

Visible-Light Induced Decarboxylative Alkylation of Quinoxalin-2(1*H*)-ones at C3-position

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730000, P. R. China

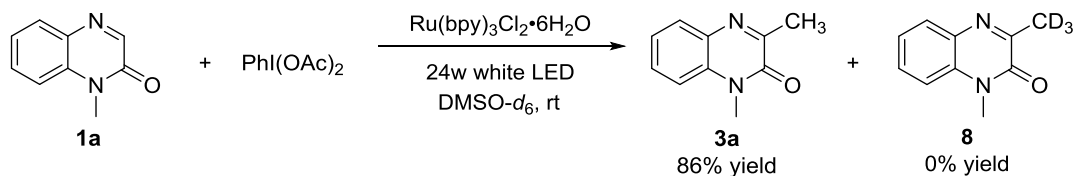
*E-mail: huyl@nwnu.edu.cn.

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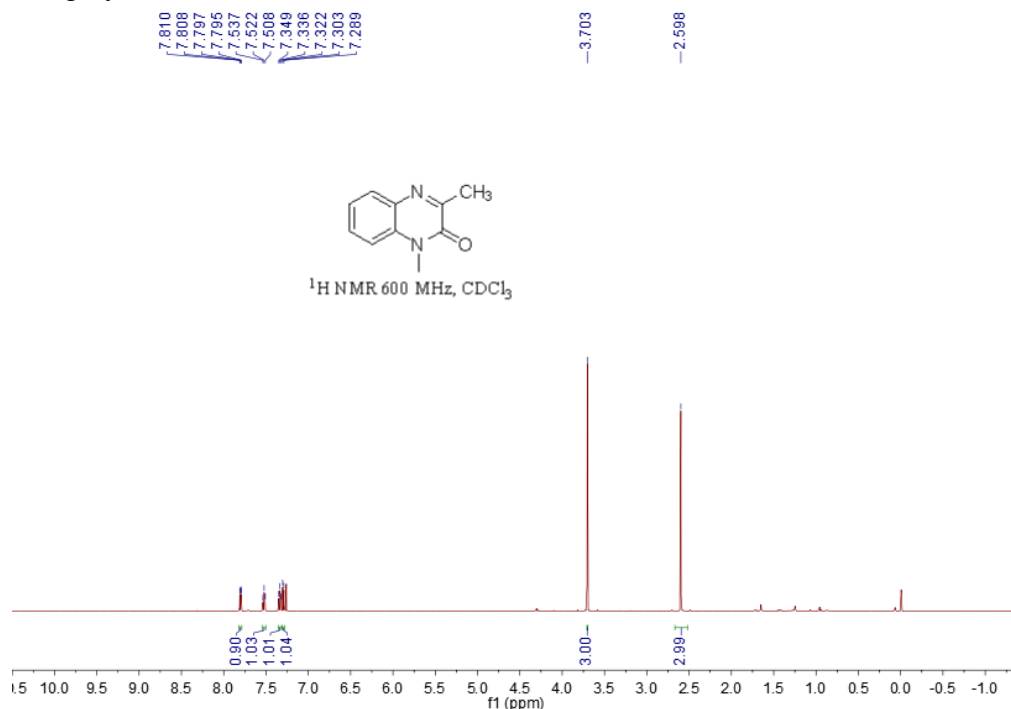
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1. Control experiments.

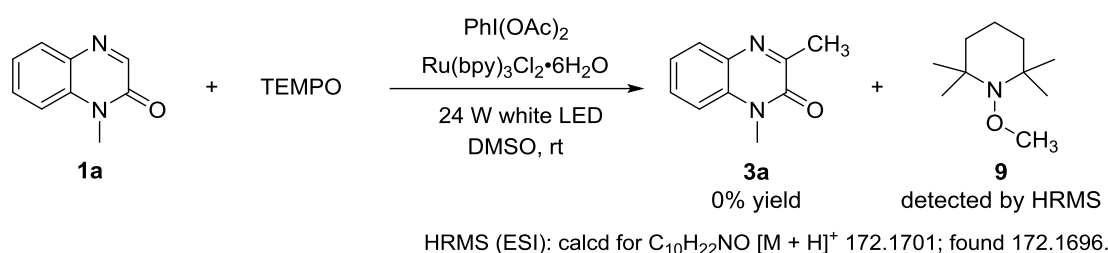
1.1. Reaction of 1a with $\text{PhI}(\text{OAc})_2$, $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ in $\text{DMSO-}d_6$ under visible-light.



In a dried Schlenk tube, 1-methylquinoxalin-2(1*H*)-one (0.2 mmol), $\text{PhI}(\text{OAc})_2$ (2.5 equiv) and $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (2.0 mg, 0.01 equiv) were mixed in $\text{DMSO-}d_6$ (2.0 mL) at room temperature. The tube was placed at a distance (app. 5 cm) from 24 W white LED, and the solution was stirred under visible-light irradiation. After the reaction was completed (monitored by TLC), the reaction mixture was quenched by saturated aqueous Na_2CO_3 solution (5 mL), and then the mixture was extracted with ethyl acetate (3×5 mL). The combined organic phase was dried over anhydrous MgSO_4 and evaporated under vacuum. The crude product was purified by column chromatography over silica gel (230–400 mesh) using EtOAc/petroleum ether as eluent to afford the 3-methylquinoxalin-2(1*H*)-ones without deuterated product after detecting by ^1H NMR.

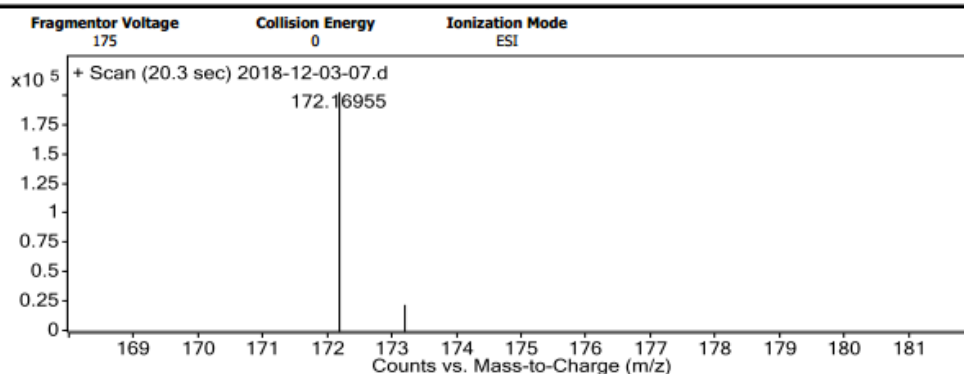


1.2. Reaction of TEMPO with $\text{PhI}(\text{OAc})_2$, $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ and **1a** under visible-light.



In a dried Schlenk tube, 1-methylquinoxalin-2(1H)-one (0.2 mmol), TEMPO (2.0 equiv), $\text{PhI}(\text{OAc})_2$ (2.5 equiv) and $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (2.0 mg, 0.01 equiv) were mixed in DMSO (2.0 mL) at room temperature. The tube was placed at a distance (app. 5 cm) from 24 W white LED, and the solution was stirred under visible-light irradiation. The mixture was stirred at r.t. for 10 h. TLC shows that the product **3a** was not formed and TEMPO- CH_3 adduct **9** was detected by HRMS.

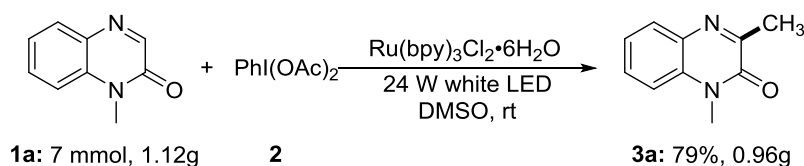
User Spectra



Peak List

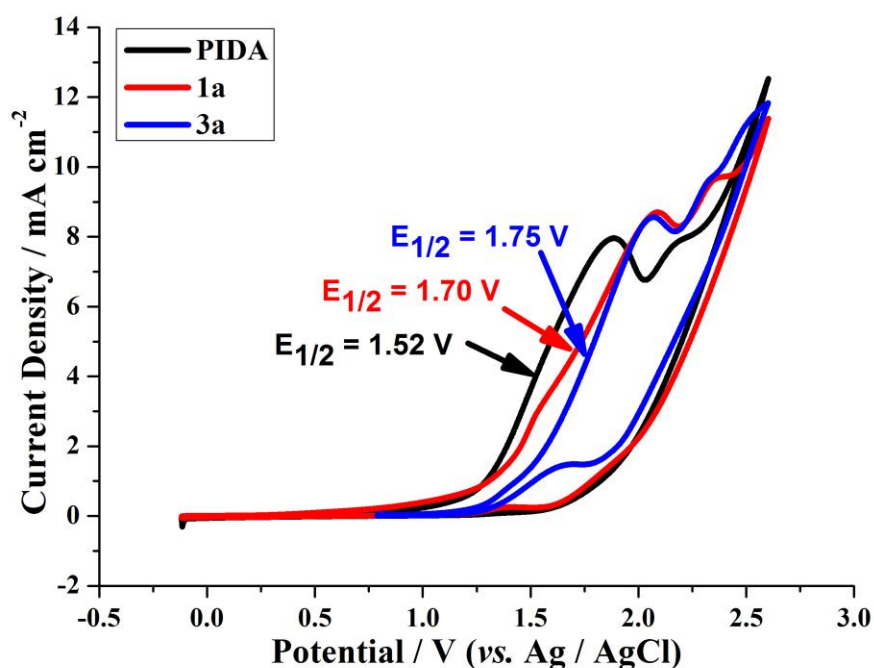
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142.26701		200766.6		
142.30001		112689.1		
143.16246	1	479416.1		
156.13854		66148.9		
156.17374		99589.5		
172.16955		203080.9	$\text{C}_{10}\text{H}_{22}\text{NO}$	$(\text{M}+\text{H})^+$
263.21157		51486.3		
319.28696		87736.1		
379.29886	1	621362.9		
380.3017	1	138397.1		
462.36833		95275.6		
496.40994	1	165619.2		
497.4124	1	53668.1		
559.49375	1	268253.1		
560.49738	1	100862.3		
651.50539		75414.8		
734.4075	1	129546.4		
735.41103	1	46656.2		

2. Gram-scale Reaction



In a dried round-bottomed flask, quinoxalin-2(1H)-ones (1.12g, 7.0 mmol), $\text{PhI}(\text{OAc})_2$ (5.635g, 17.5 mmol) and $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (52 mg, 1.0 mol%) were mixed in DMSO (70.0 mL) at room temperature. The flask was placed at a distance (app. 5 cm) from 24 W white LED, and the solution was stirred under visible-light irradiation. After the reaction was completed (monitored by TLC), the reaction mixture was quenched by saturated aqueous Na_2CO_3 solution (50 mL), and then the mixture was extracted with ethyl acetate (3×50 mL). The combined organic phase was dried over anhydrous MgSO_4 and evaporated under vacuum. The crude product was purified by column chromatography over silica gel (230–400 mesh) using EtOAc/petroleum ether as eluent to afford the desired products **3a** (0.96g, 79% yield).

3. Cyclic Voltammetry Experiment



Furthermore, we probed the mechanism of photochemical oxidative by means of cyclic voltammetric experiment: individual PIDA, **1a**, **3a**. The measurements were executed at room temperature on a PGSTAT128N Autolab workstation (Netherlands) in a three-electrode system. The reference electrode was an Ag/AgCl electrode (saturated KCl solution). A carbon rod was employed as the counter electrode for measurement. A modified glassy-carbon electrode with a diameter of 5 mm was used as the working electrode. Briefly, 2.0 mg of determinand was firstly dispersed in Nafion/ethanol (0.4 mL, 0.25% Nafion) by sonication for 1 h to achieve a well-dispersed ink. Then, 8 μ L of the uniform suspension was pipetted onto the glassy-carbon electrode and dried in open air, which makes the determinand loading is 0.2 mg cm⁻² for all samples.

The potentials vs Ag/AgCl were converted to the reversible hydrogen electrode (RHE) using the Nernst equation:

$$E(\text{vs RHE}) = E(\text{vs AgCl/Ag}) + E_{\text{AgCl/Ag}}^0 + 0.0591 \cdot \text{pH} \quad (1)$$

(where $E_{\text{AgCl/Ag}}^0$ is 0.199 V at 25 °C)

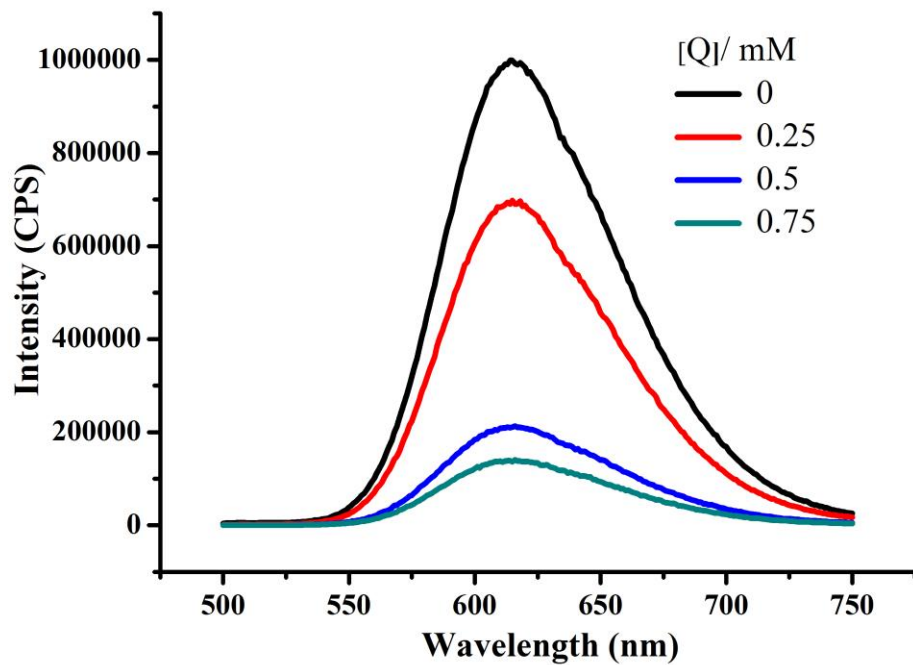
The potentials vs SCE were converted to the reversible hydrogen electrode (RHE) using the Nernst equation:

$$E(\text{vs RHE}) = E(\text{vs SCE}) + E_{\text{SCE}}^0 + 0.0591 \cdot \text{pH} \quad (2)$$

(where E_{SCE}^0 is 0.244 V at 25 °C)

In combination with the equation 1 and 2, the redox potentials of PIDA, **1a** and **3a** can be calculated as $E_{\text{PIDA}}(\text{vs SCE}) = 1.475$ V, $E_{\mathbf{1a}}(\text{vs SCE}) = 1.655$ V, $E_{\mathbf{3a}}(\text{vs SCE}) = 1.705$ V. As the redox potentials of Ru(bpy)₃Cl₂•6H₂O are well known in literature ($E_{1/2}(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}) = -0.81$ V vs. SCE, $E_{1/2}(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}) = +1.29$ V vs. SCE), in combination with the redox potentials of PIDA, **1a** and **3a**, it could be support the SET events in the proposed mechanism.

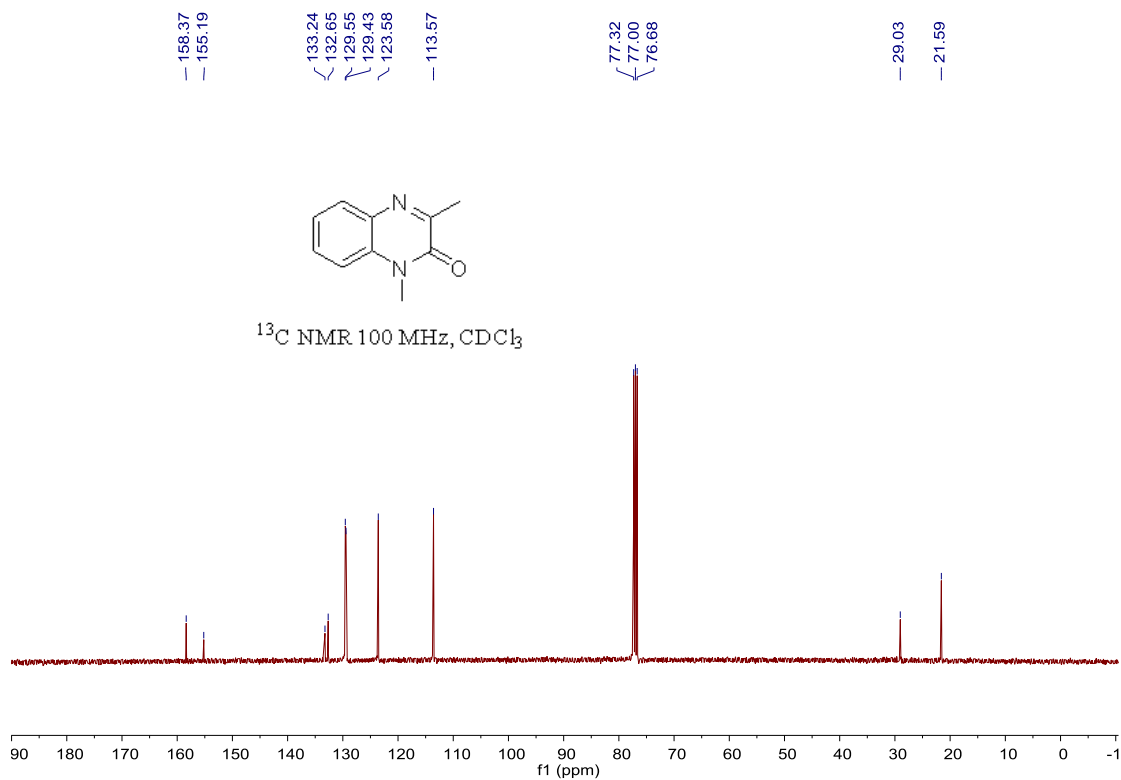
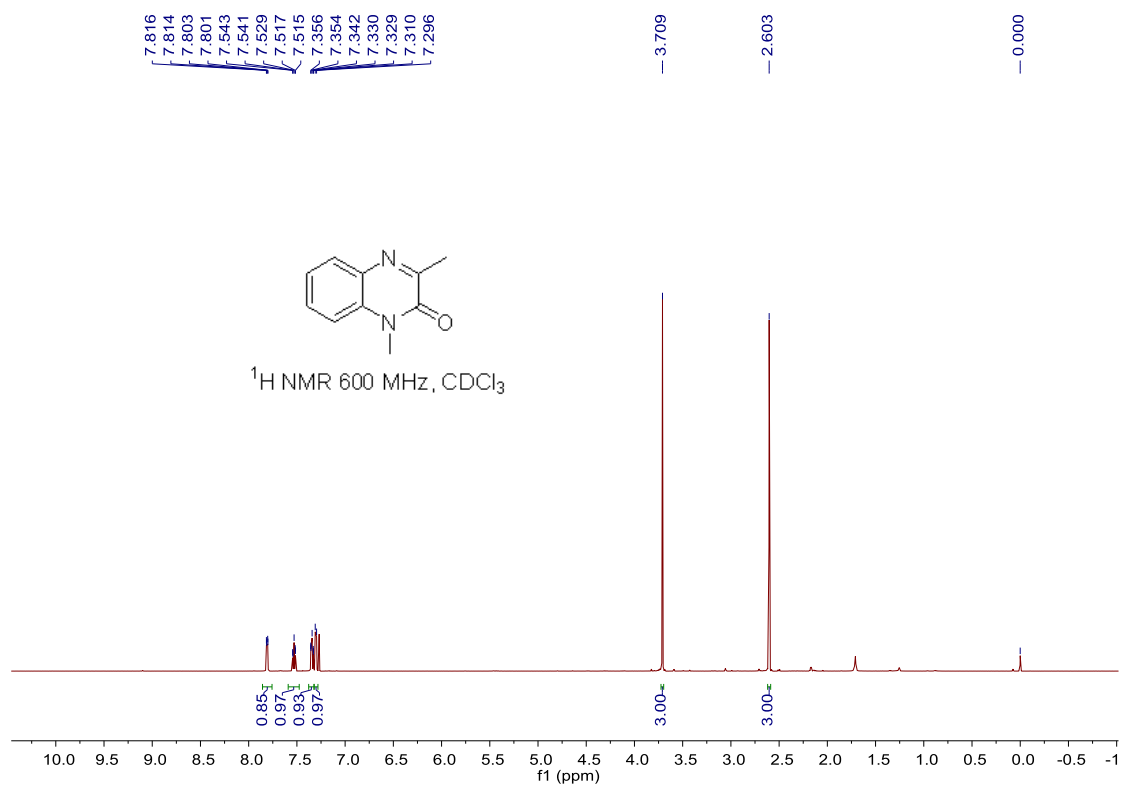
4. Emission quenching experiment



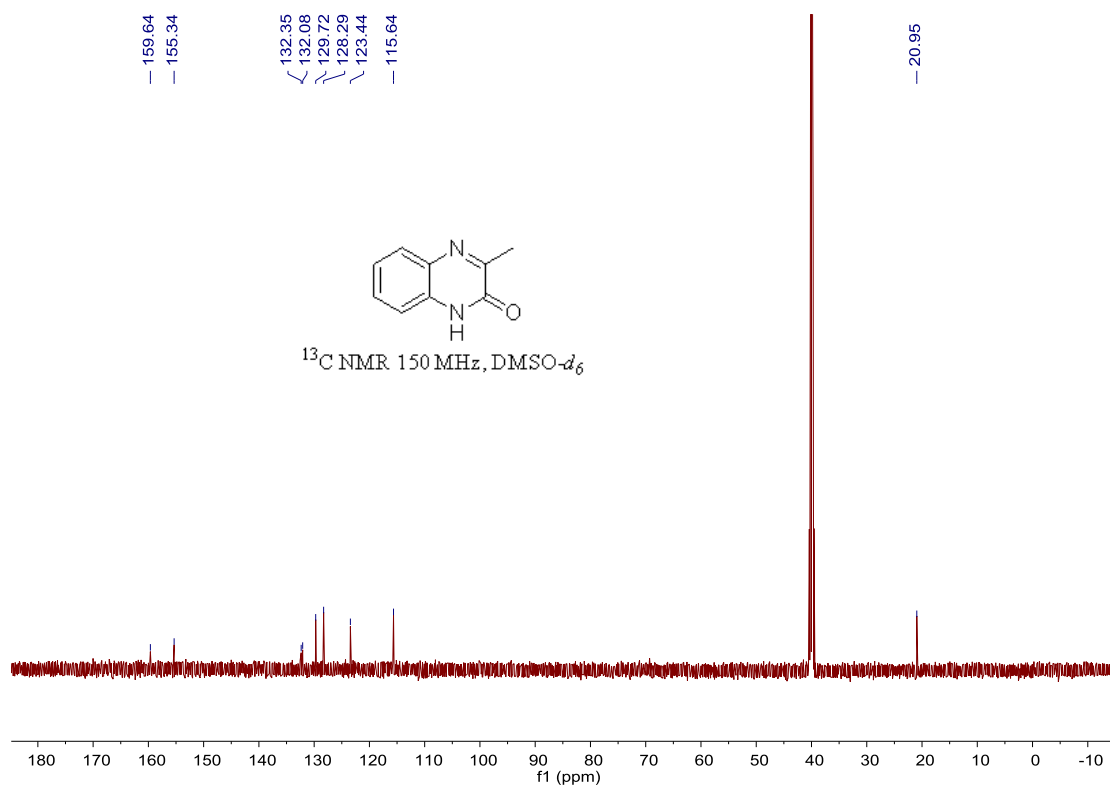
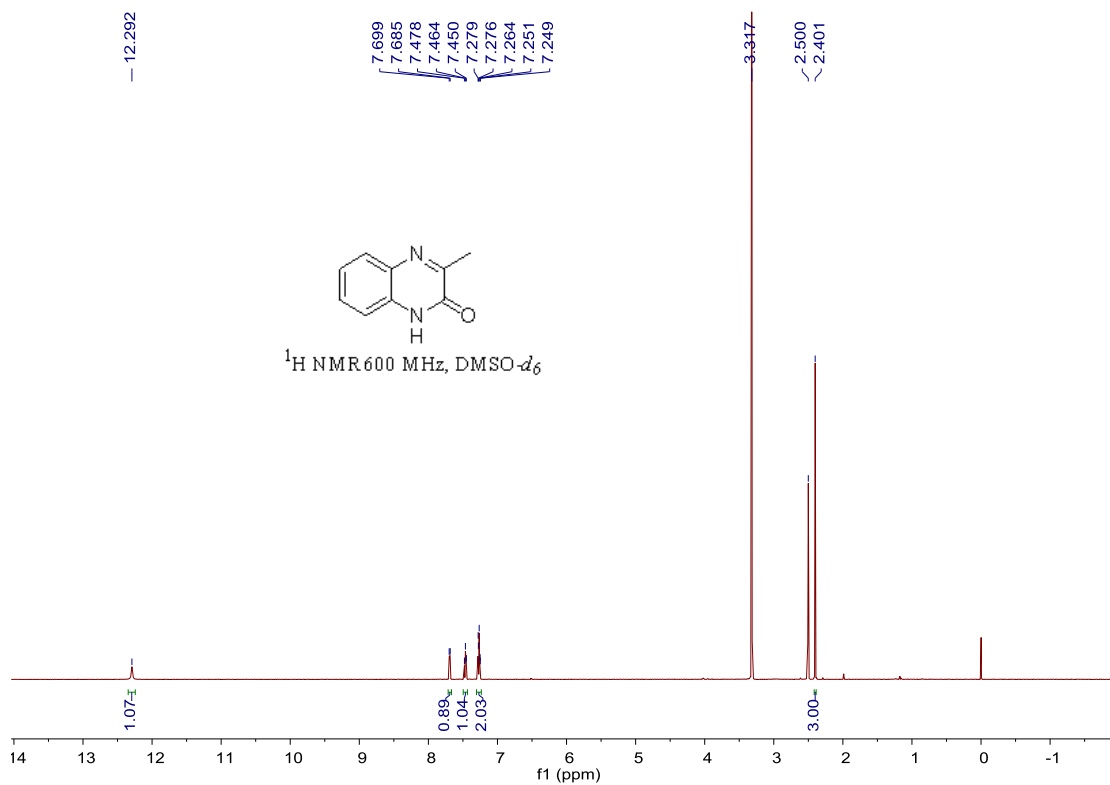
Emission intensities were recorded using a HORIBA Jobin Yvon Fluorolog3 Spectrofluorimeter. Initially, emission spectra of 10 μM Ru(bpy)₃Cl₂•6H₂O in DMSO was collected. Then, appropriate amount of quencher PIDA was added with increasing concentration and subsequent emission spectrum were recorded.

5. NMR copies of compounds 3.

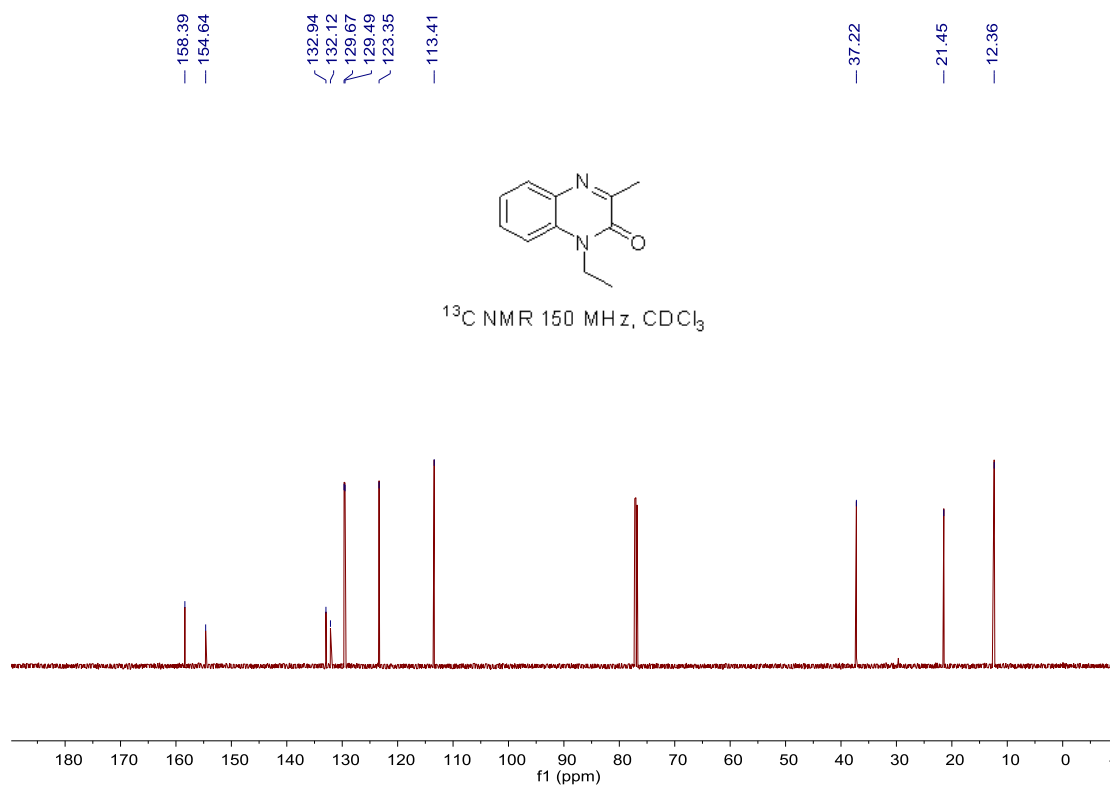
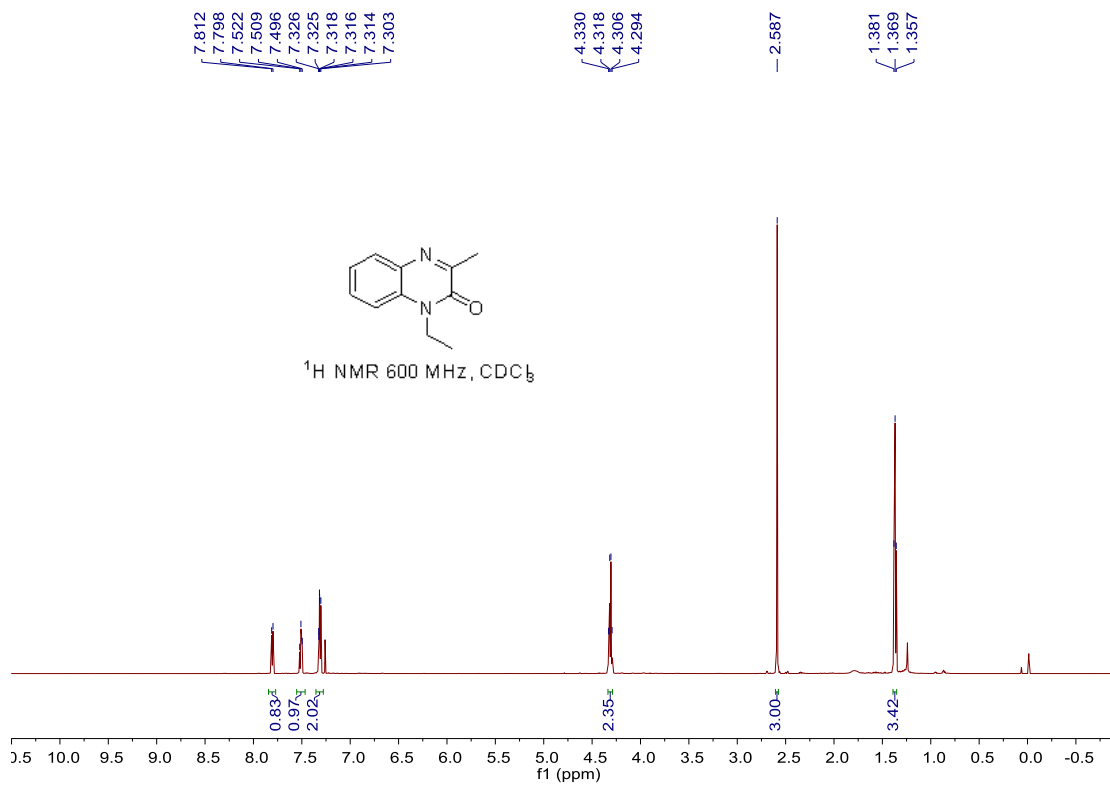
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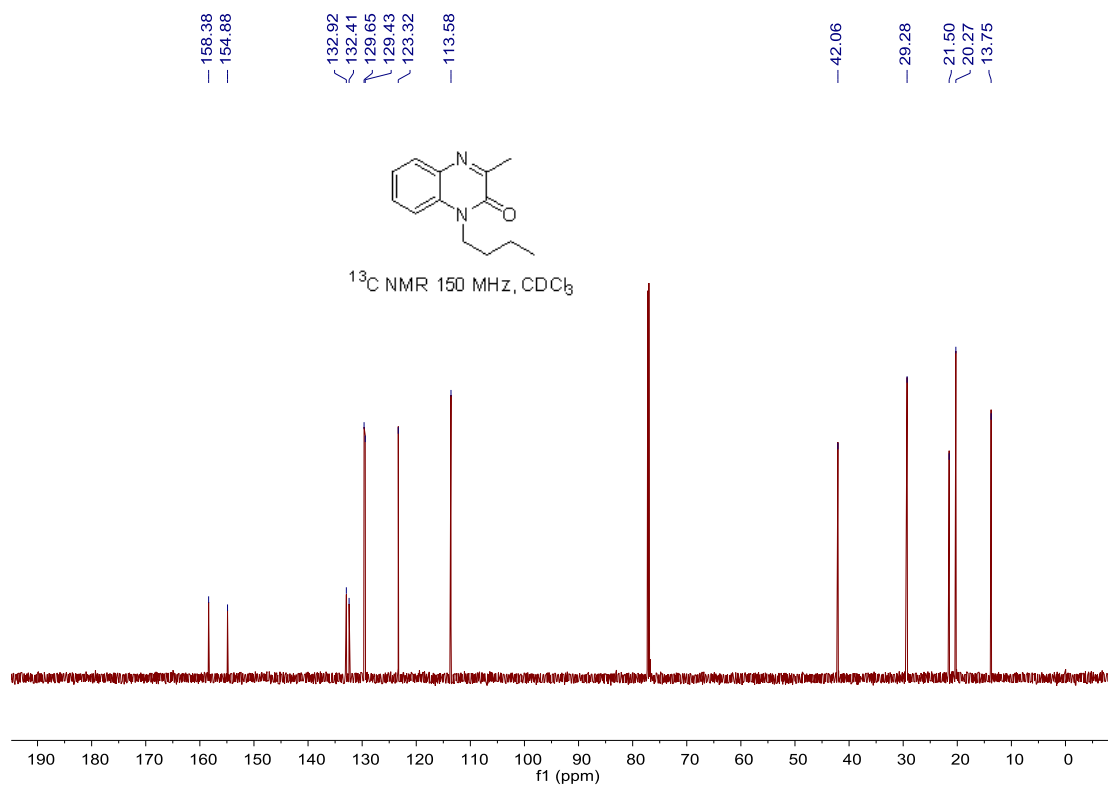
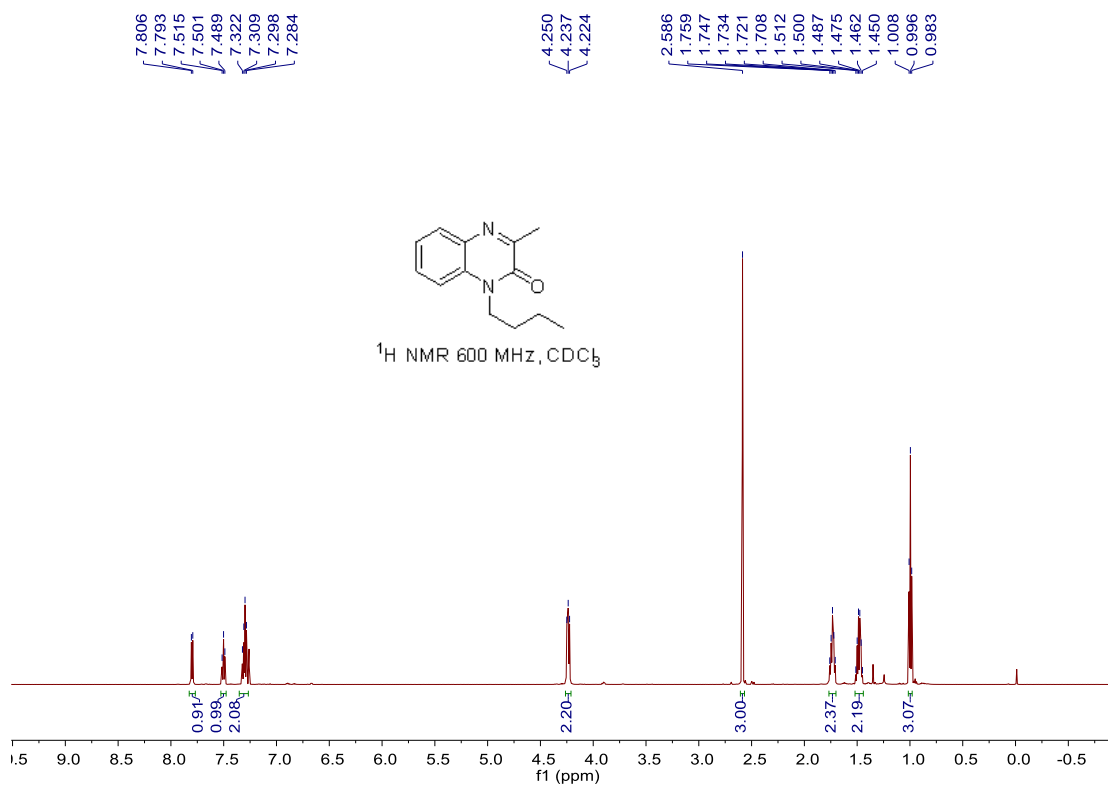
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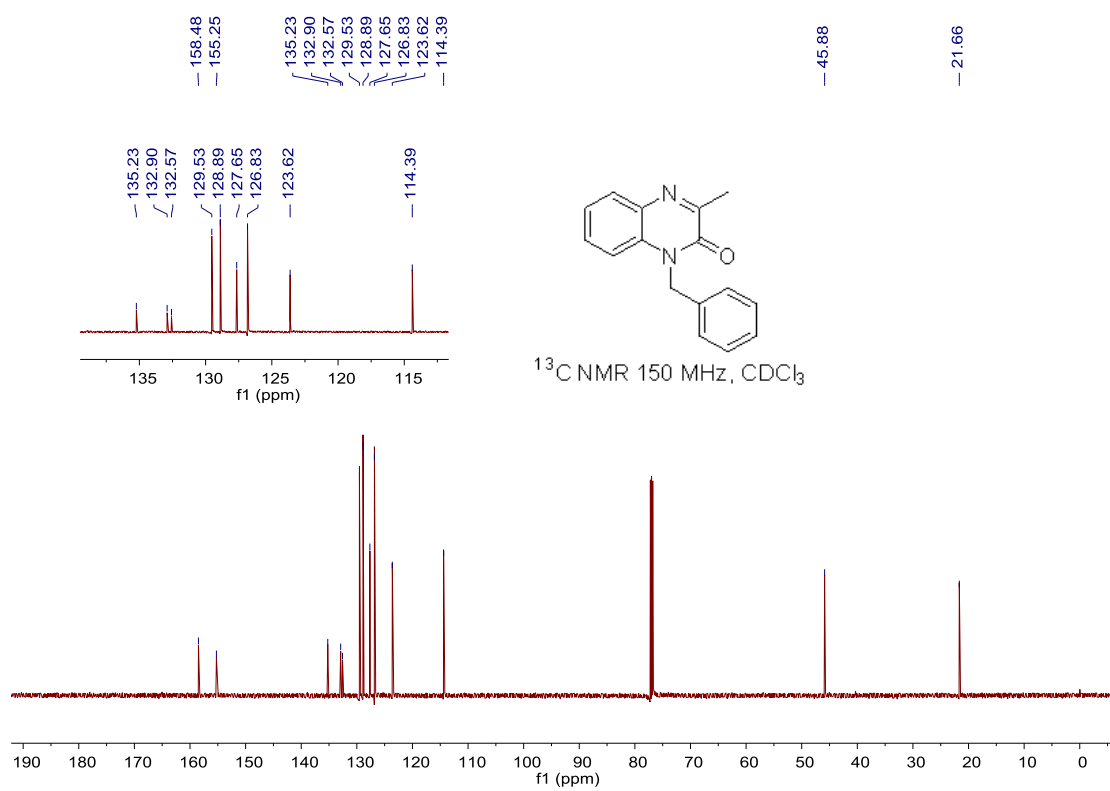
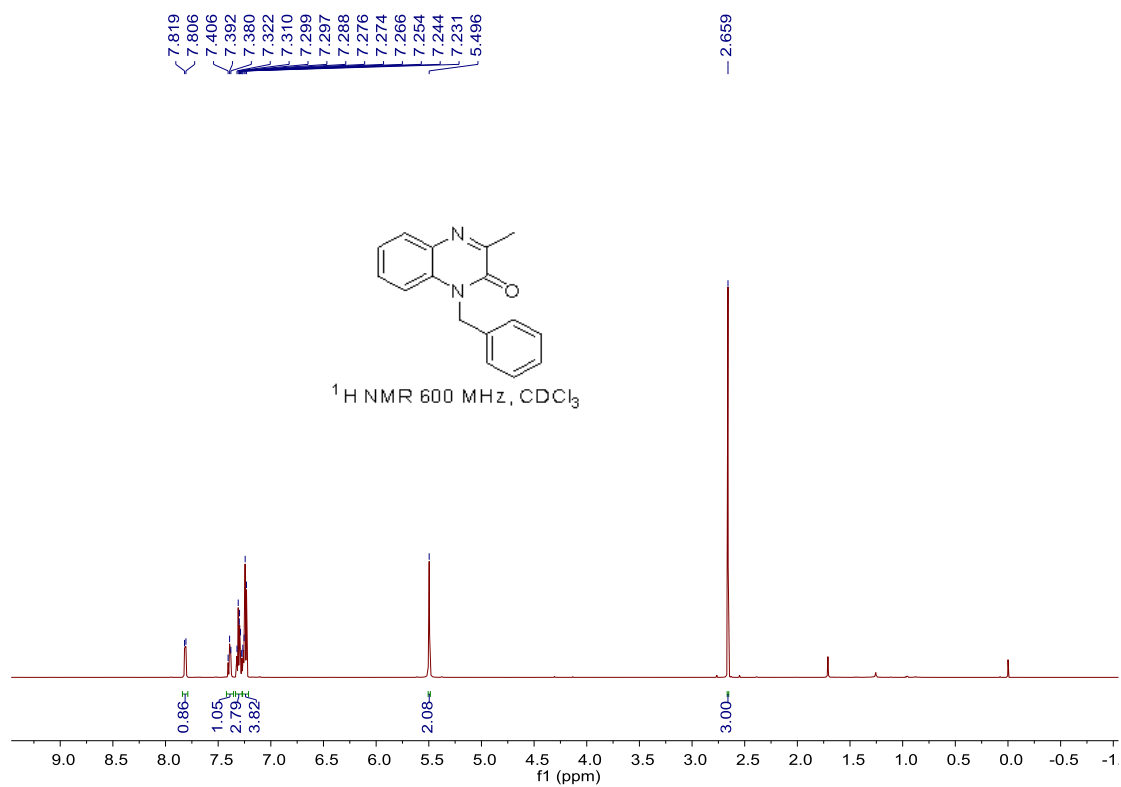
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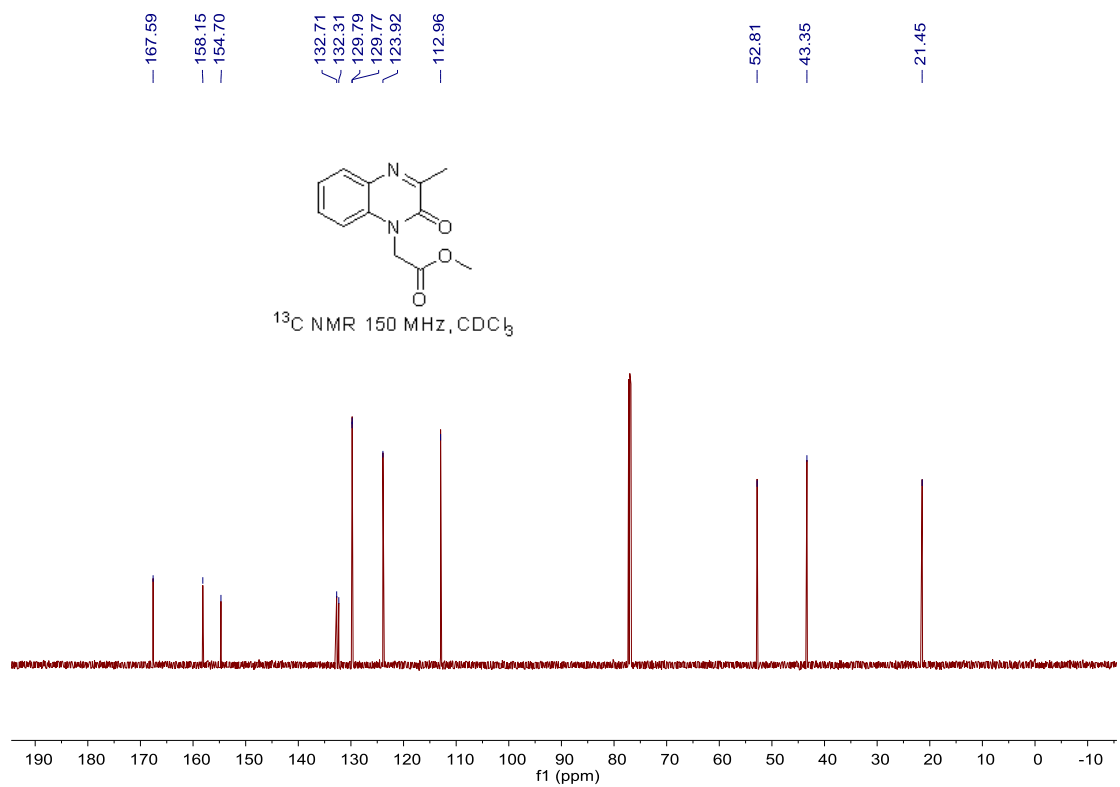
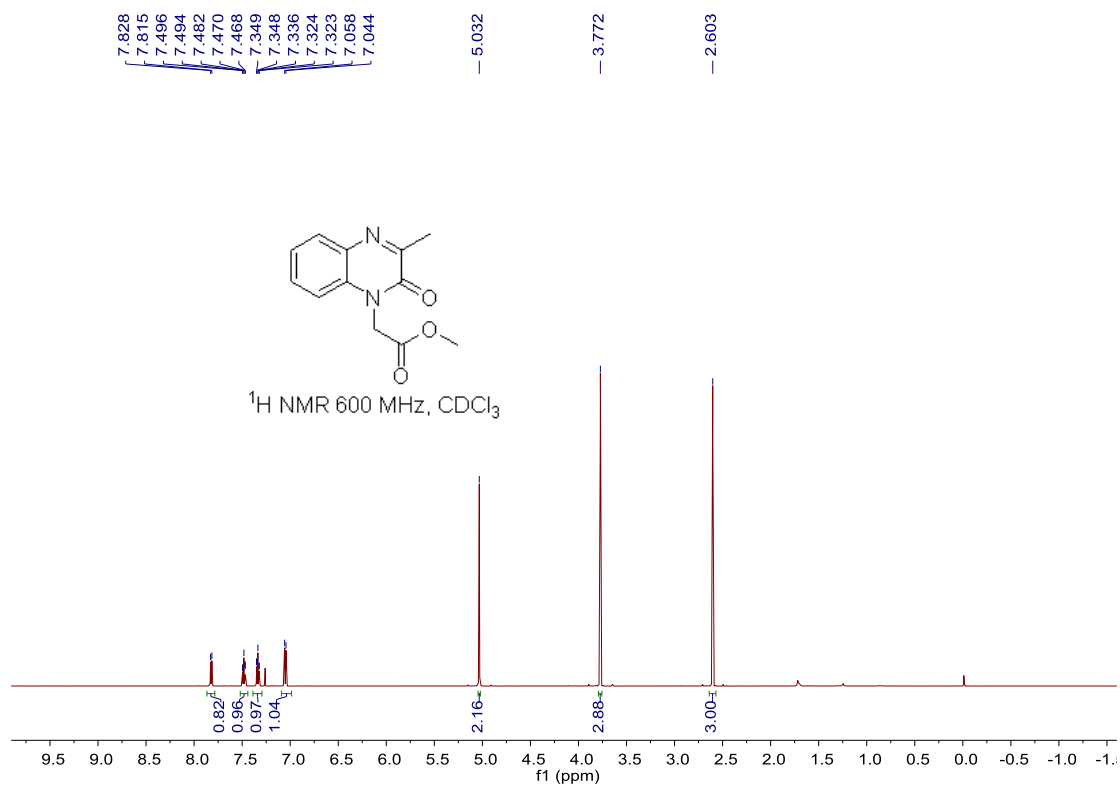
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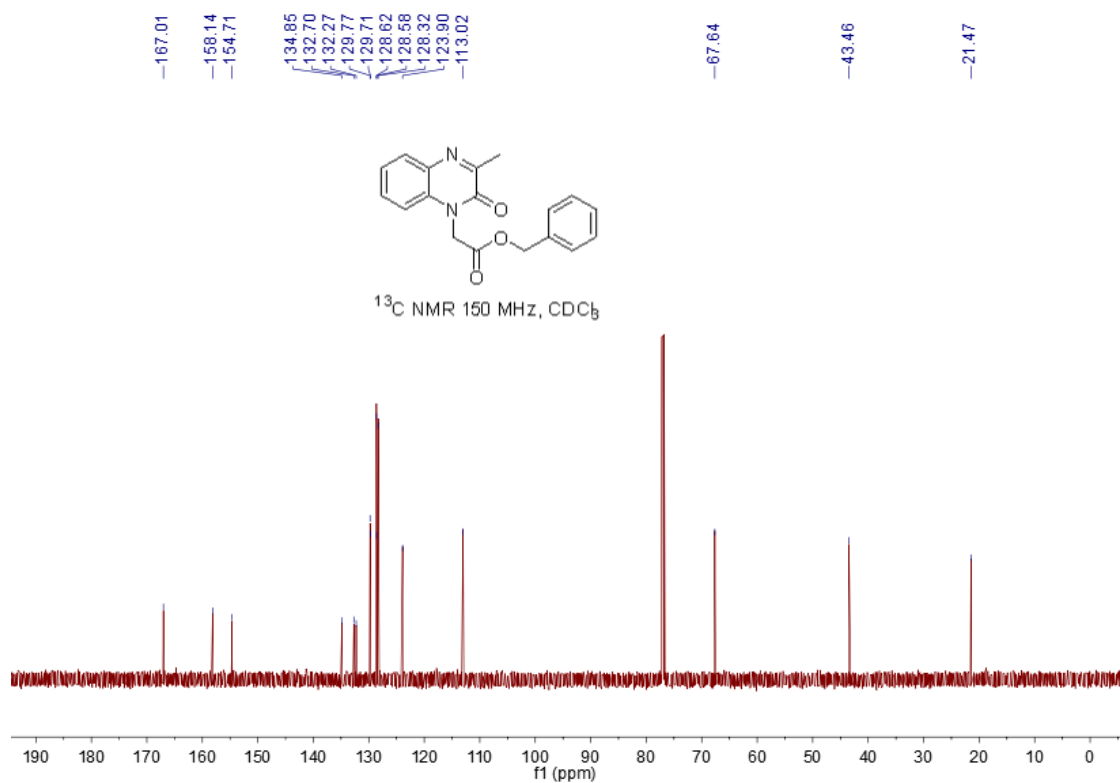
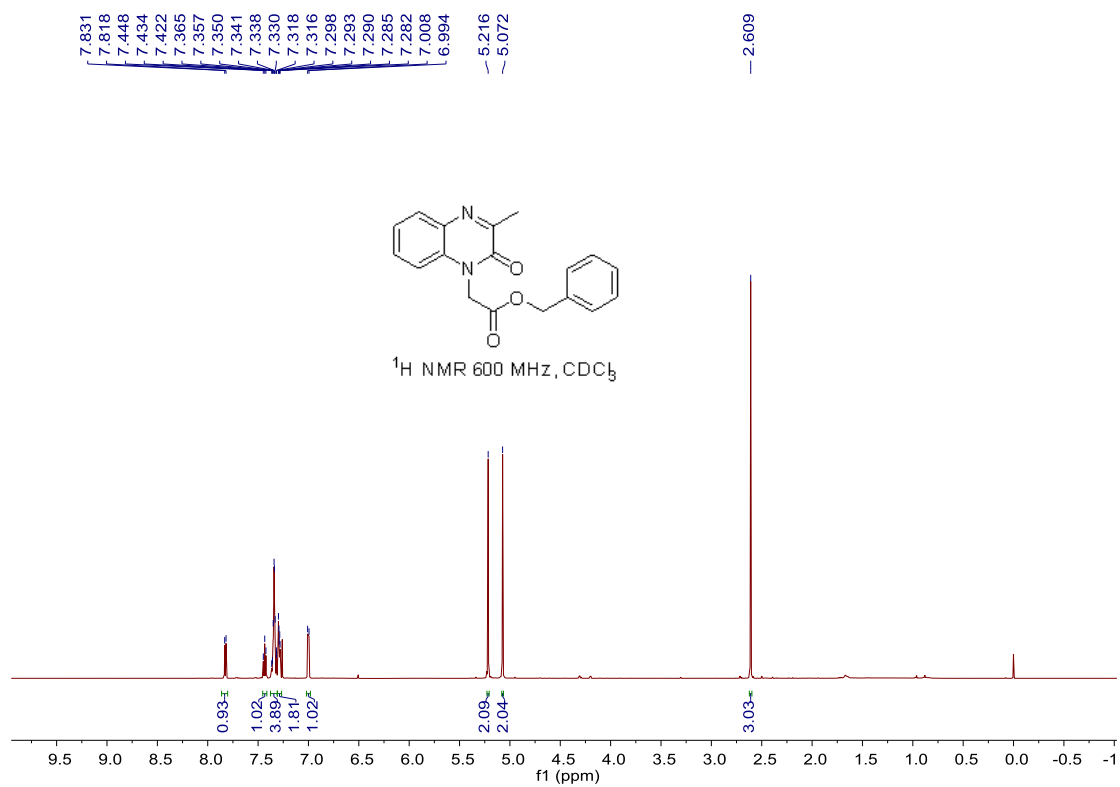
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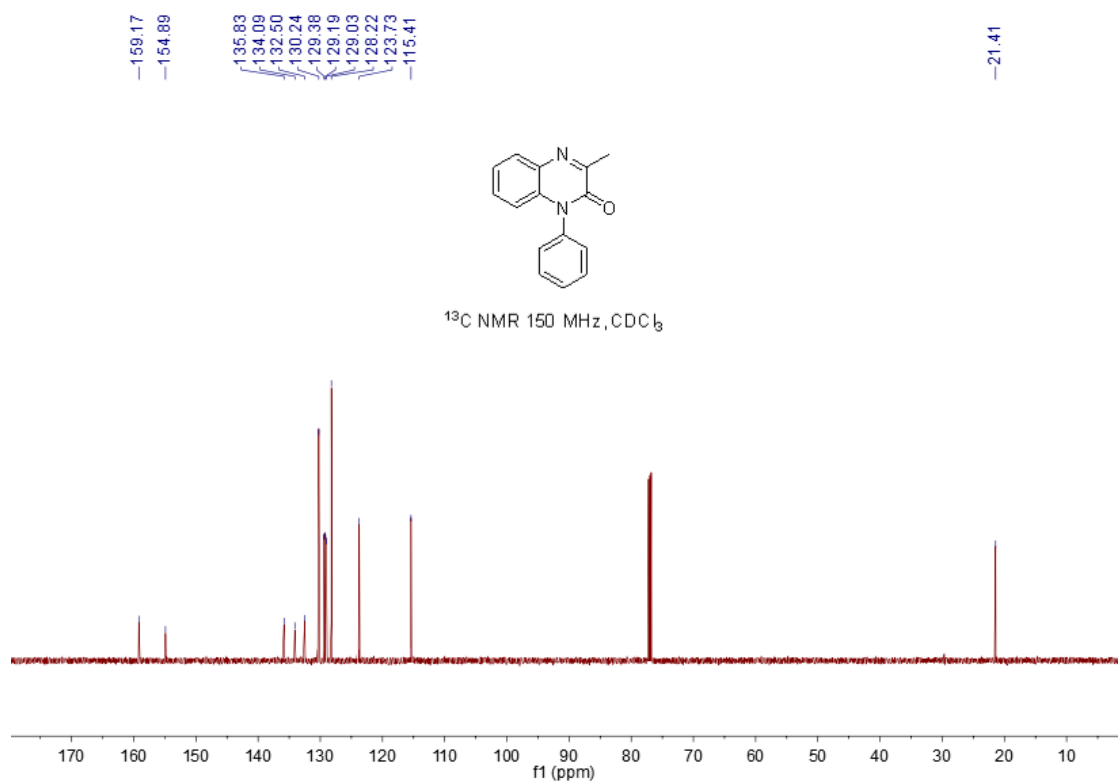
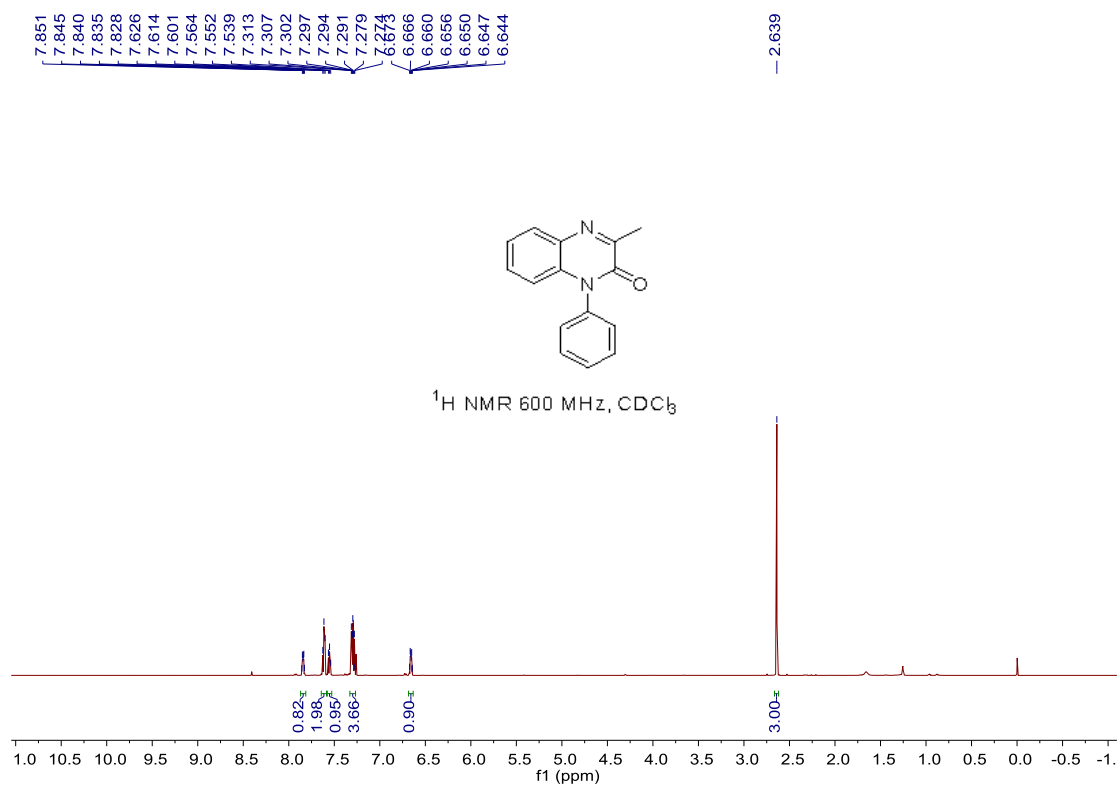
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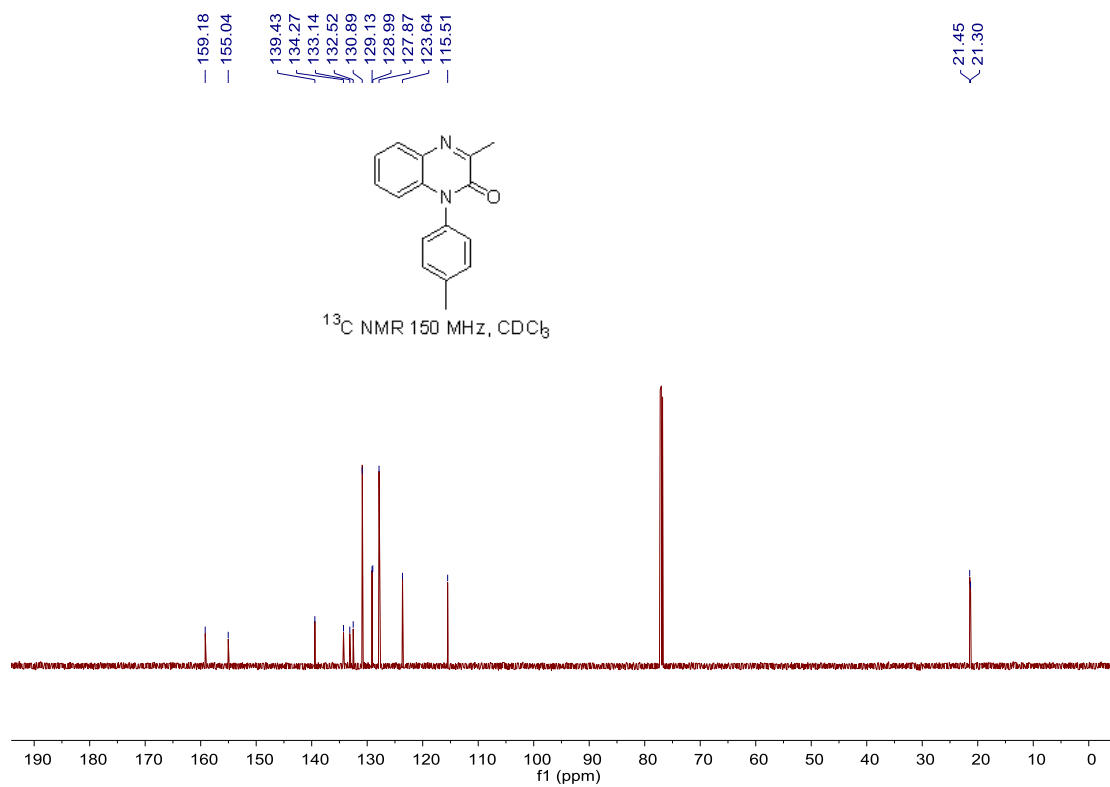
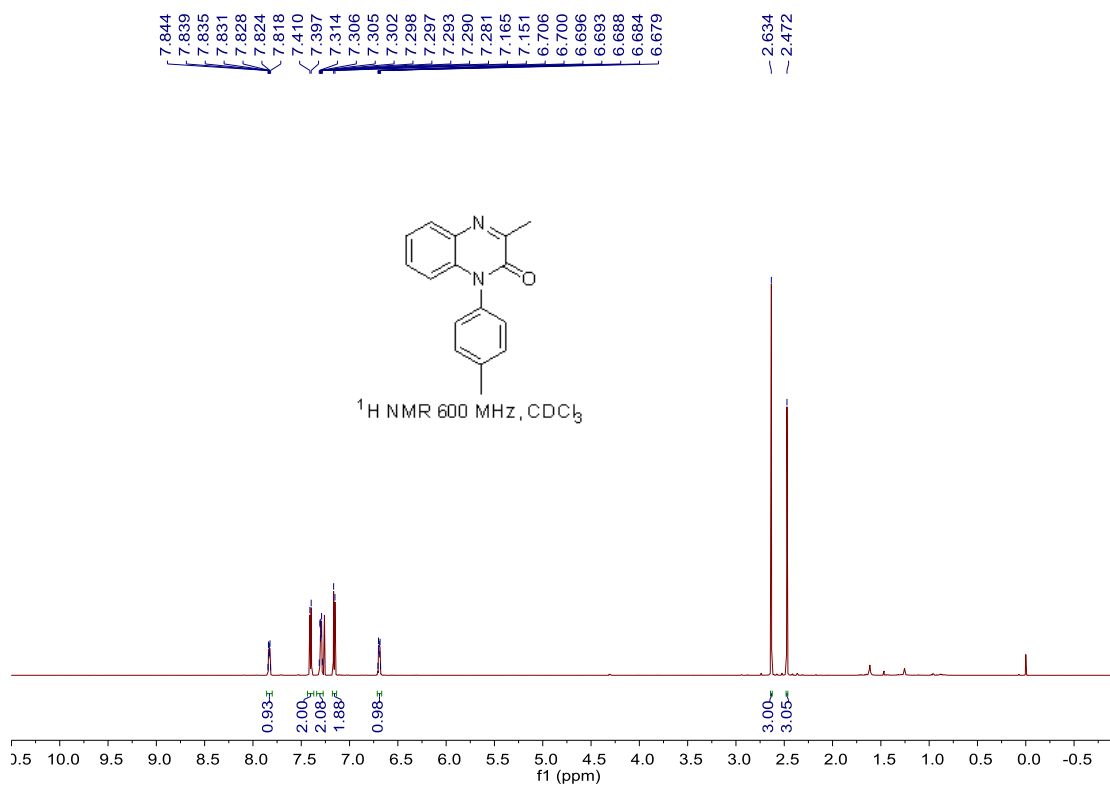
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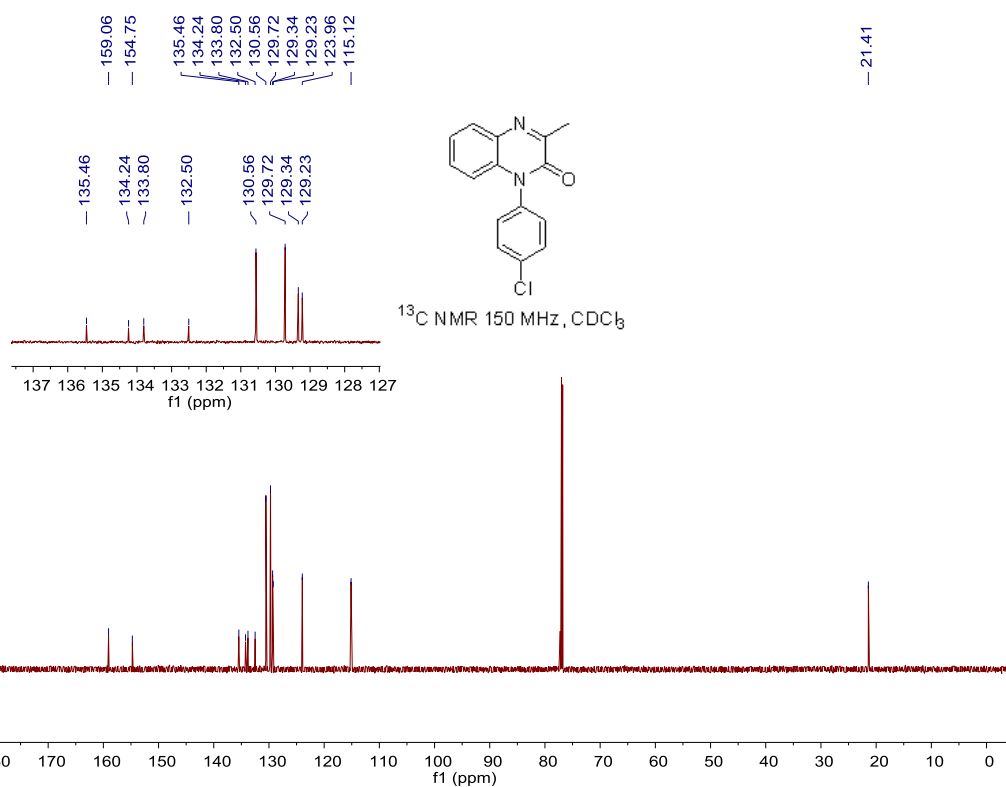
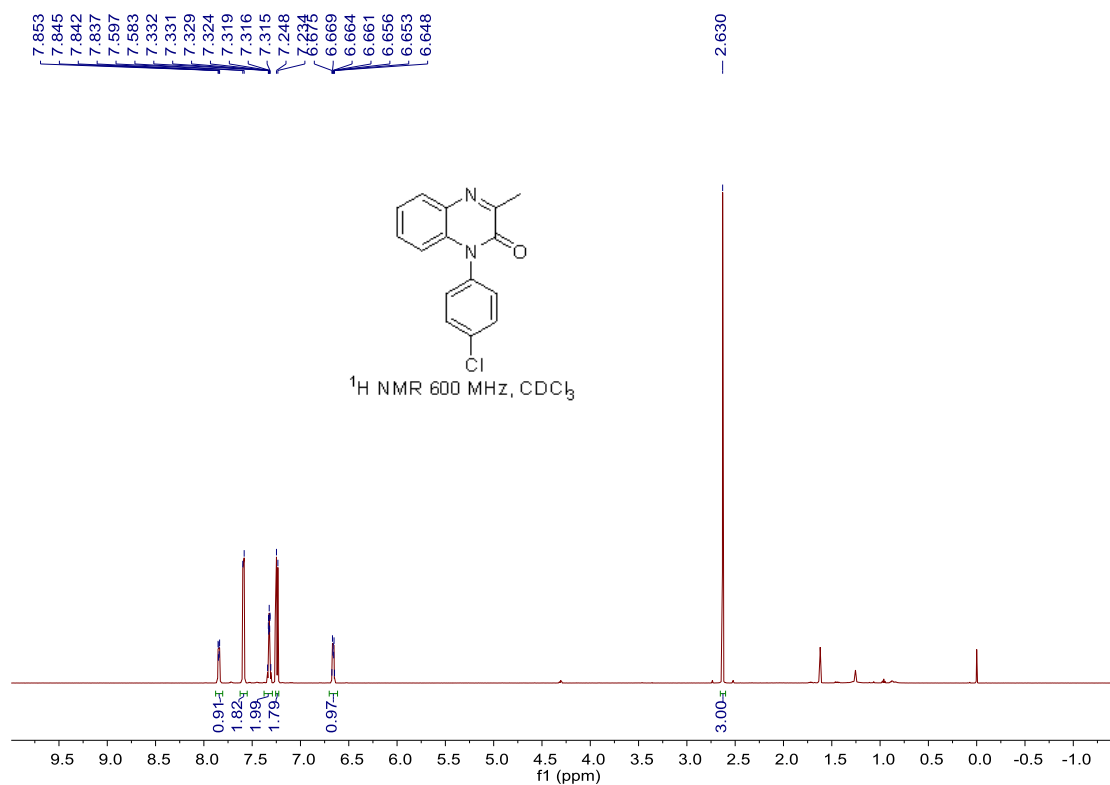
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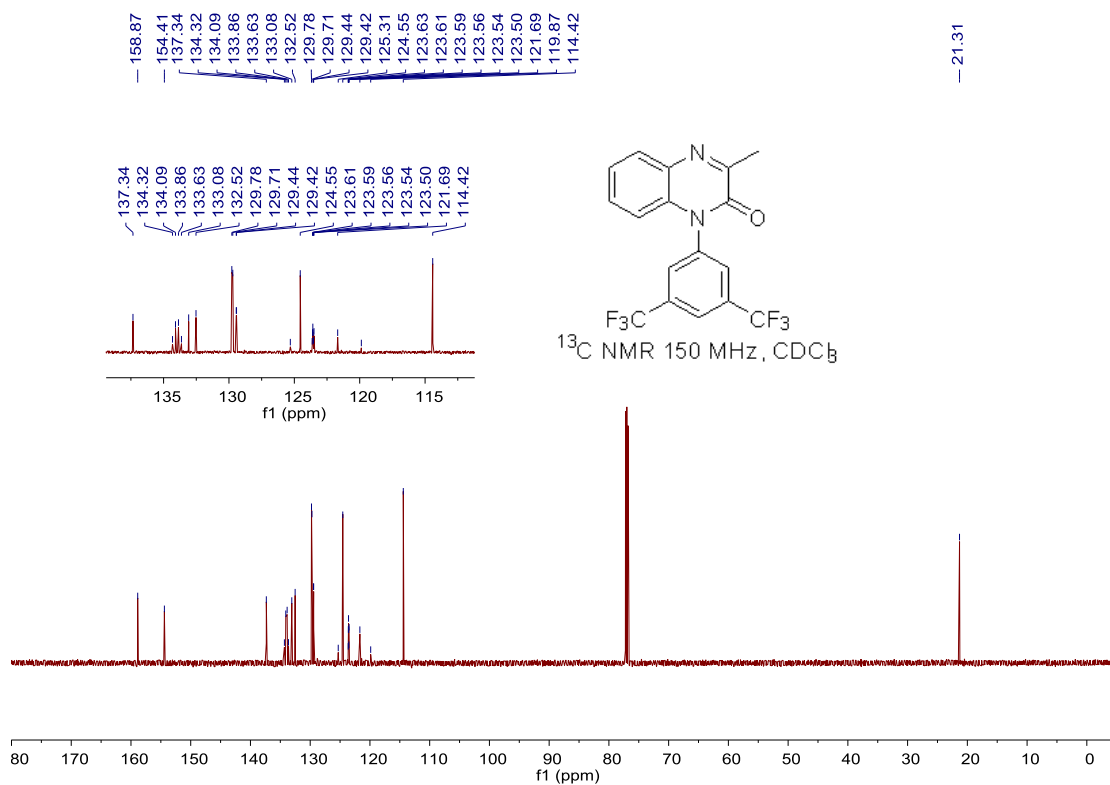
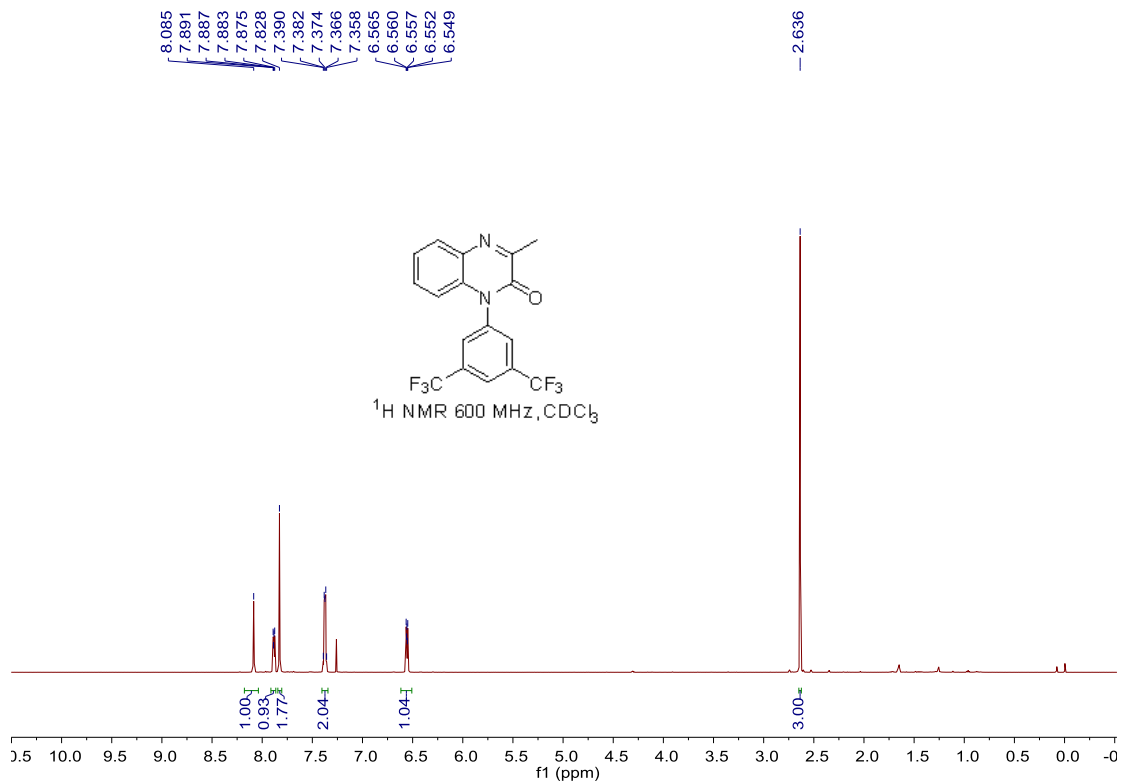
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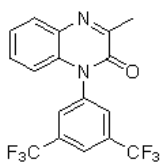
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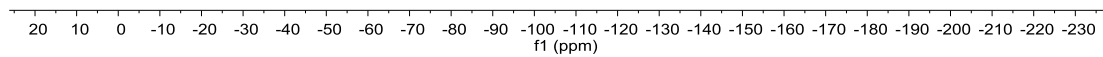
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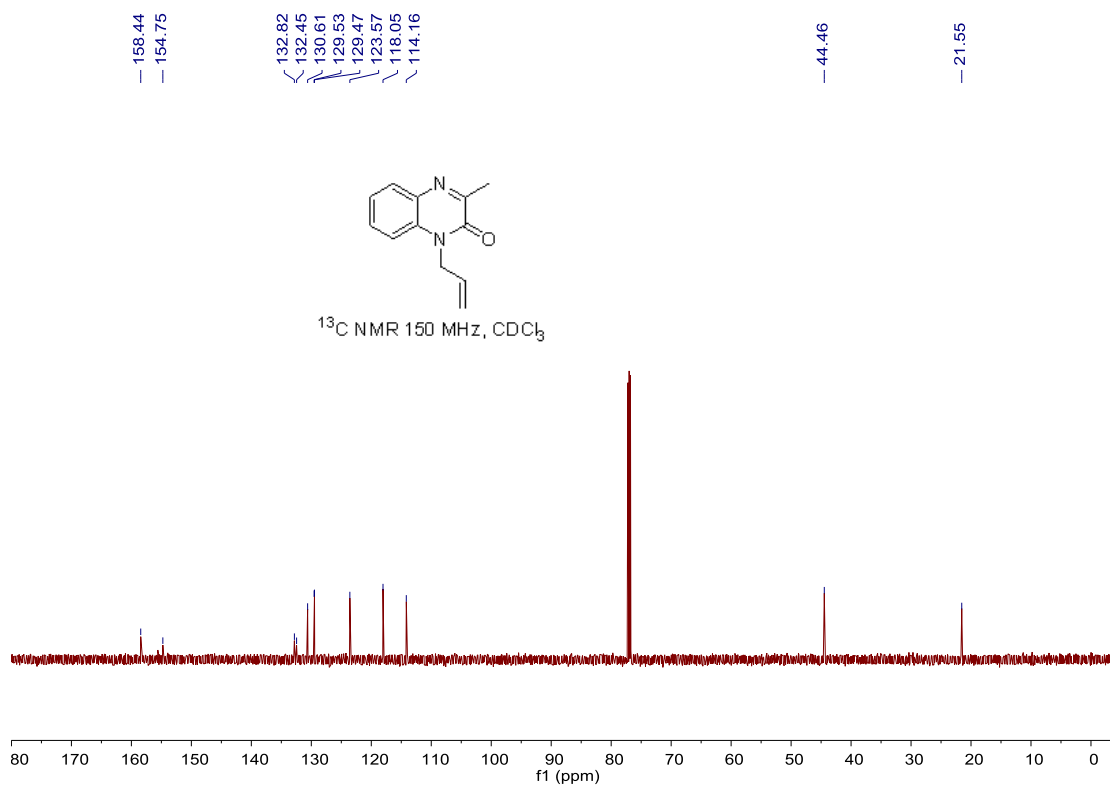
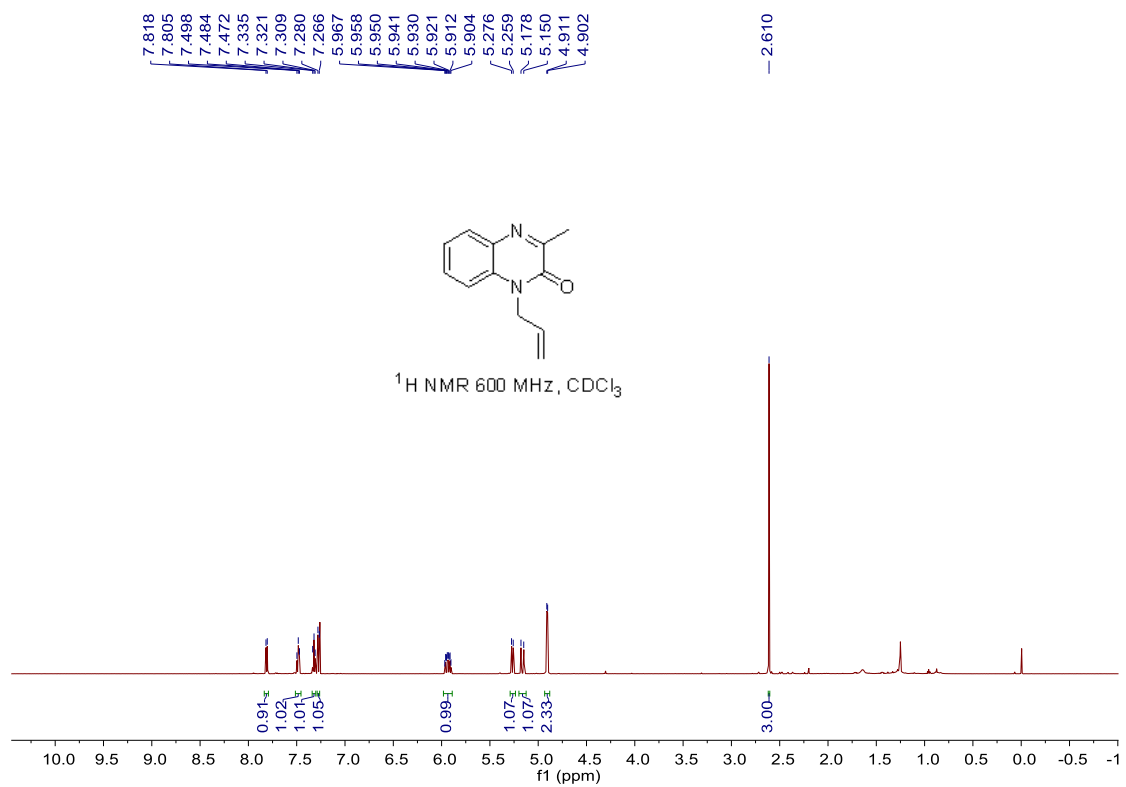
-63.25



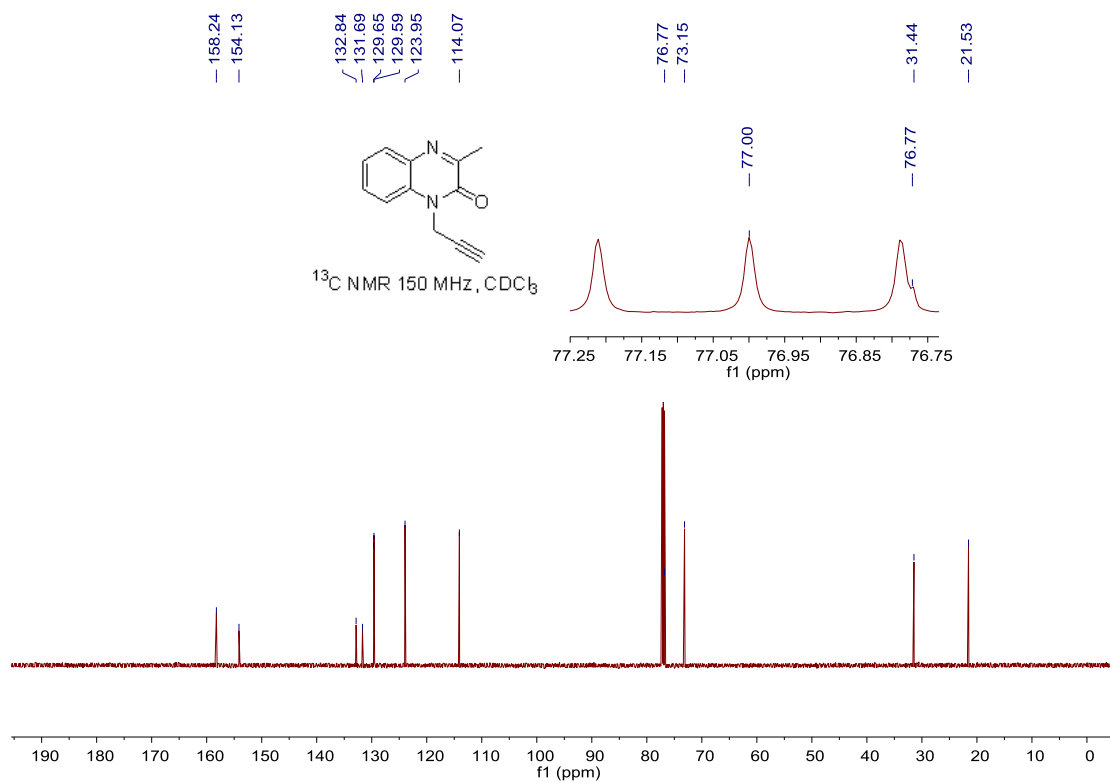
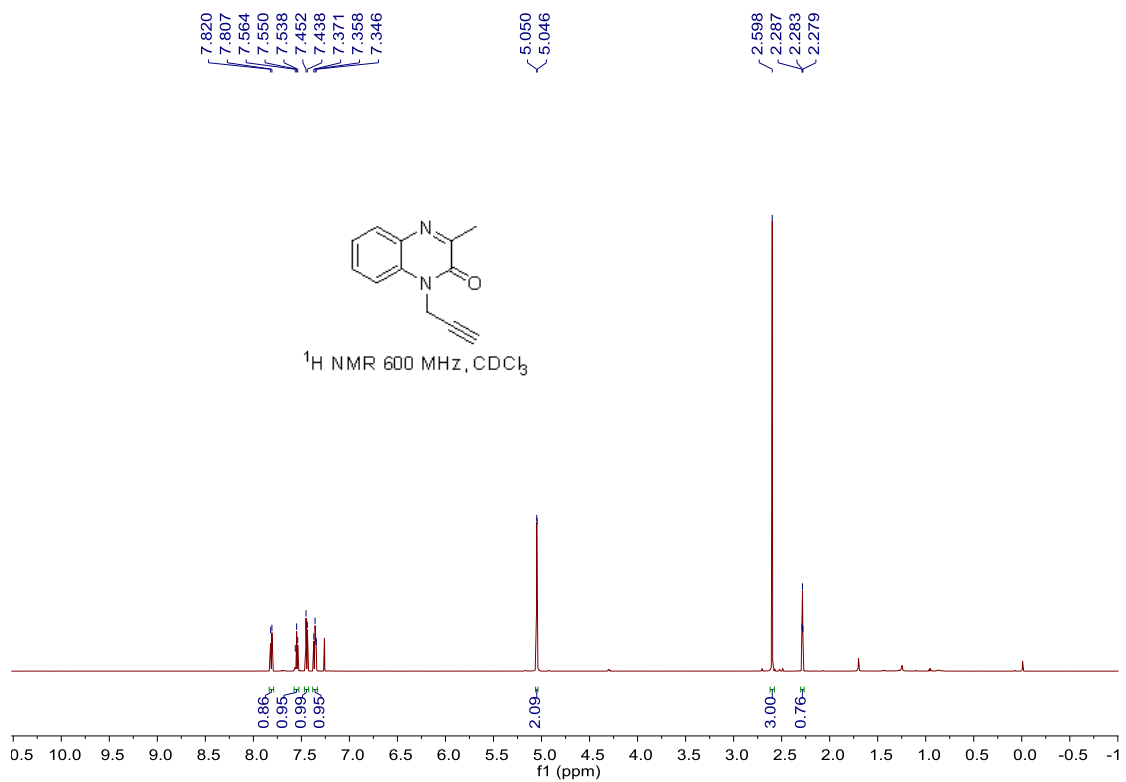
¹⁹F NMR 376 MHz, CDCl₃



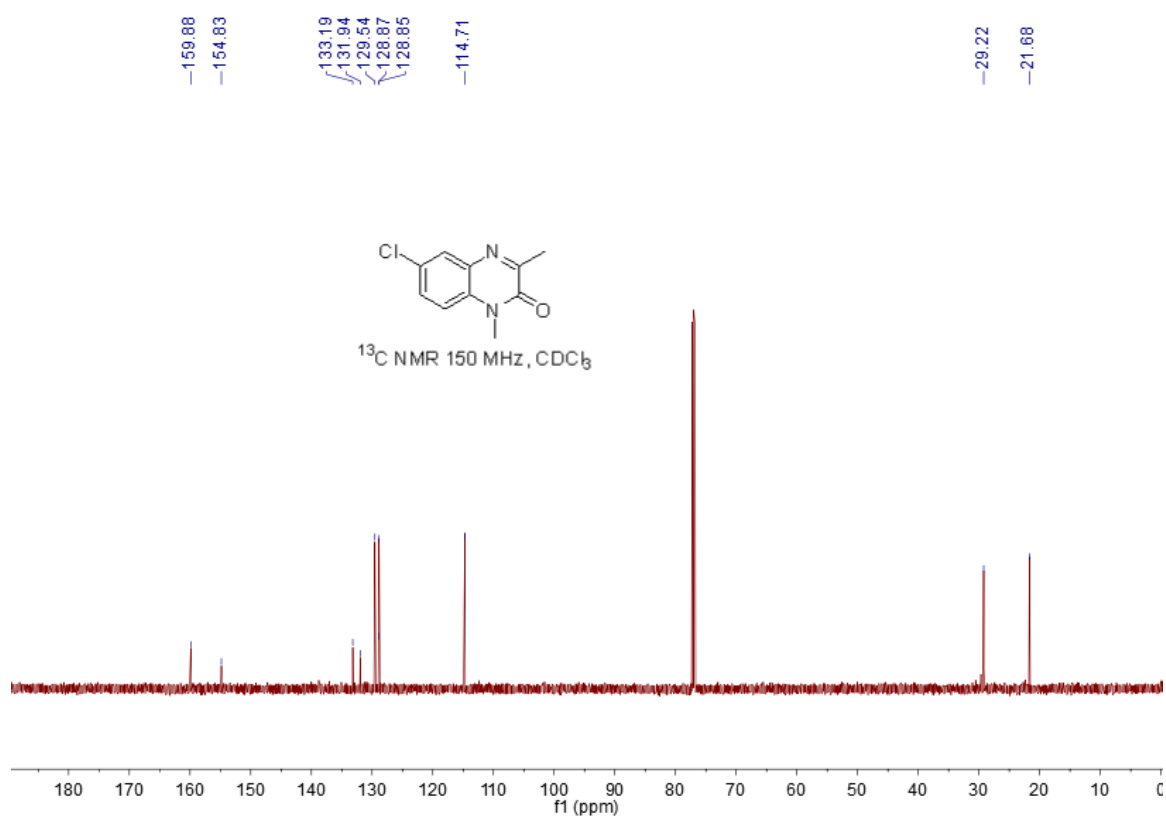
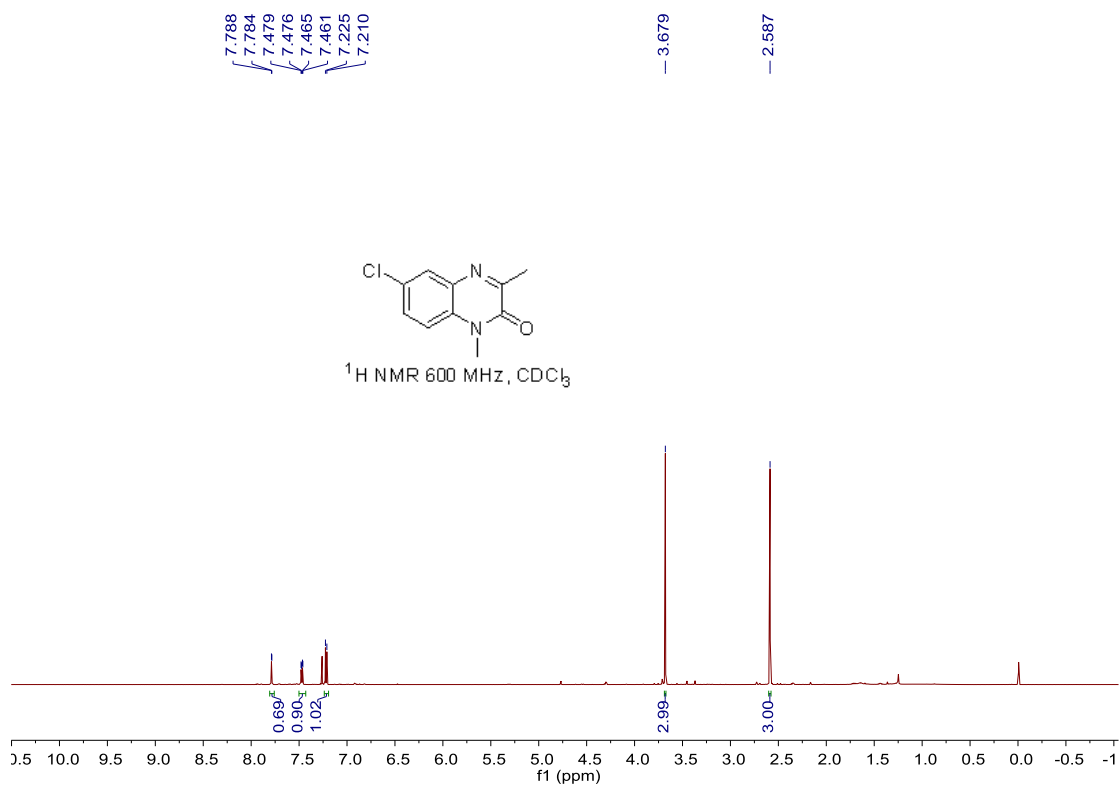
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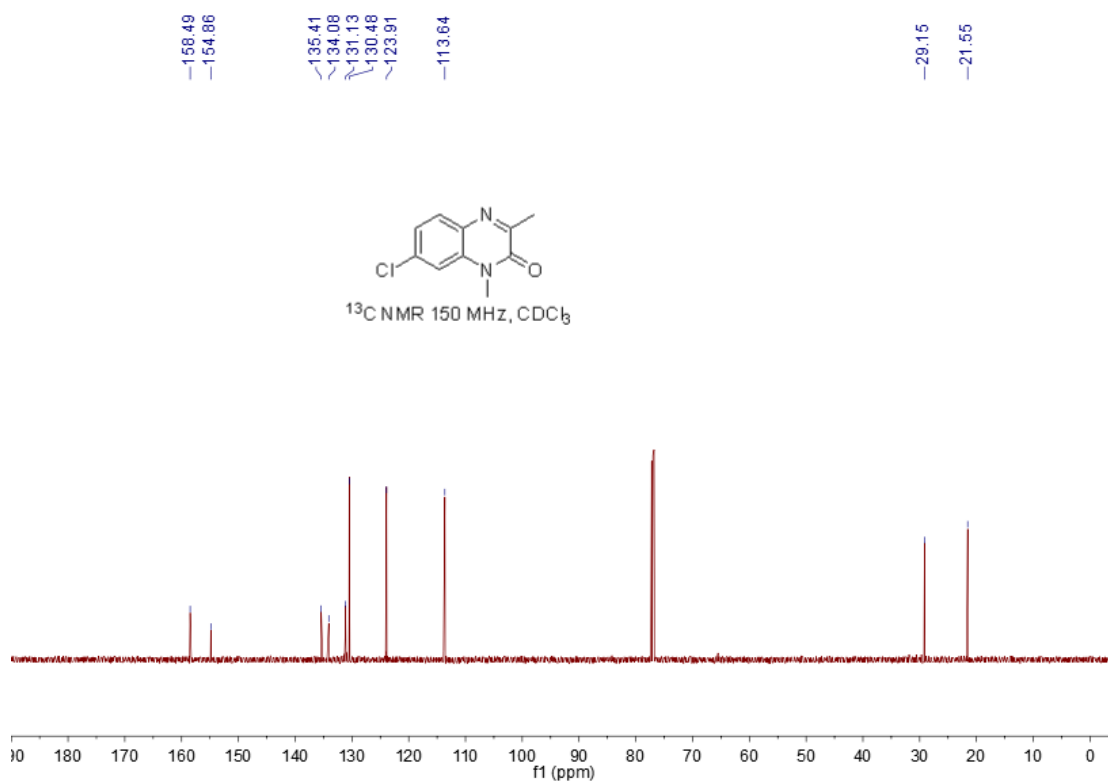
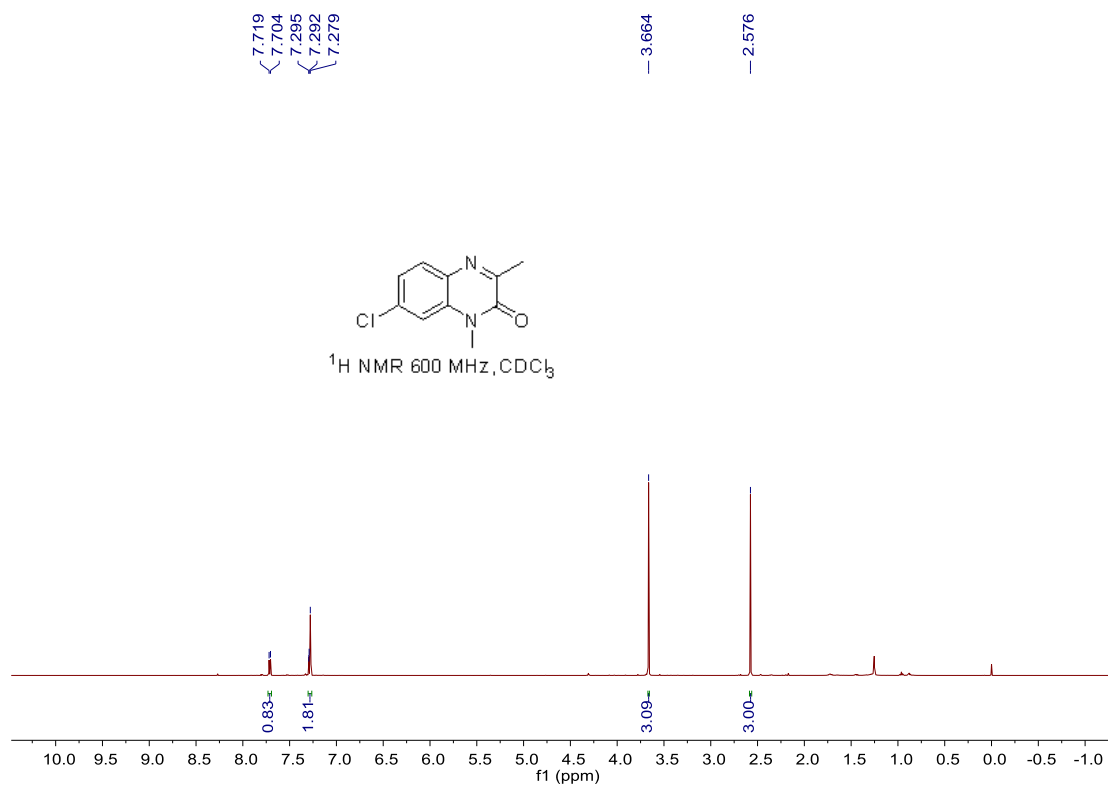
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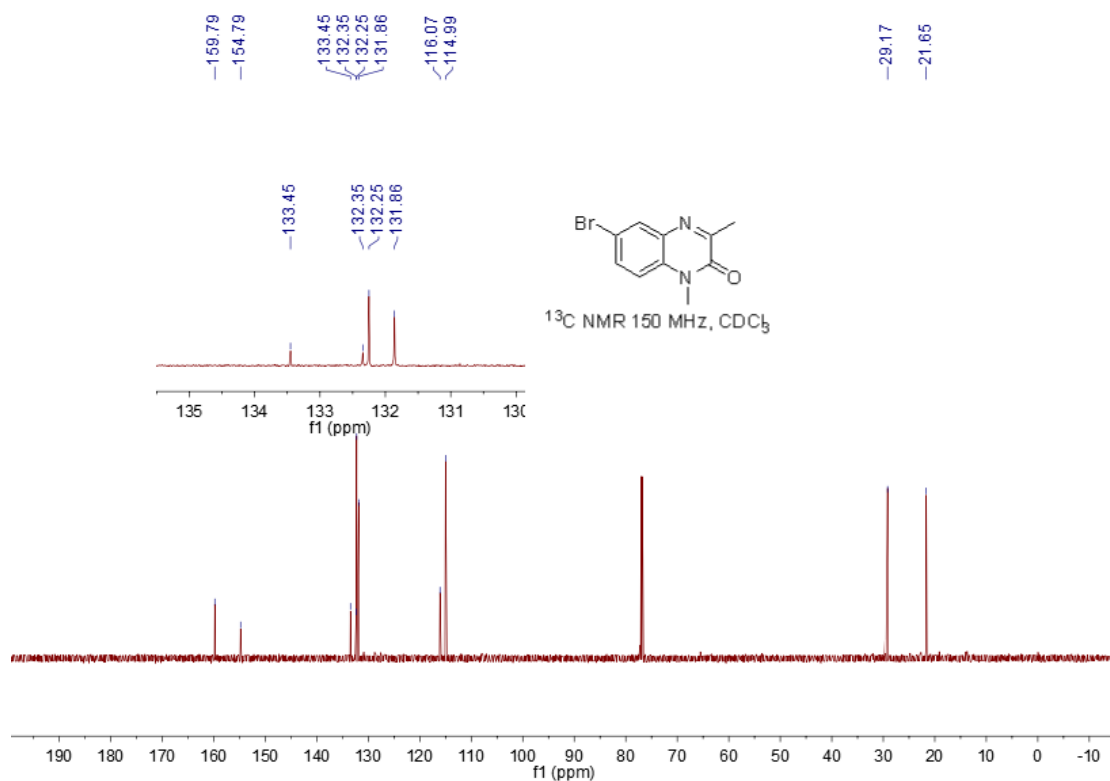
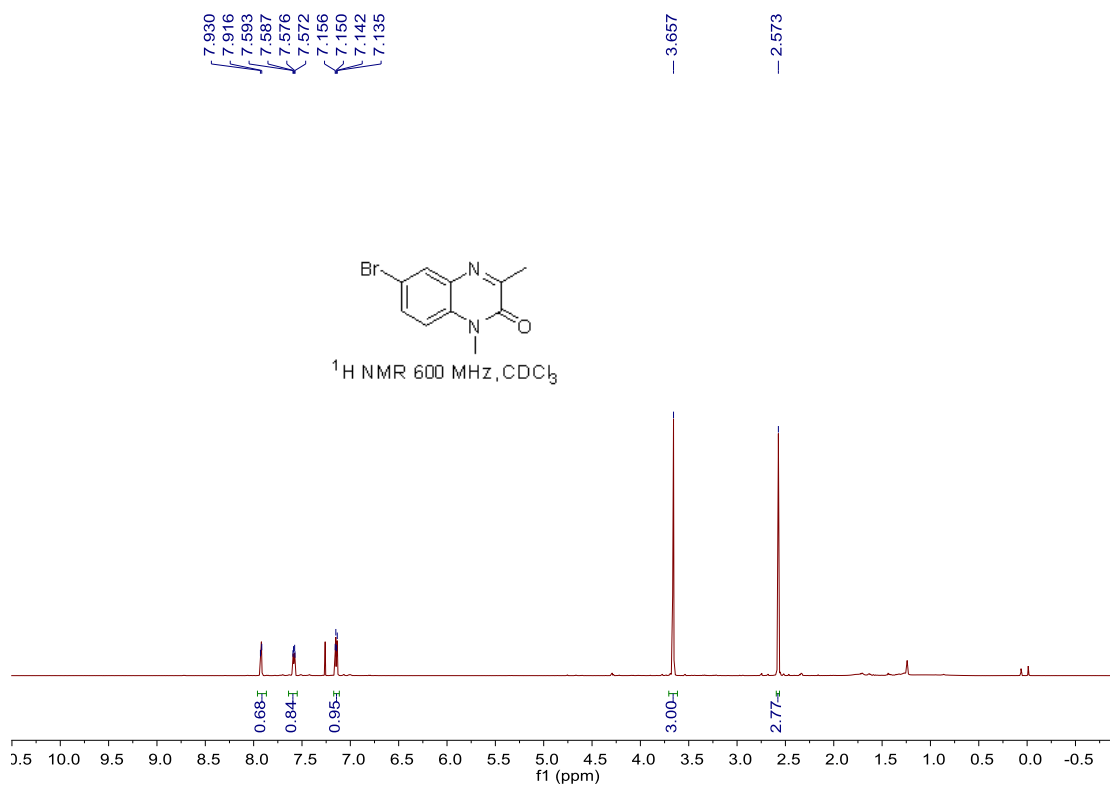
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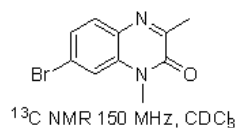
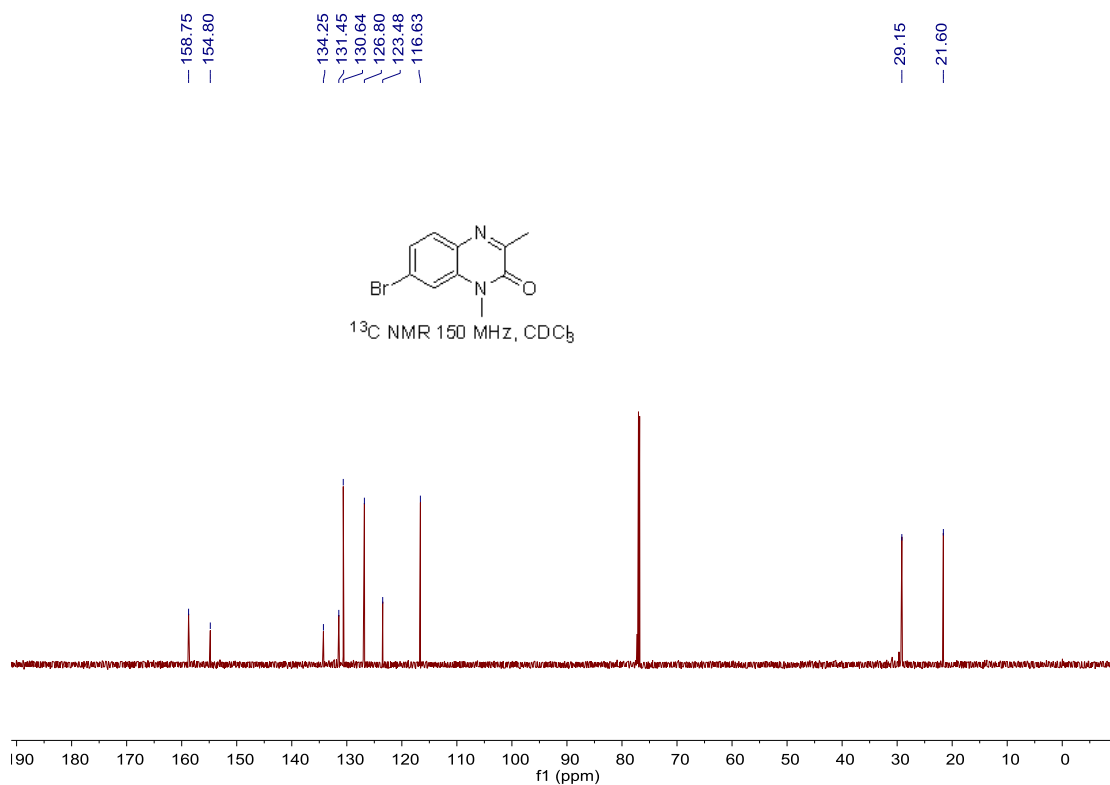
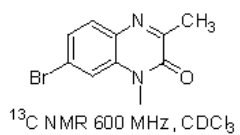
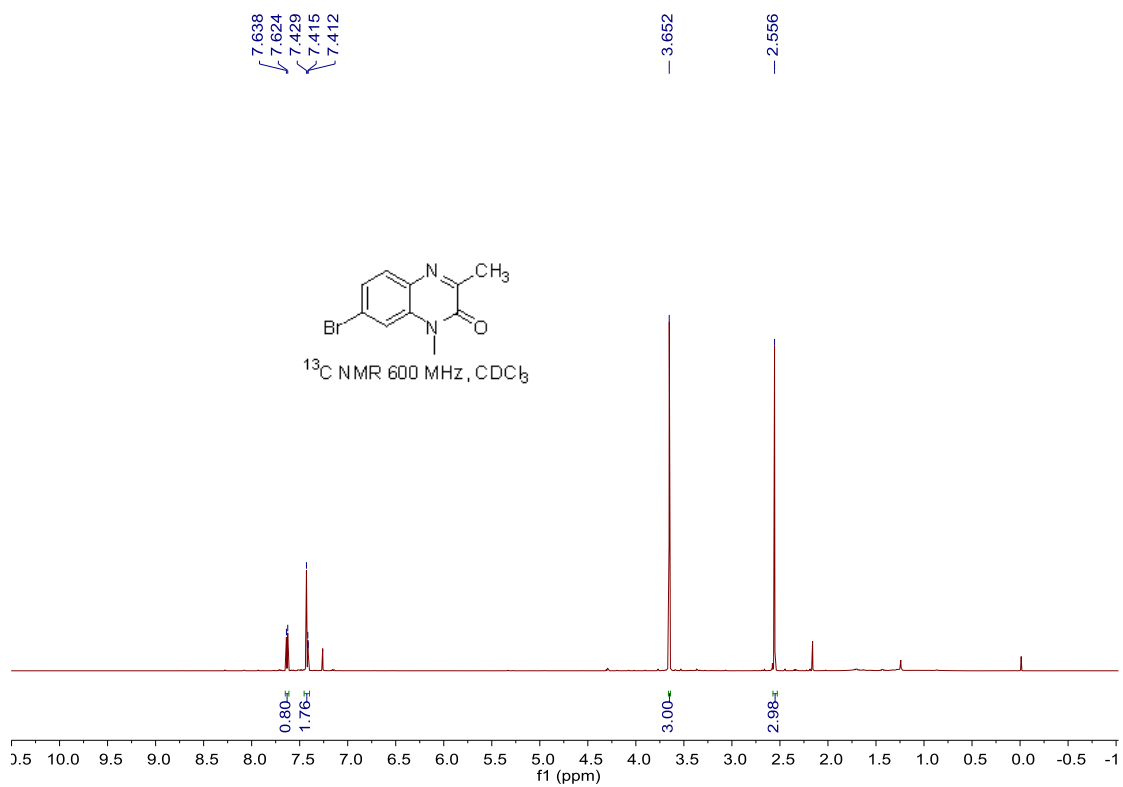
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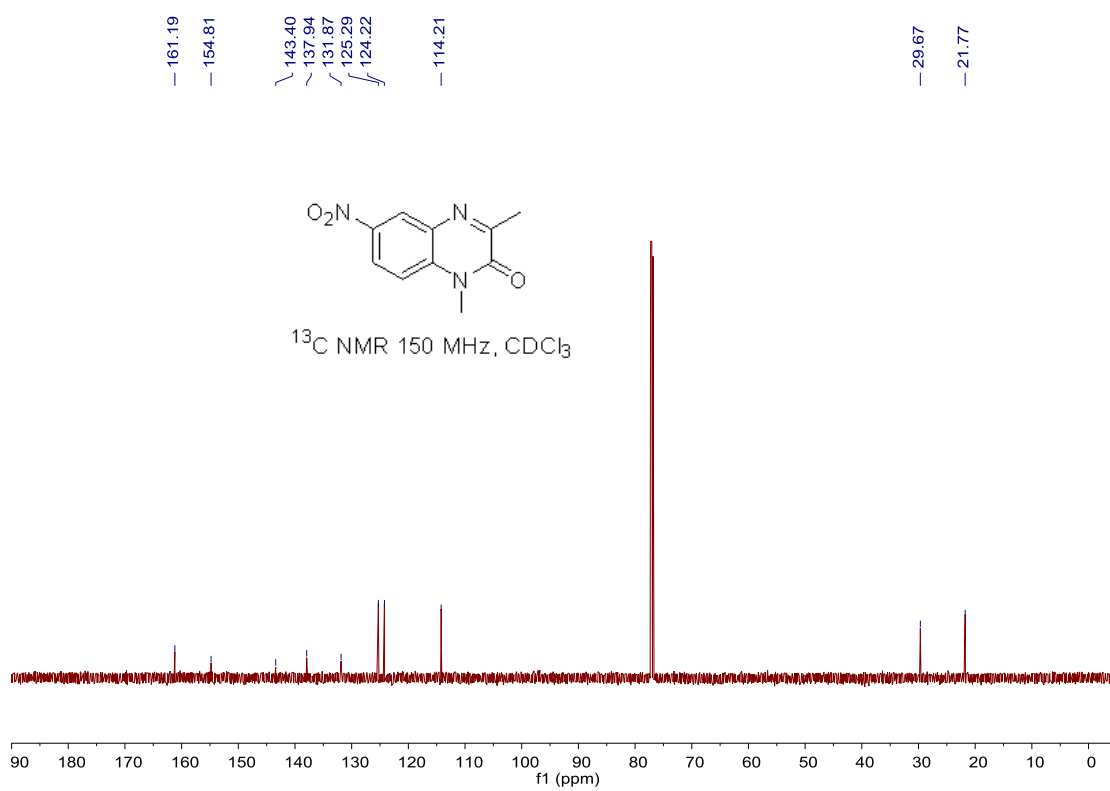
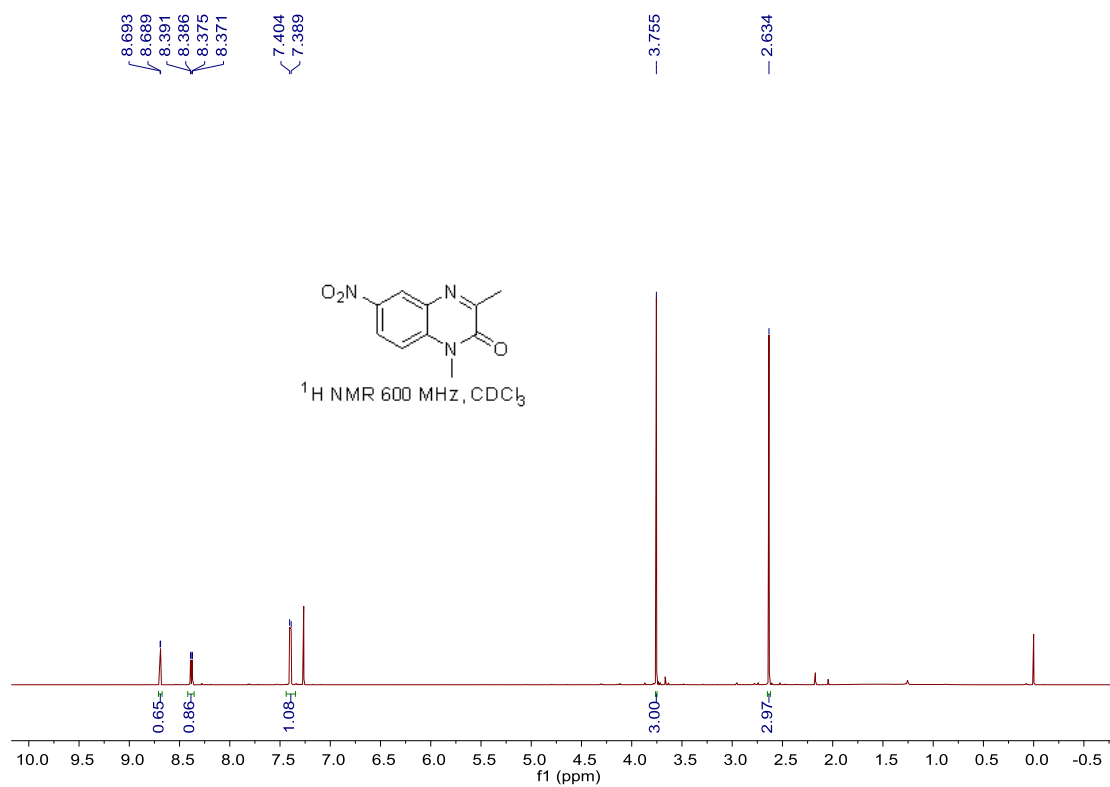
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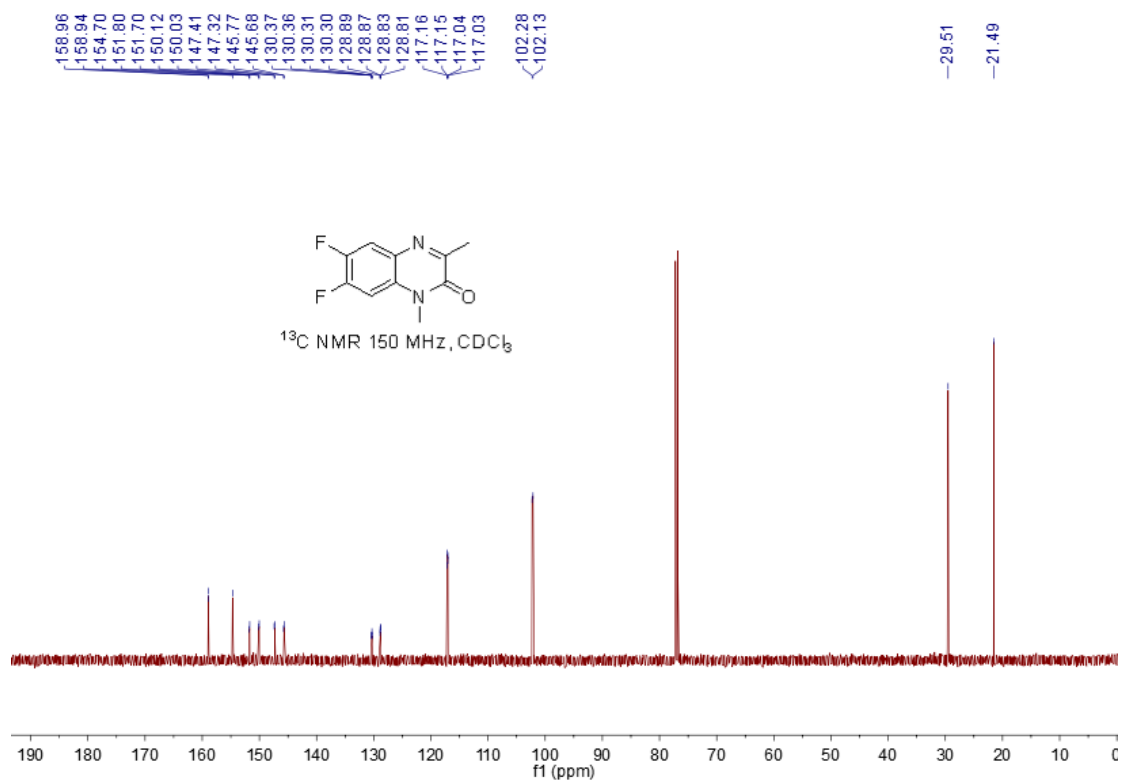
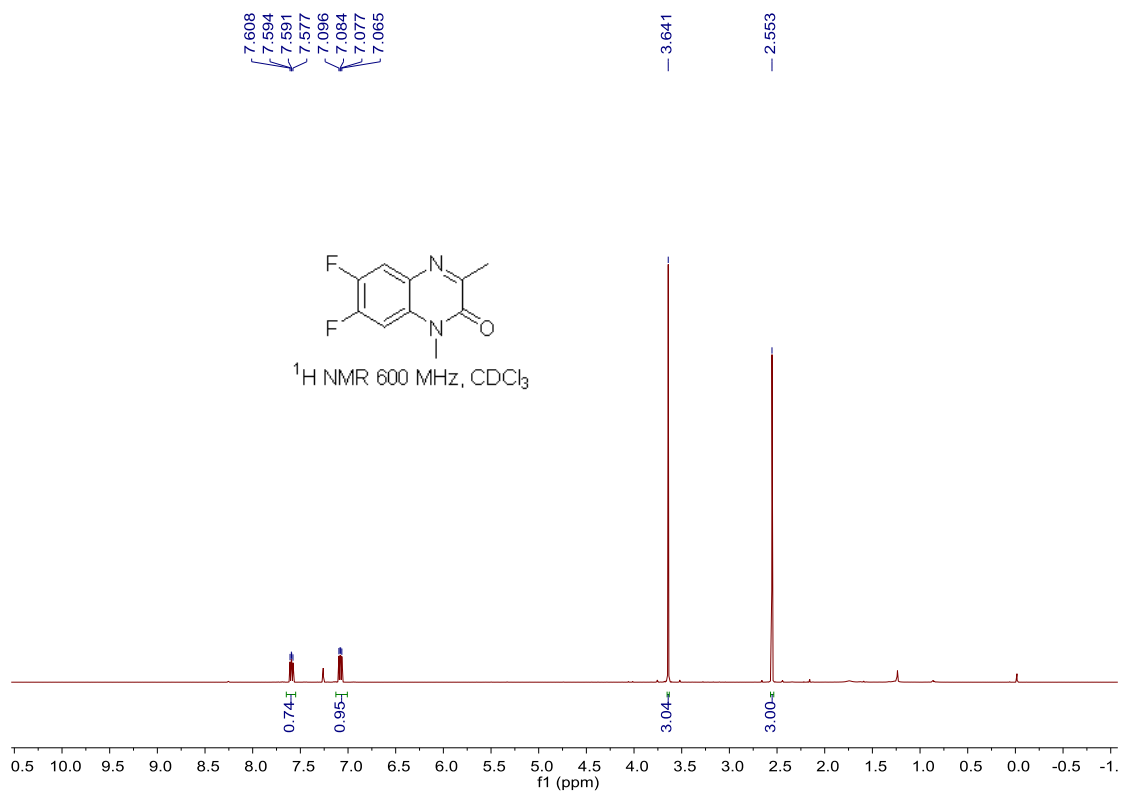
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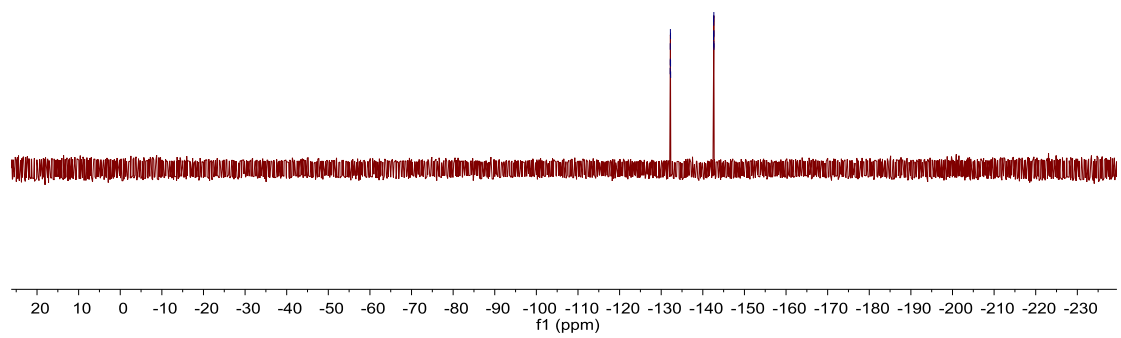
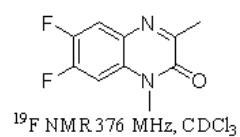
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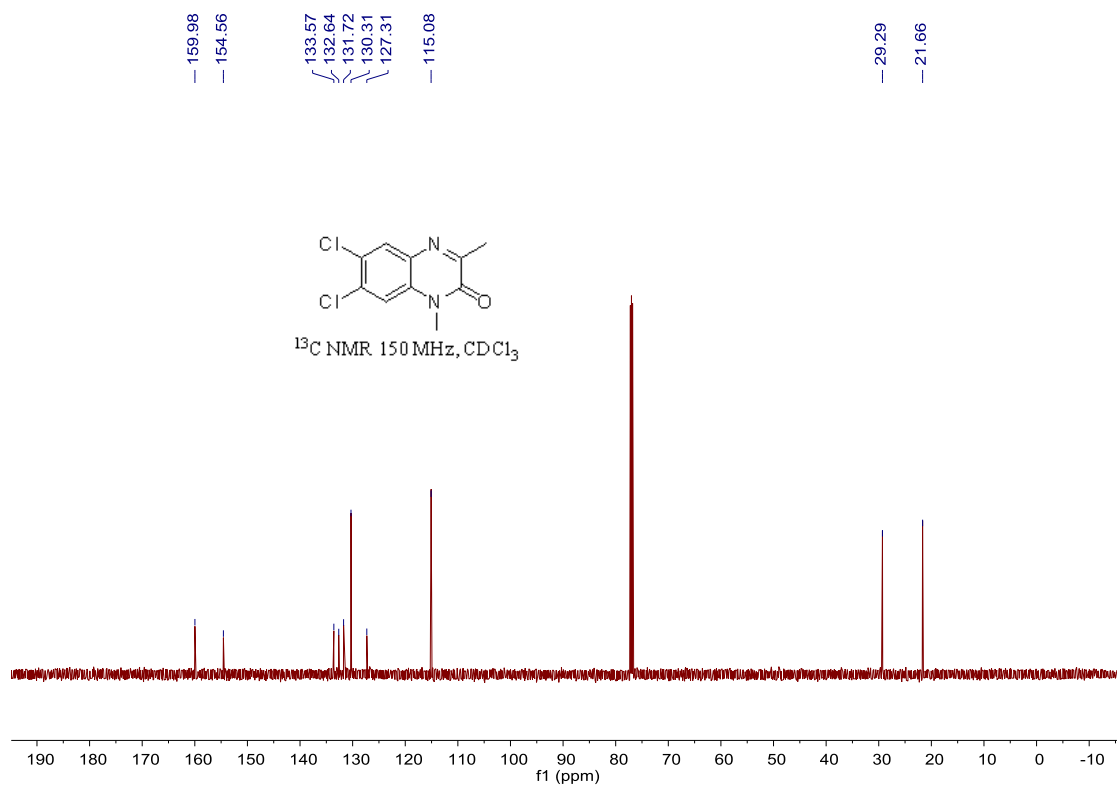
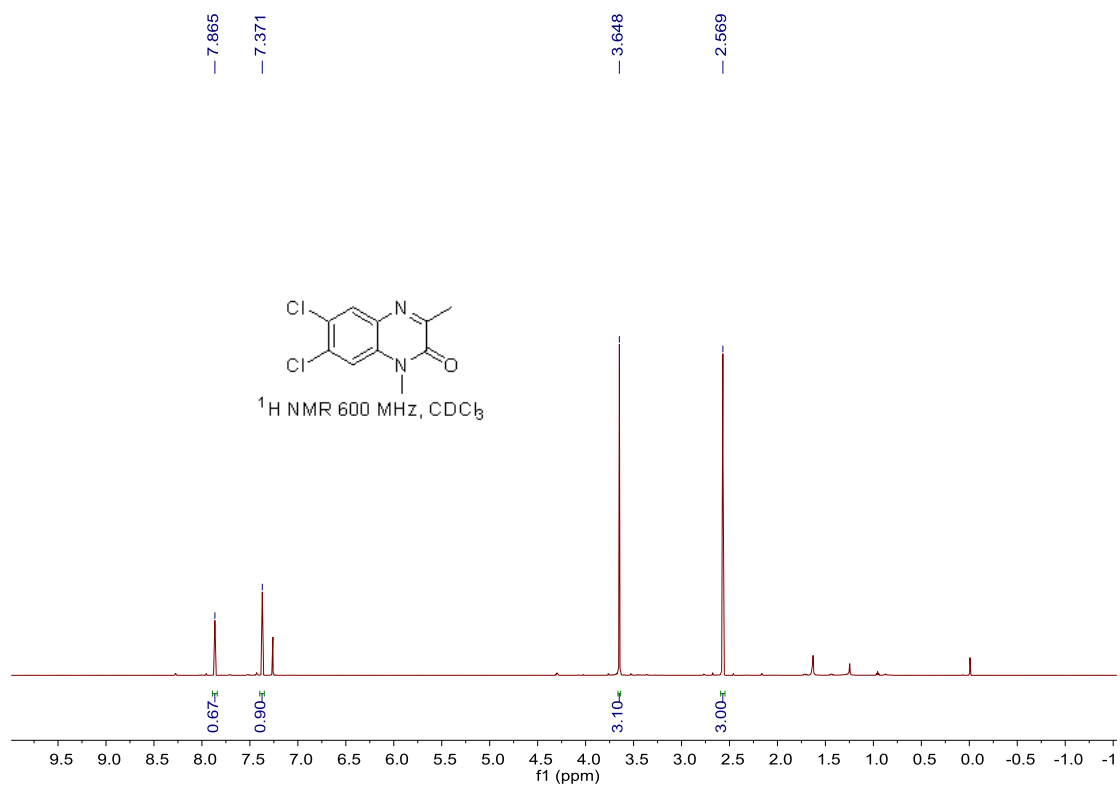
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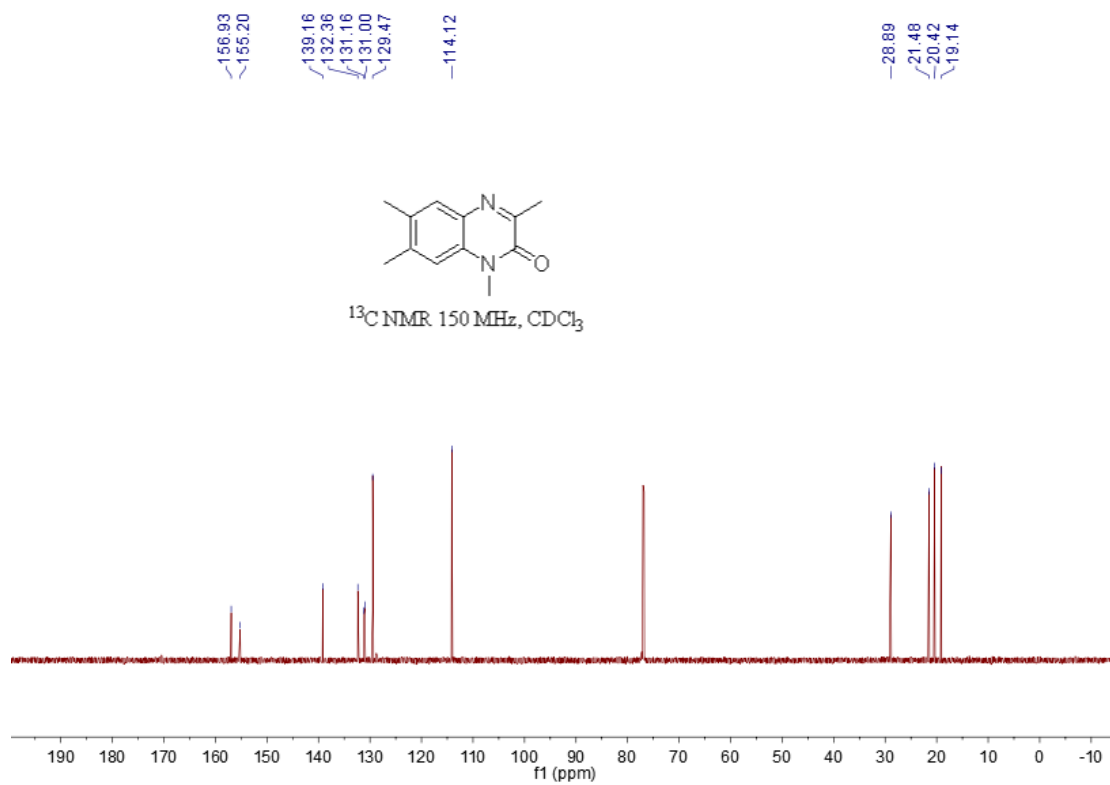
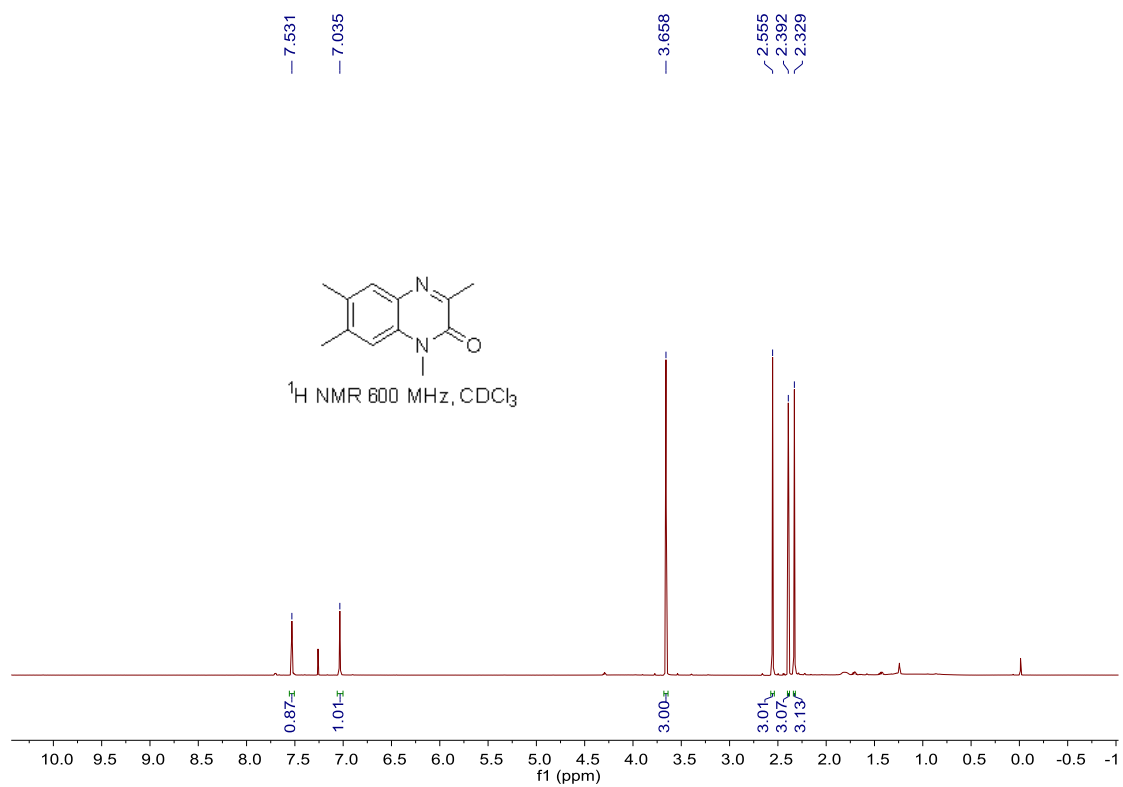
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-142.68



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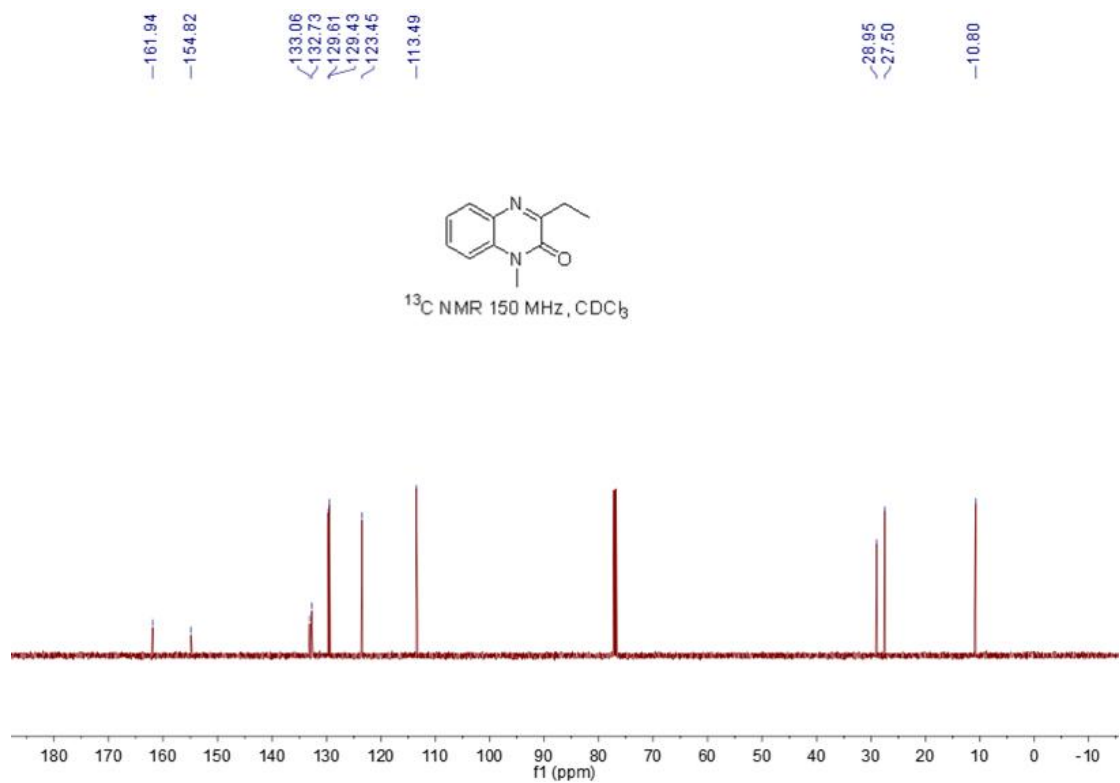
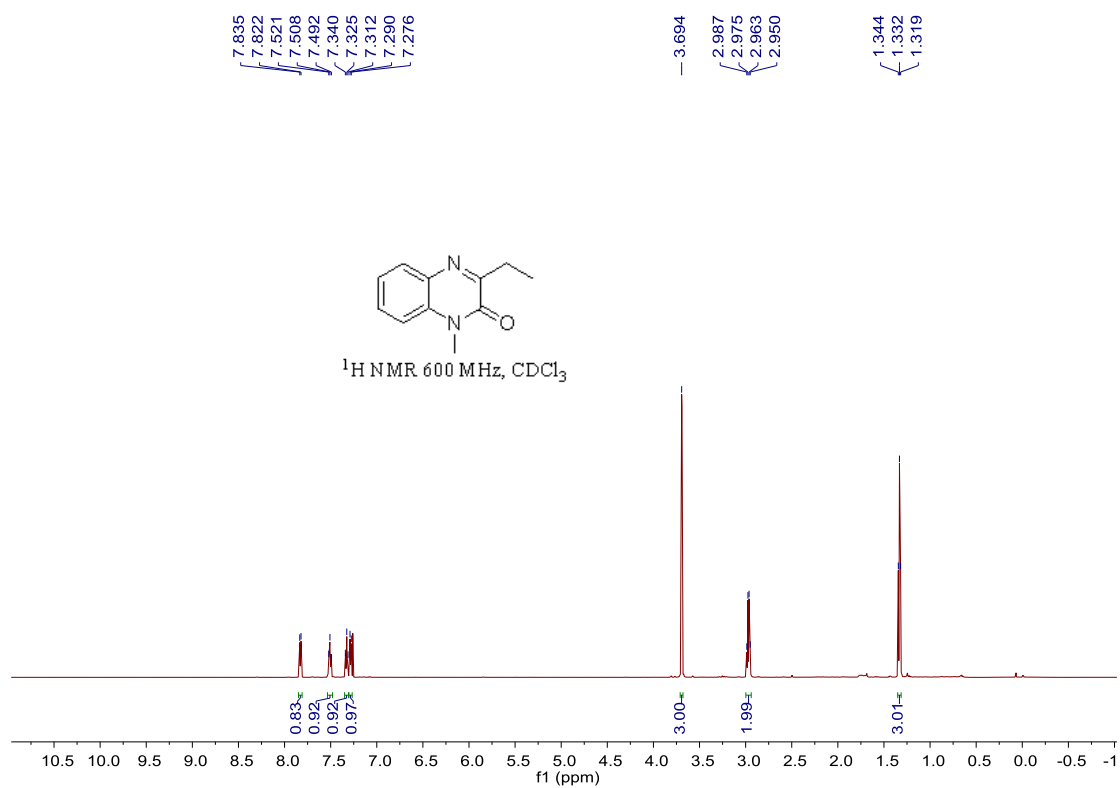


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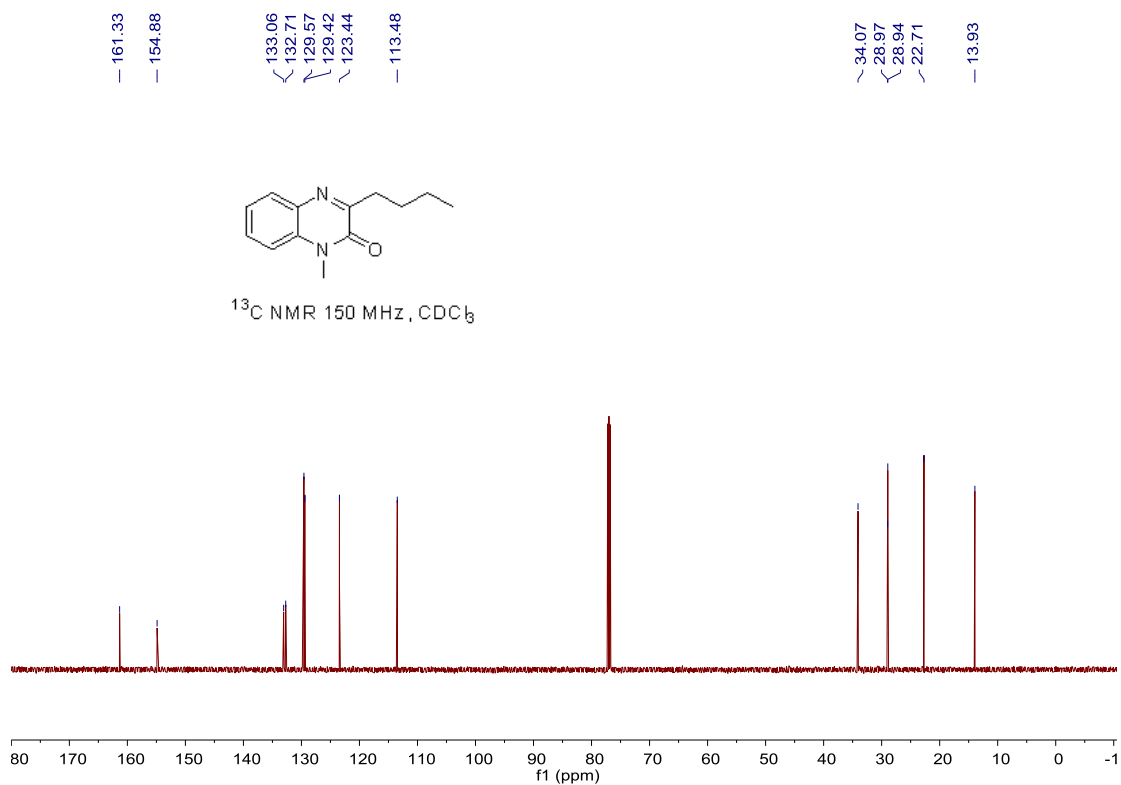
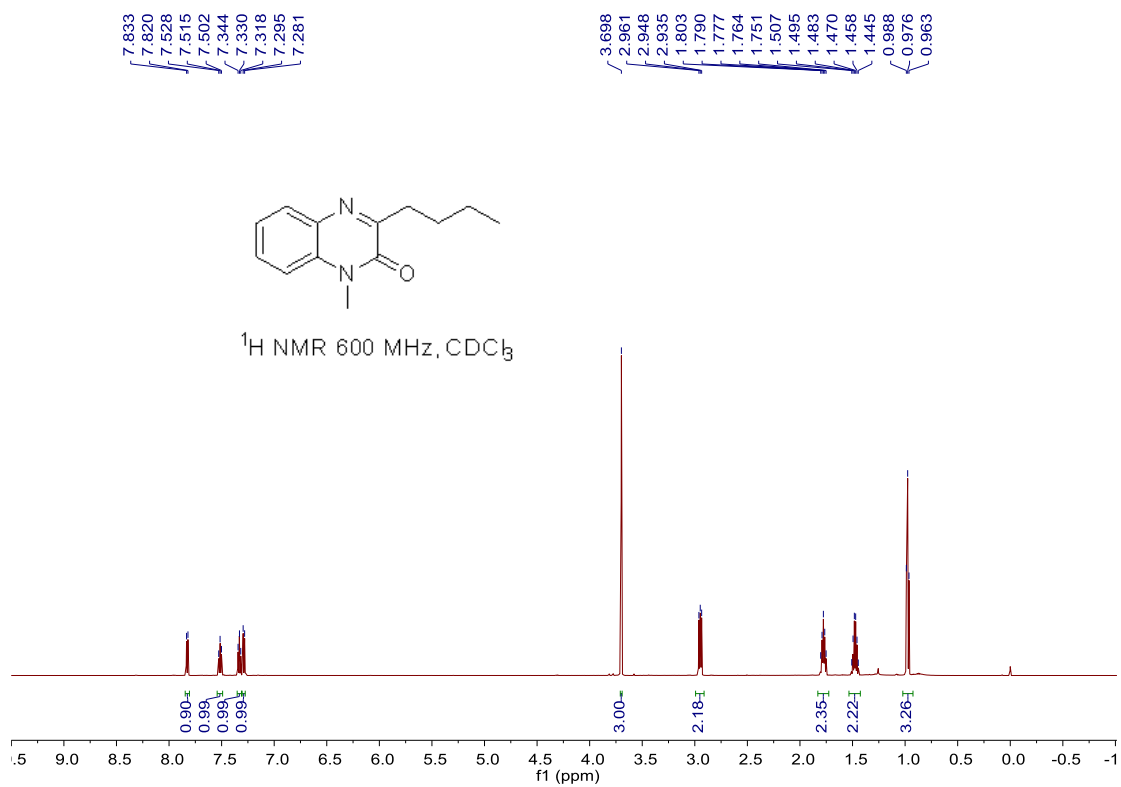


6. NMR copies of compounds 5.

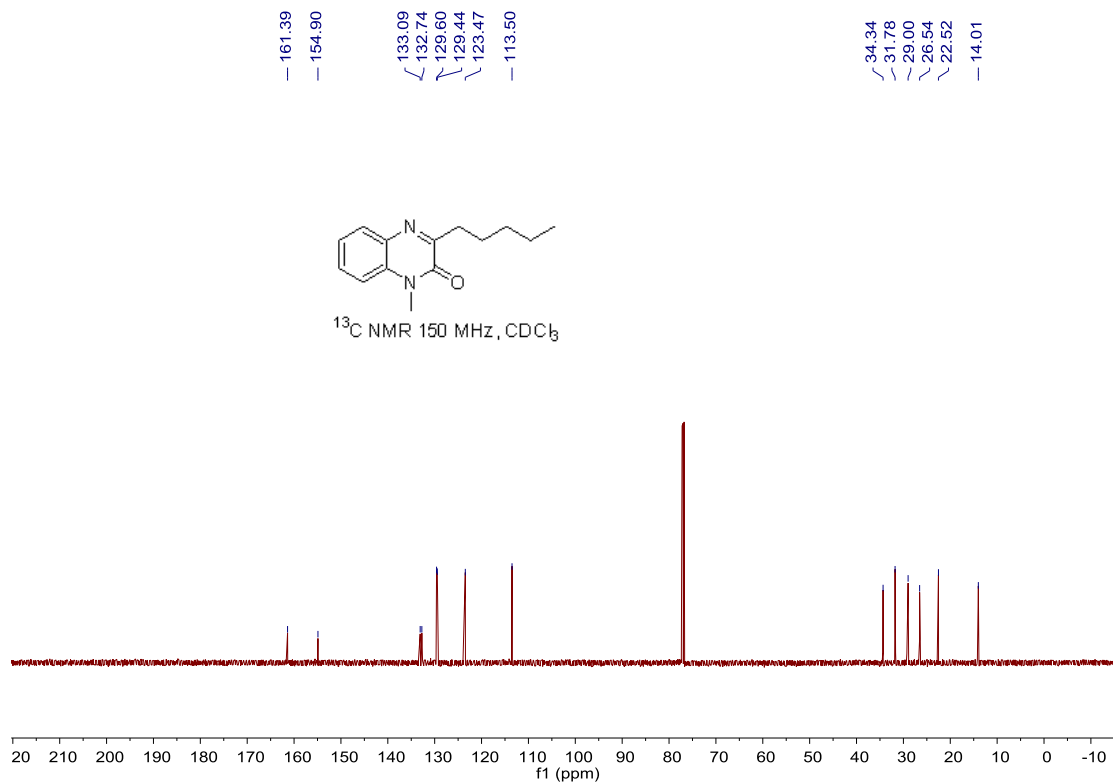
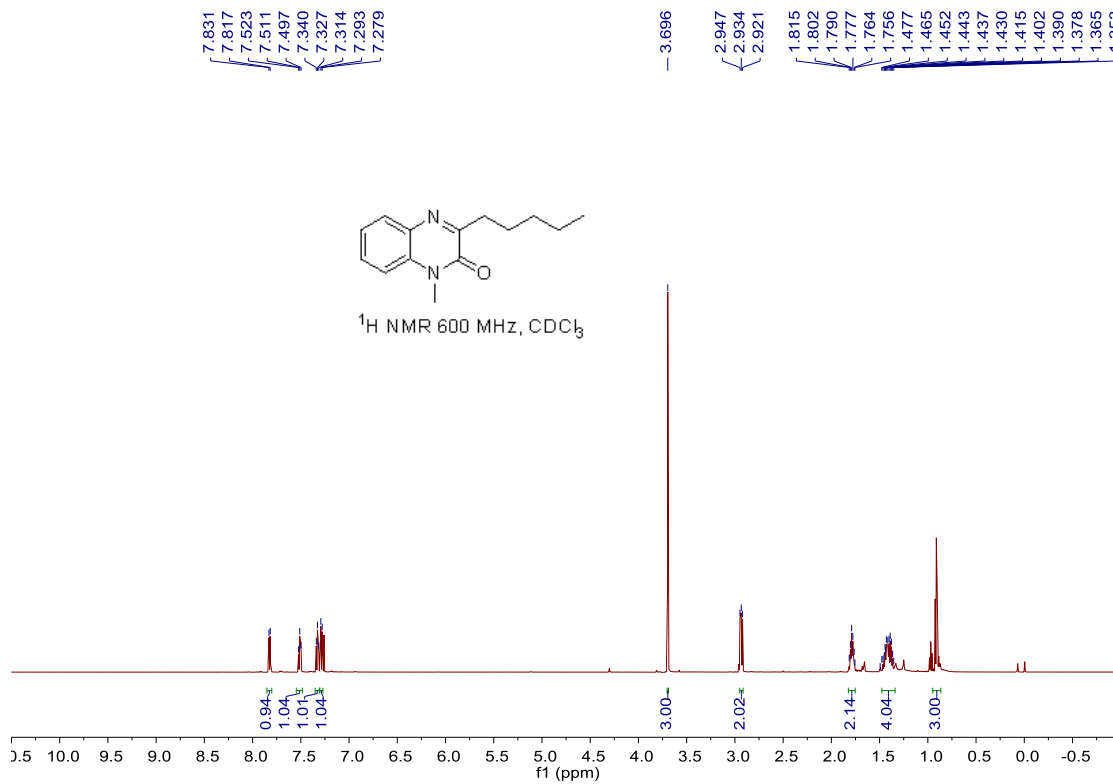
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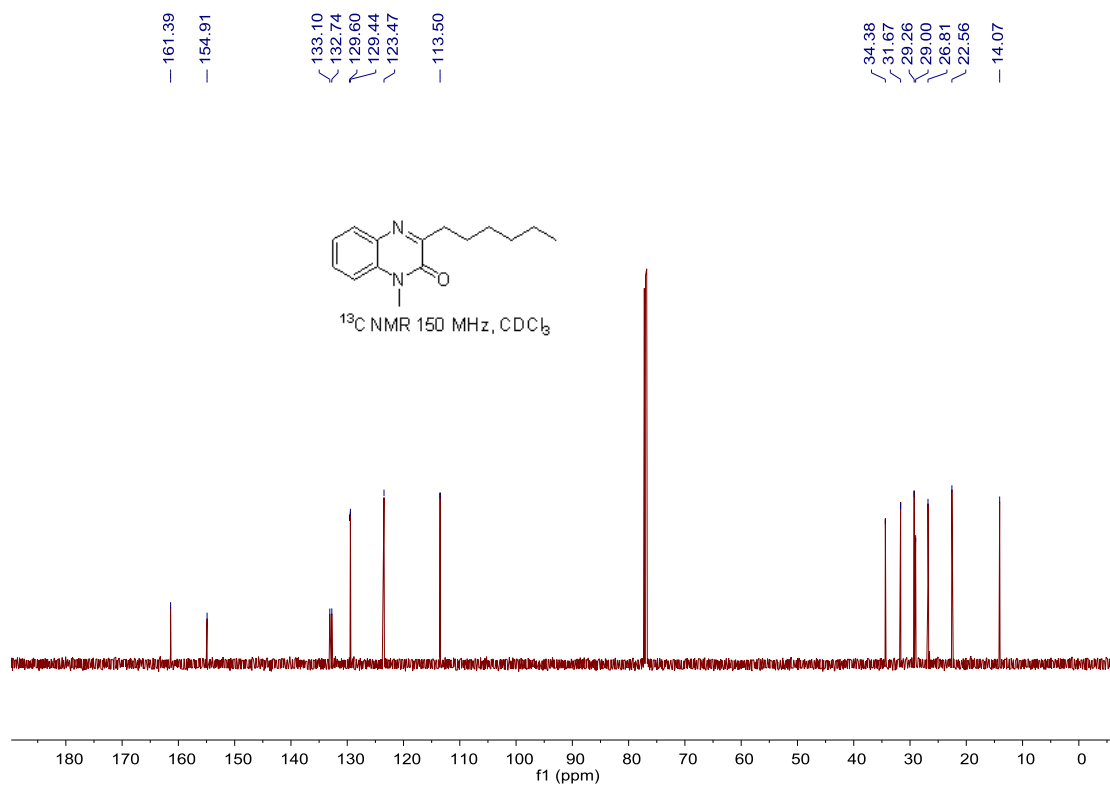
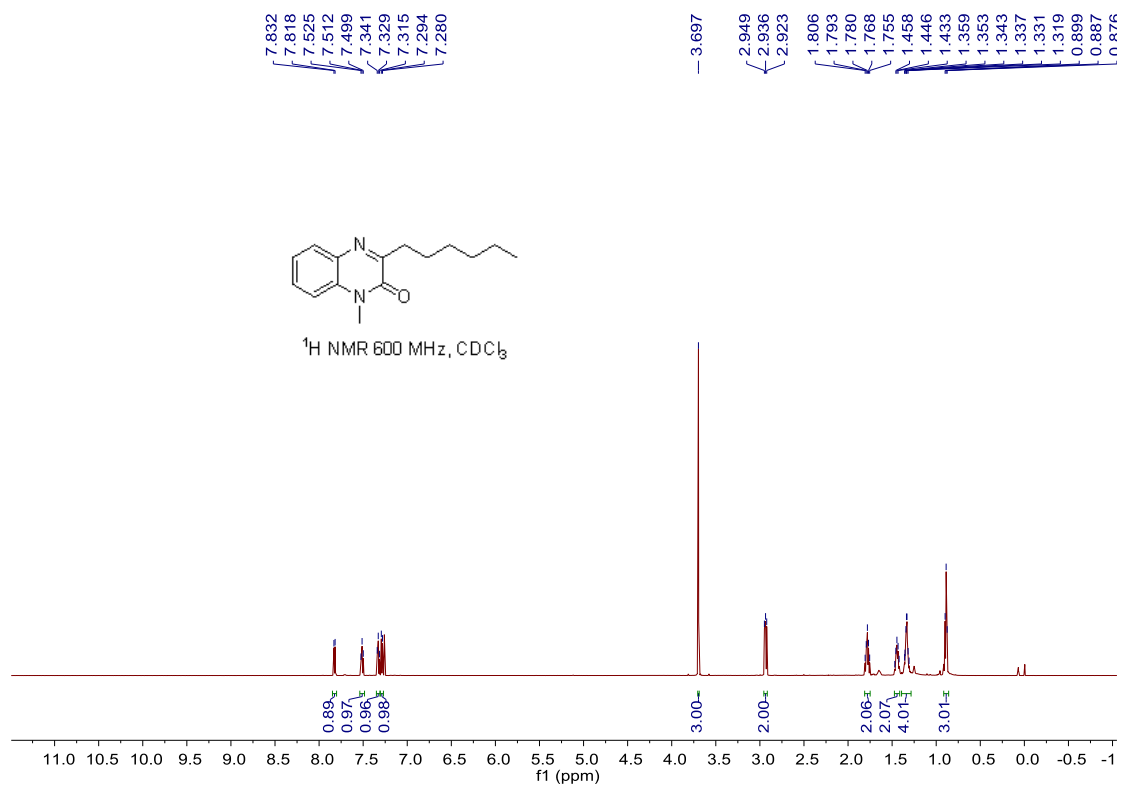
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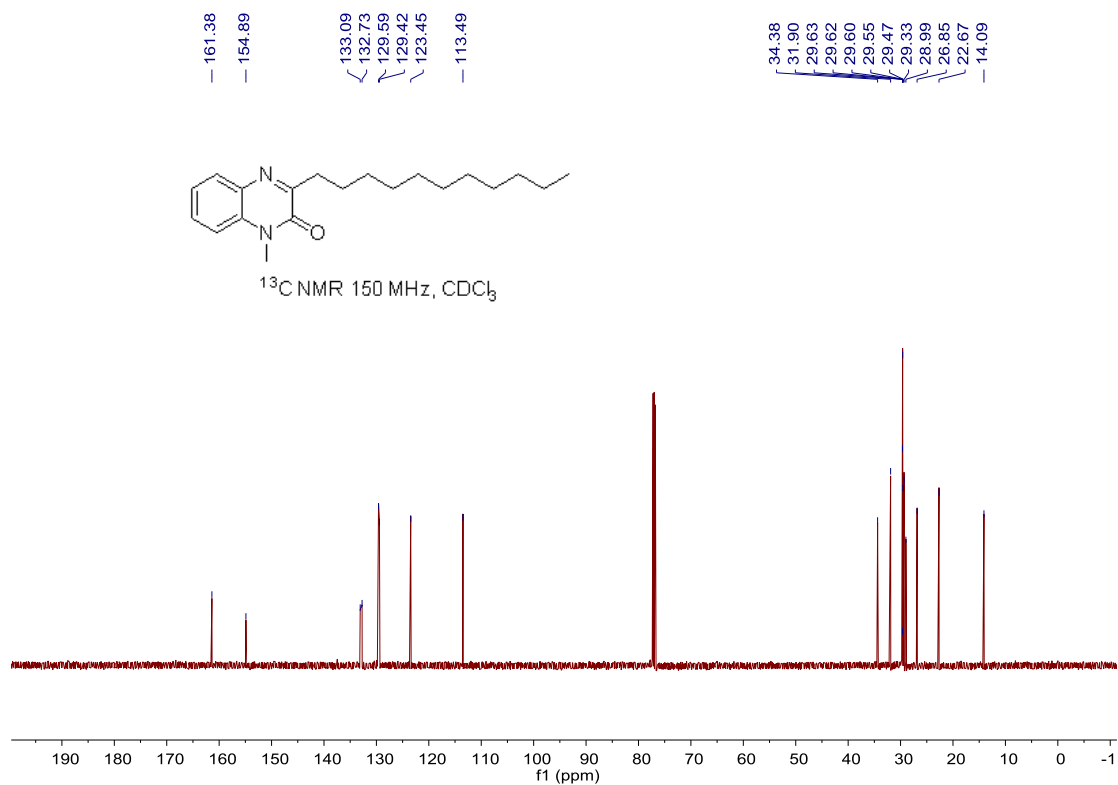
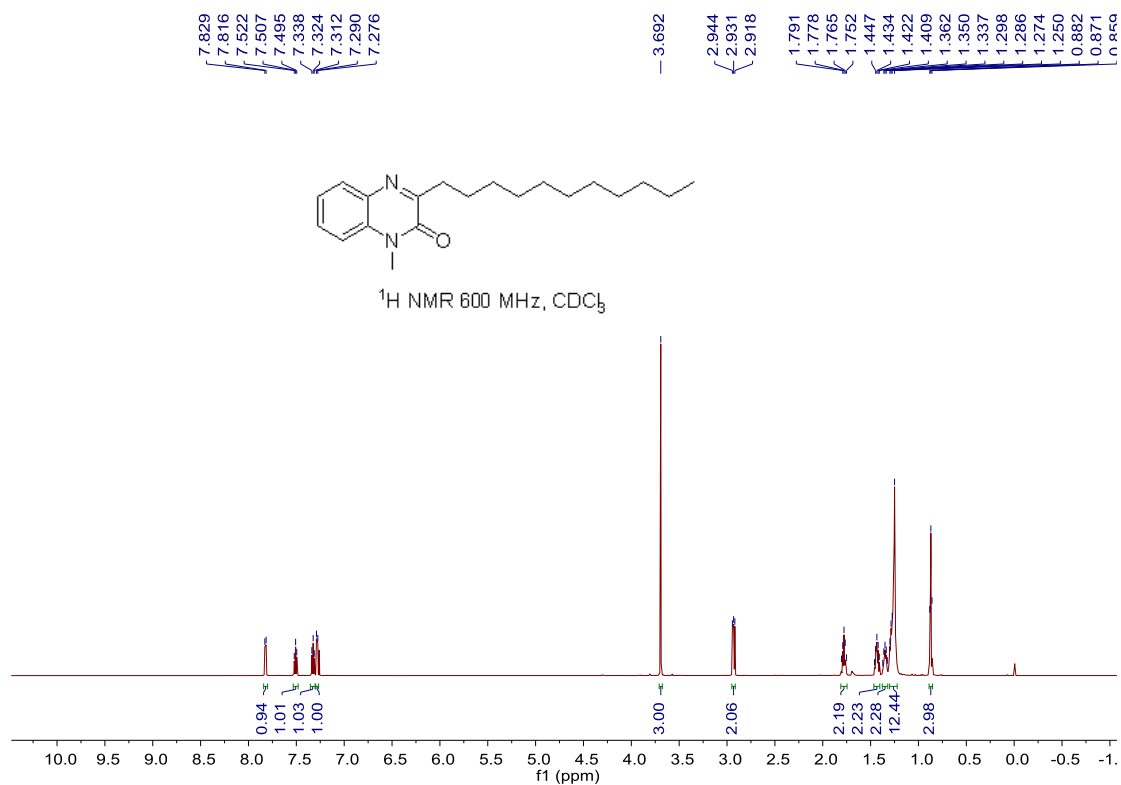
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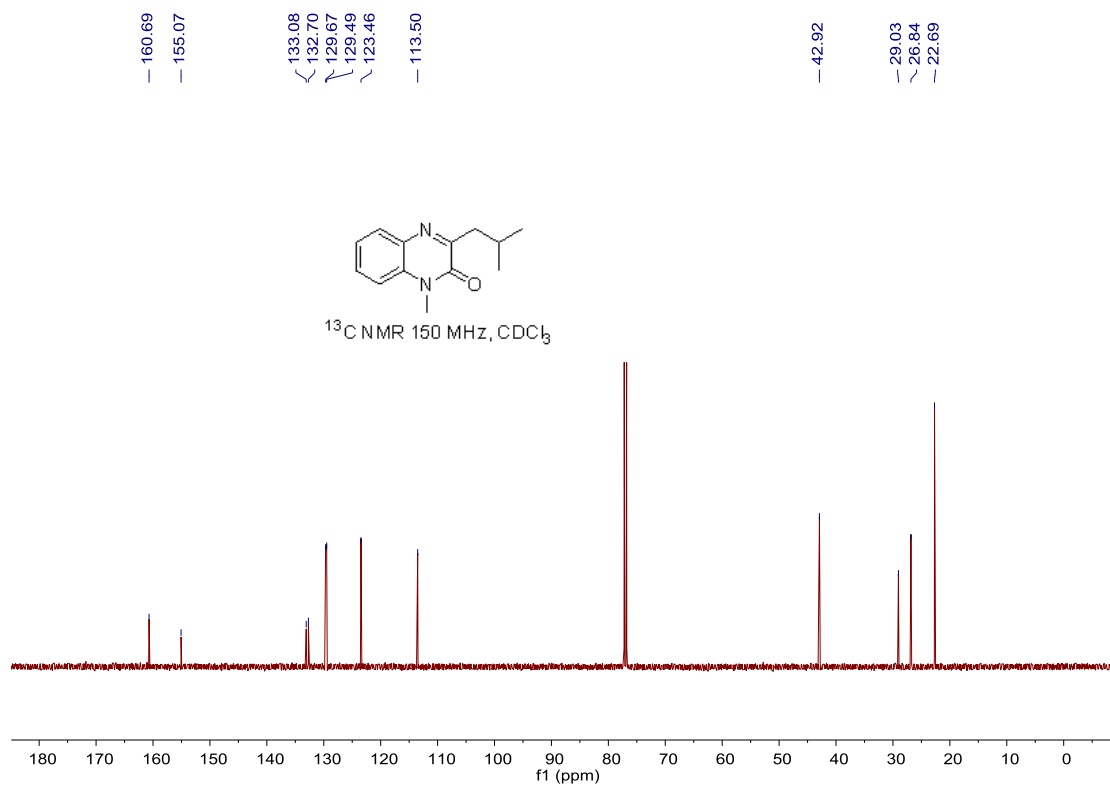
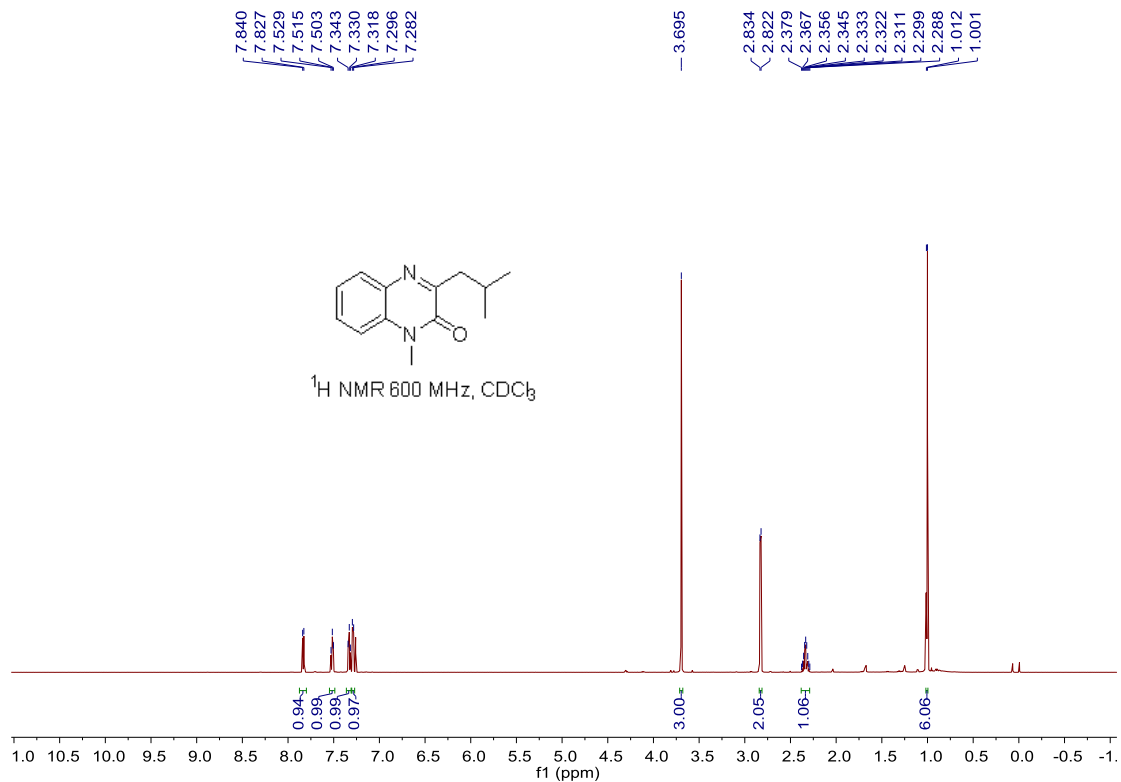
NMR copies of compound **5d**:



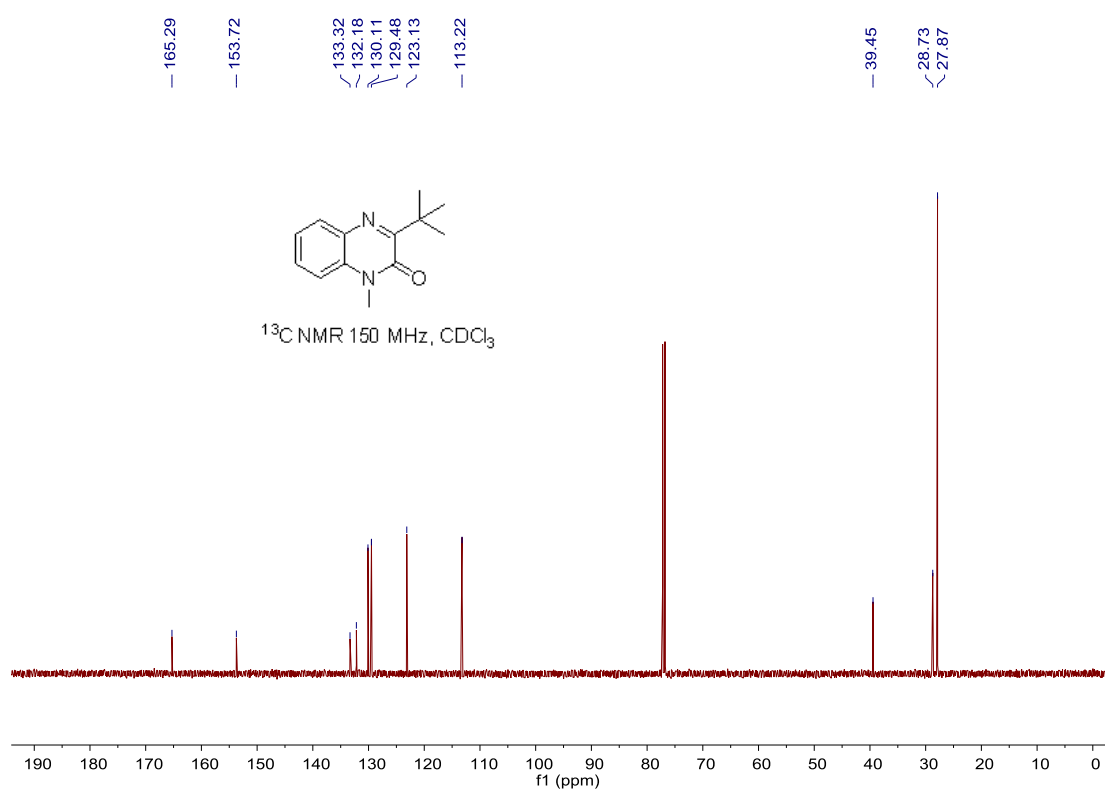
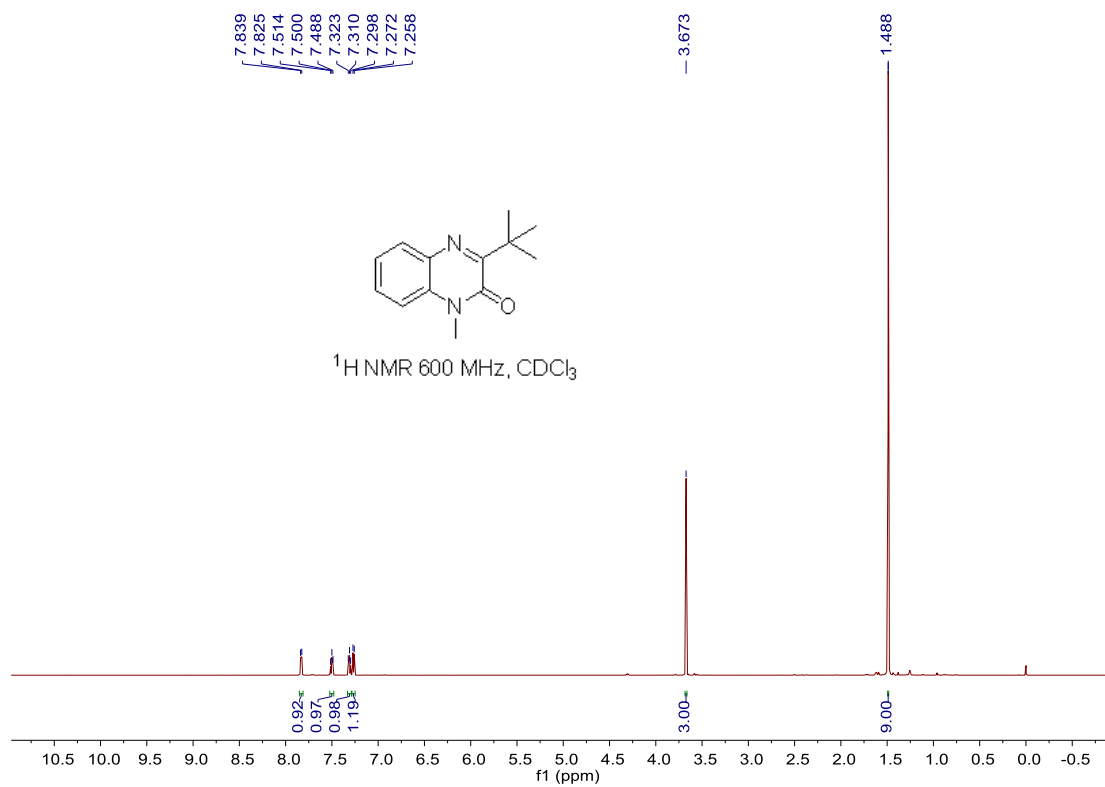
NMR copies of compound **5e**:



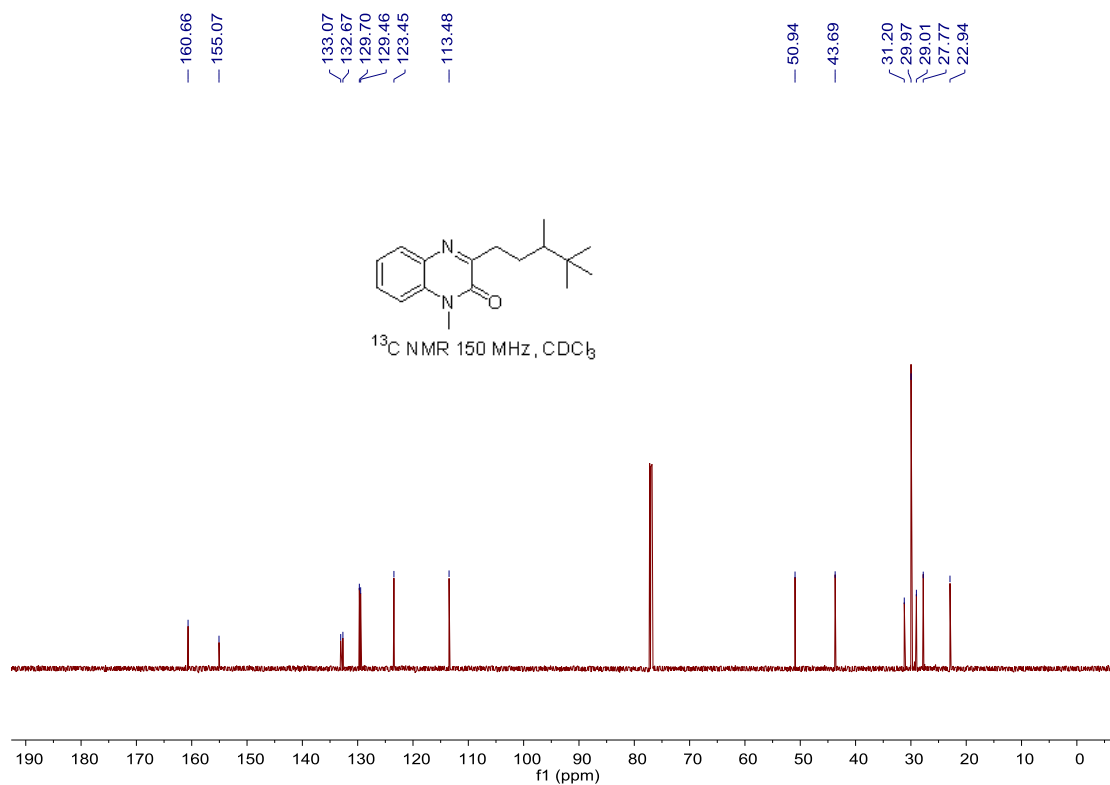
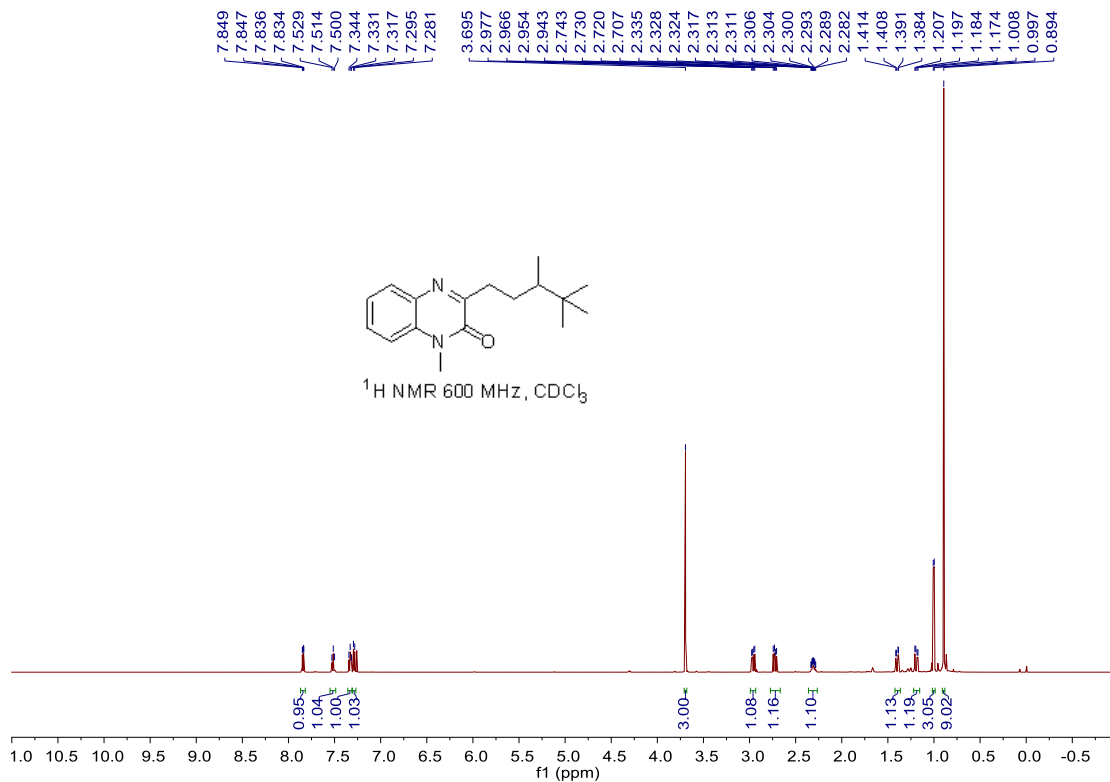
NMR copies of compound **5f**:



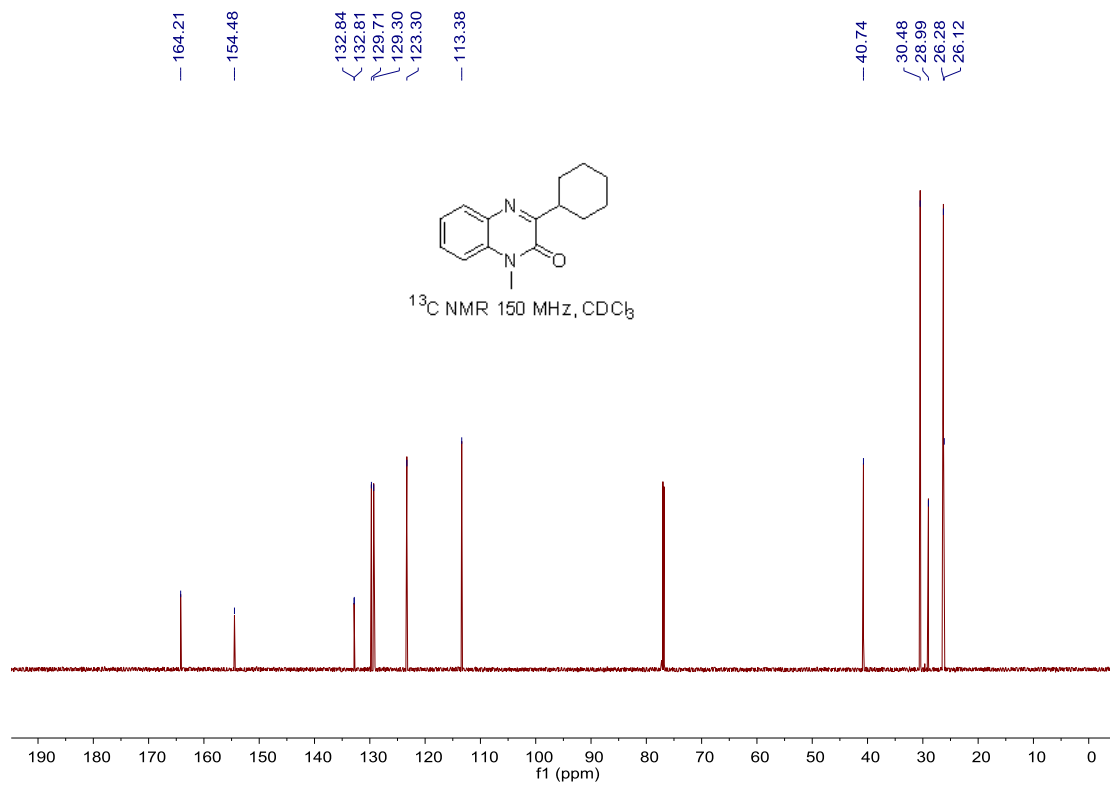
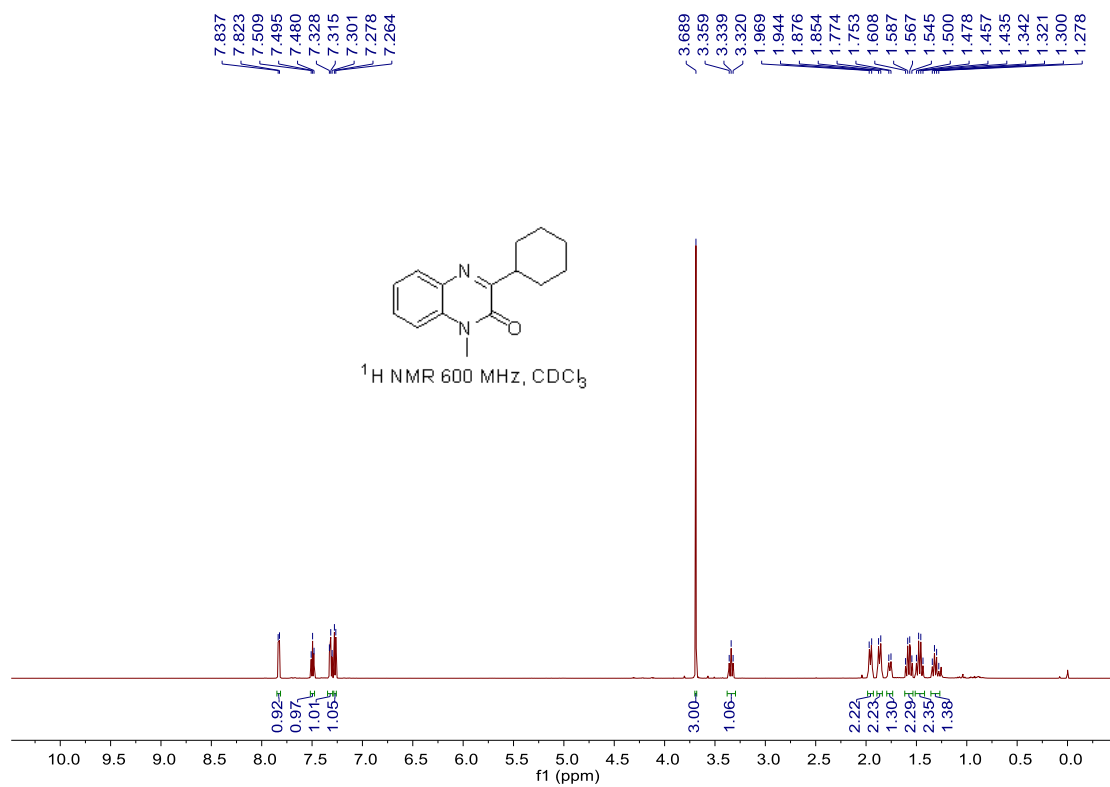
NMR copies of compound **5g**:



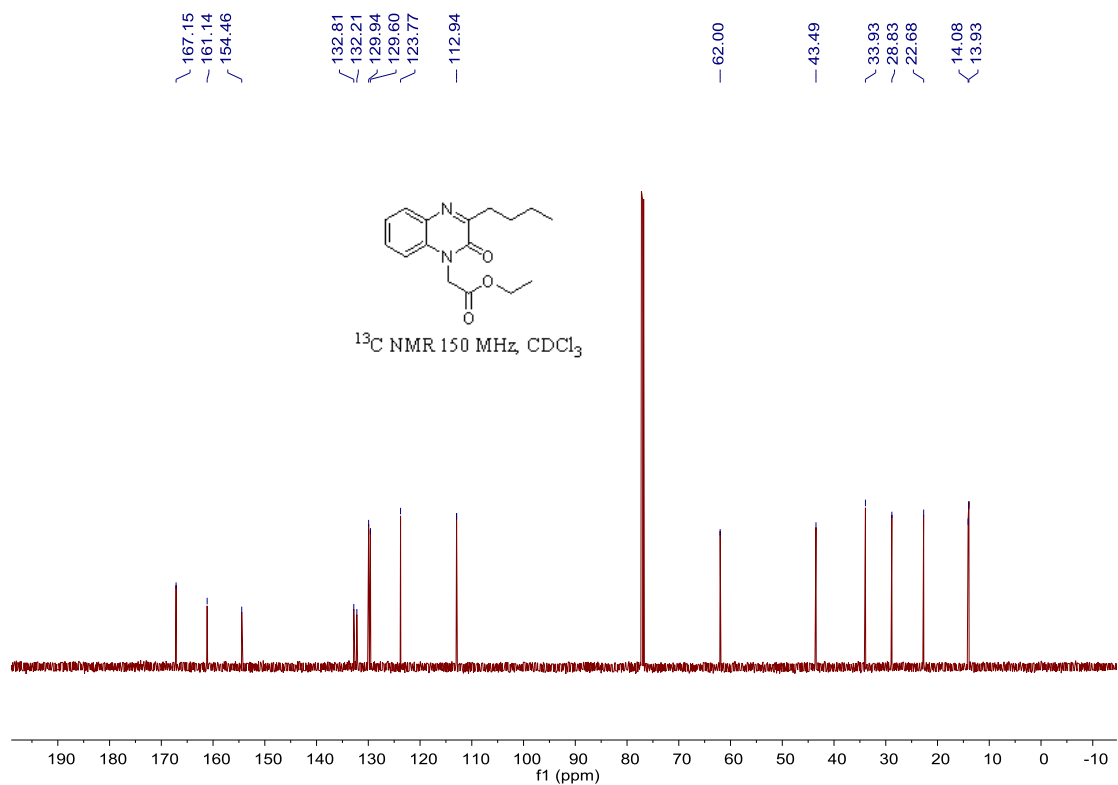
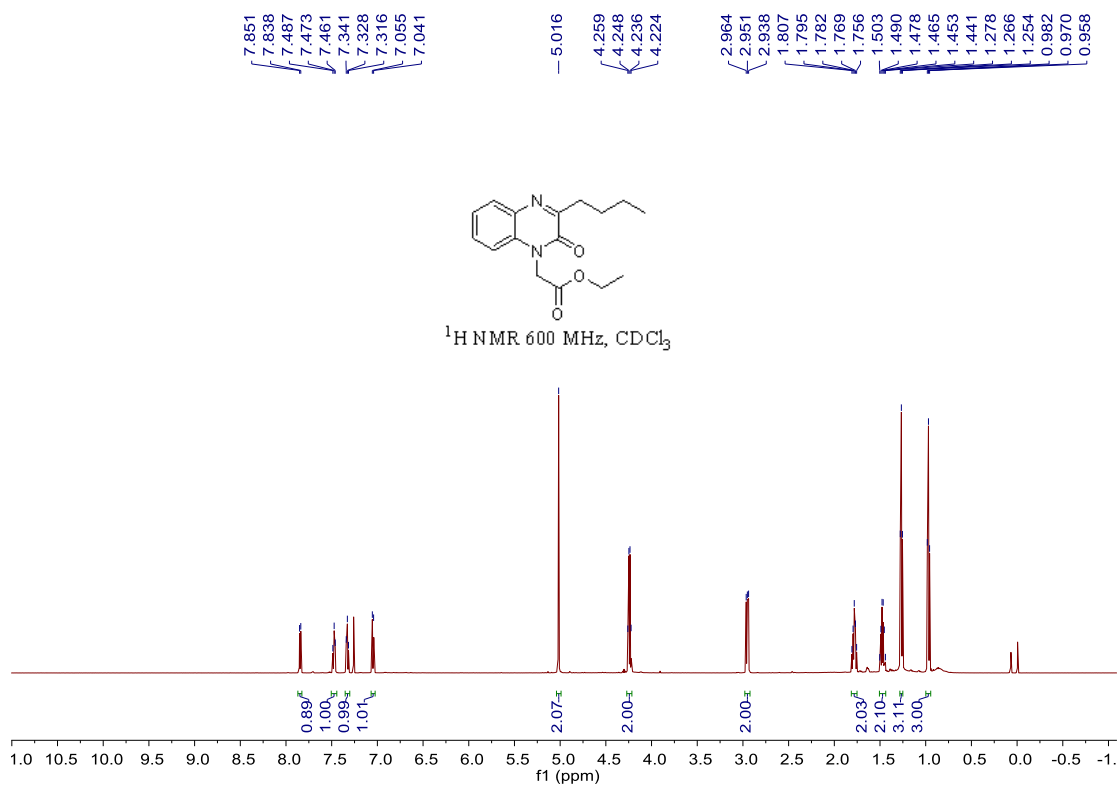
NMR copies of compound **5h**:



NMR copies of compound **5i**:



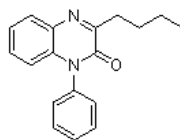
NMR copies of compound **5j**:



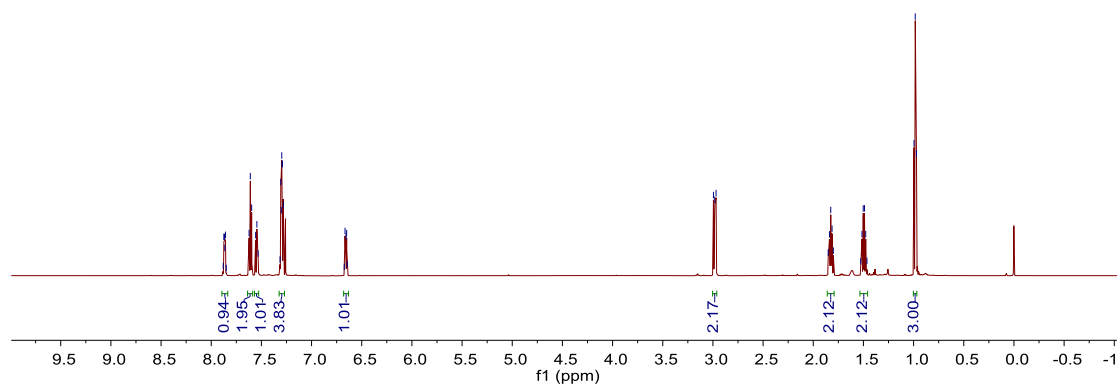
NMR copies of compound **5k**:

7.874
7.868
7.865
7.858
7.623
7.610
7.597
7.558
7.545
7.533
7.307
7.302
7.297
7.295
7.291
7.281
6.674
6.666
6.656
6.650
6.644

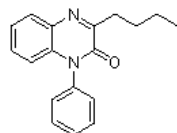
2.995
2.982
2.969
1.851
1.839
1.826
1.813
1.800
1.527
1.515
1.502
1.490
1.477
1.465
0.996
0.984
0.971



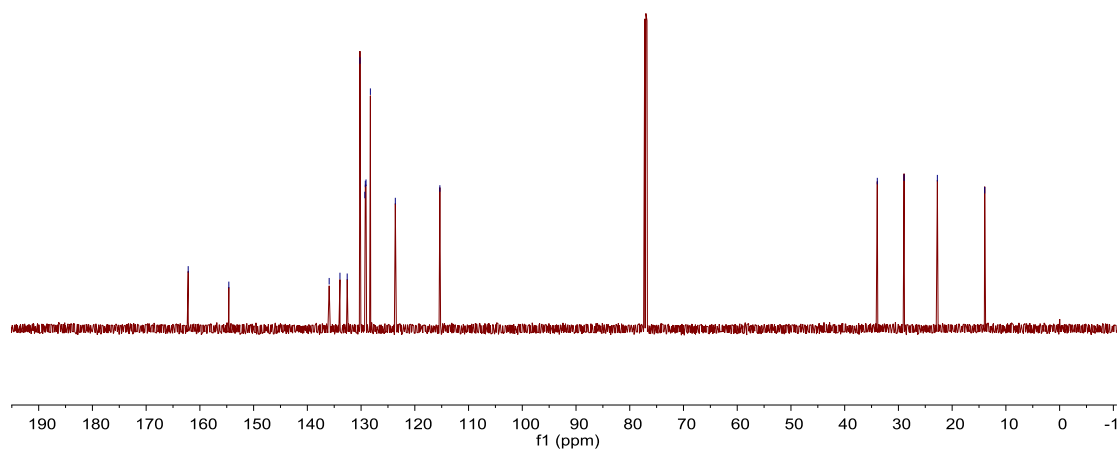
^1H NMR 600 MHz, CDCl_3



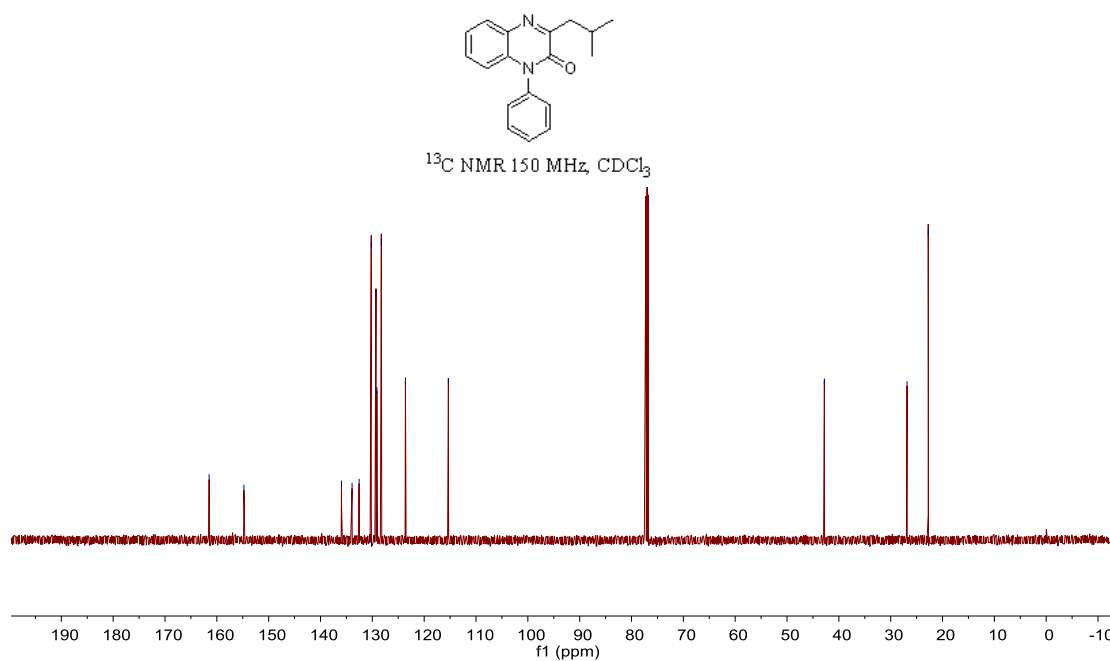
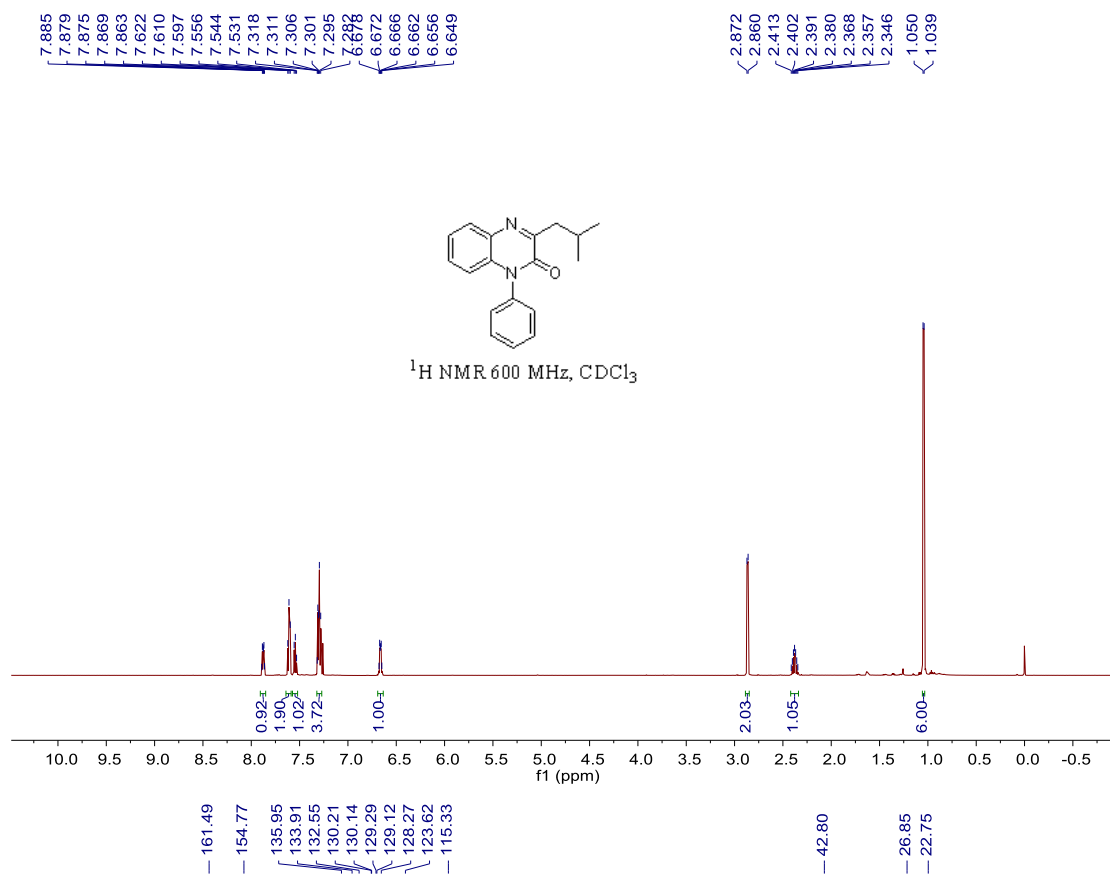
162.17
154.61
135.94
133.93
132.58
130.21
129.30
129.21
129.08
128.27
123.63
115.34
33.93
28.95
22.75
13.94



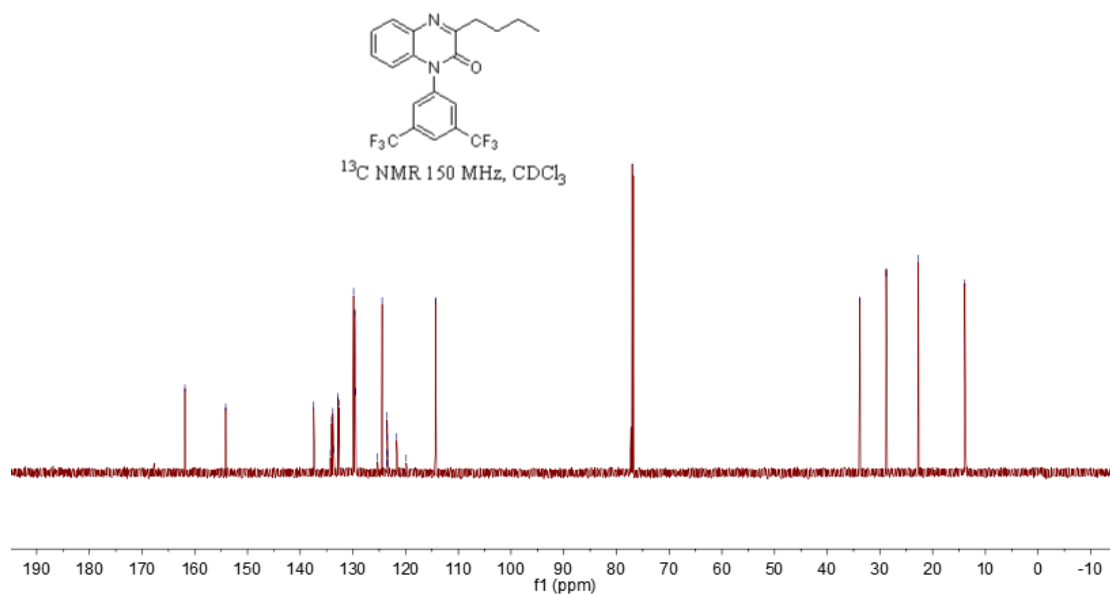
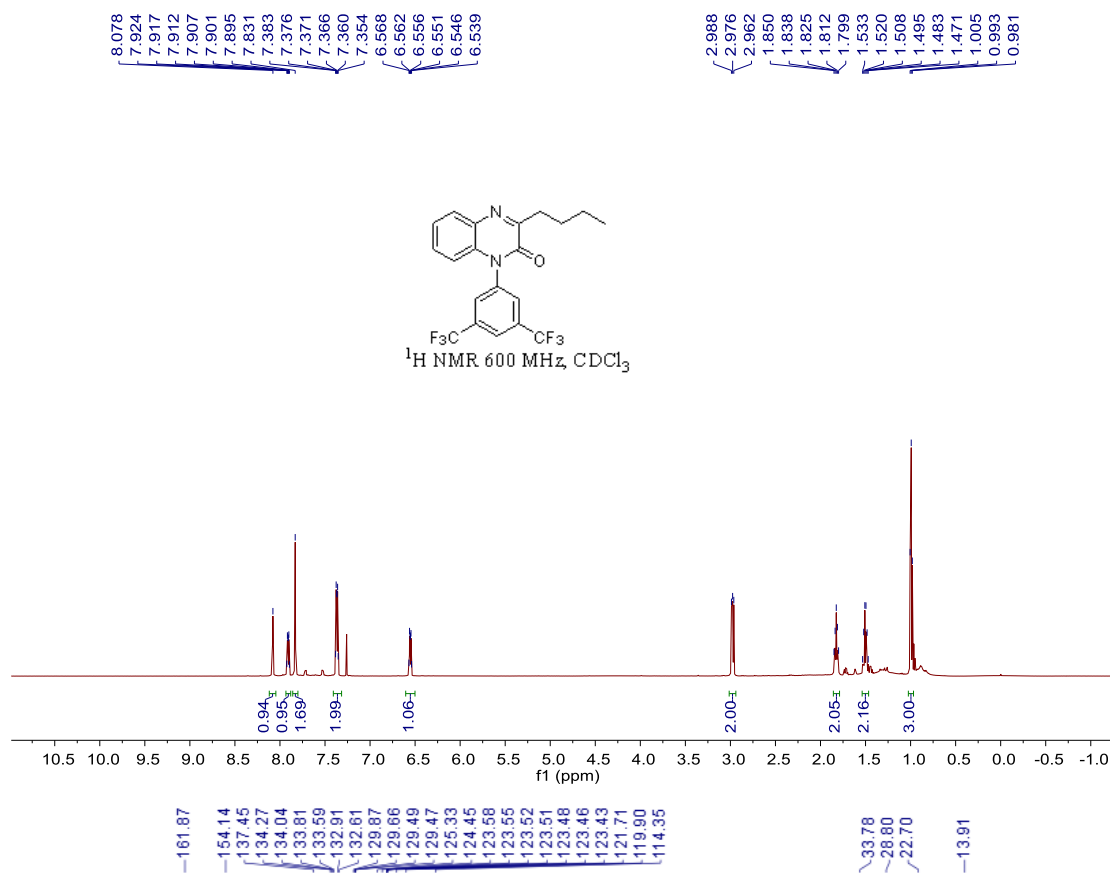
^{13}C NMR 150 MHz, CDCl_3



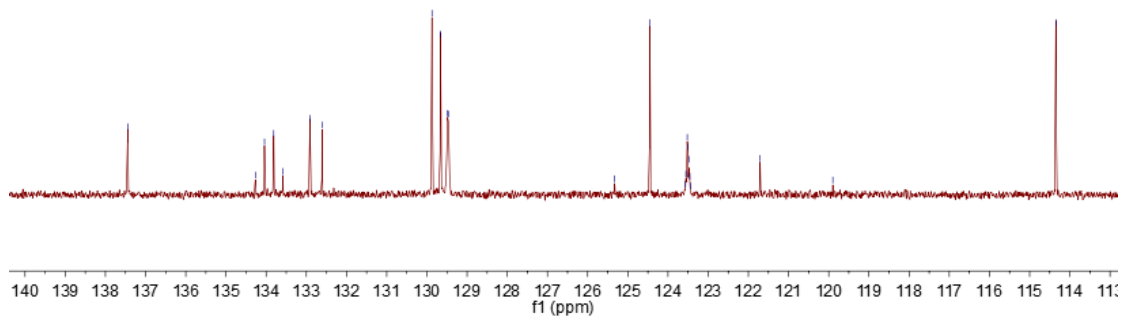
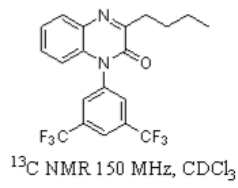
NMR copies of compound 51:



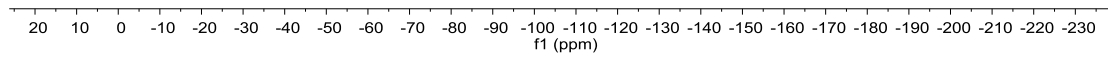
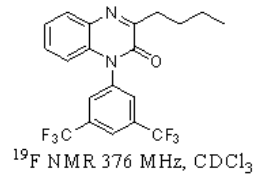
NMR copies of compound **5m**:



137.45
 134.27
 134.04
 133.81
 133.59
 132.91
 132.61
 129.87
 129.66
 129.49
 129.47
 125.33
 124.45
 123.58
 123.55
 123.52
 123.51
 123.48
 123.46
 123.43
 121.71
 119.90
 114.35

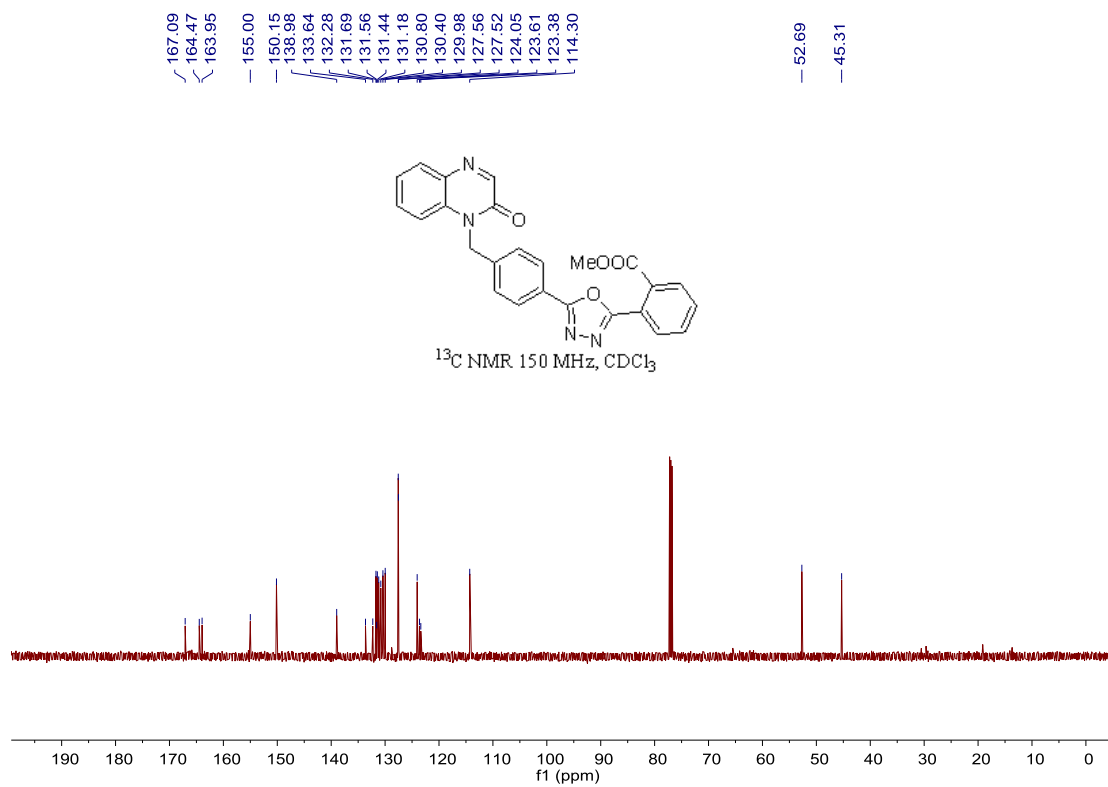
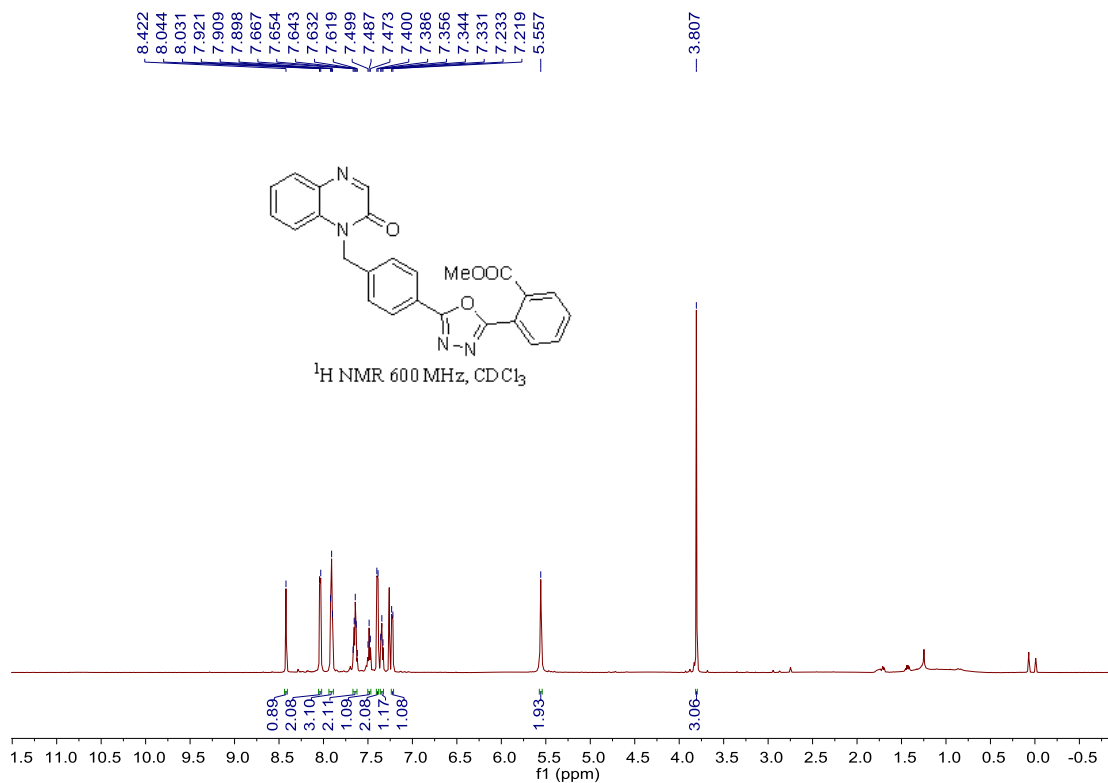


-63.25



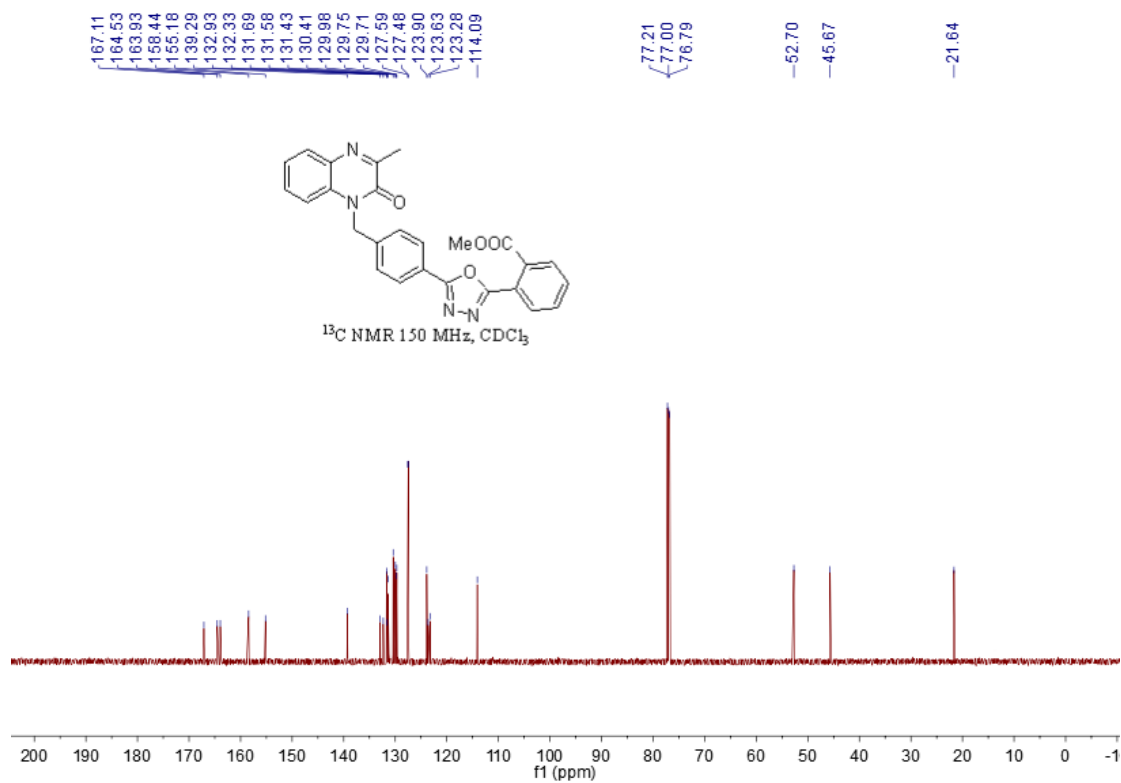
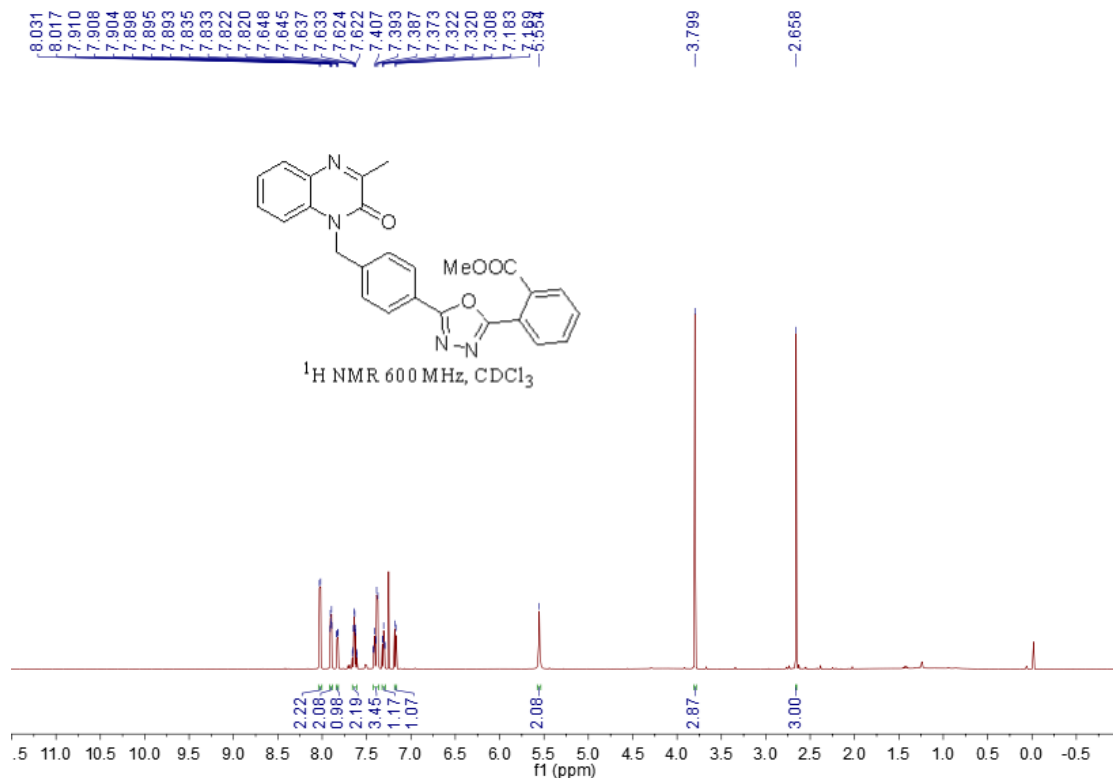
7. NMR copies of compound 6.

NMR copies of compound 6:



8. NMR copies of compounds 7.

NMR copies of compound **7a**:



NMR copies of compound **7b**:

