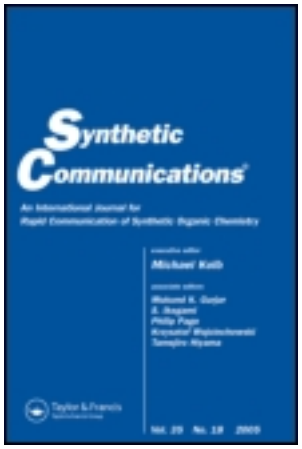

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One-Pot, Three-Component Synthesis of 5-(Alkylimino)-2-(diethoxyphosphoryl)-2,5-dihydrofuran-3,4-dicarboxylates

Javad Azizian [a], Ali Ramazani [b], Mohammad Haji [a] & Vahid Azizkhani [c]

[a] Chemistry Department, Science and Research Branch, Islamic Azad University, Tehran, Iran

[b] Department of Chemistry, Zanjan Branch, Islamic Azad University, Zanjan, Iran

[c] Chemistry Department, Payame Noor University, Abhar, Zanjan, Iran

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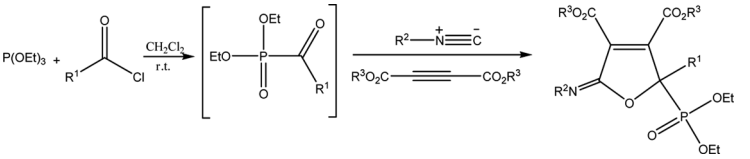
ONE-POT, THREE-COMPONENT SYNTHESIS OF 5-(ALKYLIMINO)-2-(DIETHOXYPHOSPHORYL)-2,5-DIHYDROFURAN-3,4-DICARBOXYLATES

Javad Azizian,[1] Ali Ramazani,[2] Mohammad Haji,[1] and Vahid Azizkhani[3]

[1]*Chemistry Department, Science and Research Branch, Islamic Azad University, Tehran, Iran*
[2]*Department of Chemistry, Zanjan Branch, Islamic Azad University, Zanjan, Iran*
[3]*Chemistry Department, Payame Noor University, Abhar, Zanjan, Iran*

GRAPHICAL ABSTRACT



Abstract *5-(Alkylimino)-2-(diethoxyphosphoryl)-2,5-dihydrofuran-3,4-dicarboxylates are prepared via a one-pot, three-component reaction of α-ketophosphonates, isocyanides, and dialkyl acetylenedicarboxylates at room temperature and neutral conditions. The structures of the products were deduced from their ^{1}H NMR, ^{13}C NMR, and infrared spectra and mass spectrometry.*

Keywords Alkyl isocyanide; dialkyl acetylenedicarboxylate; α-ketophosphonate; 2-phosphonofuran; three-component reaction

INTRODUCTION

Because of the unique properties of the phosphonic acid functional group, phosphono-substituted heterocyclic systems are an important class of organophosphorus compounds.[1] They are used in industrial chemistry to inhibit corrosion or as complexing, emulsifying, and dispersing agents.[2] In pharmaceutical chemistry, their enzyme inhibition, cytostatic, antiviral, antibacterial, antihypertensive, and anti-inflammatory activities have been investigated.[3]

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Address correspondence to Javad Azizian, Chemistry Department, Science and Research Branch, Islamic Azad University, P. O. Box 19395-1775, Tehran, Iran. E-mail: J_azizian@cc.sbu.ac.ir; or Ali Ramazani, Department of Chemistry, Zanjan Branch, Islamic Azad University, P. O. Box 49195-467, Zanjan, Iran. E-mail: aliramazani@gmail.com

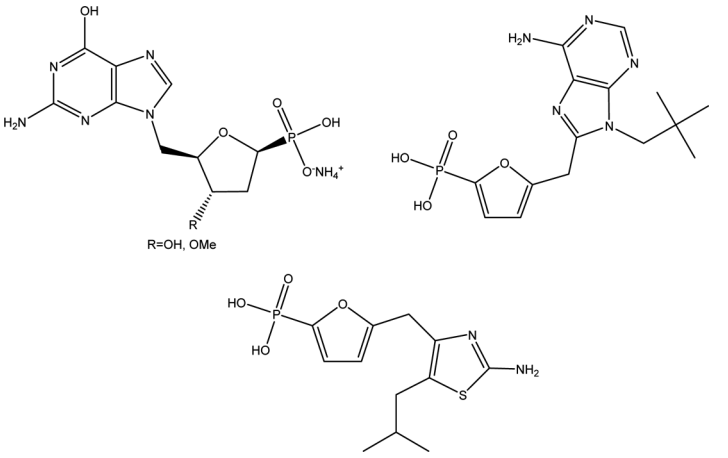


Figure 1. Some biologically active derivatives of 2-furanyl phosphonates.

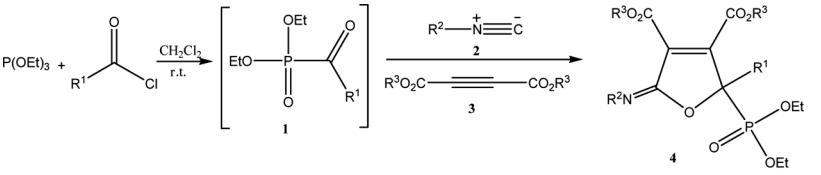
2-Furylphosphonic acid derivatives are some of the most important biologically active heterocycles. Phosphonate prodrugs based on the furan ring are used as antiviral agents in treatment of HSV (herpes simplex), HIV (human immunodeficiency virus) and HBV (hepatitis B virus) as well as to inhibit fructose-1,6-bisphosphatase (FBPase) activity in treatment of type 2 diabetes (Fig. 1).[4]

With due attention to several studies on the synthesis of phosphono-substituted heterocycles,[5] the most common synthetic methods for the preparation of 2-furyl-phosphonates involve (a) 2-litiation of furan ring with BuLi and reaction of the resulting 2-lithiofuran with dialkyl chlorophosphonate,[6] (b) reaction of 2-halofuran, 2-halo and 2-alkoxytetrahtdrofuran, 2-furaldehyde, 2-furoic acid, and 2-furanacrylic acid with trialkylphosphites in Arbuzov reaction condition,[7] and (c) reaction of phosphonate anions with 5-halo-2-one compounds.[8] To the best of our knowledge, there is no literature report of a multicomponent reaction involving the use of α-ketophosphonates for the construction of a 2-furylphosphonate ring.

As part of our studies on the design of new routes for the preparation of biologically active heterocyclic compounds and in continuation of our interest in phosphorus chemistry and isocyanide-based multicomponent reactions,[9–37] herein we report a facile method for synthesis of 2-phosphono-substituted furan derivatives **4**.

RESULTS AND DISCUSSION

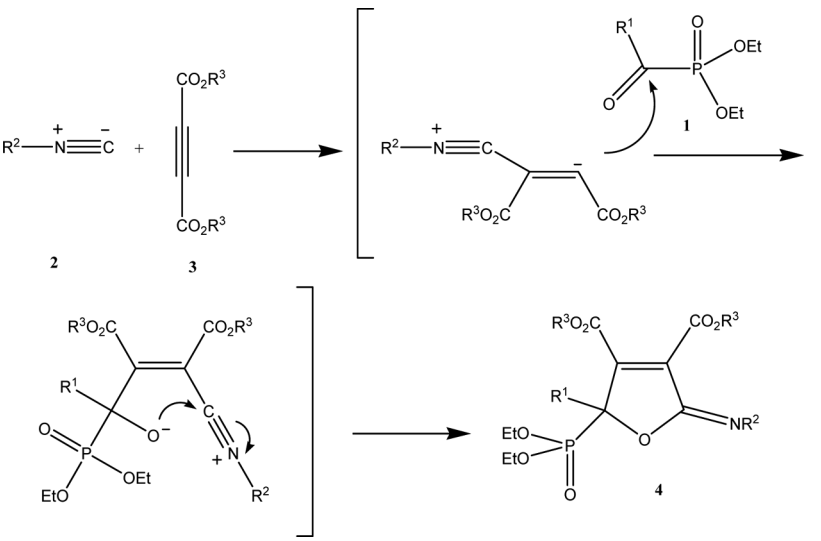
Because of the strong electron-withdrawing effect of dialkyl phosphoryl groups, the carbonyl in dialkyl α-keto phosphonates is highly electrophilic and therefore reacts rapidly with all types of nucleophiles.[38] Recently, the reaction of α-ketophosphonates with isocyanides in a Passerini manner was described by Coffinier and his coworkers.[39] In this article, we describe the three-component reaction of α-ketophosphonates **1**, isocyanides **2**, and dialkyl acetylenedicarboxylates **3** at room temperature and in neutral conditions (Scheme 1).



	R^1	R^2	R^3
4a	Me	cyclohexyl	Me
4b	Me	cyclohexyl	Et
4c	Ph	cyclohexyl	Me
4d	Ph	cyclohexyl	Et
4e	Me	1, 1, 3, 3-tetra-methylbutyl	Me
4f	Me	1, 1, 3, 3-tetra-methylbutyl	Et
4g	Ph	1, 1, 3, 3-tetra-methylbutyl	Me
4h	Ph	1, 1, 3, 3-tetra-methylbutyl	Et

Scheme 1. Three-component synthesis of sterically congested 2-phosphono-substituted furan derivatives **4a–h**.

A reasonable mechanism for this reaction based of isocyanide chemistry[40–42] is proposed in Scheme 2. The formed zwitterionic intermediate under the influence of isocyanide **2** and dialkyl acetylenedicarboxylates **3** smoothly reacts with α-keto phosphonate **1** at room temperature to afford 5-(alkylimino)-2-(diethoxyphosphoryl)-2-,5-dihydrofuran-3,4-dicarboxylates **4**. The structures of the final products **4a–h** were deduced from their elemental analyses, mass spectrometric data, and their



Scheme 2. Proposed mechanism for the formation of sterically congested 2-phosphono-substituted furan derivatives **4a–h**.

^{1}H, ^{13}C and ^{31}P NMR and infrared (IR) spectra. The mass spectrum of **4a** displayed the molecular ion peak at $m/z = 432$, which is consistent with the 1:1:1 adduct of cyclohexyl isocyanide–dimethyl acetylenedicarboxylate–diethyl acetyl phosphonate. The IR spectrum of **4a** showed strong absorptions at 1766 and 1749 cm^{-1} due to the two ester carbonyls, and at 1685 and 1261 cm^{-1} due to the C=N and P=O respectively.

The ^{1}H NMR spectra of **4a** exhibited two singlets for MeO groups ($\delta = 3.72$ and 3.76 ppm), a doublet for C-2 methyl ($\delta = 1.76$ ppm, $^{3}J_{HP} = 14.7$ Hz), and three multiplets for cyclohexyl and phosphonate methyl protons ($\delta = 1.0$–1.9 ppm), N-CH ($\delta = 3.49$ ppm), and phosphonate methylene protons ($\delta = 3.9$–4.20 ppm). The ^{1}H-decoupled ^{13}C NMR spectrum of **4a** showed 18 distinct signals, in agreement with the proposed structure, and partial assignment of these resonances is given in the Experimental section. The ^{31}P NMR spectrum of **4a** showed one signal at $\delta = 13.15$ ppm.

The ^{1}H, ^{13}C, and ^{31}P NMR spectra of compounds **4b–h** were similar to those of **4a**, except for the signals of the C-2 alkyl or aryl substituents and the alkyl substituents of alkylamino and carboxylate moieties, which exhibited characteristic signals with appropriate chemical shifts.

CONCLUSION

In summary, the reported method offers a mild, simple, and efficient route for the preparation of sterically congested 2-phosphonofuran derivatives **4** from α-ketophosphonates **1**, isocyanides **2**, and dialkyl acetylenedicarboxylates **3** (Scheme 1). Its ease of workup, good yields, and fairly mild reaction conditions make it a useful addition to modern synthetic methodologies.

EXPERIMENTAL

Starting materials and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. IR spectra were measured on a Shimadzu IR-460 spectrometer. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were measured ($CDCl_3$ solution) with a Bruker DRX-250 Avance spectrometer at 250.0, 62.9, and 101.2 MHz, respectively. Mass spectra were recorded on an Agilent Technologies (HP) 5973 mass spectrometer operating at an ionization potential of 70 eV. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. Chromatography columns were prepared from Merck silica-gel powder.

General Procedure

A solution of 0.166 g triethylphosphite (1 mmol) in 5 cm^3 CH_2Cl_2 was added dropwise at 0 °C to a magnetically stirred solution of 1 mmol acyl chloride **1** in dry CH_2Cl_2 (5 cm^3) over 15 min. The mixture was then allowed to warm to rt and stirred for 30 min. Then the mixture was cooled to 0 °C, and 1 mmol dialkyl acetylenedicarboxylate **3** was added. A solution of 1 mmol isocyanide **2** in dry CH_2Cl_2 (2 cm^3) was added dropwise to this mixture over 15 min. The mixture was stirred

for 24 h. The solvent was evaporated, and the residue was purified by flash column chromatography (silica gel, Petroleum ether/AcOEt 3:1). The characterization data of the compounds are given.

Selected Data

Dimethyl 5-(cyclohexylimino)-2-(diethoxyphosphoryl)-2-methyl-2,5-dihydrofuran-3,4-dicarboxylate (4a). Yellow viscous oil; yield 0.29 g (67%); IR (thin film) (ν_{max}, cm^{-1}): 2955, 1766, 1749, 1685, 1472, 1261, 1025; ^{1}H NMR (250 MHz, $CDCl_3$) δ_H: 1.0–1.9 (m, 2Me and 5CH_2 of cyclohexyl, 1.76 (d, $^3J_{HP} = 14.7$ Hz, Me), 3.49 (m, CH-N), 3.72 (s, MeO), 3.76 (s, MeO), 3.90–4.20 (m, 2CH_2OPO); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ_C: 16.20 (d, $^3J_{CP} = 6.3$ Hz, Me), 16.29 (d, $^3J_{CP} = 6.3$ Hz, Me), 20.38 (Me), 24.60, 25.55, 33.11 and 33.34 (5CH_2 of cyclohexyl), 52.66 and 52.82 (2MeO), 56.29 (CH-N), 63.80 (d, $^2J_{CP} = 6.9$ Hz, CH_2OPO), 64.06 (d, $^2J_{CP} = 7.5$ Hz, CH_2OPO), 87.17 (d, $^1J_{CP} = 167.9$ Hz, C), 135.27 (d, $J_{CP} = 8.2$ Hz, C-alkene), 145.12 (C-alkene), 153.76 (C=N), 161.08 and 161.63 (2C=O); ^{31}P NMR (101.2 MHz, $CDCl_3$) δ_P: 13.15; MS (*m/z*, %): 432 ($M^+ + 1$, 100), 351 (17), 293 (95), 262 (65), 212 (30), 180 (40), 155 (16), 138 (24), 109 (38), 81 (47), 43 (72). Anal. calcd. for $C_{19}H_{30}NO_8P$ (431.42): C, 52.89; H, 7.01; N, 3.24. Found: C, 53.11; H, 7.18; N, 3.41%.

Diethyl 5-(cyclohexylimino)-2-(diethoxyphosphoryl)-2-methyl-2,5-dihydrofuran-3,4-dicarboxylate (4b). Yellow viscous oil; yield 0.29 g (63%); IR (thin film) (ν_{max}, cm^{-1}): 2934, 1792, 1734, 1683, 1447, 1265, 1027; ^{1}H NMR (250 MHz, $CDCl_3$) δ_H: 1.1–2.0 (m, 4Me and 5CH_2 of cyclohexyl), 1.91 (d, $^3J_{HP} = 14.7$ Hz, Me), 3.85 (m, CH-N), 4.1–4.5 (m, 2CH_2OPO and 2CH_2O); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ_C: 13.85 and 13.95 (2Me), 16.25 (d, $^3J_{CP} = 6.3$ Hz, Me), 16.6 (d, $^3J_{CP} = 6.2$ Hz, Me), 20.06 (Me), 24.69, 25.75, 32.60 and 33.32 (5CH_2 of cyclohexyl), 56.37 (CH-N), 62.43 and 62.84 (2CH_2O), 64.69 (d, $^2J_{CP} = 7.8$ Hz, CH_2OPO), 64.93 (d, $^2J_{CP} = 7.8$, CH_2OPO), 84.24 (d, $^1J_{CP} = 152.5$ Hz, C), 134.20 and 141.24 (C-alkene), 159.33 (C=N), 160.21 and 160.50 (2C=O); ^{31}P NMR (101.2 MHz, $CDCl_3$) δ_P: 13.29 ppm; MS (*m/z*, %): 459 (M^+, 1), 379 (100), 335 (19), 196 (77), 168 (97), 127 (37), 99 (41), 81 (36), 43 (95). Anal. calcd. for $C_{21}H_{34}NO_8P$ (459.48): C, 54.89; H, 7.46; N, 3.05. Found: C, 55.12; H, 7.53; N, 3.17%.

Dimethyl 5-(cyclohexylimino)-2-(diethoxyphosphoryl)-2-phenyl-2,5-dihydrofuran-3,4-dicarboxylate (4c). Pale yellow viscous oil; yield 0.28 g (56%); IR (thin film) (ν_{max}, cm^{-1}): 2986, 1795, 1747, 1683, 1438, 1275, 1026; ^{1}H NMR (250 MHz, $CDCl_3$) δ_H: 0.9–2.1 (m, 5CH_2 of cyclohexyl), 1.14 (t, $^3J_{HH} = 7.2$ Hz, Me), 1.31 (t, $^3J_{HH} = 7.0$ Hz, Me), 3.76 (m, CH-N), 3.88 and 3.89 (s, 2MeO), 4.00–4.32 (m, 2CH_2OPO), 7.30–7.70 (m, 5H, aromatic); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ_H: 16.14 (d, $^3J_{CP} = 5.7$ Hz, Me), 16.28 (d, $^3J_{CP} = 5.7$ Hz, Me), 24.76, 25.59, 33.25 and 33.48 (5CH_2 of cyclohexyl), 53.16 and 53.42 (2MeO), 56.85 (CH-N), 65.25 (d, $^2J_{CP} = 6.9$ Hz, CH_2OPO), 65.60 (d, $^2J_{CP} = 7.5$ Hz, CH_2OPO), 90.24 (d, $^1J_{CP} = 164.0$ Hz, C), 126.21, 128.71, 129.62 and 130.73 (C-Ar), 136.10 and 147.31 (C-alkene), 159.10 (C=N), 160.30 and 161.20 (2C=O); ^{31}P NMR (101.2 MHz, $CDCl_3$) δ_P: 9.97; MS (*m/z*, %): 493 (M^+, 1), 412 (41), 358 (11), 275

(15), 244 (85), 217 (15), 105 (100), 77 (70), 51 (16). Anal. calcd. for $C_{24}H_{32}NO_8P$ (493.49): C, 58.41; H, 6.54; N, 2.84. Found: C, 58.57; H, 6.71; N, 2.96%.

Diethyl 5-(cyclohexylimino)-2-(diethoxyphosphoryl)-2-phenyl-2,5-dihydrofuran-3,4-dicarboxylate (4d). Pale yellow viscous oil; yield 0.29 g (55%); IR (thin film) (ν_{max}, cm^{-1}): 2984, 1797, 1743, 1685, 1449, 1267, 1028; ^1H NMR (250 MHz, $CDCl_3$) δ_H: 1.10–1.90 (m, 4Me and 5 CH_2 of cyclohexyl), 3.74 (m, CH-N), 3.90–4.40 (m, $2CH_2OPO$ and $2CH_2O$), 7.21–7.80 (m, 5H, aromatic); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ_C: 13.32 and 13.41 (2Me), 16.22 (d, $^3J_{CP} = 5.7$ Hz, Me), 16.34 (d, $^3J_{CP} = 5.7$ Hz, Me), 24.67, 25.70, 33.39 and 33.51 ($5CH_2$ of cyclohexyl), 56.58 (CH-N), 62.40 and 62.84 ($2CH_2O$), 65.17 (d, $^2J_{CP} = 7.3$ Hz, CH_2OPO), 65.50 (d, $^2J_{CP} = 7.5$ Hz, CH_2OPO), 90.05 (d, $^1J_{CP} = 165.7$ Hz, C), 126.80, 128.24, 129.32 and 130.88 (C-Ar), 135.12 and 145.65 (C-alkene), 159.14 (C=N), 160.56 and 161.08 (2C=O); ^{31}P NMR (101.2 MHz, $CDCl_3$) δ_P: 12.49; MS (m/z, %): 522 ($M^+ + 1$, 51), 441 (48), 385 (35), 334 (31), 302 (42), 258 (95), 212 (43), 135 (65), 105 (100), 77 (50). Anal. calcd. for $C_{26}H_{36}NO_8P$ (521.54): C, 59.88; H, 6.95; N, 2.68. Found: C, 59.74; H, 7.11; N, 2.84%.

Dimethyl 2-(diethoxyphosphoryl)-2-methyl-5-[(1,1,3,3-tetramethylbutylimino)]-2,5-dihydrofuran-3,4-dicarboxylate (4e). Yellow viscous oil; yield 0.29 g (60%); IR (thin film) (ν_{max}, cm^{-1}): 2955, 1748, 1679, 1619, 1438, 1263, 1022; ^1H NMR (250 MHz, $CDCl_3$) δ_H: 0.96 (s, Me_3C), 0.99 (t, $^3J_{HH} = 6.25$ Hz, Me), 1.31 and 1.41 (2 Me), 1.35 (t, $^3J_{HH} = 6.50$ Hz, Me), 1.94 (d, $^3J_{HP} = 15.0$ Hz, Me), 1.90 (d, $^2J_{HH} = 17.5$ Hz, CH), 2.03 (d, $^2J_{HH} = 17.5$ Hz, CH), 3.80 and 3.82 (2MeO), 4.11–4.31 (m, $2CH_2OPO$) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ_C: 16.32 (d, $^3J_{CP} = 5.7$ Hz, Me), 16.41 (d, $^3J_{CP} = 5.6$ Hz, Me), 22.50, 29.37 and 30.23 (3Me), 31.36 (Me_3C), 31.58 (CMe_3), 50.78 (CH_2), 52.74 and 54.11 (2MeO), 56.70 (Me2C-N), 63.90 (d, $^2J_{CP} = 6.7$, CH_2OPO), 64.10 (d, $^2J_{CP} = 6.8$, CH_2OPO), 88.10 (d, $^1J_{CP} = 165.6$, C), 134.20 and 141.50 (C-alkene), 156.30 (C=N), 164.00, 166.50 (2C=O) ppm; ^{31}P NMR (101.2 MHz, $CDCl_3$) δ_P: 15.20 ppm; MS (m/z, %): 462 ($M^+ + 1$, 5), 429 (48), 385 (19), 196 (77), 168 (97), 127 (37), 99 (41), 81 (36), 43 (95). Anal. calcd. for $C_{21}H_{36}NO_8P$ (461.49): C, 54.65; H, 7.86; N, 3.03. Found: C, 54.82; H, 7.73; N, 3.14%.

Diethyl 2-(diethoxyphosphoryl)-2-methyl-5-[(1,1,3,3-tetramethylbutylimino)]-2,5-dihydrofuran-3,4-dicarboxylate (4f). Yellow viscous oil; yield 0.28 g (57%); IR (thin film) (ν_{max}, cm^{-1}): 2983, 1734, 1678, 1620, 1446, 1265, 1024; ^1H NMR (250 MHz, $CDCl_3$) δ_H: 0.90–1.10 (m, Me and Me_3C), 1.20–1.47 (m, 3Me), 1.52 (d, $^2J_{HH} = 14.5$ Hz, CH), 1.64 (d, $^2J_{HH} = 14.5$ Hz, CH), 1.89 (d, $^3J_{HP} = 14.5$ Hz, Me), 4.11–4.42 (m, $2CH_2OPO$ and $2CH_2O$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ_C: 13.84 and 13.97 (2 Me), 16.38 (d, $^3J_{CP} = 6.0$, Me), 16.46 (d, $^3J_{CP} = 5.7$, Me), 20.63, 29.45 and 30.30 (3Me), 31.42 (Me_3C), 31.62 (CMe_3), 53.25 (CH_2), 55.36 (Me_2C-N), 59.27 and 60.63 ($2CH_2O$), 63.62 (d, $^2J_{CP} = 6.2$ Hz, CH_2OPO), 63.92 (d, $^2J_{CP} = 6.3$ Hz, CH_2OPO), 86.4 (d, $^1J_{CP} = 162.8$ Hz, C), 136.70 and 143.60 (C-alkene), 157.40 (C=N), 159.27 and 161.30 (2C=O); ^{31}P NMR (101.2 MHz, $CDCl_3$) δ_P: 15.26; MS (m/z, %): 490 ($M^+ + 1$, 5), 443 (87), 405 (10), 379 (32), 331 (90), 196 (35), 168 (41), 149 (57), 109 (21), 43 (75). Anal. calcd. for $C_{23}H_{40}NO_8P$ (489.55): C, 56.43; H, 8.23; N, 2.86. Found: C, 56.61; H, 8.41; N, 3.00%.

Diemthyl 2-(diethoxyphosphoryl)-2-phenyl-5-[(1,1,3,3-tetramethylbutylimino)]-2,5-dihydrofuran-3,4-dicarboxylate (4g). Pale yellow viscous oil; yield 0.3 g (54%); IR (thin film) (ν_{max}, cm^{-1}): 2954, 1765, 1747, 1678, 1473, 1261, 1024; ^1H NMR (250 MHz, $CDCl_3$) δ_H: 0. 9 (t, $^3J_{HH} = 7.0$ Hz, Me), 1.07 (s, Me_3C), 1.32 (t, $^3J_{HH} = 7.0$ Hz, Me), 1.54 (s, Me_2C), 1.64 (d, $^2J_{HH} = 15$ Hz, CH), 1.97 (d, $^2J_{HH} = 15$ Hz, CH), 3.75 and 3.84 (s, 2MeO), 4.10–4.30 (m, $2CH_2OPO$), 7.41–7.76 (m, 5H, Aromatic); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ_C: 16.11 (d, $^3J_{CP} = 5.8$ Hz, Me), 16.34 (d, $^3J_{CP} = 6.2$ Hz, Me), 29.80 and 30.84 (2 Me), 31.5 (Me3C), 31.64 (CMe_3), 50.80 (CH_2), 54.13 (Me_2C-N), 54.35 and 56.85 (2MeO), 63.96 (d, $^2J_{CP} = 7.3$ Hz, CH_2OPO), 64.41 (d, $^2J_{CP} = 7.2$ Hz, CH_2OPO), 90.24 (d, $^1J_{CP} = 165.2$ Hz, C), 126.12, 128.25, 128.68 and 129.52 (4C, aromatic), 134.27 and 144.16 (C-alkene), 155.60 (C=N), 161.10 and 161.30 (2C=O); ^{31}P NMR (101.2 MHz, $CDCl_3$) δ_P: 13.51; MS (m/z, %): 523 (M^+, 1), 491 (51), 379 (100), 347 (20), 242 (30), 211 (36), 105 (32), 57 (20). Anal. calcd. for $C_{26}H_{38}NO_8P$ (523.56): C, 59.65; H, 7.32; N, 2.67. Found: C, 59.74; H, 7.21; N, 2.81%.

Diethyl 2-(diethoxyphosphoryl)-2-phenyl-5-[(1,1,3,3-tetramethylbutylimino)]-2,5-dihydrofuran-3,4-dicarboxylate (4h). Pale yellow viscous oil; yield 0.29 g (52%); IR (thin film) (ν_{max}, cm^{-1}): 2983, 1734, 1678, 1446, 1264, 1024 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ_H: 0.9 (t, $^3J_{HH} = 7.0$ Hz, Me), 1.07 (s, Me_3C), 1.20 (t, $^3J_{HH} = 7.2$ Hz, Me), 1.31 (t, $^3J_{HH} = 7.5$ Hz, Me), 1.43 (t, $^3J_{HH} = 7.2$ Hz, Me), 1.54 (s, Me_2C), 1.63 (d, $^2J_{HH} = 15$ Hz, CH), 1.98 (d, $^2J_{HH} = 15$ Hz, CH), 3.80–4.50 (m, $2CH_2O$, $2CH_2OPO$), 7.40–7.80 (m, 5H, aromatic); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ_C: 13.90 and 14.41 (2Me), 16.07 (d, $^3J_{CP} = 6.3$ Hz, Me), 16.21 (d, $^3J_{CP} = 6.1$ Hz, Me), 29.74 and 30.26 (2Me), 31.64 (Me_3C), 31.88 (CMe_3), 53.10 (Me2C), 55.61 and 58.26 ($2CH_2O$), 61.82 (CH_2), 63.91 (d, $^2J_{CP} = 6.9$ Hz, CH_2OPO), 64.23 (d, $^2J_{CP} = 6.3$ Hz, CH_2OPO), 90.41 (d, $^1J_{CP} = 165.4$ Hz, C), 126.86, 128.74, 129.36, 134.21 (4C, aromatic), 135.23 and 142.32 (C-alkene), 150.61 (C=N), 160.44 and 161.65 (2C=O); ^{31}P NMR (101.2 MHz, $CDCl_3$) δ_P: 13.53; MS (m/z, %): 552 ($M^+ + 1$, 10), 505 (100), 393 (92), 256 (17), 211 (50), 105 (56), 77 (15), 57 (31), 41 (15). Anal. calcd. for $C_{28}H_{42}NO_8P$ (551.61): C, 60.97; H, 7.67; N, 2.54. Found: C, 61.11; H, 7.78; N, 2.70%.

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