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Synthesis and Characterization of a Series of Chromone–Hydrazones †

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Abstract: Chromones, a class of aromatic heterocyclic compounds, possess intriguing biological and optical properties, making them ideal for spectroscopic detection. Hydrazones, known for their chelating abilities, can selectively bind to metal ions. This study presents a series of novel chromone-hydrazone derivatives synthesized from 3-formylchromone and three different hydrazines compounds. The structures of these synthesized compounds were confirmed through spectral analysis using ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy.

Keywords: Chromone; Hydrazone; Synthesis

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1. Introduction

Chromones, a class of aromatic heterocyclic compounds, have garnered significant attention due to their diverse biological activities and optical properties. These compounds possess a wide range of biological applications [1,2]. Additionally, chromones' unique structural features and photophysical properties make them promising candidates for various spectroscopic applications, such as chemosensors and fluorescent probes [3,4].

Hydrazones, derived from the condensation of hydrazine with carbonyl compounds, are known for their chelating abilities and have been extensively studied for their applications in metal ion sensing [5–7]. The incorporation of hydrazine moieties into chromone derivatives can enhance their metal-binding affinity and selectivity, leading to the development of novel chemosensors with improved performance [8,9].

This study aims to explore the synthesis and characterization of a series of chromone-hydrazone derivatives. By combining the structural features of chromones and hydrazones, we hypothesize that these compounds will exhibit enhanced chemosensing properties and offer potential applications in various fields, including environmental monitoring and biological analysis.

2. Experimental Section

2.1. Instruments and Reagents

The The reagents and solvents were obtained from commercial suppliers (Acros (Fukuoka, Japan), Aldrich (St. Louis, MO, USA), and Fluka) and were used as received.

For FT-IR spectroscopy, solid samples were taken neat on a Thermo Scientific IR200 FT-IR spectrophotometer, only significant absorptions are listed.

^{1}H-NMR and ^{13}C-NMR spectra were performed on a MAGRITEK 90 MHZ spectrometer at 298 K in $CDCl_3$ solutions. Chemical shifts were reported relative to TMS as an internal standard.

2.2. Synthesis

3-Formylchromone was prepared by the VilsmeiereHaack synthesis (Scheme 1) [10].

The synthesis of benzaldehyde-hydrazone; benzophenone-hydrazone and benzil-bis-hydrazone are described in [10–12].

Synthesis of chromone hydrazones: The synthesis of chromone hydrazones are shown in scheme 2. Aromatic hydrazines (1.00 mmol), 3-formylchromone (1.00 mmol or 2.00 mmol in case of (**III**)), and a few drops of pTSA acid were dissolved in 25 mL of ethanol, and the mixture was stirred and refluxed for 6 h. The precipitate was recrystallized in ethanol, and dried in vacuo. All compounds were prepared similarly shown in Scheme 2 and characterized as below.

3-((E)-(((E)-benzylidene) hydrazinylidene) methyl)-4H-chromen-4-one (I): Yield 40% as yellow powder; IR (KBr, cm^{-1}): 3085 (=C-H); 1663 (C=O); 1609 (C=N); 1460 (C=C ar); 1227 (C-O).

^{1}H NMR (90 MHz, $CDCl_3$) δ (ppm): 8,86 (s, 2H, H-C=N); 8,33 (s, 1H, H-C-O), 7,25-7,8 (m, 9H, Ar-H).

(e)-3-(((diphenmethylen)hydrazineylidene) methyl)-4h-chromen 4one (II): Yield 60% as yellow powder; IR (KBr, cm^{-1}): 3050 (=C-H); 1650 (C=O); 1608 (N=C); 1262 (C-O).

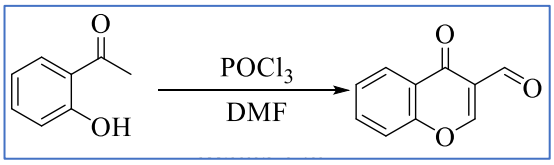
^{1}H NMR (90 MHz, $CDCl_3$) δ (ppm): 8,30 (s,1H, H-C=N); 8,14 (s, 1H, H-C-O); 7,38-8,03 (m, 14H, H Ar).

(e)-3-(((diphényle méthyl) hydrazine lydienne) méthyl) -4h-chromen-4-one (III): Yield 50% as yellow powder; IR (KBr, cm^{-1}): 3058 (=C-H); 1665(C=O); 1605 (C=N); 1226 (C-O).

^{1}H NMR (90 MHz, $CDCl_3$) δ (ppm): 8,7 (s, 2H, H-C=N); 8,3 (s, 2H, H-C-O); 7,3-8,2 (m, 18H, Ar-H).

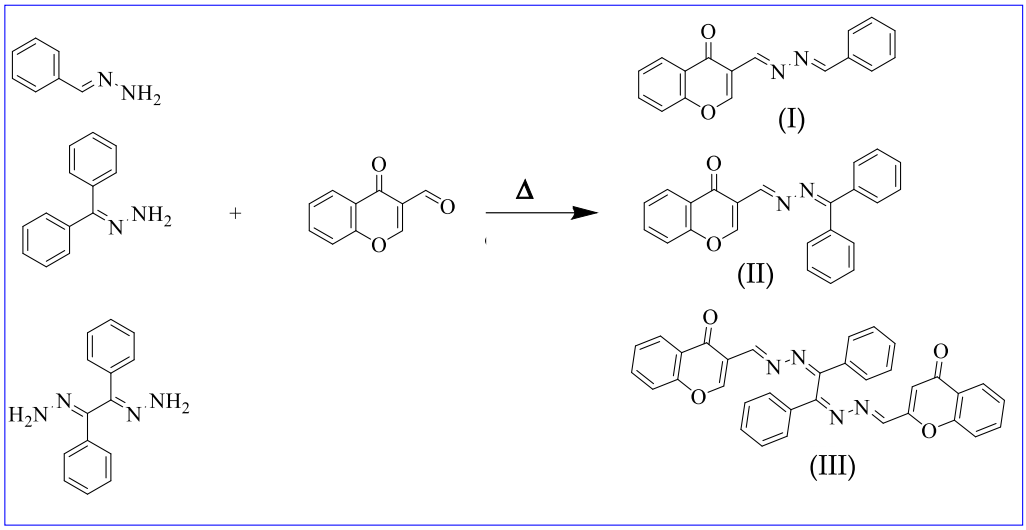
3. Result and Discussion

3-Formylchromone was prepared and obtained with a 75% yield via the Vilsmeier-Haack synthesis, as shown in Scheme 1 below.



Scheme 1. Synthesis of 3-formylchromone.

The chromone-hydrazone probes (I), (II), and (III) were successfully synthesized through a condensation reaction between 3-formylchromone and benzaldehyde-hydrazone, benzophenone-hydrazone, and benzil-bis-hydrazone, respectively, as shown in Scheme 2. The probes were obtained as yellow solids with good yields ranging from 40% to 60%. The structures of chromone-hydrazone probes (I), (II), and (III) were fully characterized using FT-IR, ^{1}H NMR, and ^{13}C NMR.



Scheme 2. Synthetic pathway for chromone-hydrazone derivatives (I), (II), and (III).

Infrared (FT-IR) spectroscopy analysis of the chromone-hydrazones (I, II, and III) further supported their proposed structures. The key characteristic bands observed in the IR spectra are summarized in the table below. The characteristic IR bands of the chromone-hydrazones, presented in Table 1, provide valuable insights into the presence and nature of the functional groups within these compounds.

Table 1. Characteristic IR spectral data of the chromone-hydrazones (I, II, and III).

	ν (=CH) cm^{-1}	ν (C=O) cm^{-1}	ν (-C=N) cm^{-1}	(C-O) cm^{-1}	ν (N-N) cm^{-1}
(I)	3085	1663	1609	1227	1095
(II)	3050	1650	1608	1262	1071
(III)	3058	1656	1605	1226	1042

As an example, the IR spectrum of chromone-hydrazone (II).

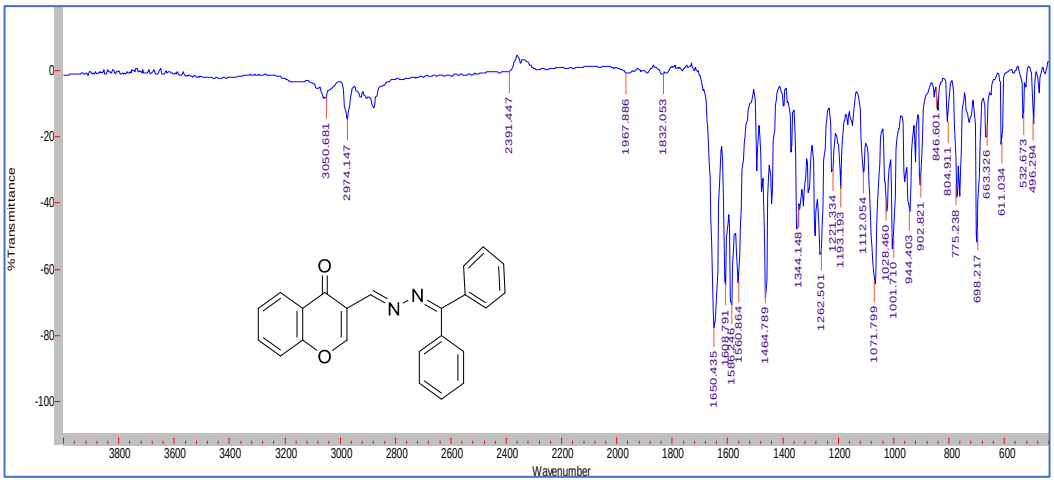


Figure 1. IR spectrum of chromone-hydrazone (II).

The ^1H NMR spectra of chromone-hydrazones (I, II, and III) were recorded using $CDCl_3$ as the solvent. The spectral data provide further evidence supporting the proposed structures of the ligands. Below is the ^1H NMR spectrum of chromone-hydrazone (III).

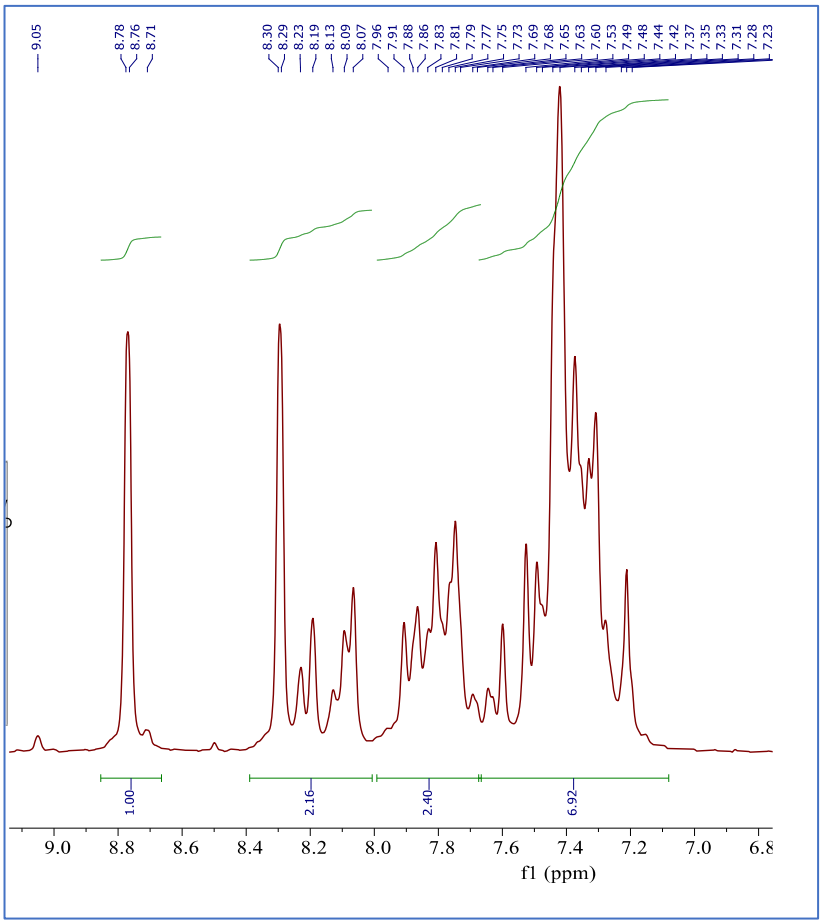


Figure 2. ^{1}H NMR spectrum of chromone-hydrazone (**III**).

4. Conclusions

In summary, we synthesized a series of three chromone-hydrazone ligands via a rapid and efficient method. These ligands, possessing multiple coordination sites and strong chelating abilities, were designed to selectively bind metal cations of environmental and health concern. Complexation and detection studies are underway to assess their potential.

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Conflicts of Interest: The author declares no conflict of interest.

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