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# Supporting Information

# Oxidative Alkylation of Heterocycles: C($sp^2$)−H/C($sp^3$)−H Cross-Coupling in Transition Metal-Free Mode

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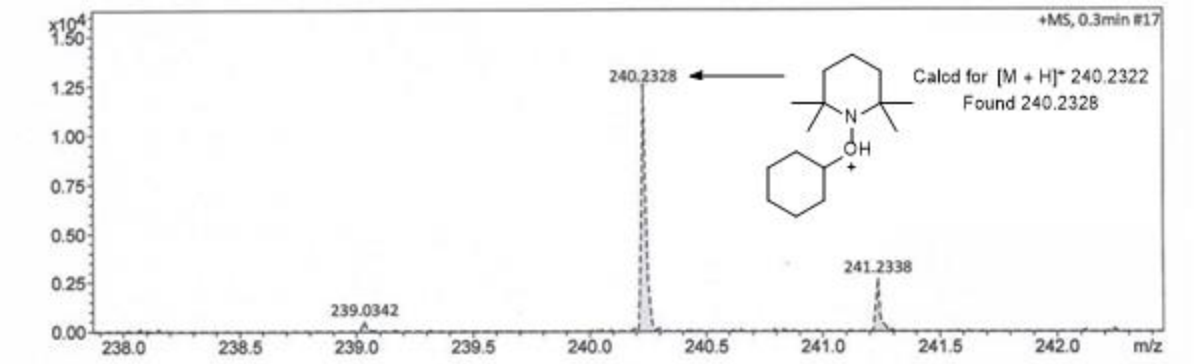
# Table of Contents

# Mechanistic Investigations:

**1. Reaction inhibition by BHT and TEMPO:**

In a sealed reaction tube, reaction between quinoxaline-2-one (0.1 mmol) and cyclohexane (2.0 mmol, 20 eq) was set up using di-*tert*-butylperoxide (DTBP) (0.3 mmol, 3 eq), *butylated hydroxytoluene (BHT)* (0.3 mmol, 3eq) in DCE (0.5 mL). The reaction mixture was stirred at 130 °C (oil bath) for 4h. No desire product was formed and the quinoxaline-2-one was remained intact.

In a separate sealed reaction tube, reaction between quinoxaline-2-one (0.1 mmol) and cyclohexane (2.0 mmol, 20 eq) was set up using di-*tert*-butylperoxide (DTBP) (0.3 mmol, 3 eq), *2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)* (0.3 mmol, 3eq) in DCE (0.5 mL). The reaction mixture was stirred at 130 °C (oil bath) for 4h. An aliquot portion of the reaction mixture was subjected to mass spectrometry (HR-MS) to identify the reactive intermediate (Figure S1). In ESI we were able to detect cyclohexyl radical adduct with TEMPO.




| Meas. m/z | # | Ion Formula | m/z | err [ppm] | Mean err [ppm] | rdb | N-Rule | e⁻ Conf | mSigma | Std I | Std Mean m/z | Std I VarNorm | Std m/z Diff | Std Comb Dev |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 240.232780 | 1 | C15H30NO | 240.232191 | -2.5 | 1719.3 | 1.5 | ok | even | 29.8 | 45.1 | n.a. | n.a. | n.a. | n.a. |

**Figure S1: HR-MS of radical quenching experiment with TEMPO**

**2. Studies of reaction mechanism by gas chromatography (GC):**

At first, authentic stander sample of *tert*-butanol (MS-a) and acetone (MS-b) was diluted with DCE and subjected to GC separately to know the retention time. Then, in a sealed reaction tube, reaction between quinoxaline-2-one (0.1 mmol) and cyclohexane (2.0 mmol, 20 eq) was set up using di-*tert*-butylperoxide (DTBP) (0.3 mmol, 3 eq) in DCE (0.5 mL). The reaction mixture was stirred at 130 °C (oil bath) for 4 h. The reaction mixture was cooled to room

temperature and from the reaction mixture 10 µL aliquot was added to DCE (490 µL) to prepare the sample solution of crude reaction mixture for GC. From this sample solution 1 µL aliquot was injected to the GC instrument (Shimadzu, Nexis GC-2030) and retention time was recorded (MS-c). After comparing the retention time with MS-a (1.810 min) and MS-b (1.955 min), we concluded that both acetone and *tert*-butanol was formed during the course of the reaction.

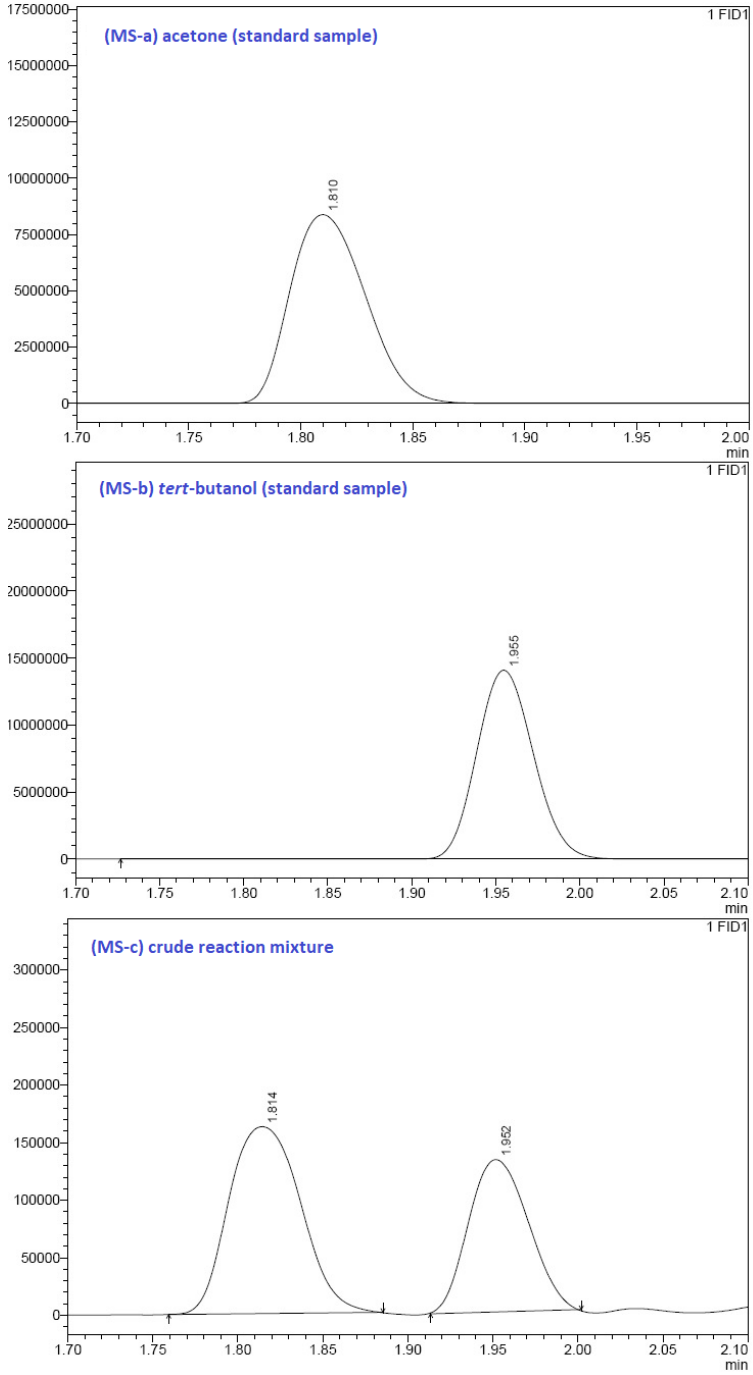
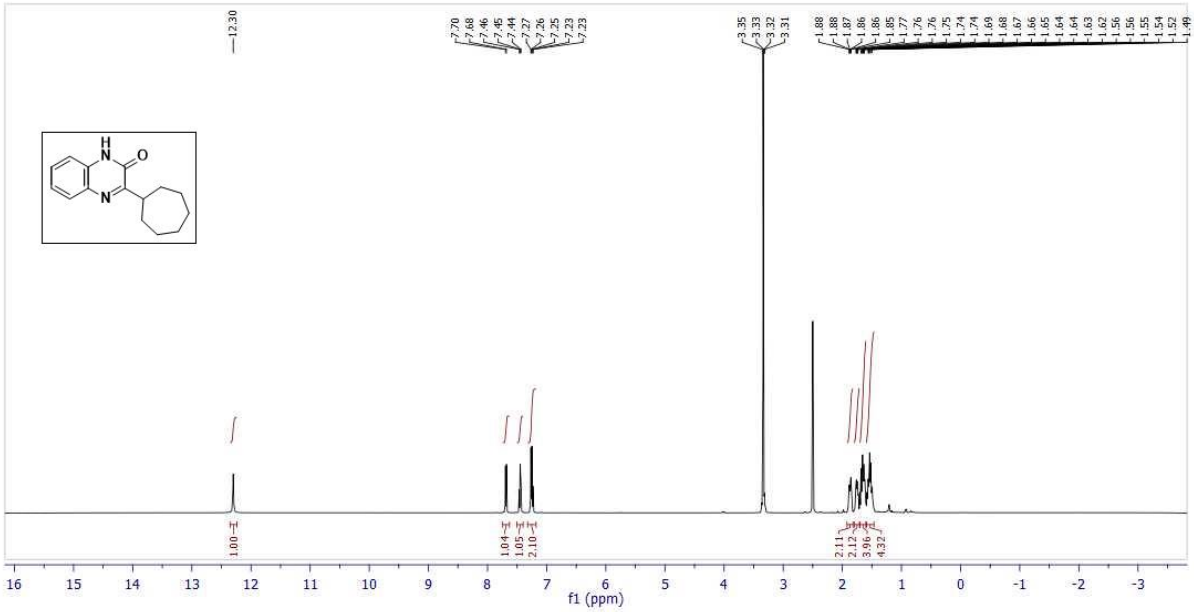
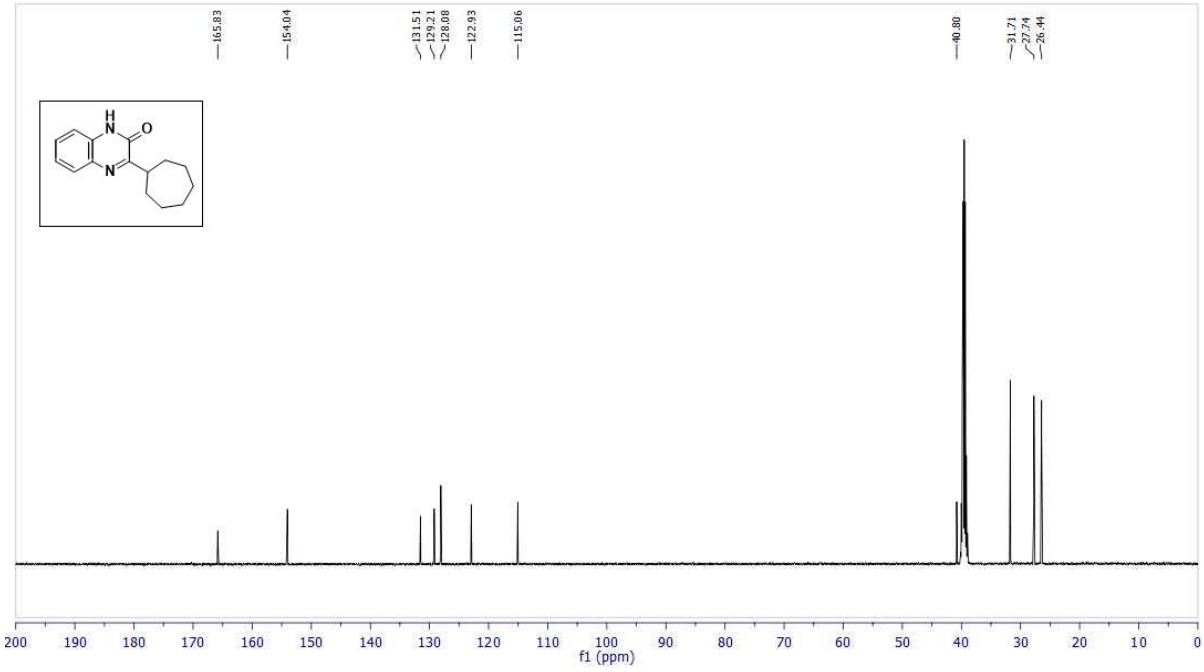



**Figure S2: Identification of acetone and *tert*-butanol during the course of the reaction through GC**

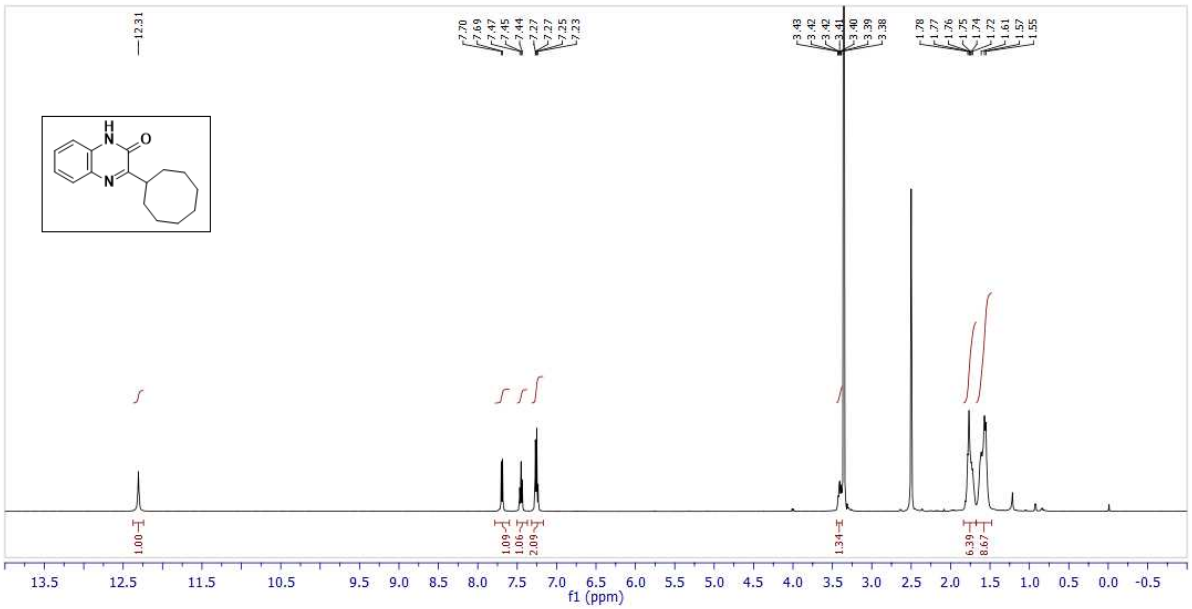
**$^{1}$H NMR spectrum of 3a (500 MHz, DMSO-d6):**



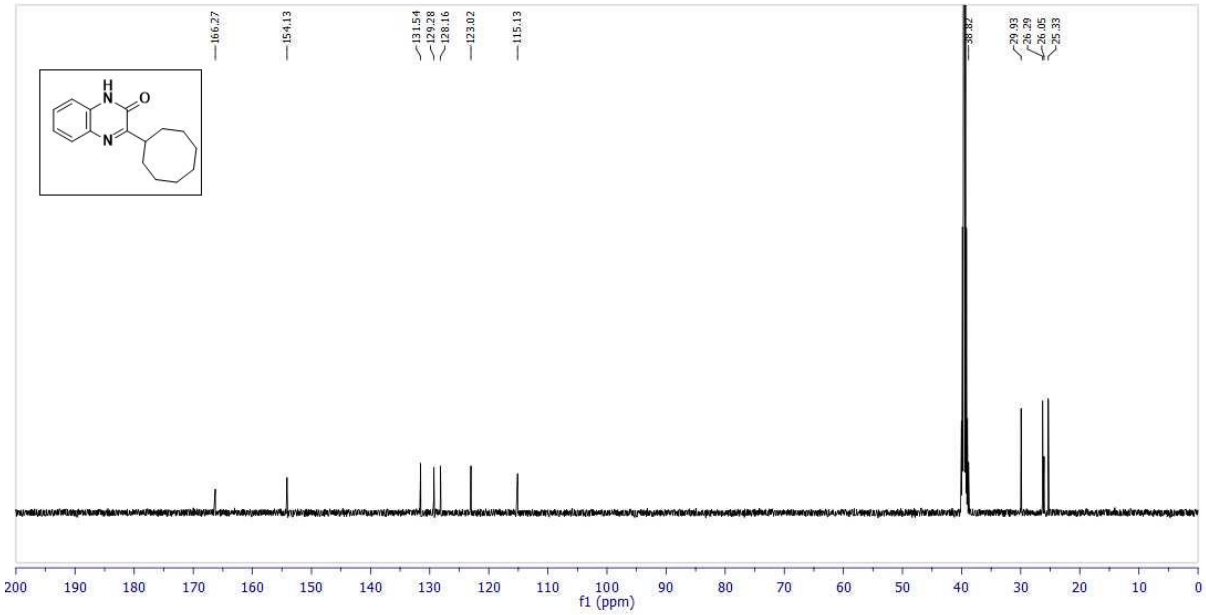

**$^{13}$C NMR spectrum of 3a (126 MHz, DMSO-d6):**



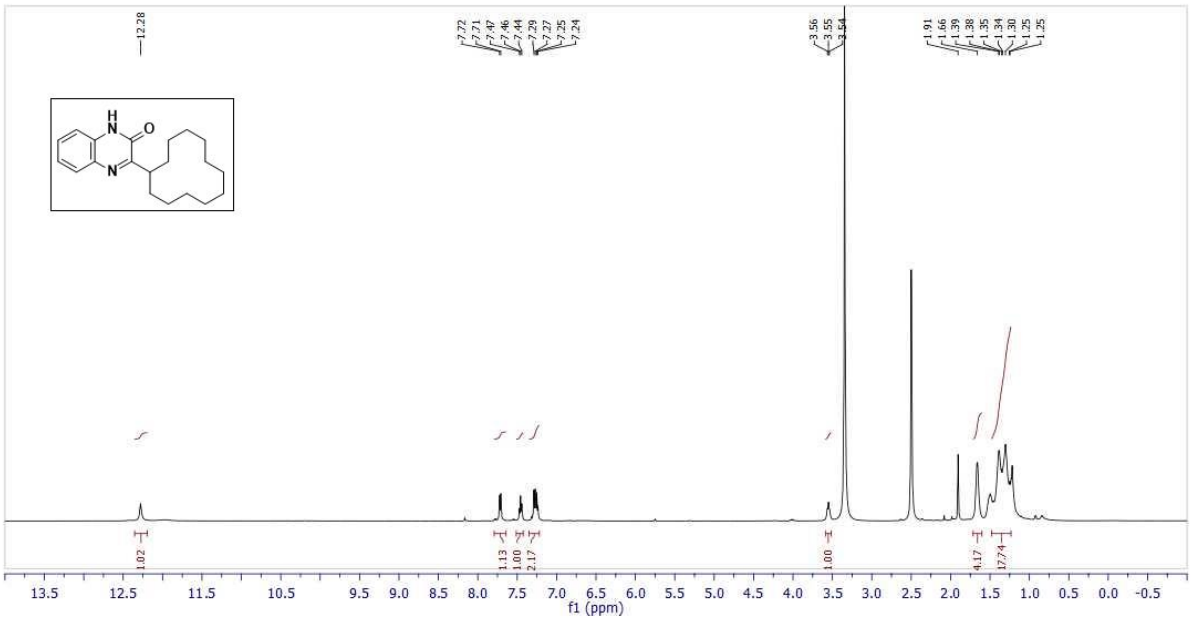
**$^{1}$H NMR spectrum of 3b (500 MHz, DMSO-d6):**



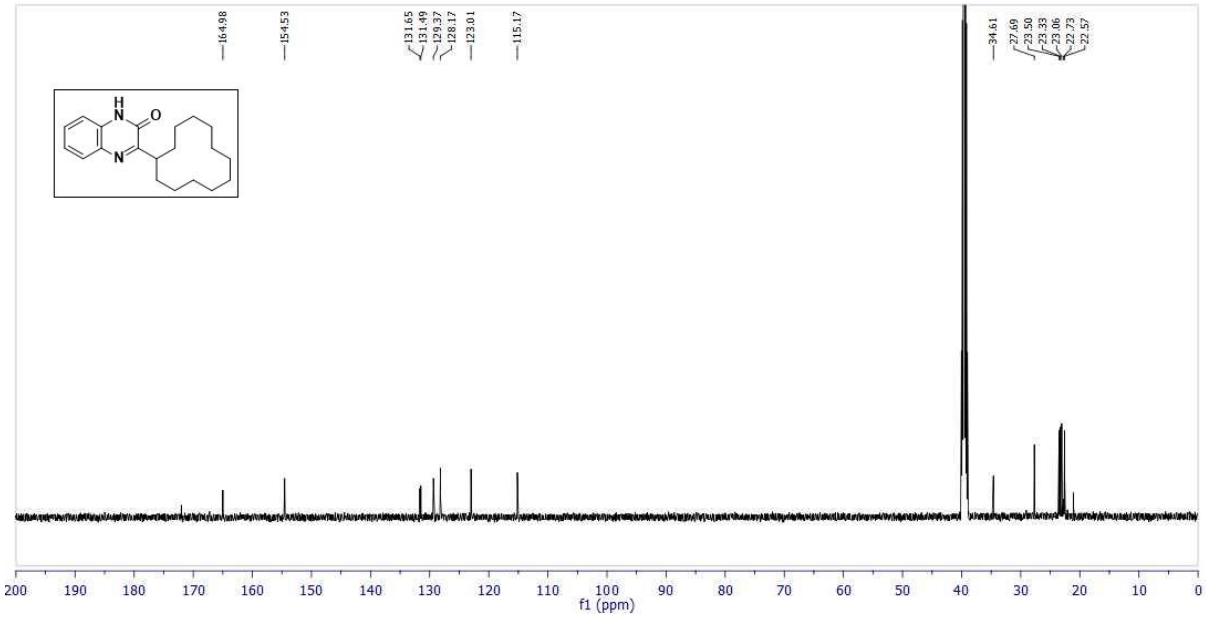

**$^{13}$C NMR spectrum of 3b (126 MHz, DMSO-d6):**



**$^{1}$H NMR spectrum of 3c (500 MHz, DMSO-d6):**




**$^{13}$C NMR spectrum of 3c (126 MHz, DMSO-d6):**



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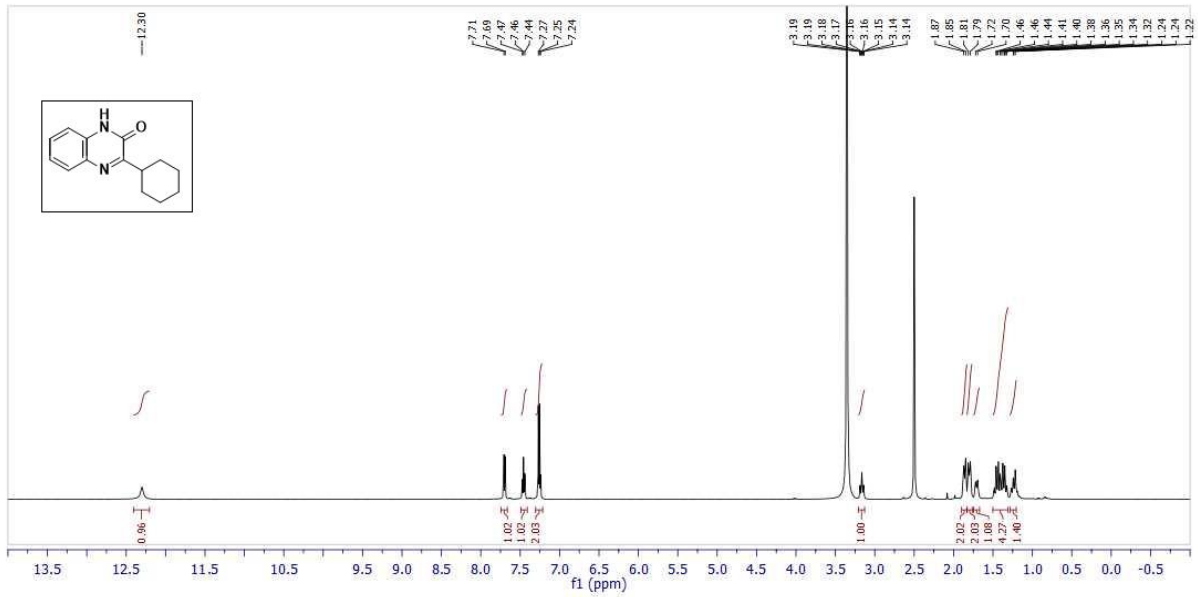
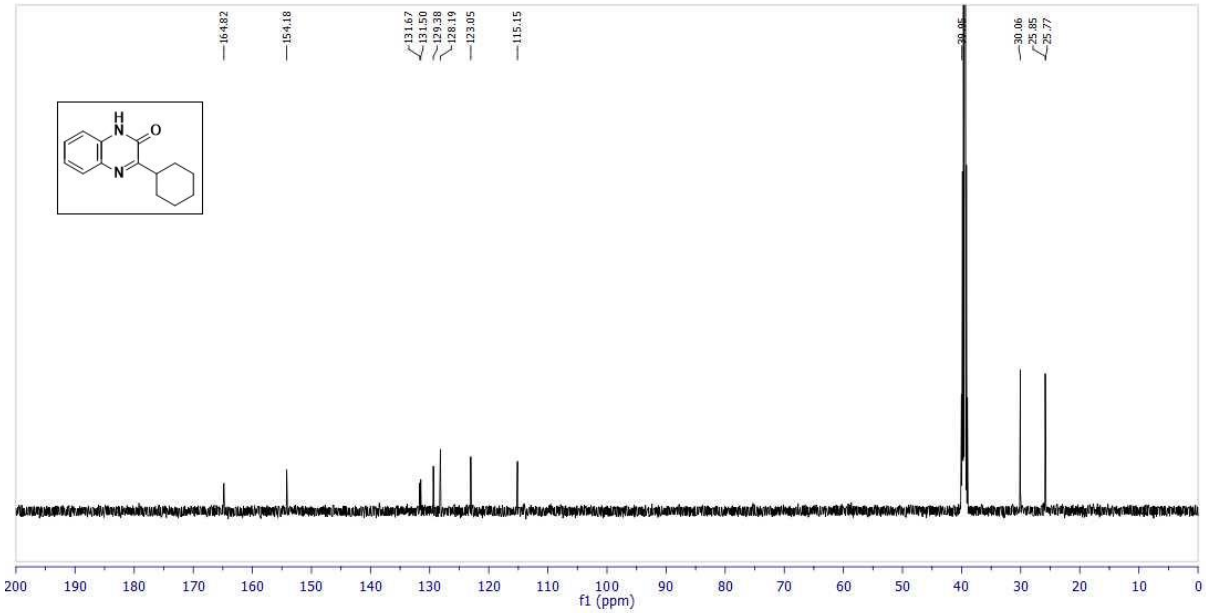
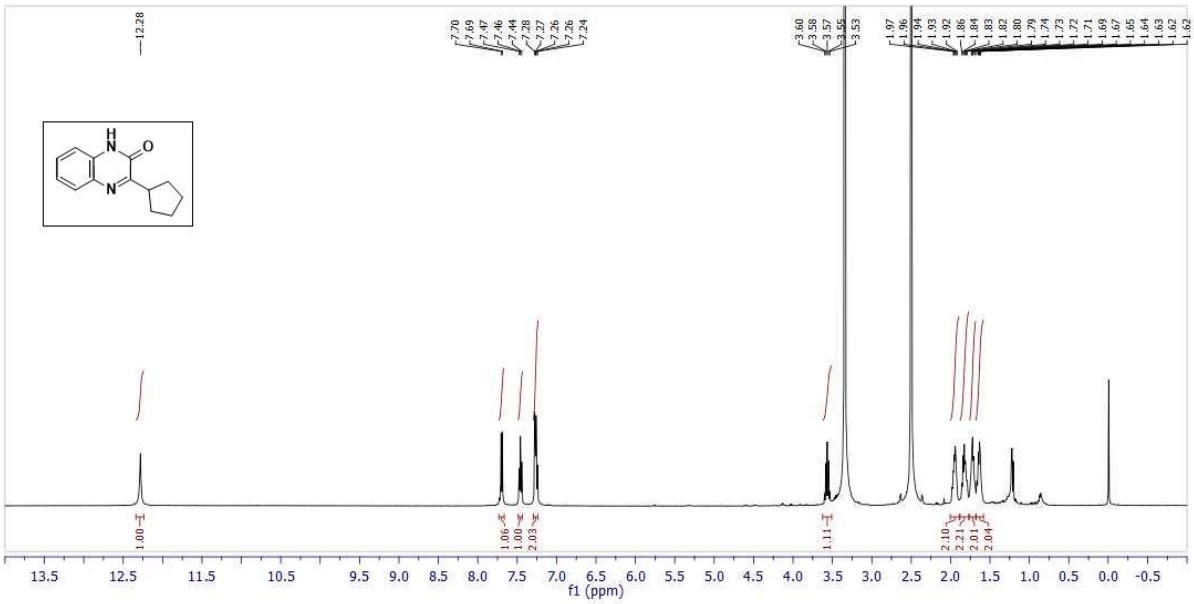


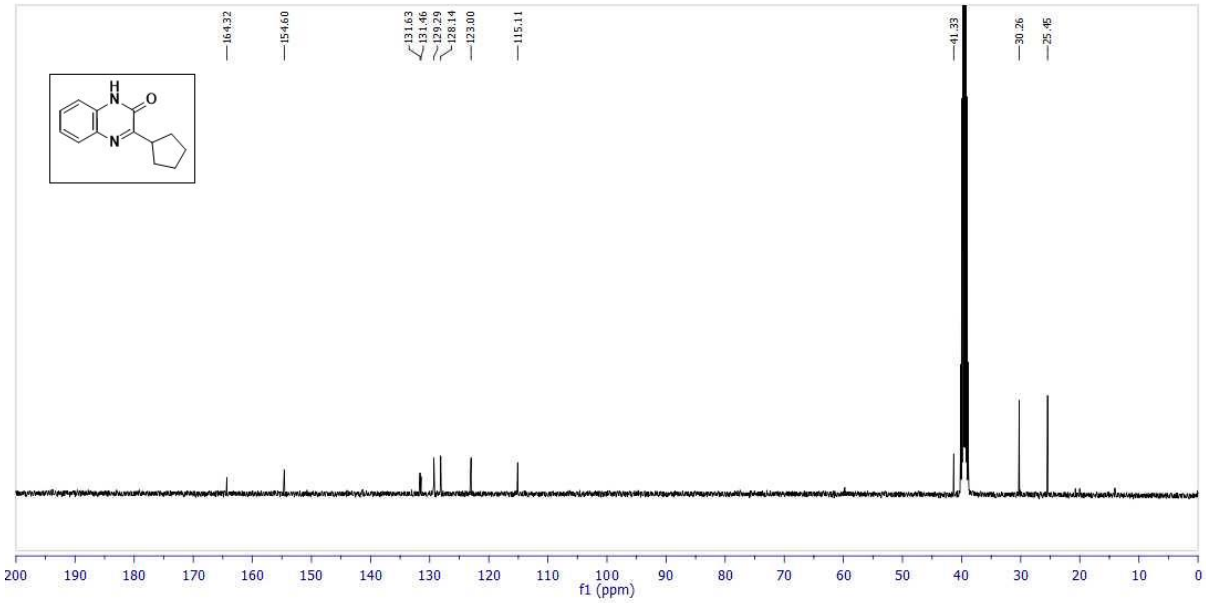

**$^{13}$C NMR spectrum of 3d (126 MHz, DMSO-d6):**



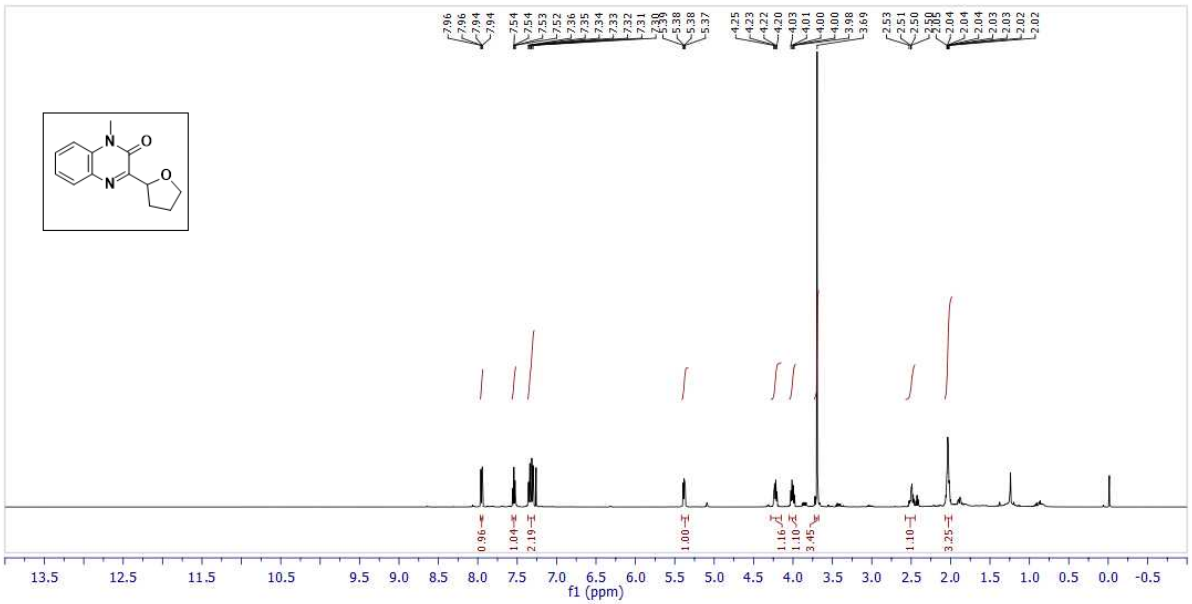
**$^{1}$H NMR spectrum of 3e (500 MHz, DMSO-d6):**



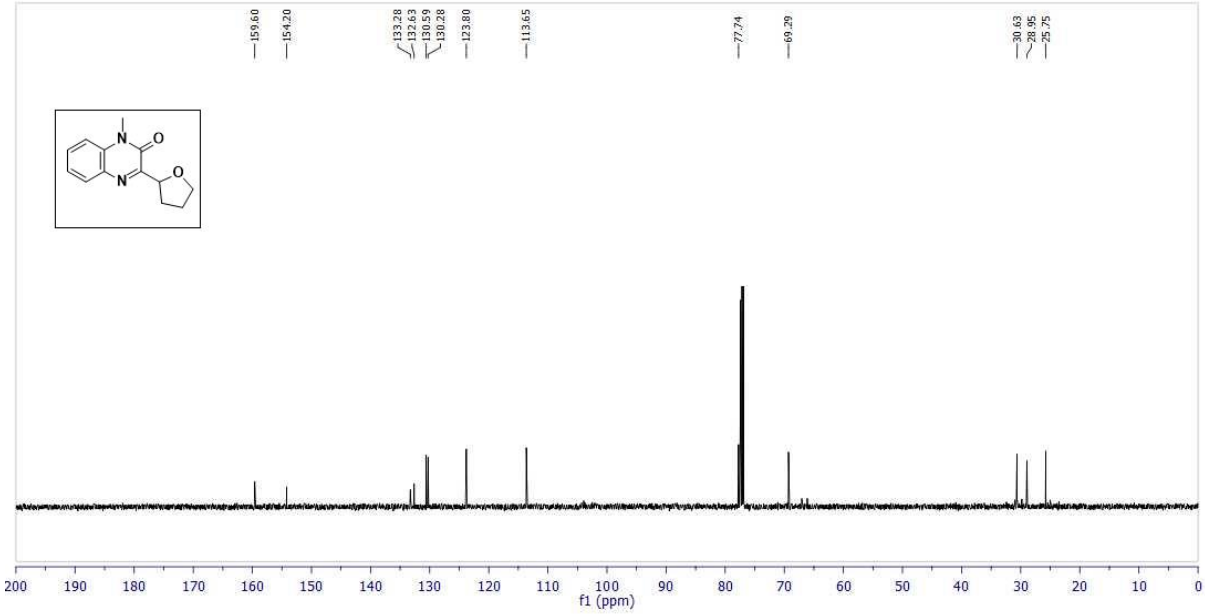

**$^{13}$C NMR spectrum of 3e (101 MHz, DMSO-d6):**



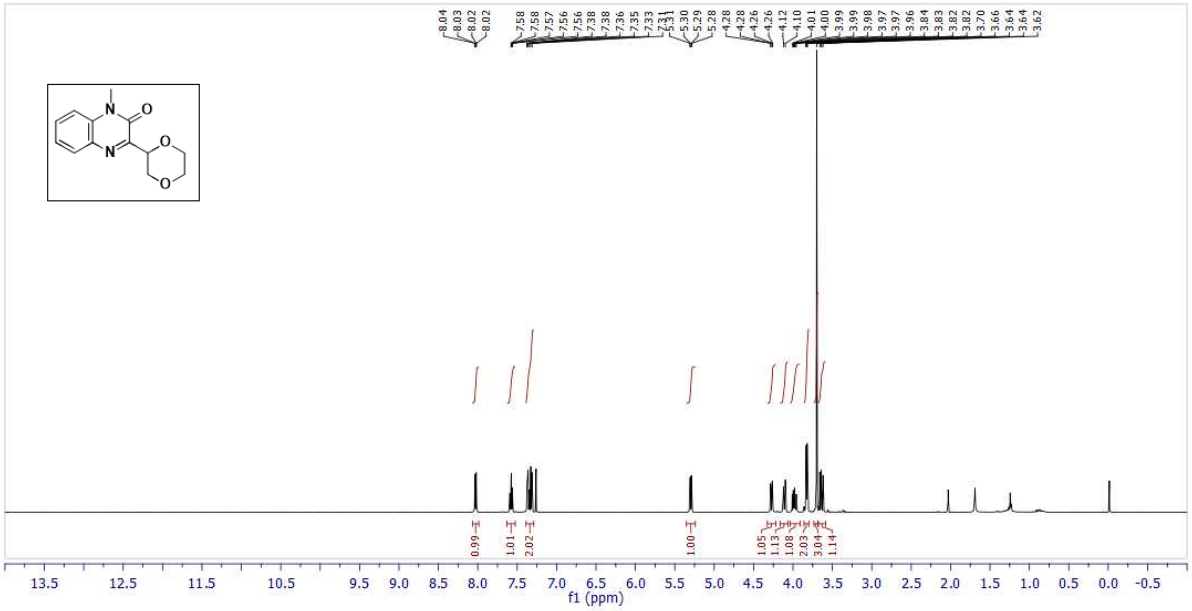
**$^{1}$H NMR spectrum of 3f (500 MHz, $CDCl_3$):**



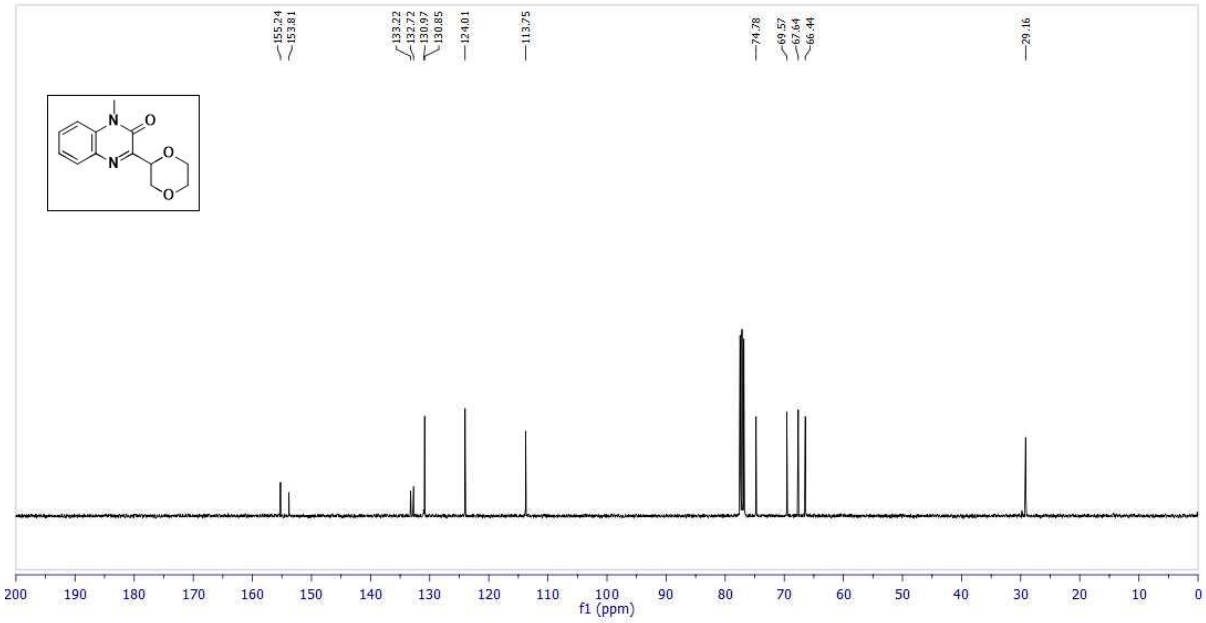

**$^{13}$C NMR spectrum of 3f (126 MHz, $CDCl_3$):**



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




**$^{13}$C NMR spectrum of 3g (101 MHz, $CDCl_3$):**



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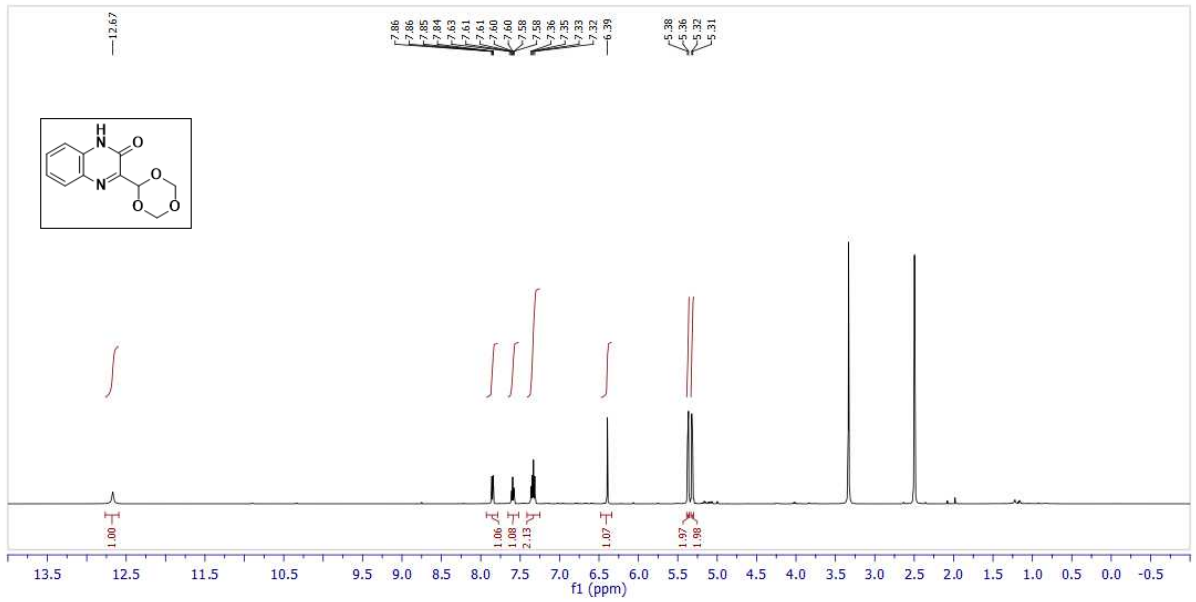
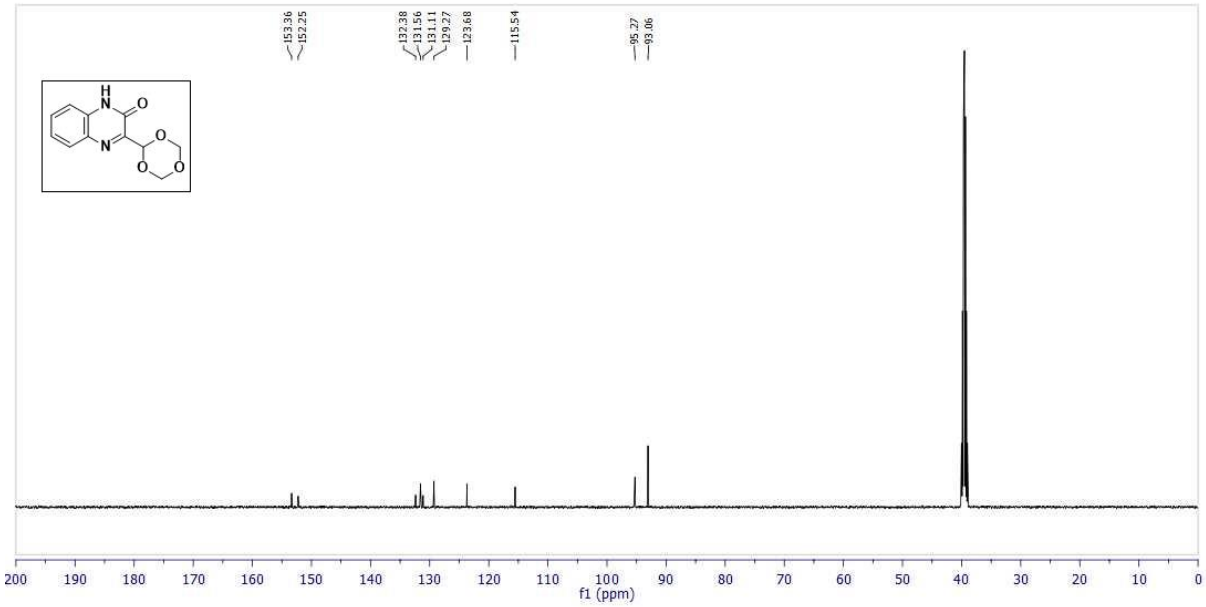
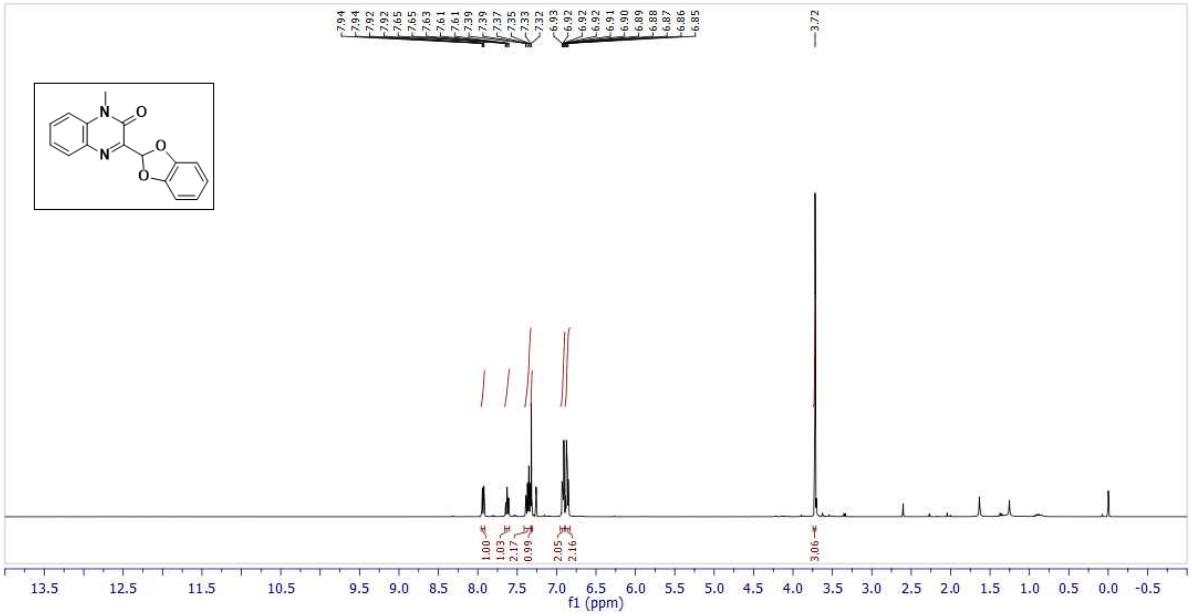


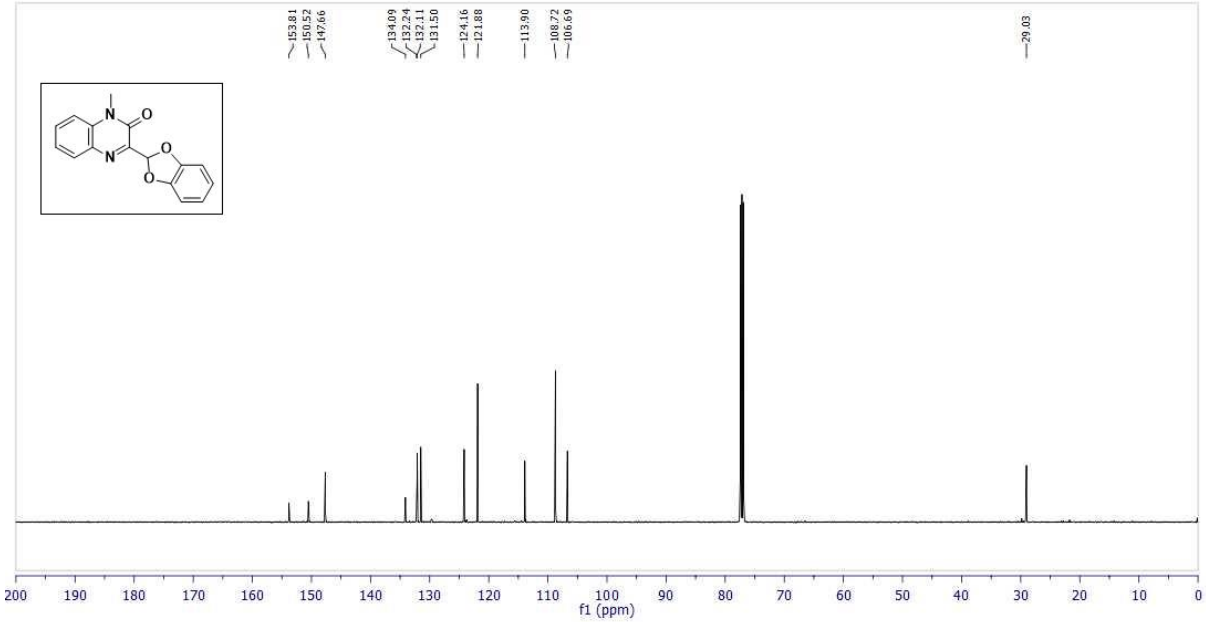

**$^{13}$C NMR spectrum of 3h (126 MHz, DMSO-d6):**



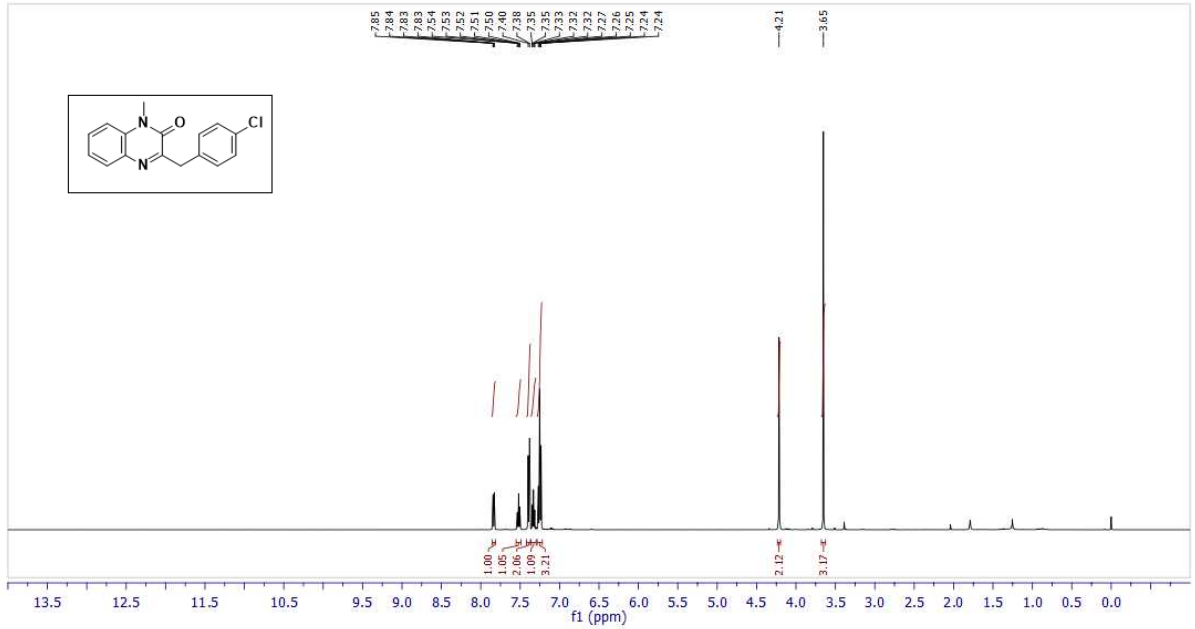
**$^{1}$H NMR spectrum of 3i (400 MHz, $CDCl_3$):**



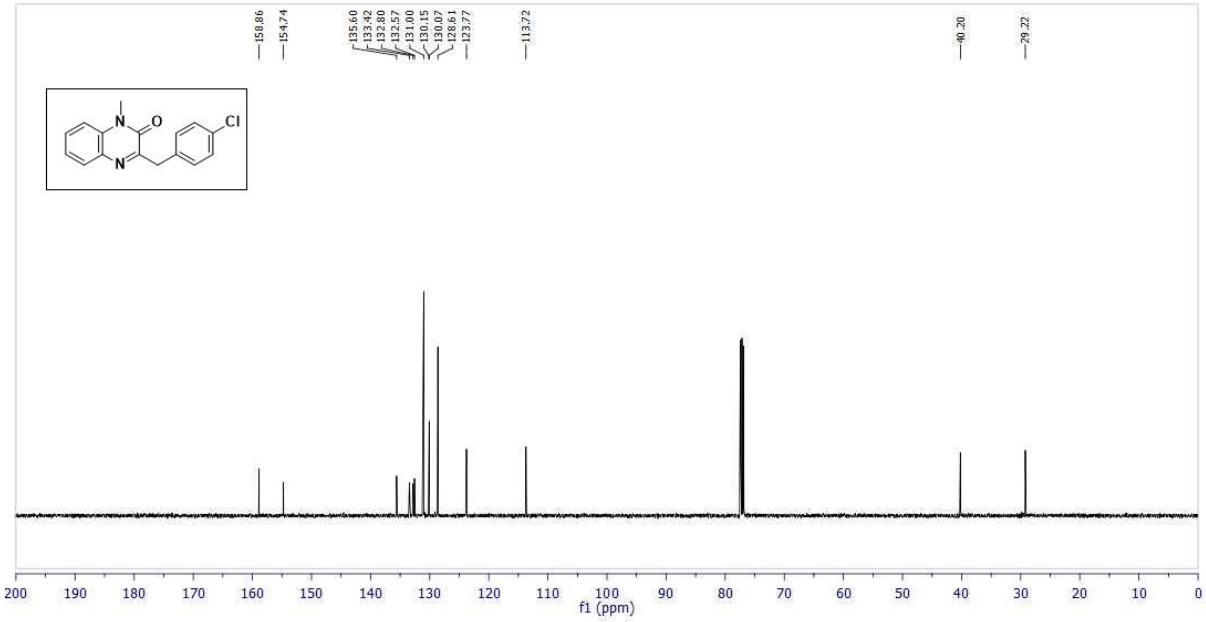

**$^{13}$C NMR spectrum of 3i (126 MHz, $CDCl_3$):**



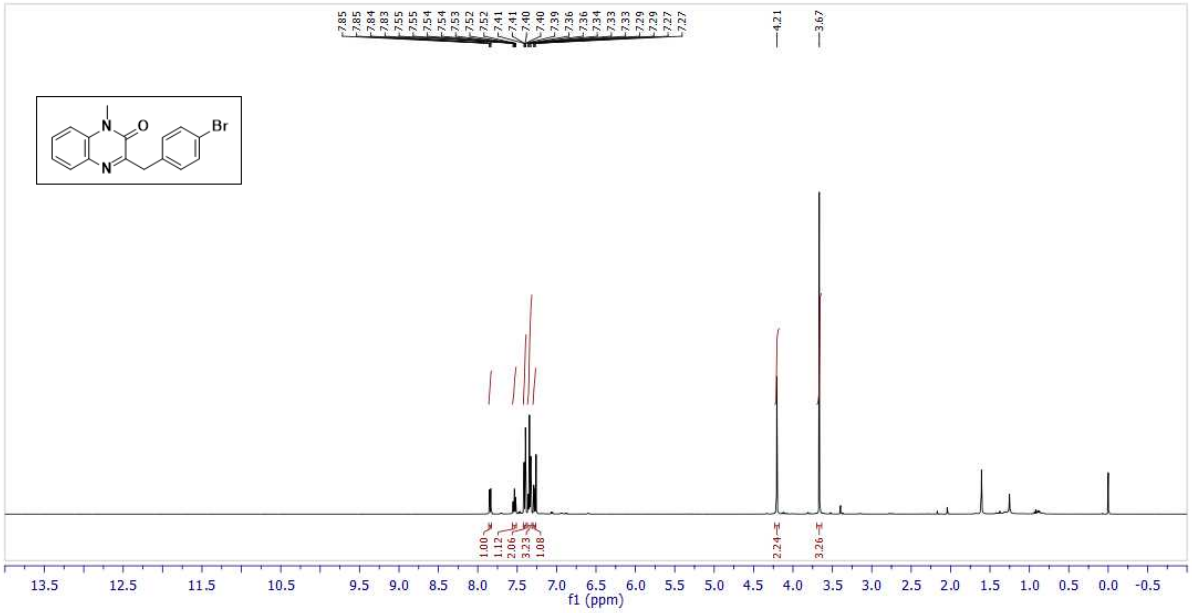
**$^{1}$H NMR spectrum of 3j (500 MHz, $CDCl_3$):**



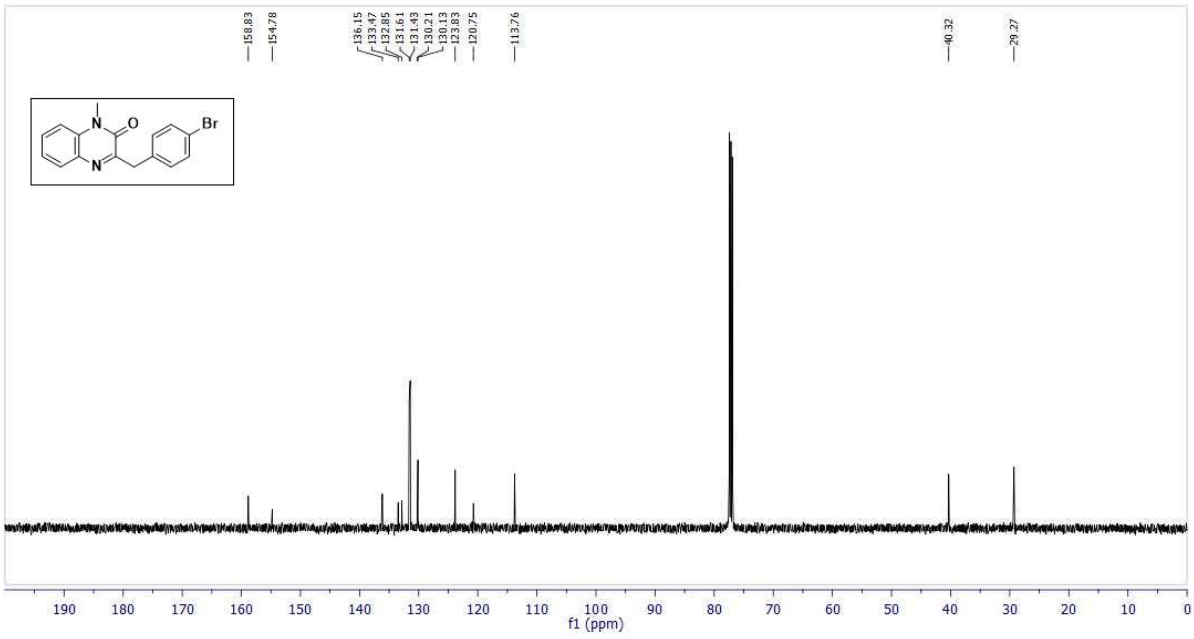

**$^{13}$C NMR spectrum of 3j (126 MHz, $CDCl_3$):**



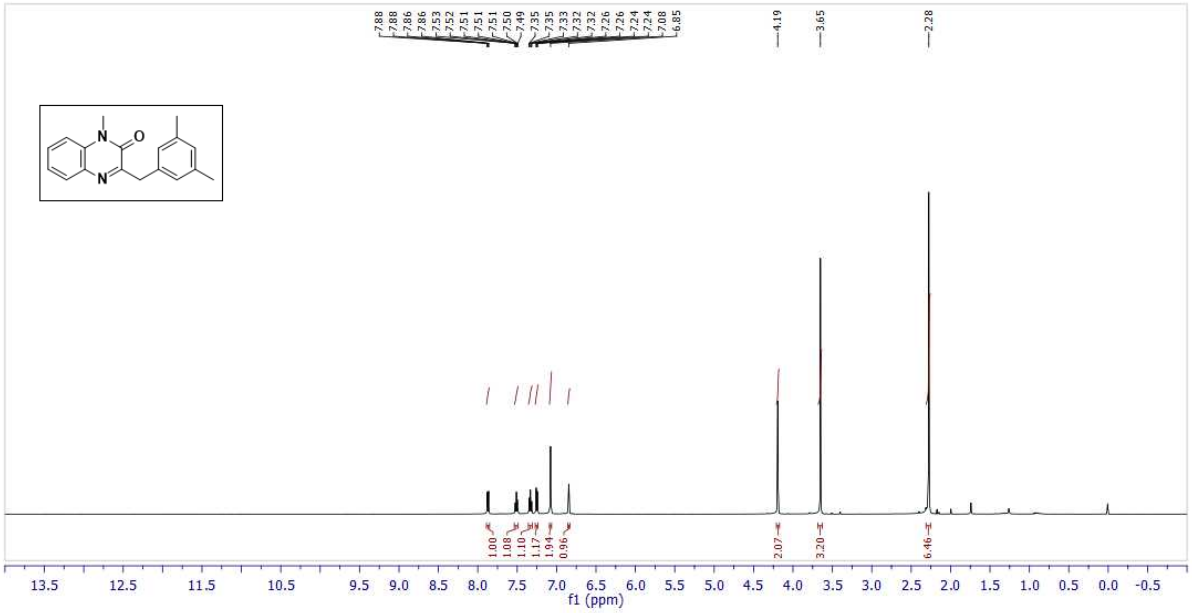
**$^{1}$H NMR spectrum of 3k (500 MHz, $CDCl_3$):**



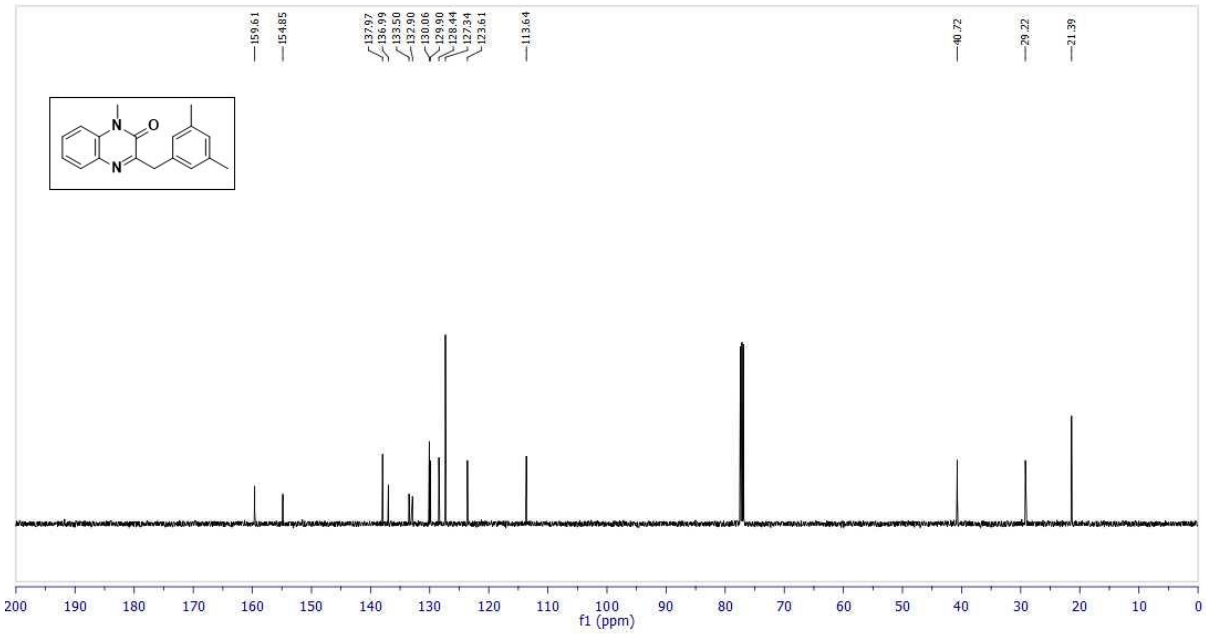

**$^{13}$C NMR spectrum of 3k (126 MHz, $CDCl_3$):**



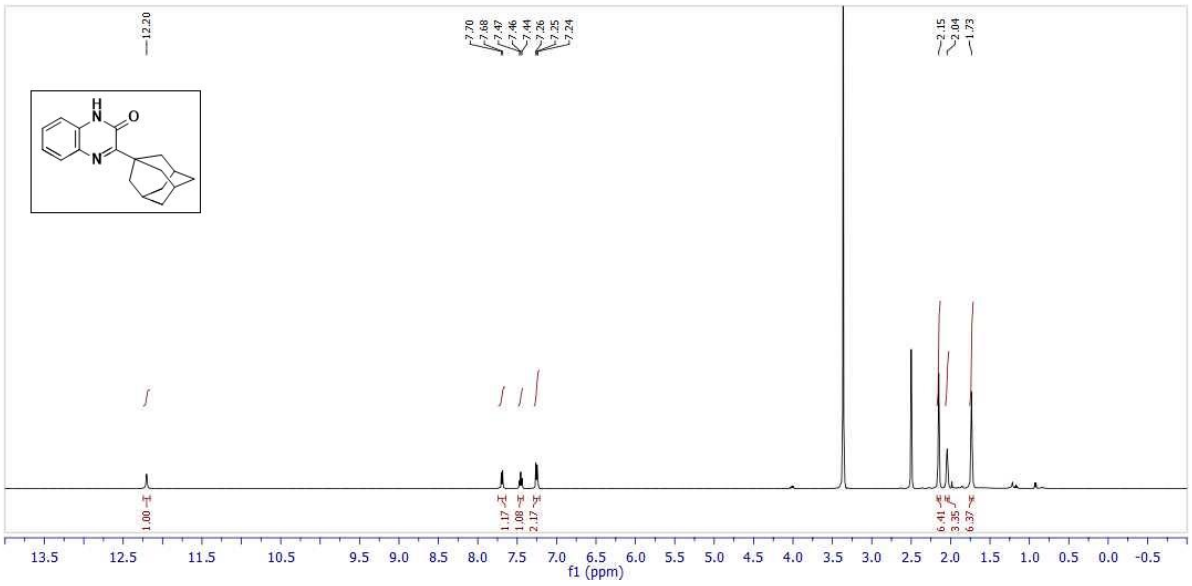
**$^{1}$H NMR spectrum of 3l (500 MHz, $CDCl_3$):**



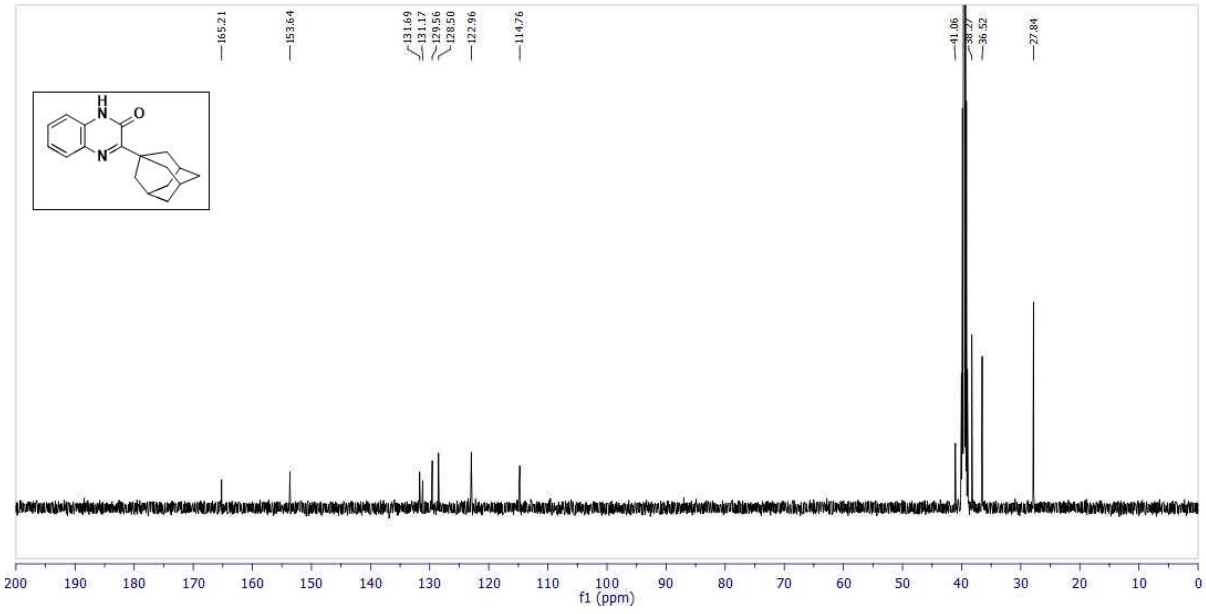

**$^{13}$C NMR spectrum of 3l (126 MHz, $CDCl_3$):**



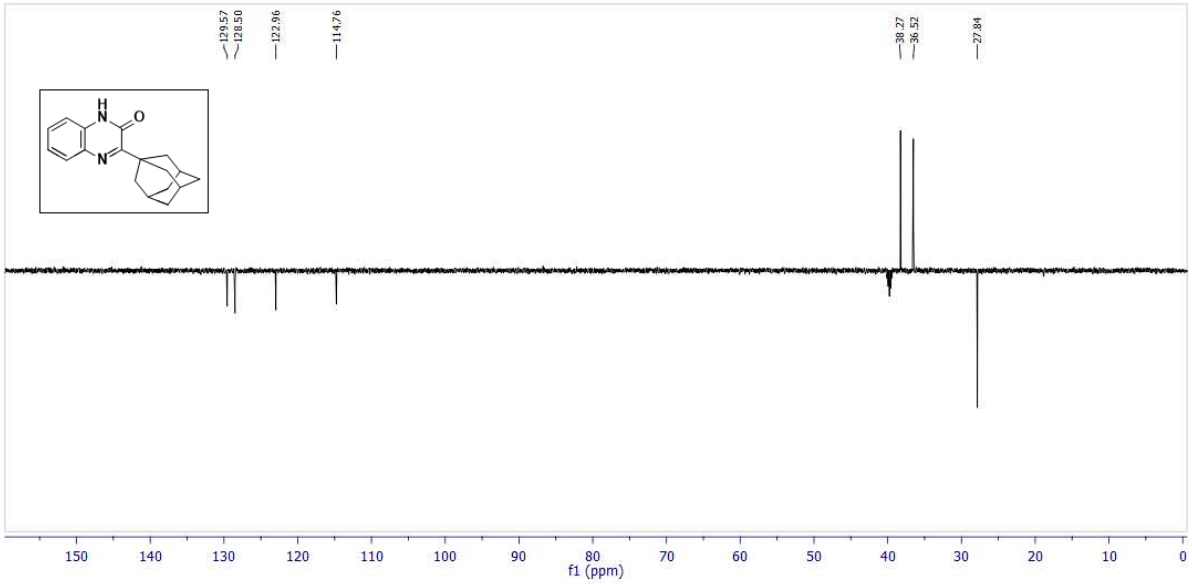
**$^{1}$H NMR spectrum of 3m (500 MHz, DMSO-d6):**



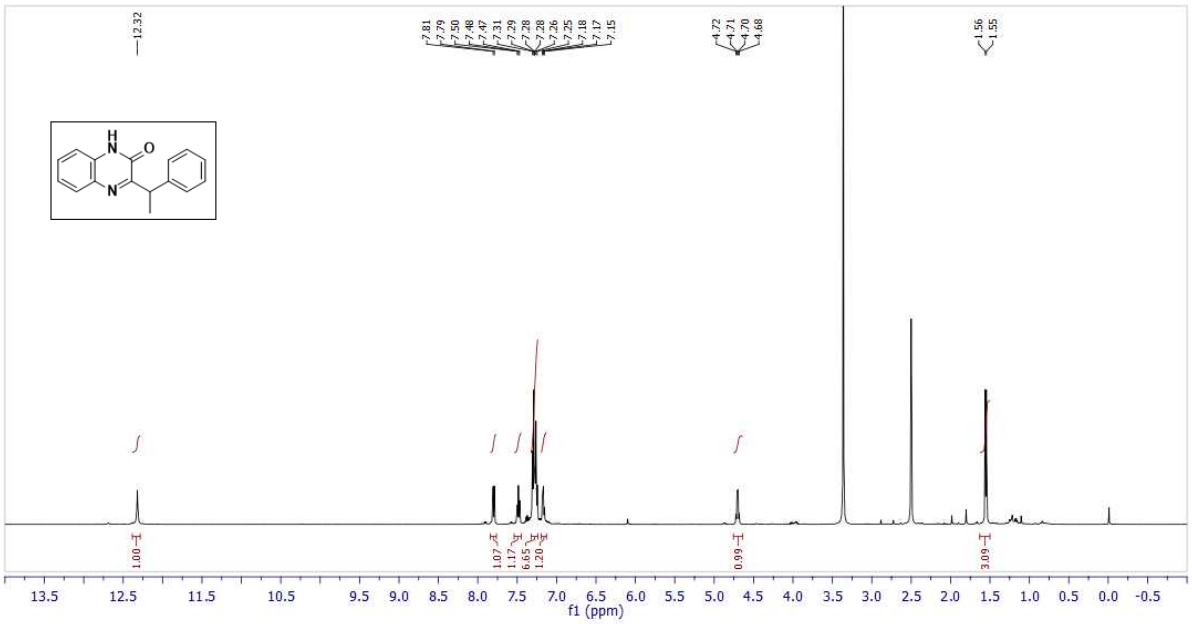

**$^{13}$C NMR spectrum of 3m (126 MHz, DMSO-d6):**



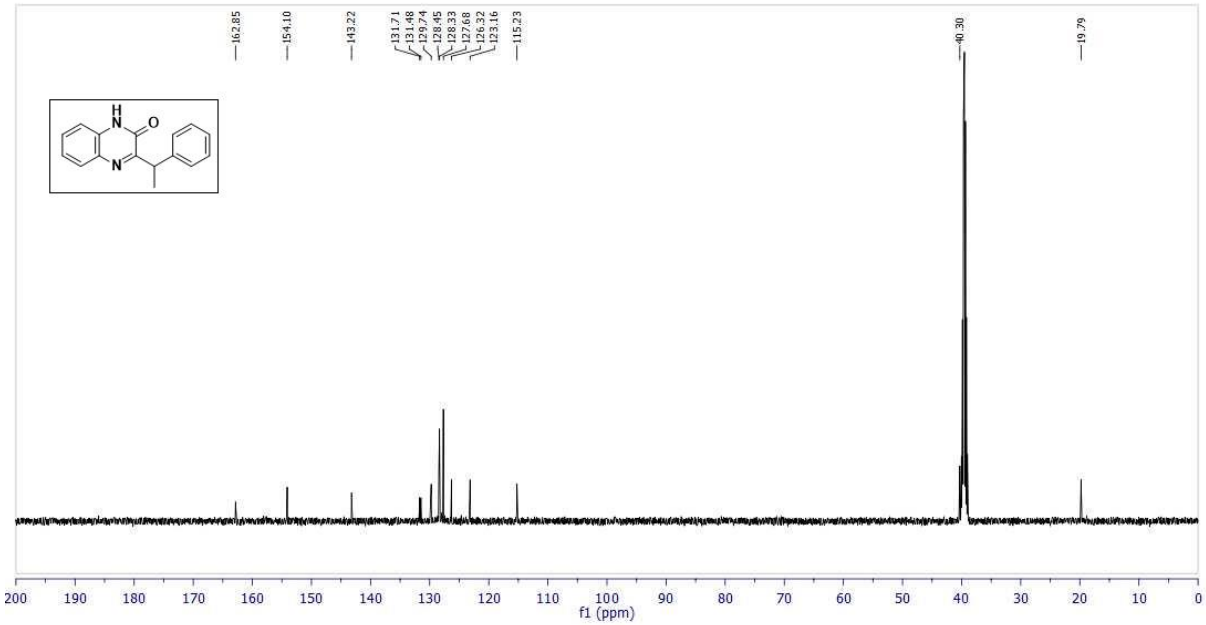
**DEPT135 NMR spectrum of 3m (126 MHz, DMSO-d6):**



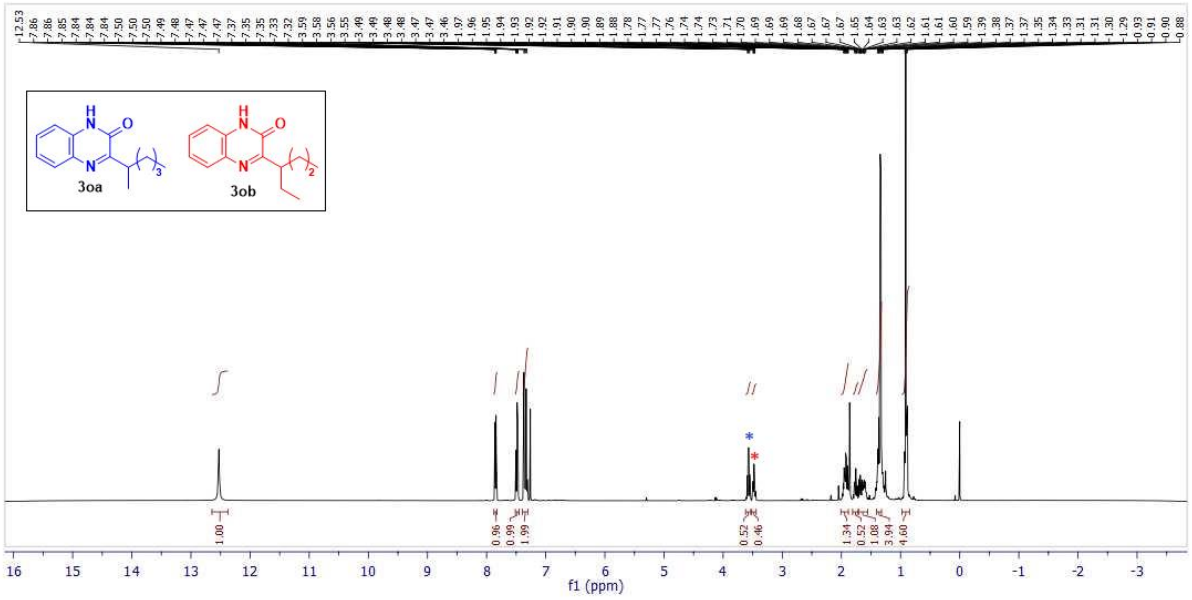
**$^{1}$H NMR spectrum of 3n (500 MHz, DMSO-d6):**



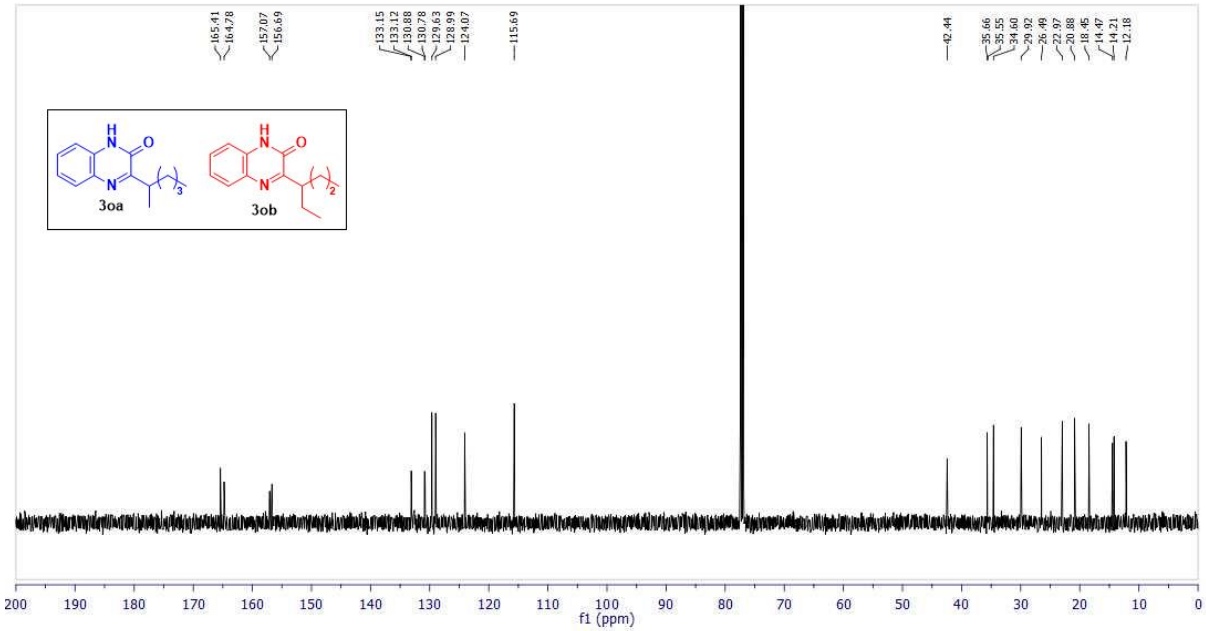

**$^{13}$C NMR spectrum of 3n (126 MHz, DMSO-d6):**



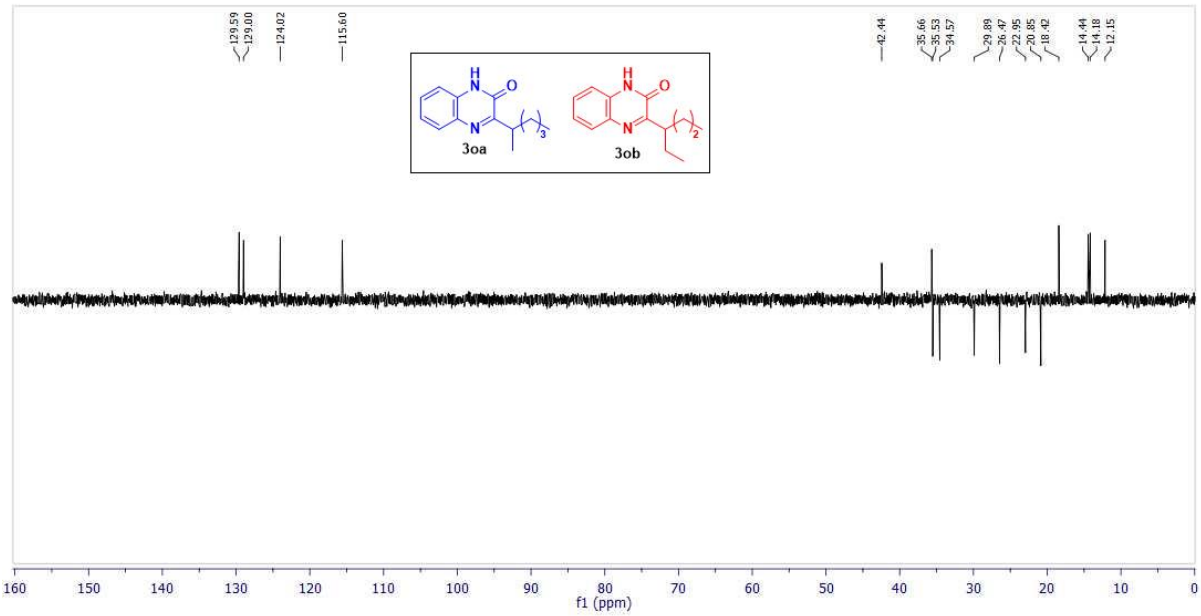
**$^{1}$H NMR spectrum of 3o (500 MHz, $CDCl_3$):**



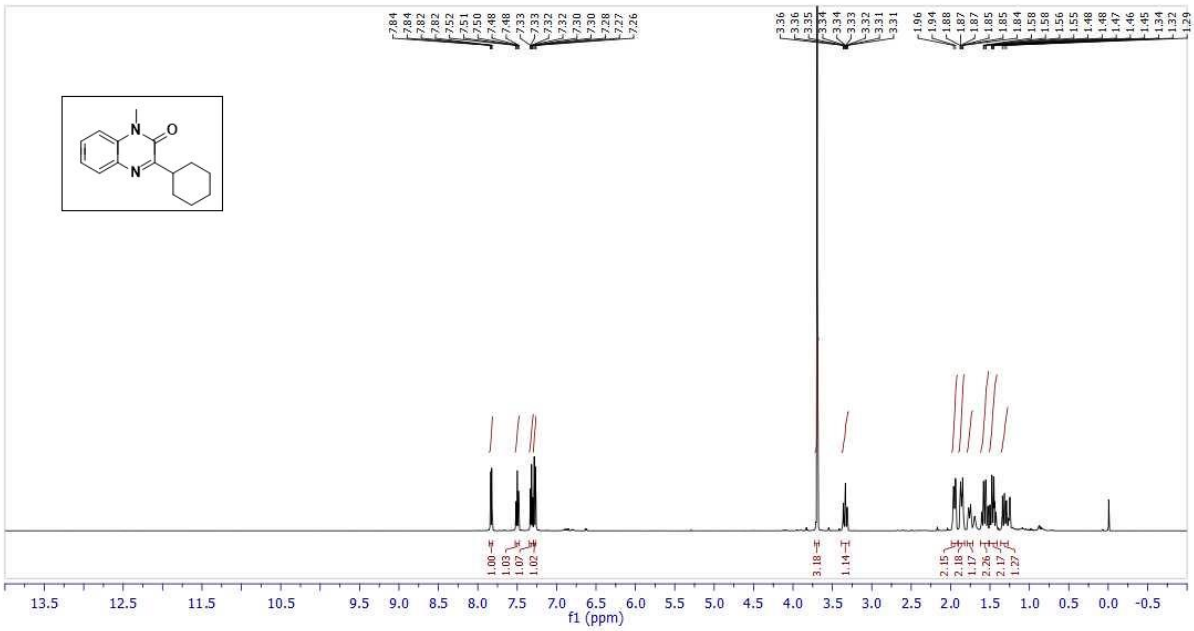

**$^{13}$C NMR spectrum of 3o (126 MHz, $CDCl_3$):**



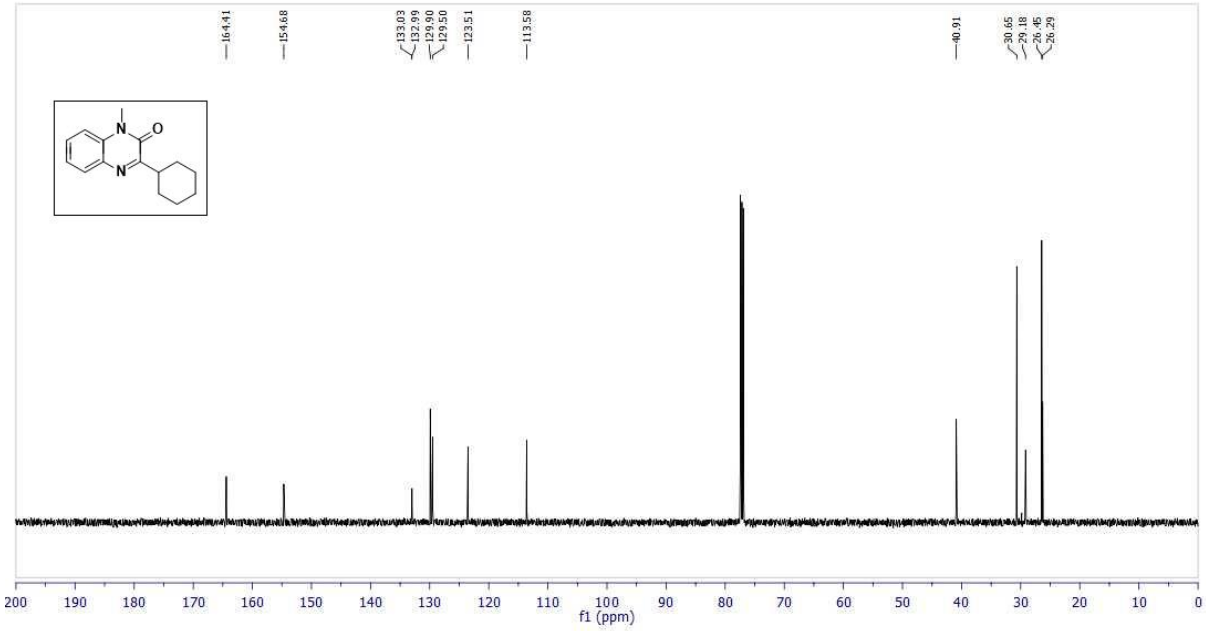
**DEPT135 NMR spectrum of 3o (101 MHz, $CDCl_3$):**



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




**$^{13}$C NMR spectrum of 4a (126 MHz, $CDCl_3$):**



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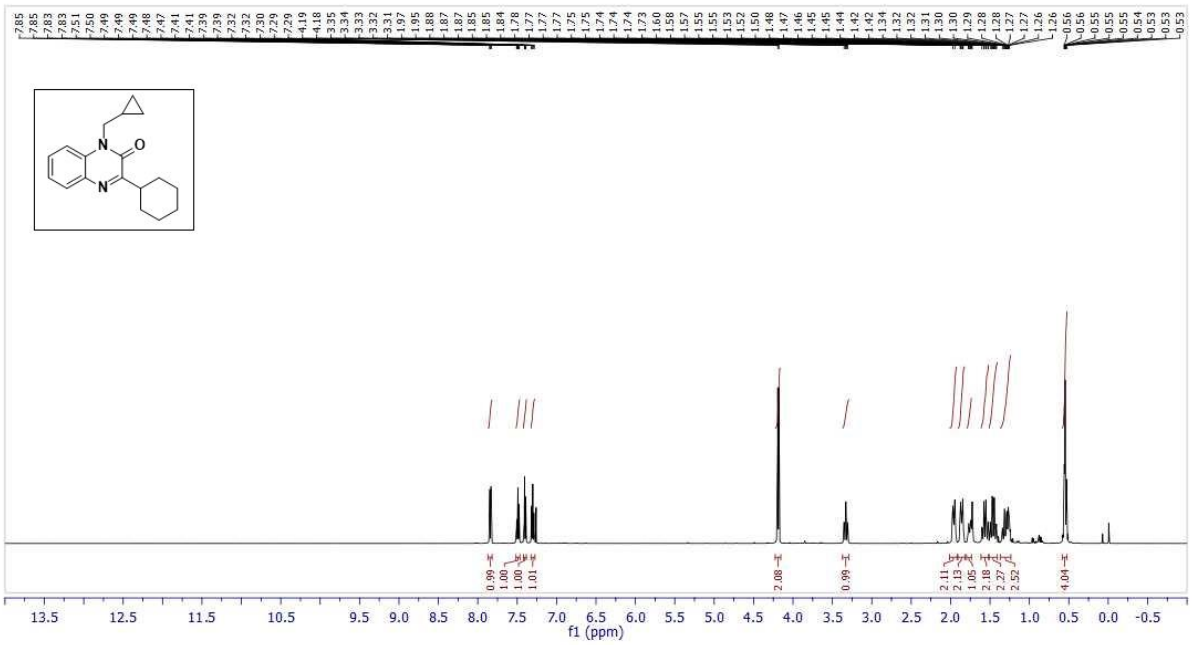


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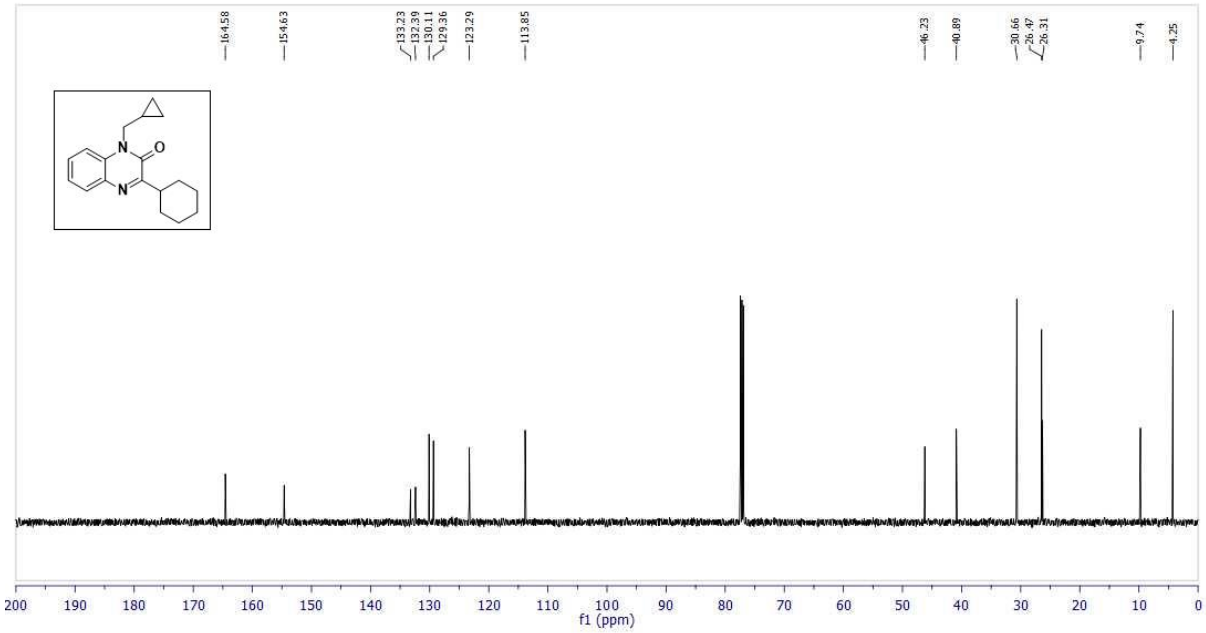

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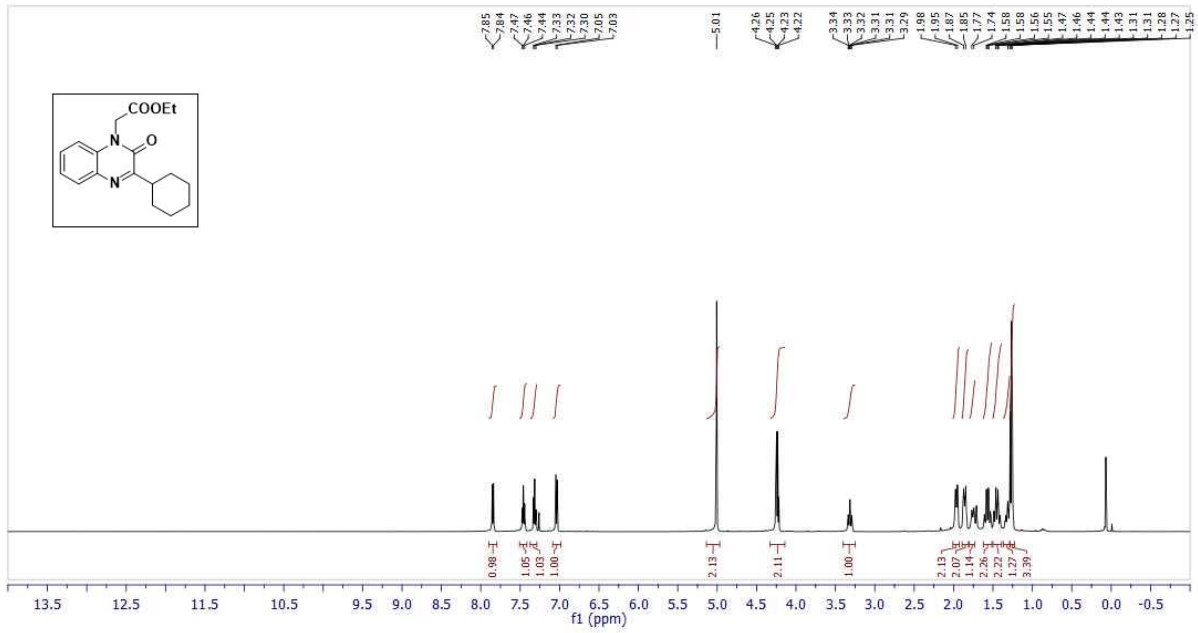


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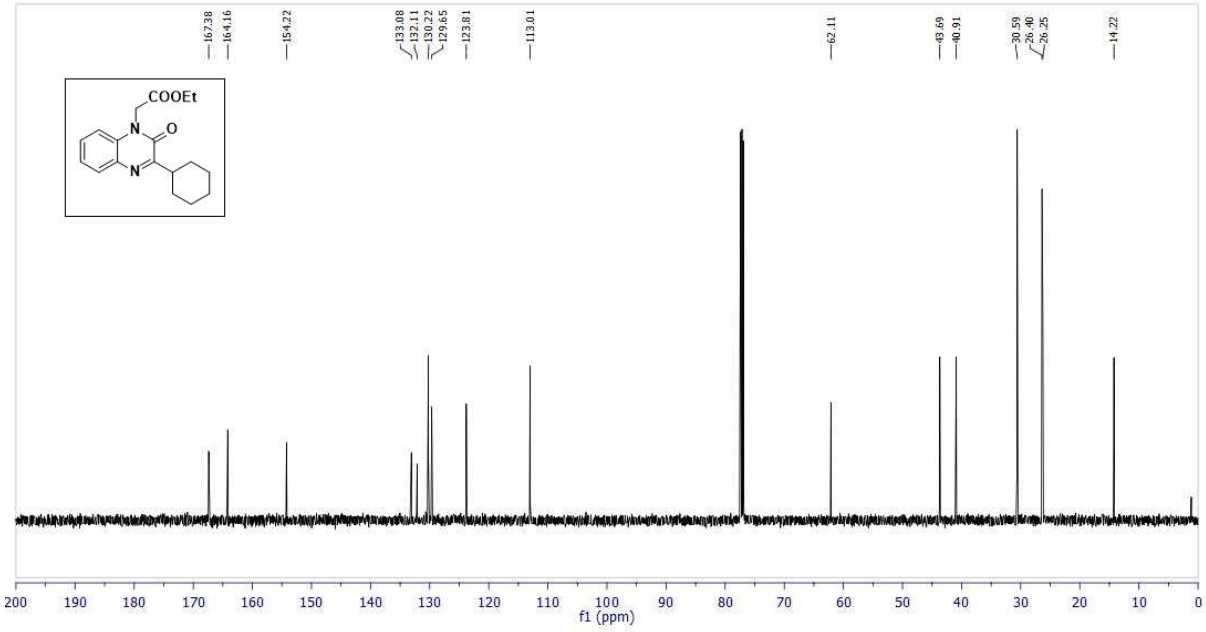

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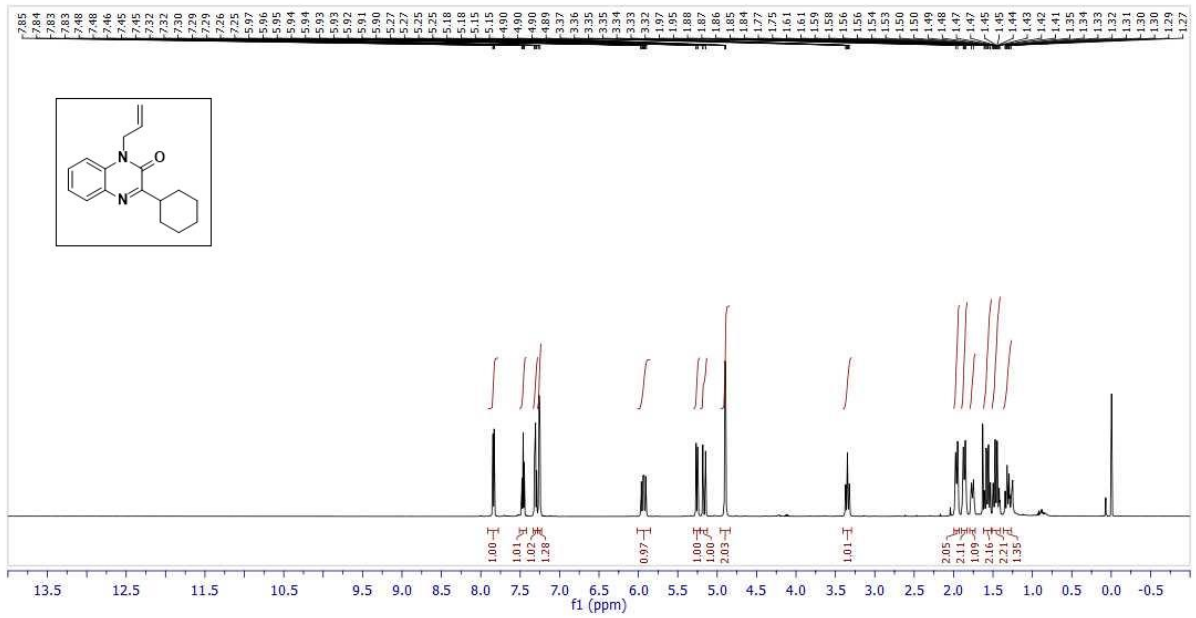

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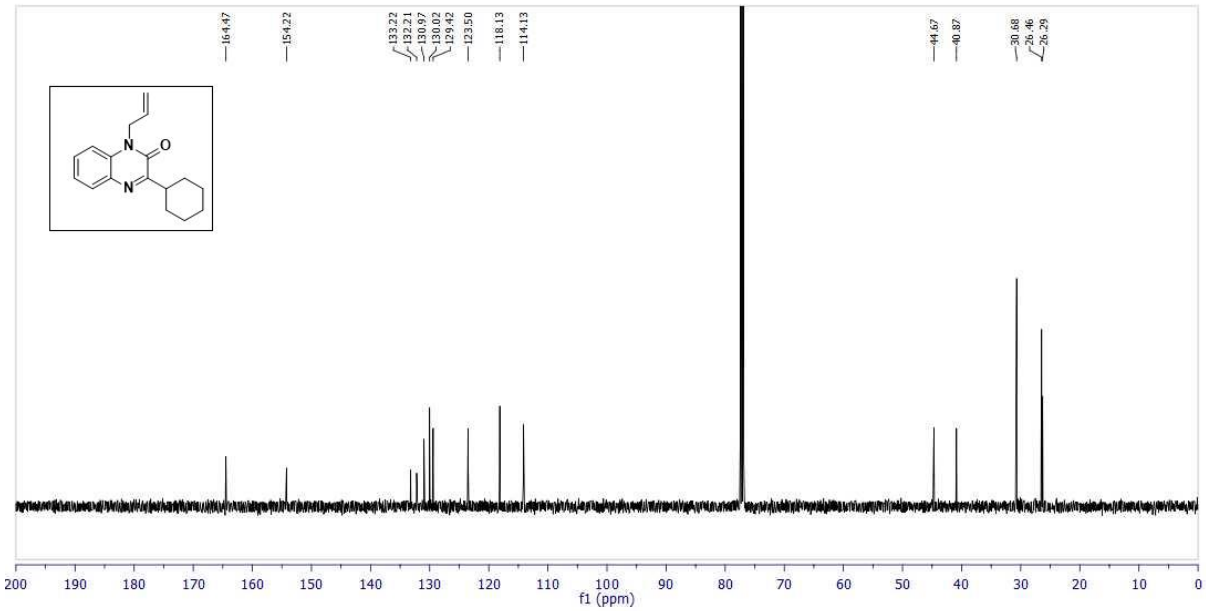
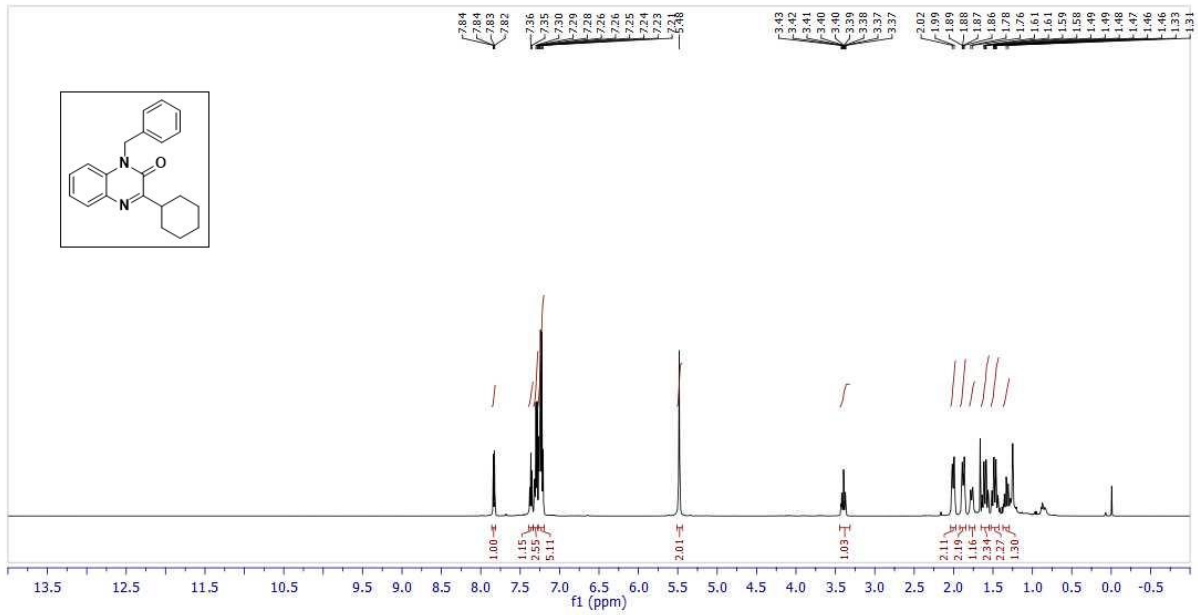
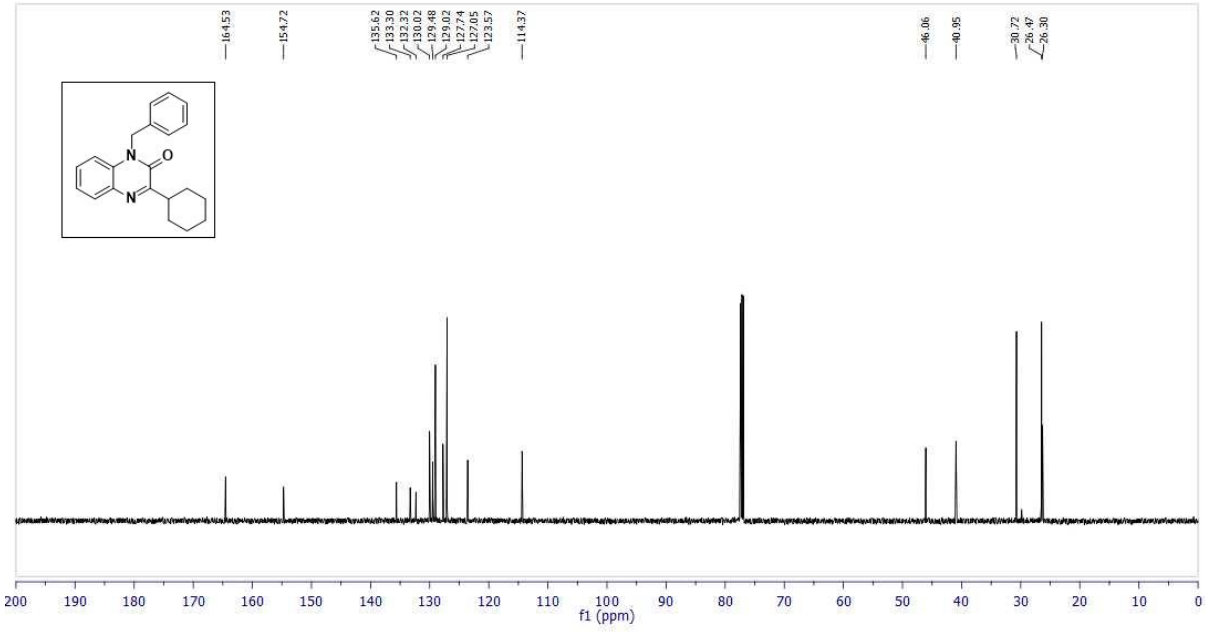


**$^{1}$H NMR spectrum of 4e (500 MHz, $CDCl_3$):**




**$^{13}$C NMR spectrum of 4e (126 MHz, $CDCl_3$):**



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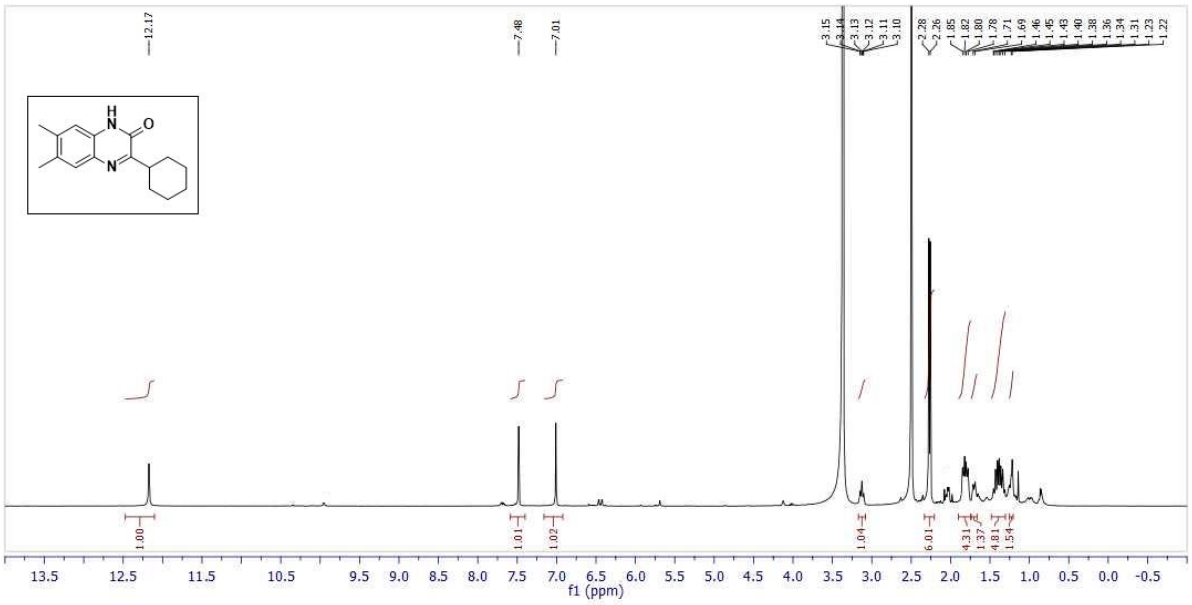


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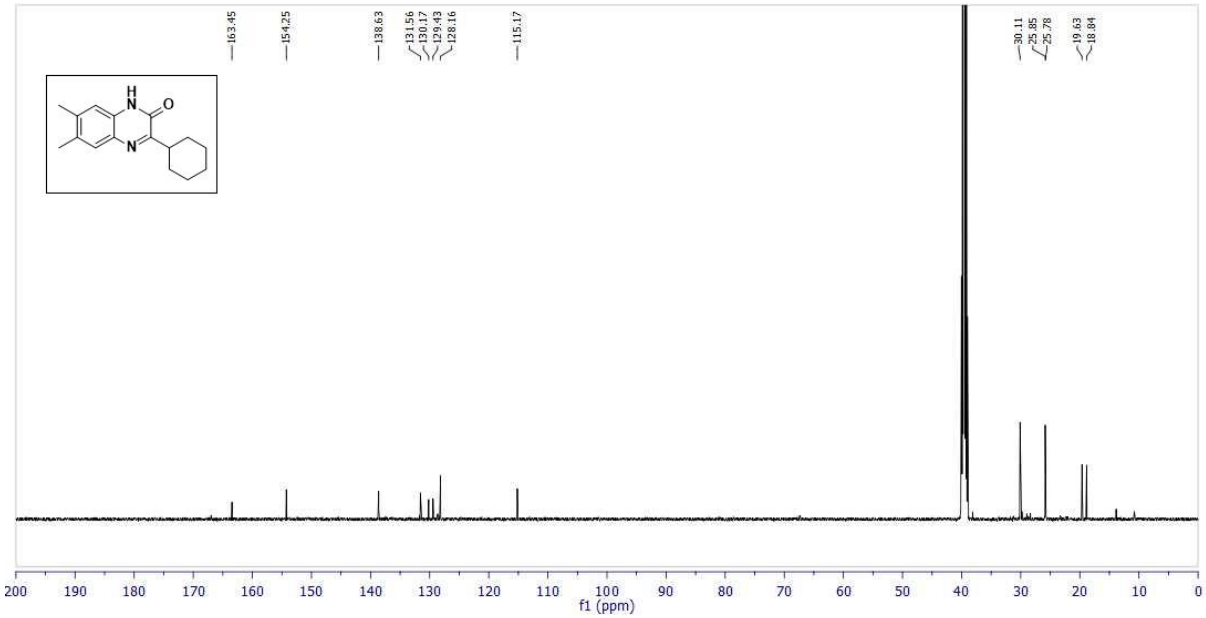
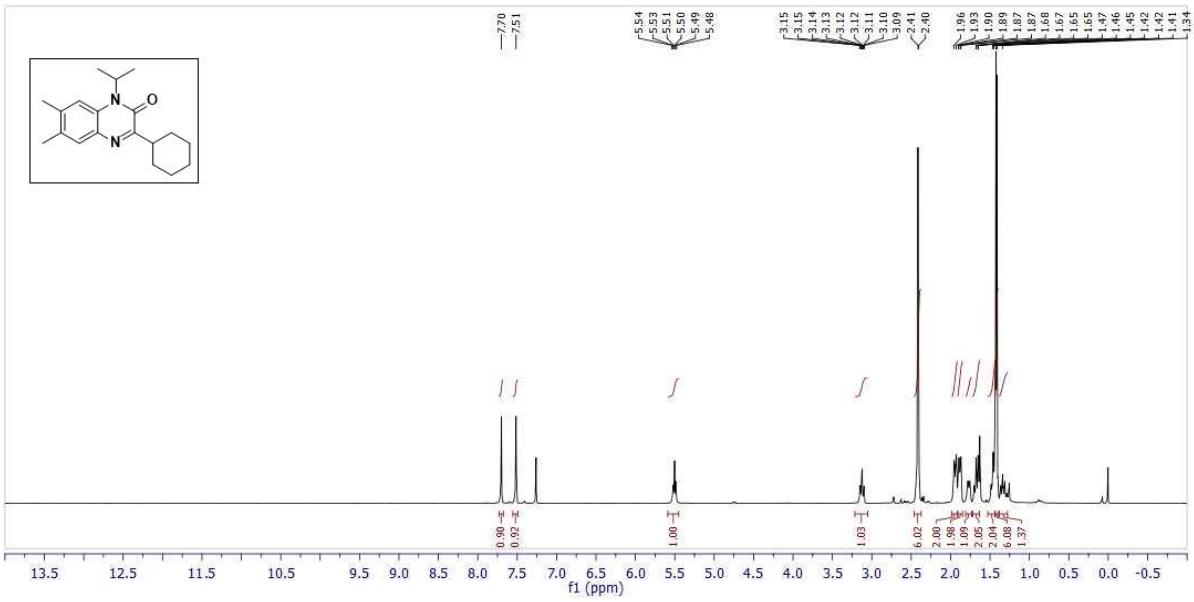
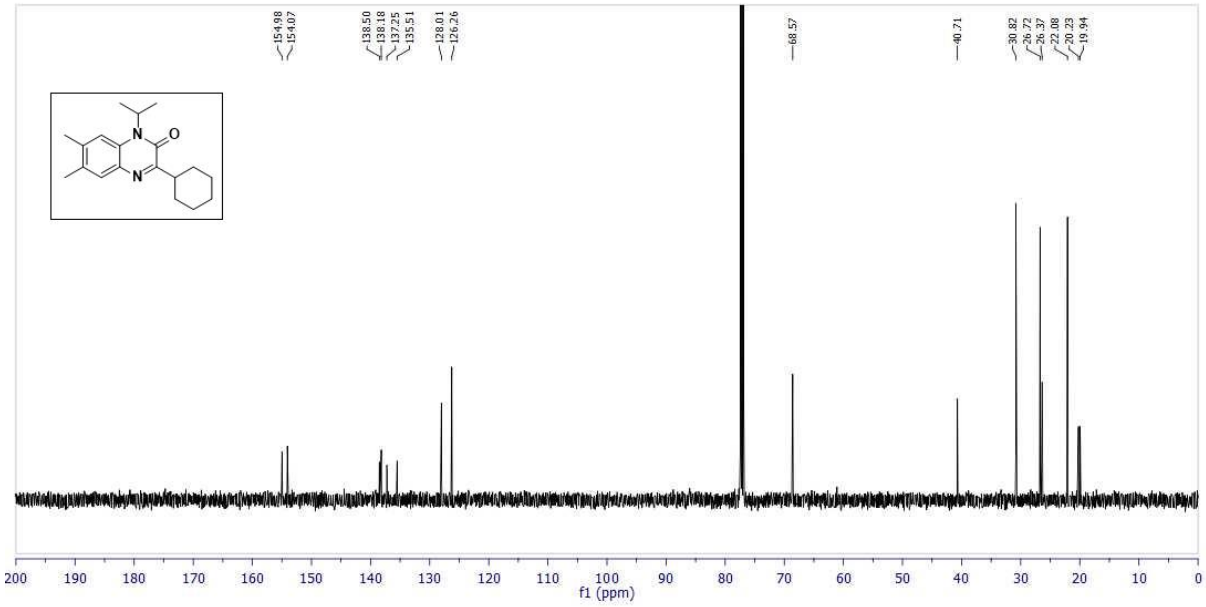


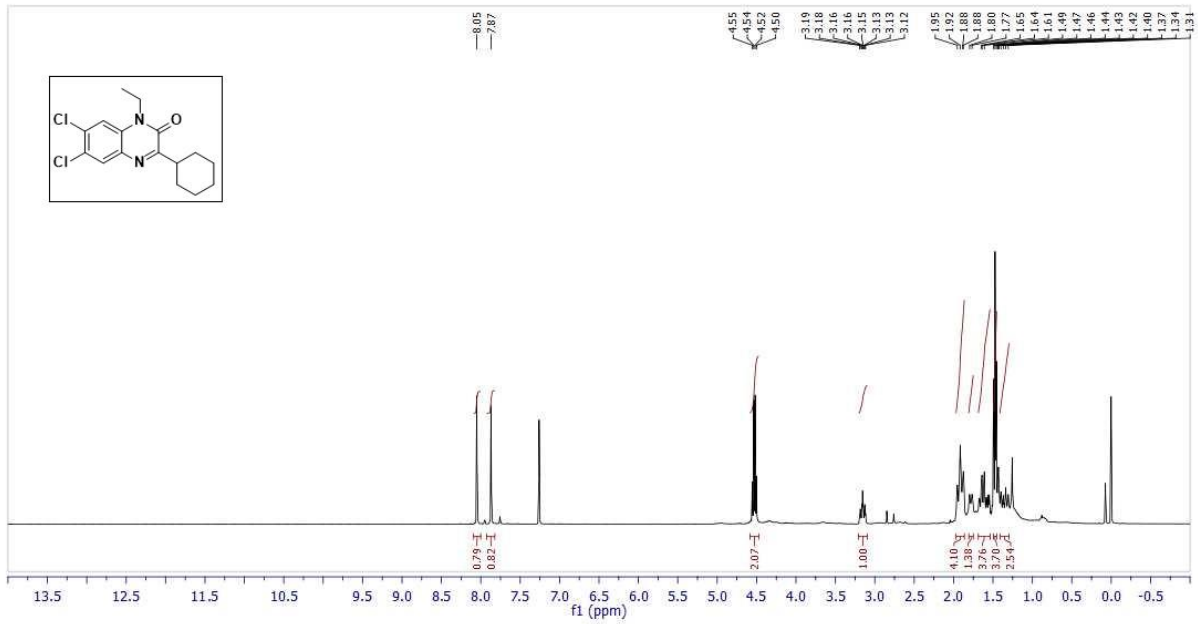
**$^{1}$H NMR spectrum of 4g (500 MHz, $CDCl_3$):**



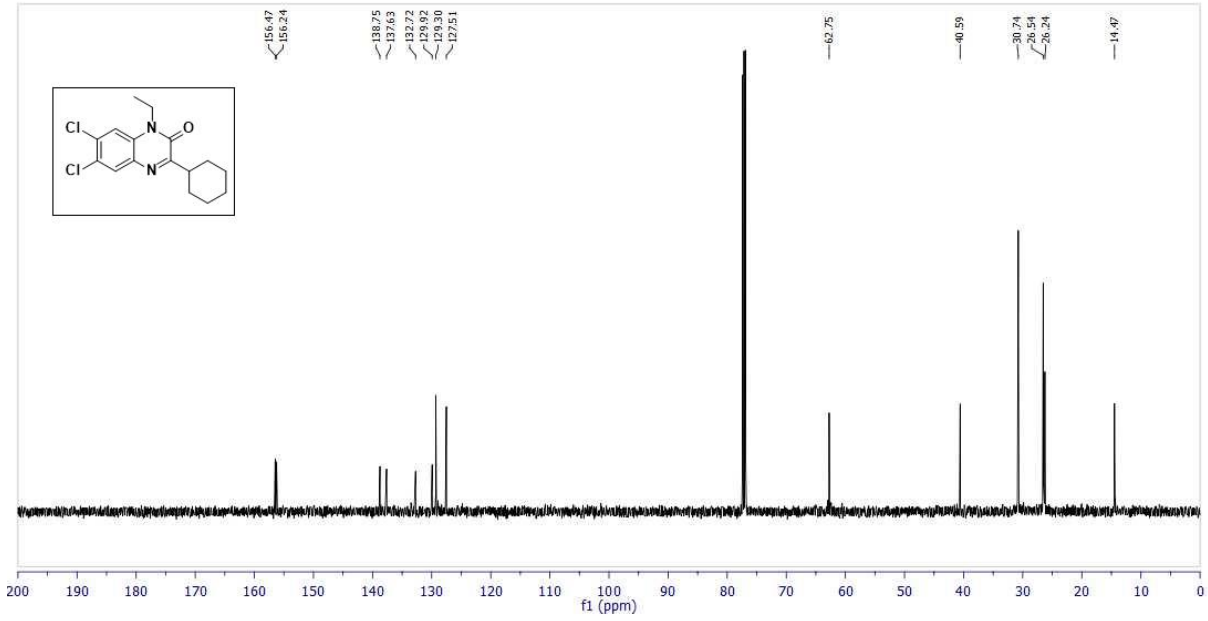

**$^{13}$C NMR spectrum of 4g (126 MHz, $CDCl_3$):**



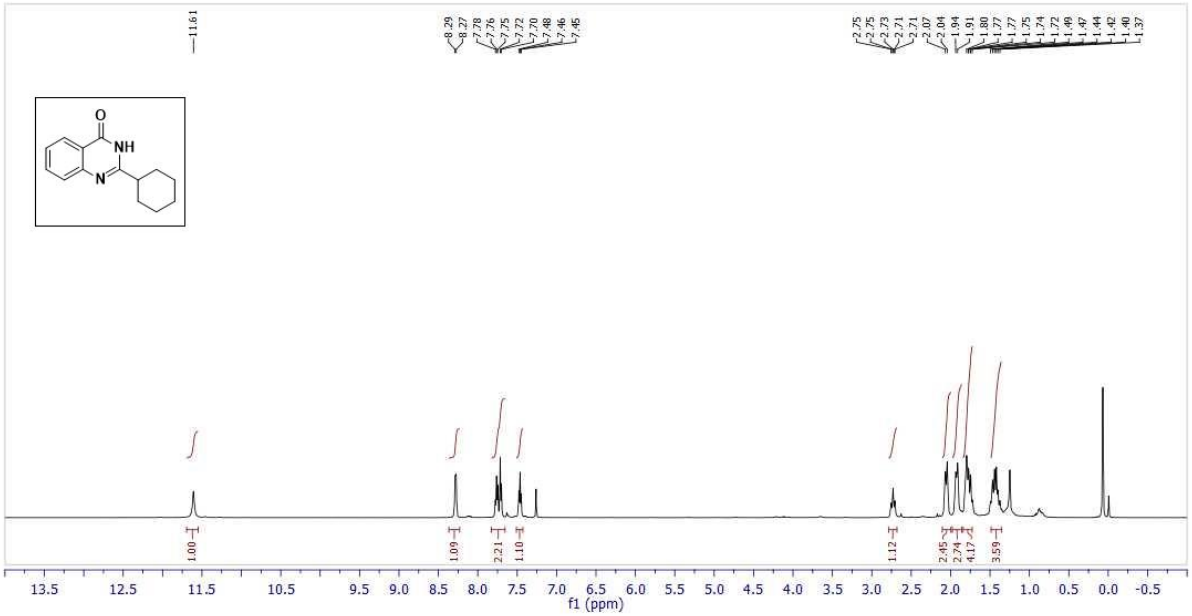
**$^{1}$H NMR spectrum of 4h (400 MHz, $CDCl_3$):**



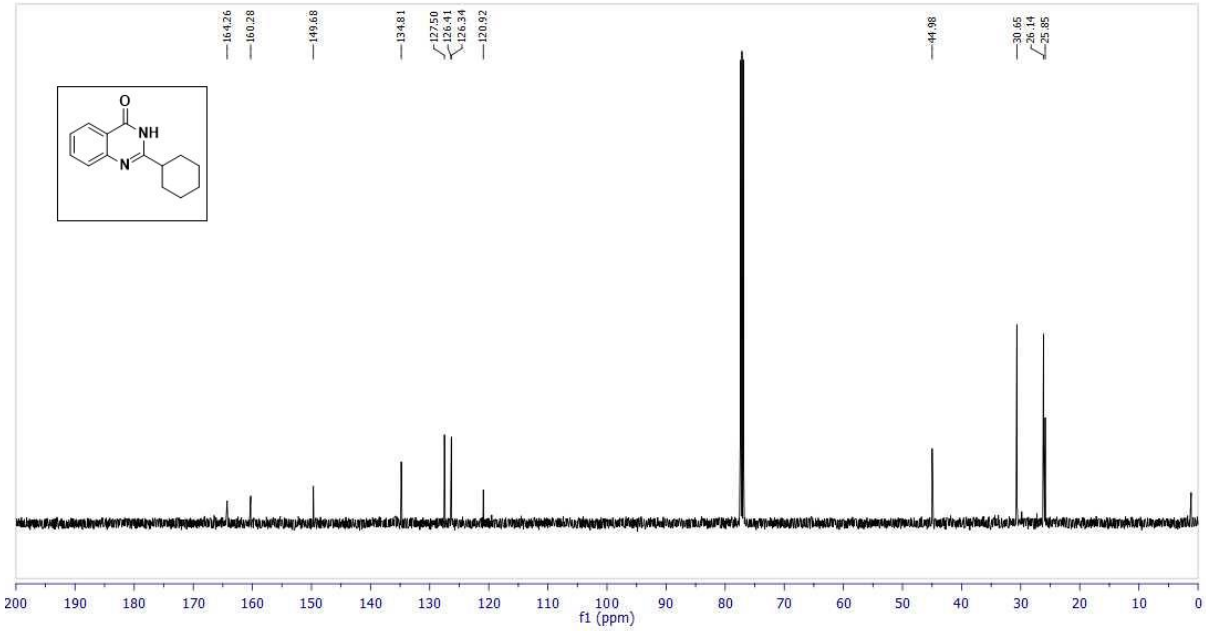

**$^{13}$C NMR spectrum of 4h (126 MHz, $CDCl_3$):**



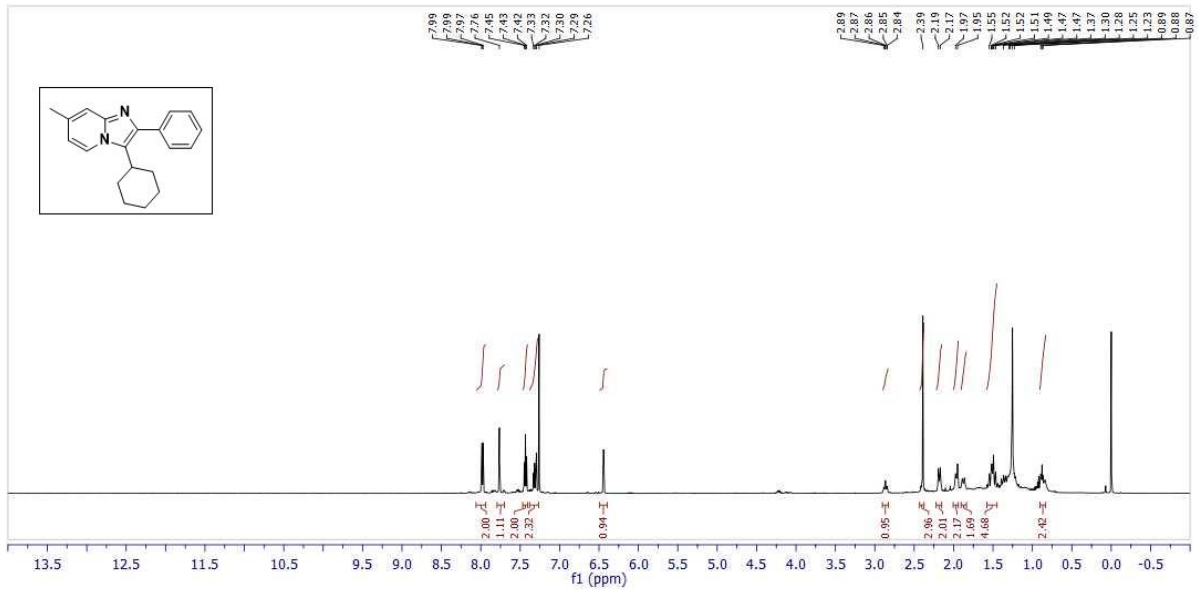
**$^{1}$H NMR spectrum of 4i (500 MHz, $CDCl_3$):**



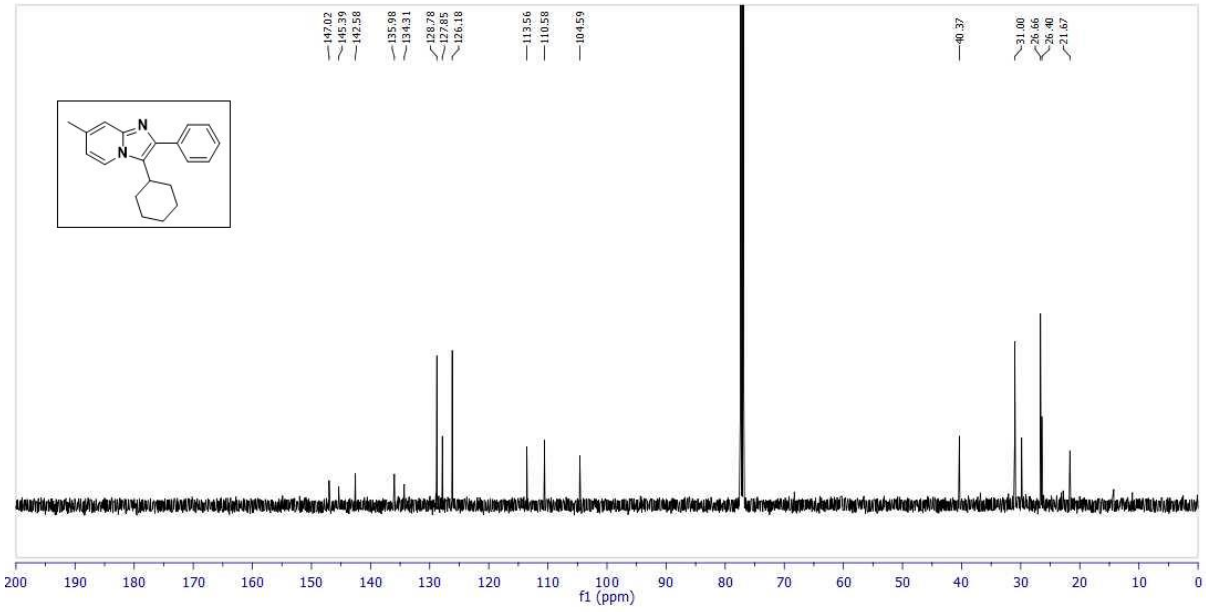

**$^{13}$C NMR spectrum of 4i (126 MHz, $CDCl_3$):**



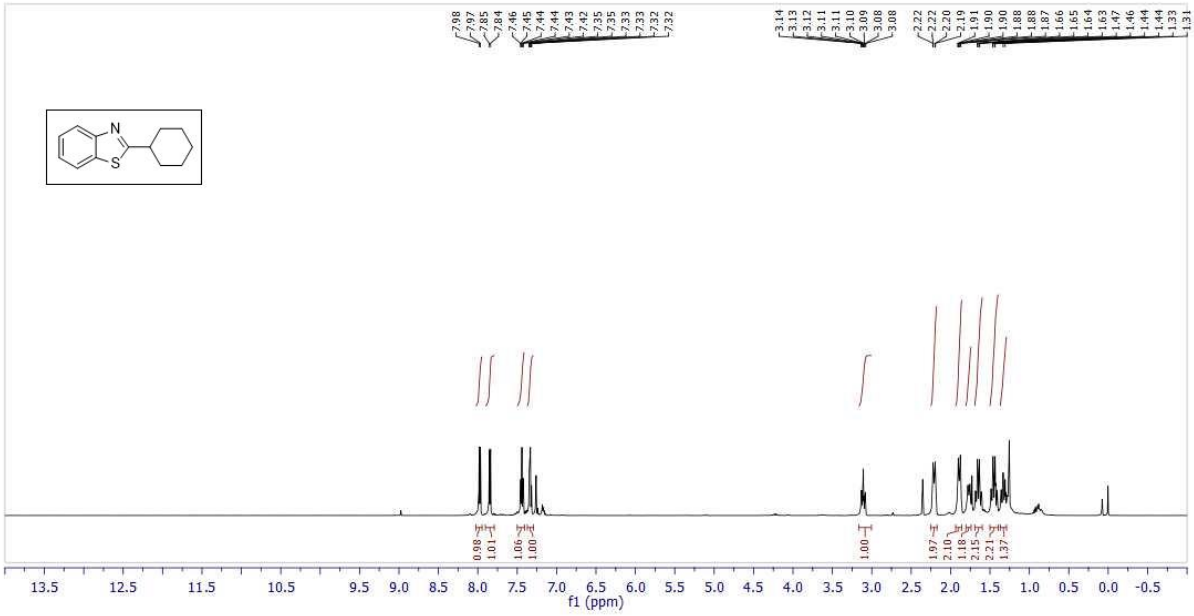
**$^{1}$H NMR spectrum of 4j (500 MHz, $CDCl_3$):**



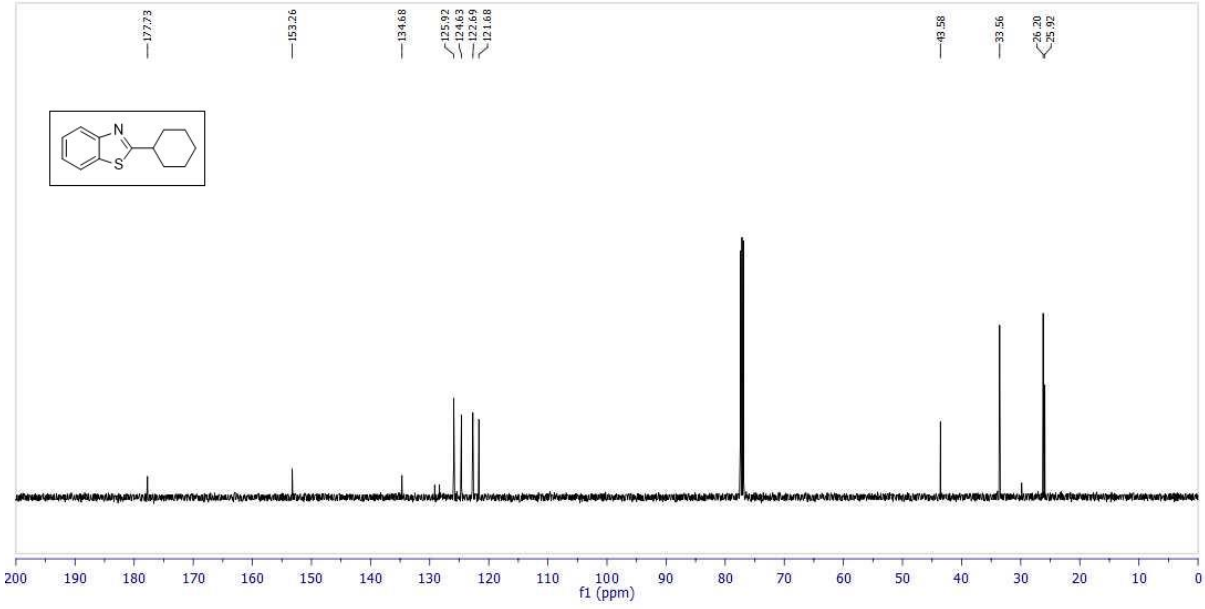

**$^{13}$C NMR spectrum of 4j (126 MHz, $CDCl_3$):**



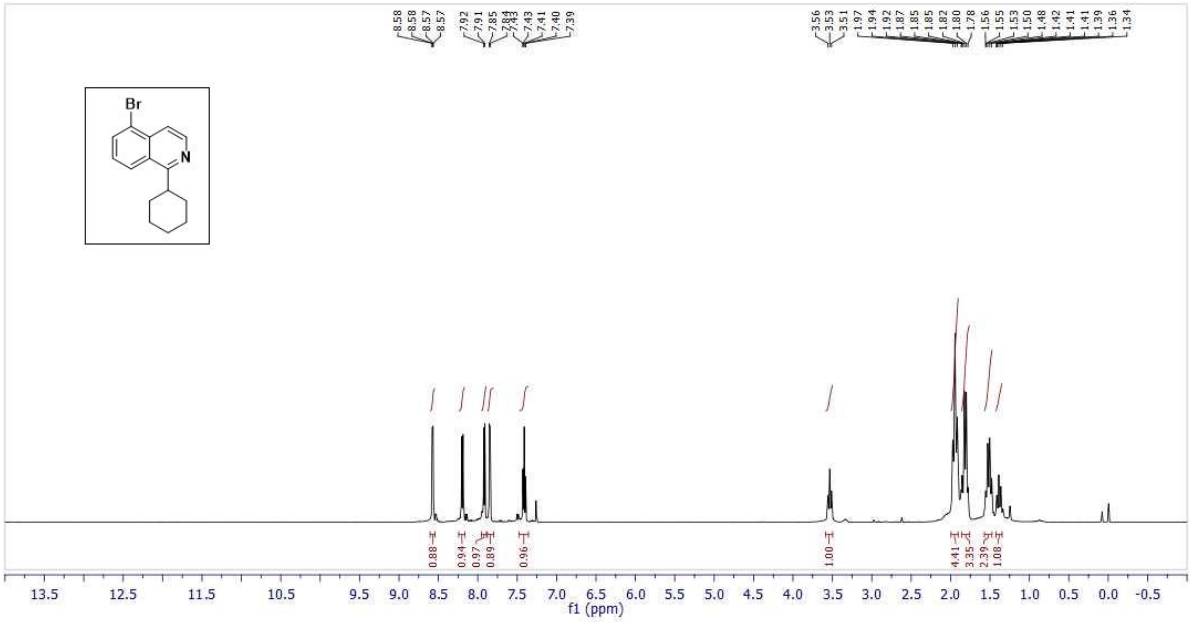
**$^{1}$H NMR spectrum of 4k (500 MHz, $CDCl_3$):**



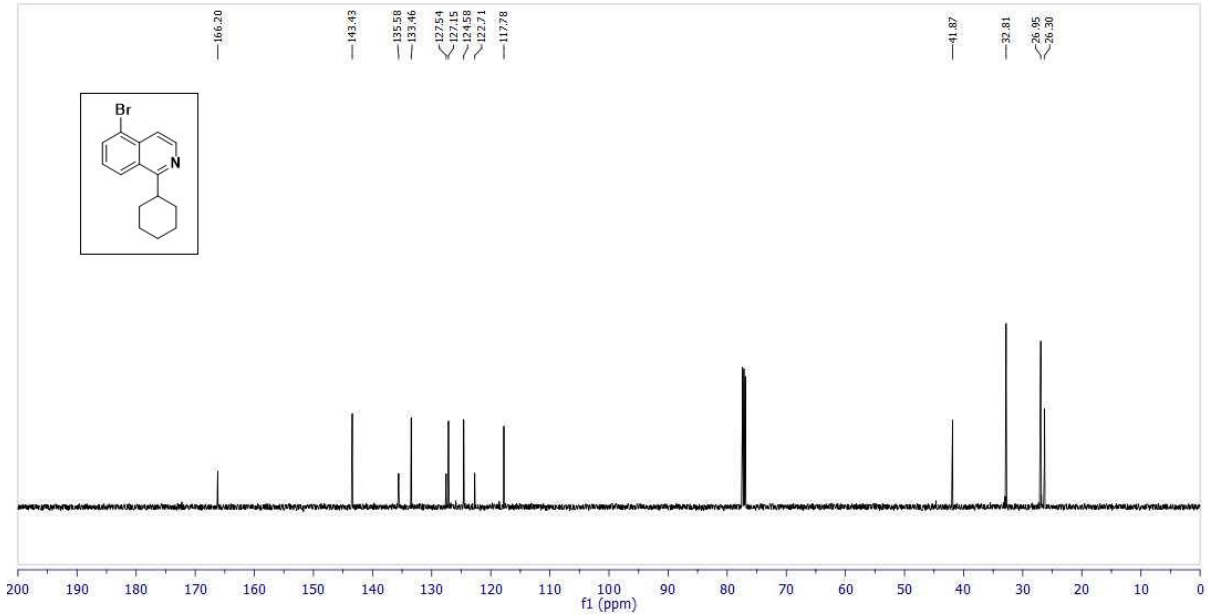
**$^{13}$C NMR spectrum of 4k (126 MHz, $CDCl_3$):**



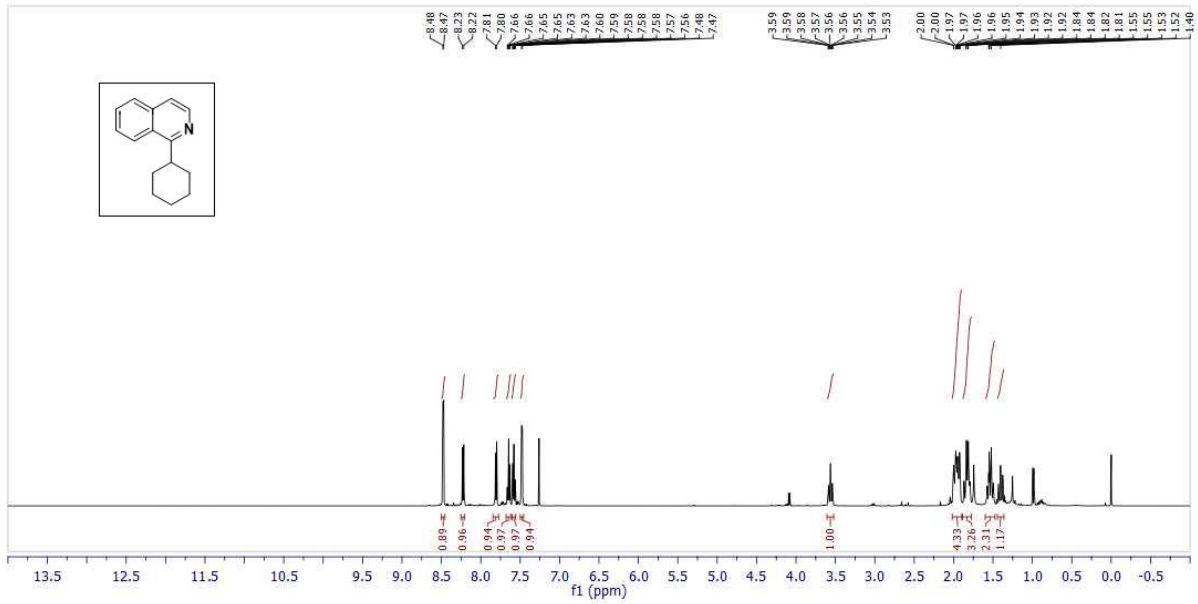
**$^{1}$H NMR spectrum of 4l (500 MHz, $CDCl_3$):**



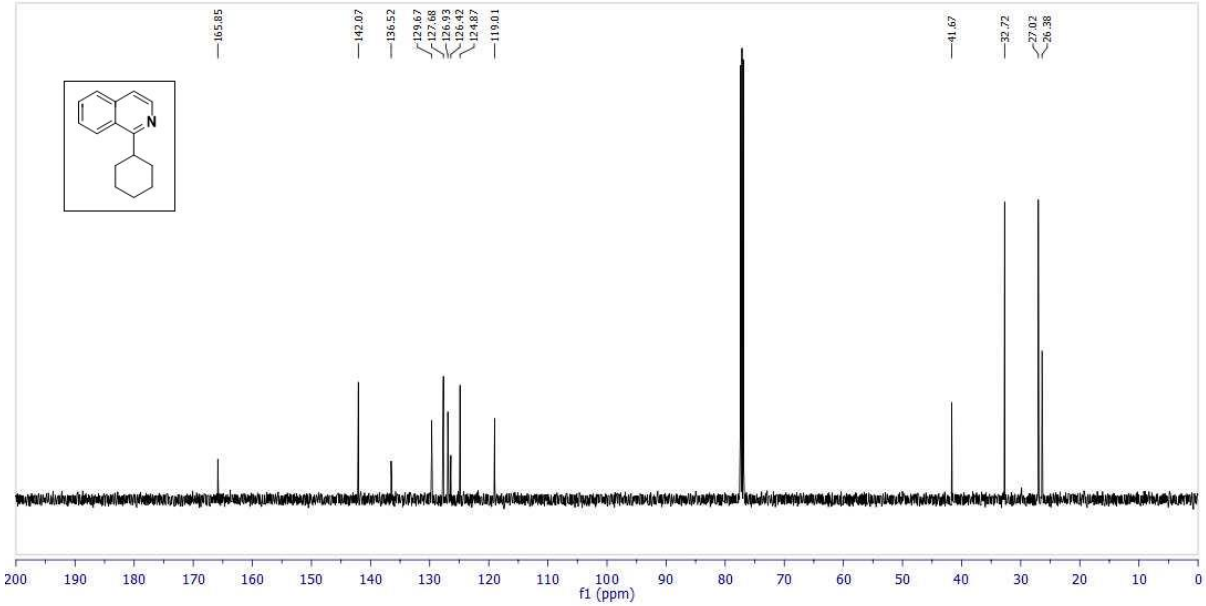

**$^{13}$C NMR spectrum of 4l (126 MHz, $CDCl_3$):**



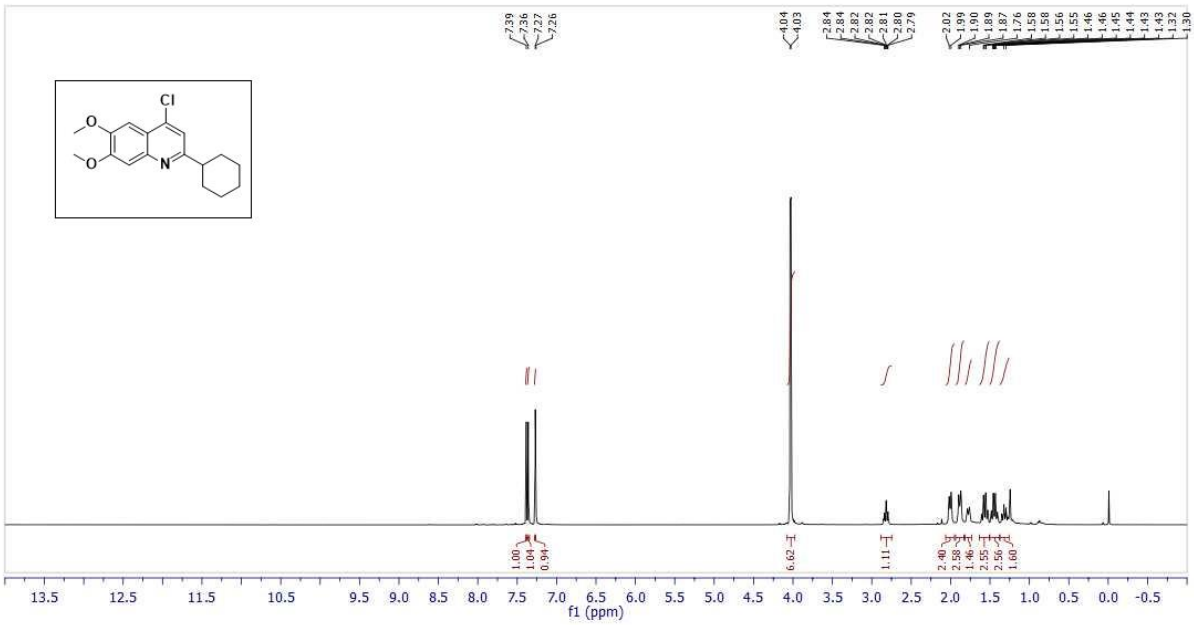
**$^{1}$H NMR spectrum of 4m (500 MHz, $CDCl_3$):**



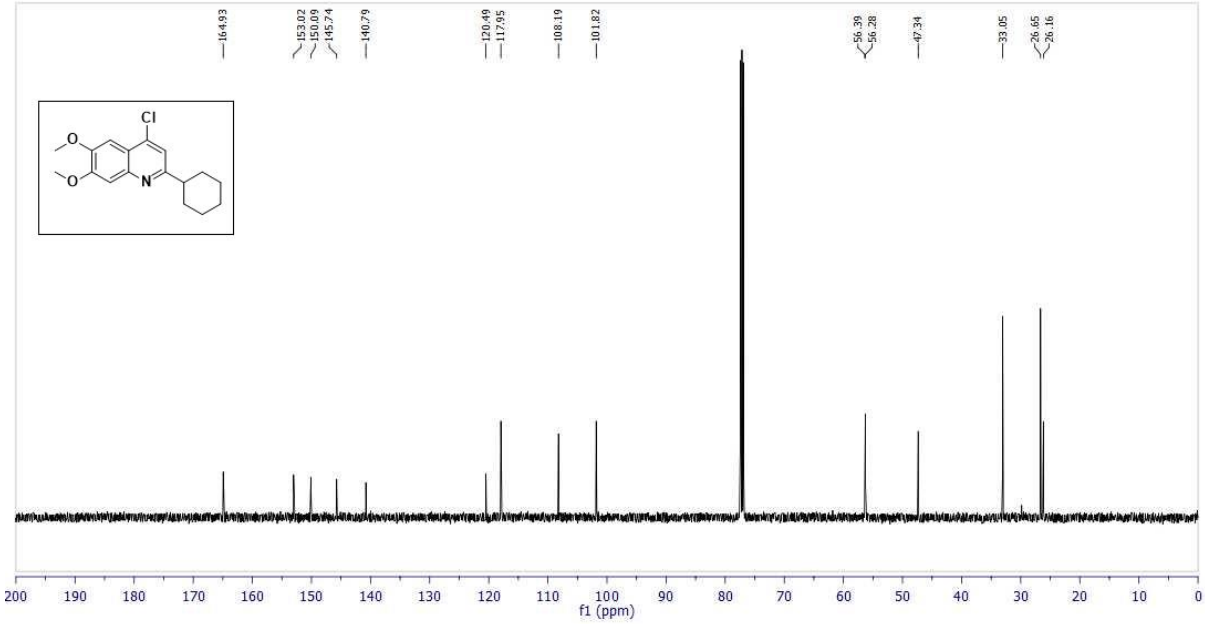

**$^{13}$C NMR spectrum of 4m (126 MHz, $CDCl_3$):**



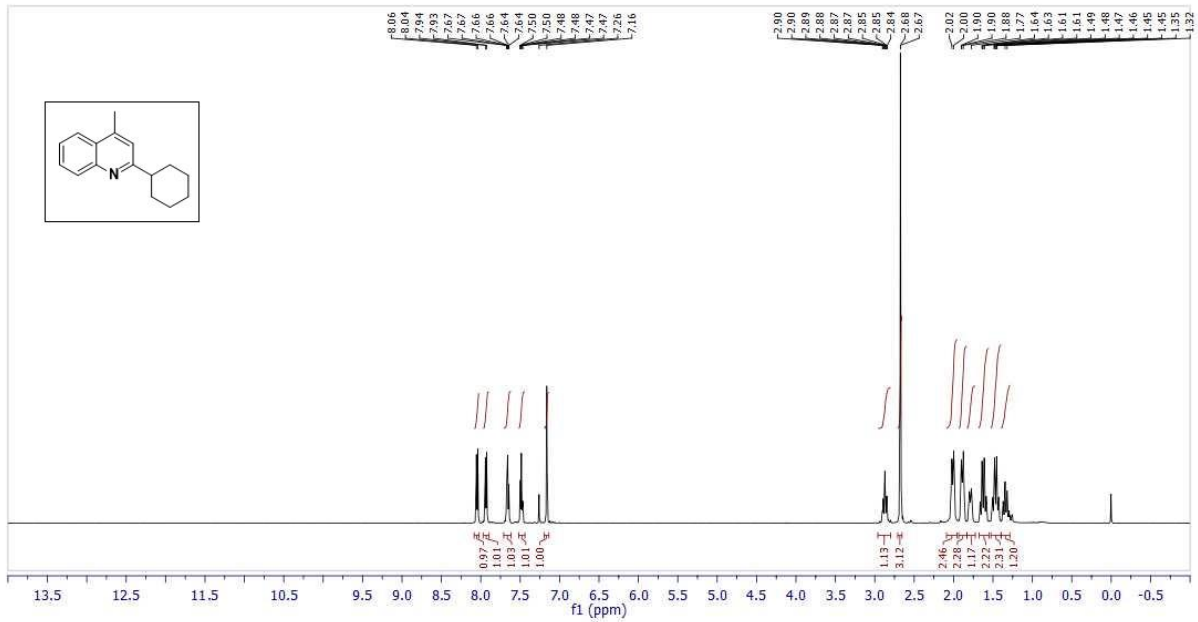
**$^{1}$H NMR spectrum of 4n (500 MHz, $CDCl_3$):**



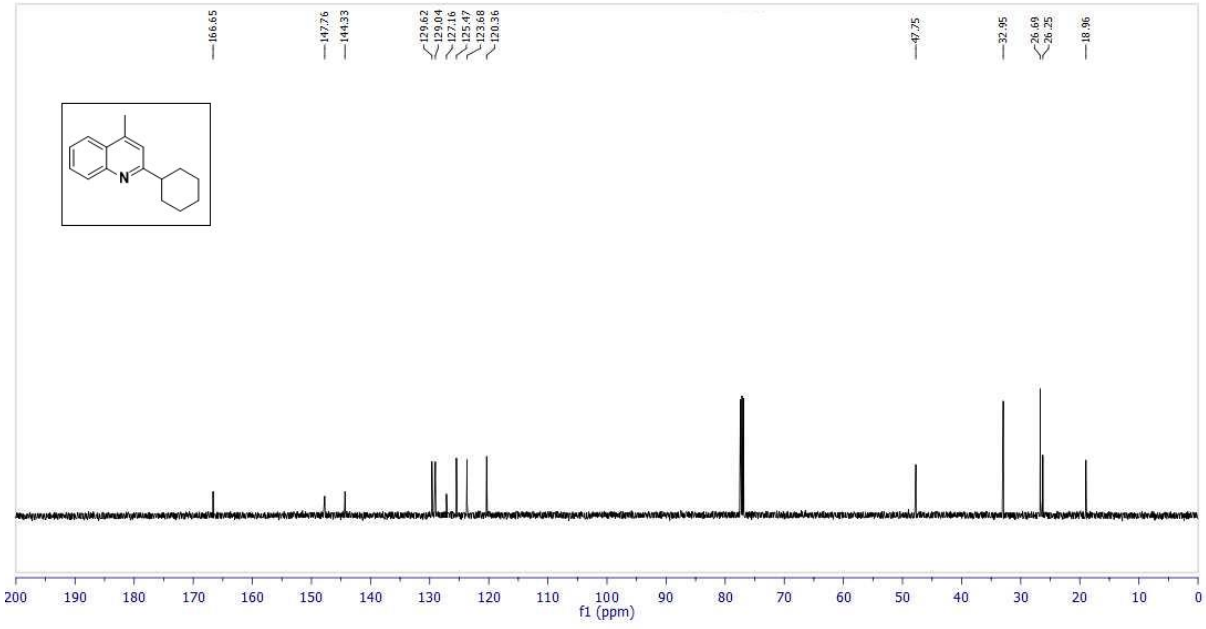

**$^{13}$C NMR spectrum of 4n (126 MHz, $CDCl_3$):**



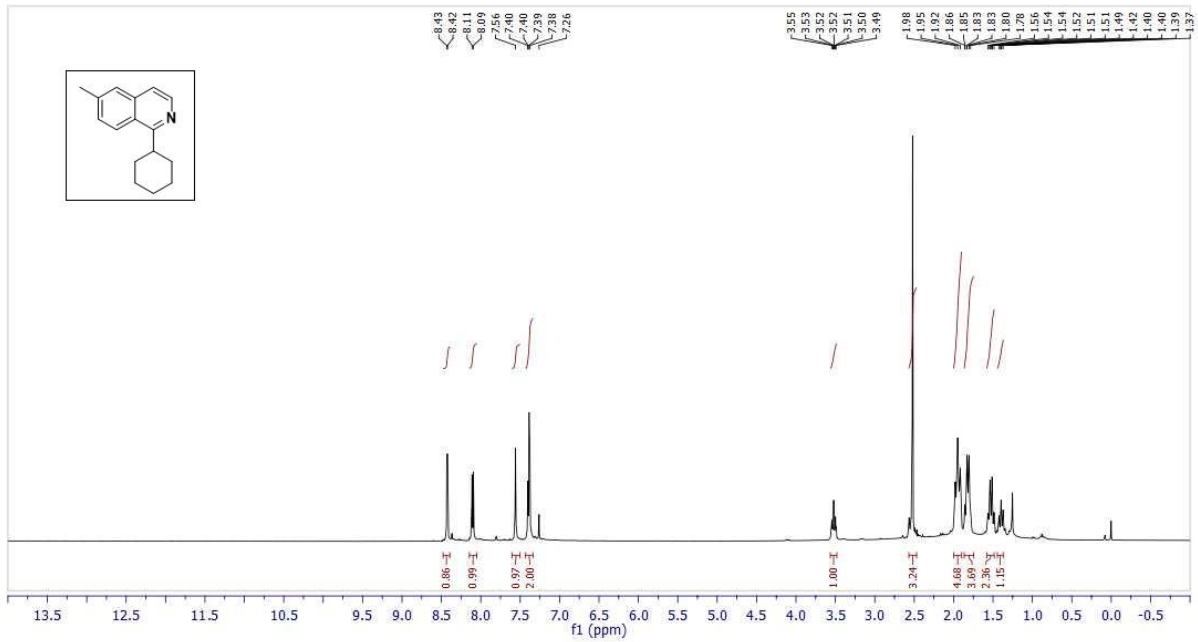
**$^{1}$H NMR spectrum of 4o (500 MHz, $CDCl_3$):**



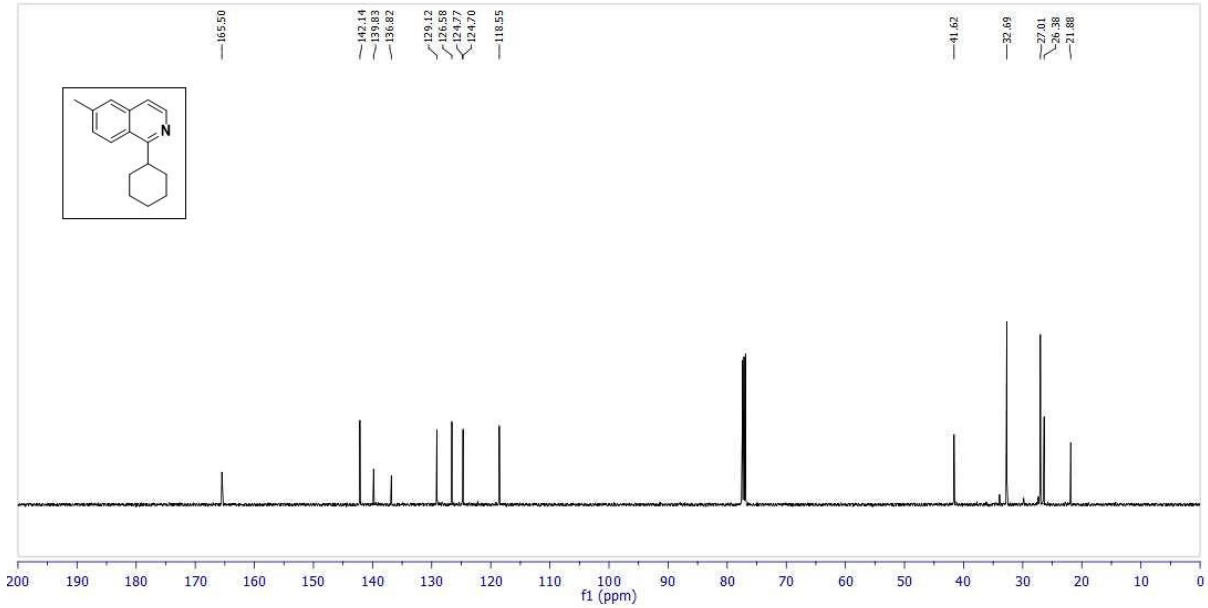

**$^{13}$C NMR spectrum of 4o (126 MHz, $CDCl_3$):**



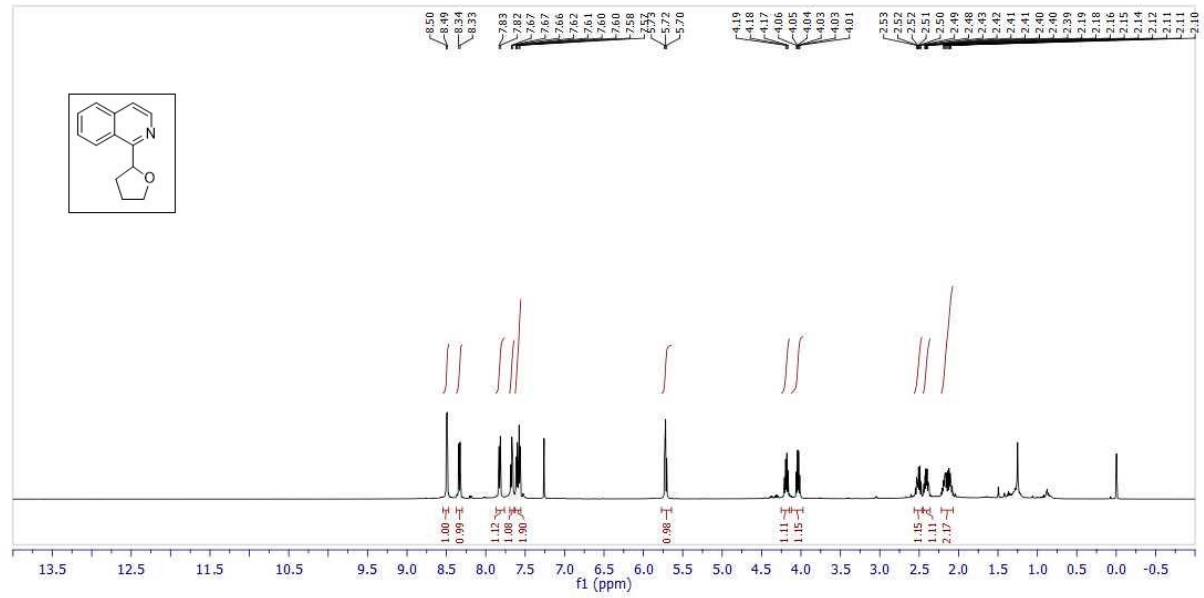
**$^{1}$H NMR spectrum of 4p (500 MHz, $CDCl_3$):**



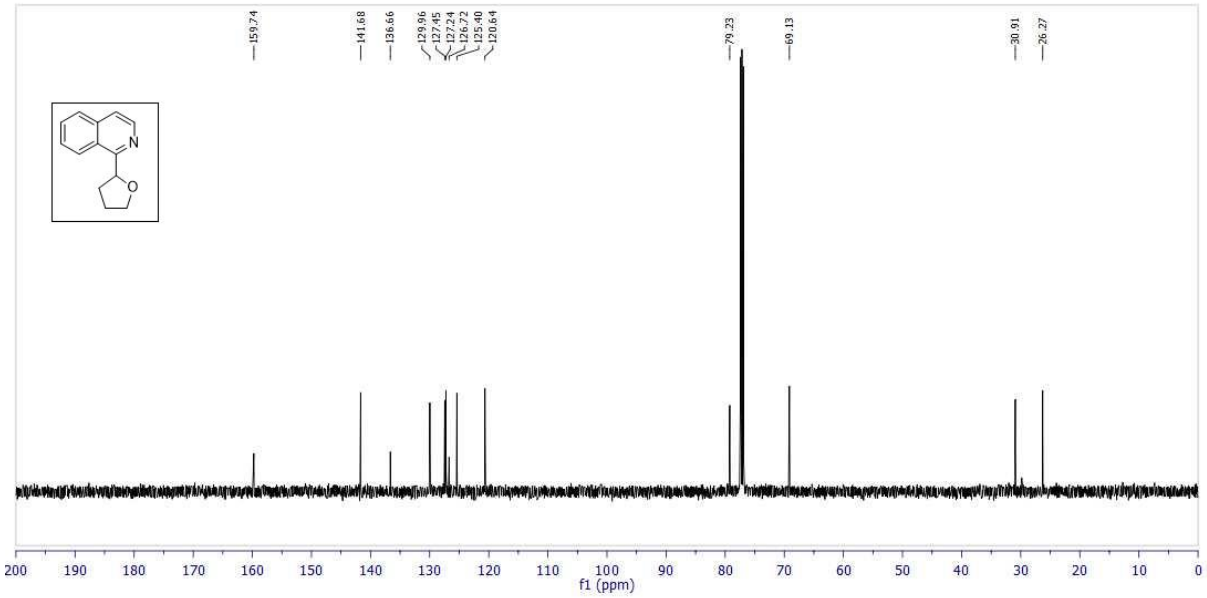

**$^{13}$C NMR spectrum of 4p (126 MHz, $CDCl_3$):**



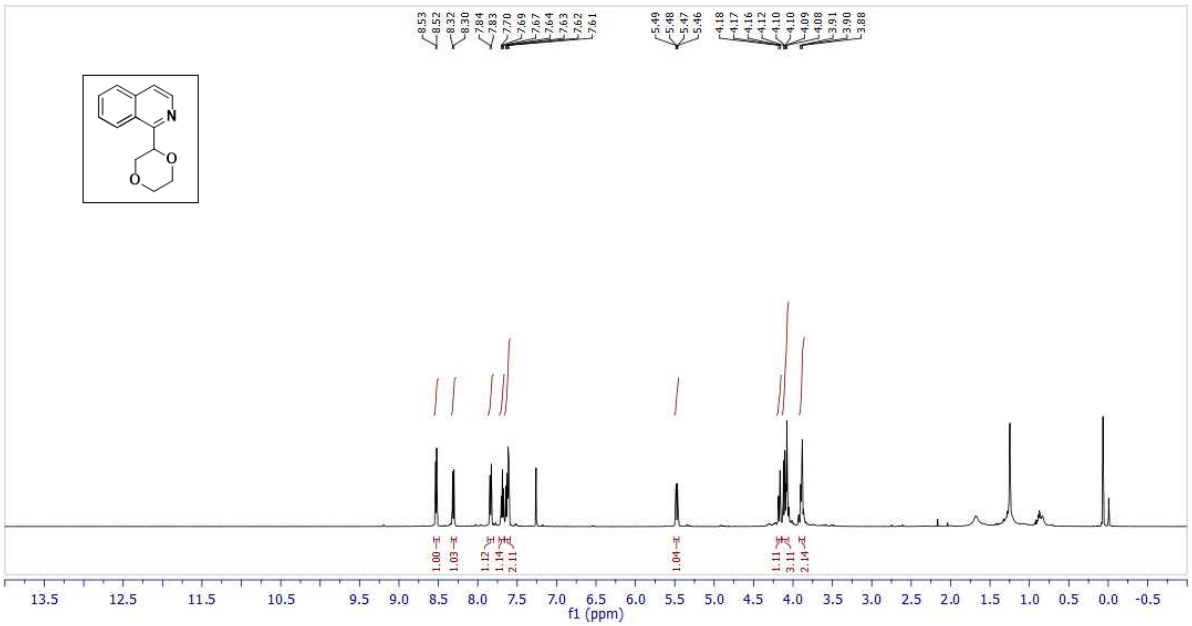
**$^{1}$H NMR spectrum of 4q (500 MHz, $CDCl_3$):**



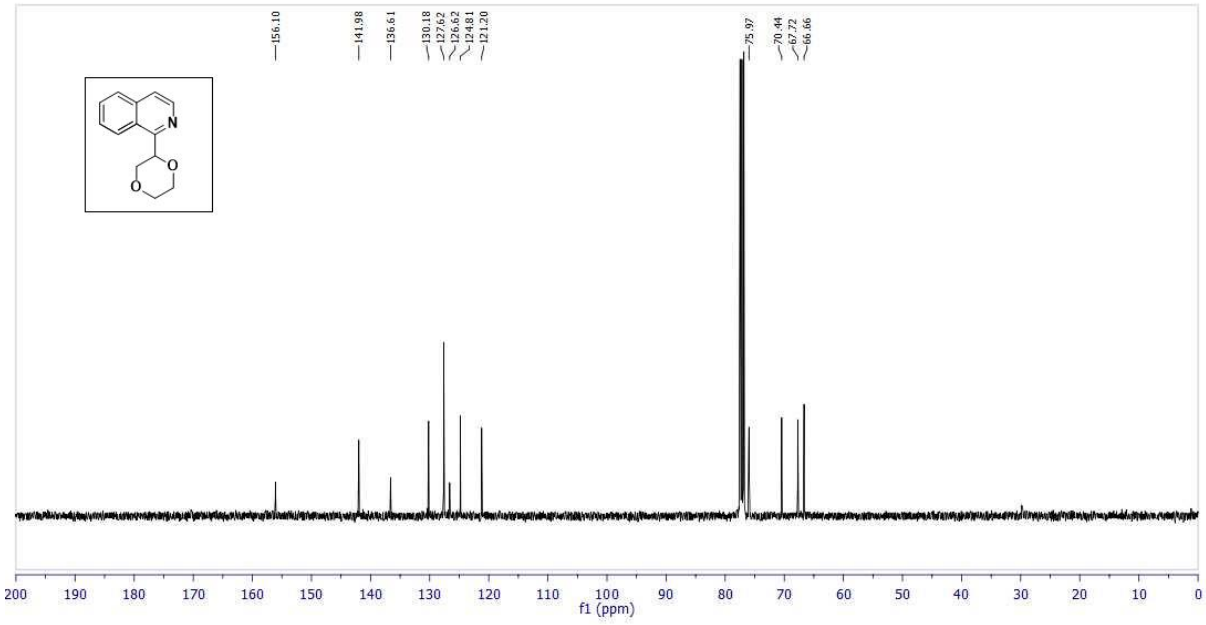

**$^{13}$C NMR spectrum of 4q (126 MHz, $CDCl_3$):**



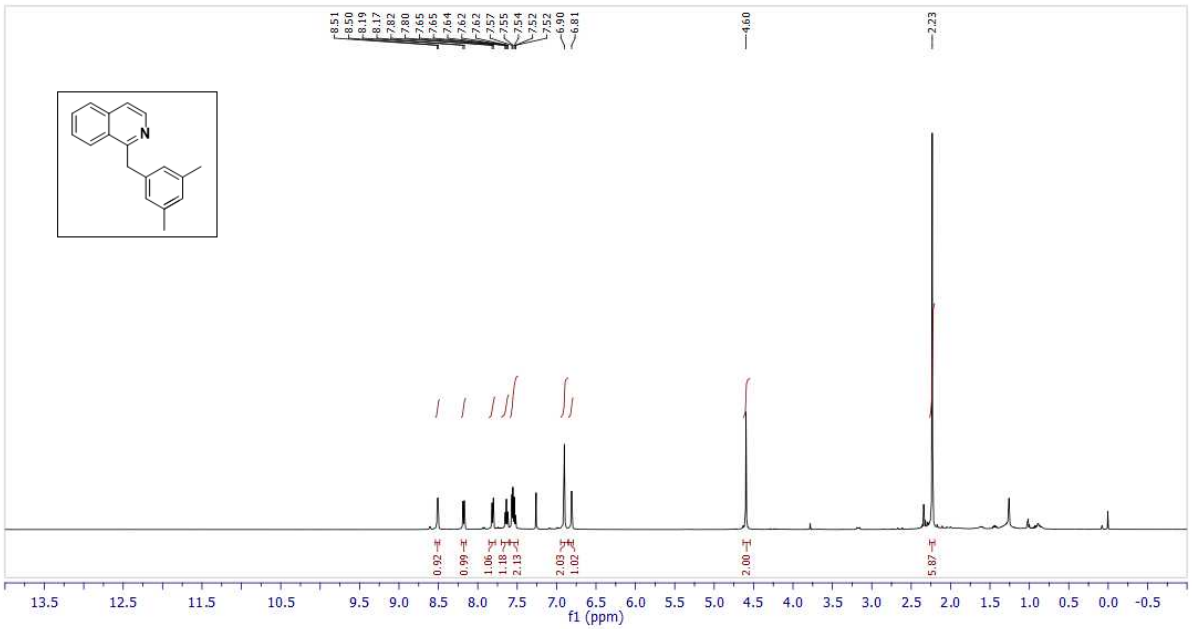
**$^{1}$H NMR spectrum of 4r (500 MHz, $CDCl_3$):**



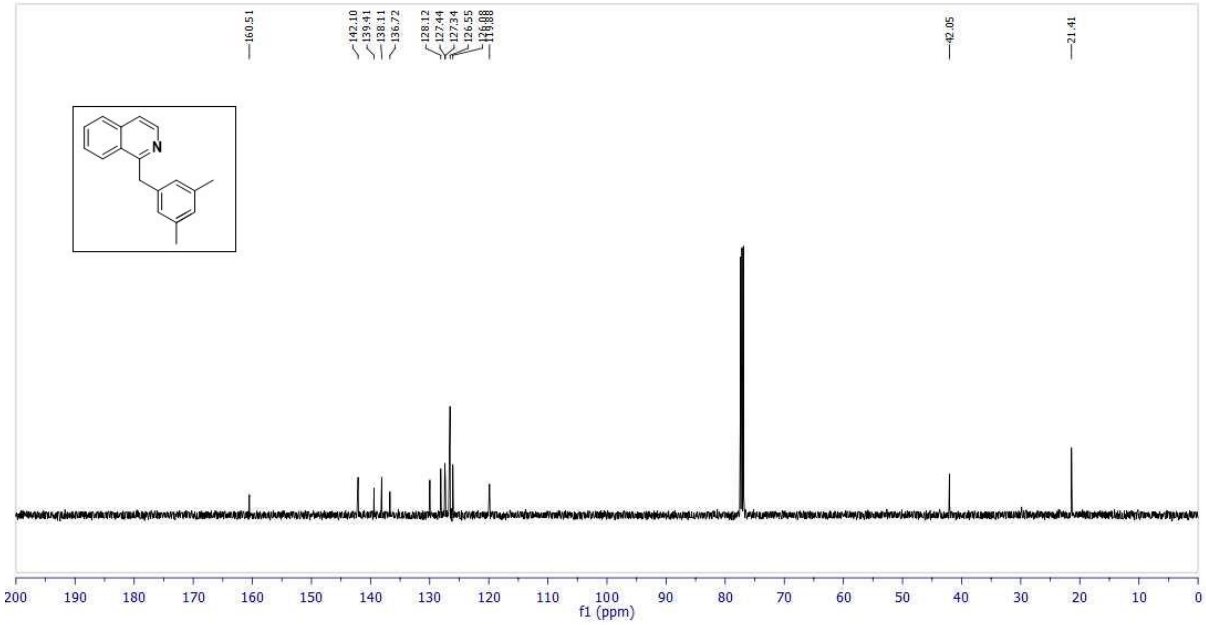

**$^{13}$C NMR spectrum of 4r (101 MHz, $CDCl_3$):**



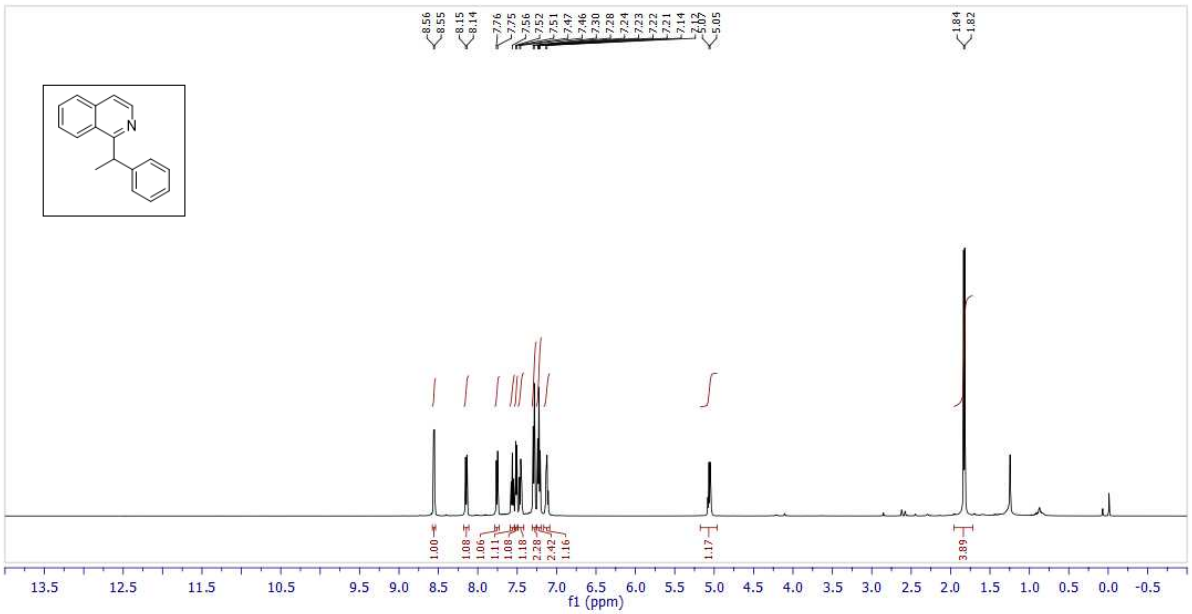
**$^{1}$H NMR spectrum of 4s (500 MHz, $CDCl_3$):**



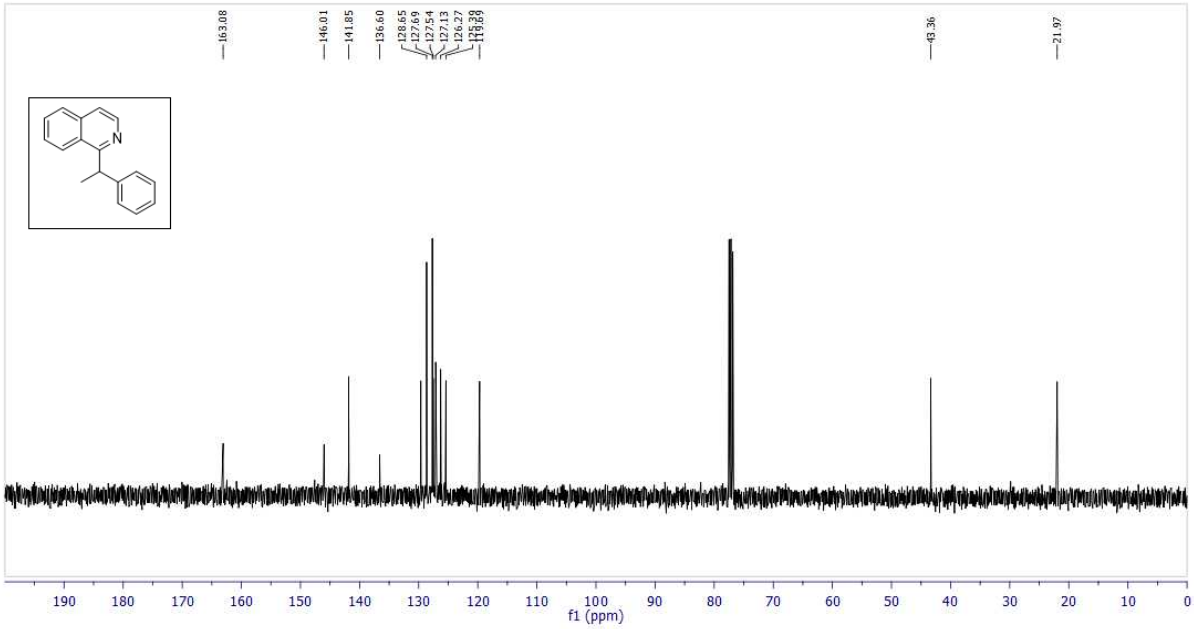

**$^{13}$C NMR spectrum of 4s (126 MHz, $CDCl_3$):**



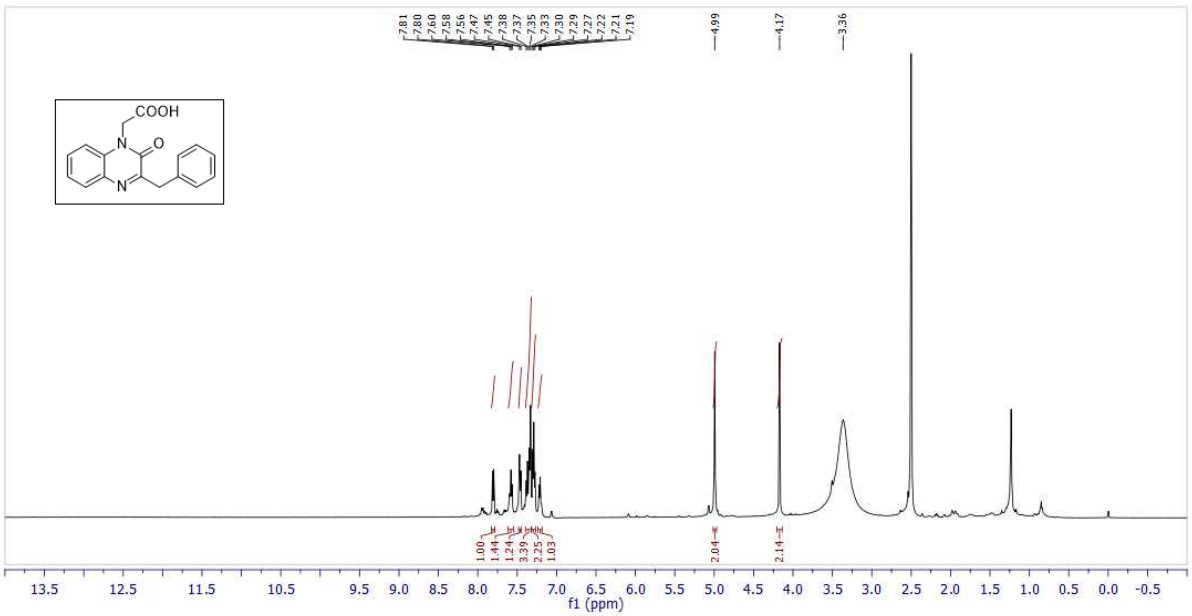
**$^{1}$H NMR spectrum of 4t (500 MHz, $CDCl_3$):**



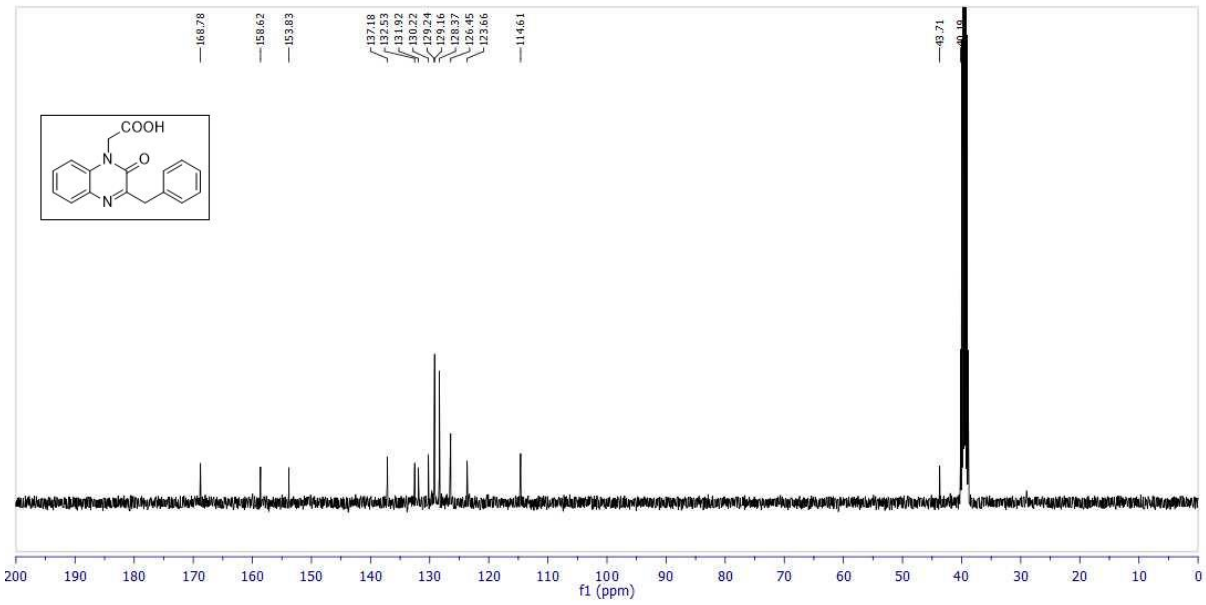

**$^{13}$C NMR spectrum of 4t (101 MHz, $CDCl_3$):**



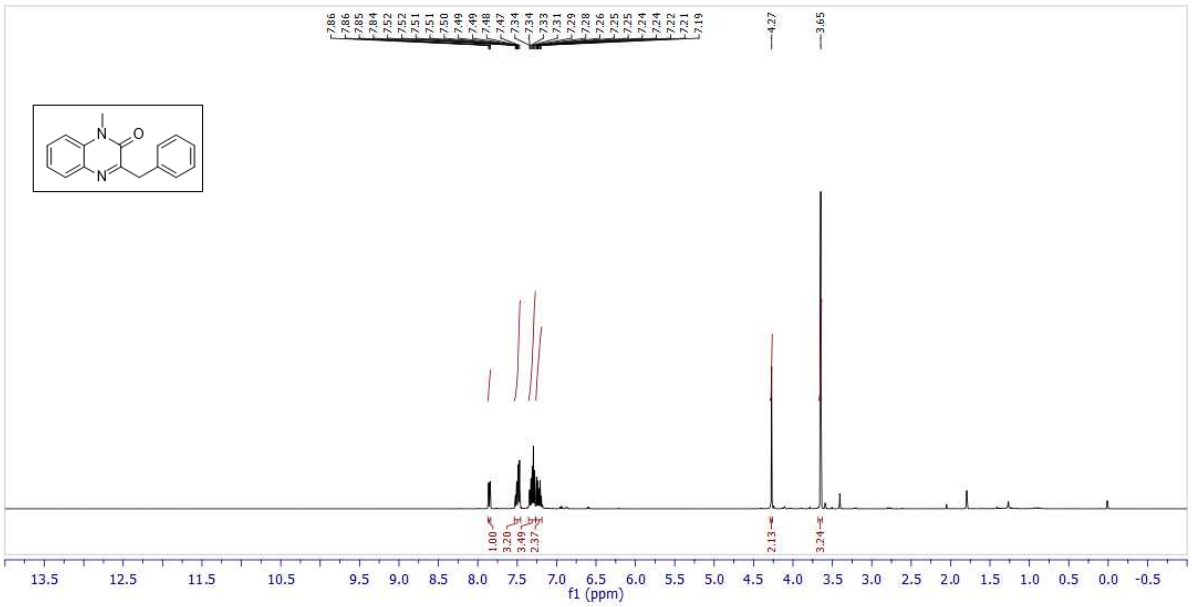
**$^{1}$H NMR spectrum of 7 (500 MHz, DMSO-d6):**




**$^{13}$C NMR spectrum of 7 (101 MHz, DMSO-d6):**



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




**$^{13}$C NMR spectrum of 8 (126 MHz, $CDCl_3$):**