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## ULTRASOUND-PROMOTED KABACHNIK-FIELDS SYNTHESIS OF NOVEL CHROMONYL $\alpha$ -AMINOPHOSPHONATE DERIVATIVES INCORPORATING NITROGEN HETEROCYCLES USING CdI<sub>2</sub> NANOPARTICLES AS AN EFFICIENT CATALYST: EVALUATION OF THEIR ANTIFUNGAL PROPERTIES

Mohamed Hussien,<sup>1,2</sup> Tarik E. Ali,<sup>3\*</sup> Ibrahim El-Tantawy El Sayed,<sup>2</sup> Abdelaleem Hassan Abdelaleem,<sup>2</sup> and H. M. Torkey<sup>1</sup>

<sup>1</sup>Pesticide Formulation Department, Central Agricultural Pesticide Laboratory, Agricultural Research Center, Dokki, Giza, 12618, Egypt.

<sup>2</sup>Department of Chemistry, Faculty of Science, Menoufia university, Shebin El-Kom, 32511, Egypt.

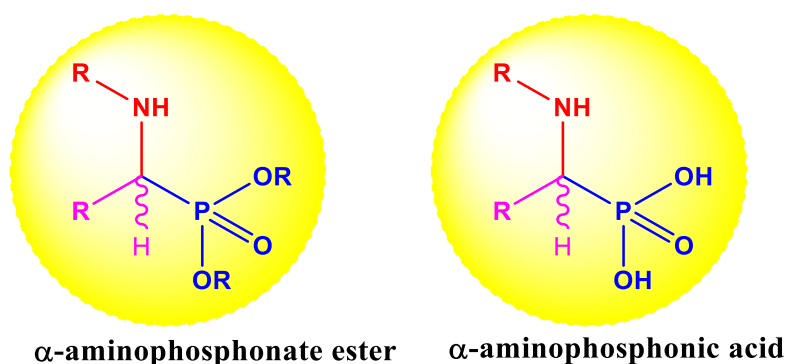
<sup>3</sup>Department of Chemistry, Faculty of Education, Ain Shams University, Roxy, Cairo, 11711, Egypt. \*E-mail: tarik\_elsayed1975@yahoo.com

**Abstract** – Synthesis of some novel chromonyl  $\alpha$ -aminophosphonate esters clubbed with nitrogen heterocycles, was achieved. The methodology based on one-pot three-components reaction of 4-oxo-4*H*-chromene-3-carboxaldehydes, *N*-aminoheterocycles and diethyl phosphite in the presence of CdI<sub>2</sub> nanoparticles as an efficient catalyst under conventional heating at 80 °C or ultrasound (US) irradiation at 50 °C. The mild reaction conditions, operational simplicity and excellent yields are the essential advantages of this protocol. The antifungal properties of the products were evaluated. Most of them recorded inhibitory effects towards plant pathogenic fungi nearly to the standard control. The hybridization between diethyl  $\alpha$ -aminophosphonate and 6-methylchromone moieties with antipyrine, morpholine or 1,2,4-triazine in one molecular frame led to promising antifungal agents against plant pathogenic fungi.

## INTRODUCTION

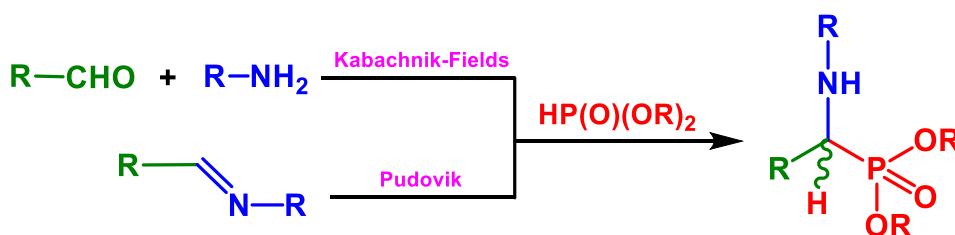
Synthetic pesticides have surely aided in increasing agricultural yields and guaranteeing food supplies in developed countries. For many years, there has been concern about pesticide persistence in the environment

and its impact on quality of life and ecosystems,<sup>1</sup> leading to prohibitions of using synthetic pesticides.<sup>2</sup> Furthermore, rising resistance has posed a threat to the efficacy of some currently available pesticides, prompting the search for new classes of active chemicals.<sup>3-5</sup> 4-Oxo-4*H*-chromenes are an essential class of oxygen-containing heterocyclic compounds.<sup>6</sup> They are well known to be powerful pharmacophores in several drugs and flavonoids.<sup>7</sup> In addition, several chromones demonstrated numerous medicinal and biological functions including antioxidant,<sup>8</sup> anticancer,<sup>9</sup> antifungal,<sup>10</sup> anti-HIV<sup>11</sup> and anti-inflammatory.<sup>12</sup> On the other hand, nitrogen heterocycles are known to exhibit diverse biological activities such as antimicrobial,<sup>13</sup> antiviral,<sup>14</sup> anticonvulsant<sup>15</sup> and antifungal.<sup>16</sup> The  $\alpha$ -aminophosphonate esters have a lot of attention in medicinal chemistry because of their wide range of applications, including antibiotic,<sup>17</sup> anticancer,<sup>18</sup> enzyme inhibition,<sup>19</sup> peptidomimetic uses<sup>20</sup> and pharmacological properties.<sup>21</sup> This class of substances can be hydrolyzed to the corresponding  $\alpha$ -aminophosphonic acids (Figure 1), which are the basis for various biologically active molecules, for example Alafosfalin and Glyphosate.<sup>22,23</sup>



**Figure 1.** The structure of  $\alpha$ -aminophosphonate esters and their acids analogues

Generally, there are several methods for construction of dialkyl  $\alpha$ -aminophosphonates.<sup>24</sup> However, both *Kabachnik-Fields* and *Pudovik* routes are the most favourable used. Synthesis of dialkyl  $\alpha$ -aminophosphonates was cited in one-pot through three-component of aldehyde, amine and dialkyl phosphite (*Kabachnik-Fields* reaction).<sup>25</sup> Also, it is well-known that Schiff bases can react with dialkyl phosphite to give the same  $\alpha$ -aminophosphonates (*Pudovik* reaction).<sup>26</sup> Both reaction types were performed in the presence or absence of a catalyst and solvent (Figure 2).



**Figure 2.** The main synthetic routes for design of  $\alpha$ -aminophosphonates

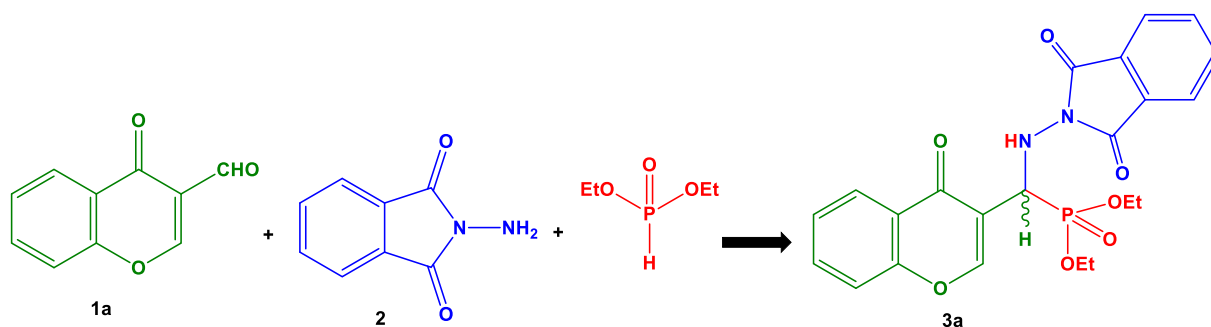
Up to now, a few cases were reported for the *Kabachnik-Fields* type synthesis of 4-oxo-4*H*-chromenyl  $\alpha$ -aminophosphonates containing different nitrogen heterocycles.<sup>27,28</sup> Based on these facts and the vast range of biological activities of 4-oxo-4*H*-chromene, nitrogen heterocycles and  $\alpha$ -aminophosphonate scaffolds, we believe that combining of these skeletons in one molecular frame will result in high biological activities especially antifungal activity. In continuation of our work on construction of new phosphorus compounds through one-pot three-component reactions,<sup>29,30</sup> we would like to report the synthesis of new chromonyl  $\alpha$ -aminophosphonate derivatives containing some bioactive nitrogen heterocycles such as phthalimide, antipyrine, pyridine, morpholine and 1,2,4-triazine. Especially, these nitrogen heterocycles are interesting because they have a variety of biological activities and therapeutic applications.<sup>31-35</sup> The antifungal properties of the obtained compounds were evaluated.

## RESULTS AND DISCUSSION

A series of ten novel  $\alpha$ -aminophosphonate esters clubbed with 4-oxo-4*H*-chromene and nitrogen heterocycles were designed by the *Kabachnik-Fields* reaction. The strategy for design of these novel scaffold depends on condensation of one-pot three-components reaction of 6-substituted-4-oxo-4*H*-chromene-3-carboxaldehyde (**1a,b**), N-aminoheterocycles and diethyl phosphite. In order to obtain the target compounds, we will use several techniques to optimize the better reaction conditions to build the target compounds in clean and high yields.

### Optimization of the required method

We checked different conditions to find an appreciate procedure for conversion of the mentioned aldehyde and amines to the corresponding diethyl  $\alpha$ -aminophosphonate. For optimization study, the reaction of 4-oxo-4*H*-chromene-3-carboxaldehyde (**1a**)<sup>36</sup> with N-aminophthalimide (**2**) and diethyl phosphite was selected as a model reaction (Scheme 1).



Scheme 1

When the three-components reacted under catalyst- and solvent-free conditions for 10 hours at room temperature, about 18% of product, namely diethyl {[[(1,3-dioxoisindolin-2-yl)amino](4-oxo-4*H*-chromen-3-yl)methyl}phosphonates (**3a**) was isolated (Entry 1). However, when the reaction was carried out without a catalyst and solvent at 80 °C, it gave the desired product **3a** in 43% yield (Entry 2), while in the presence of benzene or absolute ethanol at 78 °C for 10 hours, low products in 46 and 53% yields, respectively, were obtained (Entries 3 and 4). It is well-known that Lewis acids are good catalysts for formation of  $\alpha$ -aminophosphonates.<sup>37</sup> Thus, we decided to use some testing Lewis acids such as AlCl<sub>3</sub>, BF<sub>3</sub>·Et<sub>2</sub>O, ZnCl<sub>2</sub>, FeCl<sub>3</sub> and CdI<sub>2</sub> (10 mol%). It was found that CdI<sub>2</sub> as a catalyst led to considerable product yield 87% in 3 hours (Entries 5–9). Therefore, the effect of the quantity of CdI<sub>2</sub> was examined. Reducing of the amount of the catalyst to 5 mol% and 7.5 mol% decreased the yield of the product to be 64% and 72% yields, respectively (Entries 10 and 11), whereas, increasing of the amount of CdI<sub>2</sub> to 12.5 mol% did not promote the conversion more than 87% yield (Entry 12).

**Table 1.** Optimization of various catalysts and reaction conditions for the model reaction

Entry	Catalyst	Solvent	Time (h)	Temp (°C)	Yield (%) <sup>*</sup>
1	--	--	10	25	18%
2	--	--	10	80	43%
3	--	benzene	10	78	46%
4	--	EtOH	10	78	53%
5	AlCl <sub>3</sub> (10 mol%)	--	3	80	68%
6	BF <sub>3</sub> ·Et <sub>2</sub> O (10 mol%)	--	3	80	59%
7	ZnCl <sub>2</sub> (10 mol%)	--	3	80	79%
8	FeCl <sub>3</sub> (10 mol%)	--	3	80	81%
<b>9</b>	<b>CdI<sub>2</sub> (10 mol%)</b>	--	<b>3</b>	<b>80</b>	<b>87%</b>
10	CdI <sub>2</sub> (5 mol%)	--	3	80	64%
11	CdI <sub>2</sub> (7.5 mol%)	--	3	80	72%
12	CdI <sub>2</sub> (12.5 mol%)	--	3	80	87%
<b>13</b>	<b>CdI<sub>2</sub> (NP, 10 mol%)</b>	--	<b>3</b>	<b>80</b>	<b>90%</b>
<b>14</b>	<b>CdI<sub>2</sub> (NP, 10 mol%), US</b>	--	<b>1.25</b>	<b>25</b>	<b>91%</b>
<b>15</b>	<b>CdI<sub>2</sub> (NP, 10 mol%), US</b>	--	<b>1</b>	<b>50</b>	<b>94%</b>

<sup>\*</sup>Reagents: aldehyde (1.0 mmol), amine (1.0 mmol), and diethyl phosphite (1.0 mmol)

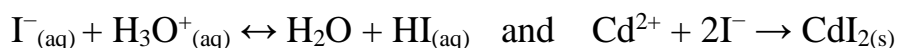
Nanomaterial-based catalysts are typically heterogeneous catalysts that have been broken down into metal nanoparticles to improve the catalytic process. Because metal nanoparticles have a large surface area, they can increase the catalytic activity.<sup>38,39</sup> Nanoparticle catalysts can be easily separated and recycled.<sup>40</sup> Thus, we tried to use the efficient catalyst CdI<sub>2</sub> as nanoparticles to improve the yield of the target product **3a**. When the reaction of 4-oxo-4*H*-chromene-3-carboxaldehyde (**1a**) with N-aminophthalimide (**2**) and diethyl phosphonate was performed at 80 °C in the presence of CdI<sub>2</sub> nanoparticles as catalyst (10 mol%), the yield increased to 90% in 3 hours (Entry 13). Next, we tried to do this reaction in a shorter time with better yields

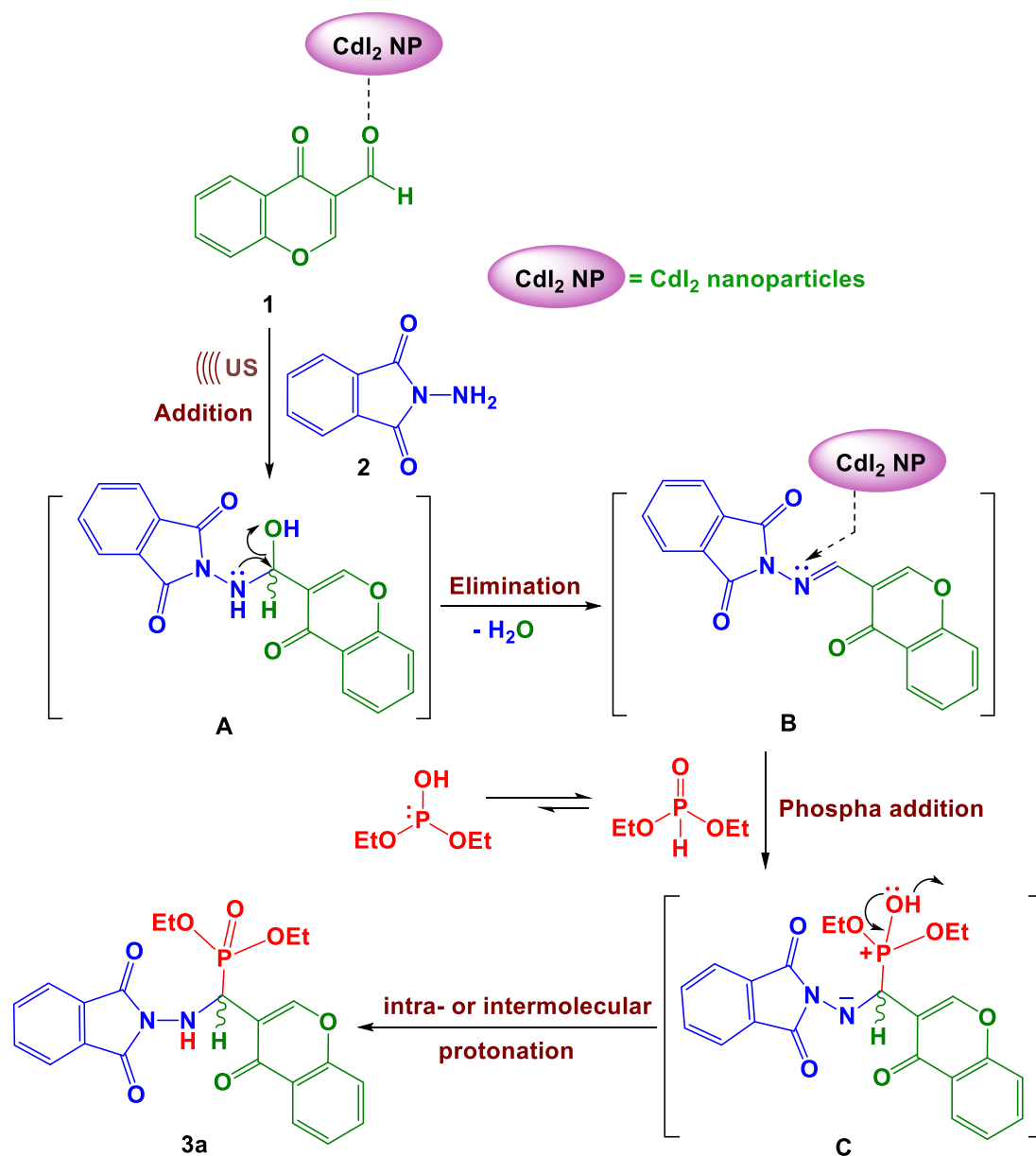
by using ultrasonication effect. Basically, ultrasound-assisted synthesis has a number of advantages over traditional synthesis techniques, including the ability to carry out reactions at room temperature and in much less time, saving both time and electricity, and a shortened work-up procedure.<sup>41</sup> In addition, it is practically good yield of product, simple instrument with reaction parameter control, and, most importantly, an environmentally friendly, neat, and clean synthetic procedure.<sup>42</sup> Thus, when the mentioned reaction for synthesis product **3a**, was carried out by three-components reaction in the presence of CdI<sub>2</sub> nanoparticle (10 mol%) under ultrasonication at room temperature, it needed about 1.25 hour to give the product in 91% yield (Entry 14). But, when the reaction was repeated under the same reaction condition at 50 °C, it gave the final product **3a** in 94% as excellent yield after 1 hour (Entry 15).

The role of CdI<sub>2</sub> nanoparticles to catalyze the formation of the product **3a** was explained in Scheme 2. The reaction of 4-oxo-4*H*-chromene-3-carboxaldehyde (**1a**) with *N*-aminophthalimide (**2**) in the presence of CdI<sub>2</sub> nanoparticles produced the intermediate **A** that was converted to the Schiff base **B** by water elimination. The nucleophilic attack of diethyl phosphite at azomethine bond of the Schiff base **B** with help of CdI<sub>2</sub> nanoparticles formed zwitterionic specie **C** that could undergo intra- or intermolecular protonation to give diethyl  $\alpha$ -aminophosphonate **3a** (Scheme 2). The using of CdI<sub>2</sub> is more convenient for preparative target  $\alpha$ -aminophosphonate. It may be due to being recrystallized and dehydrated salt. In addition, it has strong polarization effects which facilitates the addition of diethyl phosphite to azomethine bond.<sup>43</sup>

### Preparation of CdI<sub>2</sub> nanoparticles

A solution of cadmium nitrate (0.5 M) in distilled water (50 mL) was magnetically stirred with a solution of 15 g/L of cetyltrimethylammonium bromide (CTAB, 100 mL) at 80 °C for 1 hour. Then 50 mL of aqueous solution of sodium iodide (1 M) was added and magnetically stirred for another hour. The separated solid was filtered, washed, and dried in a locked furnace for 48 hours at 110 °C. The chemical processes that occurred during the production of cadmium iodide are listed below. Cadmium ions (Cd<sup>2+</sup>) were coupled with iodine (I<sup>-</sup>) in the bath to generate the insoluble CdI<sub>2</sub>.<sup>44</sup>

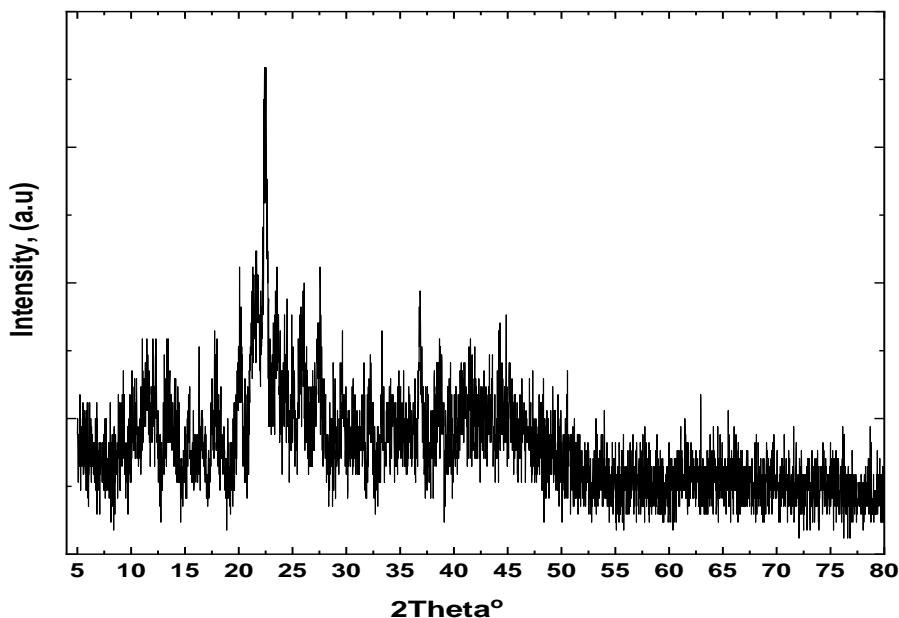




### The XRD analysis of CdI<sub>2</sub> nanoparticles

By using the X-ray diffraction (XRD) technique, we investigated the structure of produced material. The intensities were computed using a step scanning approach with tiny intervals to study structural characteristics describing crystalline size ( $D_v$ ) and lattice strain ( $\epsilon$ ). At each fixed value of 2 hours, a period of 10 seconds was captured, resulting in a fair number of counts. The XRD spectra of prepared CdI<sub>2</sub> powder are shown in Figure 3. No impurities are found there. A polycrystalline hexagonal structure is shown by XRD investigation (JCPDS Data file: 01-087-0300-hexagonal). Boulderer's equation was used to compute the average grain size, average lattice strain, and average dislocation to be 21 nm, 3.409E-03, and 1.885E-03, respectively, based on instrumental and structural variables, crystallite size, and lattice strains.<sup>45,46</sup>

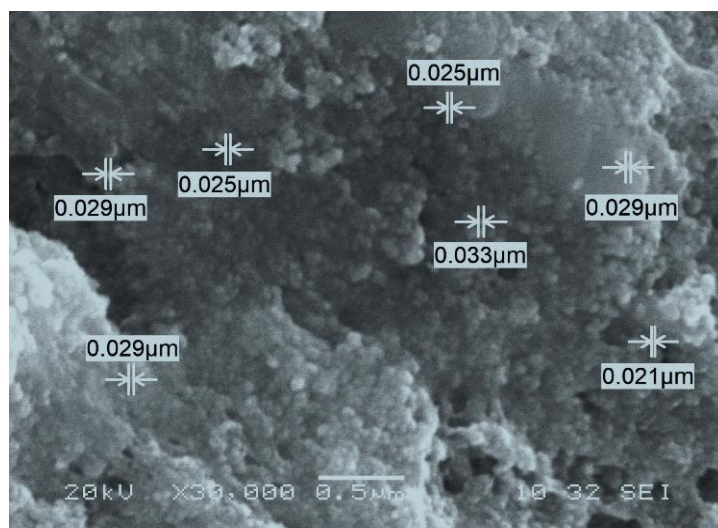
$D = \frac{0.9\lambda}{\beta \cos \theta}$ , as  $D$  was the crystallite size,  $\lambda$  was the X-ray wavelength, and  $\beta$  was the full width at half maximum (FWHM).<sup>47</sup> Lattice strain ( $\epsilon$ ) was determined via  $\epsilon = \frac{\beta \cos \theta}{4}$ , while dislocation density ( $\delta$ ) was obtained through  $\delta = \frac{1}{D^2}$ .



**Figure 3.** The XRD of CdI<sub>2</sub> nanoparticles

### The SEM analysis of CdI<sub>2</sub> nanoparticles

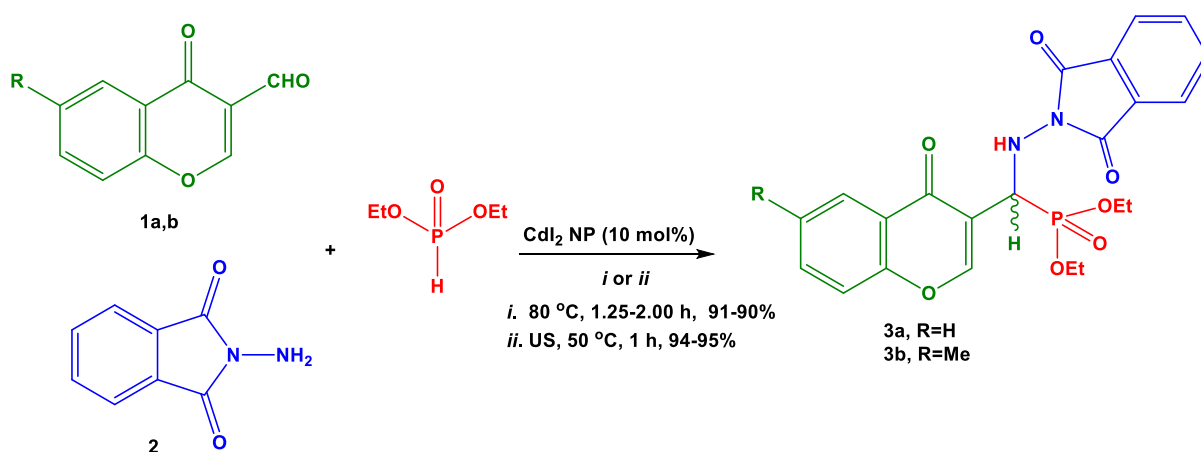
The SEM technique provided a wide range of relevant data. SEM can provide a more accurate view of the structure of the processed samples. Inconsistencies in current species descriptions can be explained by researchers. The SEM approach also produces spatial pictures of the samples under investigation. SEM also aided in the identification of the researched species by identifying new morphological traits and details. The advancement of fast electron microscopy equipment allows us to gain a better understanding of the structure of many materials.<sup>48</sup> The effectiveness and activity of catalysts are dependent on morphological characteristics (size, shape, kind of exposed facets, etc.) as is common in the field of catalysis.<sup>49</sup> Because CdI<sub>2</sub> is a promising catalyst, many researchers have been directed to morphological tuning. A branch, a tetrapod, a nanorod, a triangular prism, a pine tree, and porous microcubes are all useful forms.<sup>50</sup> Figure 4 shows the morphological structure of CdI<sub>2</sub>. The SEM images revealed that the particles had a smooth surface with a stacked layered/sheet-like morphological structure with average particle size of about 27 nm.<sup>51</sup> According to prior research, the structure might provide several active sites and improve carrier migration, making it an excellent candidate for catalysts.<sup>52</sup> This discrepancy is most likely due to the use of vigorous stirring in the highly visible co-precipitation process for CdI<sub>2</sub> dispersion.



**Figure 4.** The SEM of CdI<sub>2</sub> nanoparticles

Having determined the optimal reaction conditions, we can explore the substrate scope of the CdI<sub>2</sub> nanoparticles promoted the three-component reaction of 6-substituted-4-oxo-4*H*-chromene-3-carboxaldehyde (**1a,b**), *N*-aminoheterocycles and diethyl phosphite. Thus, a series of ten novel  $\alpha$ -aminophosphonate esters **3a,b**, **5a,b**, **7a,b**, **9a,b** and **11a,b** that incorporated 4-oxo-4*H*-chromene moiety and nitrogen heterocycles, were designed by the *Kabachnik-Fields* reaction.

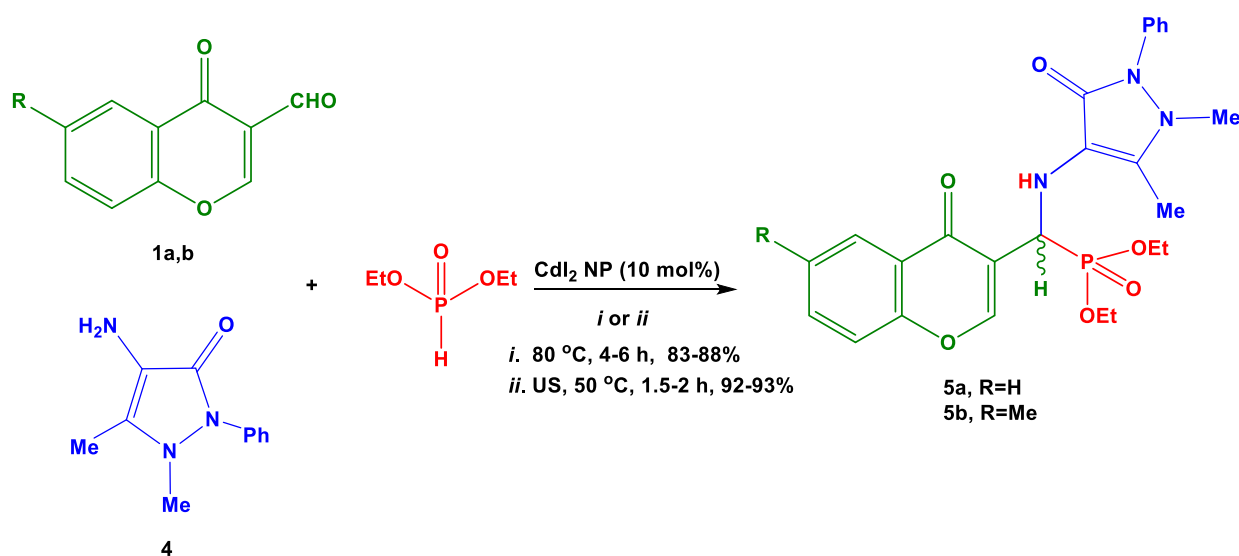
Our strategy was based on the design of these novel  $\alpha$ -aminophosphonates scaffold by one-pot three-components in the presence of CdI<sub>2</sub> nanoparticles as an efficient catalyst under conventional at 80 °C or ultrasound (US) irradiation at 50 °C. Thus, the reaction of 6-methyl-4-oxo-4*H*-chromene-3-carboxaldehyde (**1b**) with *N*-aminophthalimide (**2**) and diethyl phosphite under conventional at 80 °C for 2 hours and ultrasound irradiation at 50 °C for 1 hour in the presence of CdI<sub>2</sub> nanoparticles (10 mol%), was performed. The reaction afforded the novel diethyl {[(1,3-dioxoisindolin-2-yl)amino]}(6-methyl-4-oxo-4*H*-chromen-3-yl)methyl}phosphonate (**3b**) (Scheme 3).



**Scheme 3**

The IR spectra of the products **3a,b** displayed the absorption bands for the following functional groups: NH (3126, 3108  $\text{cm}^{-1}$ ),  $\text{C}=\text{O}_{\text{isoindole-dione}}$  (1786, 1736  $\text{cm}^{-1}$ ),  $\text{C}=\text{O}_{\text{chromone}}$  (1642, 1636  $\text{cm}^{-1}$ ),  $\text{P}=\text{O}$  (1283, 1280  $\text{cm}^{-1}$ ) and  $\text{P}-\text{O}-\text{C}$  (1009, 995  $\text{cm}^{-1}$ ). Their  $^1\text{H}$ -NMR spectra recorded the characteristic protons at  $\delta$  1.11, 1.20 ( $\text{CH}_3$ ), 4.13, 4.18 ( $\text{CH}_2\text{O}$ ), 5.20 (d,  $J_{\text{PCH}} = 19.6$  and 22.4 Hz,  $\text{P}-\text{CH}$ ), and 5.90, 5.93 (NH) ppm, while the aromatic protons appeared in the expected region  $\delta$  6.92–8.92 ppm.<sup>53</sup> Further, the  $^{13}\text{C}$ -NMR spectra of these products exhibited the specific carbon atoms at  $\delta$  14.8, 14.9 (2  $\text{CH}_3$ ), 60.3, 61.5 (2  $\text{OCH}_2$ ), 49.3, 51.3 (d,  $J_{\text{PC}} = 152.9$  and 135.0 Hz,  $\text{P}-\text{CH}$ ),<sup>54</sup> 166.6, 165.8 (2  $\text{C}=\text{O}_{\text{isoindole-dione}}$ ) and 175.8, 173.6 ( $\text{C}=\text{O}_{\text{chromone}}$ ) ppm. Also, the  $^{31}\text{P}$ -NMR spectrum of product **3b** confirmed the structure by recording a singlet at  $\delta$  23.24 ppm.<sup>55</sup> Additionally, their mass spectra recorded the molecular ion peaks at  $m/z$  456 ( $\text{M}^+$ , 1%) and 470 ( $\text{M}^+$ , 1%), respectively.

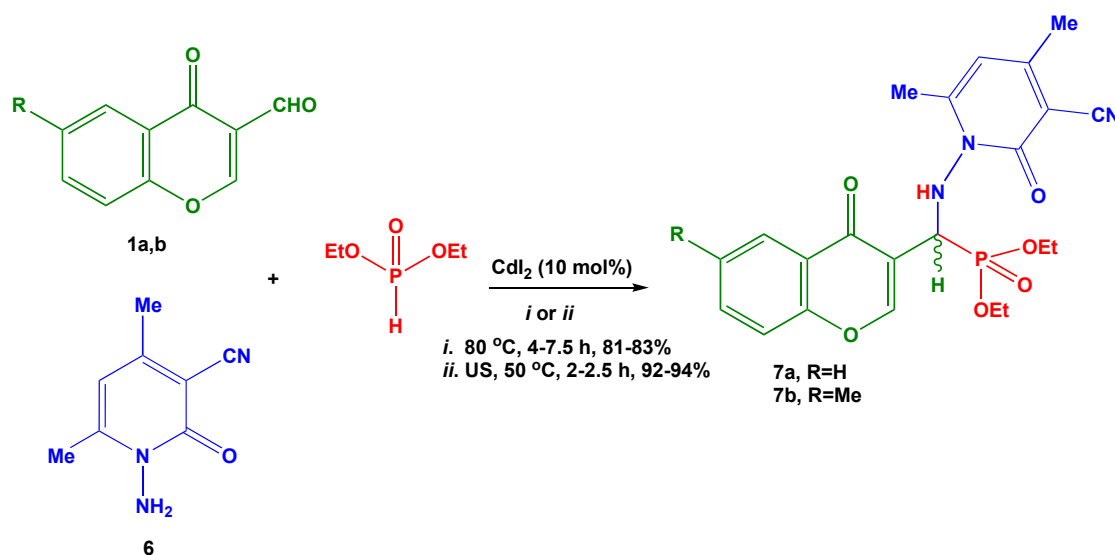
Alternatively, 4-aminoantipyrene (**4**) was ready to react with the chromonyl aldehydes **1a,b** and diethyl phosphite under the previous optimized reaction conditions. The reactions isolated the  $\alpha$ -chromonyl- $\alpha$ -(aminoantipyrene)phosphonates **5a,b** (Scheme 4).



The molecular ion peaks of the prepared compounds **5a,b** were rerecorded in their mass spectra. Also, the IR spectra of compounds **5a,b** clearly showed characteristic absorption bands corresponding to NH (3227, 3273  $\text{cm}^{-1}$ ), conjugated  $\text{C}=\text{O}_{\text{antipyrene}}$  and  $\text{C}=\text{O}_{\text{chromone}}$  (1654 and 1636  $\text{cm}^{-1}$ ),  $\text{P}=\text{O}$  (1203, 1206  $\text{cm}^{-1}$ ) and  $\text{P}-\text{O}-\text{C}$  (1045, 1036  $\text{cm}^{-1}$ ). The  $^1\text{H}$ -NMR spectra of these  $\alpha$ -aminophosphonates revealed characteristic resonances for the aromatic protons in region  $\delta$  6.83–8.99 ppm, a singlet for protons of NH groups nearly around  $\delta$  5.91 ppm, two  $\text{CH}_3$  groups attached to pyrazole moieties nearly  $\delta$  2.10 and 2.75 ppm, and an important doublet for  $\text{P}-\text{CH}$  protons  $\delta$  5.17 ( $J_{\text{PCH}} = 21.6$  Hz) and 5.92 ( $J_{\text{PCH}} = 21.6$  Hz) ppm. In their  $^{13}\text{C}$ -NMR spectra,

there are four characteristic signals appeared in the aliphatic region of stronger fields at  $\delta$  14.6–14.7 ( $\text{CH}_3$ ethoxy), 10.1–10.7 ( $\text{CH}_3$ antipyridine), 38.2–38.3 ( $\text{CH}_3$ Nantipyridine) and 60.6–62.3 ( $\text{OCH}_2$ ethoxy) ppm. Resonances due to  $\text{C}=\text{O}$ antipyridine and  $\text{C}=\text{O}$ chromone appeared at  $\delta$  161.6 and 174.8–176.8 ppm, respectively, while the carbon atoms of P–C linkages in **5a,b** were exhibited as doublets at  $\delta$  50.0 ( $J_{\text{PC}}=149.3$  Hz) and 50.5 ( $J_{\text{PC}}=143.5$  Hz) ppm, respectively.

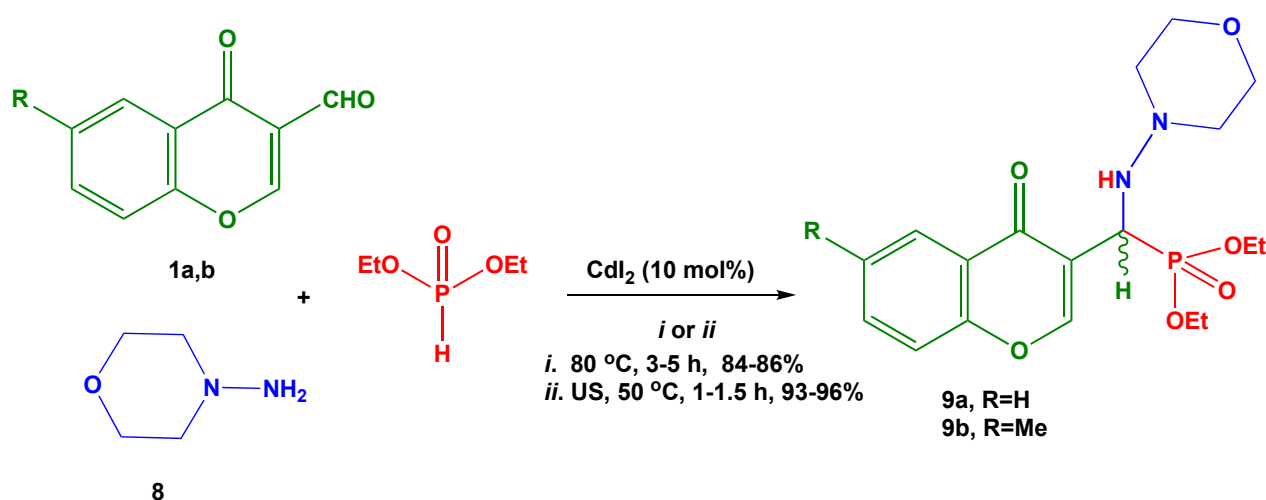
By using the optimized protocols, we also obtained diethyl {[3-cyano-4,6-dimethyl-2-oxopyridin-1(2*H*)-yl]amino}(6-substituted-4-oxo-4*H*-chromen-3-yl)methyl}phosphonates (**7a,b**) (Scheme 5). An addition of diethyl phosphite to a mixture 6-substituted-3-formylchromones (**1a,b**) and 1-amino-4,6-dimethyl-2-oxo-1,2-dihydro-pyridine-3-carbonitrile (**6**) and further heated at 80 °C or ultrasonated at 50 °C in the presence of  $\text{CdI}_2$  nanoparticles (10 mol%) yielded the desired products **7a,b** in high yields (Scheme 5).



The absorption bands for compounds **7a,b** were detected around 3267, 2225, 1654, 1639–1633, 1207 and 1019–1017  $\text{cm}^{-1}$  for NH,  $\text{C}\equiv\text{N}$ ,  $\text{C}=\text{O}$ pyridone,  $\text{C}=\text{O}$ chromone, P=O, and P–O–C, respectively, in the IR spectra. The phosphorus chemical shift for the product **7a** was showed at  $\delta$  24.01 ppm in its  $^{31}\text{P}$ -NMR spectrum. The  $^1\text{H}$ -NMR spectra of both products **7a,b** revealed the specific H-5<sub>pyridone</sub> protons ring around  $\delta$  6.36 ppm. Also, the presence of the methyl and methylene protons of  $\text{POCH}_2\text{CH}_3$  were observed at  $\delta$  1.13–1.26 and 4.15–4.22 ppm, respectively. A doublet at region  $\delta$  4.91–5.07 ppm with coupling constant  $J_{\text{PCH}}=22.4$ –23.6 Hz, ascribed to the protons at carbon atoms which attached to phosphorus atom and singlets for the protons NH appeared between  $\delta$  5.90–6.14 ppm. Their  $^{13}\text{C}$ -NMR spectra exhibited doublets for P–CH around  $\delta$  47.5–50.8 ppm with characteristic coupling constant  $J_{\text{PC}}=145.8$ –160.8 Hz. It also gave signals at  $\delta$  12.0–14.1 and 59.5–61.5 ppm for methyl and methylene carbons of  $\text{POCH}_2\text{CH}_3$  moiety. The other specific singlets at  $\delta$  114.4–115.1 ppm due to the nitrile groups. The MS further verified the synthesized compounds,

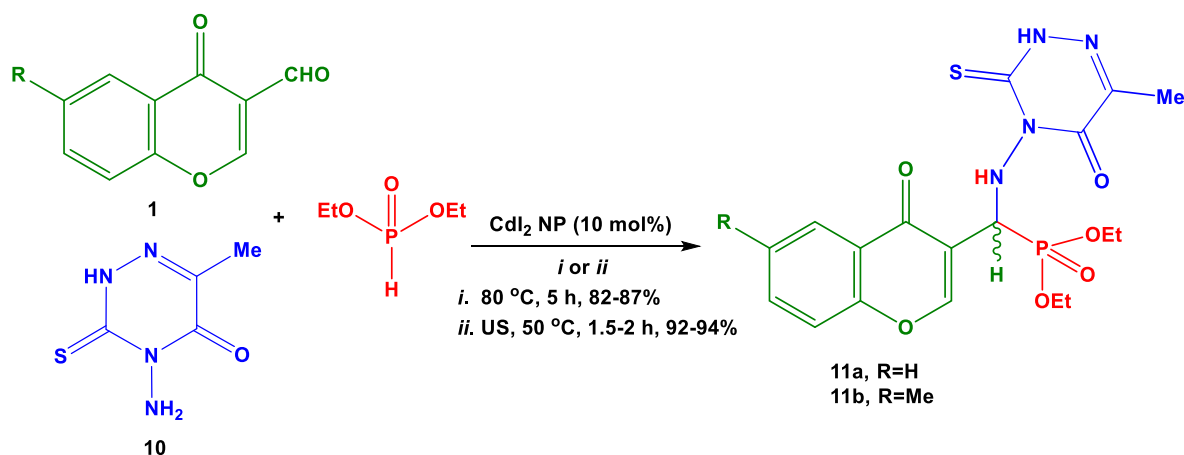
and their molecular ion peaks  $m/z$  457 (24%) and 471 (56%) values were in good agreement with the calculated mass.

An equimolar amounts of 6-substituted-3-formylchromones (**1a,b**) and 4-aminomorpholine (**8**) reacted with diethyl phosphite in the presence of 10 mol% of  $\text{CdI}_2$  nanoparticles under thermal heating at 80 °C or by help of ultrasound irradiation at 50 °C. The expected products namely, diethyl{(morpholinoamino)(6-substituted-4-oxo-4*H*-chromen-3-yl)methyl}phosphonates (**9a,b**) were isolated in excellent yields (Scheme 6).



The molecular ion peaks of the products **9a,b** were observed in their mass spectra at 396 ( $\text{M}^+$ , 43%) and 410 ( $\text{M}^+$ , 1%), respectively. Also, their  $^1\text{H-NMR}$  spectra exhibited the specific protons of diethoxy groups in range  $\delta$  1.06–1.14 ( $\text{CH}_3$ ) and 3.64–4.13 ( $\text{CH}_2\text{O}$ ) ppm, while the P–CH protons appeared as doublets at  $\delta$  5.28 ( $J_{\text{PCH}}=21.6$  Hz) and 5.11 ( $J_{\text{PCH}}=21.6$  Hz) ppm, respectively. The aliphatic protons of morpholine ring in these products were resonated around  $\delta$  3.10 (t,  $J=4.8$  Hz,  $\text{NCH}_2$ ) and 3.76, 3.77 (t,  $J=4.8$  and Hz,  $\text{OCH}_2$ ) ppm. Moreover, their  $^{13}\text{C-NMR}$  spectra recorded the specific carbon atoms of the diethoxy groups in range  $\delta$  12.3–14.9 ( $\text{CH}_3$ ) and 61.0–62.5 ( $\text{CH}_2\text{O}$ ) ppm, while the P–CH carbons appeared as doublets at  $\delta$  52.7 ( $J_{\text{PC}}=162.0$  Hz) and 53.4 ( $J_{\text{PC}}=136.7$  Hz) ppm, respectively. The aliphatic carbon atoms of morpholine ring were resonated at  $\delta$  60.4, 59.8 ( $\text{NCH}_2$ ) and 66.2, 67.7 ( $\text{OCH}_2$ ) ppm.

Next, a mixture of 4-amino-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2*H*)-one (**10**) and 6-substituted-3-formylchromones (**1a,b**), was subjected to react with diethyl phosphite in the presence of 10 mol% of nanoparticles  $\text{CdI}_2$  under the optimized reaction conditions, to furnish the interesting diethyl {(6-substituted-4-oxo-4*H*-chromen-3-yl)[(6-methyl-5-oxo-3-thioxo-2,5-dihydro-1,2,4-triazin-4(3*H*)-yl)-amino]methyl}phosphonates (**11a,b**) (Scheme 7).



Scheme 7

The mass spectrometry and elemental analysis supported the structures **11a,b**. The IR spectra of these products showed the characteristic absorption bands 3285, 3252 (NH), 3185, 3129 (NH), 1657, 1651 ( $\text{C}=\text{O}_{\text{chromone}}$ ), 1680, 1686 ( $\text{C}=\text{O}_{\text{triazine}}$ ), 1209, 1218 (P=O), 1156, 1165 (C=S) and 1045, 1039 (P–O–C)  $\text{cm}^{-1}$ . Their  $^1\text{H}$ -NMR spectra recorded the specific CH–P protons as doublets at  $\delta$  5.13, 5.10 ppm with coupling constants 21.6, 22.0 Hz, respectively. In addition, the protons of  $\text{CH}_3\text{CH}_2\text{O}$  groups appeared as triplets at ( $\delta$  1.05–1.06 ppm,  $\text{CH}_3$ ) and quartets at ( $\delta$  4.12–4.15 ppm,  $\text{OCH}_2$ ), while the NH protons of  $\alpha$ -aminophosphonate and 1,2,4-triazine moieties were showed as singlets around  $\delta$  6.45 and 13.65 ppm, respectively. Furthermore, the  $^{13}\text{C}$ -NMR spectra of the  $\alpha$ -aminophosphonates **11a,b** displayed the carbon atoms of P–C moieties as doublets at  $\delta$  51.0 and 52.3 ppm with coupling constant in values 147.0 and 134.6 Hz, respectively. Also, the carbon atoms of  $\text{CH}_3\text{CH}_2\text{O}$  groups were revealed around  $\delta$  14.7 and 61.4 ppm, while the peaks that were reported at  $\delta$  166.6, 175.1–172.3 and 176.8–174.1 ppm due to the  $\text{C}=\text{O}_{\text{triazine}}$ ,  $\text{C}=\text{O}_{\text{pyrone}}$  and  $\text{C}=\text{S}_{\text{triazine}}$  groups, respectively.

## EVALUATION OF ANTIFUNGAL ACTIVITIES

The ten synthesized compounds were tested *in vitro* for their antifungal activities against five plant pathogenic fungi, namely *Alternaria alternata*, *Cochliobolus lunatus*, *Penicillium oxalicum*, *Fusarium oxysporum*, and *Pestalotia* sp. (Table 2). The antifungal properties were tested by agar well diffusion method.<sup>56</sup> The synthesized compounds showed a wide range of antifungal activities against the pathogens tested. The products **5a,b**, **9a,b**, and **11a,b** exhibited excellent antifungal activities while both products **3a,b** showed weak inhibition effects on the growth of the used organisms in comparison with the standard control. Also, the moderate effects against the five plant pathogenic fungi, were observed in case of both products **7a,b**. Generally, the relationship between the structure and activity indicated that the introduction of diethyl  $\alpha$ -aminophosphonate group linked with chromone ring and nitrogen heteroaryl group can achieve

promising antifungal properties. The existence of methyl group in chromone ring instead of hydrogen atom at position 6 in all products exhibited significant improvements in the antifungal effects. Interestingly, the insertion of antipyrine, morpholine or 1,2,4-triazine system caused excellent inhibitory effects nearly to the standard control more than isoindole-1-one and pyridine rings. The products **5a,b**, **9b** and **11b** recorded the most inhibitory effects towards plant pathogenic fungi nearly to the standard control. Thus, it can be concluded that hybridization between diethyl  $\alpha$ -aminophosphonate and 6-methylchromone moieties with antipyrine, morpholine or 1,2,4-triazine in one molecular frame led to promising antifungal agents against plant pathogenic fungi.

**Table 2.** The *in vitro* antifungal activities as inhibition zone (cm) for the synthesized compounds

Compound	Fungal strains				
	<i>Alternaria alternata</i>	<i>Cochliobolus lunatus</i>	<i>Penicillium oxalicum</i>	<i>Fusarium oxysporum</i>	<i>Pestalotia</i> sp.
<b>3a</b>	1.30	1.43	1.56	1.63	1.03
<b>3b</b>	1.46	1.36	1.40	1.26	1.30
<b>5a</b>	3.20	3.43	4.06	2.82	2.80
<b>5b</b>	3.20	3.33	4.26	3.16	2.96
<b>7a</b>	1.96	2.00	2.26	2.06	2.03
<b>7b</b>	1.80	1.76	2.56	2.42	2.33
<b>9a</b>	3.06	3.10	3.36	3.20	3.23
<b>9b</b>	3.08	3.30	3.40	3.23	3.33
<b>11a</b>	2.90	2.93	2.93	3.03	2.73
<b>11b</b>	3.06	3.03	3.33	3.10	2.76
<b>Propiconazole *25%</b>	3.25	3.75	4.50	3.20	3.00

\*(Tilzole 250 EC ) Propiconazole 25% (10 Microliter/10 mL H<sub>2</sub>O)

## CONCLUSION

We have suggested CdI<sub>2</sub> nanoparticles as an effective catalyst for preparing of some novel 4-oxo-4*H*-chromenyl  $\alpha$ -aminophosphonate esters incorporating nitrogen heterocycles. The target compounds were achieved by reaction of 4-oxo-4*H*-chromene-3-carboxaldehydes with *N*-aminoheterocycles and diethyl phosphite as one-pot three-components in the presence of CdI<sub>2</sub> nanoparticles under conventional heating at 80 °C or ultrasound (US) irradiation at 50 °C. The mild reaction conditions, operational simplicity and excellent yields are the essential advantages of both this protocol and catalyst. Some of the products recorded inhibitory effects towards plant pathogenic fungi nearly to the standard control.

## EXPERIMENTAL

The melting point was determined in an open capillary tube on a digital Stuart SMP-3 apparatus. Infrared

spectra were measured on FT-IR (Nicolet IS10) spectrophotometer using KBr disks and Perkin-Elmer 293 spectrophotometer using KBr disks. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were measured a Bruker spectrometer (400 and 100 MHz), using  $\text{DMSO-}d_6$  as a solvent and TMS ( $\delta$ ) as an internal standard. The  $^{31}\text{P}$ -NMR spectra were measured on a Bruker (162 MHz) spectrophotometer using  $\text{DMSO-}d_6$  as a solvent, TMS as an internal standard and 85%  $\text{H}_3\text{PO}_4$  as an external reference. Mass spectra were recorded on direct probe controller inlet part to single quadrupole mass analyzer in (Thermo-Scientific GCMS). Elemental microanalyses were performed Perkin-Elmer 2400II at the Chemical War department, Ministry of Defense. The purity of the synthesized compounds was checked by thin layer chromatography (TLC) and elemental microanalysis.

**General procedure for synthesis of the target compounds 3a,b, 5a,b, 7a,b, 9a,b and 11a,b.**

**Method A:** A mixture of the aldehyde **1a,b** (2.5 mmol), *N*-aminoheterocycle (2.5 mmol), diethyl phosphite (2.9 mmol, 0.40 mL) and nanoparticles  $\text{CdI}_2$  (10 mol%, 0.091 g), was heated under reflux at 80 °C for 1.25–7.5 h. TLC was used to check achievement of the reaction each 0.5 h. The mixture was treated with water (10 mL), and the organic phase was extracted with EtOAc, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and reduced the volume under vacuum. The formed solid was filtered off and crystallized from MeOH or EtOH.

**Method B:** A mixture of aldehyde **1a,b** (2.5 mmol), *N*-aminoheterocycle (2.5 mmol), diethyl phosphite (2.9 mmol, 0.40 mL) and nanoparticles  $\text{CdI}_2$  (10 mol%, 0.091 g), was ultrasonated at 50 °C for 1–2.5 h. TLC was used to check achievement of the reaction each 0.5 h. The mixture was treated with water (10 mL), and the organic phase was extracted with EtOAc, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and reduced the volume under vacuum. The formed solid was filtered off and crystallized from MeOH or EtOH.

**Diethyl {[ (1,3-dioxoisindolin-2-yl)amino] (4-oxo-4H-chromen-3-yl)methyl} phosphonate (3a):** Pale yellow in 91% (**Method A**, 1.25 h) and 94% (**Method B**, 1 h) yields, mp 92–94 °C. IR (KBr), ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3126 (br, NH), 2982, 2929, 2849 (C–H<sub>aliph</sub>), 1786 (C=O<sub>isoindole</sub>), 1739 (C=O<sub>isoindole</sub>), 1636 (C=O<sub>pyrone</sub>), 1616, 1560 (C=C), 1280 (P=O), 995 (P–O–C).  $^1\text{H}$ -NMR (400 MHz,  $\text{DMSO-}d_6$ ): 1.20 (t, 6H,  $J=7.2$  Hz, 2  $\text{CH}_3$ ), 4.13 (q, 4H,  $J=6.8$  Hz, 2  $\text{CH}_2\text{O}$ ), 5.20 (d, 1H,  $J_{\text{PCH}}=19.6$  Hz P–CH), 5.90 (s, 1H, NH), 6.93 (t, 1H,  $J=7.2$  Hz, H-6<sub>chromone</sub>), 7.00 (d, 1H,  $J=7.6$  Hz, H-8<sub>chromone</sub>), 7.32 (t, 1H,  $J=8.0$  Hz, H-7<sub>chromone</sub>), 7.83–7.96 (m, 4H, Ar–H<sub>isoindole</sub>), 8.17 (d, 1H,  $J=8.8$  Hz, H-5<sub>chromone</sub>), 8.92 (s, 1H, H-2<sub>chromone</sub>).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{DMSO-}d_6$ ): 14.8 (2  $\text{CH}_3$ ), 49.3 (d,  $J_{\text{PC}}=152.9$  Hz, P–CH), 61.5 (2  $\text{CH}_2\text{O}$ ), 116.8 (C-3<sub>chromone</sub>), 118.7 (C-8<sub>chromone</sub>), 120.1 (C-4,7<sub>isoindole</sub>), 124.2 (C-4<sub>a</sub>chromone), 125.2 (C-6<sub>chromone</sub>), 126.4 (C-5<sub>chromone</sub>), 130.5 (C-3<sub>a</sub>,7<sub>a</sub>isoindole), 134.0 (C-5,6<sub>isoindole</sub>), 135.2 (C-7<sub>chromone</sub>), 150.4 (C-2<sub>chromone</sub>), 154.2 (C-8<sub>a</sub>chromone), 166.6 (2 C=O), 175.8 (C=O). MS ( $m/z$ , I%): 456 ( $\text{M}^+$ , 1%). Anal. Calcd for  $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_7\text{P}$  (456.39): C, 57.90%; H, 4.64%; N, 6.14%. Found: C, 57.72%; H, 4.50%; N, 6.01%.

**Diethyl** **[[[(1,3-dioxoisindolin-2-yl)amino](6-methyl-4-oxo-4H-chromen-3-yl)methyl]phosphonate (3b)**: Orange in 90% (*Method A*, 2 h) and 95% (*Method B*, 1 h) yields, mp 99–101 °C. IR (KBr), ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3108 (br, NH), 2982, 2926, 2849 (C–H<sub>aliph</sub>), 1783 (C=O<sub>isindole</sub>), 1736 (C=O<sub>isindole</sub>), 1642 (C=O<sub>pyrone</sub>), 1616 (C=C), 1283 (P=O), 1009 (P–O–C). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): 1.11 (t, 6H, *J*=7.2 Hz, 2 CH<sub>3</sub>), 2.26 (s, 3H, CH<sub>3</sub>), 4.18 (q, 4H, *J*=7.2 Hz, 2 CH<sub>2</sub>O), 5.20 (d, 1H, *J*<sub>PCH</sub>=22.4 Hz P–CH), 5.93 (s, 1H, NH), 6.92–6.82 (m, 1H, H–8<sub>chromone</sub>), 7.03–7.15 (m, 1H, H–7<sub>chromone</sub>), 7.84–7.90 (m, 4H, Ar–H<sub>isindole</sub>), 8.09–8.07 (dd, 1H, *J*=5.6 and 3.2 Hz, H–5<sub>chromone</sub>), 8.91 (s, 1H, H–2<sub>chromone</sub>). <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>): 14.9 (2 CH<sub>3</sub>), 20.5 (CH<sub>3</sub>), 51.3 (d, *J*<sub>PC</sub>=135.0 Hz, P–CH), 60.3 (2 CH<sub>2</sub>O), 115.5 (C–3<sub>chromone</sub>), 118.2 (C–8<sub>chromone</sub>), 120.1 (C–4,7<sub>isindole</sub>), 124.9 (C–4a), 125.6 (C–6<sub>chromone</sub>), 126.2 (C–5<sub>chromone</sub>), 130.4 (C–3a,7a<sub>isindole</sub>), 135.8 (C–5,6<sub>isindole</sub>), 136.8 (C–7<sub>chromone</sub>), 150.8 (C–2<sub>chromone</sub>), 156.2 (C–8a), 165.8 (2 C=O), 173.6 (C=O). <sup>31</sup>P-NMR (162 MHz, DMSO-*d*<sub>6</sub>): 23.24 ppm. MS (*m/z*, I%): 470 (M<sup>+</sup>, 1%). Anal. Calcd for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O<sub>7</sub>P (470.42): C, 58.73%; H, 4.93%; N, 5.96%. Found: C, 58.35%; H, 4.90%; N, 5.83%.

**Diethyl** **[[[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)amino](4-oxo-4H-chromen-3-yl)methyl]phosphonate (5a)**: Cumin in 83% (*Method A*, 4 h) and 92% (*Method B*, 1.5 h) yields, mp 123–125 °C. IR (KBr), ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3223 (br, NH), 3070 (C–H<sub>arom</sub>), 2981, 2934, 2905 (C–H<sub>aliph</sub>), 1654 (C=O<sub>antipyrene</sub>), 1636 (C=O<sub>pyrone</sub>), 1601, 1560 (C=C), 1206 (P=O), 1045 (P–O–C). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): 1.06 (t, 6H, *J*=6.8 Hz, 2 CH<sub>3</sub>), 2.10 (s, 3H, CH<sub>3</sub>), 2.75 (s, 3H, CH<sub>3</sub>N), 4.22 (q, 4H, *J*=6.8 Hz, 2 CH<sub>2</sub>O), 5.17 (d, 1H, *J*<sub>PCH</sub>=21.6 Hz P–CH), 5.92 (s, 1H, NH), 6.84–7.00 (m, 2H, Ph–H), 7.22–7.54 (m, 4H, Ph–H and H–6<sub>chromone</sub>), 7.69–7.75 (m, 1H, H–8<sub>chromone</sub>), 7.84–7.88 (m, 1H, H–7<sub>chromone</sub>), 8.15 (d, 1H, *J*=8.0 Hz, H–5<sub>chromone</sub>), 8.99 (s, 1H, H–2<sub>chromone</sub>). <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>): 10.1 (CH<sub>3</sub>), 14.6 (2 CH<sub>3</sub>), 38.2 (CH<sub>3</sub>N) 50.0 (d, *J*<sub>PC</sub>=149.3 Hz, P–CH), 62.3 (2 CH<sub>2</sub>O), 115.5 (C–3<sub>chromone</sub>), 118.7 (C–8<sub>chromone</sub>), 119.8 (C–4<sub>antipyrene</sub>), 122.2 (C–4<sub>phenyl</sub>), 124.2 (C–4a<sub>chromone</sub>), 125.5 (C–6<sub>chromone</sub>), 126.1 (C–2,6<sub>phenyl</sub>), 126.9 (C–5<sub>chromone</sub>), 130.5 (C–3,5<sub>phenyl</sub>), 136.1 (C–3<sub>antipyrene</sub>), 137.8 (C–7<sub>chromone</sub>), 138.4 (C–1<sub>phenyl</sub>), 150.1 (C–2<sub>chromone</sub>), 155.6 (C–8a<sub>chromone</sub>), 161.6 (C=O<sub>antipyrene</sub>), 174.8 (C=O). MS (*m/z*, I%): 497 (M<sup>+</sup>, 4%). Anal. Calcd for C<sub>25</sub>H<sub>28</sub>N<sub>3</sub>O<sub>6</sub>P (497.49): C, 60.36%; H, 5.67%; N, 8.45%. Found: C, 60.18%; H, 5.53%; N, 8.32%.

**Diethyl** **[[[(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)amino](6-methyl-4-oxo-4H-chromen-3-yl)methyl]phosphonate (5b)**: Cumin in 88% (*Method A*, 6 h) and 93% (*Method B*, 2 h) yields, mp 203–205 °C. IR (KBr), ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3273 (br, NH), 3061 (C–H<sub>arom</sub>), 2982, 2931, 2905 (C–H<sub>aliph</sub>), 1654 (C=O<sub>antipyrene</sub>), 1636 (C=O<sub>pyrone</sub>), 1621, 1560 (C=C), 1203 (P=O), 1036 (P–O–C). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): 1.06 (t, 6H, *J*=7.2 Hz, 2 CH<sub>3</sub>), 2.10 (s, 3H, CH<sub>3</sub>), 2.22 (s, 3H, CH<sub>3</sub>), 2.74 (s, 3H, CH<sub>3</sub>N), 4.25 (q, 4H, *J*=7.2 Hz, 2 CH<sub>2</sub>O), 5.08 (d, 1H, *J*<sub>PCH</sub>=22.8 Hz P–CH), 5.91 (s, 1H, NH), 6.83 (d, 1H, *J*=7.6 Hz, H–8<sub>chromone</sub>), 6.89 (d, 1H, *J*=8.4 Hz, H–7<sub>chromone</sub>), 7.22–7.28 (m, 1H, Ph–H), 7.40–7.48 (m, 4H, Ph–H), 7.86

(s, 1H,  $J=8.0$  Hz, H-5<sub>chromone</sub>), 8.19 (s, 1H, H-2<sub>chromone</sub>).  $^{13}\text{C}$ -NMR (100 MHz, DMSO- $d_6$ ): 10.7 (CH<sub>3</sub>), 14.7 (2 CH<sub>3</sub>), 22.7 (CH<sub>3</sub>), 37.3 (CH<sub>3</sub>N), 50.5 (d,  $J_{\text{PC}}=143.5$  Hz, P-CH), 60.6 (2 CH<sub>2</sub>O), 115.5 (C-3<sub>chromone</sub>), 118.8 (C-8<sub>chromone</sub>), 118.7 (C-4<sub>antipyrine</sub>), 122.3 (C-4<sub>phenyl</sub>), 124.7 (C-4<sub>a</sub>chromone), 125.3 (C-6<sub>chromone</sub>), 126.1 (C-2,6<sub>phenyl</sub>), 126.7 (C-5<sub>chromone</sub>), 129.9 (C-3,5<sub>phenyl</sub>), 136.0 (C-3<sub>antipyrine</sub>), 137.6 (C-7<sub>chromone</sub>), 138.3 (C-1<sub>phenyl</sub>), 150.5 (C-2<sub>chromone</sub>), 155.8 (C-8<sub>a</sub>chromone), 161.6 (C=O<sub>antipyrine</sub>), 176.8 (C=O).  $^{31}\text{P}$ -NMR (162 MHz, DMSO- $d_6$ ): 22.49 ppm. MS ( $m/z$ , I%): 511 (M<sup>+</sup>, 25%). Anal. Calcd for C<sub>26</sub>H<sub>30</sub>N<sub>3</sub>O<sub>6</sub>P (511.51): C, 61.05%; H, 5.91%; N, 8.22%. Found: C, 60.91%; H, 5.80%; N, 8.09%.

**Diethyl [[(3-cyano-4,6-dimethyl-2-oxopyridin-1(2H)-yl)amino](4-oxo-4H-chromen-3-yl)methyl]phosphonate (7a):** Yellow in 81% (*Method A*, 4 h) and 92% (*Method B*, 2 h) yields, mp > 300 °C. IR (KBr), ( $\nu_{\text{max}}$ , cm<sup>-1</sup>): 3267 (br, NH), 3070 (C-H<sub>arom</sub>), 2987, 2937, 2902, 2864 (C-H<sub>aliph</sub>), 2225 (C≡N), 1654 (C=O<sub>pyridone</sub>), 1633 (C=O<sub>pyrone</sub>), 1563, 1539 (C=C), 1207 (P=O), 1017 (P-O-C).  $^1\text{H}$ -NMR (400 MHz, DMSO- $d_6$ ): 1.13 (t, 6H,  $J=6.8$  Hz, 2 CH<sub>3</sub>), 2.31 (s, 3H, CH<sub>3</sub>), 2.42 (s, 3H, CH<sub>3</sub>), 4.22 (q, 4H,  $J=6.8$  Hz, 2 CH<sub>2</sub>O), 4.91 (d, 1H,  $J_{\text{PCH}}=23.6$  Hz, P-CH), 5.90 (s, 1H, NH), 6.36 (s, 1H, H-5<sub>pyridone</sub>), 6.90–6.95 (m, 1H, H-6<sub>chromone</sub>), 6.97–7.02 (m, 1H, H-8<sub>chromone</sub>), 7.27–7.37 (m 1H, H-7<sub>chromone</sub>), 7.88 (d, 1H,  $J=3.2$  Hz, H-5<sub>chromone</sub>), 8.50 (s, 1H, H-2<sub>chromone</sub>).  $^{13}\text{C}$ -NMR (100 MHz, DMSO- $d_6$ ): 12.0 (2 CH<sub>3</sub>), 18.8 (CH<sub>3</sub>), 20.7 (CH<sub>3</sub>), 47.5 (d,  $J_{\text{PC}}=145.8$  Hz, P-CH), 59.5 (2 CH<sub>2</sub>O), 96.5 (C-3<sub>pyridone</sub>), 108.6 (C-5<sub>pyridone</sub>), 115.1 (C≡N), 115.8 (C-3<sub>chromone</sub>), 118.7 (C-8<sub>chromone</sub>), 124.1 (C-4<sub>a</sub>chromone), 125.5 (C-6<sub>chromone</sub>), 126.8 (C-5<sub>chromone</sub>), 136.6 (C-7<sub>chromone</sub>), 150.5 (C-2<sub>chromone</sub>), 151.5 (C-6<sub>pyridone</sub>), 153.2 (C-8<sub>a</sub>chromone), 155.1 (C-4<sub>pyridone</sub>), 159.7 (C=O), 175.9 (C=O).  $^{31}\text{P}$ -NMR (162 MHz, DMSO- $d_6$ ): 24.01 ppm. MS ( $m/z$ , I%): 457 (M<sup>+</sup>, 24%). Anal. Calcd for C<sub>22</sub>H<sub>24</sub>N<sub>3</sub>O<sub>6</sub>P (457.42): C, 57.77%; H, 5.29%; N, 9.19%. Found: C, 57.60%; H, 5.18%; N, 9.12%.

**Diethyl [[(3-cyano-4,6-dimethyl-2-oxopyridin-1(2H)-yl)amino](6-methyl-4-oxo-4H-chromen-3-yl)methyl]phosphonate (7b):** Yellow in 83% (*Method A*, 7.5 h) and 94% (*Method B*, 2.5 h) yields, mp > 300 °C. IR (KBr), ( $\nu_{\text{max}}$ , cm<sup>-1</sup>): 3267 (br, NH), 3035 (C-H<sub>arom</sub>), 2982, 2934, 2902, 2867 (C-H<sub>aliph</sub>), 2225 (C≡N), 1654 (C=O<sub>pyridone</sub>), 1639 (C=O<sub>pyrone</sub>), 1619, 1566, 1545 (C=C), 1207 (P=O), 1019 (P-O-C).  $^1\text{H}$ -NMR (400 MHz, DMSO- $d_6$ ): 1.20–1.26 (m, 6H, 2 CH<sub>3</sub>), 2.24 (s, 3H, CH<sub>3</sub>), 2.33 (s, 3H, CH<sub>3</sub>), 2.42 (s, 3H, CH<sub>3</sub>), 4.15–4.17 (m, 4H, 2 CH<sub>2</sub>O), 5.07 (d, 1H,  $J_{\text{PCH}}=22.4$  Hz, P-CH), 6.14 (s, 1H, NH), 6.36 (s, 1H, H-5<sub>pyridone</sub>), 6.86 (d, 1H,  $J=8.4$  Hz, H-8<sub>chromone</sub>), 7.70 (t, 1H,  $J=8.4$  Hz, H-7<sub>chromone</sub>), 8.21 (s, 1H, H-5<sub>chromone</sub>), 8.48 (s, 1H, H-2<sub>chromone</sub>).  $^{13}\text{C}$ -NMR (100 MHz, DMSO- $d_6$ ): 14.1 (2 CH<sub>3</sub>), 18.8 (CH<sub>3</sub>), 20.8 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 50.8 (d,  $J_{\text{PC}}=160.5$  Hz, P-CH), 61.5 (2 CH<sub>2</sub>O), 97.9 (C-3<sub>pyridone</sub>), 107.7 (C-5<sub>pyridone</sub>), 114.4 (C≡N), 116.5 (C-3<sub>chromone</sub>), 118.0 (C-8<sub>chromone</sub>), 124.1 (C-4<sub>a</sub>chromone), 125.6 (C-6<sub>chromone</sub>), 126.8 (C-5<sub>chromone</sub>), 134.9 (C-7<sub>chromone</sub>), 150.4 (C-2<sub>chromone</sub>), 151.4 (C-6<sub>pyridone</sub>), 155.1 (C-8<sub>a</sub>chromone), 156.2 (C-4<sub>pyridone</sub>), 159.7 (C=O), 174.3 (C=O). MS ( $m/z$ , I%): 471 (M<sup>+</sup>, 56%). Anal. Calcd for C<sub>23</sub>H<sub>26</sub>N<sub>3</sub>O<sub>6</sub>P (471.45): C, 58.60%; H,

5.56%; N, 8.91%. Found: C, 58.45%; H, 5.45%; N, 8.80%.

**Diethyl {(morpholinoamino)(4-oxo-4H-chromen-3-yl)methyl}phosphonate (9a):** Pale yellow in 84% (*Method A*, 3 h) and 93% (*Method B*, 1 h) yields, mp 234–236 °C. IR (KBr), ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3276 (br, NH), 3070 (C–H<sub>arom</sub>), 2979, 2931, 2855 (C–H<sub>aliph</sub>), 1657 (C=O<sub>pyrone</sub>), 1610, 1557 (C=C), 1221 (P=O), 1045 (P–O–C). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): 1.06 (t, 3H, *J*=7.2 Hz, CH<sub>3</sub>), 1.14 (t, 3H, *J*=7.2 Hz, CH<sub>3</sub>), 3.10 (t, 4H, *J*=4.8 Hz, 2 NCH<sub>2</sub>), 3.64–3.73 (m, 4H, 2 CH<sub>2</sub>O), 3.77 (t, 4H, *J*=4.8 Hz, 2 OCH<sub>2</sub>), 5.28 (d, 1H, *J*<sub>PCH</sub>=21.6 Hz, P–CH), 5.92 (s, 1H, NH), 7.45–7.56 (m, 2H, H–6 and H–8), 7.64–7.71 (m, 1H, H–7<sub>chromone</sub>), 8.12 (dd, 1H, *J*=8.0 Hz and 1.2 Hz, H–5<sub>chromone</sub>), 8.60 (s, 1H, H–2<sub>chromone</sub>). <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>): 12.3 (CH<sub>3</sub>), 13.2 (CH<sub>3</sub>), 52.7 (d, *J*<sub>PC</sub>=162.0 Hz, P–CH), 60.4 (C–3,5<sub>morpholine</sub>), 62.5 (CH<sub>2</sub>O), 62.5 (CH<sub>2</sub>O), 66.2 (C–2,6<sub>morpholine</sub>), 114.2 (C–3<sub>chromone</sub>), 119.0 (C–8<sub>chromone</sub>), 122.5 (C–4<sub>a</sub>chromone), 125.5 (C–6<sub>chromone</sub>), 126.4 (C–5<sub>chromone</sub>), 134.8 (C–7<sub>chromone</sub>), 154.7 (C–2<sub>chromone</sub>), 158.5 (C–8<sub>a</sub>chromone), 177.8 (C=O). MS (*m/z*, I%): 396 (M<sup>+</sup>, 43%). Anal. Calcd for C<sub>18</sub>H<sub>25</sub>N<sub>2</sub>O<sub>6</sub>P (396.38): C, 54.54%; H, 6.36%; N, 7.07%. Found: C, 54.40%; H, 6.29%; N, 6.98%.

**Diethyl {(6-methyl-4-oxo-4H-chromen-3-yl)(morpholinoamino)methyl}phosphonate (9b):** Pale yellow in 86% (*Method A*, 5 h) and 96% (*Method B*, 1.5 h) yields, mp > 300 °C. IR (KBr), ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3185 (br, NH), 3061 (C–H<sub>arom</sub>), 2979, 2922, 2861 (C–H<sub>aliph</sub>), 1654 (C=O<sub>pyrone</sub>), 1619, 1560 (C=C), 1209 (P=O), 1045 (P–O–C). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): 1.13 (t, 6H, *J*=6.8 Hz, 2 CH<sub>3</sub>), 2.28 (s, 3H, CH<sub>3</sub>), 3.10 (t, 4H, *J*=4.8 Hz, 2 NCH<sub>2</sub>), 3.76 (t, 4H, *J*=4.8 Hz, 2 OCH<sub>2</sub>), 4.13 (q, 4H, *J*=6.8 Hz, 2 CH<sub>2</sub>O), 5.11 (d, 1H, *J*<sub>PCH</sub>=21.6 Hz, P–CH), 5.92 (s, 1H, NH), 6.89 (d, 1H, *J*=8.4 Hz, H–8<sub>chromone</sub>), 7.60 (d, 1H, *J*=8.4 Hz, H–7<sub>chromone</sub>), 8.19 (s, 1H, H–5<sub>chromone</sub>), 8.57 (s, 1H, H–2<sub>chromone</sub>). <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>): 14.9 (2 CH<sub>3</sub>), 20.7 (CH<sub>3</sub>), 53.4 (d, *J*<sub>PC</sub>=136.7 Hz, P–CH), 59.8 (C–3,5<sub>morpholine</sub>), 61.0 (2 CH<sub>2</sub>O), 67.7 (C–2,6<sub>morpholine</sub>), 115.7 (C–3<sub>chromone</sub>), 117.8 (C–8<sub>chromone</sub>), 123.6 (C–4<sub>a</sub>chromone), 125.2 (C–6<sub>chromone</sub>), 126.4 (C–5<sub>chromone</sub>), 132.1 (C–7<sub>chromone</sub>), 152.0 (C–2<sub>chromone</sub>), 155.8 (C–8<sub>a</sub>chromone), 173.8 (C=O). MS (*m/z*, I%): 410 (M<sup>+</sup>, 1%). Anal. Calcd for C<sub>19</sub>H<sub>27</sub>N<sub>2</sub>O<sub>6</sub>P (410.41): C, 55.61%; H, 6.63%; N, 6.83%. Found: C, 55.47%; H, 6.50%; N, 6.74%.

**Diethyl {[{(6-methyl-5-oxo-3-thioxo-2,5-dihydro-1,2,4-triazin-4(3H)-yl)amino](4-oxo-4H-chromen-3-yl)methyl}phosphonate (11a):** Cumin in 82% (*Method A*, 5 h) and 92% (*Method B*, 1.5 h) yields, mp 230–232 °C. IR (KBr), ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3252 (br, NH), 3129 (br, NH), 3073 (C–H<sub>arom</sub>), 2984, 2934, 2902, 2867 (C–H<sub>aliph</sub>), 1686 (C=O<sub>triazinone</sub>), 1651 (C=O<sub>pyrone</sub>), 1603, 1565 (C=C), 1218 (P=O), 1156 (C=S), 1039 (P–O–C). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): 1.05 (t, 6H, *J*=7.2 Hz, 2 CH<sub>3</sub>), 2.17 (s, 3H, CH<sub>3</sub>), 4.12 (q, 4H, *J*=6.8 Hz, 2 CH<sub>2</sub>O), 5.13 (d, 1H, *J*<sub>PCH</sub>=21.6 Hz, P–CH), 6.45 (s, 1H, NH), 7.31 (d, 1H, *J*=7.6 Hz, H–8<sub>chromone</sub>), 7.48 (t, 1H, *J*=6.8 Hz, H–6<sub>chromone</sub>), 7.61 (t, 1H, *J*=7.6 Hz, H–7<sub>chromone</sub>), 7.79 (d, 1H, *J*=8.4 Hz, H–5<sub>chromone</sub>),

8.76 (s, 1H, H-2<sub>chromone</sub>), 13.65 (s, 1H, NH). <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>): 14.7 (2 CH<sub>3</sub>), 18.4 (CH<sub>3</sub>), 51.0 (d, *J*<sub>PC</sub>=147.0 Hz, P-CH), 61.4 (2 CH<sub>2</sub>O), 115.3 (C-3<sub>chromone</sub>), 118.7 (C-8<sub>chromone</sub>), 123.2 (C-4<sub>a</sub>chromone), 125.4 (C-6<sub>chromone</sub>), 127.3 (C-5<sub>chromone</sub>), 137.5 (C-7<sub>chromone</sub>), 146.8 (C-6<sub>triazinone</sub>), 150.4 (C-2<sub>chromone</sub>), 156.2 (C-8<sub>a</sub>chromone), 166.6 (C=O<sub>triazinone</sub>), 175.1 (C=O<sub>pyrone</sub>), 176.8 (C=S). MS (*m/z*, I%): 452 (M<sup>+</sup>, 7%). Anal. Calcd for C<sub>18</sub>H<sub>21</sub>N<sub>4</sub>O<sub>6</sub>PS (452.42): C, 47.79%; H, 4.68%; N, 12.38%; S, 7.09%. Found: C, 47.61%; H, 4.55%; N, 12.29%; S, 7.00%.

**Diethyl {(6-methyl-4-oxo-4*H*-chromen-3-yl)[(6-methyl-5-oxo-3-thioxo-2,5-dihydro-1,2,4-triazin-4(3*H*)-yl)amino]methyl}phosphonate (11b):** cumin in 87% (*Method A*, 5 h) and 94% (*Method B*, 2 h) yields, mp 235–236 °C. IR (KBr), (*v*<sub>max</sub>, cm<sup>-1</sup>): 3285 (br, NH), 3185 (br, NH), 3070 (C-H<sub>arom</sub>), 2979, 2929, 2861 (C-H<sub>aliph</sub>), 1680 (C=O<sub>triazinone</sub>), 1657 (C=O<sub>pyrone</sub>), 1619, 1560 (C=C), 1209 (P=O), 1165 (C=S), 1045 (P-O-C). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): 1.06 (t, 6H, *J*=6.8 Hz, 2 CH<sub>3</sub>), 2.17 (s, 3H, CH<sub>3</sub>), 2.19 (s, 3H, CH<sub>3</sub>), 4.15 (q, 4H, *J*=6.8 Hz, 2 CH<sub>2</sub>O), 5.10 (d, 1H, *J*<sub>PCH</sub>=22.0 Hz, P-CH), 6.45 (s, 1H, NH), 6.78–6.90 (m, 1H, H-8<sub>chromone</sub>), 7.07–7.17 (m, 1H, H-7<sub>chromone</sub>), 7.95 (d, 1H, *J*=8.4 Hz, H-5<sub>chromone</sub>), 8.76 (s, 1H, H-2<sub>chromone</sub>), 13.65 (s, 1H, NH). <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>): 14.8 (2 CH<sub>3</sub>), 18.5 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 52.3 (d, *J*<sub>PC</sub>=134.8 Hz, P-CH), 61.4 (2 CH<sub>2</sub>O), 116.8 (C-3<sub>chromone</sub>), 118.1 (C-8<sub>chromone</sub>), 125.7 (C-4<sub>a</sub>chromone), 126.3 (C-6<sub>chromone</sub>), 127.3 (C-5<sub>chromone</sub>), 135.2 (C-7<sub>chromone</sub>), 148.6 (C-6<sub>triazine</sub>), 151.3 (C-2<sub>chromone</sub>), 154.2 (C-8<sub>a</sub>chromone), 166.6 (C=O<sub>triazinone</sub>), 172.3 (C=O<sub>pyrone</sub>), 174.1 (C=S). MS (*m/z*, I%): 466 (M<sup>+</sup>, 8%). Anal. Calcd for C<sub>19</sub>H<sub>23</sub>N<sub>4</sub>O<sub>6</sub>PS (466.45): C, 48.92%; H, 4.97%; N, 12.01%; S, 6.87%. Found: C, 48.75%; H, 4.83%; N, 11.95%; S, 6.79%.

### Evaluation of antifungal activity

The antifungal activities of the synthesized compounds were screened against five plant pathogenic fungi, namely *Alternaria alternata*, *Cochliobolus lunatus*, *Penicillium oxalicum*, *Fusarium oxysporum* and *Pestalotia* sp. They were obtained from the Microbiology Research Laboratory, Department of Biology, King Khalid University, Abha, Saudi Arabia. The fungal species were grown on potato dextrose agar (PDA) and incubated at 27 °C for 5 days, then a spore suspension was made by taking five 5 agar discs from the growing culture of each species in 50 mL distilled water in the falcon tube and shaking vigorously to obtain a homogeneous solution of the spore suspension (about 5 × 10<sup>4</sup> colony forming unit). The antifungal properties were tested by agar well diffusion method.<sup>56</sup> The PDA agar was prepared and left to cool and mixed with 100 μL of the fungal spore suspension. The petri dish was slowly moved with clockwise and reversed to ensure the spread of spore suspension in the whole dish. Wells of 4 mm were made with the help of sterile a cork borer. The compounds were dissolved in DMSO which has no inhibition activity to get concentration of 1000 μg/mL. 50 μL of each compound was inoculated into each well. Also, 50 μL from Propiconazole as antifungal standard was used as a positive control. The plates were incubated at

27 °C and the inhibition zone was measured after 3 days. The antifungal activities of tested compounds were calculated by measuring the mean surface area of the zones of inhibition of each compound.

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