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Isothiazoles. Part 11: 3-Azahexatrienes from 2-Arylpropenamidines: Electrocyclization to 6-Aminonicotinic Acid Derivatives

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Abstract—A new synthesis of 6-aminonicotinic acid derivatives was developed starting from the readily available 3-substituted acrylamidines **1** and electron-poor alkynes **2**. By nucleophilic addition of the basic amidinic NH to the electron-poor triple bond, the intermediate azatrienes **4** were obtained. Through thermally induced electrocyclization compounds **4** afforded the pyridines **3** by alcohol elimination or oxidation. Another approach was the direct cyclization of acrylamidines with the dienyne system as a backbone.

Introduction

It is well known that 1-azabutadienes are excellent starting materials for the synthesis of five- and six-membered heterocycles.[1,2] Recently, we reported the base-catalyzed ring opening of 3-amino-4-aryl-isothiazole 1,1-dioxides to 2-arylpropenamidines incorporating the 1-azadiene system in their structure. By this method a large number of compounds with different substituents on C-3 can easily be obtained in good yields.[3] In this paper we report on the suitability of these compounds as starting materials for the synthesis of highly substituted pyridines. 2-Arylpropenamidines react easily with various acetylenic compounds allowing the preparation of derivatives of 6-aminonicotinic acid in good yields.

Results and Discussion

3,3-Dialkoxy-*N*,*N*-diethylamino-2-(4-methoxyphenyl)propenamidines **1a**,**b** were reacted with methyl propiolate (**2a**) at reflux in anisole to give compounds **3a**,**b** in 50% yield. When the reaction was performed at room temperature in toluene, besides compounds **3a**,**b**, compounds **4a**,**b** were obtained as the major products (Scheme 1). Therefore, pyridines **3** are not generated through a Diels–Alder cycloaddition reaction but through an addition reaction affording the azatriene intermediates **4** which undergo electrocyclic ring closure to the intermediates **5a**,**b** followed by alcohol elimination.

This result is in agreement with the literature data, since 1-azabutadiene derivatives show, in general, little aptitude to give Diels–Alder cycloaddition reactions.[4–7]

The structures of compounds **3** and **4** were confirmed by analytical and spectroscopic data showing for **3a**,**b** the characteristic signals associated with the alkoxy groups and the singlet in the range of 8.60–8.70 ppm clearly associated with the pyridine hydrogen H-2. The spectra of compounds **4a**,**b** were mainly characterized by the methoxy groups and an AX system clearly associated with the H-2 and H-3 protons. The configuration of the azatriene system was assigned by performing NOESY and NOE difference experiments demonstrating the *Z* configuration of the amidinic double bond due to a clear relationship between the H-3 (8.1 ppm) and the signals of the diethylamino group. The *E*-configuration of the C-2 C-3 double bond was confirmed by a clear NOE effect between the methoxycarbonyl group and both H-2 and H-3 which, in turn, did not show any effect on each other.

As an extension of this synthetic scheme the reaction was generalized to dimethyl acetylenedicarboxylate (Scheme 2). Also in this case, it is possible to perform the reaction between **1a**,**b** and **2b** in one step, operating at reflux in anisole, affording directly the pyridine compounds **3c,d** or in two steps, at room temperature in toluene, isolating the intermediate triene derivatives which were always obtained as a mixture of two stereoisomers. In fact, from the reaction between **1b** and **2b** the mixture of isomeric azatrienes **4d**

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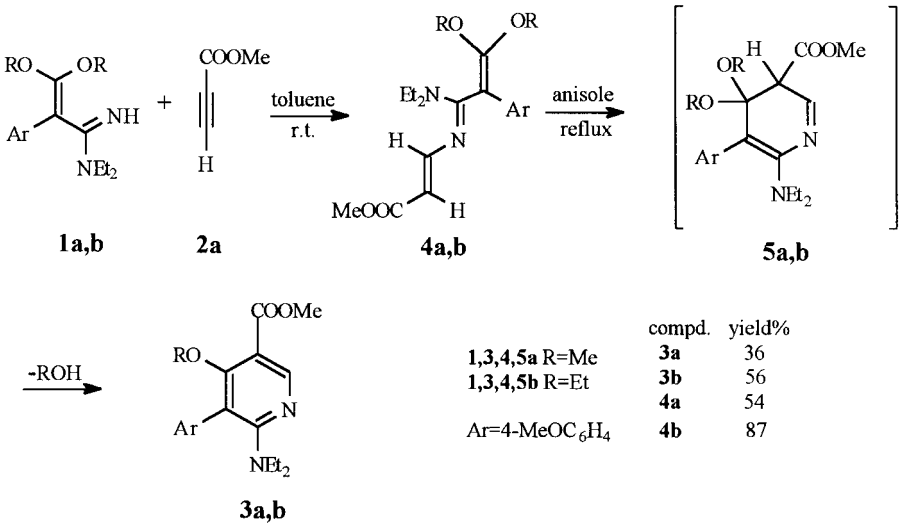
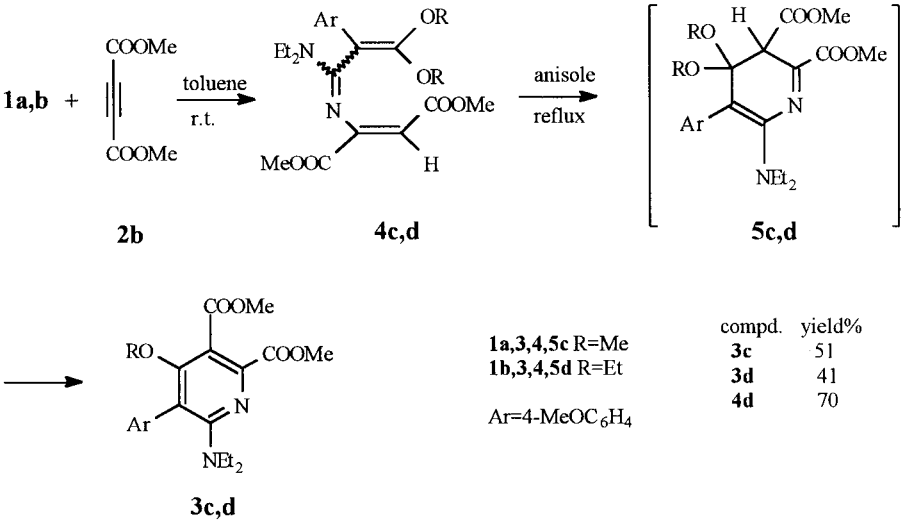
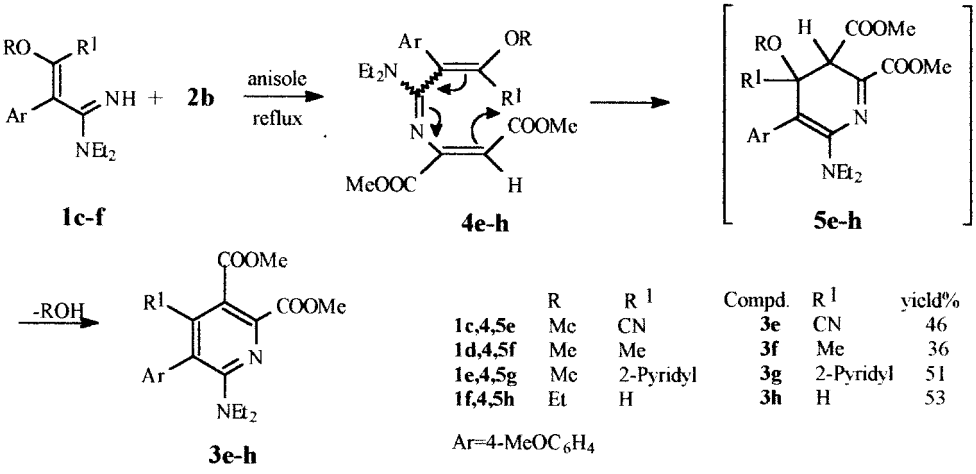


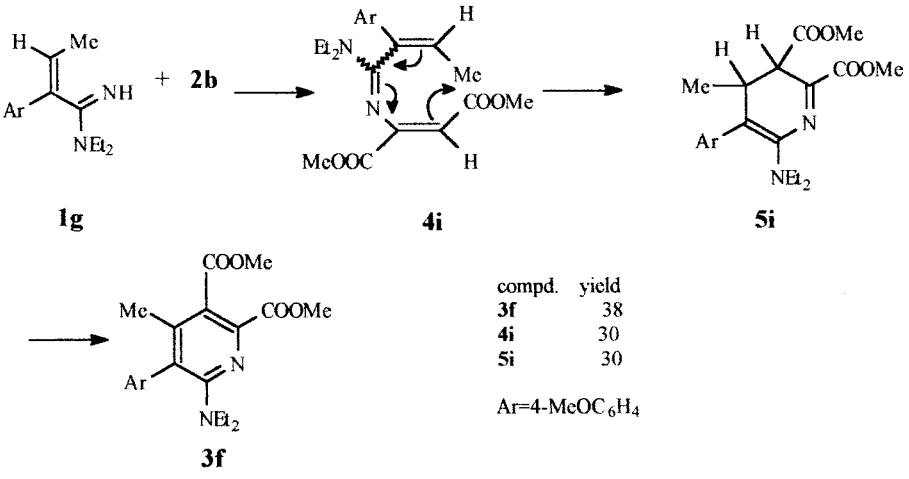
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

was isolated and analyzed: the main features in the ^{1}H NMR spectra are a singlet associated with H-2 (A isomer: 5.22 ppm, B isomer 5.72 ppm) and the signals associated with the COOMe groups shifted by 0.1–0.2 ppm in each isomer with respect to the other (A isomer: 3.55, 3.65 ppm; B isomer: 3.48, 3.60 ppm). NOE difference and NOESY experiments showed, for each isomer, NOE effect between H-2 and the two COOMe groups, confirming the *Z* configuration of the C-2 C-3 double bond in both isomers. In consequence, we can conclude that the difference between isomer A and isomer B must consist in the configuration of the amidinic double bond.

As shown, the use of 3,3-dialkoxypropenamidines **1a**,**b** allowed the synthesis of 4-alkoxy-6-amino-nicotinic acid derivatives. With the aim to obtain nicotinic derivatives with different substituents on C-4 we have considered the synthetic scheme described above utilizing as key starting material dimethyl acetylenedicarboxylate and propenamidines **1c**–**f** substituted on C-3 both with an alkoxy group, as leaving group, and a different group (Scheme 3).

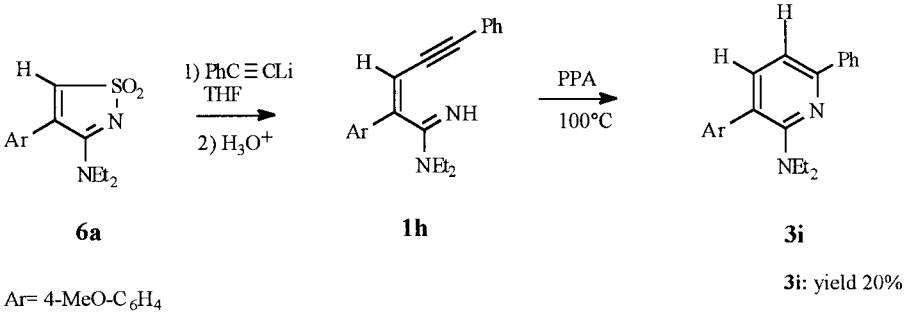
In this case the reaction pathway is the same as described above. The azatrienes **4e**–**h** were electrocyclized, giving the intermediates **5e**–**h** which aromatized with alcohol elimination affording pyridines **3e**–**h**.

Using propenamidine **1g**, lacking the alkoxy leaving group on C-3, a different aromatization process has to be considered in the formation of the pyridine **3f** (Scheme 4). Indeed, intermediate dihydronicotinic derivative **5i** are formed which spontaneously oxidized to **3f**. Confirmation was given from the reaction of **1g** and **2b** in toluene at room temperature, by isolating compound **4i** which, in anisole at reflux, afforded **5i** besides its aromatic counterpart **3f**.

As shown, the electrocyclization of the azatriene systems **4** appears a good method to synthesize the pyridine ring but suffers from the fact that only electron-poor alkynes reacted quite easily with compounds **1**. Reaction with phenylacetylene, 2-butyn-1,4-diol and other electron-rich alkynes gave only intractable tars. This limitation could be overcome starting from amidines like **1h** incorporating in their backbone the 1-aza 1,3-hexadien-5-yne system, which could be obtained according to a known procedure from 3-amino-4-aryl-isothiazole 1,1-dioxides **6a**.[3] Pyridine **3i** was obtained heating **1h** in polyphosphoric acid at 100°C for 3 h (Scheme 5), according to a literature method.[8]

Conclusion

By this method a large number of nicotinic acid derivatives can be easily synthesized. The synthetic usefulness of this new method rests upon the possibility of synthesizing tri-, tetra- or penta-substituted pyridines by the opportune choice of the C-3 substituent on the propenamidines and of the acetylenic substrate used as the reactive partner. Furthermore, the simplicity of this procedure and the easy availability of the material used is also noteworthy.



Scheme 5.

Experimental

^{1}H NMR spectra were obtained in $CDCl_3$ as the solvent with Bruker AC 200, Bruker Avance 300 and Varian Gemini 200 instruments. Melting points were determined using a Buchi 510 (capillary) or an Electrothermal 9100 apparatus. IR spectra were recorded on a Jasco IR Report 100 spectrophotometer. Compounds **1a–h** have already been described.[3] Reagents **2a**,**b** are commercially available (Aldrich).

Synthesis of nicotinic derivatives 3a–h. General procedure

Compound **1** (1 mmol) was dissoved in anisole (4 mL) and a solution of **2** (1 mmol) in anisole (1 mL) was added dropwise under stirring at room temperature. The reaction mixture was then refluxed and the end of the reaction checked by TLC (AcOEt/cyclohexane 1:1 or CH_2Cl_2/MeOH 10:1). The solvent was evaporated at reduced pressure affording an oil which was purified by column chromatography on silica gel (eluent: AcOEt/cyclohexane 0:100 to 100:0) and crystallized with the solvent indicated affording compound **3**.

Synthesis of 4a,b,d,e,g. General procedure

Compounds **1** and **2** (1 mmol each) were dissolved in toluene (5 mL) and stirred at room temperature. The end of the reaction was checked by TLC (AcOEt/cyclohexane 1:1 or CH_2Cl_2/MeOH 10:1). The solvent was evaporated at reduced pressure affording a yellow oil which was purified by column chromatography on silica gel (eluent: AcOEt/cyclohexane 0:100 to 100:0) affording compound **4** besides a minor amount of **3**.

6-Diethylamino-4-methoxy-5-(4-methoxyphenyl)nicotinic acid methyl ester 3a. Yield 36%. Mp 88–89°C (white crystals from CH_2Cl_2/pentane). IR (nujol) 1700 cm^{-1} (C═O); ^{1}H NMR 0.92 (t, 6H, CH_3, J=7 Hz); 3.18 (q, 4H, CH_2, J=7 Hz); 3.39 (s, 3H, OCH_3); 3.85 (s, 3H, OCH_3); 3.88 (s, 3H, OCH_3); 6.93 (d, 2H, aryl-H, J=9 Hz); 7.76 (d, 2H, aryl-H, J=9 Hz); 8.72 (s, 1H, H-2). Calcd for $C_{19}H_{24}N_2O_4$ (344.41) C, 66.26, H, 7.02, N, 8.13; found C, 66.52, H, 6.94, N, 8.35.

6-Diethylamino-4-ethoxy-5-(4-methoxyphenyl)nicotinic acid methyl ester 3b. Yield 56%. Mp 94°C (white crystals from CH_2Cl_2/Et_2O). IR (nujol) 1700 cm^{-1} (C═O); ^{1}H NMR 0.88–0.97 (m, 9H, CH_3); 3.19 (q, 4H, CH_2, J=7 Hz); 3.55 (q, 2H, OCH_2, J=7 Hz); 3.84 (s, 3H, OCH_3); 3.86 (s, 3H, OCH_3); 6.92 (d, 2H, aryl-H, J=9 Hz); 7.26 (d, 2H, aryl-H, J=9 Hz); 8.72 (s, 1H, H-2). Calcd for $C_{20}H_{26}N_2O_4$ (358.44) C, 67.02, H, 7.31, N, 7.82; found C, 67.27, H, 7.35, N, 7.99.

6-Diethylamino-4-methoxy-5-(4-methoxyphenyl)pyridine-2,3-dicarboxylic acid dimethyl ester 3c. Yield 51%. Mp 120°C (white crystals from CH_2Cl_2/Et_2O). IR (nujol) 1700 cm^{-1} (C═O), 1720 cm^{-1} (C═O); ^{1}H NMR 0.92 (t, 6H, CH_3, J=7 Hz); 3.15 (q, 4H, CH_2, J=7 Hz); 3.31 (s, 3H, OCH_3); 3.85 (s, 3H, $COOCH_3$); 3.91 (s, 3H, $COOCH_3$); 3.93 (s, 3H, OCH_3); 6.94 (d, 2H, aryl-H, J=9 Hz); 7.29 (d, 2H, aryl-H, J=9 Hz). Calcd for $C_{21}H_{26}N_2O_6$ (402.45) C, 62.67, H, 6.51, N, 6.96; found C, 62.30, H, 6.80, N, 6.73.

6-Diethylamino-4-ethoxy-5-(4-methoxyphenyl)pyridine-2,3-dicarboxylic acid dimethyl ester 3d. Yield 41%. Pale yellow oil. IR (nujol) 1700 cm^{-1} (C═O), 1720 cm^{-1} (C═O); ^{1}H NMR 0.88–0.97 (m, 9H, CH_3); 3.14 (q, 4H, CH_2, J=7 Hz); 3.46 (q, 2H, OCH_2, J=7 Hz); 3.85 (s, 3H, OCH_3); 3.89 (s, 3H, OCH_3); 3.92 (s, 3H, OCH_3); 6.93 (d, 2H, aryl-H, J=9 Hz); 7.29 (d, 2H, aryl-H, J=9 Hz). Calcd for $C_{22}H_{28}N_2O_6$ (416.47) C, 63.45, H, 6.78, N, 6.73; found C, 63.10, H, 6.58, N, 6.50.

4-Cyano-6-diethylamino-5-(4-methoxyphenyl)pyridine-2,3-dicarboxylic acid dimethyl ester 3e. Yield 46%. Mp 110–111°C (white crystals from CH_2Cl_2/Et_2O). IR (nujol) 1700 cm^{-1} (C═O), 1720 cm^{-1} (C═O), 2240 cm^{-1} (CN); ^{1}H NMR 0.94 (t, 6H, CH_3, J=7 Hz); 3.23 (q, 4H, CH_2, J=7 Hz); 3.86 (s, 3H, OCH_3); 3.92 (s, 3H, OCH_3); 3.96 (s, 3H, OCH_3); 7.00 (d, 2H, aryl-H, J=9 Hz); 7.28 (d, 2H, aryl-H, J=9 Hz). Calcd for $C_{21}H_{23}N_3O_5$ (397.43), C, 63.47, H, 5.83, N, 10.57; found C, 63.17, H, 5.77, N, 10.66.

6-Diethylamino-5-(4-methoxyphenyl)-4-methylpyridine-2,3-dicarboxylic acid dimethyl ester 3f. Yield 36%. Mp 121–122°C (yellow crystals from CH_2Cl_2/Et_2O). IR (nujol) 1700 cm^{-1} (C═O), 1720 cm^{-1} (C═O); ^{1}H NMR 0.85 (t, 6H, CH_3, J=7 Hz); 2.02 (s, 3H, CH_3); 3.10 (q, 4H, CH_2, J=7 Hz); 3.86 (s, 3H, OCH_3); 3.90 (s, 3H, OCH_3); 3.94 (s, 3H, OCH_3); 6.96 (d, 2H, aryl-H, J=9 Hz); 7.10 (d, 2H, aryl-H, J=9 Hz). Calcd for $C_{21}H_{26}N_2O_5$ (386.40) C, 65.27, H, 6.78, N, 7.25; found C, 65.00, H, 6.56, N, 7.47.

6′-Diethylamino-5′-(4-methoxyphenyl)-[2,4′]bipyridinyl-2′,3′-dicarboxylic acid dimethyl ester 3g. Yield 51%. Mp 176–178°C (yellow crystals from CH_2Cl_2/Et_2O). IR (nujol) 1700 cm^{-1} (C═O), 1720 cm^{-1} (C═O); ^{1}H NMR 0.94 (t, 6H, CH_3, J7 Hz); 3.26 (q, 4H, CH_2, J7 Hz); 3.57 (s, 3H, OCH_3); 3.70 (s, 3H, OCH_3); 3.90 (s, 3H, OCH_3); 6.70 (d, 2H, aryl-H, J9 Hz); 7.00–7.15 (m, 3H, pyridyl-H); 7.52–7.58 (m, 1H, pyridyl-H); 7.90–8.00 (m, 1H, pyridyl-H); 8.55–8.65 (m, 1H, pyridyl-H). Calcd for $C_{25}H_{27}N_3O_5$ (449.51) C, 66.80, H, 6.05, N, 9.35; found C, 66.98, H, 6.25, N, 9.57.

6-Diethylamino-5-(4-methoxyphenyl)pyridine-2,3-dicarboxylic acid dimethyl ester 3h. Yield 53%. Mp 108–110°C (white crystals from CH_2Cl_2/Et_2O). IR (nujol) 1700 cm^{-1} (C═O), 1730 cm^{-1} (C═O); ^{1}H NMR 0.97 (t, 6H, CH_3, J7 Hz); 3.27 (q, 4H, CH_2, J7 Hz); 3.83 (s, 3H, $COOCH_3$); 3.84 (s, 3H, $COOCH_3$); 3.98 (s, 3H, OCH_3); 6.93 (d, 2H, aryl-H, J9 Hz); 7.29 (d, 2H, aryl-H, J9 Hz); 7.82 (s, 1H, H-4). Calcd for $C_{20}H_{24}N_2O_5$ (372.42) C, 64.50, H, 6.50, N, 7.52; found C, 64.23, H, 6.65, N, 7.40.

3-[1-Diethylamino-3,3-dimethoxy-2-(4-methoxyphenyl)-allylideneamino]acrylic acid methyl ester 4a. Yield 54%. IR (nujol) 1600–1620 cm^{-1} (C═N), (C═C); 1690 cm^{-1} (C═O); Mp 137–139°C (white crystals from CH_2Cl_2/Et_2O). ^{1}H NMR 0.87 (t, 3H, CH_3, J7 Hz); 1.16 (t, 3H, CH_3, J7 Hz); 3.10–3.35, 3.35–3.50, 3.80–3.95 (3m, 4H, CH_2); 3.60 (s, 3H, OCH_3); 3.63 (s, 3H, OCH_3); 3.74 (s, 3H, OCH_3); 3.79 (s, 3H, OCH_3); 5.63 (d, 1H, H-2, J=13);

6.84 (d, 2H, aryl-H, *J*9 Hz); 7.18 (d, 2H, aryl-H, *J*9 Hz); 8.09 (d, 1H, H-3, *J*=13). Calcd for $C_{20}H_{28}N_2O_5$ (376.45) C, 63.81, H, 7.50, N, 7.44; found C, 63.60, H, 7.60, N, 7.29.

3-[1-Diethylamino-3,3-diethoxy-2-(4-methoxyphenyl)-allylideneamino]acrylic acid methyl ester 4b. Yield 87%. Pale yellow oil. IR (nujol) 1600–1620 cm^{-1} (C═N), (C═C); 1690 cm^{-1} (C═O); ^1H NMR 0.84 (t, 3H, CH_3, *J*7 Hz); 1.10–1.13 (m, 9H, CH_3); 3.25 (q, 2H, CH_2, *J*7 Hz); 3.50–4.10 (m, 6H, CH_2); 3.61 (s, 3H, OCH_3); 3.67 (s, 3H, OCH_3); 5.60 (d, 1H, H-2, *J*=13); 6.81 (d, 2H, aryl-H, *J*9 Hz); 7.22 (d, 2H, aryl-H, *J*9 Hz); 8.07 (d, 1H, H-3, *J*=13). Calcd for $C_{22}H_{32}N_2O_5$ (404.51) C, 65.32, H, 7.97, N, 6.93; found C, 65.10, H, 7.69, N, 6.85.

2-[1-Diethylamino-3,3-diethoxy-2-(4-methoxyphenyl)-allylideneamino]but-2-enedioic acid dimethyl ester 4d (mixture of two inseparable isomers, 1:1 ratio). Yield 70%. Pale yellow oil. IR (nujol) 1600–1620 cm^{-1} (C═N), (C═C); 1690 cm^{-1} (C═O); 1710 cm^{-1} (C═O); ^1H NMR 0.80–0.95 (m, 6H, CH_3); 1.12-1.34 (m, 18H, CH_3); 3.18–3.35 (m, 4H, CH_2); 3.51–3.65 (m, 4H, CH_2); 3.48, 3.55, 3.60, 3.65, 3.77, 3.78 (6s, 18H, OCH_3); 5.22 (s, 1H, H-2); 5.72 (s, 1H, H-2); 6.77 (d, 2H, aryl-H, *J*9 Hz); 6.82 (d, 2H, aryl-H, *J*9 Hz); 7.31 (d, 4H, aryl-H). Calcd for $C_{24}H_{34}N_2O_7$ (462.54) C, 62.32, H, 7.41, N, 6.06; found C, 62.54, H, 7.20, N, 6.25.

2-[3-Cyano-1-diethylamino-3-methoxy-2-(4-methoxyphenyl)allylideneamino]but-2-enedioic acid dimethyl ester 4e (mixture of two inseparable isomers, 4:1 ratio). Yield 70%. Pale yellow oil. IR (nujol) 1600–1620 cm^{-1} (C═N), (C═C); 1690 cm^{-1} (C═O); 1710 cm^{-1} (C═O); 2240 cm^{-1}(CN); ^1H NMR 0.80–0.90, 1.10–1.40 (2m, 12H, CH_3); 3.25–3.88 (2m, 8H, CH_2); 3.44, 3.56, 3.60, 3.65, 3.79, 3.80, 3.85, 3.90 (8s, 24H, OCH_3); 5.80, 5.90 (2s, 2H, H-2); 6.85 (d, 2H, aryl-H, *J*9 Hz); 6.90 (d, 2H, aryl-H, *J*9 Hz); 7.33 (d, 2H, aryl-H, *J*9 Hz); 7.45 (d, 2H, aryl-H, *J*9 Hz). Calcd for $C_{22}H_{27}N_3O_6$ (429.47) C, 61.53, H, 6.34, N, 9.78; found C, 61.77, H, 6.13, N, 9.56.

2-[1-Diethylamino-3-methoxy-2-(4-methoxyphenyl)-3-pyridin-2-ylallylideneamino]but-2-enedioic acid dimethyl ester 4g (mixture of two isomers, 1:1 ratio). Yield 61%. Yellow oil. IR (nujol) 1600–1620 cm^{-1} (C═N), (C═C); 1700 cm^{-1} (C═O); 1710 cm^{-1} (C═O); ^1H NMR 0.76–1.59 (m, 12H, CH_3); 3.20–3.89 (m, 8H, CH_2); 3.42, 3.50, 3.58, 3.62, 3.65, 3.68, 3.70, 3.83 (8s, 24H, OCH_3); 5.46 (s, 1H, H-2); 5.86 (s, 1H, H-2); 6.52–6.65, 6.70–6.83, 7.10–7.26, 7.47–7.87 (4m, 12H, pyridyl-H+aryl-H); 8.55–8.65 (m, 1H); 8.70–8.80 (m, 1H). Calcd for $C_{26}H_{31}N_3O_6$ (481.55) C, 64.85, H, 6.49, N, 8.73; found C, 64.98, H, 6.40, N, 8.61.

Isolation of dihydronicotinic derivative 5i. 1g and **2b** were reacted in anisole at reflux and the reaction stopped after 2 h. A mixture of **3f**, **5i** and **4i** were obtained and purified by column chromatography on silica gel (eluent: AcOEt/cyclohexane 0:100 to 100:0).

6-Diethylamino-5-(4-methoxyphenyl)-4-methylpyridine-2,3-dicarboxylic acid dimethyl ester 3f. Yield 38%.

2-[1-Diethylamino-3-methyl-2-(4-methoxyphenyl)but-2-enylideneamino]but-2-enedioic acid dimethyl ester 4i (mixture of two isomers). Yield 30%. Yellow oil. IR (nujol) 1600–1620 cm^{-1} (C═N), (C═C); 1690 cm^{-1} (C═O); 1710 cm^{-1} (C═O); ^1H NMR 0.60–1.50 (m, 12H, CH_3); 1.74 (d, 3H, CH_3); 1.85 (d, 3H, CH_3); 3.26–3.40, 3.66–3.80 (2m, 8H, CH_2); 3.30, 3.34, 3.55, 3.58, 3.78 3.80 (6s, 18H, OCH_3); 5.81, 5.90 (2s, 2H, H-2); 6.05, 6.25 (2q, 2H, H-3′, *J*7 Hz); 6.70–6.85 (m, 4H, aryl-H); 7.15–7.30 (m, 4H, aryl-H). Calcd for $C_{21}H_{28}N_2O_5$ (388.46) C, 64.93, H, 7.27, N, 7.21; found C, 64.65, H, 7.32, N, 7.00.

6-Diethylamino-5-(4-methoxyphenyl)-4-methyl-3,4-dihydropyridine-2,3-dicarboxylic acid dimethyl ester 5i. Yield 30%. Mp 148°C (white crystals from CH_2Cl_2/Et_2O). IR (nujol) 1700 cm^{-1} (C═O); 1720 cm^{-1} (C═O); ^1H NMR 1.00–1.20 (m, 6H, CH_3); 1.25 (s, 3H, CH_3); 2.80–2.95 (m, 1H); 2.96–3.20 (m, 1H) 3.25–3.55 (m, 2H); 3.57 (s, 1H, H-3); 3.60, 3.76, 3.88 (3s, 9H, OCH_3); 3.70–3.85 (m, 1H, H-4); 6.82 (d, 2H, aryl-H, *J*9 Hz); 7.06 (d, 2H, aryl-H, *J*9 Hz). Calcd for $C_{21}H_{28}N_2O_5$ (388.46) C, 64.93, H, 7.27, N, 7.21; found C, 65.15, H, 7.30, N, 7.35.

Diethyl-[3-(4-methoxyphenyl)-6-phenylpyridin-2-yl]amine 3i. Compound **1h** (107 mg, 0.32 mmol) and polyphosphoric acid (1 mL) were heated at 100°C for 3 h. The reaction mixture was cooled at room temperature and neutralized with a 2N NaOH solution. The crude mixture was extracted with Et_2O, dried with Na_2SO_4 and the solvent evaporated under reduced pressure, yielding an oil which was crystallized with CH_2Cl_2/Et_2O. Mp 134–136°C. Yield 20% (white powder). ^1H NMR 1.03 (t, 6H, CH_3, *J*7 Hz); 3.24 (q, 4H, CH_2, *J*7 Hz); 3.86 (s, 3H, OCH_3); 6.96 (d, 2H, aryl-H, *J*9 Hz); 7.28–7.50 (m, 5H, aryl-H); 7.48 (d, 2H, aryl-H, *J*9 Hz); 8.06–8.12 (m, 2H, aryl-H). Calcd for $C_{21}H_{24}N_2O$ (332.45) C 79.48 H 7.28 N 8.43 found C 79.32 H 7.19 N 8.30.

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