

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. ^1H and ^{13}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

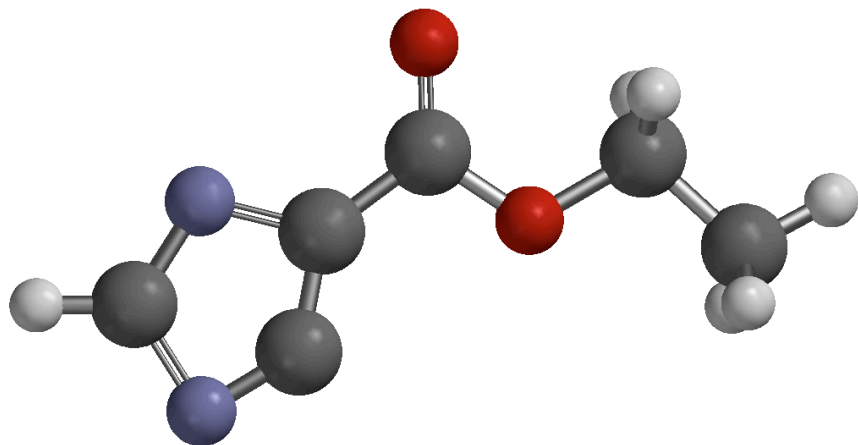
ATOM	X	Y	Z
C	1.011832	-0.180464	0.001801
C	1.417124	1.252988	0.006192
N	2.693409	1.362672	0.010297
C	3.114673	0.047932	0.011196
N	2.121825	-0.894006	0.004223
H	4.162175	-0.221695	0.013313
C	-0.359567	-0.751652	-0.004944
O	-0.610179	-1.929365	-0.018923

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

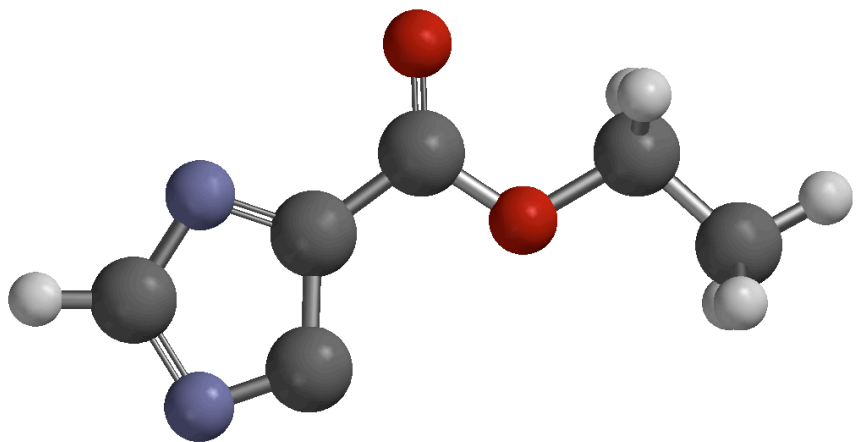
Triplet E = -492.201045077 au (UB3LYP/6-311+G**// UB3LYP/6-311+G**)

This molecule has 0 imaginary frequencies

Zero point vibrational energy: 72.386 kcal/mol



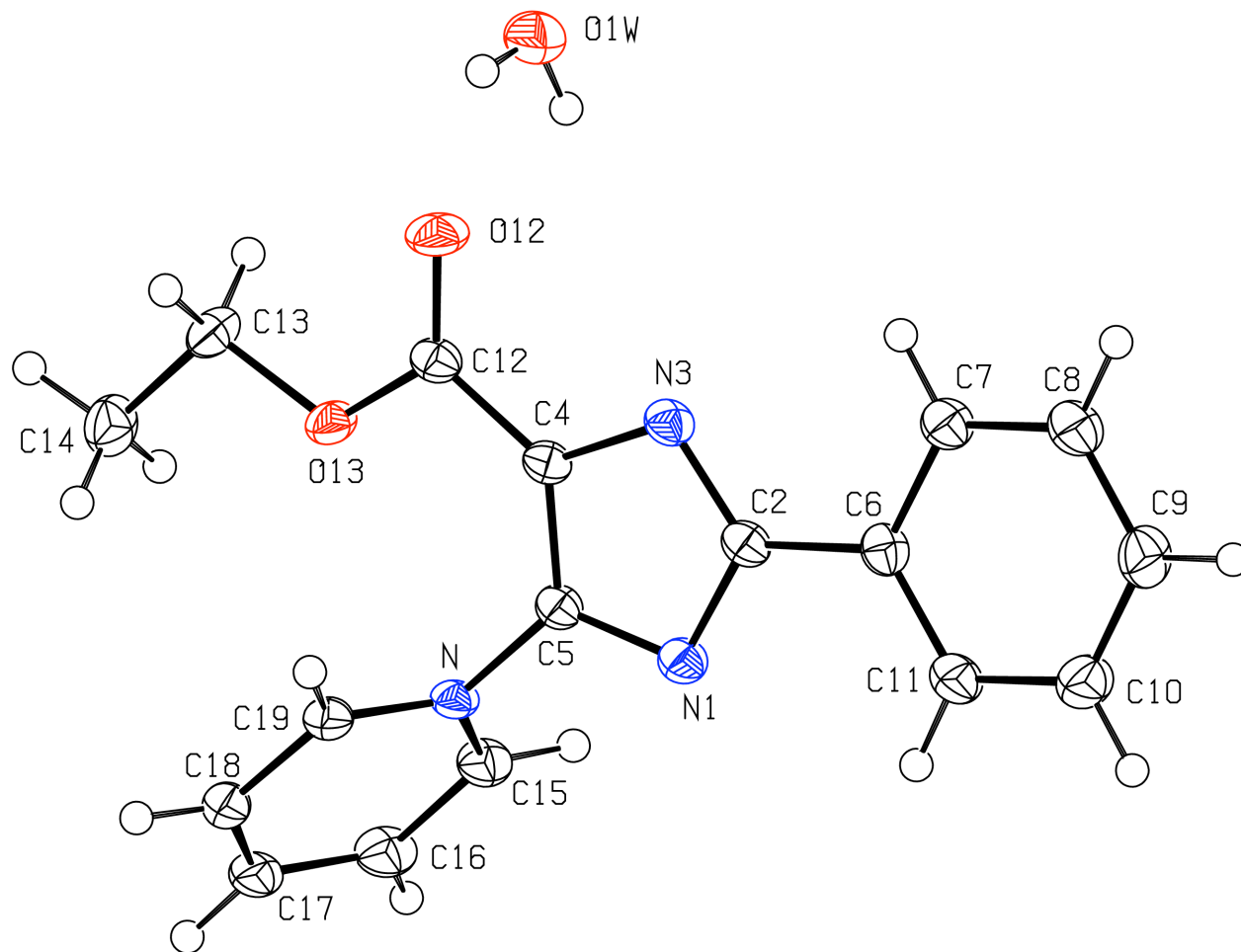
Singlet E = -492.186747449 au (B3LYP/6-311+G**// B3LYP/6-311+G**)



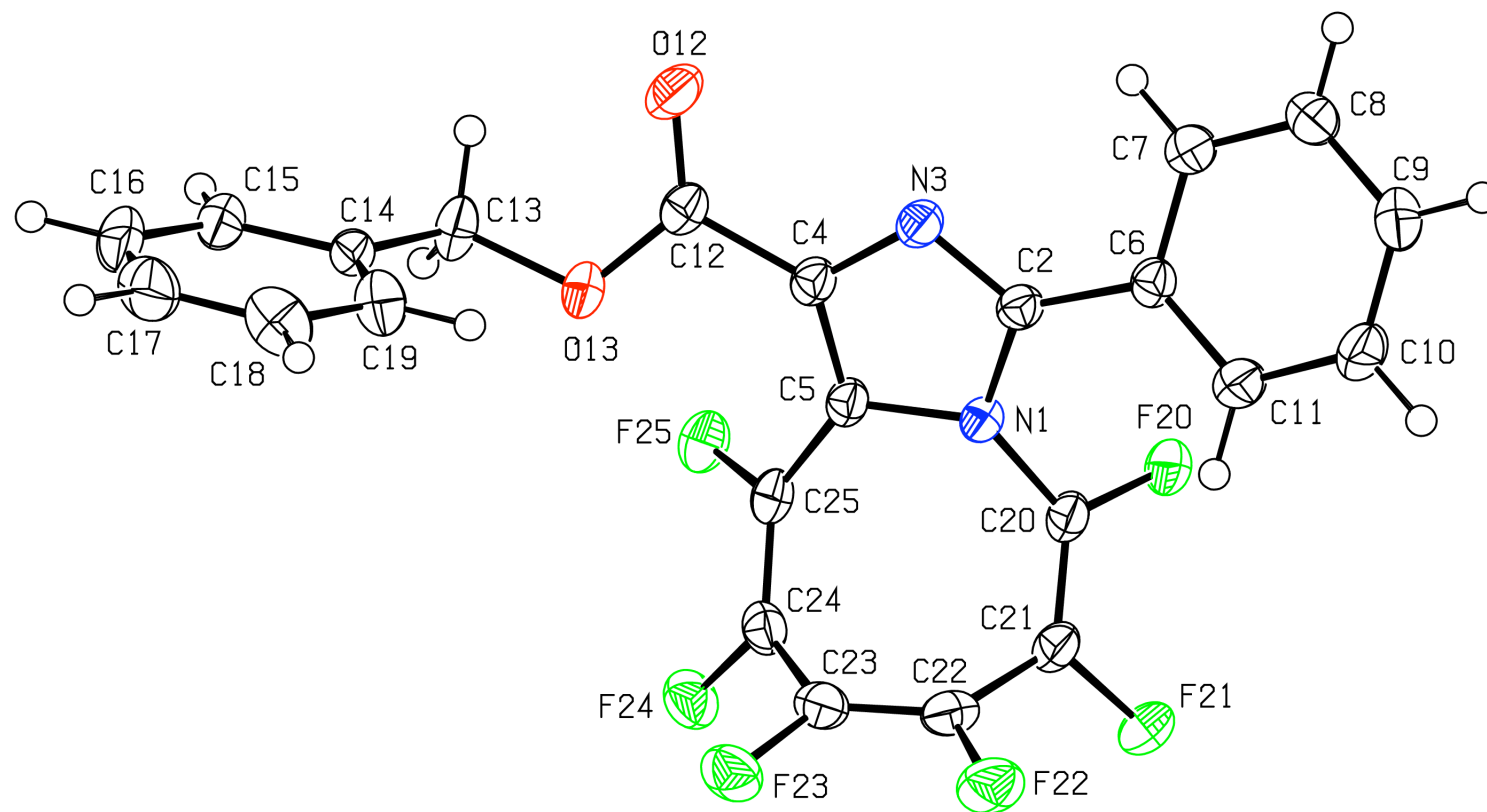
Triplet E = -492.201045077 au (UB3LYP/6-311+G**// UB3LYP/6-311+G**)

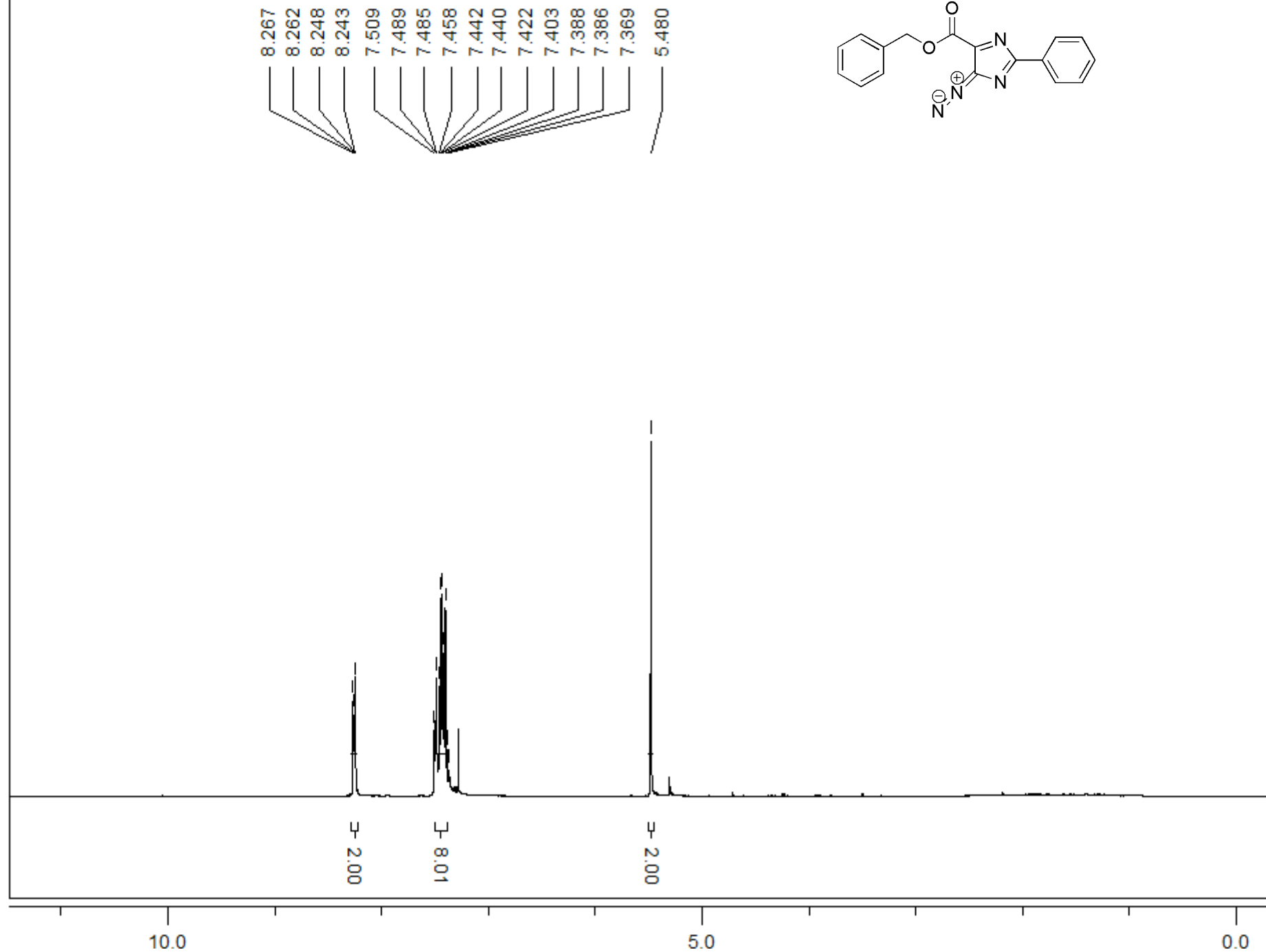
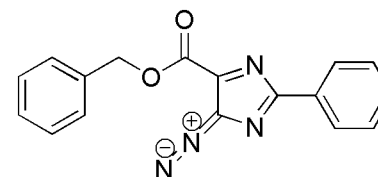
Therefore triplet is ground state, with a triplet to singlet gap of 9.0 Kcal mol⁻¹

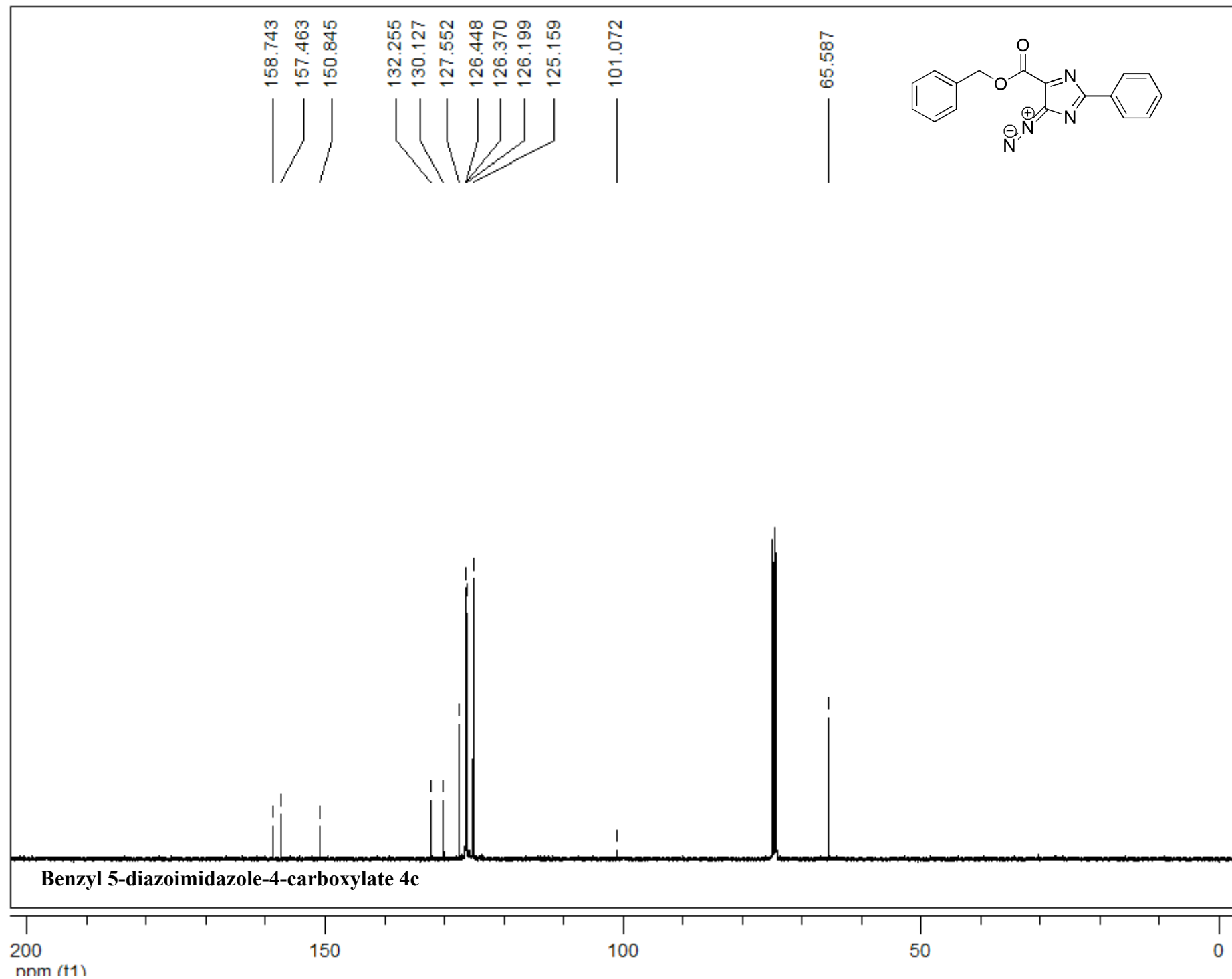
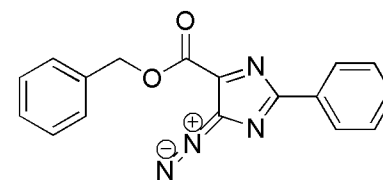
X-Ray crystal structure of 1-(4-ethoxycarbonyl-2-phenylimidazolidin-4-yl)pyridinium inner salt **8**.



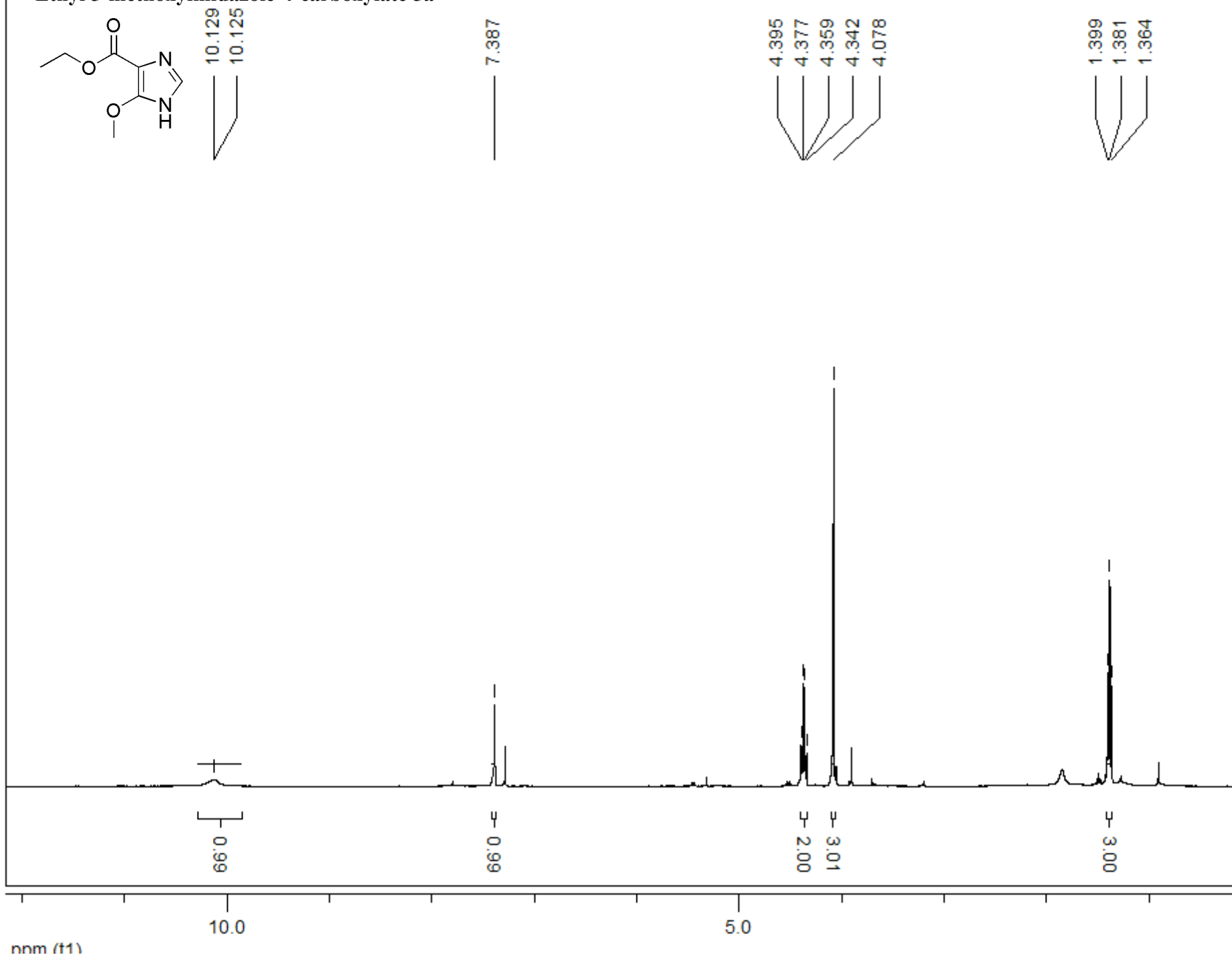
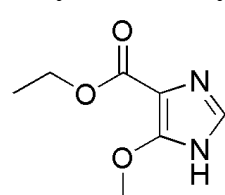
X-Ray crystal structure of benzyl 5,6,7,8,9,10-hexafluoro-2-phenylimidazo[1,5-*a*]azocine-4-carboxylate **11**.

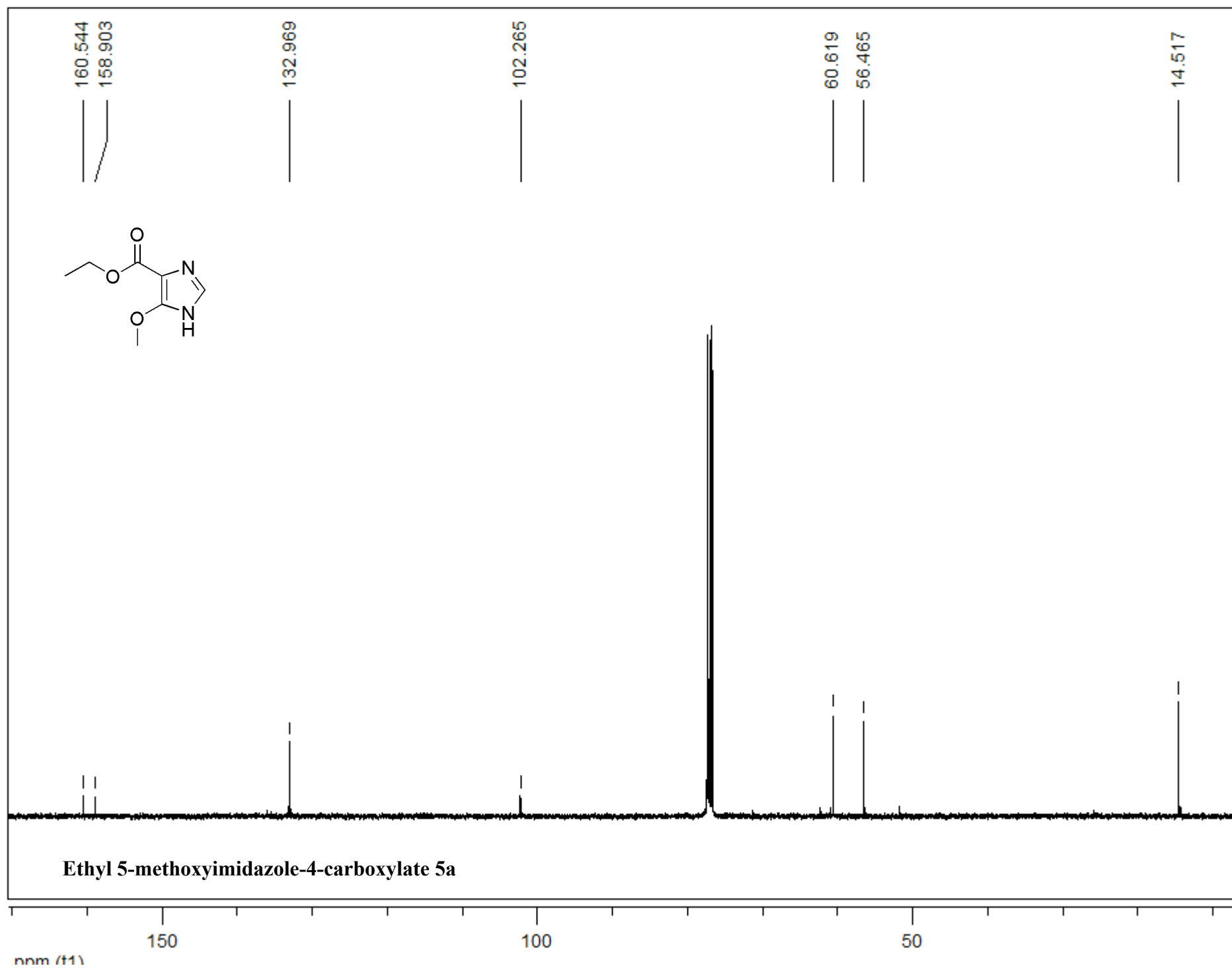


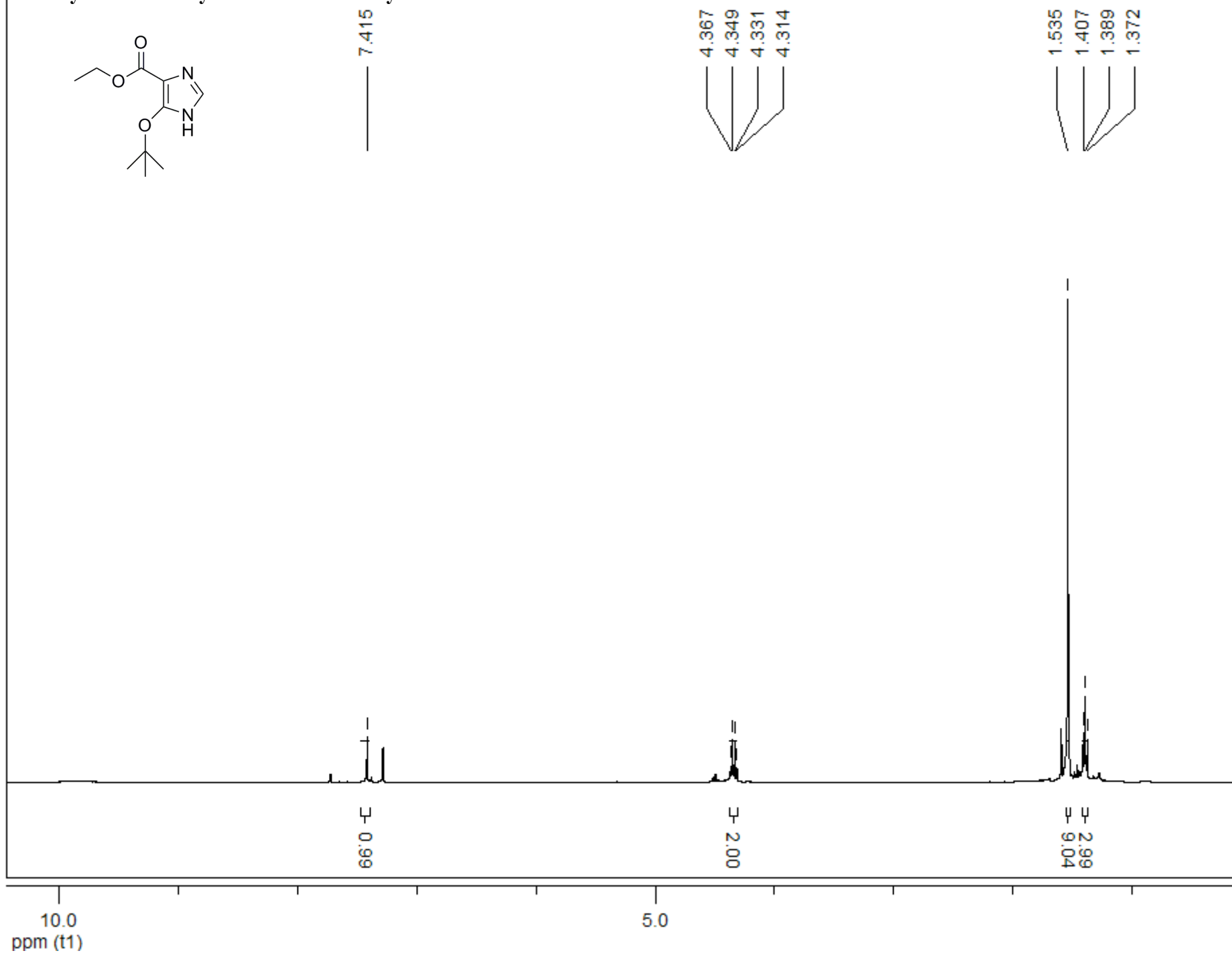
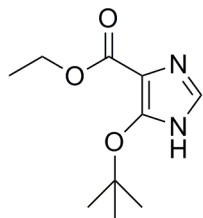
Benzyl 5-diazoimidazole-4-carboxylate 4c

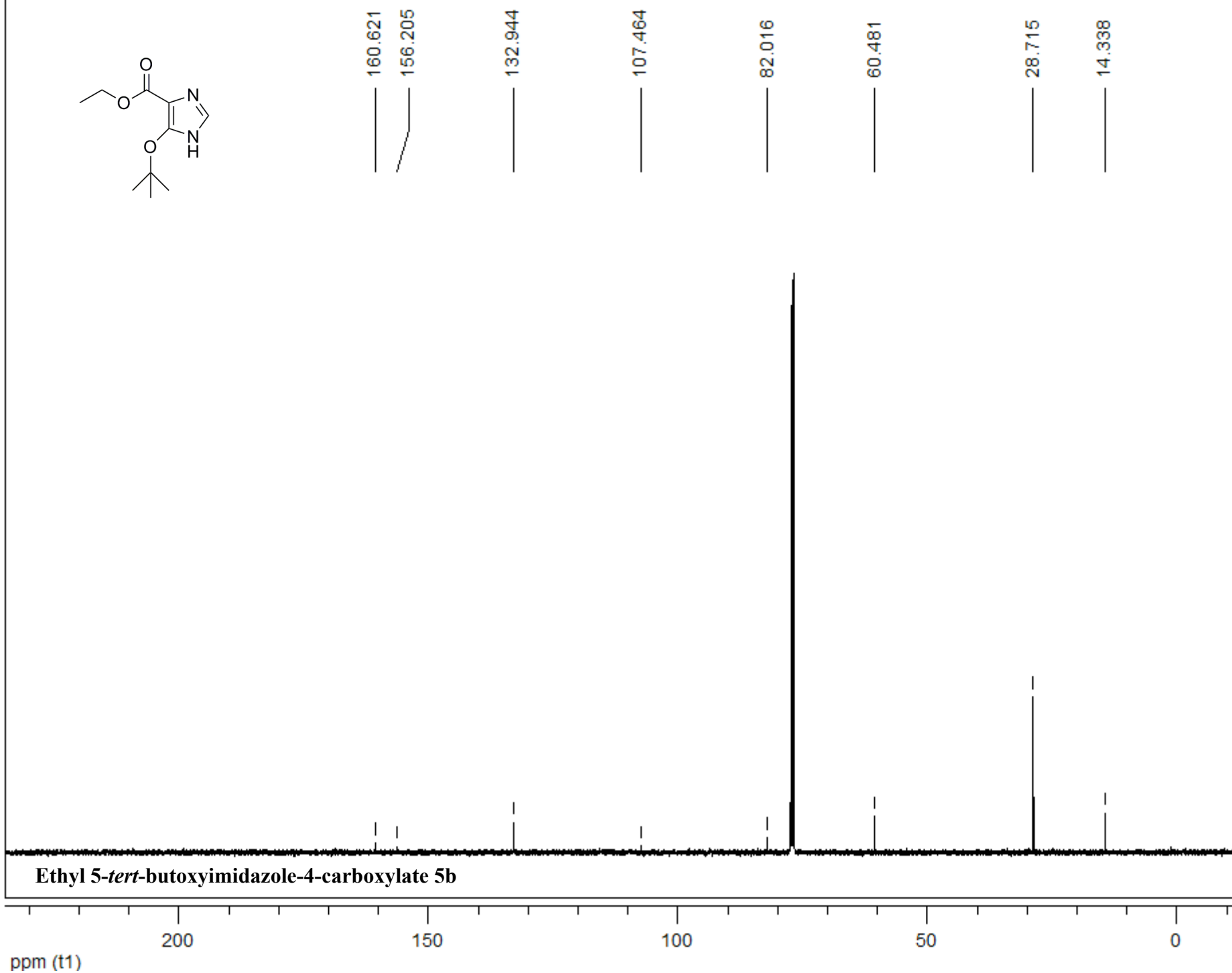
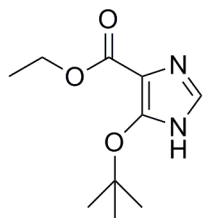


Ethyl 5-methoxyimidazole-4-carboxylate 5a

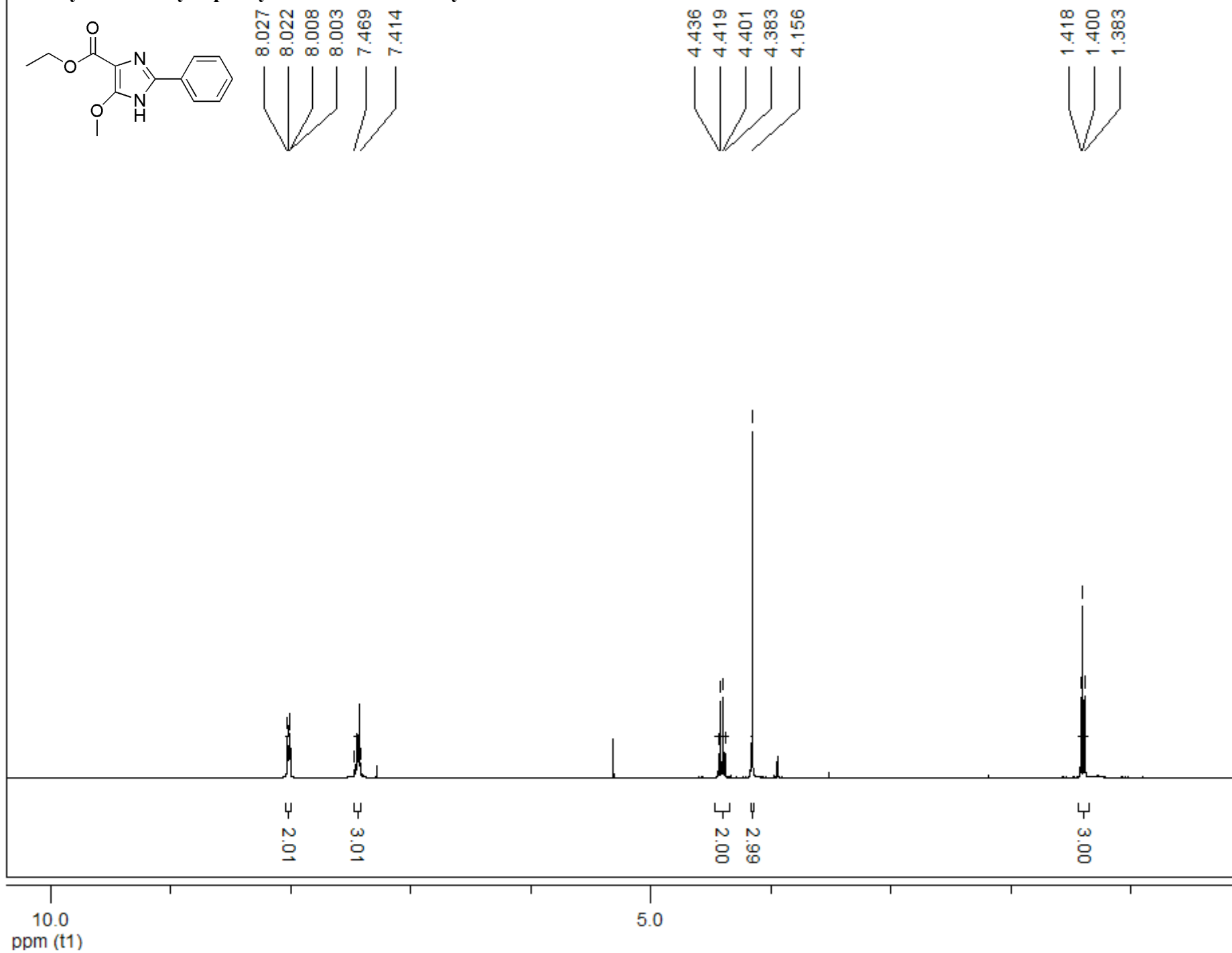


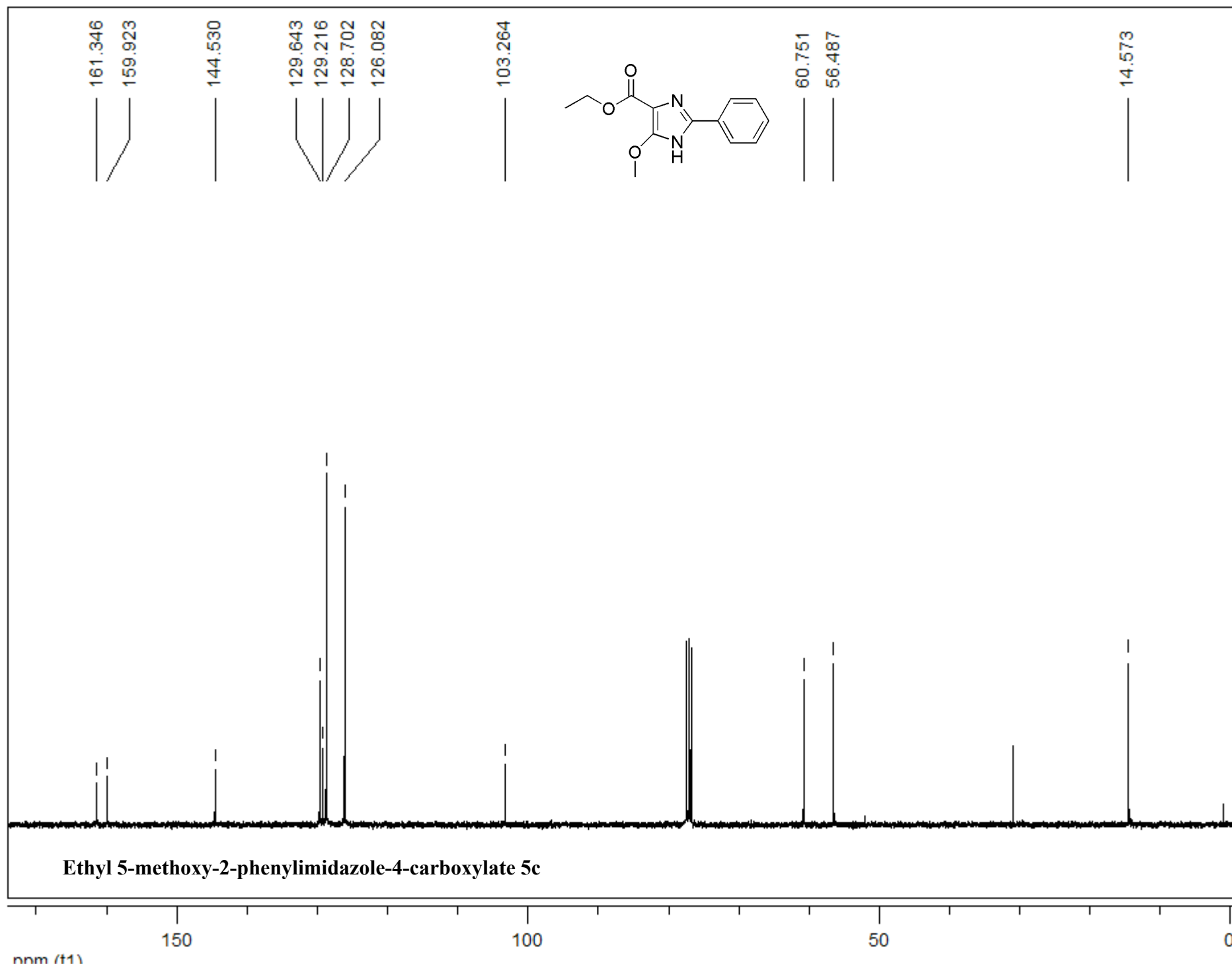


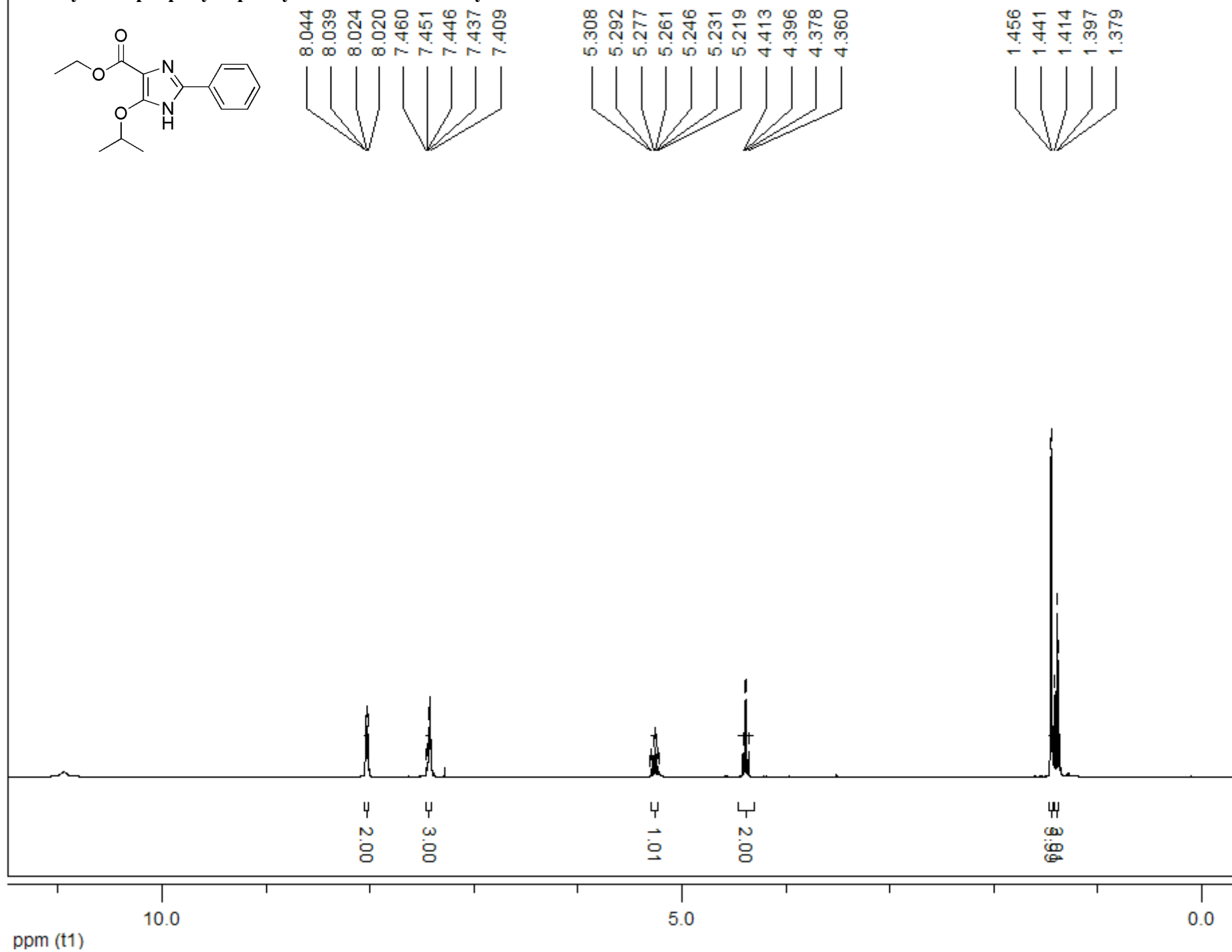
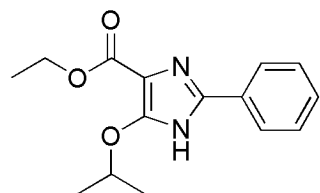
Ethyl 5-*tert*-butoxyimidazole-4-carboxylate 5b

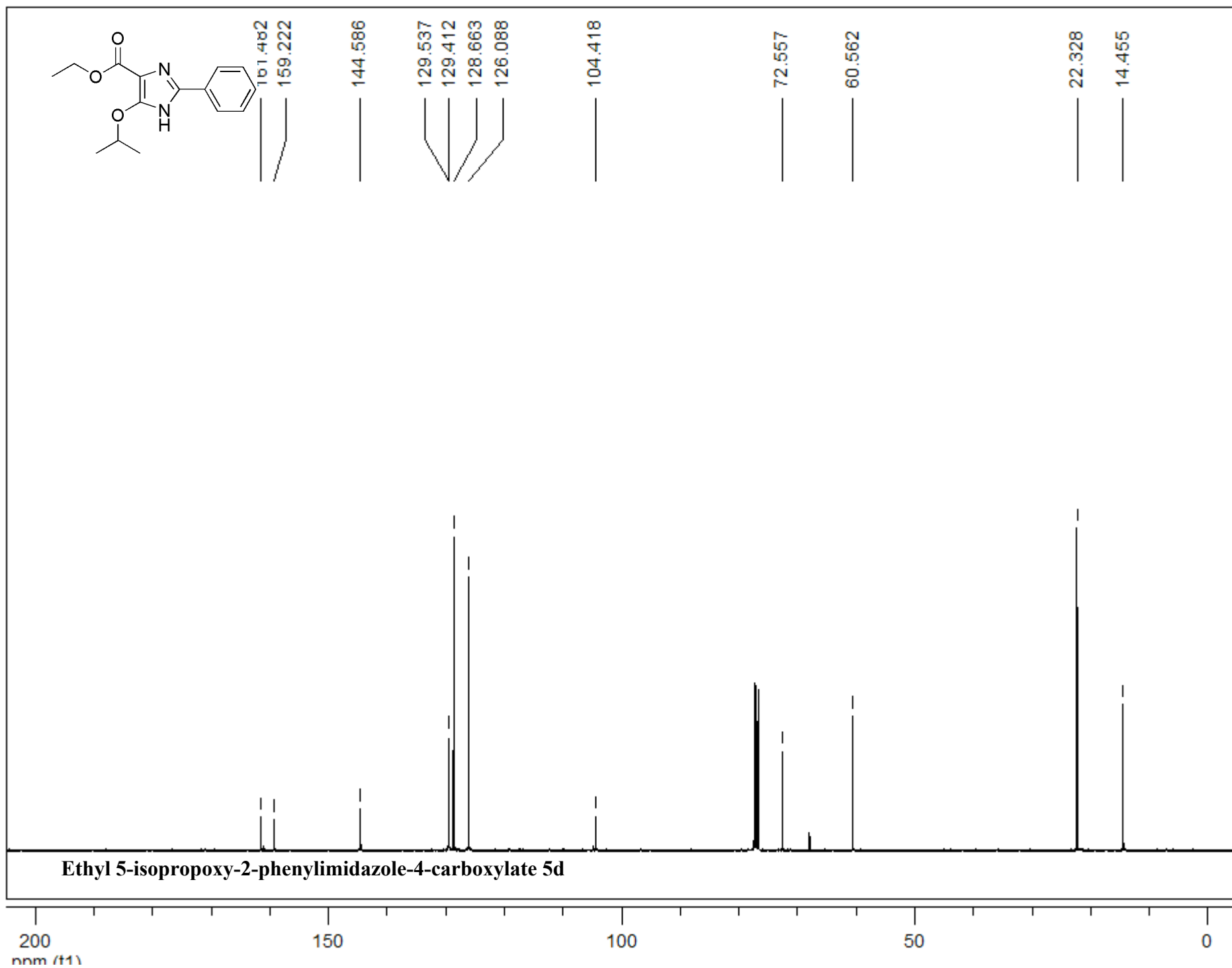


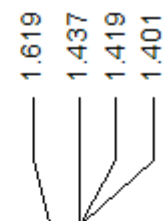
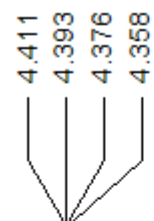
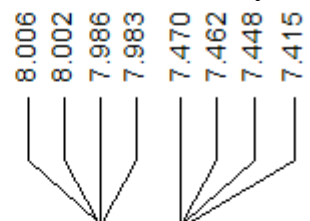
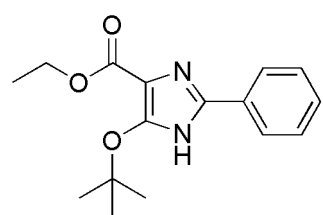
Ethyl 5-methoxy-2-phenylimidazole-4-carboxylate 5c





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



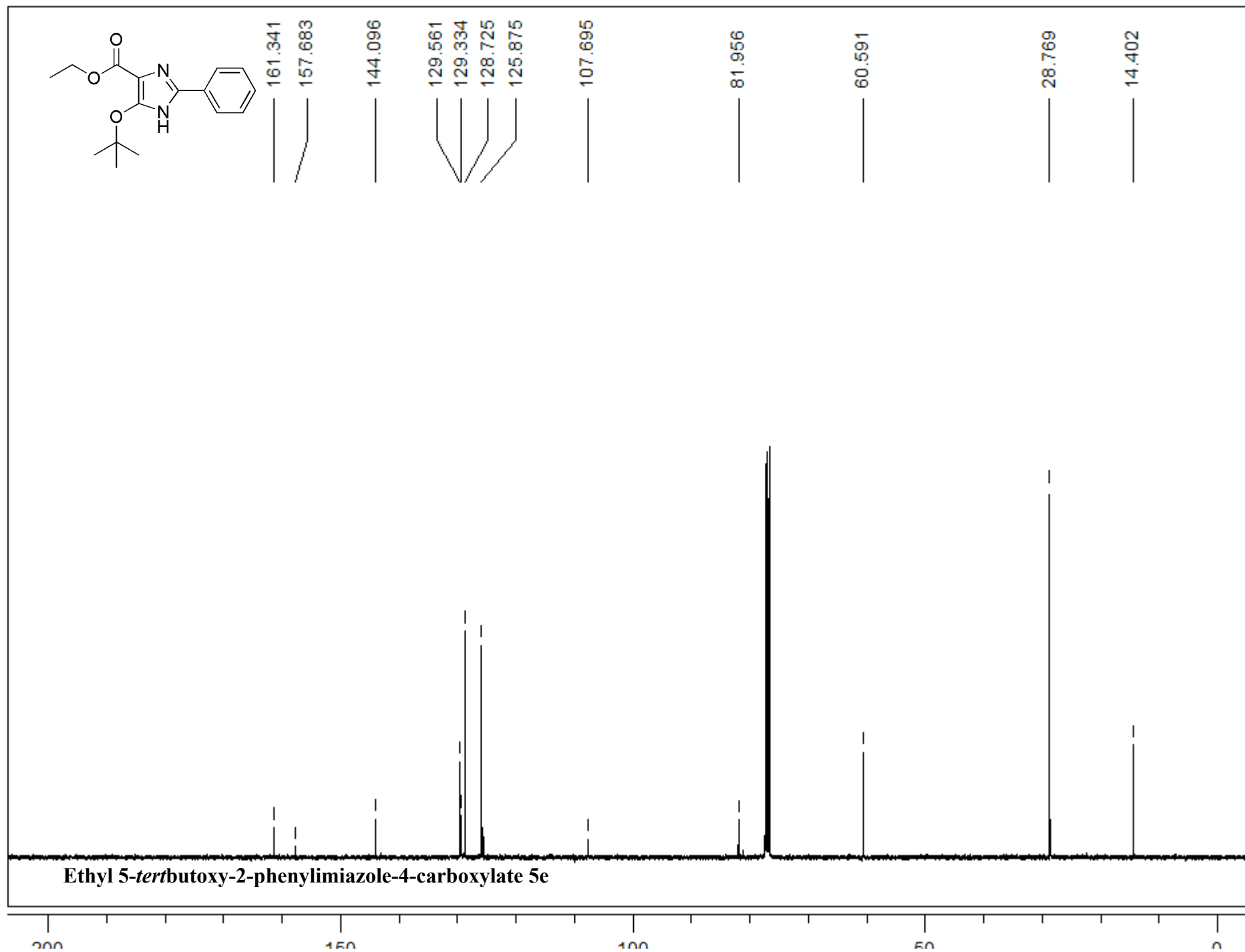
Ethyl 5-*tert*-butoxy-2-phenylimidazole-4-carboxylate 5e

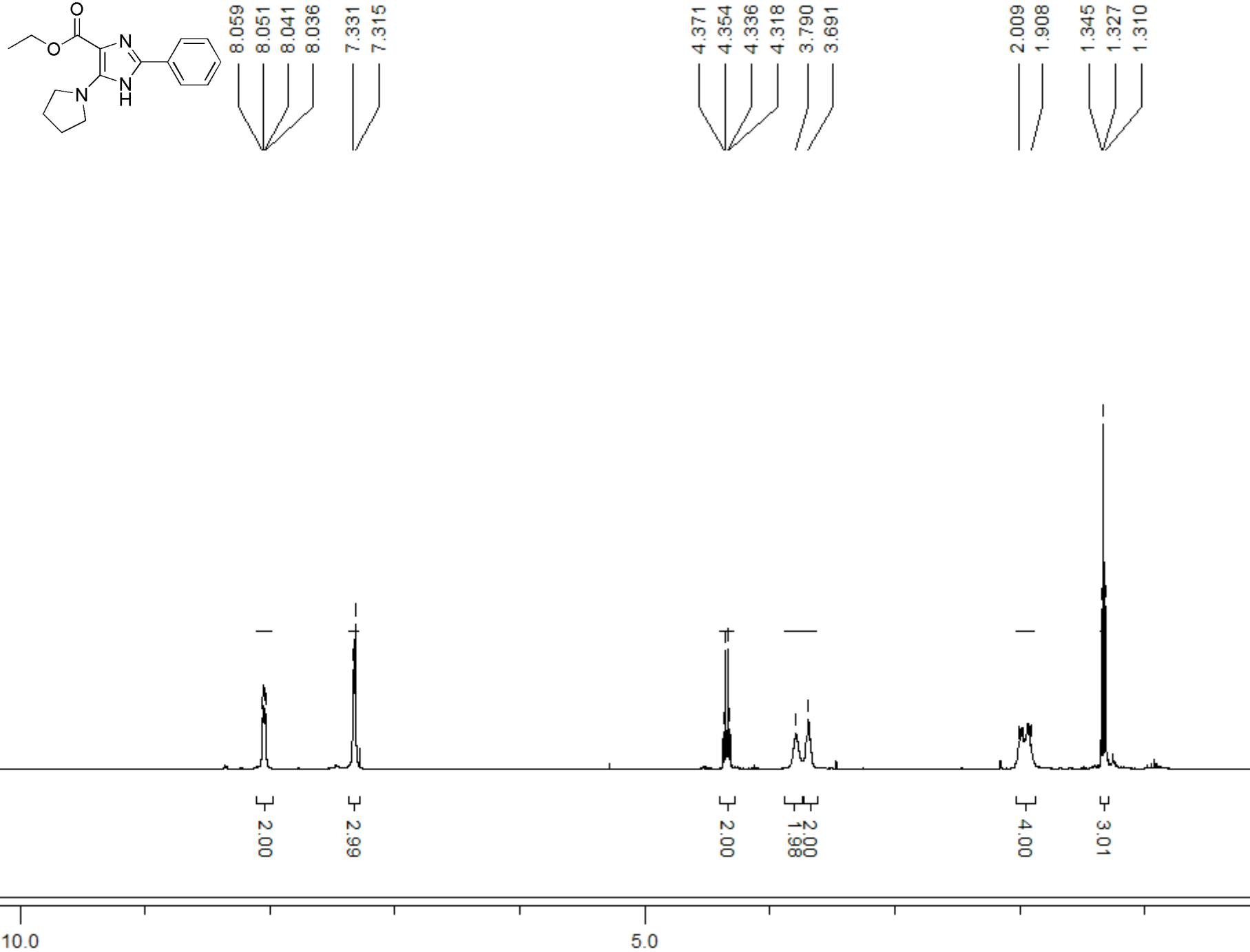
ppm (t1)

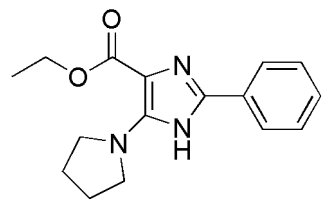
10.0

5.0

0.0



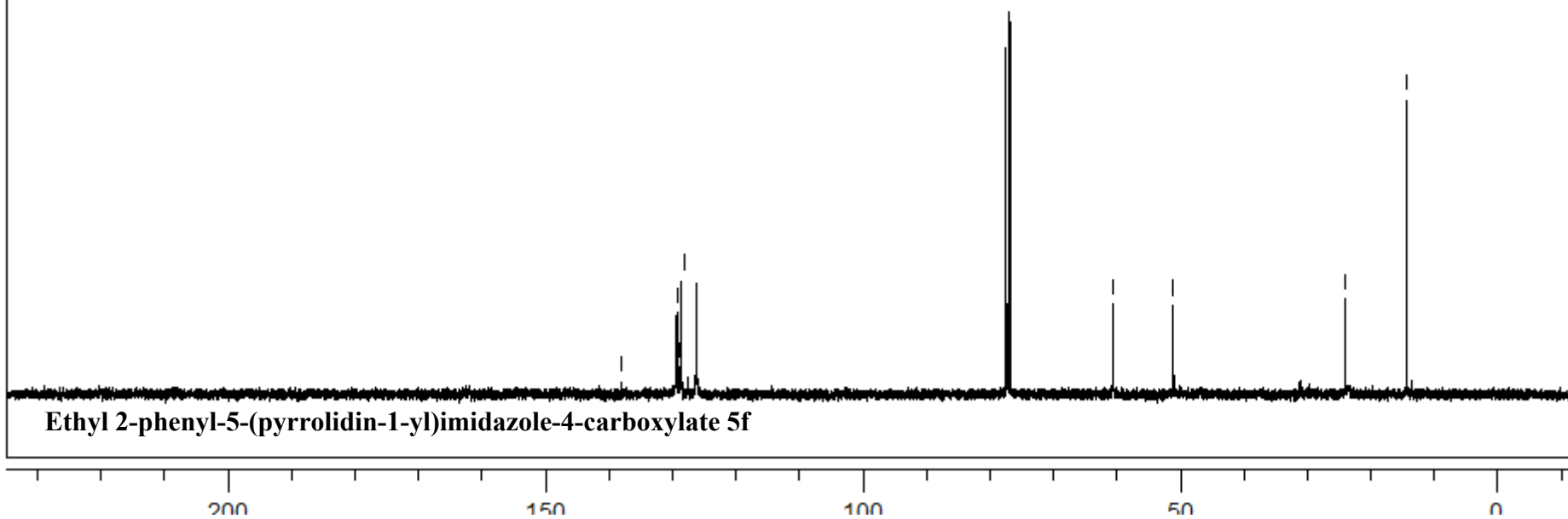
Ethyl 2-phenyl-5-(pyrrolidin-1-yl)imidazole-4-carboxylate 5f



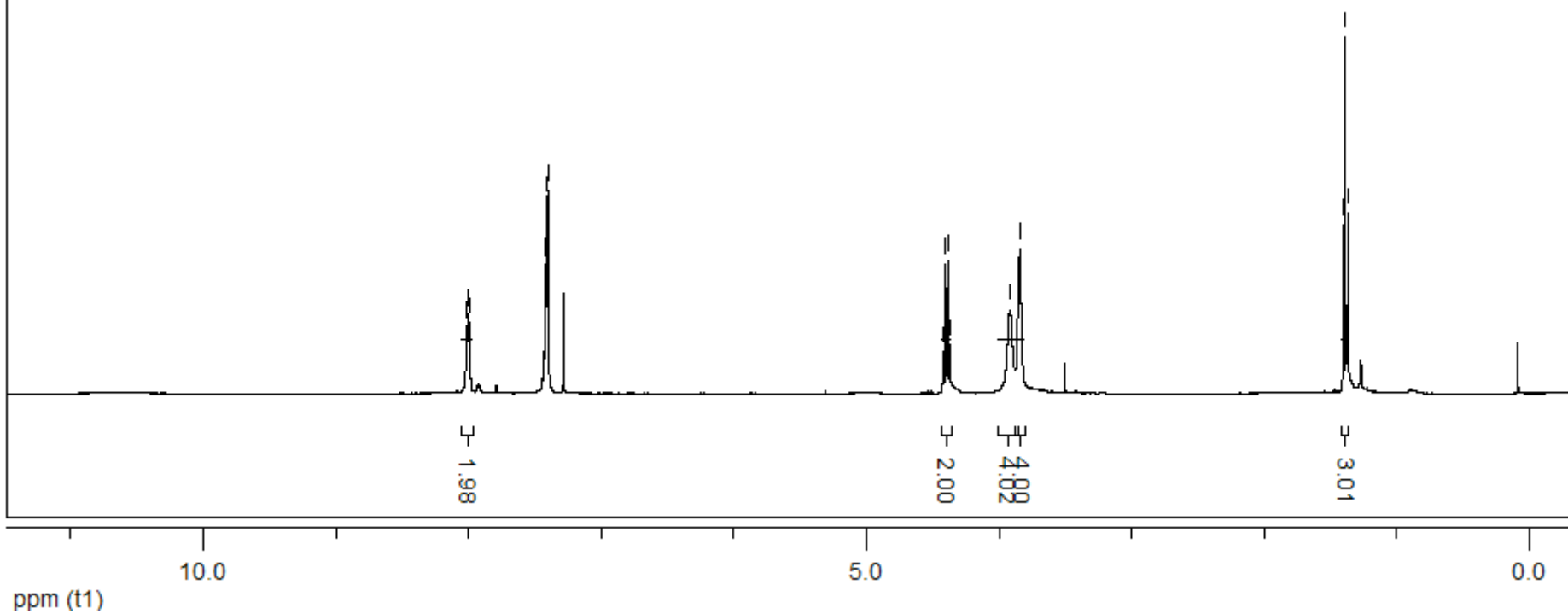
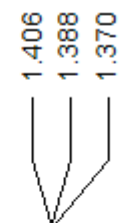
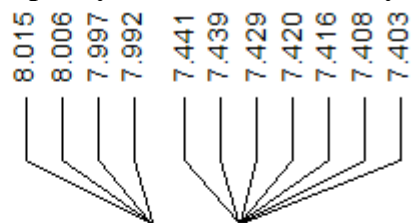
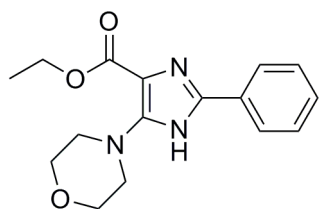
138.129
129.376
129.290
128.924
128.557
126.223

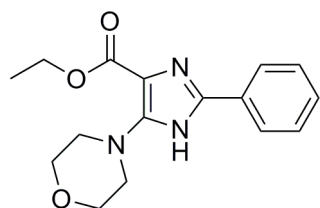
60.643
51.123

23.932
14.347



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

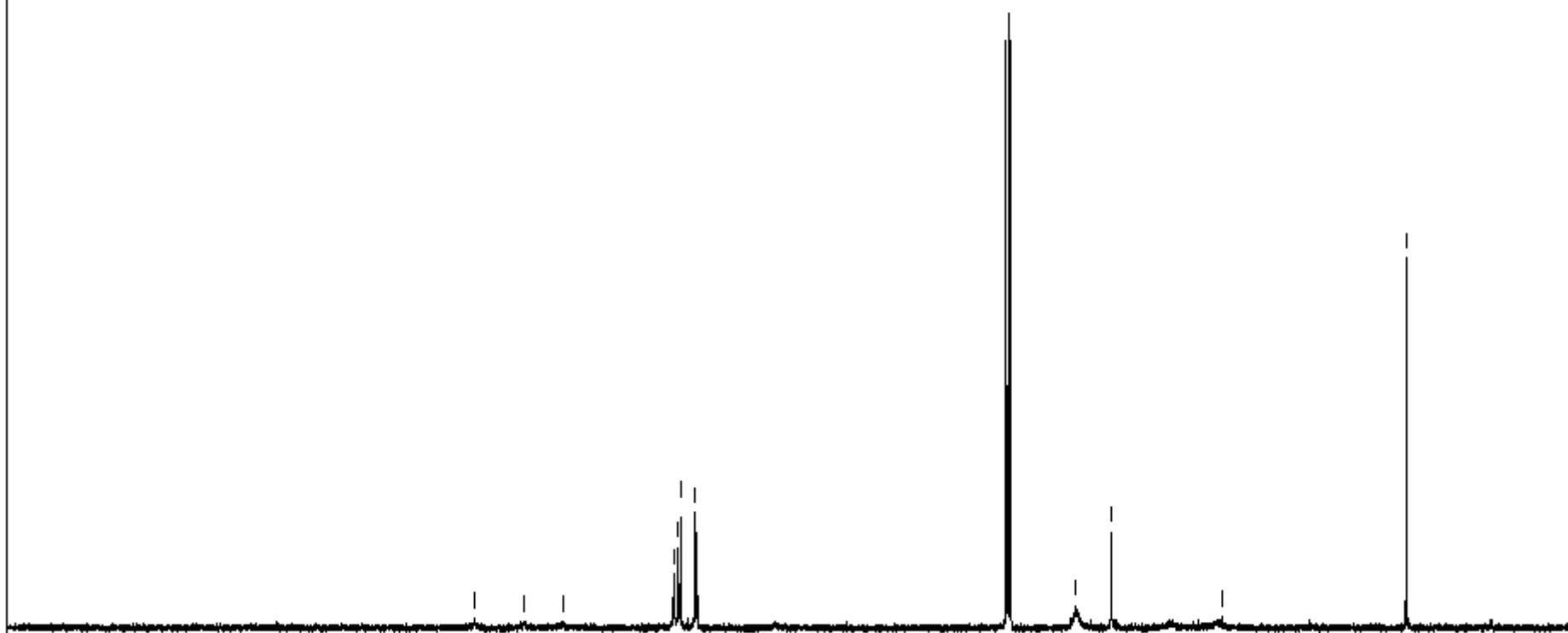
126.338

66.409

60.867

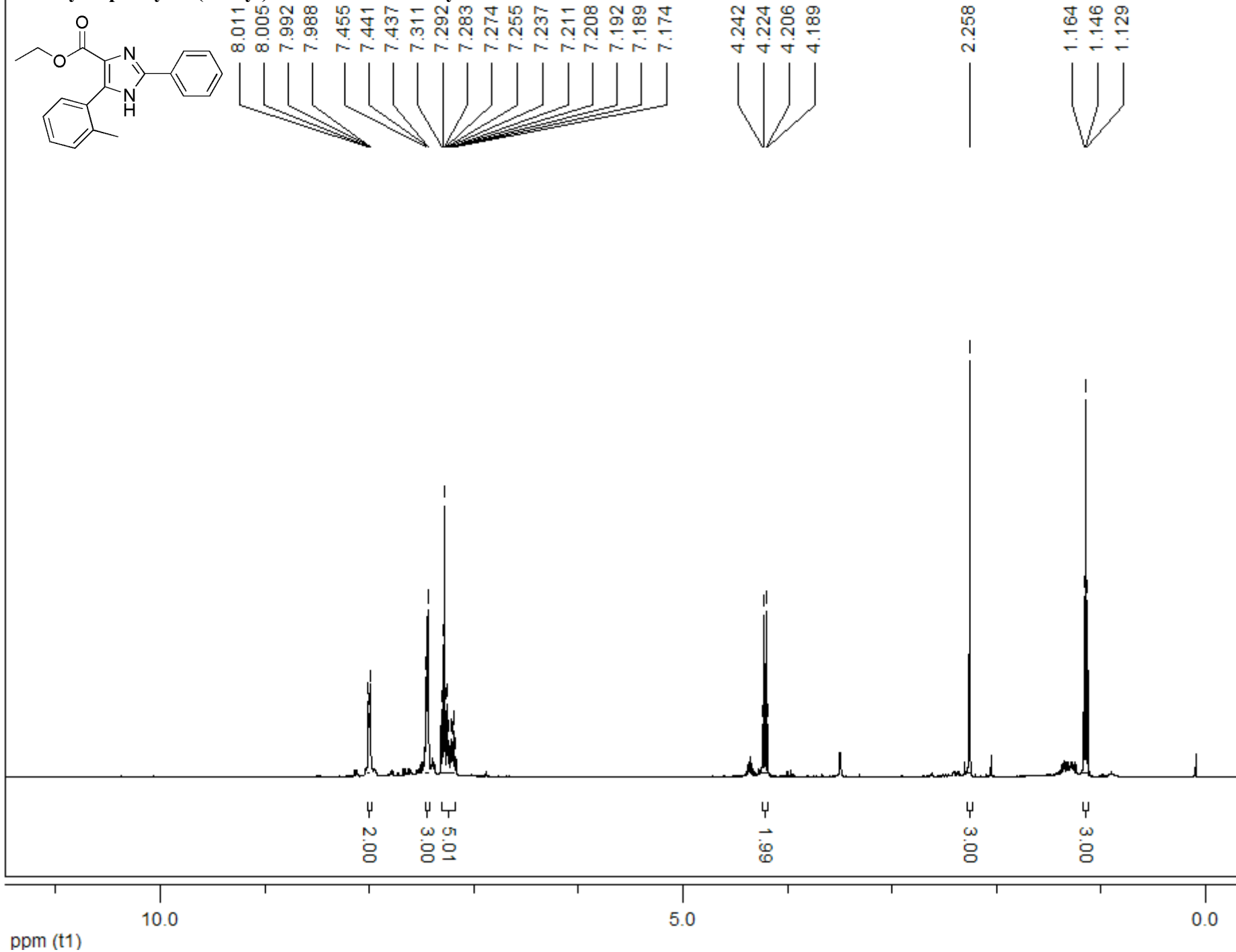
43.505

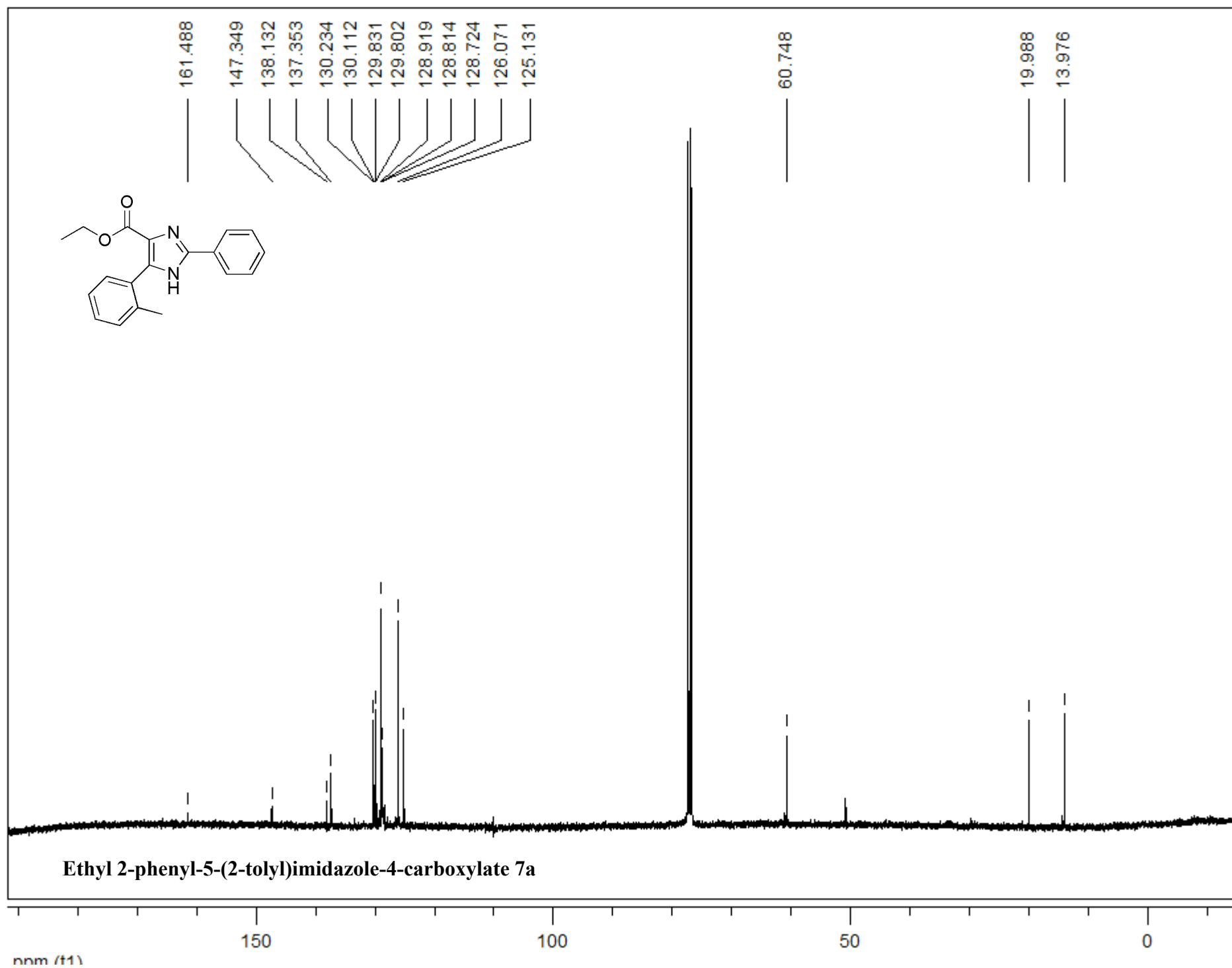
14.349

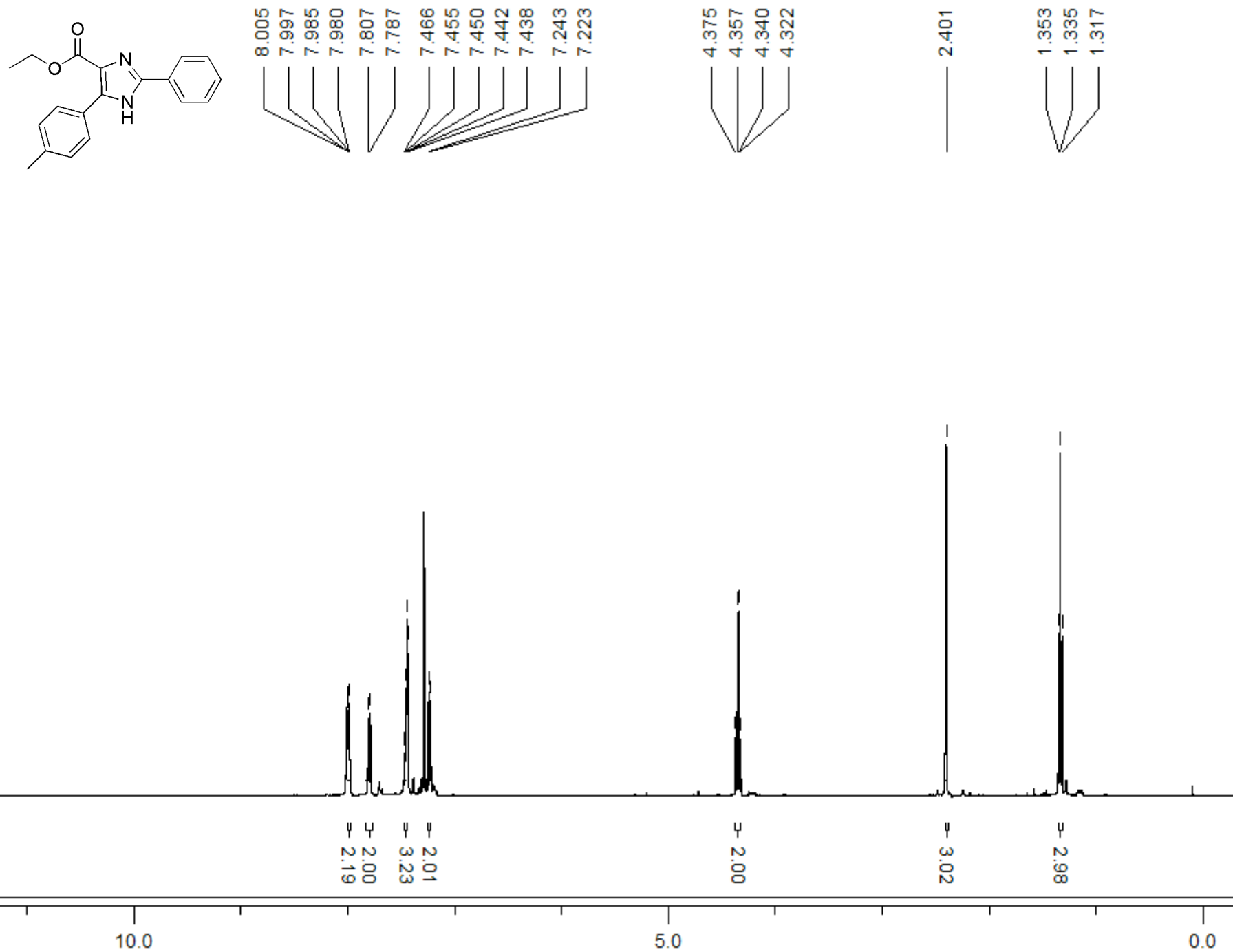


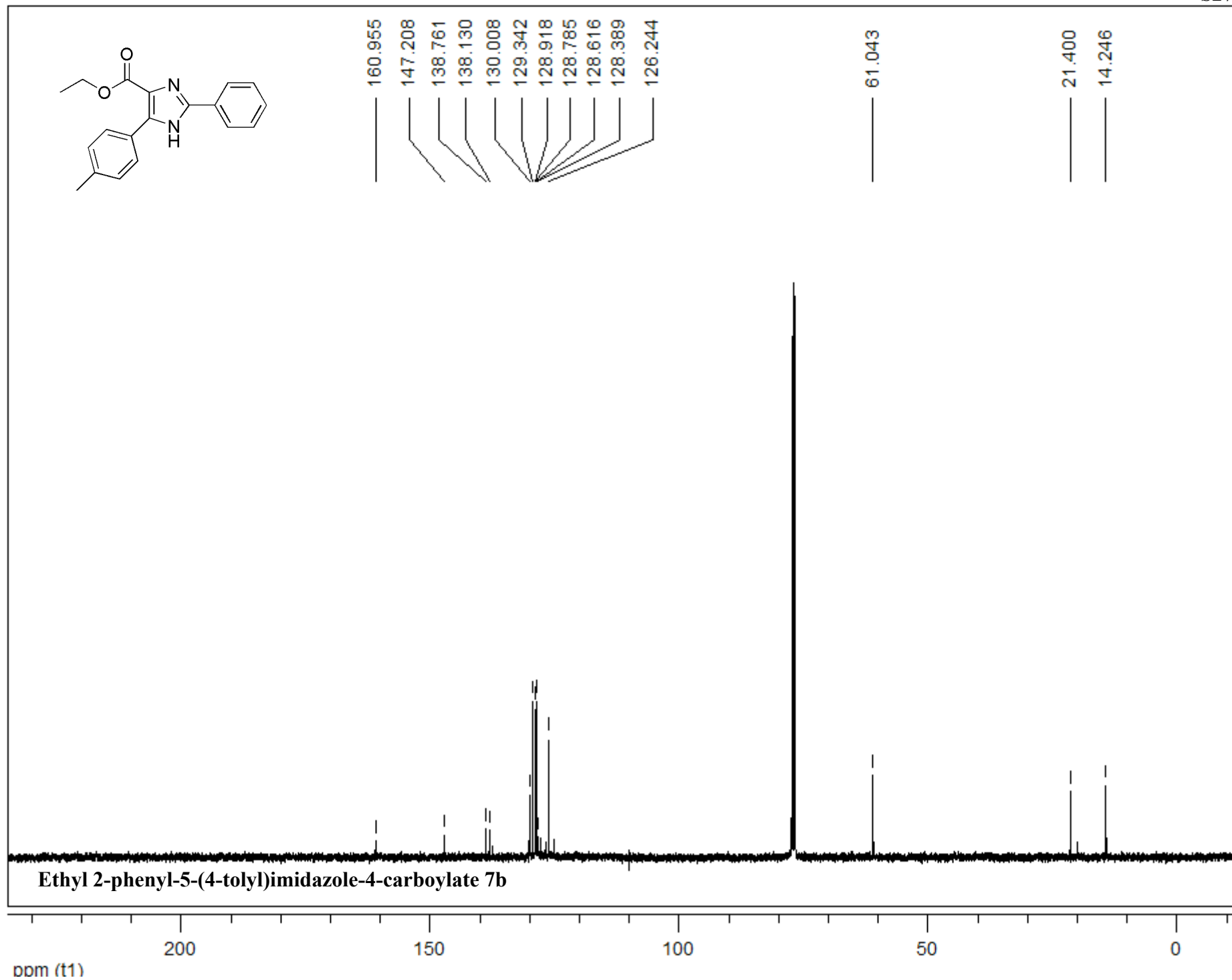
Ethyl 5-(morpholin-4-yl)-2-phenylimidazole-4-carboxylate 5g

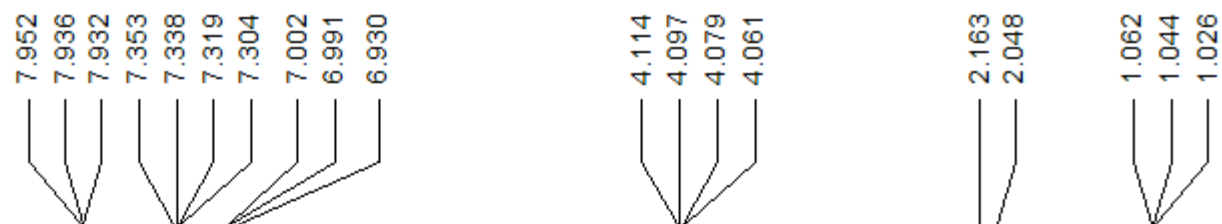
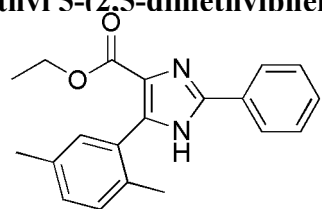
ppm (f1)

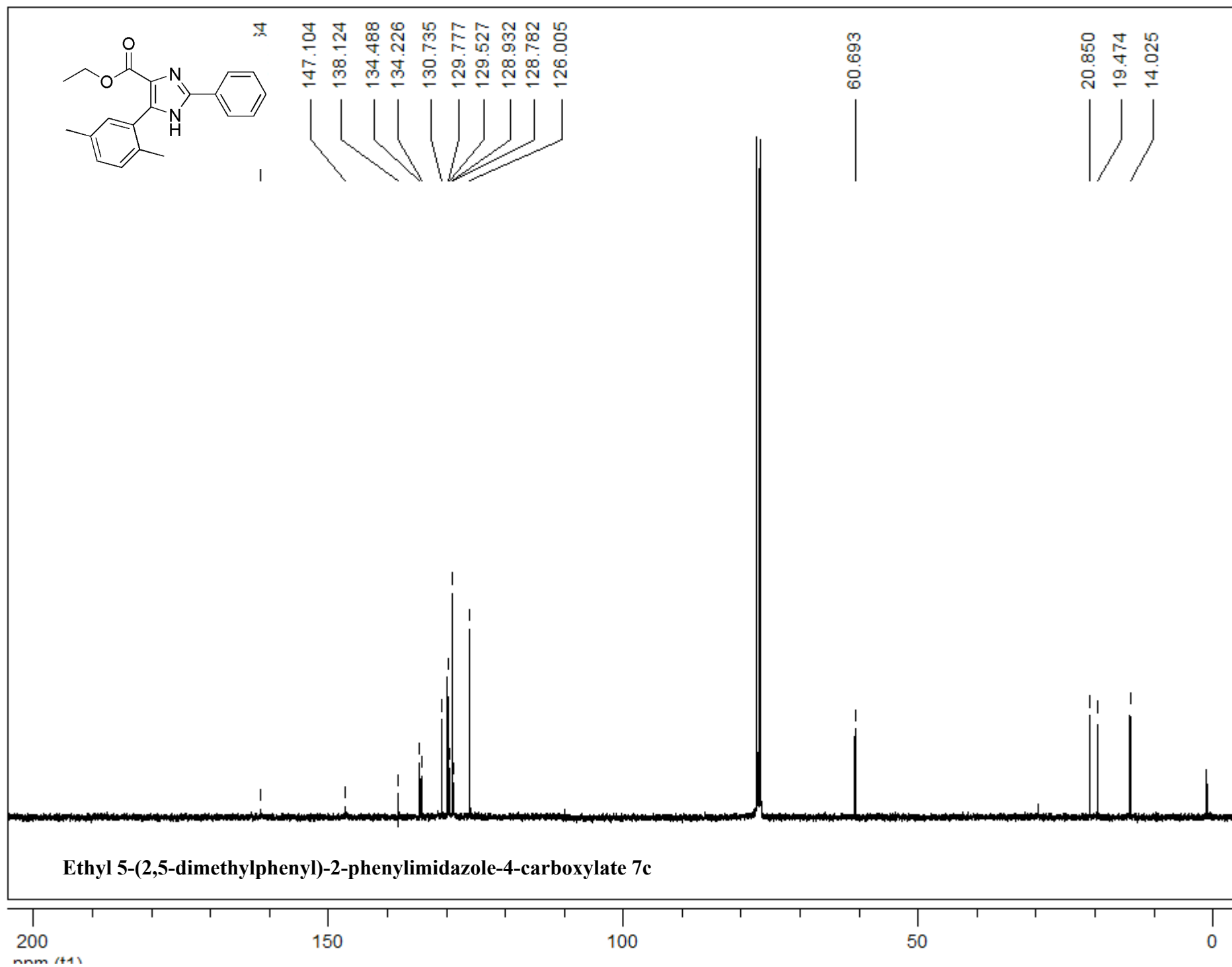
Ethyl 2-phenyl-5-(2-tolyl)imidazole-4-carboxylate 7a



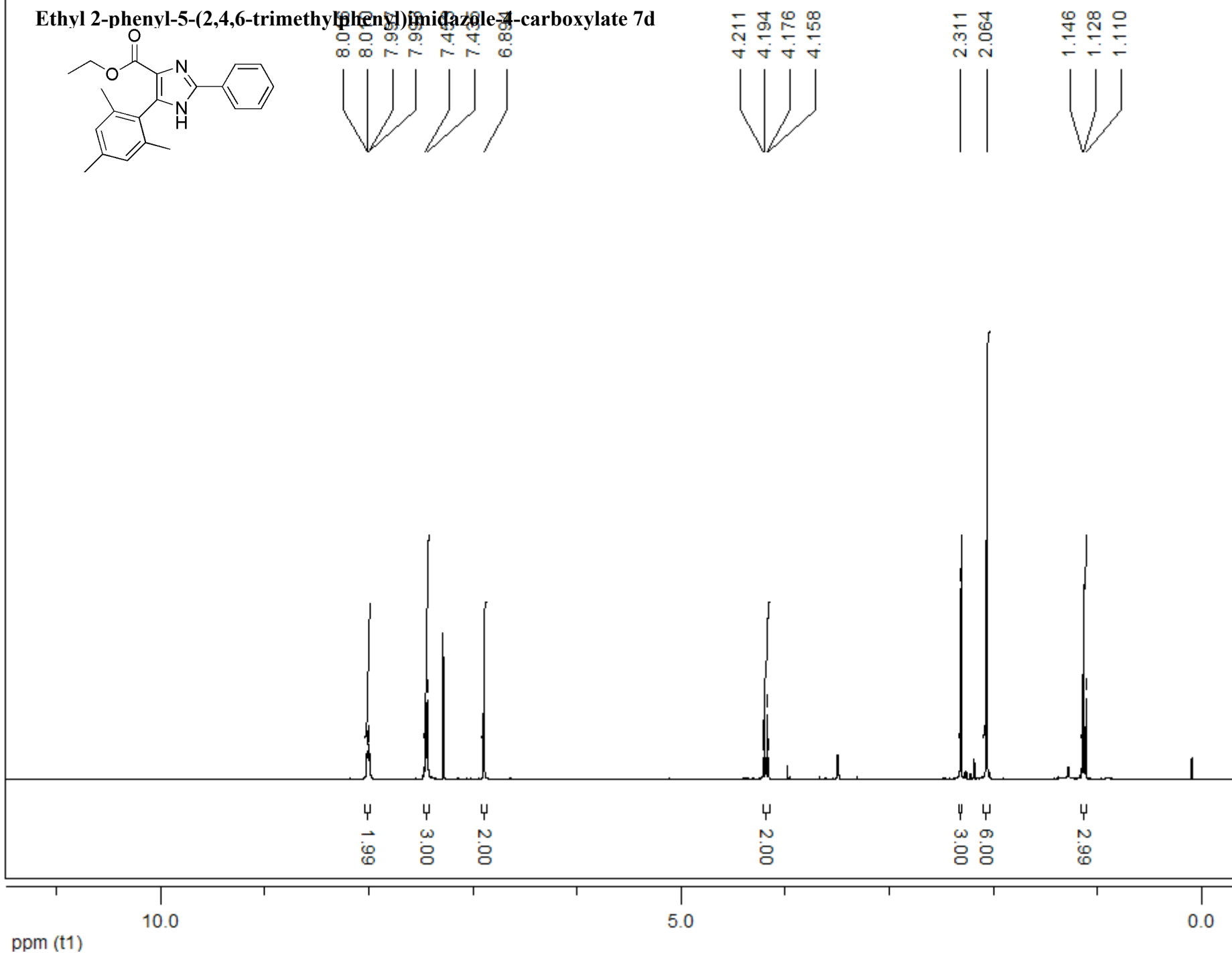
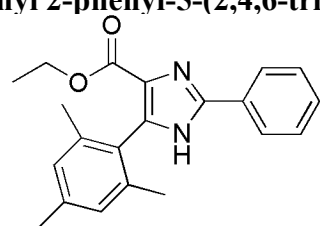
Ethyl 2-phenyl-5-(4-tolyl)imidazole-4-carboxylate 7b

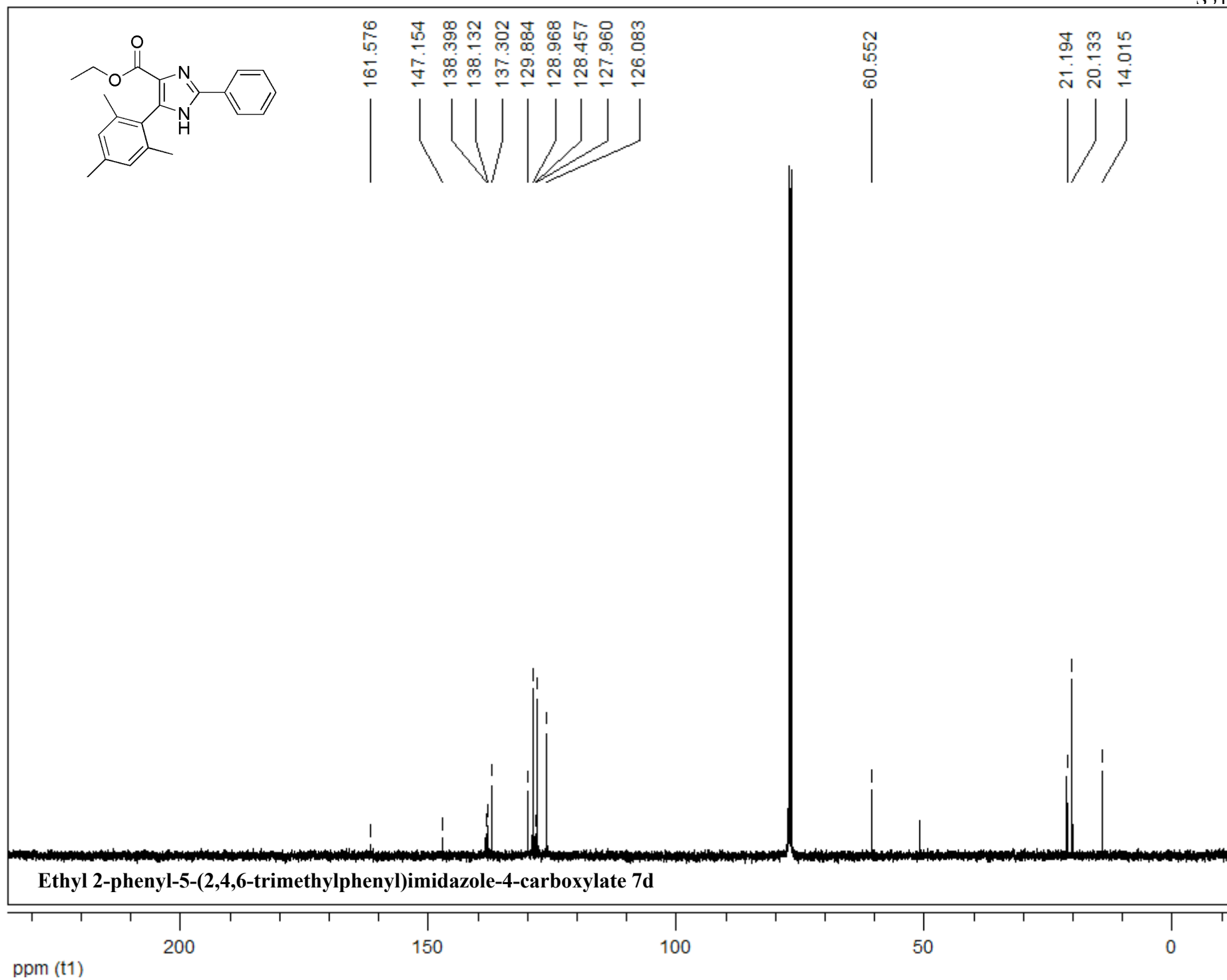


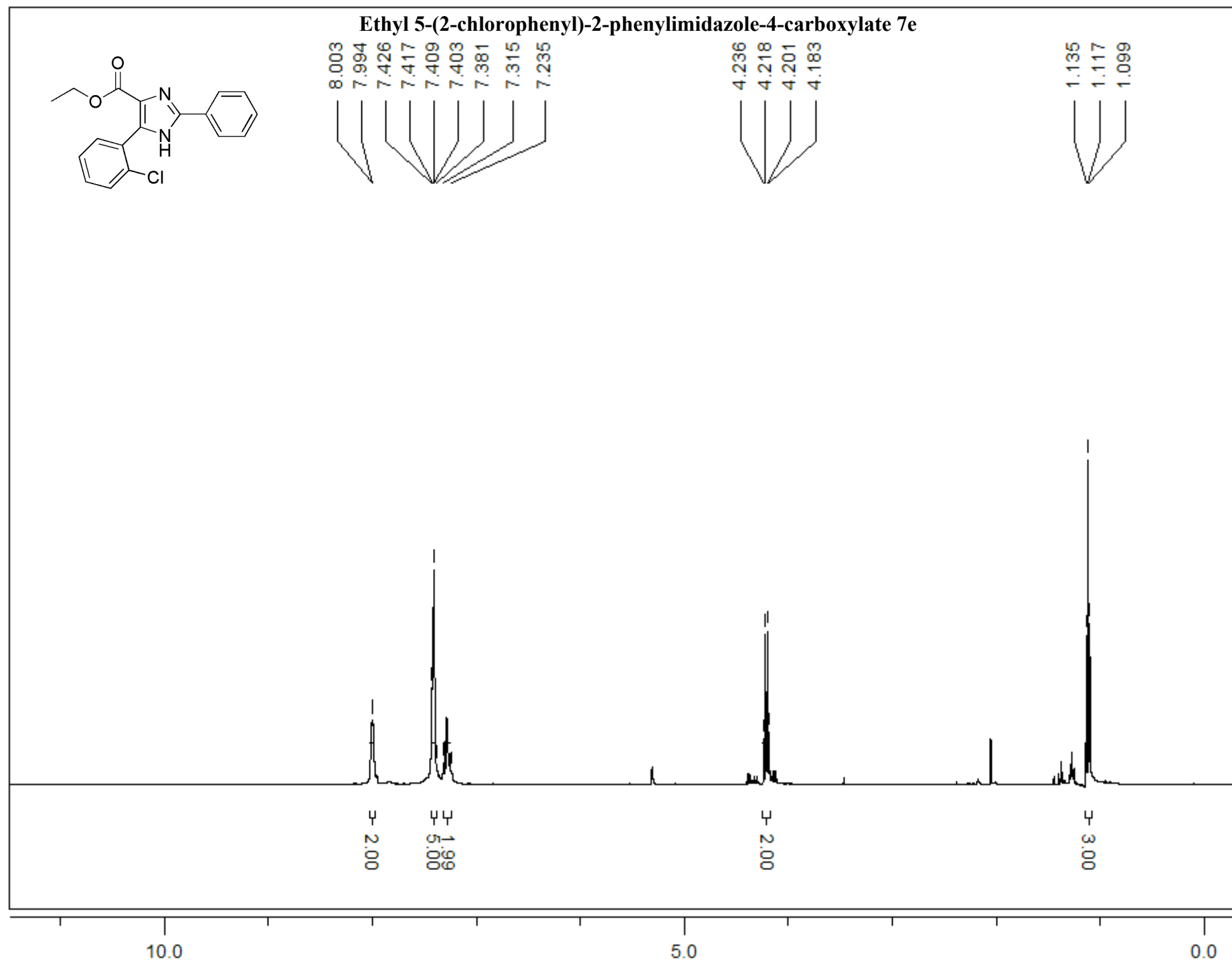
Ethyl 5-(2,5-dimethylphenyl)-2-phenylimidazole-4-carboxylate 7c

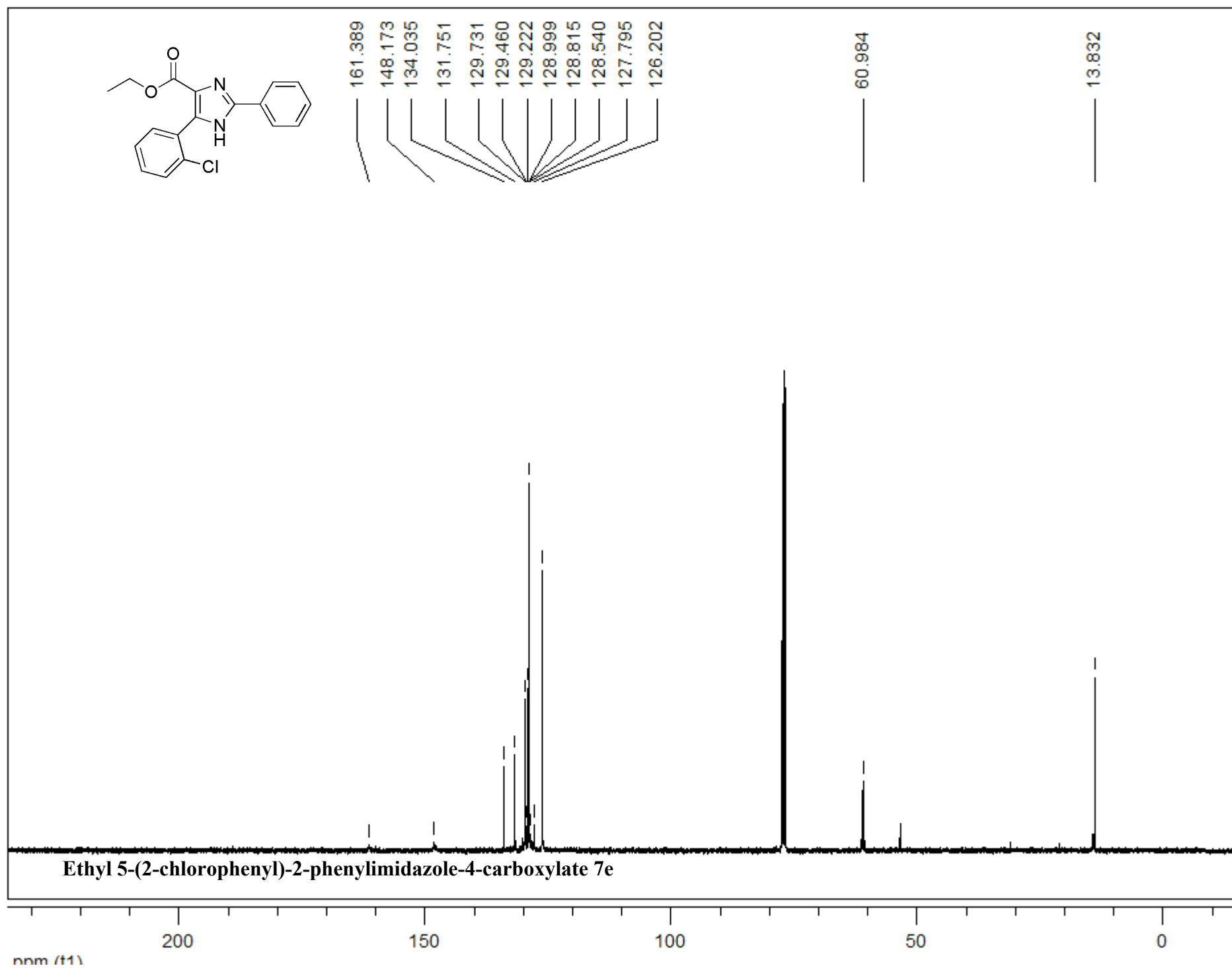


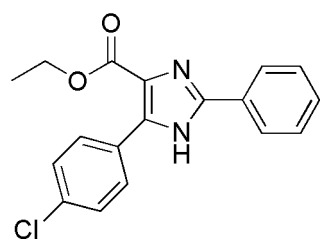
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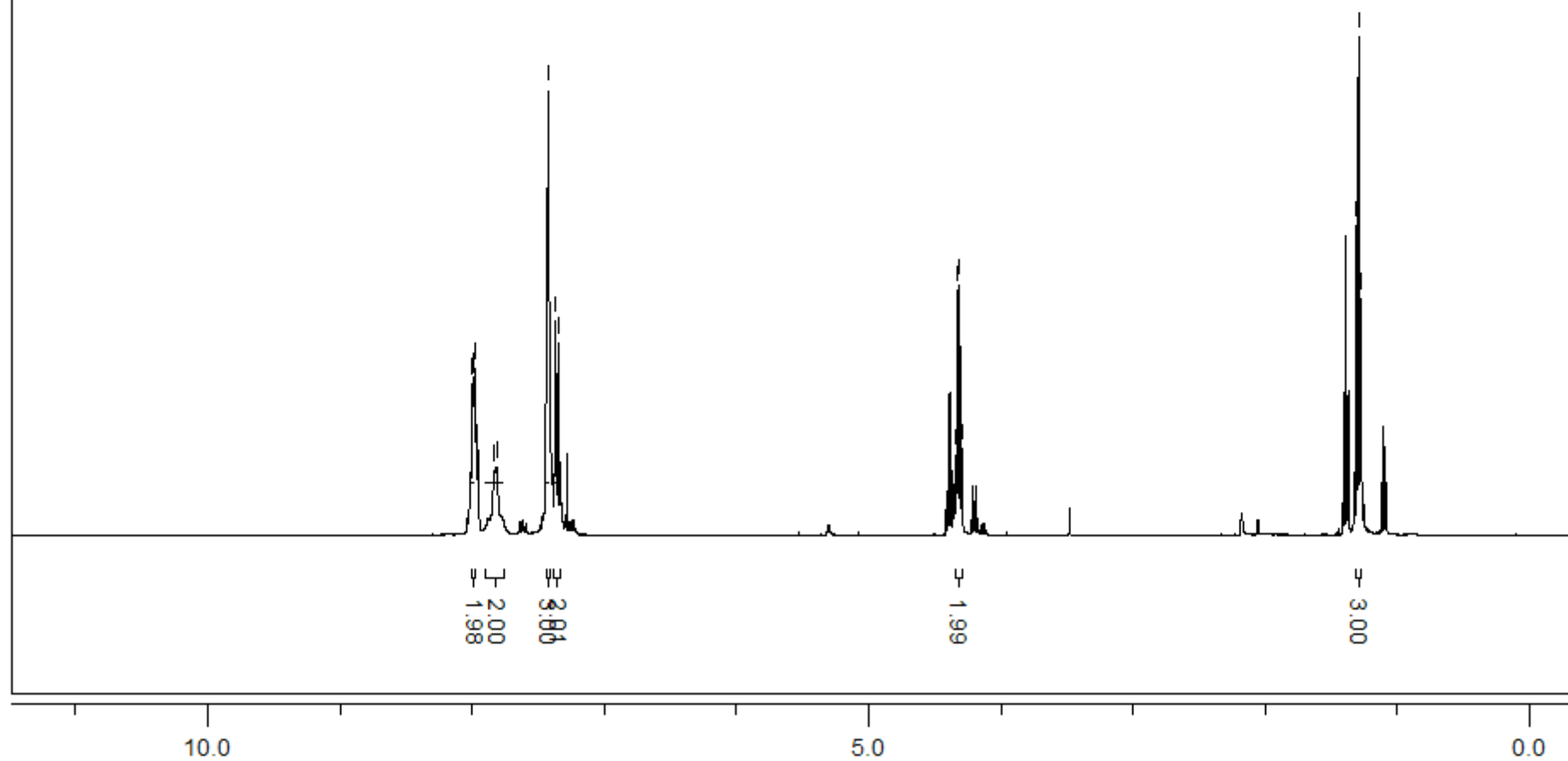


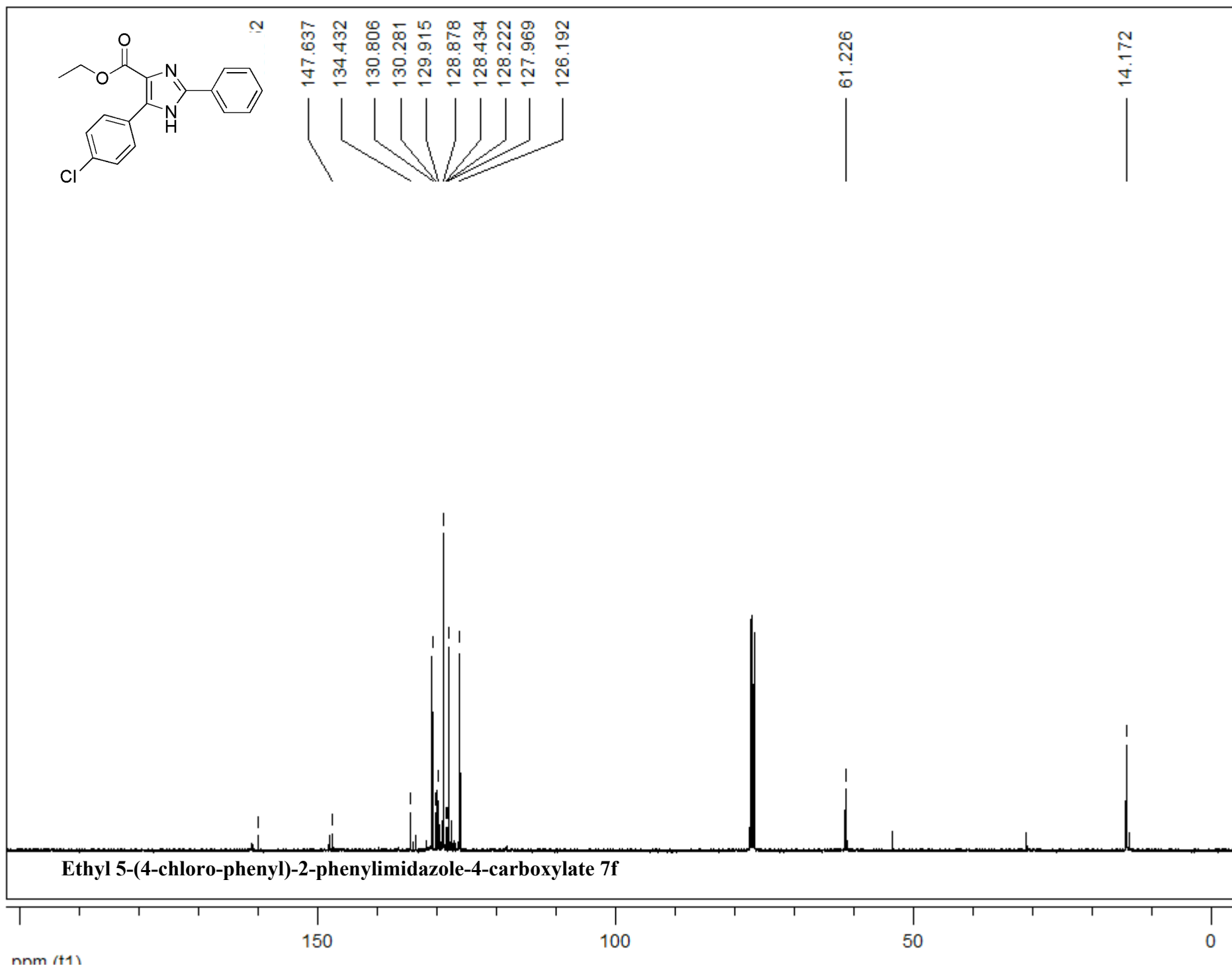
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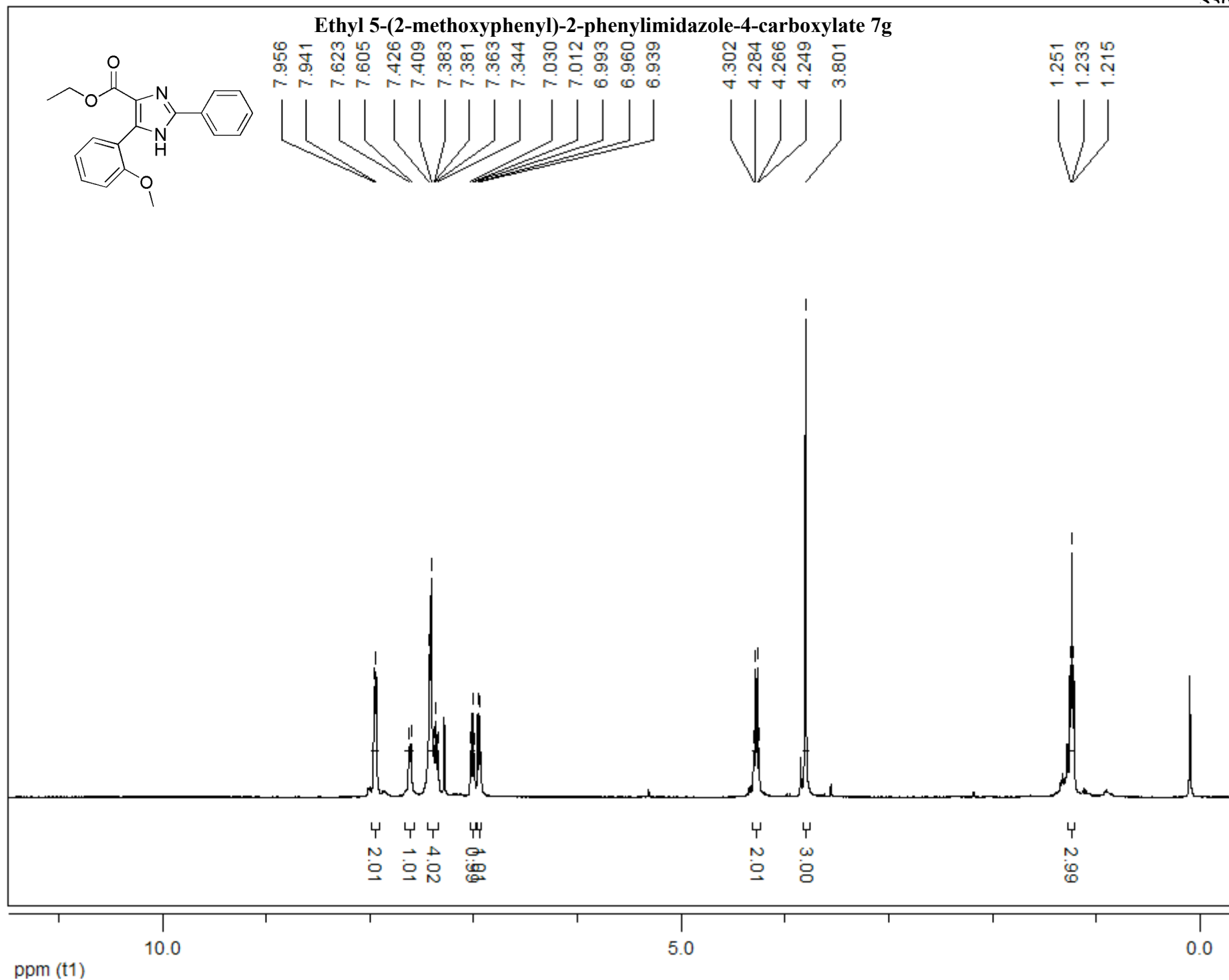
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7.830
7.815
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7.423
7.371
7.350

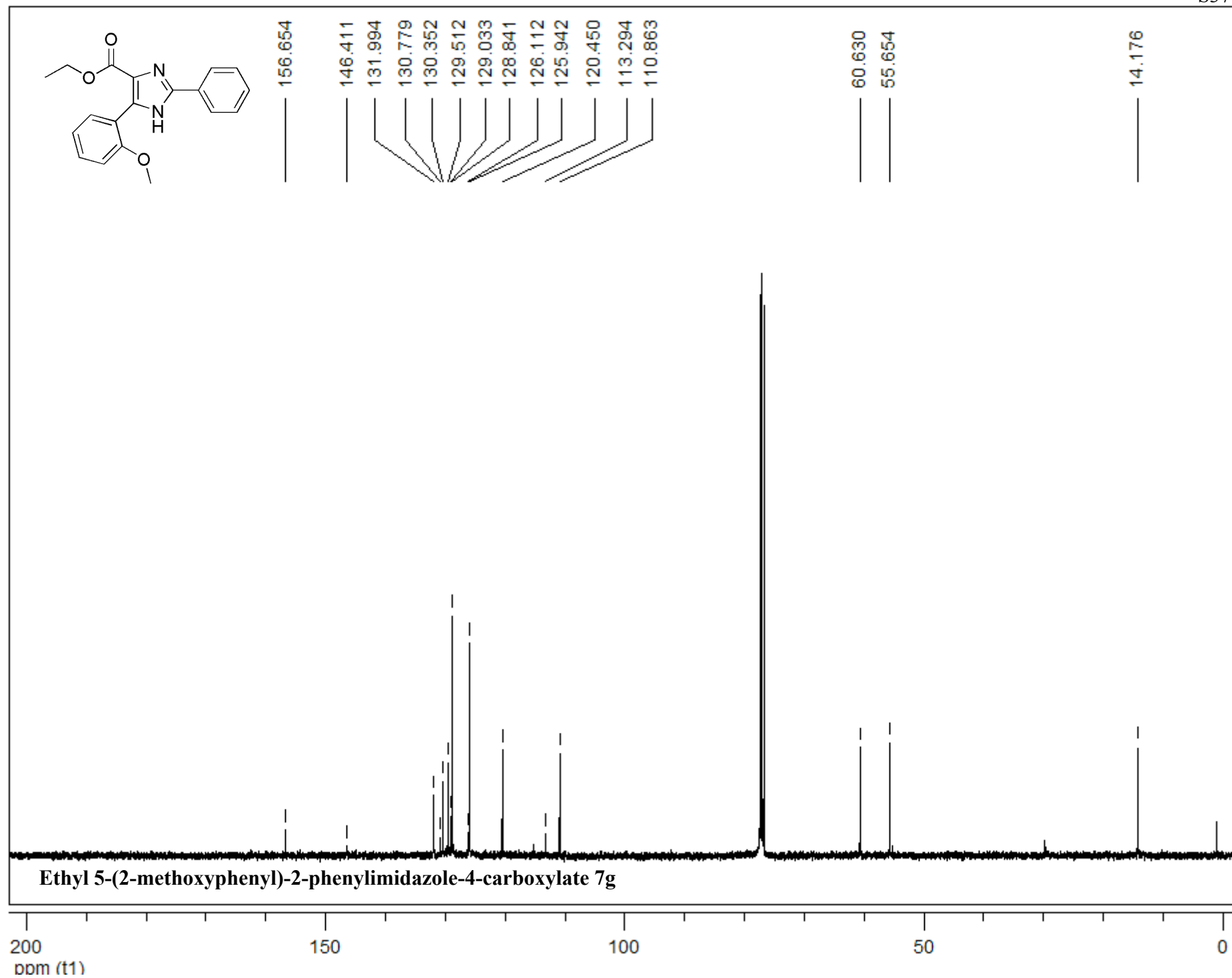
4.347
4.329
4.312
4.294

1.312
1.294
1.276

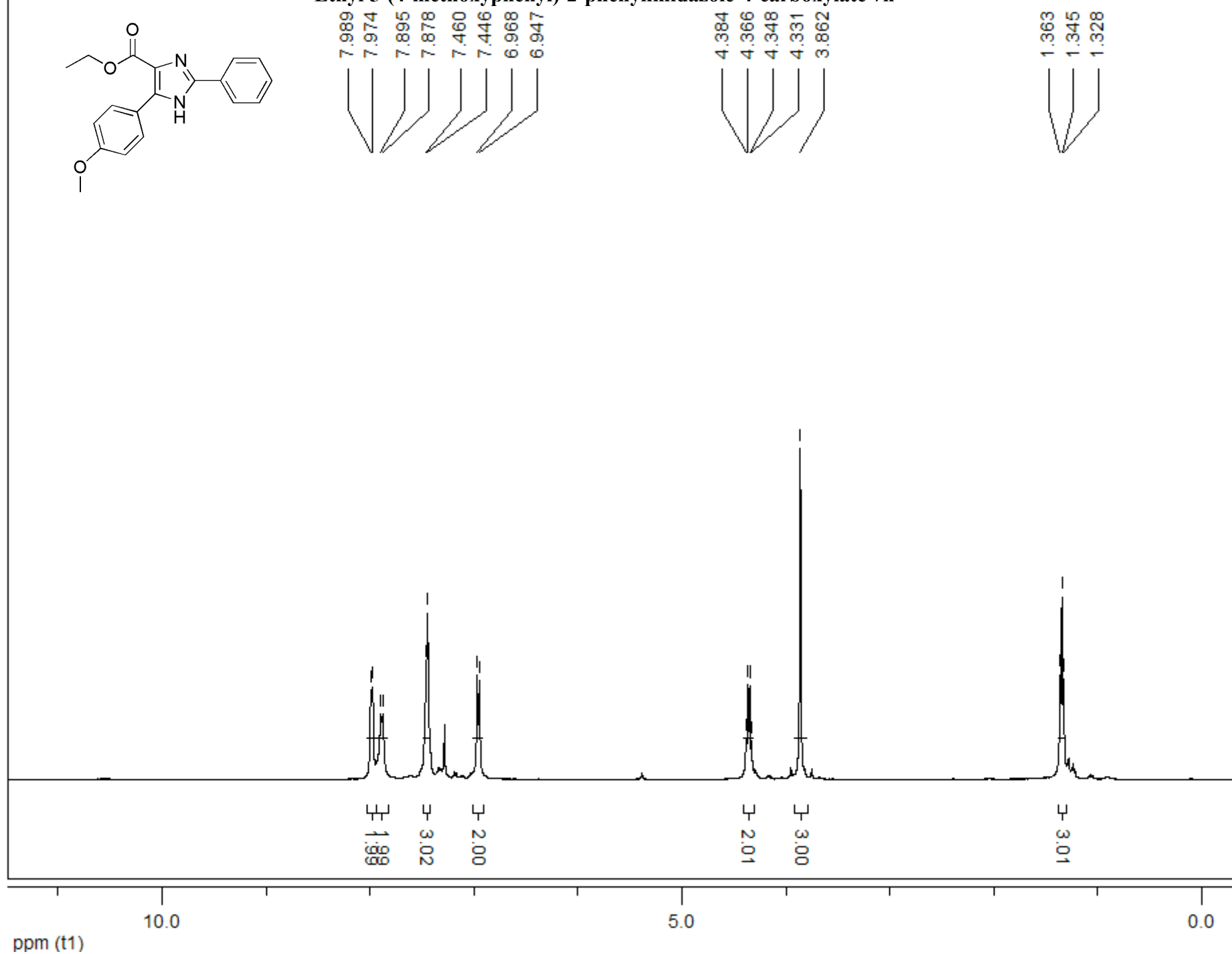
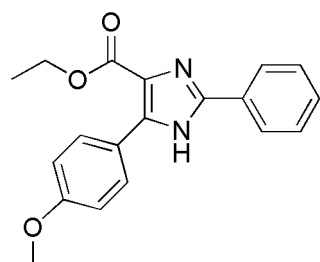


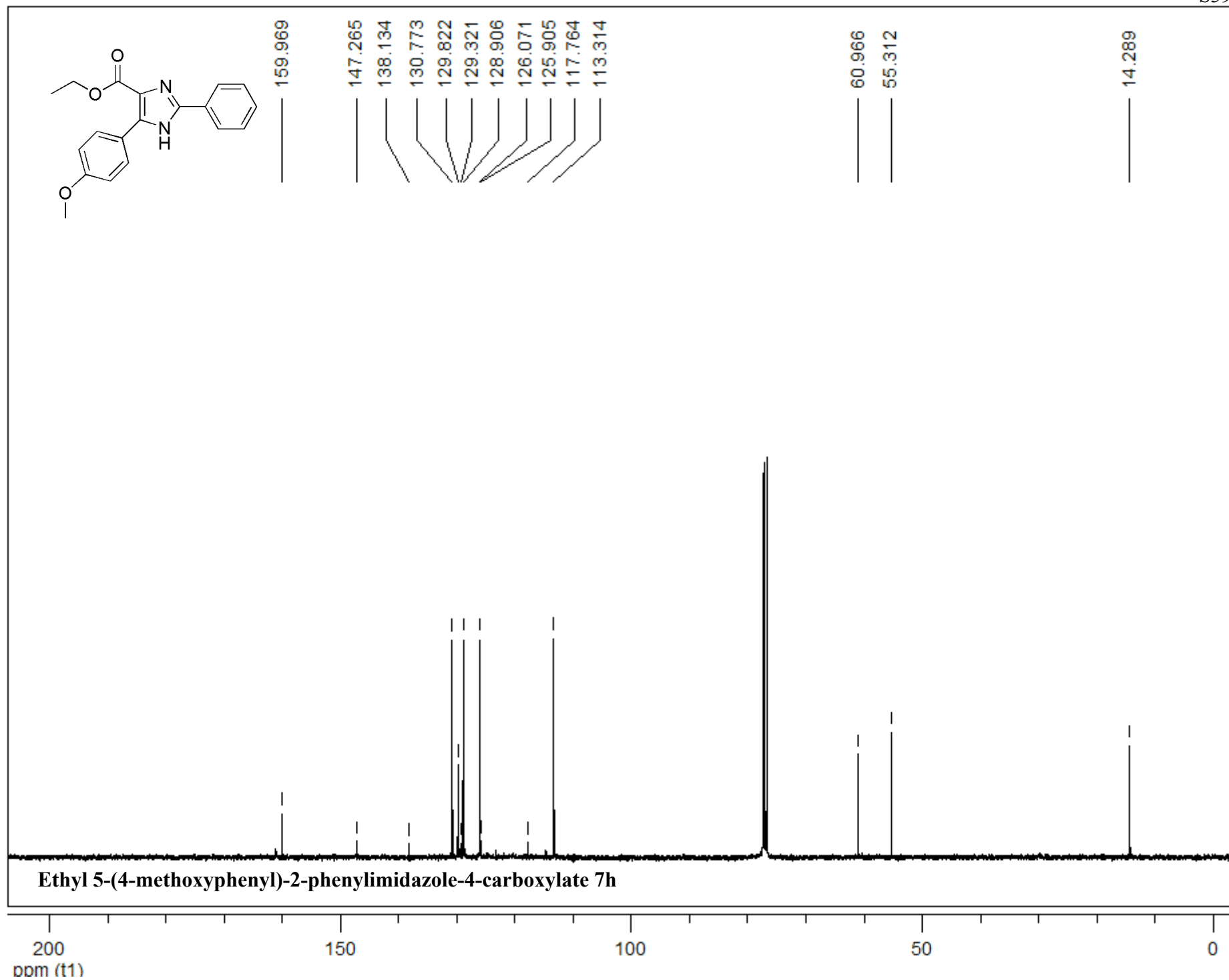


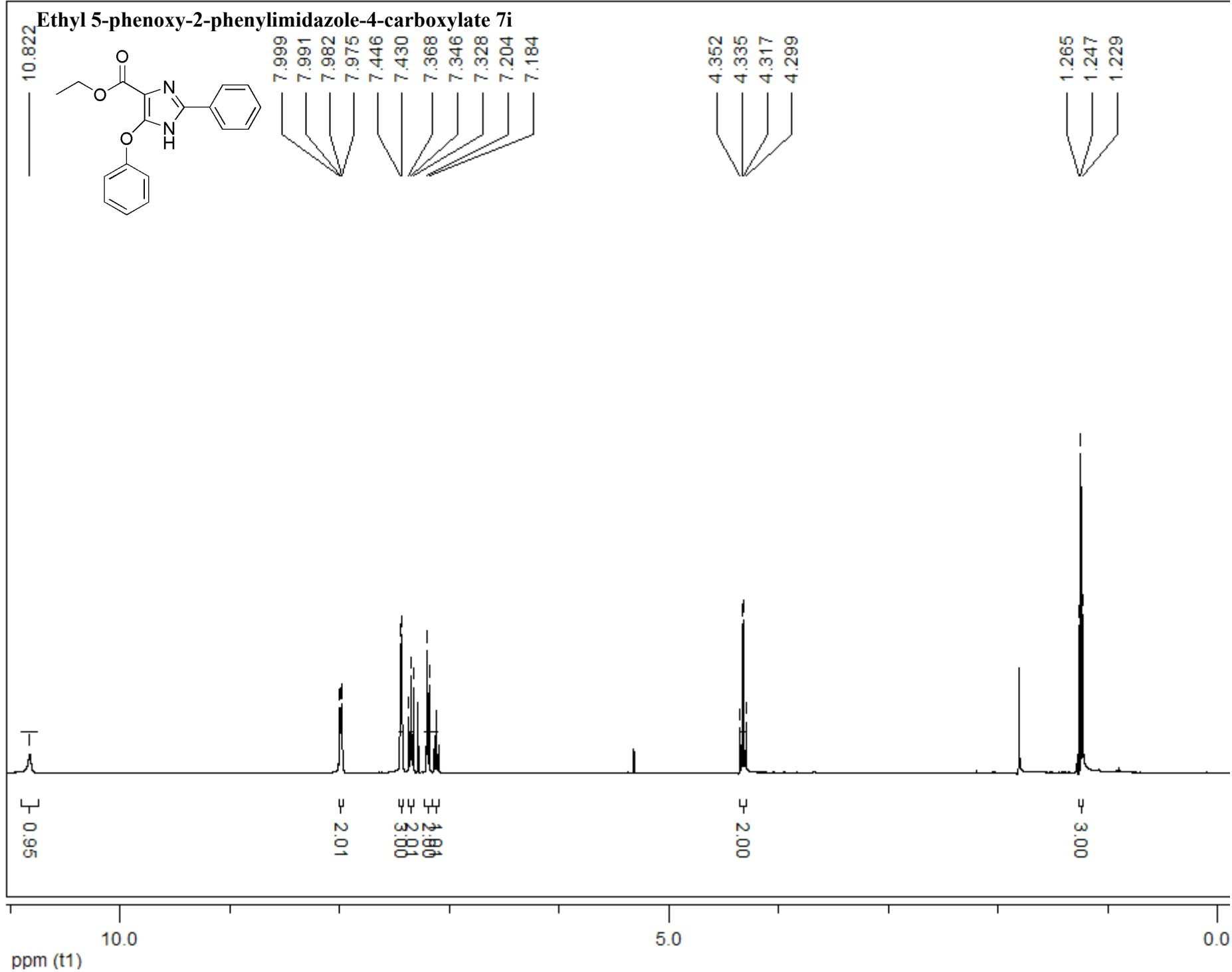


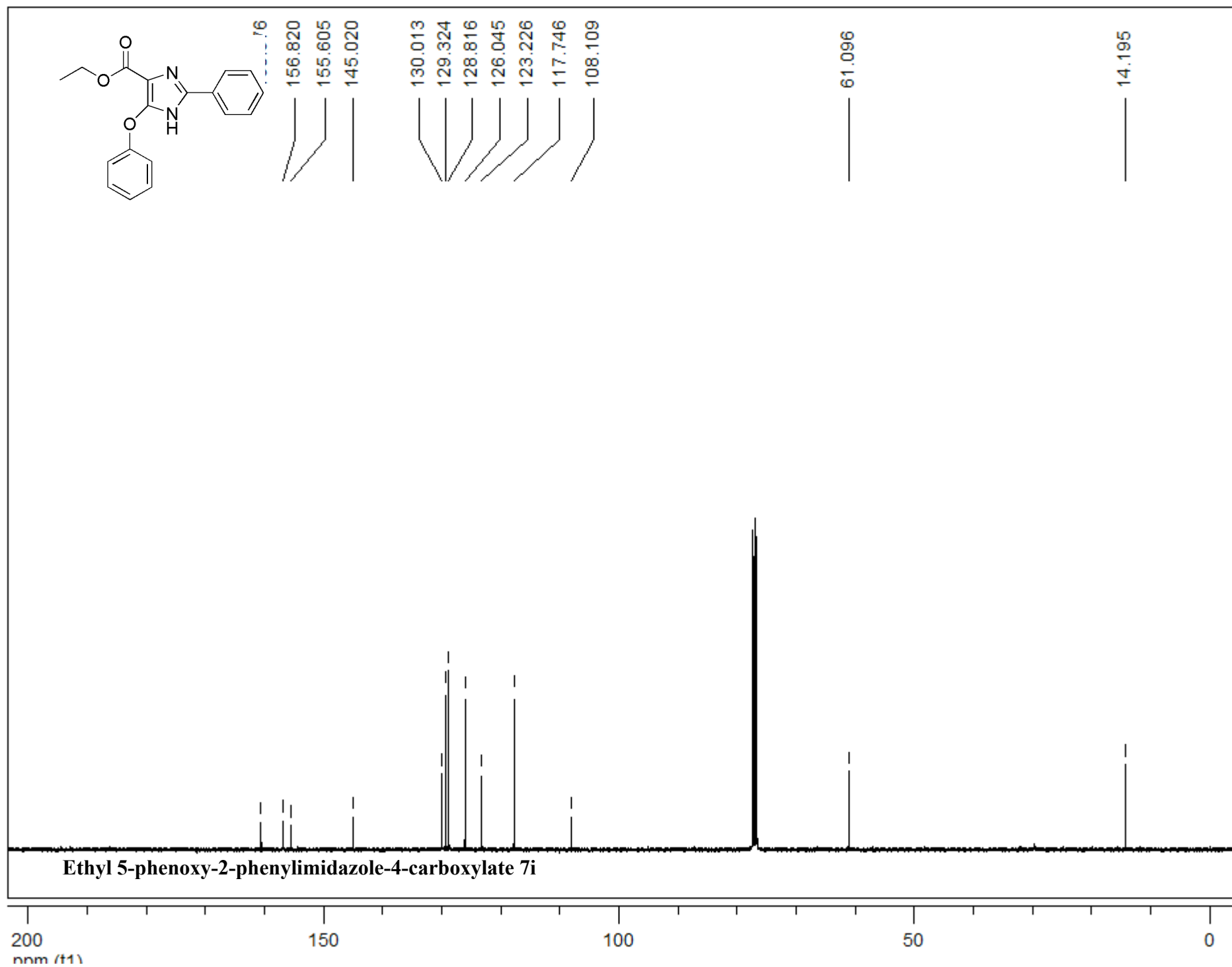


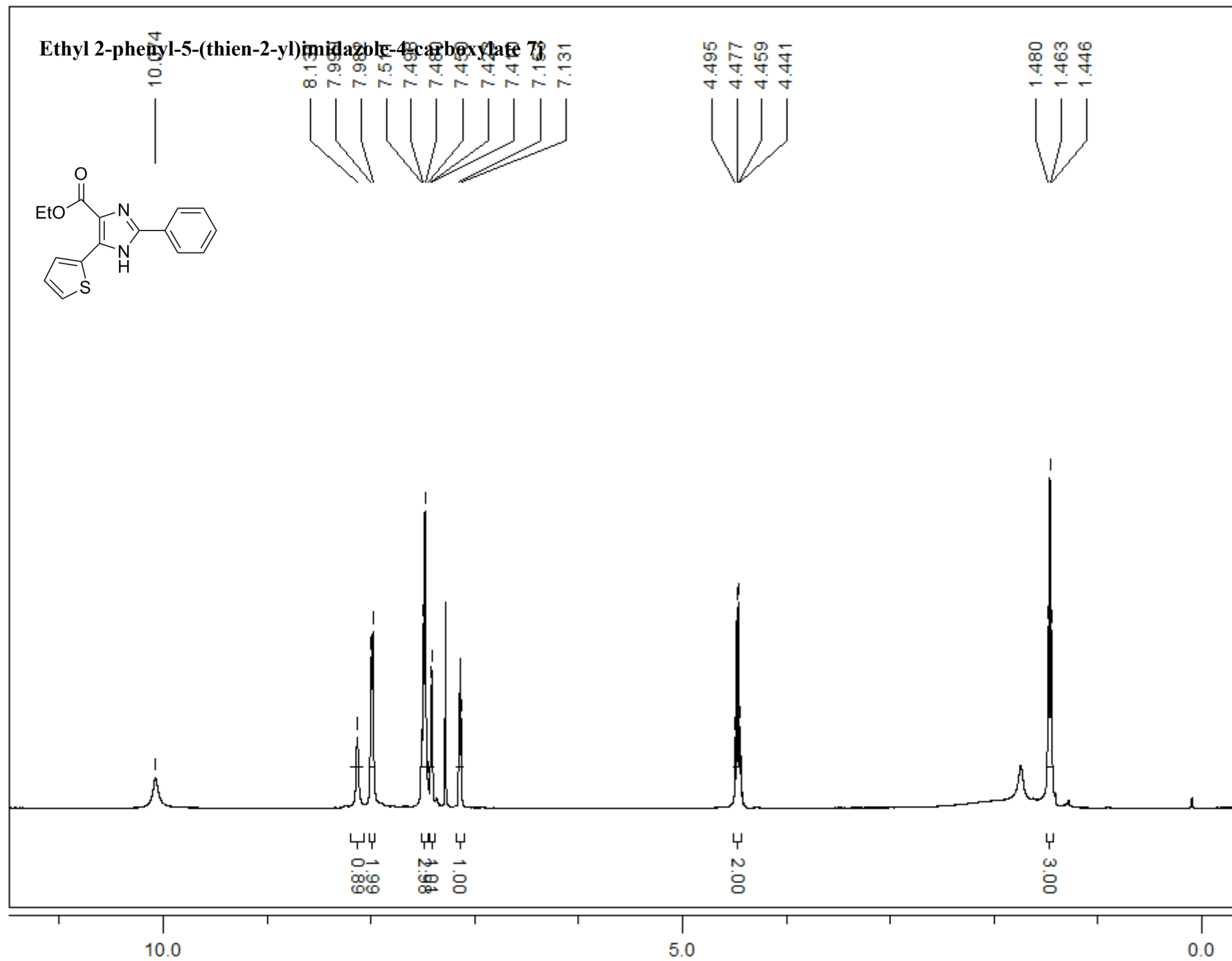
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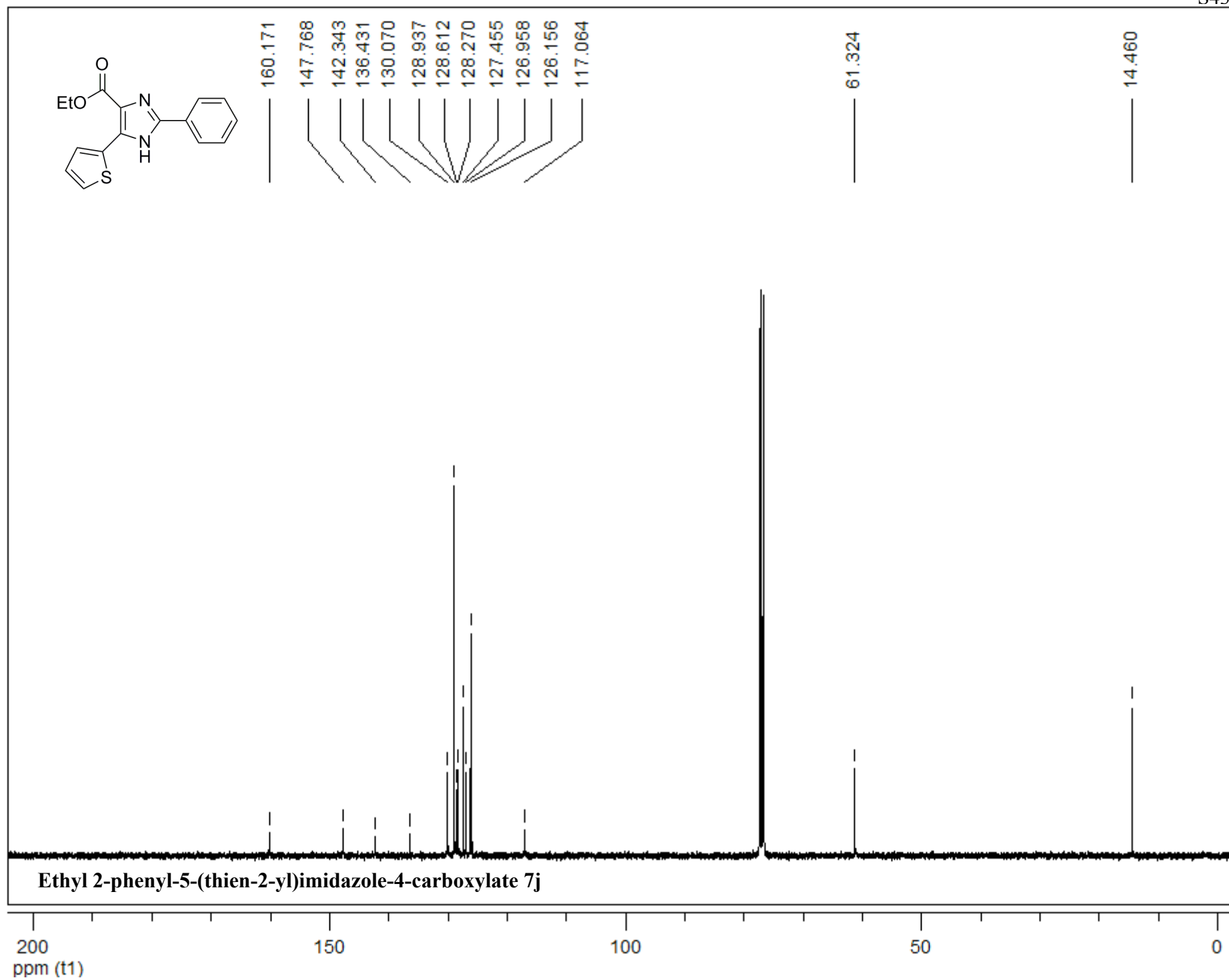




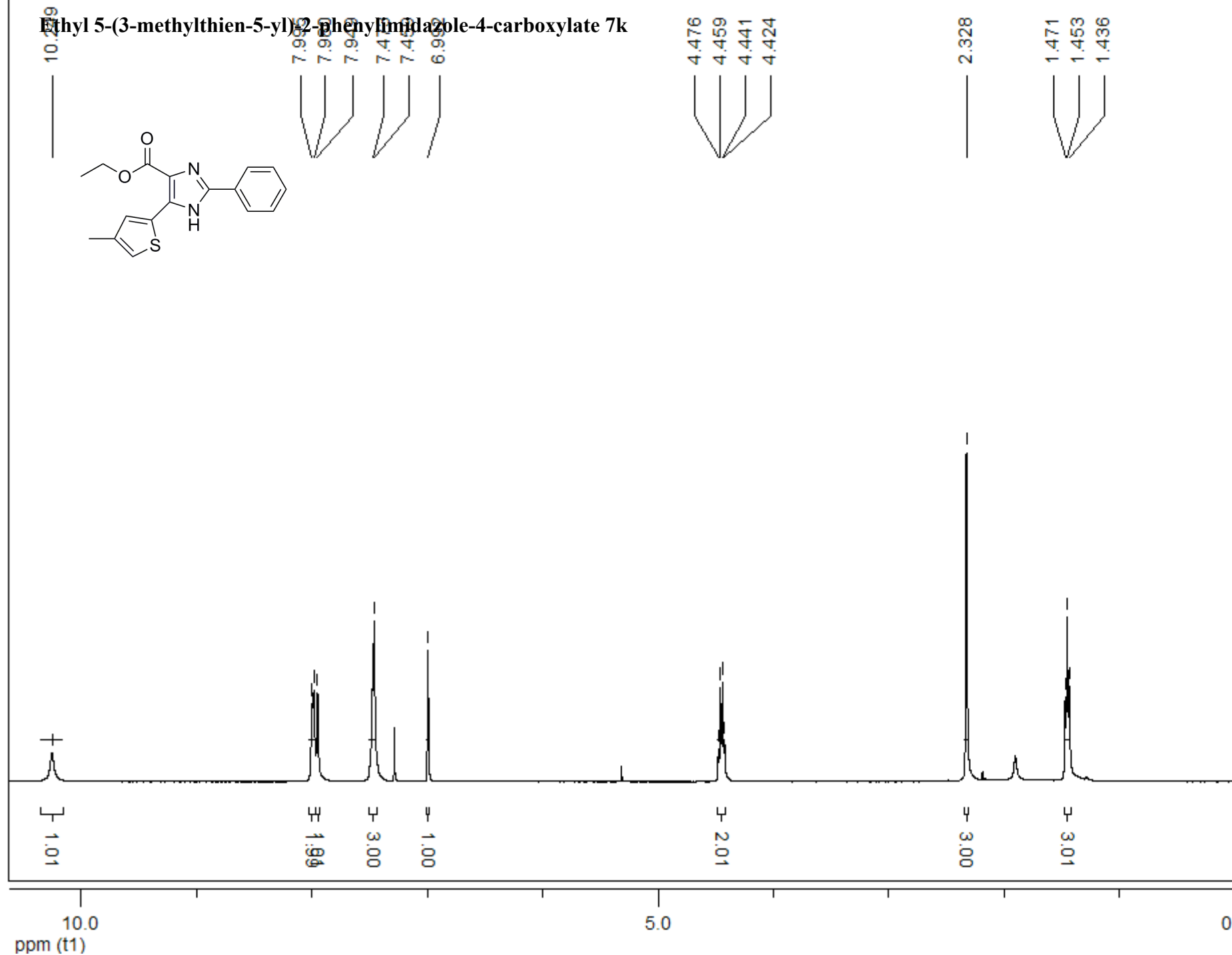


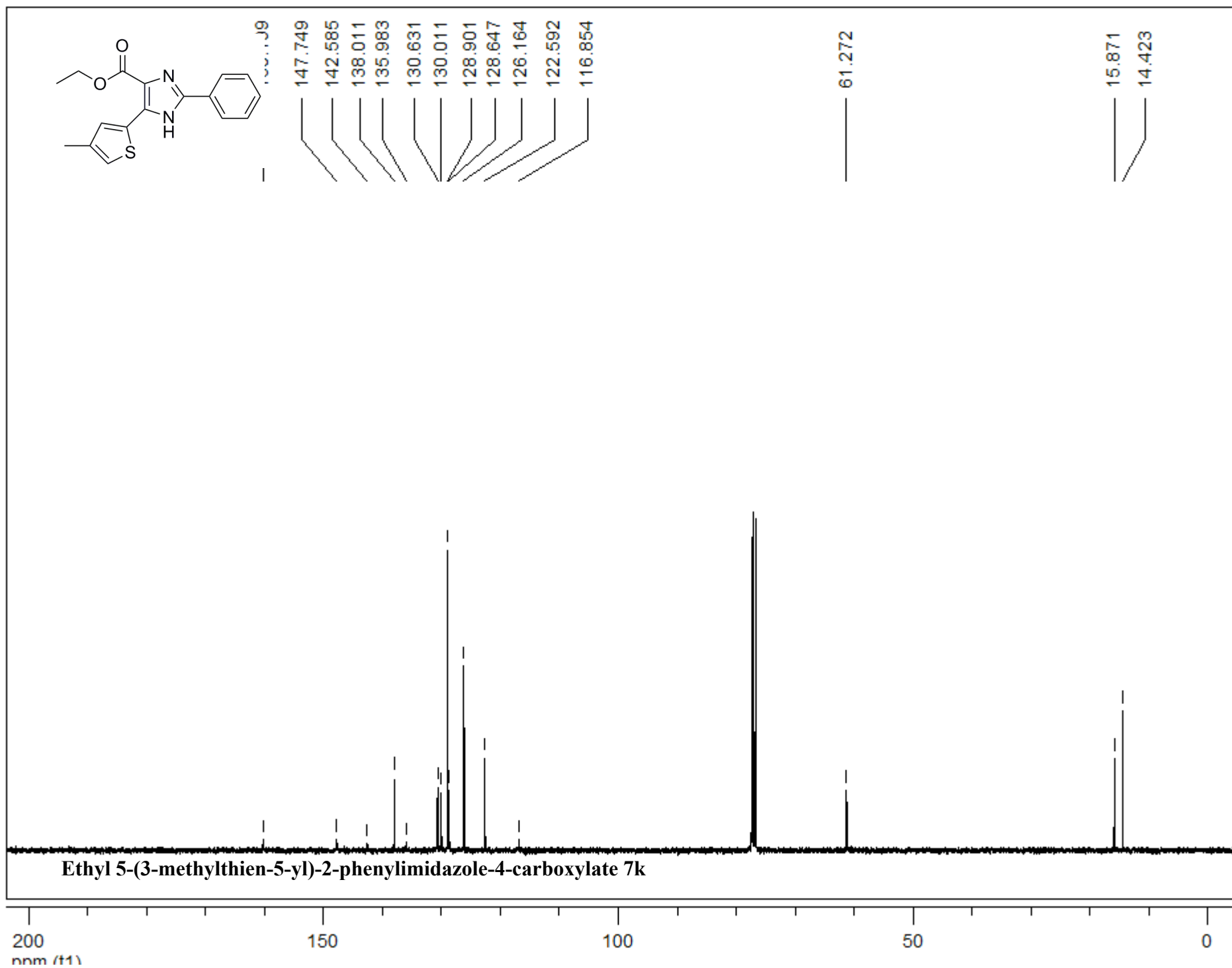




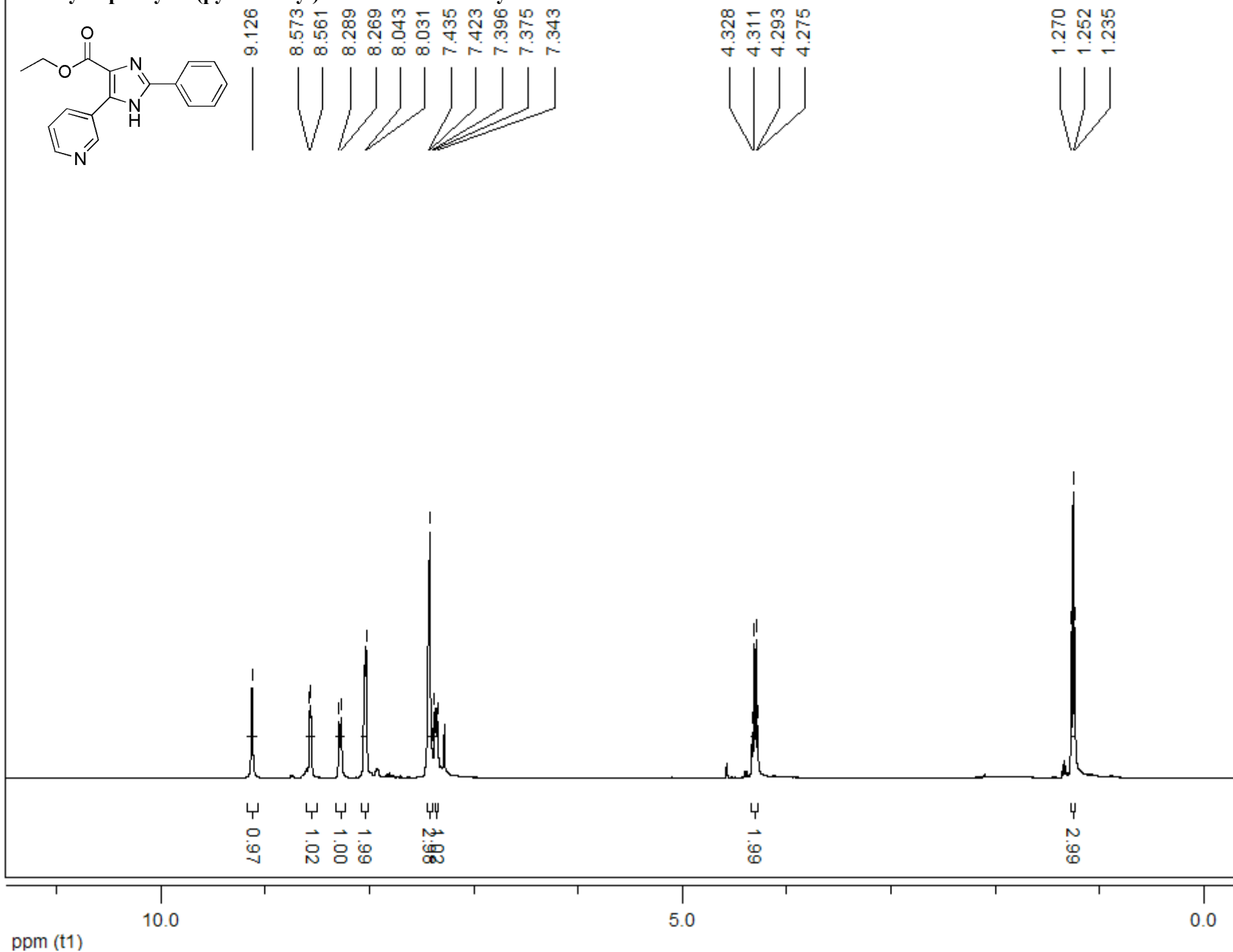


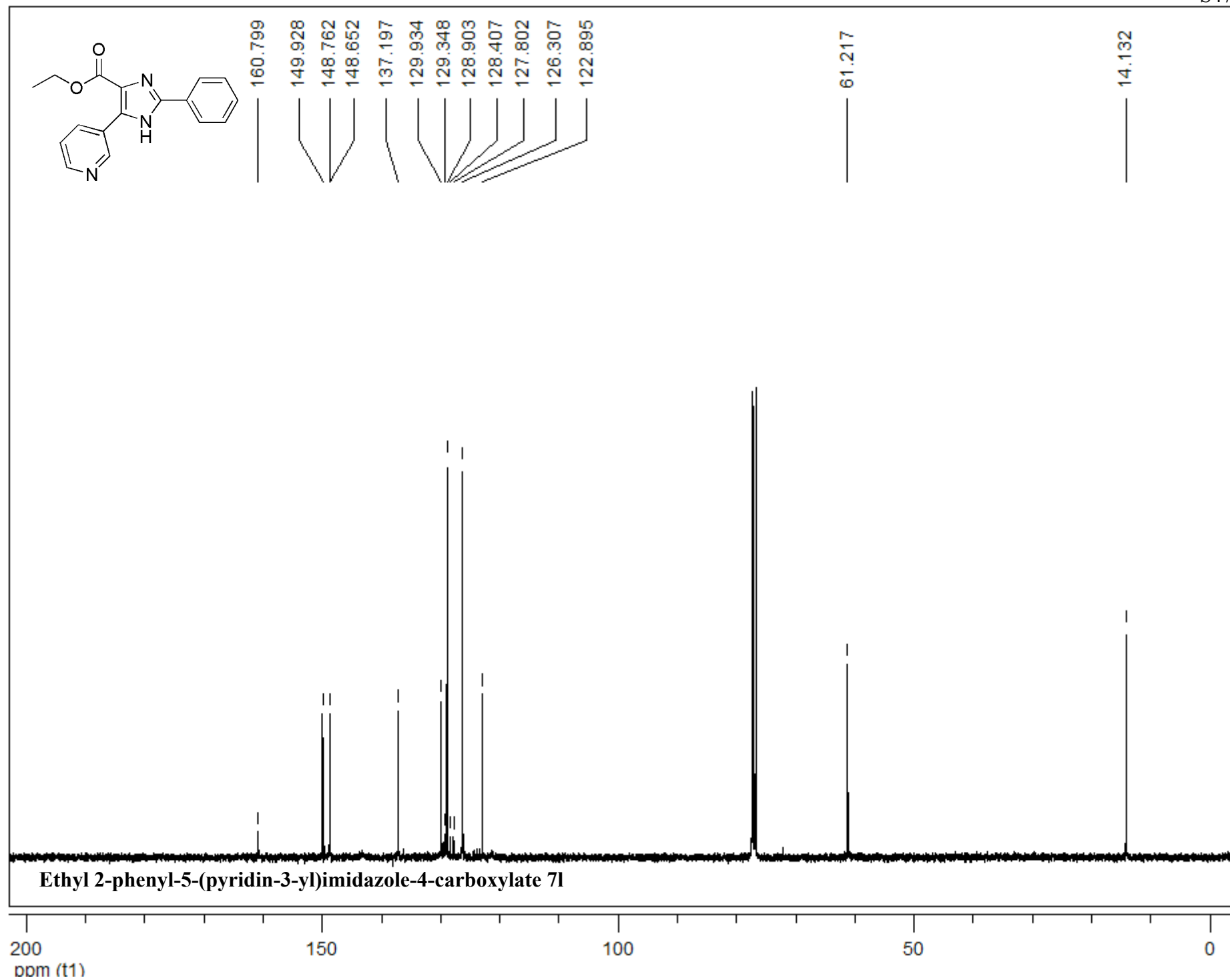
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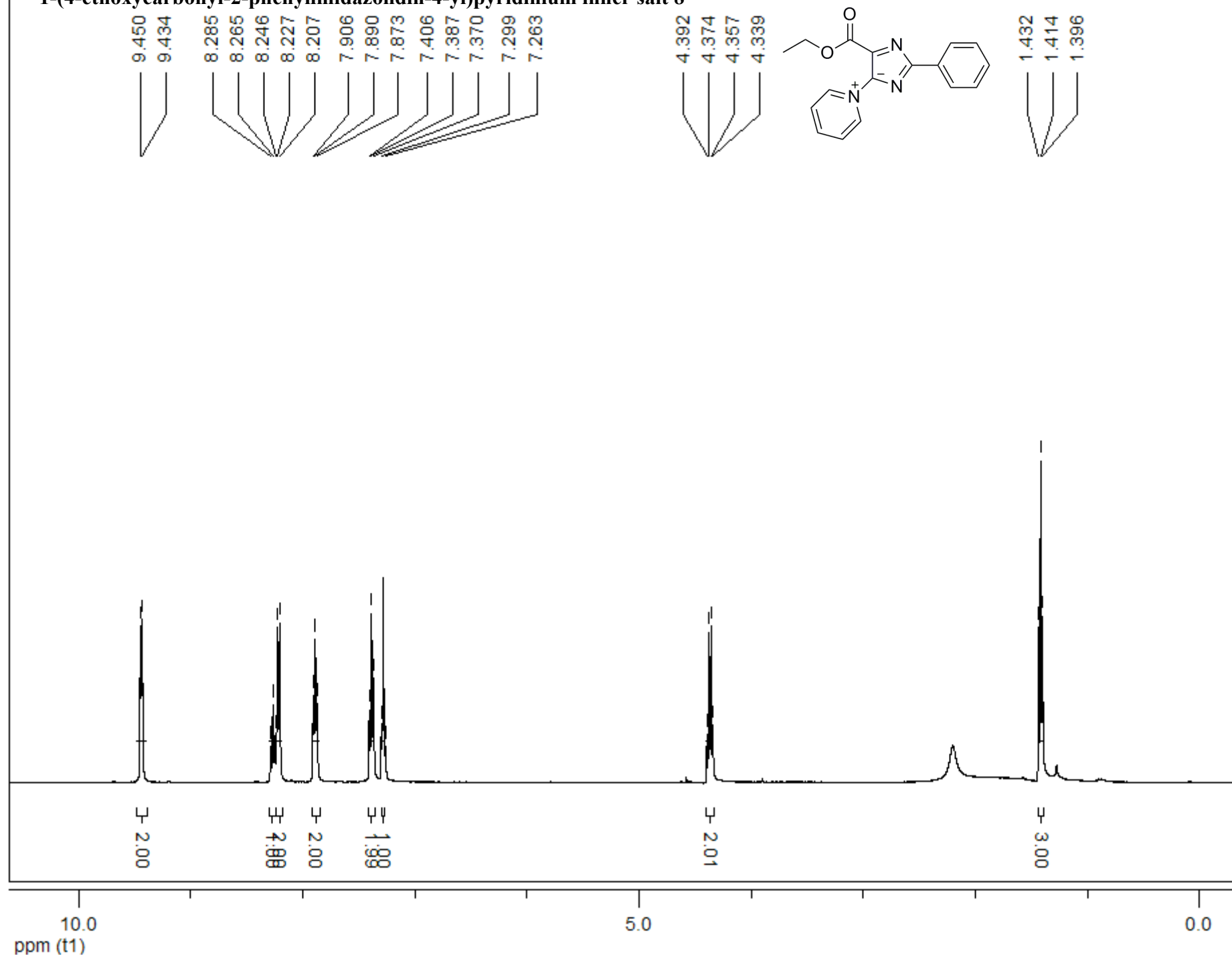


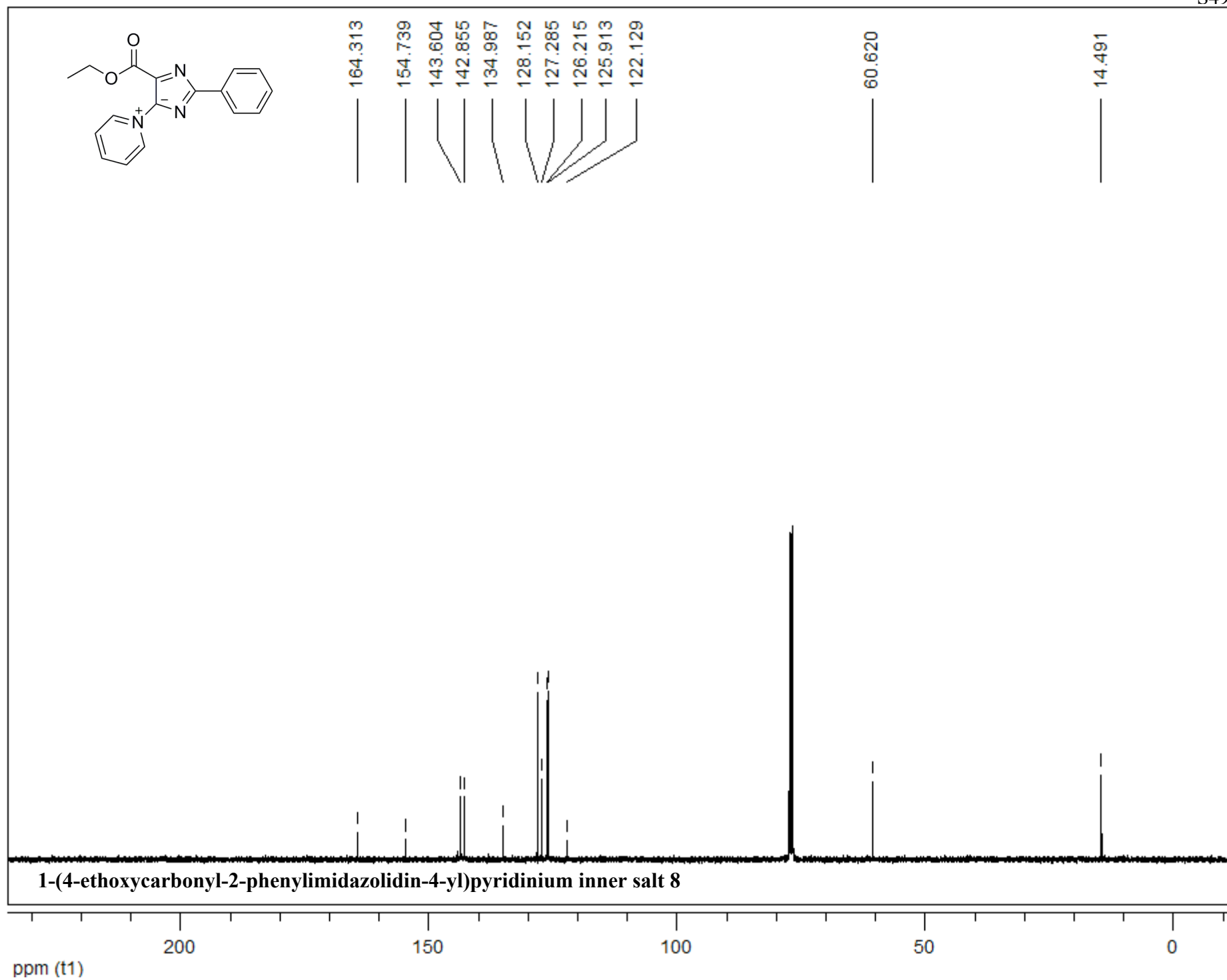


Ethyl 2-phenyl-5-(pyridin-3-yl)imidazole-4-carboxylate 7l

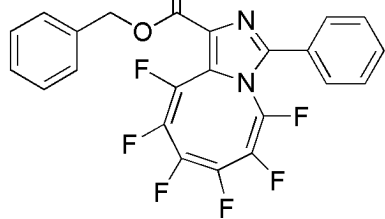




1-(4-ethoxycarbonyl-2-phenylimidazolidin-4-yl)pyridinium inner salt 8

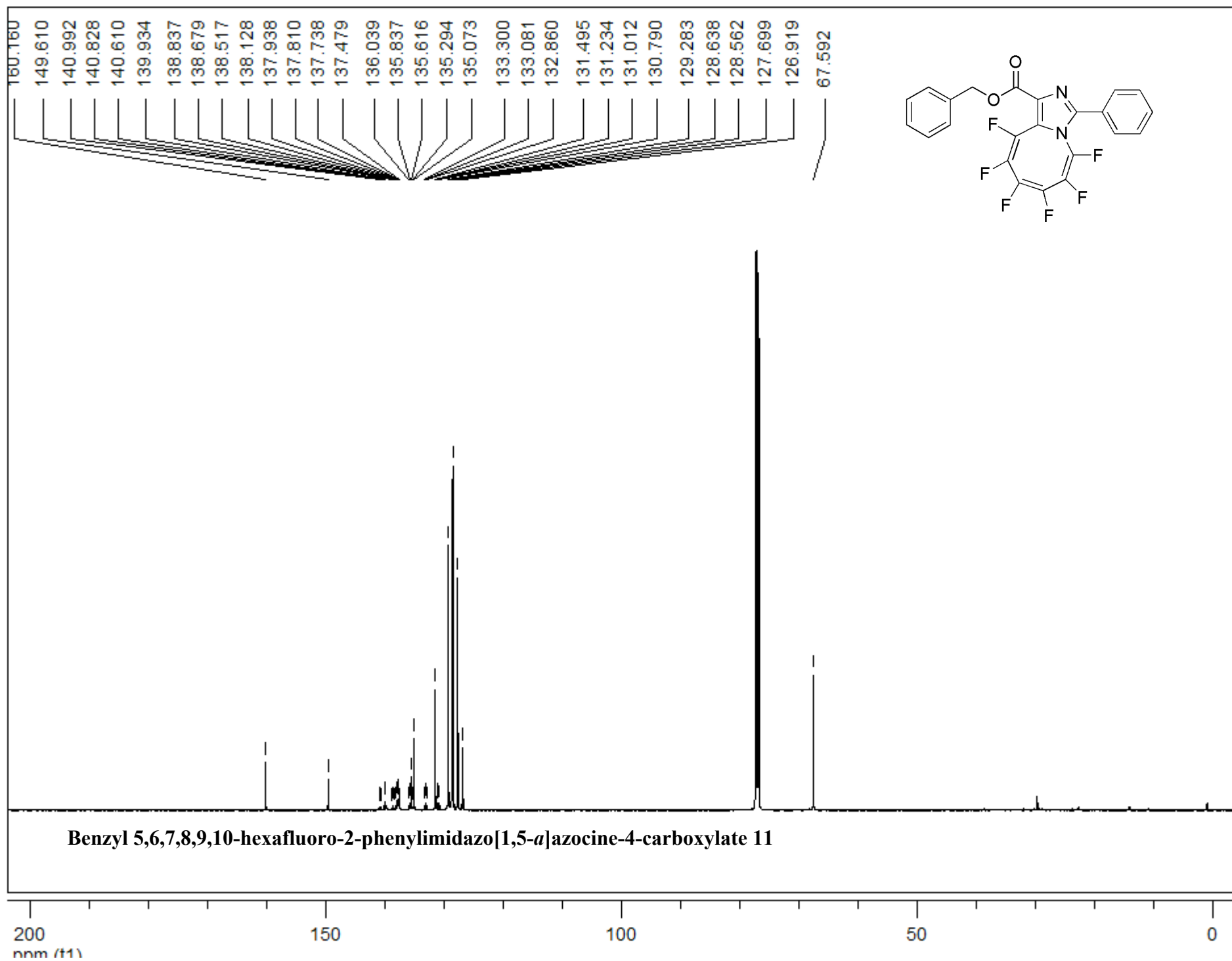


Renzi 5 6 7 8 9 10-hexafluoro-2-phenylimidazo[1,5-a]azocine-4-carboxylate 11

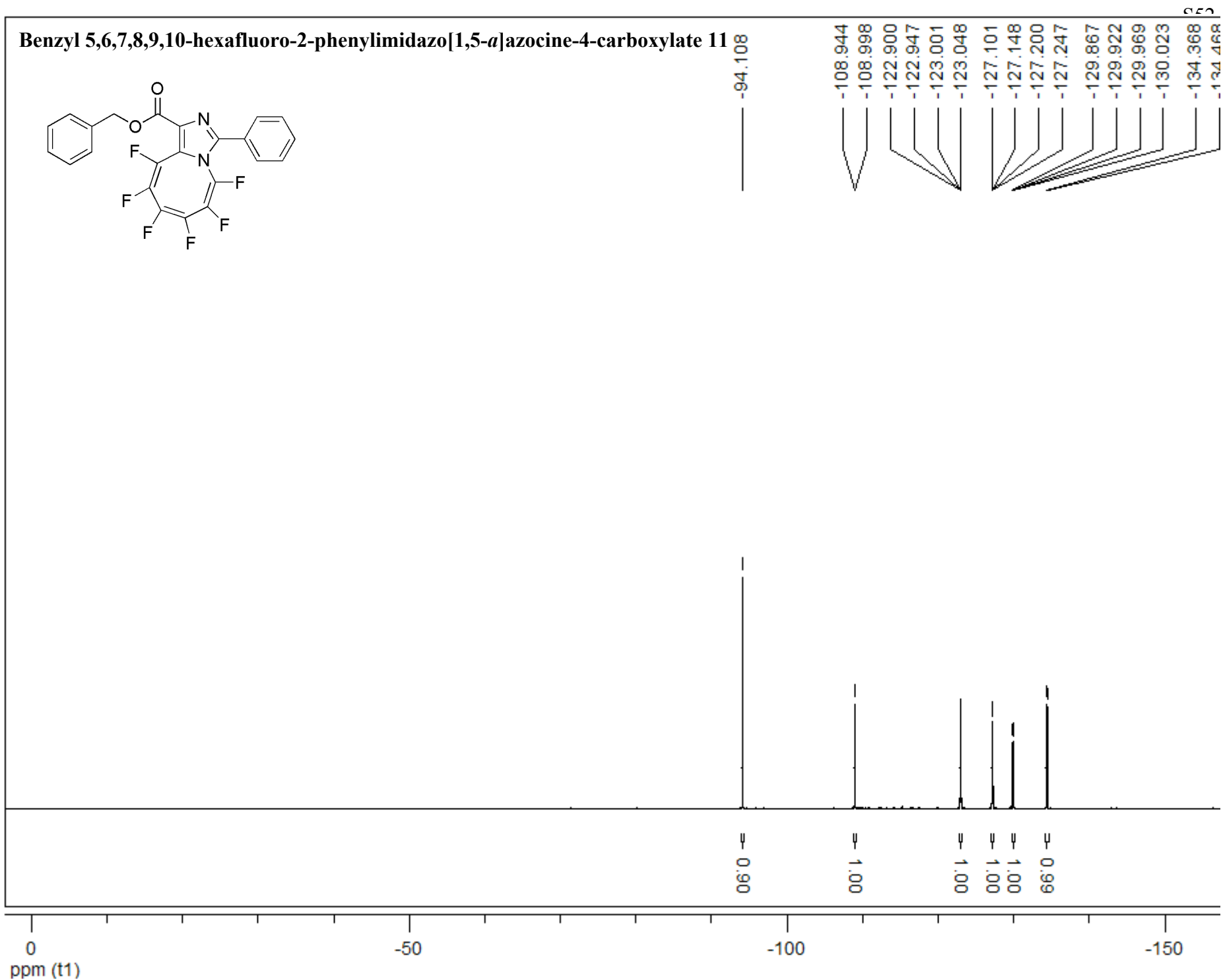
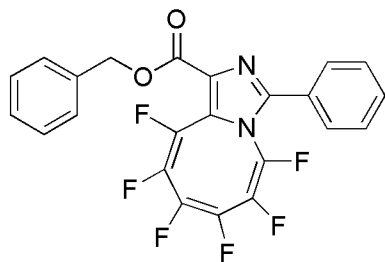


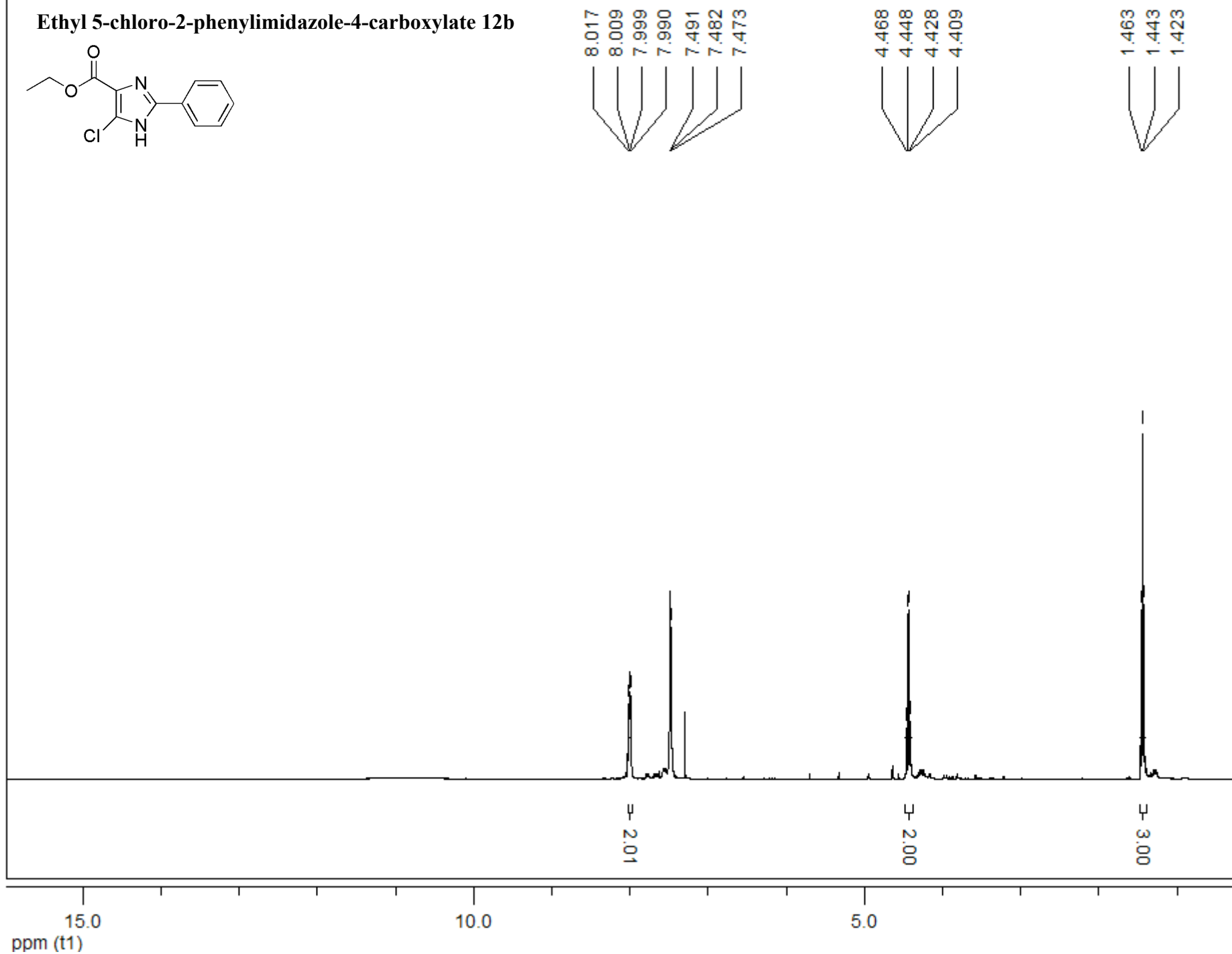
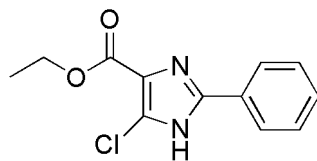
2.00
3.81
1.99

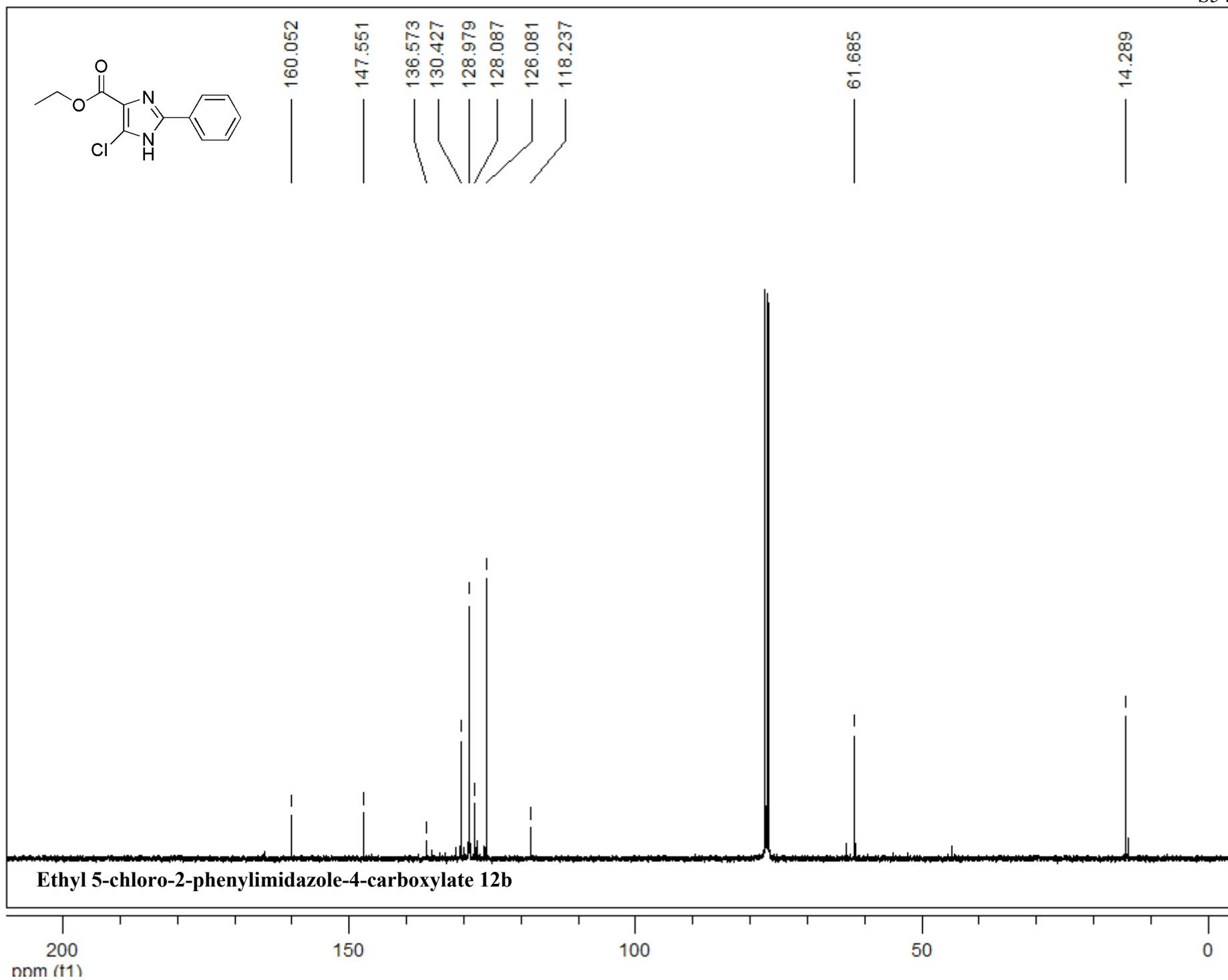
ppm (t1)



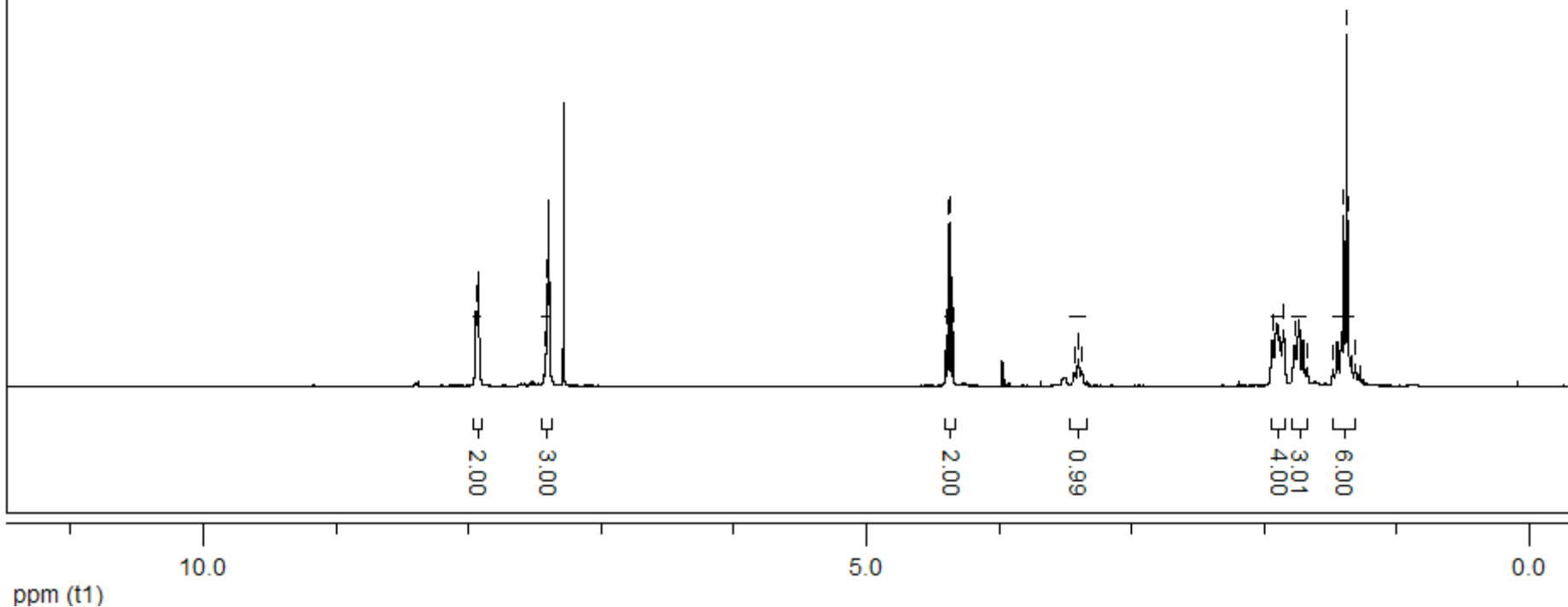
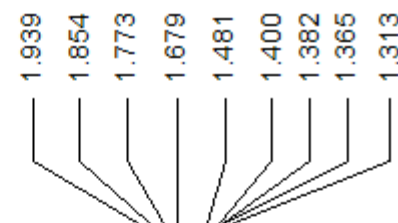
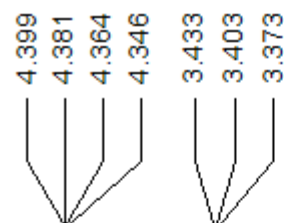
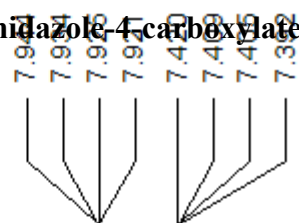
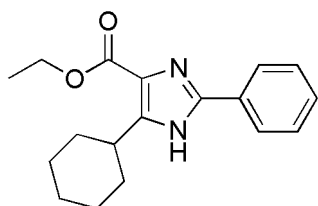
Benzyl 5,6,7,8,9,10-hexafluoro-2-phenylimidazo[1,5-a]azocine-4-carboxylate 11

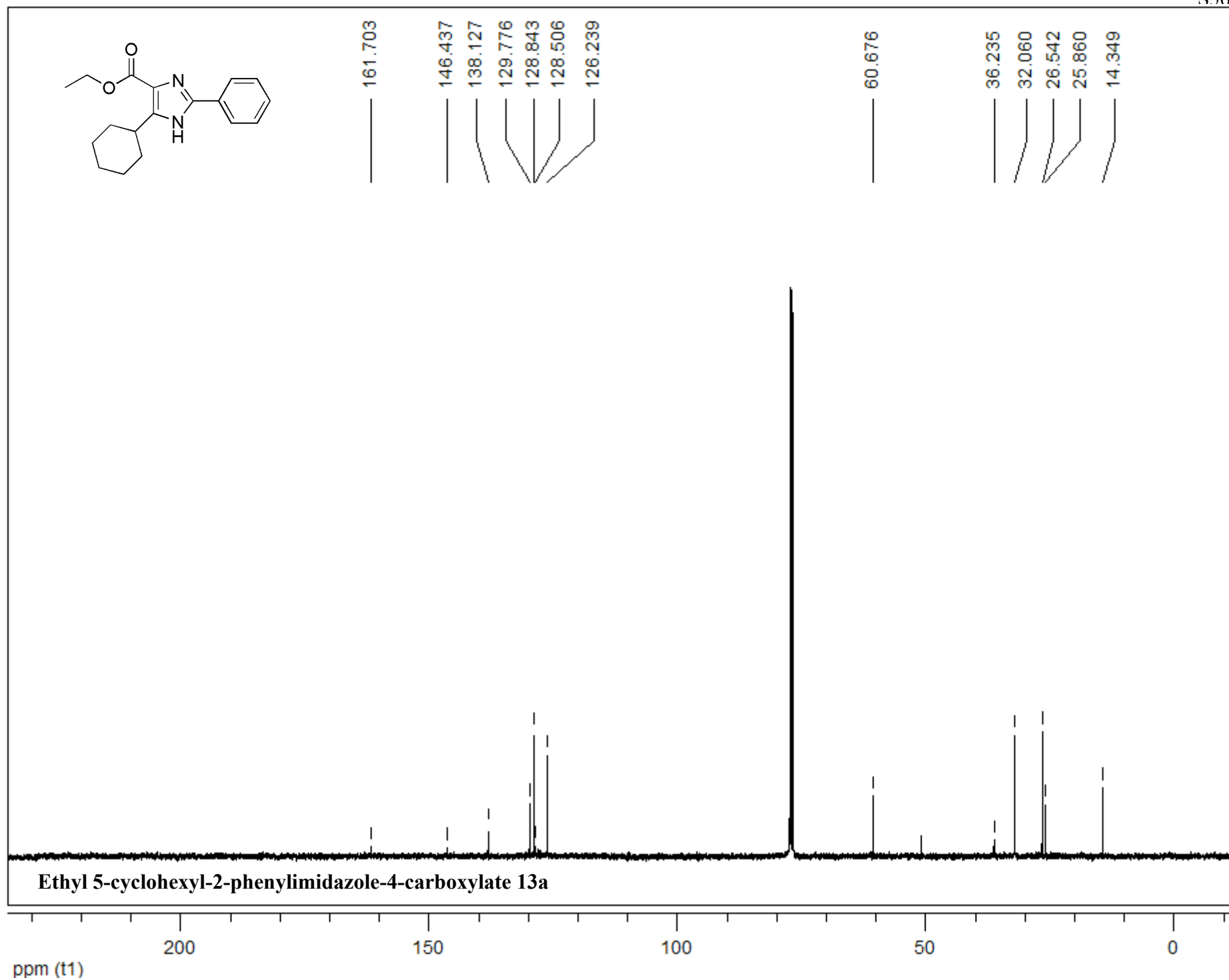


Ethyl 5-chloro-2-phenylimidazole-4-carboxylate 12b



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





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

