

Supporting Information

Uncatalyzed diastereoselective synthesis of alkyliminofurochromone-derived benzylmalononitriles *via* a three-component cascade reaction: Competition between Diels-Alder cycloaddition and Michael addition

Mohammad Bagher Teimouri,^{*a} Zahra Mokhtare,^a Hamid Reza Khavasi^b

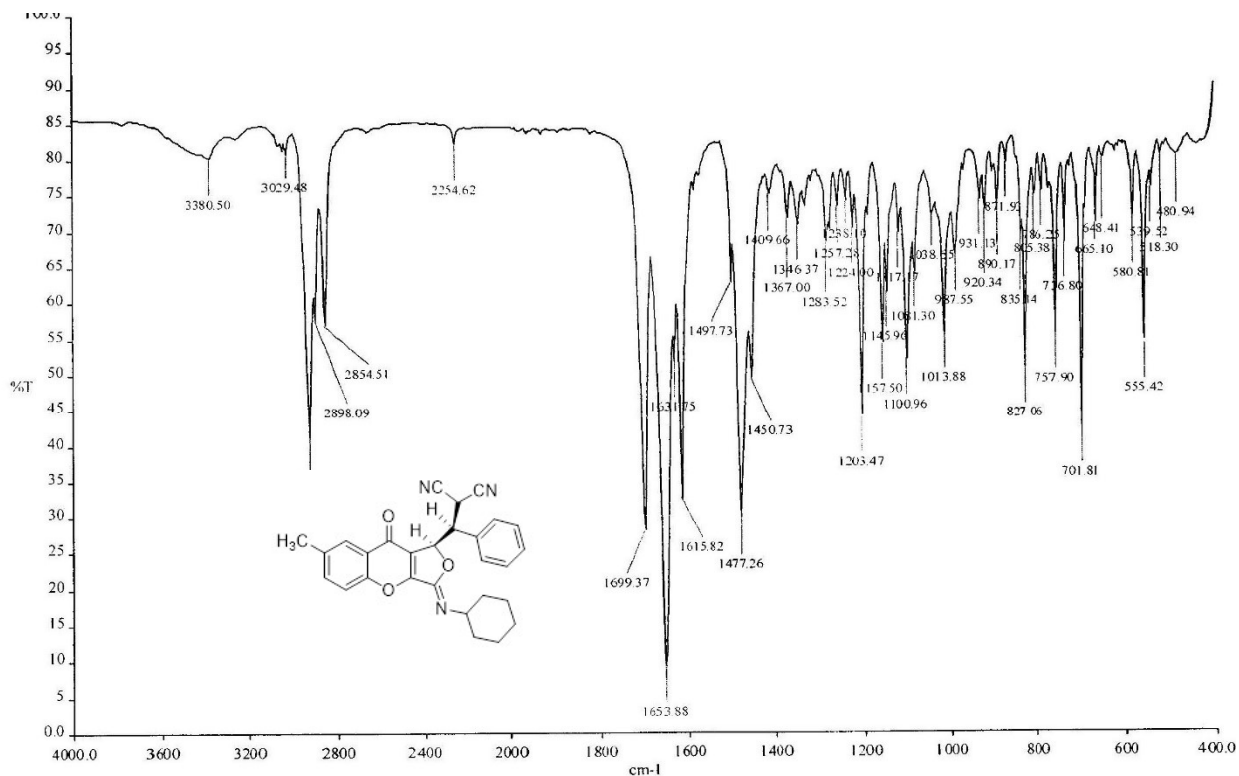
^a *Faculty of Chemistry, Kharazmi University, Mofateh Ave., Tehran, Iran*

^b *Department of Inorganic Chemistry and Catalysis, Shahid Beheshti University, Evin, Tehran, Iran*

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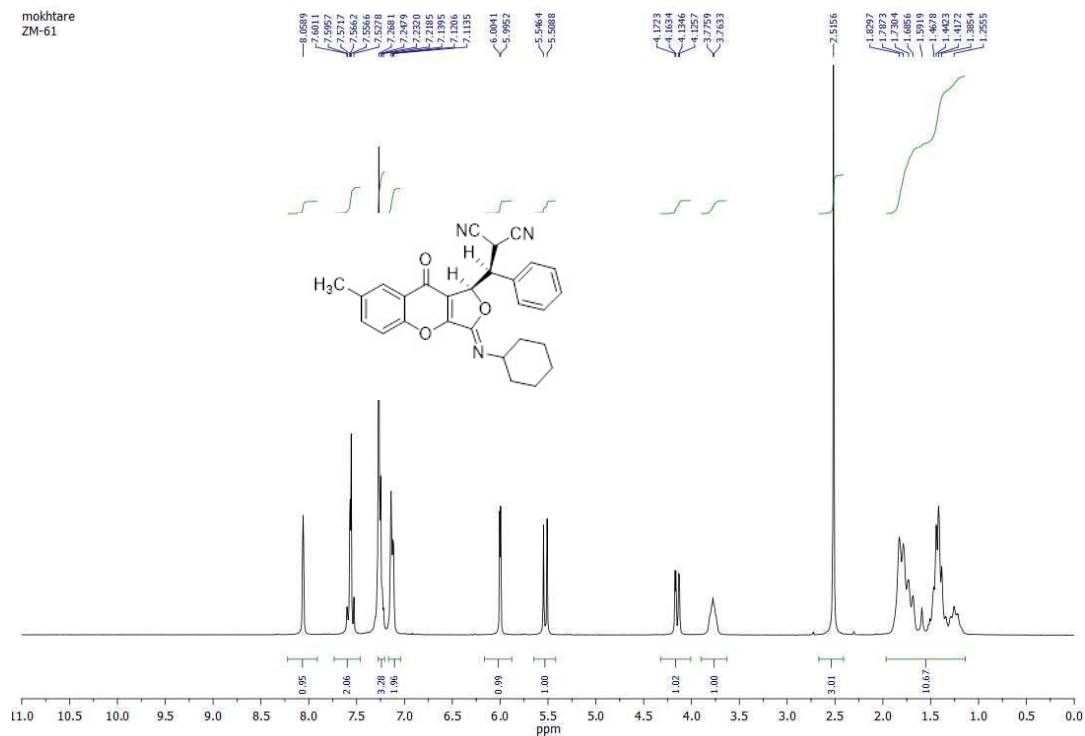
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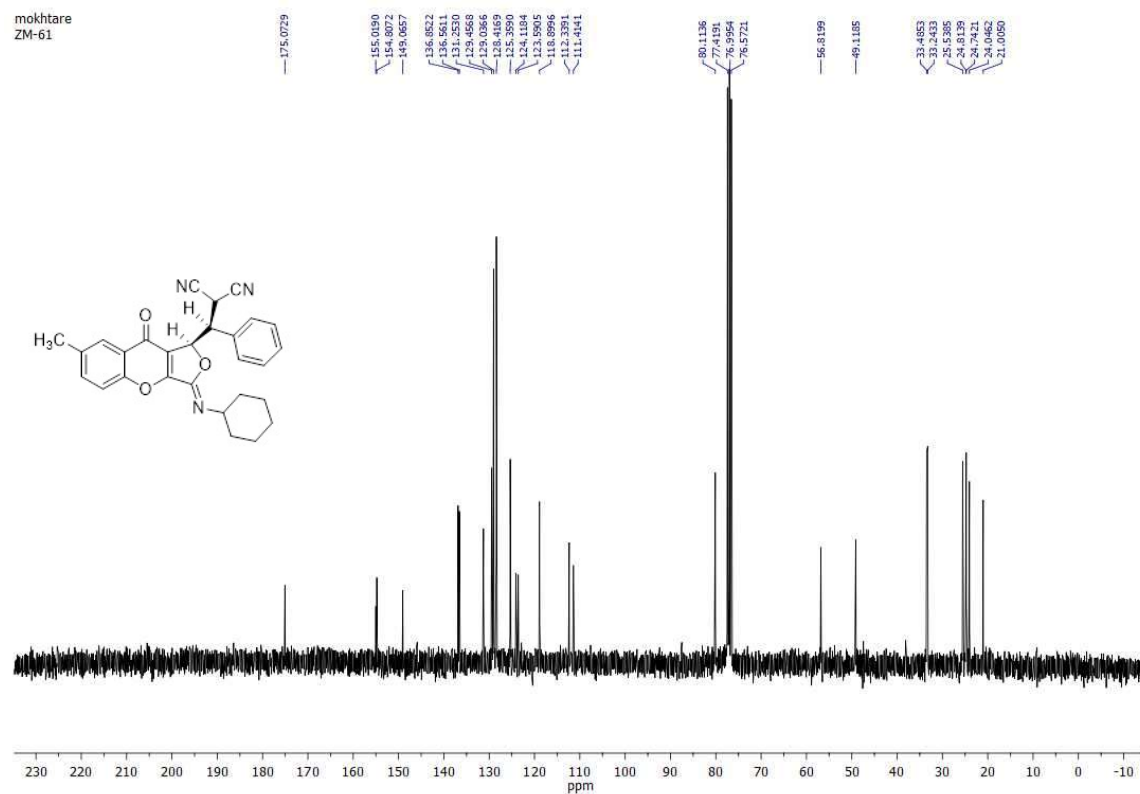
Ms. Mokhtare

Sample: ZM-61

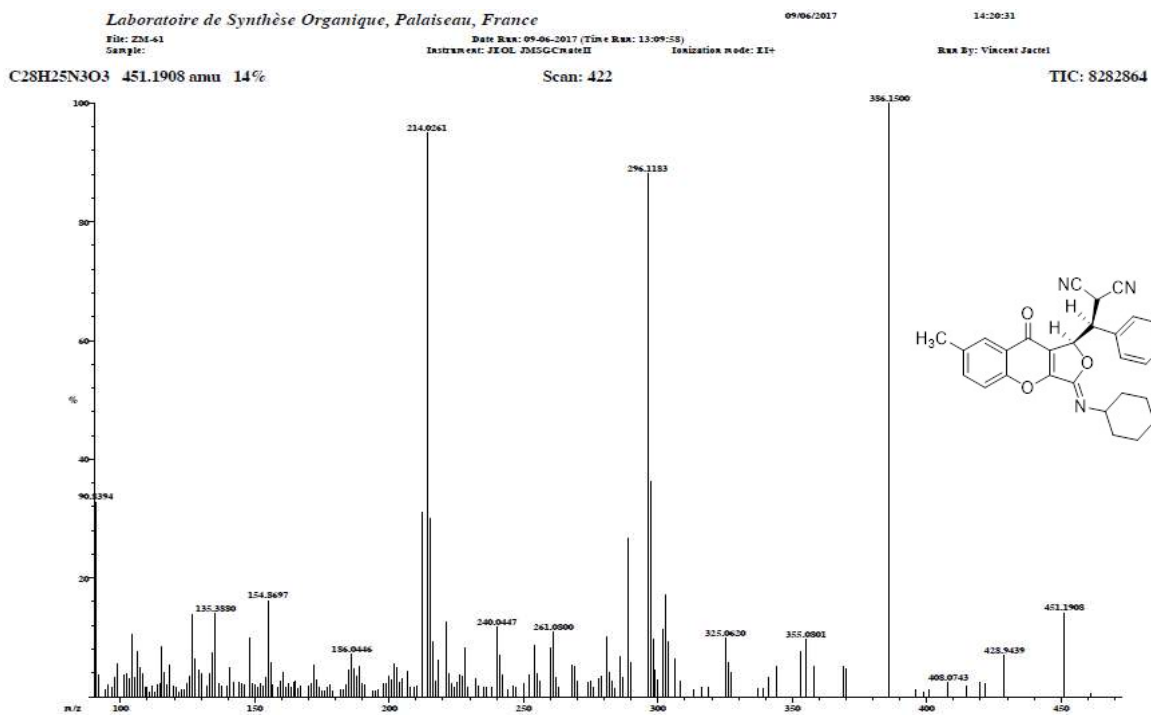
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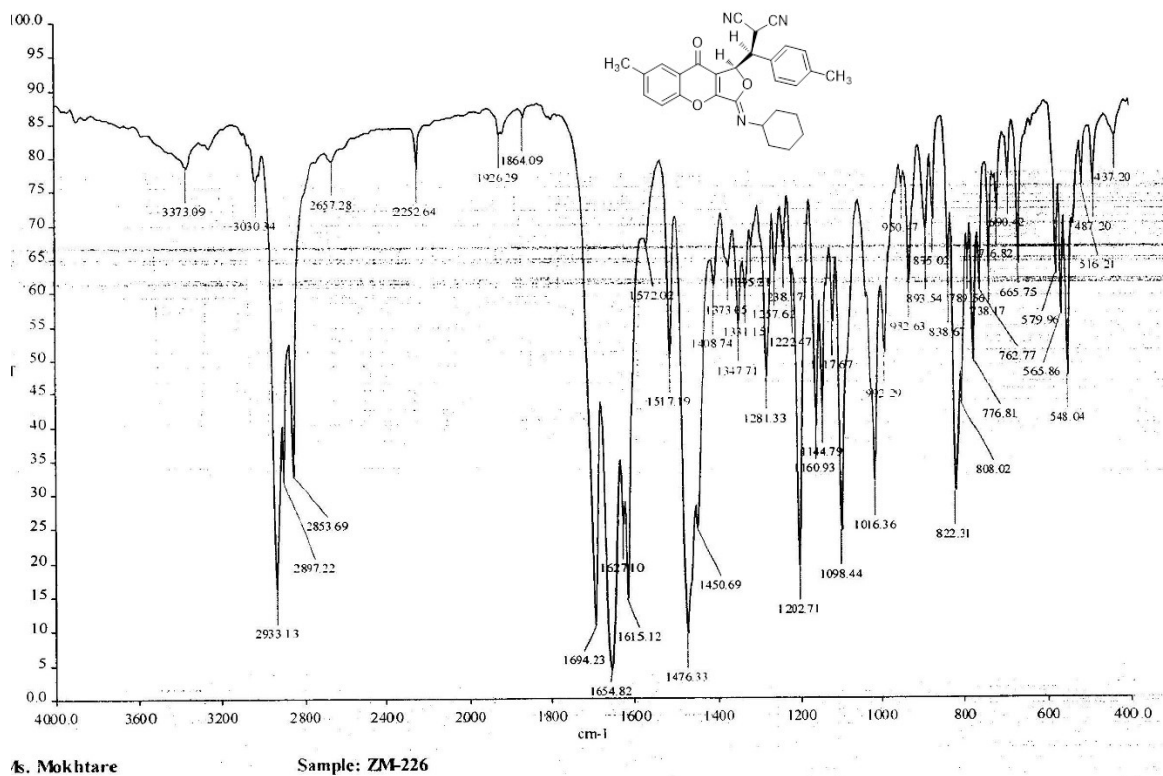
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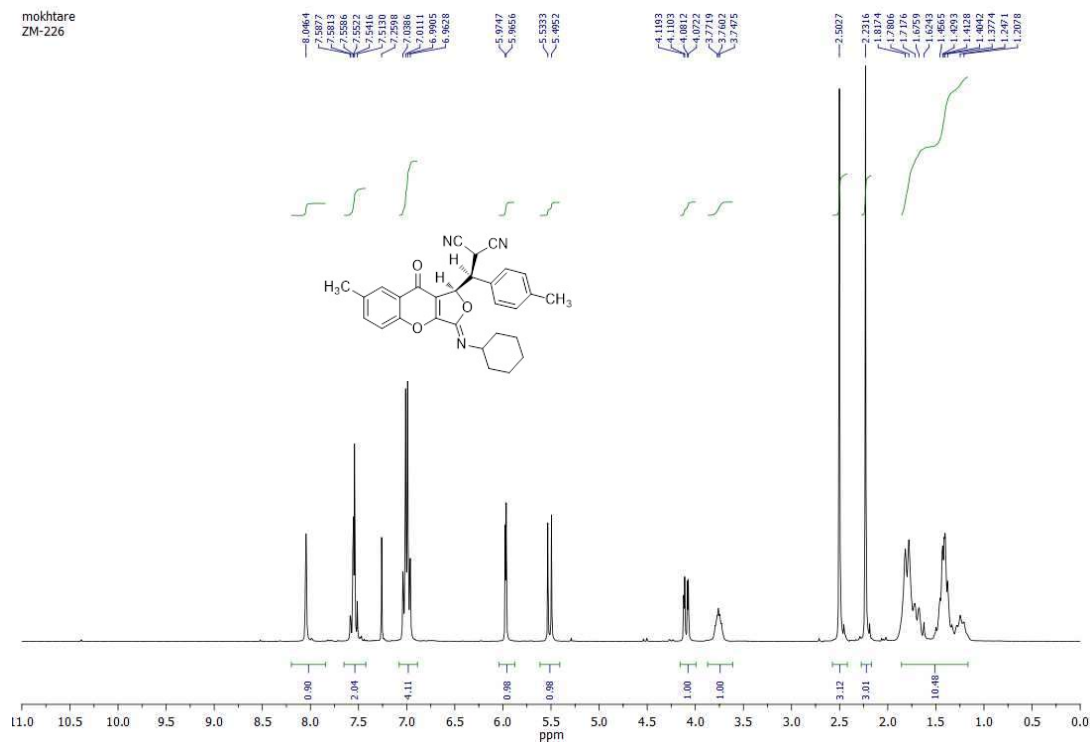
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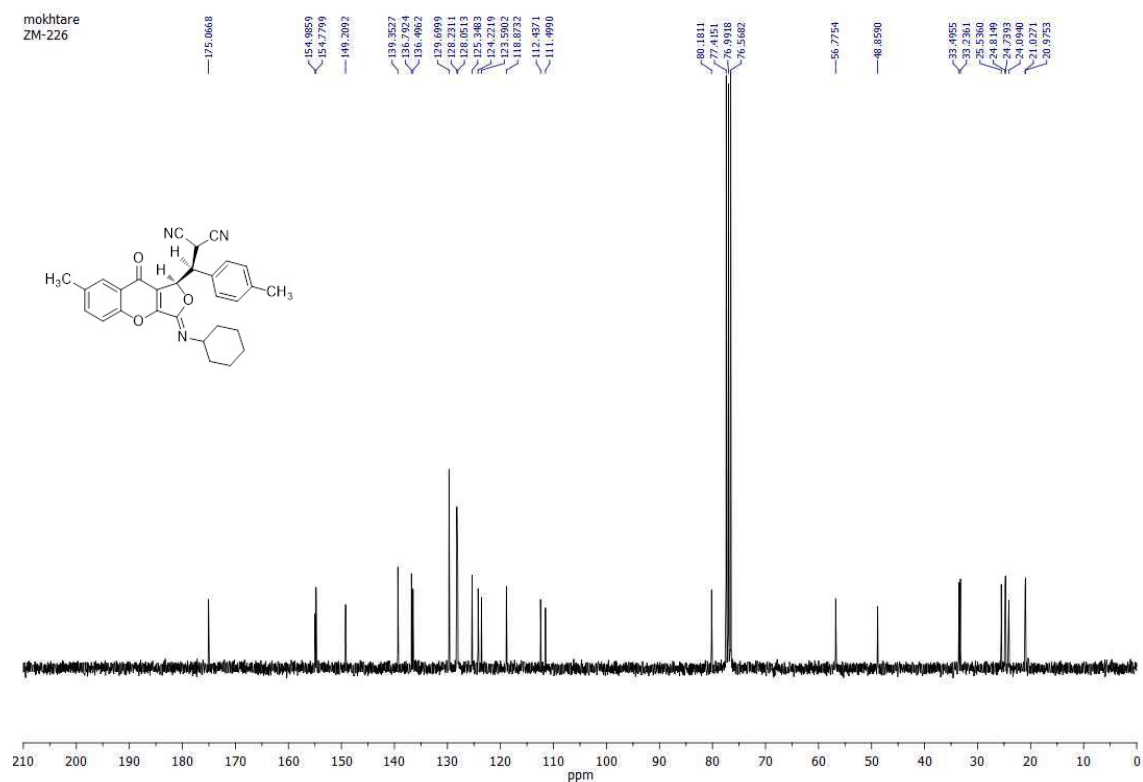
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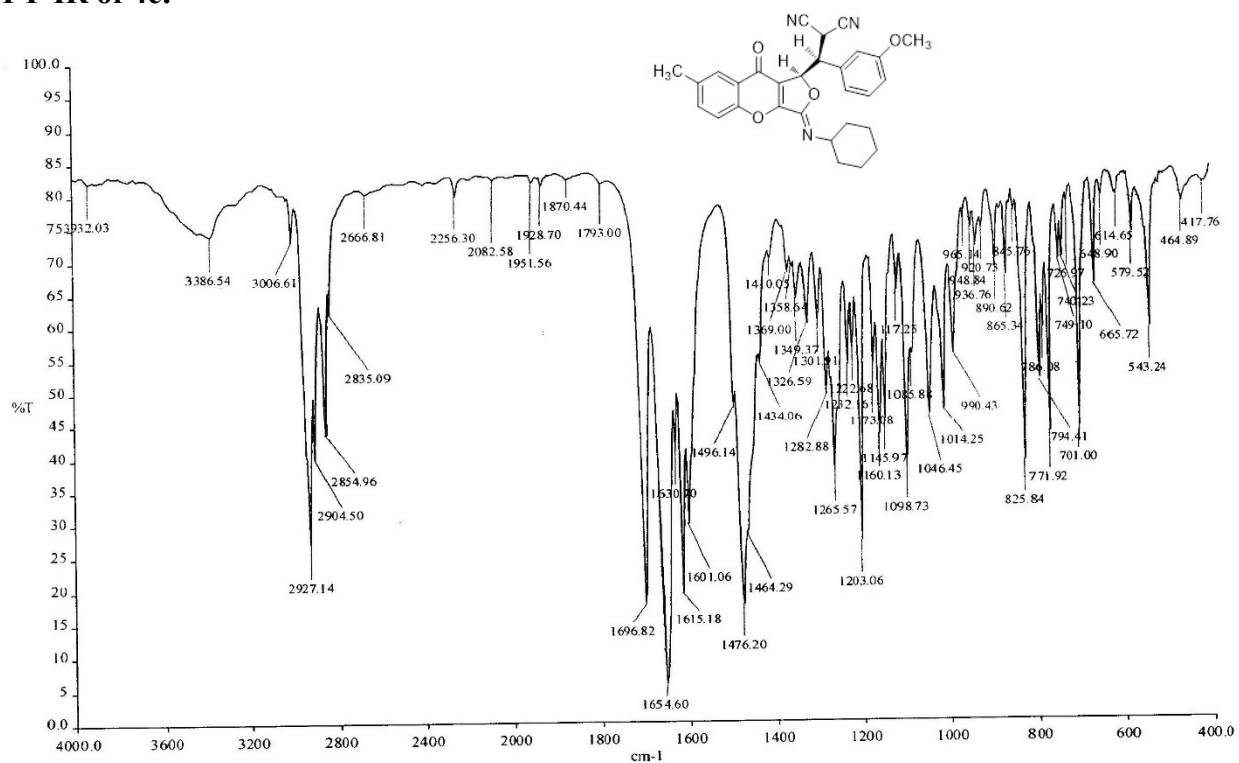
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¹³C NMR (75 MHz, CDCl₃) of 4b:



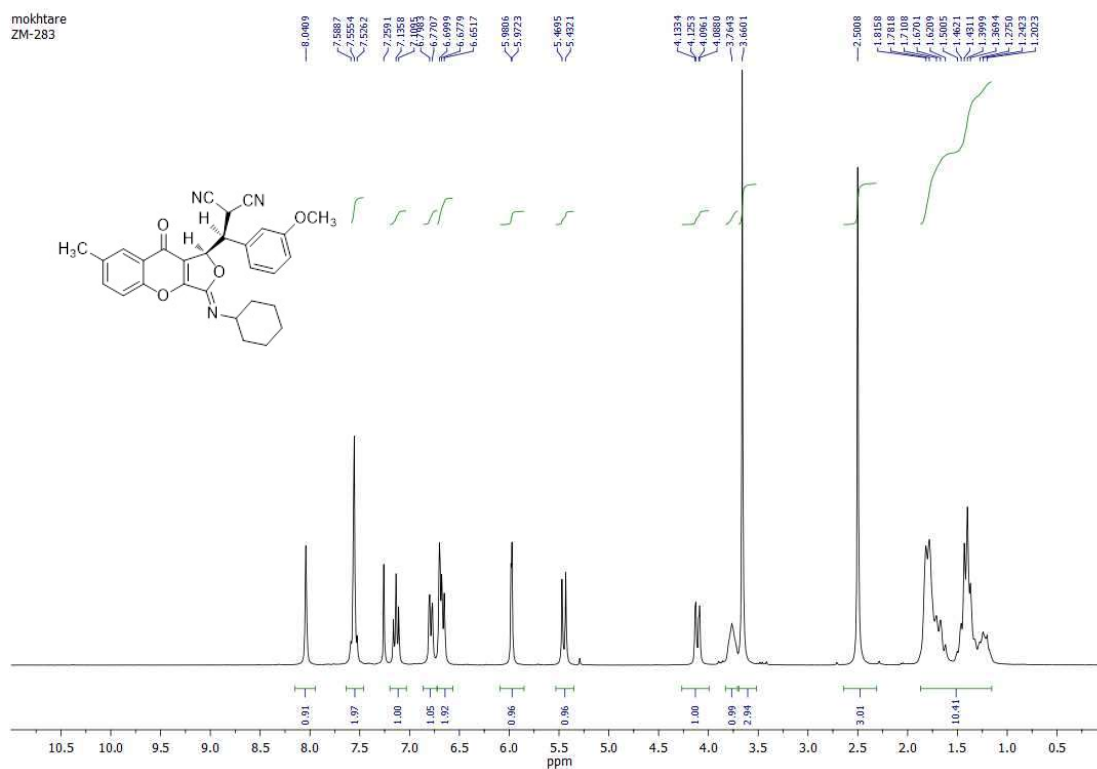
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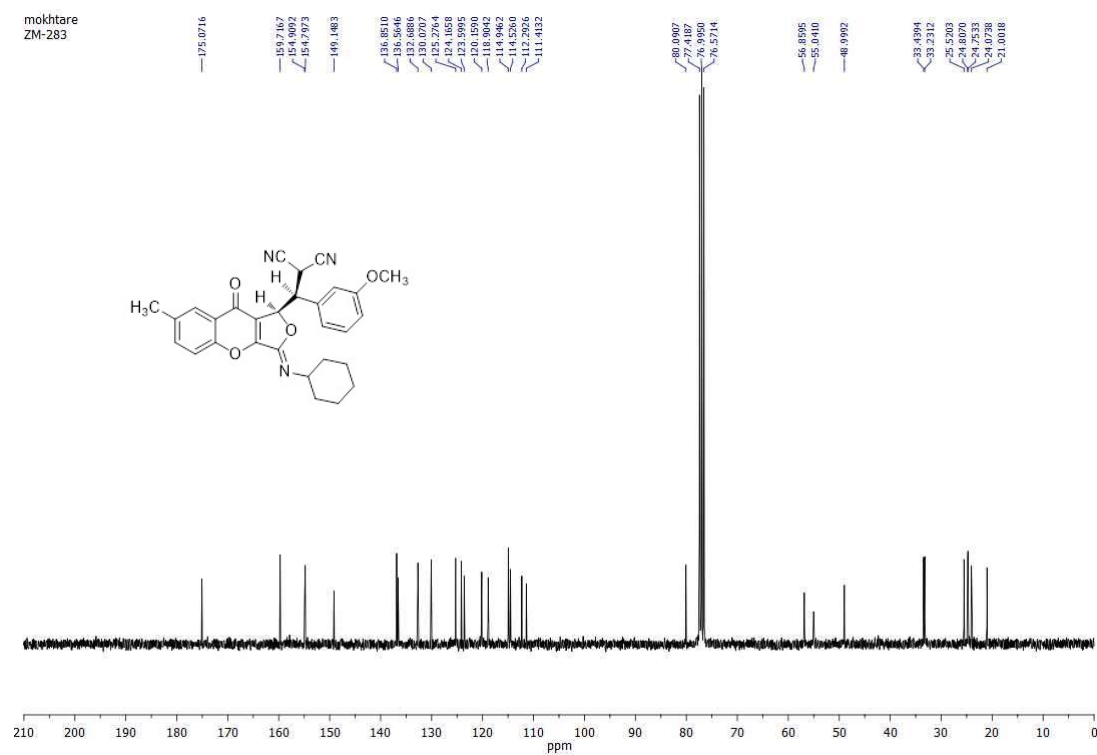
Ms. Mokhtare

Sample: ZM-283

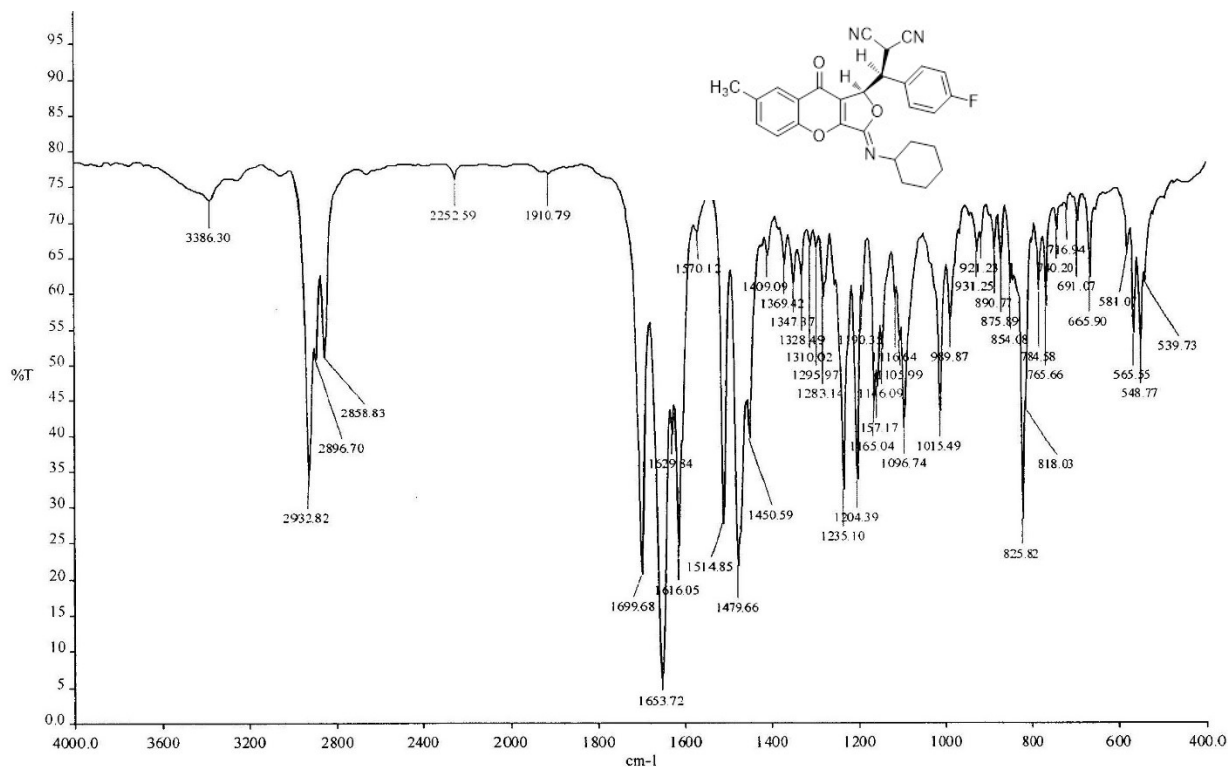
¹H NMR (300 MHz, CDCl₃) of 4c:



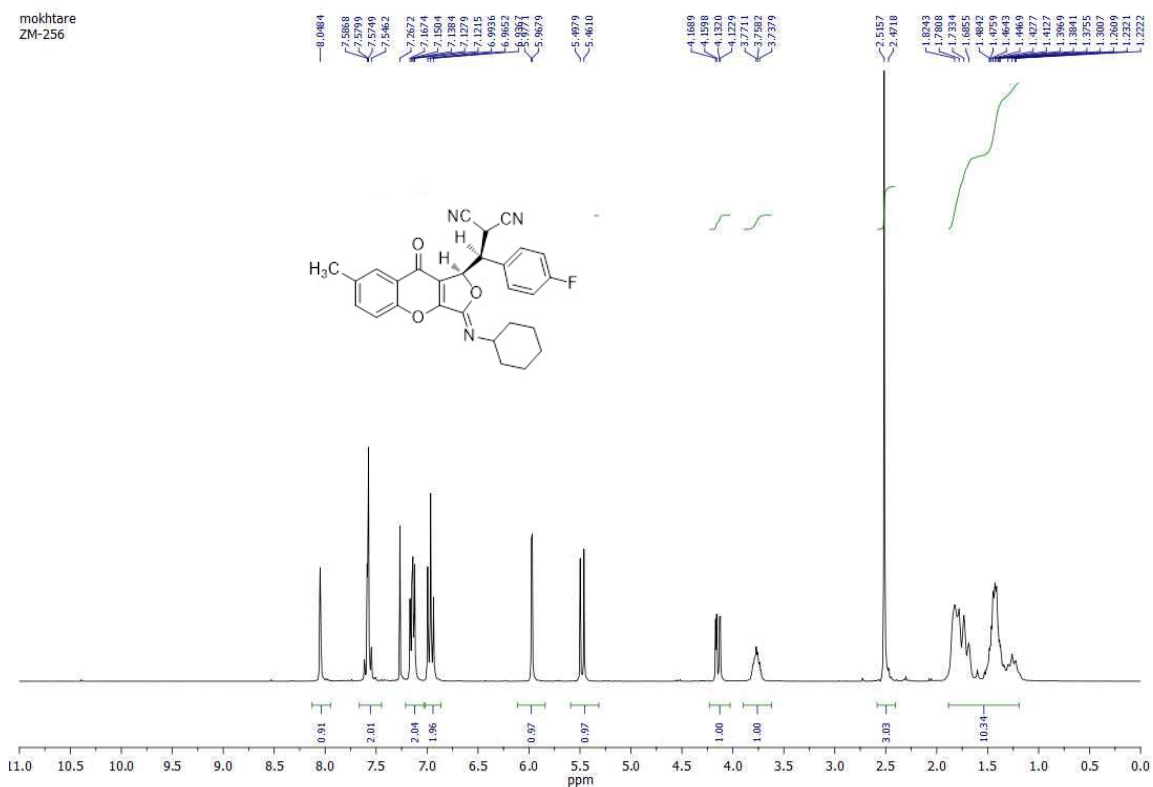
¹³C NMR (75 MHz, CDCl₃) of 4c:



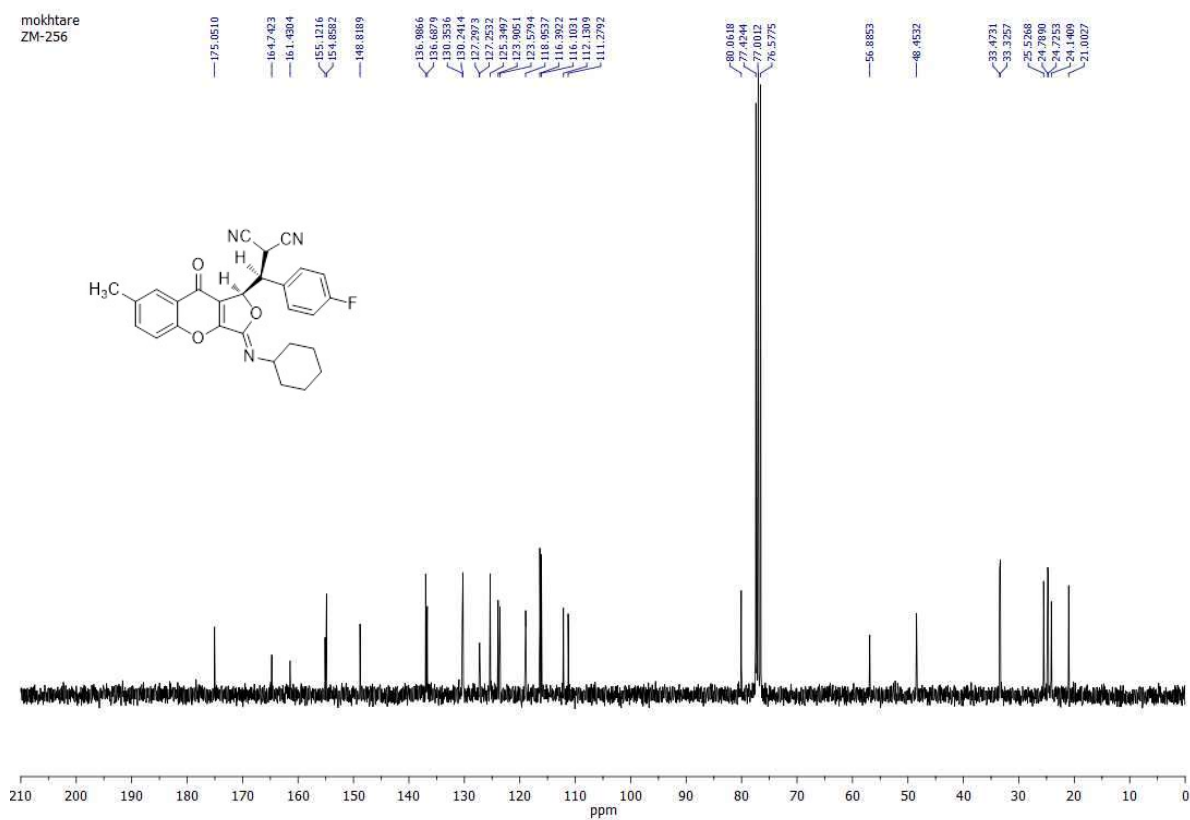
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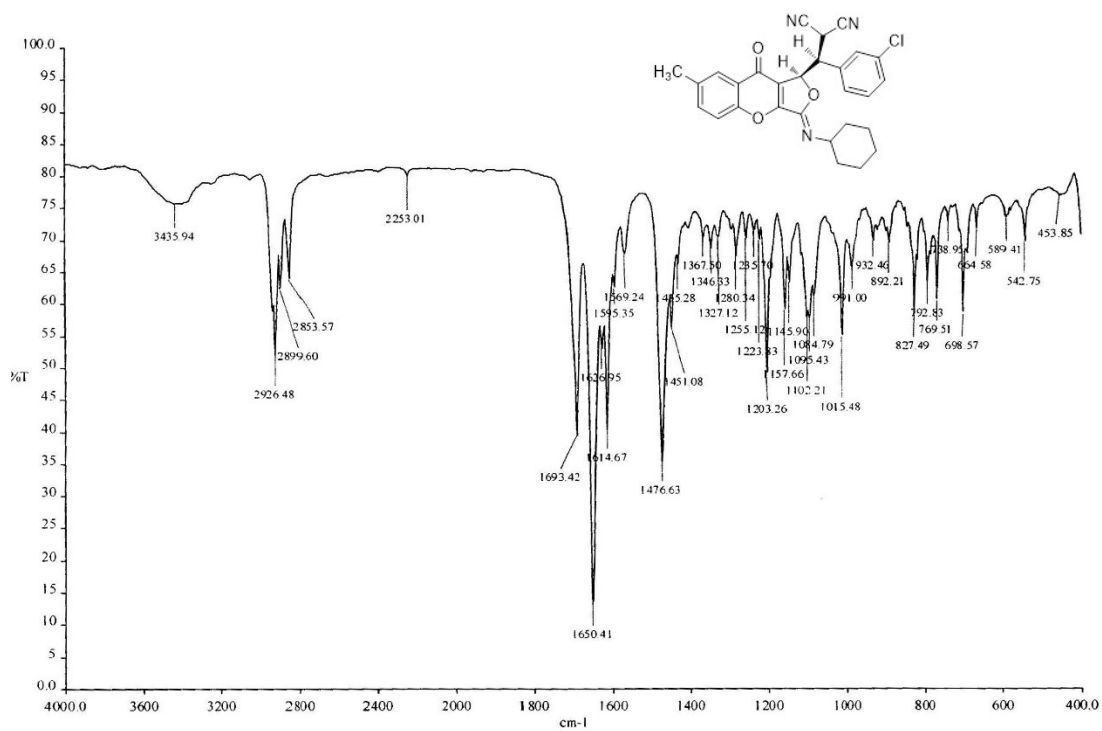
Ms. Mokhtare Sample: ZM-256
¹H NMR (300 MHz, CDCl₃) of 4d:



^{13}C NMR (75 MHz, CDCl_3) of 4d:



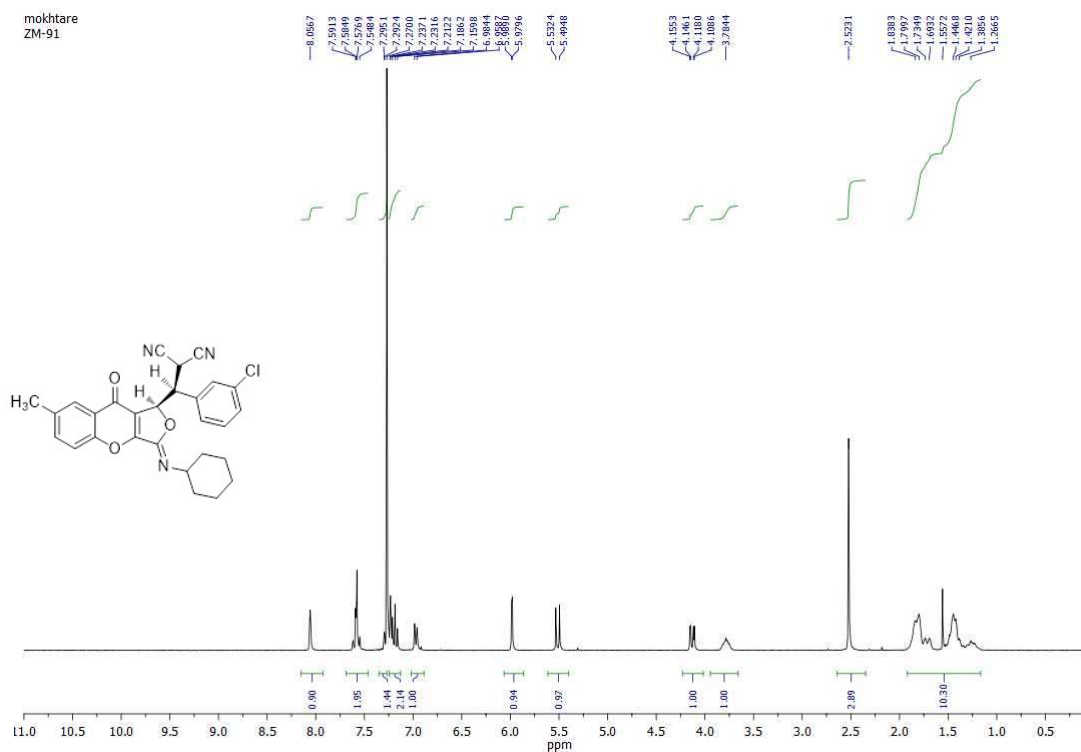
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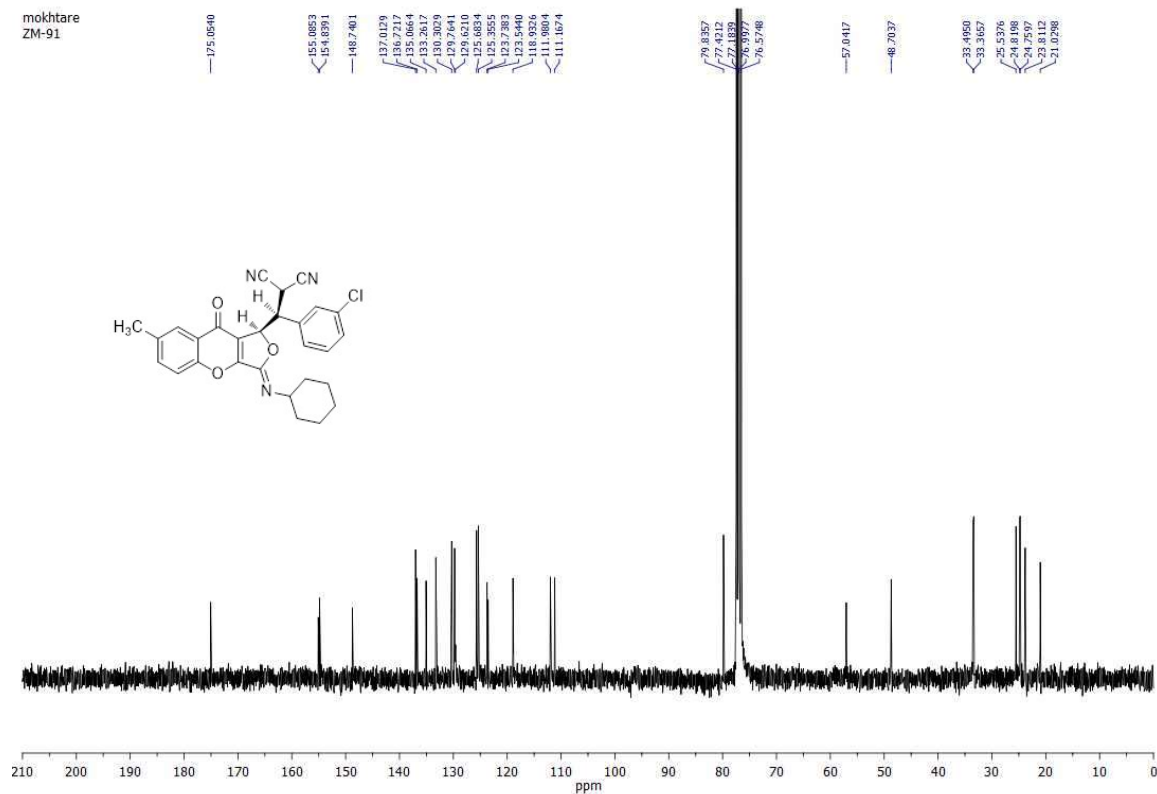
S. Mokhtare

Sample: ZM-91

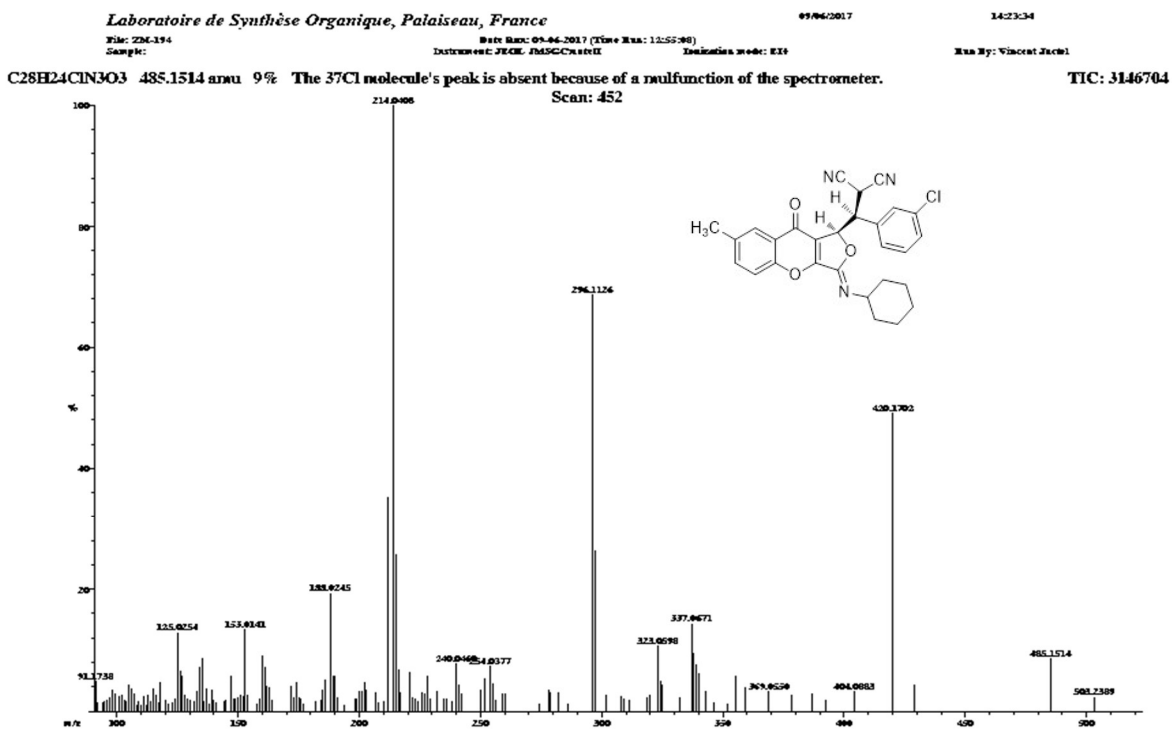
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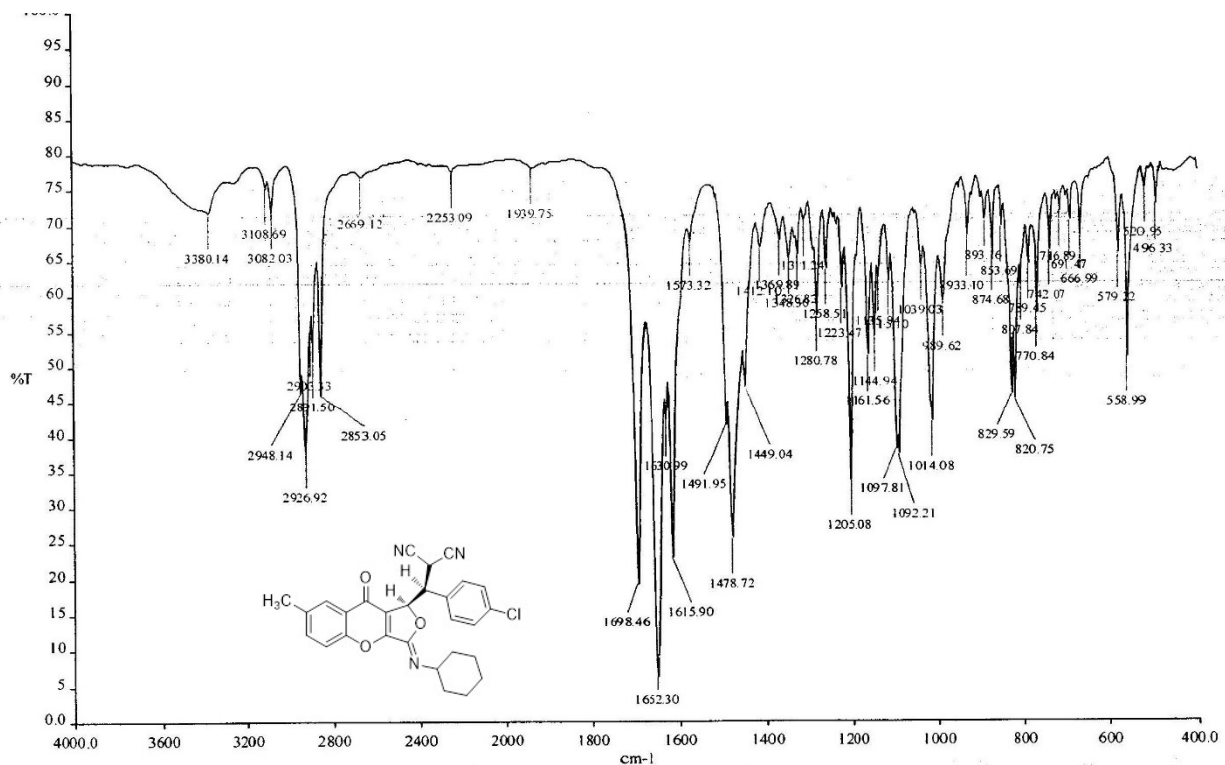
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HRMS of 4e:

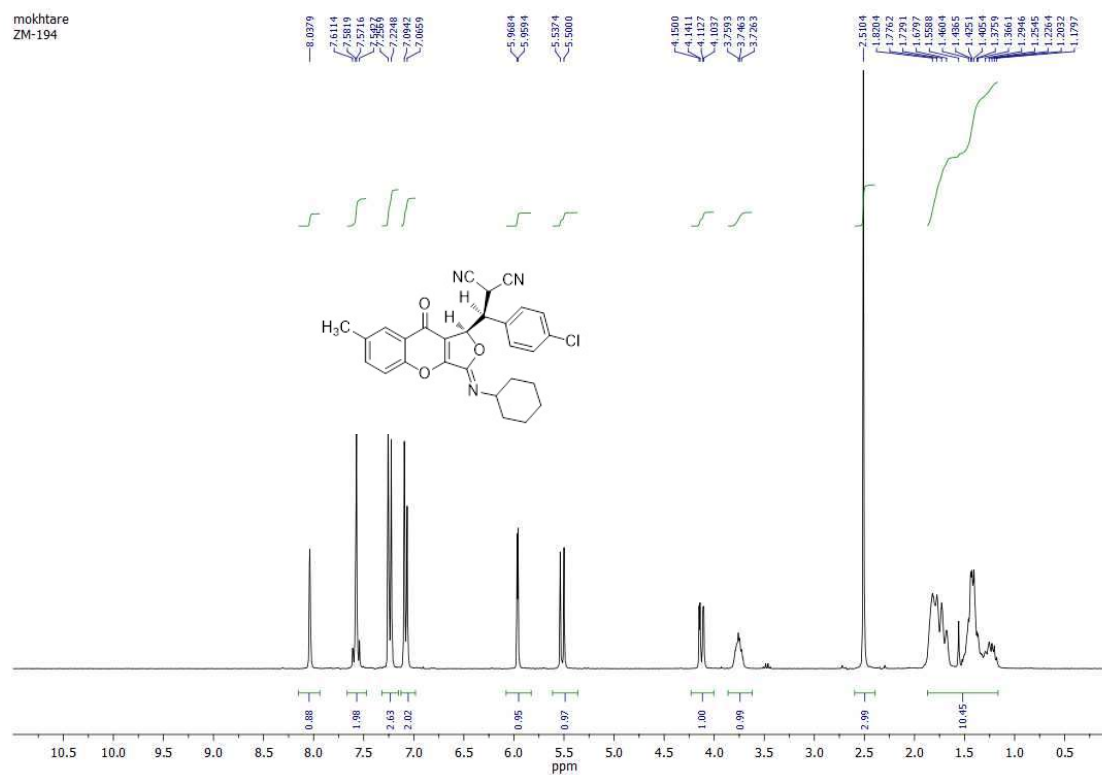


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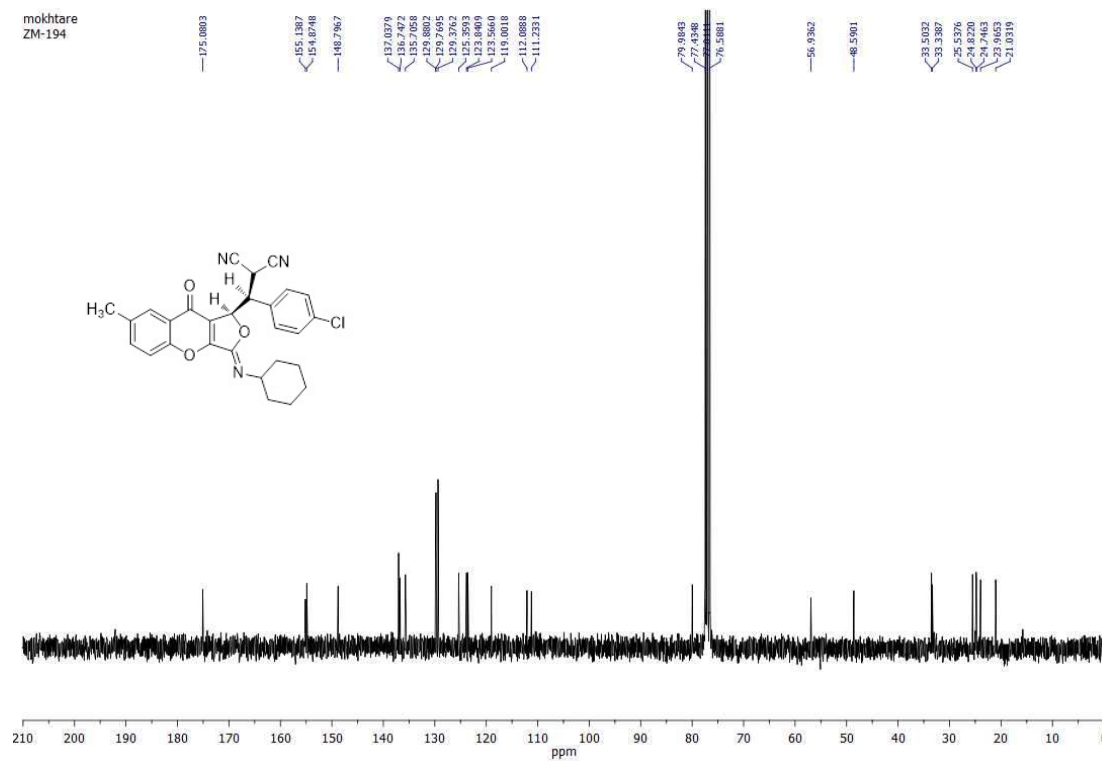


Ms. Mokhtare Sample: ZM-194

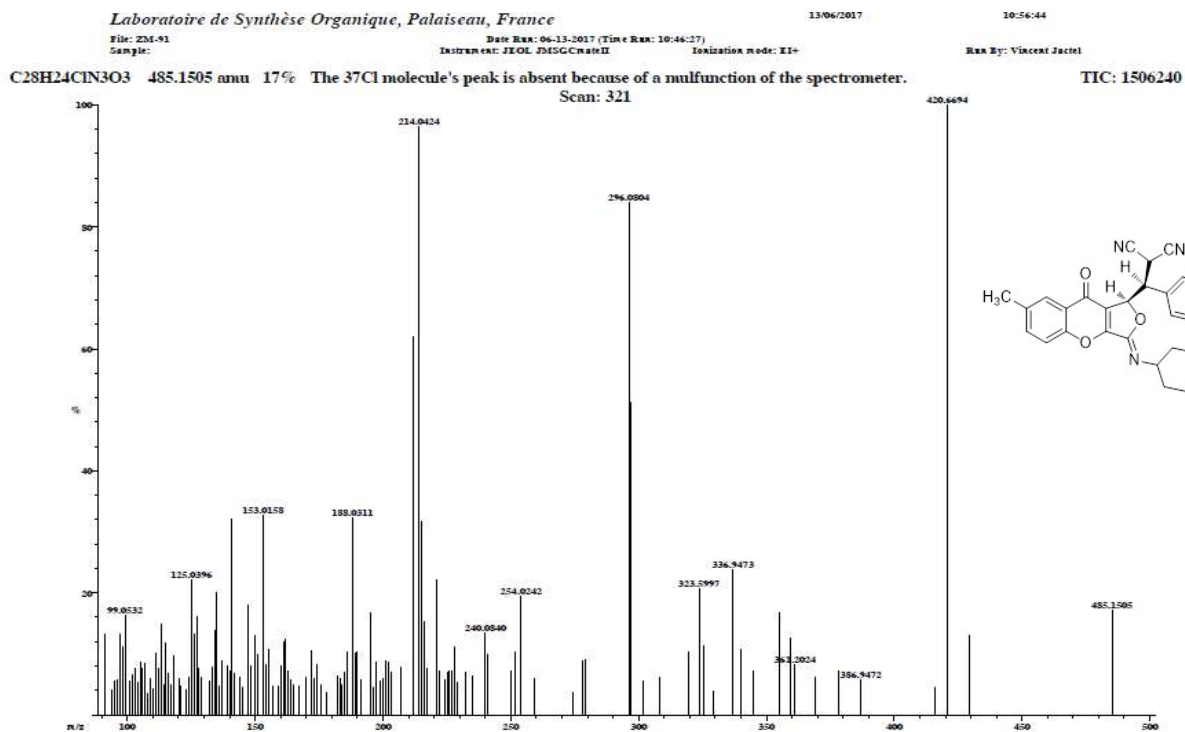
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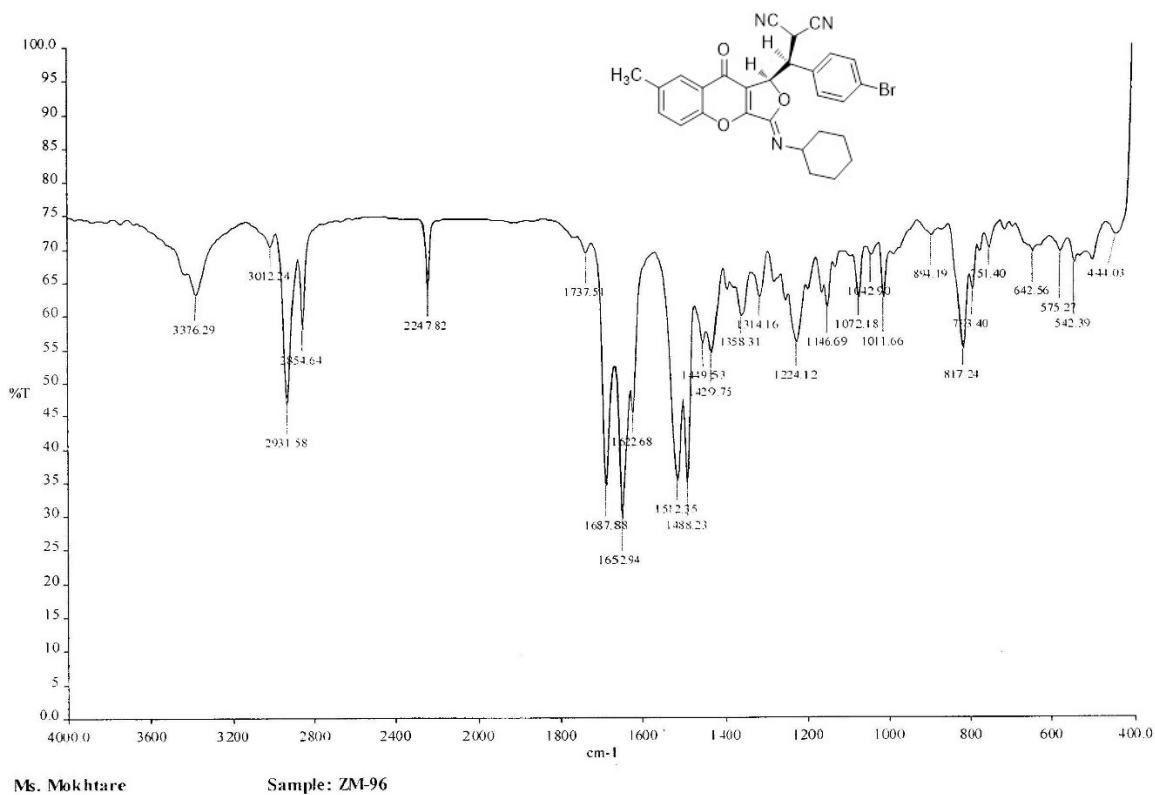
^{13}C NMR (75 MHz, CDCl_3) of 4f:



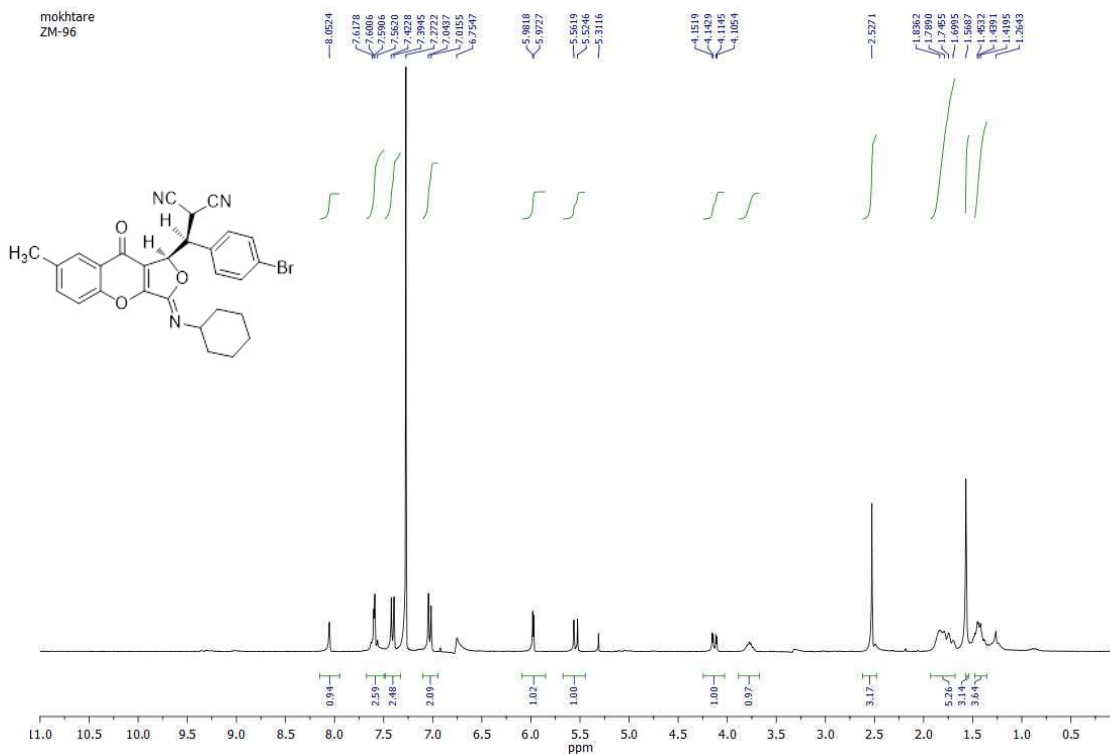
HRMS of 4f:



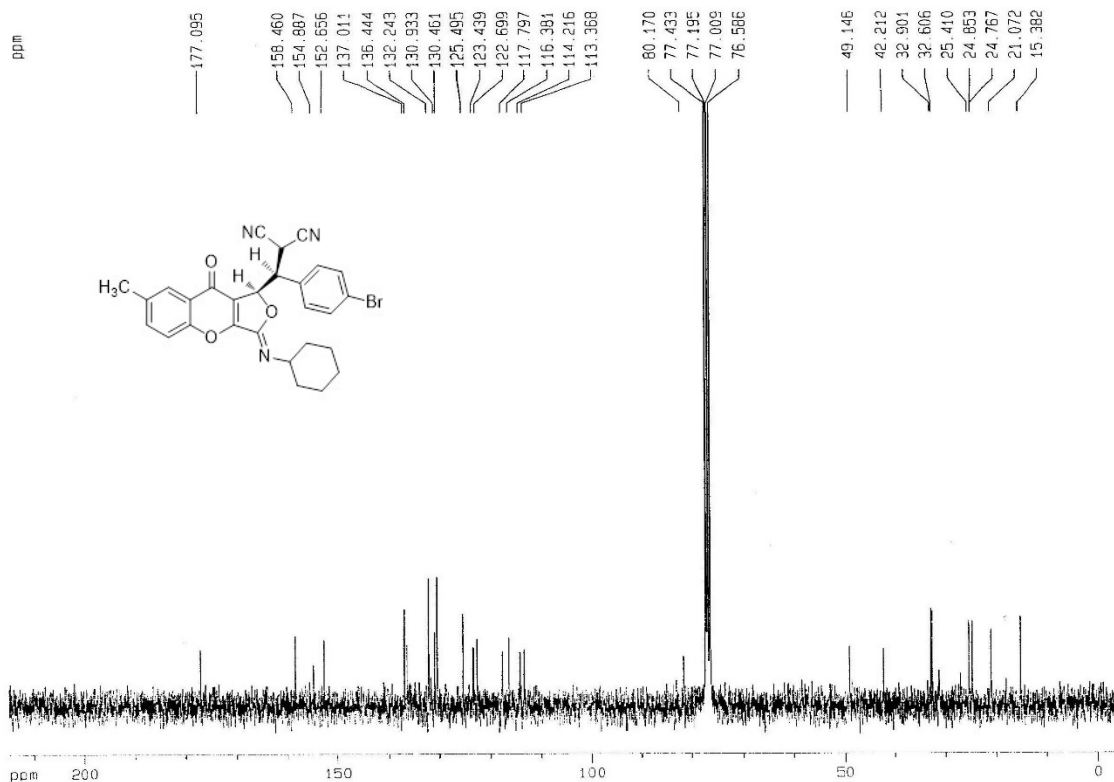
FT-IR of 4g:



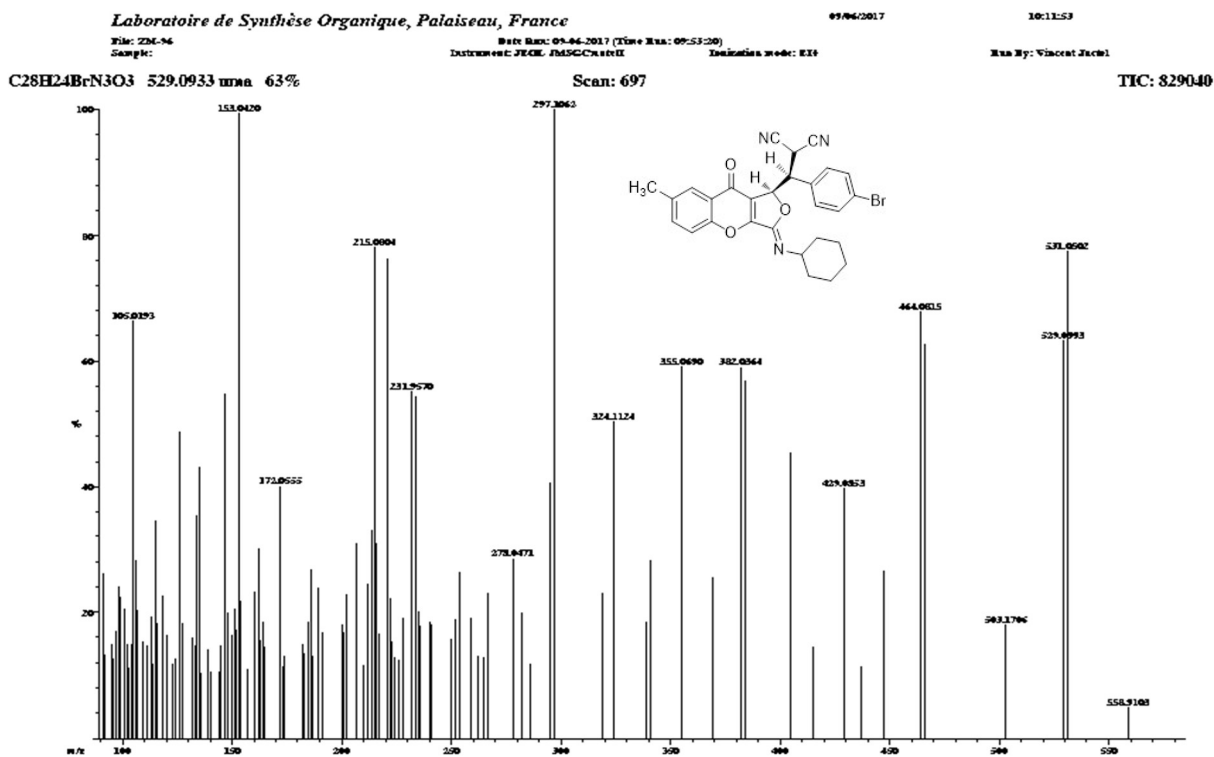
¹H NMR (300 MHz, CDCl₃) of 4g:



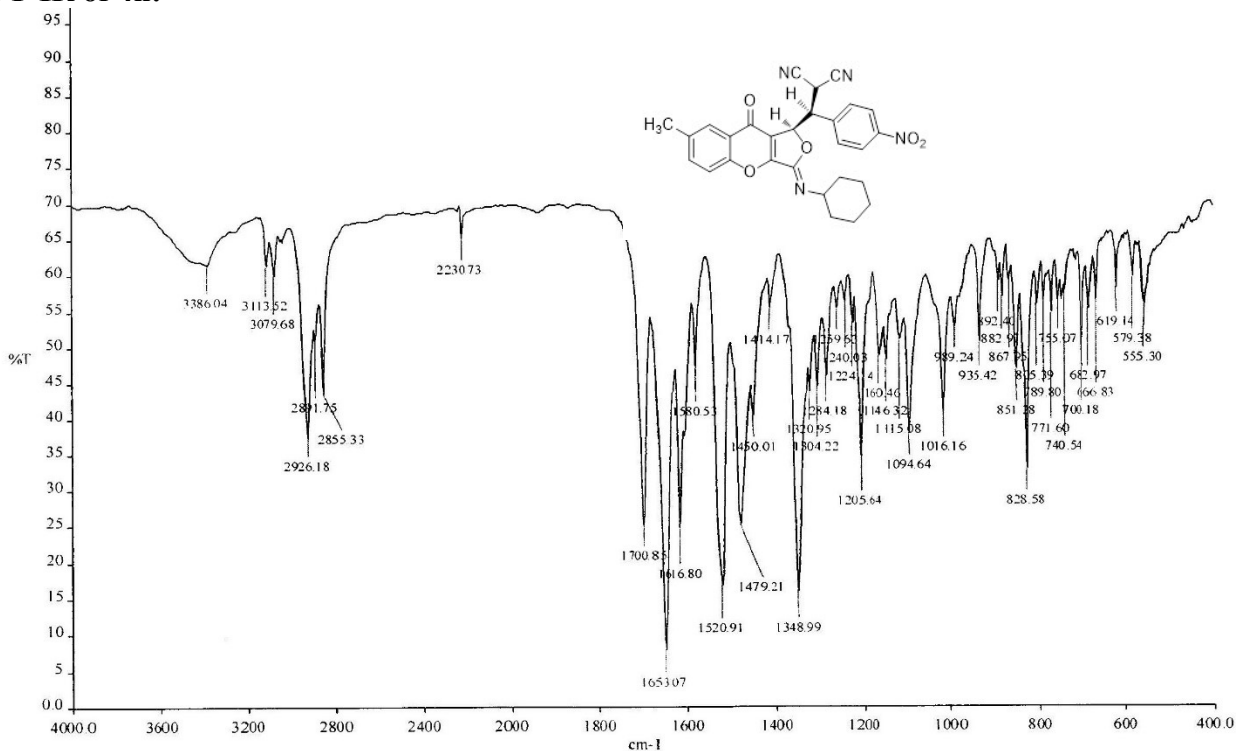
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HRMS of 4g:



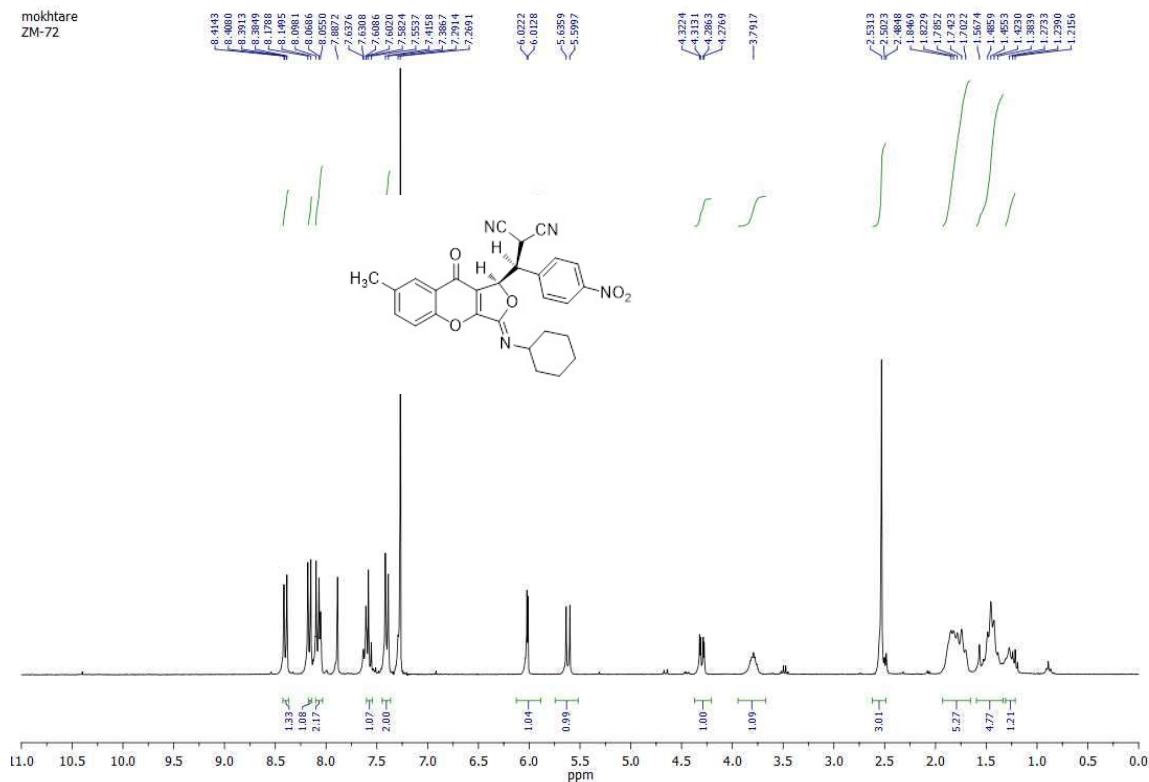
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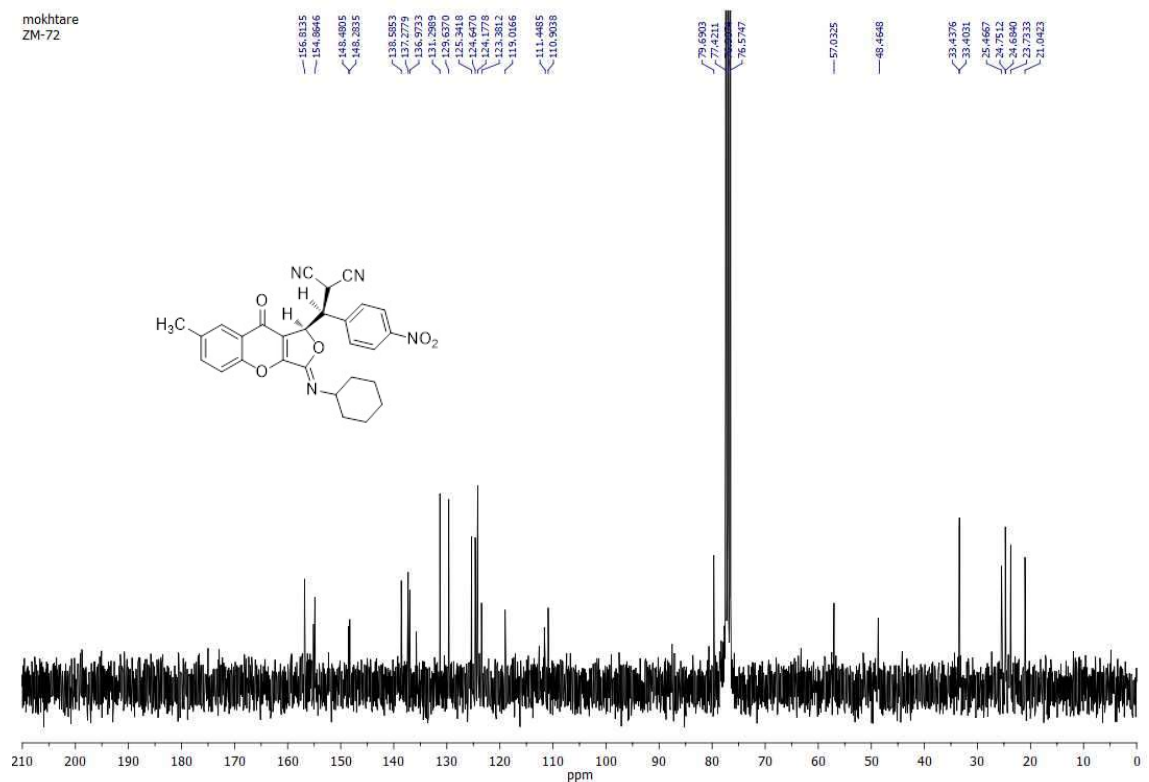
Ms. Mokhtare

Sample: ZM-72

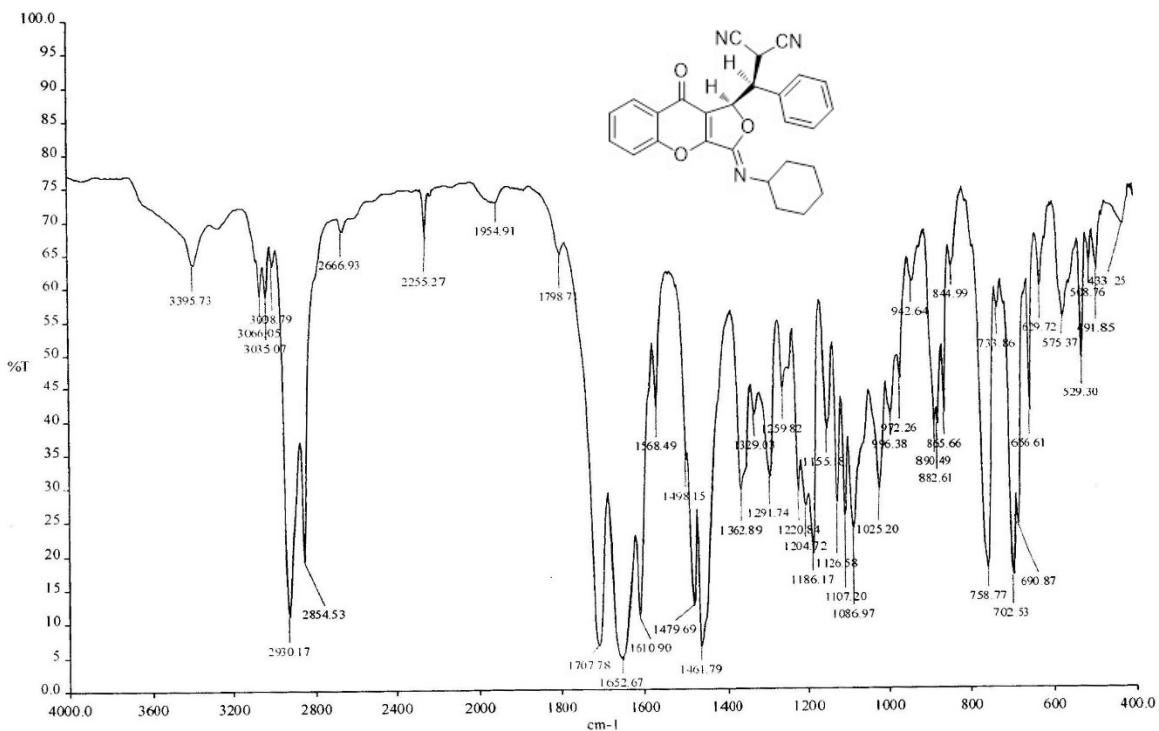
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¹³C NMR (75 MHz, CDCl₃) of 4h:



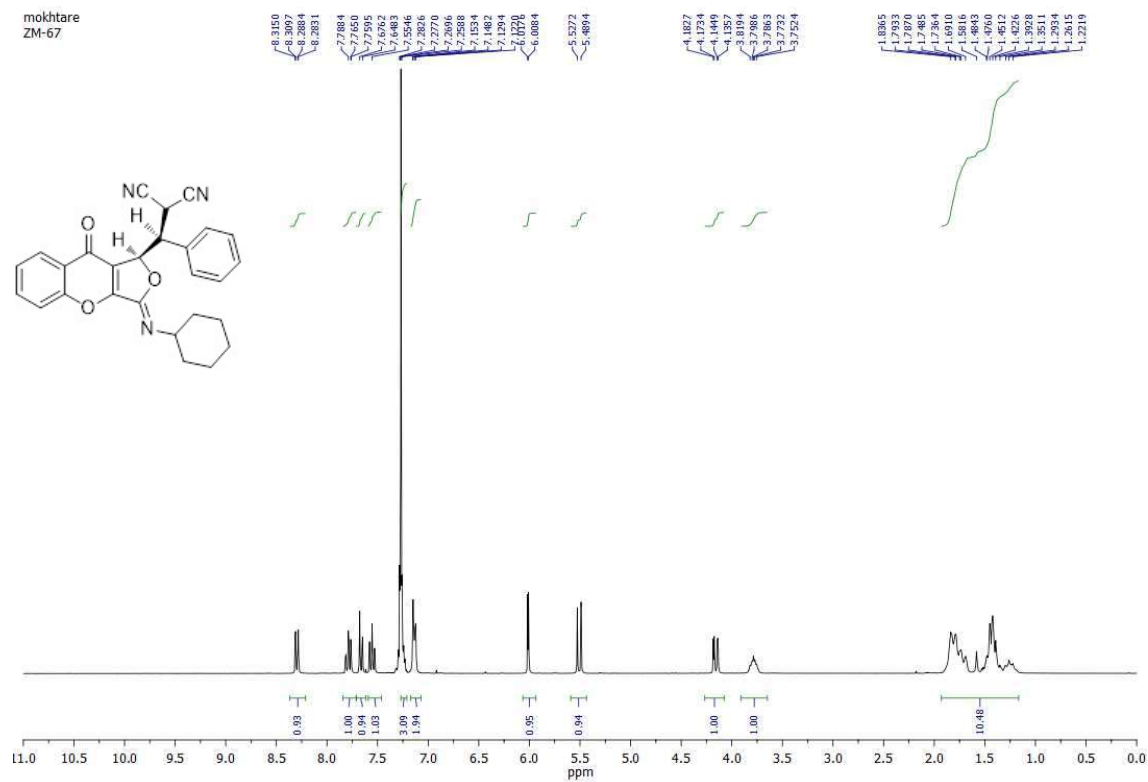
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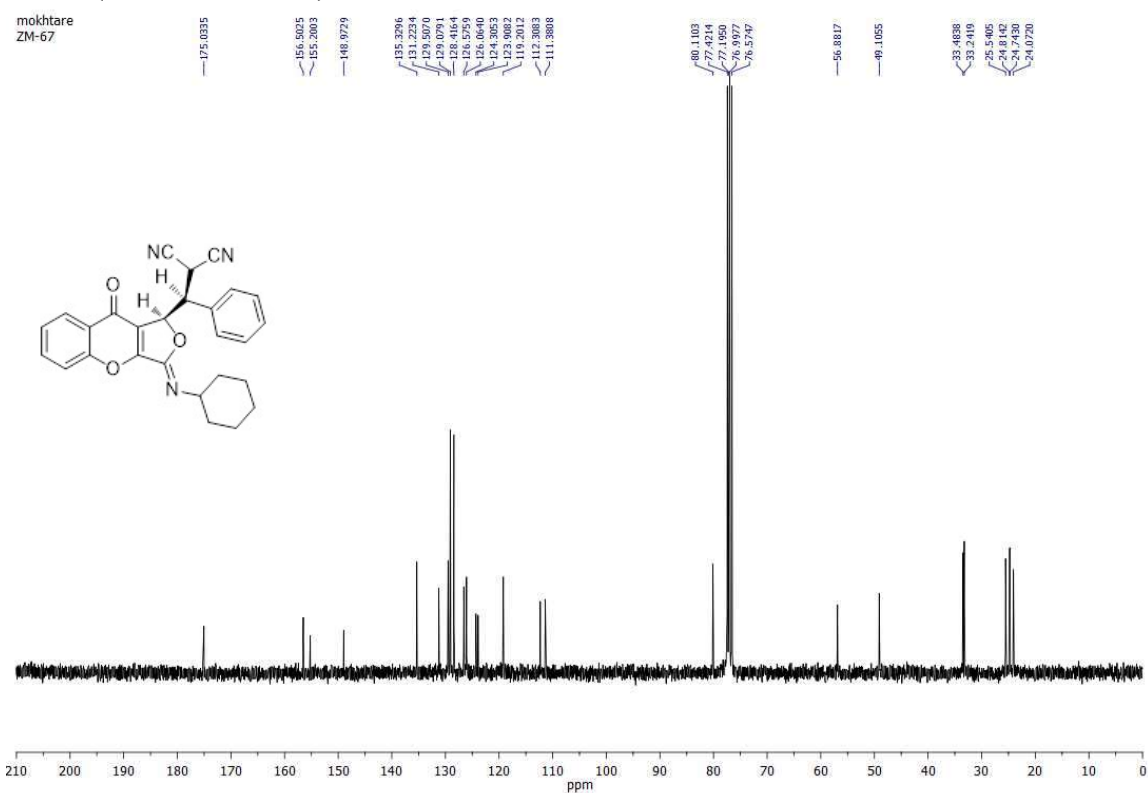
Ms. Mokhtare

Sample: ZM 67

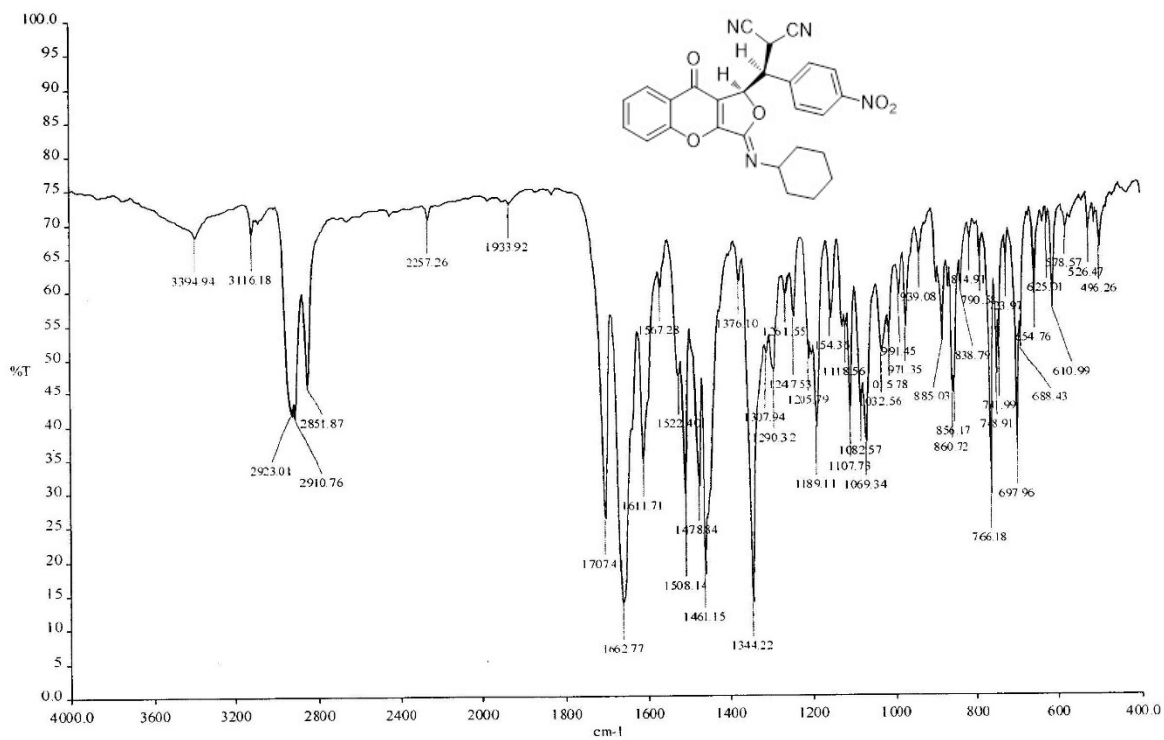
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¹³C NMR (75 MHz, CDCl₃) of 4i:



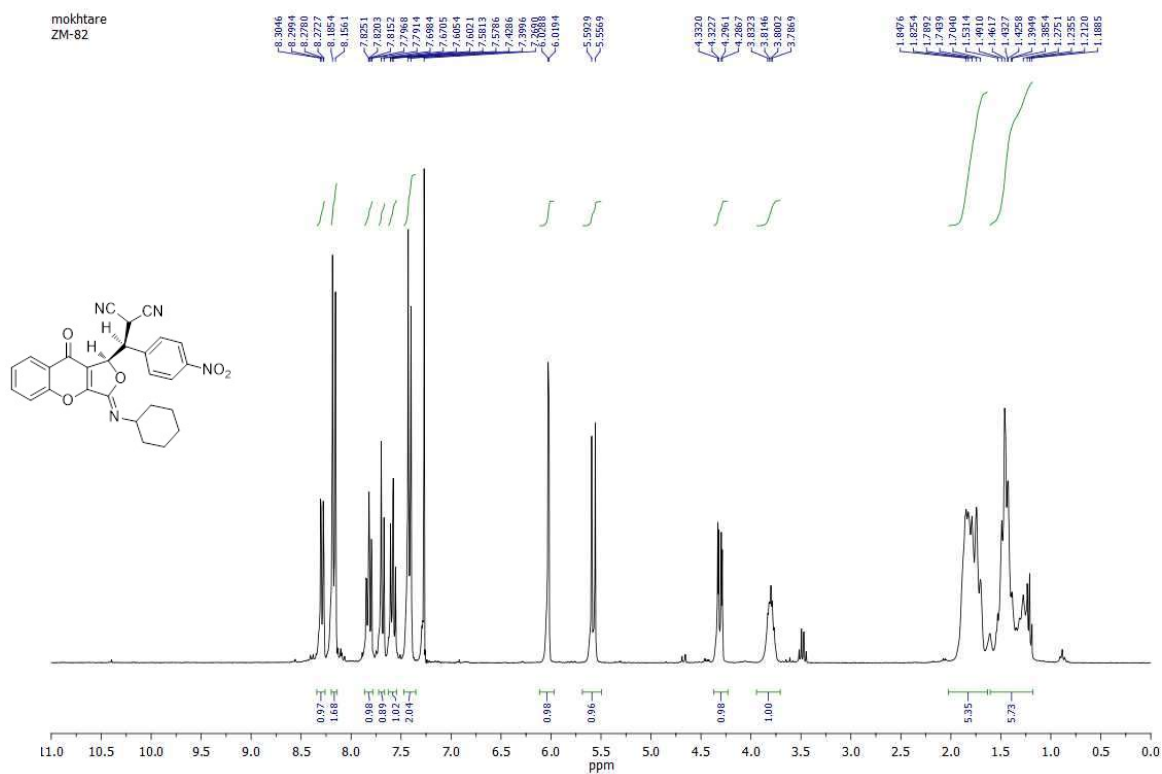
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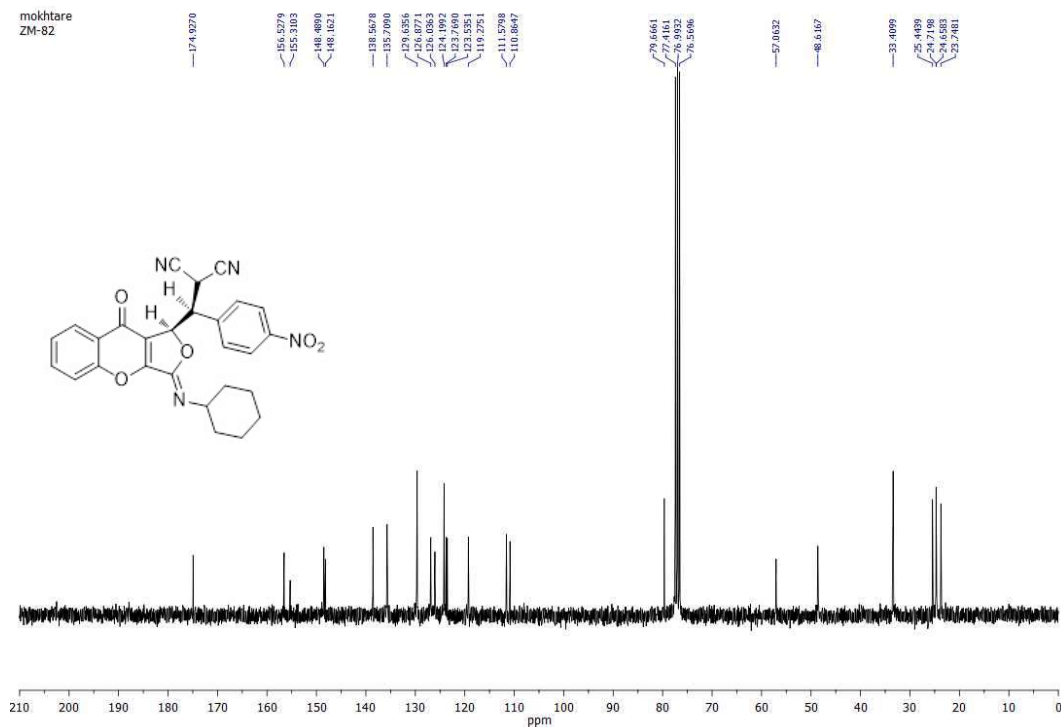
Ms. Mokhtare

Sample: ZM-82

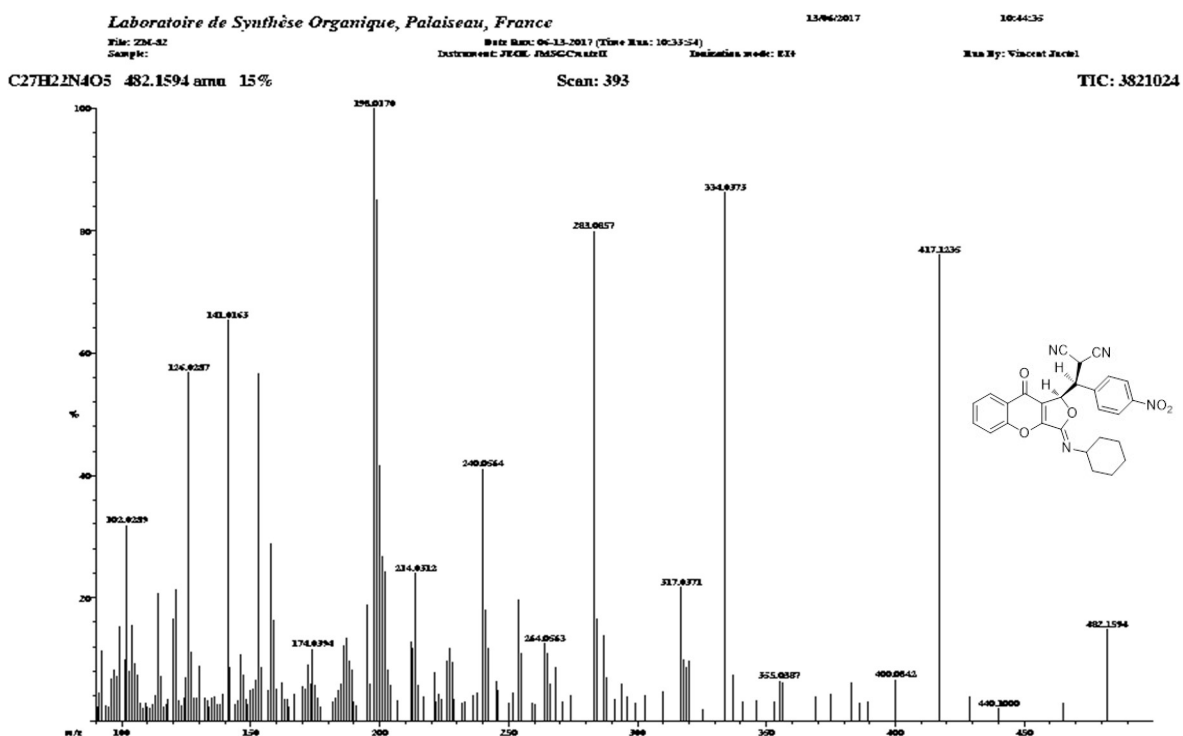
¹H NMR (300 MHz, CDCl₃) of 4j:



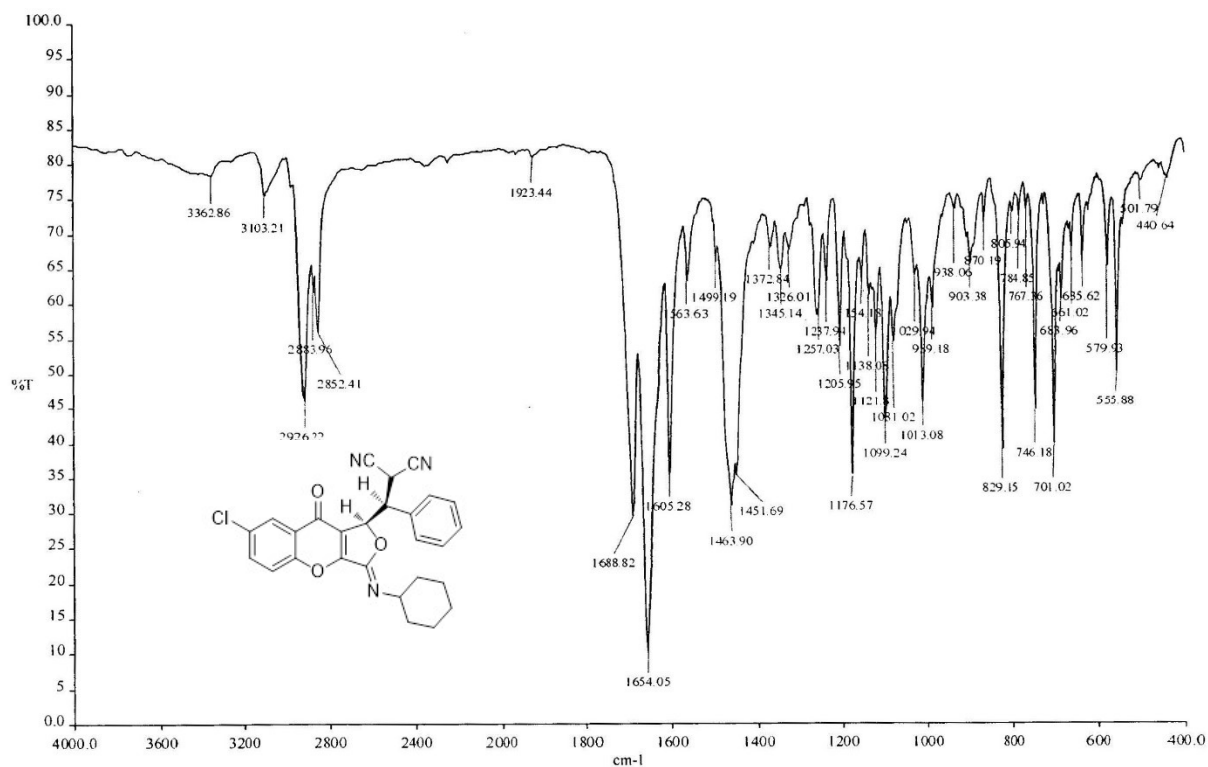
¹³C NMR (75 MHz, CDCl₃) of 4j:



HRMS of 4j:



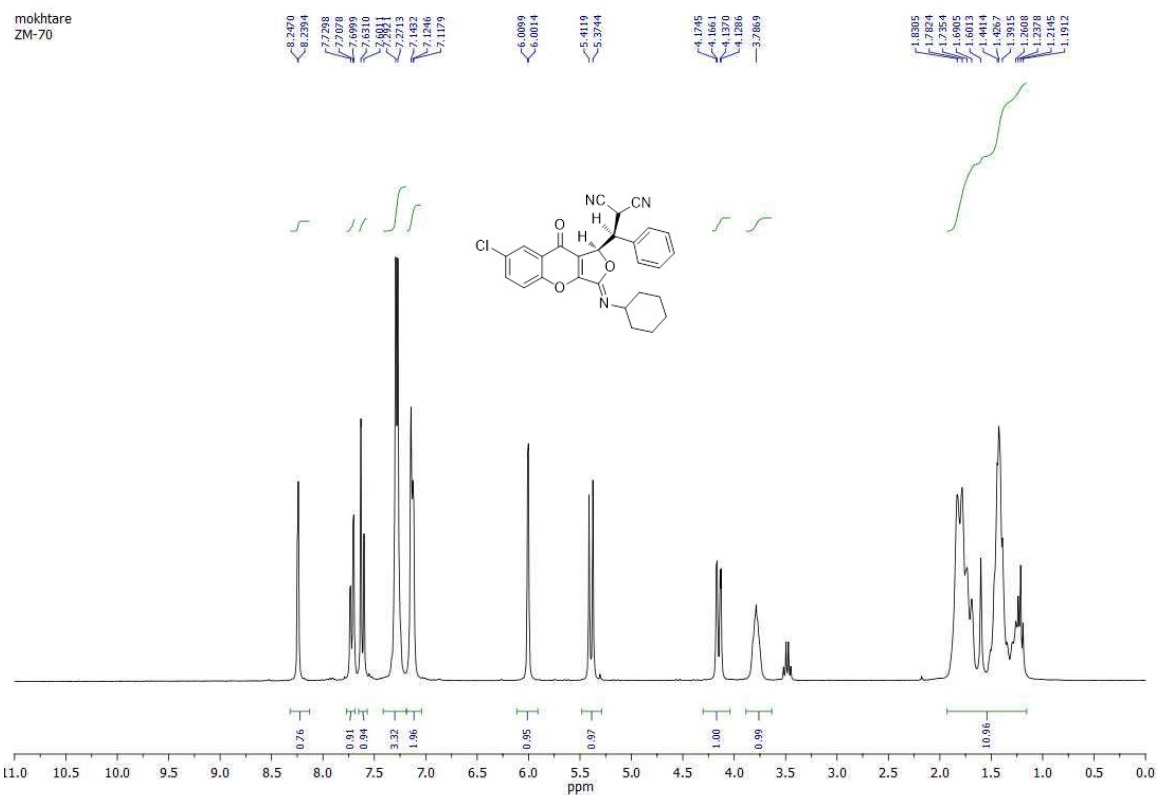
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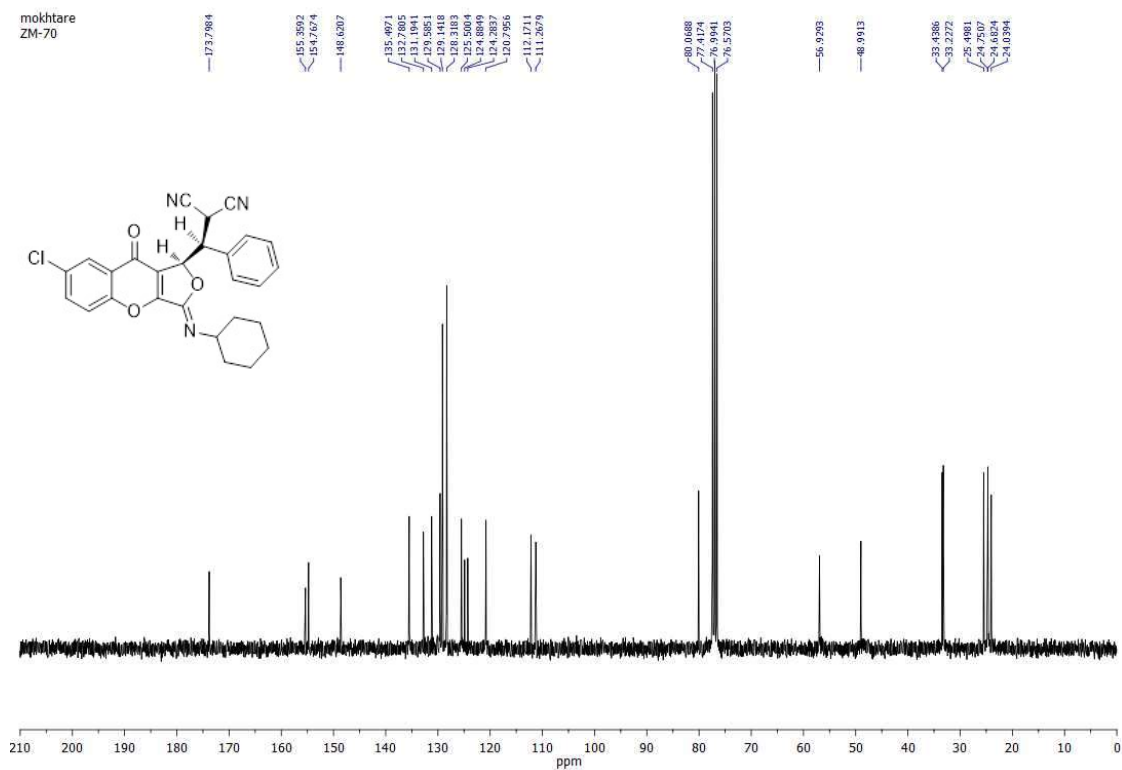
Ms. Mokhtare

Sample: ZM-70

¹H NMR (300 MHz, CDCl₃) of 4k:



¹³C NMR (75 MHz, CDCl₃) of 4k:



HRMS of 4k:

Laboratoire de Synthèse Organique, Palaiseau, France

09/06/2007

15:38:47

File: ZM-70

Date Run: 09-06-2017 (Time Run: 15:34:34)

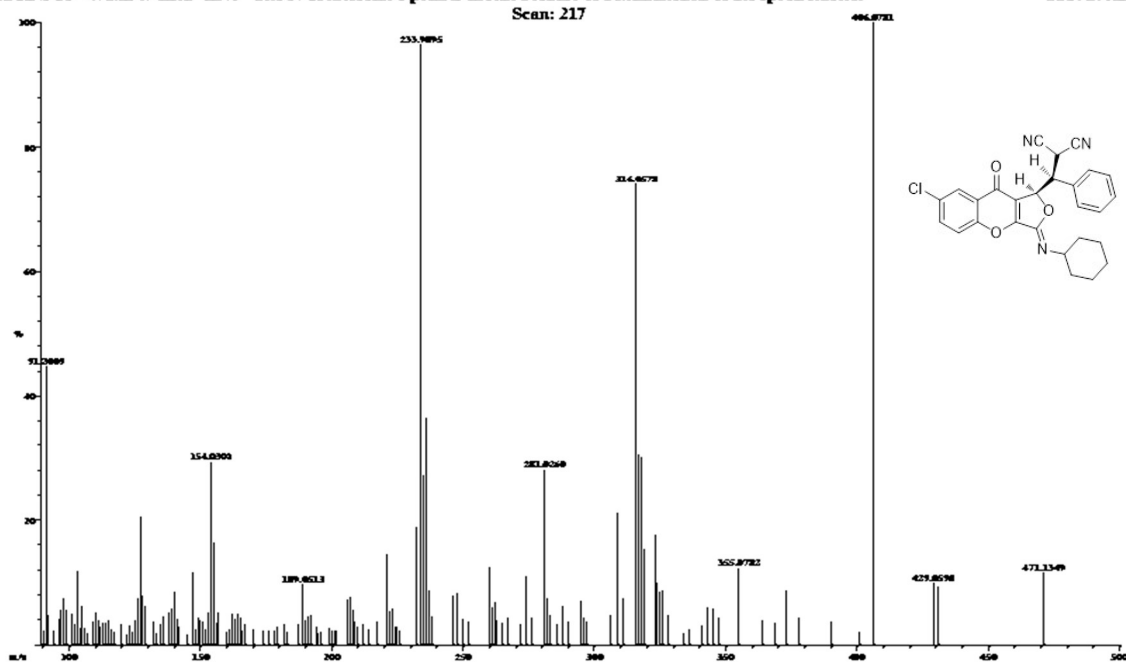
Instrument: JEOL JMSGCX5000

Injection mode: ESI+

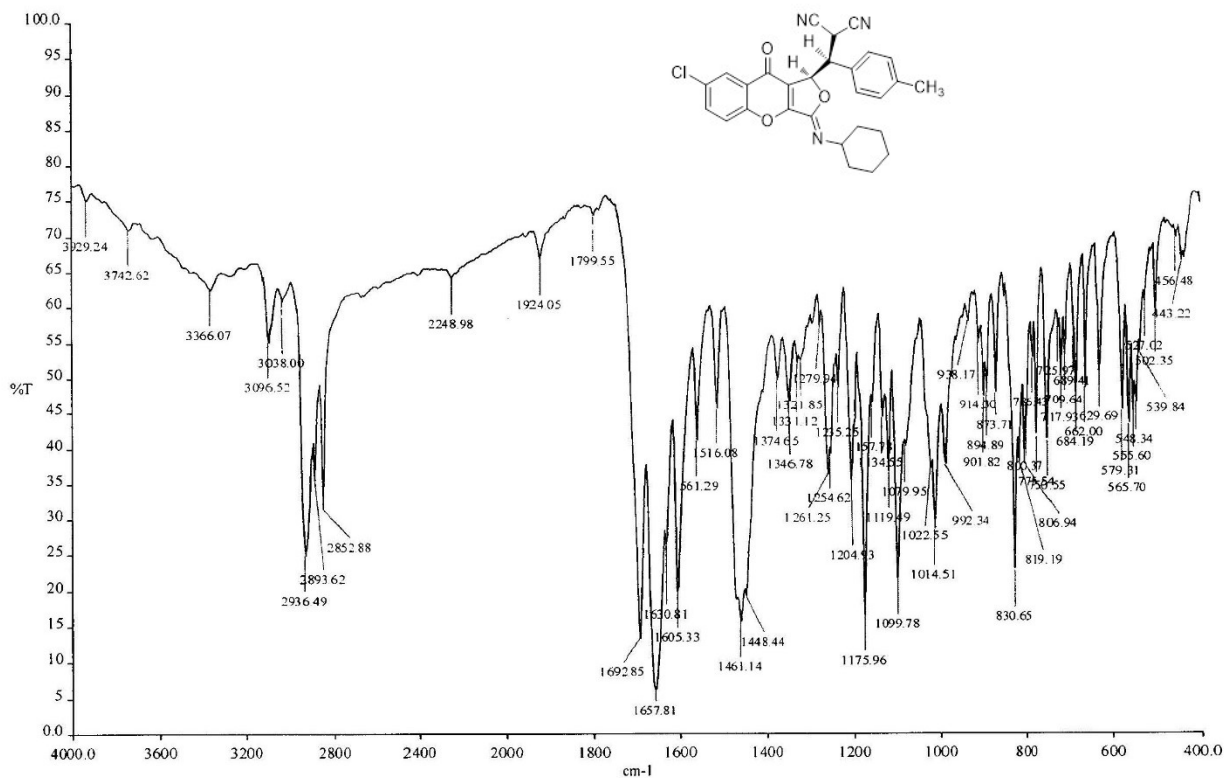
Run By: Vincent Jozel

C₂₇H₂₂ClN₃O₃ 471.1349 amu 12% The ³⁷Cl molecule's peak is absent because of a malfunction of the spectrometer.

TIC: 2701152



FT-IR of 4l:

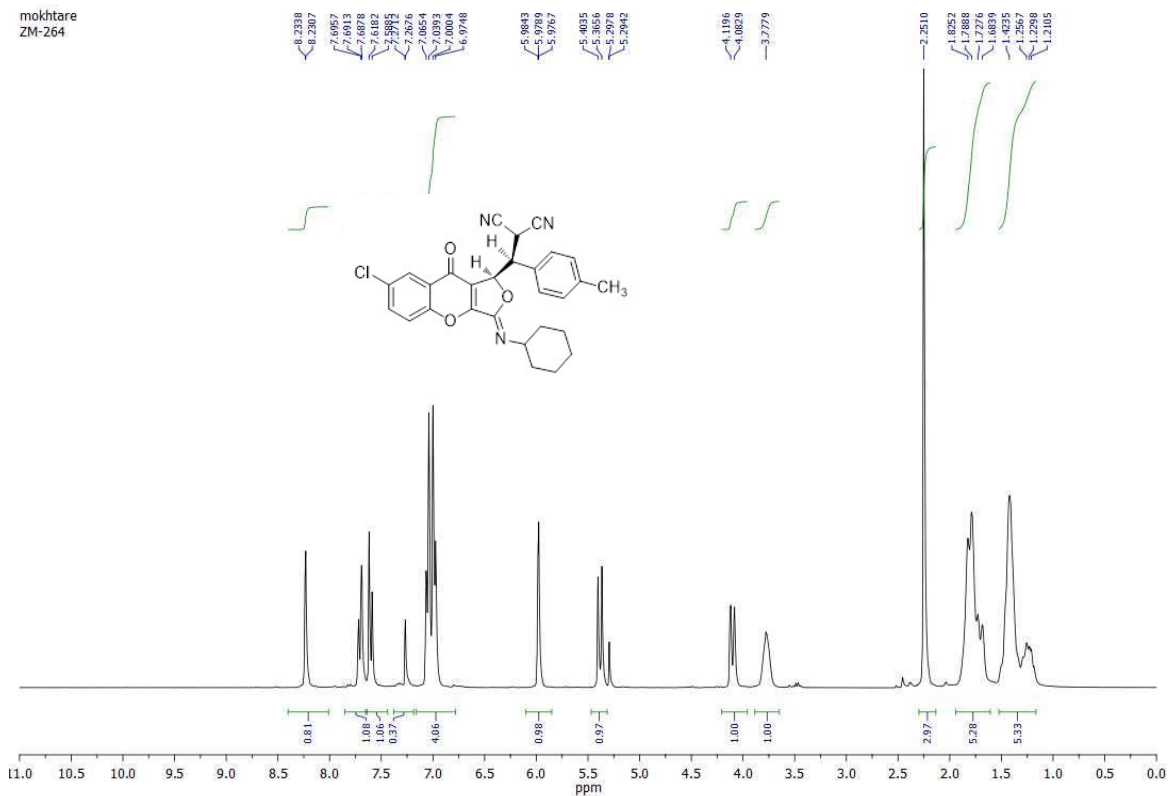


Ms. Mokhtare

Sample: ZM-264

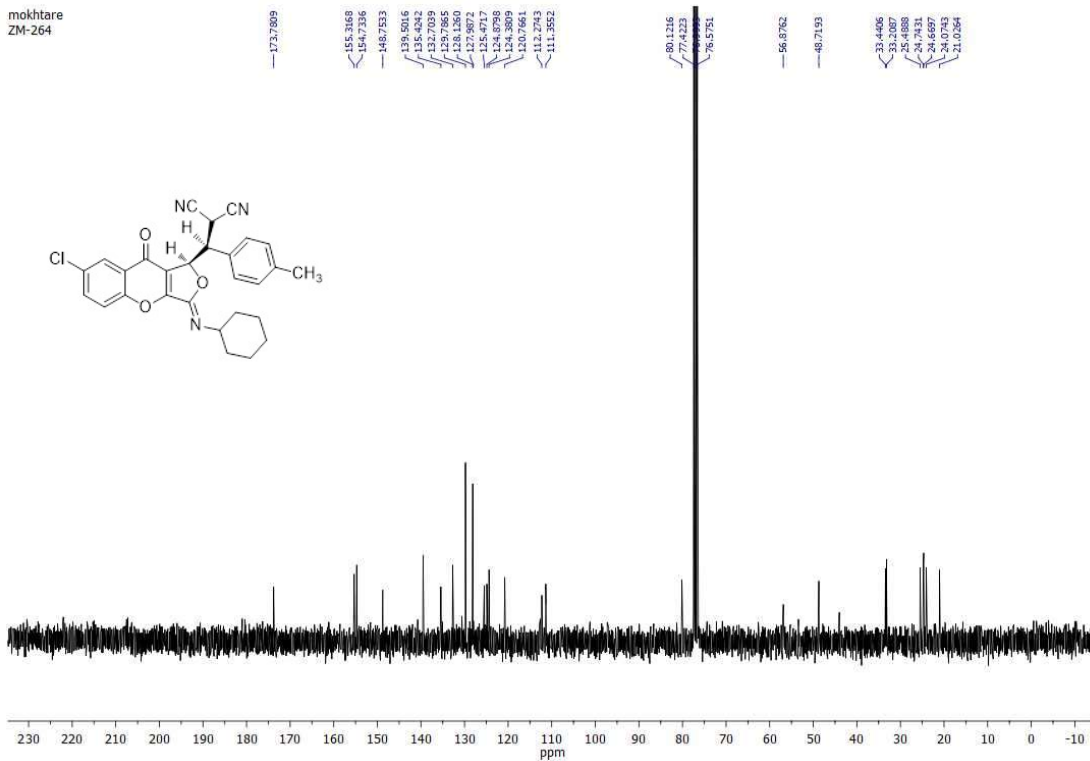
¹H NMR (300 MHz, CDCl₃) of 4l:

mokhtare
ZM-264

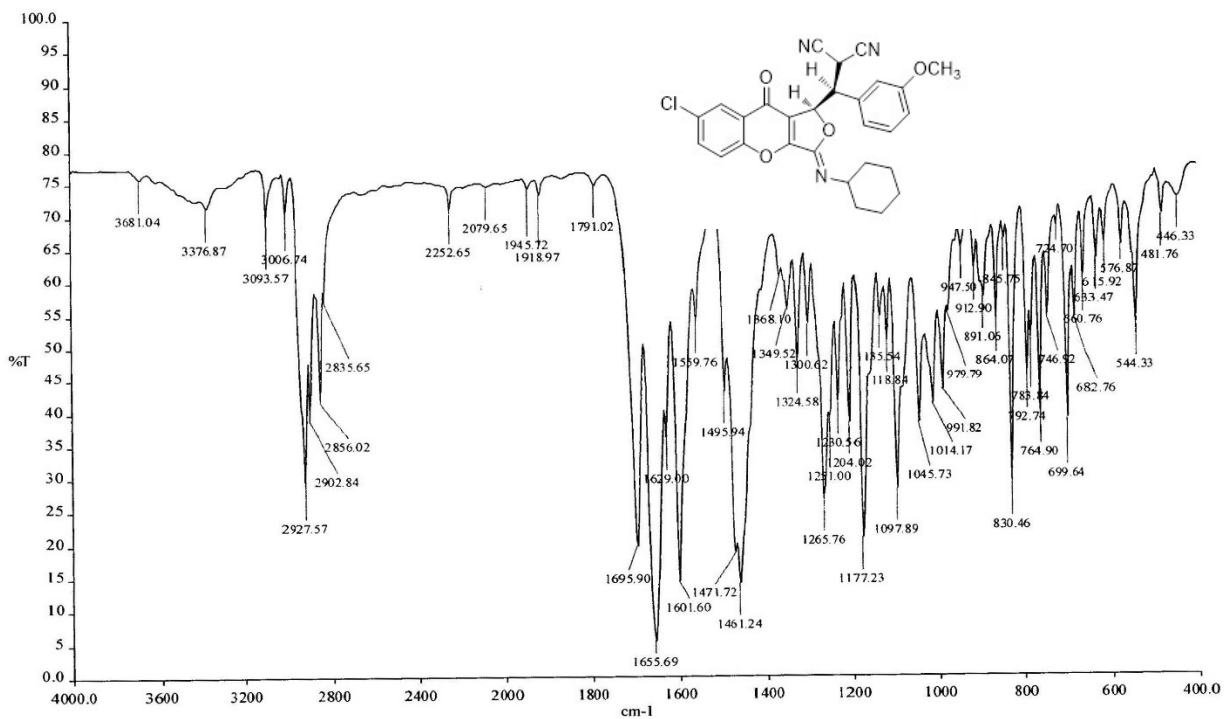


¹³C NMR (75 MHz, CDCl₃) of 4l:

mokhtare
ZM-264



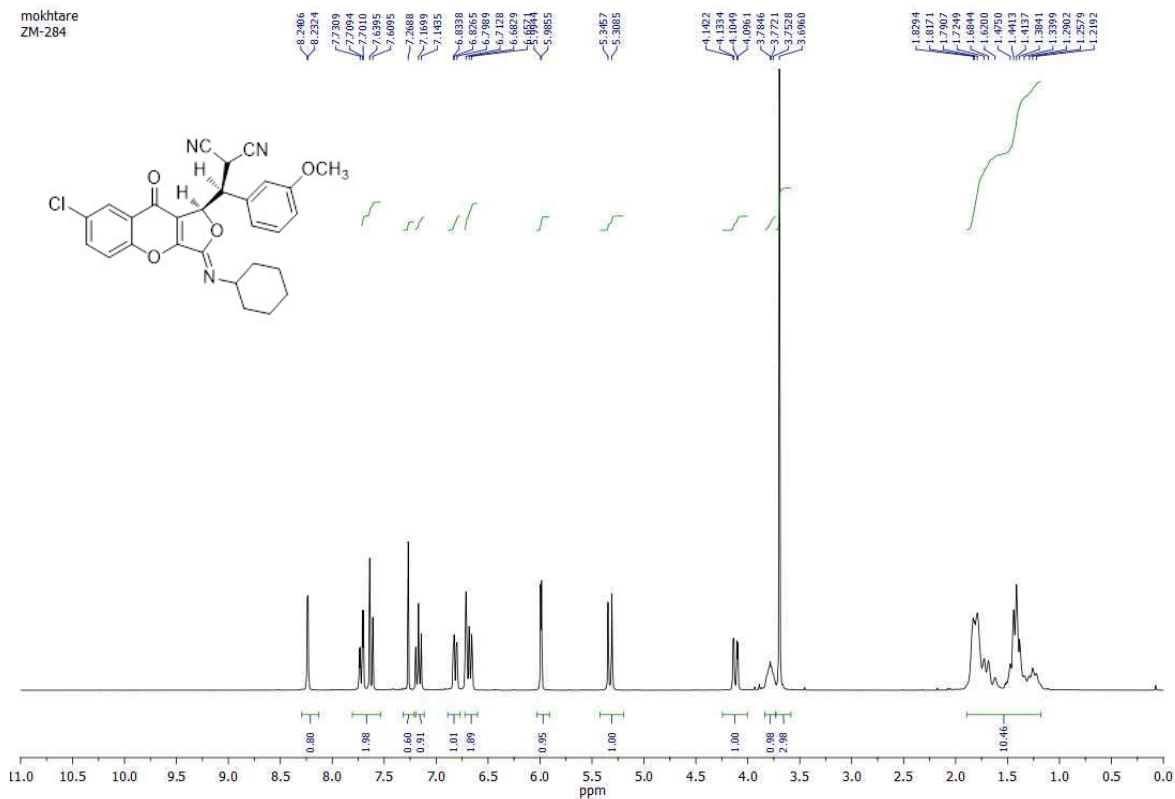
FT-IR of 4m:



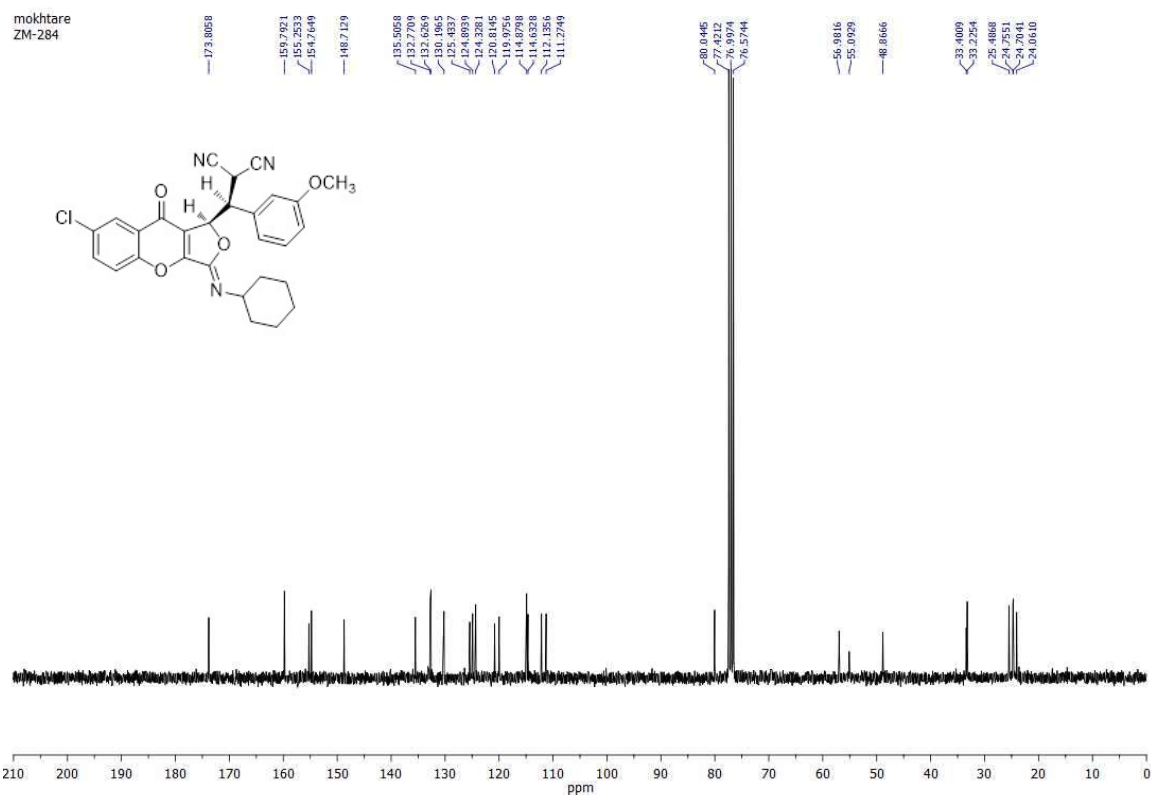
Ms. Mokhtare

Sample: ZM-284

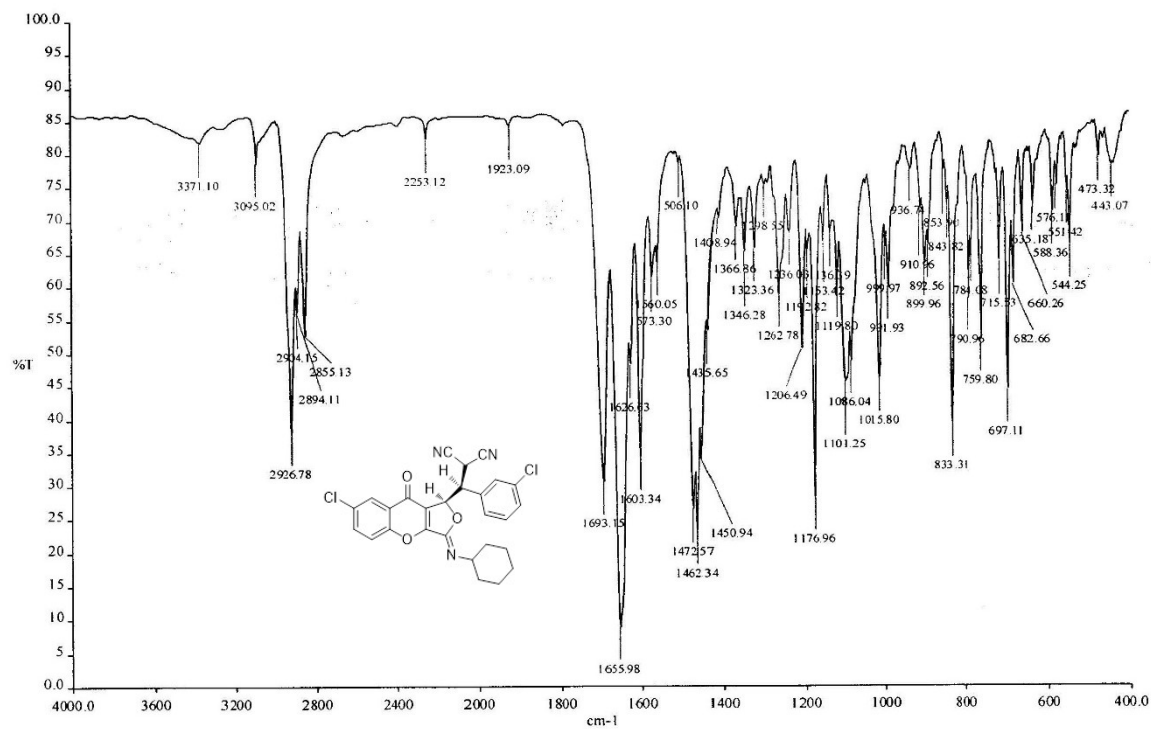
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¹³C NMR (75 MHz, CDCl₃) of 4m:



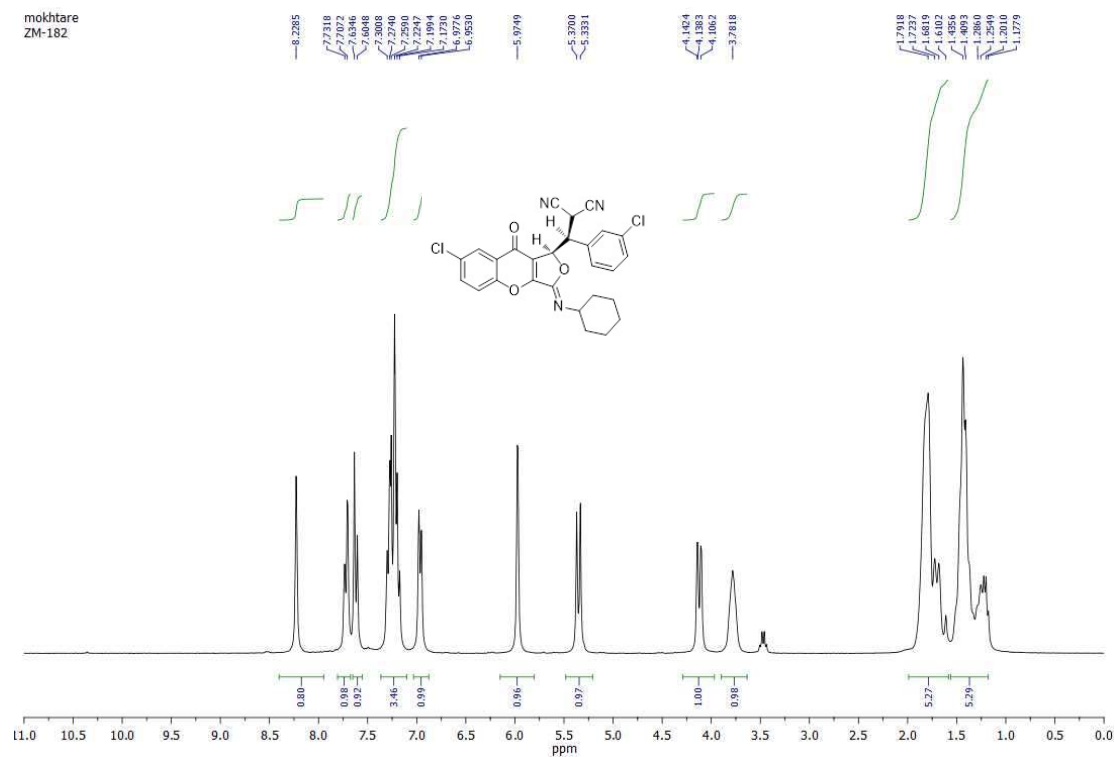
FT-IR of 4n:



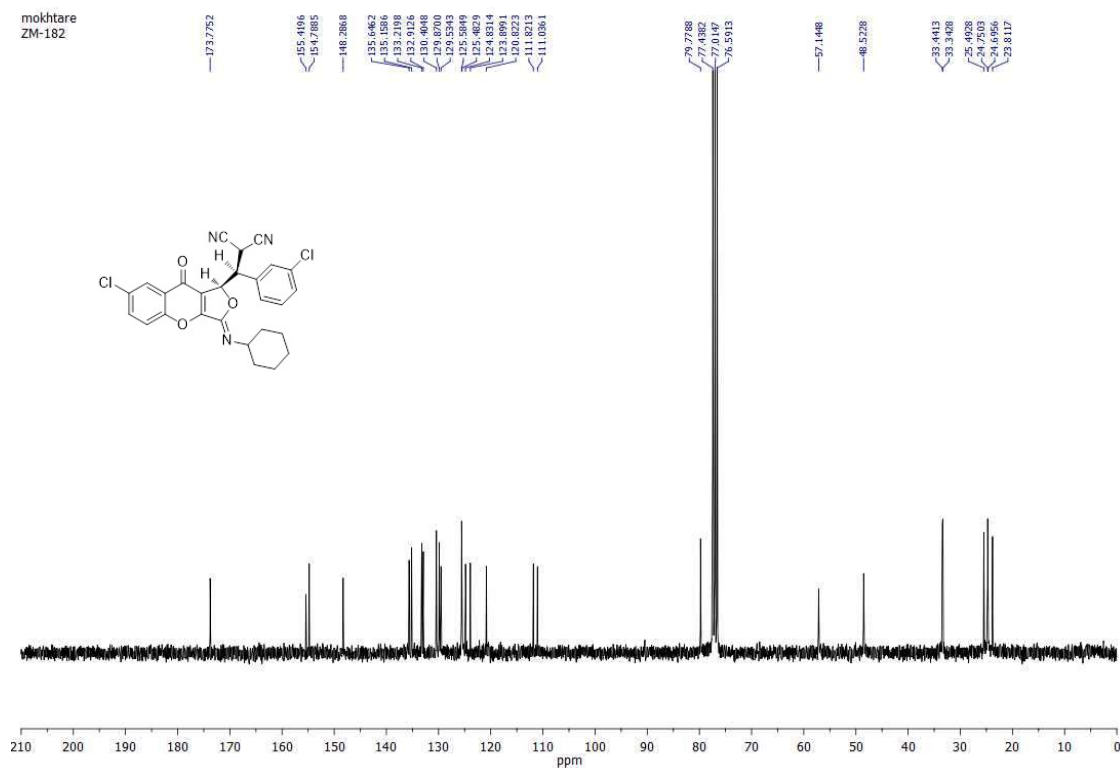
Ms. Mokhtare

Sample: ZM-182

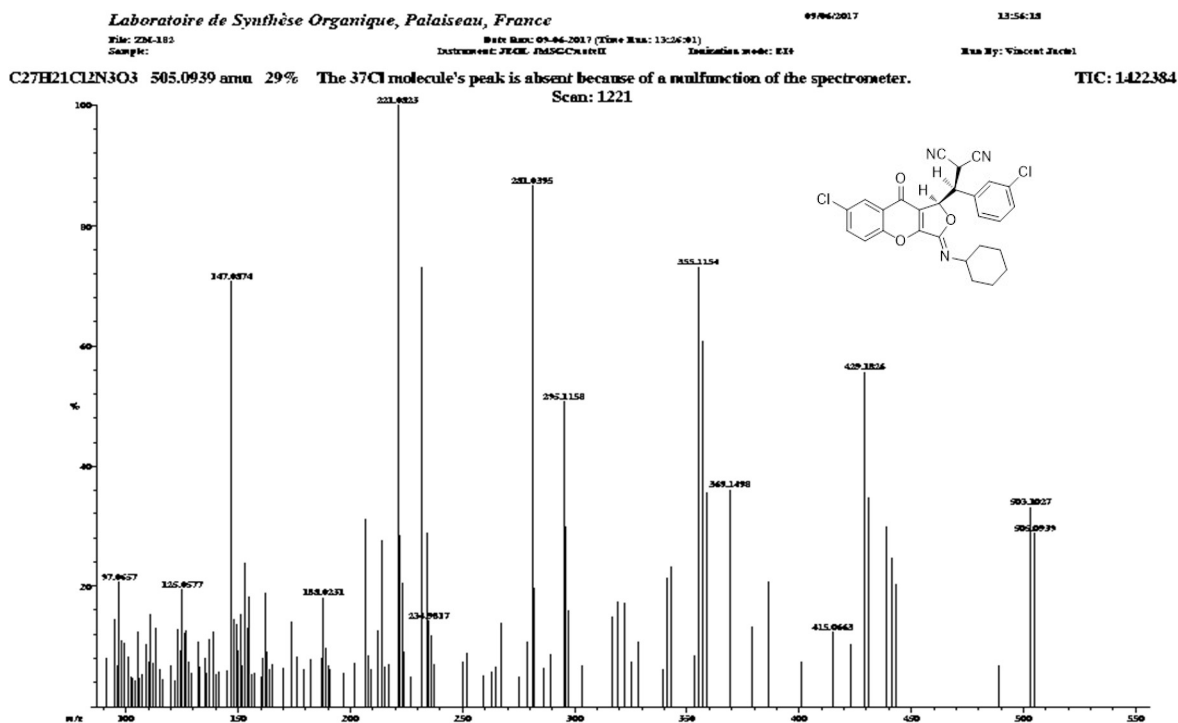
¹H NMR (300 MHz, CDCl₃) of 4n:



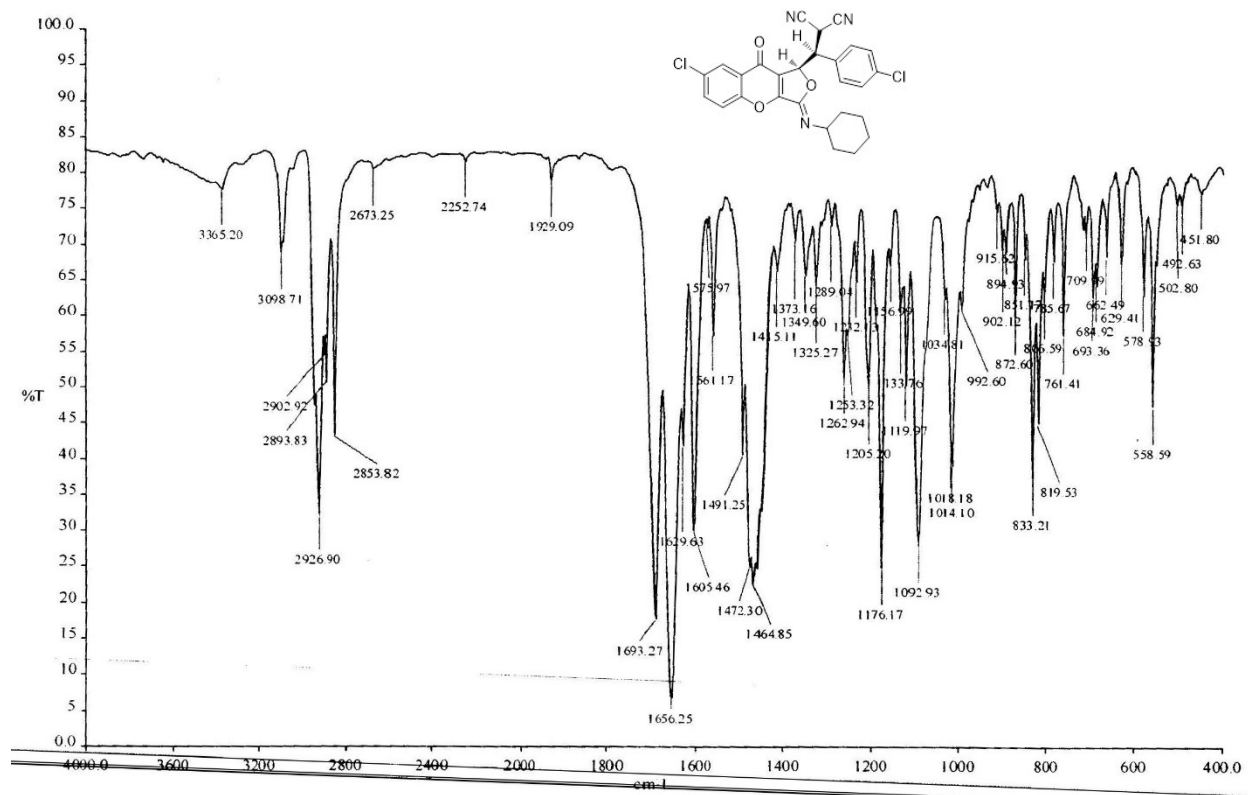
¹³C NMR (75 MHz, CDCl₃) of 4n:



HRMS of 4n:



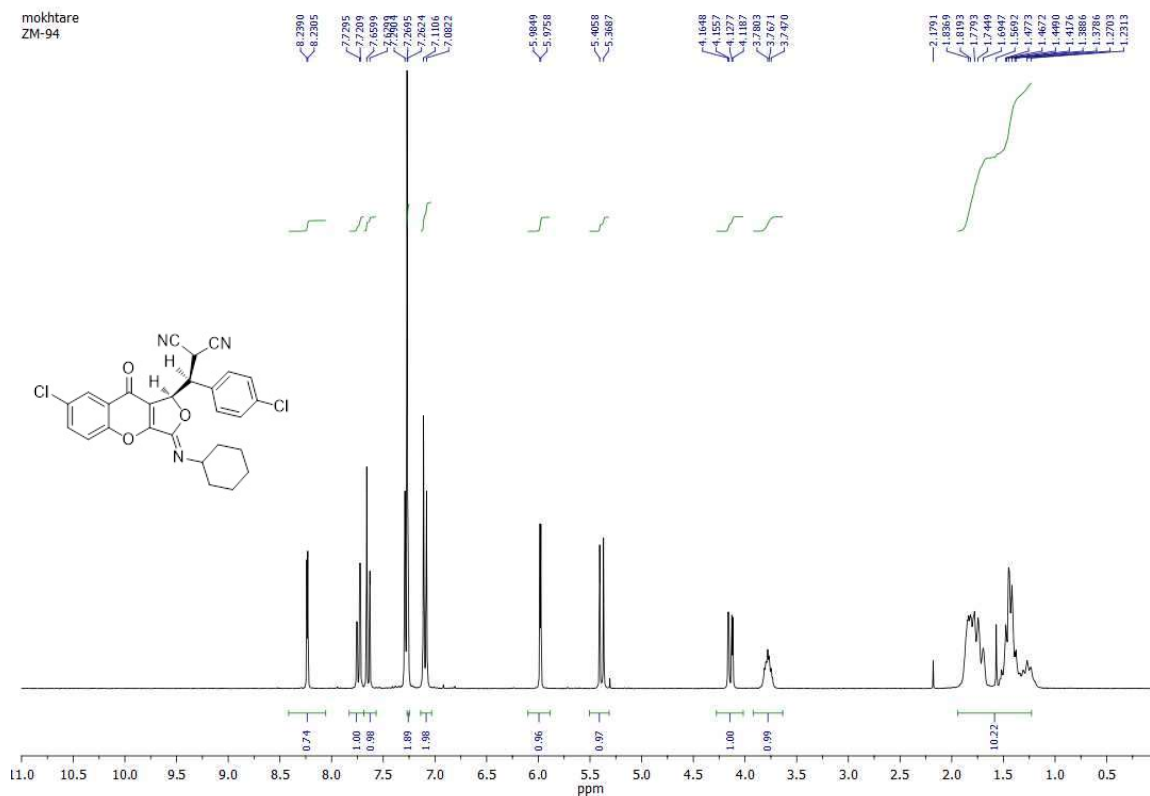
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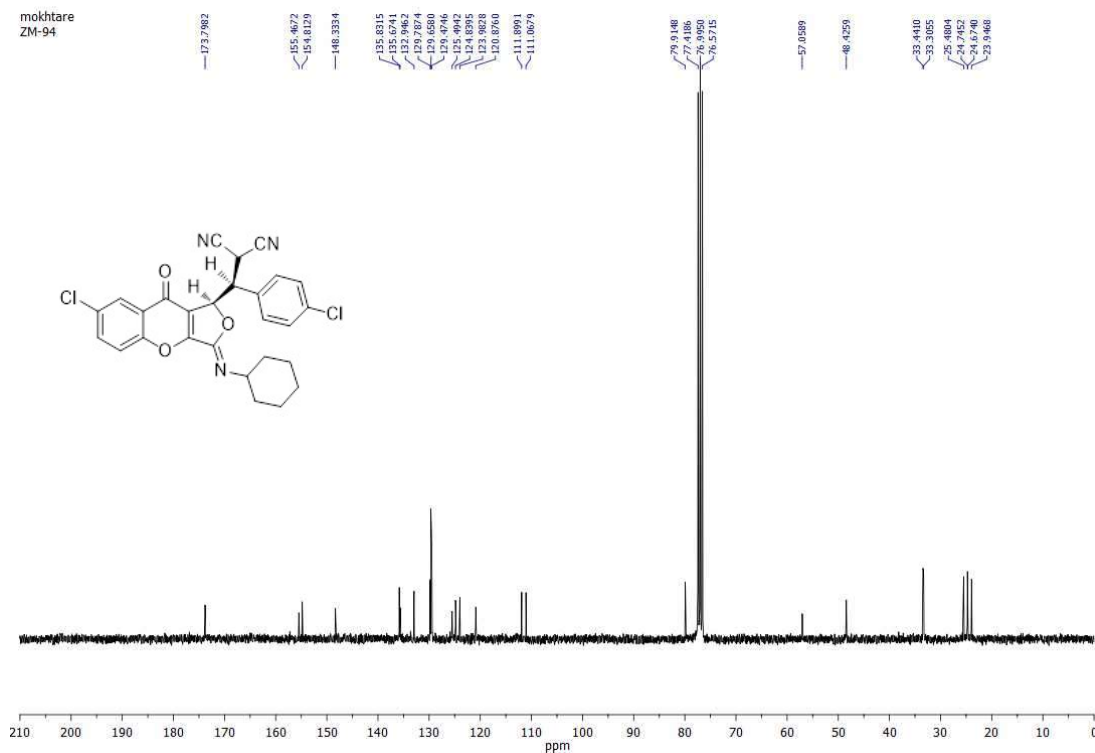
Ms. Mokhtar

Sample: ZM-94

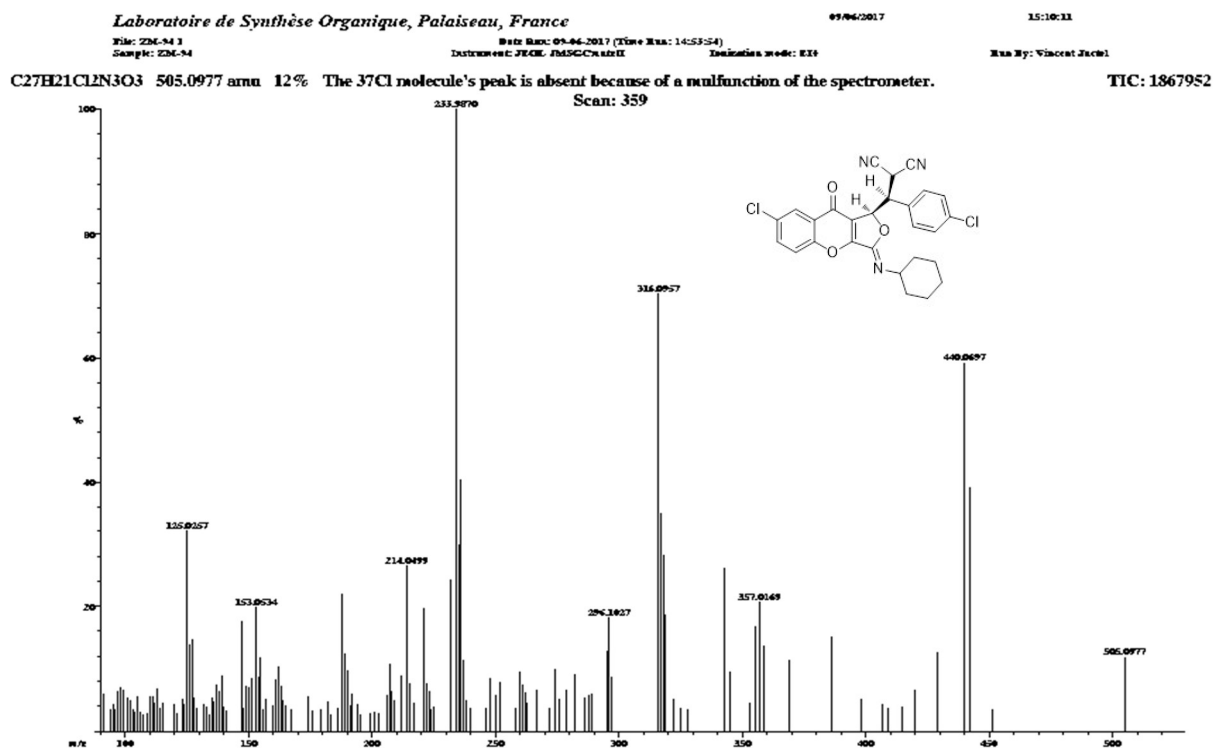
¹H NMR (300 MHz, CDCl₃) of 4o:



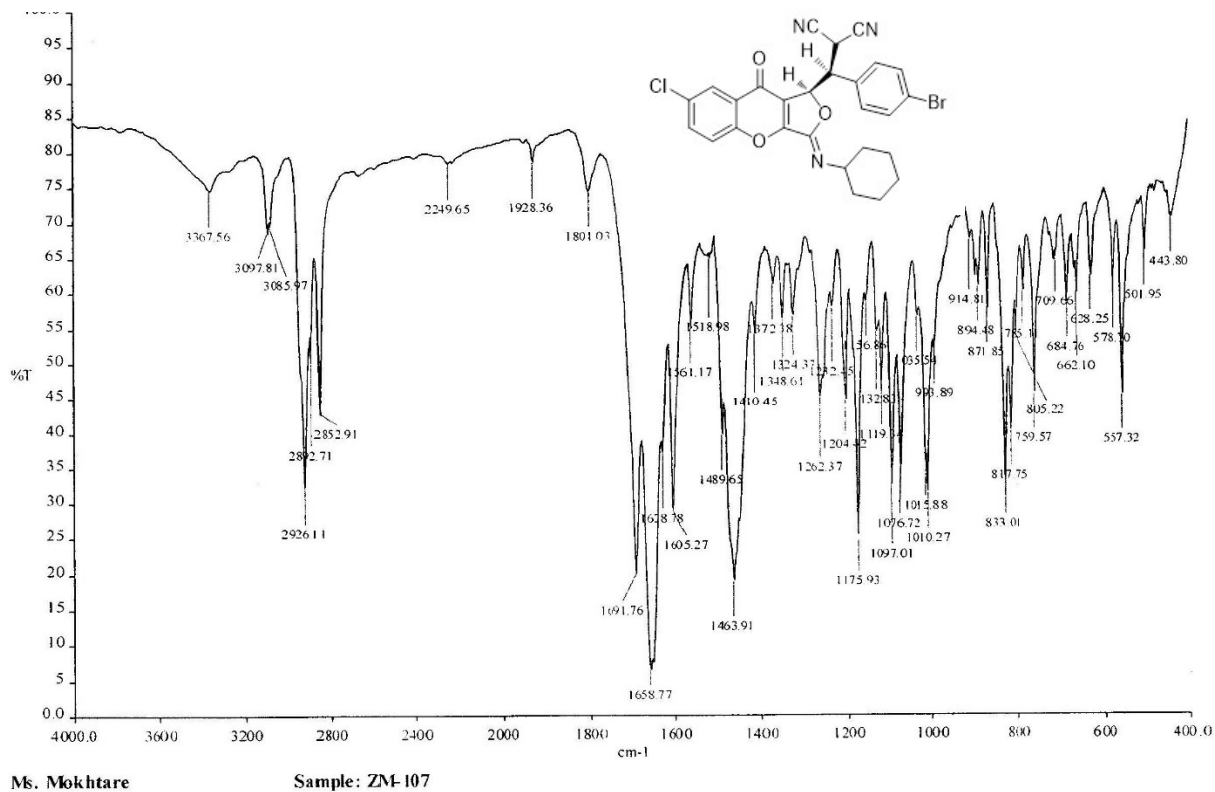
¹³C NMR (75 MHz, CDCl₃) of 4o:



HRMS of 4o:

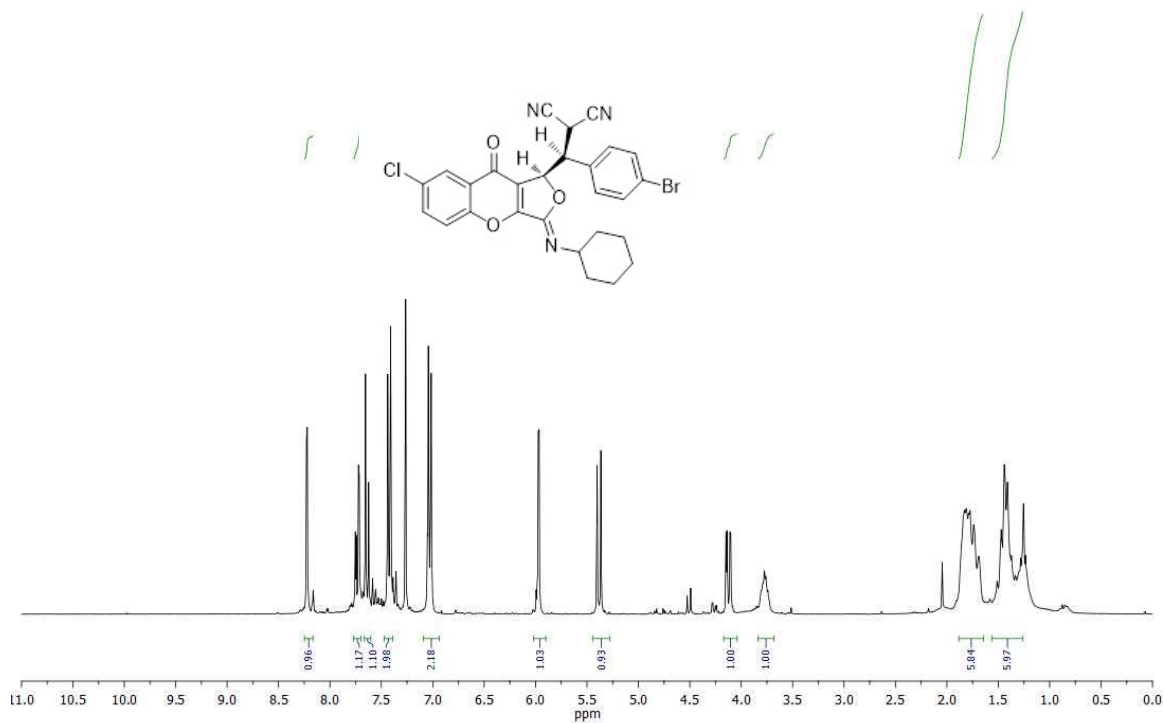


FT-IR of 4p:



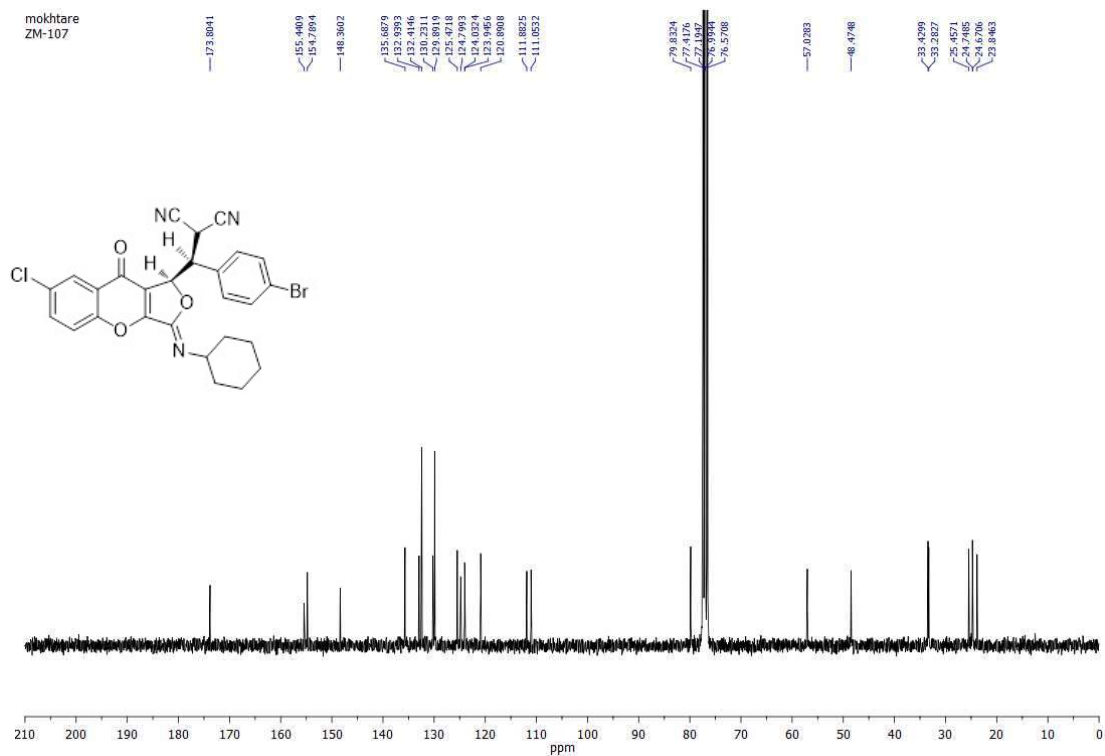
¹H NMR (300 MHz, CDCl₃) of 4p:

mokhtare
ZM-107

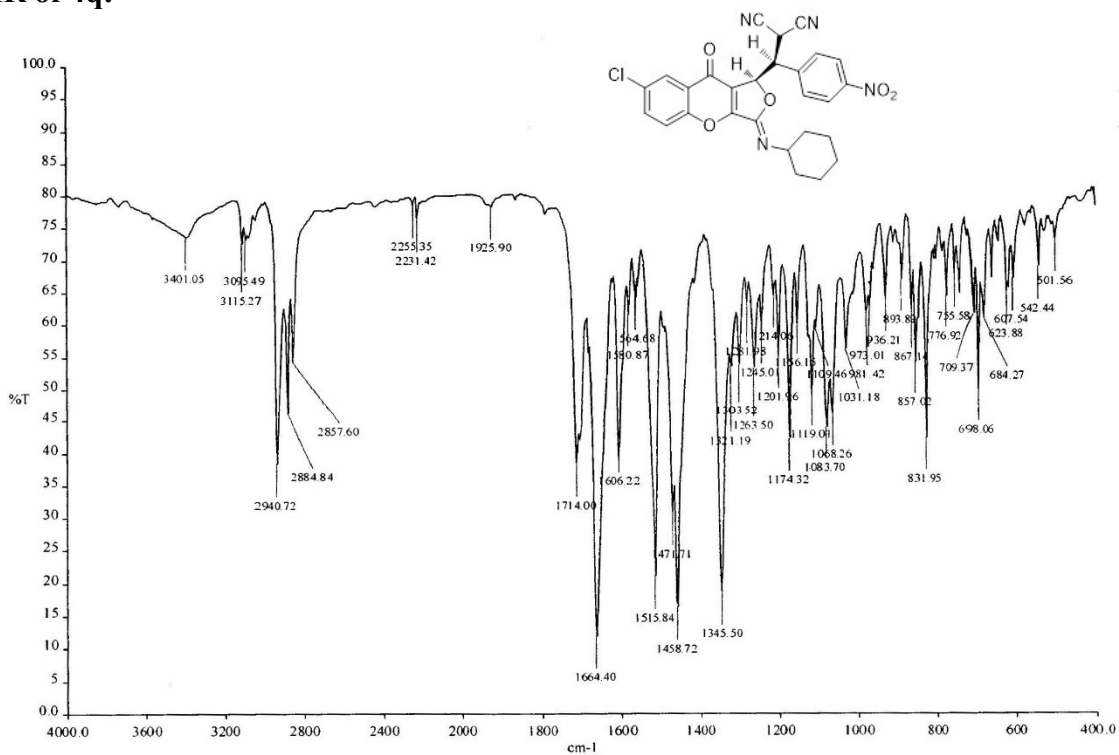


¹³C NMR (75 MHz, CDCl₃) of 4p:

mokhtare
ZM-107



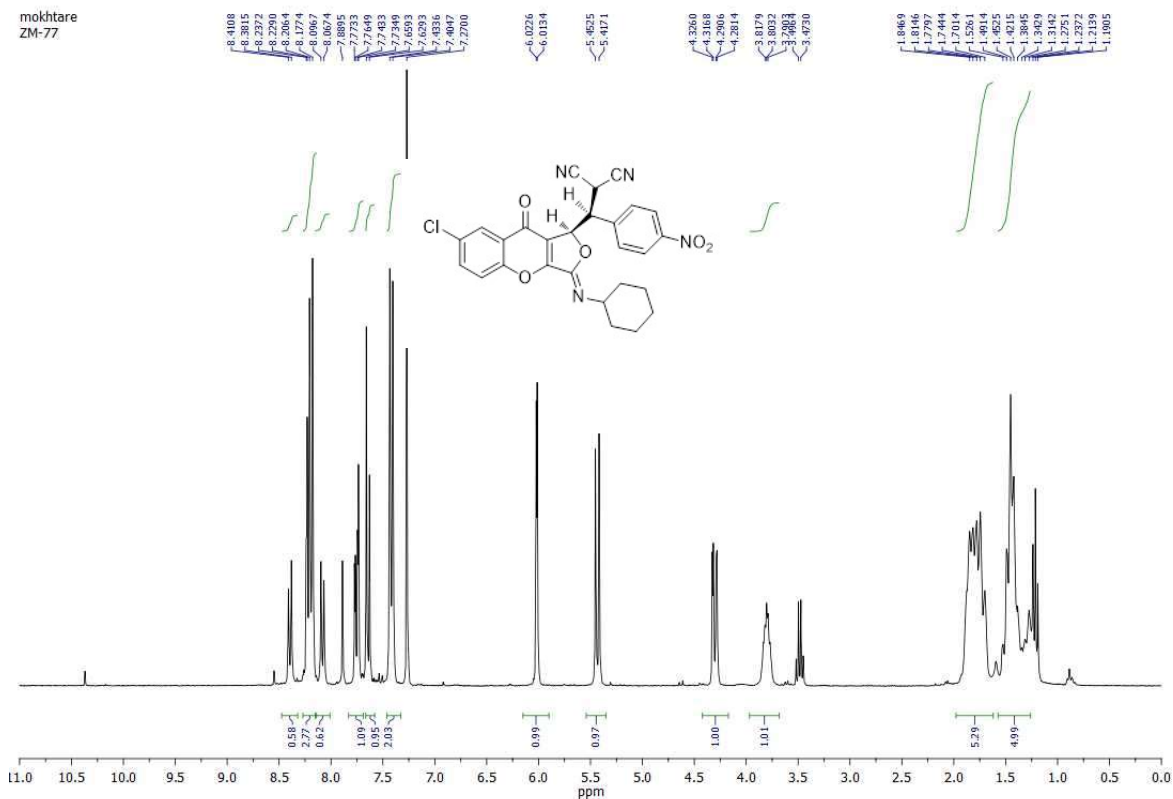
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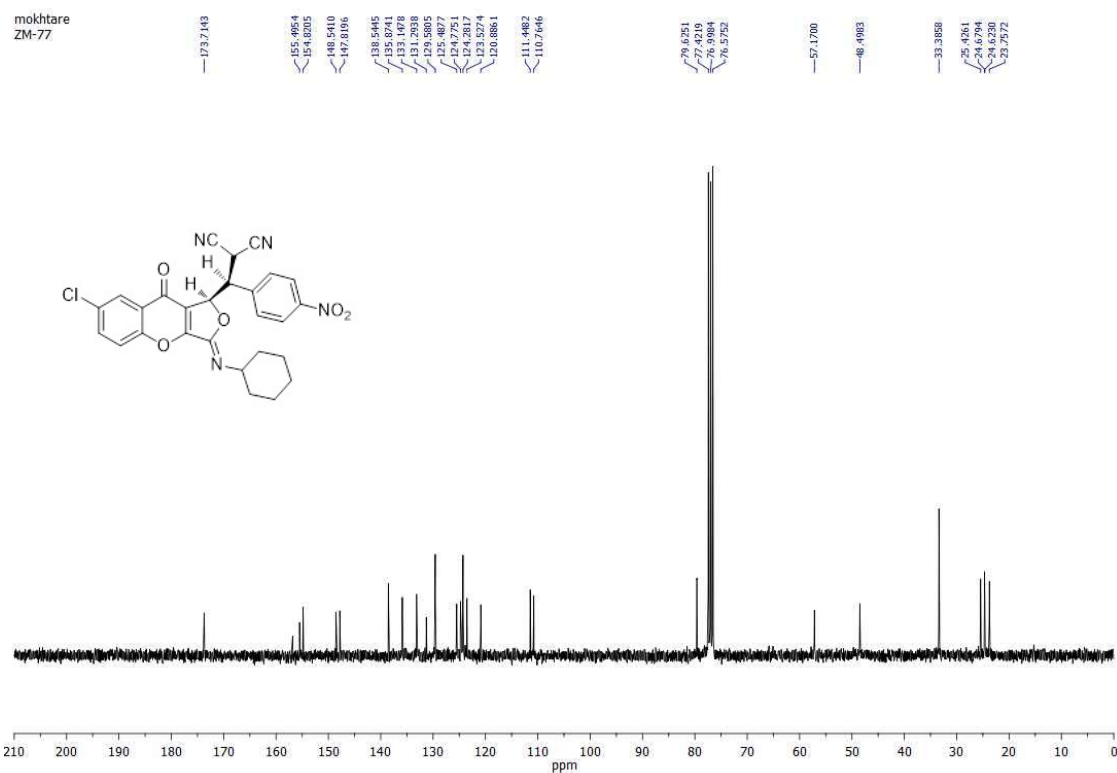
Ms. Mokhtare

Sample: ZM-71

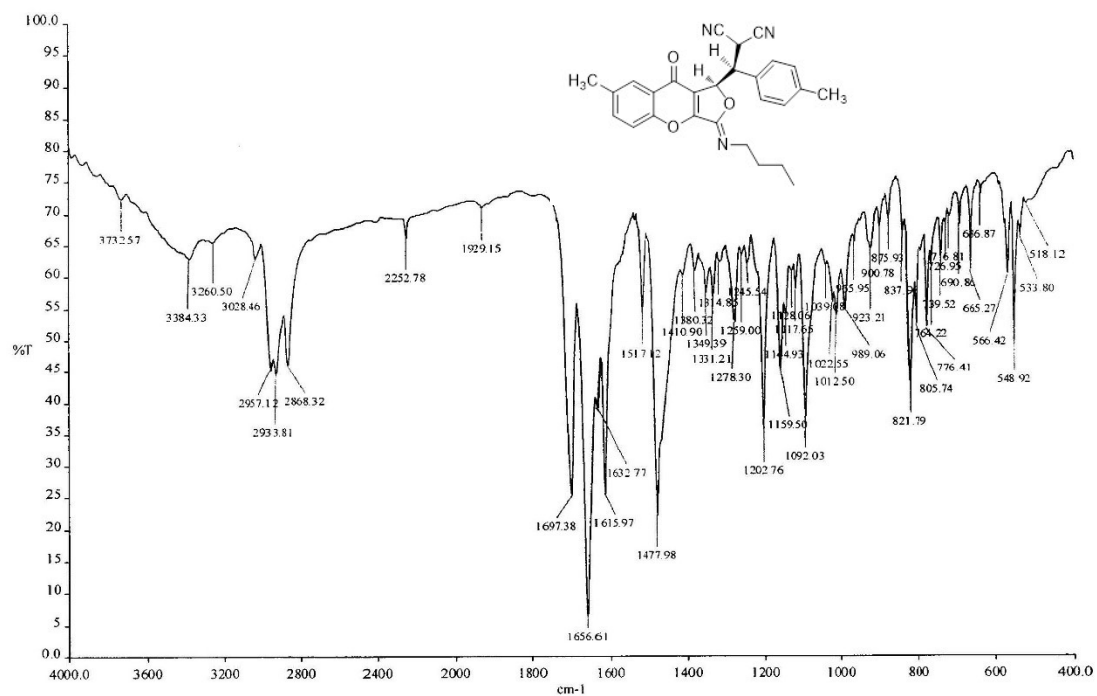
¹H NMR (300 MHz, CDCl₃) of 4q:



¹³C NMR (75 MHz, CDCl₃) of 4q:



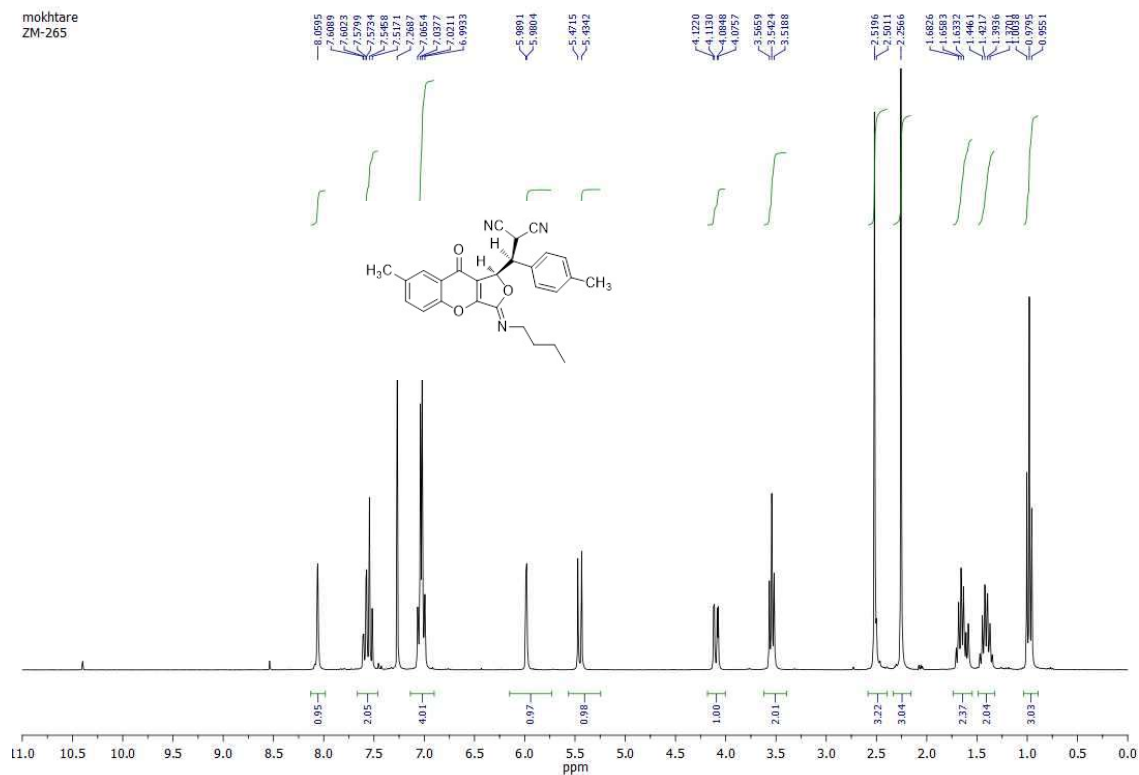
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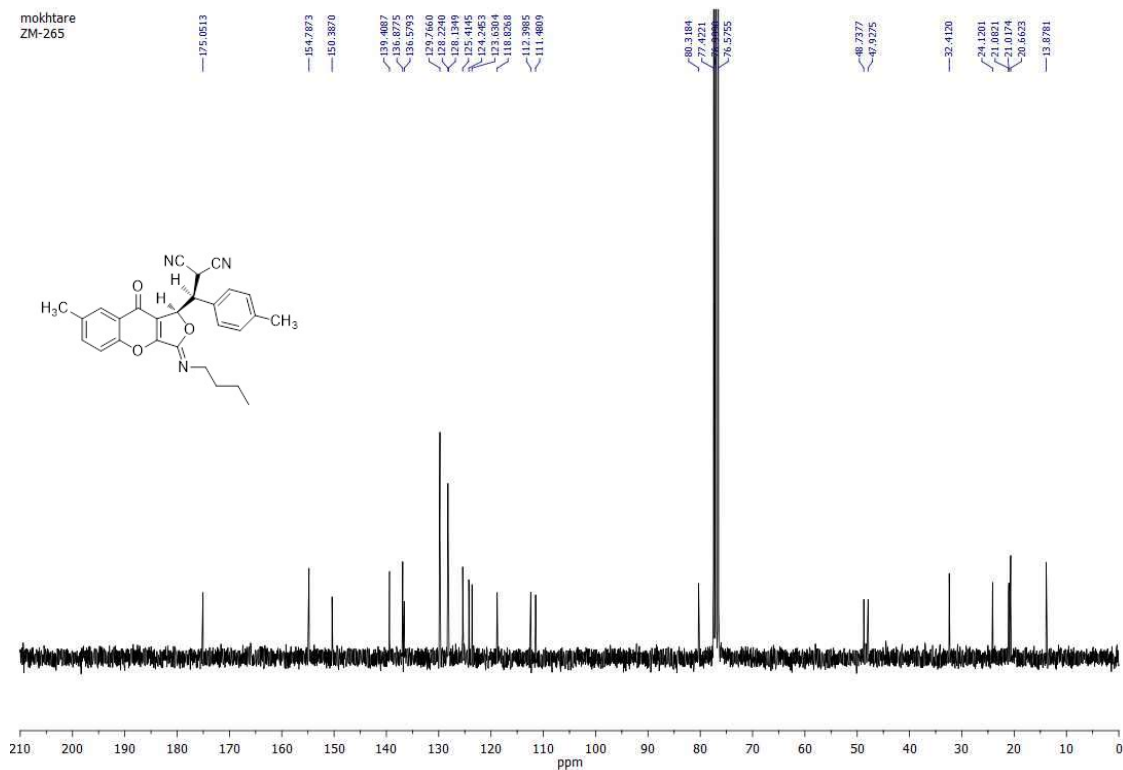
Ms. Mokhtare

Sample: ZM-265

¹H NMR (300 MHz, CDCl₃) of 4r:



¹³C NMR (75 MHz, CDCl₃) of 4r:



Single crystal structure of **4p**:

The yellow plate shape crystals of compound **4p** were obtained from methanol after 4 days. In order to have strong document about the molecular structure of product, the crystals of compound **4p** were also studied by single crystal X-ray diffraction studies. A suitable single crystal of **4p** was selected and mounted on a glass fiber. The X-ray diffraction data collection was done on a STOE IPDS-II diffractometer with graphite-monochromated Mo-K α radiation at room temperature. Diffraction data were collected in a series of ω scans in 1° oscillations and integrated using the Stoe X-Area [1] software package. A numerical absorption correction was applied using X-RED [2] and X-SHAPE [3] software. The data were corrected for Lorentz and polarizing effects. The structures were solved by direct methods [4] and subsequent difference Fourier maps and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [5]. All refinements were performed using the X-STEP32 crystallographic software package [6]. The data collection and refinement processes are summarized in Table 1.

Table 1. Crystal data and structure refinement parameters for compound **4p**.

Compound	4p
Net formula	<u>C₂₇H₂₁BrClN₃O₃</u>
<i>M_w</i> /g mol ⁻¹	550.82
Crystal size/mm	<u>0.45</u> × <u>0.15</u> × <u>0.05</u>
<i>T</i> /K	298
Radiation	Mo K α
Diffractometer	STOE IPDS 2T
Crystal system	Triclinic
Crystal shape, color	Plate, yellow
space group	<i>P</i> -1
<i>a</i> /Å	8.8254(15)
<i>b</i> /Å	9.1172(14)
<i>c</i> /Å	16.392(2)
α /°	94.438(12)
β /°	90.270(13)
γ /°	111.705(13)
<i>V</i> /Å ³	1221.0(3)
<i>Z</i>	2
calc. density/g cm ⁻³	1.498
μ /mm ⁻¹	1.83
<i>F</i> (000)	560
θ range/°	2.4–27.0
<i>h</i>	–11→11
<i>k</i>	–11→10

l	-20→20
R_{int}	0.151
$R[F^2 > 2\sigma(F^2)]$	0.069
$wR(F^2)$	0.165
S	0.82
Measured reflections	11405
Independent reflections	5326
Reflections with $I > 2\sigma(I)$	2009
Parameters	316
$\Delta\rho_{\text{min}}$ and $\Delta\rho_{\text{max}}/ \text{e } \text{\AA}^{-3}$	-0.51 and 0.70

The structural data have been deposited at the Cambridge Crystallographic Data Center (CCDC No 2049904). These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/structures.

Description of the crystal structure **4p**:

The plate yellow crystals of compound **4p** were studied by single crystal X-ray diffraction analysis. Structural studies indicated this compound is crystallized in triclinic crystal system. The molecular structure of compound **4p** is shown in Fig. 1 and the selected bond lengths and angles are collected in Table 2. As it is shown in Fig. 1, the structure of compound **4p** the desired compound is successfully synthesized. (Please write some details about the spectroscopic properties of the compound and their agreement with the crystal structure). The N3-C22 and N3-C21 bond lengths are 1.487(6) and 1.246(6) Å which are in agreement with double and single carbon-nitrogen bond lengths, respectively. The C9-N1 (1.109(7) Å) and C10-N2 (1.108(7) Å) bonds are considerably shorter than these bonds which confirm the presence of C≡N bond in malononitrile unit.

The crystal structure of compound **4p** is stabilized by several CHO and CHN intermolecular hydrogen bond interactions (see Fig. 2a). The oxygen atoms of ketone functionality and chromene ring involve with C-H...O interactions with the hydrogen atoms of the neighboring molecules (see green dashed lines in Fig. 2a). The nitrogen atoms of the malononitrile functionality also form intermolecular C-H...N hydrogen bond interactions with the phenyl rings (see pink dashed lines in Fig. 2a and Fig. 3). The strong C-H... π and π ... π interactions between the aromatic and heterocyclic rings of the compound further stabilize the crystal packing of compound **1** (see Fig. 2b).

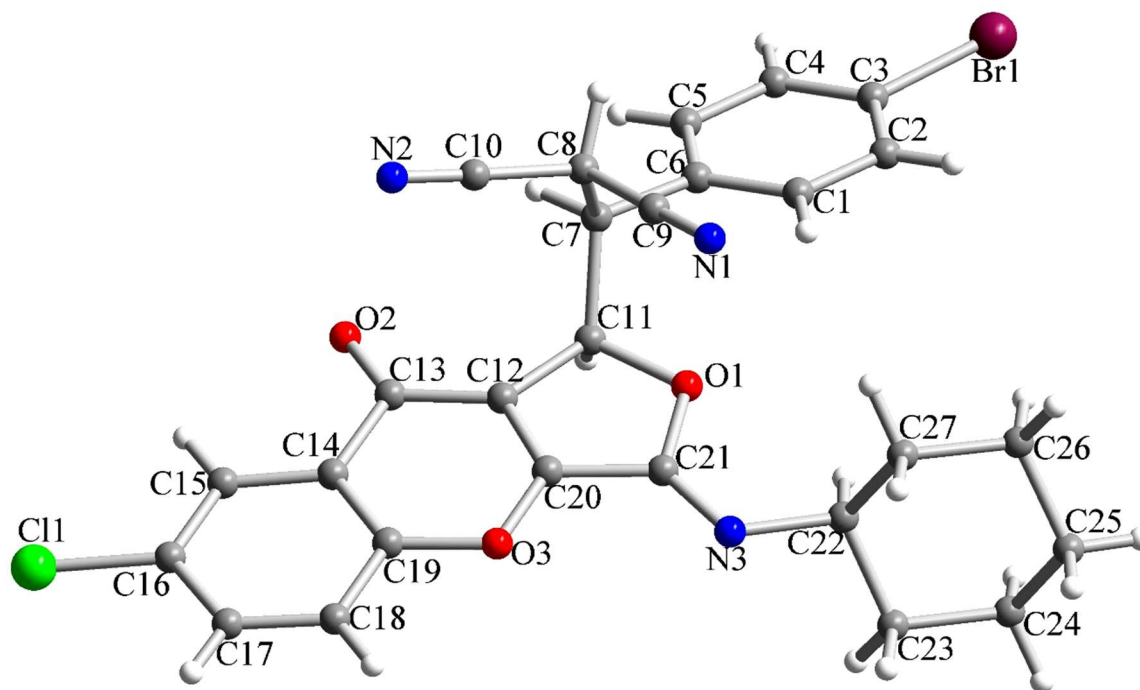


Fig. 2. Molecular structure of compound **4p** with atom labeling scheme.

Table 2. Selected bond lengths and angles in the crystal structure of compound **4p**.

Bond	Length/Å	Bond	Angle/°
C3–Br1	1.893(5)	C6–C7–C8	113.0(4)
C16–Cl1	1.717(5)	C6–C7–C11	109.8(4)
C9–N1	1.109(7)	C8–C7–C11	116.0(4)
C10–N2	1.108(7)	C21–N3–C22	117.8(4)
C22–N3	1.487(6)	C21–O1–C11	110.5(4)
C21–N3	1.246(6)	C20–O3–C19	115.8(4)
C11–O1	1.453(6)	N1–C9–C8	178.4(8)
C13–O2	1.227(6)	N2–C10–C8	178.7(7)
C19–O3	1.374(6)	N3–C21–O1	124.4(5)
C20–O3	1.336(5)	N3–C21–C20	129.7(5)
C21–O1	1.392(6)	N3–C22–C23	109.2(4)
C6–C7	1.529(7)	O1–C11–C12	104.1(4)
C7–C8	1.536(7)	O1–C11–C7	109.5(4)
C7–C11	1.548(7)	O1–C21–C20	105.9(4)
C8–C9	1.466(8)	O2–C13–C12	125.0(5)
C8–C10	1.470(8)	O2–C13–C14	122.9(5)
C11–C12	1.505(6)	O3–C20–C12	126.6(4)
		O3–C20–C21	121.7(4)
		O3–C19–C14	122.7(4)
		O3–C19–C18	115.9(5)

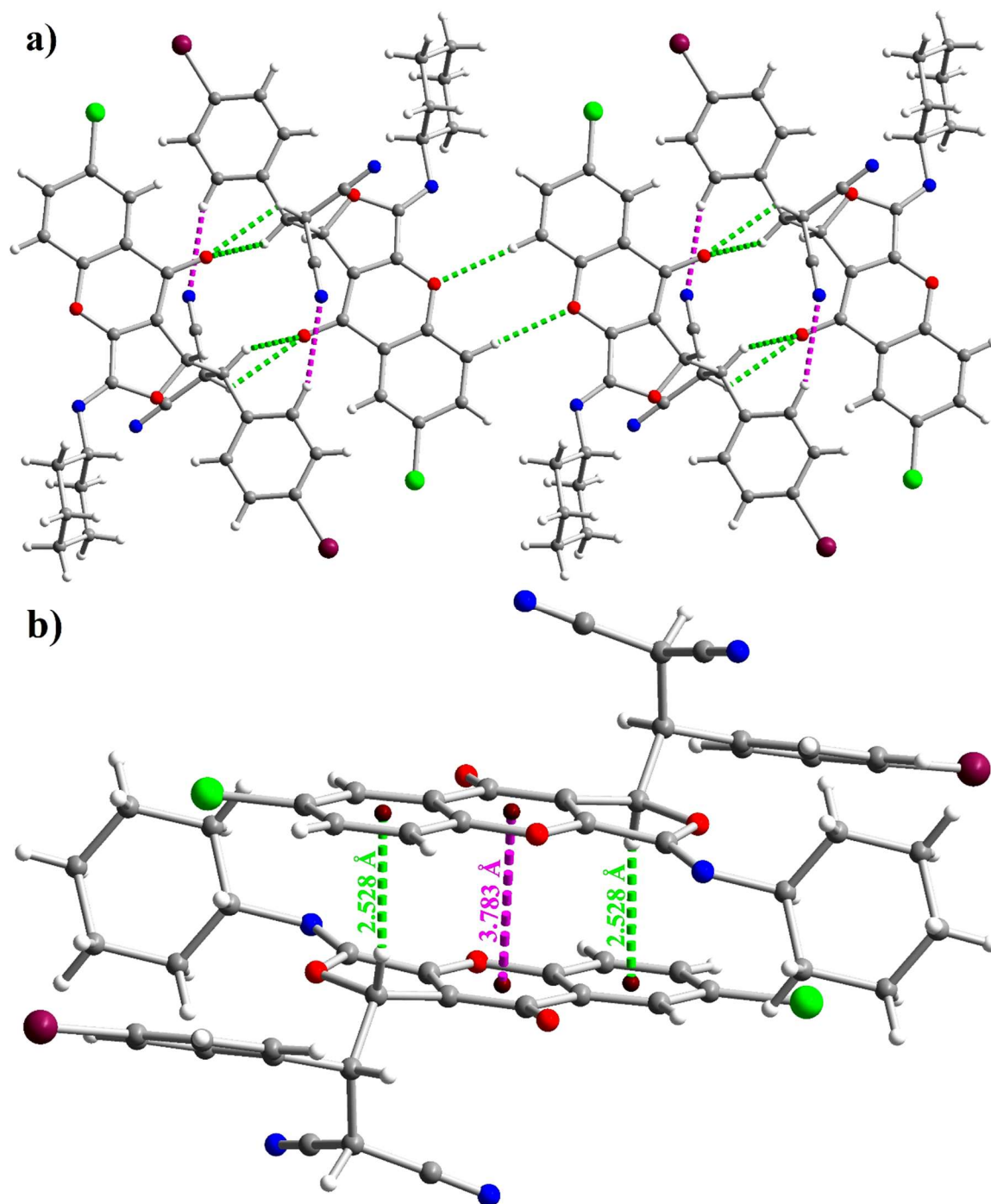


Fig. 2. a) Intermolecular C-H...O (green dashed lines) and C-H...N (pink dashed lines) interactions; b) C-H... π (green dashed lines) and π ... π (pink dashed lines) interactions in the crystal structure of **4p**.

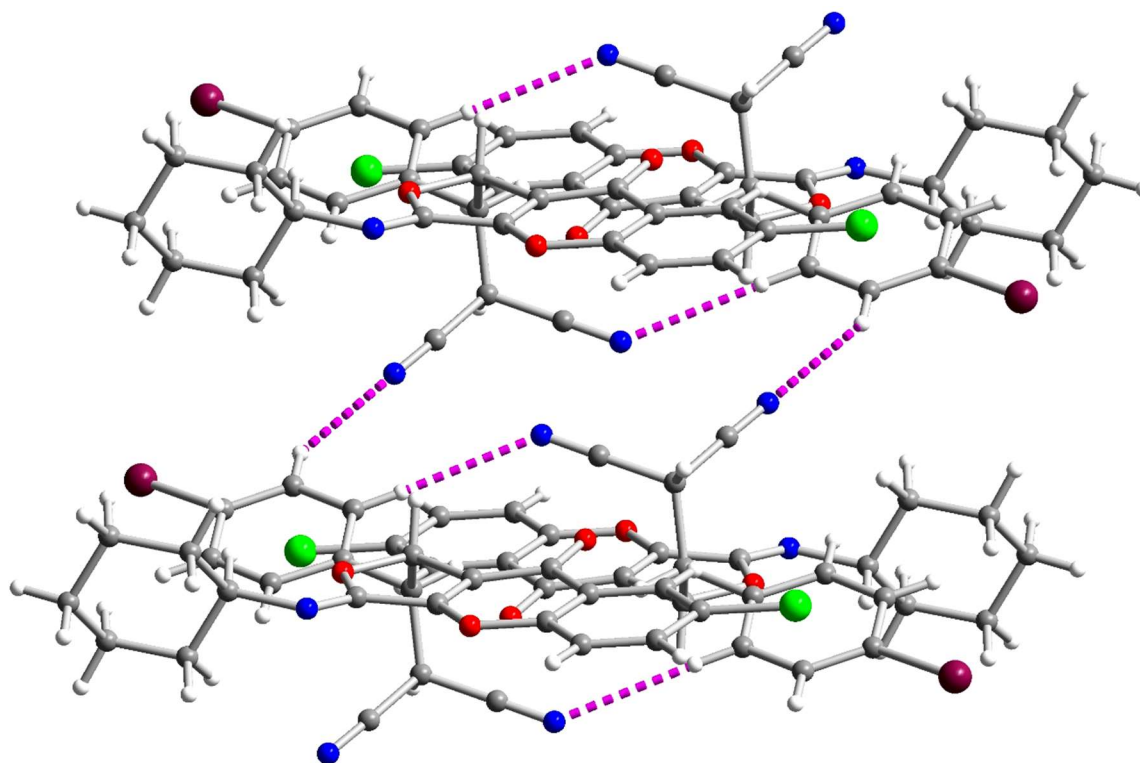


Fig. 3. Intermolecular C–H···N interactions in the crystal structure of **4p** shown as pink dashed lines.

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