

**Carbene reactivity of 4-diazo-4*H*-imidazoles towards nucleophiles and aromatic compounds****Matthew R. Smith, Alexander J. Blake, Christopher J. Hayes, Malcolm F. G. Stevens, and Christopher J. Moody****SUPPORTING INFORMATION****Contents**

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## General experimental details

### General

All solvent and chemical reagents obtained commercially were used without further purification or drying. All irradiation experiments were carried out in glass vessels using a 300W lamp emitting a wavelength range of 300-600 nm. All chromatography was carried out using silica gel unless otherwise stated.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 298K on a 400 MHz instrument, unless otherwise stated. Chemical shifts are quoted in ppm using residual undeuterated solvent as the internal reference. Mass spectra were recorded on a time of flight spectrometer using electrospray ionization. Infrared spectra were recorded on an FT IR spectrometer in attenuated total reflectance (ATR) mode.

### Computational Methods

Geometry optimisations were performed at the B3LYP/6-311+G\*\* level of theory for the singlet carbene and UB3LYP/6-311+G\*\* for the triplet carbene using Q-Chem,. Zero point vibrational energies were calculated for all structures and the absence of imaginary frequencies was used to characterise the structures as minima on their potential energy surfaces.

### Coordinates (Angstroms) for Singlet imidazole carbene

ATOM	X	Y	Z
C	0.956067	-0.193053	-0.000987
C	1.533156	1.030869	0.003502
N	2.740282	1.392918	0.002917
C	3.166337	0.072385	0.001479
N	2.178553	-0.847644	-0.001105
H	4.213811	-0.186677	0.002764
C	-0.398298	-0.746028	-0.002352
O	-0.659581	-1.920954	-0.005672

O	-1.302628	0.255532	0.000779
C	-2.700050	-0.143830	-0.000045
H	-2.881730	-0.757953	-0.884735
H	-2.881813	-0.761169	0.882387
C	-3.536850	1.117415	0.002255
H	-3.337153	1.724622	-0.883531
H	-3.337336	1.721351	0.890325
H	-4.596954	0.850629	0.001654

**Singlet** E = -492.186747449 au (B3LYP/6-311+G\*\*// B3LYP/6-311+G\*\*)

This molecule has 0 imaginary frequencies

Zero point vibrational energy: 72.103 kcal/mol

#### **Coordinates (Angstroms) for Triplet imidazole carbene**

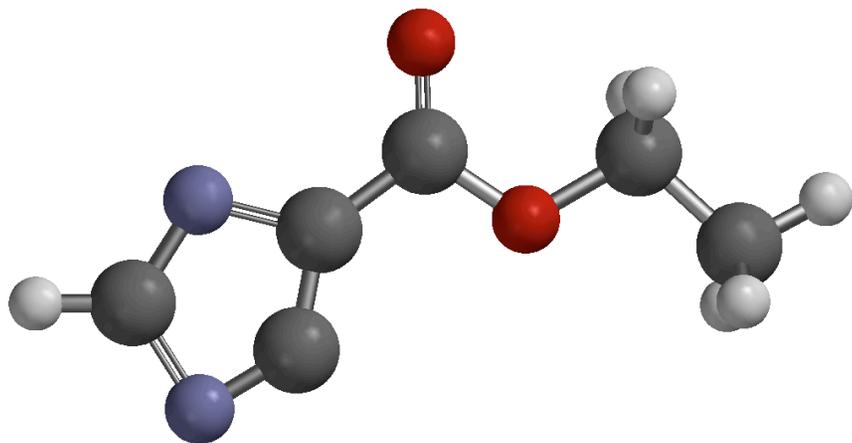
ATOM	X	Y	Z
C	1.011832	-0.180464	0.001801
C	1.417124	1.252988	0.006192
N	2.693409	1.362672	0.010297
C	3.114673	0.047932	0.011196
N	2.121825	-0.894006	0.004223
H	4.162175	-0.221695	0.013313
C	-0.359567	-0.751652	-0.004944
O	-0.610179	-1.929365	-0.018923

O	-1.269181	0.237865	0.007220
C	-2.664473	-0.169081	0.003038
H	-2.839274	-0.780837	-0.885040
H	-2.840581	-0.794498	0.881270
C	-3.509676	1.086155	0.012159
H	-3.312076	1.699980	-0.869331
H	-3.314364	1.685995	0.903770
H	-4.567962	0.812209	0.008637

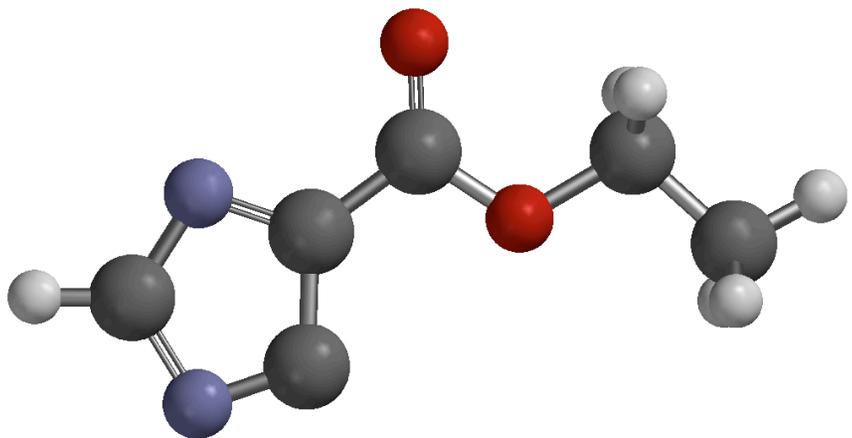
**Triplet** E = -492.201045077 au (UB3LYP/6-311+G\*\*// UB3LYP/6-311+G\*\*)

This molecule has 0 imaginary frequencies

Zero point vibrational energy: 72.386 kcal/mol



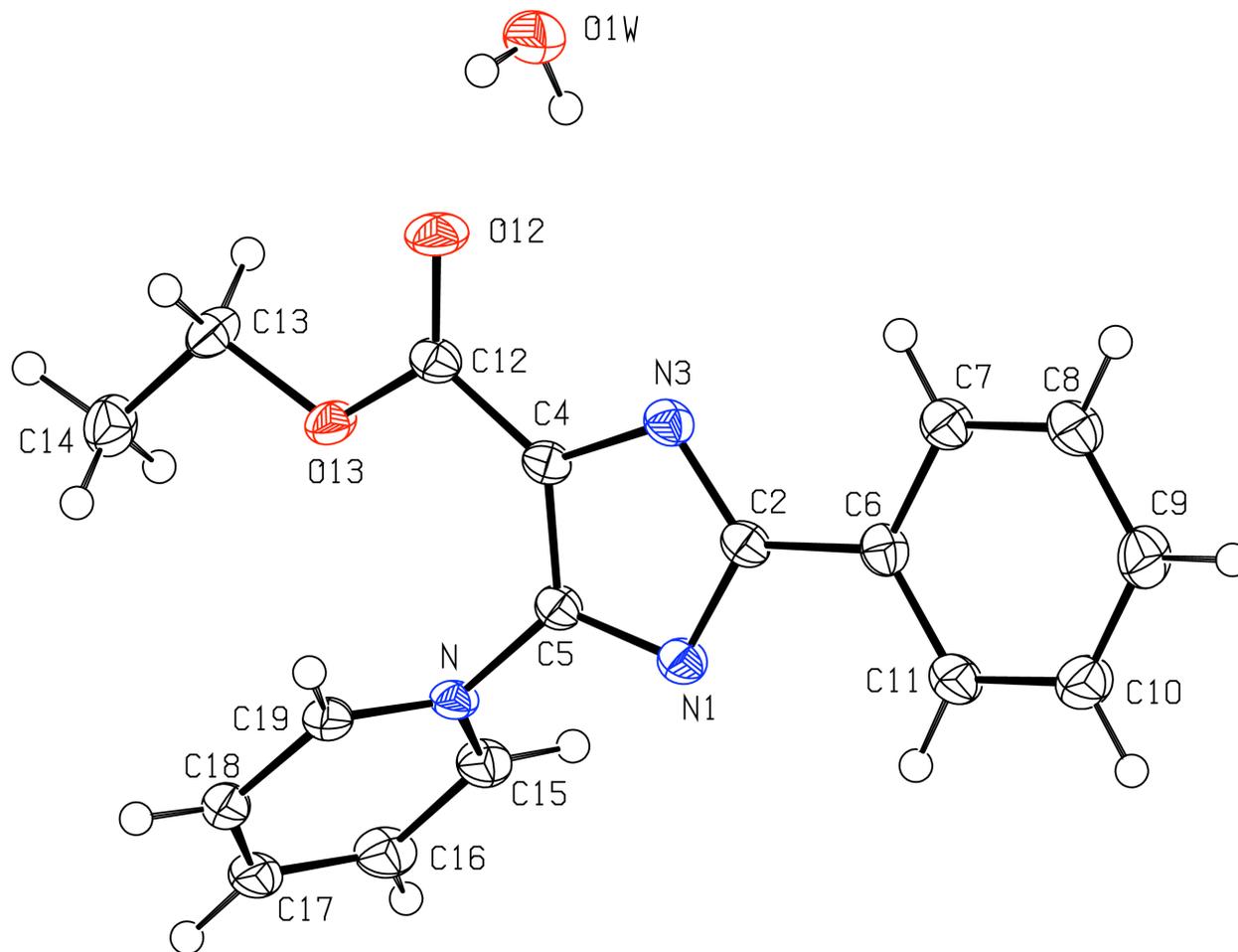
**Singlet**  $E = -492.186747449$  au (B3LYP/6-311+G\*\*// B3LYP/6-311+G\*\*)



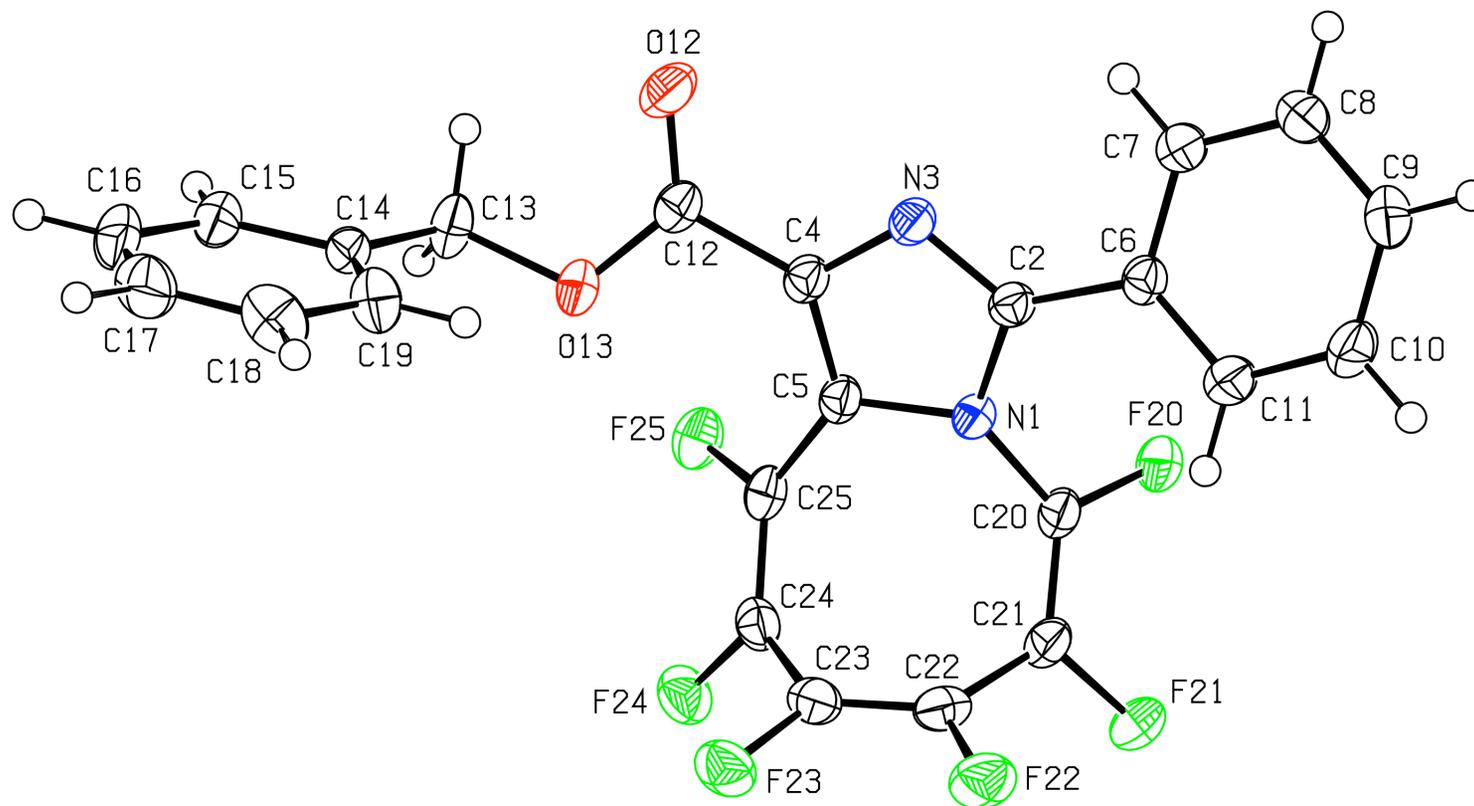
**Triplet**  $E = -492.201045077$  au (UB3LYP/6-311+G\*\*// UB3LYP/6-311+G\*\*)

Therefore triplet is ground state, with a triplet to singlet gap of  $9.0 \text{ Kcal mol}^{-1}$

X-Ray crystal structure of 1-(4-ethoxycarbonyl-2-phenylimidazolidin-4-yl)pyridinium inner salt **8**.

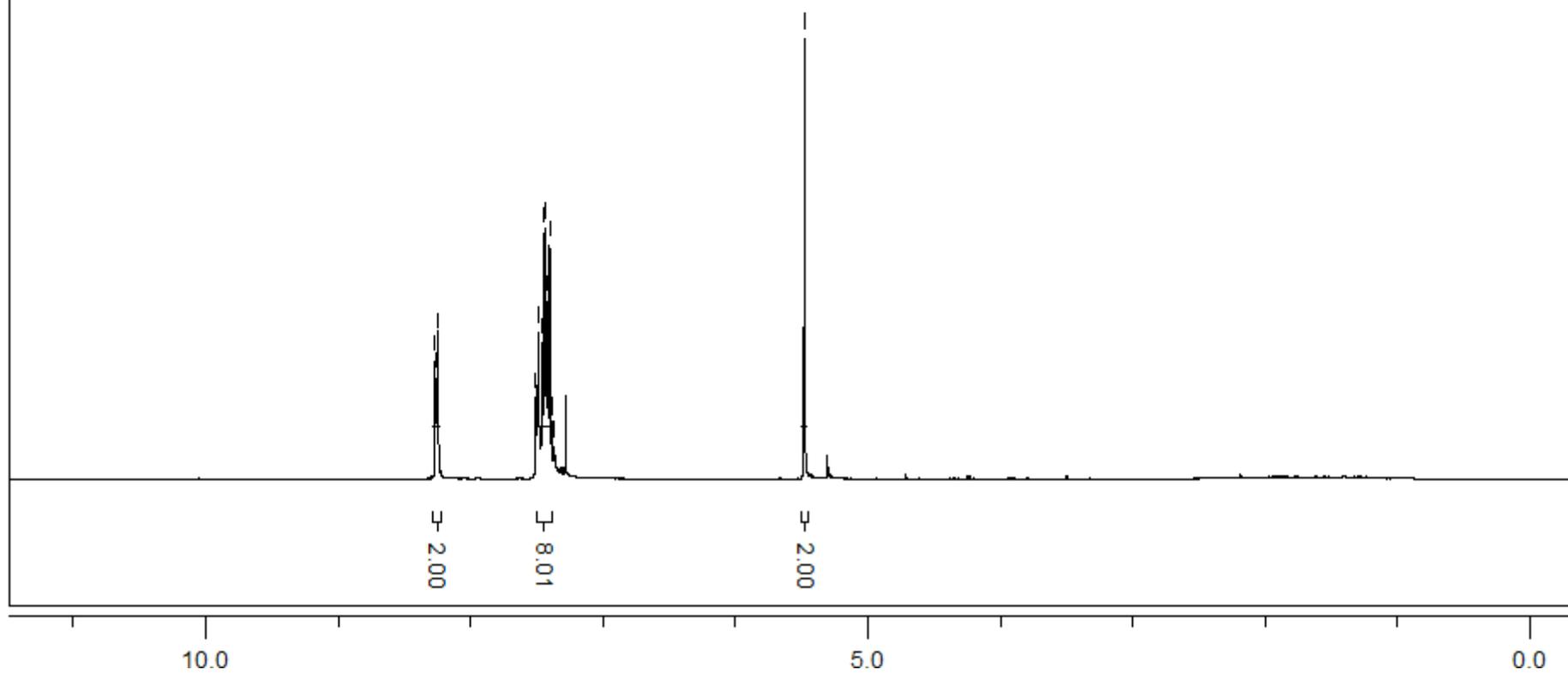
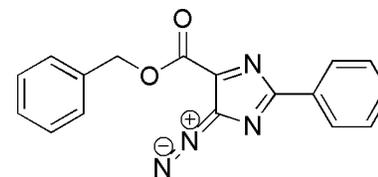


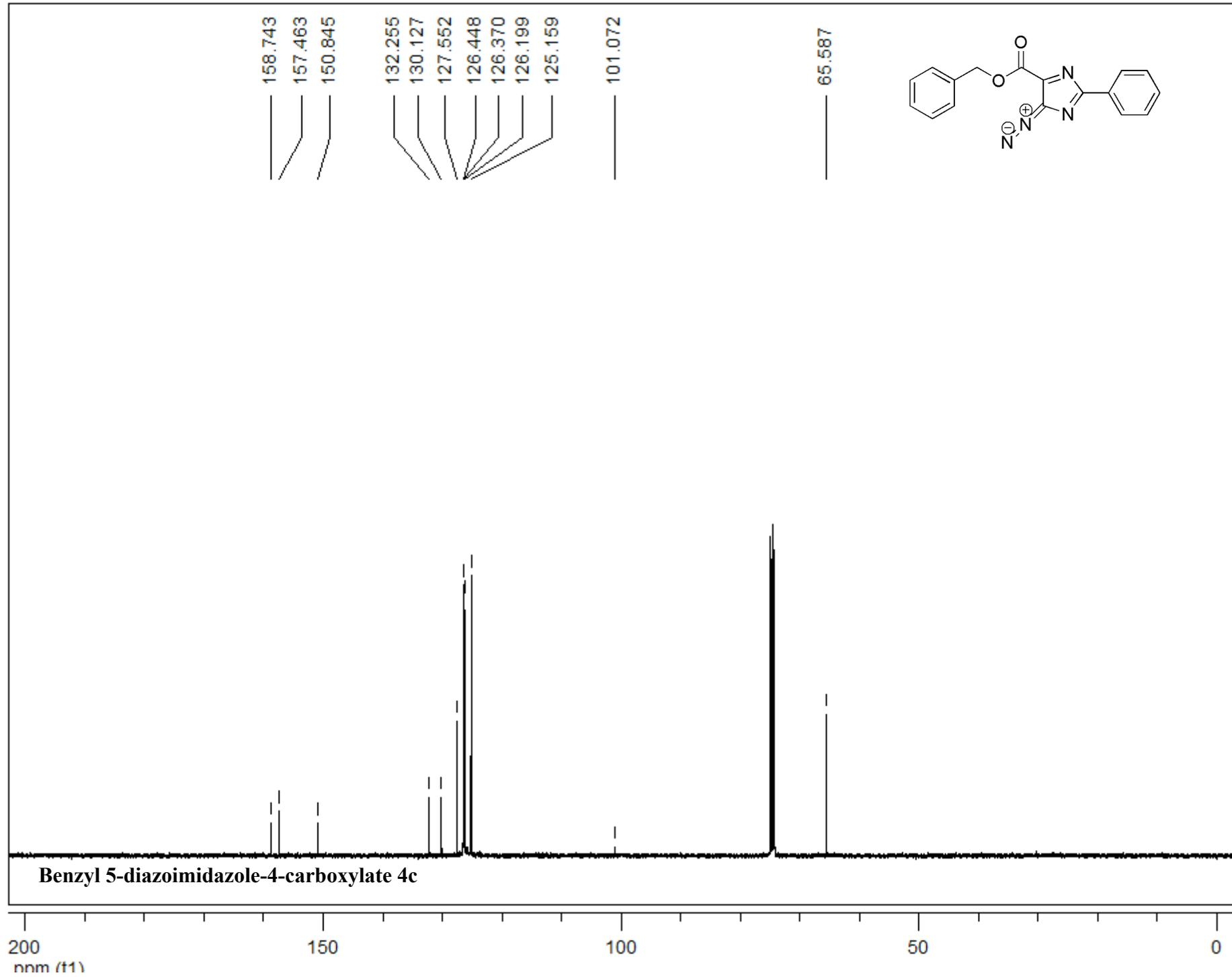
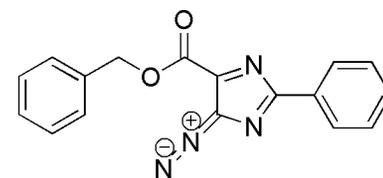
X-Ray crystal structure of benzyl 5,6,7,8,9,10-hexafluoro-2-phenylimidazo[1,5-*a*]azocine-4-carboxylate **11**.



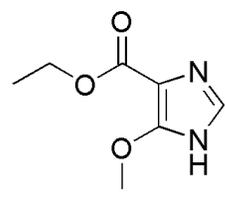
## Benzyl 5-diazoimidazole-4-carboxylate 4c

8.267  
8.262  
8.248  
8.243  
7.509  
7.489  
7.485  
7.458  
7.442  
7.440  
7.422  
7.403  
7.388  
7.386  
7.369  
5.480





## Ethyl 5-methoxyimidazole-4-carboxylate 5a

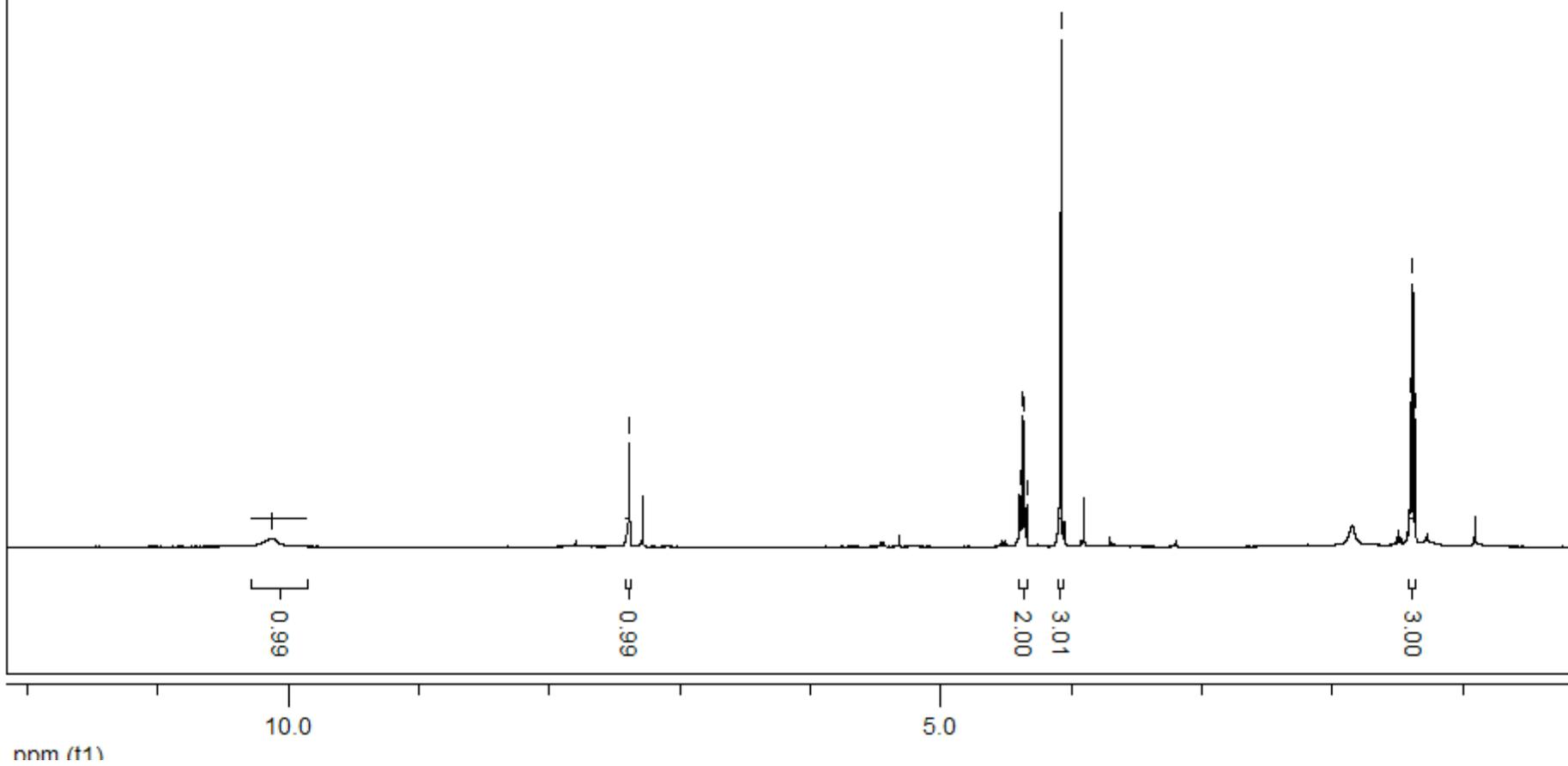


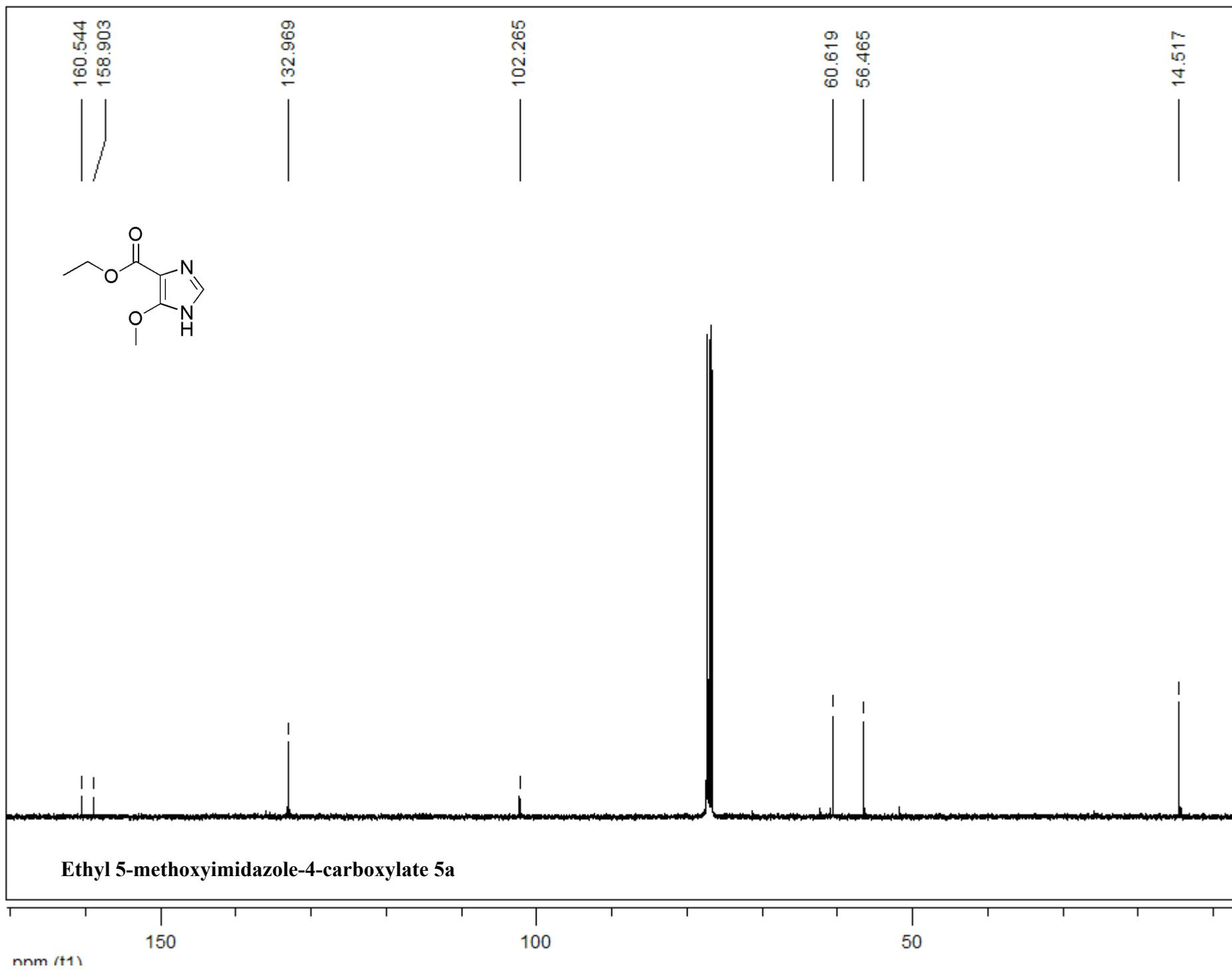
10.129  
10.125

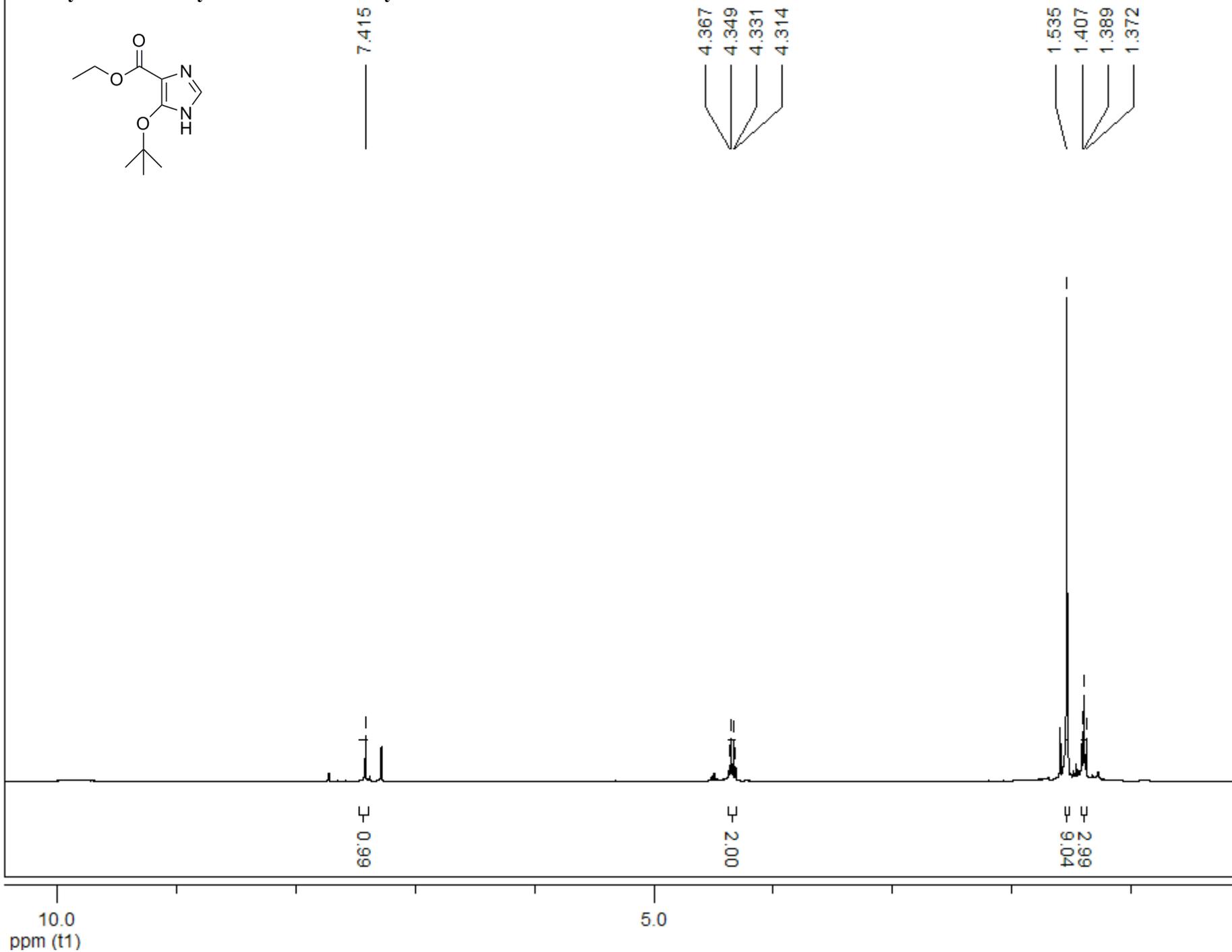
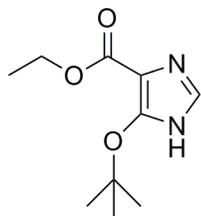
7.387

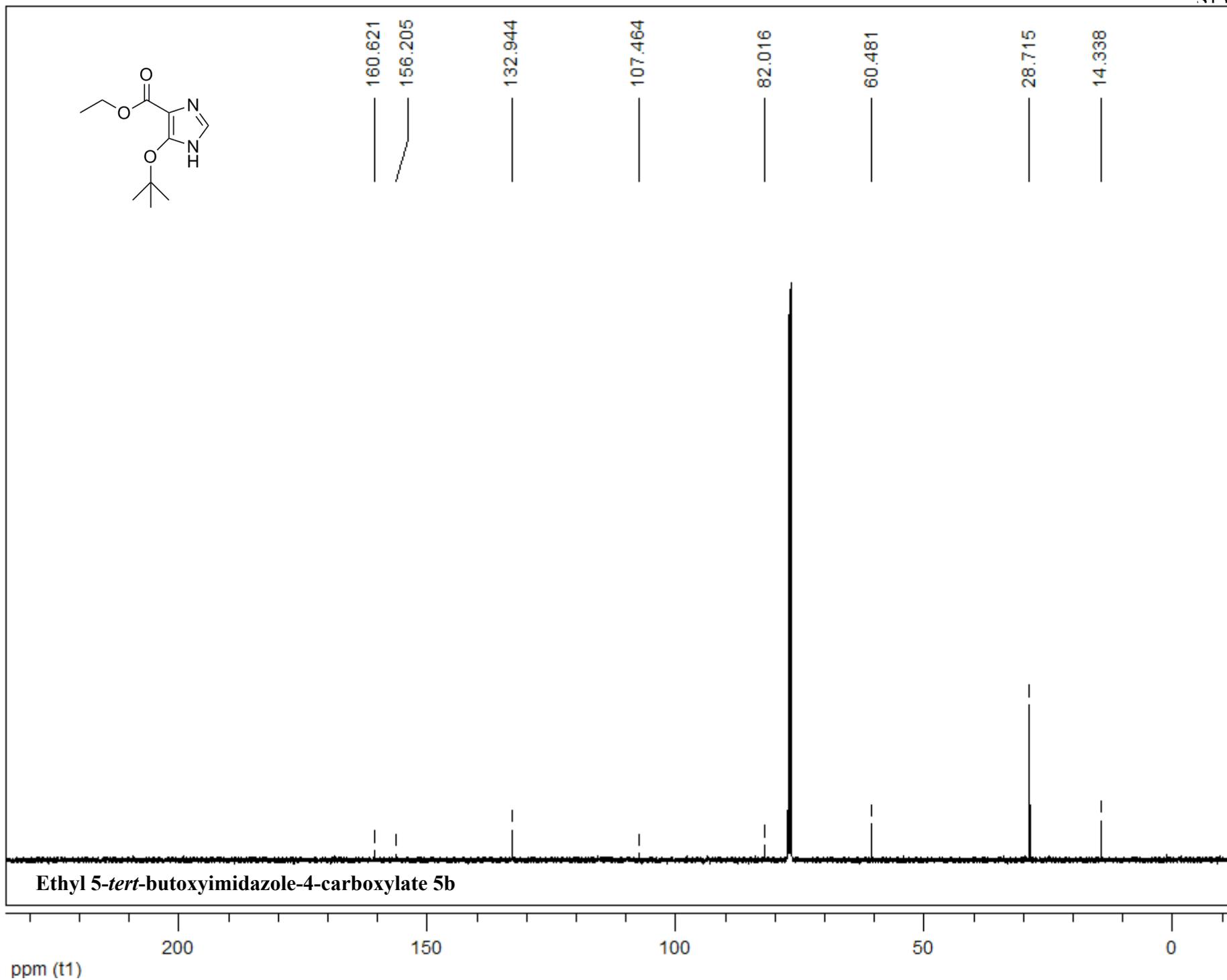
4.395  
4.377  
4.359  
4.342  
4.078

1.399  
1.381  
1.364

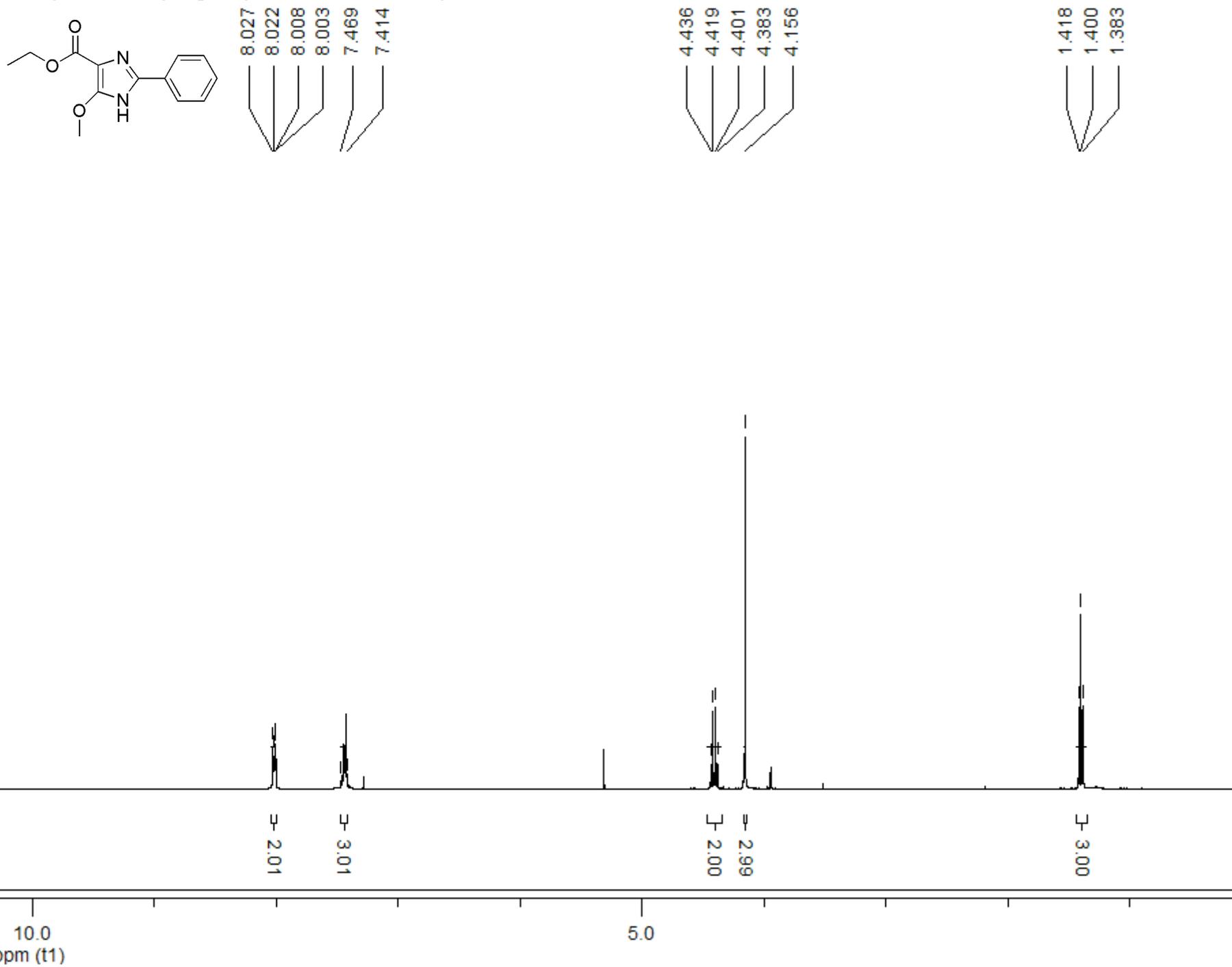


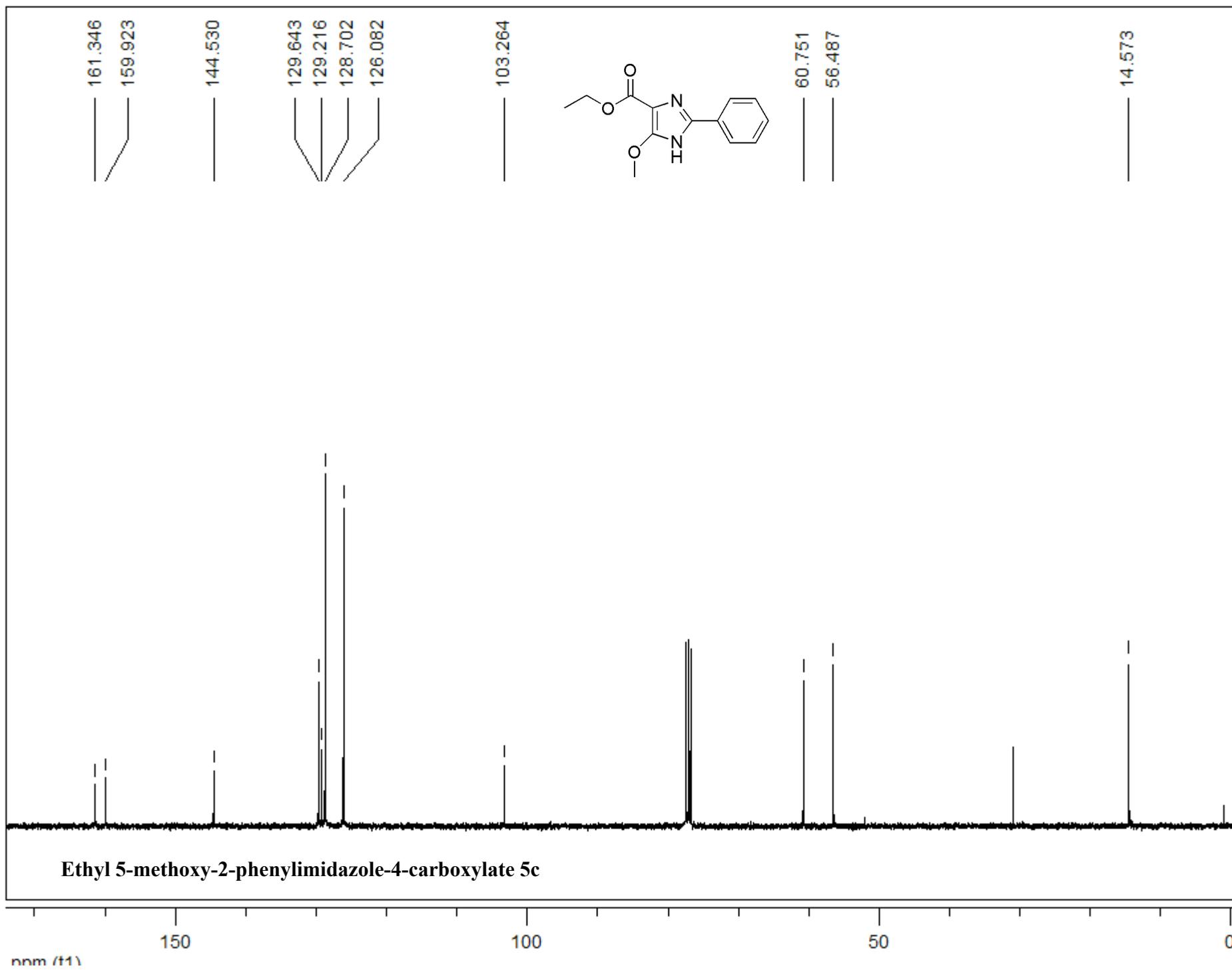


Ethyl 5-*tert*-butoxyimidazole-4-carboxylate 5b

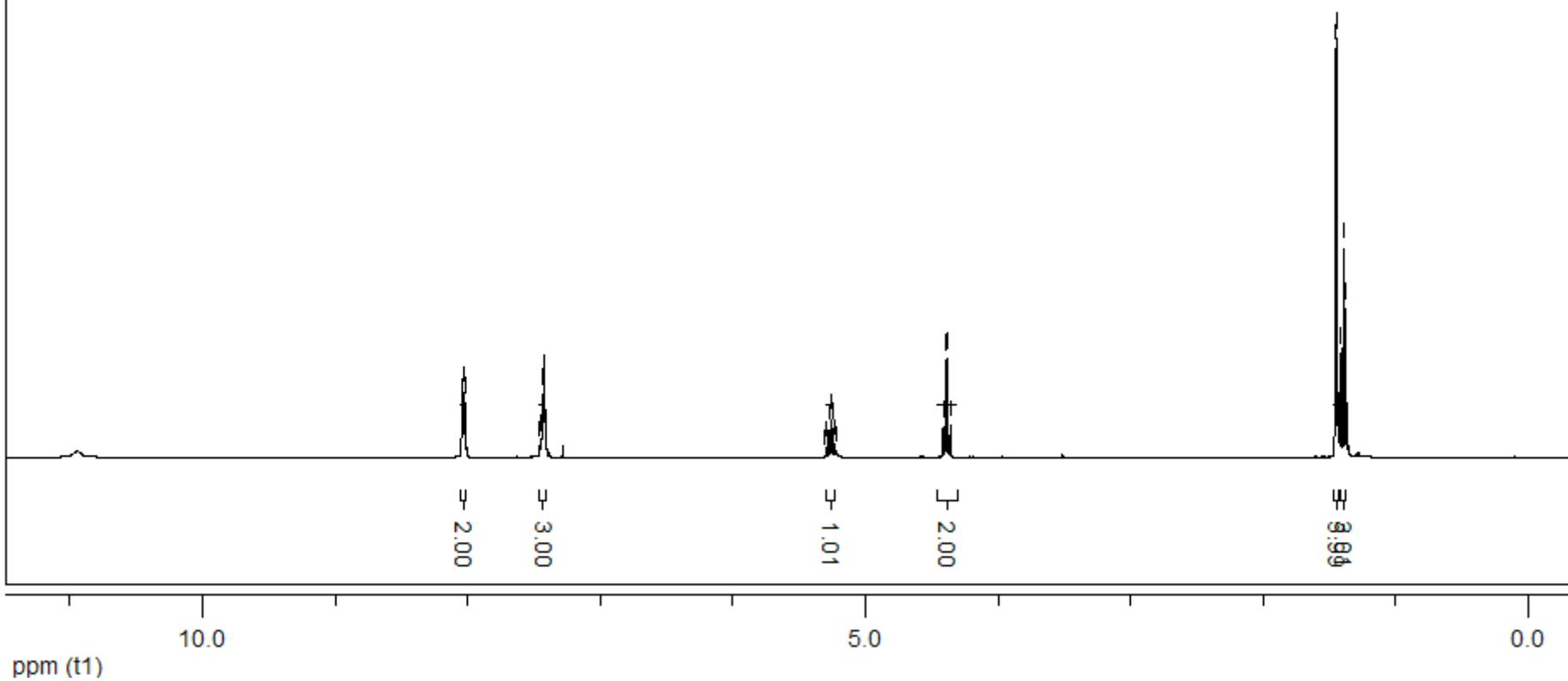
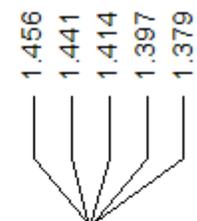
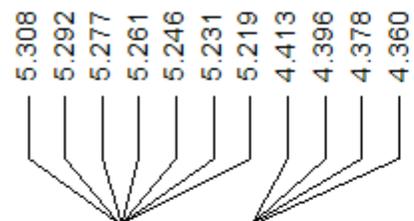
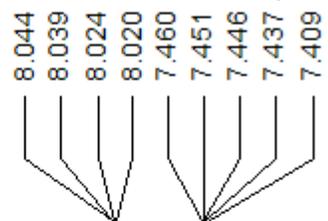
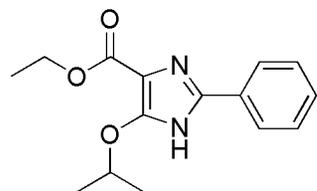


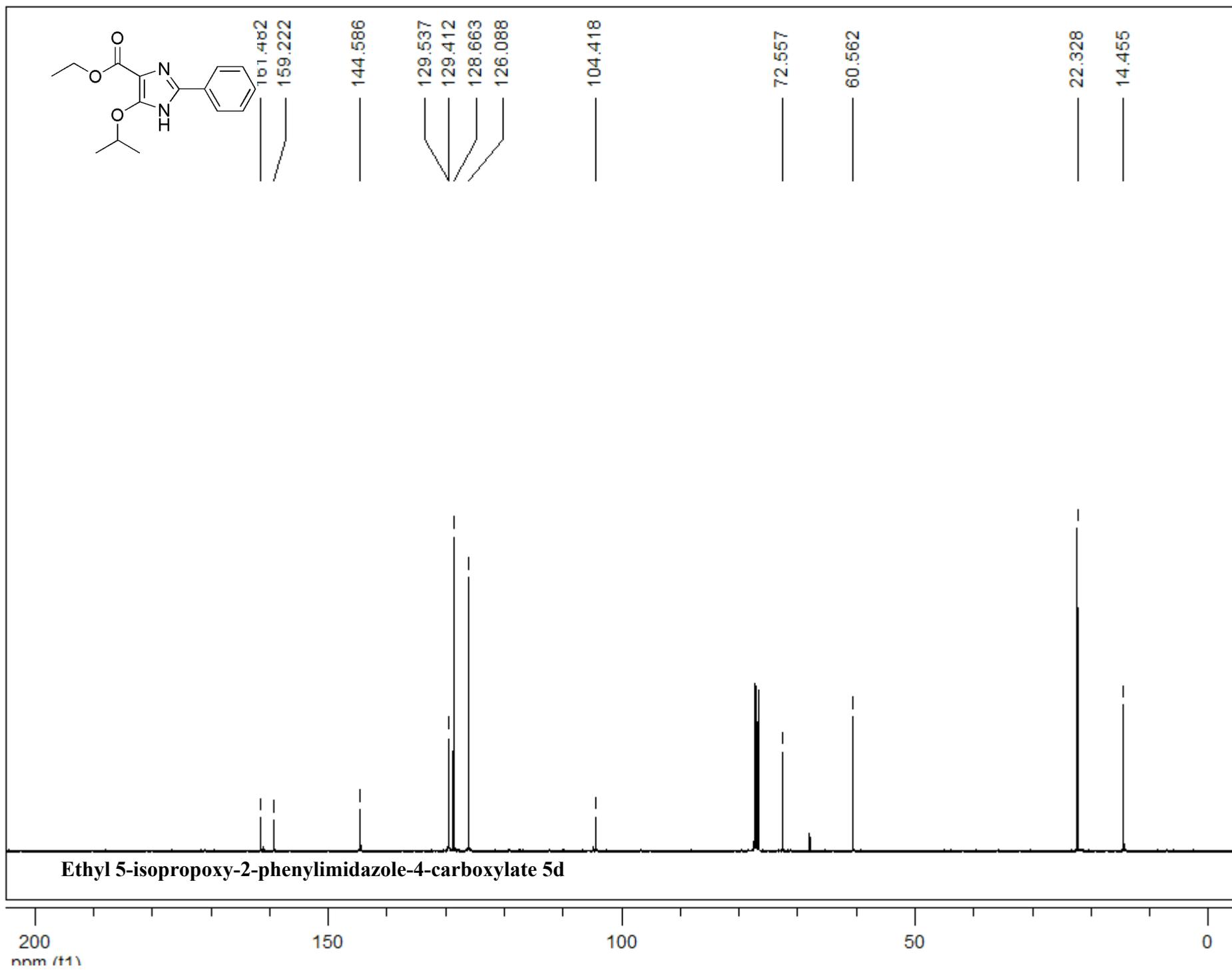
## Ethyl 5-methoxy-2-phenylimidazole-4-carboxylate 5c

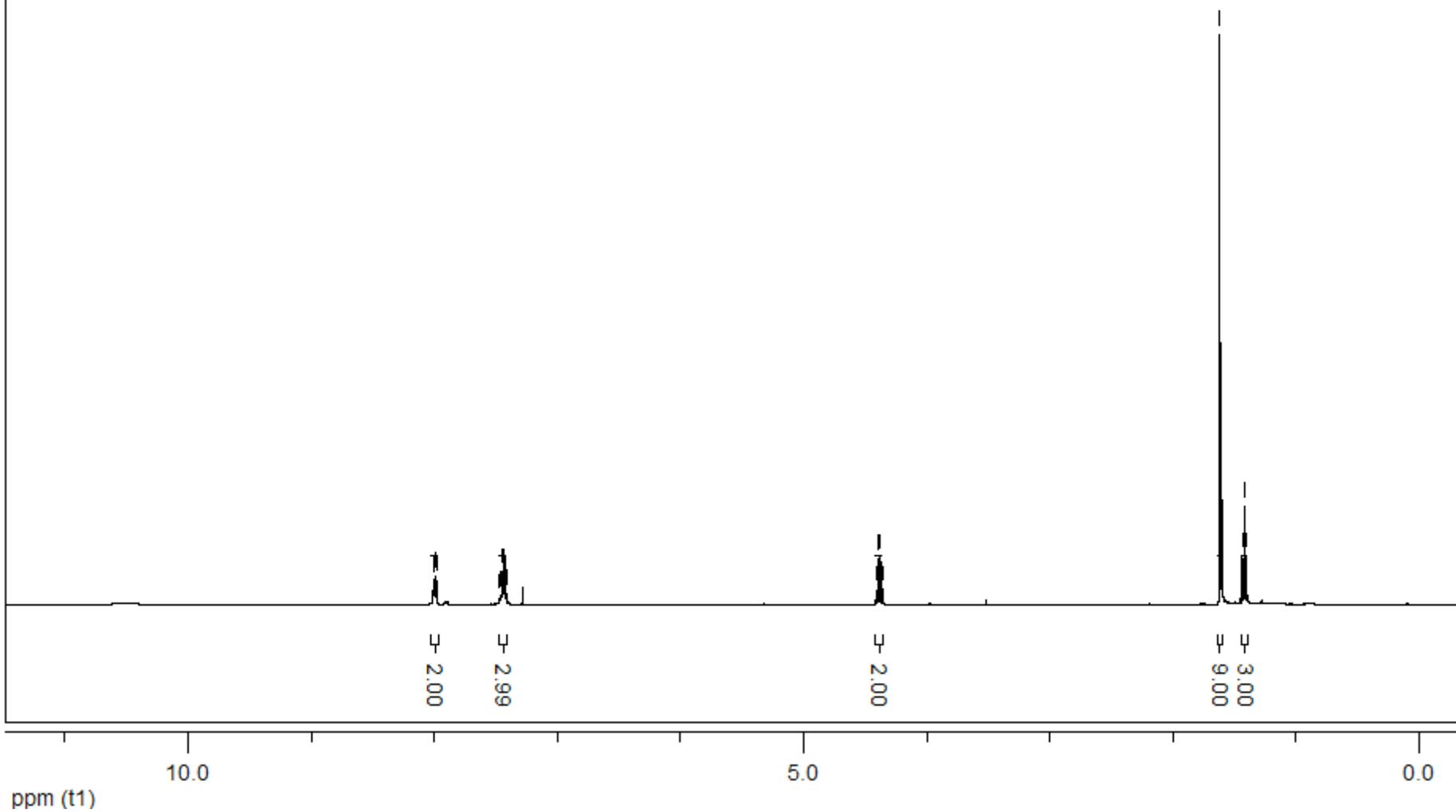
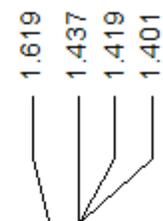
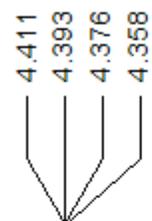
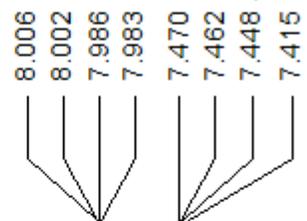
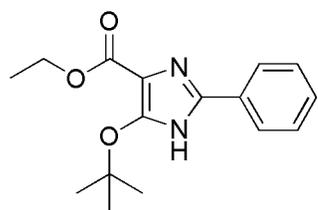


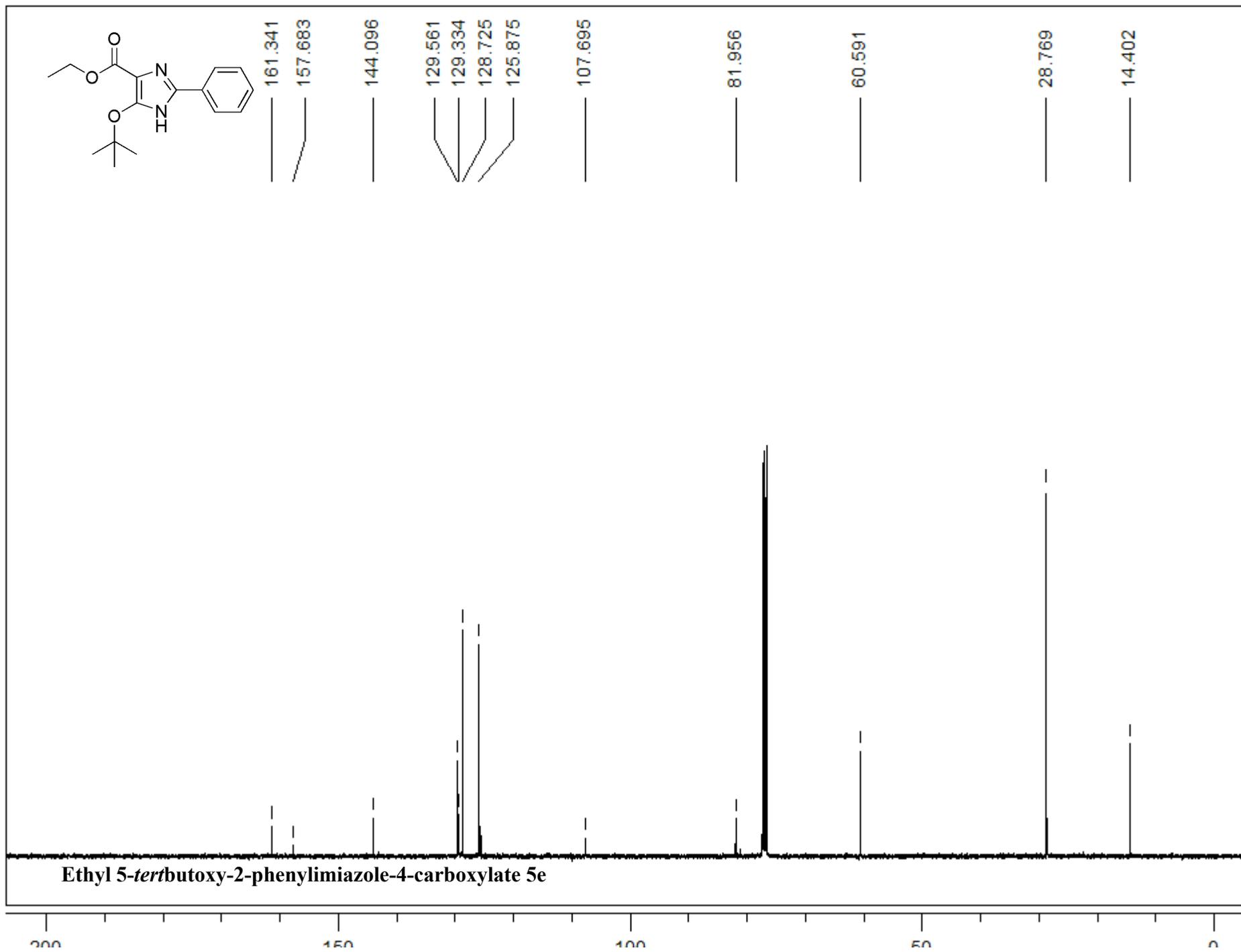


## Ethyl 5-isopropoxy-2-phenylimidazole-4-carboxylate 5d

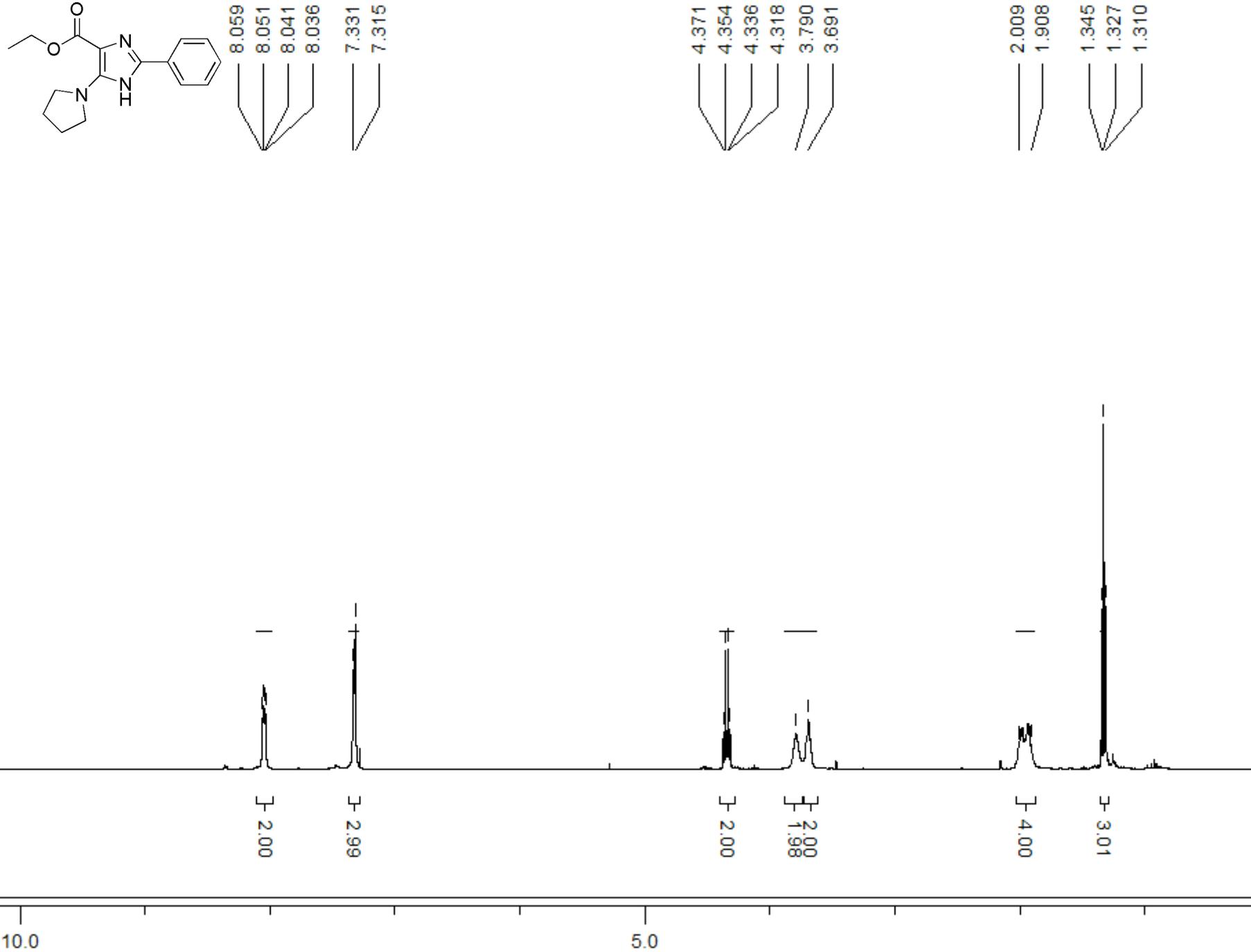


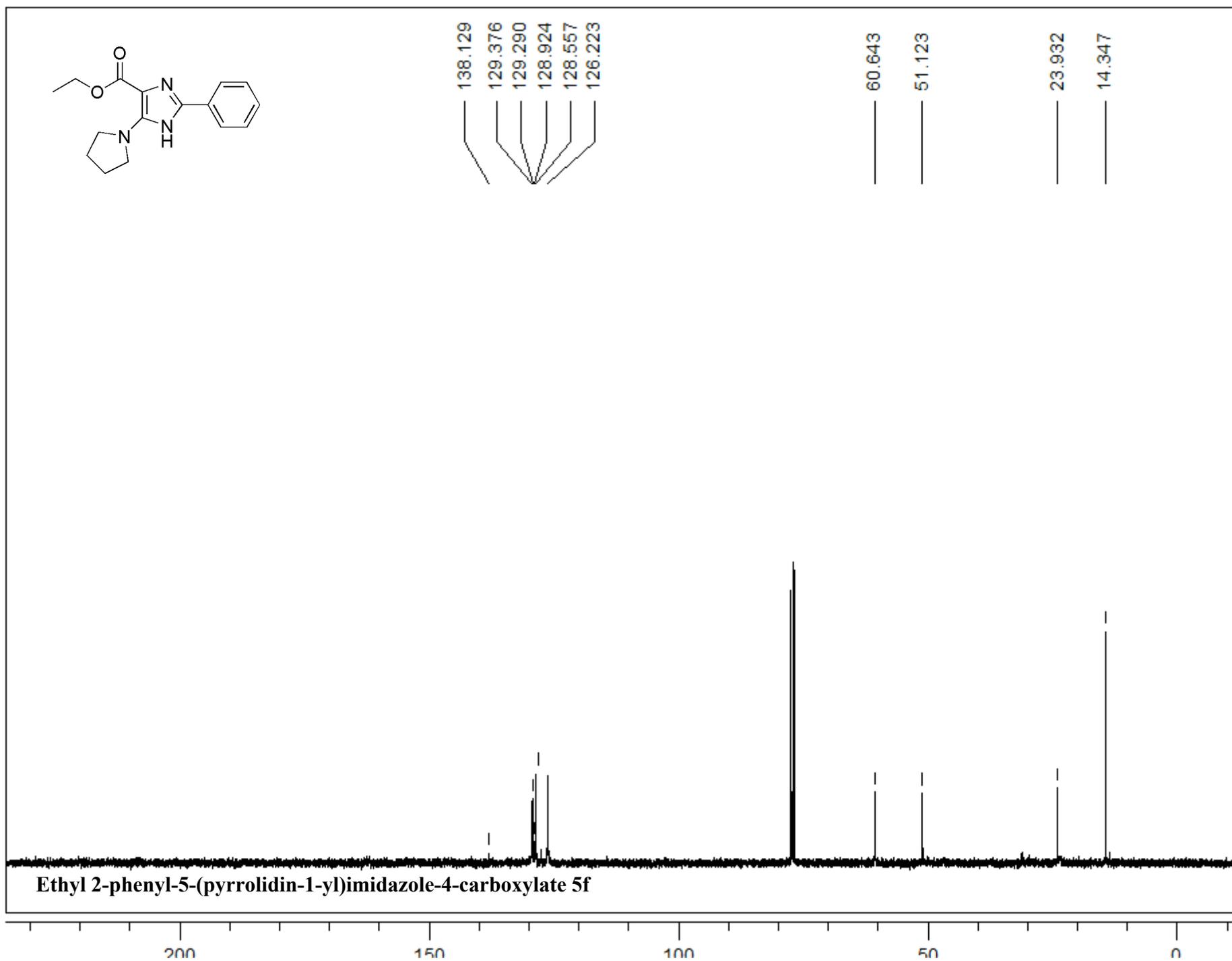


Ethyl 5-*tert*-butoxy-2-phenylimidazole-4-carboxylate 5e

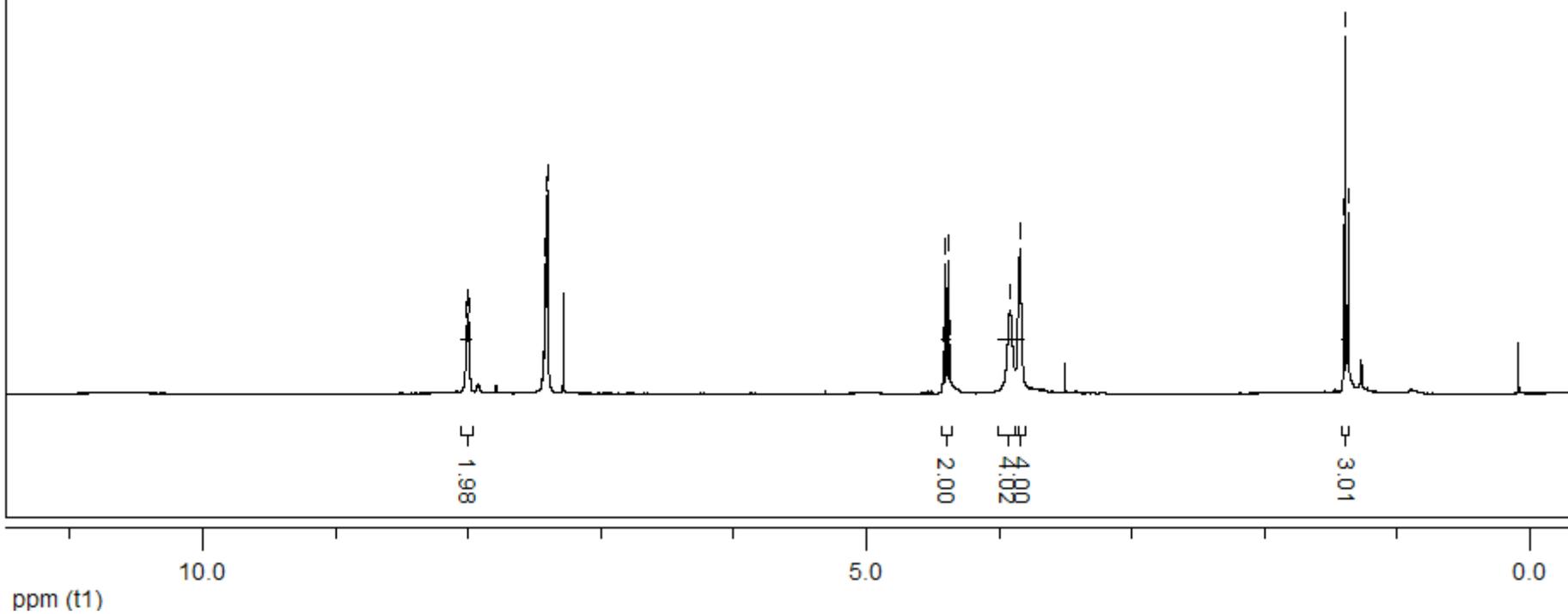
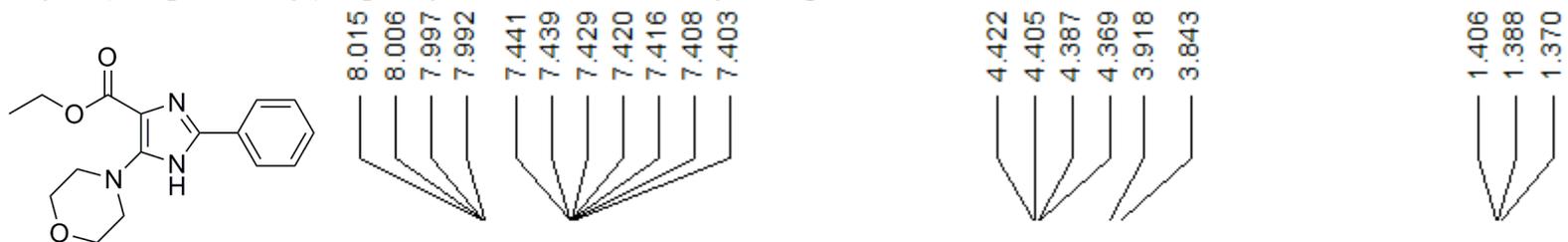


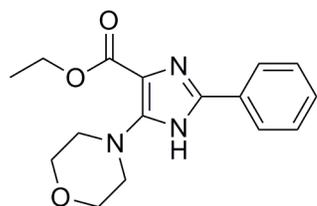
Ethyl 2-phenyl-5-(pyrrolidin-1-yl)imidazole-4-carboxylate 5f





## Ethyl 5-(morpholin-4-yl)-2-phenylimidazole-4-carboxylate 5g





161.048

153.370

147.235

129.755

129.026

128.658

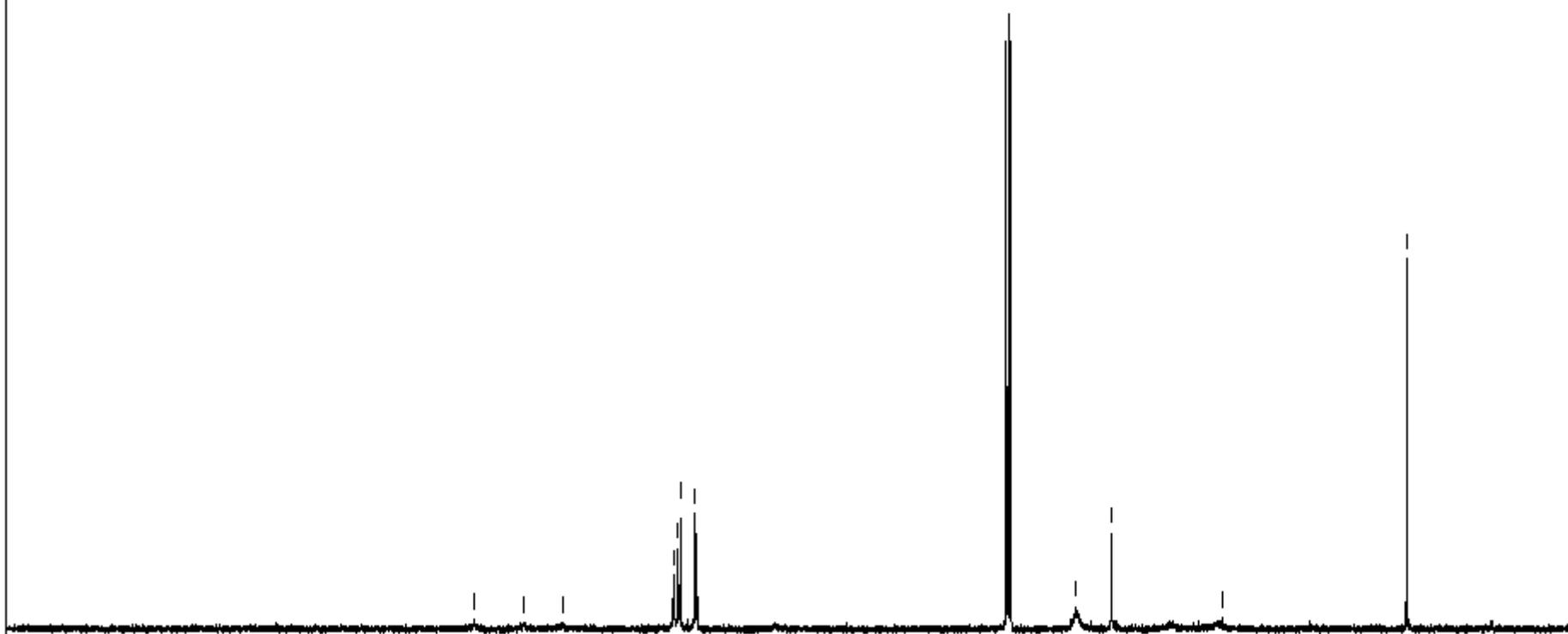
126.338

66.409

60.867

43.505

14.349



Ethyl 5-(morpholin-4-yl)-2-phenylimidazole-4-carboxylate 5g

ppm (f1)

200

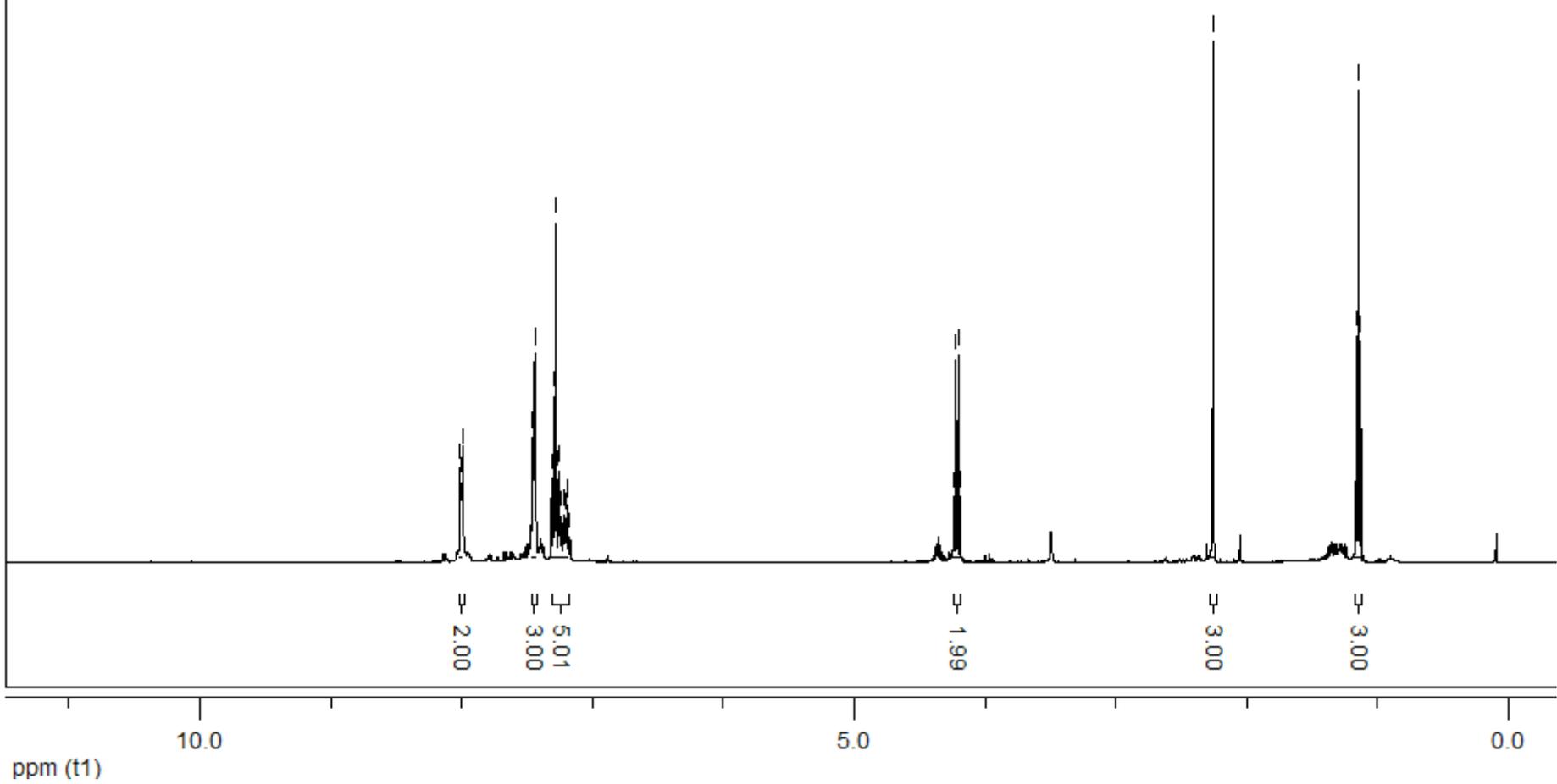
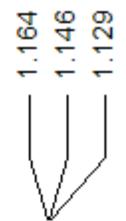
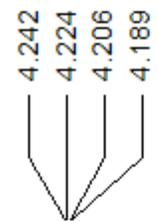
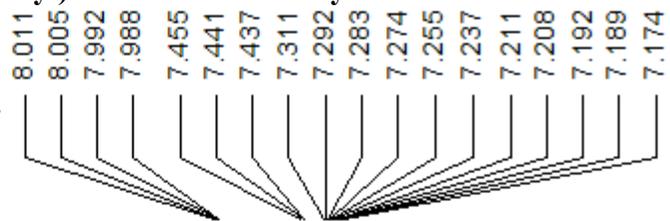
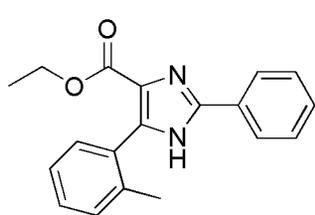
150

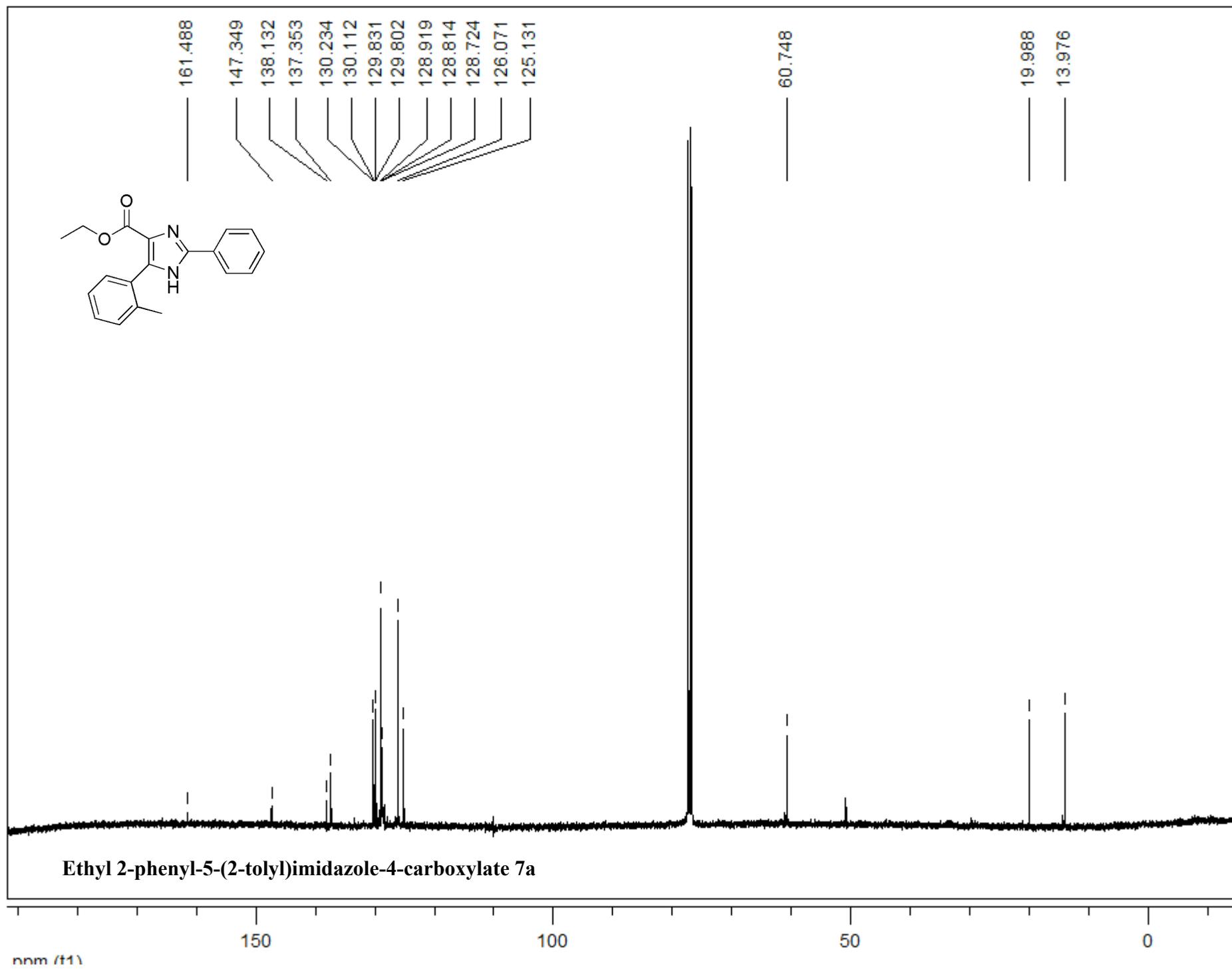
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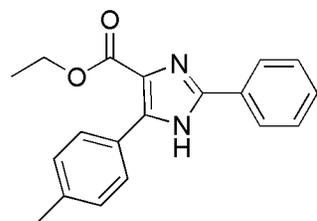
50

0

**Ethyl 2-phenyl-5-(2-tolyl)imidazole-4-carboxylate 7a**





**Ethyl 2-phenyl-5-(4-tolyl)imidazole-4-carboxylate 7b**

8.005  
7.997  
7.985  
7.980  
7.807  
7.787  
7.466  
7.455  
7.450  
7.442  
7.438  
7.243  
7.223

4.375  
4.357  
4.340  
4.322

2.401

1.353  
1.335  
1.317

2.19  
2.00  
3.23  
2.01

2.00

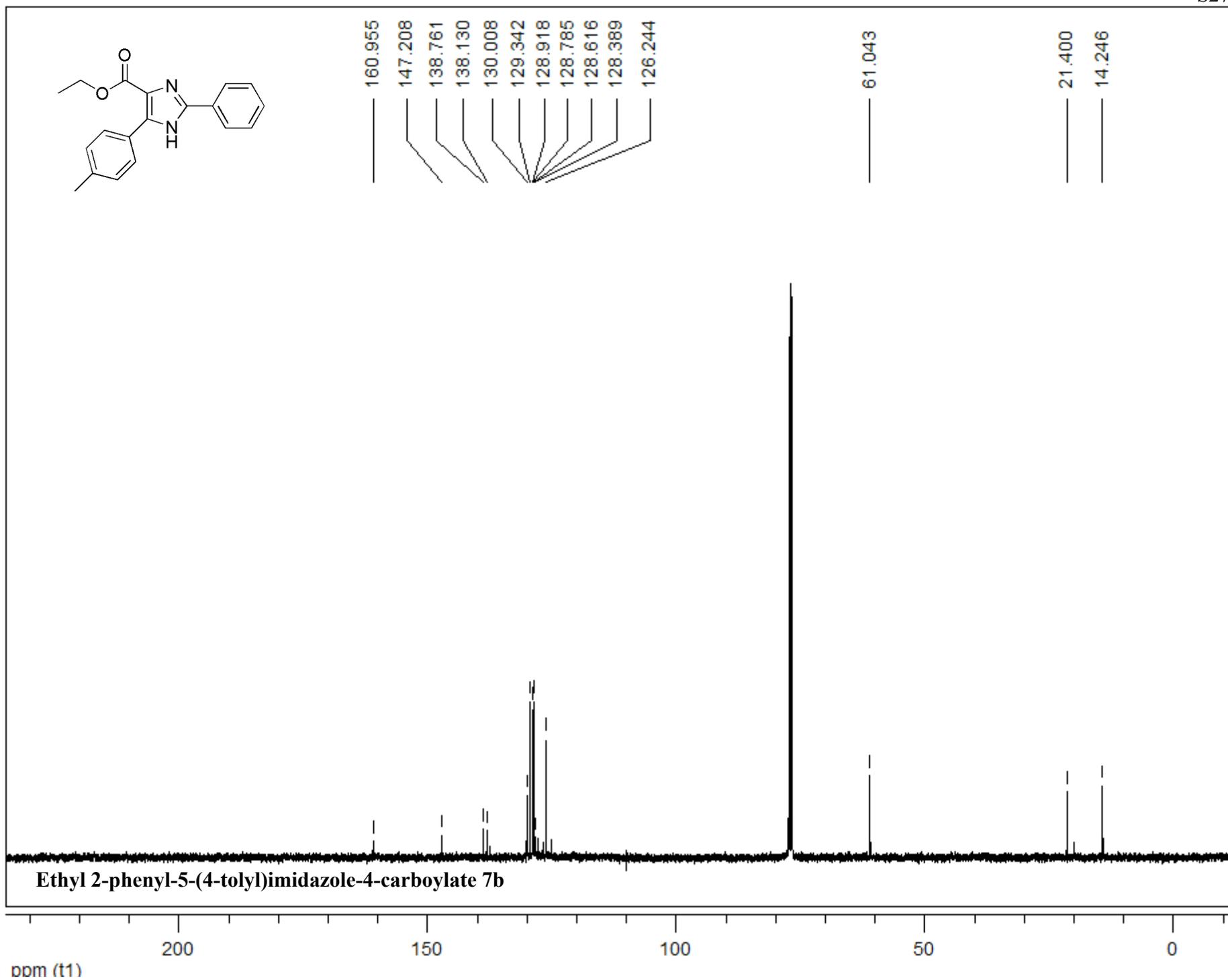
3.02

2.98

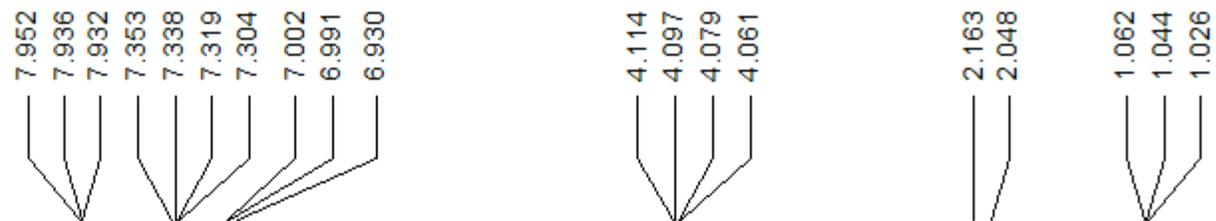
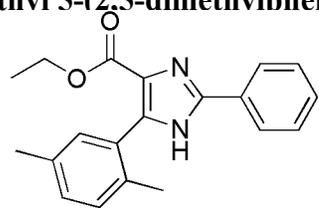
10.0

5.0

0.0



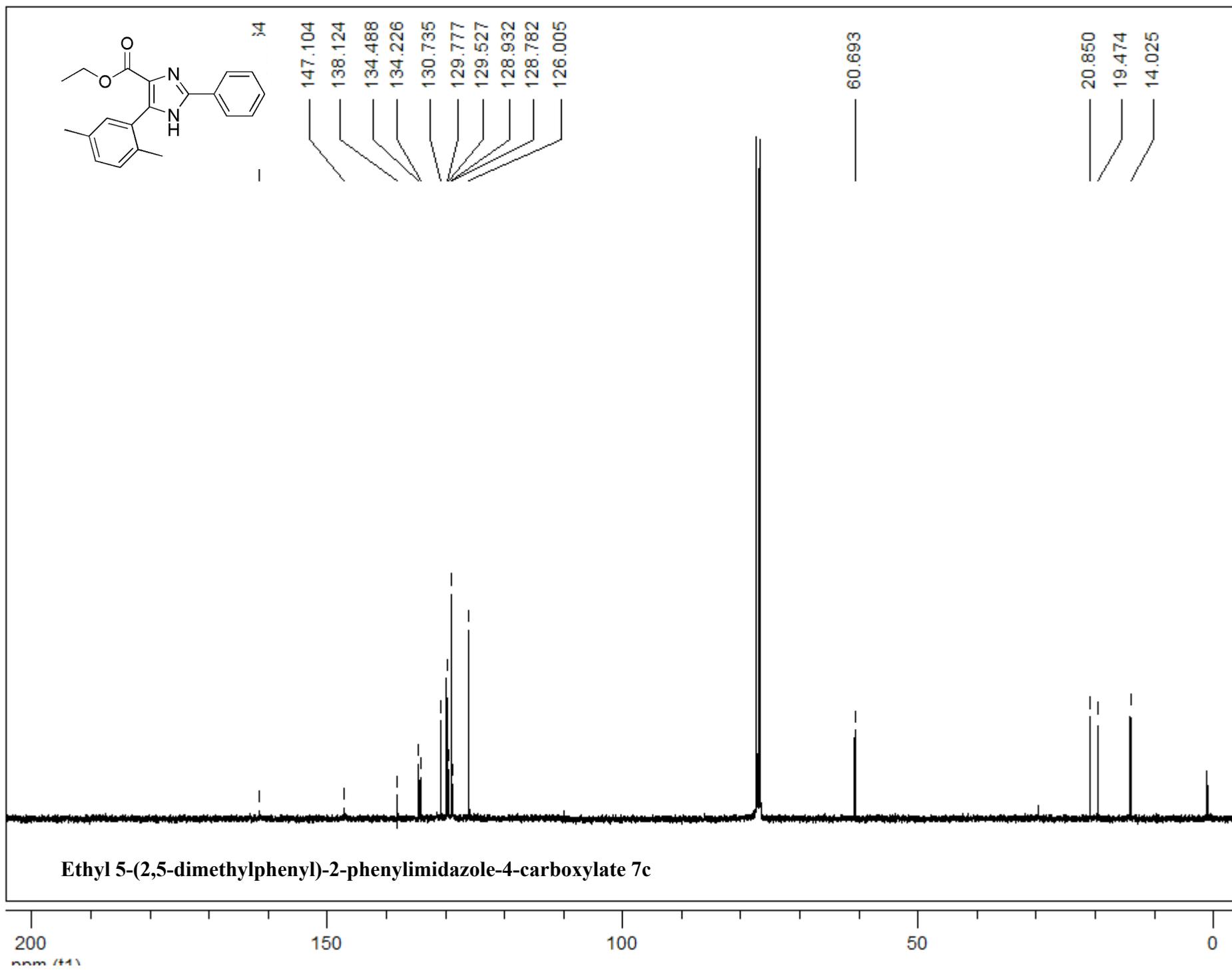
Ethyl 5-(2,5-dimethylphenyl)-2-phenylimidazole-4-carboxylate 7c



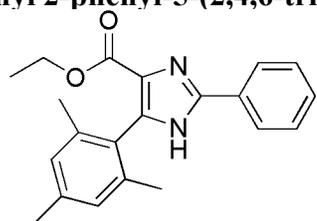
100

50

00



Ethyl 2-phenyl-5-(2,4,6-trimethylphenyl)imidazole-4-carboxylate 7d



8.010  
8.008  
7.997  
7.995  
7.977  
7.975  
7.955  
6.889

4.211  
4.194  
4.176  
4.158

2.311  
2.064

1.146  
1.128  
1.110

1.99

3.00

2.00

2.00

3.00

6.00

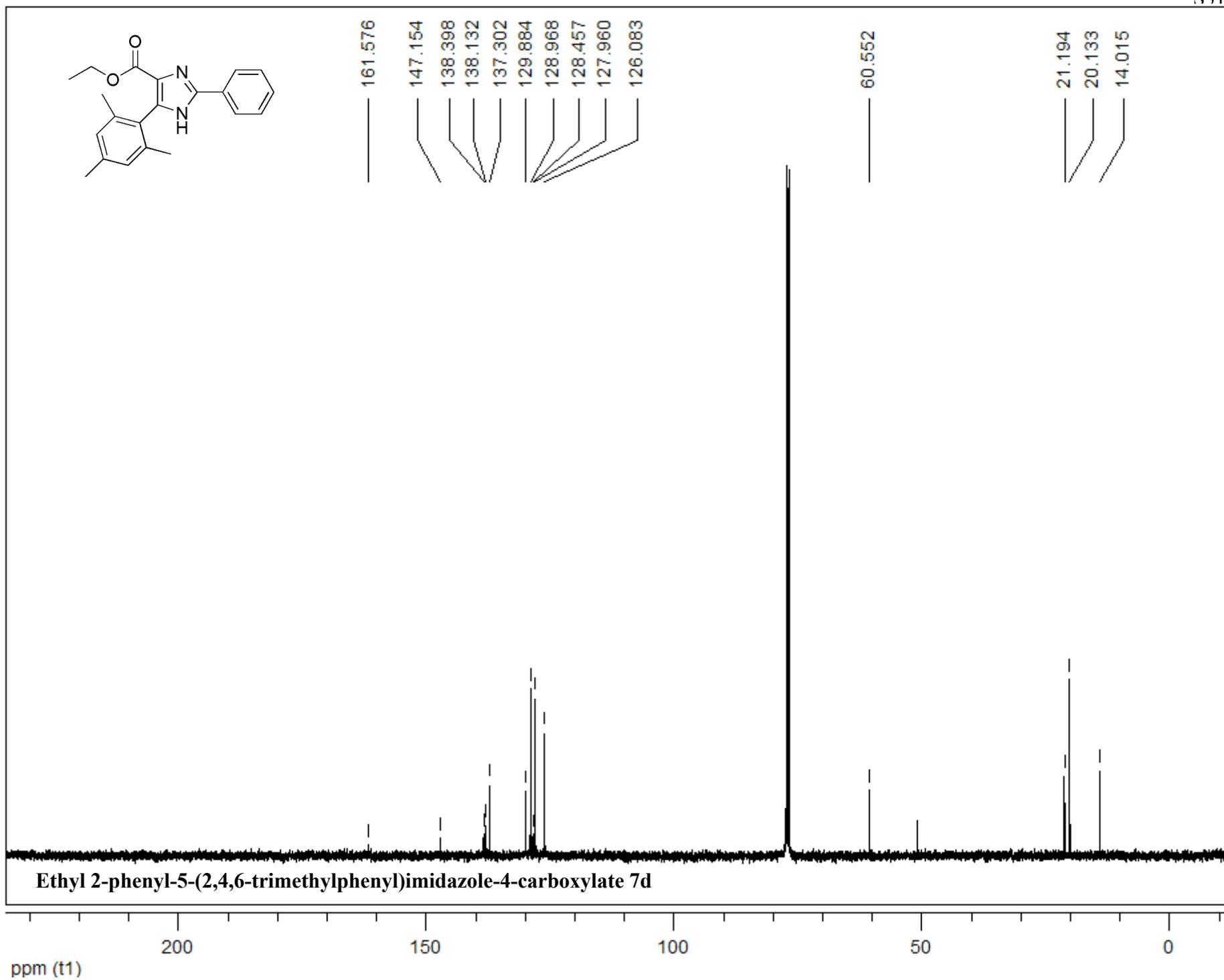
2.99

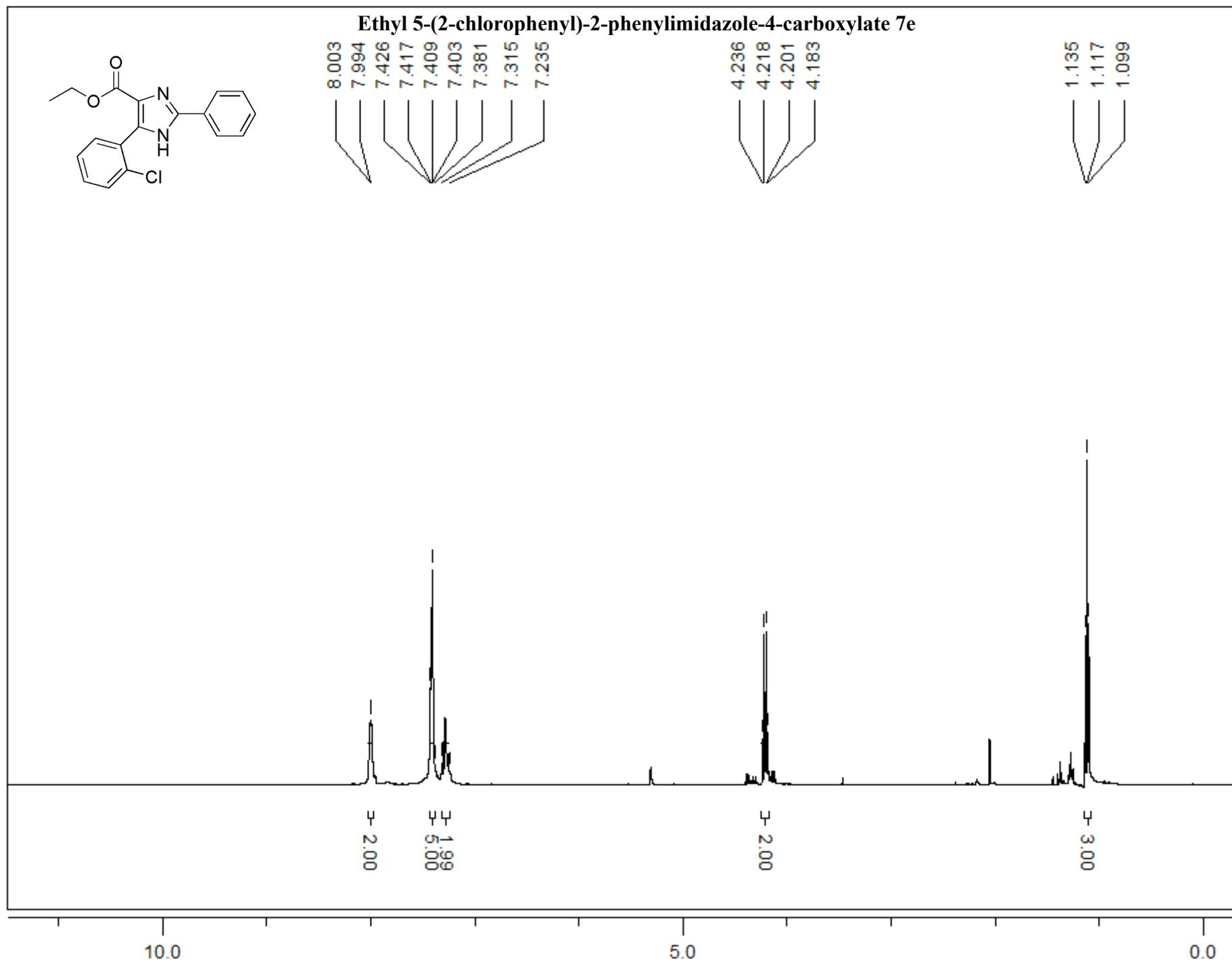
ppm (t1)

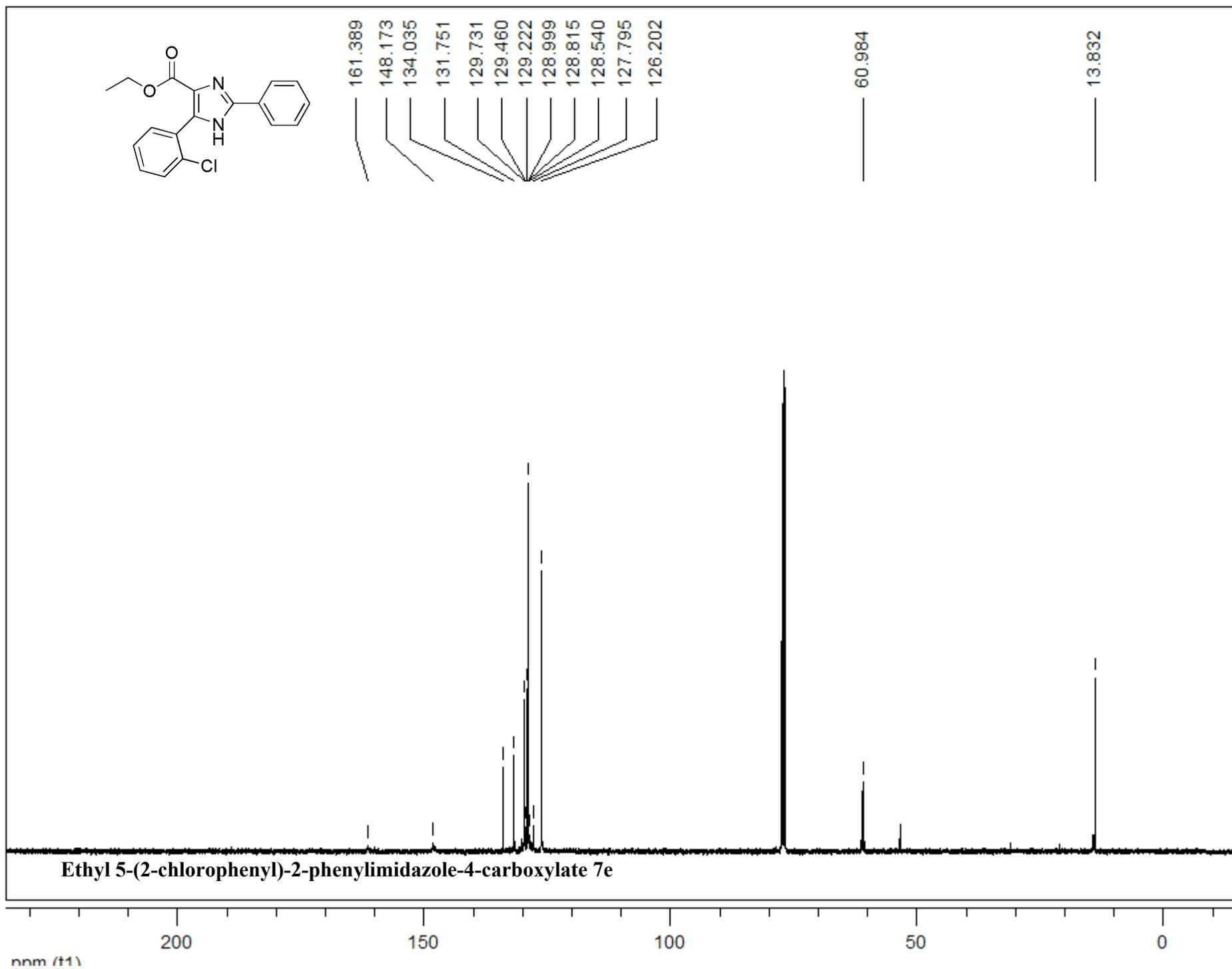
10.0

5.0

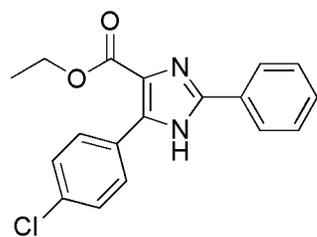
0.0







Ethyl 5-(4-chloro-phenyl)-2-phenylimidazole-4-carboxylate 7f



8.001  
7.993  
7.983  
7.976  
7.830  
7.815  
7.435  
7.427  
7.423  
7.371  
7.350

4.347  
4.329  
4.312  
4.294

1.312  
1.294  
1.276

1.98  
2.00

3.84

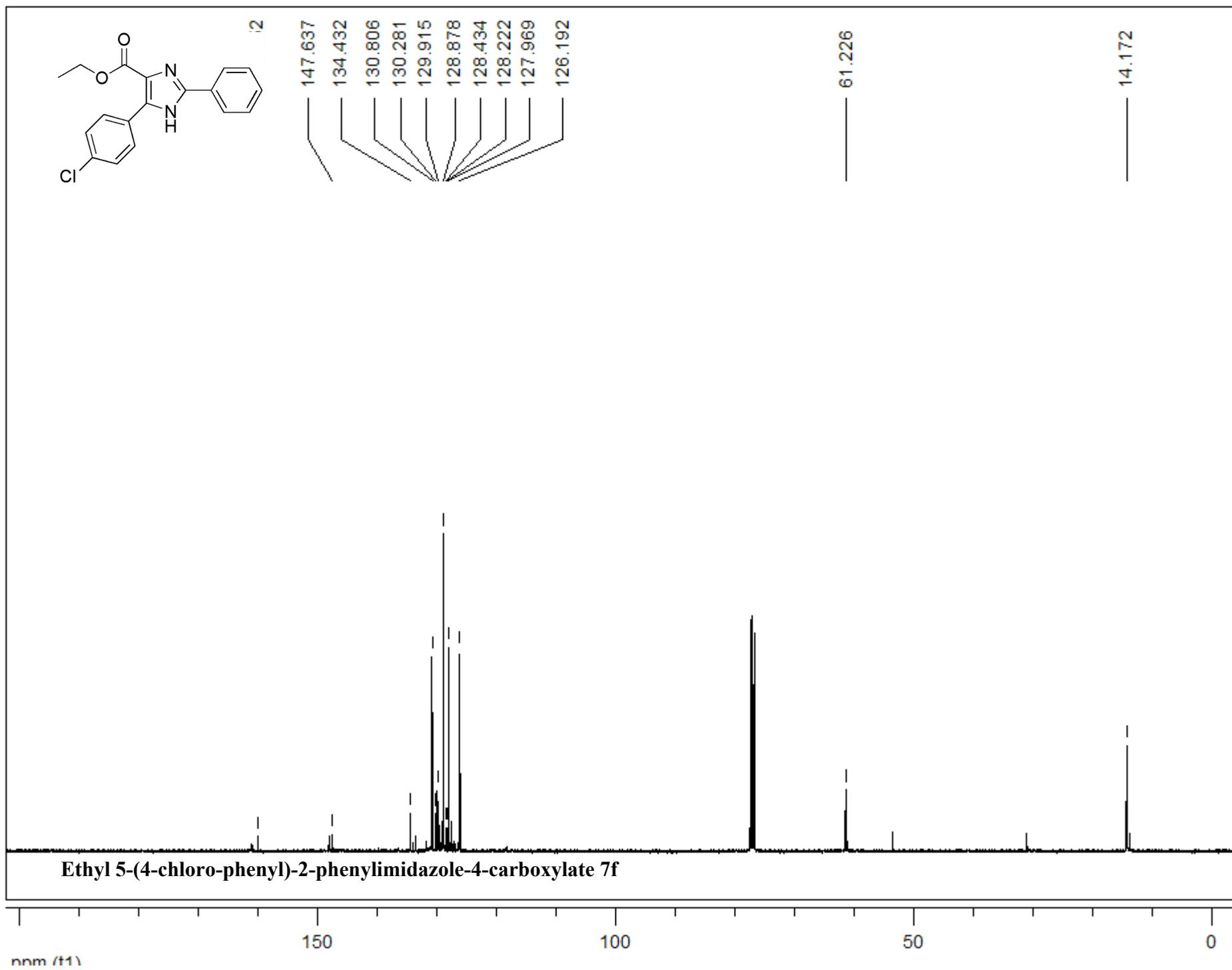
1.99

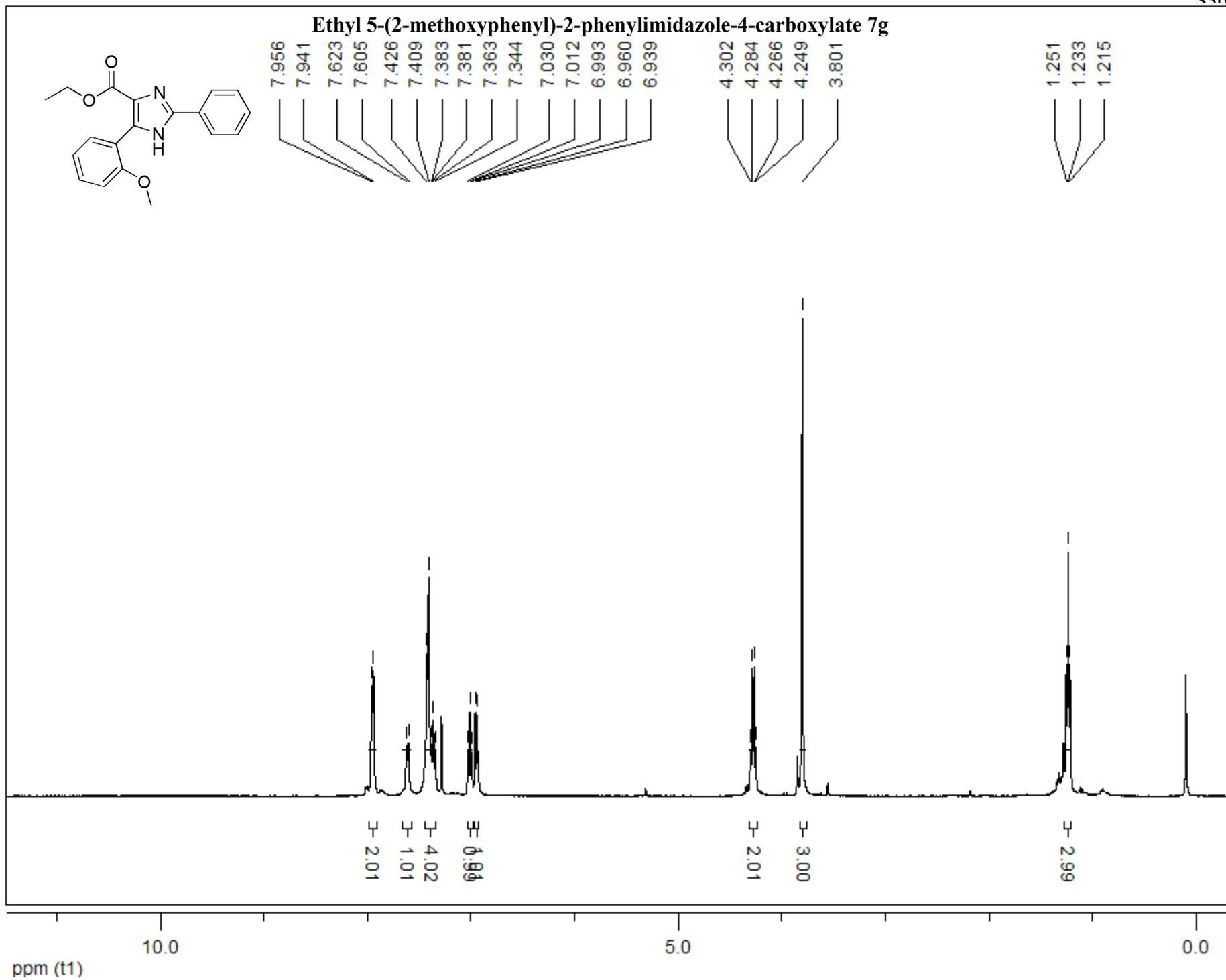
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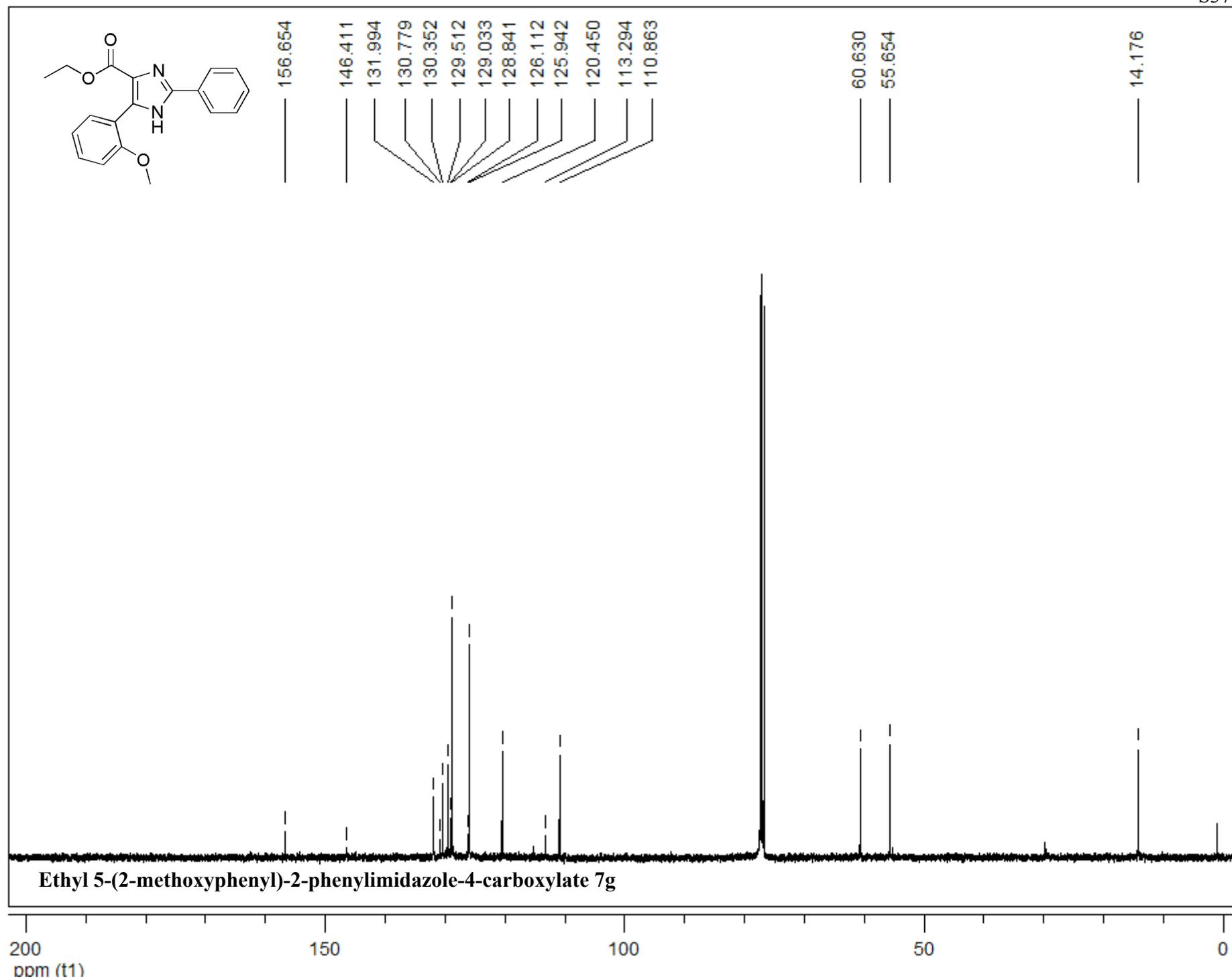
10.0

5.0

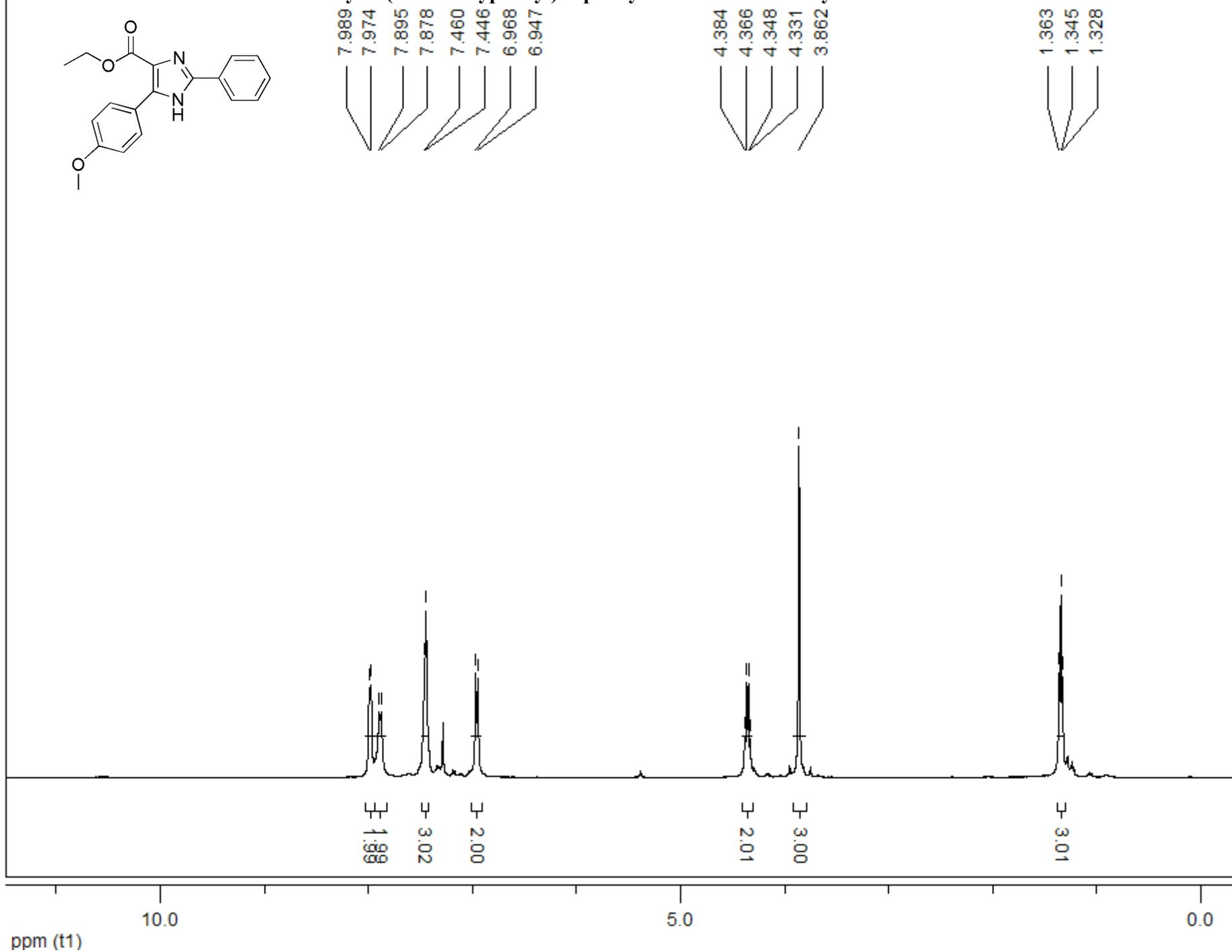
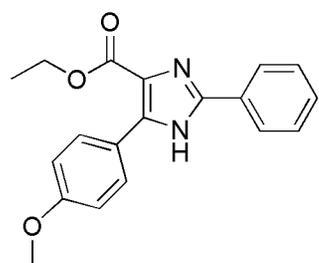
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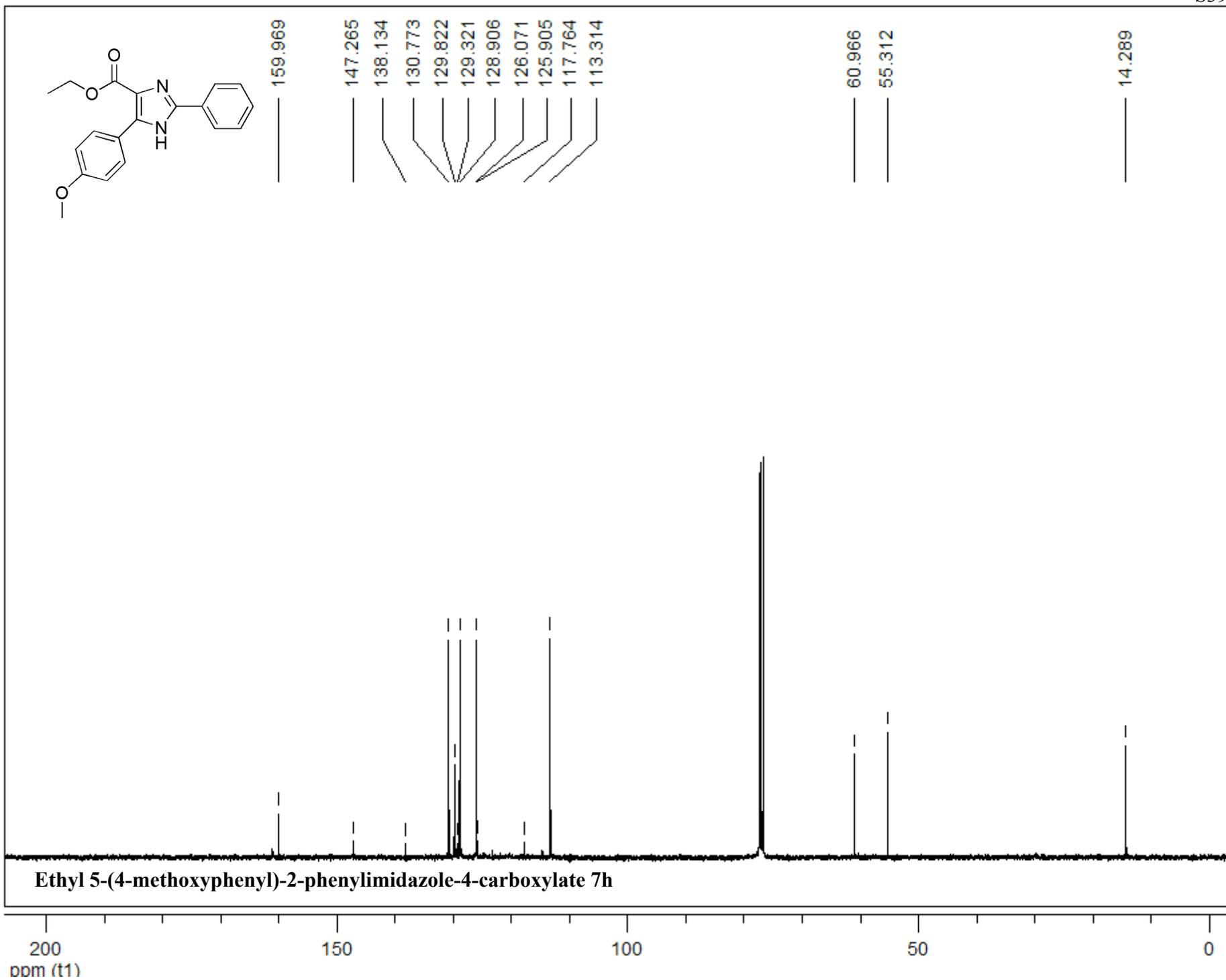


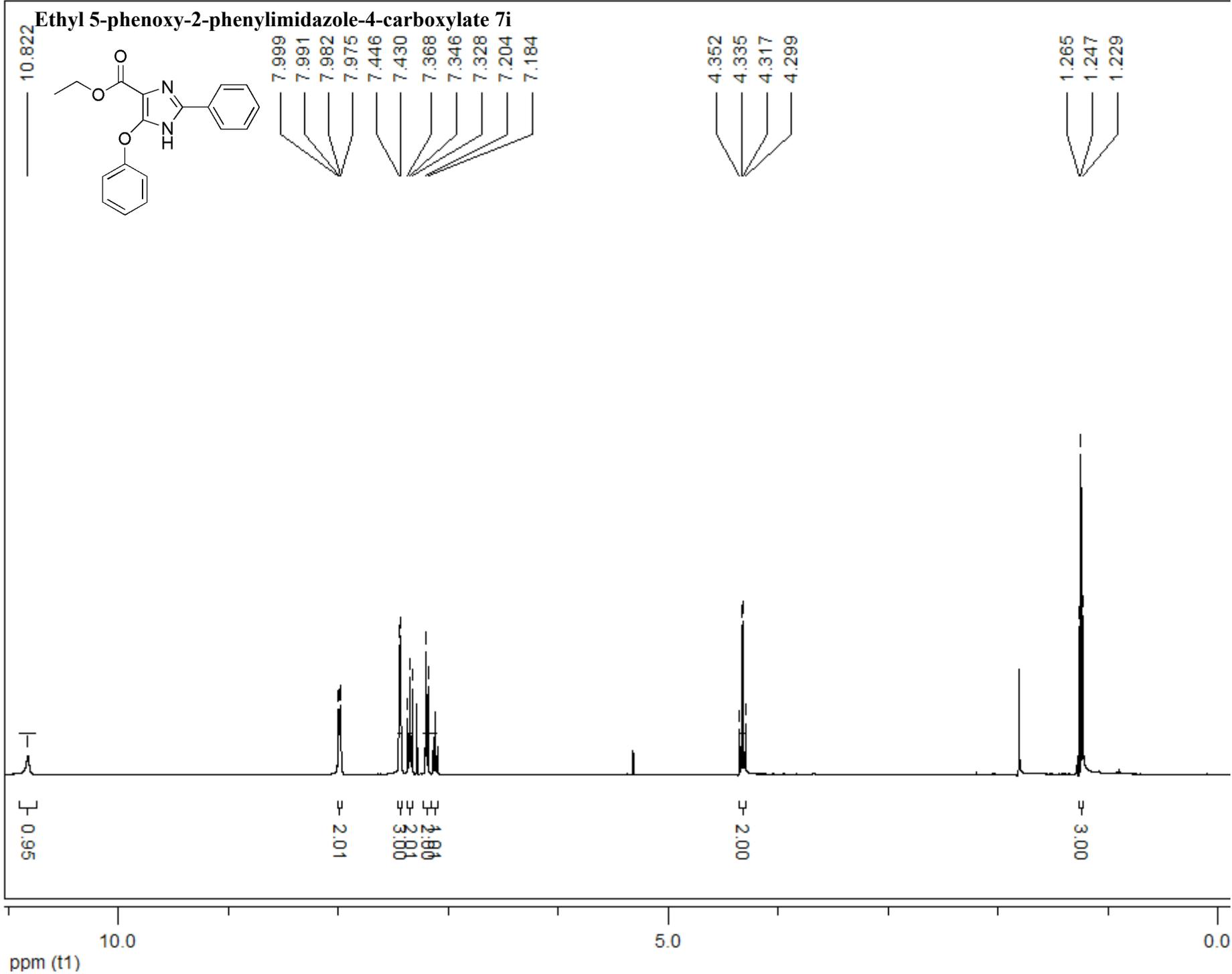


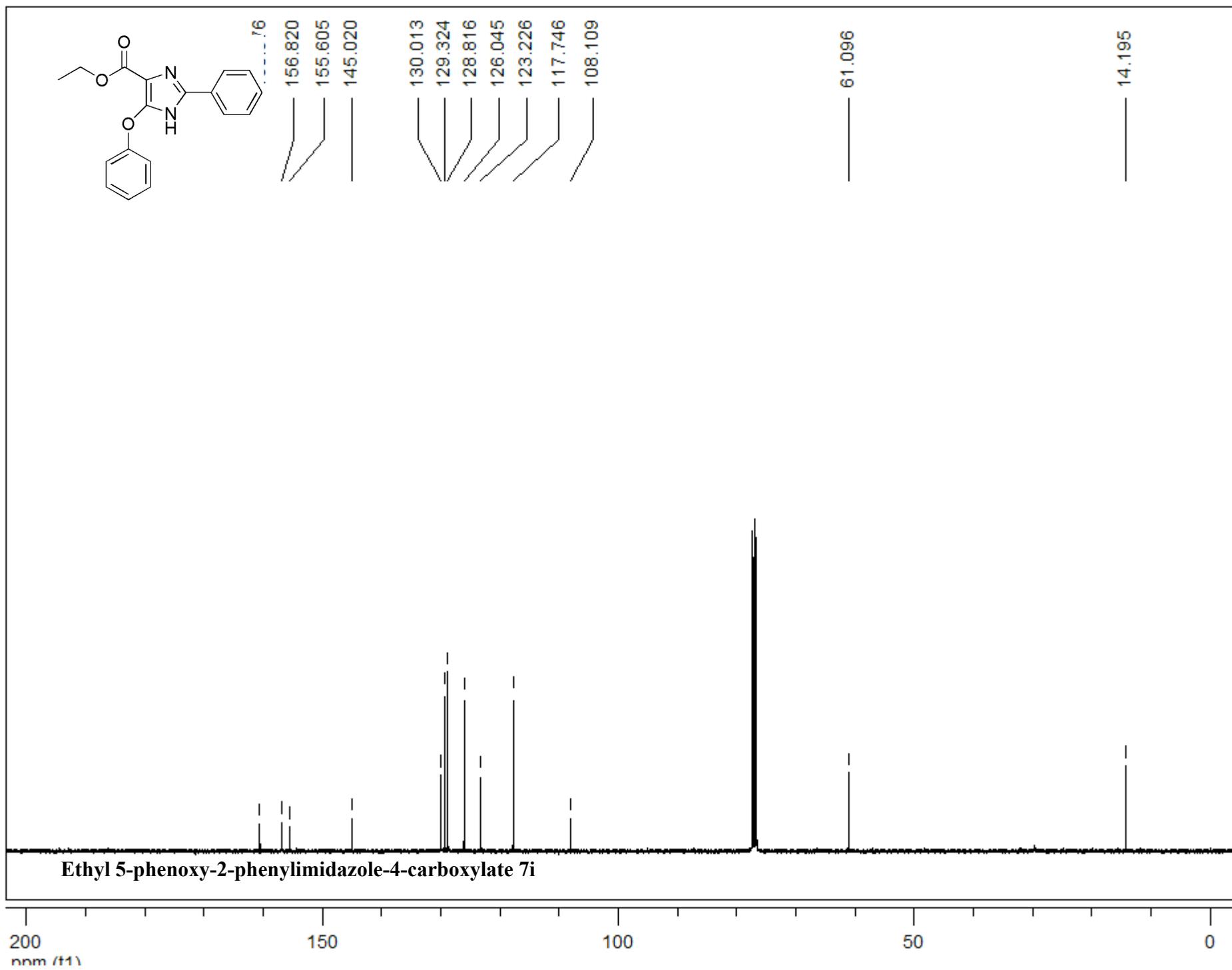


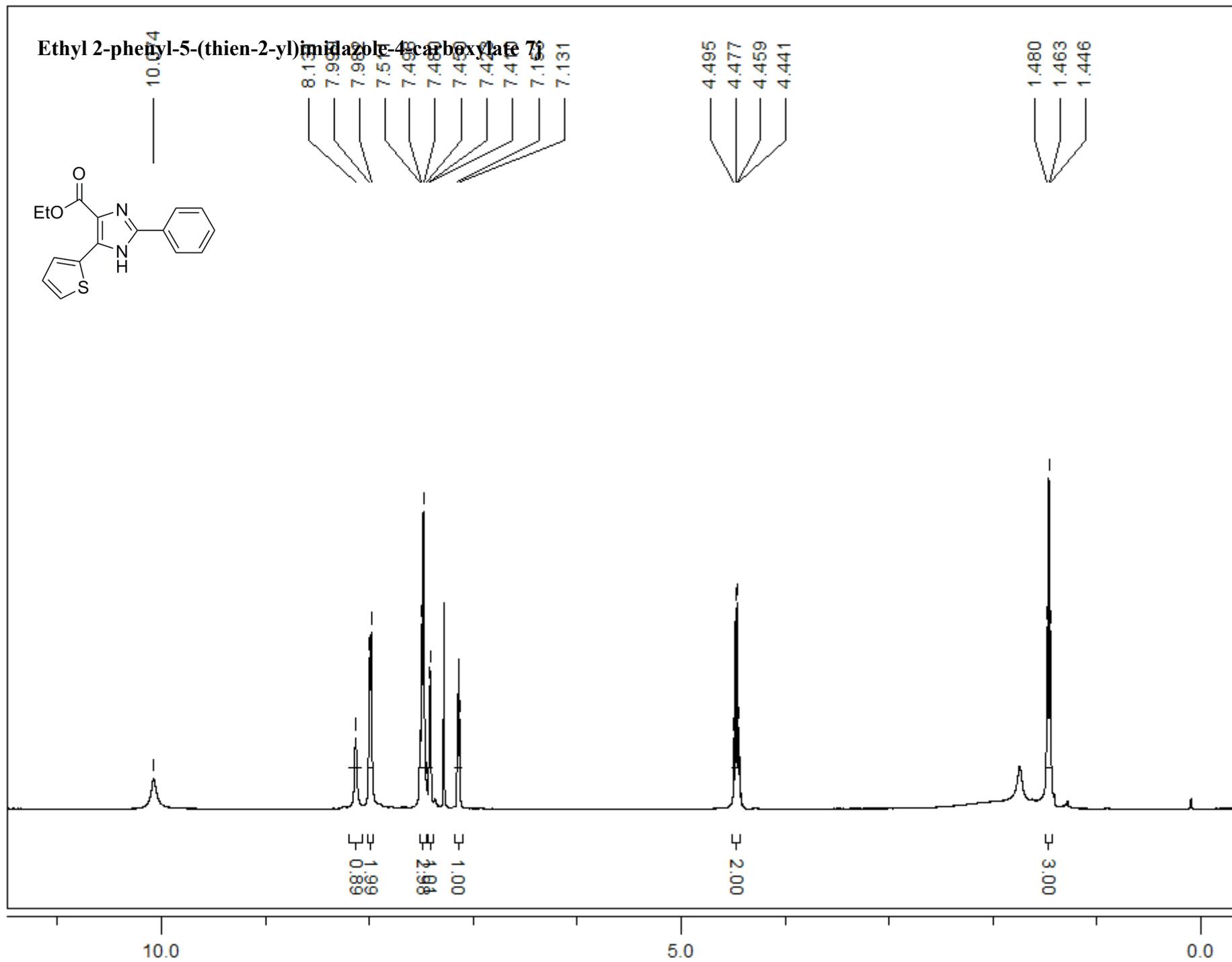
Ethyl 5-(4-methoxyphenyl)-2-phenylimidazole-4-carboxylate 7h

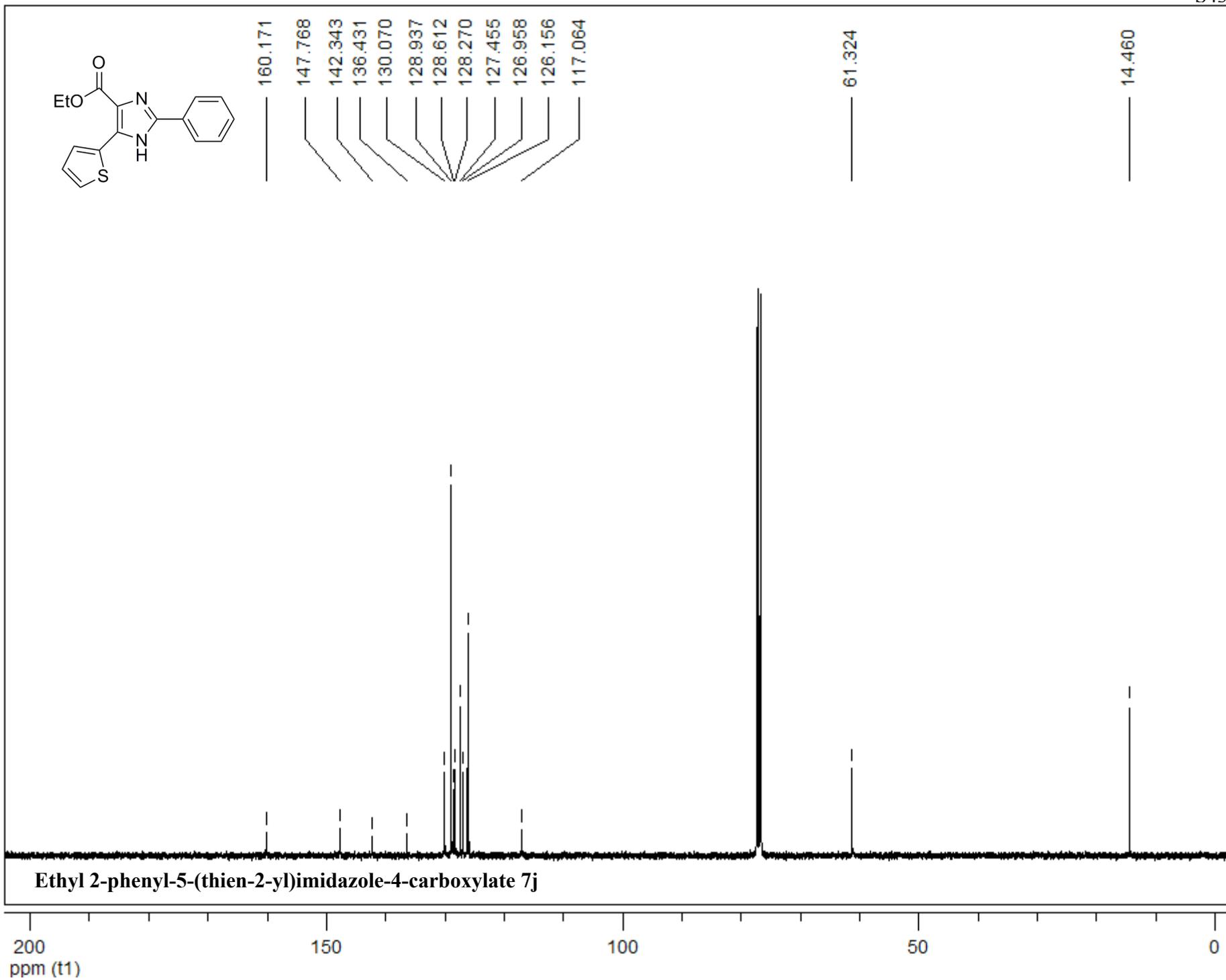




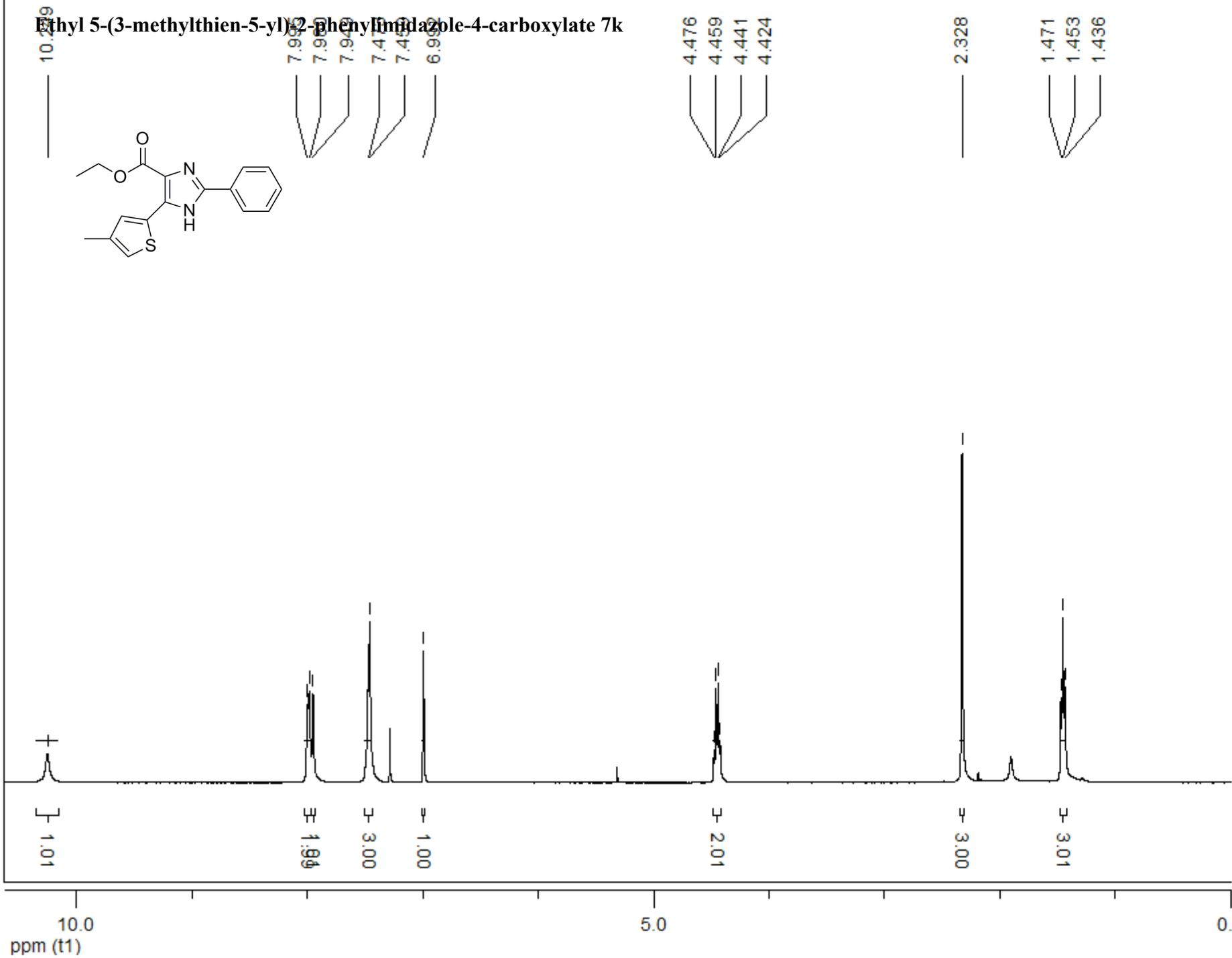
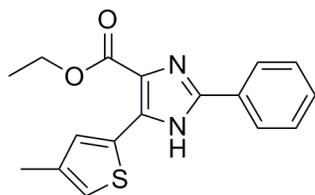


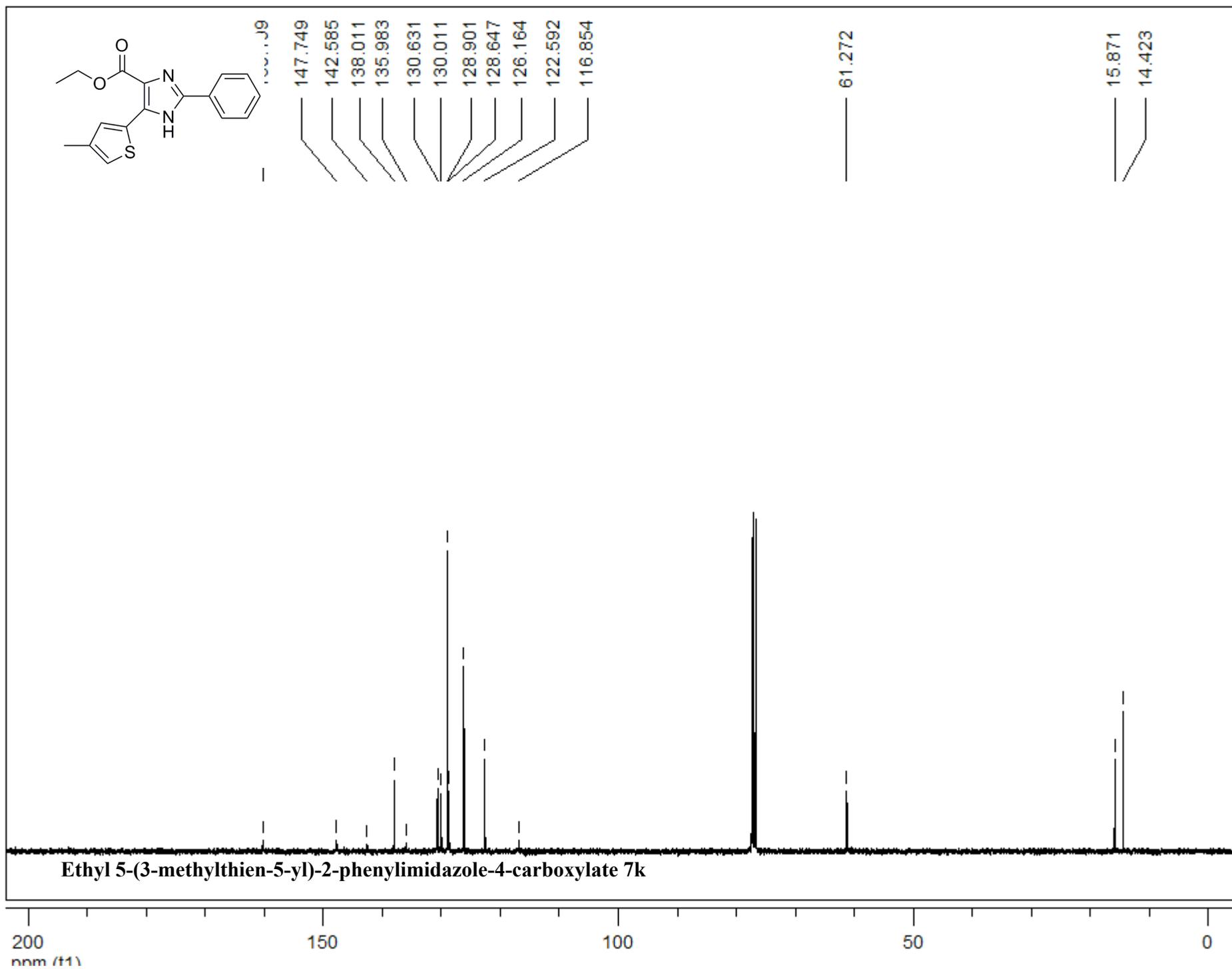




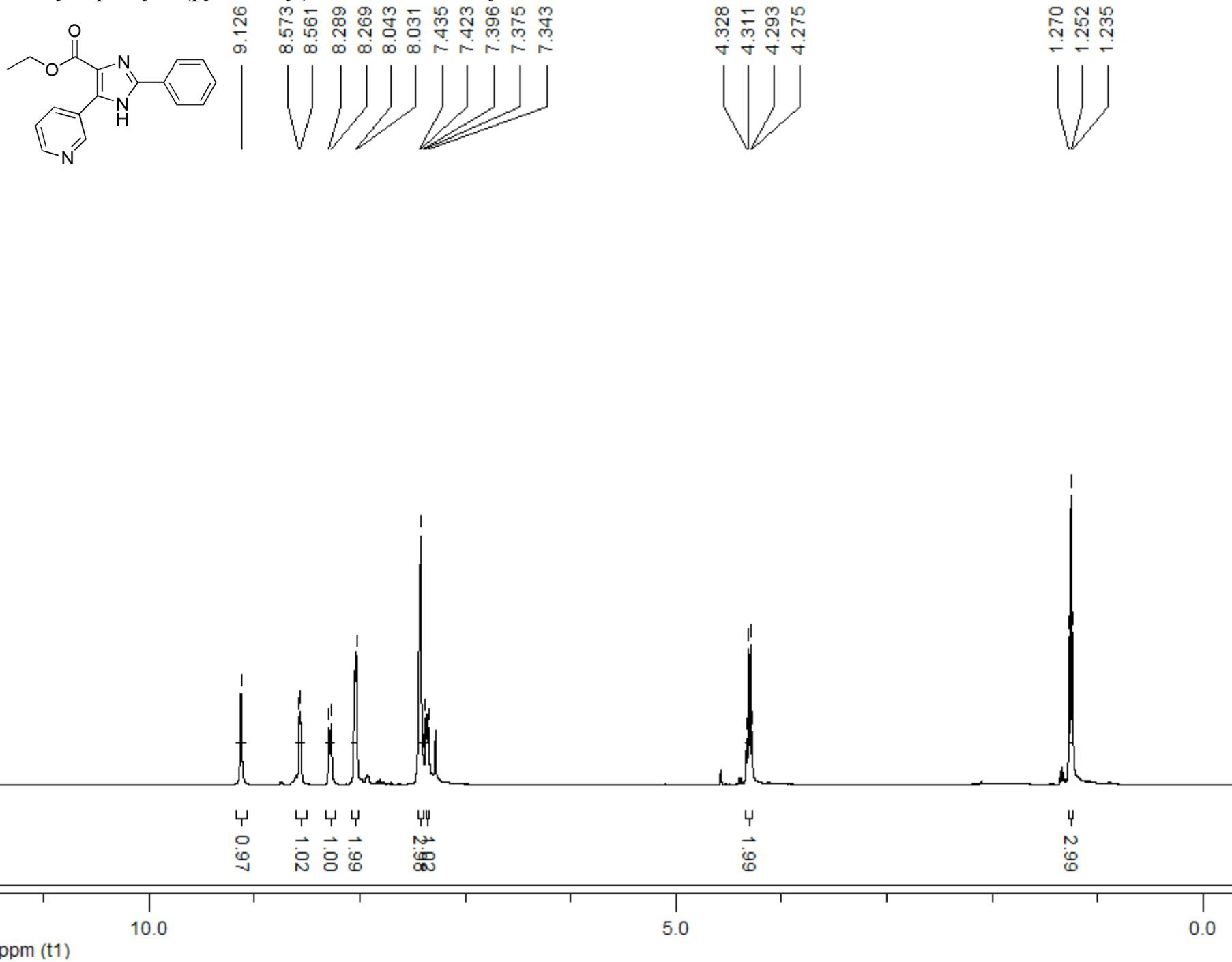


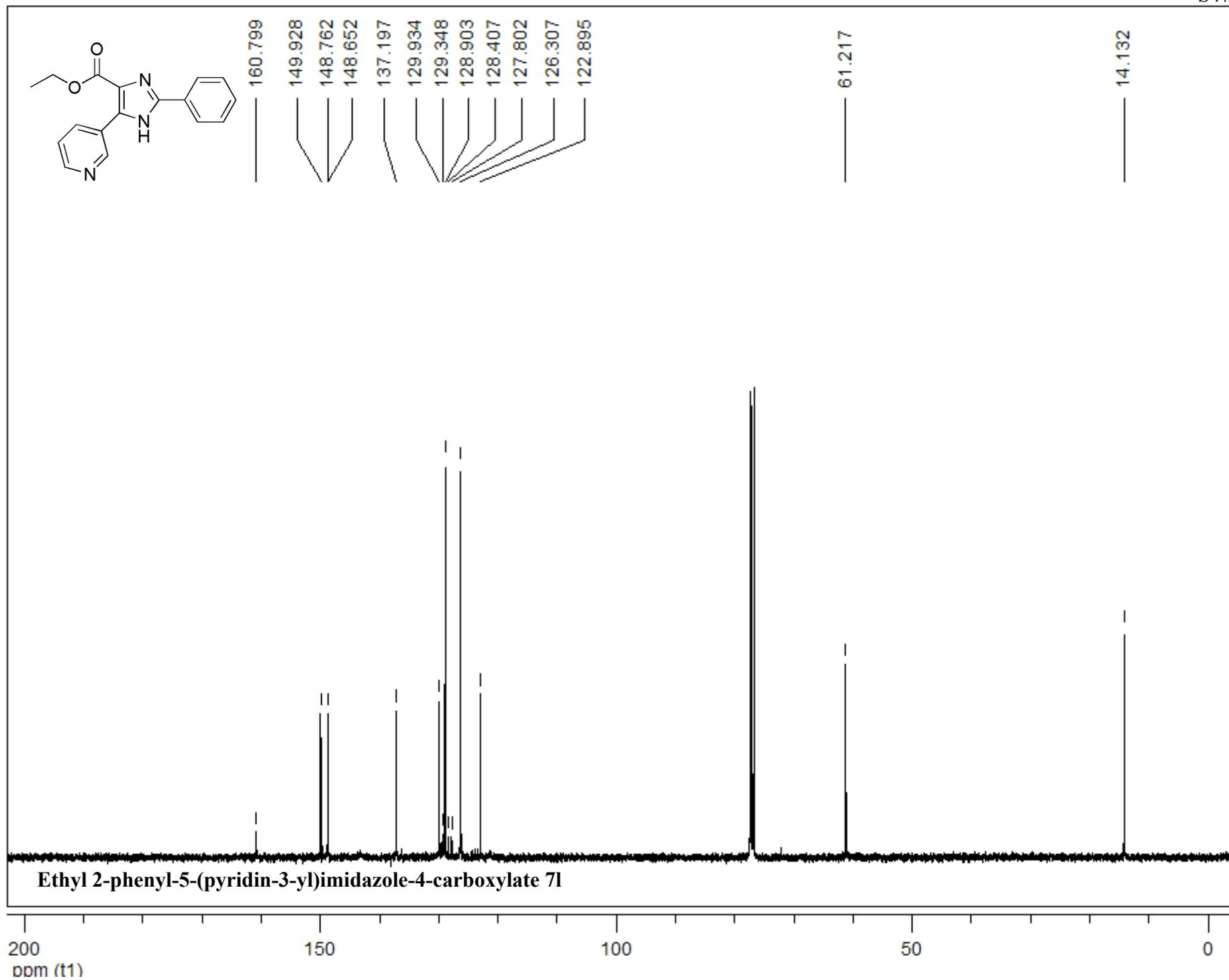
Ethyl 5-(3-methylthien-5-yl)-2-phenylimidazole-4-carboxylate 7k



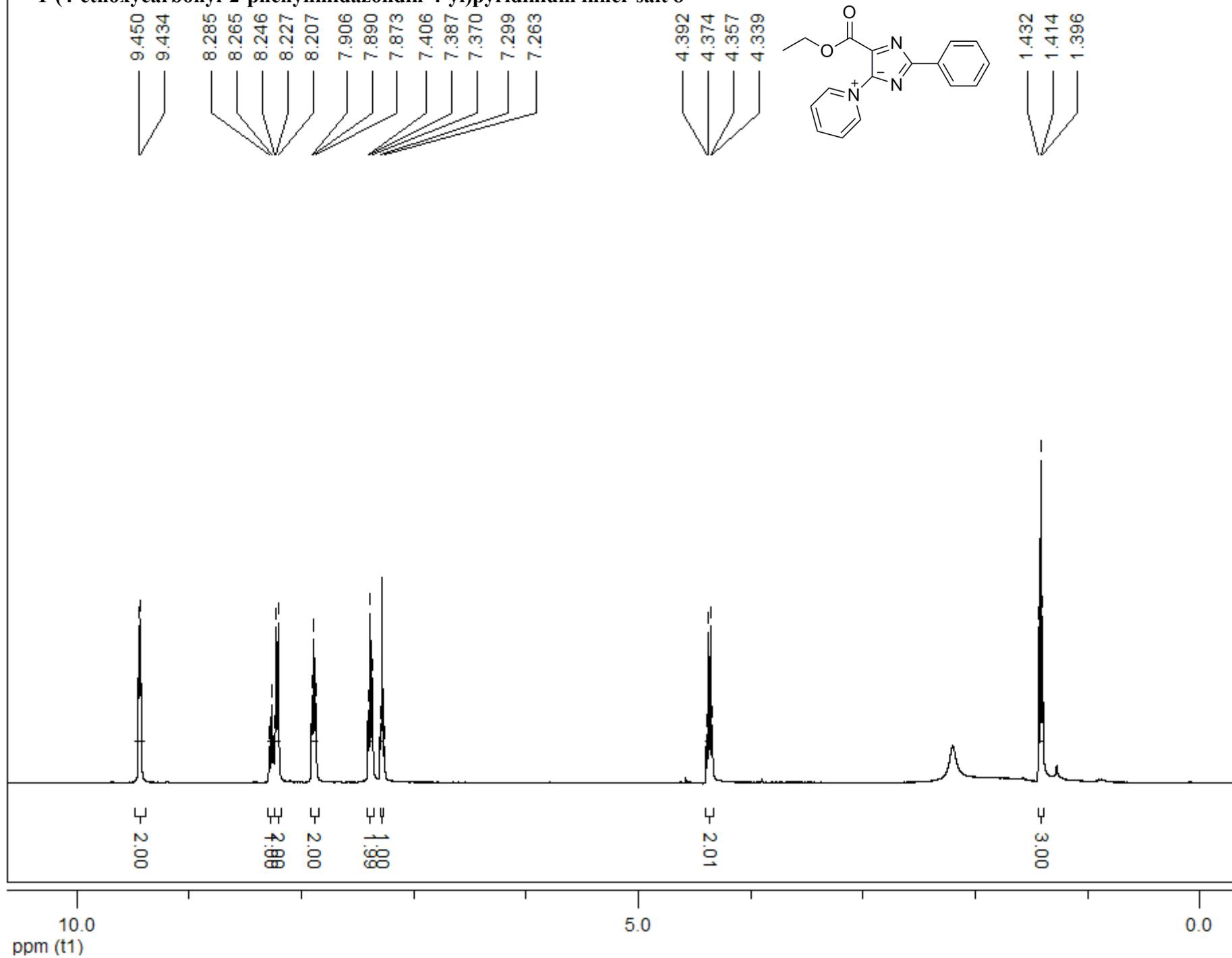


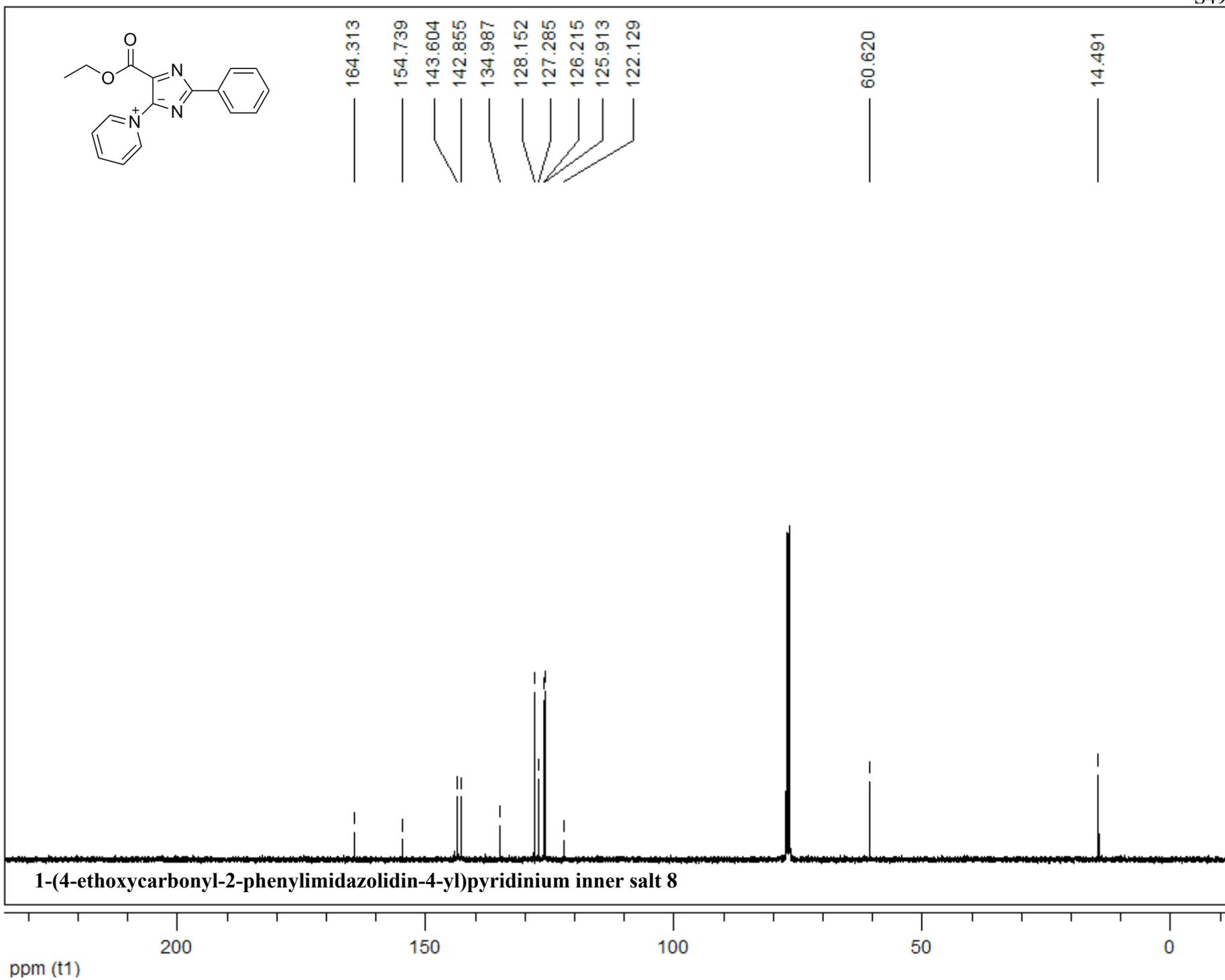
## Ethyl 2-phenyl-5-(pyridin-3-yl)imidazole-4-carboxylate 71



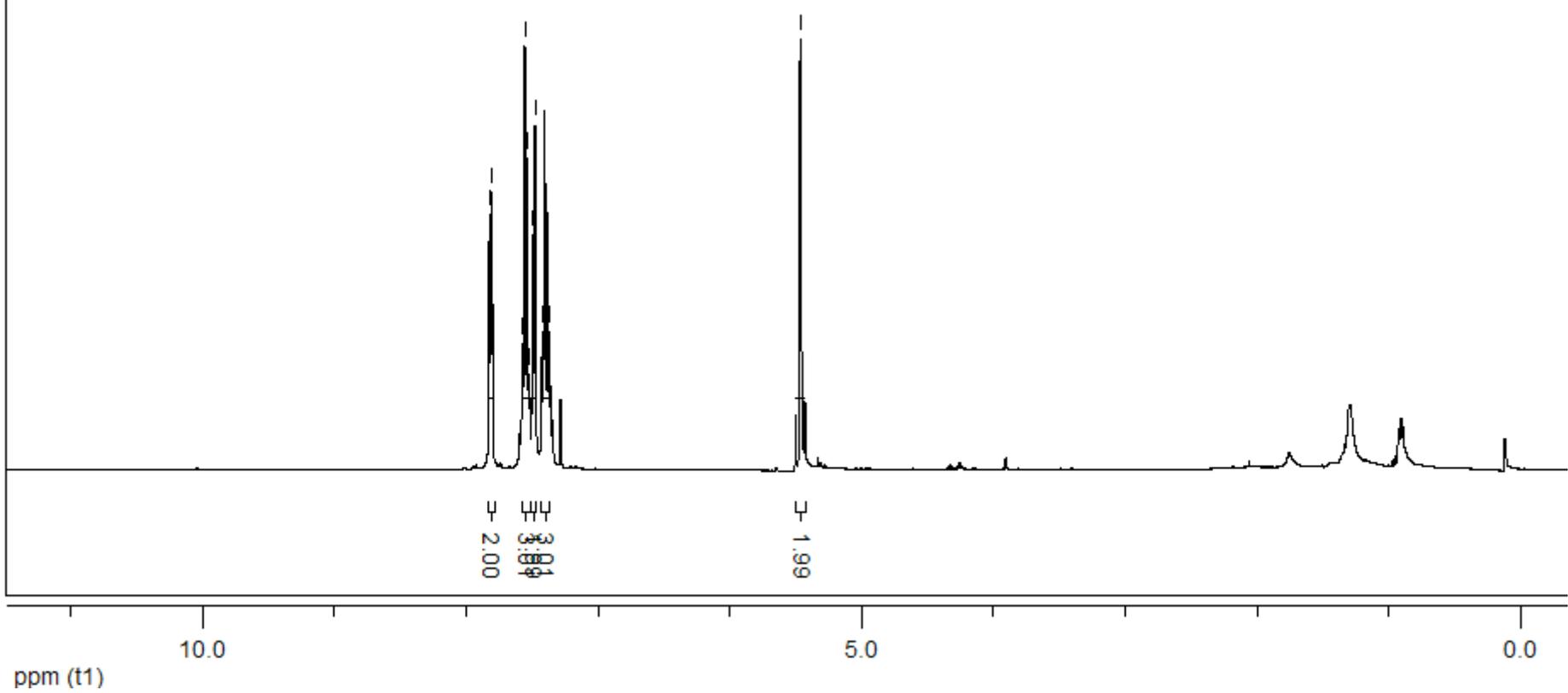
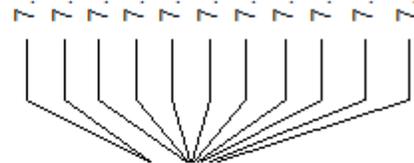
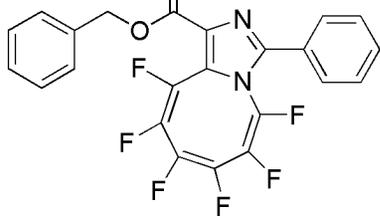


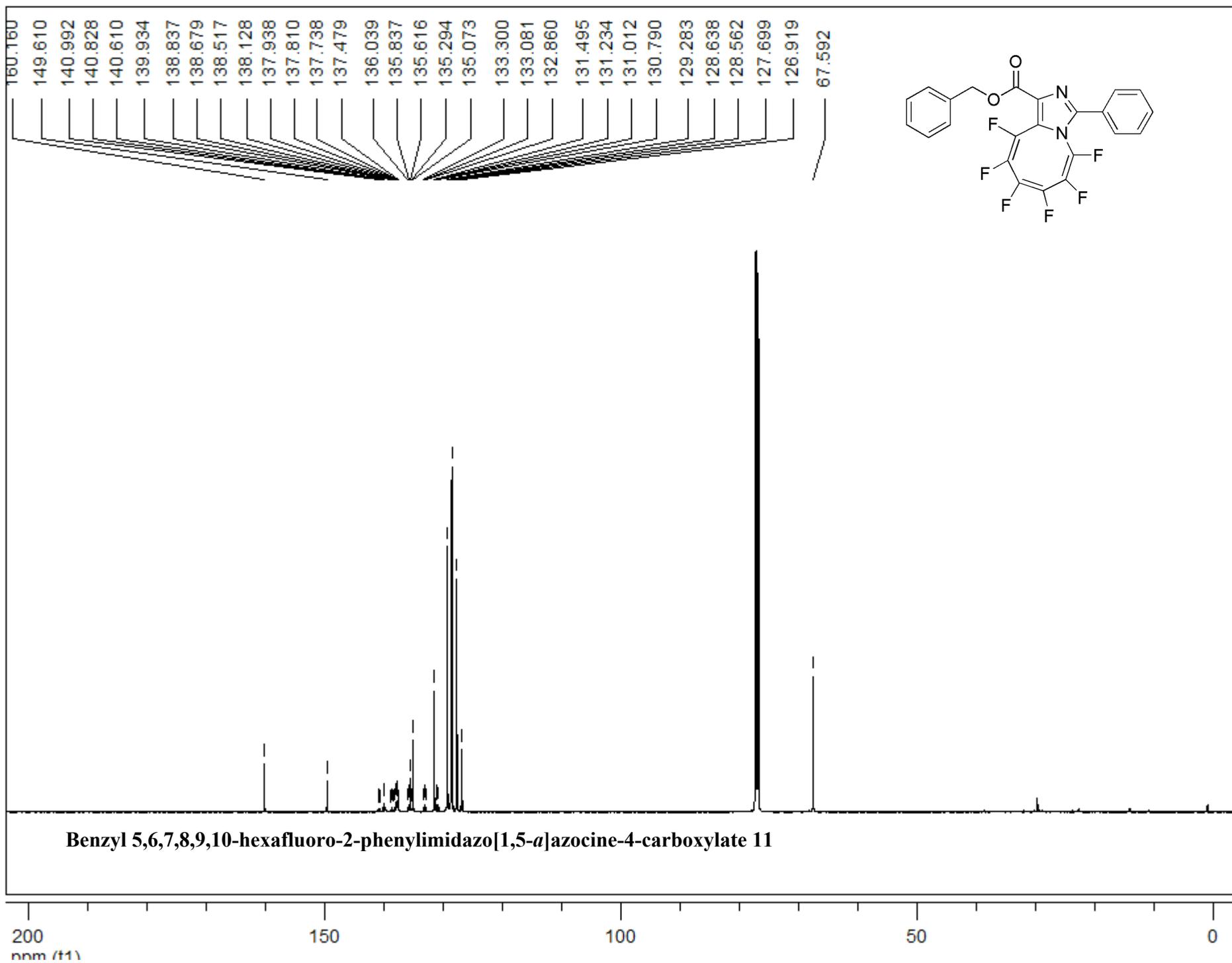
## 1-(4-ethoxycarbonyl-2-phenylimidazolidin-4-yl)pyridinium inner salt 8



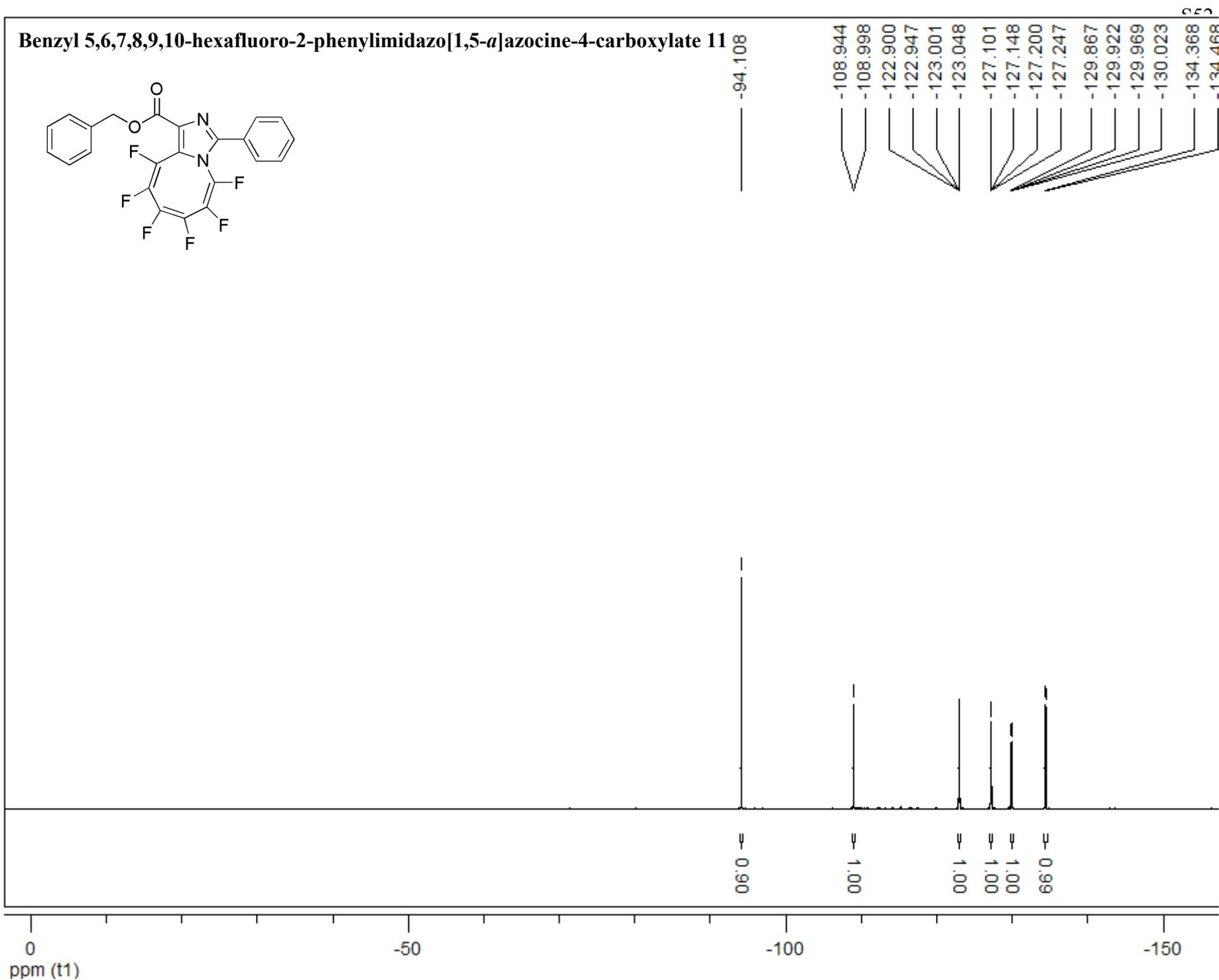
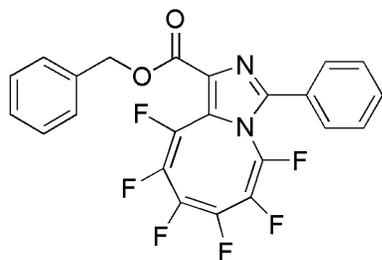


Benzyl 5,6,7,8,9,10-hexafluoro-2-phenylimidazo[1,5-a]azocine-4-carboxylate 11

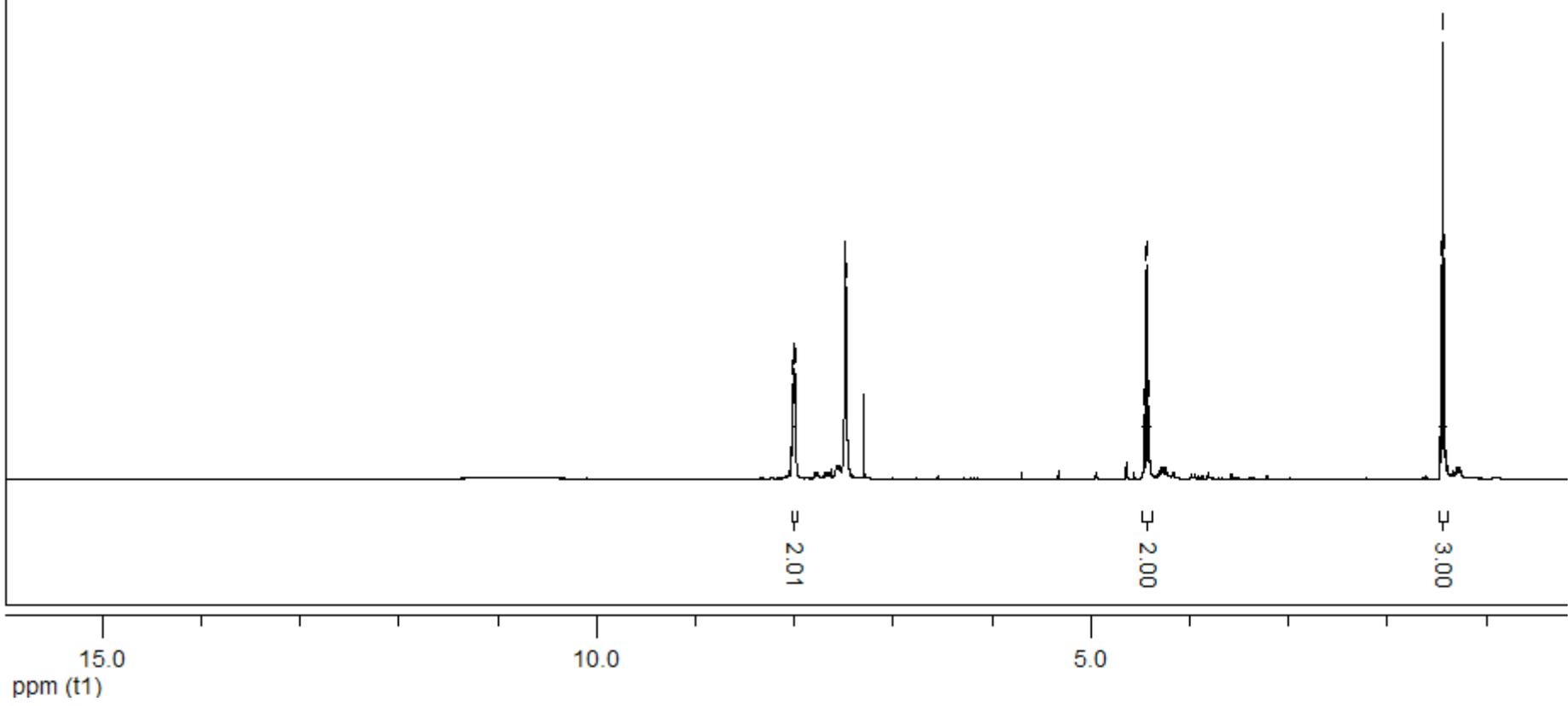
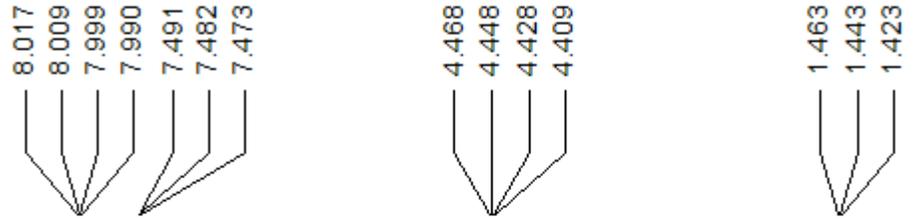
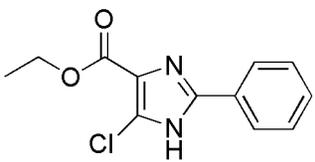


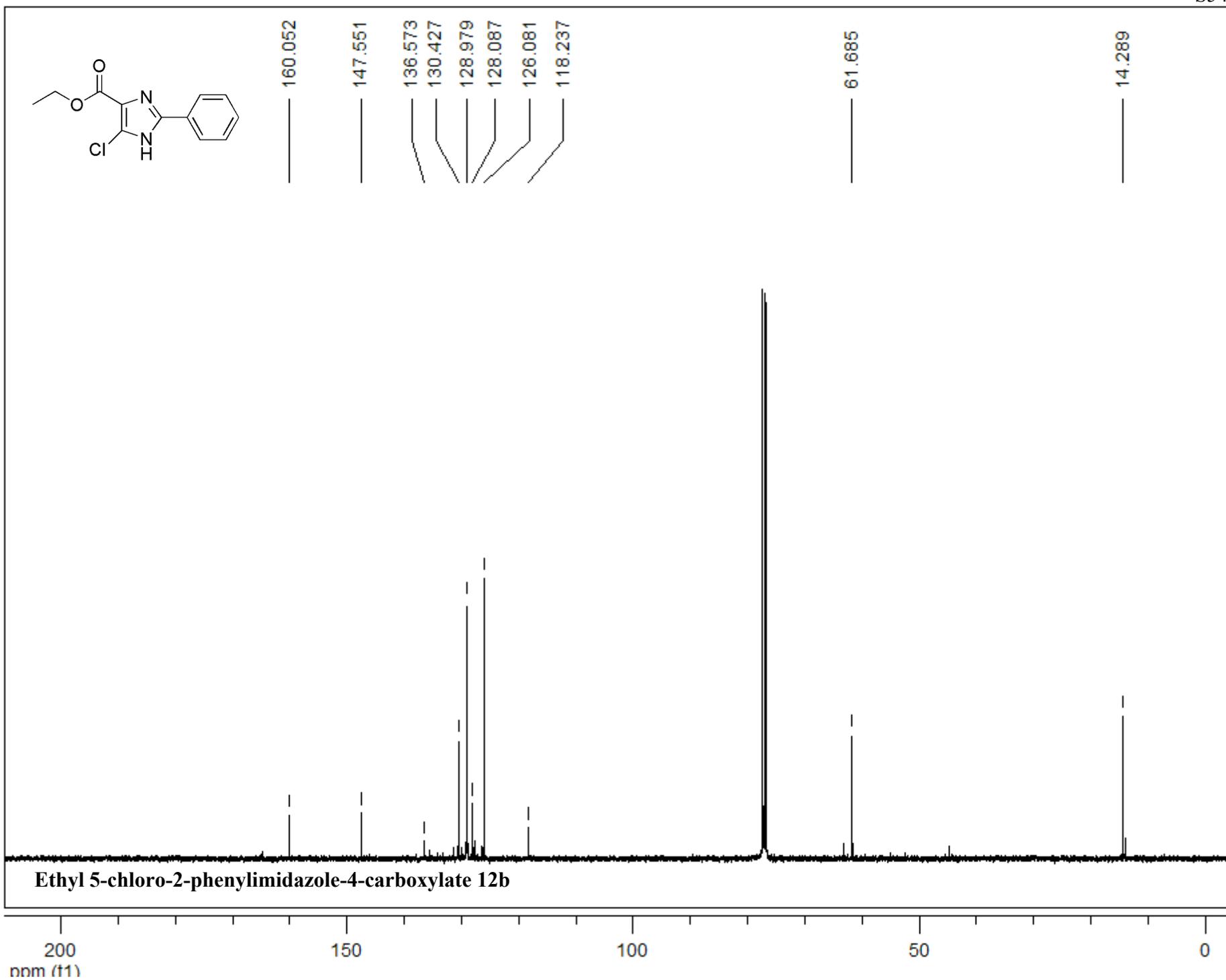


Benzyl 5,6,7,8,9,10-hexafluoro-2-phenylimidazo[1,5-a]azocine-4-carboxylate 11

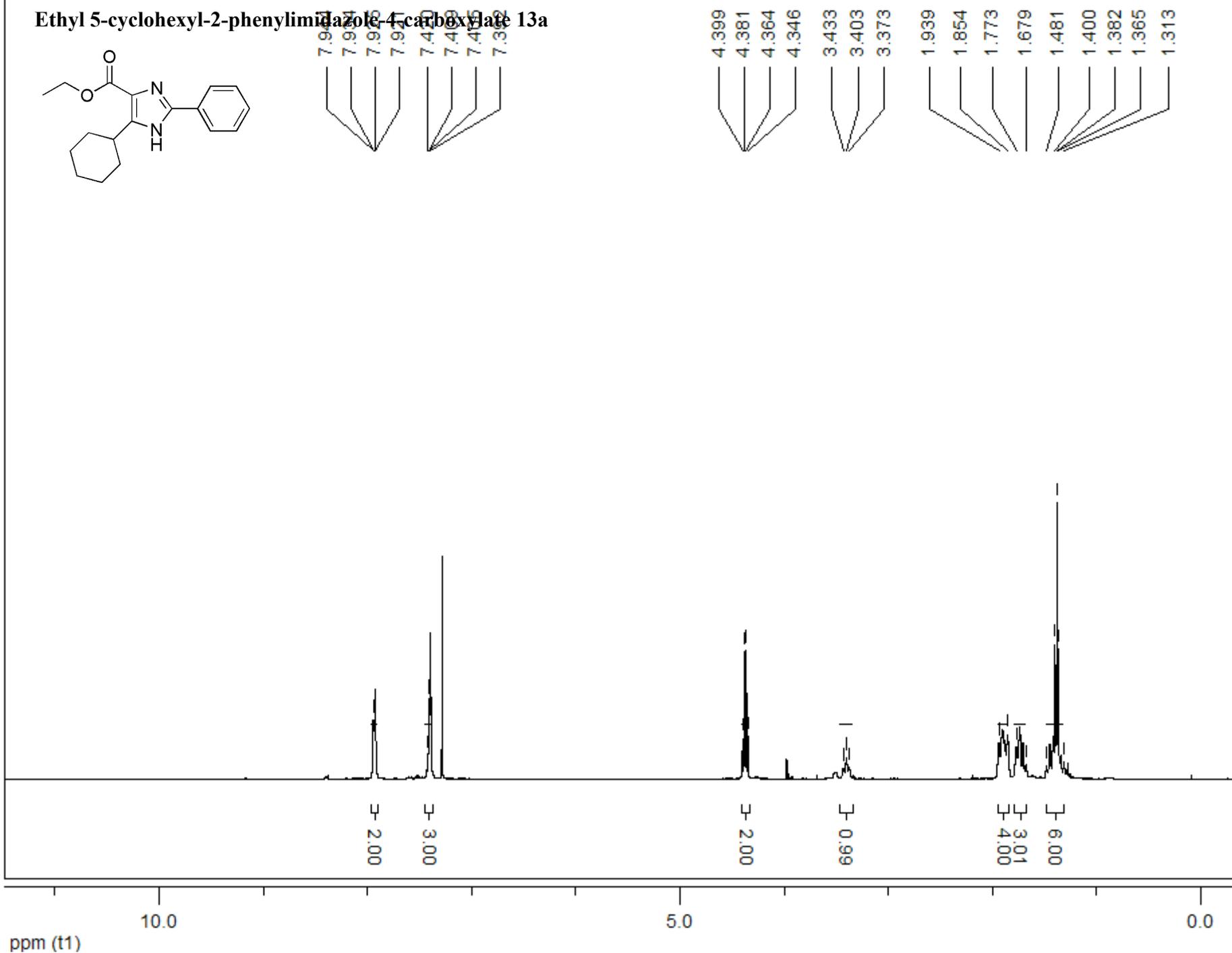
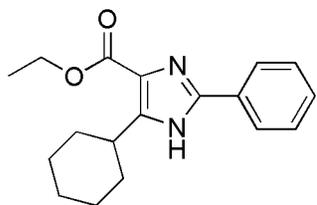


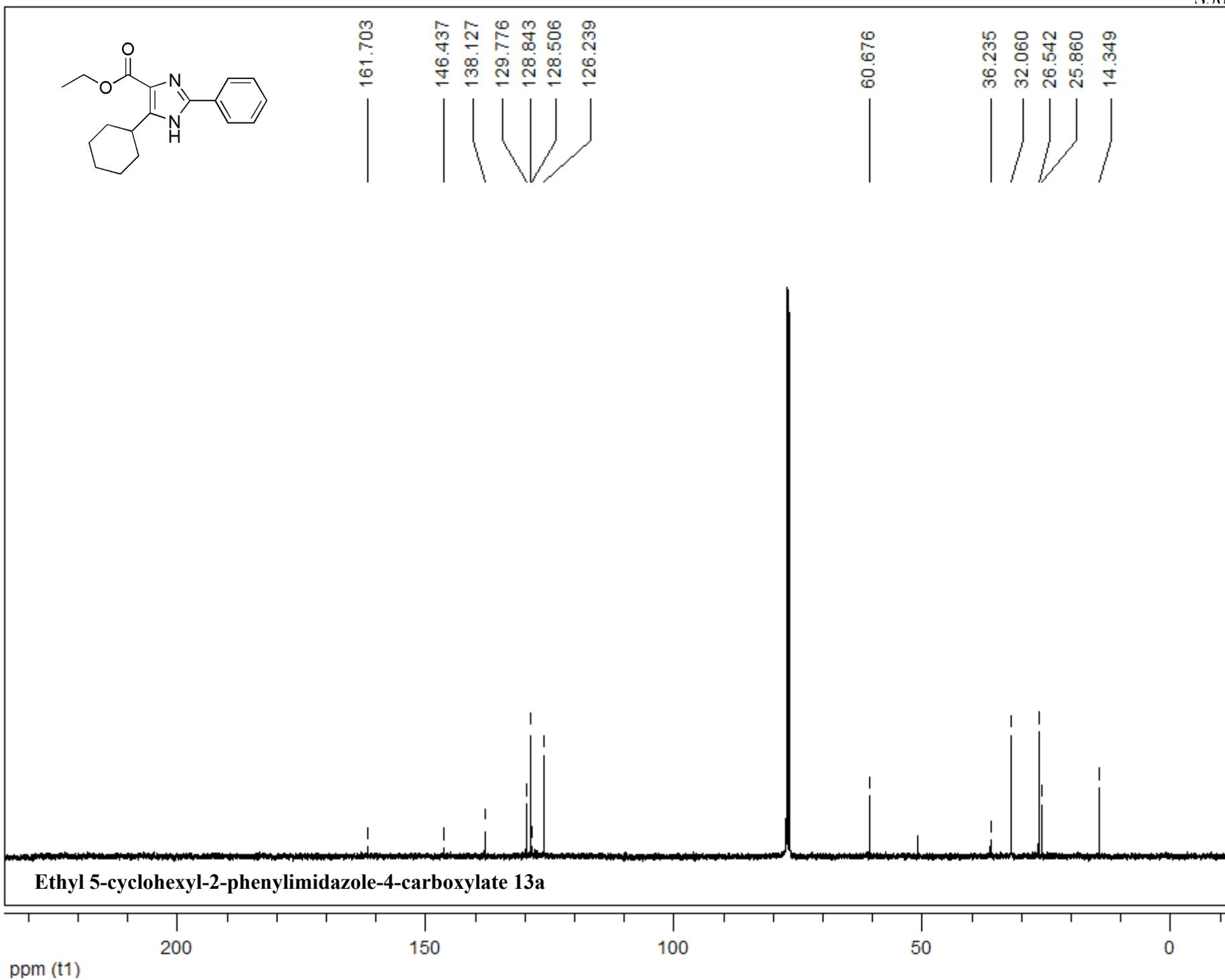
Ethyl 5-chloro-2-phenylimidazole-4-carboxylate 12b





Ethyl 5-cyclohexyl-2-phenylimidazole-4-carboxylate 13a





Ethyl 5-cycloheptyl-2-phenylimidazole-4-carboxylate 13b

