

## Supporting Information

### Synthesis of unsymmetrical urea from aryl- or pyridyl carboxamides and aminopyridines using $\text{PhI}(\text{OAc})_2$ via *in situ* formation of aryl- or pyridyl isocyanates

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*Department of Pharmaceutical Technology (Process Chemistry),*

*National Institute of Pharmaceutical Education and Research,*

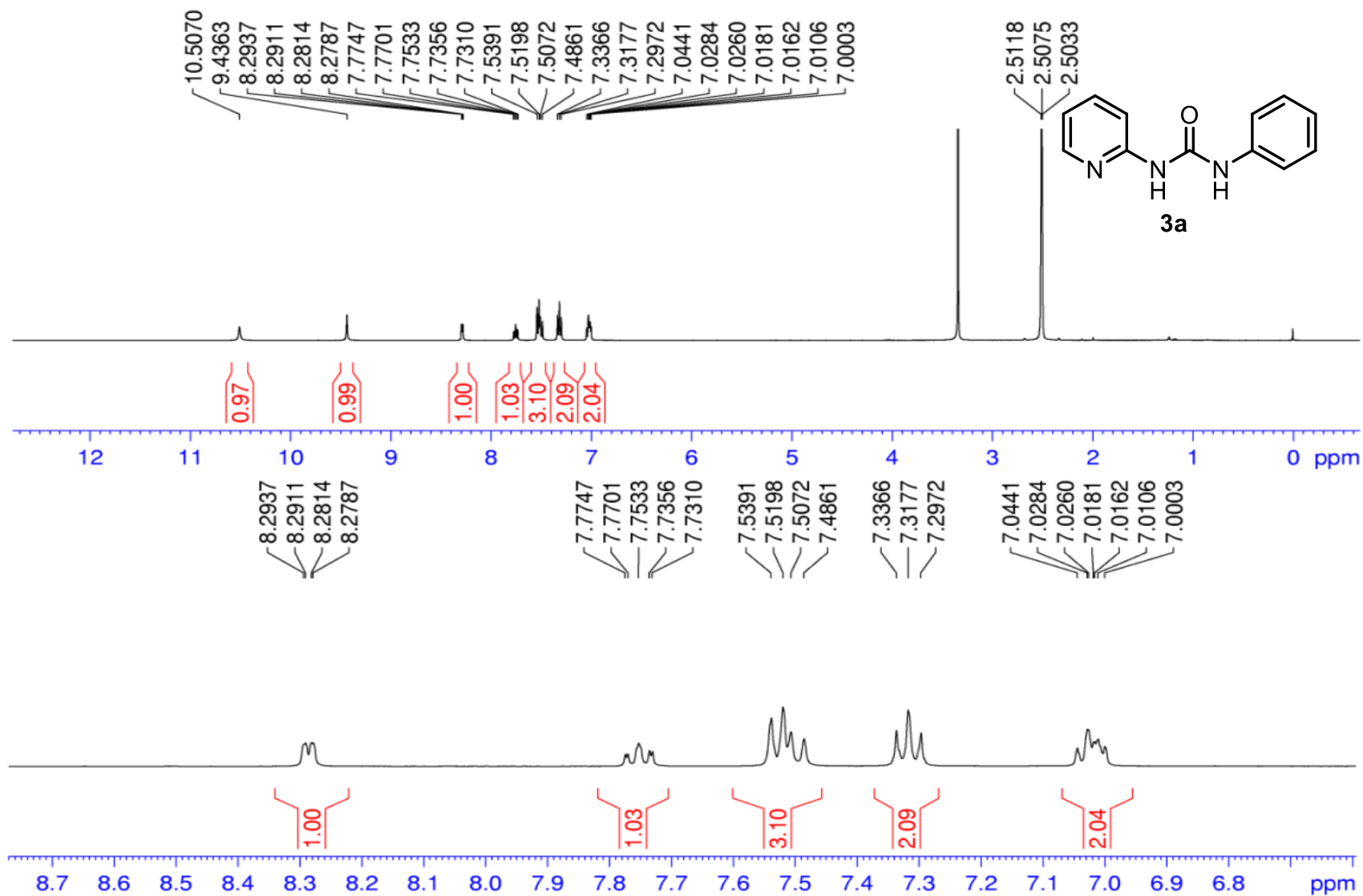
*S. A. S. Nagar, Punjab 160062,*

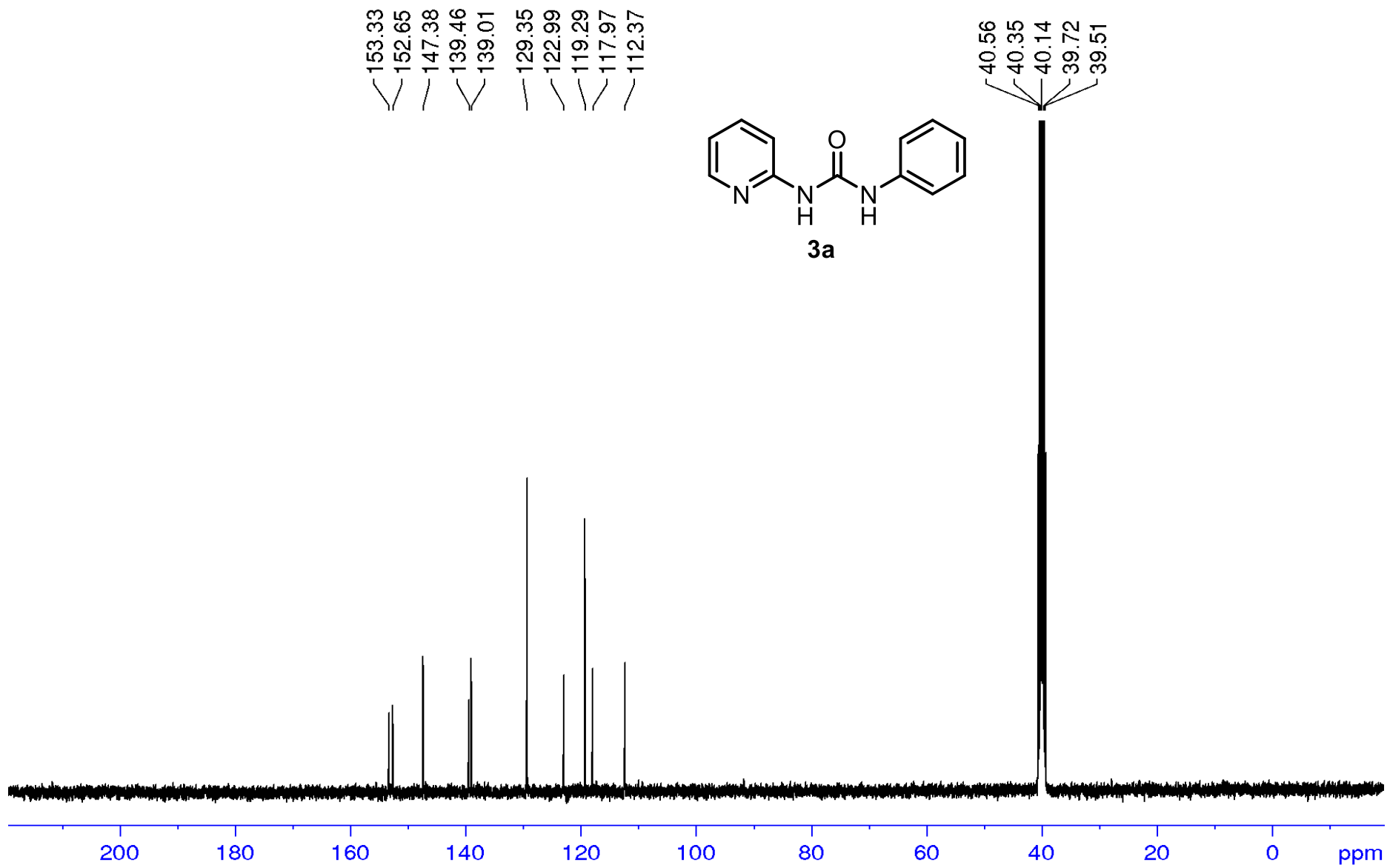
*India*

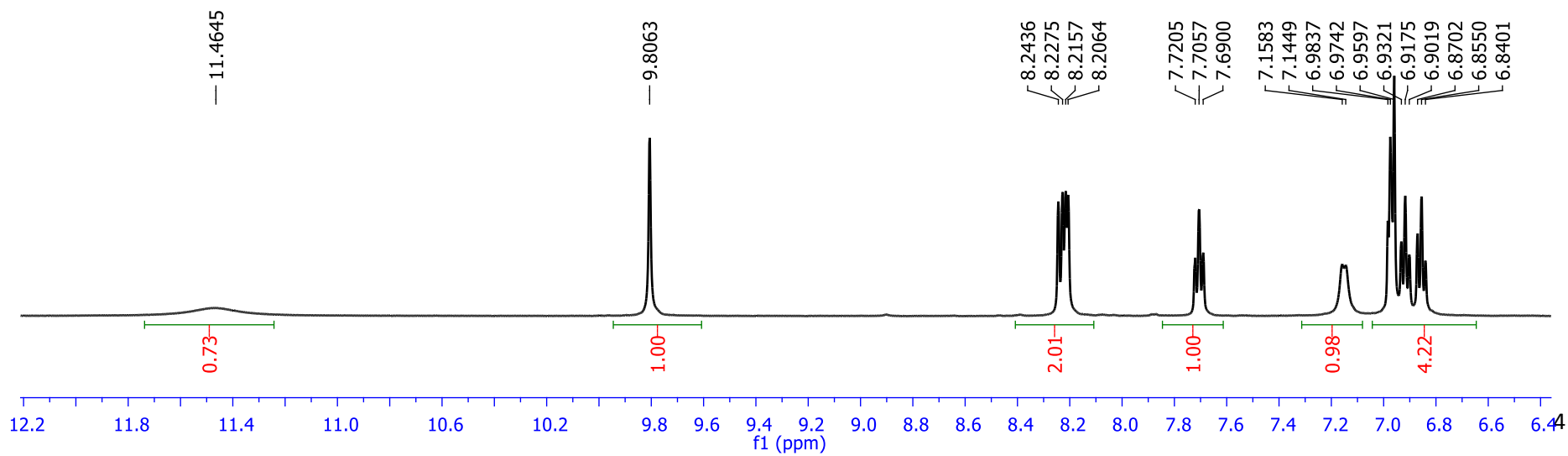
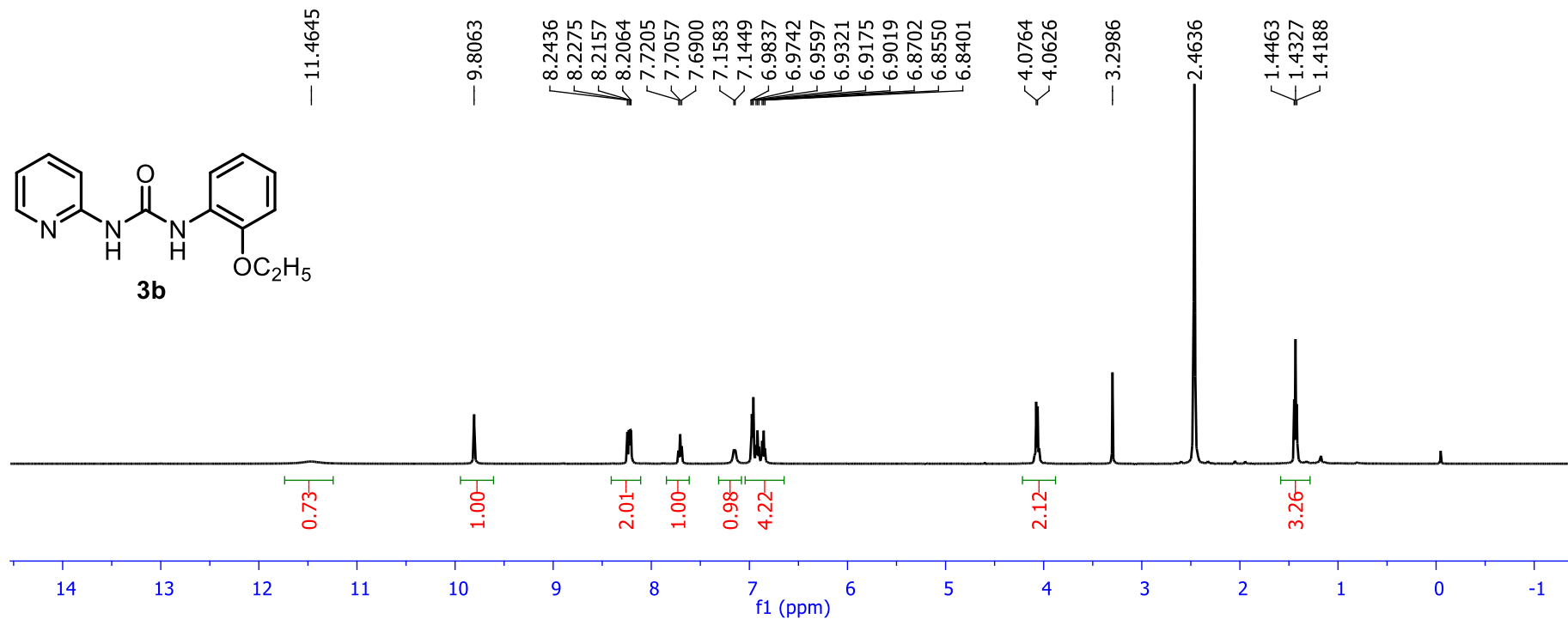
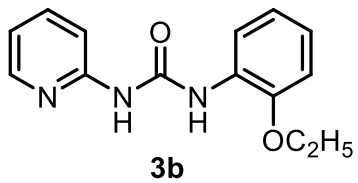
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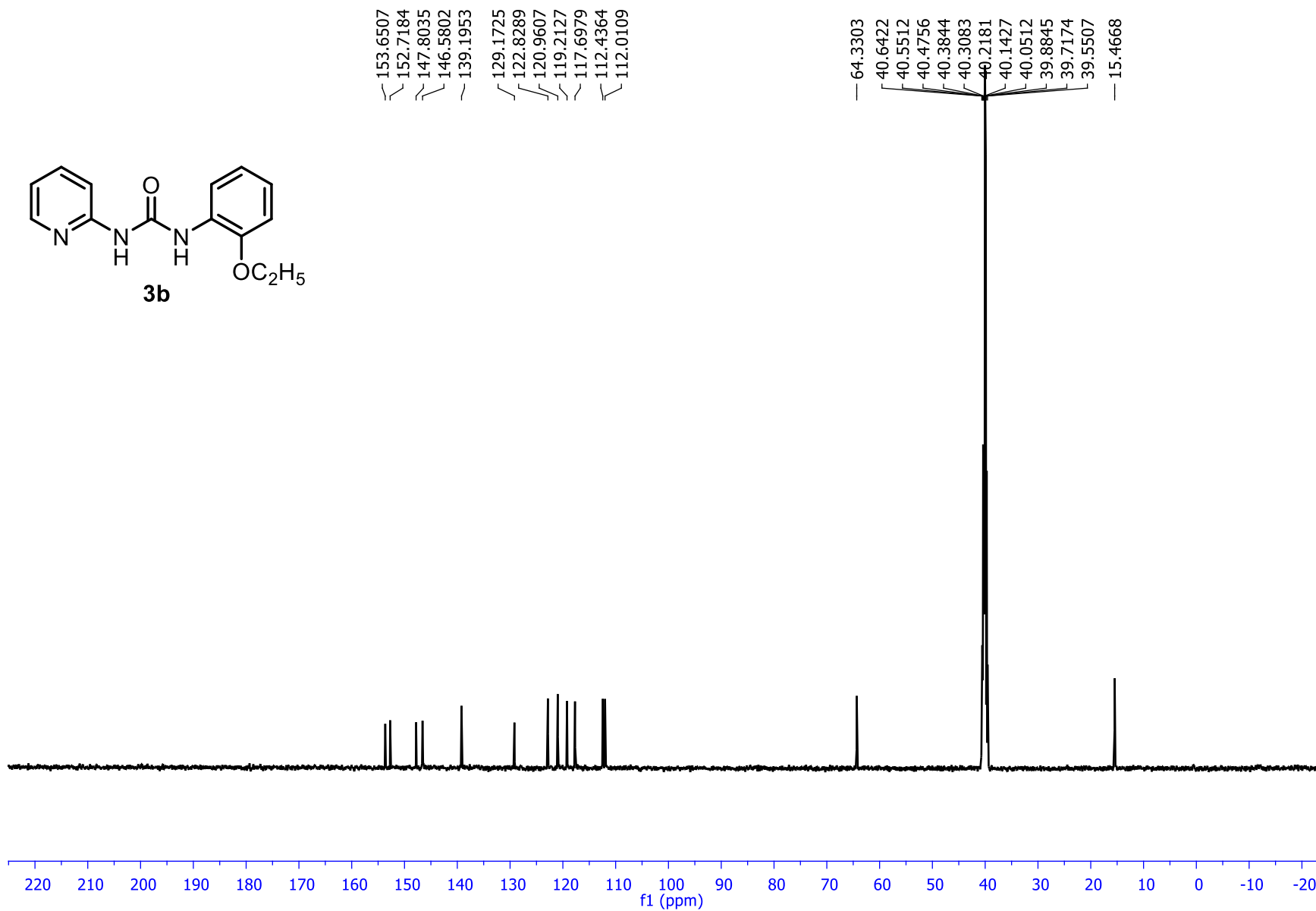
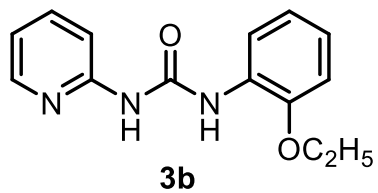
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# I. <sup>1</sup>H and <sup>13</sup>C SPECTRA:

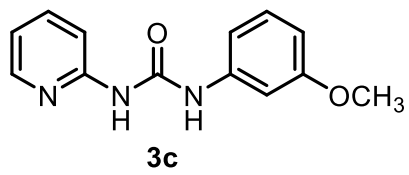






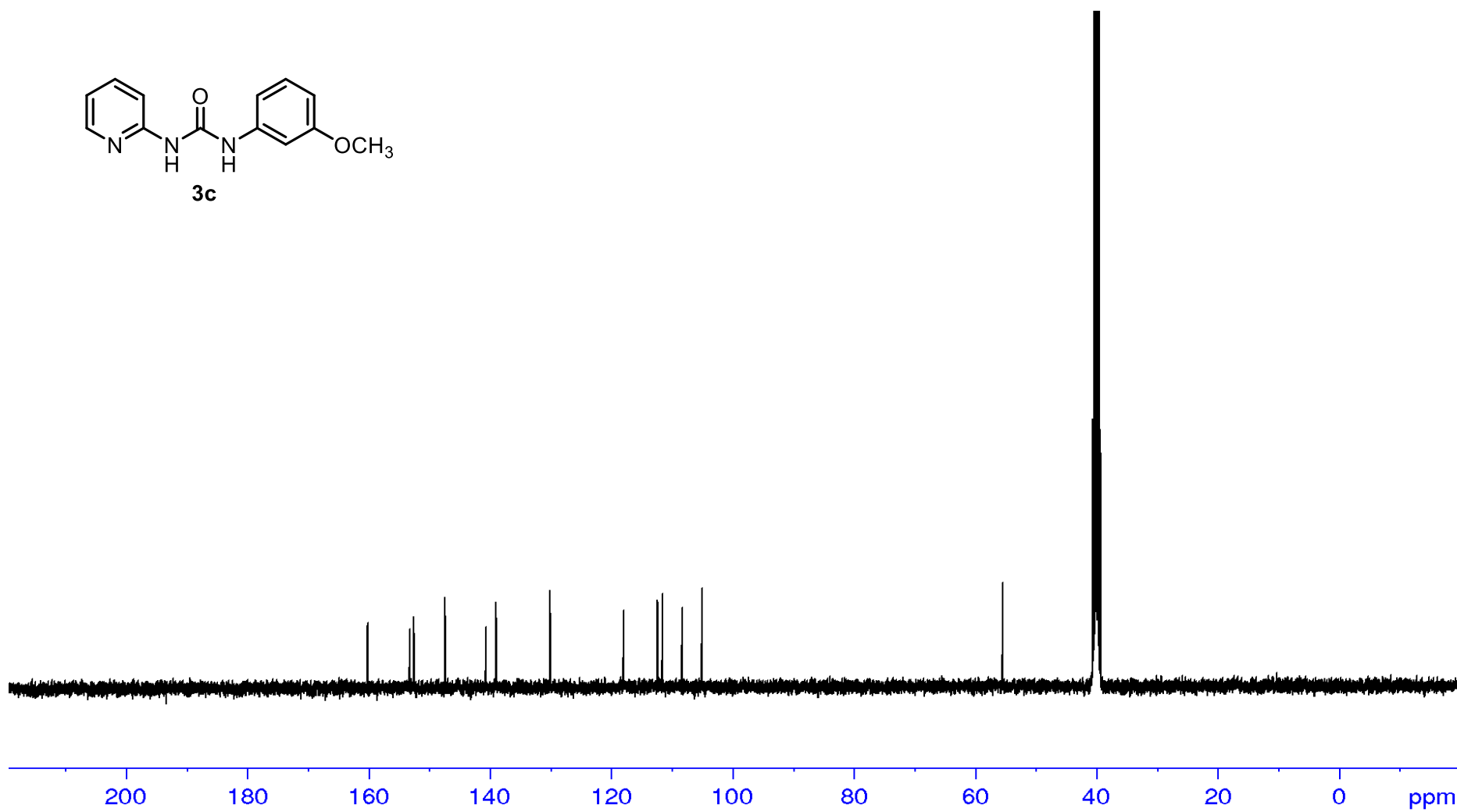


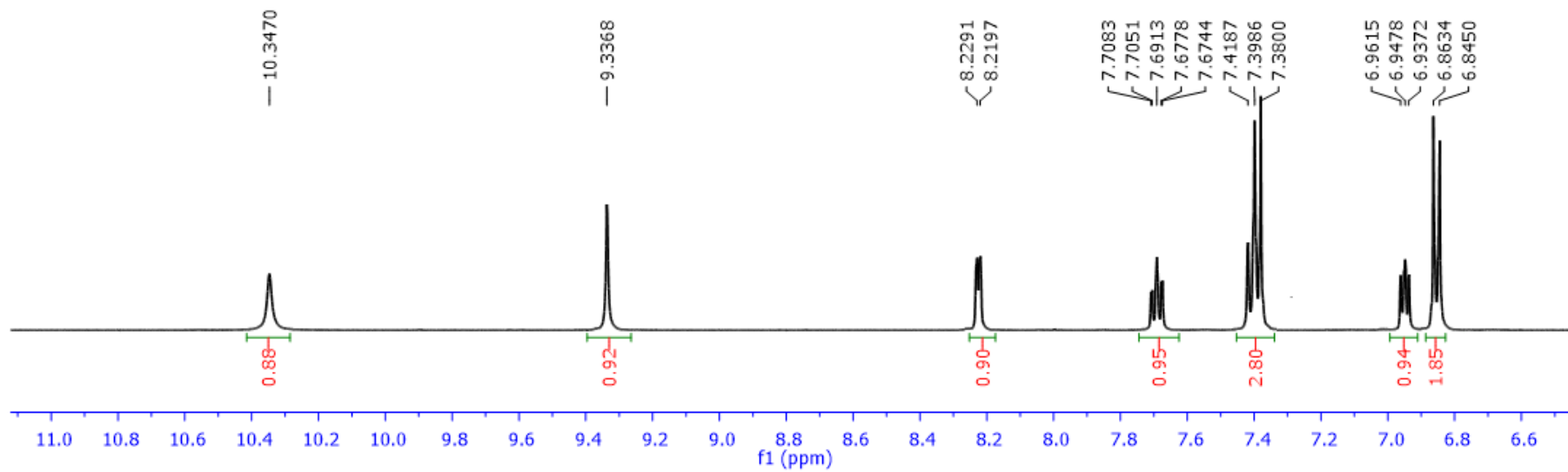
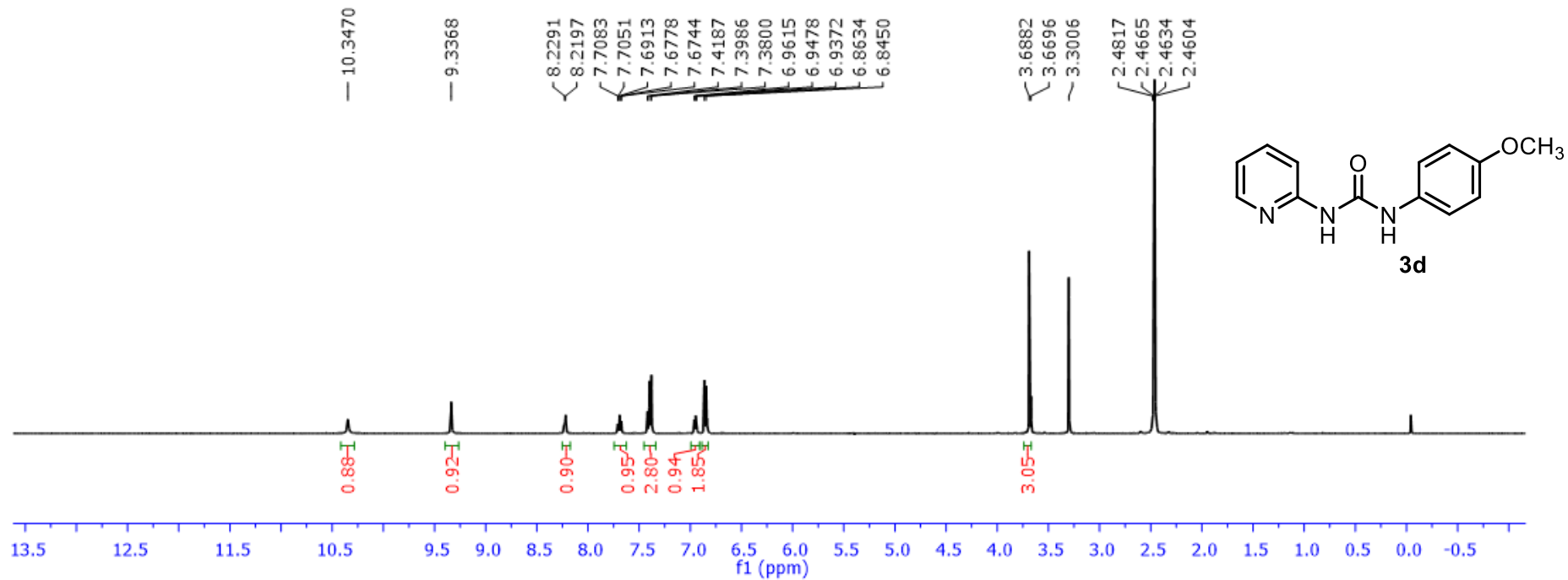




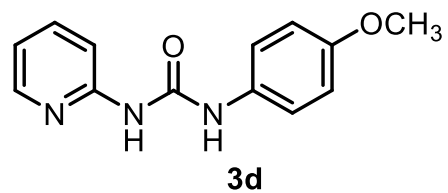
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105.08

55.48  
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40.37  
40.16  
39.95  
39.75  
39.54  
39.33





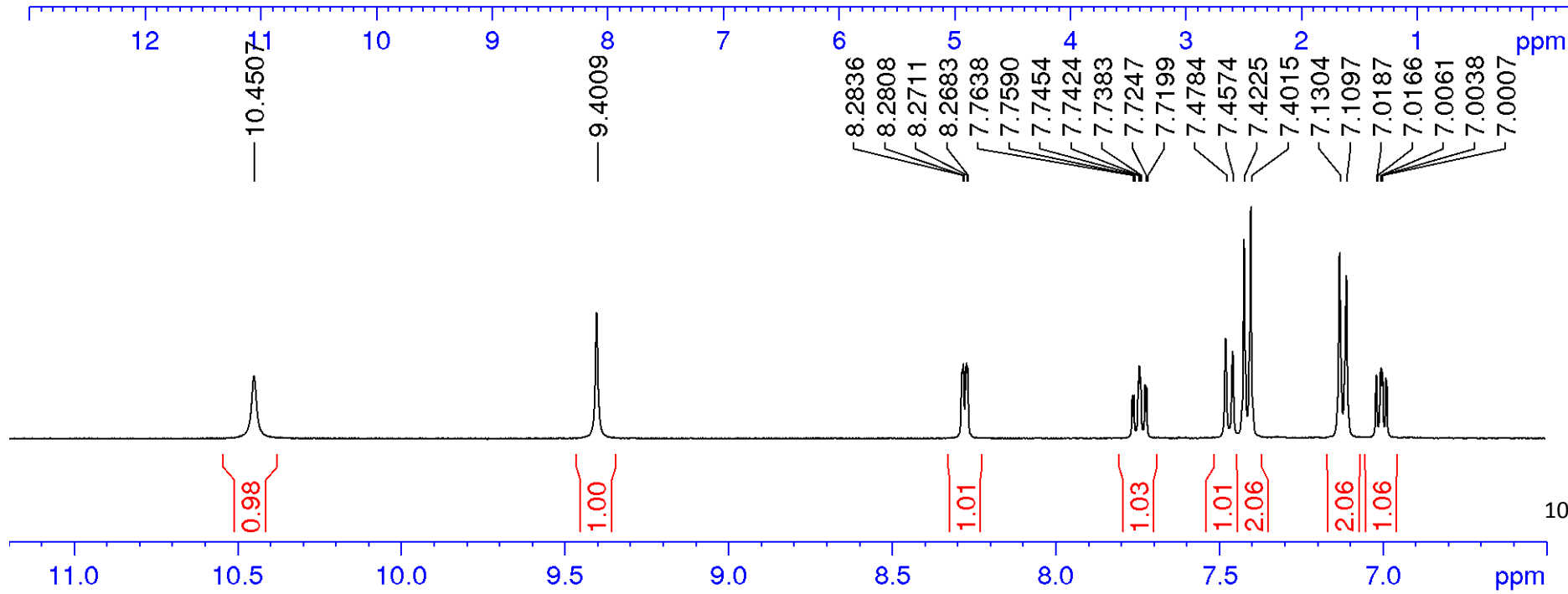
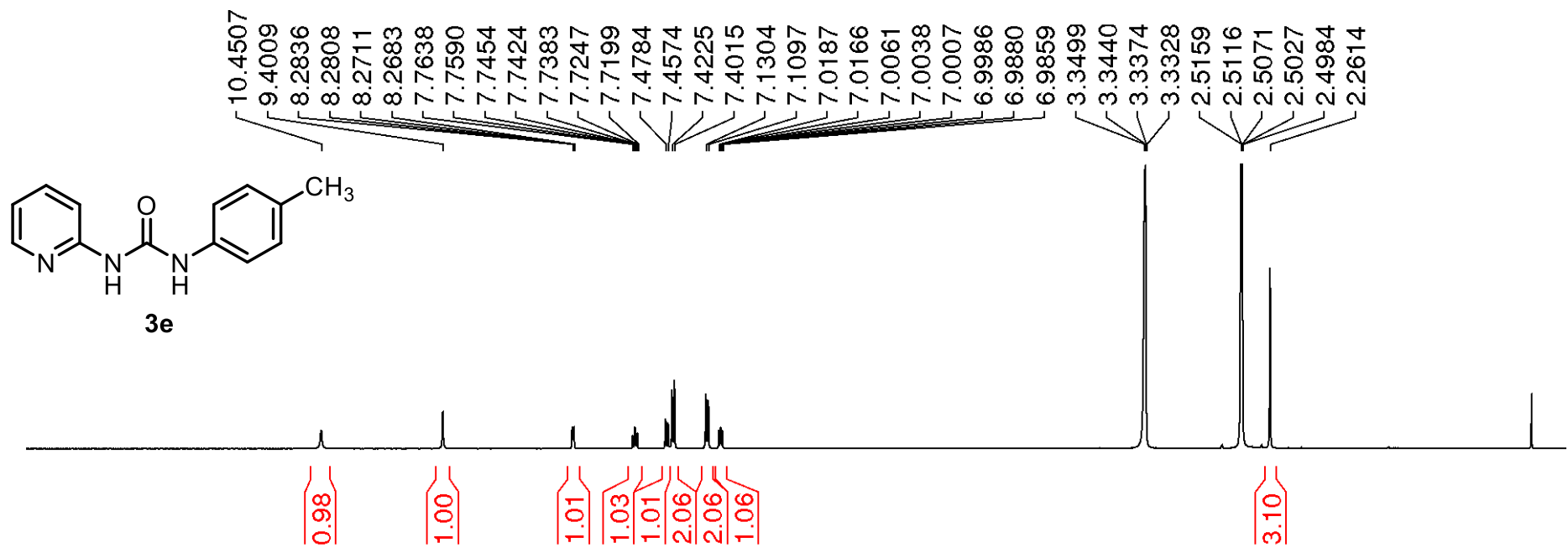


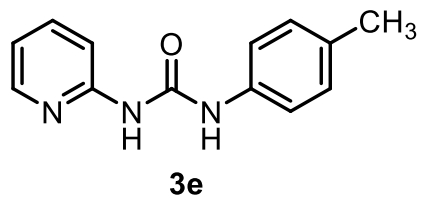


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153.41  
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147.27  
138.99  
132.35  
121.18  
120.52  
117.83  
114.52  
114.42  
112.31

55.65  
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40.20  
39.99  
39.78  
39.57  
39.36  
39.15

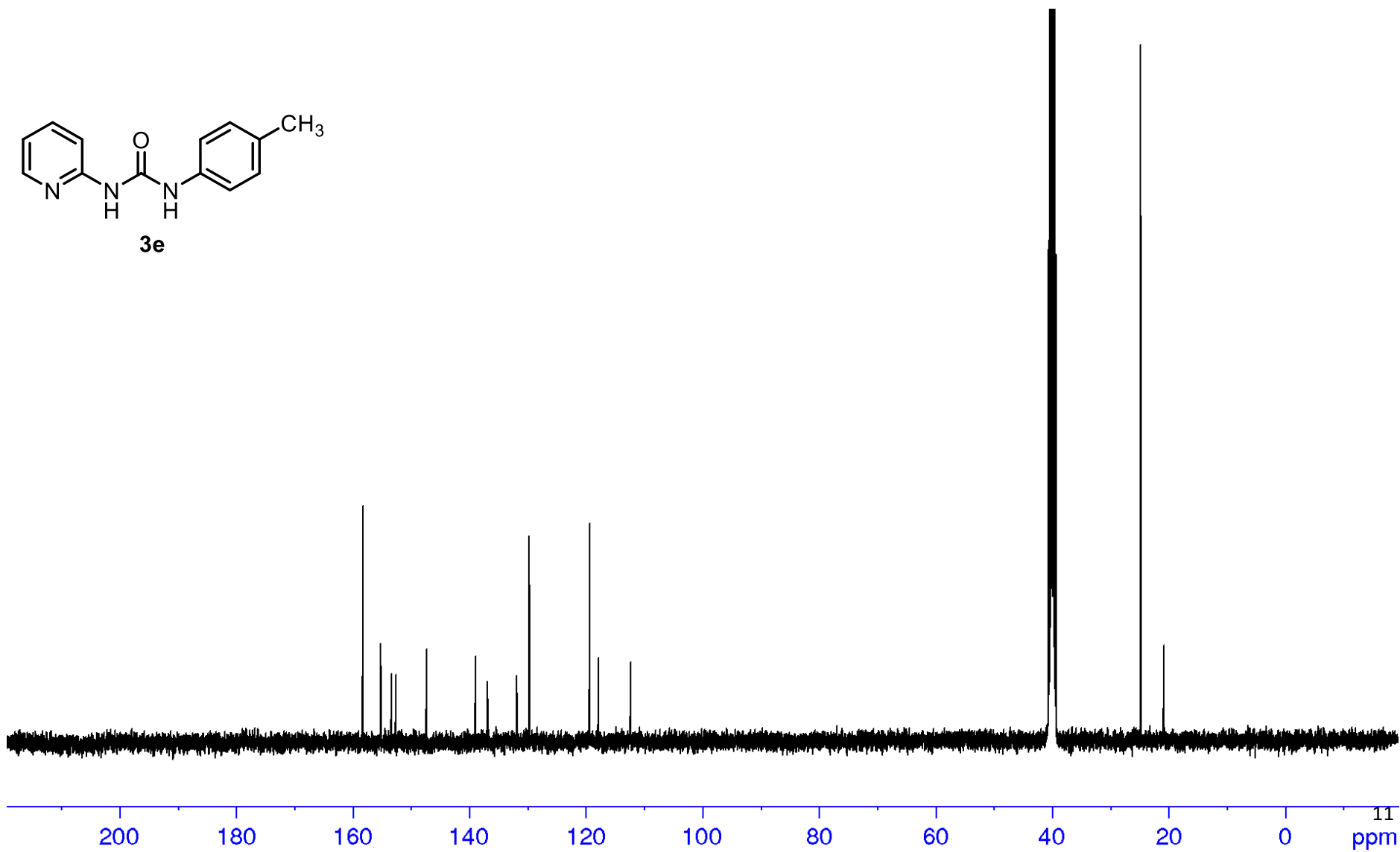


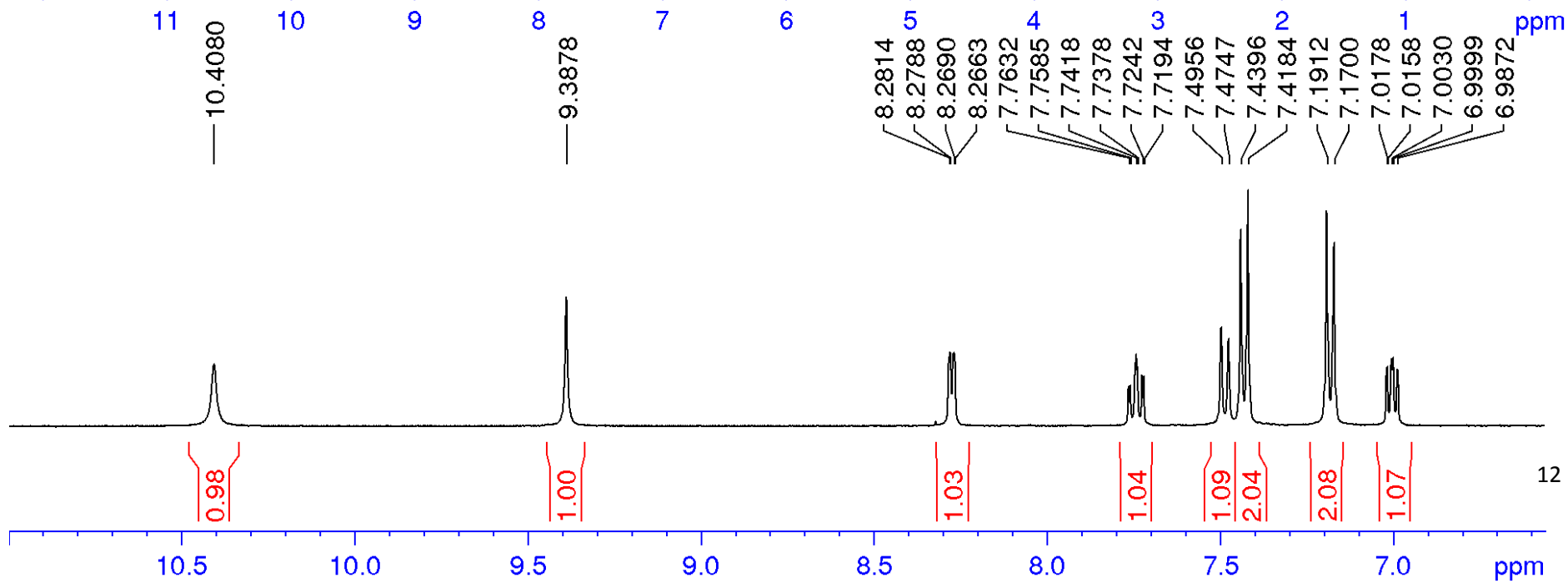
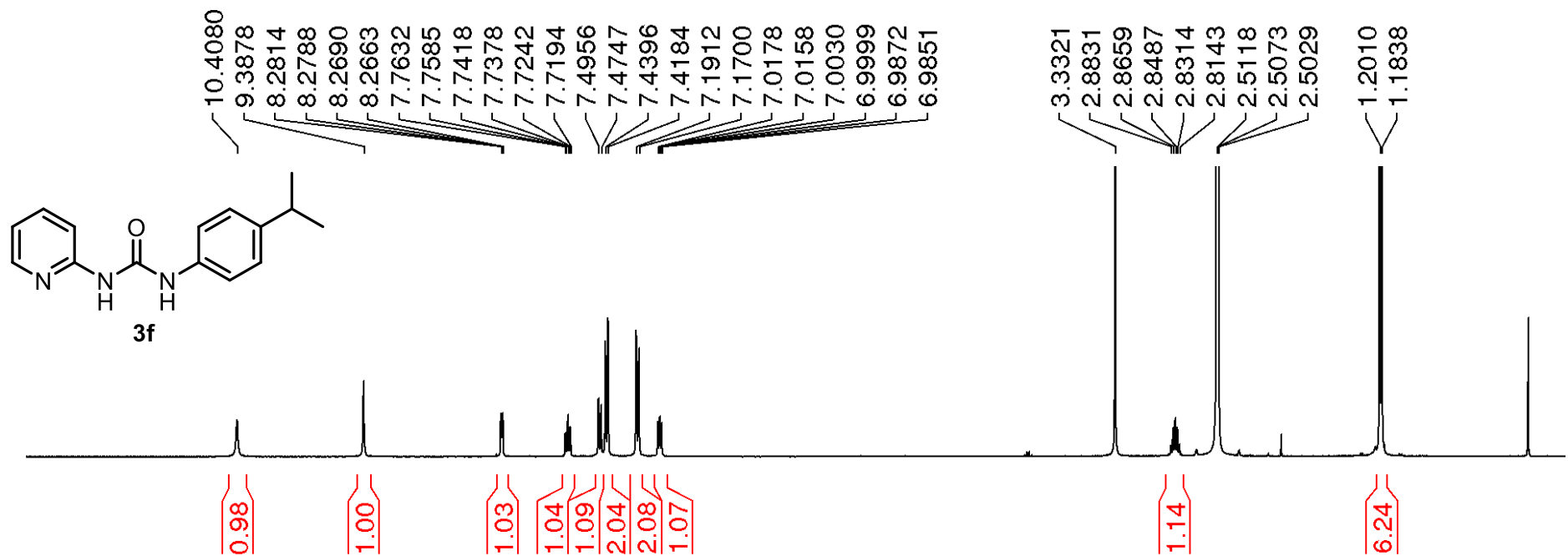


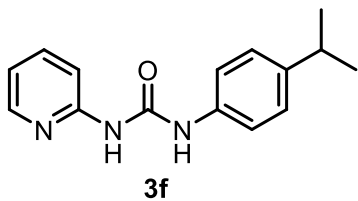


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155.23  
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147.32  
138.98  
136.90  
131.86  
129.73  
119.33  
117.86  
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39.32  
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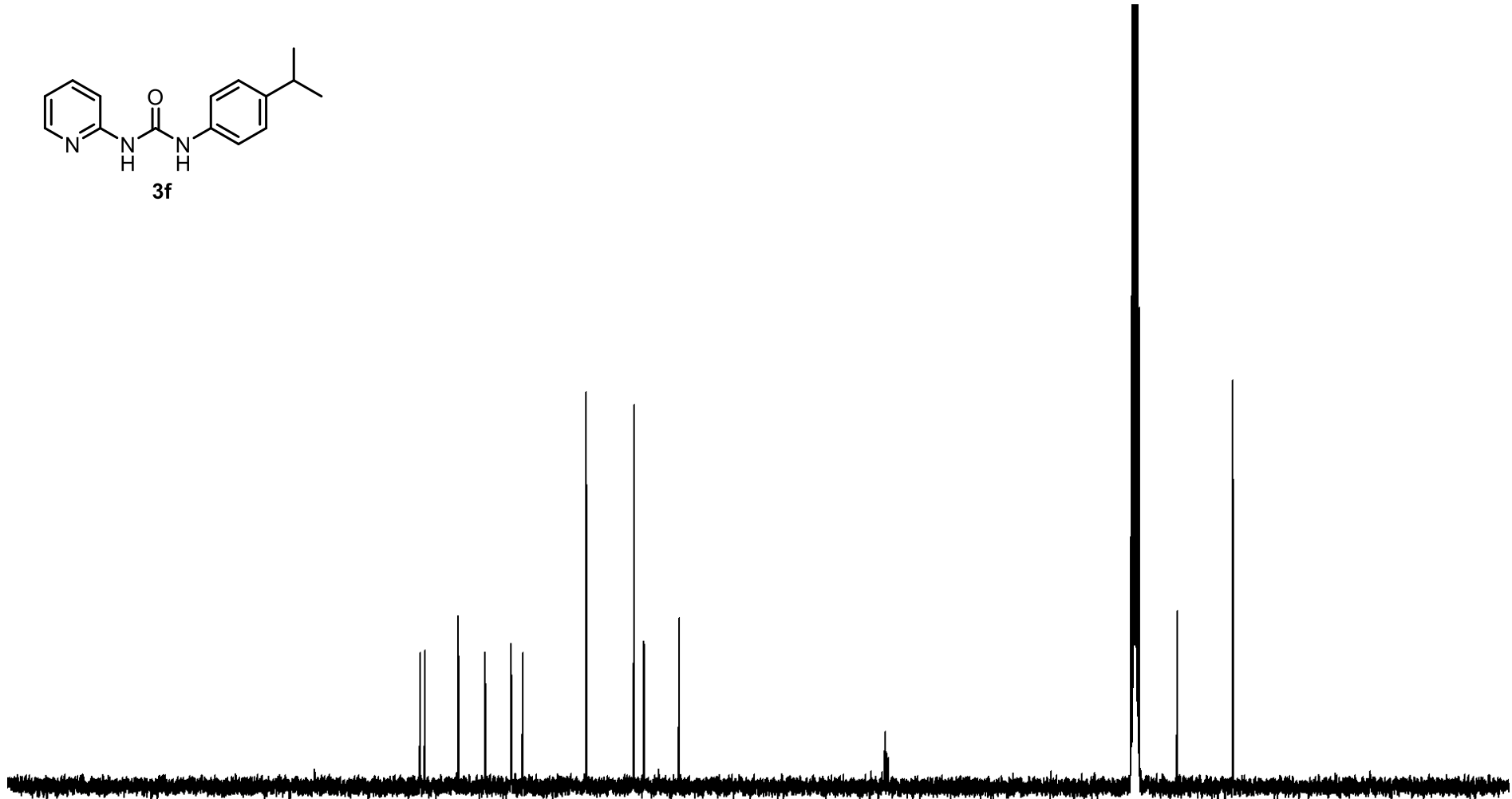




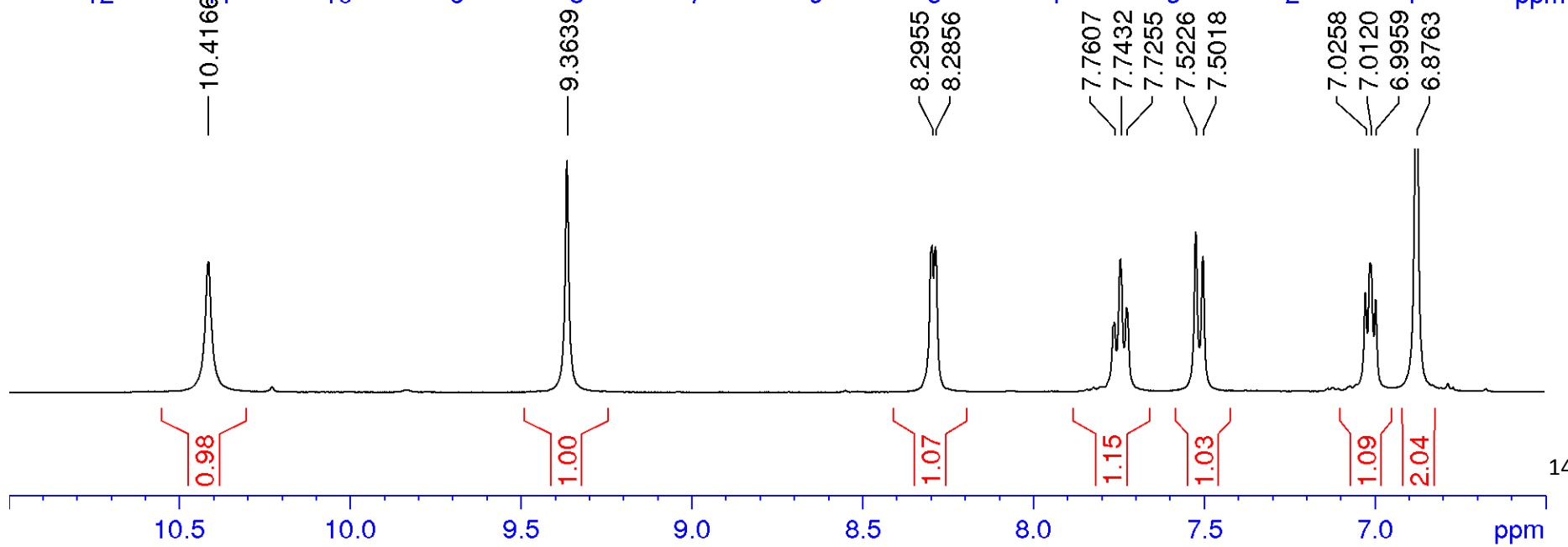
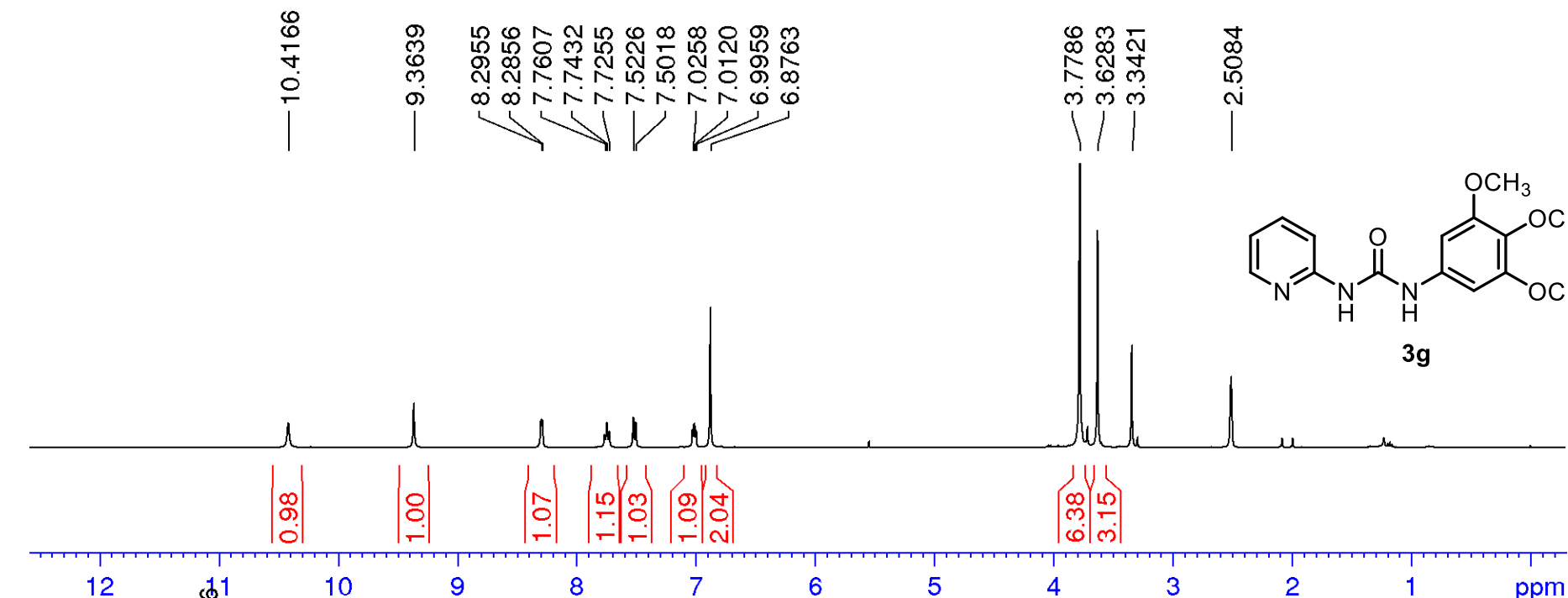
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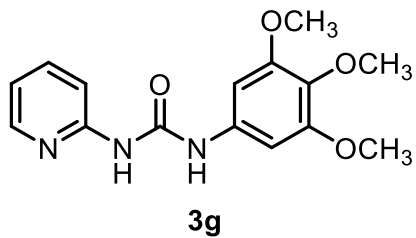
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79.41  
79.07

40.55  
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40.13  
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39.30  
33.27  
24.46



200 180 160 140 120 100 80 60 40 20 0 ppm



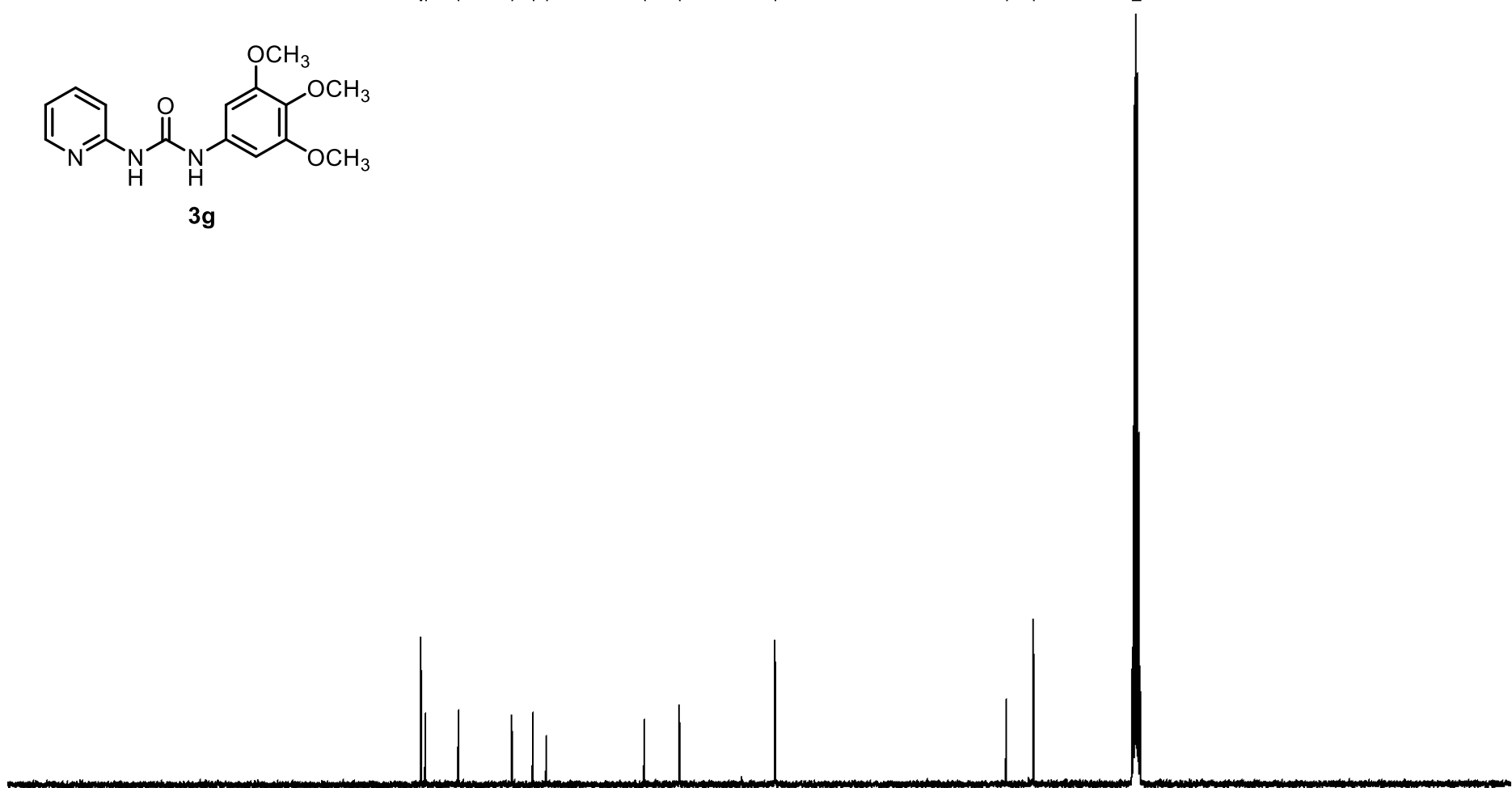


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153.33  
152.62  
147.41  
138.95  
135.60  
133.47

117.92  
112.38

97.20

60.58  
56.25  
40.61  
40.40  
40.19  
39.98  
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39.56  
39.36



200

180

160

140

120

100

80

60

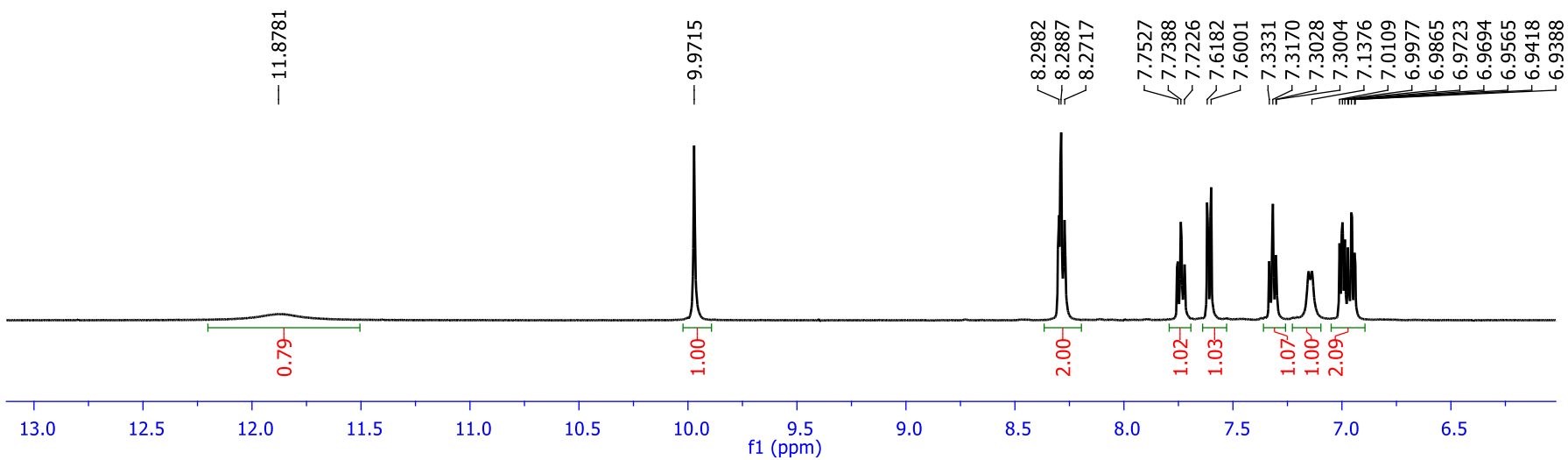
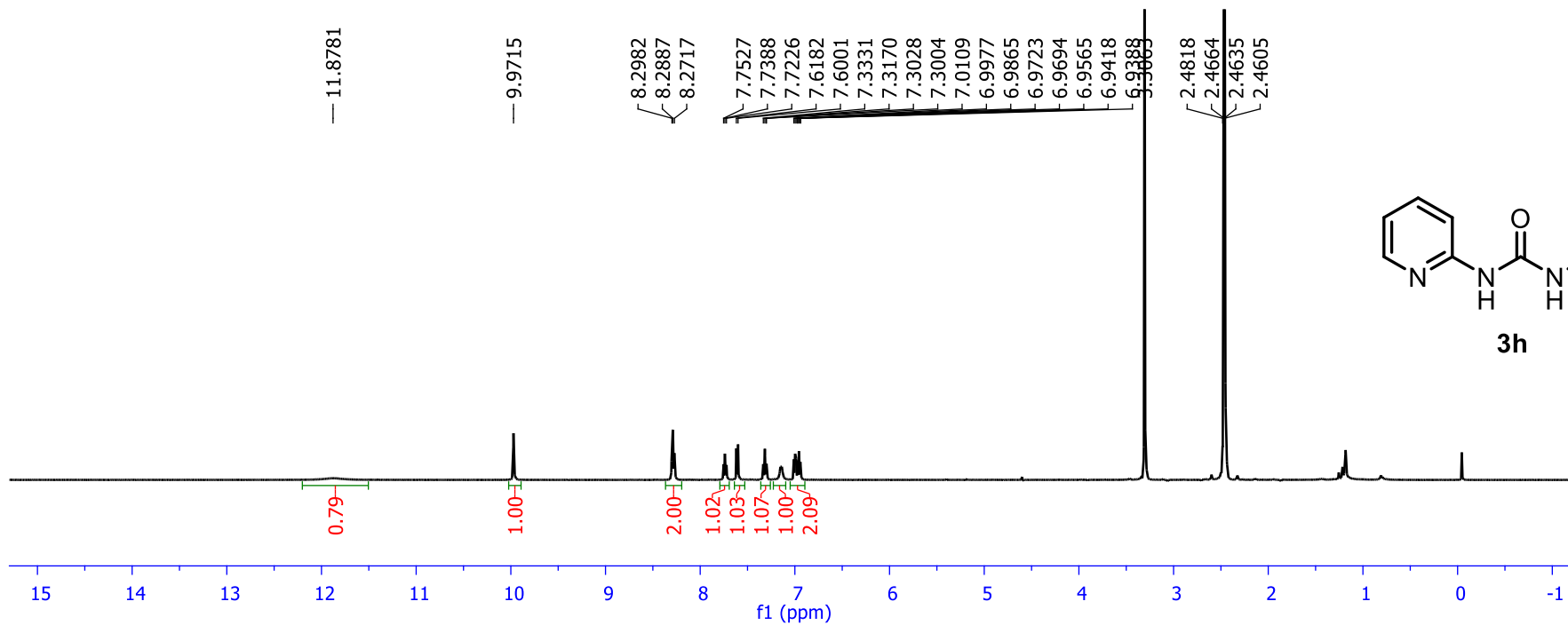
40

20

0

ppm

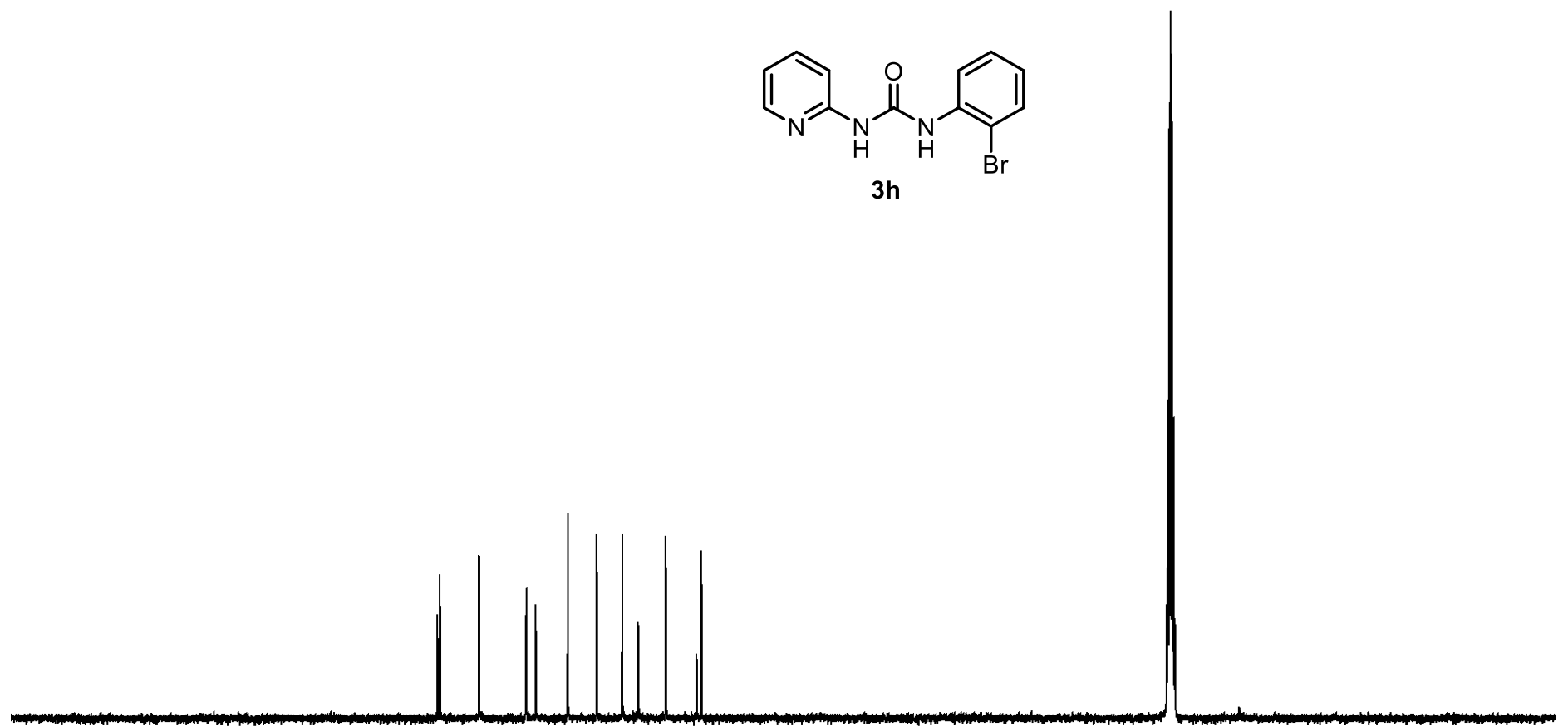
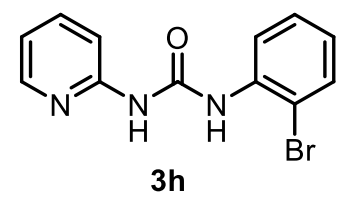
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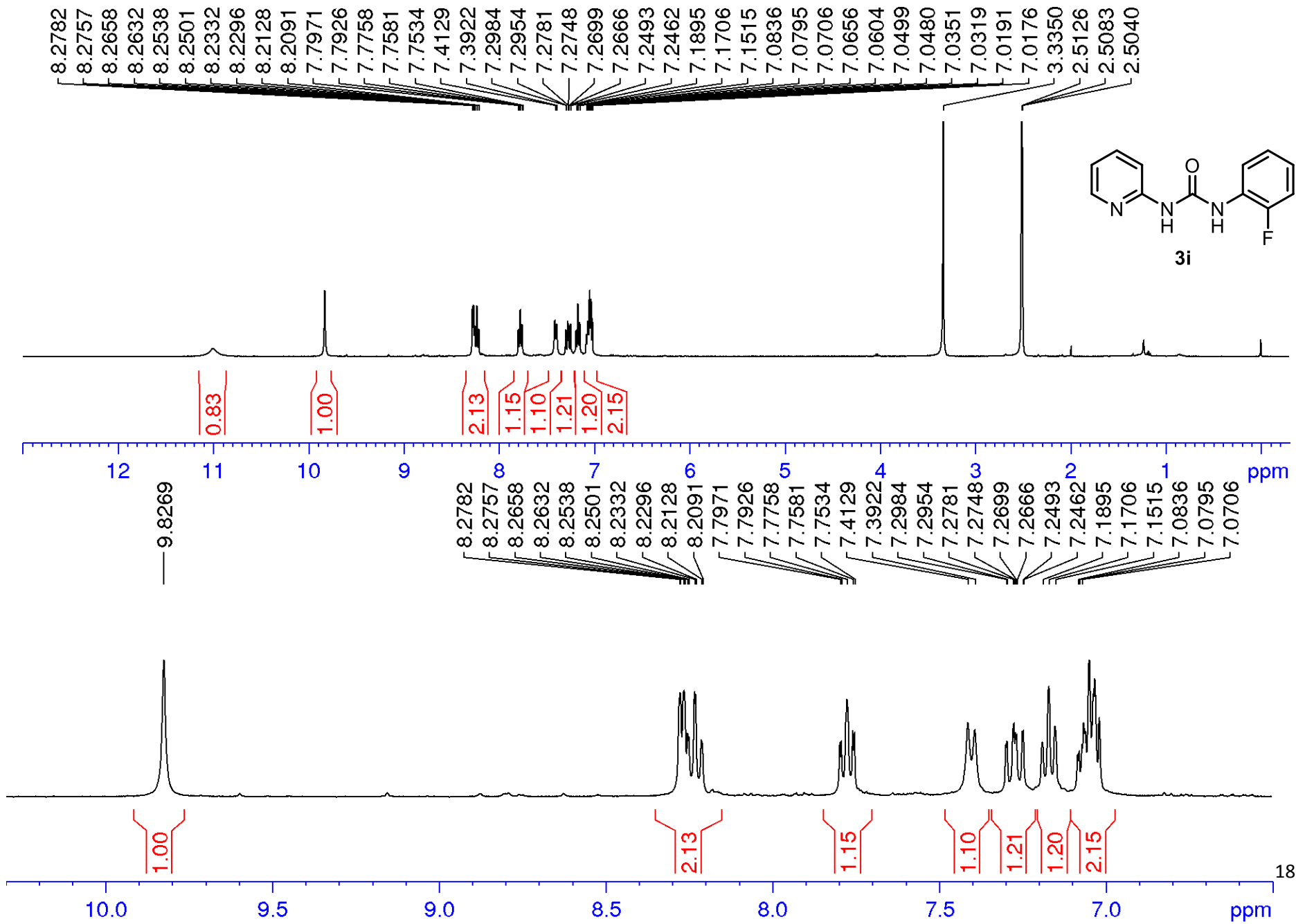


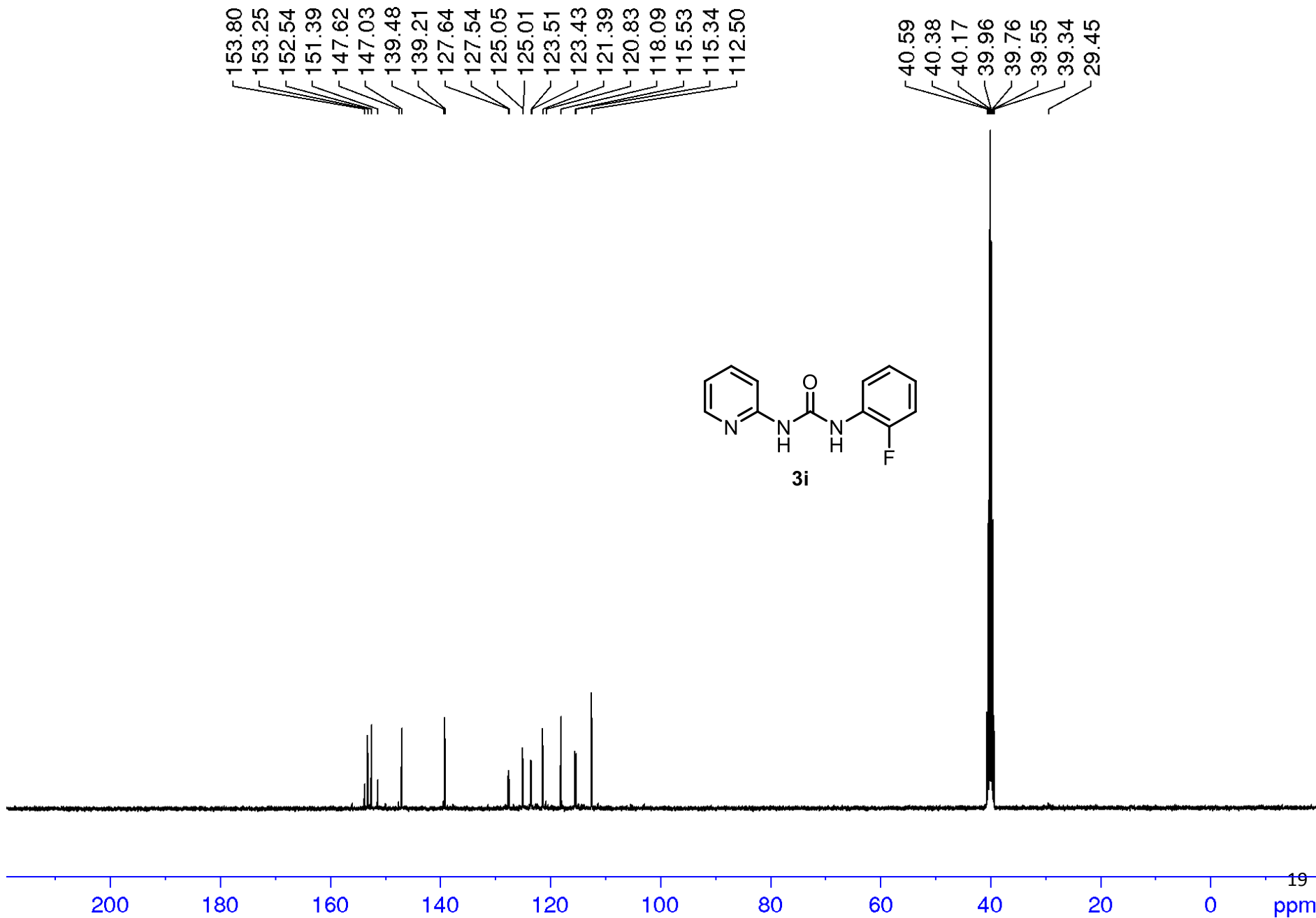
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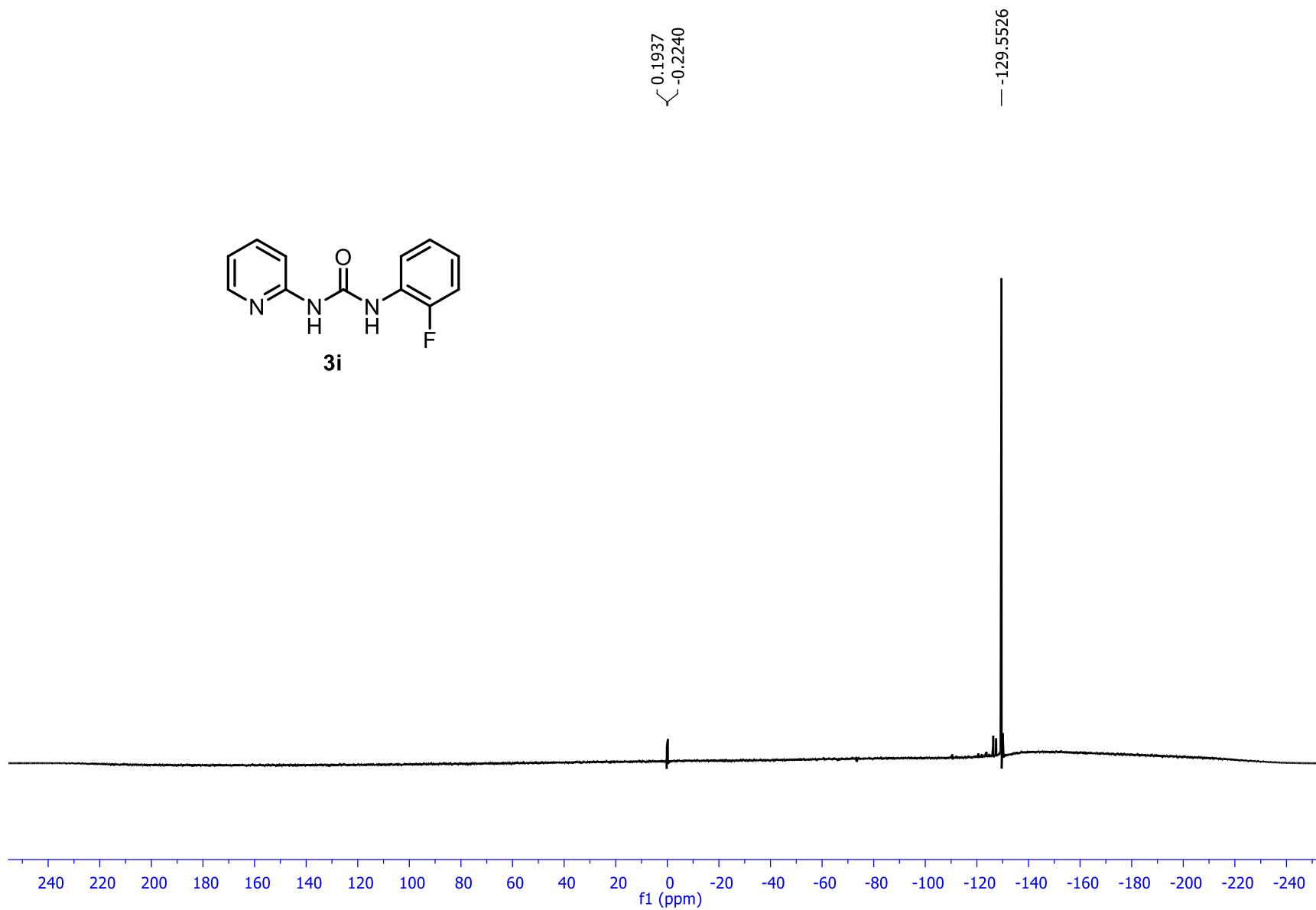
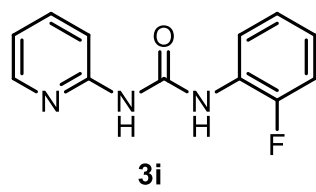
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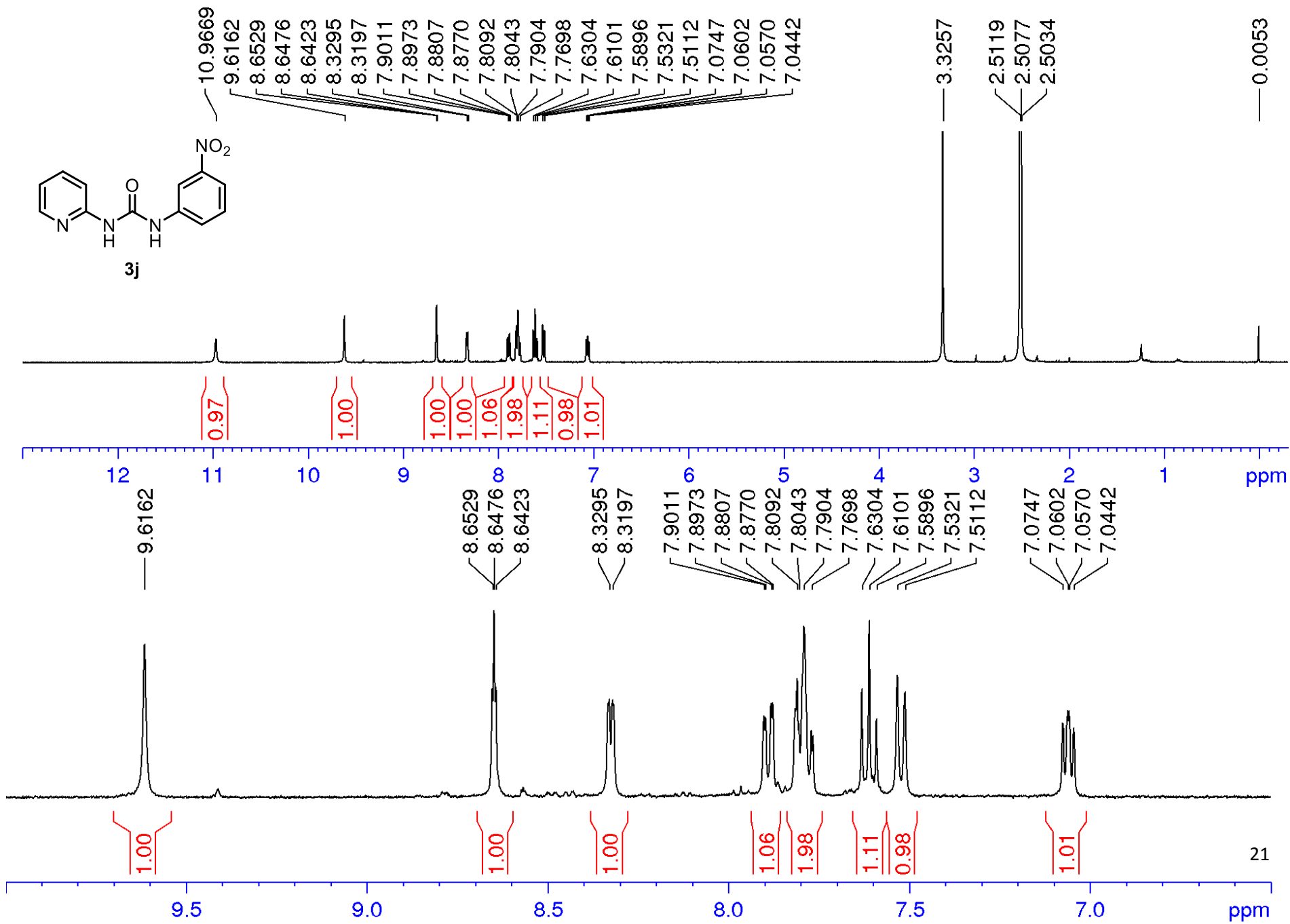
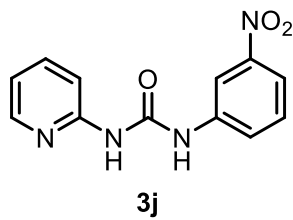


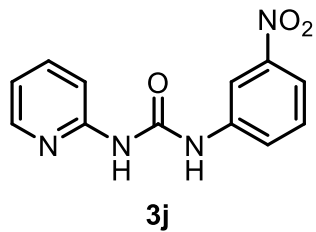
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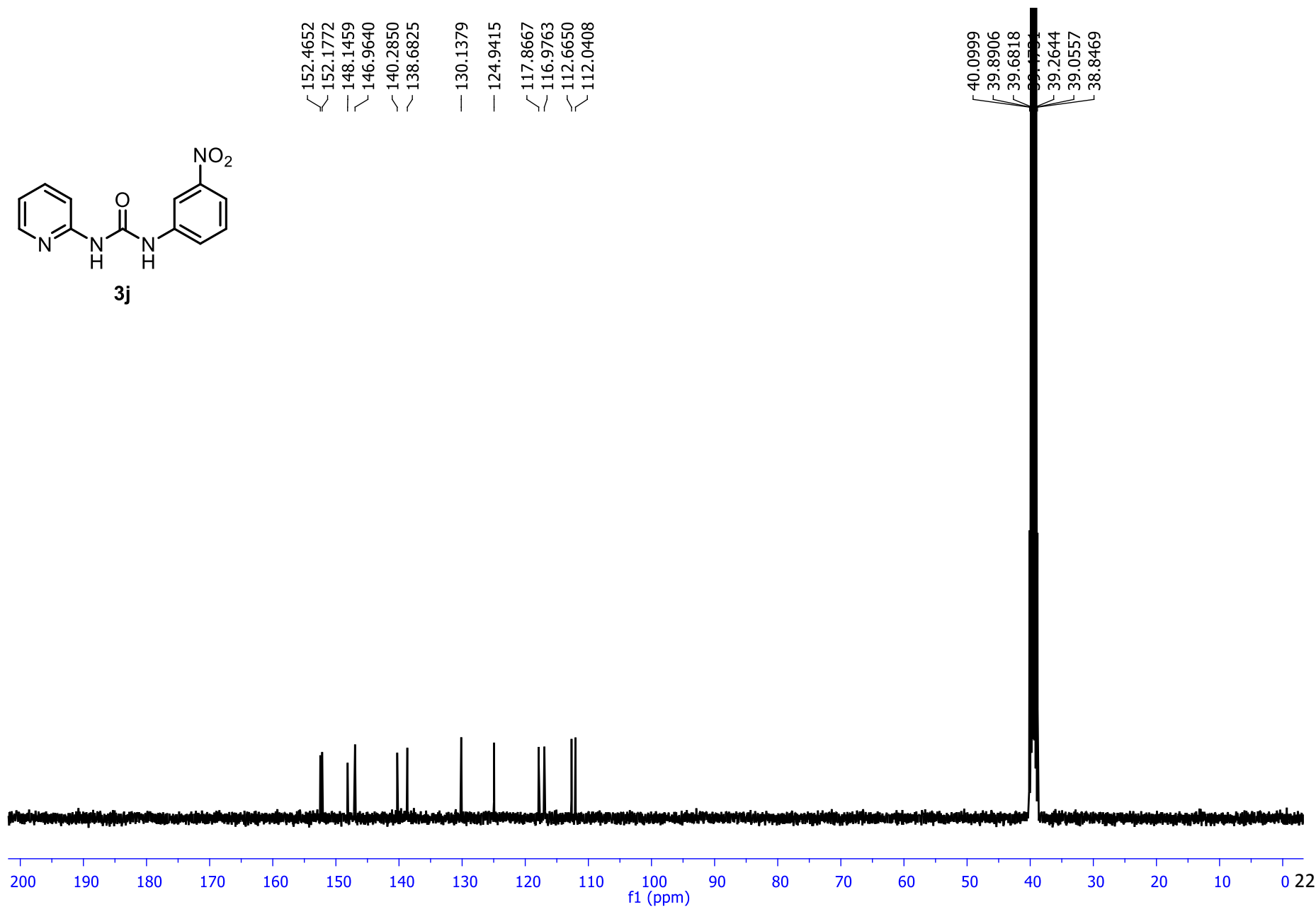


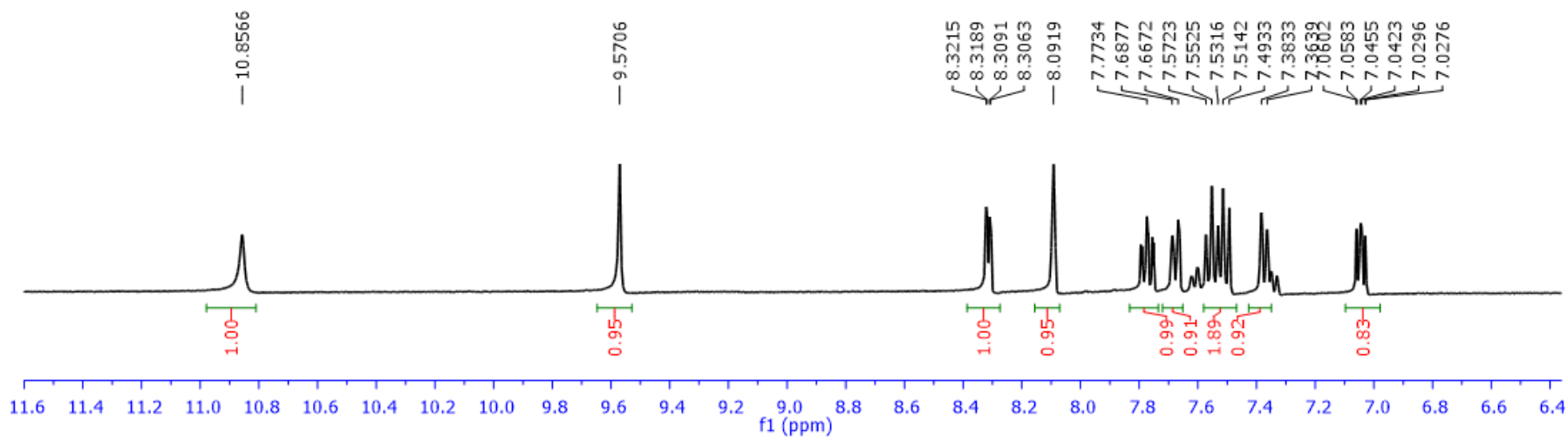
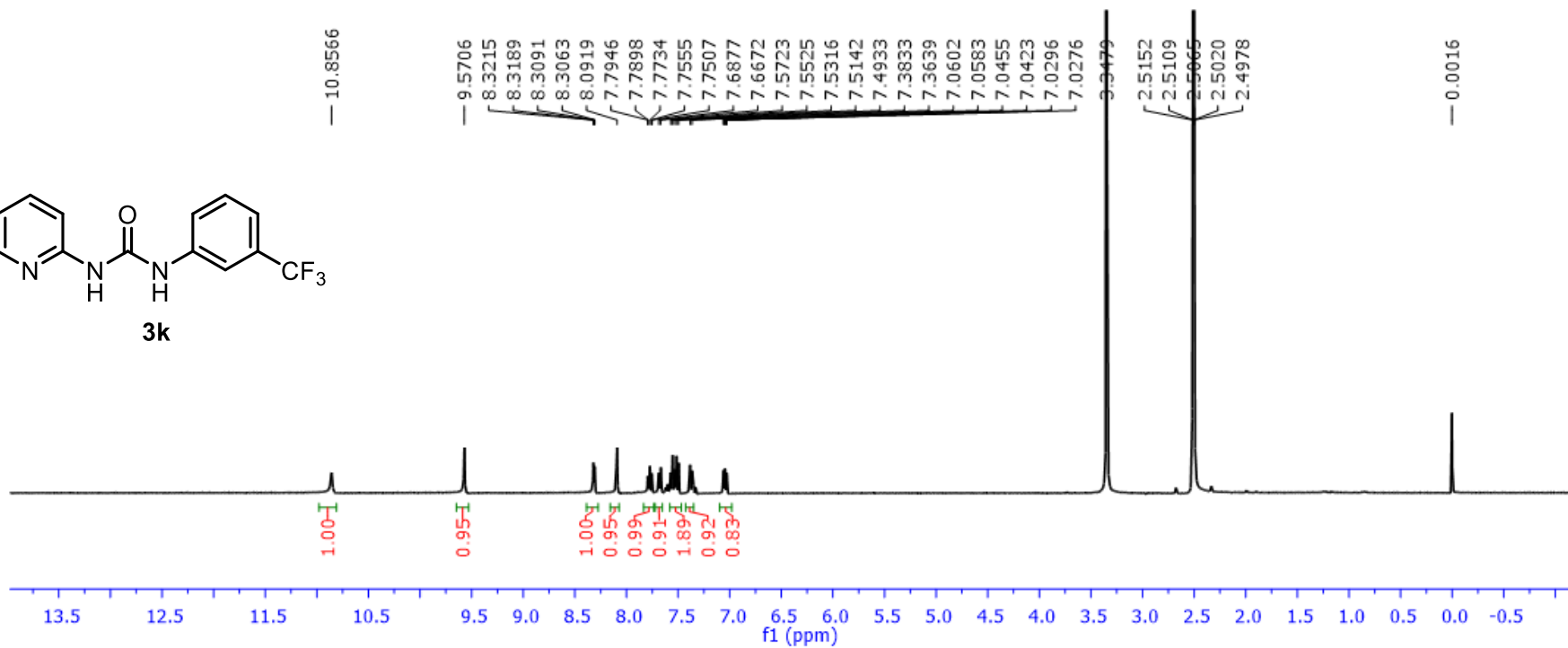
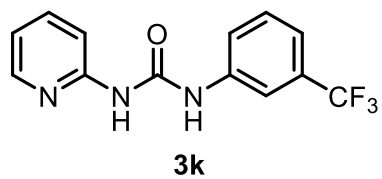


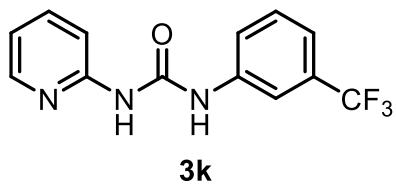


- 152.4652
- 152.1772
- 148.1459
- 146.9640
- 140.2850
- 138.6825
- 130.1379
- 124.9415
- 117.8667
- 116.9763
- 112.6650
- 112.0408

- 40.0999
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- 39.6818
- 39.1791
- 39.2644
- 39.0557
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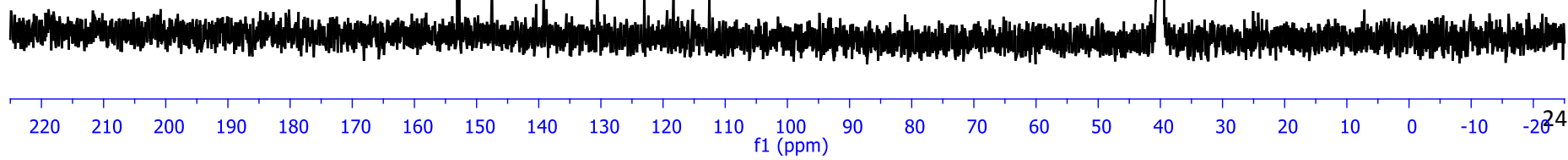




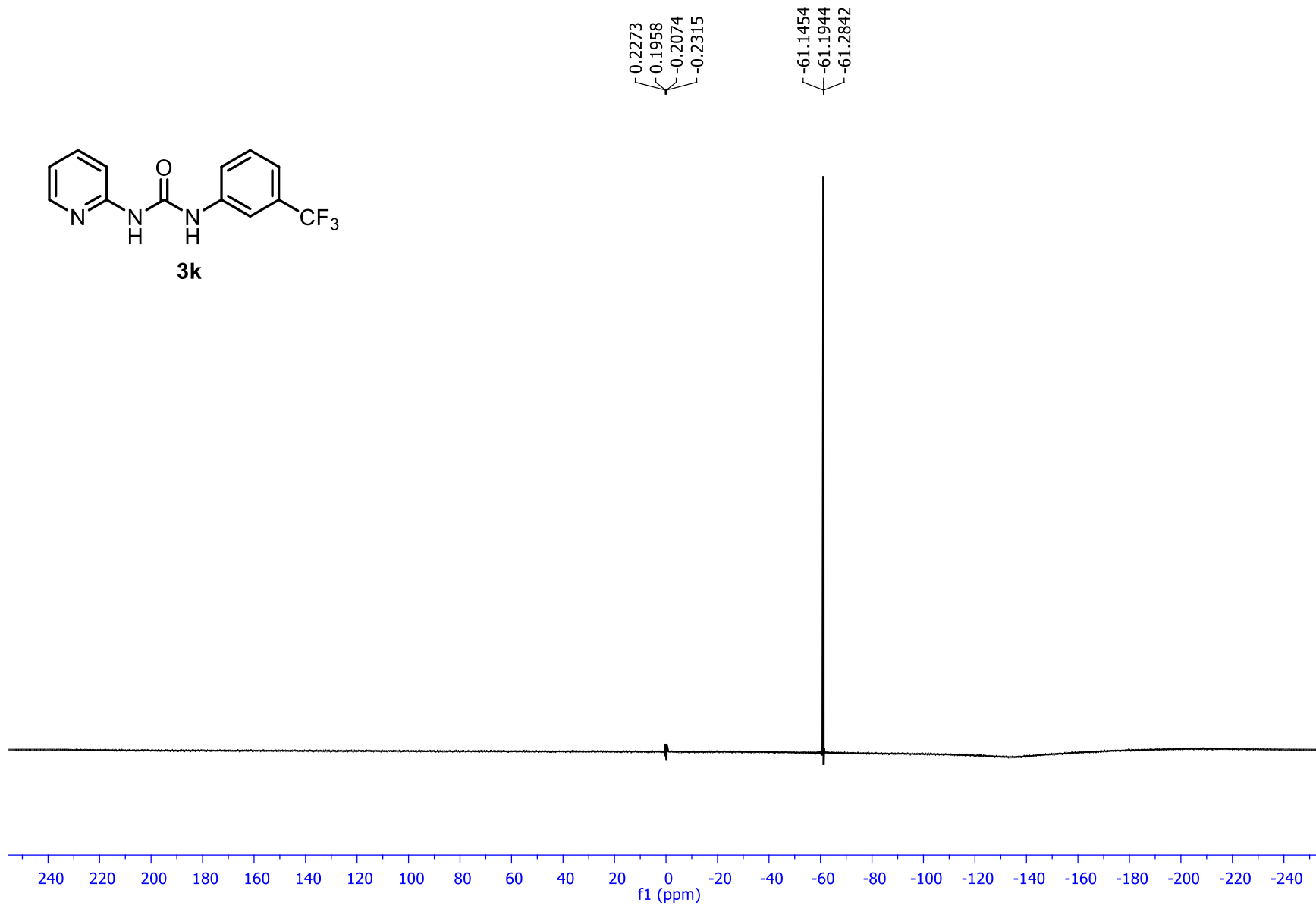
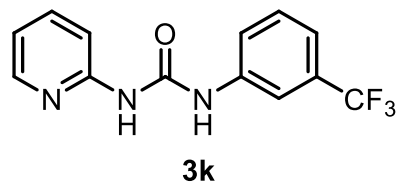


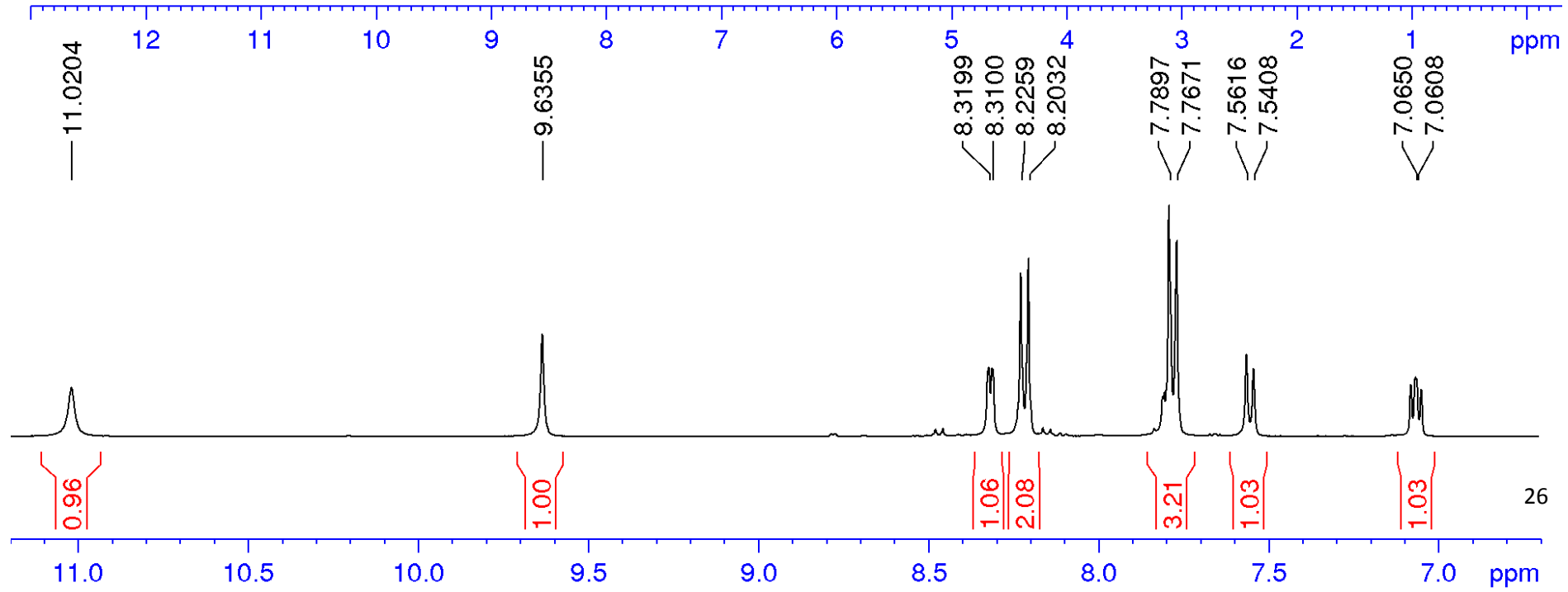
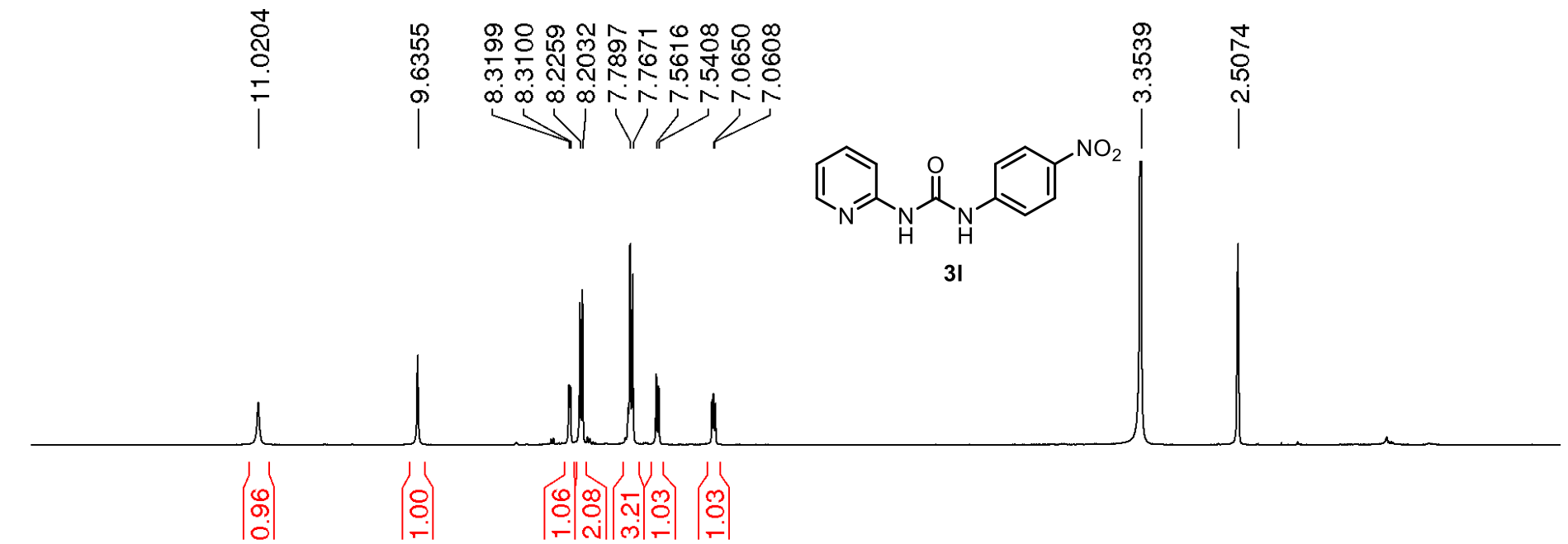
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— 139.2160  
} 130.5687  
} 123.0273  
} 118.3157  
} 112.5411

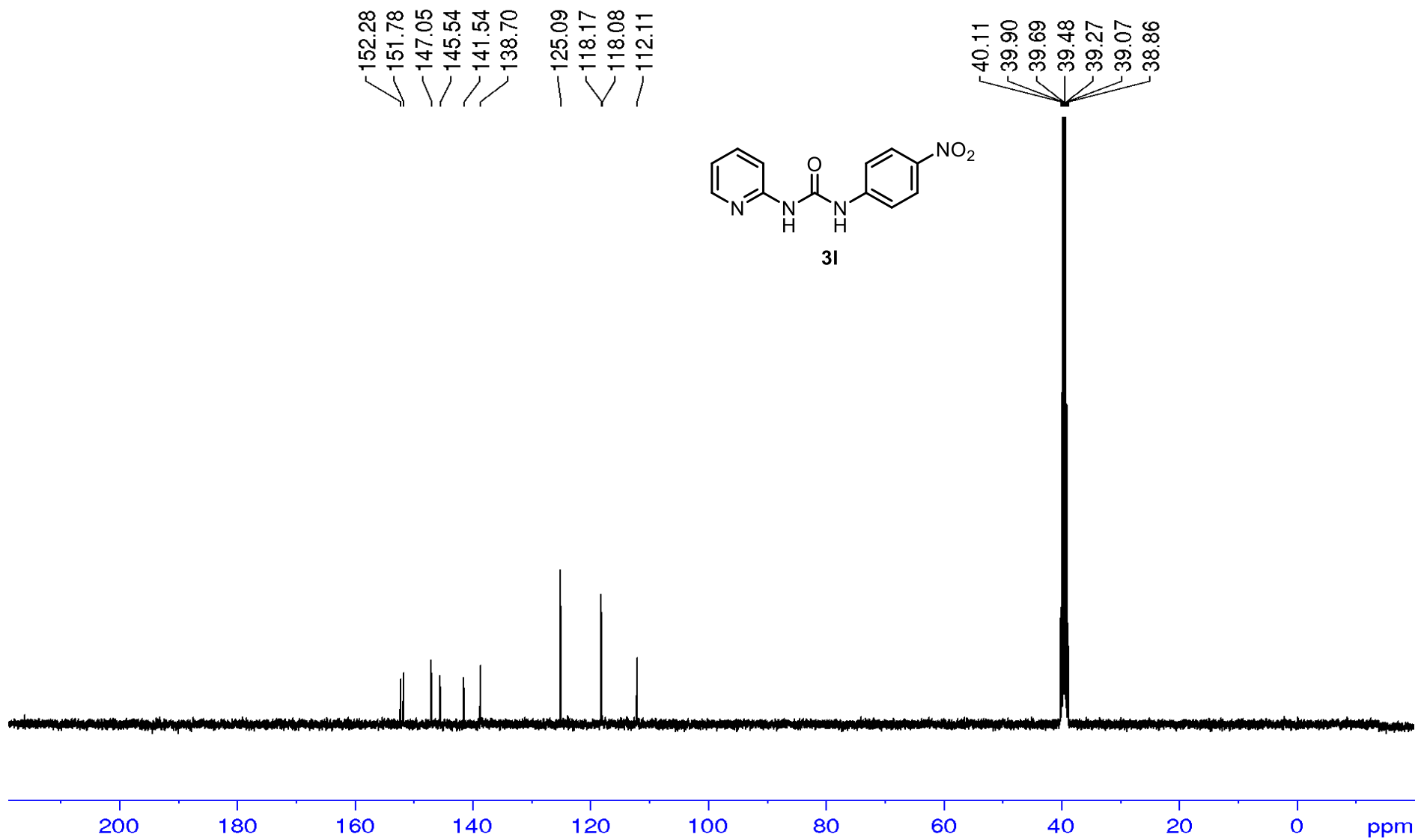
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39.6754  
39.5089

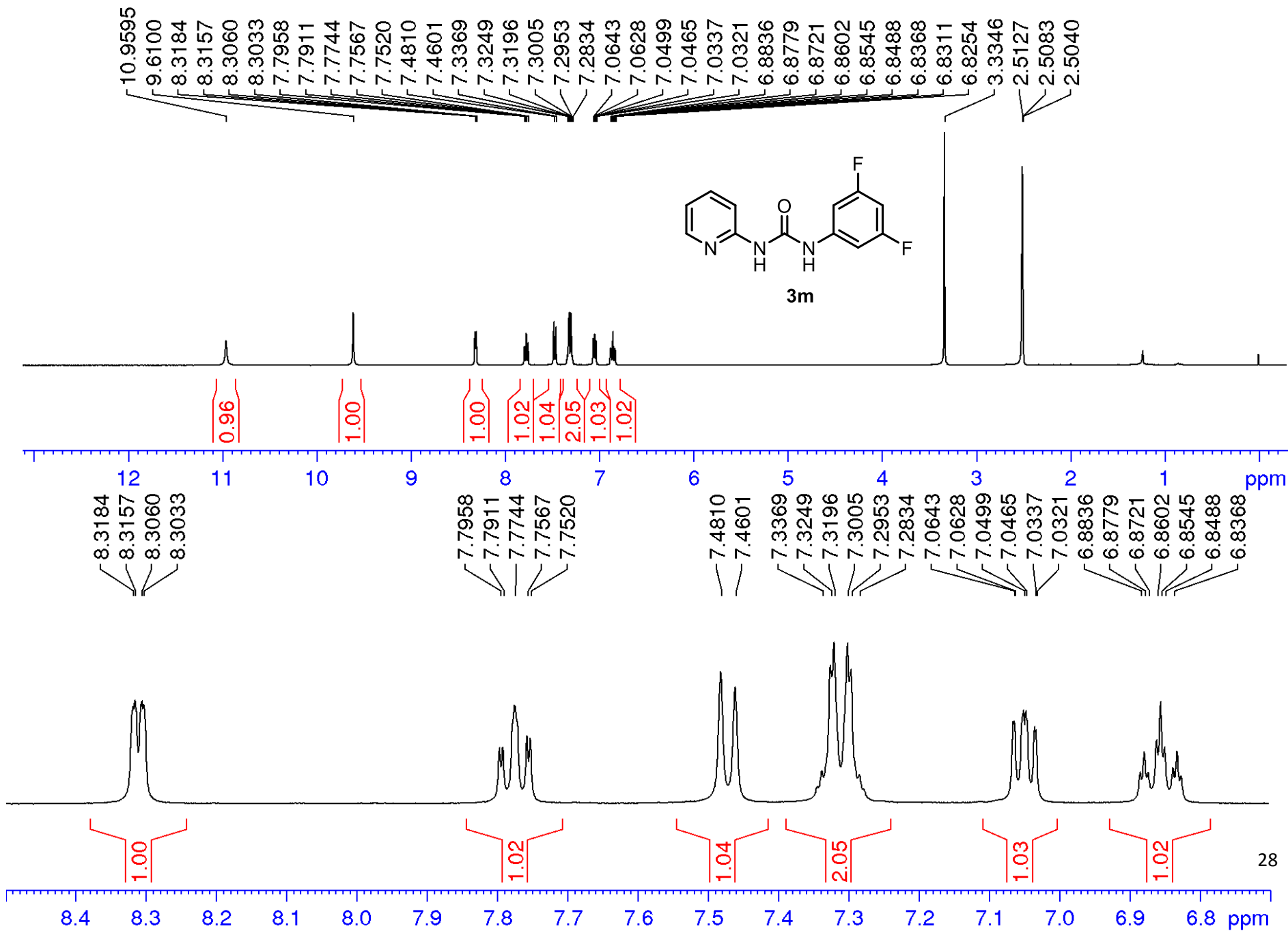


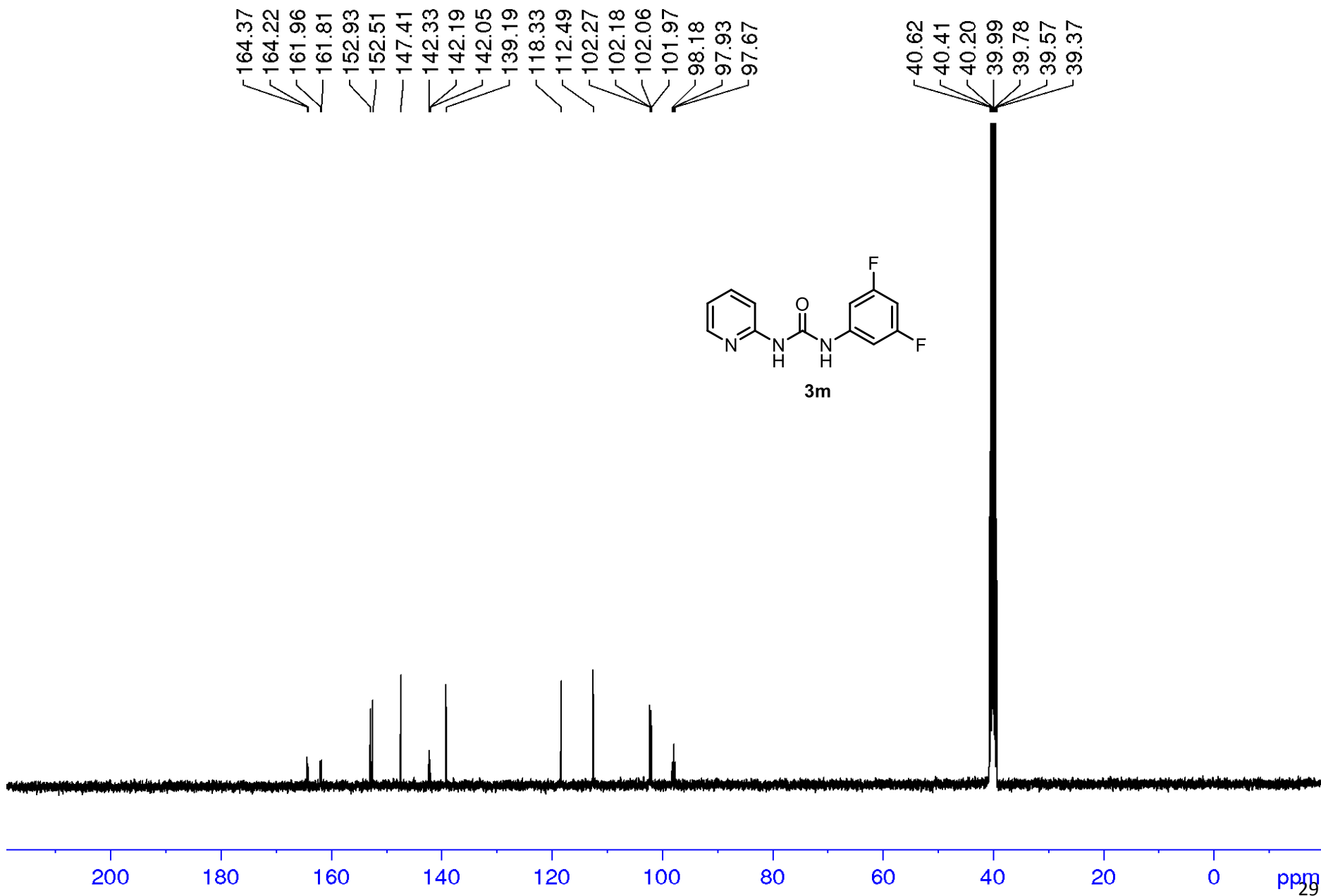


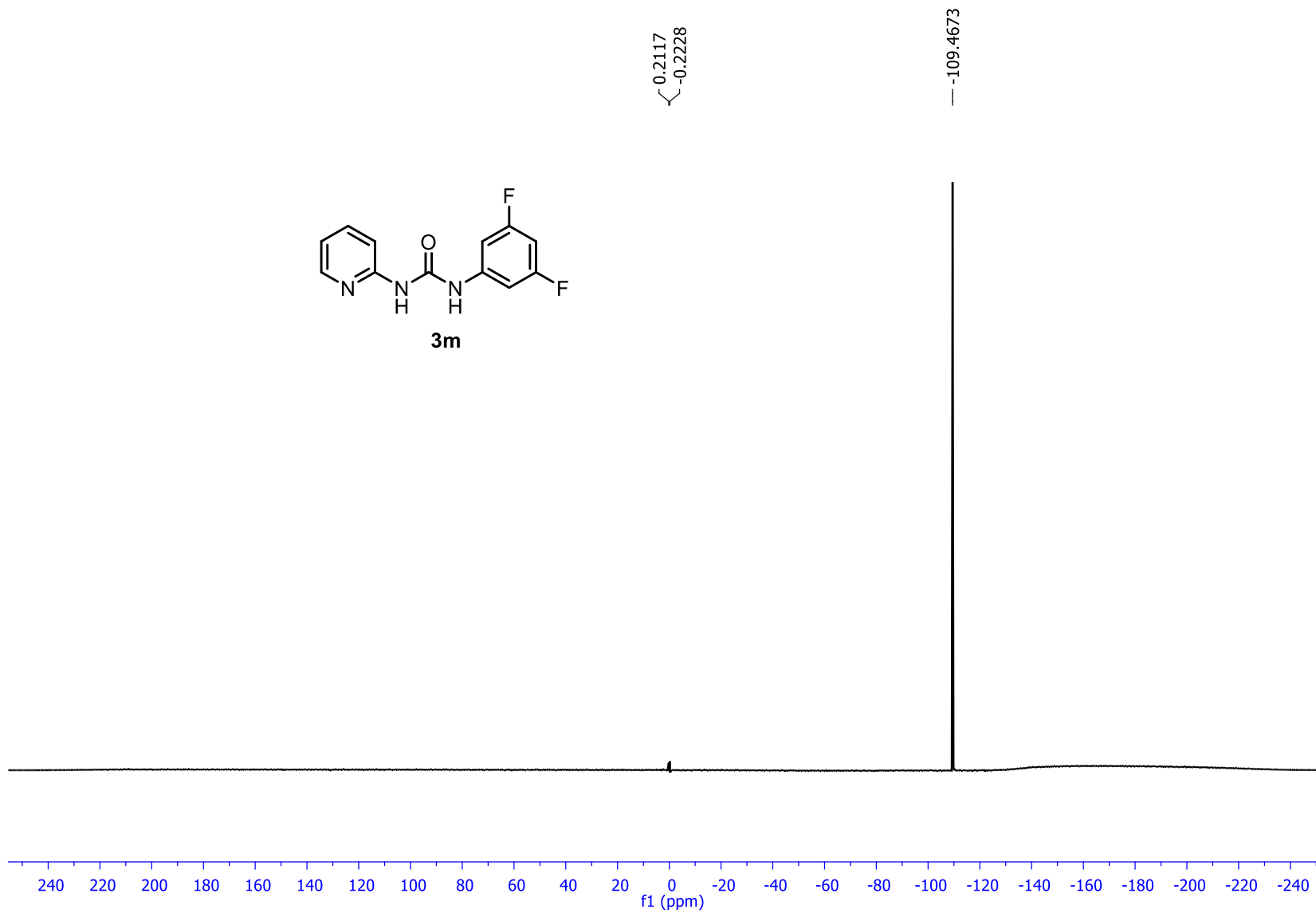
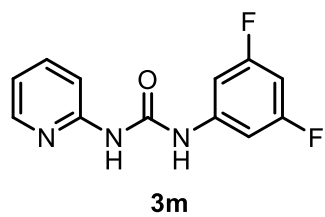


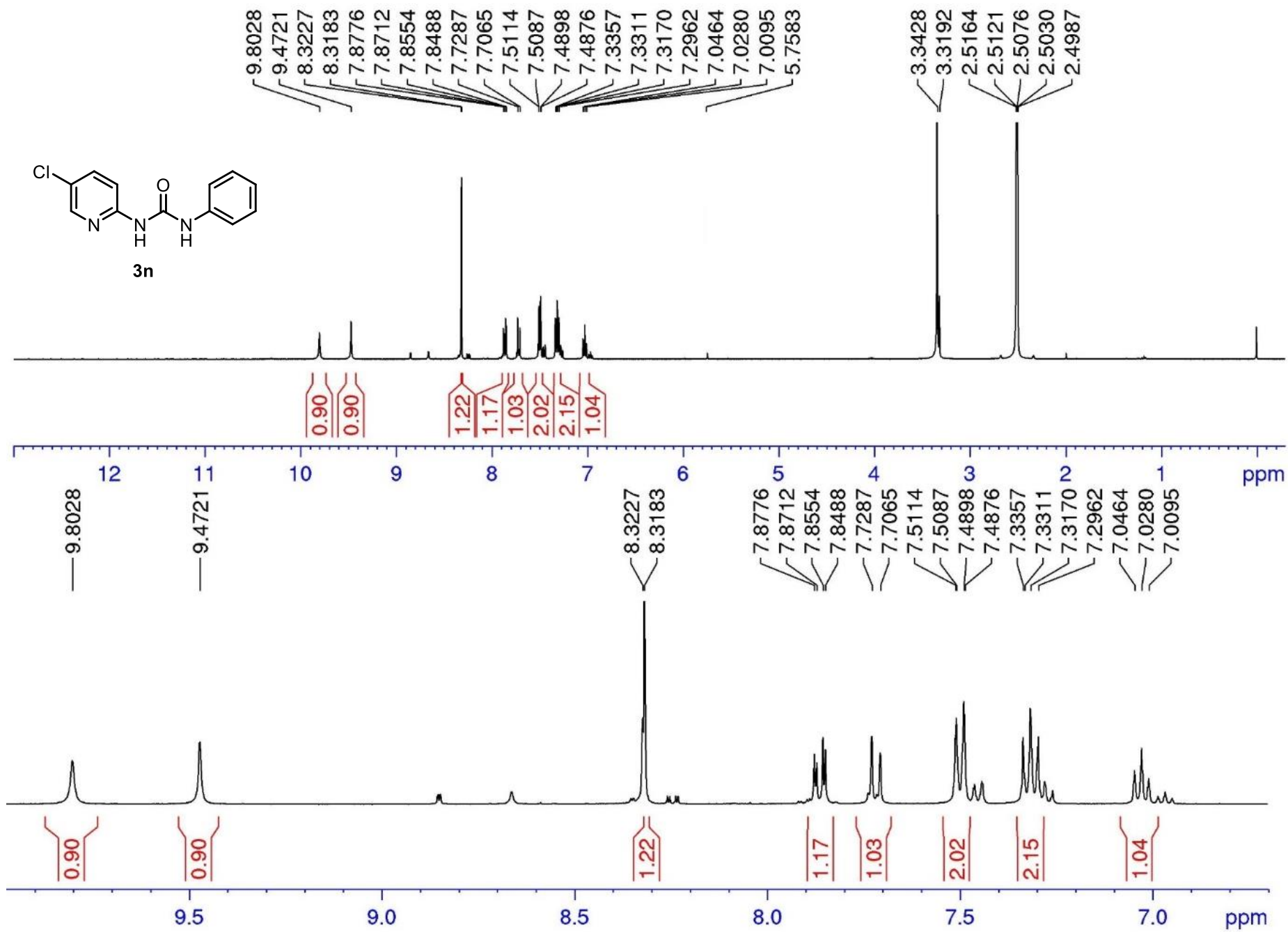


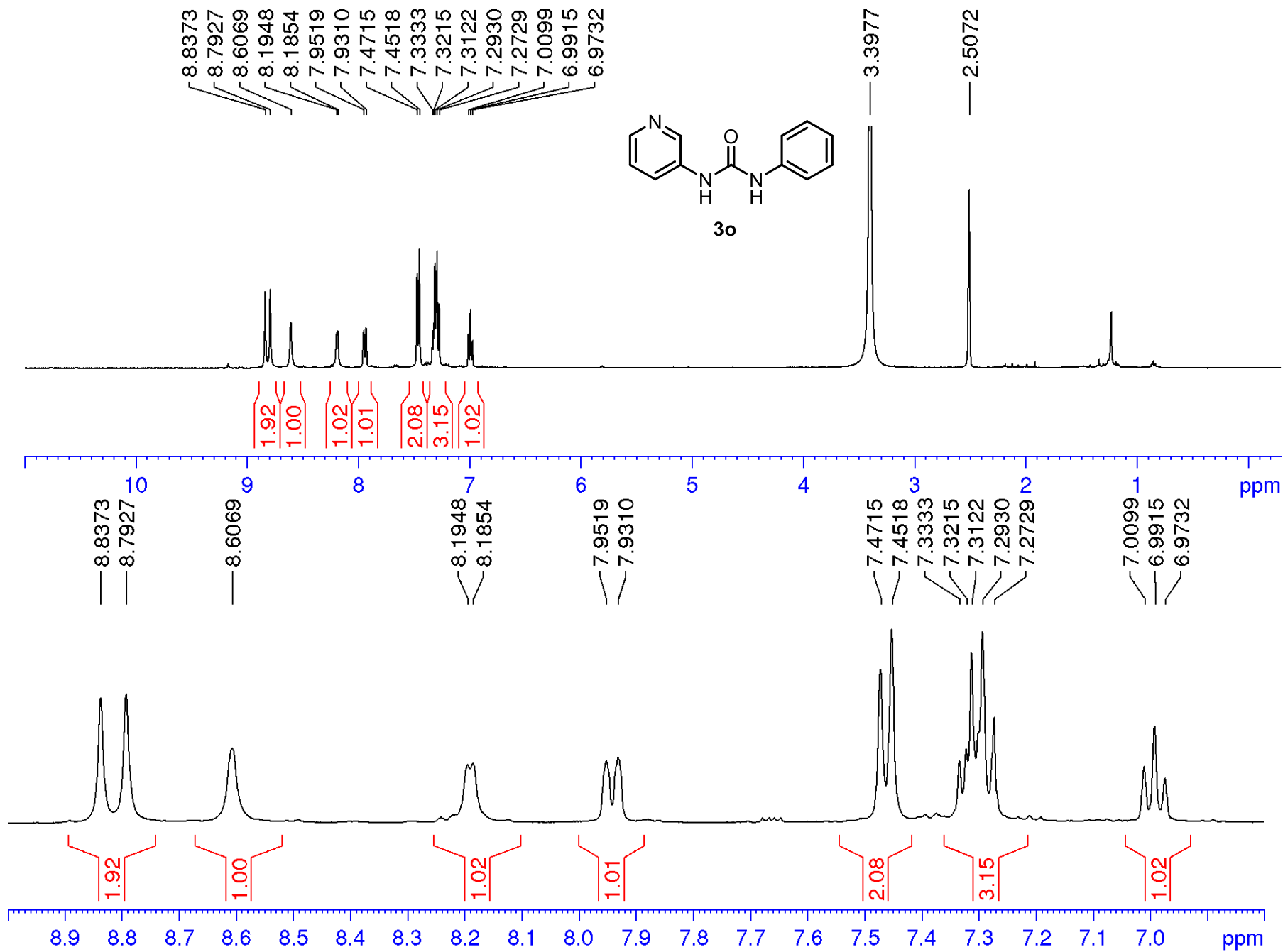






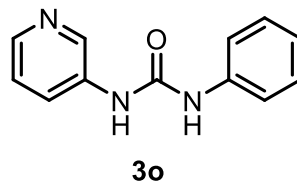




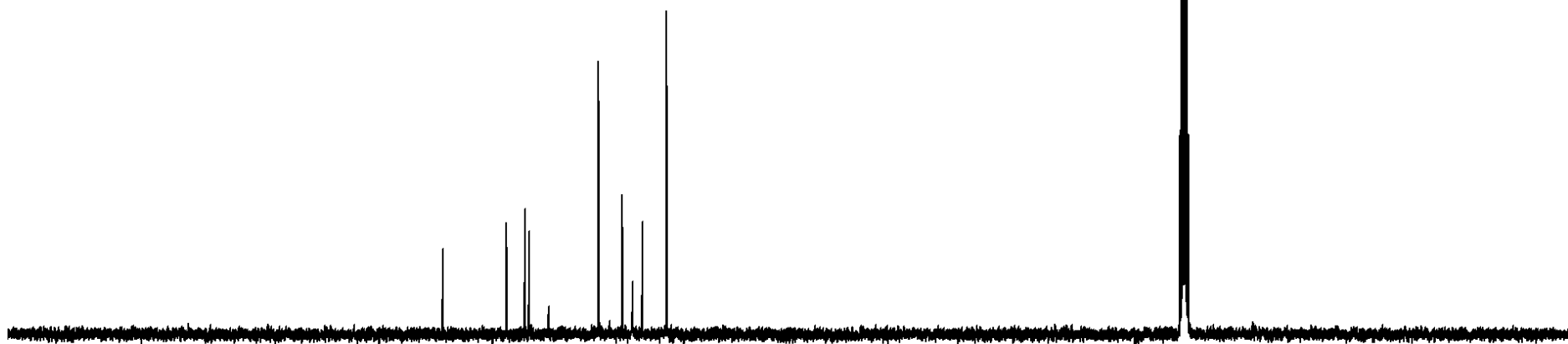




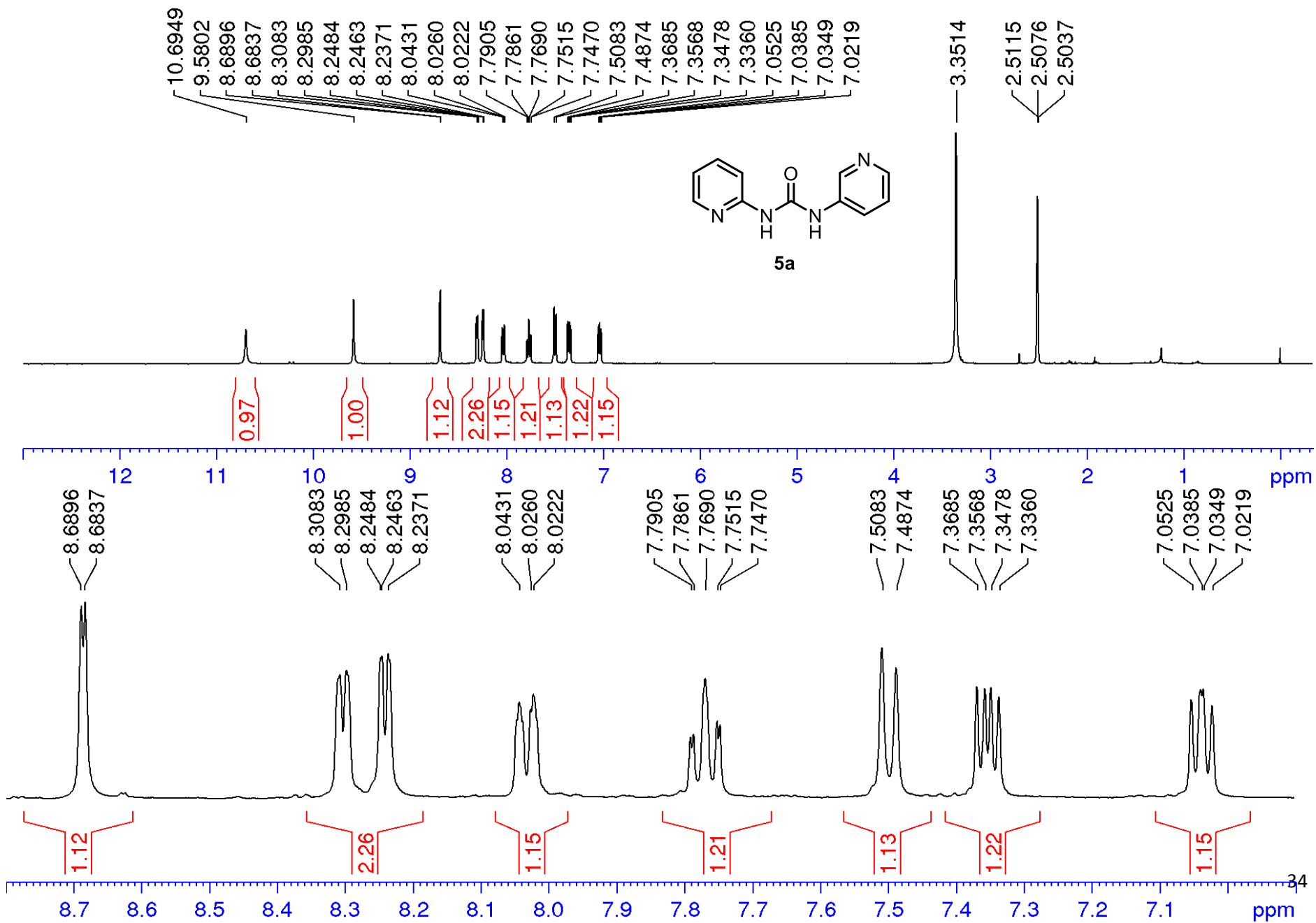
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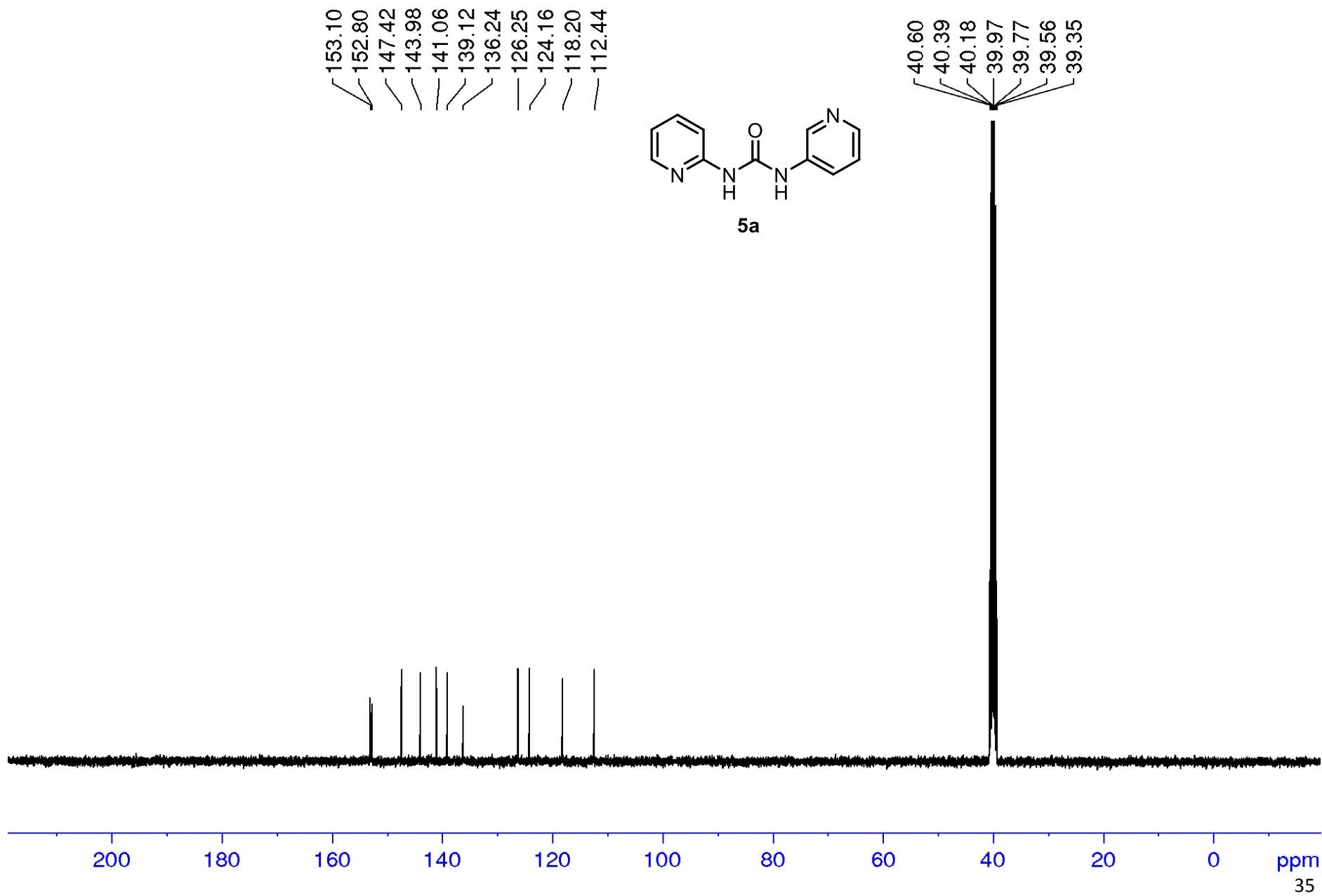


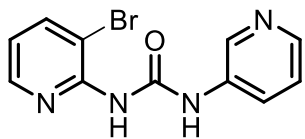
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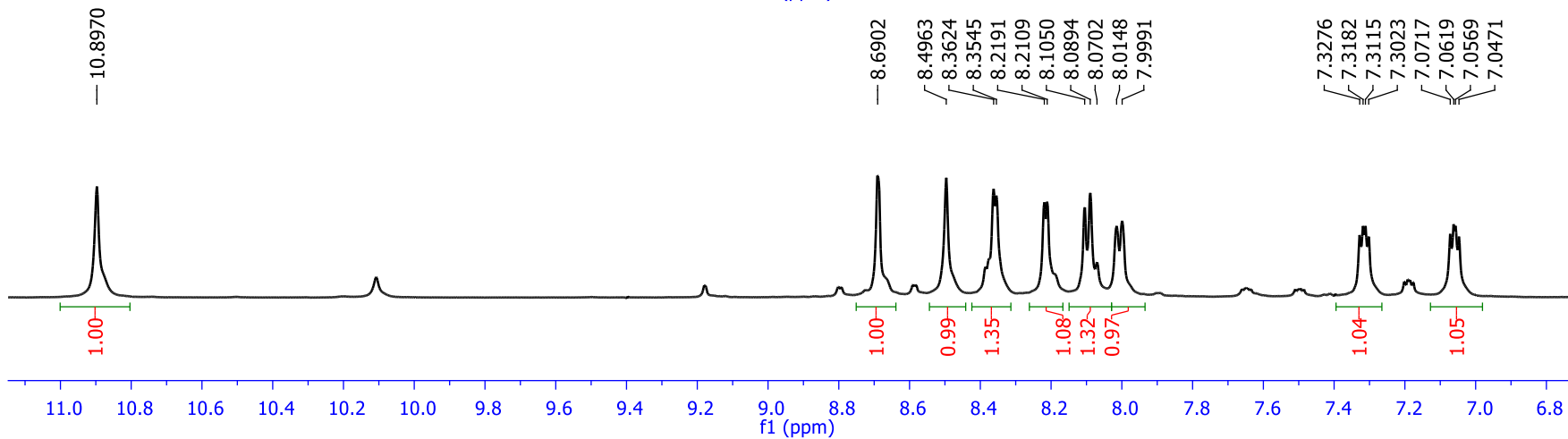
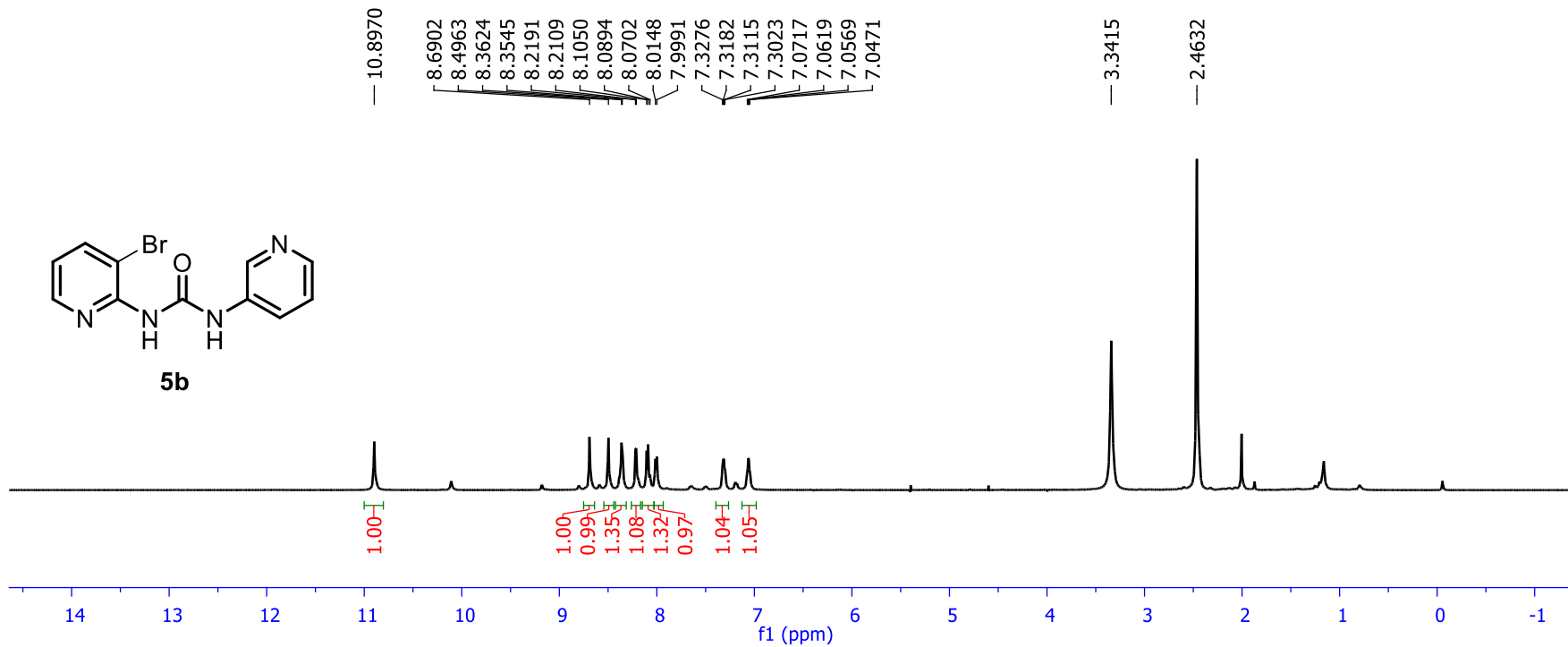
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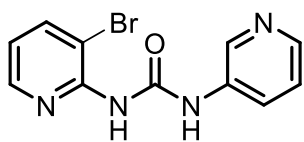






**5b**

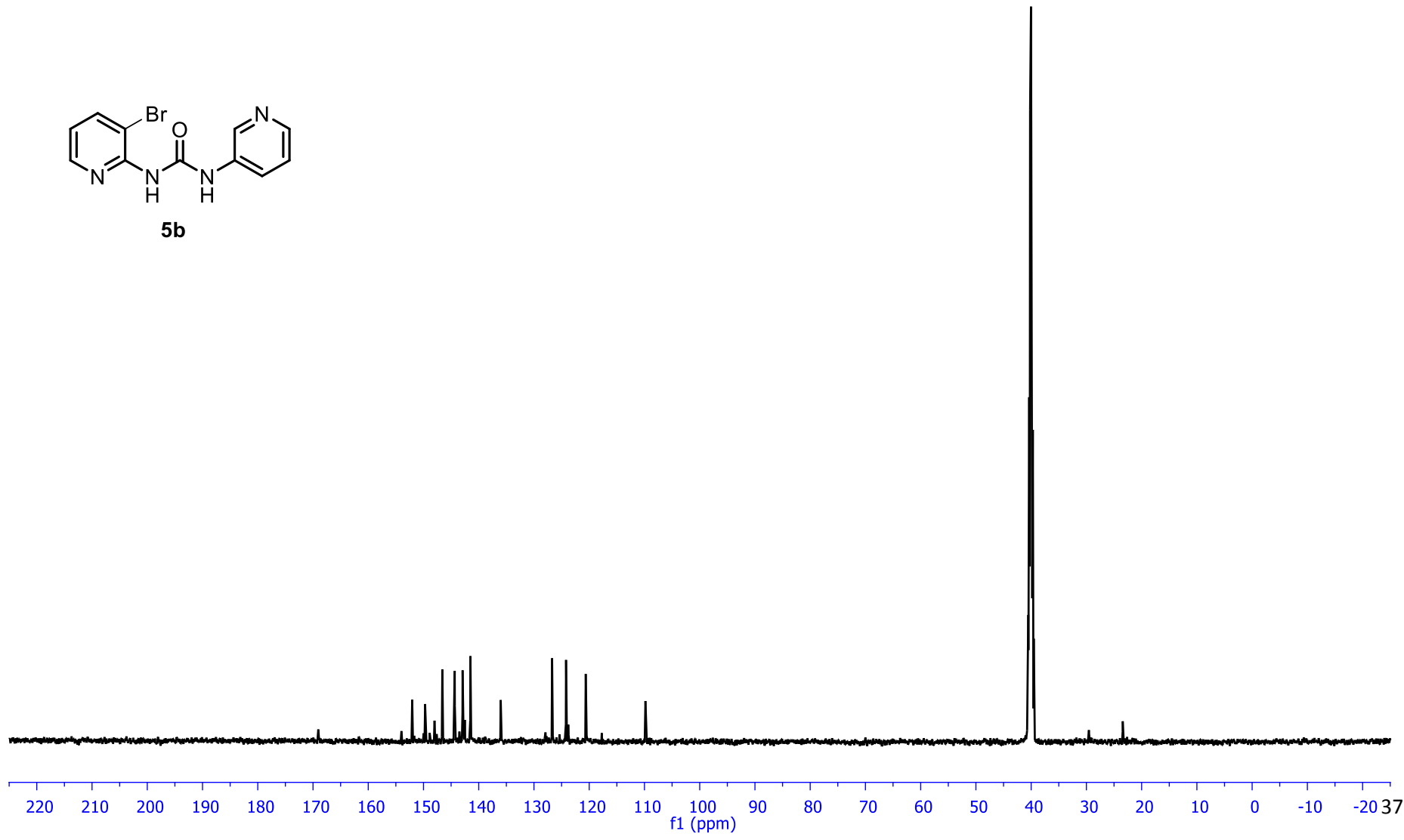


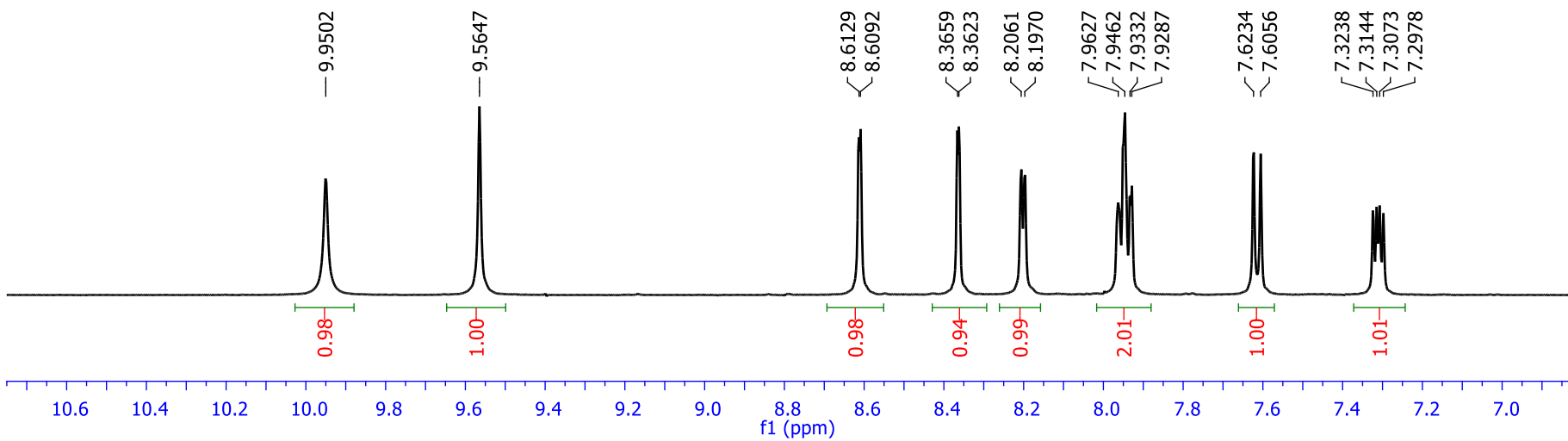
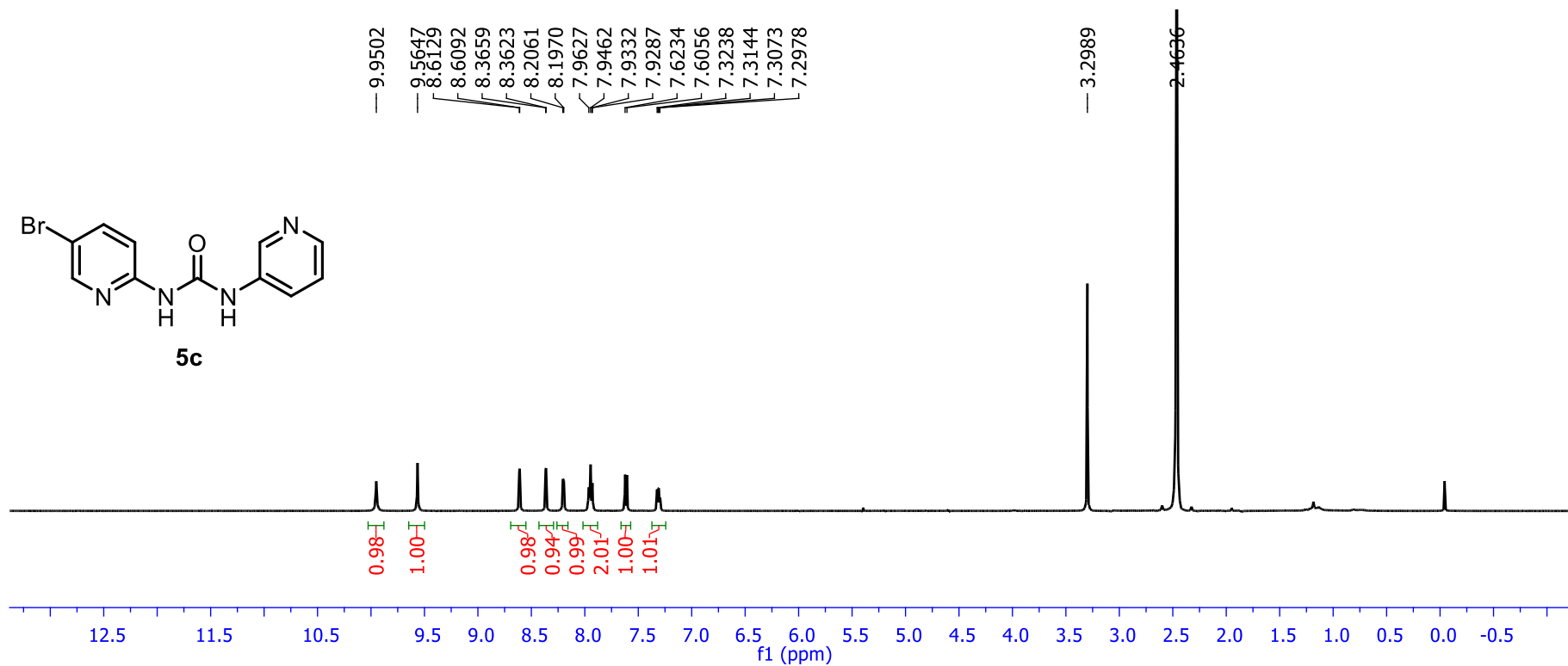
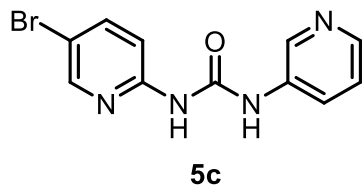


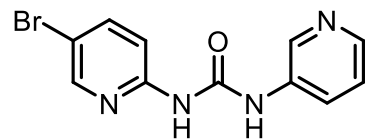
5b

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109.8184

40.6174  
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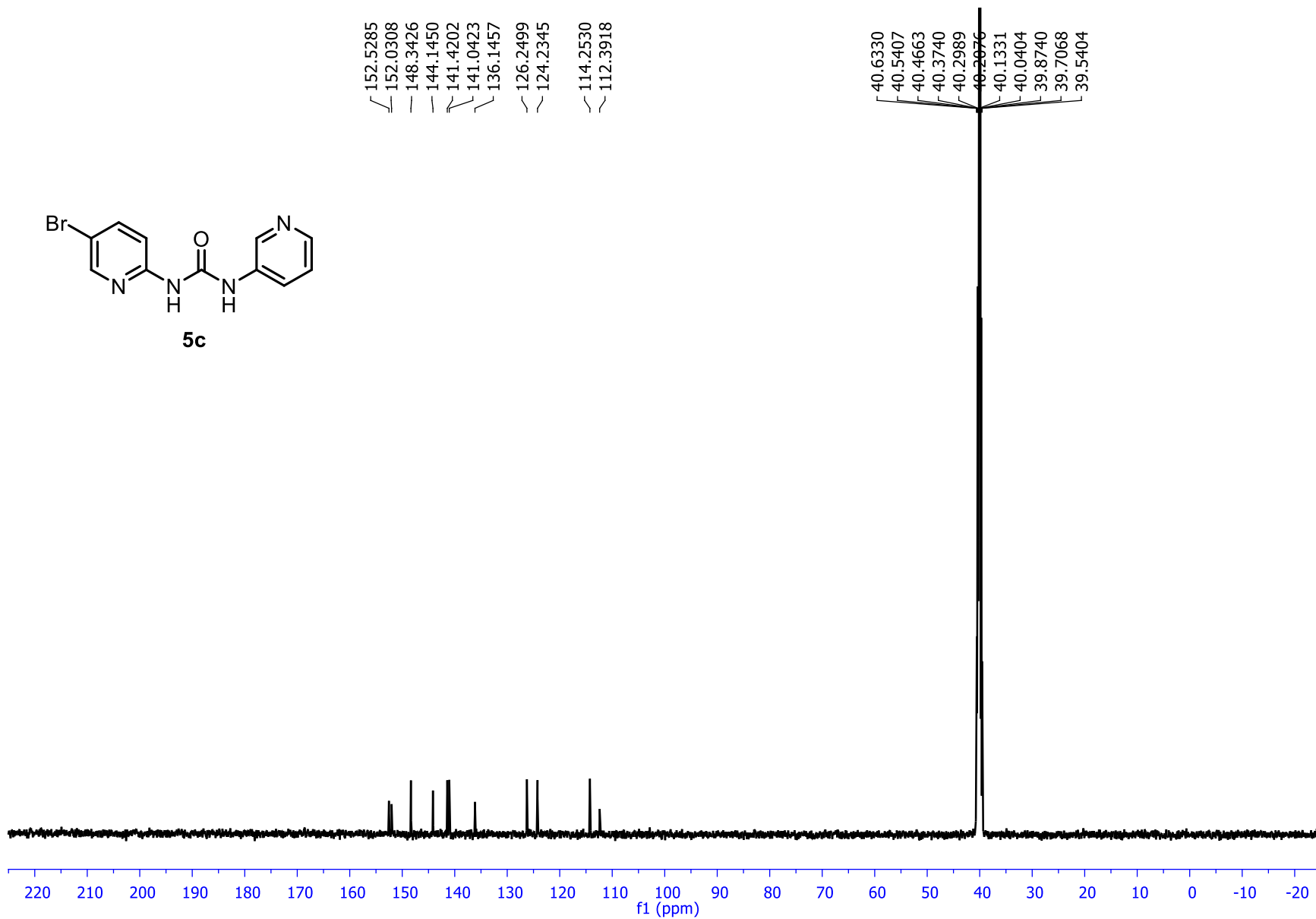


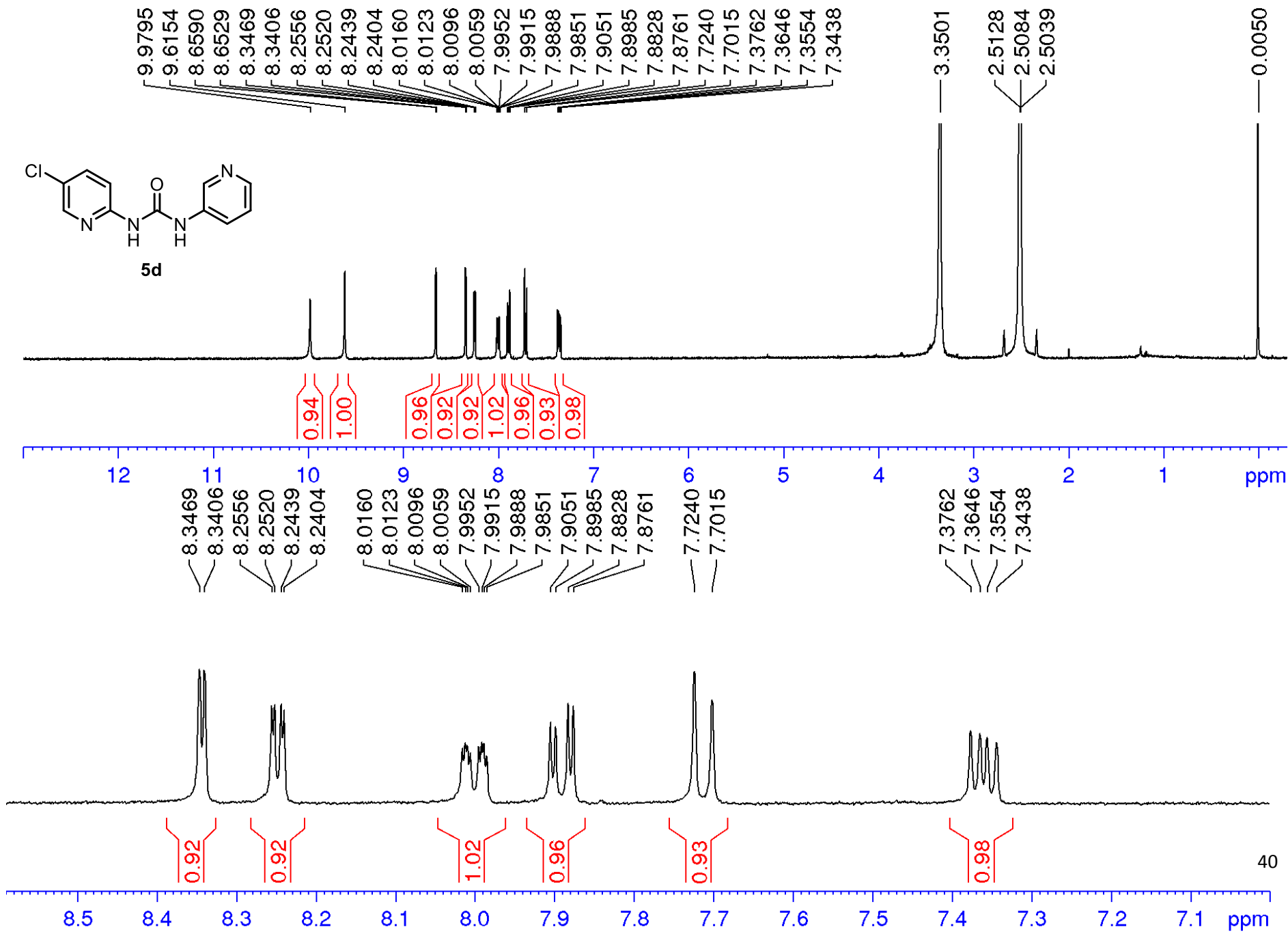


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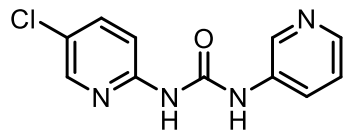
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114.2530  
112.3918

40.6330  
40.5407  
40.4663  
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39.5404





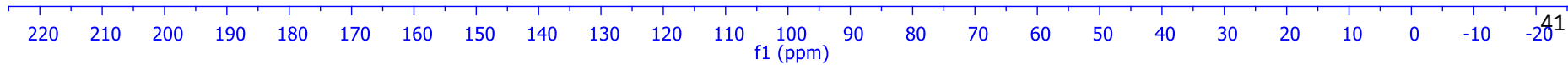


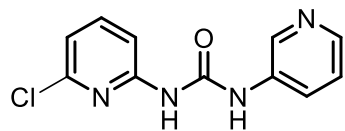


5d

152.5437  
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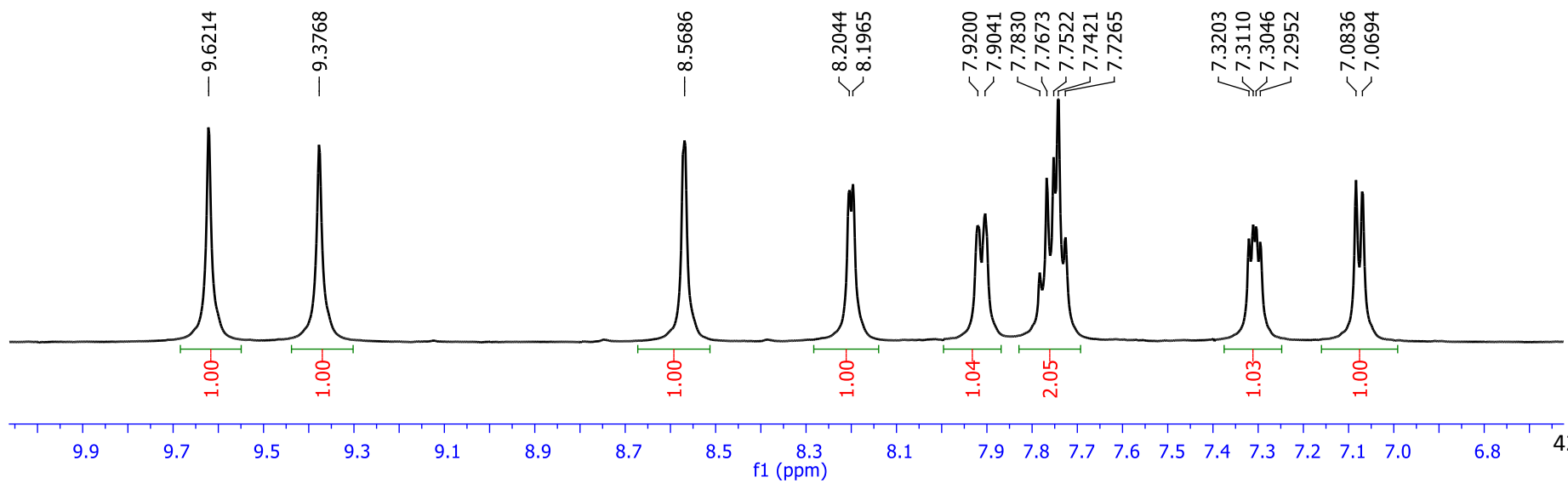
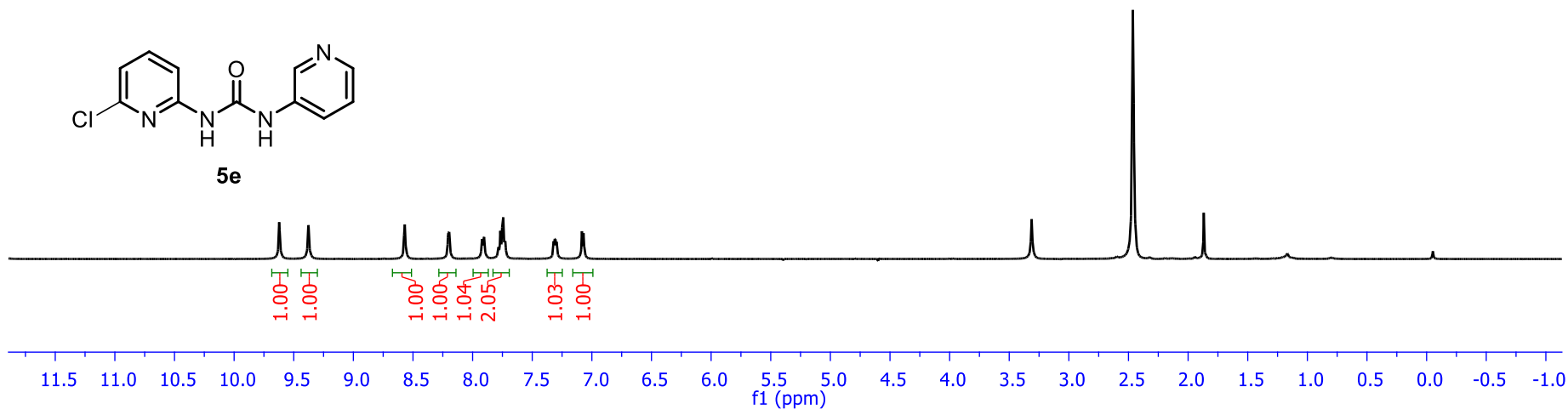
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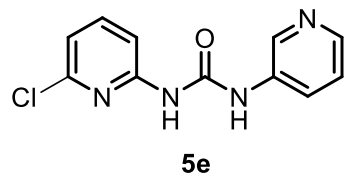




5e

9.6214  
9.3768  
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8.2044  
8.1965  
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7.7421  
7.7203  
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7.0694  
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2.4629



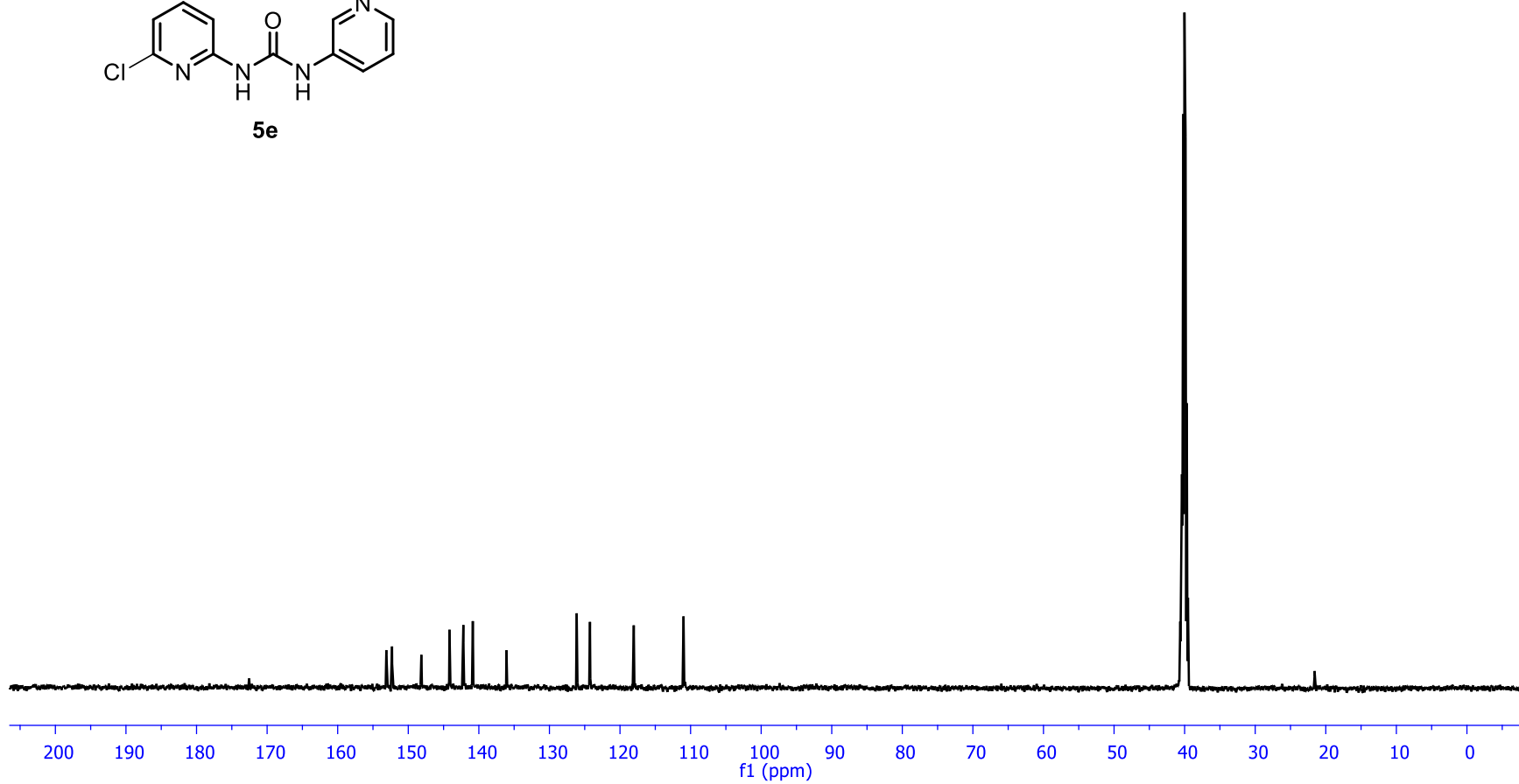


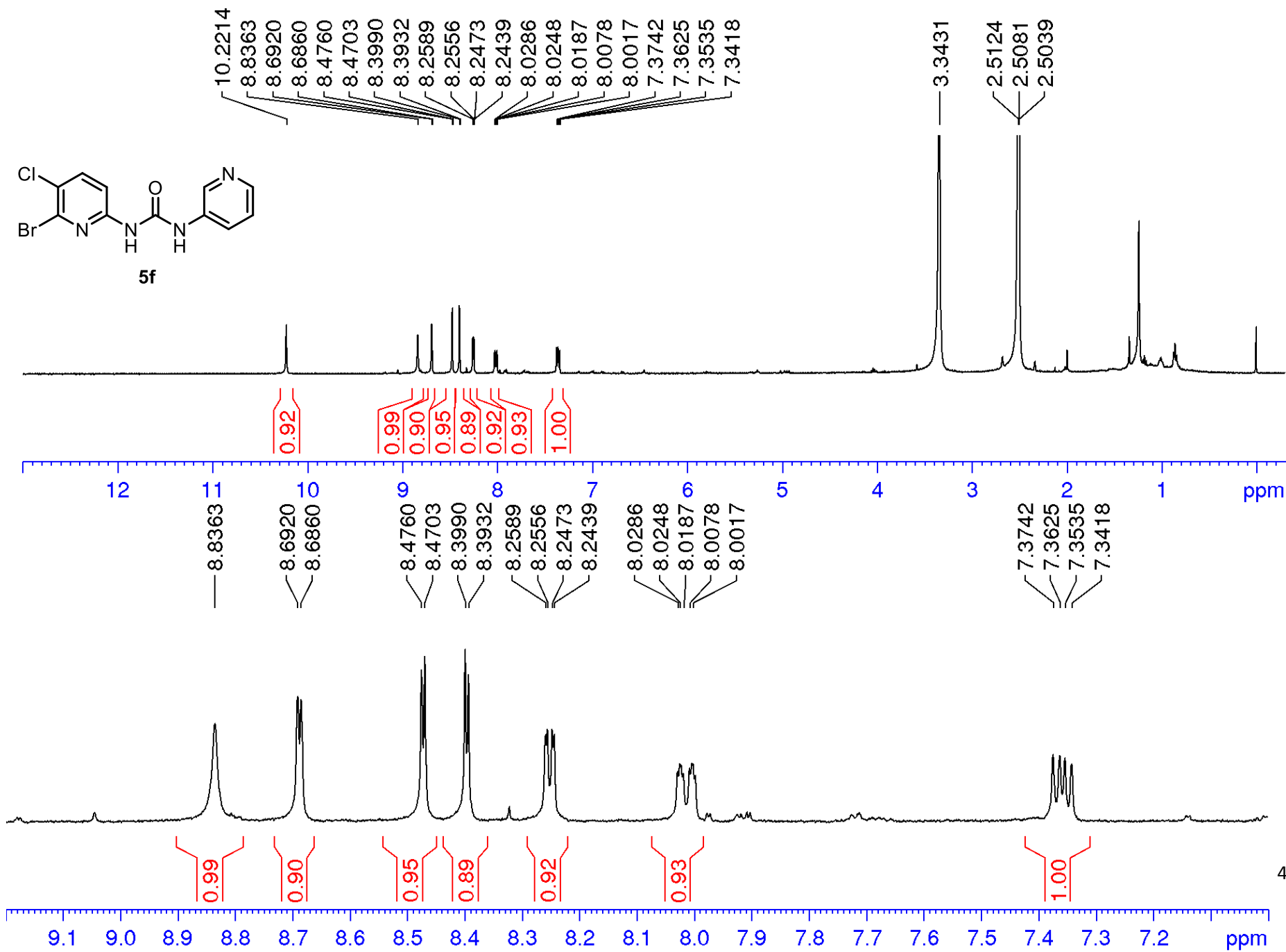
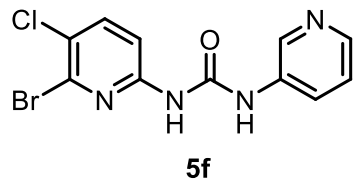
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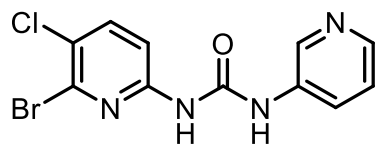
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111.0039

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39.6941  
39.5273



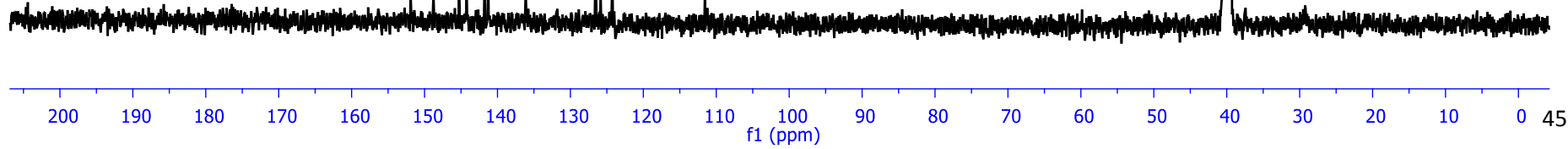


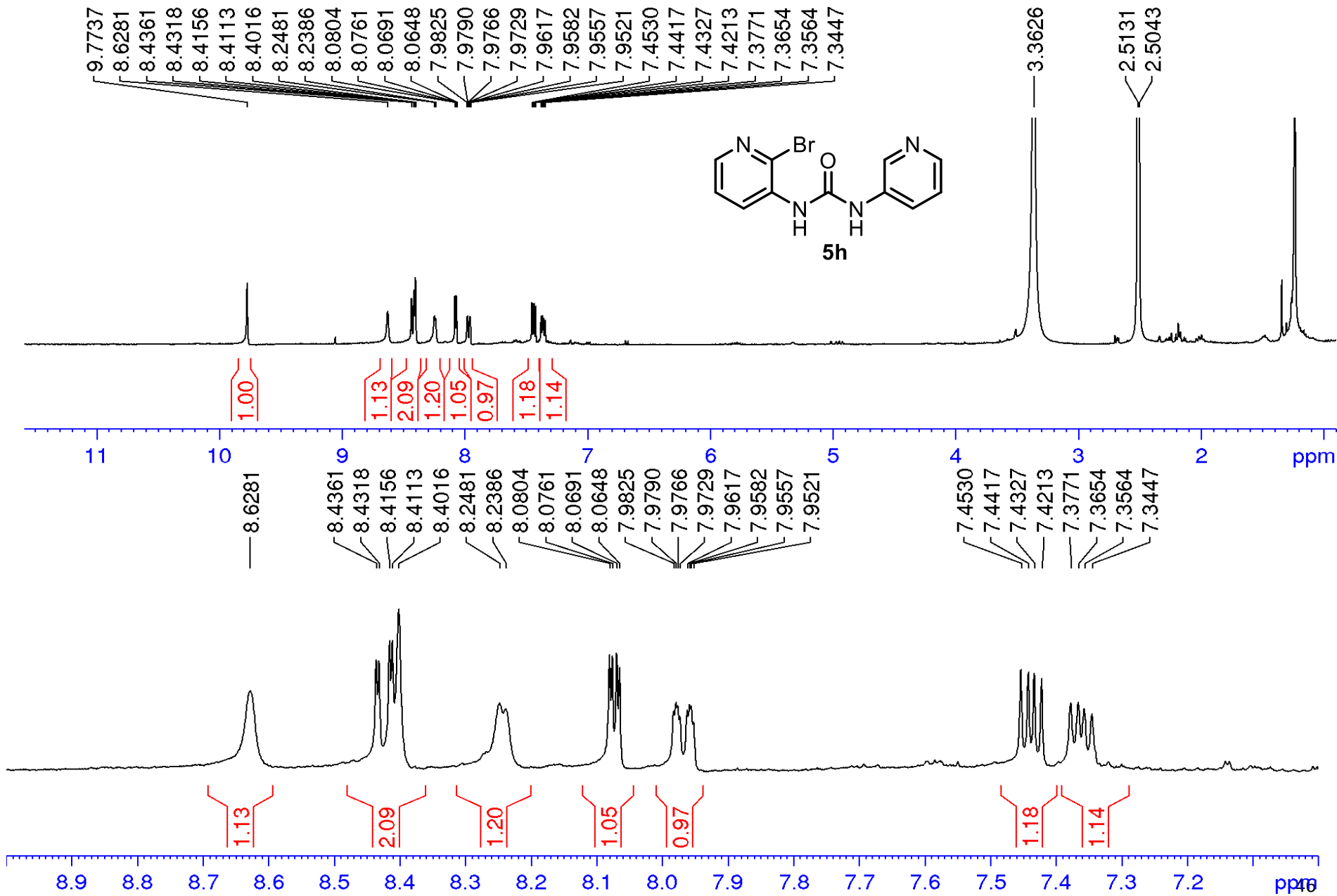


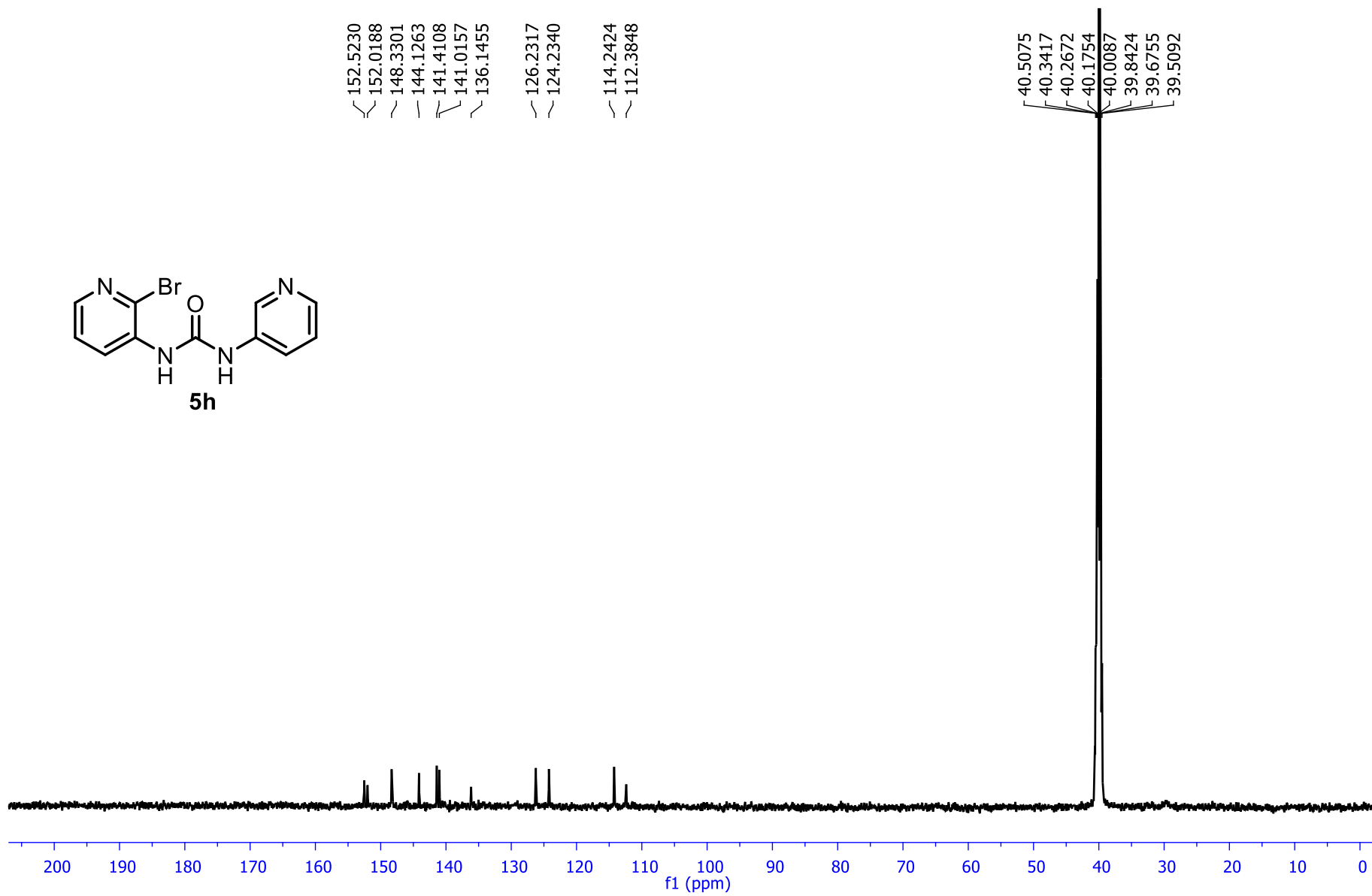
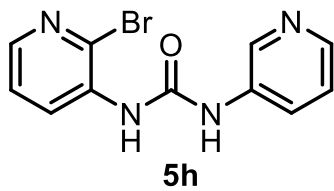
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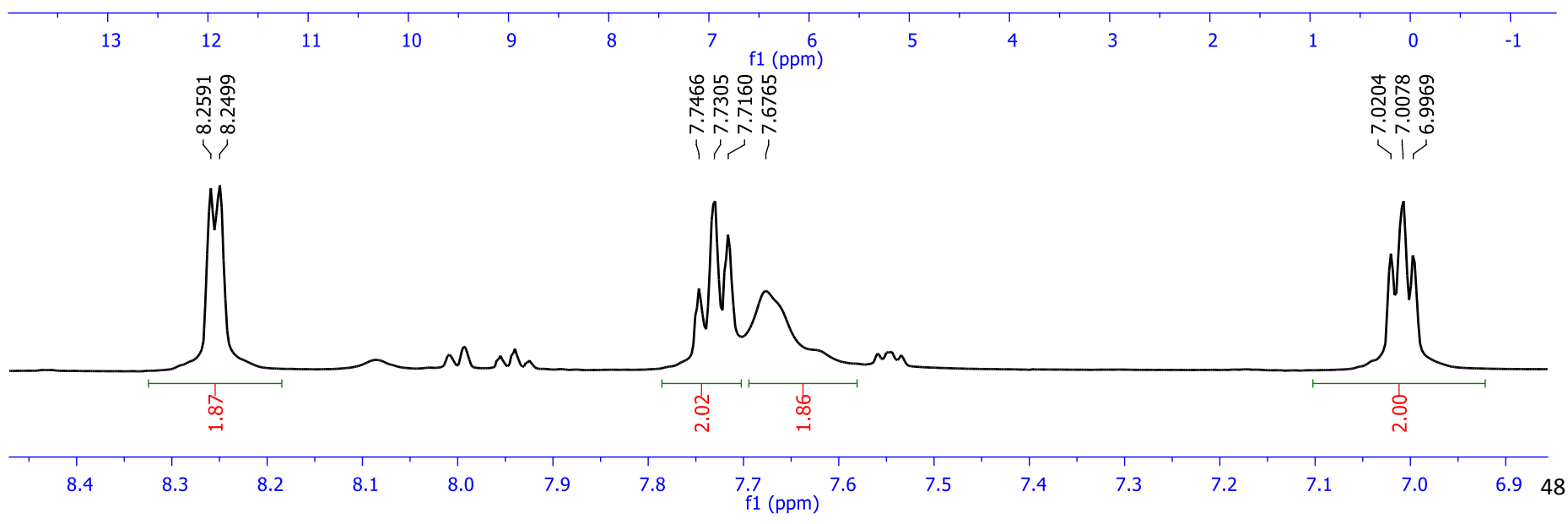
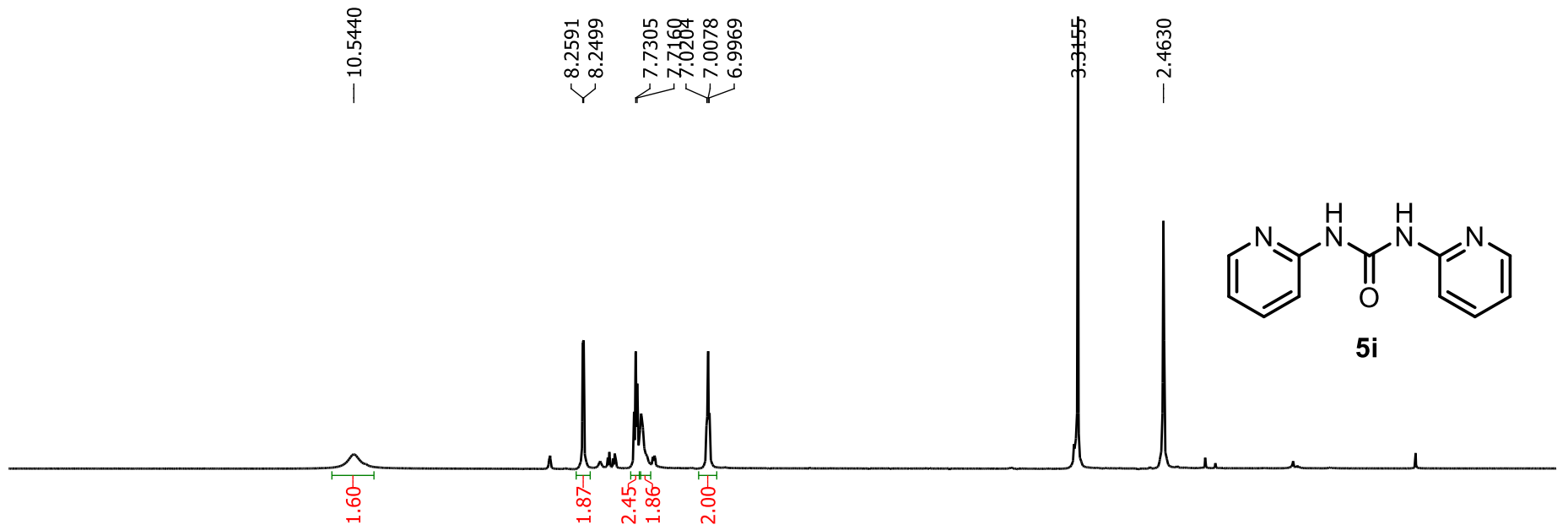
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- 145.2730
- 144.2587
- 141.7452
- 141.2600
- 136.1373
- 126.5611
- 124.2420
- 111.5383

- 40.5064
- 40.4170
- 40.3394
- 40.2497
- 40.1718
- 40.0059
- 39.9159
- 39.7495
- 39.5820
- 39.4157

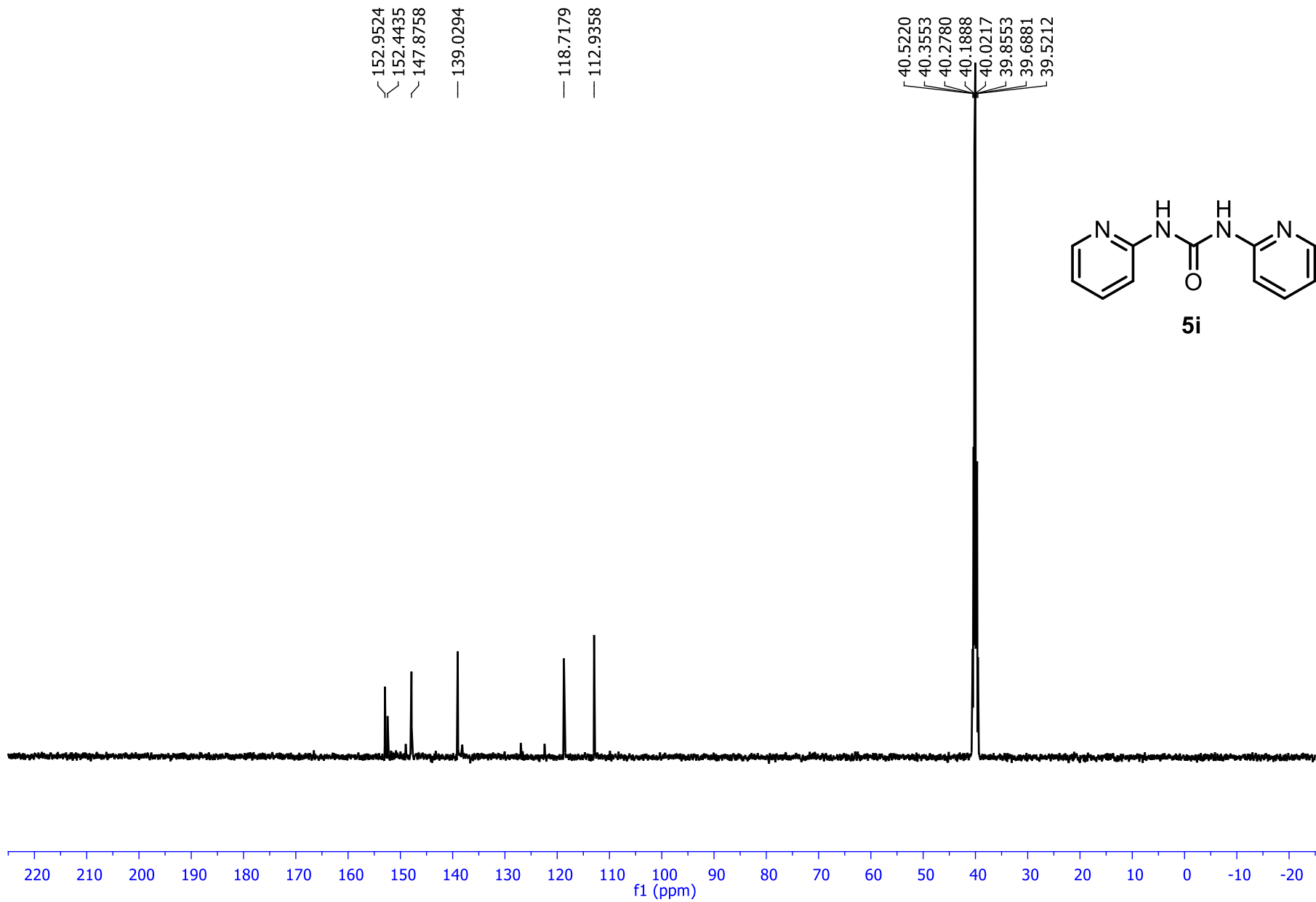


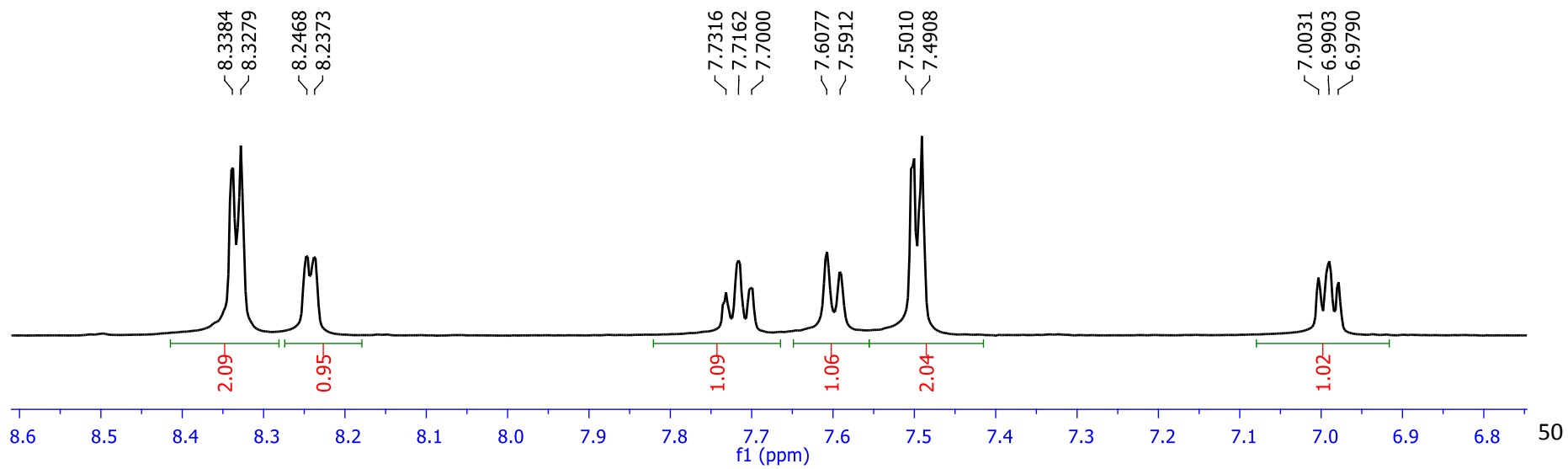
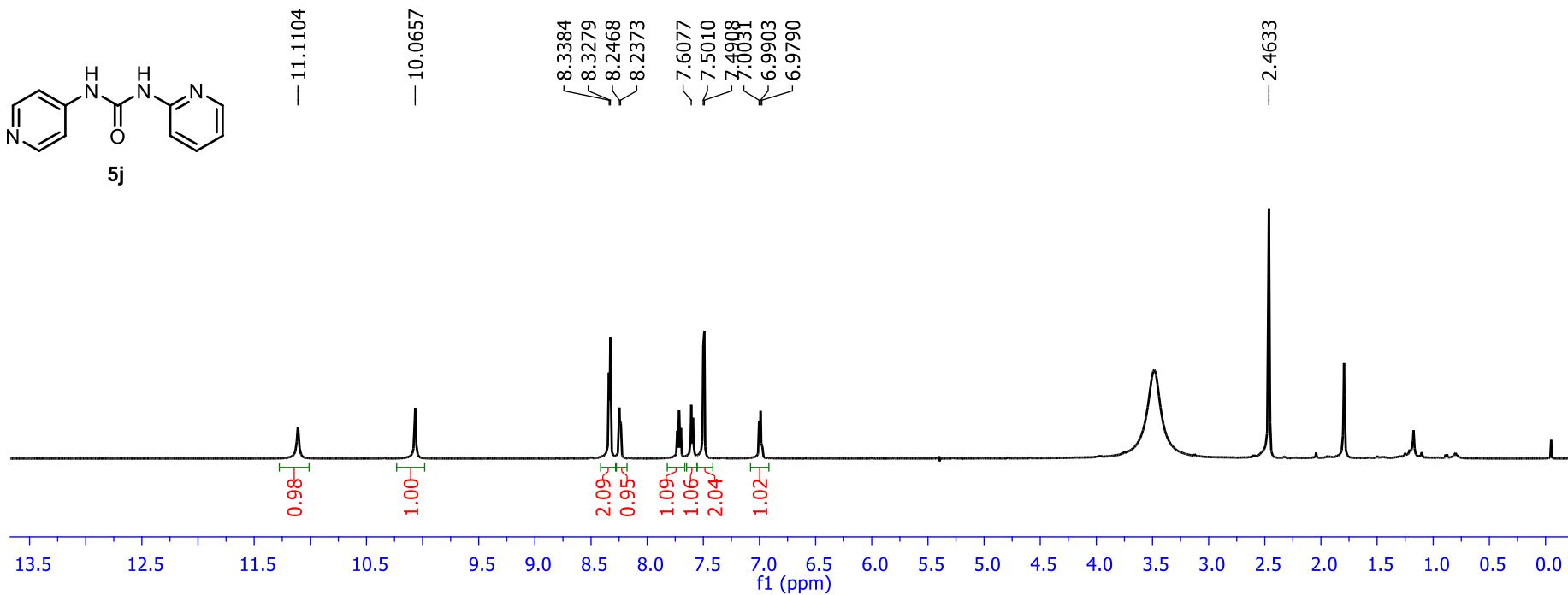
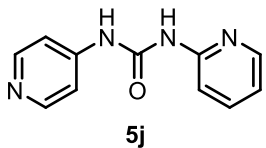


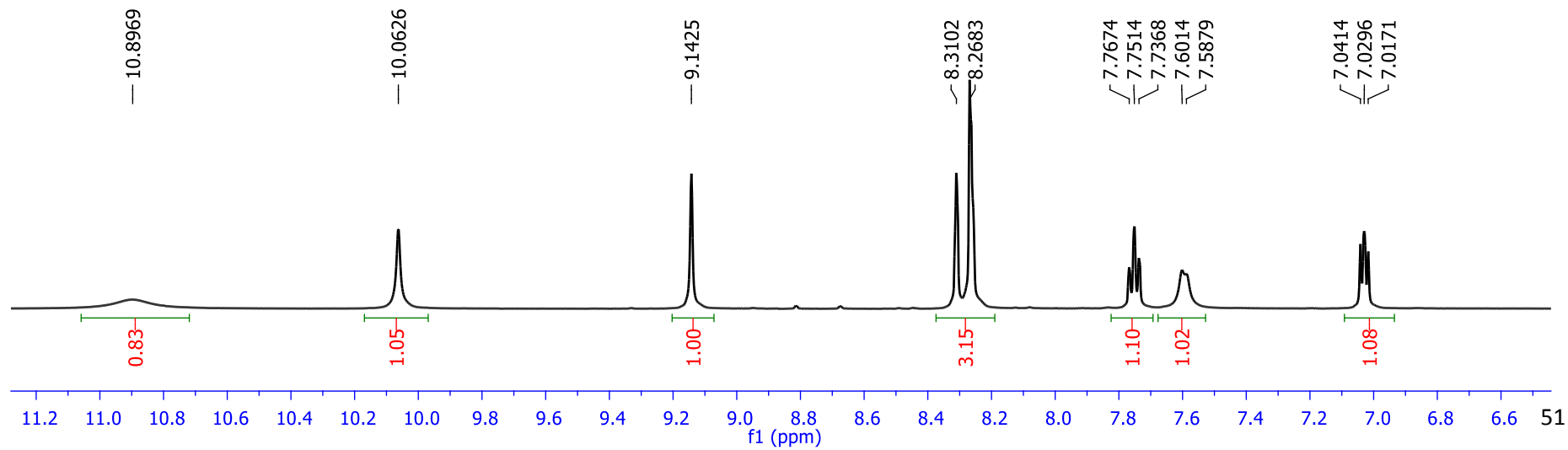
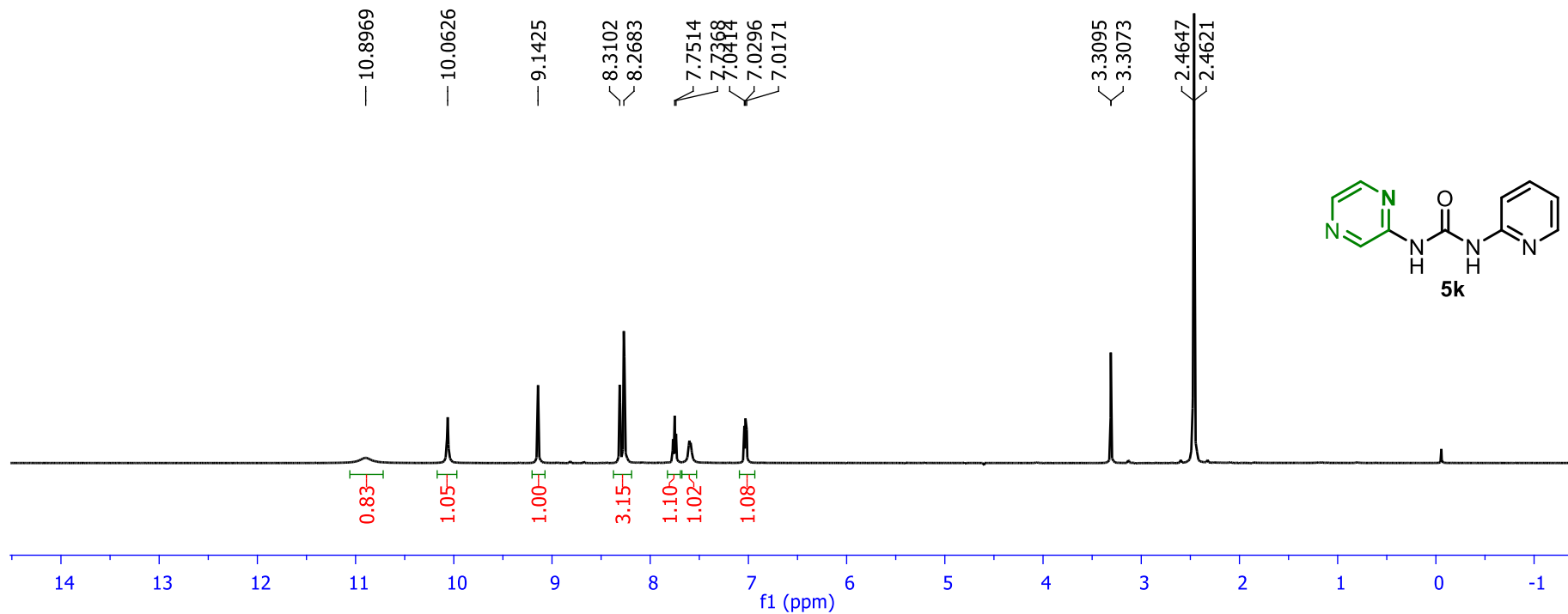


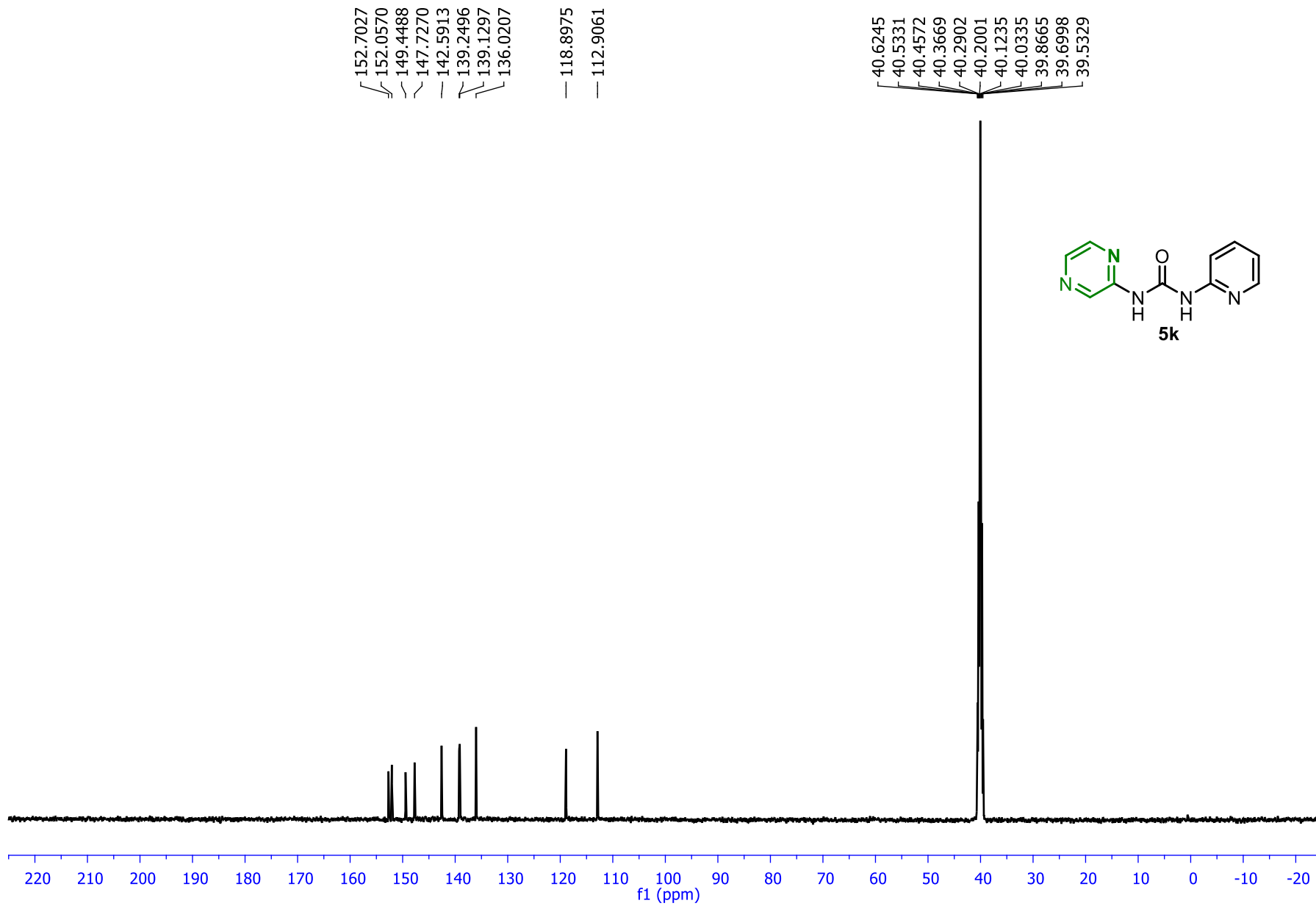


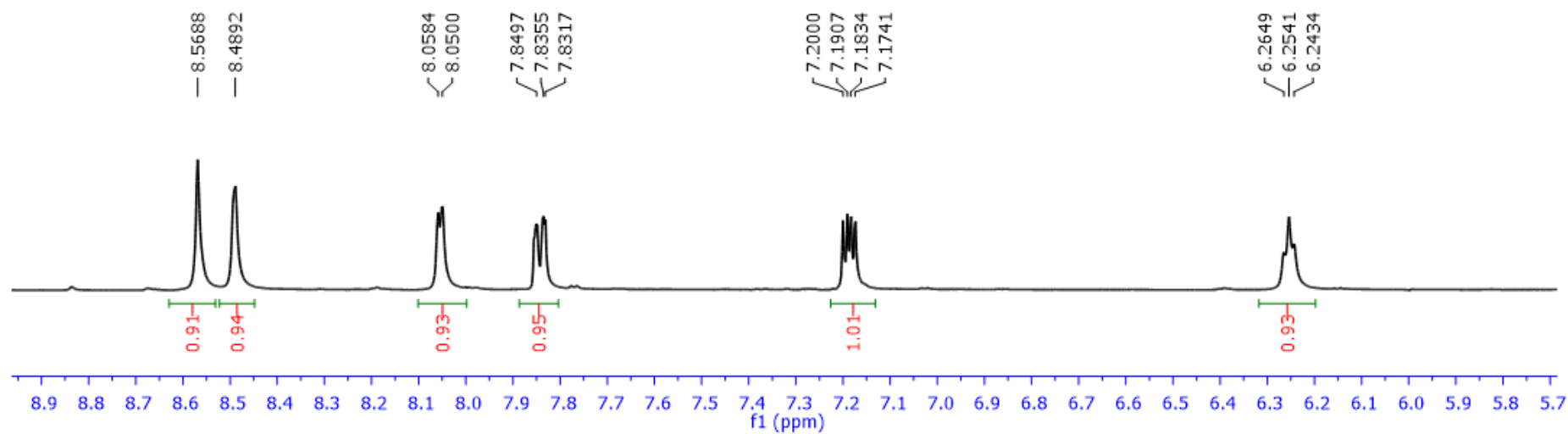
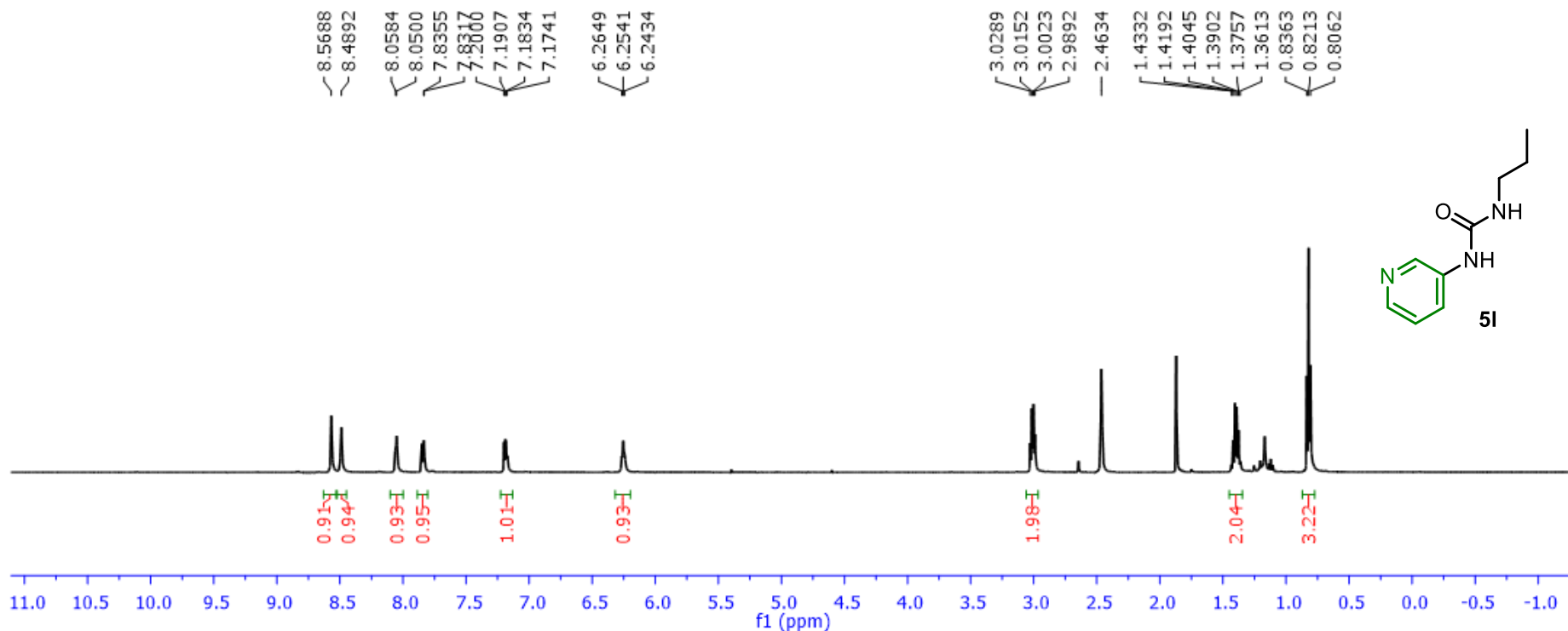
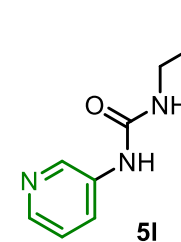


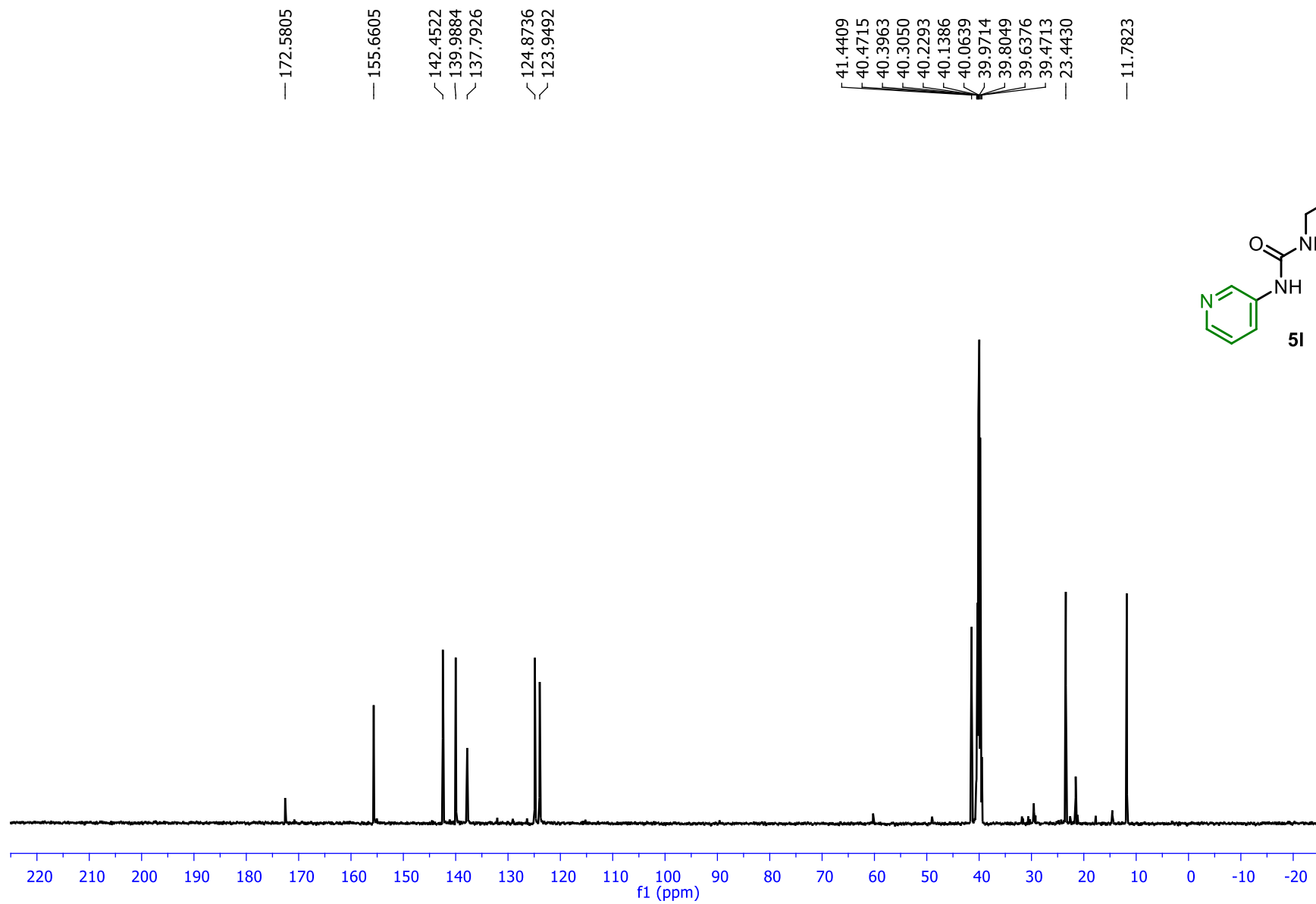


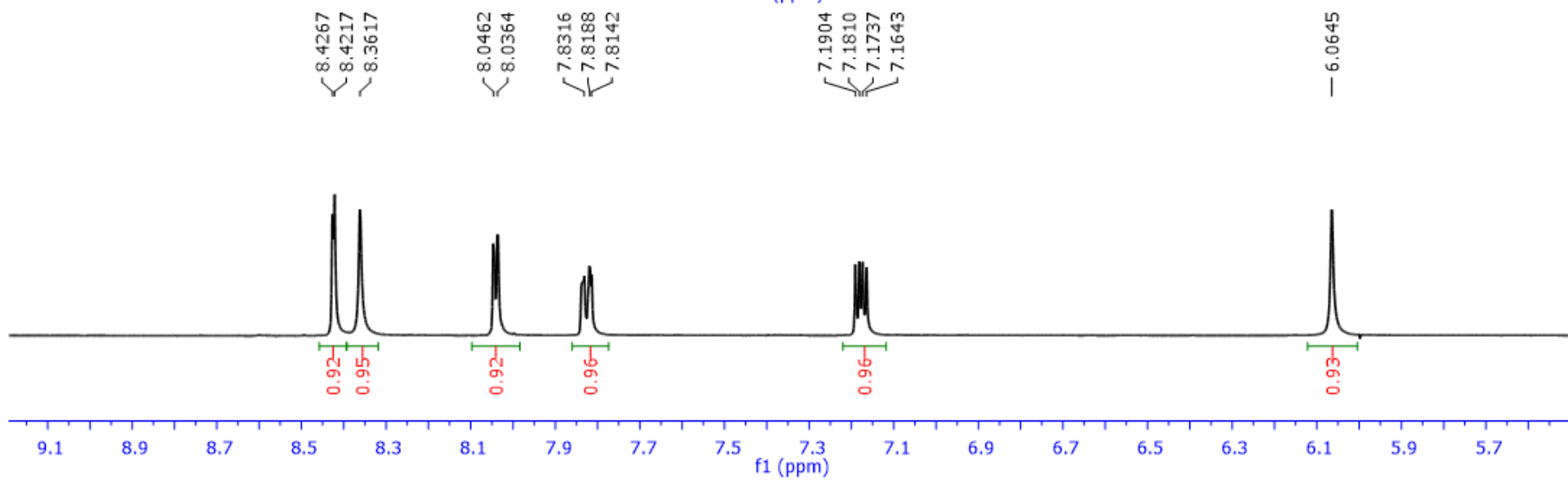
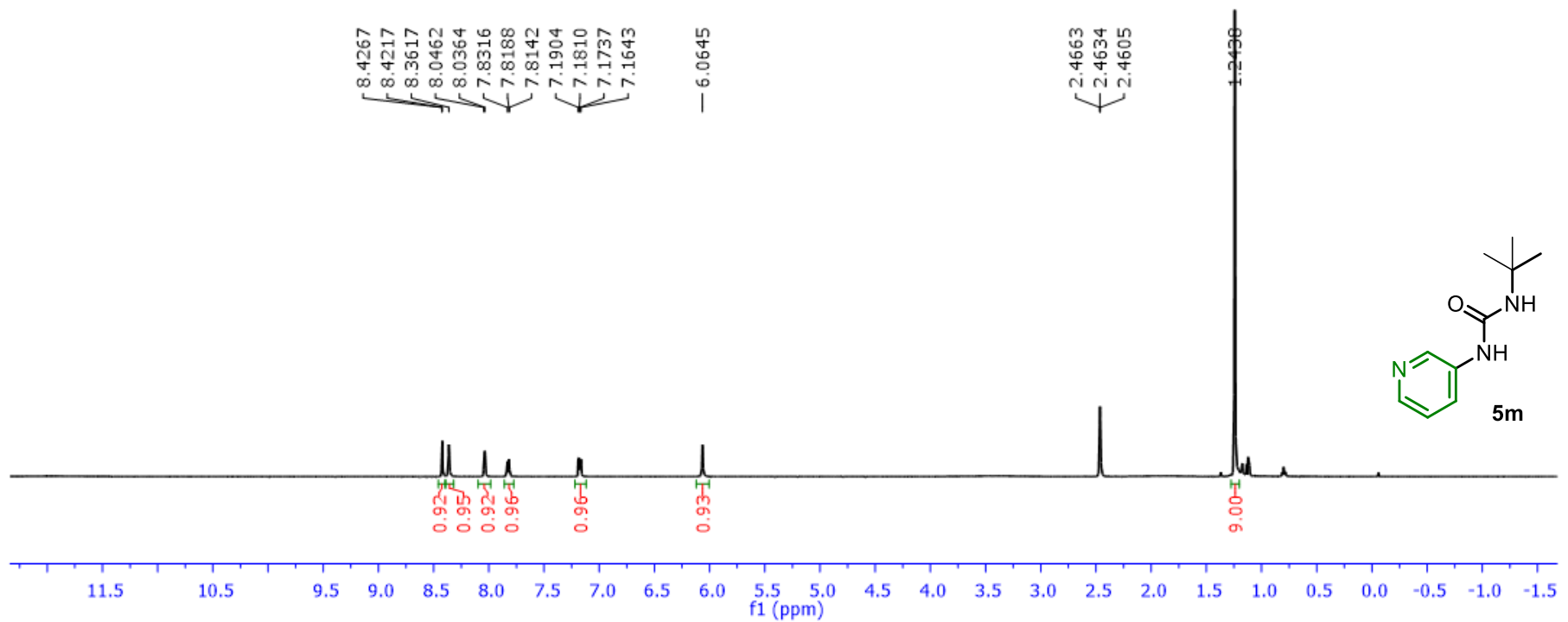


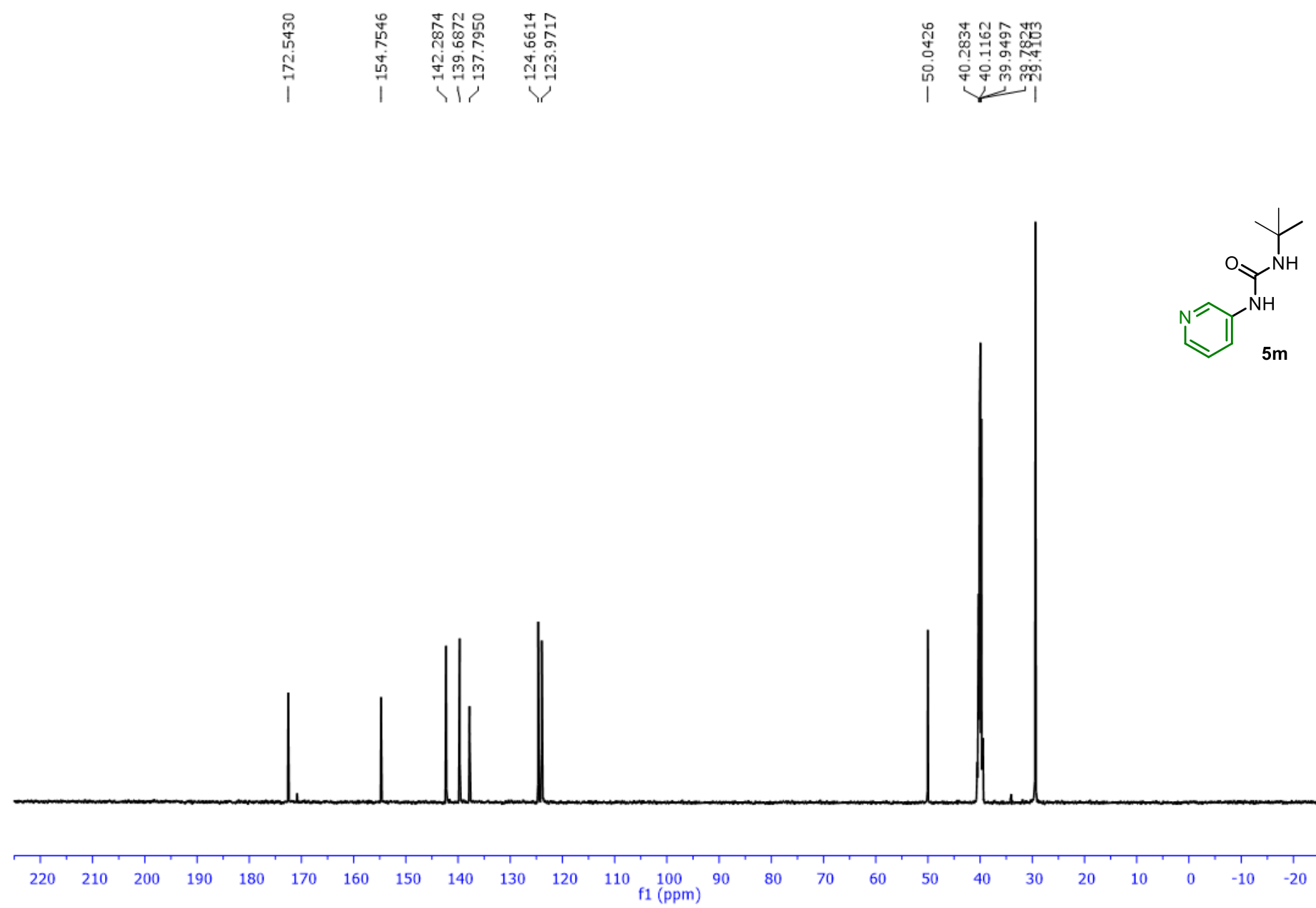
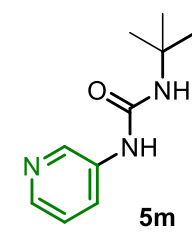




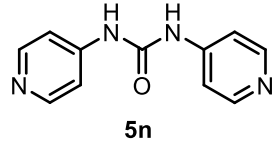












— 11.4723

{ 8.3011  
8.2911

{ 7.4858  
7.4739

3.3149

{ 2.4634  
2.4605

1.71

4.00

4.05

13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

f1 (ppm)

{ 8.3011  
8.2911

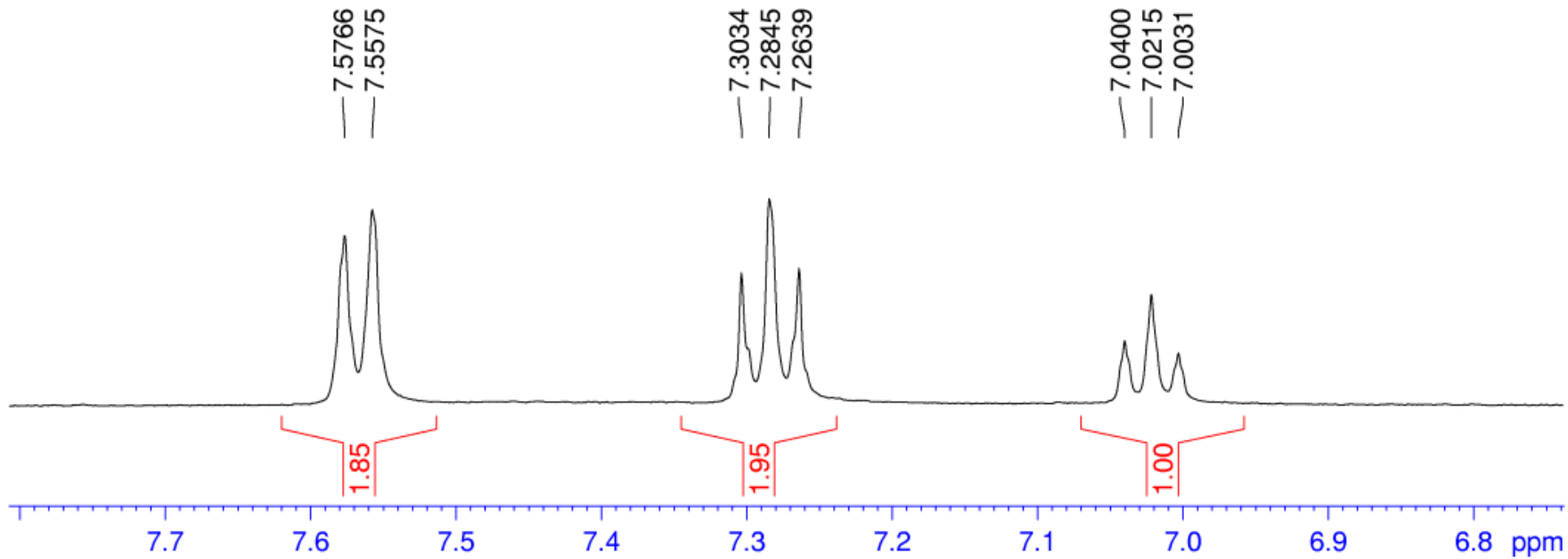
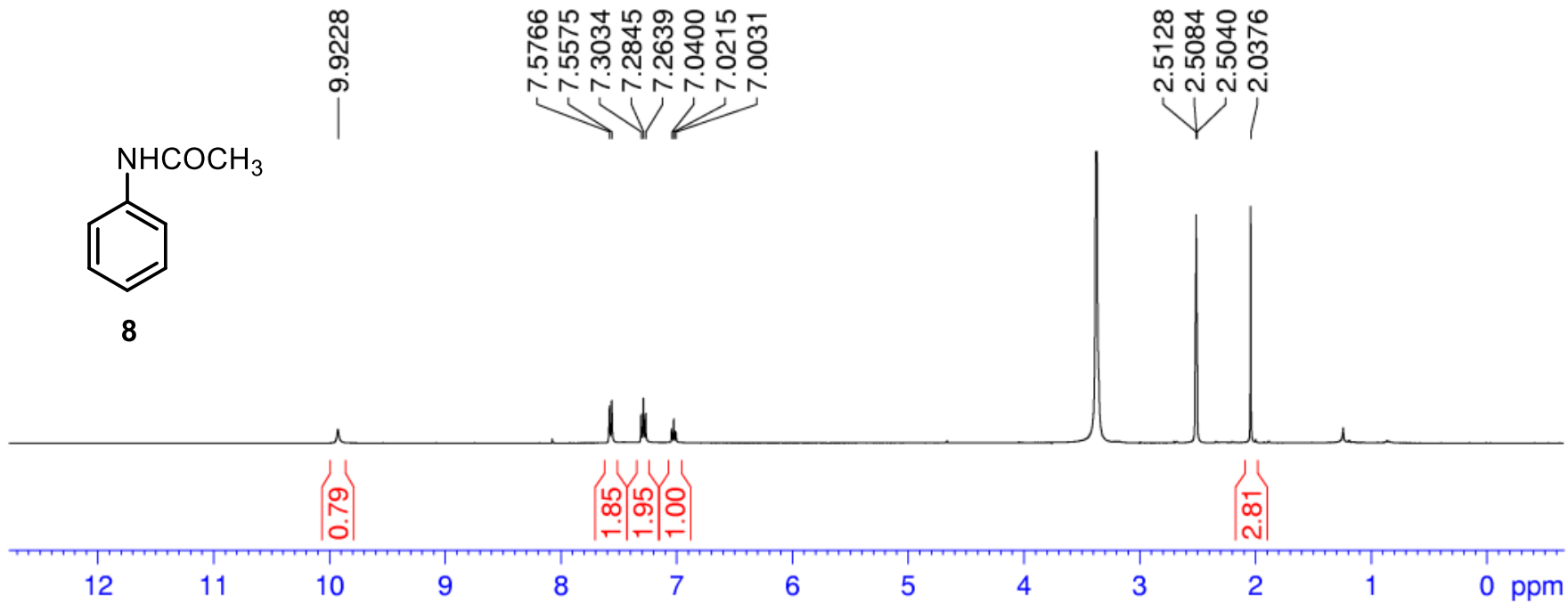
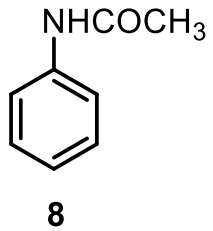
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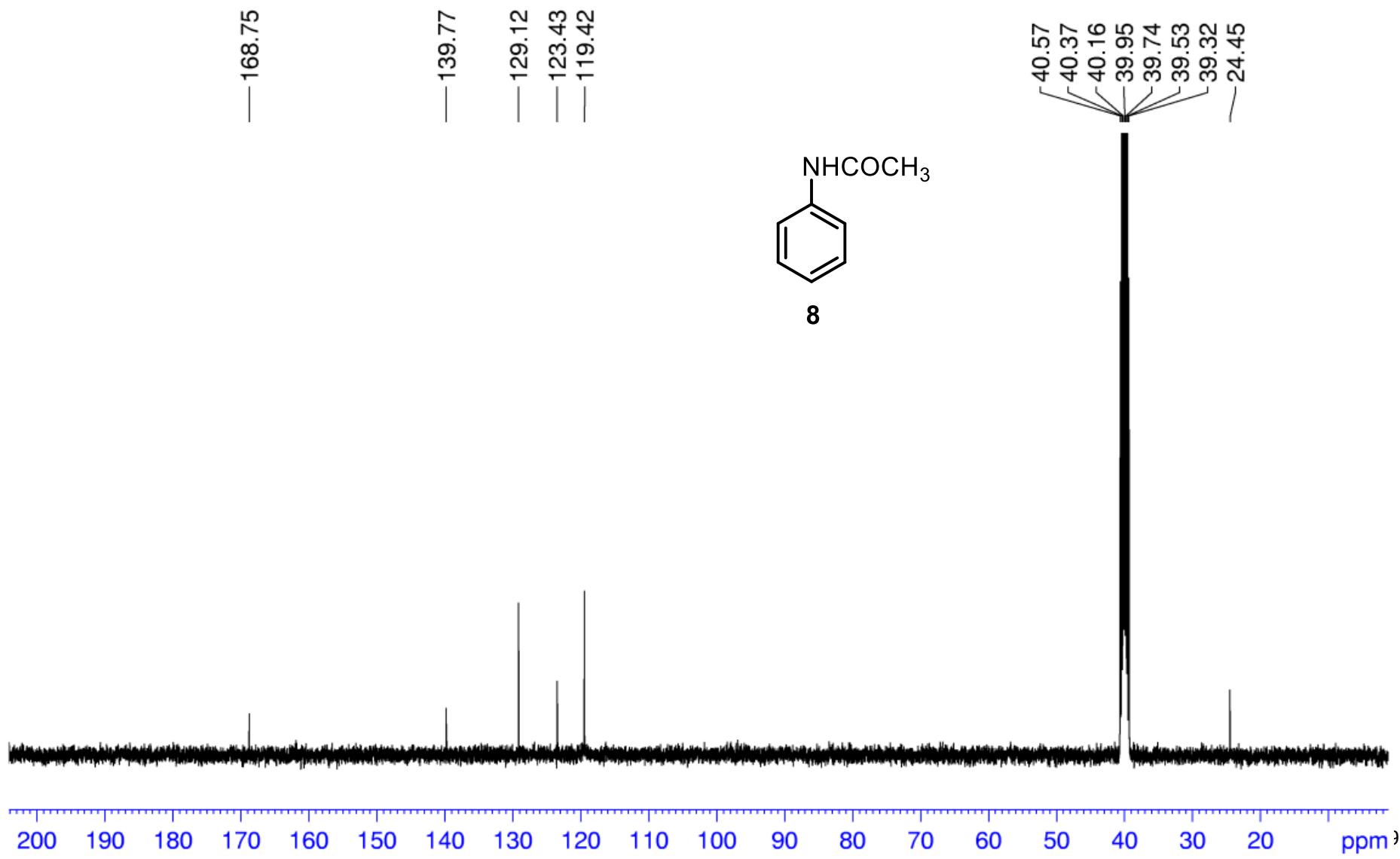
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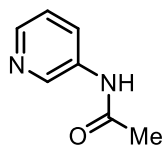
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8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 57

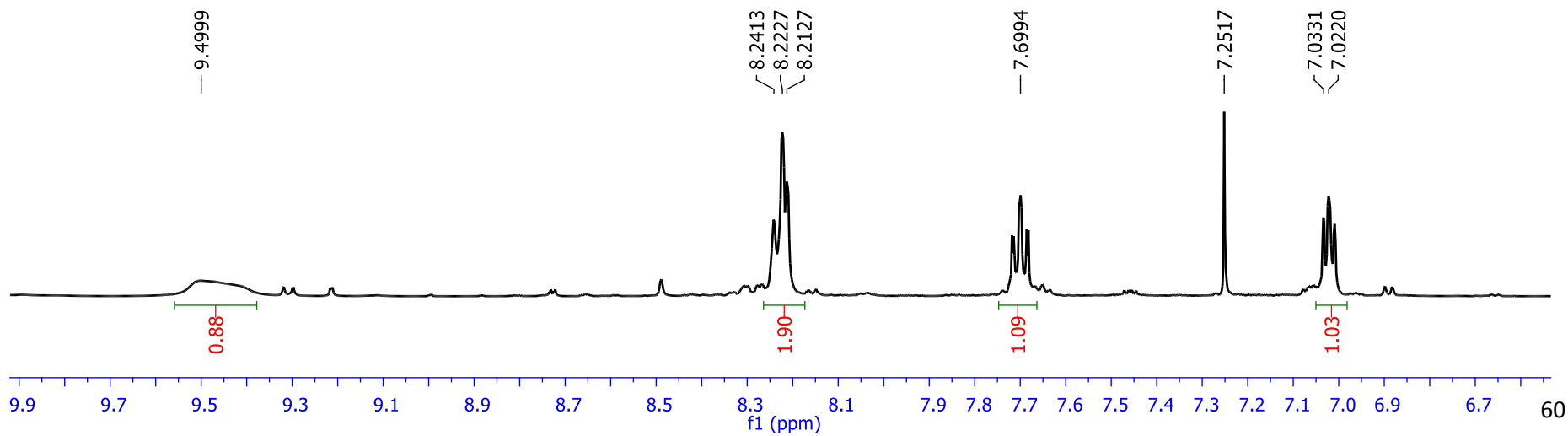
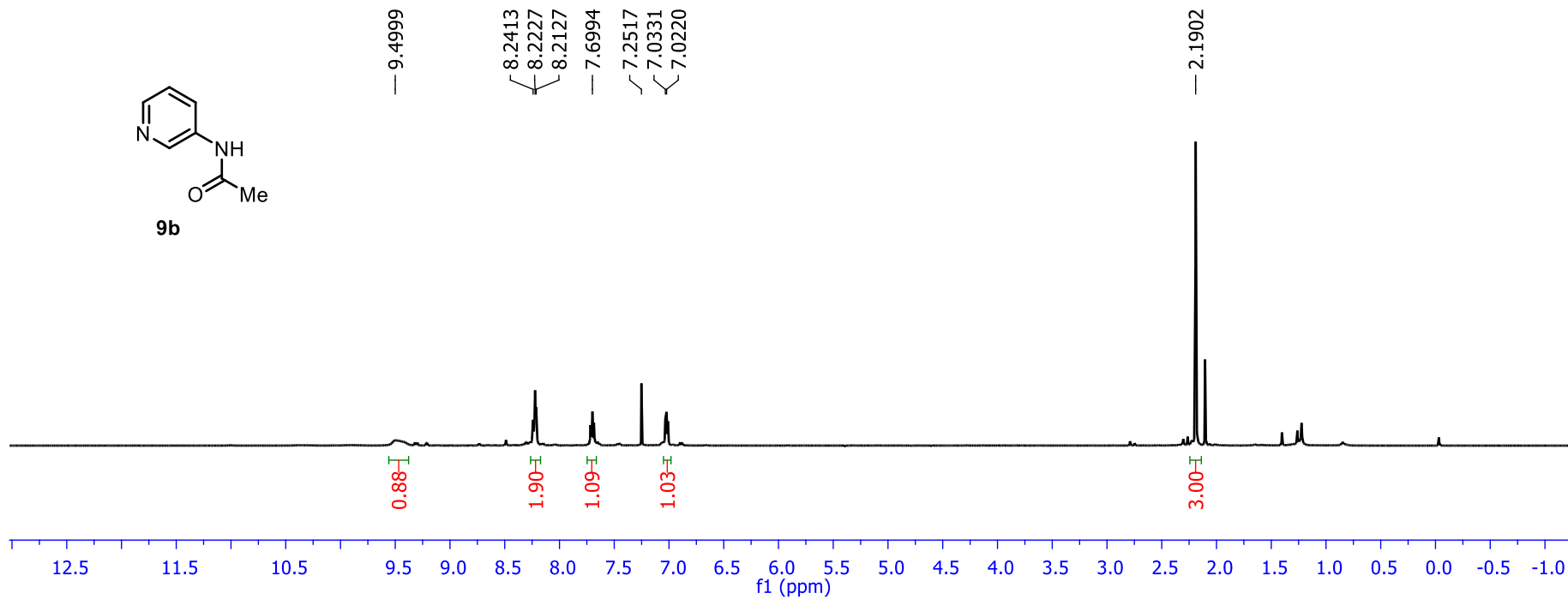
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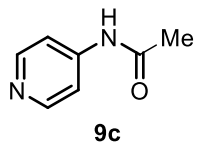






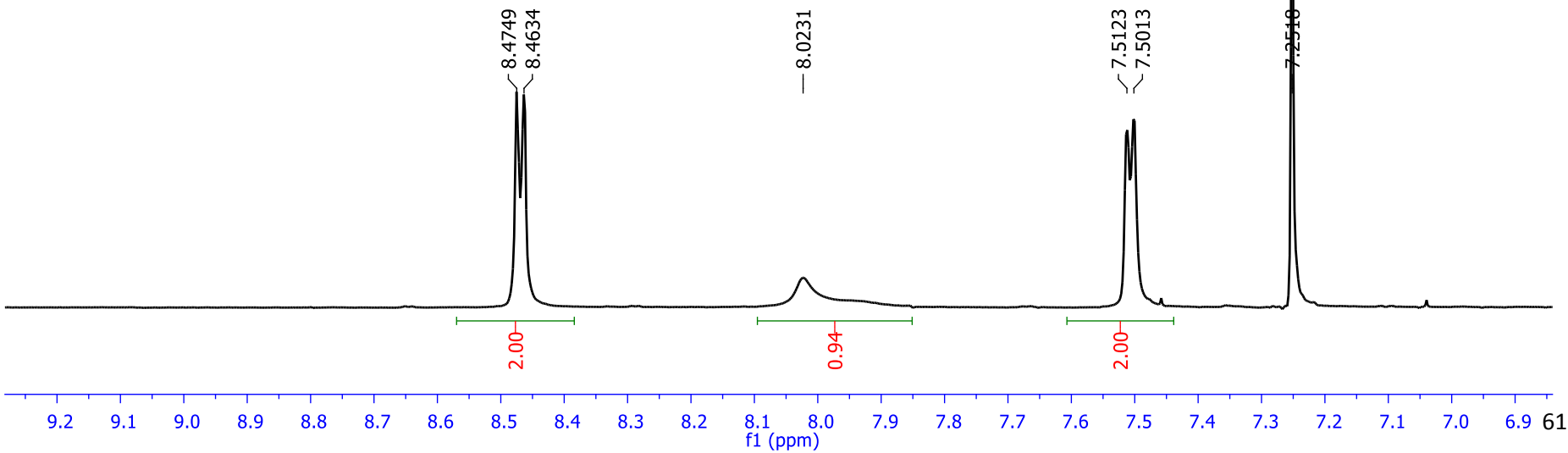
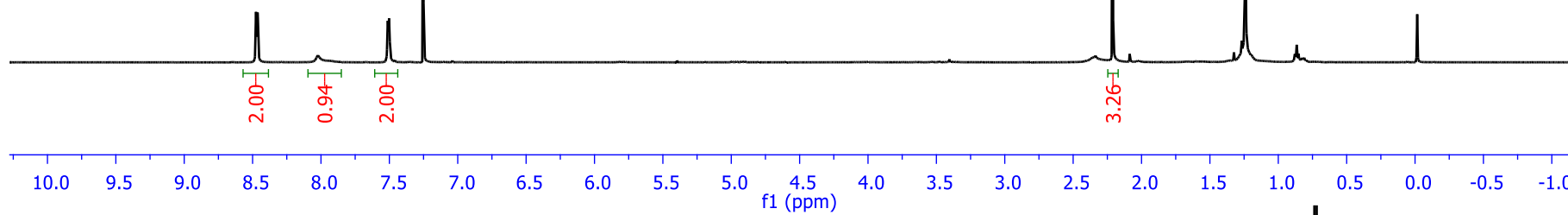
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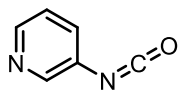




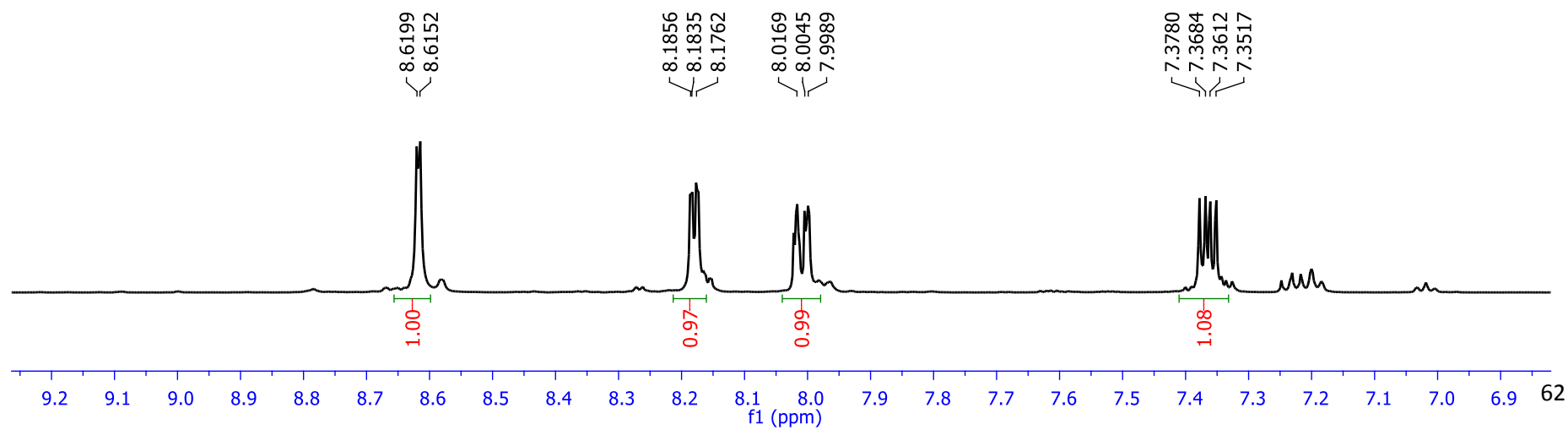
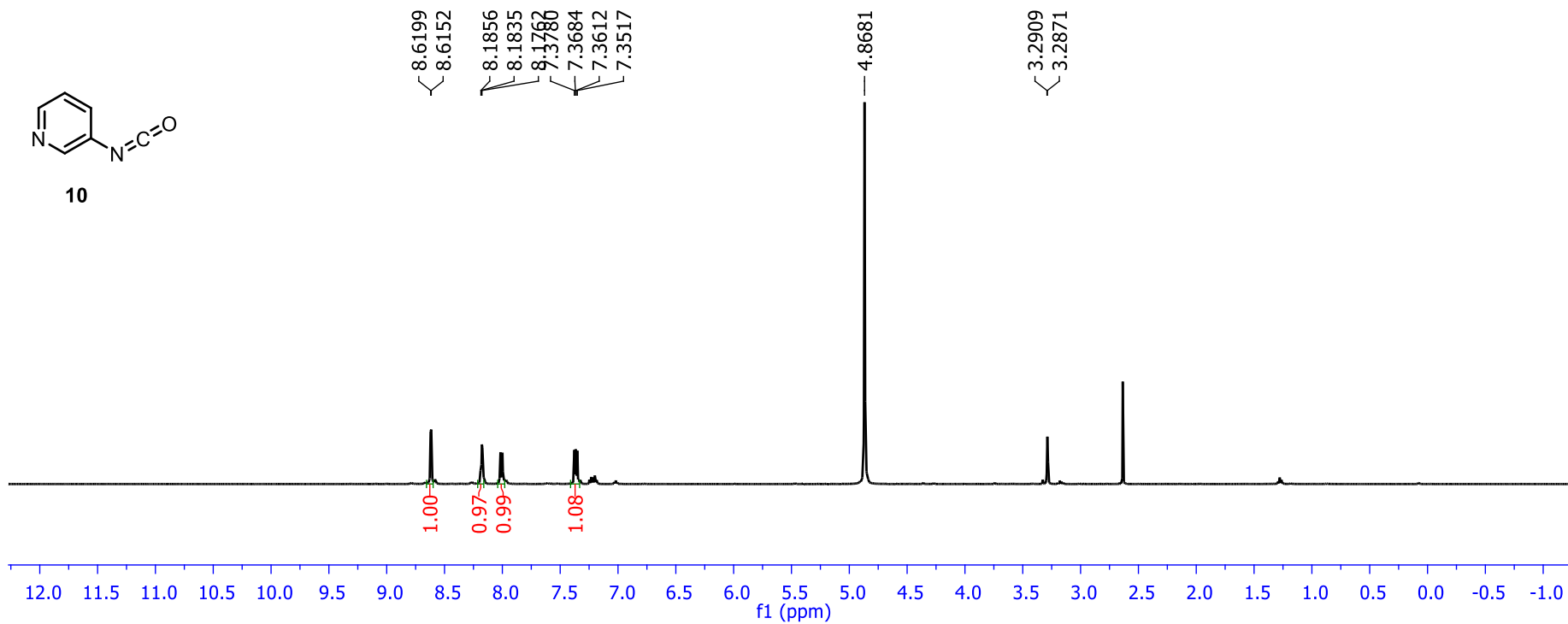
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— 8.0231  
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7.2518

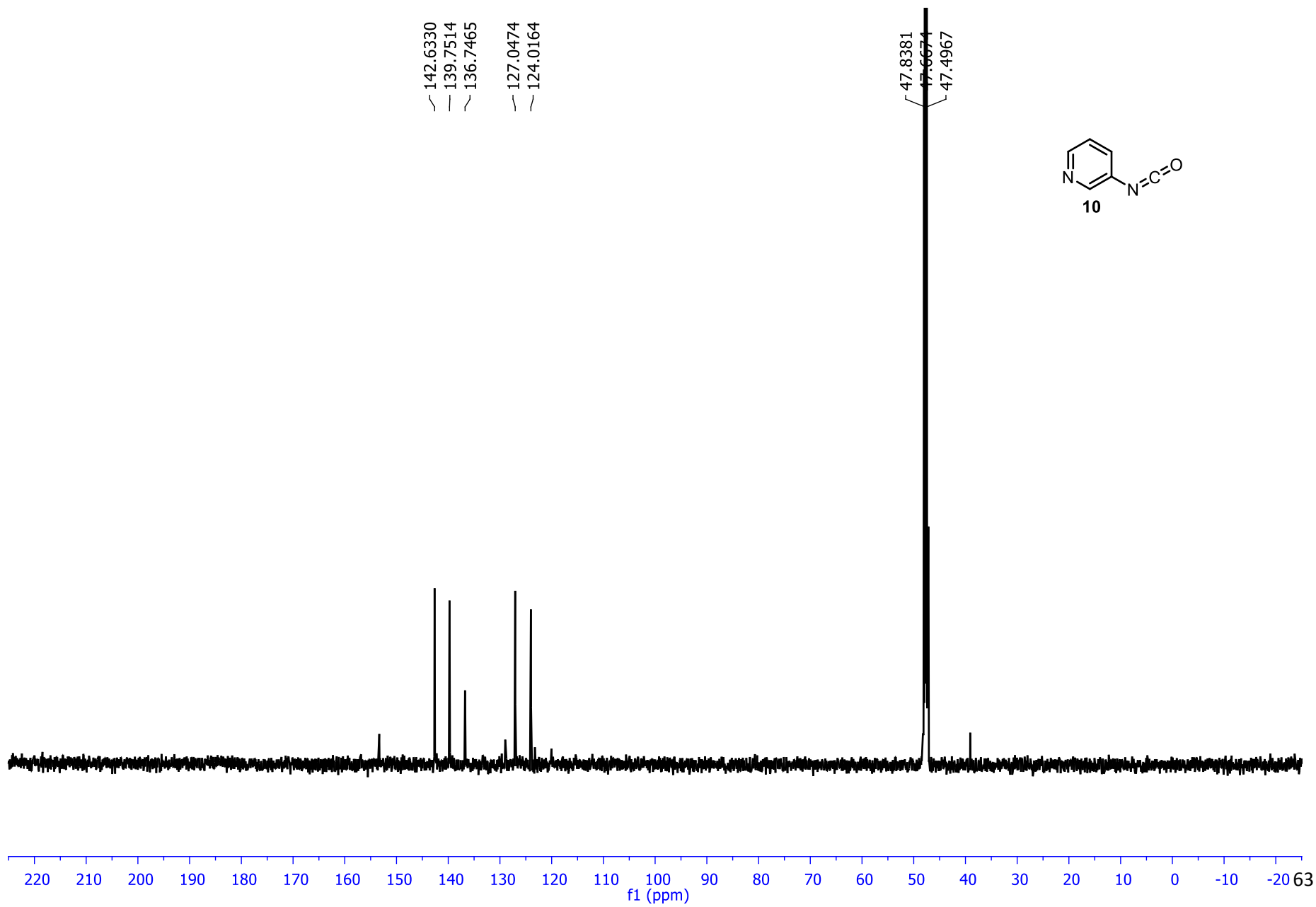
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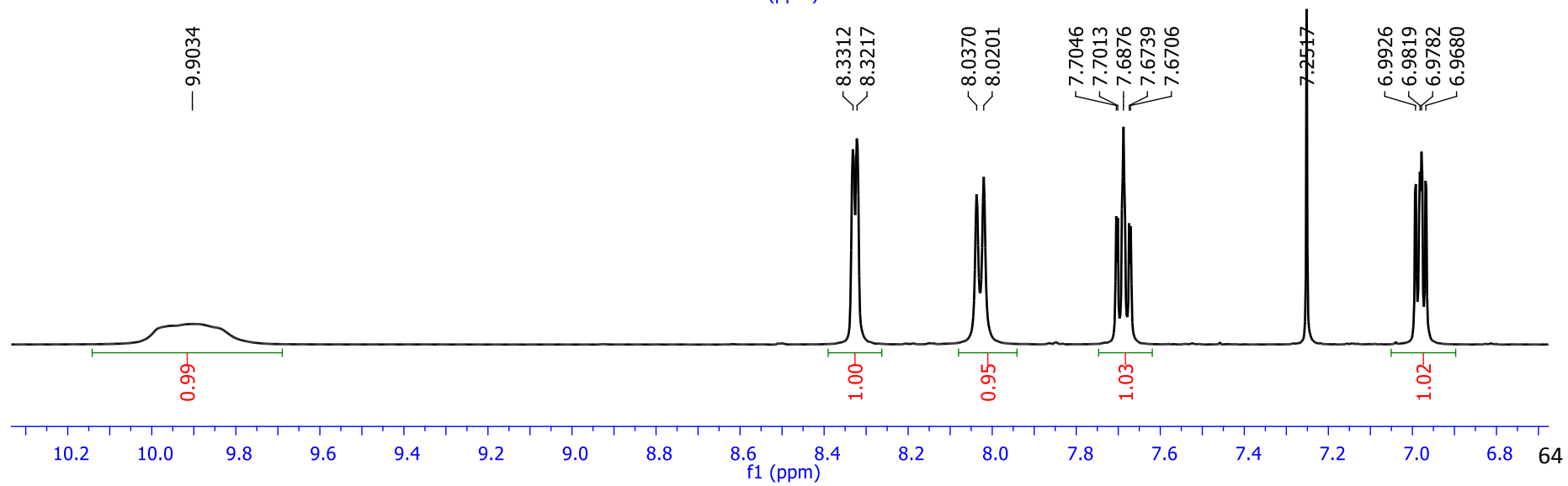
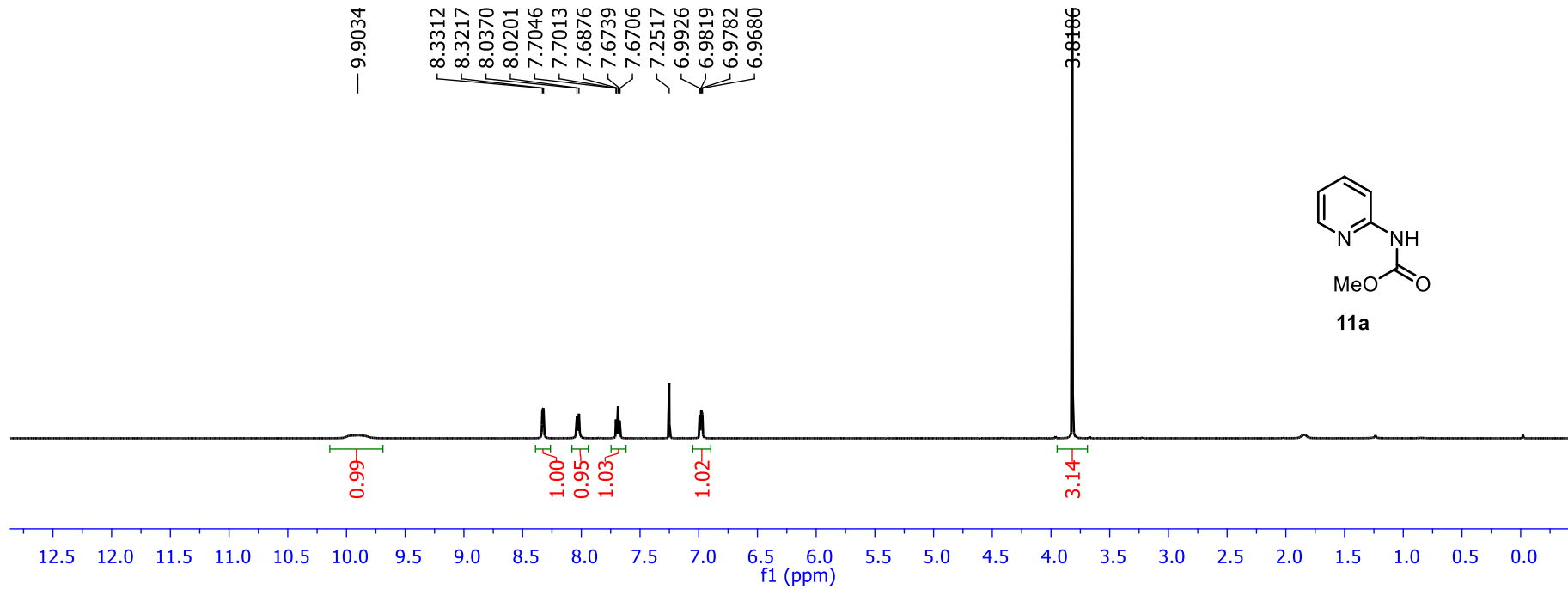
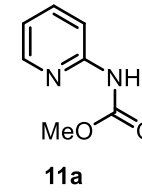




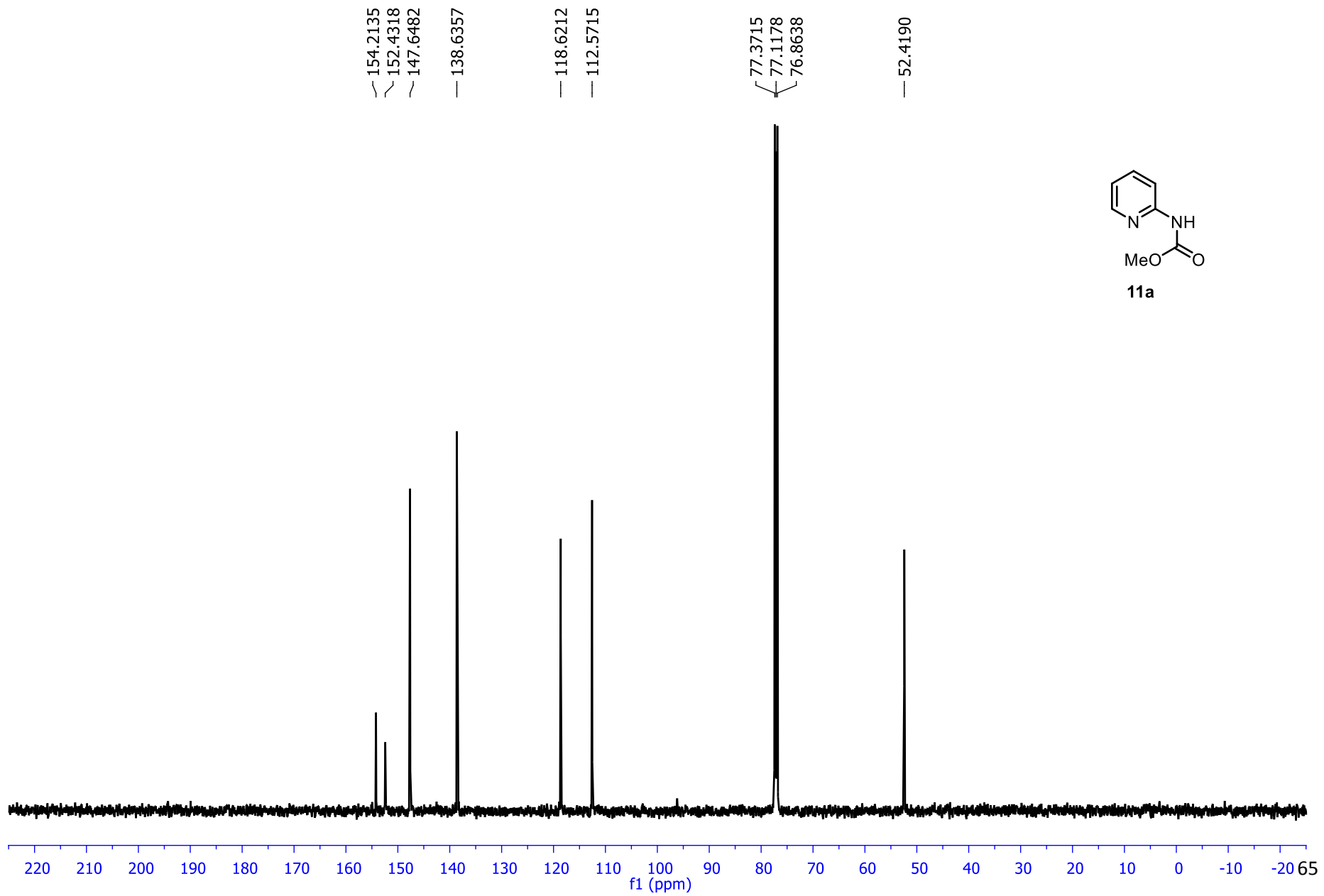
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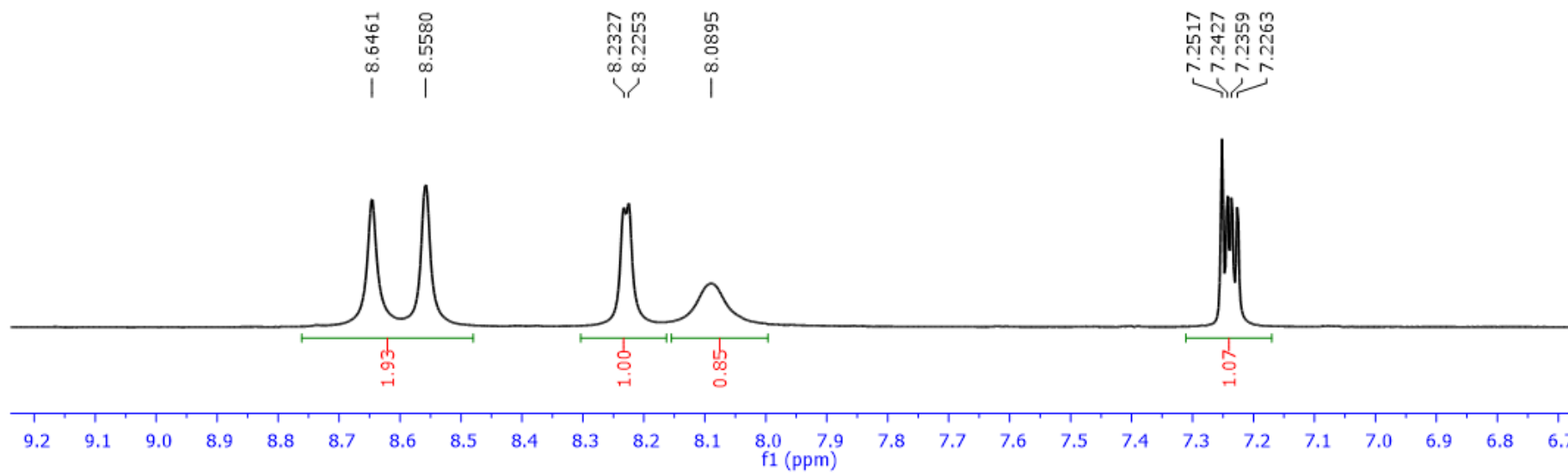
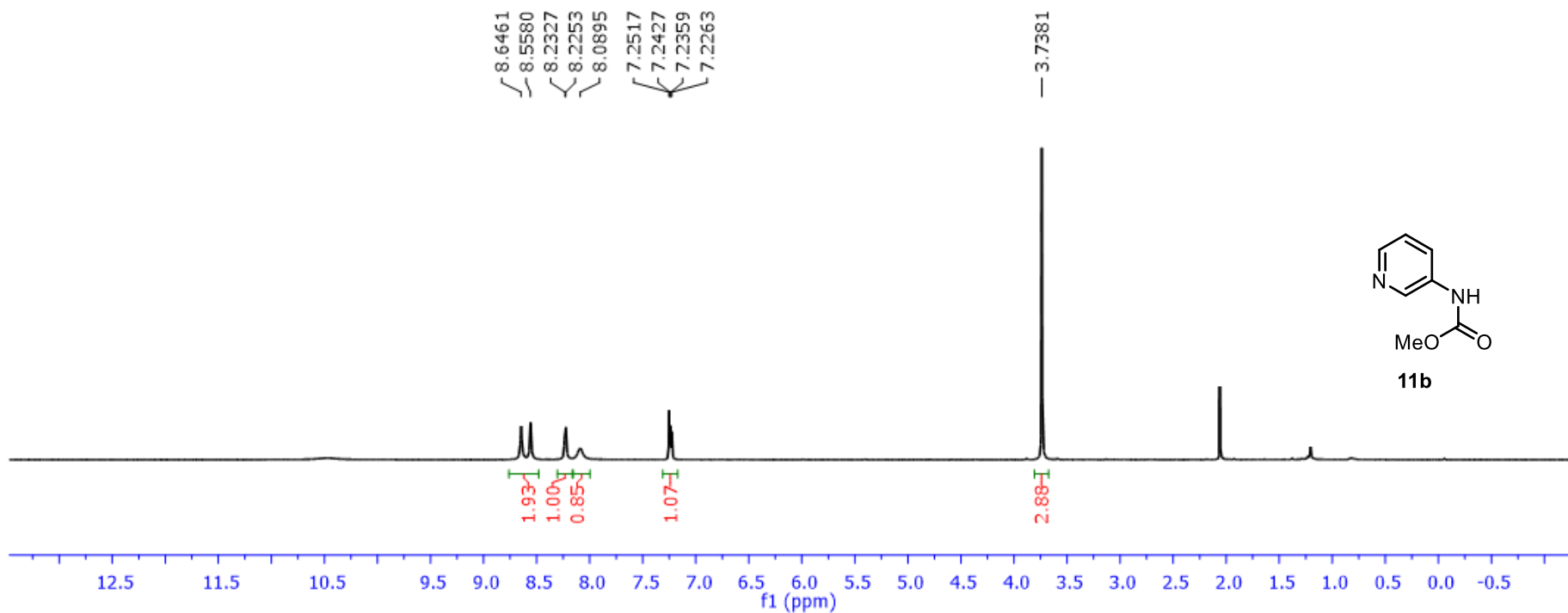


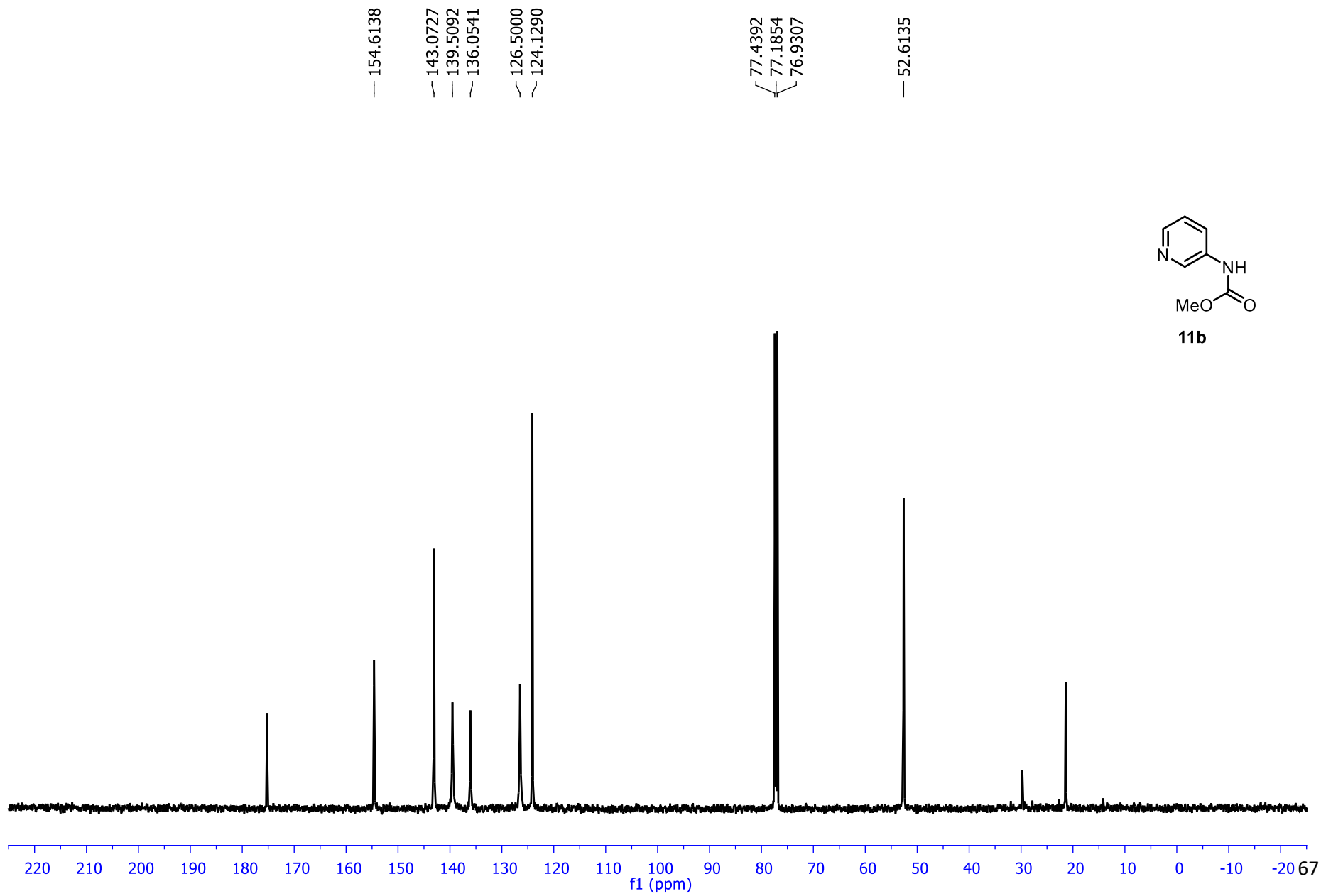
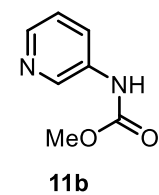


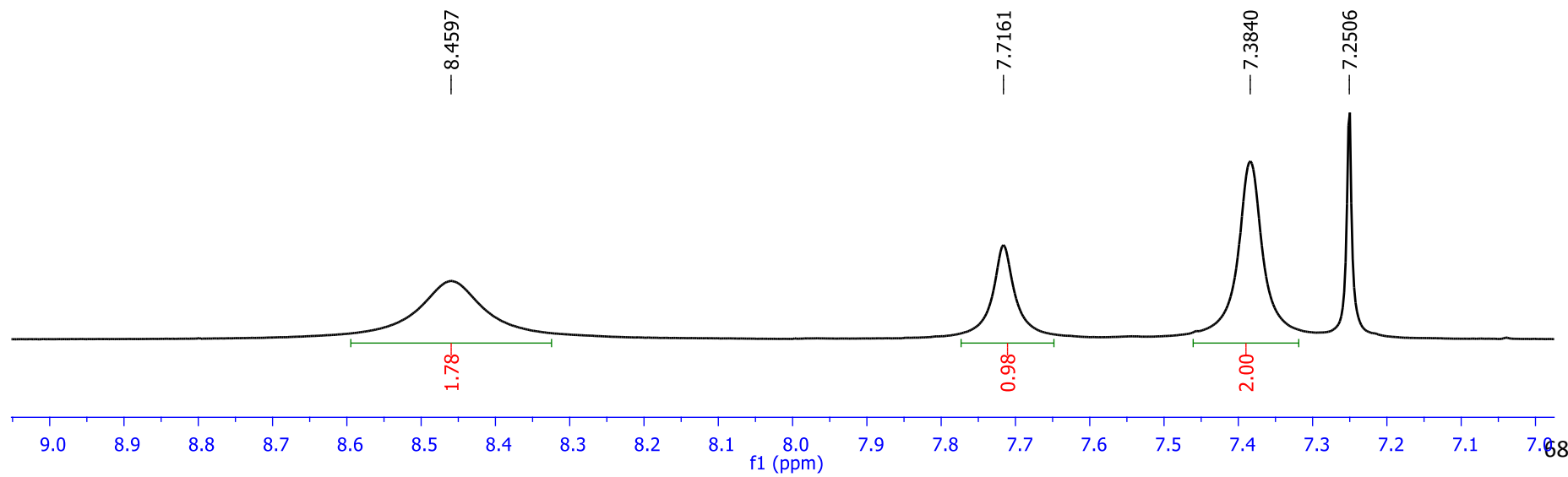
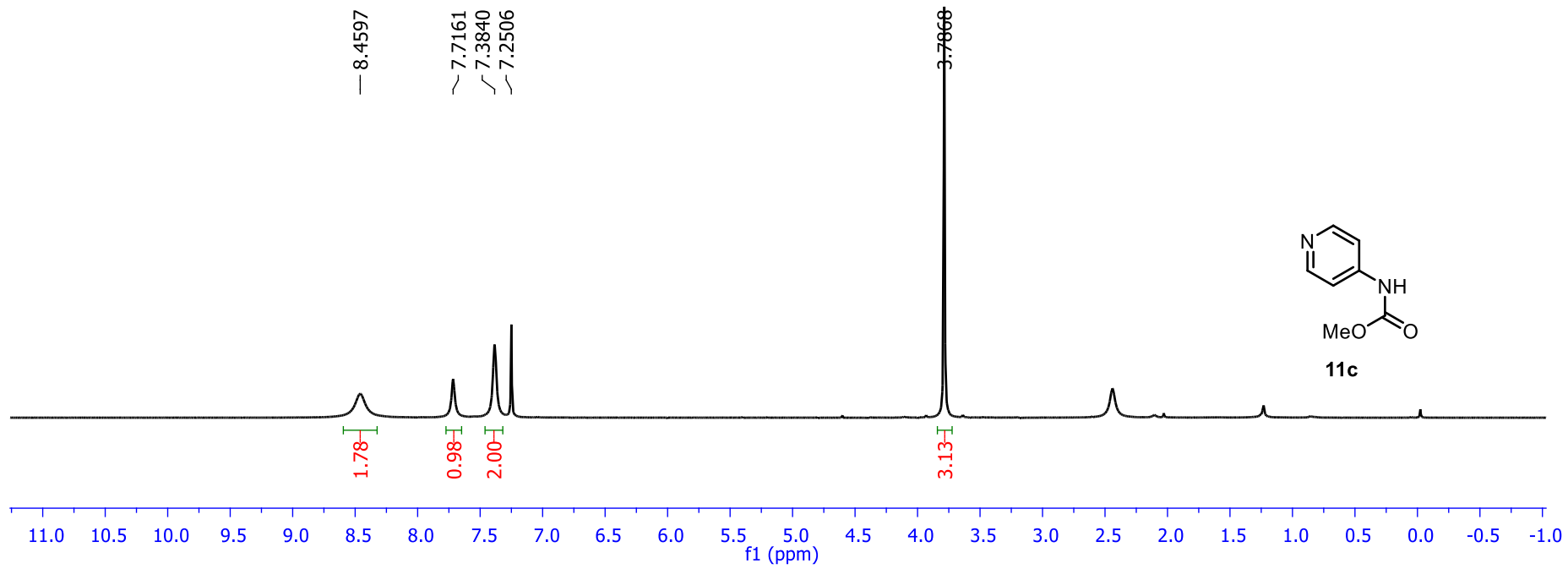


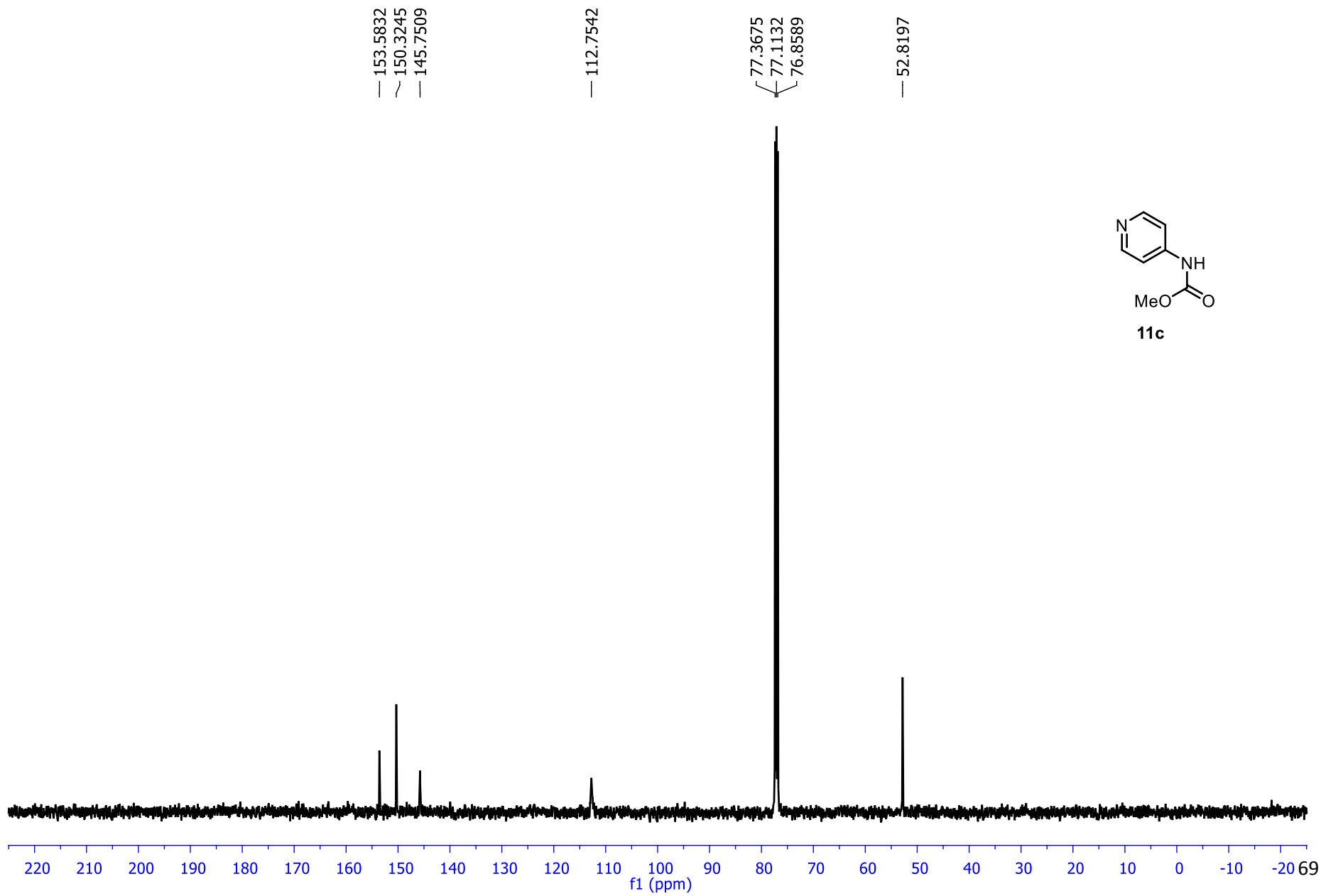




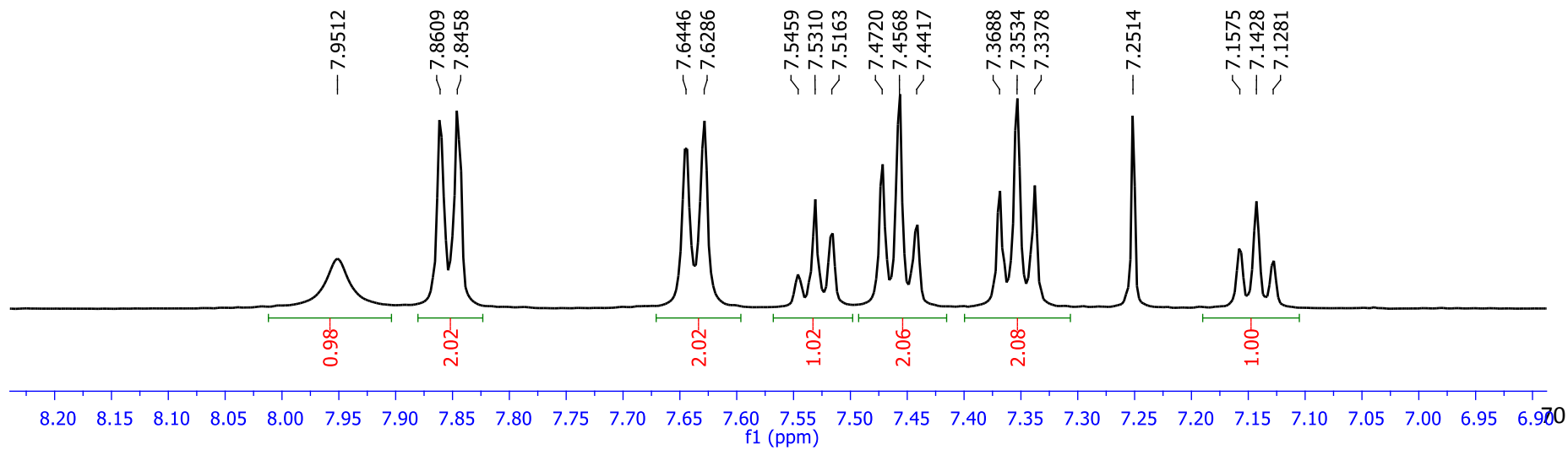
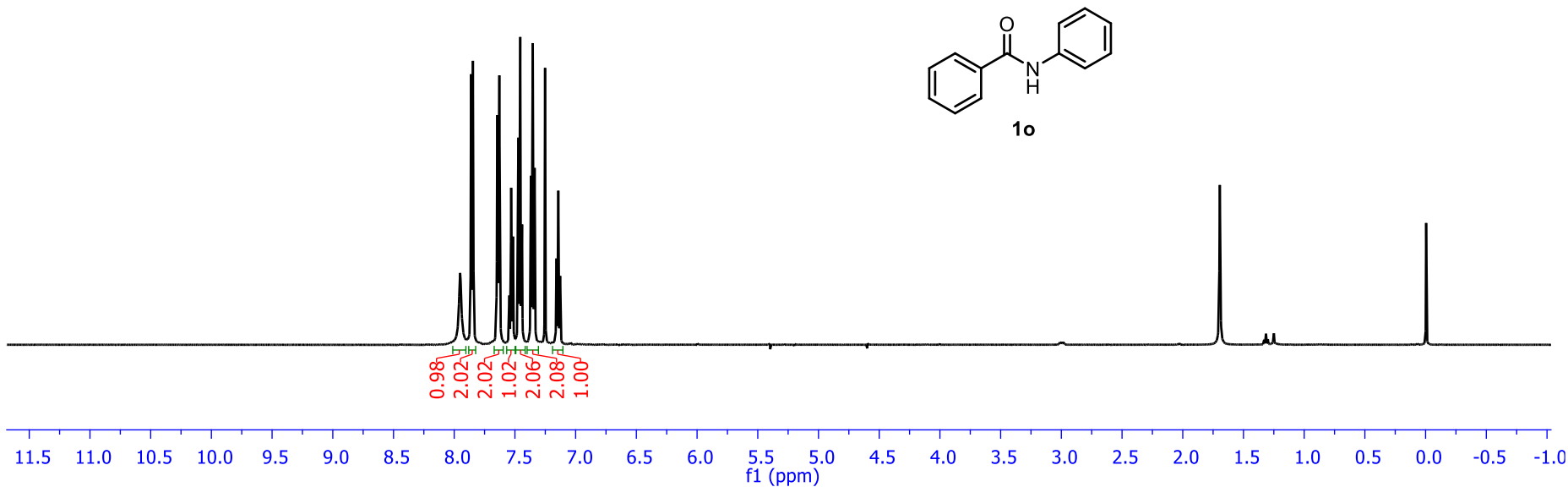
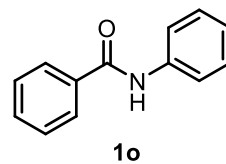


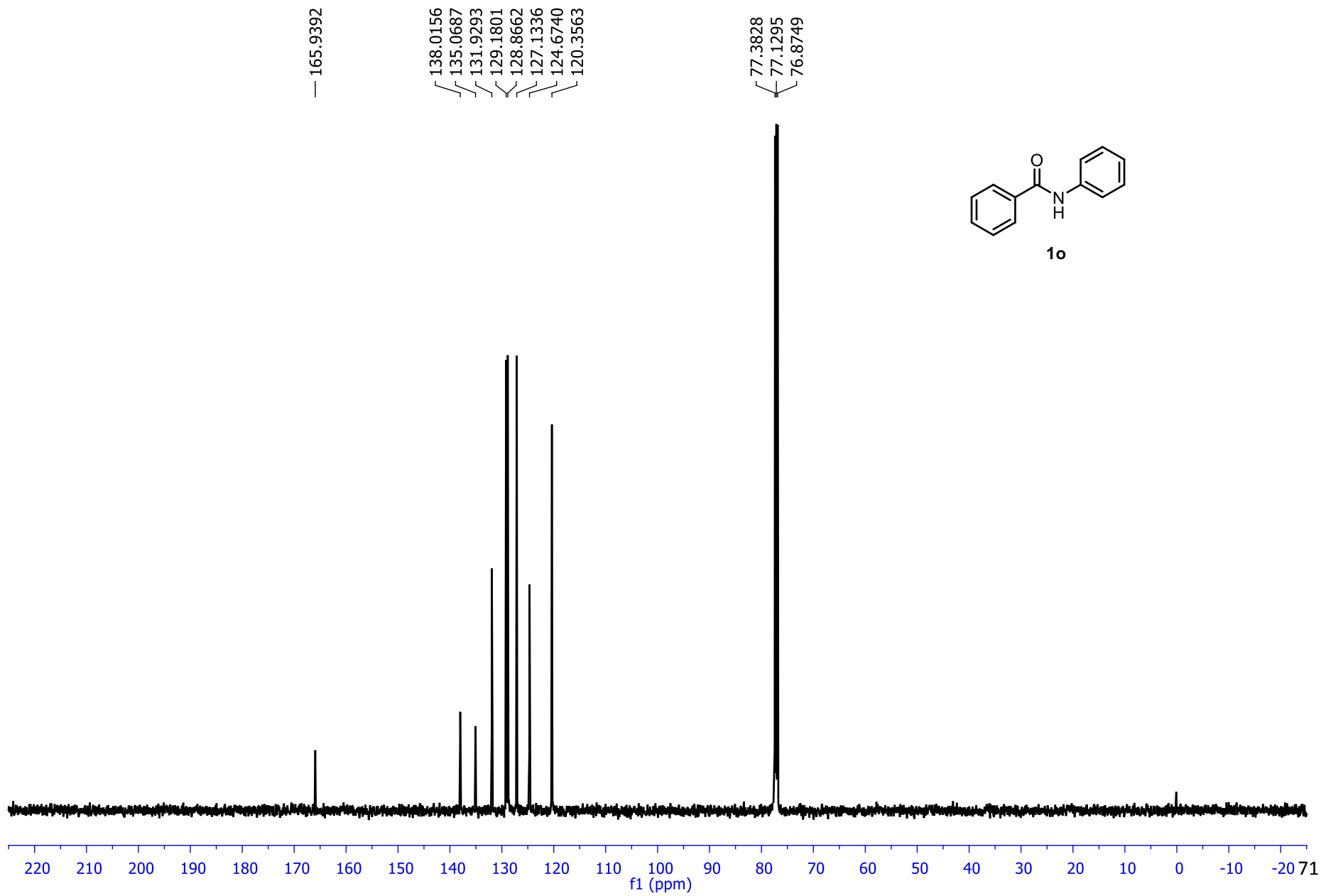


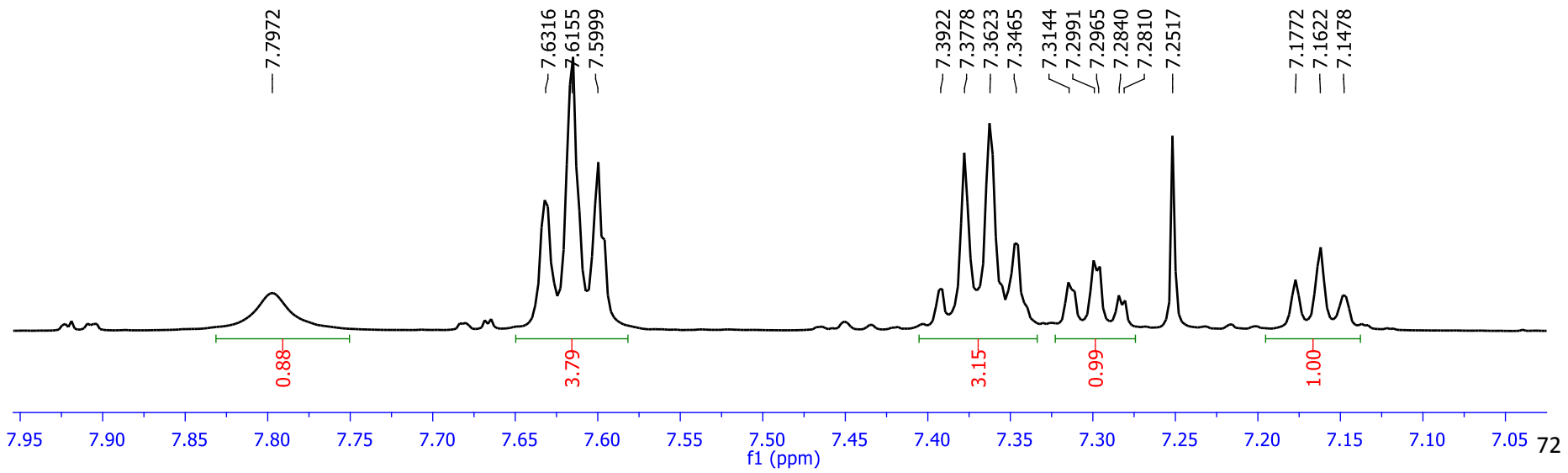
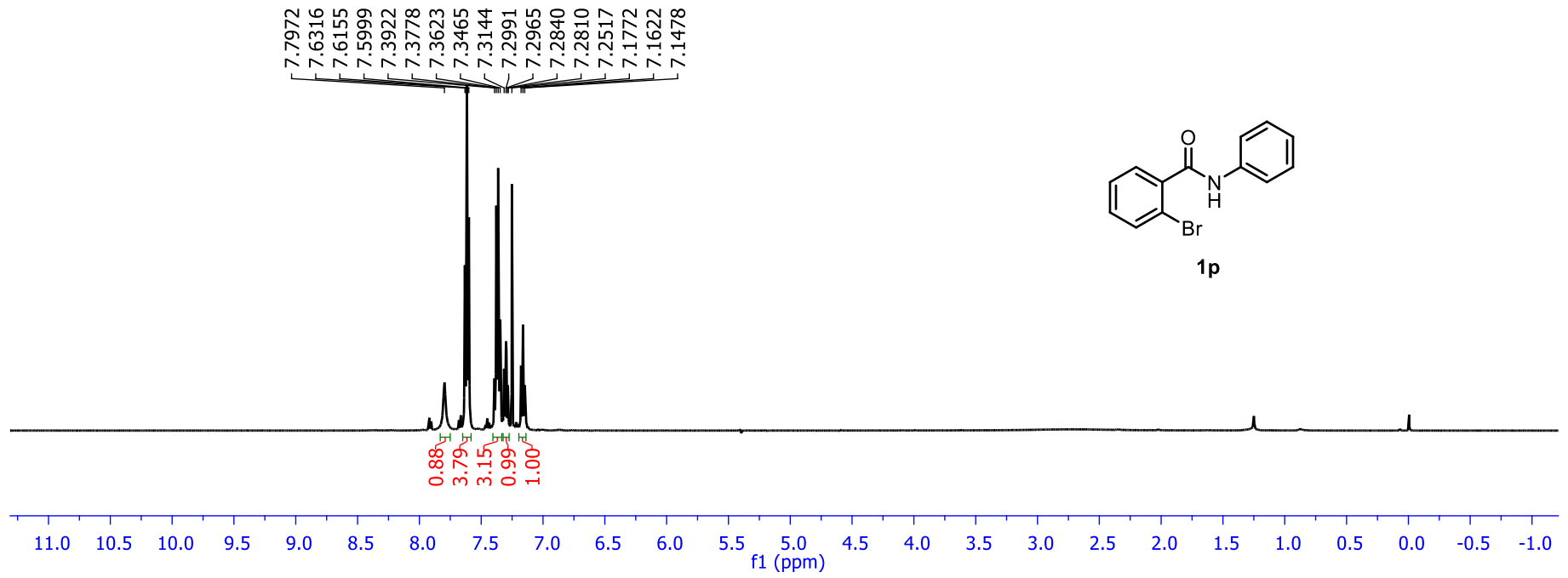




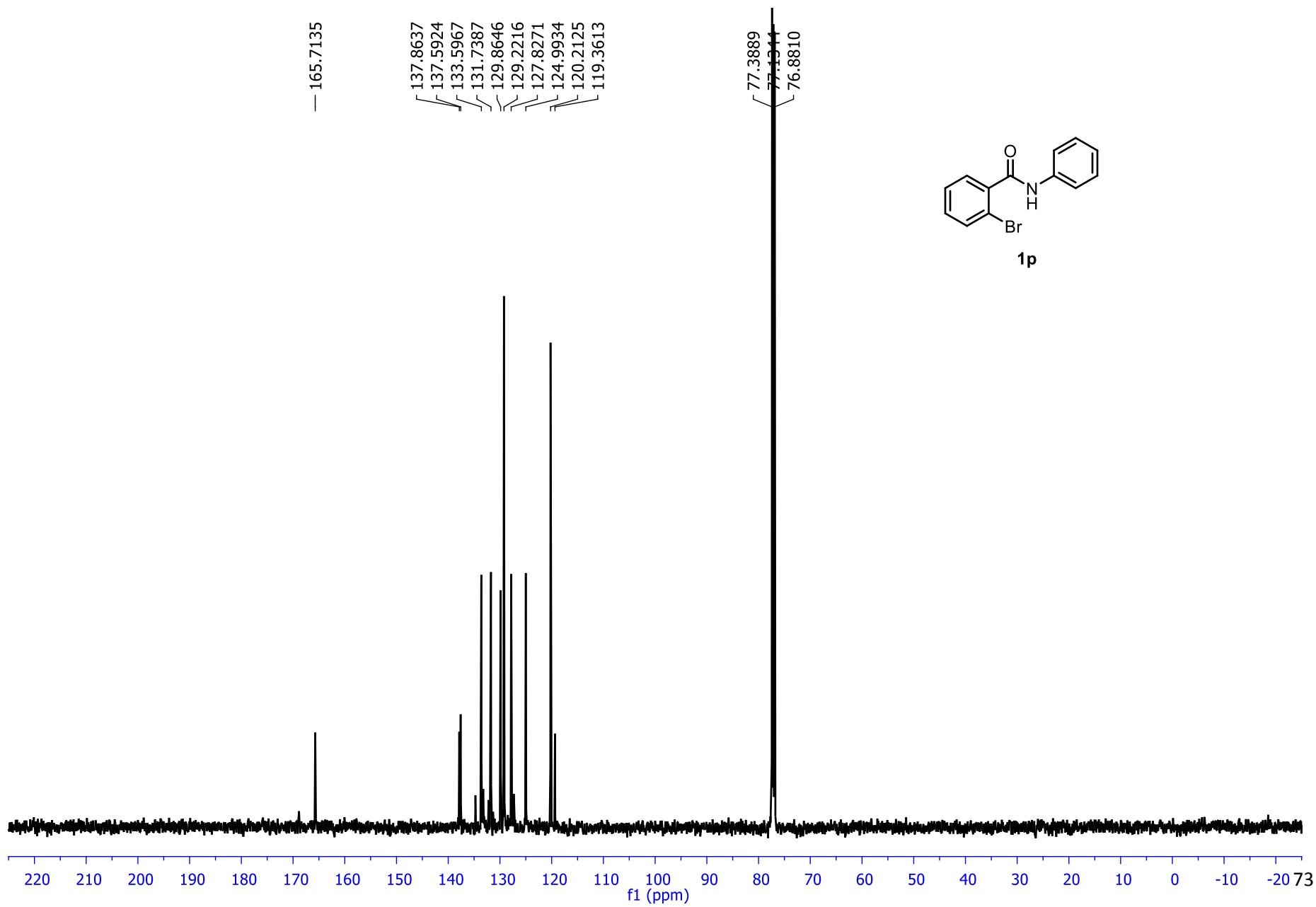
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7.4568  
7.4417  
7.3688  
7.3534  
7.3378  
7.2514  
7.1575  
7.1428  
7.1281











## II. X-ray Data

For the determination of X-ray crystal structure of compound **3k** a single crystal was selected and mounted with paratone oil on a glass fiber using gum. The data was collected at 293 K on a CMOS based Bruker D8 Venture PHOTON 100 diffractometer equipped with a INCOATEC micro-focus source with graphite monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) operation at 50 kV and 30 mA. For the integration of diffraction profiles SAINT program was used. Absorption correction was done applying SADABS program. The crystal structure was solved SIR 92 and refined by full matrix least square method using SHELXL- 97 WinGX system, Ver 1.70.01. All the non-hydrogen atoms in the structure were located the Fourier map and refined anisotropically. The hydrogen atoms were fixed by HFIX in the ideal positions and refined using riding model with isotropic thermal parameters. CIF file is attached with the supporting information.

## Datablock: shelx

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Bond precision: C-C = 0.0043 A                      Wavelength=0.71073  
Cell:                    a=14.7883(11)        b=5.8469(5)            c=16.4107(16)  
                          alpha=90            beta=115.755(3)       gamma=90  
Temperature:        293 K

	Calculated	Reported
Volume	1278.00(19)	1278.00(19)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C13 H10 F3 N3 O	C13 H10 F3 N3 O
Sum formula	C13 H10 F3 N3 O	C13 H10 F3 N3 O
Mr	281.24	281.24
Dx,g cm-3	1.462	1.462
Z	4	4
Mu (mm-1)	0.126	0.126
F000	576.0	576.0
F000'	576.37	
h,k,lmax	19,7,21	19,7,21
Nref	3188	3115
Tmin,Tmax	0.960,0.967	0.652,0.746
Tmin'	0.960	

Correction method= # Reported T Limits: Tmin=0.652 Tmax=0.746  
AbsCorr = MULTI-SCAN

Data completeness= 0.977                      Theta(max)= 28.329

R(reflections)= 0.0864( 2317)                wR2(reflections)= 0.2591( 3115)

S = 1.025    Npar= 181

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