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Furoyl Phosphonates

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Abstract—A series of furoyl phosphonates bearing methyl, methoxymethyl, and diethoxyphosphorylmethyl groups in the furan ring have been synthesized via the Arbuzov reaction from the corresponding acid chlorides. NMR spectral parameters of the prepared compounds were studied. The values of coupling constants between the phosphorus nuclei and the carbon nuclei of the furan ring have been examined with relation to the location of the acylphosphoryl group in the furan ring, the nature of second substituent, and location of the latter with respect to the phosphorus-containing substituent in the furan ring. The substitution in position 4 of the furan ring of 3-furoyl phosphonates has been shown to strongly decrease the value of the coupling constant between the phosphorus nucleus and the C^2 atom of the heterocycle. The interaction between the phosphorus nuclei has not been detected in the spectra of the compounds containing both diethoxyphosphorylmethyl and acylphosphonate fragments.

Keywords: acyl phosphonate, furoyl chloride, the Arbuzov reaction, spin-spin coupling constant

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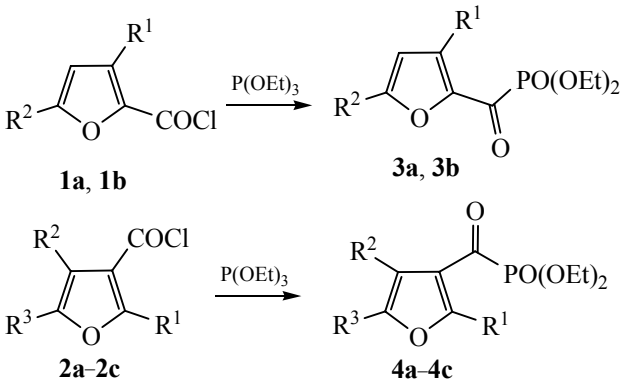
Acyl phosphonates have been extensively studied [1,2] as available compounds capable of wide range of chemical transformations. At the same time, first furan derivatives of class have been synthesized quite recently [3]. Since then, no attempts to utilize furoyl phosphonates in organic synthesis have been reported.

In this work we have proposed the methods of preparation of furoyl phosphonates containing the substituents allowing their further functionalization. For instance, methyl and methoxymethyl groups have been chosen in view of the pathway to halomethyl compounds, alkoxycarbonyl group can be used in a wide range of transformations as well, and diethoxyphosphorylmethyl group is a CH-acidic center.



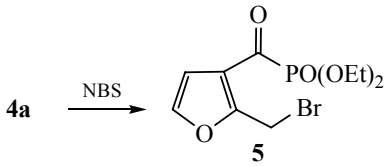
$R^1 = CH_3$, $R^2 = H$ (**1a**, **3a**); $R^1 = H$, $R^2 = CH_3$ (**1b**, **3b**); $R^1 = CH_3$, $R^2 = R^3 = H$ (**2a**, **4a**); $R^1 = R^3 = H$, $R^2 = CH_3$ (**2b**, **4b**); $R^1 = R^2 = H$, $R^3 = CH_3$ (**2c**, **4c**).

Phosphorylation of acid chlorides of methylfuran-2- (**1a, 1b**) and 3-carboxylic acids (**2a–2c**) was carried out in benzene in the presence of slight excess of triethyl phosphite. The reaction was complete in 2–3 h and led to formation of the corresponding phosphonate **3a, 3b** and **4a–4c**. Diethyl ethanephosphonate was found as the only side product. Reduction of the carbonyl group and formation of 1,1-bis(phosphonates) characteristic of the reaction with trimethyl phosphite [3] were not observed.

The phosphonates **3a, 3b** and **4a–4c** were colorless high-boiling oils gradually turning yellow when exposed to light. Structure of the compounds was elucidated using NMR spectroscopy data. ^{31}P NMR spectra of compounds **3a, 3b** and **4a–4c** contained signals of the phosphorus nuclei in the range of –1.2 to –3.1 ppm. The ^{13}C signal of the carbonyl carbon atom in the 2-furoyl derivatives was a doublet around 182 ppm ($^1J_{PC}$ = ≈180 Hz). In the case of the 3-furoyl compounds, the doublet of the carbonyl carbon atom

was located at 192–194 ppm, its $^1J_{PC}$ coupling constant being the same.

In order to investigate the possibility of functionalization of the prepared phosphonate at the methyl group, we attempted the bromination of compound **4a** with *N*-bromosuccinimide initiated with azobisisobutyronitrile. The reaction was carried out in carbon tetrachloride.

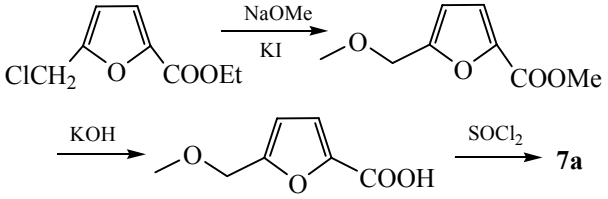


The bromination occurred selectively at the methyl group. ^{1}H NMR spectrum of the product **5** contained the signal of bromomethyl group protons at 4.71 ppm. ^{13}C signal of the corresponding carbon atom was observed at 21.15 ppm. The ^{31}P signal of phosphorus atom shifted downfield from –1.76 ppm (compound **4**) to –2.84 ppm.

The synthesized bromide readily eliminated hydrogen bromide on cooling. When treated with the solution of urotropine in chloroform at room temperature, it formed urotropine hydrobromide within 10 min after mixing the reagents. Hence, formation of the 2-bromomethyl derivative of 3-furoyl phosphonate was reliably registered by spectral methods, but its application in further transformations was limited due to hydrogen bromide elimination followed by formation of the polymer.

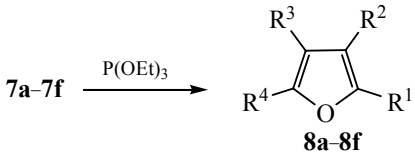
In view of that, we attempted phosphorylation of 2-chloromethyl-3-furoyl chloride. The reaction was carried out in benzene in the presence of slight excess of triethyl phosphite. The process was not selective even at room temperature. A complex set of products was formed, as reflected in the presence of 11 signals of phosphorus nuclei over –13.24 to 20.03 ppm in the ^{31}P NMR spectrum of the reaction mixture. The presence of phosphonate signals was especially surprising, since substitution of chlorine in ethyl 2-chloromethyl-3-furoate under conditions of the Arbuzov reaction required heating to 165–170°C.

Hence, introduction and necessary transformations of the acylphosphoryl group should precede any other functionalization of the furan ring. Methoxymethyl group is convenient in this instance, since it can be easily converted into bromomethyl one upon treatment with triphenylphosphine dibromide, being fairly inert under conditions of majority of transformations involving carbonyl group of acyl phosphonate. In view of that, we studied the synthesis of isomeric methoxymethyl derivatives of 2- and 3-furoyl phosphonates. The corresponding acid chlorides **7a–7f** prepared from available alkyl halomethylfuroates (the scheme of preparation of compound **7a** given below exemplifies the procedure) were chosen as the starting compounds.



Addition of 5 mol % of potassium iodide as catalyst allowed smooth substitution even in the case of relatively inert ethyl 4-chloromethyl-3-furoate. Synthesis of the acid chlorides was never accompanied by cleavage of the ether bond in the methoxymethyl fragment.

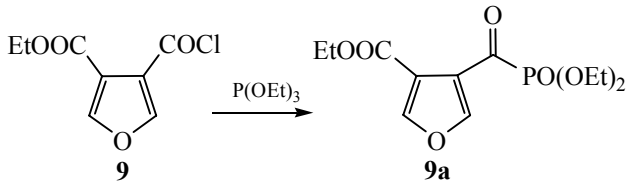
Phosphorylation of the corresponding acid chlorides **7a–7f** was carried out similarly to that of compounds **1** and **2**. The Arbuzov reaction occurred within 2–3 h to yield furoyl phosphonates **8a–8f**. Their spectral parameters were close to those of the methyl derivatives **3** and **4**.



R^1 = C(O)P(O)(OEt)$_2$, R^2 = R^3 = H, R^4 = CH_2OCH_3 (**8a**);
R^1 = C(O)P(O)(OEt)$_2$, R^2 = H, R^3 = CH_2OCH_3, R^4 = Me (**8b**);
R^1 = C(O)P(O)(OEt)$_2$, R^2 = CH_2OCH_3, R^3 = R^4 = H (**8c**);
R^1 = CH_2OCH_3, R^2 = C(O)P(O)(OEt)$_2$, R^3 = R^4 = H (**8d**);
R^1 = R^4 = H, R^2 = C(O)P(O)(OEt)$_2$, R^3 = CH_2OCH_3 (**8e**);
R^1 = R^3 = H, R^2 = CH_2OCH_3, R^4 = C(O)P(O)(OEt)$_2$ (**8f**).

The ester group is another moiety convenient for further transformations and inert under the conditions of phosphorylation. The available 4-(ethoxycarbonyl)-3-furoyl chloride **9** is of special interest among the alkoxycarbonyl derivatives of furoyl chlorides: it potentially opens the way to preparation of the phosphorylated analogs of 3-functionalyzed furans, found in natural compounds. The acid chloride **9** was phosphorylated via the Arbuzov reaction similarly to the above-described compounds, to afford the acyl phosphonate **9a**. The obtained compound was stabile below

80°C but was decomposed below its boiling point when heated in vacuum.

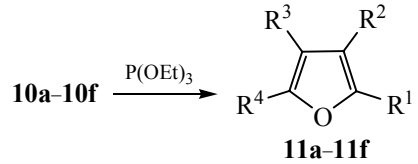


9 **9a**

Analysis of the spectral data revealed that for the studied furoyl phosphonates the ^{31}P chemical shift ranged between –1.9 and –3.6 ppm. It was independent of the location of the phosphorus-containing fragment in the furan ring and the presence of the other substituents. On the contrary, the value of the coupling constant between the phosphorus and the carbonyl carbon atom depended on the substitution pattern of the furan ring, being of 184–188 Hz in 2-furoyl phosphonates and decreases to 181–183 Hz in the case of the 3-furoyl derivatives. When position 4 of the furan ring was occupied by methyl or methoxymethyl group (as in the case of compounds **4b** and **8e**), the $^{1}J_{PC}$ value was down to 178.3 Hz and 180.4 Hz, respectively. The change of the $^{2}J_{PC}$ value (the interaction between the phosphorus atom and the adjacent carbon atom of the furan ring) revealed certain specific features as well. In the case of furoyl phosphonates, it was several times higher than the coupling constant typical of furylmethane phosphonates. On top of that, its value depended on the location of the acyl phosphonate group in the furan ring. In 2-furoyl phosphonates, $^{2}J_{PC}$ ranged between 89 and 91 Hz if position 3 of the furan ring is not occupied. In the presence of methyl (**3a**) or the methoxymethyl (**8c**) group $^{2}J_{PC}$ value decreased to 60.1 Hz and 60.6 Hz, respectively. In 3-furoyl phosphonates, the $^{2}J_{PC}$ value was 68–70 Hz, except for the 2-methoxymethyl derivative **8d** exhibiting the $^{2}J_{PC}$ value as high as 86.5 Hz.

We have earlier applied the NMR spectroscopy method to study the interaction of the phosphorus nuclei of diethoxyphosphorylmethyl groups located at various positions of the furan ring [4,5]. In the present work, phosphorylation of the corresponding (diethoxyphosphorylmethyl)furoyl chlorides **10a–10f** afforded the bis(phosphonates) **11a–11f**, and the influence of two different phosphorus atoms on the parameters of the ^{13}C and ^{31}P NMR spectra was examined.

Phosphorylation of the phosphorus-containing acid chlorides **10a–10f** was carried out with triethyl phosphite via the Arbuzov reaction as described above. The obtained bis(phosphonates) **11a–11f** were highly viscous syrups decomposing on heating in vacuum.



11a–11f

$R^1 = C(O)P(O)(OEt)_2$, $R^2 = R^3 = H$, $R^4 = CH_2P(O)(OEt)_2$ (**11a**); $R^1 = C(O)P(O)(OEt)_2$, $R^2 = H$, $R^3 = CH_2P(O)(OEt)_2$, $R^4 = Me$ (**11b**); $R^1 = C(O)P(O)(OEt)_2$, $R^2 = CH_2P(O)(OEt)_2$, $R^3 = R^4 = H$ (**11c**); $R^1 = CH_2P(O)(OEt)_2$, $R^2 = C(O)P(O)(OEt)_2$, $R^3 = R^4 = H$ (**11d**); $R^1 = R^4 = H$, $R^2 = C(O)P(O)(OEt)_2$, $R^3 = CH_2P(O)(OEt)_2$ (**11e**); $R^1 = R^3 = H$, $R^2 = CH_2P(O)(OEt)_2$, $R^4 = C(O)P(O)(OEt)_2$ (**11f**).

The ^{31}P chemical shifts of the acyl phosphonate group (from –2.1 to –3.6 ppm) and of the methanephosphonate one (23.7–25.6 ppm for β-substituted furans and 20.5–21.6 ppm for α-substituted ones) in compounds **11a–11f** coincided with the values for compounds containing a single phosphorus atom. The coupling between the phosphorus atoms was never observed in the ^{31}P NMR spectra. The value of the coupling constant between the phosphorus atom and the C^2 carbon atom of the furan ring in compound **11c** ($^{2}J_{PC}$ = 58.9 Hz) was lower than that observed for 2-furoyl phosphonates and bis(phosphonates) **11a, 11b** ($^{2}J_{PC}$ = 90 Hz).

The effects of location of the acylphosphonate fragment and the nature of second substituent on the $^{3}J_{PC}$ constant of the coupling between the acyl phosphorus atom and the carbon atoms of the furan ring can be exemplified by the series of compounds **3a**, **8c**, **11c**; **4a**, **8d**, **11d**; and **4b**, **8e**, **11e**, **9a**. For compounds **3a**, **8c**, and **11c**, the $^{3}J_{P(C^3)}$ value somewhat increased in the $CH_3 < CH_2OCH_3 < CH_2PO(OEt)_2$ substituent series, being close to 9 Hz. In that case, the transfer of the interaction was opposite to the direction of the electronic density polarization in the furan ring induced by the oxygen atom. For compounds **4a**, **8d**, and **11d**, two coupling types with constants $^{3}J_{P(C^4)}$ and $^{3}J_{P(C^2)}$ were possible. The former one was not revealed, meaning that the magnetic interaction in the direction perpendicular to the direction of polarization of the electronic density was absent. The value of the second constant was independent of the nature of the substituent in the position 2, being close to 15 Hz at the average. That reflected the transfer of the magnetic interaction codirectional with the polarization of heterocycle. Hence, transfer of the magnetic interaction

between the phosphorus and carbon nuclei in the latter case was more efficient.

The situation was more complicated for the series of compounds **4b**, **8e**, **11e**, **9a**. In that case, the spin-spin coupling constants $^3J_{P(C^4)}$ and $^3J_{P(C^2)}$ were observed on top of the increase in the electron-accepting properties of the substituent located in position 4 of the heterocycle [CH_3 < CH_2OCH_3 < $CH_2PO(OEt)_2$ < COOEt]. The $^3J_{P(C^4)}$ value was only slightly varied, being of 10.5 Hz on the average. The so high value has been never observed previously for phosphonomethyl derivatives. The $^3J_{P(C^2)}$ value for compounds **4b**, **8e**, **11e** ranged between 3.7 and 3.9 Hz, being much lower than has been earlier observed. The $^3J_{P(C^2)}$ value was decreased to 2.8 Hz with the appearance of ethoxycarbonyl group in the structure; that was probably characteristic exclusively for acyl phosphonates, since such effect has not been observed for phosphonomethyl compounds.

The changes of the $^2J_{PC}$ and $^3J_{PC}$ coupling constants between the phosphorus atom of the phosphonomethyl group and the carbon atoms of the furan ring could be followed using bis(phosphonates) **11c–11e**. In the case of the phosphonate **11c**, $^2J_{PC^3}$ and $^3J_{PC^2}$ coupling constants exhibited the usual values of 9.3 and 9.8 Hz, respectively, whereas the coupling constant $^3J_{PC^4}$ was not observed. In the case of phosphonate **11d**, $^2J_{PC^2}$ and $^3J_{PC^3}$ were as large as 14.7 Hz and 7.4 Hz, respectively. Comparison of the listed values showed that the relationship between the coupling constant value and the orientation of the P–C magnetic interaction with respect to the direction of electronic density polarization in the furan ring earlier established for the phosphonomethyl derivatives [4, 5] was observed in presence of the acyl phosphonate substituent as well. For the phosphonate **11e**, the $^2J_{PC^4}$ constant value was typical (9.8 Hz), and the coupling constant $^3J_{PC^5}$ was smaller than usual (7.8 Hz). The $^3J_{PC^3}$ coupling constant was unexpectedly high (5.9 Hz). Probably, in such compounds the P^3 phosphorus atom of the acylphosphonate group efficiently interacted with the C^4 carbon atom (cf. the series of compounds **4b**, **8e**, **11e**, **9a**), and also the magnetic interaction of the P^4 phosphonomethyl phosphorus atom with the C^5 carbon atom of the furan ring was significantly enhanced in presence of the acylphosphonate moiety.

In summary, it was shown that phosphorylation of furoyl chlorides with triethyl phosphite under conditions of the Arbuzov reaction led to formation of furoyl phosphonates. The method was applicable for the wide range of compounds bearing different substituents in the furan ring. It was established that magnetic interactions between the phosphorus atom and carbon atoms of the furan ring in diethoxyphosphorylmethyl derivatives of furoyl phosphonates differed significantly from that operative in bis(di-ethoxyphosphorylmethyl)furans. The presence of the acyl phosphonate group significantly altered the generally observed values of the J_{PC} coupling constants. Magnetic interaction between phosphorus nuclei of the phosphonomethyl and acyl phosphonate groups was not revealed in the spectra.

EXPERIMENTAL

^1H, ^{13}C, and ^{31}P NMR spectra were registered using a Bruker DPX-400 spectrometer (400.13 MHz ^1H, 161.97 MHz ^{31}P, 100.16 MHz ^{13}C) in $CDCl_3$.

Methyl methoxymethylfuroates *(general procedure)*. 30 mmol of ethyl chloromethyl- or bromomethylfuroate dissolved in 30 mL of toluene and 1.5 mmol of finely crumbled potassium iodide were added to a solution of sodium methylate prepared via dissolution of 36 mmol of sodium in 20 mL of methanol. The reaction mixture was refluxed with stirring during 10 h. After cooling, the precipitate was filtered off, the solvent was removed on a rotary evaporator, and the residue distilled in vacuum.

Methyl 5-methoxymethyl-2-furoate. Yield 66%, colorless oil, bp 94–96°C (1 mmHg). ^1H NMR spectrum, δ, ppm: 3.28 s (3H, CH_3O), 3.77 s (3H, $\underline{C}H_3OOC$), 4.34 s (2H, OCH_2-furan), 6.34 d (1H, H^4-furan, J_{HH} = 3.4 Hz), 7.03 d (1H, H^3-furan, J_{HH} = 3.4 Hz).

Methyl 5-methyl-4-methoxymethyl-2-furoate. Yield 53%, colorless oil, bp 92°C (1 mmHg). ^1H NMR spectrum, δ, ppm: 2.32 s (3H, CH_3-furan), 3.28 s (3H, CH_3O), 3.81 s (3H, $\underline{C}H_3OOC$), 4.21 s (2H, OCH_2-furan), 7.03 s (1H, H^3-furan).

Methyl 3-methoxymethyl-2-furoate. Yield 66%, colorless oil, bp 79–80°C (1 mmHg). ^1H NMR spectrum, δ, ppm: 3.35 s (3H, CH_3O), 3.84 s (3H, $\underline{C}H_3OOC$), 4.62 s (2H, OCH_2-furan), 6.57 br.s (1H, H^4-furan), 7.45 br.s (1H, H^5-furan).

Methyl 2-methoxymethyl-3-furoate. Yield 46%, colorless oil, bp 76°C (1 mmHg). ^1H NMR spectrum, δ, ppm: 3.38 s (3H, CH_3O), 3.83 s (3H, $\underline{C}H_3OOC$), 4.72 s (2H, OCH_2-furan), 6.68 br.s (1H, H^4-furan), 7.35 br.s (1H, H^5-furan).

Methyl 4-methoxymethyl-3-furoate. Yield 64%, colorless oil, bp 67°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 3.41 s (3H, CH_3O), 3.80 s (3H, $\underline{C}H_3OOC$), 4.54 s (2H, OCH_2-furan), 7.41 br.s (1H, H^5-furan), 7.95 d (1H, H^2-furan, J_{HH} = 1.6 Hz).

Methyl 5-methoxymethyl-3-furoate. Yield 70%, colorless oil, bp 87°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 3.34 s (3H, CH_3O), 3.81 s (3H, $\underline{C}H_3OOC$), 4.37 s (2H, OCH_2-furan), 6.15 s (1H, H^4-furan), 7.97 s (1H, H^2-furan).

Methoxymethylfuroic acids *(general procedure)*. 30 mmol of methyl methoxymethylfuroate was added to a solution of 40 mmol of potassium hydroxide in a mixture of 5 mL of water and 40 mL of ethanol. The obtained mixture was refluxed with stirring during 7 h and then evaporated to dryness on a rotary evaporator. The residue was dissolved in the minimum amount of water and acidified with concentrated hydrochloric acid to pH 2–3. The formed precipitate was filtered off and dried in air to constant mass.

5-Methoxymethyl-2-furoic acid. Yield 71%, colorless crystals with mp 69–70°C.

5-Methyl-4-methoxymethyl-2-furoic acid. Yield 99%, colorless crystals with mp 82°C.

3-Methoxymethyl-2-furoic acid. Yield 93%, colorless crystals with mp 146°C.

2-Methoxymethyl-3-furoic acid. Yield 72%, colorless crystals with mp 792°C.

4-Methoxymethyl-3-furoic acid. Yield 90%, colorless crystals with mp 135°C.

5-Methoxymethyl-3-furoic acid. Yield 96%, colorless crystals with mp 94°C.

Methoxymethylfuroyl chlorides *(general procedure)*. 45 mmol of thionyl chloride and 5 drops of DMF were added to a suspension of 30 mmol of methoxymethylfuroic acid in 40 mL of benzene. The obtained mixture was refluxed with stirring during 8 h. The target product was isolated via vacuum distillation.

5-Methoxymethyl-2-furoyl chloride. Yield 75%, colorless oil with bp 92°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 3.42 s (3H, CH_3O), 4.48 s (2H, OCH_2-furan), 6.56 d (1H, H^4-furan, J_{HH} = 3.6 Hz), 7.47 d (1H, H^3-furan, J_{HH} = 3.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 58.80 (CH_3O), 66.53 (OCH_2-furan), 111.70 (C^4-furan), 125.67 (C^3-furan), 145.53 (C^2-furan), 155.27 (C^5-furan), 160.39 (C=O).

5-Methyl-4-methoxymethyl-2-furoyl chloride. Yield 45%, colorless oil with bp 106°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 2.42 s (3H, CH_3-furan), 3.37 s (3H, CH_3O), 4.29 s (2H, OCH_2-furan), 7.46 s (1H, H^3-furan). ^{13}C NMR spectrum, δ_C, ppm: 12.60 (CH_3-furan), 58.14 (CH_3O), 65.07 (OCH_2-furan), 121.13 C^4-furan), 127.15 (C^3-furan), 143.74 (C^2-furan), 151.99 (C^5-furan), 159.41 (C=O).

3-Methoxymethyl-2-furoyl chloride. Yield. 73%, colorless oil with bp 69–70°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 3.43 s (3H, CH_3O), 4.65 s (2H, OCH_2-furan), 6.78 br.s (1H, H^4-furan), 7.66 br.s (1H, H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: 58.84 (CH_3O), 66.28 (OCH_2-furan), 114.22 (C^4-furan), 138.02 (C^3-furan), 148.38 (C^2-furan), 147.91 (C^5-furan), 156.43 (C=O).

2-Methoxymethyl-3-furoyl chloride. Yield 67%, colorless oil with bp 68–69°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 3.40 s (3H, CH_3O), 4.68 s (2H, OCH_2-furan), 6.81 d (1H, H^4-furan, J_{HH} = 2.0 Hz), 7.43 d (1H, H^5-furan, J_{HH} = 2.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 58.84 (CH_3O), 64.92 (OCH_2-furan), 112.61 (C^4-furan), 128.67 (C^3-furan), 142.73 (C^5-furan), 159.14 (C^2-furan), 161.66 (C=O).

4-Methoxymethyl-3-furoyl chloride. Yield 86%, colorless oil with bp 68°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 3.45 s (3H, CH_3O), 4.51 s (2H, OCH_2-furan), 7.51 s (1H, H^5-furan), 8.23 s (1H, H^2-furan). ^{13}C NMR spectrum, δ_C, ppm: 58.81 (CH_3O), 65.20 (OCH_2-furan), 122.70, 122.91 ($C^{3,4}$-furan), 143.29 (C^2-furan), 154.05 (C^5-furan), 159.22 (C=O).

5-Methoxymethyl-3-furoyl chloride. Yield 75%, colorless oil with bp 90°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 3.37 s (3H, CH_3O), 4.39 s (2H, OCH_2-furan), 6.69 s (1H, H^4-furan), 8.17 s (1H, H^2-furan). ^{13}C NMR spectrum, δ_C, ppm: 58.16 (CH_3O), 65.83 (OCH_2-furan), 108.58 (C^4-furan), 124.83 (C^3-furan), 151.90 (C^2-furan), 154.81 (C^5-furan), 159.67 (C=O).

Synthesis of diethyl methyl- and methoxymethylfuroyl phosphonates *(general procedure)*. A solution of 20 mmol of methylfuroyl or methoxymethylfuroyl chloride in 10 mL of benzene was added to a solution of 30 mmol of triethyl phosphite in 20 mL of benzene. Heat evolution was observed, and temperature of the reaction mixture reached 28–35°C. After spontaneous cooling to room temperature, the formed mixture was heated with stirring at 70°C during 3 h and then distilled in vacuum.

Diethyl 3-methyl-2-furoyl phosphonate (3a). Yield 73%. Colorless oil with bp 146–147°C (2 mmHg). ^{1}H NMR spectrum, δ, ppm: 1.37 t (6H, CH_3-phosphonate, J_{HH} = 7.0 Hz), 2.39 s (3H, CH_3-furan), 4.29 d.q (4H, CH_2OP, J_{HH} = 7.0 Hz, J_{PH} = 14.4 Hz), 6.42 br.s (1H, H^4-furan), 7.58 br.s (1H, H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: 11.78 (CH_3-furan), 16.36 d (CH_3-phosphonate, $^3J_{PC}$ = 5.8 Hz), 63.92 d (CH_2OP, $^2J_{PC}$ = 7.0 Hz), 116.22 d (C^4-furan, $^4J_{PC}$ = 2.8 Hz), 134.83 d (C^3-furan, $^3J_{PC}$ = 8.6 Hz), 147.42 d (C^5-furan), 148.73 d (C^2-furan, $^2J_{PC}$ = 60.1 Hz), 186.49 d (C=O, $^1J_{PC}$ = 184.0 Hz). ^{31}P NMR spectrum, δ_P, ppm: –1.30.

Diethyl 5-methyl-2-furoyl phosphonate (3b). Yield 73%. Colorless oil with bp 146–147°C (2 mmHg). ^{1}H NMR spectrum, δ, ppm: 1.18 t (6H, CH_3-phosphonate, J_{HH} = 7.2 Hz), 2.25 s (3H, CH_3-furan), 4.03–4.10 m (4H, CH_2OP), 6.12 d (1H, H^4-furan, J_{HH} = 3.6 Hz), 7.67 d (1H, H^3-furan, J_{HH} = 3.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.99 (CH_3-furan), 16.14 d (CH_3-phosphonate, $^3J_{PC}$ = 5.6 Hz), 63.88 d (CH_2OP, $^2J_{PC}$ = 6.8 Hz), 110.19 (C^4-furan), 127.94 (C^3-furan), 151.12 d (C^2-furan, $^2J_{PC}$ = 90.8 Hz), 161.38 (C^5-furan), 183.20 d (C=O, $^1J_{PC}$ = 187.5 Hz). ^{31}P NMR spectrum, δ_P, ppm: –2.23.

Diethyl 2-methyl-3-furoyl phosphonate (4a). Yield 70%. Colorless oil with bp 132–133°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 1.30 t (6H, CH_3-phosphonate, J_{HH} = 7.2 Hz), 2.54 d (3H, CH_3-furan, J_{PH} = 1.2 Hz), 4.18 d. q (4H, CH_2OP, J_{HH} = 7.2 Hz, J_{PH} = 14.0 Hz), 6.07 br.s (1H, H^4-furan), 7.21 br.s (1H, H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: 14.61 (CH_3-furan), 16.27 d (CH_3-phosphonate, $^3J_{PC}$ = 5.7 Hz), 63.68 d (CH_2OP, $^2J_{PC}$ = 7.1 Hz), 111.01 (C^4-furan), 120.36 d (C^3-furan, $^2J_{PC}$ = 68.8 Hz), 140.82 (C^5-furan), 161.52 d (C^2-furan, $^3J_{PC}$ = 15.0 Hz), 193.82 d (C=O, $^1J_{PC}$ = 181.5 Hz). ^{31}P NMR spectrum, δ_P, ppm: –1.76.

Diethyl 4-methyl-3-furoyl phosphonate (4b). Yield 59%. Colorless oil with bp 121°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 1.33 t (6H, CH_3-phosphonate, J_{HH} = 7.2 Hz), 2.16 s (3H, CH_3-furan), 4.16–4.26 m (4H, CH_2OP), 7.20 br.s (1H, H^5-furan), 8.70 br.d (1H, H^2-furan, J_{PH} = 1.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 9.23 (CH_3-furan), 16.28 d (CH_3-phosphonate, $^3J_{PC}$ = 5.5 Hz), 63.90 d (CH_2OP, $^2J_{PC}$ = 7.0 Hz), 119.86 d (C^4-furan, $^3J_{PC}$ = 10.7 Hz), 126.06 d (C^3-furan, $^2J_{PC}$ = 69.0 Hz), 141.31 (C^5-furan), 154.96 d (C^2-furan, $^3J_{PC}$ = 3.8 Hz), 194.12 d (C=O, $^1J_{PC}$ = 178.Hz). ^{31}P NMR spectrum, δ_P, ppm: –3.15.

Diethyl 5-methyl-3-furoyl phosphonate (4c). Yield 87%. Colorless oil with bp 129°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 1.33 t (6H, CH_3-phosphonate, J_{HH} = 7.0 Hz), 2.29 s (3H, CH_3-furan), 4.15–4.23 m (4H, CH_2OP), 6.37 s (1H, H^4-furan), 8.54 s (1H, H^2-furan). ^{13}C NMR spectrum, δ_C, ppm: 13.19 (CH_3-furan), 16.29 d (CH_3-phosphonate, $^3J_{PC}$ = 5.6 Hz), 63.89 d (CH_2OP, $^2J_{PC}$ = 6.8 Hz), 103.11 d (C^4-furan, $^3J_{PC}$ = 8.3 Hz), 128.35 d (C^3-furan, $^2J_{PC}$ = 69.0 Hz), 152.19 (C^5-furan), 154.64 (C^2-furan, $^3J_{PC}$ = 3.8 Hz), 192.90 d (C=O, $^1J_{PC}$ = 180.1 Hz).). ^{31}P NMR spectrum, δ_P, ppm: –2.69.

Diethyl 5-methoxymethyl-2-furoyl phosphonate (8a). Yield 65%. Colorless oil with bp 164–165°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 1.25 t (6H, CH_3-phosphonate, J_{HH} = 7.2 Hz), 3.29 s (3H, CH_3O), 4.15 d. q (4H, CH_2OP, J_{HH} = 7.2 Hz, J_{PH} = 14.4 Hz), 4.38 s (2H, O–CH_2-furan), 6.45 d (1H, H^4-furan, J_{HH} = 3.6 Hz), 7.76 d (1H, H^3-furan, J_{HH} = 3.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.12 d (CH_3-phosphonate, $^3J_{PC}$ = 5.6 Hz), 58.63 (CH_3O), 64.08 d (CH_2OP, $^2J_{PC}$ = 6.8 Hz), 66.45 (OCH_2-furan), 111.39 (C^4-furan), 126.57 (C^3-furan), 151.63 d (C^2-furan, $^2J_{PC}$ = 89.9 Hz), 159.80 (C^5-furan), 184.48 d (C=O, $^1J_{PC}$ = 188.4 Hz). ^{31}P NMR spectrum, δ_P, ppm: –2.67.

Diethyl 4-methoxymethyl-5-methyl-2-furoyl phosphonate (8b). Yield 72%. Colorless oil with bp 183–184°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 1.24 t (6H, CH_3-phosphonate, J_{HH} = 7.2 Hz), 2.30 s (3H, CH_3-furan), 3.22 s (3H, CH_3O), 4.07–4.15 m (4H, CH_2OP), 4.16 s (2H, O–CH_2-furan), 7.76 s (1H, H^3-furan). ^{13}C NMR spectrum, δ_C, ppm: 13.41 (CH_3-furan), 16.19 d (CH_3-phosphonate, $^3J_{PC}$ = 5.6 Hz), 57.92 (CH_3O), 63.98 d (CH_2OP, $^2J_{PC}$ = 6.7 Hz), 65.02 (OCH_2-furan), 120.92 (C^4-furan), 128.29 (C^3-furan), 150.18 d (C^2-furan, $^2J_{PC}$ = 90.8 Hz), 159.21 (C^5-furan), 183.34 d (C=O, $^1J_{PC}$ = 187.6 Hz). ^{31}P NMR spectrum, δ_P, ppm: –2.34.

Diethyl 3-methoxymethyl-2-furoyl phosphonate (8c). Yield 59%. Colorless oil with bp 155–156°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 1.29 br.s (6H, CH_3-phosphonate), 3.32 s (3H, CH_3O), 4.19–4.23 m (4H, CH_2OP), 4.59 s (2H, O–CH_2-furan), 6.67 br.s (1H, H^4-furan), 7.59 br.s (1H, H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: 16.00 d (CH_3-phosphonate, $^3J_{PC}$ = 6.3 Hz), 16.28 d (CH_3-phosphonate, $^3J_{PC}$ = 5.6 Hz), 58.66 (CH_3O), 63.99 d (CH_2OP, $^2J_{PC}$ = 6.9 Hz), 66.40 (OCH_2-furan), 113.62 (C^4-furan), 136.97 d (C^3-furan, $^3J_{PC}$ = 9.0 Hz), 147.89 (C^5-furan), 147.30 d (C^2-furan, $^2J_{PC}$ = 60.6 Hz), 186.71 d (C=O, $^1J_{PC}$ = 186.1 Hz. ^{31}P NMR spectrum, δ_P, ppm: –1.93.

Diethyl 2-methoxymethyl-3-furoyl phosphonate (8d). Yield 75%. Colorless oil with bp 163°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 1.28 t (6H, CH_3-phosphonate, J_{HH} = 7.0 Hz), 3.32 s (3H, CH_3O), 4.15 d.q (4H, CH_2OP, J_{HH} = 7.0 Hz, J_{PH} = 14.0 Hz), 4.63 s (2H, O–CH_2-fran), 7.11 br.s (1H, H^4-furan), 7.36 br.s (1H, H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: 16.26 d (CH_3-phosphonate, $^3J_{PC}$ = 5.4 Hz), 58.68 (CH_3O), 63.39 d (CH_2OP, $^2J_{PC}$ = 7.0 Hz), 65.54 (OCH_2-furan), 111.15 (C^4-furan), 122.06 d (C^3-furan, $^2J_{PC}$ = 86.5 Hz), 142.63 (C^5-furan), 158.75 d (C^2-furan, $^3J_{PC}$ = 15.2 Hz), 194.36 d (C=O, $^1J_{PC}$ = 183.7 Hz). ^{31}P NMR spectrum, δ_P, ppm: –2.36.

Diethyl 4-methoxymethyl-3-furoyl phosphonate (8e). Yield 73%. Colorless oil with bp 151°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 1.29 t (6H, CH_3-phosphonate, J_{HH} = 7.0 Hz), 3.34 s (3H, CH_3O), 4.13–4.17 m (4H, CH_2OP), 4.63 s (2H, O–CH_2-furan), 7.38 s (1H, H^5-furan), 8.68 s (1H, H^2-furan). ^{13}C NMR spectrum, δ_C, ppm: 16.21 d (CH_3-phosphonate, $^3J_{PC}$ = 5.Hz), 58.64 (CH_3O), 63.99 d (CH_2OP, $^2J_{PC}$ = 6.9 Hz), 65.97 (OCH_2-furan), 122.40 d (C^4-furan, $^3J_{PC}$ = 11.1 Hz), 124.96 d (C^3-furan, $^2J_{PC}$ = 70.1 Hz), 141.96 (C^5-furan), 154.96 d (C^2-furan, $^3J_{PC}$ = 3.8 Hz), 193.83 d (C=O, $^1J_{PC}$ = 180.4 Hz). ^{31}P NMR spectrum, δ_P, ppm: –3.44.

Diethyl 5-methoxymethyl-3-furoyl phosphonate (8f). Yield 75%. Colorless oil with bp 156–158°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm: 1.21 t (6H, CH_3-phosphonate, J_{HH} = 7.0 Hz), 3.20 s (3H, CH_3O), 4.05–4.11 m (4H, CH_2OP), 4.25 s (2H, OCH_2-furan), 6.59 s (1H, H^4-furan), 8.53 s (1H, H^2-furan). ^{13}C NMR spectrum, δ_C, ppm: 16.15 d (CH_3-phosphonate, $^3J_{PC}$ = 5.4 Hz), 57.91 (CH_3O), 63.88 d (CH_2OP, $^2J_{PC}$ = 6.8 Hz), 65.67 (OCH_2-furan), 106.44 d (C^4-furan, $^3J_{PC}$ = 7.9 Hz), 127.78 d (C^3-furan, $^2J_{PC}$ = 70.0 Hz), 153.06 (C^2-furan), 153.91 (C^5-furan), 192.90 d (C=O, $^1J_{PC}$ = 181.6 Hz). ^{31}P NMR spectrum, δ_P, ppm: –3.10.

Diethyl 2-bromomethyl-3-furoyl phosphonate (5). 4.5 g of *N*-bromosuccinimide and 0.2 g of azobisisobutyronitrile were added to a solution of 5.6 g of furoylphosphonate **4a** in 100 mL of carbon tetrachloride. The reaction mixture was heated until the beginning of vigorous reaction, and after completion of heat evolution it was refluxed with stirring until disappearance of *N*-bromosuccinimide crystals. After that, the formed mixture was left overnight for crystallization. On the next day the precipitate was filtered off, the solvent was removed from the filtrate on a rotary evaporator, and the residue was incubated in vacuum (1 mmHg) during 1 h at room temperature. Brown oil, 6.9 g, was obtained. Its major component was phosphonate **5**. ^{1}H NMR spectrum, δ, ppm: 1.32 t (6H, CH_3-phosphonate, J_{HH} = 7.2 Hz), 4.20 d. q (4H, CH_2OP, J_{HH} = 7.2 Hz, J_{PH} = 14.8 Hz), 4.71 s (2H, CH_2Br), 7.15 d (1H, H^4-furan, J_{HH} = 2.0 Hz), 7.40 d (1H, H^5-furan, J_{HH} = 2.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.30 d (CH_3-phosphonate, $^3J_{PC}$ = 5.7 Hz), 21.15 (CH_2Br), 64.12 d (CH_2OP, $^2J_{PC}$ = 7.1 Hz), 111.83 (C^4-furan), 121.39 d (C^3-furan, $^2J_{PC}$ = 68.7 Hz), 143.09 (C^5-furan), 156.65 d (C^2-furan, $^3J_{PC}$ = 14.9 Hz), 194.37 d (C=O, $^1J_{PC}$ = 185.0 Hz). ^{31}P NMR spectrum, δ_P, ppm: –2.84.

Synthesis of furoyl phosphonates 9a and 11a–11f *(general procedure)*. A solution of 20 mmol of acid chloride in 10 mL of benzene was added to a solution of 30 mmol of triethyl phosphite in 20 mL of benzene. Stirring of the reagents caused spontaneous heating of the reaction mixture to 28–35°C. After complete heat evolution, the formed mixture was heated with stirring at 70°C during 3 h. The volatile products were removed on a rotary evaporator, and the fraction with bp 30–60°C (1 mmHg) was further distilled off. The residual substance was the target product.

Diethyl 4-(ethoxycarbonyl)-3-furoyl phosphonate (9a). Yield 68%. Yellow oil. ^{1}H NMR spectrum, δ, ppm: 1.29 t (6H, CH_3-phosphonate, J_{HH} = 7.0 Hz), 1.32 t (3H, CH_3-ester, J_{HH} = 7.0 Hz), 4.16–4.23 m (4H, CH_2OP), 4.27 q (2H, CH92°C, J_{HH} = 7.0 Hz), 7.94 s (1H, H^5-furan), 8.68 s (1H, H^2-furan). ^{13}C NMR spectrum, δ_C, ppm: 14.03 (CH_3-ester), 16.21 d (CH_3-phosphonate, $^3J_{PC}$ = 5.6 Hz), 61.13 (CH_2O-ester), 64.30 d (CH_2OP, $^2J_{PC}$ = 7.1 Hz), 117.84 d (C^4-furan, $^3J_{PC}$ = 10.3 Hz), 125.01 d (C^3-furan, $^2J_{PC}$ = 74.6 Hz), 148.86 (C^5-furan), 153.82 d (C^2-furan, $^3J_{PC}$ = 2.8 Hz), 192.28 d (C=O, $^1J_{PC}$ = 184.6 Hz). ^{31}P NMR spectrum, δ_P, ppm: –3.48.

Diethyl 5-(diethoxyphosphorylmethyl)-2-furoyl phosphonate (11a). Yield 95%. Light brown syrup. ^{1}H NMR spectrum, δ, ppm: 1.22 t (6H, CH_3-phosphonate, J_{HH} = 7.2 Hz), 1.27 t (6H, CH_3-acyl phosphonate, J_{HH} = 7.2 Hz), 3.27 d (2H, CH_2P, J_{PH} = 22.0 Hz), 4.00–4.08 m (4H, CH_2OP-phosphonate), 4.13–4.21 m (4H, CH_2OP-acyl phosphonate), 6.41 d (1H, H^4-furan, J_{HH} = 3.6 Hz), 7.73 d (1H, H^3-furan, J_{HH} = 3.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.24 d (CH_3-phosphonates, $^3J_{PC}$ = 4.4 Hz), 27.23 d (CH_2P, $^1J_{PC}$ = 141.0 Hz), 62.67 d (CH_2OP, $^2J_{PC}$ = 6.4 Hz), 64.09 d (CH_2OP-acyl, $^2J_{PC}$ = 6.8 Hz), 111.94 d (C^4-furan, $^3J_{PC}$ = 6.0 Hz), 127.36 (C^3-furan), 151.52 d (C^2-furan, $^2J_{PC}$ = 90.8 Hz), 154.79 d (C^5-furan, $^2J_{PC}$ = 8.3 Hz), 183.88 d (C=O, $^1J_{PC}$ =

188.6 Hz). ^{31}P NMR spectrum, δ_P, ppm: 20.54 (P^5), –2.67 (P^2).

Diethyl 4-(diethoxyphosphorylmethyl)-5-methyl-2-furoyl phosphonate (11b). Yield 83%. Brown syrup. ^{1}H NMR spectrum, δ, ppm: 1.01–1.12 m (12H, CH_3-phosphonate), 2.14 s (3H, CH_3-furan), 2.66 d (2H, CH_2P, J_{PH} = 20.4 Hz), 3.83 br.s (4H, CH_2OP), 3.97 br.s (4H, CH_2OP-acyl phosphonate), 7.56 s (1H, H^3-furan). ^{13}C NMR spectrum, δ_C, ppm: 12.16 (CH_3-furan), 16.08 br.s (CH_3-phosphonate), 22.81 d (CH_2P, $^1J_{PC}$ = 148.2 Hz), 62.02 br.s (CH_2OP-phosphonate), 63.78 br.s (CH_2OP-acyl phosphonate), 114.27 d (C^4-furan, $^2J_{PC}$ = 9.3 Hz), 128.59 (C^3-furan), 149.87 d (C^2-furan, $^2J_{PC}$ = 90.3 Hz), 158.76 d (C^5-furan, $^3J_{PC}$ = 9.2 Hz), 183.14 d (C=O, $^1J_{PC}$ = 187.8 Hz). ^{31}P NMR spectrum, δ_P, ppm: 24.84 (P^4), –2.42 (P^2).

Diethyl 3-(diethoxyphosphorylmethyl)-2-furoyl phosphonate (11c). Yield 87%. Brown syrup. ^{1}H NMR spectrum, δ, ppm: 1.04–1.16 br.s (12H, CH_3-phosphonate), 3.32 d (2H, CH_2P, J_{PH} = 22.4 Hz), 3.85–4.10 m (8H, CH_2OP), 6.54 br.s (1H, H^4-furan), 7.48 br.s (1H, H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: 15.89 d (CH_3-phosphonate, $^3J_{PC}$ = 5.5 Hz), 16.16 d (CH_3-acyl phosphonate, $^3J_{PC}$ = 5.0 Hz, 23.45 d (CH_2P, $^1J_{PC}$ = 138.9 Hz), 62.16 d (CH_2OP-phosphonate, $^2J_{PC}$ = 6.5 Hz), 63.85 d (CH_2OP-acyl phosphonate, $^2J_{PC}$ = 6.8 Hz), 115.76 (C^4-furan), 128.32 t (C^3-furan, $^2J_{PC}$ = $^3J_{PC}$ = 9.3 Hz), 147.56 (C^5-furan), 148.40 d. d (C^2-furan, $^2J_{PC}$ = 58.5 Hz, $^3J_{PC}$ = 9.8 Hz), 186.87 d (C=O, $^1J_{PC}$ = 186.8 Hz). ^{31}P NMR spectrum, δ_P, ppm: 23.73 (P^3), –2.16 (P^2).

Diethyl 2-(diethoxyphosphorylmethyl)-3-furoyl phosphonate (11d). Yield 69%. Yellow syrup. ^{1}H NMR spectrum, δ, ppm: 1.25 t (6H, CH_3-phosphonate, J_{HH} = 7.0 Hz), 1.35 t (6H, CH_3-acyl phosphonate, J_{HH} = 7.2 Hz), 3.73 d (2H, CH_2P, J_{PH} = 22.8 Hz), 4.07 d. q (4H, CH_2OP-phosphonate, J_{HH} = 7.0 Hz, J_{PH} = 14.8 Hz), 4.22 d. q (4H, CH_2OP-acyl phosphonate, J_{HH} = 7.2 Hz, J_{PH} = 14.6 Hz), 7.18 d (1H, H^4-furan, J_{PH} = 2.0 Hz), 7.36 d. d (1H, H^5-furan, J_{HH} = 2.0 Hz, J_{PH} = 2.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.24 d (CH_3-phosphonate, $^3J_{PC}$ = 6.2 Hz), 16.32 d (CH_3-acyl phosphonate, $^3J_{PC}$ = 6.0 Hz), 27.15 d (CH_2P, $^1J_{PC}$ = 137.5 Hz), 62.52 d (CH_2OP-phosphonate, $^2J_{PC}$ = 6.9 Hz), 63.89 d (CH_2OP-acyl phosphonate, $^2J_{PC}$ = 7.0 Hz), 111.44 (C^4-furan), 121.44 d. d (C^3-furan, $^2J_{PC}$ = 86.5 Hz, $^3J_{PC}$ = 7.4 Hz), 142.24 (C^5-furan), 158.75 t (C^2-furan, $^3J_{PC}$ = $^3J_{PC}$ = 4.7 Hz), 194.03 d (C=O, $^1J_{PC}$ = 183.6 Hz). ^{31}P NMR spectrum, δ_P, ppm: 20.59 (P^2), –2.23 (P^3).

Diethyl 4-(diethoxyphosphorylmethyl)-3-furoyl phosphonate (11e). Yield 73%. Dark yellow syrup. ^{1}H NMR spectrum, δ, ppm: 1.11 t (6H, CH_3-phosphonate, J_{HH} = 7.0 Hz), 1.21 t (6H, CH_3-acyl phosphonate, J_{HH} = 7.0 Hz), 3.21 d (2H, CH_2P, J_{PH} = 21.2 Hz), 3.87–3.94 m (4H, CH_2OP-phosphonate), 4.04–4.12 m (4H, CH_2OP-acyl phosphonate), 7.39 s (1H, H^5-furan), 8.63 s (1H, H^2-furan). ^{13}C NMR spectrum, δ_C, ppm: 16.16 d (CH_3-phosphonates, $^3J_{PC}$ = 5.5 Hz), 20.75 d (CH_2P, $^1J_{PC}$ = 141.5 Hz), 61.96 d (CH_2OP-phosphonate, $^2J_{PC}$ = 6.4 Hz), 63.88 d (CH_2OP-acyl phosphonate, $^2J_{PC}$ = 6.8 Hz), 114.44 t (C^4-furan, $^2J_{PC}$= $^3J_{PC}$ = 11.Hz), 124.95 d. d (C^3-furan, $^2J_{PC}$ = 70.1 Hz, $^3J_{PC}$ = 5.9 Hz), 141.16 (C^5-furan, $^3J_{PC}$ = 7.8 Hz), 154.70 d (C^2-furan, $^3J_{PC}$ = 3.9 Hz), 194.83 d (C=O, $^1J_{PC}$ = 180.6 Hz). ^{31}P NMR spectrum, δ_P, ppm: 25.55 (P^4), –3.62 (P^3).

Diethyl 5-(diethoxyphosphorylmethyl)-3-furoyl phosphonate (11f). Yield 85%. Light brown syrup. ^{1}H NMR spectrum, δ, ppm: 1.28 t (6H, CH_3-phosphonate, J_{HH} = 7.2 Hz), 1.33 t (6H, CH_3-acyl phosphonate, J_{HH} = 7.2 Hz), 3.21 d (2H, CH_2P, J_{PH} = 20.2 Hz), 4.04–4.10 m (4H, CH_2OP-phosphonate), 4.16–4.24 m (4H, CH_2OP-acyl phosphonate), 6.63 d (1H, H^4-furan, J_{PH} = 3.6 Hz), 8.60 s (1H, H^2-furan). ^{13}C NMR spectrum, δ_C, ppm: 16.29–16.34 br.s (CH_3-phosphonates), 26.50 d (CH_2P, $^1J_{PC}$ = 143.0 Hz), 62.52 d (CH_2OP-phosphonate, $^2J_{PC}$ = 6.4 Hz), 64.02 d (CH_2OP-acyl phosphonate, $^2J_{PC}$ = 6.8 Hz), 106.44 t (C^4-furan, $^2J_{PC}$ = $^3J_{PC}$ = 7.8 Hz), 128.42 d (C^3-furan, $^2J_{PC}$ = 69.3 Hz), 152.66 (C^2-furan), 148.69 d (C^5-furan, $^2J_{PC}$ = 9.2 Hz), 192.88 d (C=O, $^1J_{PC}$ = 181.5 Hz). ^{31}P NMR spectrum, δ_P, ppm: 25.55 (P^5), –3.62 (P^3).

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