2(5*H*)-FURANONE AZIDES IN THE SYNTHESIS OF IMINOPHOSPHORANES AND AMINES

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Abstract The synthesis and characterization of previously unknown azides, iminophosphoranes and amines from commercially available mucochloric and mucobromic acids is reported. The interaction of 5-alkoxy-3,4-dihalo-2(5*H*)-furanones with sodium azide resulted in the regioselective formation of 4-azidoderivatives of furanone. A series of novel iminophosphoranes was obtained from the reaction of corresponding azides with triphenylphosphine. Reduction of iminophosphoranes with stannous chloride dihydrate led to the heterocycles, possessing an amino group at carbon atom C(4) of the unsaturated γ-lactone ring.

Keywords: 2(5*H*)-furanone, unsaturated lactone, organic azide, iminophosphorane, Staudinger reaction, amine

Organic azides are among the generally recognized as both theoretically significant and practically valuable starting compounds in the synthesis of molecules with desired structures and properties. The attractiveness and demand for this class of compounds is primarily associated with their availability, high and diverse reactivity [1–4]. Due to the structural features of the azide group, these energy-rich and versatile intermediates are involved in numerous important chemical reactions, including the copper-catalyzed azide-alkyne [3+2] cycloaddition, popularized as "click reaction" [5, 6], Staudinger reduction and ligation [1, 7], the aza-Wittig reaction [8], the Schmidt family of reactions [1, 2, 4], direct C–H amination reactions [9], etc. Organic azides exhibiting unique reactivity patterns, have become effective and widely used tools in heterocyclic chemistry [2, 6, 10], total synthesis of natural products [11], drug development and modern chemical biology [2, 6, 12], materials science [13] and other fields.

Azides of heterocyclic series have attracted much recent interest for their great diversity, rich chemistry, the ability to produce the biologically active and other practically useful organic compounds [14]. Such chemically and biologically active heterocycles include azides of 2(5*H*)-furanone series.

Previously, as part of our ongoing projects in the field of chemistry of five-membered *O*- and *N*-heterocycles, we have developed the selective methods for the synthesis of various sulfur- [15–18] and nitrogen-containing derivatives [19–21] on the basis of commercially available 3,4-dihalo-2(5*H*)-furanones. Among the synthesized compounds, furanone derivatives with pronounced antimicrobial and antifungal activity were found, as well as heterocycles that demonstrated a synergistic effect when combined with aminoglycoside antibiotics and antifungal agents against microorganisms in mono- and mixed cultures [18, 22, 23].

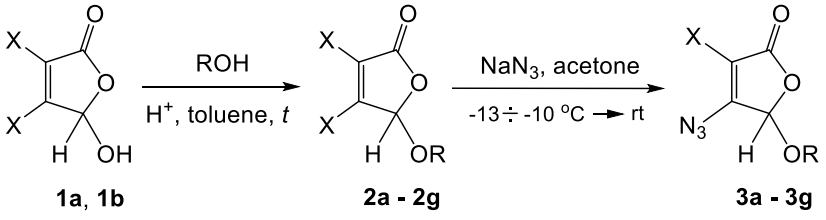
The introduction of an active azide group into the 2(5*H*)-furanone fragment is intended to expand the synthetic potential of unsaturated γ-lactones to create novel highly functionalized nitrogen-containing molecules. Despite the fact that azido derivative of 2(5*H*)-furanone was first obtained more than 50 years ago [24], the chemical reactivity of furanone-based azides has been poorly explored. Scant information is available in the literature regarding nitrogen possessing derivatives of 2(5*H*)-furanone, directly obtained from the corresponding azides [25–28]. Substantial attention has been paid to the thermolysis and photolysis reactions of various 5-alkoxy-4-azido-3-halo-2(5*H*)-furanones, resulting in the formation of highly reactive halocyanoketenes [29–33]. The latter have proven to be valuable intermediates in cycloaddition reactions with various unsaturated compounds, studied in a systematic manner.

In this paper we report the synthesis of a series of 4-azido-3-halo-2(5*H*)-furanones, possessing alkoxy or halogenalkoxy substituent in the fifth position of unsaturated γ-lactone ring, and their conversion to the corresponding novel amines and iminophosphoranes.

RESULTS AND DISCUSSION

The starting 5-alkoxy and 5-halogenalkoxy derivatives of 2(5*H*)-furanone **2a**–**2g** were synthesized from commercially available mucochloric **1a** and mucobromic **1b** acids and alcohols under acid catalysis conditions [33–37] (Scheme 1). Further, by reacting the 3,4-dihalofuranones **2a**–**2g** with sodium azide, the corresponding 4-azido derivatives **3a**–**3g** in the form of low melting substances were isolated in high yields. The reactions were carried out by adding sodium azide to the cooled acetone solutions of furanones **2a**–**2g**. Under these conditions, high regioselectivity was observed for the formation of azides **3a**–**3g**, which are the products of nucleophilic substitution of the halogen atom at the unsaturated carbon atom C(4) of the γ-lactone ring with azide group.

Scheme 1



1a, **1b** **2a - 2g** **3a - 3g**

X = Cl		**1a**		
X = Br		**1b**		
X = Cl,	R = Me	**2a**	**3a**	(95%)
X = Cl,	R = Et	**2b**	**3b**	(98%)
X = Cl,	R = Pr^i	**2c**	**3c**	(91%)
X = Cl,	R = CH_2CH_2Cl	**2d**	**3d**	(93%)
X = Cl,	R = $CH(CH_2Cl)_2$	**2e**	**3e**	(99%)
X = Cl,	R = *l*-menthyl	**2f**	**3f**	(95%)
X = Br,	R = Me	**2g**	**3g**	(97%)

It should be noted that when reactions between compounds **2b**–**2f** and sodium azide were performed in methanol, previously used in the synthesis of some furanone azides [33, 38], reaction mixtures contained small (3–15%) amounts of 4-azido-5-methoxyfuranone **3a**, which is formed via a side reaction, namely, as a result of the methanol nucleophilic attack at the atom C(5) of the lactone ring.

The structure of 4-azido derivatives of furanone **3a**–**3g** was confirmed by IR and NMR spectroscopy. Along with the narrow intense signals at 1780–1764 cm^{-1} and 1654–1640 cm^{-1} typical for the stretching vibrations of the C=O and C=C bonds of the lactone cycle, in the IR spectra of azides **3a**–**3g**, characteristic absorption bands of stretching vibrations of the azide group appeared in two regions: 2149–2128 cm^{-1} (antisymmetric vibrations) and 1309–1297 cm^{-1} (symmetric vibrations).

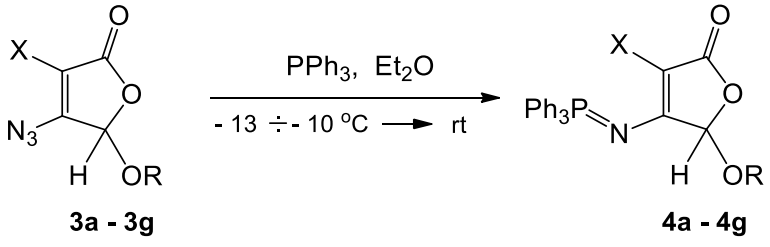
Analysis of proton and carbon NMR spectra revealed a clear trend of a significant upfield shift ($\Delta\delta$ ~ 15–17 ppm in $CDCl_3$) for the signal of the vinyl carbon atom C(3) of the five-membered ring in the $^{13}C\{^1H\}$ NMR spectra of azides **3a**–**3g** in comparison with the spectra of the starting 3,4-

dihalofuranones **2a**–**2g**. The structure of compound **3c** was determined by single crystal X-ray diffraction (Fig. 1).

Reactions of organic azides with phosphorus-containing nucleophilic reagents (for example, with phosphines) at the terminal nitrogen atom of the azide group proceed easily with the loss of a nitrogen molecule and the formation of iminophosphoranes, which are valuable intermediates in organic synthesis and chemical biology. The readily available iminophosphoranes are increasingly employed in the construction of nitrogen-containing heterocycles, natural products and P–N backbone polymers, as "superbases" and versatile ligands for homogeneous catalysis [1, 7, 8, 11, 39, 40].

The 2(5*H*)-furanone azides **3a–3g** were involved in the Staudinger reaction with triphenylphosphine. Mixing equimolar amounts of azides **3a–3g** and triphenylphosphine in diethyl ether yields the corresponding iminophosphoranes **4a–4g** (Scheme 2). In all cases, the target products **4a–4g** were precipitated during the reaction and, after recrystallization from ethanol were obtained in the form of colorless, crystalline substances.

Scheme 2



X = Cl, R = Me	**3a**	**4a** (71%)
X = Cl, R = Et	**3b**	**4b** (78%)
X = Cl, R = Pr^i	**3c**	**4c** (72%)
X = Cl, R = CH_2CH_2Cl	**3d**	**4d** (68%)
X = Cl, R = $CH(CH_2Cl)_2$	**3e**	**4e** (86%)
X = Cl, R = *l*-menthyl	**3f**	**4f** (86%)
X = Br, R = Me	**3g**	**4g** (66%)

In the ^{1}H NMR spectra of iminophosphoranes **4a**–**4g**, the signal of the methine proton at the carbon atom C(5) appears in the range of 4.8–5.7 ppm as a doublet with $^4J_{PH}$ = 0.9–1.8 Hz. In the $^{13}C\{^1H\}$ NMR spectra of compounds **4a**–**4f** in comparison with the spectra of azides **3a**–**3f**, the upfield shift ($\Delta\delta$ ~ 10–13 ppm) for the signal of the carbon atom C(3) of the lactone ring and the downfield shift ($\Delta\delta$ ~ 11–14 ppm) for the C(4) signal were observed. The $^{31}P\{^1H\}$ NMR spectra of novel compounds **4a**–**4g** display the signal of the phosphorus atom in the range of 11.6–13.0 ppm, that is consistent with the literature [41].

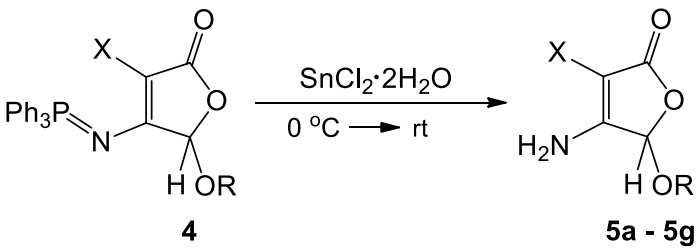
The molecular structures of iminophosphoranes **4a**, **4f,** and **4g** were characterized by single crystal X-ray diffraction (Fig. 2). Compound **4g** crystallizes as a crystal solvate with one molecule of chloroform, while its chlorine analogue **4a** crystallizes in its individual form.

Iminophosphorane moiety can be used as a common precursor of various useful compounds including amines, which display various reactivity profiles and potent biological applications. The literature contains several examples of 5-alkoxy-3-halo-2(5*H*)-furanones, possessing an NHR or NR_2 substituent at carbon atom C(4) of the lactone ring, exhibited antitumor activity against various tumor cells lines [42, 43].

Different synthetic procedures have been described for the preparation of amines from the corresponding iminophosphoranes, based on the acid and alkaline hydrolysis, ammonolysis or the treatment with reducing agents [2]. We have shown, that under acid hydrolysis conditions iminophosphorane **4a** is converted to 4-amino-2(5*H*)-furanone **5a**, but the desired product was isolated only in low yield (26%). Much better results were obtained with stannous chloride dihydrate as a reducing agent (Scheme 3). The reactions were carried out in a suitable organic (methanol, acetone, acetonitrile) or water-organic medium, and the corresponding 4-aminoderivatives of 2(5*H*)-furanone **5a**–**5g** were isolated in 67–84% yields using silica gel column

chromatography. Amine **5a** was previously obtained by reduction of 4-azido-3,5-dichloro-2(5*H*)-furanone in methanol [26], aminofuranones **5b**–**5f** have not been described in the literature.

Scheme 3



X = Cl, R = Me	**a** (67%)
X = Cl, R = Et	**b** (75%)
X = Cl, R = Pr^i	**c** (68%)
X = Cl, R = CH_2CH_2Cl	**d** (77%)
X = Cl, R = $CH(CH_2Cl)_2$	**e** (70%)
X = Cl, R = *l*-menthyl	**f** (84%)
X = Br, R = Me	**g** (72%)

The formation of an amino group is evidenced by the presence in the ^{1}H NMR spectra of compounds **5a**–**5g** recorded in $CDCl_3$ of a broadened singlet in the range of 4.9–5.0 ppm. These aminofuranones displayed in the IR spectra a group of broadened bands at 3500–3150 cm^{-1}, corresponding to antisymmetric and symmetric stretching vibrations and vibrations of the hydrogen-bonded amino groups, as well as a narrow intense band at 1598–1618 cm^{-1}, characteristic of the deformation vibrations of the primary amino group.

According to the X-ray data the crystals of 4-aminoderivatives of 2(5*H*)-furanone **5a** and **5b** are isostructural. Compounds **5a** and **5b** crystallize in the noncentrosymmetric (but at the same time achiral) space group *Pna*2$_1$ (Fig. 3a, b). The main structure-forming interactions in a crystal are classical hydrogen bonds. Both hydrogen atoms of the amino group participate in hydrogen bonding, and the oxygen atom of the carbonyl group forms a bifurcate interaction (Fig. 3d). The combination of hydrogen bonds of both types leads to the formation of a branched three-dimensional network of hydrogen bonds.

Crystal **5e** is not isostructural to the previous one (Fig. 3c). Only one hydrogen atom of the amino group is involved in hydrogen bonding, that results in the formation of infinite chains (Fig. 3e).

In conclusion, novel derivatives of 2(5*H*)-furanone, bearing alkoxy or halogenalkoxy substituent in the fifth position of unsaturated γ-lactone ring, and an azide, amine or iminophosphorane moiety at carbon atom C(4) were synthesized from 3,4-dihalo-5-hydroxy-2(5*H*)-furanones. These nitrogen-containing compounds will continue to be investigated in order to expand their synthetic possibilities for the construction of various *N*-heterocyclic cores.

EXPERIMENTAL

IR spectra of synthesized compounds were recorded on a Bruker Tensor-27 Fourier-transform spectrometer fitted with a Pike MIRacle ATR accessory (diamond/ZnSe crystal plate). NMR spectra were measured on a Bruker Avance III 400 spectrometer at 400.17 MHz (^{1}H), 100.62 MHz (^{13}C) and 161.99 MHz (^{31}P) at 25°C for solutions in $CDCl_3$, acetone-d_6, and CD_3OD. The chemical shifts (δ) are expressed in parts per million (ppm) and are calibrated using residual undeuterated solvent peak as an internal reference. High-resolution mass spectra (HRMS) were obtained by electrospray ionisation (ESI) with positive (+) ion detection on a Bruker Daltonics micrOTOF–QIII quadrupole time-of-flight mass spectrometer. The melting points were measured on a Boetius hot stage and were not corrected. Analytical thin layer chromatography (TLC) was carried out on Sorbfil PTLC-AF-A-UF plates using acetone–toluene mixtures as the eluent and UV light (254 nm) as the visualizing agent. Silica gel 60A (Acros Organics, 70–230 mesh, 0.060–0.200

mm) was used for open column chromatography. Optical rotations were measured on a JASCO P–2200 polarimeter at λ 589 nm and at 25°C (concentration *c* is given as g/100 mL).

Single crystal X-ray diffraction analysis was performed on a Bruker D8 QUEST automatic three-circle diffractometer with a PHOTON III two-dimensional detector and an IμS DIAMOND microfocus X-ray tube (λ[MoK_α] 0.71073 Å) at *T* 150(2) K (compound **3c**), a Bruker Kappa Apex DUO diffractometer (λ[MoK_α] 0.71073 Å) at *T* 150(2) K (compound **4a**), a Rigaku XtaLab Synergy S automatic three-circle diffractometer (λ[CuK_α] 1.54184 Å) at *T* 100(2) K (compounds **4f**, **5b** and **5e**), a Bruker Kappa Apex automatic diffractometer (λ[CuK_α] 1.54184 Å) at *T* 150 K (compound **4g**) and a Bruker Smart Apex II CCD automatic three-circle diffractometer (λ[MoK_α] 0.71073 Å) at *T* 150 K (compound **5a**).

Data collection and indexing, determination, and refinement of unit cell parameters for crystals **3c**, **4a**, **4g**, and **5a** were carried out using the APEX3 software package. Numerical absorption correction based on the crystal shape, additional spherical absorption correction, and systematic error correction were performed using the SADABS [44]. Data collection and indexing, determination, and refinement of unit cell parameters for crystals **4f**, **5b**, and **5e** were carried out using the CrysAlisPro software package, the absorption correction was performed using ABSPACK.

Using OLEX2 [45], the structures were solved by direct methods using the SHELXT program [46] and refined by full-matrix least-squares on F^2 using the SHELXL program [47].

Nonhydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at the calculated positions and refined using a riding model (exception for crystal **5a**, in which all hydrogen atoms were located from difference Fourier series and were refined isotropically). H(N) hydrogen atoms were located from difference Fourier series and were refined isotropically at the final stage of structure refinement. Analysis of intermolecular contacts and figures were performed using PLATON [48] and Mercury [49]. The crystallographic data for all structures have been deposited in the Cambridge Crystallographic Data Centre, the supplementary publication numbers and the principal crystallographic characteristics are summarized in the Tables 1 and 2. X-Ray diffraction data were obtained from the Collective Spectro-Analytical Center of FRC Kazan Scientific Center of RAS by support of the State Assignment of the Federal Research Center "Kazan Scientific Center", Russian Academy of Sciences.

3,4-Dichloro-5-methoxyfuran-2(5*H*)-one (**2a**) [34], 3,4-dichloro-5-ethoxyfuran-2(5*H*)-one (**2b**) [34], 3,4-dichloro-5-isopropoxyfuran-2(5*H*)-one (**2c**) [33], 3,4-dichloro-5-(2-chloroethoxy)furan-2(5*H*)-one (**2d**) [35], 3,4-dichloro-5-(1,3-dichloropropan-2-yloxy)furan-2(5*H*)-one (**2e**) [35], 5(*S*)-3,4-dichloro-5-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyloxy]furan-2(5*H*)-one (**2f**) [36] and 3,4-dibromo-5-methoxyfuran-2(5*H*)-one (**2g**) [37] were synthesized by known procedures. Sodium azide (Diaem), triphenylphosphine (Acros Organics), and tin (II) chloride dihydrate (Reakhim) were used without additional purification.

4-Azido-3-chloro-5-methoxyfuran-2(5*H*)-one (3a) was synthesized according to a slightly modified procedure generally following [50]. To a solution of 1.66 g (9.1 mmol) of furanone **2a** in acetone (20 mL) cooled to –13 ÷ –10°C with intense stirring was added 1.77 g (27.3 mmol) of sodium azide in small portions. The mixture was stirred under cooling for 20 minutes and warmed up to room temperature, and stirred for 3 hours. A white precipitate of NaCl was formed during the reaction. The reaction mixture was evaporated to dryness and the obtained orange oily residue was subjected to water–chloroform extraction. The organic layer was dried over magnesium sulfate and evaporated to dryness. A light yellow oily residue crystallized on cooling. Yield 95%, mp 65–66°C

(decom.) (mp 67–68°C (decom.) [50]), R_f 0.57 (acetone–toluene, 1 : 6). IR spectrum, ν, cm^{-1}: 2148 (N_3 asym), 1780, 1771 (C=O), 1645 (C=C), 1301 (N_3 sym). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.62 s (3H, OCH_3), 5.76 s (1H, H^5). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 56.82 (OCH_3), 98.63 (C^5), 108.25 (C^3), 150.41 (C^4), 164.24 (C^2).

4-Azido-3-chloro-5-ethoxyfuran-2(5*H*)-one (3b) was synthesized as described for compound **3a** from furanone **2b** (1.12 g, 5.7 mmol) and sodium azide (1.11 g, 17.1 mmol). Yield 98%, yellow oil, R_f 0.57 (acetone–toluene, 1 : 6). IR spectrum, ν, cm^{-1}: 2135 (N_3 asym), 1776 (C=O), 1649 (C=C), 1305 (N_3 sym). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.32 t (3H, ABX_3 system, X part, CH_3, $^3J_{AX} = {}^3J_{BX}$ 7.1 Hz), 3.82 m (1H, ABX_3 system, A part, OCH_A, $^2J_{AB}$ –9.4, $^3J_{AX}$ 7.1 Hz), 3.98 m (1H, ABX_3 system, B part, OCH_B, $^2J_{AB}$ –9.4, $^3J_{BX}$ 7.1 Hz), 5.83 s (1H, H^5). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 14.80 (CH_3), 66.53 (OCH_2), 97.84 (C^5), 107.62 (C^3), 150.67 (C^4), 164.46 (C^2). Found, %: C 35.24; H 3.05; Cl 17.38; N 20.70. $C_6H_6ClN_3O_3$. Calculated, %: C 35.40; H 2.97; Cl 17.41; N 20.64.

4-Azido-3-chloro-5-isopropoxyfuran-2(5*H*)-one (3c) was synthesized as described for compound **3a** from furanone **2c** (5.17 g, 24.5 mmol) and sodium azide (4.78 g, 73.5 mmol). Yield 91%, light yellow solid, mp 50°C (decom.) (mp 51.5–52.5°C [33]), R_f 0.59 (acetone–toluene, 1 : 6). IR spectrum, ν, cm^{-1}: 2149 (N_3 asym), 1764 (C=O), 1648 (C=C), 1308 (N_3 sym). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.30, 1.32 both d (3H, CH_3, ^3J 6.2 Hz), 4.15 septet (1H, OCH, ^3J 6.2 Hz), 5.91 s (1H, H^5). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 21.80, 22.98 (CH_3), 75.13 (OCH), 96.99 (C^5), 107.59 (C^3), 150.62 (C^4), 164.58 (C^2).

4-Azido-3-chloro-5-(2-chloroethoxy)furan-2(5*H*)-one (3d) was synthesized as described for compound **3a** from furanone **2d** (1.53 g, 6.6 mmol) and sodium azide (1.29 g, 19.8 mmol). Yield 93%, light yellow solid, mp 41°C (decom.), R_f 0.46 (acetone–toluene, 1 : 6). IR spectrum, ν, cm^{-1}: 2144 (N_3 asym), 1777 (C=O), 1644 (C=C), 1297 (N_3 sym). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.62–3.78 m (2H, CH_2Cl), 3.93–4.05, 4.09–4.21 both m (1H, OCH_2), 5.92 s (1H, H^5). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 41.98 (CH_2Cl), 70.02 (OCH_2), 97.73 (C^5), 108.16 (C^3), 150.46 (C^4), 164.03 (C^5). Found, %: C 30.36; H 2.04; Cl 29.77; N 17.58. $C_6H_5Cl_2N_3O_3$. Calculated, %: C 30.28; H 2.12; Cl 29.79; N 17.65.

4-Azido-3-chloro-5-(1,3-dichloropropan-2-yloxy)furan-2(5*H*)-one (3e) was synthesized as described for compound **3a** from furanone **2e** (1.40 g, 5.0 mmol) and sodium azide (0.98 g, 15.0 mmol). Yield 99%, light yellow solid, mp 64°C (decom.), R_f 0.58 (acetone–toluene, 1 : 6). IR spectrum, ν, cm^{-1}: 2145 (N_3 asym), 1776 (C=O), 1643 (C=C), 1305 (N_3 sym). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.64–3.96 m (4H, CH_2Cl), 4.21–4.30 m (1H, OCH), 6.02 s (1H, C^5H). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 43.13, 43.43 (CH_2), 79.88 (OCH), 97.67 (C^5), 108.69 (C^3), 150.25 (C^4), 163.73 (C^2). Found, %: C 29.26; H 2.15; Cl 37.12; N 14.62. $C_7H_6Cl_3N_3O_3$. Calculated, %: C 29.35; H 2.11; Cl 37.12; N 14.67.

5(*S*)-4-Azido-3-chloro-5-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyloxy]furan-2(5*H*)-one (3f) was synthesized as described for compound **3a** from furanone **2f** (0.92 g, 3.0 mmol) and sodium azide (0.59 g, 9.0 mmol). Yield 95%, light yellow solid, mp 78–80°C (decom.) (mp 70–72°C [51]), R_f 0.66 (acetone–toluene, 1 : 6), $[\alpha]_D^{20}$ +45.1 (*c* 1.0, MeOH). IR spectrum, ν, cm^{-1}: 2960, 2945, 2924, 2871 (C–H), 2128 (N_3 asym), 1769 (C=O), 1654 (C=C), 1309 (N_3 sym). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.79 d (3H, CH_3, *i*-Pr, ^3J 7.0 Hz), 0.93 d (6H, CH_3, *i*-Pr, H^{12}, ^3J 6.8 Hz), 0.82–1.17 m (3H, H^7, H^9, H^{10}), 1.29–1.48 m (2H, H^8, H^{11}), 1.62–1.73 m (2H, H^9, H^{10}), 2.11–2.27 m (2H, H^7, H^{13}), 3.58 ddd (1H, H^6, ^3J 10.7, ^3J 4.4 Hz), 5.77 s (1H, H^5). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 15.91, 20.92 [CH_3 (*i*-Pr)], 22.03 (C^{12}), 22.87 (C^{10}), 25.21 (C^{13}), 31.59

(C^8), 33.83 (C^9), 42.17 (C^7), 48.05 (C^{11}), 83.29 (C^6), 98.82 (C^5), 108.99 (C^3), 150.77 (C^4), 164.54 (C^2). Mass spectrum (HRMS), *m/z*: 336.1079 [*M* + Na]$^+$ (calculated for $C_{14}H_{20}ClN_3NaO_3^+$: 336.1085).

4-Azido-3-bromo-5-methoxyfuran-2(5*H*)-one (3g) was synthesized as described for compound **3a** from furanone **2g** (0.20 g, 0.7 mmol) and sodium azide (0.07 g, 1.1 mmol). Yield 97%, light yellow solid, mp 74°C (decomp.) (mp 74–75°C [52]), R_f 0.70 (acetone–toluene, 1 : 6). IR spectrum, ν, cm^{-1}: 2137 (N_3 asym), 1777 (C=O), 1640 (C=C), 1304 (N_3 sym). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.63 s (3H, OCH_3), 5.77 s (1H, H^5). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 56.70 (OCH_3), 96.06 (C^3), 99.58 (C^5), 154.13 (C^4), 164.71 (C^4). Found, %: C 25.62; H 1.74; Br 34.15; N 17.93. $C_5H_4BrN_3O_3$. Calculated, %: C 25.66; H 1.72; Br 34.15; N 17.96.

3-Chloro-5-methoxy-4-[(triphenyl-λ^5-phosphanylidene)amino]furan-2(5*H*)-one (4a). To a solution of 0.42 g (2.2 mmol) of azide **3a** in diethyl ether (10 mL) cooled to –13 ÷ –10°C with stirring was added a solution of 0.58 g (2.2 mmol) triphenylphosphine in ether (15 mL). The formation of a yellow oily solid was observed. The mixture was stirred under cooling for an hour and warmed up to room temperature, and stirred for 20 hours. The yellow precipitate was filtered off, washed with ether, dried and recrystallized from ethanol. Yield 71%, colorless crystals, mp 201°C, R_f 0.39 (acetone–toluene, 1 : 6). IR spectrum, ν, cm^{-1}: 1752 (C=O), 1600, 1585, 1573 (C=C arom), 1390 (P=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.96 s (3H, OCH_3), 4.90 d (1H, H^5, $^4J_{PH}$ 0.9 Hz), 7.46–7.55 m (6H, H^m_{arom}), 7.56–7.63 m (3H, H^p_{arom}), 7.64–7.75 m (6H, H^o_{arom}). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 54.99 s (OCH_3), 96.82 d (C^3, $^3J_{PC}$ 19.7 Hz), 99.79 d (C^5, $^3J_{PC}$ 13.0 Hz), 128.86 d (C^m, $^3J_{PC}$ 12.7 Hz), 128.92 d (C^i, $^1J_{PC}$ 103.1 Hz), 132.55 d (C^o, $^2J_{PC}$ 10.4 Hz), 132.67 d (C^p, $^4J_{PC}$ 2.8 Hz), 162.69 s (C^4), 169.50 s (C^2). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), δ_P, ppm: 12.73. Mass spectrum (HRMS), *m/z*: 424.0863 [*M* + H]$^+$ (calculated for $C_{23}H_{20}ClNO_3P^+$: 424.0864).

3-Chloro-5-ethoxy-4-[(triphenyl-λ^5-phosphanylidene)amino]furan-2(5*H*)-one (4b) was synthesized as described for compound **4a** from azide **3b** (1.24 g, 6.1 mmol) and triphenylphosphine (1.60 g, 6.1 mmol). Yield 78%, colorless crystals, mp 198°C, R_f 0.42 (acetone–toluene, 1 : 6). IR spectrum, ν, cm^{-1}: 1764, 1753 (C=O), 1600, 1586, 1573 (C=C arom), 1385 (P=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.89 t (3H, ABX_3 system, X part, CH_3, $^3J_{AX} = {}^3J_{BX}$ 7.2 Hz), 2.78 m (1H, ABX_3 system, A part, OCH_A, $^2J_{AB}$ –9.0, $^3J_{AX}$ 7.2 Hz), 3.50 m (1H, ABX_3 system, B part, OCH_B, $^2J_{AB}$ –9.0, $^3J_{BX}$ 7.2 Hz), 4.92 d (1H, H^5, $^4J_{PH}$ 0.9 Hz), 7.43–7.56 m (6H, H^m_{arom}), 7.56–7.65 m (3H, H^p_{arom}), 7.66–7.77 m (6H, H^o_{arom}). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 14.62 s (CH_3), 64.03 s (OCH_2), 97.12 d (C^3, $^3J_{PC}$ 20.5 Hz), 98.91 d (C^5, $^3J_{PC}$ 12.1 Hz), 128.81 d (C^m, $^3J_{PC}$ 12.6 Hz), 128.98 d (C^i, $^1J_{PC}$ 103.1 Hz), 132.62 d (C^o, $^2J_{PC}$ 13.6 Hz), 132.66 s (C^p), 162.95 s (C^4), 169.61 s (C^2). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), δ_P, ppm: 12.48. Mass spectrum (HRMS), *m/z*: 438.1018 [*M* + H]$^+$ (calculated for $C_{24}H_{22}ClNO_3P^+$: 438.1020).

3-Chloro-5-isopropoxy-4-[(triphenyl-λ^5-phosphanylidene)amino]furan-2(5*H*)-one (4c) was synthesized as described for compound **4a** from azide **3c** (0.98 g, 4.5 mmol) and triphenylphosphine (1.18 g, 4.5 mmol). Yield 72%, colorless crystals, mp 163–165°C, R_f 0.51 (acetone–toluene, 1 : 6). IR spectrum, ν, cm^{-1}: 1752, 1738 (C=O), 1596, 1586, 1572 (C=C arom), 1397 (P=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.84, 1.11 both d (3H, CH_3, ^3J 6.2 Hz), 3.56 septet (1H, OCH, $^3J_{HH}$ 6.2 Hz), 5.29 d (1H, H^5, $^4J_{PH}$ 1.1 Hz), 7.44–7.55 m (6H, H^m_{arom}), 7.56–7.65 m (3H, H^p_{arom}), 7.65–7.78 m (6H, H^o_{arom}). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 21.70, 23.24 both s (CH_3), 72.45 s (OCH), 97.12 d (C^3, $^3J_{PC}$ 16.7 Hz), 98.87 d (C^5, $^3J_{PC}$ 14.4 Hz), 128.85 d (C^m, $^3J_{PC}$ 12.7 Hz), 129.48 d (C^i, $^1J_{PC}$ 103.8 Hz), 132.61 d (C^o, $^2J_{PC}$ 10.3 Hz), 132.64 d (C^p, $^4J_{PC}$ 4.9 Hz),

163.05 s (C^4), 169.85 s (C^2). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), δ_P, ppm: 11.64. Mass spectrum (HRMS), *m/z*: 452.1179 $[M + H]^+$ (calculated for $C_{25}H_{24}ClNO_3P^+$: 452.1177).

3-Chloro-5-(2-chloroethoxy)-4-[(triphenyl-λ^5-phosphanylidene)amino]furan-2(5*H*)-one (4d) was synthesized as described for compound **4a** from azide **3d** (0.43 g, 1.8 mmol) and triphenylphosphine (0.47 g, 1.8 mmol). Yield 68%, colorless crystals, mp 203°C, R_f 0.60 (acetone–toluene, 1 : 6). IR spectrum, ν, cm^{-1}: 1747 (C=O), 1596, 1584, 1572 (C=C arom), 1380 (P=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.11–3.27, 3.54–3.70 both m (1H, OCH_2), 3.30–3.49 m (2H, CH_2Cl), 5.07 d (1H, H^5, $^4J_{PH}$ 1.1 Hz), 7.46–7.57 m (6H, H^m_{arom}), 7.58–7.66 m (3H, H^p_{arom}), 7.67–7.79 m (6H, H^o_{arom}). ^1H NMR spectrum (acetone-d_6), δ, ppm: 3.06–3.18, 3.56–3.69 both m (1H, OCH_2), 3.36–3.52 m (2H, CH_2Cl), 5.13 s (1H, H^5), 7.59–7.69 m (6H, H^m_{arom}), 7.69–7.78 m (3H, H^p_{arom}), 7.79–7.90 m (6H, H^o_{arom}). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 41.97 s (CH_2Cl), 67.66 s (OCH_2), 96.90 d (C^3, $^3J_{PC}$ 18.3 Hz), 98.87 d (C^5, $^3J_{PC}$ 14.1 Hz), 128.87 d (C^i, $^1J_{PC}$ 103.2 Hz), 128.95 d (C^m, $^3J_{PC}$ 12.7 Hz), 132.64 d (C^o, $^2J_{PC}$ 10.5 Hz), 132.81 d (C^p, $^4J_{PC}$ 2.7 Hz), 162.37 s (C^4), 169.33 s (C^2). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), δ_P, ppm: 12.76. $^{31}P\{^1H\}$ NMR spectrum (acetone-d_6), δ_P, ppm: 12.30. Mass spectrum (HRMS), *m/z*: 472.0629 $[M + H]^+$ (calculated for $C_{24}H_{21}Cl_2NO_3P^+$: 472.0631).

3-Chloro-5-(1,3-dichloropropan-2-yloxy)-4-[(triphenyl-λ^5-phosphanylidene)amino]furan-2(5*H*)-one (4e) was synthesized as described for compound **4a** from azide **3e** (0.49 g, 1.7 mmol) and triphenylphosphine (0.45 g, 1.7 mmol). Yield 86%, colorless crystals, mp 147°C, R_f 0.42 (acetone–toluene, 1 : 6). IR spectrum, ν, cm^{-1}: 1755 (C=O), 1601, 1569, 1483 (C=C arom), 1370 (P=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.48–3.84 m (4H, CH_2Cl), 3.88–4.01 m (1H, OCH), 5.56 d (1H, H^5, $^4J_{PH}$ 1.1 Hz), 7.42–7.57 m (6H, H^m_{arom}), 7.57–7.65 m (3H, H^p_{arom}), 7.65–7.79 m (6H, H^o_{arom}). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 43.15, 43.19 both s (CH_2), 76.78 s (OCH), 96.01 d (C^3, $^3J_{PC}$ 11.3 Hz), 100.16 d (C^5, $^3J_{PC}$ 20.0 Hz), 129.00 d (C^m, $^3J_{PC}$ 12.7 Hz), 129.19 d (C^i, $^1J_{PC}$ 103.4 Hz), 132.52 d (C^o, $^2J_{PC}$ 10.5 Hz), 132.82 d (C^p, $^4J_{PC}$ 2.7 Hz), 161.79 s (C^4), 169.22 s (C^2). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), δ_P, ppm: 12.97. Mass spectrum (HRMS), *m/z*: 520.0396 $[M + H]^+$ (calculated for $C_{25}H_{22}Cl_3NO_3P^+$: 520.0397).

5(*S*)-3-Chloro-5-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyloxy]-4-[(triphenyl-λ^5-phosphanylidene)amino]furan-2(5*H*)-one (4f) was synthesized as described for compound **4a** from azide **3f** (0.41 g, 1.3 mmol) and triphenylphosphine (0.34 g, 1.3 mmol). Yield 86%, colorless crystals, mp 235–236°C, R_f 0.65 (acetone–toluene, 1 : 6), $[\alpha]_D^{20}$ +13.3 (*c* 1.0, $CHCl_3$). IR spectrum, ν, cm^{-1}: 2957, 2915, 2835 (C–H), 1750 (C=O), 1606, 1585, 1573 (C=C arom), 1361 (P=N). ^1H NMR spectrum (acetone-d_6), δ, ppm: 0.78, 0.81 both d (3H, CH_3, *i*-Pr, ^3J 7.0 Hz), 0.89 d (3H, H^{12}, ^3J 6.6 Hz), 0.84–1.11 m (3H, H^7, H^9, H^{10}), 1.24–1.34 m (1H, H^{11}), 1.35–1.49 m (1H, H^8), 1.57–1.70 m (2H, H^9, H^{10}), 2.06–2.17 m (1H, H^7), 2.47 septet of doublets (1H, H^{13}, ^3J 7.0, ^3J 2.4 Hz), 3.57 ddd (1H, H^6, ^3J 10.6, ^3J 4.3 Hz), 5.66 d (1H, H^5, $^4J_{PH}$ 1.8 Hz), 7.57–7.66 m (6H, H^m_{arom}), 7.66–7.74 m (3H, H^p_{arom}), 7.75–7.87 m (6H, H^o_{arom}). $^{13}C\{^1H\}$ NMR spectrum (acetone–d_6), δ, ppm: 17.67, 22.37 both s (CH_3, *i*-Pr), 23.56 s (C^{12}), 24.93 s (C^{10}), 26.94 s (C^{13}), 33.33 s (C^8), 36.00 s (C^9), 44.34 s (C^7), 50.41 s (C^{11}), 83.14 s (C^6), 96.01 d (C^3, $^3J_{PC}$ 8.8 Hz), 103.74 d (C^5, $^3J_{PC}$ 24.0 Hz), 130.84 d (C^m, $^3J_{PC}$ 12.6 Hz), 132.12 d (C^i, $^1J_{PC}$ 102.7 Hz), 134.33 d (C^o, $^2J_{PC}$ 10.3 Hz), 134.55 d (C^p, $^4J_{PC}$ 2.8 Hz), 165.06 d (C^4, $^2J_{PC}$ 2.5 Hz), 170.48 s (C^2). $^{31}P\{^1H\}$ NMR spectrum (acetone-d_6), δ_P, ppm: 12.86. Mass spectrum (HRMS), *m/z*: 548.2119 $[M + H]^+$ (calculated for $C_{32}H_{36}ClNO_3P^+$: 548.2116).

3-Bromo-5-methoxy-4-[(triphenyl-λ^5-phosphanylidene)amino]furan-2(5*H*)-one (4g) was synthesized as described for compound **4a** from azide **3g** (0.12 g, 0.5 mmol) and

triphenylphosphine (0.14 g, 0.5 mmol). Recrystallization from $CHCl_3$. Yield 66%, colorless crystals, mp 195–196°C, R_f 0.52 (acetone–toluene, 1 : 6). IR spectrum, ν, cm^{-1}: 3060, 3009, 2931, 2834 (C–H), 1756, 1744 (C=O), 1597, 1572 (C=C arom), 1399 (P=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.86 s (3H, OCH_3), 4.79 s (1H, H^5), 7.35–8.00 m (15H, H_{arom}). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 55.10 s (OCH_3), 85.38 d (C^3, $^3J_{PC}$ 22.6 Hz), 100.20 d (C^5, $^3J_{PC}$ 10.7 Hz), 128.71 d (C^i, $^1J_{PC}$ 103.2 Hz), 128.86 d (C^m, $^3J_{PC}$ 12.6 Hz), 132.59 d (C^o, $^2J_{PC}$ 10.5 Hz), 132.69 d (C^p, $^4J_{PC}$ 2.8 Hz), 165.72 s (C^4), 169.76 s (C^2). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), δ_P, ppm: 12.49. Mass spectrum (HRMS), *m/z*: 468.0366 $[M + H]^+$ (calculated for $C_{23}H_{20}BrNO_3P^+$: 468.0359).

4-Amino-3-chloro-5-methoxyfuran-2(5*H*)-one (5a). To a mixture of 0.30 g (0.7 mmol) of iminophosphorane **4a** in methanol (8 mL) cooled to 0°C with stirring was added a mixture of 0.47 g (2.1 mmol) $SnCl_2 \cdot 2H_2O$ and 8 mL of methanol. The reaction mixture was stirred for 24 hours at room temperature, the completion of the reaction was monitored by TLC. The colorless precipitate was filtered off, and the filtrate was evaporated to dryness. The resulting colorless oily residue was purified by column chromatography on silica gel with a gradual increase in the polarity of the eluent (acetone–toluene, from 1 : 6 to 1 : 2). The main fraction was evaporated to dryness, and the residue was recrystallized from chloroform. Yield 67%, colorless ctystals, mp 122°C (mp 122−123°C [26]), R_f 0.27 (acetone-toluene, 1 : 4). IR spectrum, ν, cm^{-1}: 3335, 3172 broad (NH_2), 1726 (C=O), 1659 (C=C), 1618 (NH_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.54 s (3H, OCH_3), 4.92 br s (2H, NH_2), 5.68 s (1H, H^5). ^1H NMR spectrum (acetone-d_6), δ, ppm: 3.46 s (3H, OCH_3), 5.78 s (1H, H^5), 6.84 br. s (2H, NH_2). $^{13}C\{^1H\}$ NMR spectrum (acetone-d_6), δ_C, ppm: 56.38 (OCH_3), 88.78 (C^3), 99.93 (C^5), 160.01 (C^4), 168.35 (C^2). Mass spectrum (HRMS), *m/z*: 185.9931 $[M + Na]^+$ (calculated for $C_5H_6ClNNaO_3^+$: 185.9928).

4-Amino-3-chloro-5-ethoxyfuran-2(5*H*)-one (5b) was synthesized as described for compound **5a** from furanone **4b** (0.26 g, 0.6 mmol) and $SnCl_2 \cdot 2H_2O$ (0.41 g, 1.8 mmol) in acetone. Recrystallization from CCl_4–$CHCl_3$ (2 : 1). Yield 75%, colorless crystals, mp 105°C, R_f 0.14 (acetone–toluene, 1 : 6). IR spectrum, ν, cm^{-1}: 3363, 3196 broad (NH_2), 1727 (C=O), 1652 (C=C), 1615 (NH_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 t (3H, ABX_3 system, X part, CH_3, $^3J_{AX} = {}^3J_{BX}$ 7.1 Hz), 3.68 m (1H, ABX_3 system, A part, OCH_A, $^2J_{AB}$ –9.4, $^3J_{AX}$ 7.1 Hz), 3.96 m (1H, ABX_3 system, B part, OCH_B, $^2J_{AB}$ –9.4, $^3J_{BX}$ 7.1 Hz), 4.93 br s (2H, NH_2), 5.72 s (1H, H^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ_C, ppm: 14.96 (CH_3), 64.98 (OCH_2), 91.06 (C^3), 97.19 (C^5), 156.41 (C^4), 166.84 (C^2). Mass spectrum (HRMS), *m/z*: 178.0256 $[M + H]^+$ (calculated for $C_6H_9ClNO_3^+$: 178.0265).

4-Amino-3-chloro-5-isopropoxyfuran-2(5*H*)-one (5c) was synthesized as described for compound **5a** from furanone **4c** (0.50 g, 1.1 mmol) and $SnCl_2 \cdot 2H_2O$ (0.74 g, 3.3 mmol) in methanol. Recrystallization from CCl_4–$CHCl_3$ (3 : 1). Yield 68%, colorless crystals, mp 137–138°C, R_f 0.28 (acetone–toluene, 1 : 6). IR spectrum, ν, cm^{-1}: 3413, 3301, 3189 broad (NH_2), 1741 (C=O), 1657 (C=C), 1598 (NH_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.28, 1.30 both d (3H, CH_3, $^3J_{HH}$ 6.2 Hz), 4.12 septet (1H, OCH, $^3J_{HH}$ 6.2 Hz), 4.89 broad s (2H, NH_2), 5.76 s (1H, H^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ_C, ppm: 22.06, 23.20 (CH_3), 73.60 (OCH), 91.05 (C^3), 96.34 (C^5), 156.81 (C^4), 167.00 (C^2). Mass spectrum (HRMS), *m/z*: 192.0418 $[M + H]^+$ (calculated for $C_7H_{11}ClNO_3^+$: 192.0422).

4-Amino-3-chloro-5-(2-chloroethoxy)furan-2(5*H*)-one (5d) was synthesized as described for compound **5a** from furanone **4d** (0.61 g, 1.3 mmol) and $SnCl_2 \cdot 2H_2O$ (0.88 g, 3.9 mmol) in the mixture CH_3CN–H_2O (3 : 1). Recrystallization from $CHCl_3$. Yield 77%, colorless crystals, mp 109°C, R_f 0.37 (acetone–toluene, 1 : 4). *ИК* spectrum, ν, cm^{-1}: 3434, 3300, 3193 broad (NH_2), 1748 (C=O), 1668 (C=C), 1608 (NH_2). ^1H NMR spectrum (CD_3OD), δ, ppm: 3.68–3.80 m (2H, CH_2Cl),

3.88–4.03 m (2H, OCH_2), 5.88 s (1H, H^5). $^{13}C\{^1H\}$ NMR spectrum (CD_3OD), δ_C, ppm: 43.32 (CH_2Cl), 69.86 (OCH_2), 87.22 (C^3), 99.09 (C^5), 160.72 (C^4), 170.17 (C^2). Mass spectrum (HRMS), *m/z*: 211.9868 $[M + H]^+$ (calculated for $C_6H_8Cl_2NO_3^+$: 211.9876).

4-Amino-3-chloro-5-(1,3-dichloropropan-2-yloxy)furan-2(5*H*)-one (5e) was synthesized as described for compound **5a** from furanone **4e** (0.21 g, 0.4 mmol) and $SnCl_2 \cdot 2H_2O$ (0.27 g, 1.2 mmol) in the acetone–water mixture (2 : 1). Recrystallization from CCl_4–$CHCl_3$ (1 : 3). Yield 70%, colorless crystals, mp 169°C, R_f 0.23 (acetone–toluene, 1 : 8). IR spectrum, ν, cm^{-1}: 3427, 3289, 3250, 3183 broad (NH_2), 1751 (C=O), 1665 (C=C), 1607 (NH_2). ^1H NMR spectrum ($CDCl_3$, δ, ppm): 3.56–3.98 m (4H, CH_2Cl), 4.11–4.23 m (1H, OCH), 4.97 br s (2H, NH_2), 5.86 s (1H, H^5). ^1H NMR spectrum (acetone-d_6), δ, ppm: 3.81–4.00 m (4H, CH_2Cl), 4.34–4.44 m (1H, OCH), 6.13 s (1H, H^5), 6.90 br s (2H, NH_2). $^{13}C\{^1H\}$ NMR spectrum (acetone-d_6), δ_C, ppm: 44.97, 45.34 (CH_2), 80.27 (OCH), 88.75 (C^3), 99.28 (C^5), 159.92 (C^4), 167.92 (C^2). Mass spectrum (HRMS), *m/z*: 259.9641 $[M + H]^+$ (calculated for $C_7H_9Cl_3NO_3^+$: 259.9643).

5(*S*)-4-Amino-3-chloro-5-[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyloxy]furan-2(5*H*)-one (5f) was synthesized as described for compound **5a** from furanone **4f** (0.22 g, 0.4 mmol) and $SnCl_2 \cdot 2H_2O$ (0.27 g, 1.2 mmol) in methanol. Recrystallization from CCl_4–$CHCl_3$ (3 : 1). Yield 84%, colorless crystals, mp 154–155°C, R_f 0.47 (acetone– toluene, 1 : 8), $[\alpha]_D^{20}$ +50.5 (*c* 1.0, MeOH). IR spectrum, ν, cm^{-1}: 3483, 3308, 3189 broad (NH_2), 2958, 2919, 2867 (C–H), 1738 (C=O), 1647 (C=C), 1607 (NH_2). ^1H NMR ($CDCl_3$), δ, ppm: 0.80, 0.91 both d (3H, CH_3, *i*-Pr, ^3J 7.0 Hz), 0.89 d (3H, H^{12}, ^3J 6.4 Hz), 0.82–1.12 m (3H, H^7, H^9, H^{10}), 1.26–1.50 m (2H, H^8, H^{11}), 1.55–1.72 m (2H, H^9, H^{10}), 2.01–2.30 m (2H, H^7, H^{13}), 3.54 ddd (1H, H^6, ^3J 10.7, ^3J 4.3 Hz), 5.10 br. s (2H, NH_2), 5.72 s (1H, H^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ, ppm: 15.84, 20.90 [CH_3 (*i*-Pr)], 21.98 (C^{12}), 22.83 (C^{10}), 25.68 (C^{13}), 31.47 (C^8), 33.84 (C^9), 42.32 (C^7), 47.93 (C^{11}), 82.91 (C^6), 90.31 (C^3), 98.56 (C^5), 157.30 (C^4), 167.33 (C^2). Mass spectrum (HRMS), *m/z*: 310.1186 $[M + Na]^+$ (calculated for $C_{14}H_{22}ClNNaO_3^+$: 310.1180).

4-Amino-3-bromo-5-methoxyfuran-2(5*H*)-one (5g) was synthesized as described for compound **5a** from furanone **4g** (0.14 g, 0.3 mmol) and $SnCl_2 \cdot 2H_2O$ (0.20 g, 0.9 mmol) in methanol. Recrystallization from $CHCl_3$. Yield 72%, colorless crystals, mp 147–149°C, R_f 0.51 (acetone–toluene, 1 : 2). IR spectrum, ν, cm^{-1}: 3324, 3171 broad (NH_2), 1719 (C=O), 1656 (C=C), 1610 (NH_2). ^1H NMMR spectrum ($CDCl_3$), δ, ppm: 3.53 s (3H, CH_3), 4.92 br. s (2H, NH_2), 5.69 s (1H, H^5). ^1H NMR spectrum (acetone-d_6), δ, ppm: 3.46 s (3H, CH_3), 5.79 s (1H, C^5H), 6.90 br. s (2H, NH_2). $^{13}C\{^1H\}$ NMR spectrum (acetone-d_6), δ_C, ppm: 56.28 (CH_3), 75.74 (C^3), 100.72 (C^5), 162.89 (C^4), 168.60 (C^2). Mass spectrum (HRMS), *m/z*: 207.9604 $[M + H]^+$ (calculated for $C_5H_7BrNO_3^+$: 207.9604).

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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Table 1. Crystallographic data and X-ray structural experiment parameters for the single crystals **3c**, **4a**, **4f** and **4g**

Compound	**3c**	**4a**	**4f**	**4g**
Empirical formula	$C_7H_8ClN_3O_3$	$C_{23}H_{19}ClNO_3P$	$C_{32}H_{35}ClNO_3P$	$C_{23}H_{19}BrNO_3P$, $CHCl_3$
Formula weight	217.61	423.81	548.03	587.64
Crystal system	orthorhombic	triclinic	monoclinic	triclinic
Space group	*Pbcn* (No. 60)	*P*–1 (No. 2)	$P2_1$ (No. 4)	*P*–1 (No. 2)
Unit cell parameters: *a*, *b*, *c*, Å; α, β, γ, deg	10.9712(4), 11.4339(4), 15.2844(6); 90, 90, 90	9.1226(7), 10.0937(8), 13.4536(11); 93.115(2), 108.402(2), 116.775(2)	10.05570(10), 14.49330(10), 10.73010(10); 90, 112.254(2), 90	10.4780(8), 16.2126(13), 16.4848(13); 63.064(2), 82.839(2), 83.215(3)
Unit cell volume, $Å^3$	1917.33(12)	1020.80(14)	1447.33(3)	2471.1(3)
Z / *Z*'	8 / 1	2 / 1	2 / 1	4 / 2
Calculated density, g cm^{-3}	1.508	1.379	1.258	1.580
Absorption coefficient, mm^{-1}	0.384	0.290	1.949	2.080
F(000)	896	440	580	1184
θ range for data collection, deg	2.573–25.999	1.640–30.643	4.452–76.687	1.964–26.999
Index ranges	$-13 \le h \le 13$, $-14 \le k \le 14$, $-18 \le l \le 18$	$-13 \le h \le 11$, $-14 \le k \le 14$, $-19 \le l \le 19$	$-12 \le h \le 12$, $-18 \le k \le 18$, $-13 \le l \le 13$	$-11 \le h \le 13$, $-19 \le k \le 20$, $-17 \le l \le 21$
Total / independent reflection number (R_{int})	23010 / 1893 (0.0503)	26450 / 6243 (0.0346)	19354 / 5865 (0.0268)	21496 / 10617 (0.0374)
R_σ	0.0243	0.0331	0.0232	0.0626
T_{max} / T_{min}		0.981 / 0.914	0.720 / 0.602	0.607 / 0.326
Final *R* indices [$I > 2\sigma(I)$]	1618	5079	5811	7914
Data / restraints / parameters	1893 / 0 / 129	6243 / 0 / 263	5865 / 1 / 346	10617 / 0 / 597
GOOF	1.058	0.967	1.045	0.967
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0279, *wR*2 = +0.0638	*R*1 = 0.0533, *wR*2 = 0.1424	*R*1 = 0.0262, *wR*2 = 0.0687	*R*1 = 0.0385, *wR*2 = 0.0815
R indices (all data)	*R*1 = 0.0359, *wR*2 = 0.0673	*R*1 = 0.0669, *wR*2 = 0.1475	*R*1 = 0.0263, *wR*2 = 0.0688	*R*1 = 0.0608, *wR*2 = 0.0748

Flack parameter	-	-	0.005(5)	-
Largest diff. peak and hole, e Å^{-3}	0.272 and –0.224	0.671 and –0.437	0.198 and –0.315	0.714 and –0.634
CCDC	2305614	2305615	2305617	2305613

Table 2. Crystallographic data and X-ray structural experiment parameters for the single crystals **5a**, **5b** and **5e**

Compound	**5a**	**5b**	**5e**
Empirical formula	$C_5H_6ClNO_3$	$C_6H_8ClNO_3$	$C_7H_8Cl_3NO_3$
Formula weight	163.56	177.58	260.49
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	*Pna*2$_1$ (No. 33)	*Pna*2$_1$ (No. 33)	*I*2/*a* (No. 15)
Unit cell parameters: *a*, *b*, *c*, Å; α, β, γ, deg	12.054(4), 8.075(2), 7.483(2); 90, 90, 90	12.22740(10), 8.36590(10), 7.86530(10); 90, 90, 90	13.4497(3), 6.6546(2), 22.7655(6); 90, 99.814(3), 90
Unit cell volume, Å^3	728.3(4)	804.567(16)	2007.75(9)
Z / Z'	4 / 1	4 / 1	8 / 1
Calculated density, g cm^{-3}	1.492	1.466	1.724
Absorption coefficient, mm^{-1}	0.470	3.912	8.144
F(000)	336	368	1056
θ range for data collection, deg	3.036–25.967	6.411–76.235	3.941–76.446
Index ranges	$-13 \le h \le 14$, $-9 \le k \le 9$, $-9 \le l \le 9$	$-14 \le h \le 14$, $-9 \le k \le 10$, $-9 \le l \le 9$	$-16 \le h \le 16$, $-8 \le k \le 8$, $-27 \le l \le 28$
Total / independent reflection number (R_{int})	3671 / 1379 (0.0274)	20037 / 1631 (0.0390)	9442 / 2066 (0.0290)
R_σ	0.0309	0.0136	0.0178
Final R indices [$I > 2\sigma(I)$]	1334	1623	2001
Data / restraints / parameters	1379 / 1 / 115	1631 / 1 / 109	2066 / 0 / 135
GOOF	1.056	1.114	1.101
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0243, $wR2$ = 0.0600	$R1$ = 0.0207, $wR2$ = 0.0536	$R1$ = 0.0293, $wR2$ = 0.0801
R indices (all data)	$R1$ = 0.0252, $wR2$ = 0.0605	$R1$ = 0.0208, $wR2$ = 0.0537	$R1$ = 0.0301, $wR2$ = 0.0807
Flack parameter	0.05(3)	–0.003(6)	-
Largest diff. peak and hole, e Å^{-3}	0.132 and –0.220	0.180 and –0.190	0.404 and –0.256
CCDC	2305612	2305616	2305618

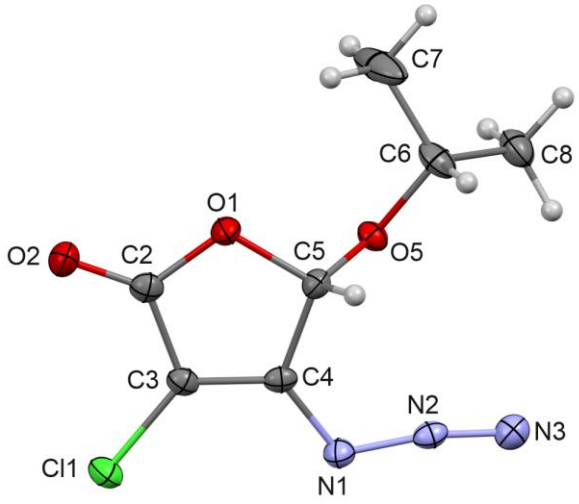
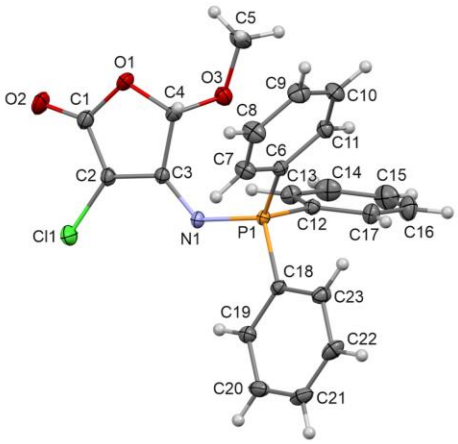


Fig. 1.

a)



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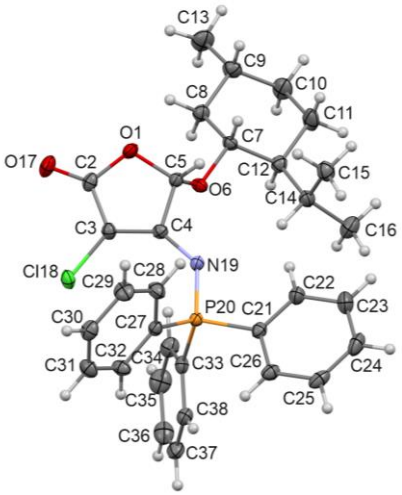

c)

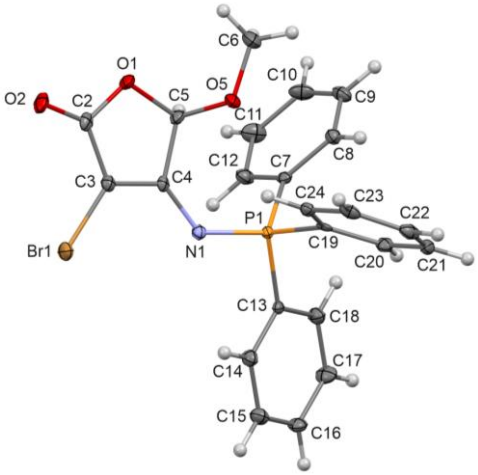

Fig. 2.

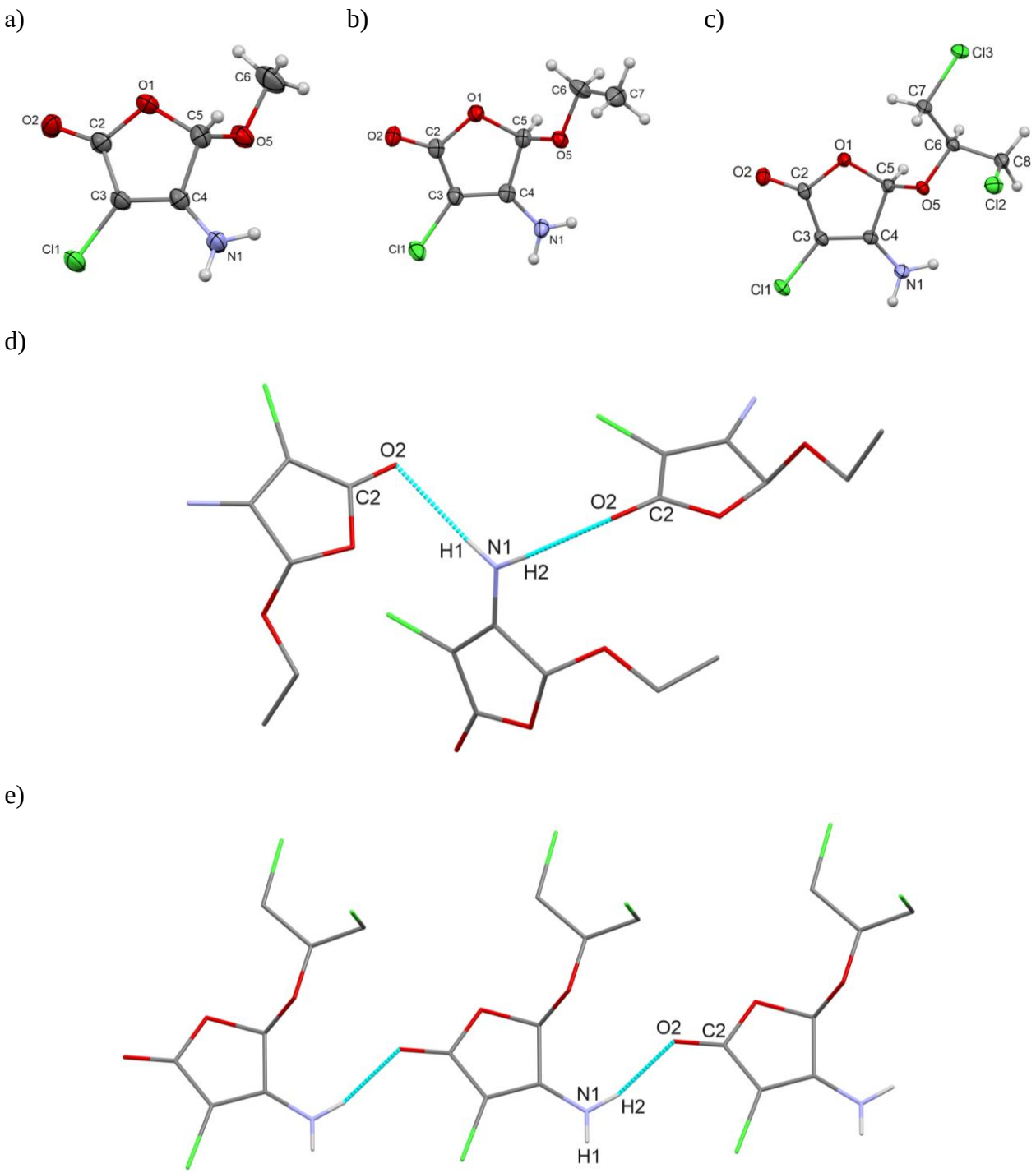

Fig. 3.

FIGURE CAPTIONS

Fig. 1. Molecular structure of azide **3c** in the crystal.

Fig. 2. Molecular geometry of iminophosphoranes (a) **4a**, (b) **4f**, (c) **4g** in the crystal.

Fig. 3. Molecular geometry of amines (a) **5a**, (b) **5b**, (c) **5e** in the crystal. (d) The system of hydrogen bonds in the crystal **5b** (for the crystal **5a** the picture is similar). (e) Hydrogen-bonded chain of molecules in the crystal **5e**.