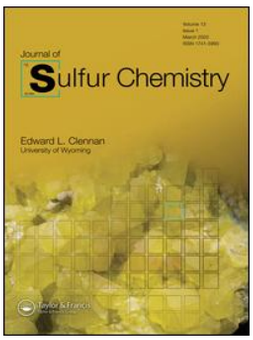

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A convenient one-pot synthesis of novel functionalized thiophene, thieno[2,3-*b*] thiophene, thiopyran, and thiopyrano[2,3-*b*]thiopyran bearing phosphonate groups

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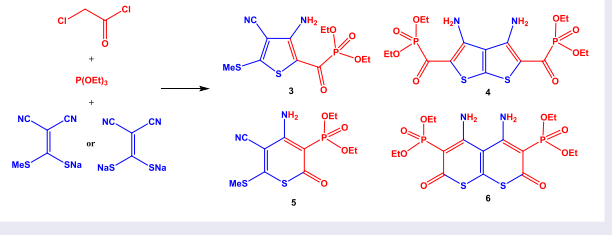
ABSTRACT

Design of some novel functionalized thiophene, thieno[2,3-*b*] thiophene, thiopyran and thiopyrano[2,3-*b*]thiopyran bearing phosphonate groups was described in one-pot through simple two steps. The methodology depended on the reaction of three-component of chloroacetyl chloride with triethyl phosphite in the presence of sodium 2,2-dicyanoethene-1,1-bis(thiolate) or sodium (2,2-dicyano-1-methylthioethen-1-yl)thiolate in a certain sequence.



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Synthesis; one-pot; thiophene; thiopyran; phosphonate

1. Introduction

Sulfur-containing heterocyclic compounds have a broad range of biological and pharmacological activities [1]. Thiophene and thiopyran compounds as classes of sulfur-containing heterocycles are rapidly becoming important classes of therapeutic agents and are likely to replace many existing pharmaceuticals in the near future [2]. They are reported to possess variable pharmaceutical applications such as anti-inflammatory [3], antifungal [4,5], anticancer [6,7] and antimicrobial [8,9] agents. Substituted thiophenes and thiopyrans and their derivatives are known since the 1950s. One of the most recent synthetic pathways for their preparation is based on the cyclisation of ketene dithioacetals, obtained from carbon disulfide in basic media [10–13]. The intermediates of ketene dithioacetal disodium salt are reacted generally with the methylene active halides in order to obtain

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thiophenes and thiopyrans [14–16]. On the other hand, Acyl phosphonate is a useful member of the class of organophosphorus compounds that can be used as a reagent to access P-atom containing organic structures. Having a phosphonate group in the structure may enhance the biological activity of a parent structure [17,18]. Acyl phosphonates are used in many reactions and they act as electrophiles and easily react with electron-rich reagents [19]. In continuation of our work in the development of expected bioactive phosphorus compounds [20–24], we herein describe the synthesis of novel and expected biologically active phosphonate-containing thiophenes and thiopyrans. To the best of our knowledge, there has been no report available on the synthesis of thiophenes and thiopyrans bearing phosphonate groups, which were synthesized in the present study.

2. Results and discussion

2.1. Chemistry

In this paper, and as a consequence of our previous work, on the simple synthesis of heterocyclic compounds bearing phosphonate groups of biological interest [25,26], we investigated a novel efficient protocol that was developed for the construction of functionalized thiophene, thieno[2,3-b]thiophene, thiopyran and thiopyrano[2,3-b]thiopyran *via* three-component reaction in different sequences in refluxing tetrahydrofuran. The starting materials sodium 2,2-dicyanoethene-1,1-bis(thiolate) (**1**) [27] and sodium (2,2-dicyano-1-methylthioethen-1-yl)thiolate (**2**) [28] were prepared according to the reported methods in the literature (Figure 1).

Firstly, one-pot three-component condensation of sodium 1-cyano-2-methylthioethylene-2-thiolate (**2**), chloroacetyl chloride and triethyl phosphite in a certain sequence afforded diethyl[(3-amino-4-cyano-5-methylthio)thiophene-2-carbonyl] phosphonate (**3**) (Figure 1). Thus, heating of triethyl phosphite with chloroacetyl chloride for 3 h at 150°C formed the intermediate **A** [29]. When compound **2** was added to the intermediate **A** and stirred in THF for one hour at room temperature gave the nonisolable intermediate **B** which underwent cyclization by increasing the temperature to 50°C in the presence of triethylamine to isolate diethyl[3-amino-4-cyano-5-methylthiothiophene-2-carbonyl]phosphonate (**3**) (Figure 2). In the same manner, tetraethyl[3,4-diaminothieno[2,3-*b*]thiophene-2,5-dicarbonyl]bis(phosphonate) (**4**) was constructed in using a one-pot three-component reaction. Therefore, the intermediate **A** was stirred with half equimolar amount of sodium 2,2-dicyanoethene-1,1-bis(thiolate) (**1**) in THF for one hour at room temperature, followed by heating for 3 h at 50°C in the presence of triethylamine to isolate the target product **4** as shown in Figure 2.

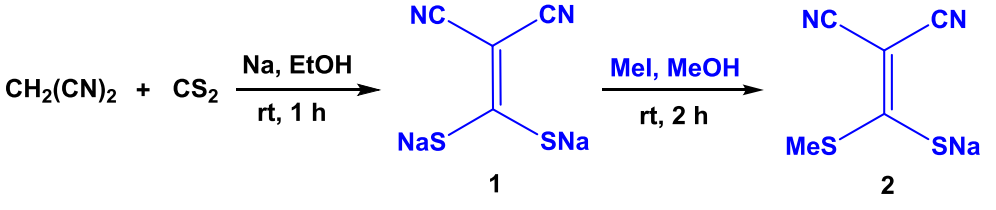

Figure 1. The preparation of starting materials **1** and **2**.

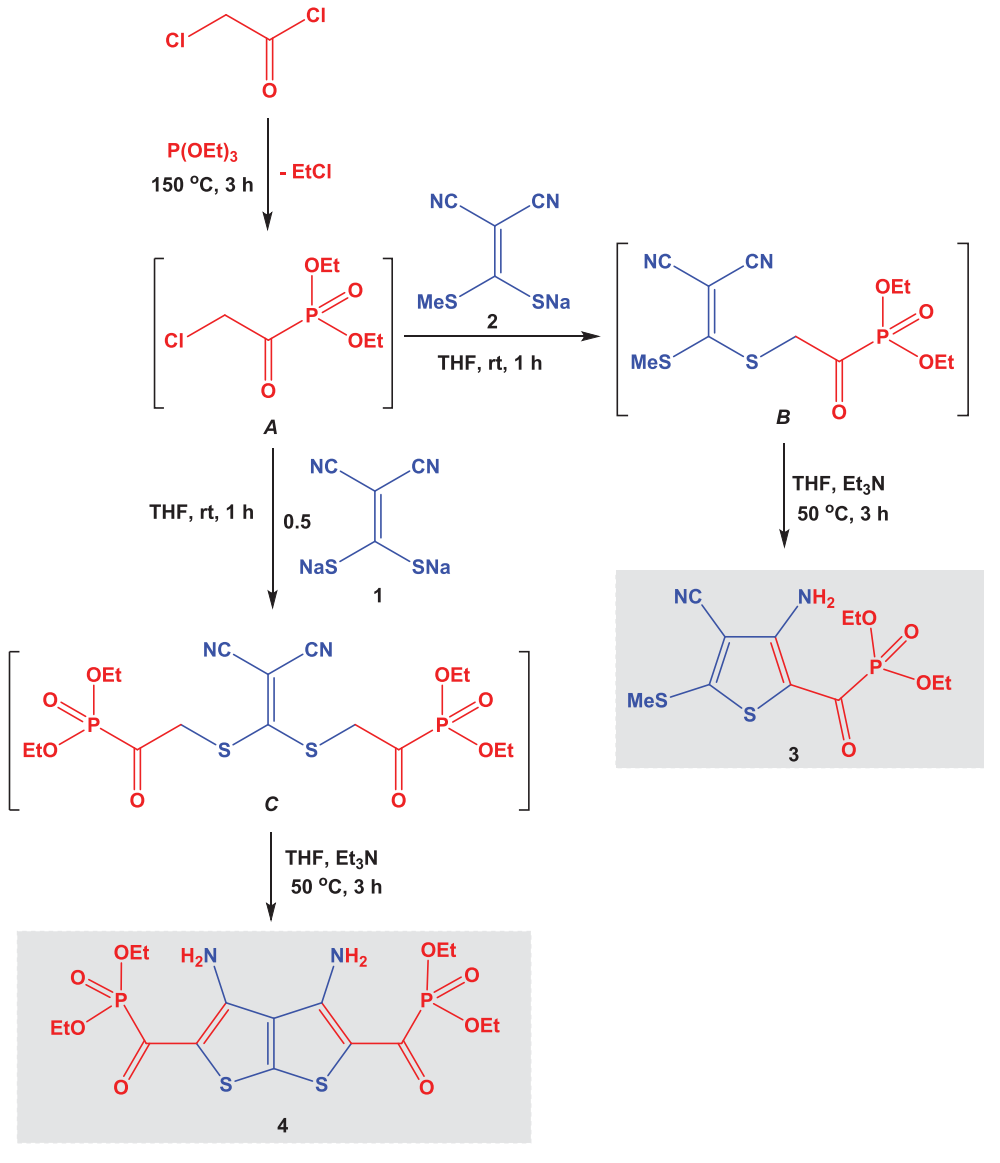

Figure 2. The reaction of chloroacetyl chloride with triethyl phosphite then with substrates **1** and **2**.

Using the same protocol, the prepared sodium 1-cyano-2-methylthioethylene-2-thiolate (**2**) reacted with an equimolar amount of chloroacetyl chloride in THF at room temperature for 1 h to give the nonisolable chloroacetyl derivative **D**. Then, triethyl phosphite was added to the previous mixture and stirred at 60−70°C for 3 h, followed by the addition of a few drops of triethylamine to isolate diethyl(4-amino-5-cyano-6-methylthio-2-oxo-2*H*-thiopyran-3-yl) phosphonate (**5**) in good yield (Figure 3).

Finally, sodium 2,2-dicyanoethene-1,1-bis(thiolate) (**1**) was stirred with two-fold equivalents of chloroacetyl chloride in THF at room temperature for 1 h to give the intermediate **D**. Adding of triethyl phosphite then heating under reflux at 60−70°C for 3 h generated the

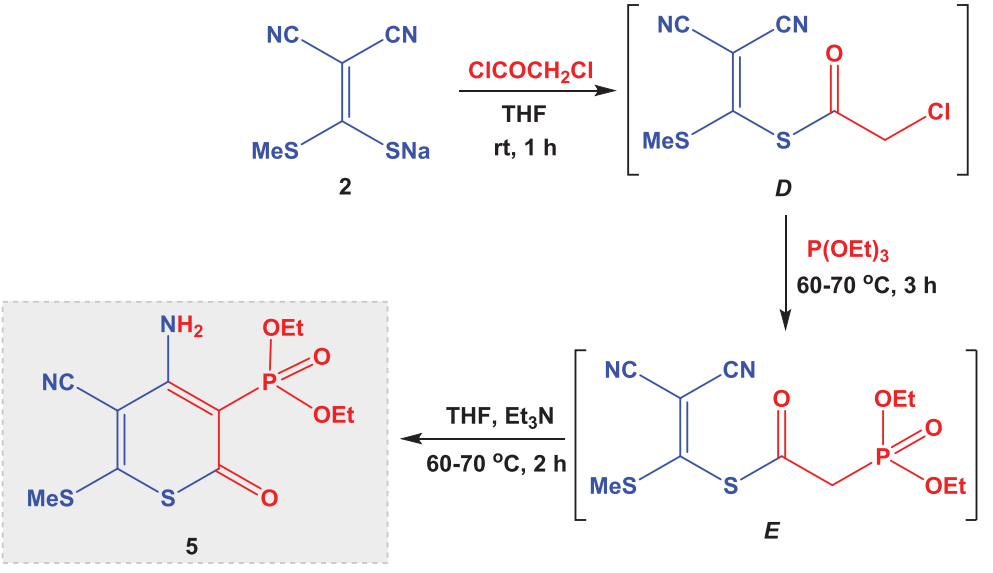

Figure 3. The reaction of chloroacetyl chloride with substrate **2** then with triethyl phosphite.

intermediate **H** that underwent cyclization by th help of triethylamine after another 3 h at the same temperature to yield the interesting system **6** in moderate yield (Figure 4).

2.2. Spectral characterization

The structures of all synthesized compounds **3**–**6** were deduced by IR, NMR and MS spectral and elemental analysis. The IR spectra of compounds **3** and **5** displayed important absorption bands at 3385–3102 (NH_2), 2257–2225 (CN), 1680–1706 (C=O), 1234–1147 (*P*=O) and 1004–1020 (P–O–C) cm^{-1}. The ^{1}H-NMR spectra of products **3** and **5** exhibited singlets in the region δ 2.98–2.92 ppm due to the methylsulfanyl protons. The NH_2 protons in product **3** resonated as two singlets at δ 7.04 and 7.06 ppm while the same group also resonated as one singlet at δ 6.41 ppm in product **5**. The diethyl phosphonate protons in both products were displayed at δ 1.03–0.77 (CH_3) and 4.01–3.42 (OCH_2). Moreover, their ^{13}C-NMR spectra exhibited the characteristic carbon atoms MeS, CN, CH_3 and OCH_2 in the regions δ 16.5–19.7, 114.9–112.2, 16.7–14.4 and 61.9–57.7 ppm, respectively. The carbon atom of the C=O group in compound **3** resonated as a doublet at δ 184.2 with coupling constant 252 Hz, while the carbon atom C–3 in product **5** appeared as a doublet at δ 105.1 ppm with coupling constant 236 Hz [30]. The presence of phosphonate groups in both products was confirmed by ^{31}P-NMR spectra that showed peaks at δ 23.07 and 26.32 ppm, respectively [31].

Infrared spectra of both compounds **4** and **6** showed new absorption bands for the NH_2 groups at 3385–3167 cm^{-1} and so endorsed the presence of C=O groups at 1667 and 1668 cm^{-1}, respectively. Their ^{1}H-NMR spectra showed two characteristic signals at δ 9.20 and 9.22 for NH_2 protons in product **4** and also two singlets at δ 5.79 and 5.97 ppm for the two NH_2 groups in product **6** [32]. The ethoxy protons in both products appeared in the regions

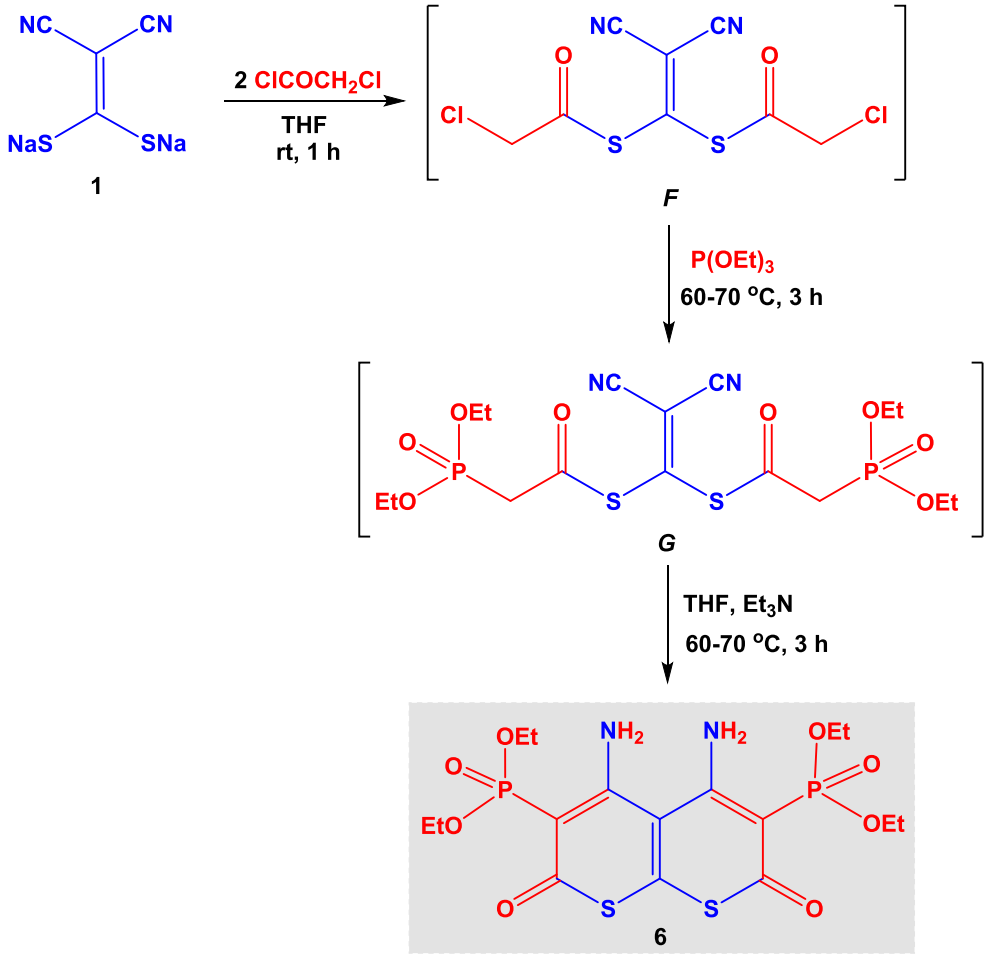

Figure 4. The reaction of chloroacetyl chloride with substrate **1** then with triethyl phosphite.

δ 1.03−1.15 (t, J = 6.8 Hz, CH_3) and 3.52−3.69 (m, OCH_2) ppm. Furthermore, the ^{13}C-NMR spectrum of structure **4** revealed signals at δ 16.9, 17.6 (2 CH_3), 58.1, 58.9 (2 OCH_2) and 190.9 (d, J_{PC} = 253 Hz, 2 C=O), while compound **6** exhibited specific carbon atoms at δ 15.1, 15.8 (2 CH_3), 57.7, 58.7 (2 OCH_2), 103.2 (d, J_{PC} = 228 Hz, C−3,6) and 189.0 (C=O). The ^{31}P-NMR spectra of compounds **4** and **6** appeared at δ 22.51 and 24.55 ppm, respectively, as expected. Furthermore, their mass spectral data confirmed the proposed structures.

3. Conclusion

A facile route was used to synthesize novel functionalized thiophene, thieno[2,3-*b*] thiophene, thiopyran and thiopyrano[2,3-*b*]thiopyran bearing phosphonates. The simple and efficient one-pot three-component approach and the catalyst-free and mild reaction conditions make the present methodology a good synthetic procedure. We hope that this

approach may be of value to others seeking novel synthetic fragments with unique properties for medicinal chemistry.

4. Experimental

4.1. General remarks

The melting points were measured on a digital Stuart SMP-3 apparatus in an open capillary tube. Infrared spectra were measured on FT-IR spectrophotometer (Nicolet iS10) using KBr disks. The NMR spectra were recorded on a Bruker 400 MHz instrument in DMSO using TMS as an internal standard. Mass spectra were recorded on direct probe controller inlet part to single quadropole mass analyzer in (Thermo Scientific GCMS). Elemental microanalysis was performed on Perkin-Elmer 2400II at the Chemical War department, Ministry of Defense, Egypt. The purity of the synthesized compounds was checked by thin layer chromatography (TLC) and elemental microanalysis.

4.2. Synthesis of diethyl(3-amino-4-cyano-5-methylsulfanylthiophene-2-carbonyl) phosphonate (3)

A mixture of triethyl phosphite (2.5 mmol, 0.41 ml) and chloroacetyl chloride (3 mmol, 0.24 ml) was heated under reflux at 150°C for 3 h. The excess materials were removed under pressure. A solution of compound **2** (2.5 mmol, 0.44 g) in THF (10 ml) was added and stirred for 1 h at room temperature followed by adding a few drops of triethylamine and heated at 50°C for 3 h. The mixture was concentrated under pressure. The formed solid was filtered off, washed with water and crystallized from methanol to give a beige solid in 81% yield, mp 143−145°C. IR (KBr), (ν_{max}, cm^{-1}): 3341, 3184 (NH_2), 2976, 2922 (C−H_{aliph}), 2257 (CN), 1680 (C=O), 1615 (C=C), 1234 (*P*=O), 1004 (P−O−C). ^{1}H-NMR (400 MHz, DMSO-d_6): 0.77 (t, 3H, J = 6.8 Hz, CH_3), 1.03 (t, 3H, J = 6.8 Hz, CH_3), 2.98 (s, 3H, SCH_3), 3.98−4.01 (m, 4H, 2 OCH_2), 7.04, 7.06 (ss, 2H, NH_2). ^{13}C-NMR (100 MHz, DMSO-d_6): 14.4 (CH_3), 14.8 (CH_3), 16.5 (SCH_3), 61.4 (OCH_2), 61.9 (OCH_2), 98.8 (C−4), 107.6 (C−2), 114.9 (C≡N), 152.9 (C−3), 160.9 (C−5), 184.2 (d, J_{PC} = 252 Hz, C=O). ^{31}P-NMR (162 MHz, DMSO-d_6): 23.07 ppm. MS (*m/z*, I %): 334 (M^+, 6%). Anal. Calcd for $C_{11}H_{15}N_2O_4PS_2$ (334.34): C, 39.52%; H, 4.52%; N, 8.38%; S, 19.18%. Found: C, 39.34%; H, 4.41%; N, 8.19%; S, 18.99%.

4.3. Synthesis of tetraethyl[3,4-diaminothieno[2,3-b]thiophene-2,5-dicarbonyl]bis (phosphonate) (4)

A mixture of triethyl phosphite (5 mmol, 0.82 ml) and chloroacetyl chloride (6 mmol, 0.48 ml) was heated under reflux at 150°C for 3 h. The excess materials were removed under pressure. A solution of compound **1** (2.5 mmol, 0.46 g) in THF (20 ml) was added and stirred for 1 h at room temperature followed by adding a few drops of triethylamine and heated at 50°C for 3 h. The formed solid was filtered off, washed with water and crystallized from dioxane-ethanol (1:2) to give yellow solid in 69% yield, mp 252−253°C. IR (KBr), (ν_{max}, cm^{-1}): 3385, 3275, 3250, 3167 (NH_2), 2981, 2955, 2904 (C−H_{aliph}), 1667 (C=O), 1598 (C=C), 1262 (*P*=O), 1024 (P−O−C). ^{1}H-NMR (400 MHz,

DMSO-d_6): 1.03 (t, 6H, J = 6.8 Hz, 2 CH_3), 1.15 (t, 6H, J = 7.2 Hz, 2 CH_3), 3.54−3.69 (m, 8H, 4 OCH_2), 9.20, 9.22 (ss, 2H, NH_2). ^{13}C-NMR (100 MHz, DMSO-d_6): 16.9 (2 CH_3), 17.6 (2 CH_3), 58.1 (2 OCH_2), 58.9 (2 OCH_2), 108.4 (C−2,5), 125.7 (C−3a), 146.6 (C−6a), 150.8 (C−3,4), 190.9 (d, J_{PC} = 253 Hz, 2 C=O). ^{31}P-NMR (162 MHz, DMSO-d_6): 22.51 ppm. MS (*m/z*, I %): 498 (M^+, 22%). Anal. Calcd for $C_{16}H_{24}N_2O_8P_2S_2$ (498.44): C, 38.56%; H, 4.85%; N, 5.62%; S, 12.86%. Found: C, 38.41%; H, 4.71%; N, 5.43%; S, 12.72%.

4.4. Synthesis of diethyl(4-amino-5-cyano-6-methylsulfanyl-2-oxo-2H-thiopyran-3-yl) phosphonate (5)

A mixture of chloroacetyl chloride (3 mmol, 0.24 ml) and compound **2** (2.5 mmol, 0.44 g) in THF (15 ml) was stirred for 1 h at room temperature. Triethyl phosphite (2.5 mmol, 0.41 ml) was added to the previous mixture and heated under reflux at 60−70°C for 3 h. A few drops of triethylamine was added, and the mixture was heated at 60−70°C for 2 h. The mixture was concentrated under pressure. The formed solid was filtered off, washed with water and crystallized from ethanol to give yellow solid in 72% yield, mp 168−170°C. IR (KBr), (ν_{max}, cm^{-1}): 3385, 3284, 3102 (NH_2), 2934, 2893 (C−H_{aliph}), 2225 (C≡N), 1706 (C=O), 1604 (C=C), 1147 (P = O), 1020 (P−O−C). ^{1}H-NMR (400 MHz, DMSO-d_6): 1.03 (t, 6H, J = 6.8 Hz, CH_3), 2.92 (s, 3H, SCH_3), 3.42 (q, 4H, J = 6.8 Hz, 2 OCH_2), 6.41 (s, 2H, NH_2). ^{13}C-NMR (100 MHz, DMSO-d_6): 16.2 (CH_3), 16.7 (CH_3), 19.7 (SCH_3), 57.7 (OCH_2), 58.6 (OCH_2), 101.1 (C−5), 105.1 (d, J_{PC} = 236 Hz, C−3), 112.2 (CN), 153.0 (C−4), 158.8 (C−6), 180.0 (C=O).^{31}P-NMR (162 MHz, DMSO-d_6): 26.32 ppm. MS (*m/z*, I %): 334 (M^+, 10%). Anal. Calcd for $C_{11}H_{15}N_2O_4PS_2$ (334.34): C, 39.52%; H, 4.52%; N, 8.38%; S, 19.18%. Found: C, 39.42%; H, 4.44%; N, 8.21%; S, 19.02%.

4.5. Synthesis of tetraethyl(4,5-diamino-2,7-dioxo-2H,7h-thiopyrano[2,3-b]thiopyran-3,6-diyl)bis(phosphonate) (6)

A mixture of chloroacetyl chloride (6 mmol, 0.48 ml) and compound **1** (2.5 mmol, 0.46 g) in THF (5 ml) was stirred for 1 h at room temperature. Triethyl phosphite (5 mmol, 0.82 ml) was added to the previous mixture and heated under reflux at 60−70°C for 3 h. A few drops of triethylamine was added, and the mixture was heated at 60−70°C for 2 h. The formed solid was filtered off, washed with water and crystallized from ethanol to give orange solid in 75% yield, mp 218−220°C (dec). IR (KBr), (ν_{max}, cm^{-1}): 3385, 3279, 3252, 3167 (NH_2), 2984, 2904 (C−H_{aliph}), 1668 (C=O), 1590 (C=C), 1260 (P=O), 1022 (P−O−C). ^{1}H-NMR (400 MHz, DMSO-d_6): 1.03 (t, 6H, J = 6.8 Hz, 2 CH_3), 1.15 (t, 6H, J = 7.2 Hz, 2 CH_3), 3.52−3.69 (m, 8H, 4 OCH_2), 5.79, (s, 2H, NH_2), 5.97 (s, 2H, NH_2). ^{13}C-NMR (100 MHz, DMSO-d_6): 15.1 (2 CH_3), 15.8 (2 CH_3), 57.7 (2 OCH_2), 58.7 (2 OCH_2), 103.2 (d, J_{PC} = 228 Hz, C−3,6), 110.1 (C−4a), 146.6 (C−6a), 158.7 (C−5), 189.0 (2 C=O). ^{31}P-NMR (162 MHz, DMSO-d_6): 24.55 ppm. MS (*m/z*, I %): 498 (M^+, 36%). Anal. Calcd for $C_{16}H_{24}N_2O_8P_2S_2$ (498.04): C, 38.56%; H, 4.85%; N, 5.62%; S, 12.86%. Found: C, 38.43%; H, 4.68%; N, 5.47%; S, 12.74%.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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