

Supporting Information

Copper-catalytic Oxidation of Arylmethyl Triazines with H₂O toward the Oxidant-free Synthesis of Aroyl Triazines

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^b School of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou, 310014, China;

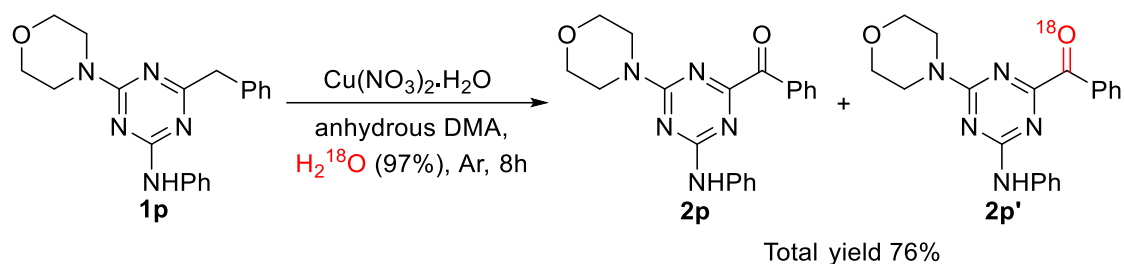
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S1 Investigation of oxygen source



Procedure: To a mixture of **1p** (86.8 mg, 0.25 mmol), H_2^{18}O (97% labeled) (10 μL , 1.2 mmol) in DMA (3 mL) was added $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (10 mol%). The resulting mixture was then sealed and stirred for 8 h at 110°C under Argon. Product was isolated by flash chromatography with petroleum ether and ethyl acetate (v/v 10/1) as the eluent, 68 mg, 76% yield. LCMS of the reaction product (**Figure 1**), **1p** (**Figure 2**) and **2p** (**Figure 3**) showed that both ^{18}O labeled and unlabeled products (**2p** and **2p'**) were produced under the optimized conditions, which confirmed that H_2O was the oxygen source in this oxidation transformation.

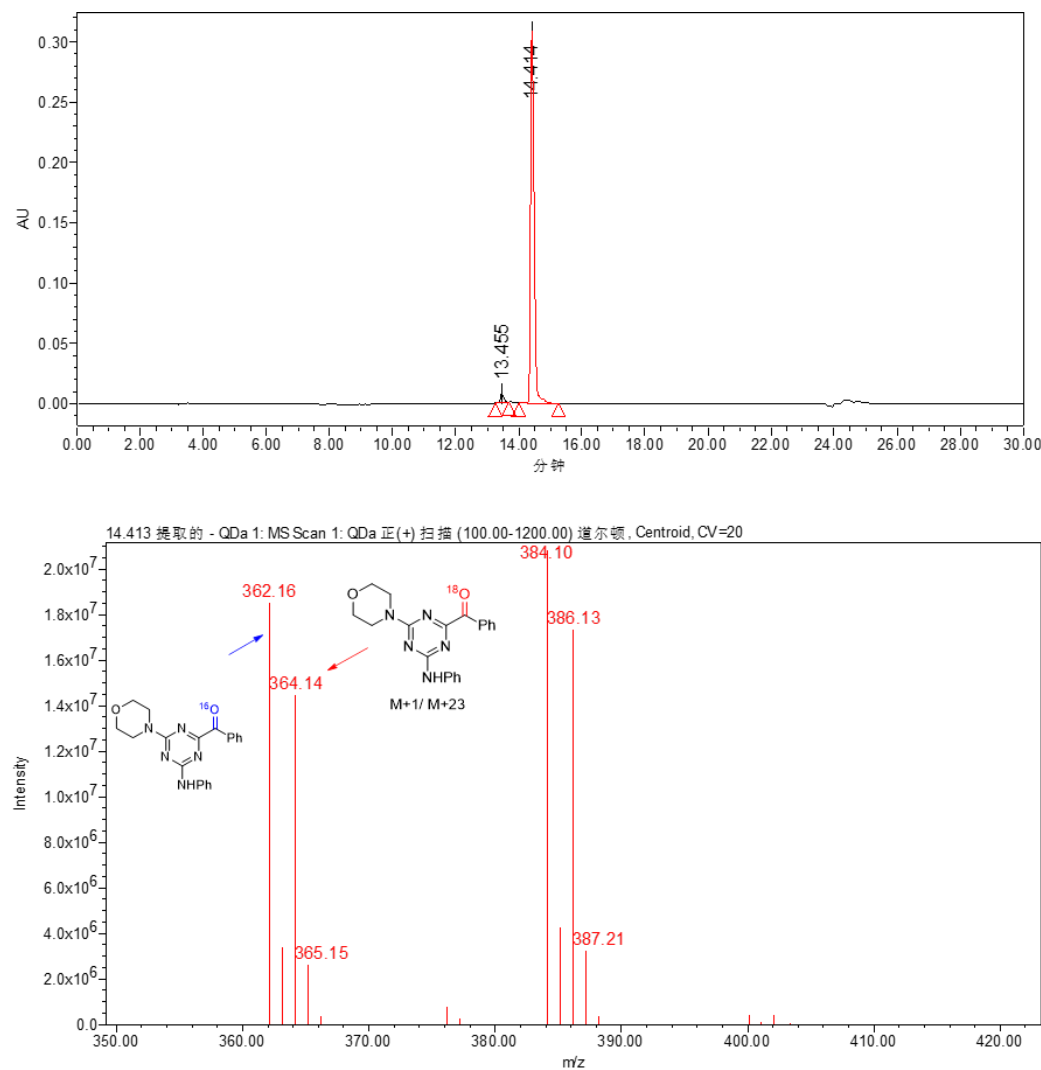


Figure 1. Reaction was performed with H_2^{18}O (97% labeled)

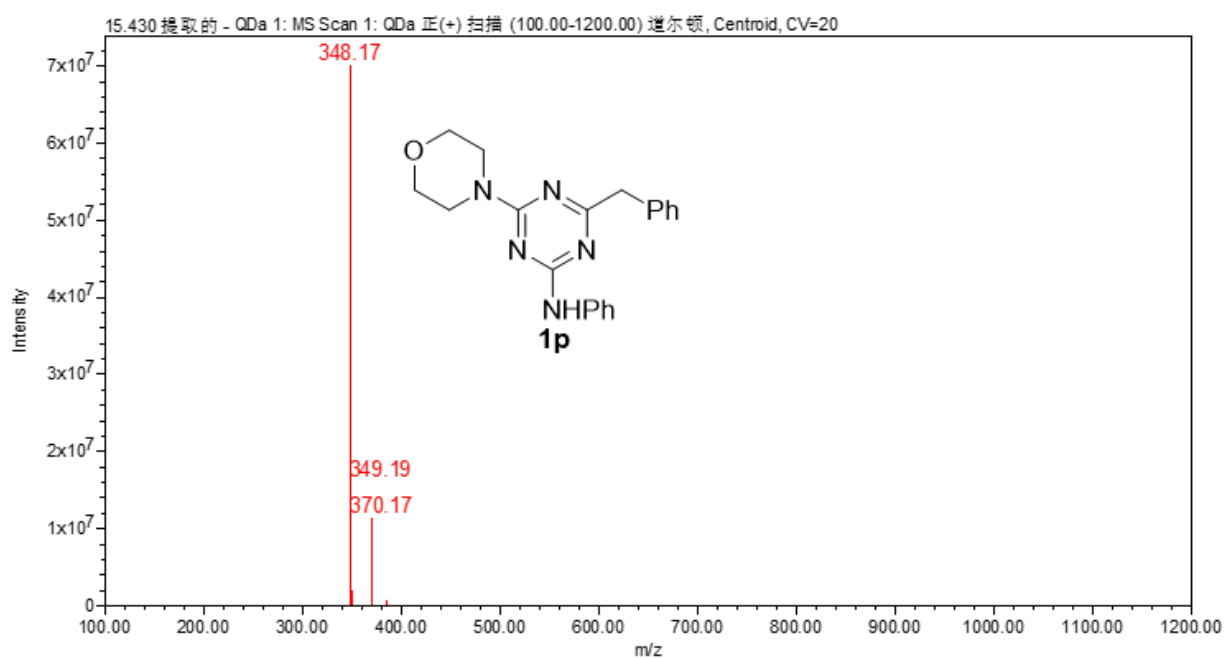
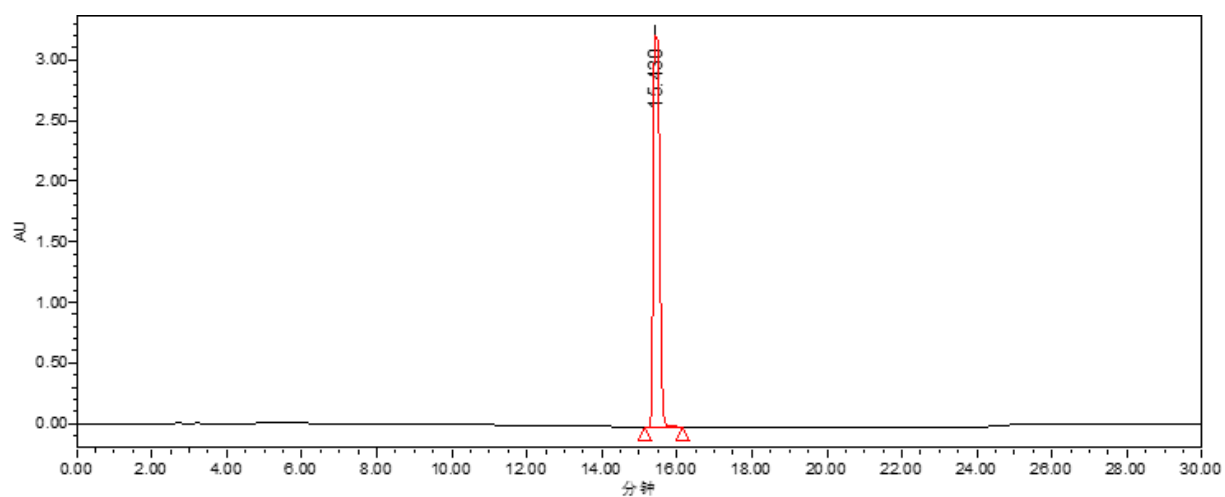


Figure 2. LCMS of **1p**

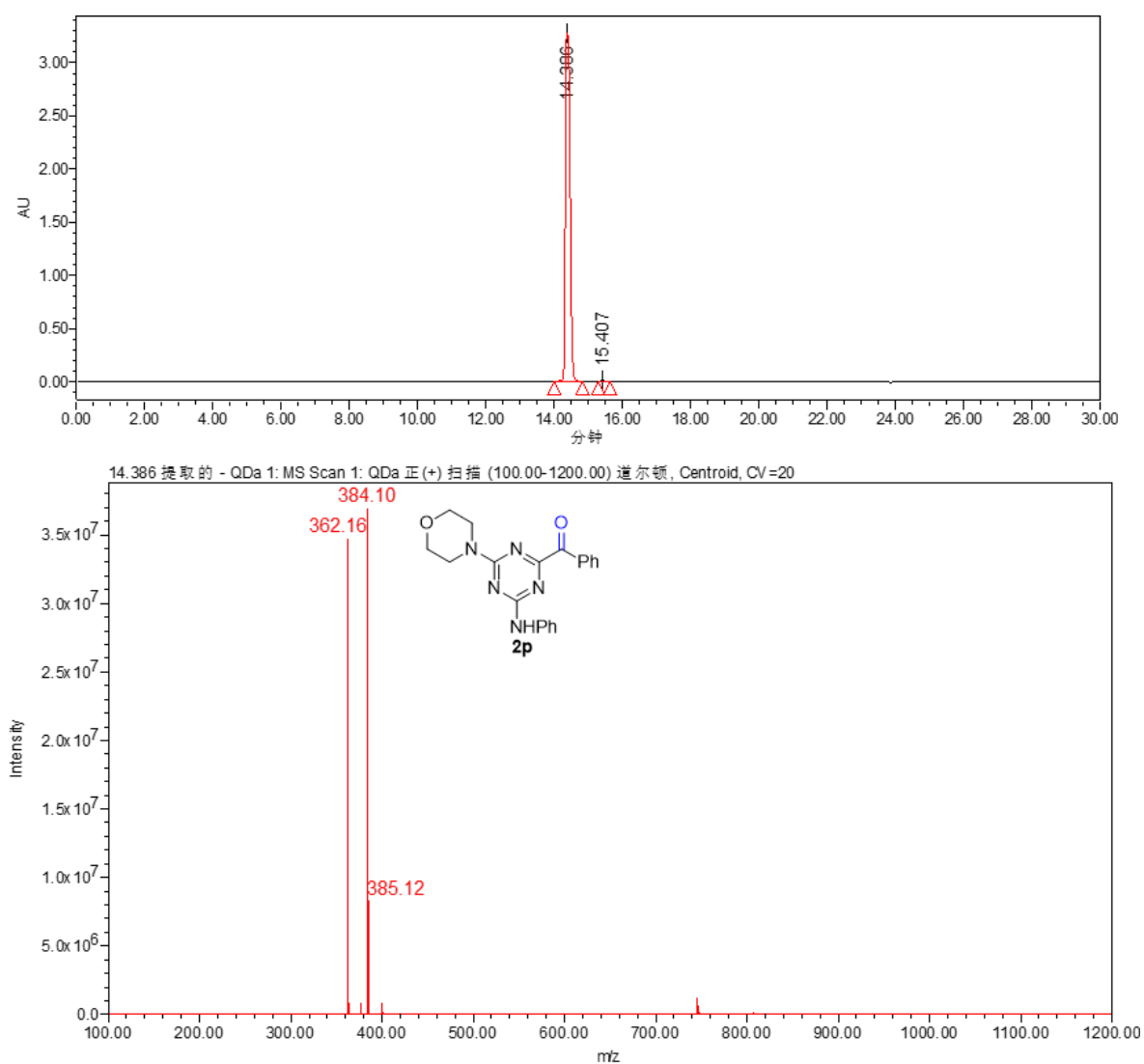
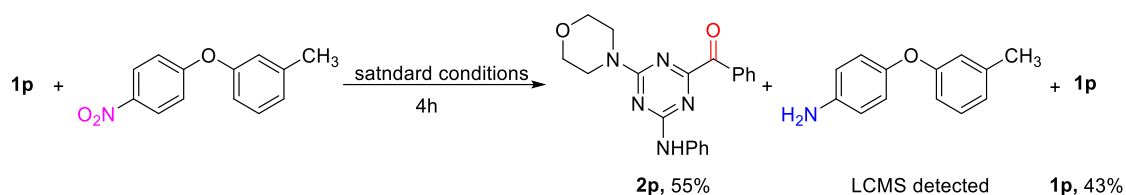


Figure 3. Reaction was performed with H₂O

S2 Hydrogen capture experiment



Procedure: To a mixture of **1p** (86.8 mg, 0.25 mmol), H₂O (10 uL, 1.2 mmol), 1-methyl-3-(4-nitrophenoxy)benzene (58.0 mg, 0.25 mmol) in DMA (3 mL) was added Cu(NO₃)₂·3H₂O (10 mol%). The resulting mixture was then sealed and stirred for 4 h at 120°C under Argon, 4-(m-tolyloxy)aniline was observed by LCMS (Figure 4). The result above indicated that hydrogen release was involved in this reaction.

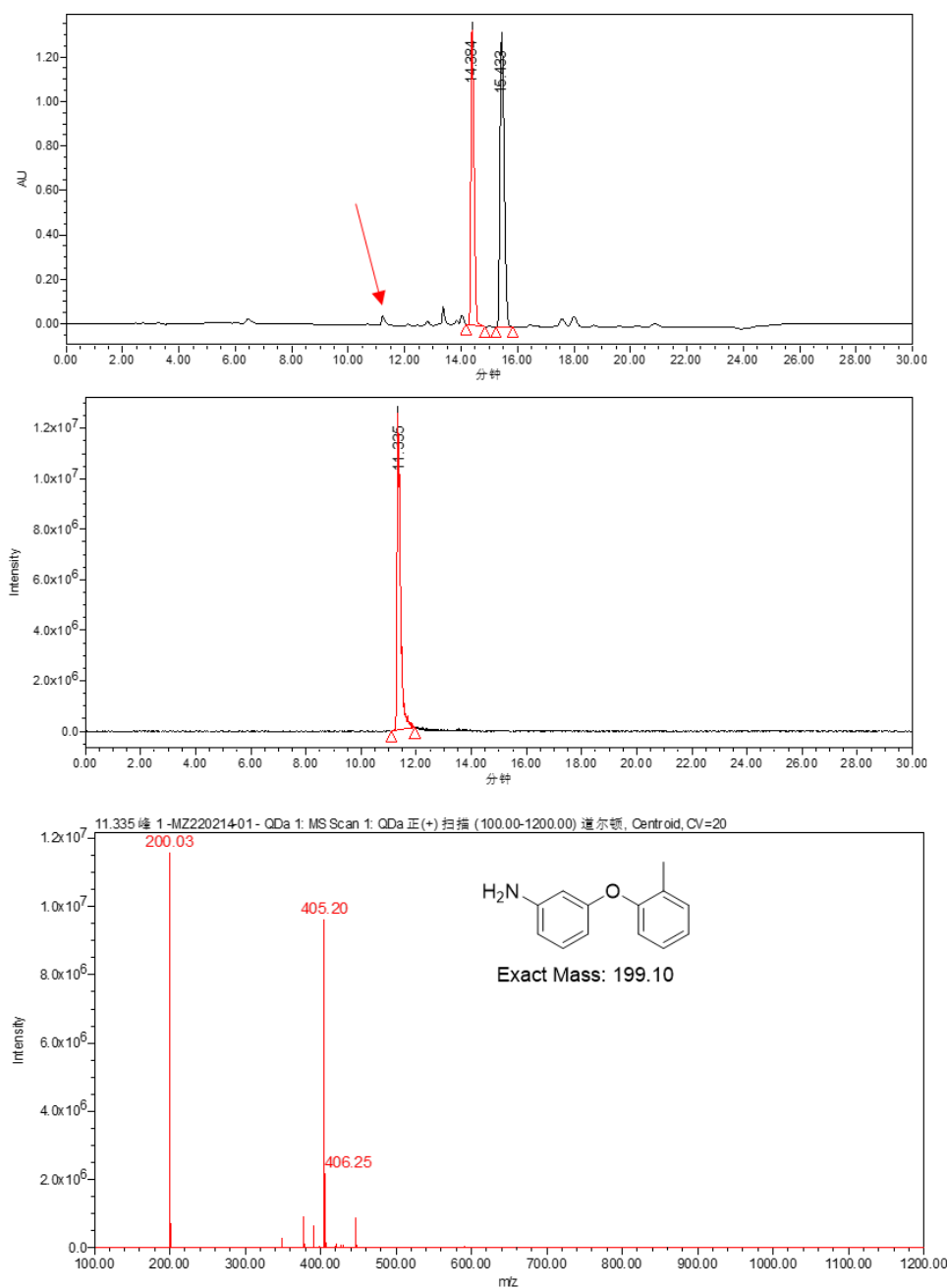
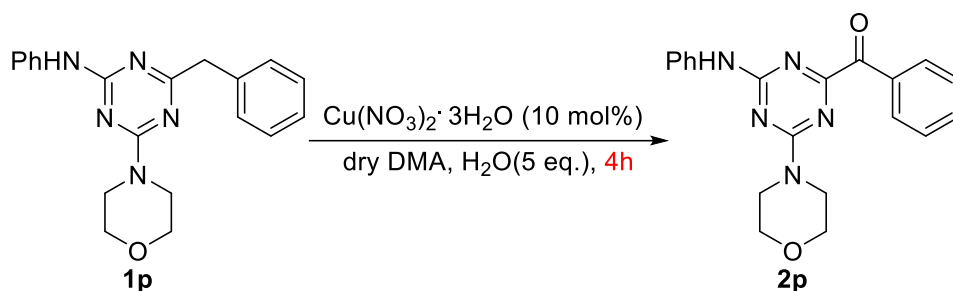


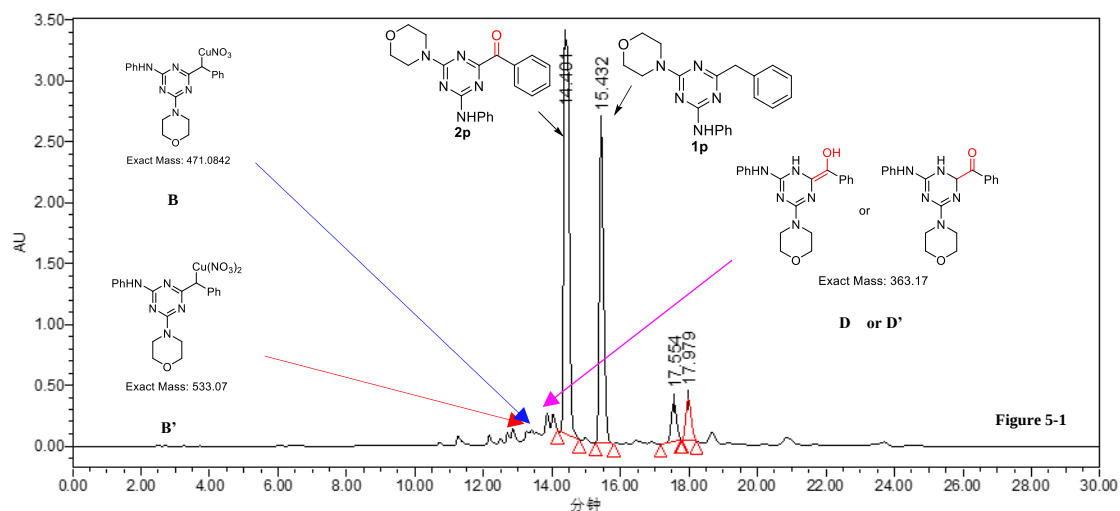
Figure 4. 4-(m-tolyloxy)aniline was observed by LCMS.

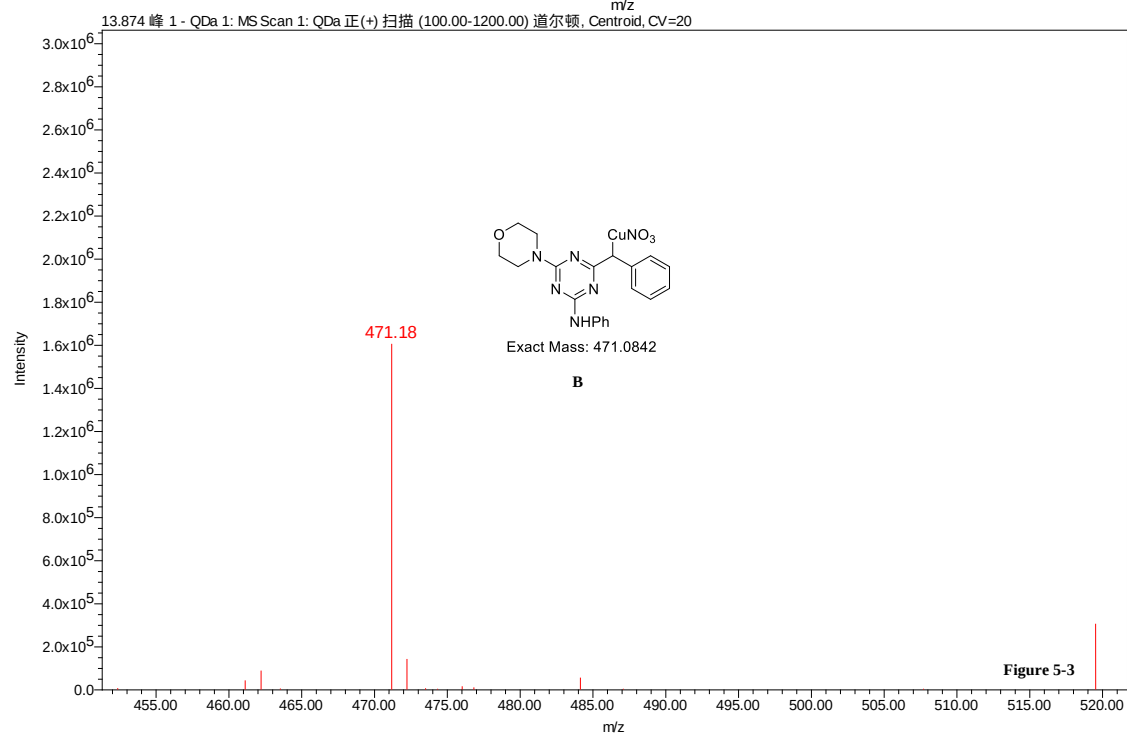
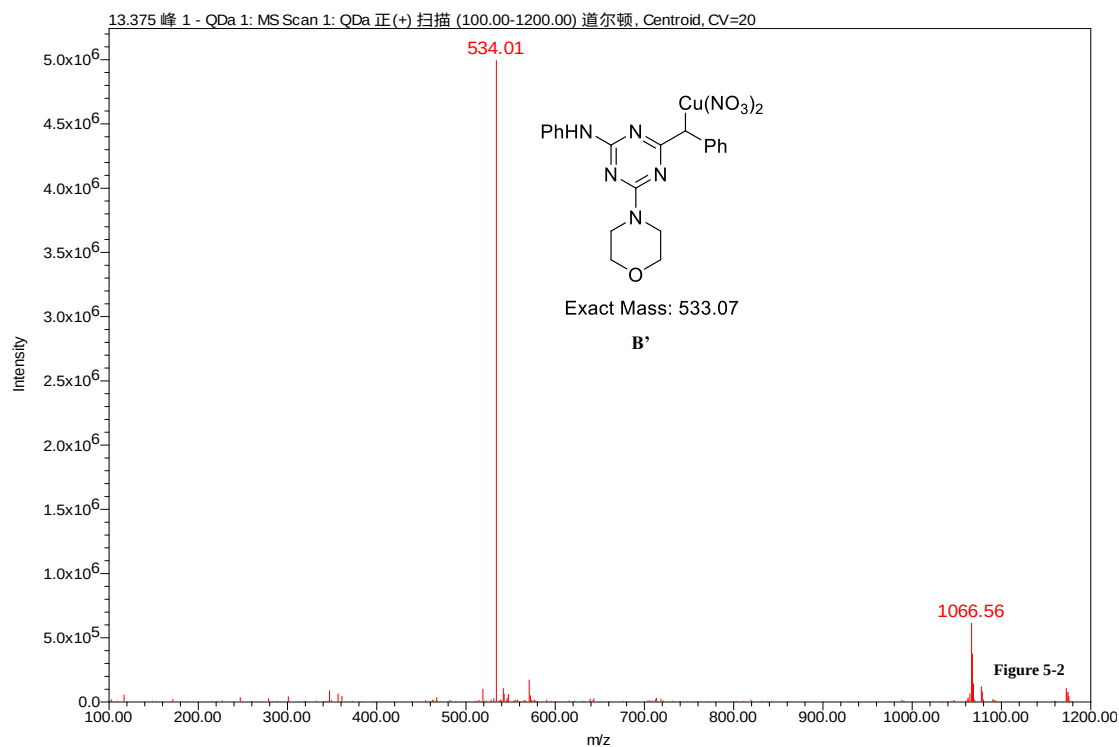
S3 Intermediates capture experiment

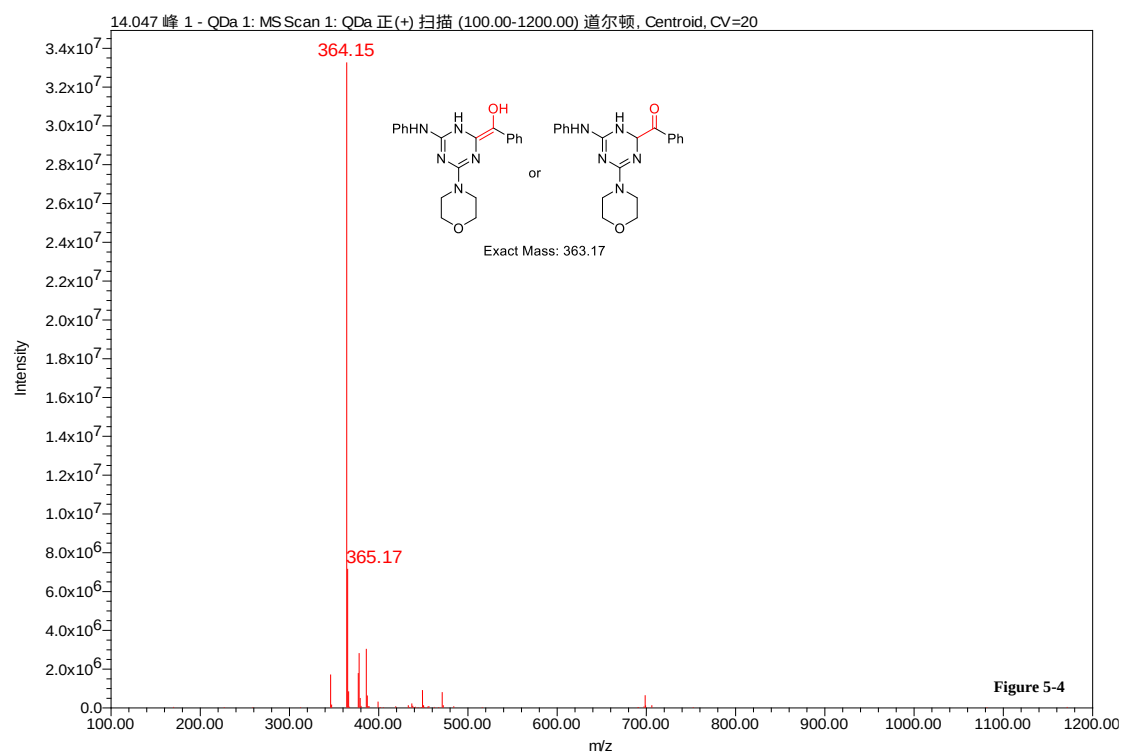


Procedure: To a mixture of **1p** (86.8 mg, 0.25 mmol), H_2O (10 μL , 1.2 mmol) in DMA (3 mL) was added $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (10 mol%). The resulting mixture was then sealed and stirred for 4 h at 120°C under Argon, 4-(m-tolyloxy)aniline was observed by LCMS (**Figure 5**). The results showed that **B**, **B'** and **D** or **D'** may be the intermediates in the reaction.

Figure 5. Possible Intermediates were observed by LCMS. (Figure 5-1) HPLC of the reaction mixture after 4h; (Figure 5-2) LCMS of intermediate **B'**; (Figure 5-3) LCMS of intermediate **B**; (Figure 5-4) LCMS of intermediate **D** and **D'**;





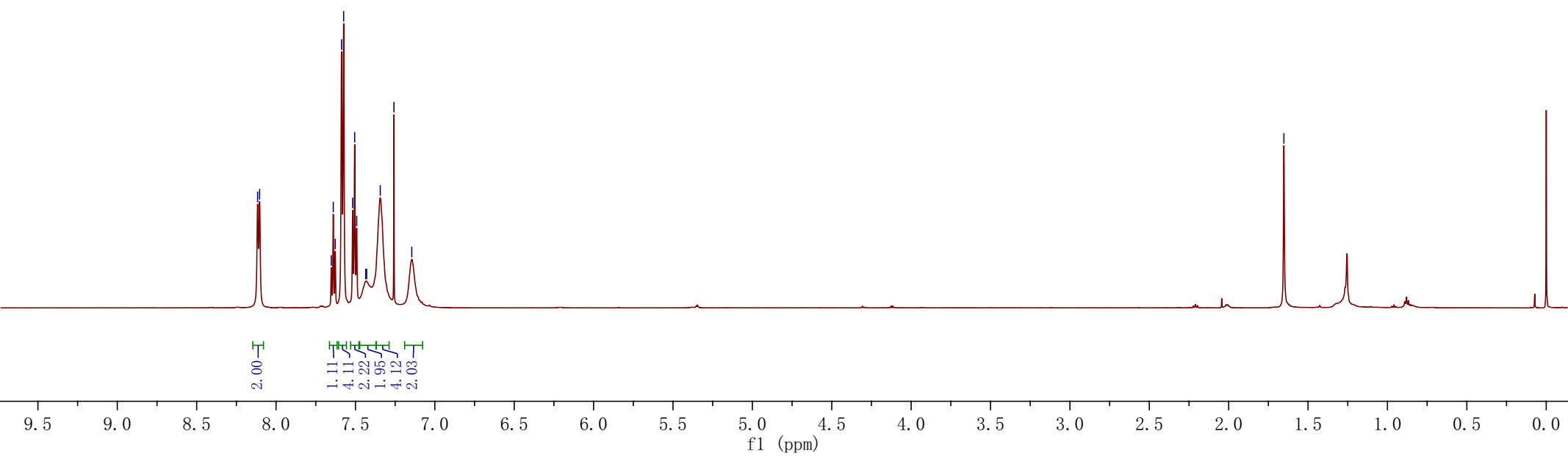
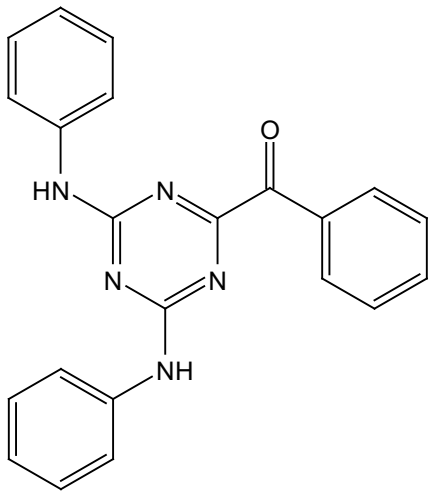


S4 The ^1H -NMR and ^{13}C -NMR spectra of products

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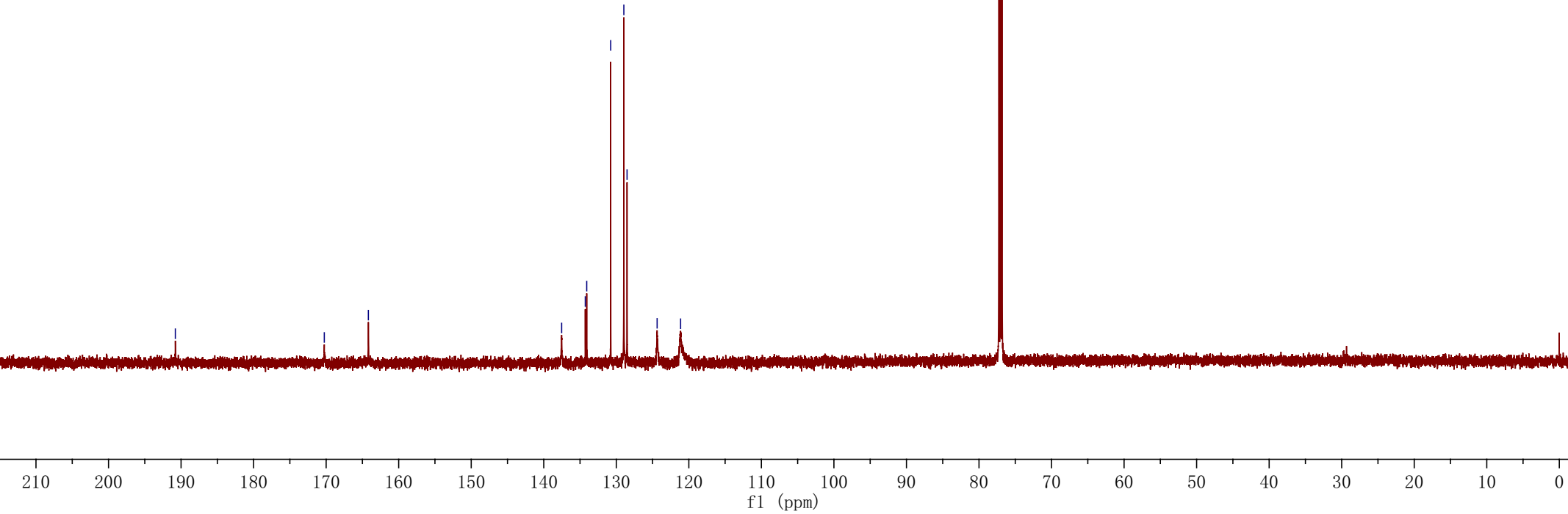
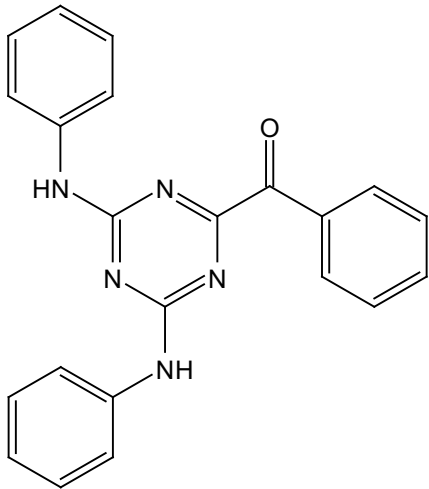
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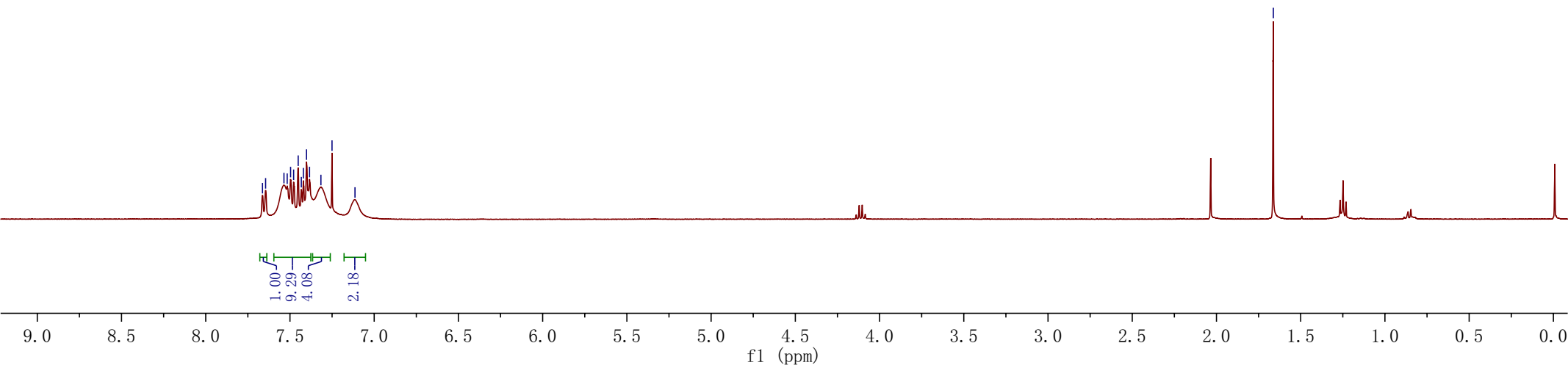
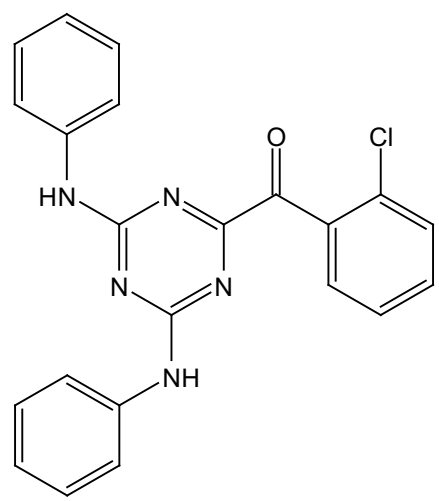
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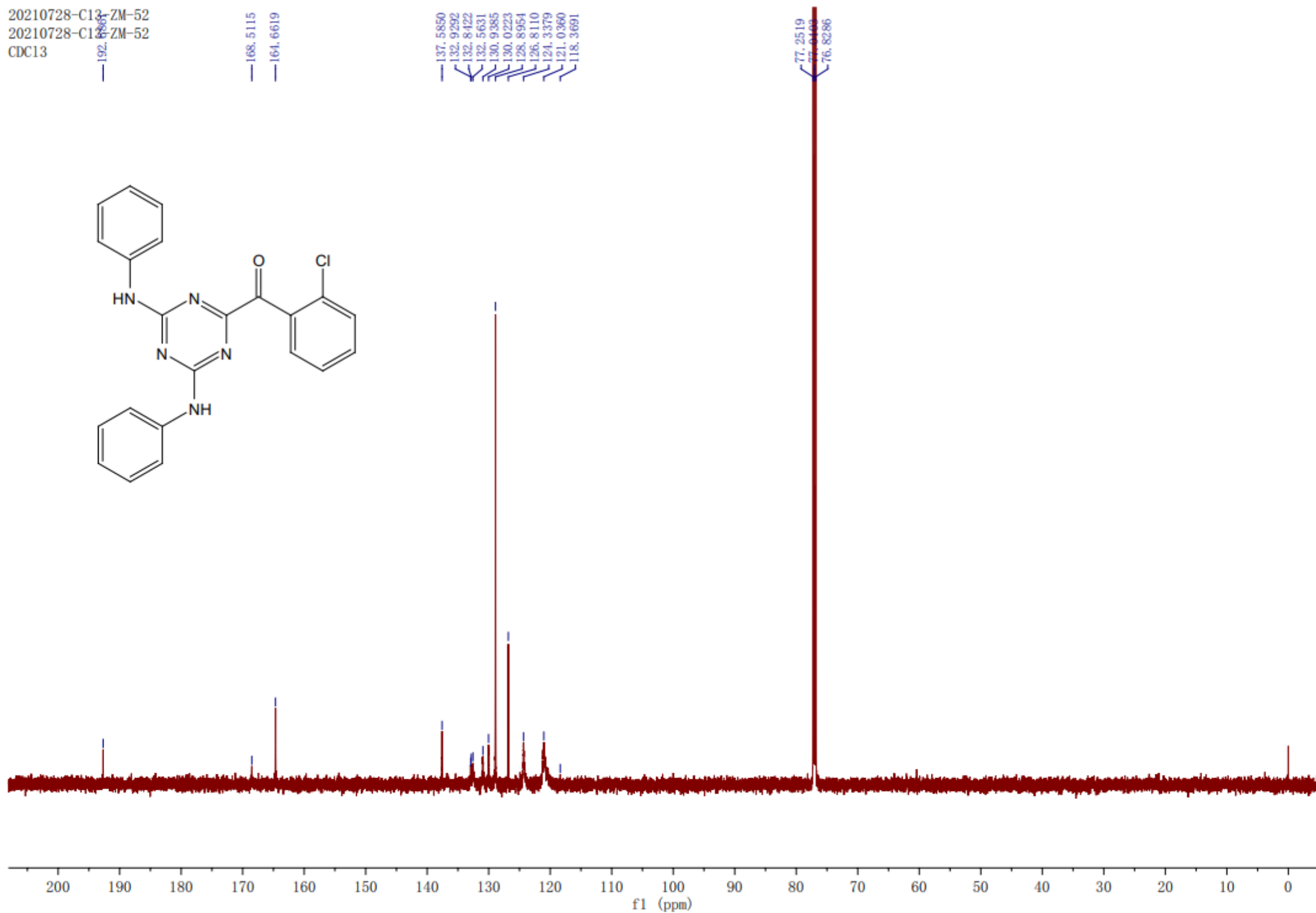
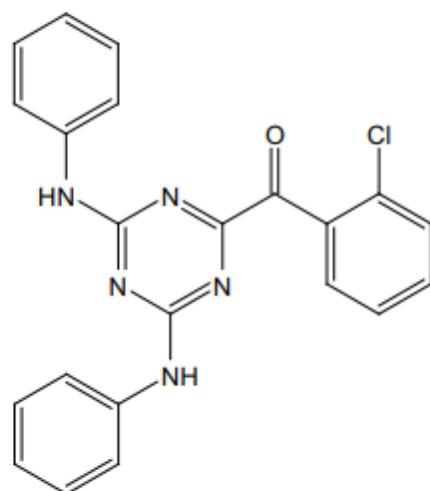
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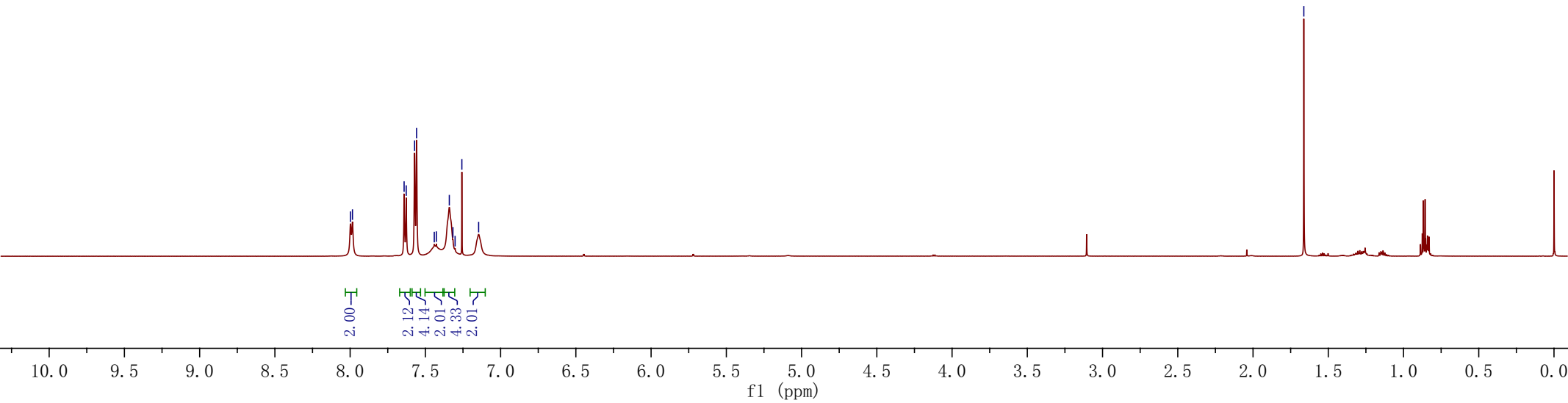
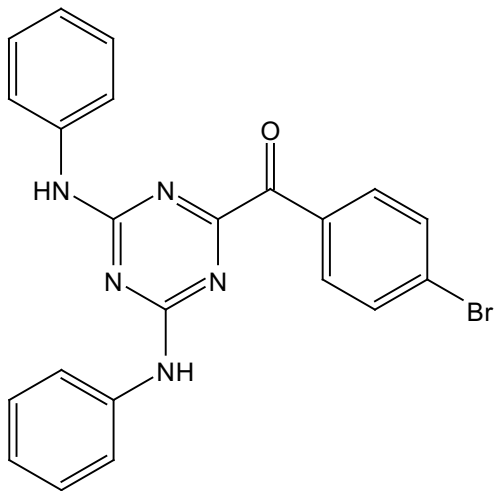
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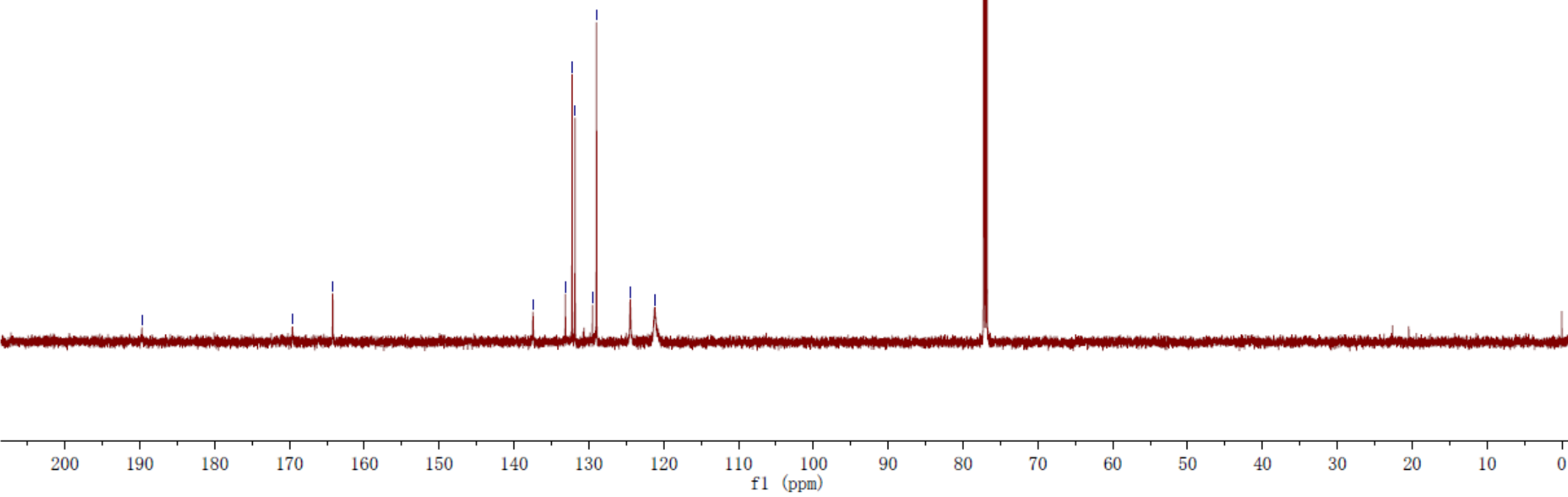
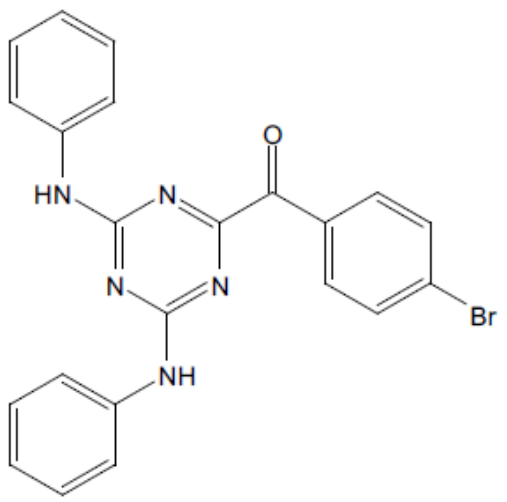
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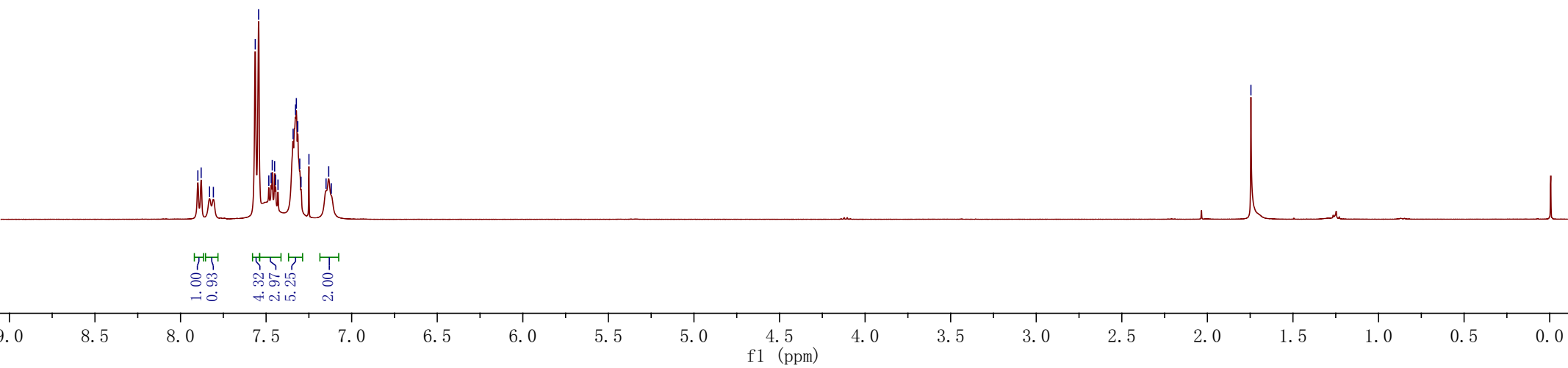
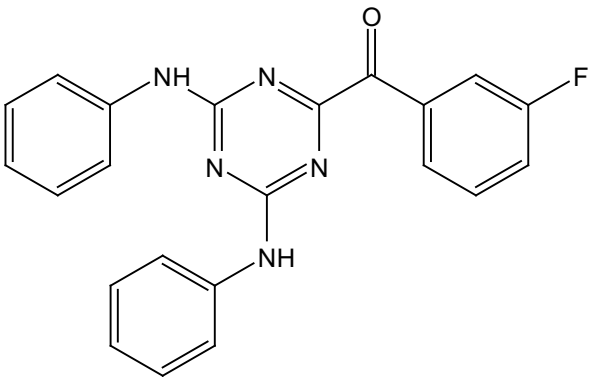
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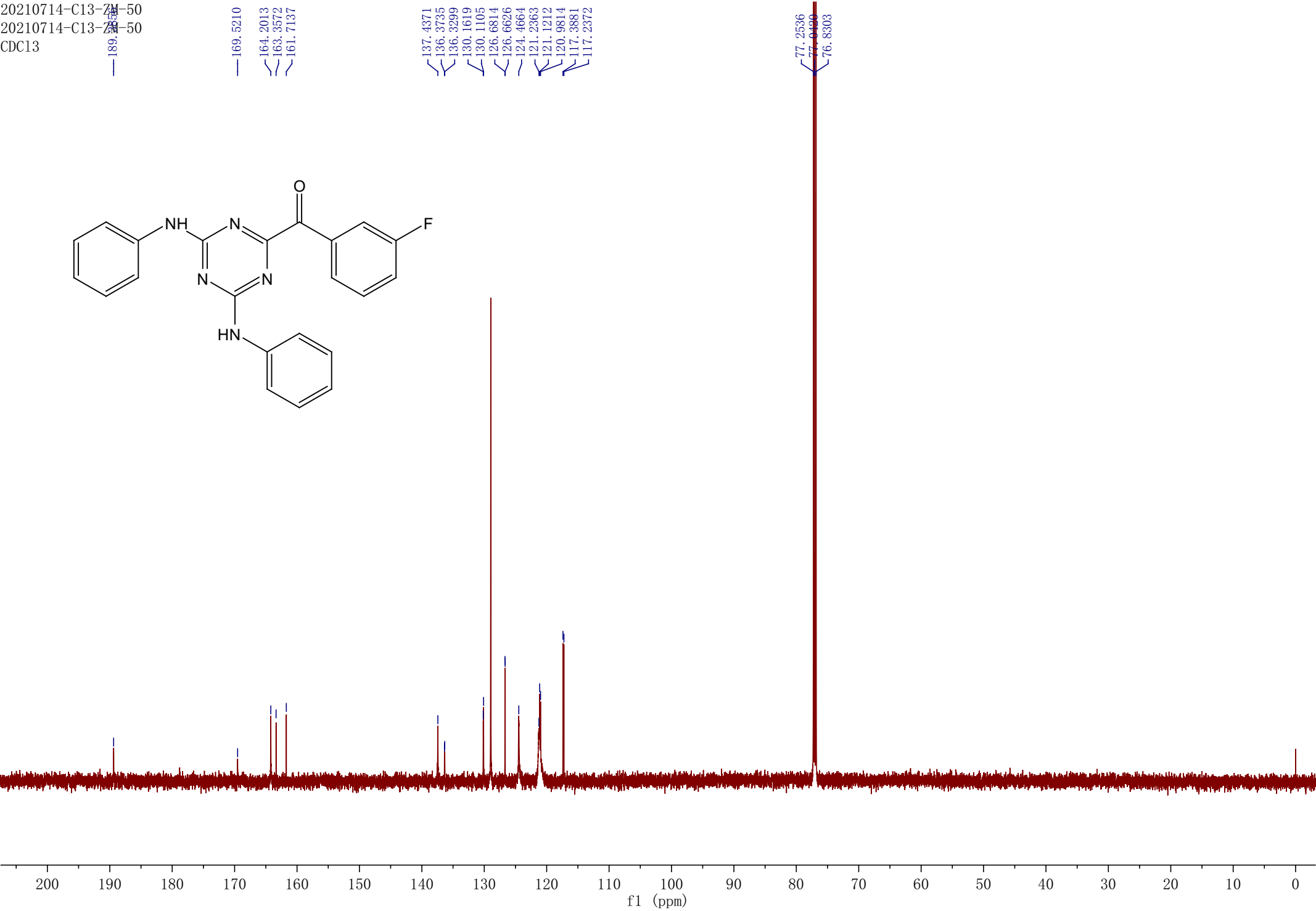
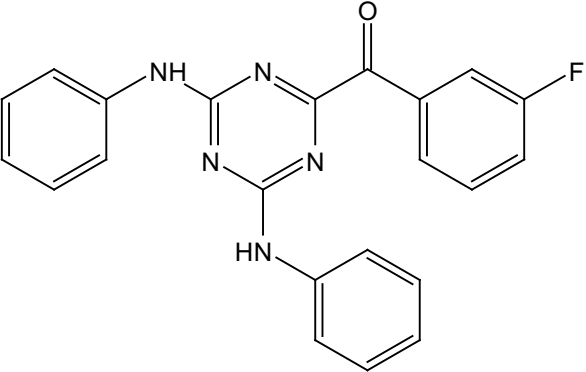
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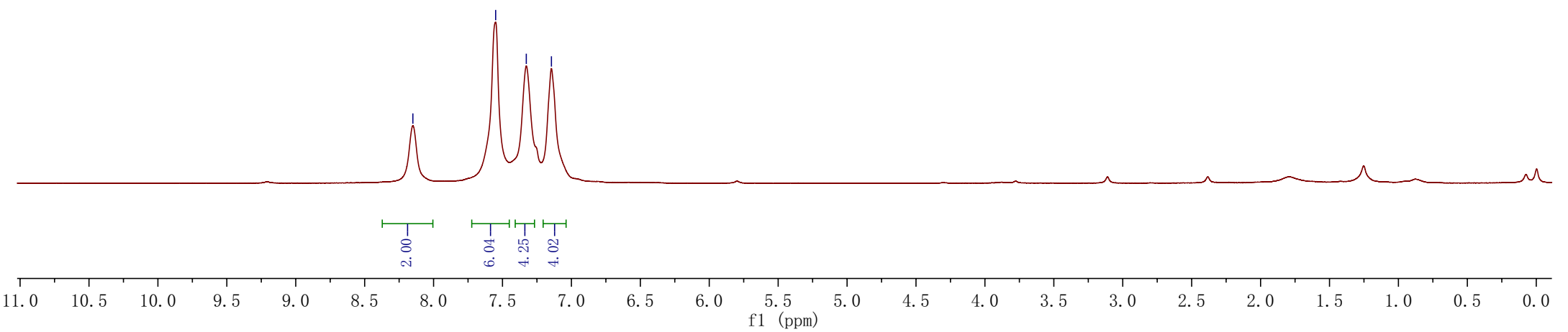
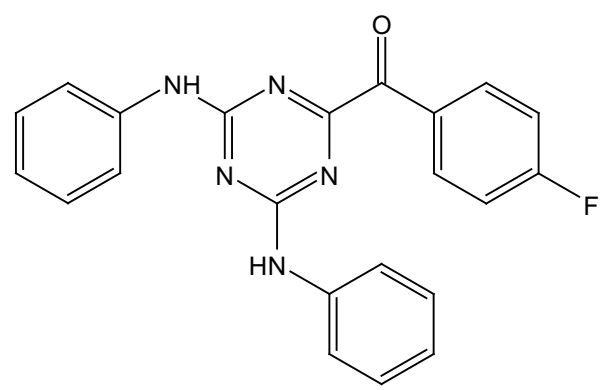


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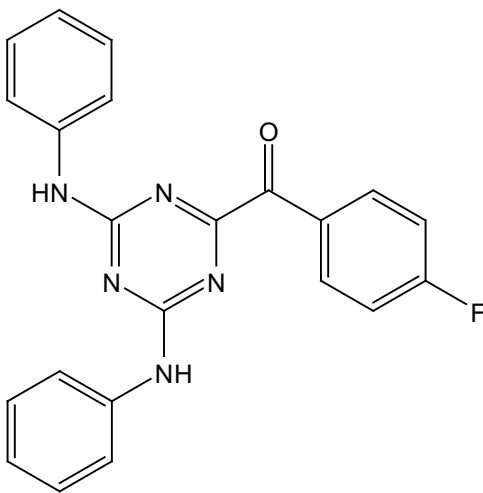


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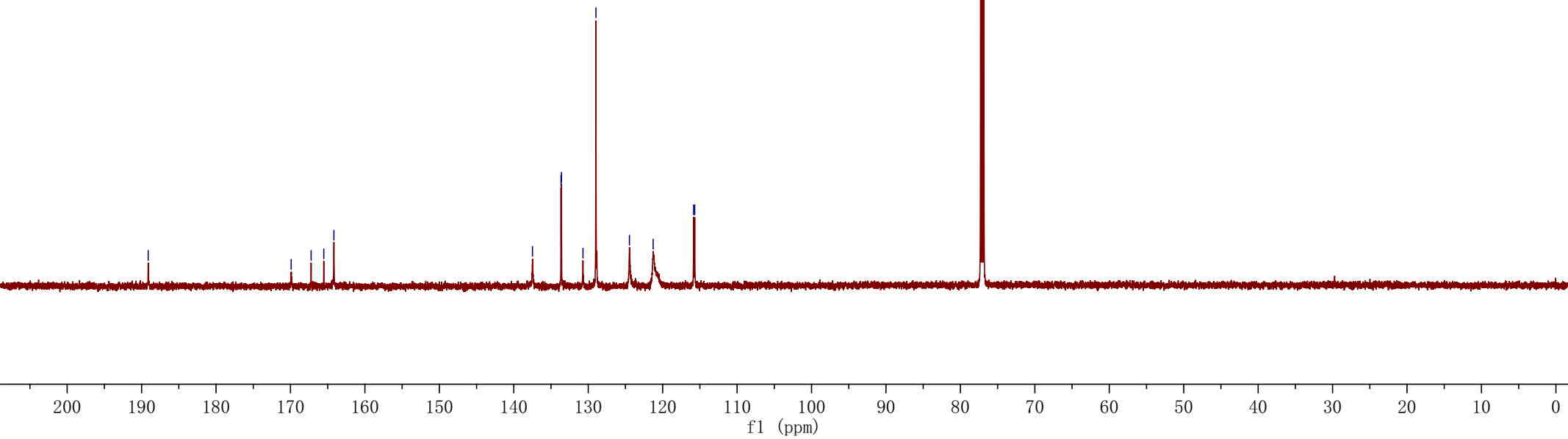
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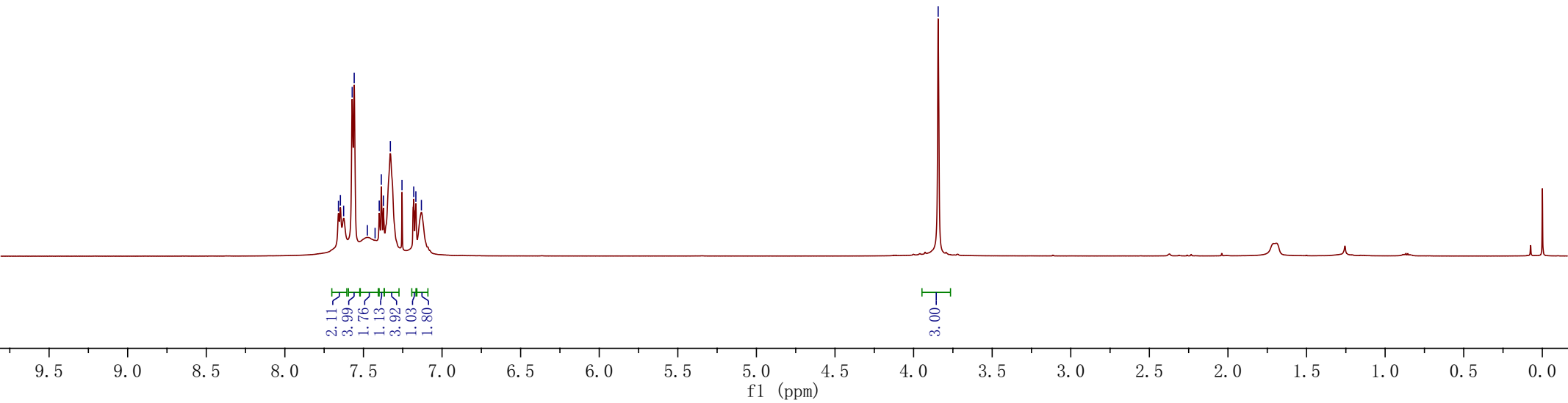
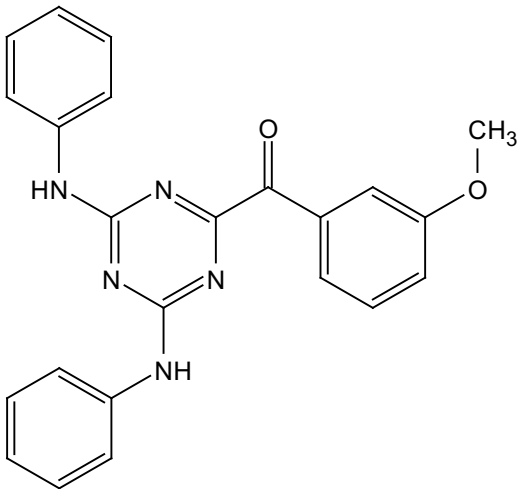
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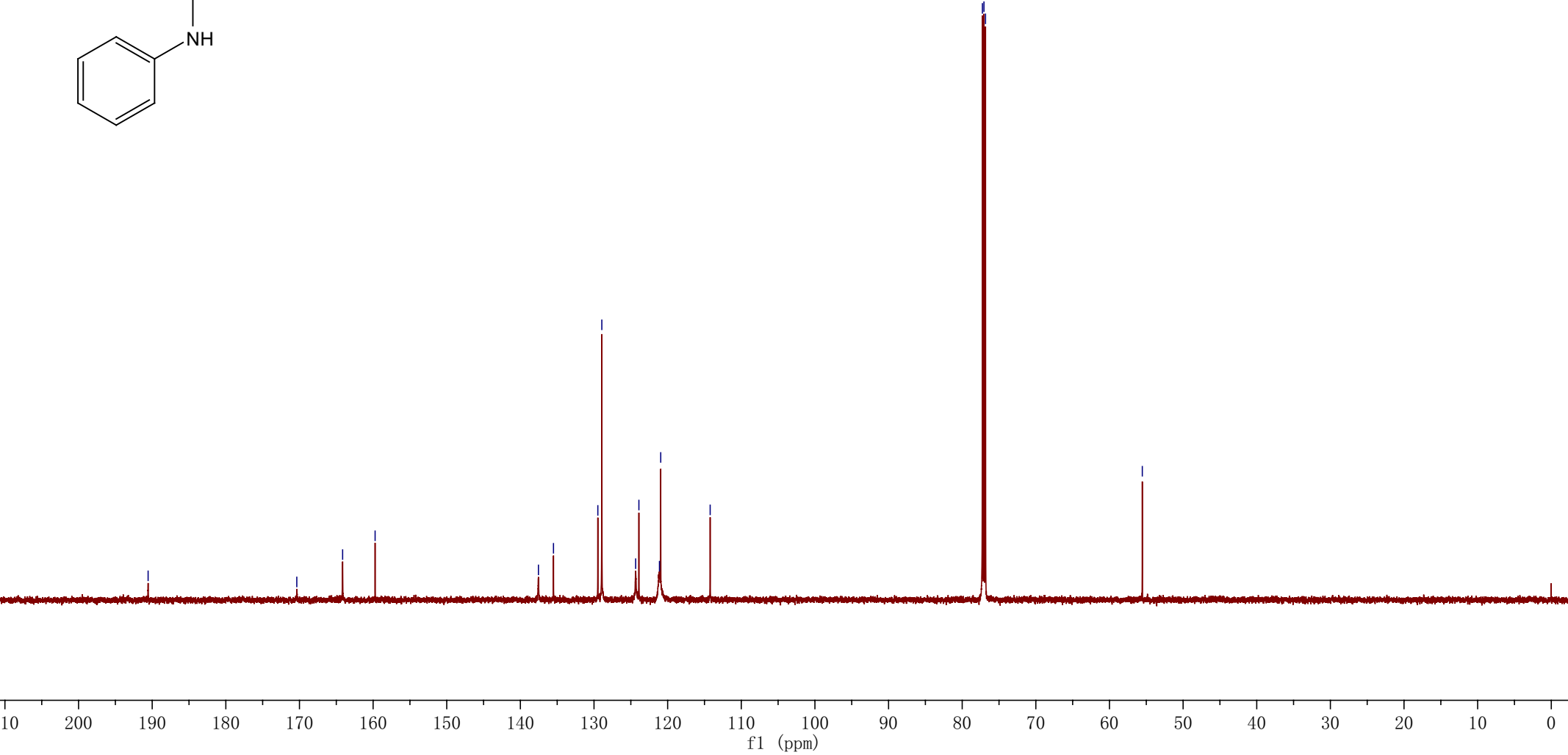
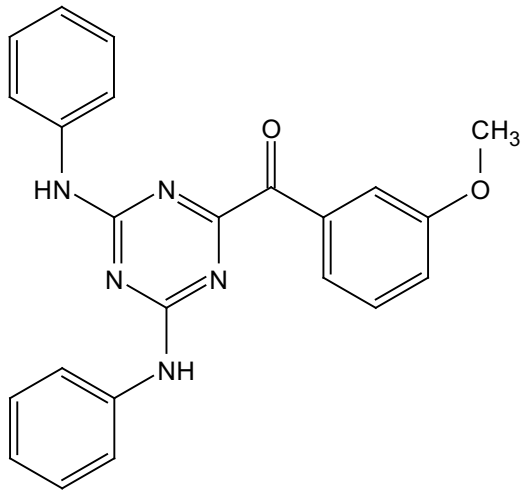
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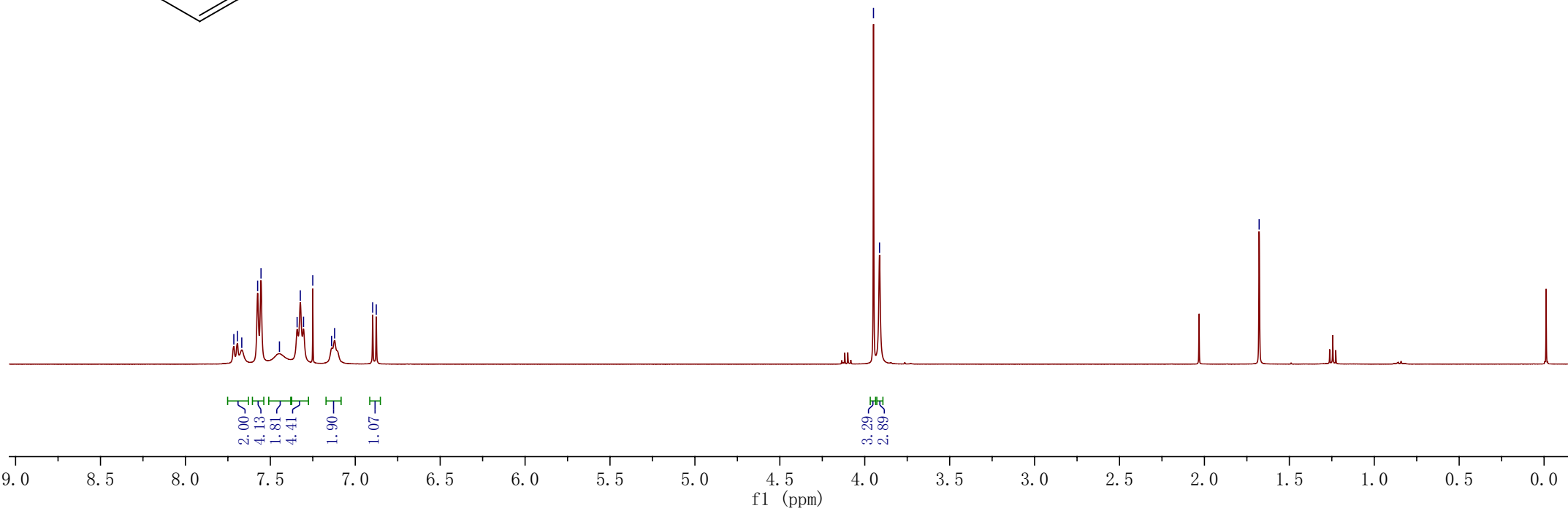
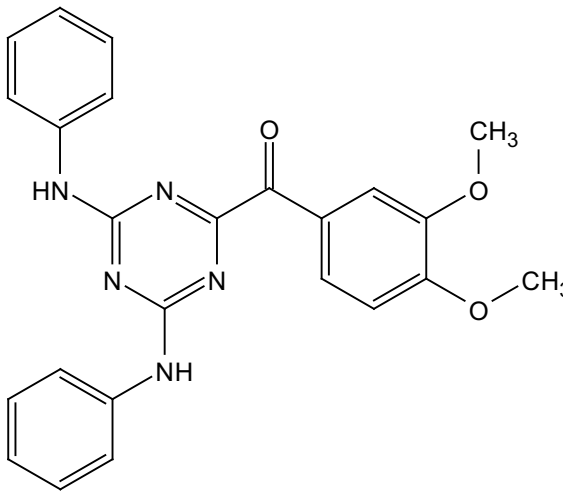


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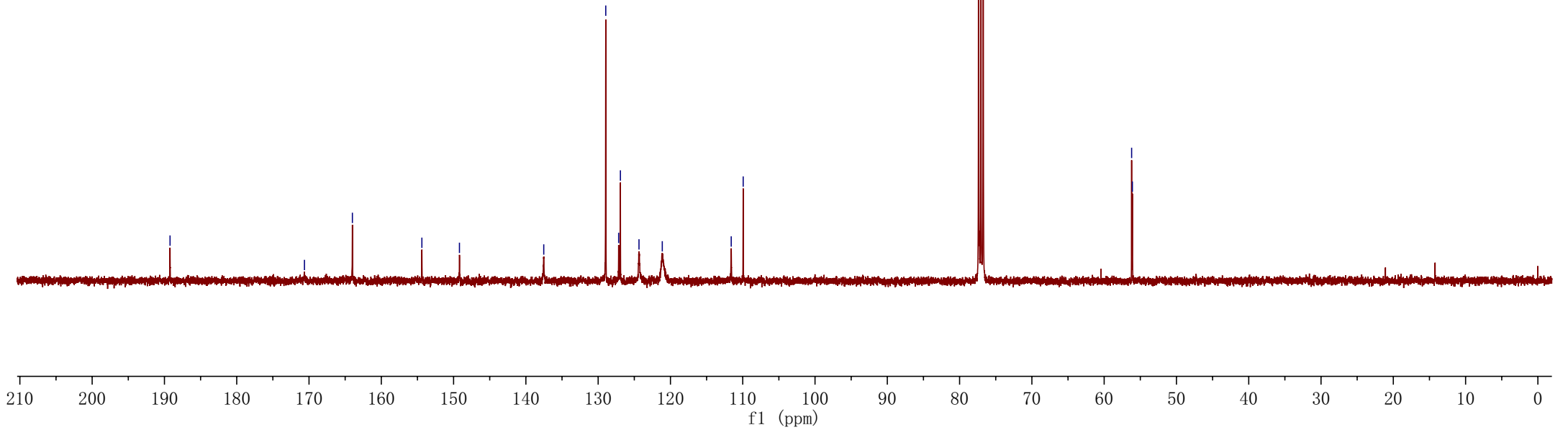
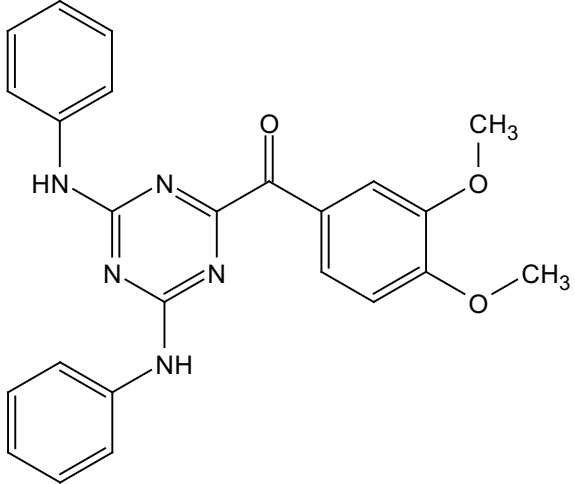
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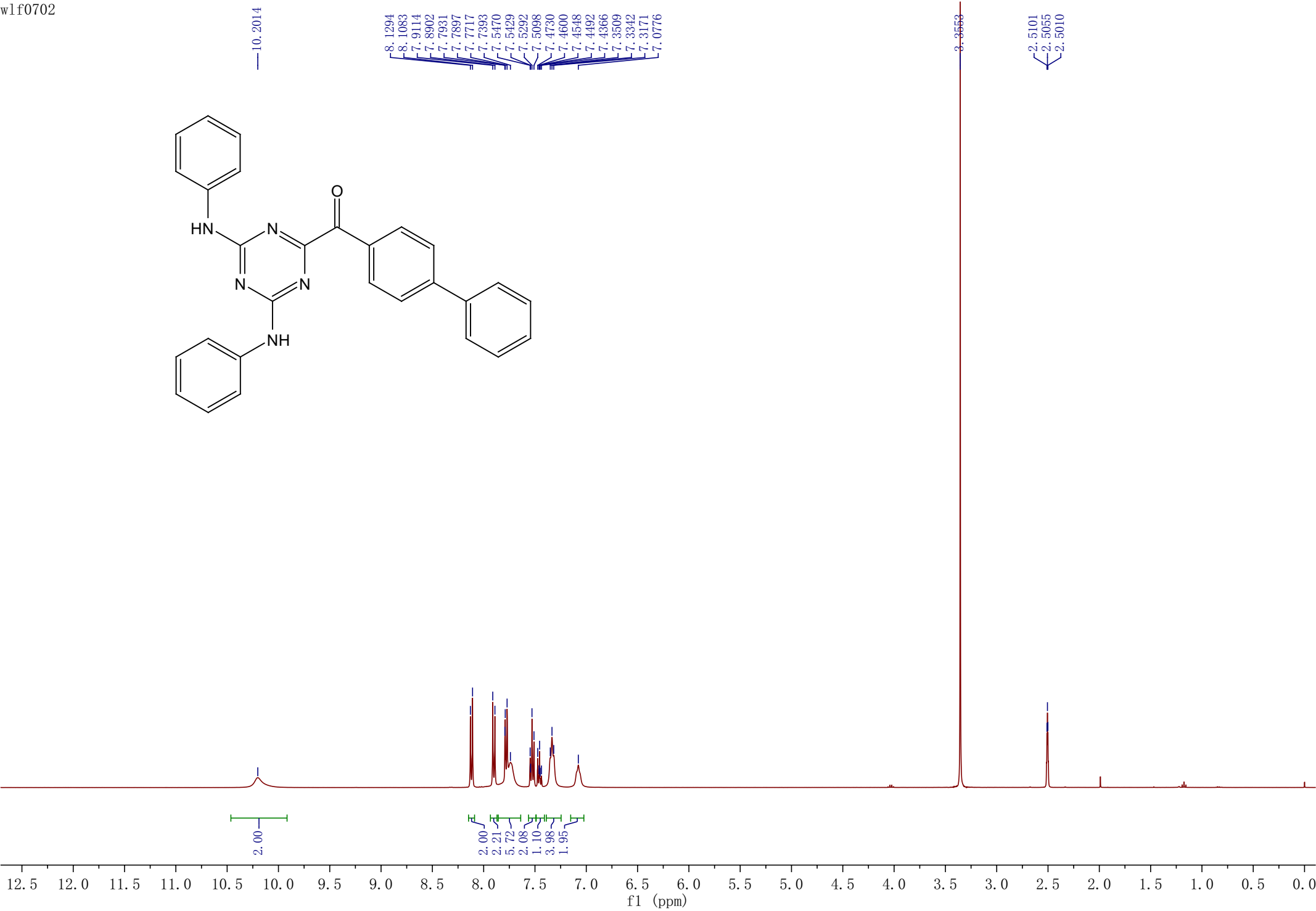


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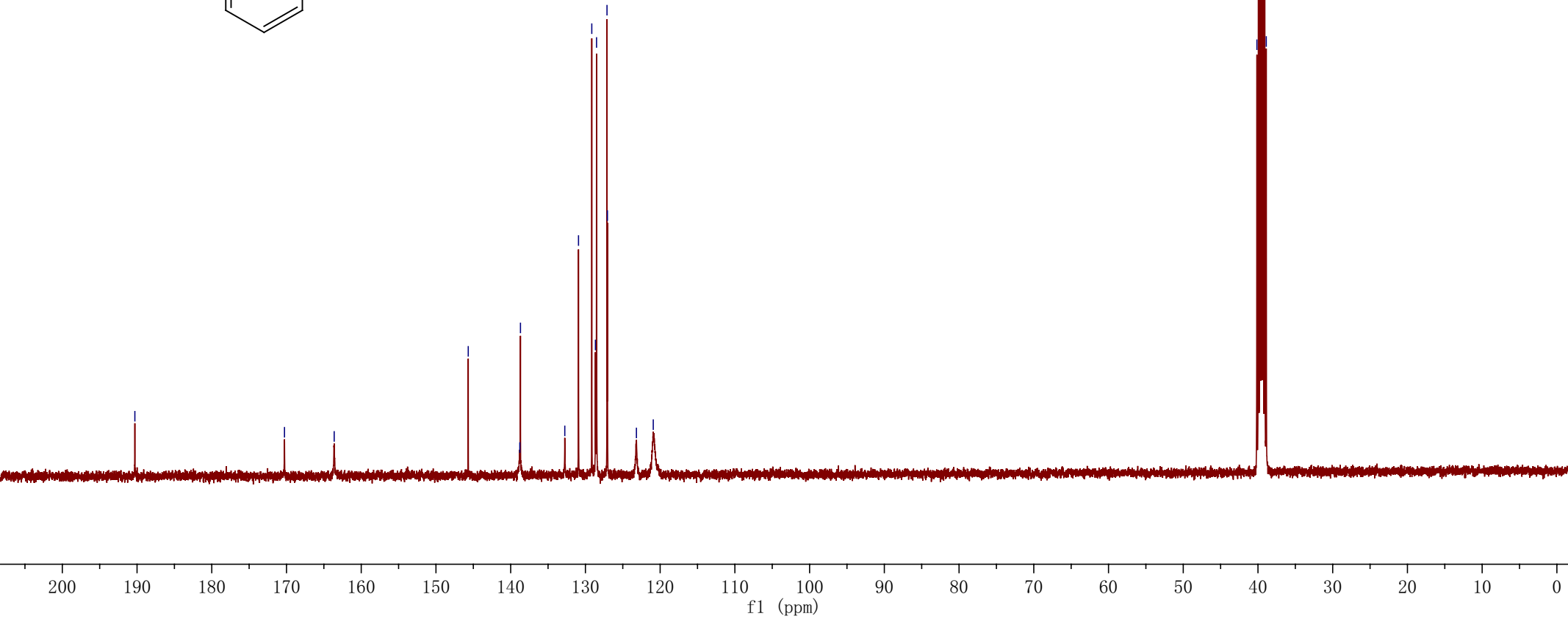
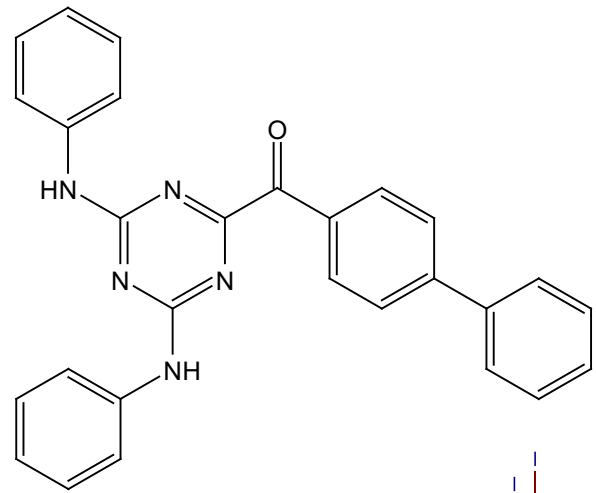
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wlf0702

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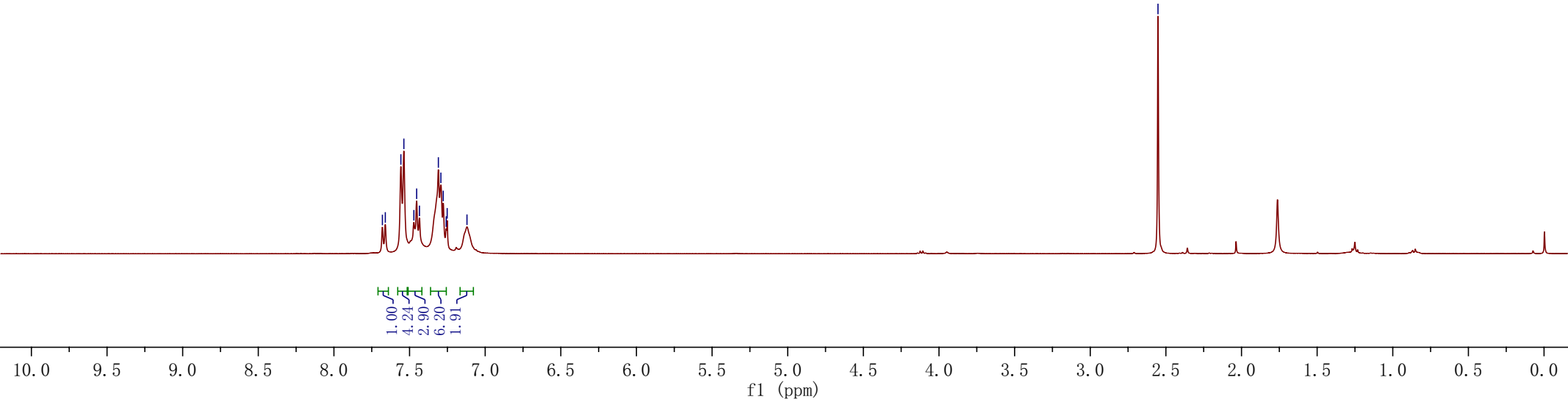
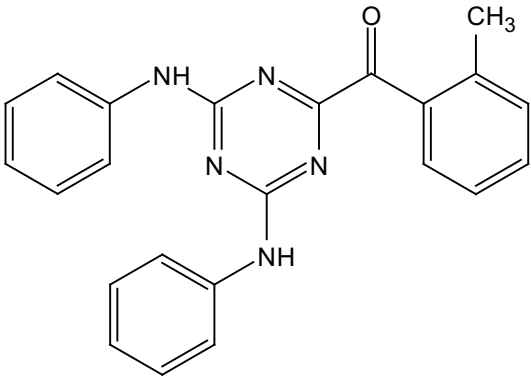
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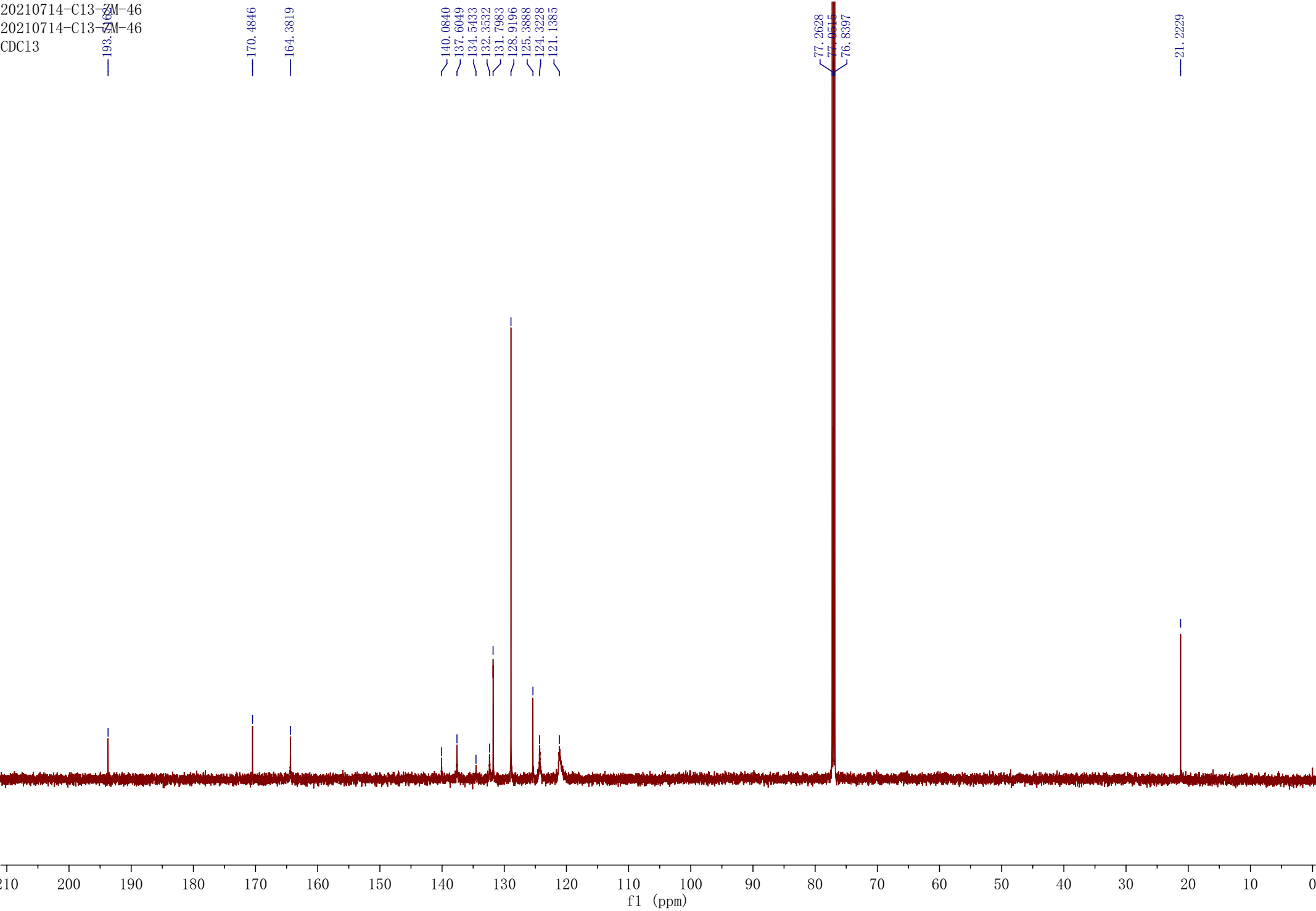
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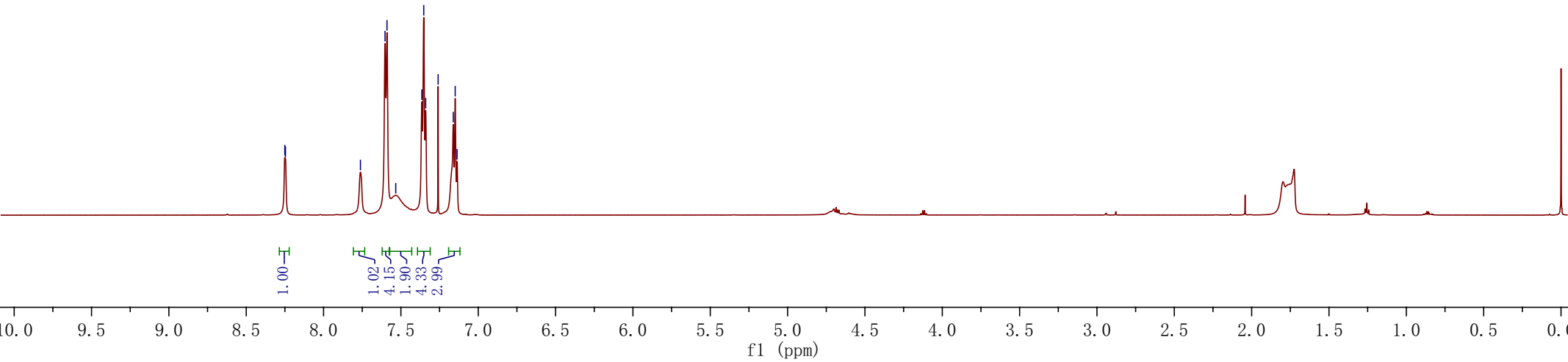
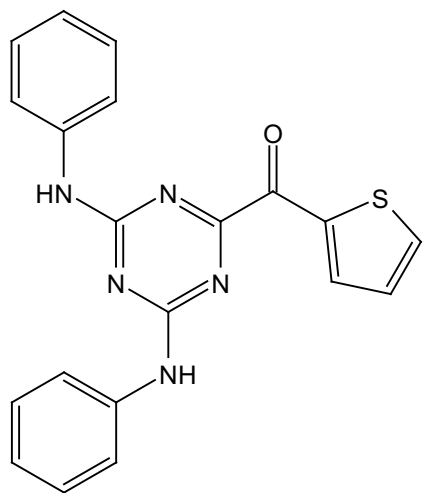


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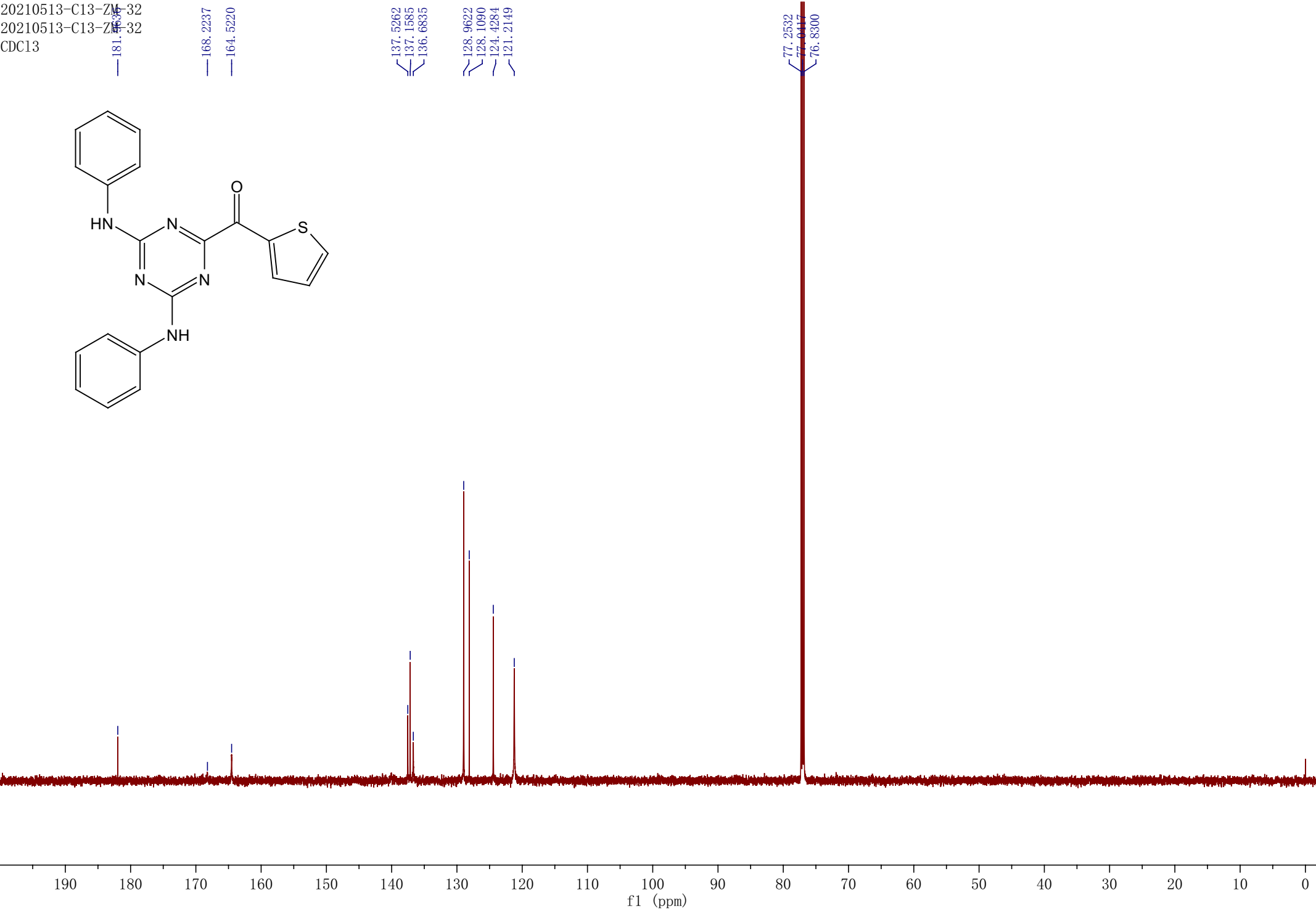
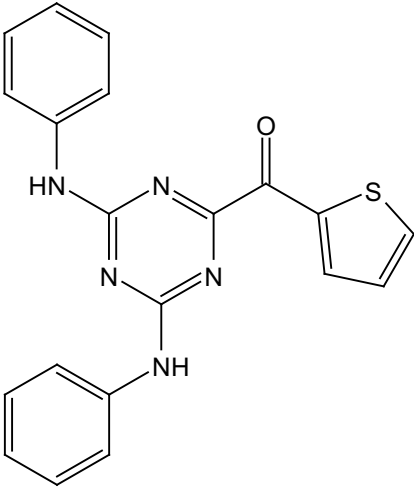


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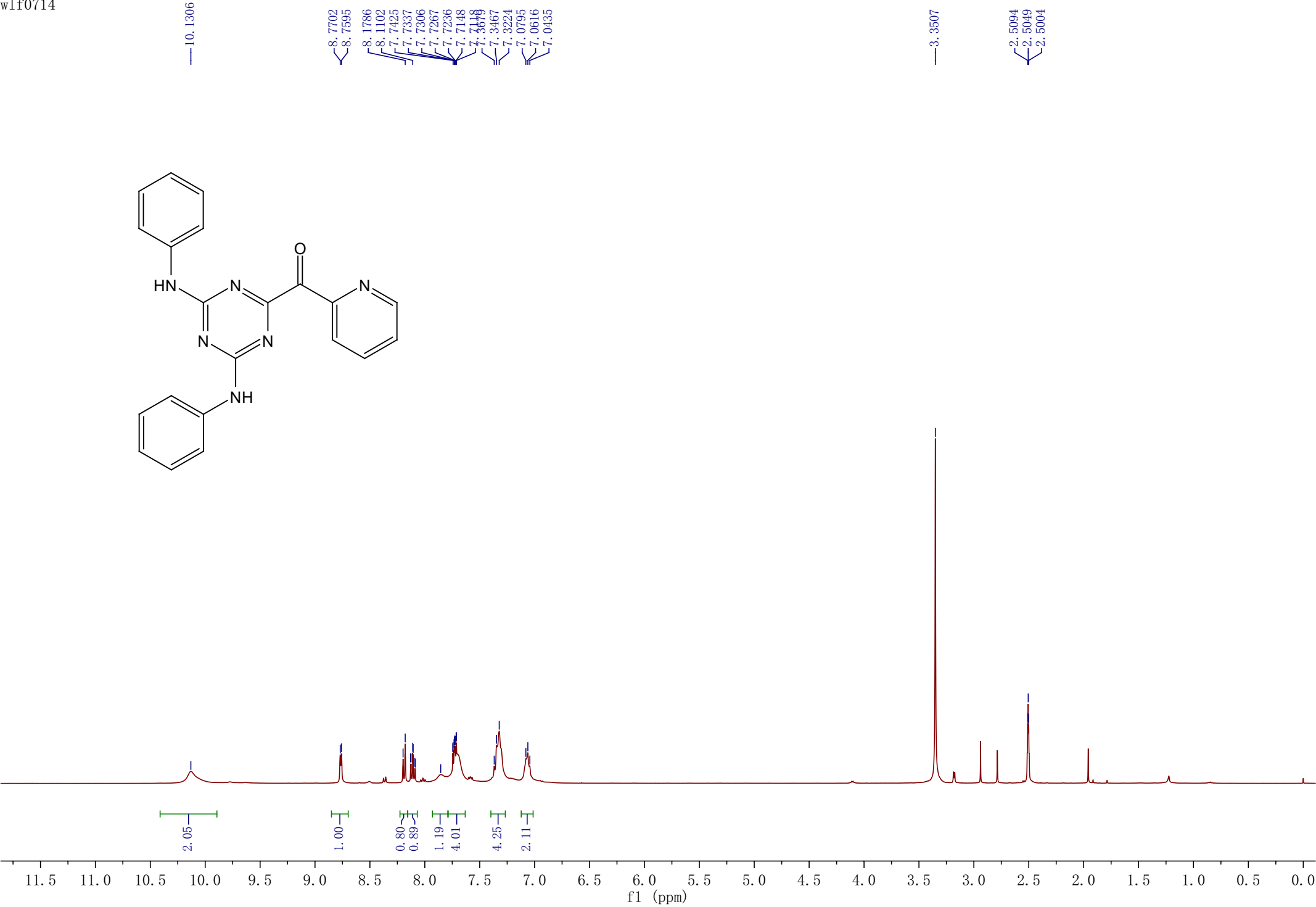
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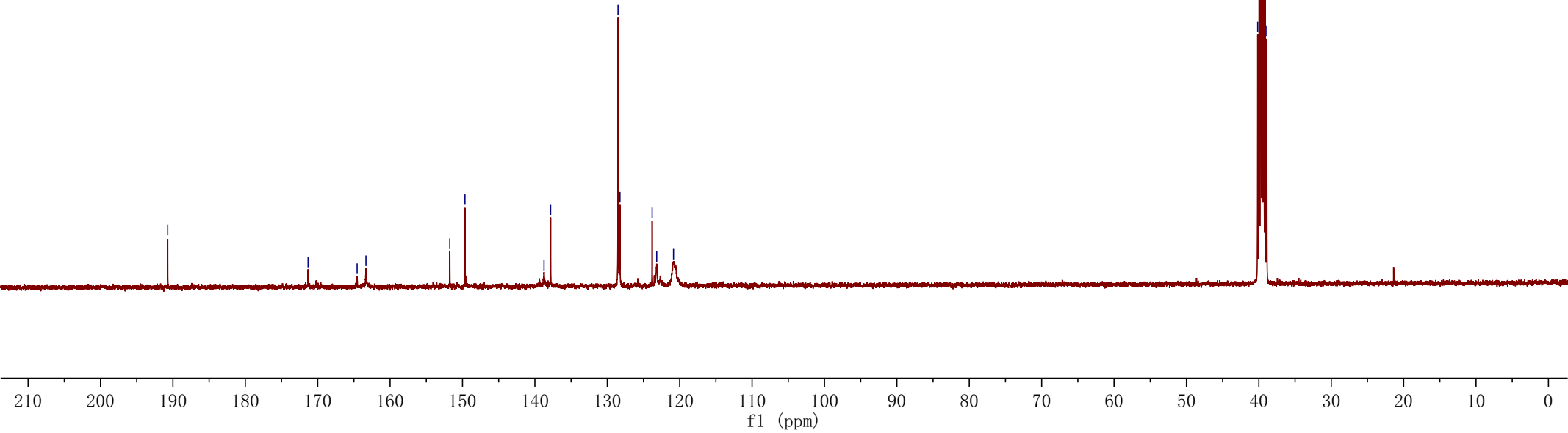
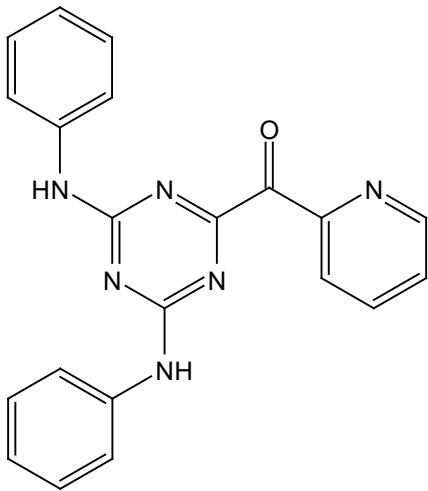


wlf0714



wlf0714

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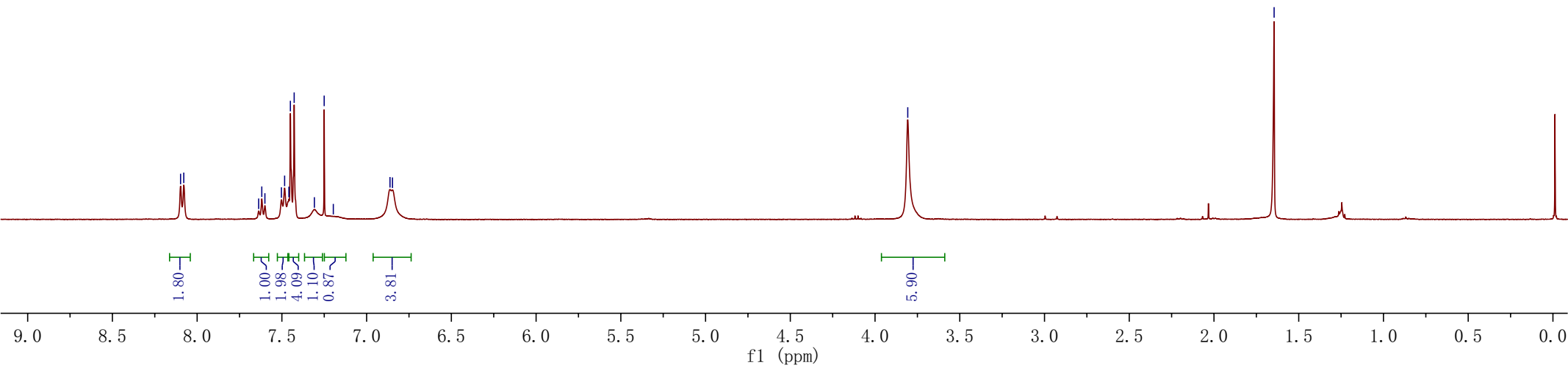
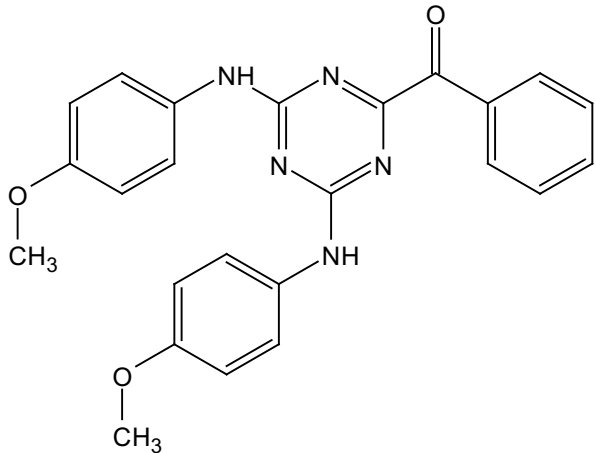


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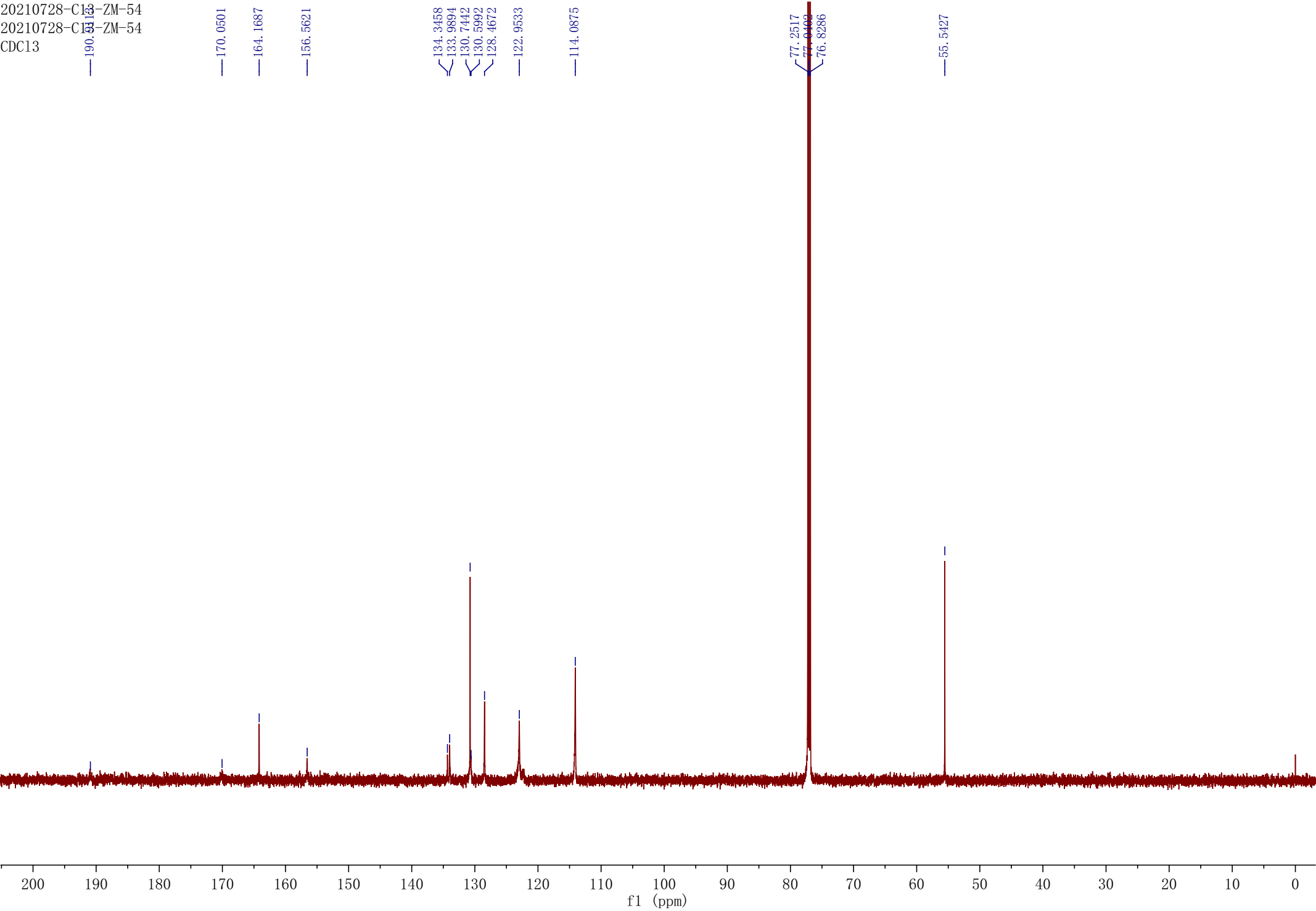
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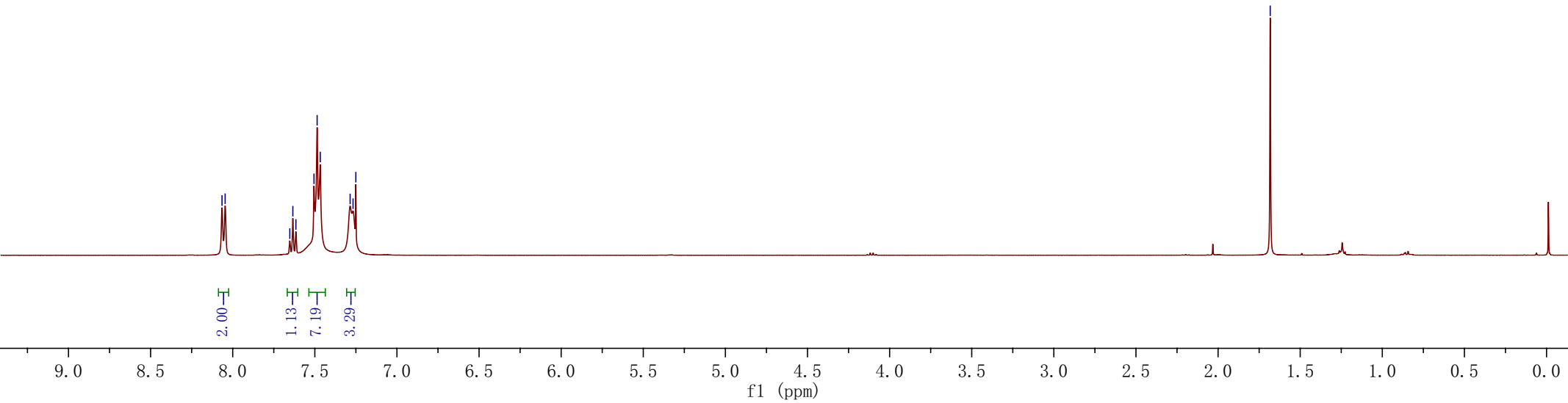
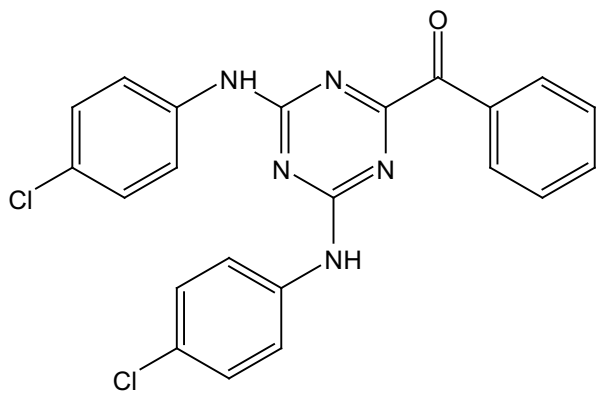
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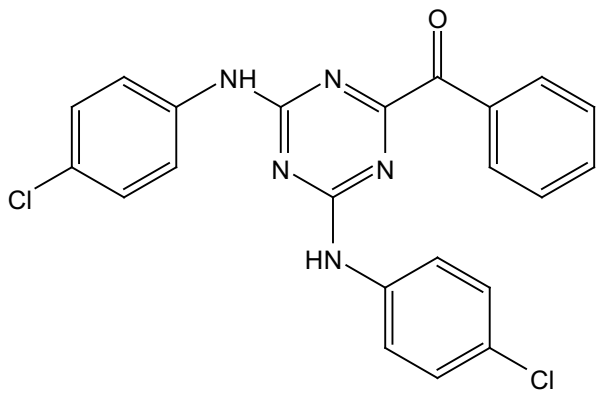
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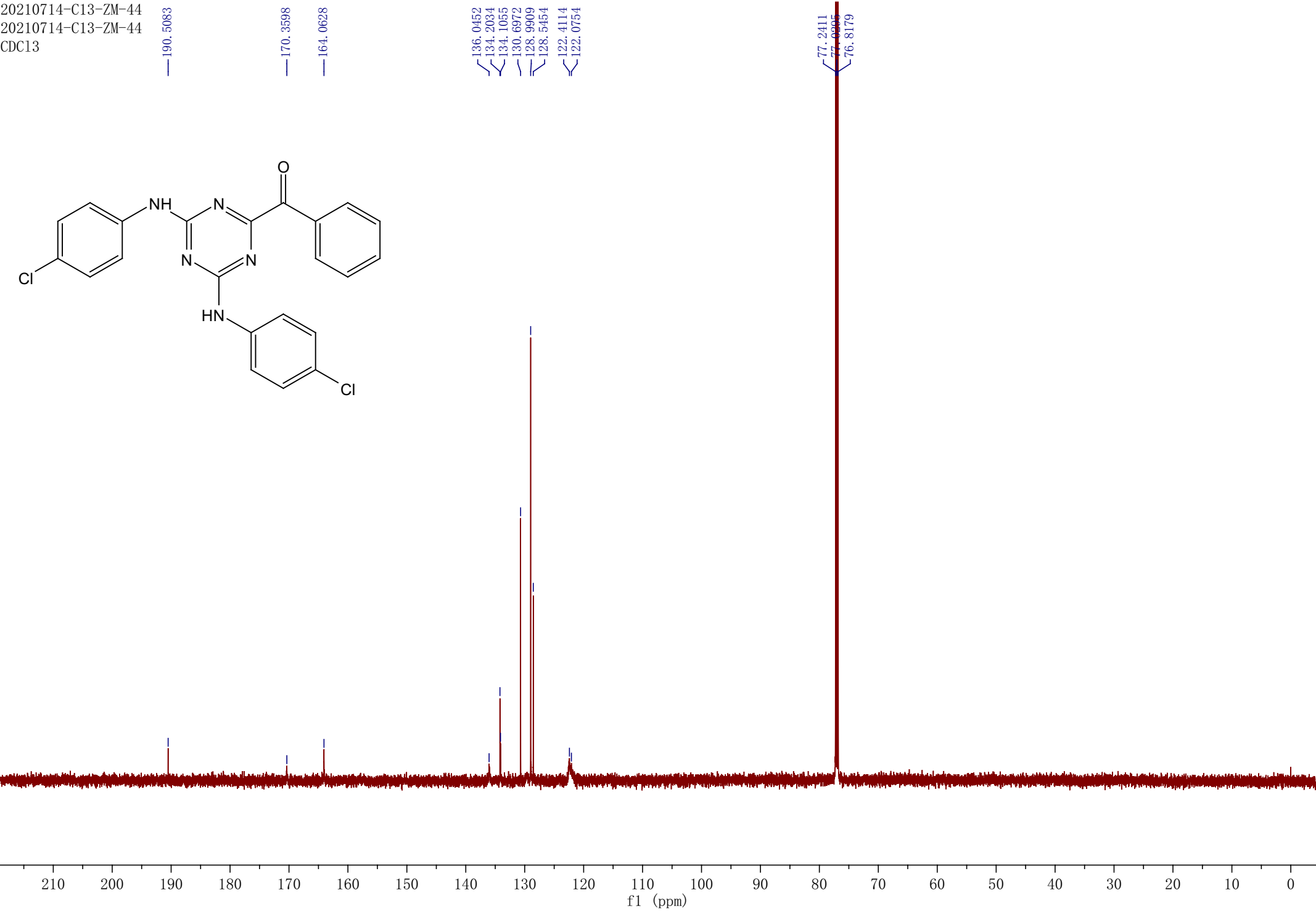
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CDC13



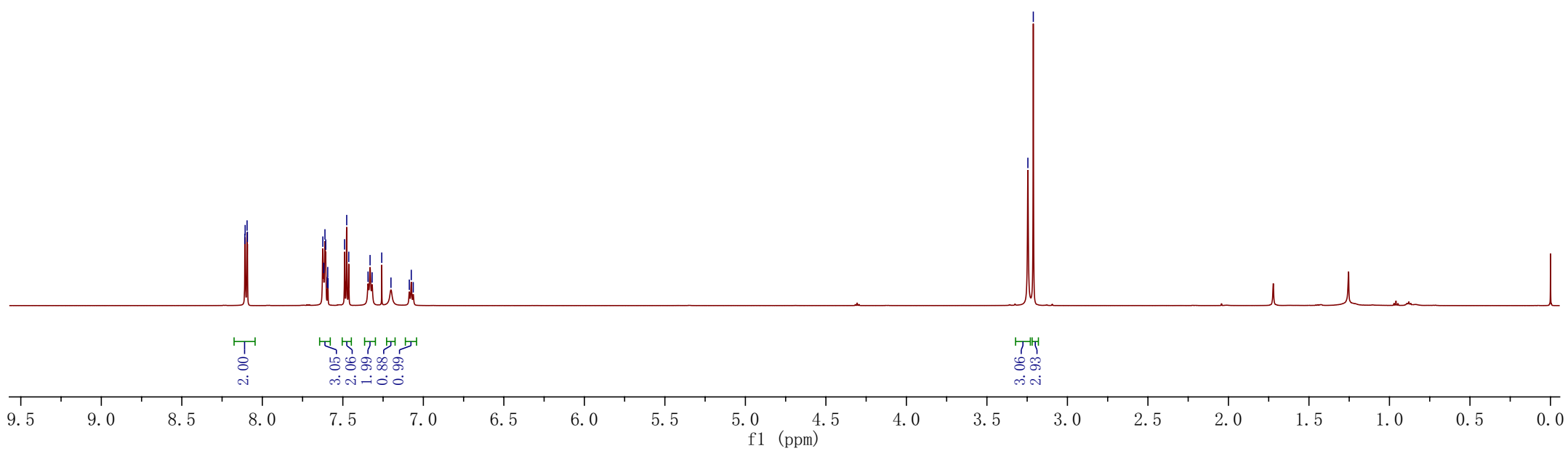
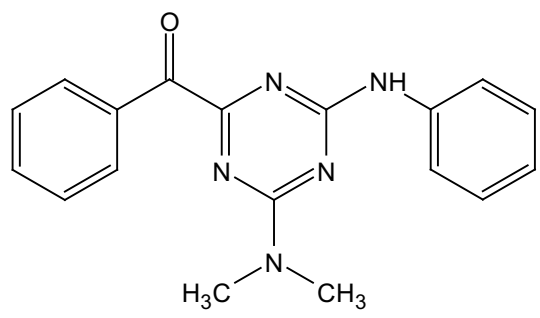
190.5083
170.3598
164.0628
136.0452
134.2034
134.1055
130.6972
128.9909
128.5454
122.4114
122.0754
77.2411
77.0995
76.8179



20191210-H1-WHF-ZM-P2
20191210-H1-WHF-ZM-P2
CDC13

8.1084
8.1067
8.0948
8.0926
7.6242
7.6187
7.6111
7.6063
7.5959
7.5939
7.5919
7.4893
7.4760
7.4633
7.3436
7.3309
7.3181
7.2584
7.2012
7.0872
7.0750
7.0628

3.2456
3.2118



20191216-C13-WHF-ZM-P2
20191216-C13-WHF-ZM-P2
CDC13

191.2441

169.6574

165.0178

163.5683

138.4738

134.5145

133.7765

130.7207

128.8850

128.3509

123.3037

119.8946

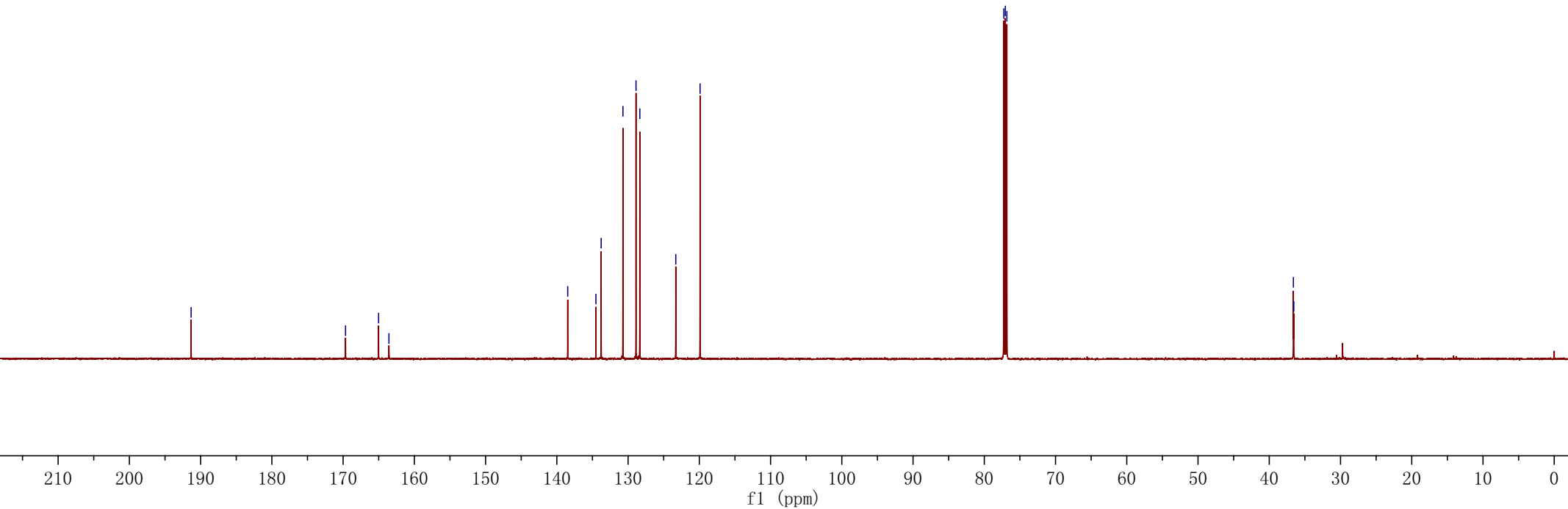
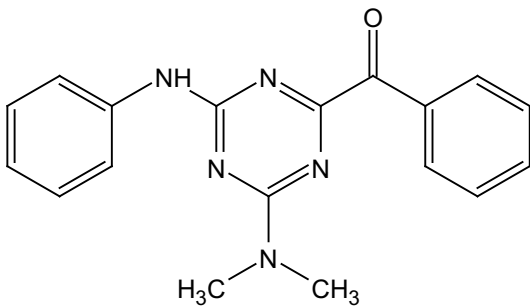
77.2548

77.0432

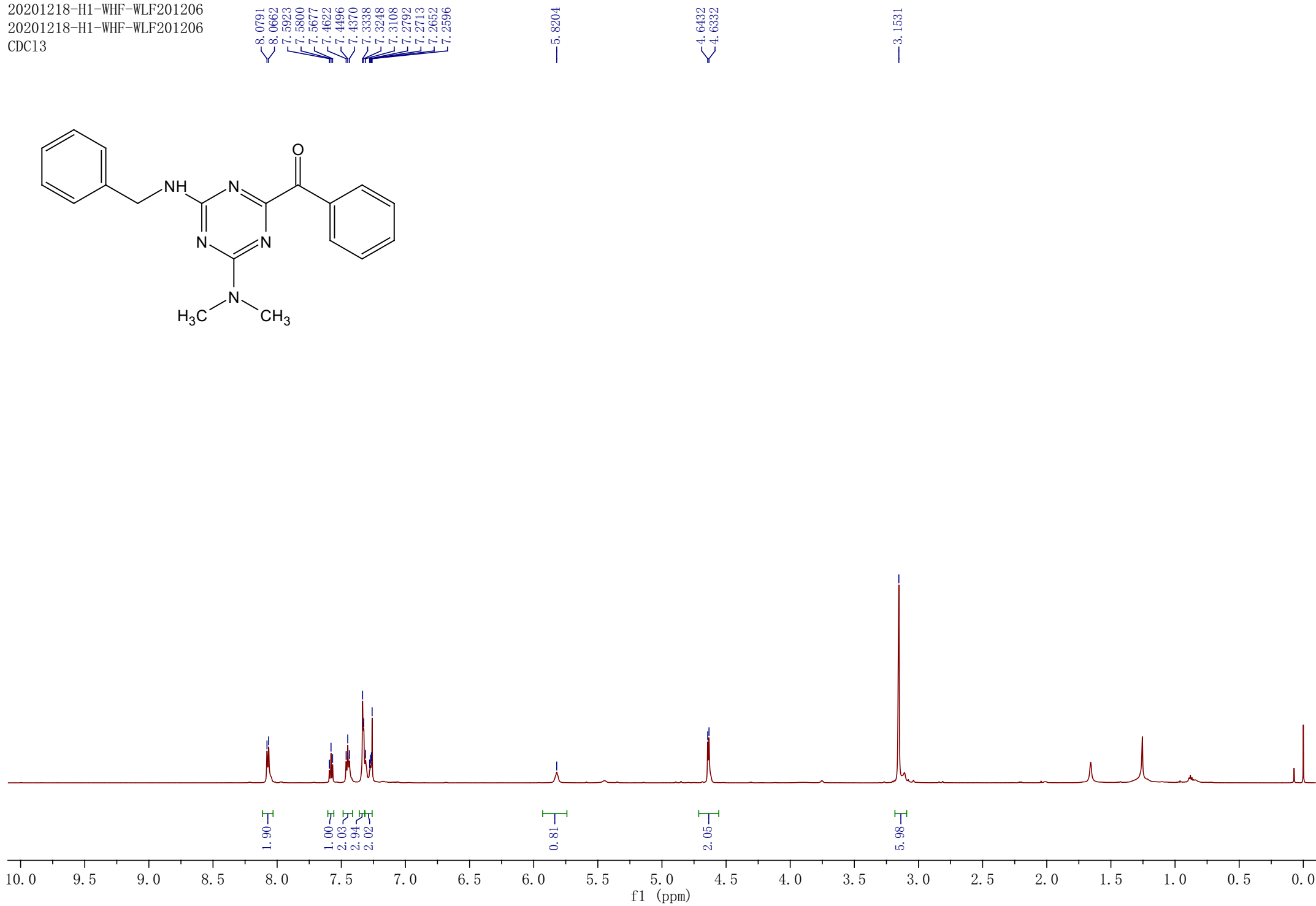
76.8315

36.6151

36.5597



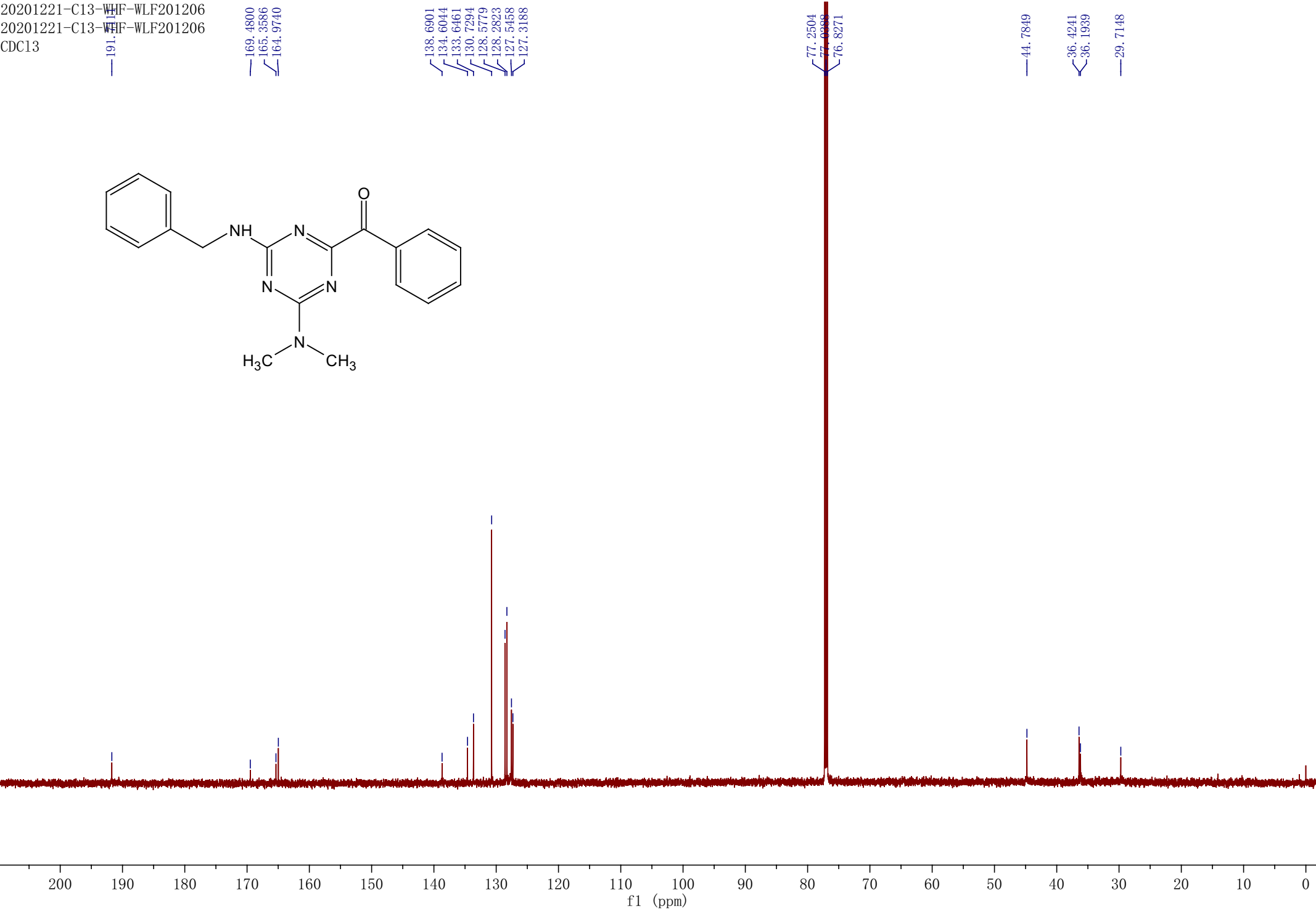
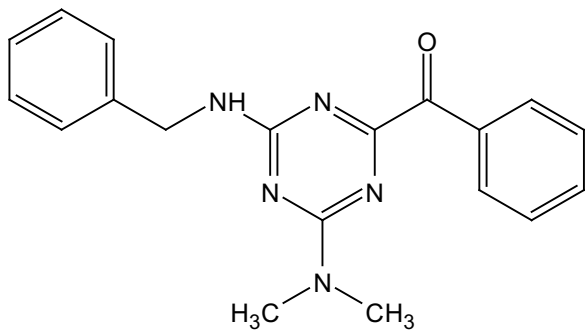
20201218-H1-WHF-WLF201206
20201218-H1-WHF-WLF201206
CDC13



20201221-C13-WF-WLF201206
20201221-C13-WF-WLF201206
CDC13

191.111
169.4800
165.3586
164.9740
138.6901
134.6044
133.6461
130.7294
128.5779
128.2823
127.5458
127.3188

77.2504
77.0289
76.8271
44.7849
36.4241
36.1939
29.7148

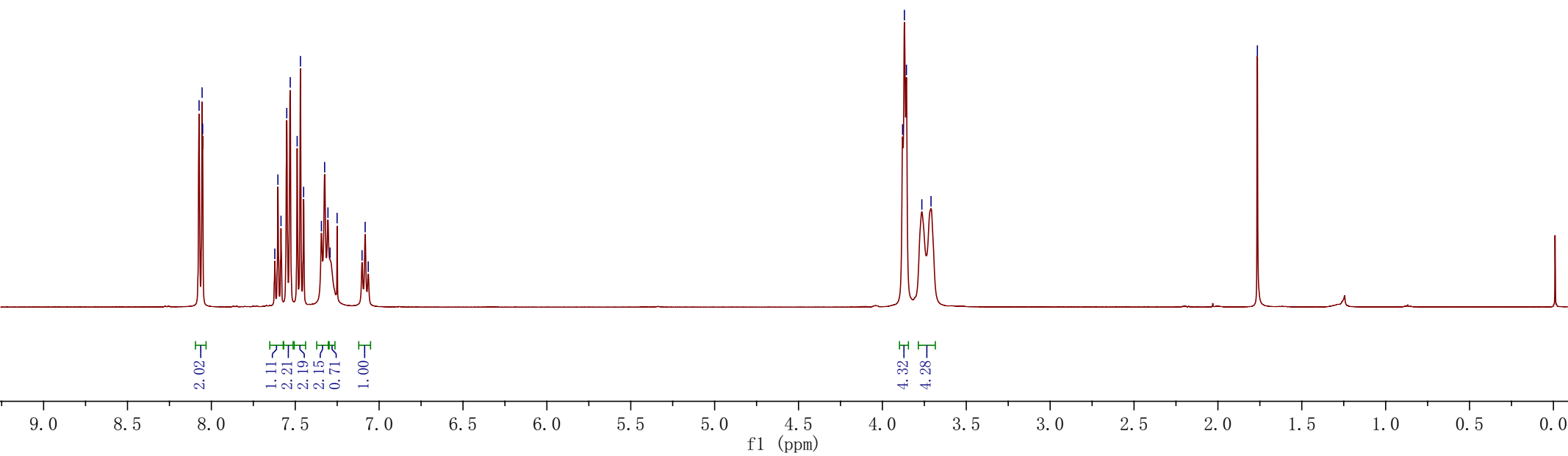
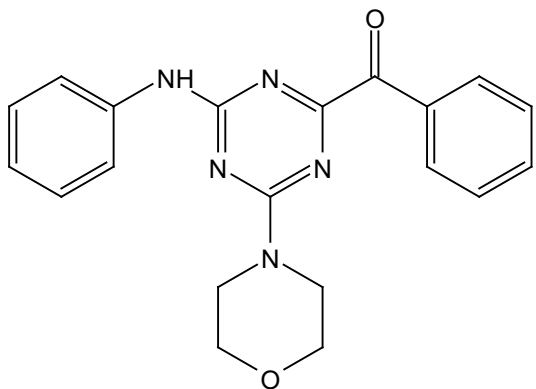


PROTON_01
ZM-48

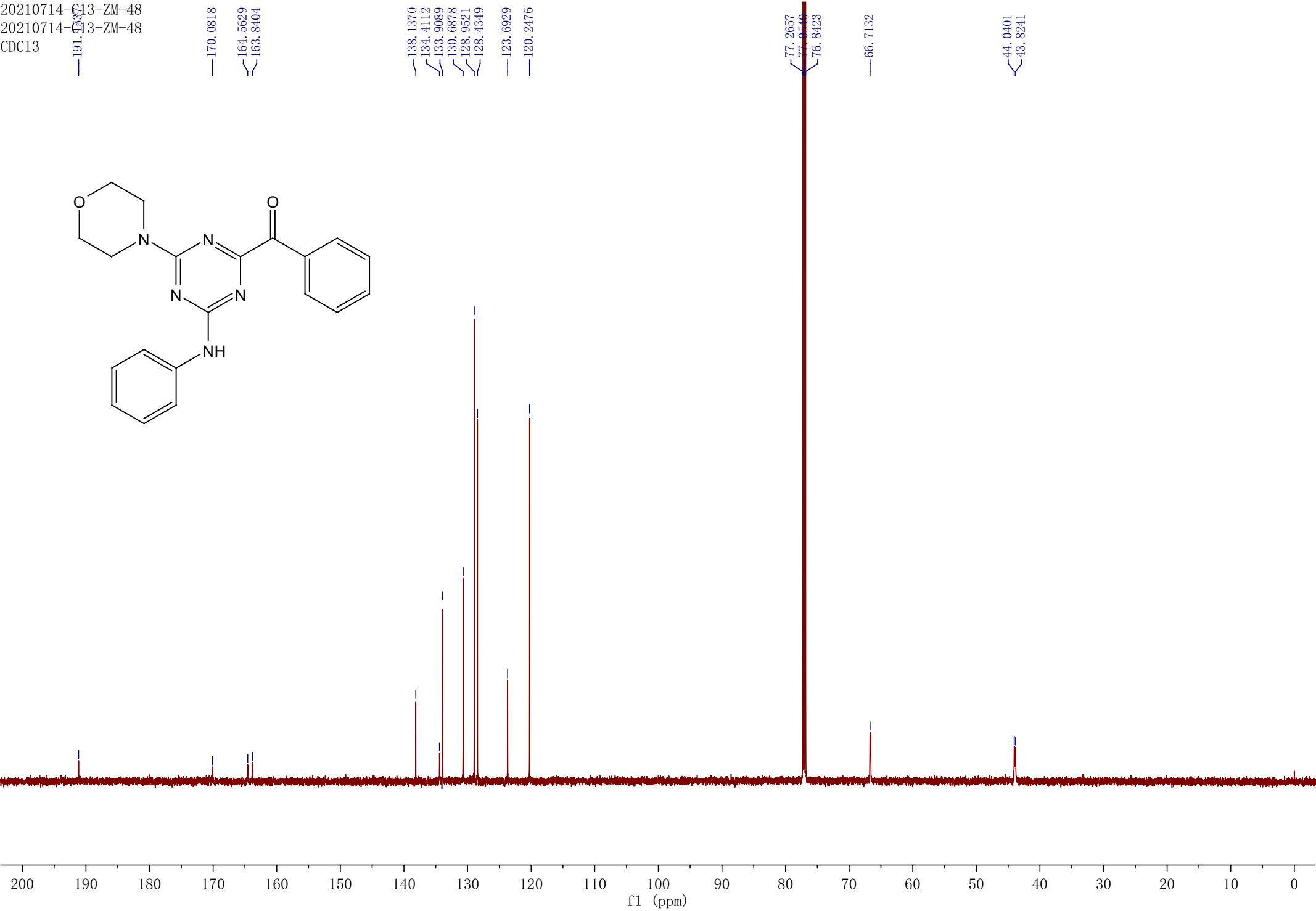
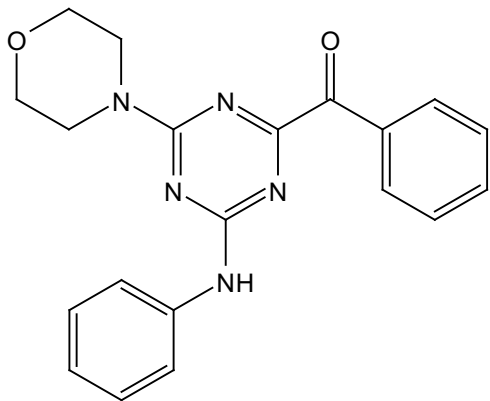
8.0732
8.0552
8.0521
7.6220
7.6033
7.5849
7.5505
7.5298
7.4886
7.4689
7.4500
7.3440
7.3248
7.3050
7.2925
7.2504
7.1017
7.0832
7.0649

3.8796
3.8687
3.8568
3.7648
3.7101

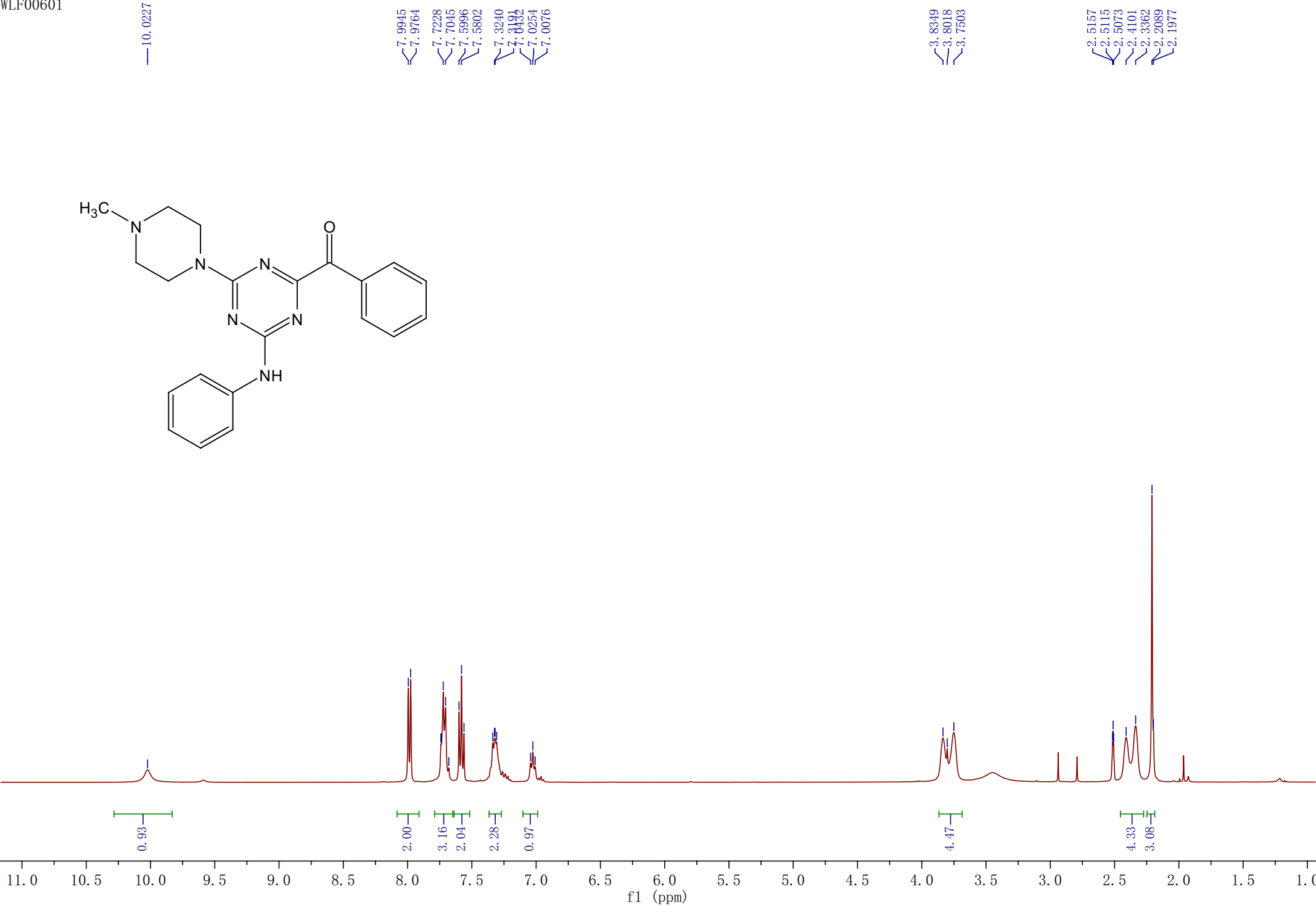
1.7647



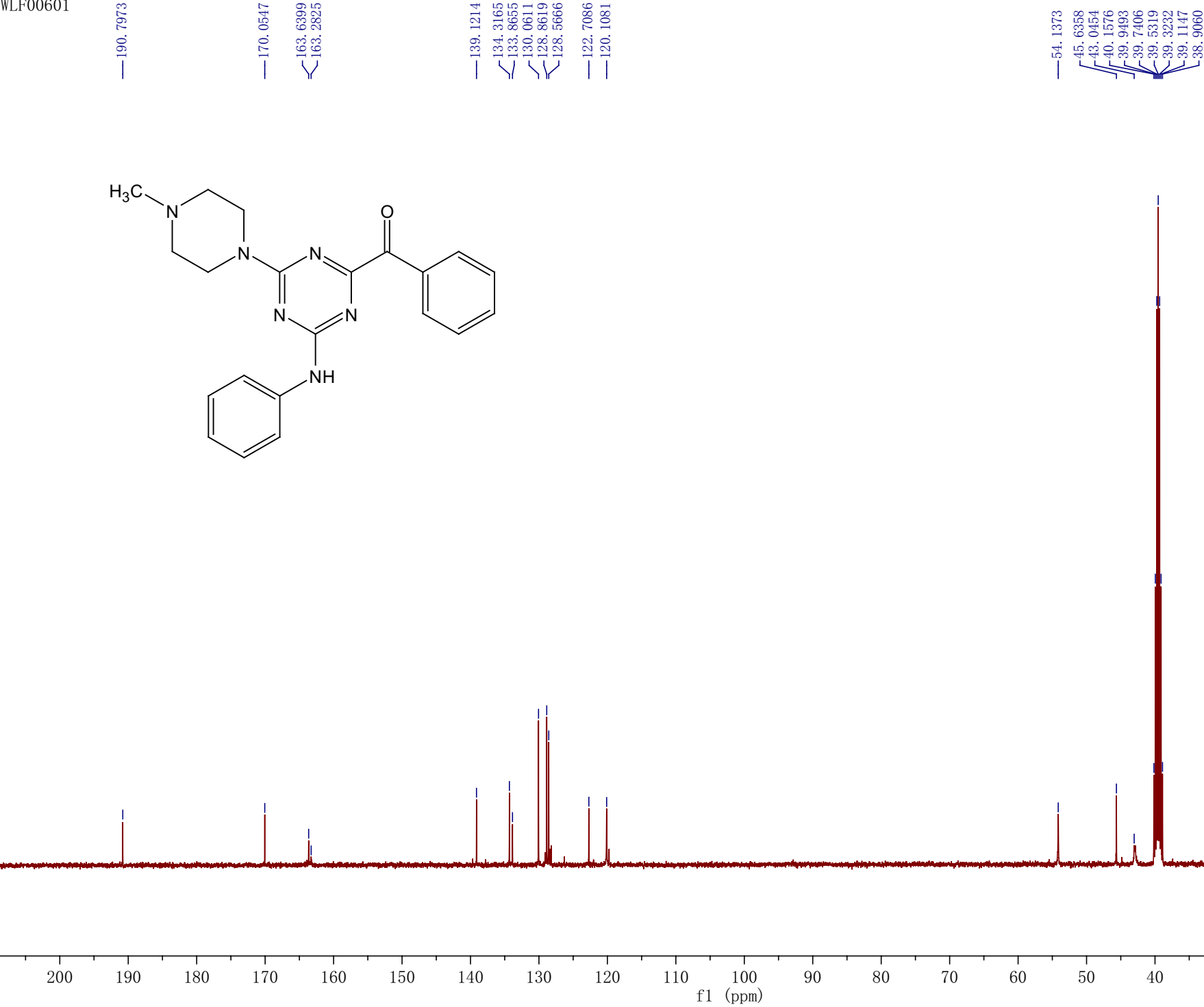
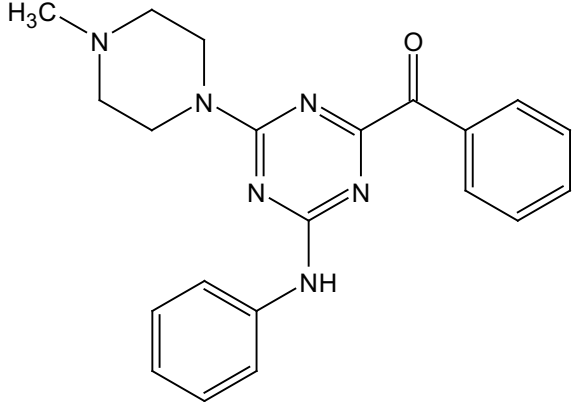
20210714-G13-ZM-48
20210714-G13-ZM-48
CDC13



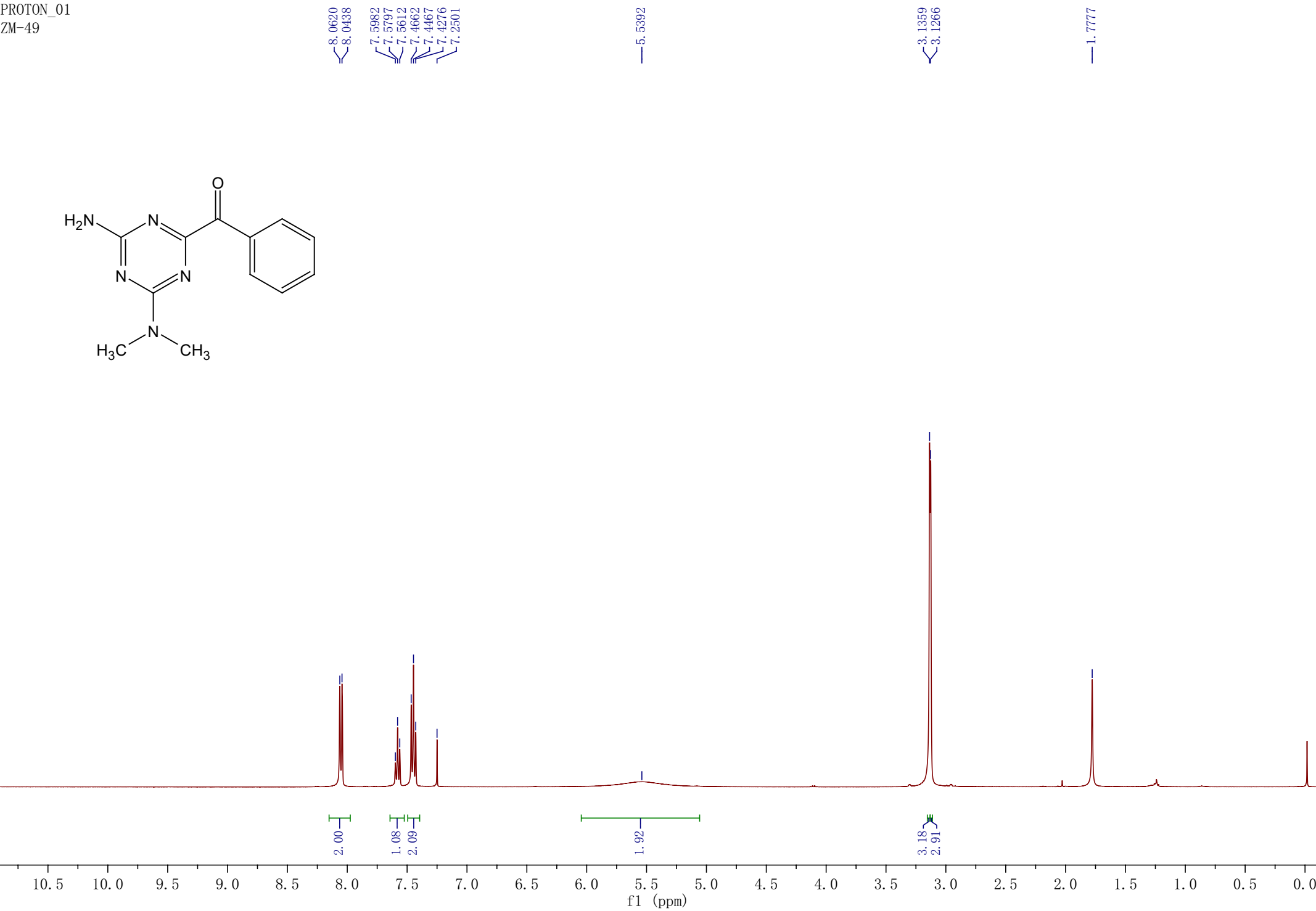
WLF00601



WLF00601



PROTON_01
ZM-49



20210714-C13-M-49
20210714-C13-M-49
CDC13

191.4823

169.7248

166.6679

165.1391

134.5685

133.7180

130.6951

128.3190

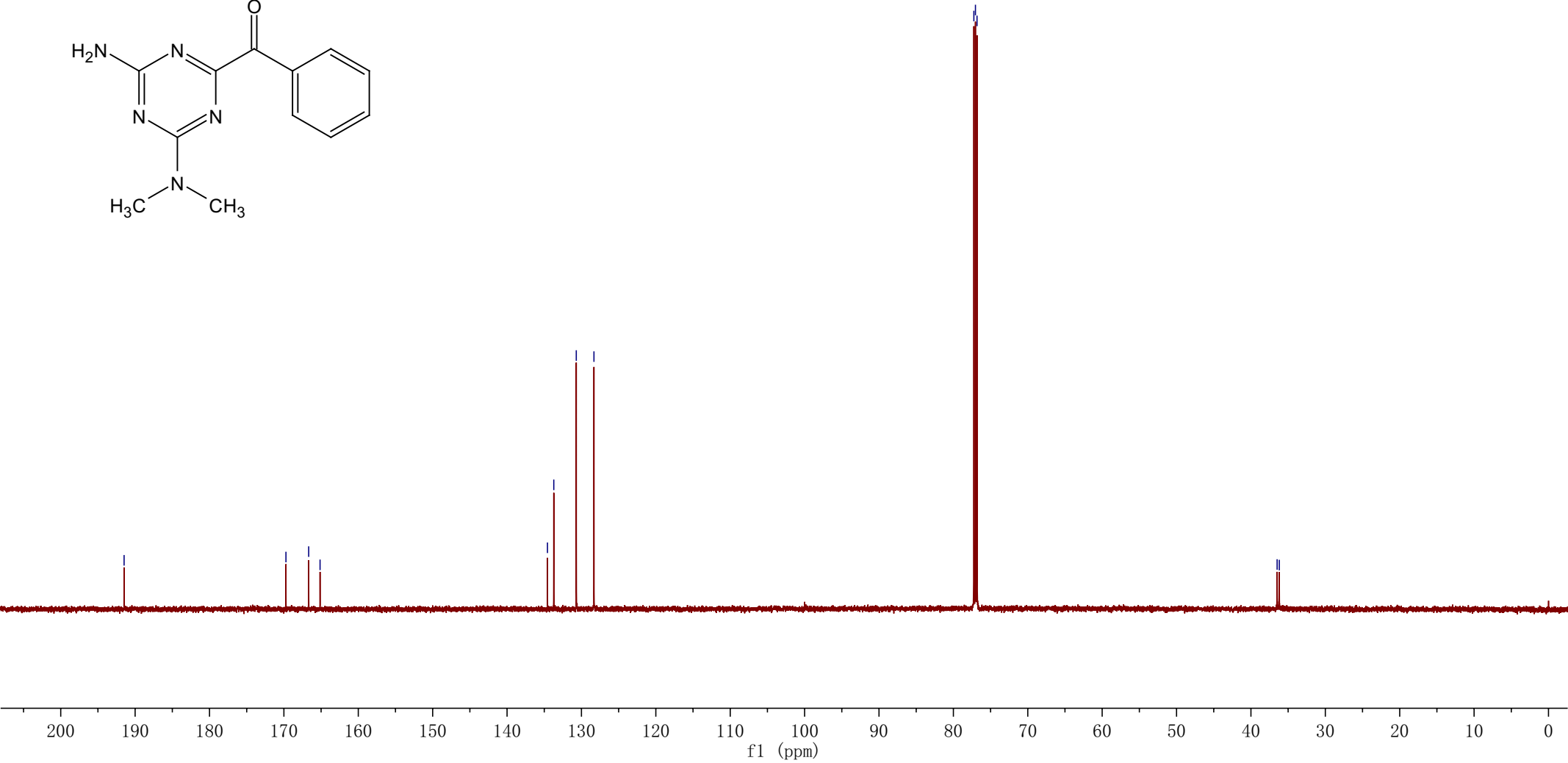
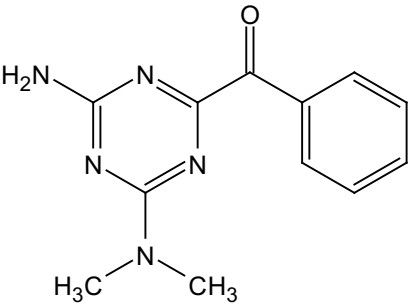
77.2461

77.0345

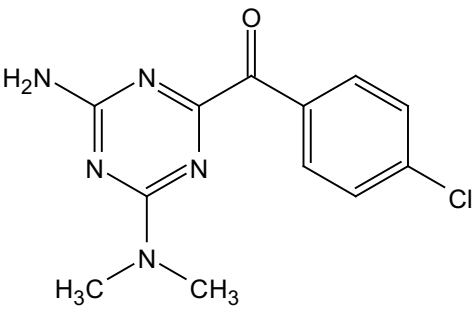
76.8228

36.4803

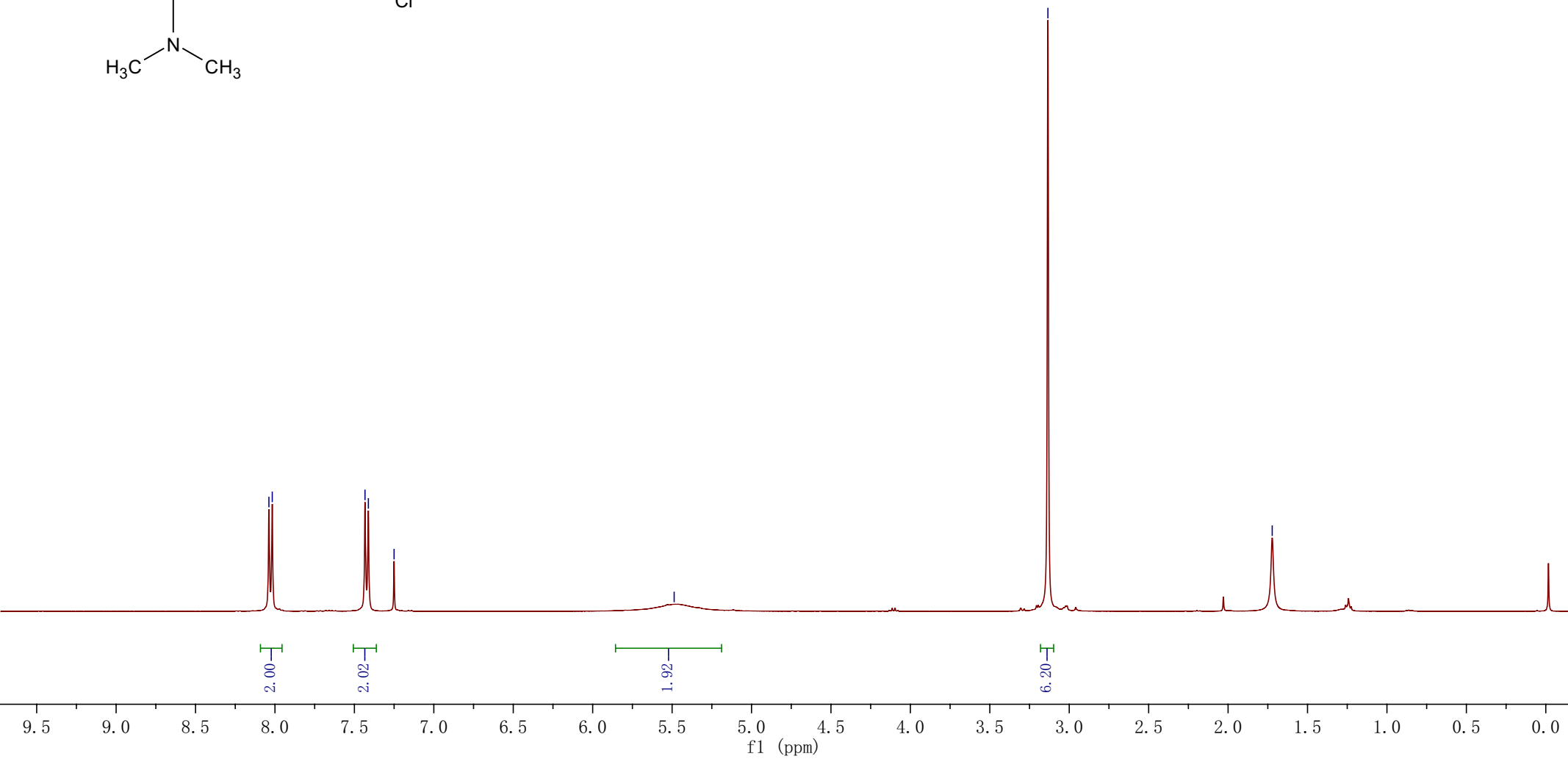
36.1896



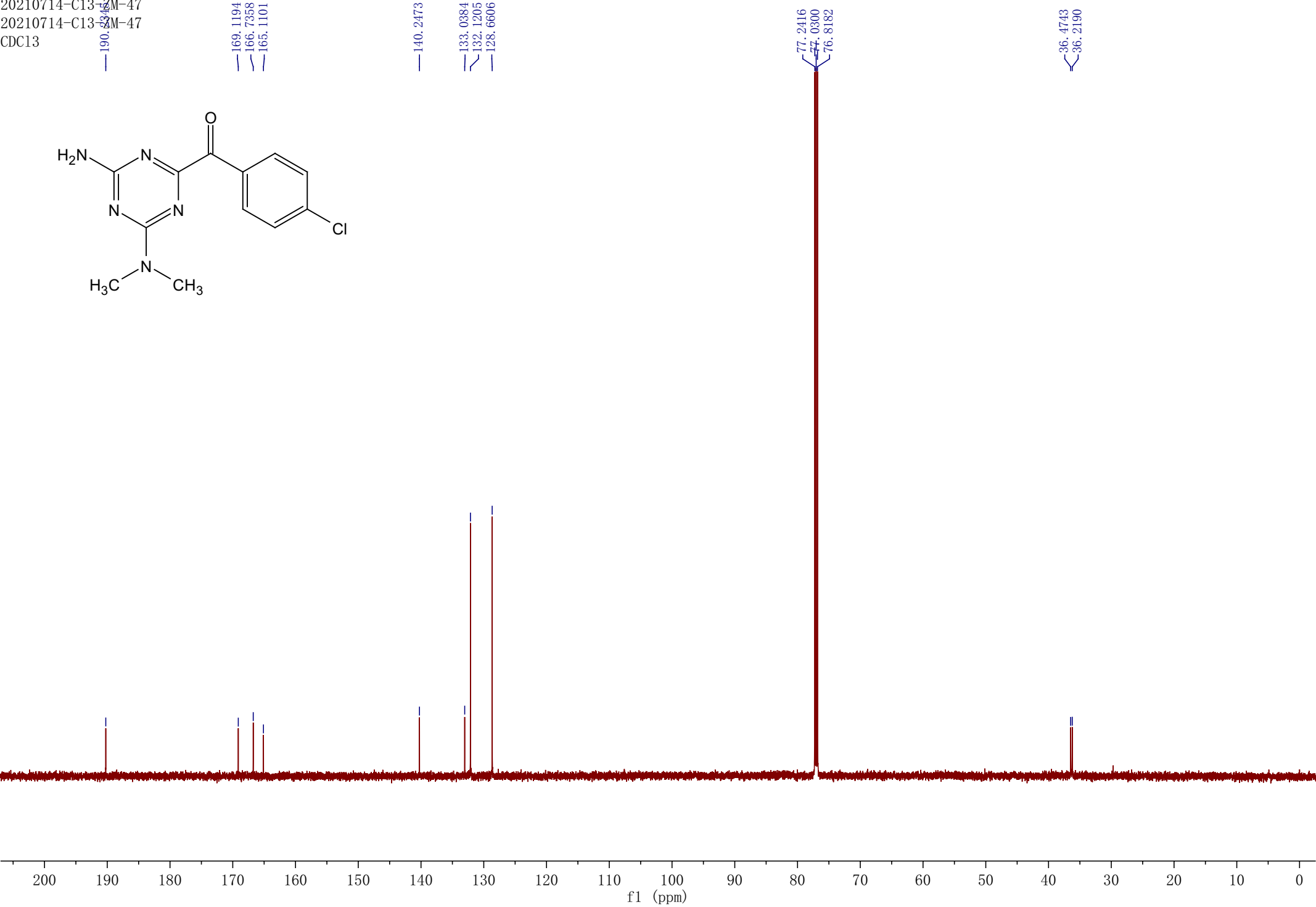
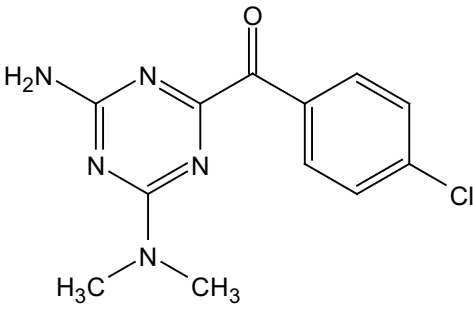
PROTON_01
zm-47



8.0382
8.0170
7.4332
7.4120
7.2502
5.4870
3.1343
1.7222



20210714-C13-ZM-47
20210714-C13-ZM-47
CDC13



20210513-H1-ZM-33
20210513-H1-ZM-33
CDC13

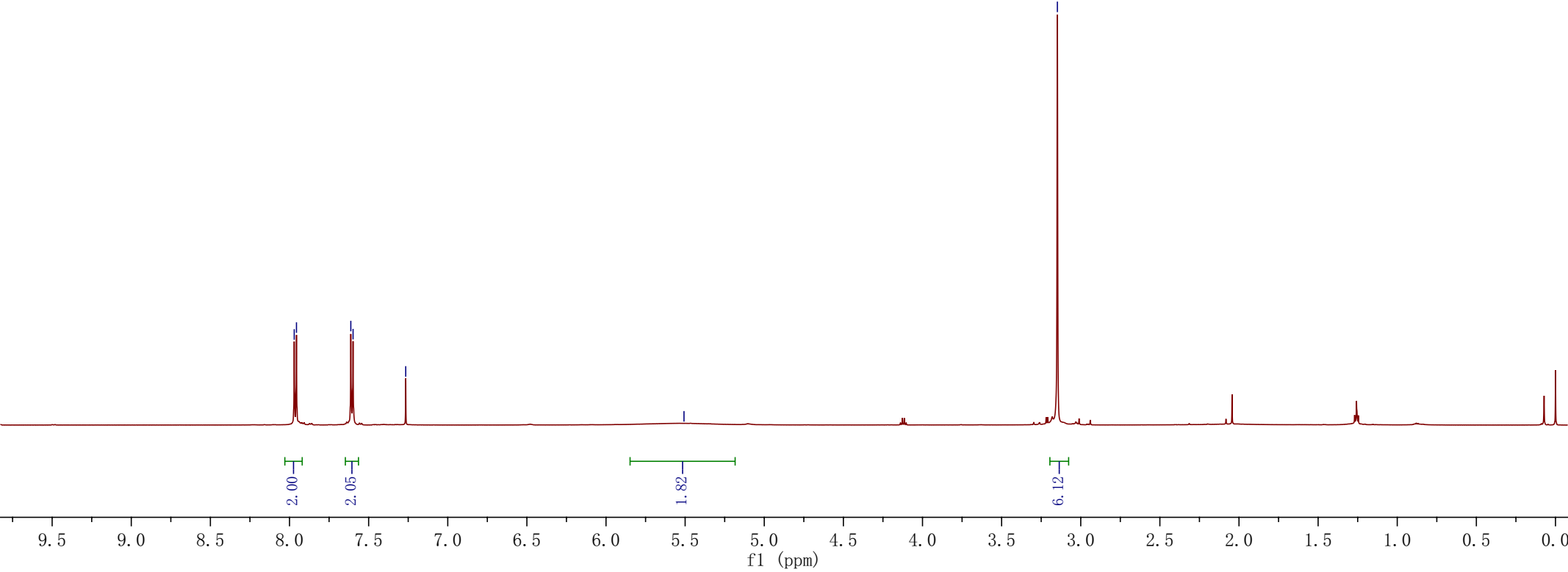
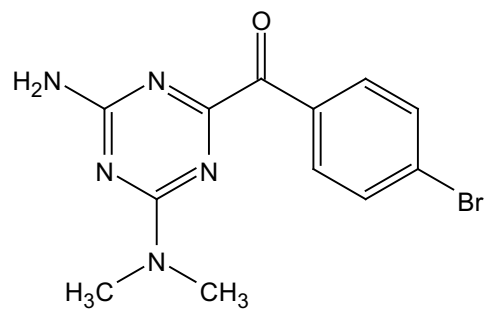
7.9703
7.9560

7.6126
7.5984

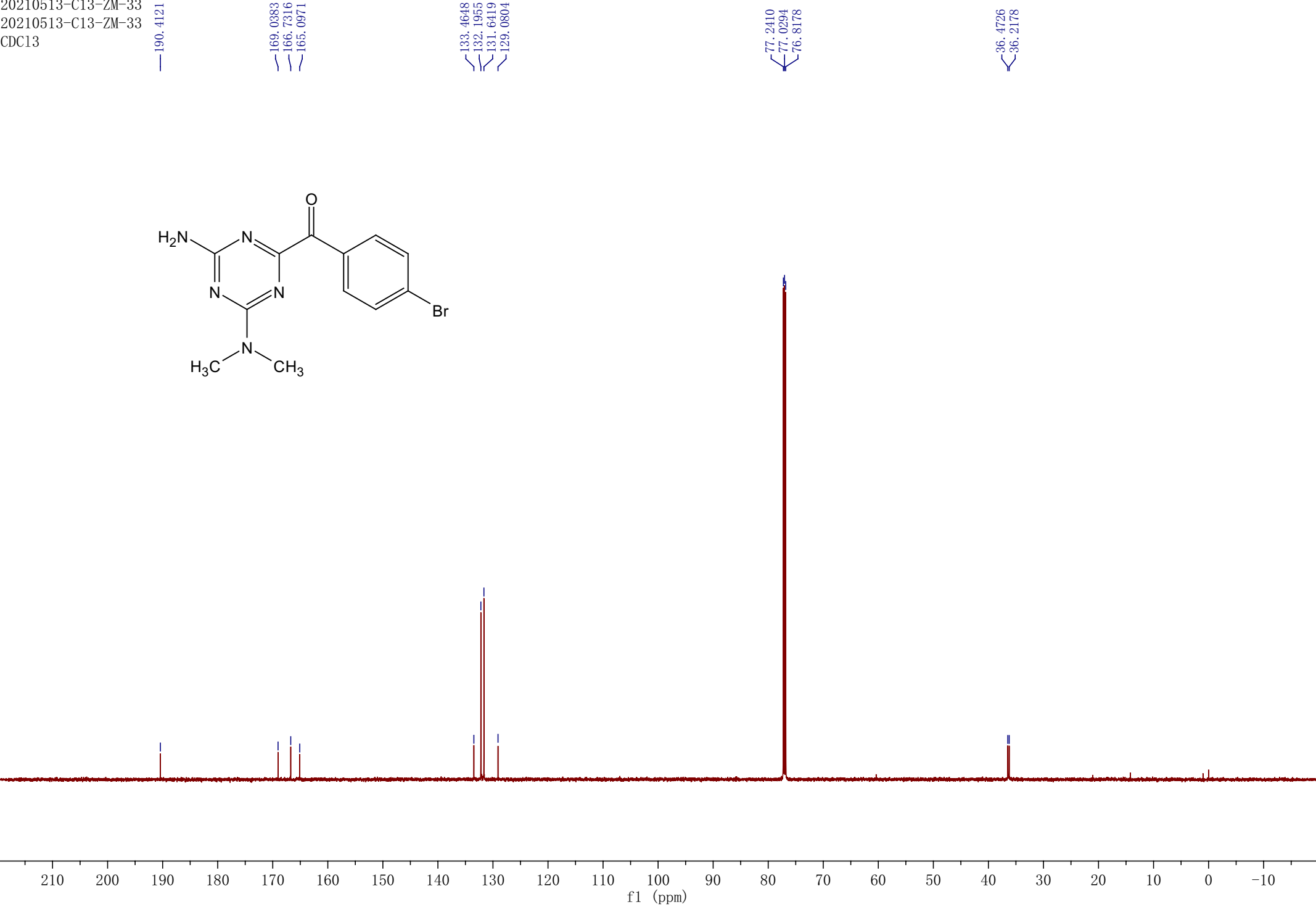
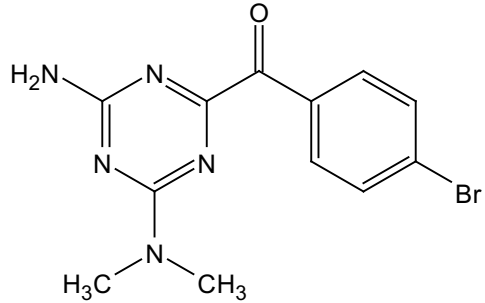
7.2656

5.5072

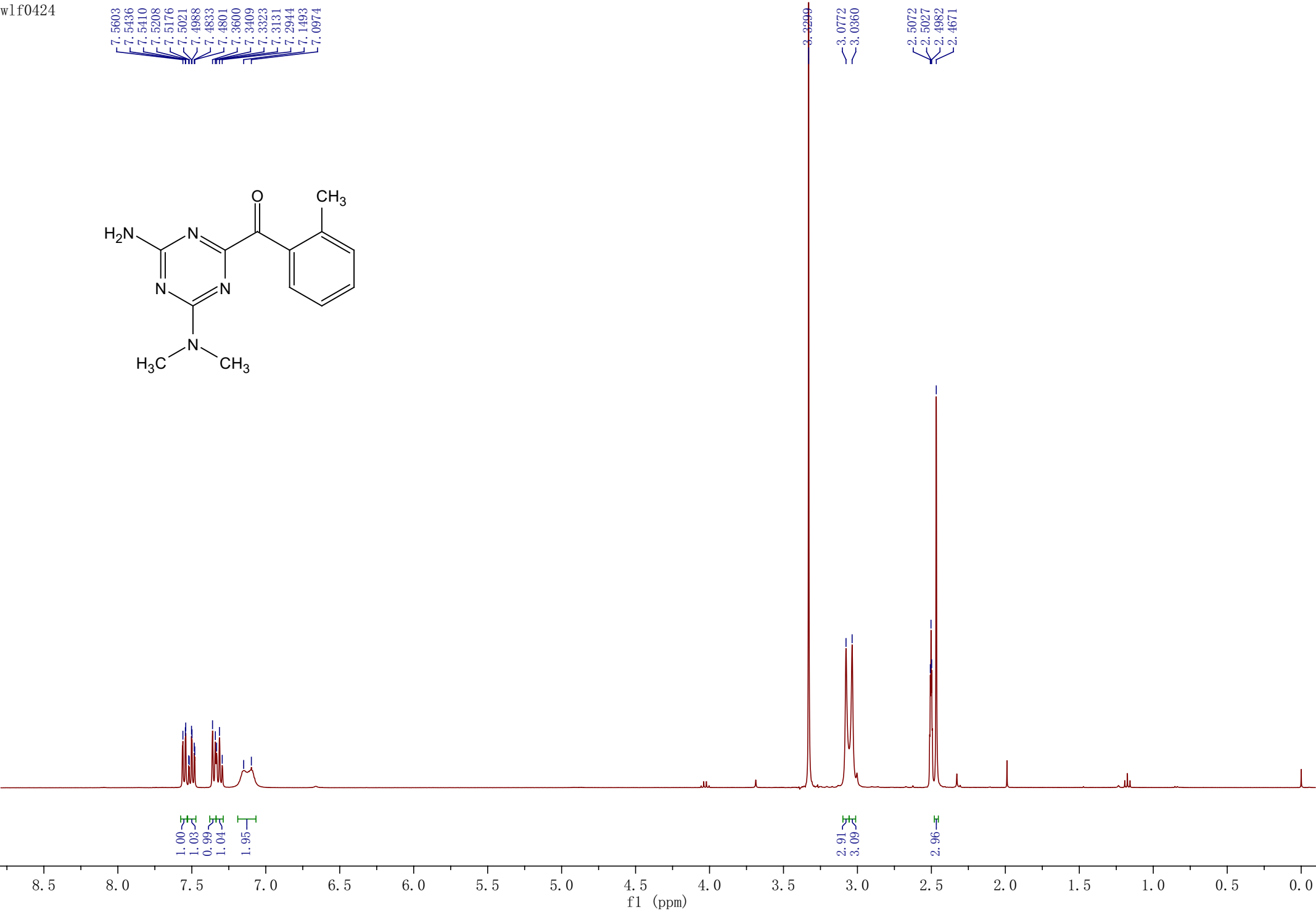
3.1477



20210513-C13-ZM-33
20210513-C13-ZM-33
CDC13



wlf0424



wlf0424

