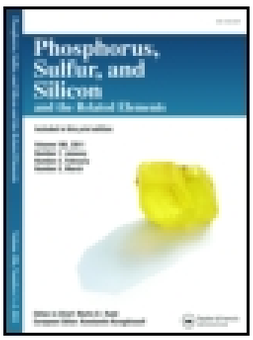

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Reaction of 2-imino-2*H*-chromene-3-carboxamide with phosphorus sulfides: Synthesis of novel 2-sulfido-2,3-dihydro-4*H*-chromeno[2,3-*d*][1,3,2]diaza-phosphinines.

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Reaction of 2-imino-2*H*-chromene-3-carboxamide with phosphorus sulfides: Synthesis of novel 2-sulfido-2,3-dihydro-4*H*-chromeno[2,3-*d*][1,3,2]diaza-phosphinines.

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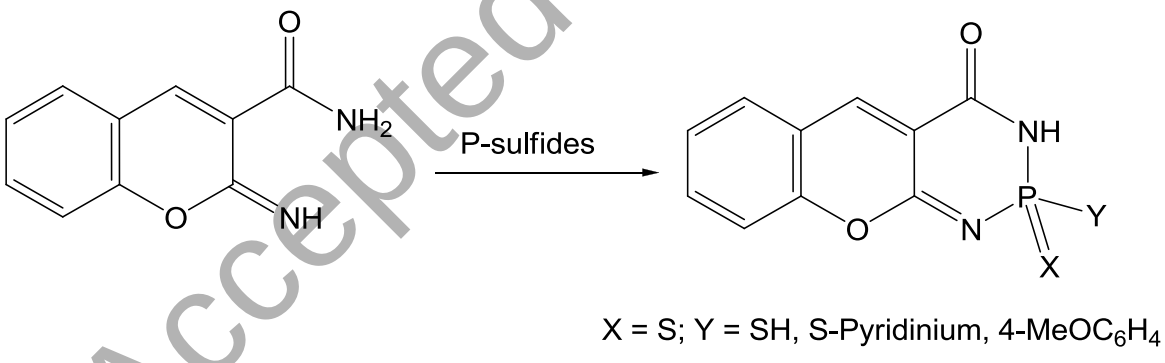
Abstract

Novel 2-sulfido-2,3-dihydro-4*H*-chromeno[2,3-*d*][1,3,2]diazaphosphinines are obtained in a simple one-pot procedure via treatment of 2-imino-2*H*-chromene-3-carboxamide with various phosphorus sulfides. Possible reaction mechanisms are proposed. The structure of the obtained products is confirmed by elemental analyses and spectral tools.

Graphic Abstract



Keywords: Chromene, 1,3,2-diazaphosphinine, phosphorus sulfides

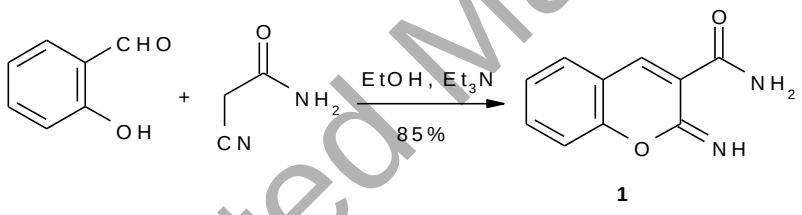
INTRODUCTION

Fused polycyclic chromene compounds have received much synthetic attention[1,2] because of their important biological properties such as antioxidant,[3] anticancer,[4] and antimicrobial activity.[5] On the other hand, phosphorus compounds

continue to attract a great interest because of the diversity of structures and pharmacological activities, especially when they are associated with different heterocycles.[6] For example, they were used as antitumor,[7] antineoplastic,[8] anti-inflammatory[9] and biodegradable insecticide agents.[10] Considering the above facts and our research program on the development of new biologically active heterocyclic organophosphorus compounds,[11-14] we herein report the synthesis of some novel chromeno[2,3-*d*][1,3,2]diazaphinine-2-sulfides *via* treatment of 2-imino-2*H*-chromene-3-carboxamide (**1**) with various phosphorus sulfides.

RESULTS AND DISCUSSION

The starting material 2-imino-2*H*-chromene-3-carboxamide (**1**) was prepared according to the reported method by a *Knovenagel* condensation and intramolecular cyclization of salicylaldehyde with cyanoacetamide in absolute ethanol containing a few drops of triethylamine (Scheme 1).[15]



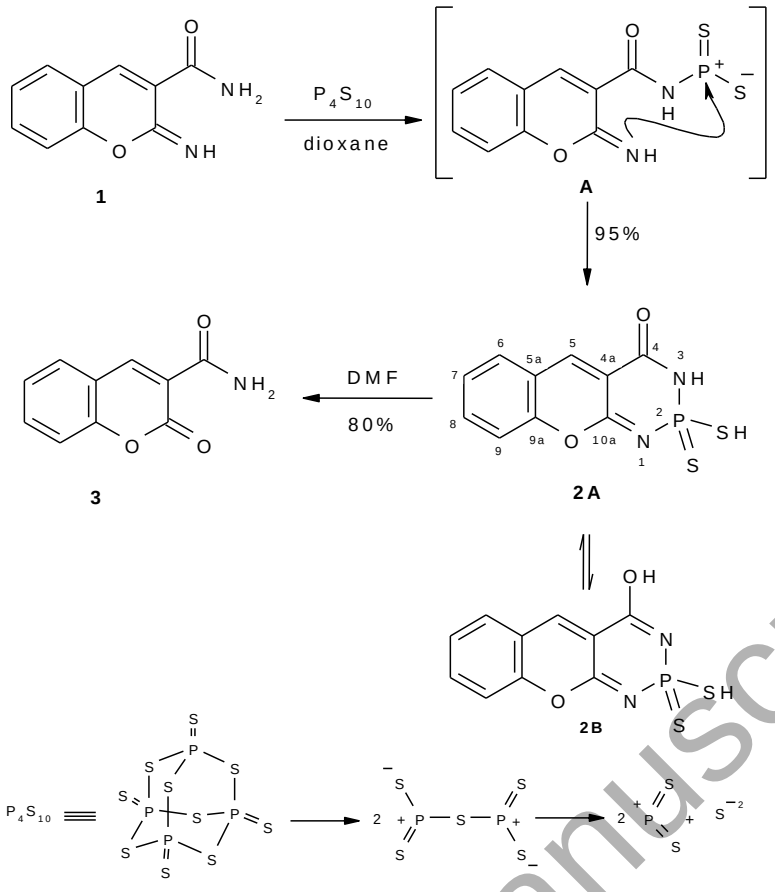
Scheme 1.

The presence of two active nucleophilic and two electrophilic centers in the molecule of 2-imino-2*H*-chromene-3-carboxamide (**1**) provides alternative opportunities in the direction of the reaction with electrophilic and nucleophilic phosphorus reagents such as phosphorus sulfides. Its synthetic precursor opens wide opportunities for the use of chromene systems in the synthesis of diverse fused phosphorus heterocyclic compounds.

Phosphorus decasulfide and Lawesson's reagent (LR) have been used as versatile reagents for thionation processes and the construction of phosphorus and

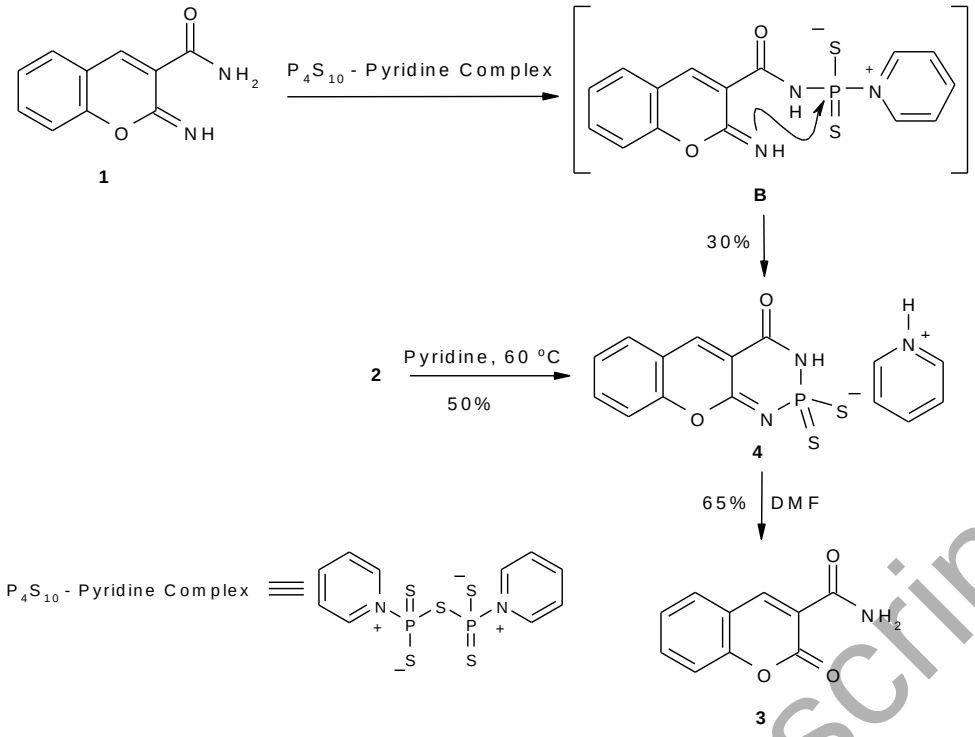
sulfur heterocycles.[16,17] Also, a series of hetaryl-substituted carbinols were converted into the corresponding thiols and sulfides by treatment with LR.[18] In addition, some secondary alcohols bearing ferrocenyl and a hetaryl substituent reacted with LR to give unexpected tetra-substituted ethane or disubstituted methane derivatives with no sulfur atom in the molecule.[19]

Thus, reaction of **1** with phosphorus decasulfide in dry dioxane under reflux for 7 hours afforded the unexpected 2-sulfanyl-2-sulfido-2,3-dihydro-4*H*-chromeno[2,3-*d*][1,3,2]diazaphinin-4-one (**2A**) which apparently exists in another *enol* form **2B** according to its spectral data (Scheme 2). Although P_4S_{10} is an effective reagent for the thionation of amides,[20] its reaction with **1** did not result in any thionated product. This may be due to the high reactivity of NH functional groups towards P_4S_{10} which lead to cyclization instead of thionation reactions.[21] Also, we observed the formation of an interesting hydrolysis product, the known 2-oxo-2*H*-chromene-3-carboxamide (**3**),[22] obtained as yellow crystal needles, which was formed during the purification of compound **2** by a crystallization process from hot polar solvent such as DMF. The structure of **2** was proved by spectroscopic means. Its IR spectrum indicated the presence of OH, NH and C=O functions with bands at 3361, 3200 and 1710 cm^{-1}, respectively. Also, its ^1H NMR spectrum revealed D_2O-exchangeable signals at δ 6.79 (SH), 7.89 (NH), 8.05 (OH) and 5-H proton at δ 8.35 and 8.85 ppm. Moreover, its ^{13}C NMR spectrum showed the specific signals of C-5 and C-4 at δ 146.4, 148.3 and 160.7, 163.0 ppm, respectively, thus supporting the existence of this product in two tautomeric forms. Furthermore, its mass spectrum exhibited the expected molecular ion peak at *m/z* 282 (M^+, 5%).



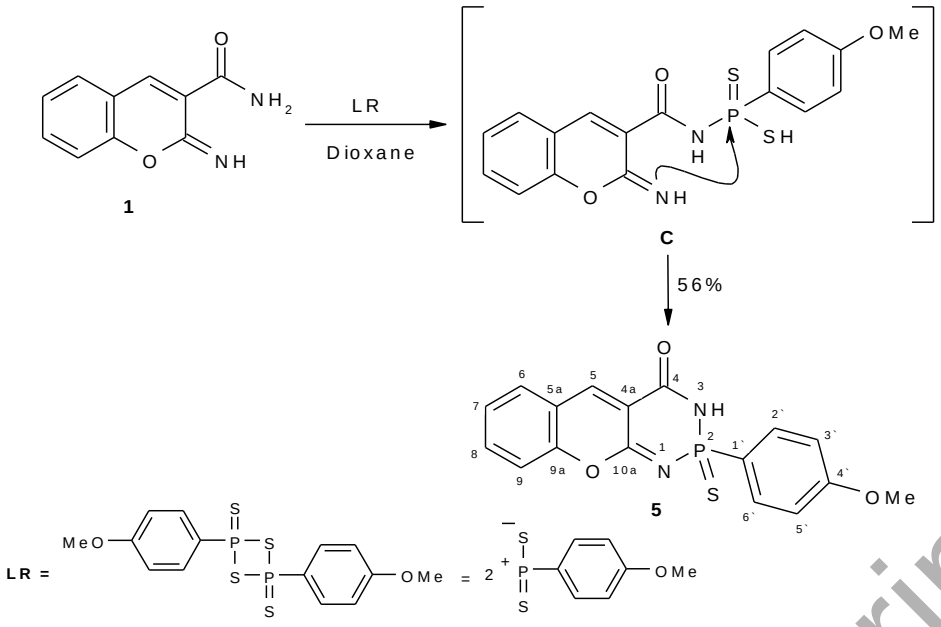
Scheme 2.

When the above reaction was carried out via reaction of **1** with the P_4S_{10}-pyridine complex in dry pyridine, the pyridinium chromeno[2,3-*d*][1,3,2]diazaphosphinine sulfide **4** was isolated as the sole product without any traces of thionated compounds (Scheme 3). Also, the sulfide **4** was obtained with higher yield by warming compound **2** in dry pyridine for 15 minutes. In the same manner, **4** underwent hydrolysis into the corresponding coumarin **3** through heating in DMF. The IR spectrum of **4** exhibited carbonyl bands at 1699 cm^{-1} and two NH groups at 3291 and 3149 cm^{-1}. Its ^1H NMR spectrum displayed the aromatic protons of the pyridine ring and two D_2O-exchangeable signals for NH protons, while its ^{13}C NMR revealed three characteristic signals for the pyridine ring at δ 125.6 ($C_{\beta,\beta'}$), 133.9 (C_γ) and 135.9 ($C_{\alpha,\alpha'}$) ppm. The suggested structure of compound **4** was further corroborated by the molecular ion peak at *m/z* 361 (M^+, 2%) in its mass spectrum.



Scheme 3.

Next, treatment of compound **1** with Lawesson's reagent in dry dioxan, led to 2-(4-methoxyphenyl)-4-oxo-2-sulfido-2,3-dihydro-4*H*-chromeno[2,3-*d*][1,3,2]diaza-phosphinine (**5**) (Scheme 4). The formation of a diazaphosphinine ring can be explained on the basis of nucleophilic attack of the NH_2 group at the phosphorus atom of LR, followed by intramolecular cyclization via removal of H_2S affording the desired fused triheterocyclic system (Scheme 4). The mass spectrum of **5** showed its molecular ion peak at *m/z* 356 (M^+, 56%). The ^{1}H NMR spectrum of **5** exhibited a characteristic broad singlet at δ 6.25 ppm attributable to NH proton and a singlet at δ 3.74 ppm (OCH_3). Further proof for the structure of **5** arose from the ^{13}C NMR data which displayed a methoxy signal δ 55.3 ppm and a carbonyl signal at δ 160.5 ppm. Also, the ^{31}P NMR spectrum of **5** showed a phosphorus atom signal at δ 54.6 ppm. Finally, the IR and mass spectra were in agreement with the suggested structure.



Scheme 4.

EXPERIMENTAL

Melting points were determined in an open capillary tube on a digital Stuart SMP-3 apparatus. IR spectra were measured on a FT-IR (Nicolet IS10) spectrophotometer and Perkin-Elmer 293 spectrophotometers using KBr disks. ^{1}H and ^{13}C NMR spectra were measured on a Gemini-300BB spectrometer (400 and 100 MHz), using DMSO-d_6 as solvent and TMS (δ) as internal standard. ^{31}P-NMR spectra were measured on a Bruker (162 MHz) spectrophotometer using DMSO-d_6 as solvent, TMS as an internal standard and 85% H_3PO_4 as external reference. Mass spectra were recorded on a Gas Chromatographic GCMSqp 1000 ex Shimadzu instrument at 70 eV. Elemental microanalyses were performed on a Perkin-Elmer 2400II at the Chemical War department, Ministry of Defense. Phosphorus decasulfide and Lawesson's reagent used in this work were purchased from Sigma-Aldrich and were used without further purification. The reactions were performed in air without any an inert atmosphere. The purity of the synthesized compounds was checked by thin layer chromatography (TLC) and elemental microanalysis.

2-Imino-2*H*-chromene-3-carboxamide (1)

A solution of 2-cyanoacetamide (1.68 g, 20 mmol) in absolute ethanol (40 mL) was stirred with salicylaldehyde (2.44 mL, 20 mmol) in the presence of NEt_3 (0.4 mL) for 30 min. The formed solid was filtered off, washed with EtOH and crystallized from EtOH to give yellow crystals in 85% yield; mp. 188-190 °C (lit.[15] 184-185 °C). IR (ν_{max}, cm^{-1}): 3419 (br, OH), 3312, 3289, 3140 (3 NH), 3060 (C-H_{arom}), 1698 (C=O), 1636 (C=N), 1601, 1568 (C=C). MS (*m/z*, I %): 189 [$(M+1)^+$, 10%], 188 (M^+, 70%). Anal. calcd. for $C_{10}H_8N_2O_2$ (188.18): C, 63.82%; H, 4.28%; N, 14.89%. Found: C, 63.51%; H, 3.99%; N, 14.61%.

2-Sulfanyl-2-sulfido-2,3-dihydro-4*H*-chromeno[2,3-*d*][1,3,2]diazaphosphinin-4-one (2A) and 4-hydroxy-2-sulfanyl-2-sulfido-2*H*-chromeno[2,3-*d*][1,3,2]diaza-phosphinine (2B)

A mixture of **1** (0.94 g, 5 mmol) and P_4S_{10} (2.22 g, 5 mmol) in dry dioxane (30 mL) was heated under reflux for 7 h. The formed solid was filtered off, washed with EtOH and crystallized from diluted EtOH to give an orange solid in 95% yield; mp. 124-125 °C. IR (ν_{max}, cm^{-1}): 3361 (br, OH), 3200 (br, NH), 1710 (C=O), 1633 (C=N), 1611, 1569 (C=C), 700 (P=S). ^{1}H NMR: 6.79 (br, 1H, SH exchangeable with D_2O), 6.91, 7.23 (two t, 1H, *J* = 7.6 and 7.2 Hz, 7-H), 6.98, 7.19 (two d, 1H, *J* = 7.6 and 8.4 Hz, 9-H), 7.40-7.48, 7.68-7.75 (two m, 1H, 8-H), 7.50, 7.95 (two d, 1H, *J* = 8.4 and 8.0 Hz, 6-H), 7.89, 8.05 (two s, 1H, NH and OH exchangeable with D_2O), 8.35, 8.85 (two s, 1H, 5-H). ^{13}C NMR: 115.4, 116.6 (C-9), 116.8, 118.9 (C-4a), 119.4, 119.7 (C-5a), 124.4, 125.5 (C-7), 128.5, 130.3 (C-6), 133.4, 134.6 (C-8), 146.4, 148.3 (C-5), 154.5 (C-9a), 158.3 (C-10a), 160.7, 163.0 (C-4). MS (*m/z*, I %): 282 (M^+, 5%). Anal. calcd. for $C_{10}H_7N_2O_2PS_2$ (282.27): C, 42.55%; H, 2.50%; N, 9.92%; S, 22.72%. Found: C, 42.22%; H, 2.23%; N, 9.58%; S, 22.48%.

2-Oxo-2*H*-chromene-3-carboxamide (3)

A solution of **2** or **4** (0.2 g) in DMF (10 mL) was boiled for 10 min. The solution was left to cool. The formed solid was filtered off and dried to give yellow crystals in 65−80% yield; mp. 278-280 °C (lit.[22] 280-281 °C). IR (ν_{max}, cm^{-1}): 3388, 3149 (NH_2), 3055 (C-H_{arom}), 1737 (C=$O_{lactone}$), 1678 (2 C=O_{amide}), 1602, 1564 (C=C).

Pyridinium 4-oxo-2,3-dihydro-2-sulfido-4*H*-chromeno[2,3–*d*][1,3,2]diazaphosphinine 2-sulfide (4)

Method A: A solution of **2** (0.2 g) in dry pyridine (10 mL) was warmed at 60 °C for 15 min. The solid formed after cooling was filtered off, washed with diethyl ether and dried to give a yellow solid in 50% yield; mp. 202-203 °C.

Method B: A solution of P_4S_{10} (2.22 g, 5 mmol) in pyridine (20 mL) was heated under reflux for 2 h to form the pyridine complex. A solution of **1** (0.94 g, 5 mmol) in dry pyridine (10 mL) was added to the above solution and refluxed for 5 h. The formed solid was filtered off, washed with diethyl ether and crystallized from dioxane to give a yellow solid in 30% yield; mp. 203-205°C. IR, (ν max, cm^{-1}): 3291 (NH), 3149 (NH), 3066, 3024 (C-H_{arom}), 1699 (C=O), 1610 (C=N), 1599, 1562 (C=C), 679 (P=S). ^{1}H NMR: 7.41 (t, 1H, J = 7.6 Hz, 7-H), 7.47 (d, 1H, J = 8.4 Hz, 9-H), 7.61 (d, 1H, J = 8.4 Hz, H_β), 7.70-7.77 (m, 3H, 8-H, $H_{\beta'}$, H_γ), 7.88 (d, 1H, J = 8.0 Hz, 6-H), 7.96 (d, 1H, J = 8.0 Hz, H_α), 8.16 (d, 1H, J = 6.6 Hz, $H_{\alpha'}$), 8.89 (s, 1H, 5-H), 9.77 (s, 1H, NH, exchangeable with D_2O), 10.31 (brs, 1H, NH, exchangeable with D_2O). ^{13}C NMR: 116.4 (C-9), 116.5 (C-4a), 118.9 (C-5a), 125.2 (C-7), 125.6 ($C_{\beta,\beta'}$), 130.7 (C-6), 133.9 (C_γ), 134.4 (C-8), 135.9 ($C_{\alpha,\alpha'}$), 148.3 (C-5), 153.9 (C-9a), 159.3 (C-10a), 193.6 (C-4). MS (*m/z*, I %): 361 (M^+, 2%). Anal. calcd. for $C_{15}H_{12}N_3O_2PS_2$ (361.37): C, 49.85%; H, 3.35%; N, 11.63%; S, 17.75%. Found: C, 49.51%; H, 3.13%; N, 11.30%; S, 17.48%.

2-(4-Methoxyphenyl)-4-oxo-2-sulfido-2,3-dihydro-4*H*-chromeno[2,3-*d*][1,3,2]diaza-phosphinine (5)

LR (1 g, 5 mmol) was added to a solution of **1** (0.94 g, 5 mmol) in dry dioxane (30 mL). The mixture was heated under reflux for 7 h. The formed solid was filtered off and washed with hot dioxan to give a yellow solid in 56% yield; mp. 250−252 °C. IR, (*v* max, cm^{-1}): 3367 (br, NH), 3051 (C-H_{arom}), 1720 (C=O), 1673 (C=N), 1611, 1598 (C=C), 1077 (O-C), 651 (P=S). ^{1}H NMR: 3.74 (s, 3H, OCH_3), 6.25 (d, 1H, J_{NHP} = 100 Hz, NH exchangeable with D_2O), 6.77 (d, 2H, *J* = 8.0 Hz, 3'-H, 5'-H), 6.85 (d, 1H, *J* = 7.5 Hz, 9-H), 7.37 (t, 1H, *J* = 8.0 Hz, 7-H), 7.47 (d, 2H, *J* = 8.0 Hz, 2'-H, 6'-H), 7.55 (t, 1H, *J* = 7.8 Hz, 8-H), 7.74 (d, 1H, *J* = 8.0 Hz, 6-H), 8.87 (s, 1H, 5-H). ^{13}C NMR: 55.3 (OCH_3), 110.6 (C-3',5'), 113.1 (C-9), 116.8 (C-4a), 118.0 (C-5a), 125.6 (C-7), 129.1 (C-2',6'), 130.7 (C-6), 132.8 (C-1'), 135.0 (C-8), 147.4 (C-5), 150.0 (C-4'), 154.0 (C-9a), 157.9 (C-10a), 160.5 (C-4). ^{31}P NMR: 54.6 ppm. MS (*m/z*, I %): 358 [$(M+2)^+$, 17%), 356 (M^+, 56%). Anal. calcd. for $C_{17}H_{13}N_2O_3PS$ (356.33): C, 57.30%; H, 3.68%; N, 7.86%; S, 9.00%. Found: C, 57.02%; H, 3.43%; N, 7.57%; S, 8.69%.

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