

## SUPPLEMENTARY MATERIAL

### Transition Metal-Free Synthesis of Halobenzo[*b*]furans from *O*-Arylcarbamates via *o*-Lithiation Reactions

Claudia Feberero <sup>1</sup>, Cintia Virumbrales <sup>1</sup>, Carlos Sedano <sup>1</sup>, Lorena Renedo <sup>1</sup>, Samuel Suárez-Pantiga <sup>1</sup> and Roberto Sanz <sup>1,\*</sup>

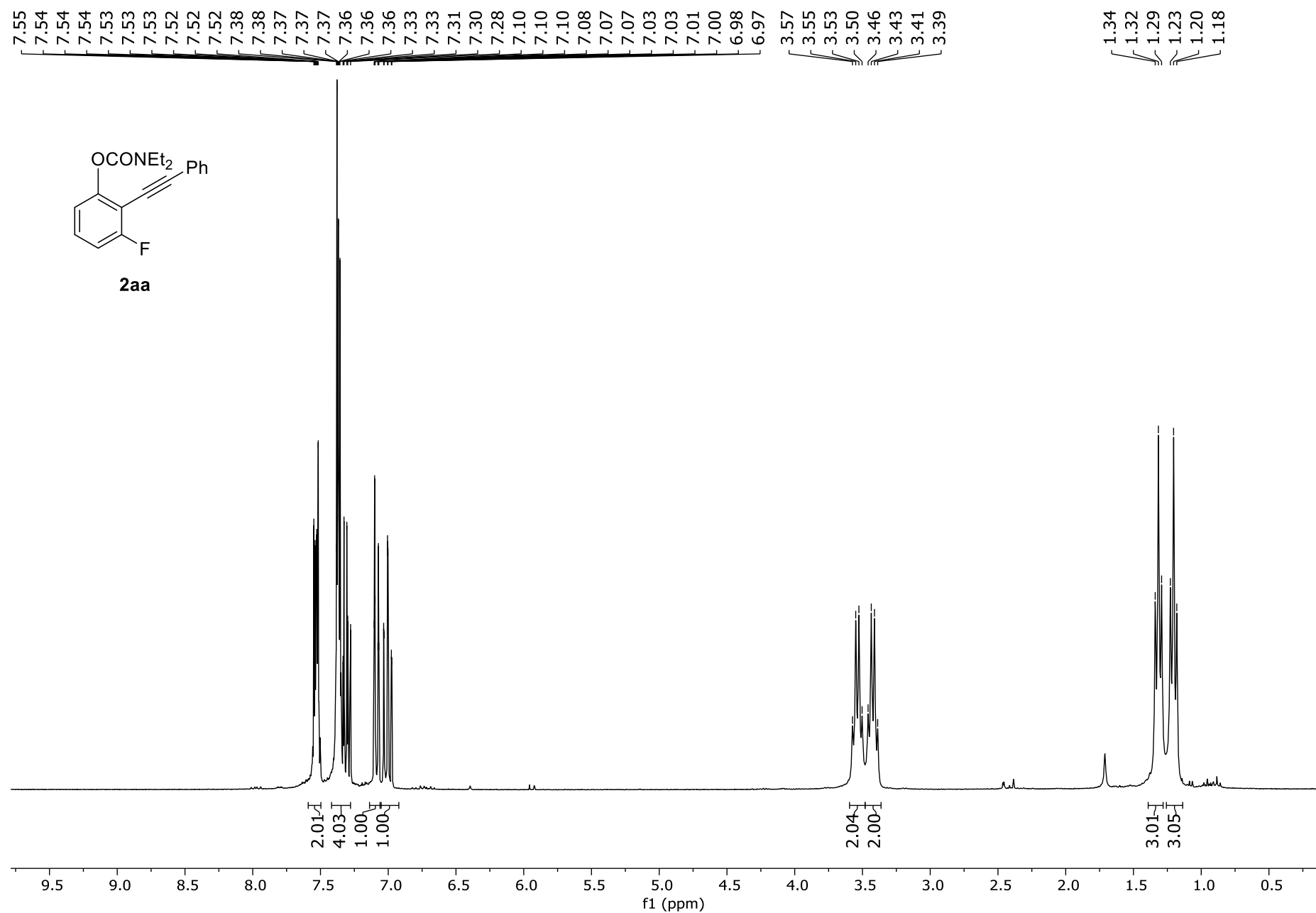
<sup>1</sup> Área de Química Orgánica, Departamento de Química, Facultad de Ciencias, Universidad de Burgos, Pza. Misael Bañuelos s/n, 09001 Buros, Spain; rsd@ubu.es

\* Correspondence: rsd@ubu.es

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<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of compounds <b>2-9</b> .....	S2-S79
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<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)

— 164.7

— 161.4

— 153.3

— 153.3

— 131.7

— 129.4

— 129.2

— 128.8

— 128.4

— 123.0

— 118.5

— 118.5

— 112.5

— 112.2

— 107.5

— 107.3

— 98.6

— 98.5

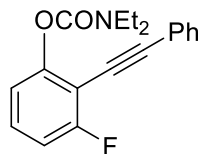
— 78.5

— 42.5

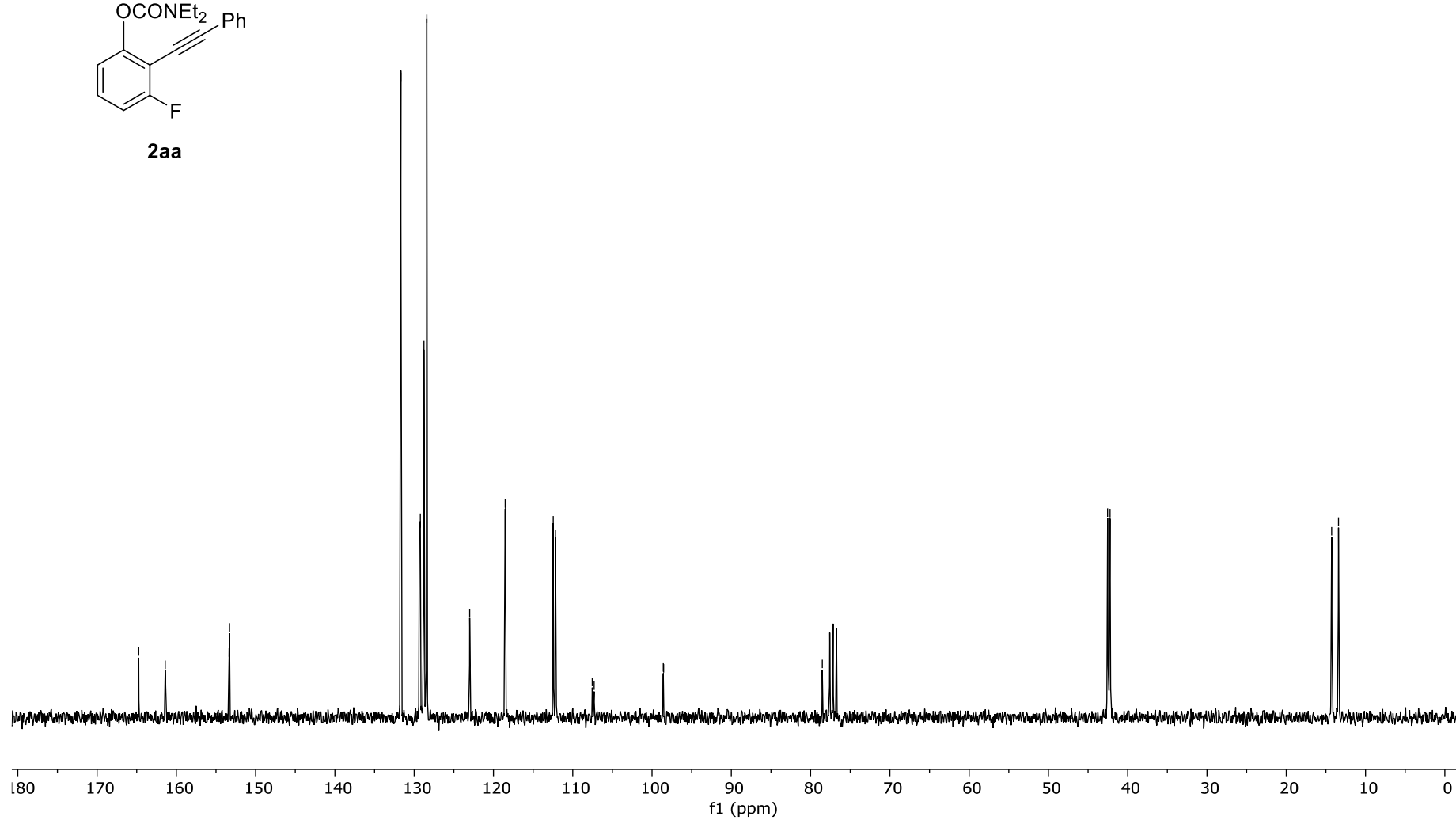
— 42.2

— 14.3

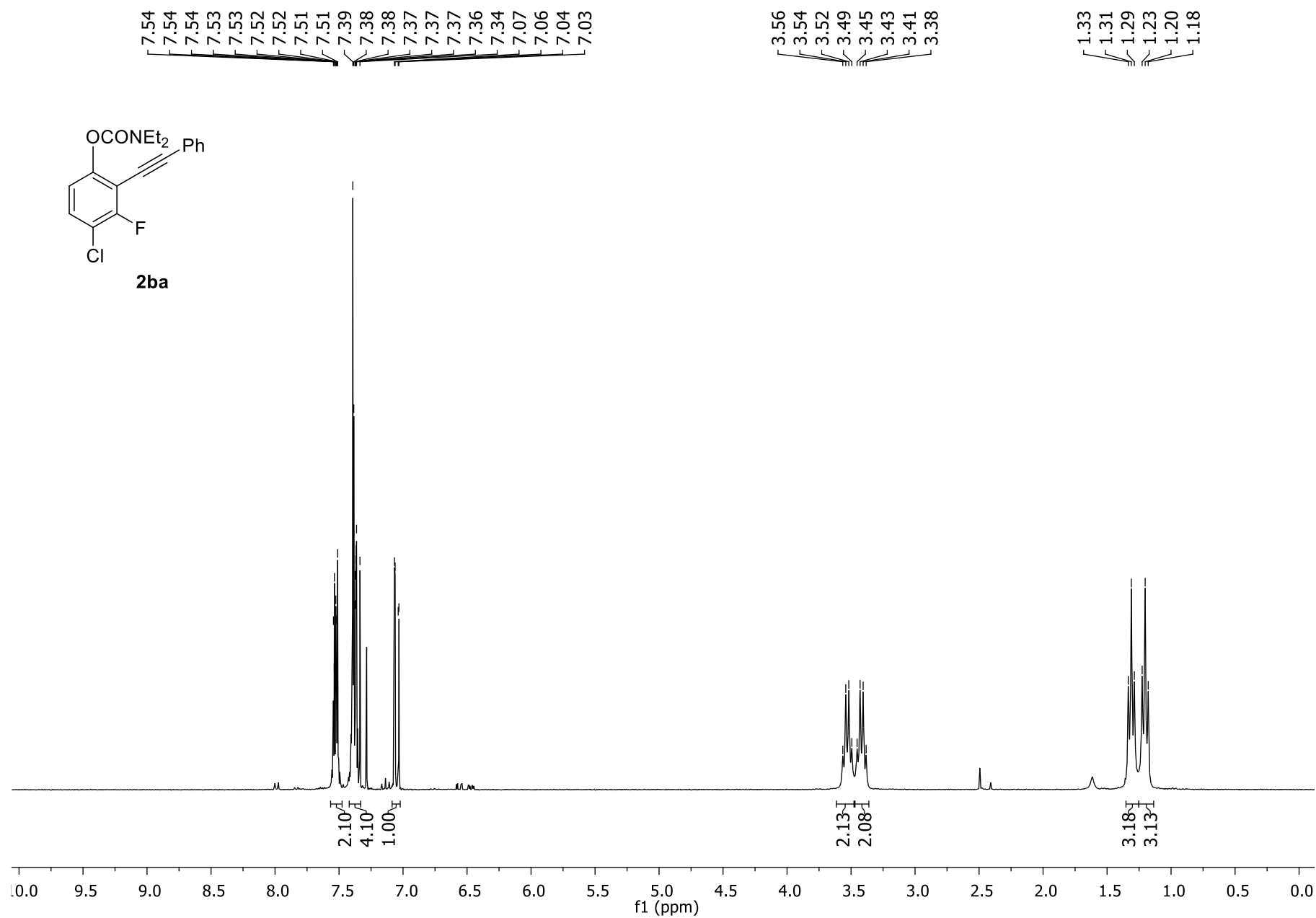
— 13.4



**2aa**



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



<sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)

160.0  
156.7  
153.1  
151.7  
151.6

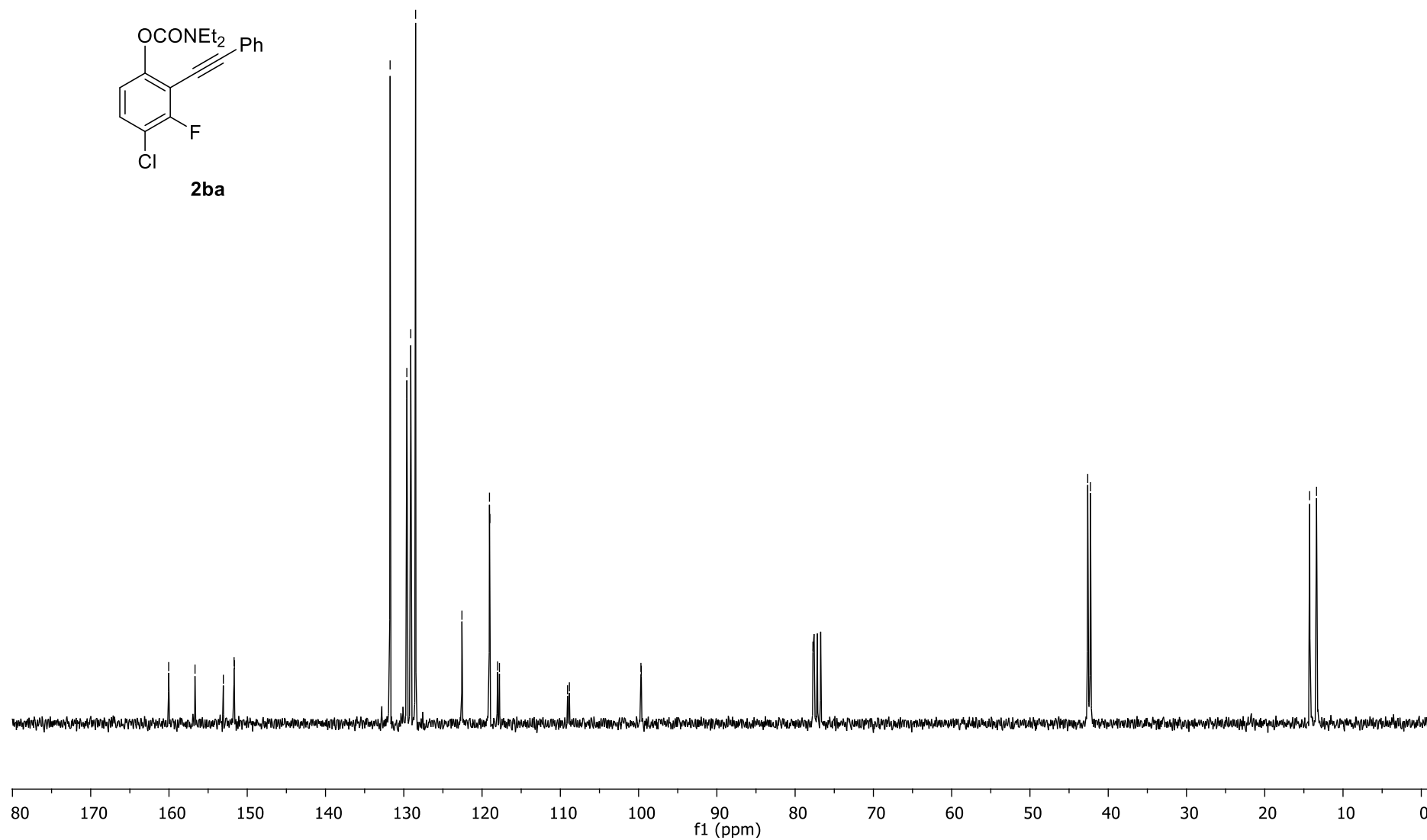
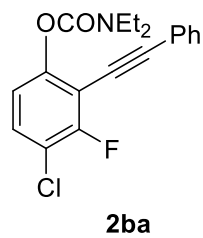
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117.8  
109.1  
108.8

99.7  
99.6

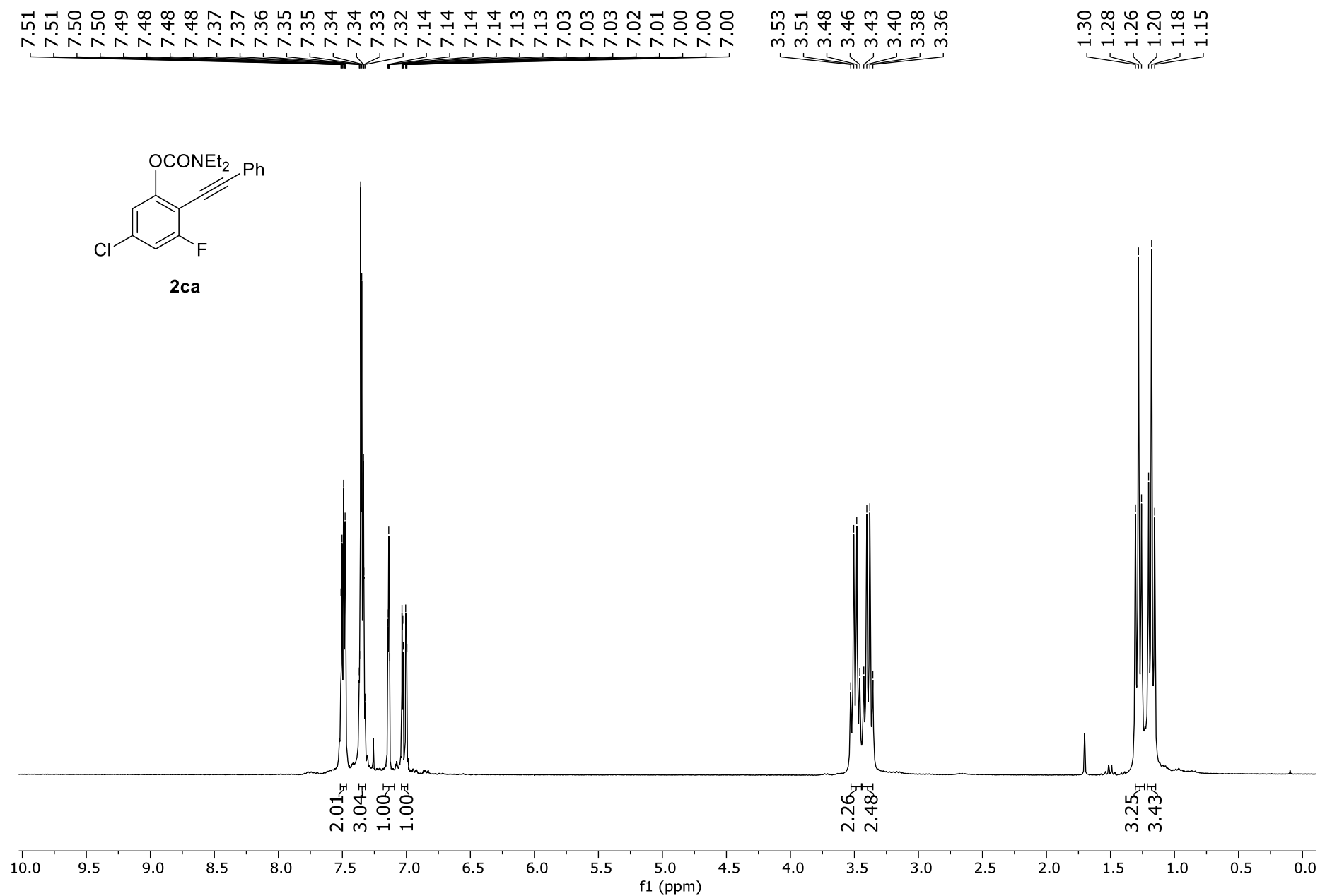
— 77.7

42.6  
42.3

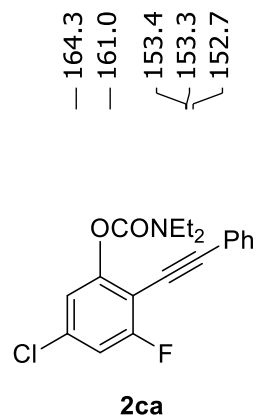
14.3  
13.4



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



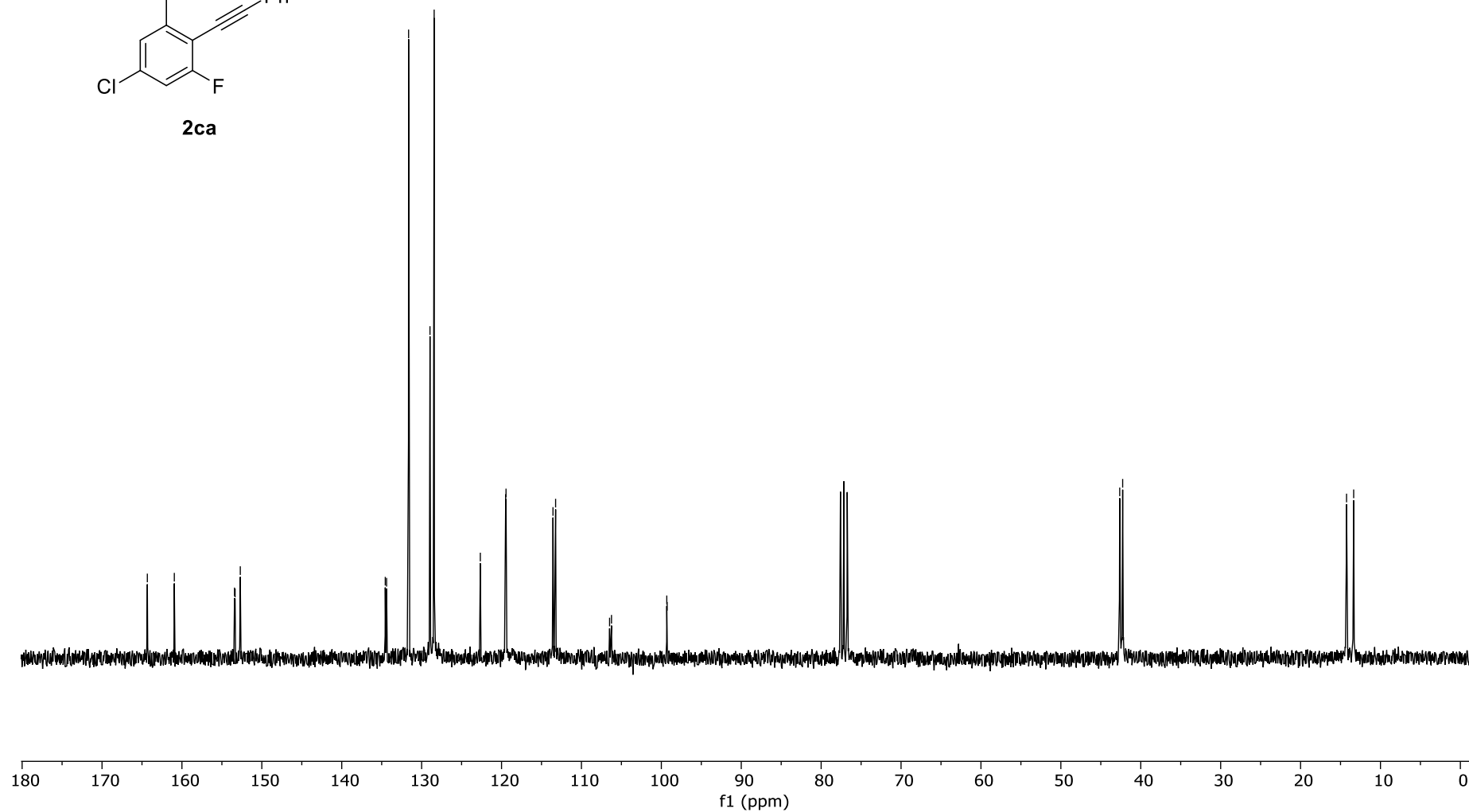
$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



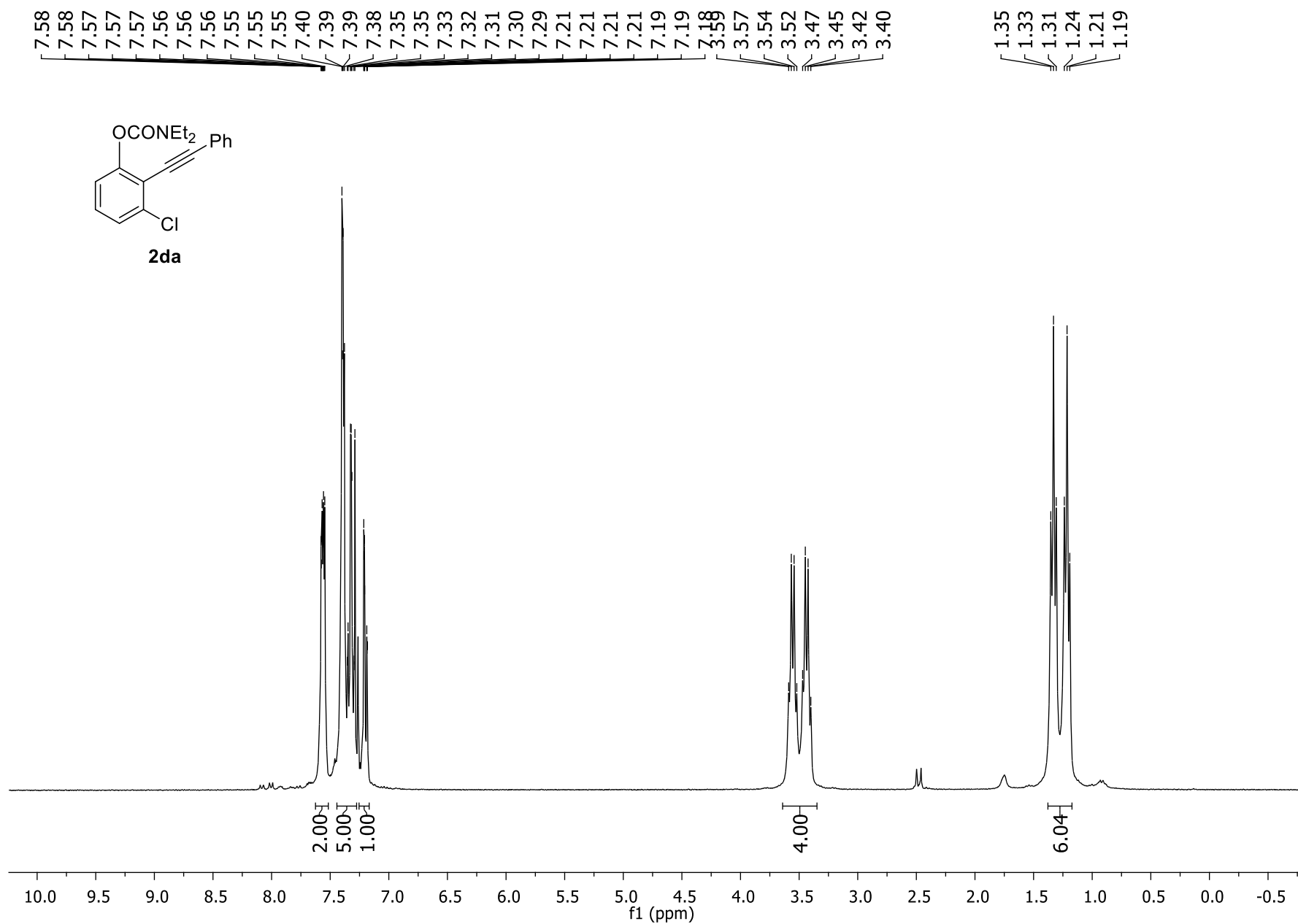
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153.4  
153.3  
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129.0  
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122.7  
119.5  
119.4  
113.6  
113.2  
106.5  
106.2  
99.3  
99.3

42.6  
42.3

14.2  
13.4

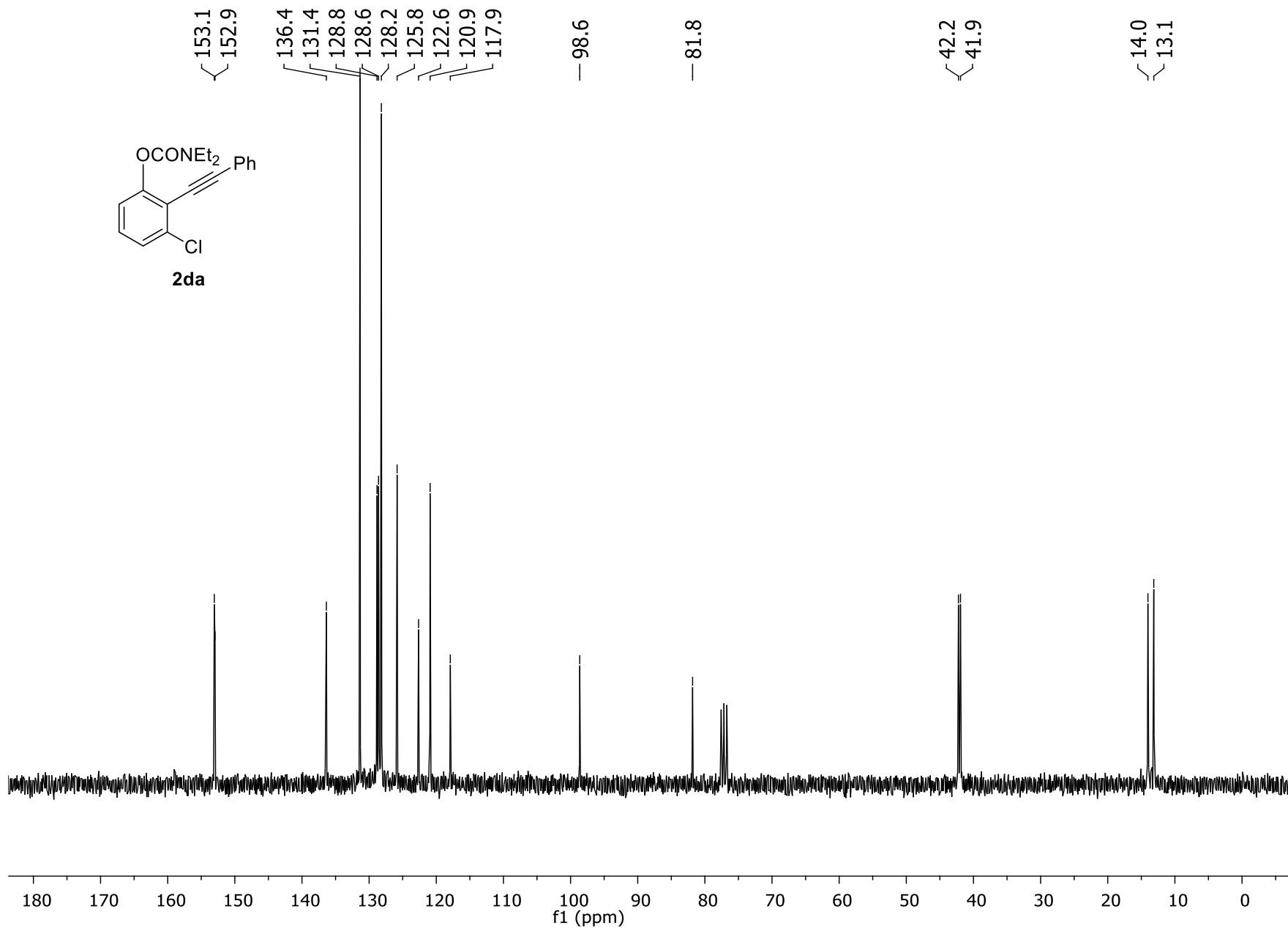
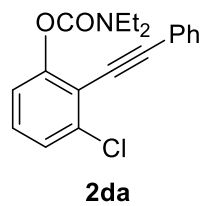


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

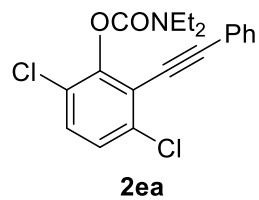




<sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)



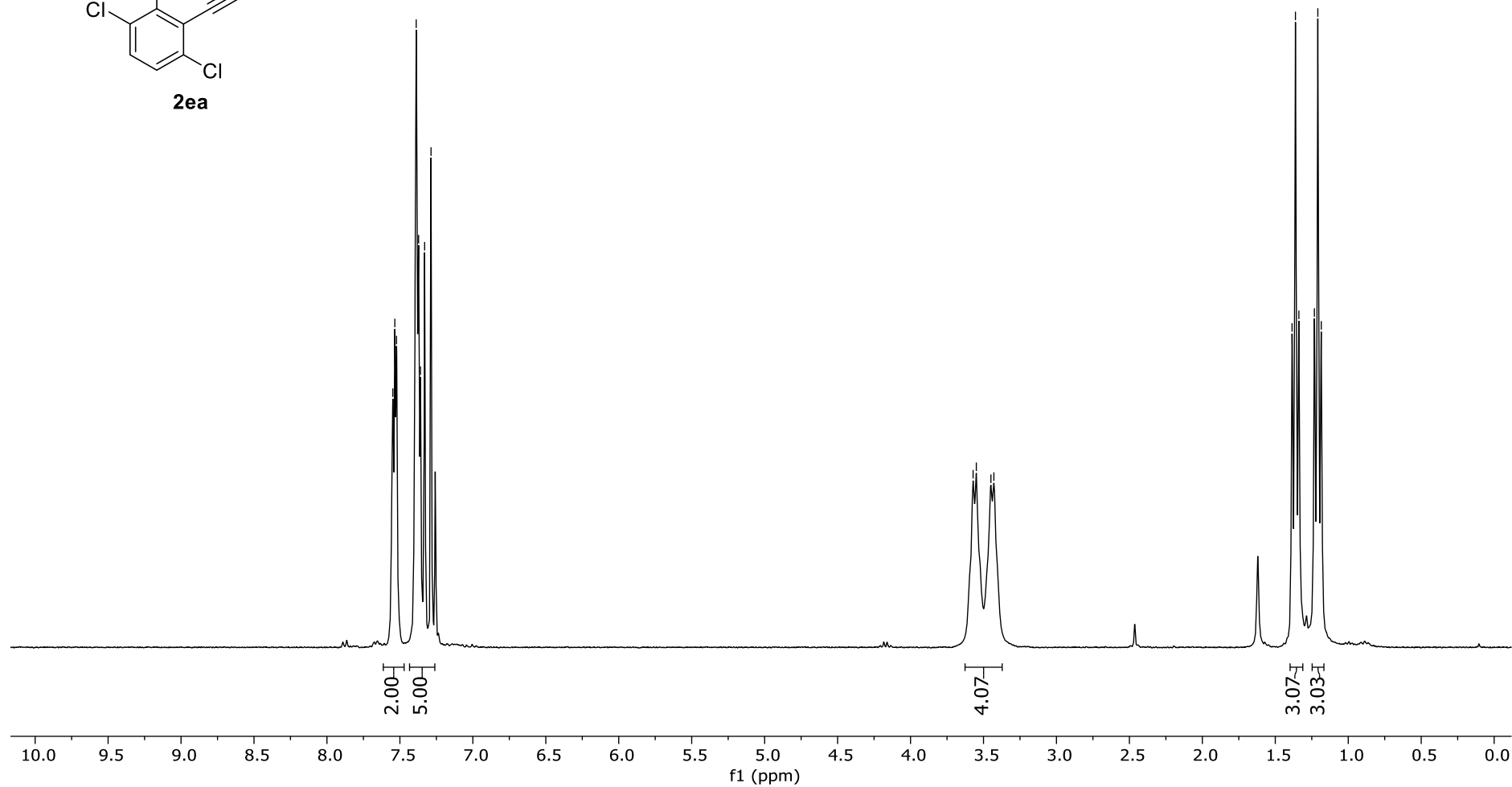
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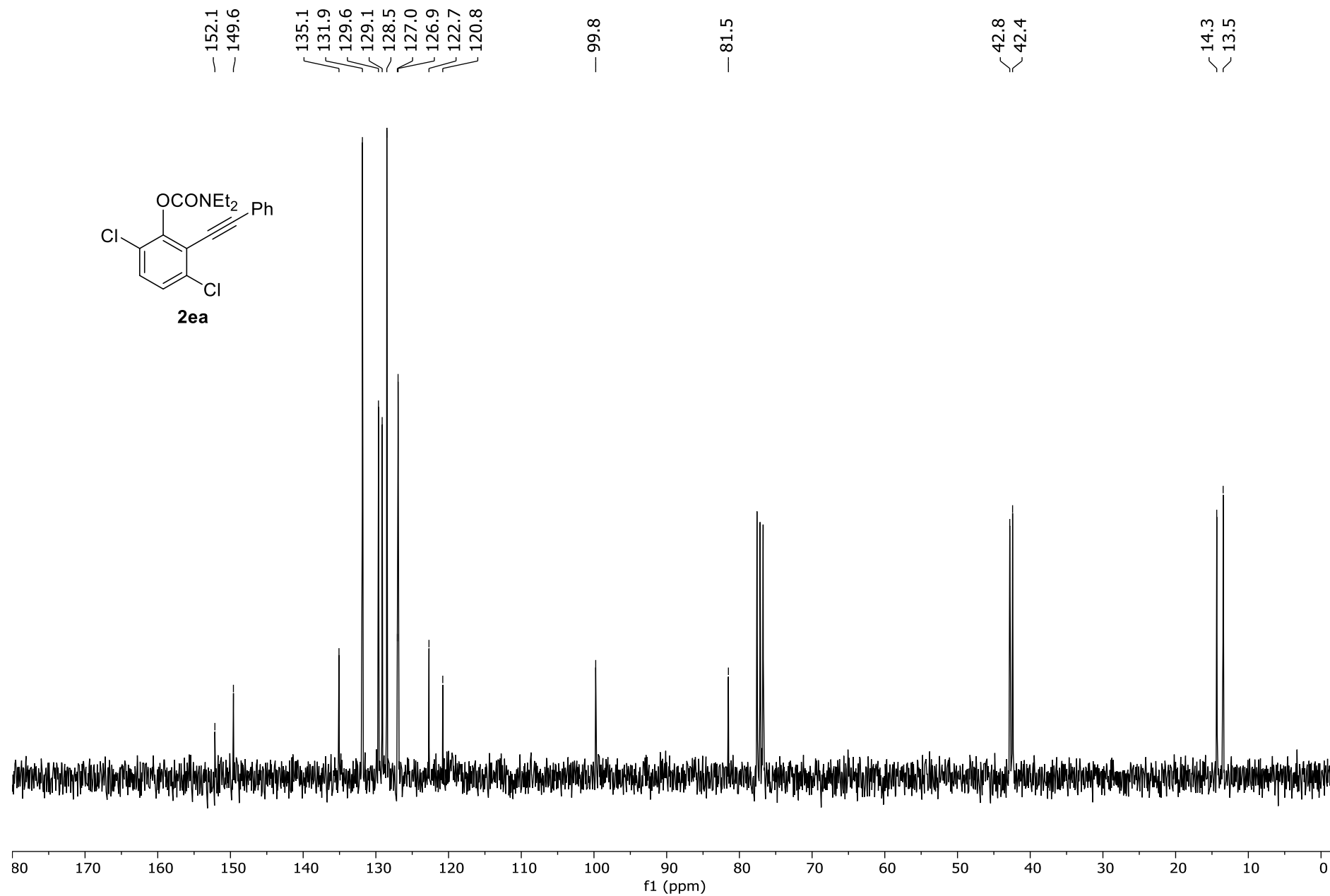
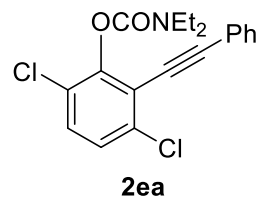
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7.39  
7.37  
7.36  
7.33  
7.29

3.57  
3.55  
3.45  
3.43

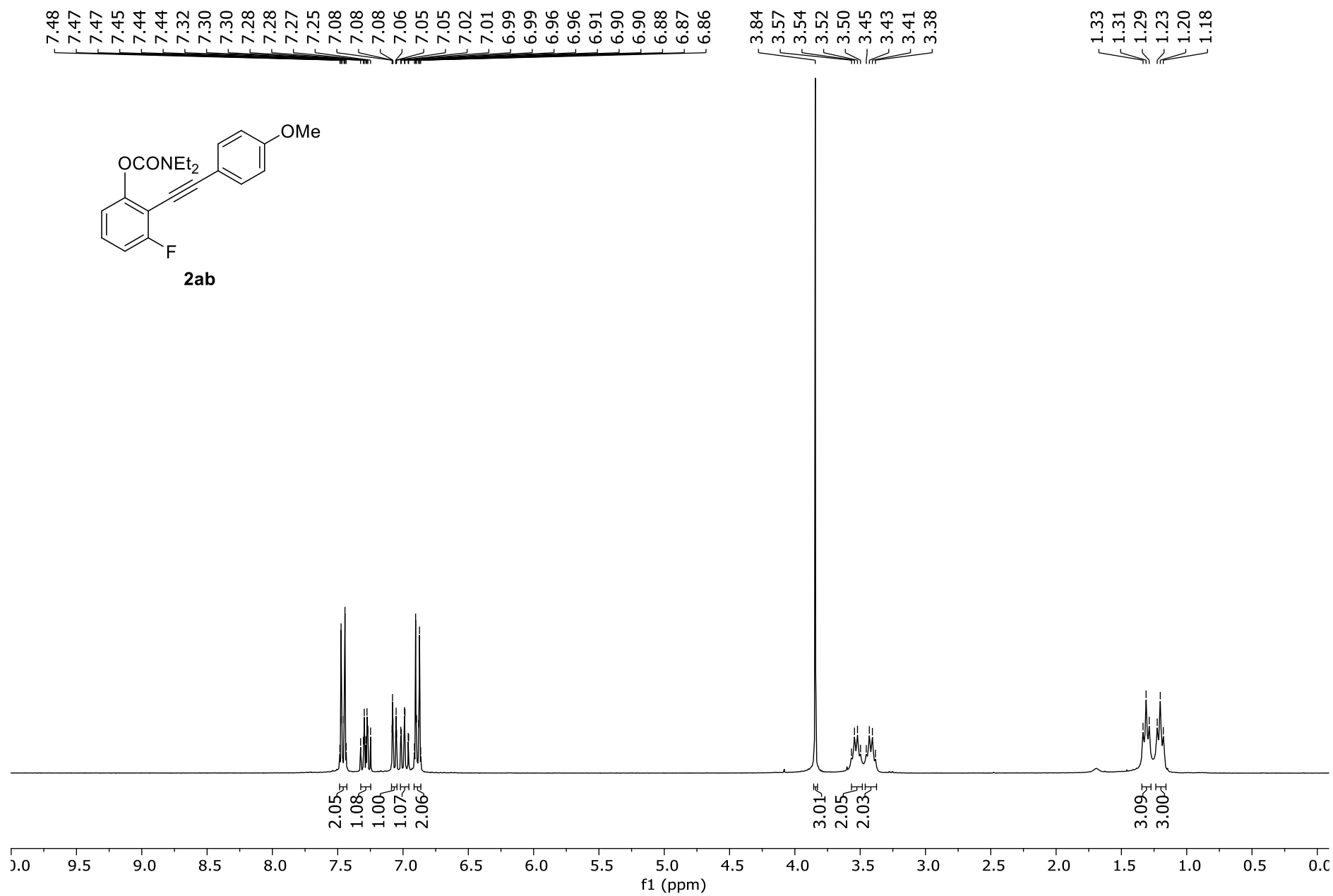
1.39  
1.36  
1.34  
1.23  
1.21  
1.18



$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



<sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)

~ 164.7  
~ 161.3  
~ 160.1  
~ 153.4  
~ 153.3  
~ 153.2

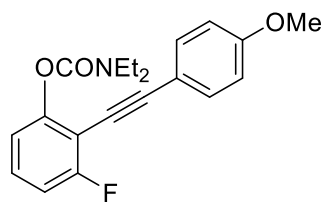
~ 133.2  
~ 129.0  
~ 128.8  
~ 118.5  
~ 118.4  
~ 115.2  
~ 114.1  
~ 112.4  
~ 112.2  
~ 107.9  
~ 107.6  
— 98.7

— 77.2

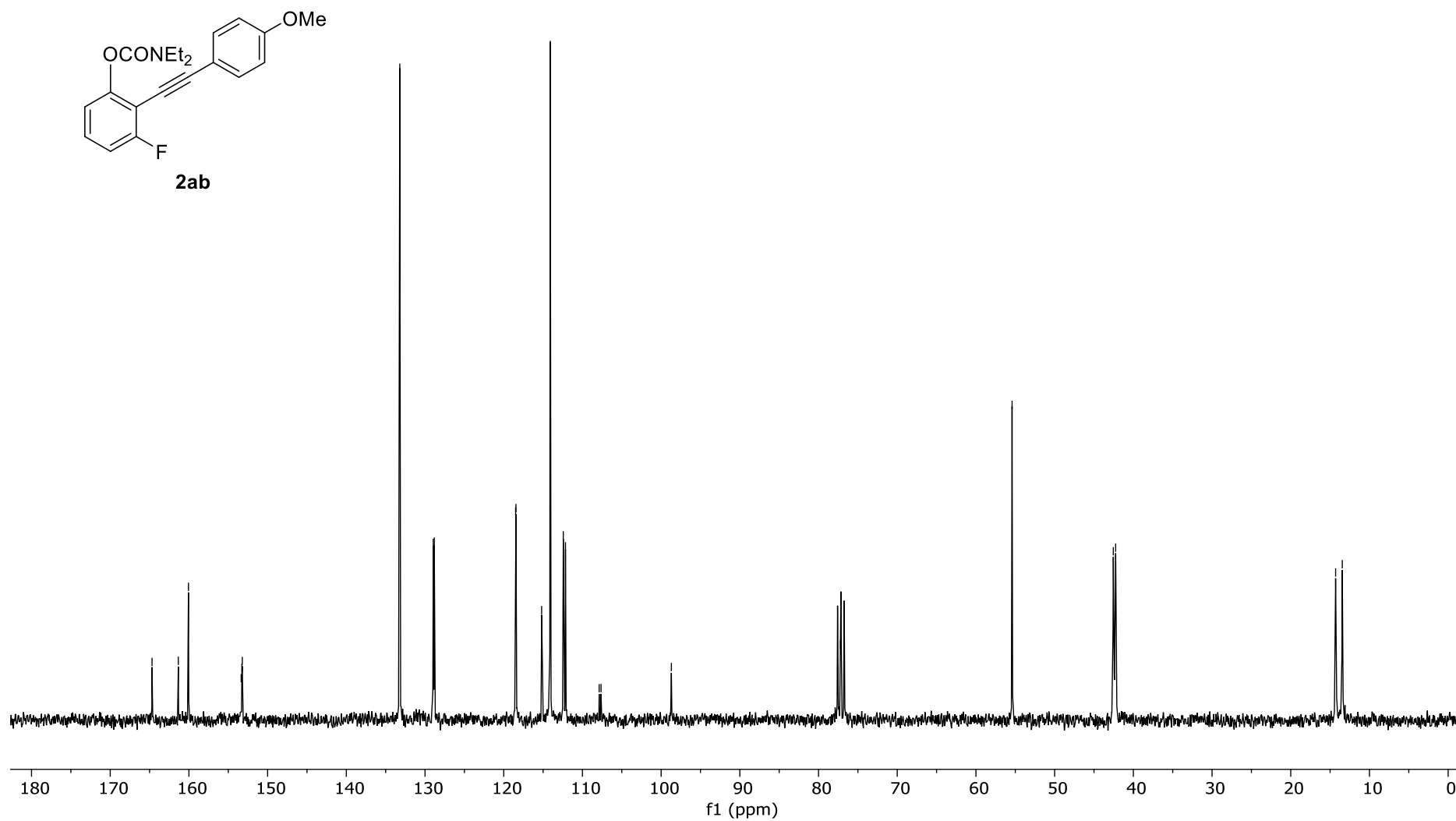
— 55.4

~ 42.5  
~ 42.2

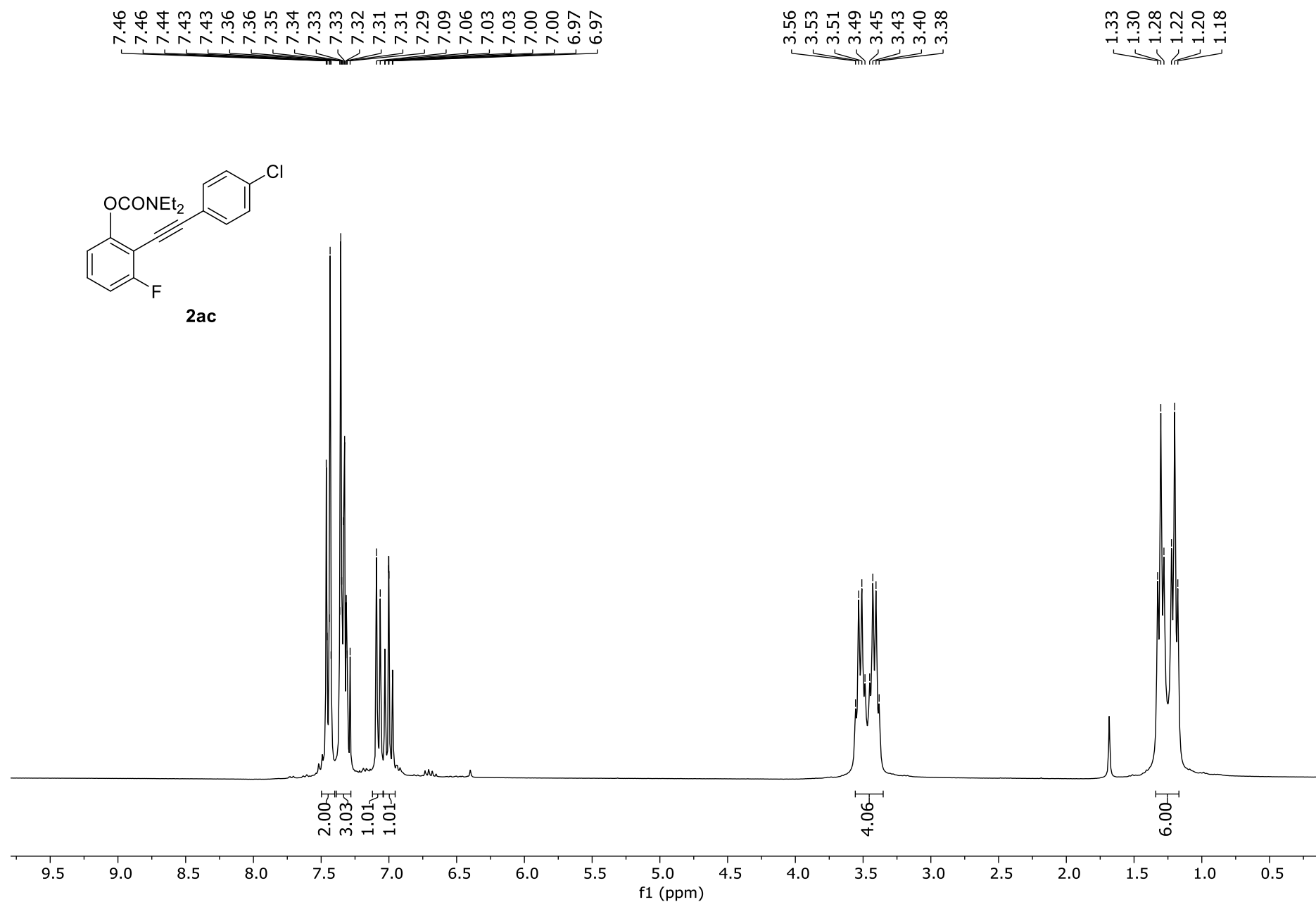
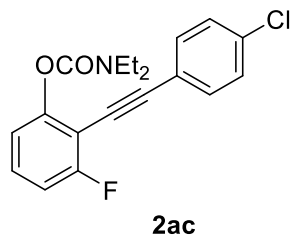
~ 14.3  
~ 13.5



**2ab**



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )

— 164.8  
— 161.4  
{ 153.4  
  153.3  
  153.2

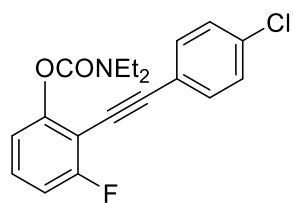
{ 134.9  
  132.9  
  129.6  
  129.5  
  128.8  
  121.5  
  118.6  
  118.5  
  112.5  
  112.2  
  107.3  
  107.0

— 97.3

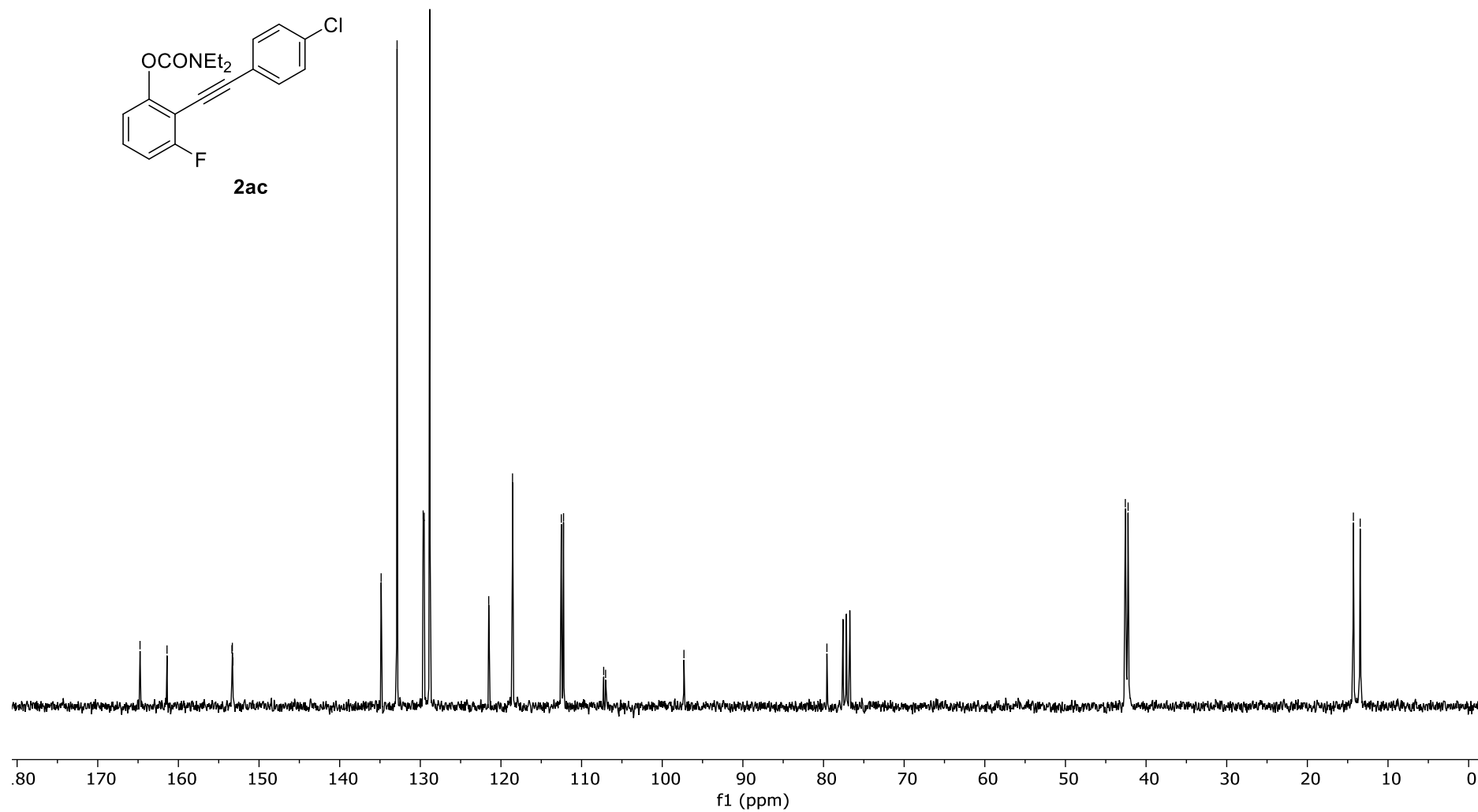
— 79.6

{ 42.6  
  42.2

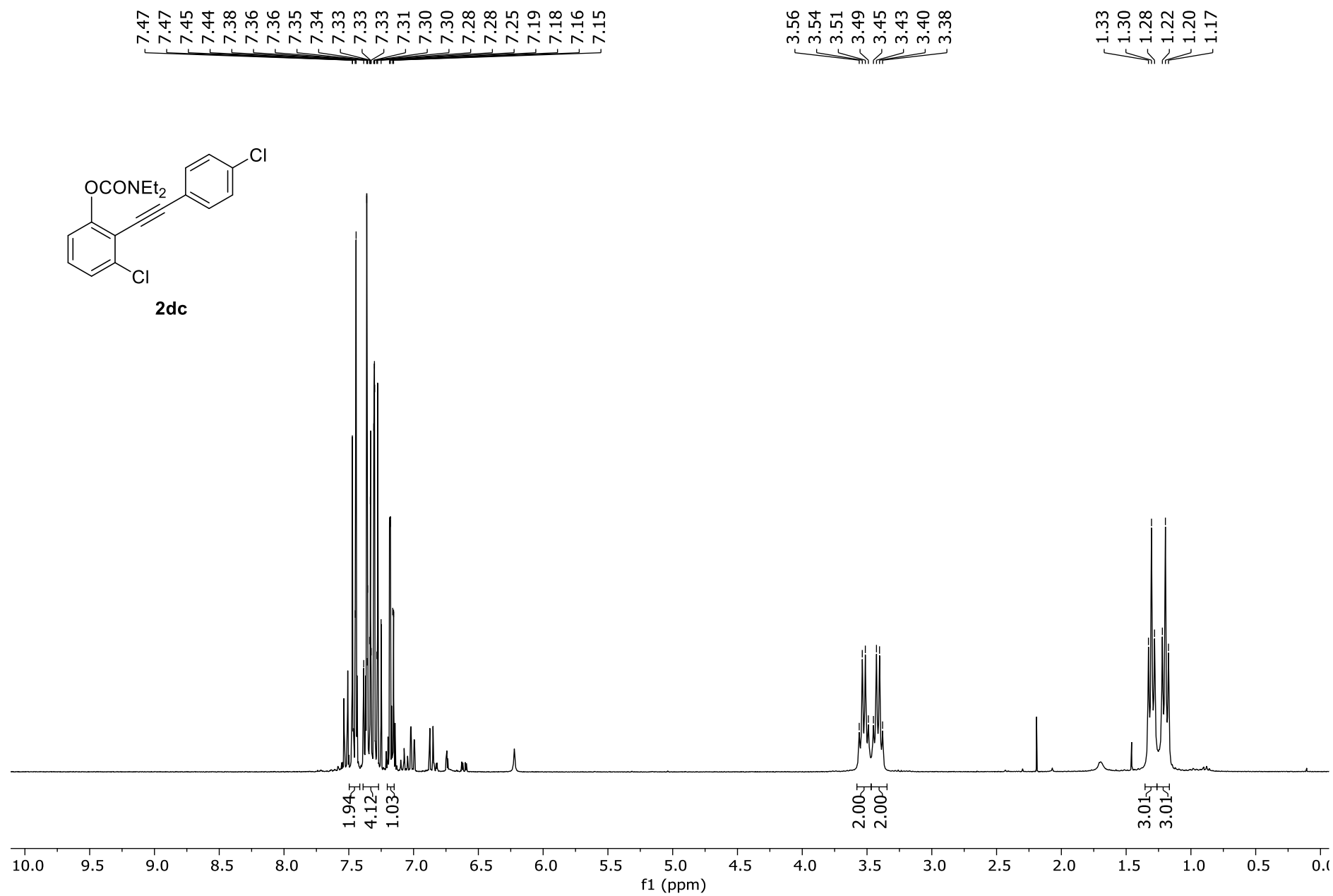
{ 14.3  
  13.4



**2ac**

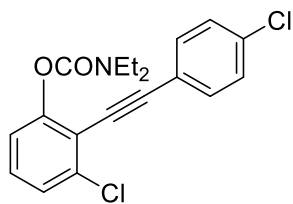


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

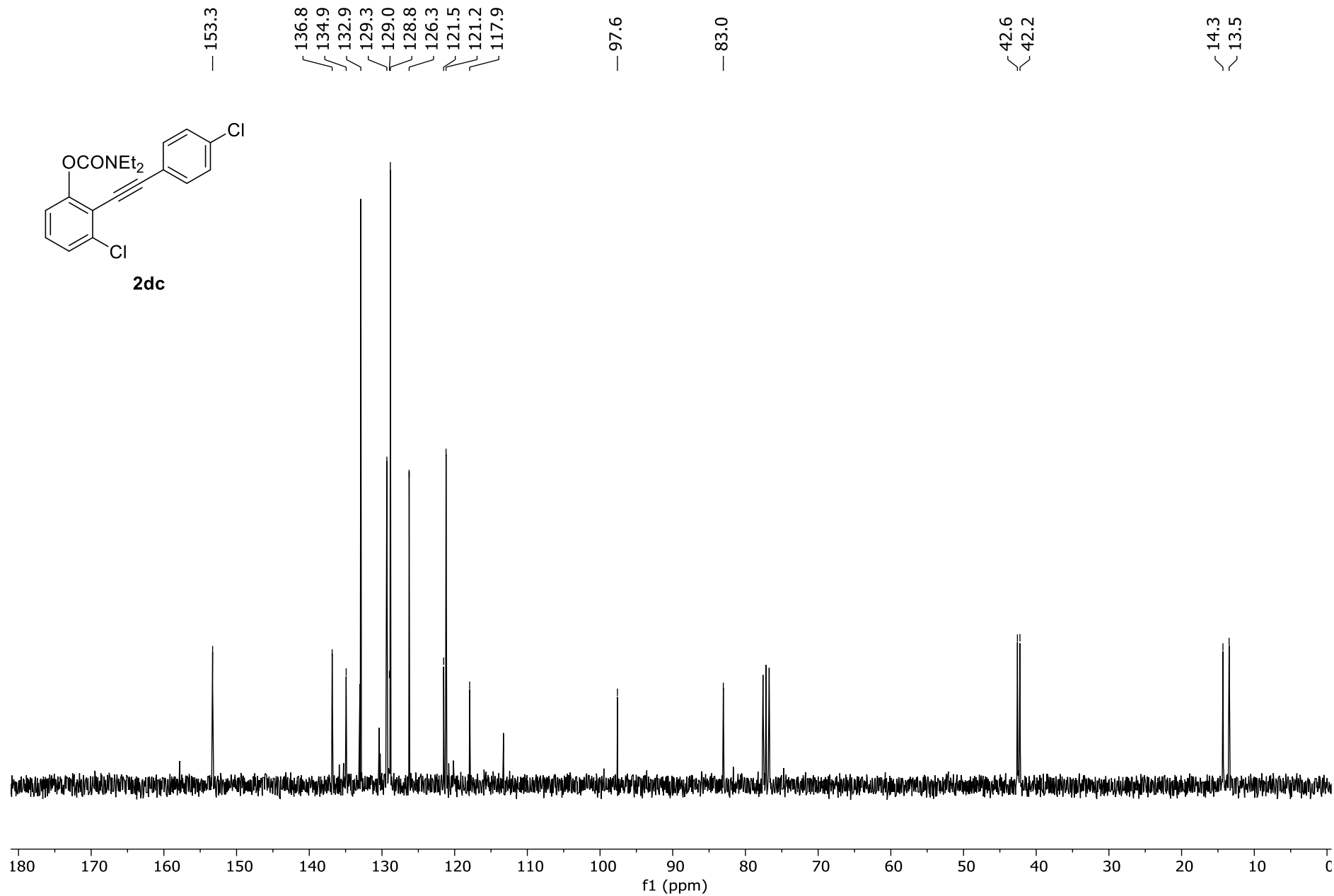




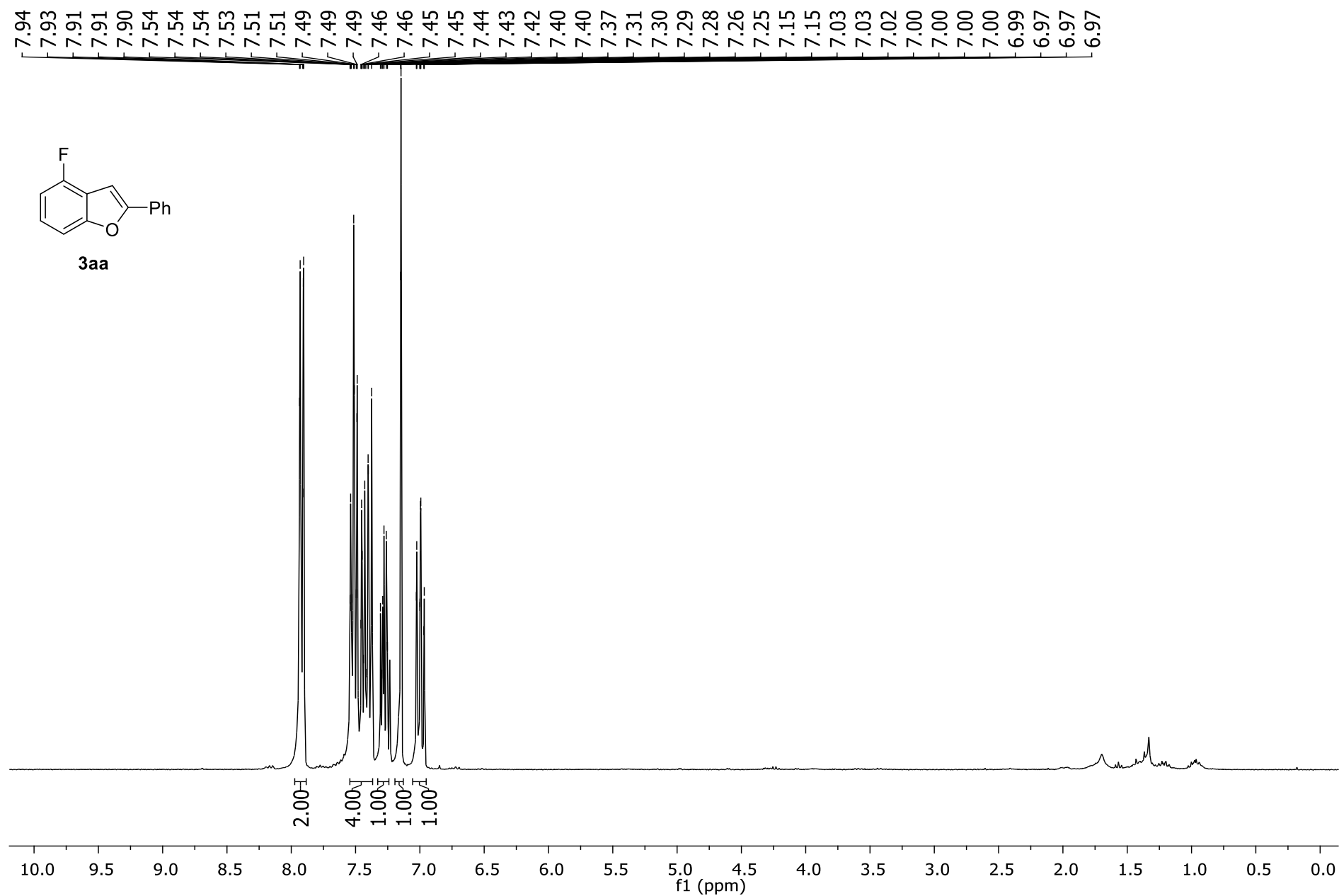
$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



**2dc**

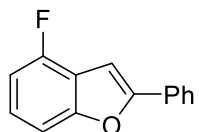


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

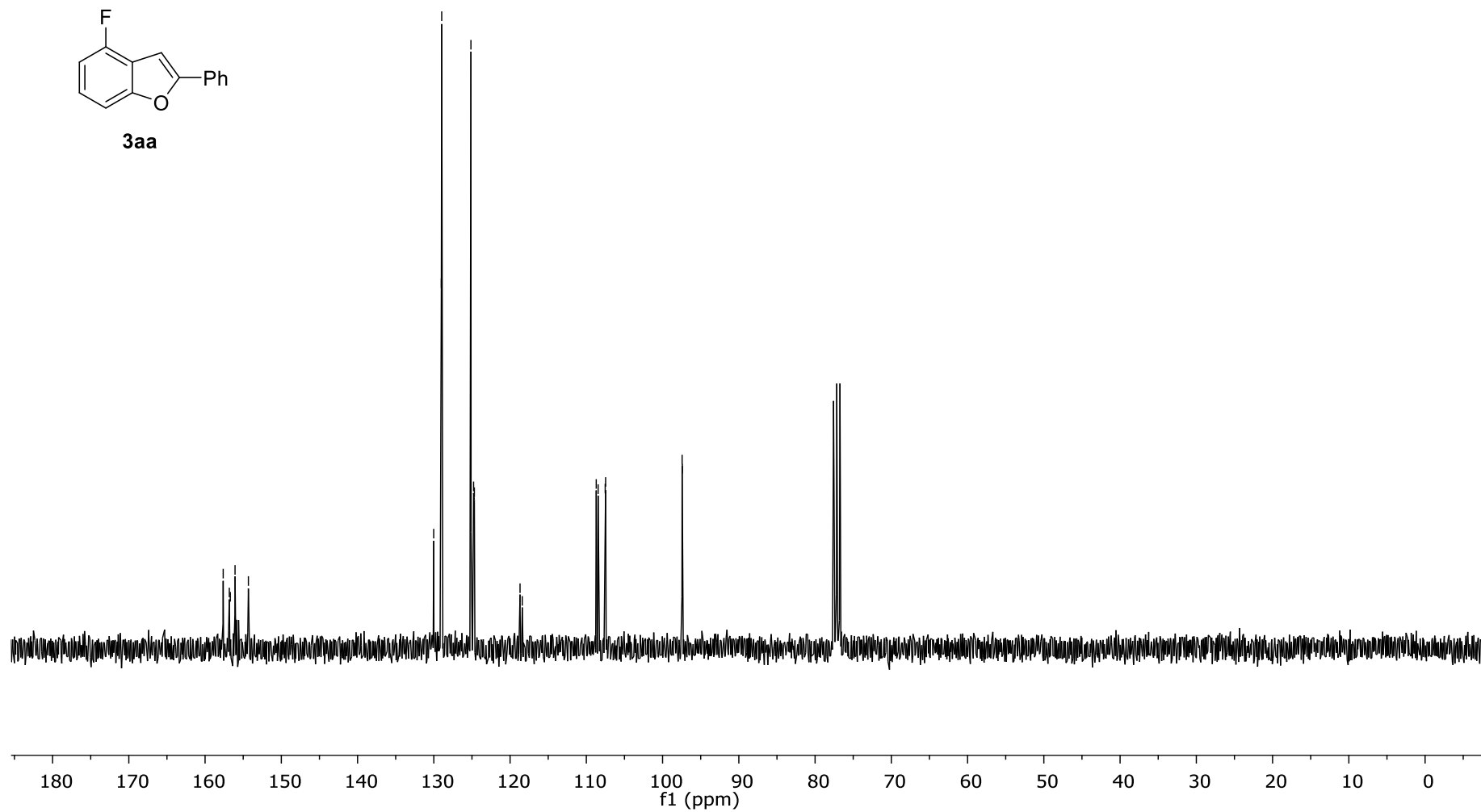


$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )

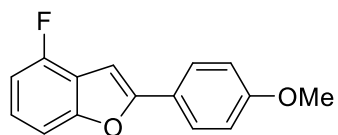
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156.1  
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129.0  
129.0  
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118.7  
118.4  
108.7  
107.5  
107.5  
97.4  
97.4



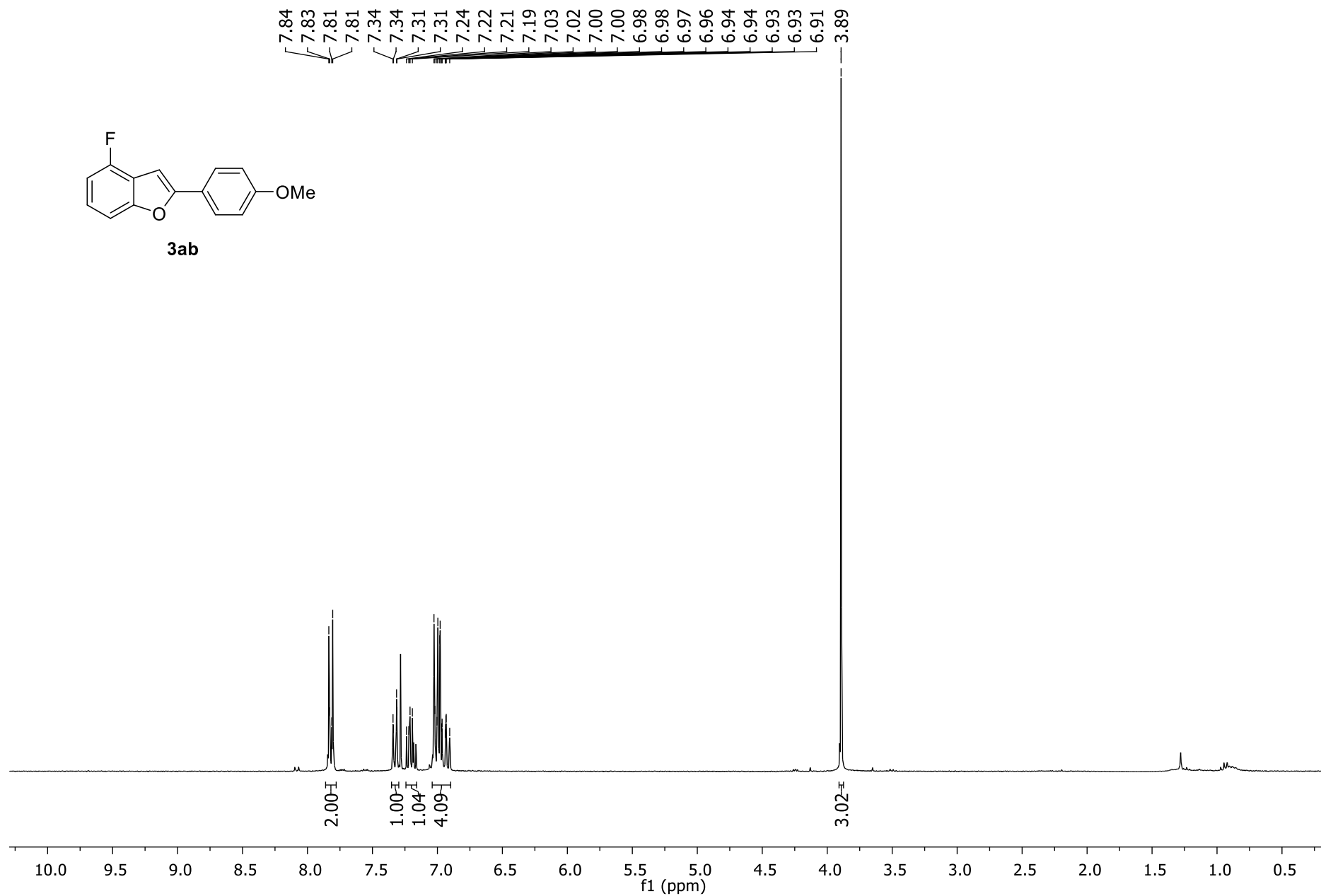
**3aa**



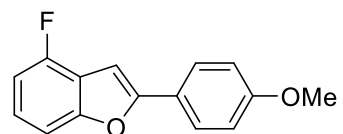
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



**3ab**



$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



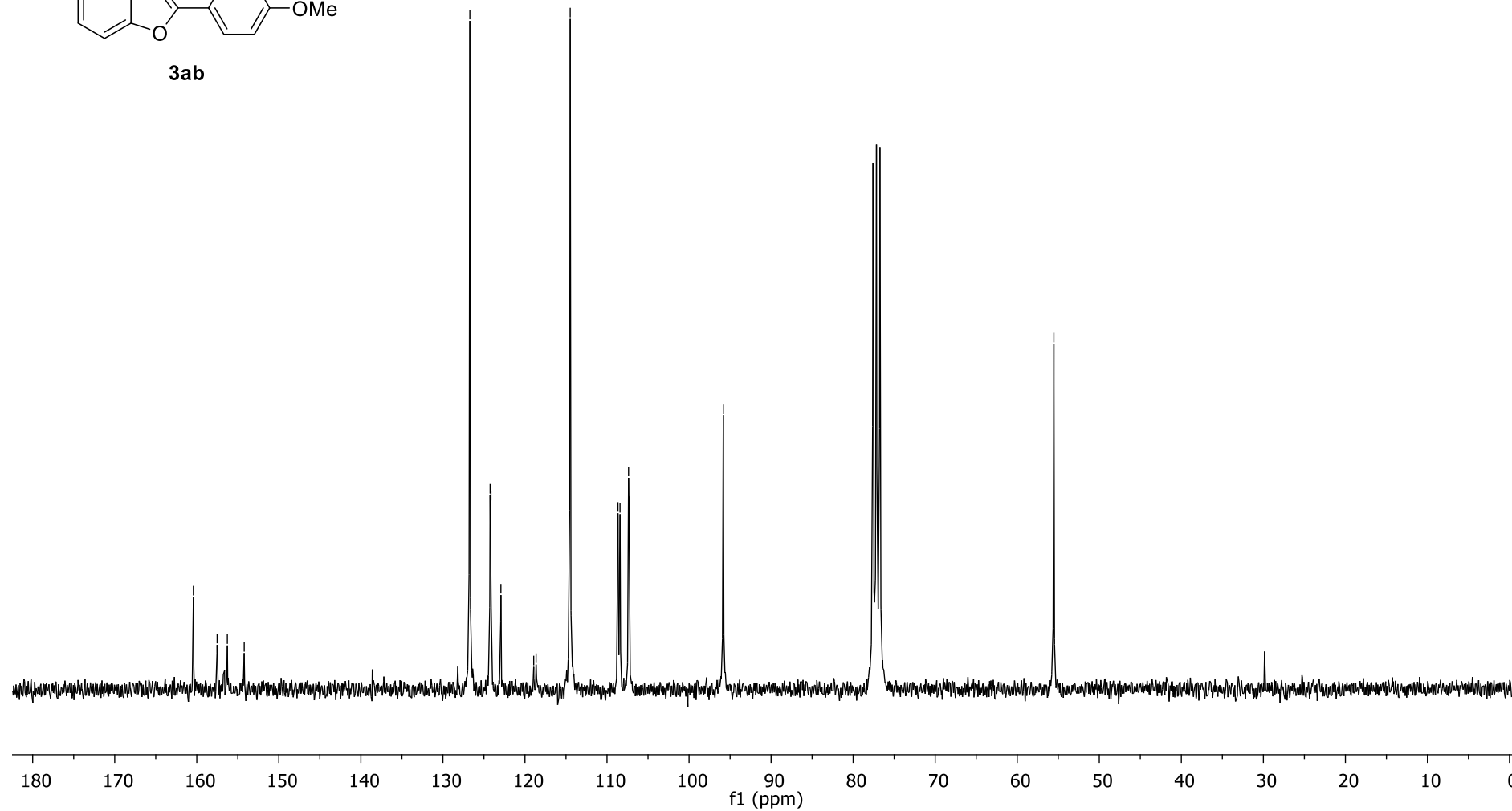
**3ab**

160.4  
157.5  
156.3  
154.2

126.7  
124.2  
124.1  
122.9  
118.9  
118.6  
114.5  
108.7  
108.4  
107.4  
107.3

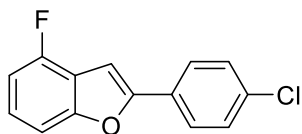
95.8

55.5

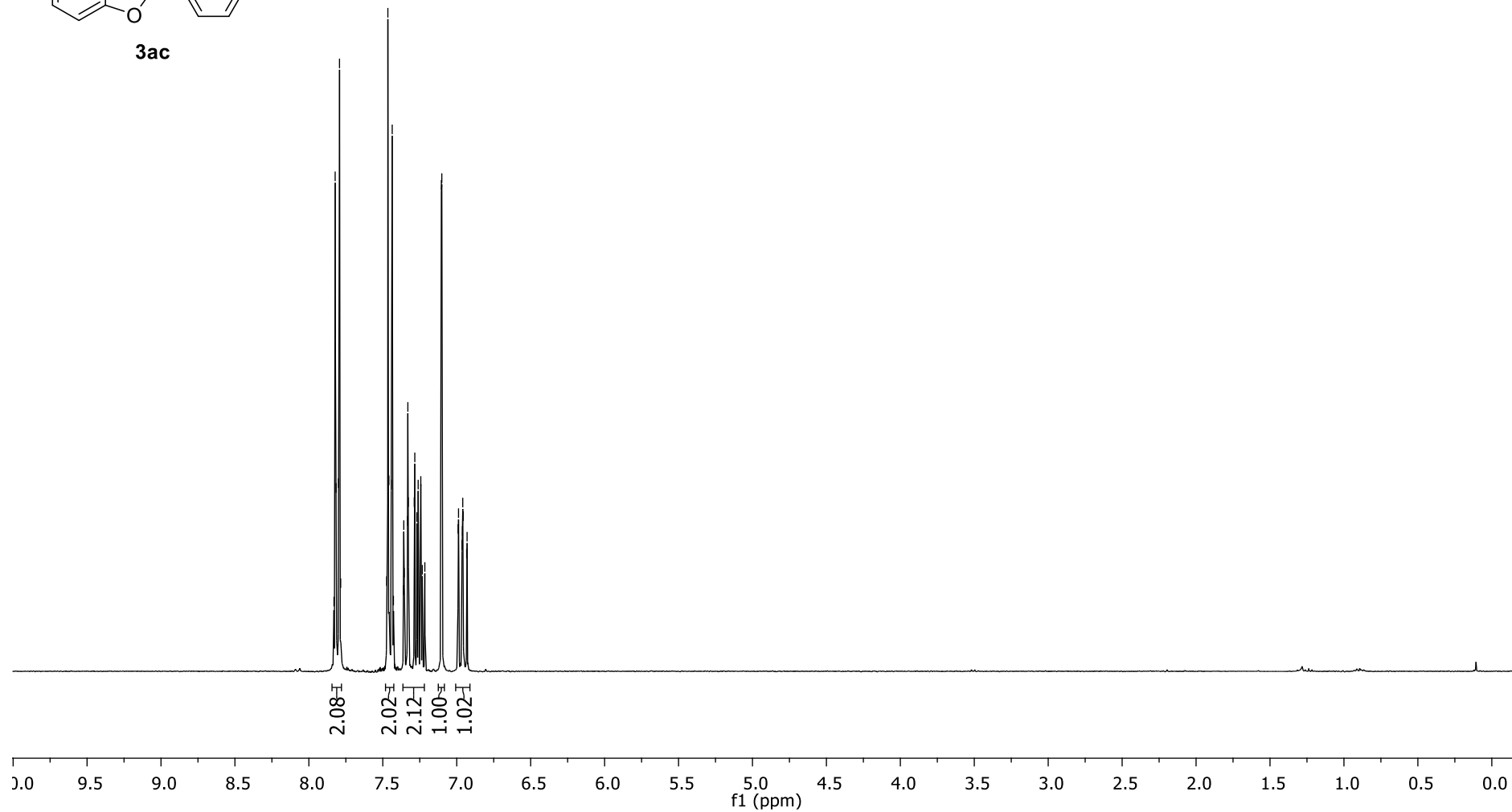


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

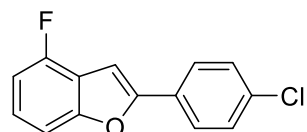
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7.82  
7.80  
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7.44  
7.44  
7.43  
7.36  
7.36  
7.36  
7.33  
7.33  
7.33  
7.29  
7.28  
7.27  
7.26  
7.24  
7.23  
7.22  
7.10  
7.10  
6.99  
6.99  
6.96  
6.96  
6.96  
6.96  
6.93  
6.93



**3ac**



$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



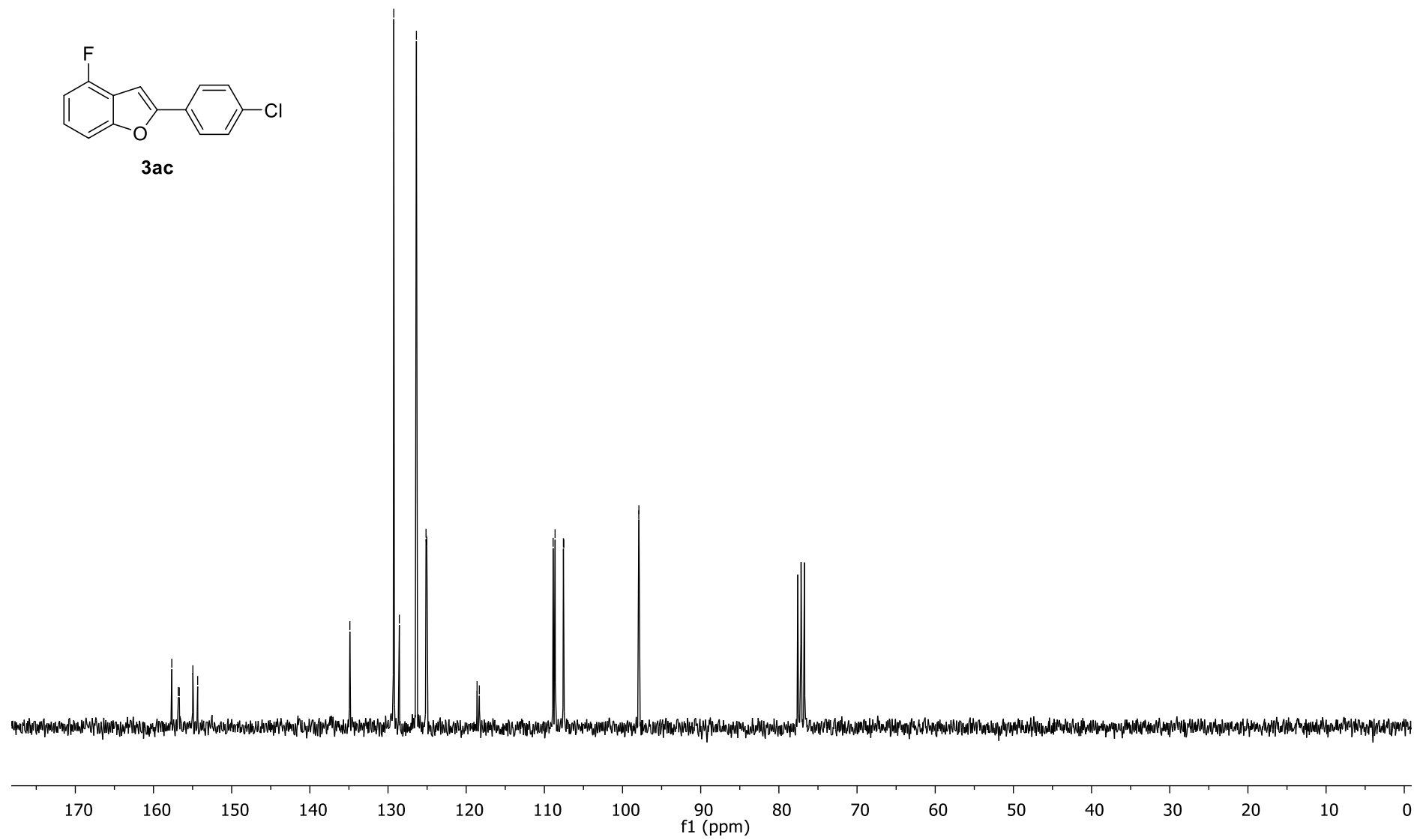
**3ac**

157.7  
156.8  
156.7  
155.0  
154.4

134.9  
129.3  
128.6  
126.4  
125.1  
125.0  
118.6  
118.3

108.9  
108.6  
107.6  
107.5

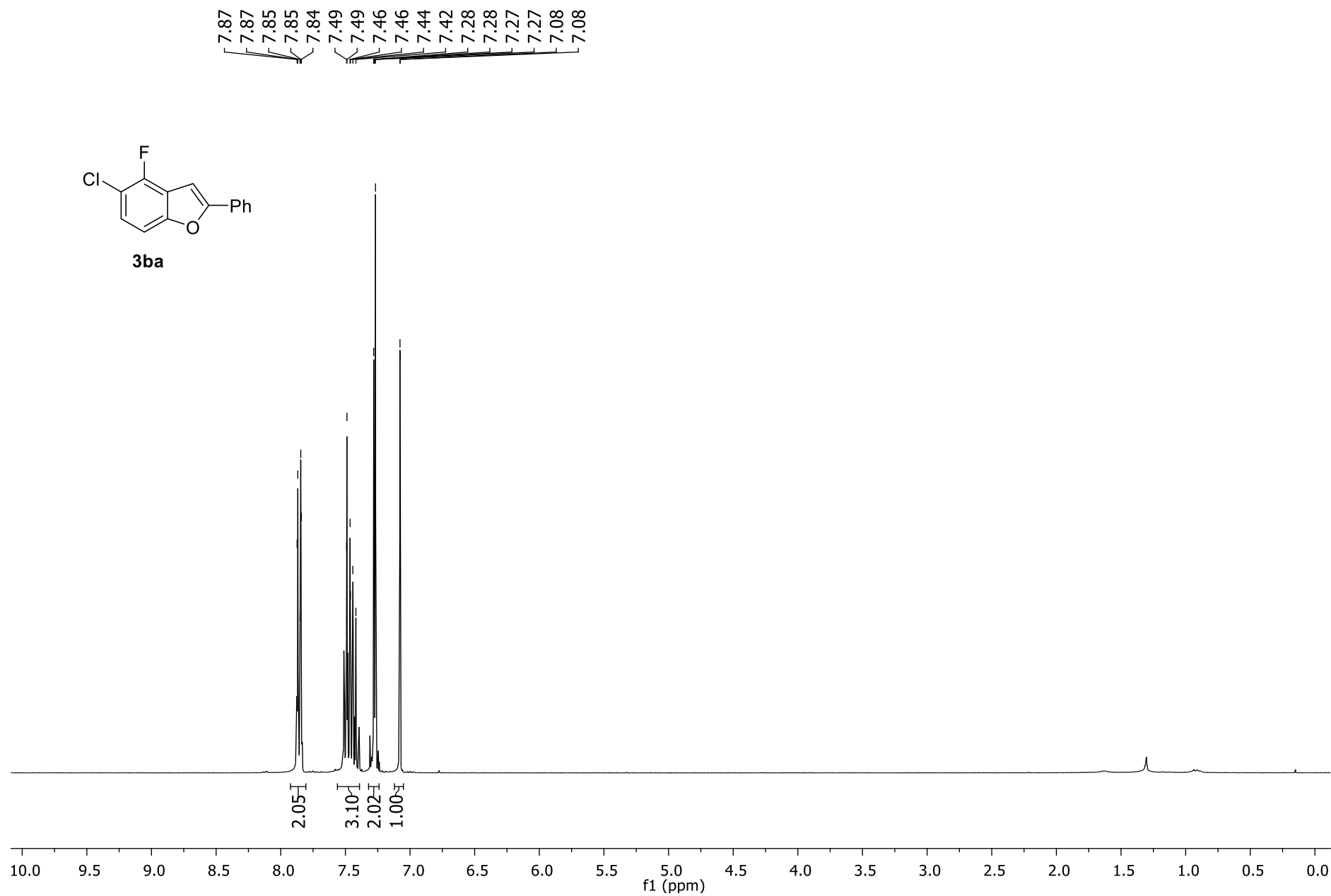
97.9  
97.9



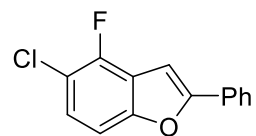
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



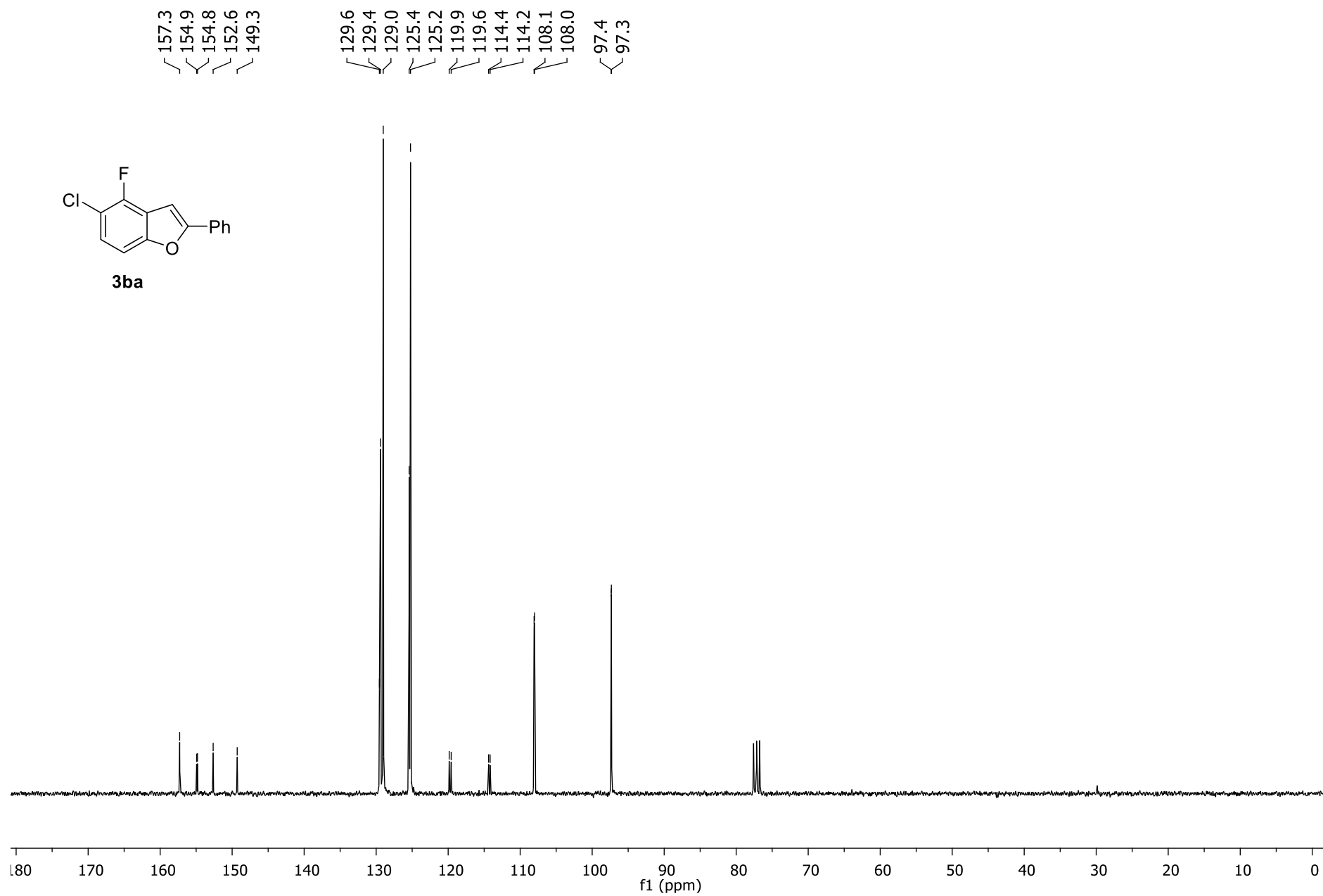
**3ba**





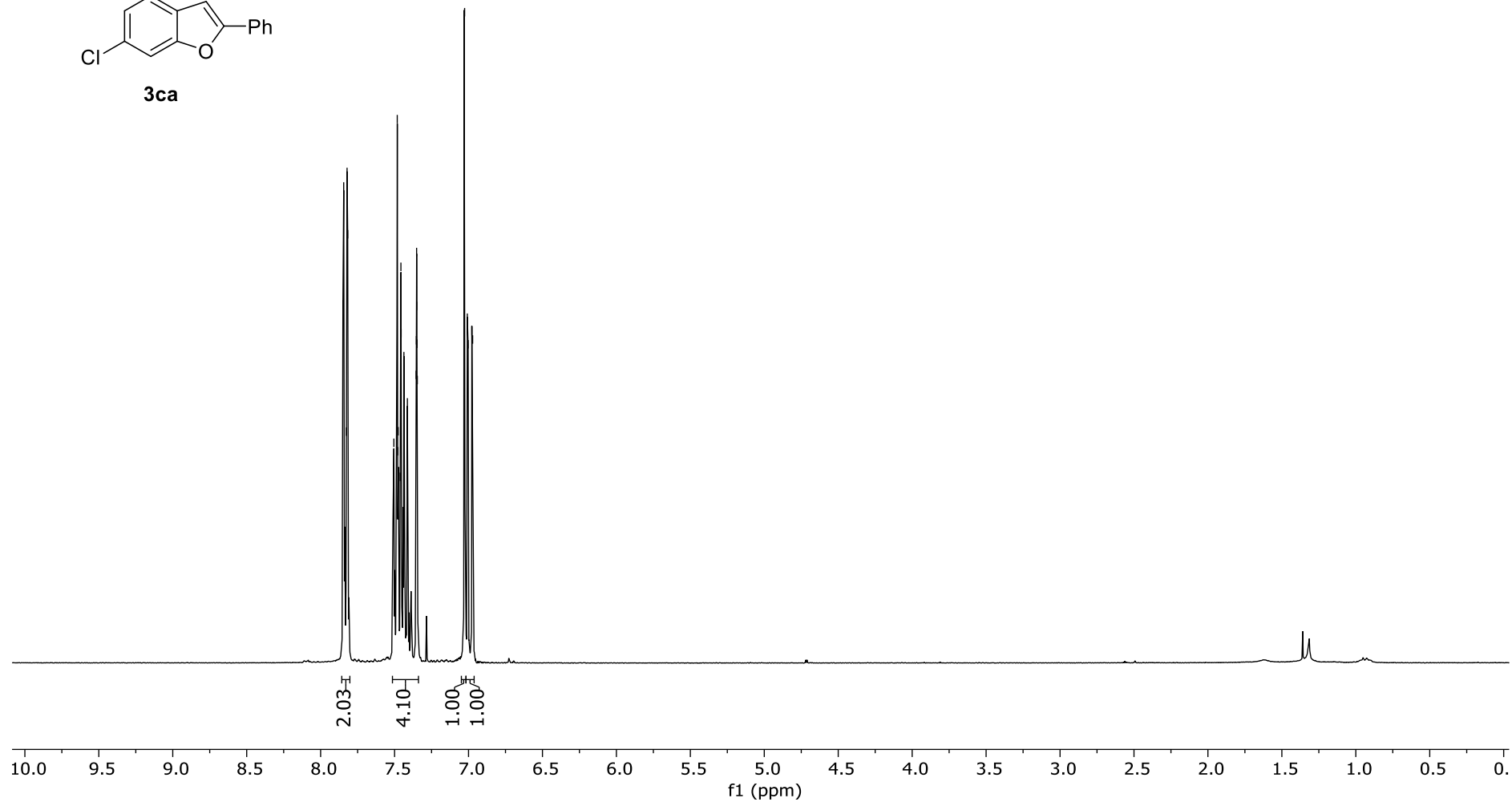
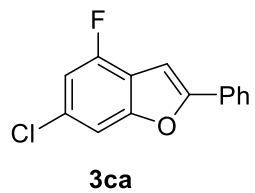
<sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)

**3ba**

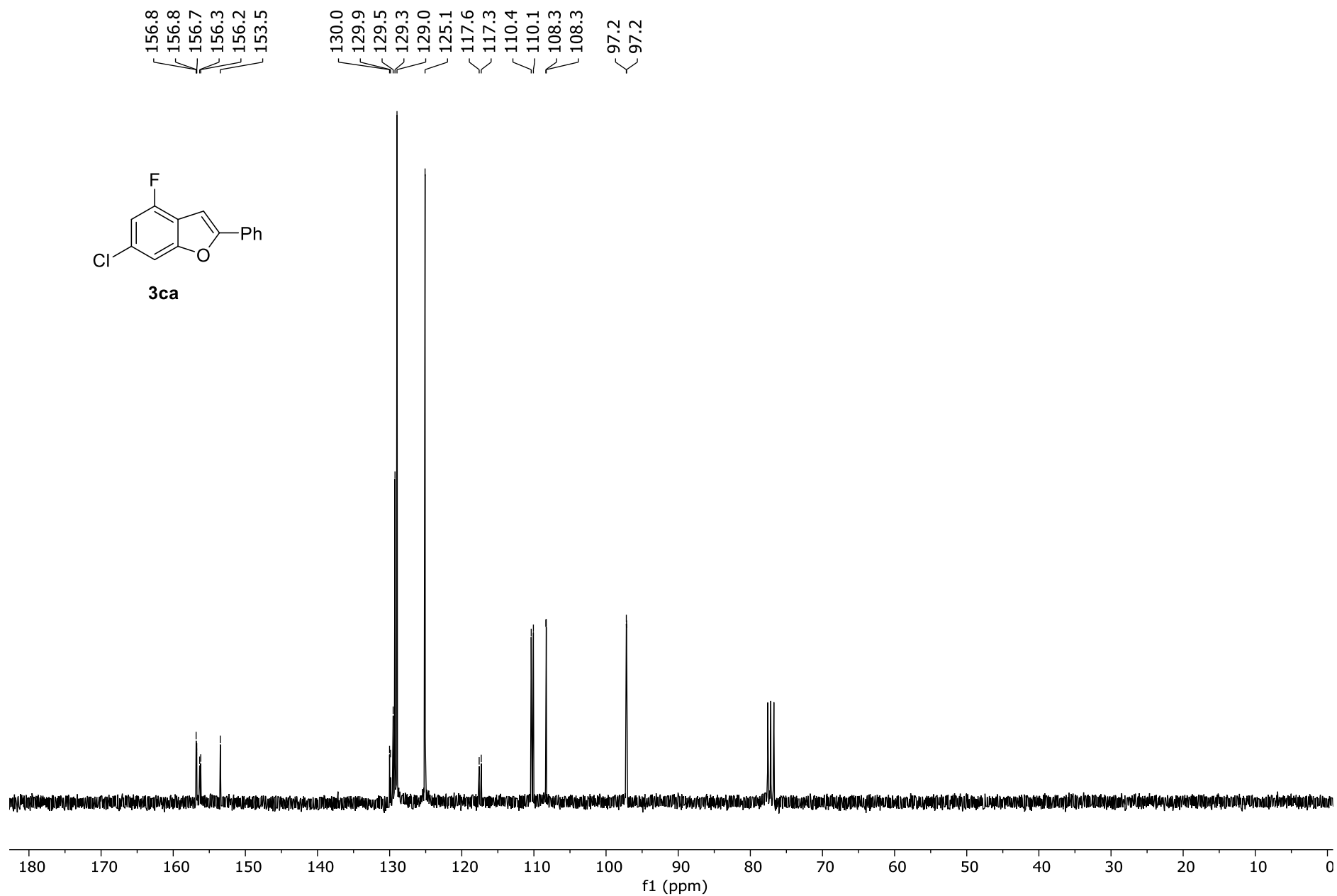
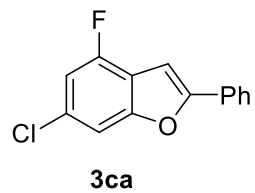


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

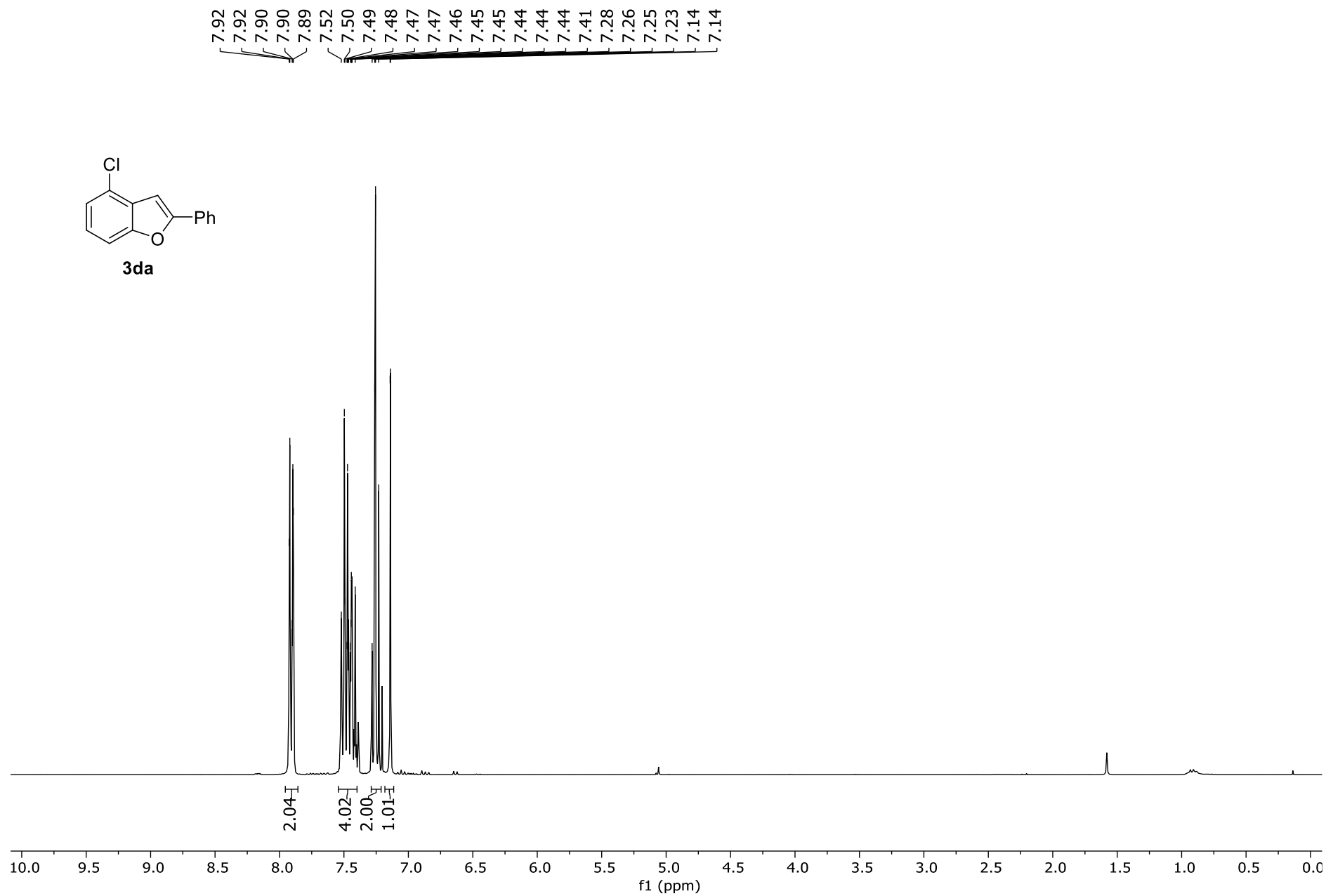
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7.46  
7.44  
7.41  
7.35  
7.35  
7.35  
7.35  
7.35  
7.35  
7.03  
7.03  
7.01  
7.00  
6.98  
6.97



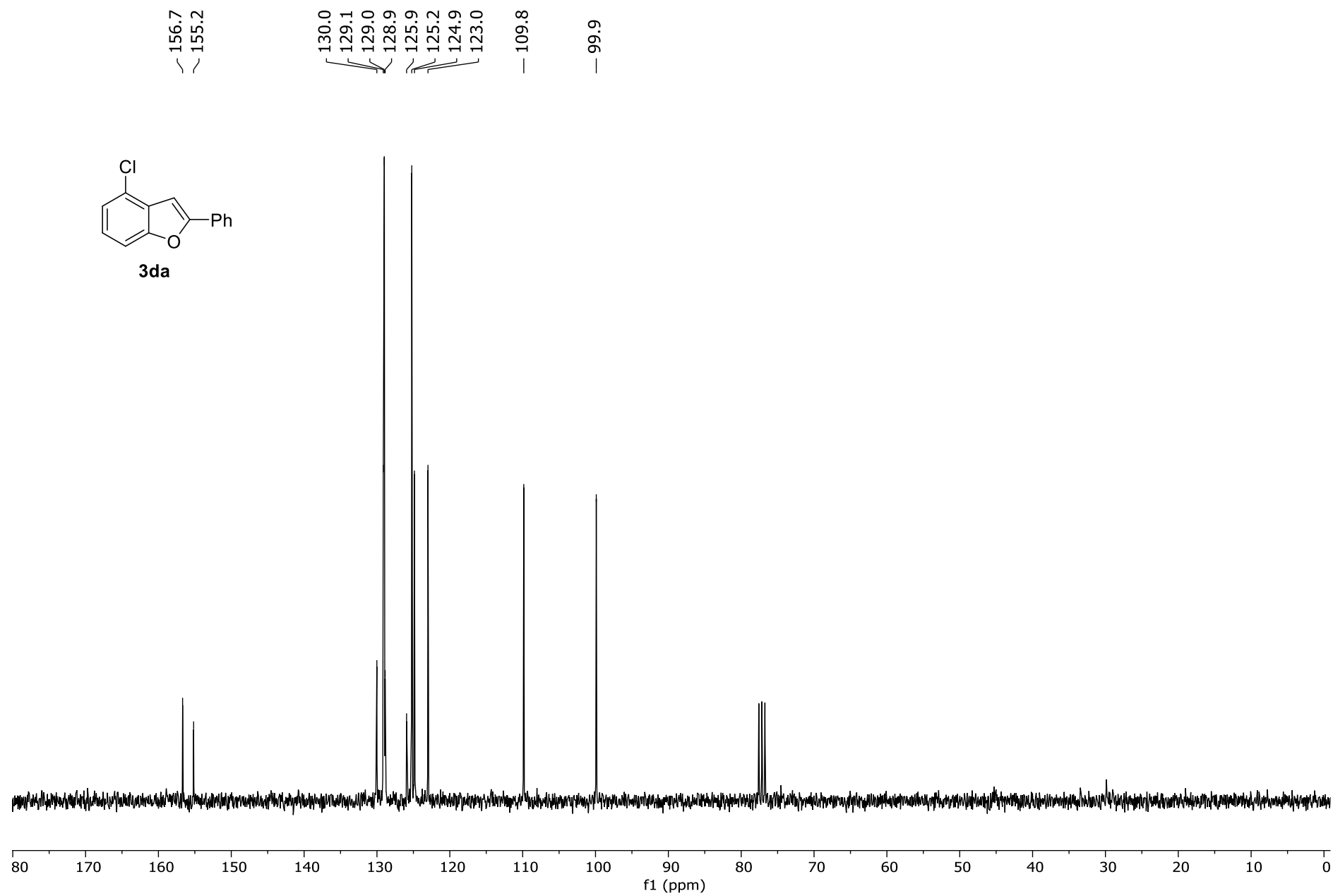
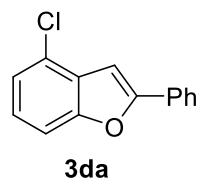
$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



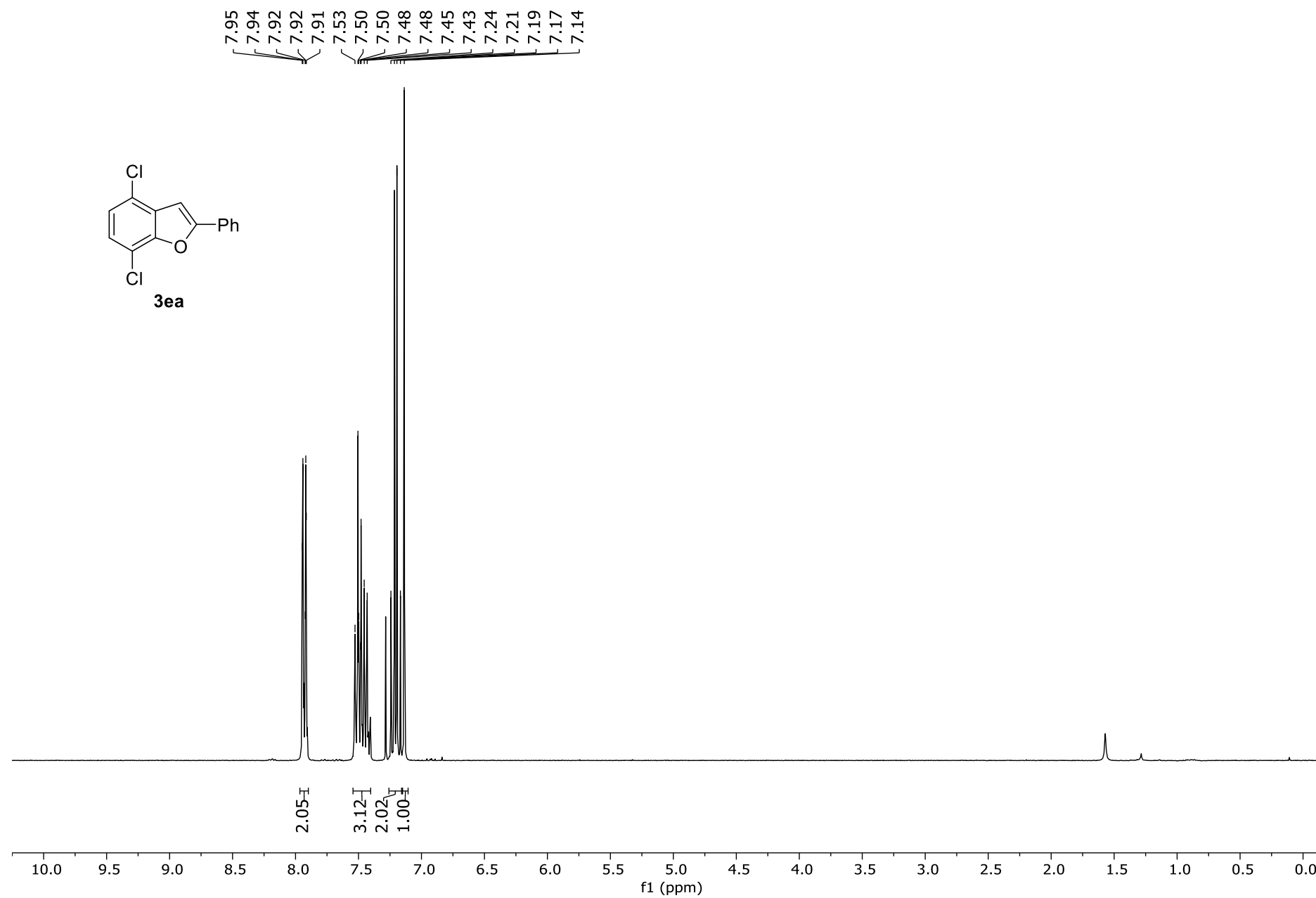
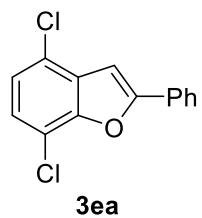
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



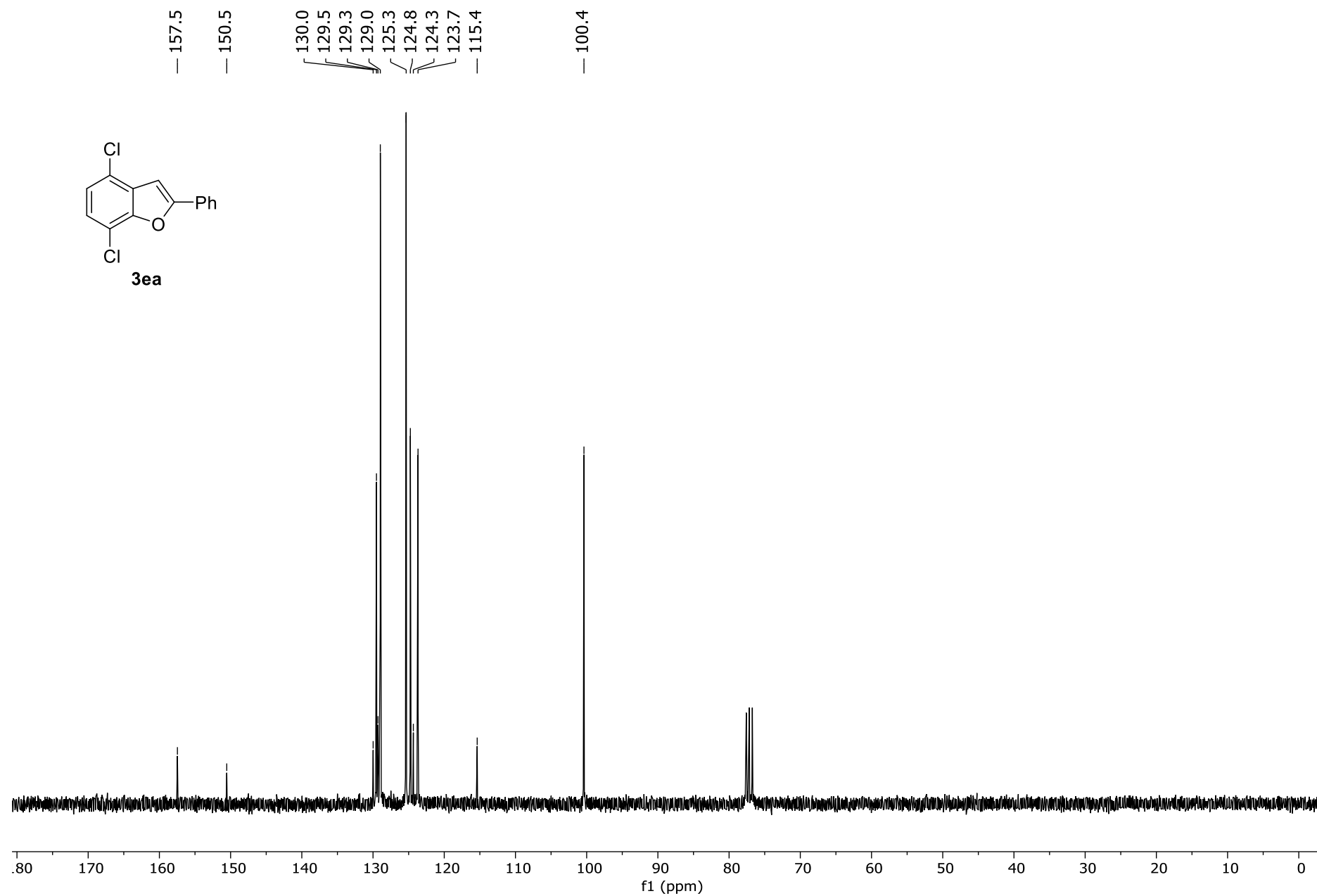
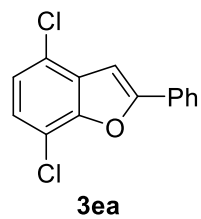
$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



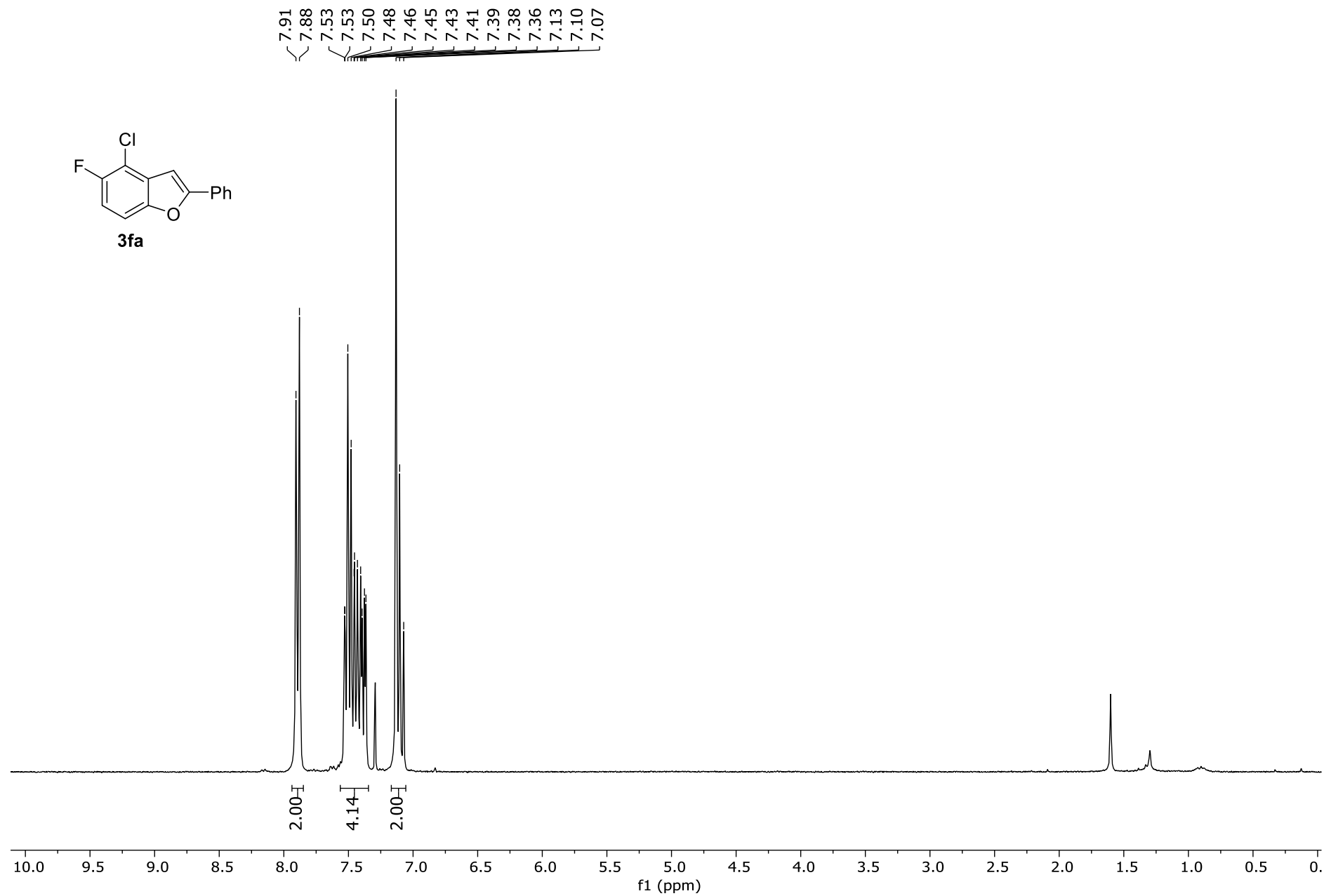
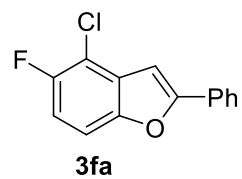
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )

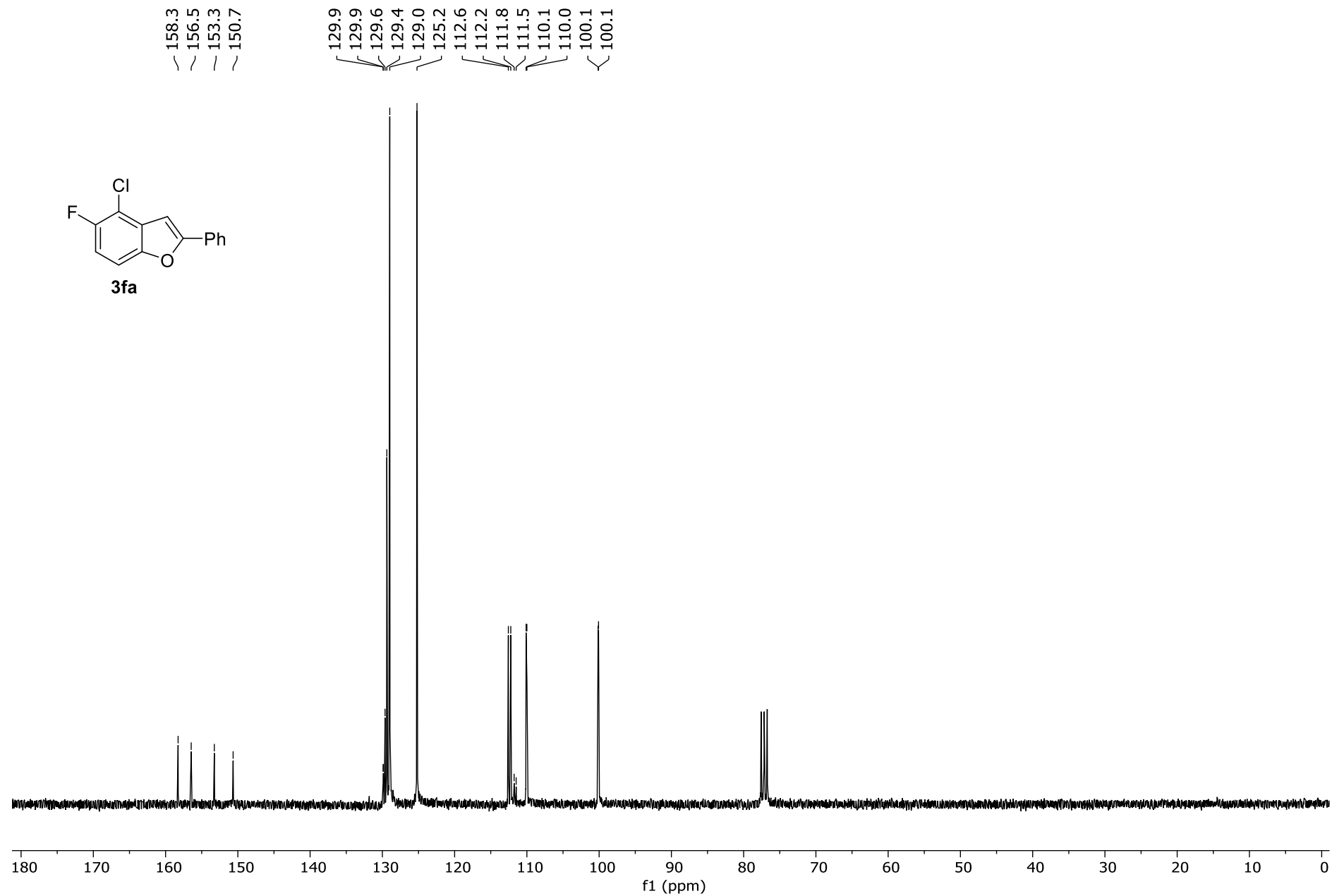
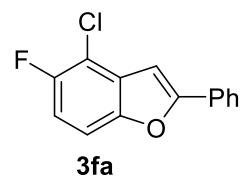


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

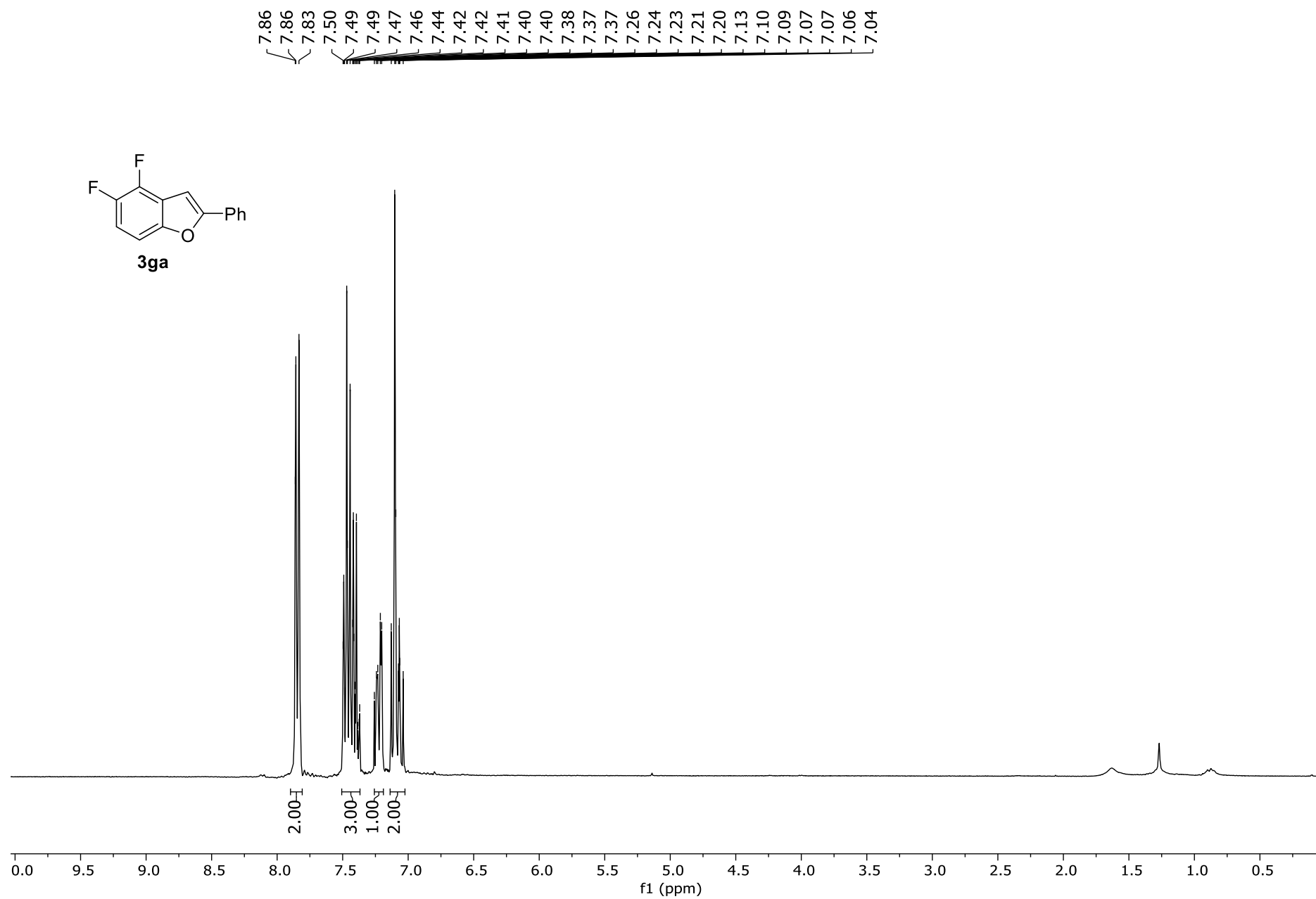
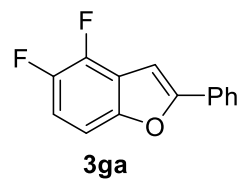




$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )

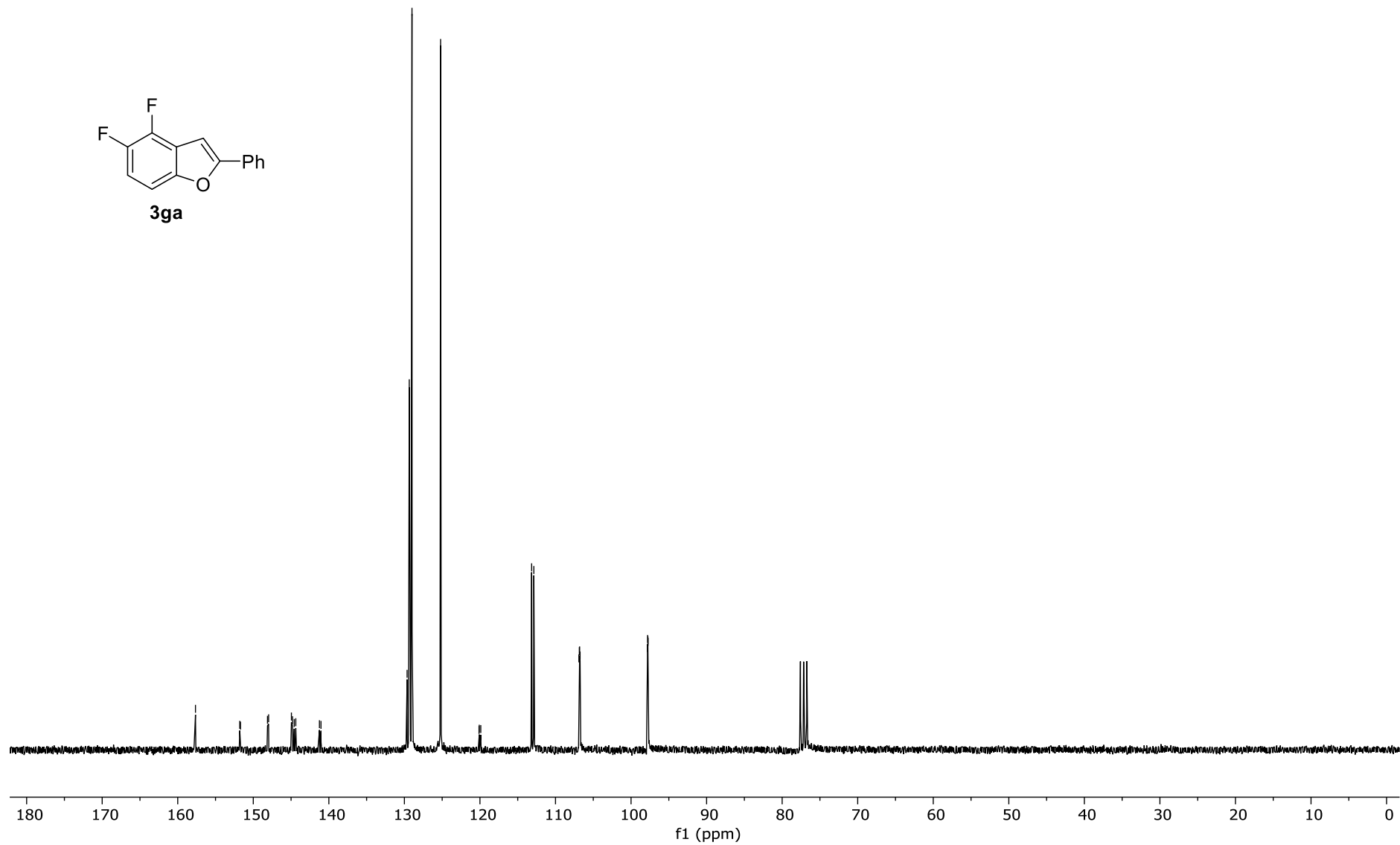
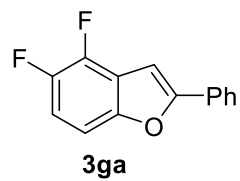


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

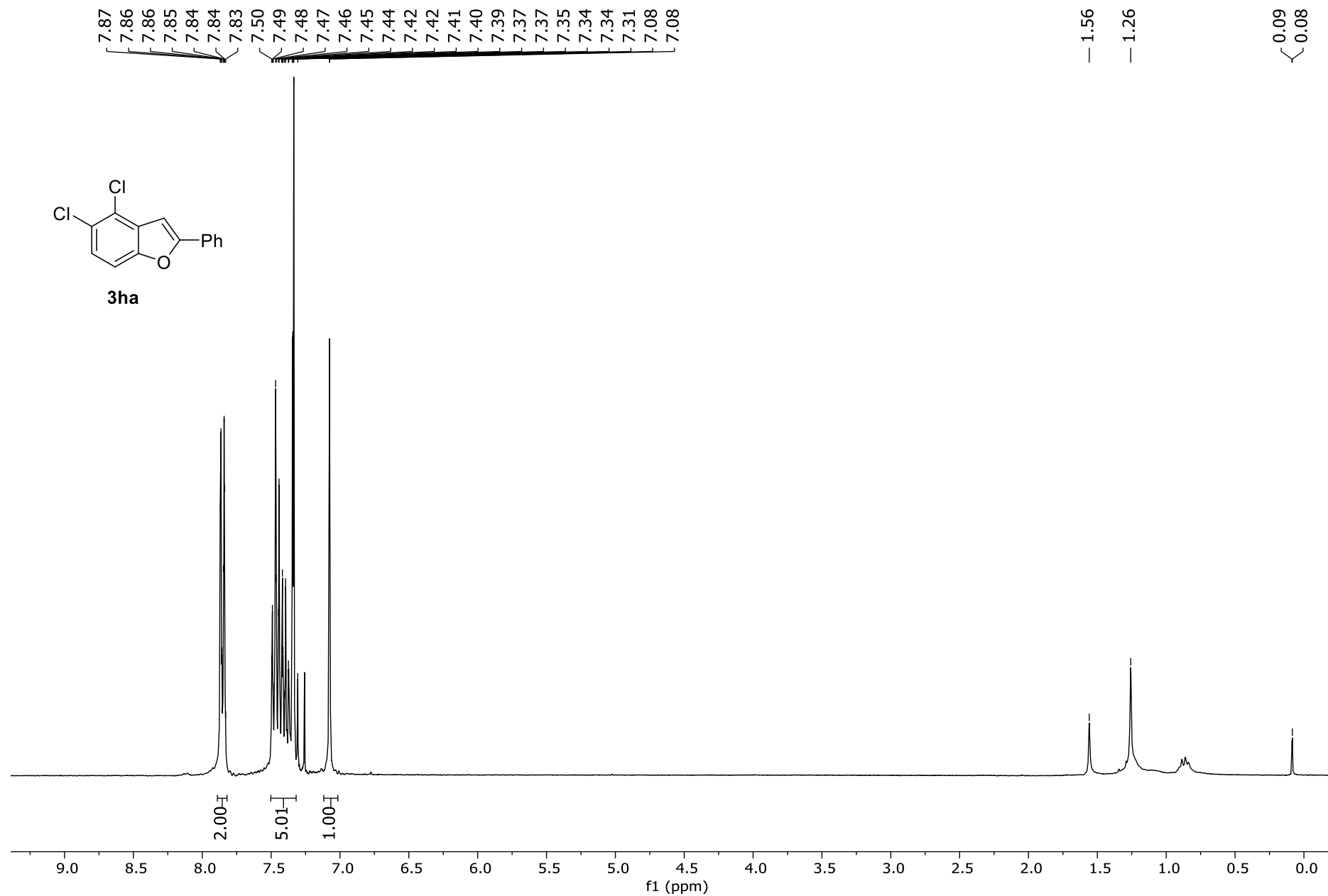
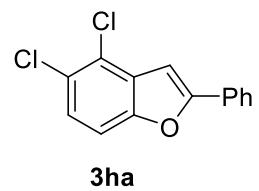


$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )

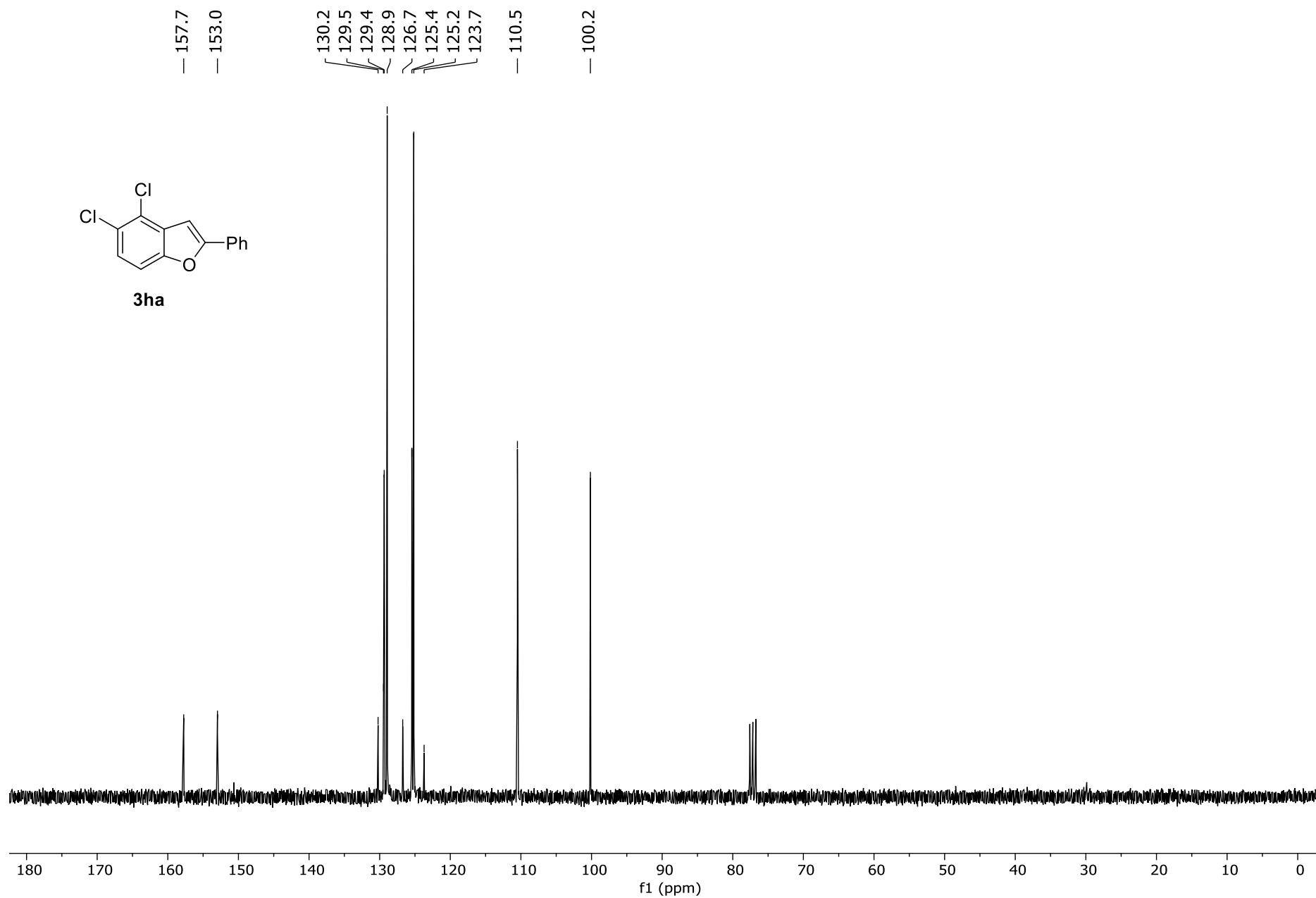
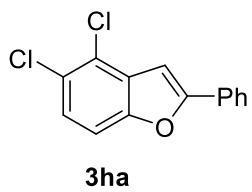
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141.0  
129.6  
129.4  
129.0  
125.2  
120.1  
120.1  
119.9  
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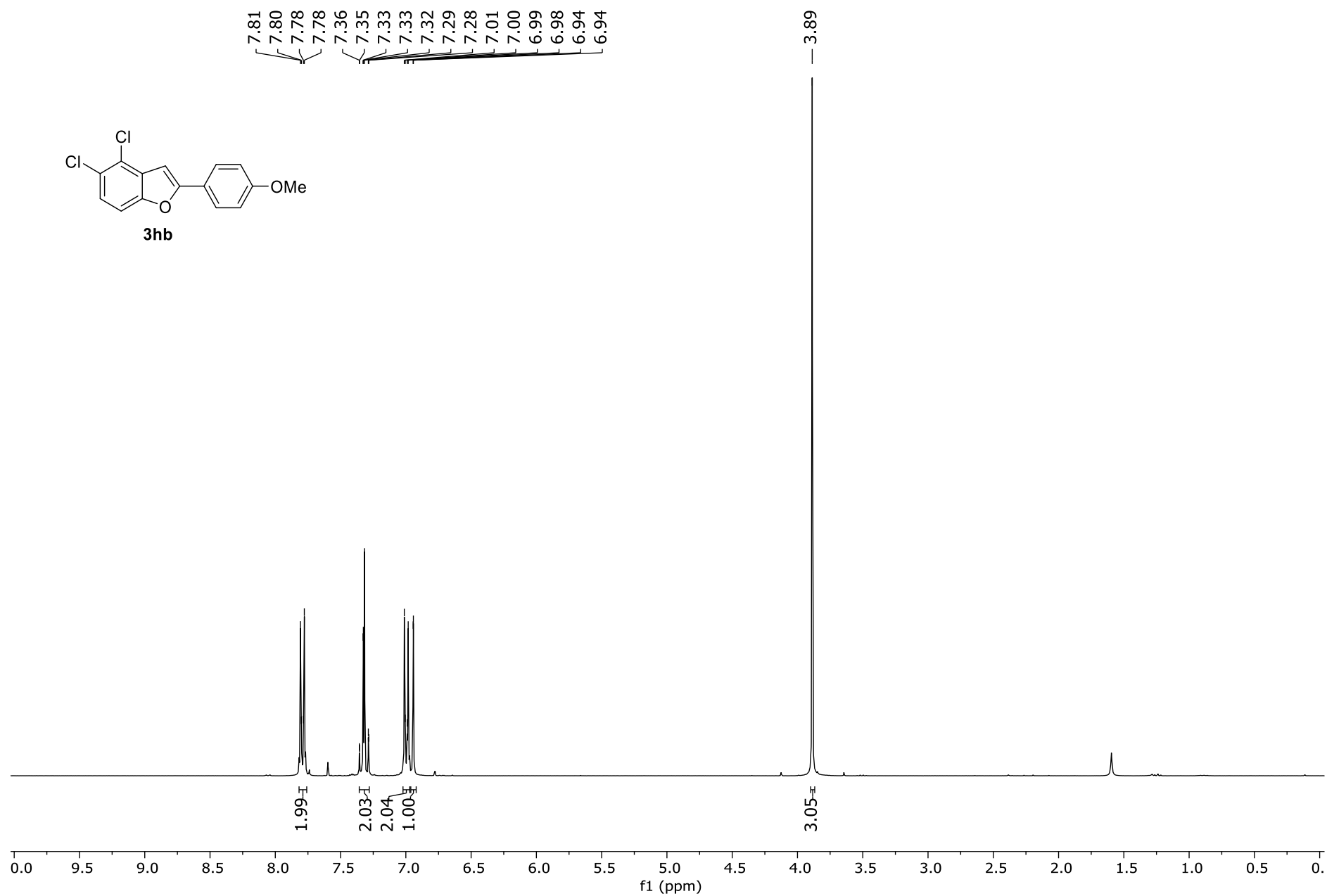
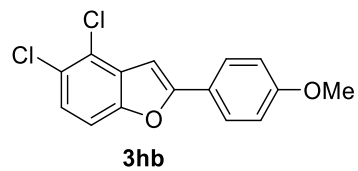
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



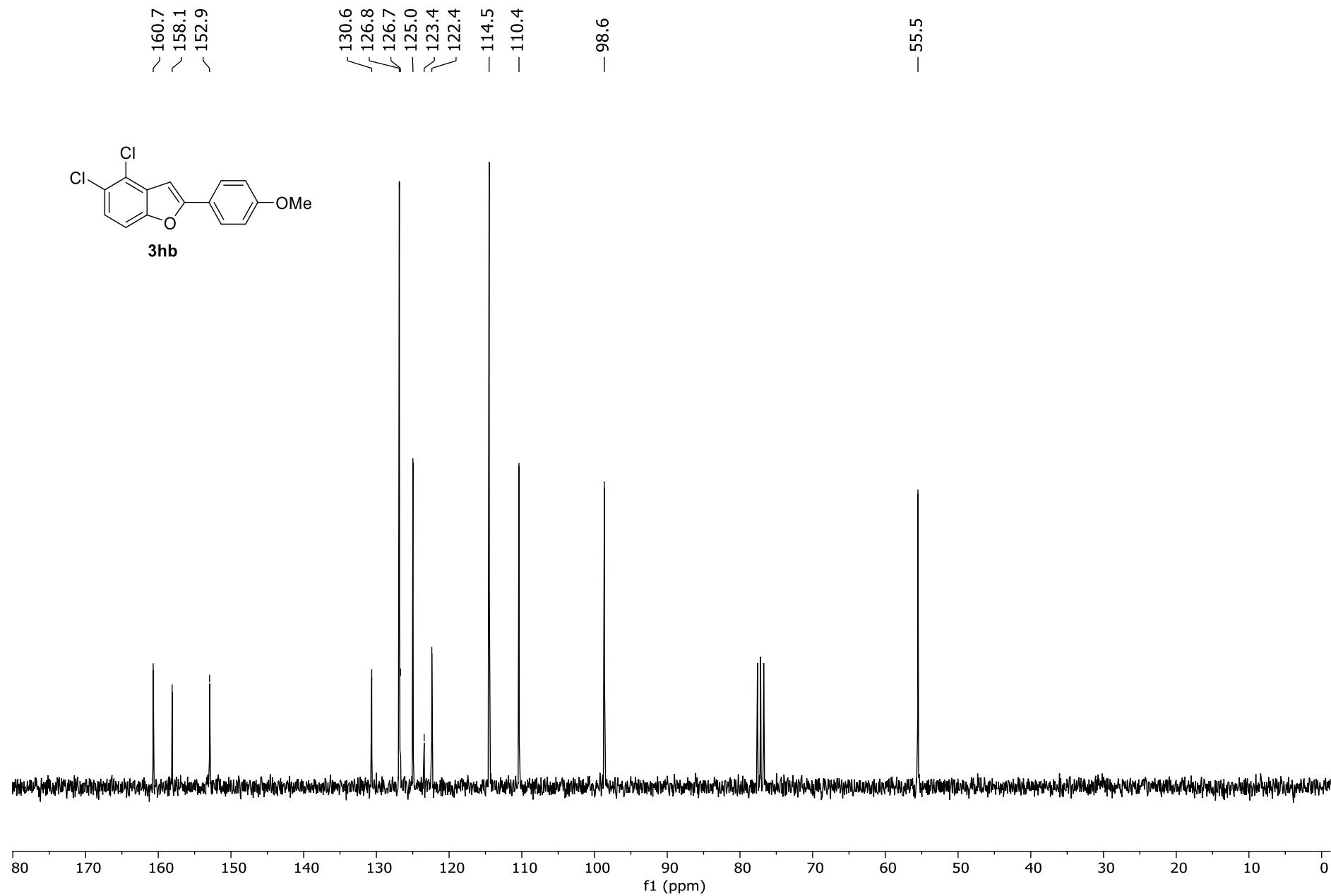
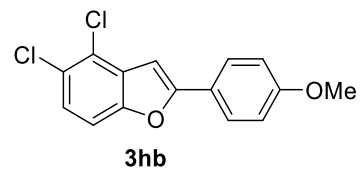
$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



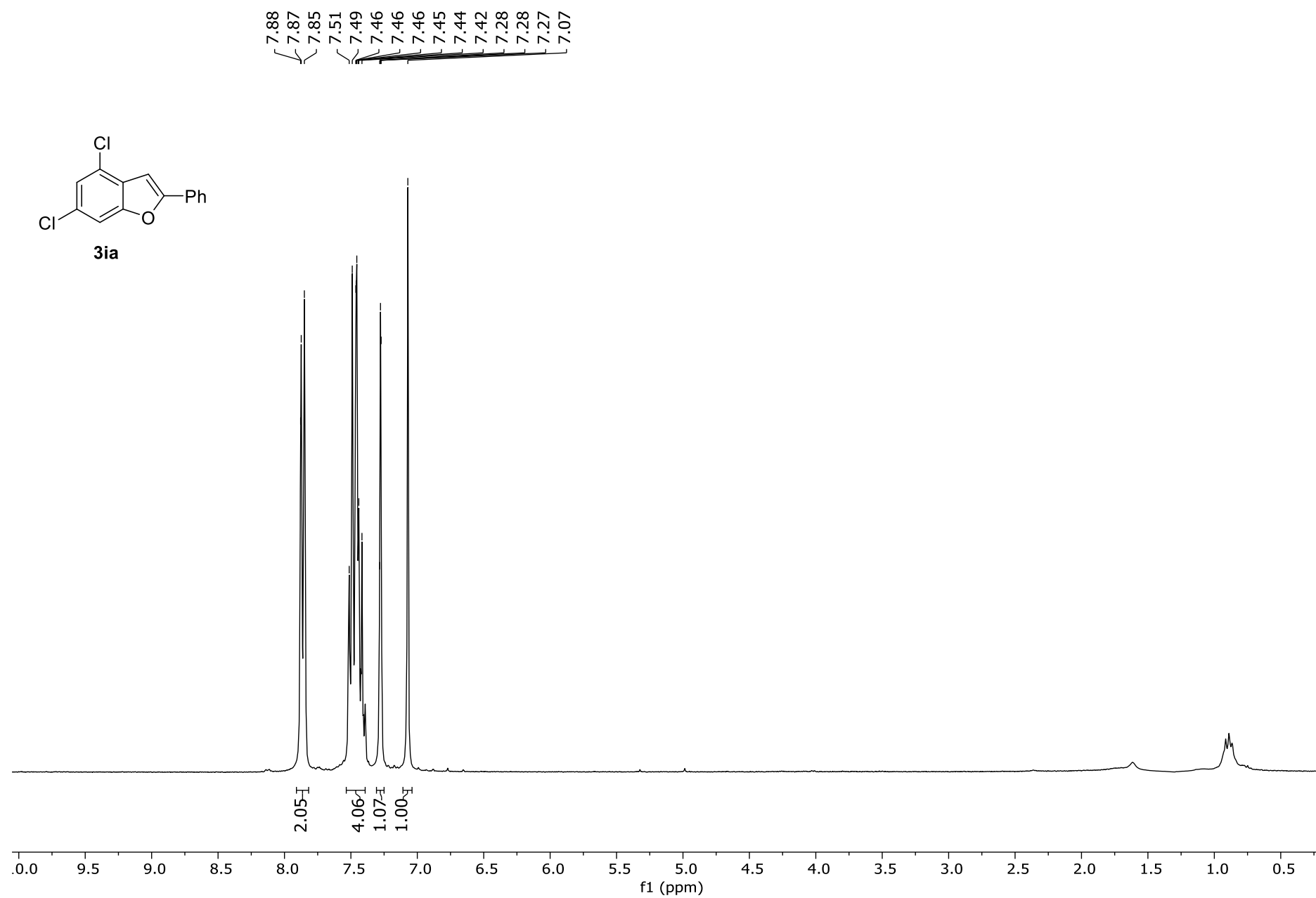
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



<sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)

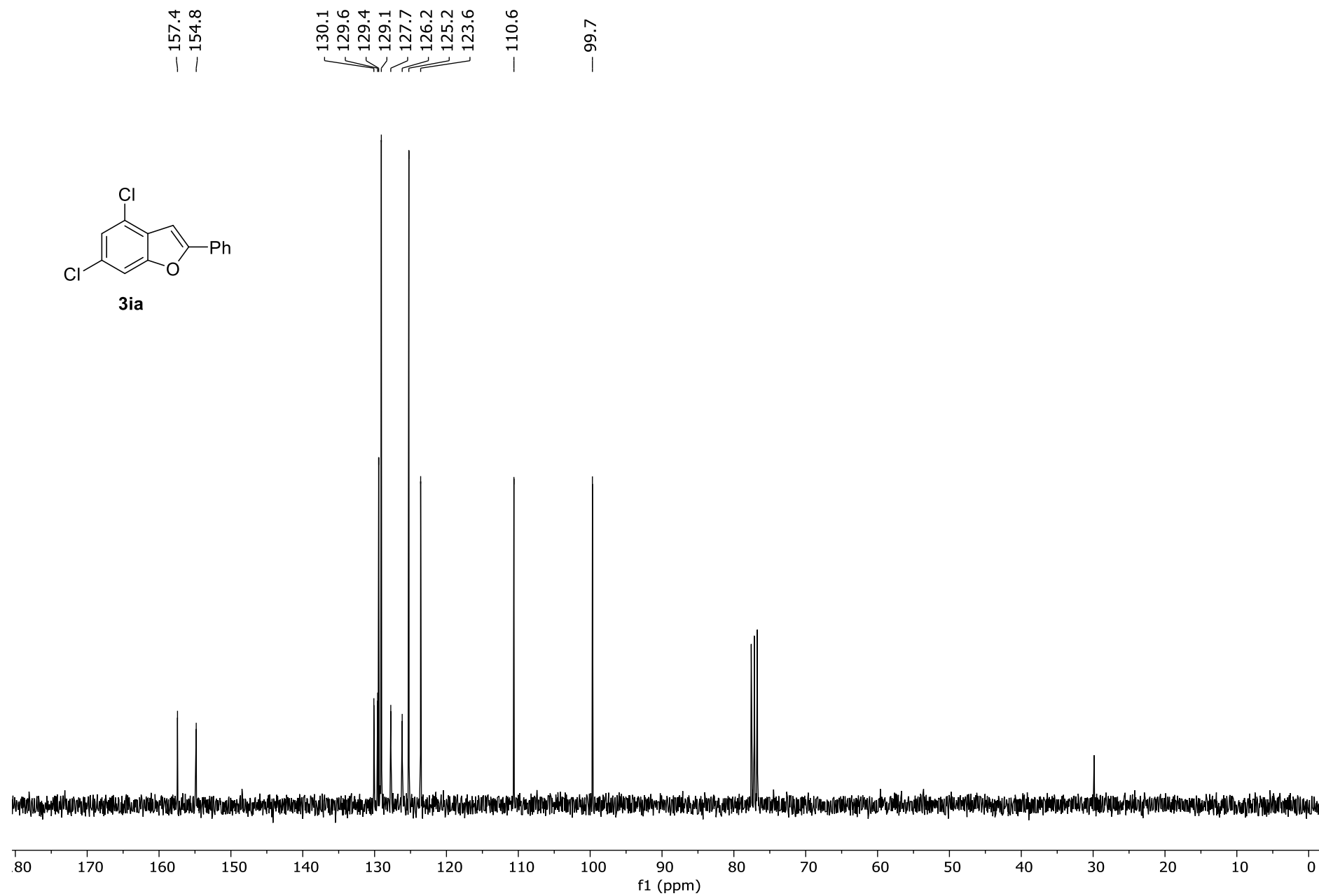
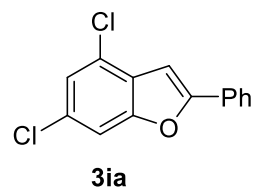


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

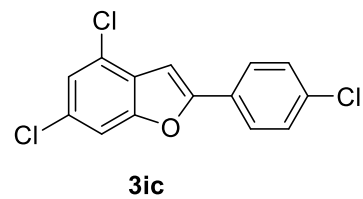




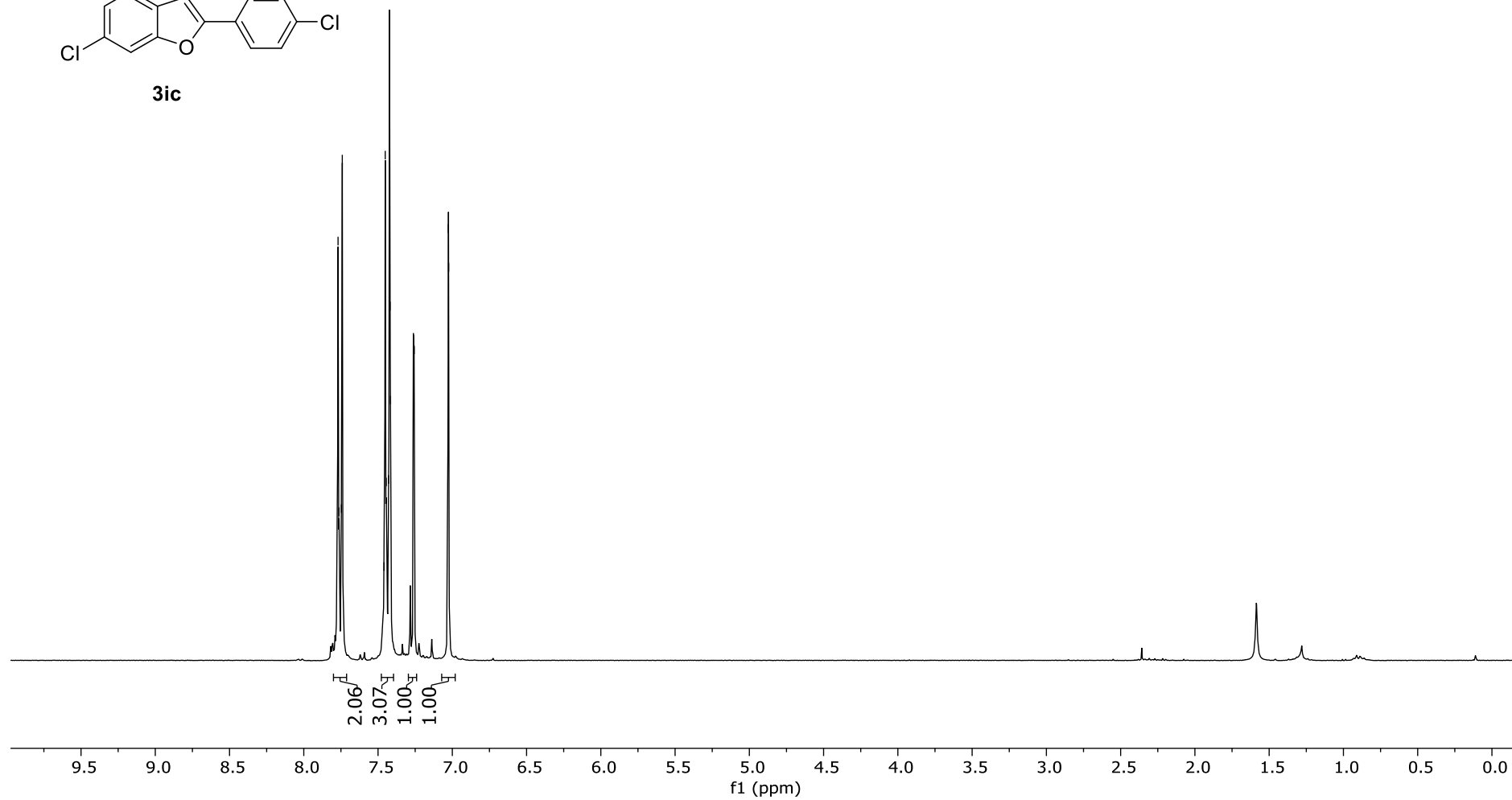
$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



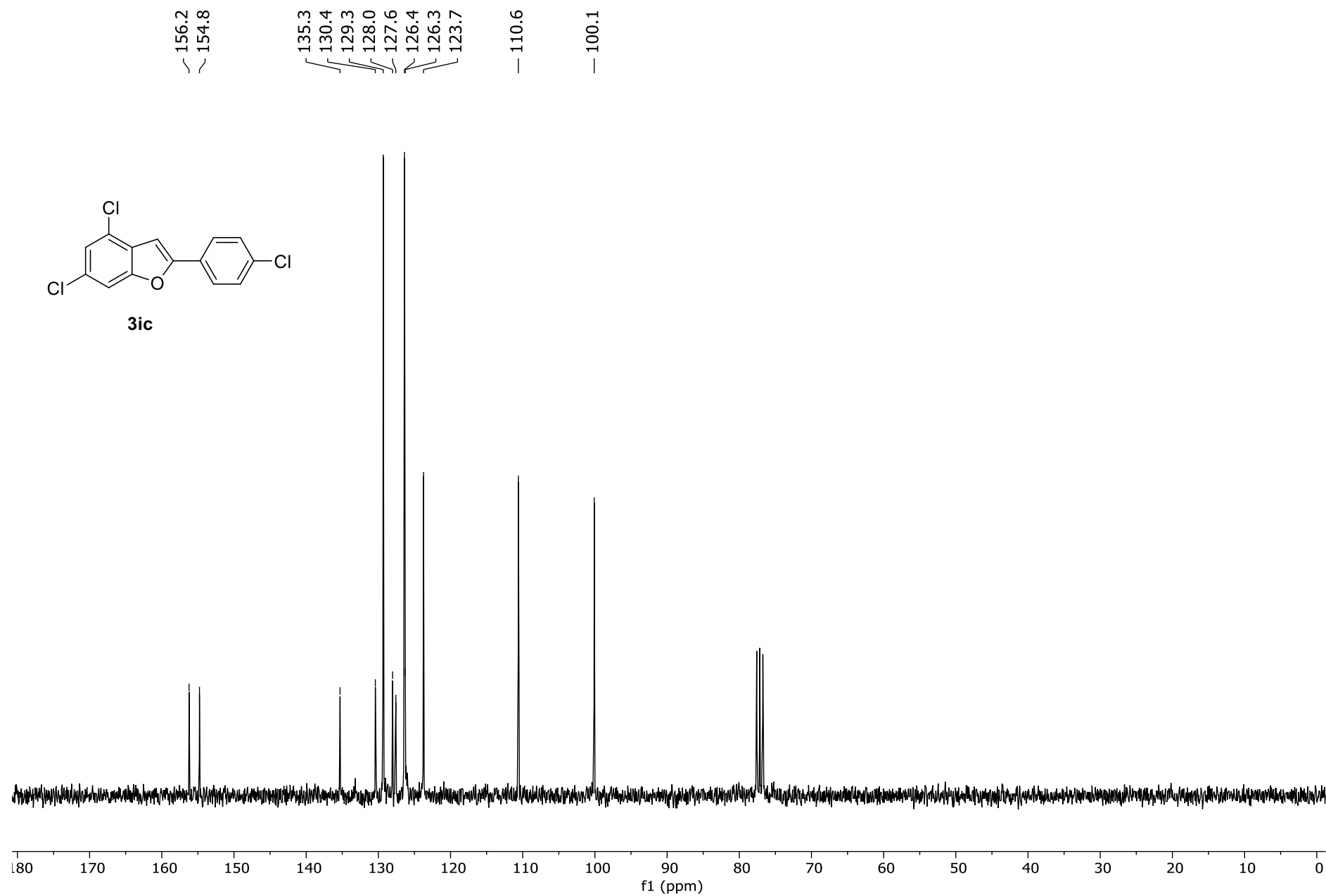
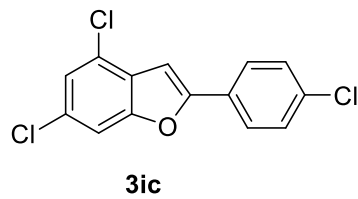
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



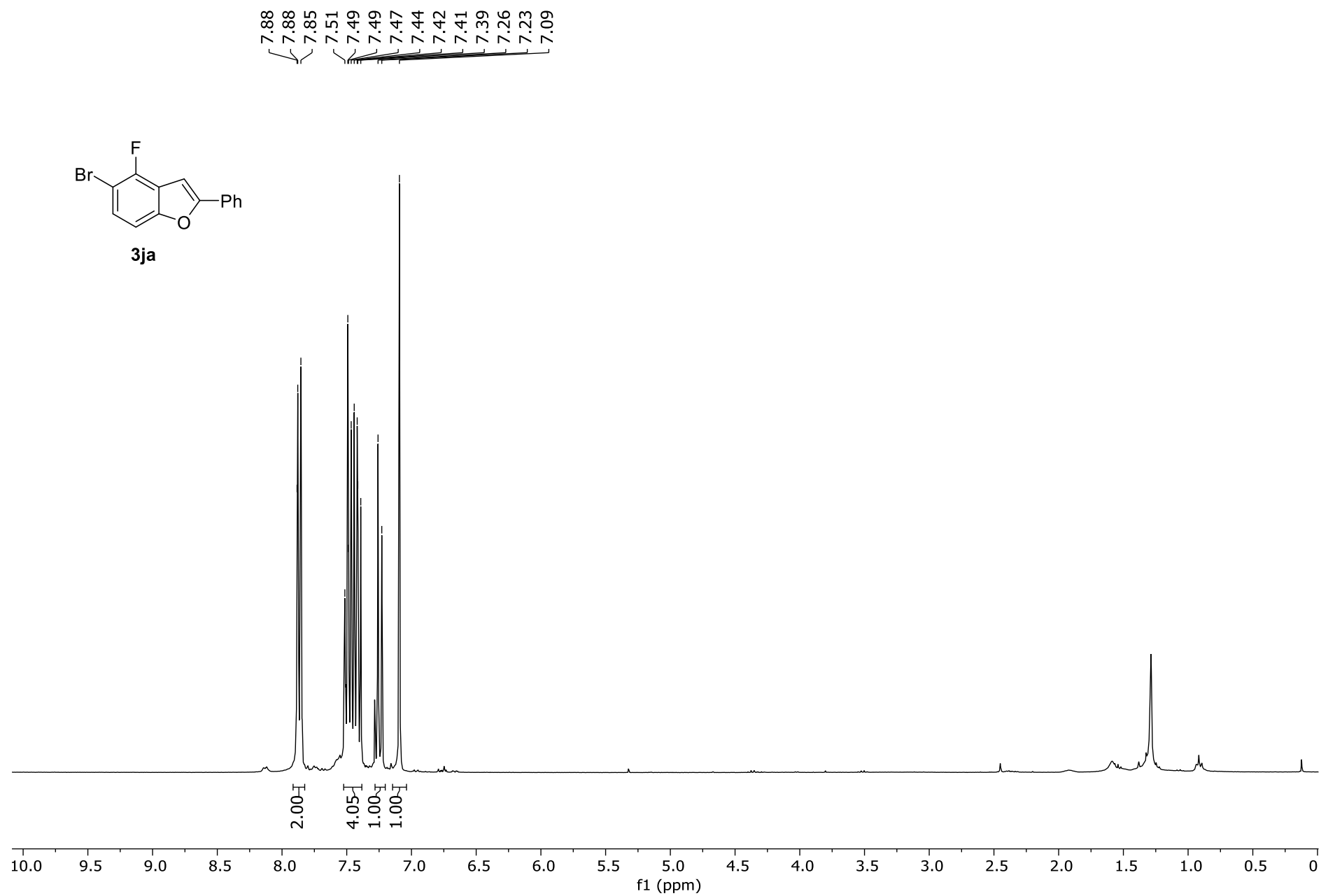
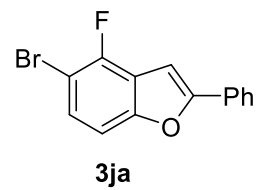
7.77  
7.76  
7.75  
7.74  
7.46  
7.45  
7.44  
7.43  
7.42  
7.42  
7.26  
7.26  
7.03  
7.02



$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

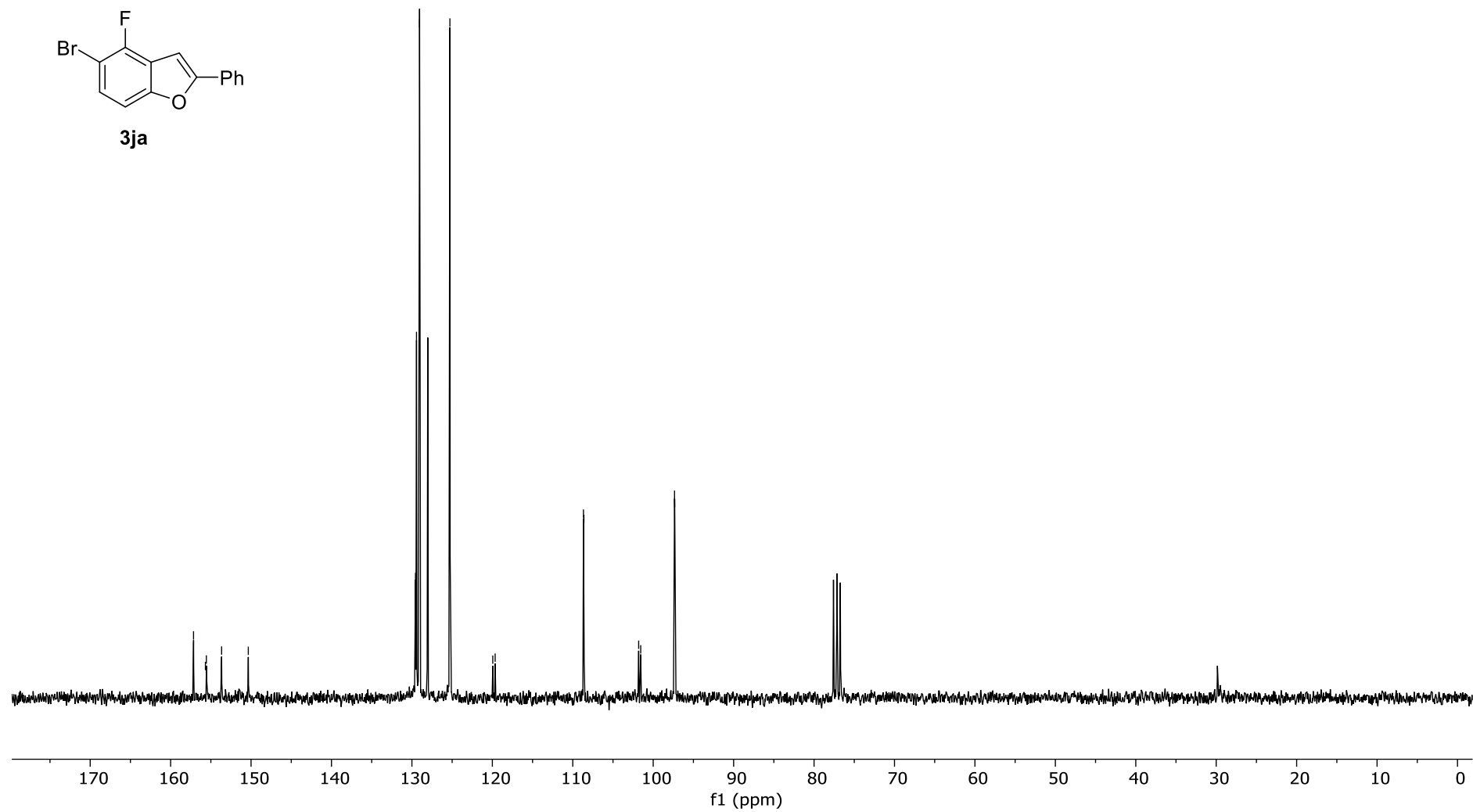
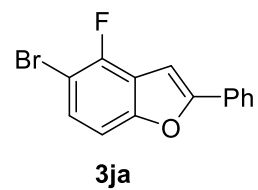


$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )

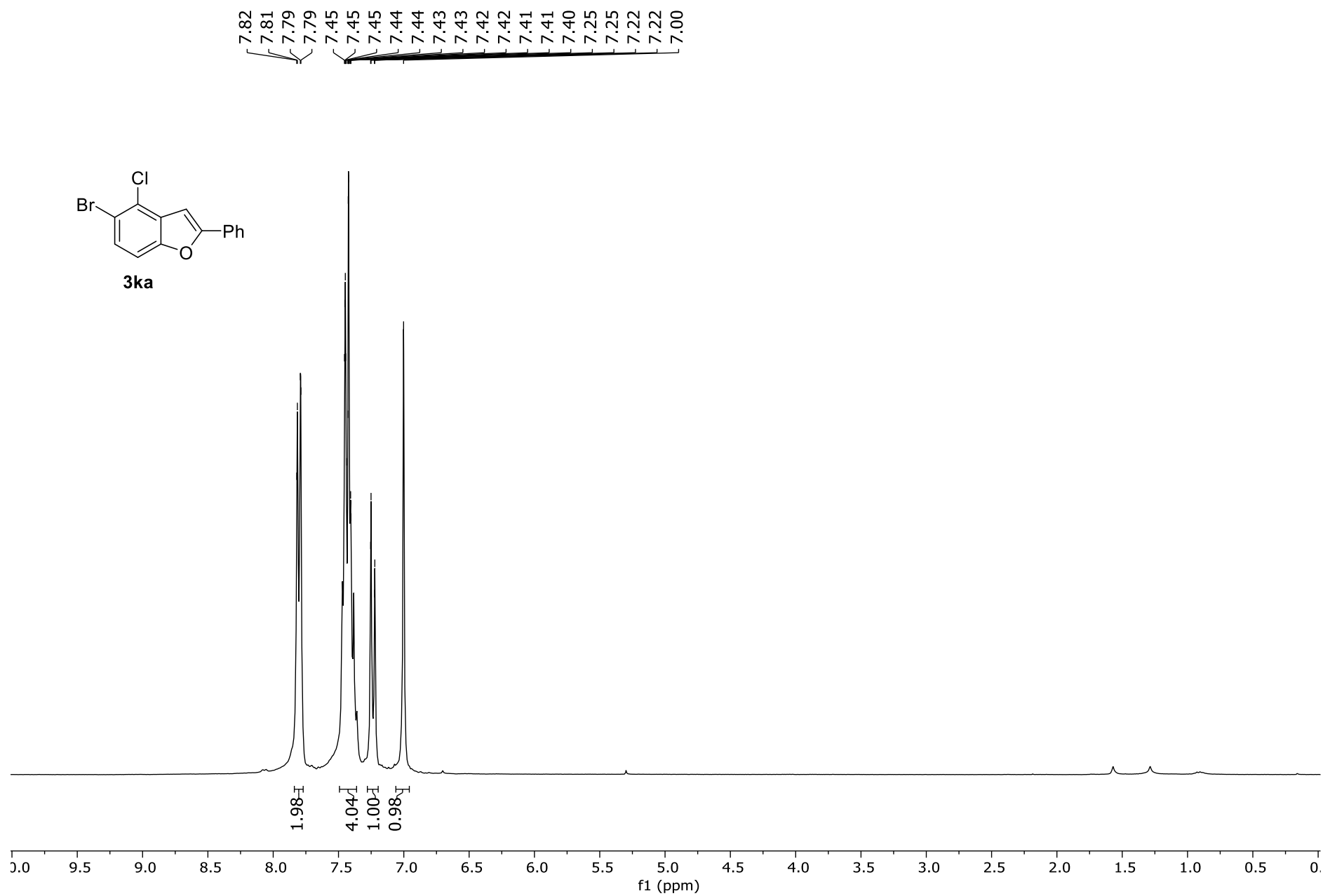
157.2  
155.7  
155.6  
153.7  
150.3

129.6  
129.4  
129.1  
128.0  
125.3  
119.9  
119.7

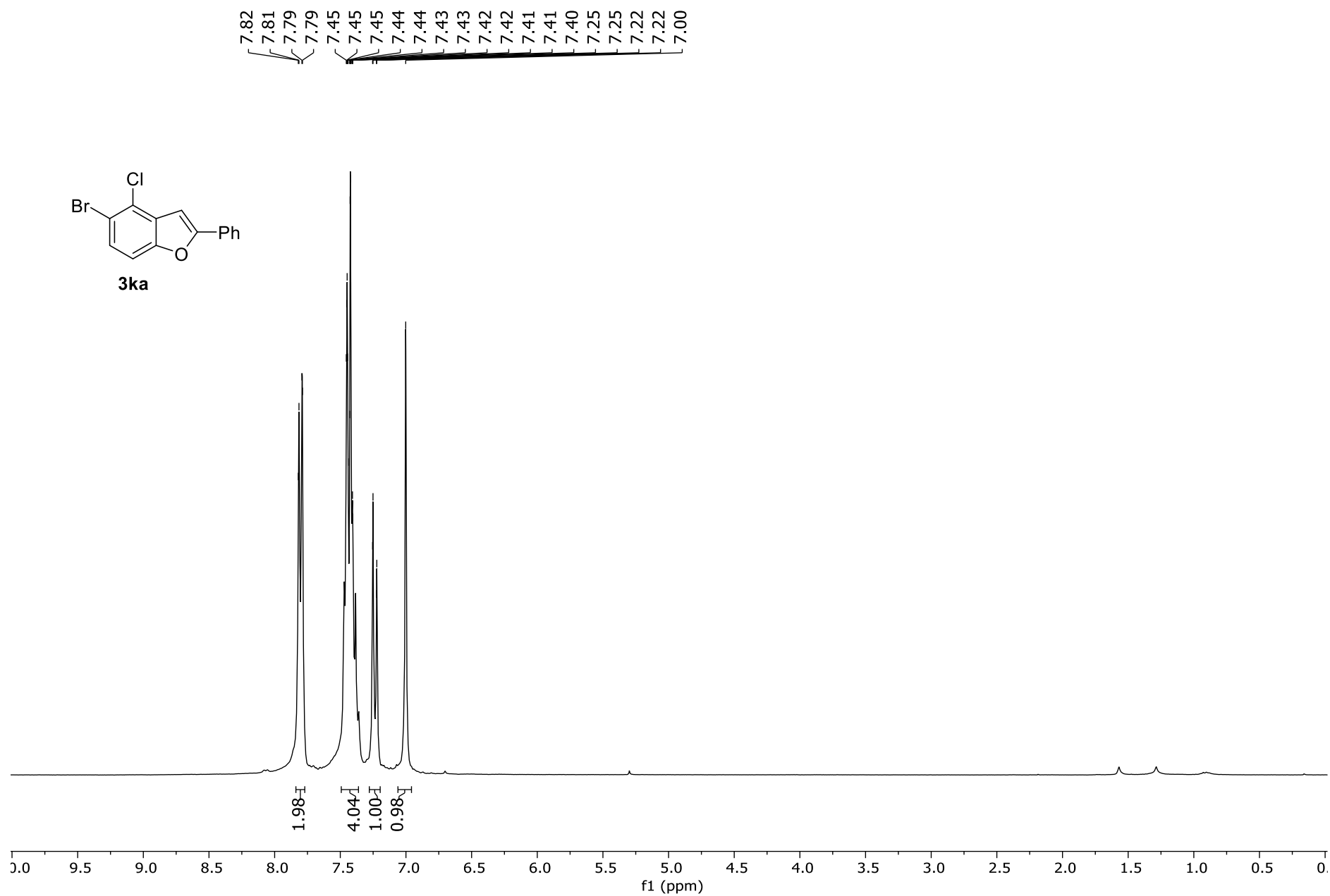
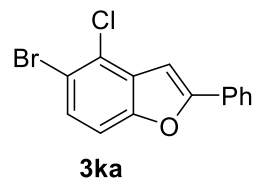
108.7  
108.6  
101.8  
101.6  
97.3  
97.3



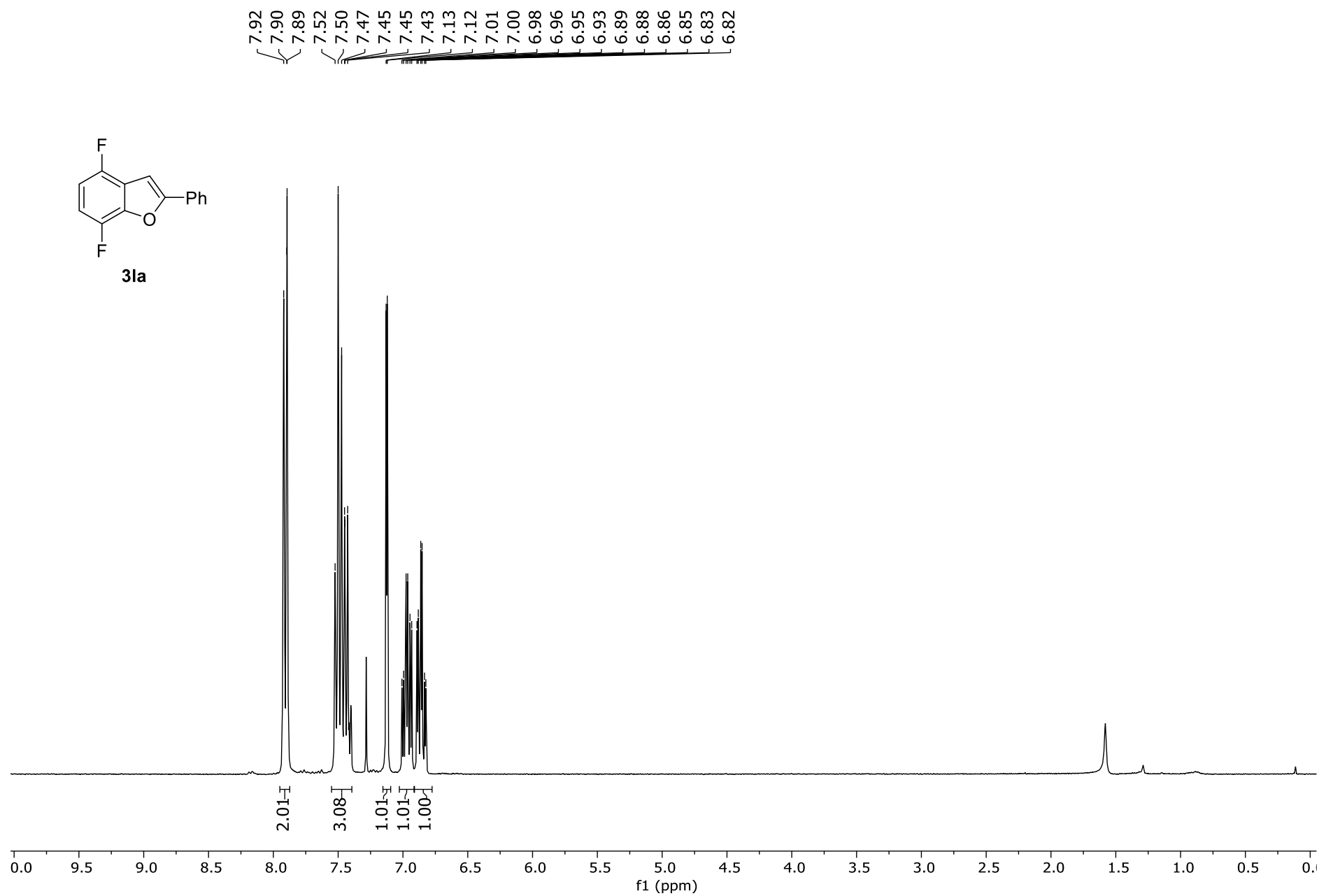
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)

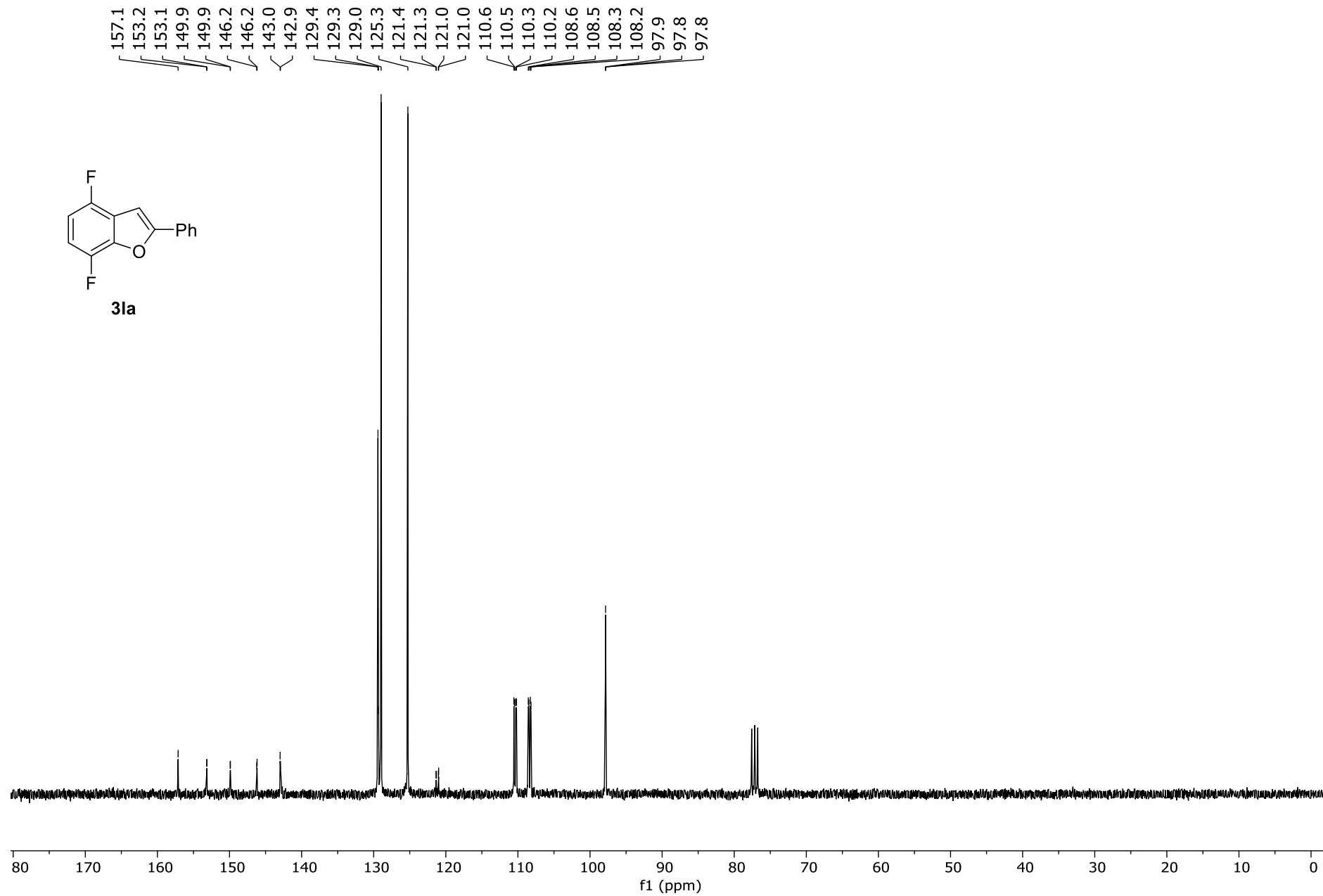
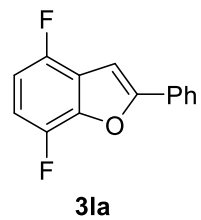


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

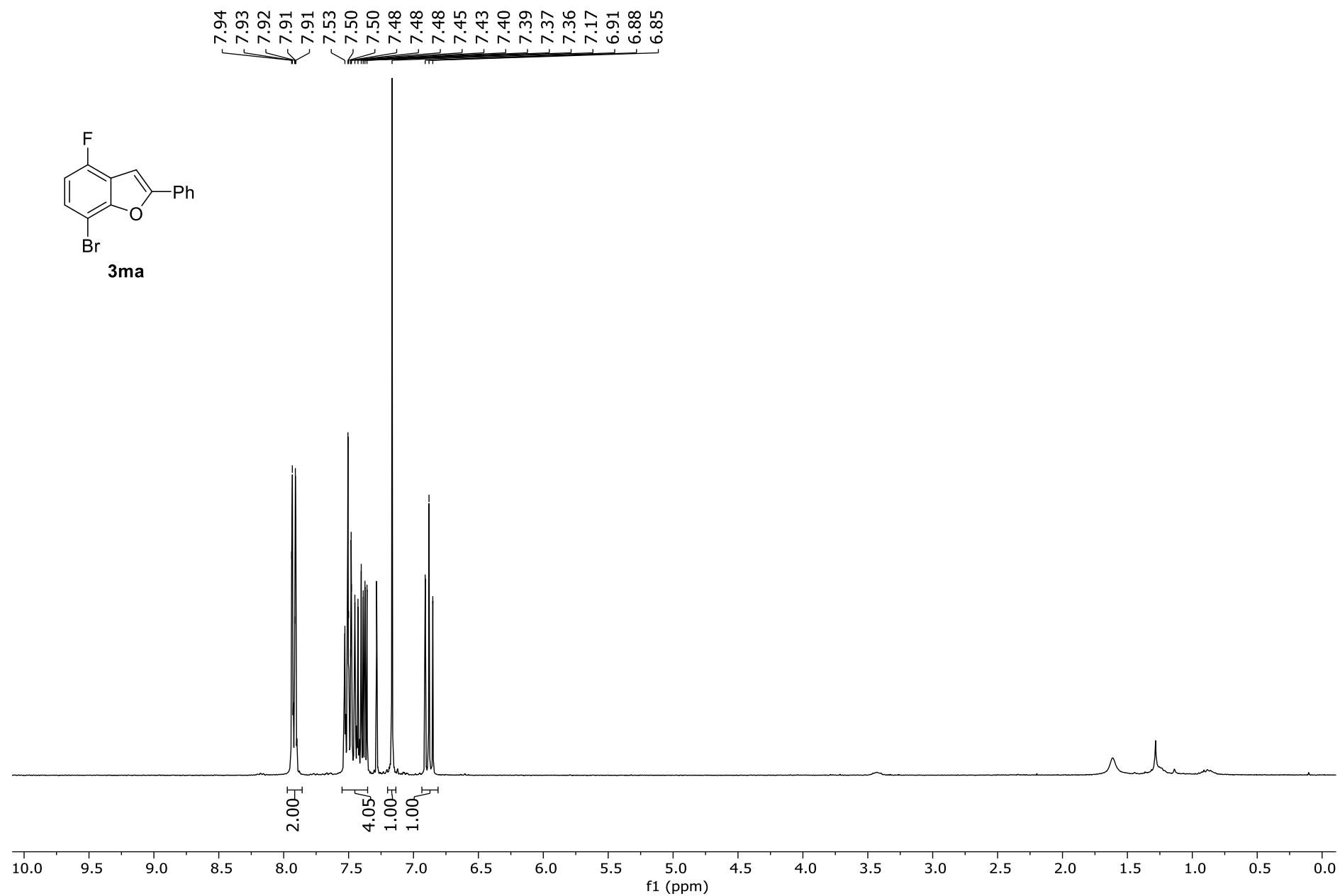




$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

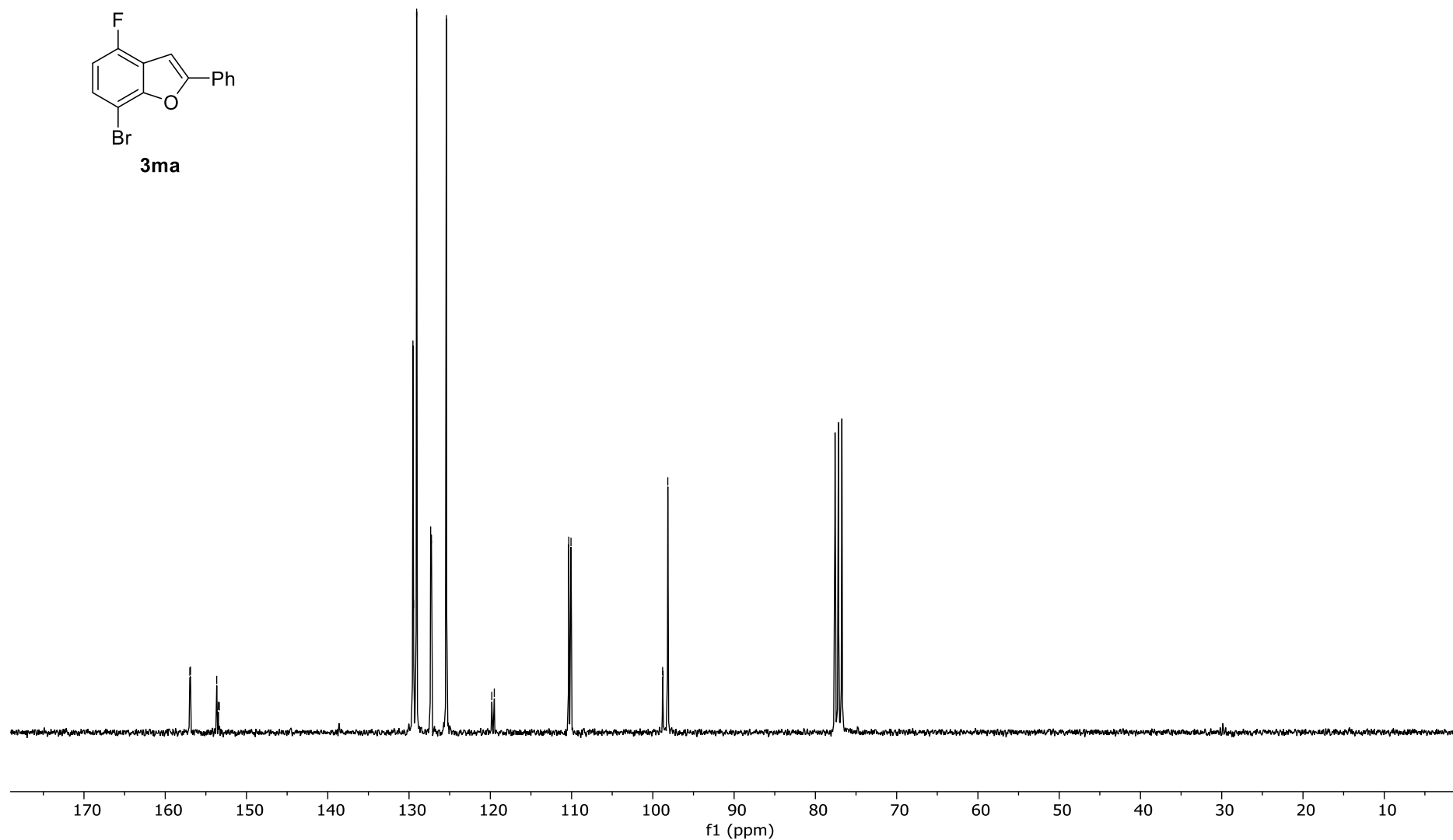
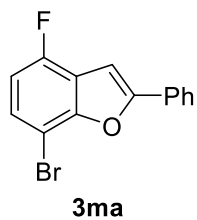


$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )

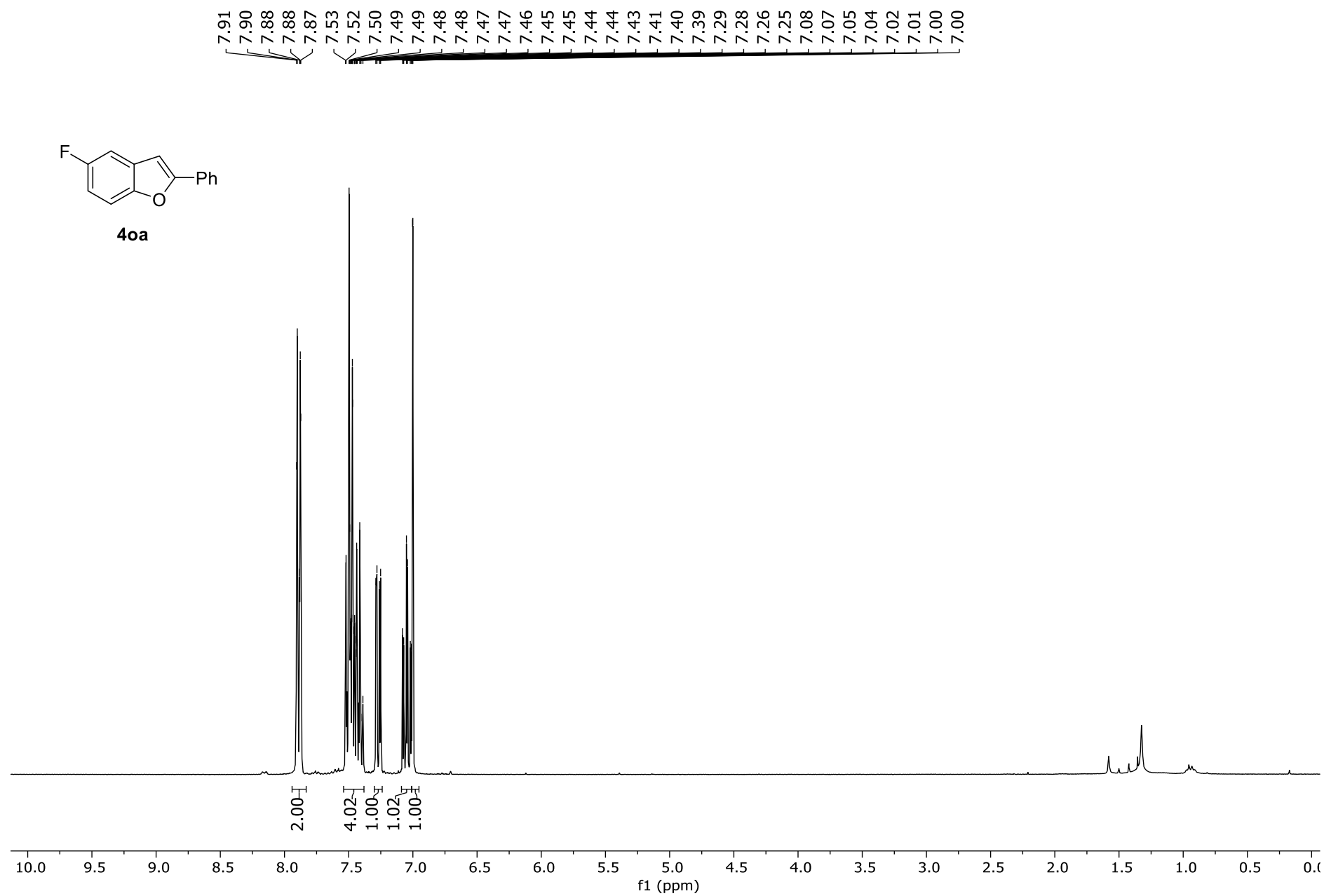
157.0  
156.9  
153.7  
153.5  
153.3

129.5  
129.4  
129.1  
127.3  
127.2  
125.4  
119.8  
119.5  
110.3  
110.1

98.8  
98.7  
98.2



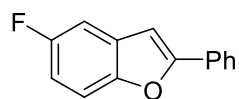
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



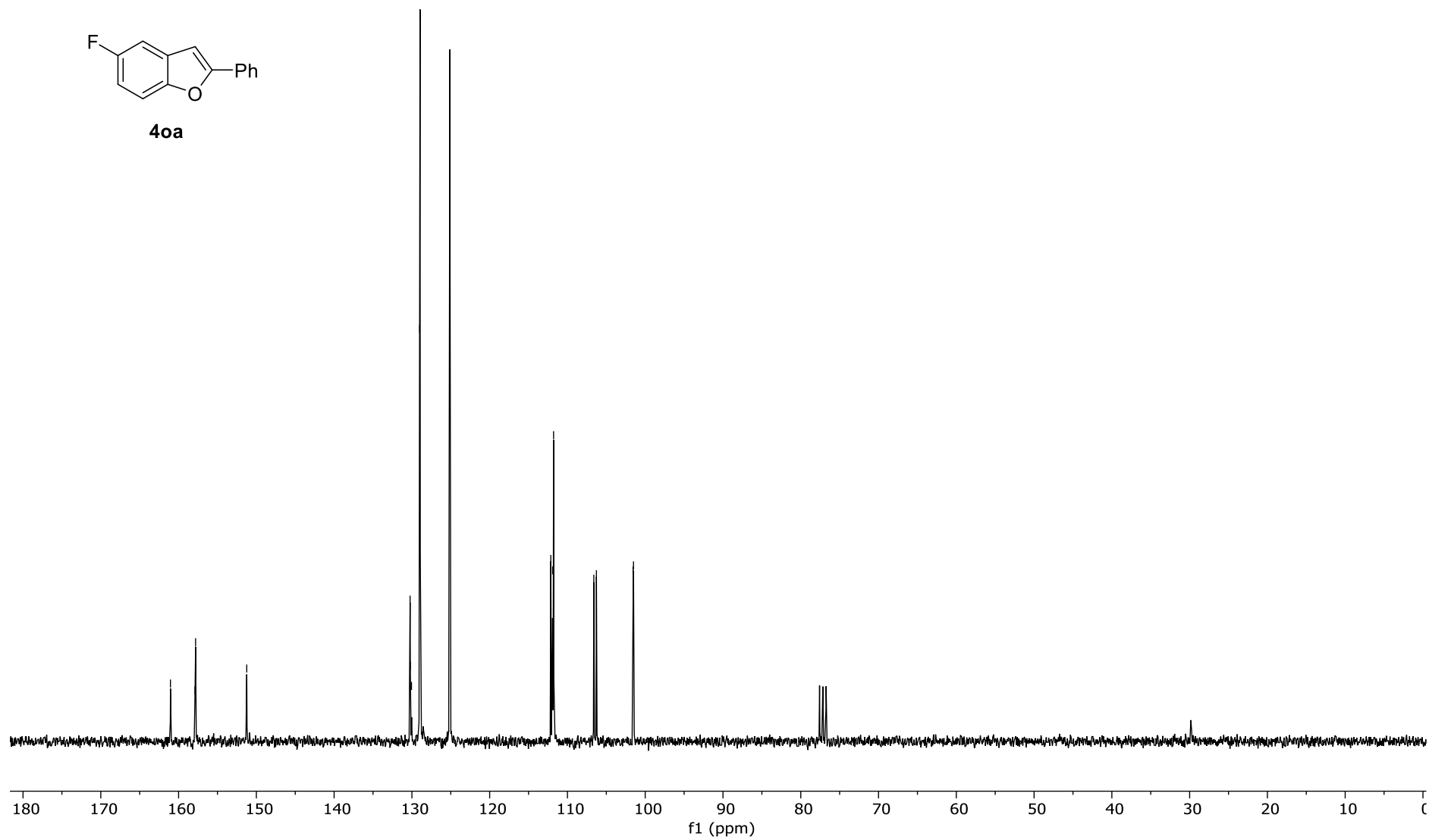
$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )

161.0  
157.9  
157.8  
— 151.2

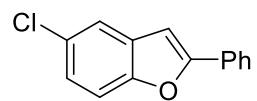
130.2  
130.2  
130.1  
129.0  
128.9  
125.1  
112.1  
111.9  
111.8  
106.6  
106.3  
101.6  
101.5



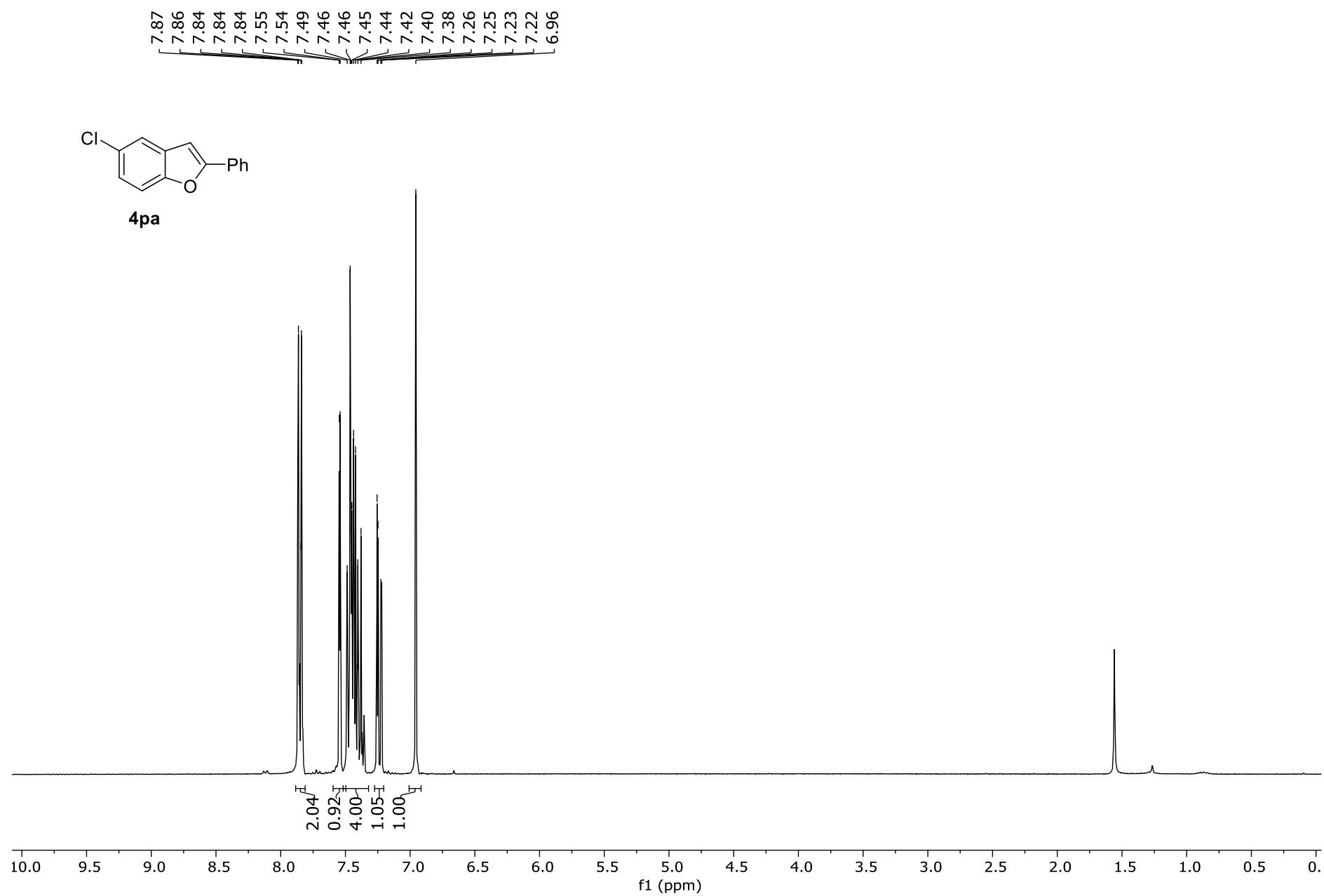
**4oa**



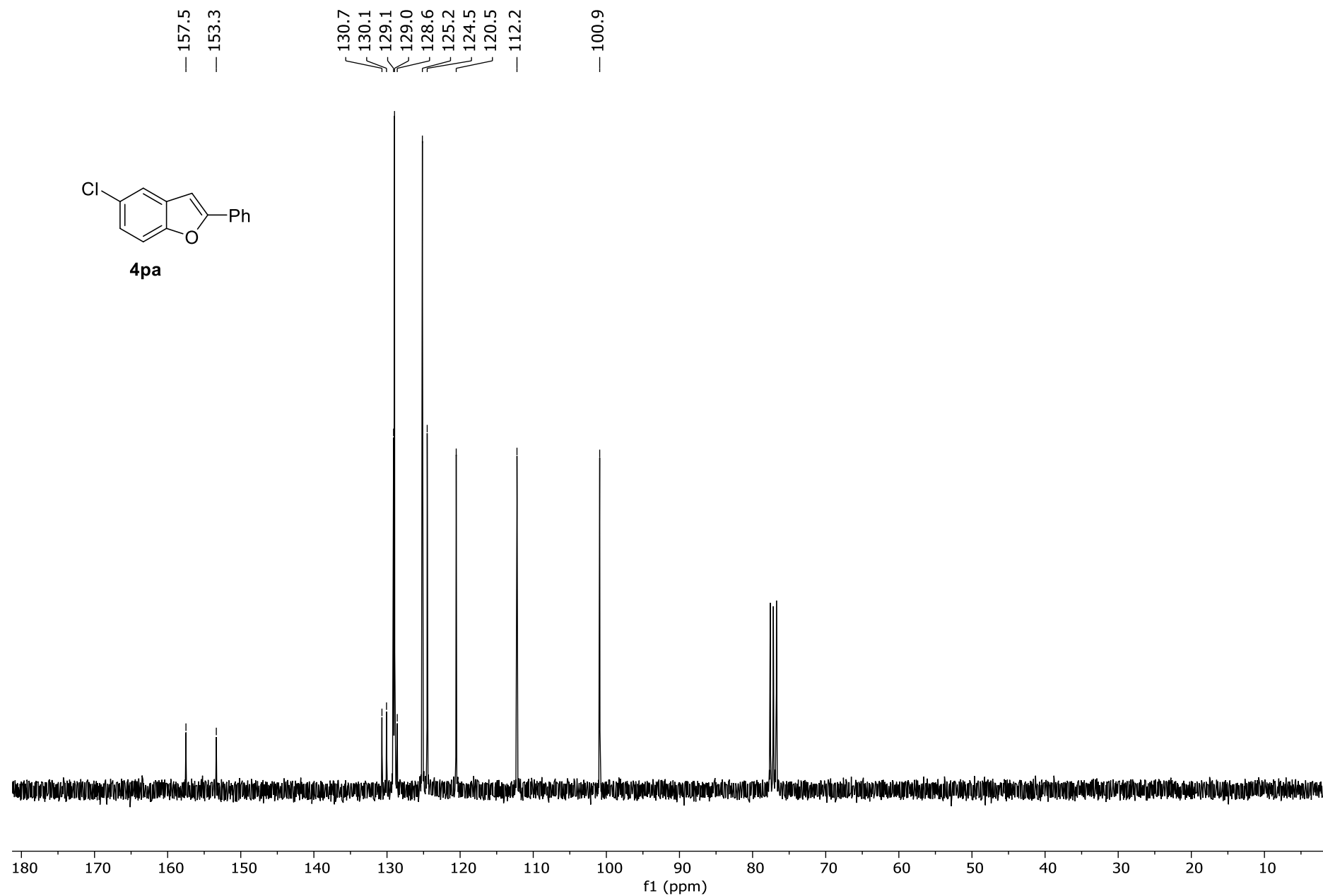
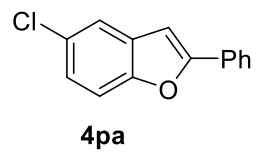
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



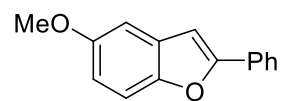
**4pa**



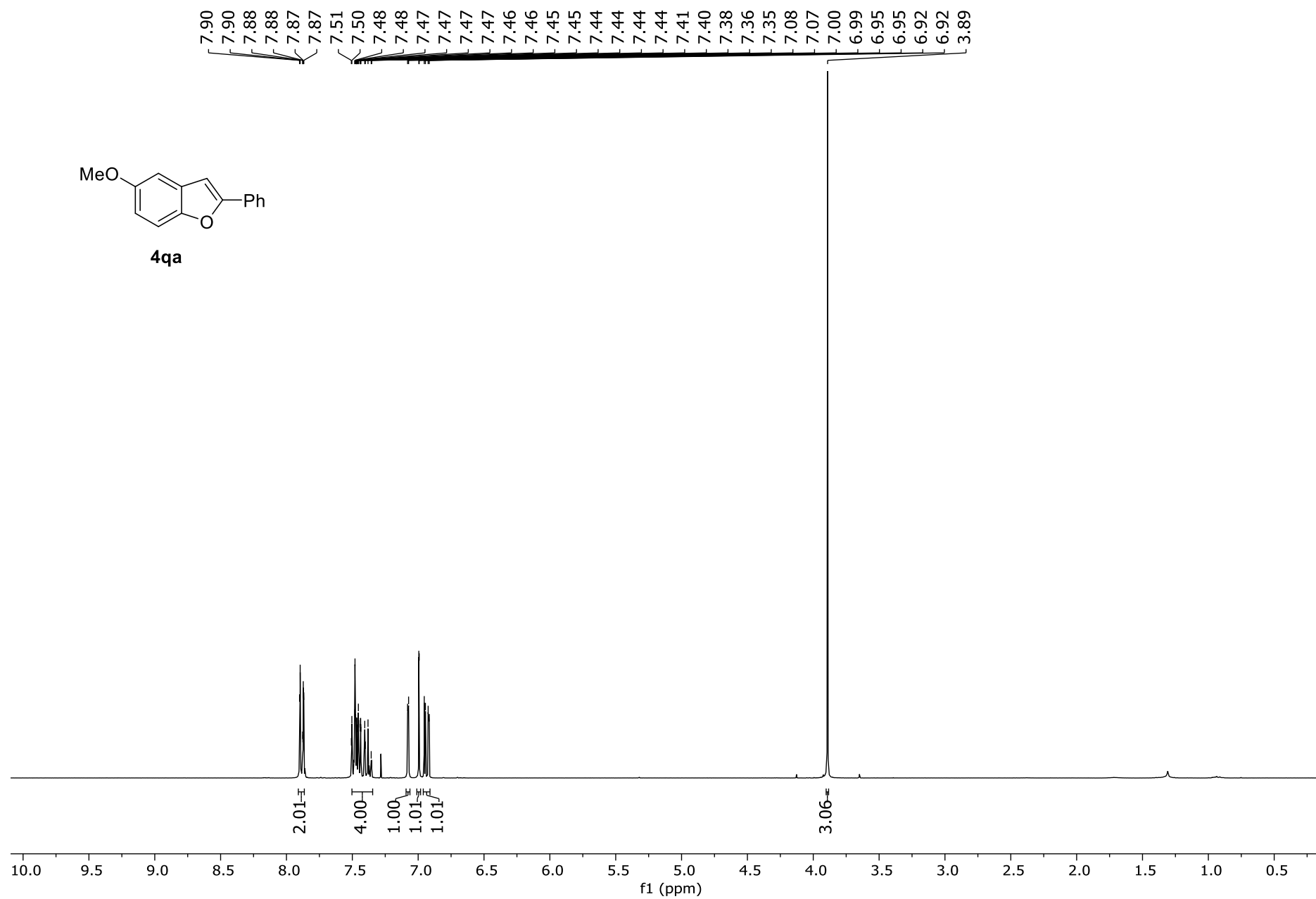
$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

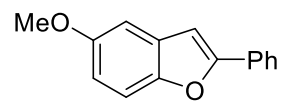


**4qa**

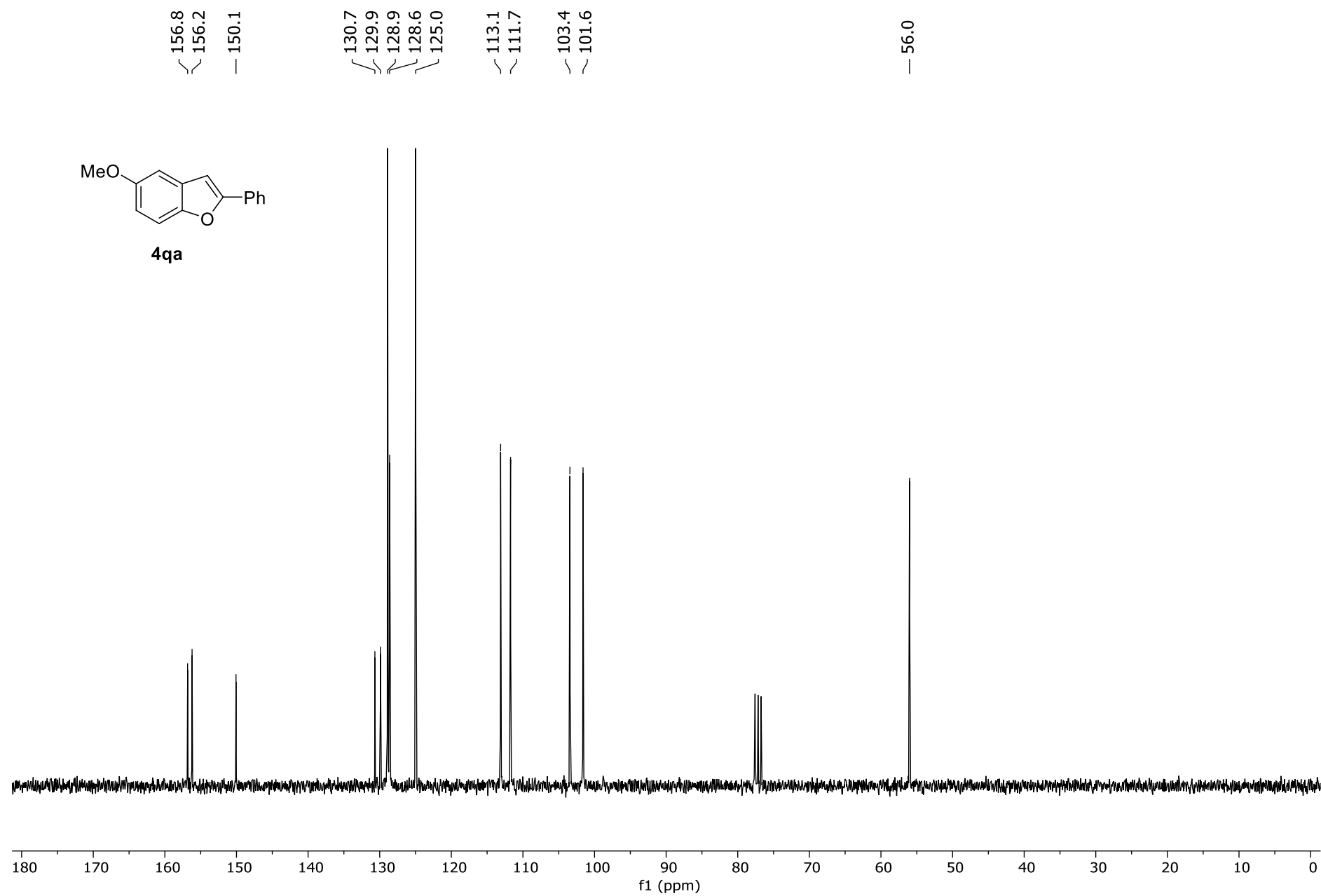




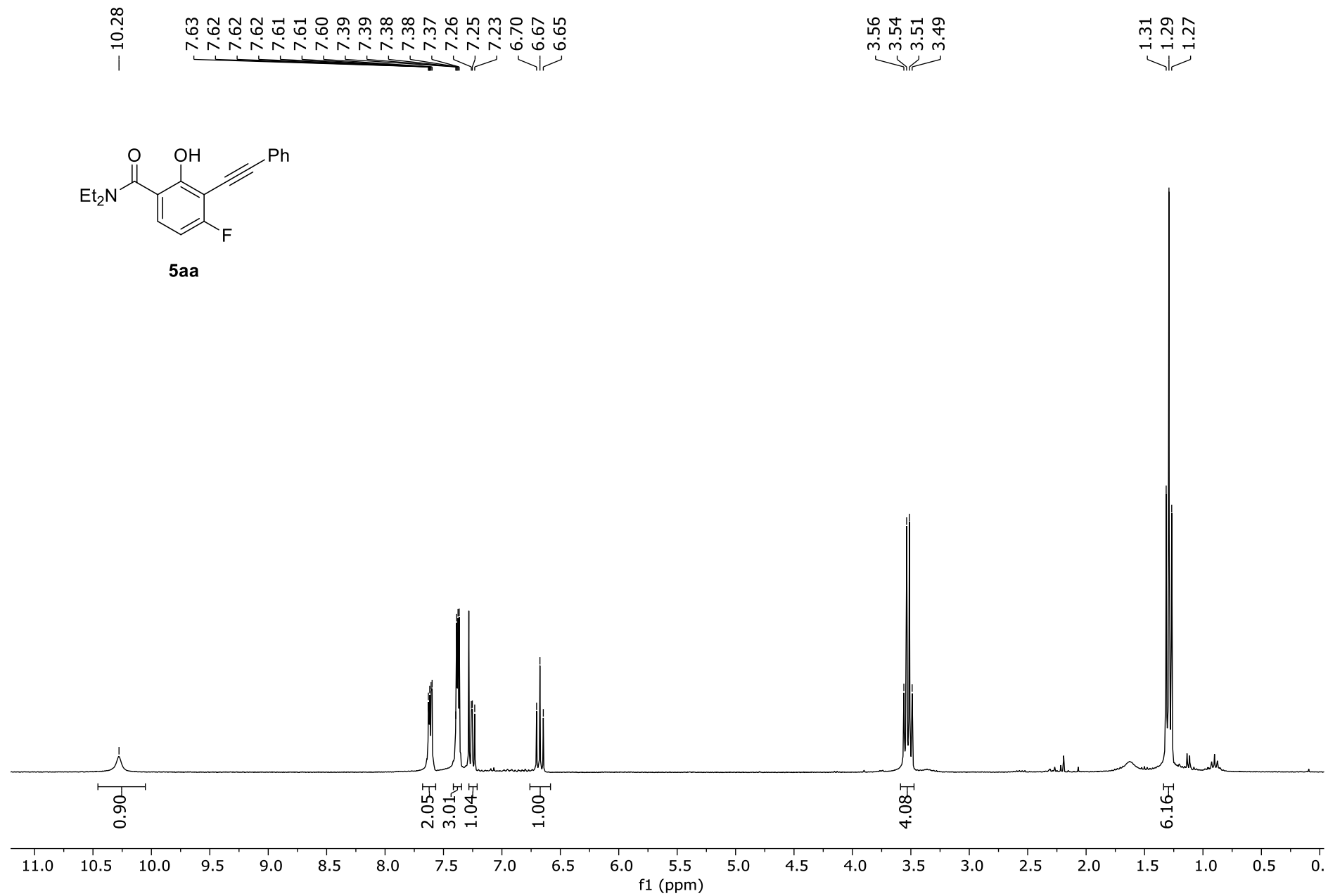
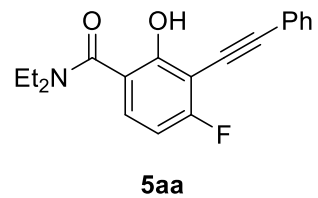
$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



**4qa**



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



<sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)

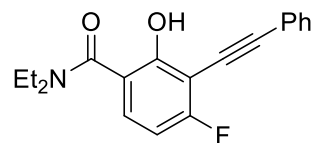
170.1  
166.0  
162.6  
160.7  
160.6

131.8  
128.7  
128.3  
128.2  
128.1  
122.8  
114.9  
114.8

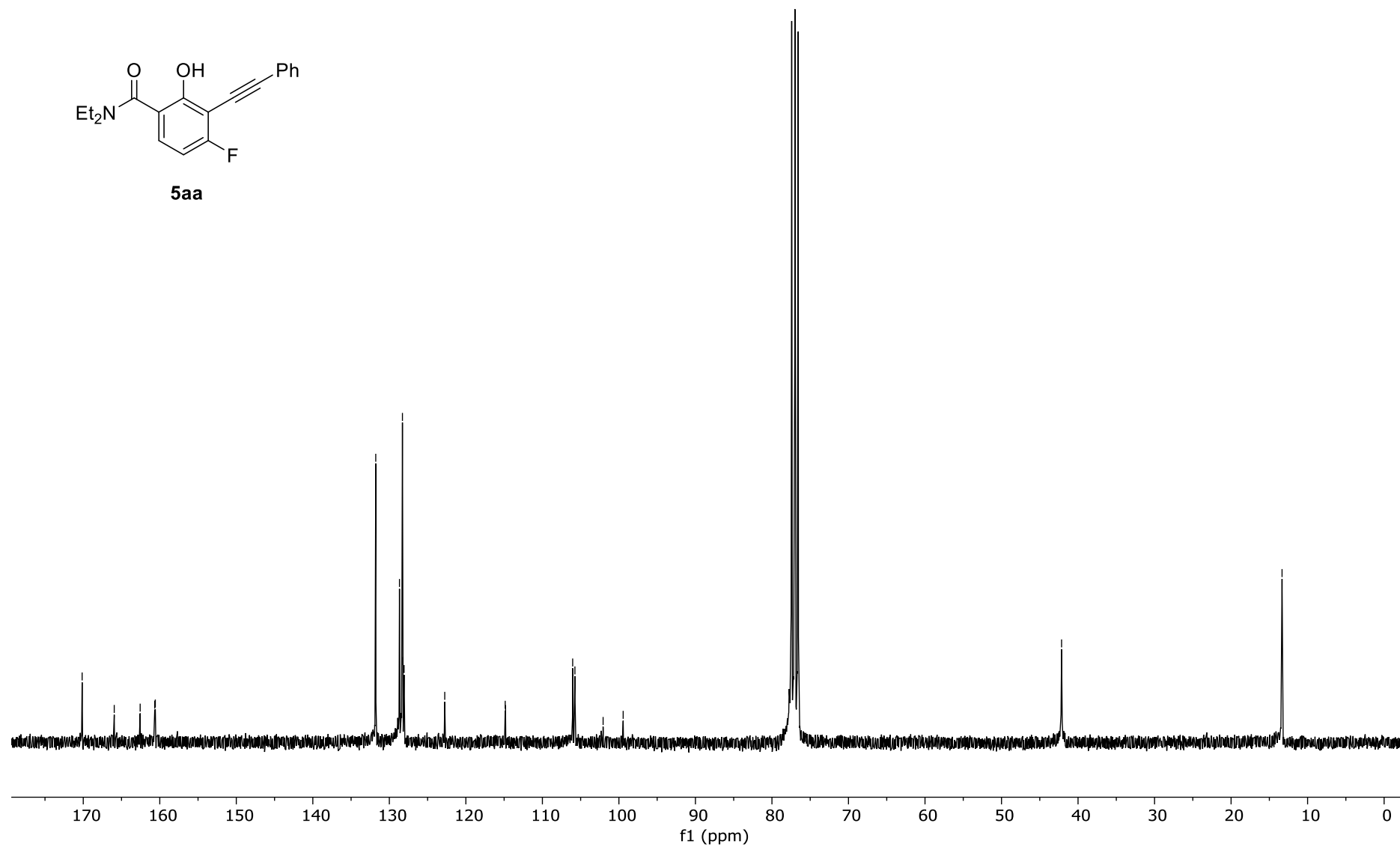
106.0  
105.7  
102.1  
99.4

— 42.2

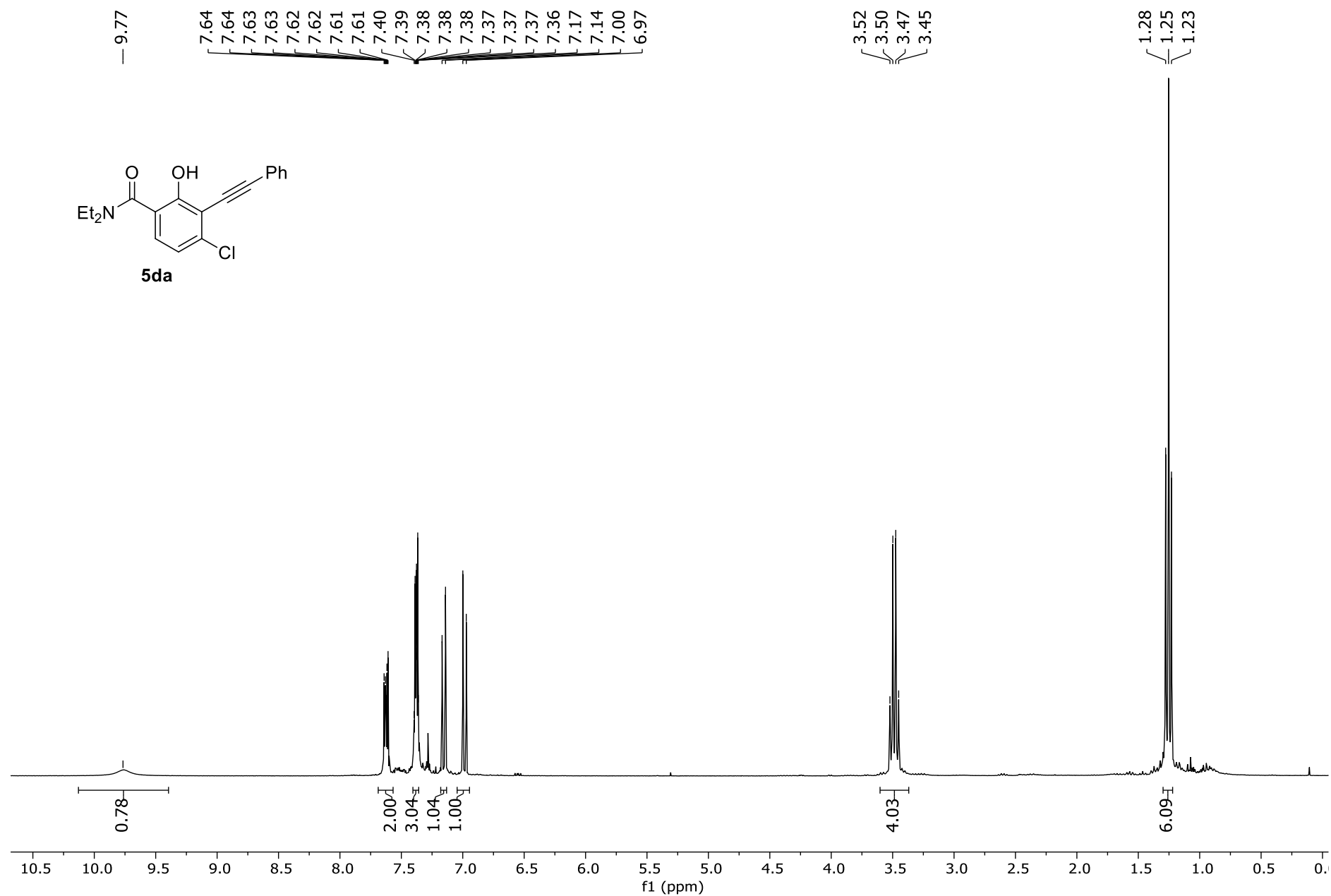
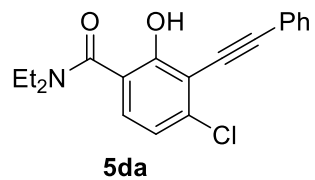
— 13.3



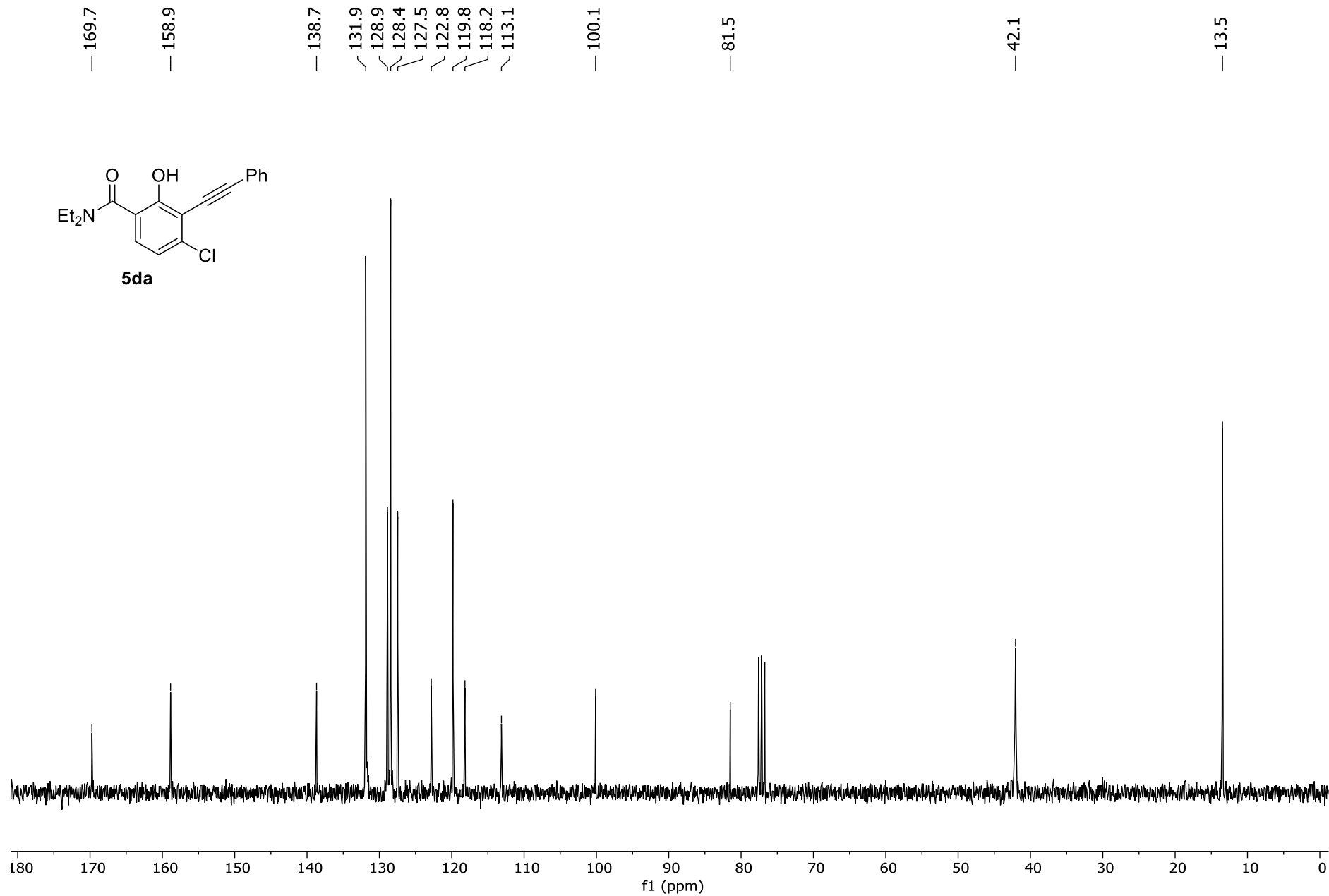
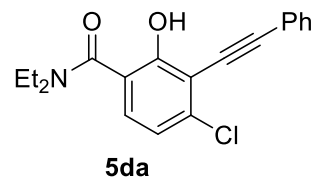
**5aa**



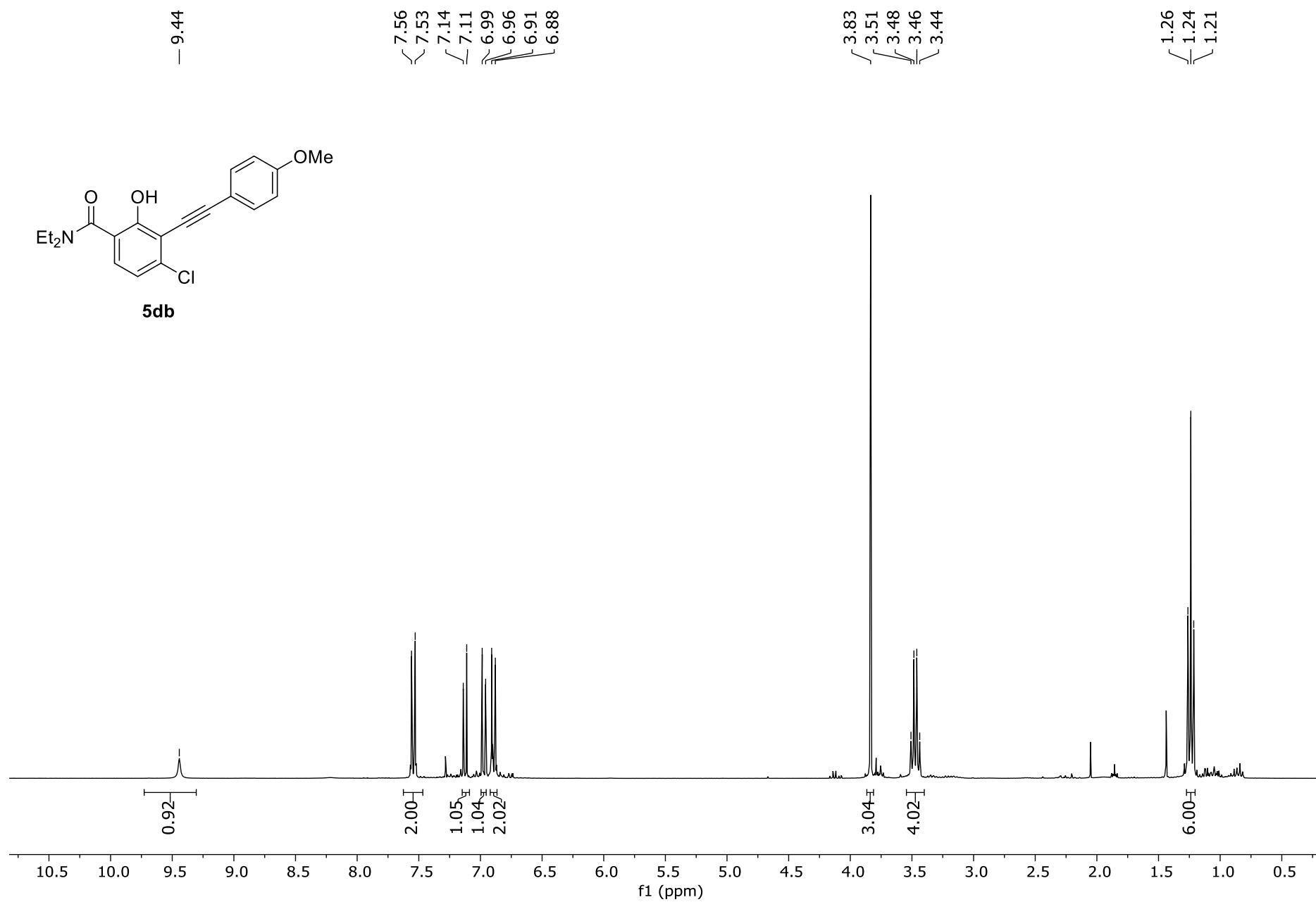
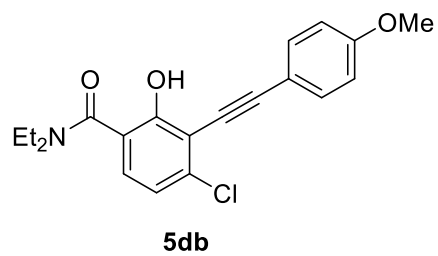
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



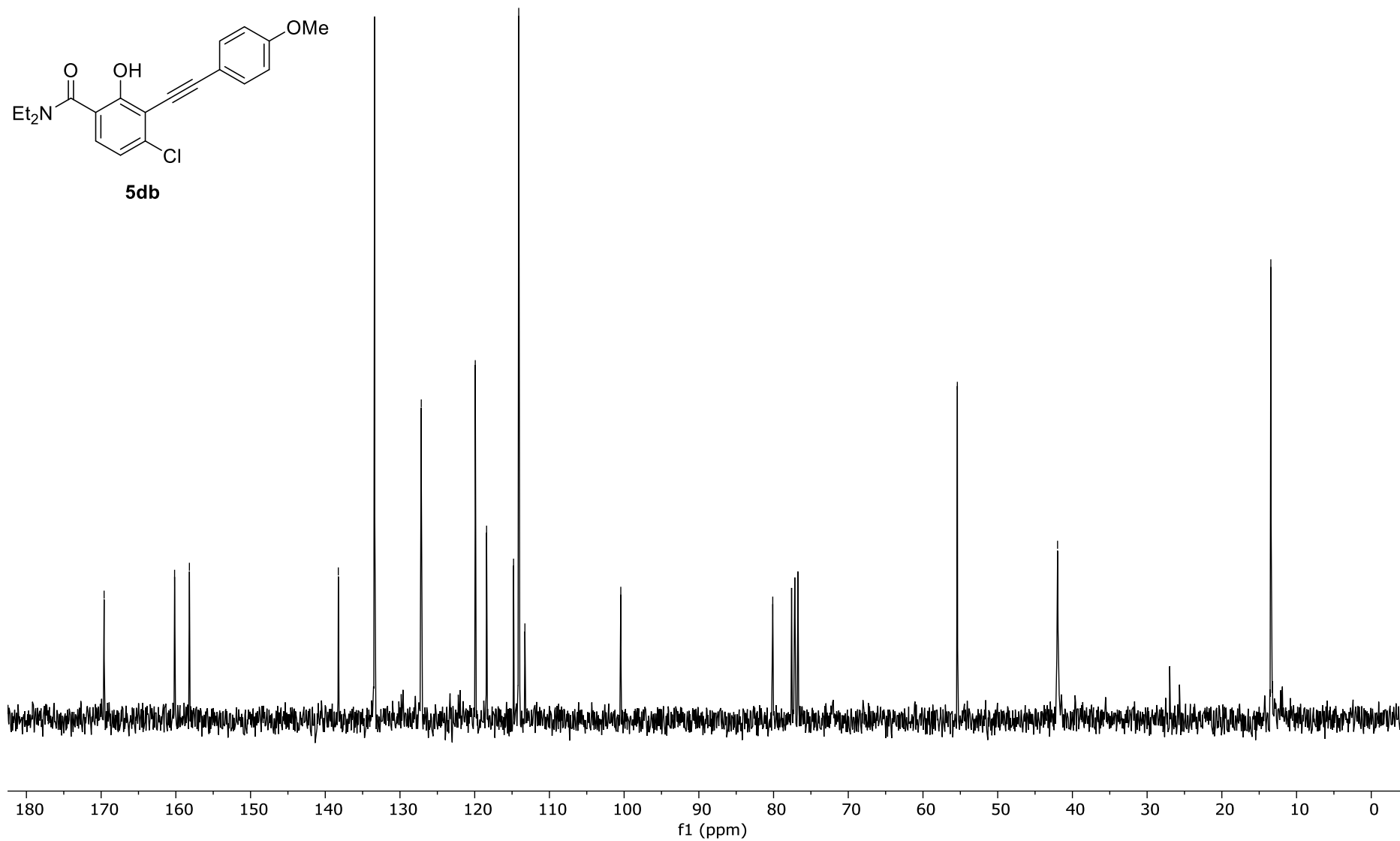
$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



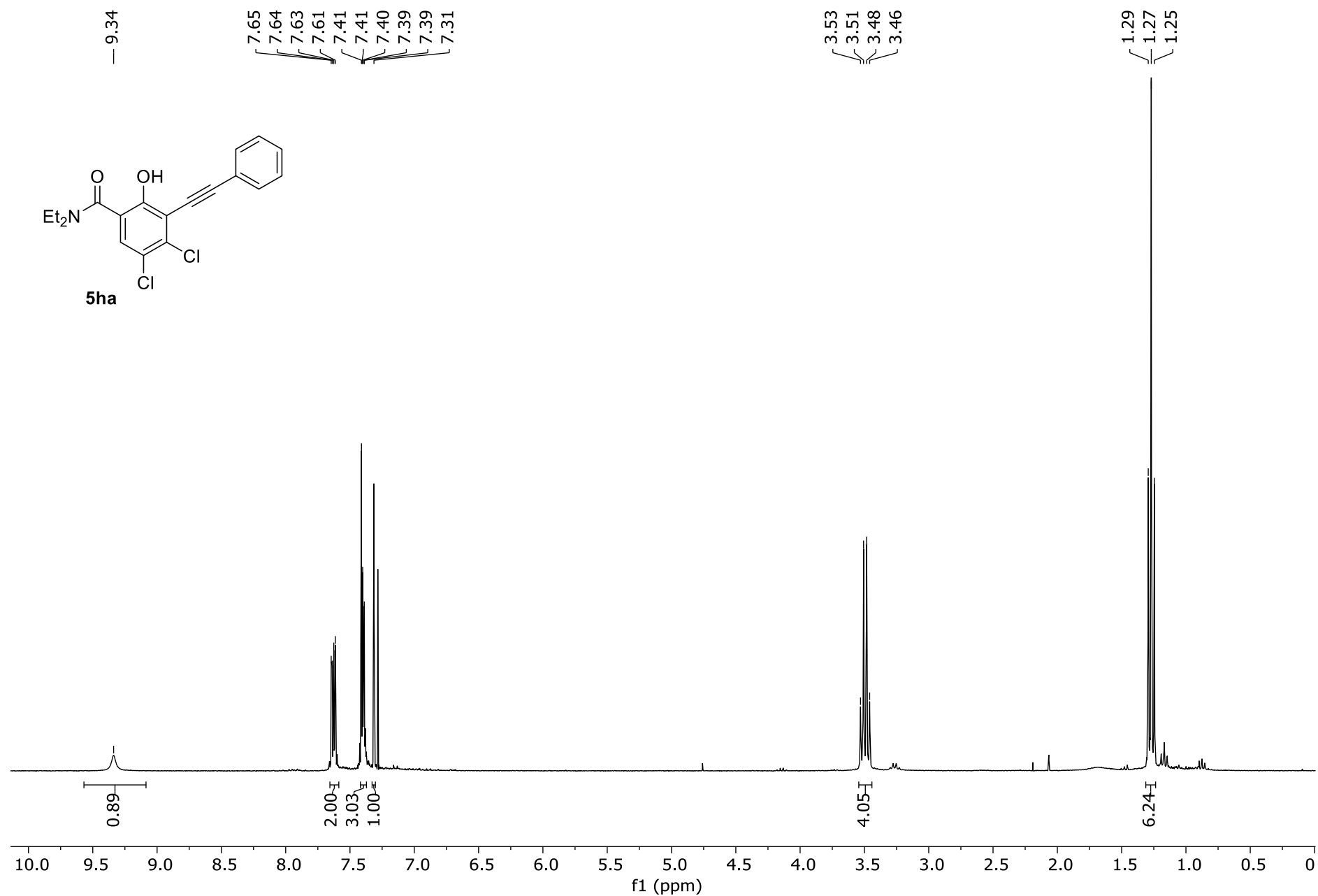
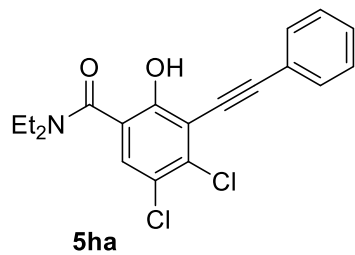
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



<sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)

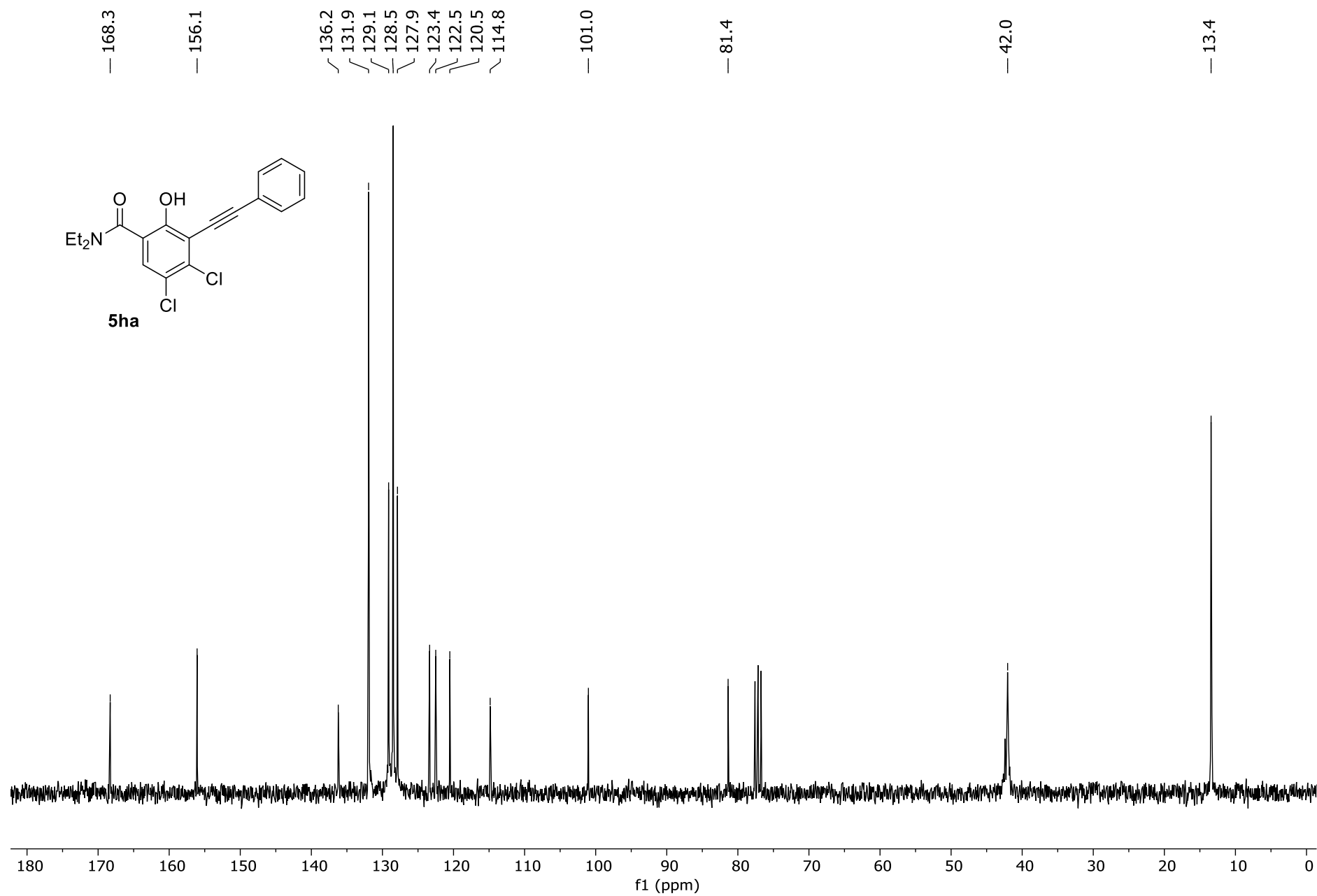
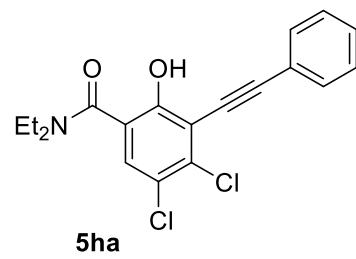


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

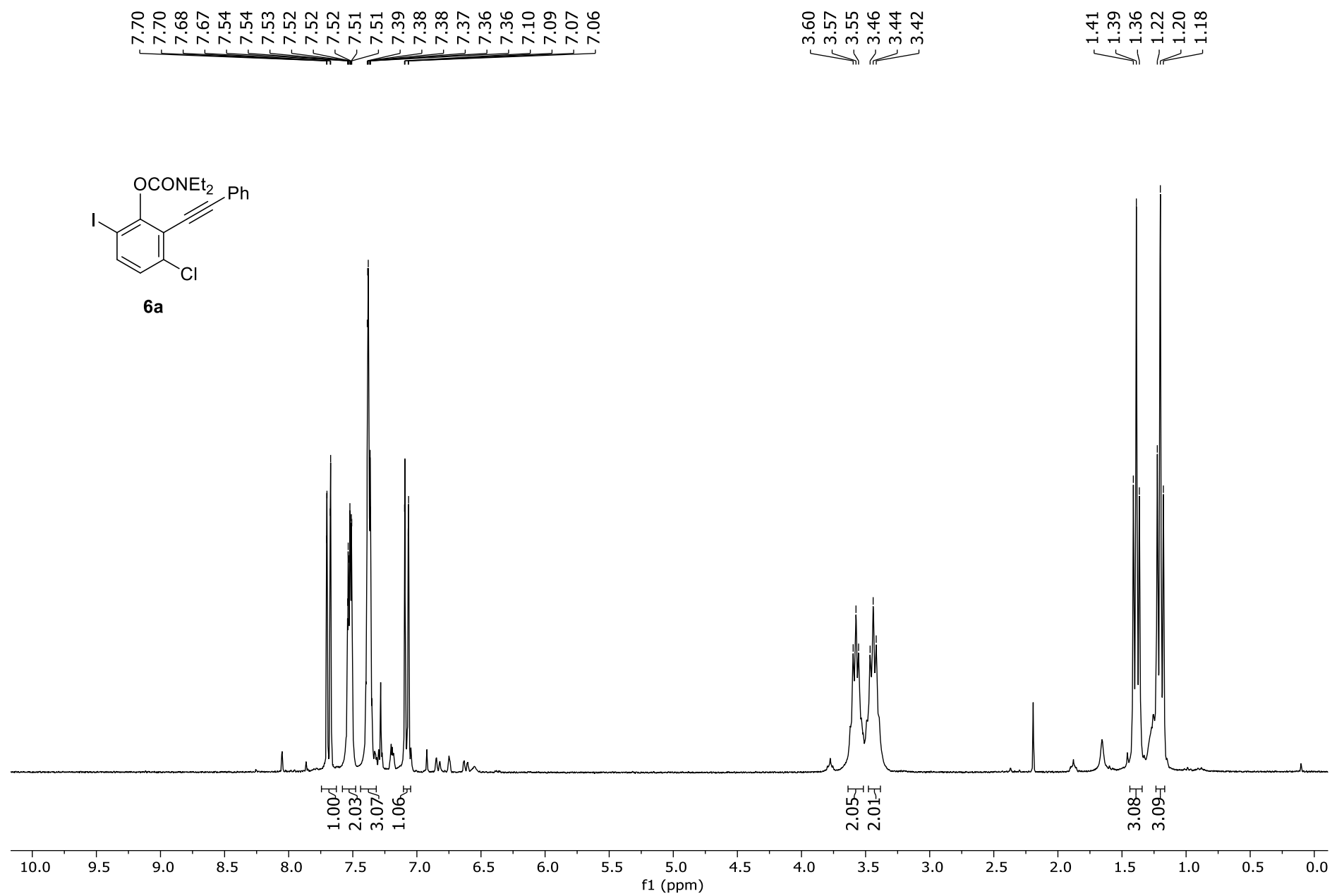
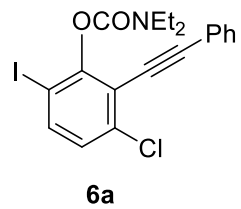




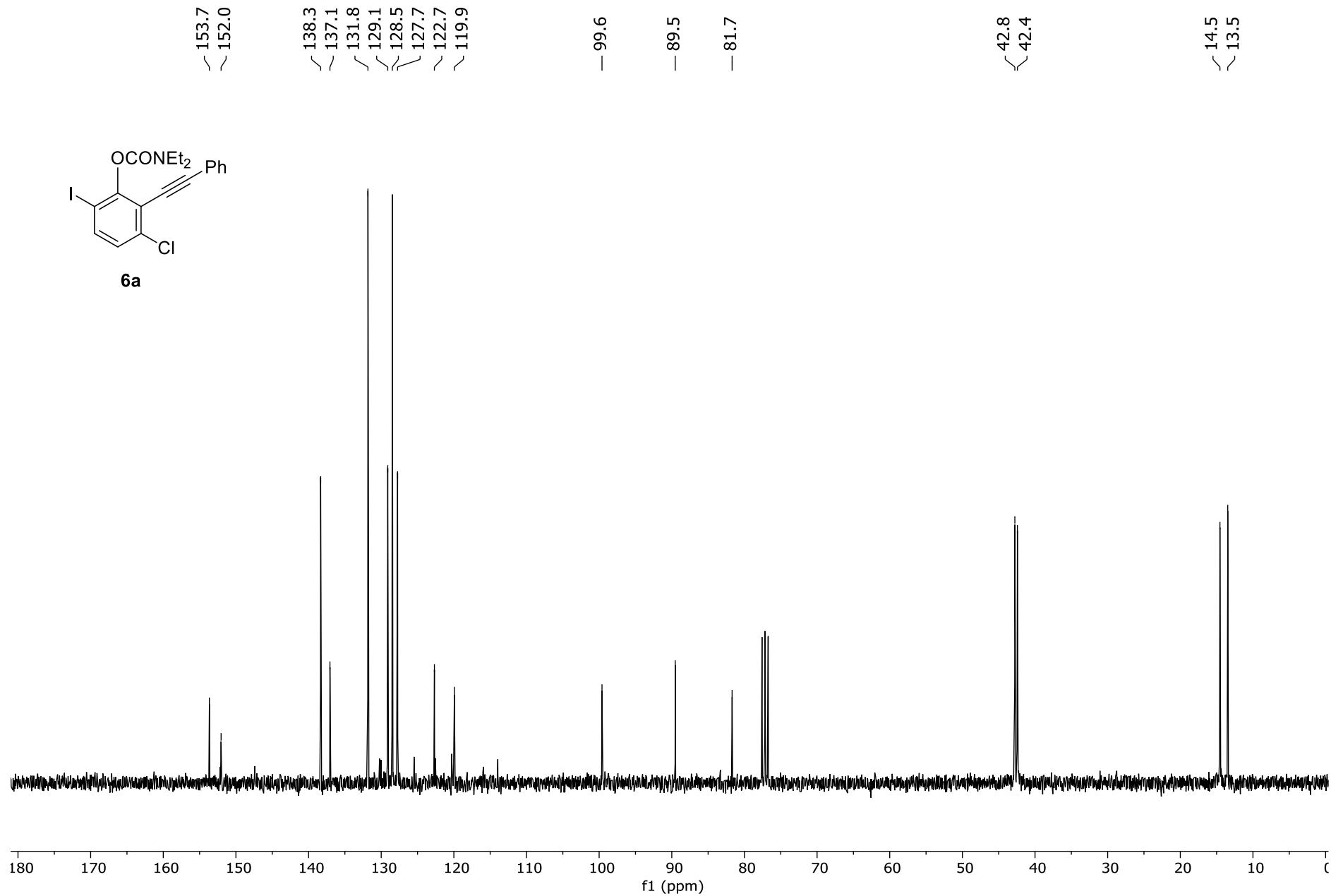
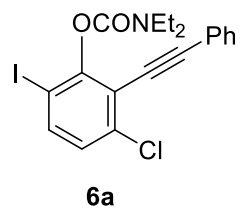
$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



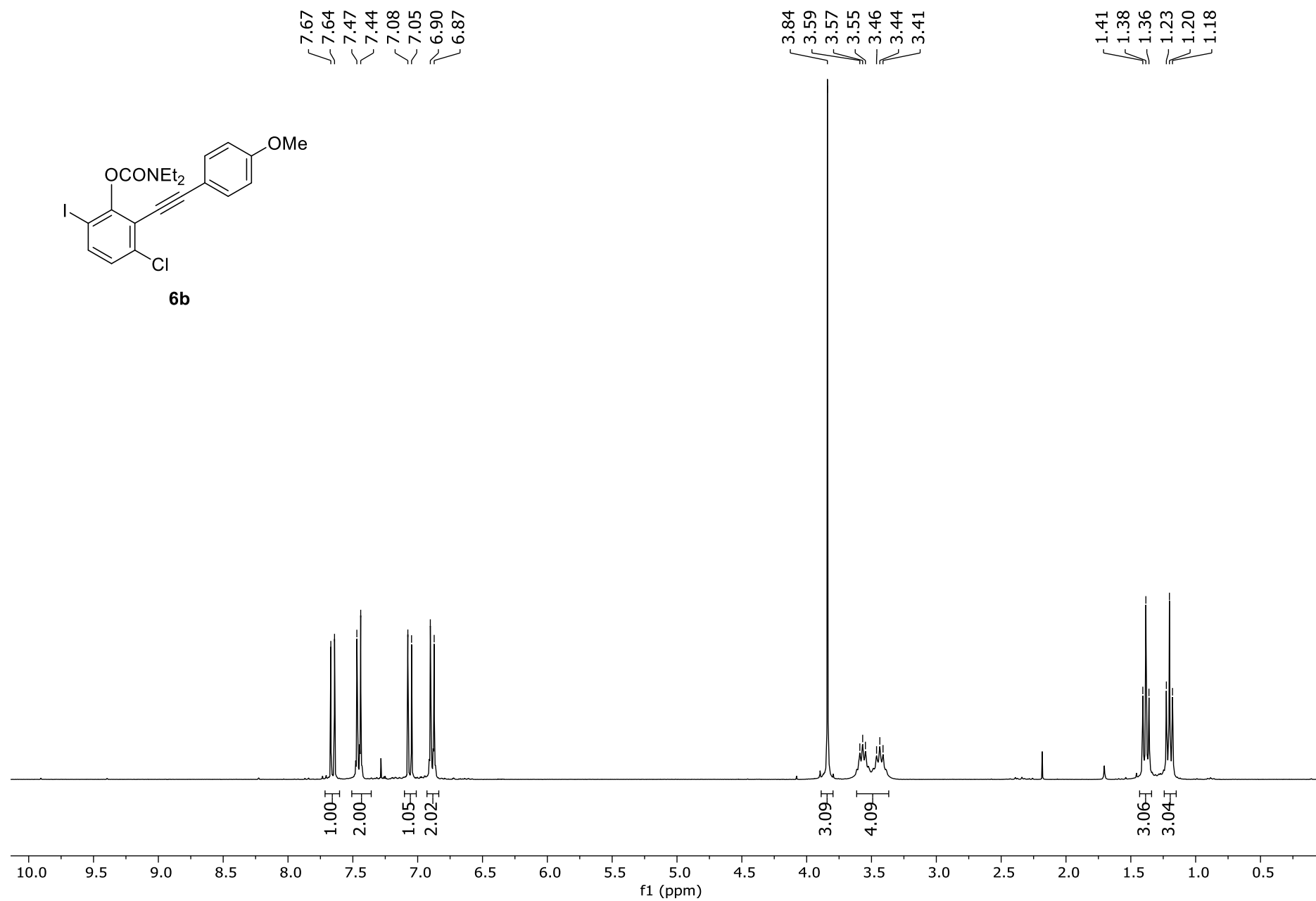
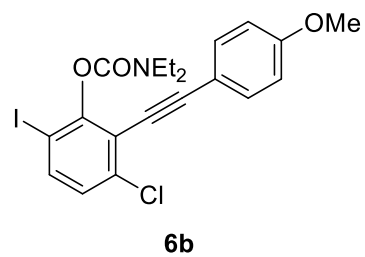
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



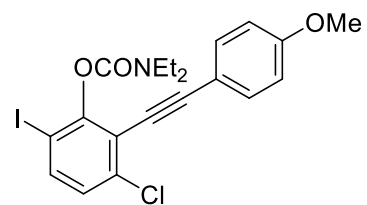
$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



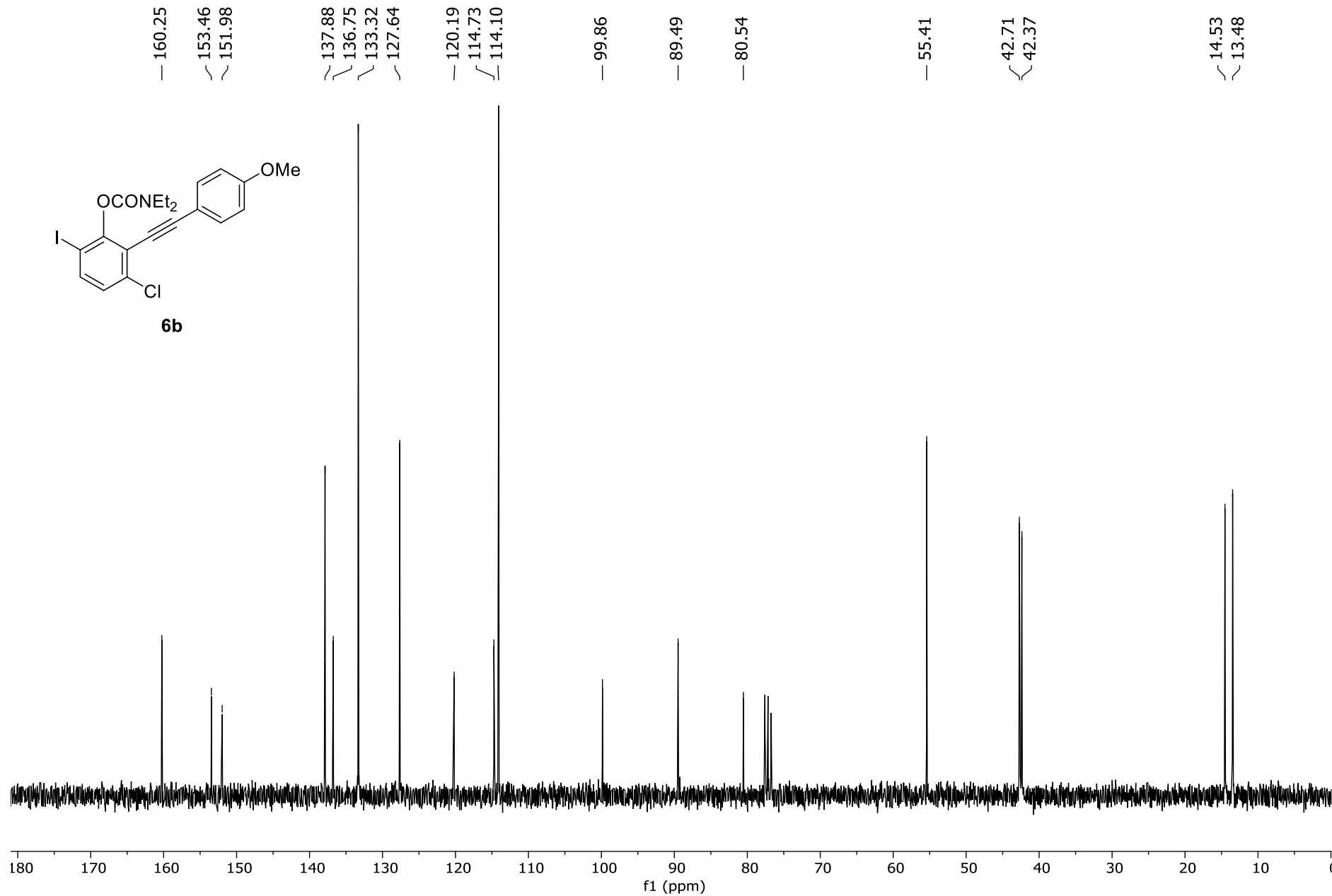
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



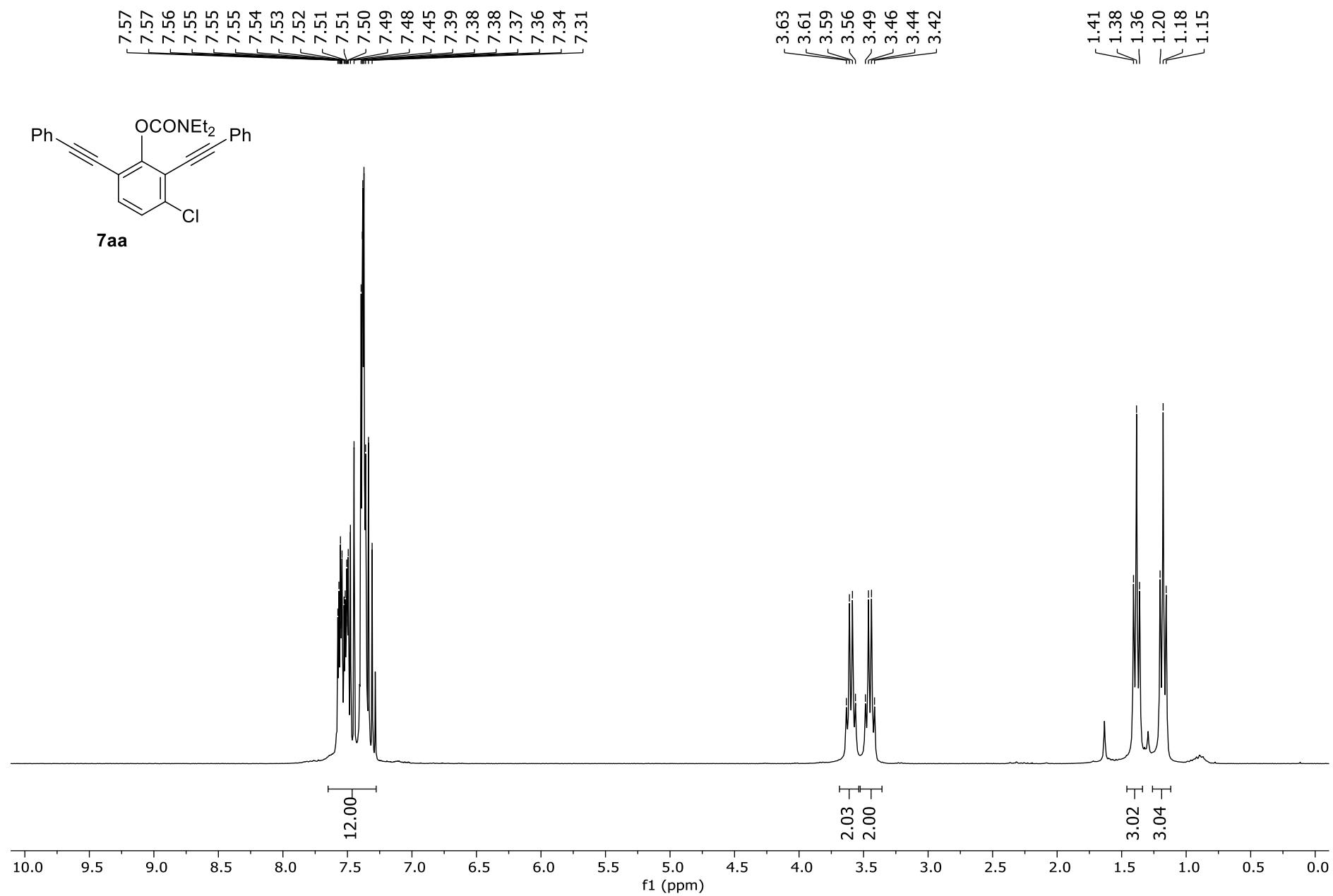
$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



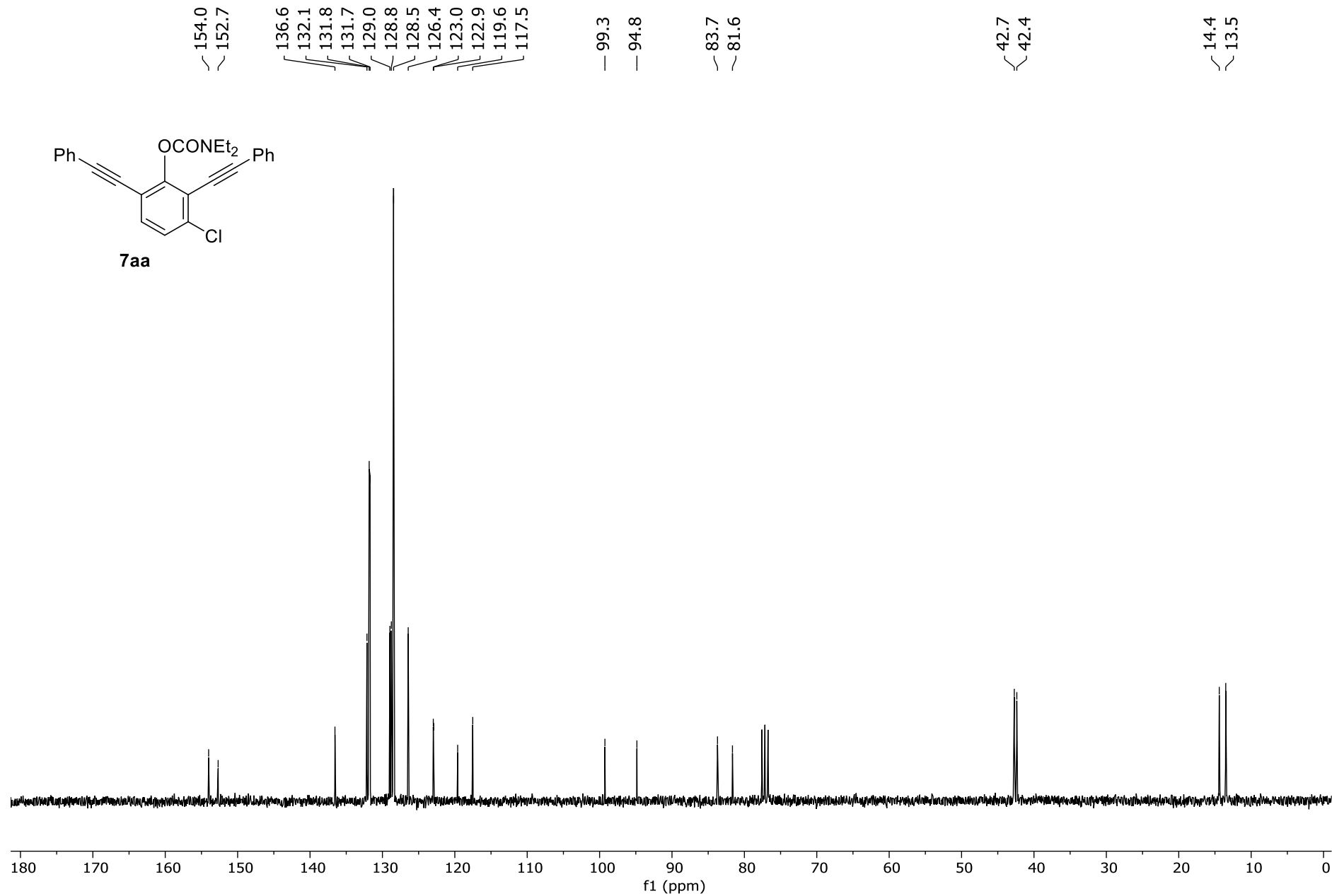
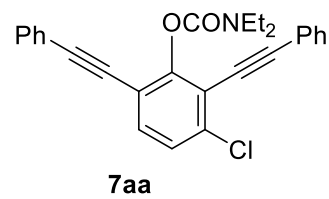
**6b**



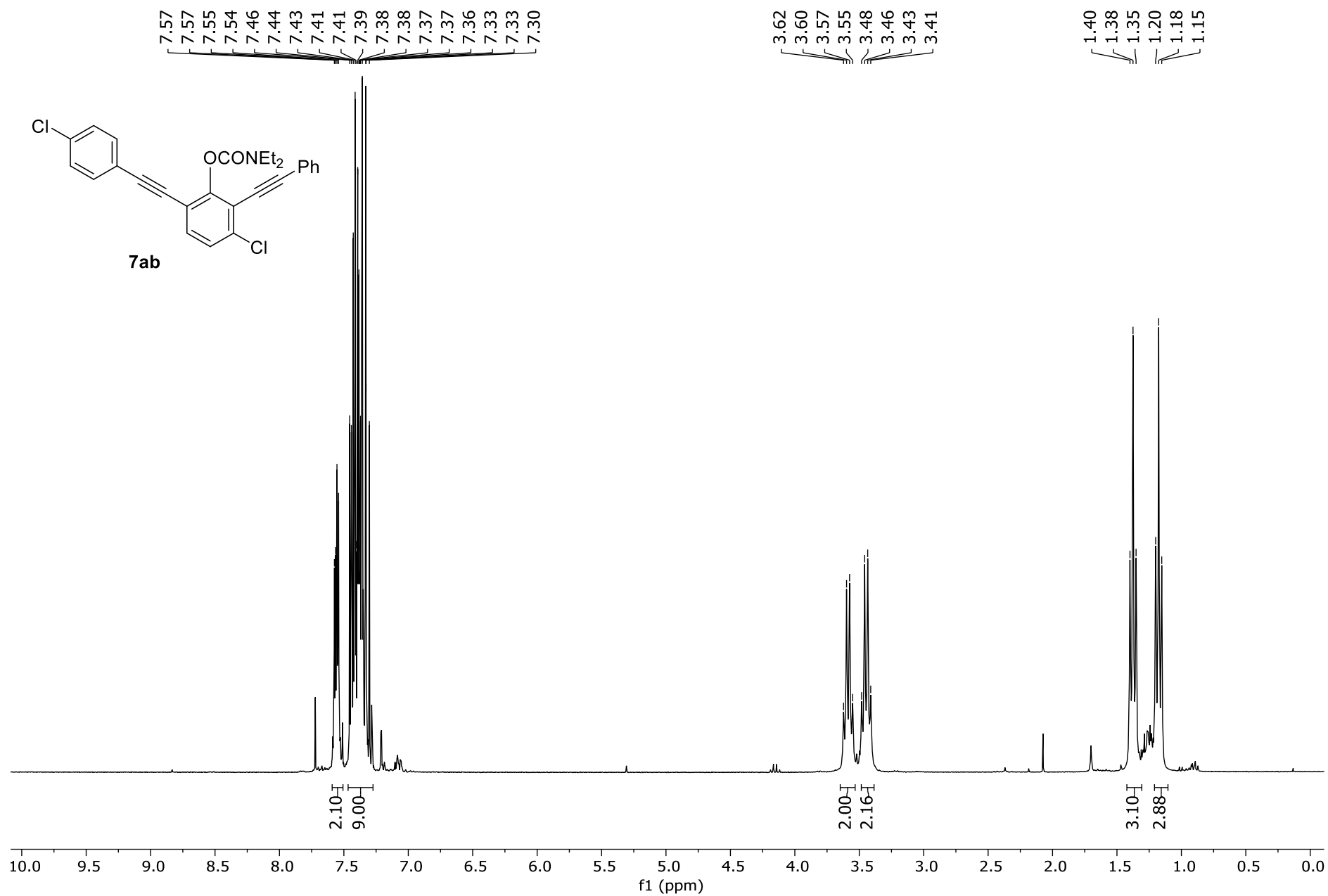
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



<sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )





<sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)

154.0  
152.6  
136.8  
134.8  
132.8  
132.0  
131.8  
129.0  
128.8  
128.4  
126.4  
122.8  
121.4  
119.6  
117.2

99.4

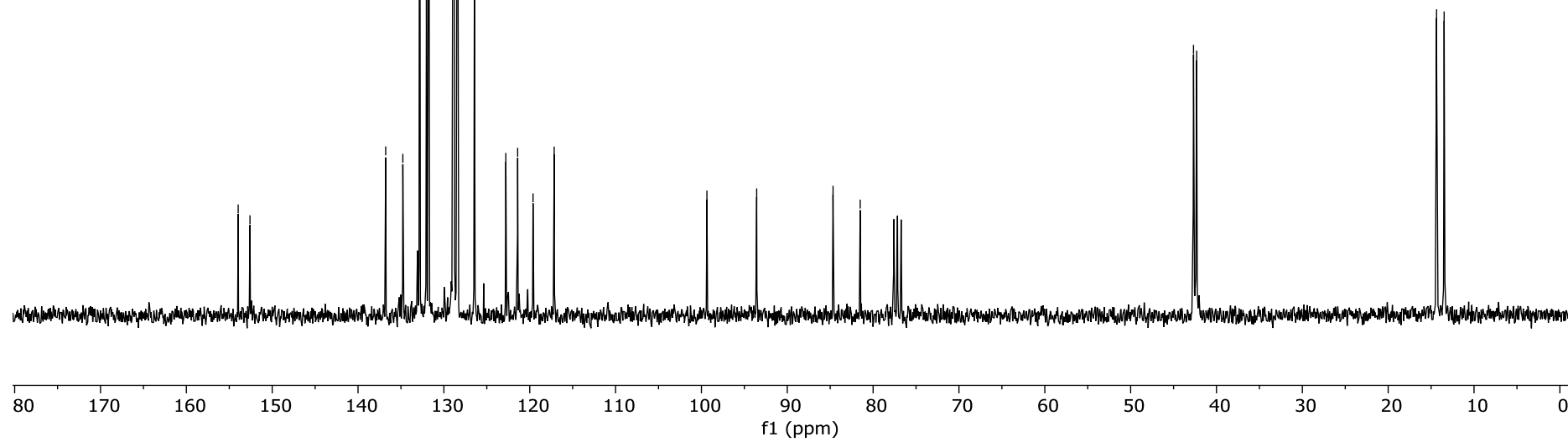
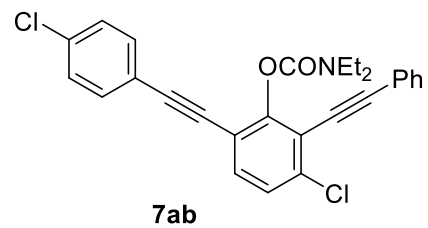
93.6

84.7

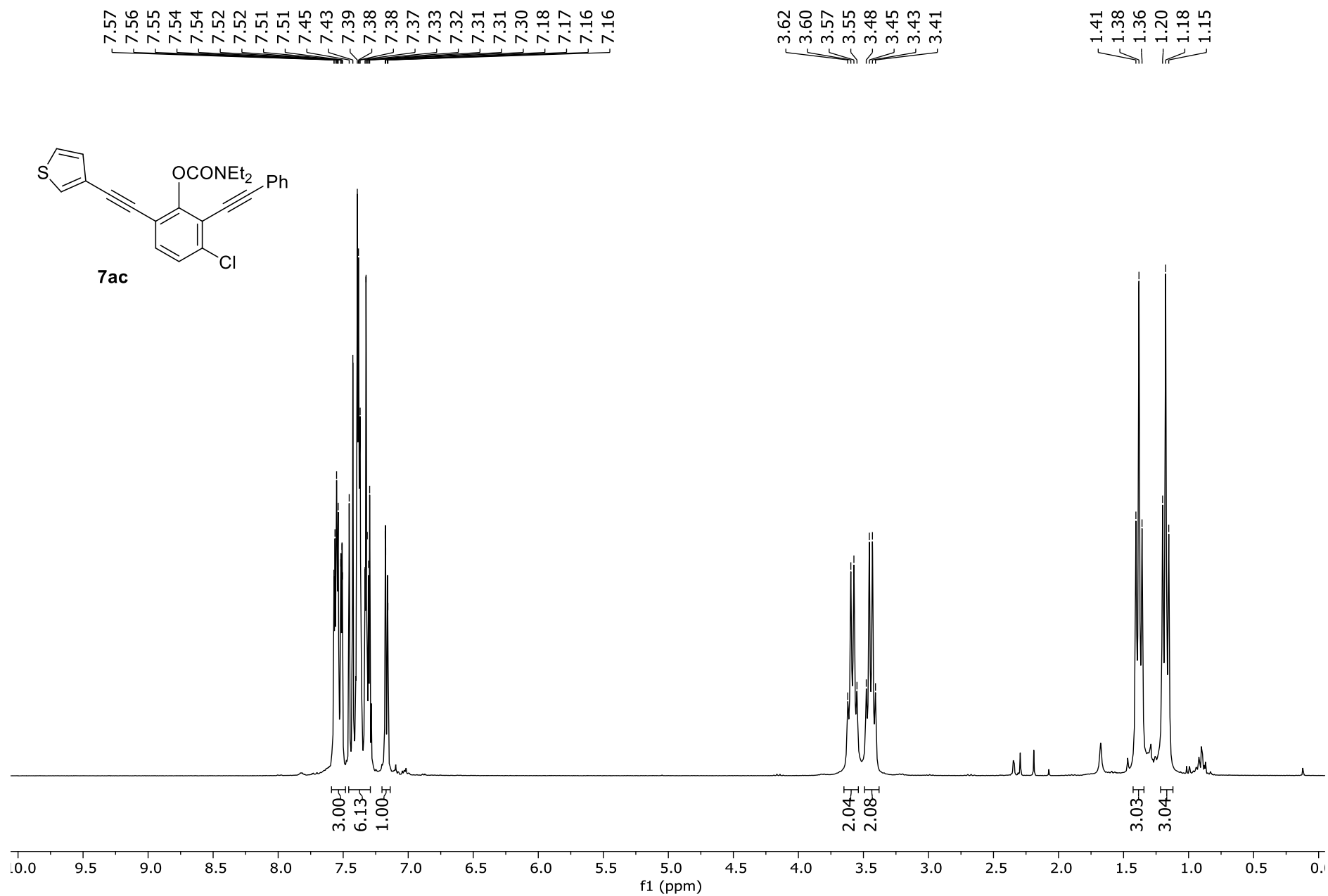
81.5

42.7  
42.3

14.4  
13.5



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )

~153.9  
~152.6  
136.5  
132.0  
131.8  
129.8  
129.2  
129.0  
128.4  
126.4  
125.6  
122.9  
122.0  
119.6  
117.4

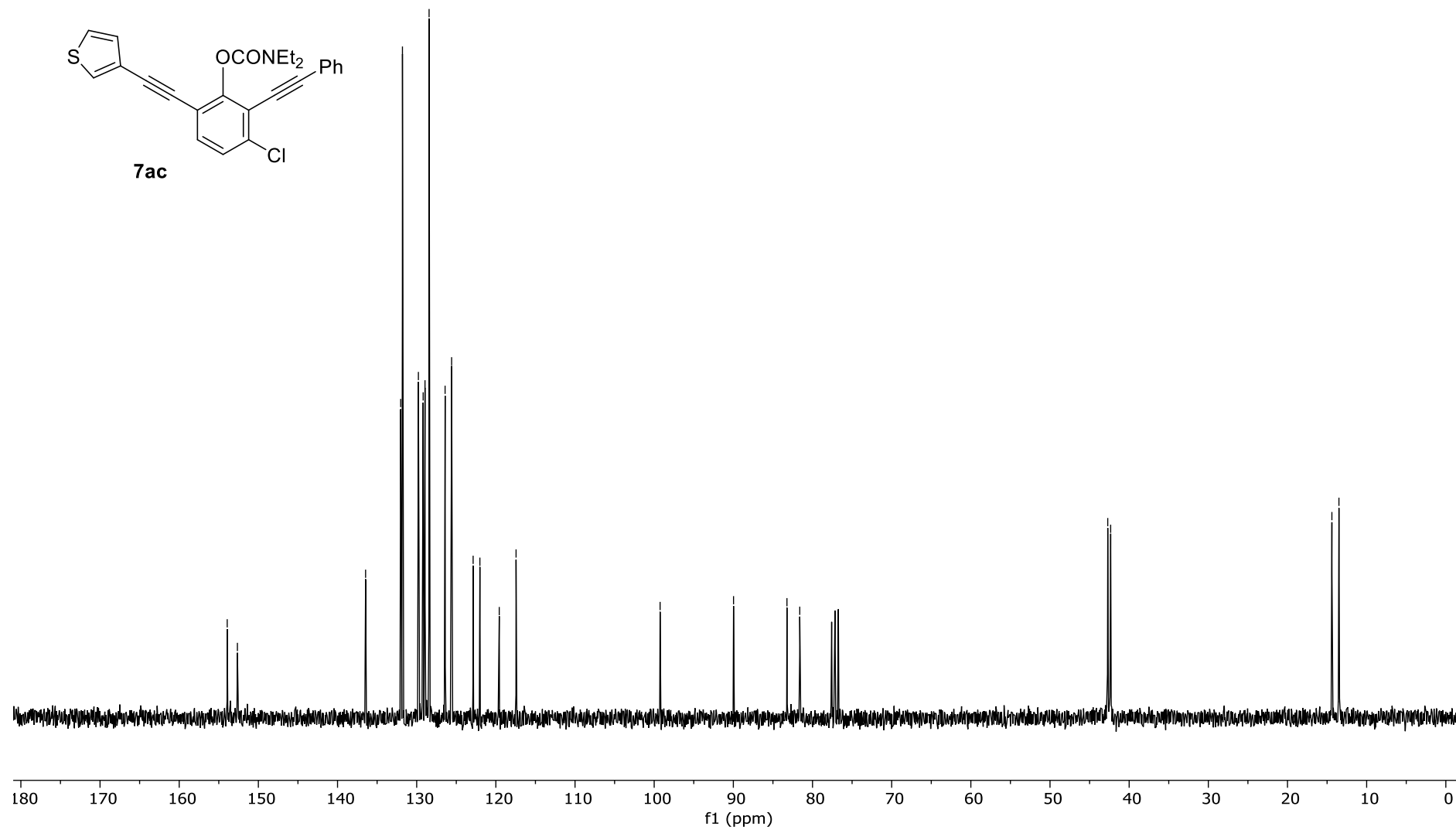
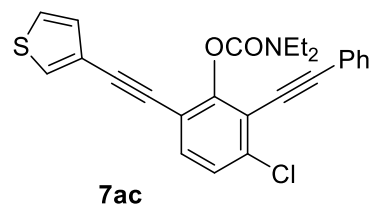
— 99.3

— 90.0

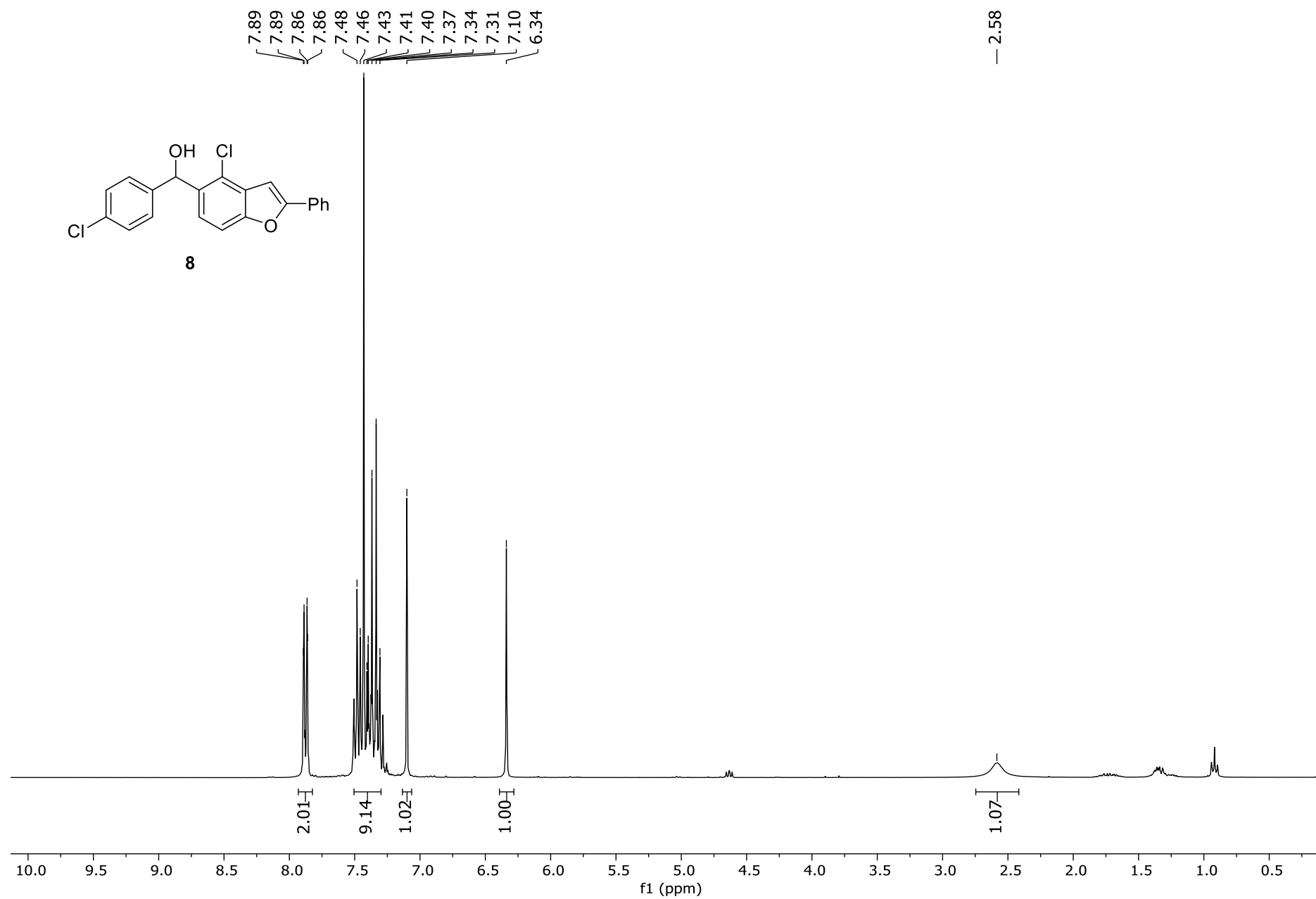
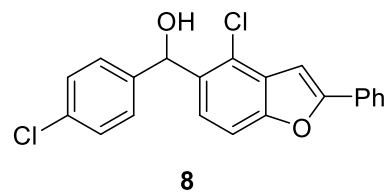
~83.2  
~81.6

~42.7  
~42.3

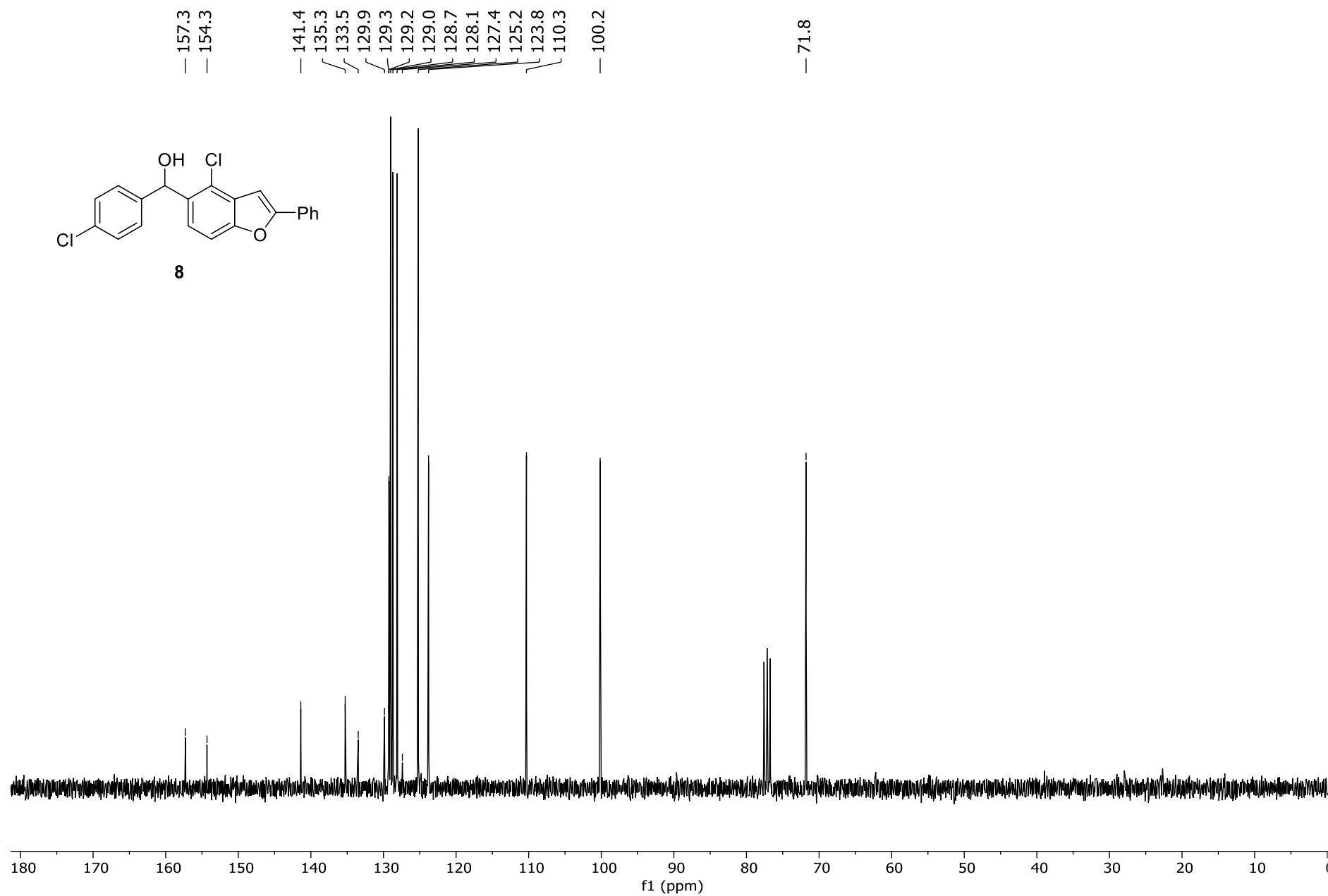
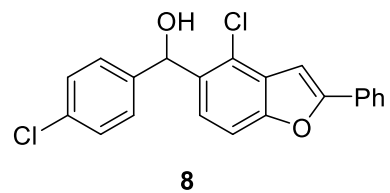
~14.4  
~13.5



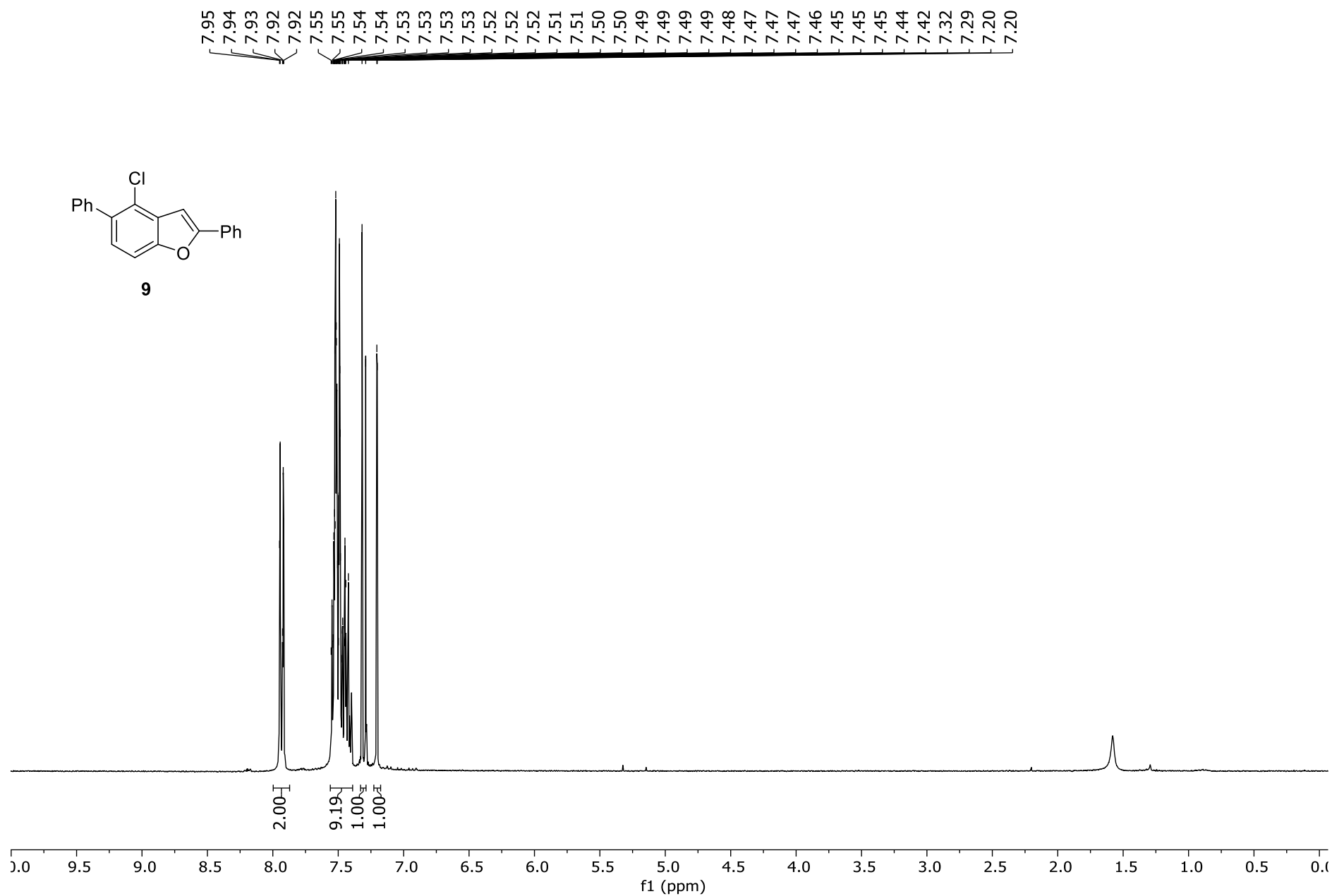
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)

