# Cycloaddition Reactions of Neutral 2-Azadienes with Enamines − Regiospecific Synthesis of Highly Substituted Dihydropyridines and Pyridines

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The reaction between electronically neutral 2-azadienes and enamines affords isoquinolines, bicyclic pyridine derivatives, tetrasubstituted 1,2-dihydropyridines, and pyridines. Dimerization of heterodienes gives pentasubstituted 2,3-dihydropyridines and pyridines in a regioselective fashion.

Six-membered nitrogen heterocycles are among the most useful heterocycles and their utility has been widely demonstrated in the chemistry of natural products, in material sciences, and in pharmaceutical chemistry.[1] In particular, pyridine ring systems have received considerable attention not only because of their widespread occurrence in nature,[1] but also for their remarkable versatility in the synthesis of enantiopure organic compounds[2] and in coordination chemistry.[3] Because pyridine derivatives occupy a unique position in medicinal and preparative organic chemistry, many synthetic pathways to these compounds have been developed.[4,5] The development of strategies for the preparation of these heterocycles has two main approaches: either modification of a preformed pyridine nucleus, or formation through heterocycloaddition. In the latter strategy, 2-azabutadiene systems have proven to be efficient Diels−Alder partners for dienophiles.[6] In this process, the simultaneous creation of two new C−C bonds is complemented by the potential for regiocontrol in the newly formed six-membered ring, and highly substituted adducts may be obtained when polysubstituted reagents are used. However, general synthetic applications of these cycloadditions suffer from important limitations in the substitution patterns that may be accessed[7] and, as far as we know, this strategy has not to date been used for the preparation of the less easily available, highly substituted nonfunctionalized pyridines.

2-Azadienes substituted with strongly electron-donating groups are excellent reagents in *normal* Diels−Alder reactions.[6,8] Cycloaddition reactions of electron-poor azadienes with enamines have been described.[9,10] In the case of neutral 2-azadienes, however, although these substrates react with a wide range of dienophiles,[6c,11] reactions with enamines have been limited to 1,4-disubstituted azadienes, the process requiring very high temperatures[12] or Lewis acids as catalyst,[13] with very low reported yields.[12,13] In this context, we have been involved in the synthesis of neutral[11] and electron-poor azadienes[9] as well as in the preparation of nitrogen-heterocyclic compounds.[5a,5c,14] As a continuation of our work on the [4+2] cycloaddition chemistry of 2-azadienes, we aim here to explore a new and effective strategy for the preparation of pyridine derivatives through dimerization of electronically neutral 2-azadienes and their reaction with enamines.

## Results and Discussion

### The Reaction between 2-Azadienes and Enamines

The reaction between 2-azadienes **1**, easily prepared by aza Wittig treatment of *N*-vinylic phosphazenes and aldehydes,[11] with enamines has been explored, and here we report a general procedure for the preparation of pyridine derivatives, based on the cyclization of 2-azadiene **1** with an electron-rich olefin, such as an enamine, and subsequent aromatization. *N*-(Cyclohex-1-enyl)pyrrolidine (**2**, $n = 2$) reacted with azadienes **1** at 80 °C in $CHCl_3$, affording tetrahydroisoquinolines **6** in good yields (Scheme 1, Table 1, Entries 1−4). Formation of compounds **6** can be explained by [4+2] cycloaddition reaction between heterodienes **1** and enamine **2** to give adduct **4**, with subsequent loss of pyrrolidine and aromatization of products **5** under the reaction conditions resulting in tetrahydroisoquinolines **6**. An X-ray diffraction analysis was performed and confirmed the structure proposed for compound **6c** (Figure 1). A similar set of products was obtained under the same reaction conditions when *N*-(cyclopent-1-enyl)pyrrolidine **3** ($n = 1$) was treated with 3,4-diphenyl-1-(2-thienyl)-2-aza-1,3-butadiene (**1**), yielding bicyclic pyridine compounds **7** (Scheme 1, Table 1, Entry 5). It is noteworthy that cyclopentenopyridines constitute part of the skeleton of pyridine monoterpene alkaloids.[15] However, when 3-pyridyl-substituted azadienes **1** ($R^1$ = 3-pyr) were used and the reaction was performed in refluxing toluene, tricyclic pyridine **9** was also isolated, in addition to the expected cyclic products **7b** and **7c** (Scheme 1, Table 1, Entries 6 and 7). Formation of compound **9** can be explained by a [2+2+2] tandem cycloaddi-

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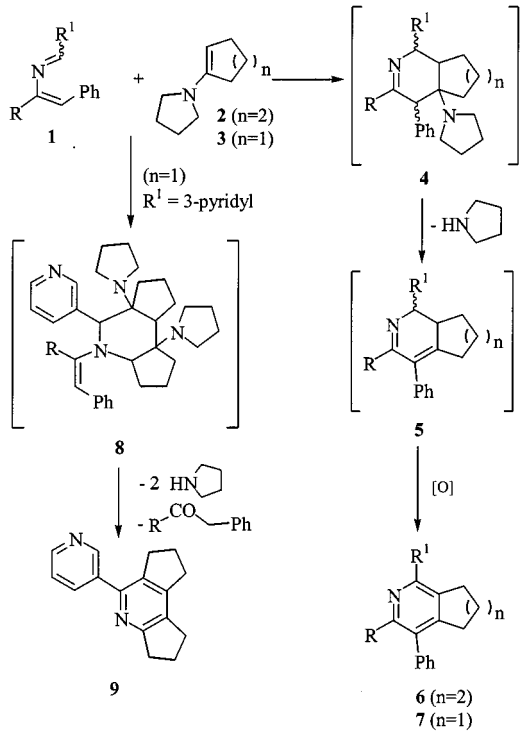



Scheme 1. Cycloaddition reactions between 2-azadienes and cyclic enamines

Table 1. Pyridine derivatives **6**, **7**, **9**, **12**, and **13** obtained

| Entry | Compd. | R | $R^1$ | Reaction conditions $T$ [°C] | $t$ [h] | Yield (%)[a] |
|---|---|---|---|---|---|---|
| 1 | **6a** | 2-thienyl | 3-pyridyl | 80 | 72 | 60 |
| 2 | **6b** | phenyl | 2-pyrrolyl | 80 | 152 | 72 |
| 3 | **6c** | phenyl | phenyl | 80 | 48 | 71 |
| 4 | **6d** | 2-furyl | phenyl | 80 | 72 | 55 |
| 5 | **7a** | phenyl | 2-thienyl | 80 | 55 | 48 |
| 6 | **7b** + **9** | phenyl | 3-pyridyl | 110 | 30 | 46/25[b] |
| 7 | **7c** + **9** | 2-furyl | 3-pyridyl | 110 | 16 | 49/25[b] |
| 8 | **12a** | phenyl | phenyl | 110/25 | 192/5[c] | 52/40[c] |
| 9 | **12b** | 2-furyl | phenyl | 110/25[c] | 42/24[c] | 60/54[c] |
| 10 | **13a** | phenyl | phenyl | 105 | 12 | 90[d] |
| 11 | **13b** | 2-furyl | phenyl | 105 | 12 | 94[e] |
| 12 | **13c** | 3-pyridyl | 3-pyridyl | 60 | 120 | 53 |
| 13 | **13d** | 2-thienyl | 2-thienyl | 110 | 144 | 38 |

[a] Yields are for isolated compounds. – [b] Yield of isolated compound **9**. – [c] Reaction was performed in the presence of lithium perchlorate/diethyl ether (LP-$Et_2O$). – [d] Obtained from **12a**. – [e] Obtained from **12b**.

tion reaction between 2-azadienes **1** and two molecules of enamine **3**.

Less nucleophilic enamines such as β-enamino ketones do not seem to be sufficiently electron-rich as dienophiles to participate in a [4+2] cycloaddition reaction with cyclic heterodienes such as 1,2,3-triazines.[16] However, acyclic 2-azadienes derived from β-amino acids even reacted with enamines such as β-enamino esters, resulting in the formation of dihydropyridine derivatives.[9a]

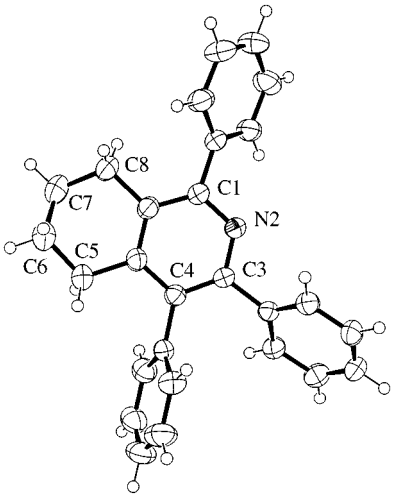
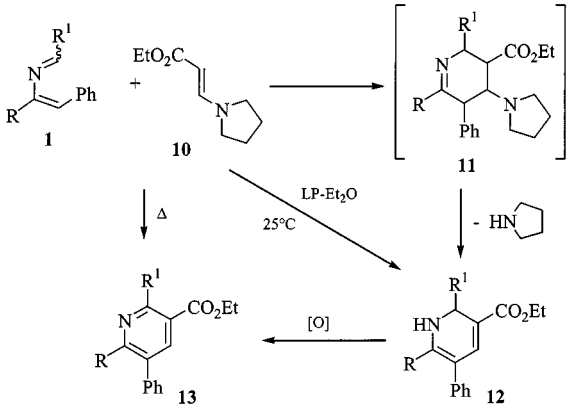



Figure 1. ORTEP view of isoquinoline **6c**

Treatment of electronically neutral 2-azadienes **1**, incorporating heterocyclic (3-pyridyl or 2-thienyl) substituents in the 1-positions, with β-enamino ester **10** at 110 °C, using toluene as solvent, afforded tetrasubstituted pyridines **13c** and **13d** (Scheme 2, Table 1, Entries 12 and 13) in a regioselective fashion. Formation of these compounds may be explained by [4+2] cycloaddition reactions between heterodienes **1** and enamine **10**, followed by aromatization of the 1,2-dihydropyridines **12** (Scheme 2). In fact, when 1-phenyl heterodienes **1** were used, it was possible to isolate these uncommon 1,2-dihydropyridines **12**. Thus, treatment of electronically neutral 1-phenyl-2-azadienes **1** ($R^1$ = Ph) with β-enamino ester **10** at 110 °C resulted in the formation of 1,2-dihydropyridines **12a** and **12b** (Scheme 2).




Scheme 2. Cycloaddition reactions between 2-azadienes and *trans*-pyrrolidineacrylate

Dihydropyridines **12** were also obtained under catalysis, when the reaction was performed in the presence of lithium perchlorate in a nonaqueous solvent such as diethyl ether (LP-$Et_2O$) at room temperature, similarly to previously reported processes,[9c] but with a lower yield (Table 1, Entries 8 and 9). Compounds **12** were characterized on the basis of their spectroscopic data, which indicated that they had been isolated as single regioisomers. Thus, in the $^1$H NMR spec-

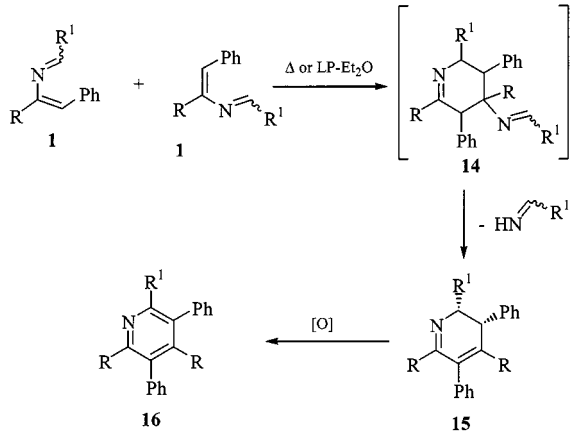
trum of **12a** (R = $R^1$ = phenyl), 4-H resonated as a singlet at $\delta_H$ = 7.70, while 2-H showed absorption at $\delta_H$ = 5.75 as a well-resolved doublet with a coupling constant of 4.2 Hz due to the influence of the proton bound to the nitrogen atom, and changing to a singlet when $D_2O$ was added. Compounds **12a** and **12b** underwent aromatization to give nicotine esters **13a** and **13b** (Scheme 2) on oxidation with *p*-benzoquinone (Table 1, Entries 10 and 11).

Dihydropyridines are important heterocycles in medicinal chemistry.[17,18] Among these compounds, derivatives containing the 1,2-dihydropyridine system without stabilizing electron-withdrawing groups on the ring are relatively rare and little information is available concerning their chemistry,[19] although they have been reported to be implicated in thermal rearrangements to give 2,3-dihydropyridines,[19f] and as pivotal intermediates in the biosynthesis of the indole alkaloids.[19h]

### Dimerization of Electronically Neutral 2-Azadienes 1

Dimerizations of electron-poor 2-azadienes derived from α-[20] and β-amino acids,[9b] in which one molecule acts as the dienophile and the other as a heterodiene, have been reported. In the case of 2-azadienes derived from α-amino acids[10e][20b−20d] without substitution in the 4-position, dimerization in the presence of Lewis acid (aluminium trichloride)[20a] resulted in adducts of regioselectivities different from those obtained when the process took place in the absence of catalyst. With 2-azadienes derived from β-amino acids (substitution in the 4-position), however, the same regioselectivity was observed irrespective of whether the reaction was thermal, or performed in the presence of lithium perchlorate (LP-$Et_2O$)[9b]. Therefore, while studying the [4+2] cycloaddition reactions of 2-azadienes, we also explored the dimerization reaction of these substrates, since they could also be considered to be functionalized enamines. In our case, when the dimerization of 2-azadienes **1** was performed (Scheme 3) in the presence of lithium perchlorate in a nonaqueous solvent such as diethyl ether (LP-$Et_2O$), similarly to the previously reported process,[9b] 2,3-dihydropyridines **15** (Table 2, Entries 1 and 2) or pyridines **16** (Table 2, Entry 4) were obtained in a regioselective fashion. Analogous selectivity was observed when the dimerization was performed at 160 °C without solvent, but in this case only the aromatic compounds **16** were obtained (Table 2, Entries 5 and 6). [Pyridine **16** was obtained not only when the (1*E*,3*Z*)-1-(5-methyl-2-furyl)-4-phenyl-3-(3-pyridyl)-2-azabuta-1,3-diene but also when the (1*Z*,3*Z*)-diene was used.]

Formation of compounds **15** and **16** can be interpreted in terms of a [4+2] cycloaddition in which one molecule acts as the dienophile and the other as heterodiene to afford the nonisolable tetrahydropyridines **14**, which then lose a molecule of imine under the reaction conditions to give dihydropyridines **15**. Compounds **16** may be formed by aromatization of derivatives **15**, and can also be obtained directly by treatment of compounds **15** with *p*-benzoquinone (Table 2, Entry 3).




Scheme 3. Dimerization reactions of 2-azadienes

Table 2. Compounds **15** and **16** obtained

| Entry | Comp. | R | $R^1$ | Reaction conditions $T$ [°C] | time [h] | Yield (%)[a] |
|---|---|---|---|---|---|---|
| 1 | **15a** | 2-thienyl | 3-pyridyl | 25[b] | 72 | 71 |
| 2 | **15b** | 2-thienyl | 2-thienyl | 25[b] | 48 | 45 |
| 3 | **16b** | 2-thienyl | 2-thienyl | 105 | 40 | 67[c] |
| 4 | **16c** | 2-furyl | phenyl | 25[b] | 96 | 54 |
| 5 | **16d** | 2-furyl | 3-pyridyl | 160 | 2 | 71 |
| 6 | **16e** | 3-pyridyl | 5-Me-2-furyl | 160[d][e] | 2[d]/4[e] | 60[d]/63[e] |

[a] Yields of isolated compounds purified by flash chromatography. − [b] Reaction was performed in the presence of LP-$Et_2O$. [c] Obtained by oxidation of **15b** with quinone. − [d] Obtained from (*E*,*Z*) isomer of 2-azadiene. − [e] Obtained from (*Z*,*Z*) isomer of 2-azadiene.

The structural assignments for compounds **15** and **16** were performed on the basis of their spectroscopic data and mass spectrometry. For instance, in **15a** (R = 2-thienyl, $R^1$ = 3-pyridyl) the protons at C-2 and C-3 showed doublet absorptions at δ = 5.57 and 4.26 ($^3J_{HH}$ = 1.6 Hz), results consistent with a *cis* configuration between the two protons. $^1$H NMR NOE experiments confirmed the structure of 2,3-dihydropyridine **15a**; at room temperature in $CDCl_3$, selective saturation at δ = 5.57 (2-H) afforded significant NOEs (9%) with the adjacent proton (3-H) and the pyridine-2-H proton (7%) (Figure 2), while selective saturation at δ = 4.26 (3-H) afforded significant NOEs (9%) on the adjacent proton (2-H), on the thienyl proton (14%), and on the phenyl group proton (15%). Aromatization of compound

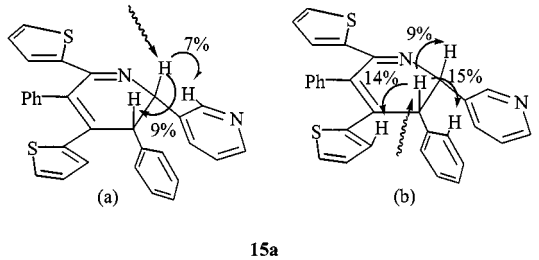



Figure 2. (a) Selective saturation of 2-H; (b) selective saturation of 3-H

**15b** (R = $R^1$ = 2-thienyl) with *p*-benzoquinone similarly resulted in symmetric compound **16b** (Table 2, Entry 3).

In summary, the heterodienes examined in our work all undergo efficient [4+2] cycloaddition with enamines, with a high degree of regiochemical control possible. The reaction provides a potentially useful route towards new tetrahydroisoquinolines and bicyclic pyridines, as well as towards highly substituted dihydropyridines and pyridines bearing a variety of aryl and heterocyclic substituents.

## Experimental Section

**General:** Melting points were determined with a Buchi SPM-20 apparatus and are uncorrected. − Analytical TLC was performed on 0.25 mm silica gel plates (Merck). Viewing was by exposure to UV light. − Solvents for extraction and chromatography were technical grade and were 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 prior to use: $CHCl_3$ and $CH_2Cl_2$ ($P_2O_5$), ethanol ($CH_3MgI$), toluene (Na). All reactions were performed in oven-dried (125 °C) or flame-dried glassware under dry $N_2$. − Column chromatography was carried out on silica gel (Merck, 70−230 mesh). − Mass spectra (EI) were obtained with a Hewlett Packard 5890 spectrometer, using an ionization voltage of 70 eV. Data are reported in the *m*/*z* form (intensity relative to base peak = 100). − Infrared (IR) spectra were recorded with a Nicolet IRFT Magna 550 spectrometer, either as neat liquids or as solids in NaCl. Absorptions are reported in $cm^{-1}$. − $^1H$ NMR spectra were recorded with a Varian 300 MHz spectrometer, using tetramethylsilane (δ = 0.00) as internal reference in $CDCl_3$ solution.$^{13}C$ NMR spectra were recorded at 75 MHz with chloroform (δ = 77.0) as an internal reference. $^{31}P$ NMR spectra were recorded at 120 MHz with 85% phosphoric acid as an external reference. Chemical shifts are given in ppm (δ). Coupling constants *J* are reported in Hertz. − Elemental analyses were determined with a Leco CHNS 932 instrument. − Crystallographic data (excluding structure factors) for structure **6c** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-152819. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail:deposit@ccdc.cam.ac.uk]. − 2-Azadienes **1** were prepared as described in the literature.[11a]

**General Procedure for [4+2] Cycloaddition Reactions between 2-Azadienes 1 and Cyclic Enamines 2 and 3:** Cyclic enamine (5 mmol) was added to a solution of 2-azadiene **1** (5 mmol) in $CHCl_3$ or toluene (10 mL), and the mixture was stirred at a suitable temperature (see Table 1) until TLC indicated the disappearance of the 2-azadiene. Evaporation of the solvent under reduced pressure afforded an oil that was chromatographed on silica gel to give compounds **6**, **7**.

**4-Phenyl-1-(3-pyridyl)-3-(2-thienyl)-5,6,7,8-tetrahydroisoquinoline (6a):** The general procedure was followed, using (1*E*,3*Z*)-4-phenyl-1-(3-pyridyl)-3-(2-thienyl)-2-azabuta-1,3-diene (1.45 g) and 1-(cyclohex-1-enyl)pyrrolidine (**2**, 0.75 g) in $CHCl_3$. Chromatographic separation (5:1, hexane/ethyl acetate) gave 1.10 g (60%) of **6a** as a white solid, m.p. 170−172 °C. − IR (KBr): $\tilde{\nu}$ = 1543 (C=N). − $^1H$ NMR ($CDCl_3$): δ = 1.71−1.73 (m, 4 H, $CH_2$), 2.41−2.43 (m, 2 H, $CH_2$), 2.80−2.82 (m, 2 H, $CH_2$), 6.27 (d, $^3J_{HH}$ = 3.9 Hz, 1 H, HC=), 6.73 (dd, $^3J_{HH}$ = 3.9 Hz, $^3J_{HH}$ = 5.1 Hz, 1 H, HC=), 7.17 (d, $^3J_{HH}$ = 5.1 Hz, 1 H, HC=), 7.22−7.54 (m, 6 H, aromatic H), 7.98−8.01 (m, 1 H, HC=), 8.64−8.66 (m, 1 H, HC=), 8.91 (d, $^4J_{HH}$ = 2.1 Hz, 1 H, HC=). − $^{13}C$ NMR ($CDCl_3$): δ = 22.4 ($CH_2$), 22.5 ($CH_2$), 28.1 ($CH_2$), 28.6 ($CH_2$), 123.0 (HC=), 127.1−129.5 (HC=), 132.9−153.9 (m, aromatic C). − MS (70 eV): *m*/*z* (%) = 368 (87) [$M^+$]. − $C_{24}H_{20}N_2S$ (368): calcd. C 78.23, H 5.47 N 7.60; found C 78.18, H 5.58, N 7.49.

**3,4-Diphenyl-1-(1*H*-2-pyrrolyl)-5,6,7,8-tetrahydroisoquinoline (6b):** The general procedure was followed, using a diastereomeric mixture [50:50, (1*E*,3*Z*)/(1*Z*,3*Z*)] of 3,4-diphenyl-1-(2-pyrrolyl)-2-azabuta-1,3-diene (1.36 g) and 1-(cyclohex-1-enyl)pyrrolidine (**2**, 0.75 g) in $CHCl_3$. Chromatographic separation (20:1, hexane/ethyl acetate) gave 1.26 g (72%) of **6b** as a white solid, m.p. 181−182 °C. − IR (KBr): $\tilde{\nu}$ = 3442 (NH), 1561 (C=N). − $^1H$ NMR ($CDCl_3$): δ = 1.69−1.85 (m, 2 H, $CH_2$), 1.86−1.94 (m, 2 H, $CH_2$), 2.50 (t, $^3J_{HH}$ = 6.4 Hz, 2 H, $CH_2$), 3.04 (t, $^3J_{HH}$ = 6.4 Hz, 2 H, $CH_2$), 6.34−6.37 (m, 1 H, HC=), 6.73−6.76 (m, 1 H, HC=), 6.92−6.95 (m, 1 H, HC=), 7.07−7.31 (m, 10 H, aromatic H), 10.13 (s, 1 H, NH). − $^{13}C$ NMR ($CDCl_3$): δ = 22.3 ($CH_2$), 22.7 ($CH_2$), 27.9 ($CH_2$), 29.4 ($CH_2$), 110.0 (HC=), 110.8 (HC=), 118.9−152.9 (m, aromatic C). − MS (70 eV): *m*/*z* (%) = 350 (100) [$M^+$]. − $C_{25}H_{22}N_2$ (350): calcd. C 85.68, H 6.33 N 7.99; found C 85.78, H 6.38, N 7.99.

**1,3,4-Triphenyl-5,6,7,8-tetrahydroisoquinoline (6c):** The general procedure was followed, using a diastereomeric mixture [40:60, (1*E*,3*Z*)/(1*Z*,3*Z*)] of 1,3,4-triphenyl-2-azabuta-1,3-diene (1.42 g) and 1-(cyclohex-1-enyl)pyrrolidine (**2**, 0.75 g) in $CHCl_3$. Chromatographic separation (20:1, hexane/ethyl acetate) gave 1.28 g (71%) of **6c** as a white solid, m.p. 162−163 °C. − IR (KBr): $\tilde{\nu}$ = 1550 (C=N). − $^1H$ NMR ($CDCl_3$): δ = 1.65−1.67 (m, 4 H, $CH_2$), 2.42−2.47 (m, 2 H, $CH_2$), 2.69−2.72 (m, 2 H, $CH_2$), 7.02−7.55 (m, 15 H, aromatic H). − $^{13}C$ NMR ($CDCl_3$): δ = 22.4 ($CH_2$), 22.5 ($CH_2$), 28.1 ($CH_2$), 28.7 ($CH_2$), 126.8−157.9 (m, aromatic C). − MS (70 eV): *m*/*z* (%) = 361 (100) [$M^+$]. − $C_{27}H_{23}N$ (361): calcd. C 89.71, H 6.41, N 3.87; found C 89.31, H 6.22, N 3.85.

**3-(2-Furyl)-1,4-diphenyl-5,6,7,8-tetrahydroisoquinoline (6d):** The general procedure was followed, using (1*E*,3*Z*)-3-(2-furyl)-1,4-diphenyl-2-azabuta-1,3-diene (1.43 g) and 1-(cyclohex-1-enyl)pyrrolidine (**2**, 0.75 g) in $CHCl_3$. Chromatographic separation (20:1, hexane/ethyl acetate) gave 0.97 g (55%) of **6d** as a white solid, m.p. 177−178 °C. − IR (KBr): $\tilde{\nu}$ = 1561 (C=N). − $^1H$ NMR ($CDCl_3$): δ = 1.51−1.57 (m, 4 H, $CH_2$), 2.42 (t, $^3J_{HH}$ = 6.4 Hz, 2 H, $CH_2$), 2.72 (t, $^3J_{HH}$ = 6.4 Hz, 2 H, $CH_2$), 5.47 (d, $^3J_{HH}$ = 3.5 Hz, 1 H, CH=) 6.15−6.16 (m, 1 H, HC=), 7.20−7.61 (m, 11 H, aromatic H). − $^{13}C$ NMR ($CDCl_3$): δ = 22.4 ($CH_2$), 22.6 ($CH_2$), 28.2 ($CH_2$), 28.6 ($CH_2$), 110.8 (HC=), 111.3 (HC=), 127.5−157.3 (m, aromatic C). − MS (70 eV): *m*/*z* (%) = 351 (100) [$M^+$]. − $C_{25}H_{21}NO$ (351): calcd. C 85.44, H 6.02, N 3.99; found C 85.31, H 5.98, N 3.76.

**2,3-Diphenyl-4,5-trimethylene-6-(2-thienyl)pyridine (7a):** The general procedure was followed, using a diastereomeric mixture [40:60, (1*E*,3*Z*)/(1*Z*,3*Z*)] of 3,4-diphenyl-1-(2-thienyl)-2-azabuta-1,3-diene (1.45 g) and 1-(cyclopent-1-enyl)pyrrolidine (**3**, 0.67 g) in $CHCl_3$. Chromatographic separation (10:1, hexane/ethyl acetate) gave 0.85 g (48%) of **7a** as a brown solid, m.p. 161−162 °C. − IR (KBr): $\tilde{\nu}$ = 1555 (C=N). − $^1H$ NMR ($CDCl_3$): δ = 2.11−2.31 (m, 2 H, $CH_2$), 2.84 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, $CH_2$), 3.29 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, $CH_2$), 7.12−7.65 (m, 13 H, aromatic H). − $^{13}C$ NMR ($CDCl_3$): δ = 24.9 ($CH_2$), 32.9 ($CH_2$), 33.1 ($CH_2$), 123.7−155.2 (m, aromatic C). − MS (70 eV): *m*/*z* (%) = 353 (64) [$M^+$]. − $C_{24}H_{19}NS$ (353): calcd. C 81.55, H 5.42, N 3.96; found C 81.39, H 5.48, N 3.99.

**2,3-Diphenyl-4,5-trimethylene-6-(3-pyridyl)pyridine (7b) and Bis(2,3:4,5-trimethylene)-6-(3-pyridyl)pyridine (9):** The general procedure was followed, using a diastereomeric mixture [50:50, (1*E*,3*Z*)/(1*Z*,3*Z*)] of 3,4-diphenyl-1-(3-pyridyl)-2-azabuta-1,3-diene (1.42 g) and 1-cyclopent-1-enylpyrrolidine (**3**, 0.67 g) in toluene. Separation and purification by column chromatography (10:1, hexane/ethyl acetate) gave 0.80 g (46%) of **7b** along with 0.29 g (25%) of **9**.

**Compound 7b:** White solid, m.p. 121−122 °C. − IR (KBr): $\tilde{\nu}$ = 1546 (C=N). − $^1$H NMR ($CDCl_3$): δ = 2.08−2.16 (m, 2 H, $CH_2$), 2.87 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, $CH_2$), 3.29 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, $CH_2$), 7.14−7.44 (m, 11 H, aromatic H), 8.24−8.29 (m, 1 H, HC=), 8.63 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, HC=), 9.13 (dd, $^4J_{HH}$ = 2.1 Hz, $^5J_{HH}$ = 0.6 Hz, 1 H, HC=). − $^{13}$C NMR ($CDCl_3$): δ = 25.8 ($CH_2$), 32.9 ($CH_2$), 33.1 ($CH_2$), 123.2−140.2 (m, aromatic C), 149.1 (C=N), 149.3 (HC=), 149.6 (HC=), 155.4 (C=N). − MS (70 eV): *m*/*z* (%) = 348 (90) [$M^+$]. − $C_{25}H_{20}N_2$ (348): calcd. C 86.17, H 5.79, N 8.04; found C 86.84, H 6.05, N 8.22.

**Compound 9:** White solid, m.p. 104−105 °C. − IR (KBr): $\tilde{\nu}$ = 1580 (C=N). − $^1$H NMR ($CDCl_3$): δ = 2.06−2.16 (m, 4 H, $CH_2$), 2.79 (t, $^3J_{HH}$ = 7.2 Hz, 4 H, $CH_2$), 3.05 (t, $^3J_{HH}$ = 7.2 Hz, 4 H, $CH_2$), 7.27−7.39 (m, 1 H, HC=), 7.64−7.68 (m, 1 H, HC=), 8.61−8.64 (m, 2 H, HC=). − $^{13}$C NMR ($CDCl_3$): δ = 23.6 ($CH_2$), 29.9 ($CH_2$), 34.3 ($CH_2$), 123.2 (HC=), 132.3−138.8 (m, aromatic C), 148.9 (HC=), 149.2 (HC=), 164.5 (C=N). − MS (70 eV): *m*/*z* (%) = 236 (100) [$M^+$]. − $C_{16}H_{16}N_2$ (236): calcd. C 81.32, H 6.82, N 11.85; found C 81.39, H 6.88, N 11.84.

**2-(2-Furyl)-4,5-trimethylene-3-phenyl-6-(3-pyridyl)pyridine (7c) and Bis(2,3:4,5-trimethylene)-6-(3-pyridyl)pyridine (9):** The general procedure was followed, using (1*E*,3*Z*)-3-(2-furyl)-4-phenyl-1-(3-pyridyl)-2-azabuta-1,3-diene (1.37 g) and 1-cyclopent-1-enylpyrrolidine (**3**, 0.67 g) in toluene. Separation and purification by column chromatography (10:1, hexane/ethyl acetate) gave 0.83 g (49%) of **7c** along with 0.29 g (25%) of **9**.

**Compound 7c:** White solid, m.p. 114−115 °C. − IR (KBr): $\tilde{\nu}$ = 1554 (C=N). − $^1$H NMR ($CDCl_3$): δ = 2.04−2.14 (m, 2 H, $CH_2$), 2.74 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, $CH_2$), 3.20 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, $CH_2$), 5.83 (dd, $^3J_{HH}$ = 3.3 Hz, $^4J_{HH}$ = 0.6 Hz, 1 H, HC=), 6.23 (dd, $^3J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 2.1 Hz, 1 H, HC=), 7.17−7.49 (m, 7 H, aromatic H), 8.24−8.28 (m, 1 H, HC=), 8.64 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, HC=), 9.09 (d, $^4J_{HH}$ = 1.5 Hz, 1 H, HC=). − $^{13}$C NMR ($CDCl_3$): δ = 25.3 ($CH_2$), 32.7 ($CH_2$), 32.8 ($CH_2$), 111.1 (HC=), 111.7 (HC=), 123.0−149.3 (m, aromatic C), 151.3 (HC=), 155.6 (C=N). − MS (70 eV): *m*/*z* (%) = 338 (100) [$M^+$]. − $C_{23}H_{18}N_2O$ (338): calcd. C 81.63, H 5.36, N 8.28; found C 81.69, H 5.38, N 8.29.

**Compound 9:** Spectroscopic data described under the previous compound **7b**.

**General Procedure A for [4+2] Cycloaddition Reactions between 2-Azadienes 1 and β-Enamino Ester 10:** $LiClO_4$ (5.32 g, 0.050 mol) and ethyl *trans*-3-pyrrolidin-1-ylacrylate (0.85 g, 5 mmol) were added to a solution of 2-azadiene **1** (5 mmol) in $Et_2O$ (10 mL). The mixture was stirred at room temperature until TLC indicated the disappearance of 2-azadiene. The reaction mixture was poured into $CH_2Cl_2$ (20 mL), washed with a saturated solution of $NaHCO_3$, extracted with $CH_2Cl_2$ (3 × 20 mL), and dried ($MgSO_4$). Removal of solvent under vacuum afforded an oil that was chromatographed on silica gel to give compounds **12**.

**General Procedure B for [4+2] Cycloaddition Reactions between 2-Azadienes 1 and β-Enamino Ester 10:** Ethyl *trans*-3-pyrrolidin-1-ylacrylate (0.85 g, 5 mmol) was added to a solution of 2-azadiene **1** (5 mmol) in $CHCl_3$ or toluene (10 mL), and the mixture was stirred at the required temperature (see Table 1) until TLC indicated the disappearance of 2-azadiene. Removal of solvent under vacuum afforded an oil that was chromatographed on silica gel to give compounds **12** and **13**.

**Ethyl 1,2-Dihydro-2,5,6-triphenylpyridine-3-carboxylate (12a):** General procedure A was followed, using a diastereomeric mixture [40:60, (1*E*,3*Z*)/(1*Z*,3*Z*)] of 1,3,4-triphenyl-2-azabuta-1,3-diene (1.42 g), with a 5 h reaction time. Chromatographic separation (20:1, hexane/ethyl acetate) afforded 0.57 g (30%) of **12a**. Following general procedure B, the same azadiene was used, with toluene as solvent. Chromatographic separation (20:1, hexane/ethyl acetate) gave 0.99 g (52%) of **12a** as an orange oil, $R_f$ = 0.40 (1:2, ethyl acetate/hexane). − IR (KBr): $\tilde{\nu}$ = 3335 (NH), 1685 (COO), 1214 (C−O). − $^1$H NMR ($CDCl_3$): δ = 1.25 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, $CH_3$), 4.12−4.19 (m, 2 H, $OCH_2$), 5.00 (d, $^3J_{HH}$ = 4.2 Hz, 1 H, NH), 5.75 (d, $^3J_{HH}$ = 4.2 Hz, 1 H, CH), 7.00−7.69 (m, 15 H, aromatic H), 7.70 (s, 1 H, HC=). − $^{13}$C NMR ($CDCl_3$): δ = 14.4 ($CH_3$), 54.3 (CH), 60.0 ($OCH_2$), 108.5−146.4 (m, aromatic C, C=C and HC=), 166.5 (COO). − MS (70 eV): *m*/*z* (%) = 381 (28) [$M^+$]. − $C_{26}H_{23}NO_2$ (381): calcd. C 81.86, H 6.08, N 3.67; found C 81.45, H 5.94, N 3.58.

**Ethyl 6-(2-Furyl)-1,2-dihydro-2,5-diphenylpyridine-3-carboxylate (12b):** General procedure A was followed, using (1*E*,3*Z*)-3-(2-furyl)-1,4-diphenyl-2-azabuta-1,3-diene (1.43 g), with a reaction time of 24 h. Chromatographic separation (15:1, hexane/ethyl acetate) gave 1.00 g (54%) of **12b**. Following general procedure B, the same azadiene was used, with toluene as solvent. Chromatographic separation (15:1, hexane/ethyl acetate) gave 1.11 g (60%) of **12b** as an orange oil, $R_f$ = 0.12 (1:2, ethyl acetate/hexane). − IR (KBr): $\tilde{\nu}$ = 3429 (NH), 1722 (COO), 1253 (C−O). − $^1$H NMR ($CDCl_3$): δ = 1.26 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, $CH_3$), 4.10−4.50 (m, 2 H, $OCH_2$), 5.55 (d, $^3J_{HH}$ = 4.0 Hz, 1 H, NH), 5.74−5.78 (m, 2 H, CH and HC=), 6.24 (dd, $^3J_{HH}$ = 4.0 Hz, $^3J_{HH}$ = 1.8 Hz, 1 H, HC=), 7.10−7.67 (m, 12 H, aromatic H and HC=). − $^{13}$C NMR ($CDCl_3$): δ = 13.7 ($CH_3$), 52.9 (CH), 61.4 ($OCH_2$), 111.5 (HC=), 113.7 (HC=), 126.2−147.9 (m, aromatic C, C=C and HC=), 166.4 (COO). − MS (70 eV): *m*/*z* (%) = 371 (60) [$M^+$]. − $C_{24}H_{21}NO_3$ (371): calcd. C 77.61, H 5.70, N 3.77; found C 77.05, H 5.64, N 3.82.

**Ethyl 5-Phenyl-2,6-bis(3-pyridyl)nicotinate (13c):** General procedure B was followed, using a diastereomeric mixture [40:60, (1*E*,3*Z*)/(1*Z*,3*Z*)] of 4-phenyl-1,3-bis(3-pyridyl)-2-azabuta-1,3-diene (1.45 g) in $CHCl_3$. Chromatographic separation (2:1, hexane/ethyl acetate) gave 1.01 g (53%) of **13c** as a yellow solid, m.p. 120−121 °C. − IR (KBr): $\tilde{\nu}$ = 1721 (COO), 1583 (C=N), 1257 (C−O). − $^1$H NMR ($CDCl_3$): δ = 1.15 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, $CH_3$), 4.25 (q, $^3J_{HH}$ = 7.2 Hz, 2 H, $OCH_2$), 7.18−8.04 (m, 9 H, aromatic H), 8.29 (s, 1 H, HC=), 8.51−8.53 (m, 1 H, HC=), 8.67−8.74 (m, 2 H, HC=), 8.85−8.86 (m, 1 H, HC=). − $^{13}$C NMR ($CDCl_3$): δ = 13.8 ($CH_3$), 61.8 ($OCH_2$), 122.8−141.1 (m, aromatic C), 148.8−159.5 (m, aromatic C), 166.8 (COO). − MS (70 eV): *m*/*z* (%) = 381 (39) [$M^+$]. − $C_{24}H_{19}N_3O_2$ (381): calcd. C 75.57, H 5.02, N 11.02; found C 75.68, H 5.21, N 10.91.

**Ethyl 5-Phenyl-2,6-bis(2-thienyl)nicotinate (13d)**: General procedure B was followed, using a diastereomeric mixture [40:60, (1*E*,3*Z*)/(1*Z*,3*Z*)] of 4-phenyl-1,3-bis(2-thienyl)-2-azabuta-1,3-diene (1.47 g) in toluene. Chromatographic separation (20:1, hexane/ethyl acetate) gave 0.39 g (20%) of **13d** as a yellow solid, m.p. 104−106 °C. − IR (KBr): $\tilde{\nu}$ = 1721 (COO), 1228 (C−O). − $^1$H NMR ($CDCl_3$): δ =

1.31 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, $CH_3$), 4.36 (q, $^3J_{HH}$ = 7.2 Hz, 2 H, $OCH_2$), 6.67 (dd, $^3J_{HH}$ = 3.8 Hz, $^4J_{HH}$ = 1.0 Hz, 1 H, HC=), 6.81 (dd, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 4.0 Hz, 1 H, HC=), 7.10 (dd, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 3.8 Hz, 1 H, HC=) 7.25−7.53 (m, 8 H, aromatic H), 7.84 (s, 1 H, HC=). − $^{13}$C NMR ($CDCl_3$): δ = 14.0 ($CH_3$), 61.8 ($OCH_2$), 122.5−150.7 (m, aromatic C), 167.9 (COO). − MS (70 eV): *m*/*z* (%) = 391 (64) [$M^+$]. − $C_{22}H_{17}N_2O_2S_2$ (391): calcd. C 67.49, H 4.38, N 3.58; found C 67.55, H 4.63, N 3.99.

**General Procedure for Aromatization of Compounds 12:** *p*-Benzoquinone (0.216 g, 2 mmol) was added to a solution of compound **12** (2 mmol) in dioxane (5 mL), and the mixture was stirred at 105 °C for 12 h. The solvent was evaporated under reduced pressure, and the resulting oil was purified by silica gel column chromatography.

**Ethyl 2,5,6-Triphenylnicotinate (13a):** Treatment of compound **12a** (0.76 g) according to the general procedure and subsequent chromatographic separation (15:1, hexane/ethyl acetate) afforded 0.68 g (90%) of **13a** as a pale yellow solid, m.p. 124−125 °C. − IR (KBr): ν̃ = 1732 (COO), 1246 (C−O). − $^1$H NMR ($CDCl_3$): δ = 1.09 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, $CH_3$), 4.20 (q, $^3J_{HH}$ = 7.2 Hz, 2 H, $OCH_2$), 7.21−7.69 (m, 15 H, aromatic H), 8.14 (s, 1 H, HC=). − $^{13}$C NMR ($CDCl_3$): δ = 13.7 ($CH_3$), 61.5 ($OCH_2$), 125.4−141.6 (m, aromatic C), 156.3 (C=N), 158.2 (C=N), 168.1 (COO). − MS (70 eV): *m*/*z* (%) = 379 (73) [$M^+$]. − $C_{26}H_{21}NO_2$ (379): calcd. C 82.30, H 5.58, N 3.69; found C 82.95, H 5.63, N 3.72.

**Ethyl 6-(2-Furyl)-2,5-diphenylnicotinate (13b):** Treatment of compound **12b** (0.74 g) according to the general procedure and subsequent chromatographic separation (2:1, hexane/ethyl acetate) afforded 0.69 g (94%) of **13b** as a yellow solid, m.p. 117−118 °C. − IR (KBr): ν̃ = 1722 (COO), 1253 (C−O). − $^1$H NMR ($CDCl_3$): δ = 1.13 (t, $^3J_{HH}$= 7.2 Hz, 3 H, $CH_3$), 4.18 (q, $^3J_{HH}$ = 7.2 Hz, 2 H, $OCH_2$), 6.28−6.33 (m, 2 H, HC=), 7.34−7.67 (m, 11 H, aromatic H), 8.03 (s, 1 H, HC=). − $^{13}$C NMR ($CDCl_3$): δ = 13.7 ($CH_3$), 61.4 ($OCH_2$), 111.5 (HC=), 113.7 (HC=), 124.5−147.7 (m, aromatic C), 152.0 (C=N), 157.5 (C=N), 167.7 (COO). − MS (70 eV): *m*/*z* (%) = 369 (100) [$M^+$]. − $C_{24}H_{19}NO_3$ (369): calcd. C 78.03, H 5.18, N 3.79; found C 77.95, H 5.24, N 3.82.

**General Procedure A for Dimerization of Compounds 1:** $LiClO_4$ (5.32 g, 0.050 mol) was added to a solution of 2-azadiene **1** (5 mmol) in $Et_2O$ (10 mL) and the mixture was stirred at room temperature until TLC indicated the disappearance of 2-azadiene. The reaction mixture was poured into $CH_2Cl_2$ (20 mL), washed with a saturated solution of $NaHCO_3$, and dried ($MgSO_4$). Removal of solvent under reduced pressure afforded an oil that was chromatographed on silica gel to give compounds **15** or **16**.

**General Procedure B for Dimerization of Compounds 1:** 2-Azadiene **1** (5 mmol) was stirred at 160 °C without solvent until TLC indicated its disappearance. The crude product from the reaction was chromatographed on silica gel to give compounds **16**.

**2,3-Dihydro-3,5-diphenyl-2-(3-pyridyl)-4,6-bis(2-thienyl)pyridine (15a):** General procedure A was followed, using (1*E*,3*Z*)-4-phenyl-1-(3-pyridyl)-3-(2-thienyl)-2-azabuta-1,3-diene (1.45 g), with a reaction time of 72 h. Chromatographic separation (2:1, hexane/ethyl acetate) gave 0.84 g (71%) of **15a** as a pale yellow solid, m.p. 186−188 °C. − IR (KBr): ν̃ = 1537 (C=N). − $^1$H NMR ($CDCl_3$): δ = 4.26 (d, $^3J_{HH}$ = 1.6 Hz, 1 H, CH), 5.57 (d, $^3J_{HH}$ = 1.6 Hz, 1 H, CH), 6.29 (d, $^3J_{HH}$ = 3.6 Hz, 1 H, HC=), 6.67−6.75 (m, 3 H, HC=), 7.05 (d, $^3J_{HH}$ = 5.0 Hz, 1 H, HC=), 7.21−7.76 (m, 13 H, aromatic H), 8.52 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.7 Hz, 1 H, HC=), 8.77 (d, $^3J_{HH}$ = 2.3 Hz, 1 H, HC=). − $^{13}$C NMR ($CDCl_3$): δ = 50.0 (CH), 64.9 (CH), 123.5−144.4 (m, C=C and aromatic C), 148.8 (HC=), 149.1 (HC=), 160.5 (C=N). − MS (70 eV): *m*/*z* (%) = 474 (100) [$M^+$]. − $C_{30}H_{22}N_2S_2$ (474): calcd. C 75.91, H 4.67, N 5.90; found C 75.95, H 4.64, N 5.92.

**2,3-Dihydro-3,5-diphenyl-2,4,6-tris(2-thienyl)pyridine (15b):** General procedure A was followed, using a diastereomeric mixture [40:60, (1*E*,3*Z*)/(1*Z*,3*Z*)] of 4-phenyl-1,3-bis(2-thienyl)-2-azabuta-1,3-diene (1.47 g), with a reaction time of 48 h. Chromatographic separation (10:1, hexane/ethyl acetate) gave 0.54 g (45%) of **15b** as a brown solid, m.p. 167−168 °C. − IR (KBr): ν̃ = 1595 (C=N). − $^1$H NMR ($CDCl_3$): δ = 4.36 (d, $^3J_{HH}$ = 1.6 Hz, 1 H, CH), 5.73 (d, $^3J_{HH}$ = 1.6 Hz, 1 H, CH), 6.30 (d, $^3J_{HH}$ = 3.6 Hz, 1 H, HC=), 6.67−7.51 (m, 18 H, aromatic H). − $^{13}$C NMR ($CDCl_3$): δ = 50.4 (CH), 63.0 (CH), 124.3−144.4 (m, C=C and aromatic C), 158.6 (C=N). − MS (70 eV): *m*/*z* (%) = 479 (40) [$M^+$]. − $C_{29}H_{21}NS_3$ (479): calcd. C 72.61, H 4.41, N 2.92; found C 72.75, H 4.40, N 2.94.

**3,5-Diphenyl-2,4,6-tris(2-thienyl)pyridine (16b):** *p*-Benzoquinone (0.216 g, 2 mmol) was added to a solution of compound **15b** (0.96 g, 2 mmol) in dioxane (5 mL), and the mixture was stirred at 105 °C for 40 h. The solvent was evaporated under reduced pressure, and the resulting oil was purified by silica gel column chromatography (10:1, hexane/ethyl acetate) to give 0.64 g (67%) of **16b** as a white solid, m.p. 187−188 °C. − IR (KBr): ν̃ = 1608 (C=N). − $^1$H NMR ($CDCl_3$): δ = 6.28−6.35 (m, 3 H, HC=), 6.52−6.55 (m, 1 H, HC=), 6.75−6.78 (m, 2 H, HC=), 6.93−6.95 (m, 1 H, HC=), 7.14−7.28 (m, 12 H, aromatic H). − $^{13}$C NMR ($CDCl_3$): δ = 125.7−130.3 (m, aromatic C), 132.1−148.2 (m, aromatic C). − MS (70 eV): *m*/*z* (%) = 477 (20) [$M^+$]. − $C_{29}H_{19}NS_3$ (477): calcd. C 72.92, H 4.01, N 2.93; found C 72.95, H 4.14, N 2.92.

**2,4-Bis(2-furyl)-3,5,6-triphenylpyridine (16c):** General procedure A was followed, using (1*E*,3*Z*)-3-(2-furyl)-1,4-diphenyl-2-azabuta-1,3-diene (1.43 g), with a reaction time of 96 h. Chromatographic separation (5:1, hexane/ethyl acetate) gave 0.59 g (54%) of **16c** as a brown solid, m.p. 196−197 °C. − IR (KBr): ν̃ = 1538 (C=N). − $^1$H NMR ($CDCl_3$): δ = 5.64 (d, $^3J_{HH}$ = 3.3 Hz, 1 H, HC=), 5.71 (d, $^3J_{HH}$ = 3.3 Hz, 1 H, HC=), 6.03 (dd, $^3J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 1.8 Hz, 1 H, HC=), 6.26 (dd, $^3J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 1.8 Hz, 1 H, HC=), 6.99−7.46 (m, 17 H, aromatic H). − $^{13}$C NMR ($CDCl_3$): δ = 110.5 (HC=), 111.4 (HC=), 112.1 (HC=), 112.9 (HC=), 126.8−158.6 (m, aromatic C). − MS (70 eV): *m*/*z* (%) = 439 (100) [$M^+$]. − $C_{31}H_{21}NO_2$ (439): calcd. C 84.72, H 4.82, N 3.19; found C 84.85, H 4.78, N 3.22.

**4,6-Bis(2-furyl)-3,5-diphenyl-2-(3-pyridyl)pyridine (16d):** General procedure B was followed, using (1*E*,3*Z*)-3-(2-furyl)-4-phenyl-1-(3-pyridyl)-2-azabuta-1,3-diene (1.37 g), with a reaction time of 2 h. Chromatographic separation (5:1, hexane/ethyl acetate) gave 0.78 g (71%) of **16d** as a white solid, m.p. 204−205 °C. − IR (KBr): ν̃ = 1534 (C=N). − $^1$H NMR ($CDCl_3$): δ = 5.62 (dd, $^3J_{HH}$ = 3.3 Hz, $^4J_{HH}$ = 0.8 Hz, 1 H, HC=), 5.67 (d, $^3J_{HH}$ = 3.5 Hz, 1 H, HC=), 5.99 (dd, $^3J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 1.8 Hz, 1 H, HC=), 6.24 (dd, $^3J_{HH}$ = 3.5 Hz, $^3J_{HH}$ = 1.8 Hz, 1 H, HC=), 6.96−7.71 (m, 14 H, aromatic H), 8.44 (dd, $^3J_{HH}$ = 4.7 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, HC=), 8.62 (d, $^4J_{HH}$ = 1.5 Hz, 1 H, HC=). − $^{13}$C NMR ($CDCl_3$): δ = 110.3 (HC=), 111.3 (HC=), 112.2 (HC=), 112.9 (HC=), 122.5−154.0 (m, aromatic C). − MS (70 eV): *m*/*z* (%) = 440 (45) [$M^+$]. − $C_{30}H_{20}N_2O_2$ (440): calcd. C 81.80, H 4.58, N 6.36; found C 81.85, H 4.54, N 6.32.

**6-(5-Methyl-2-furyl)-3,5-diphenyl-2,4-bis(3-pyridyl)pyridine (16e):** General procedure B was followed, using (1*E*,3*Z*)-1-(5-methyl-2-furyl)-4-phenyl-3-(3-pyridyl)-2-azabuta-1,3-diene (1.44 g), with a reaction time of 2 h. Chromatographic separation (5:1, hexane/

ethyl acetate) gave 0.70 g (60%) of **16e** as a brown solid. When general procedure B was followed, using (1*Z*,3*Z*)-1-(5-methyl-2-furyl)-4-phenyl-3-(3-pyridyl)-2-azabuta-1,3-diene (1.44 g) and a 4 h reaction time, chromatographic separation (5:1, hexane/ethyl acetate) gave 0.74 g (63%) of **16e** as brown solid, m.p. 131−132 °C. − IR (KBr): $\tilde{\nu}$ = 1564 (C=N). − $^1$H NMR ($CDCl_3$): δ = 2.23 (s, 3 H, $CH_3$), 5.64 (dd, $^3J_{HH}$ = 3.0 Hz, 1 H, HC=), 5.83 (m, 1 H, HC=), 6.80−7.72 (m, 14 H, aromatic H), 8.04 (s, 1 H, HC=), 8.12 (d, $^3J_{HH}$ = 4.8 Hz, 1 H, HC=), 8.42 (d, $^3J_{HH}$ = 4.8 Hz, 1 H, HC=), 8.68 (s, 1 H, HC=). − $^{13}$C NMR ($CDCl_3$): δ = 13.7 ($CH_3$), 107.8 (HC=), 114.3 (HC=), 121.9−137.5 (m, aromatic C), 146.9−153.7 (m, aromatic C). − MS (70 eV): *m*/*z* (%) = 465 (70) [$M^+$]. − $C_{32}H_{23}N_3O$ (465): calcd. C 82.56, H 4.98, N 9.03; found C 82.62, H 5.07, N 9.11.

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