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A New and Efficient Synthesis of Imidazo[1,5-a] pyridine Derivatives by a Tandem Aza-Wittig / Electrocyclic Ring Closure of *N*-vinylic phosphazenes.

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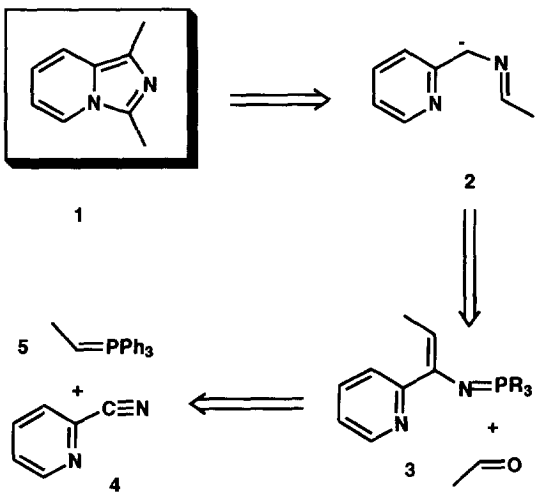
Abstract: Imidazo[1,5-a]pyridines **1** are prepared by reaction of *N*-vinylic phosphazene **3**, obtained from phosphorus ylide **5** and 2-cyanopyridine **4**, with aldehydes. Formation of fused heterocycles **1** can be explained through aza-Wittig reaction of phosphazene **3**, followed by 1,5-electrocyclic ring closure of the resulting aldimines **2**. Phosphazene **3** undergoes pyrido annelation by reaction with Diethyl Ketomalonate to give isoquinoline derivative **9**.

Fused imidazopyridine ring systems represent an important class of compounds not only for their theoretical interest but also from a pharmacological point of view[1]. These heterocyclic structures form part of the skeleton of natural alkaloids[2], as well as of potent short-acting neuromuscular blocking agents[3], of reversible inhibitors of the H^+, K^+-ATPase enzyme[4] with a potent antisecretory activity[5] and of sedative-hypnotics of the nervous system[6]. Imidazo[1,5-a]pyridine skeleton is a basic structure of synthetic drugs such as Pirmogrel, with human clinical applications as effective platelet aggregation and thromboxane synthetase inhibitors[7]. Although several procedures for the synthesis of imidazo[1,5-a]pyridines have been reported, the preparation of such compounds is far from simple[1].

In recent years, we have described the synthesis of 1-azadienes[8] and secondary *E*-allylamines[9] through Wittig reaction of functionalized ylides, as well as the usefulness of phosphazenes in the preparation of acyclic[10] and heterocyclic[11] compounds. Phosphazenes[12], nitrogen analogues of the isoelectronic phosphorus ylides, react with carbonyl compounds and lead to a very efficient and mild-condition method for the construction of carbon-nitrogen double bonds. This strategy has been used recently in the preparation of acyclic imines[13], of rigid bicyclic guanidine[14], of genotoxic heterocyclic amine Trp-P2[15], of azulenes[16] and in an elegant route to the synthesis of alkaloids such as Leucettamine B[17] and Lavendamycin[18]. Likewise, we have

also used the aza-Wittig reaction of *N*-vinylic phosphazenes in the synthesis of 2-azadienes derived from α-[19] and β-aminoacid derivatives[20]. Following on from our previous studies on the reactivity and the synthetic utility of phosphazenes, here we aim to explore a new and effective strategy for the preparation of imidazo[1,5-a]pyridines **1** from *N*-vinylic phosphazene **3**. Retrosynthetically, we envisaged the preparation of fused heterocycles **1** by tandem Aza-Wittig Reaction/ Electrocyclic Ring closure of functionalized phosphazene **3**, obtained from the reaction between phosphonium ylide **5** and 2-cyanopyridine **4** (Scheme 1).

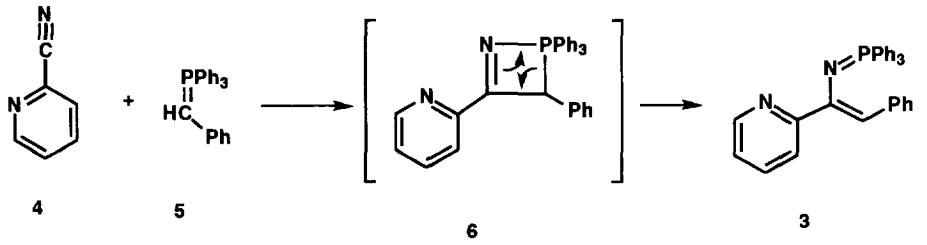


Scheme 1

RESULTS AND DISCUSSION

Preparation of Phosphazene **3**.

The preparation of the required *N*-vinylic phosphazene **3** was accomplished very easily, and in high yield, by reaction of the commercially available 2-cyanopyridine **4** and phosphorus ylide **5** in benzene. This strategy had been used previously in the preparation of functionalized phosphazenes by reaction of phosphorus ylides[21-23] and simple phosphazenes[24] with aryl nitriles. The structure of compound **3** is supported by the spectroscopic data. Thus, the *^{31}P-NMR* spectrum shows an absorption at δ_P 3.8 ppm, while in the *^{1}H-NMR* spectrum, the vinylic proton resonates at δ_H 6.27 ppm as a well resolved doublet with coupling constant of $^4J_{PH}$ 6.0 Hz and the *^{13}C-NMR* spectrum shows an absorption at δ_C 111.6 ($^3J_{PC}$ 20.6 Hz). Formation of phosphazene **3** can be explained through [2+2] cycloaddition[21,24,25] followed by ring opening of the unstable cyclic adduct containing pentavalent phosphorus **6**.



4 5 6 3

Scheme 2

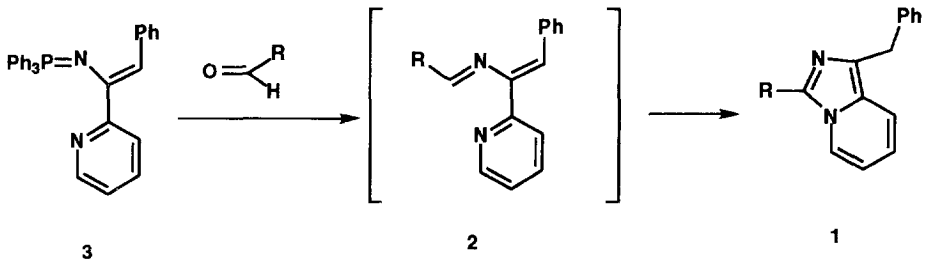
Aza-Wittig Reaction of Phosphazene **3** with Aldehydes. Synthesis of Imidazo[1,5-a]pyridines **1**.

Aza-Wittig reaction of phosphazene **3** with aliphatic, heteroaromatic, aromatic and functionalized aldehydes (see Table) in Chloroform (*TLC* control) leads to the formation of imidazo[1,5-a]pyridines **1** in excellent yields. Pure compounds were obtained after flash-chromatography and show satisfactory microanalyses. Compounds **1** were characterized by their spectroscopic data and mass spectrometry, which shows a molecular ion at *m/z* 284 (62 %) for compound **1a**. The ^1H-*NMR* spectrum of fused heterocycle **1a** indicates a benzylic methylene group at δ_H 4.35 ppm and pyridine protons, of which one shows a well resolved doublet at δ_H 8.17 ppm ($^3J_{HH}$ 7.2 Hz) for H-5 and a characteristic high field shift absorption in the region of δ 6.62-6.45 ppm for H-6 and H-7.

Table Imidazo[1,5-a]pyridines **1** obtained

Compound	R	reaction time (h)	reaction temperature (°C)	Yield (%)[a]	m.p. (°C)
a	Ph-	168	25	79	oil[b]
b	4-NO_2-Ph	86	25	78	126-127
c	4-Cl-Ph-	120	25	80	oil[b]
d	4-Me-Ph-	192	25	74	oil[b]
e	3-Pyr-	70	25	82	89-90
f	^{i}Bu-	30	80	76	oil[b]
g	Cyclohexyl-	90	80	65	oil[b]
h	COOEt	0.5	25	73	oil[b]

[a] Yield of isolated purified product. [b]Purified by flash chromatography.

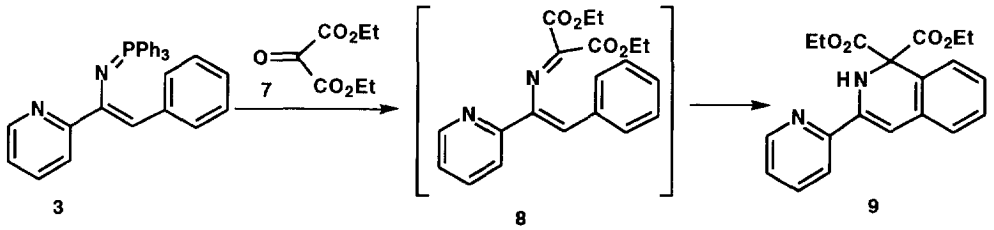


Scheme 3

The formation of bicyclic heterocycles **1** could be assumed *via* imidazo annelation of imino functionalized pyridines **2** generated "in situ" from Aza-Wittig reaction of phosphazene **3** and aldehydes. Therefore, the 1,5-electrocyclic ring closure process leads to a new approach to the formation of the imidazo ring, it is well known that 1,5-electrocyclic reaction is important in Heterocyclic Chemistry for the synthesis of five membered heterocycles[26]. On the other hand, several examples of synthesis of heterocyclic compounds by means of Aza-Wittig reactions followed by 1,6-electrocyclic reactions have been reported in recent years[18,22,27-29]. However, to the best of our knowledge, we report here the first application of tandem Aza-Wittig reaction/1,5-electrocyclic ring closure strategy in the preparation of fused heterocycles **1**, with a wide range of aliphatic, heteroaromatic and aromatic substituents. It is noteworthy that the use of ethyl glyoxalate leads to imidazo[1,5-a] pyridine derived from α-aminoacid **1h**.

Aza-Wittig Reaction of Phosphazene **3** with Diethyl Ketomalonate. Preparation of Dihydroisoquinoline Derivative **9**

In order to test the scope of the Aza-Wittig reaction of phosphazene **3** and the synthetic usefulness of this compound **3** as a key intermediate in organic synthesis, the Aza-Wittig reaction with diethyl ketomalonate was explored. Thus, the treatment of *N*-vinylic phosphazene **3** with carbonyl compound **7** in CH_2Cl_2 at room temperature gave a very high yield of 3-pyridyldihydroisoquinoline derivative **9** (Scheme 4). This result suggests that the process involves initial Aza-Wittig reaction to give the unsaturated ketimine **8** which subsequently undergoes 1,6-electrocyclic ring-closure leading to the formation of bicyclic heterocycle **9**. It is noteworthy that, while the aryl group is involved in the heterocyclization process in this case, the imidazo annelation for the preparation of compound **1** involves the pyridyl group.



Scheme 4

In summary, the present study demonstrates that Tandem Aza-Wittig/Electrocyclic Ring Closure strategy affords a new entry to fused heterocycles **1** and **9**. Phosphazene **3** undergoes imidazo annelation through 1,5-electrocyclic ring closure of aldimine **2** to give imidazo[1,5-a]pyridines, while pyrido annelation through 1,6-electrocyclic reaction of Aza-Wittig ketimine **8** leads to isoquinoline derivative **9**. Because of its simplicity, easy access of the starting material, the good yields in the phosphazene preparation and in the heterocyclization step, the investigated reaction provides an efficient method for the preparation of fused heterocycles **1** and **9**.

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EXPERIMENTAL SECTION

General. Melting points were determined with a Buchi SPM-20 apparatus and are uncorrected. Analytical *TLC* was performed on 0.25mm silica gel plates (Merck). Visualization was accomplished by *UV* light and iodine. Solvents for extraction and chromatography were technical grade and distilled from the indicated drying agents: CH_2Cl_2 *(P_2O_5)*; *n*-hexane and diethyl ether (sodium benzophenone ketyl); ethyl acetate (K_2CO_3). All solvents used in reactions were freshly distilled from appropriate drying agents before use: C_6H_6 (sodium benzophenone ketyl);$CHCl_3$ *(P_2O_5)*. All other reagents were recystallized or distilled as necessary. Column (flash) chromatography was carried out on aluminum oxide, activated, neutral, Brockmann I (Aldrich, ~150 mesh) and silica gel (Merck, 70-230 mesh). Mass spectra were obtained on a Hewlett Packard 5890 spectrometer. Infrared spectra were taken on a Nicolet IRFT Magna 550 spectrometer. ^{1}*H-NMR* spectra were recorded on a Bruker 250 MHz spectrometer using tetramethylsilane (0.00 ppm) or chloroform (7.26 ppm) as an internal reference in $CDCl_3$ solutions. ^{13}*C-NMR* spectra were recorded at 75 MHz with chloroform (77.0 ppm) as an internal reference in $CDCl_3$ solutions. ^{31}*P-NMR* spectra were recorded at 120 MHz with 85% phosphoric acid as an external reference. Elemental analyses were performed in a Perkin Elmer Model 240 instrument. Chemical shifs are given in ppm *(δ)*; multiplicities are indicated by s (singlet), d (doublet), dd (double-doublet), t (triplet) q (quadruplet) or m (multiplet). Coupling constants, *J*, are reported in hertz. Infrared spectra *(IR)* were obtained as neat liquids, or as solids in *KBr*. Peaks are reported in cm^{-1}. Mass spectra *(EI)* were obtained with a ionization voltage of 70 eV. Data are reported in the form m/z (intensity relative to base = 100). All reactions were performed in oven (125 °C) or flame-dried glassware under an inert atmosphere of dry N_2.

1,1,1,4-tetraphenyl-3-(2-pyridinyl)-2-aza-1,λ^5-phosphabuta-1,3-diene (3). To a slurry of 24.00 g (50 mmol) of benzyltriphenylphosphonium iodide in 25 ml of anhydrous benzene was added, under nitrogen, 31.250 ml of a 1.6 M solution of methyllithium (50 mmol) in ether. The clear red solution was heated to reflux; a precipitate formed before the boiling point was reached. The mixture was cooled at 0°C and a solution of 2-cyanopyridine (5.202 g, 50 mmol) in benzene (20 ml) was added. The reaction mixture was stirred at room temperature until *TLC* indicated the disappearance of the nitrile (120 h). After addition of 50 ml of CH_2Cl_2, filtration of the lithium salts and evaporation of solvents, the brown oils obtained were purified by flash chromatography in neutral aluminum oxide (Ethyl acetate) to give 20.98 (92 %) of compound **3**; m.p. 156-157 °C (Ethyl acetate);

^{1}H-NMR (250 MHz) 8.17-6.72 (m, 24 H, arom.+ Pyr.), 6.27 (d, $^4J_{PH}$= 6Hz, 1H, HC=); *^{13}C-NMR* (75 MHz) 146.4-127.8 (C arom.+C pyr.), 123.1 (d, $^1J_{PC}$= 203 Hz, C arom-P), 111.6 (d, $^3J_{PC}$=20.6 Hz, HC=) ; *^{31}P-NMR* (120 MHz) 3.8; *IR* (*KBr*) 3.053, 2999, 1558, 1436, 1400, 1117, 696, 528; *MS* (70 eV) 456 (M^+, 6). Anal. Calcd. for $C_{31}H_{25}N_2P$ (456.18): C, 81.55; H, 5.52; N, 6.14. Found: C, 81.58; H, 5.56; N, 6.15.

General Procedure for the Preparation of imidazo[1,5-a]pyridines: To a solution of the phosphazene **1** (1.368 g, 3 mmol) in dried $CHCl_3$ (10 ml) was added a solution of the aldehyde (3 mmol) in $CHCl_3$ (5 ml) and the mixture was stirred at an appropiate temperature (see Table) until *TLC* indicated the disappearance of the phosphazene. After evaporation of the solvent the residue was purified by flash chromatography on neutral aluminun oxide.

1-benzyl-3-phenylimidazo[1,5-a]pyridine (1a). Reaction with benzaldehyde (0.318 g, 3 mmol) gave 0.673 g (79 %) of the compound **1a** as an orange oil (R_f= 0.29, *n*-hexane/ethyl acetate, 2/1). Data for **1a**: *^{1}H-NMR* (250 MHz) 8.17 (d, $^3J_{HH}$= 7.2Hz, 1H, HC=), 7.79 (d, $^3J_{HH}$= 7 Hz, 2H, arom.), 7.54-7.20 (m, 9H, arom and HC=), 6.62-6.45 (m, 2H, HC=), 4.35 (s, 2H, CH_2); *^{13}C-NMR* (75 MHz) 140.2-125.8 (m, C arom. and C=), 120.9 (HC=), 118.0 (HC=), 117.4 (HC=), 112.6 (HC=), 33.9 (CH_2); *IR* (*film*) 3064, 3030, 2919, 1607, 1498, 1456, 1078, 699; *MS* (70 eV) 284 (M^+, 62). Anal. Calcd. for $C_{20}H_{16}N_2$ (284.13): C, 84.47; H, 5.68; N, 9.86. Found: C, 84.44; H, 5.67; N, 9.84.

1-benzyl-3-(4-nitrophenyl)imidazo[1,5-a]pyridine (1b). Reaction with 4-nitrobenzaldehyde (0.453 g, 3 mmol) gave 0.770 g (78 %) of the compound **1b** as an orange solid. Data for **1b**: m.p.126-127°C (*n*-hexane/diethyl ether), *^{1}H-NMR* (250 MHz) 8.35 (d, $^3J_{HH}$= 8.7 Hz, 2H, arom.), 8.29 (d, $^3J_{HH}$= 6.5 Hz, 1H, HC=), 8.00 (d, $^3J_{HH}$= 8.7 Hz, 2H, arom.), 7.70-7.19 (m, 6H, arom and HC=), 6.72-6.64 (m, 2H, HC=), 4.33 (s, 2H, CH_2); *^{13}C-NMR* (75 MHz) 146.7 (CNO_2), 139.8-124.3 (m, C arom. and C=), 121.2 (HC=), 119.11 (HC=), 118.7 (HC=), 114.4 (HC=), 34.2 (CH_2); *IR* (*KBr*) 3083, 2916, 1590, 1511, 1330, 1111, 853, 698; *MS* (70 eV) 329 (M^+, 6). Anal. Calcd. for $C_{20}H_{15}N_3O_2$ (329.12): C, 72.92; H, 4.59; N, 12.76. Found: C, 72.90; H, 4.57; N, 12.75.

1-benzyl-3-(4-chlorophenyl)imidazo[1,5-a]pyridine (1c). Reaction with 4-chlorobenzaldehyde (0.322 g, 3 mmol) gave 0.763 g (80 %) of the compound **1c** as a brown oil (R_f= 0.35, *n*-hexane/ethyl acetate, 2/1). Data for **1c**: *^{1}H-NMR* (250 MHz) 8.12 (d, $^3J_{HH}$= 7 Hz, 1H, HC=), 7.73 (d, $^3J_{HH}$= 6.6 Hz, 2H, arom.), 7.47 (d, $^3J_{HH}$= 6.6 Hz, 2H, arom.), 7.44-7.18 (m, 6H, arom. and HC=), 6.60-6.50 (m, 2H, HC=), 4.31 (s, 2H, CH_2);*^{13}C-NMR* (75 MHz) 140.1-126.0 (m, C arom. and C=), 120.8 (HC=), 118.2 (HC=), 117.8 (HC=), 113.2 (HC=), 33.9 (CH_2); *IR* (*film*) 3029, 2930, 1599, 1510, 1094, 837, 720; *MS* (70 eV) 318 (M^+, 40). Anal. Calcd. for $C_{20}H_{15}N_2Cl$ (318.09): C, 75.45; H, 4.75; N, 8.80. Found: C, 75.46; H, 4.74; N, 8.83.

1-benzyl-3-(4-methylphenyl)imidazo[1,5-a]pyridine (1d). Reaction with 4-methyl-benzaldehyde (0.360 g, 3 mmol) gave 0.662 g (74 %) of the compound **1d** as a brown oil (R_f= 0.34, n-hexane/ethyl acetate, 2/1). Data for **1d**: *^{1}H-NMR* (250 MHz) 8.15 (d, $^3J_{HH}$= 7 Hz, 1H, HC=), 7.65 (d, $^3J_{HH}$= 8.1 Hz, 2H, arom.), 7.33-7.26 (m, 8H, arom. and HC=), 6.60-6.40(m, 2H, HC=), 4.31 (s, 2H, CH_2), 2.42 (s, 3H, CH_3); *^{13}C-NMR* (75 MHz) 140.4-126.0 (m, C arom. and C=), 121.3 (HC=), 118.2 (HC=), 117.5 (HC=), 112.7 (HC=), 34.1 (CH_2), 21.3 (CH_3); *IR* (*film*) 3028, 2925, 1669, 1499, 1458, 1261, 1077, 828, 741, 700; *MS* (70 eV) 298 (M^+, 51). Anal. Calcd. for $C_{21}H_{18}N_2$ (298.15): C, 84.52; H, 6.09; N, 9.39. Found: C, 84.54; H, 6.07; N, 9.36.

1-benzyl-3-(3-pyridyl)imidazo[1,5-a]pyridine (1e). Reaction with 3-pyridinecarboxaldehyde (0.321 g, 3 mmol) gave 0.702 g (82 %) of the compound **1e** as a solid. Data for **1e**: m.p. 89-90°C (*n*-hexane/CH_2Cl_2), *^{1}H-NMR* (250 MHz) 9.06 d, $^4J_{HH}$= 2.1 Hz, 1H, Pyr.), 8.63 (q, $^3J_{HH}$= 4.8 Hz, $^4J_{HH}$= 1.7 Hz, 1H, Pyr.), 8.17-8.08 (m, 2H, Pyr. and HC=), 7.71-7.18 (m, 7H, arom., Pyr. and HC=), 6.66-6.51 (m, 2H, HC=), 4.32 (s, 2H, CH_2); *^{13}C-NMR* (75 MHz) 149.1 (C Pyr.), 148.1 (C Pyr.), 140.1-123.8 (m, C arom., C Pyr. and C=), 120.8 (HC=), 118.4 (HC=), 118.3 (HC=), 113.7 (HC=), 34.3 (CH_2); *IR* (*KBr*) 3058, 2923, 1591, 1440, 1193, 1125, 724, 702, 543; *MS* (70 eV) 285 (M^+, 83). Anal. Calcd. for $C_{19}H_{15}N_3$ (285.13): C, 79.96; H, 5.30; N, 14.73. Found: C, 80.01; H, 5.29; N, 14.74.

1-benzyl-3-isobuthylimidazo[1,5-a]pyridine (1f). Reaction with isovaleraldehyde (0.258 g, 3 mmol) gave 0.602 g (76 %) of the compound **1f** as a yellow oil (R_f= 0.30, *n*-hexane/ethyl acetate, 3/1). Data for **1f**: *^{1}H-NMR* (250 MHz) 7.55 (d, $^3J_{HH}$= 7Hz, 1H, HC=), 7.19-7.03 (m, 6H, arom. and HC=), 6.42-6.32 (m, 2H, HC=), 4.17 (s, 2H, CH_2), 2.75 (d, $^3J_{HH}$= 7.3Hz, 2H, CH_2), 2.10 (q, $^3J_{HH}$= 7.3 Hz, $^3J_{HH}$= 6.6 Hz, 1H, CH), 0.91 (d, $^3J_{HH}$= 6.6 Hz, 6H, CH_3); *^{13}C-NMR* (75 MHz) 140.3-125.5 (m, C arom. and C=), 120.1(HC=), 117.6 (HC=), 115.9 (HC=), 111.4 (HC=), 35.1 (CH_2), 33.5 (CH_2), 27.3 (CH), 22.2 (CH_3); *IR (film)* 3064, 2958, 2926, 1689, 1590, 1454, 1082, 740, 699; *MS* (70 eV) 264 (M^+, 65). Anal. Calcd. for $C_{18}H_{20}N_2$ (264.16): C, 81.77; H, 7.63; N, 10.60. Found: C, 81.80; H, 7.64; N, 10.62.

1-benzyl-3-cyclohexylimidazo[1,5-a]pyridine (1g). Reaction with cyclohexanecarboxaldehyde (0.336 g, 3 mmol) gave 0.566 g (65 %) of the compound **1g** as a yellow oil (R_f= 0.36, *n*-hexane/ethyl acetate, 2/1). Data for **1g**: *^{1}H-NMR* (250 MHz) 7.60 (d, $^3J_{HH}$= 6.9 Hz, 1H, HC=), 7.29-7.00 (m, 6H, arom. and HC=), 6.42-6.30 (m, 2H, HC=), 4.26 (s, 2H, CH2), 2.90 (m, 1H, CH), 2.02-1.36 (m, 10 H, CH_2); *^{13}C-NMR* (75 MHz) 140.9-125.3 (m, C arom. and C=), 119.8 (HC=), 117.6 (HC=), 115.7 (HC=), 111.0 (HC=), 35.2 (CH), 33.6 (CH_2), 30.2 (CH_2), 25.8 (CH_2), 25.4 (CH_2); *IR (film)* 3027, 2928, 2854, 1635, 1497, 1453, 1086, 739, 700 ; *MS* (70 eV) 290 (M^+, 90). Anal. Calcd. for $C_{20}H_{22}N_2$ (290.18): C, 82.71; H, 7.64; N,9.65. Found: C, 82.68; H, 7.64; N, 9.66.

Ethyl 1-benzylimidazo[1,5-a]pyridine-3-carboxylate (1h). Reaction with ethyl glyoxalate (0.306 g, 3 mmol) gave 0.613 g (73 %) of the compound **1h** as a yellow oil (R_f= 0.29, *n*-hexane/ethyl acetate, 1/1) Data for **1h**: *^{1}H-NMR* (250 MHz) 9.27 (d, $^3J_{HH}$= 6.9 Hz, 1H, HC=), 7.32-7.17 (m, 6H, arom and HC=), 6.89-6.78 (m, 2H, HC=), 4.51 (q, 2H, OCH_2), 4.35 (s, 2H, CH_2), 1.46 (t, 2H, CH_3); *^{13}C-NMR* (75 MHz) 159.7 (COO), 139.4-126.3 (m, C arom. and C=), 125.6 (HC=), 121.7 (HC=), 117.9 (HC=), 115.3 (HC=), 61.1 (OCH_2), 34.5 (CH_2), 14.6 (CH_3); *IR (film)* 3063, 3031, 2984, 2931, 1732, 1686, 1460, 1228, 1080, 1035, 754, 701; *MS* (70 eV) 280 (M^+, 93). Anal. Calcd. for $C_{17}H_{16}N_2O_2$ (280.12): C, 72.83; H, 5.76; N, 10.00. Found: C, 72.84; H, 5.74, N, 9.99.

Diethyl 2-Pyridyl-1,2-dihydro-1,1-isoquinolinedicarboxylate (9). To a solution of the phosphazene **3** (1.368 g, 3 mmol) in dried $CHCl_3$ (10 ml) was added a solution of diethyl ketomalonate (0.522 g, 3 mmol) in $CHCl_3$ (3 ml) and the mixture was stirred at room temperature for 20 h. After evaporation of the solvent the residue was purified by flash chromatography on silicagel (ether/ *n*-hexane 1/5) to give 0.898 g (85 %) of compound **4** as a yellow solid. Data for 4: m.p. 108-109 °C(CH_2Cl_2/*n*-hexane); *^{1}H-NMR* (250 MHz) 8.65-8.63 (m, 1H, Pyr.), 7.54-7.12 (m, 8 H, arom., Pyr. and HC=), 4.54 (q, 2H, OCH_2), 4.22 (q, 2H, OCH_2), 4.14 (s, 1H, NH), 1.40 (t, 3H, CH_3), 1.15 (t, 3H, CH_3); *^{13}C-NMR* (75 MHz) 176.3 (COO), 170.0 (COO). 152.9-123.0 (m, C arom., C Pyr. and HC=), 85.9 (C-N), 66.0 (OCH_2), 63.2 (OCH_2), 14.2 (CH_3), 14.1 (CH_3); *IR (KBr)* 3386, 3064, 2985, 1753, 1756, 1616, 1327, 1230, 1043, 696; *MS* (70 eV) 352 (M^+, 10). Anal. Calcd. for $C_{20}H_{20}N_2O_4$ (352.14): C, 68.15; H, 5.72; N, 7.95. Found: C, 68.14; H, 5.72; N, 9.94.

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