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Synthesis of Symmetrical *N*-(Het)aryl-*C*-phosphonoacetamidines

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Abstract—A series of new symmetrical *C*-phosphonylated acetamidines was obtained by the reaction of diethyl chloroethynylphosphosphonate with a number of primary aromatic and heteroaromatic amines.

Keywords: symmetrical phosphorus-containing amidines, *C*-phosphonylated acetamidines, primary aromatic amines

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Amidines have attracted considerable interest due to the high reactivity caused by the presence in their structure of an amino group coupled to a multiple C=N bond [1, 2]. The synthetic potential of compounds of this class is extremely large. Amidines and their derivatives are used as key intermediates in the synthesis of various classes of organic compounds [3–5], including nitrogen-containing heterocycles [6], metallacycles, and coordination compounds [7–10]. This structural fragment is part of a large number of natural compounds [3]. Due to the unique structure, amidines are highly basic compounds and can act as superbases [11, 12]. In addition, amidines exhibit a wide range of biological activity, and therefore are of interest to be prospective precursors for drug design [13–15].

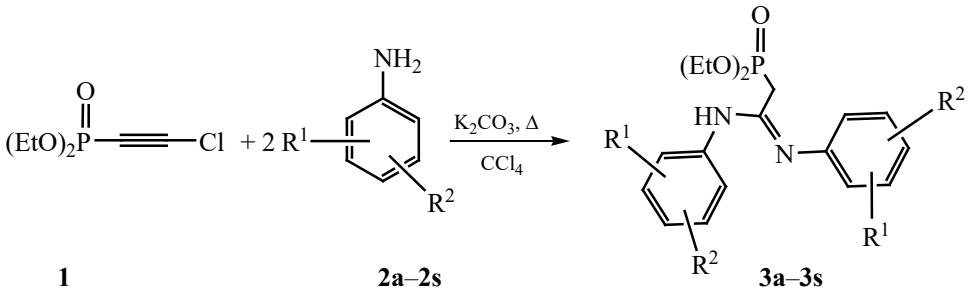
The introduction of an aryl or heteroaryl group to the nitrogen atom weakens the basic properties of amidines and increases lipophilicity, which, in turn, opens the way to the creation of new compounds with diverse biological activity [16, 17]. Compounds containing an *N*-arylamidine fragment are effective anti-inflammatory and analgesic agents [18–20]. Amidines having aryl substituents at the nitrogen atom are precursor compounds for the synthesis of biologically important heterocycles, such as imidazoles [21, 22], benzimidazoles [23], quinazolines and quinazolinones [24–27], pyrimidines [28], etc.

Modification of the structure of amidines by the introduction of a phosphonate group allows us to expand their synthetic and biological potential [29–33]. Phosphonates and their derivatives are widely used in biochemistry [34], organic synthesis [35], medical [36–38] and agrochemistry [39]. Amidines containing a phosphoryl group have been first described in [40, 41]. To date, there are only a few examples of the synthesis of *C*-phosphorylated amidines [42–50]. However, the synthesis of symmetric phosphonylated amidines is presented by single examples [40, 41, 49, 51]. Thus, a method for the synthesis of *N*-alkylated symmetric amidines by the reaction of *gem*-dichlorovinylphosphonate with primary amines has been reported in [51]. An alternative approach to the preparation of symmetric phosphonoamidines is the reaction of phosphorylated ketenimines with amines [40].

In continuation of the studies in the field of chemistry of phosphorus-containing amidines [49, 50, 52, 53], we synthesized a number of new symmetrical *C*-phosphonoacetamidines based on the reaction of diethyl 2-chloroethynylphosphonate with primary aromatic and some heteroaromatic amines. Earlier, we have showed the possibility of obtaining symmetrical *N*-arylphosphonoacetamidines from chloroacetylenephosphonates [49]. Herein, we expanded the range of primary aryl amines introduced into the reaction and investigated the effect of various substituents in the aromatic ring on the reaction output.

It was found that the reactions of diethyl 2-chloroethynylphosphonate **1** [54] with primary aryl amines **2a**–**2q** lead to the formation of the corresponding *N*-arylphosphonoacetamidines **3a**–**3q** with a yield of 30–93% (Scheme 1, see table). The reactions proceeded in anhydrous carbon tetrachloride at 80°C in the presence of 1 equiv. of K_2CO_3

Scheme 1.



as an acceptor of released hydrogen chloride for 10–49 h with a reagent ratio of 1 : 2 = 1 : 2. It should be noted that in order to avoid the undesired formation of amides due to the reaction of intermediate ynaminophosphonates even with trace amounts of water, the reaction must be carried out in an argon atmosphere using an anhydrous solvent and amines.

Analyzing data on similar reactions involving primary aryl amines bearing a substituent in the *para*-position [49], it can be noted that in the case of *meta*-substituted aryl amines, a longer time is required to achieve complete conversion (up to 40–49 h). Thus, in the reaction of chloroacetylenephosphonate **1** with *m*-toluidine **2a**, complete conversion was achieved in 40 h, the yield of the target amidine was 79%, while the reaction with *p*-toluidine proceeded in 10 h with the formation of the corresponding amidine with a yield of 86% [49]. A similar result was obtained in the case of other *meta*-substituted anilines **2b**–**2i**. The highest yield of the target symmetric amidines (91–93%) was achieved by the reaction with 4-isopropyl- (**2b**), 4-chloro- (**2j**) and 4-trifluoromethoxyaniline (**2k**). As expected, the reaction time in this case was 10–15 h.

When using 3-halo-substituted arylamines, the highest yield (73%) was achieved in the case of *m*-chloroaniline **2e**. In contrast to *para*-haloanilines [49], the reactivity of arylamines having an Hlg substituent in the *meta* position decreases in the following order: Cl > Br > F (see table).

The reactions of aromatic amines **2d**, **2h**, and **2i** bearing acceptor substituents (Ac, NO_2, CF_3) with diethyl 2-chloroethylphosphonate **1** take place within 45–49 h, leading to the formation of the corresponding amidines with a satisfactory yield (59–63%).

In the case of disubstituted aromatic amines **2l**–**2q** best results were achieved when using 3,4-dichloroaniline **2m**: the reaction time was 14 h, while the yield of the target product was 80%. For the remaining disubstituted anilines used, complete conversion was achieved in 46–48 h, while the yield of the corresponding amidines did not exceed 60% (see Table). Similar results were obtained in the case of 5-amino-2-methylisoindole-1,3-dione **2r** and 2,3-dihydrobenzo[1,4]dioxin-6-amine **2s**: yield of the target amidines in this case was 44 and 53%, respectively.

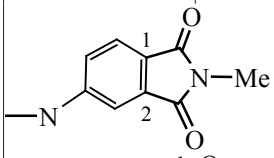
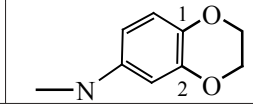
Structure and composition of the obtained symmetrical *C*-phosphonylated acetamidines was proved using IR and ^{1}H, ^{13}C, ^{31}P, ^{19}F NMR spectroscopy, as well as mass spectrometry (see Table). Thus, in the ^{1}H NMR spectra of phosphonoacetamidines **3a**–**3s**, there is a characteristic doublet signal of protons of the methylene fragment PCH_2 in the region of 2.95–3.05 ppm with the spin-spin coupling constant of $^{2}J_{HP}$ = 21.6–22.3 Hz. In the ^{13}C NMR spectra the carbon atom attached to the phosphorus atom manifests as a doublet signal with at 28.72–30.90 ppm with the spin-spin coupling constant of $^{1}J_{CP}$ = 131.3–132.7 Hz, which is typical for phosphonates with sp^3-hybridized carbon atom. The carbon of the azomethine fragment resonates in a weak field at 147.09–149.21 ppm with a spin-spin coupling constant of $^{2}J_{CP}$ = 6.6–7.3 Hz. The chemical shift of the phosphorus atom in acetamidines **3a**–**3s** is recorded in the range of 21.02–22.59 ppm.

The IR spectra of compounds **3a**–**3s** contain strong absorption bands in the regions of 1019–1065 and 1227–1291 cm^{-1} due to stretching vibrations of the P–O–C and P=O bonds, respectively. The absorption in the regions of 3102–3371 (NH) and 1493–1607 cm^{-1} (C=N) is due to the vibrations of amidine fragment.

Data of single crystal X-ray diffraction analysis using the example of diethyl (2-{[3-(trifluoromethyl)phenyl]-amino}-2-{[3-(trifluoromethyl)phenyl]imino}ethyl)-phosphonate **3i** (see Figure) also undoubtedly confirm the structure of the obtained phosphonoacetamidines **3a**–**3s**.

In summary, the reactions of 2-chloroethynylphosphonate with primary aryl amines yields a new series of symmetrical *N*-(het)aryl-*C*-phosphonoacetamidines. The

Yields, reaction time, ^{31}P NMR and mass spectrometry data for symmetrical phosphonoacetamides **3a**–**3s**

Comp. no.	R^1	R^2	Time, h	Yield, %	mp, °C	m/z $[M + H]^+$	δ_P, ppm
3a	3-Me	H	40	79	76–78	375.1832	22.53
3b	4-*i*-Pr	H	10	91	101–103	453.2276	22.54
3c	3-OMe	H	44	55	–	407.1743	22.41
3d	3-Ac	H	49	62	92–94	431.1730	21.95
3e	3-Cl	H	45	71	85–87	415.0810	21.61
3f	3-Br	H	46	68	88–90	504.9735	21.63
3g	3-F	H	48	53	–	383.1344	21.74
3h	3-NO_2	H	49	59	109–111	437.1237	21.28
3i	3-CF_3	H	45	63	75–77	483.1254	21.53
3j	4-Cl	H	10	93	104–106	415.0727	21.85
3k	4-OCF_3	H	15	92	125–127	537.1013	21.71
3l	3-OMe	4-OMe	46	56	–	467.1959	22.95
3m	3-Cl	4-Cl	14	80	95–97	482.9975	21.35
3n	3-Cl	4-OMe	48	59	–	475.0906	22.16
3o	3-NO_2	4-Me	46	55	106–108	465.1521	21.48
3p	2-Me	3-Cl	47	30	73–75	443.1057	22.66
3q	2-Cl	3-NO_2	49	45	122–124	527.0265	21.62
3r			48	44	–	513.1527	21.02
3s			40	53	133–135	463.1612	22.59

obtained phosphorylated amidines may be of interest as promising building blocks in organic synthesis and for the preparation of substances with a potentially wide spectrum of biological activity.

EXPERIMENTAL

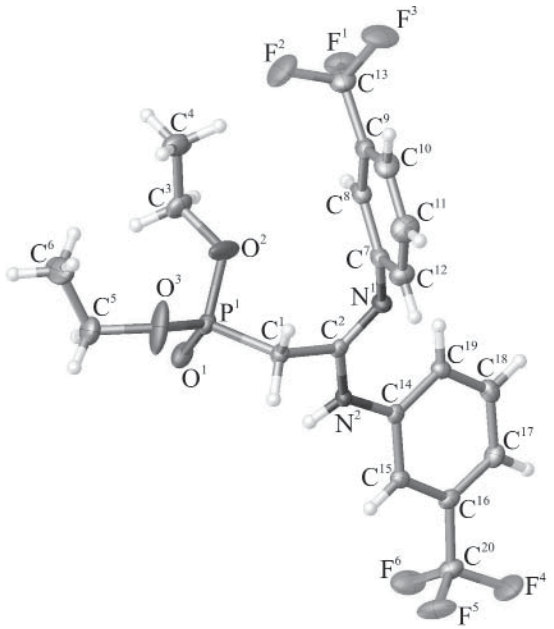
NMR spectra were recorded on a Bruker Ascend 400 spectrometers [400.13 (^1H), 100.61 (^{13}C), 161.98 (^{31}P) and 376.50 MHz (^{19}F)] from DMSO-d_6 solutions. Chemical shifts of phosphorus are given relative to the external 85% phosphoric acid. The signals in the ^1H, ^{13}C NMR spectra were assigned using two-dimensional homo- and heteronuclear NMR spectroscopy NOESY, HMQC, HSQC techniques. IR spectra were recorded on a Shimadzu IRAffinity-1 spectrometer from KBr pellets. High-resolution mass spectra (ESI)were recorded on a Bruker MicrOTOF mass spectrometer; the ionization chamber temperature 180°C; the ionization voltage 70 and 100 eV). Melting points were measured on a Kofler table (VEB Wägetechnik Rapido, PHMK 81/2969).

Single crystal X-ray diffraction analysis was performed on an Agilent Technologies Xcalibur diffractometer at 100 K. Crystals of compound **3i** are monoclinic, $C_{20}H_{21}F_6N_2O_3P$, space group P_{21}/c, the unit cell parameters: $a = 15.7826(8)$ Å, $b = 10.7262(5)$ Å, $c = 26.2490(12)$ Å, $\beta = 97.252(5)°$, $V = 4408.1(4)$ Å^3, $Z = 8$, $d_{calc} = 1.454$ g/cm^3, $\mu(MoK_\alpha) = 0.199$ mm^{-1}, $F(000) = 1984.0$, $R_1 = 0.0504$ (8156 reflections), $wR_2 = 0.1264$ (10099).

General procedure for the synthesis of *C*-phosphonoacetamidines. To a solution of 1 mmol of diethyl 2-chloroethynylphosphonate **1** [31] in 10 mL of anhydrous carbon tetrachloride was added with vigorous stirring at room temperature 2 mmol of the corresponding amine **2a**–**2s**. The resulting mixture was boiled for 10–49 h in an argon atmosphere. The reaction progress was monitored by ^{31}P NMR method. After the reaction completed, the mixture was filtered, and the solvent was distilled off. The residue was recrystallized from hexane.

Diethyl {2-[(3-methylphenyl)amino]-2-(3-methylphenylimino)ethyl}phosphonate (3a). Yield 79%, white crystals, mp 76–78°C. IR spectrum, ν, cm^{-1}: 1022 (P–O–C), 1232 (P=O), 3038 (CH_3), 3291 (NH). ^{1}H NMR spectrum, δ, ppm: 1.18 t (6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 2.27 s [6H, CH_3(Ph)], 2.98 d (2H, P–CH_2, $^2J_{HP}$ = 21.8 Hz), 3.93 d. q (4H, $POCH_2$, $^3J_{HH}$ = 7.0, $^3J_{HP}$ = 14.2 Hz), 6.60 d (1H, CH^p_{NH}, $^3J_{HH}$ = 7.8 Hz), 6.64 s (1H, CH^o_{NH}), 6.78 d (1H, $CH^o_{N=}$, $^3J_{HH}$ = 6.5 Hz), 6.79 d (1H, $CH^p_{N=}$, $^3J_{HH}$ = 6.4 Hz), 7.15 t (2H, CH^m_{NH}, $CH^m_{N=}$, $^3J_{HH}$ = 7.7 Hz), 7.52 d (1H, CH^o_{NH}, $^3J_{HH}$ = 8.3 Hz), 7.54 s (1H, $CH^o_{N=}$), 8.49 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.59 d (CH_3, $^3J_{CP}$ = 5.9 Hz), 21.50 (CH_{3NH}), 21.76 ($CH_{3N=}$), 28.88 d (PCH_2, $^1J_{CP}$ = 132.1 Hz), 62.24 d ($POCH_2$, $^2J_{CP}$ = 6.6 Hz), 116.64 (CH^o_{NH}), 119.00 (CH^o_{NH}), 119.83 (CH^p_{NH}), 122.77 ($CH^o_{N=}$), 122.94 ($CH^o_{N=}$), 123.03 ($CH^p_{N=}$), 128.74 ($CH^m_{N=}$), 128.97 (CH^m_{NH}), 137.95 ($C^m_{N=}$), 138.28 (C^m_{NH}), 141.19 ($C^{ipso}_{N=}$), 147.09 d (=C^2, $^2J_{CP}$ = 6.6 Hz), 150.32 (C^{ipso}_{NH}). ^{31}P NMR spectrum: δ_P 22.53 ppm. Mass spectrum, *m/z*: 375.1832 $[M + H]^+$ (calcd. $C_{20}H_{27}N_2O_3P$: 375.1821 $[M + H]^+$).

Diethyl {2-[(4-isopropylphenyl)amino]2-[(4-isopropylphenyl)imino]ethyl}phosphonate (3b). Yield 91%, reddish crystals, mp 101–103°C. IR spectrum, ν, cm^{-1}: 1025 (P–O–C), 1260 (P=O), 1605 (C=N), 2959 (CH_3), 3333 (NH). ^{1}H NMR spectrum, δ, ppm: 1.16 t (6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 1.17 d (6H, CH_3, $^3J_{HH}$ = 6.5 Hz), 1.19 d (6H, CH_3, $^3J_{HH}$ = 5.4 Hz), 2.83 d. sept (2H, CH, $^3J_{HH}$ = 6.9 Hz), 2.97 d (2H, PCH_2, $^2J_{HP}$ = 21.6 Hz), 3.89 d. q (4H, $POCH_2$, $^3J_{HH}$ = 7.1, $^3J_{HP}$ = 14.3 Hz), 6.71 d (2H, $CH^o_{N=}$, $^3J_{HH}$ = 8.1 Hz), 7.13 d (4H, CH^p, $^3J_{HH}$ = 8.4 Hz), 7.61 d (2H, CH^o_{NH}, $^3J_{HH}$ = 8.3 Hz), 8.53 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.61 d (CH_3, $^3J_{CP}$ = 5.9 Hz), 24.51 (CH_{3NH}), 24.58 ($CH_{3N=}$), 28.72 d (P–CH_2, $^1J_{CP}$ = 131.4 Hz), 33.27 (CH), 62.20 d ($POCH_2$, $^2J_{CP}$ = 6.5 Hz), 119.55 (CH^o_{NH}), 121.89 ($CH^o_{N=}$), 126.56 (CH^m_{NH}), 126.91 ($CH^m_{N=}$), 139.04 ($C^{ipso}_{N=}$), 142.09 (C^p_{NH}), 142.19 ($C^p_{N=}$), 147.15 d (=C^2, $^2J_{CP}$ = 6.9 Hz), 148.16 (C^{ipso}_{NH}). ^{31}P NMR spectrum: δ_P 22.54 ppm. Mass spectrum, *m/z*: 453.2276 $[M + Na]^+$ (calcd. $C_{24}H_{35}N_2O_3P$: 453.2278 $[M + Na]^+$).



General view of the molecule of compound **3i** in the crystal (CCDC 1832056).

Diethyl {2-[(3-methoxyphenyl)amino]-2[(3-methoxyphenyl)imino]ethyl}phosphonate (3c). Yield 55%, pale yellow oil. IR spectrum, ν, cm^{-1}: 1047 (P–O–C), 1251 (P=O), 1593 (C=N), 3332 (NH). ^{1}H NMR spectrum, δ, ppm: 1.19 t (6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 3.01 d (2H, PCH_2, $^2J_{HP}$ = 21.7 Hz), 3.72 s (3H, OCH_3), 3.74 s (3H, OCH_3), 3.94 d. q (4H, $POCH_2$, $^3J_{HH}$ = 7.0, $^3J_{HP}$ = 14.9 Hz), 6.41 d (1H, $CH^o_{N=}$, $^3J_{HH}$ = 7.8 Hz), 6.44 s (1H, CH^o_{NH}), 6.56 d (2H, CH^p_{NH}, $CH^o_{N=}$, $^3J_{HH}$ = 7.8 Hz), 7.18 t (2H, CH^m_{NH}, $CH^m_{N=}$, $^3J_{HH}$ = 8.0 Hz), 7.24 br. d (1H, $CH^p_{N=}$, $^3J_{HH}$ = 7.4 Hz), 7.51 br. s (1H, CH^o_{NH}), 8.64 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.56 d (CH_3, $^3J_{CP}$ = 5.9 Hz), 29.11 d (PCH_2, $^1J_{CP}$ = 131.7 Hz), 55.33 (OCH_3), 62.29 d ($POCH_2$, $^2J_{CP}$ = 6.4 Hz), 105.61 (CH^o_{NH}), 107.36 (CH^p_{NH}), 107.55 (CH^o_{NH}), 108.32 ($CH^o_{N=}$), 111.96 ($CH^o_{N=}$), 114.35 ($CH^o_{N=}$), 129.62 ($CH^m_{N=}$), 129.86 (CH^m_{NH}), 142.31 ($C^{ipso}_{N=}$), 147.30 d (=C^2, $^2J_{CP}$ = 6.9 Hz), 151.63 (C^{ipso}_{NH}), 159.91 ($C^m_{N=}$), 160.29 (C^m_{NH}). ^{31}P NMR spectrum: δ_P 22.41 ppm. Mass spectrum, *m/z*: 407.1743 $[M + H]^+$ (calcd. $C_{20}H_{27}N_2O_5P$: 407.1730 $[M + H]^+$).

Diethyl {2-[(3-acetylphenyl)amino]-2-[(3-acetylphenyl)imino]ethyl}phosphonate (3d). Yield 62%, white crystals, mp 92–94°C. IR spectrum, ν, cm^{-1}: 1029 (P–O–C), 1246 (P=O), 3355 (NH). ^{1}H NMR spectrum,

δ, ppm: 1.15 t (6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 2.56 s (3H, CH_{3NH}), 2.58 s (3H, $CH_{3N=}$), 3.00 d (2H, PCH_2, $^2J_{HP}$ = 21.7 Hz), 3.92 d. q (4H, $POCH_2$, $^3J_{HH}$ = 7.1, $^3J_{HP}$ = 14.5 Hz), 7.11 d (1H, $CH^o_{N=}$, $^3J_{HH}$ = 7.8 Hz), 7.41–7.47 m (3H, $CH^m_{NH,N=}$, CH^p_{NH}), 7.59 s (1H, $CH^o_{N=}$), 7.60 d (1H, CH^o_{NH}, $^3J_{HH}$ = 7.4 Hz), 8.06 d (1H, $CH^p_{N=}$, $^3J_{HH}$ = 7.9 Hz), 8.29 s (1H, CH^o_{NH}), 9.11 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.58 d (CH_3, $^3J_{CP}$ = 5.9 Hz), 27.21 (CH_{3NH}), 27.29 ($CH_{3N=}$), 29.35 d (PCH_2, $^1J_{CP}$ = 132.1 Hz), 62.32 d ($POCH_2$, $^2J_{CP}$ = 6.5 Hz), 118.60 (CH^o_{NH}), 121.91 (CH^p_{NH}), 122.29 (CH^o_{NH}), 122.62 ($CH^o_{N=}$), 124.07 ($CH^p_{N=}$), 126.98 ($CH^o_{N=}$), 129.39 ($C^m_{N=}$), 129.53 (CH^m_{NH}), 131.62 ($C^m_{N=}$), 137.98 (C^m_{NH}), 141.45 ($C^{ipso}_{N=}$), 148.13 d (=C^2, $^2J_{CP}$ = 6.7 Hz), 150.43 (C^{ipso}_{NH}), 198.25 (C=O_{NH}), 198.47 (C=$O_{N=}$). ^{31}P NMR spectrum: δ_P 21.95 ppm Mass spectrum, *m/z*: 431.1730 [*M* + H]$^+$ (calcd. $C_{22}H_{27}N_2O_5P$: 431.1732 [*M* + H]$^+$).

Diethyl {2-[(3-chlorophenyl)amino]-2-[(3-chlorophenyl)imino]ethyl}phosphonate (3e). Yield 71%, white crystals, mp 85–87°C. IR spectrum, ν, cm^{-1}: 1022 (P–O–C), 1049 (C–Cl), 1227 (P=O), 3126 (NH). ^1H NMR spectrum, δ, ppm: 1.17 t (6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 2.98 d (2H, PCH_2, $^2J_{HP}$ = 21.7 Hz), 3.93 d. q (4H, OCH_2, $^3J_{HH}$ = 7.0, $^3J_{HP}$ = 14.0 Hz), 6.79 d (1H, CH^p_{NH}, $^3J_{HH}$ = 7.9 Hz), 6.92 s (1H, CH^o_{NH}), 7.03 d (1H, $CH^o_{N=}$, $^3J_{HH}$ = 7.6 Hz), 7.05 d (1H, $CH^p_{N=}$, $^3J_{HH}$ = 7.5 Hz), 7.30 t (1H, CH^m_{NH}, $^3J_{HH}$ = 8.0 Hz), 7.31 t (1H, $CH^m_{N=}$, $^3J_{HH}$ = 8.0 Hz), 7.51 d (1H, CH^o_{NH}, $^3J_{HH}$ = 8.2 Hz), 8.01 s (1H, $CH^o_{N=}$), 9.08 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.57 d (CH_3, $^3J_{CP}$ = 6.6 Hz), 29.51 d (PCH_2, $^1J_{CP}$ = 131.3 Hz), 62.35 d ($POCH_2$, $^2J_{CP}$ = 6.6 Hz), 117.96 (CH^o_{NH}), 118.85 ($CH^o_{N=}$), 120.79 (CH^p_{NH}), 122.01 ($CH^o_{N=}$), 122.13 (CH^o_{NH}), 122.38 ($CH^p_{N=}$), 130.59 ($CH^m_{N=}$), 130.74 (CH^m_{NH}), 133.32 ($C^m_{N=}$), 133.54 (C^m_{NH}), 142.40 ($C^{ipso}_{N=}$), 148.22 (=C^2, $^2J_{CP}$ = 6.6 Hz), 151.52 (C^{ipso}_{NH}). ^{31}P NMR spectrum: δ_P 21.61 ppm Mass spectrum, *m/z*: 415.0810 [*M* + H]$^+$ (calcd. $C_{18}H_{21}Cl_2N_2O_3P$: 415.0822 [*M* + H]$^+$).

Diethyl {2-[(3-bromophenyl)amino]-2-[(3-bromophenyl)imino]ethyl}phosphonate (3f). Yield 68%, pale yellow crystals, mp 88–90°C. IR spectrum, ν, cm^{-1}: 1020 (P–O–C), 1050 (C–Br), 1227 (P=O), 3121 (NH). ^1H NMR spectrum, δ, ppm: 1.18 t (6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 2.98 d (2H, PCH_2, $^2J_{HP}$ = 21.7 Hz), 3.94 d. q (4H, $POCH_2$, $^3J_{HH}$ = 7.2, $^3J_{HP}$ = 14.4 Hz), 6.83 d (1H, $CH^o_{N=}$, $^3J_{HH}$ = 7.8 Hz), 7.07 s (1H, CH^o_{NH}), 7.16 d (1H, CH^p_{NH}, $^3J_{HH}$ = 8.7 Hz), 7.18 d (1H, $CH^p_{N=}$, $^3J_{HH}$ = 8.5 Hz), 7.23 t (1H, CH^m_{NH}, $^3J_{HH}$ = 7.8 Hz), 7.25 t (1H, $CH^m_{N=}$, $^3J_{HH}$ = 8.1 Hz), 7.58 d (1H, CH^o_{NH}, $^3J_{HH}$ = 8.1 Hz), 8.13 s (1H, $CH^o_{N=}$), 9.06 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.60 d (CH_3, $^3J_{CP}$ = 5.8 Hz), 29.51 d (PCH_2, $^1J_{CP}$ = 132.7 Hz), 62.37 d ($POCH_2$, $^1J_{CP}$ = 6.6 Hz), 118.36 (CH^o_{NH}), 121.16 ($CH^o_{N=}$), 121.71 ($CH^o_{N=}$), 121.85 ($C^m_{N=}$), 122.10 (C^m_{NH}), 124.84 (CH^o_{NH}), 125.04 (CH^p_{NH}), 125.27 ($CH^p_{N=}$), 130.90 ($CH^m_{N=}$), 131.04 (CH^m_{NH}), 142.54 ($C^{ipso}_{N=}$), 148.21 d (=C^2, $^2J_{CP}$ = 7.3 Hz), 151.69 (C^{ipso}_{NH}). ^{31}P NMR spectrum: δ_P 21.63 ppm. Mass spectrum, *m/z*: 504.9735 [*M* + H]$^+$ (calcd. $C_{18}H_{21}Br_2N_2O_3P$: 504.9709 [*M* + H]$^+$).

Diethyl {2-[(3-fluorophenyl)amino]-2-[(3-fluorophenyl)imino]ethyl}phosphonate (3g). Yield 53%, orange oil. IR spectrum, ν, cm^{-1}: 1026 (P–O–C), 1243 (P=O), 1601 (C–Cl). ^1H NMR spectrum, δ, ppm: 1.17 t (6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 3.02 d (2H, PCH_2, $^2J_{HP}$ = 21.7 Hz), 3.93 d. q (4H, OCH_2, $^3J_{HH}$ = 7.1, $^3J_{HP}$ = 15.1 Hz), 6.68 d (1H, $CH^o_{N=}$, $^3J_{HF}$ = 12.2 Hz), 6.70 d (1H, CH^p_{NH}, $^3J_{HH}$ = 8.0 Hz), 6.79 q (2H, $CH^o_{N=}$, $CH^p_{1N=}$, $^3J_{HH}$ = 7.9, $^3J_{HF}$ = 8.2 Hz), 7.30 q (2H, CH^m_{NH}, $CH^m_{N=}$, $^3J_{HH}$ = 7.8 Hz), 7.37 d (1H, CH^o_{NH}, $^3J_{HH}$ = 8.1 Hz), 7.85 d (1H, CH^o_{NH}, $^3J_{HF}$ = 12.2 Hz), 9.11 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.50 d (CH_3, $^3J_{CP}$ = 6.1 Hz), 29.38 d (PCH_2, $^1J_{CP}$ = 131.7 Hz), 62.33 d ($POCH_2$, $^2J_{CP}$ = 6.5 Hz), 106.19 d (CH^o_{NH}, $^2J_{CF}$ = 26.9 Hz), 108.70 d (CH^p_{NH}, $^2J_{CF}$ = 21.0 Hz), 109.07 d ($CH^o_{N=}$, $^2J_{CF}$ = 20.8 Hz), 109.11 d ($CH^p_{N=}$, $^2J_{CF}$ = 22.2 Hz), 115.23 (CH^o_{NH}), 118.18 ($CH^o_{N=}$), 130.38 d ($CH^m_{N=}$, $^3J_{CF}$ = 9.6 Hz), 130.57 d (CH^m_{NH}, $^3J_{CF}$ = 9.7 Hz), 142.73 d ($C^{ipso}_{N=}$, $^3J_{CF}$ = 11.3 Hz), 148.03 d (=C^2, $^2J_{CP}$ = 7.0 Hz), 151.99 d (C^{ipso}_{NH}, $^3J_{CF}$ = 9.9 Hz), 162.59 d ($C^m_{N=}$, $^1J_{CF}$ = 240.1 Hz), 163.03 d (C^m_{NH}, $^1J_{CF}$ = 242.8 Hz). ^{19}F NMR spectrum, δ_F, ppm: –113.28, –112.35. ^{31}P NMR spectrum: δ_P 21.74 ppm. Mass spectrum, *m/z*: 383.1344 [*M* + H]$^+$ (calcd. $C_{18}H_{21}F_2N_2O_3P$: 383.1331 [*M* + H]$^+$).

Diethyl {2-[(3-nitrophenyl)amino]-2-[(3-nitrophenyl)imino]ethyl}phosphonate (3h). Yield 59%, pale crystals, mp 109–111°C. IR spectrum, ν, cm^{-1}: 1019 (P–O–C), 1237 (P=O), 1520 (NO_2), 3122 (NH). ^1H NMR spectrum, δ, ppm: 1.15 t (6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 3.05 d (2H, PCH_2, $^3J_{HP}$ = 21.6 Hz), 3.93 d. q (4H, P–OCH_2, $^3J_{HH}$ = 7.0, $^3J_{HP}$ = 14.2 Hz), 7.32 d (1H, CH^o_{NH}, $^3J_{HH}$ = 7.9 Hz), 7.58 d. t (2H, CH^m, $^3J_{HH}$ = 8.2 Hz), 7.69 t (1H, CH^p_{NH}, $^4J_{HH}$ = 2.1 Hz), 7.87 t (2H, $CH^o_{N=}$, $^3J_{HH}$ = 8.2 Hz), 8.06 d (1H, $CH^p_{N=}$, $^3J_{HH}$ = 8.1 Hz), 8.81 s (1H, CH^o_{NH}), 9.59 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.49 d (CH_3, $^3J_{CP}$ = 5.9 Hz), 29.80 d (PCH_2, $^1J_{CP}$ = 132.7 Hz), 62.44 d ($POCH_2$, $^2J_{CP}$ = 6.6 Hz), 113.59 (CH^o_{NH}), 116.76 (CH^p_{NH}), 117.22 ($CH^o_{N=}$), 117.50 ($CH^o_{N=}$), 125.68 ($CH^p_{N=}$), 129.05 (CH^o_{NH}), 130.37 ($CH^m_{N=}$), 130.51

(CH^{m}_{NH}), 141.91 ($C^{ipso}_{N=}$), 148.40 ($C^{m}_{N=}$), 148.76 (C^{m}_{NH}), 149.21 d (=C^{2}, $^{2}J_{CP}$ 6.6 Hz), 150.95 (C^{ipso}_{NH}). ^{31}P NMR spectrum: δ_P 21.28 ppm. Mass spectrum, *m/z*: 437.1237 $[M + H]^+$ (calcd. $C_{18}H_{21}N_4O_7P$: 437.1221 $[M + H]^+$).

Diethyl {2-[(3-trifluoromethyl)phenyl]amino-2-[(3-trifluoromethylphenyl)imino]ethyl}phosphonate (3i). Yield 63%, white crystals, mp 75–77°C. IR spectrum, ν, cm^{-1}: 1050 (P–O–C), 1235 (P=O), 3120 (NH). ^{1}H NMR spectrum, δ, ppm: 1.15 t (6H, CH_3, $^{3}J_{HH}$ = 7.1 Hz), 3.01 d (2H, PCH_2, $^{2}J_{HP}$ = 21.7 Hz), 3.92 d. q (4H, $POCH_2$, $^{3}J_{HH}$ = 7.0, $^{3}J_{HP}$ = 14.2 Hz), 7.13 d (1H, $CH^{o}_{N=}$, $^{3}J_{HH}$ = 7.9 Hz), 7.20 s (1H, $CH^{o}_{N=}$), 7.33 d (1H, CH^{p}_{NH}, $^{3}J_{HH}$ = 7.8 Hz), 7.35 d (1H, $CH^{p}_{N=}$, $^{3}J_{HH}$ = 7.9 Hz), 7.51 t (1H, CH^{m}_{NH}, $^{3}J_{HH}$ = 7.5 Hz), 7.53 t (1H, $CH^{m}_{N=}$, $^{3}J_{HH}$ = 7.6 Hz), 7.94 d (1H, CH^{o}_{NH}, $^{3}J_{HH}$ = 8.1 Hz), 8.21 s (1H, CH^{o}_{NH}), 9.29 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.47 d (CH_3, $^{3}J_{CP}$ = 5.8 Hz), 29.60 d (PCH_2, $^{1}J_{CP}$ = 132.7 Hz), 62.33 d ($POCH_2$, $^{2}J_{CP}$ = 5.8 Hz), 115.51 q (CH^{o}_{NH}, $^{3}J_{CF}$ = 4.4 Hz), 118.72 q ($CH^{o}_{N=}$, $^{3}J_{CF}$ = 4.4 Hz), 118.82 q (CH^{p}_{NH}, $^{3}J_{CF}$ = 3.7 Hz), 119.14 q ($CH^{p}_{N=}$, $^{3}J_{CF}$ = 3.7 Hz), 123.17 (CH^{o}_{NH}), 124.68 q (CF_{3NH}, $^{1}J_{CF}$ = 272.1 Hz), 124.74 q ($CF_{3N=}$, $^{1}J_{CF}$ = 272.1 Hz), 126.09 ($CH^{o}_{N=}$), 129.72 q (C^{m}_{NH}, $^{2}J_{CF}$ = 31.0 Hz), 130.12 q ($C^{m}_{N=}$, $^{2}J_{CF}$ = 31.3 Hz), 130.18 ($CH^{m}_{N=}$), 130.33 (CH^{m}_{NH}), 141.66 ($C^{ipso}_{N=}$), 148.62 d (=C^{2}, $^{2}J_{CP}$ = 6.6 Hz), 150.56 (C^{ipso}_{NH}). ^{19}F NMR spectrum, δ_F, ppm: –61.30 (CF_3), –61.09 (CF_3). ^{31}P NMR spectrum: δ_P 21.53 ppm. Mass spectrum, *m/z*: 483.1254 $[M + H]^+$ (calcd. $C_{20}H_{21}F_6N_2O_3P$: 483.1267 $[M + H]^+$).

Diethyl {2-[(4-chlorophenyl)amino]-2-[(4-chlorophenyl)imino]ethyl}phosphonate (3j). Yield 93%, white crystals, mp 104–106°C. IR spectrum, ν, cm^{-1}: 1027 (P–O–C), 1209 (C–Cl), 1256 (P=O), 3328 (NH). ^{1}H NMR spectrum, δ, ppm: 1.17 t (6H, CH_3, $^{3}J_{HH}$ = 7.1 Hz), 2.98 d (2H, P–CH_2, $^{2}J_{HP}$ = 21.7 Hz), 3.93 d. q (4H, $POCH_2$, $^{3}J_{HH}$ = 7.0, $^{3}J_{HP}$ = 14.2 Hz), 6.84 d (2H, $CH^{o}_{N=}$, $^{3}J_{HH}$ = 8.5 Hz), 7.30 d (2H, CH^{m}_{NH}, $^{3}J_{HH}$ = 8.5 Hz), 7.32 d (2H, $CH^{m}_{N=}$, $^{3}J_{HH}$ = 9.0 Hz), 7.75 d (2H, CH^{o}_{NH}, $^{3}J_{HH}$ = 8.8 Hz), 8.95 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.57 d (CH_3, $^{3}J_{CP}$ = 5.9 Hz), 29.26 d (PCH_2, $^{1}J_{CP}$ = 132.0 Hz), 62.33 d ($POCH_2$, $^{2}J_{CP}$ = 5.8 Hz), 121.02 (CH^{o}_{NH}), 123.84 ($CH^{o}_{N=}$), 125.86 (C^{p}_{NH}), 126.53 ($C^{p}_{N=}$), 128.79 ($CH^{m}_{N=}$), 128.97 (CH^{m}_{NH}), 140.01 ($C^{ipso}_{N=}$), 147.90 d (=C^{2}, $^{2}J_{CP}$ = 6.6 Hz), 149.03 (C^{ipso}_{NH}). ^{31}P NMR spectrum: δ_P 21.85 ppm. Mass spectrum, *m/z*: 415.0727 $[M + H]^+$ (calcd. $C_{18}H_{21}Cl_2N_2O_3P$: 415.0740 $[M + H]^+$).

Diethyl {2-[(4-trifluoromethoxy)phenyl]amino-2-[(4-trifluoromethoxyphenyl)imino]ethyl}phosphonate (3k). Yield 92%, white crystals, mp 125–127°C. IR spectrum, ν, cm^{-1}: 1024 (P–O–C), 1291 (P=O), 1502 (C=N), 3150 (NH). ^{1}H NMR spectrum, δ, ppm: 1.15 t (6H, CH_3, $^{3}J_{HH}$ = 7.0 Hz), 3.01 d (2H, PCH_2, $^{2}J_{HP}$ = 21.7 Hz), 3.90 d. q (4H, $POCH_2$, $^{3}J_{HH}$ = 7.0, $^{3}J_{HP}$ = 14.2 Hz), 6.92 d (2H, $CH^{o}_{N=}$, $^{3}J_{HH}$ = 8.7 Hz), 7.27 t (4H, CH^{o}_{NH}, CH^{m}_{NH}, $^{3}J_{HH}$ = 8.9 Hz), 7.84 d (2H, $CH^{m}_{N=}$, $^{3}J_{HH}$ = 8.9 Hz), 9.08 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.49 d (CH_3, $^{3}J_{CP}$ = 5.8 Hz), 29.26 d (PCH_2, $^{1}J_{CP}$ = 131.6 Hz), 62.27 d ($POCH_2$, $^{2}J_{CP}$ = 6.4 Hz), 120.66 q (OCF_3, $^{1}J_{CF}$ = 255.3 Hz), 120.69 q (OCF_3, $^{1}J_{CF}$ = 255.3 Hz), 120.70 ($CH^{m}_{N=}$), 121.83 (CH^{m}_{NH}), 122.02 (CH^{o}_{NH}), 123.41 ($CH^{o}_{N=}$), 140.28 ($C^{ipso}_{N=}$), 143.05 (C^{p}_{NH}), 143.80 (C^{ipso}_{NH}), 148.09 d (=C^{2}, $^{2}J_{CP}$ = 7.1 Hz), 149.34 ($C^{p}_{N=}$). ^{19}F NMR spectrum: δ_F –57.11 ppm. ^{31}P NMR spectrum: δ_P 21.71 ppm. Mass spectrum, *m/z*: 537.1013 $[M + Na]^+$ (calcd. $C_{20}H_{21}F_6N_2O_5P$: 537.0984 $[M + Na]^+$).

Diethyl {2-[(3,4-dimethoxyphenyl)amino]2-[(3,4-dimethoxyphenyl)imino]ethyl}phosphonate (3l). Yield 56%, orange oil. IR spectrum, ν, cm^{-1}: 1026 (P–O–C), 1231 (P=O), 1511 (C=N), 3368 (NH). ^{1}H NMR spectrum, δ, ppm: 1.18 t (6H, CH_3, $^{3}J_{HH}$ = 7.0 Hz), 2.99 d (2H, PCH_2, $^{2}J_{HP}$ = 21.6 Hz), 3.71 s (6H, OCH_3), 3.72 s (3H, OCH_3), 3.73 s (3H, OCH_3), 3.95 d. q (4H, $POCH_2$, $^{3}J_{HH}$ = 7.5, $^{3}J_{HP}$ = 14.9 Hz), 6.32 d (1H, $CH^{o}_{N=}$, $^{3}J_{HH}$ = 6.6 Hz), 6.51 s (1H, $CH^{o}_{N=}$), 6.84 d (1H, $CH^{m}_{N=}$, $^{3}J_{HH}$ = 7.8 Hz), 6.85 d (1H, CH^{m}_{NH}, $^{3}J_{HH}$ = 8.0 Hz), 7.31 d (1H, CH^{o}_{NH}, $^{3}J_{HH}$ = 8.5 Hz), 7.41 s (1H, CH^{o}_{NH}), 8.41 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.60 d (CH_3, $^{3}J_{CP}$ = 5.9 Hz), 28.80 d (PCH_2, $^{1}J_{CP}$ = 131.8 Hz), 55.71 (OCH_3), 55.79 (OCH_3), 56.17 (OCH_3), 56.25 (OCH_3), 62.31 d ($POCH_2$, $^{2}J_{CP}$ = 6.4 Hz), 104.94 (CH^{o}_{NH}), 107.03 ($CH^{o}_{N=}$), 111.44 (CH^{o}_{NH}), 112.29 ($C^{ipso}_{N=}$), 112.55 ($CH^{m}_{N=}$), 112.96 (CH^{m}_{NH}), 113.05 ($CH^{o}_{N=}$), 135.13 (C^{p}_{NH}), 144.28 (C^{ipso}_{NH}), 144.46 ($C^{m}_{N=}$), 147.41 d (=C^{2}, $^{2}J_{CP}$ = 7.1 Hz), 148.84 (C^{m}_{NH}), 149.41 ($C^{p}_{N=}$). ^{31}P NMR spectrum: δ_P 22.95 ppm. Mass spectrum, *m/z*: 467.1959 $[M + H]^+$ (calcd. $C_{22}H_{31}N_2O_7P$: 467.1942 $[M + H]^+$).

Diethyl {2-[(3,4-dichlorophenyl)amino]2-[(3,4-dichlorophenyl)imino]ethyl}phosphonate (3m). Yield 80%, white crystals, mp 95–97°C. IR spectrum, ν, cm^{-1}: 1025 (P–O–C), 1051 (C–Cl), 1233 (P=O), 1582 (C=N), 3106 (NH). ^{1}H NMR spectrum, δ, ppm: 1.17 t (6H, CH_3, $^{3}J_{HH}$ = 7.0 Hz), 2.99 d (2H, PCH_2, $^{2}J_{HP}$ = 21.7 Hz), 3.95 d. q (4H, $POCH_2$, $^{3}J_{HH}$ = 7.1, $^{3}J_{HP}$ = 14.2 Hz), 6.84 d. d (1H, CH^{o}_{NH}, $^{3}J_{HH}$ = 8.5, $^{4}J_{HH}$ = 2.4 Hz), 7.14 d (1H, CH^{o}_{NH}, $^{4}J_{HH}$ = 2.4 Hz), 7.49–7.59 m (3H, $CH^{o}_{N=}$, CH^{m}_{NH}, $CH^{m}_{N=}$), 8.16 d (1H, CH^{o}_{NH}, $^{4}J_{HH}$ = 1.7 Hz),

9.30 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.56 d (CH_3, $^3J_{CP}$ = 5.9 Hz), 29.75 d (PCH_2, $^1J_{CP}$ = 131.3 Hz), 62.42 d ($POCH_2$, $^2J_{CP}$ = 6.5 Hz), 119.71 (CH^o_{NH}), 120.59 (CH^o_{NH}), 122.64 ($CH^o_{N=}$), 123.88 ($C^{ipso}_{N=}$), 123.96 ($CH^o_{N=}$), 124.63 (C^p_{NH}), 130.84 ($CH^m_{N=}$), 130.91 (CH^m_{NH}), 131.17 ($C^m_{N=}$), 131.38 (C^m_{NH}), 140.89 ($C^p_{N=}$), 148.73 d (=C^2, $^2J_{CP}$ = 6.9 Hz), 149.94 (C^{ipso}_{NH}). ^{31}P NMR spectrum: δ_P 21.35 ppm. Mass spectrum, *m/z*: 482.9975 $[M + H]^+$ (calcd. $C_{18}H_{19}Cl_4N_2O_3P$: 482.9960 $[M + H]^+$).

Diethyl {2-[(4-methoxy-3-chlorophenyl)amino]-2-[(4-methoxy-3-chlorophenyl)imino]ethyl}phosphonate (3n). Yield 59%, yellow oil. IR spectrum, ν, cm^{-1}: 1022 (P–O–C), 1252 (P=O), 1493 (C=N), 3317 (NH). ^{1}H NMR spectrum, δ, ppm: 1.18 t (6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 2.96 d (2H, PCH_2, $^2J_{HP}$ = 21.6 Hz), 3.81 s (6H, OCH_3), 3.94 d. q (4H, $POCH_2$, $^3J_{HH}$ = 7.1, $^3J_{HP}$ = 14.7 Hz), 6.75 d. d (1H, $CH^o_{N=}$, $^3J_{HH}$ = 8.6, $^4J_{HH}$ = 1.9 Hz), 6.93 d (1H, $CH^o_{N=}$, $^4J_{HH}$ = 1.9 Hz), 7.04 d (1H, CH^m_{NH}, $^3J_{HH}$ = 8.8 Hz), 7.07 d (1H, $CH^m_{N=}$, $^3J_{HH}$ = 9.2 Hz), 7.51 d. d (1H, CH^o_{NH}, $^3J_{HH}$ = 8.9, $^4J_{HH}$ = 1.8 Hz), 7.98 d (1H, CH^o_{NH}, $^4J_{HH}$ = 1.8 Hz), 8.79 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.59 d (CH_3, $^3J_{CP}$ = 5.9 Hz), 29.12 d (PCH_2, $^1J_{CP}$ = 131.9 Hz), 56.59 (OCH_3), 62.33 d ($POCH_2$, $^2J_{CP}$ = 6.5 Hz), 113.27 ($CH^m_{N=}$), 113.49 (CH^m_{NH}), 119.33 (CH^o_{NH}), 120.73 ($C^m_{N=}$), 121.05 (CH^o_{NH}), 121.32 (C^m_{NH}), 121.49 ($CH^o_{N=}$), 123.67 ($CH^o_{N=}$), 135.04 ($C^{ipso}_{N=}$), 144.12 (C^{ipso}_{NH}), 148.29 d (=C^2, $^2J_{CP}$ = 6.9 Hz), 149.97 (C^p_{NH}), 150.31 ($C^p_{N=}$). ^{31}P NMR spectrum: δ_P 22.16 ppm. Mass spectrum, *m/z*: 475.0906 $[M + H]^+$ (calcd. $C_{20}H_{25}Cl_2N_2O_5P$: 475.0921 $[M + H]^+$).

Diethyl {2-[(4-methoxy-3-chlorophenyl)amino]-2-[(4-methoxy-3-chlorophenyl)imino]ethyl}phosphonate (3o). Yield 55%, yellow crystals, mp 106–108°C. IR spectrum, ν, cm^{-1}: 1053 (P–O–C), 1225 (P=O), 1603 (C=N), 3105 (NH). ^{1}H NMR spectrum, δ, ppm: 1.15 t (6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 2.46 s (3H, CH_3), 2.47 s (3H, CH_3), 3.01 d (2H, PCH_2, $^2J_{HP}$ = 21.7 Hz), 3.93 d. q (4H, $POCH_2$, $^3J_{HH}$ = 7.1, $^3J_{HP}$ = 14.2 Hz), 7.12 d. d (1H, $CH^o_{N=}$, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 2.1 Hz), 7.41 t (2H, CH^m_{NH}, $CH^m_{N=}$, $^3J_{HH}$ = 8.5 Hz), 7.45 d (1H, $CH^o_{N=}$, $^4J_{HH}$ = 2.0 Hz), 7.84 d. d (1H, CH^o_{NH}, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 1.9 Hz), 8.57 d (1H, CH^o_{NH}, $^4J_{HH}$ = 1.9 Hz), 9.41 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.53 d (CH_3, $^3J_{CP}$ = 5.9 Hz), 19.37 (CH_3), 19.62 (CH_3), 29.62 d (PCH_2, $^1J_{CP}$ = 131.0 Hz), 62.41 d ($POCH_2$, $^2J_{CP}$ = 6.4 Hz), 114.62 (CH^o_{NH}), 117.59 ($CH^o_{N=}$), 124.28 (CH^o_{NH}), 126.36 (C^p_{NH}), 126.45 ($C^p_{N=}$), 127.46 (C^o_{NH}), 133.31 (CH^m_{NH}), 133.44 ($CH^m_{N=}$), 139.76 ($C^{ipso}_{N=}$), 148.75 (C^{ipso}_{NH}), 148.96 ($C^m_{N=}$), 149.05 d (=C^2, $^2J_{CP}$ = 6.2 Hz), 149.51 (C^m_{NH}). ^{31}P NMR spectrum: δ_P 21.48 ppm. Mass spectrum, *m/z*: 465.1521 $[M + H]^+$ (calcd. $C_{20}H_{25}N_4O_7P$: 465.1534 $[M + H]^+$).

Diethyl {2-[(3-chloro-2-methylphenyl)amino]-2-[(3-chloro-2-methylphenyl)imino]ethyl}phosphonate (3p). Yield 30%, yellow crystals, mp 73–75°C. IR spectrum, ν, cm^{-1}: 1025 (P–O–C), 1050 (C–Cl), 1236 (P=O), 1576 (C=N), 2978 (CH_3), 3371 (NH). ^{1}H NMR spectrum, δ, ppm: 1.18 t (6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 2.07 s (3H, CH_{3NH}), 2.37 s (3H, $CH_{3N=}$), 2.99 d (2H, PCH_2, $^2J_{HP}$ = 21.8 Hz), 3.95 d. q (4H, $POCH_2$, $^3J_{HH}$ = 7.1, $^3J_{HP}$ = 14.4 Hz), 6.66 d (1H, CH^o_{NH}, $^3J_{HH}$ = 7.4 Hz), 7.02 d (1H, CH^p_{NH}, $^3J_{HH}$ = 7.4 Hz), 7.09 t (1H, $CH^m_{N=}$, $^3J_{HH}$ = 7.5 Hz), 7.21 br. s (2H, $CH^o_{N=}$, $CH^p_{N=}$), 7.72 d (1H, CH^m_{NH}, $^3J_{HH}$ = 5.4 Hz), 8.29 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 15.33 (CH_{3NH}), 15.40 ($CH_{3N=}$), 16.54 d (CH_3, $^3J_{CP}$ = 6.0 Hz), 28.41 d (PCH_2, $^1J_{CP}$ = 130.7 Hz), 62.31 d ($POCH_2$, $^2J_{CP}$ = 6.3 Hz), 120.16 (CH^o_{NH}), 122.93 (CH^p_{NH}), 123.86 (CH^m_{NH}), 125.34 ($CH^p_{N=}$), 127.21 ($CH^o_{N=}$), 127.35 ($CH^m_{N=}$), 127.75 ($C^{ipso}_{N=}$), 130.01 (C^o_{NH}), 134.09 ($C^m_{N=}$), 134.12 (C^m_{NH}), 140.24 ($C^o_{N=}$), 148.68 d (=C^2, $^2J_{CP}$ = 6.5 Hz), 150.63 (C^{ipso}_{NH}). ^{31}P NMR spectrum: δ_P 22.66 ppm. Mass spectrum, *m/z*: 443.1057 $[M + H]^+$ (calcd. $C_{20}H_{25}Cl_2N_2O_3P$: 443.1053 $[M + H]^+$).

Diethyl {2-[(5-nitro-2-chlorophenyl)amino]-2-[(5-nitro-2-chlorophenyl)imino]ethyl}phosphonate (3q). Yield 45%, yellow crystals, mp 122–124°C. IR spectrum, ν, cm^{-1}: 1045 (P–O–C), 1278 (P=O), 1514 (NO_2), 3337 (NH). ^{1}H NMR spectrum, δ, ppm: 1.20 t (6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 3.27 d (2H, PCH_2, $^2J_{HP}$ = 22.0 Hz), 4.02 d. q (4H, $POCH_2$, $^3J_{HH}$ = 7.2, $^3J_{HP}$ = 14.6 Hz), 7.76 d (1H, $CH^m_{N=}$, $^3J_{HH}$ = 8.6 Hz), 7.80 d (1H, CH^m_{NH}, $^3J_{HH}$ = 8.8 Hz), 7.88 d (2H, CH^o_{NH}, $CH^o_{N=}$, $^3J_{HH}$ = 8.5 Hz), 7.94 d. d (1H, $CH^p_{N=}$, $^3J_{HH}$ = 8.8, $^4J_{HH}$ = 2.6 Hz), 8.99 s (1H, NH), 9.43 s (1H, CH^p_{NH}). ^{13}C NMR spectrum, δ_C, ppm: 16.51 d (CH_3, $^3J_{CP}$ = 5.9 Hz), 29.39 d (PCH_2, $^1J_{CP}$ = 132.5 Hz), 62.79 d ($POCH_2$, $^2J_{CP}$ = 6.4 Hz), 117.70 (CH^o_{NH}), 118.03 (CH^p_{NH}), 119.08 ($CH^o_{N=}$), 119.34 ($CH^p_{N=}$), 130.67 (C^o_{NH}), 130.87 ($CH^m_{N=}$), 130.93 (CH^m_{NH}), 133.70 ($C^o_{N=}$), 137.18 ($C^{ipso}_{N=}$), 146.73 ($C^m_{N=}$), 146.85 (C^m_{NH}), 147.18 (C^{ipso}_{NH}), 150.87 d (=C^2, $^2J_{CP}$ = 6.9 Hz). ^{31}P NMR spectrum: δ_P 21.62 ppm. Mass spectrum, *m/z*: 527.0265 $[M + Na]^+$ (calcd. $C_{18}H_{19}Cl_2N_4O_7P$: 527.0261 $[M + Na]^+$).

Diethyl [*N*,*N*'-bis(2-methyl-1,3-dioxo-2,3-dihydro-1*H*-isoindol-5-yl)carbamimidoylmethyl]phosphonate (3r). Yield 44%, yellow oil. IR spectrum, ν,

cm^{-1}: 1020 (P–O–C), 1280 (P=O), 1583 (C=N), 3102 (NH). ^{1}H NMR spectrum, δ, ppm: 1.16 t (6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 3.00 s (3H, NCH_3), 3.03 s (3H, NCH_3), 3.05 d (2H, PCH_2, $^2J_{HP}$ = 22.3 Hz), 3.94 d. q (4H, $POCH_2$, $^3J_{HH}$ = 7.1, $^3J_{HP}$ = 14.2 Hz), 7.22 d. d (1H, CH^o_{NH}, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.8 Hz), 7.30 d (1H, CH^m_{NH}, $^4J_{HH}$ = 1.7 Hz), 7.76 d (1H, CH^o_{NH}, $^3J_{HH}$ = 7.5 Hz), 7.78 d (1H, $CH^o_{N=}$, $^3J_{HH}$ = 7.6 Hz), 7.96 d. d (1H, $CH^o_{N=}$, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 1.7 Hz), 8.31 d (1H, $CH^m_{N=}$, $^4J_{HH}$ = 1.7 Hz), 9.77 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.54 d (CH_3, $^3J_{CP}$ = 5.9 Hz), 24.13 (NCH_3), 30.09 d (PCH_2, $^1J_{CP}$ = 131.3 Hz), 62.52 d ($POCH_2$, $^2J_{CP}$ = 6.6 Hz), 113.13 (CH^o_{NH}), 116.57 ($CH^o_{N=}$), 124.33 (CH^m_{NH}), 124.39 (CH^o_{NH}), 125.08 (C^1_{NH}), 125.14 ($CH^m_{N=}$), 125.81 ($C^1_{N=}$), 127.10 ($CH^o_{N=}$), 133.75 (C^2_{NH}), 133.83 ($C^2_{N=}$), 146.02 (C^{ipso}_{NH}), 148.58 d (=C^2, $^2J_{CP}$ = 7.3 Hz), 155.26 ($C^{ipso}_{N=}$), 168.15 (C=O), 168.36 (C=O), 168.39 (C=O). ^{31}P NMR spectrum: δ_P 21.02 ppm. Mass spectrum, *m/z*: 513.1527 $[M + H]^+$ (calcd. $C_{24}H_{25}N_4O_7P$: 513.1534 $[M + H]^+$).

Diethyl {*N*,*N*-bis(2,3-dihydrobenzo[1,4]dioxin-6-yl)-carbamimidoylmethyl}phosphonate (3s). Yield 53%, white needle crystals, mp 133–135°C. IR spectrum, ν, cm^{-1}: 1023 (dioxane), 1065 (P–O–C), 1240 (P=O), 1607 (C=N), 3335 (NH). ^{1}H NMR spectrum, δ, ppm: 1.19 t (6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 2.95 d (2H, PCH_2, $^2J_{HP}$ = 21.6 Hz), 3.93 d. q (4H, $POCH_2$, $^3J_{HH}$ = 7.1, $^3J_{HP}$ = 14.8 Hz), 4.18 t (4H, CH_2, $^3J_{HH}$ = 6.0 Hz), 4.19 t (4H, CH_2, $^3J_{HH}$ = 5.2 Hz), 6.26 d (1H, CH^o_{NH}, $^3J_{HH}$ = 8.1 Hz), 6.31 s (1H, CH^o_{NH}), 6.74 d (2H, $CH^m_{NH,N=}$, $^3J_{HH}$ = 8.6 Hz), 6.98 d (1H, $CH^o_{N=}$, $^3J_{HH}$ = 7.9 Hz), 7.45 s (1H, $CH^o_{N=}$), 8.41 br. s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 16.60 d (CH_3, $^3J_{CP}$ = 6.0 Hz), 28.80 d (PCH_2, $^1J_{CP}$ = 132.9 Hz), 62.28 d ($POCH_2$, $^2J_{CP}$ = 6.5 Hz), 64.34 (CH_2), 64.63 (CH_2), 102.89 (C^{ipso}_{NH}), 107.86 ($C^{ipso}_{N=}$), 108.64 ($CH^o_{N=}$), 110.54 (CH^o_{NH}), 112.75 ($CH^o_{N=}$), 114.95 (CH^o_{NH}), 116.95 ($CH^m_{N=}$), 117.29 (CH^m_{NH}), 138.66 ($C^1_{N=}$), 138.96 ($C^2_{N=}$), 143.09 (C^1_{NH}), 143.66 (C^2_{NH}), 147.53 d (=C^2, $^2J_{CP}$ = 7.0 Hz). ^{31}P NMR spectrum: δ_P 22.59 ppm. Mass spectrum, *m/z*: 463.1612 $[M + H]^+$ (calcd. $C_{22}H_{27}N_2O_7P$: 463.1629 $[M + H]^+$).

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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