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ULTRASOUND ASSISTED ONE POT, THREE-COMPONENT REACTION FOR FACILE DESIGN OF NOVEL 1,2,3-DIAZAPHOSPHOLE, 1,5,2-DIAZAPHOSPHININE AND 1,5,2-DIAZAPHOSPHEPINE COMPOUNDS CONTAINING COUMARIN RING

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Abstract – We have designed novel 1,2,3-diazaphosphole, 1,5,2-diazaphosphinine and 1,5,2-diazaphosphepine compounds containing a coumarin ring. The method depended on one-pot, three-component reaction of 3-(2-bromoacetyl)-2*H*-chromen-2-one (**1**) and diethyl phosphite in the presence of diamine reagent under ultrasonication effect at 50 ºC. The possible reaction mechanisms of the formation of these products were displayed and discussed. The structures of isolated products were established by elemental analyses and spectral tools.

INTRODUCTION

Ultrasound irradiation has recently emerged as a clean and green method for speeding up organic synthetic transformations.[1-3] The main advantages of ultrasound-assisted synthesis are high reaction rates, short reaction times, high yields, and mild reaction conditions. Actually, ultrasound radiation causes acoustic cavitation to overcome molecular attractive forces and stimulate molecule mixing. These results increased intimate interaction between distinct molecules, resulting in the formation of a highly reactive species, which accelerates the reaction and improves product yields. This method is carried out in order to trigger a number of organic reactions.[4-6] In contrast to the traditional approach, which provides thermal energy to the macro-system, the ultrasonic-assisted method improves reaction time, increases yield, decreases waste,

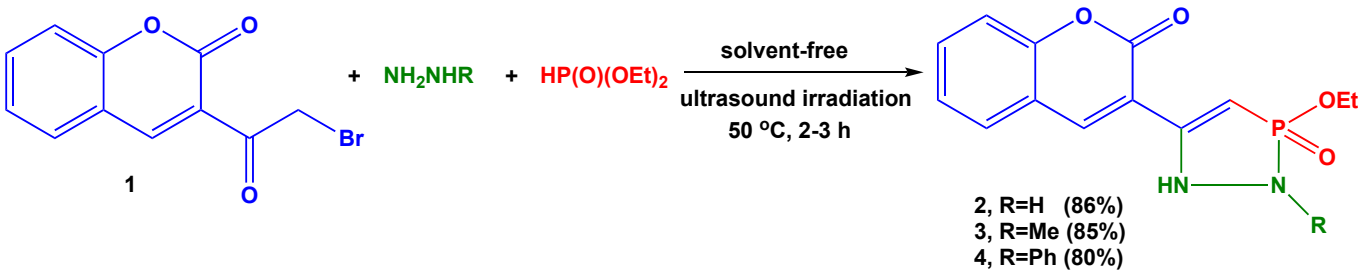
and conserves energy by providing activation energy to the microenvironment, enhancing its greener impact.[7,8] Further, multicomponent reactions have grown into a useful and potent tool in current synthetic organic chemistry due to its valuable features. Multicomponent reactions are particularly advantageous for the synthesis of diverse "drug-like" heterocyclic scaffolds.[9] On the other hand, coumarin (2-oxo-2*H*-chromene) derivatives are well recognized for their widespread biological properties such as antibacterial,[10] antifungal,[11] anticancer,[12] antimicrobial,[13] anti-inflammatory[14] and anti-HIV.[15] Similarly, the importance of phosphorus-nitrogen compounds as intermediates in organic synthesis is well documented. A variety of functionalized phosphorus-containing nitrogen heterocycles have received considerable interest because of their possible biological and pharmacological effects such as anticancer,[16] insecticidal[17] and herbicidal properties.[18] In continuation of our interest in the development of new synthetic procedures in phosphorus heterocycles,[19-22] we wish to describe a one-pot, three-component, solvent-free and catalyst-free to construct a novel series of 1,2,3-diazaphosphole, 1,5,2-diazaphosphinine and 1,5,2-diazaphosphepine compounds containing a coumarin ring *via* sequential ultrasound-assisted reaction in good yields.

RESULTS AND DISCUSSION

A one-pot, three-component reaction to synthesize of a novel series of 1,2,3-diazaphosphole, 1,5,2-diazaphosphinine and 1,5,2-diazaphosphepine compounds containing a coumarin ring was achieved by an ultrasound-assisted reaction. Although the molecular frames of coumarinyl P-heterocycles are known in the literature,[23,24] but the suggested frame of coumarin moiety with 1,5,2-diazaphosphinine and 1,5,2-diazaphosphepine are unknown. In addition, the coumarinyl-1,2,3-diazaphospholes are rare.[25] For these reasons, there is a need to synthesize these novel compounds under mild reaction conditions that may have interesting biological properties. The suggested methodology depended on one-pot reaction of 3-(2-bromoacetyl)-2*H*-chromen-2-one (**1**) and diethyl phosphite in the presence of 1,2-, 1,3-, and 1,4-diamine reagent under ultrasonication effect at 50 ^{o}C.

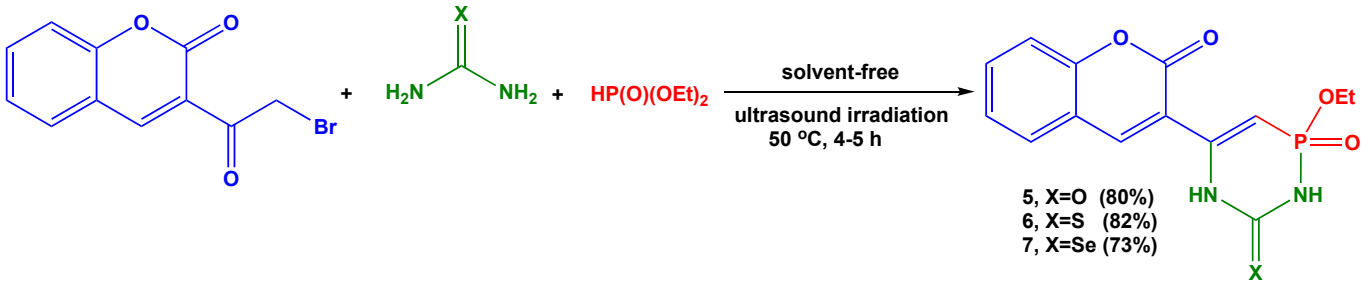
In our initial search for appropriate reaction conditions, we chose the reaction of 3-(2-bromoacetyl)-2*H*-chromen-2-one (**1**),[26] with hydrazine hydrate and diethyl phosphite as a model. When the reaction was carried out under stirring at room temperature, no product was isolated. However, repetition of the reaction at 50 and 80 ^{o}C gave the the target product of 3-(3-ethoxy-3-oxido-1,2-dihydro-1,2,3-diazaphosphol-5-yl)-2*H*-chromen-2-one (**2**) in 22% and 35% yields, respectively (Scheme 1). The reaction was performed under ultrasonication at room temperature to furnish the desired product **2** in 51% yield after 5 hours. By increasing of the reaction temperature to 50 ^{o}C for the latter reaction, the product **2** was formed in 86% yield after 2 hours (Scheme 1). The scope and generality of this protocol were illustrated with respect to other hydrazines. When methylhydrazine and phenylhydrazine were used, these reaction occurred smoothly and gave the corresponding 3-(3-ethoxy-2-methyl-3-oxido-1,2-dihydro-1,2,3-diazaphosphol-5-yl)-2*H*-

chromen-2-one (**3**) and 3-(3-ethoxy-3-oxido-2-phenyl-1,2-dihydro-1,2,3-diazaphosphol-5-yl)-2*H*-chromen-2-one (**4**), respectively, in good yields (Scheme 1).



Scheme 1

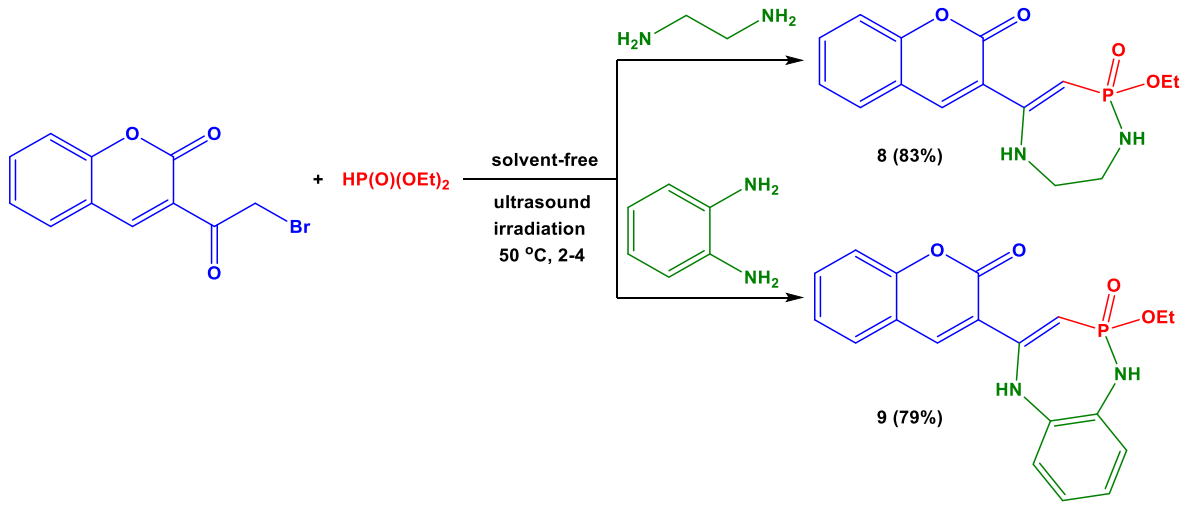
A variety of nitrogen 1,3-diamine reagent was used instead of hydrazines to design other phosphorus-nitrogen heterocycles. Thus, reaction of the substrate **1** with diethyl phosphite and each one from urea, thiourea and selenourea under ultrasound irradiation at 50 °C afforded the corresponding 2-ethoxy-4-(2-oxo-2*H*-chromen-3-yl)-2-oxido-5*H*-1,5,2-diazaphosphinines (**5**–**7**) in satisfactory yields (Scheme 2). Similarly, when ethylenediamine and 1,2-phenylenediamine were used to react with the substrate **1** and diethyl phosphite by help of ultrasound irradiation at 50 °C, the novel frames of 3-(2-ethoxy-2-oxido-1,5,6,7-tetrahydro-1,5,2-diazaphosphepin-4-yl)-2*H*-chromen-2-one (**8**) and 3-(2-ethoxy-2-oxido-1,5-dihydro-1,5,2-benzodiazaphosphepin-4-yl)-2*H*-chromen-2-one (**9**), respectively, were isolated (Scheme 3).



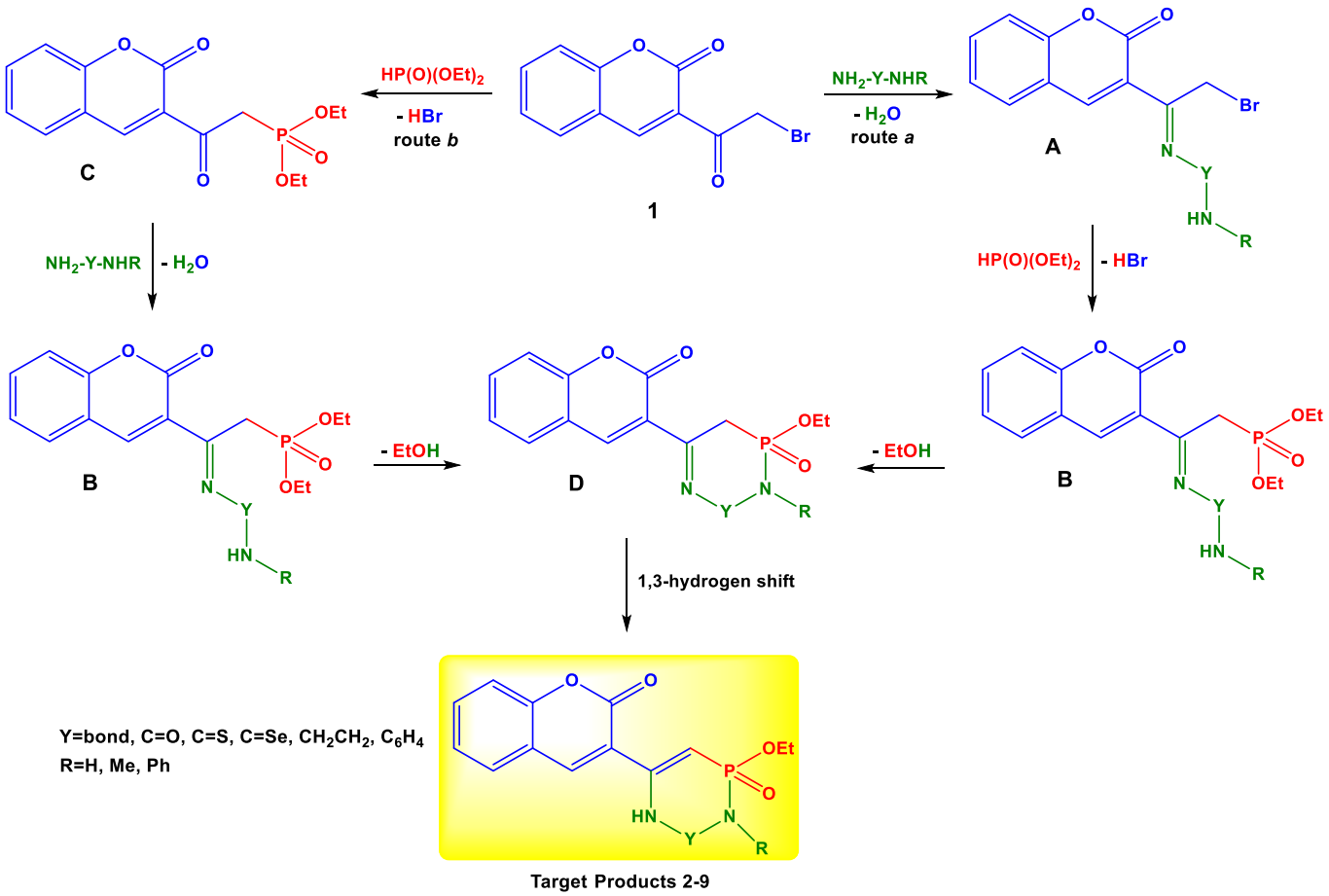
Scheme 2

The proposed mechanism is depicted in Scheme 4. The reaction underwent two routes. The first route is condensation of substrate **1** with the diamine compound to afford the corresponding hydrazone **A** (Scheme 4, route *a*). This hydrazone intermediate can react diethyl phosphite under Arbuzov reaction to form the diethyl phosphonate intermediate **B**.[27] The second route may undergo Arbuzov reaction to give the intermediate **C**, followed by condensation with the diamino compound to give the intermediate **B** (Scheme 4, route *b*). This latter intermediate underwent an intramolecular cyclization by attack of -NHR at the

phosphonate group to remove ethanol molecule forming the intermediate **D** which was rearranged into the isolated form due to 1,3-hydrogen shift (Scheme 4).



Scheme 3



Scheme 4

This three-component, solvent-free, and catalyst-free reaction progressed very cleanly under the ultrasonic condition and no undesirable side product was observed. The structure of all obtained products was confirmed by IR, mass, ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopies. The mass spectra of all synthesized compounds showed their expected molecular ion peaks. The IR spectra for all products displayed absorption bands at region 3310–3119, 1253–1239 and 1058–1023 cm^{-1}, which are respectively, related to the stretching frequencies of NH, P=O and P–O–C groups. Also, the C=O absorption bands were observed at 1714–1709 cm^{-1}. The ^{1}H-NMR spectra of all products exhibited one ethoxy group in the aliphatic region as a triplet in δ 1.09–1.21 (CH_3) and 3.89–4.11 (OCH_2) ppm.[28] Also, in the region δ 8.56–8.74 ppm, the hydrogens of C–4 in coumarin ring appeared as singlets. The hydrogens of C–4$_{diazaphosphole}$, C–3$_{diazaphosphinine}$, and C–3$_{diazaphosphepine}$ appeared as doublets in the region δ 5.98–6.04 (J_{PCH}=19.6–20.4 Hz), 6.23–6.31 (J_{PCH}=20.8–22.0 Hz) and 5.79–6.02 (J_{PCH}=19.4–23.4 Hz) ppm, respectively. Each product exhibited the distinct signals for carbon atoms. The specific carbon atoms of ethoxy group were recorded at range δ 13.6–14.3 (CH_3) and 59.2–62.0 (OCH_2) ppm. The signals of the carbon atoms C–4$_{diazaphosphole}$, C–3$_{diazaphosphinine}$, and C–3$_{diazaphosphepine}$ appeared as doublet in the region δ 101.2–102.4 (J_{PCH}=86.2–88.2 Hz), 106.4–107.2 (J_{PCH}=86.7–88.7 Hz) and 96.2–101.2 (J_{PCH}=83–85 Hz) ppm, respectively. In addition, the carbon atom C–4 of coumarin rings were observed at δ 147.2–150.1 ppm while C=O carbon atoms were found at δ 159.1–160.1 ppm. Finally, the ^{31}P-NMR spectra for some selected products **2**, **6** and **8** were showed at region δ 19.2, 15.3 and 16.8 ppm, respectively.[22]

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. ^{1}H- and ^{13}C-NMR spectra were measured a Bruker spectrometer (400 and 100 MHz), using DMSO-d_6 as a solvent and TMS (δ) as an internal standard. ^{31}P-NMR spectra were measured on a Bruker (162 MHz) spectrophotometer using DMSO-d_6 as a solvent, TMS as an internal standard and 85% H_3PO_4 as an external reference. Mass spectra were recorded on direct probe controller inlet part to single quadropole mass analyzer in (thermo scientific GCMS). Elemental microanalysis 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 2-9.

A mixture of 3-(2-bromoacetyl)-2*H*-chromen-2-one (**1**) (0.66 g, 2.5 mmol), diethyl phosphite (0.34 mL, 2.5 mmol) and 1,2-, 1,3- and 1,4-diamine reagent (2.5 mmol), was subjected to ultrasonication at 50 °C for 2–

5 h. After completion of reaction (monitored by TLC), the mixture was treated with MeOH. The formed solid was filtered off and crystallized from the proper solvent.

3-(3-Ethoxy-3-oxido-1,2-dihydro-1,2,3-diazaphosphol-5-yl)-2*H*-chromen-2-one (2): Yield 86%, yellow solid, mp 184–186 ºC. IR (KBr), (*v* max, cm^{-1}): 3210 (br, NH), 3119 (br, NH), 3056 (C–H_{arom}), 2961, 2903 (C–H_{aliph}), 1710 (C=O), 1601, 1598 (C=C), 1250 (P=O), 1029 (P–O–C). ^{1}H-NMR (400 MHz, DMSO-d_6): 1.10 (t, 3H, *J*=6.8 Hz, CH_3), 3.98 (q, 2H, *J*=6.8 Hz, OCH_2), 5.98 (d, 1H, *J*=20.4 Hz, C_4–$H_{diazaphosphole}$), 7.35 (t, 1H, *J*=6.4 Hz, H–$6_{coumarin}$), 7.43 (d, 1H, *J*=7.2 Hz, H–$8_{coumarin}$), 7.61 (t, 1H, *J*=6.8 Hz, H–$7_{coumarin}$), 8.01 (d, 1H, *J*=6.4 Hz, H–$5_{coumarin}$), 8.64 (s, 1H, H–$4_{coumarin}$), 10.01 (s, 1H, NH), 10.32 (s, 1H, NH). ^{13}C-NMR (100 MHz, DMSO-d_6): 13.9 (CH_3), 61.1 (OCH_2), 101.2 (d, J_{PC}=86.2 Hz, C–$4_{diazaphosphole}$), 115.3 (C–$8_{coumarin}$), 117.9 (C–$4a_{coumarin}$), 122.8 (C–$3_{coumarin}$), 124.2 (C–$6_{coumarin}$), 130.5 (C–$5_{coumarin}$), 133.4 (C–$7_{coumarin}$), 147.4 (C–$4_{coumarin}$), 151.2 (C–$5_{diazaphophole}$), 153.4 (C–$8a_{coumarin}$), 159.6 (C=O). ^{31}P-NMR (162 MHz, DMSO-d_6): 19.2 ppm. MS (EI, *m/z*): 292 (M^+, 15%). Anal. Calcd for $C_{13}H_{13}N_2O_4P$ (292.23): C, 53.43; H, 4.48; N, 9.59%. Found: C, 53.29; H, 4.31; N, 9.43%.

3-(3-Ethoxy-2-methyl-3-oxido-1,2-dihydro-1,2,3-diazaphosphol-5-yl)-2*H*-chromen-2-one (3): Yield 85%, yellow solid, mp 186–188 ºC. IR (KBr), (*v* max, cm^{-1}): 3192 (br, NH), 3061 (C–H_{arom}), 2958, 2919 (C–H_{aliph}), 1711 (C=O), 1602, 1596 (C=C), 1245 (P=O), 1031 (P–O–C). ^{1}H-NMR (400 MHz, DMSO-d_6): 1.08 (t, 3H, *J*=6.4 Hz, CH_3), 2.91 (s, 3H, CH_3), 3.89 (q, 2H, *J*=6.4 Hz, OCH_2), 6.01 (d, 1H, *J*=19.6 Hz, C_4–$H_{diazaphosphole}$), 7.38 (t, 1H, *J*=6.8 Hz, H–$6_{coumarin}$), 7.42 (d, 1H, *J*=6.8 Hz, H–$8_{coumarin}$), 7.59 (t, 1H, *J*=7.2 Hz, H–$7_{coumarin}$), 7.98 (d, 1H, *J*=6.8 Hz, H–$5_{coumarin}$), 8.61 (s, 1H, H–$4_{coumarin}$), 10.42 (s, 1H, NH). ^{13}C-NMR (100 MHz, DMSO-d_6): 14.1 (CH_3), 37.6 (NCH_3), 60.3 (OCH_2), 101.4 (d, J_{PC}=87.3 Hz, C–$4_{diazaphosphole}$), 115.4 (C–$8_{coumarin}$), 118.1 (C–$4a_{coumarin}$), 123.1 (C–$3_{coumarin}$), 124.7 (C–$6_{coumarin}$), 130.6 (C–$5_{coumarin}$), 133.8 (C–$7_{coumarin}$), 147.9 (C–$4_{coumarin}$), 152.0 (C–$5_{diazaphophole}$), 153.9 (C–$8a_{coumarin}$), 160.0 (C=O). MS (EI, *m/z*): 306 (M^+, 11%). Anal. Calcd for $C_{14}H_{15}N_2O_4P$ (306.26): C, 54.91; H, 4.94; N, 9.15%. Found: C, 54.79; H, 4.78; N, 9.03%.

3-(3-Ethoxy-3-oxido-2-phenyl-1,2-dihydro-1,2,3-diazaphosphol-5-yl)-2*H*-chromen-2-one (4): Yield 80%, yellow solid, mp 195–196 ºC. IR (KBr), (*v* max, cm^{-1}): 3153 (br, NH), 3059 (C–H_{arom}), 2982, 2942 (C–H_{aliph}), 1709 (C=O), 1605, 1594 (C=C), 1249 (P=O), 1033 (P–O–C). ^{1}H-NMR (400 MHz, DMSO-d_6): 1.21 (t, 3H, *J*=6.8 Hz, CH_3), 4.01 (q, 2H, *J*=6.8 Hz, OCH_2), 6.04 (d, 1H, *J*=20.0 Hz, C_4–$H_{diazaphosphole}$), 6.85–6.93 (m, 3H, Ph–H), 7.36–7.45 (m, 2H, Ph–H and H–$6_{coumarin}$), 7.55–7.59 (m, 2H, Ph–H and H–$8_{coumarin}$), 7.69 (t, 1H, *J*=7.6 Hz, H–$7_{coumarin}$), 8.05 (d, 1H, *J*=7.2 Hz, H–$5_{coumarin}$), 8.66 (s, 1H, H–$4_{coumarin}$), 11.23 (s, 1H, NH). ^{13}C-NMR (100 MHz, DMSO-d_6): 14.2 (CH_3), 62.0 (OCH_2), 102.4 (d, J_{PC}=88.2 Hz, C–$4_{diazaphosphole}$), 112.4 (C–$2,6_{phenyl}$), 115.9 (C–$8_{coumarin}$), 118.3 (C–$4a_{coumarin}$), 119.8 (C–4_{phenyl}), 123.1 (C–$3_{coumarin}$), 125.7 (C–$6_{coumarin}$), 129.6 (C–$3,5_{phenyl}$), 130.9 (C–$5_{coumarin}$), 134.1 (C–$7_{coumarin}$), 147.8 (C–$4_{coumarin}$), 150.4 (C–1_{phenyl}), 151.4 (C–$5_{diazaphophole}$), 153.7 (C–$8a_{coumarin}$), 159.9 (C=O). MS (EI, *m/z*): 368

(M^+, 8%). Anal. Calcd for $C_{19}H_{17}N_2O_4P$ (368.33): C, 61.96; H, 4.65; N, 7.61%. Found: C, 61.81; H, 4.49; N, 7.42%.

3-(2-Ethoxy-2-oxido-6-oxo-1,5,6-trihydro-1,5,2-diazaphosphinin-4-yl)-2*H*-chromen-2-one (5): Yield 80%, beige solid, mp 201–203 ºC. IR (KBr), (ν max, cm^{-1}): 3310 (br, NH), 3205 (br, NH), 3051 (C–H_{arom}), 2972, 2904 (C–H_{aliph}), 1713 (C=O), 1652 (C=O), 1599, 1576 (C=C), 1246 (P=O), 1042 (P–O–C). ^{1}H-NMR (400 MHz, DMSO-d_6): 1.12 (t, 3H, J=6.8 Hz, CH_3), 3.92 (q, 2H, J=6.8 Hz, OCH_2), 6.23 (d, 1H, J=21.4 Hz, C_3–$H_{diazaphosphinine}$), 7.44 (t, 1H, J=7.2 Hz, H–$6_{coumarin}$), 7.61 (d, 1H, J=6.8 Hz, H–$8_{coumarin}$), 7.72 (t, 1H, J=7.2 Hz, H–$7_{coumarin}$), 8.03 (d, 1H, J=7.2 Hz, H–$5_{coumarin}$), 8.74 (s, 1H, H–$4_{coumarin}$), 9.86 (s, 1H, NH), 11.12 (s, 1H, NH). ^{13}C-NMR (100 MHz, DMSO-d_6): 14.3 (CH_3), 61.4 (OCH_2), 107.2 (d, J_{PC}=88.4 Hz, C–$3_{diazaphosphinine}$), 115.8 (C–$8_{coumarin}$), 118.7 (C–$4a_{coumarin}$), 123.8 (C–$3_{coumarin}$), 125.1 (C–$6_{coumarin}$), 130.4 (C–$5_{coumarin}$), 134.1 (C–$7_{coumarin}$), 146.9 (C–$4_{coumarin}$), 150.1 (C–$4_{diazaphophinine}$), 152.8 (C–$8a_{coumarin}$), 158.2 (C=O), 159.6 (C=O). MS (EI, *m/z*): 320 (M^+, 15%). Anal. Calcd for $C_{14}H_{13}N_2O_5P$ (320.24): C, 52.51; H, 4.09; N, 8.75%. Found: C, 52.39; H, 3.91; N, 8.61%.

3-(2-Ethoxy-2-oxido-6-thioxo-1,5,6-trihydro-1,5,2-diazaphosphinin-4-yl)-2*H*-chromen-2-one (6): Yield 82%, beige solid, mp 207–209 ºC. IR (KBr), (ν max, cm^{-1}): 3260 (br, NH), 3119 (br, NH), 3049 (C–H_{arom}), 2984, 2916 (C–H_{aliph}), 1711 (C=O), 1602, 1588 (C=C), 1253 (P=O), 1154 (C=S), 1040 (P–O–C). ^{1}H-NMR (400 MHz, DMSO-d_6): 1.09 (t, 3H, J=6.4 Hz, CH_3), 3.96 (q, 2H, J=6.4 Hz, OCH_2), 6.31 (d, 1H, J=20.8 Hz, C_3–$H_{diazaphosphinine}$), 7.47 (t, 1H, J=7.6 Hz, H–$6_{coumarin}$), 7.63 (d, 1H, J=7.2 Hz, H–$8_{coumarin}$), 7.69 (t, 1H, J=7.2 Hz, H–$7_{coumarin}$), 8.08 (d, 1H, J=7.6 Hz, H–$5_{coumarin}$), 8.69 (s, 1H, H–$4_{coumarin}$), 10.14 (s, 1H, NH), 11.31 (s, 1H, NH). ^{13}C-NMR (100 MHz, DMSO-d_6): 13.9 (CH_3), 60.9 (OCH_2), 106.4 (d, J_{PC}=86.7 Hz, C–$3_{diazaphosphinine}$), 115.1 (C–$8_{coumarin}$), 118.4 (C–$4a_{coumarin}$), 122.9 (C–$3_{coumarin}$), 124.8 (C–$6_{coumarin}$), 130.6 (C–$5_{coumarin}$), 134.7 (C–$7_{coumarin}$), 147.2 (C–$4_{coumarin}$), 152.2 (C–$4_{diazaphophinine}$), 153.4 (C–$8a_{coumarin}$), 159.5 (C=O), 181.4 (C=S). ^{31}P-NMR (162 MHz, DMSO-d_6): 15.3 ppm. MS (EI, *m/z*): 336 (M^+, 5%). Anal. Calcd for $C_{14}H_{13}N_2O_4PS$ (336.30): C, 50.00; H, 3.90; N, 8.33; S, 9.53%. Found: C, 49.86; H, 3.78; N, 8.19; S, 9.39%.

3-(2-Ethoxy-2-oxido-6-selenoxo-1,5,6-trihydro-1,5,2-diazaphosphinin-4-yl)-2*H*-chromen-2-one (7): Yield 73%, pale brown solid, mp 198–199 ºC. IR (KBr), (ν max, cm^{-1}): 3243 (NH), 3156 (br, NH), 3062 (C–H_{arom}), 2991, 2973 (C–H_{aliph}), 1711 (C=O), 1603, 1585 (C=C), 1239 (P=O), 1023 (P–O–C). ^{1}H-NMR (400 MHz, DMSO-d_6): 1.21 (t, 3H, J=7.2 Hz, CH_3), 4.05 (q, 2H, J=7.2 Hz, OCH_2), 6.25 (d, 1H, J=22.0 Hz, C_3–$H_{diazaphosphinine}$), 7.38 (t, 1H, J=6.8 Hz, H–$6_{coumarin}$), 7.49 (d, 1H, J=7.2 Hz, H–$8_{coumarin}$), 7.64 (t, 1H, J=7.2 Hz, H–$7_{coumarin}$), 7.99 (d, 1H, J=6.8 Hz, H–$5_{coumarin}$), 8.56 (s, 1H, H–$4_{coumarin}$), 10.25 (s, 1H, NH), 11.42 (s, 1H, NH). ^{13}C-NMR (100 MHz, DMSO-d_6): 13.9 (CH_3), 60.8 (OCH_2), 106.8 (d, J_{PC}=88.7 Hz, C–$3_{diazaphosphinine}$), 116.1 (C–$8_{coumarin}$), 118.5 (C–$4a_{coumarin}$), 124.1 (C–$3_{coumarin}$), 125.8 (C–$6_{coumarin}$), 131.1 (C–$5_{coumarin}$), 135.2 (C–$7_{coumarin}$), 147.2 (C–$4_{coumarin}$), 150.4 (C–$4_{diazaphophinine}$), 153.1 (C–$8a_{coumarin}$), 159.2

(C=O), 180.2 (C=Se). MS (EI, *m/z*): 384, 382, 380 (M^+, 6%). Anal. Calcd for $C_{14}H_{13}N_2O_4PSe$ (383.20): C, 43.88; H, 3.42; N, 7.31%. Found: C, 43.72; H, 3.29; N, 7.14%.

3-(2-Ethoxy-2-oxido-1,5,6,7-tetrahydro-1,5,2-diazaphosphepin-4-yl)-2*H*-chromen-2-one (8): Yield 83%, pale yellow solid, mp 170–172 °C. IR (KBr), (*v* max, cm^{-1}): 3186 (br, NH), 3132 (br, NH), 3049 (C–H_{arom}), 2976, 2925 (C–H_{aliph}), 1714 (C=O), 1601, 1581 (C=C), 1242 (P=O), 1052 (P–O–C). ^{1}H-NMR (400 MHz, DMSO-d_6): 1.13 (t, 3H, *J*=6.8 Hz, CH_3), 2.78 (br, 2H, NCH_2), 2.98 (br, 2H, NCH_2), 4.11 (q, 2H, *J*=6.8 Hz, OCH_2), 5.01 (brs, 1H, NH), 5.79 (d, 1H, *J*=19.4 Hz, C_3–$H_{diazaphosphepine}$), 7.41 (t, 1H, *J*=7.2 Hz, H–$6_{coumarin}$), 7.53 (d, 1H, *J*=7.2 Hz, H–$8_{coumarin}$), 7.69 (t, 1H, *J*=6.8 Hz, H–$7_{coumarin}$), 7.97 (d, 1H, *J*=7.2 Hz, H–$5_{coumarin}$), 8.11 (brs, 1H, NH), 8.63 (s, 1H, H–$4_{coumarin}$). ^{13}C-NMR (100 MHz, DMSO-d_6): 13.6 (CH_3), 60.2 (OCH_2), 96.2 (d, J_{PC}=83.0 Hz, C–$3_{diazaphosphepine}$), 42.3 (NCH_2), 46.3 (NCH_2), 115.8 (C–$8_{coumarin}$), 118.6 (C–$4a_{coumarin}$), 123.4 (C–$3_{coumarin}$), 124.5 (C–$6_{coumarin}$), 131.1 (C–$5_{coumarin}$), 133.2 (C–$7_{coumarin}$), 147.9 (C–$4_{coumarin}$), 148.2 (C–$4_{diazaphophepine}$), 153.1 (C–$8a_{coumarin}$), 159.1 (C=O). ^{31}P-NMR (162 MHz, DMSO-d_6): 16.8 ppm. MS (EI, *m/z*): 320 (M^+, 8%). Anal. Calcd for $C_{15}H_{17}N_2O_4P$ (320.28): C, 56.25; H, 5.35; N, 8.75%. Found: C, 56.09; H, 5.21; N, 8.64%.

3-(2-Ethoxy-2-oxido-1,5-dihydro-1,5,2-benzodiazaphosphepin-4-yl)-2*H*-chromen-2-one (9): Yield 79%, yellow solid, mp 218–220 °C. IR (KBr), (*v* max, cm^{-1}): 3216 (br, NH), 3102 (br, NH), 3063 (C–H_{arom}), 2991, 2936 (C–H_{aliph}), 1710 (C=O), 1603, 1592 (C=C), 1253 (P=O), 1058 (P–O–C). ^{1}H-NMR (400 MHz, DMSO-d_6): 1.09 (t, 3H, *J*=7.2 Hz, CH_3), 4.04 (q, 2H, *J*=7.2 Hz, OCH_2), 6.02 (d, 1H, *J*=23.4 Hz, C_3–$H_{benzodiazaphosphepine}$), 6.81–6.89 (m, 2H, Ar–H), 7.08–7.22 (m, 2H, Ar–H), 7.46 (t, 1H, *J*=6.8 Hz, H–$6_{coumarin}$), 7.58 (d, 1H, *J*=7.2 Hz, H–$8_{coumarin}$), 7.71 (t, 1H, *J*=7.2 Hz, H–$7_{coumarin}$), 8.04 (d, 1H, *J*=7.2 Hz, H–$5_{coumarin}$), 8.72 (s, 1H, H–$4_{coumarin}$), 9.10 (s, 1H, NH), 10.03 (s, 1H, NH). ^{13}C-NMR (100 MHz, DMSO-d_6): 14.1 (CH_3), 59.2 (OCH_2), 101.2 (d, J_{PC}=85.0 Hz, C–$3_{benzodiazaphophepine}$), 116.1 (C–$8_{coumarin}$), 117.1 (C–$6_{benzodiazaphophepine}$), 118.2 (C–$9_{benzodiazaphophepine}$), 118.8 (C–$4a_{coumarin}$), 120.4 (C–$8_{benzodiazaphophepine}$), 121.0 (C–$7_{benzodiazaphophepine}$), 122.9 (C–$3_{coumarin}$), 125.1 (C–$6_{coumarin}$), 130.0 (C–$5_{coumarin}$), 132.8 (C–$7_{coumarin}$), 134.1 (C–$9a_{benzodiazaphophepine}$), 135.6 (C–$5a_{benzodiazaphophepine}$), 147.2 (C–$4_{coumarin}$), 148.2 (C–$4_{benzodiazaphophepine}$), 153.3 (C–$8a_{coumarin}$), 159.6 (C=O). MS (EI, *m/z*): 368 (M^+, 7%). Anal. Calcd for $C_{19}H_{17}N_2O_4P$ (368.33): C, 61.96; H, 4.65; N, 7.61%. Found: C, 61.79; H, 4.49; N, 7.46%.

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