Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary information

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

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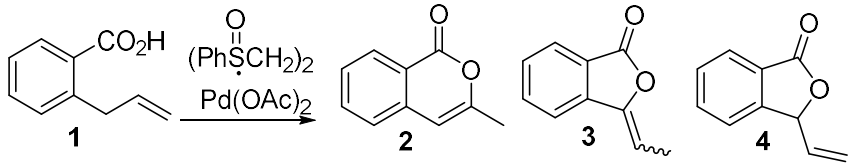
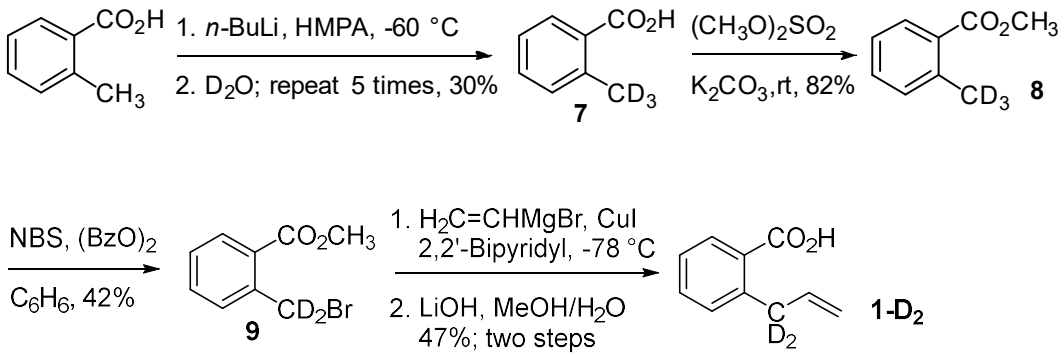
SI Table 1. Screened Reaction Conditions for the Oxidation of 2-Allylbenzoic acids (**1**)



entry	reaction condition[a]	yield (%)[b]			recovered
		2	**3** (*E*:*Z*)[c]	**4**	**1**
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_2Cl_2, 40 °C, 24h	7		75	
6	BQ, CH_2Cl_2/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

[a]2-Allylbenzoic acid (1.0 mmol), Pd catalyst (5 mol%), solvent (1.0 mL), benzoquinone (BQ, 2.0 mmol) or O_2 (1 atm).

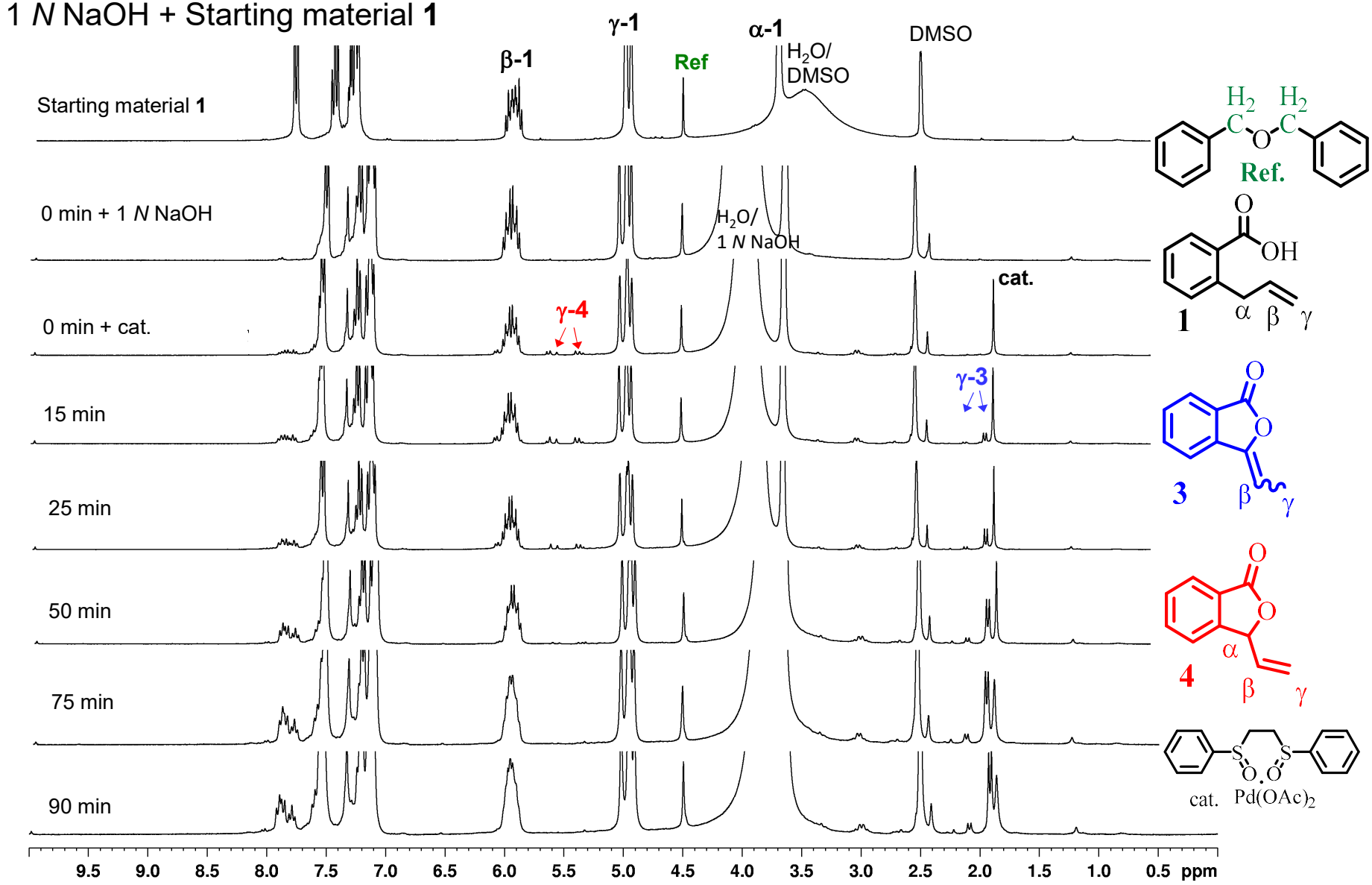
[b]Isolated yields.



SI Scheme 1. Synthesis of **1-D$_2$**

Procedure for kinetic isotope effect

White catalyst (2.5 mg, 5 μmol) was added to solution of **1** or **1-D$_2$** (16.2 mg, 100 μmol), $NaOH_{(aq)}$ (1*N*, 50 μL, 50 μmol), dibenzyl ether (1.0 mg, 5 μmol, as internal standard) and d_6-DMSO (0.7 mL). The reaction tube was heated in an oil bath (100 °C) under an atmosphere of oxygen and monitored by ^{1}H NMR at certain time intervals. For the reactions conducted under the acidic condition, $HCl_{(aq)}$ (1 *N*, 50 μL, 50 μmol) was applied instead of $NaOH_{(aq)}$. The KIE value was obtained using the initial rates method, each experiment was conducted in duplicate.



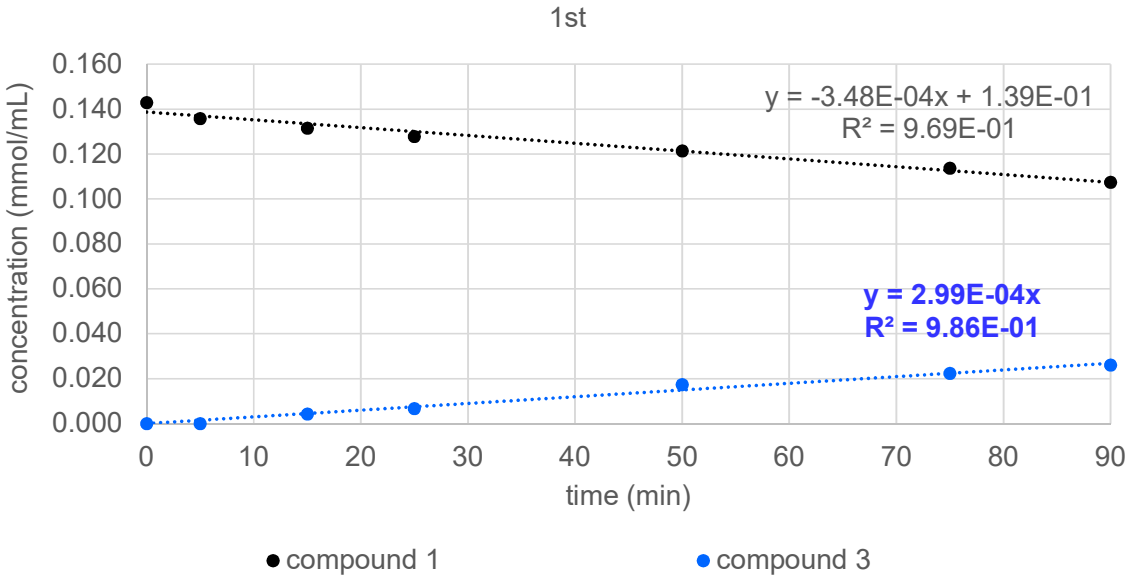
Kinetic ^{1}H NMR (300 MHz, d_6-DMSO) of **1** in base

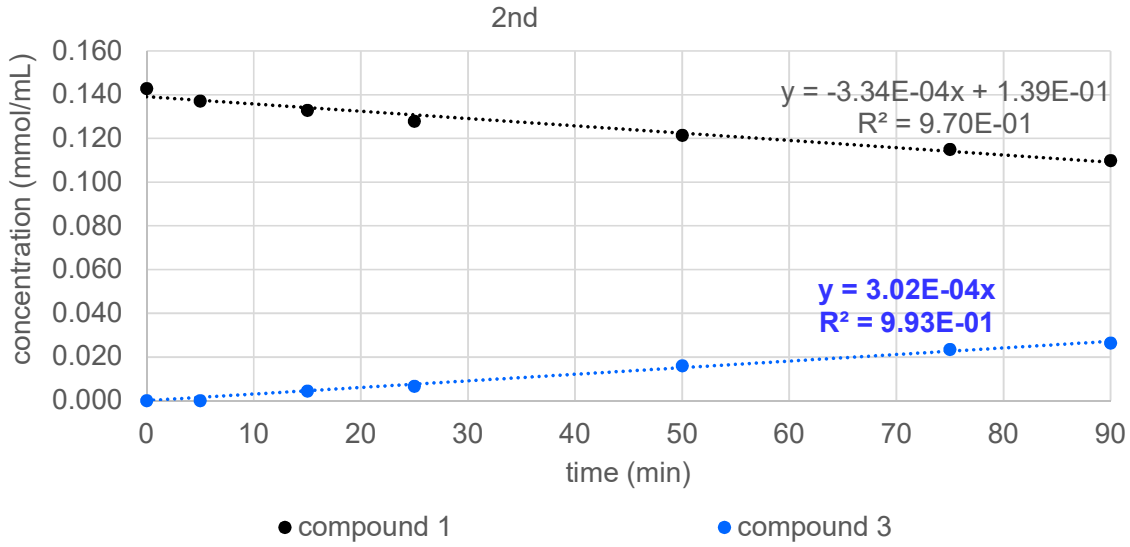
1 *N* NaOH + Starting material **1**

1st	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	concn. (mmol/mL)
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.									

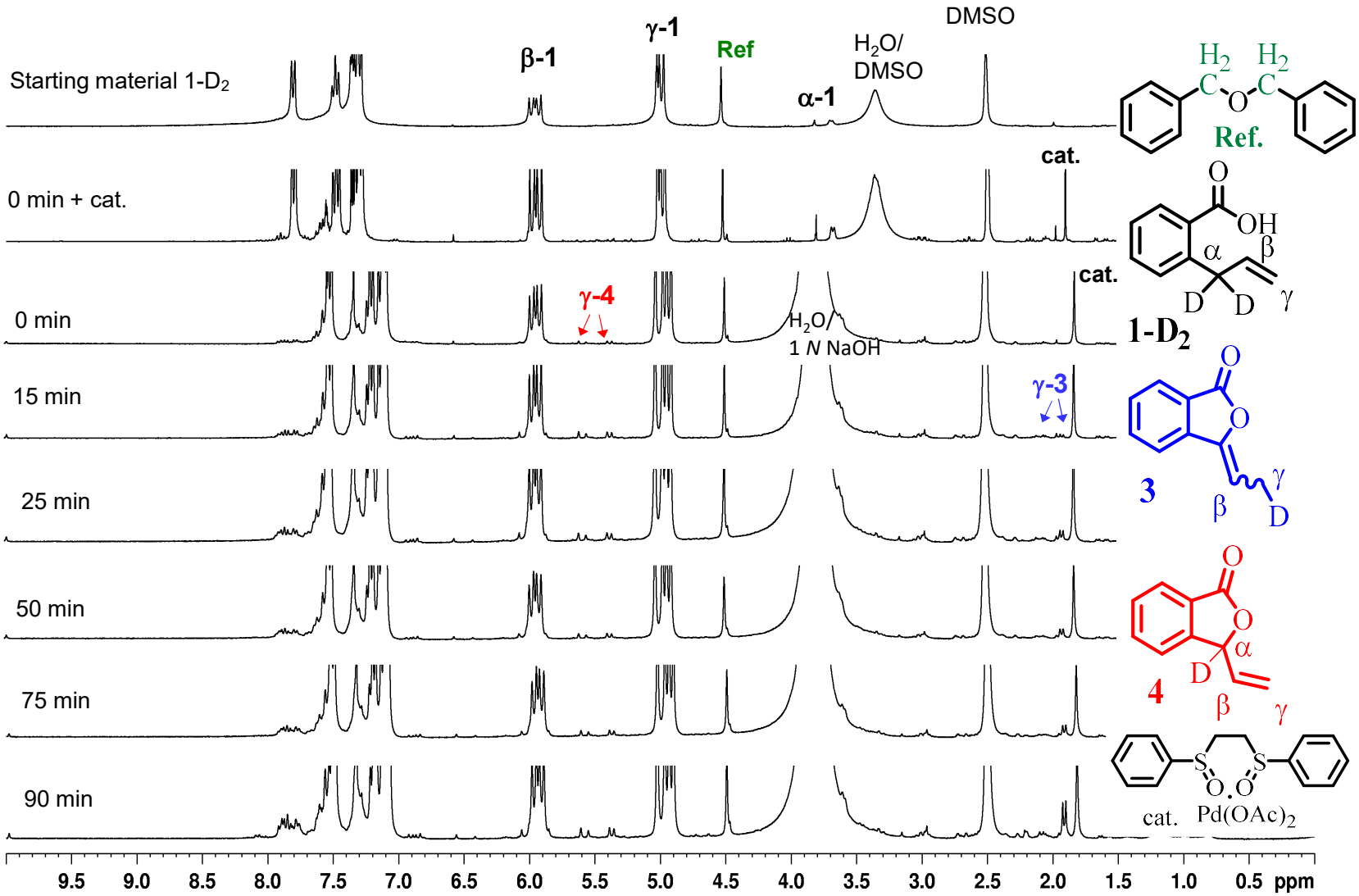
2nd	Starting material **1**			Product **3**			Intermediate **4**		
time (min)	integ. γ-**1***	mmol	concn. (mmol/mL)	integ. γ-**3***	mmol	concn. (mmol/mL)	integ. γ-**4***	mmol	concn. (mmol/mL)
0	10	0.1	0.143	0	0	0	0	0	0
5	9.593	0.0959	0.137	0	0	0.000	0.201	0.00402	0.0057
15	9.298	0.093	0.133	0.466	0.0031	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 *N* NaOH + Starting material **1**





1 *N* NaOH + Starting material **1-D$_2$**



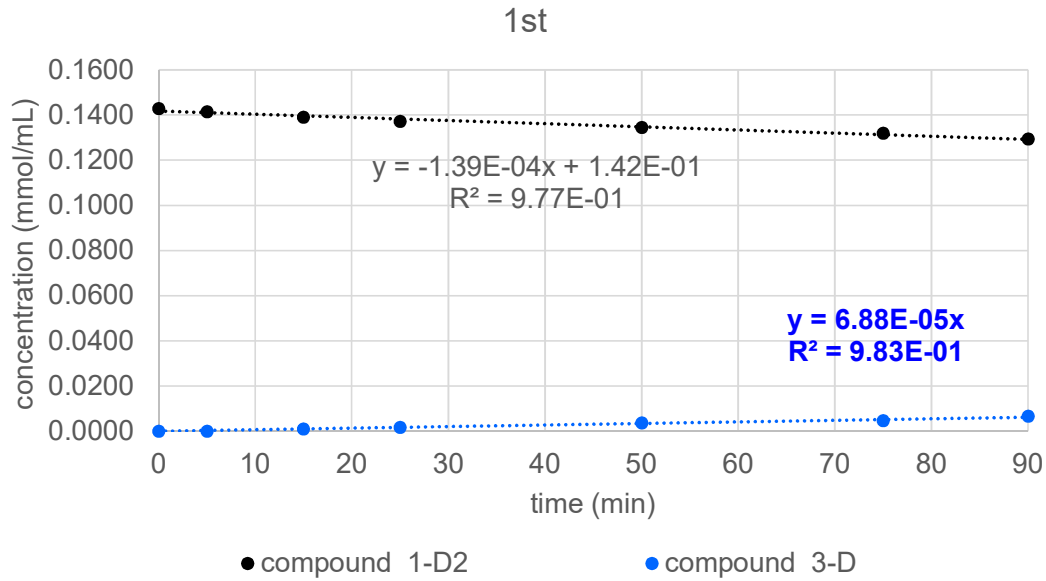
Kinetic ^{1}H NMR (300 MHz, d_6-DMSO) of **1-D$_2$** in base

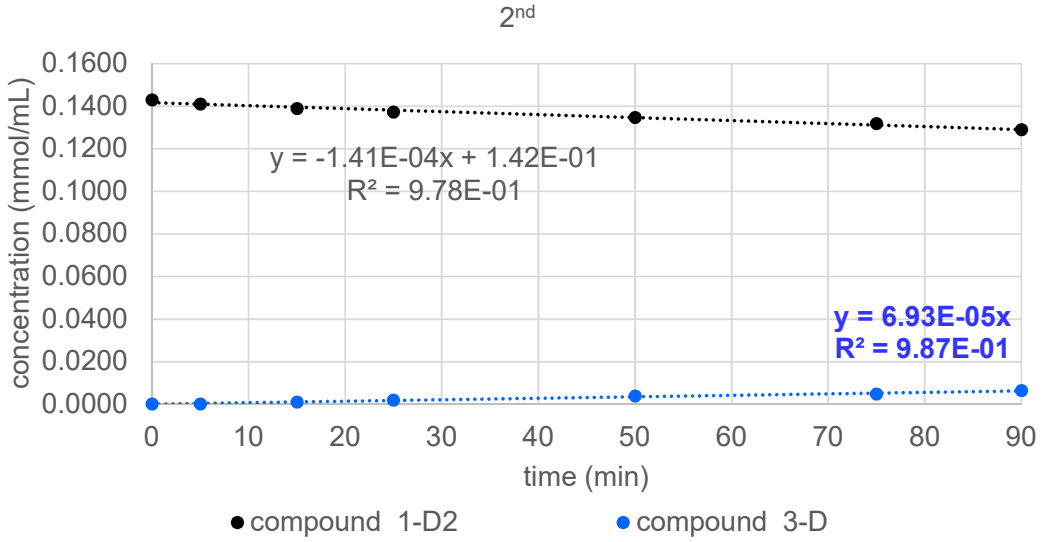
1 *N* NaOH + Starting material **1-D$_2$**

1st	Starting material **1**-D$_2$			Product **3**-D			Intermediate **4**		
time (min)	integ. γ-**1***	mmol	concn. (mmol/mL)	integ. γ-**3***	mmol	concn. (mmol/mL)	integ. γ-**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.									

2nd	Starting material **1**-D$_2$			Product **3**-D			Intermediate **4**		
time (min)	integ. γ-**1***	mmol	concn. (mmol/mL)	integ. γ-**3***	mmol	concn. (mmol/mL)	integ. γ-**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$_2$**





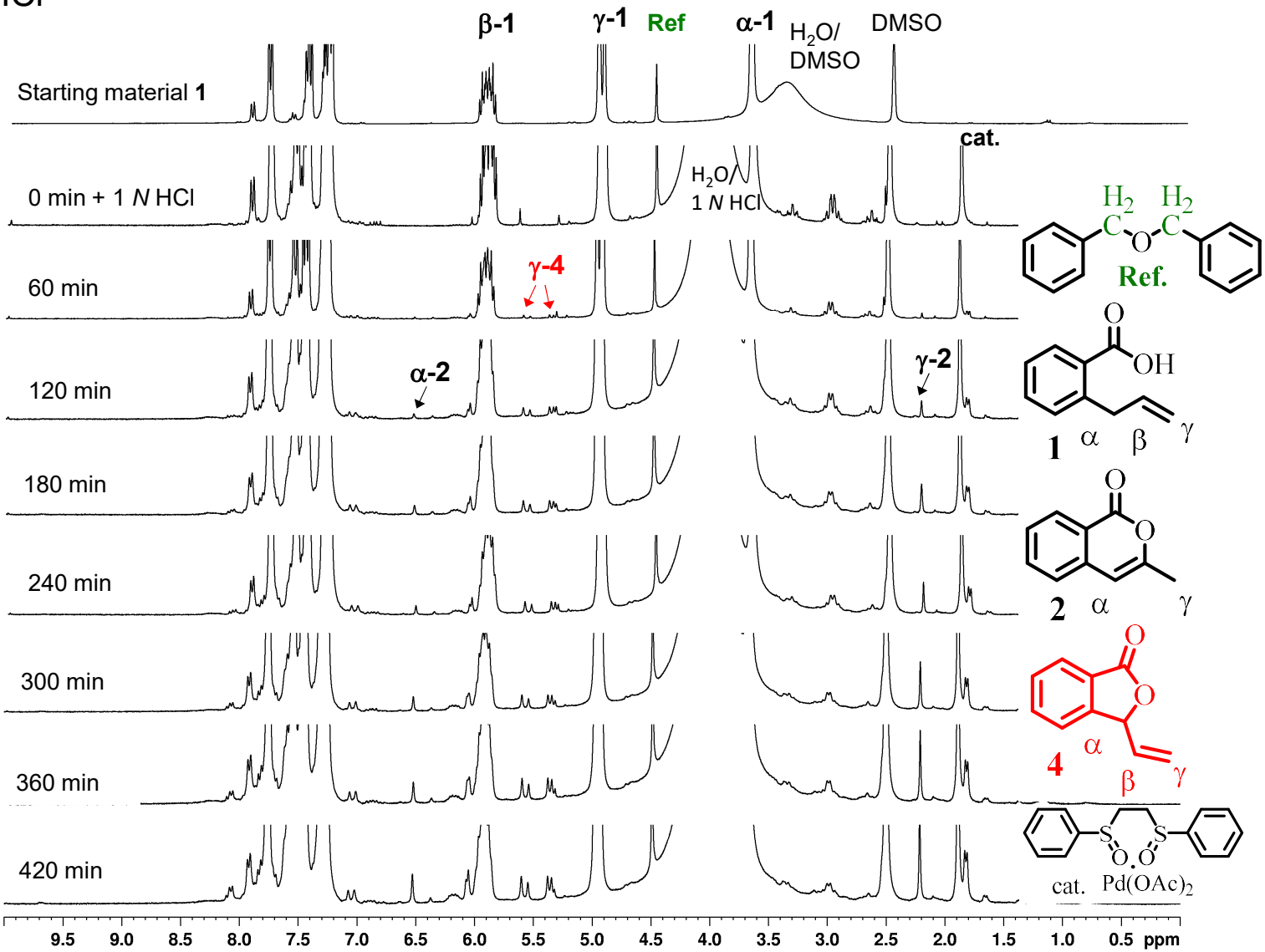
Kinetic Isotope Effect under the basic condition

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

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

$$\textbf{KIE} = \frac{k_H}{k_D} = \frac{\textbf{1:}\ \text{rate}_{ave}}{\textbf{1-D}_{\textbf{2}}\textbf{:}\ \text{rate}_{ave}} = 4.3 - 4.4$$

1 *N* HCl



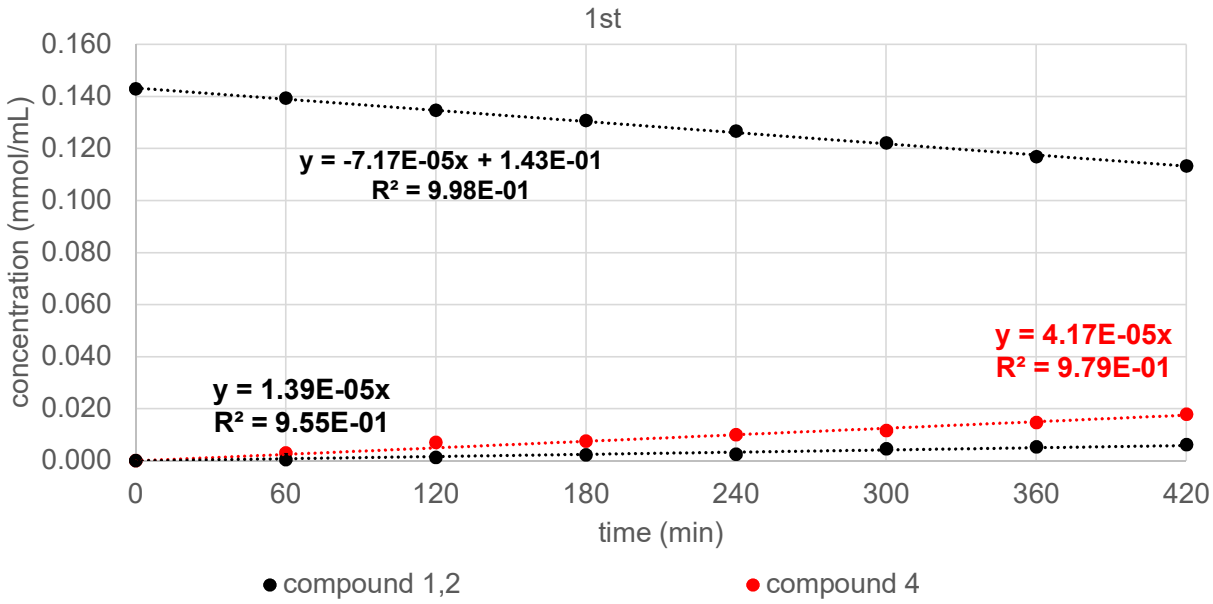
Kinetic ^{1}H NMR (300 MHz, d_6-DMSO) of **1** in acid

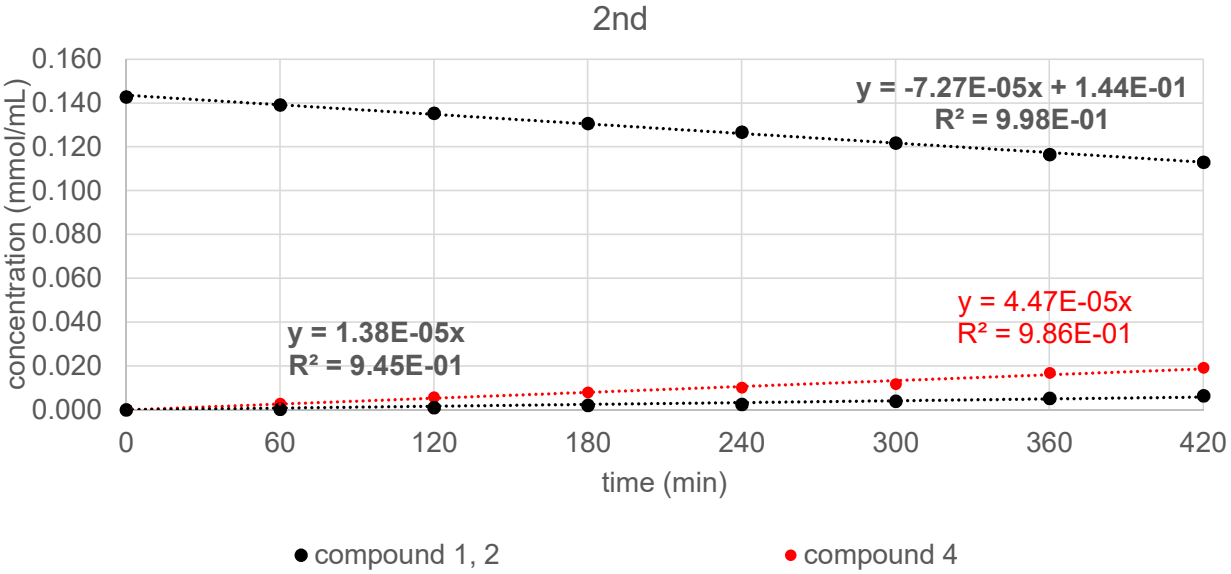
1 *N* HCl

1st	Starting material **1**			Product **4**			Product **2**		
time (min)	integ. γ-**1***	mmol	concn. (mmol/mL)	integ. γ-**4***	mmol	concn. (mmol/mL)	integ. α-**2***	mmol	concn. (mmol/mL)
0	10	0.1	0.143	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.									

2nd	SM Starting material **1**			Product **4**			Product **2**		
time (min)	integ. γ-**1***	mmol	concn. (mmol/mL)	integ. γ-**4***	mmol	concn. (mmol/mL)	integ. α-**2***	mmol	concn. (mmol/mL)
0	10	0.1	0.143	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.									

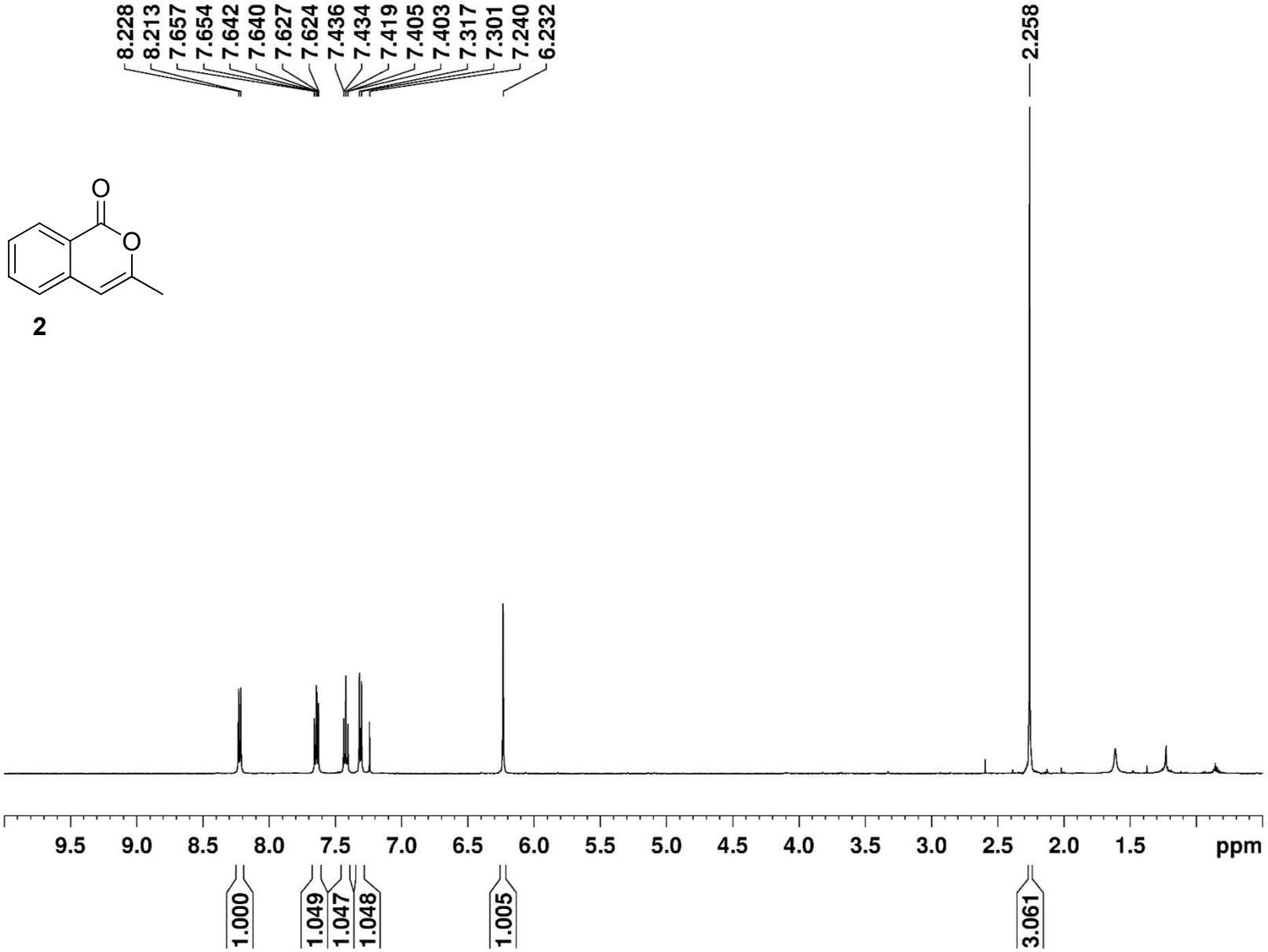
1 *N* HCl



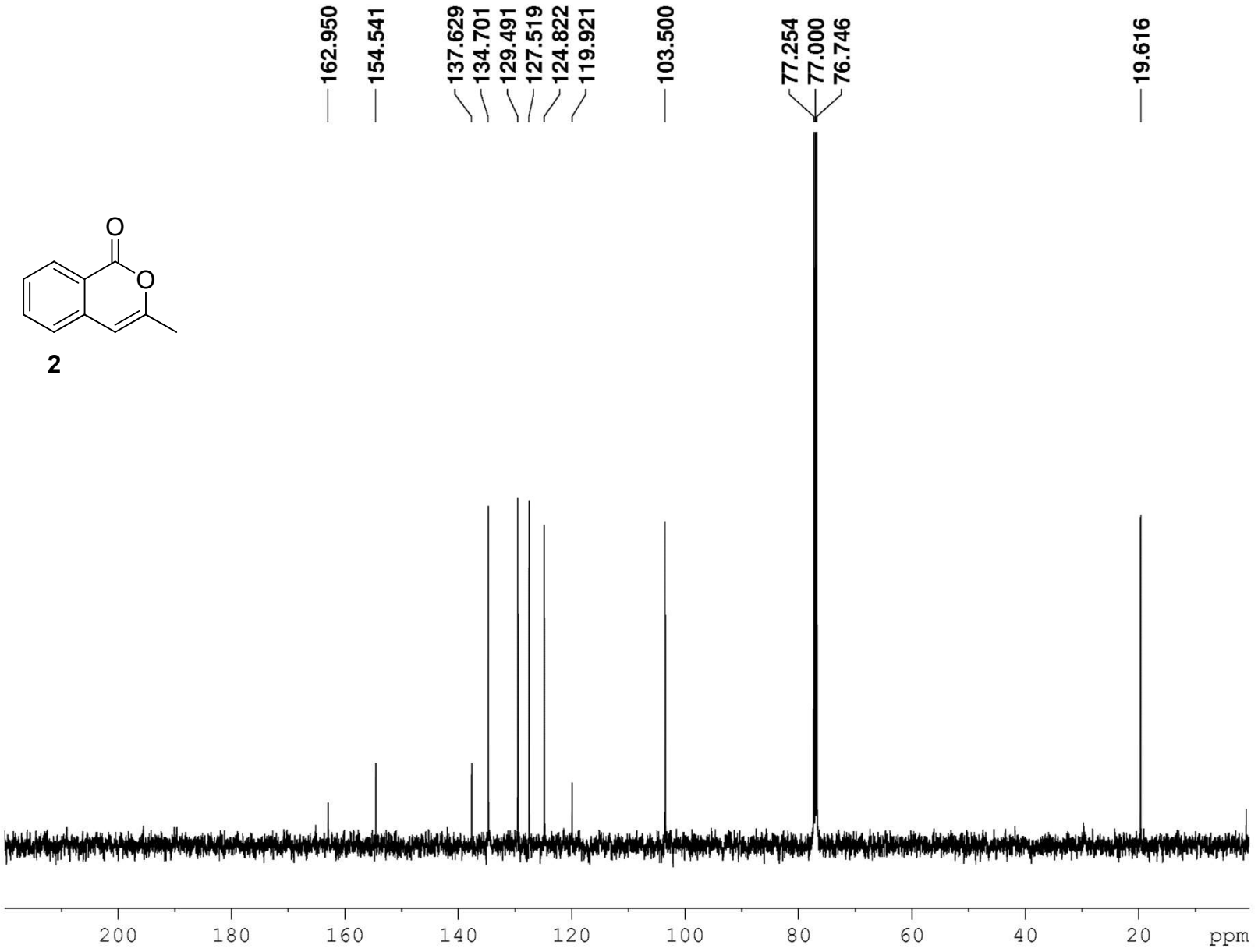


Under $HCl_{(aq)}$ (1 *N*)

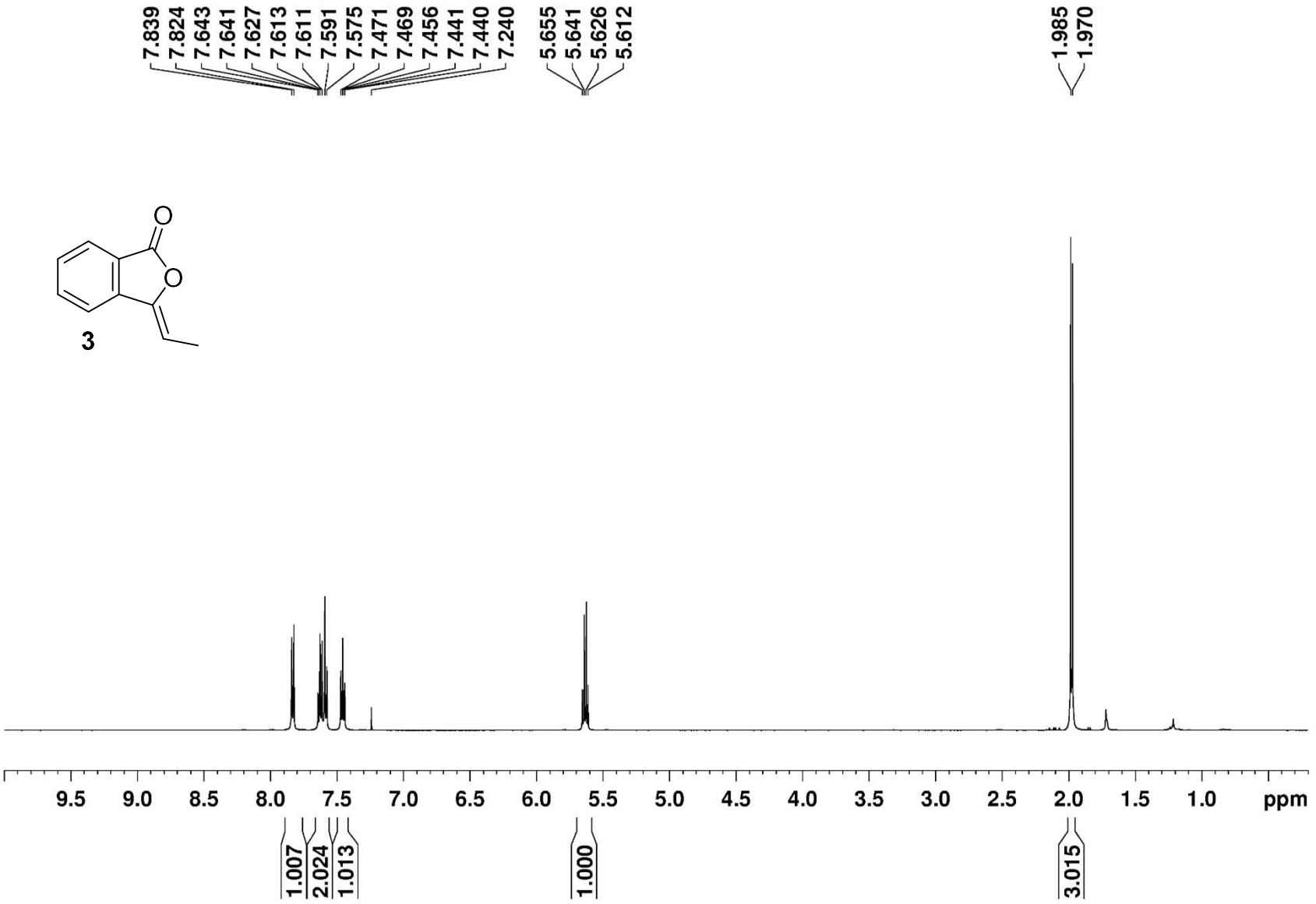
$$rate_{ave} = \frac{(4.17 \times 10^{-5} + 4.47 \times 10^{-5})}{2} = 4.32 \times 10^{-5}\ (M \cdot \min^{-1})$$



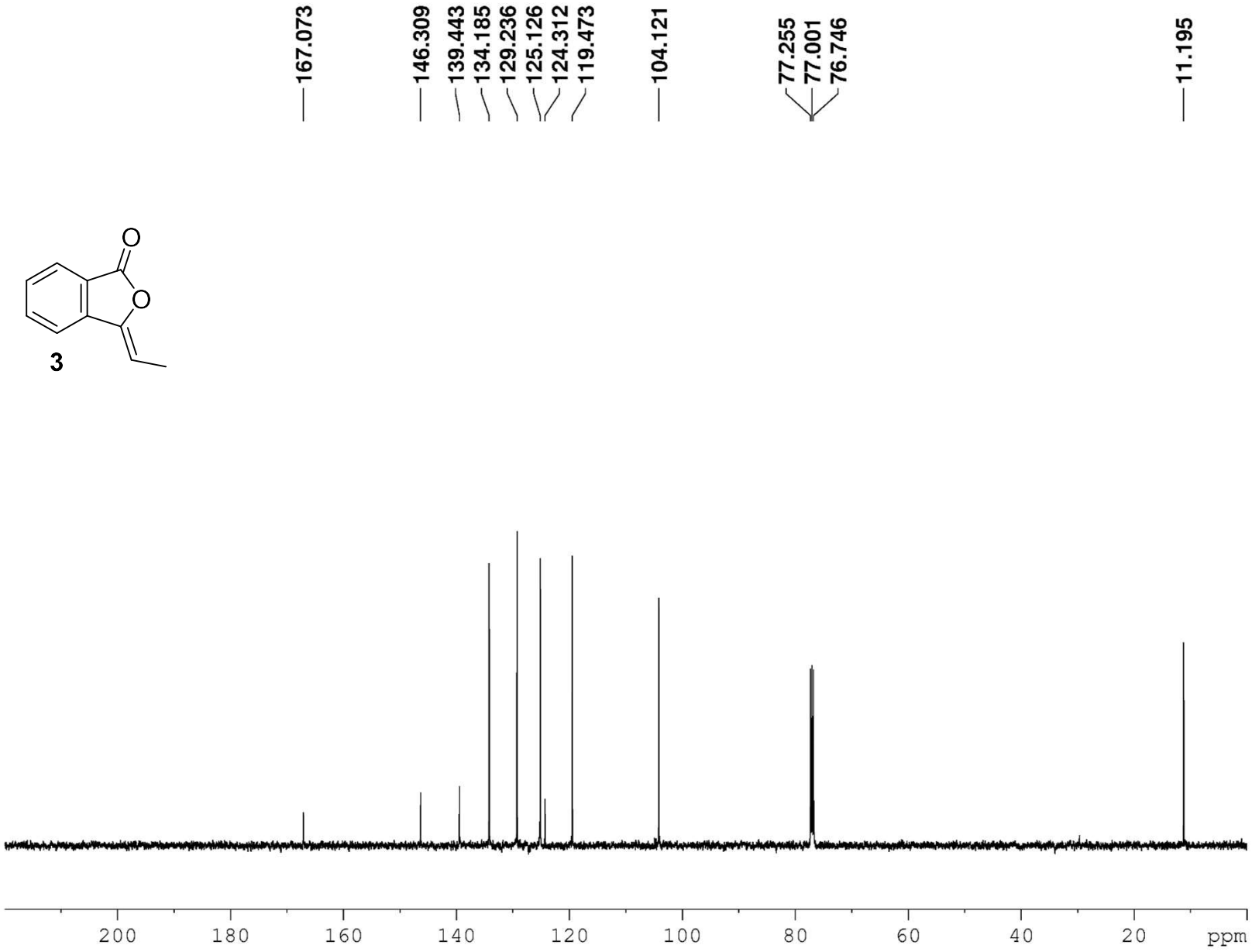
^{1}H NMR of compound **2** (500 MHz, $CDCl_3$)



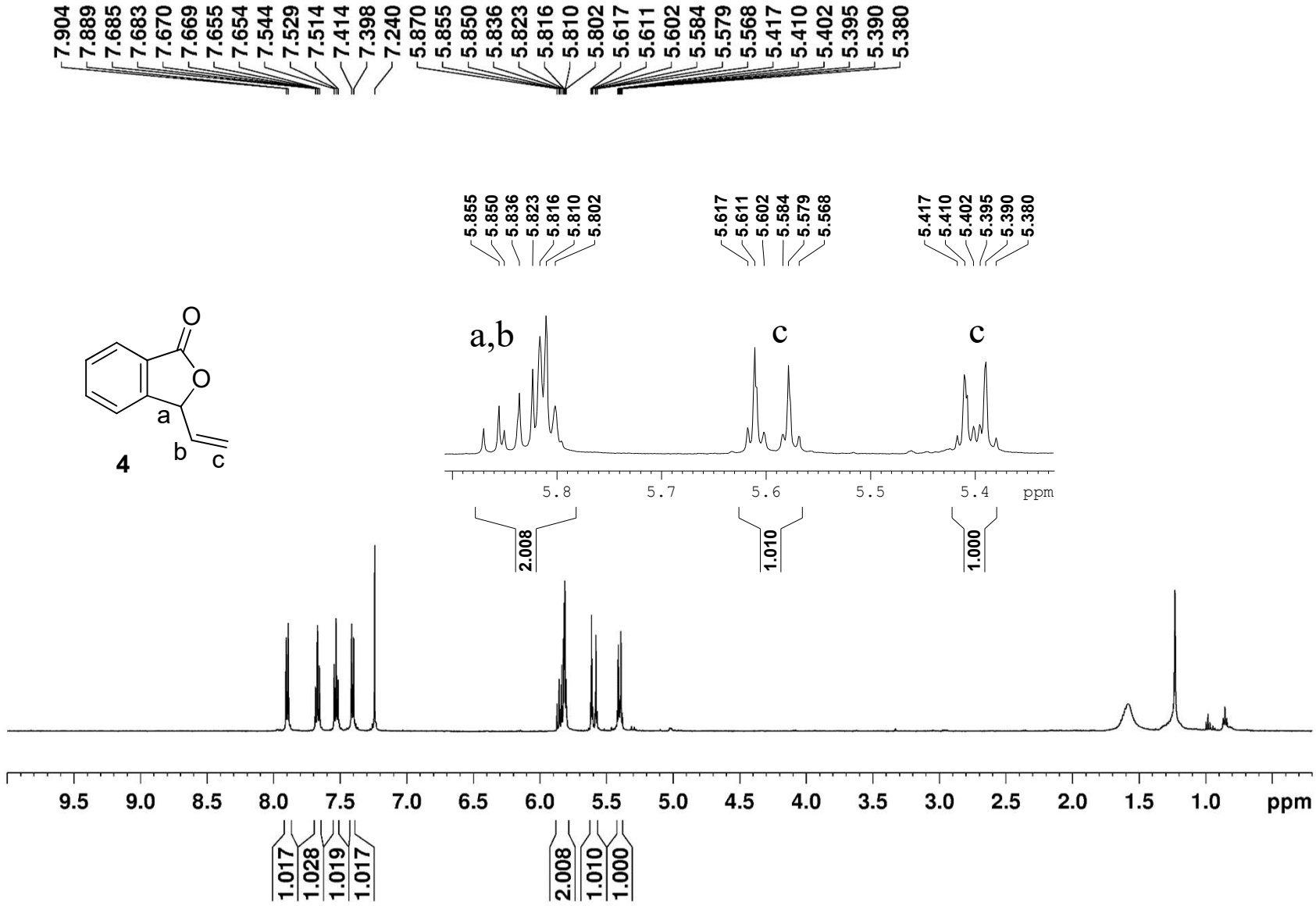
^{13}C NMR of compound **2** (125 MHz, $CDCl_3$)



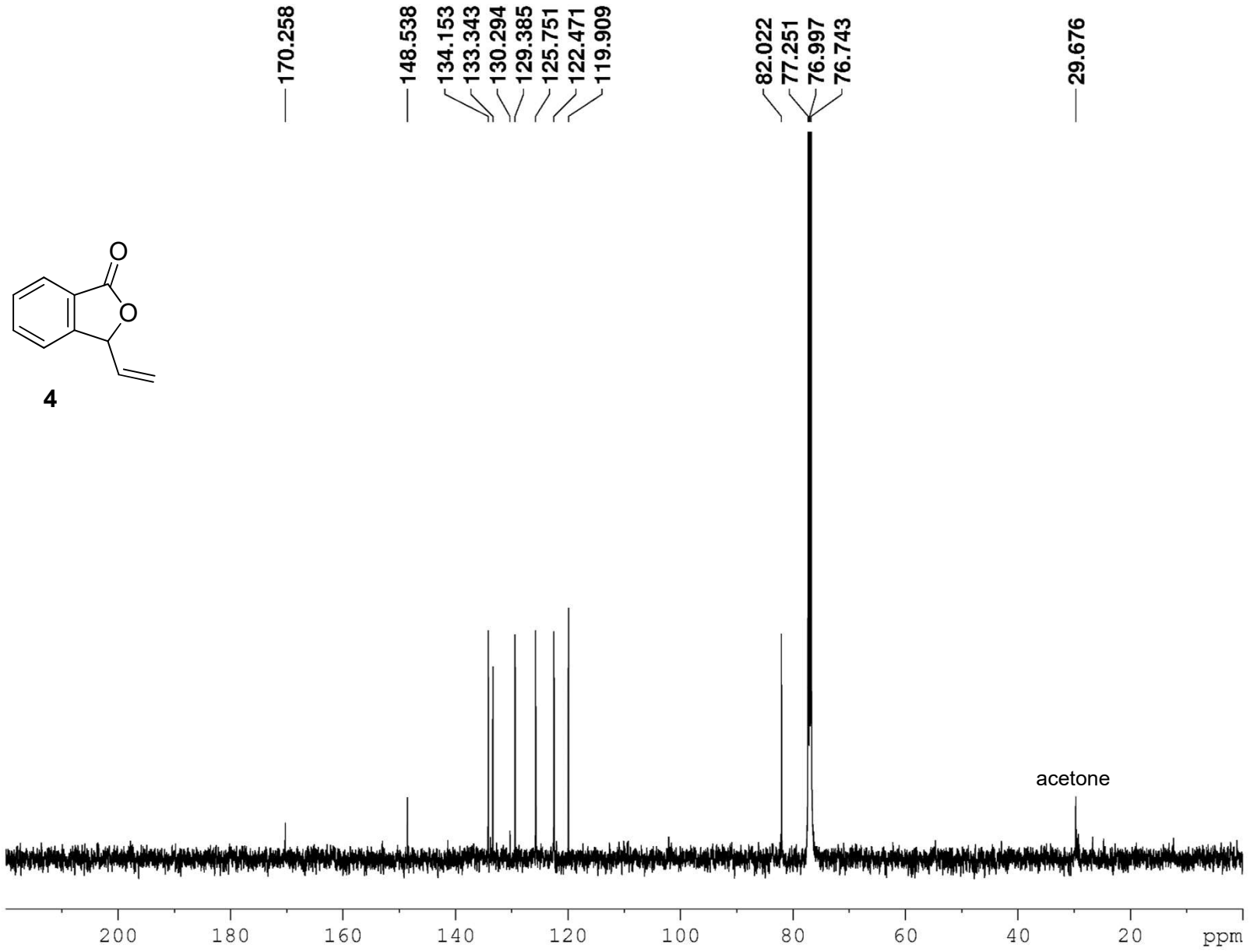
^{1}H NMR of compound **3** (500 MHz, $CDCl_3$)



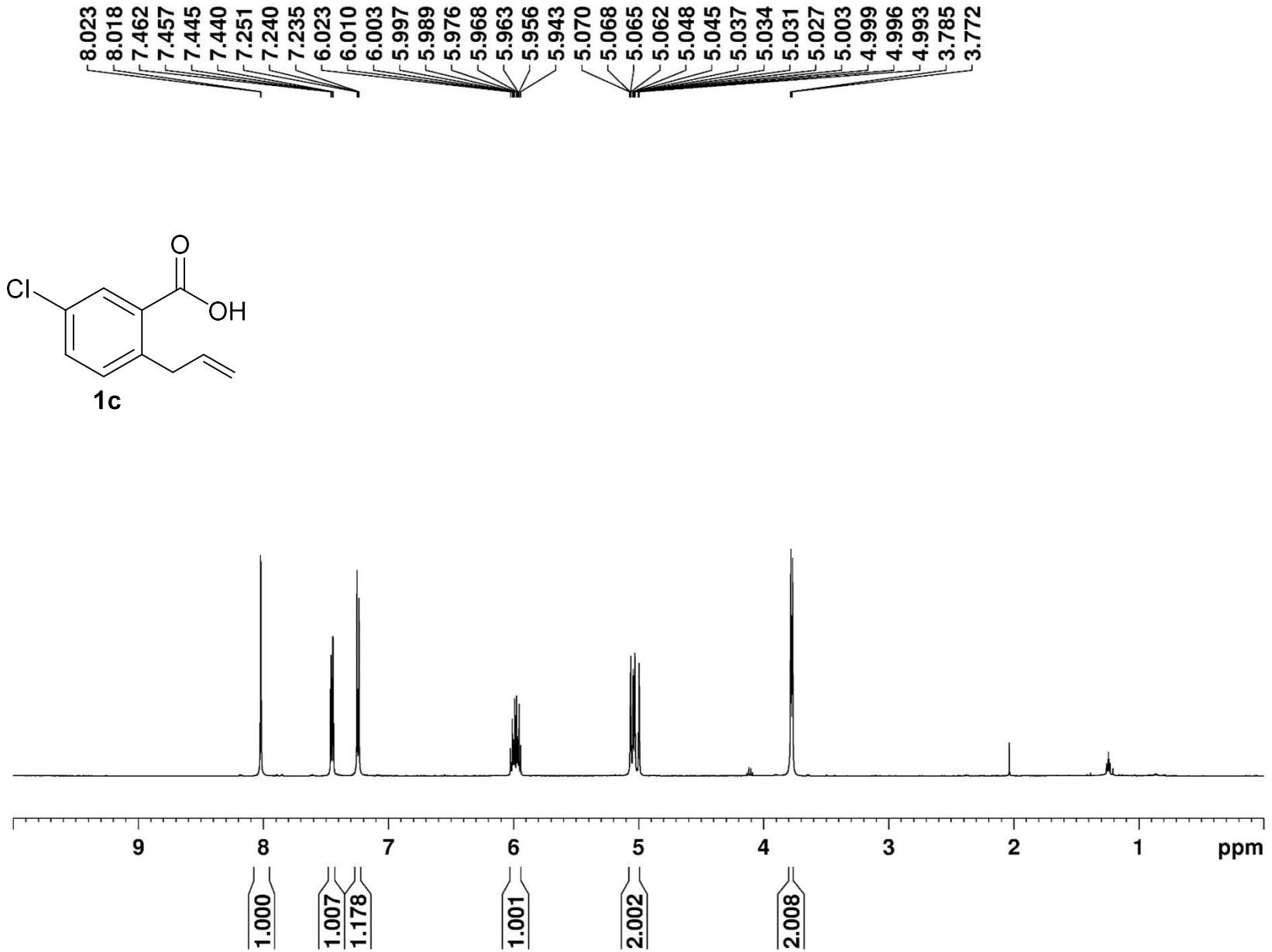
^{13}C NMR of compound **3** (125 MHz, $CDCl_3$)



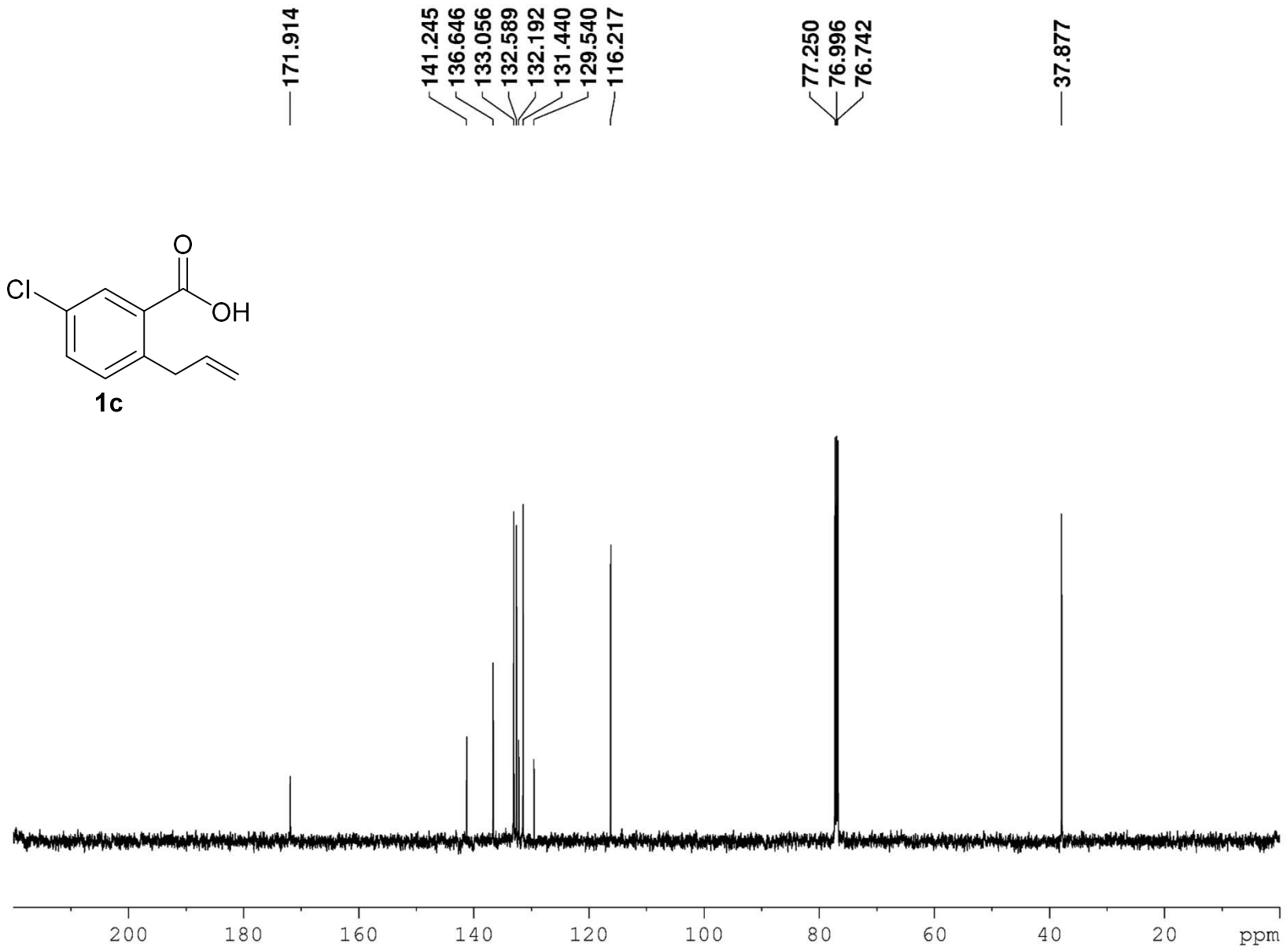
^{1}H NMR of compound **4** (500 MHz, $CDCl_3$)



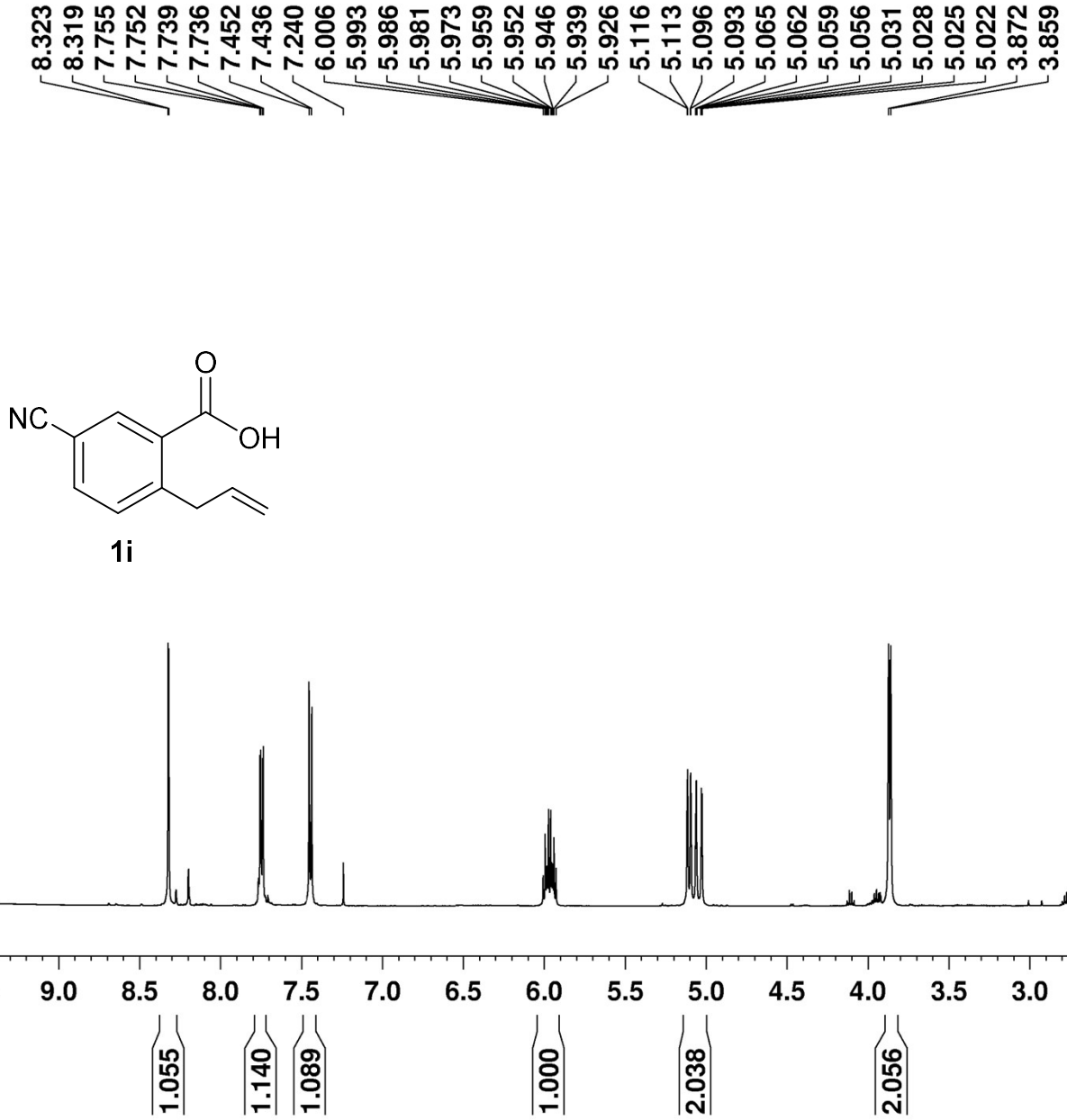
^{13}C NMR of compound **4** (125 MHz, $CDCl_3$)



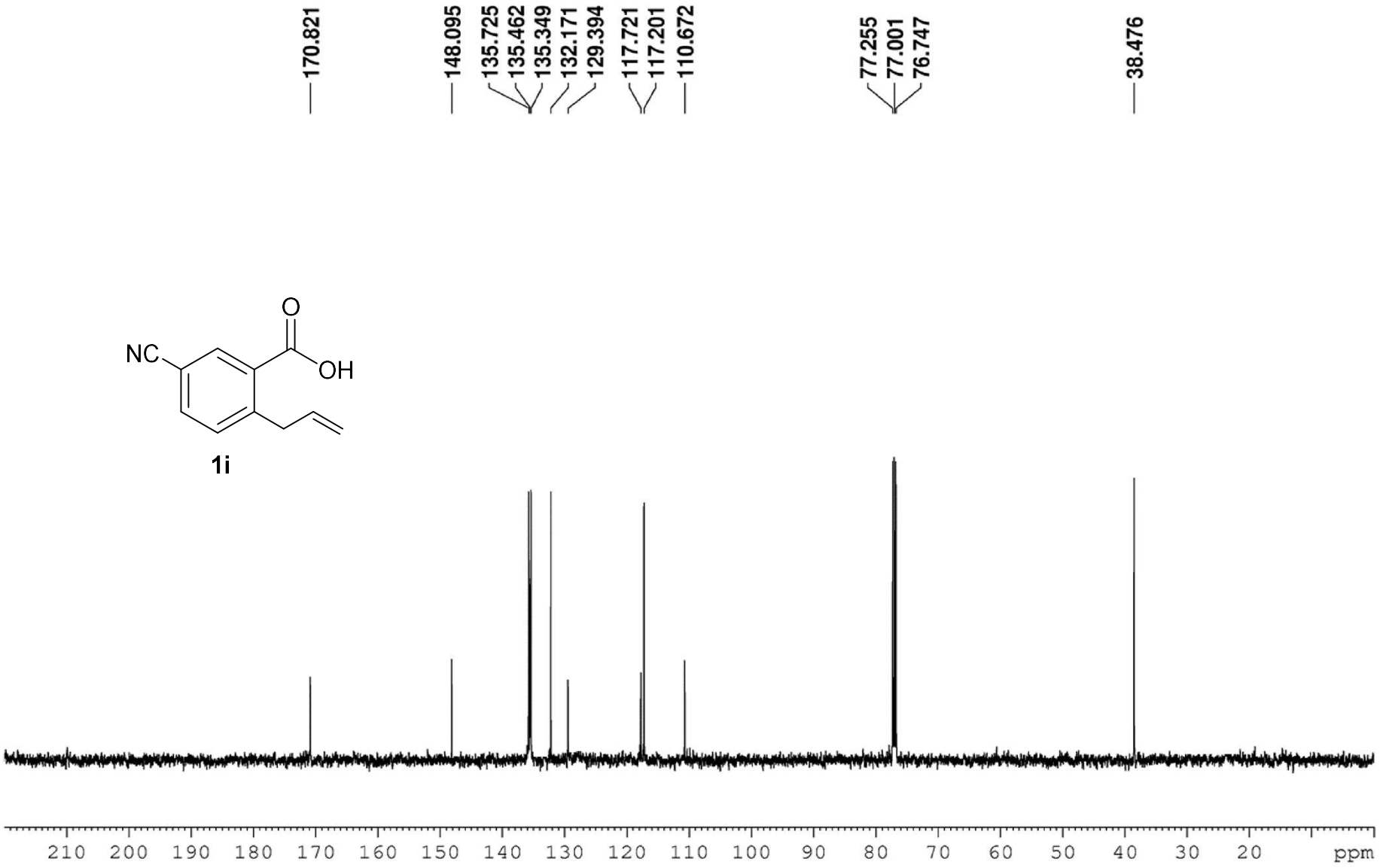
^{1}H NMR of compound **1c** (500 MHz, $CDCl_3$)



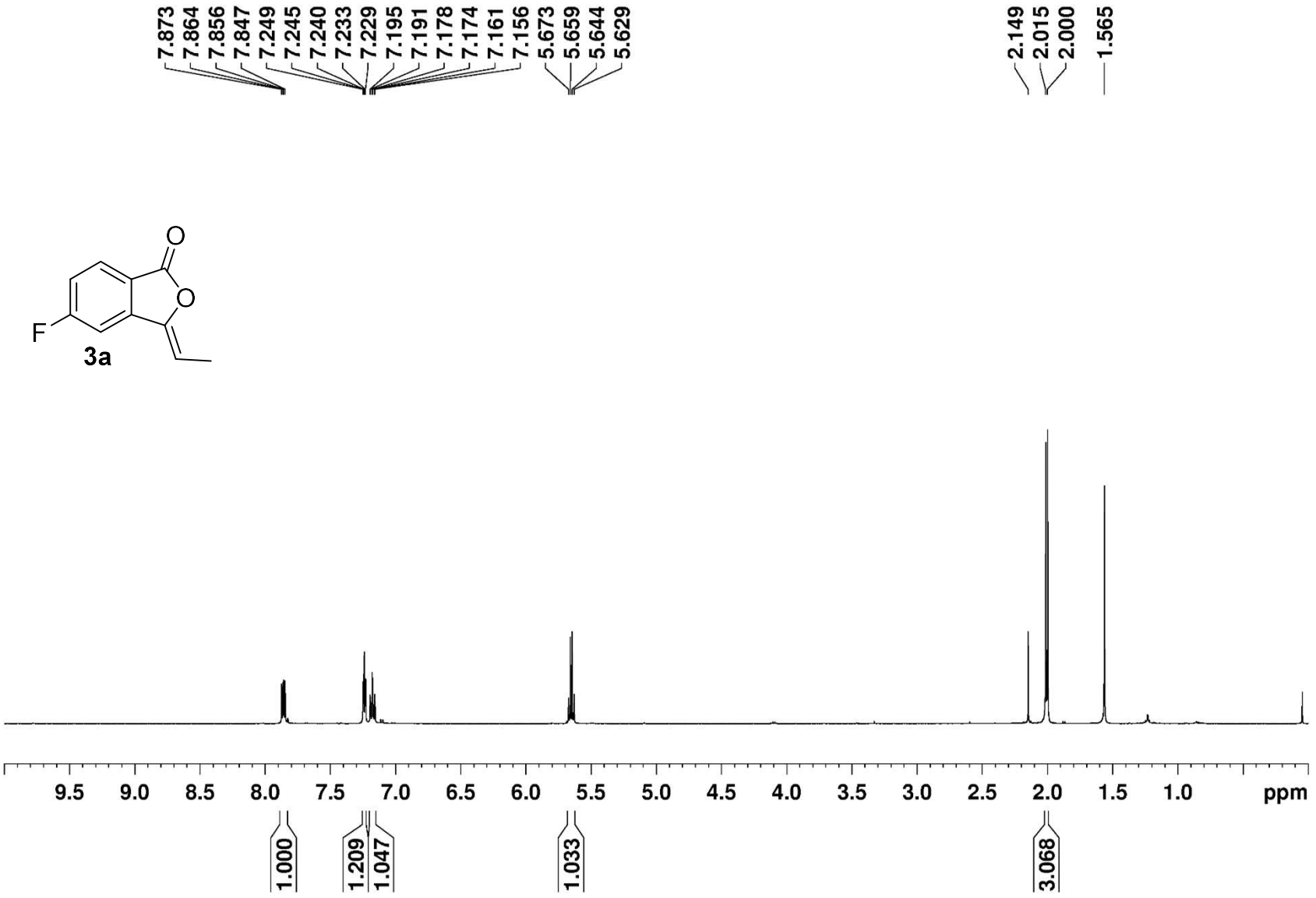
^{13}C NMR of compound **1c** (125 MHz, $CDCl_3$)



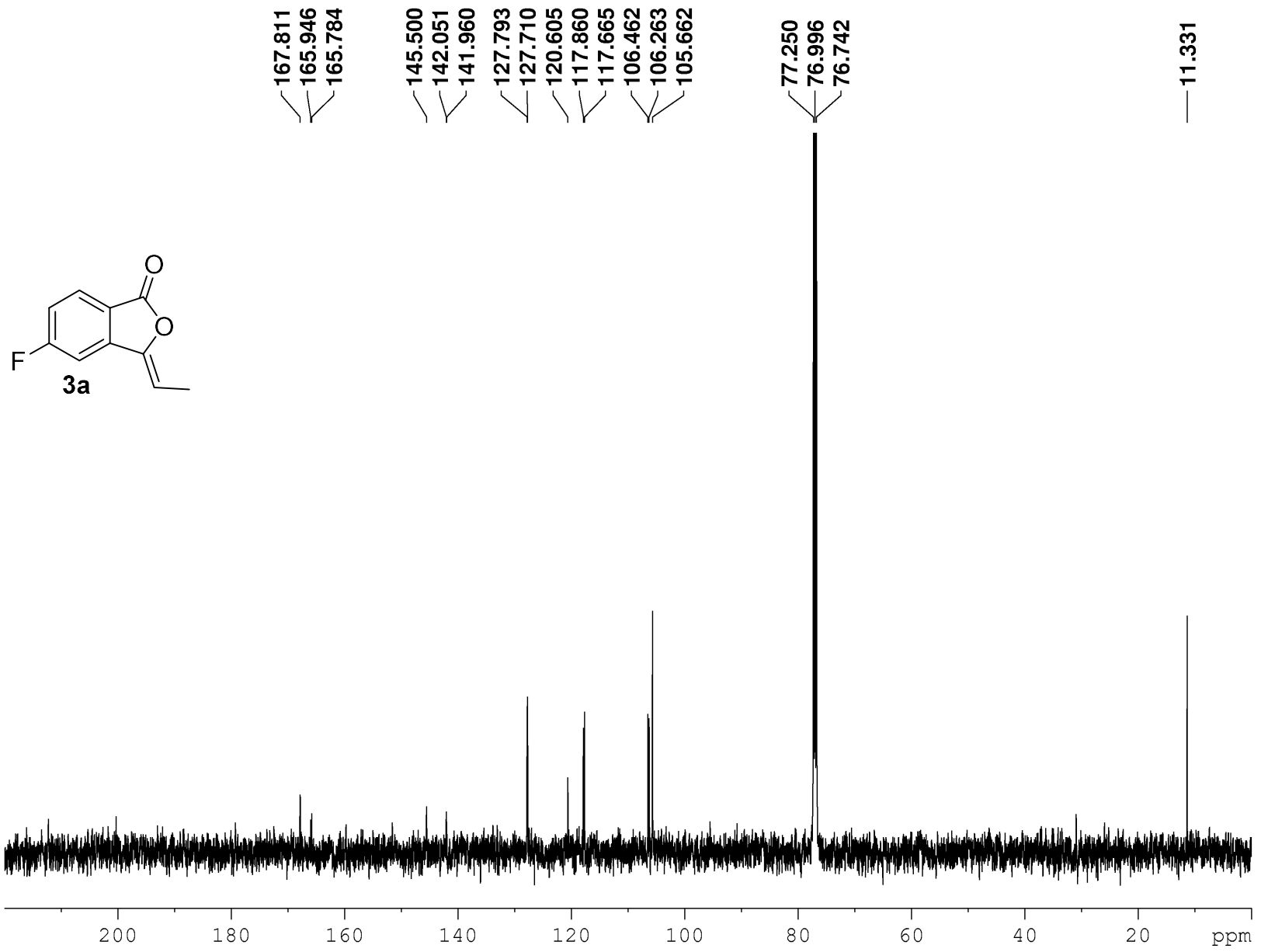
^{1}H NMR of compound **1i** (500 MHz, $CDCl_3$)



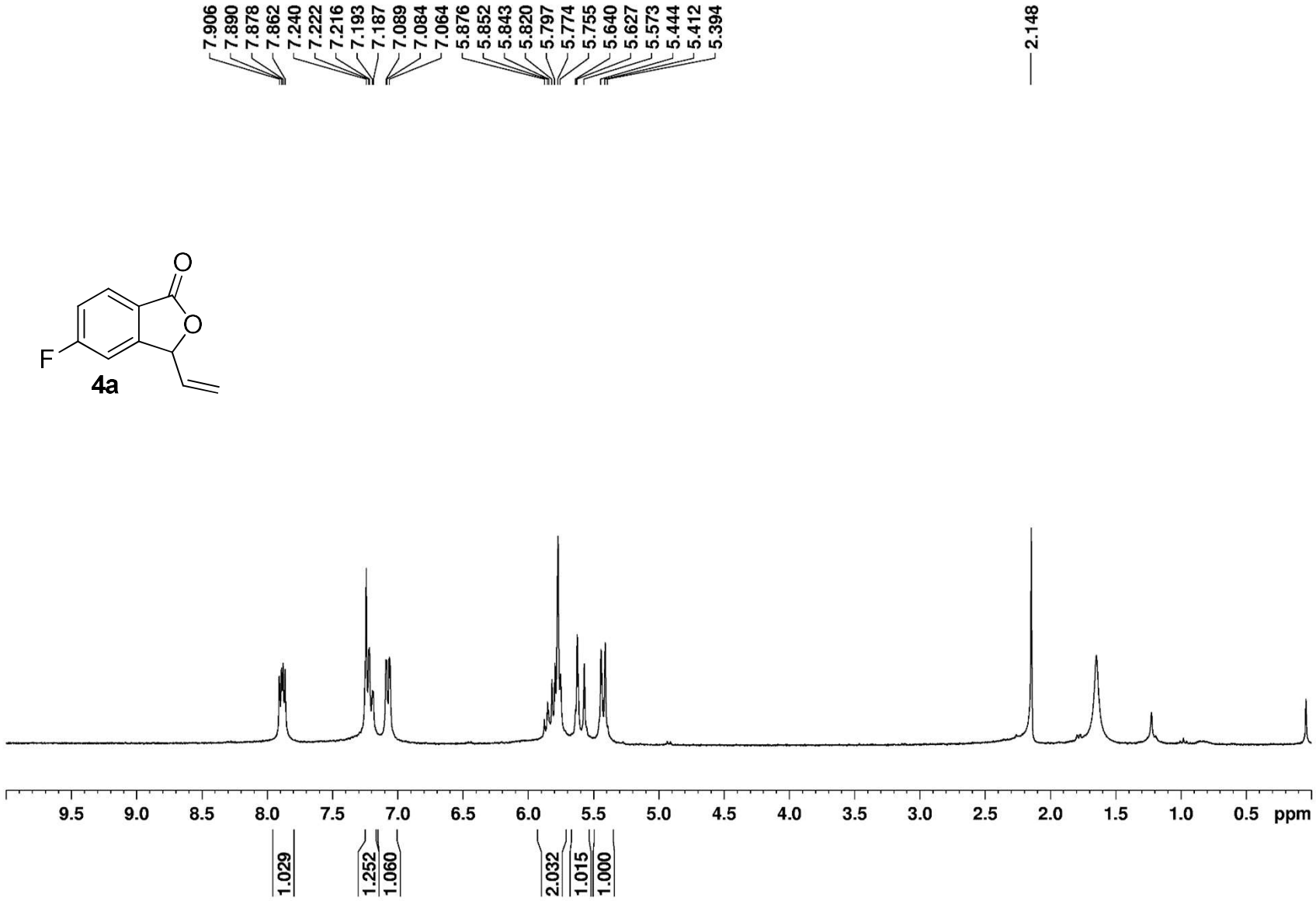
^{13}C NMR of compound **1i** (125 MHz, $CDCl_3$)



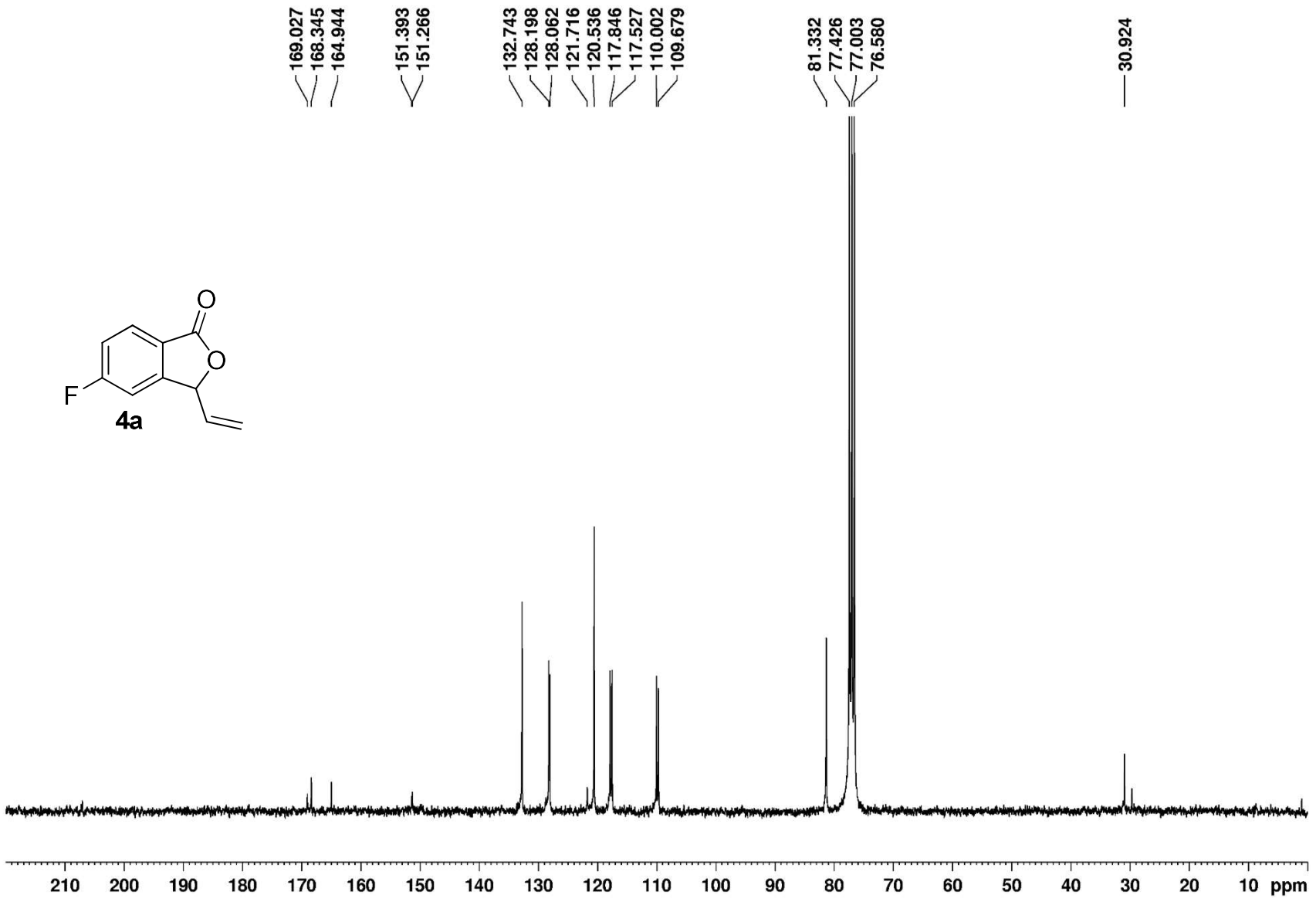
^{1}H NMR of compound **3a** (500 MHz, $CDCl_3$)



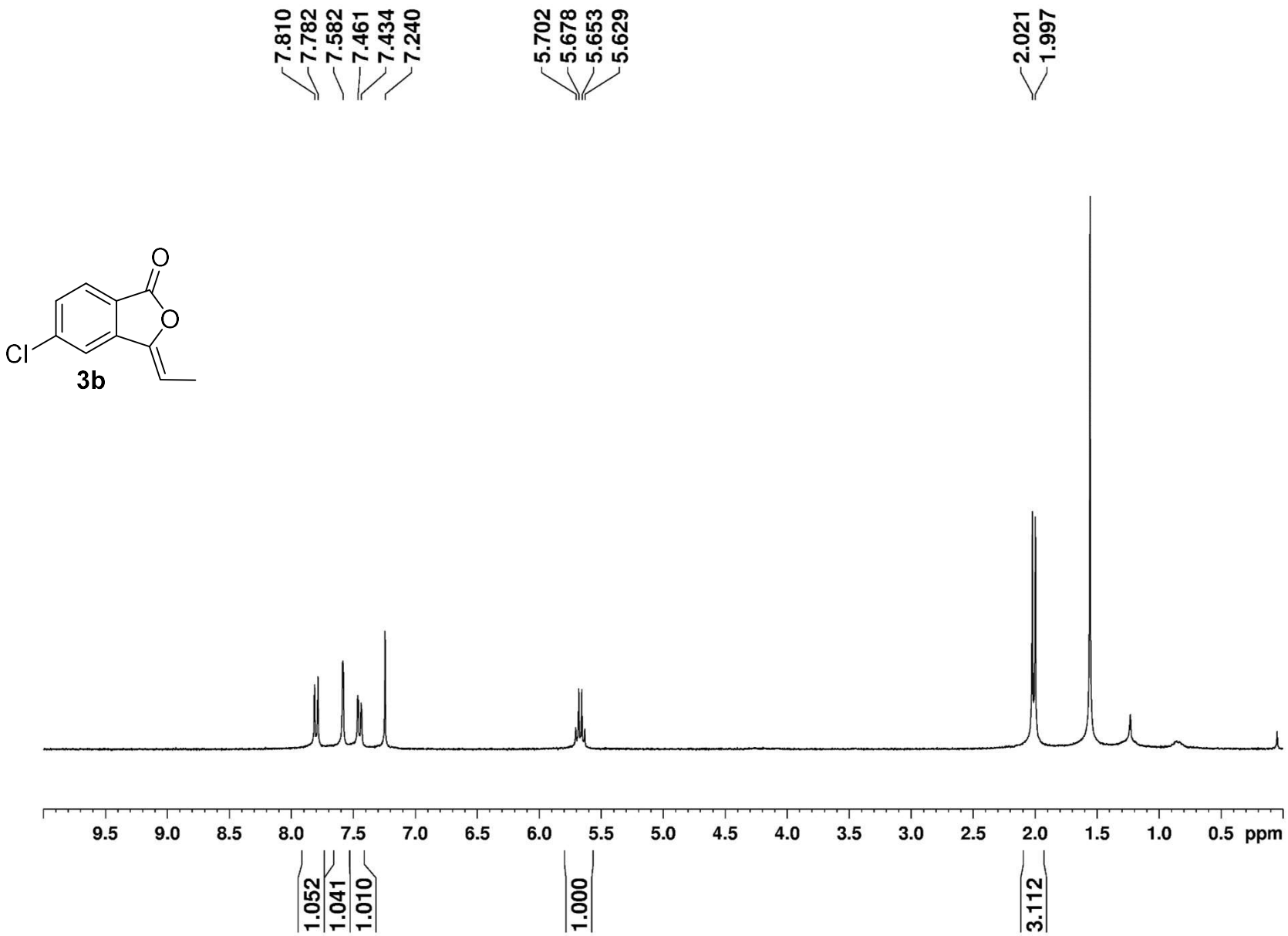
^{13}C NMR of compound **3a** (125 MHz, $CDCl_3$)



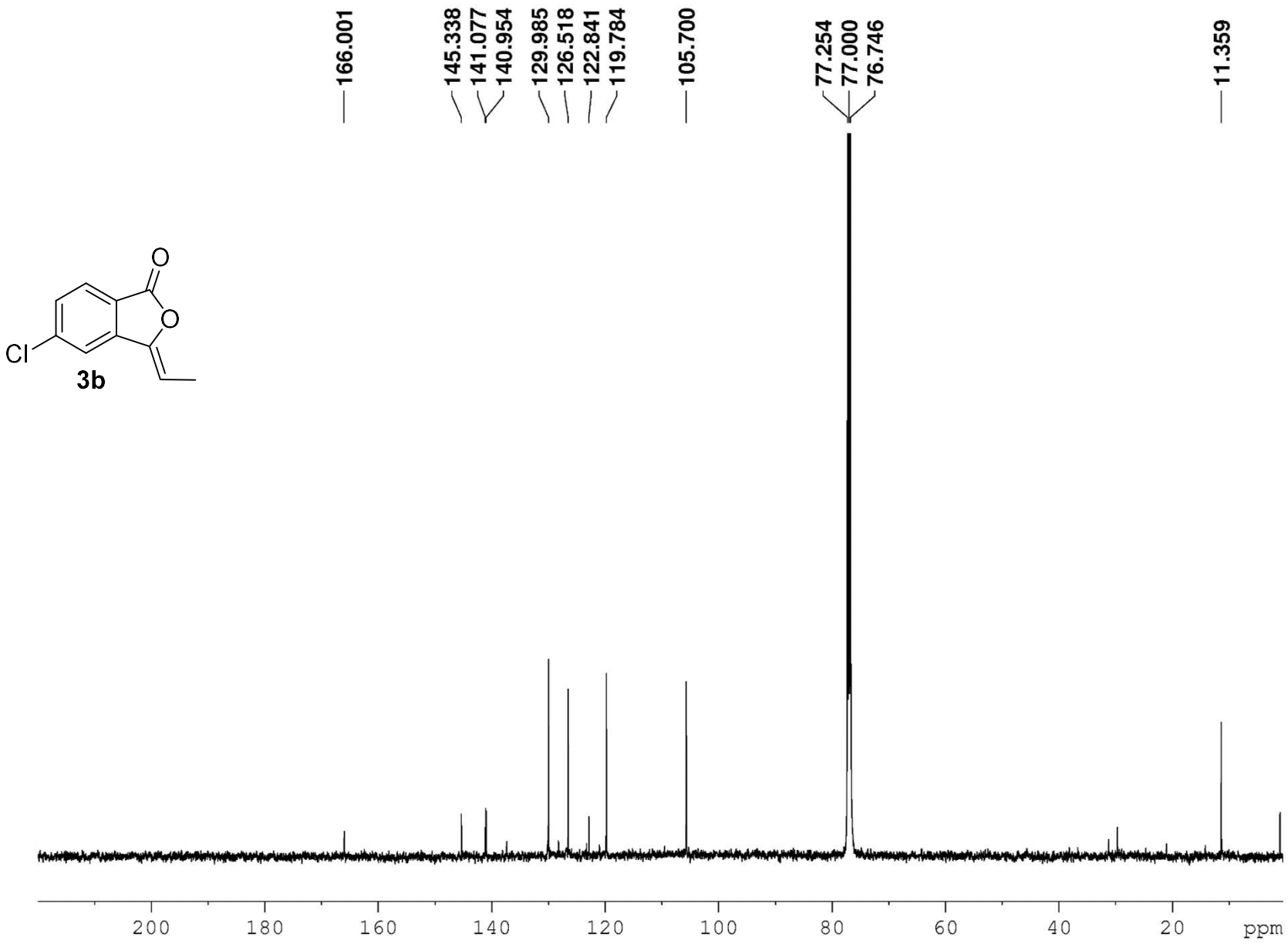
^{1}H NMR of compound **4a** (300 MHz, $CDCl_3$)



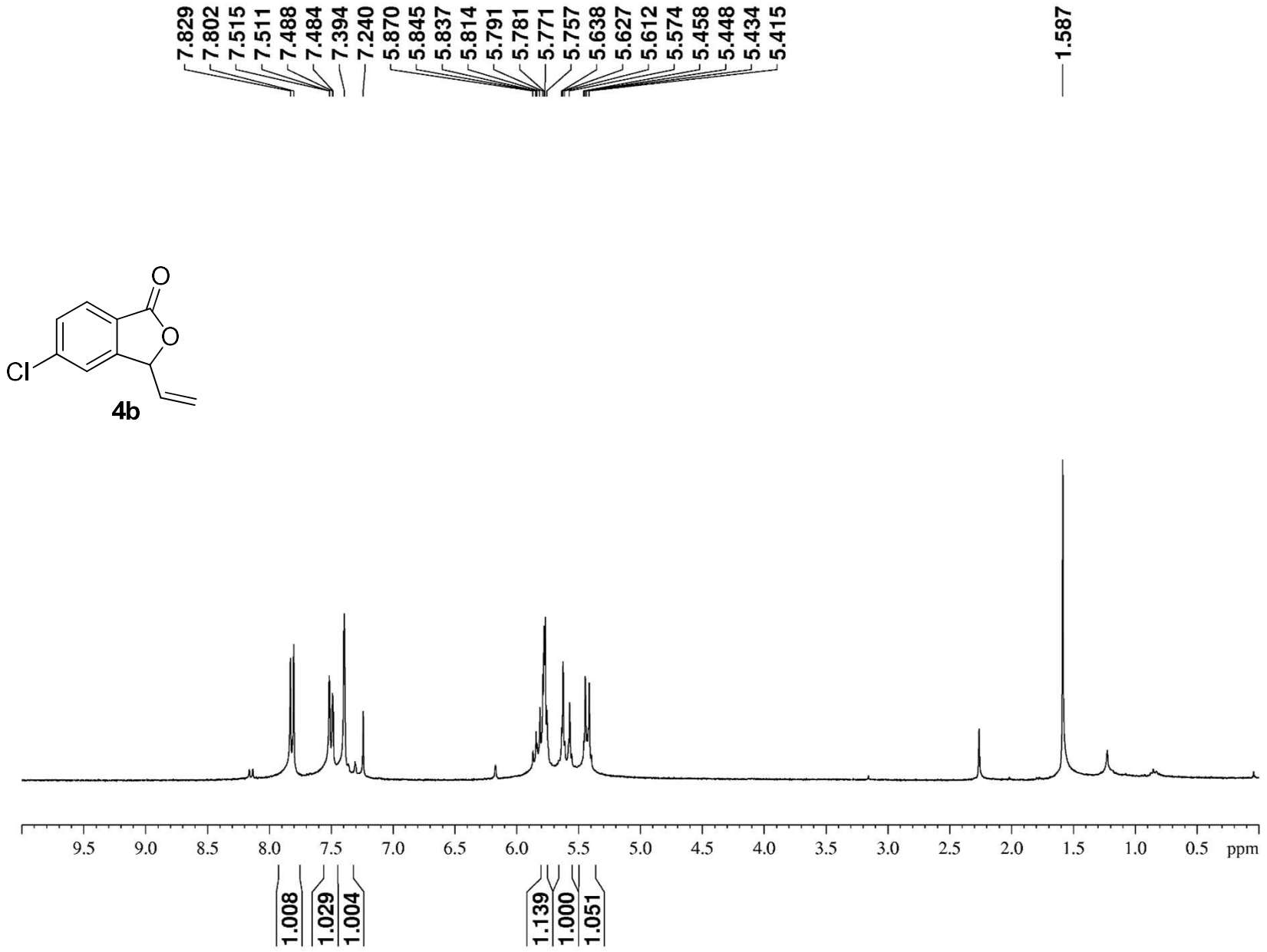
^{13}C NMR of compound **4a** (75 MHz, $CDCl_3$)



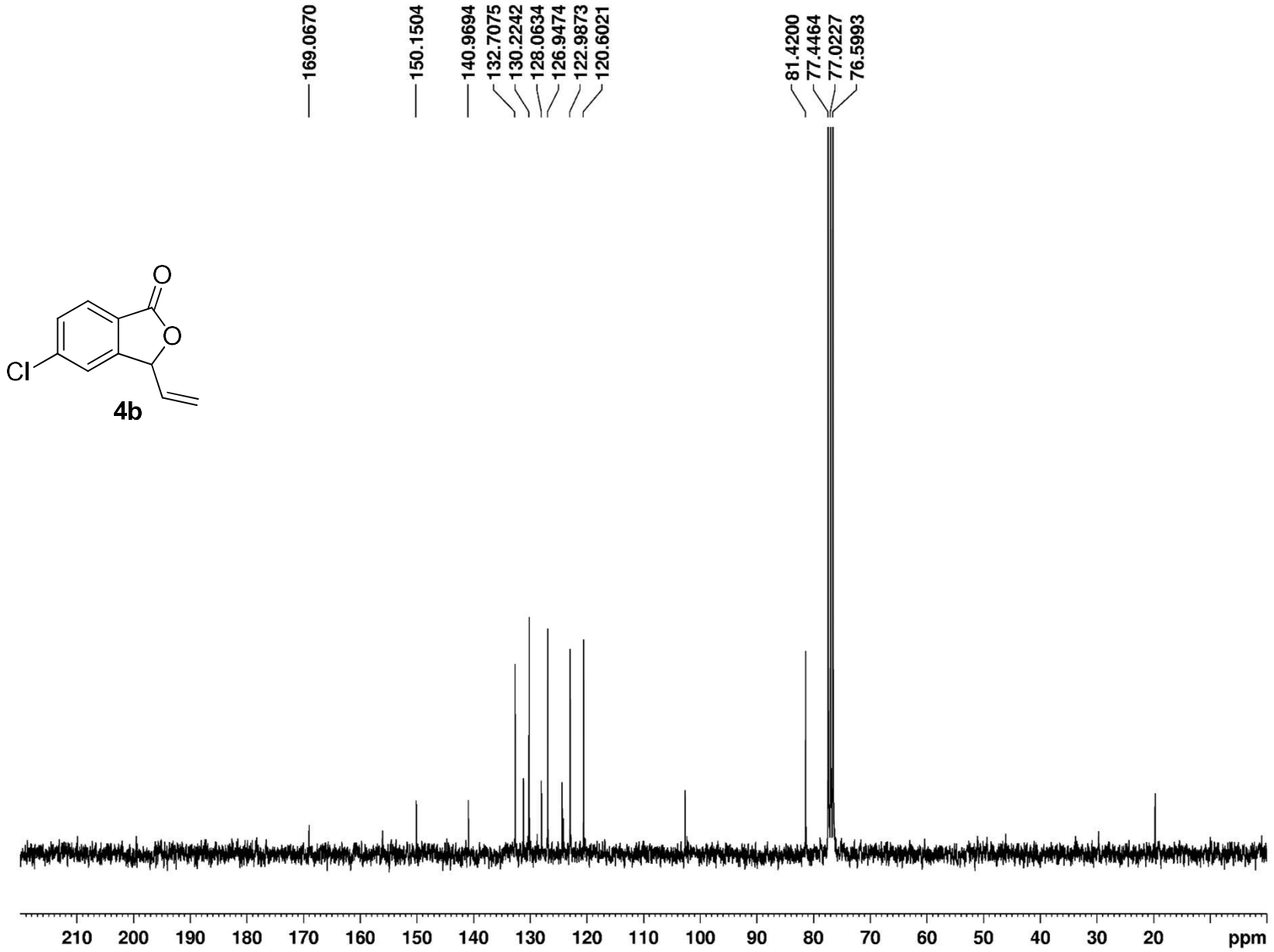
^{1}H NMR of compound **3b** (300 MHz, $CDCl_3$)



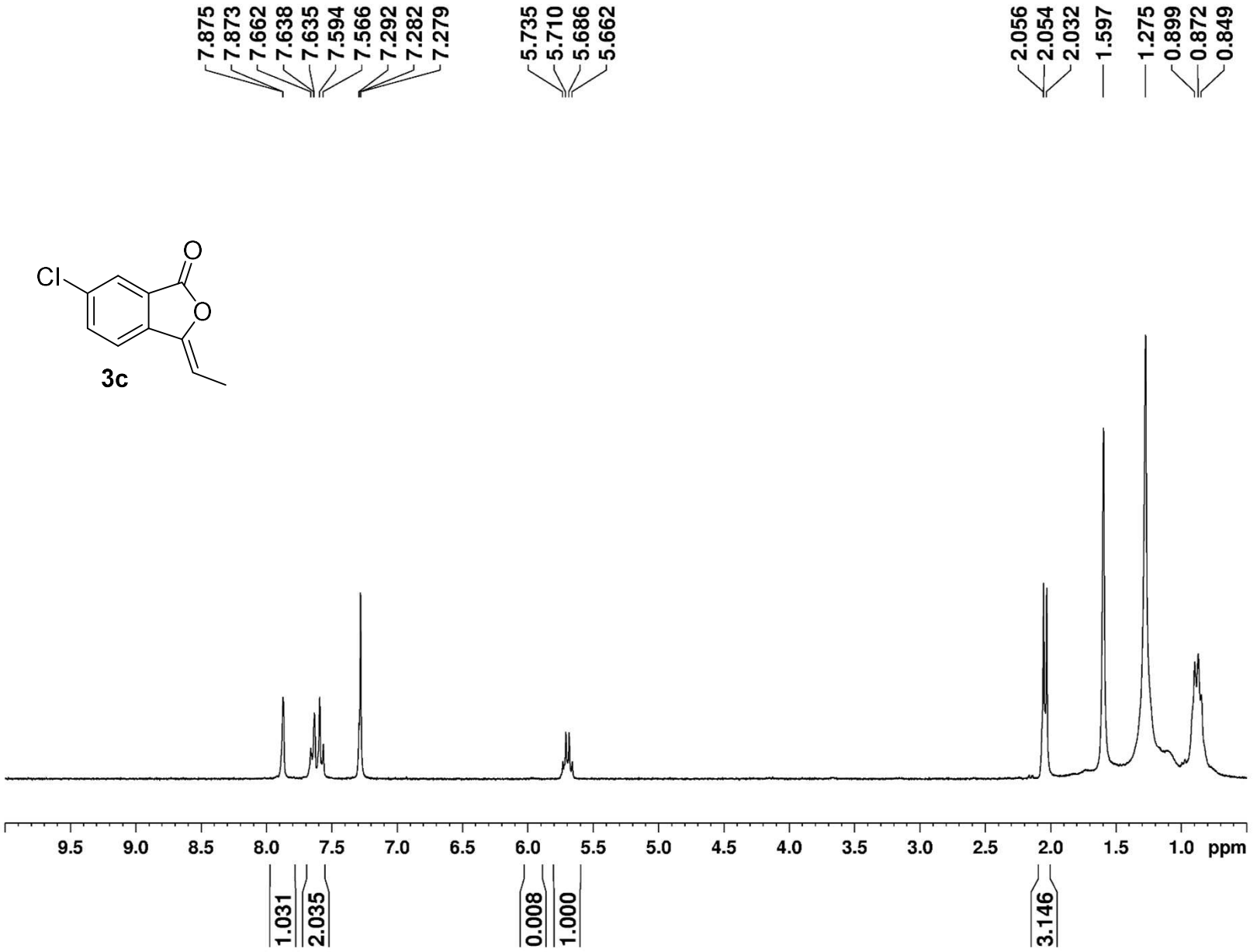
^{13}C NMR of compound **3b** (75 MHz, $CDCl_3$)



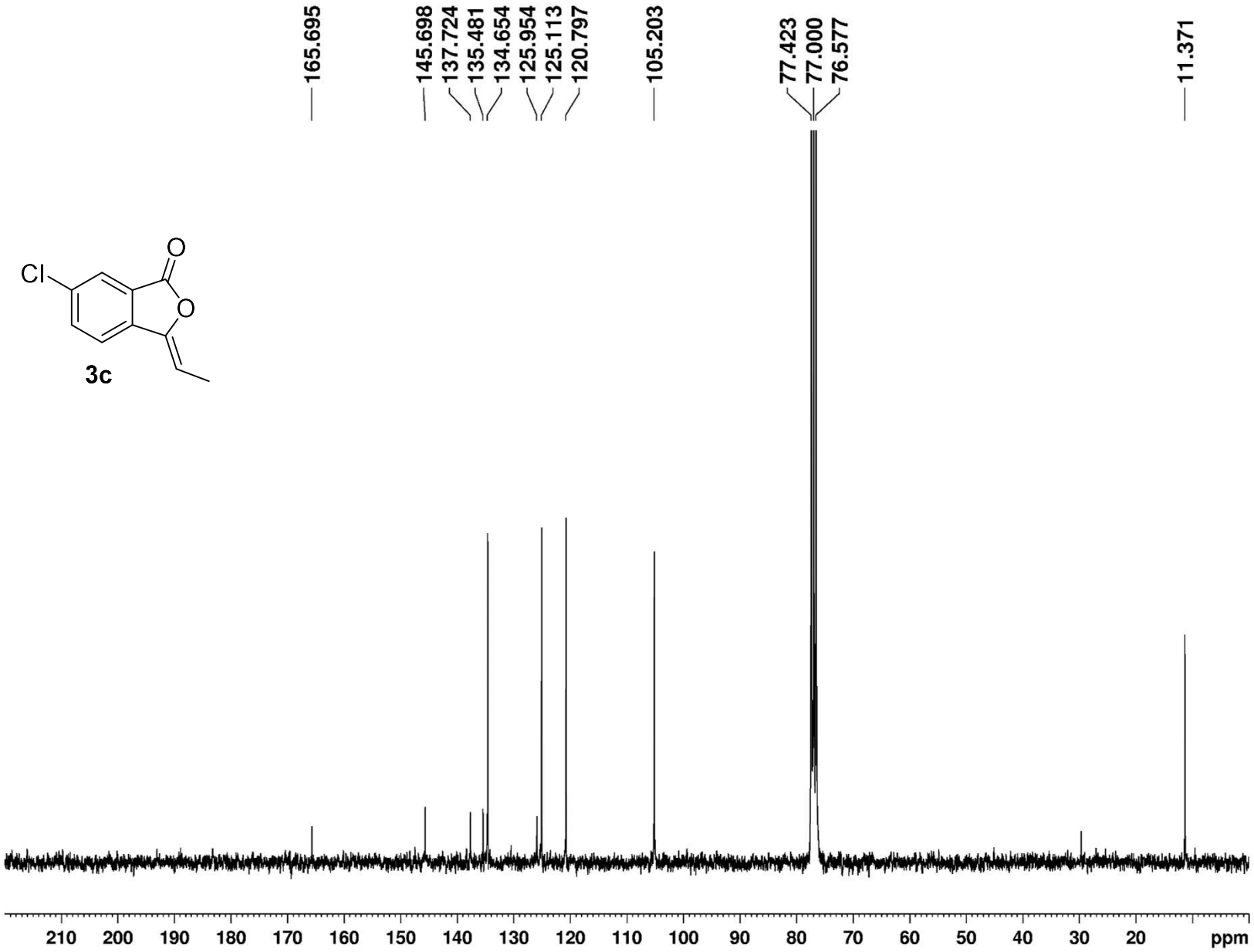
^{1}H NMR of compound **4b** (300 MHz, $CDCl_3$)



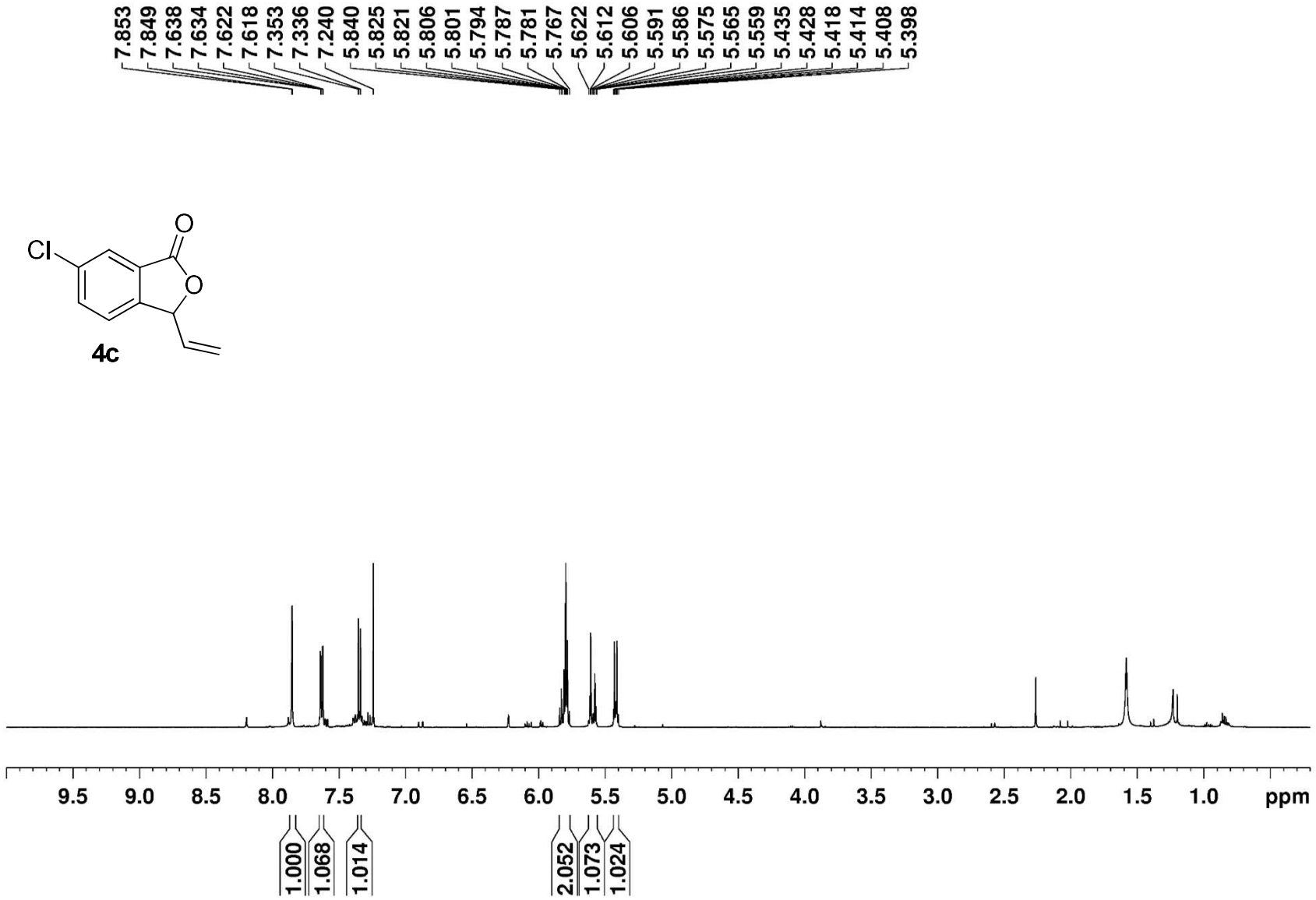
^{13}C NMR of compound **4b** (75 MHz, $CDCl_3$)



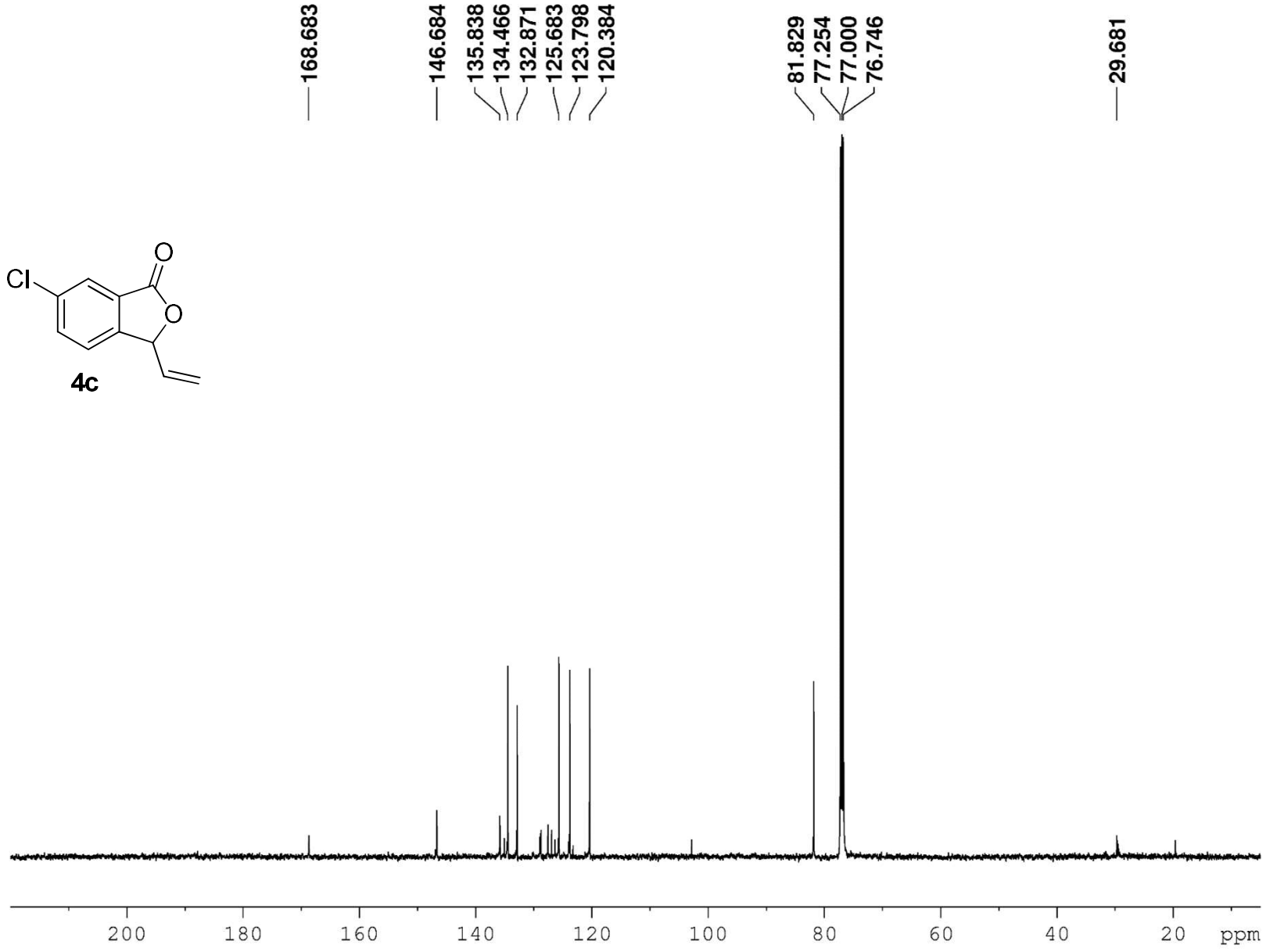
^{1}H NMR of compound **3c** (300 MHz, $CDCl_3$)



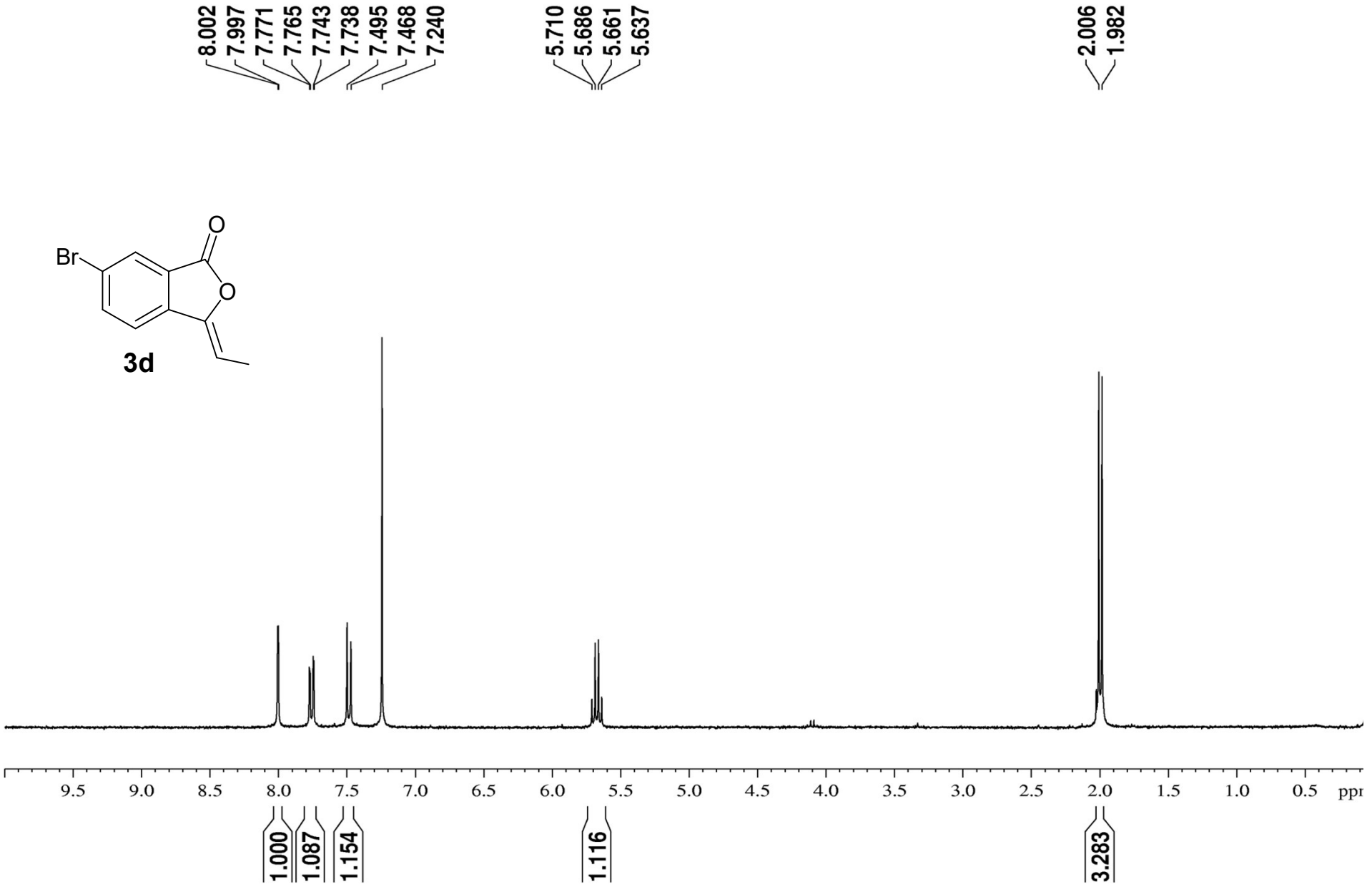
^{13}C NMR of compound **3c** (75 MHz, $CDCl_3$)



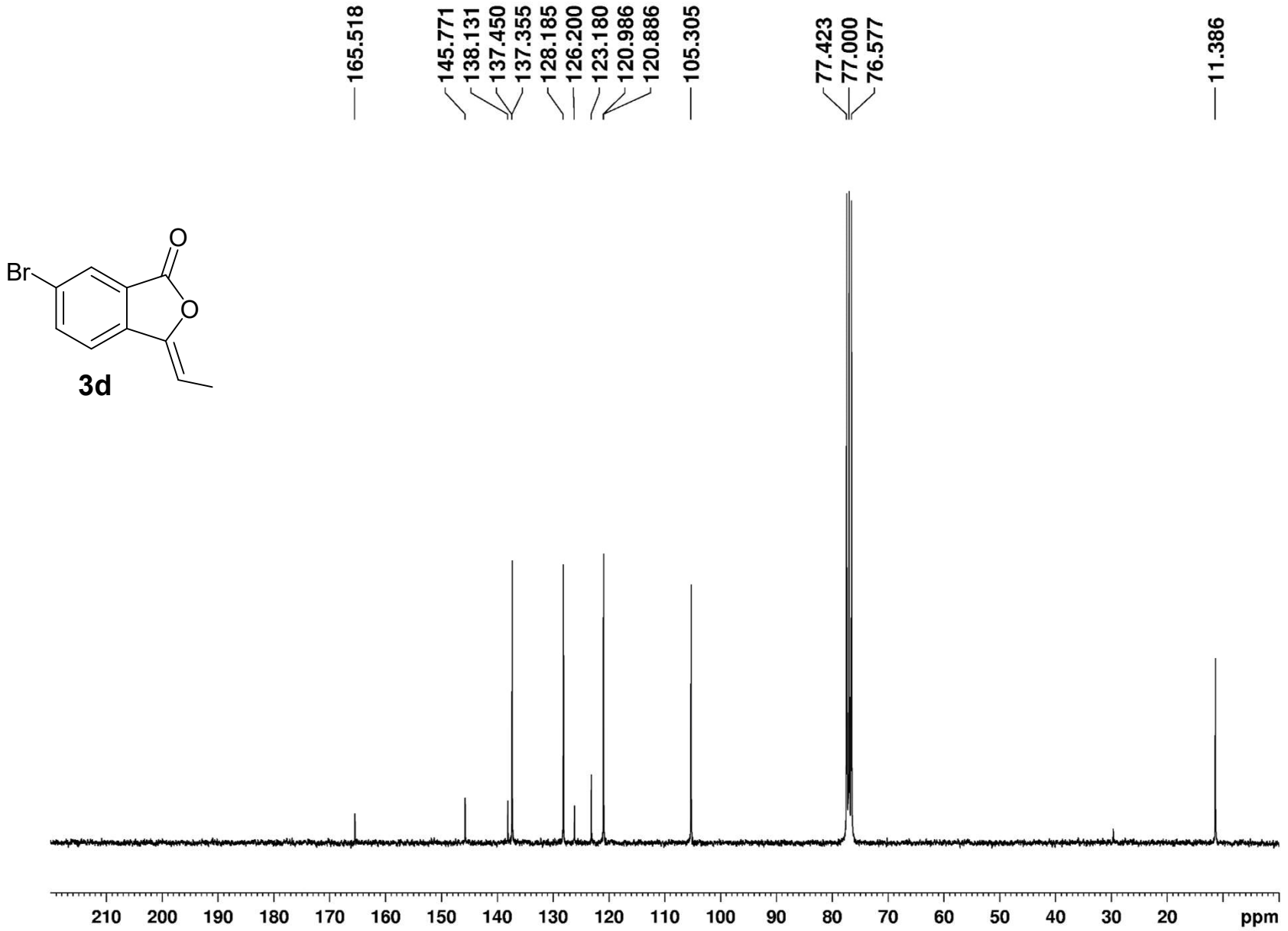
^{1}H NMR of compound **4c** (500 MHz, $CDCl_3$)



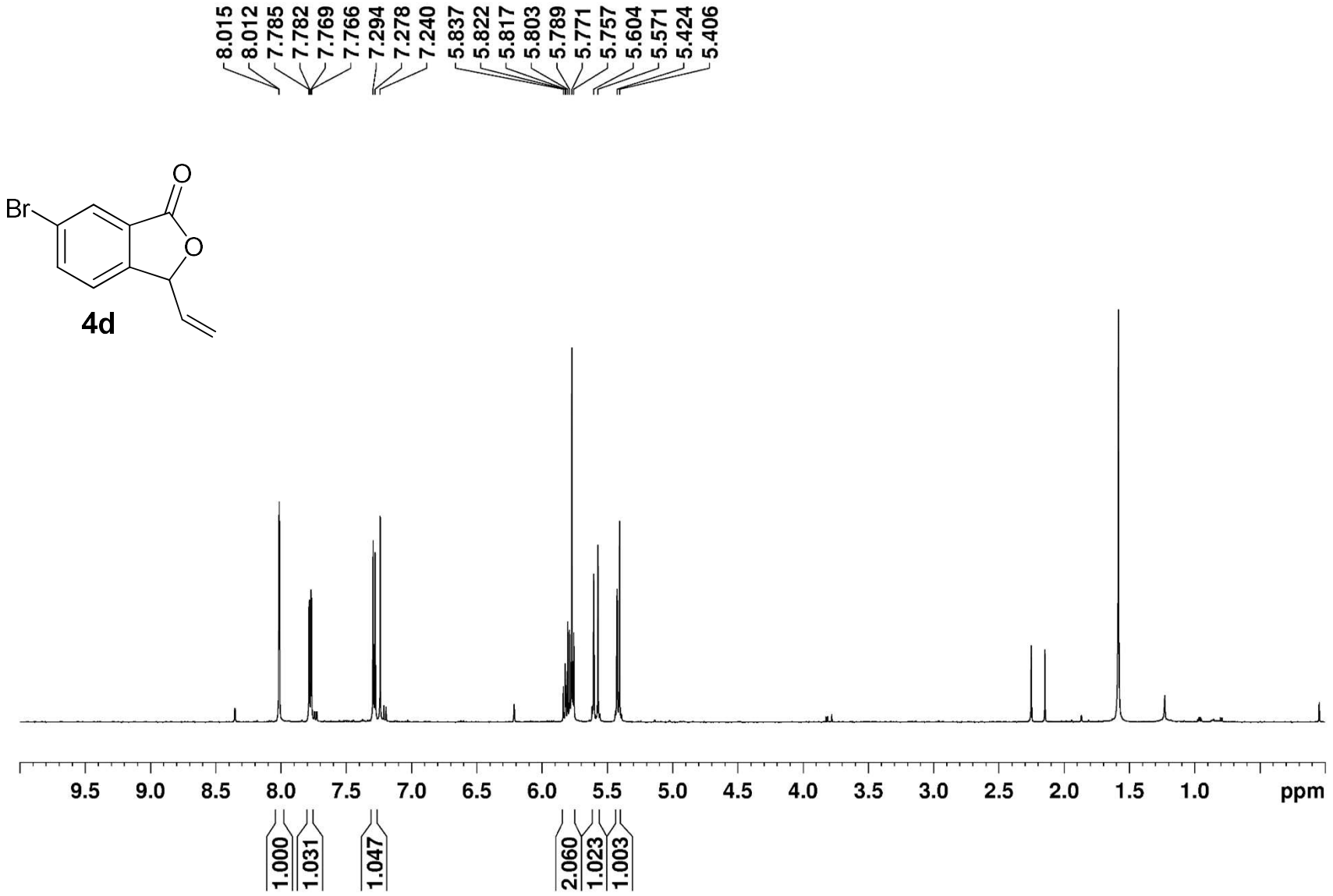
^{13}C NMR of compound **4c** (125 MHz, $CDCl_3$)



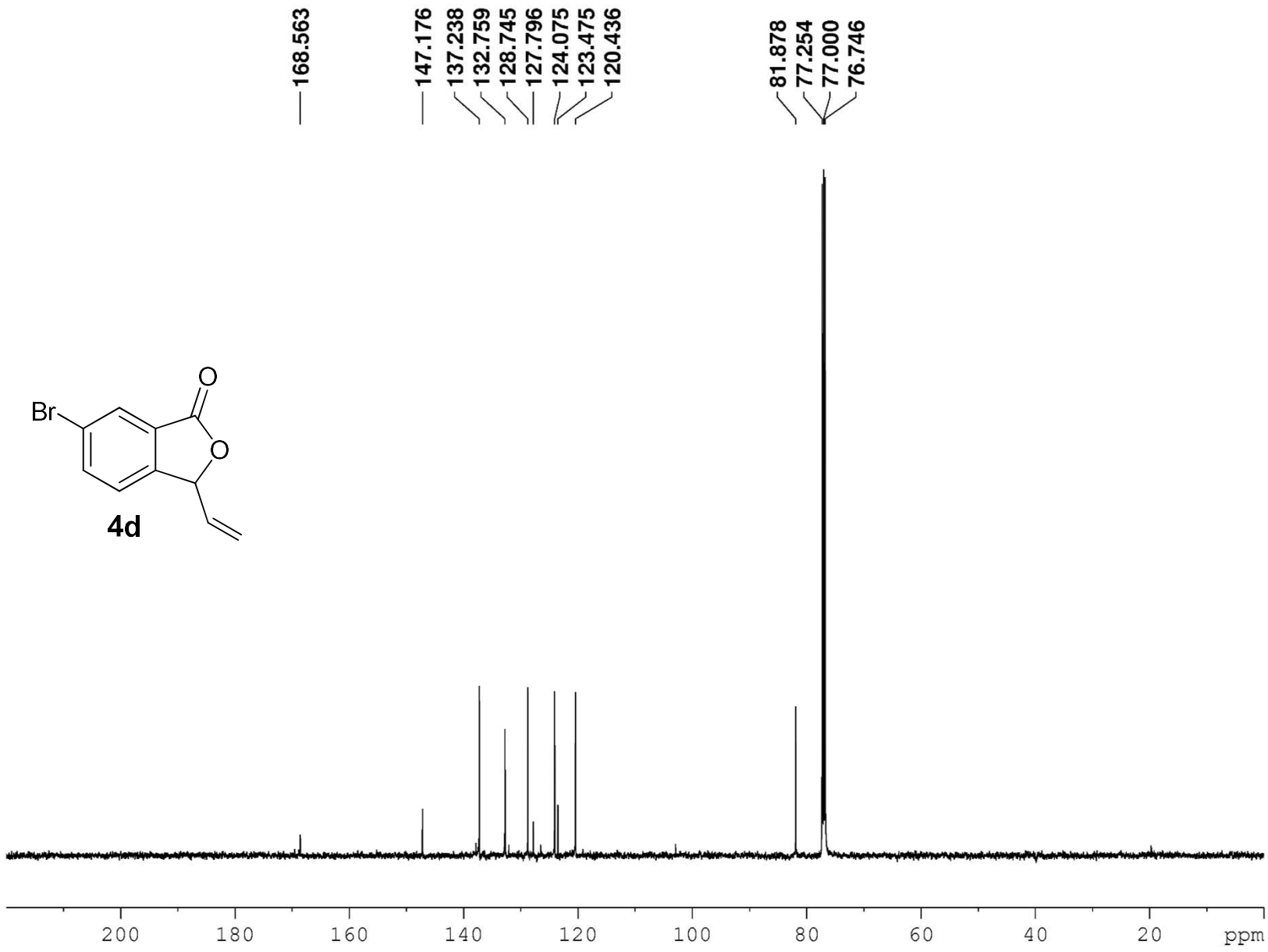
^{1}H NMR of compound **3d** (300 MHz, $CDCl_3$)



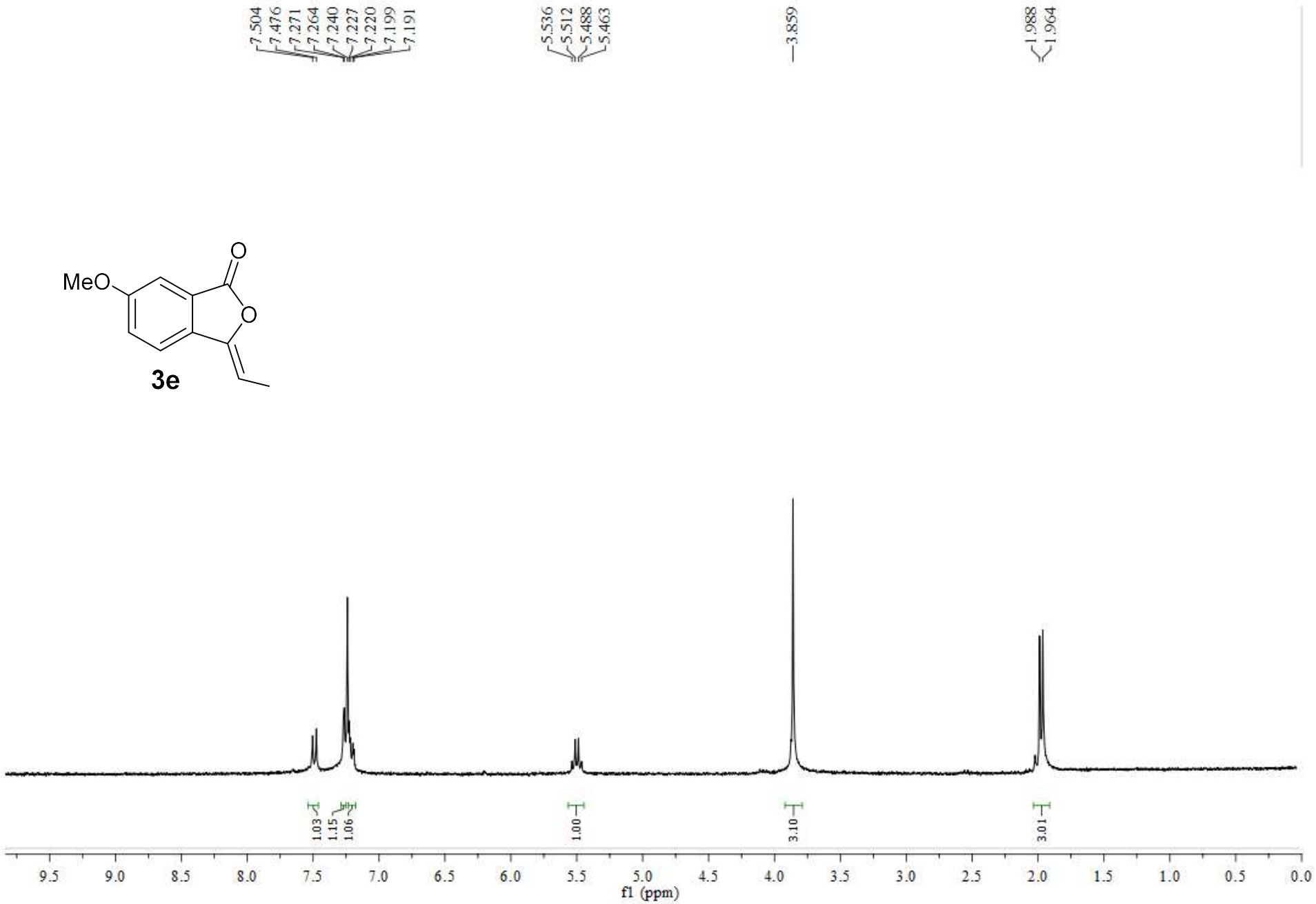
^{13}C NMR of compound **3d** (75 MHz, $CDCl_3$)



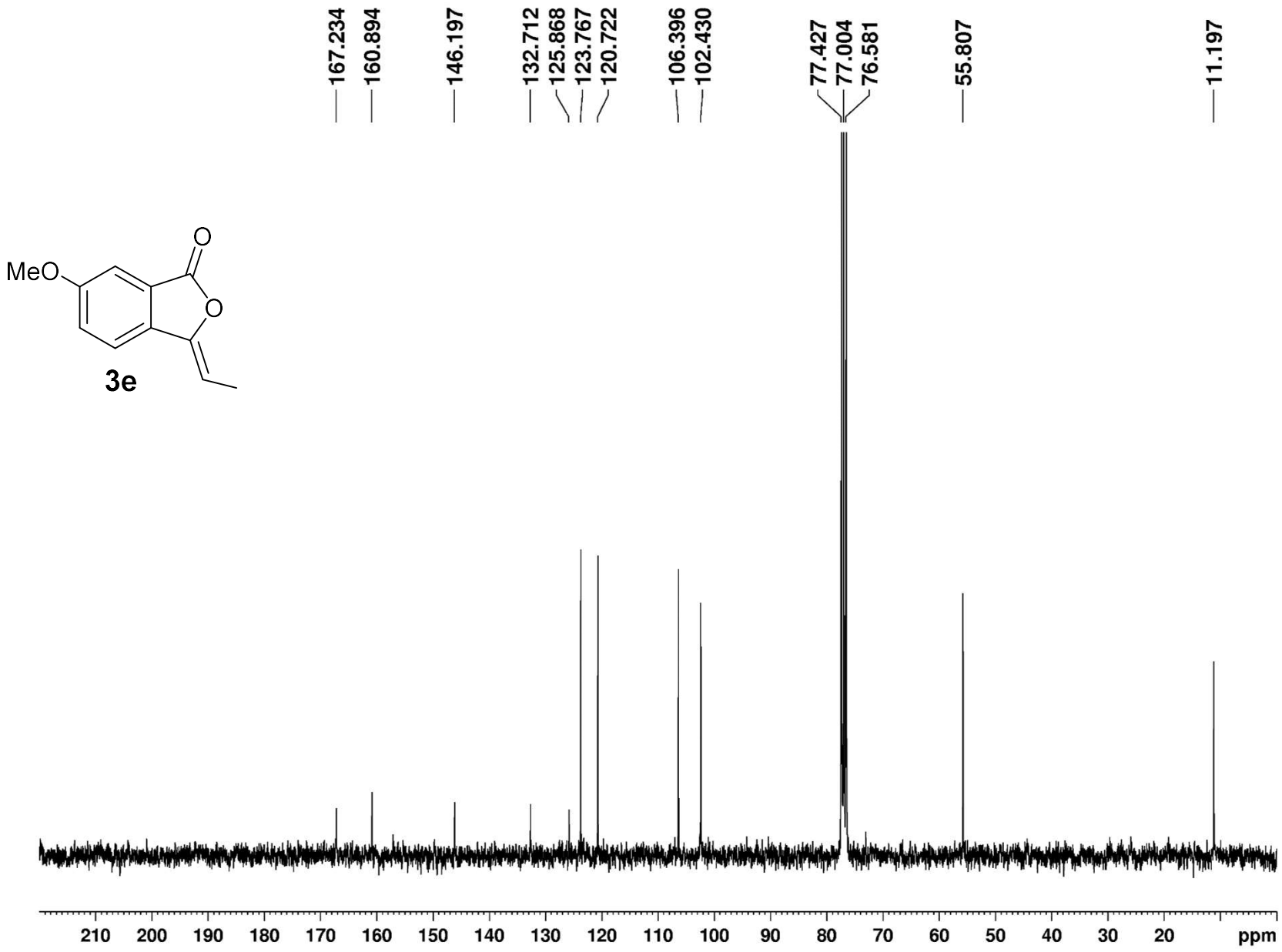
^{1}H NMR of compound **4d** (500 MHz, $CDCl_3$)



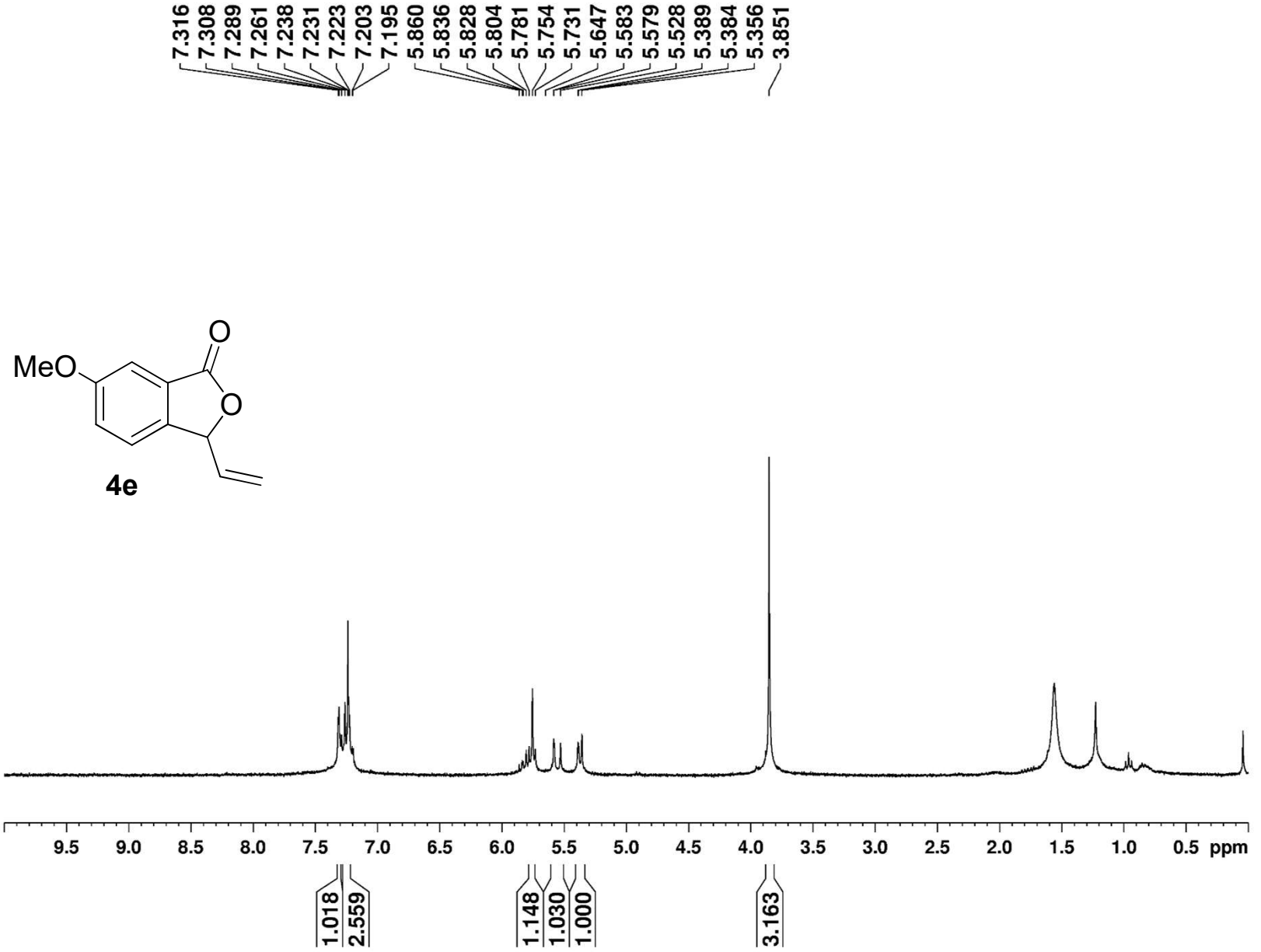
^{13}C NMR of compound **4d** (125 MHz, $CDCl_3$)



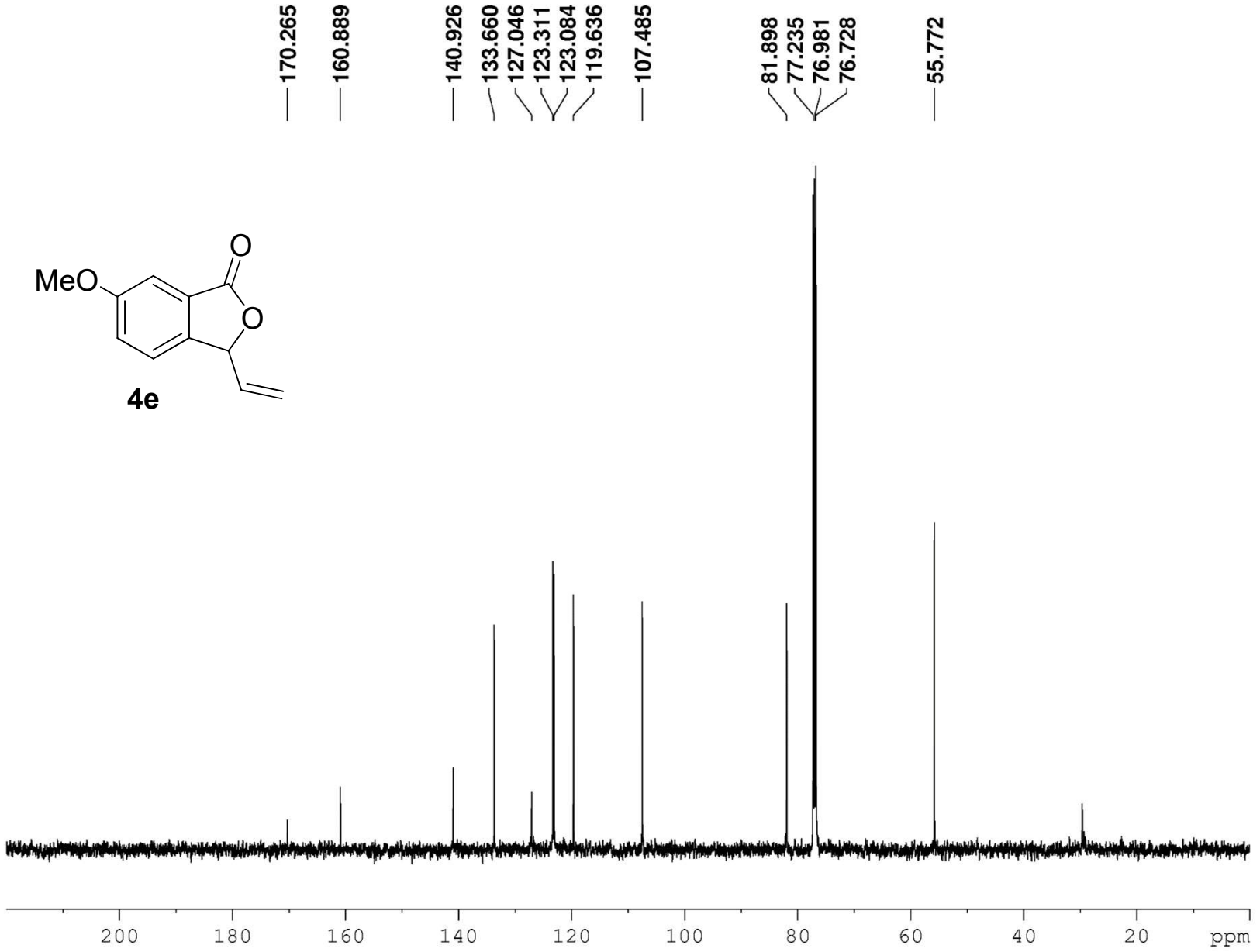
^{1}H NMR of compound **3e** (300 MHz, $CDCl_3$)



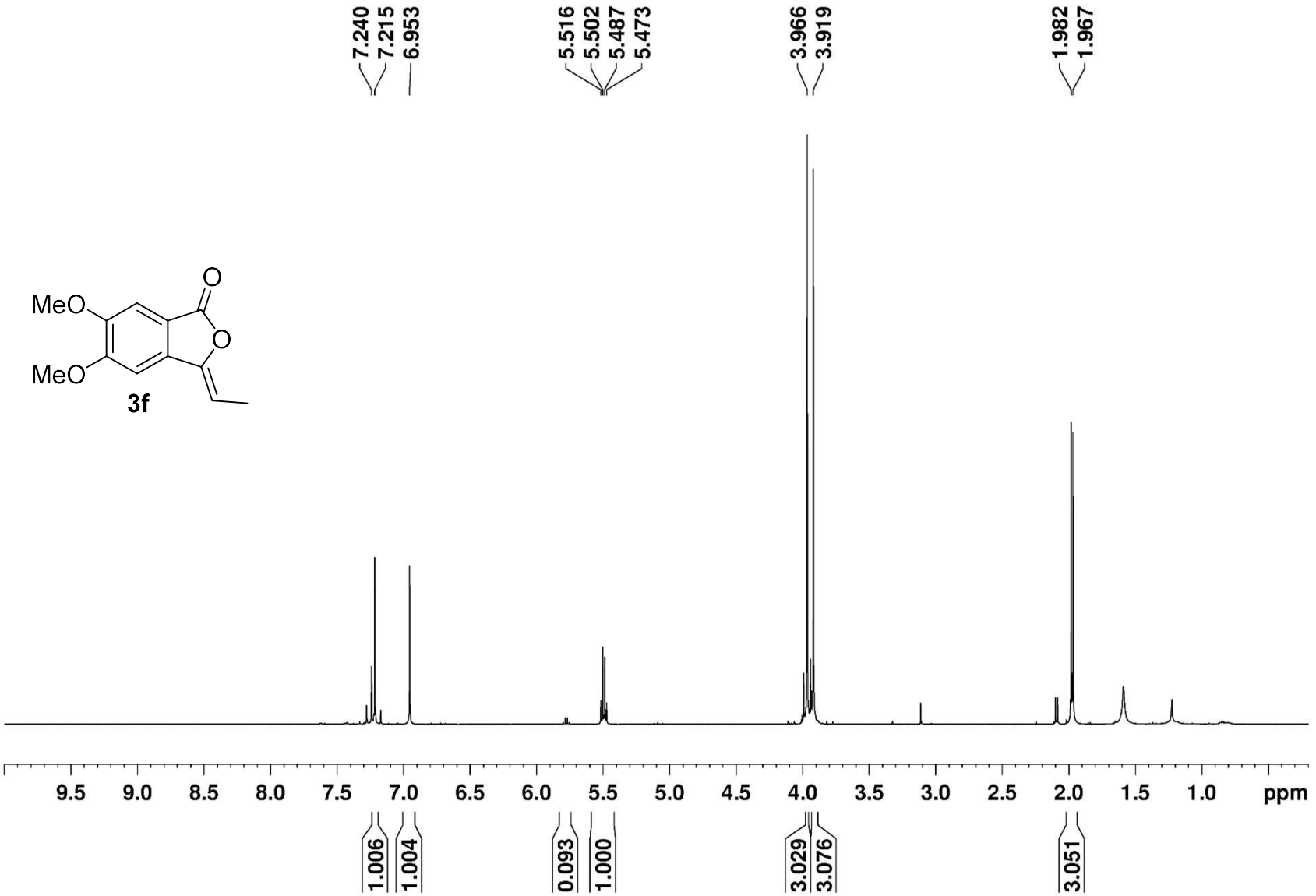
^{13}C NMR of compound **3e** (75 MHz, $CDCl_3$)



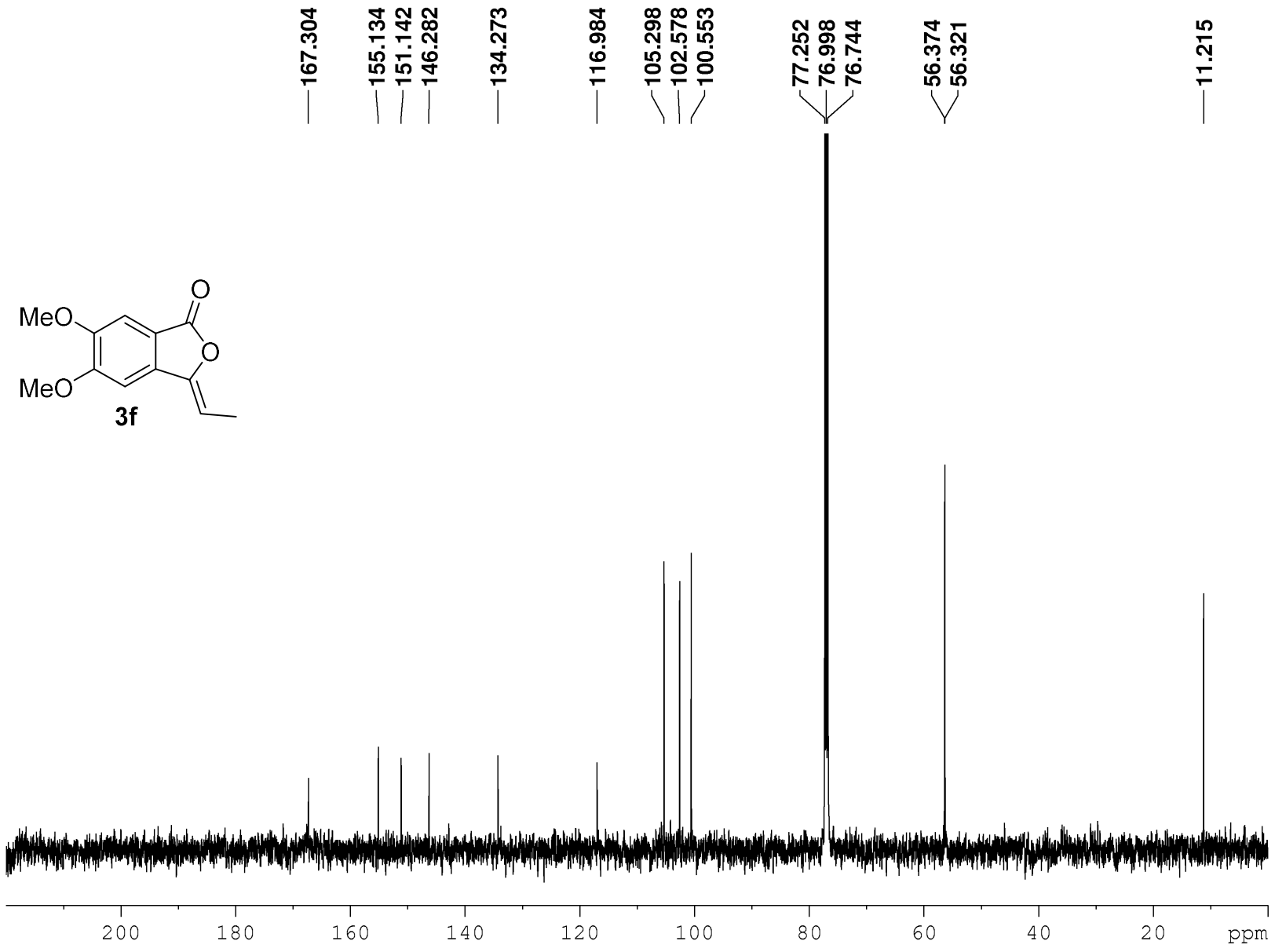
^{1}H NMR of compound **4e** (300 MHz, $CDCl_3$)



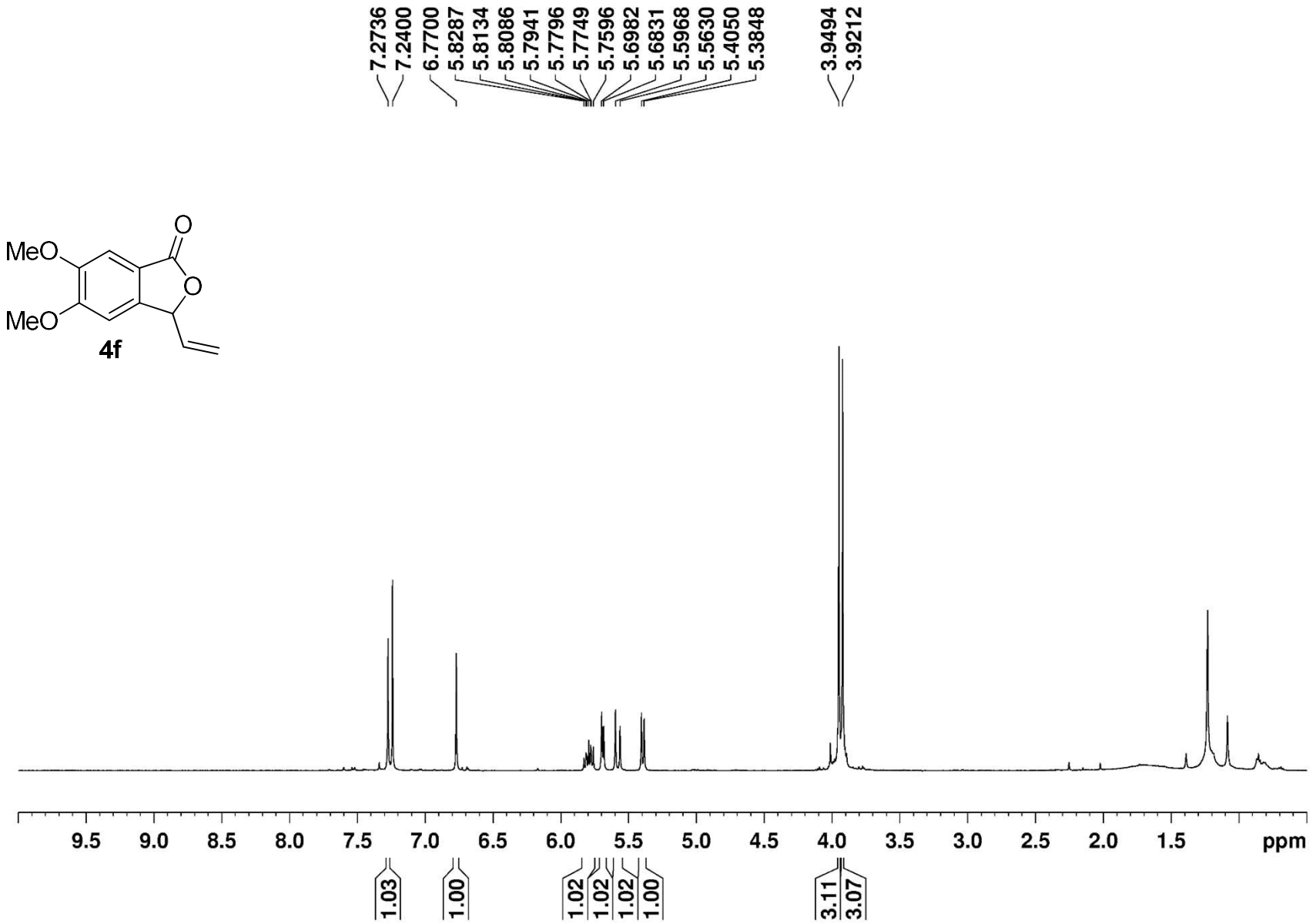
^{13}C NMR of compound **4e** (125 MHz, $CDCl_3$)



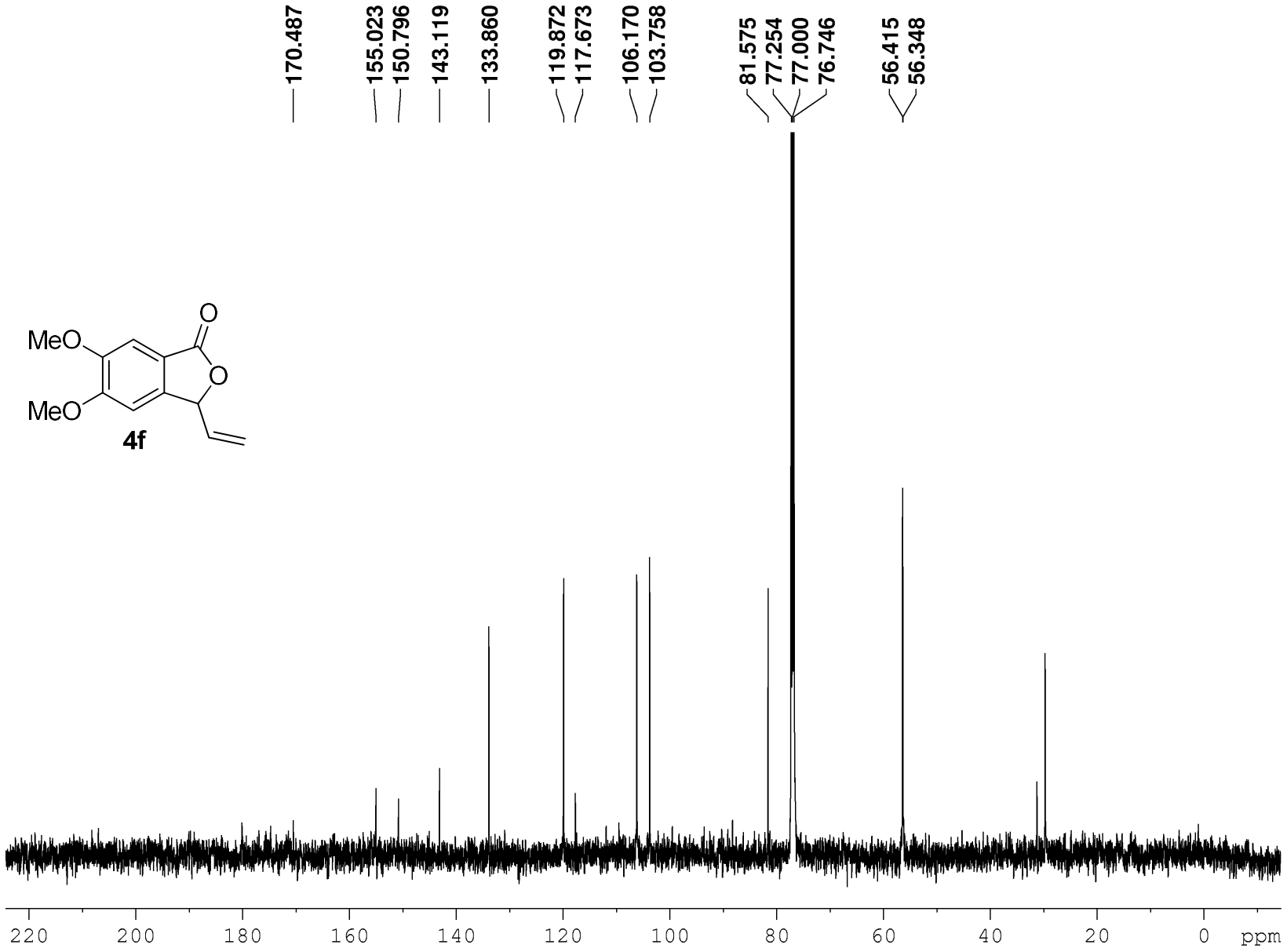
^{1}H NMR of compound **3f** (500 MHz, $CDCl_3$)



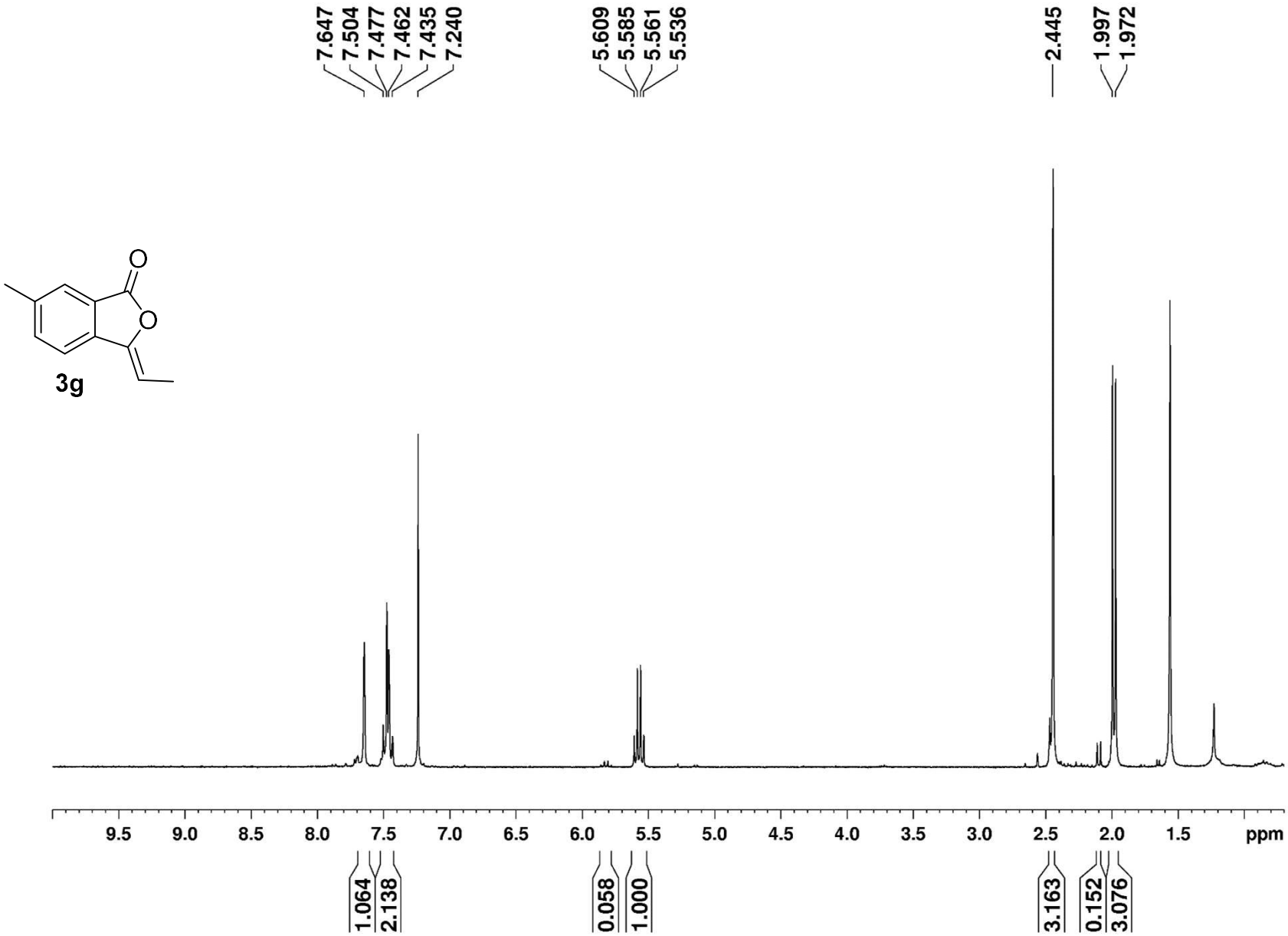
^{13}C NMR of compound **3f** (125 MHz, $CDCl_3$)



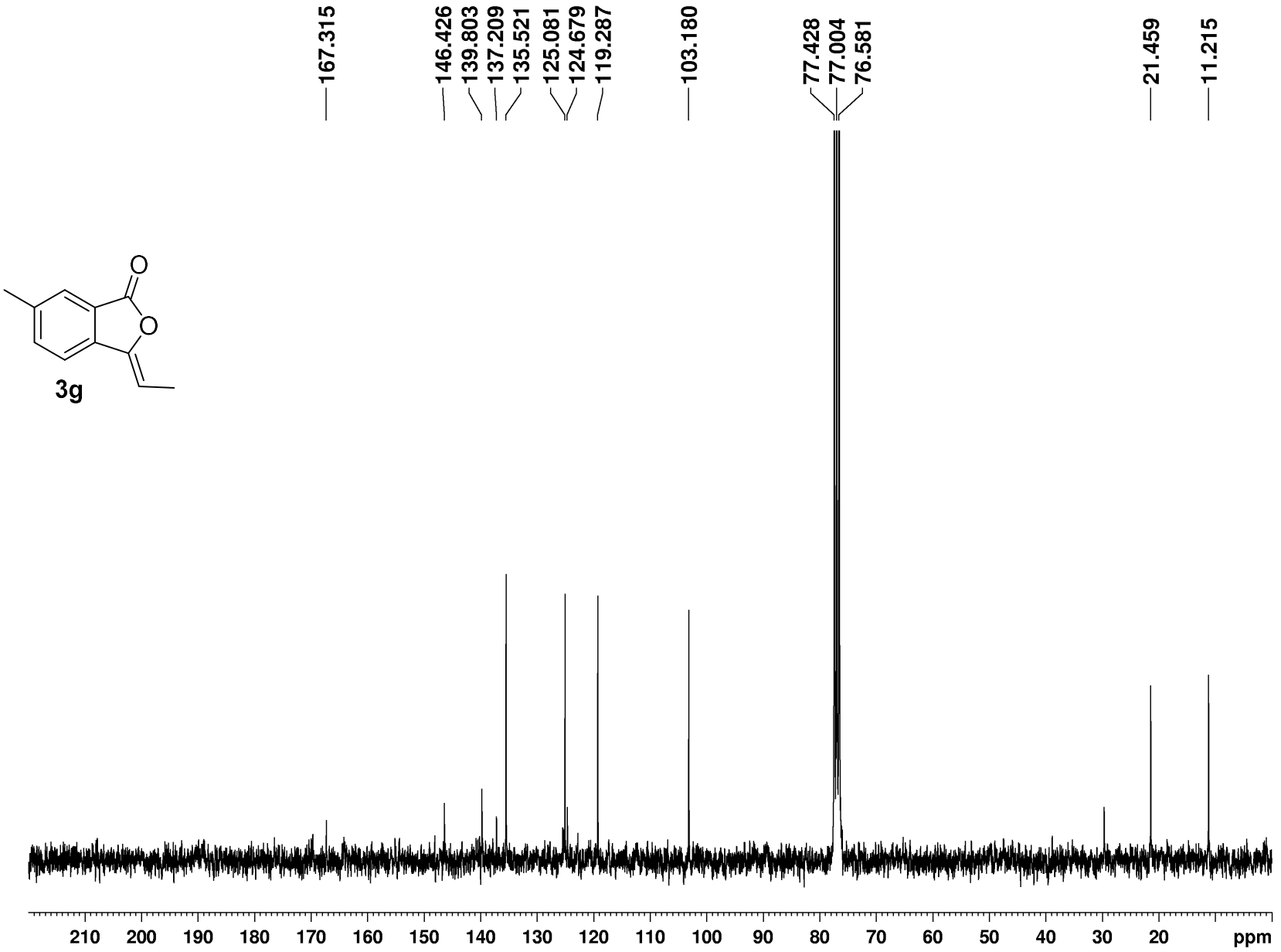
^{1}H NMR of compound **4f** (500 MHz, $CDCl_3$)



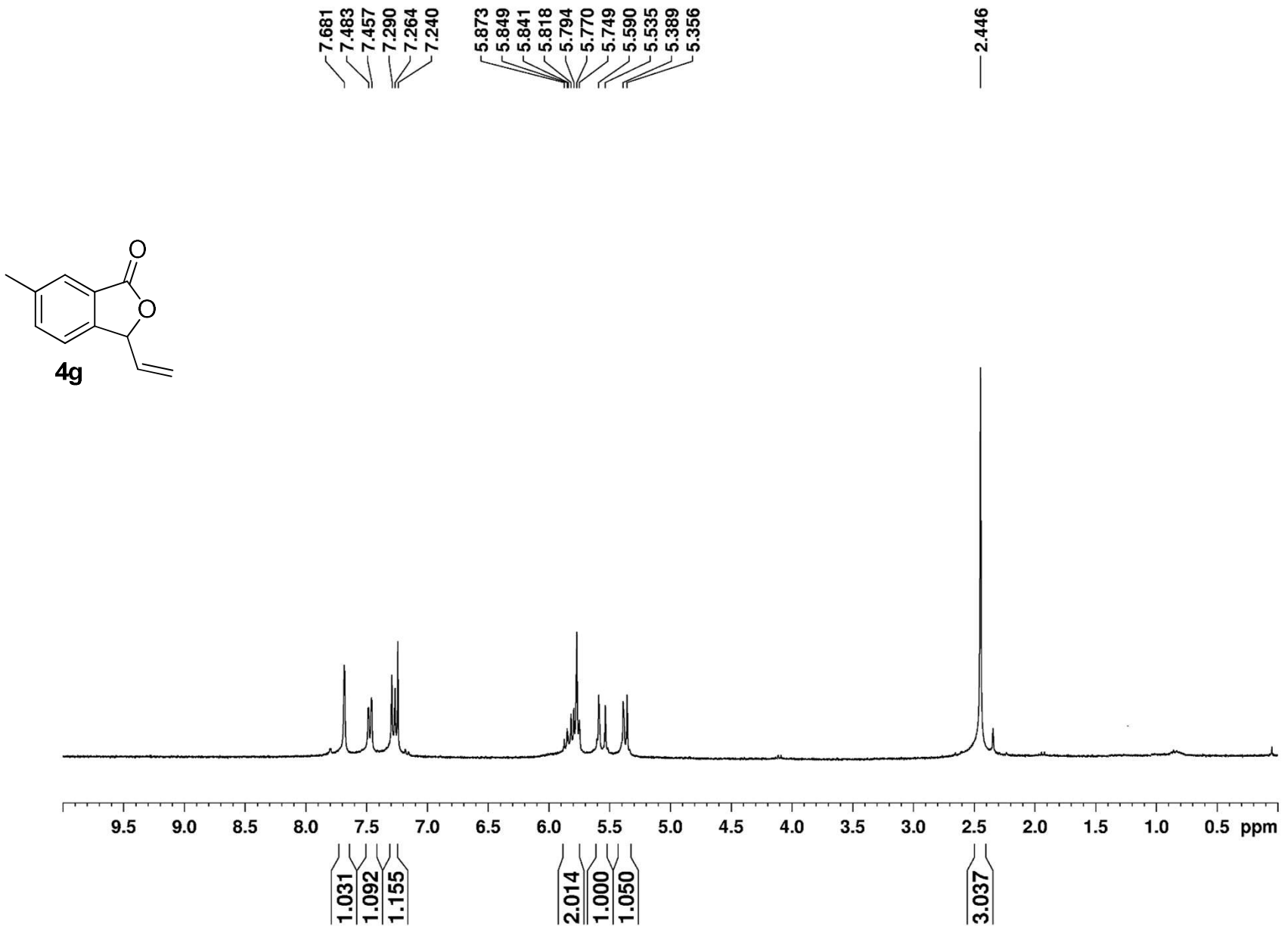
^{13}C NMR of compound **4f** (125 MHz, $CDCl_3$)



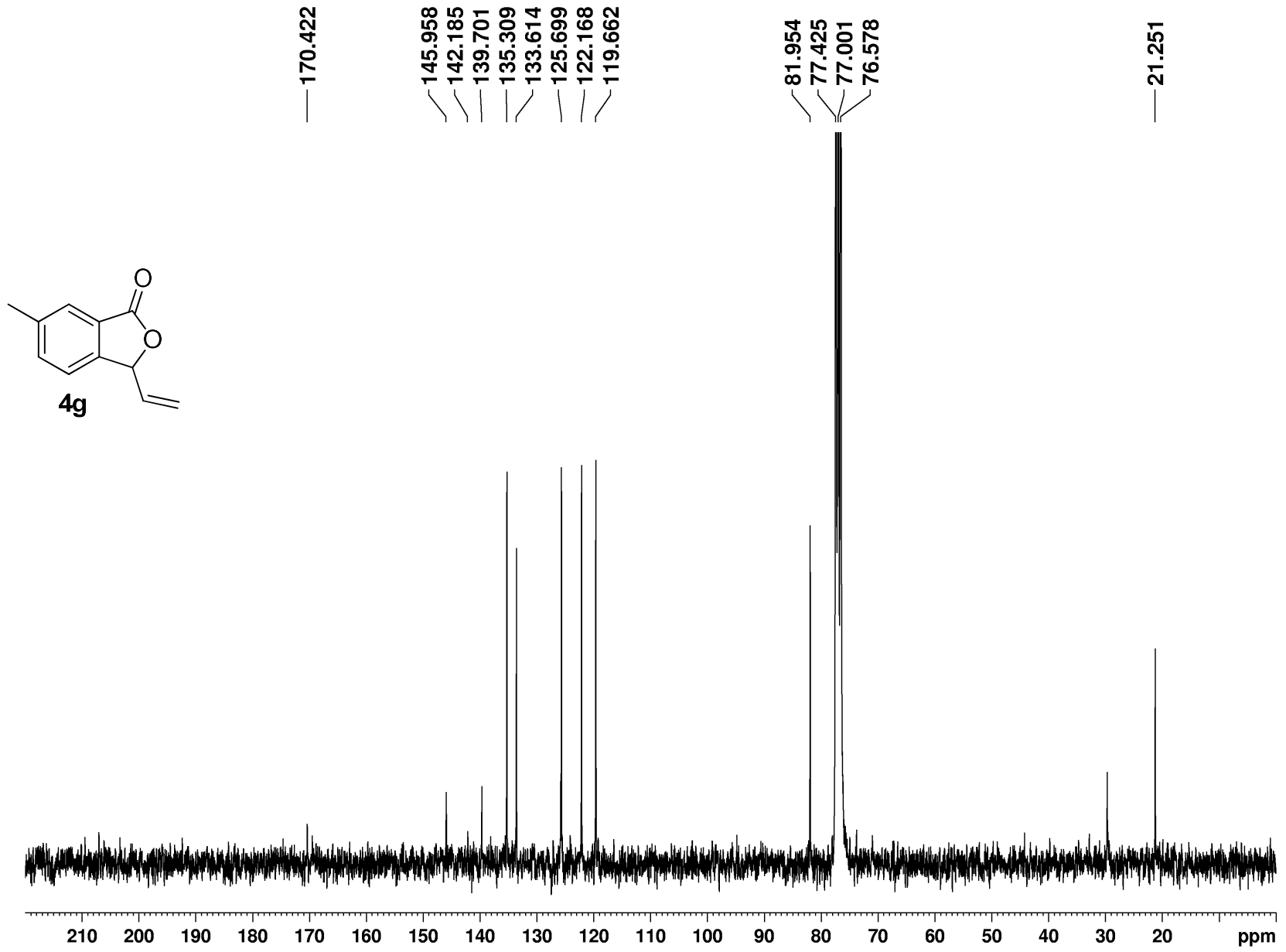
^{1}H NMR of compound **3g** (300 MHz, $CDCl_3$)



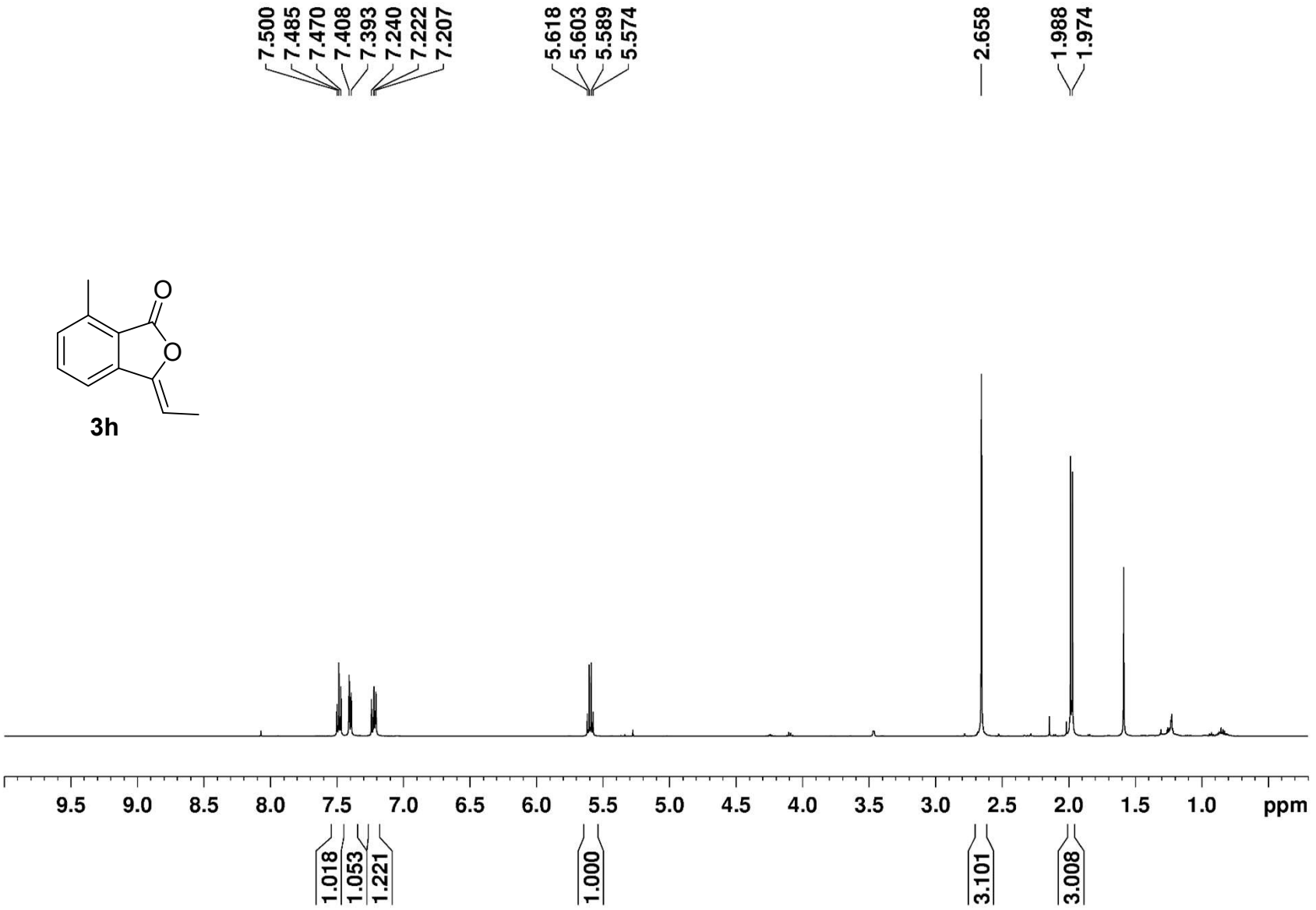
^{13}C NMR of compound **3g** (75 MHz, $CDCl_3$)



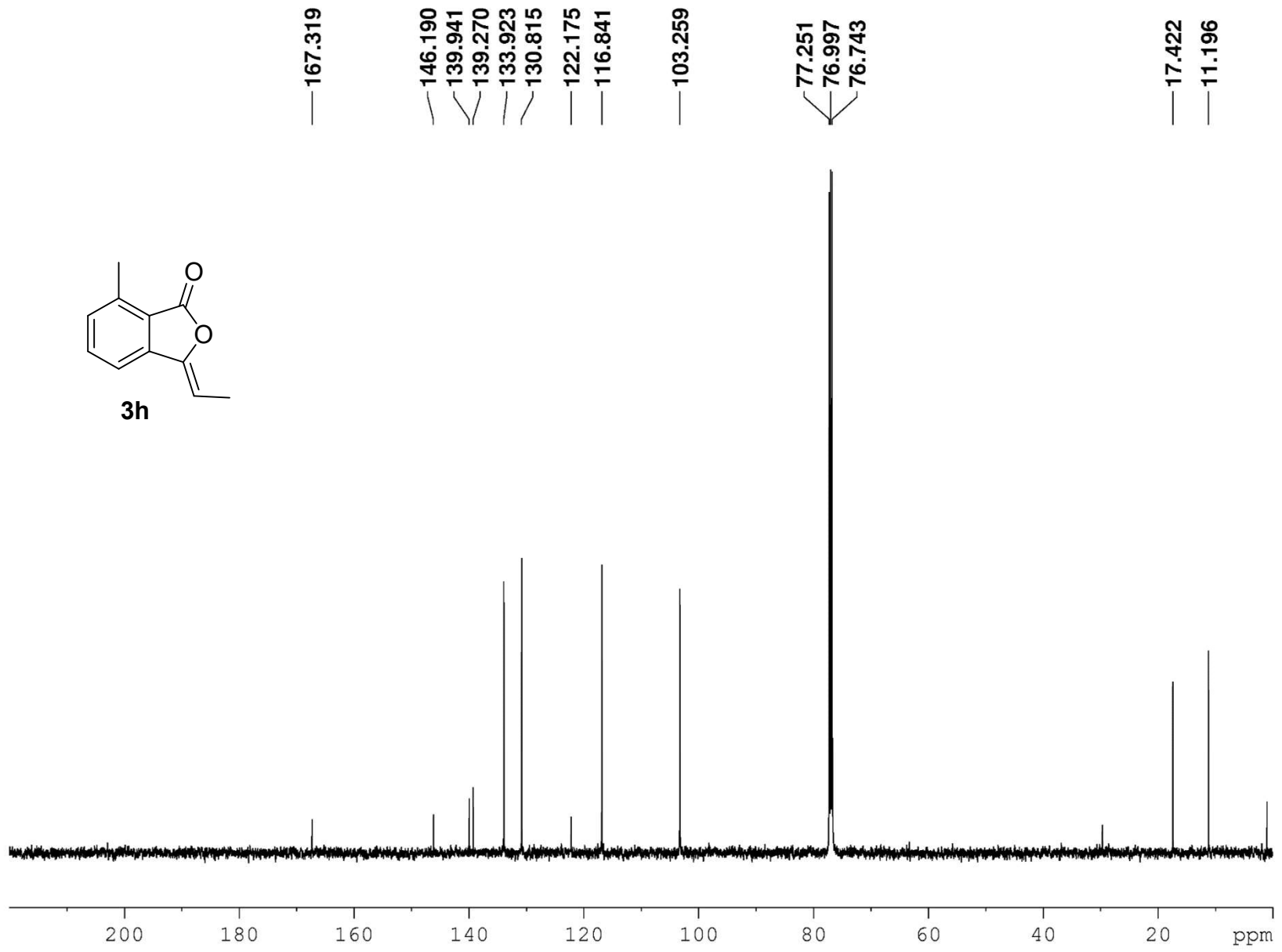
^{1}H NMR of compound **4g** (300 MHz, $CDCl_3$)



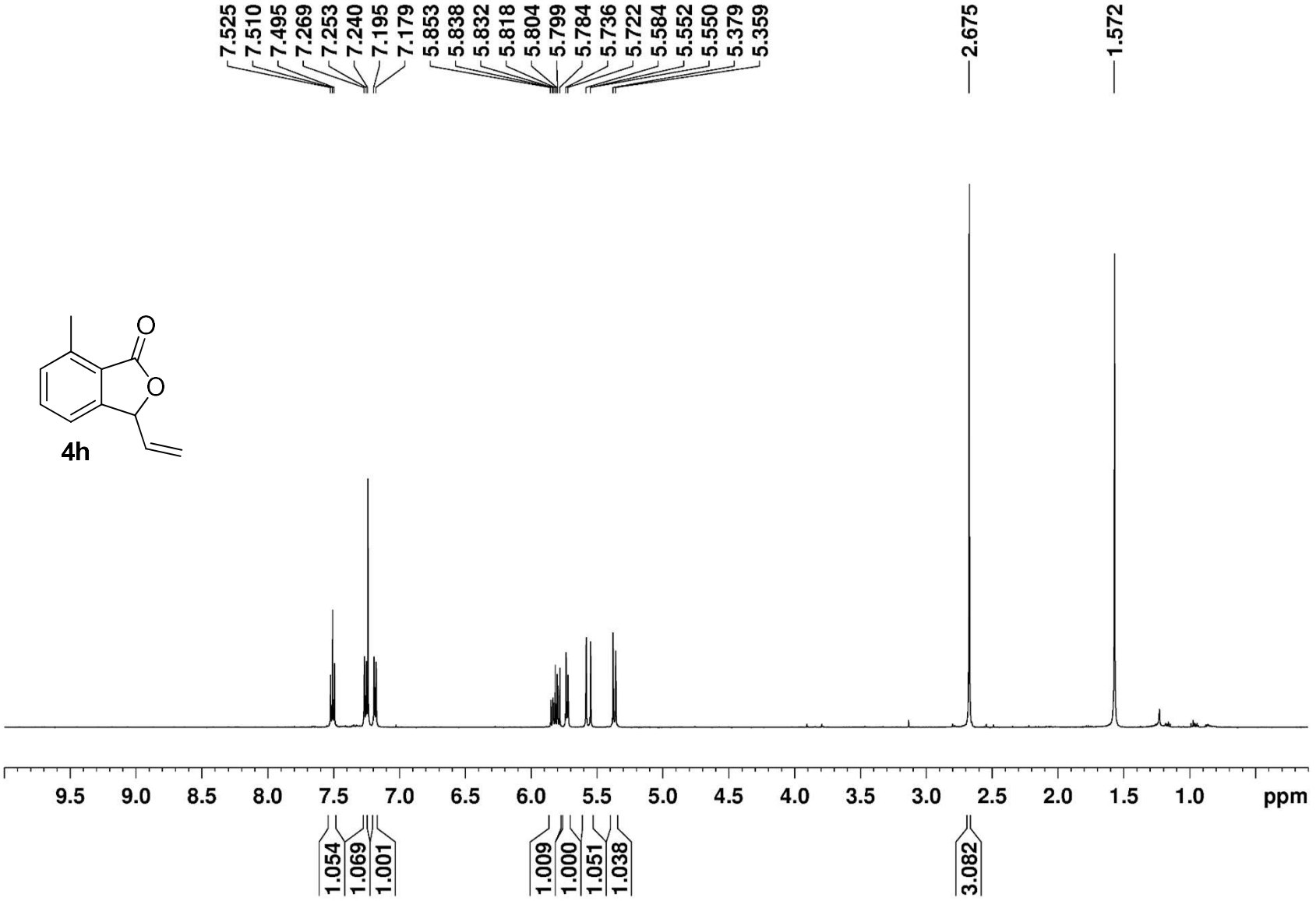
^{13}C NMR of compound **4g** (75 MHz, $CDCl_3$)



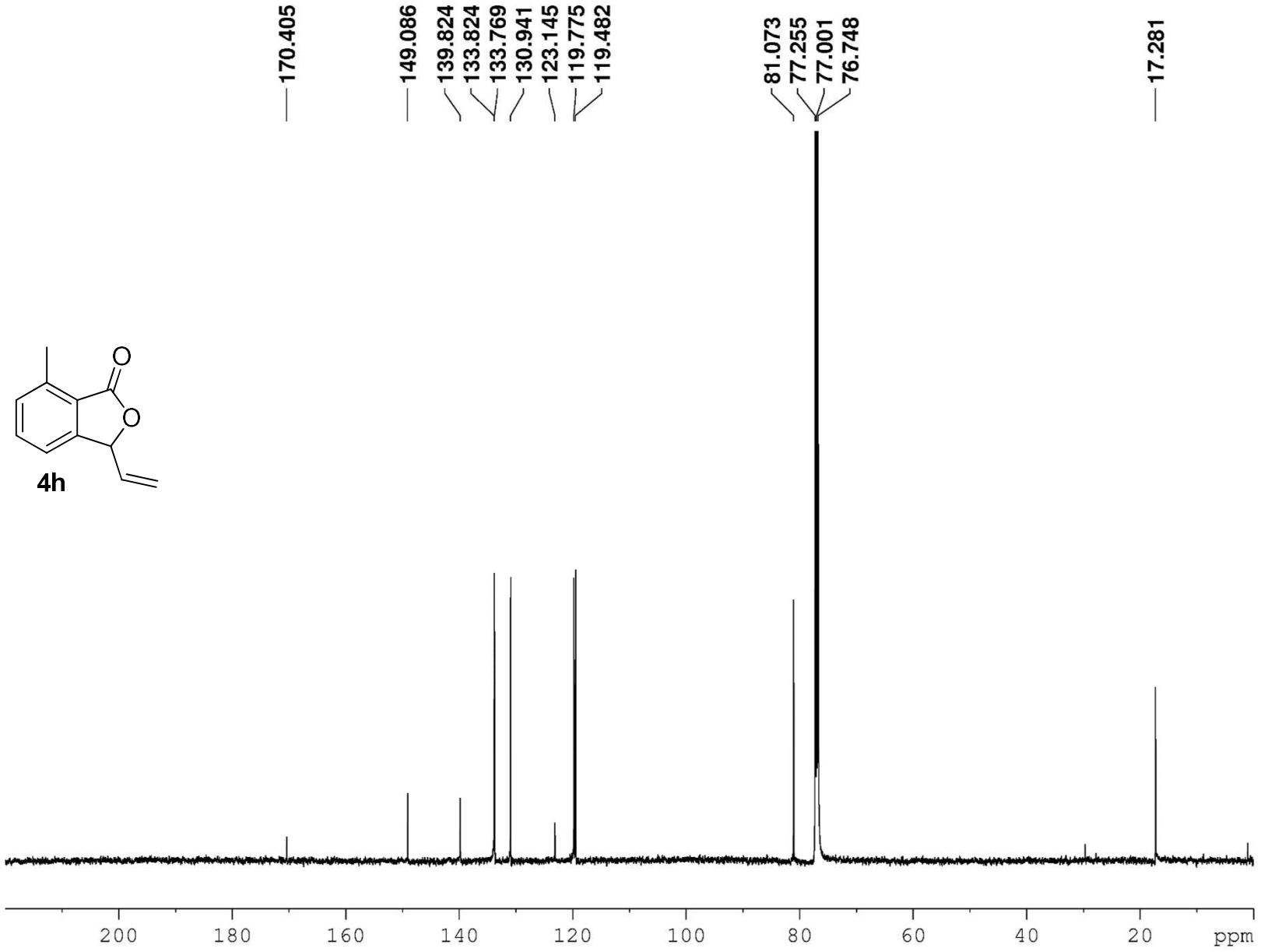
^{1}H NMR of compound **3h** (500 MHz, $CDCl_3$)



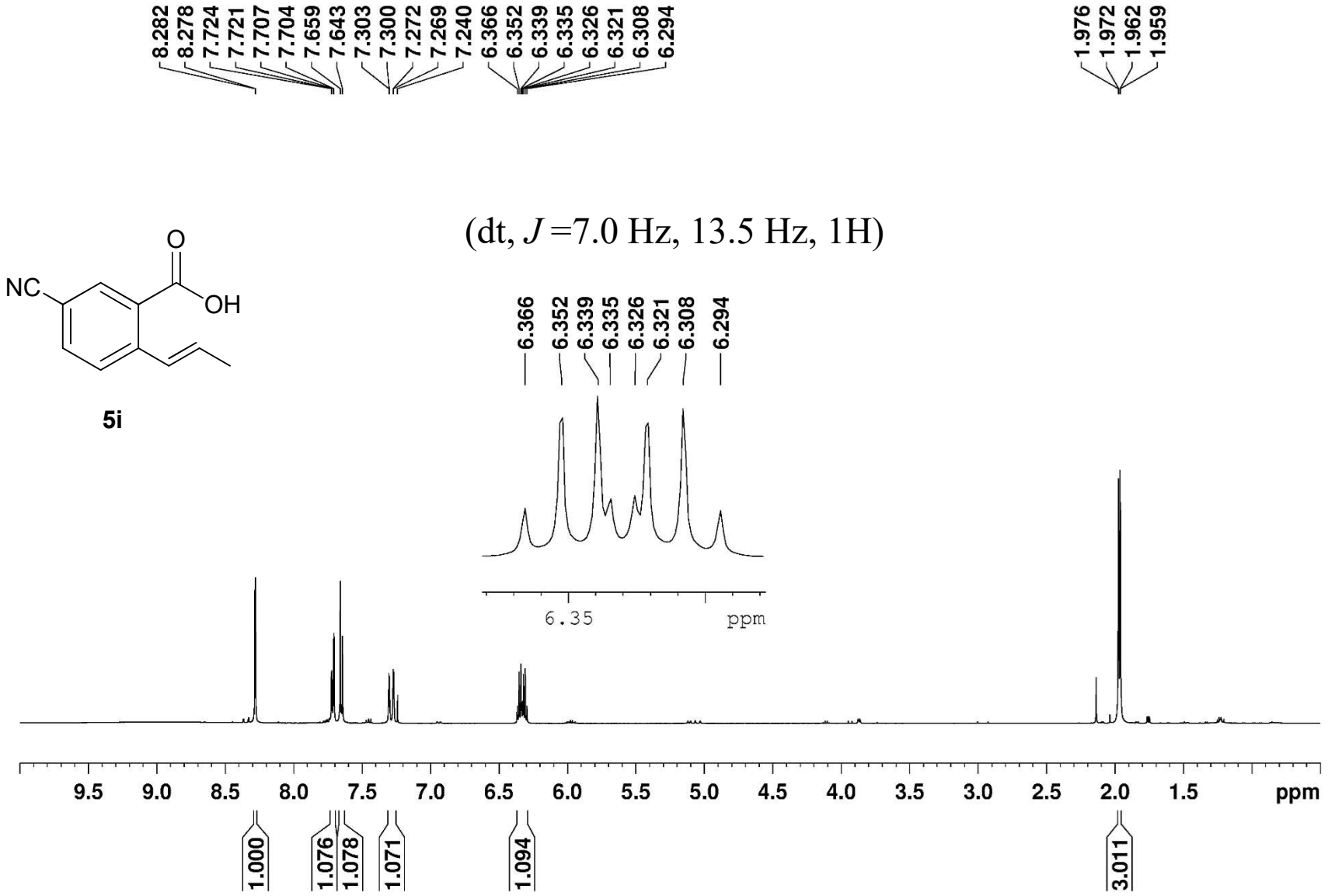
^{13}C NMR of compound **3h** (125 MHz, $CDCl_3$)



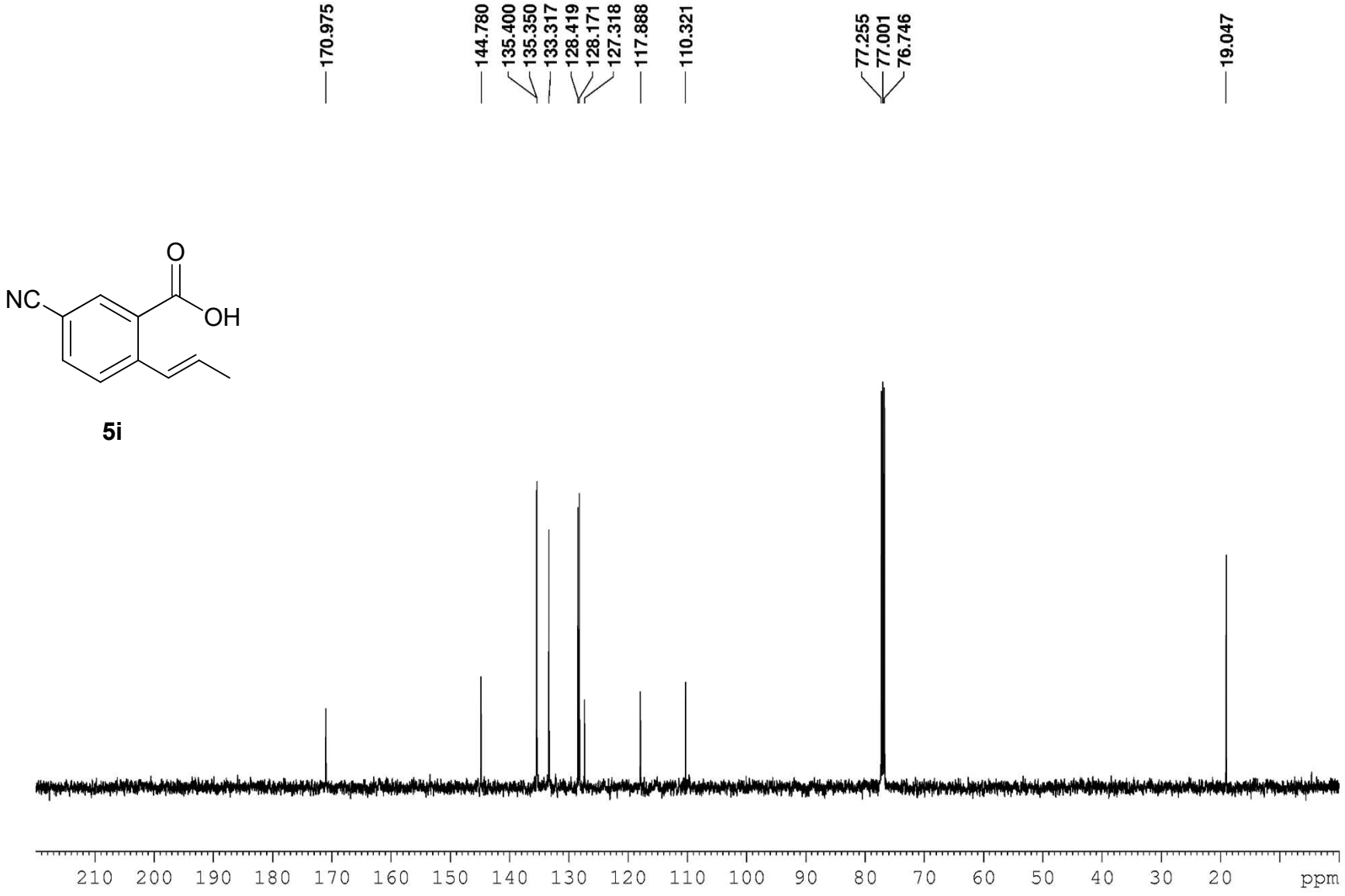
^{1}H NMR of compound **4h** (500 MHz, $CDCl_3$)



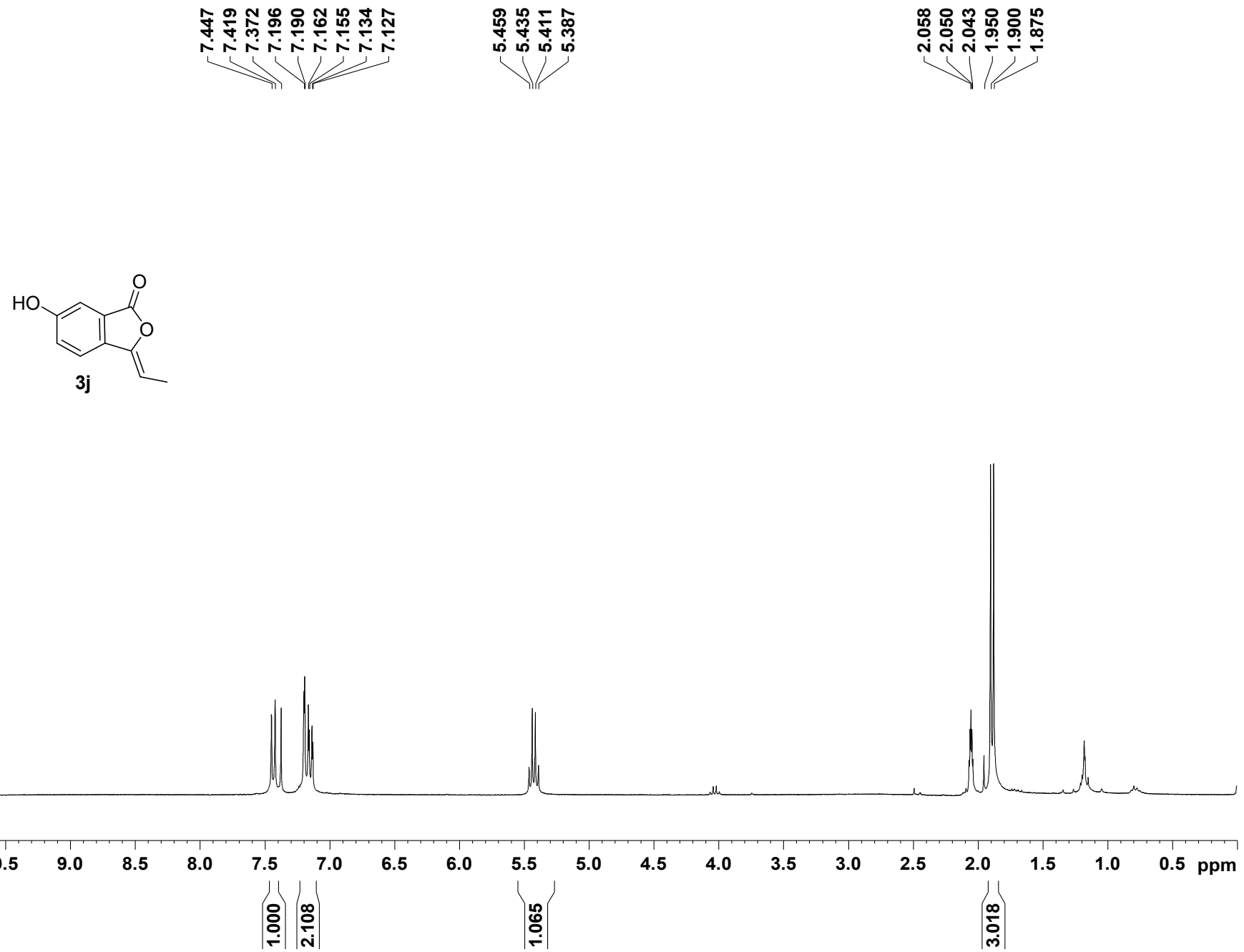
^{13}C NMR of compound **4h** (125 MHz, $CDCl_3$)



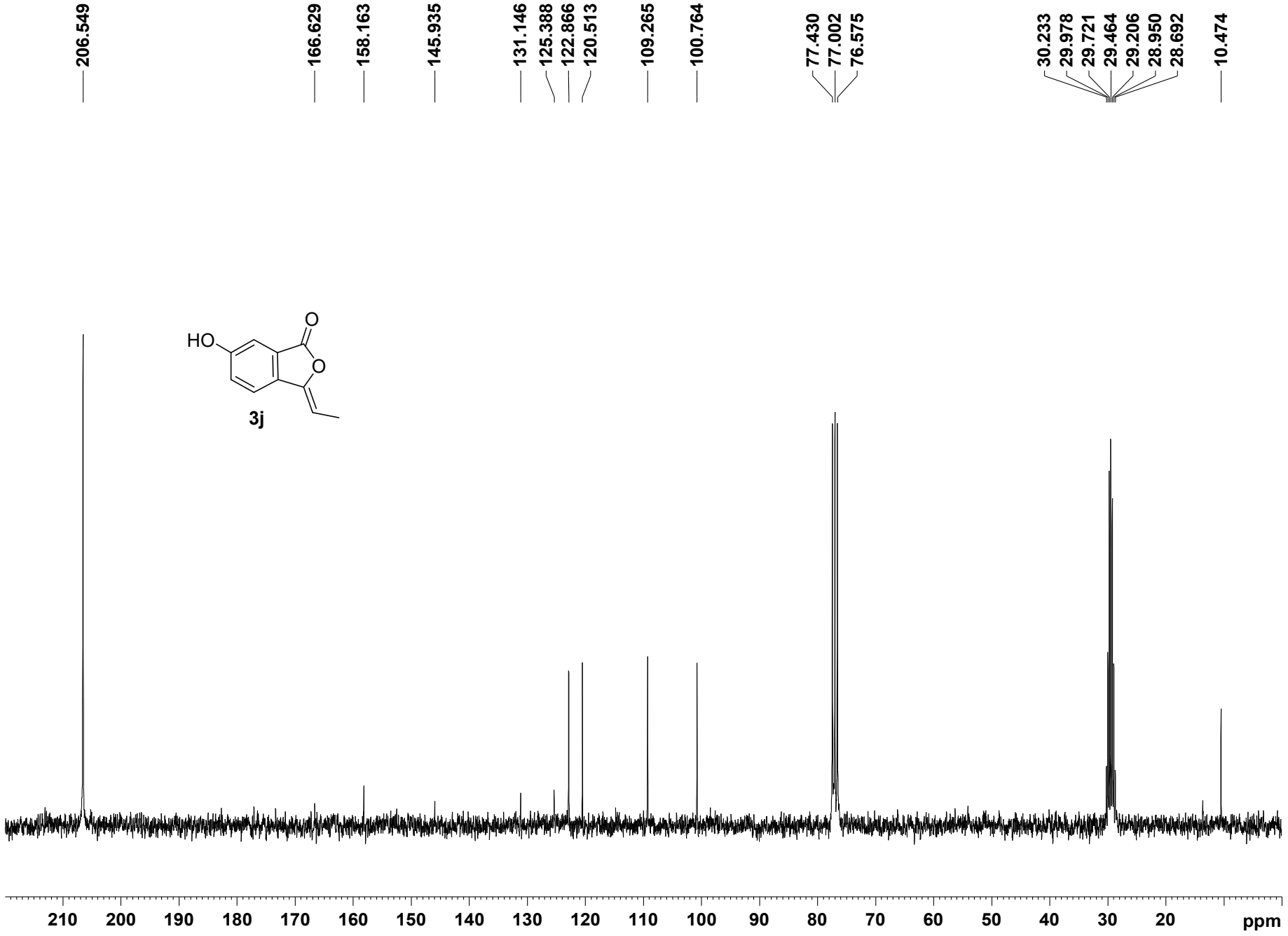
^{1}H NMR of compound **5i** (500 MHz, $CDCl_3$)



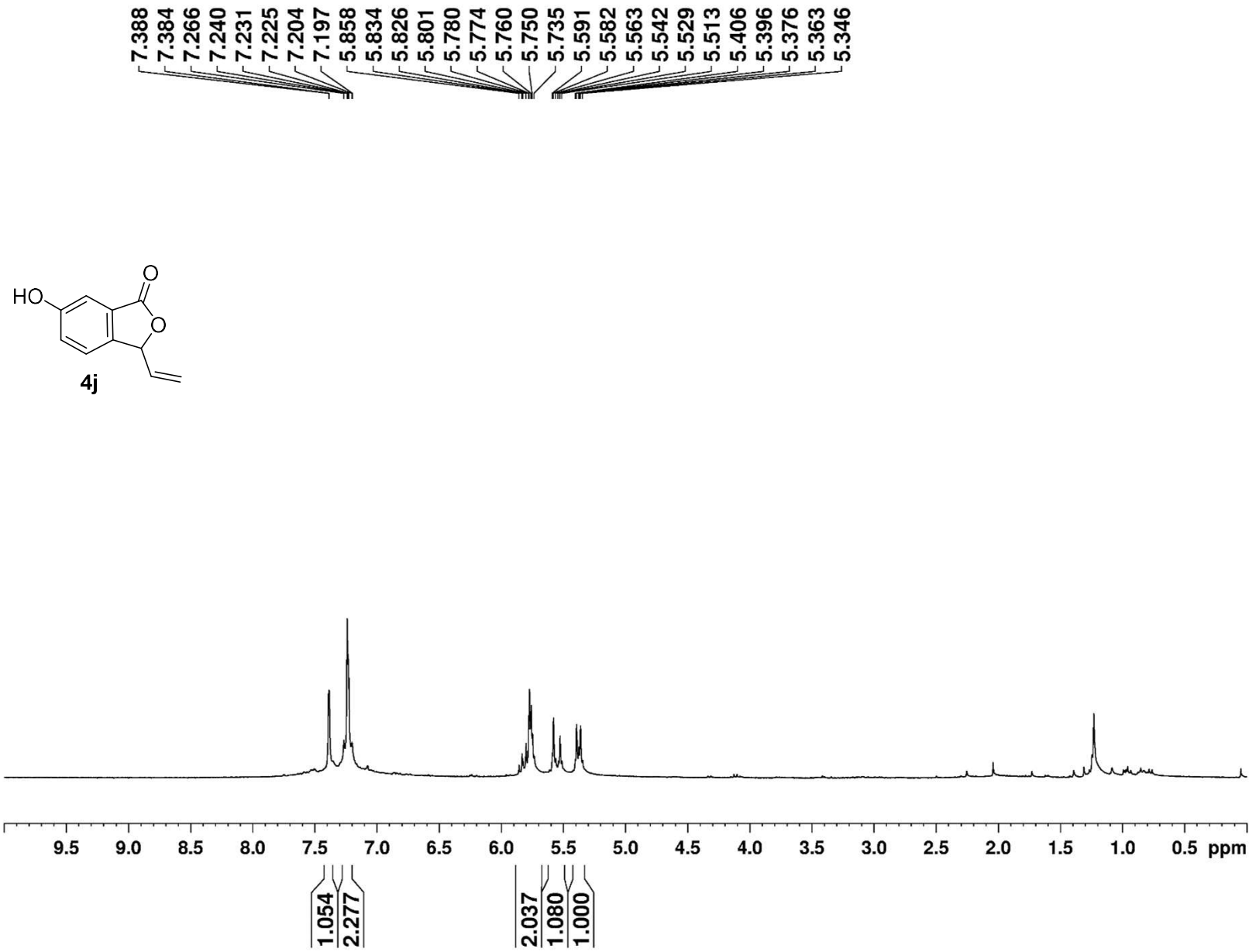
^{13}C NMR of compound **5i** (125 MHz, $CDCl_3$)



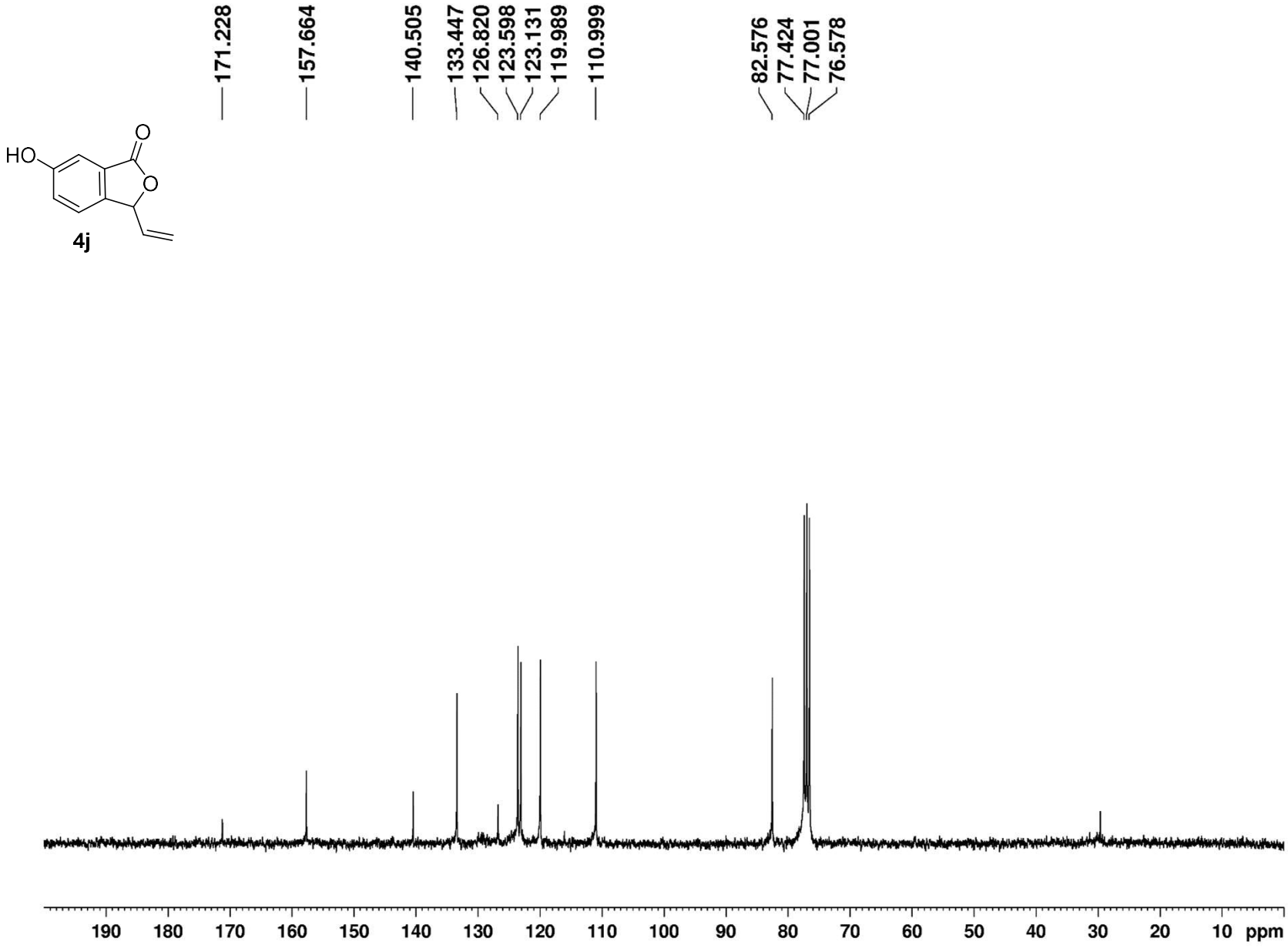
^{1}H NMR of compound **3j** (300 MHz, $CDCl_3$+ $(CD_3)_2CO$)



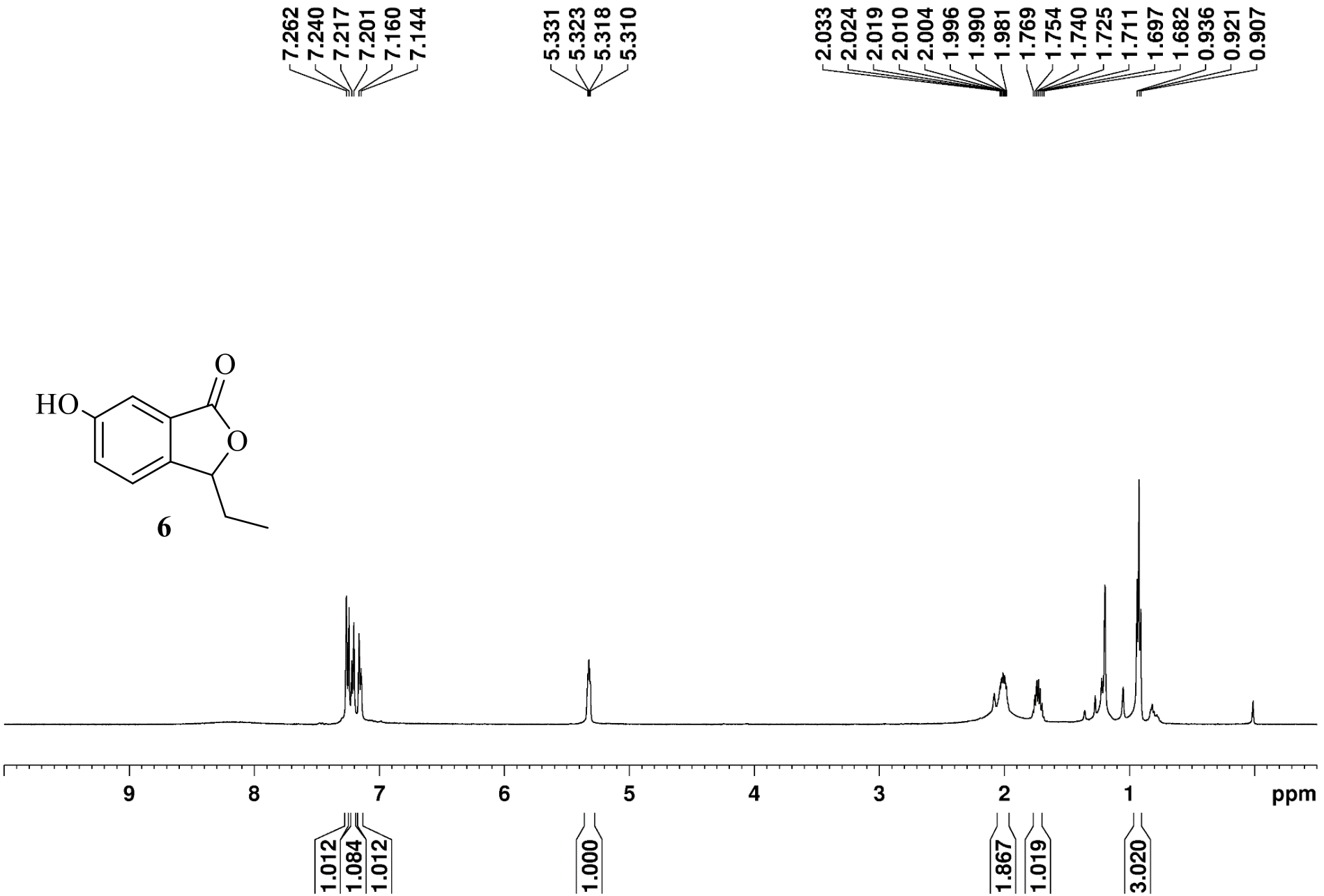
^{13}C NMR of compound **3j** (75 MHz, $CDCl_3$ + $(CD_3)_2CO$)



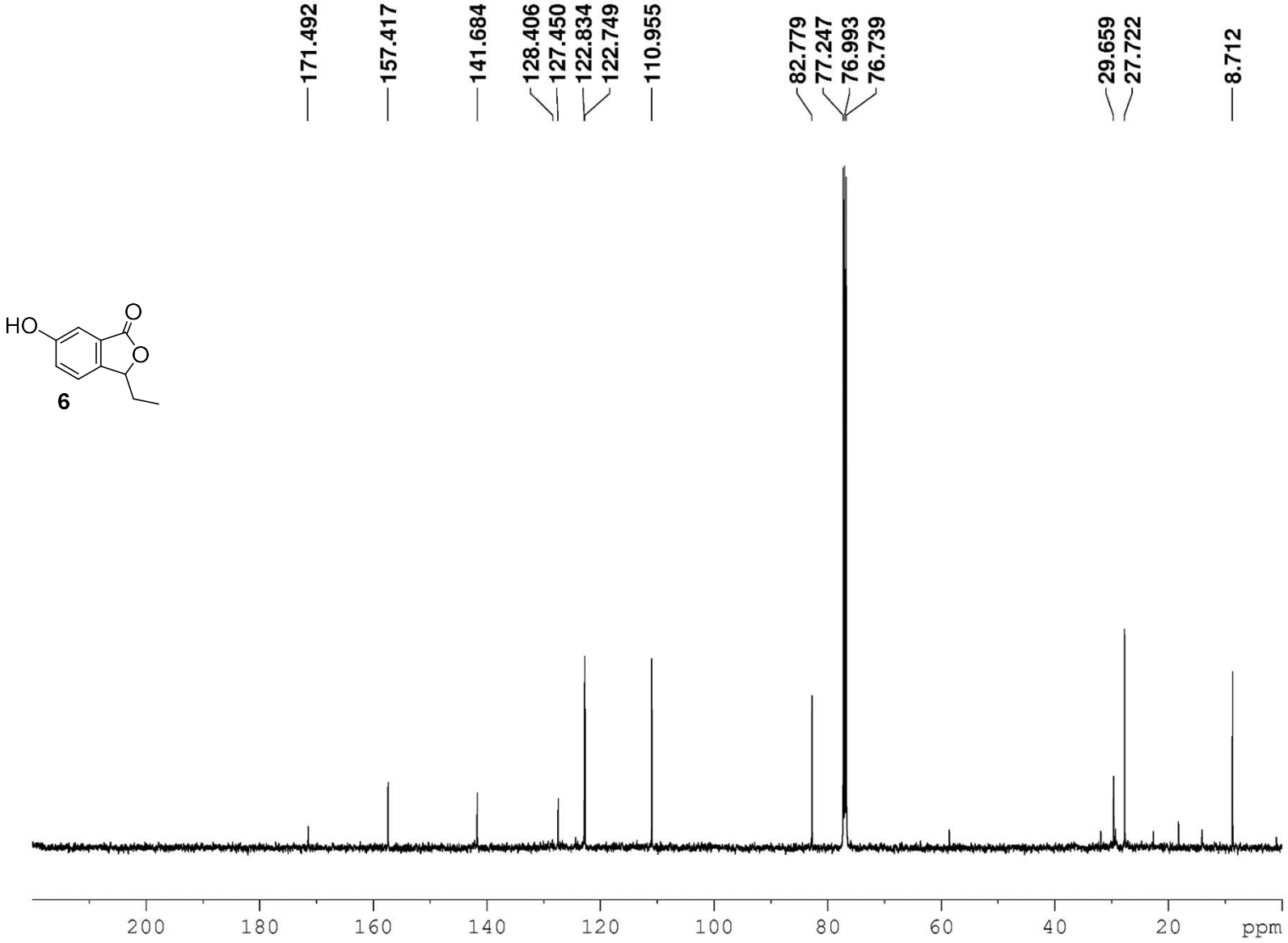
^{1}H NMR of compound **4j** (300 MHz, $CDCl_3$+ $(CD_3)_2CO$)



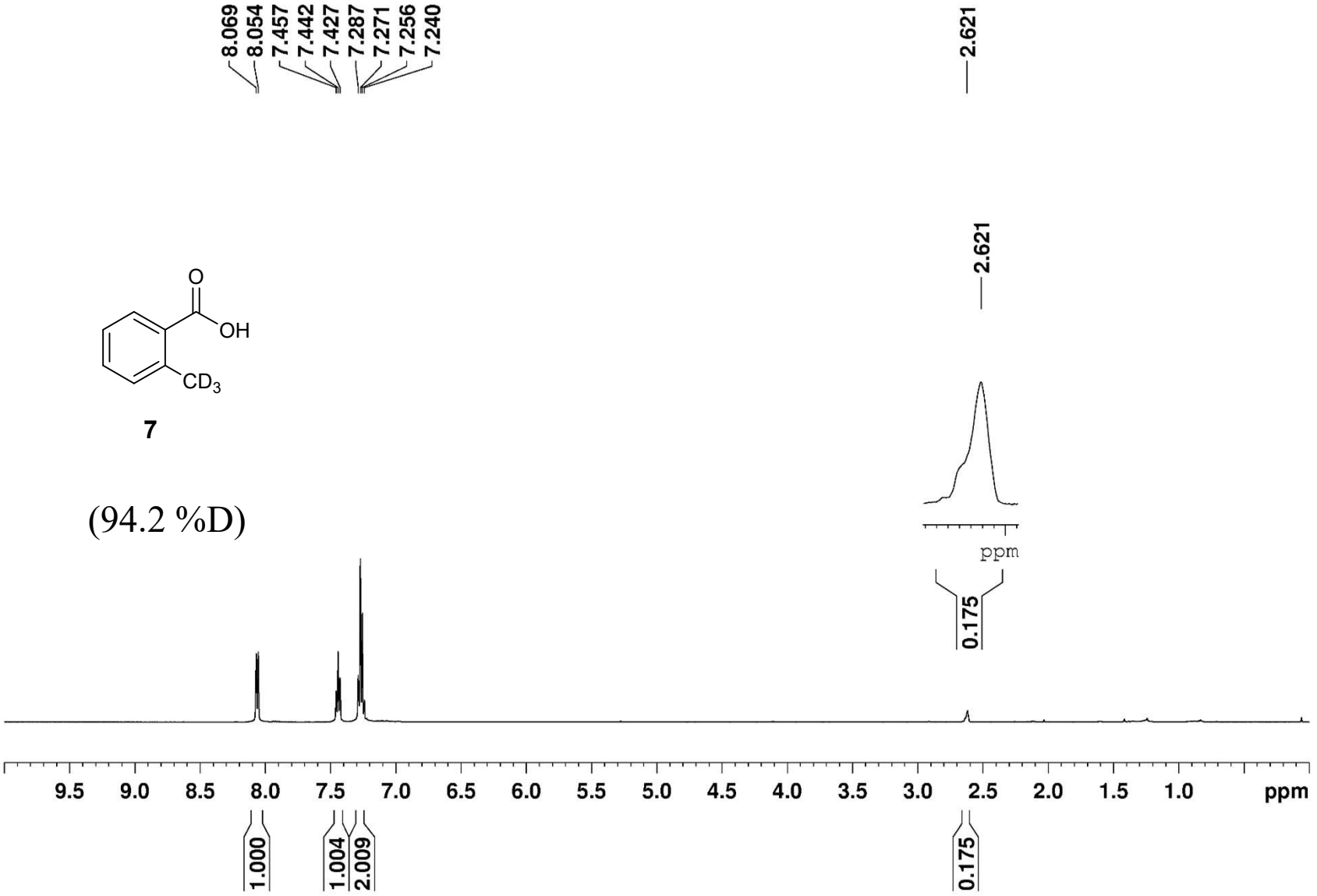
^{13}C NMR of compound **4j** (75 MHz, $CDCl_3$ + $(CD_3)_2CO$)



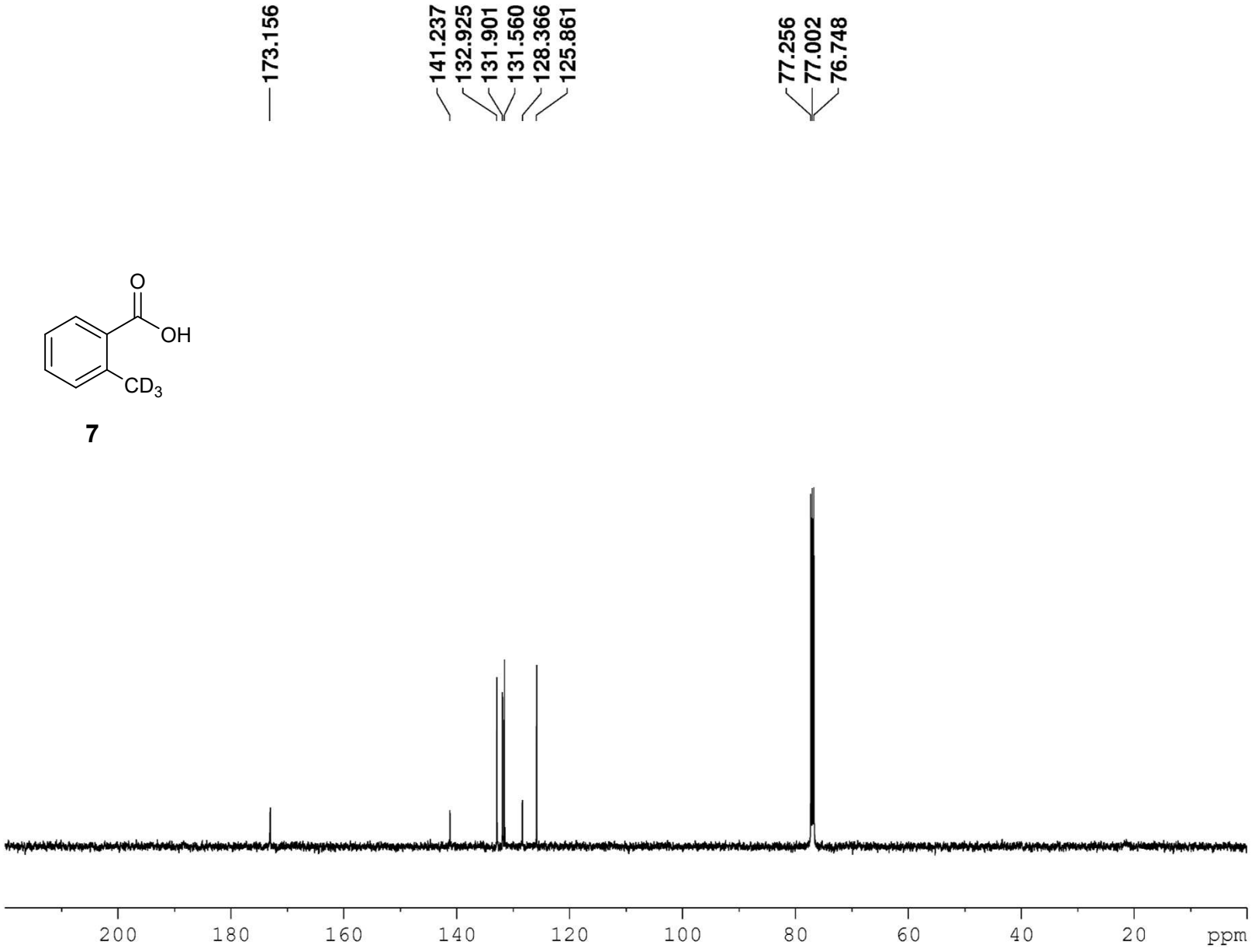
^{1}H NMR of compound **6** (500 MHz, $CDCl_3$ + $(CD_3)_2CO$)



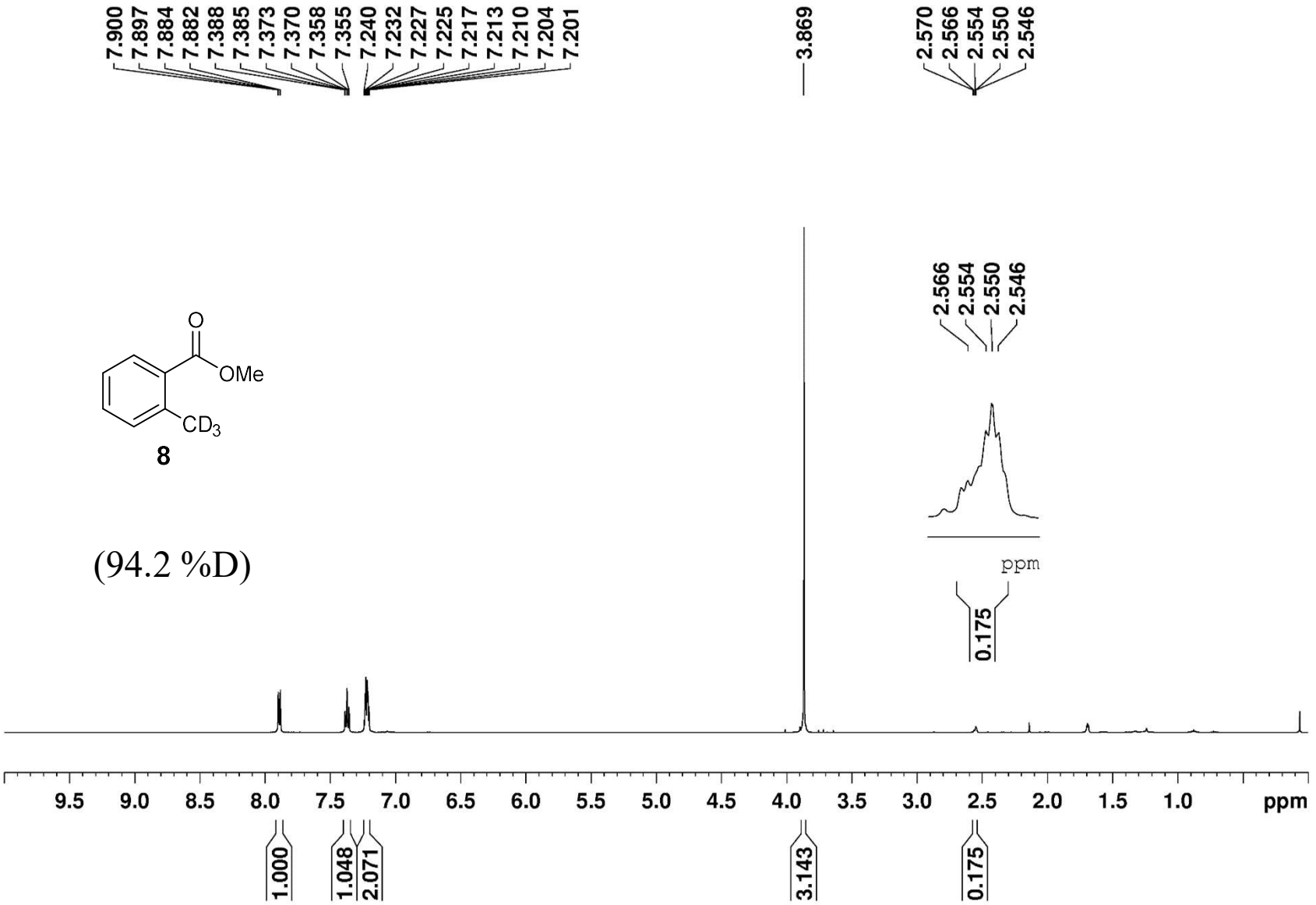
^{13}C NMR of compound **6** (125 MHz, $CDCl_3$ + $(CD_3)_2CO$)



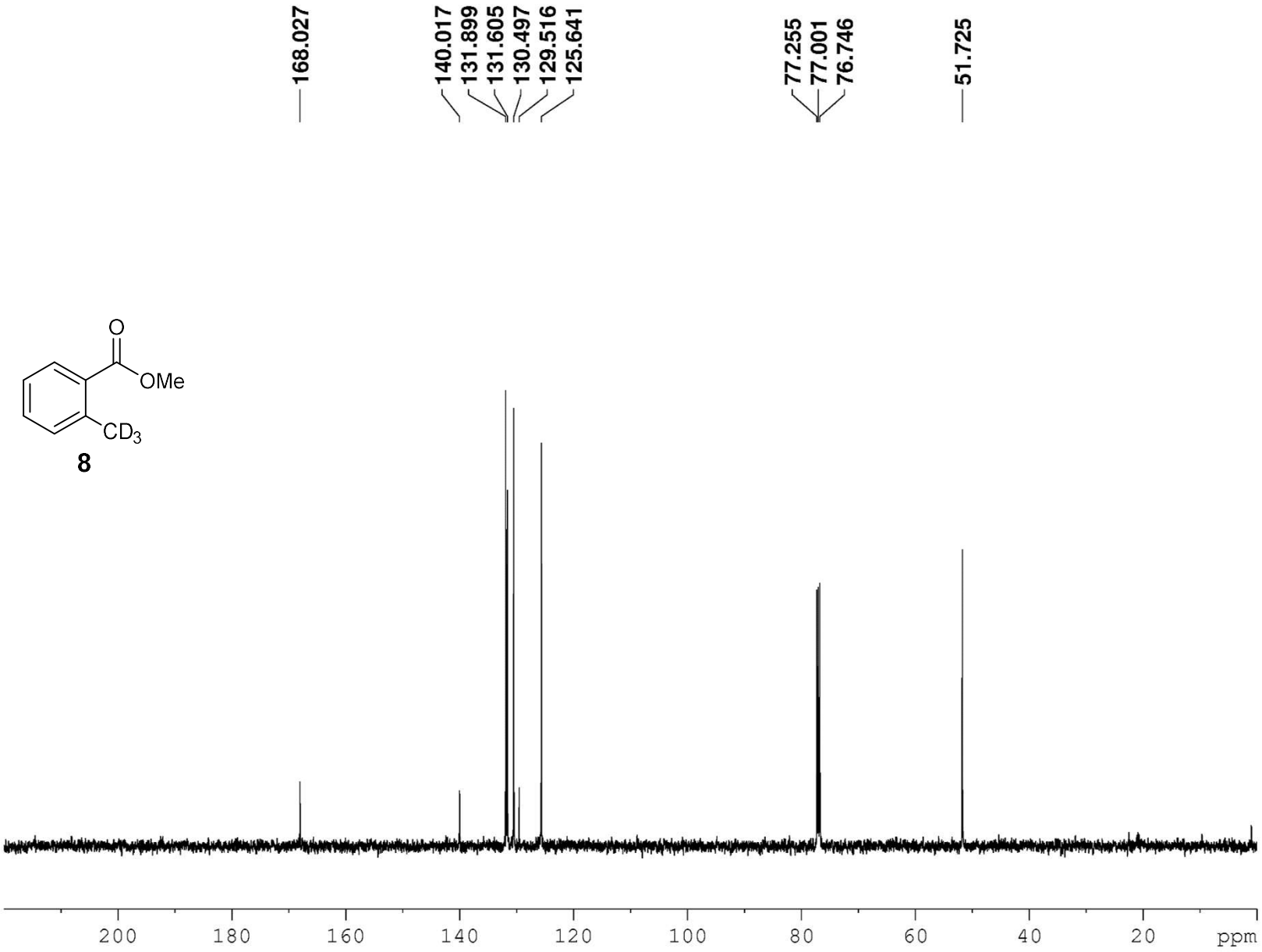
^{1}H NMR of compound **7** (500 MHz, $CDCl_3$)



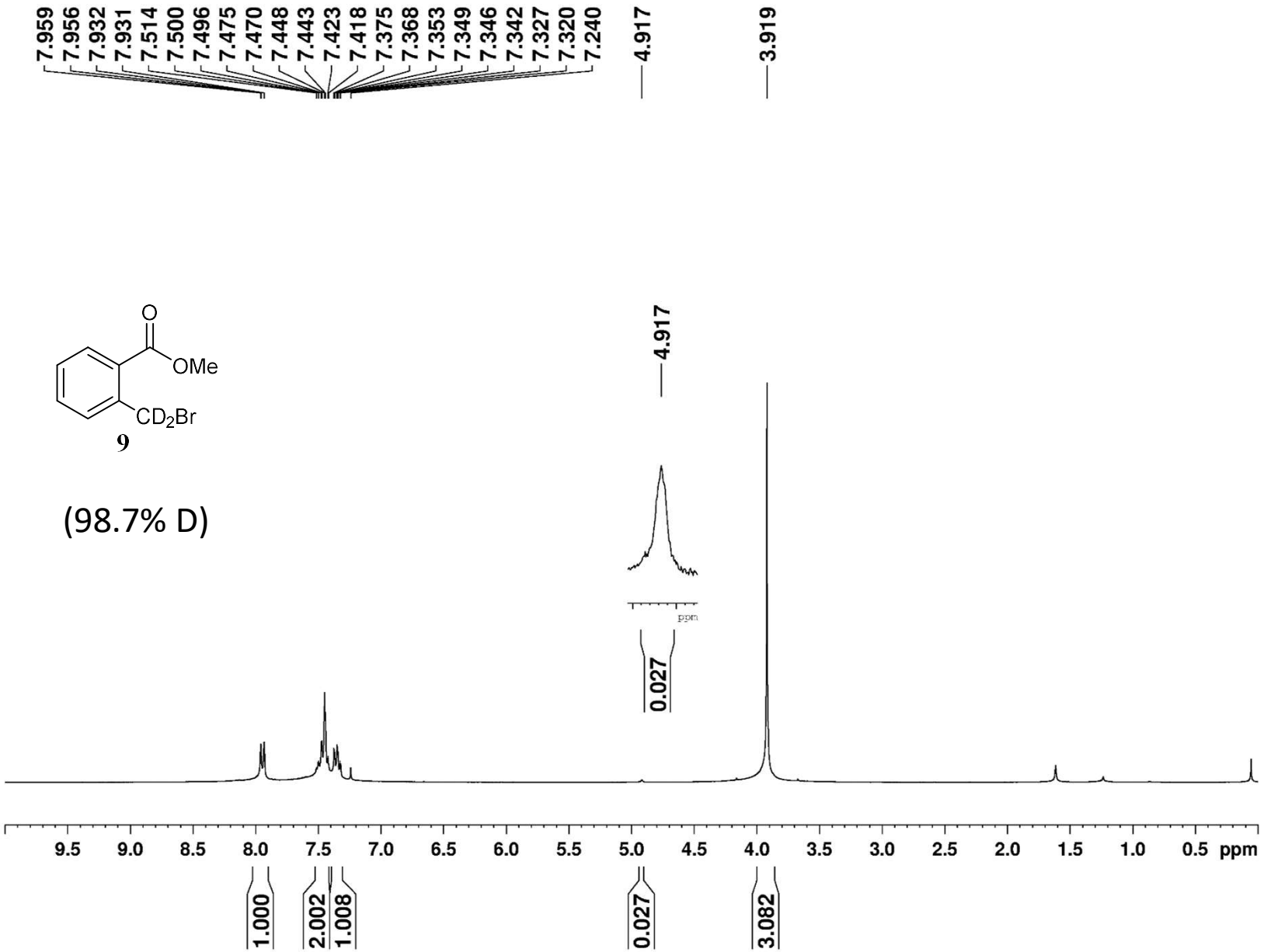
^{13}C NMR of compound **8** (125 MHz, $CDCl_3$)



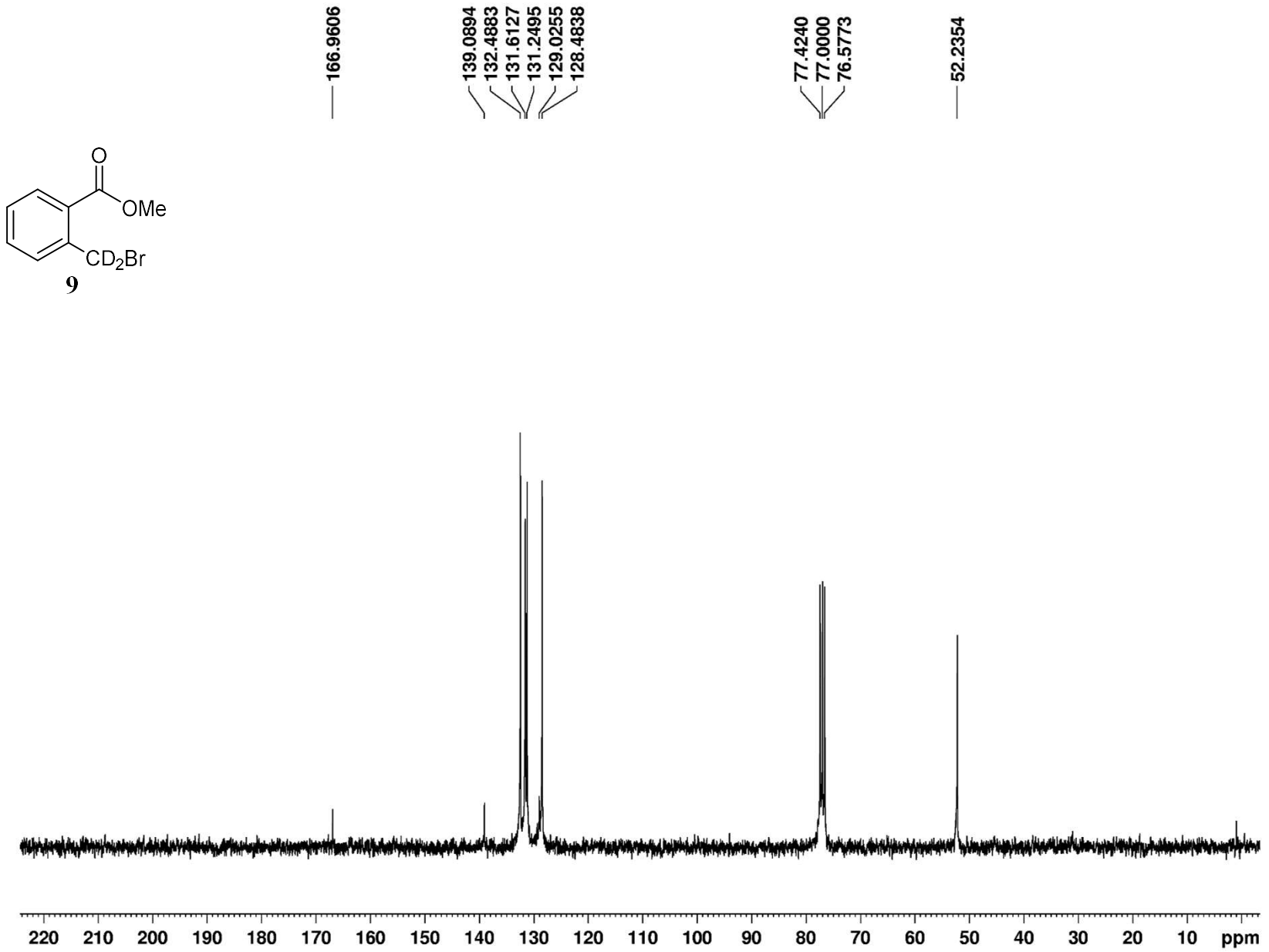
^{1}H NMR of compound **8** (500 MHz, $CDCl_3$)



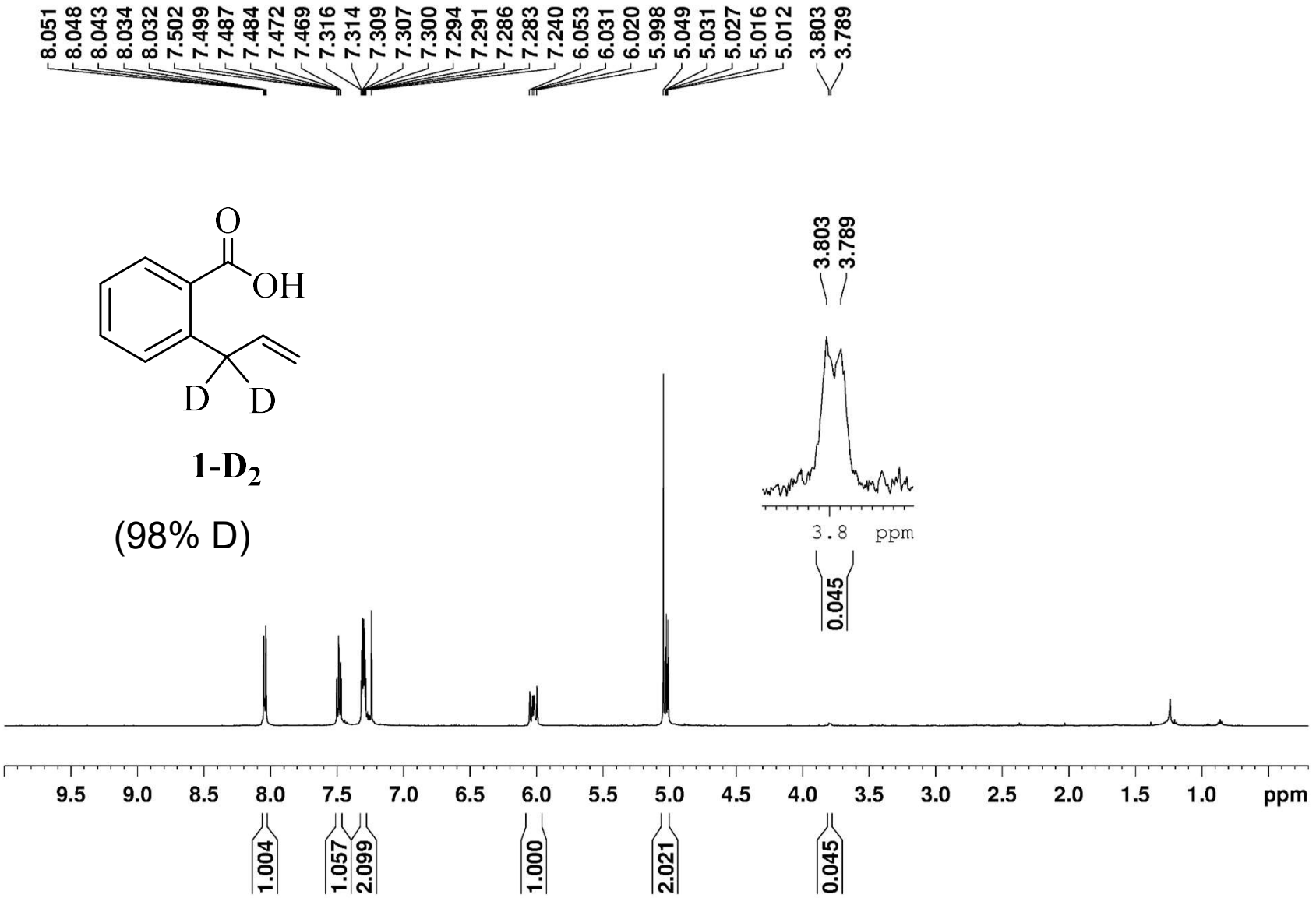
^{13}C NMR of compound **8** (125 MHz, $CDCl_3$)



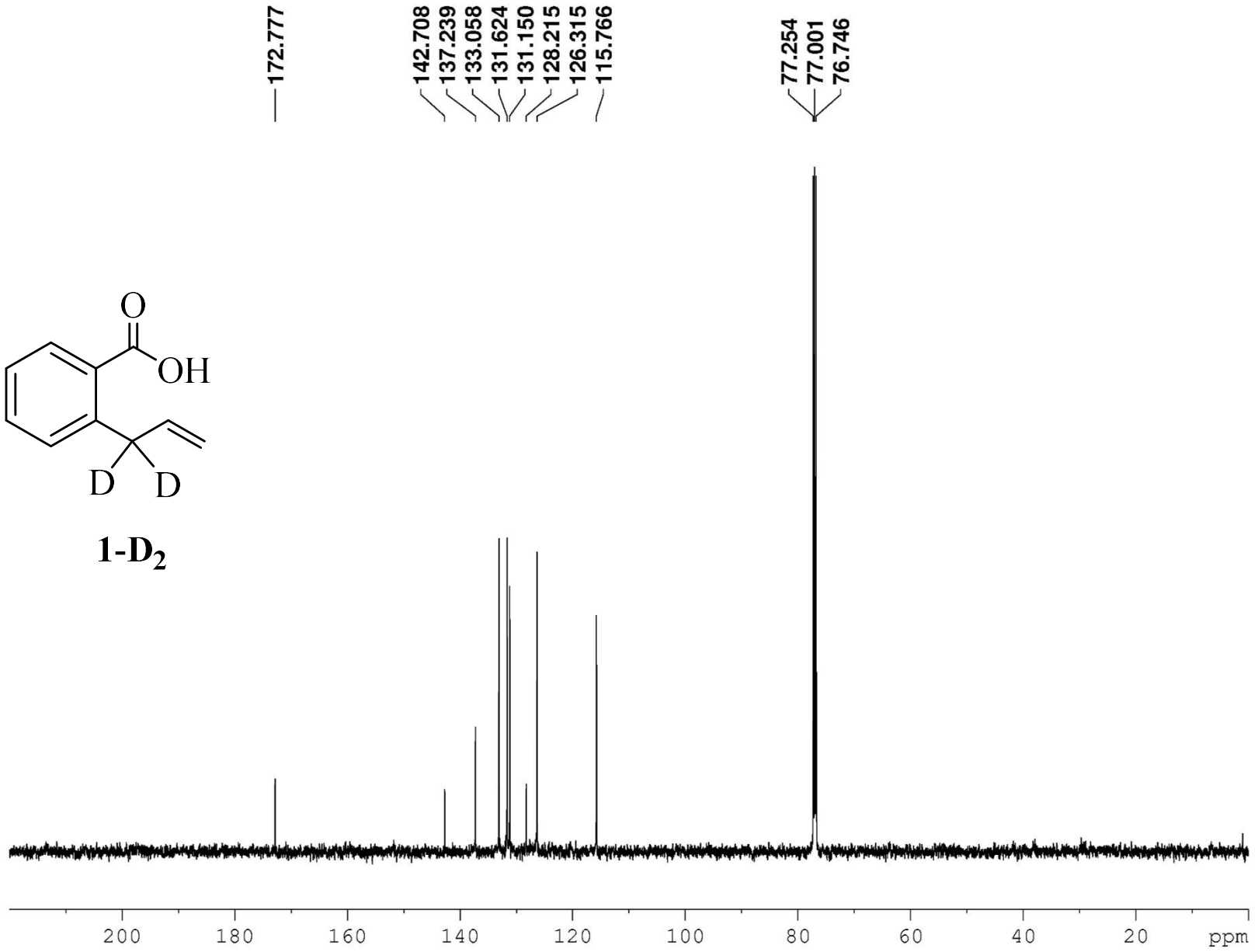
^{1}H NMR of compound **9** (300 MHz, $CDCl_3$)



^{13}C NMR of compound **9** (75 MHz, $CDCl_3$)

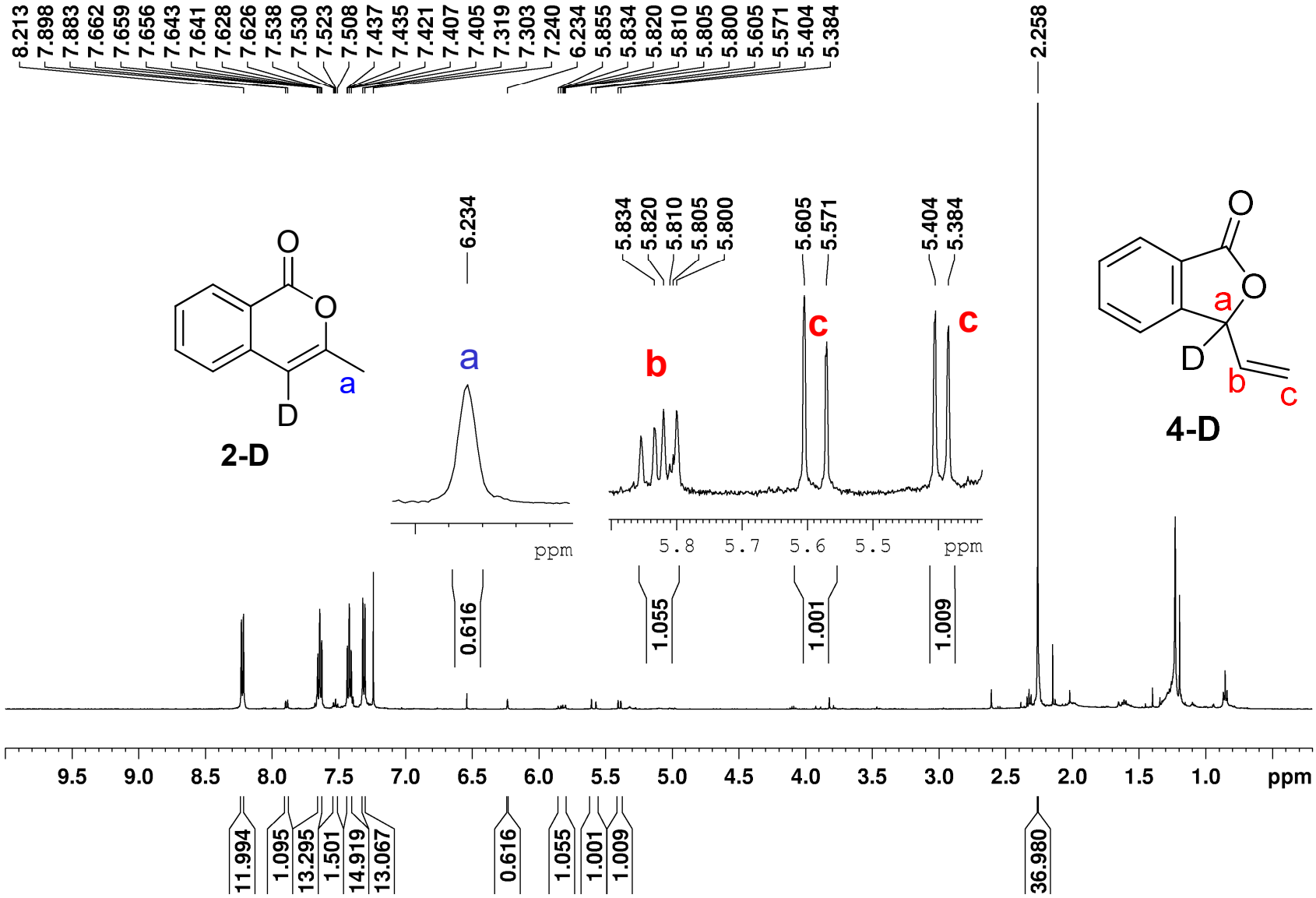


^{1}H NMR of compound **1-D$_2$** (500 MHz, $CDCl_3$)

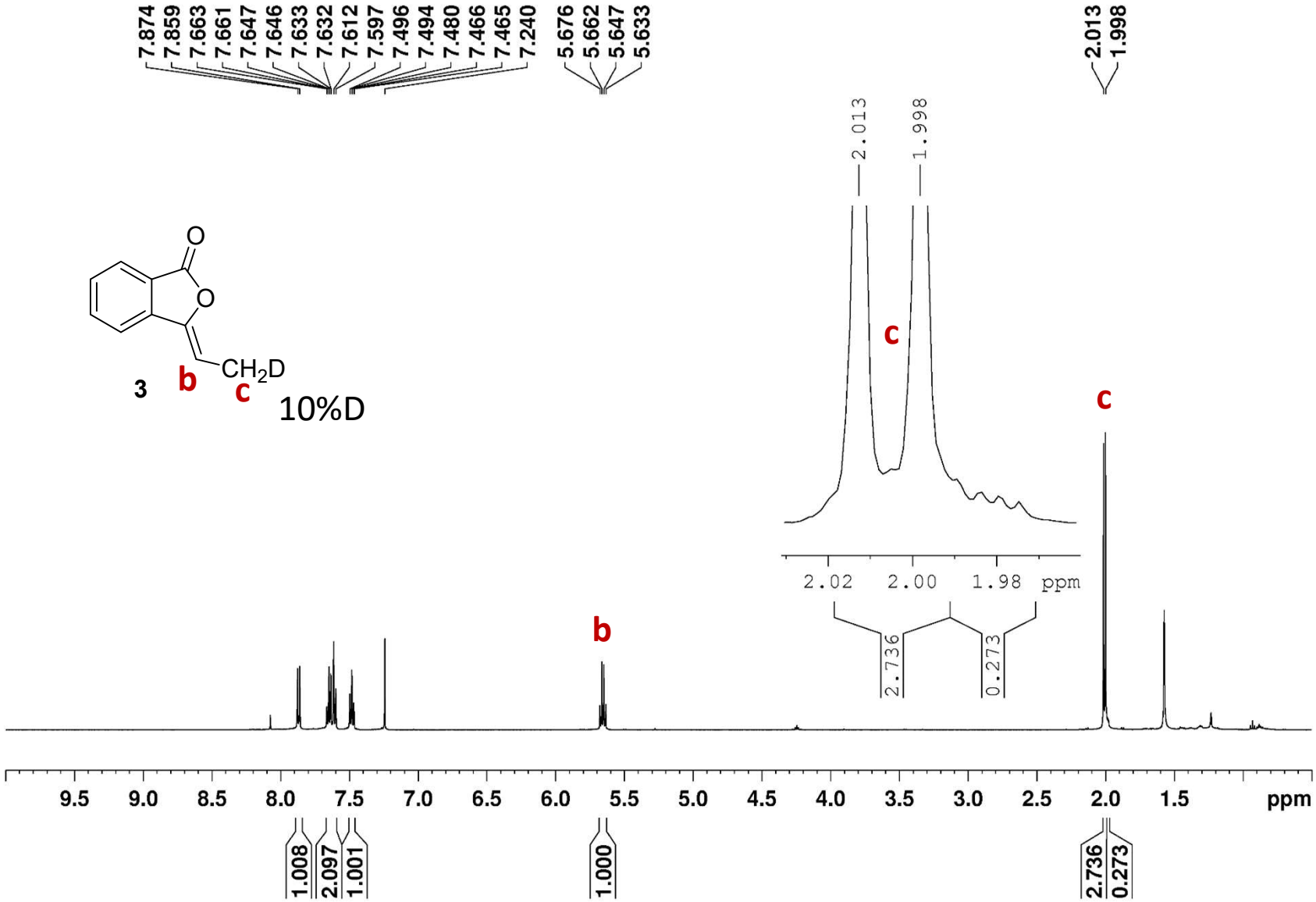


1-D_2

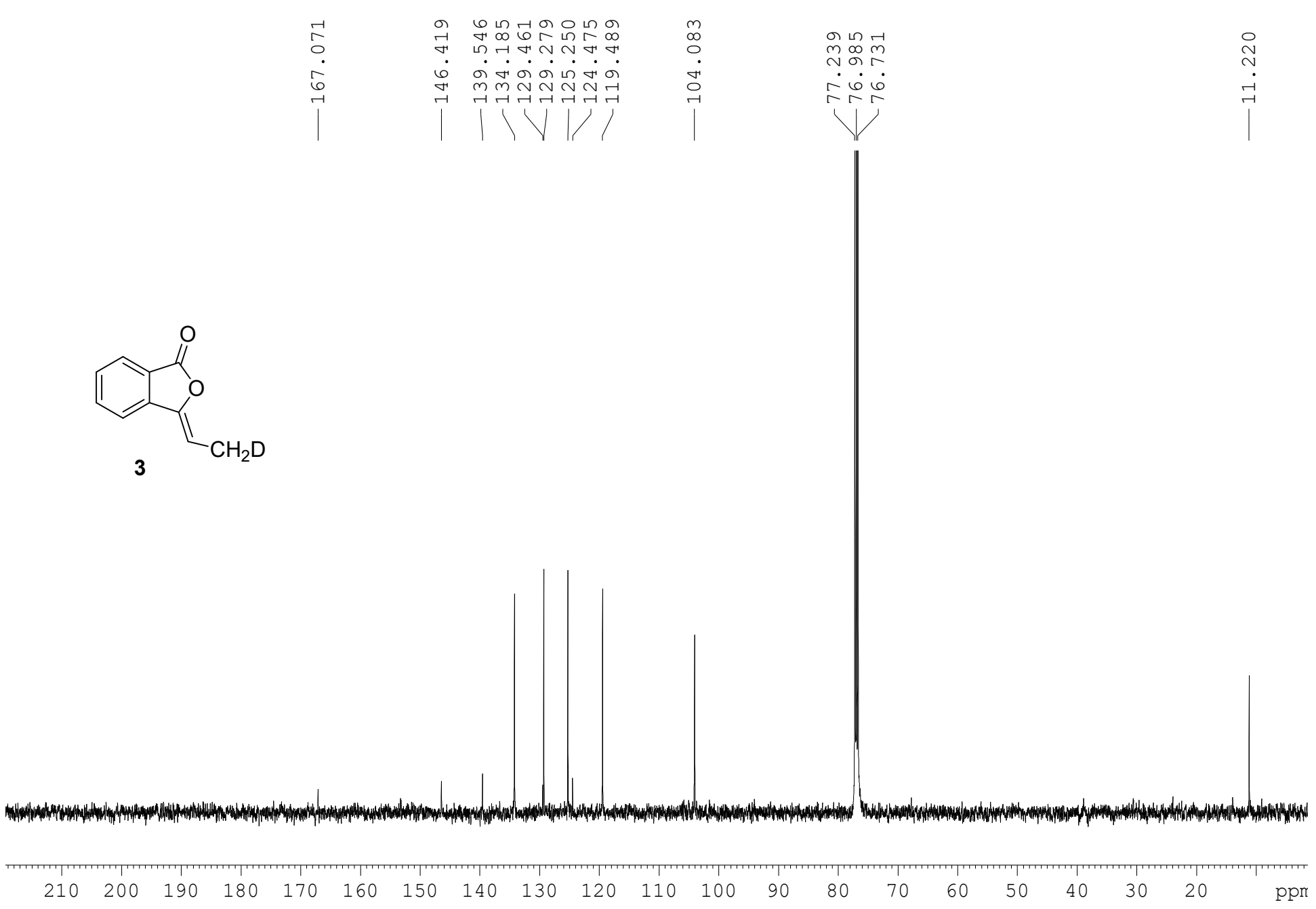
^{13}C NMR of compound **1-D_2** (125 MHz, $CDCl_3$)



^{1}H NMR of the mixture of compound **2-D and 4-D** (500 MHz, $CDCl_3$)



^{1}H NMR of compound **3-D** (500 MHz, $CDCl_3$)



^{13}C NMR of compound **3-D** (125 MHz, $CDCl_3$)