

## Supplementary information

### **Acid-base-sensitive allylic oxidation of 2-allylbenzoic acids to form phthalides**

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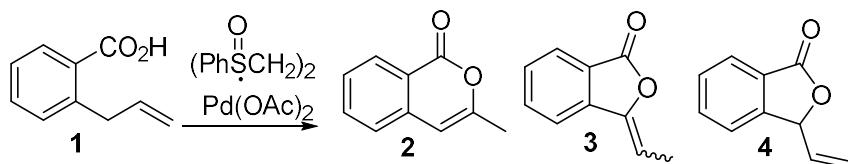
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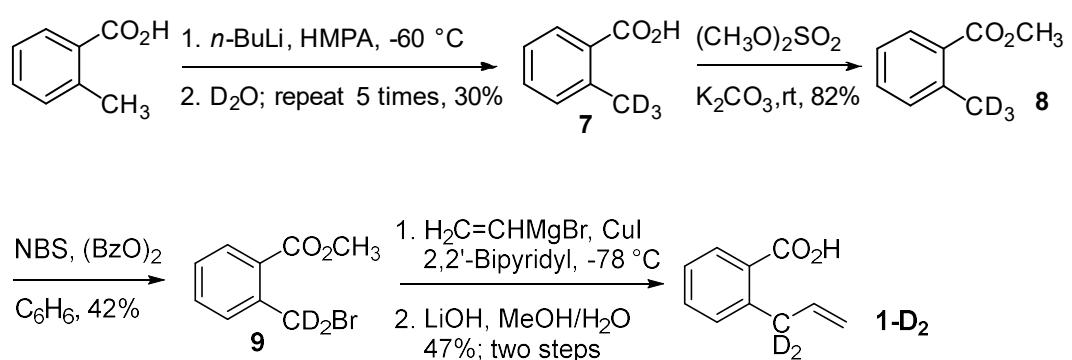
**SI Table 1.** Screened Reaction Conditions for the Oxidation of 2-Allylbenzoic acids (**1**)



entry	reaction condition <sup>a</sup>	yield (%) <sup>b</sup>			recovered <b>1</b>
		<b>2</b>	<b>3 (E:Z)<sup>c</sup></b>	<b>4</b>	
1	BQ, 1,4-dioxane, 45 °C, 24 h	75		1	
2	BQ, THF, 70 °C, 24 h	21		42	
3	BQ, ethyl acetate, 30 °C, 24 h	3		40	45
4	BQ, AcOH, 45 °C, 24 h	26		9	53
5	BQ, CH <sub>2</sub> Cl <sub>2</sub> , 40 °C, 24h	7		75	
6	BQ, CH <sub>2</sub> Cl <sub>2</sub> /AcOH (1:1), 45 °C, 24 h	70		27	
7	BQ, DMSO/AcOH (1:1), 45 °C, 24 h	25		14	49
8	BQ, DMSO/1,4-dioxane (1:1), 45 °C, 24 h	1		8	83

<sup>a</sup>2-Allylbenzoic acid (1.0 mmol), Pd catalyst (5 mol%), solvent (1.0 mL), benzoquinone (BQ, 2.0 mmol) or O<sub>2</sub> (1 atm).

<sup>b</sup>Isolated yields.

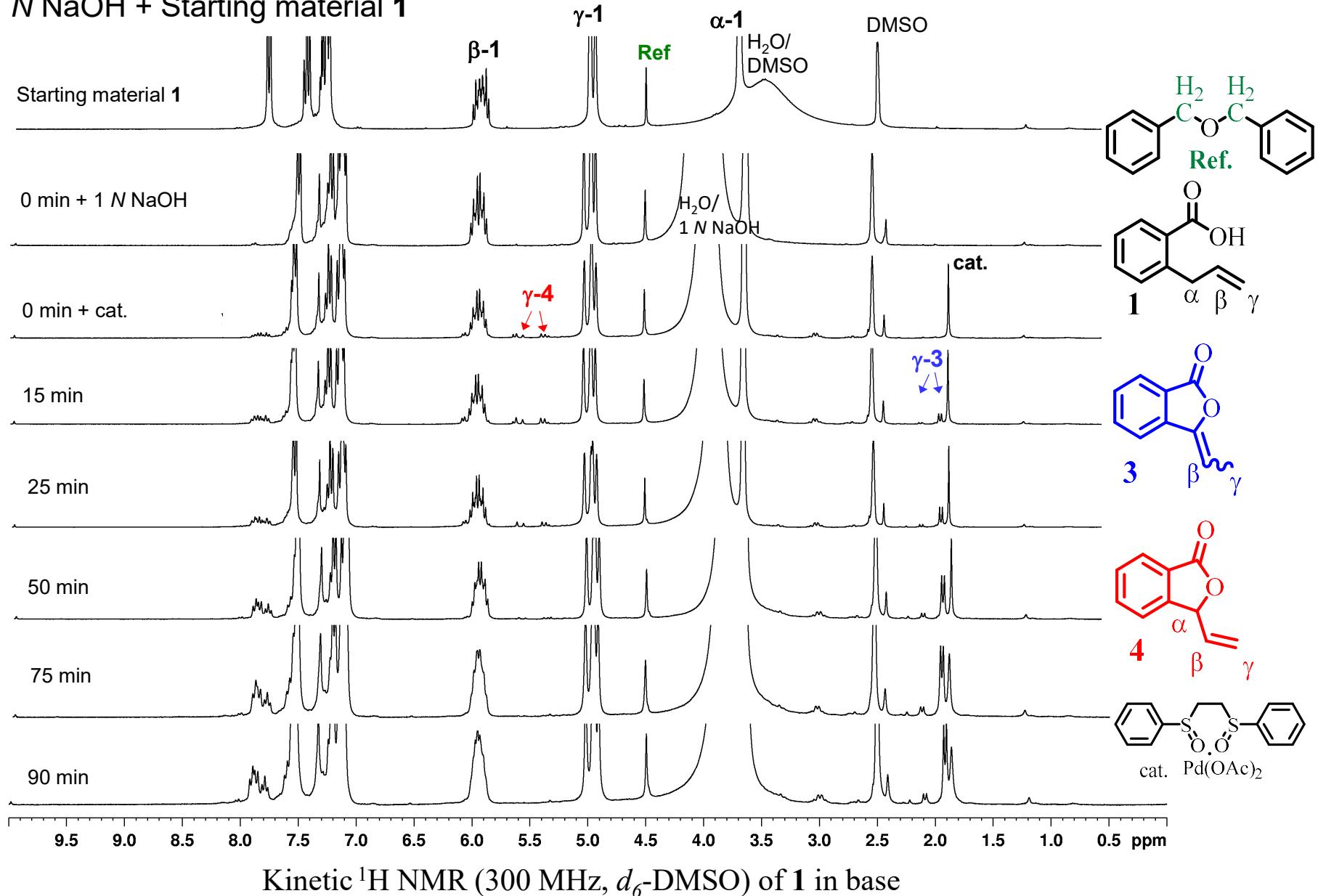


**SI Scheme 1.** Synthesis of **1-D<sub>2</sub>**

### **Procedure for kinetic isotope effect**

White catalyst (2.5 mg, 5  $\mu\text{mol}$ ) was added to solution of **1** or **1-D<sub>2</sub>** (16.2 mg, 100  $\mu\text{mol}$ ), NaOH<sub>(aq)</sub> (1*N*, 50  $\mu\text{L}$ , 50  $\mu\text{mol}$ ), dibenzyl ether (1.0 mg, 5  $\mu\text{mol}$ , as internal standard) and *d*<sub>6</sub>-DMSO (0.7 mL). The reaction tube was heated in an oil bath (100 °C) under an atmosphere of oxygen and monitored by <sup>1</sup>H NMR at certain time intervals. For the reactions conducted under the acidic condition, HCl<sub>(aq)</sub> (1 *N*, 50  $\mu\text{L}$ , 50  $\mu\text{mol}$ ) was applied instead of NaOH<sub>(aq)</sub>. The KIE value was obtained using the initial rates method, each experiment was conducted in duplicate.

1 N NaOH + Starting material **1**



## 1 N NaOH + Starting material 1

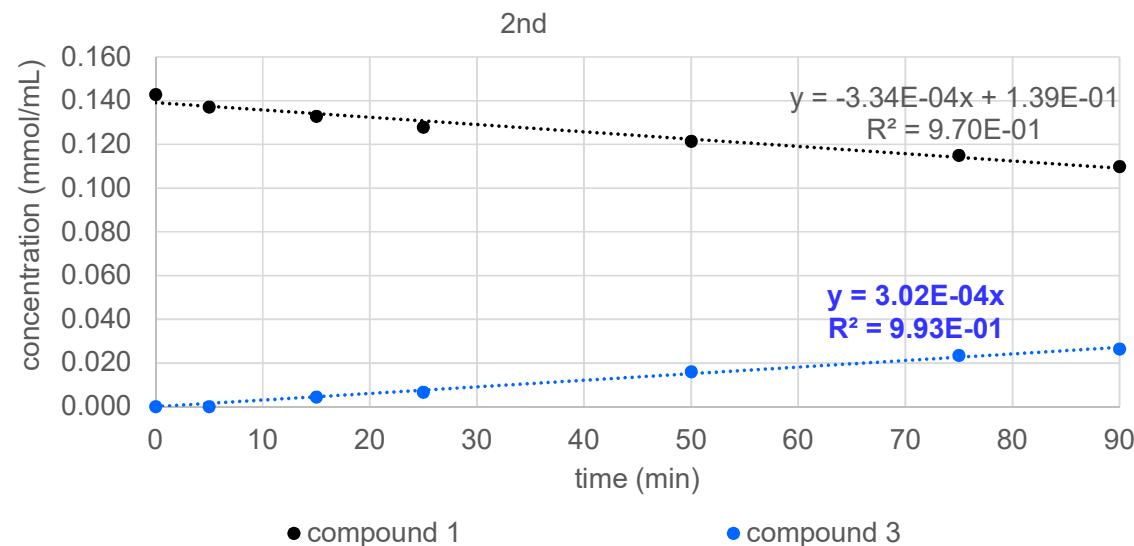
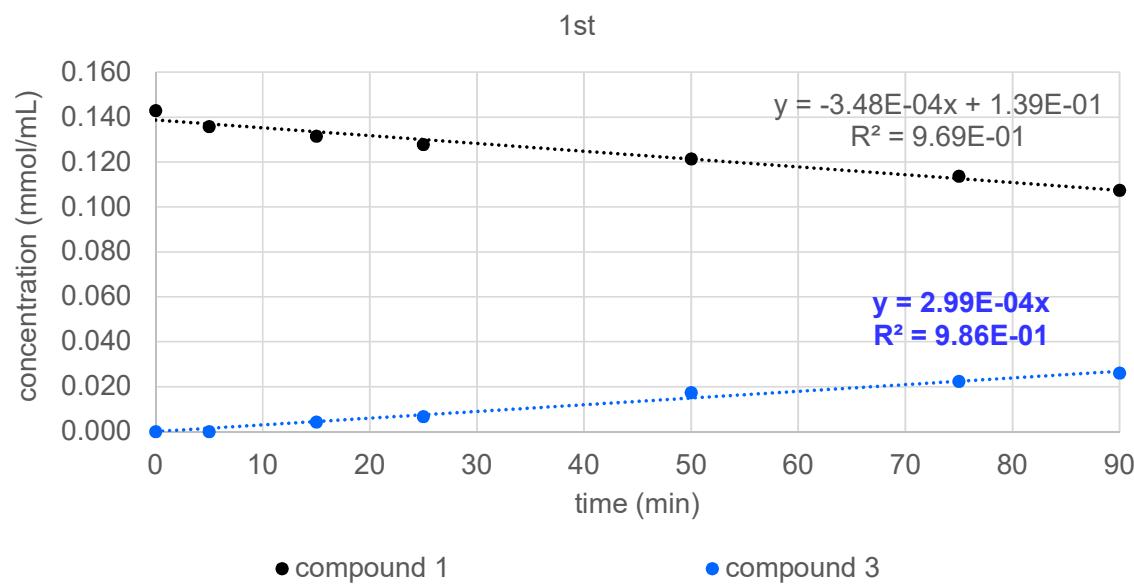
1 <sup>st</sup>	Starting material 1			Product 3			Intermediate 4		
	time (min)	integ. γ-1*	mmol	concn. (mmol/mL)	integ. γ-3*	mmol	concn. (mmol/mL)	integ. γ-4*	mmol
0	10	0.1	0.143	0	0	0	0	0	0
5	9.503	0.0950	0.136	0	0	0.000	0.246	0.00492	0.0070
15	9.206	0.0921	0.132	0.449	0.0030	0.004	0.262	0.00524	0.0075
25	8.946	0.0895	0.128	0.698	0.0047	0.007	0.281	0.00562	0.0080
50	8.498	0.0850	0.121	1.821	0.0121	0.017	0.0077	0.000154	0.0002
75	7.958	0.0796	0.114	2.341	0.0156	0.022	0.0074	0.000148	0.0002
90	7.521	0.0752	0.107	2.725	0.0182	0.026	0	0	0.0000

\*Reference to internal standard dibenzyl ether.

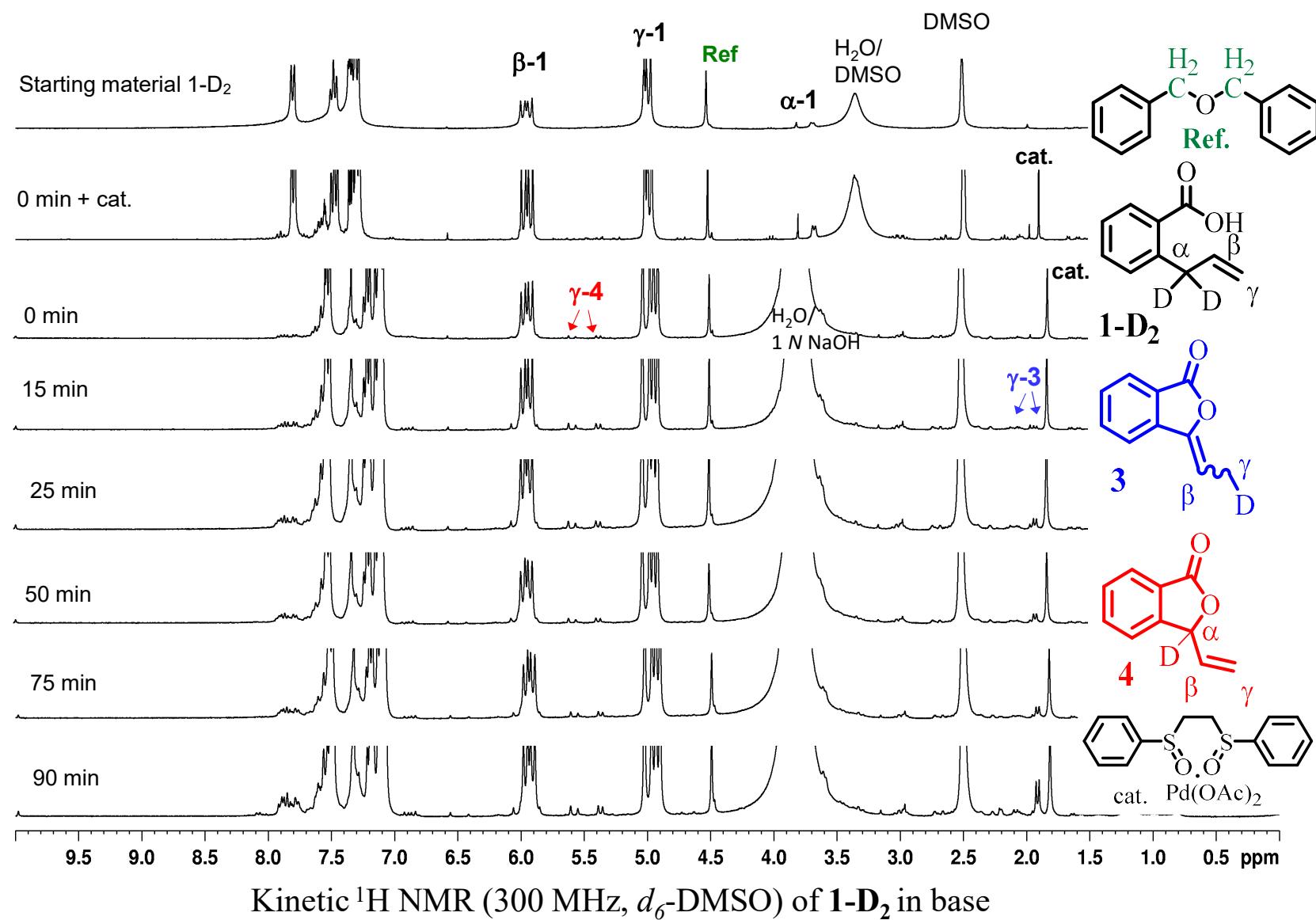
2 <sup>nd</sup>	Starting material 1			Product 3			Intermediate 4		
	time (min)	integ. γ-1*	mmol	concn. (mmol/mL)	integ. γ-3*	mmol	concn. (mmol/mL)	integ. γ-4*	mmol
0	10	0.1	0.143	0	0	0	0	0	0
5	9.593	0.0959	0.137	0	0	0.000	0.201	0.00402	0.0057
15	9.298	0.093	0.133	0.466	0.0031	0.004	0.251	0.00502	0.0072
25	8.957	0.0896	0.128	0.6875	0.0046	0.007	0.278	0.00556	0.0079
50	8.504	0.085	0.121	1.6730	0.0112	0.016	0.039	0.00079	0.0011
75	8.045	0.0805	0.115	2.462	0.0164	0.023	0.064	0.00128	0.0018
90	7.695	0.0770	0.110	2.767	0.0184	0.026	0.087	0.00174	0.0025

\*Reference to internal standard dibenzyl ether.

# $1\text{ N NaOH} + \text{Starting material 1}$



**1 N NaOH + Starting material **1-D<sub>2</sub>****



1 N NaOH + Starting material **1-D<sub>2</sub>**

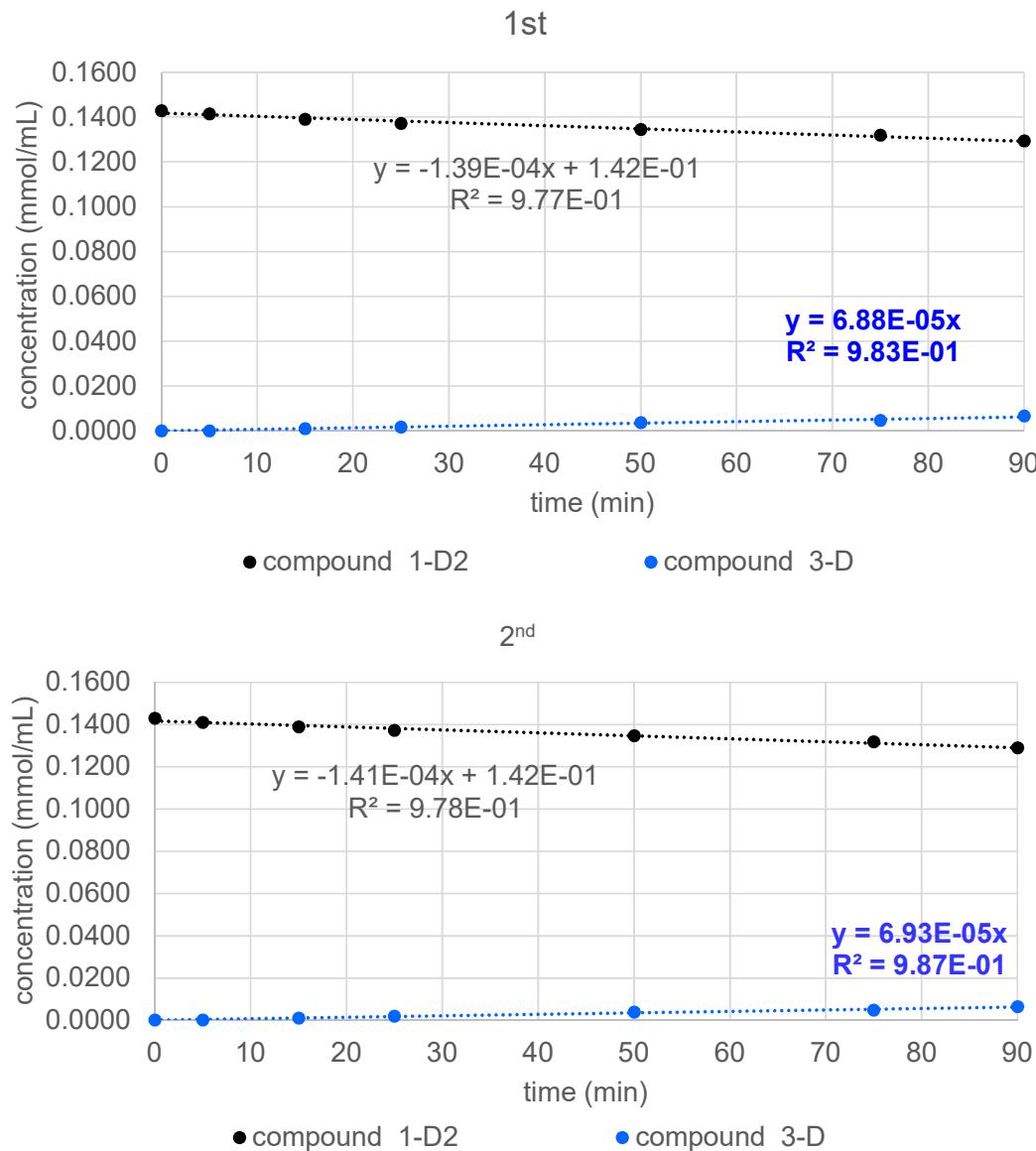
<b>1<sup>st</sup></b>	Starting material <b>1-D<sub>2</sub></b>			Product <b>3-D</b>			Intermediate <b>4</b>		
time (min)	integ. $\gamma\text{-1}^*$	mmol	concn. (mmol/mL)	integ. $\gamma\text{-3}^*$	mmol	concn. (mmol/mL)	integ. $\gamma\text{-4}^*$	mmol	concn. (mmol/mL)
0	10	0.1	0.1429	0	0	0	0	0	0
5	9.896	0.09896	0.1414	0	0	0	0.055	0.0011	0.0016
15	9.726	0.09726	0.1389	0.105	0.00063	0.0009	0.104	0.00208	0.0030
25	9.604	0.09604	0.1372	0.203	0.00122	0.0017	0.133	0.00266	0.0038
50	9.413	0.09413	0.1345	0.419	0.00251	0.0036	0.153	0.00306	0.0044
75	9.229	0.09229	0.1318	0.537	0.00322	0.0046	0.207	0.00414	0.0059
90	9.051	0.09051	0.1293	0.771	0.00463	0.0066	0.217	0.00434	0.0062

\*Reference to internal standard dibenzyl ether.

<b>2<sup>nd</sup></b>	Starting material <b>1-D<sub>2</sub></b>			Product <b>3-D</b>			Intermediate <b>4</b>		
time (min)	integ. $\gamma\text{-1}^*$	mmol	concn. (mmol/mL)	integ. $\gamma\text{-3}^*$	mmol	concn. (mmol/mL)	integ. $\gamma\text{-4}^*$	mmol	concn. (mmol/mL)
0	10	0.1	0.1429	0	0	0	0	0	0
5	9.867	0.09867	0.1410	0	0	0	0.064	0.00128	0.0018
15	9.715	0.09715	0.1388	0.105	0.00063	0.0009	0.113	0.00226	0.0032
25	9.608	0.09608	0.1373	0.209	0.00125	0.0018	0.138	0.00276	0.0039
50	9.423	0.09423	0.1346	0.452	0.00271	0.0039	0.156	0.00312	0.0045
75	9.224	0.09224	0.1318	0.558	0.00335	0.0048	0.222	0.00444	0.0063
90	9.021	0.09021	0.1289	0.745	0.00447	0.0063	0.267	0.00534	0.0076

\*Reference to internal standard dibenzyl ether.

## 1 N NaOH + Starting material 1-D<sub>2</sub>



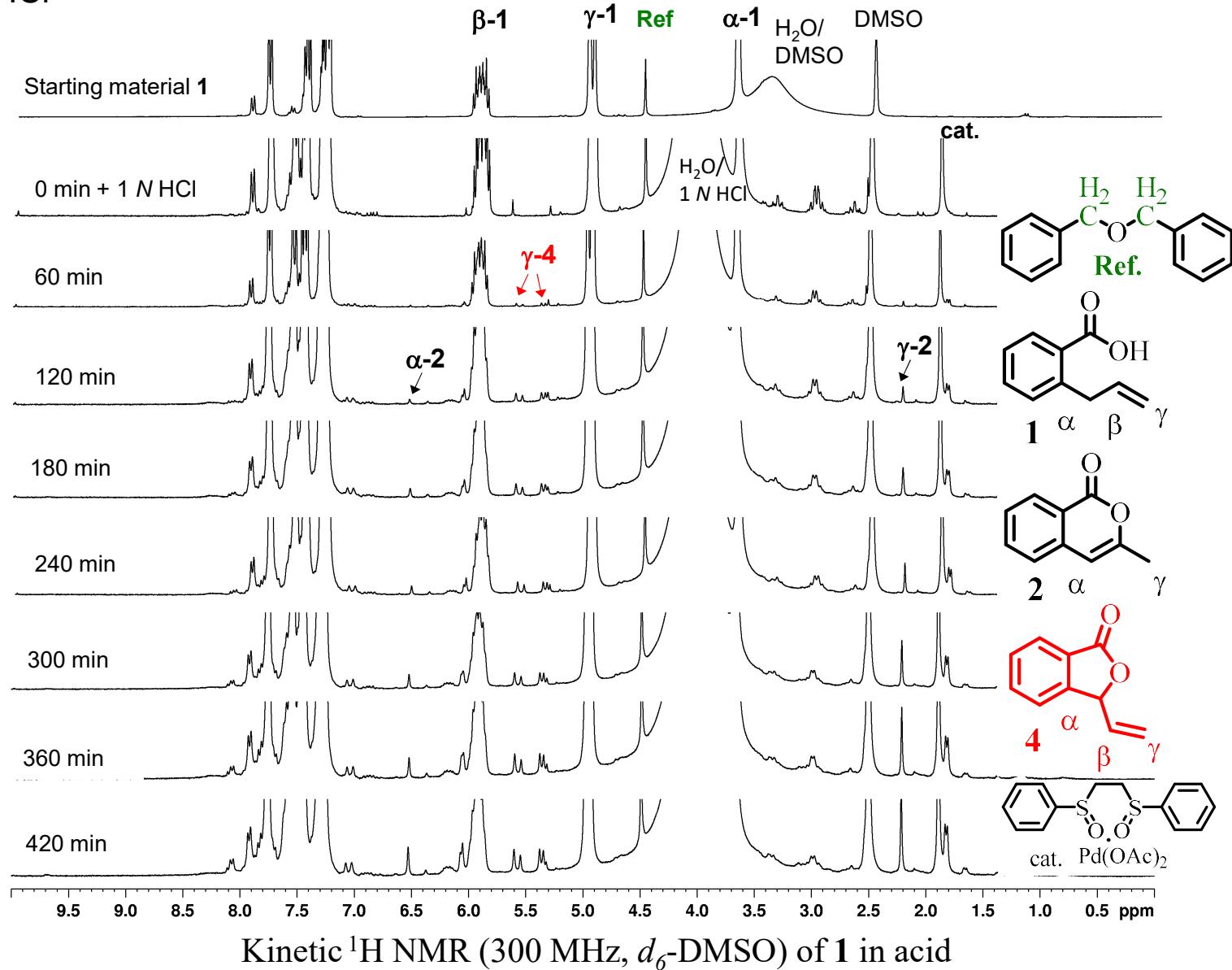
## Kinetic Isotope Effect under the basic condition

$$1: \text{rate}_{\text{ave}} = \frac{(2.99 \times 10^{-4} + 3.02 \times 10^{-4})}{2} = 3.01 \times 10^{-4} (\text{M} \cdot \text{min}^{-1})$$

$$1-\text{D}_2: \text{rate}_{\text{ave}} = \frac{(6.88 \times 10^{-5} + 6.93 \times 10^{-5})}{2} = 6.91 \times 10^{-5} (\text{M} \cdot \text{min}^{-1})$$

$$\text{KIE} = \frac{k_{\text{H}}}{k_{\text{D}}} = \frac{1: \text{rate}_{\text{ave}}}{1-\text{D}_2: \text{rate}_{\text{ave}}} = 4.3 - 4.4$$

1 N HCl



1 N HCl

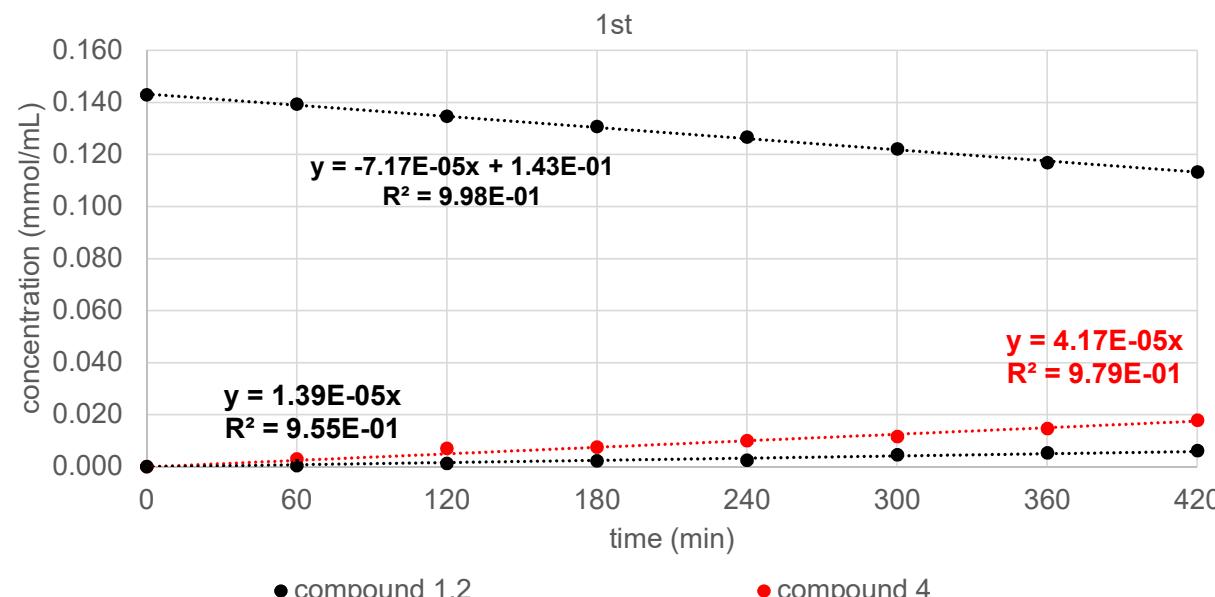
1 <sup>st</sup>	Starting material <b>1</b>			Product <b>4</b>			Product <b>2</b>			
	time (min)	integ. $\gamma\text{-1}^*$	mmol	concн. (mmol/mL)	integ. $\gamma\text{-4}^*$	mmol	concн. (mmol/mL)	integ. $\alpha\text{-2}^*$	mmol	concн. (mmol/mL)
0	10	0.1	0.143	0	0	0	0	0	0	0
60	9.752	0.0975	0.139	0.105	0.0021	0.0030	0.012	0.00024	0.0003	
120	9.423	0.0942	0.135	0.243	0.0049	0.0069	0.041	0.00082	0.0012	
180	9.155	0.0916	0.131	0.263	0.0053	0.0075	0.077	0.00154	0.0022	
240	8.870	0.0887	0.127	0.350	0.0070	0.0100	0.086	0.00172	0.0025	
300	8.547	0.0855	0.122	0.405	0.0081	0.0116	0.16	0.0032	0.0046	
360	8.174	0.0817	0.117	0.514	0.0103	0.0147	0.185	0.0037	0.0053	
420	7.930	0.0793	0.113	0.625	0.0125	0.0179	0.215	0.0043	0.0061	

\*Reference to internal standard dibenzyl ether.

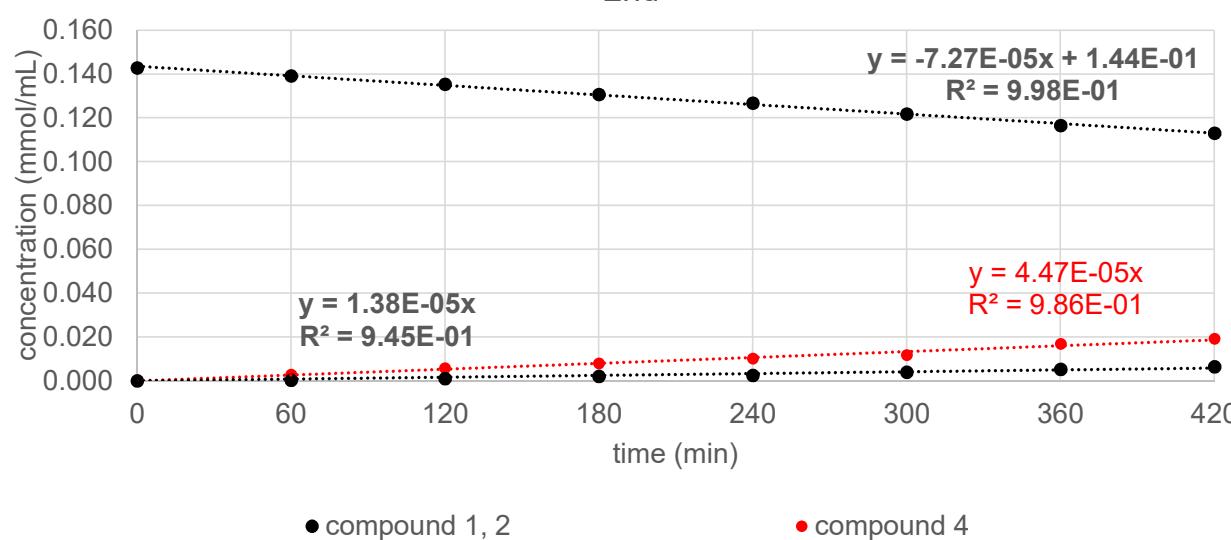
2 <sup>nd</sup>	SM Starting material <b>1</b>			Product <b>4</b>			Product <b>2</b>			
	time (min)	integ. $\gamma\text{-1}^*$	mmol	concн. (mmol/mL)	integ. $\gamma\text{-4}^*$	mmol	concн. (mmol/mL)	integ. $\alpha\text{-2}^*$	mmol	concн. (mmol/mL)
0	10	0.1	0.143	0	0	0	0	0	0	0
60	9.745	0.097	0.139	0.104	0.002	0.0030	0.011	0.0002	0.0003	
120	9.478	0.095	0.135	0.204	0.004	0.0058	0.035	0.0007	0.0010	
180	9.147	0.091	0.131	0.282	0.006	0.0081	0.074	0.0015	0.0021	
240	8.873	0.089	0.127	0.359	0.007	0.0103	0.086	0.0017	0.0025	
300	8.526	0.085	0.122	0.412	0.008	0.0118	0.141	0.0028	0.0040	
360	8.161	0.082	0.117	0.592	0.012	0.0169	0.184	0.0037	0.0053	
420	7.913	0.079	0.113	0.675	0.014	0.0193	0.227	0.0045	0.0065	

\*Reference to internal standard dibenzyl ether.

1 N HCl

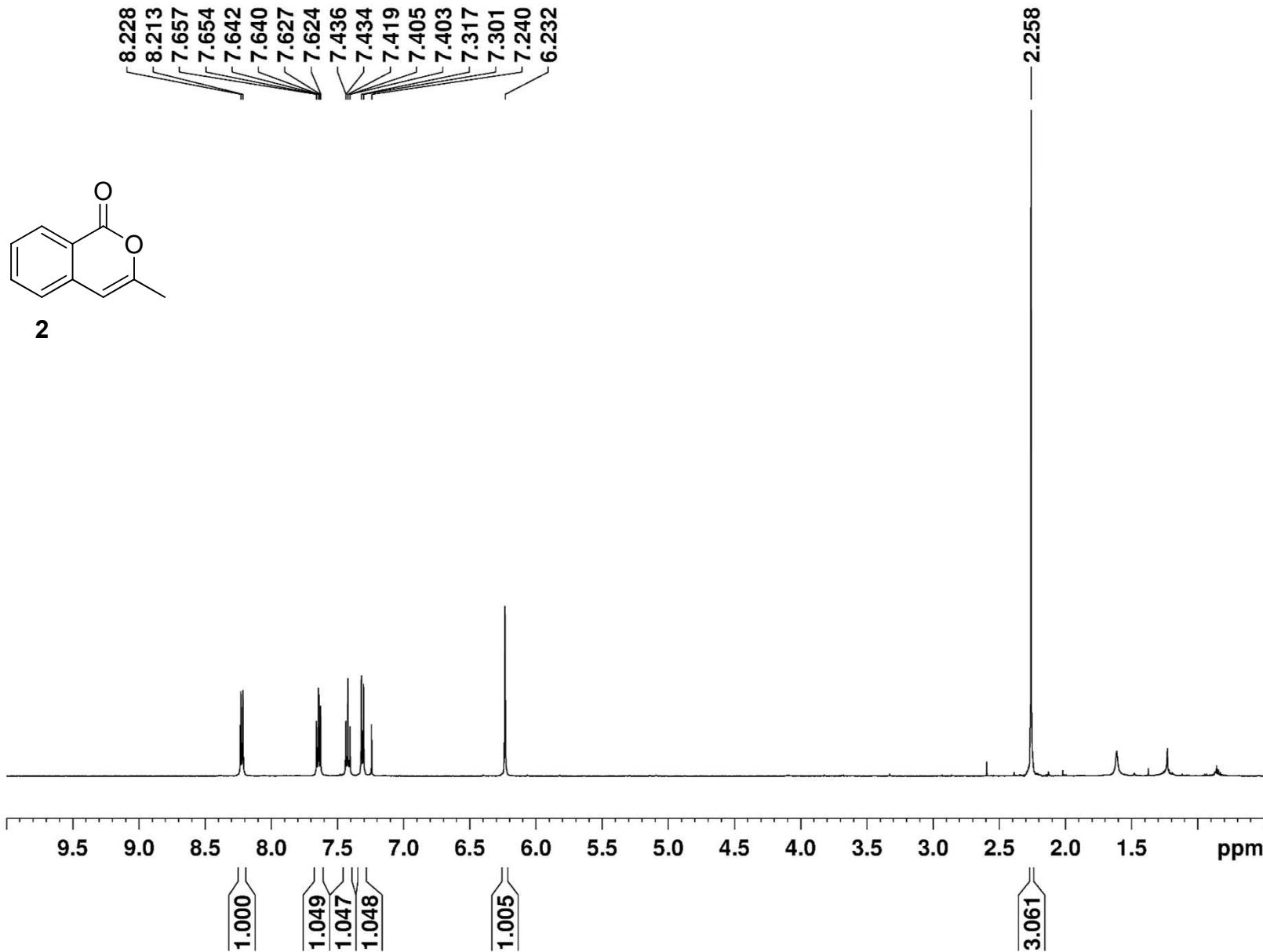


2nd

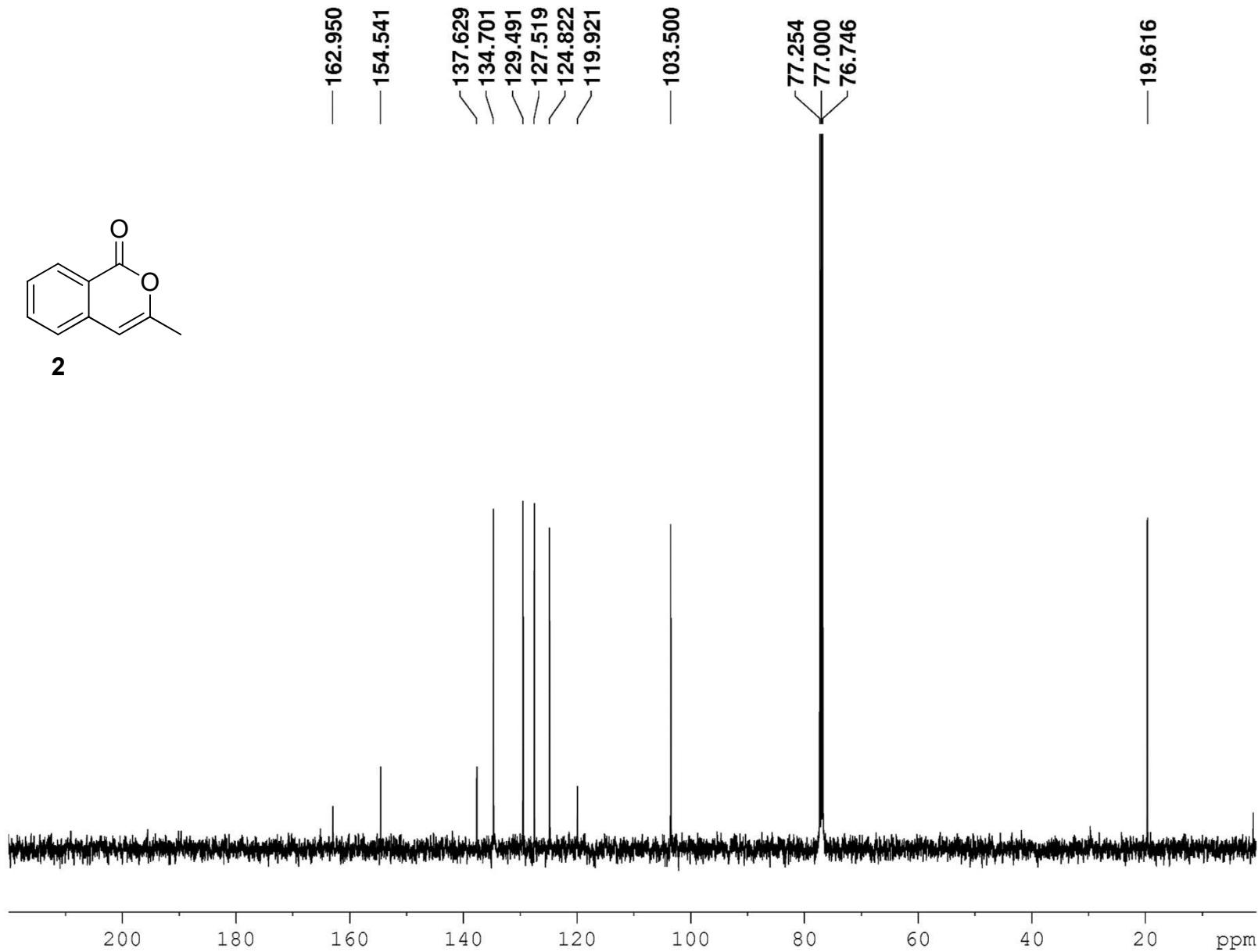
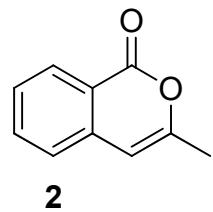


Under  $\text{HCl}_{(\text{aq})}$  (1 N)

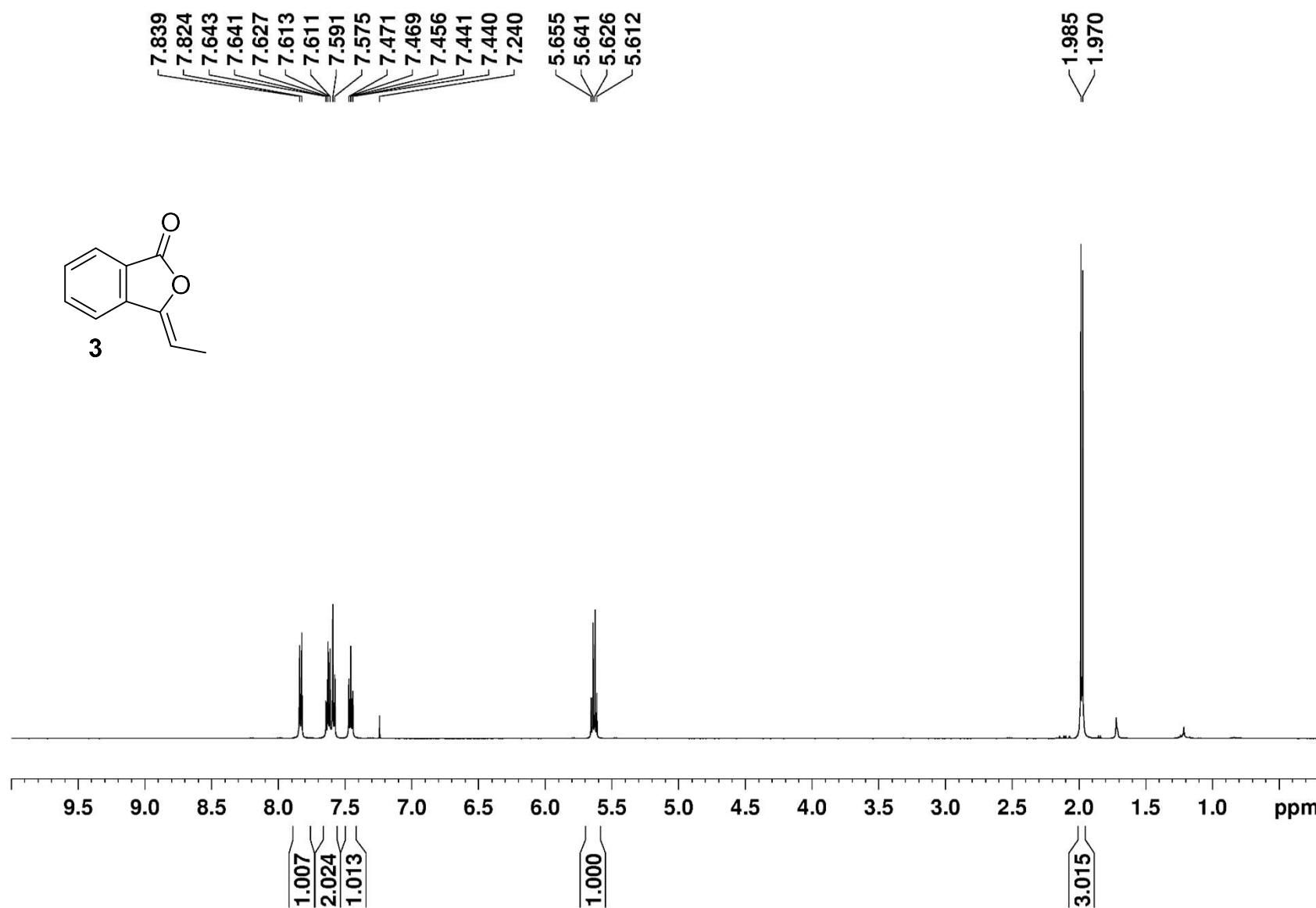
$$\text{rate}_{\text{ave}} = \frac{(4.17 \times 10^{-5} + 4.47 \times 10^{-5})}{2} = 4.32 \times 10^{-5} (\text{M} \cdot \text{min}^{-1})$$



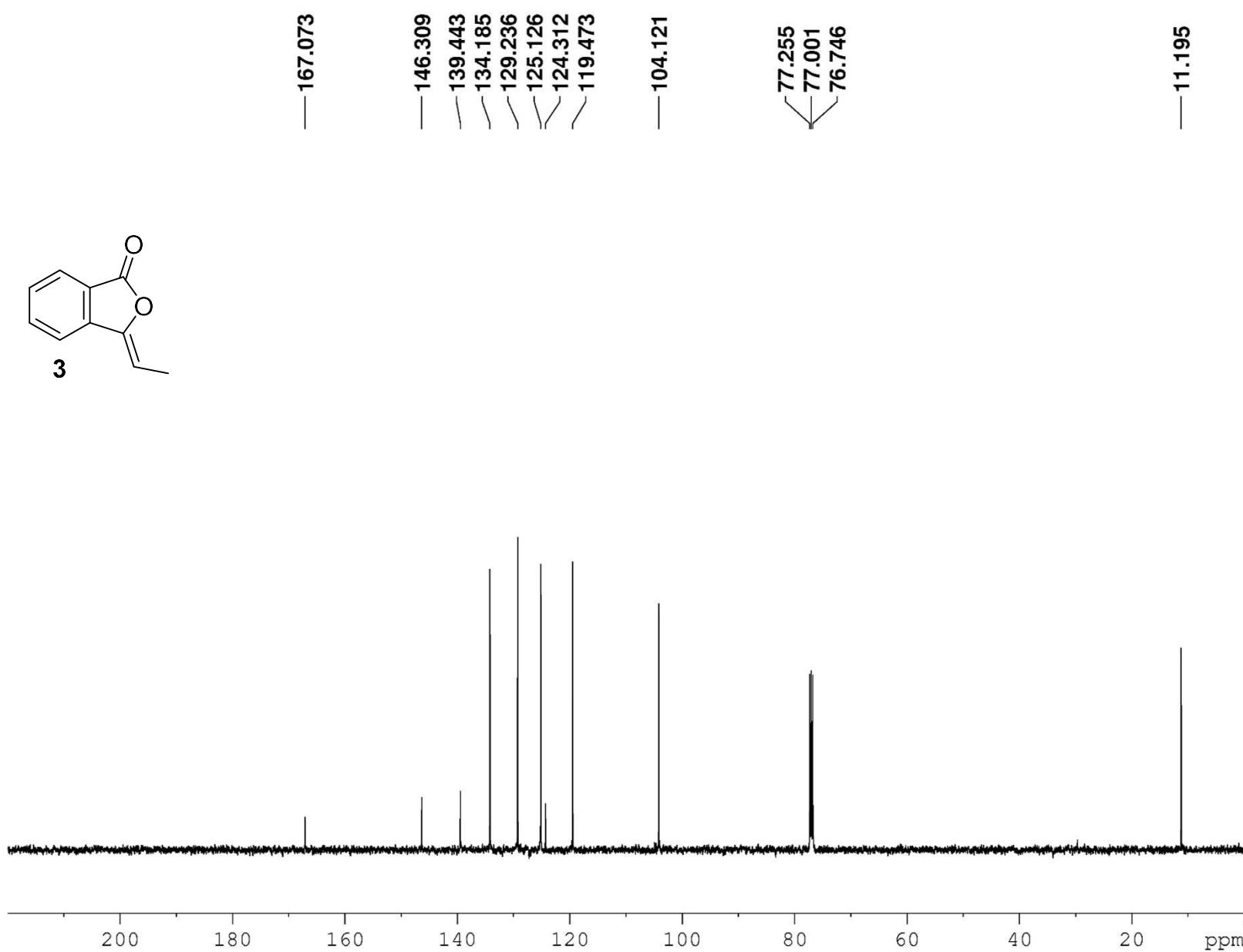
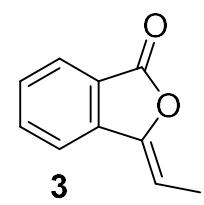
<sup>1</sup>H NMR of compound 2 (500 MHz, CDCl<sub>3</sub>)



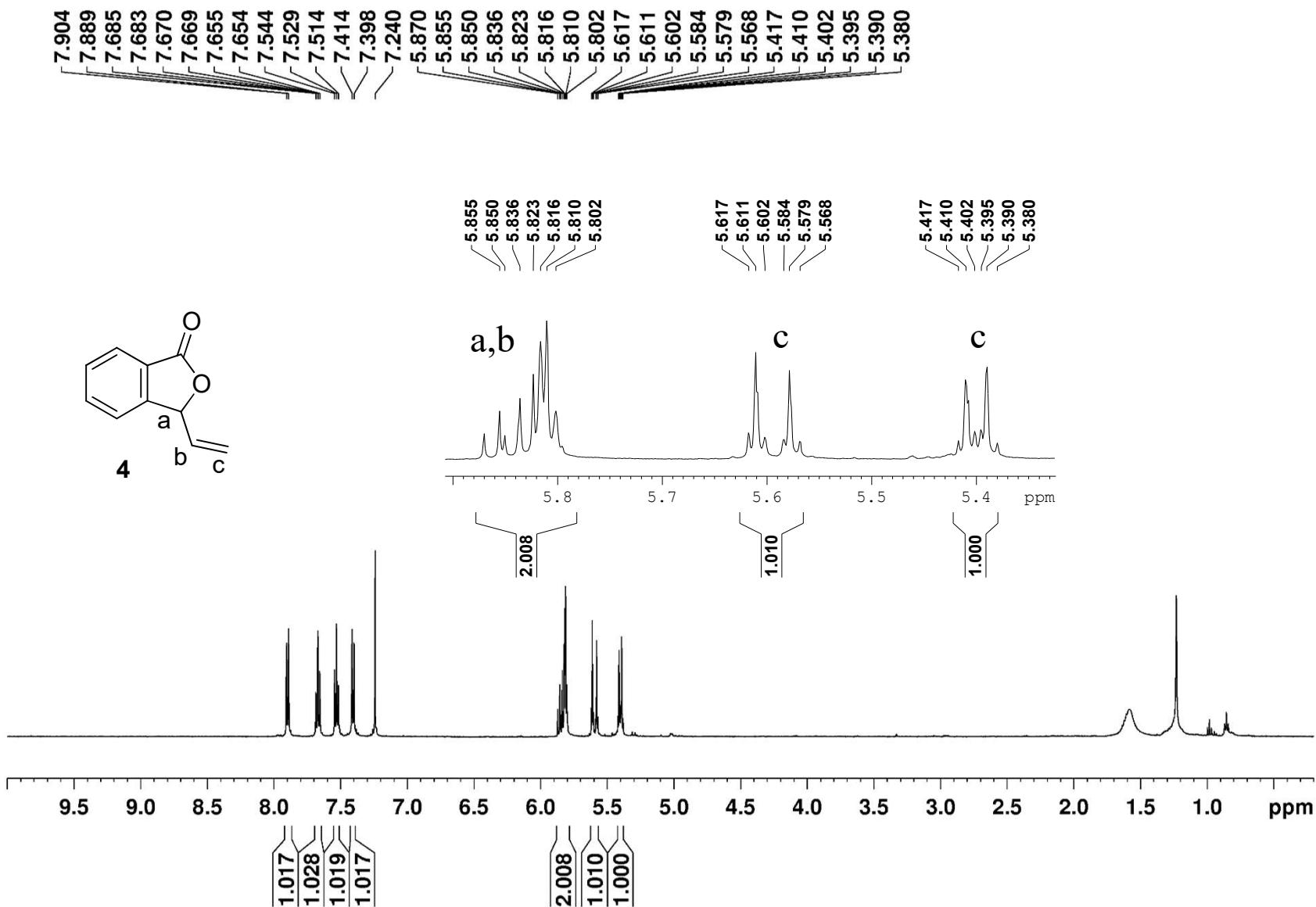
<sup>13</sup>C NMR of compound **2** (125 MHz, CDCl<sub>3</sub>)

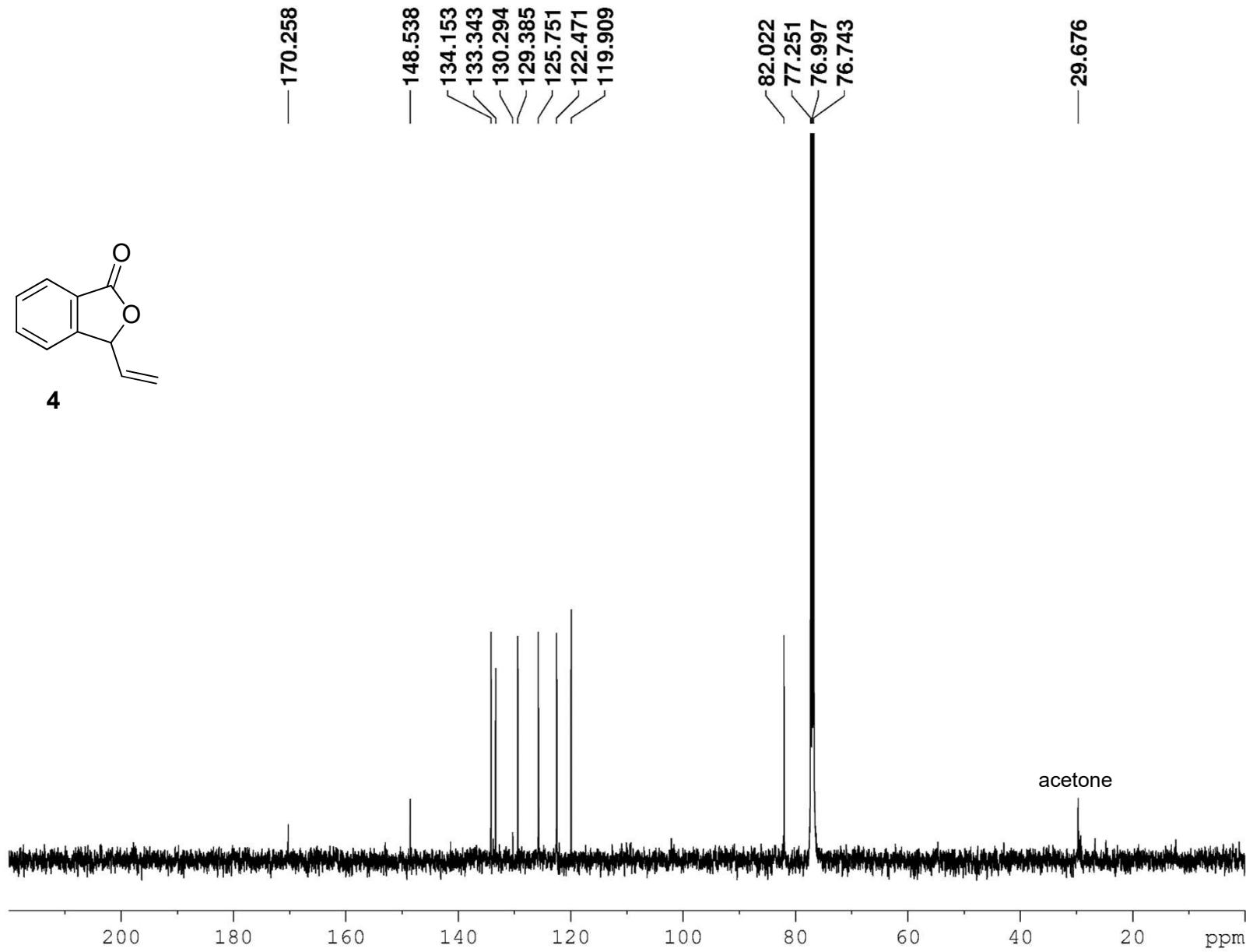
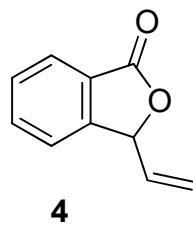


$^1\text{H}$  NMR of compound **3** (500 MHz,  $\text{CDCl}_3$ )

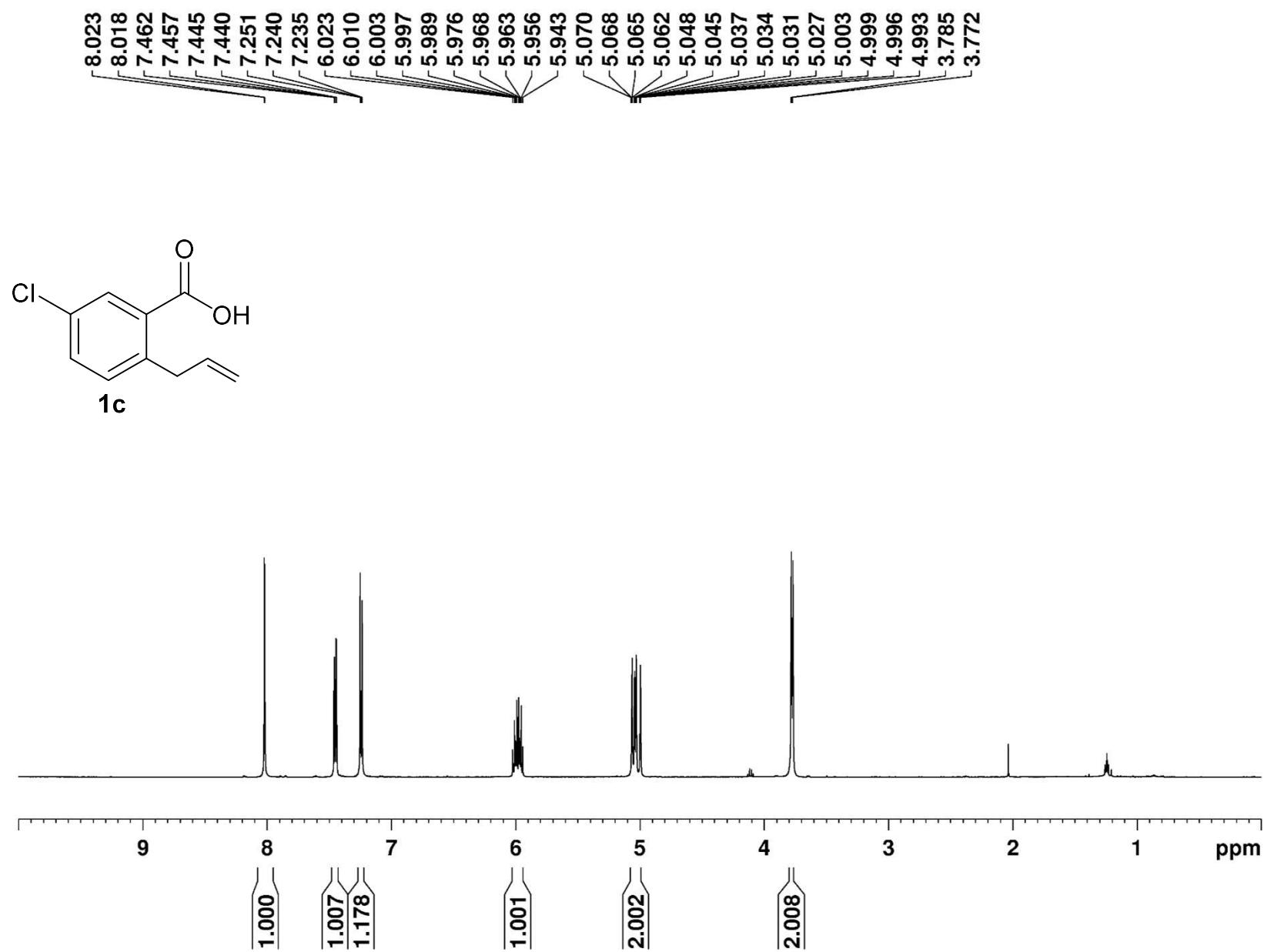


<sup>13</sup>C NMR of compound **3** (125 MHz, CDCl<sub>3</sub>)

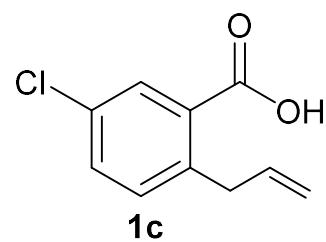




$^{13}\text{C}$  NMR of compound 4 (125 MHz,  $\text{CDCl}_3$ )



<sup>1</sup>H NMR of compound **1c** (500 MHz, CDCl<sub>3</sub>)

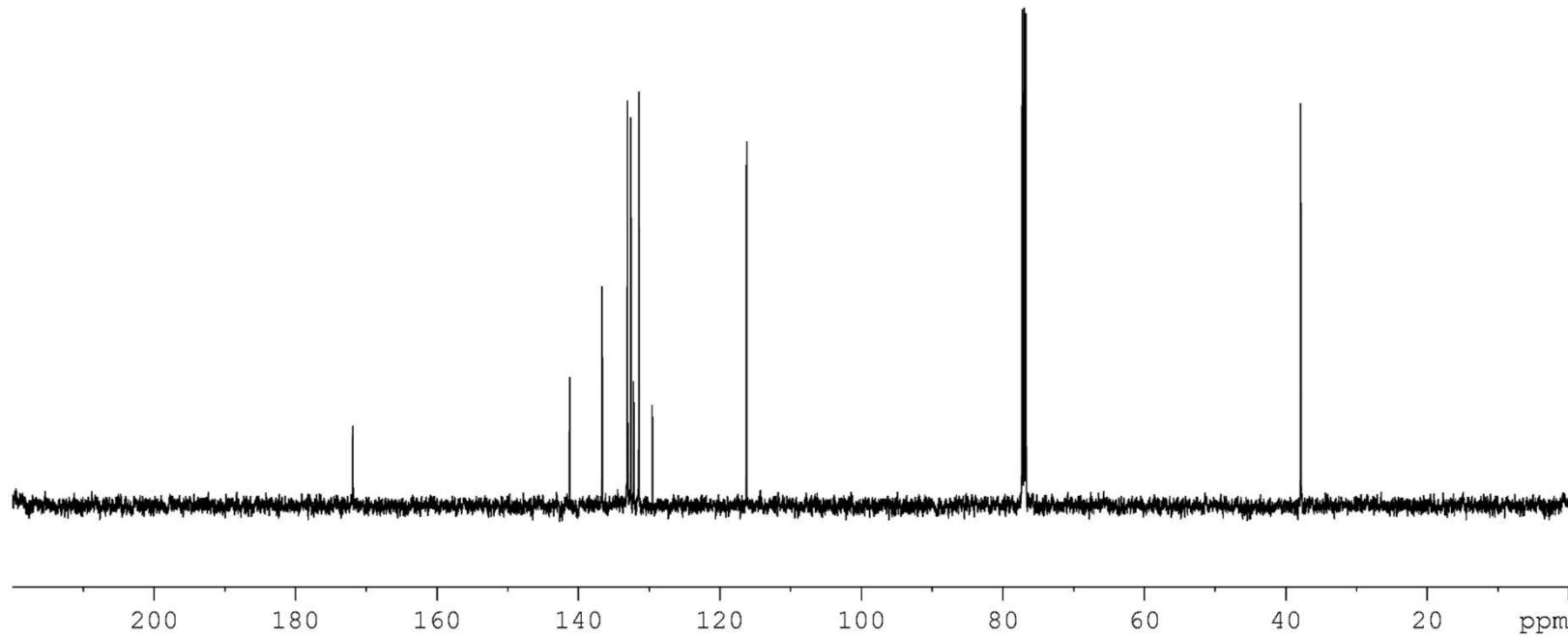


— 171.914

141.245  
136.646  
133.056  
132.589  
132.192  
131.440  
129.540  
116.217

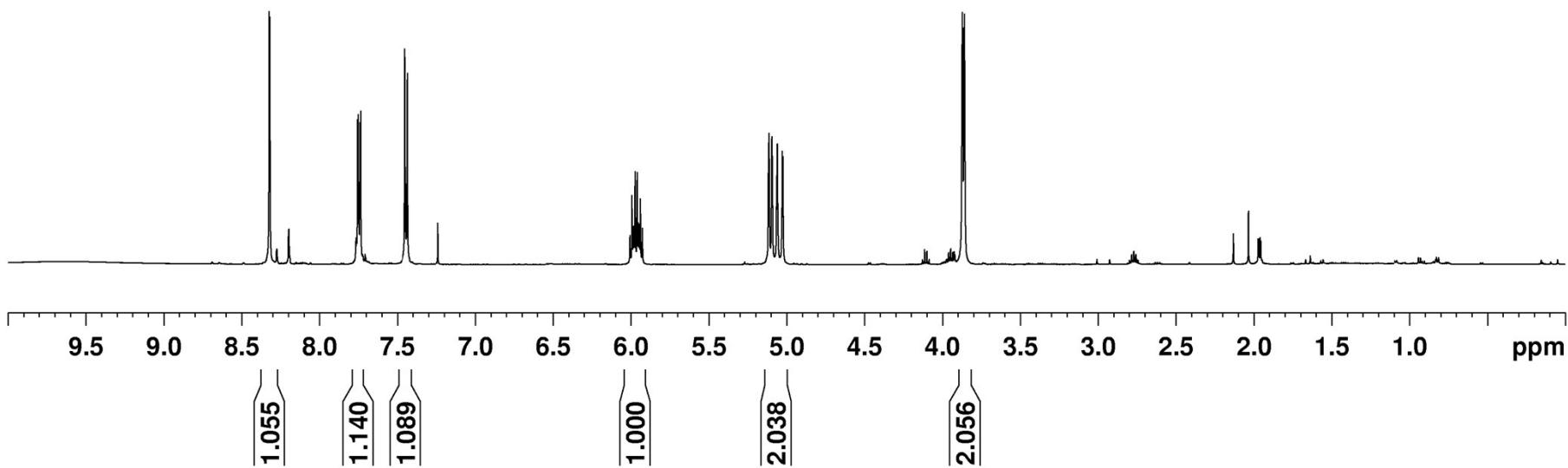
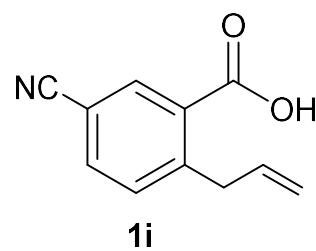
77.250  
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76.742

— 37.877

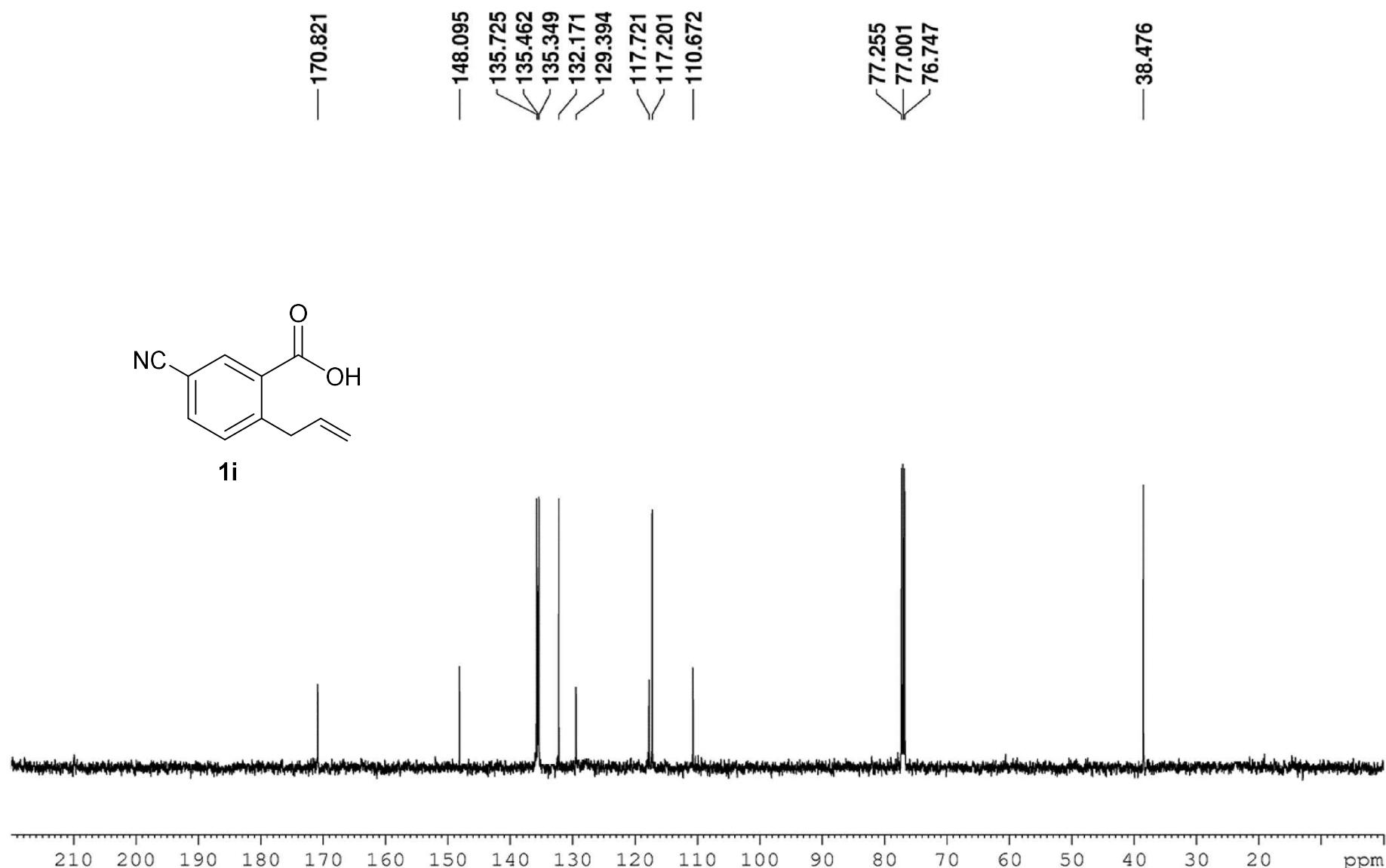


$^{13}\text{C}$  NMR of compound **1c** (125 MHz,  $\text{CDCl}_3$ )

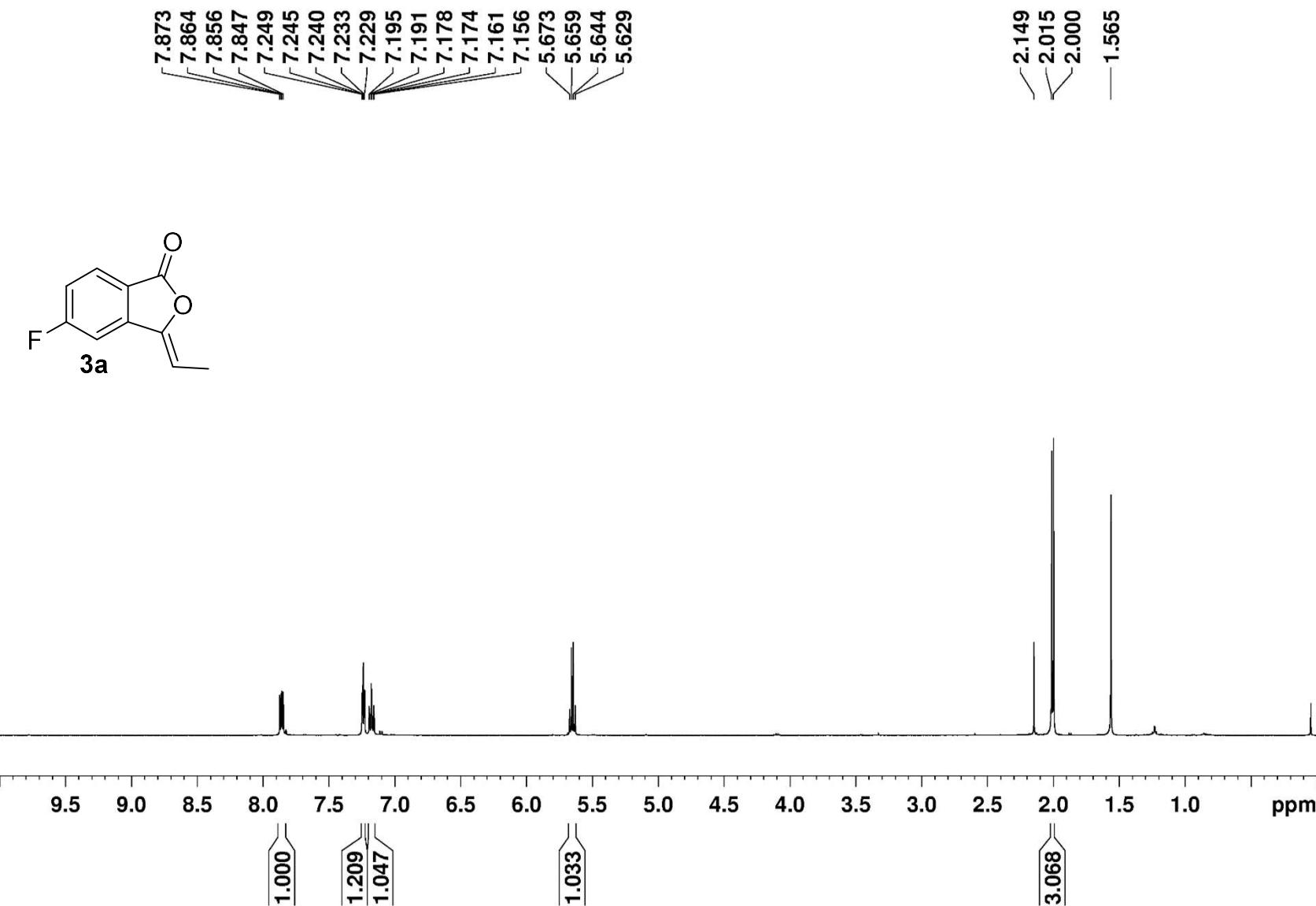
8.323  
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 7.739  
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 7.452  
 7.436  
 7.240  
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 5.993  
 5.986  
 5.981  
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 3.859



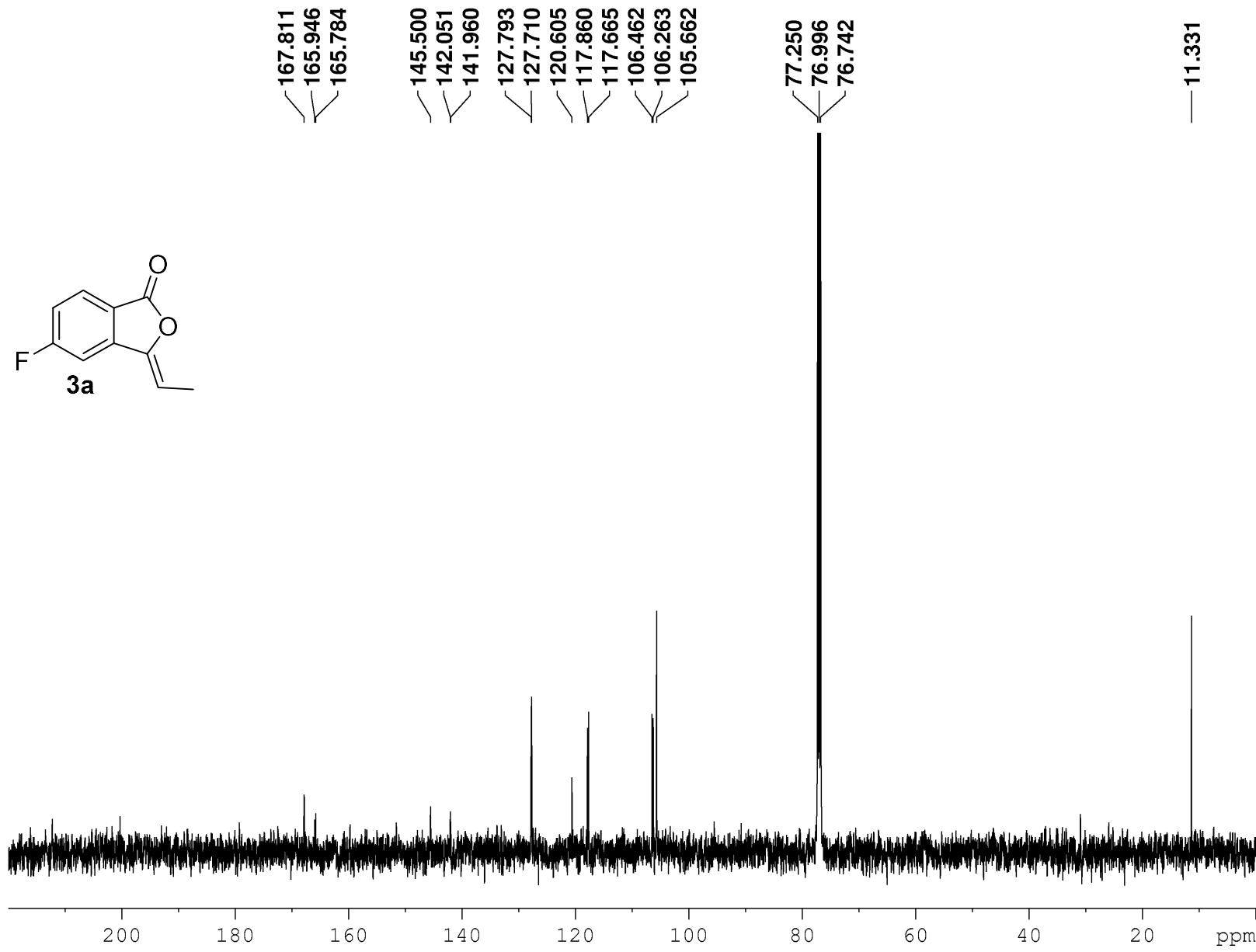
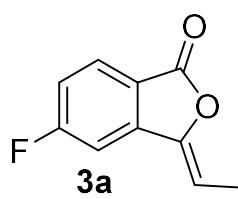
<sup>1</sup>H NMR of compound **1i** (500 MHz, CDCl<sub>3</sub>)

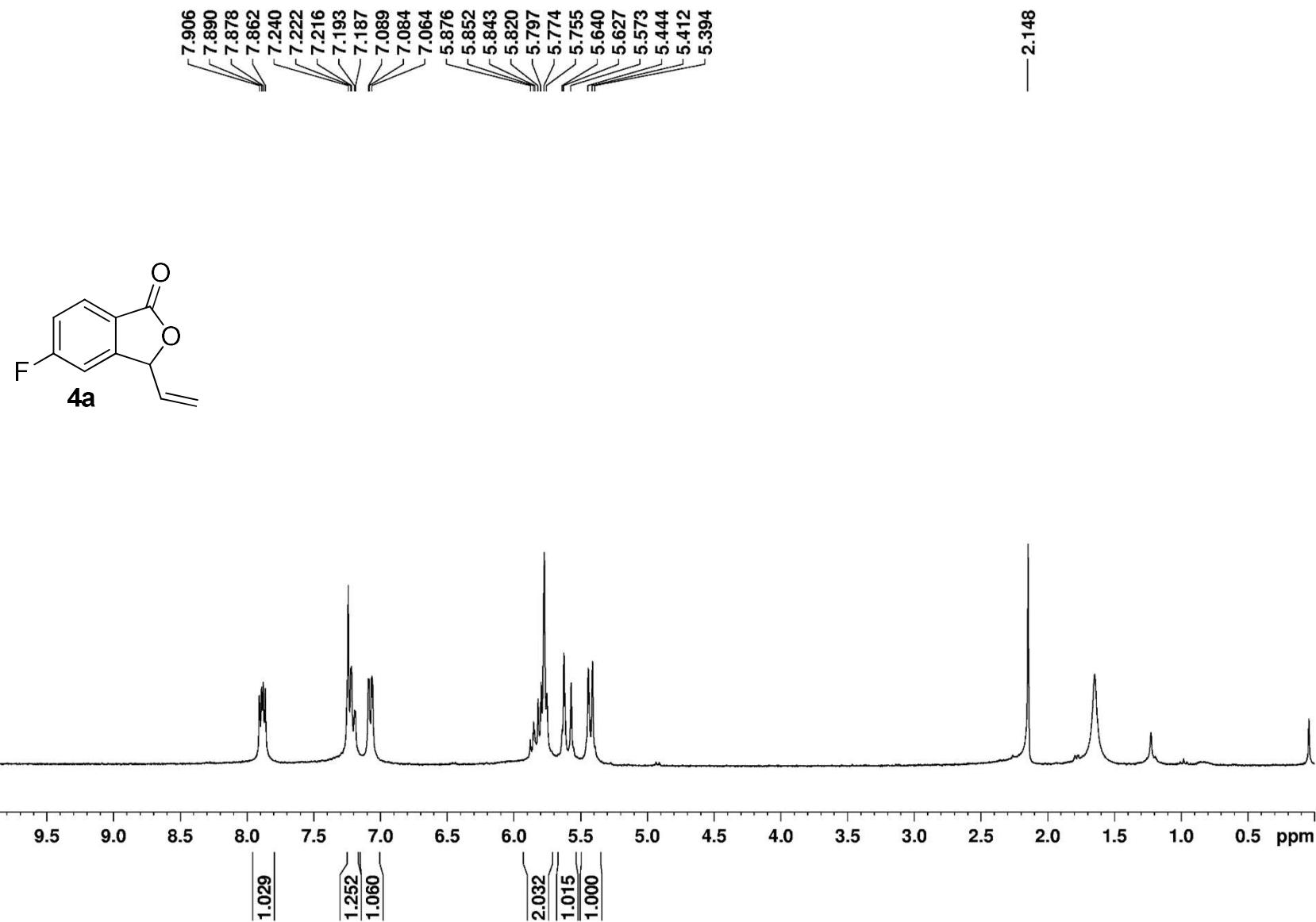


$^{13}\text{C}$  NMR of compound **1i** (125 MHz,  $\text{CDCl}_3$ )

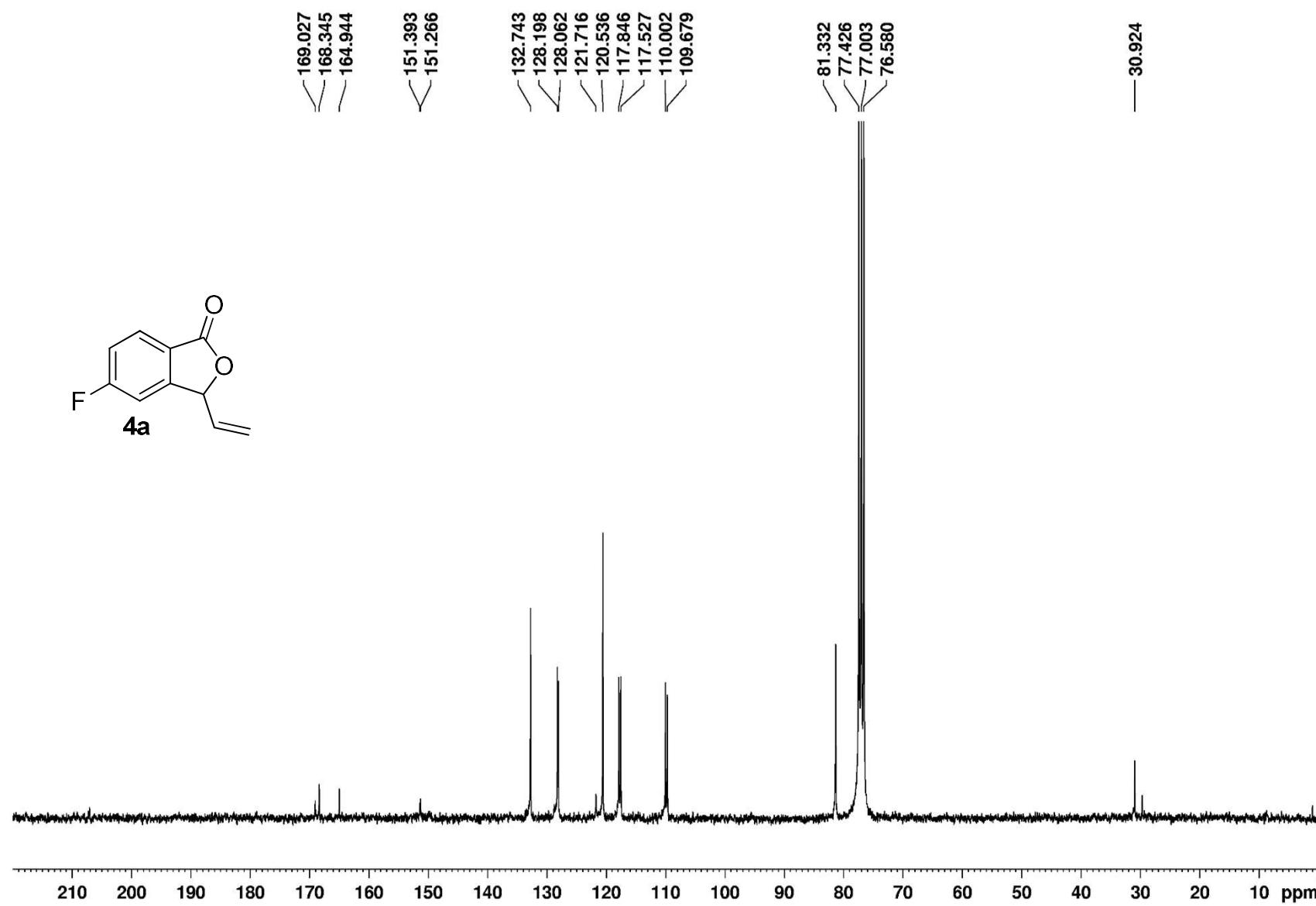


<sup>1</sup>H NMR of compound 3a (500 MHz, CDCl<sub>3</sub>)

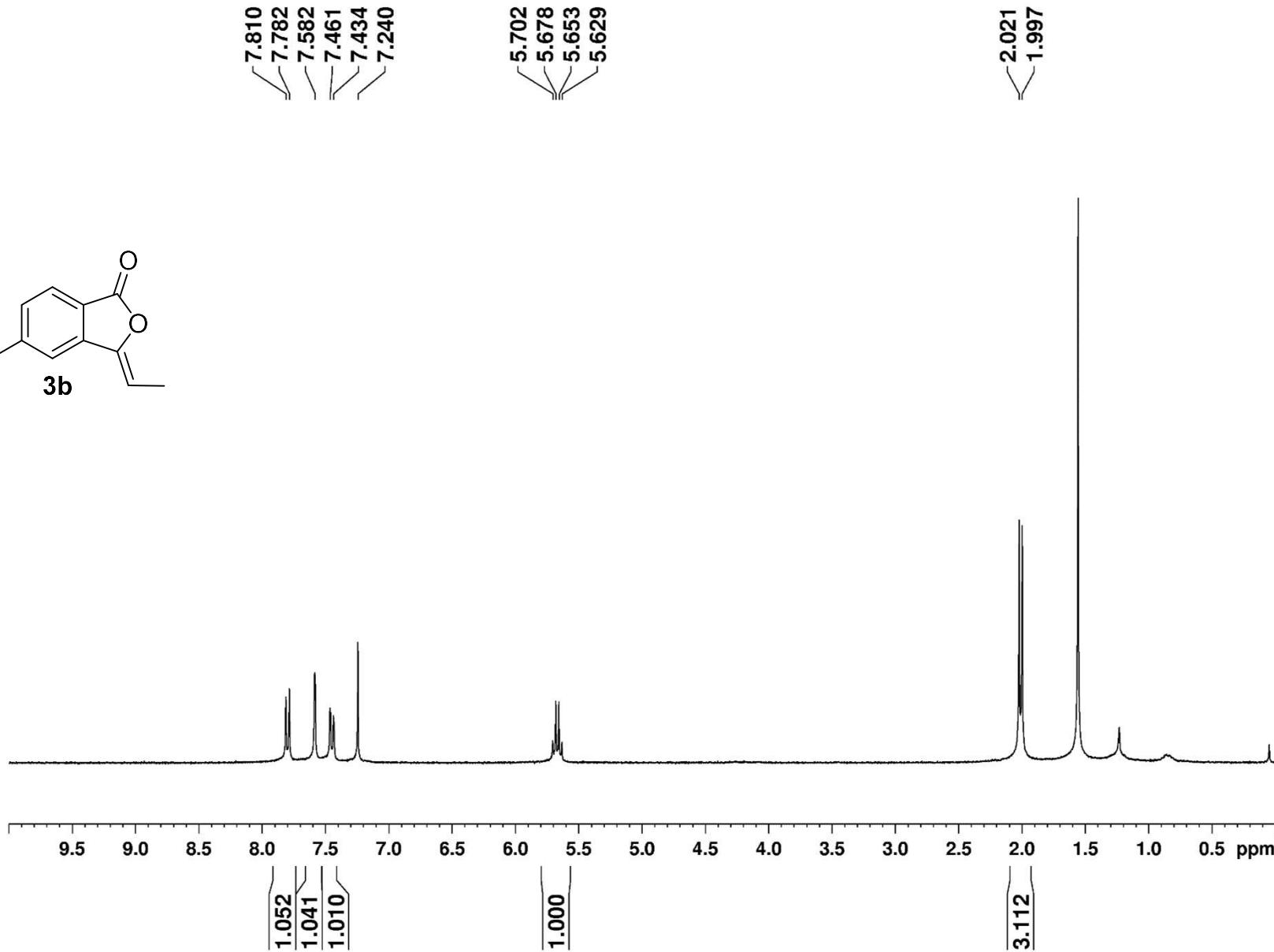
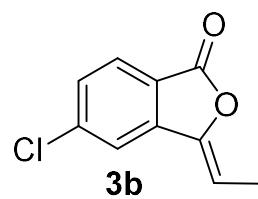




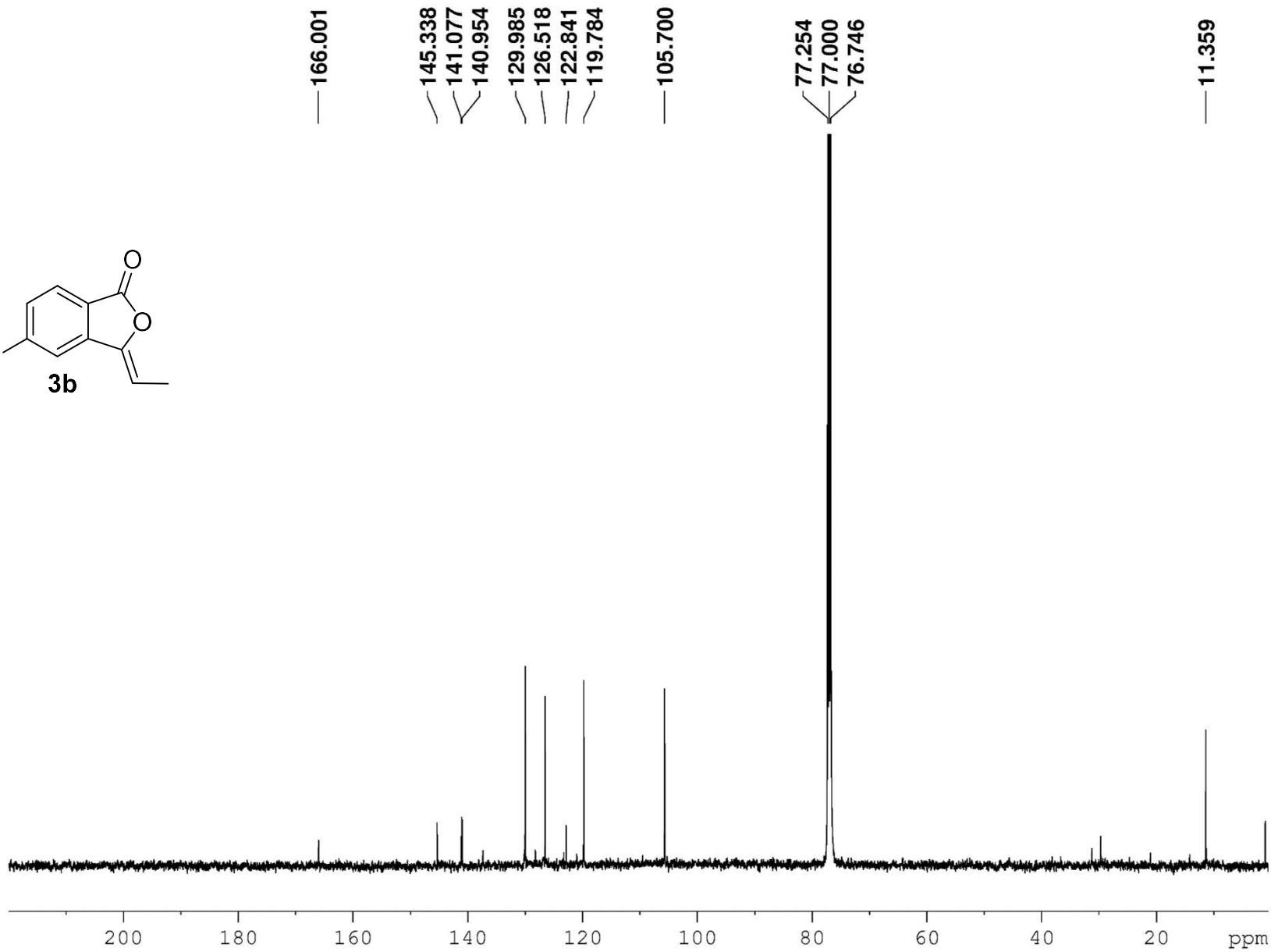
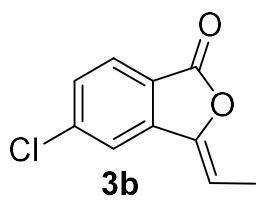
<sup>1</sup>H NMR of compound **4a** (300 MHz, CDCl<sub>3</sub>)



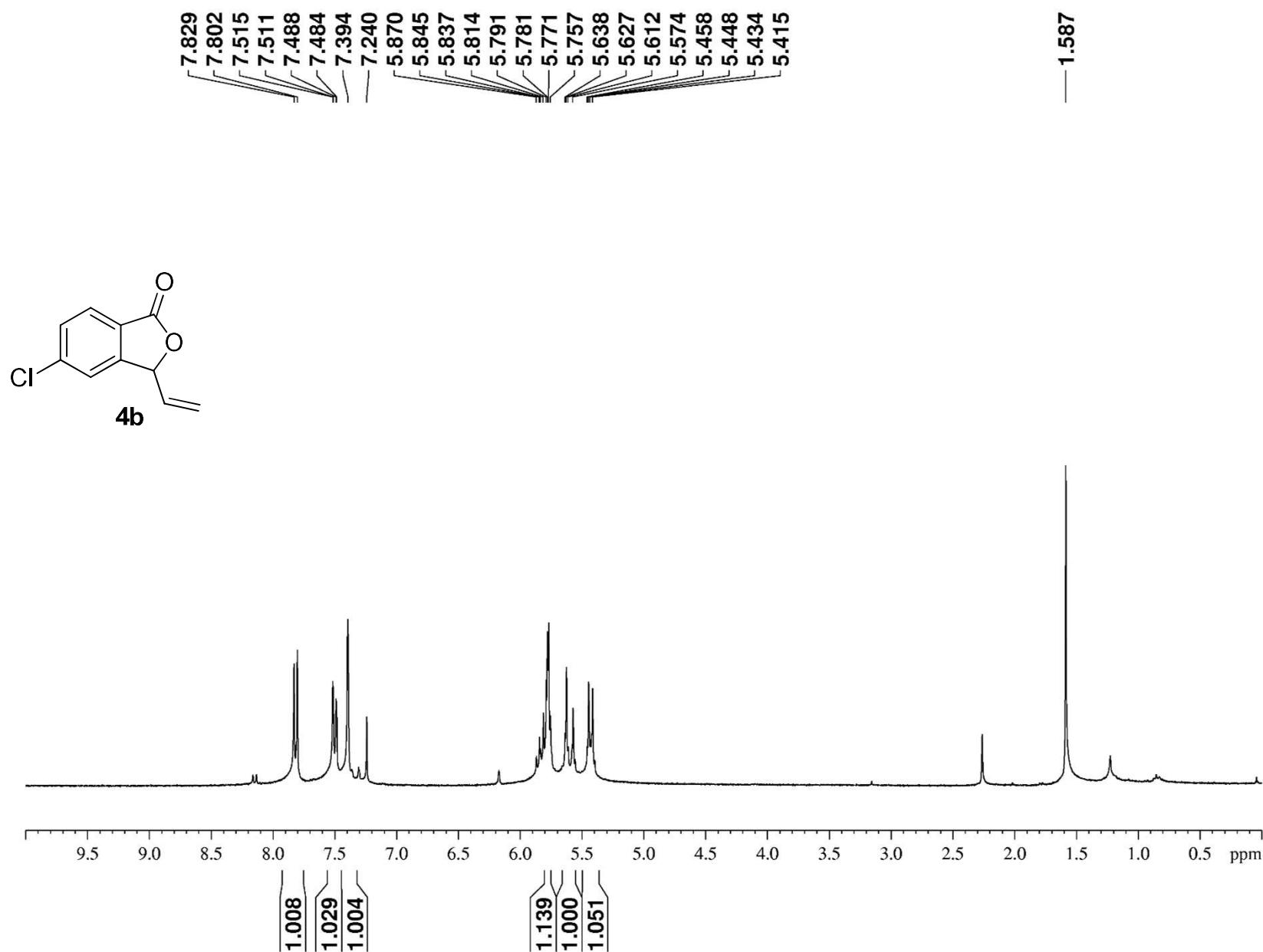
<sup>13</sup>C NMR of compound 4a (75 MHz, CDCl<sub>3</sub>)



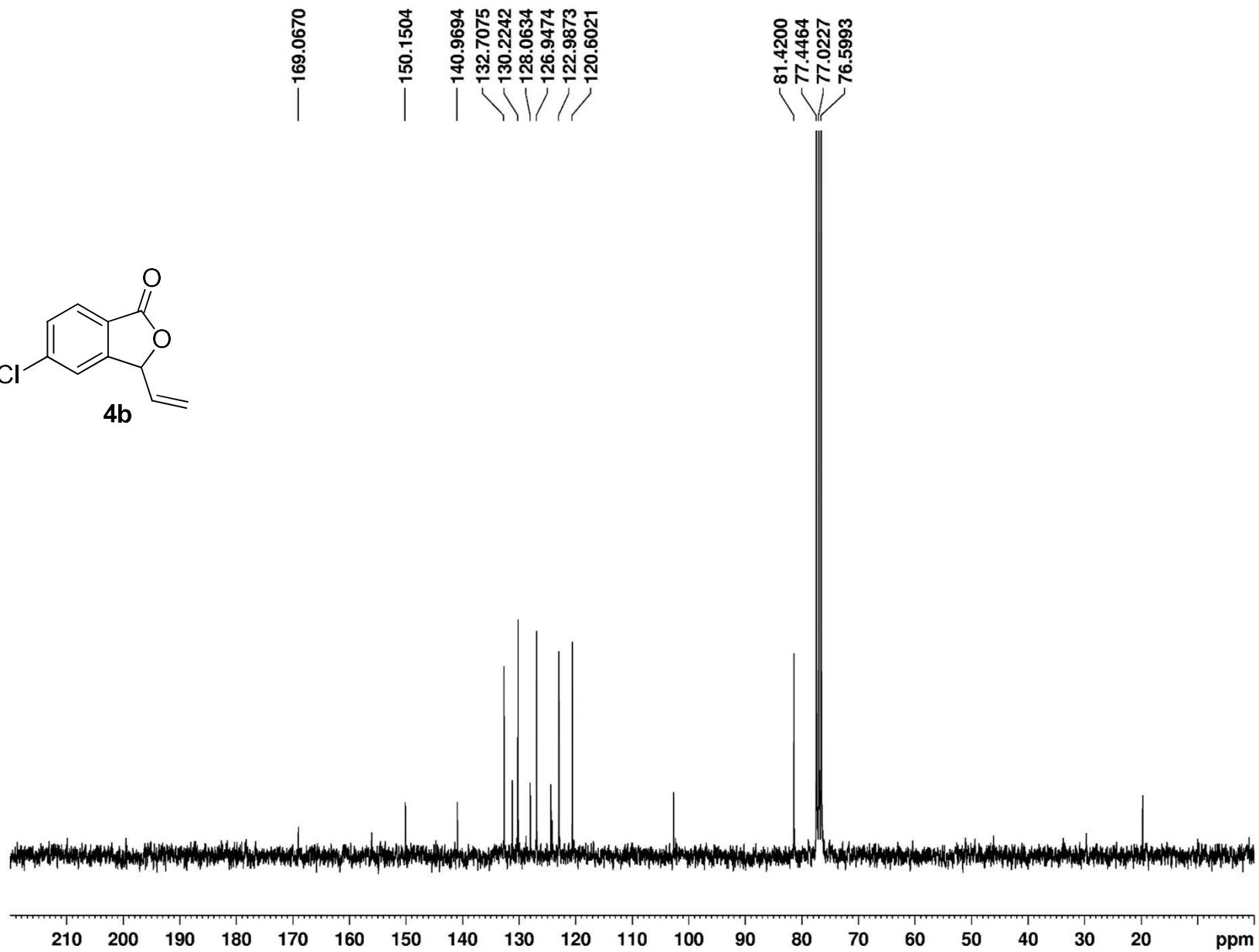
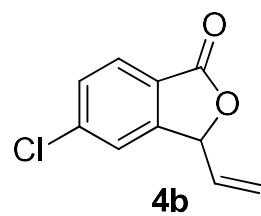
$^1\text{H}$  NMR of compound **3b** (300 MHz,  $\text{CDCl}_3$ )



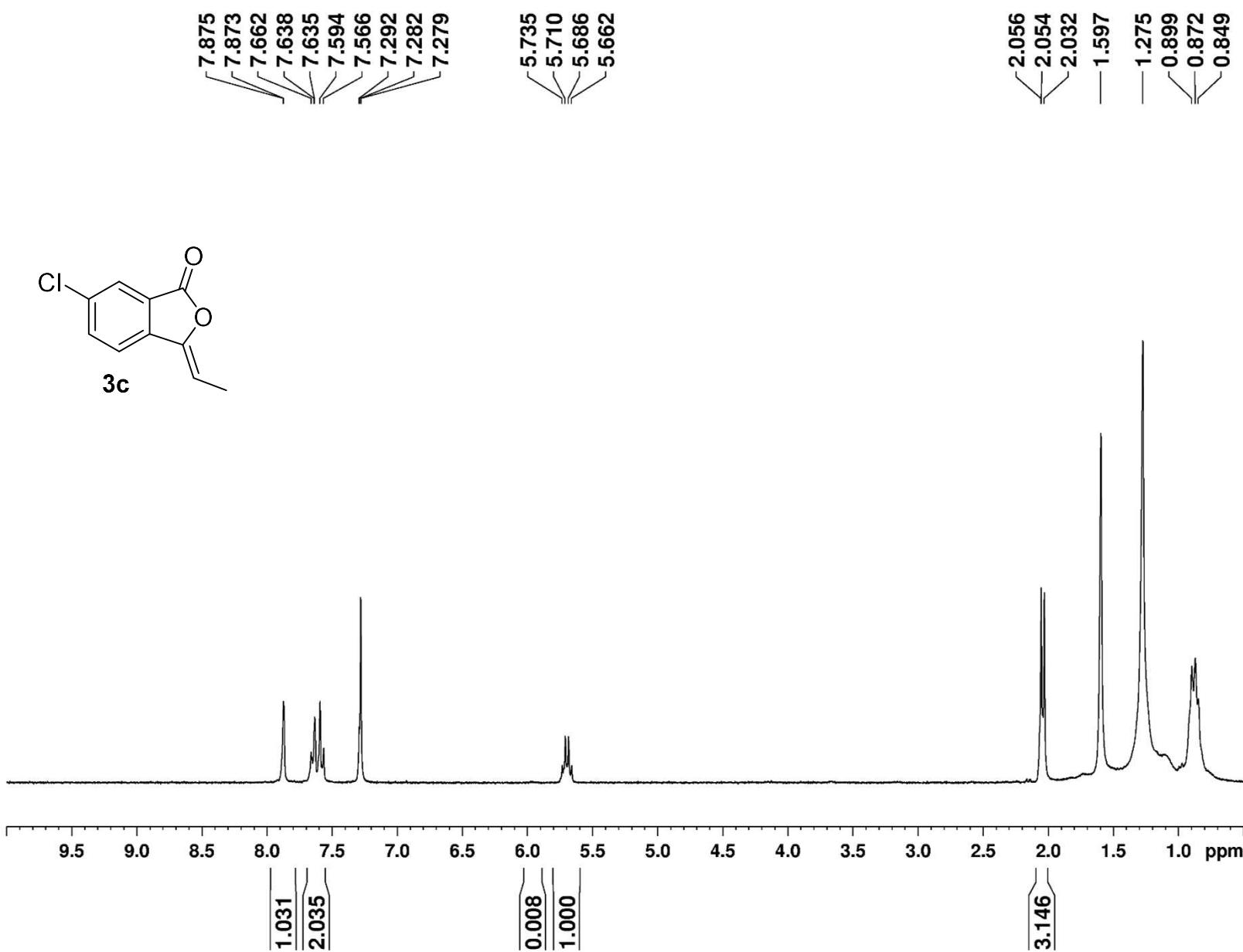
<sup>13</sup>C NMR of compound **3b** (75 MHz, CDCl<sub>3</sub>)



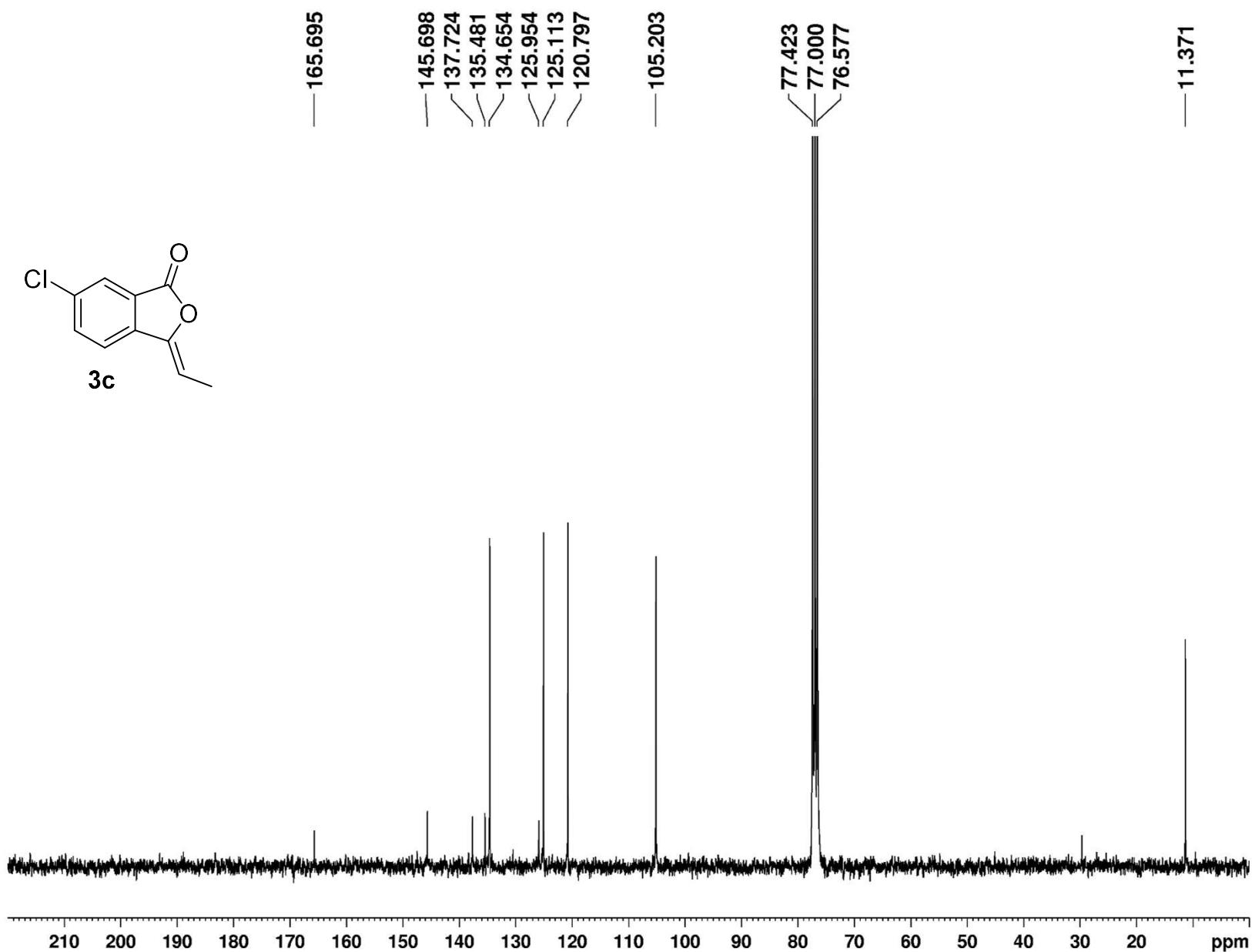
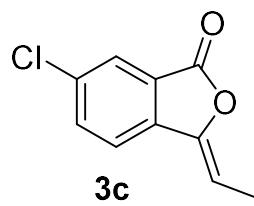
<sup>1</sup>H NMR of compound **4b** (300 MHz, CDCl<sub>3</sub>)



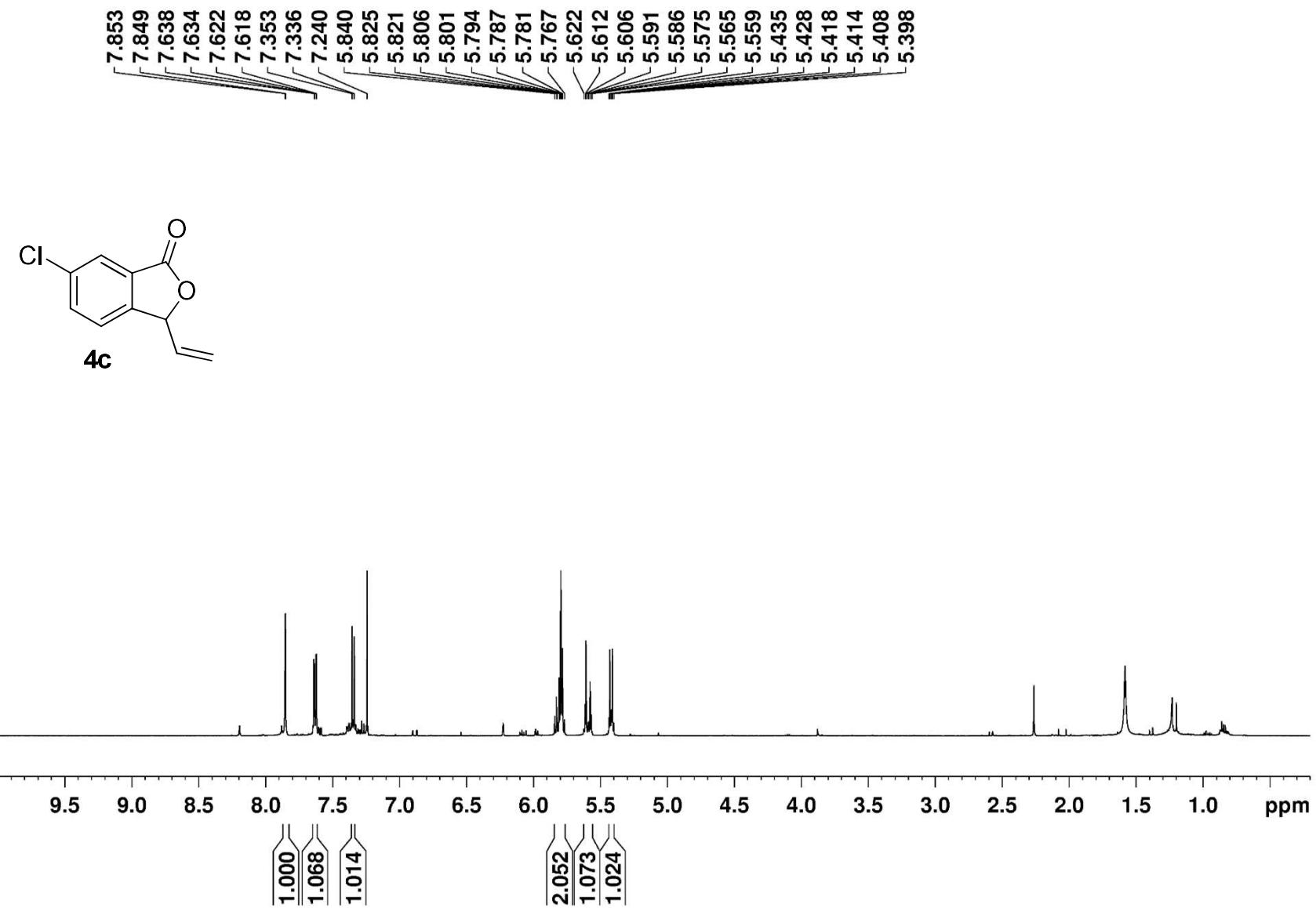
$^{13}\text{C}$  NMR of compound **4b** (75 MHz,  $\text{CDCl}_3$ )



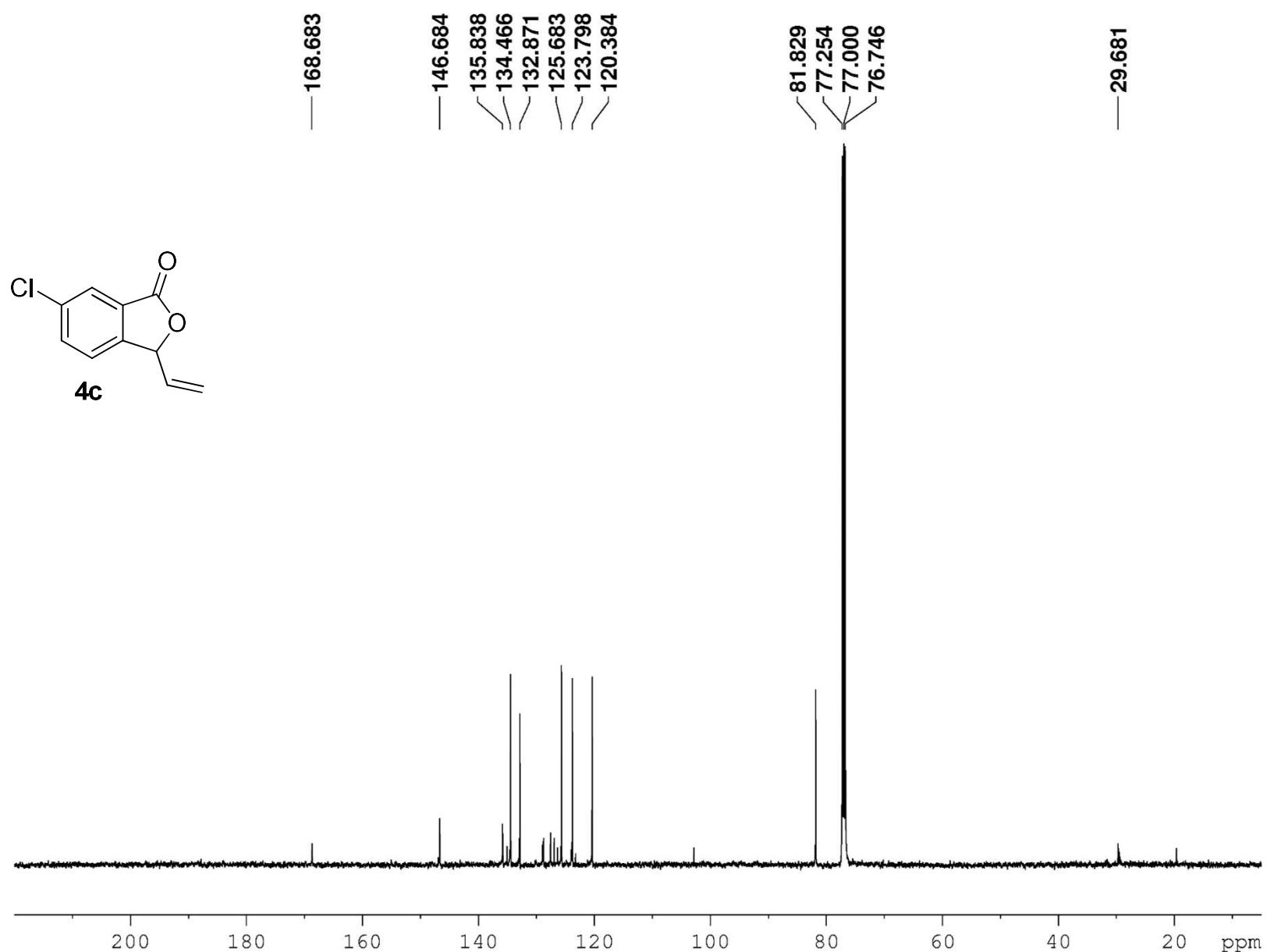
<sup>1</sup>H NMR of compound **3c** (300 MHz, CDCl<sub>3</sub>)



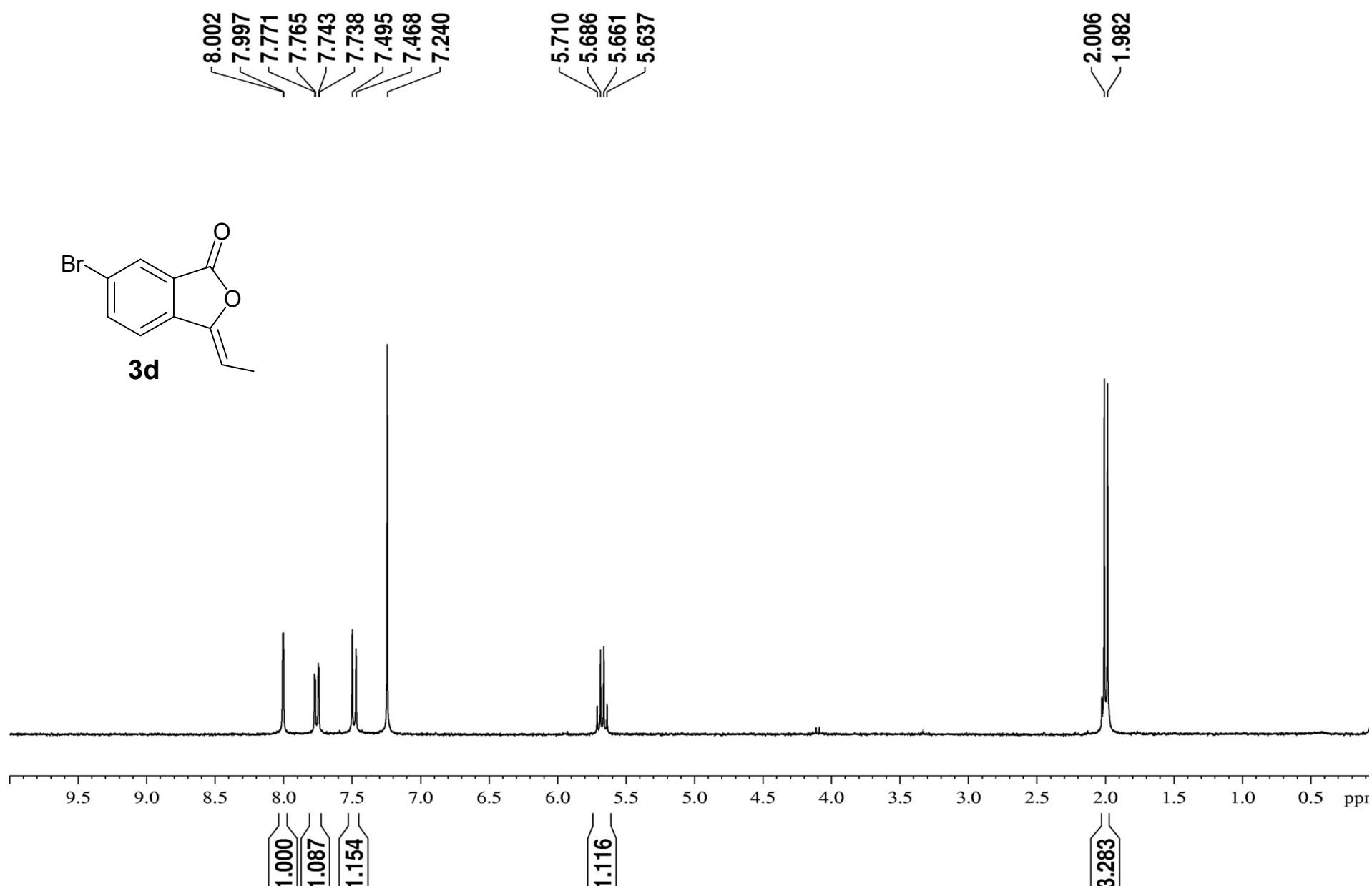
$^{13}\text{C}$  NMR of compound 3c (75 MHz,  $\text{CDCl}_3$ )



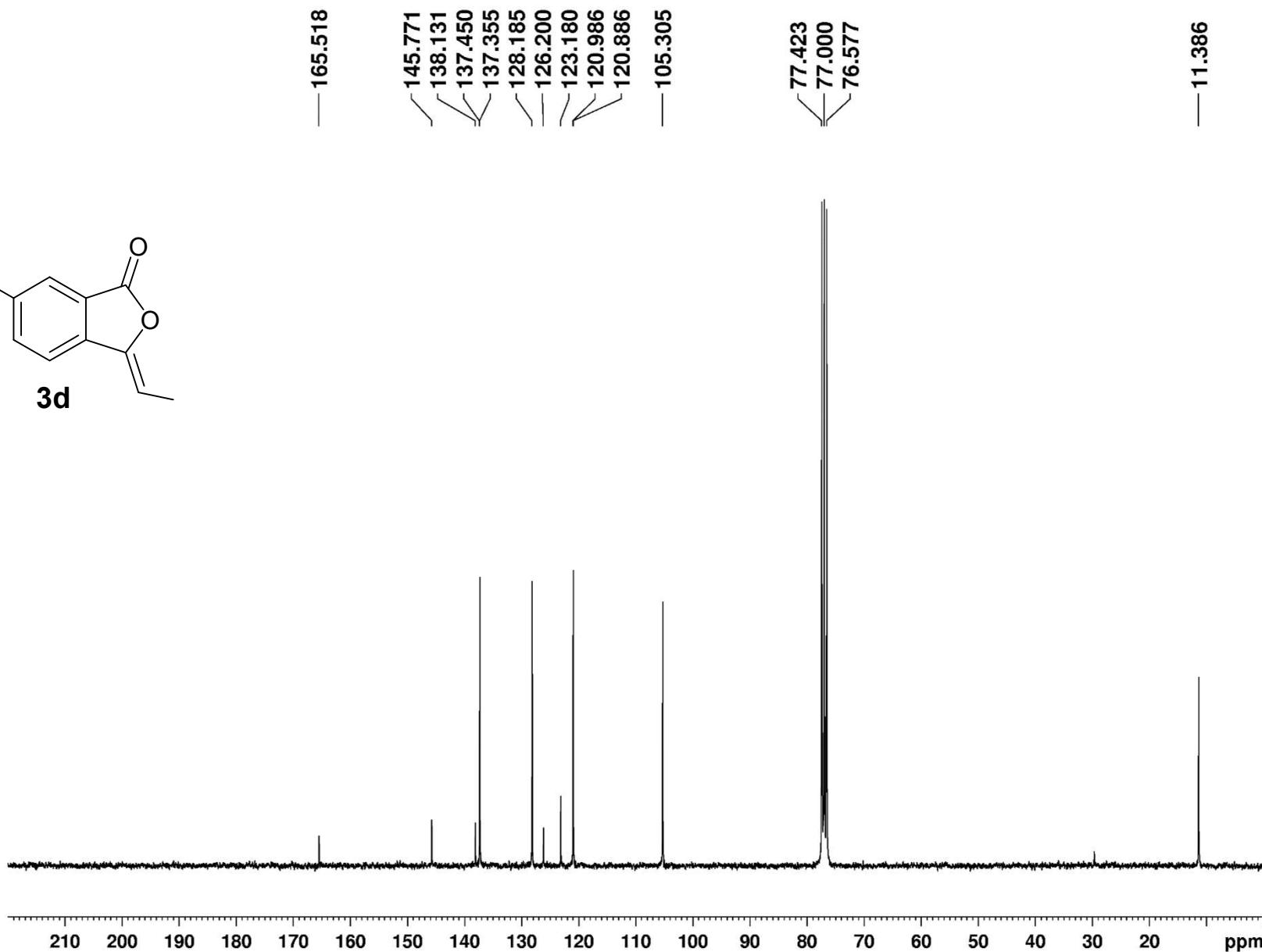
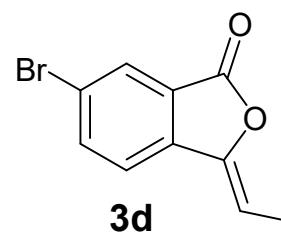
$^1\text{H}$  NMR of compound **4c** (500 MHz,  $\text{CDCl}_3$ )



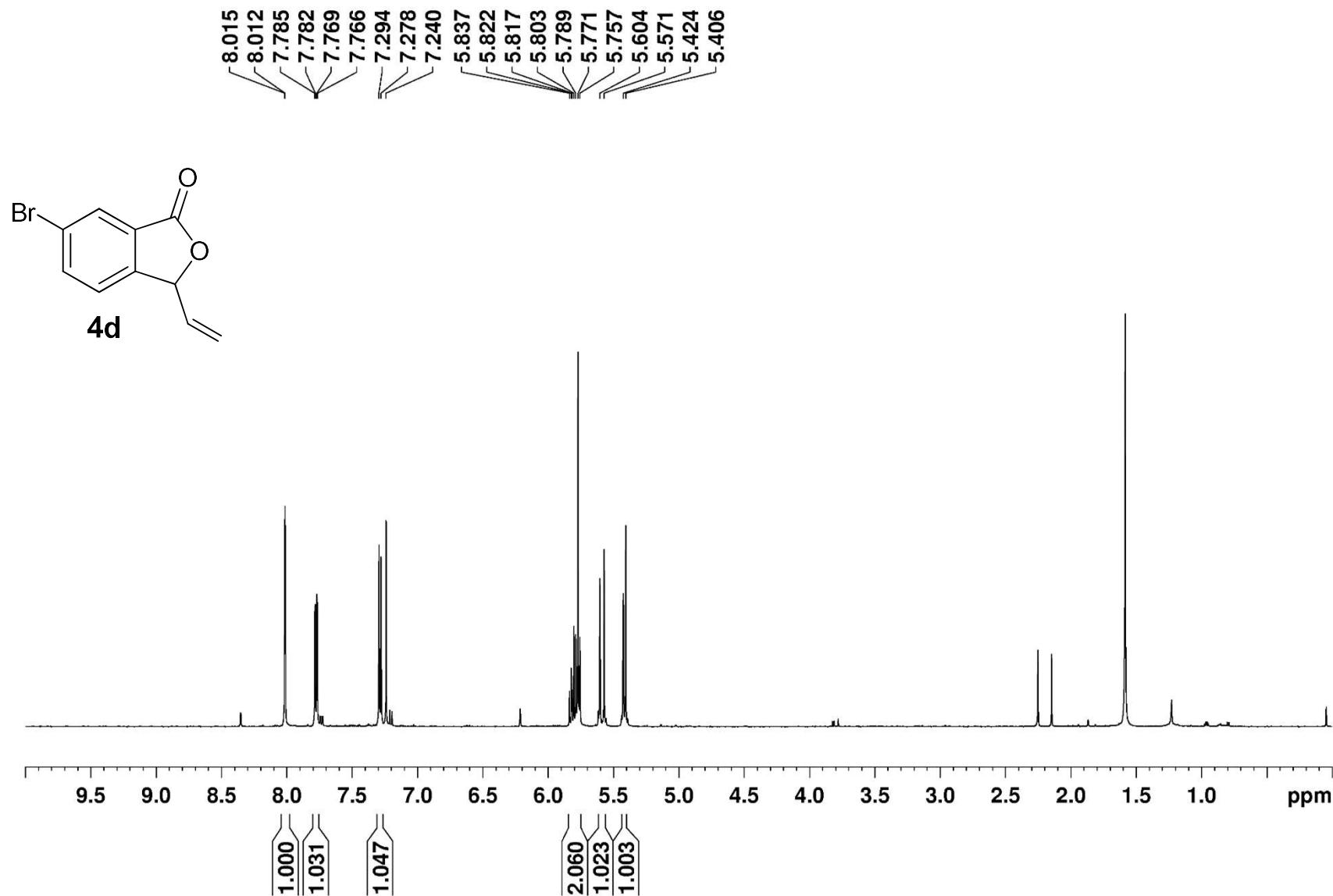
$^{13}\text{C}$  NMR of compound 4c (125 MHz,  $\text{CDCl}_3$ )



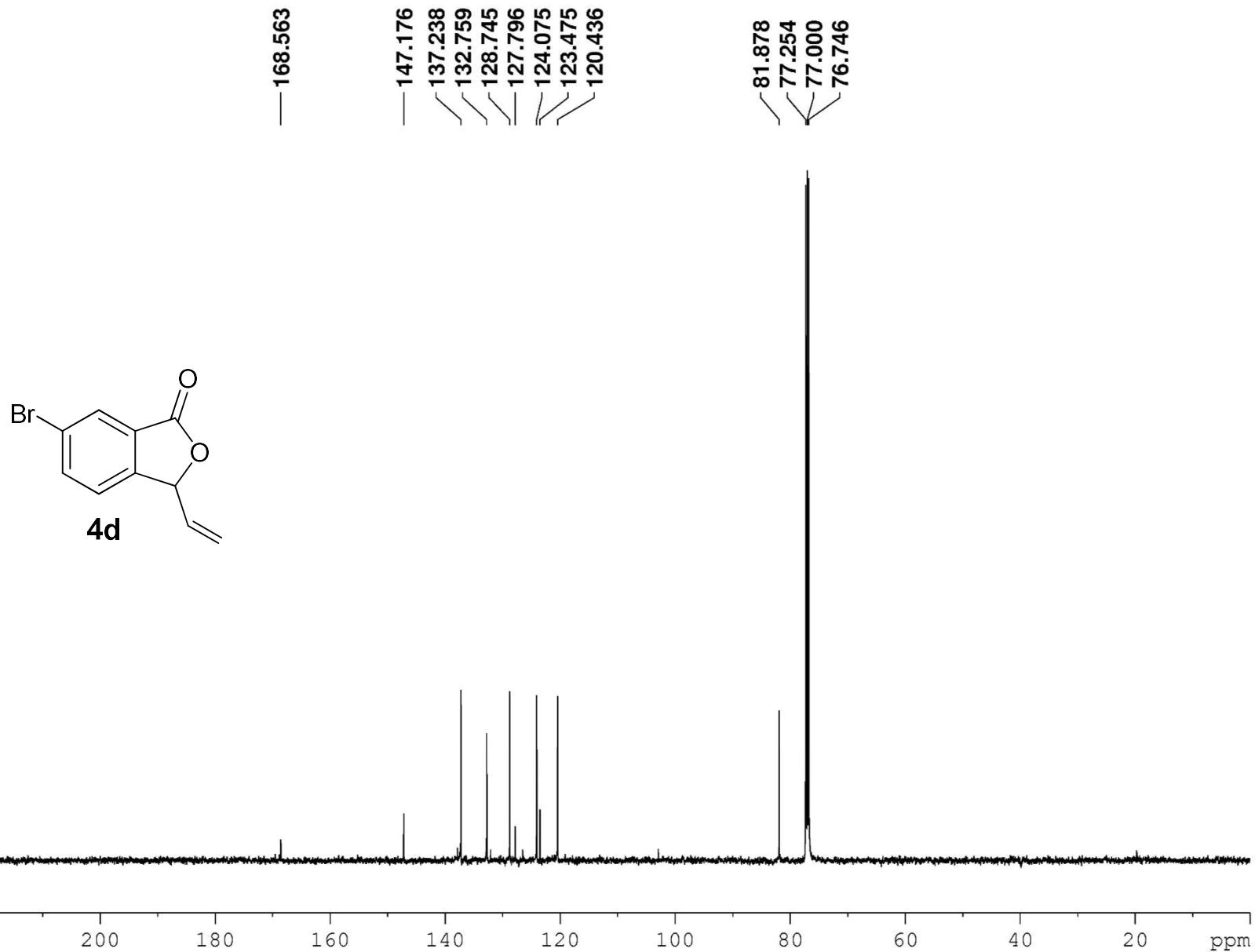
$^1\text{H}$  NMR of compound **3d** (300 MHz,  $\text{CDCl}_3$ )



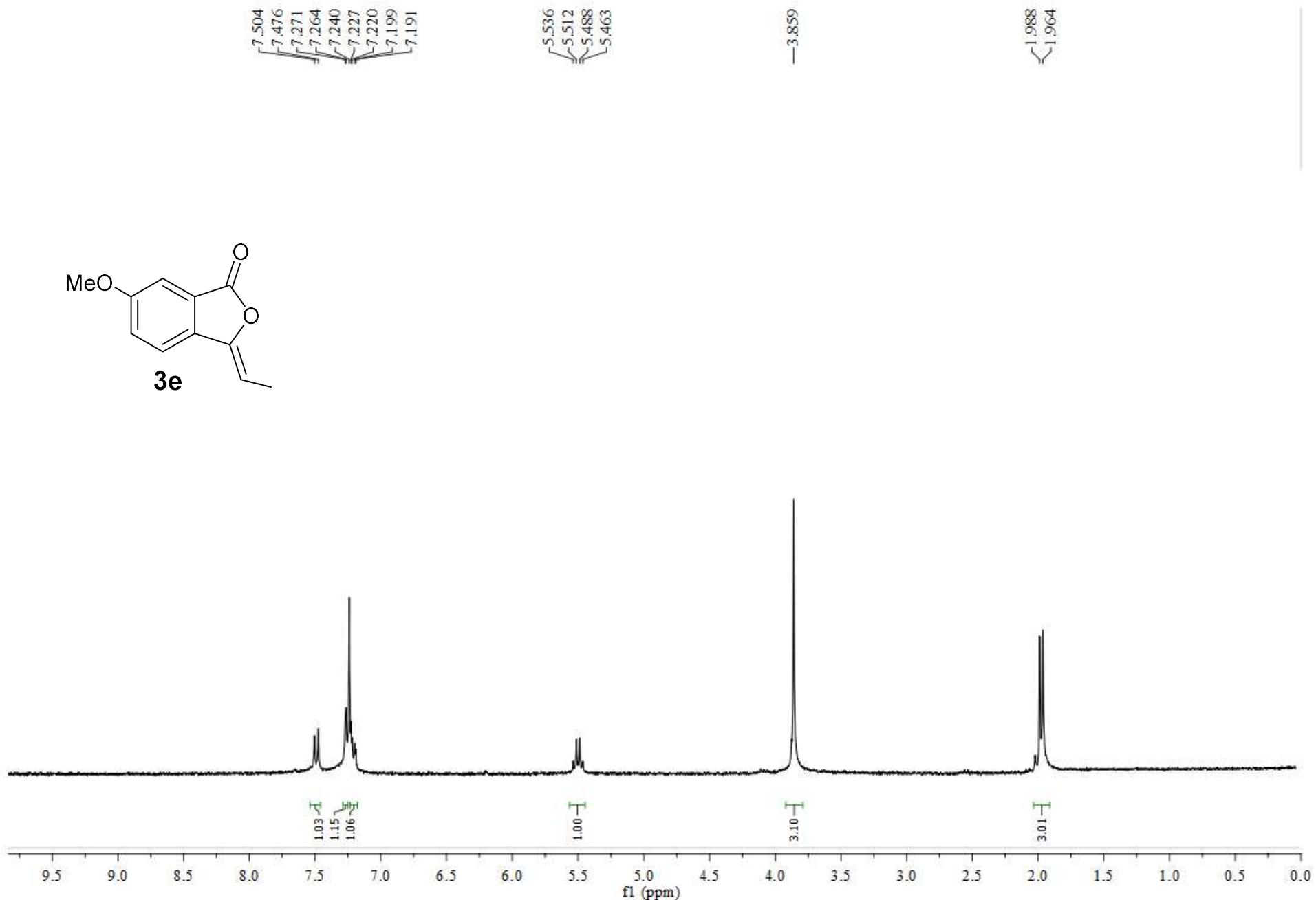
$^{13}\text{C}$  NMR of compound **3d** (75 MHz,  $\text{CDCl}_3$ )

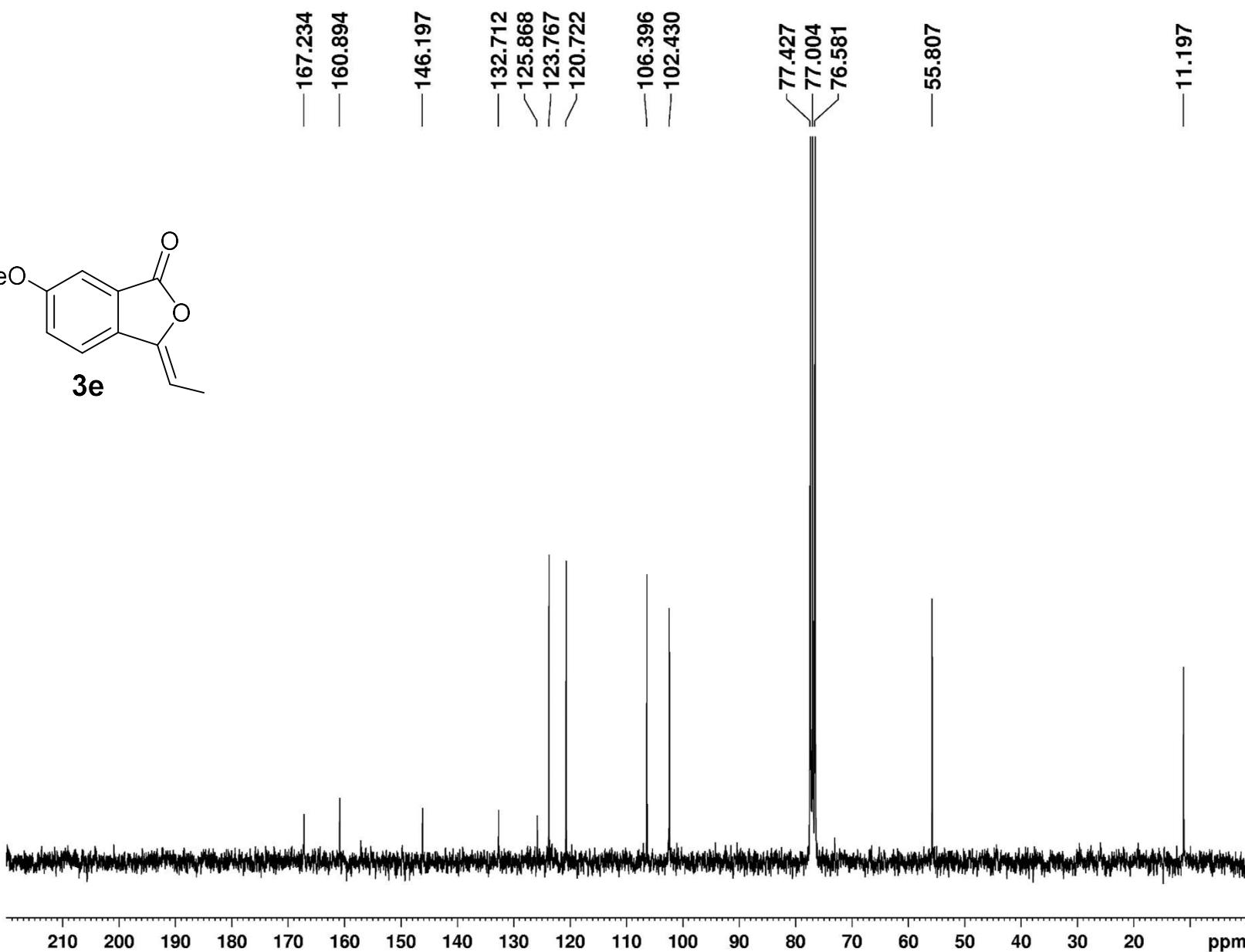
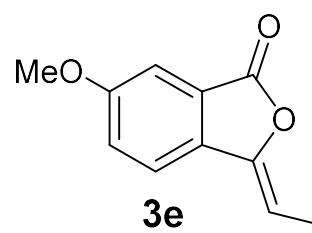


<sup>1</sup>H NMR of compound **4d** (500 MHz, CDCl<sub>3</sub>)

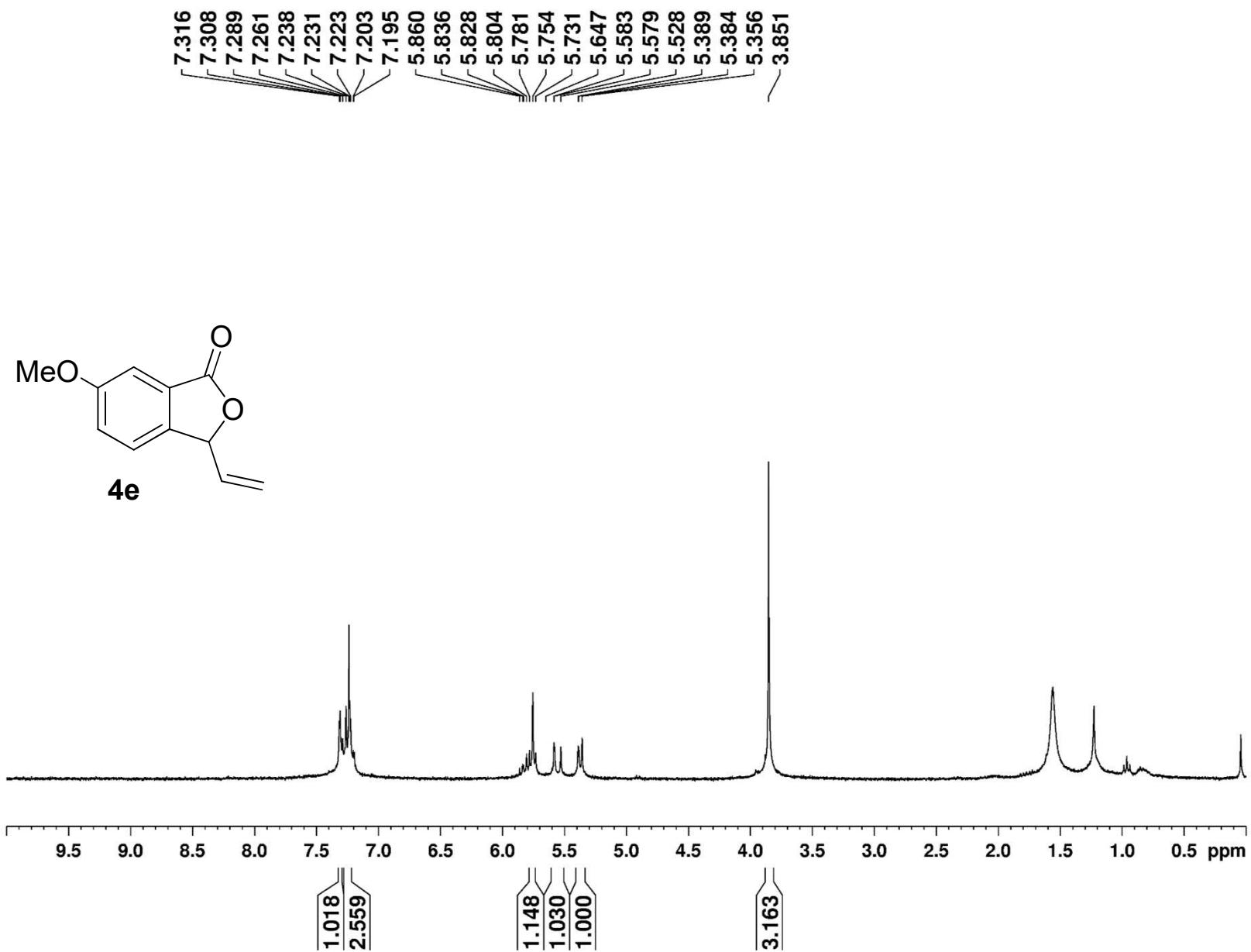


$^{13}\text{C}$  NMR of compound **4d** (125 MHz,  $\text{CDCl}_3$ )

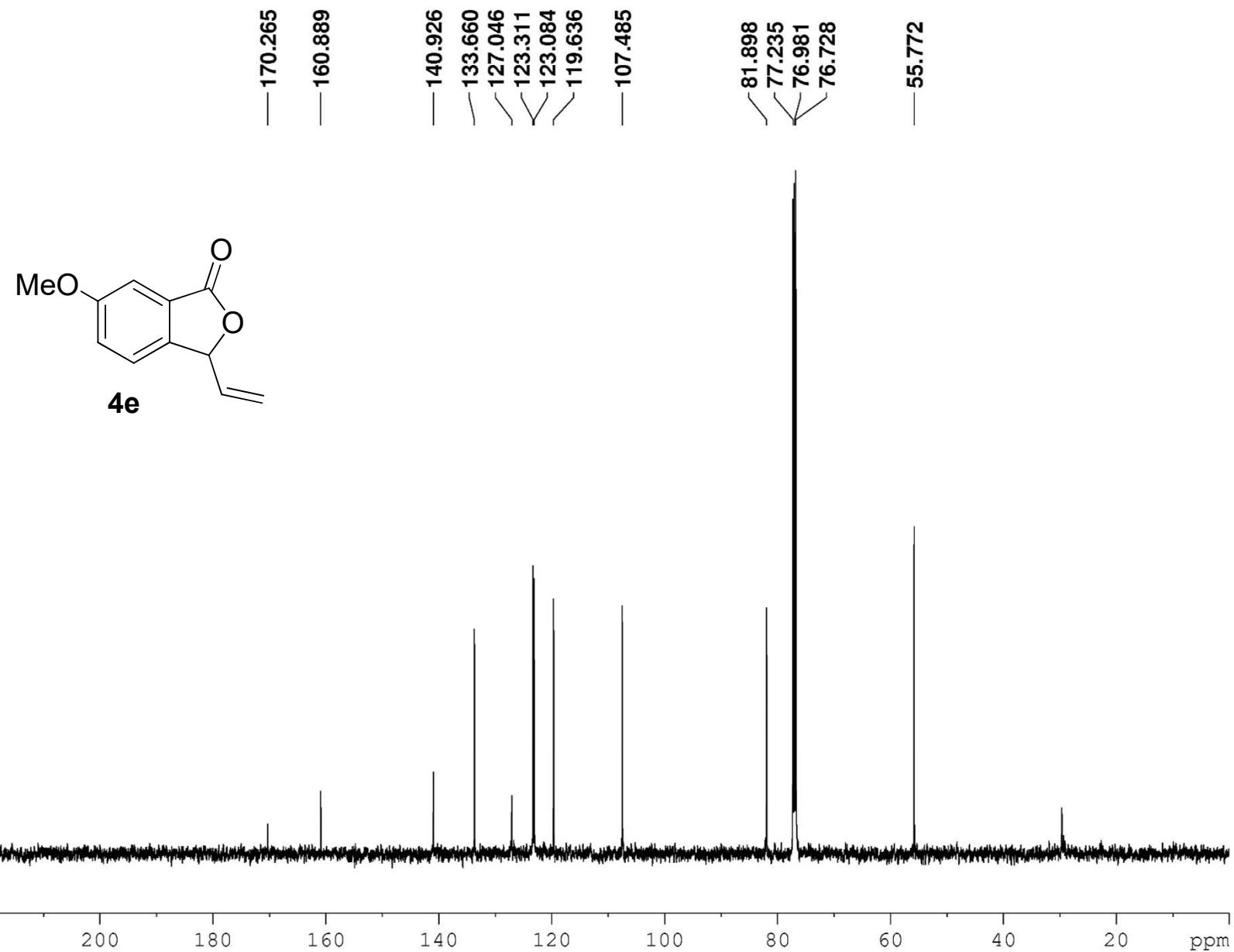




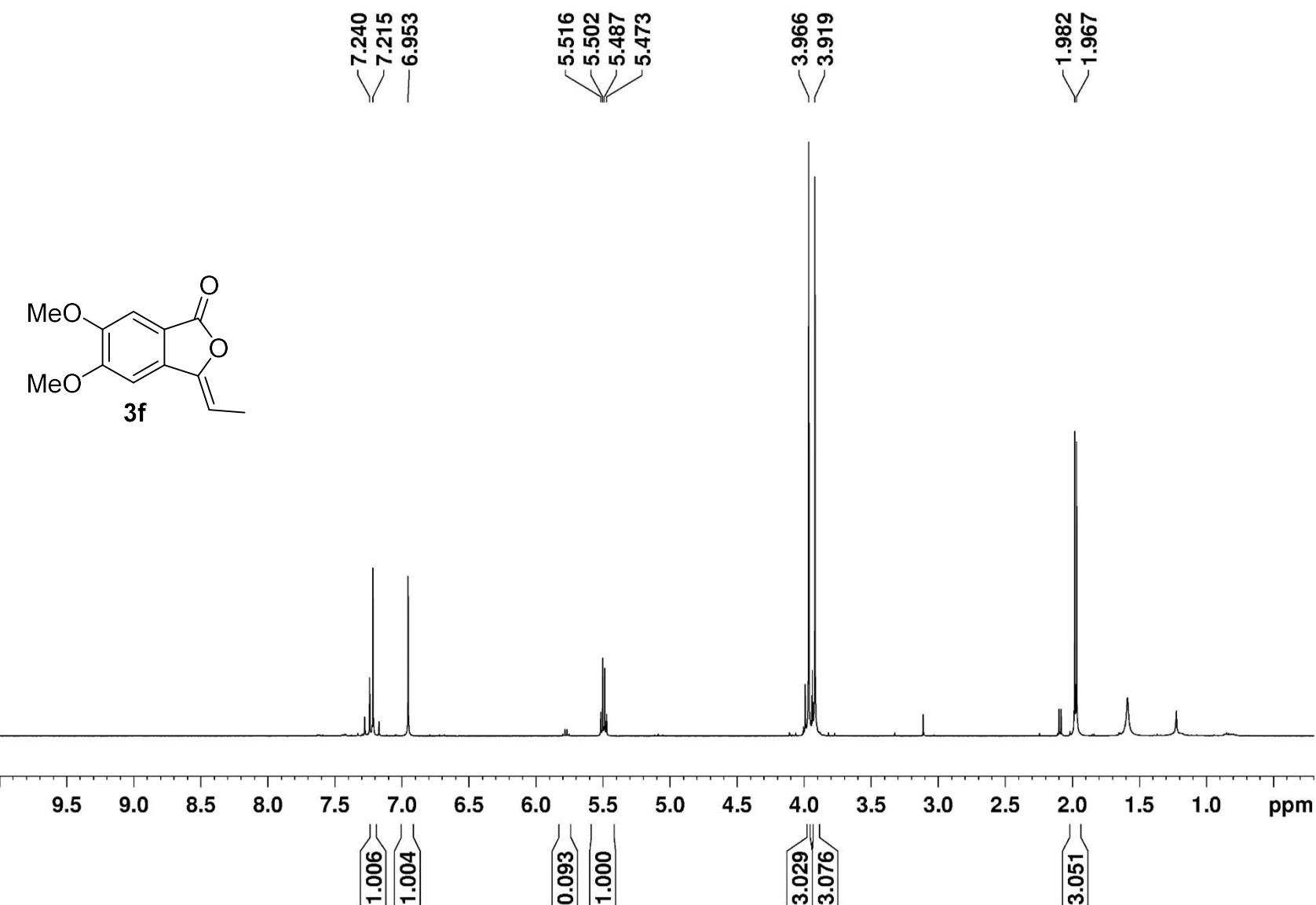
$^{13}\text{C}$  NMR of compound 3e (75 MHz,  $\text{CDCl}_3$ )



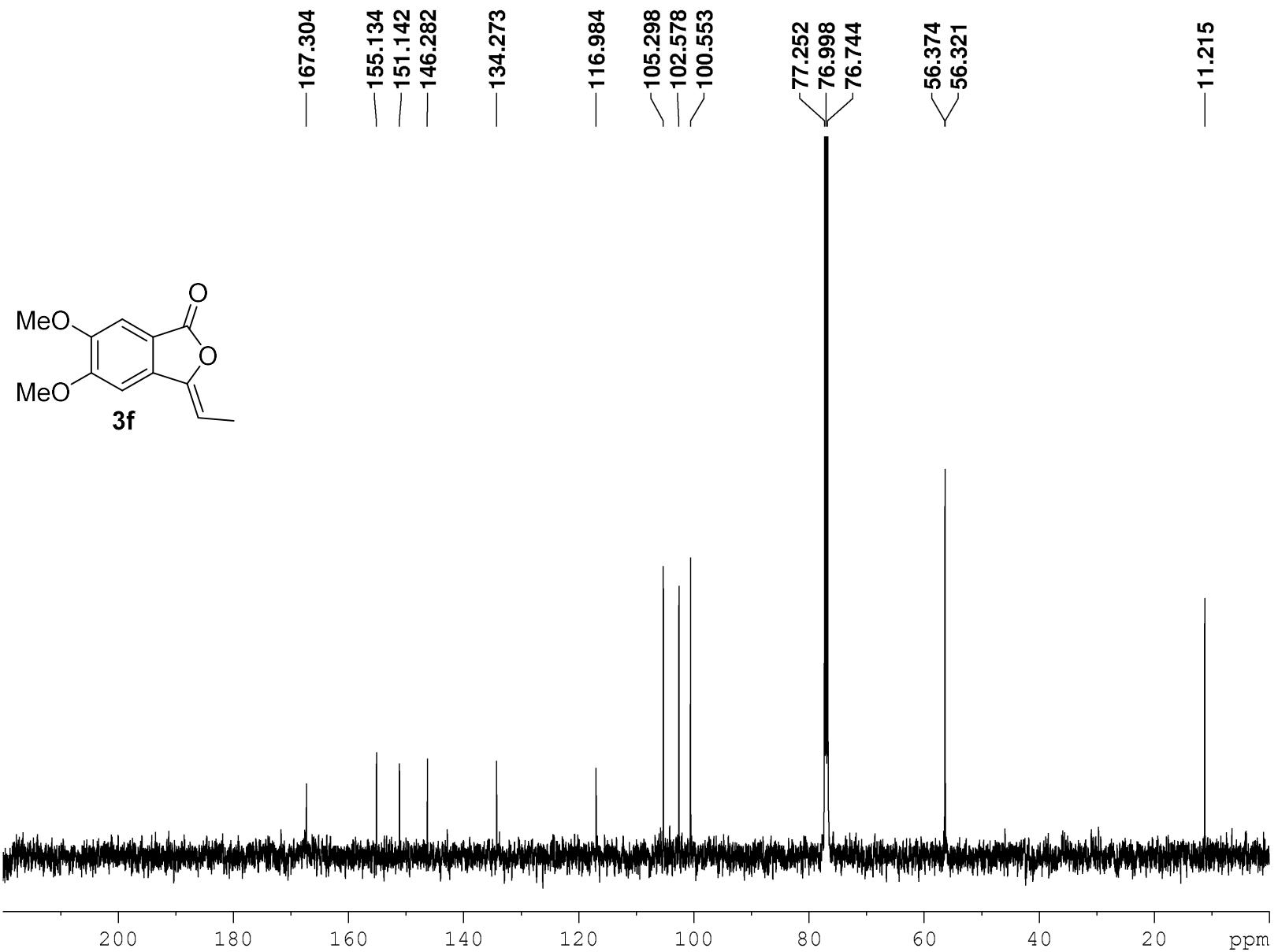
$^1\text{H}$  NMR of compound **4e** (300 MHz,  $\text{CDCl}_3$ )  
S46



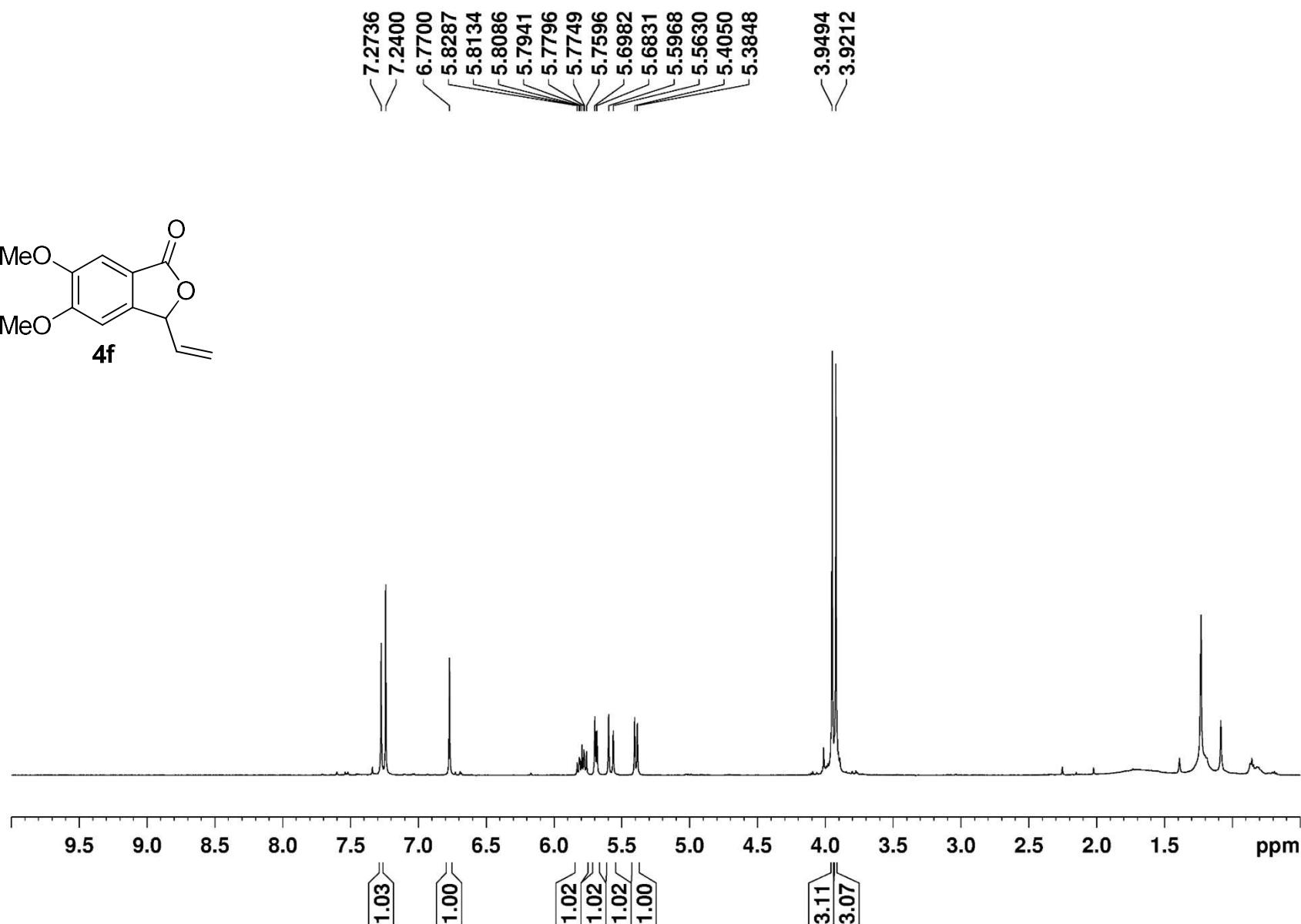
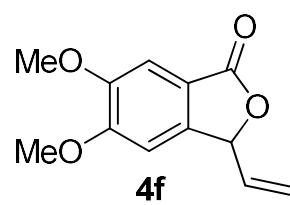
$^{13}\text{C}$  NMR of compound **4e** (125 MHz,  $\text{CDCl}_3$ )



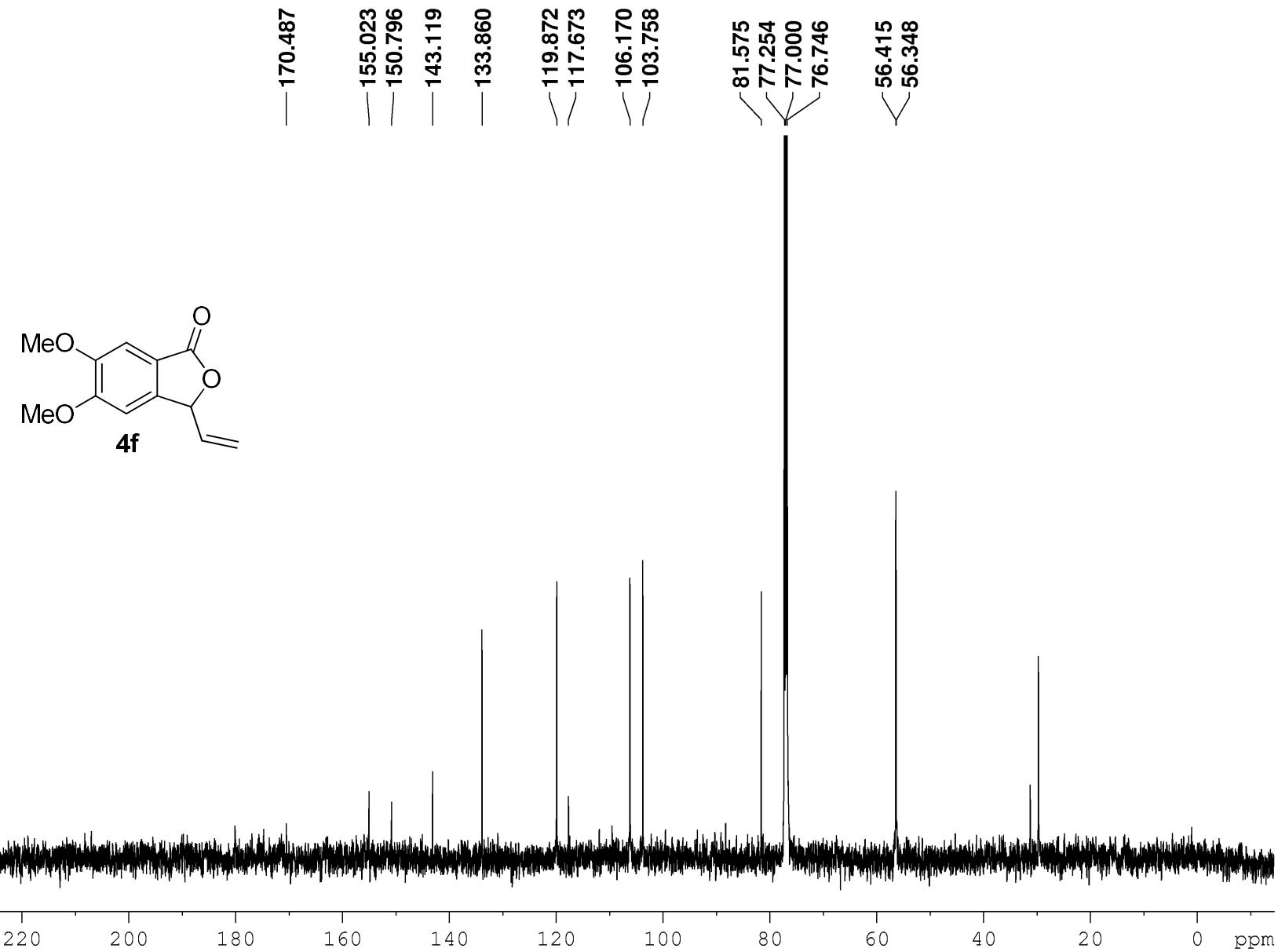
<sup>1</sup>H NMR of compound **3f** (500 MHz, CDCl<sub>3</sub>)



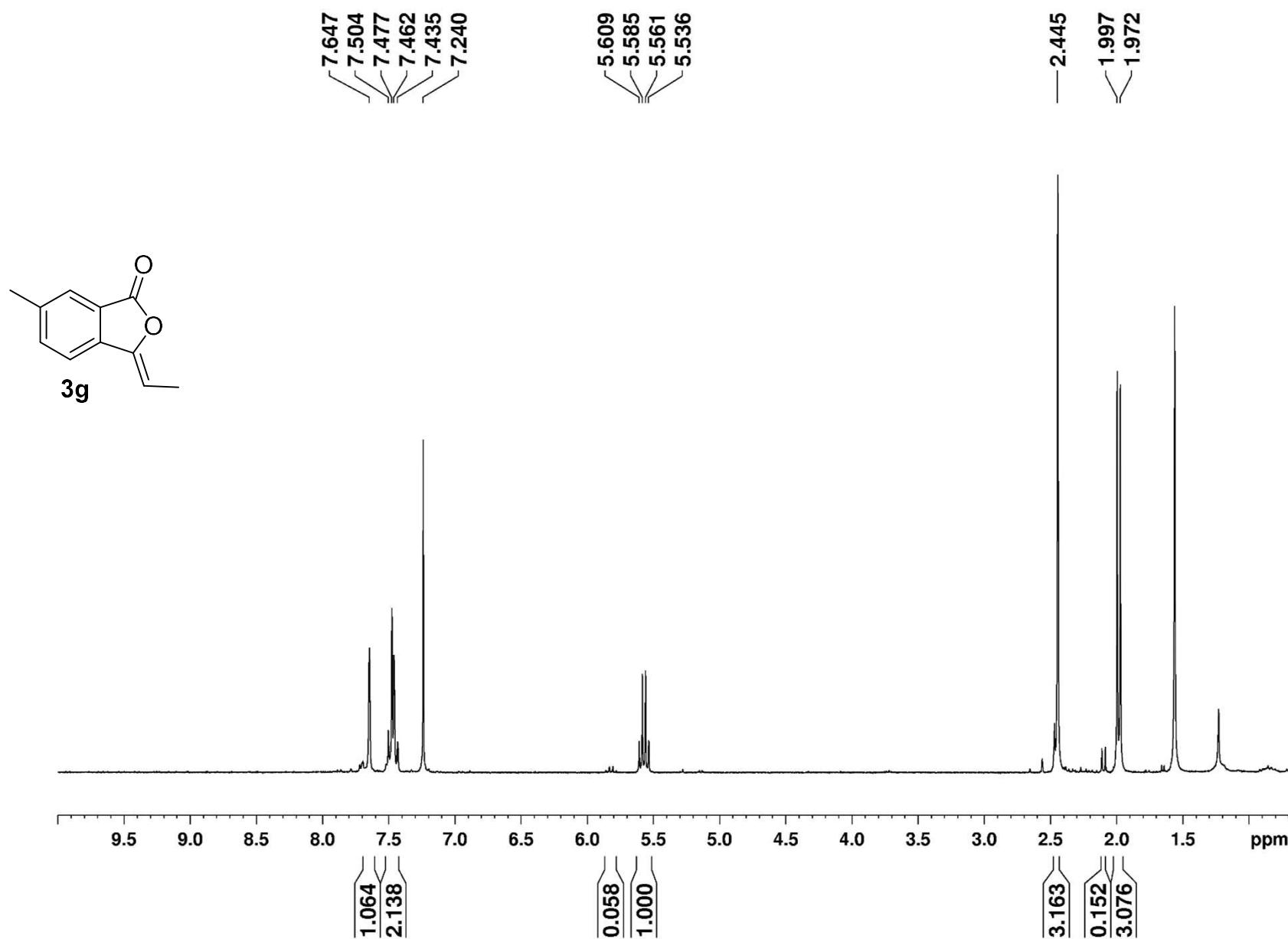
$^{13}\text{C}$  NMR of compound **3f** (125 MHz,  $\text{CDCl}_3$ )



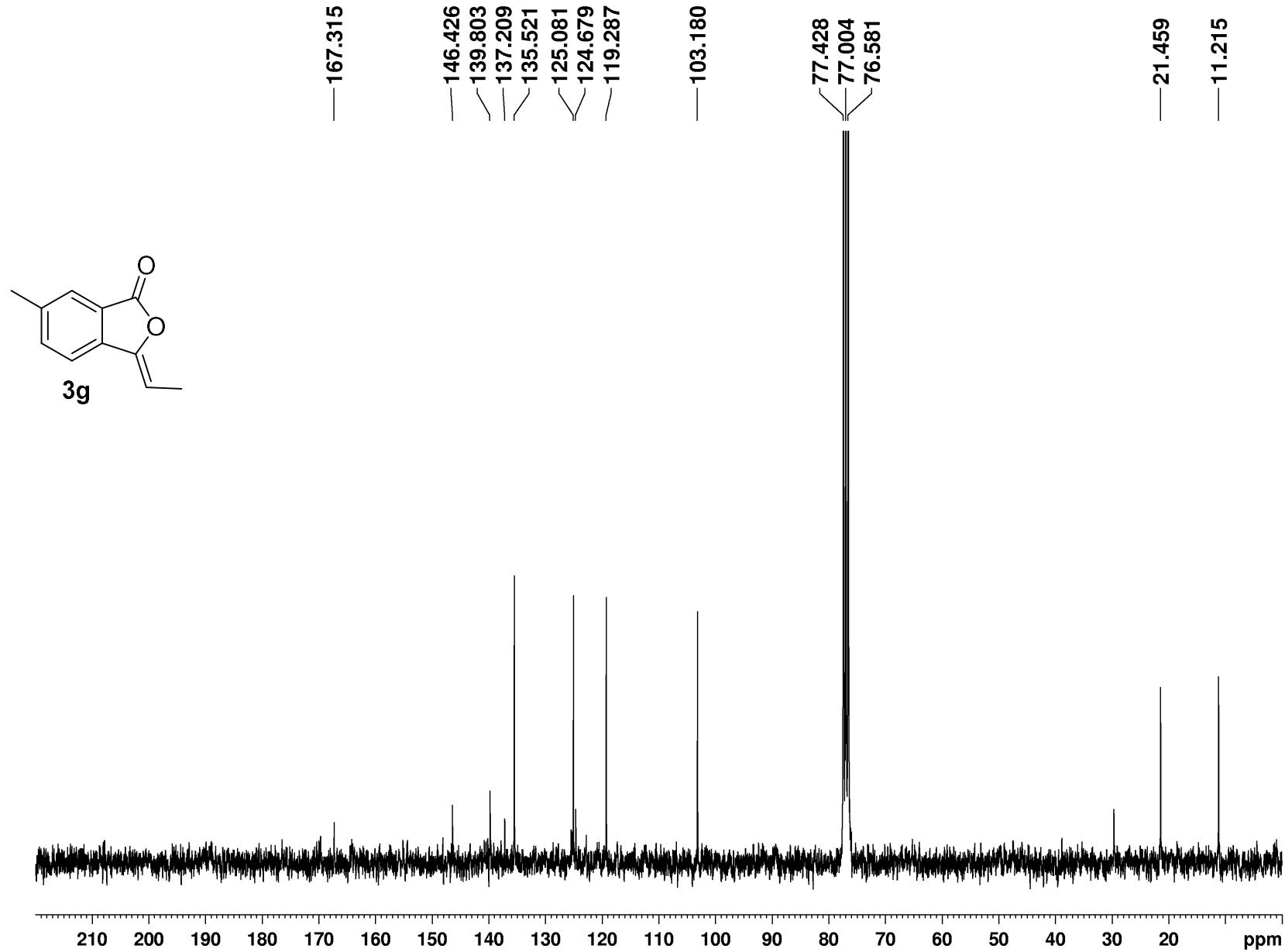
<sup>1</sup>H NMR of compound **4f** (500 MHz, CDCl<sub>3</sub>)



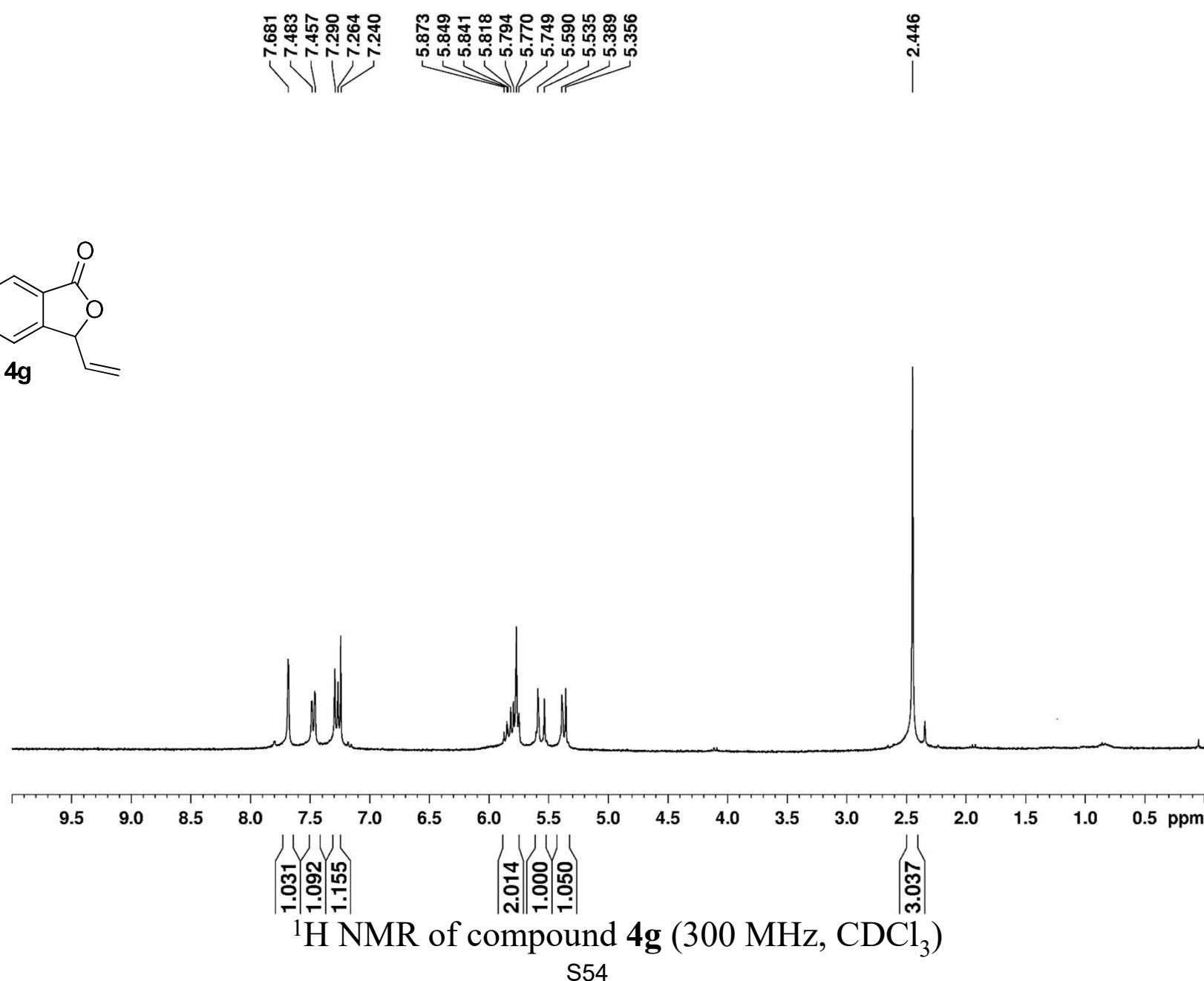
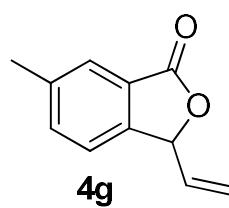
$^{13}\text{C}$  NMR of compound **4f** (125 MHz,  $\text{CDCl}_3$ )

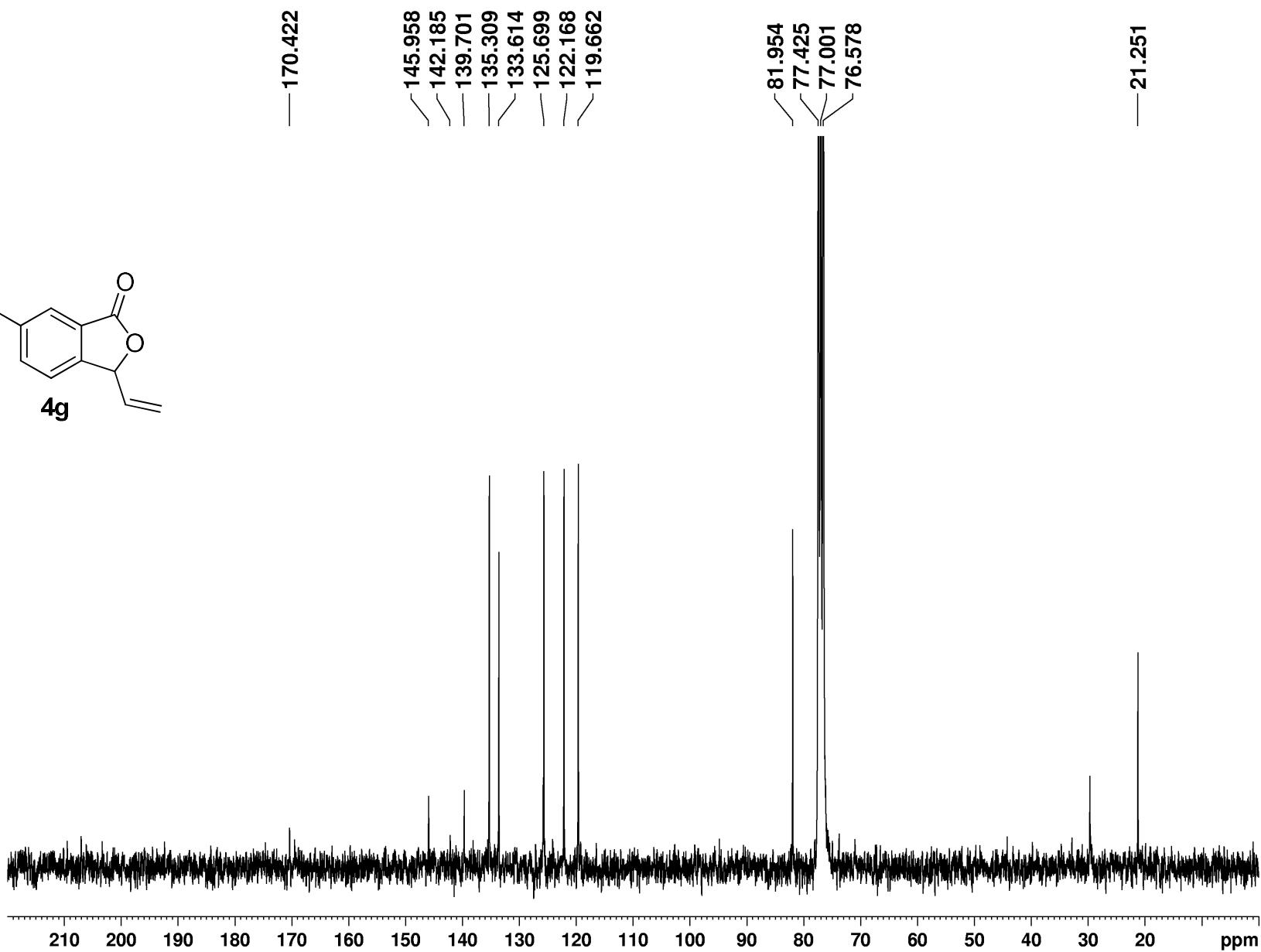
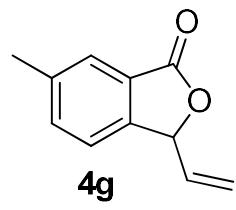


$^1\text{H}$  NMR of compound **3g** (300 MHz,  $\text{CDCl}_3$ )

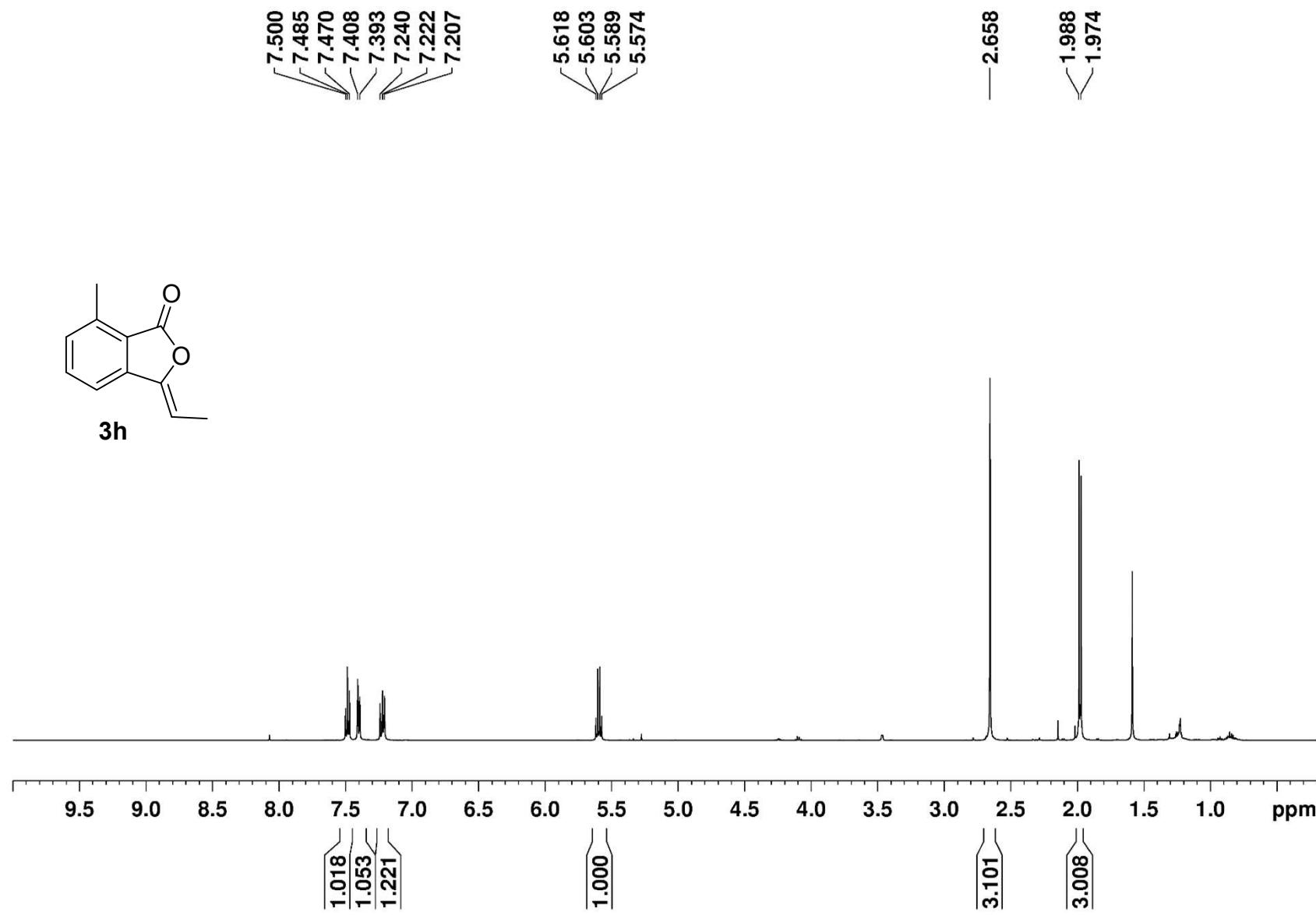


$^{13}\text{C}$  NMR of compound **3g** (75 MHz,  $\text{CDCl}_3$ )

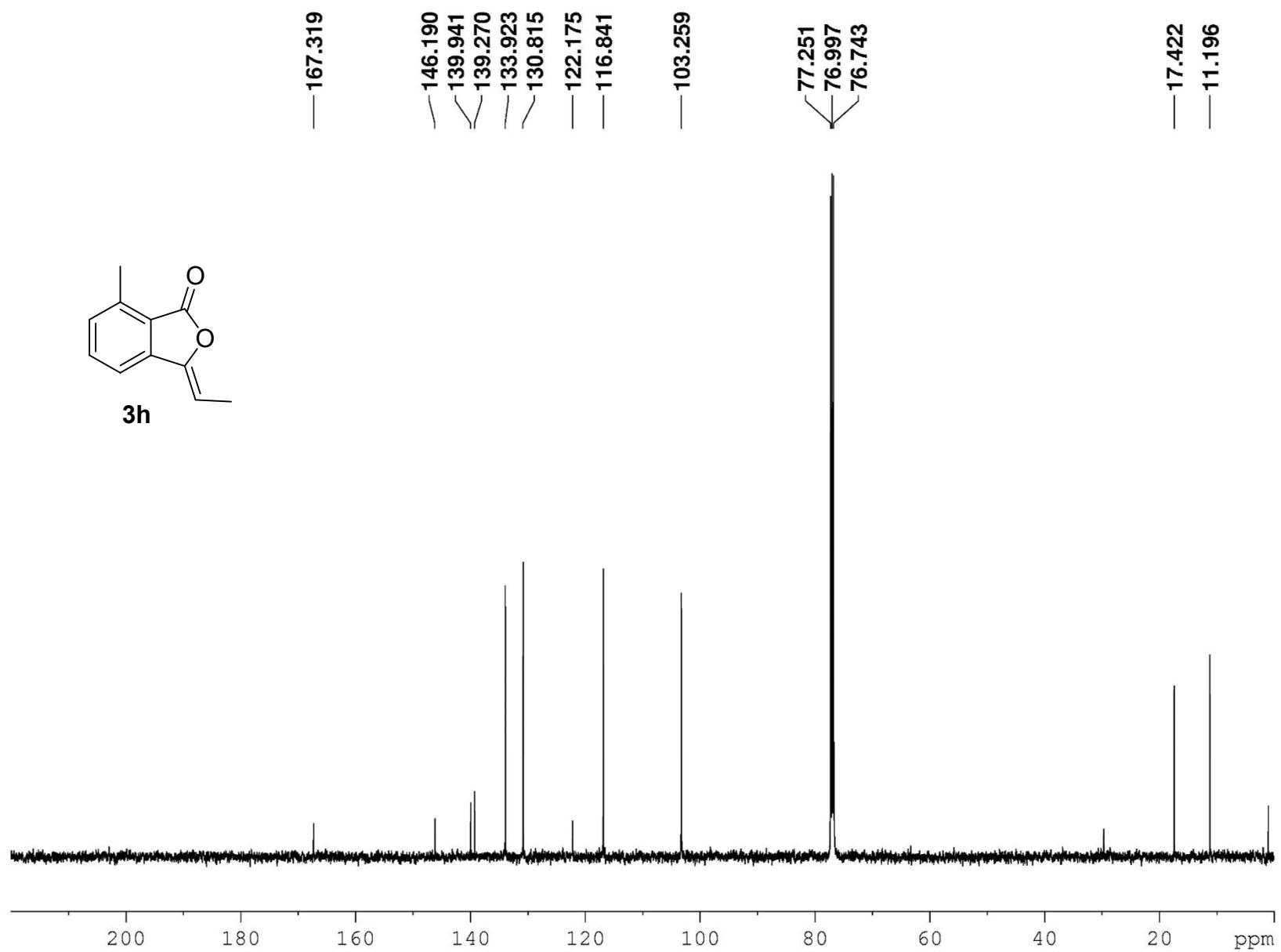
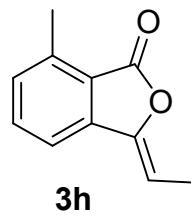




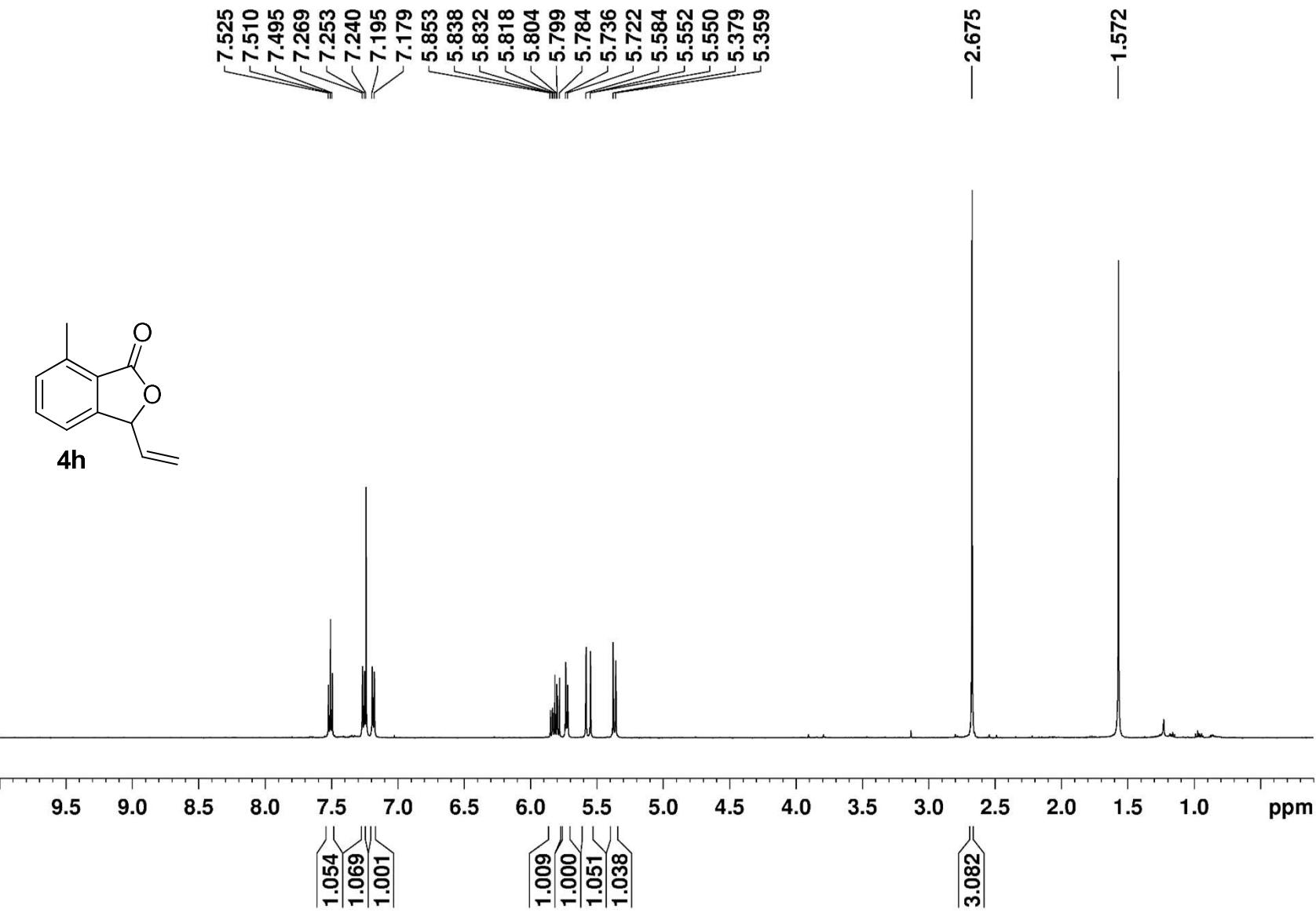
$^{13}\text{C}$  NMR of compound 4g (75 MHz,  $\text{CDCl}_3$ )



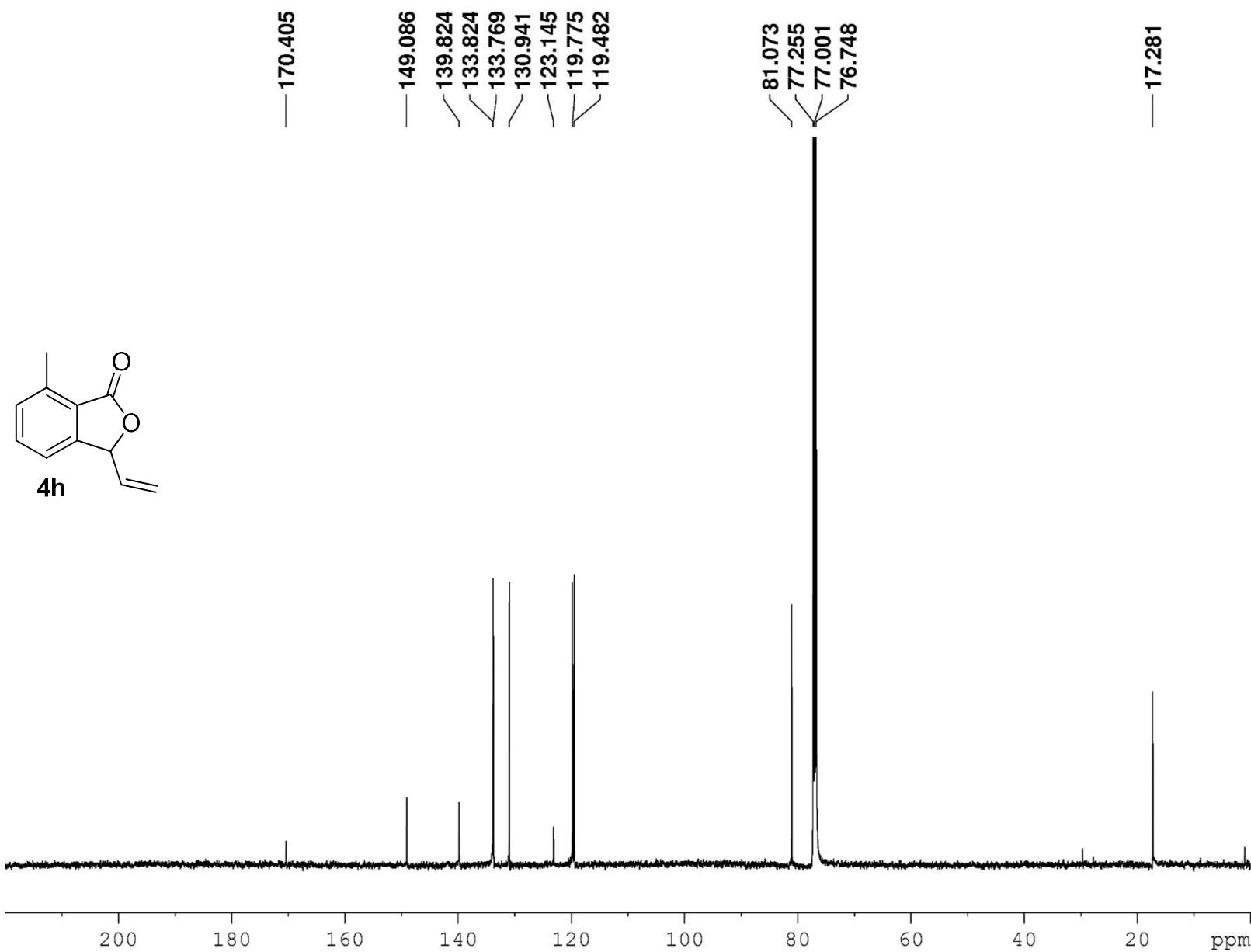
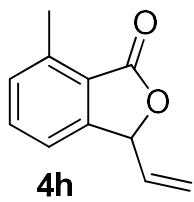
$^1\text{H}$  NMR of compound **3h** (500 MHz,  $\text{CDCl}_3$ )



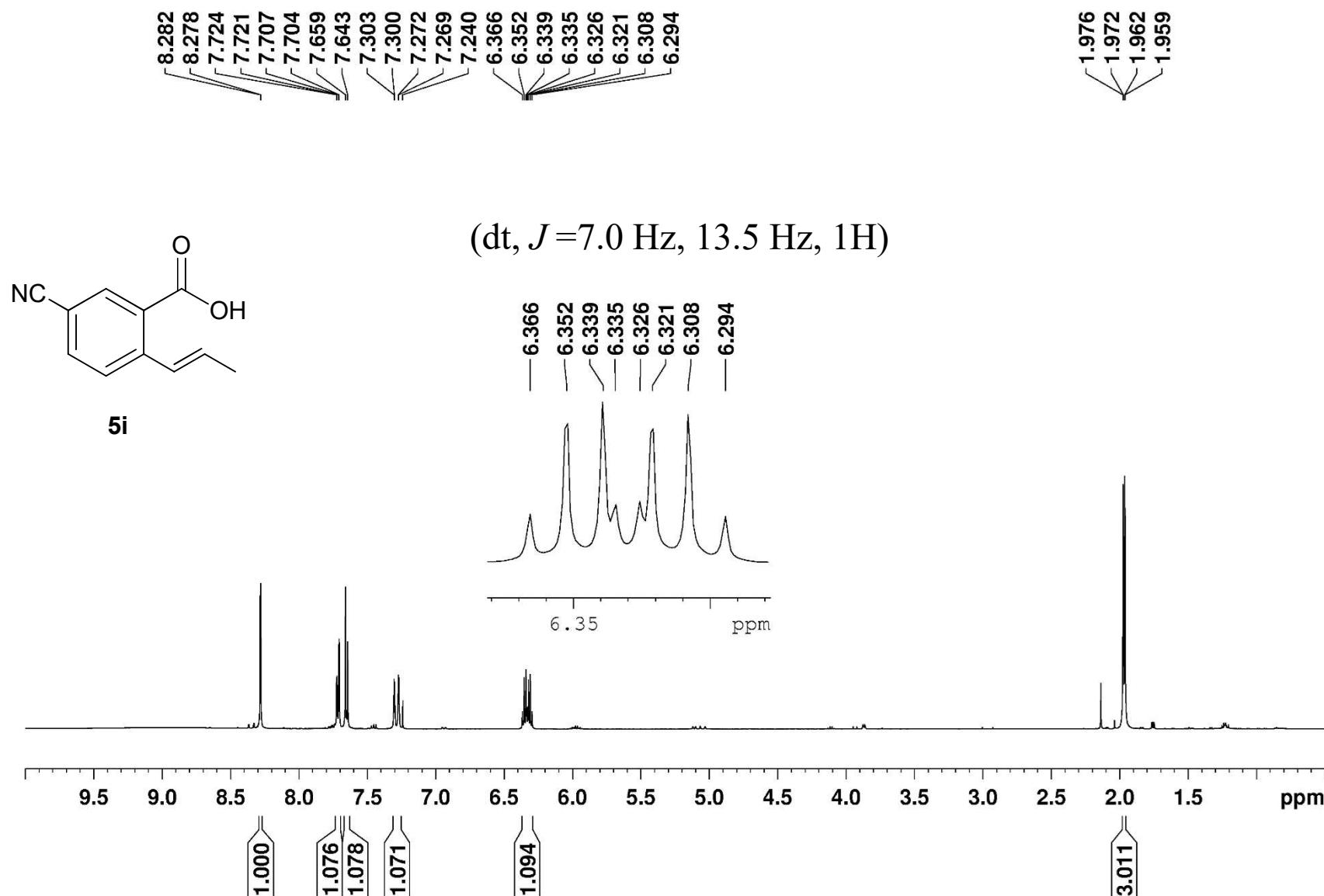
$^{13}\text{C}$  NMR of compound **3h** (125 MHz,  $\text{CDCl}_3$ )



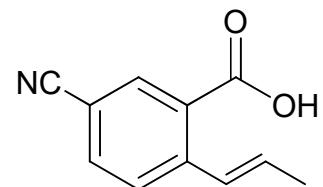
$^1\text{H}$  NMR of compound **4h** (500 MHz,  $\text{CDCl}_3$ )  
S58



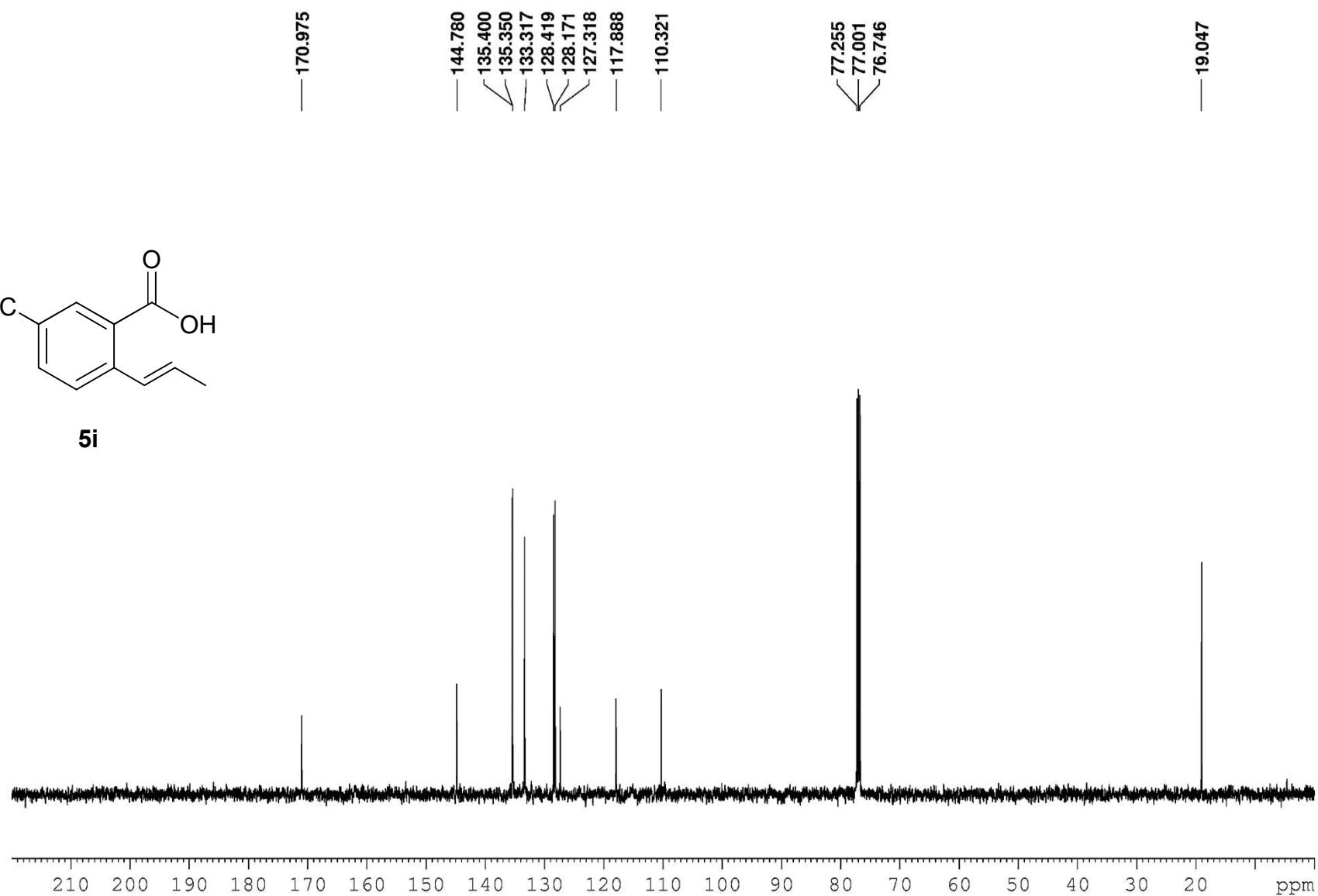
$^{13}\text{C}$  NMR of compound **4h** (125 MHz,  $\text{CDCl}_3$ )



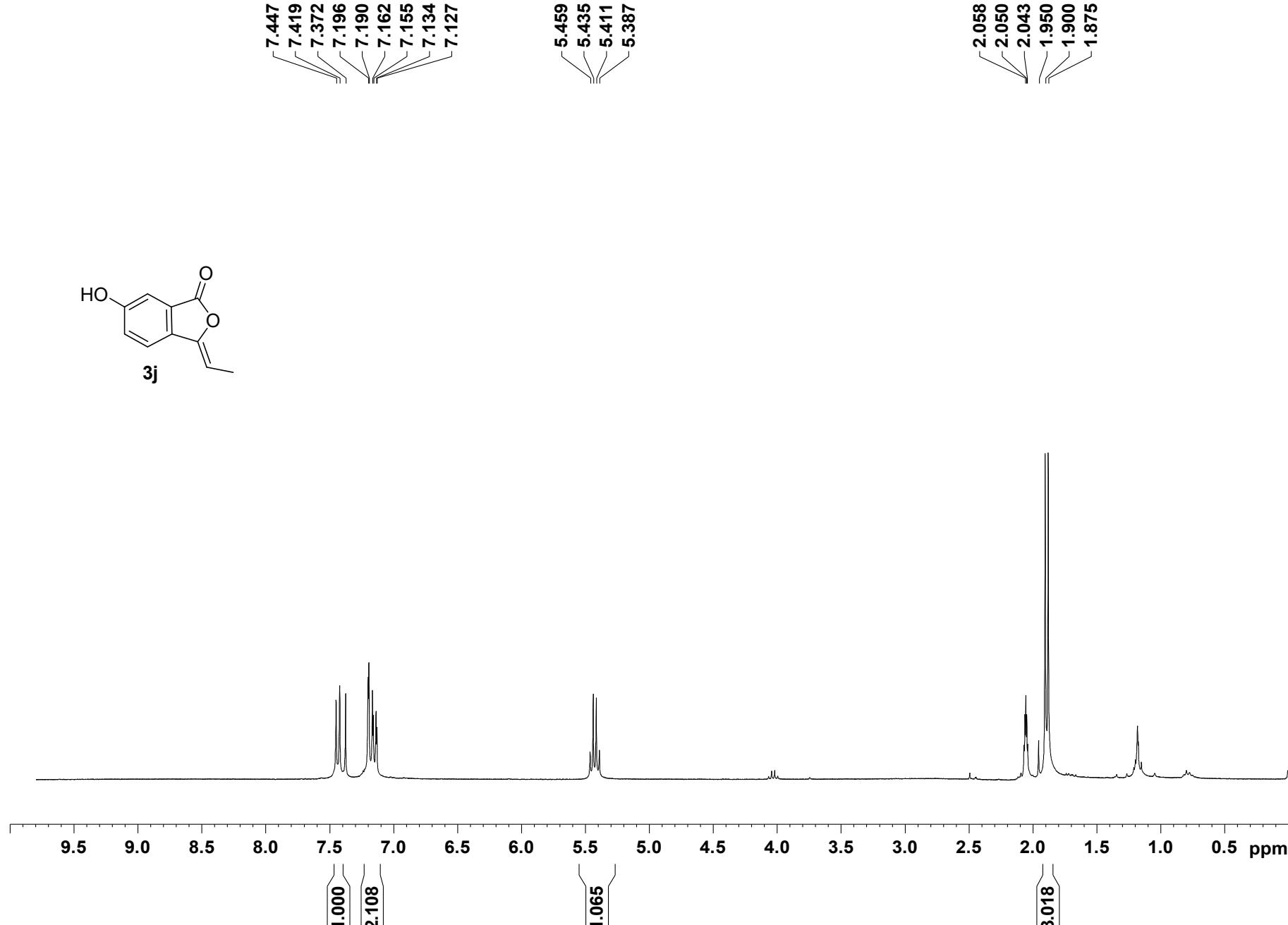
<sup>1</sup>H NMR of compound **5i** (500 MHz, CDCl<sub>3</sub>)



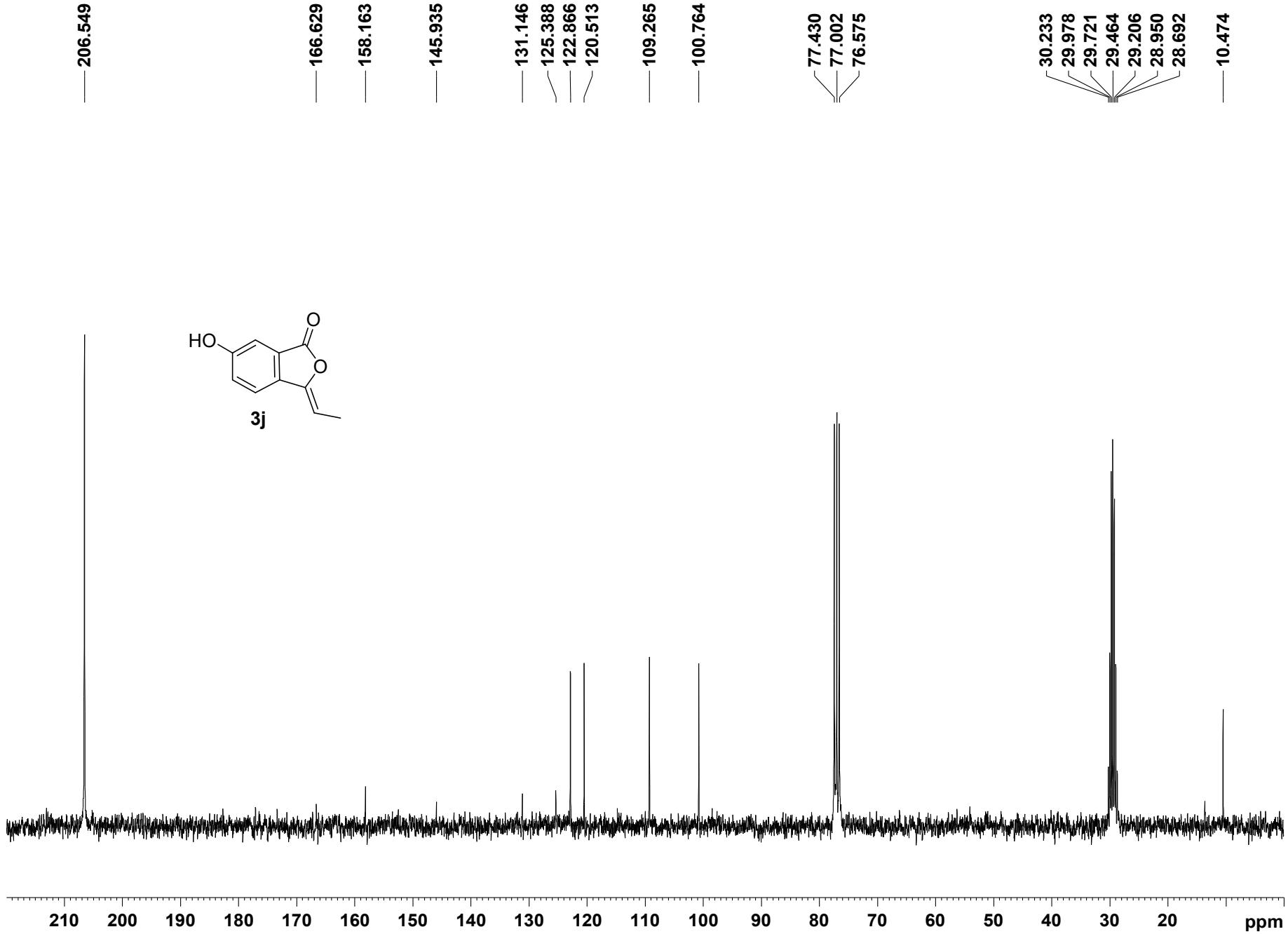
**5i**



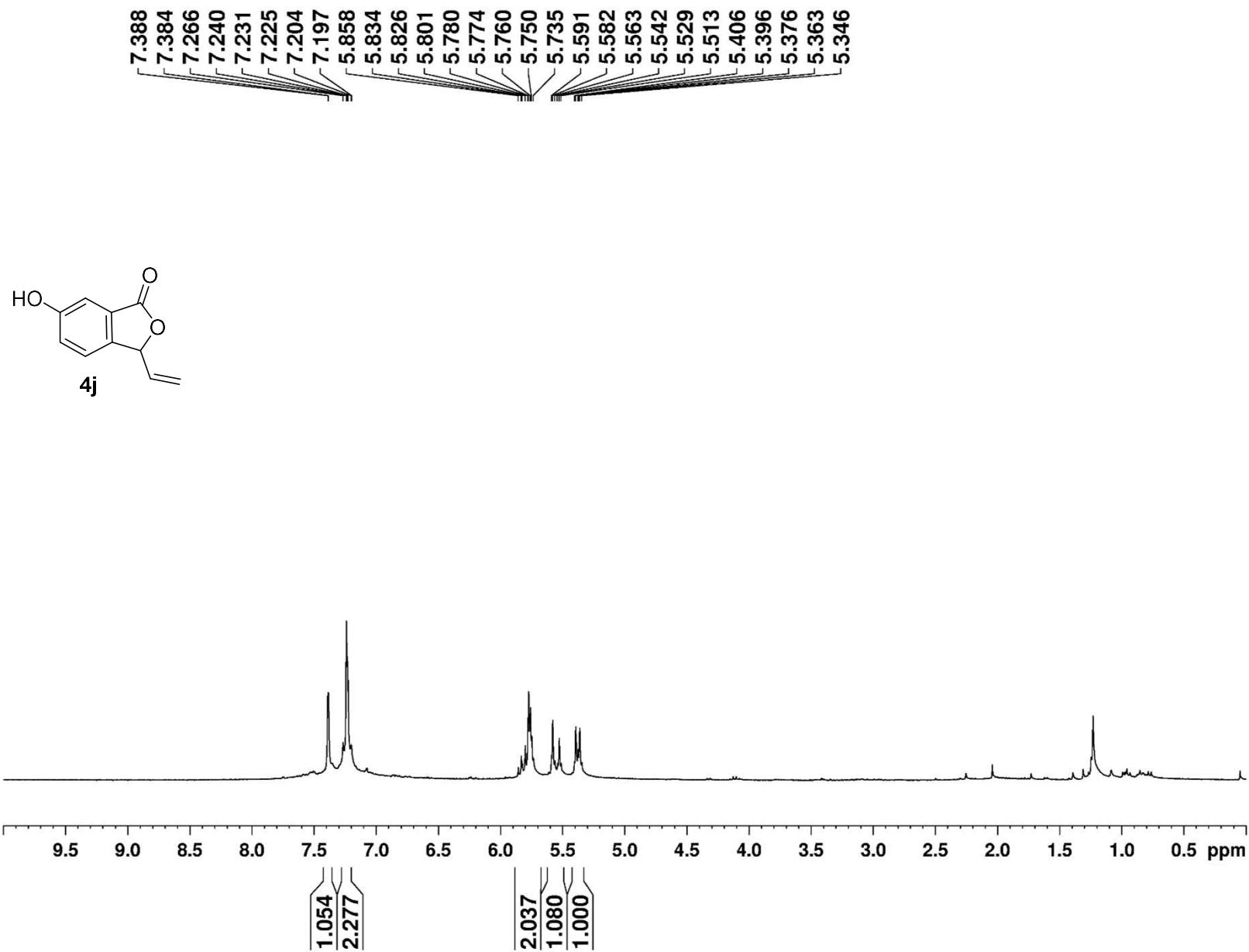
<sup>13</sup>C NMR of compound **5i** (125 MHz, CDCl<sub>3</sub>)



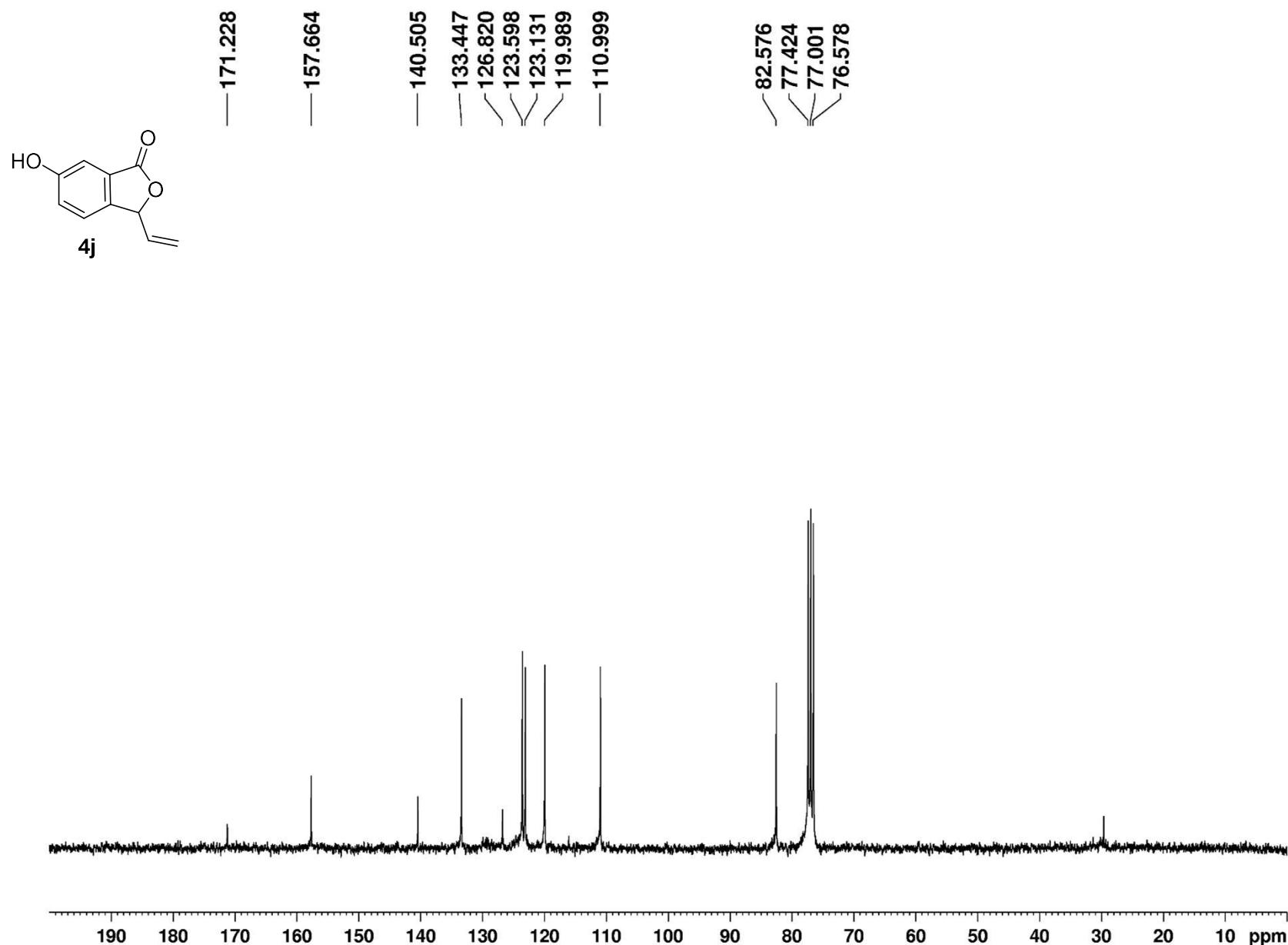
$^1\text{H}$  NMR of compound **3j** (300 MHz,  $\text{CDCl}_3 + (\text{CD}_3)_2\text{CO}$ )



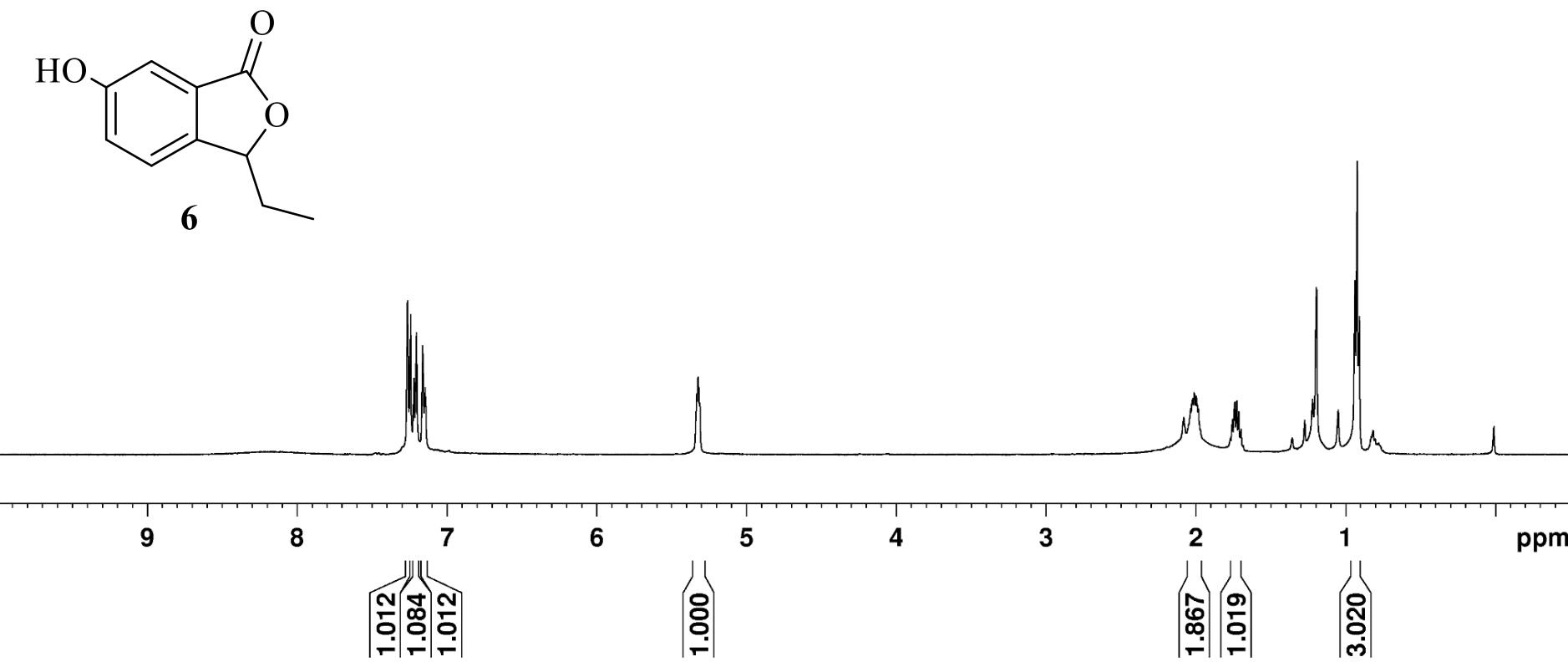
$^{13}\text{C}$  NMR of compound **3j** (75 MHz,  $\text{CDCl}_3 + (\text{CD}_3)_2\text{CO}$ )



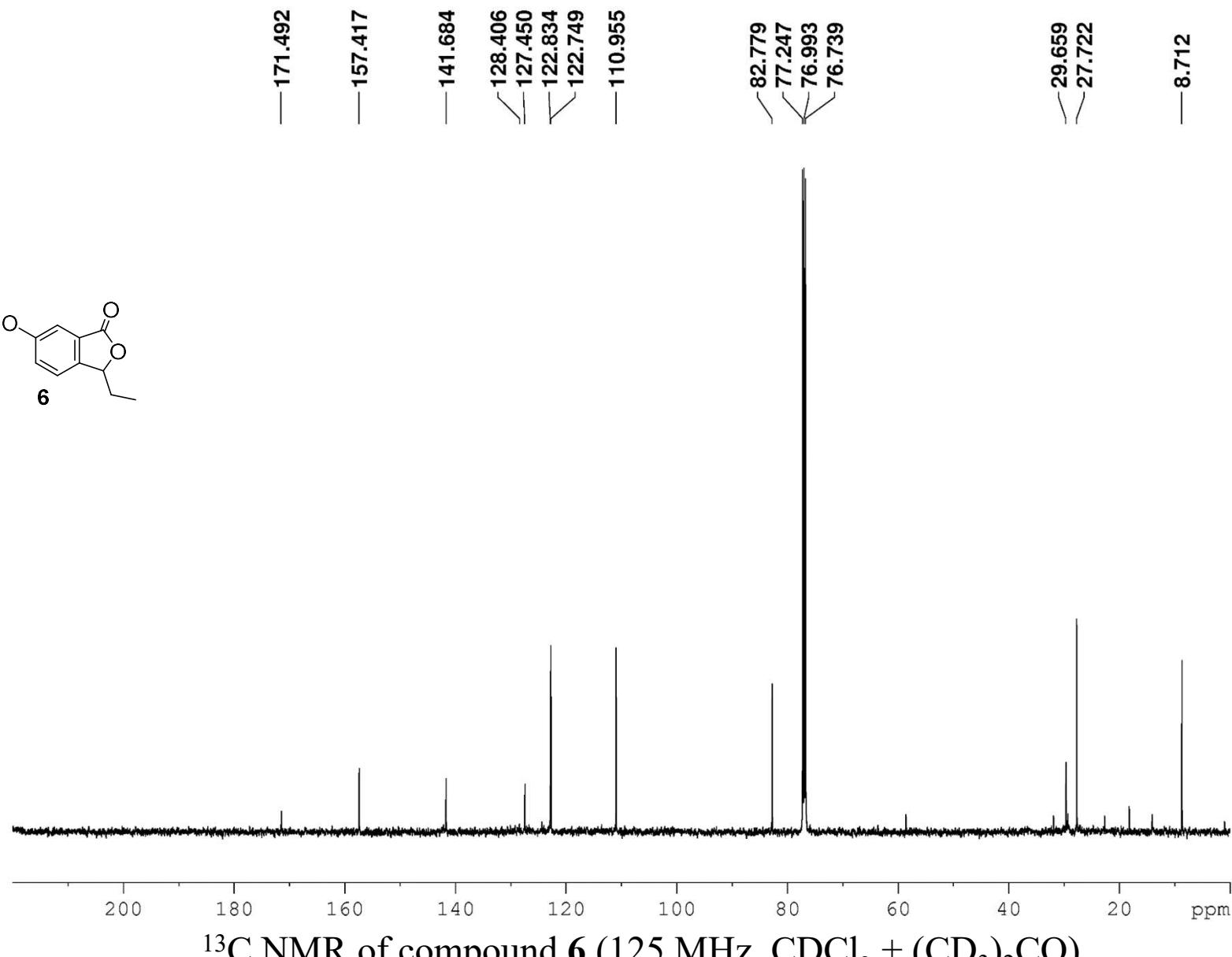
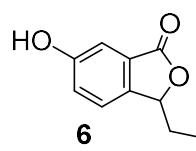
$^1\text{H}$  NMR of compound **4j** (300 MHz,  $\text{CDCl}_3 + (\text{CD}_3)_2\text{CO}$ )

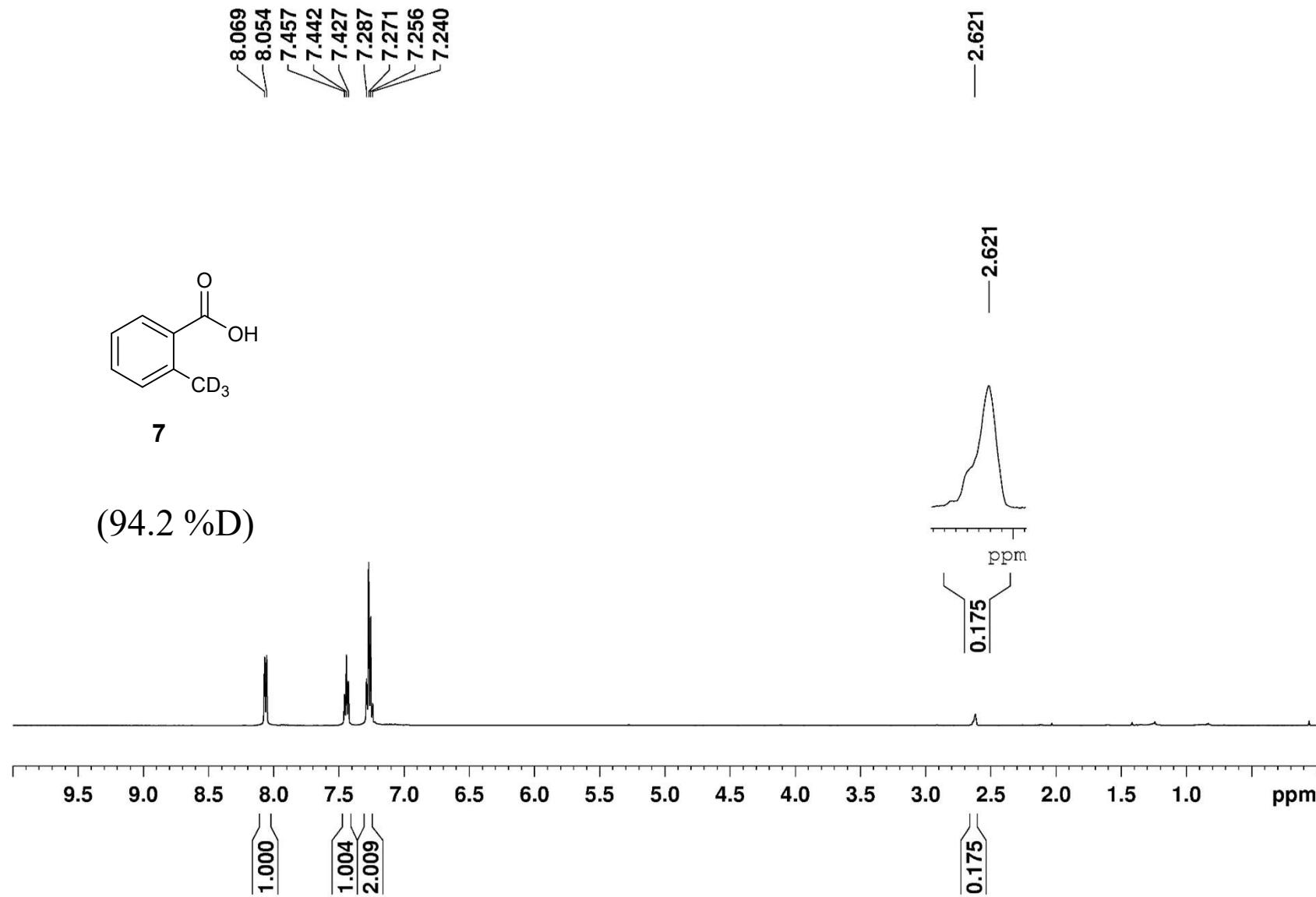


$^{13}\text{C}$  NMR of compound **4j** (75 MHz,  $\text{CDCl}_3 + (\text{CD}_3)_2\text{CO}$ )

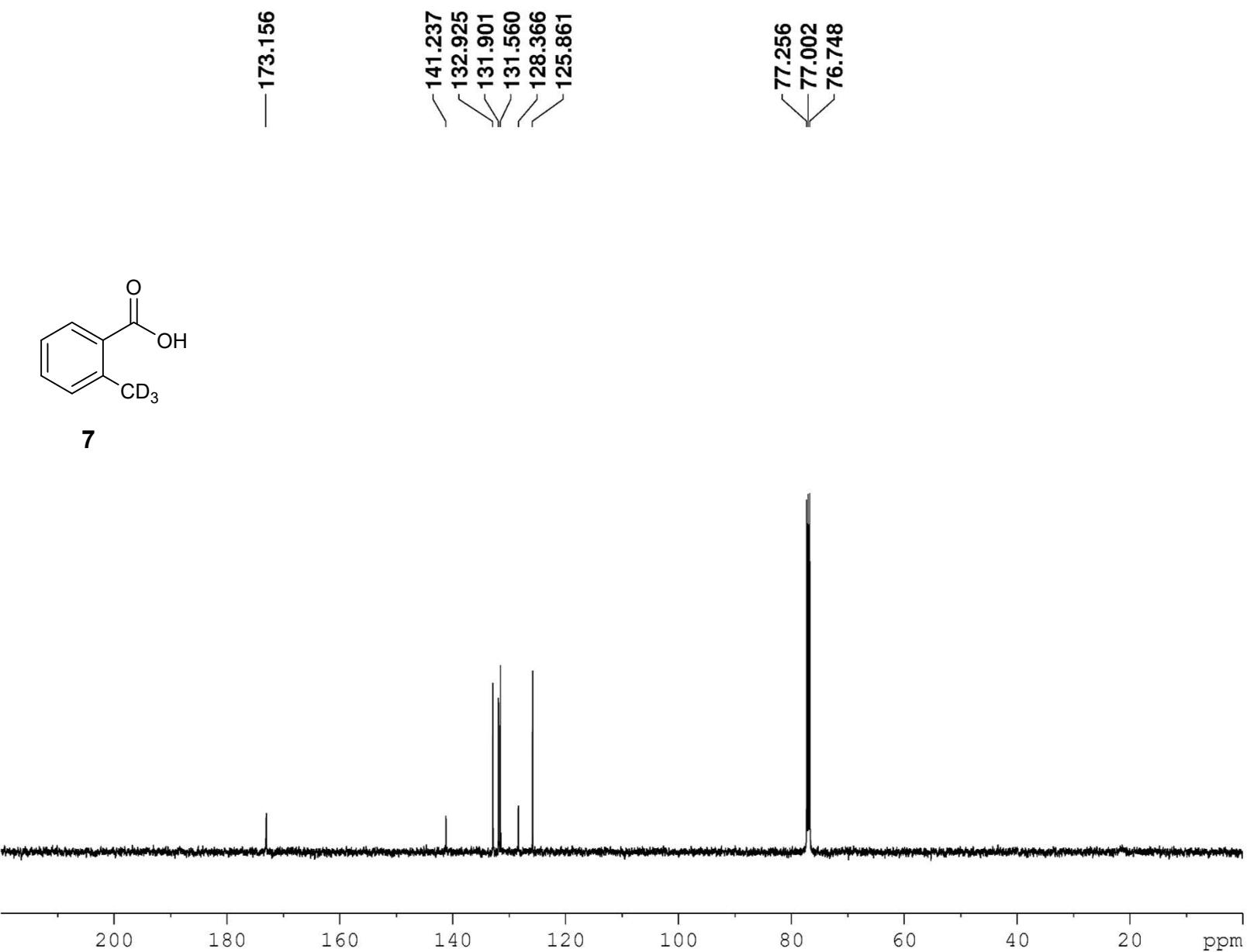


<sup>1</sup>H NMR of compound **6** (500 MHz,  $\text{CDCl}_3 + (\text{CD}_3)_2\text{CO}$ )

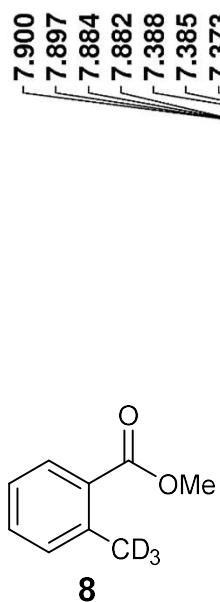




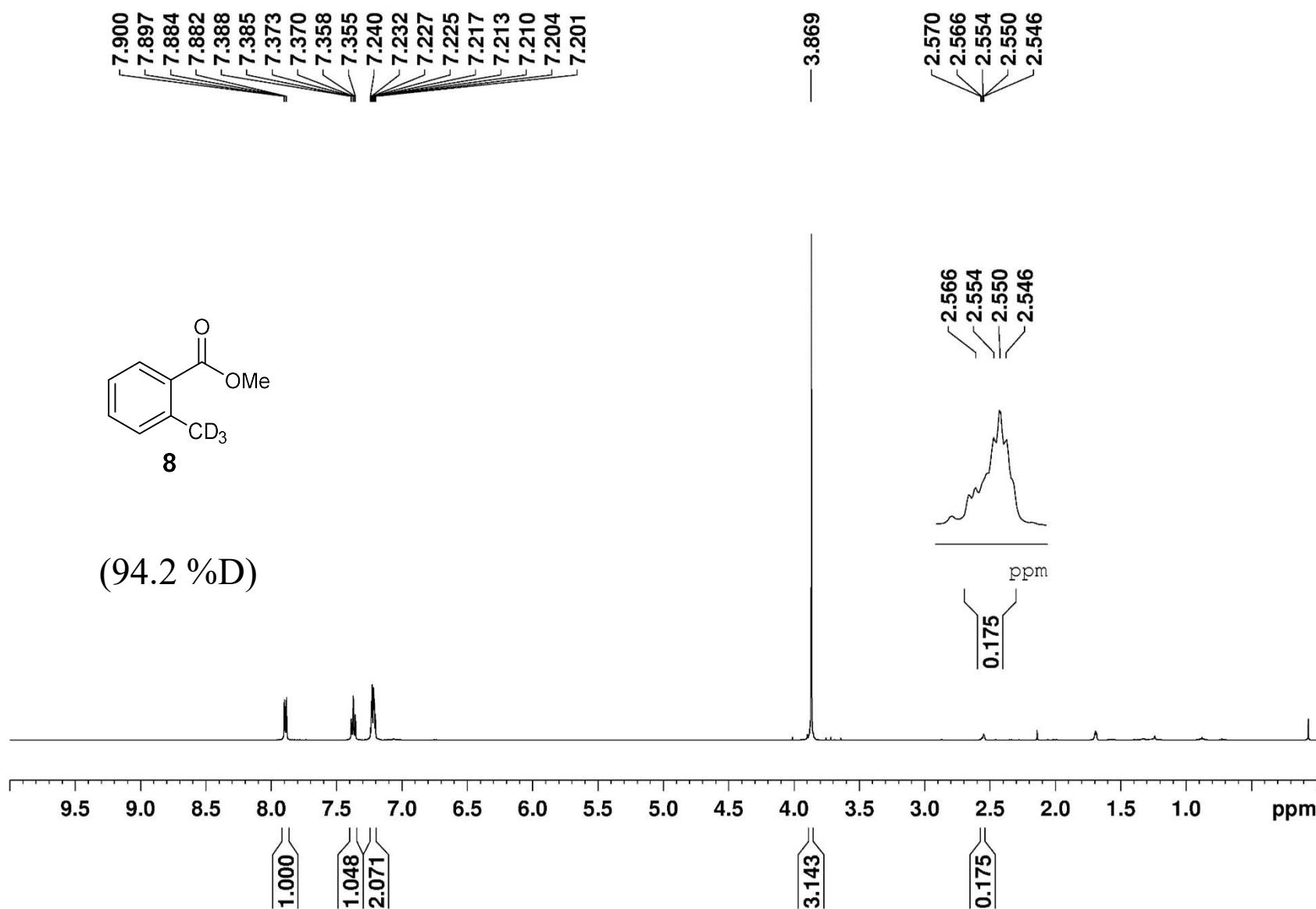
$^1\text{H}$  NMR of compound 7 (500 MHz,  $\text{CDCl}_3$ )



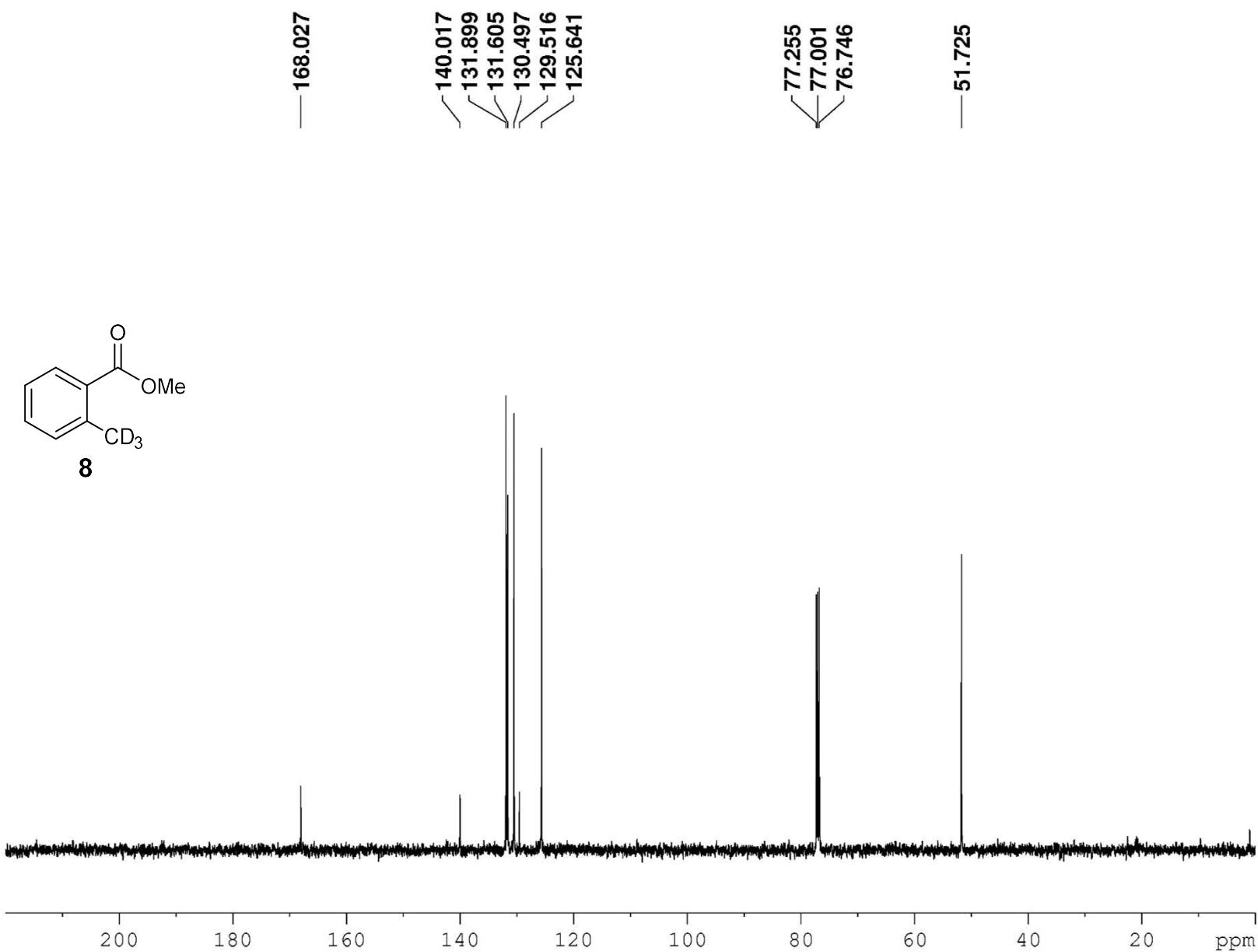
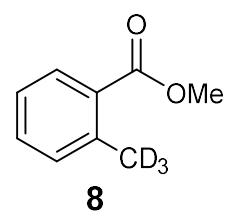
$^{13}\text{C}$  NMR of compound 8 (125 MHz,  $\text{CDCl}_3$ )



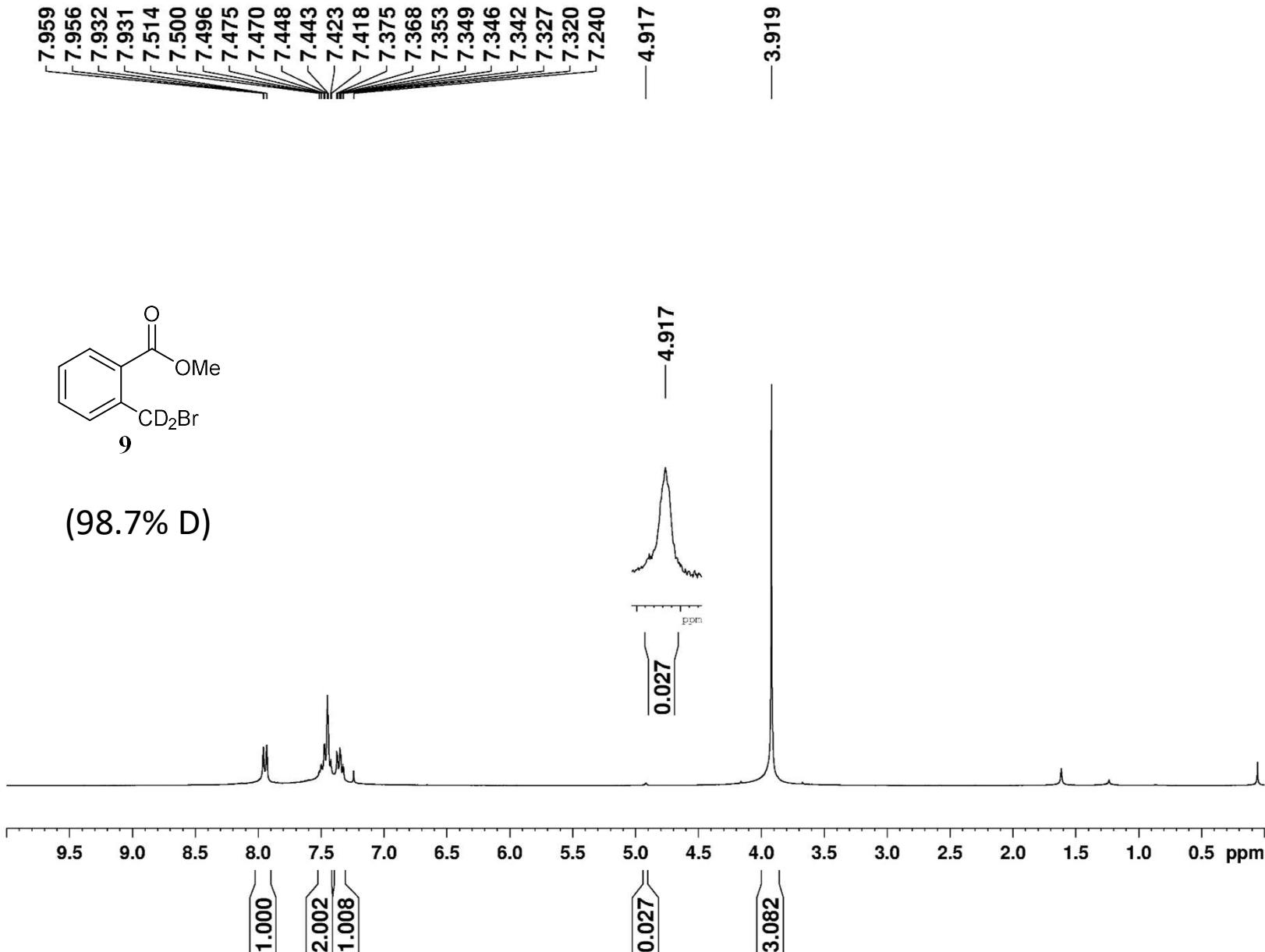
(94.2 %D)



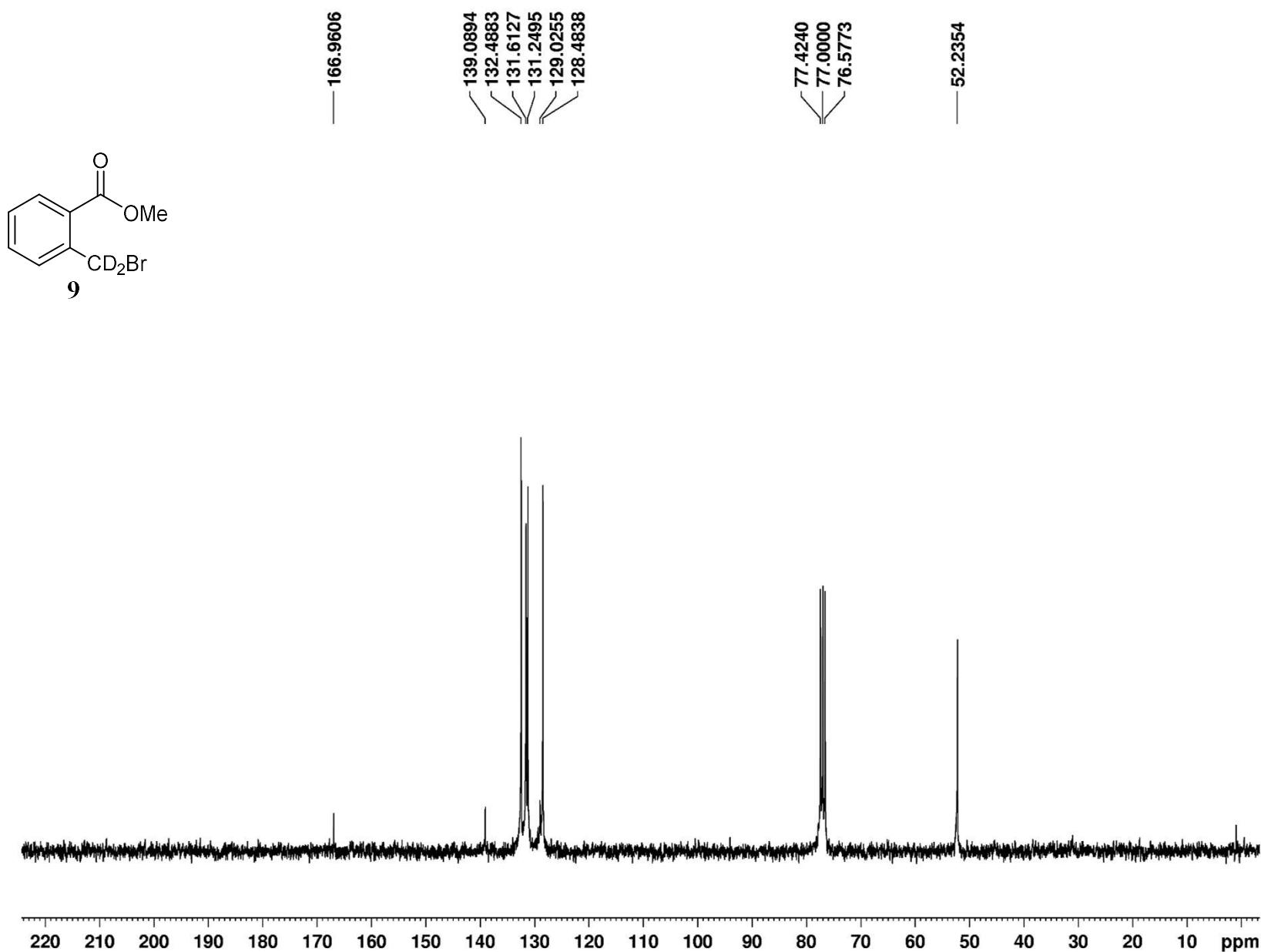
<sup>1</sup>H NMR of compound **8** (500 MHz, CDCl<sub>3</sub>)



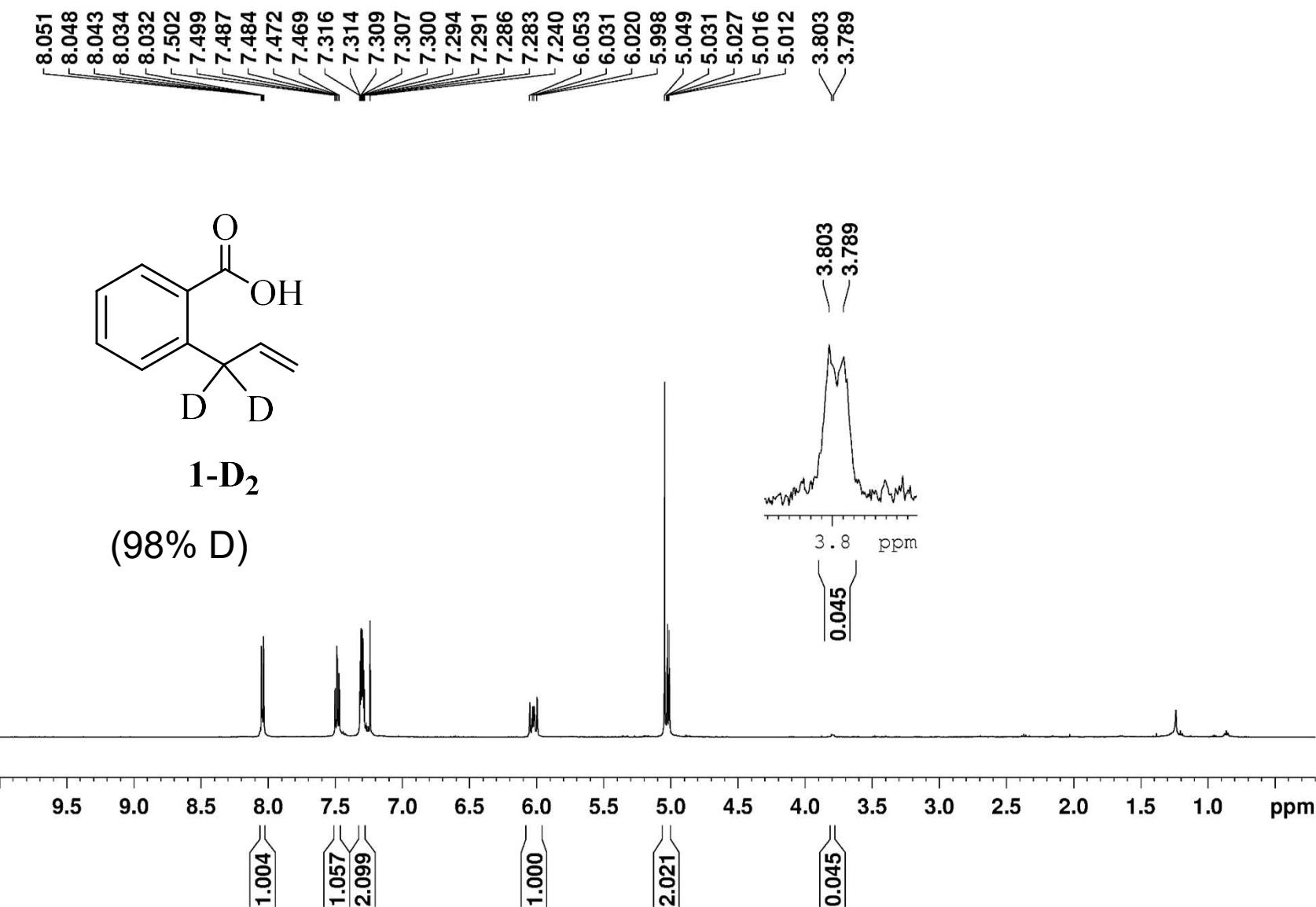
$^{13}\text{C}$  NMR of compound 8 (125 MHz,  $\text{CDCl}_3$ )



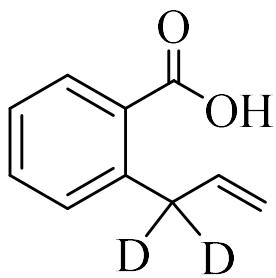
<sup>1</sup>H NMR of compound 9 (300 MHz, CDCl<sub>3</sub>)



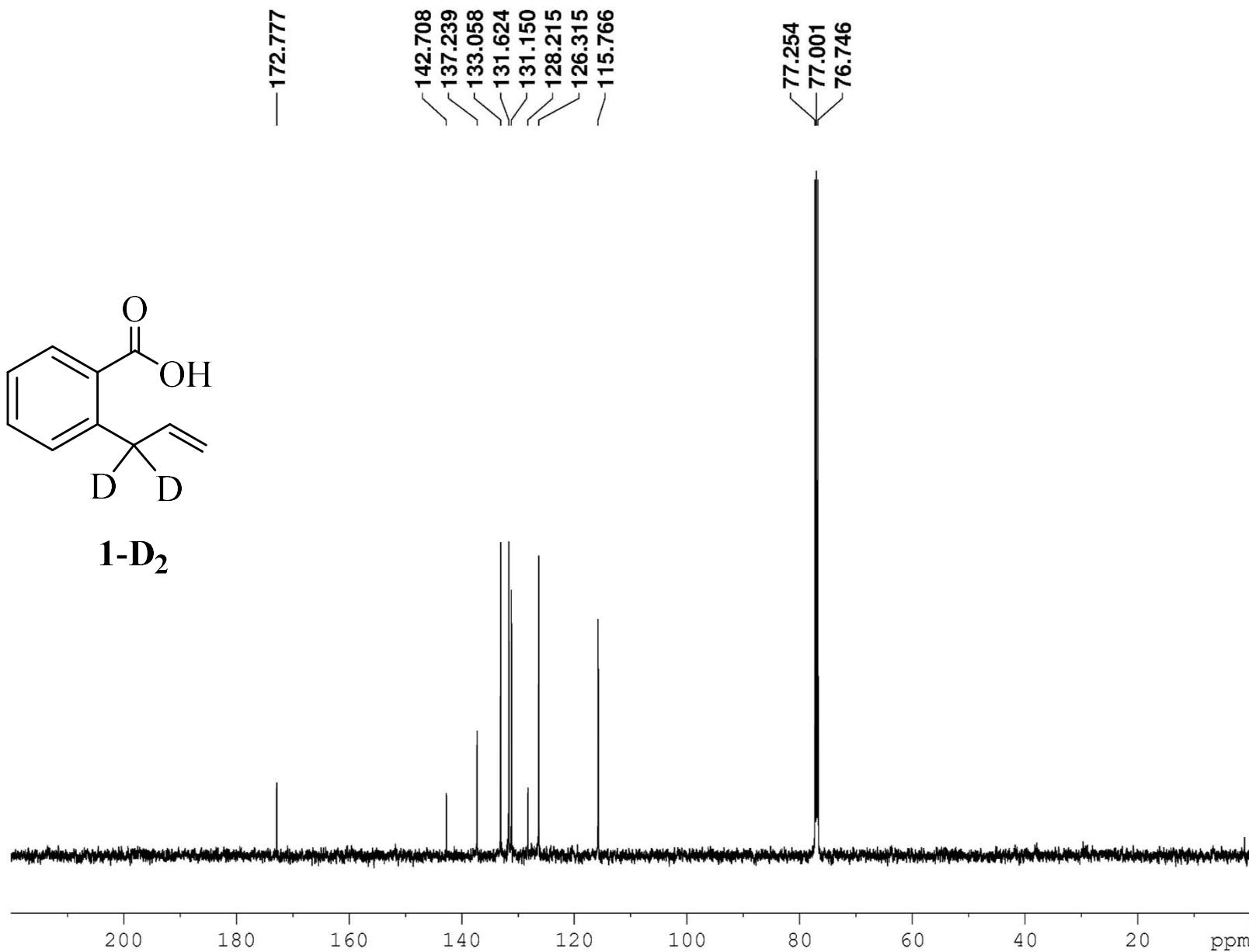
$^{13}\text{C}$  NMR of compound **9** (75 MHz,  $\text{CDCl}_3$ )



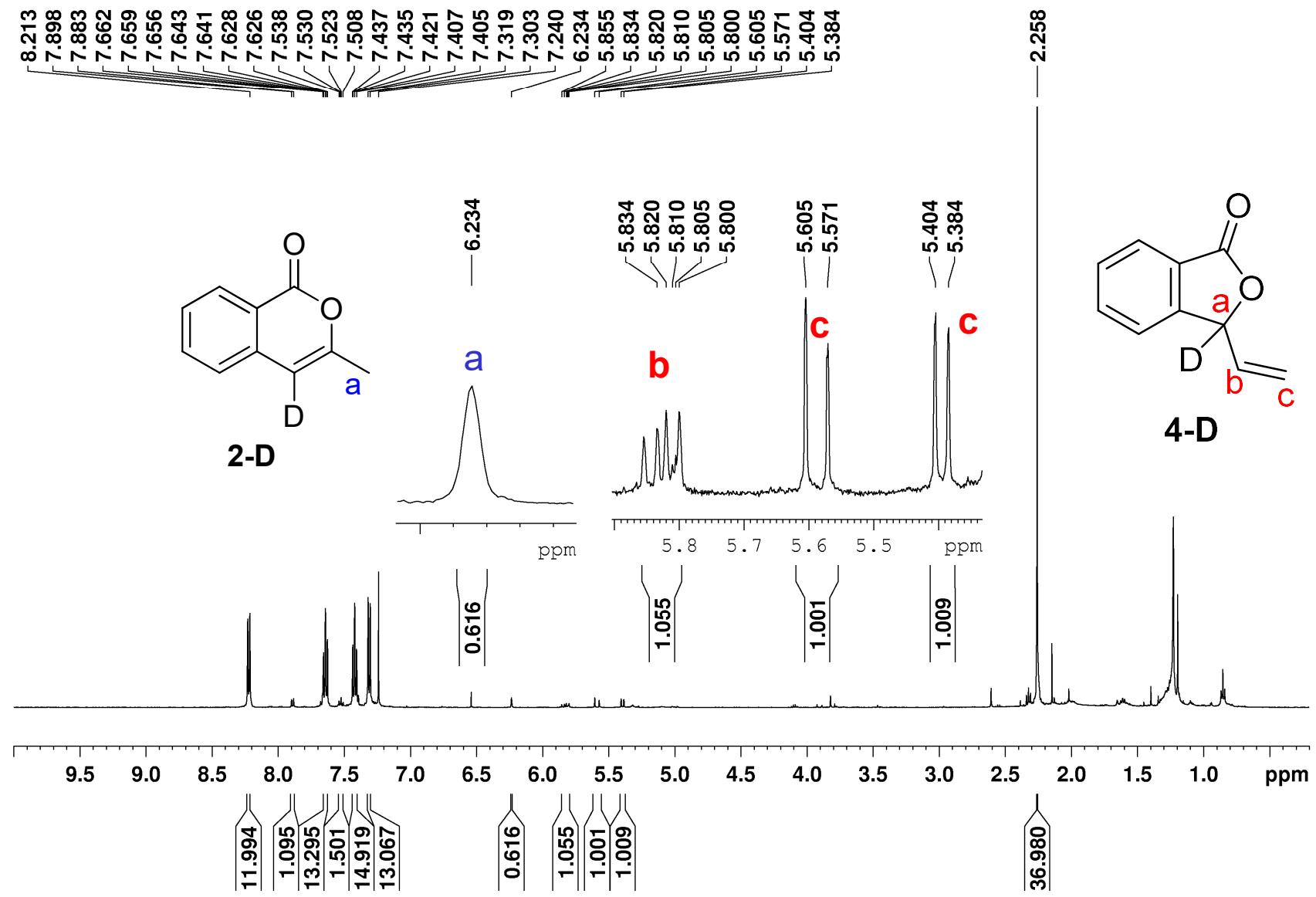
<sup>1</sup>H NMR of compound **1-D<sub>2</sub>** (500 MHz, CDCl<sub>3</sub>)



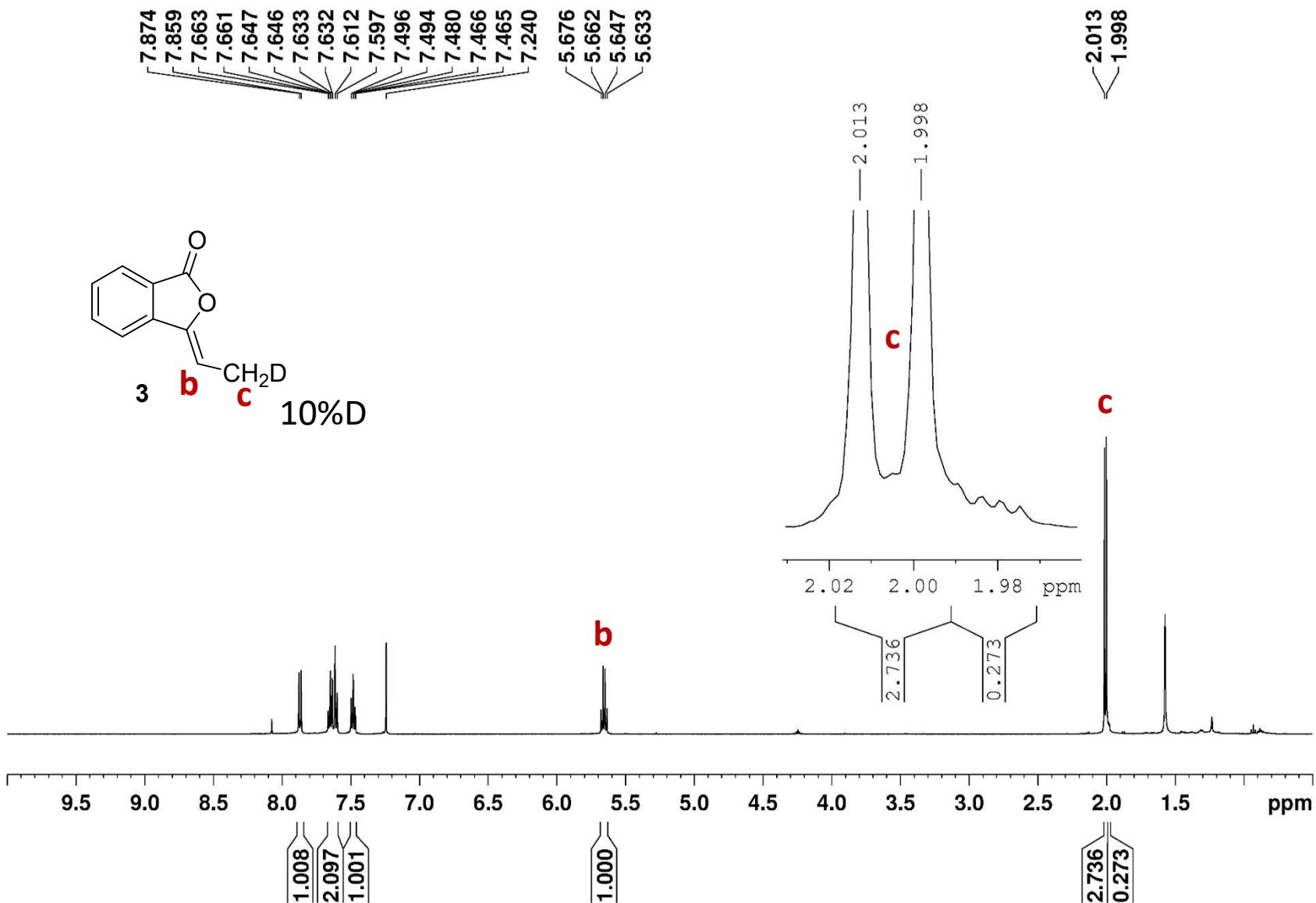
**1-D<sub>2</sub>**



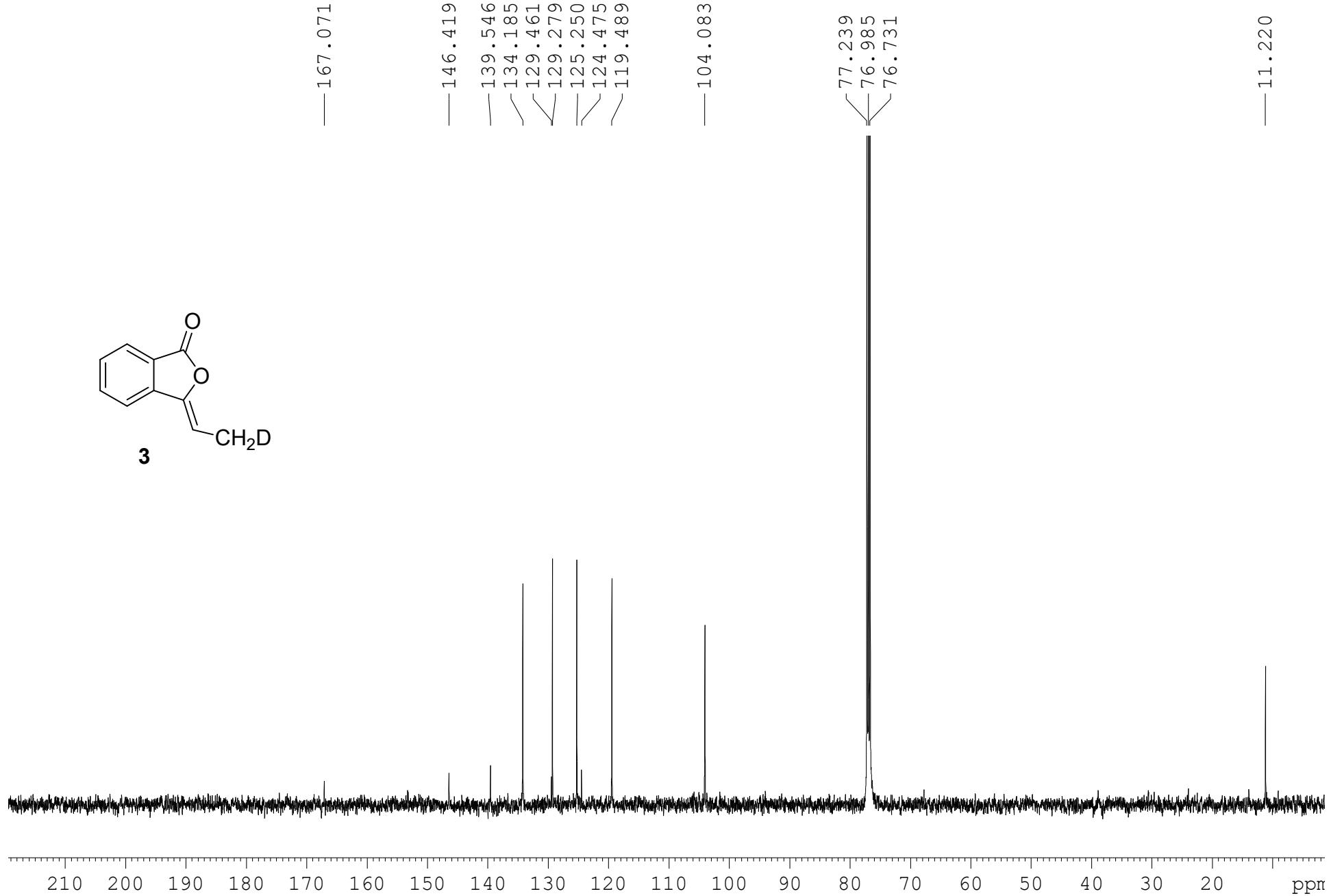
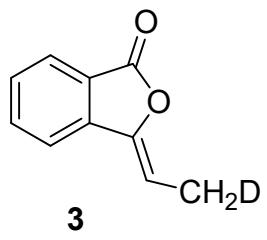
<sup>13</sup>C NMR of compound **1-D<sub>2</sub>** (125 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of the mixture of compound **2-D** and **4-D** (500 MHz, CDCl<sub>3</sub>)



$^1\text{H}$  NMR of compound **3-D** (500 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR of compound 3-D (125 MHz,  $\text{CDCl}_3$ )