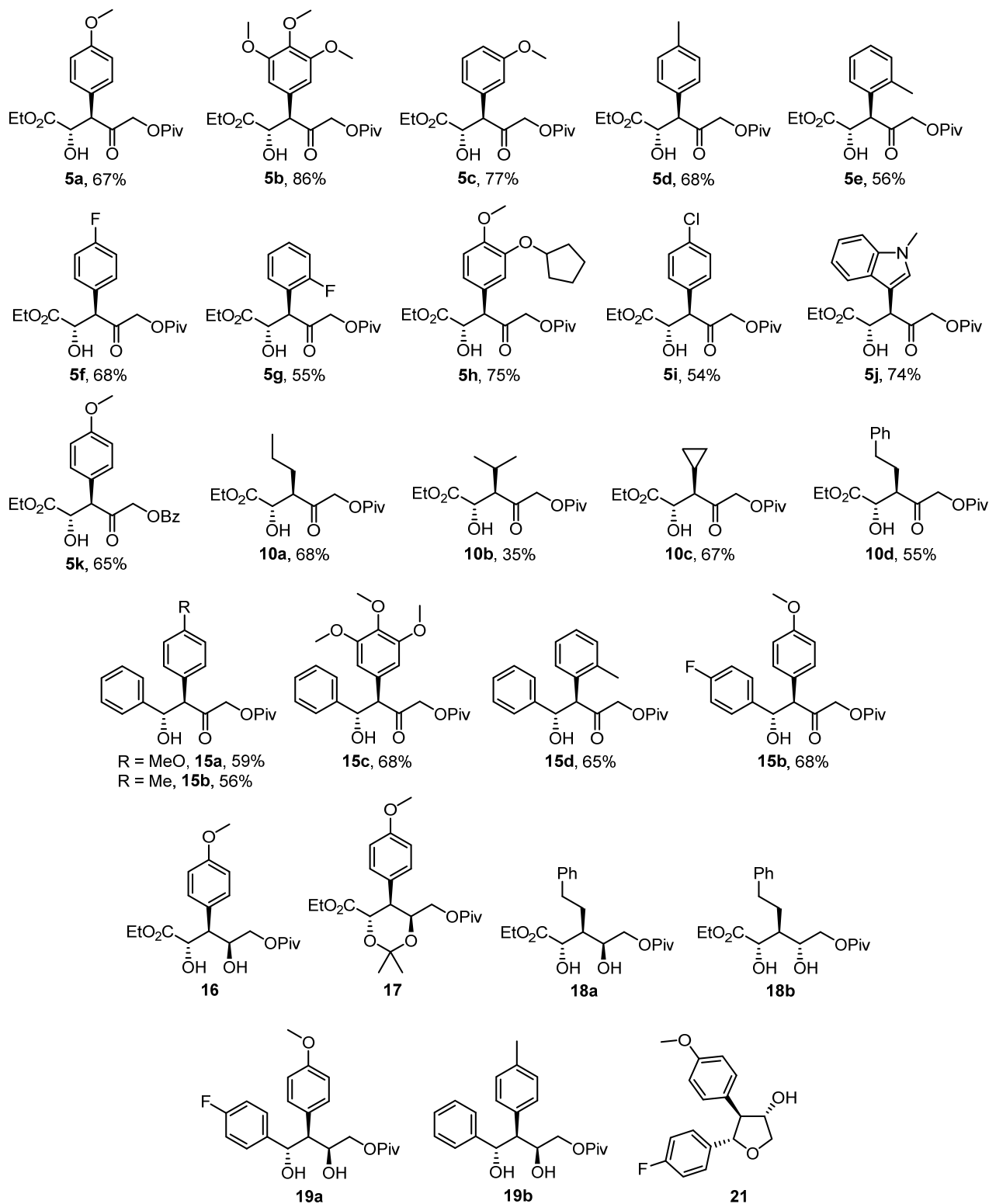
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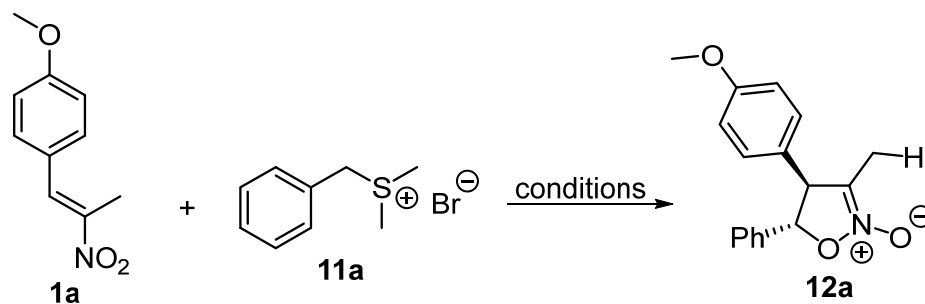
## Structures of starting compounds and intermediates



## Structures of products

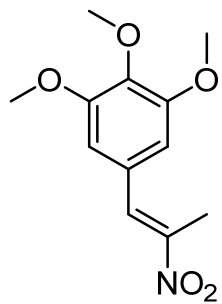


### Optimization study on [4+1]-annulation with benzylsulfonium salt **11a**

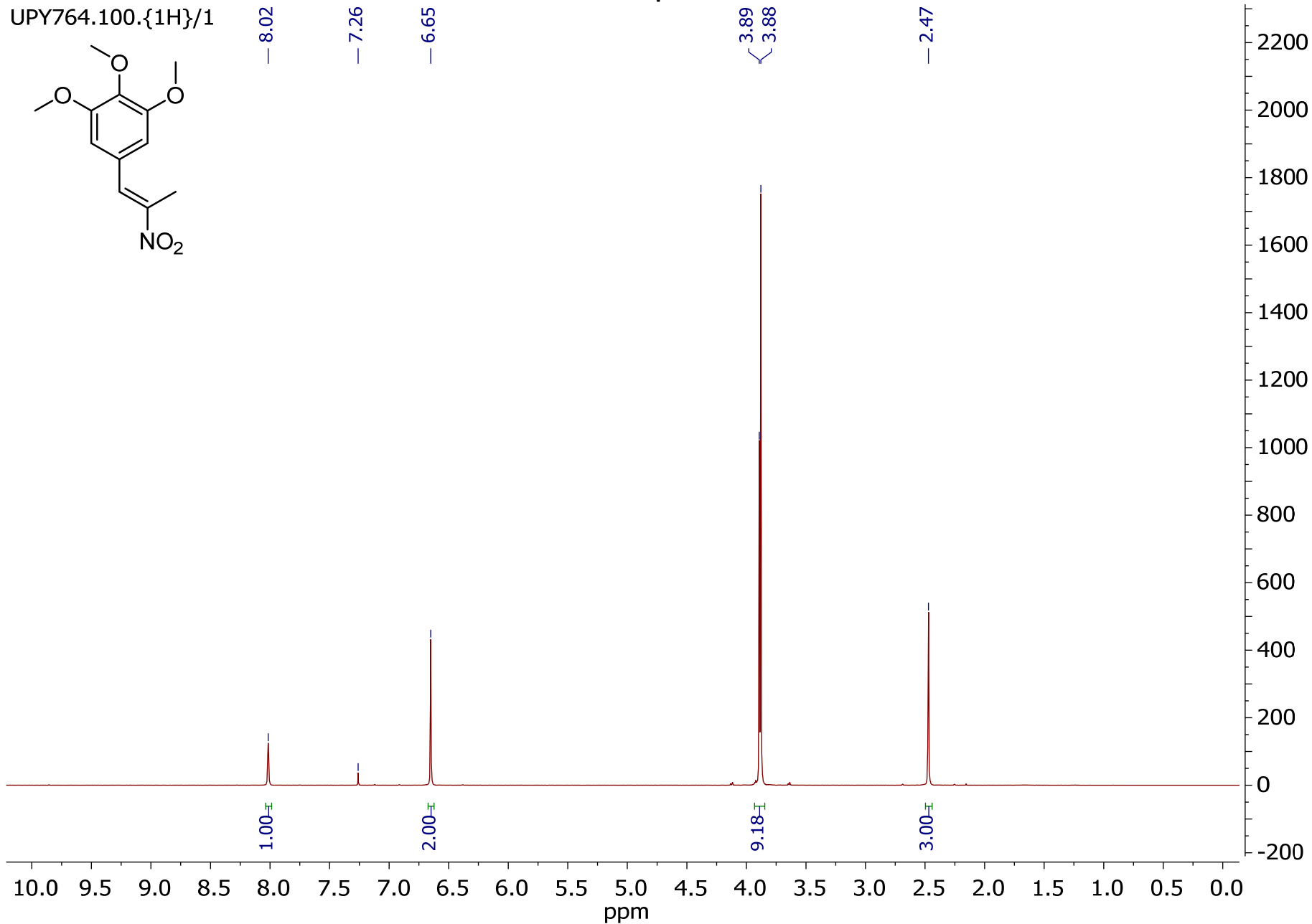


Entry	Conditions	Solvent	Time, h	Yield of <b>12a</b> , %	Recovery of <b>1a</b> , %
1	<b>11a</b> (2 equiv.) K <sub>2</sub> CO <sub>3</sub> (3 equiv.)	THF	24	13	73
2	<b>11a</b> (2 equiv.) K <sub>2</sub> CO <sub>3</sub> (3 equiv.)	MeCN	24	38	13
3	<b>11a</b> (2 equiv.) K <sub>2</sub> CO <sub>3</sub> (3 equiv.)	CH <sub>2</sub> Cl <sub>2</sub>	24	24	43
4	<b>11a</b> (1.3 equiv.) Bu <sub>4</sub> NHSO <sub>4</sub> (0.1 equiv.) 50% aq. NaOH (17 equiv.)	CH <sub>2</sub> Cl <sub>2</sub>	5	<b>63</b>	0

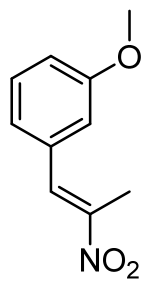
UPY764.100.{1H}/1



### NMR spectra of 1b

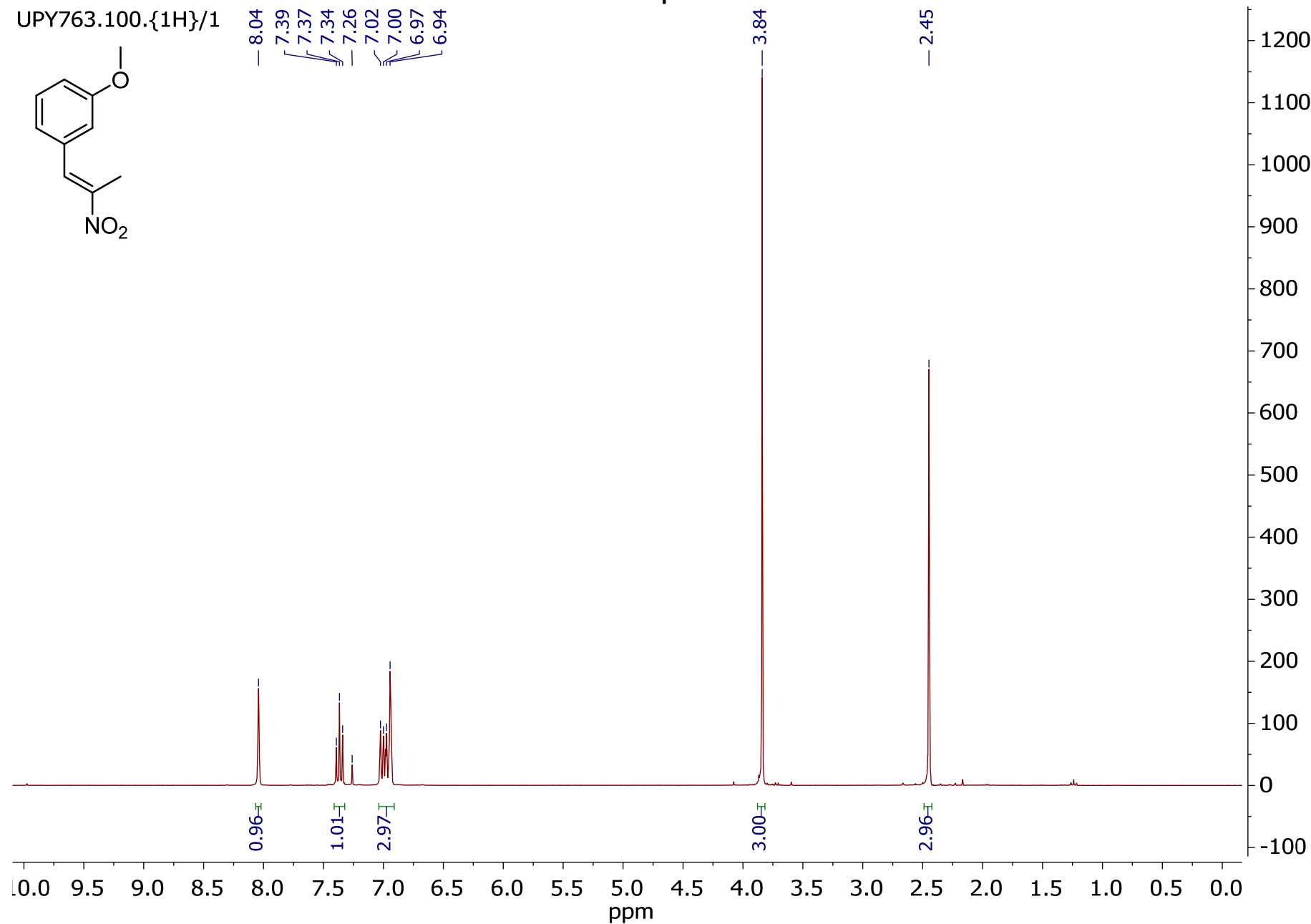


UPY763.100.{1H}/1



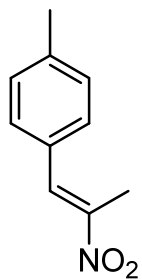
8.04  
7.39  
7.37  
7.34  
7.26  
7.02  
7.00  
6.97  
6.94

### NMR spectra of 1c



# NMR spectra of 1d

UPY780.200.{1H}/1



8.04

7.33

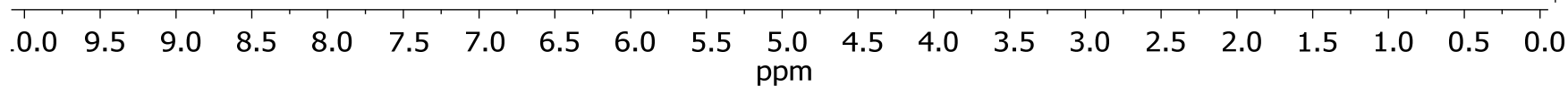
7.30

7.25

7.22

2.43

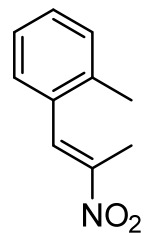
2.37





# NMR spectra of 1e

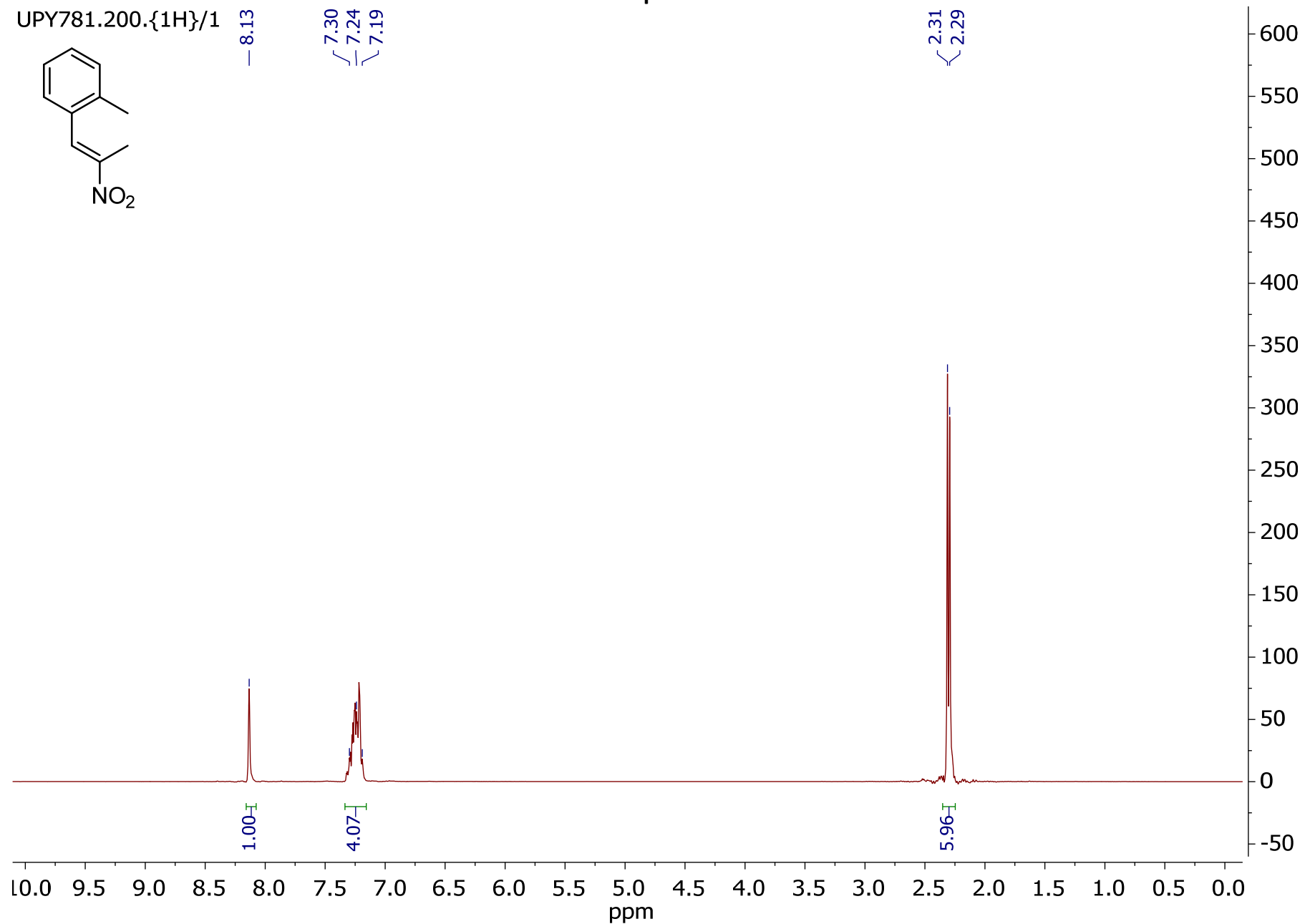
UPY781.200.{1H}/1



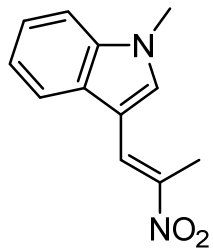
8.13

7.30  
7.24  
7.19

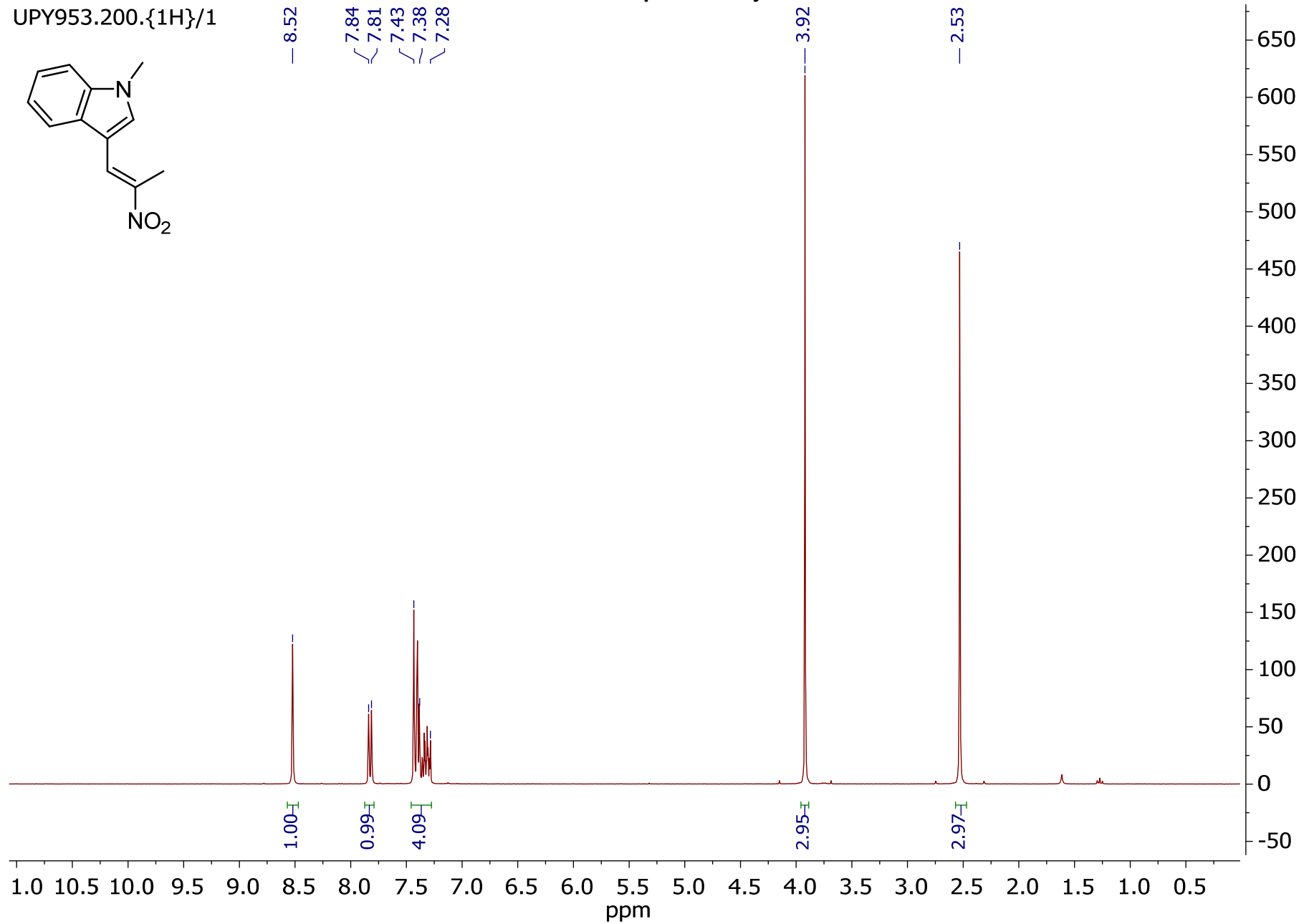
2.31  
2.29



UPY953.200.{1H}/1

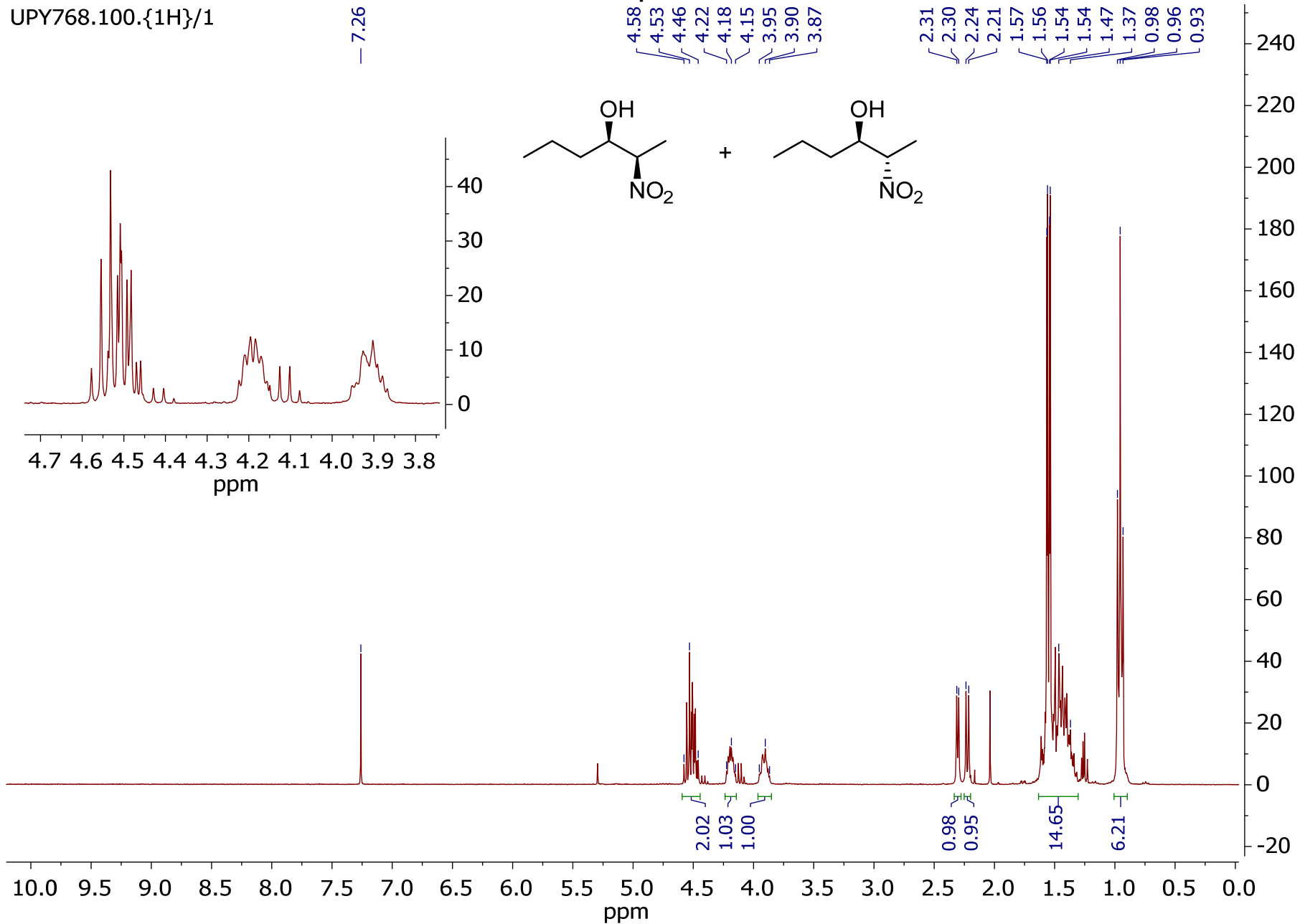


### NMR spectra of 1j

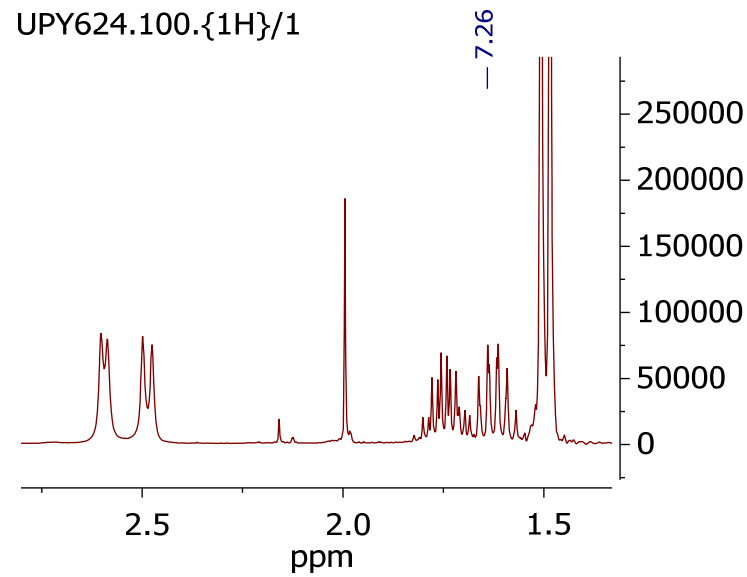


UPY768.100.{1H}/1

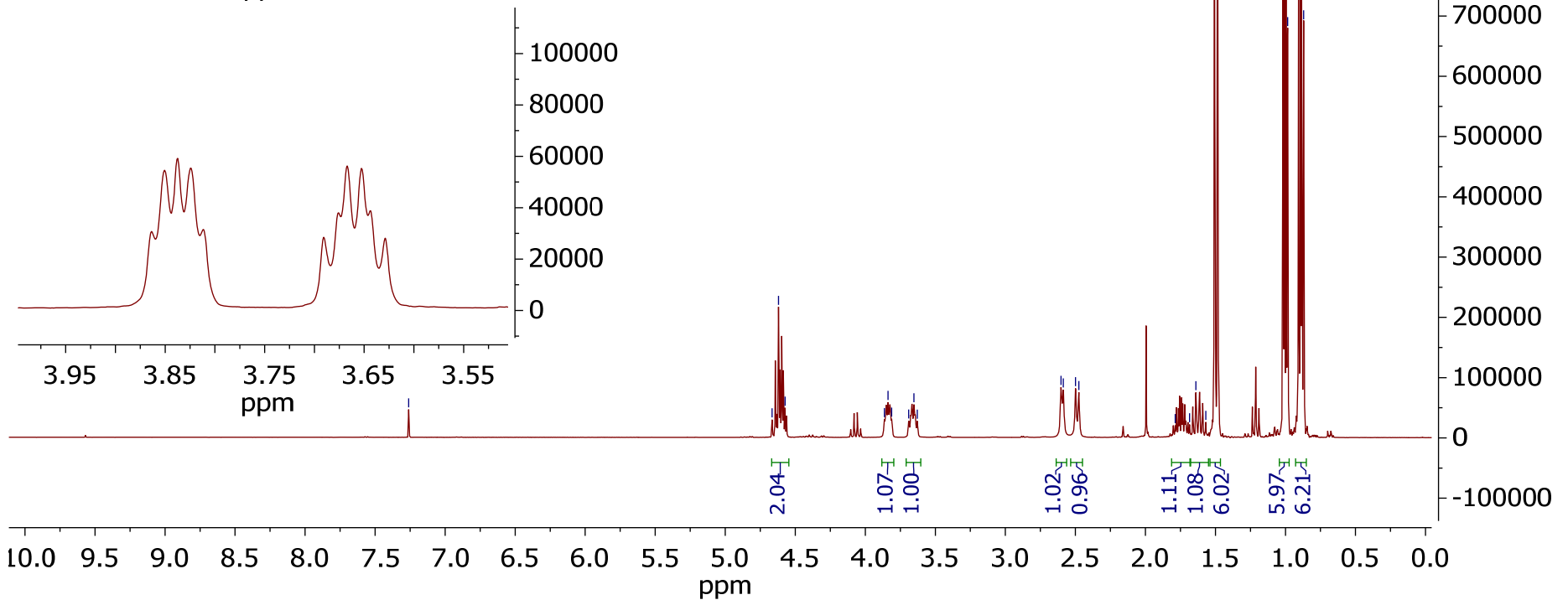
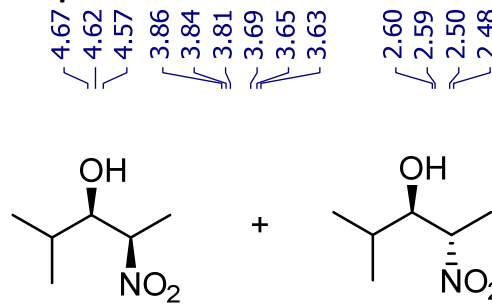
### NMR spectra of 6a



UPY624.100.{1H}/1



### NMR spectra of 6b

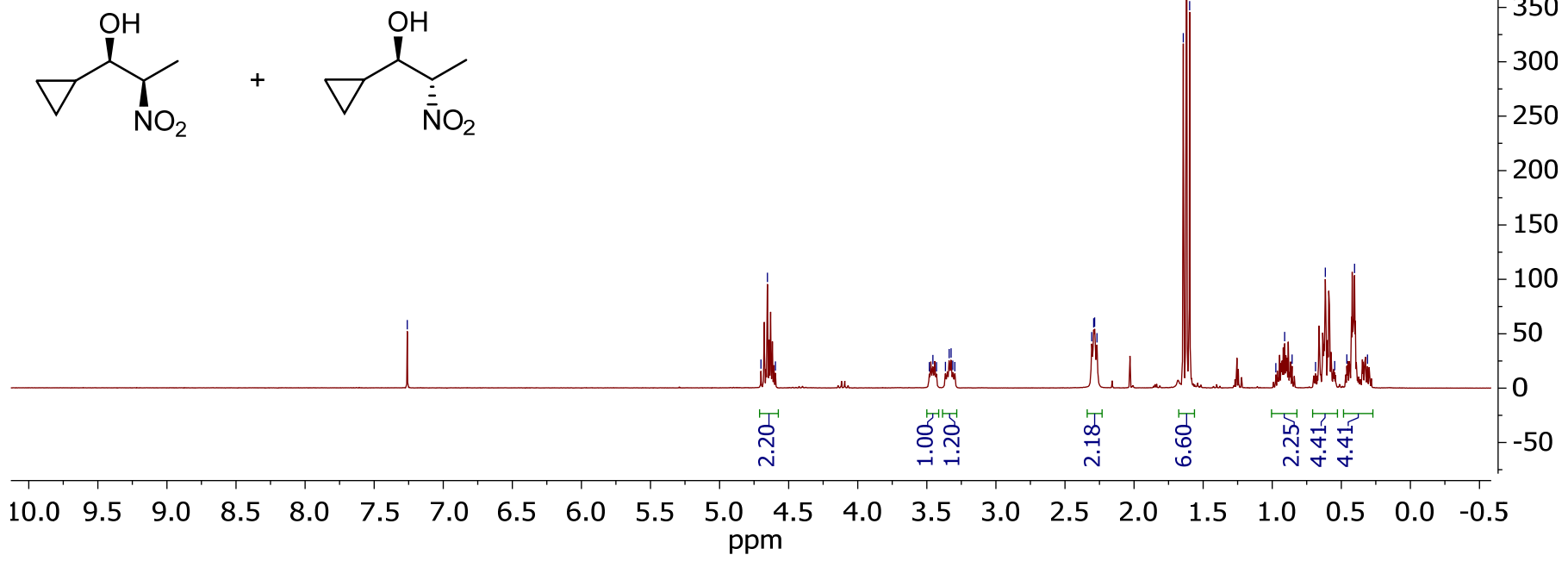
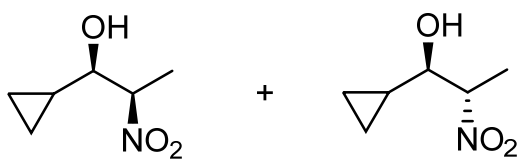
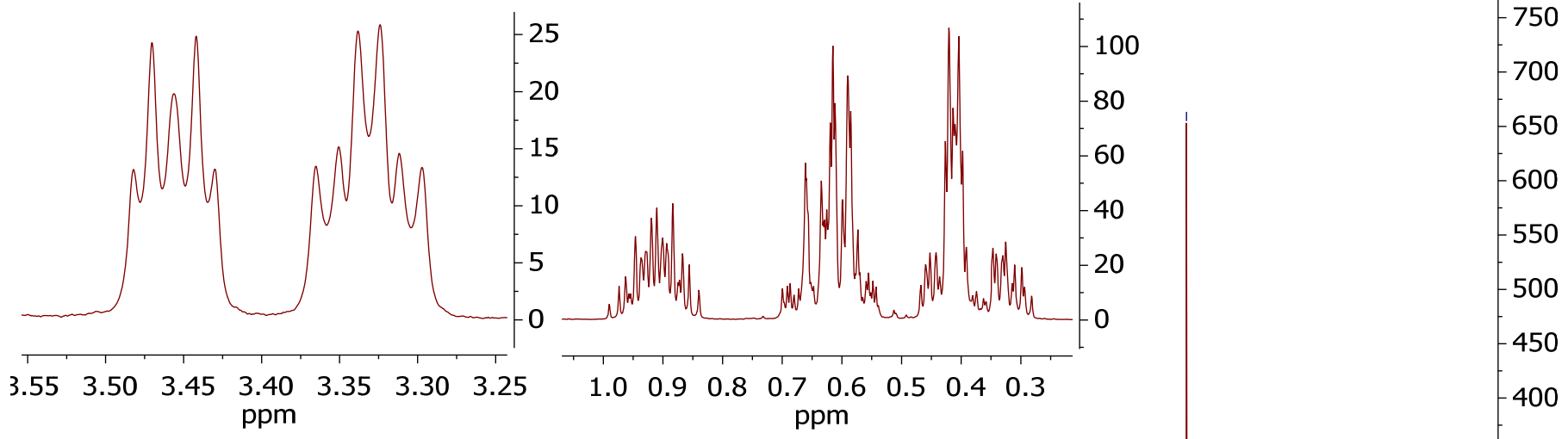


UPY766.100.{1H}/1

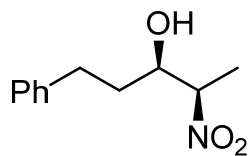
7.26

### NMR spectra of 6c

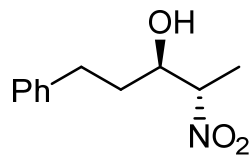
- 4.70
- 4.65
- 4.60
- 3.48
- 3.46
- 3.43
- 3.37
- 3.34
- 3.32
- 3.31
- 3.30
- 2.31
- 2.29
- 2.29
- 2.27
- 1.64
- 1.62
- 1.60
- 0.97
- 0.91
- 0.86
- 0.69
- 0.62
- 0.55
- 0.46
- 0.40
- 0.31



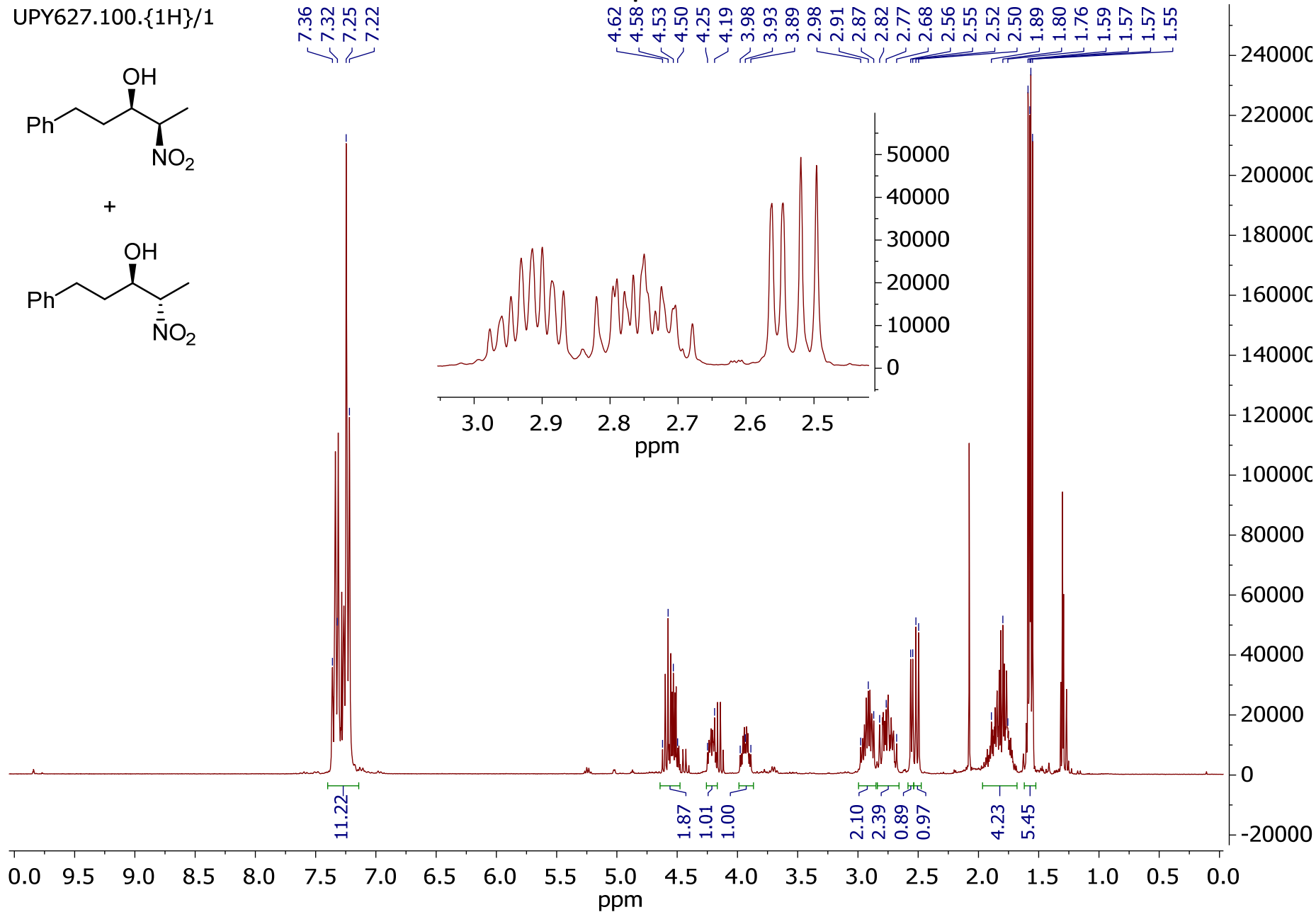
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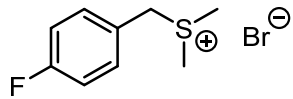
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### NMR spectra of 6d



UPY837.100.{1H}/1



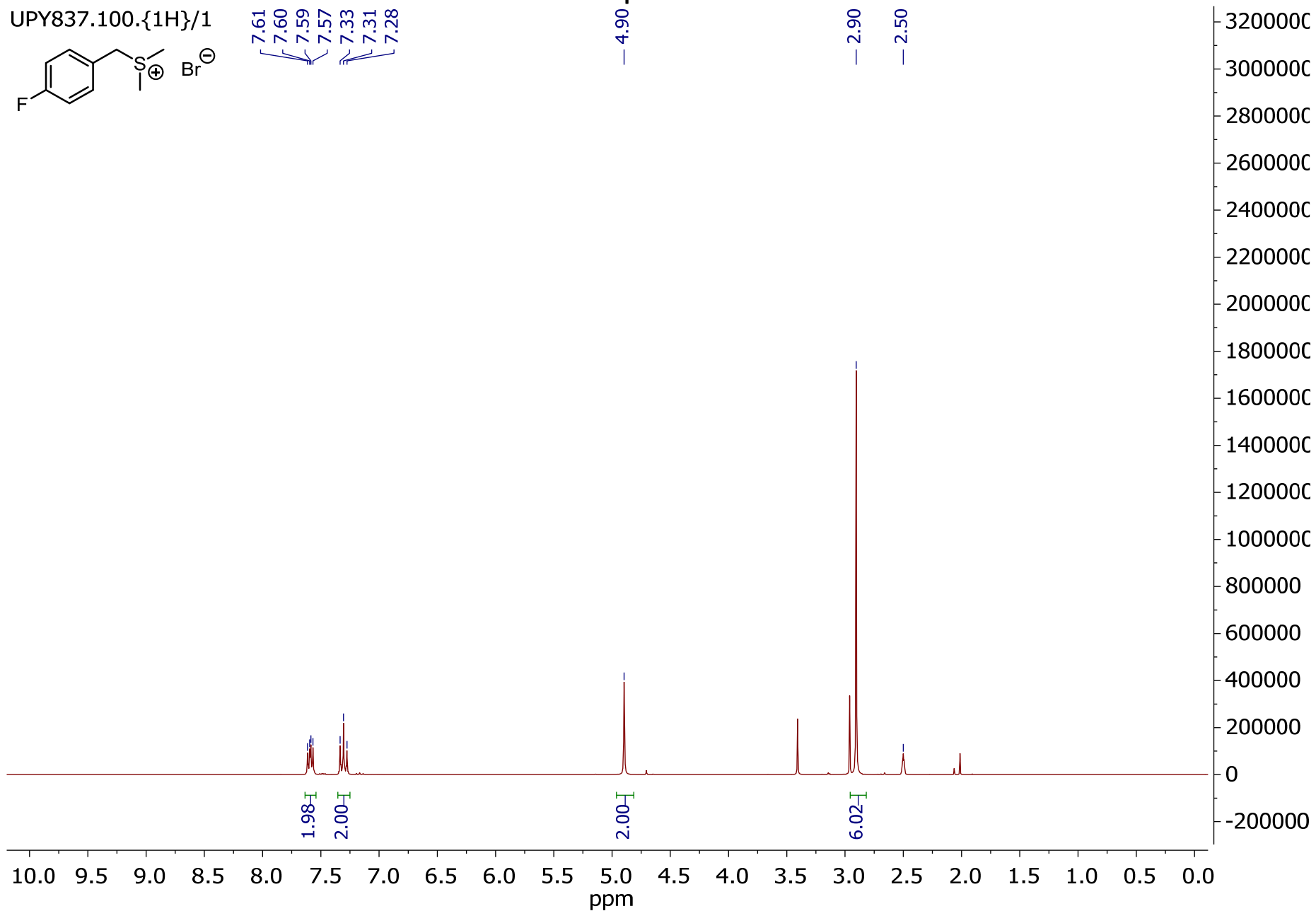
7.61  
7.60  
7.59  
7.57  
7.33  
7.31  
7.28

### NMR spectra of 11b

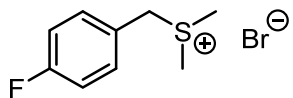
4.90

2.90

2.50



UPY837.100.{13C}/2

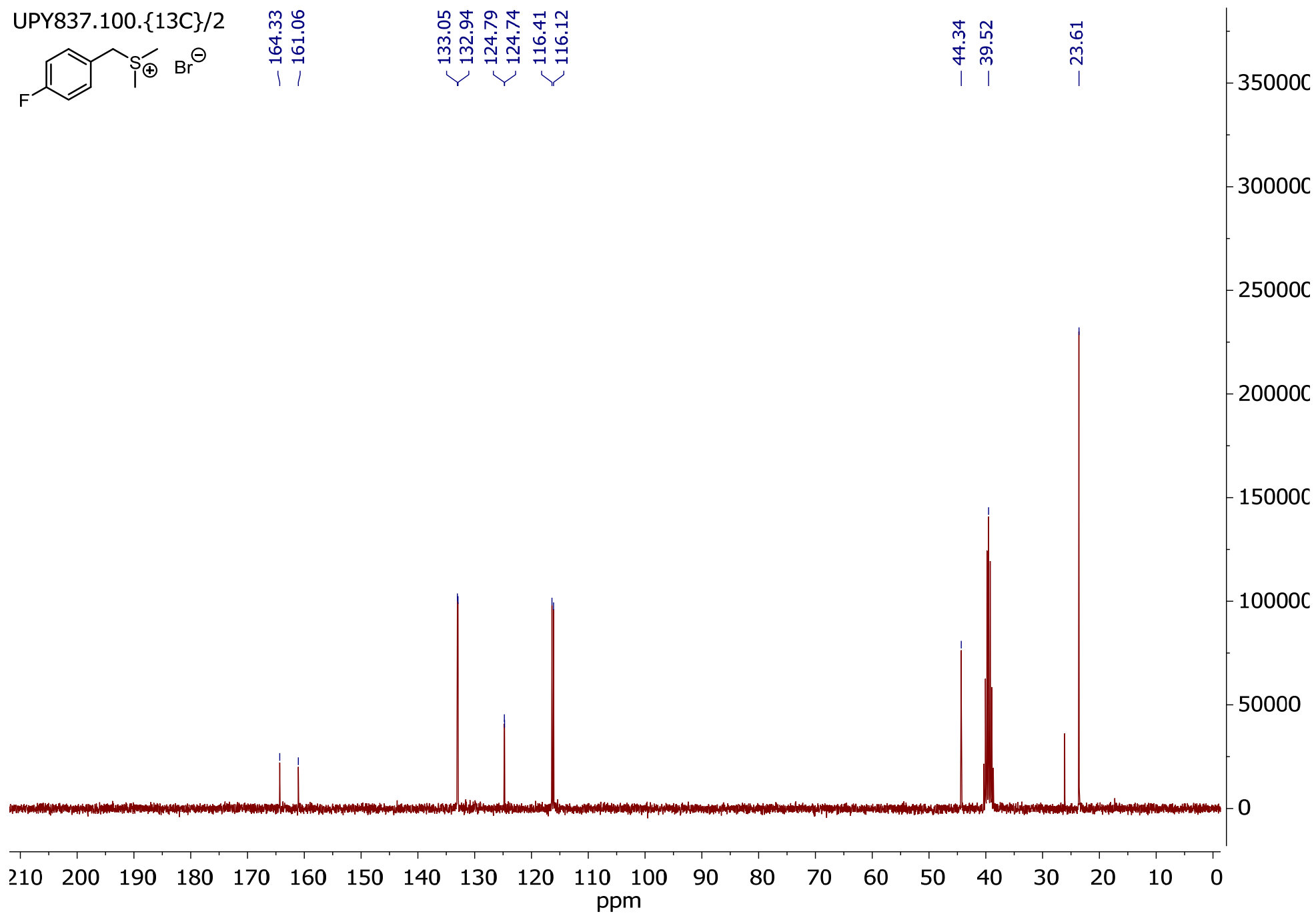


— 164.33  
— 161.06

133.05  
132.94  
124.79  
124.74  
116.41  
116.12

— 44.34  
— 39.52

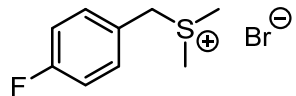
— 23.61



S16



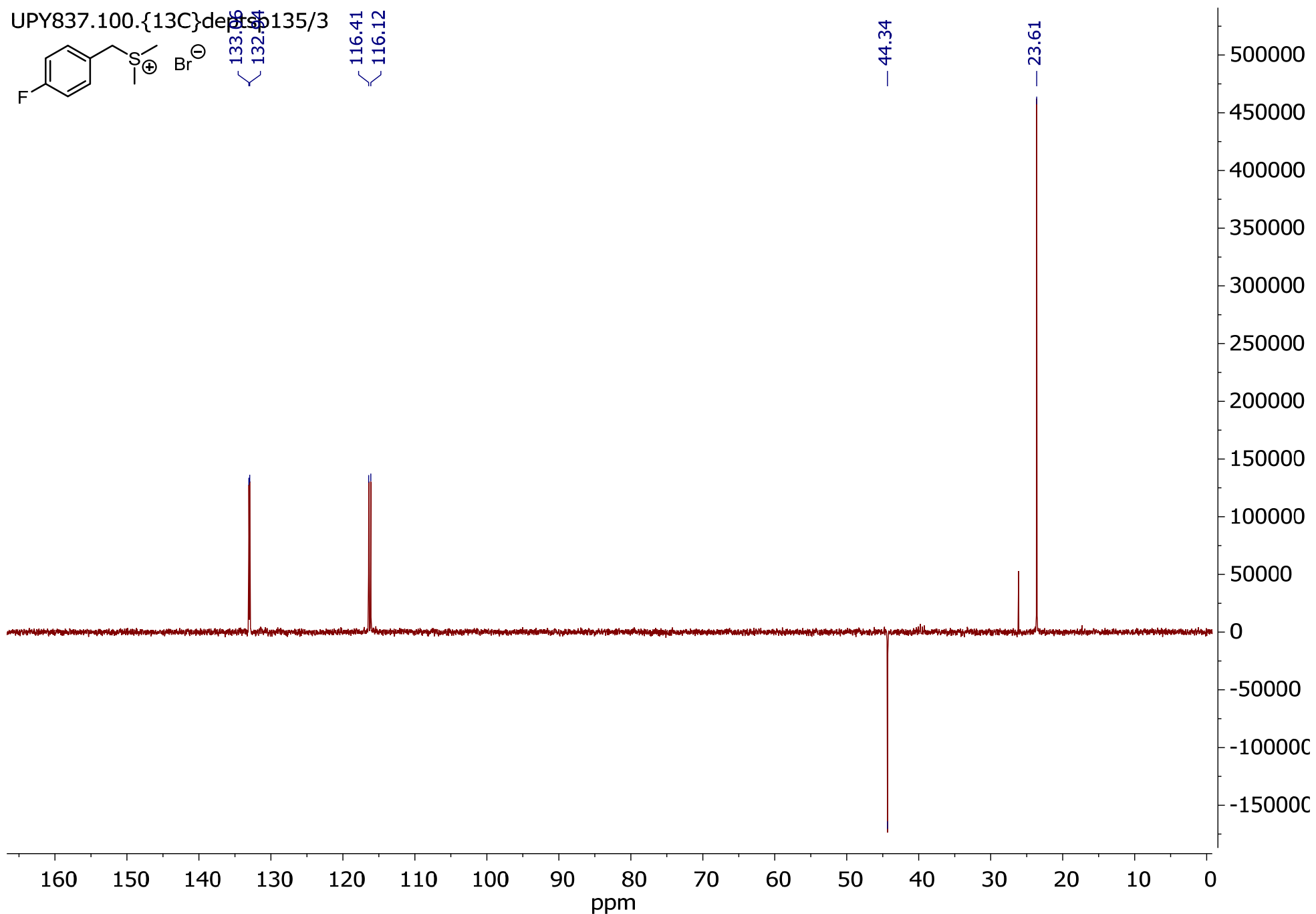
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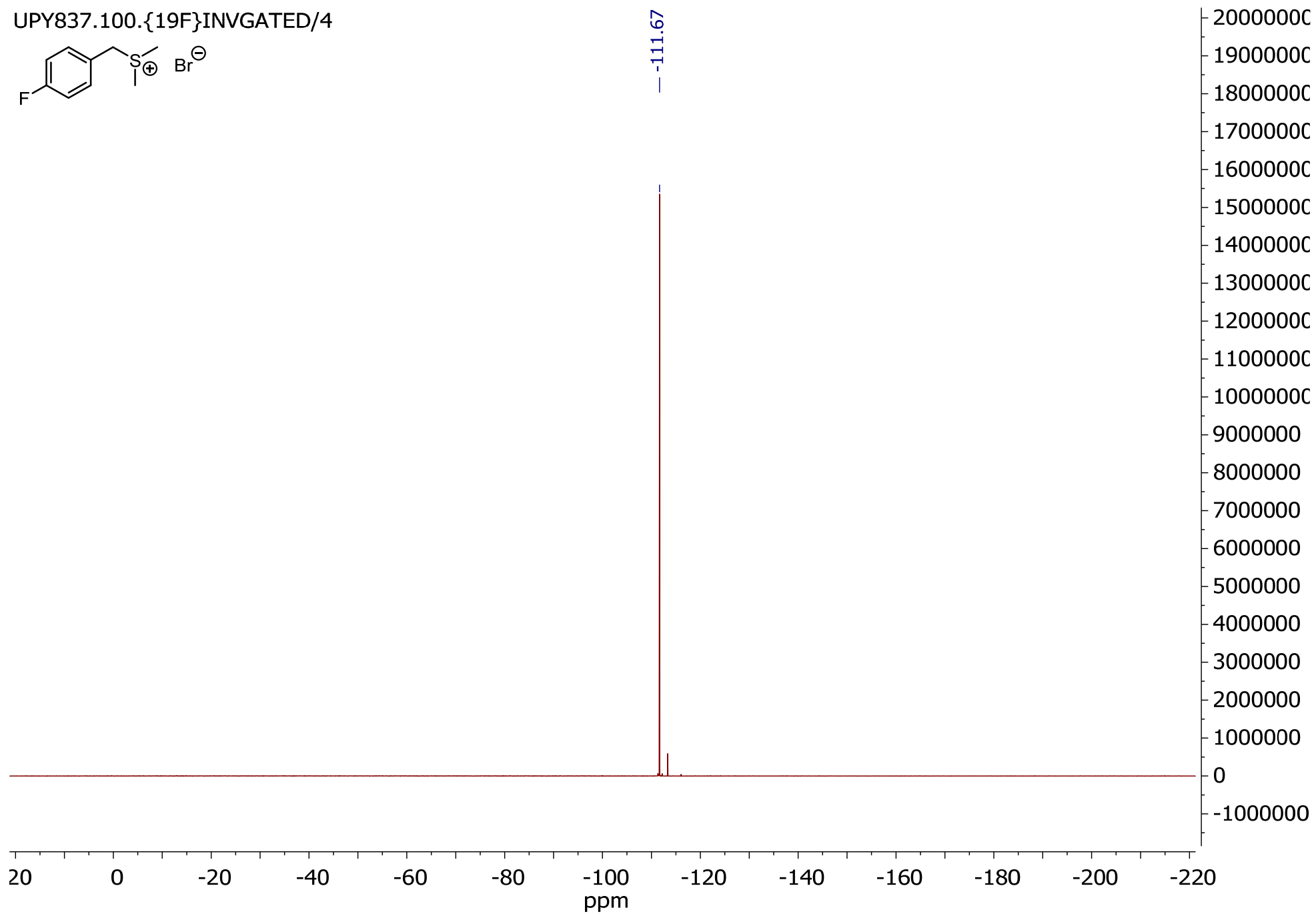
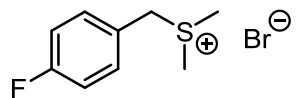
133.86  
132.84  
116.41  
116.12

44.34

23.61

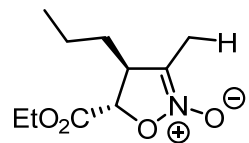


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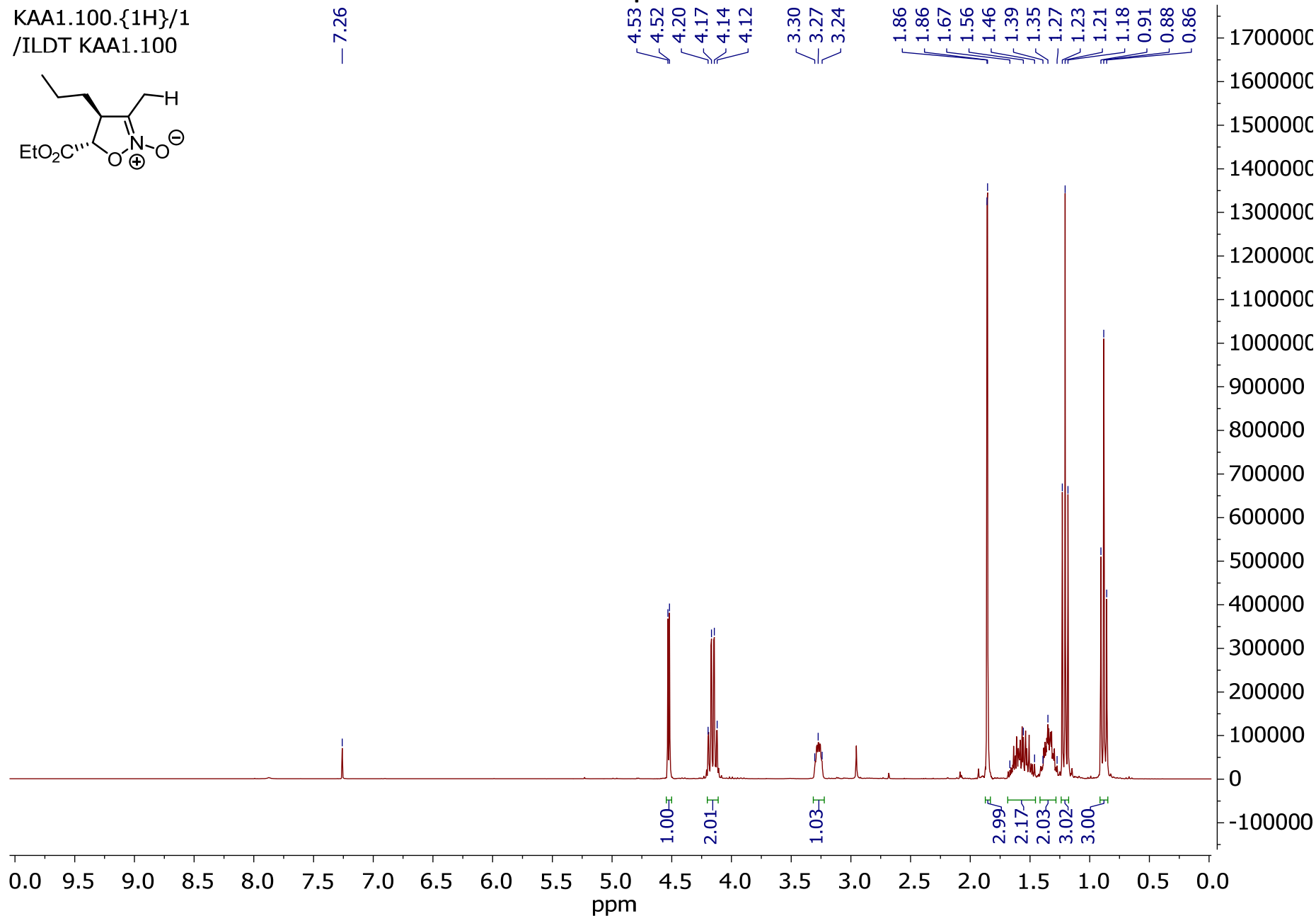
S18

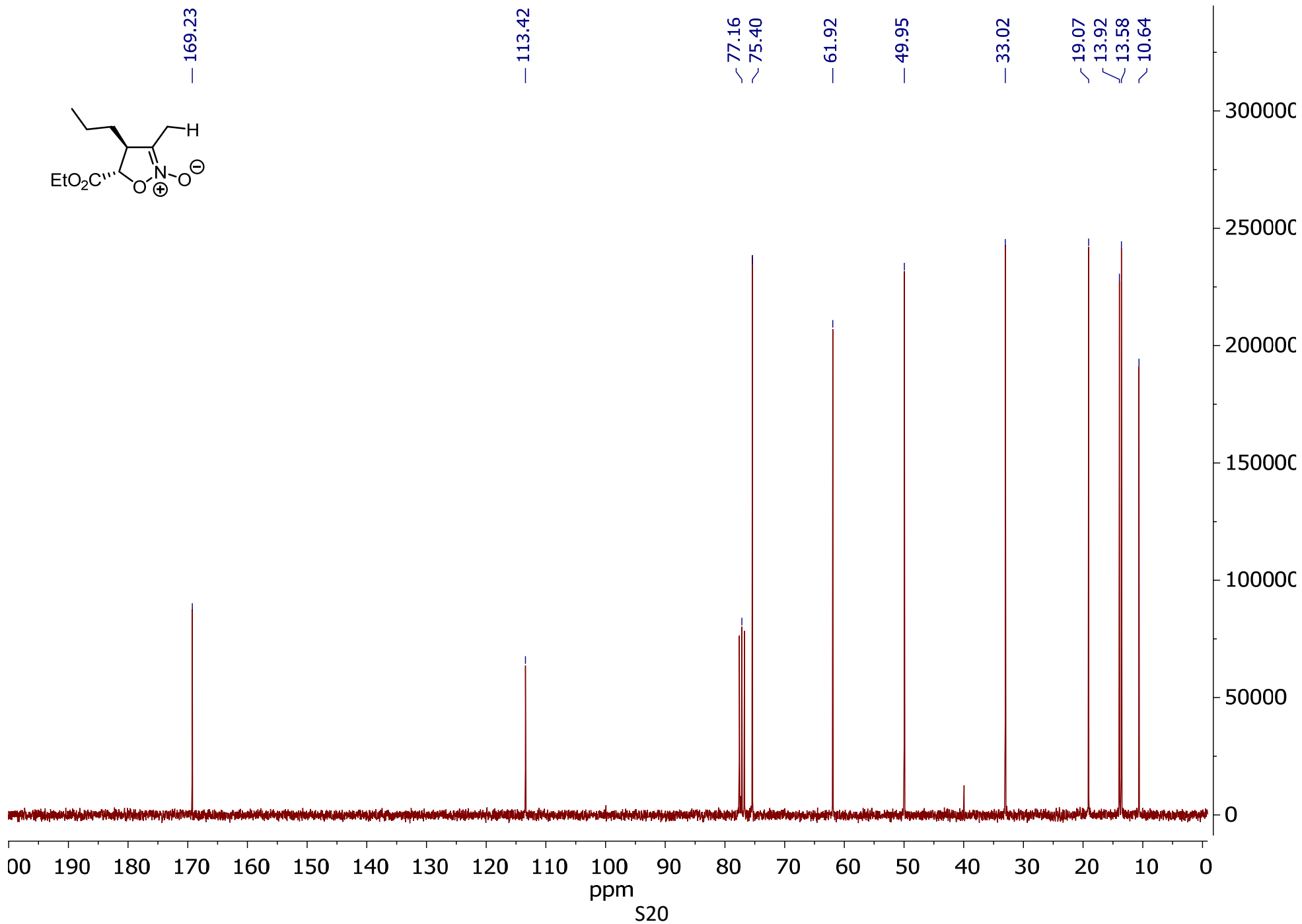
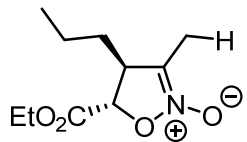
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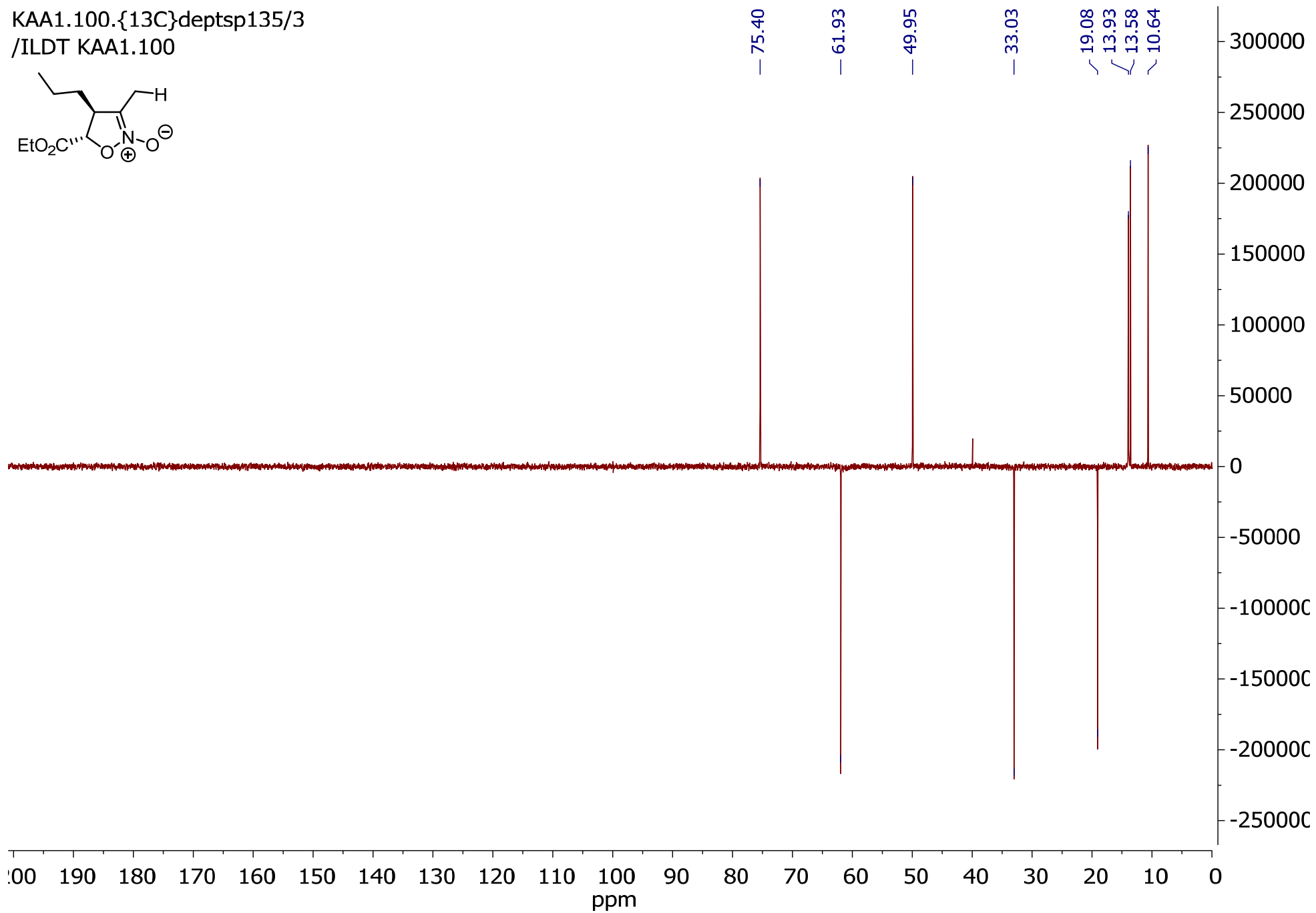
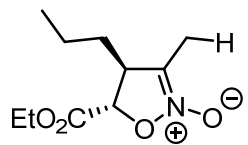
— 7.26

### NMR spectra of 8a



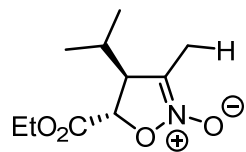


KAA1.100.{13C}deptsp135/3  
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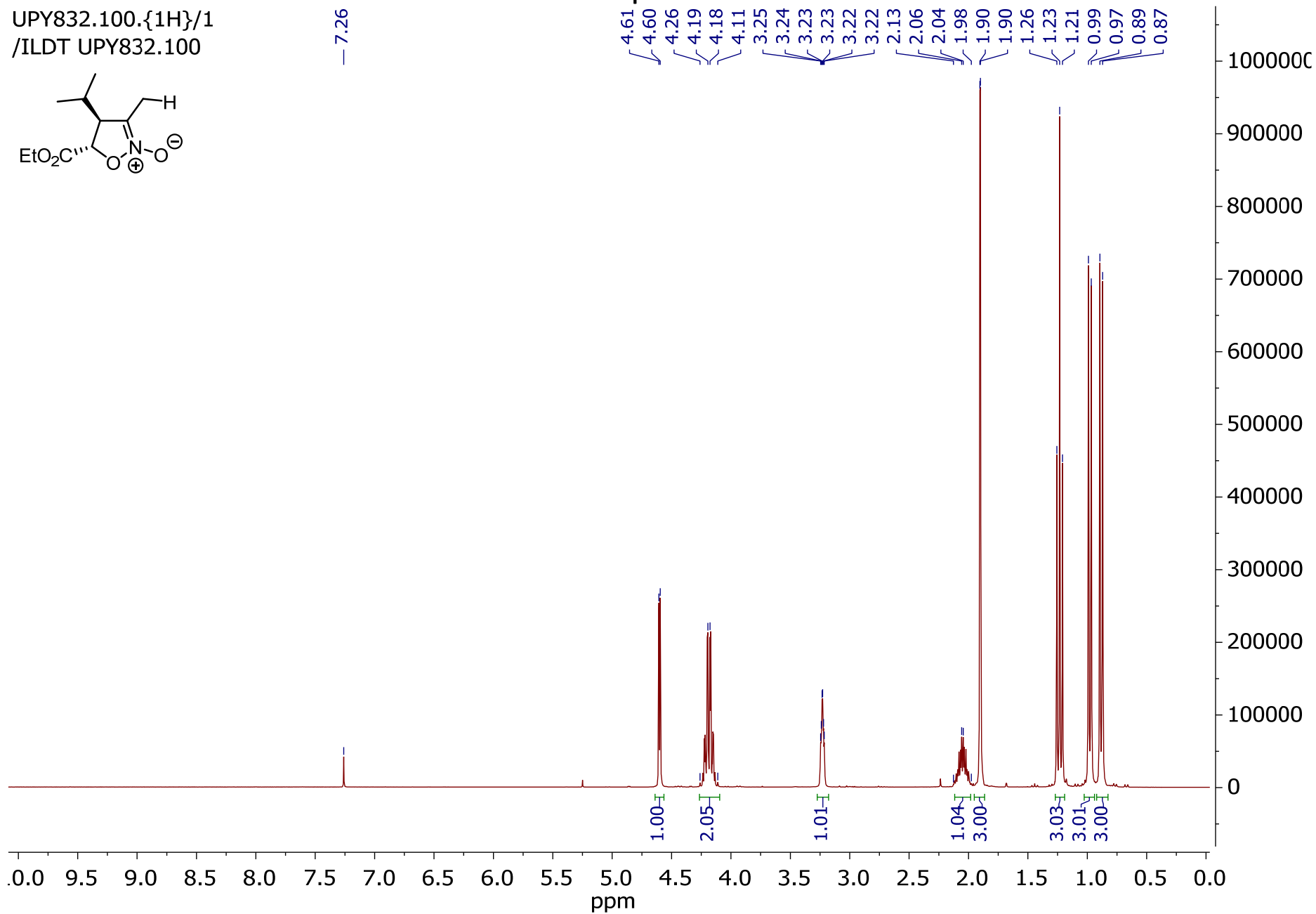
S21

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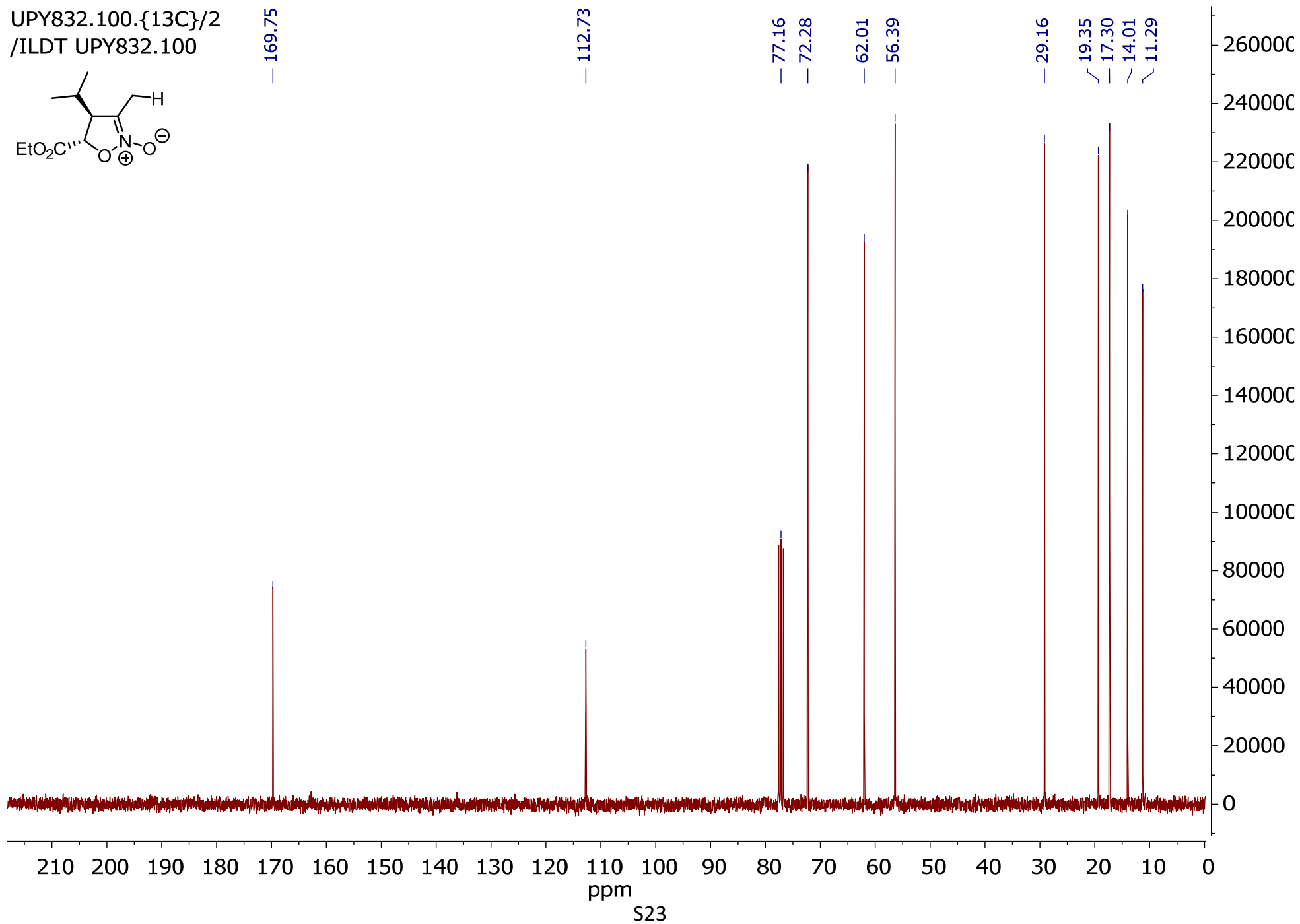
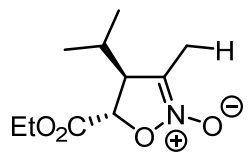


— 7.26

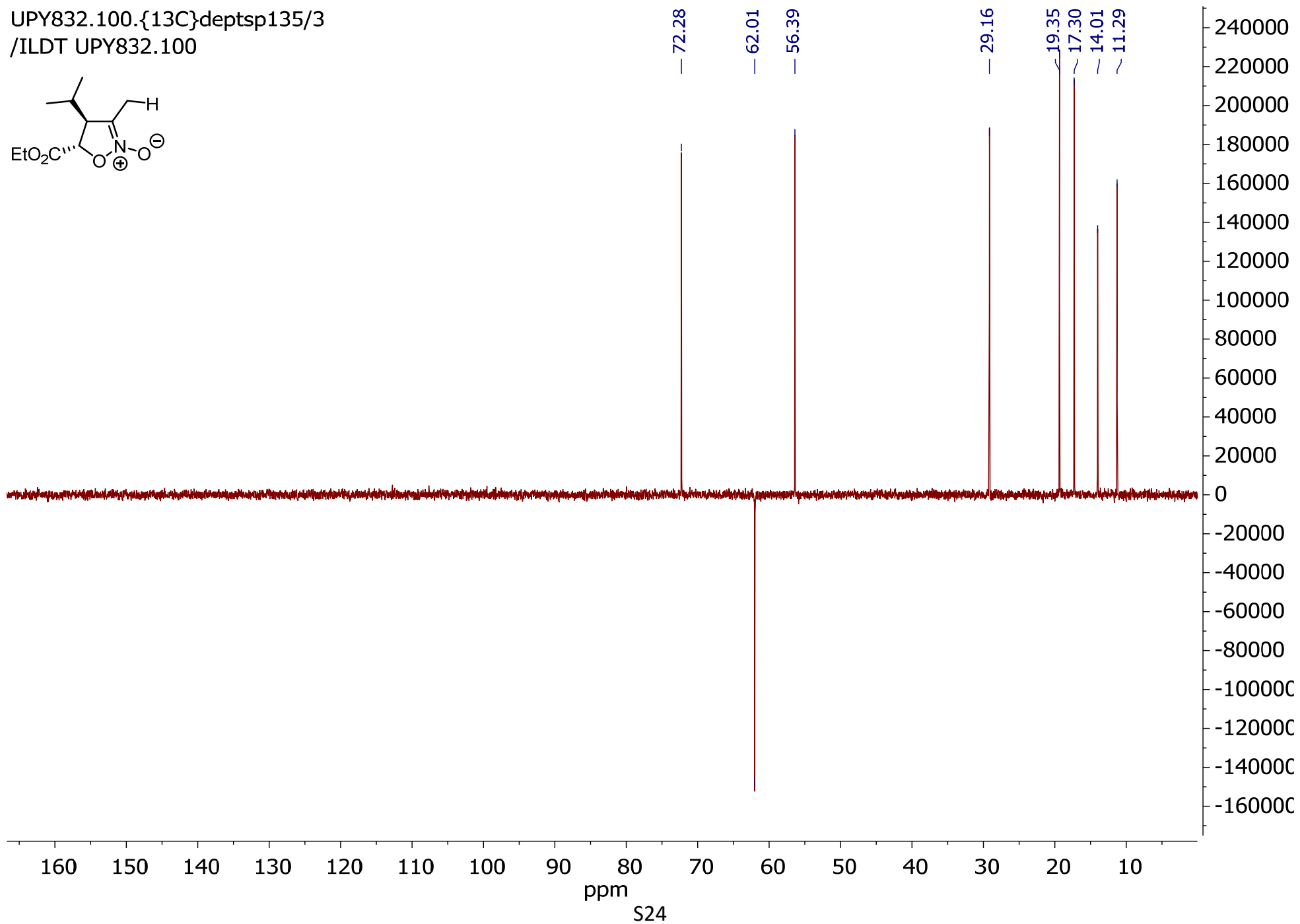
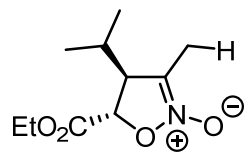
### NMR spectra of 8b



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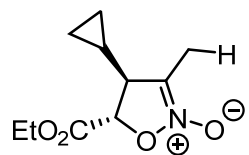


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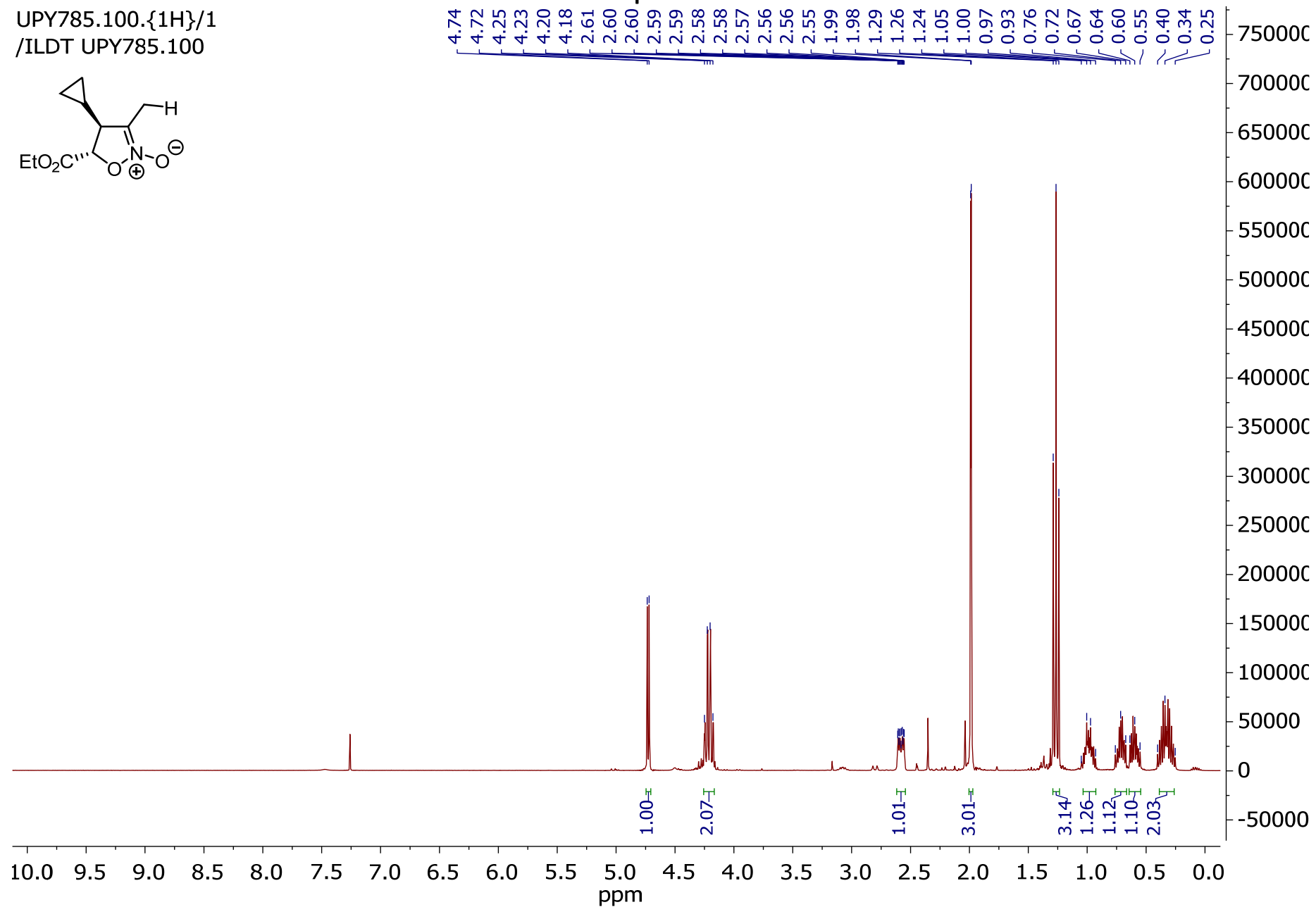


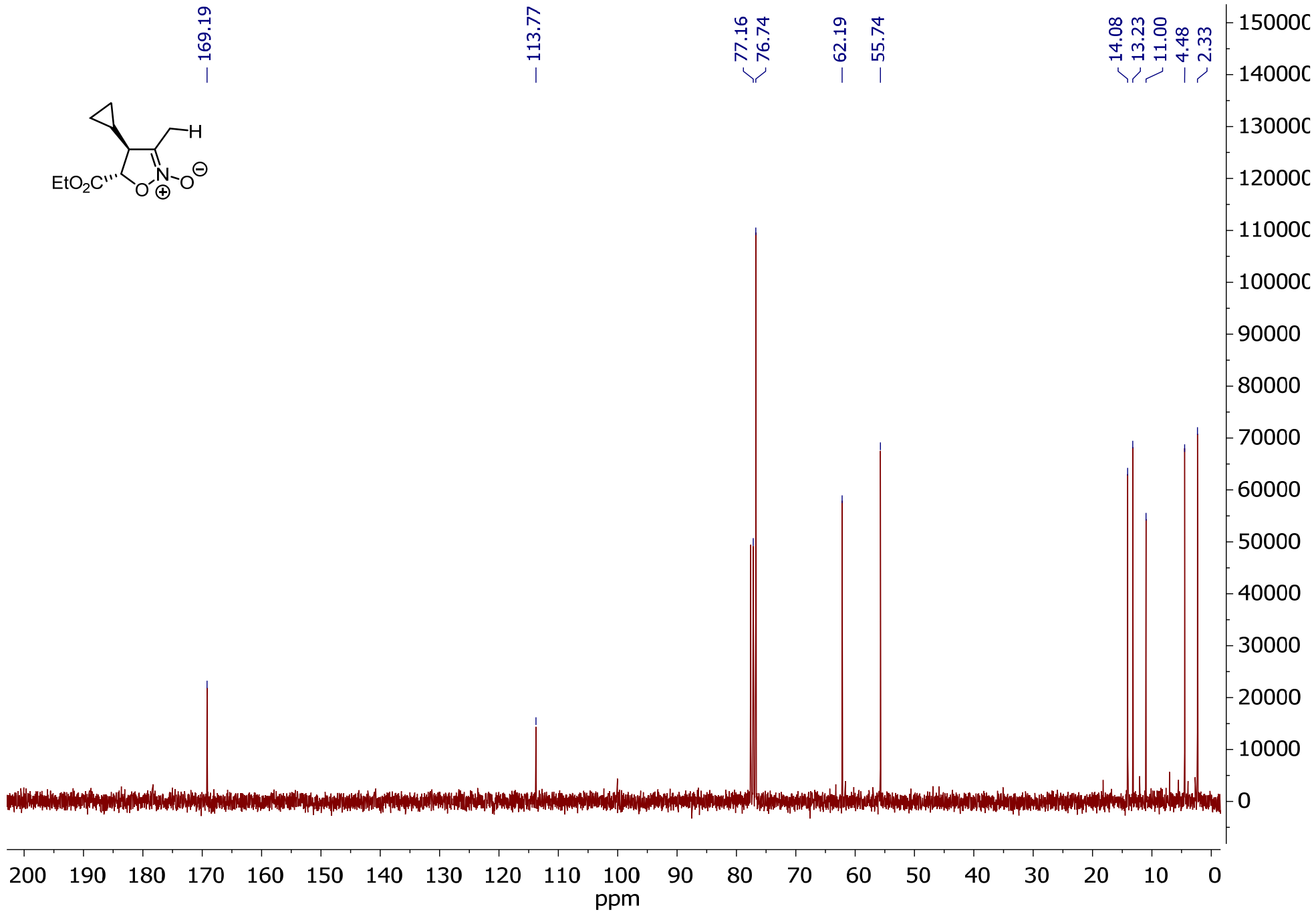
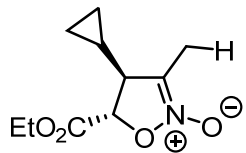


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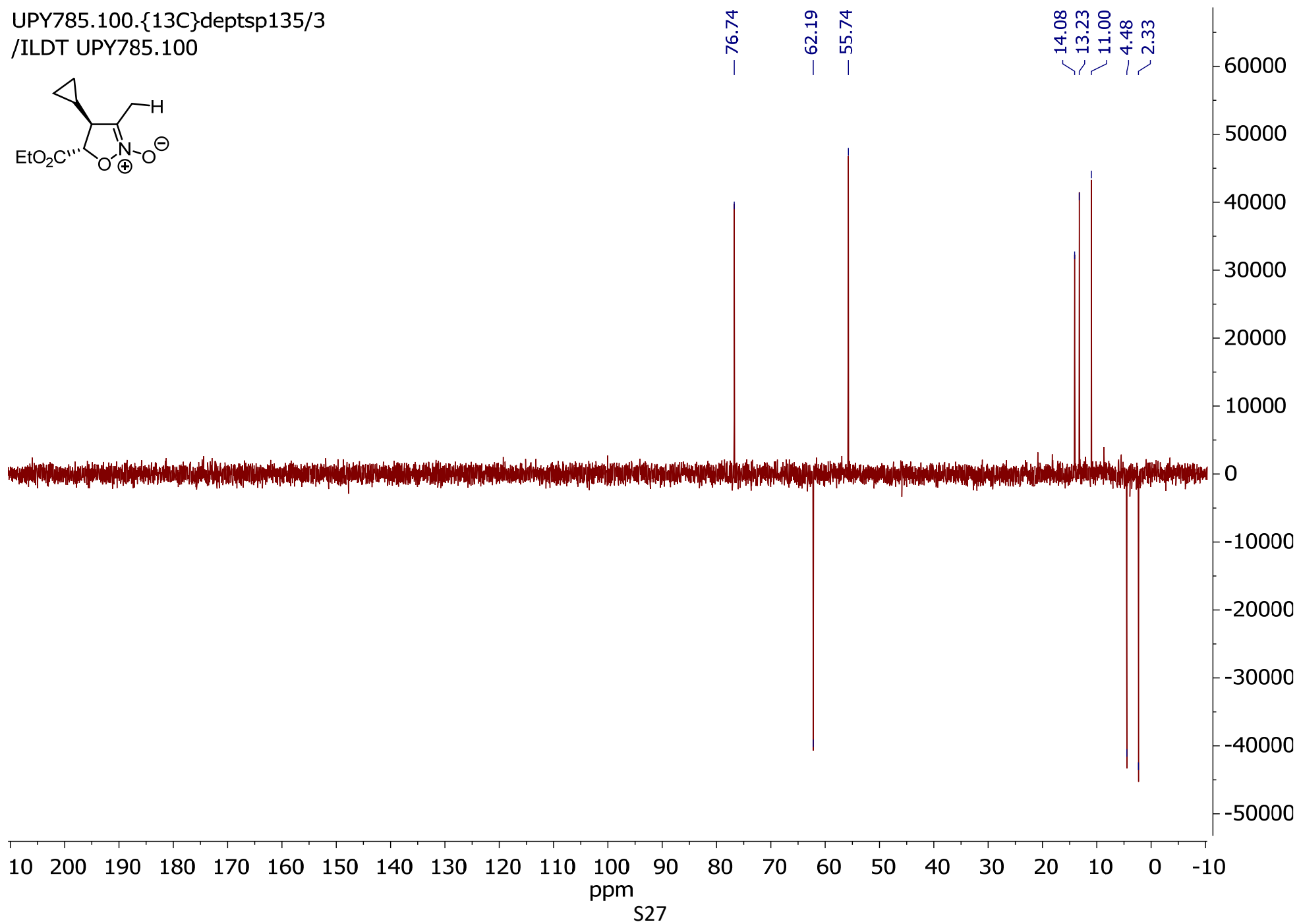
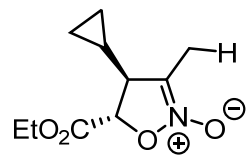


### NMR spectra of 8c



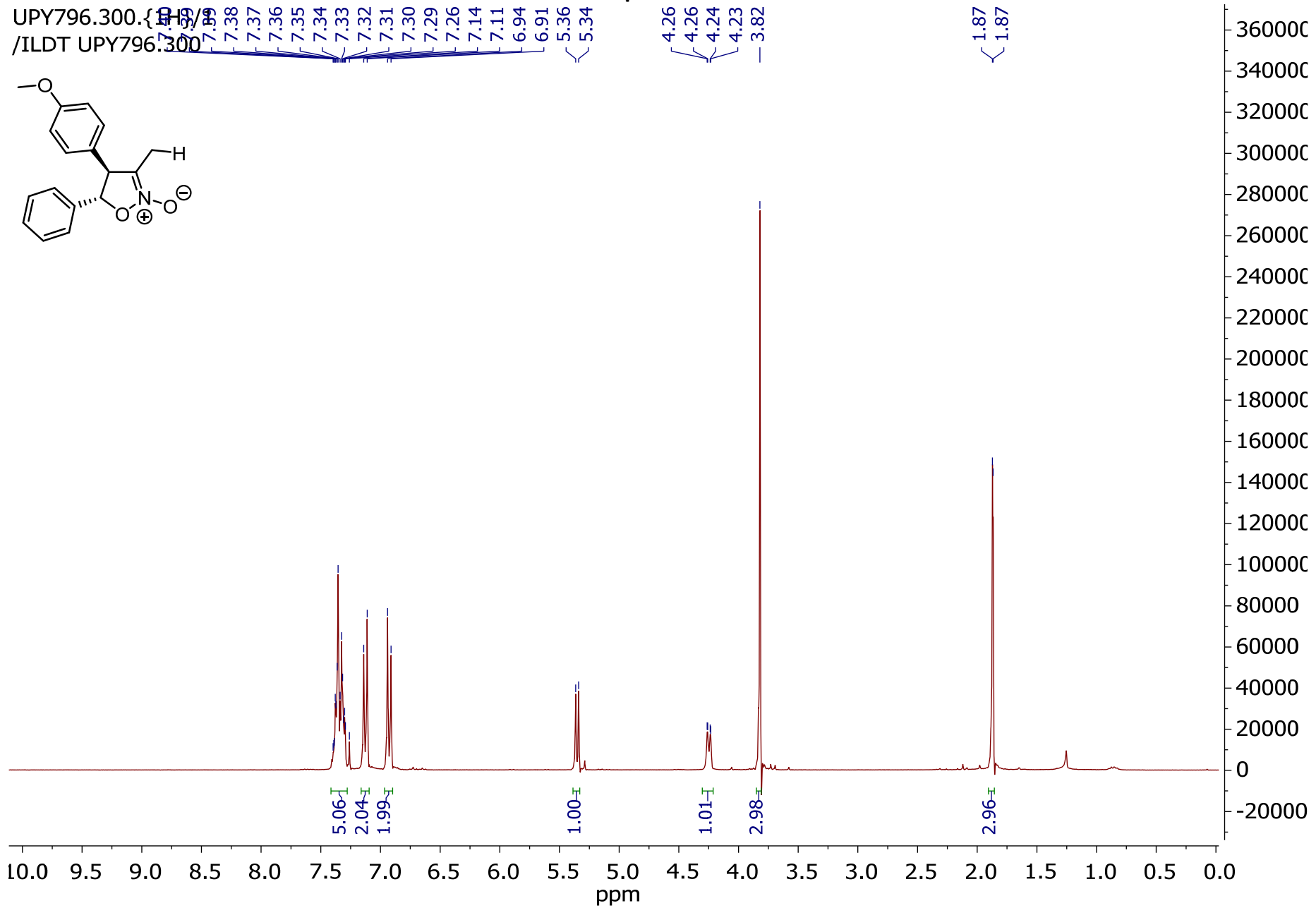
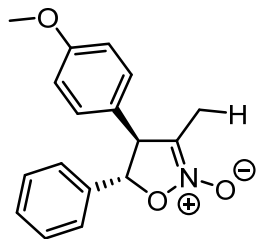


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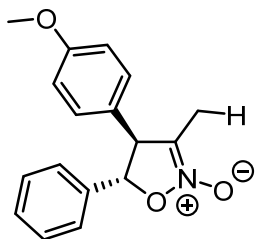


# NMR spectra of 12a

UPY796.300 (1H) /ILDT UPY796.300



UPY796.300.{13C}/2  
/ILD T UPY796.300



— 159.84

138.23

129.11

129.08

129.01

128.84

125.57

115.41

114.94

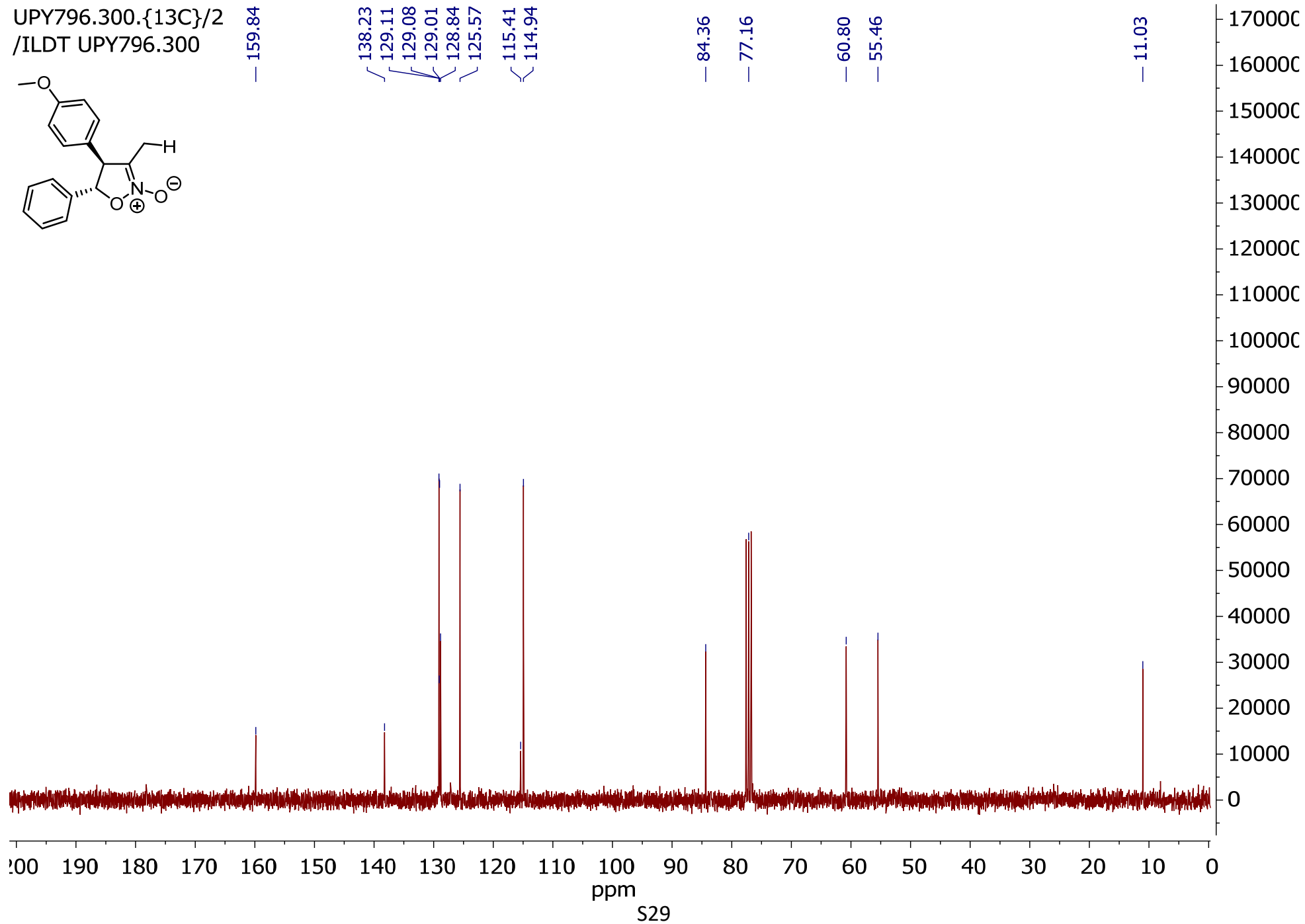
— 84.36

— 77.16

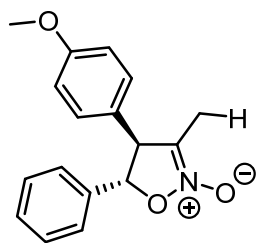
— 60.80

— 55.46

— 11.03



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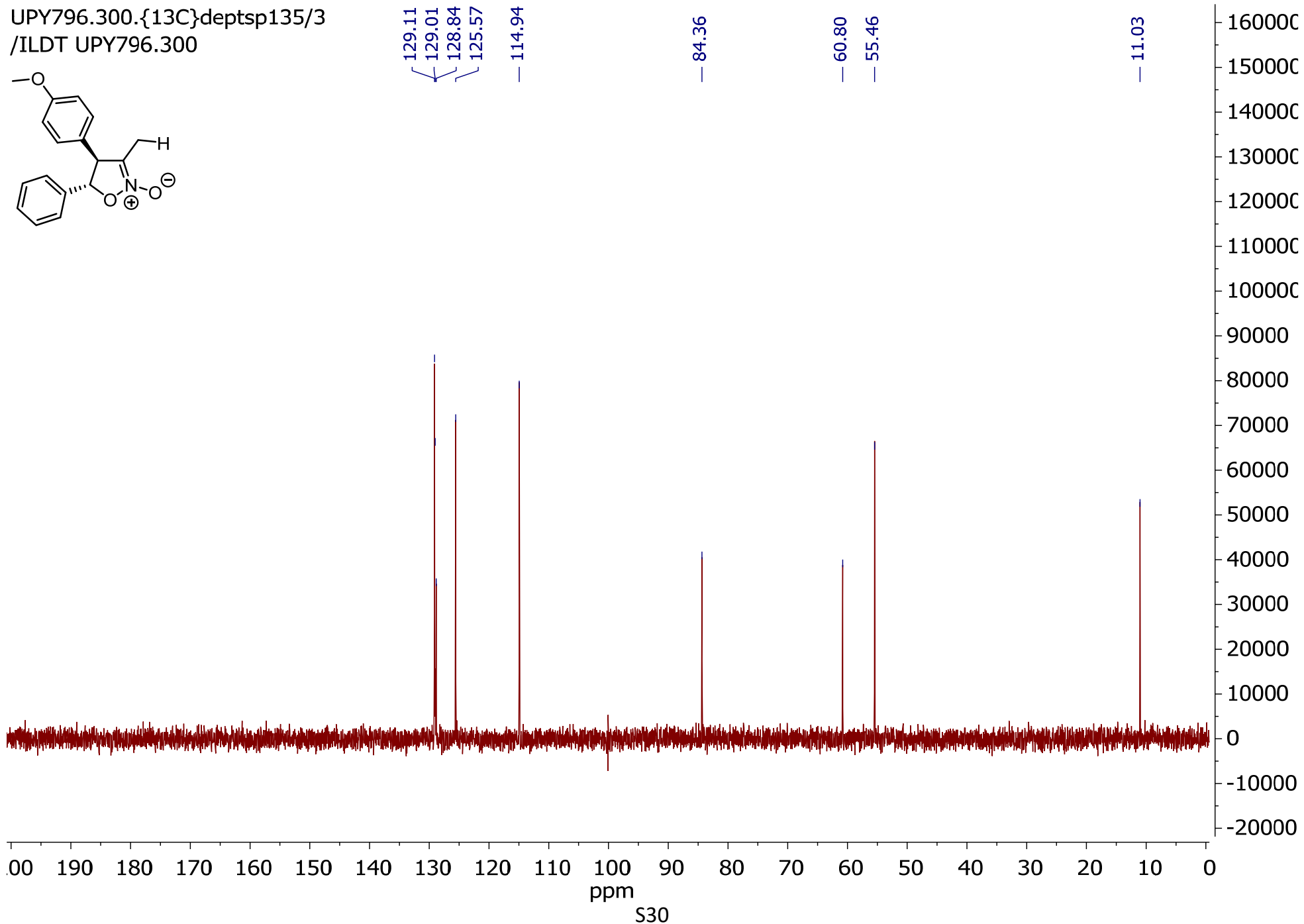
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129.01  
128.84  
125.57  
— 114.94

— 84.36

— 60.80

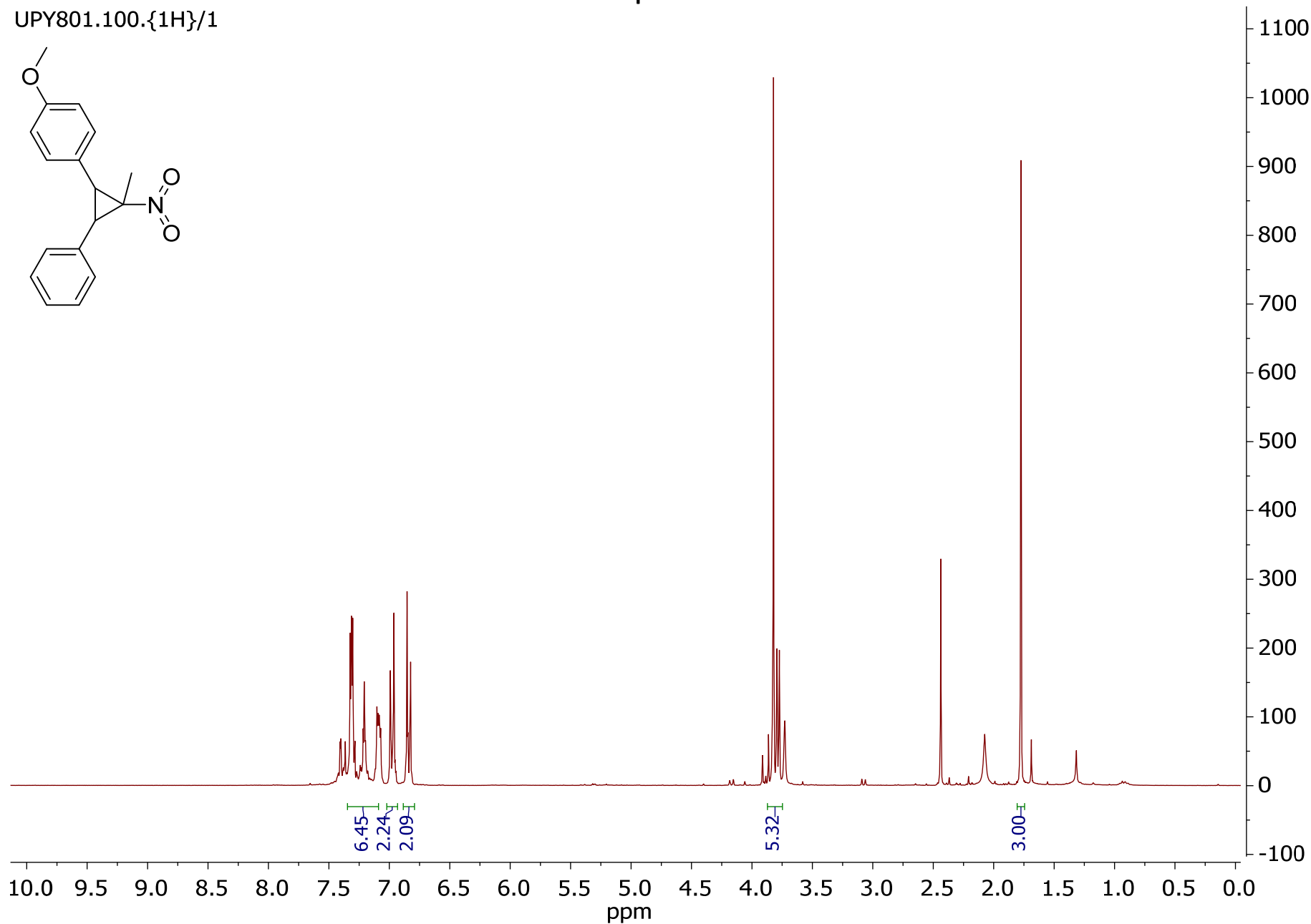
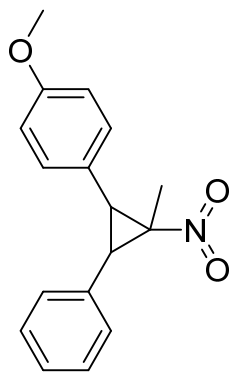
— 55.46

— 11.03

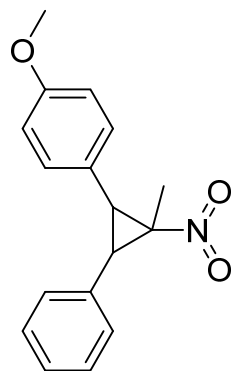


# NMR spectra of 13a

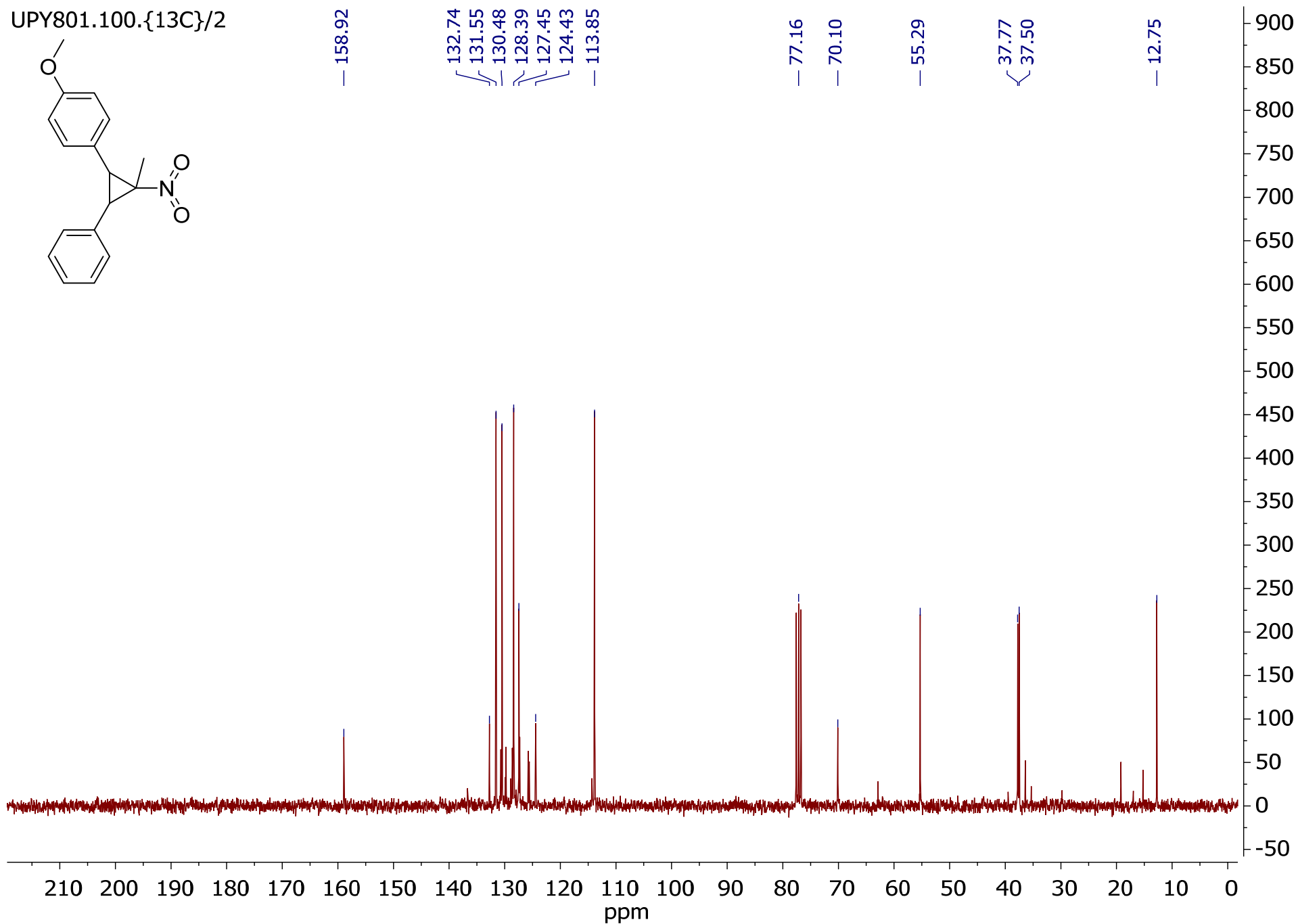
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UPY801.100.{13C}/2

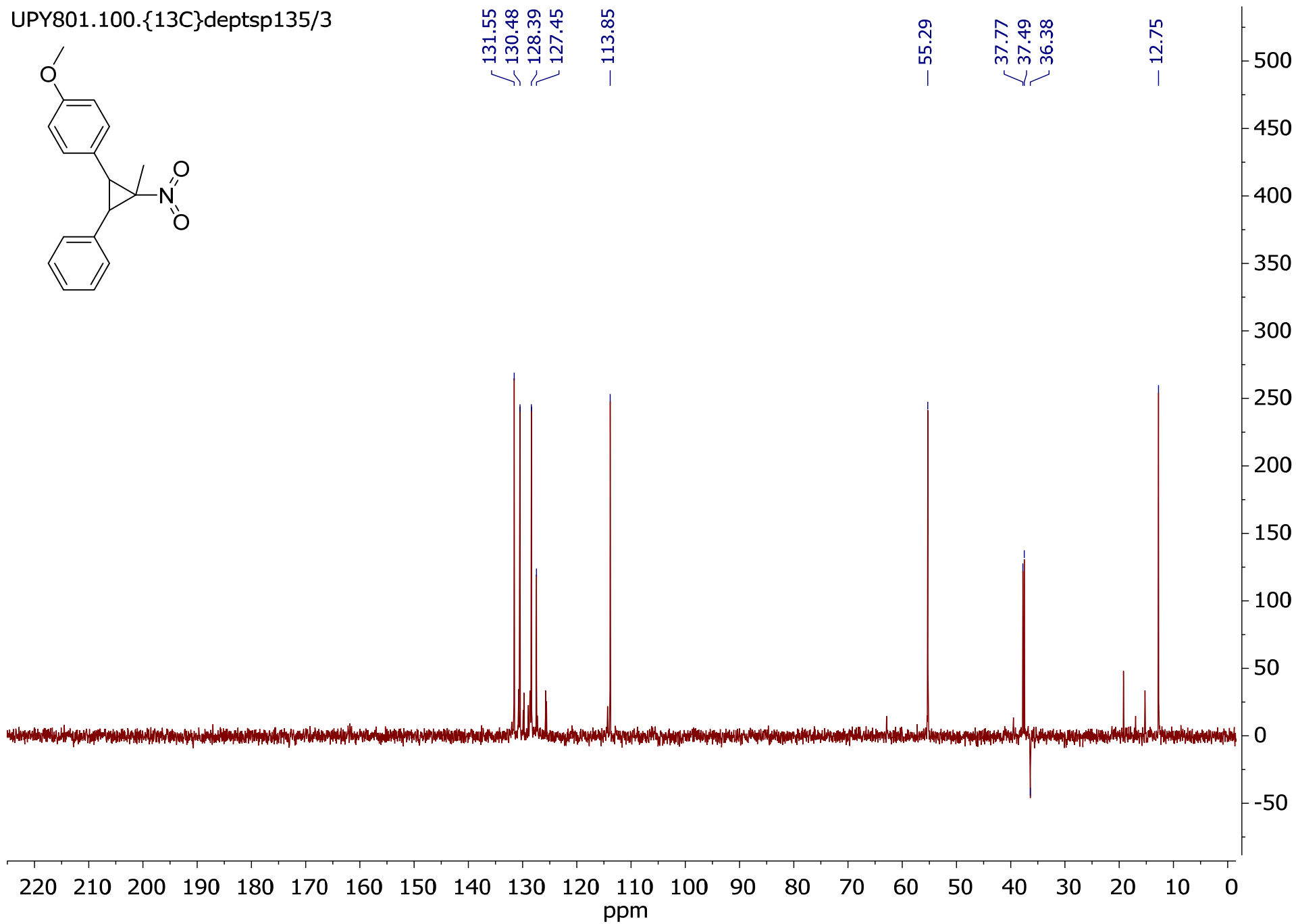
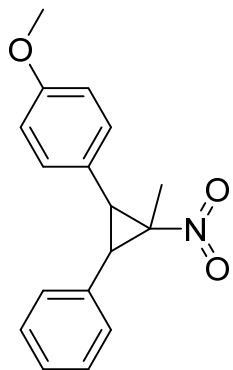


158.92  
132.74  
131.55  
130.48  
128.39  
127.45  
124.43  
113.85  
77.16  
70.10  
55.29  
37.77  
37.50  
12.75



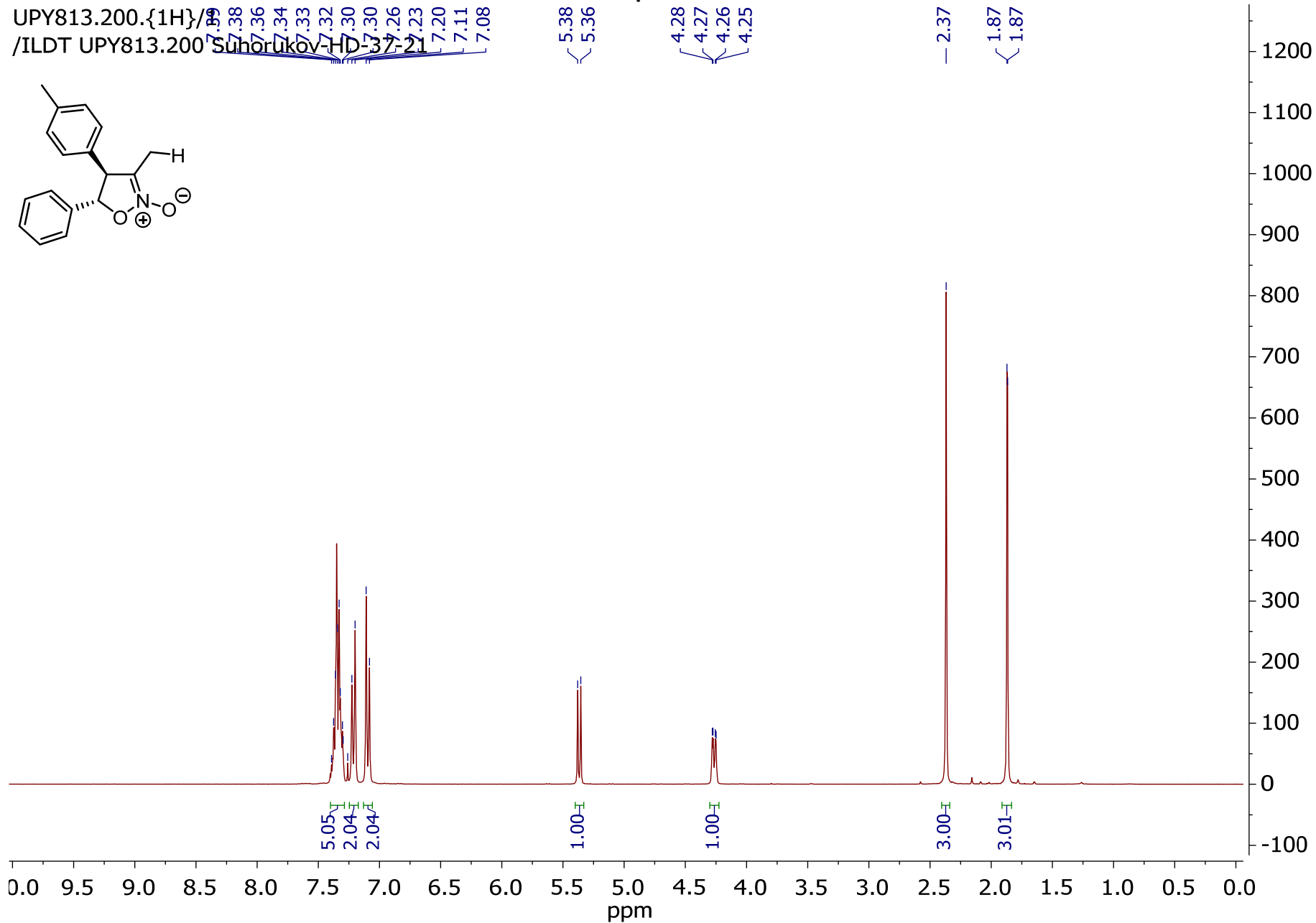


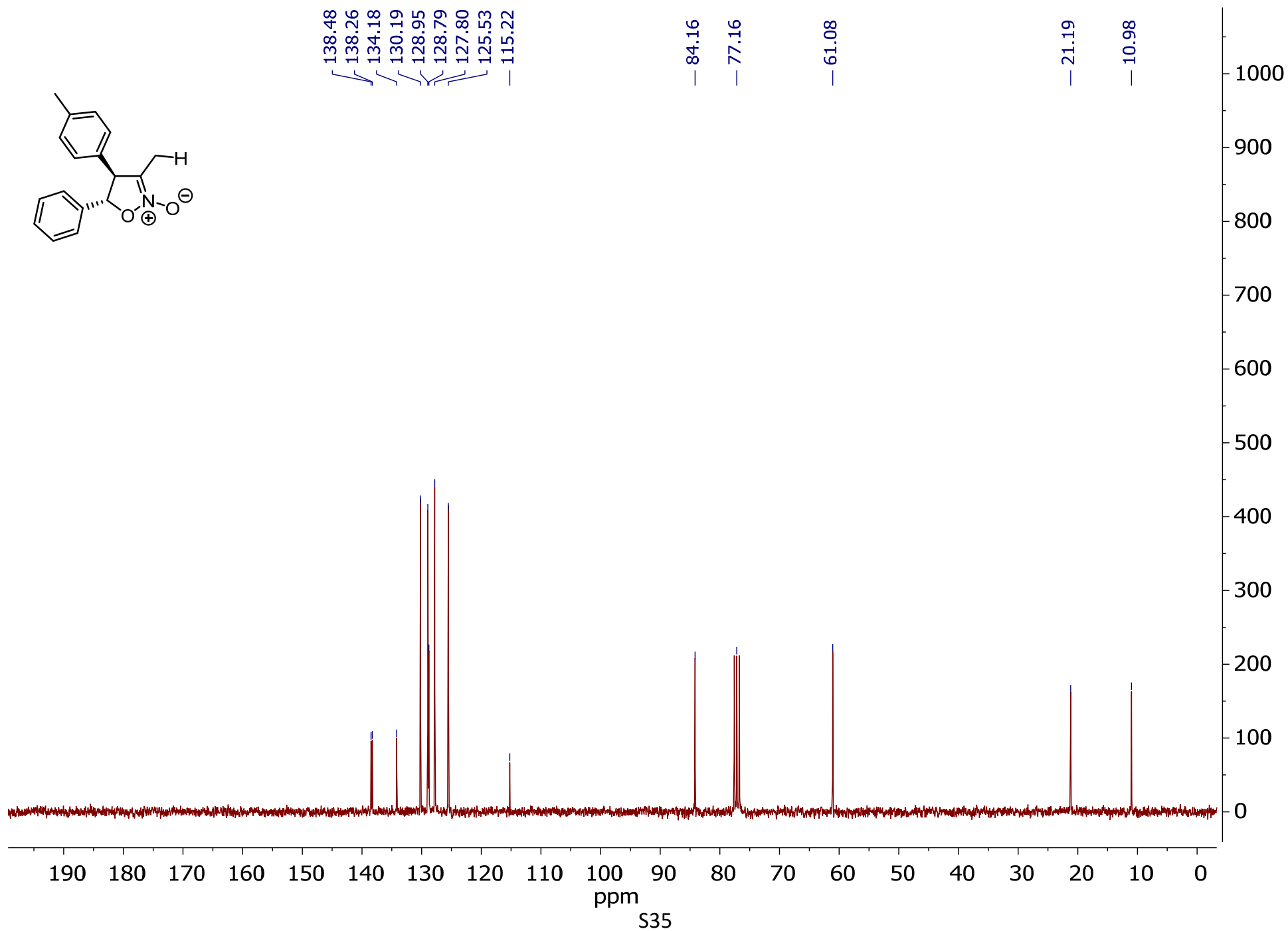
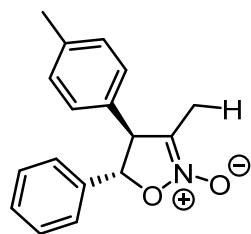
UPY801.100.{13C}deptsp135/3

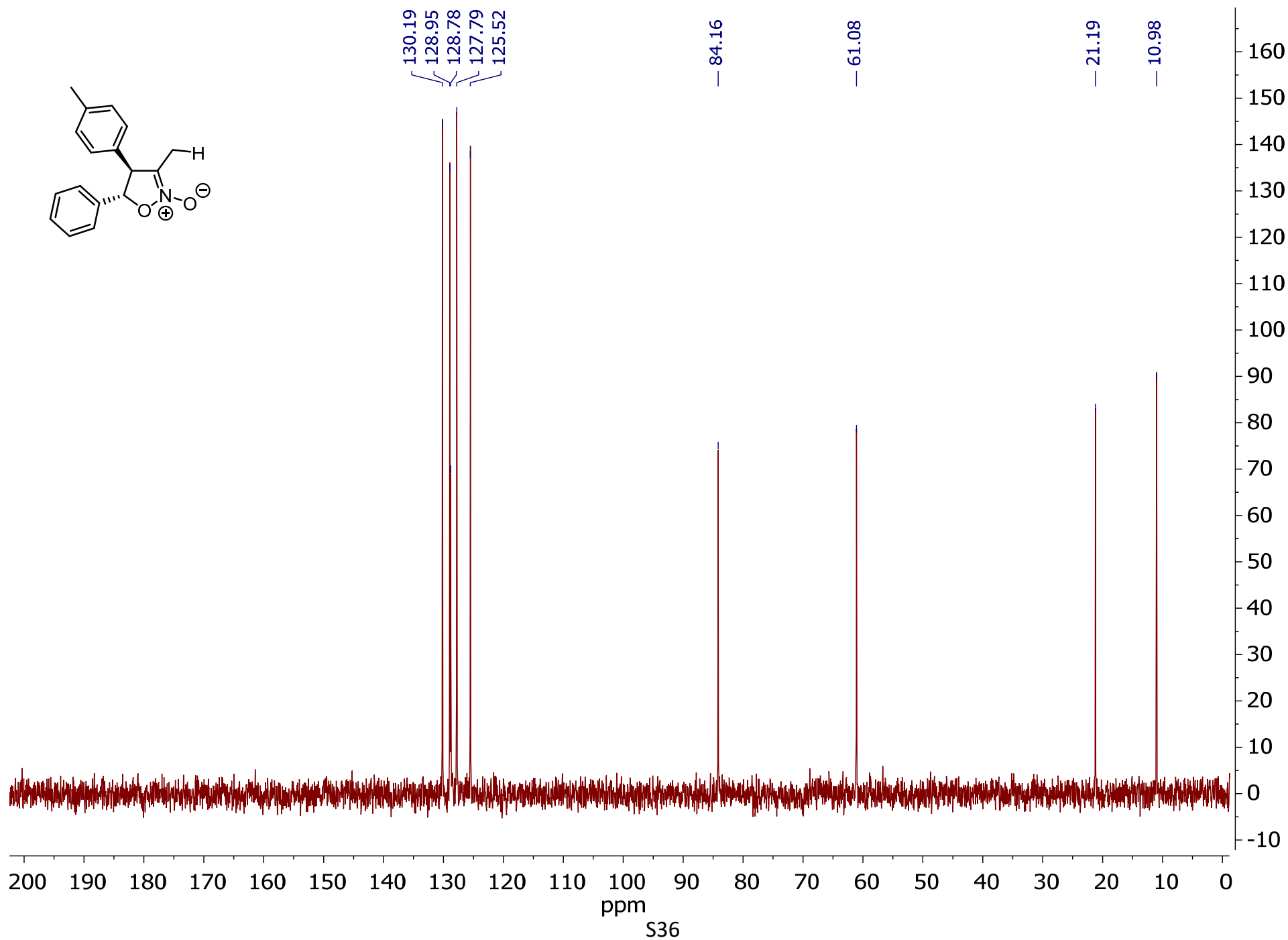
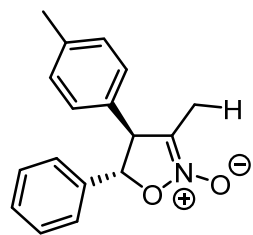


UPY813.200.{1H}/9  
/ILDTPY813.200

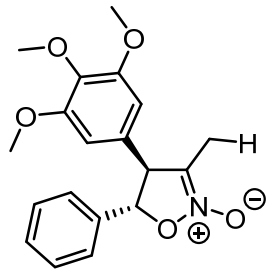
### NMR spectra of 12b



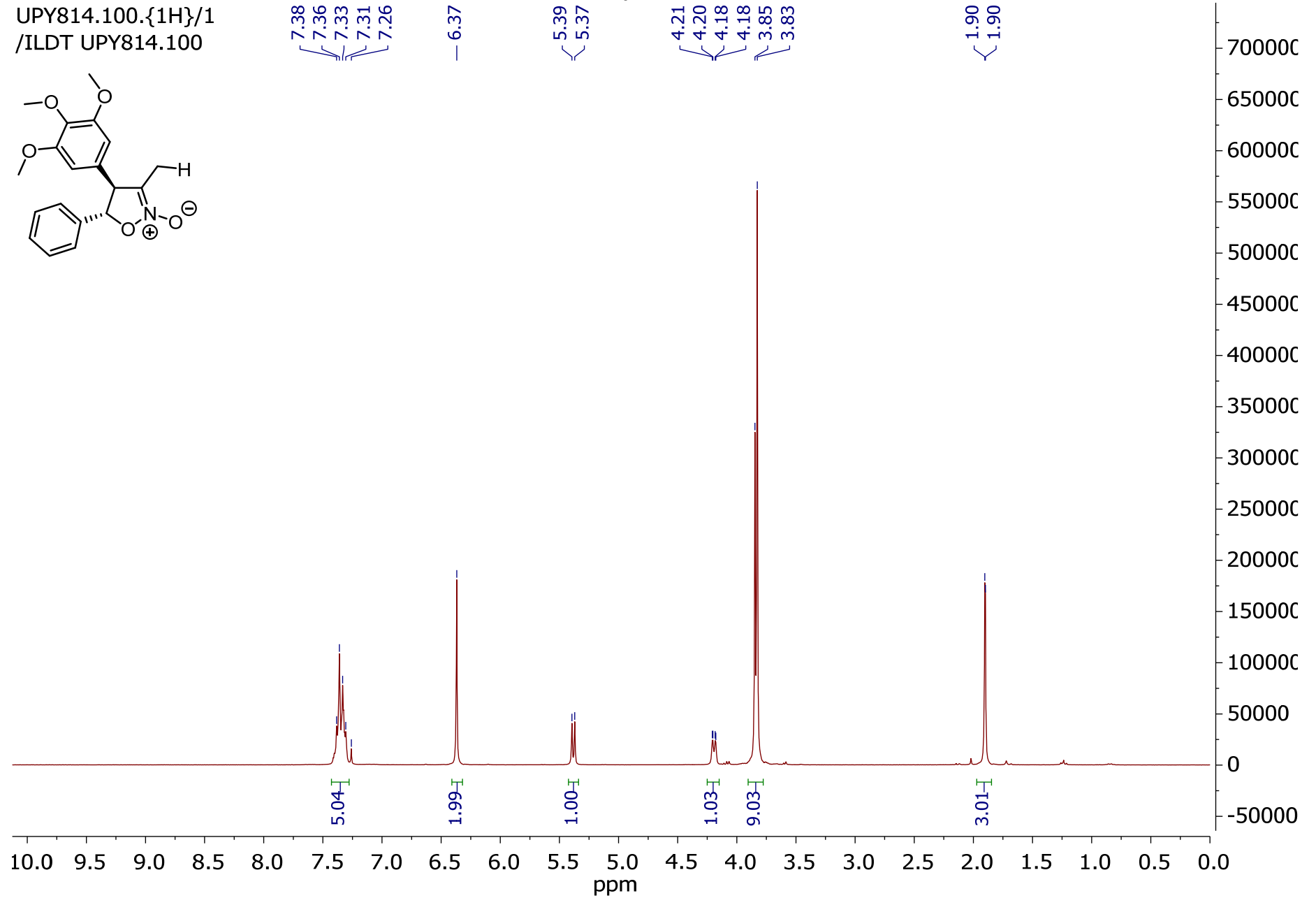




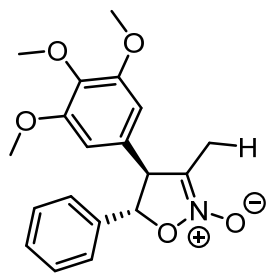
UPY814.100.{1H}/1  
/ILDY UPY814.100



### NMR spectra of 12c



UPY814.100.{13C}/2  
/ILD T UPY814.100



— 154.06

138.31

138.10

132.87

129.02

128.91

125.52

— 115.04

— 104.68

— 83.94

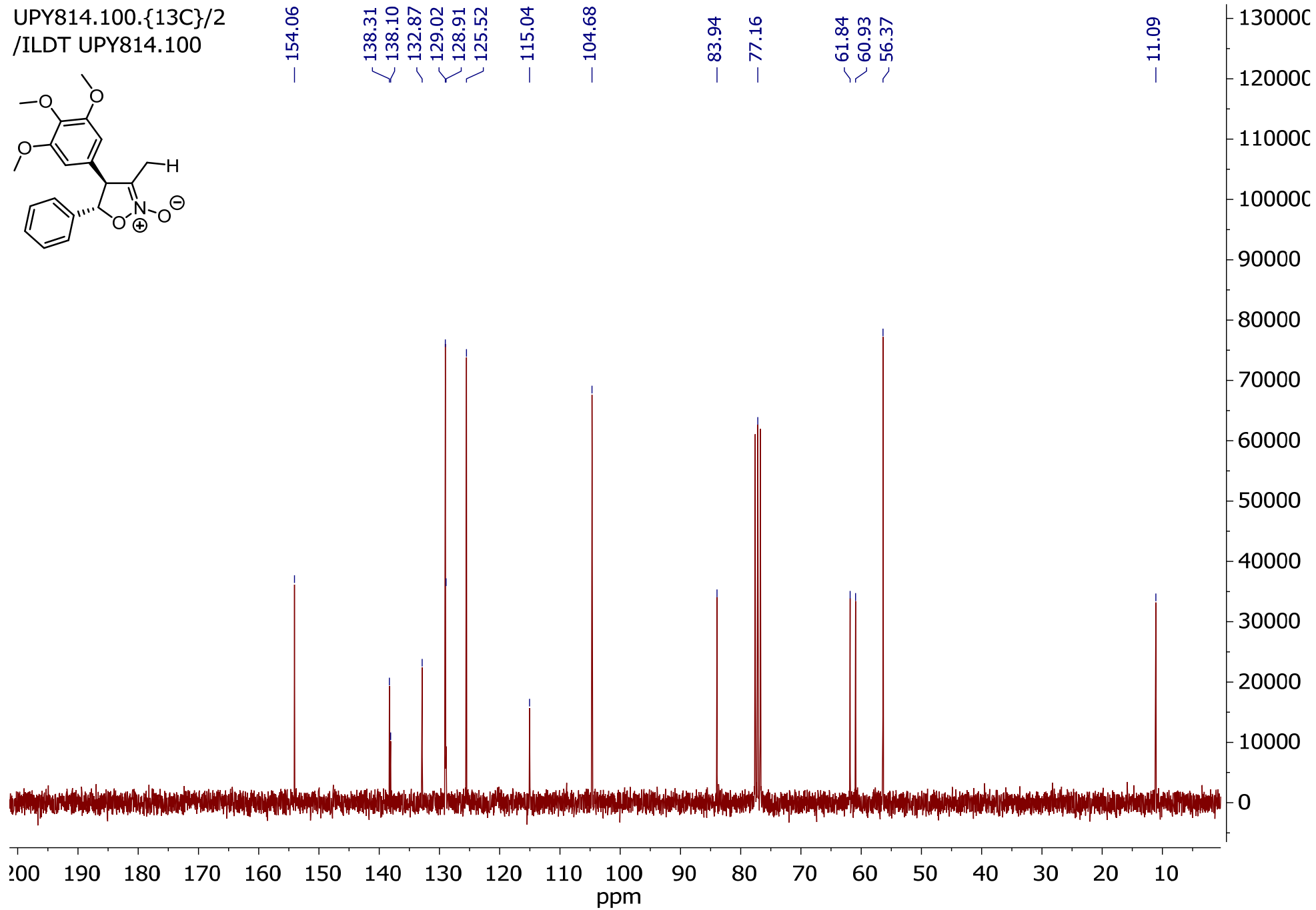
— 77.16

61.84

60.93

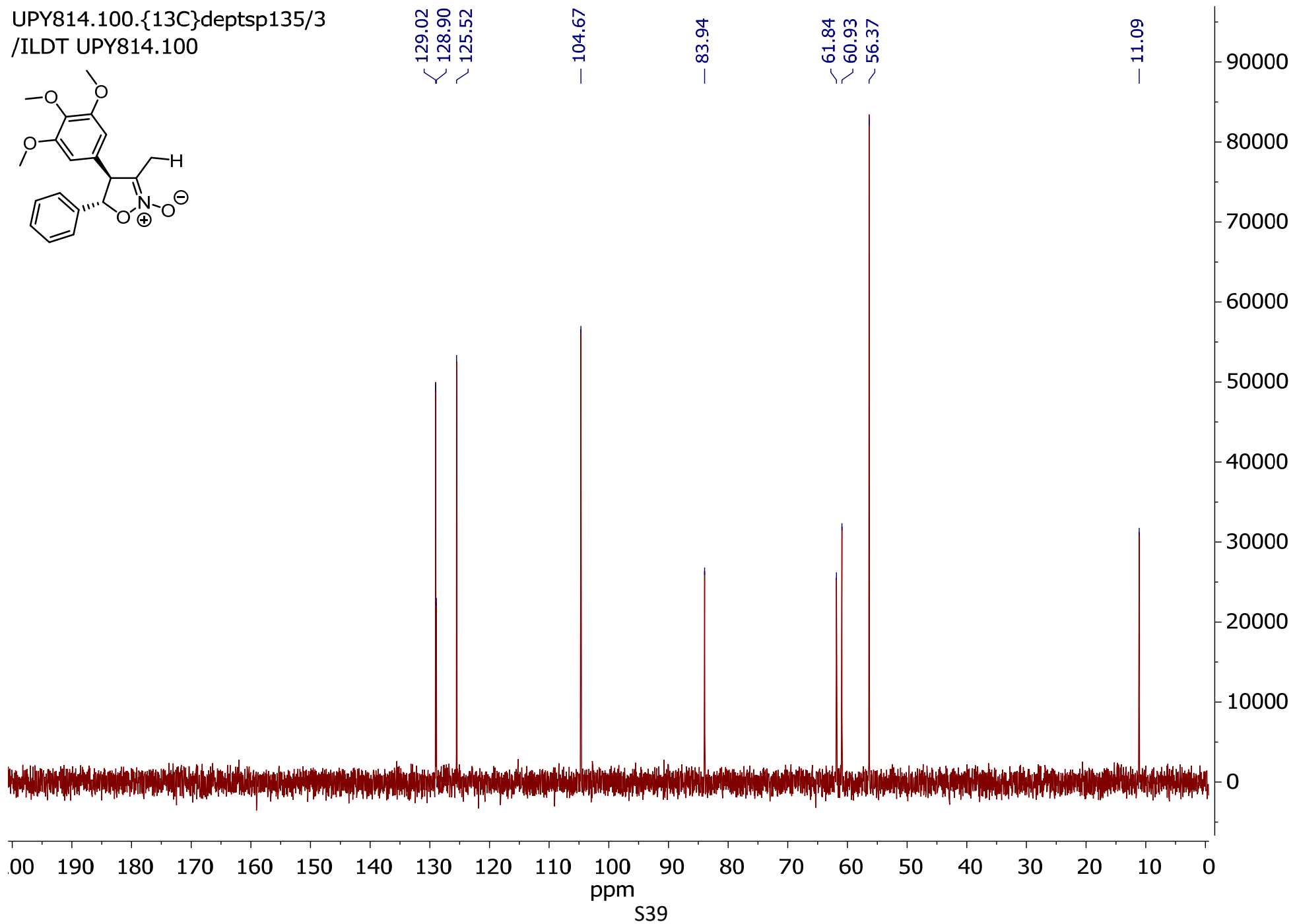
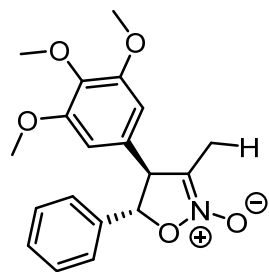
56.37

— 11.09

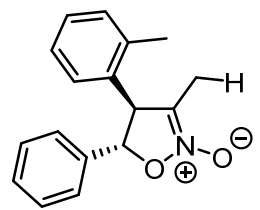
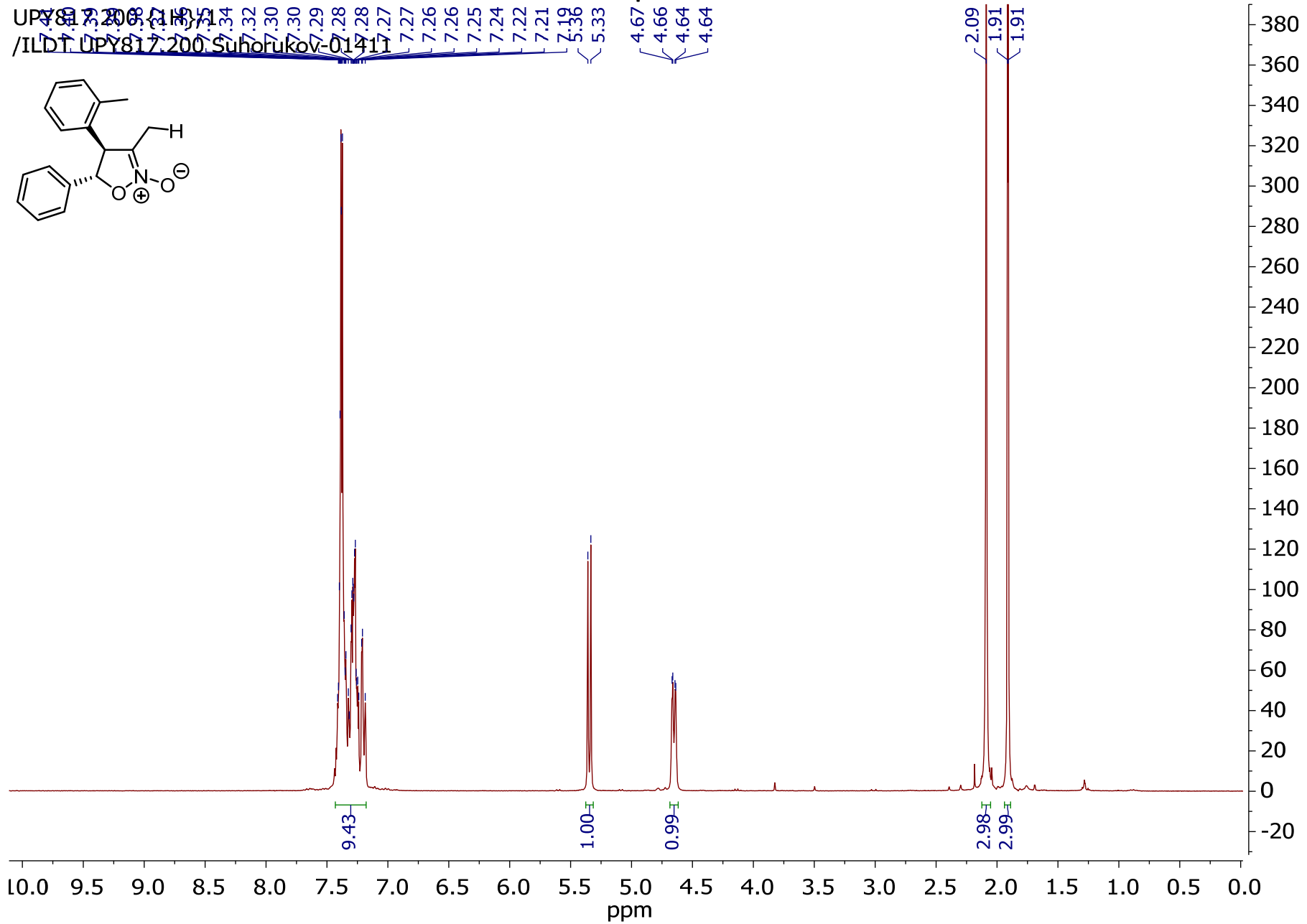


S38

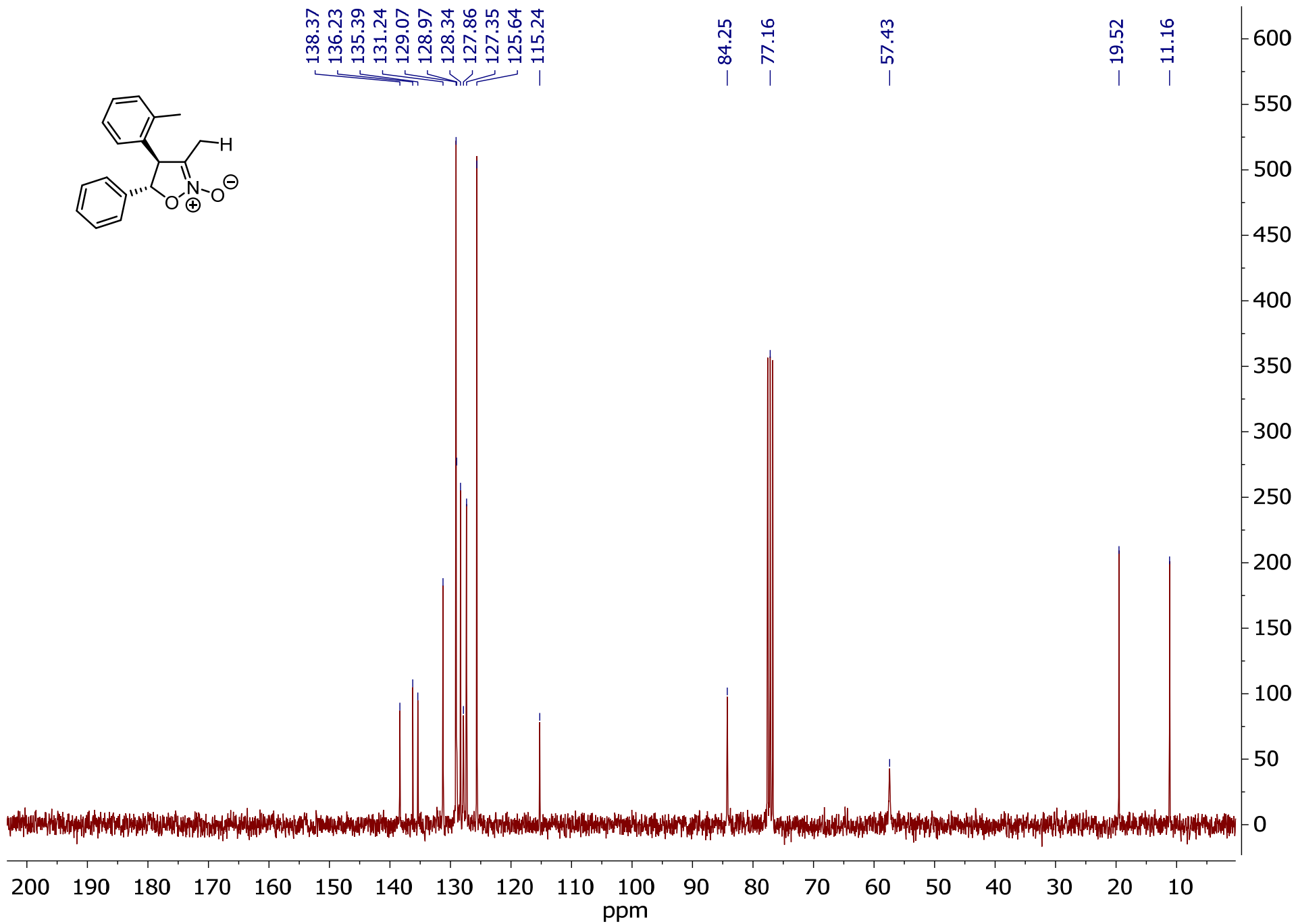
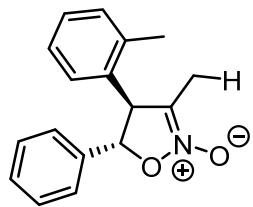
UPY814.100.{13C}deptsp135/3  
/ILD T UPY814.100



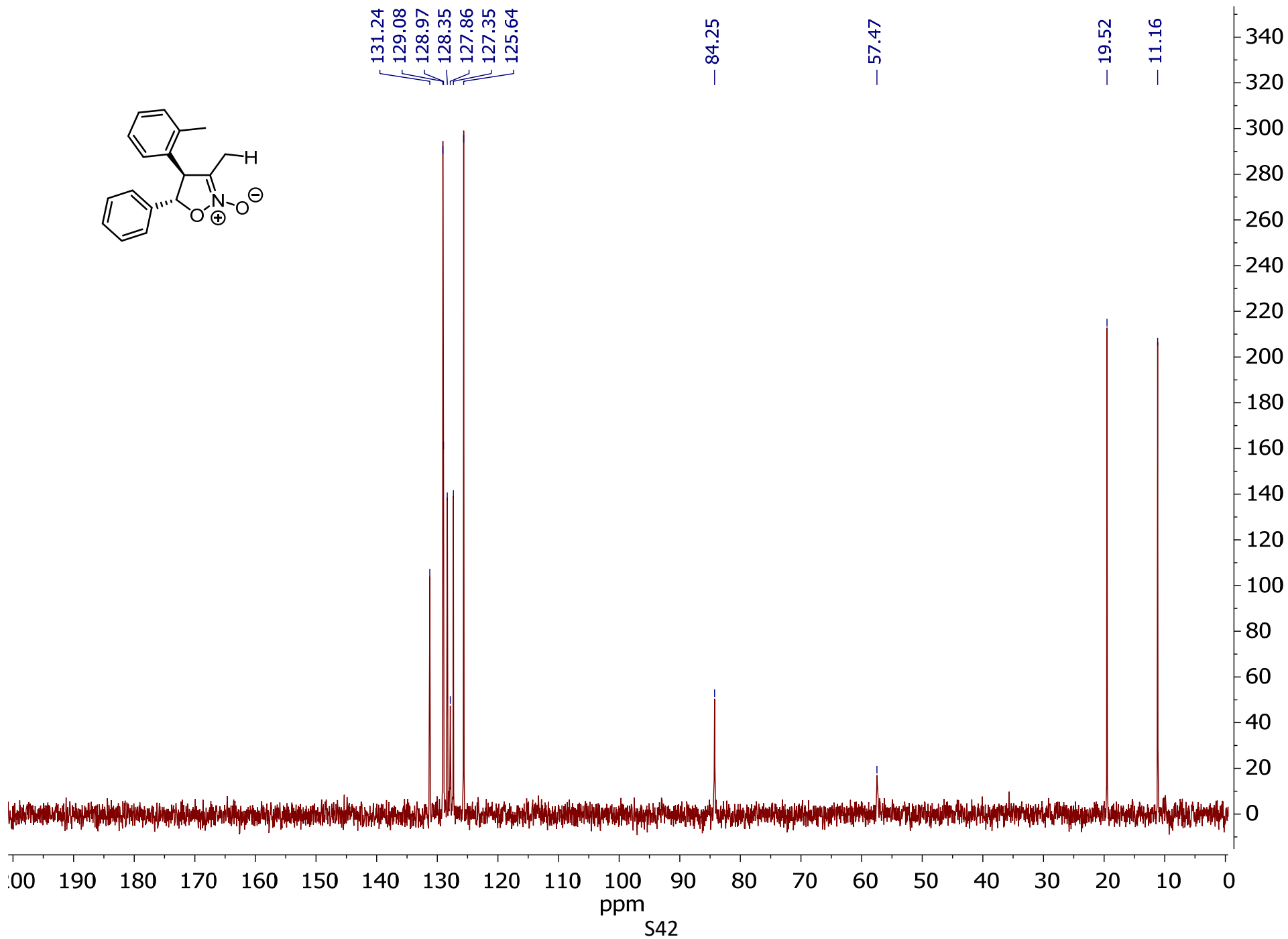
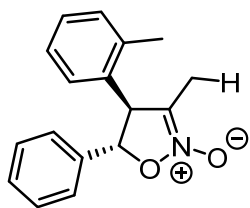
# NMR spectra of 12d



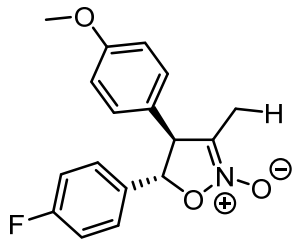




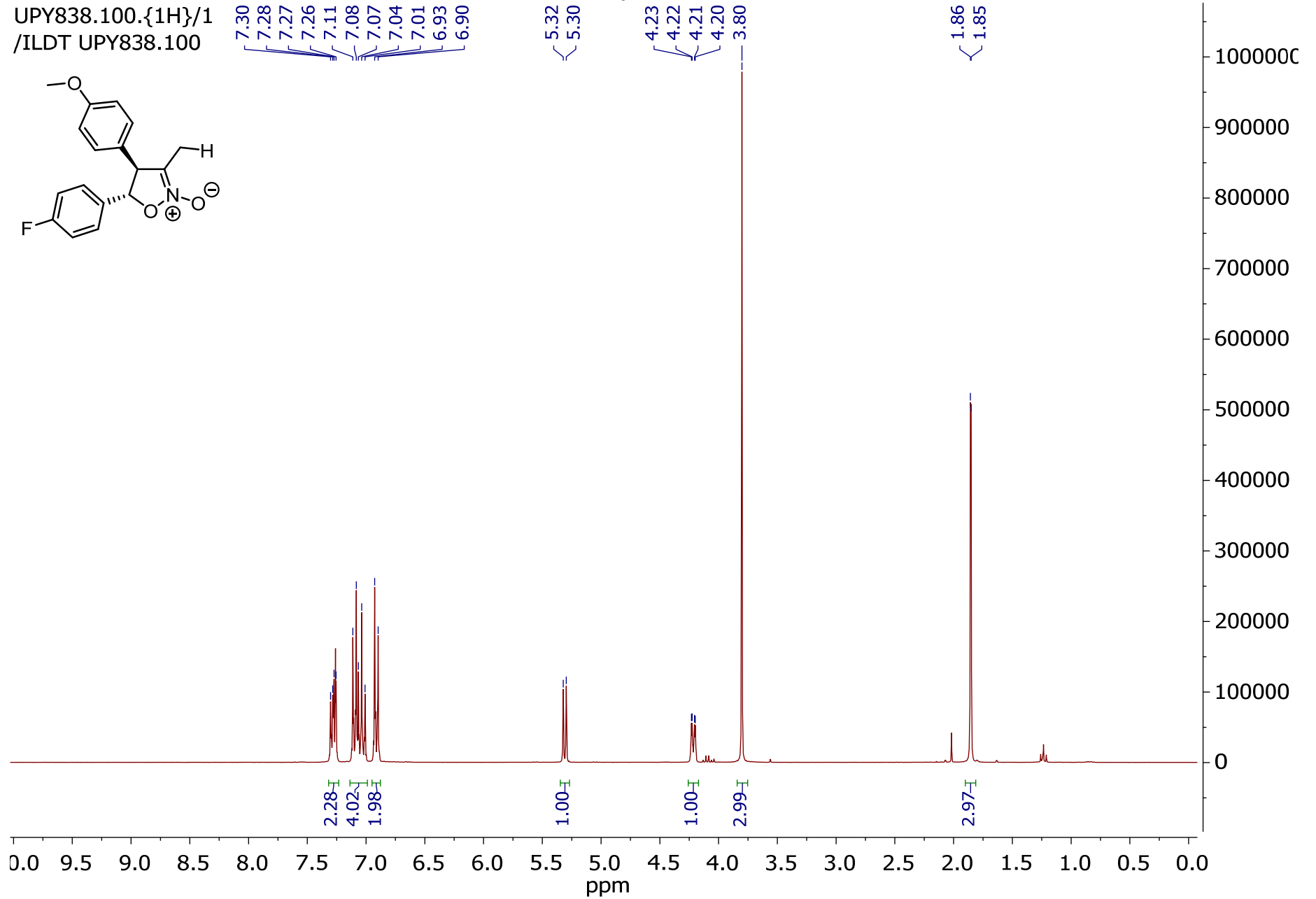
S41



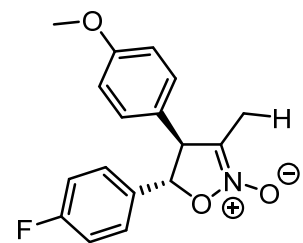
UPY838.100.{1H}/1  
/ILDY UPY838.100



### NMR spectra of 12e



UPY838.100.{13C}/  
/ILDT UPY838.100



164.15  
161.27  
159.85

133.78  
133.74  
129.06  
128.63  
127.58  
127.46  
116.09  
115.80  
115.31  
114.93

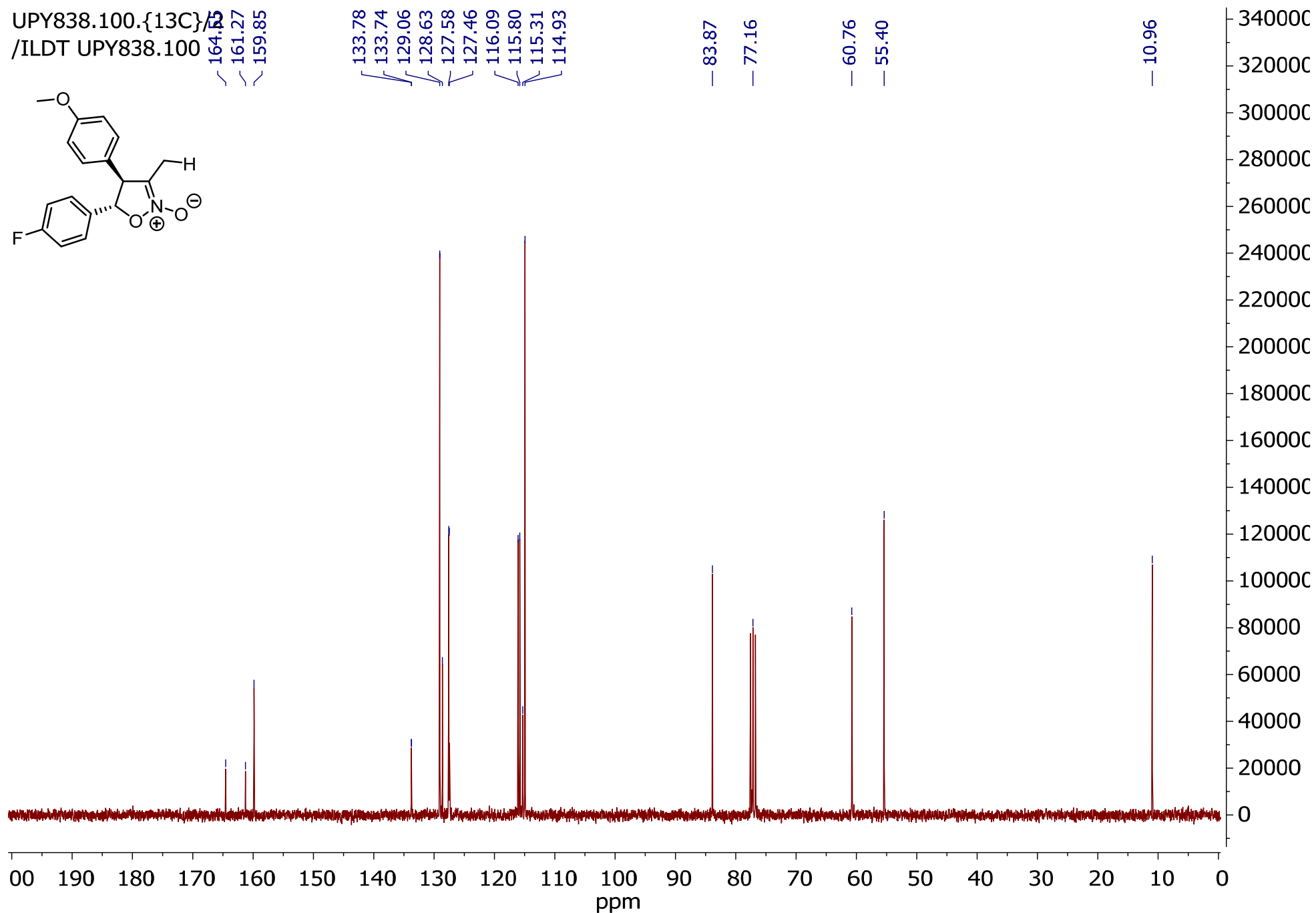
83.87

77.16

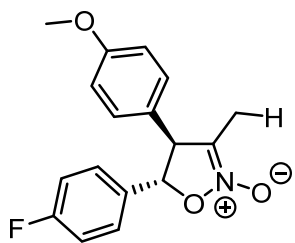
60.76

55.40

10.96



UPY838.100.{13C}deptspl3/3  
/ILDIT UPY838.100



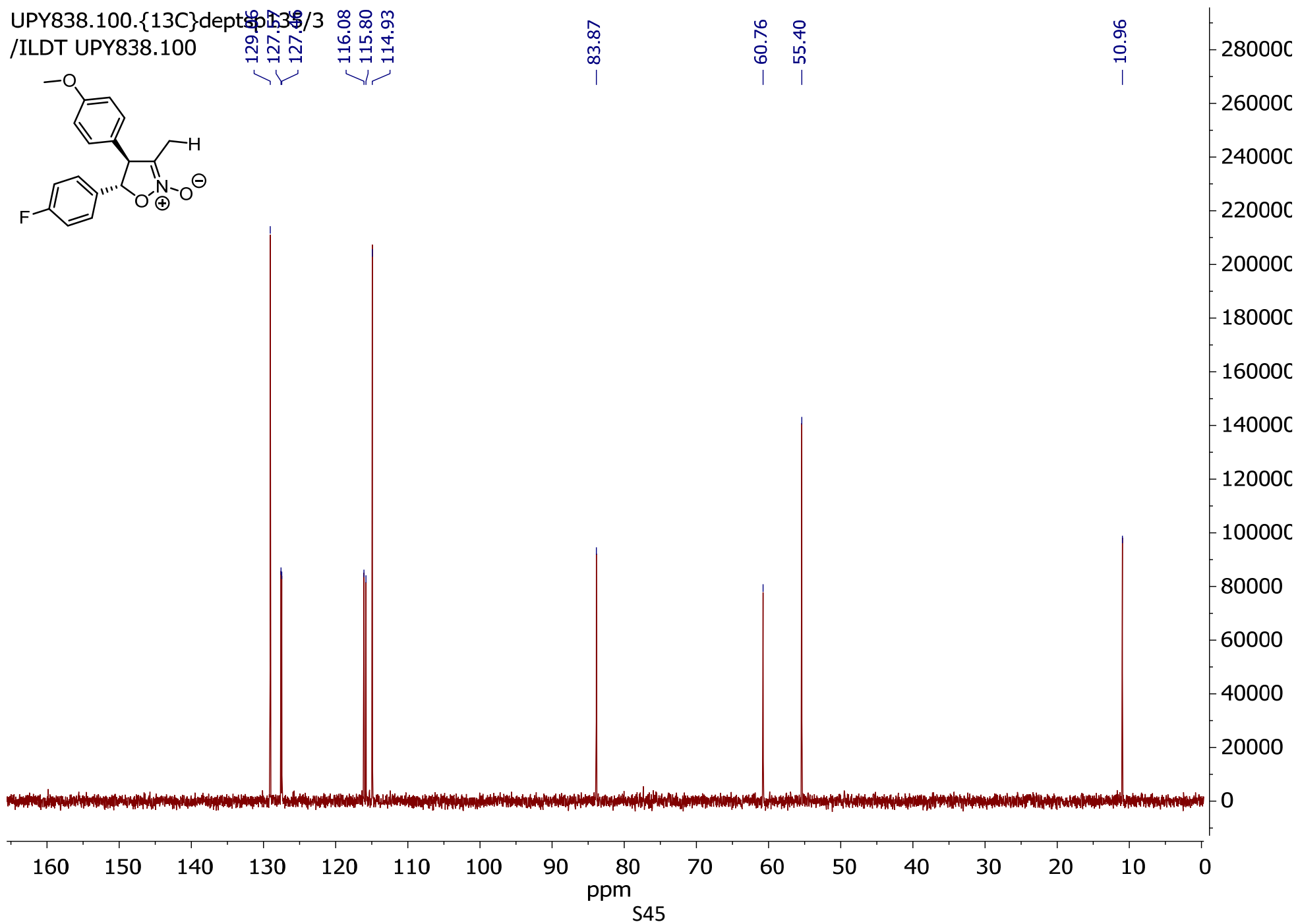
129.56  
127.57  
127.46  
116.08  
115.80  
114.93

83.87

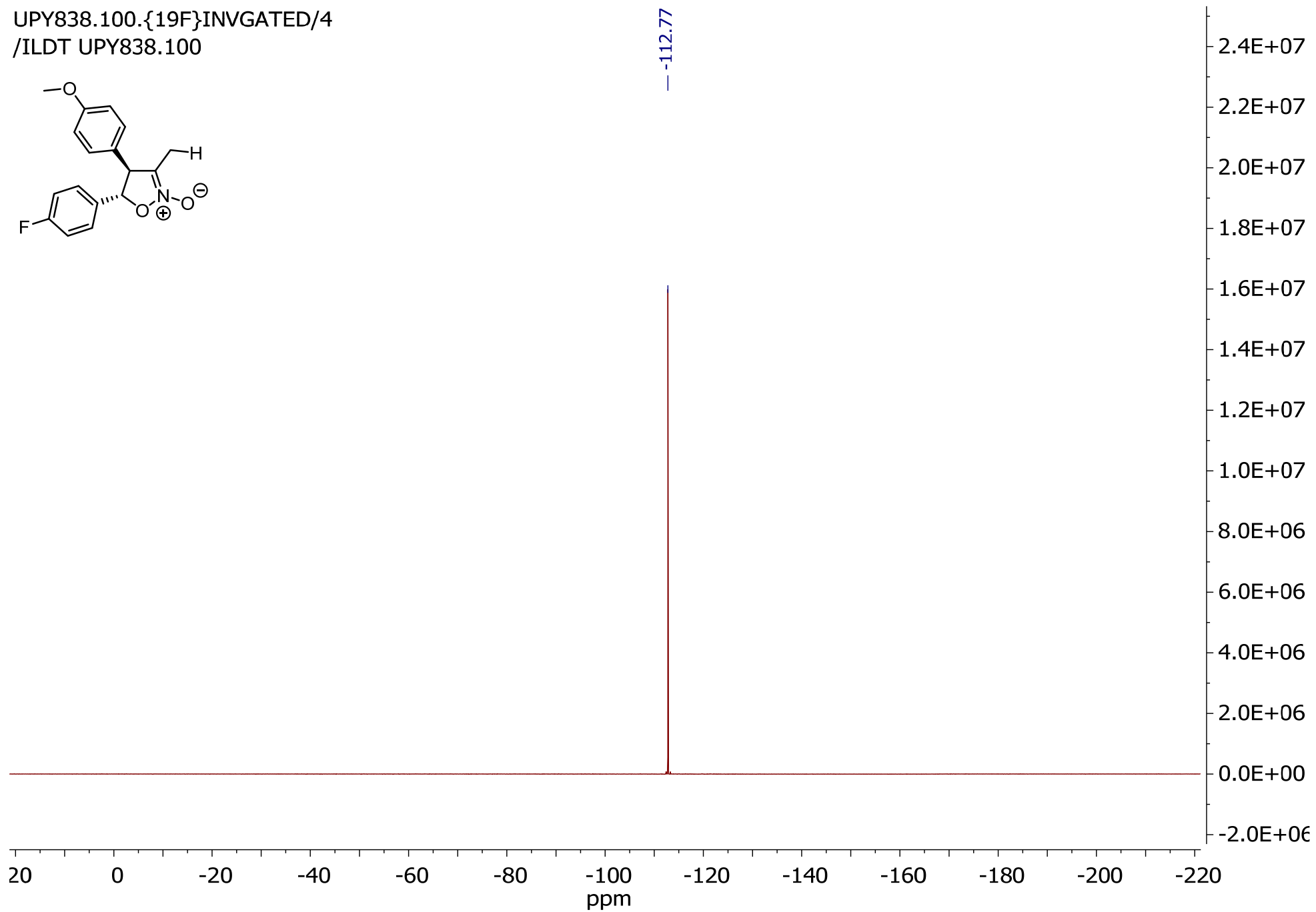
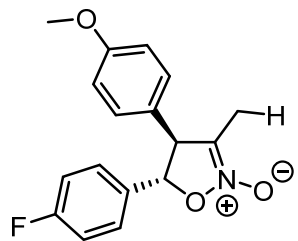
60.76

55.40

10.96



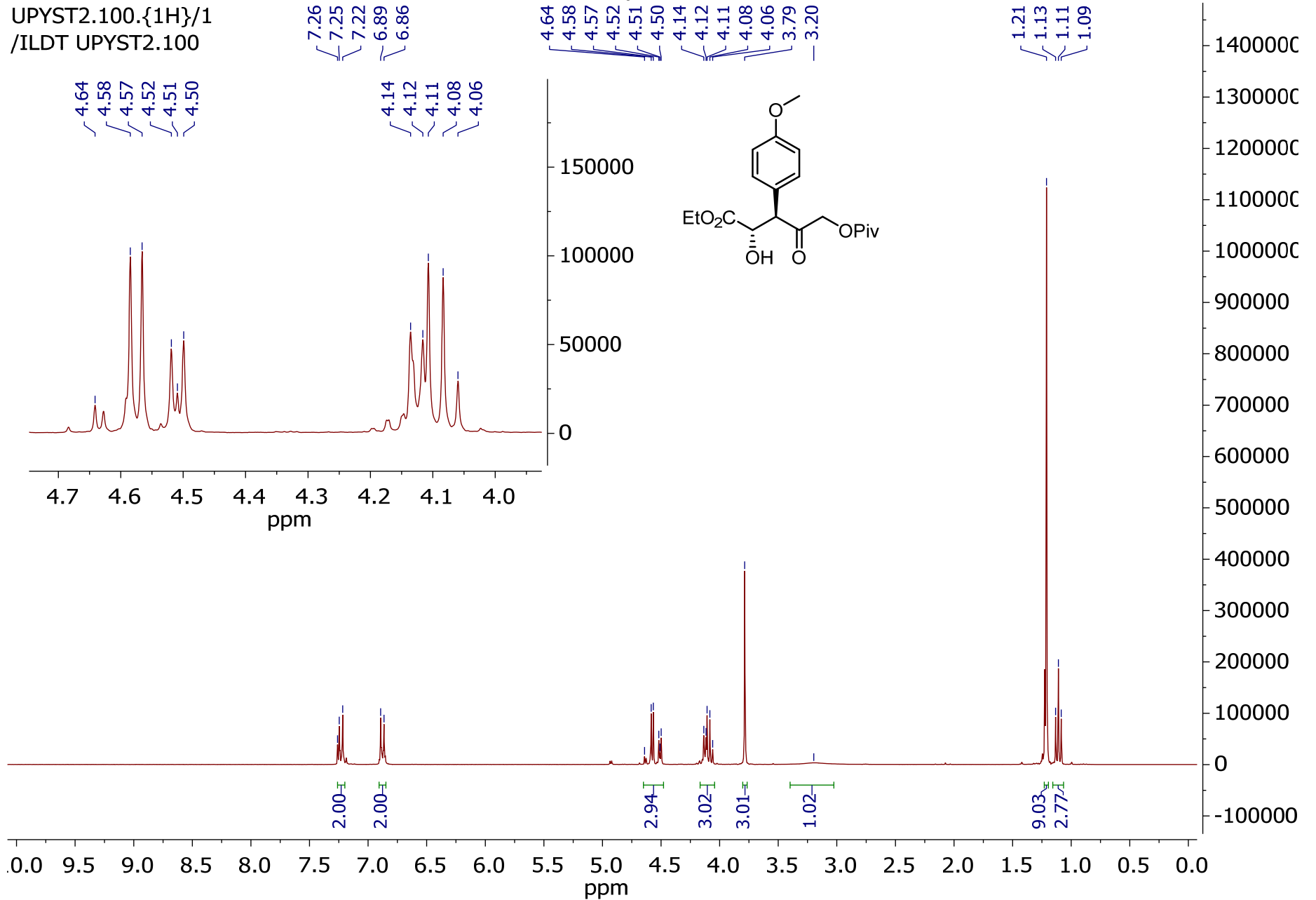
UPY838.100.{19F}INVGATED/4  
/ILDIT UPY838.100

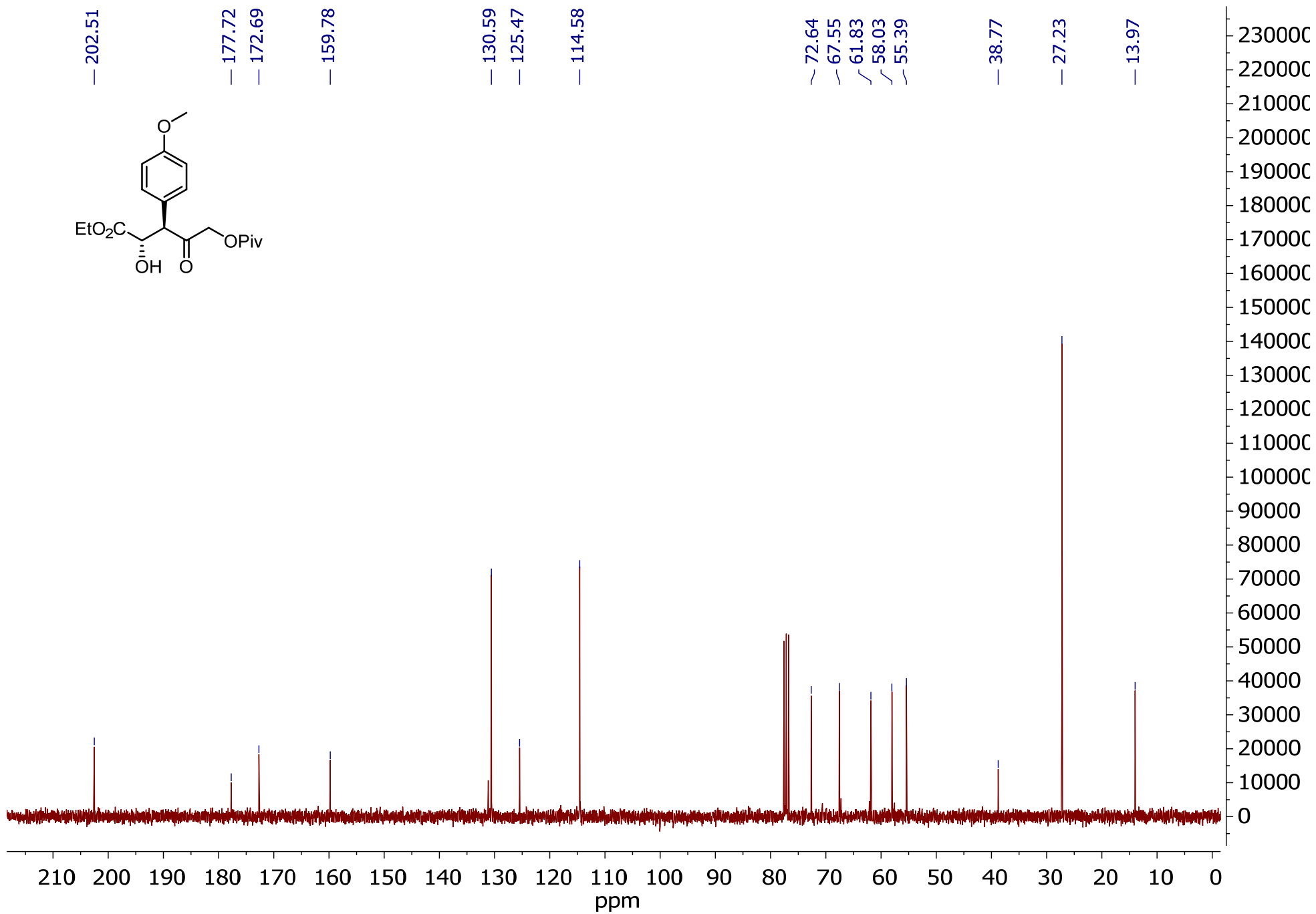
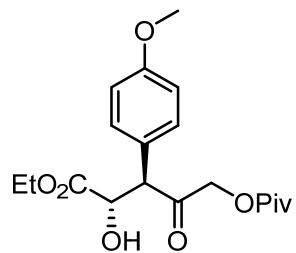


S46

UPYST2.100.{1H}/1  
/ILD T UPYST2.100

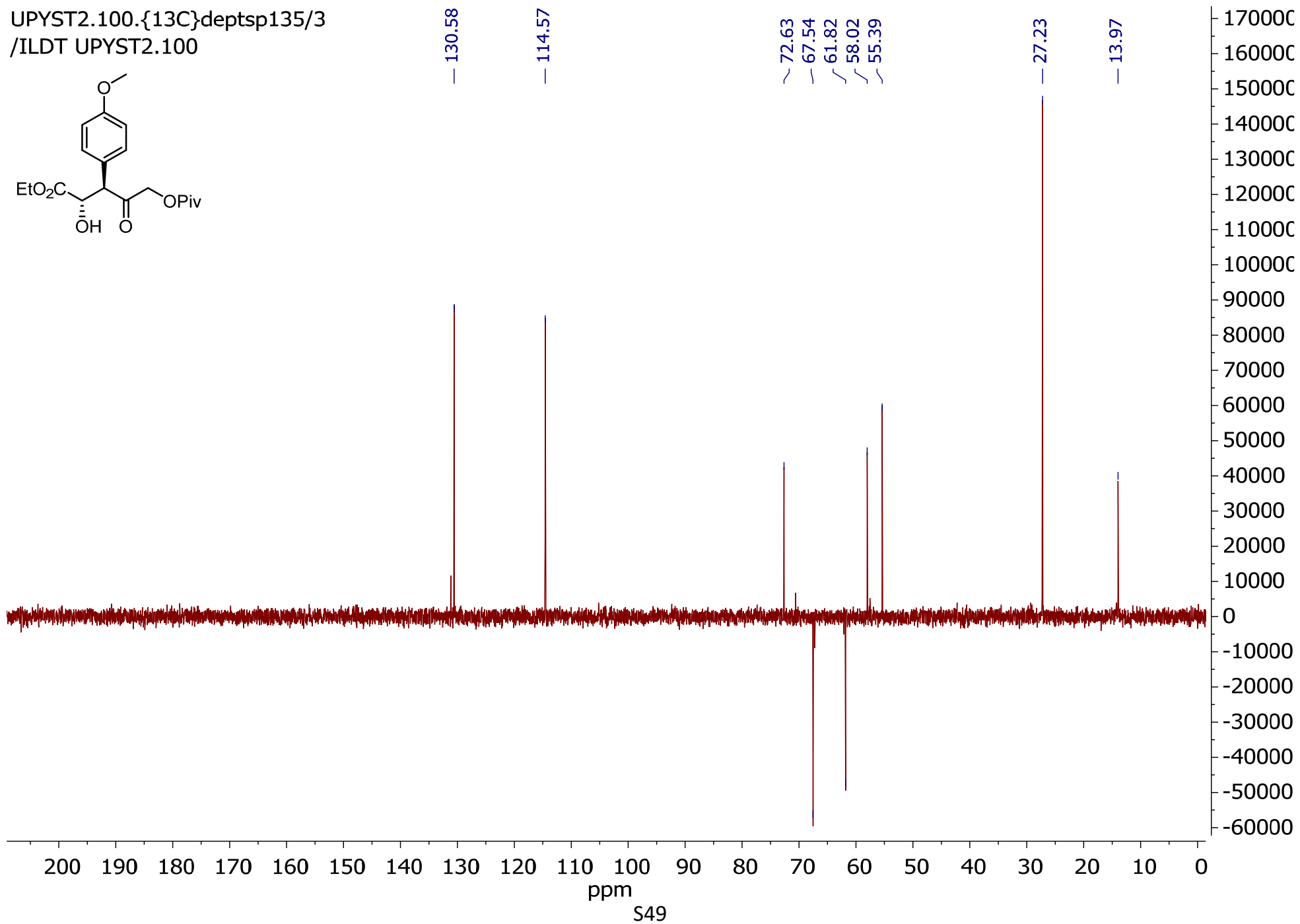
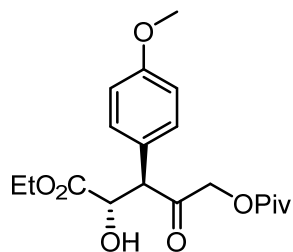
### NMR spectra of 5a

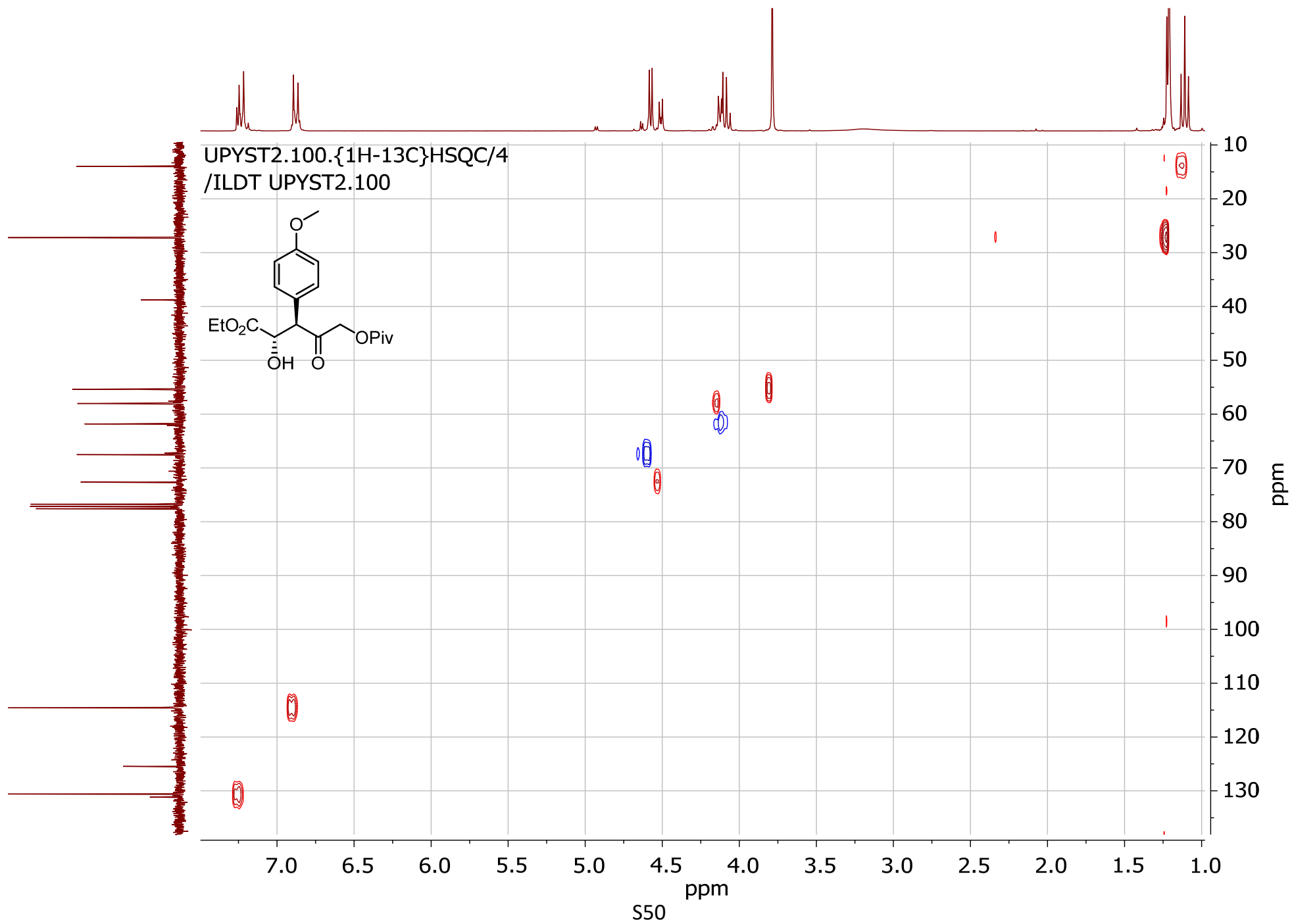




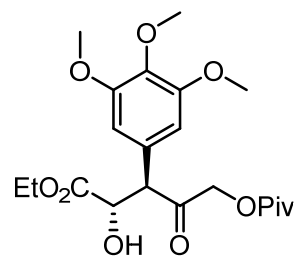


UPYST2.100.{13C}deptsp135/3  
/ILD T UPYST2.100

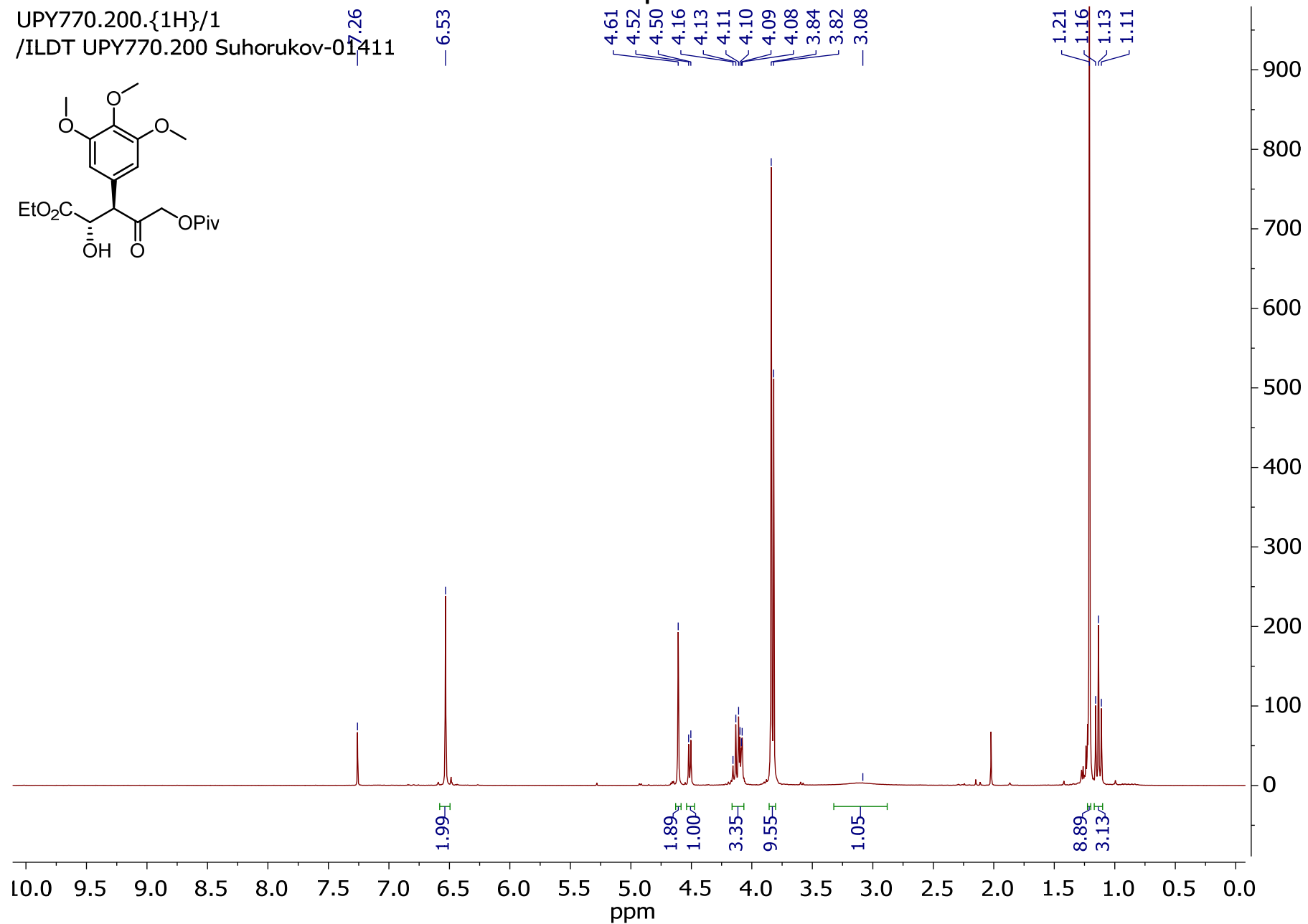


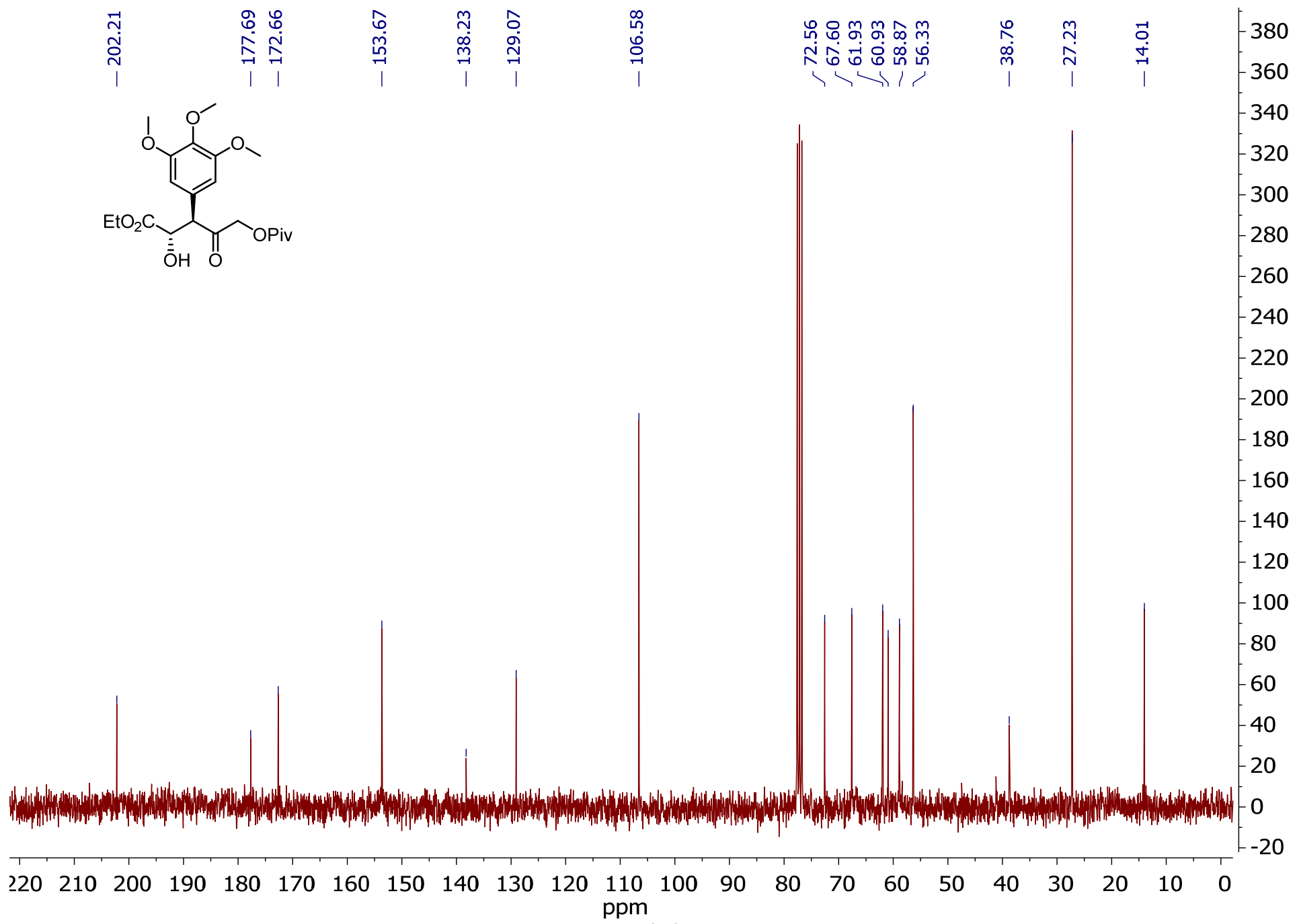
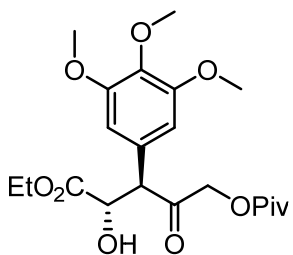


UPY770.200.{1H}/1  
/ILDT UPY770.200 Suhorukov-01411

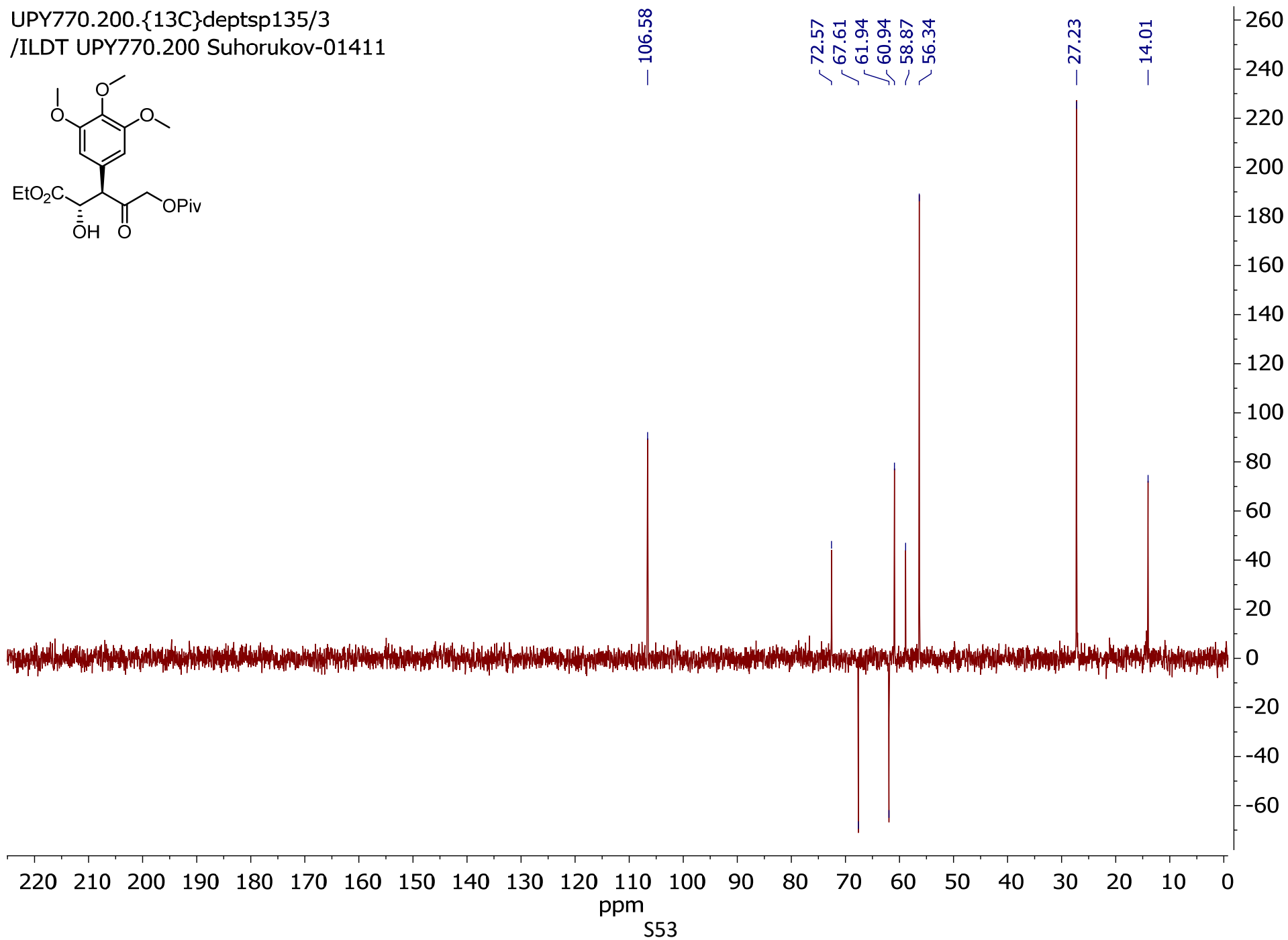
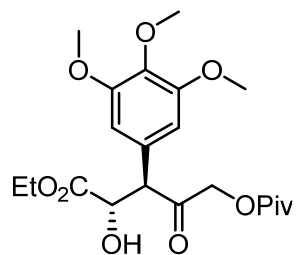


### NMR spectra of 5b

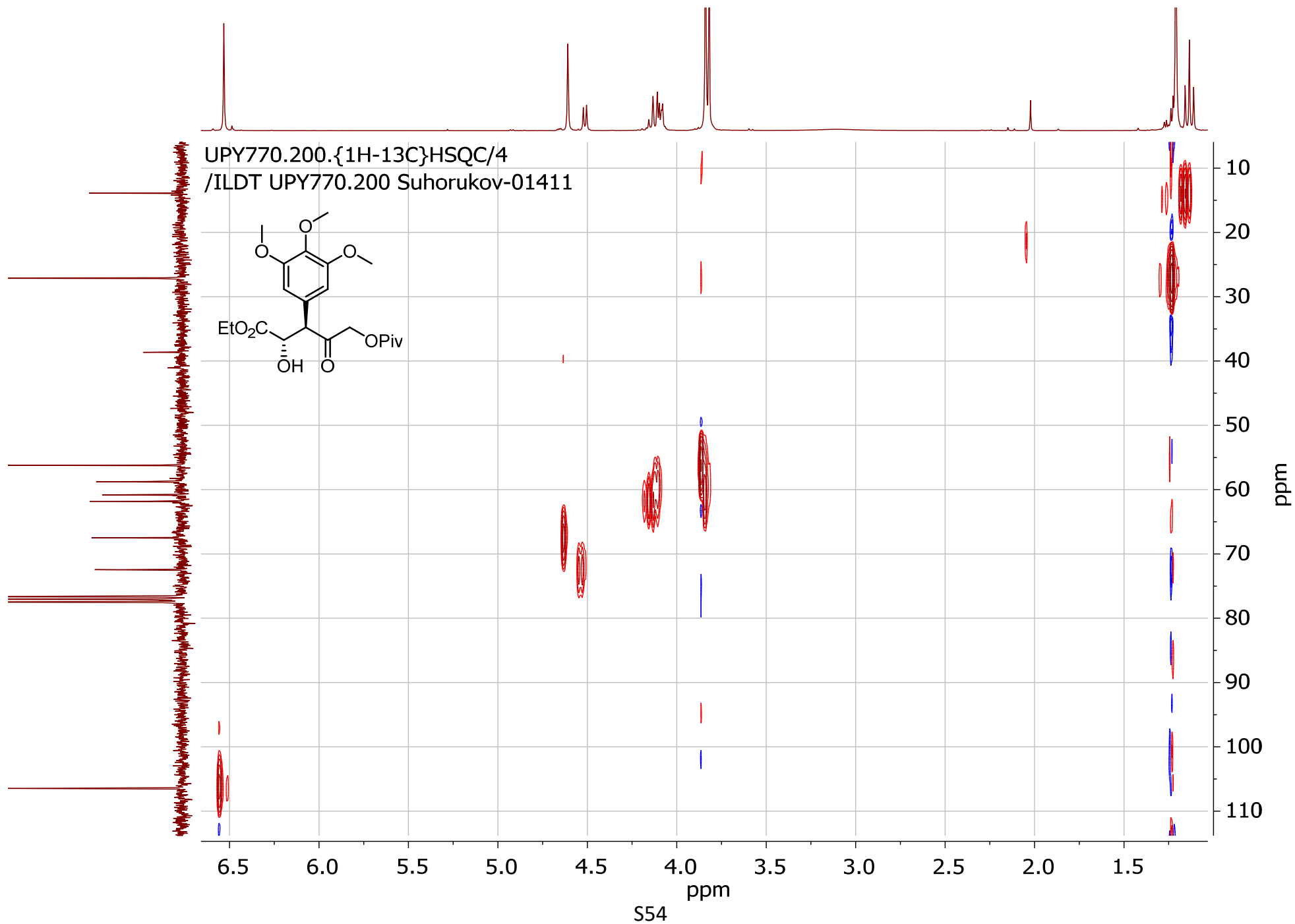
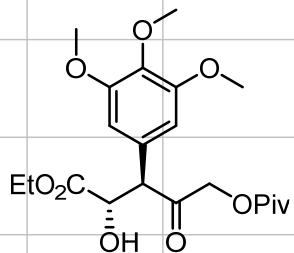


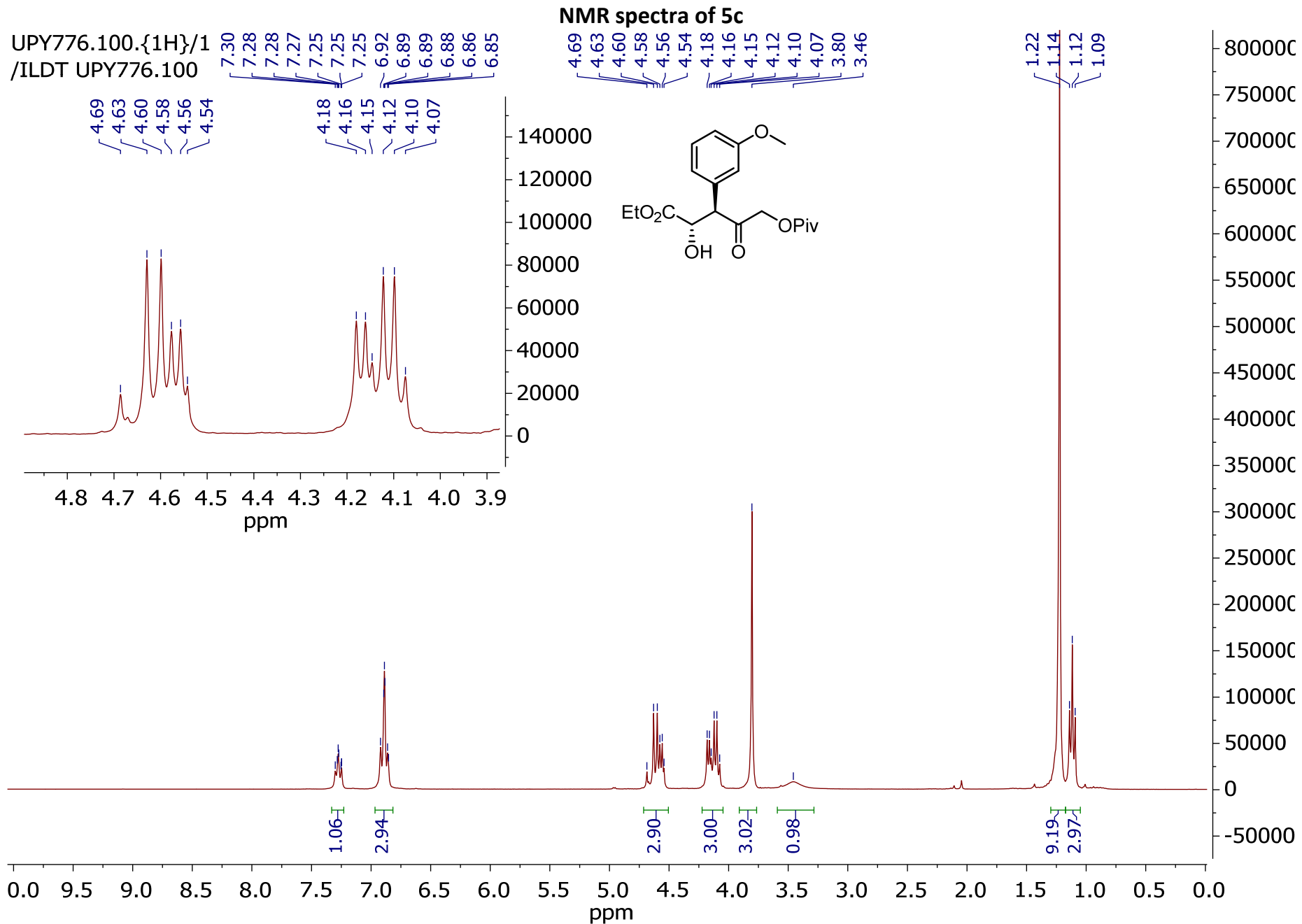


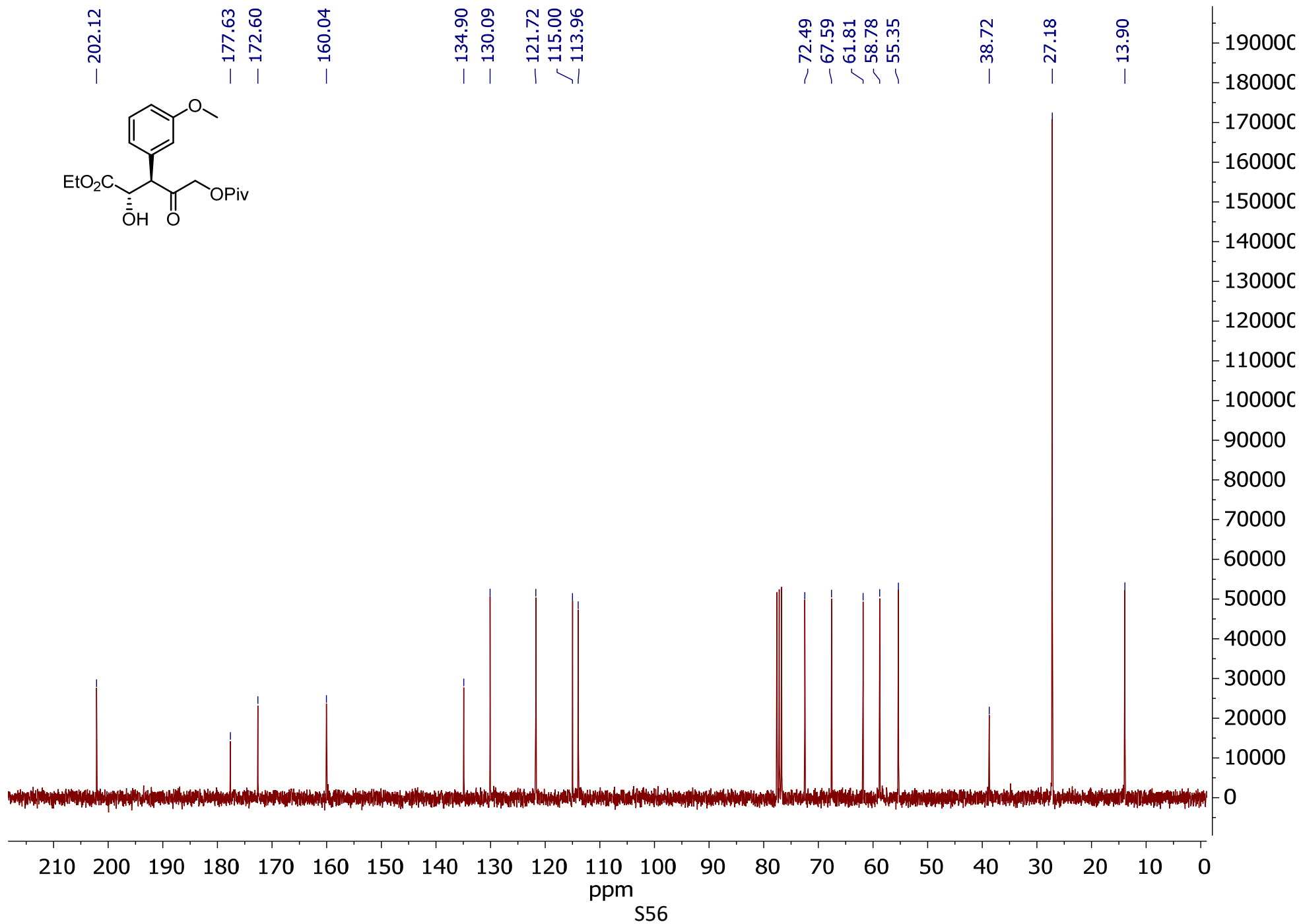
UPY770.200.{13C}depts135/3  
/ILDTP UPY770.200 Suhorukov-01411



UPY770.200.{1H-13C}HSQC/4  
/ILDT UPY770.200 Suhorukov-01411

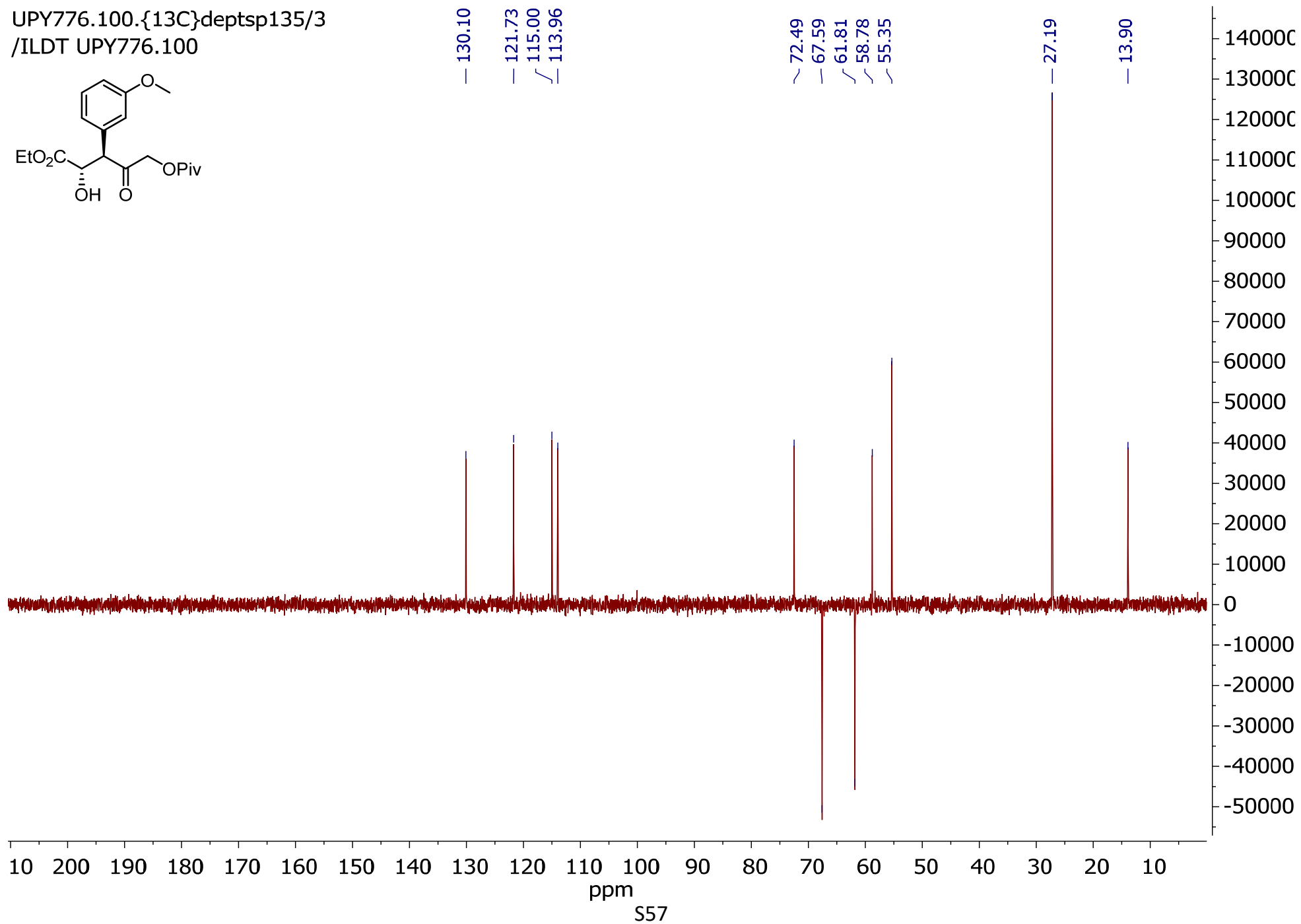
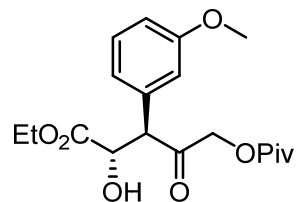






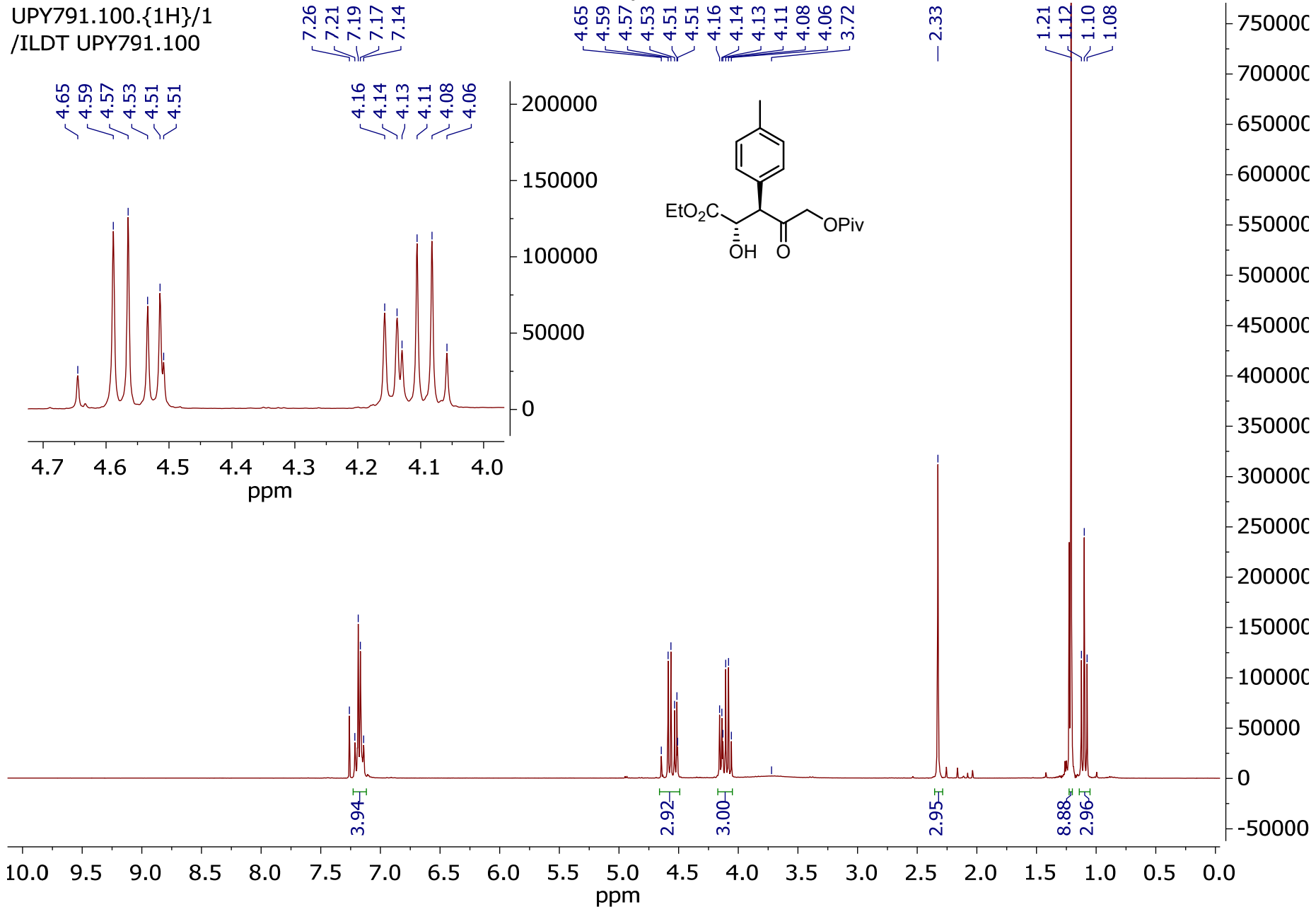


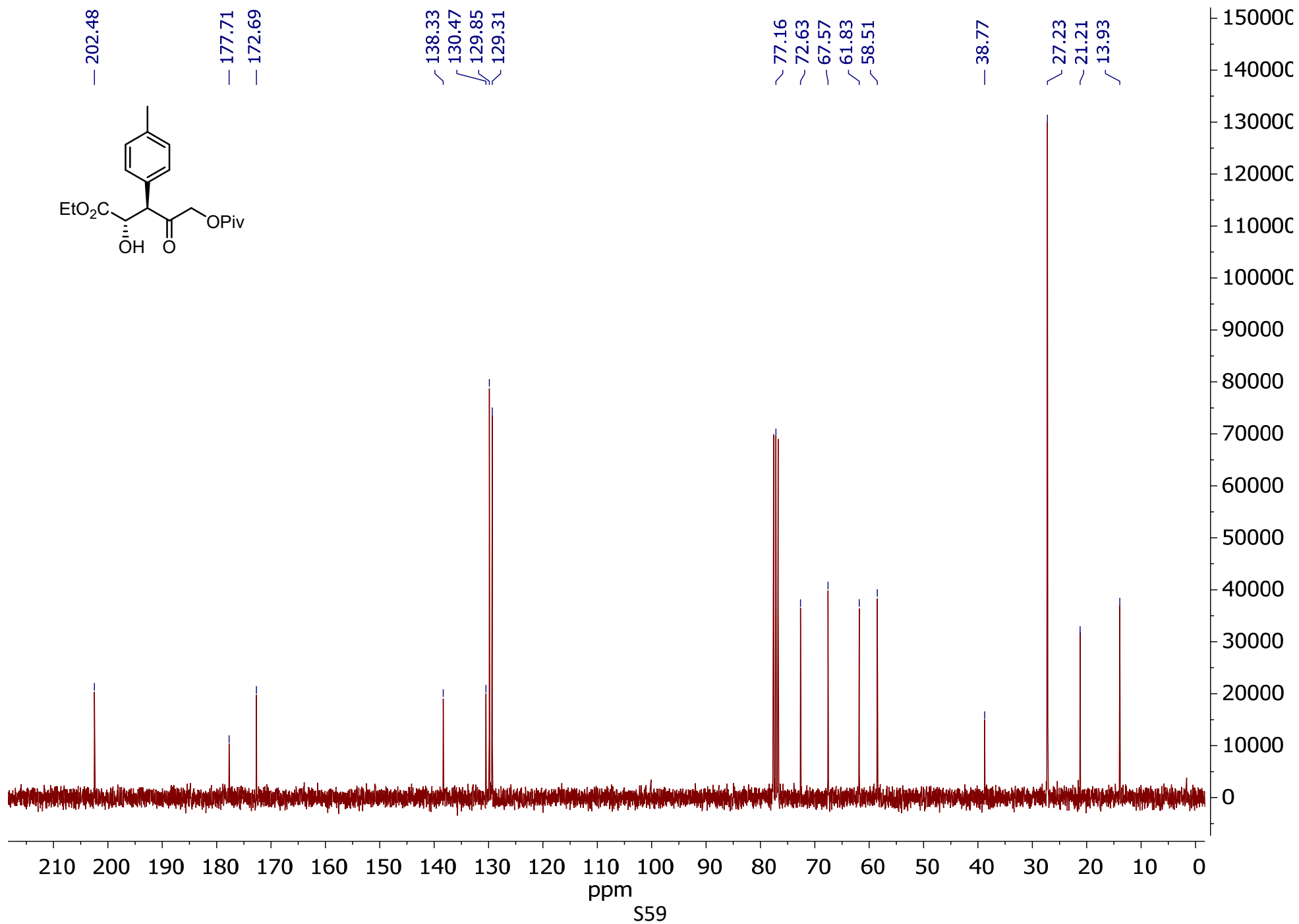
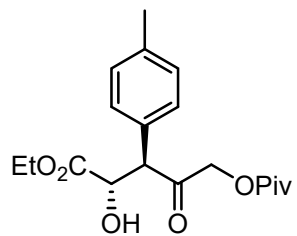
UPY776.100.{13C}depts135/3  
/ILD T UPY776.100



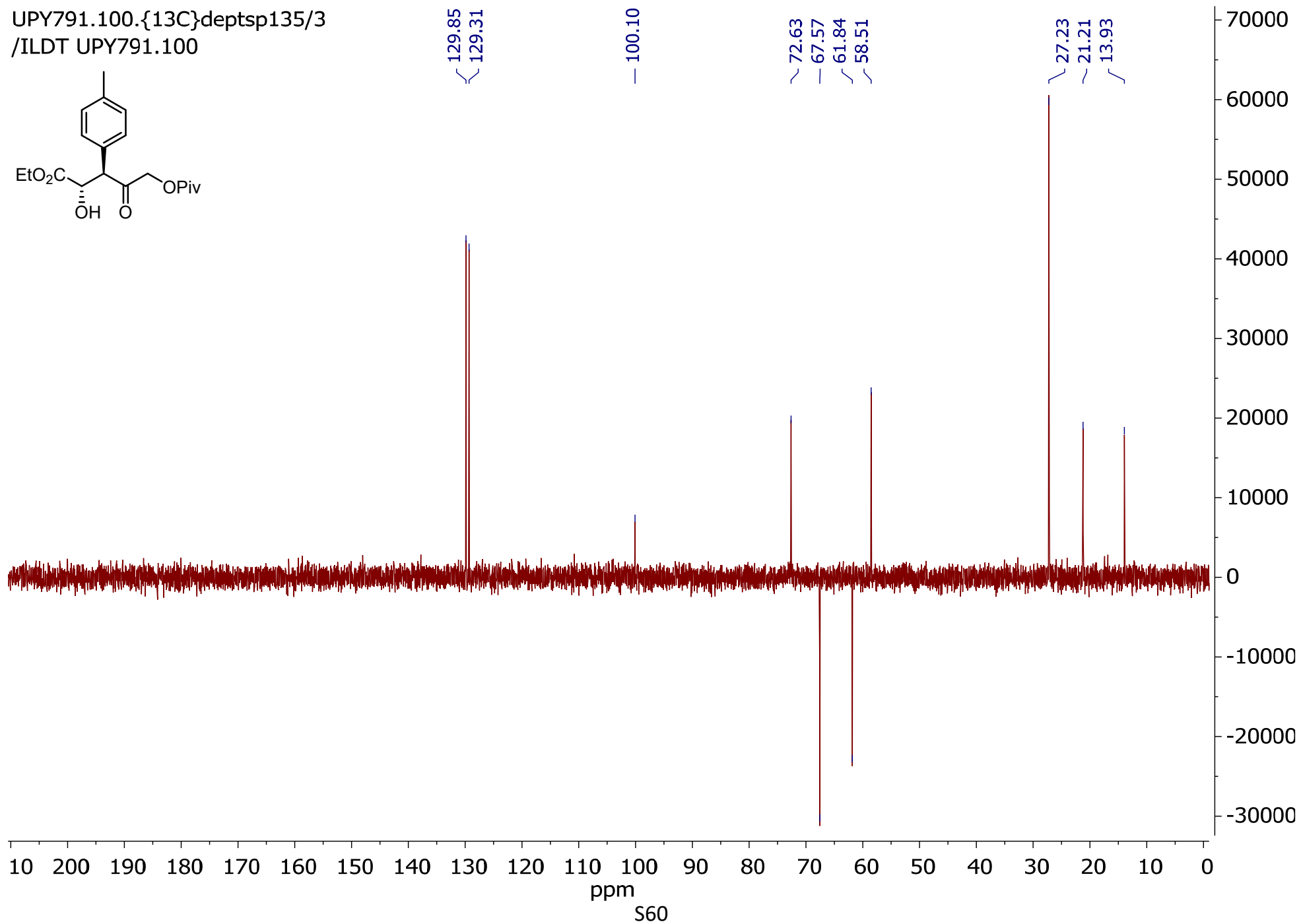
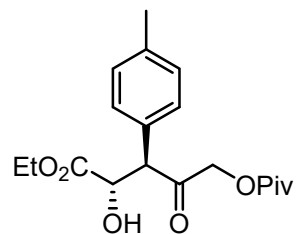
UPY791.100.{1H}/1  
/ILDY791.100

### NMR spectra of 5d

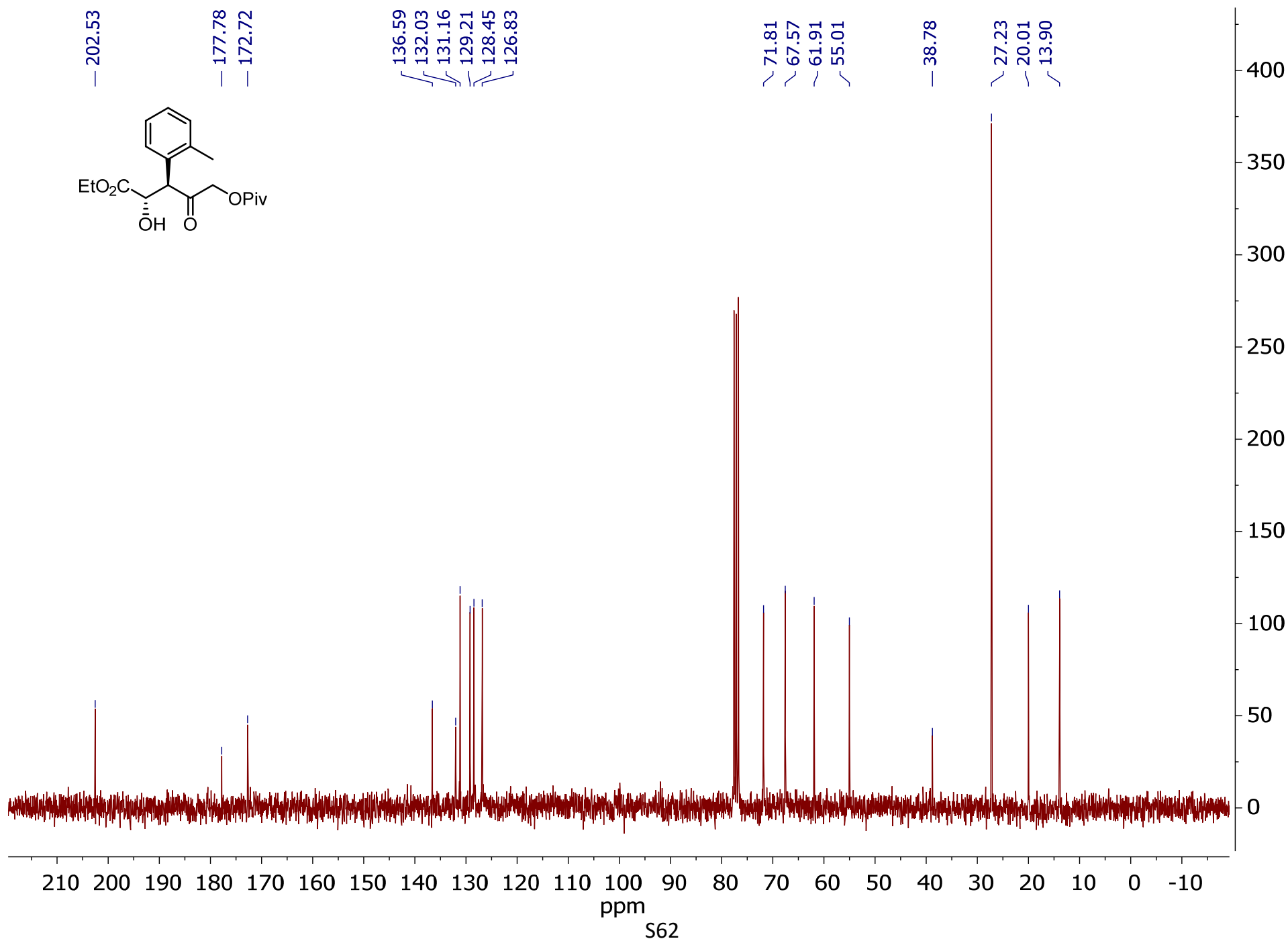
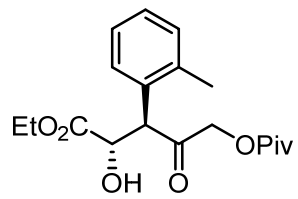




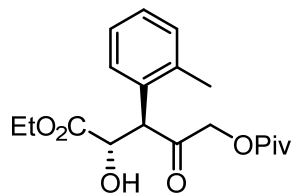
UPY791.100.{13C}deptsp135/3  
/ILD T UPY791.100







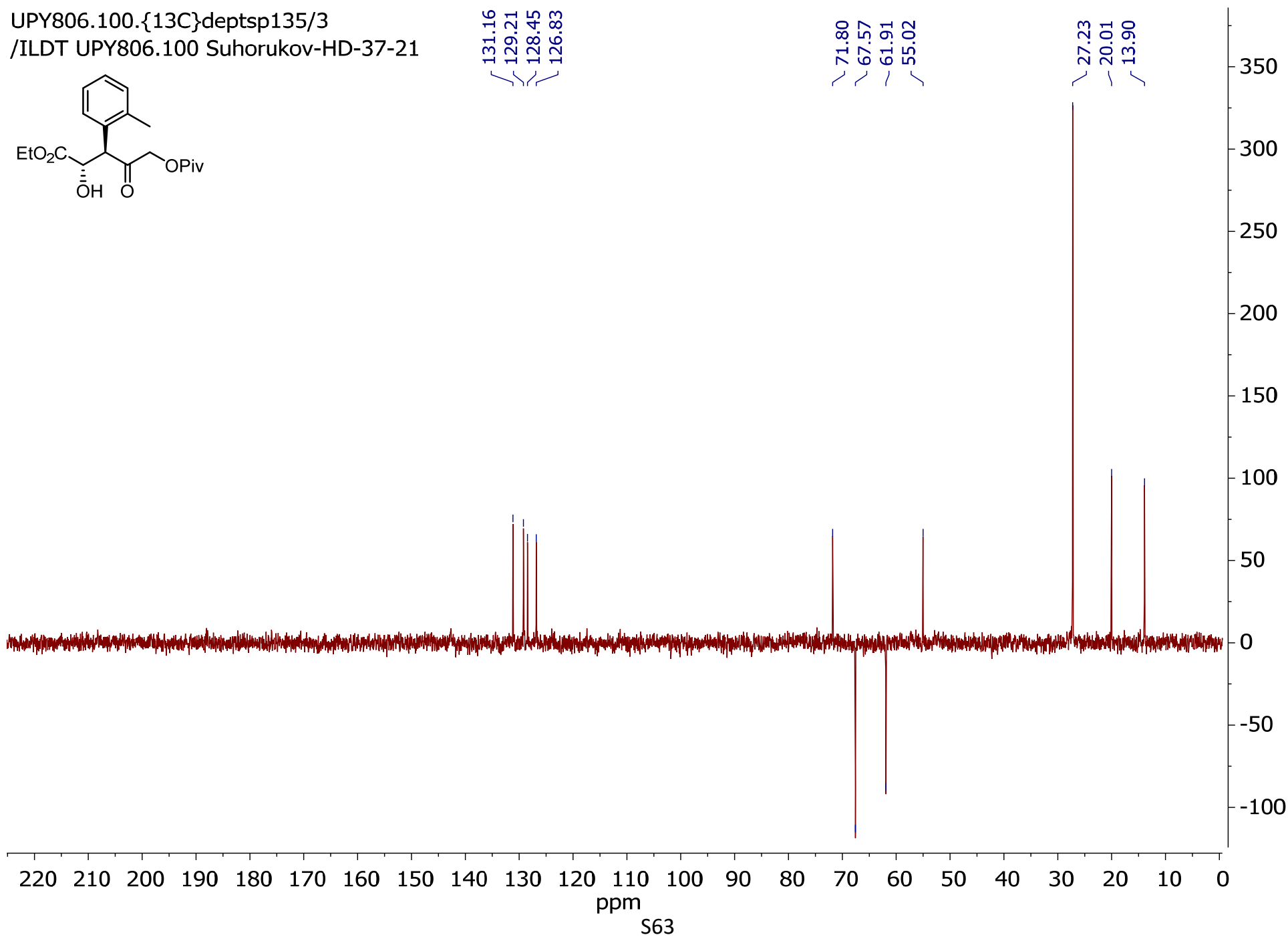
UPY806.100.{13C}depts135/3  
/ILD T UPY806.100 Suhorukov-HD-37-21



131.16  
129.21  
128.45  
126.83

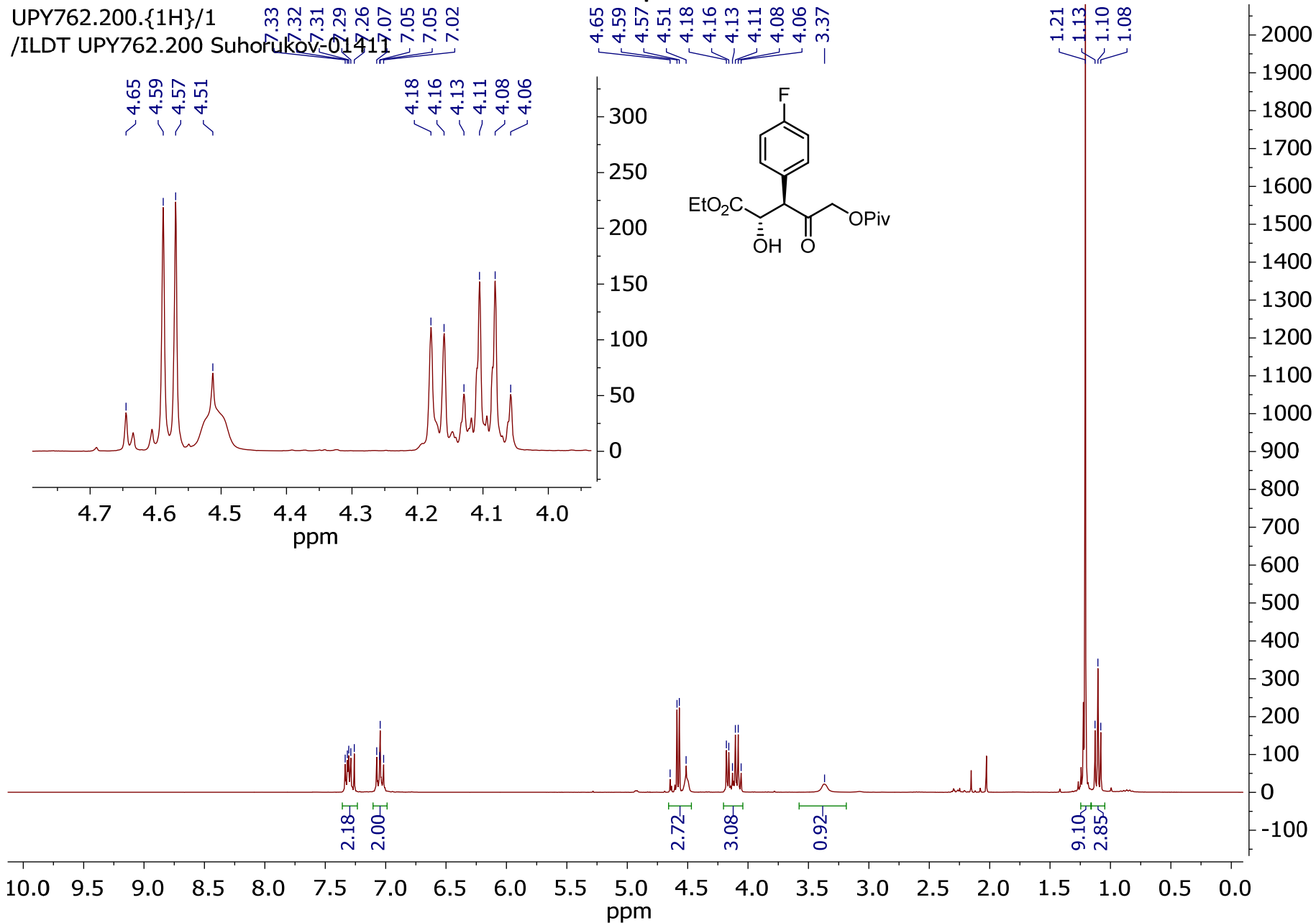
71.80  
67.57  
61.91  
55.02

27.23  
20.01  
13.90

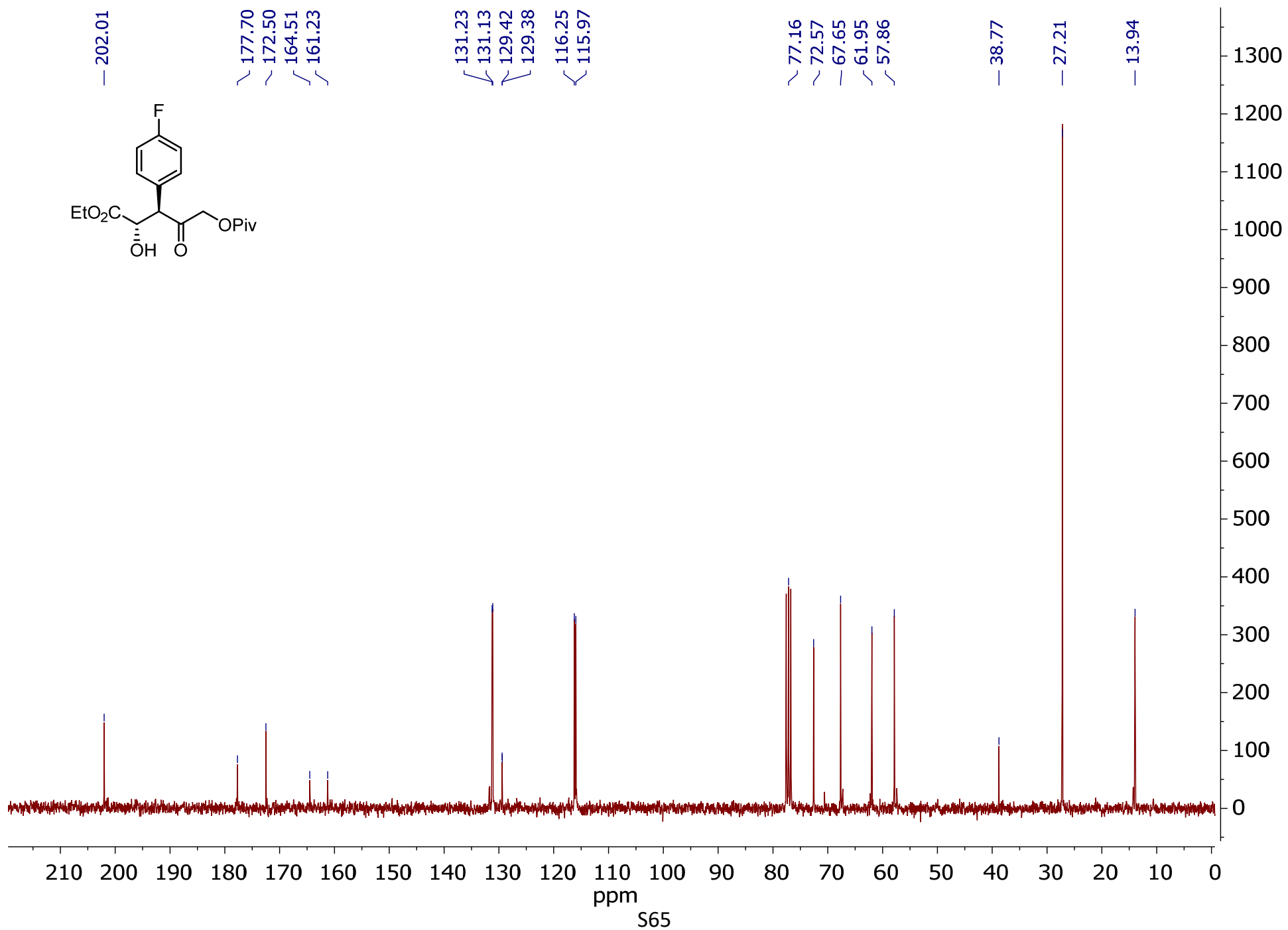
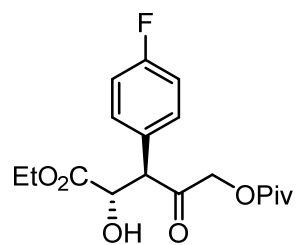


UPY762.200.{1H}/1  
/ILD T UPY762.200 Suhorukov-01411

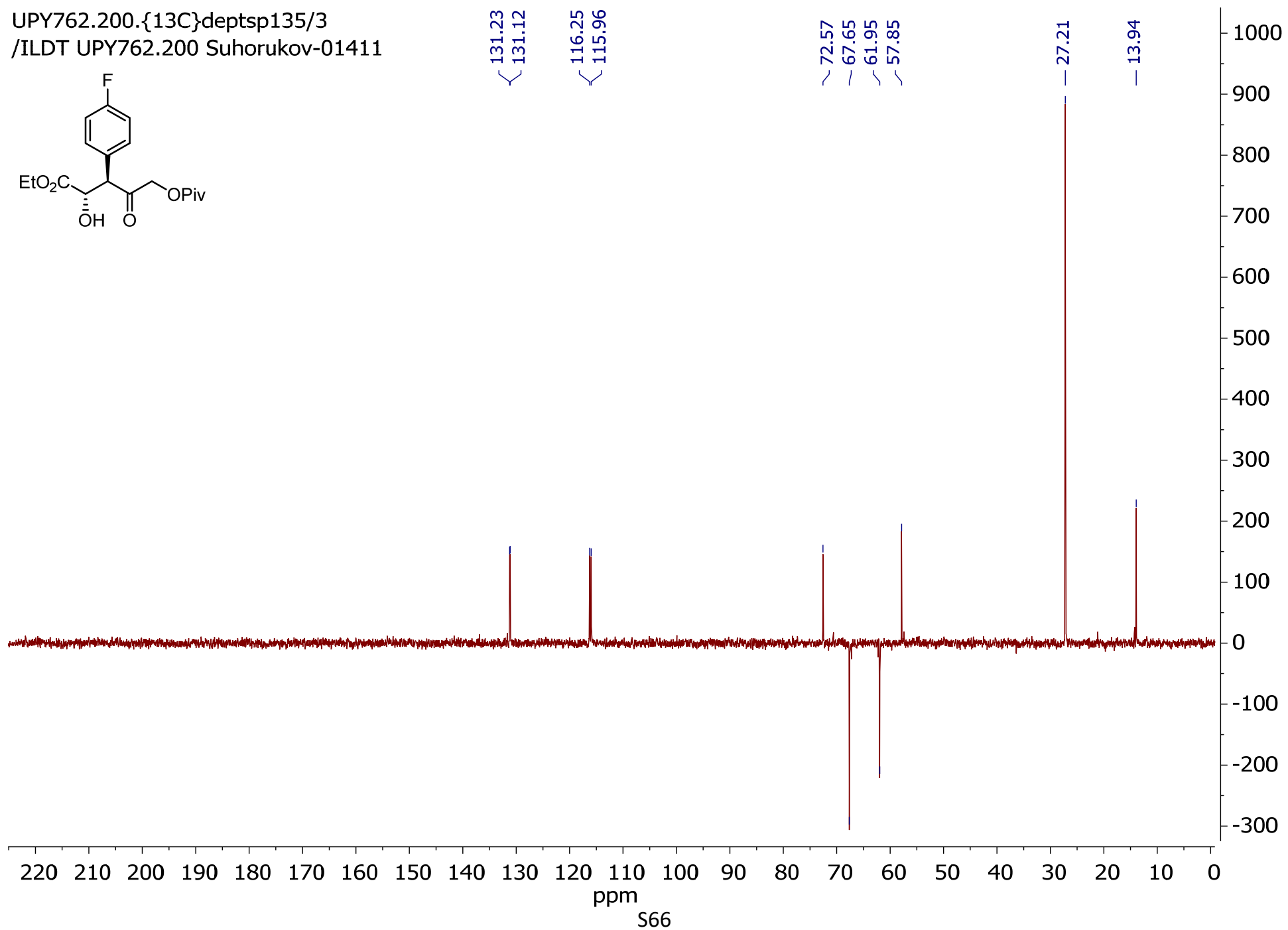
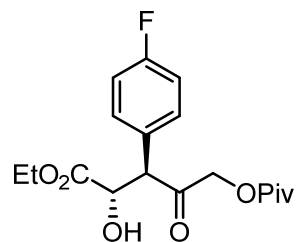
### NMR spectra of 5f



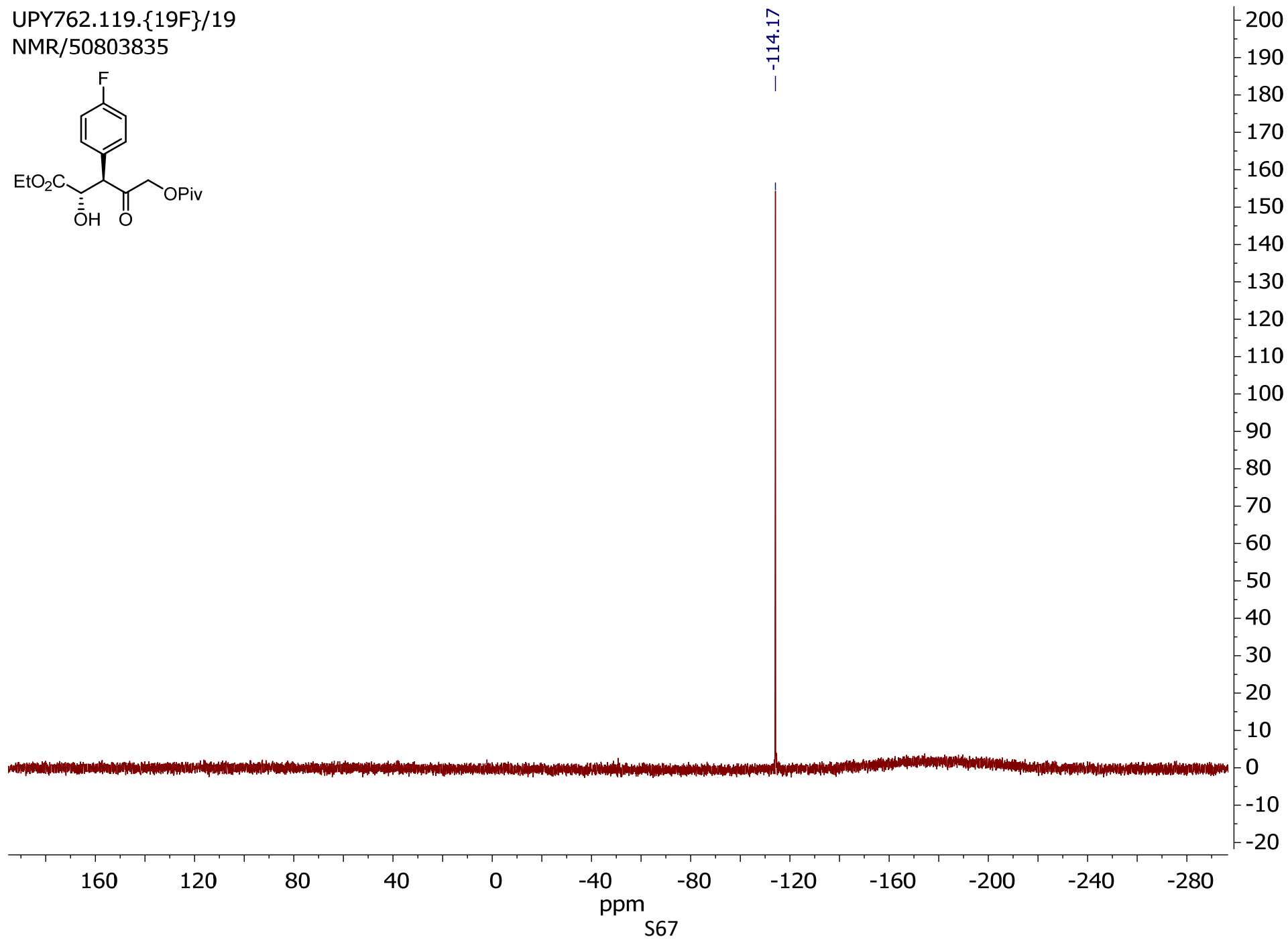
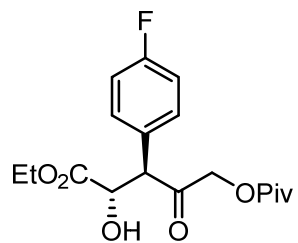




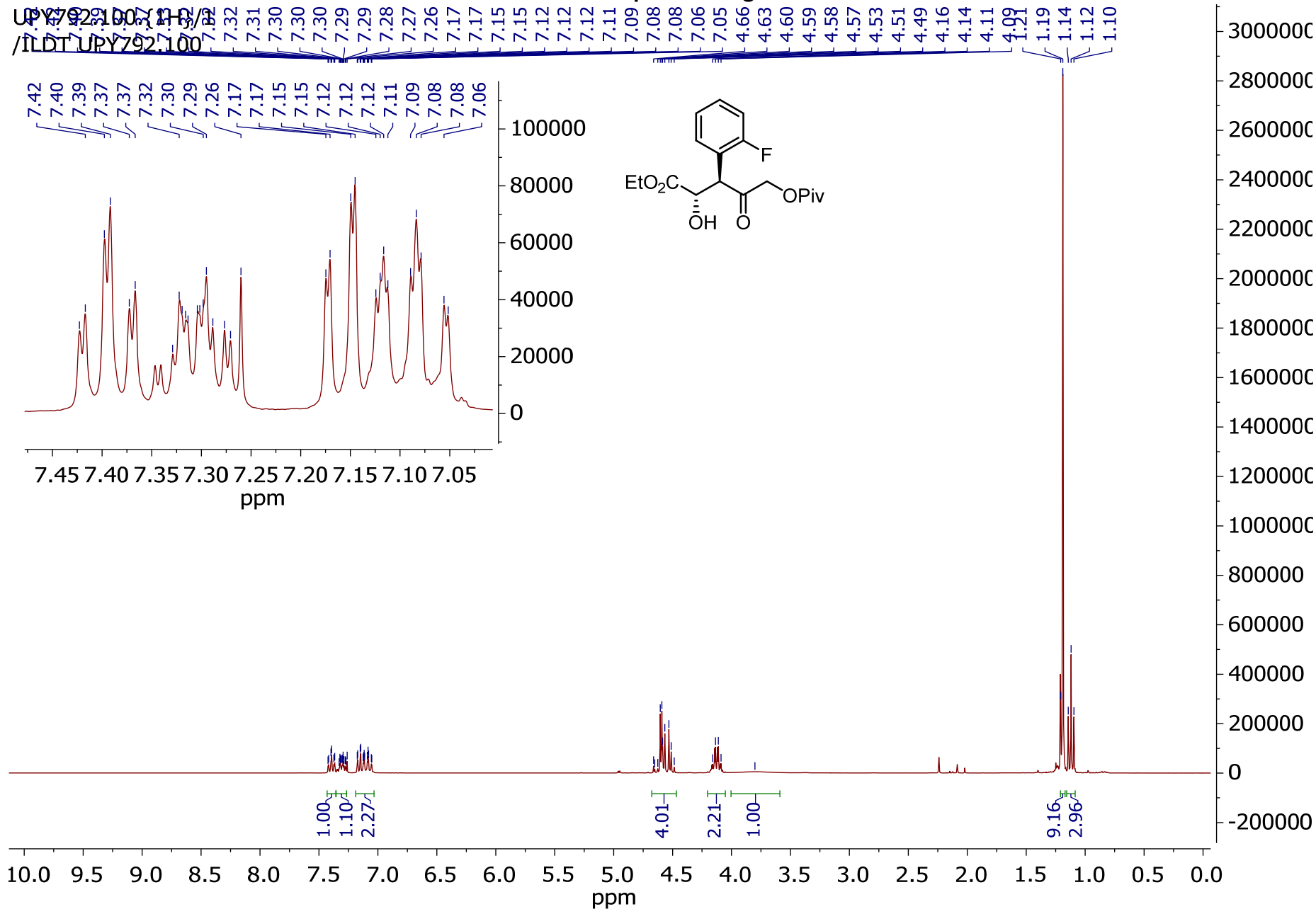
UPY762.200.{13C}deptsp135/3  
/ILDY UPY762.200 Suhorukov-01411

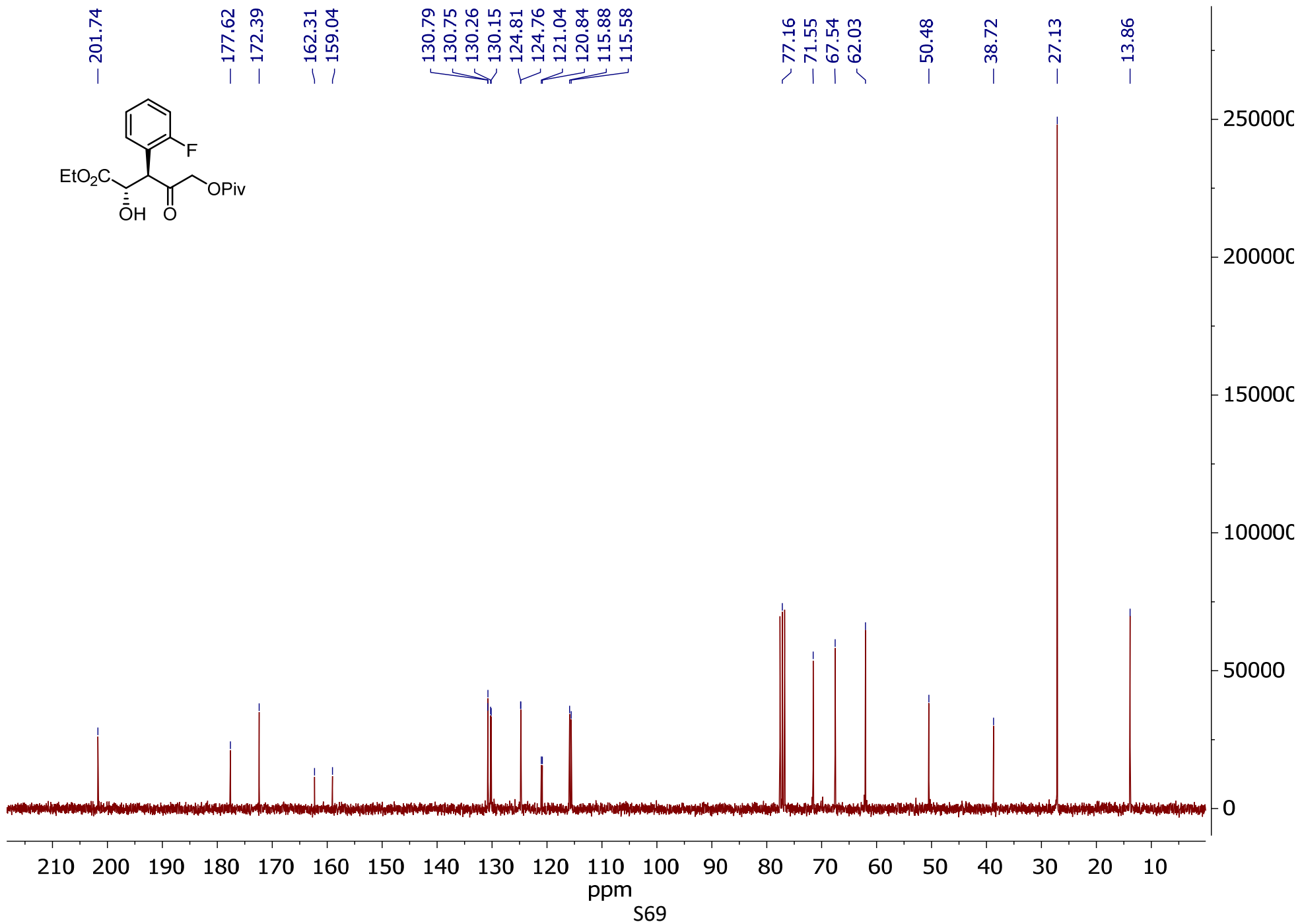
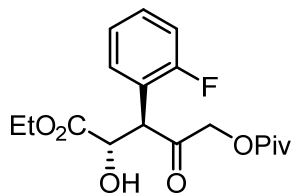


UPY762.119.{19F}/19  
NMR/50803835

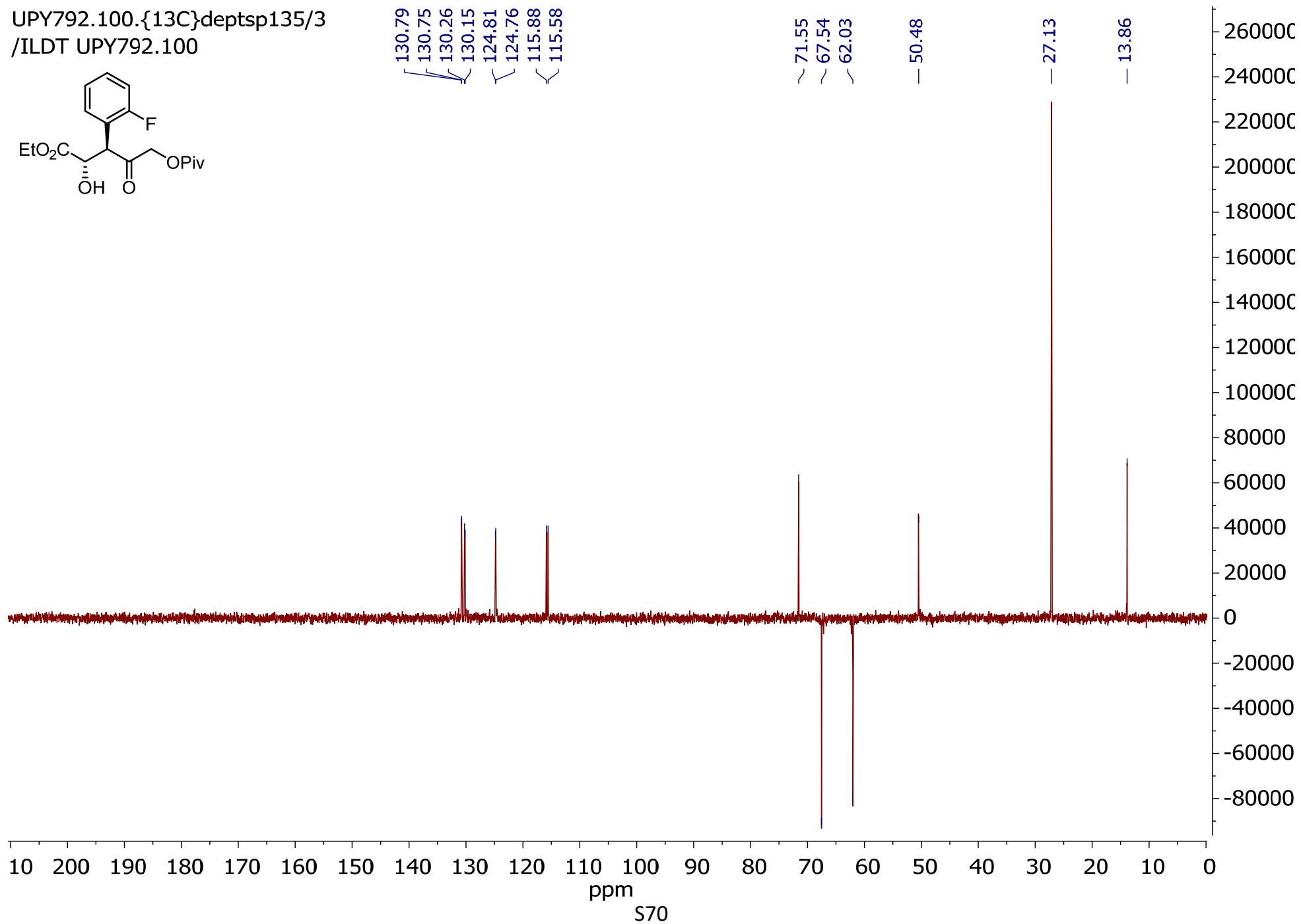
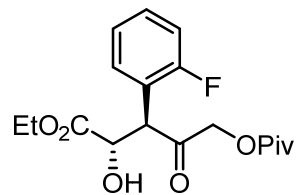


NMR spectra of 5g

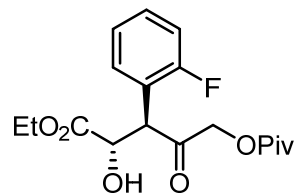




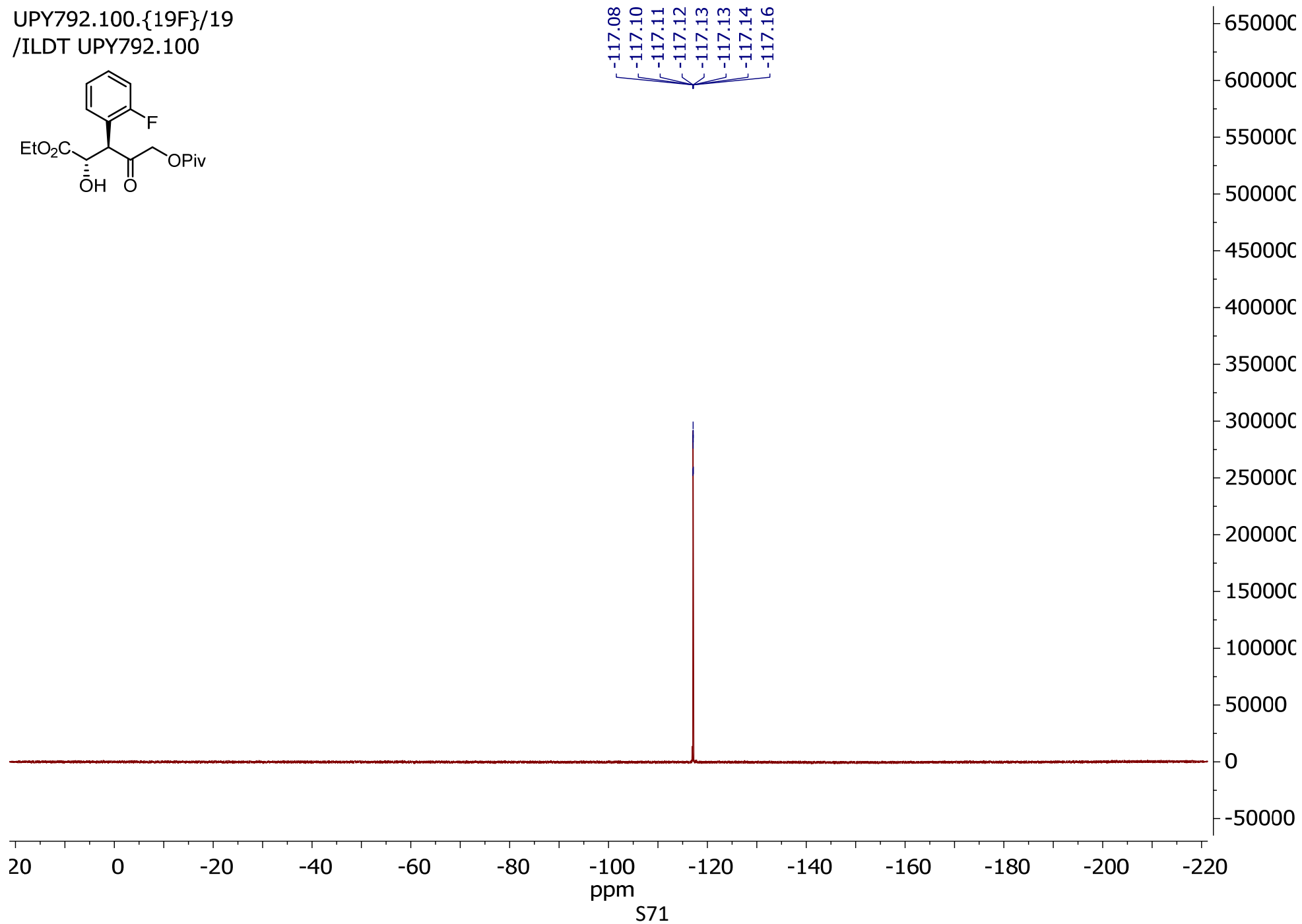
UPY792.100.{13C}depts135/3  
/ILD T UPY792.100



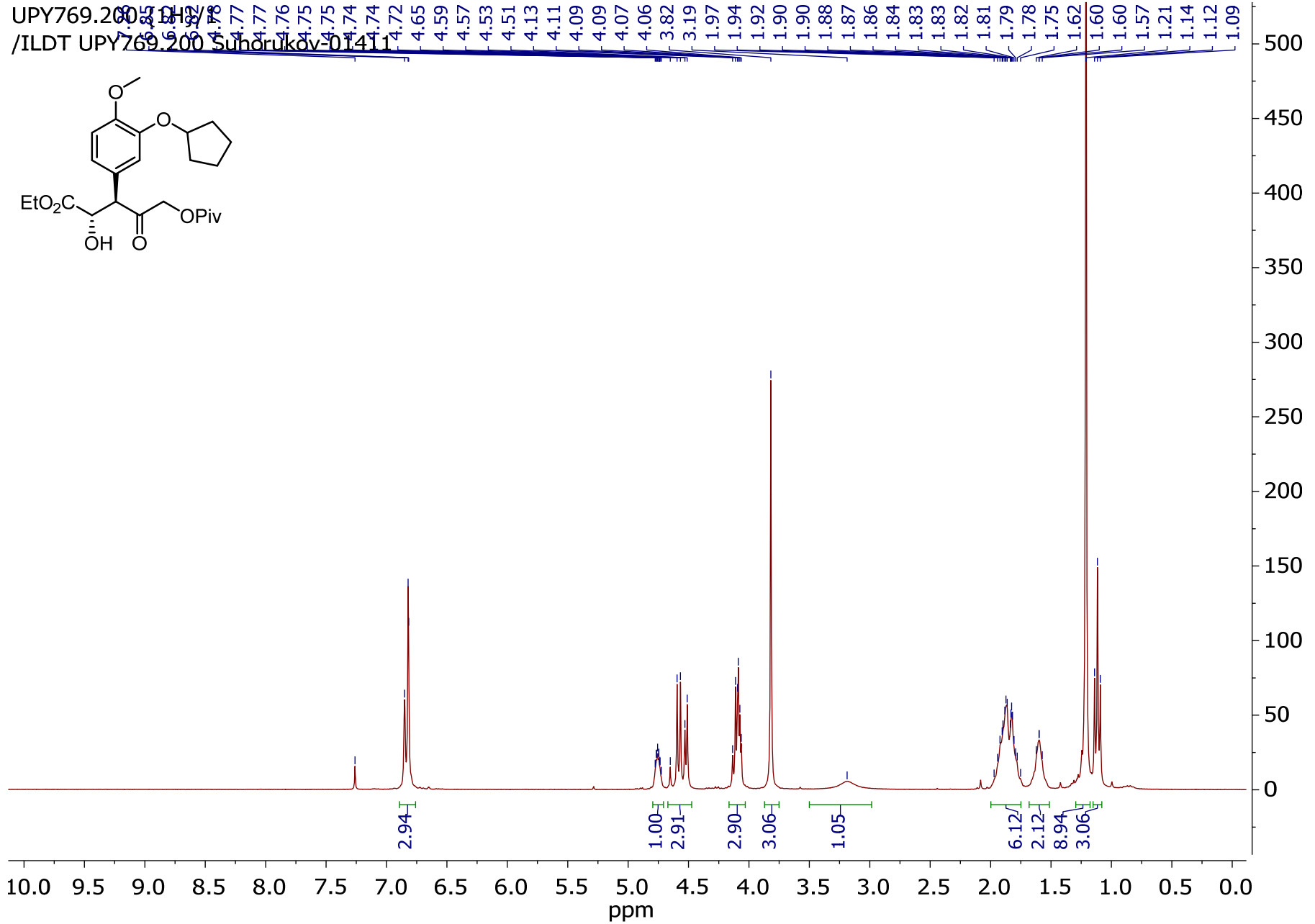
UPY792.100.{19F}/19  
/ILD T UPY792.100



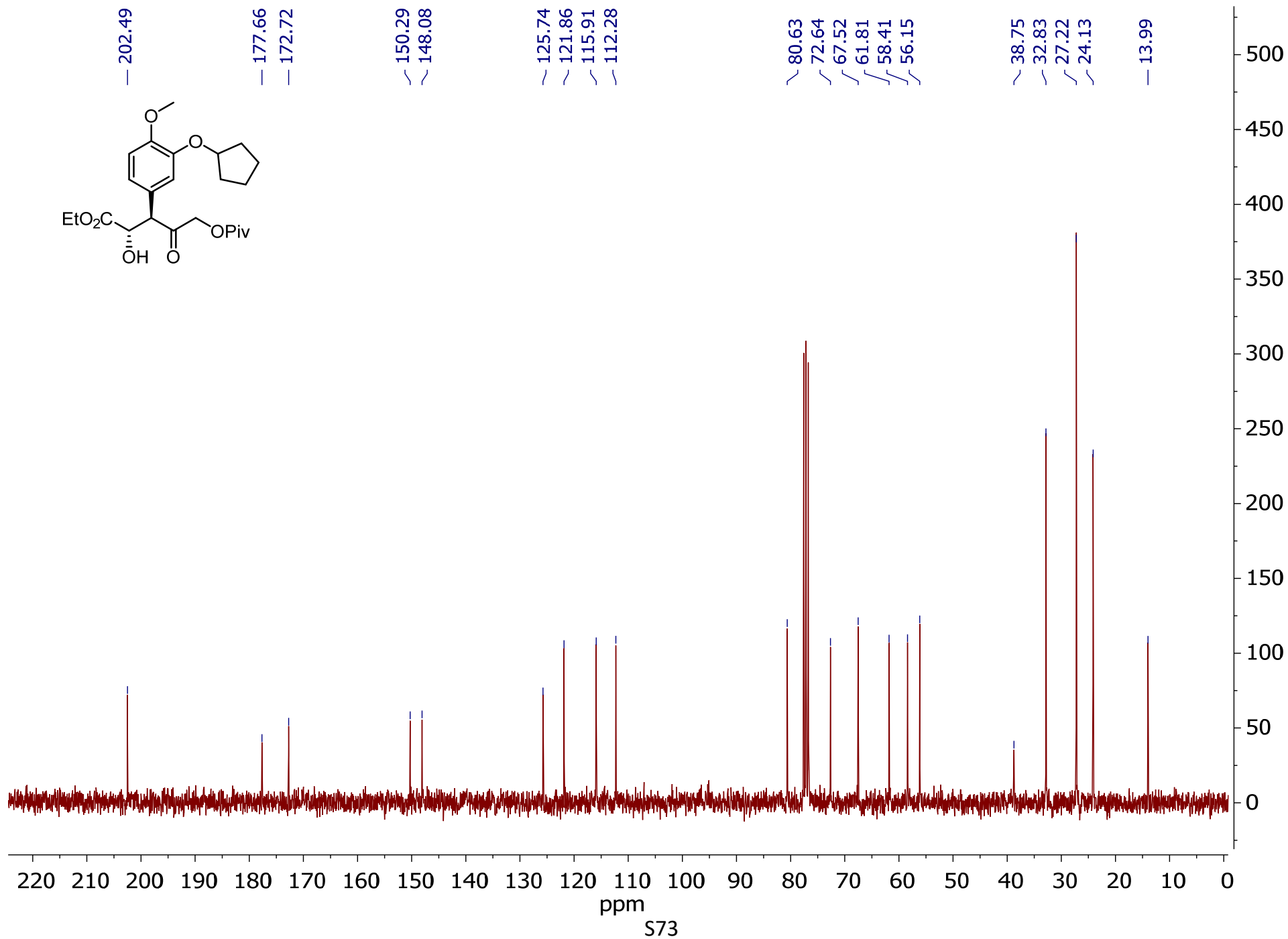
-117.08  
-117.10  
-117.11  
-117.12  
-117.13  
-117.13  
-117.14  
-117.16



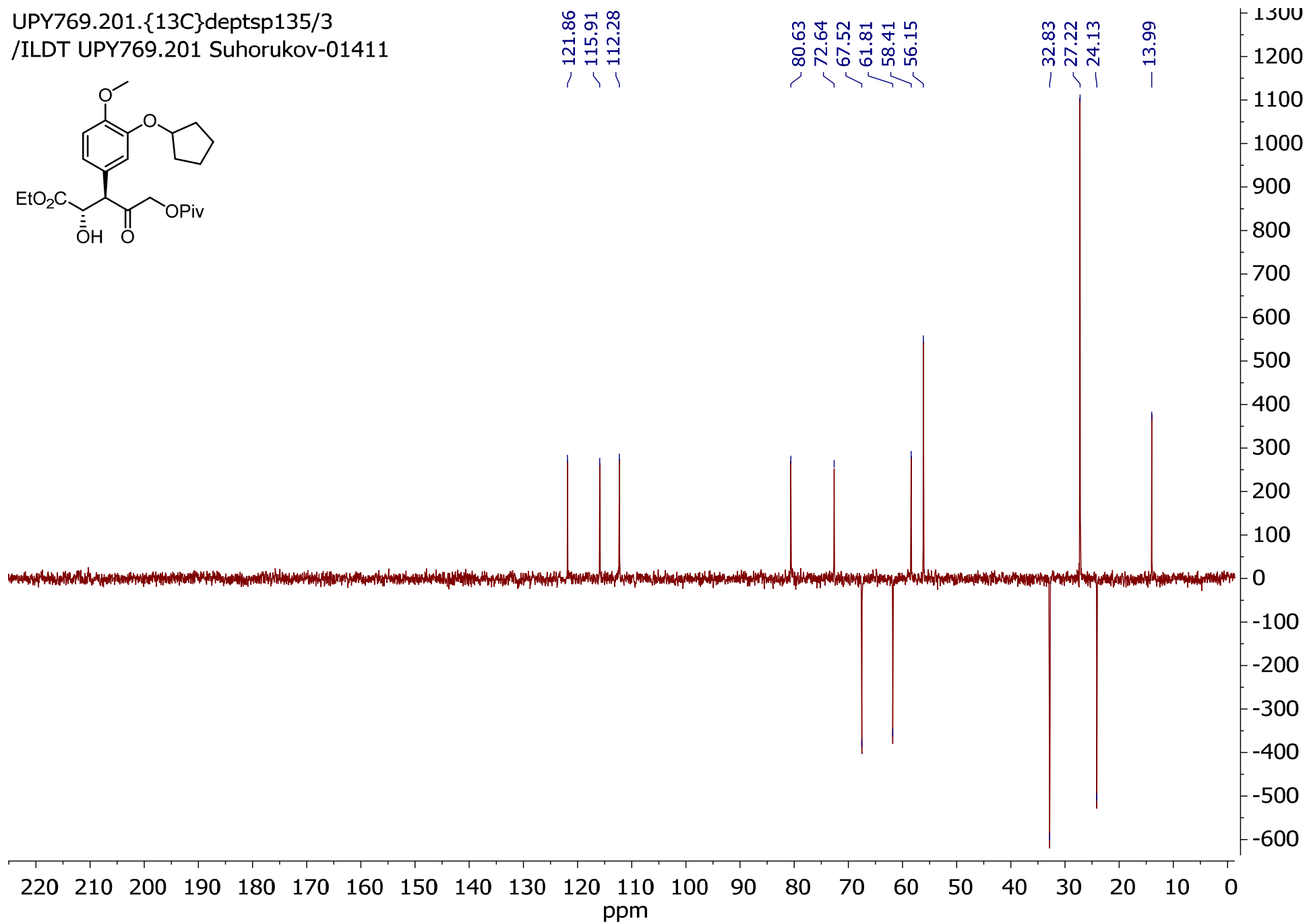
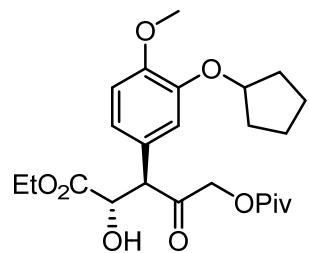
# NMR spectra of 5h

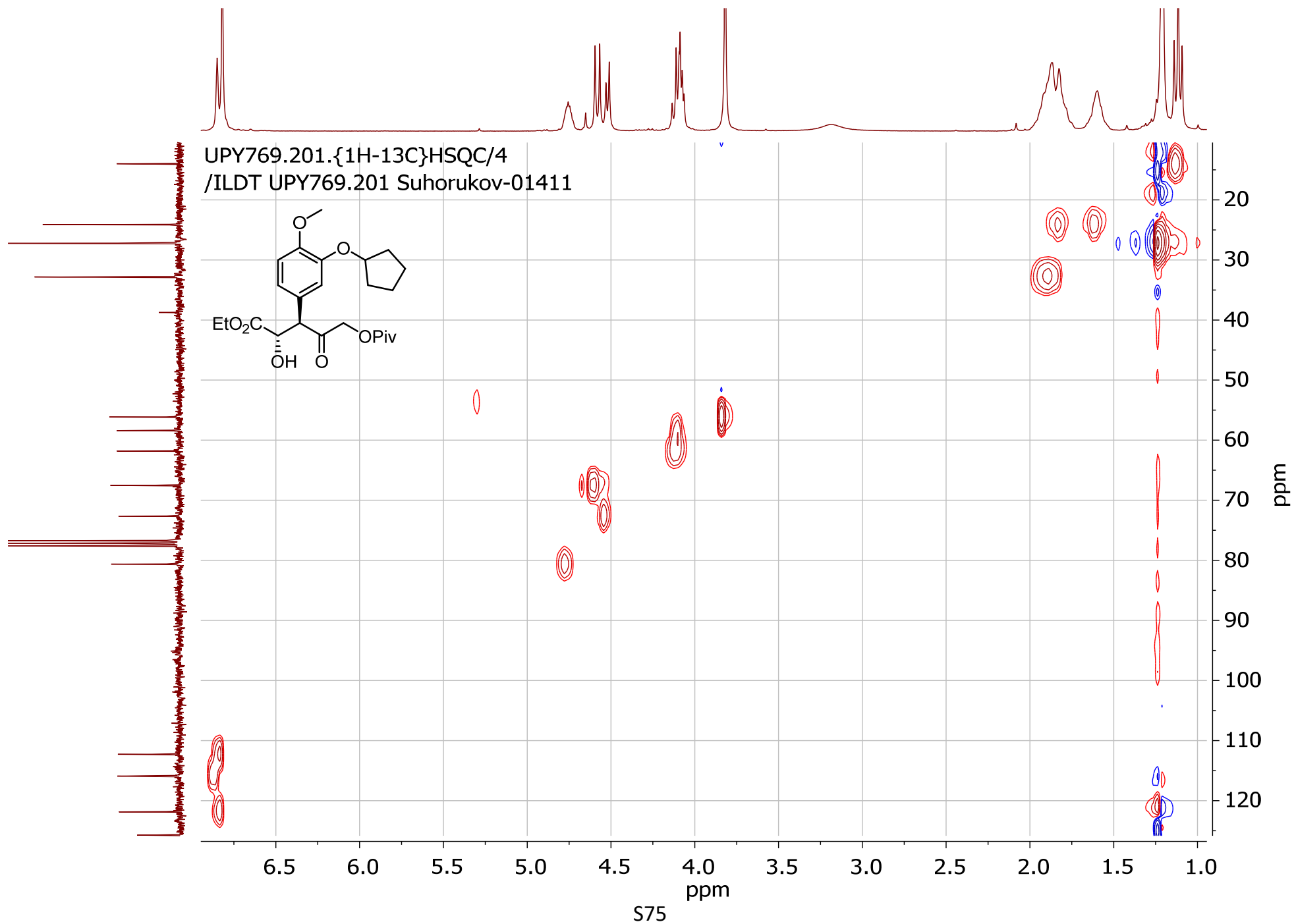






UPY769.201.{13C}deptsp135/3  
/ILDT UPY769.201 Suhorukov-01411





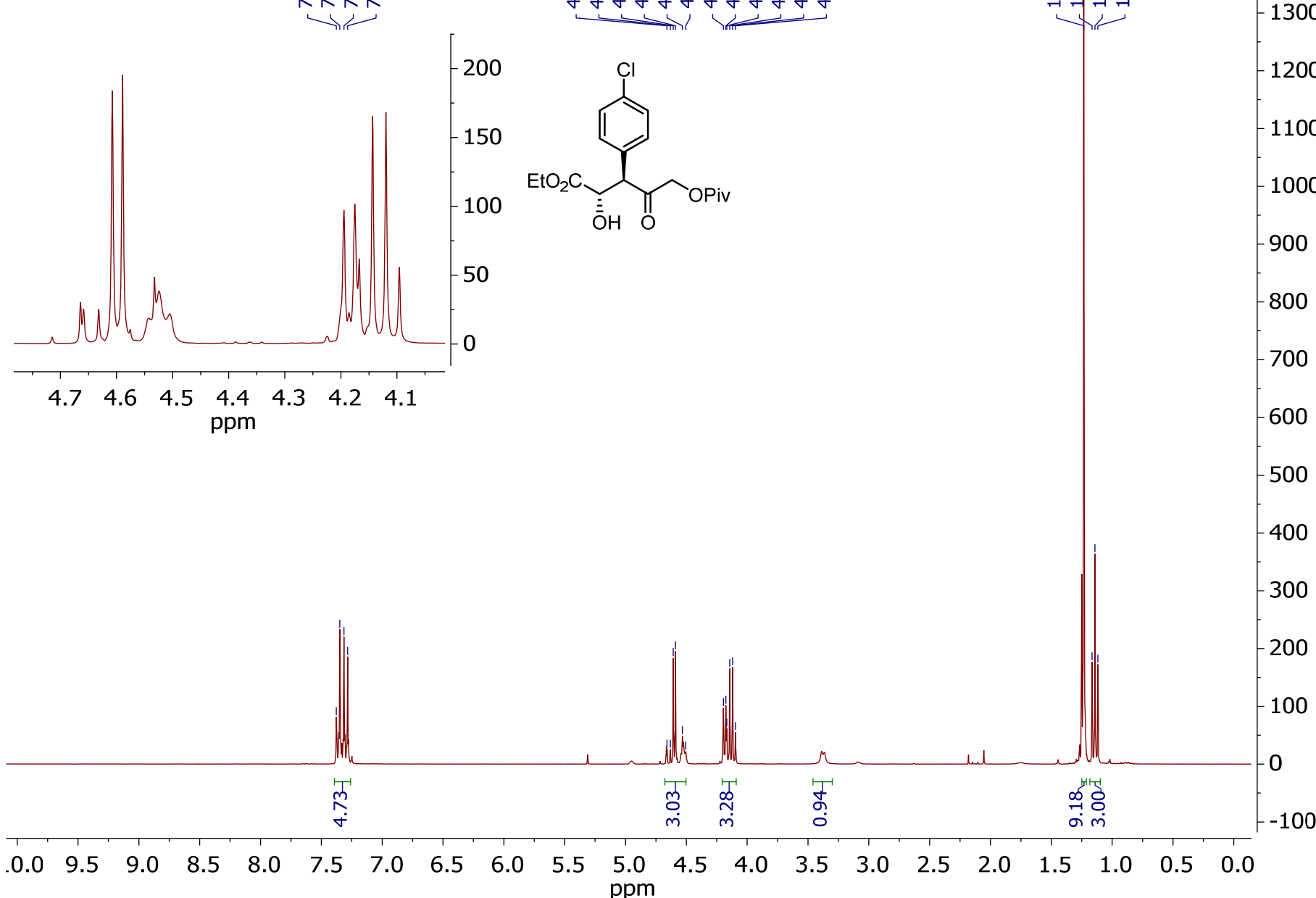
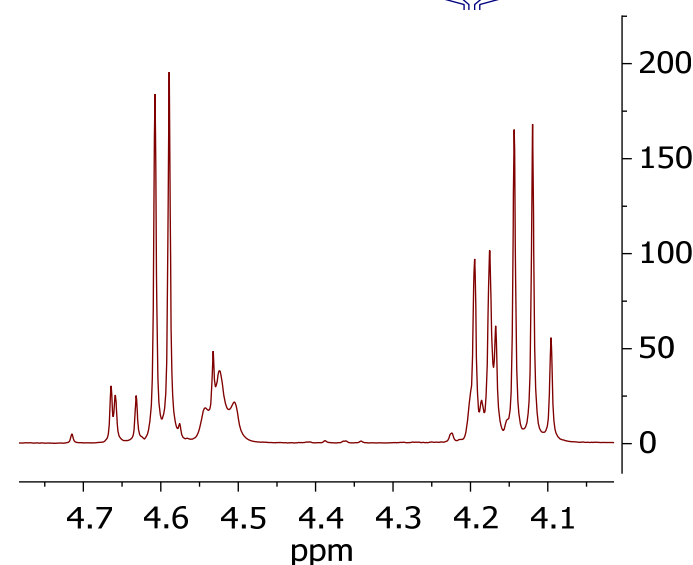
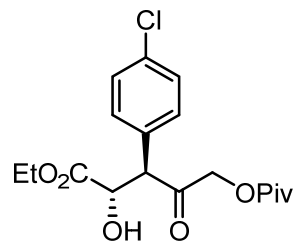
UPY949.100.{1H}/1

7.38  
7.35  
7.31  
7.28

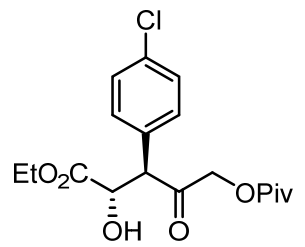
### NMR spectra of 5i

4.66  
4.63  
4.61  
4.59  
4.53  
4.51  
4.19  
4.18  
4.17  
4.14  
4.12  
4.10

1.23  
1.16  
1.14  
1.12



UPY949.000.{13C}/2



201.81  
177.71  
172.42

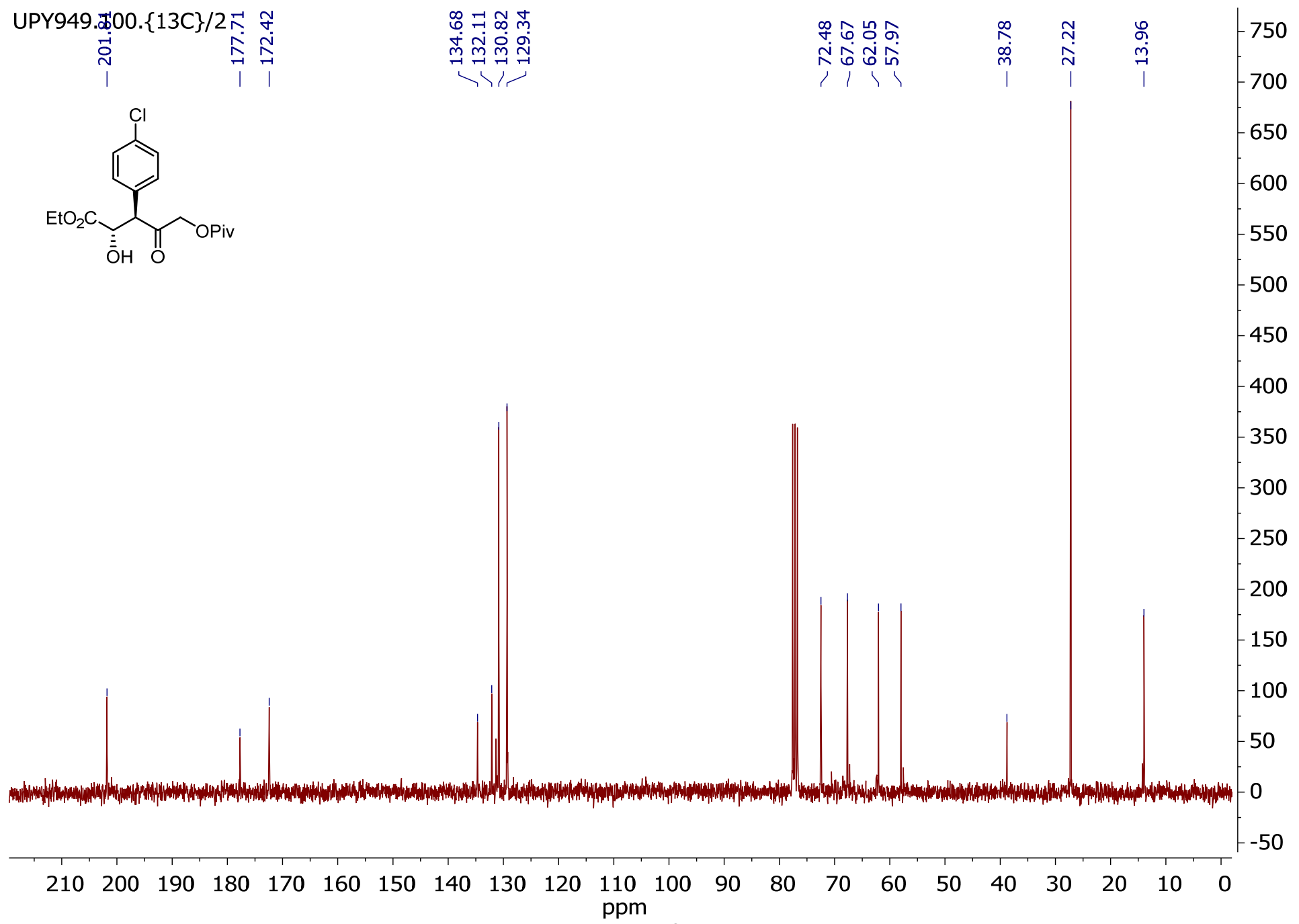
134.68  
132.11  
130.82  
129.34

72.48  
67.67  
62.05  
57.97

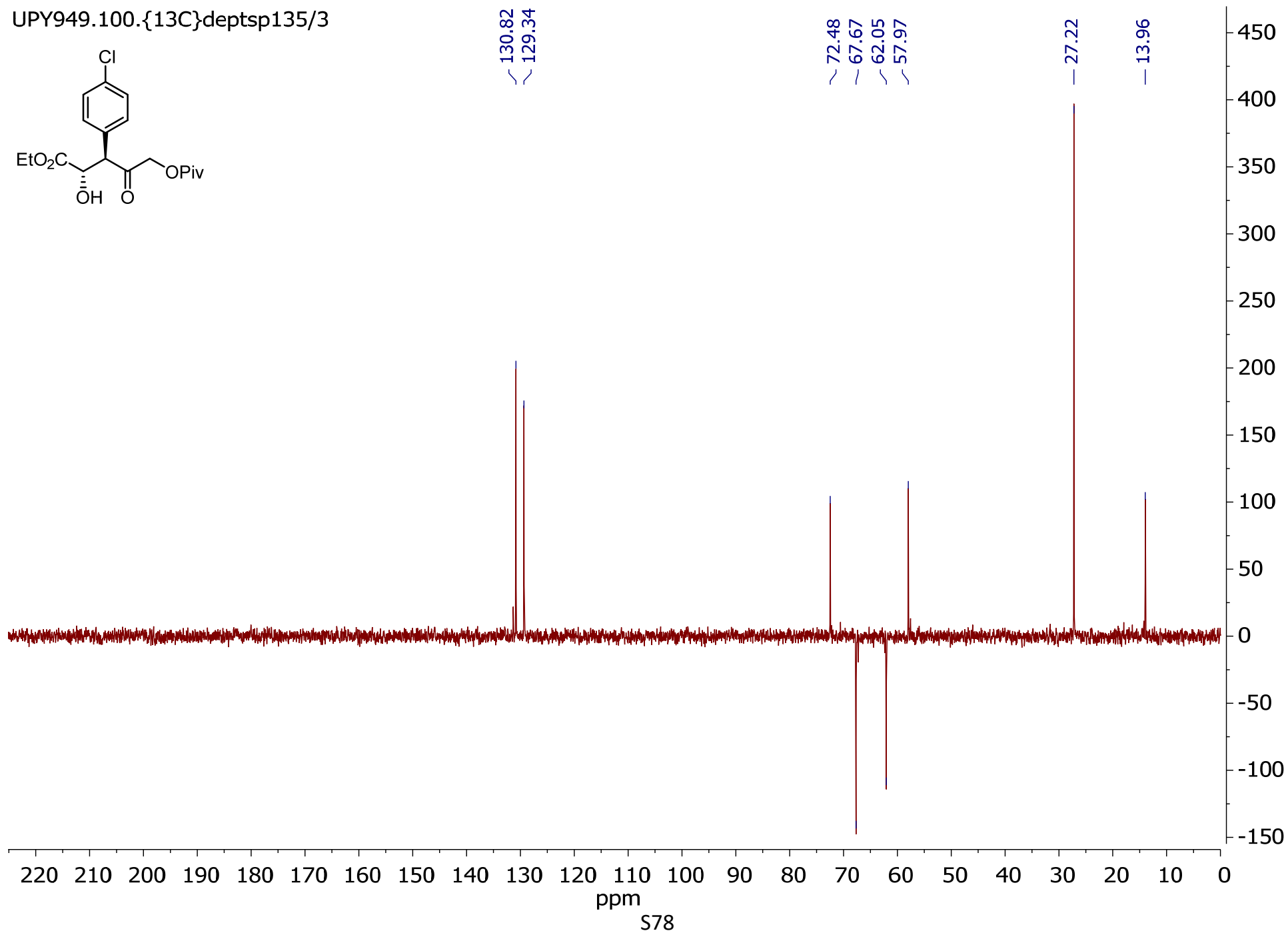
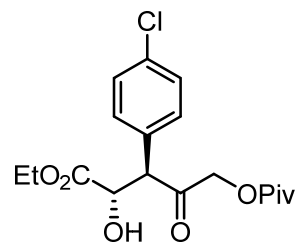
38.78

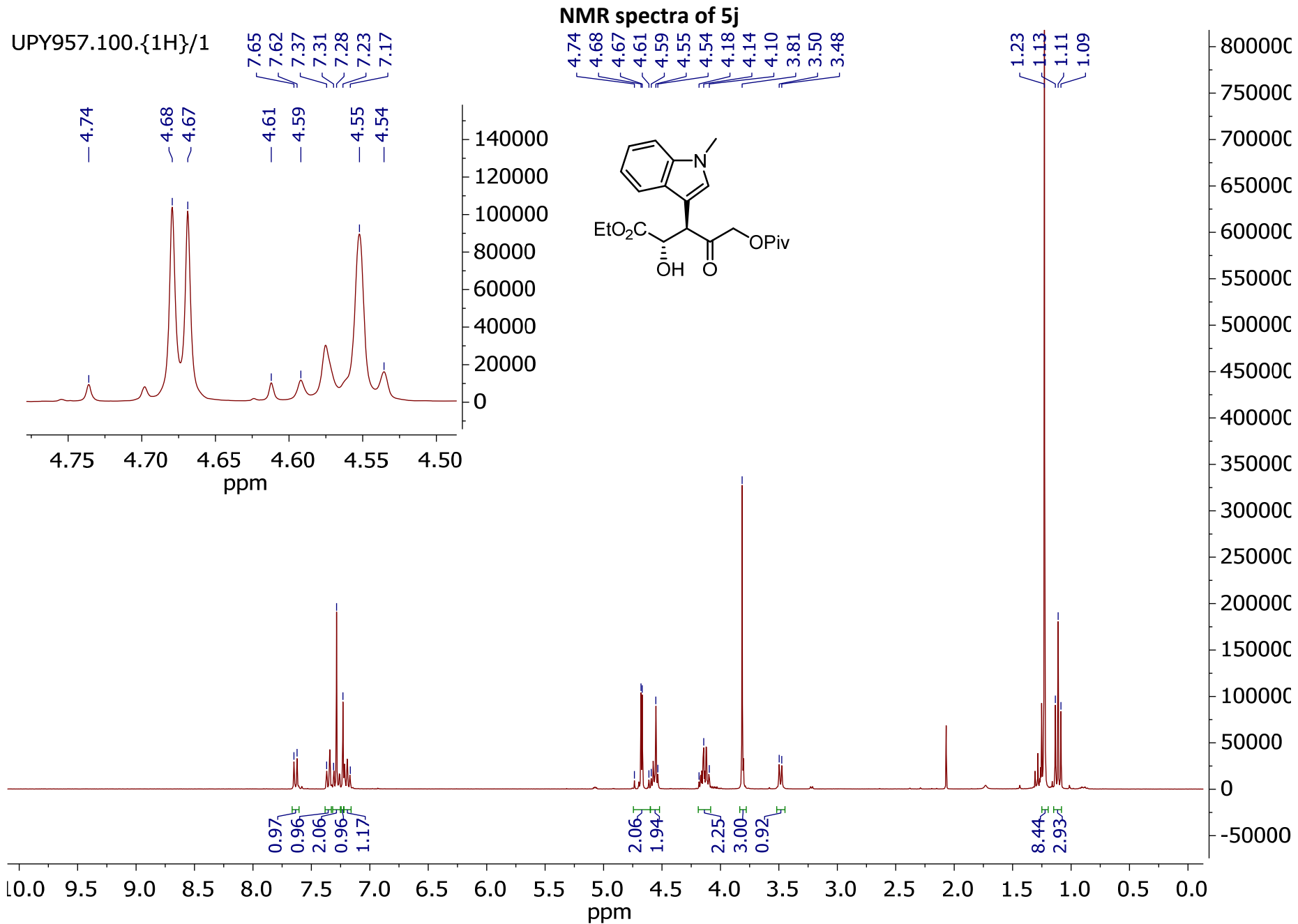
27.22

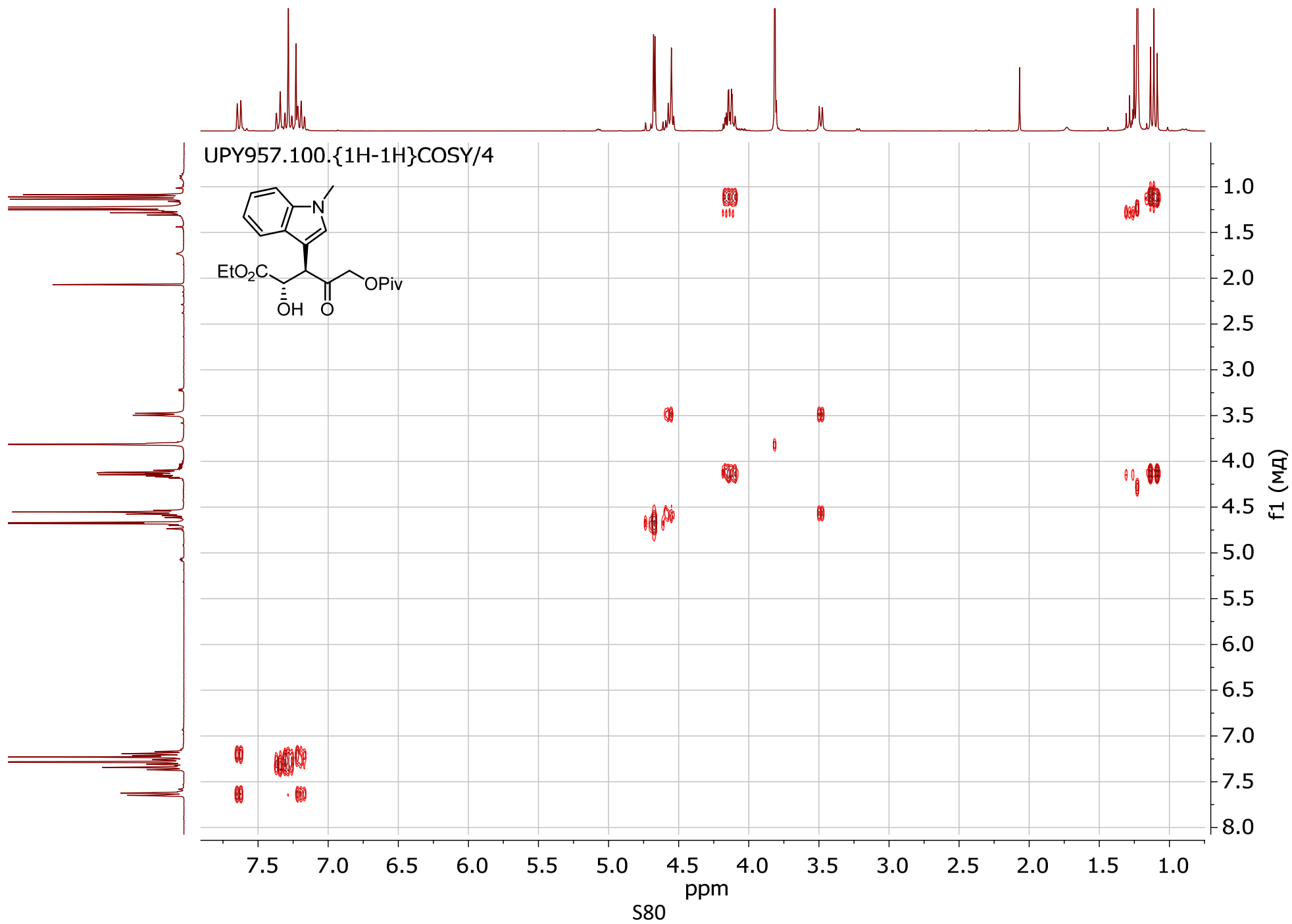
13.96



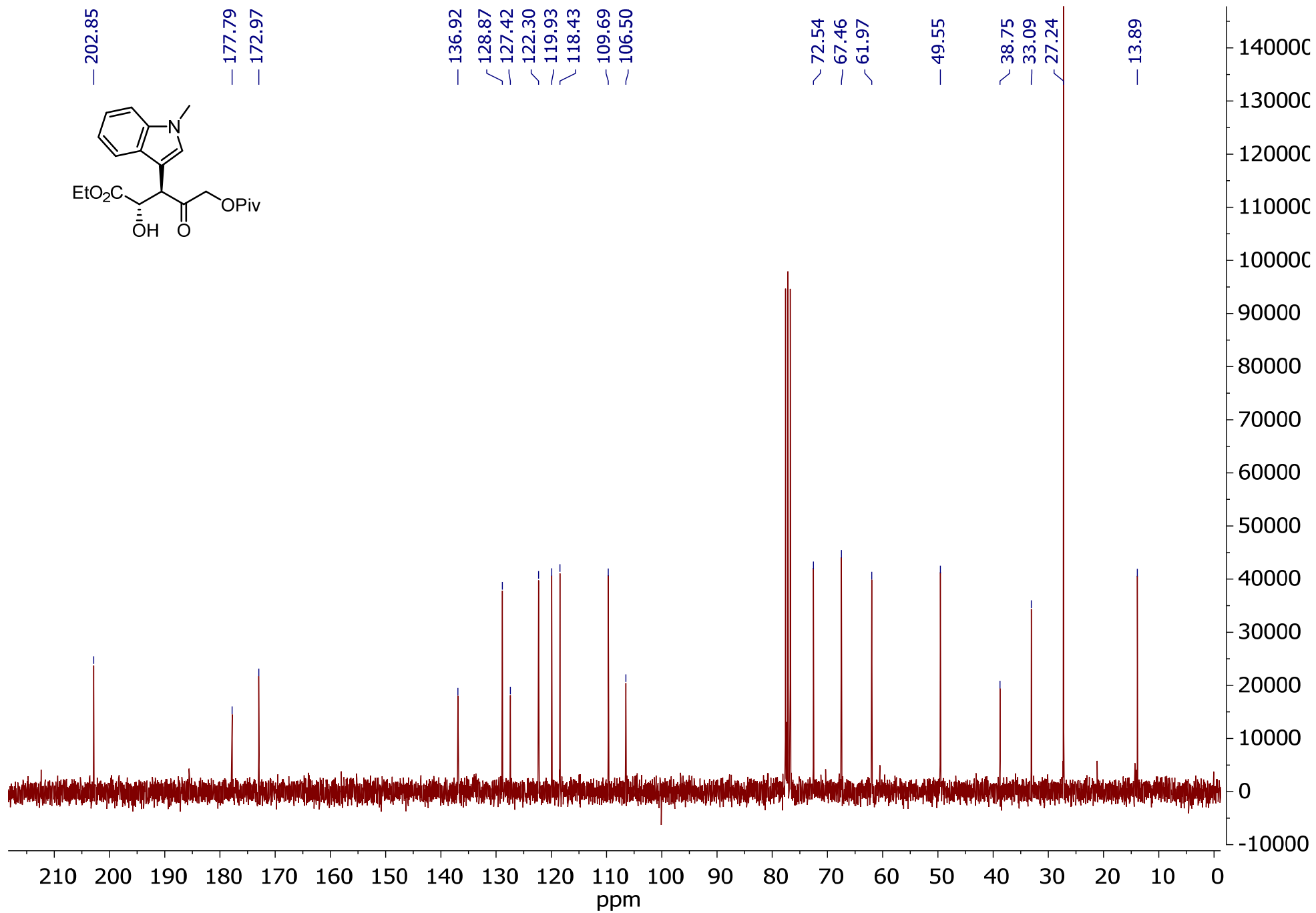
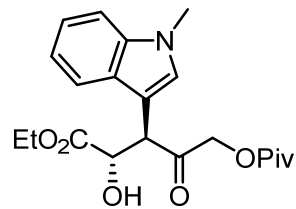
UPY949.100.{13C}deptsp135/3



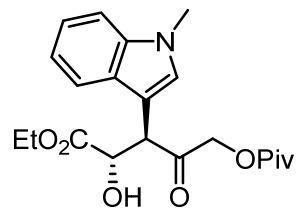








UPY957.100.{13C}depts135/3



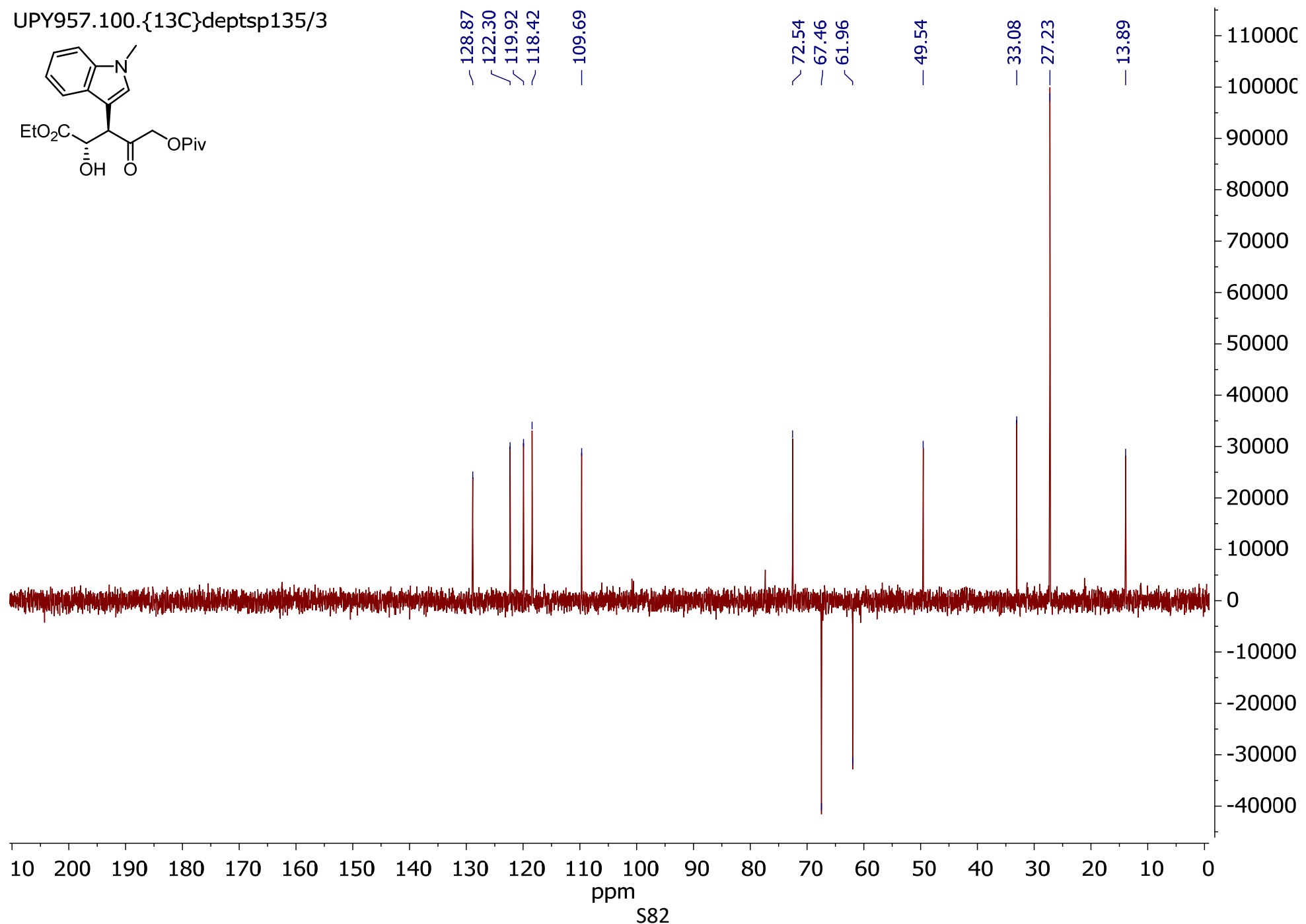
128.87  
122.30  
119.92  
118.42  
109.69

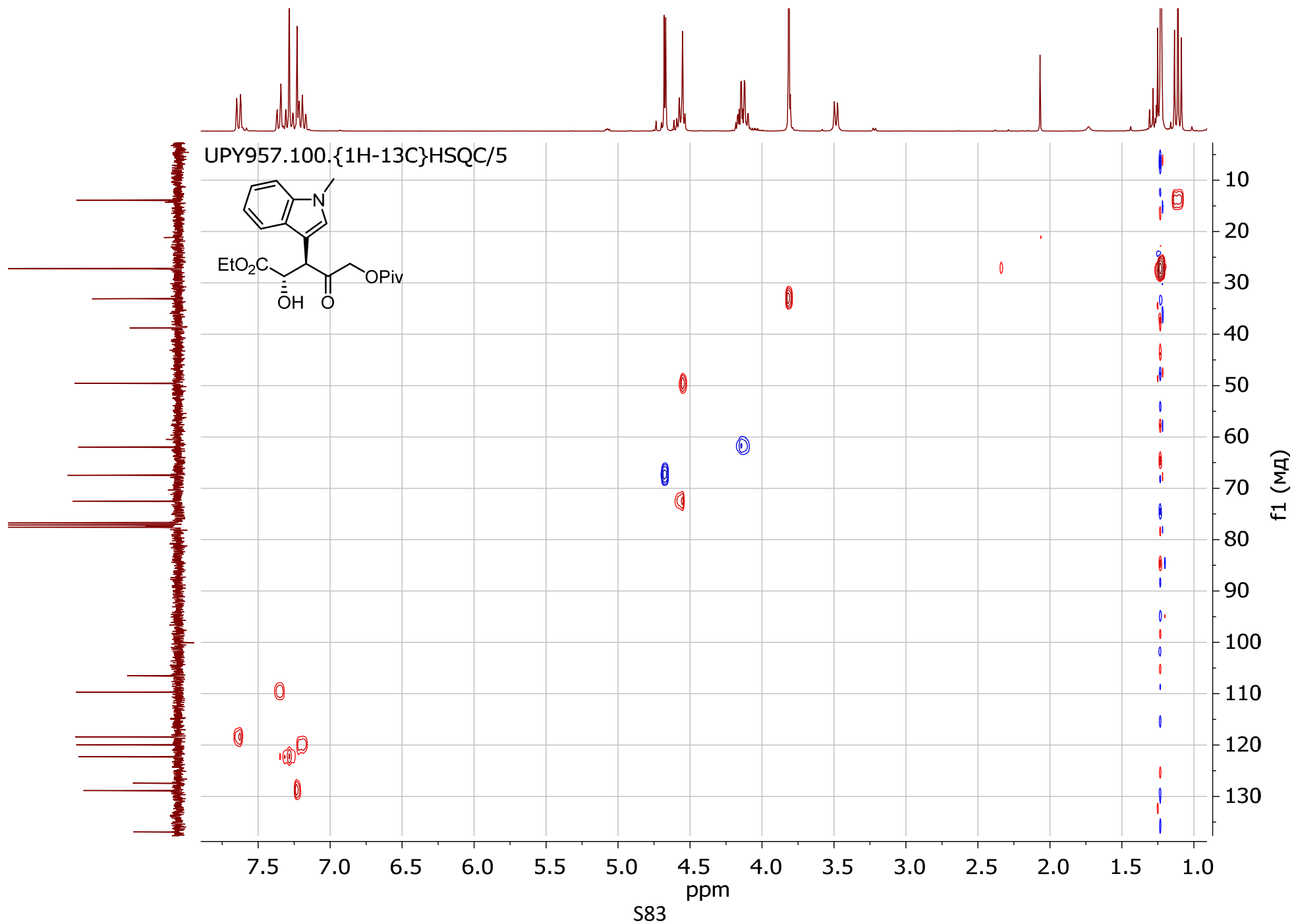
72.54  
67.46  
61.96

49.54

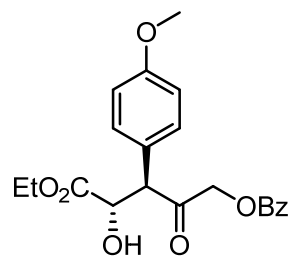
33.08  
27.23

13.89

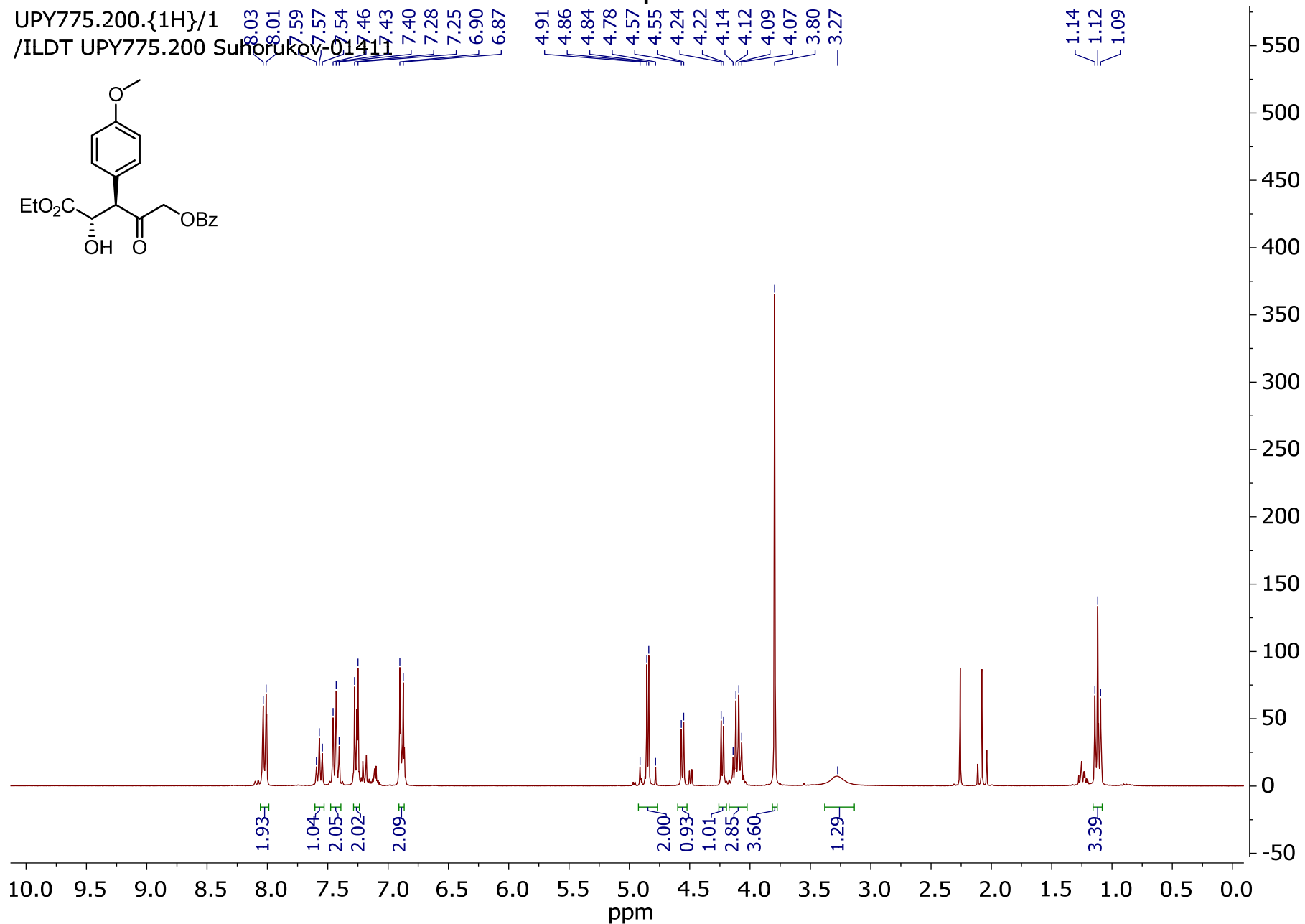


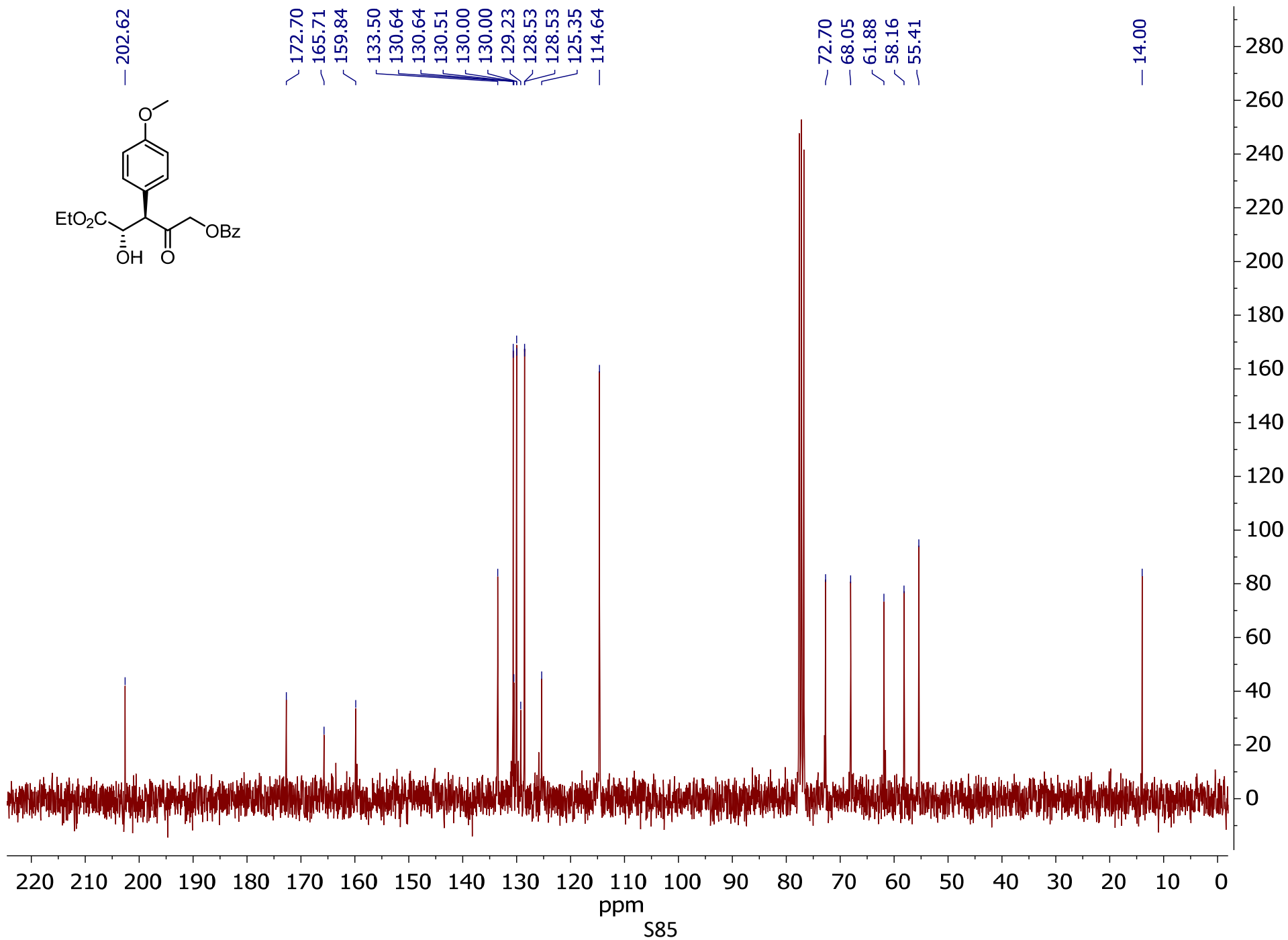
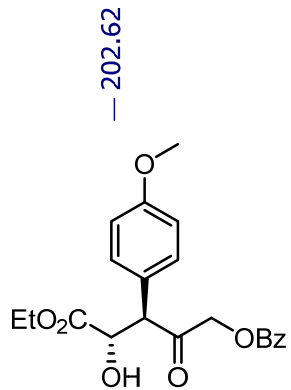


UPY775.200.{1H}/1  
/ILDT UPY775.200 Suhorukov-01411

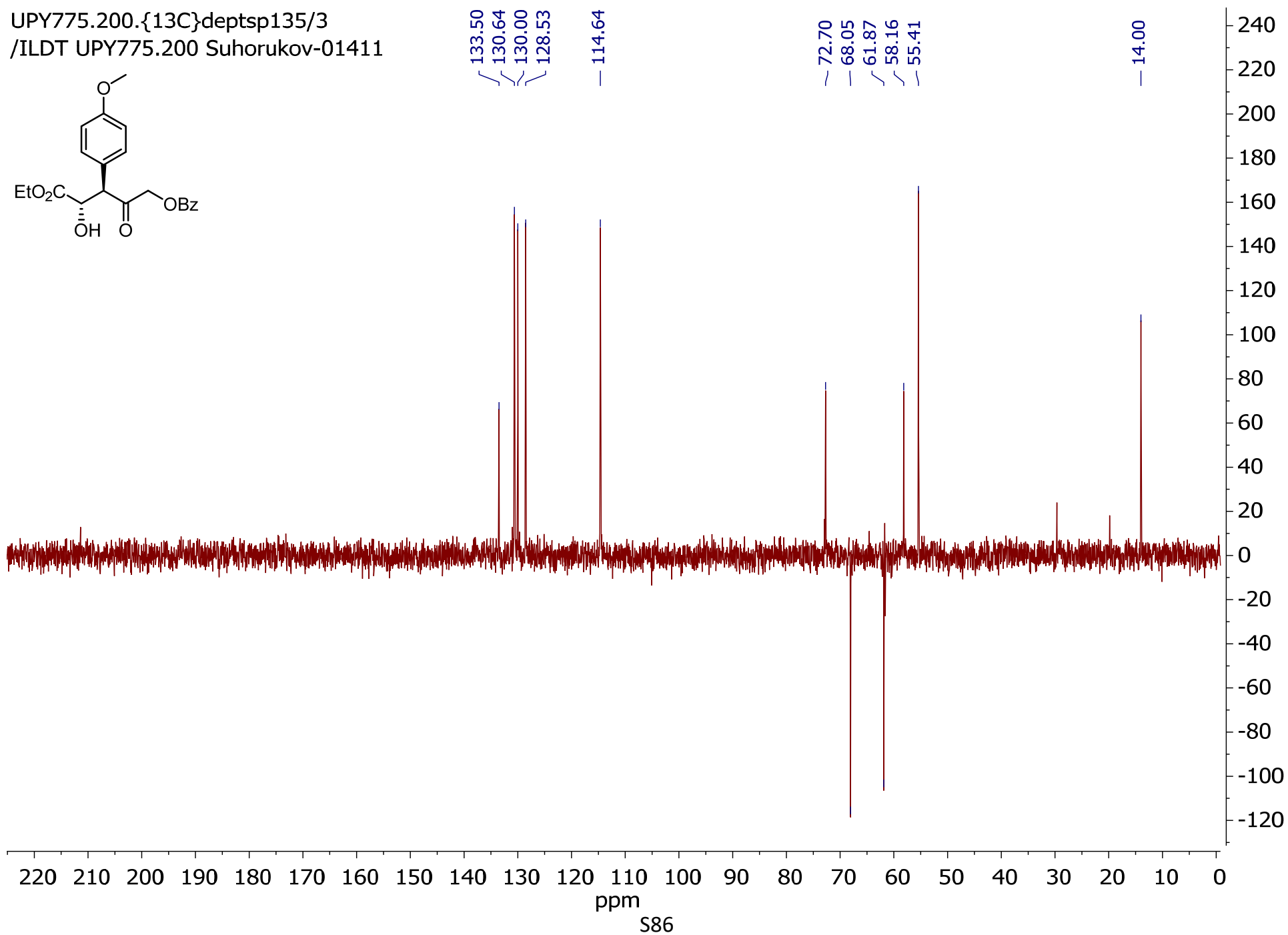
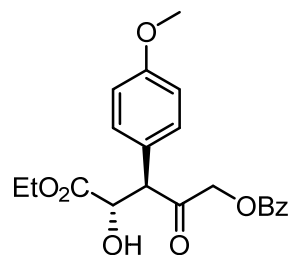


### NMR spectra of 5k



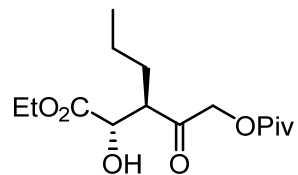


UPY775.200.{13C}deptsp135/3  
/ILD T UPY775.200 Suhorukov-01411

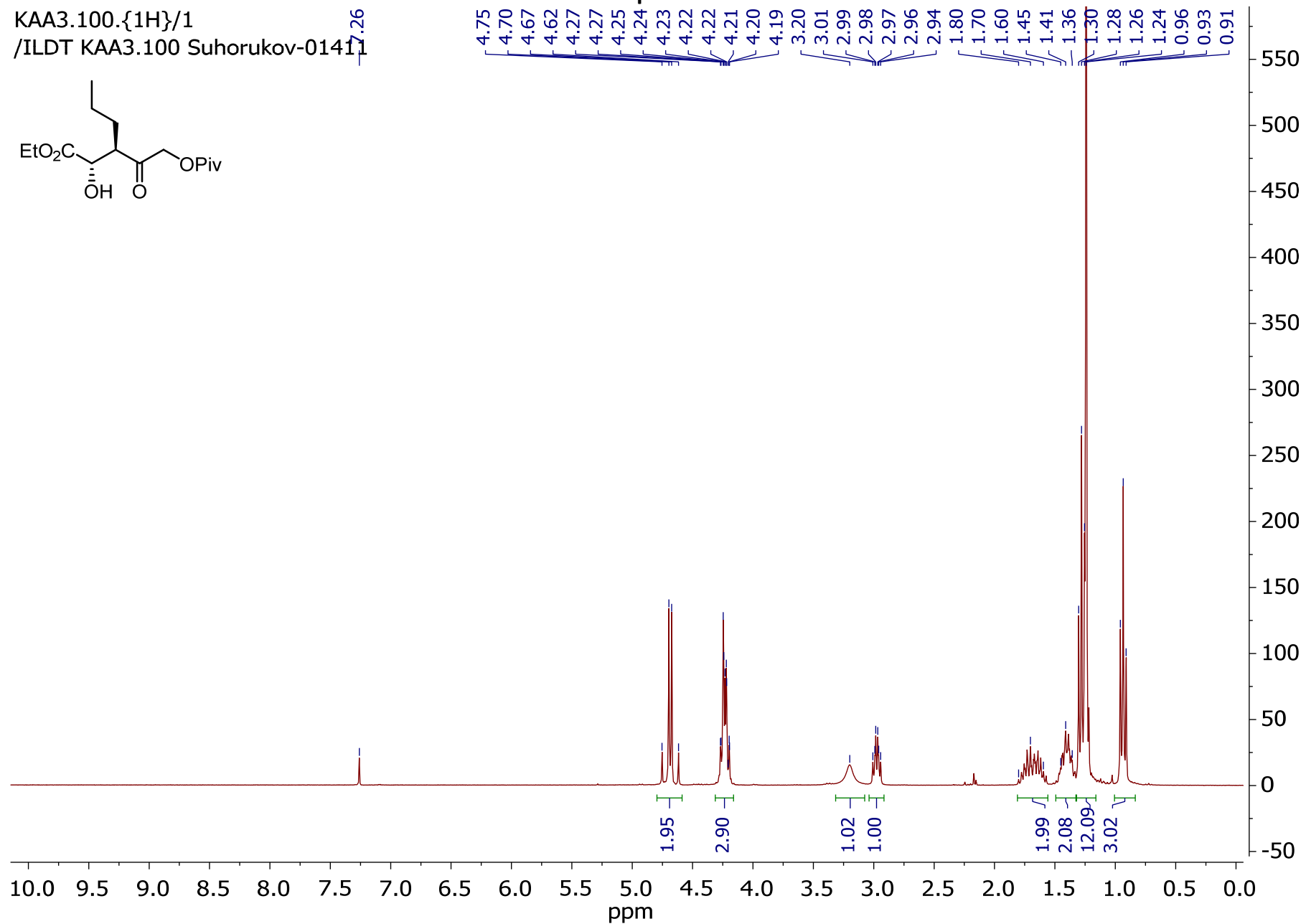




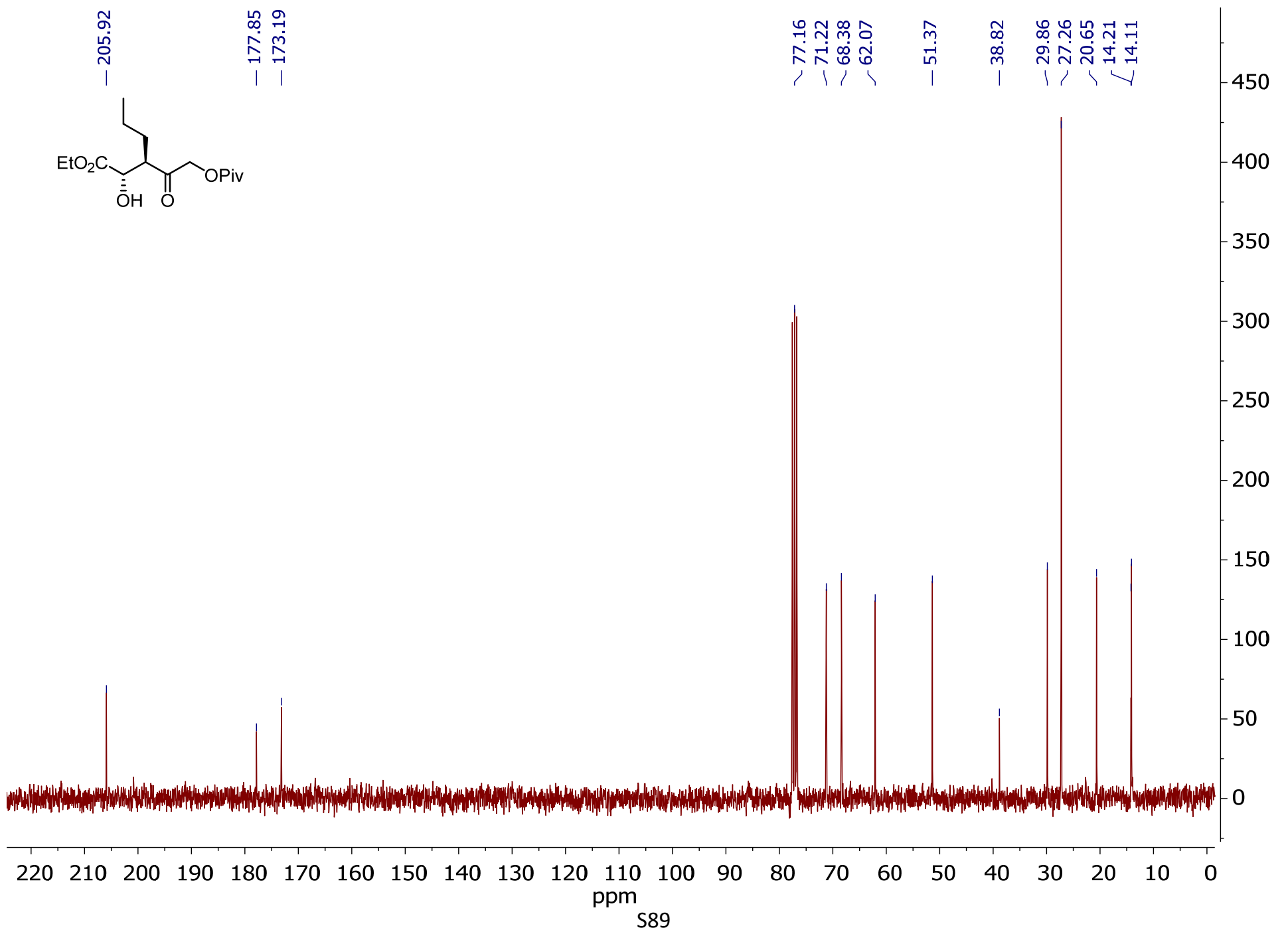
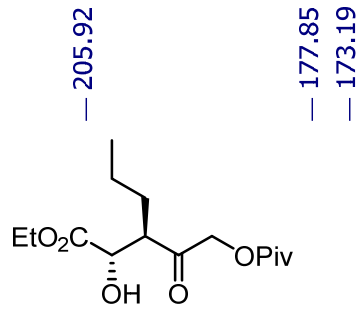
KAA3.100.{1H}/1  
/ILDT KAA3.100 Suhorukov-01411



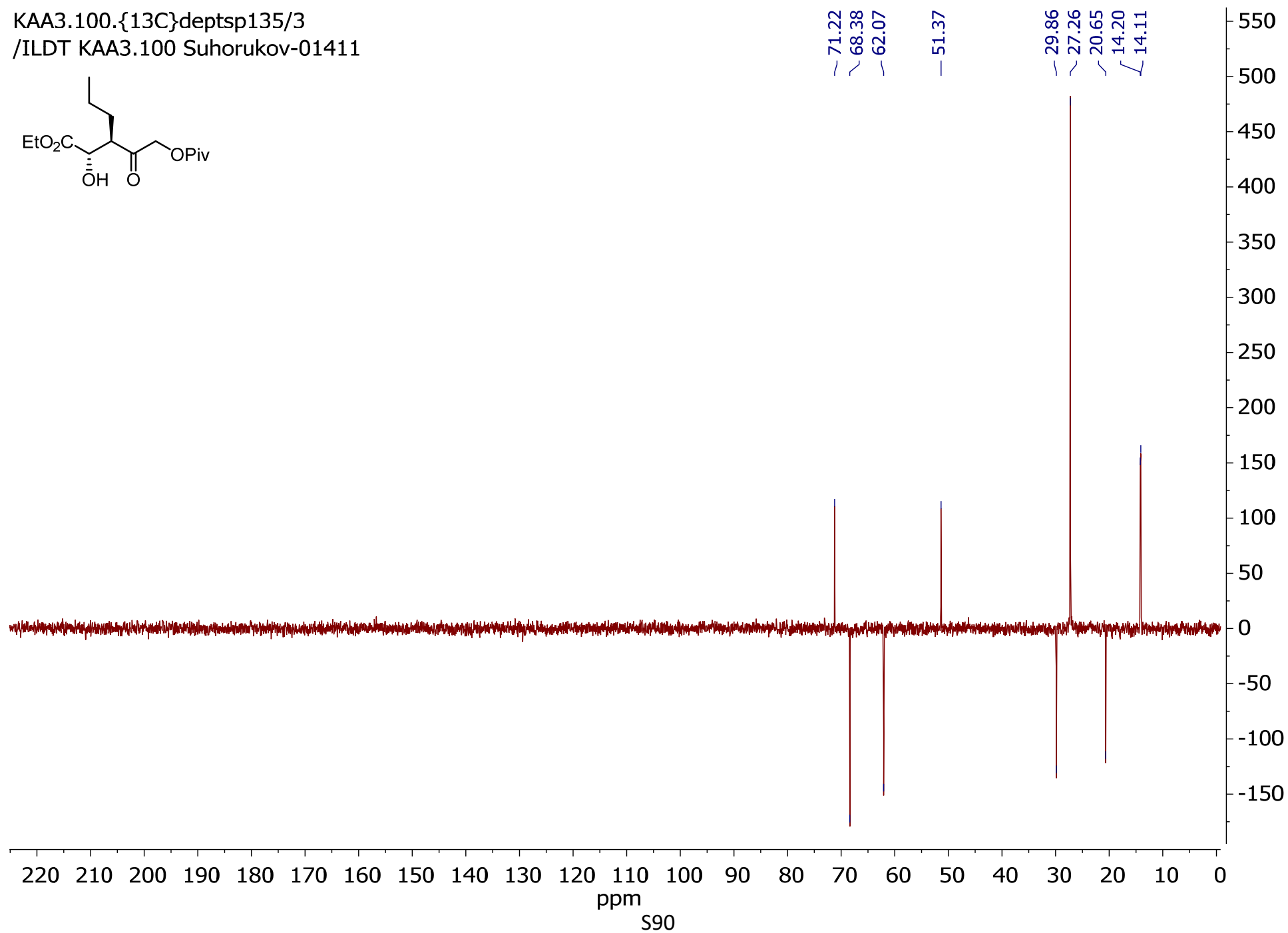
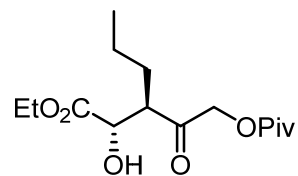
### NMR spectra of 10a

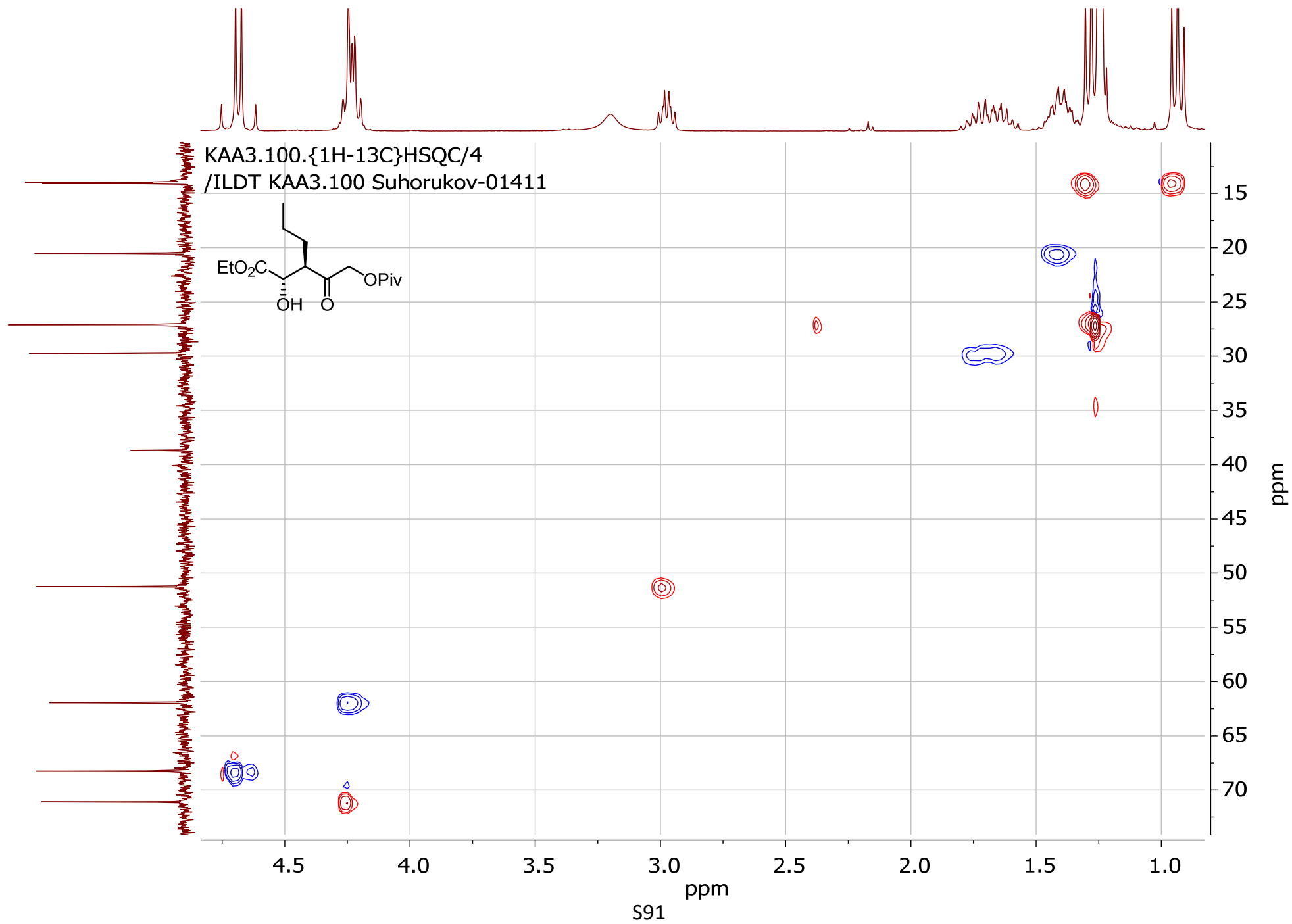




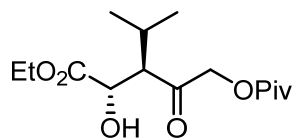


KAA3.100.{13C}deptsp135/3  
/ILDT KAA3.100 Suhorukov-01411

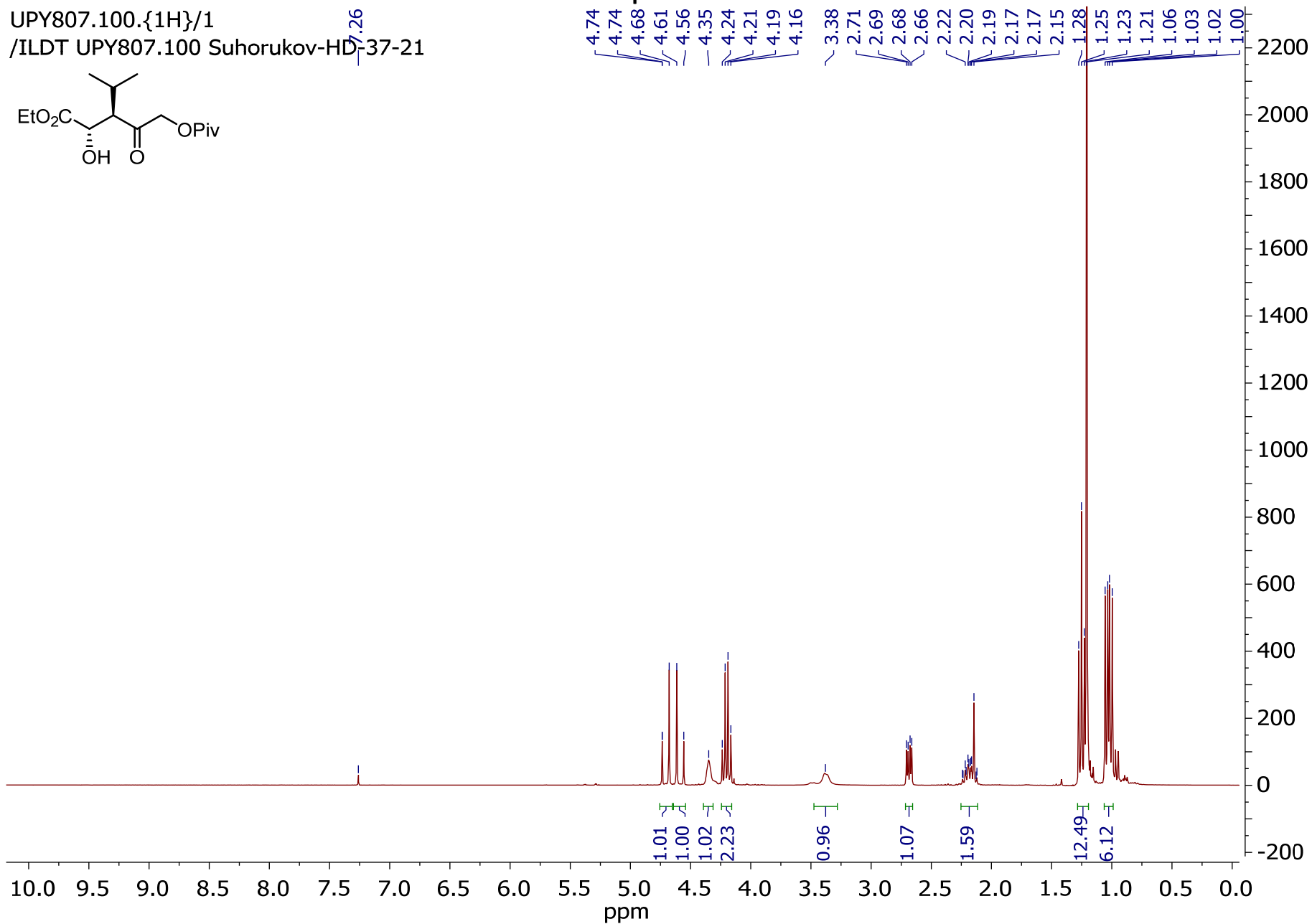




UPY807.100.{1H}/1  
/ILDY UPY807.100 Suhorukov-HD-37-21



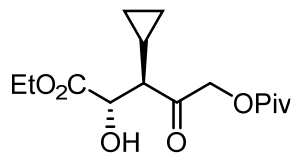
### NMR spectra of 10b



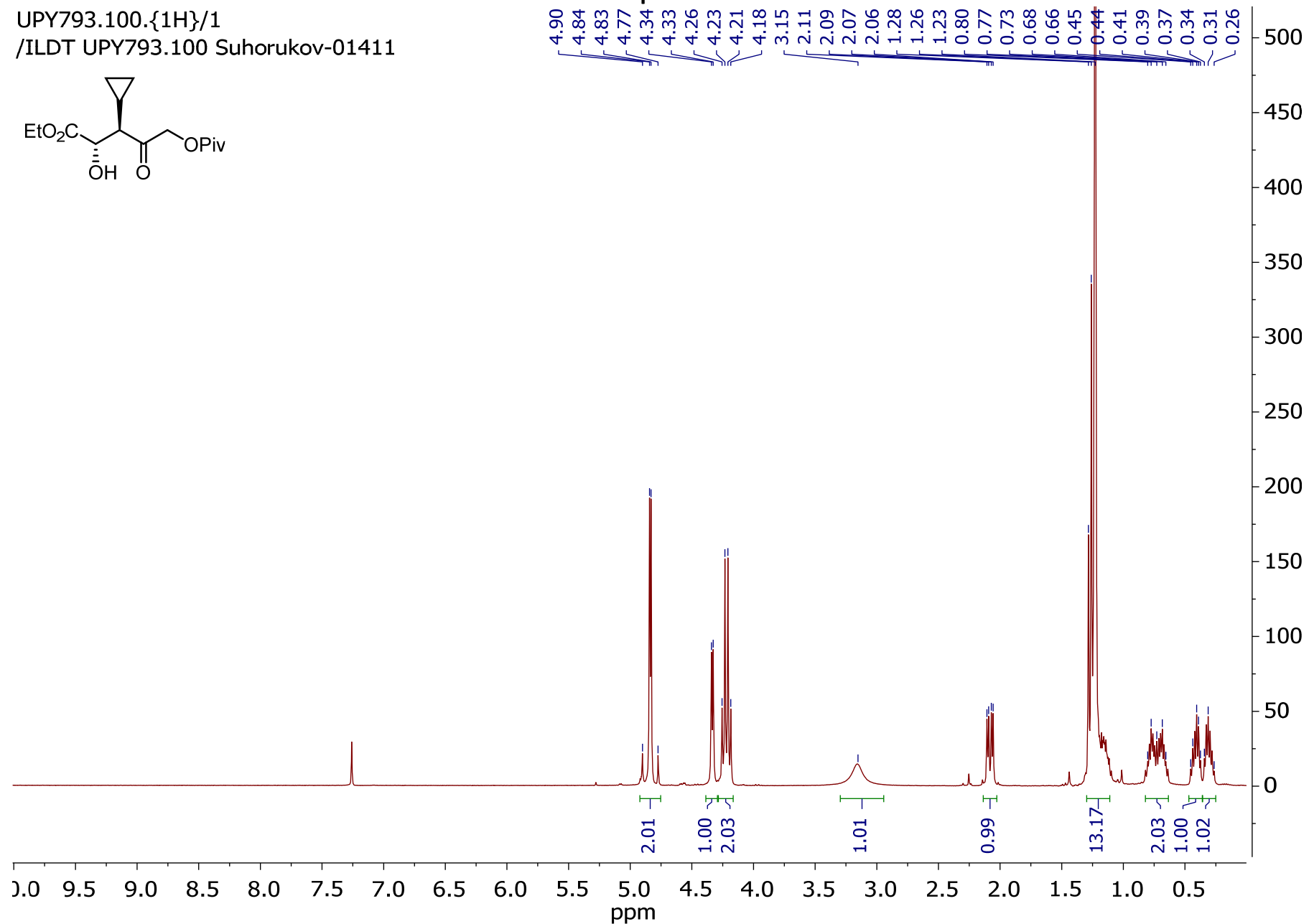




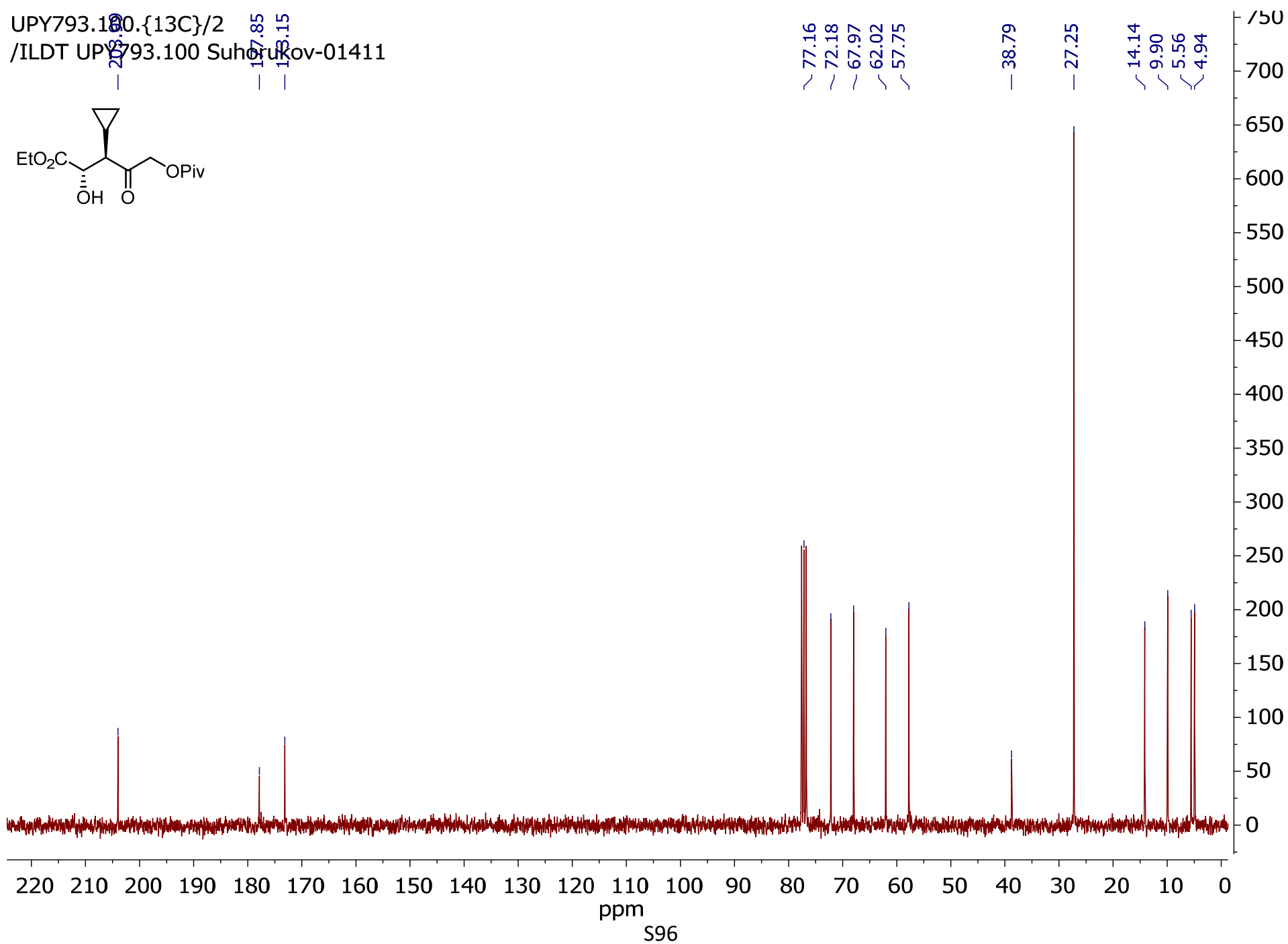
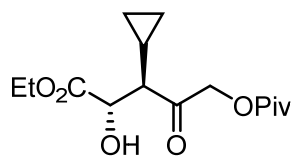
UPY793.100.{1H}/1  
/ILDY UPY793.100 Suhorukov-01411



### NMR spectra of 10c

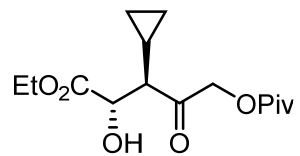


UPY793.100.{13C}/2  
/ILDT UPY793.100 Suhrkov-01411





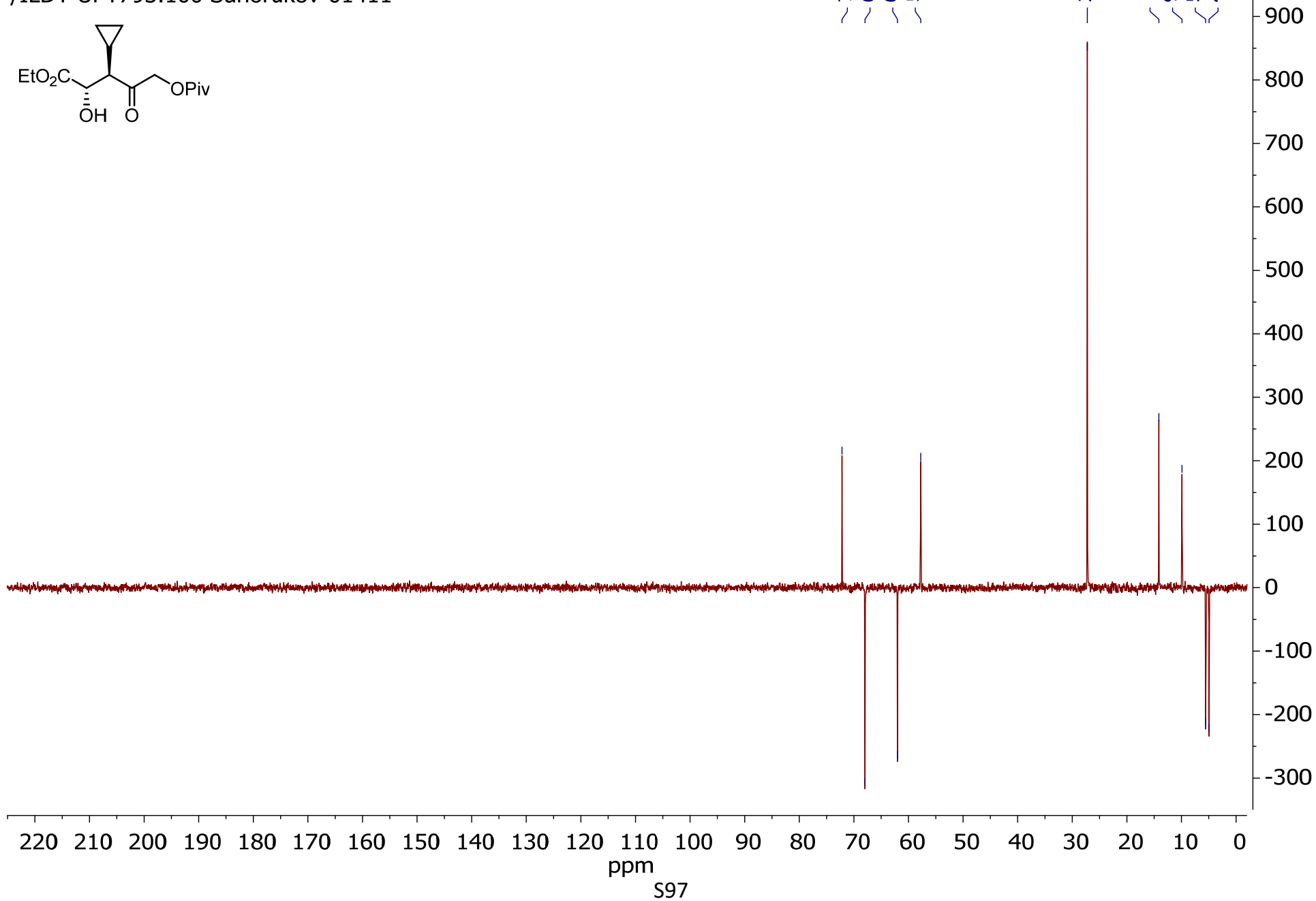
UPY793.100.{13C}deptsp135/3  
/ILDIT UPY793.100 Suhorukov-01411

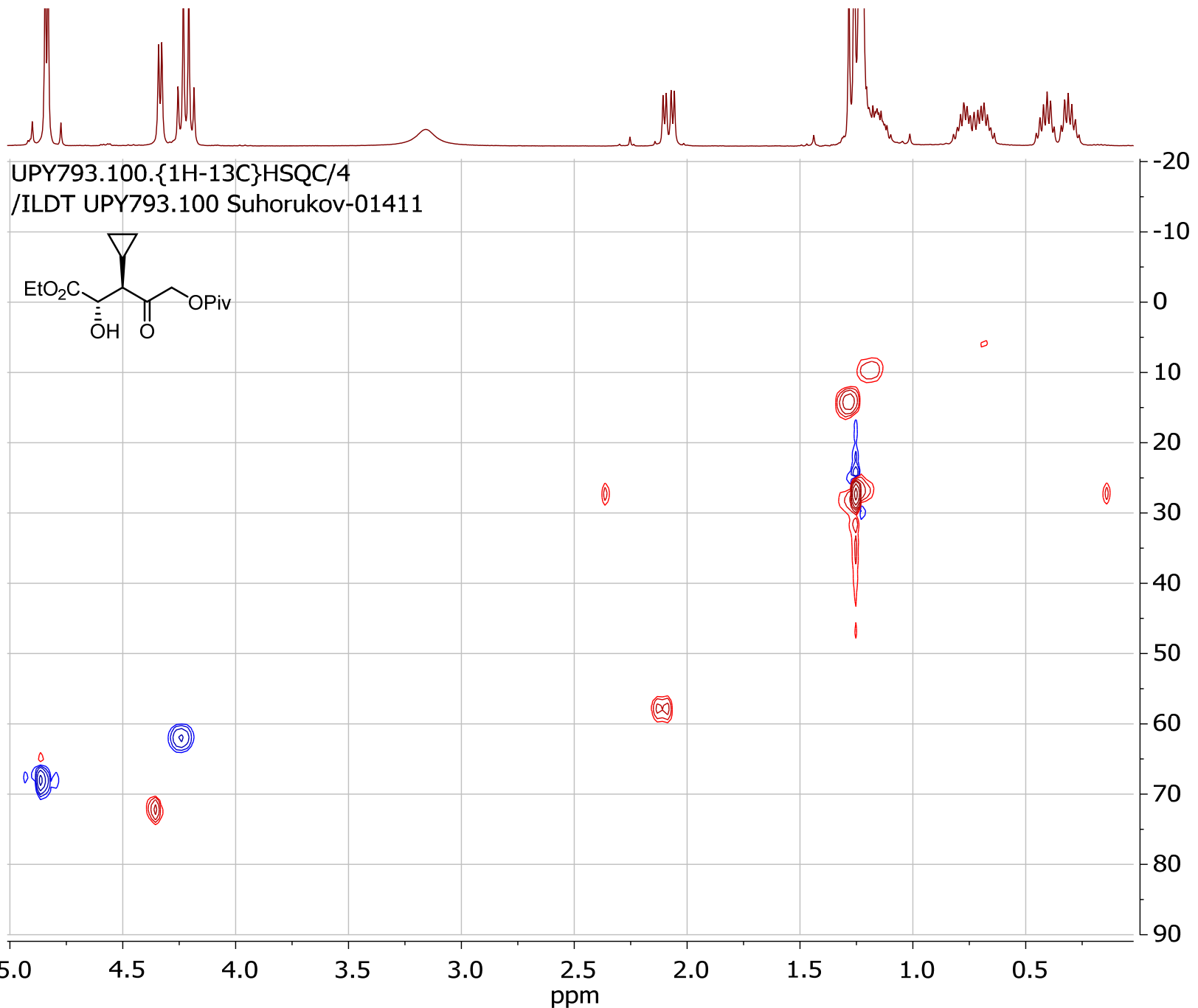


72.18  
67.97  
62.02  
57.76

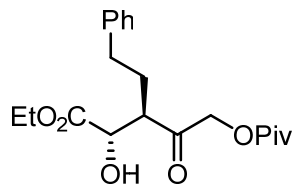
27.25

14.14  
9.90  
5.57  
4.94

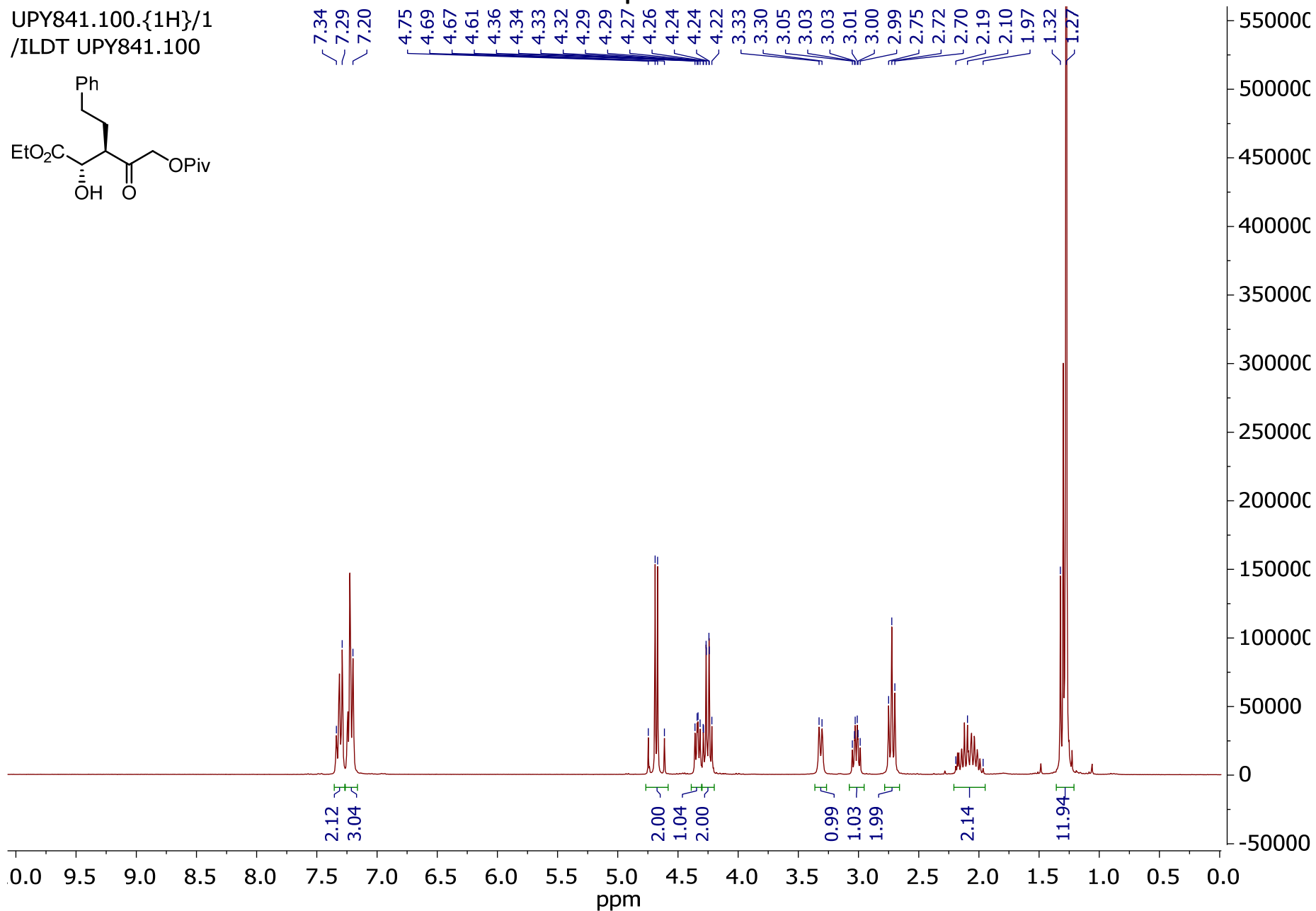


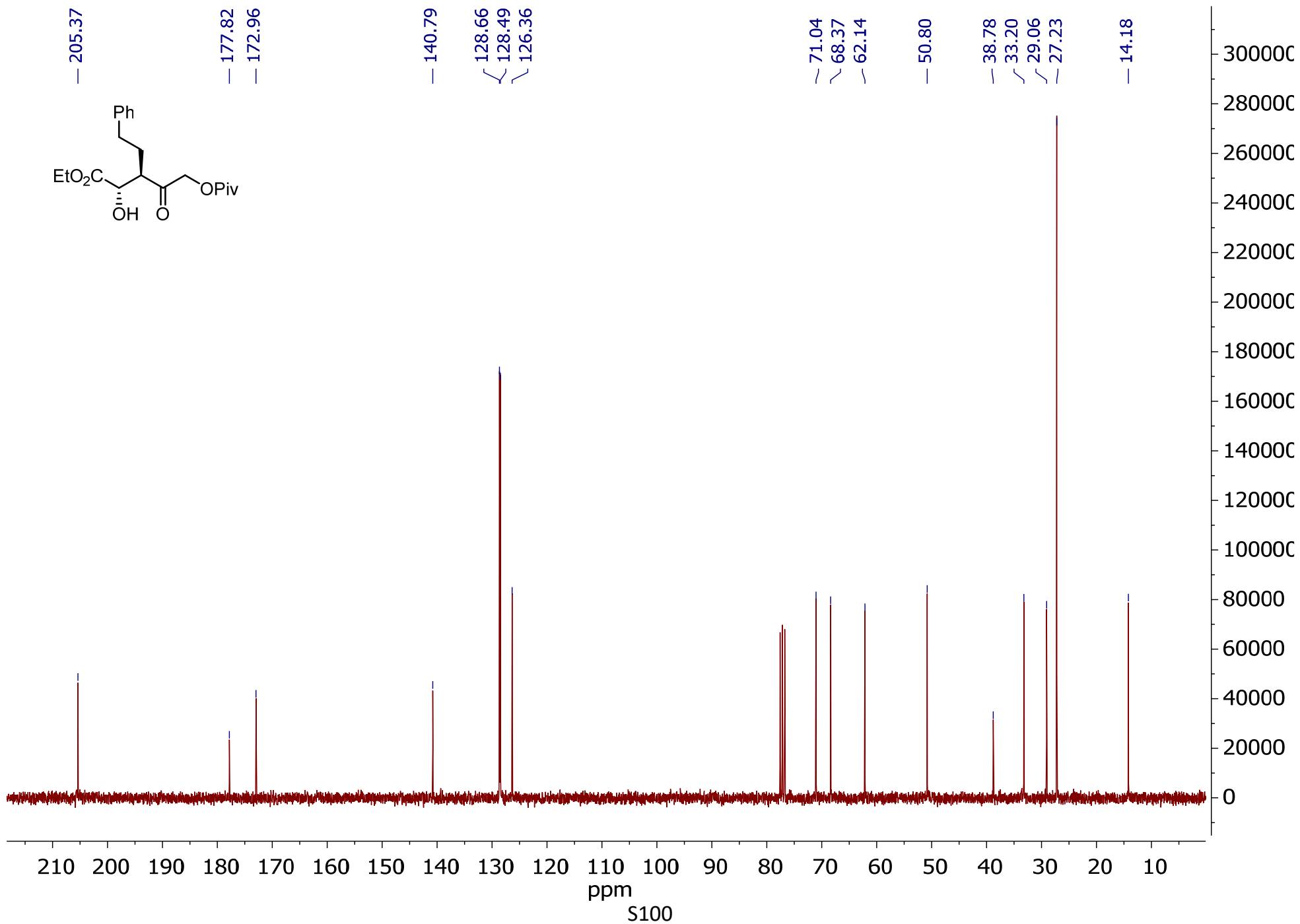
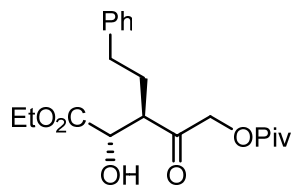


UPY841.100.{1H}/1  
/ILDT UPY841.100

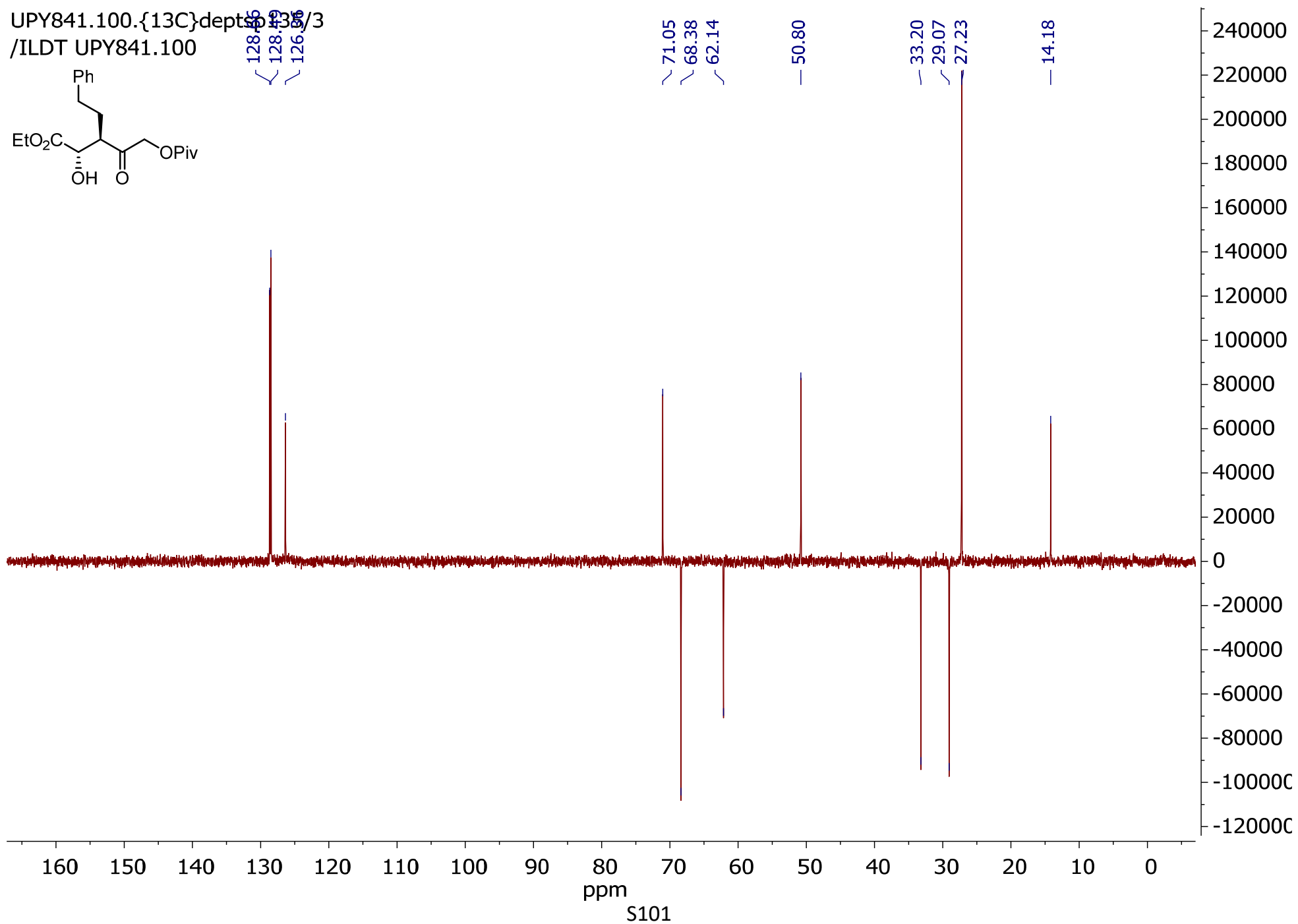
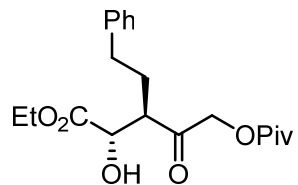


### NMR spectra of 10d

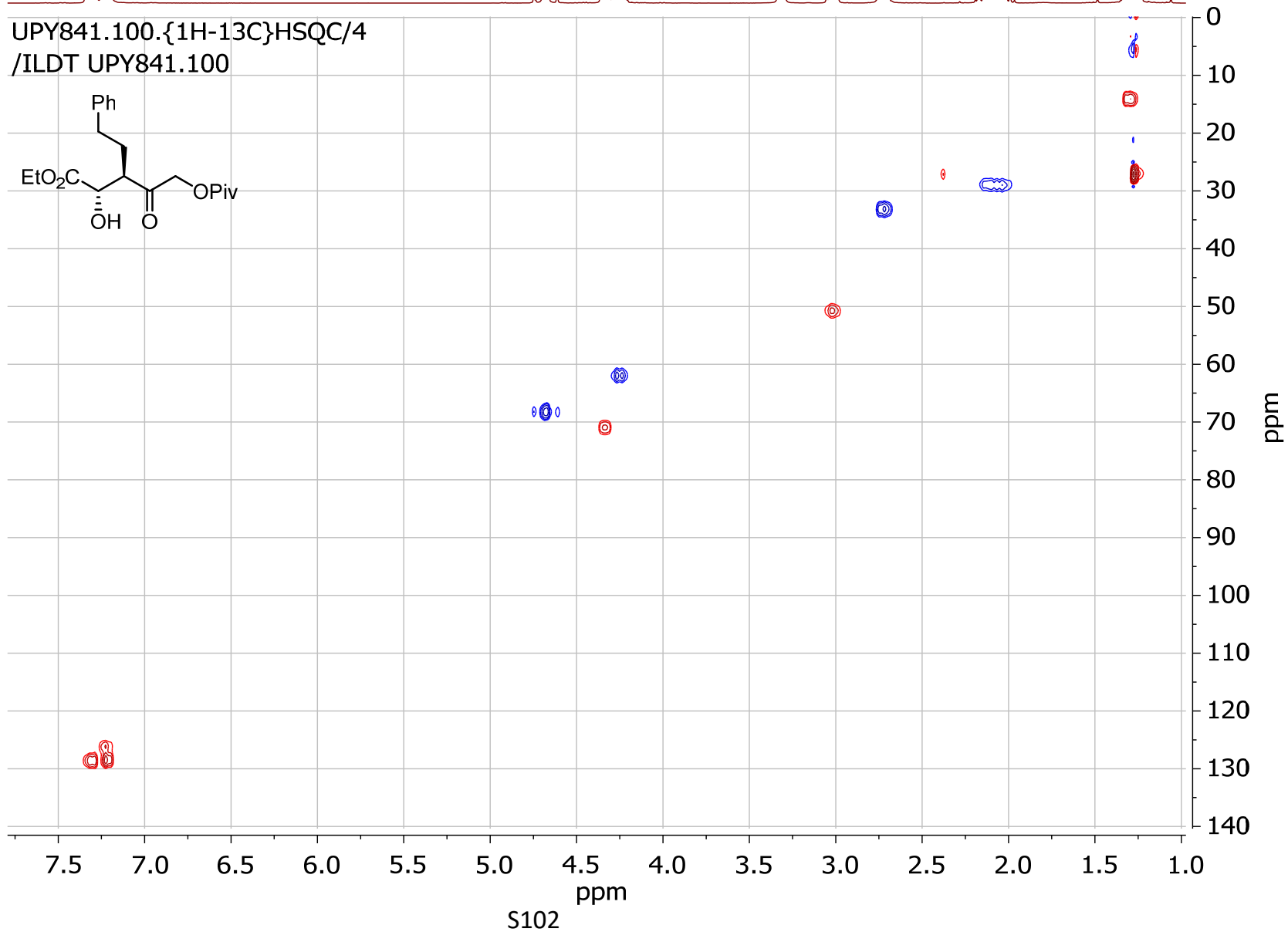
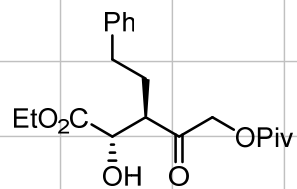




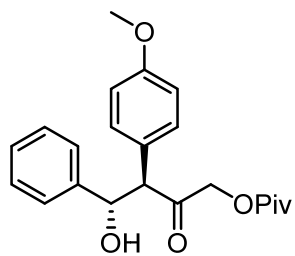
UPY841.100.{13C}depts/3  
/ILDT UPY841.100



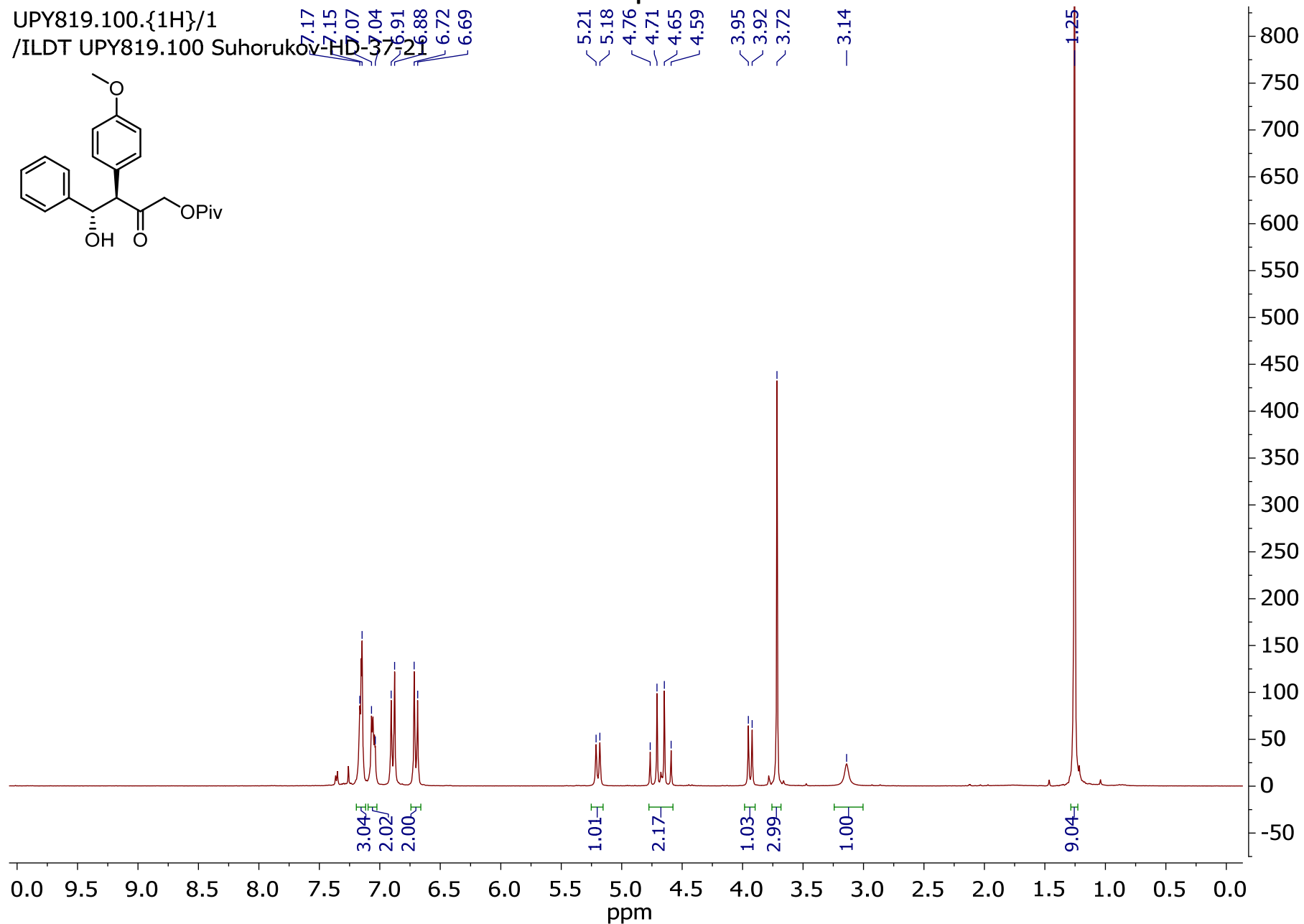
UPY841.100.{1H-13C}HSQC/4  
/ILD T UPY841.100

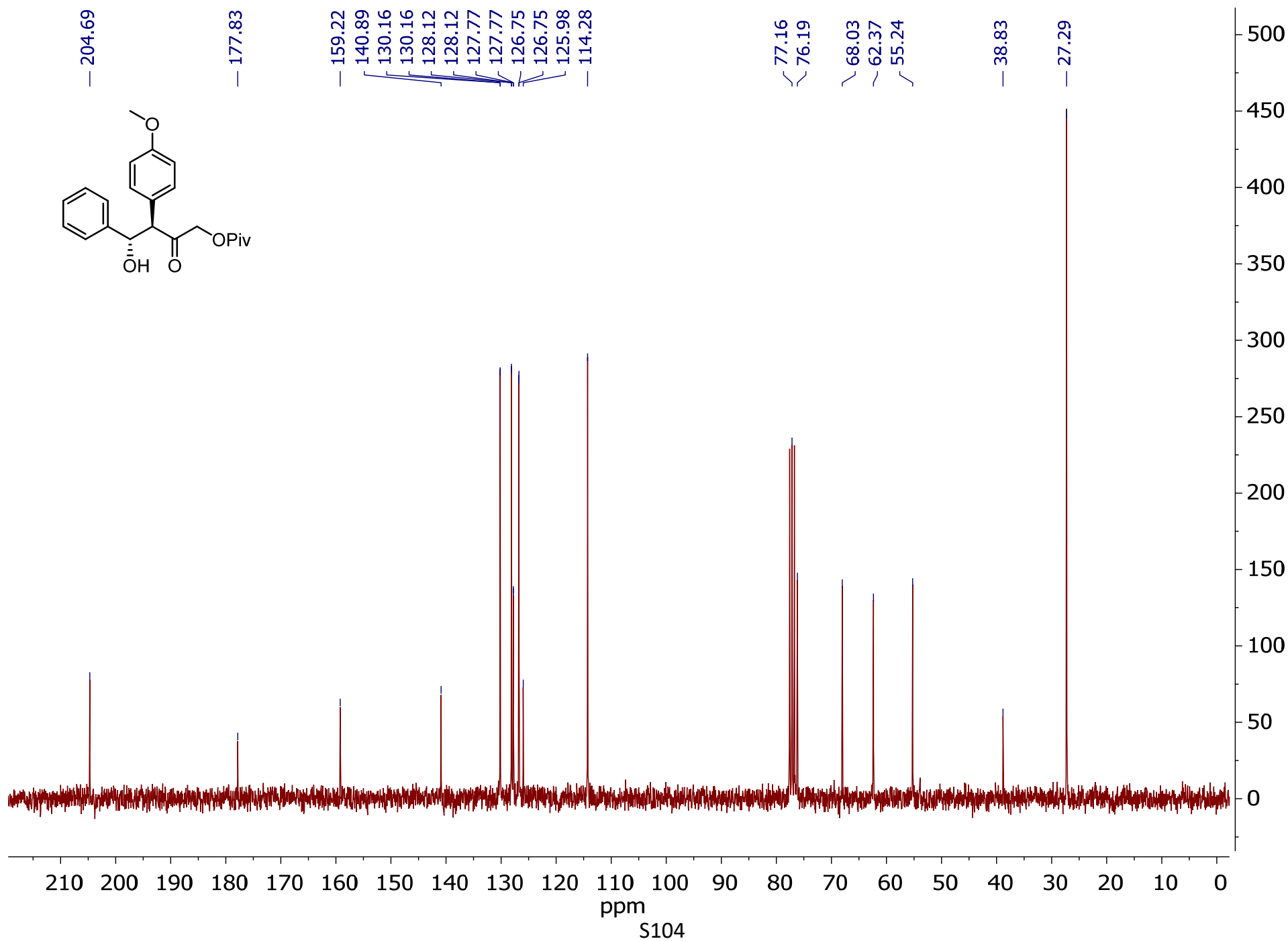
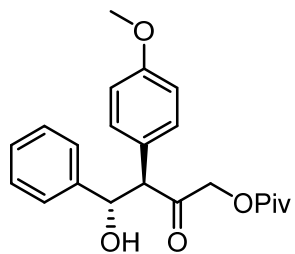


UPY819.100.{1H}/1  
/ILDT UPY819.100 Suhorukov-HD-37-21



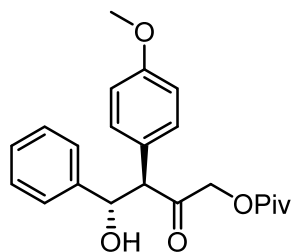
### NMR spectra of 15a







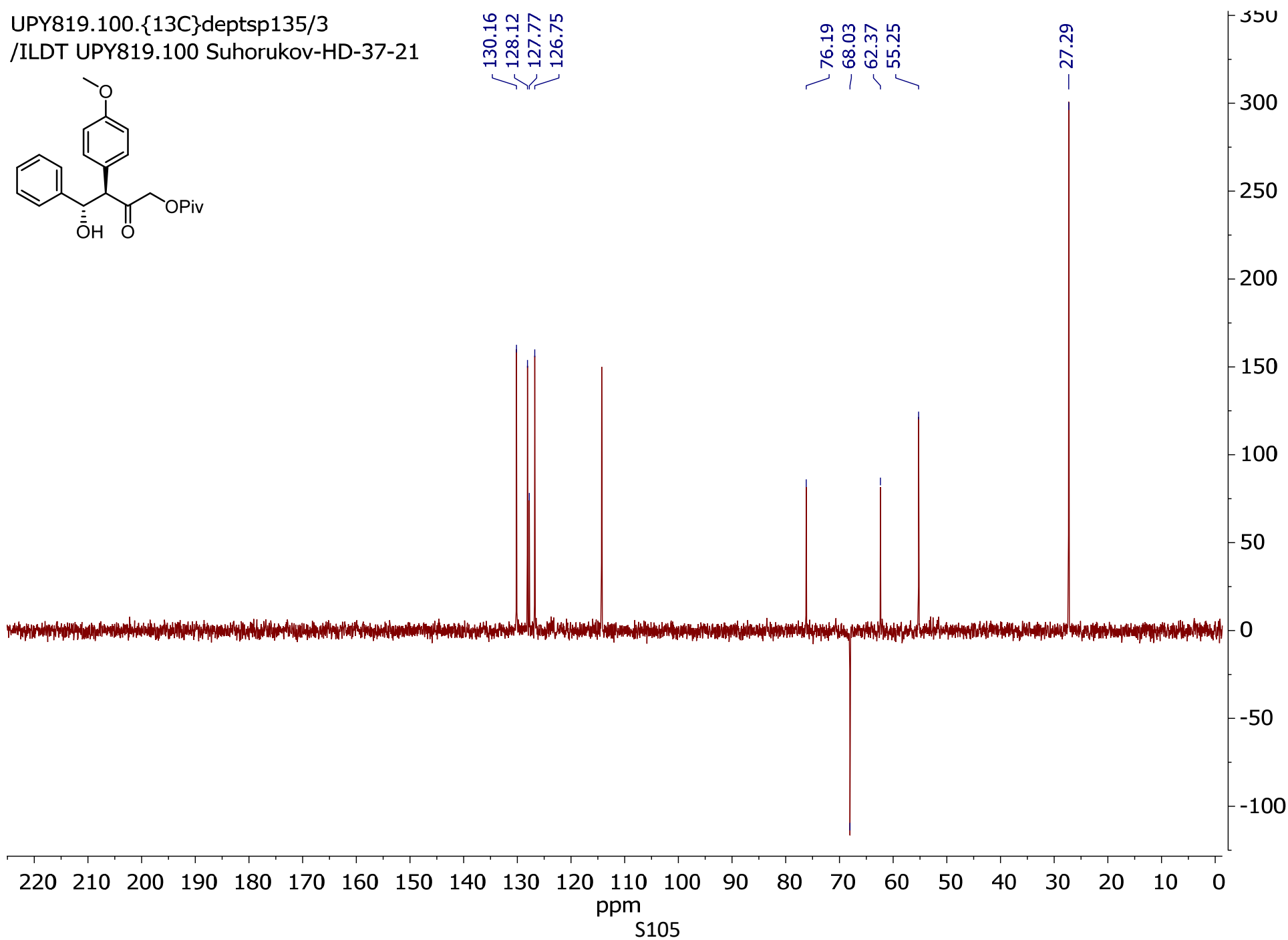
UPY819.100.{13C}deptsp135/3  
/ILDT UPY819.100 Suhorukov-HD-37-21



130.16  
128.12  
127.77  
126.75

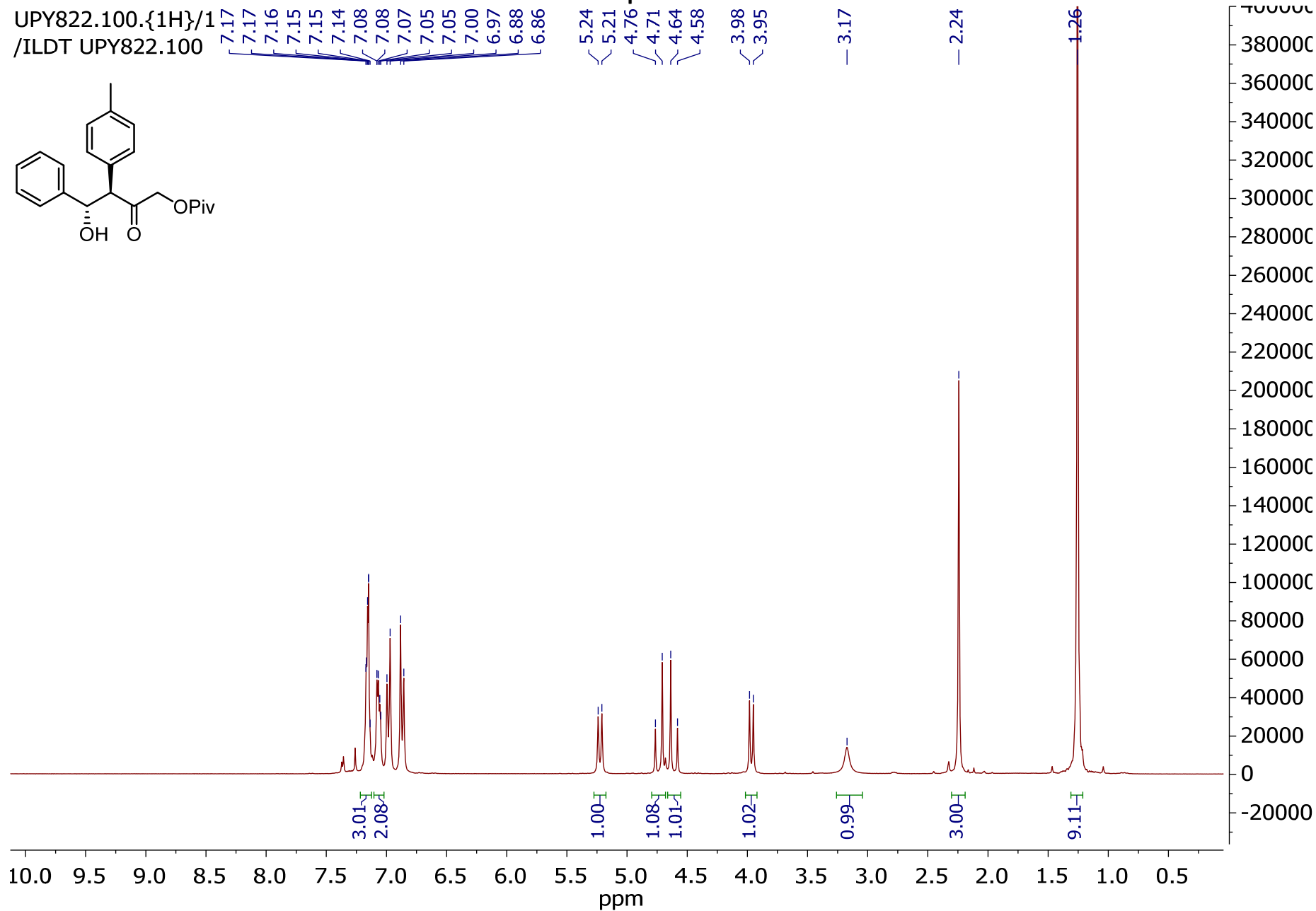
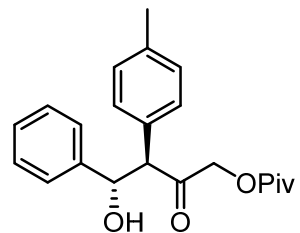
76.19  
68.03  
62.37  
55.25

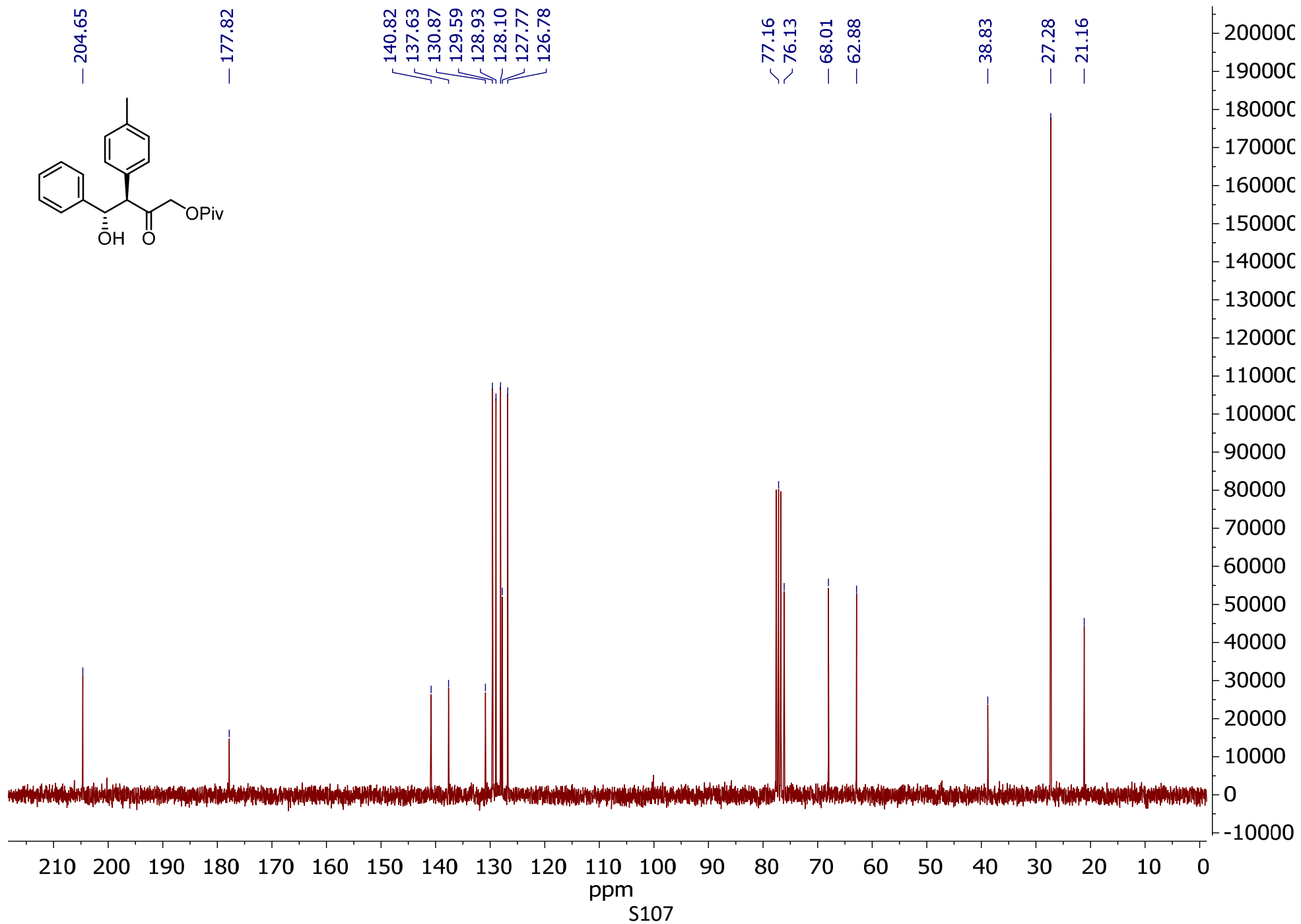
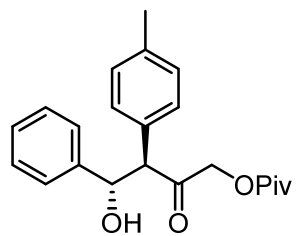
27.29



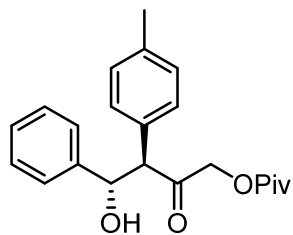
UPY822.100.{1H}/1  
/ILDT UPY822.100

### NMR spectra of 15b





UPY822.100.{13C}deptsp135/3  
/ILDIT UPY822.100



129.59  
128.93  
128.10  
127.77  
126.78

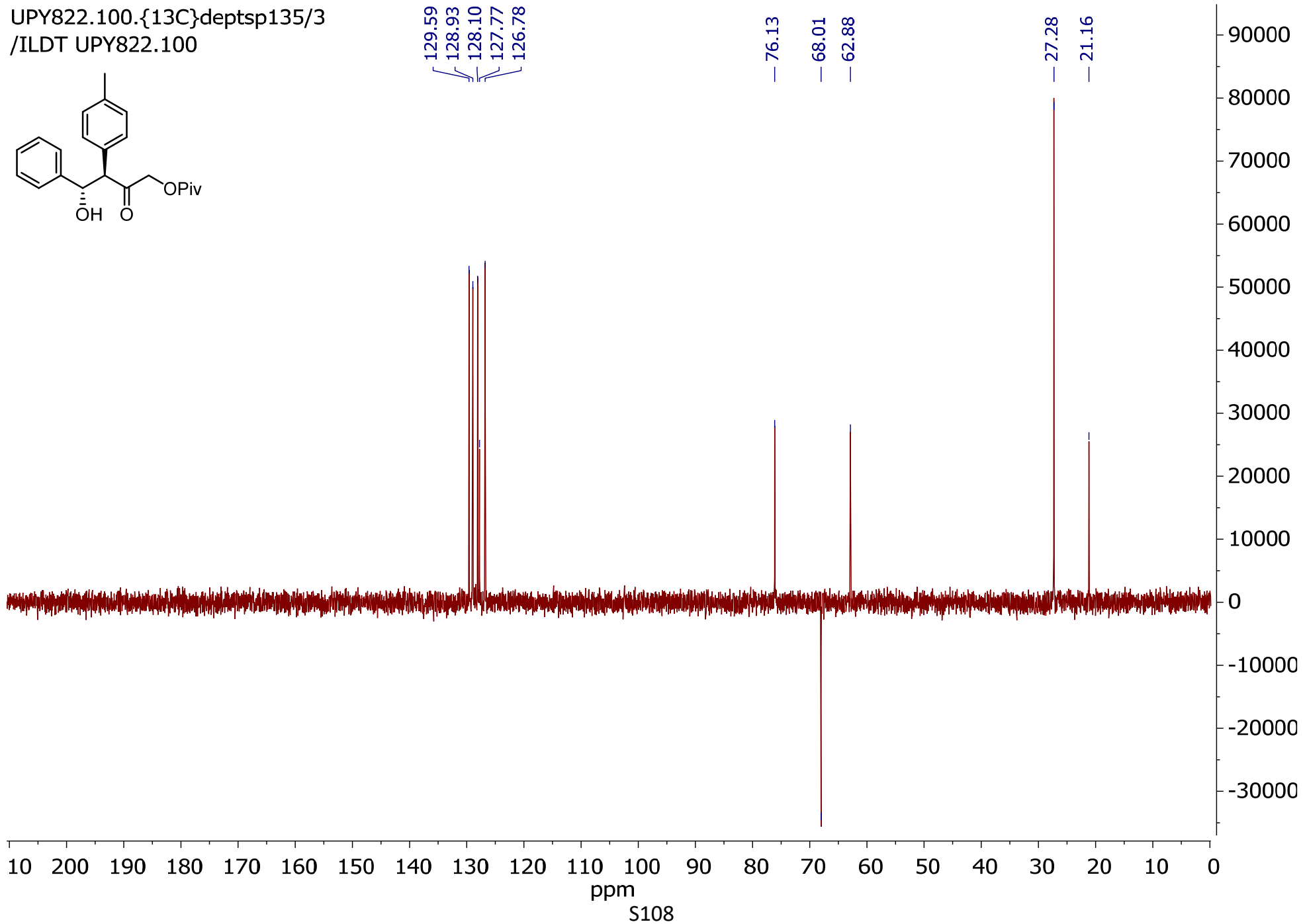
76.13

68.01

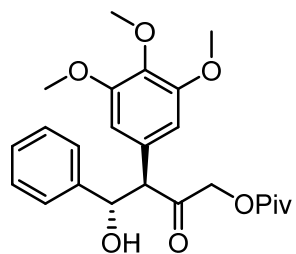
62.88

27.28

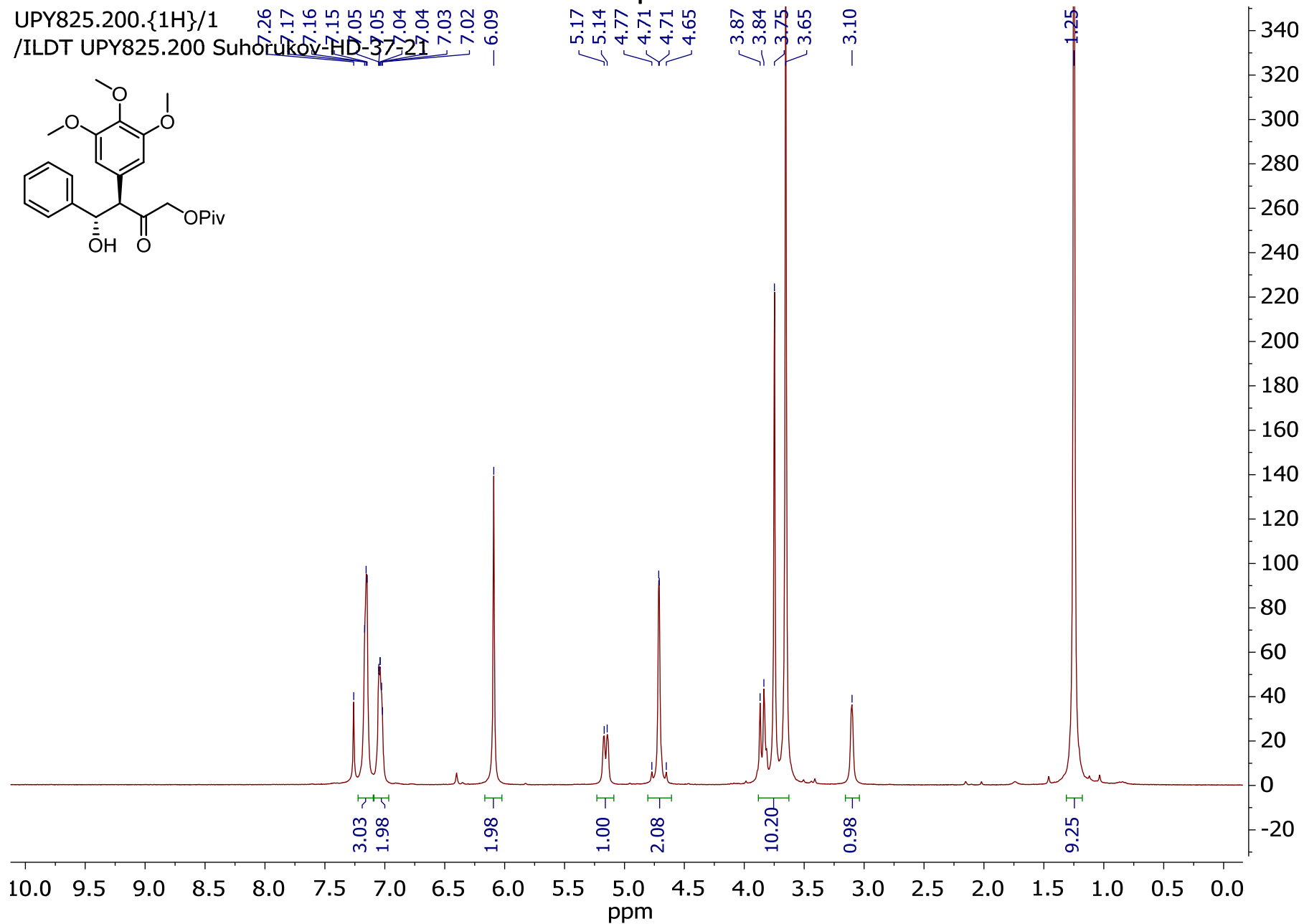
21.16

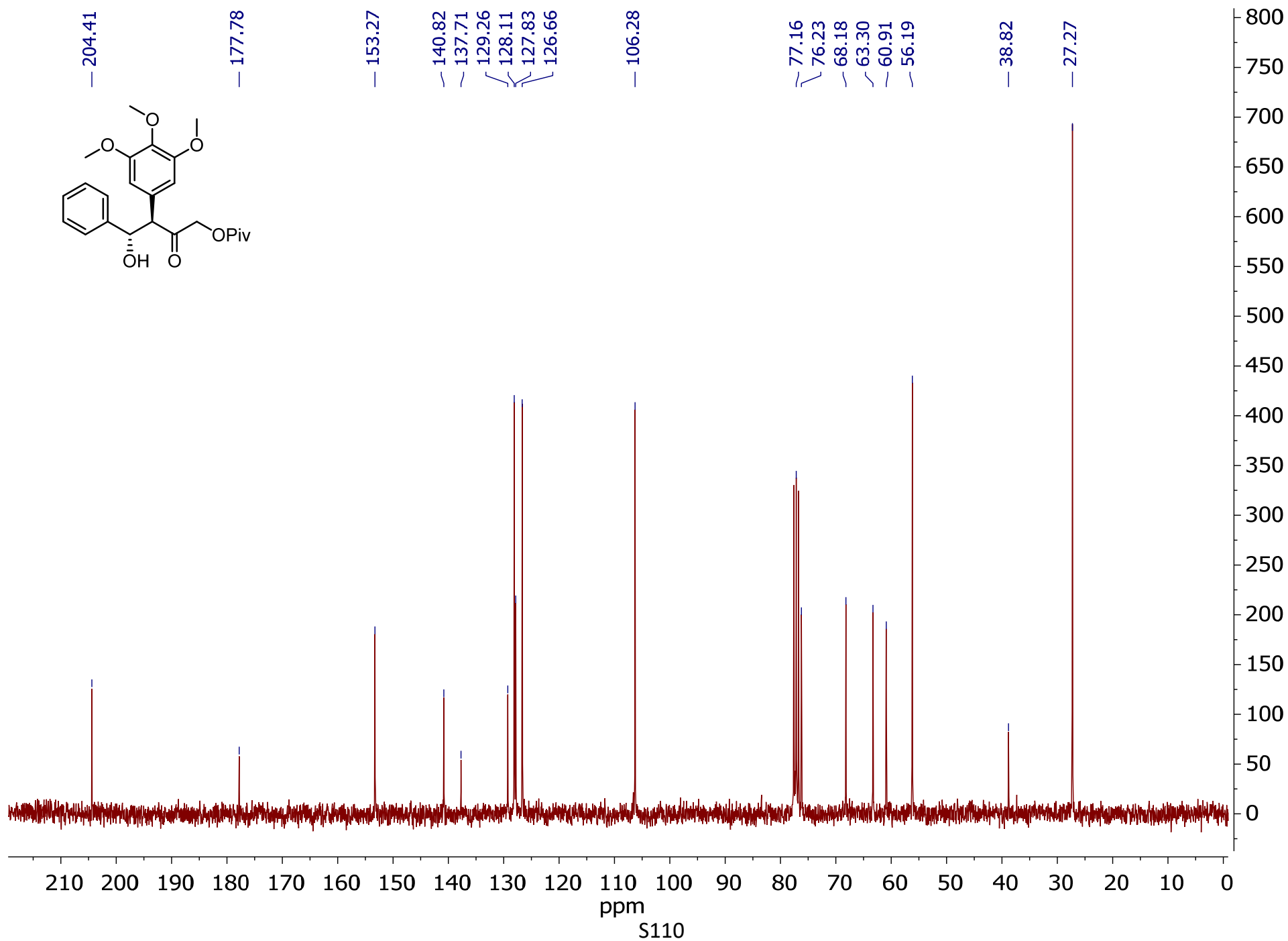
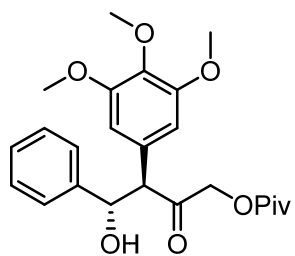


UPY825.200.{1H}/1  
/ILDT UPY825.200 Suhorukov-HD-37-21

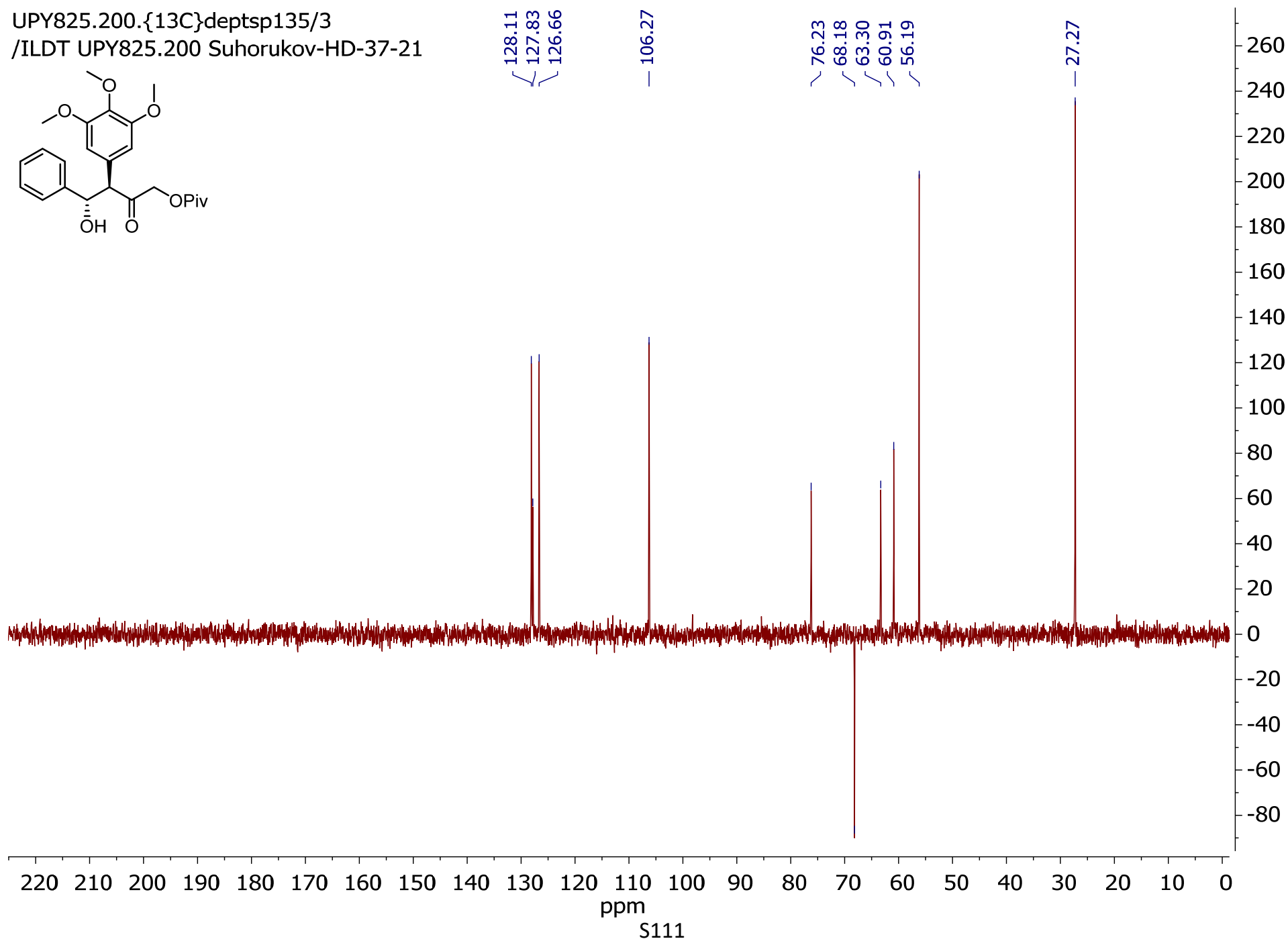
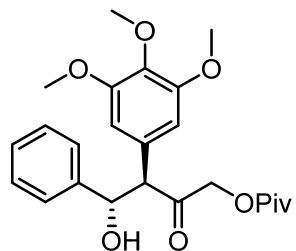


### NMR spectra of 15c



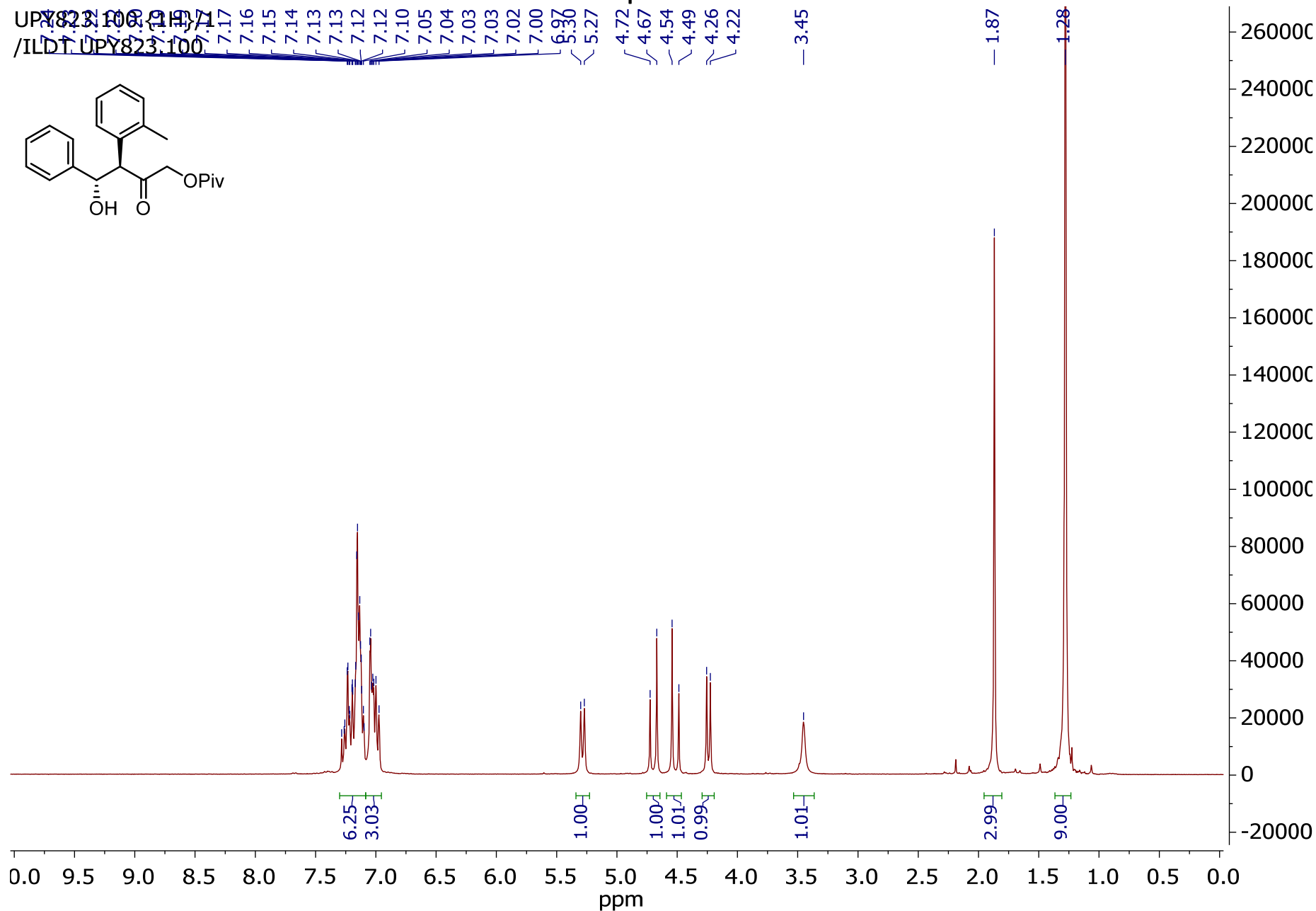
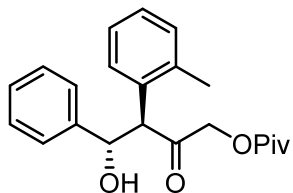


UPY825.200.{13C}deptsp135/3  
/ILDY UPY825.200 Suhorukov-HD-37-21

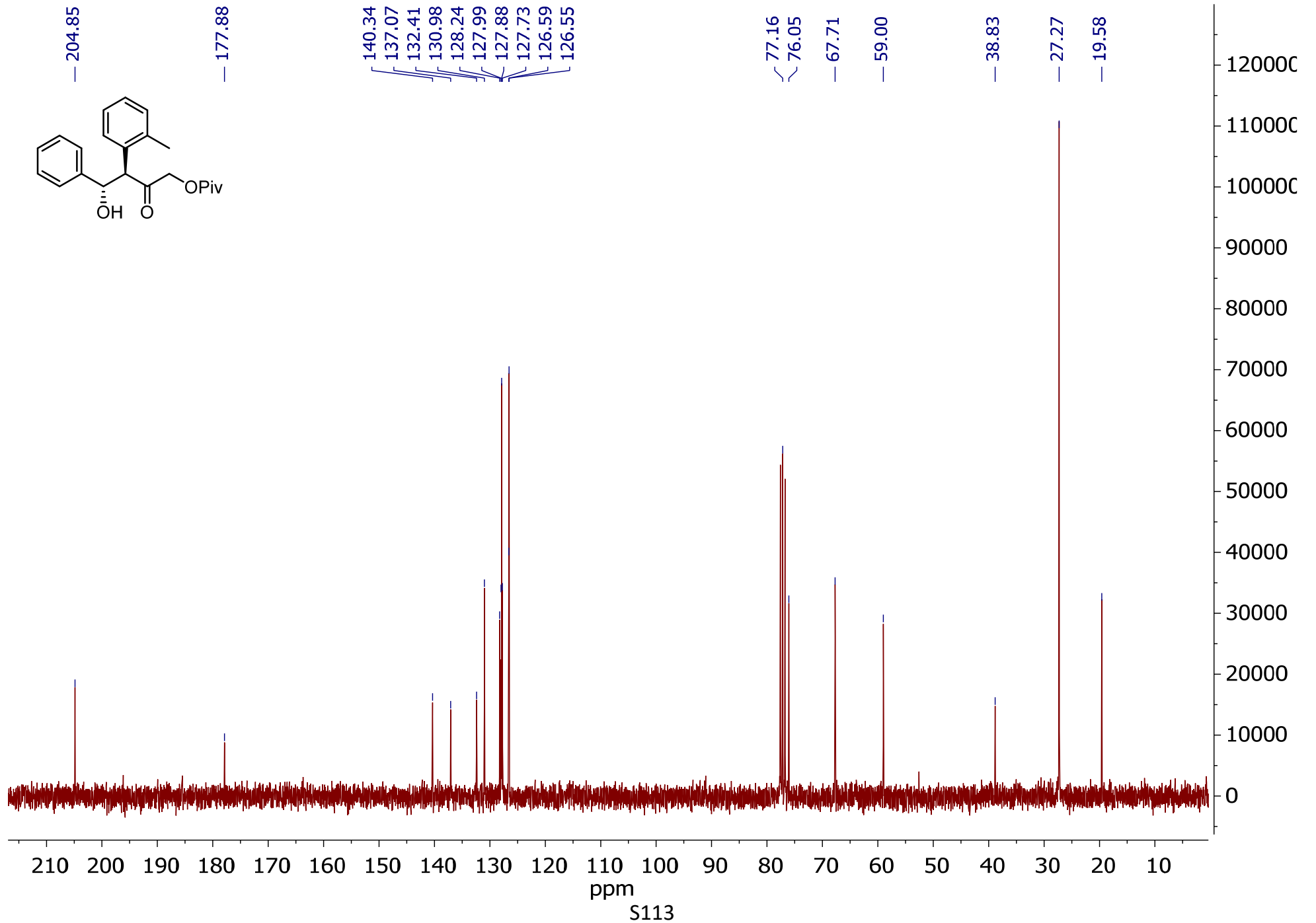
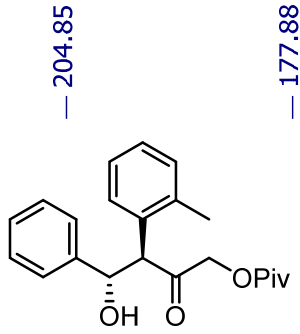


# NMR spectra of 15d

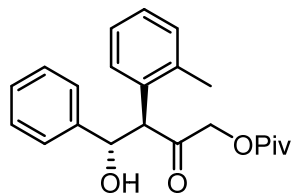
UPY823.100.11371  
/ILD.T/UPY823.100.





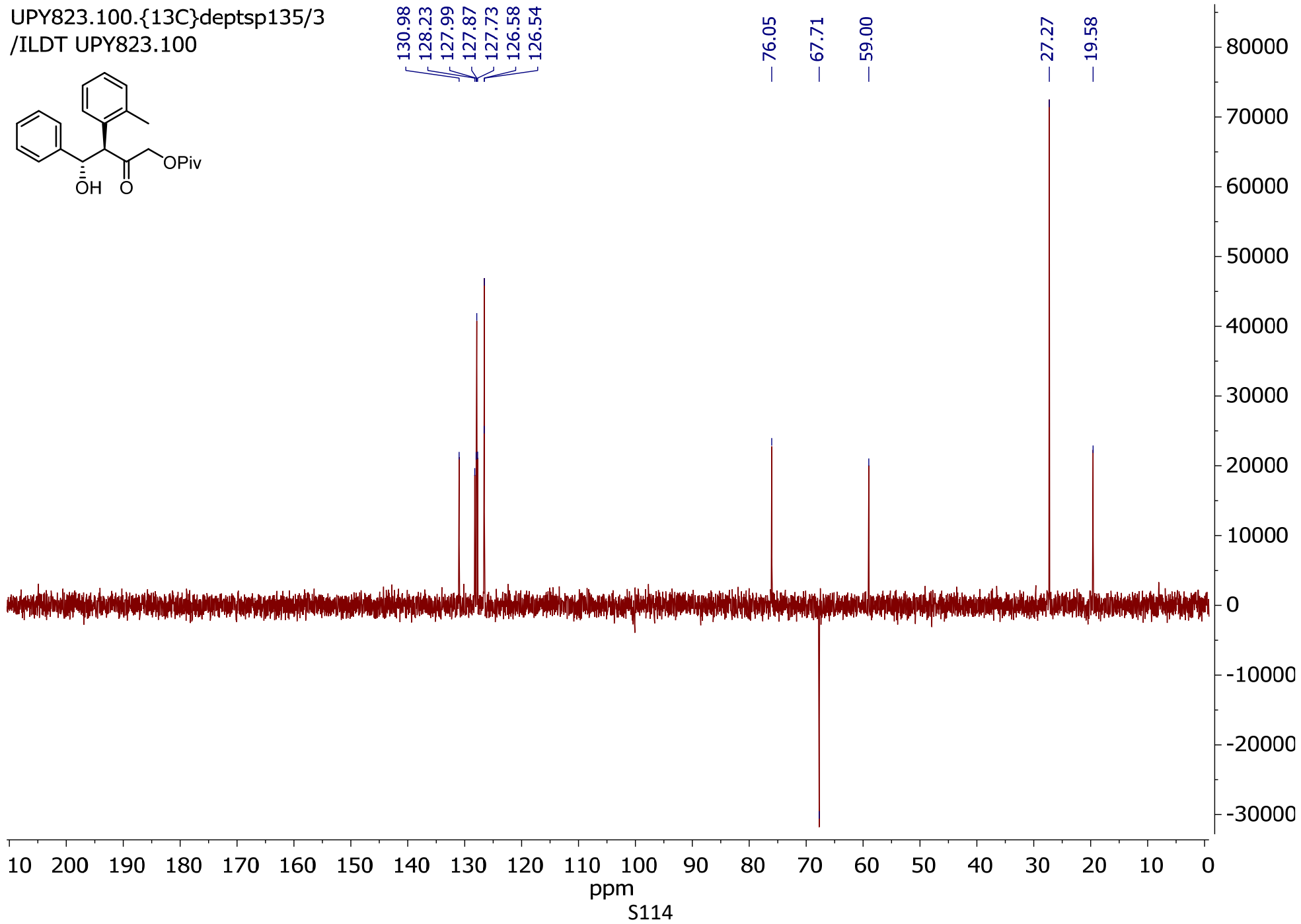


UPY823.100.{13C}deptsp135/3  
/ILDIT UPY823.100

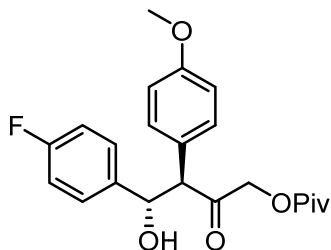


130.98  
128.23  
127.99  
127.87  
127.73  
126.58  
126.54

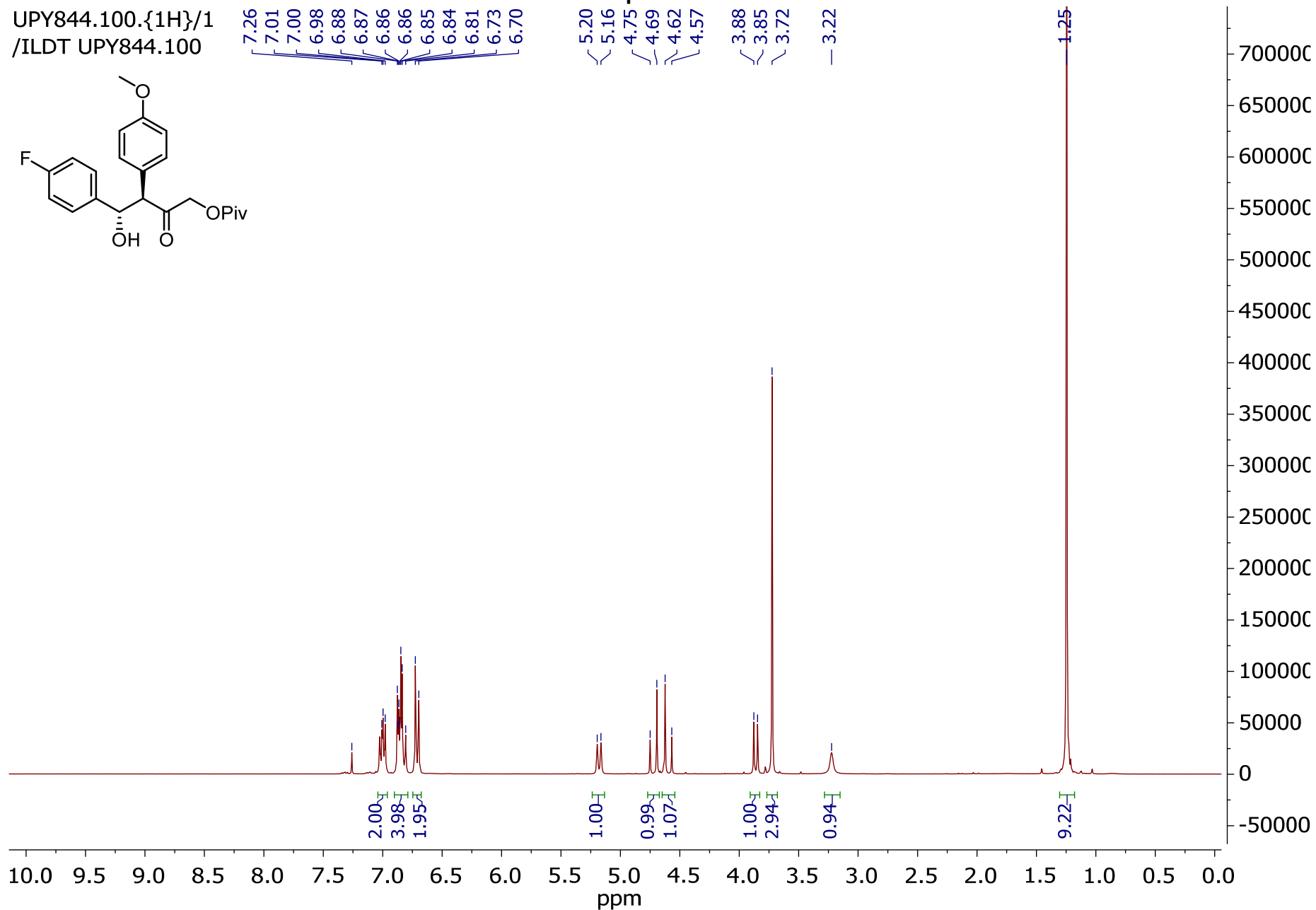
76.05  
67.71  
59.00  
27.27  
19.58



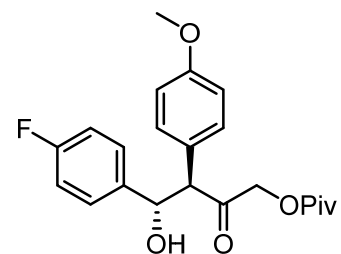
UPY844.100.{1H}/1  
/ILDT UPY844.100



### NMR spectra of 15e



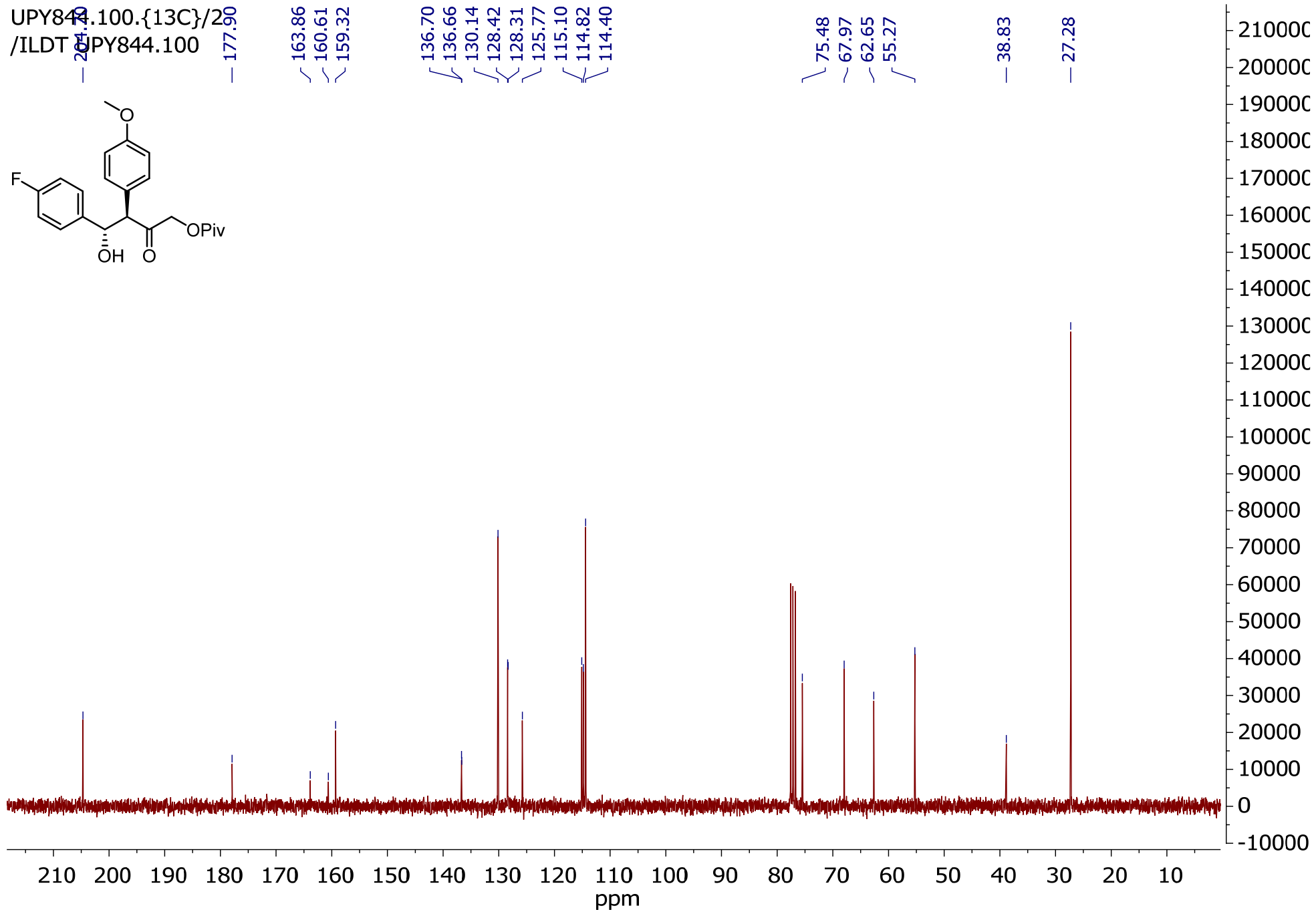
UPY844.100.{13C}/2  
/ILDTPY844.100



163.86  
160.61  
159.32  
136.70  
136.66  
130.14  
128.42  
128.31  
125.77  
115.10  
114.82  
114.40

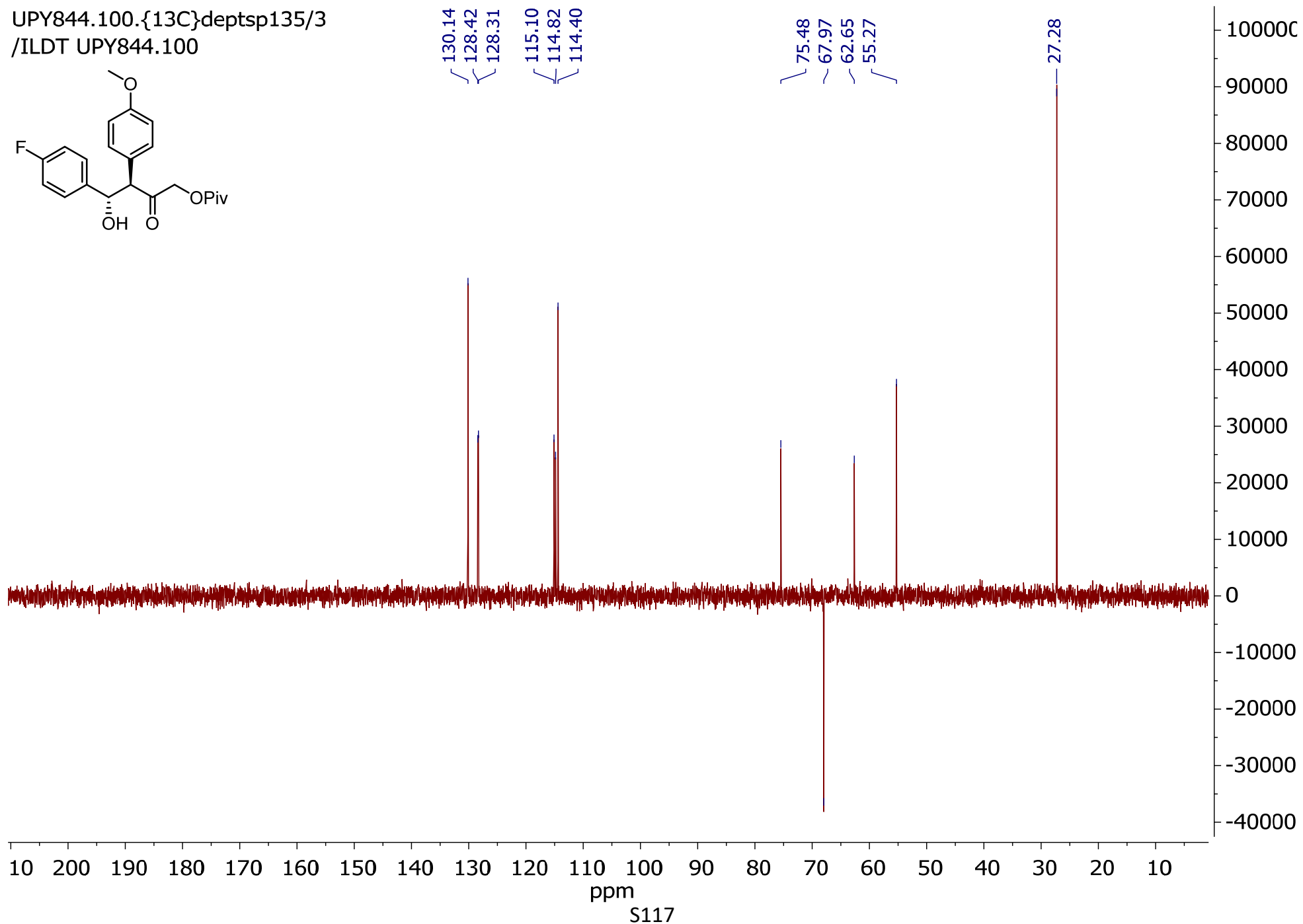
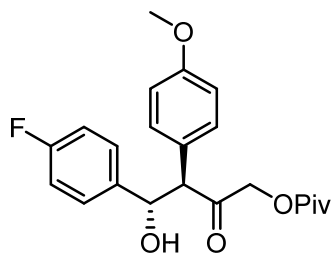
75.48  
67.97  
62.65  
55.27

38.83  
27.28

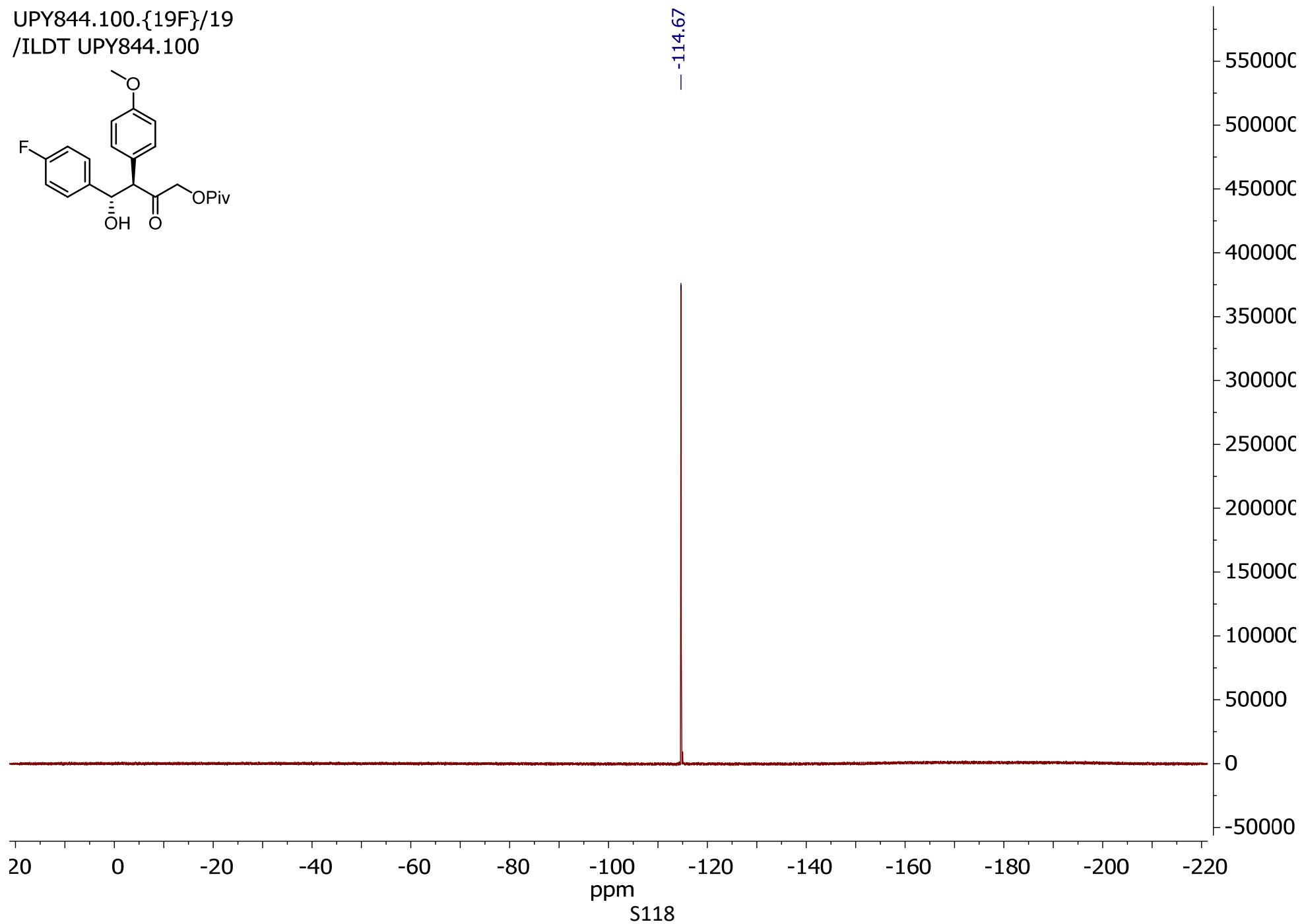
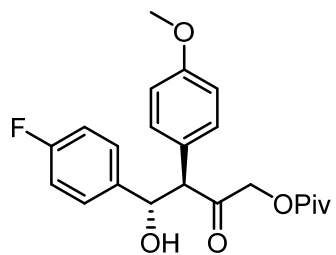


S116

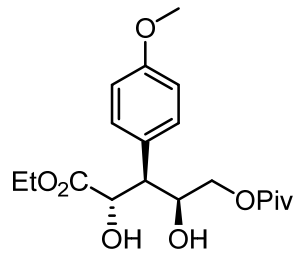
UPY844.100.{13C}deptsp135/3  
/ILDT UPY844.100



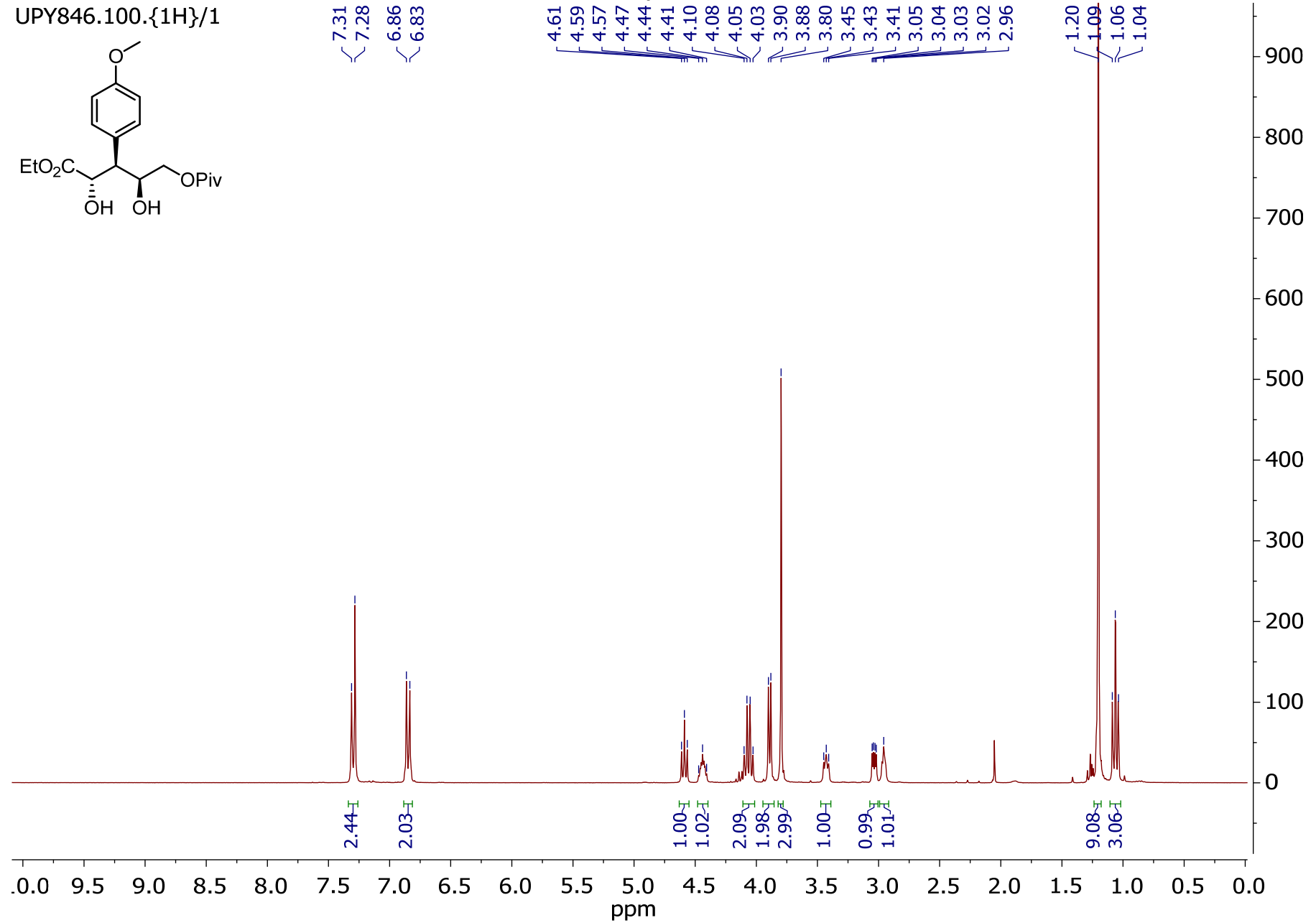
UPY844.100.{19F}/19  
/ILD T UPY844.100



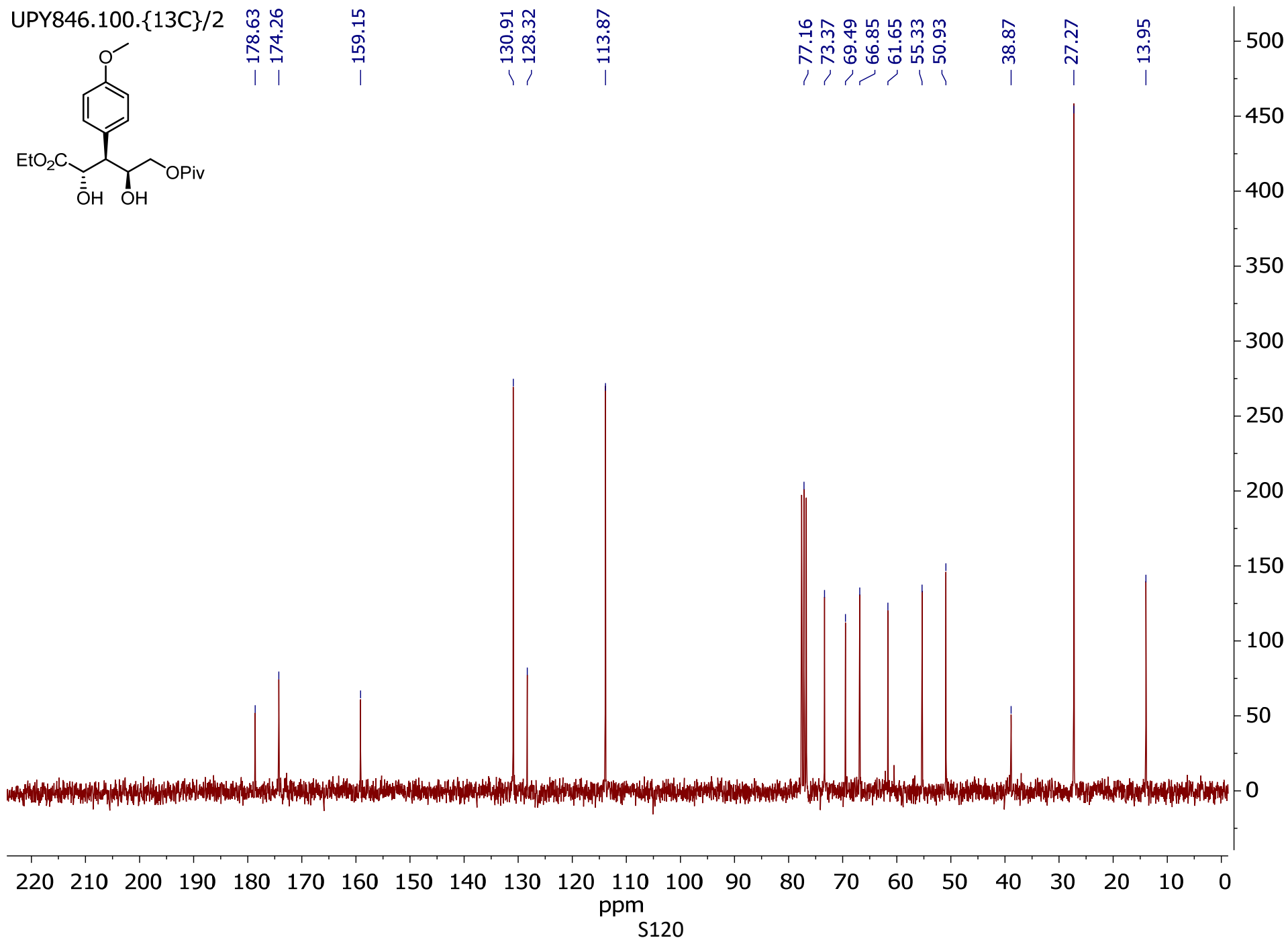
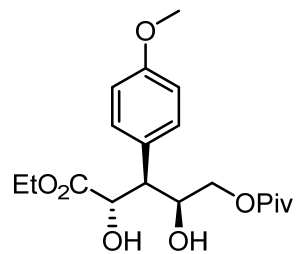
UPY846.100.{1H}/1



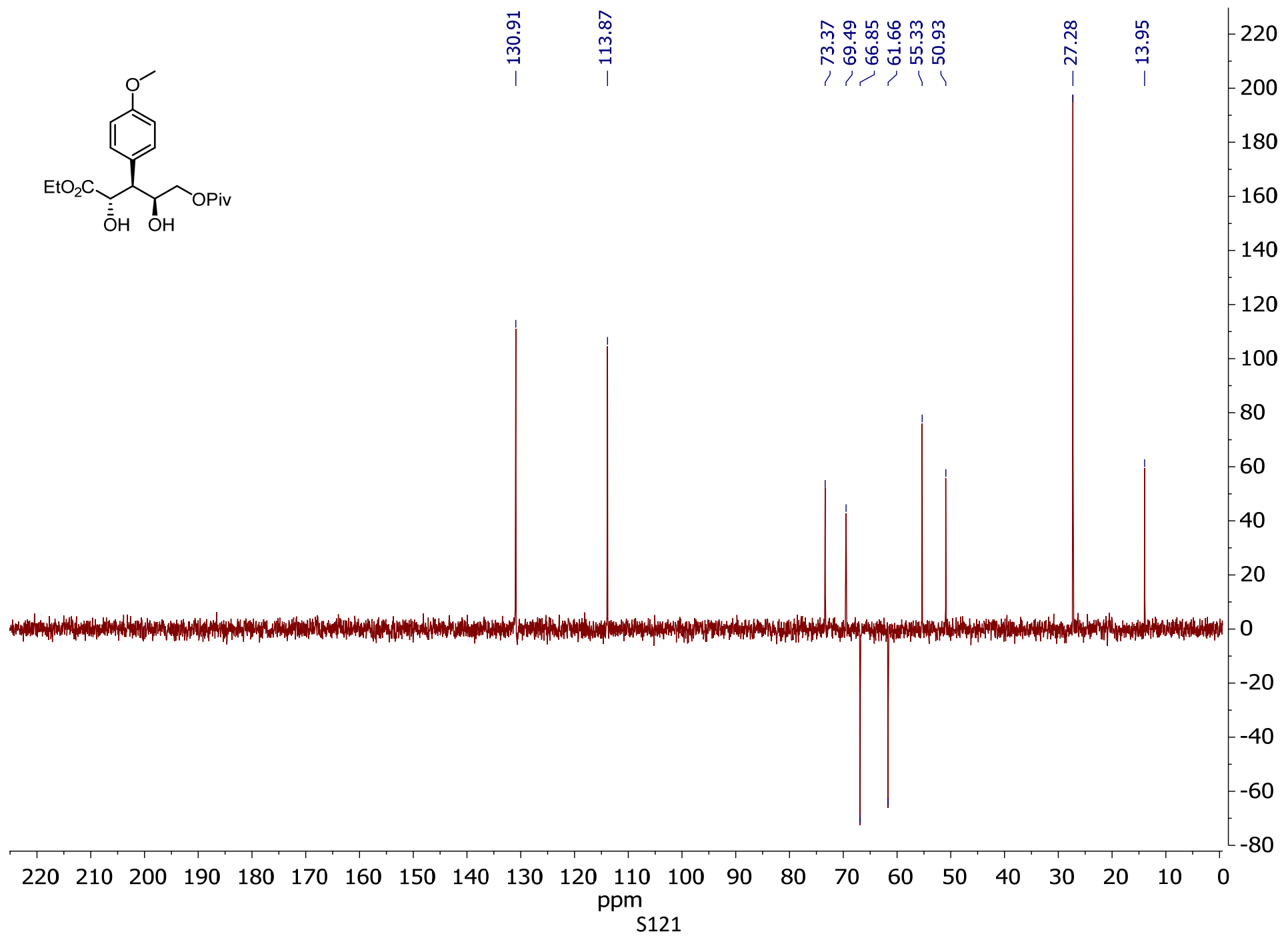
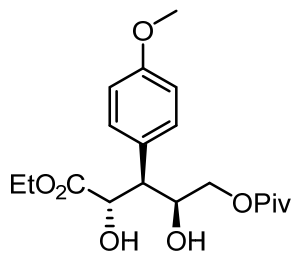
### NMR spectra of 16

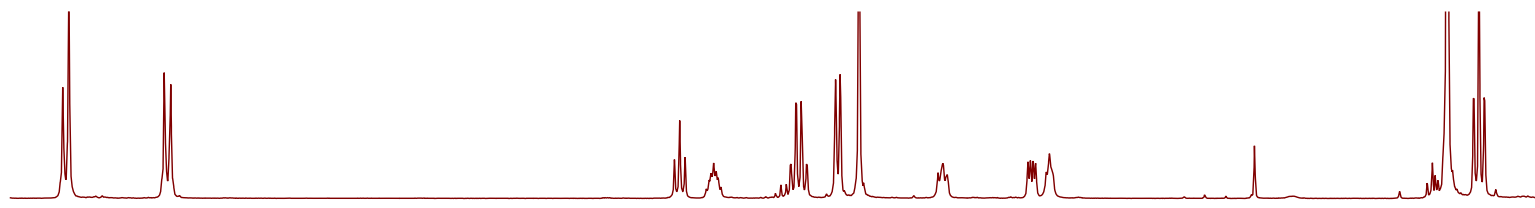


UPY846.100.{13C}/2

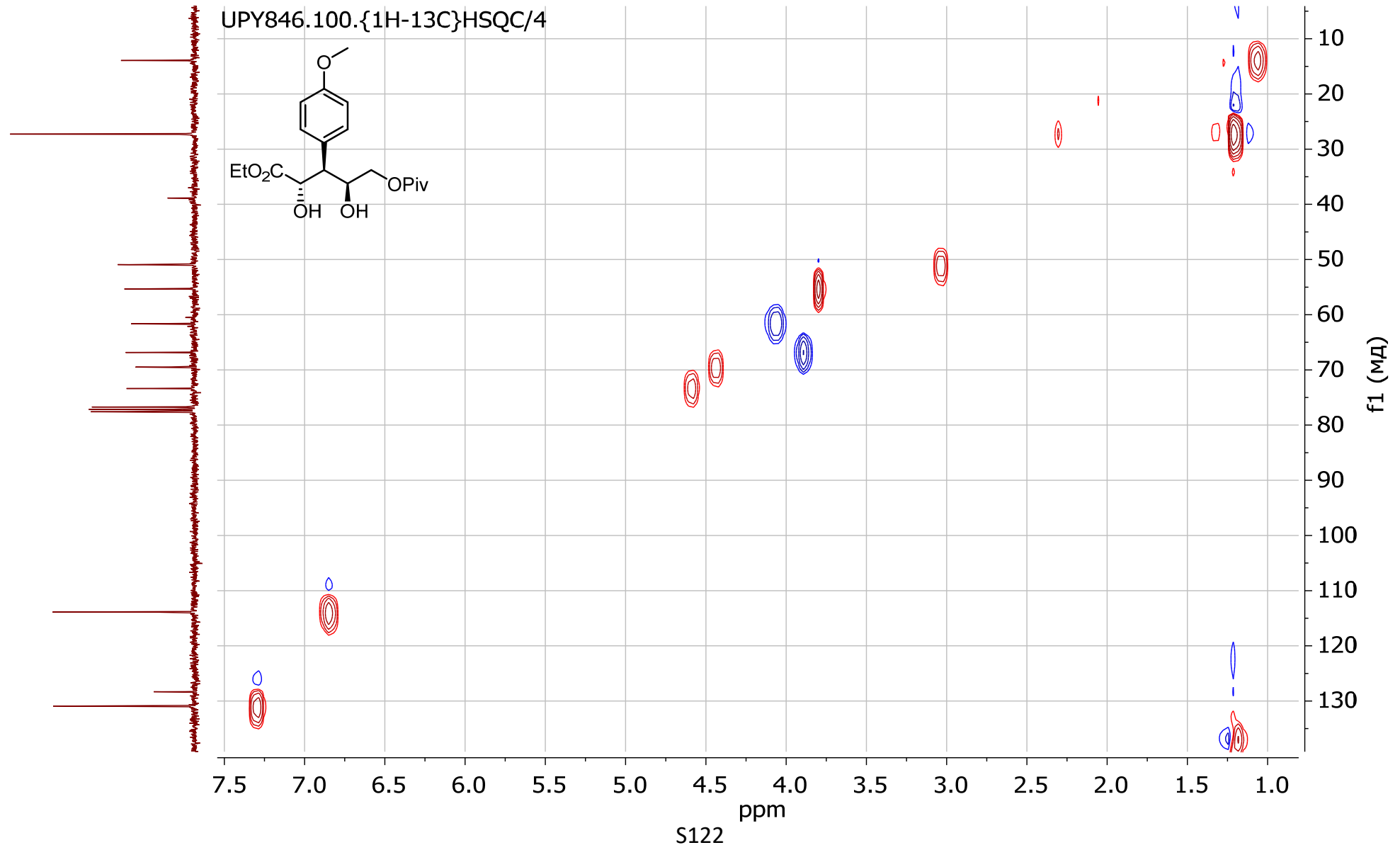
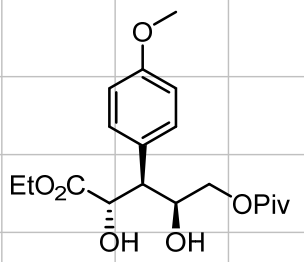








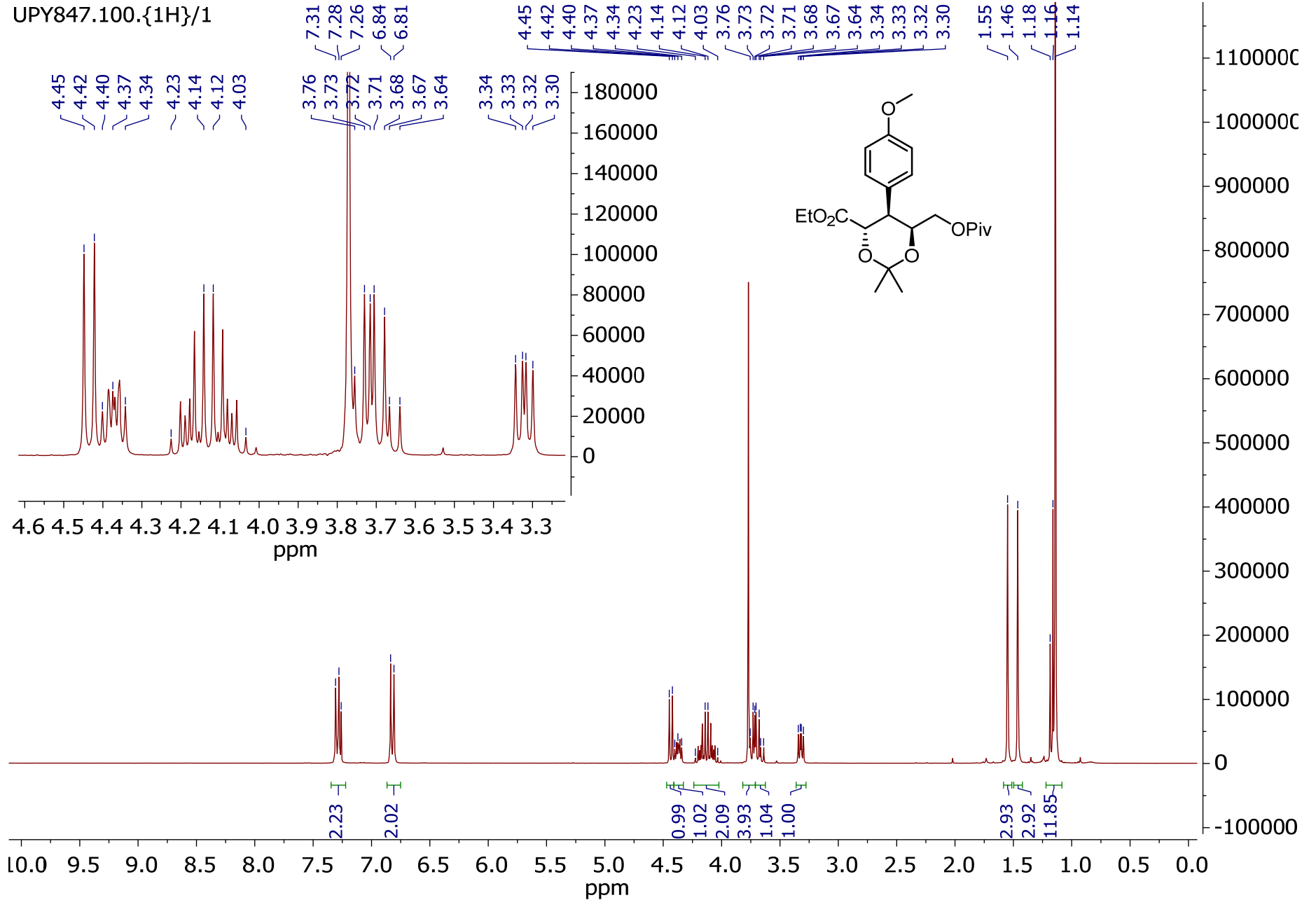
UPY846.100.{1H-13C}HSQC/4

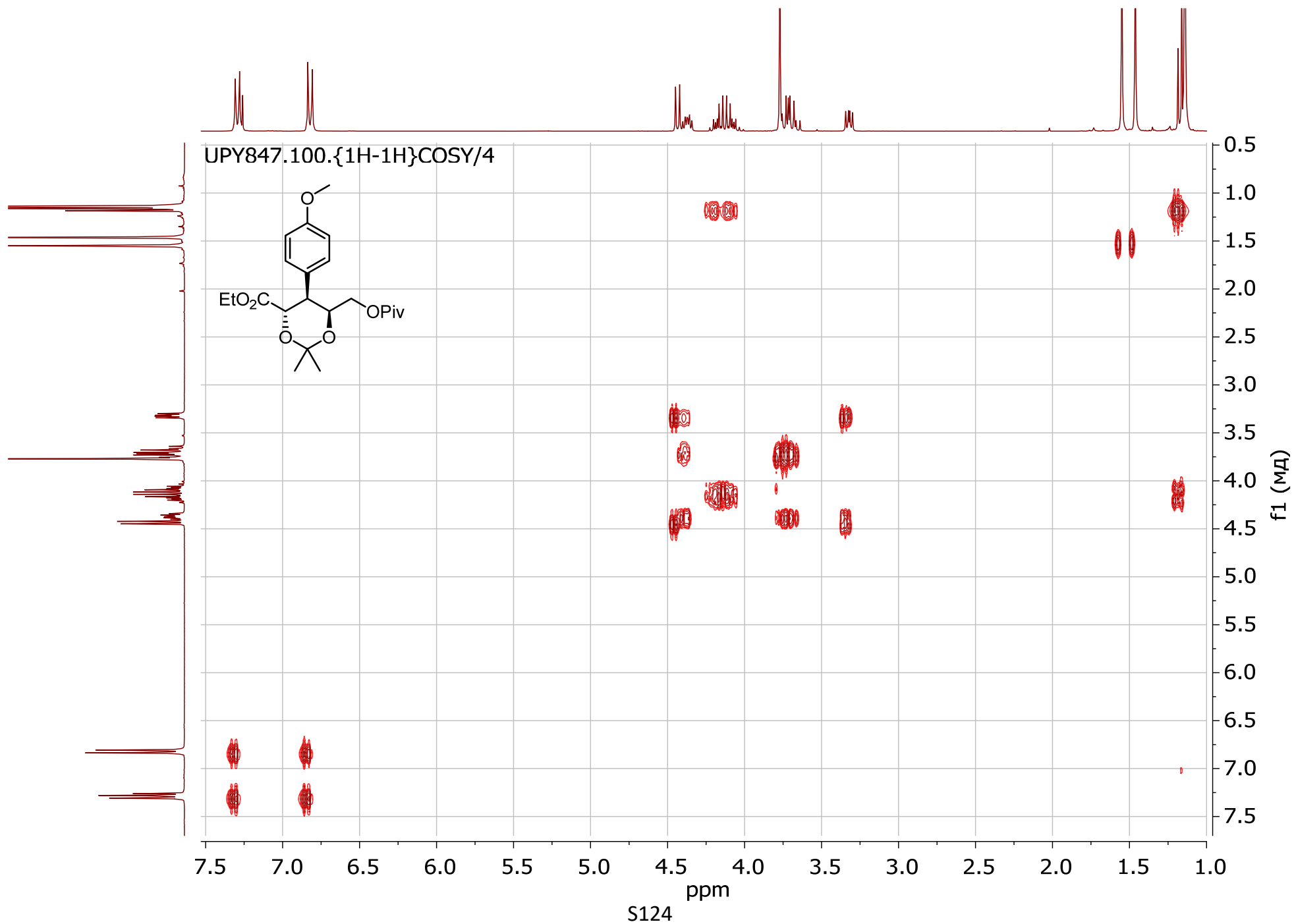


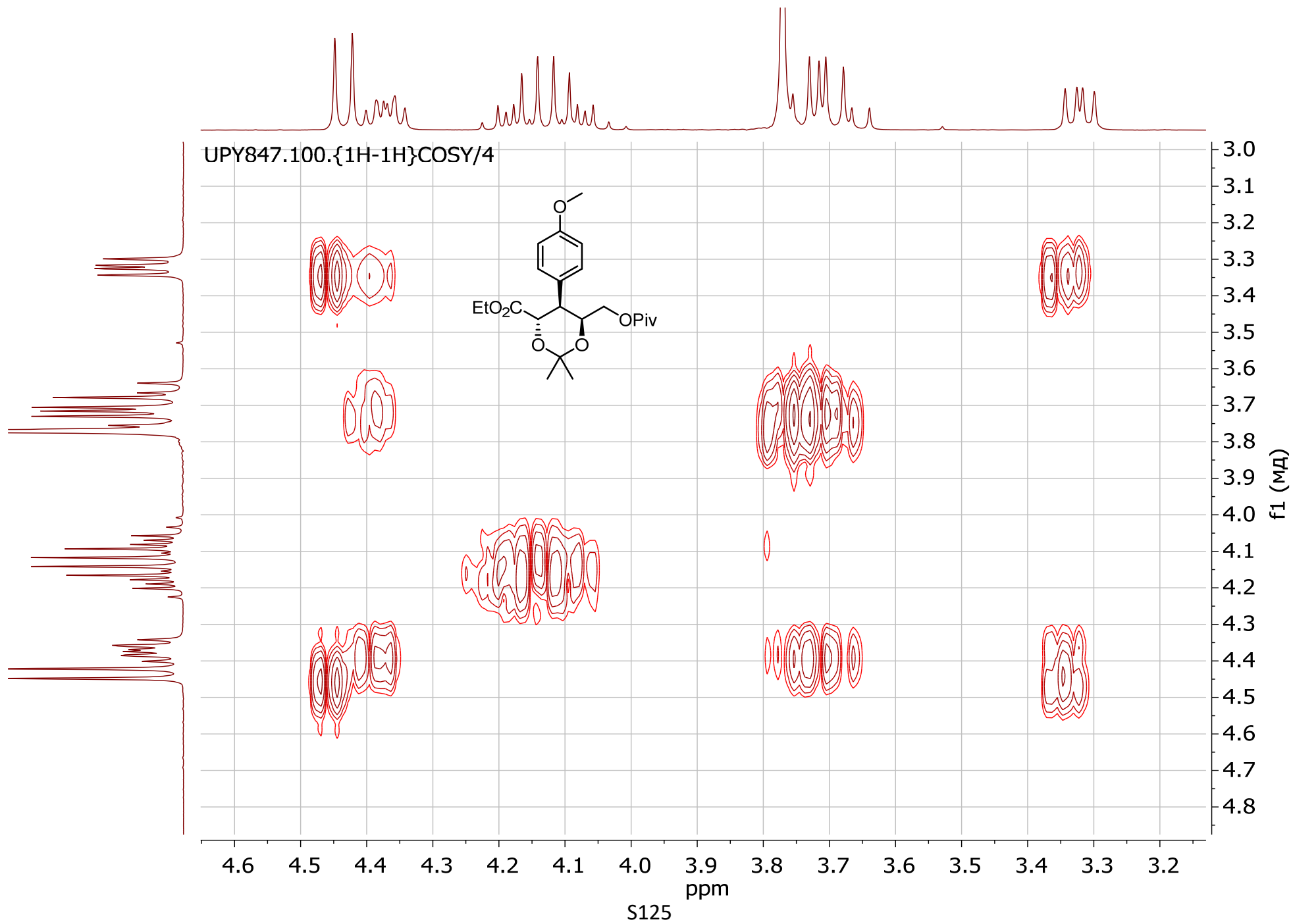
S122

NMR spectra of 17

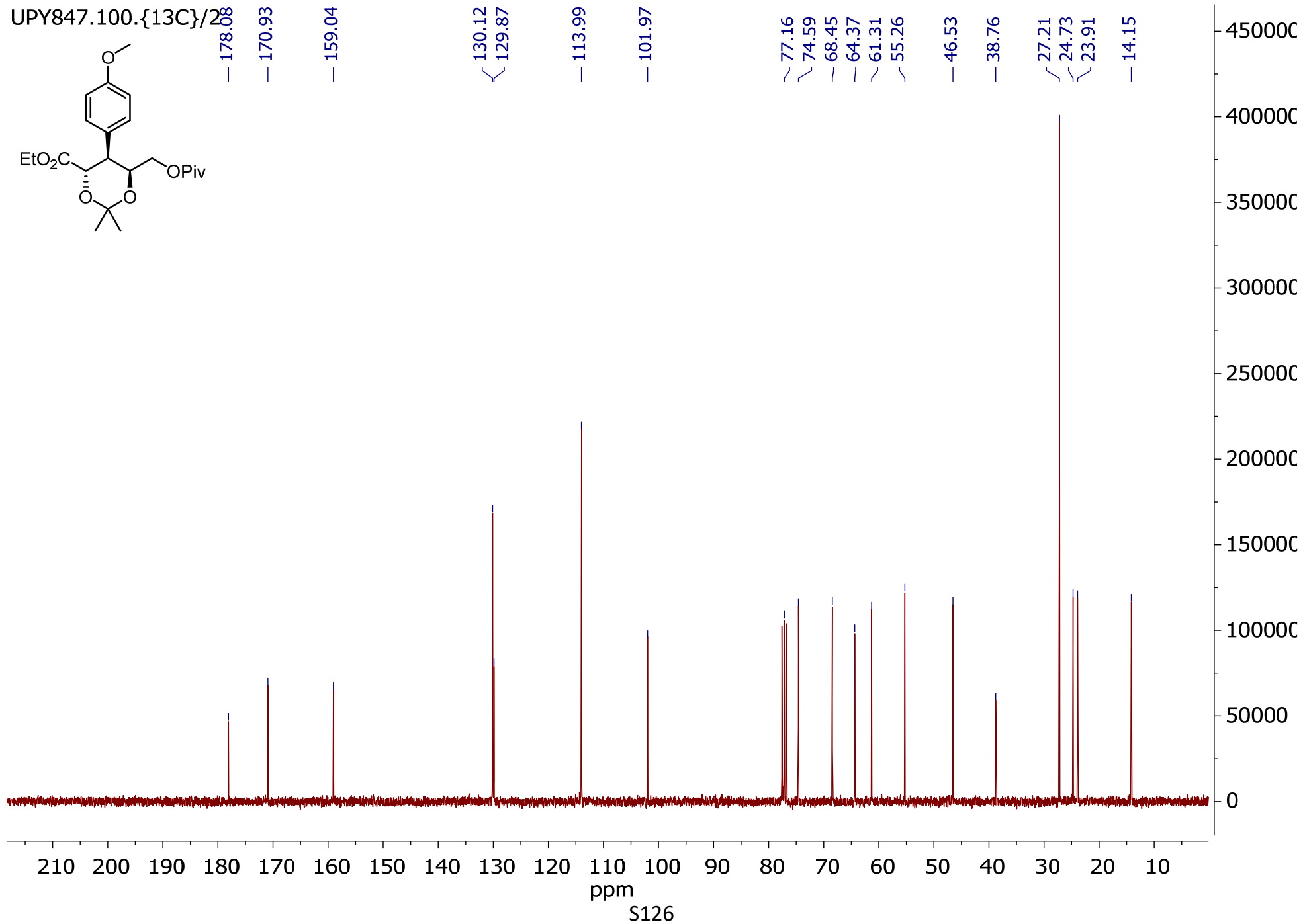
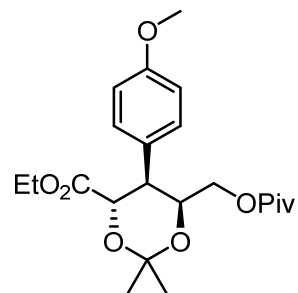
UPY847.100.1H/1



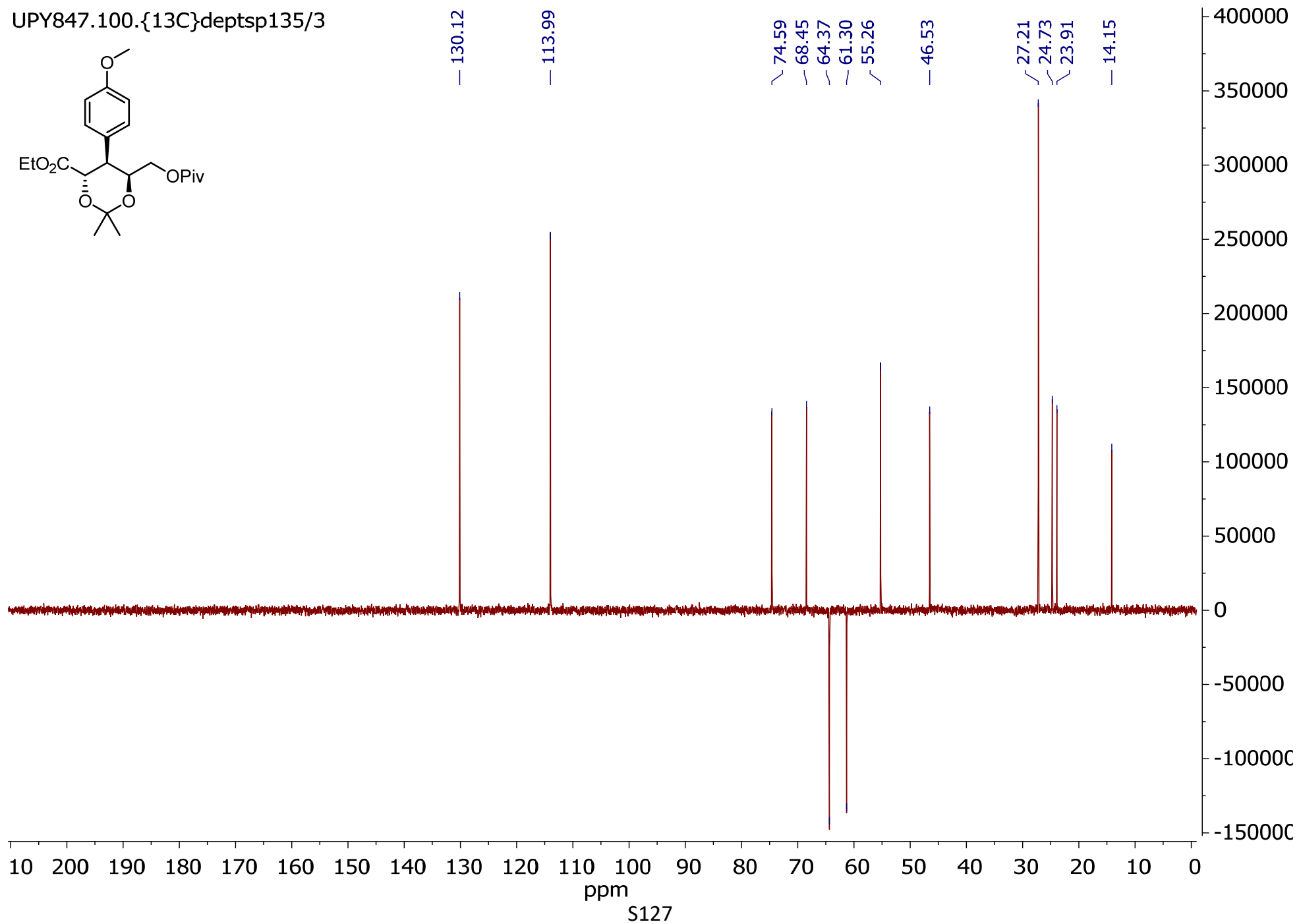
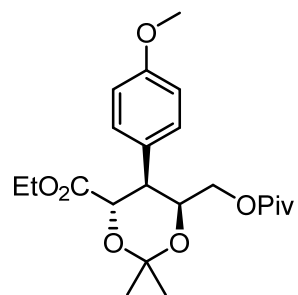


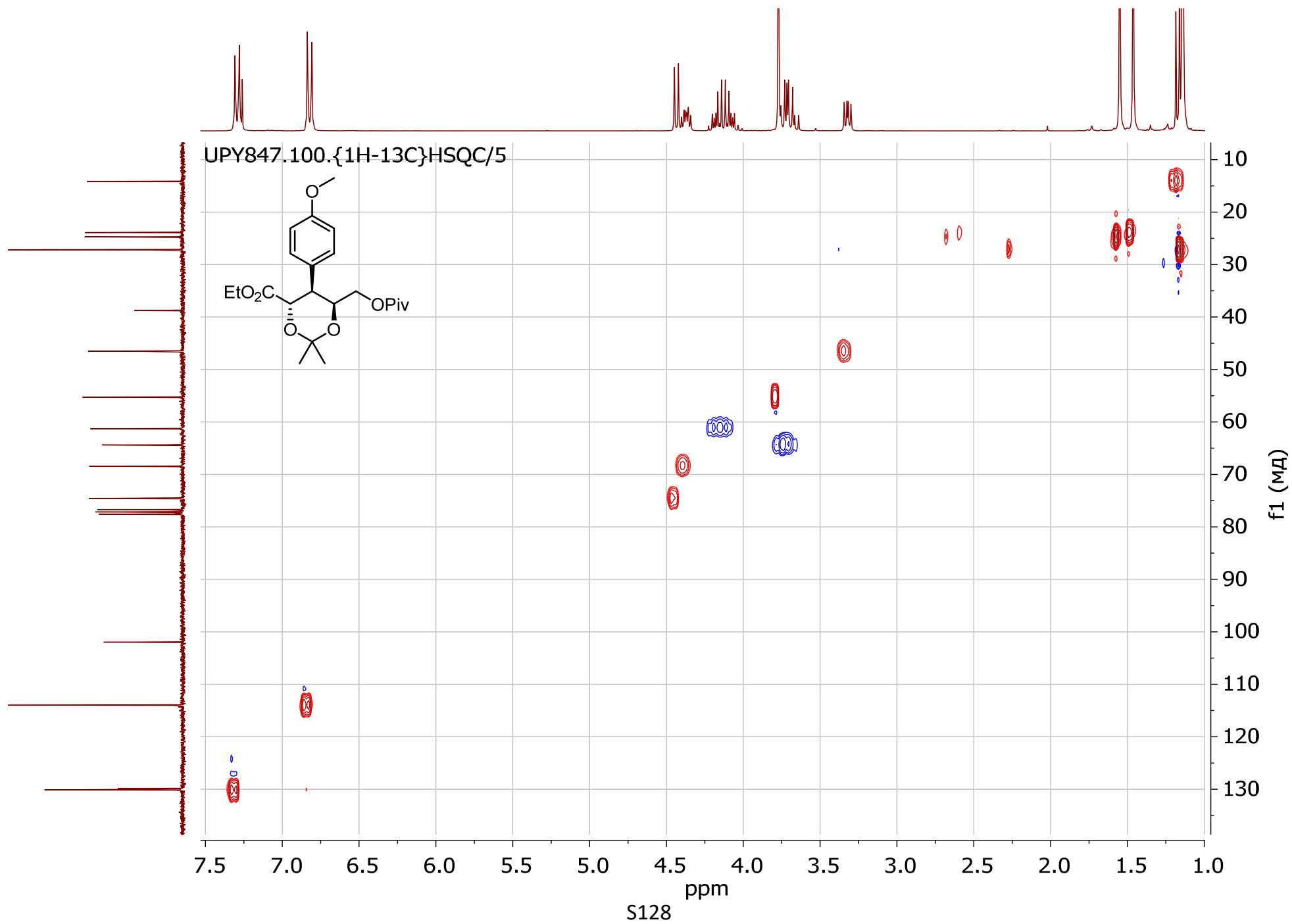


UPY847.100.{13C}/208

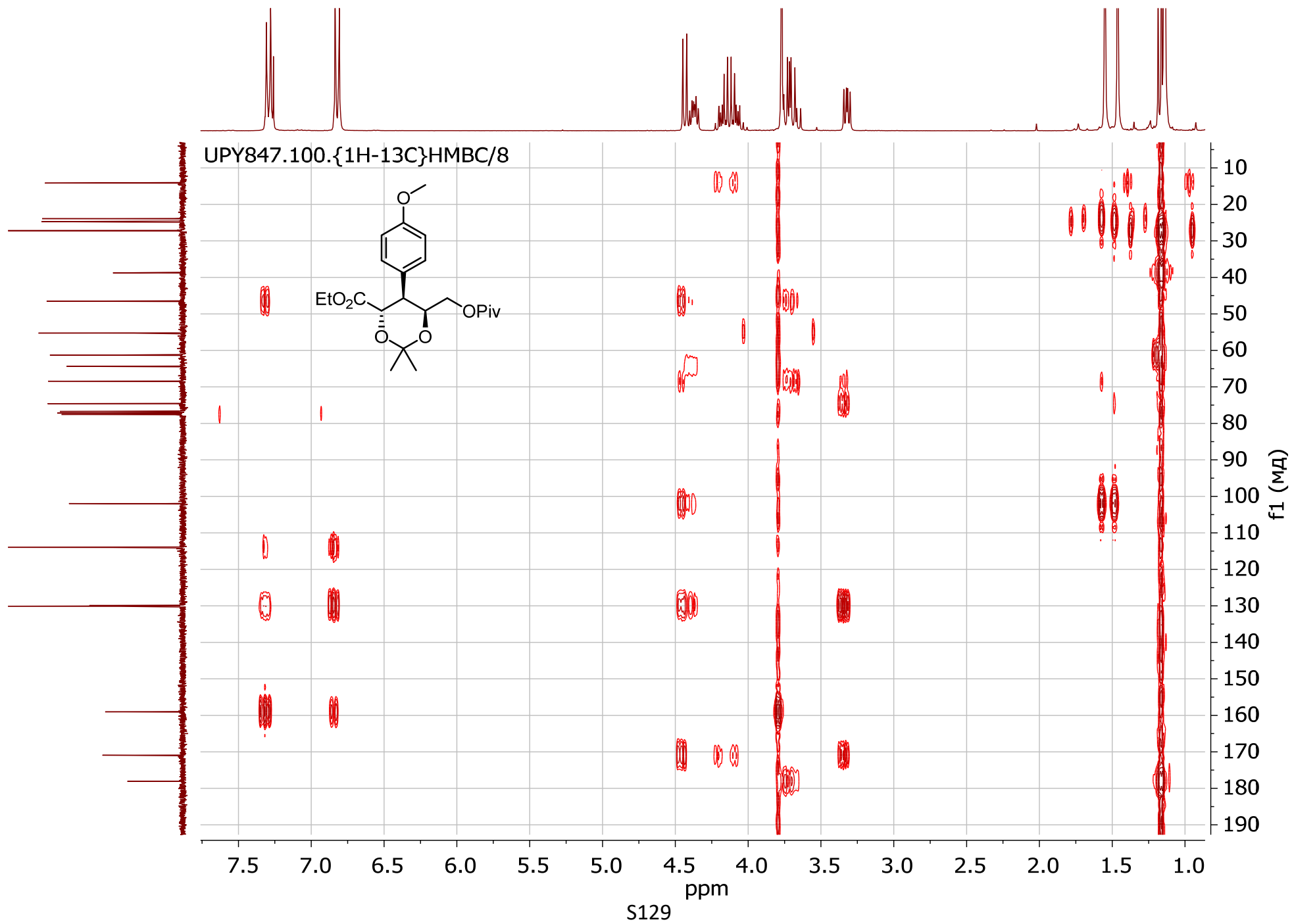


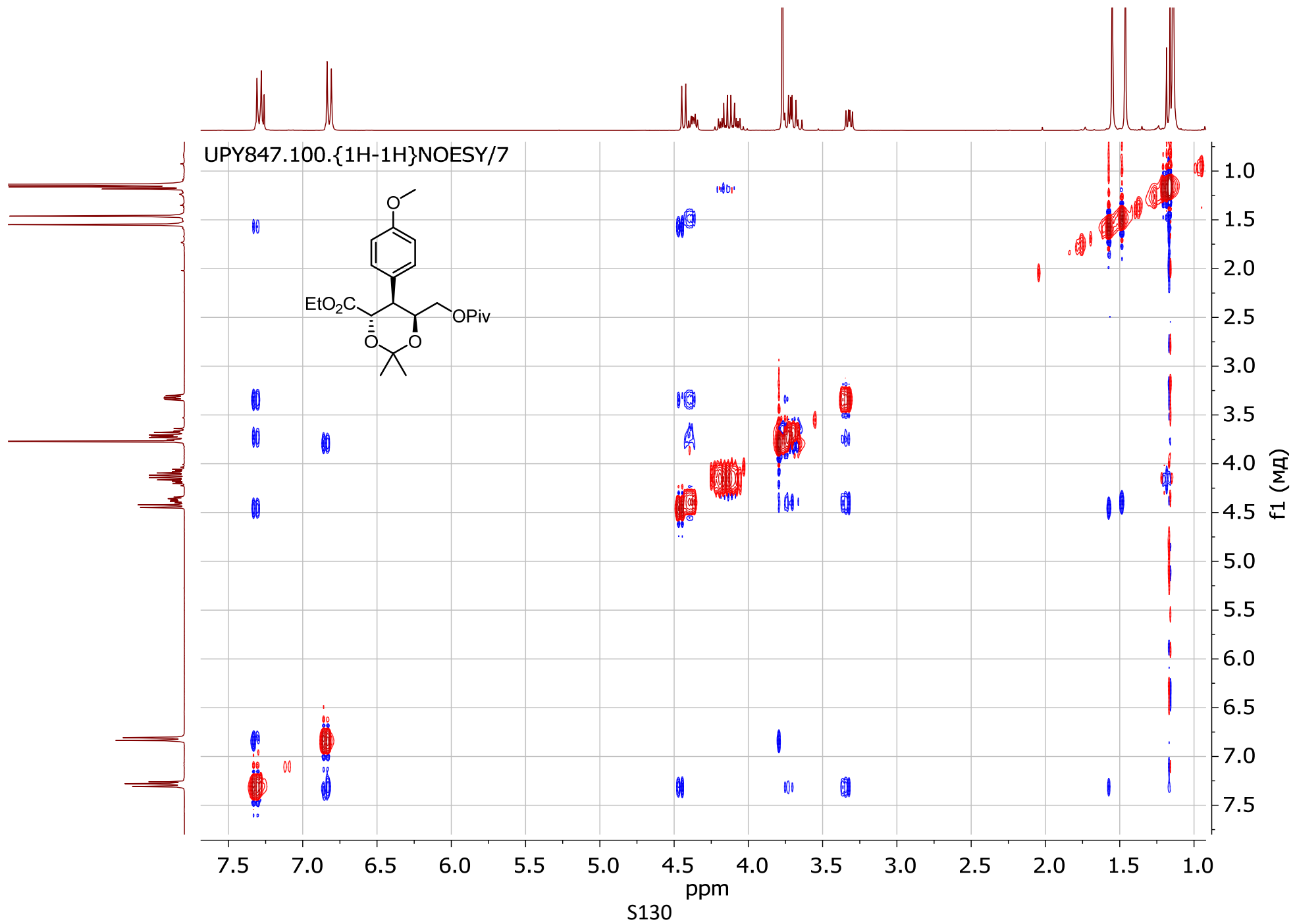
UPY847.100.{13C}deptsp135/3



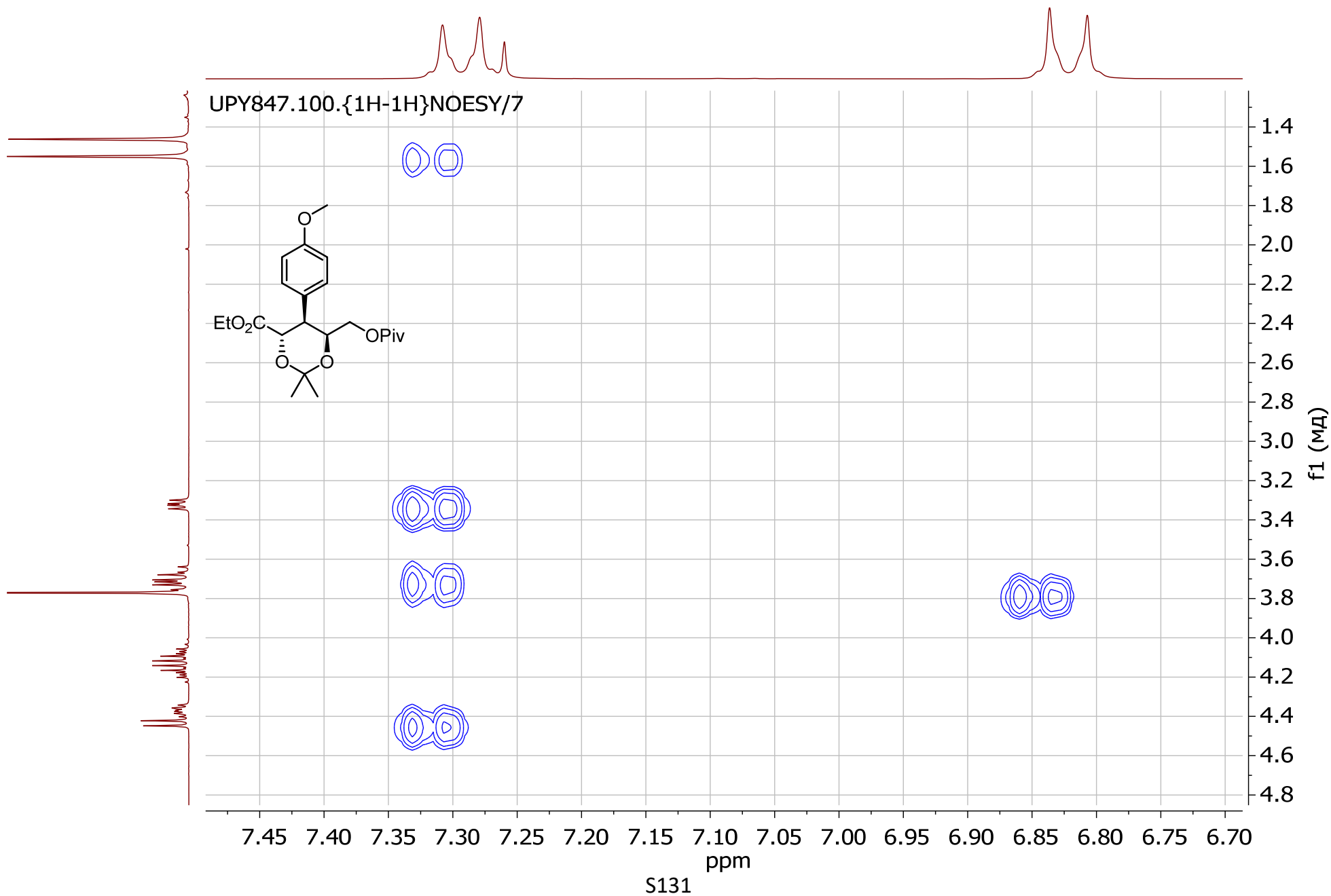
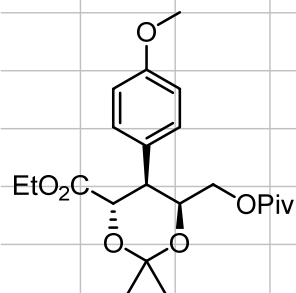




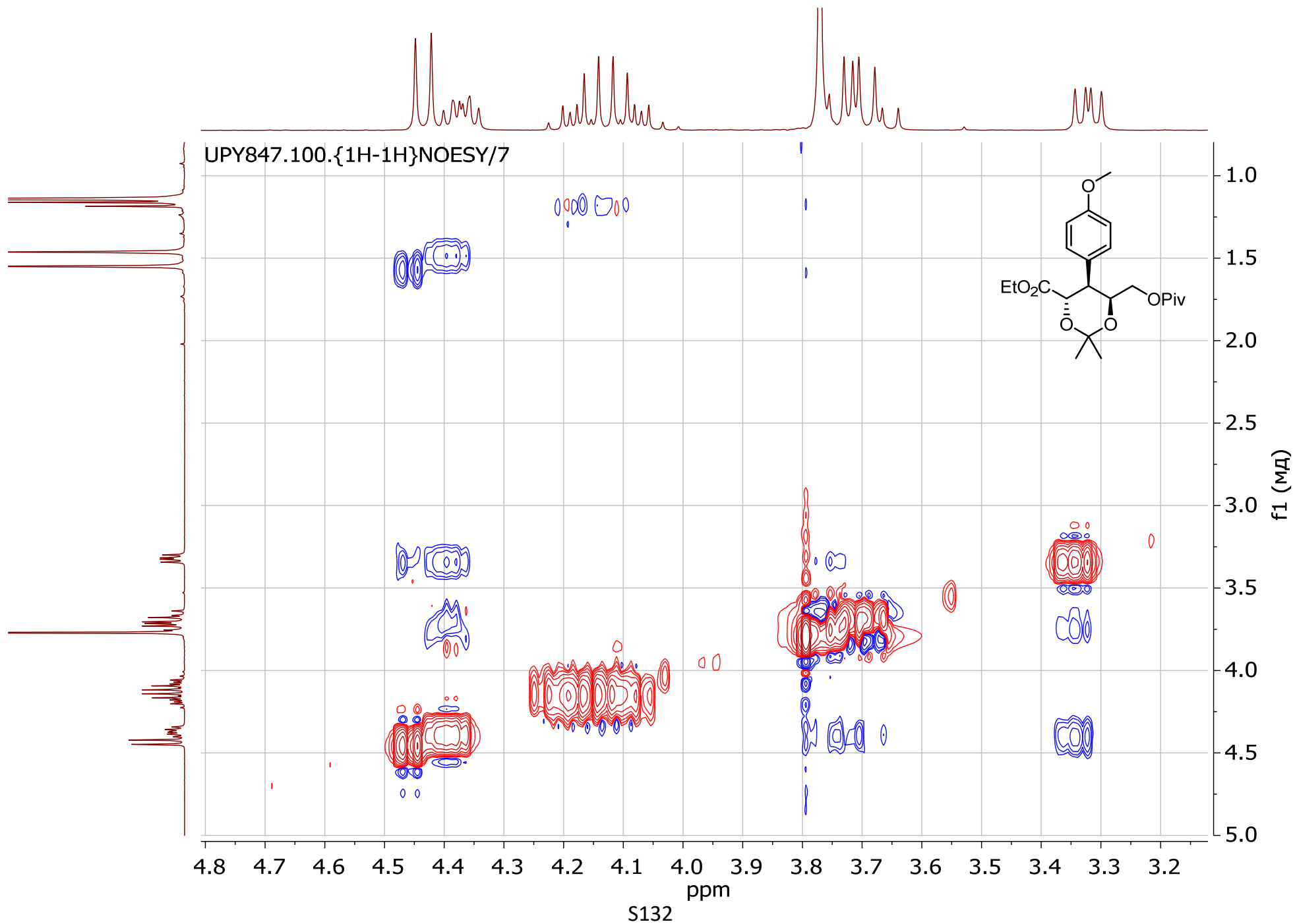




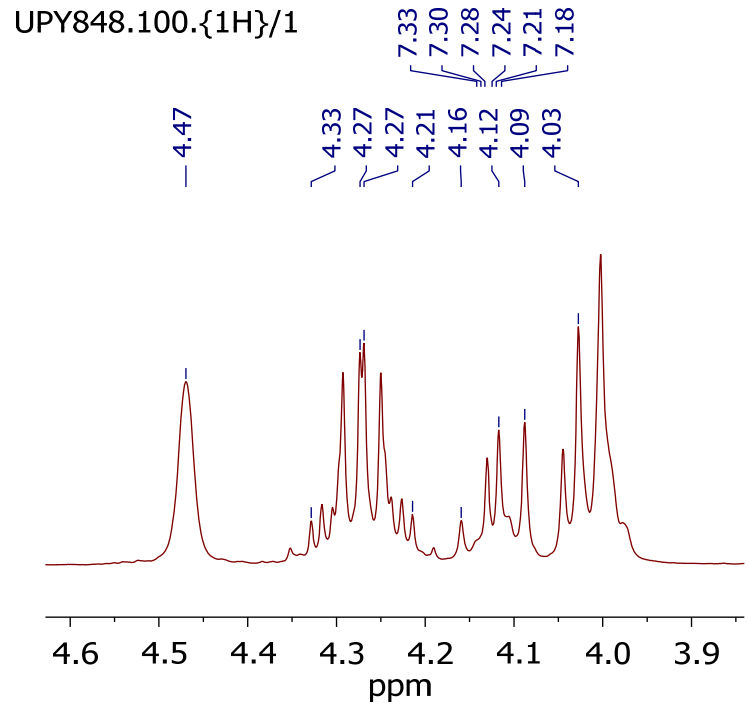
UPY847.100.{1H-1H}NOESY/7



S131

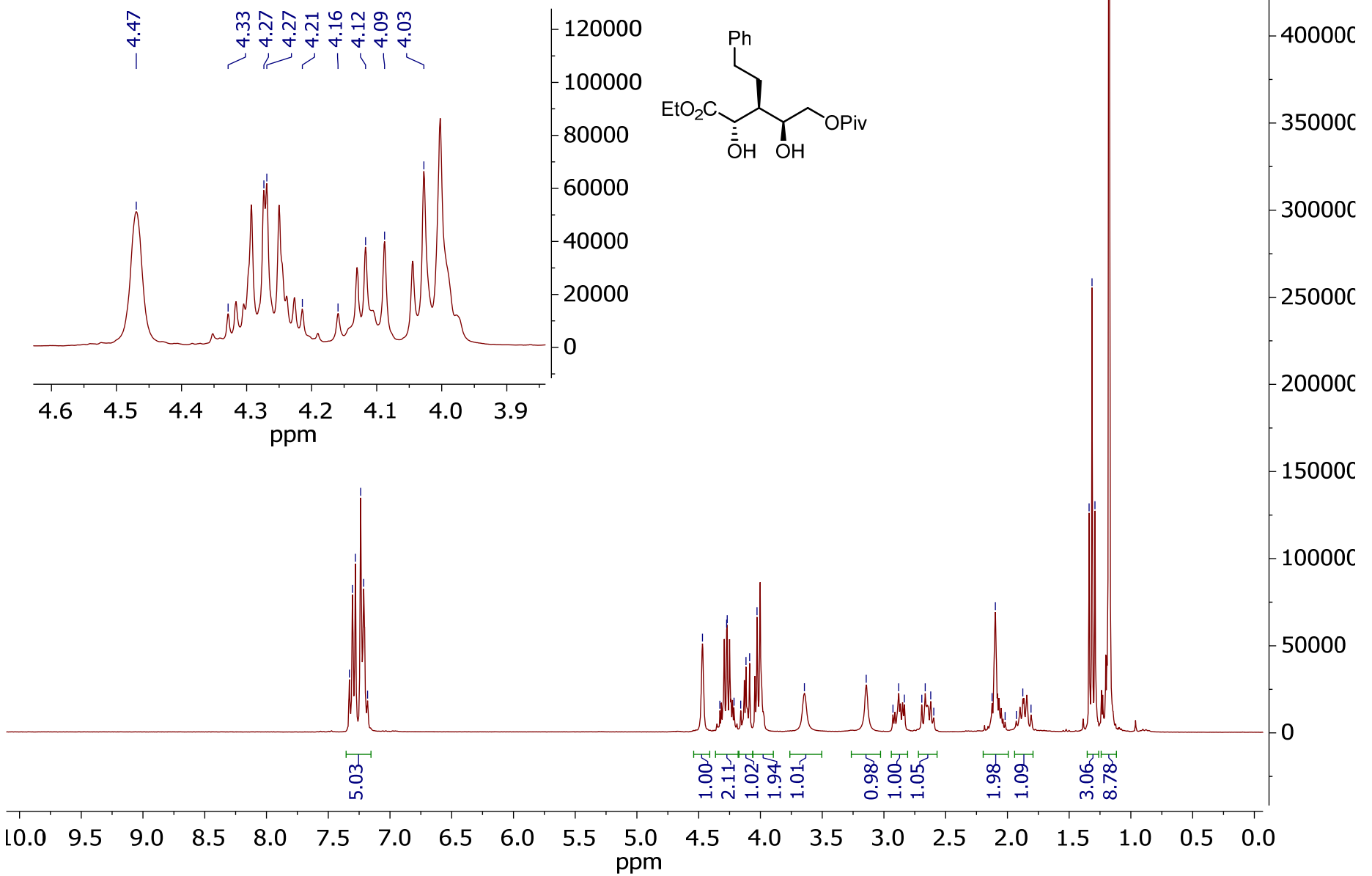
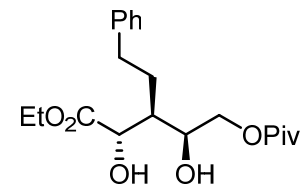


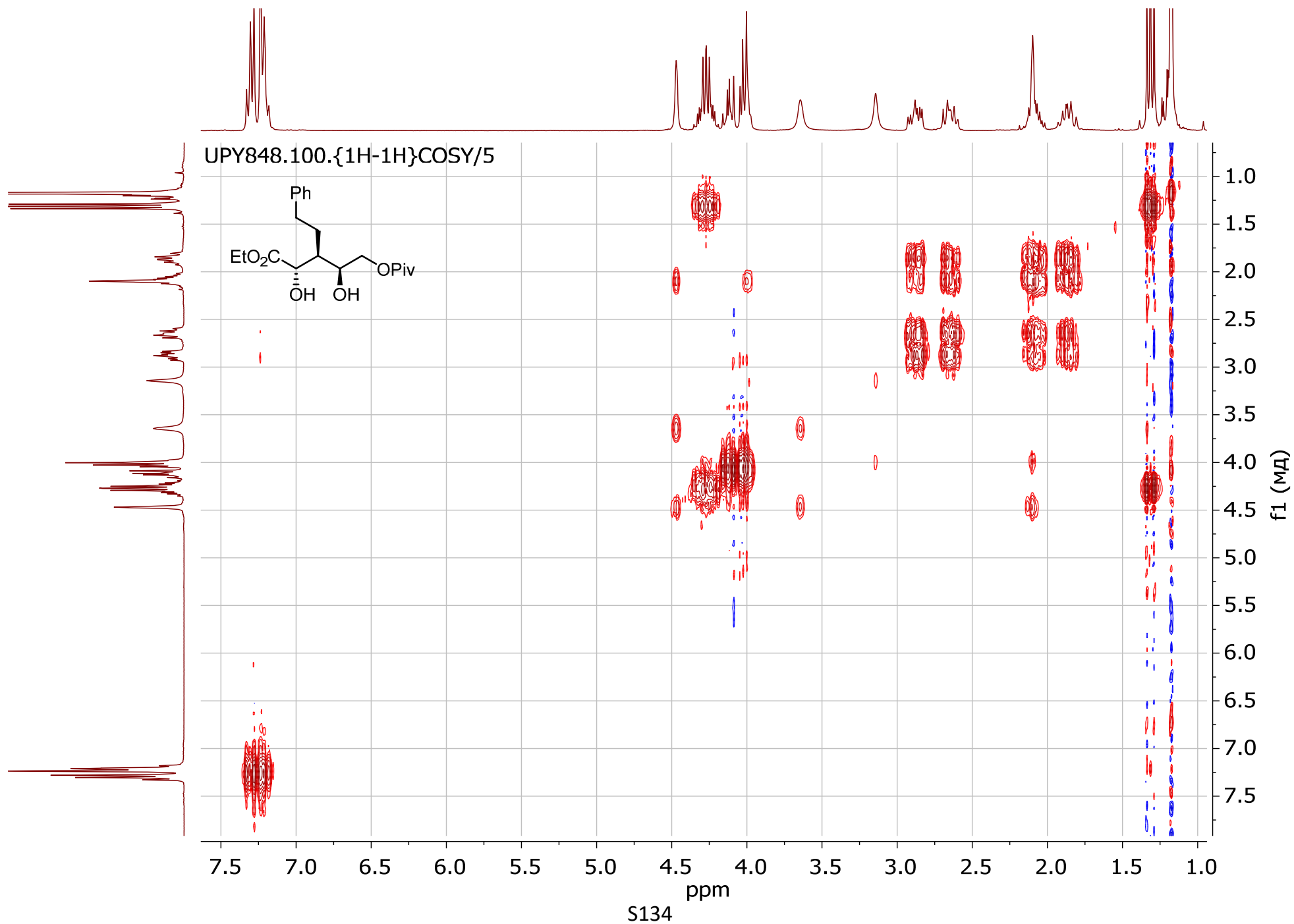
UPY848.100.{1H}/1

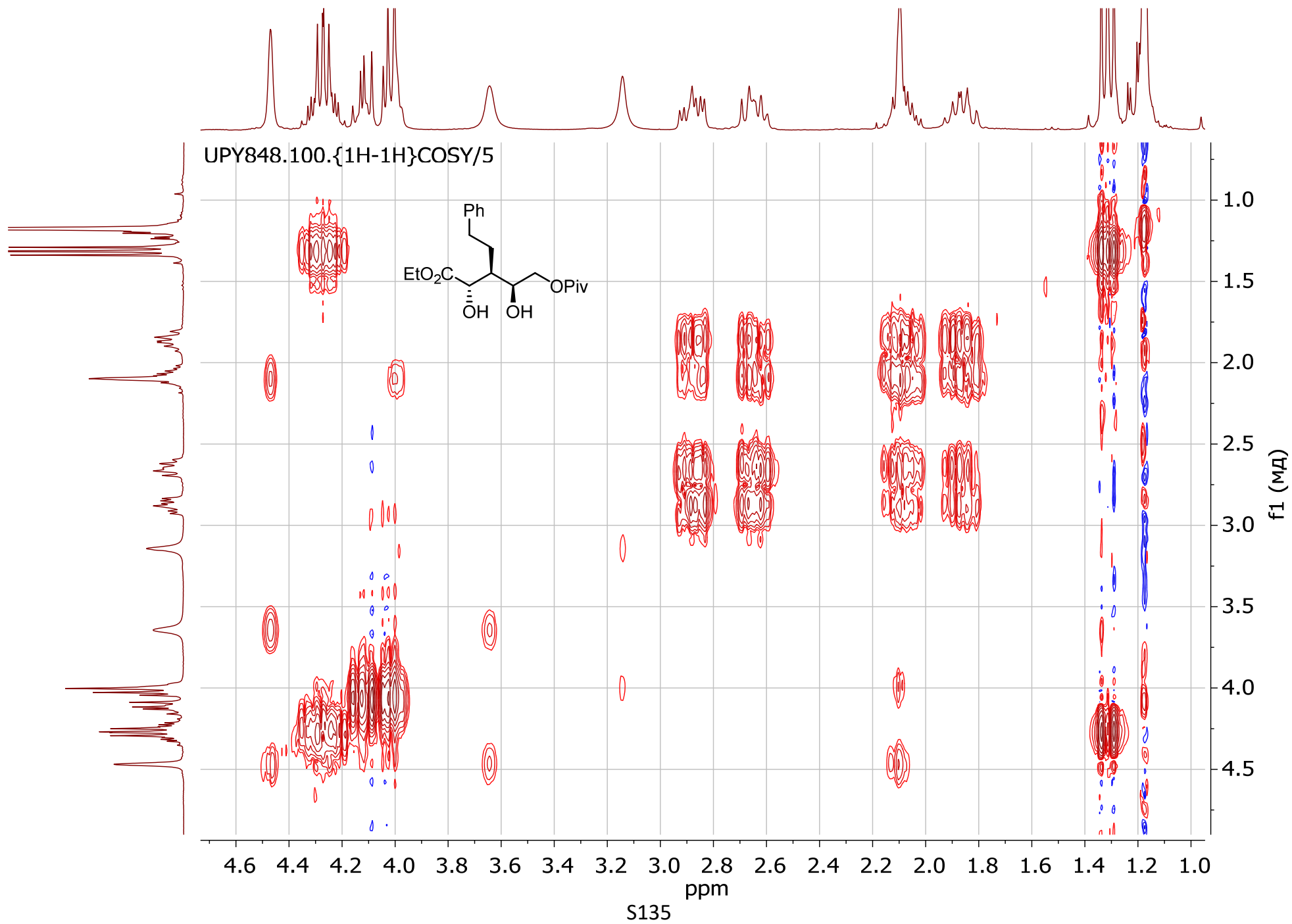


### NMR spectra of 18a

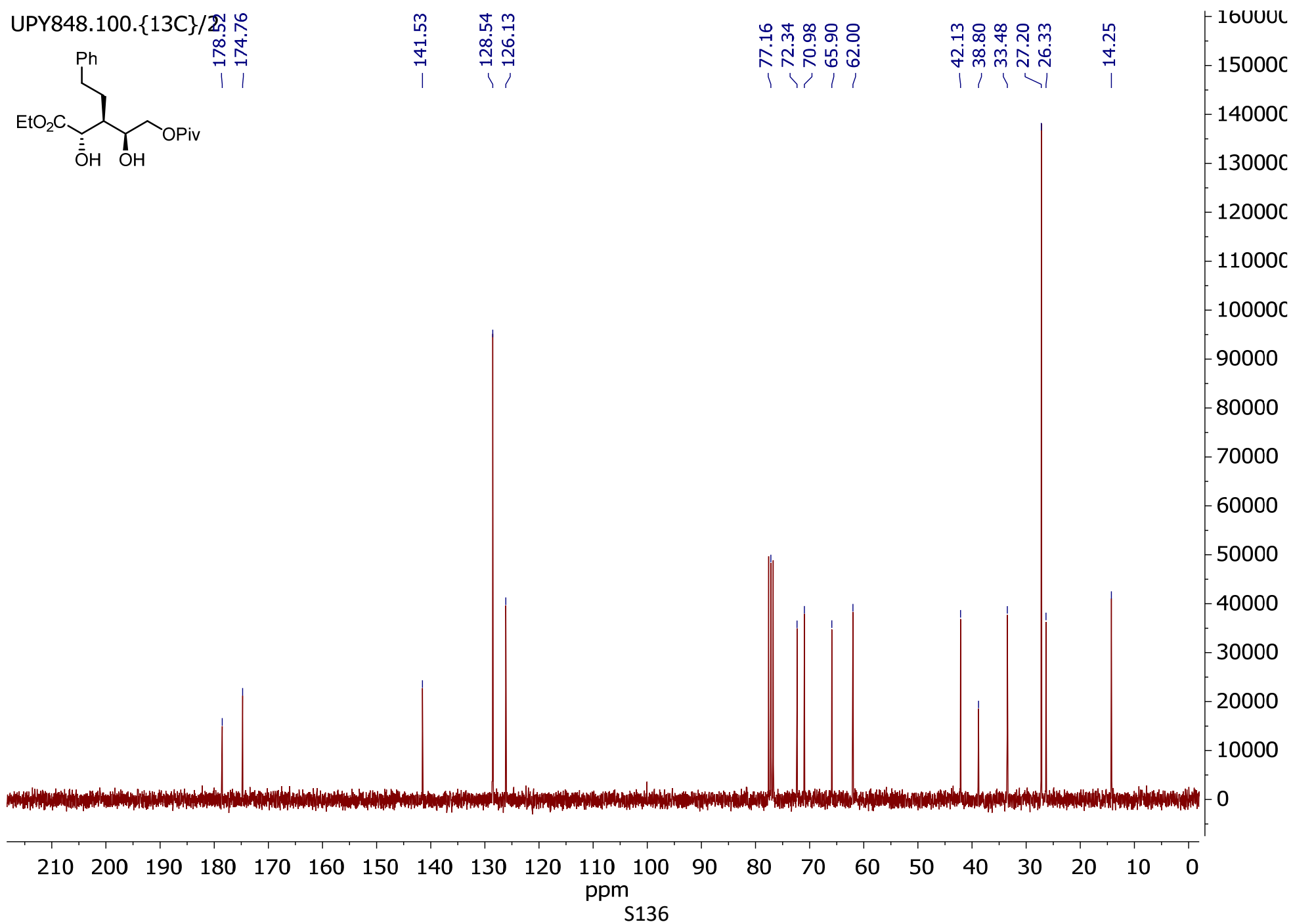
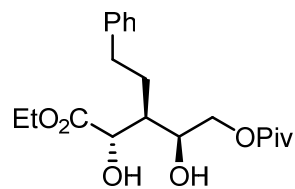
4.47  
4.33  
4.27  
4.27  
4.21  
4.16  
4.12  
4.09  
4.03  
3.64  
3.14  
2.93  
2.88  
2.83  
2.69  
2.67  
2.62  
2.60  
2.12  
2.10  
2.02  
1.93  
1.88  
1.81  
1.34  
1.31  
1.29  
1.18





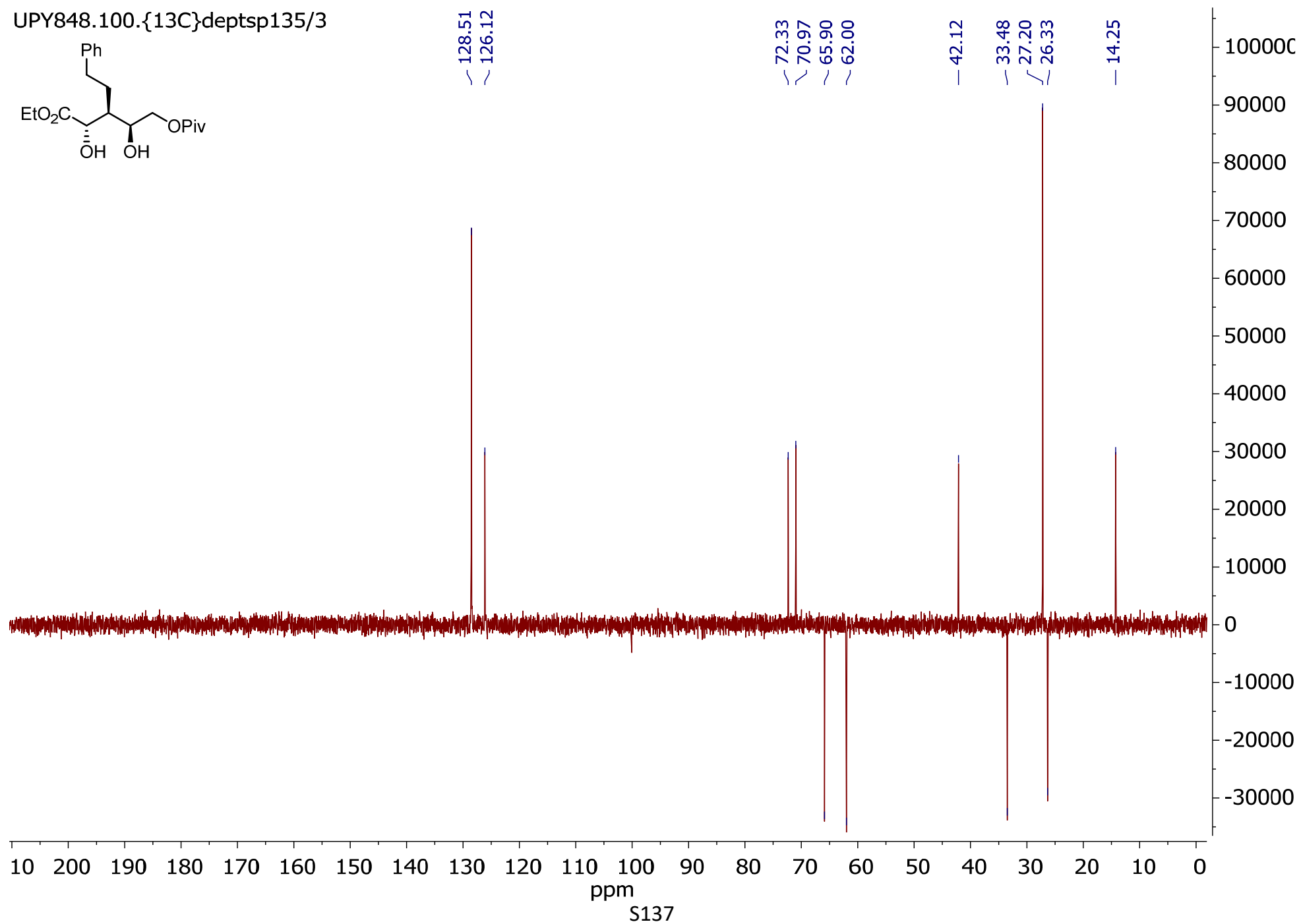
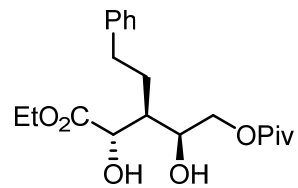


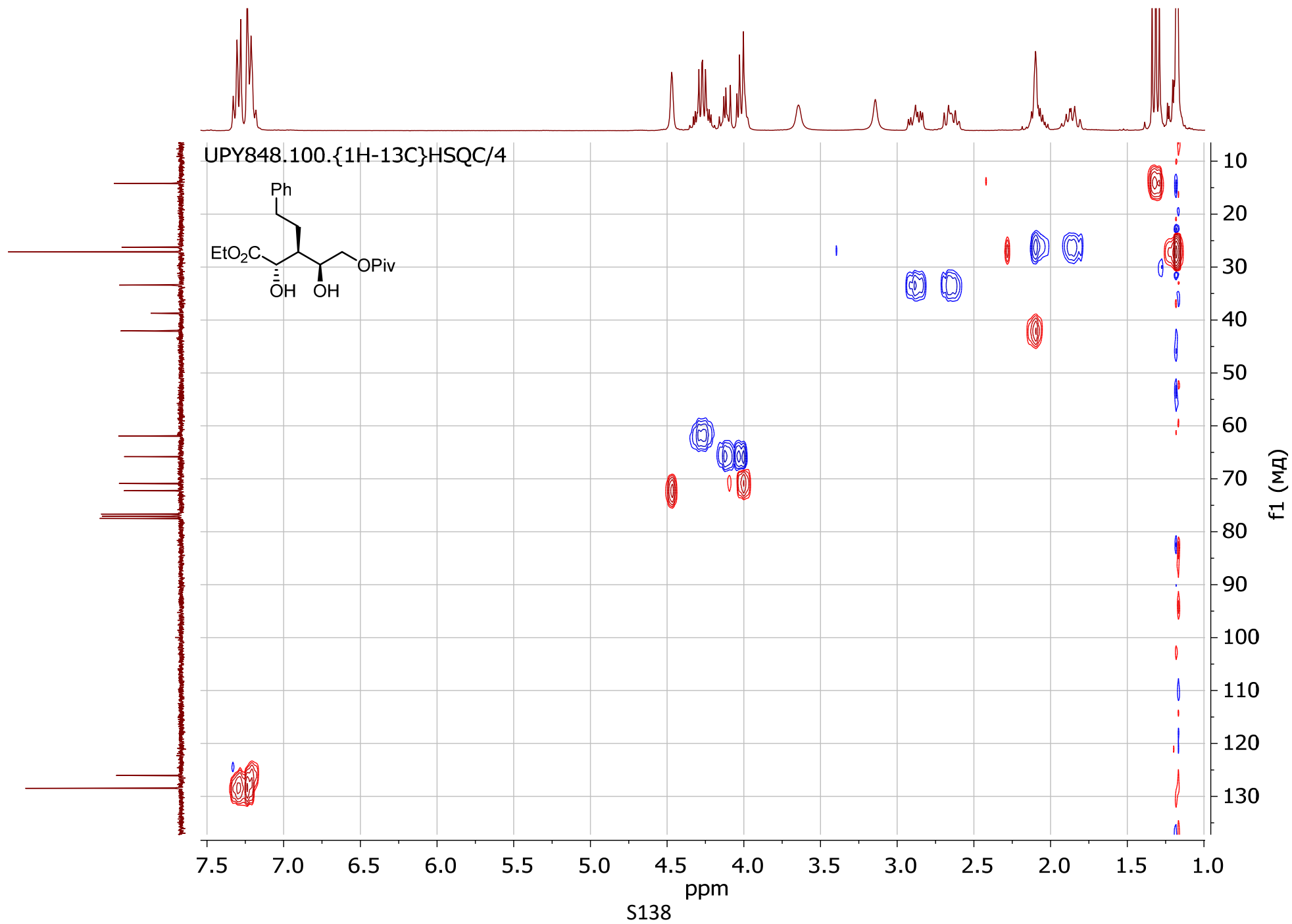
UPY848.100.{13C}/2



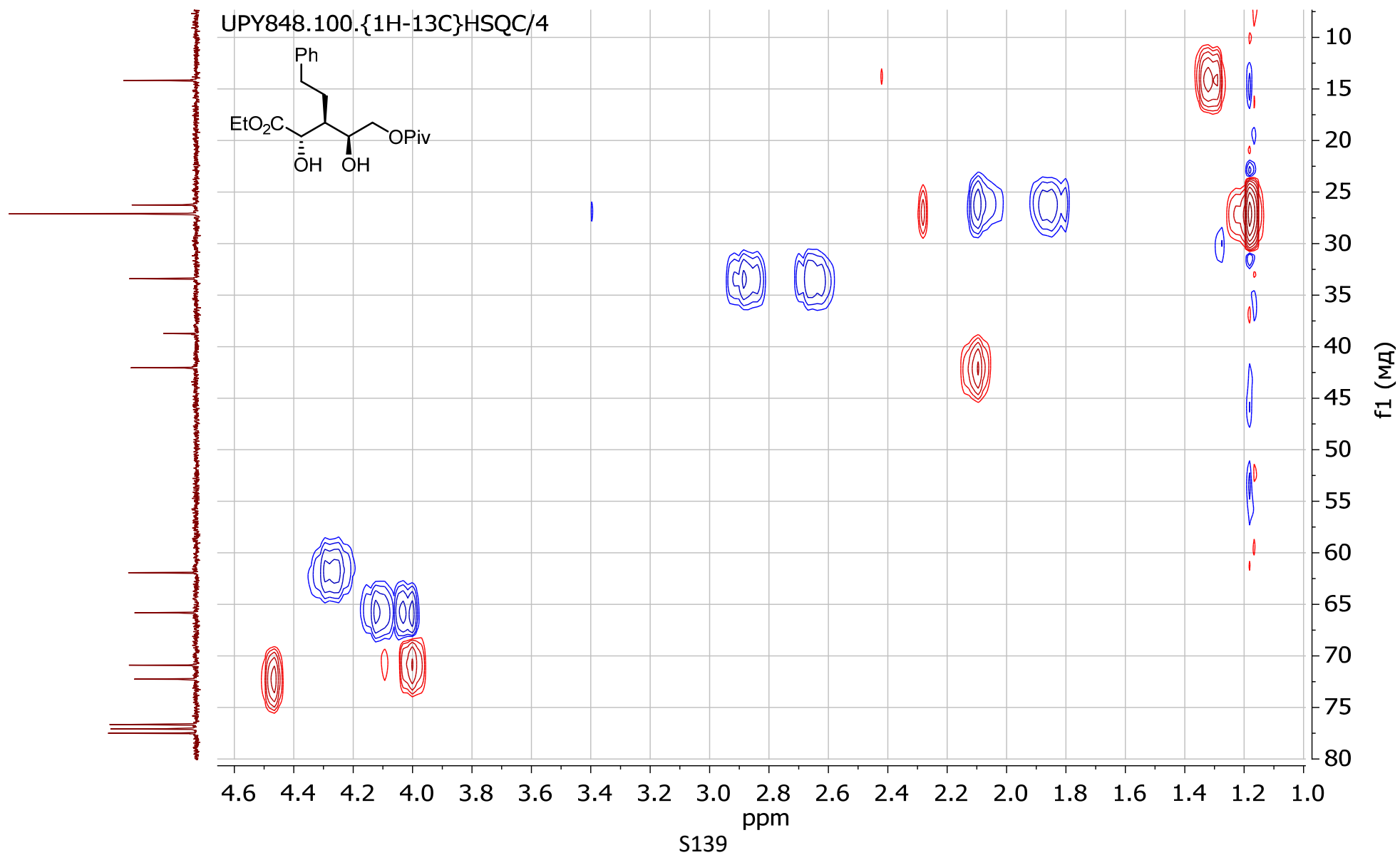
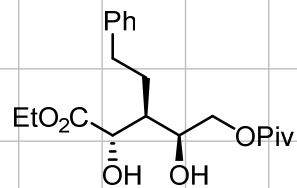


UPY848.100.{13C}deptsp135/3



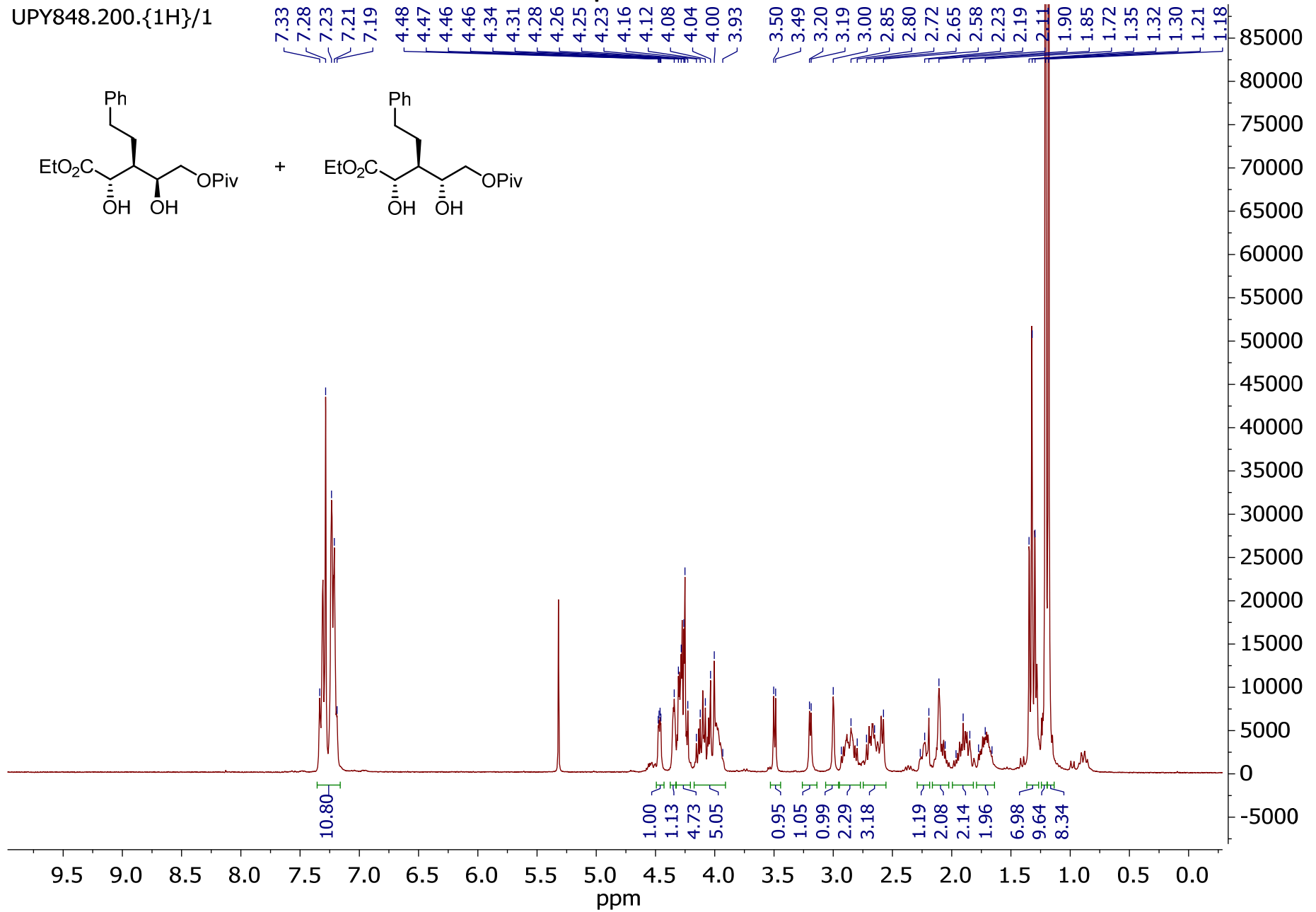
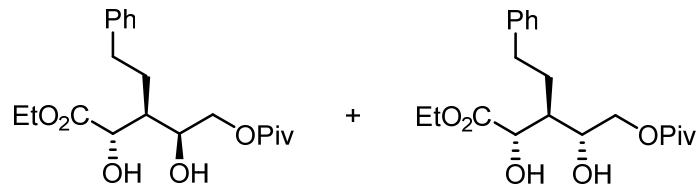


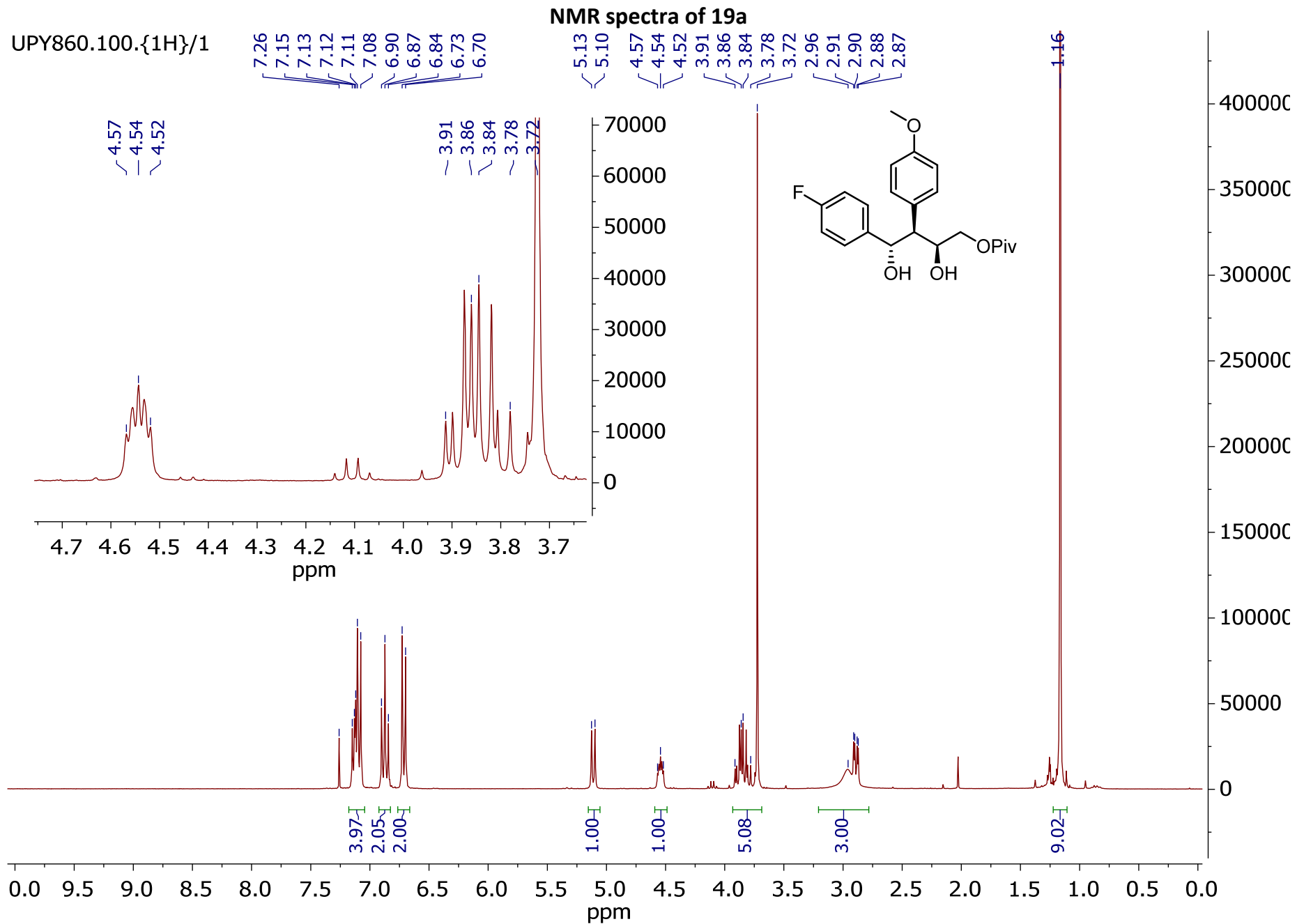
UPY848.100.{1H-13C}HSQC/4

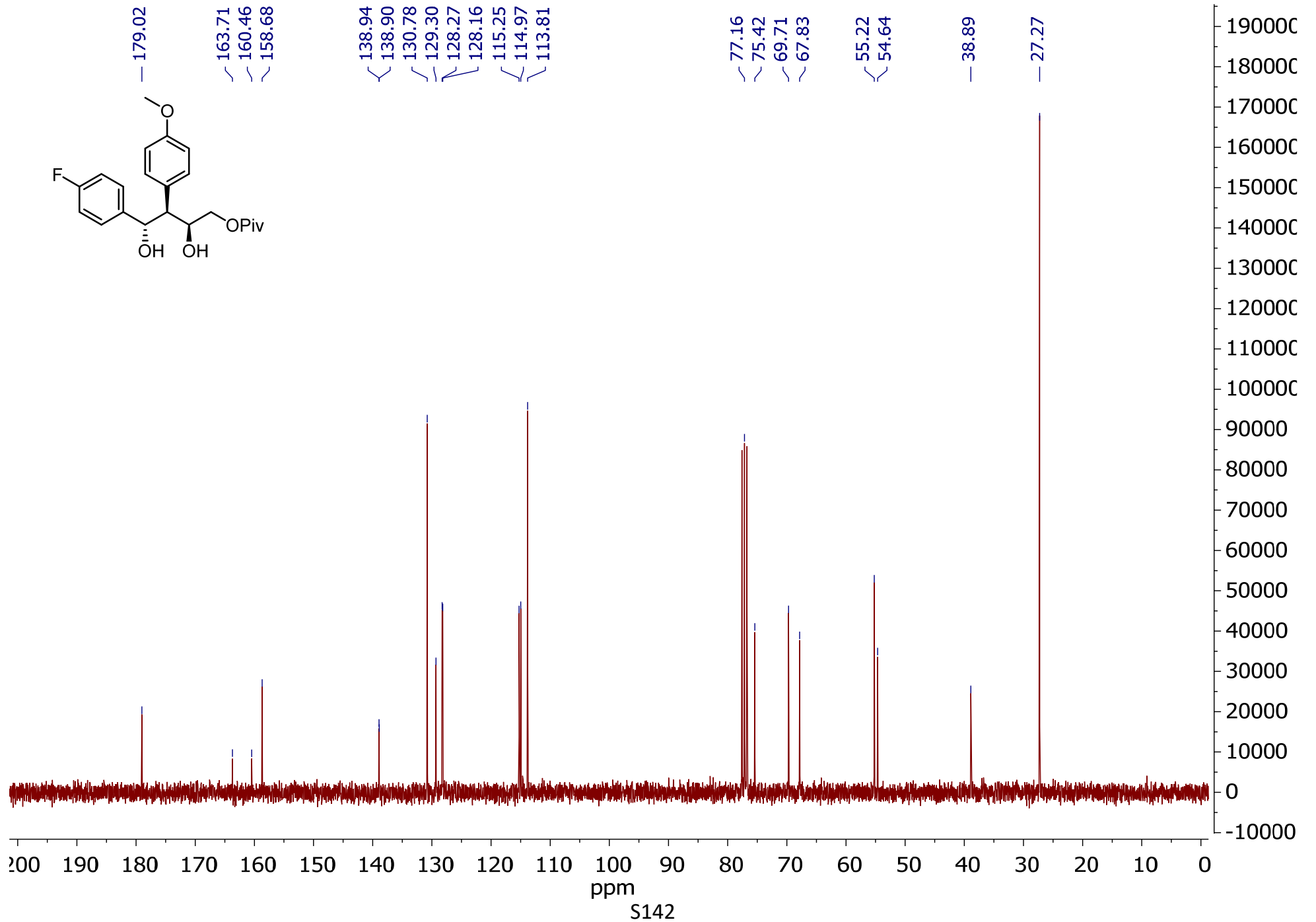
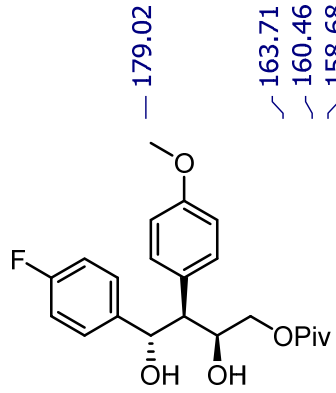


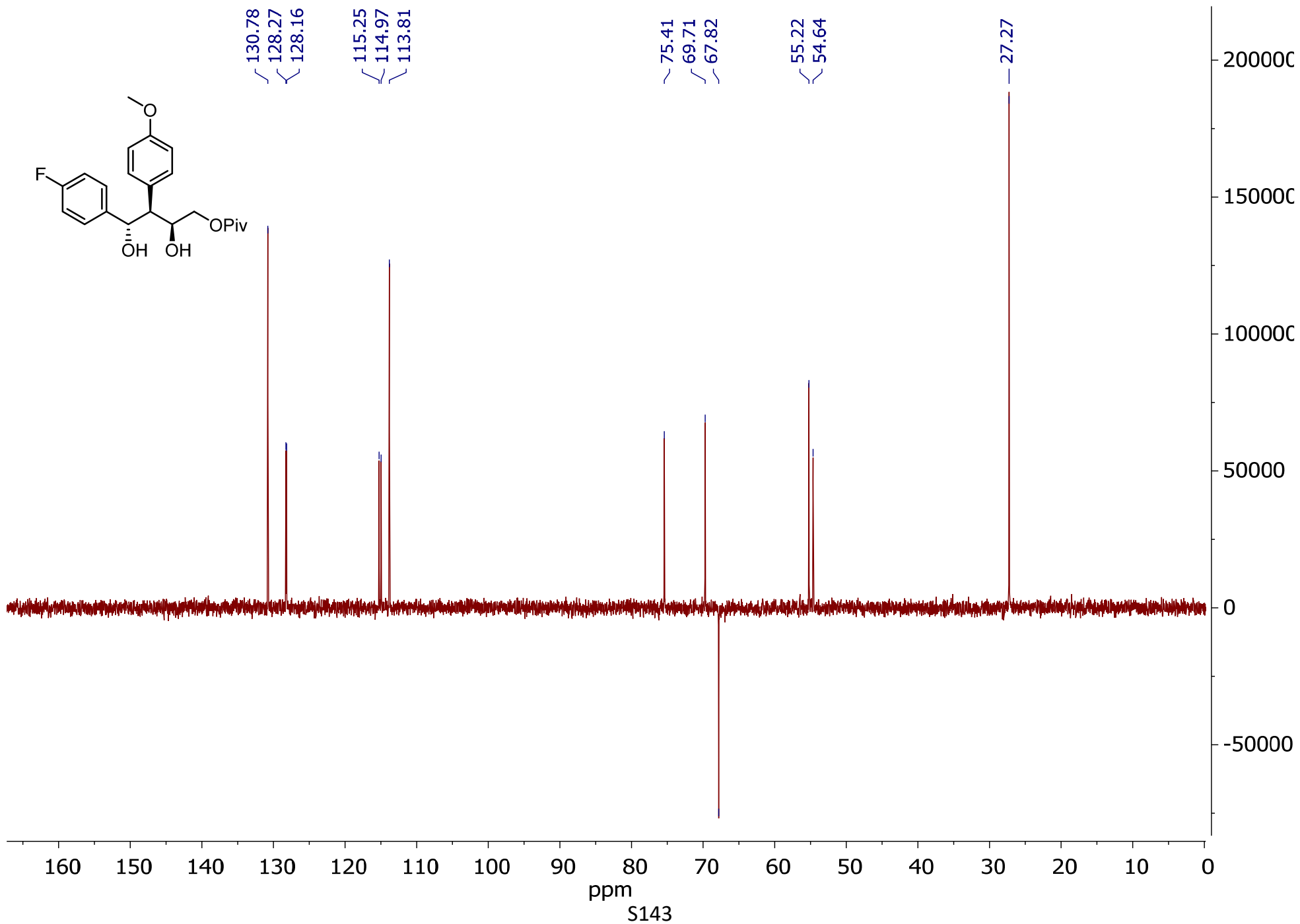
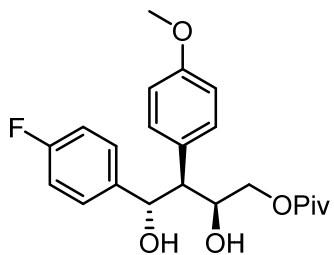
UPY848.200.{1H}/1

### NMR spectra of 18a + 18b

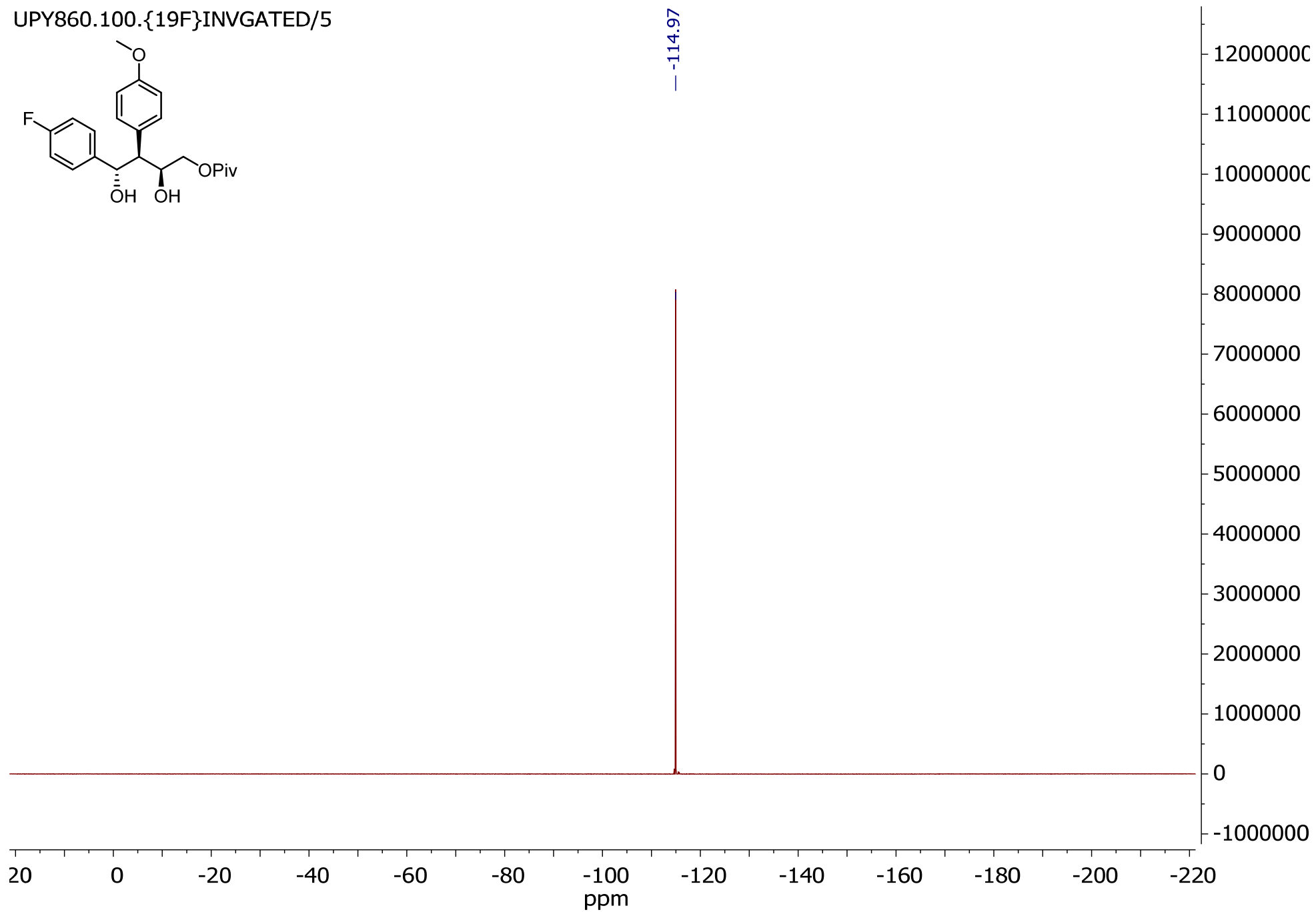
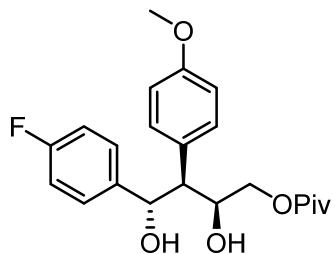






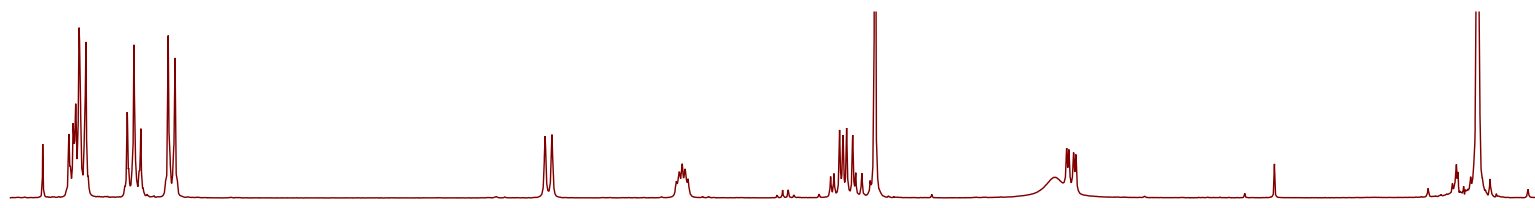


UPY860.100.{19F}INVGATED/5

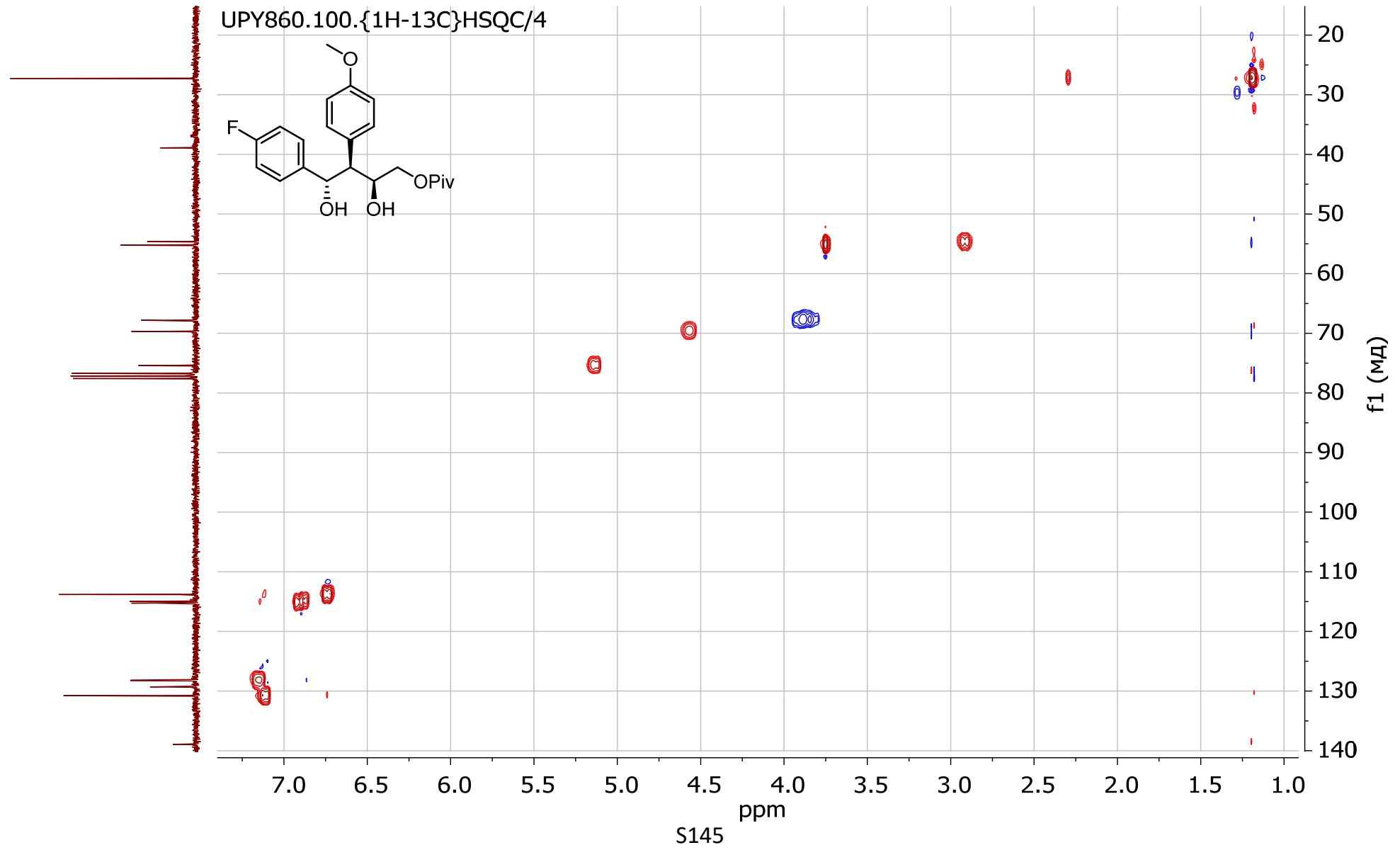
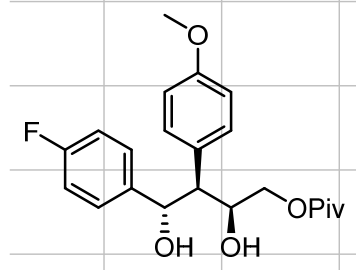


S144



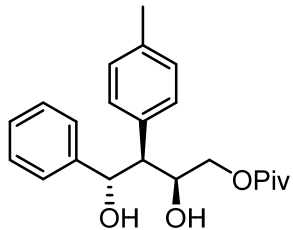


UPY860.100.{1H-13C}HSQC/4

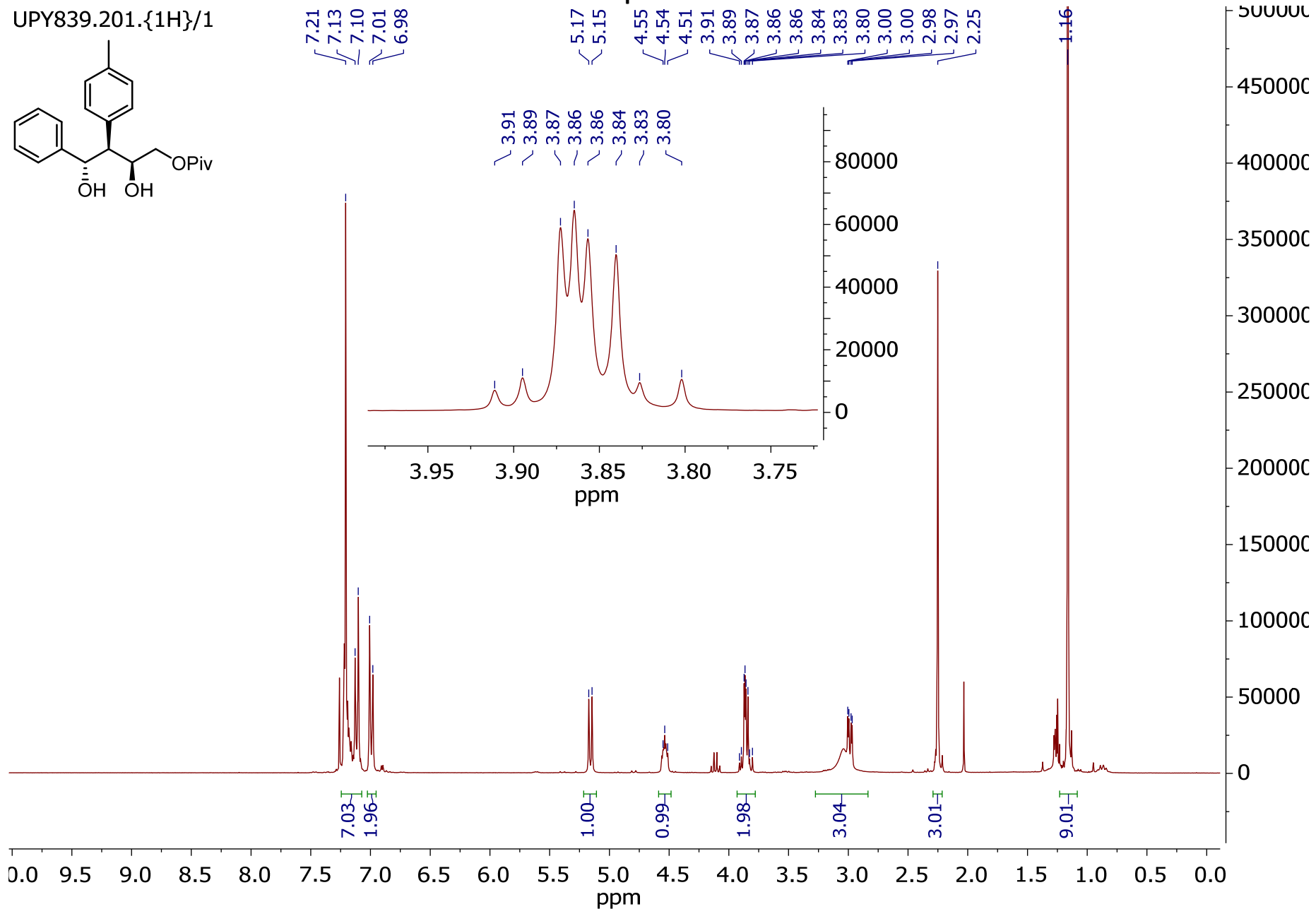


S145

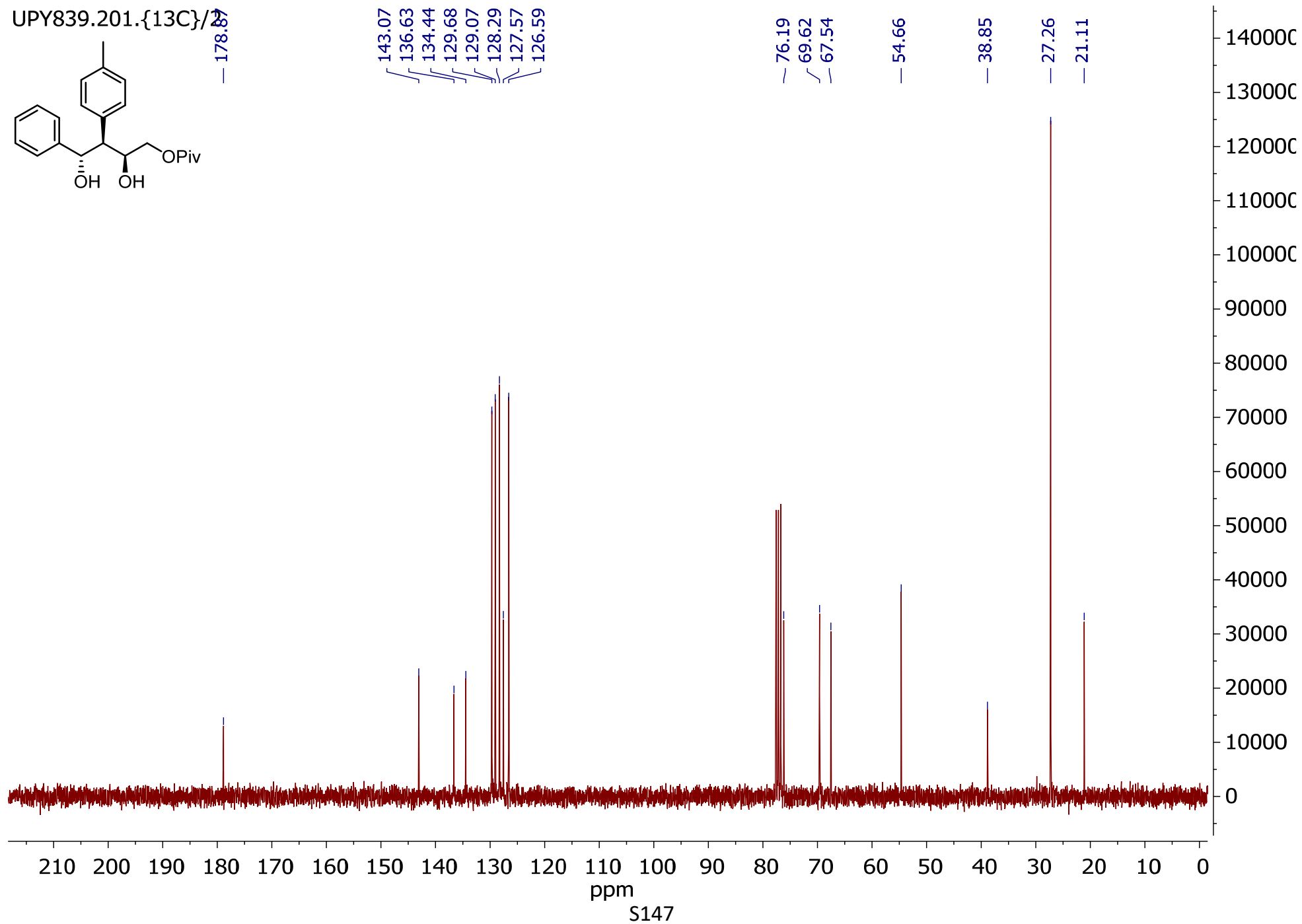
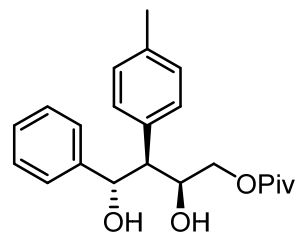
UPY839.201.{1H}/1



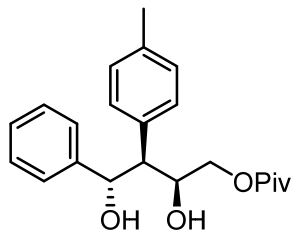
### NMR spectra of 19b



UPY839.201.{13C}/



UPY839.201.{13C}deptsp135/3



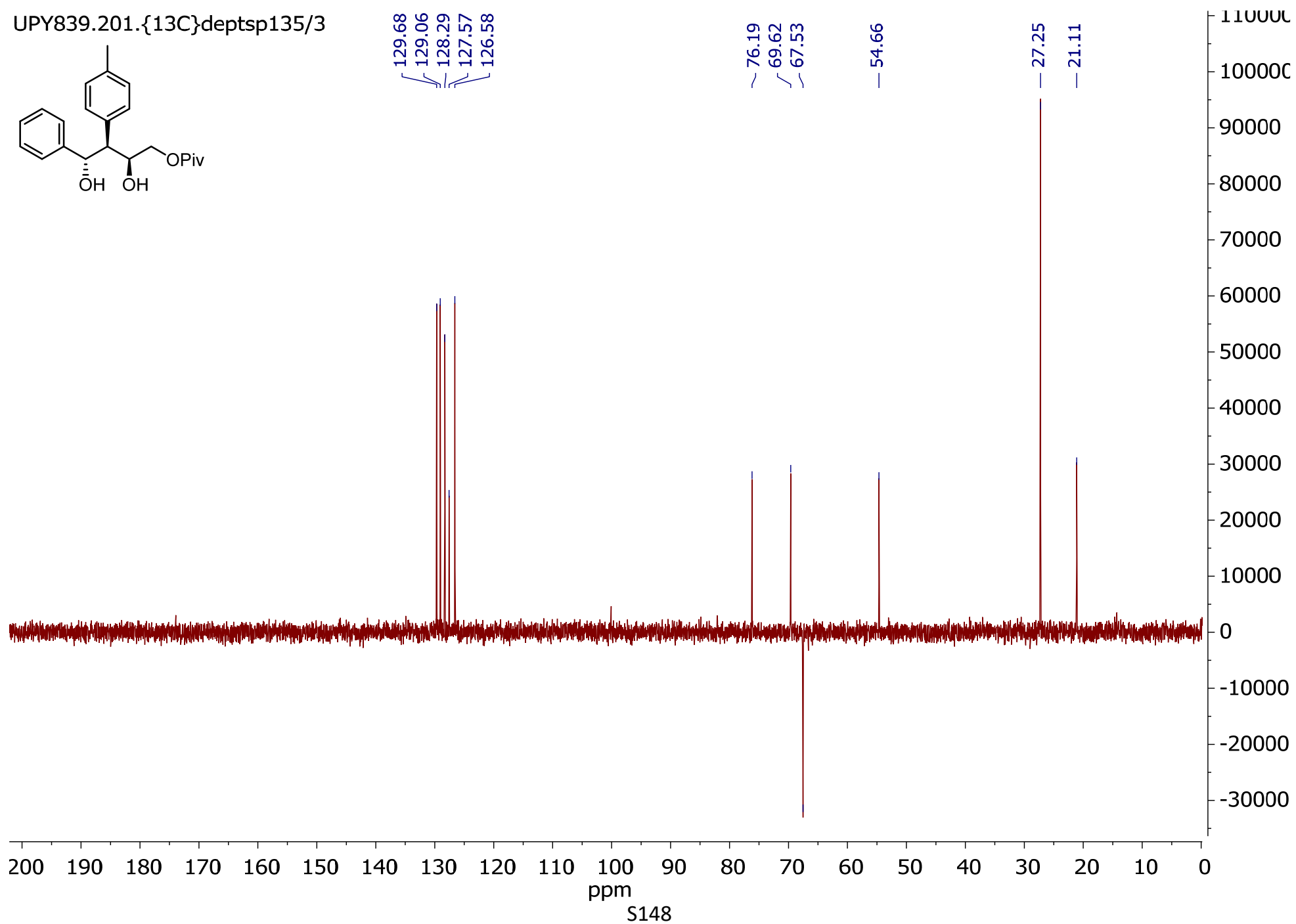
129.68  
129.06  
128.29  
127.57  
126.58

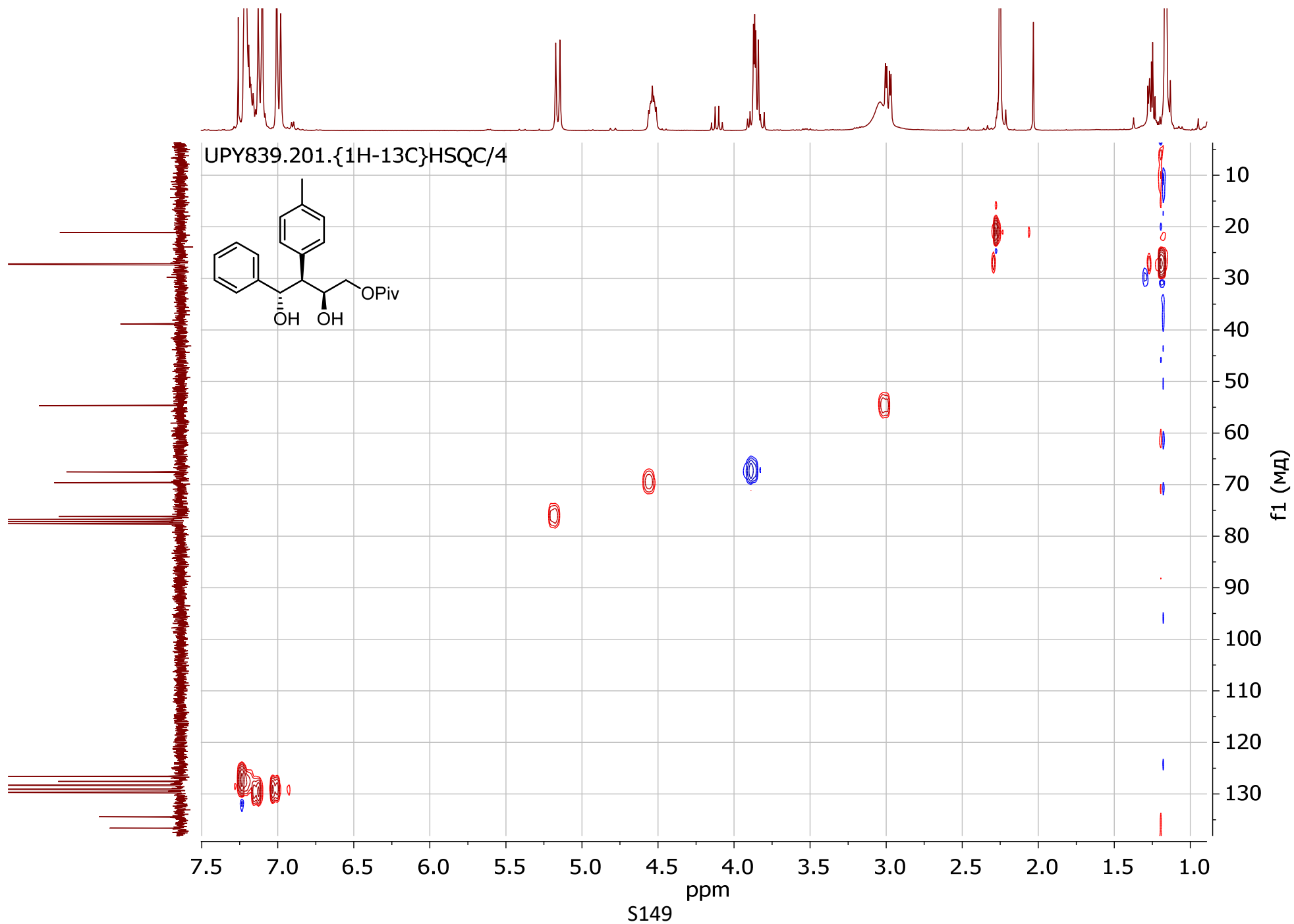
76.19  
69.62  
67.53

54.66

27.25

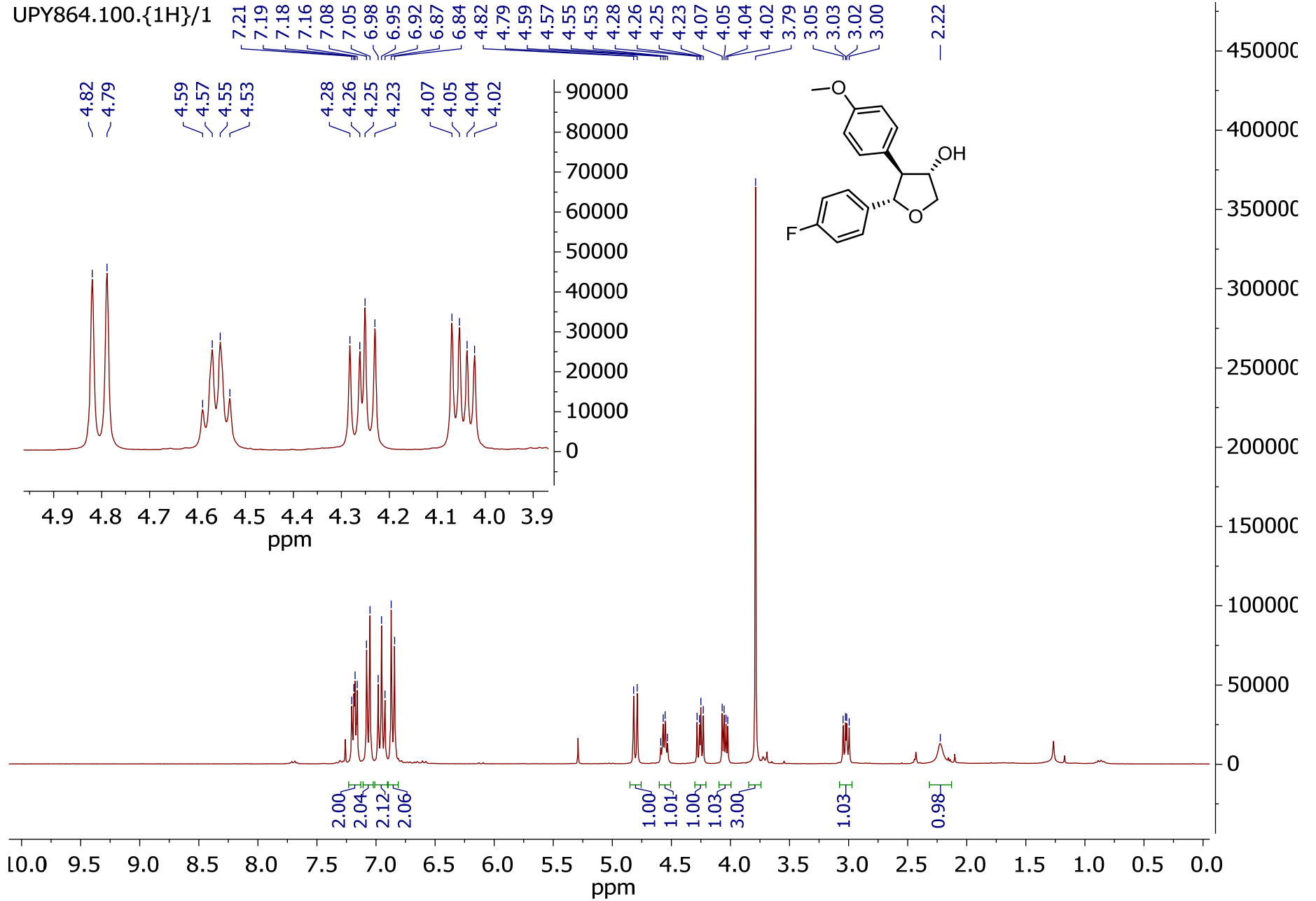
21.11

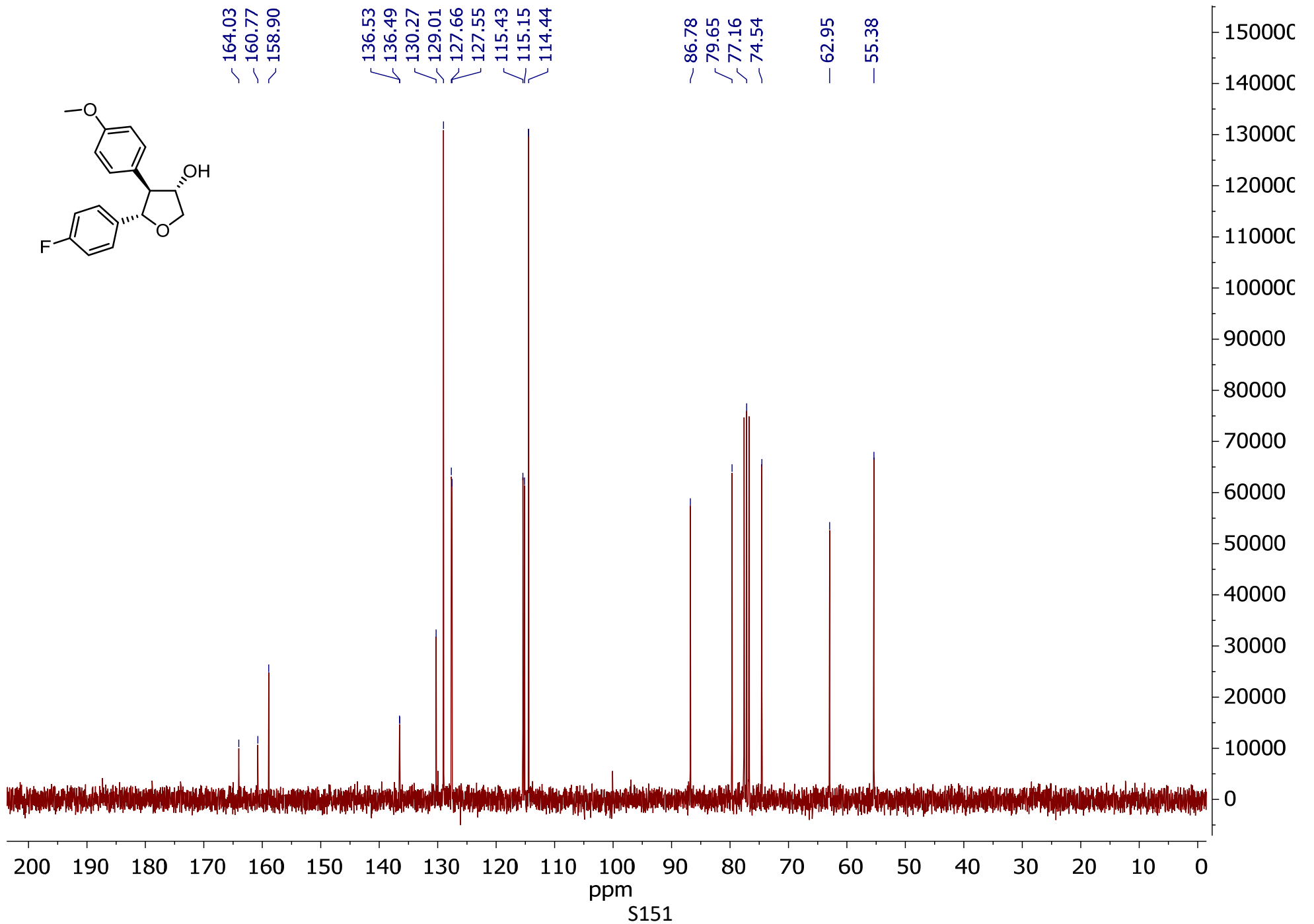
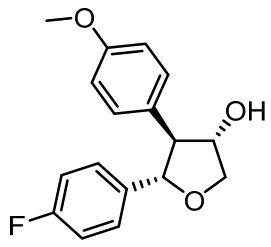


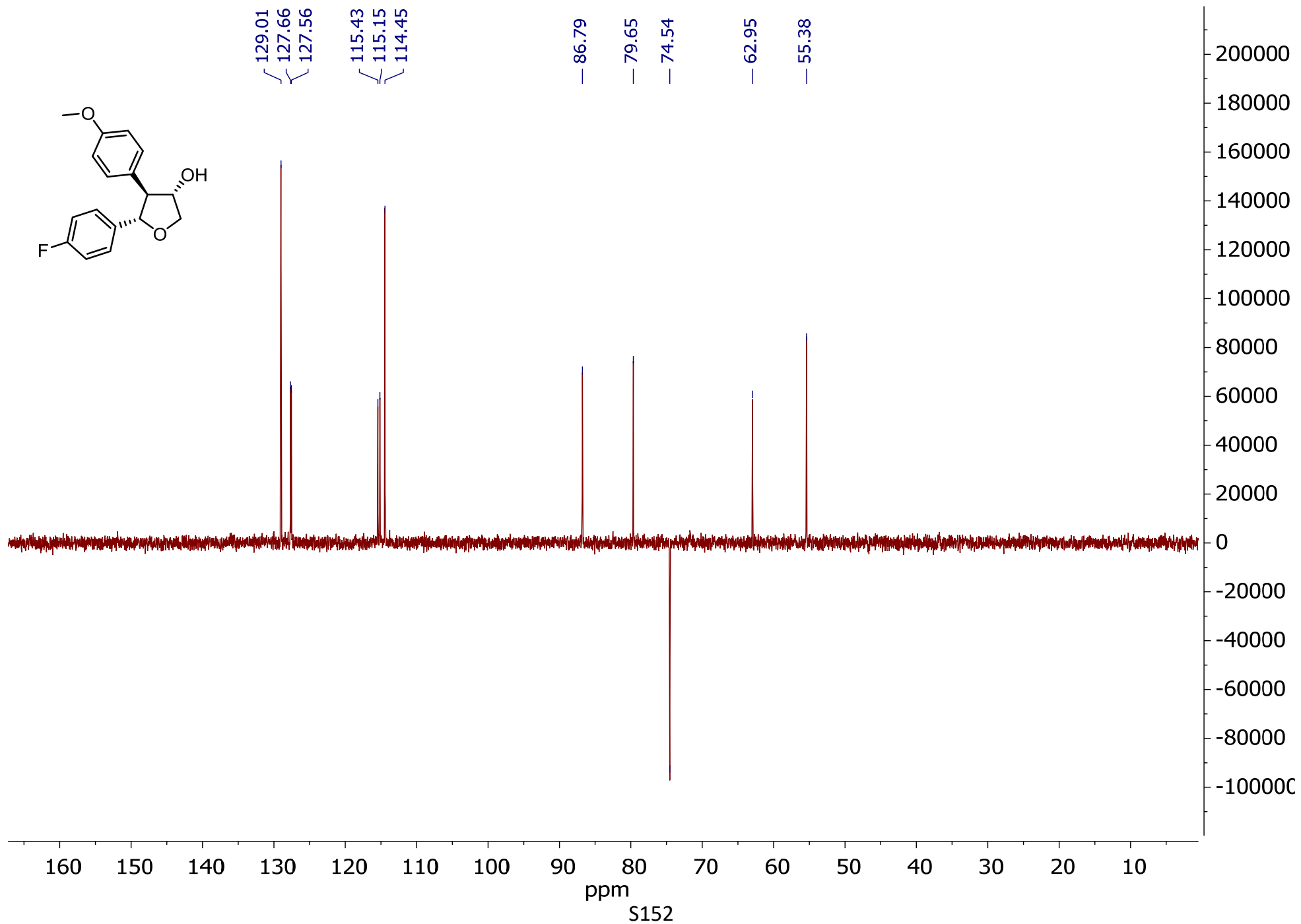
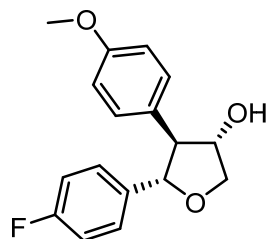


# NMR spectra of 21

UPY864.100.{1H}/1

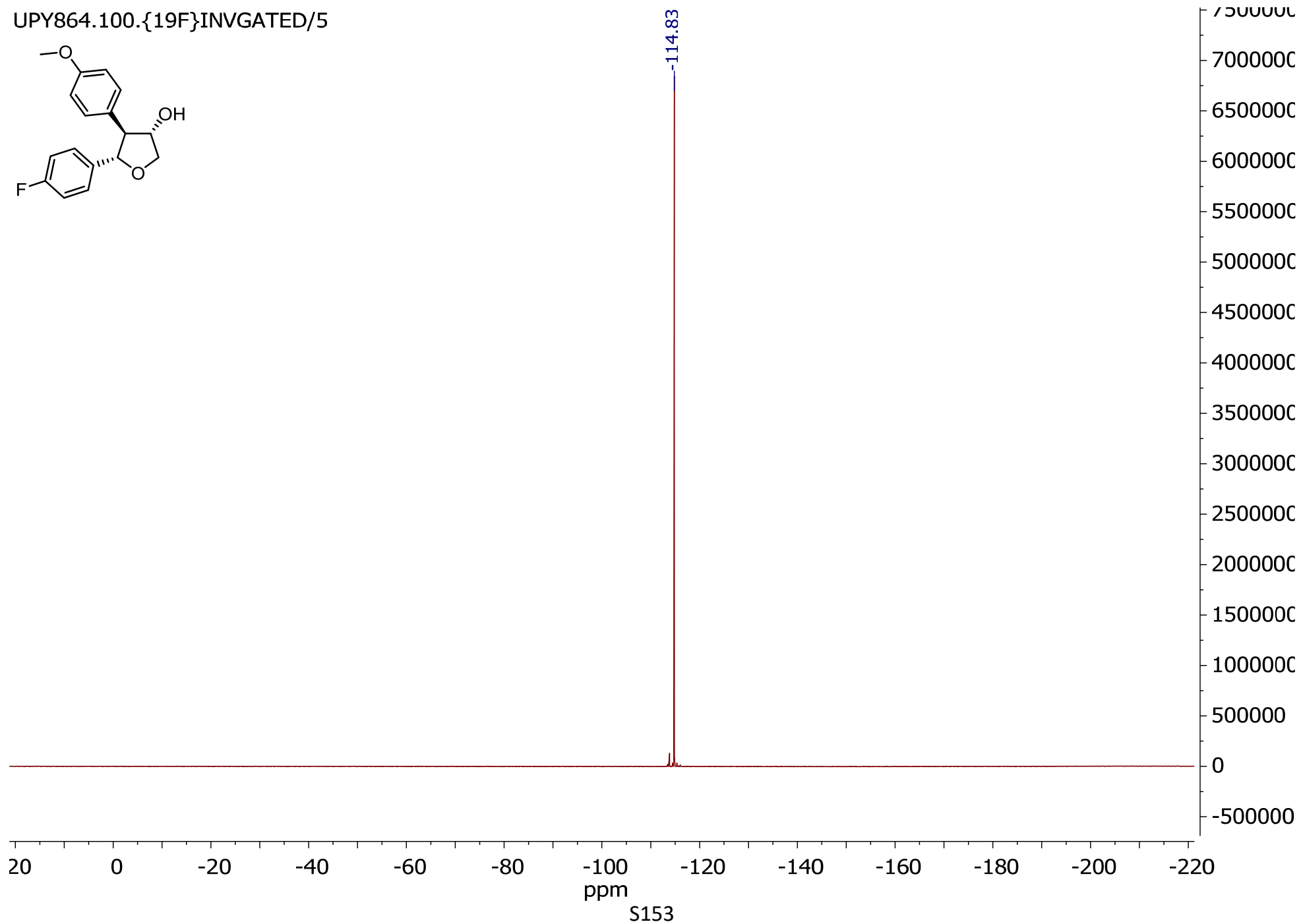
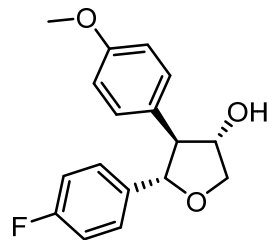


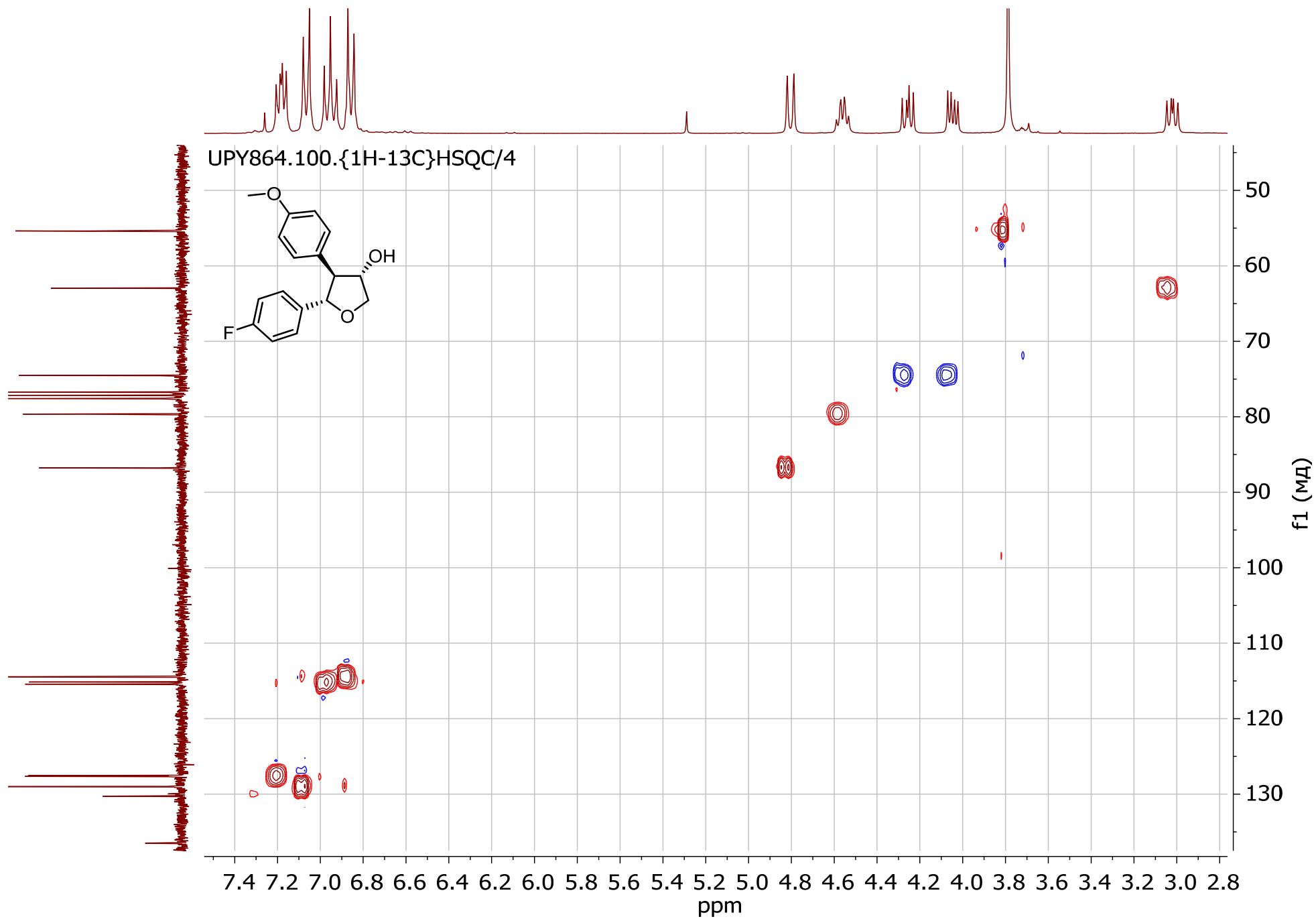




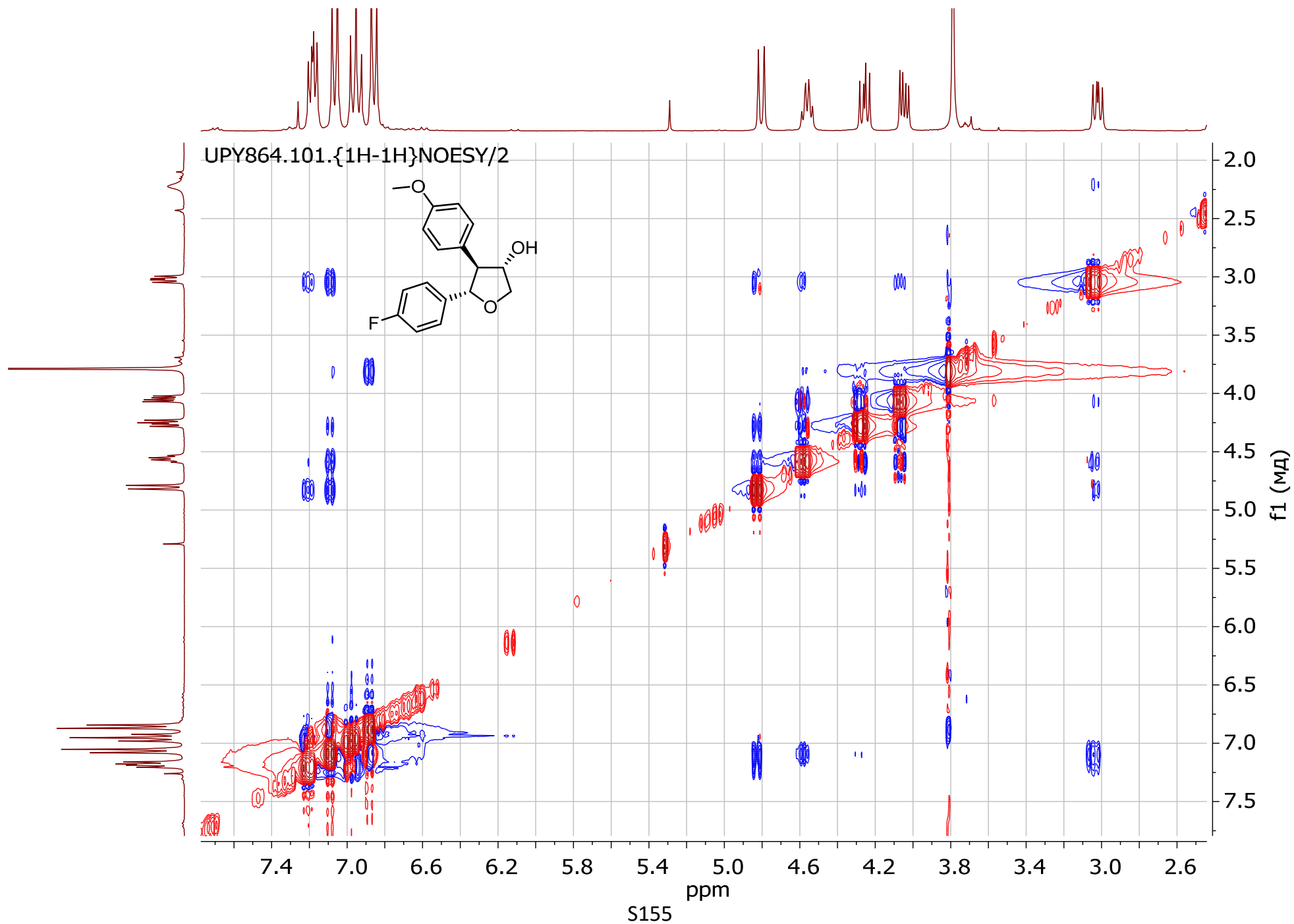


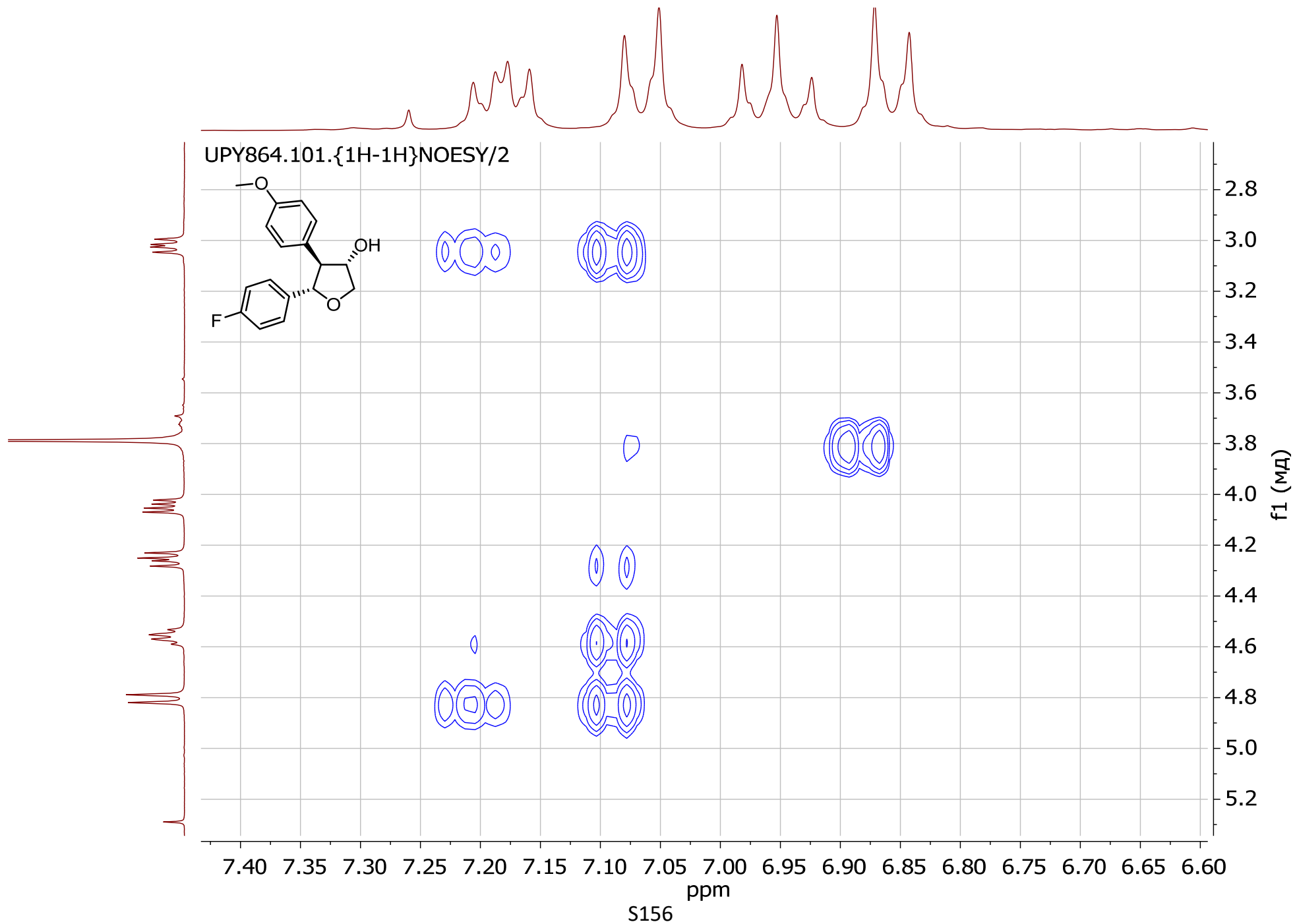
UPY864.100.{19F}INVGATED/5



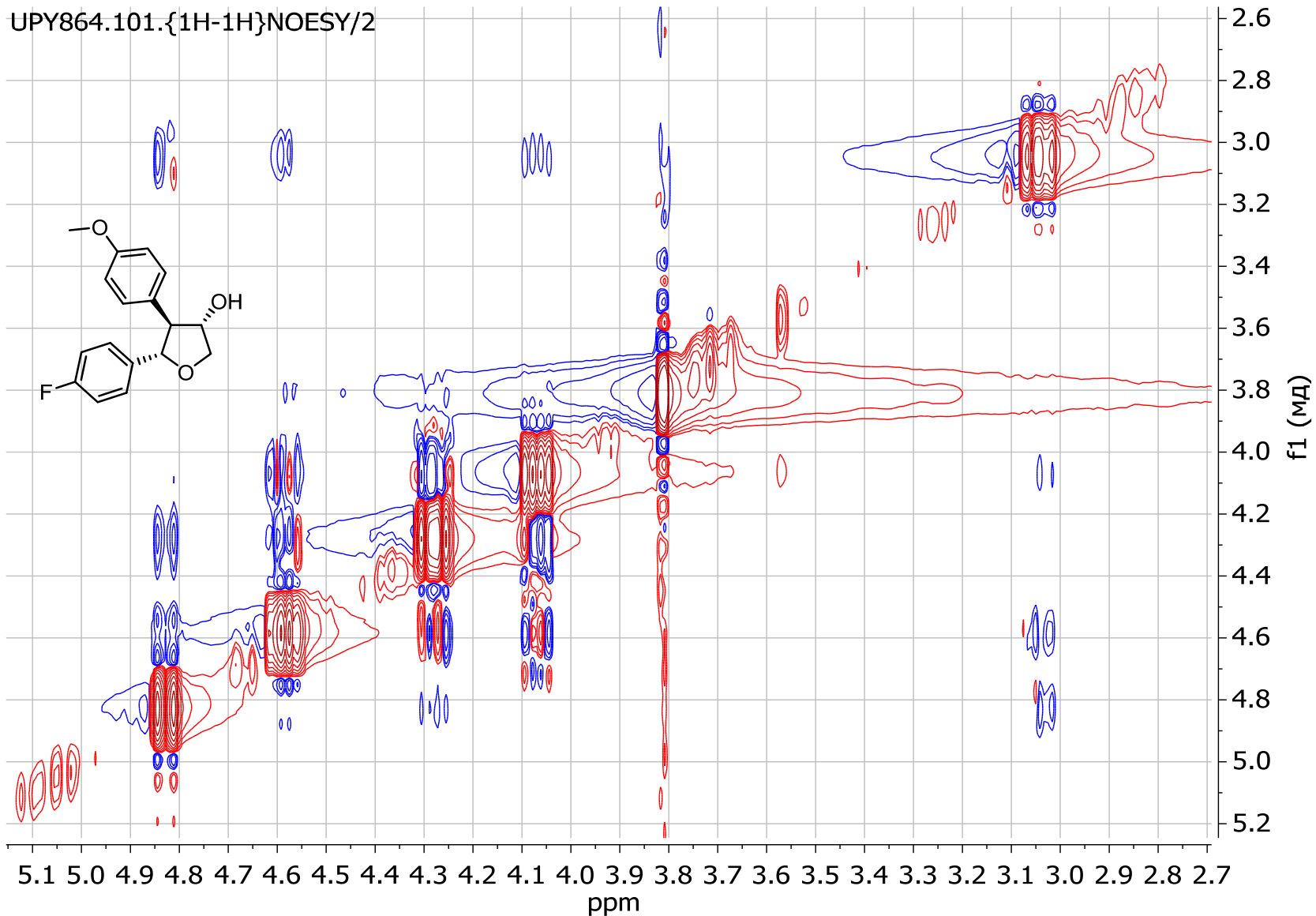
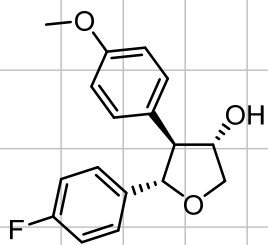


S154

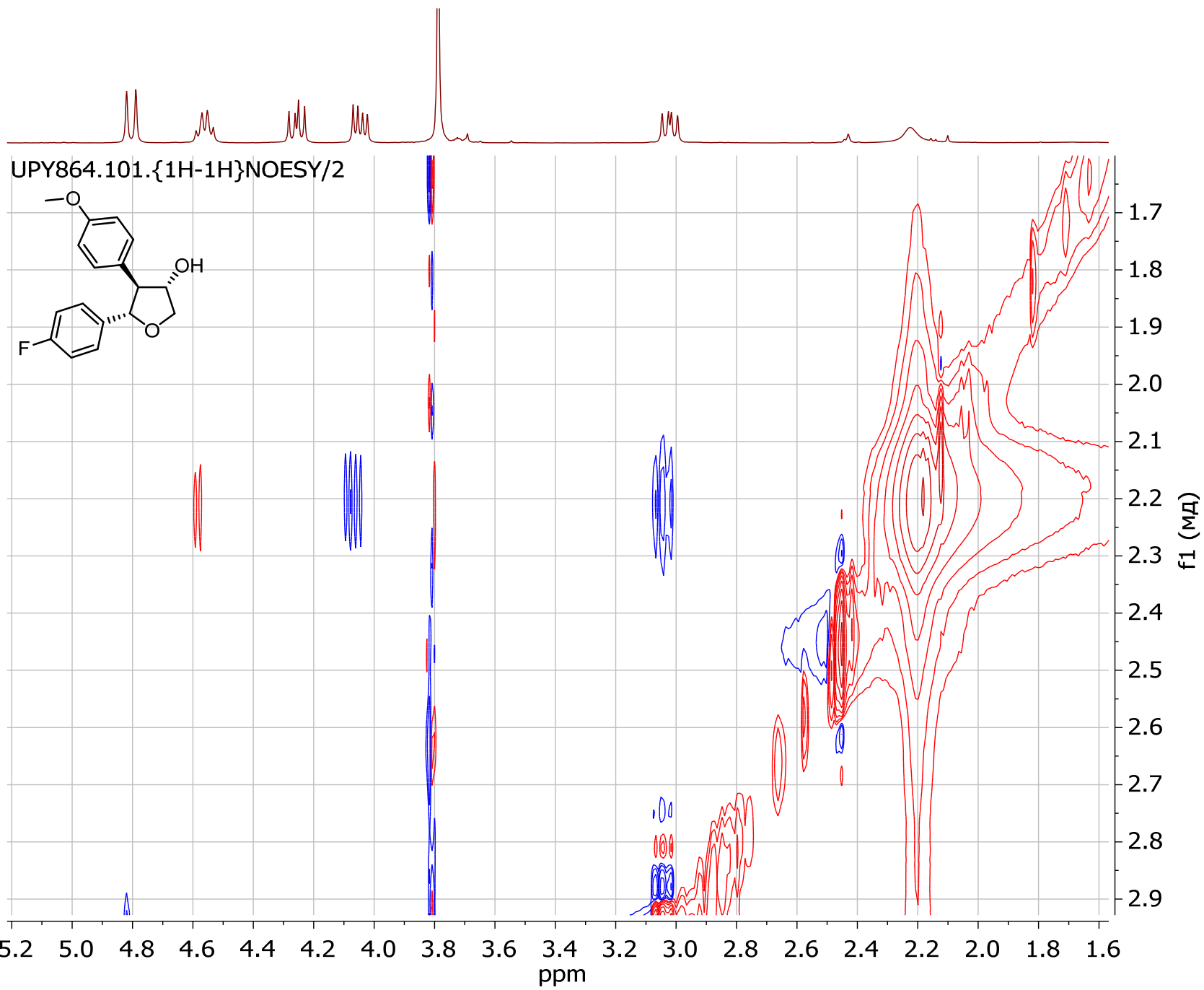




UPY864.101.{1H-1H}NOESY/2



S157



S158