JOC Article

A Versatile Strategy for the Synthesis of Functionalized 2,2′-Bi- and 2,2′:6′,2″-Terpyridines *via* Their 1,2,4-Triazine Analogues†

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A general synthetic route for the synthesis of functionalized bi- and terpyridines is reported. Functionalized 1,2,4-triazene 4-oxides **7** and **8**—obtained from the reaction of hydrazones **1** with pyridine aldehydes and followed by oxidation—are functionalized by introduction of a cyano group via nucleophilic aromatic substitution. The thus-obtained 5-cyano-1,2,4-triazines **9** and **10** undergo facile inverse-electron-demand Diels−Alder reactions with enamines and alkenes to yield functionalized bi- and terpyridines, respectively. The substituent at position 6 of the 1,2,4-triazene 4-oxides must be aromatic or heteroaromatic in order to allow their facile synthesis, but other substituents and reagents may vary. Each step of the synthetic route allows diversification, which makes the approach particularly useful for the facile synthesis of a large variety of functionalized bi- and terpyridines.

Introduction

Organic molecules bearing 2,2′-bipyridine and 2,2′:6′,2″-terpyridine moieties have a geometry that is favorable for the coordination of various metal ions, and therefore, such molecules are widely used in coordination chemistry. On the basis of functionalized 2,2′-bipyridine and 2,2′:6′,2″-terpyridine ligands and their complexes, highly sensitive analytical reagents,[1] various sensor systems,[2−4] reagents for enantioselective synthesis,[5] and luminescent agents for labeled peptide synthesis[6] were created. 2,2′:6′,2″-Terpyridines are attractive building blocks for supramolecular chemistry too.[7,8] Due to their high emission quantum yields, bi-and terpyridines bearing aromatic substituents in the β-position are particularly interesting for photophysical applications.[9,10]

The most common methods of synthesizing functionalized 2,2′-bipyridines and 2,2′:6′,2″-terpyridines are based on the coupling of single pyridine building blocks[11] or the formation of the central (rarely both terminal) pyridine rings starting from the corresponding open-chain intermediates.[12,13]

We have recently communicated a new synthetic strategy for the synthesis of functionalized bi- and terpyridines via Diels−Alder reaction of their corresponding 1,2,4-triazines.[14,15] Herein we describe the scope and limitation of the method and report the full experimental details. The strategy is based on the high reactivity of 1,2,4-triazines in nucleophilic substitution reactions and the possibility of their transformation into pyridines by the Diels−Alder reaction.[16,17] 1,2,4-Triazine *N*-oxides bearing a pyridine ring at position 3 and any aromatic substituents at position 6 serve as starting material of

† Dedicated to Prof. Theodor Troll on the occasion of his 60th birthday.

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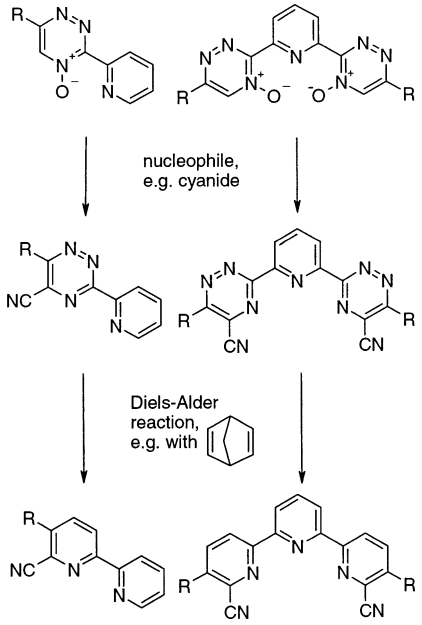
SCHEME 1



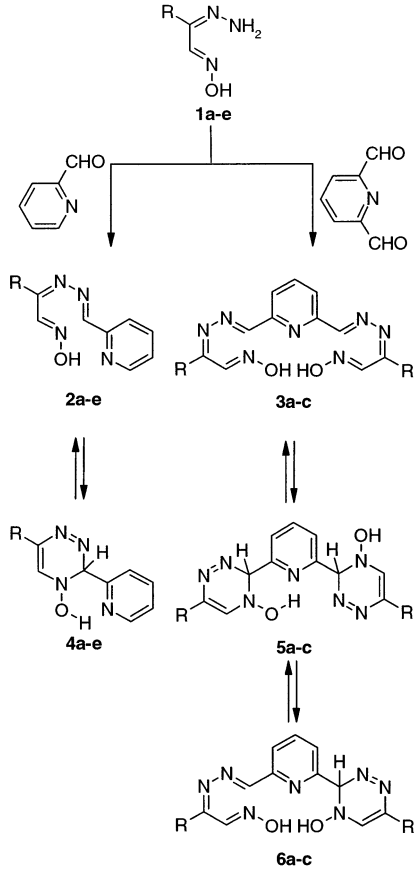
R = C_6H_5 (**a**), $CH_3C_6H_4$ (**b**), $CH_3OC_6C_4$ (**c**), thienyl-2 (**d**), naphthyl-2 (**e**)

the sequence. By nucleophilic attack at position 5 another functional group is introduced, which results in 3-fold substituted 1,2,4-triazines. A Diels−Alder reaction transforms these precursors into bi- or terpyridines. Depending on the alkene used as reaction partner, additional functionality may be introduced at positions 3 and 4 of the new pyridine rings. Reaction with norbornadiene leads to bi- and terpyridines showing the same substitution pattern as the 1,2,4-triazine precursors. Scheme 1 summarizes the key steps of the sequence. With each step molecular diversity may be introduced, which makes the approach particularly interesting for library synthesis.

Results and Discussion

Synthesis of 1,2,4-Triazine 4-Oxides. A previously established method[18] for the synthesis of 1,2,4-triazine 4-oxides was adapted for preparations reported here. The reaction of hydrazones of isonitroso acetophenones **1a**−**e** with pyridine-2-carboxaldehyde or pyridine-2,6-dicarboxaldehyde results in 3-aryl-1-hydroxy-6-(2-pyridyl)-1,4,5-triazahexatrienes **2a**−**e** and 2,6-bis(3-aryl-1-hydroxy-1,4,5-triazahexatriene-6-yl)pyridine **3a**−**c** (Scheme 2). The open-chain compounds **2** exist in equilibrium with their cyclic form of 6-aryl-4-hydroxy-3-(2-pyridyl)-3,4-dihydro-1,2,4-triazines **4a**−**e**, which is typical for 4-hydroxy-3,4-dihydro-1,2,4-triazines.[19] As previously shown,[19] the ratio of the cyclic (**4**) and the open-chain isomers (**2**) can be determined easily by ^{1}H NMR spectroscopy and depends on the solvent. Spectra of compounds **3** are more complicated due to ring-chain isomers: (1) both the 1,2,4-triazine rings are in the open-chain form as in compound

SCHEME 2



R = C_6H_5 (**a**), $CH_3C_6H_4$ (**b**), $CH_3OC_6C_4$ (**c**), thienyl-2 (**d**), naphthyl-2 (**e**)

3, (2) both are in the cyclic form as in compound **5**, and (3) one of the 1,2,4-triazines is in the cyclic form, the second one in the open-chain form as in compound **6** (Scheme 2) (see the Supporting Information for NMR spectra of compounds **2c** and **3b**).

Oxidative aromatization proceeded without being affected by the ratio of the ring-chain isomers. The intermediate compounds **2a**−**e** were treated with Pb_3O_4 in acetic acid yielding the corresponding 6-aryl-3-(2′-pyridyl)-1,2,4-triazine 4-oxides **7a**−**e**. The same reaction of **3a**−**c** with Pb_3O_4 resulted in 2,6-bis(6-phenyl-1,2,4-triazin-3-yl 4-oxide)pyridines **8a**−**c** (Scheme 3).

An advantage of this approach over typical methods for the synthesis of 1,2,4-triazines is the presence of the *N*-oxide group in the 1,2,4-triazine ring of the resulting compounds **7** and **8**. This allows the direct introduction of another substituent by means of a nucleophilic substitution of hydrogen (S_N^H).[16] The direct cyanation of the 1,2,4-triazine 4-oxide has been chosen for S_N^H functionalization of the bi- and terpyridine precursors **7** and **8**. The reaction proceeds easily. Functional group interconversion of the cyano group gives access to many useful derivatives. The cyano group in 5-cyano-1,2,4-triazines can readily be substituted by water, various aliphatic alcohols, amines, or carbanions to give a wide variety of 1,2,4-triazines.[16] Furthermore, the electron-withdrawing cyano group increases the reactivity of the heterocycle in the inverse electron demand Diels−Alder reaction with electron rich dienophiles (vide infra). The cyanation of **7**

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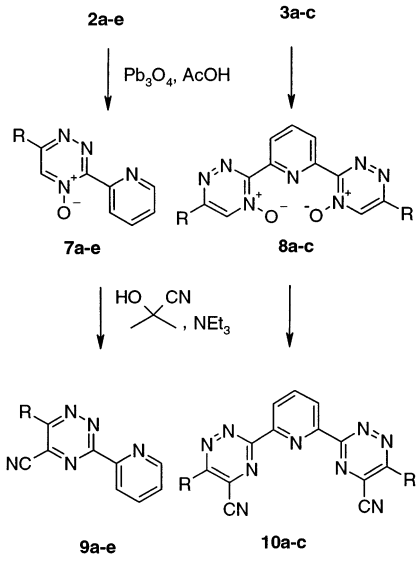
SCHEME 3

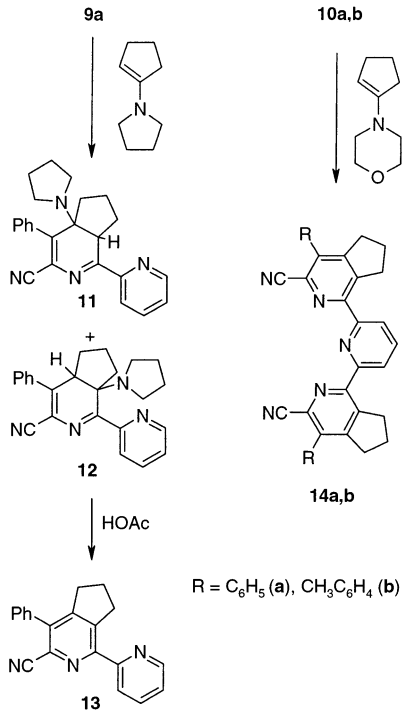


and **8** was achieved by reaction with acetone cyanohydrine in the presence of triethylamine in dichloromethane, affording 6-aryl-5-cyano-3-(2′-pyridyl)-1,2,4-triazines **9a**−**e** and 2,6-bis(6-aryl-5-cyano-1,2,4-triazin-3-yl)-pyridines **10a**−**c** (Scheme 3). The in situ generated cyanide anion adds to position 5 of the 1,2,4-triazine ring resulting in the intermediate σ-adducts, which undergo dehydration to form the aromatic products **9** and **10**. The reaction proceeded smoothly with good yields.

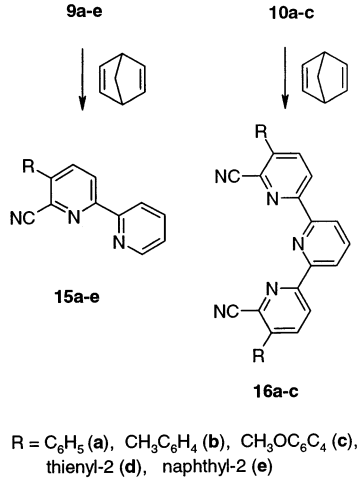
Synthesis of Bi- and Terpyridines. The transformation of cyano-1,2,4-triazines **9** and **10** into bi- and terpyridines was carried out in practically one step by Diels−Alder reaction. Bearing in mind that 1,2,4-triazines, are π-deficient heterocycles, particularly if cyano substituted, we have chosen enamines and norbornadiene as electron rich dienophiles. The reaction of cyano-1,2,4-triazine **9a** with 1-(1-pyrrolidino)cyclopentene already proceeds at room temperature, releasing nitrogen. The intermediate cycloadducts are isolated as a mixture of two regioisomers **11** and **12**. Unaffected by the ratio of the isomers, the rearomatization by elimination of pyrrolidine upon reflux in acetic acid gave 6-cyano-5-phenyl-2-(2′-pyridyl)-3,4-cyclopentenopyridine **13** (Scheme 4). The analogous 2-fold reaction of 2,6-bis(cyano-1,2,4-triazin-3-yl)pyridines **10a**,**b** with 1-(1-pyrrolidino)cyclopentene or 1-(4-morpholino)cyclopentene gave 2,6-bis(6-cyano-5-phenyl-3,4-cyclopentenopyridyl-2)pyridines **14a**,**b** with good yields (Scheme 4). The molecular structure of the terpyridine **14b** was confirmed by X-ray crystallography (see the Supporting Information).

Reaction of the cyanotriazines **9** and **10** with norbornadiene yields unsubstituted bi- and terpyridines. In this case, the reaction proceeded more slowly than the reaction with enamines. Thus refluxing the compounds **9a**−**e** with bicyclo[2.2.1]hepta-2,5-diene in toluene resulted in 6-cyano-5-phenyl-2,2′-bipyridine **15a**−**e**. The same reaction of the dinitriles **10a**−**c** yielded 6,6″-dicyano-5,5″-diphenyl-2,2′:6′,2″-terpyridine **16a**−**c** (Scheme 5). The cyano group in the 1,2,4-triazine ring facilitates the

SCHEME 4



SCHEME 5



inverse-electron-demand Diels−Alder reaction in comparison to unsubstituted pyridyl-1,2,4-triazines.

The presence of the cyano group in the bi- and terpyridines obtained hereby allows further functional group transformation, if desired. For illustration of this option, the cyano group of bipyridine **13a** was hydrolyzed in 95% sulfuric acid to give 6-carbomoyl-5-phenyl-2-(2′-pyridyl)-3,4-cyclopentenopyridine (**17**). Reflux of the amide **17** in concentrated hydrochloric acid yielded 5-phenyl-2-(2′-pyridyl)-3,4-cyclopentenopyridine-6-carboxylic acid **18**. Esterification of the acid **18** gave 6-ethoxycarbonyl-5-phenyl-2-(2′-pyridyl)-3,4-cyclopentenopyridine (**19**), which was reduced with sodium borohydride to 6-hydroxymethyl-5-phenyl-2-(2′-pyridyl)-3,4-cyclopentenopyridine (**20**) (Scheme 6).

Synthesis and Structure of 14a−Ni(NO$_3$)$_2$. The synthesized bi- and terpyridine ligands are expected to form complexes with a variety of transition metals.

SCHEME 6

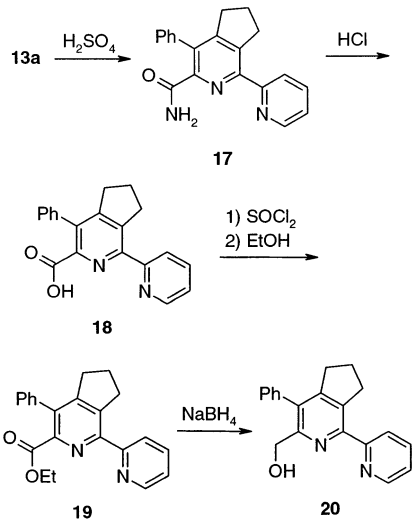


TABLE 1. Absorption and Emission Maxima and Quantum Yields of Compounds 15a−e and 16a−c in an Ethanol Solution

compd	λ_{abs},[a] nm	λ_{fl},[a] nm	Φ_{fl}[a,b]
15a	292	359	0.01
15b	295	370	0.10
15c	306	408	0.43
15d	317	393	0.10
15e	304	407	0.58
16a	302	355	0.40
16b	305	363	0.50
16c	313	402	0.60

[a] Measured in ethanol solution 10^{-5} mol/L. [b] Anthracene in ethanol solution ($\phi_{em} = 0.27$) was used as standard for determining emission quantum yields.

However, contrary to less functionalized bi- and terpyridines, the cyano group in the α-(αα″)-position causes a steric hindrance. Therefore, complexes of, e.g., two terpyridine molecules binding to one metal atom with coordination number 6 cannot be obtained. This is illustrated nicely by the nickel complex **14a**−**Ni(NO$_3$)$_2$**, which was obtained by refluxing dicyanoterpyridine **14a** with Ni(NO$_3$)$_2$·6H$_2$O in acetonitrile.[15] The molecular structure of the complex in the crystal was determined by X-ray crystallography. The Ni(II) atom is bound to the three nitrogen atoms of the terpyridine ligand and three oxygen atoms of two nitrate anions with chelate and terminal coordination. The terpyridine system is almost planar with a deviation of 0.047 Å of the metal atom from the average plane of the terpyridine.

Absorption and Emission Properties of Cyanobipyridines and Dicyanoterpyridines. Table 1 summarizes the absorption and emission maxima of cyanobipyridines **15a**−**e** and dicyanoterpyridines **16a**−**c** in ethanol. The lowest energy absorption bands of these compounds are around 300 nm. The emission maxima and relative quantum yields of **15** and **16** depend strongly on the aromatic substituents.[20] An increase in electron donor properties of the substituent causes a bathochromic shift of the emission and an increase in quantum yields.

(20) A comparison of the corresponding aryl-substituted bi- and terpyridines (see ref 9) with the cyano-substituted compounds shows a bathochromic shift of the emission of 15−25 nm.

Conclusion

Functionalized bi- and terpyridines can be obtained from 1,2,4-triazine 4-oxides. The sequence of triazine 4-oxide formation, introduction of an additional cyano group by nucleophilic substitution of hydrogen, and transformation of the 1,2,4-triazine rings into pyridines by Diels−Alder reaction tolerates many functional groups. Most steps result in a high chemical yield. The variety of substituents is limited by the fact that the substituent at position 6 of the 1,2,4-triazines must be aromatic or heteroaromatic. Each step of the synthesis allows diversification, if desired. The presented examples may be well extended by the use of other nucleophiles or dienophiles.

Functionalized bi- and terpyridines and their metal complexes are important building blocks for the construction of chemosensors, self-organized assemblies, or photoactive molecular devices. The synthetic procedure presented facilitates the preparation of such compounds.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz in $CDCl_3$, unless otherwise stated. The multiplicity of the ^{13}C signals was determined using the DEPT technique and quoted as (+) for CH_3 or CH, (−) for CH_2, and (C_{quat}) for quaternary carbons. Starting hydrazones **1a**−**e** were synthesized according to the described method.[21]

6-Phenyl-3-(2-pyridyl)-1,2,4-triazine 4-Oxide (7a). General Procedure 1 (GP1). Pyridine 2-carboxaldehyde (1 g, 9.2 mmol) was added to a stirred solution of isonitrosoacetophenone hydrazone **1a** (1.5 g, 9.2 mmol) in ethanol (10 mL). The reaction mixture was kept at room temperature for 12 h. The resulting precipitate was filtered off, washed with ethanol to give **2a** (2.1 g, 8.3 mmol, 90%). Over 1 h at room temperature, Pb_3O_4 (5.69 g, 8.3 mmol) was added to the suspension of intermediate **2a** (2.1 g, 8.3 mmol) in acetic acid (11 mL). The mixture was stirred at room temperature for an additional 3 h and then diluted with water (35 mL). The precipitate was filtered off, washed with water, and recrystallized from ethanol to yield **7a** (1.1 g, 54%). Mp: 173−174 °C. ^{1}H NMR (DMSO-d_6, 250 MHz): δ 7.58 (m, 4H), 8.00 (m, 2H), 8.23 (m, 2H), 8.78 (m, 1H), 9.32 (s, 1H). IR (KBr): ν (cm^{-1}) 1240, 1374, 1424, 1555, 3061. EI MS (70 eV): *m*/*z* 250 (23) [M$^+$], 116 (100). Anal. Calcd for $C_{14}H_{10}N_4O$ (250.3): C, 67.19; H, 4.03; N, 22.39. Found: C, 67.14; H, 4.13; N, 22.42.

6-(4-Methylphenyl)-3-(2-pyridyl)-1,2,4-triazine 4-Oxide (7b). Following GP1, **1b** (2.12 g, 12 mmol) and 2-pyridinecarboxaldehyde (1.28 g. 12 mmol) were reacted to yield 2.87 g (90%) of the intermediate **2b**. Compound **2b** (2.66 g, 10 mmol) and Pb_3O_4 (6.85 g, 10 mmol) gave 1.4 g (5.3 mmol, 52%) of **7b**. Mp: 209−210 °C. ^{1}H NMR: δ 2.43 (s, 3H), 7.36 (m, 2H), 7.48 (m, 1H), 7.92 (m, 3H), 8.21 (br. d, 1H), 8.61 (s, 1H), 8.87 (m, 1H). ^{13}C NMR: δ 21.5 (+), 125.6 (+), 125.9 (+), 127.0 (+), 128.7 (C_{quat}), 130.2 (+), 131.86 (+), 136.7 (+), 142.6 (C_{quat}), 147.6 (C_{quat}), 150.1 (+), 155.4 (C_{quat}), 157.2 (C_{quat}). IR (KBr): ν (cm^{-1}) 1244, 1366, 1420, 1446, 1552, 1581, 3054. EI MS (70 eV): *m*/*z* 264 (29) [M$^+$], 248 (5) [M − O$^+$], 130 (100). Anal. Calcd for $C_{15}H_{12}N_4O$ (264.3): C, 68.17; H, 4.58; N, 21.20. Found: C, 68.03; H, 4.52; N, 20.92.

6-(4-Methoxyphenyl)-3-(2-pyridyl)-1,2,4-triazine 4-Oxide (7c). According to GP1, **1c** (1.13 g, 5.9 mmol) and 2-pyridinecarboxaldehyde (0.63 g. 5.9 mmol) gave 1.64 g (98%) of the intermediate **2c**. In the second step, **2c** (1.6 g, 5.7 mmol) and Pb_3O_4 (3.89 g, 5.7 mmol) yielded 0.7 g (44%) of **7c**. Mp: 207−209 °C. ^{1}H NMR: δ 3.89 (s, 3H), 7.07 (m, 2H), 7.49 (m, 1H), 7.90 (m, 1H), 8.04 (m, 2H), 8.22 (m, 1H), 8.60 (s, 1H),

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8.89 (br.d, 1H). IR (KBr): ν (cm^{-1}) 1244, 1516, 1576, 1603, 2839, 3050. EI MS (70 eV): *m/z* 280 (29) [M^+], 146 (100). Anal. Calcd for $C_{15}H_{12}N_4O_2$ (280.3): C, 64.28; H, 4.32; N, 19.99. Found: C, 63.86; H, 4.38; N, 20.13.

3-(2-Pyridyl)-6-(2-thienyl)-1,2,4-triazine 4-Oxide (7d). Following GP1, compound **1d** (1.23 g, 7.4 mmol) and 2-pyridinecarboxaldehyde (0.79 g. 7.4 mmol) gave 1.77 g (93%) of **2d**. In the second step, **2d** (1.62 g, 6.3 mmol) and Pb_3O_4 (4.3 g, 6.3 mmol) yielded 680 mg (43%) of **7d**. Mp: 202−204 °C. ^{1}H NMR: δ 7.32 (m, 1H), 7.62 (m, 1H), 7.96 (dd, 1H), 8.02 (m, 2H), 8.16 (m, 1H), 8.79 (m, 1H), 9.49 (s, 1H). ^{13}C NMR: δ 125.9 (+), 126.2 (+), 129.5 (+), 130.5 (+), 131.6 (+), 132.8 (+), 135.8 (C_{quat}), 137.1 (+), 148.5 (C_{quat}), 150.1 (+), 153.5 (C_{quat}), 156.2 (C_{quat}). IR (KBr): ν (cm^{-1}) 1240, 1374, 1438, 1561, 3086. EI MS (70 eV): *m/z* 256 (29) [M^+], 122 (100). Anal. Calcd for $C_{12}H_8N_4OS$ (256.3): C, 56.24; H, 3.15; N, 21.86. Found: C, 56.05; H, 3.18; N, 21.64.

6-(2-Naphthyl)-3-(2-pyridyl)-1,2,4-triazine 4-Oxide (7e). Following GP1, **1e** (1.41 g, 6.6 mmol) and 2-pyridinecarboxaldehyde (0.71 g, 6.6 mmol) were reacted to give 1.68 g (84%) of the intermediate **2e**. Compound **2e** (1.68 g, 5.6 mmol) and Pb_3O_4 (3.81 mg, 5.6 mmol) yielded 0.85 g (51%) of **7e**. Mp: 203−205 °C. ^{1}H NMR: δ 7.6 (m, 1H), 7.7 (m, 2H), 8.0 (m, 4H), 8.2 (m, 1H), 8.31 (d, 1H), 8.63 (br.s, 1H), 8.84 (s, 1H), 8.95 (br.d, 1H). IR (KBr): ν (cm^{-1}) 1242, 1348, 1369, 1552, 1580, 2853, 3031. EI MS (70 eV): *m/z* 300 (48) [M^+], 166 (100). Anal. Calcd for $C_{18}H_{12}N_4O$ (300.3): C, 71.99; H, 4.03; N, 18.66. Found: C, 71.69; H, 4.13; N, 18.54.

2,6-Bis(6-phenyl-1,2,4-triazin-3-yl 4-oxide)pyridine (8a). General Procedure 2 (GP2). A solution of pyridine 2,6-dicarboxaldehyde (1.35 g, 10 mmol) in ethanol was added to a stirred solution of isonitrosoacetophenone hydrazone **1a** (3.26 g, 20 mmol) in ethanol. The reaction mixture was heated under reflux for 1 h. The resulting precipitate was separated by filtration and washed with ethanol to give intermediate **3a** (4.12 g, 97%). To a stirred suspension of **3a** (3.50 g, 8.2 mmol) in glacial acetic (20 mL) acid was added Pb_3O_4 (11.3 g, 16.5 mmol), and the mixture was kept at room temperature for 5 h. The precipitate was separated by filtration and washed with acetic acid, water, and ethanol to give **8a** (1.14 g, 33%). Mp: 270−273 °C dec. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 7.62 (m, 6H), 8.26 (m, 7H), 9.44 (s, 2H). IR (KBr): ν (cm^{-1}) 1244, 1368, 1420, 1555, 3059. EI MS (70 eV): *m/z* 421 (10) [M^+], 102 (100). Anal. Calcd for $C_{23}H_{15}N_7O_2$ (421.4): C, 65.55; H, 3.59; N, 23.27. Found: C, 65.75; H, 3.39; N, 23.38.

2,6-Bis[6-(4-methylphenyl)-1,2,4-triazin-3-yl 4-oxide]-pyridine (8b). Following GP2, **1b** (3.54 g, 20 mmol) and 2,6-pyridinedicarboxaldehyde (1.35 g, 10 mmol) yielded 4.03 g (89%) of the intermediate **3b**. In the second step, **3b** (4.0 g, 8.8 mmol) and Pb_3O_4 (12.10 g, 17.7 mmol) gave 1.34 g (34%) of **8b**. Mp: 303−305 °C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.45 (s, 6H), 7.61 (d, 4H, 4-methylphenyl), 8.19 (d, 4H), 2.28−2.31 (m, 3H), 9.46 (s, 2H). IR (KBr): ν (cm^{-1}) 1244, 1366, 1422, 1557, 2920, 3056. EI MS (70 eV): *m/z* 449 (26) [M^+], 116 (78), 130 (100). Anal. Calcd for $C_{25}H_{19}N_7O_2$ (449.5): C, 66.81; H, 4.26; N, 21.81. Found: C, 66.43; H, 4.24; N, 21.56.

2,6-Bis-(6-(4-methoxyphenyl)-1,2,4-triazin-3-yl 4-oxide)-pyridine (8c). Following GP2, **1c** (1.4 g, 7.3 mmol) and 2,6-pyridinedicarboxaldehyde (0.49 g, 3.6 mmol) yielded 1.49 g (85%) of the intermediate **3c**. In the second step, **3c** (1.49 g, 3.1 mmol) and Pb_2O_3 (4.25 g, 6.2 mmol) gave 0.54 g (36%) of **8c**. Mp: 293−295 °C. ^{1}H NMR: δ 3.87 (s, 6H), 7.17 (m, 4H), 8.25 (m, 7H), 9.41 (s, 2H). IR (KBr): ν (cm^{-1}) 1244, 1306, 1368, 1421, 1519, 1605, 2841, 3052. EI MS (70 eV): *m/z* 481 (3) [$M]^+$, 132 (100). Anal. Calcd for $C_{25}H_{19}N_7O_4$ (481.5): C, 62.37; H, 3.98; N, 20.36. Found: C, 62.42; H, 4.13; N, 20.67.

5-Cyano-6-phenyl-3-(2-pyridyl)-1,2,4-triazine (9a). General Procedure 3 (GP3). To a solution of 1,2,4-triazine-4-oxide **7a** (500 mg, 2.0 mmol) in dichloromethane (10 mL) were added acetone cyanohydrine (204 mg, 0.22 mL, 2.4 mmol) and triethylamine (202 mg 0.28 mL, 2.0 mmol). The reaction mixture was heated under reflux until complete conversion of the starting material was confirmed by TLC (approximately 1 h). Solvents were removed under reduced pressure, and the residue was dissolved in ethyl acetate and filtered through silica gel to give **9a** (388 mg, 1.5 mmol, 75%). Mp: 128−129 °C. ^{1}H NMR: δ 7.51 (m, 1H), 7.60 (m, 3H), 7.94 (m, 1H), 8.09 (m, 2H), 8.65 (m, 1H), 8.90 (m, 1H). IR (KBr): ν (cm^{-1}) 1391, 1440, 1580, 2239, 3058. EI MS (70 eV): *m/z* 259 (4) [$M]^+$, 231 (21) [$M - N_2]^+$, 129 (100). Anal. Calcd for $C_{15}H_9N_5$ (259.3): C, 69.49; H, 3.50; N, 27.01. Found: C, 69.35; H, 3.47; N, 27.14.

5-Cyano-6-(4-methylphenyl)-3-(2-pyridyl)-1,2,4-triazine (9b). Following GP3, **7b** (970 mg, 3.7 mmol) yielded 883 mg (88%) of **9b**. Mp: 145−146 °C. ^{1}H NMR: δ 2.48 (s, 3H), 7.44 (m, 2H), 7.54 (m, 1H), 7.98 (m, 1H), 8.07 (m, 2H), 8.69 (br.d, 1H), 8.94 (m, 1H). ^{13}C NMR: δ 21.6 (+), 114.7 (C_{quat}), 124.5 (+), 126.4 (+), 128.2 (C_{quat}), 129.0 (+), 130.2 (+), 132.3 (C_{quat}), 137.6, 143.0 (C_{quat}), 150.8 (+), 150.8 (C_{quat}), 157.2 (C_{quat}), 160.6 (C_{quat}). IR (KBr): ν (cm^{-1}) 1386, 1578, 1606, 2240, 3049. EI MS (70 eV): *m/z* 273 (10) [$M]^+$, 245 (18), [$M - N_2]^+$, 141 (100). Anal. Calcd for $C_{16}H_{11}N_5$ (273.3): C, 70.32; H, 4.06; N, 25.63. Found: C, 69.97; H, 4.00; N, 25.63.

5-Cyano-6-(4-methoxyphenyl)-3-(2-pyridyl)-1,2,4-triazine (9c). Following GP3, **7c** (530 mg, 1.9 mmol) yielded 383 mg (70%) of **9c**. Mp: 139−140 °C. ^{1}H NMR: δ 3.93 (s, 3H), 7.02 (m, 1H), 7.15 (m, 2H), 7.58 (m, 1H), 8.20 (m, 2H), 8.70 (m, 1H), 8.97 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 55.6 (+), 114.8 (C_{quat}), 115.0 (+), 123.2 (C_{quat}), 124.5 (+), 126.5 (+), 130.9 (+), 131.6 (C_{quat}), 138.1 (+), 150.5 (C_{quat}), 150.5 (+), 156.6 (C_{quat}), 159.9 (C_{quat}), 163.1 (C_{quat}). IR (KBr): ν (cm^{-1}) 1388, 1604, 2232, 3057. EI MS (70 eV): *m/z* 289 (5) [$M]^+$, 157 (100). Anal. Calcd for $C_{16}H_{11}N_5O$ (289.3): C, 66.43; H, 3.83; N, 24.21. Found: C, 66.58; H, 4.04; N, 24.70.

5-Cyano-6-(2-thienyl)-3-(2-pyridyl)-1,2,4-triazine (9d). Following GP3, **7d** (450 mg, 1.8 mmol) yielded 335 mg (72%) of **9d**. Mp: 197−199 °C. ^{1}H NMR: δ 7.35 (dd, 1H, *J* 5.1 Hz, 3.9 Hz), 7.59 (m, 1H), 7.82 (dd, 1H, *J* 5.1 Hz, 0.8 Hz), 8.02 (m, 1H), 8.45 (dd, 1H, *J* 3.9 Hz, 0.8 Hz), 8.71 (br.d, 1H), 8.96 (br.d, 1H). ^{13}C NMR: δ 114.7 (C_{quat}), 124.4 (+), 126.5 (+), 128.8 (C_{quat}), 129.5 (+), 131.5 (+), 134.1 (+), 134.7 (C_{quat}), 137.9 (+), 150.6 (C_{quat}), 150.7 (+), 151.51 (C_{quat}), 160.0 (C_{quat}). IR (KBr): ν (cm^{-1}) 1386, 1420, 1482, 1526, 2231, 3057, 3109. EI MS (70 eV): *m/z* 265 (9) [$M]^+$, 237 (17), [$M - N_2]^+$. Anal. Calcd for $C_{13}H_7N_5S$ (265.3): C, 58.86; H, 2.66; N, 26.40. Found: C, 58.49; H, 2.43; N, 26.51.

5-Cyano-6-(2-naphthyl)-3-(2-pyridyl)-1,2,4-triazine (9e). Following GP3, **7e** (430 mg, 1.4 mmol) yielded 394 mg (1.3 mmol, 89%) of **9e**. Mp: 169−170 °C. ^{1}H NMR: δ 7.61 (m, 3H), 8.02 (m, 4H), 8.22 (m, 1H), 8.71 (m, 2H), 8.97 (m, 1H). ^{13}C NMR: δ 114.7 (C_{quat}), 124.6 (+), 124.8 (+), 126.5 (+), 127.3 (+), 127.9 (+), 128.3 (C_{quat}), 128.6 (+), 129.3 (+), 129.5 (+), 130.2 (+), 132.7 (C_{quat}), 132.9 (C_{quat}), 134.7 (C_{quat}), 137.7 (+), 150.8 (C_{quat}), 150.8 (+), 157.2 (C_{quat}), 160.65 (C_{quat}). IR (KBr): ν (cm^{-1}) 1391, 1479, 1578, 2236, 3059. EI MS (70 eV): *m/z* 309 (7) [M^+], 177 (100). Anal. Calcd for $C_{19}H_{11}N_5$ (309.3): C, 73.78; H, 3.58; N, 22.64. Found: C, 73.81; H, 3.88; N, 22.62.

2,6-Bis(5-cyano-6-phenyl-1,2,4-triazine-3-yl)pyridine (10a). Following GP3, **8a** (700 mg, 1.7 mmol) yielded 460 mg (63%) of **10a**. Mp: 176−177 °C. ^{1}H NMR: δ 7.75 (m, 6H), 0.8.15 (m, 4H), 8.48 (dd, 1H, *J* 7.8 Hz, *J* 7.8 Hz), 8.85 (d, 2H, *J* 7.8 Hz). IR (KBr): ν (cm^{-1}) 1378, 1441, 2241, 3068. EI MS (70 eV): *m/z* 439 (4) [M^+], 129 (100). Anal. Calcd for $C_{25}H_{13}N_9$ (439.4): C, 68.33; H, 2.98; N, 28.69. Found: C, 67.93; H, 2.71; N, 28.39.

2,6-Bis(5-cyano-6-(4-methylphenyl)-1,2,4-triazine-3-yl)-pyridine (10b). Following GP3, **8b** (1 g, 2.2 mmol) yielded 728 mg (70%) of **10b**. Mp: 239−241 °C. ^{1}H NMR: δ 2.45 (s, 6H, CH_3), 7.42 (d, 4H), 8.01 (d, 4H), 8.29 (dd, 1H), 8.82 (d, 2H). IR (KBr): ν (cm^{-1}) 1375, 1607, 2240, 3049. EI MS (70 eV): *m/z* 467 (3) [M^+], 141 (100). Anal. Calcd for $C_{27}H_{17}N_9$ (467.5): C, 69.37; H, 3.67; N, 26.96. Found: C, 69.52; H, 3.68; N, 26.75.

2,6-Bis(5-cyano-6-(4-methoxyphenyl)-1,2,4-triazine-3-yl)pyridine (10c). Following GP3, **8c** (350 mg, 0.7 mmol) yielded 316 mg (87%) of **10c**. Mp: 237−239 °C. ^{1}H NMR: δ 3.94 (s, 6H), 7.17 (d, 4H), 8.22 (d, 4H), 8.29 (dd, 1H), 8.89 (d, 2H). IR (KBr): ν (cm^{-1}) 1377, 1603, 2232, 3056. EI MS (70 eV): *m*/*z* 499 (7) [M$^+$], 157 (100). Anal. Calcd for $C_{27}H_{17}N_9O_2$ (499.5): C, 64.93; H, 3.43; N, 25.24. Found: C, 64.45; H, 3.67; N, 25.03.

6-Cyano-5-phenyl-2-(2′-pyridyl)-3,4-cyclopentenopyridine (13). 1-(1-Pyrrolidino)cyclopentene (302 mg, 2.2 mmol) was added to a solution of 5-cyano-6-phenyl-3-(2-pyridyl)-1,2,4-triazine **9a** (0.52 g, 2.0 mmol) in benzene (10 mL). The reaction mixture was stirred at room temperature for 1 h and then heated under reflux for 1 h. The solvent was evaporated in vacuo and the residue refluxed in acetic acid (3 mL) for 30 min. The precipitated crystals of **13** were filtered off and washed first with acetic acid and then with ethanol. Yield: 0.58 g (97%). Mp: 192−193 °C. ^{1}H NMR (250 MHz, DMSO-d_6) δ 2.11 (m, 2H), 2.90 (m, 2H), 3.57 (m, 2H), 7.50 (m, 6H), 7.94 (m, 1H), 8.32 (m, 1H), 8.67 (m, 1H). IR(KBr): ν (cm^{-1}) 1409, 1541, 1572, 2230, 2956, 3059. EI MS (70 eV): *m*/*z* 297 (100) [M$^+$]. Anal. Calcd for $C_{20}H_{15}N_3$ (297.36): C, 80.78; H, 5.08; N, 14.13. Found: C, 80.74; H, 4.98; N, 14.27.

2,6-Bis(6-cyano-5-phenyl-3,4-cyclopentenopyridyl-2)-pyridine (14a). 1-(4-Morpholino)cyclopentene (178 mg, 1.16 mmol) was added to the solution of the compound **10a** (255 mg, 0.58 mmol) in toluene, and the resulting mixture was kept at room temperature for 1 h and then heated under reflux for 1 h. The solvent was removed in vacuo, and the residue was heated under reflux in 3 mL of acetic acid. The crystals were separated by filtration and recrystallized from DMF yielding **14a** (230 mg, 77%). Mp: >300 °C dec. ^{1}H NMR (DMSO-d_6, 250 MHz) δ: 2.15 (m, 4H), 2.93 (t, 4H), 3.45 (t, 4H), 7.6 (m, 10H), 8.25 (m, 3H). EI/MS (70 eV): *m*/*z* 515 (100) [M$^+$]. Anal. Calcd for $C_{35}H_{25}N_5$ (515.6): C, 81.53; H, 4.89; N, 13.58. Found: C, 81.62; H, 4.81; N, 13.60.

Complex 14a−Ni(NO$_3$)$_2$.[15] A solution of $Ni(NO_3)_2 \cdot 6H_2O$ (84.4 mg, 0.29 mmol) in 3 mL of acetonitrile was added to a solution of **14a** (150 mg, 0.29 mmol) in acetonitrile (5 mL). The resulting mixture was heated under reflux for 15 min. Crystals formed after cooling and were separated by filtration, dissolved in hot acetonitrile, and kept at room temperature for 12 h resulting in green crystals suitable for X-ray analysis. Yield: 152 mg, 75%. Mp: >300 °C. $C_{35}H_{25}N_5-Ni(NO_3)_2$ (698.3).

2,6-Bis(6-cyano-5-(4-methylphenyl)-3,4-cyclopentenopyridin-2-yl)pyridine (14b). 1-(1-Pyrrolidino)cyclopentene (288 mg, 2.1 mmol) was added to a solution of compound **10b** (470 mg, 1 mmol) in benzene. The resulting mixture was stirred at room temperature for 1 h and heated under reflux for 1 h. The solvent was removed in vacuo, the residue was heated under reflux in 3 mL of acetic acid, and the crystals obtained were separated by filtration and washed with acetic acid to give **14b** (525 mg, 97%). Mp: 278−279 °C. ^{1}H NMR: δ 2.08 (m, 4H), 2.45 (s, 6H)2.94 (t, 4H), 3.46 (t, 4H), 7.33 (d, 4H), 7.36 (d, 4H), 8.03 (dd, 1H), 8.29 (d, 2H). ^{13}C NMR: δ 21.4 (+), 25.2 (−), 32.6 (−), 34.1 (−), 117.58 (C_{quat}), 123.8 (+), 128.9 (+), 129.5 (+), 130.1 (C_{quat}), 131.4 (C_{quat}), 137.7 (+), 138.4 (C_{quat}), 139.2 (C_{quat}), 143.2 (C_{quat}), 152.2 (C_{quat}), 155.7 (C_{quat}). IR (KBr): ν (cm^{-1}) 1375, 1404, 1544, 1570, 2231, 2871, 2946, 2968, 3026. EI MS (70 eV): *m*/*z* 543 (100) [M]$^+$. Anal. Calcd for $C_{37}H_{29}N_5$ (543.7): C, 81.74; H, 5.38; N, 12.88. Found: C, 81.65; H, 5.48; N, 12.79.

6-Cyano-5-phenyl-2,2′-bipyridine (15a). General Procedure 4 (GP4). A mixture of 5-cyano-6-phenyl-1,2,4-triazine **9a** (110 mg, 0.42 mmol) and 10 equiv of bicyclo[2.2.1]hepta-2,5-diene (386 mg, 0.45 mL, 4.2 mmol) in toluene (10 mL) was heated under reflux for 12 h. The solvent was evaporated under reduced pressure, and the residue was stirred with ethanol (10 mL) for 15 min and separated by filtration to give **15a** (103 mg, 95%). Mp: 189−190 °C. ^{1}H NMR: δ 7.43 (m, 1H), 7.54 (m, 3H), 7.63 (m, 2H), 7.93 (m, 1H), 8.00 (d, 1H, *J* 8.2 Hz), 8.55 (br.d, 1H), 8.72 (m, 1H), 8.78 (d, 1H, *J* 8.2 Hz). ^{13}C NMR: δ 117.2 (C_{quat}), 122.0 (+), 124.3 (+), 124.9 (+), 128.8 (+), 129.1 (+), 129.6 (+), 131.4 (C_{quat}), 135.1 (C_{quat}), 138.1 (+), 138.7 (+), 141.9 (C_{quat}), 148.6 (+), 153.4 (C_{quat}), 155.1 (C_{quat}). IR (KBr): ν (cm^{-1}) 1437, 1586, 2228, 3056. UV (CH_3CN): λ_{max} (log ϵ) 290 (4.28). EI MS (70 eV): *m*/*z* 257 (100) [M$^+$]. Anal. Calcd for $C_{17}H_{11}N_3$ (257.3): C, 79.36; H, 4.31; N, 16.33. Found: C, 79.40; H, 4.56; N, 16.84.

6-Cyano-5-(4-methylphenyl)-2,2′-bipyridine (15b). Following GP4, **9b** (550 mg, 2.0 mmol) yielded 490 mg (90%) of **15b**. Mp: 187−188 °C. ^{1}H NMR: δ 2.44 (s, 3H), 7.34 (d, 2H), 7.38 (m, 1H, 7.53 (d, 2H), 7.88 (m, 1H), 7.96 (d, 1H), 8.52 (m, 1H), 8.69 (m, 1H), 8.70 (d, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.3 (+), 117.4 (C_{quat}), 121.6 (+), 124.1 (+), 124.7 (+), 128.6 (+), 129.8 (+), 131.2 (C_{quat}), 132.3 (C_{quat}), 137.4 (+), 138.5 (+), 139.7 (C_{quat}), 141.8 (C_{quat}), 149.1 (+), 153.9 (C_{quat}), 155.6 (C_{quat}). IR (KBr): ν (cm^{-1}) 1441, 1583, 2230, 2919, 3019. UV (CH_3-CN): λ_{max} (log ϵ) 292 (4.56). EI MS (70 eV): *m*/*z* 271 (100) [M$^+$]. Anal. Calcd for $C_{18}H_{13}N_3$ (271.3): C, 79.68; H, 4.83; N, 15.49. Found: C, 79.71; H, 4.90; N, 15.51.

6-Cyano-5-(4-methoxyphenyl)-2,2′-bipyridine (15c). Following GP4, **9c** (320 mg, 1.1 mmol) gave 290 mg (92%) of **15c**. Mp: 183−184 °C. ^{1}H NMR: δ 3.88 (s, 3H), 7.06 (d, 2H), 7.39 (m, 1H), 7.59 (d, 2H), 7.88 (m, 1H), 7.95 (d, 1H, *J* 8.4 Hz), 8.51 (m, 1H), 8.70 (d, 1H, *J* 8.4 Hz), 8.70 (m, 1H). ^{13}C NMR: δ 55.4 (+), 114.6 (+), 117.5 (C_{quat}), 121.7 (+), 124.1 (+), 124.7 (+), 127.4 (C_{quat}), 130.1 (+), 131.0 (C_{quat}), 137.5 (+), 138.3 (+), 141.5 (C_{quat}), 149.0 (+), 153.8 (C_{quat}), 155.2 (C_{quat}), 160.7 (C_{quat}). IR (KBr): ν (cm^{-1}) 1441, 1518, 1611, 2232, 2843, 2956, 3049. UV (CH_3CN): λ_{max} (log ϵ) 302 (4.31). EI MS (70 eV): *m*/*z* 287 (100) [M]$^+$, 272 (12), 244 (23). Anal. Calcd for $C_{18}H_{13}N_3O$ (287.3): C, 75.25; H, 4.56; N, 14.62. Found: C, 75.25; H, 4.78; N, 14.82.

6-Cyano-5-(2-thienyl)-2,2′-bipyridine (15d). Following GP4, **9d** (210 mg, 0.8 mmol) yielded 187 mg (89%) of **15d**. Mp: 178−179 °C. ^{1}H NMR: δ 7.21 (dd, 1H, *J* 5.2 Hz, 3.8 Hz), 7. 39 (m, 1H), 7.54 (dd, 1H, *J* 5.2 Hz, 1.1 Hz), 7.80 (dd, 1H, *J* 3.8 Hz, 1.1 Hz), 7.88 (m, 1H), 8.06 (d, 1H, *J* 8.5 Hz), 8.50 (br.d, 1H), 8.67 (d, 1H, *J* 8.5 Hz), 8.70 (m, 1H). ^{13}C NMR: δ 117.5 (C_{quat}), 121.7 (+), 124.2 (+), 124.8 (+), 128.5 (+), 128.7 (+), 129.4 (C_{quat}), 134.4 (C_{quat}), 136.3 (C_{quat}), 137.6 (+), 137.8 (+), 149.0 (+), 153.5 (C_{quat}), 155.3 (C_{quat}). IR (KBr): ν (cm^{-1}) 1449, 1543, 1573, 1587, 2227, 3003. UV (CH_3CN): λ_{max} (log ϵ) 314 (4.32). EI MS (70 eV): *m*/*z* 263 (100) [M]$^+$. Anal. Calcd for $C_{15}H_9N_3S$ (263.3): C, 68.42; H, 3.45; N, 15.96. Found: C, 68.45; H, 3.65; N, 16.23.

6-Cyano-5-(2-naphthyl)-2,2′-bipyridine (15e). In accordance with GP4, **9e** (200 mg, 0.65 mmol) was reacted to yield 179 mg (90%) of **15e**. Mp: 188−190 °C. ^{1}H NMR: δ 7.40 (m, 1H), 7.58 (m, 2H), 7.73 (m, 1H), 7.94 (m, 3H), 8.03 (br.d, 1H), 8.10 (d, 1H), 8.13 (d, 1H), 8.56 (br.d, 1H), 8.72 (m, 1H), 8.76 (d, 1H). ^{13}C NMR: δ 117.3 (C_{quat}), 121.8 (+), 124.2 (+), 124.8 (+), 125.8 (+), 126.9 (+), 127.3 (+), 127.8 (+), 128.5 (+), 128.6 (+), 129.0 (+), 131.5 (C_{quat}), 132.5 (C_{quat}), 133.2 (C_{quat}), 133.4 (C_{quat}), 137.6 (+), 138.8 (+), 141.8 (C_{quat}), 149.0 (C_{quat}), 153.7 (C_{quat}), 155.7 (C_{quat}). IR (KBr): ν (cm^{-1}) 1436, 1541, 2223, 3051. UV (CH_3CN): λ_{max} (log ϵ) 304 (4.43). EI MS (70 eV): *m*/*z* 307 (100) [M]$^+$. Anal. Calcd for $C_{21}H_{13}N_3$ (307.4): C, 82.07; H, 4.26; N, 13.67. Found: C, 82.08; H, 4.39; N, 13.89.

6,6″-Dicyano-5,5″-diphenyl-2,2′,6′2″-terpyridine (16a). General Procedure 5 (GP5). In accordance with GP4, compound **10a** (350 mg, 0.8 mmol) and 20 equiv of bicyclo-[2.2.1]hepta-2,5-diene (1.47 g, 1.72 mL, 16 mmol) were allowed to react. Work up in accordance with GP4 yielded 300 mg (87%) of **16a**. Mp: 287−288 °C. ^{1}H NMR: δ 7.56 (m, 6H), 7.67 (m, 4H), 8.03 (d, 2H, *J* 8.2 Hz), 8.07 (dd, 1H, *J* 7.9 Hz, *J* 7.9 Hz), 8.62 (d, 2H, *J* 7.9 Hz), 8.87 (d, 2H, *J* 8.2 Hz). ^{13}C NMR: δ 117.2 (C_{quat}), 122.5 (+), 124.0 (+), 128.8 (+), 129.1 (+), 129.6 (+), 131.4 (C_{quat}), 135.2 (C_{quat}), 138.6 (+), 141.9 (C_{quat}), 153.5 (C_{quat}), 155.8 (C_{quat}). IR (KBr): ν (cm^{-1}) 1436, 1540, 1575, 2230, 3059. UV (CH_3CN): λ_{max} (log ϵ) 301 (4.60). EI MS (70 eV): *m*/*z* 435 (100) [M]$^+$. Anal. Calcd for $C_{29}H_{17}N_5$ (435.5): C, 79.98; H, 3.93; N, 16.08. Found: C, 79.87; H, 4.06; N, 15.90.

6,6″-Dicyano-5,5″-di(4-methylphenyl)-2,2′,6′2″-terpyridine (16b). Following GP5, **10b** (570 mg, 1.22 mmol) and bicyclo[2.2.1]hepta-2,5-diene (2.24 g, 2.63 mL, 24.4 mmol) gave 480 mg (85%) of **16b**. Mp: 279−280 °C. ^{1}H NMR: δ 2.46 (s, 6H), 7.37 (d, 4H), 7.56 (d, 4H), 8.01 (d, 2H, *J* 8.2 Hz), 8.06 (dd, 1H, *J* 7.9 Hz, *J* 7.9 Hz), 8.61 (d, 2H, *J* 7.9 Hz),8.84 (d, 2H, *J* 8.2 Hz). ^{13}C NMR: δ 21.3 (+), 117.3 (C_{quat}), 122.4 (+), 123.9 (+), 128.6 (+), 129.8 (+), 131.3 (C_{quat}), 132.3 (C_{quat}), 138.4 (+), 138.5 (+), 139.8 (C_{quat}), 141.9 (C_{quat}), 153.5 (C_{quat}), 155.5 (C_{quat}). IR (KBr): ν (cm^{-1}) 1435, 1540, 1575, 2234, 3026. UV (CH_3-CN): λ_{max} (log ϵ) 304 (4.65). EI MS (70 eV): *m*/*z* 463 (100) [M$^+$]. Anal. Calcd for $C_{31}H_{21}N_5$ (463.6): C, 80.33; H, 4.57; N, 15.11. Found: C, 79.96; H, 4.71; N, 15.13.

6,6″-Dicyano-5,5″-di-(4-methoxylphenyl)-2,2′,6′2″-terpyridine (16c). Following GP5, **10c** (150 mg, 0.3 mmol) and bicyclo[2.2.1]hepta-2,5-diene (552 mg, 0.65 mL, 6 mmol) yielded 130 mg (87%) of **16c**. Mp: 263−264 °C. ^{1}H NMR: δ 3.90 (s, 6H), 7.09 (d, 4H), 7.61 (d, 4H), 8.00 (d, 2H, *J* 8.2 Hz), 8.05 (dd, 1H, *J* 7.8 Hz, 7.8 Hz), 8.60 (d, 2H, *J* 7.8 Hz), 8.83 (d, 2H, *J* 8.2 Hz). ^{13}C NMR: δ 55.5 (+), 114.6 (+), 117.5 (C_{quat}), 122.4 (+), 124.0 (+), 127.4 (C_{quat}), 130.1 (+), 131.1 (C_{quat}), 138.3 (+), 138.6 (+), 141.6 (C_{quat}), 153.5 (C_{quat}), 155.2 (C_{quat}), 160.8 (C_{quat}). IR (KBr): ν (cm^{-1}) 1433, 1516, 1609, 2234, 2837, 2955, 3067. UV (CH_3CN): λ_{max} (log ϵ) 312 (4.62). EI MS (70 eV): *m*/*z* 495 (100) [M]$^+$. Anal. Calcd for $C_{31}H_{21}N_5O_2$ (495.6): C, 75.14; H, 4.27; N, 14.13. Found: C, 75.33; H, 4.44; N, 14.18.

6-Carbamoyl-5-phenyl-2-(2′-pyridyl)-3,4-cyclopentenopyridine (17). Cyanocyclopentenopyridine **13a** (0.3 g, 1 mmol) was dissolved in 1 mL of concentrated sulfuric acid and heated at 100 °C for 6 h. The mixture was poured onto ice and was neutralized with concentrated ammonia solution. Precipitated crystals were filtered off, washed with water, and recrystallized from 2-propanol to give 0.29 g (92%) of **17**. Mp: 197−198 °C. ^{1}H NMR (DMSO-d_6, 250 MHz) δ 2.03 (m, 2H), 2.72 (t, *J* 7.7 Hz, 2H), 3.50 (t, *J* 7.7 Hz, 2H), 7.12 (br.s, 1H, amide), 7.32 (m, 6H), 7.72 (br.s, 1H, amide), 8.87 (m, 1H), 8.44 (m, 1H), 8.63−6.67 (m, 1H). IR (KBr): ν (cm^{-1}) 1427, 1577, 1661, 2361, 2953, 3058, 3176, 3400. EI MS (70 eV): *m*/*z* 315 (36) [M]$^+$, 270 (100). Anal. Calcd for $C_{20}H_{17}N_3O$ (315.38): C, 76.17; H, 5.43; N, 13.32. Found: 76.19; H, 5.54; N, 13.30.

6-Carboxy-5-phenyl-2-(2′-pyridyl)-3,4-cyclopentenopyridine Hydrochloride (18). Carbamoylcyclopentenopyridine **17** (0.19 g, 0.6 mmol) was heated under reflux in 11 M HCl for 7 h. The crystals formed after cooling were filtered off and washed with 2 mL of 11 M HCl, yielding **18** (0.16 g, 83%). Mp: 209−210 °C; ^{1}H NMR (DMSO-d_6, 250 MHz) δ 2.04−2.19 (m, 2H), 2.84 (t, *J* 7.3 Hz, 2H), 3.48 (t, *J* 7.3 Hz, 2H), 7.39 (m, 5H), 7.82 (m, 1H), 8.41 (m, 2H), 8.88 (m, 1H). IR (KBr): ν (cm^{-1}) 1448, 1547, 1690, 2970, 3055. EI MS (70 eV): *m*/*z* 316 (M$^+$, 11), 272 (100) [M$^+$ − CO_2]. Anal. Calcd for $C_{20}H_{16}N_2O_2$·HCl: C, 68.08; H, 4.86; N, 7.94. Found: C, 68.07; H, 4.56; N, 7.73.

6-Ethoxycarbonyl-5-phenyl-2-(2′-pyridyl)-3,4-cyclopentenopyridine (19). Carboxylic acid **18** (0.51 g, 1.6 mmol) was heated under reflux in 5 mL of $SOCl_2$ for 7 h. The solvent was removed in vacuo, ethanol (15 mL) was added, and the resulting solution was heated under reflux for 1 h. The mixture was concentrated in vacuo, and the residue was recrystallized from ethanol to give **19** (0.47 g, 87%). Mp: 126−127 °C. ^{1}H NMR (DMSO-d_6, 250 MHz) δ 0.97 (t, *J* 7.5 Hz, 3H), 2.07 (m, 2H), 2.82 (t, *J* 7.5 Hz, 2H), 3.53 (t, *J* 7.5 Hz, 2H), 4.03 (q, *J* 7.5 Hz, 2H), 7.35 (m, 6H), 7.87 (m, 1H), 8.33 (m, 1H), 8.66 (m, 1H). EI MS (70 eV): *m*/*z* 344 (3) [M$^+$], 270 (100). Anal. Calcd for $C_{22}H_{20}N_2O_2$ (344.42): C, 76.72; H, 5.85; N, 8.13.: Found: C, 76.67; H, 5.90; N, 8.17.

6-Hydroxymethyl-5-phenyl-2-(2′-pyridyl)-3,4-cyclopentenopyridine (20). To a solution of the ester **19** (0.41 g, 1.2 mmol) in ethanol (10 mL) was added $NaBH_4$ (0.23 g, 6 mmol). The suspension was stirred at room temperature for 1 h and then heated under reflux for 5 h. The solvent was removed in vacuo, and the residue was kept at 100 °C for 1 h. Crystals formed after cooling were filtered off and washed with water to give 0.27 g of **20** (75%). Mp: 140−141 °C. ^{1}H NMR (DMSO-d_6, 250 MHz) δ 2.03 (m, 2H), 2.70 (t, *J* 7.4 Hz, 2H), 3.46 (t, *J* 7.4 Hz, 2H), 4.38 (br.s, 2H), 4.69 (br.s 1H), 7.40 (m, 6H), 7.88 (m, 1H), 8.40 (m, 1H), 8.65 (m, 1H). EI MS (70 eV): *m*/*z* 302 (M$^+$, 100). Anal. Calcd for $C_{20}H_{18}N_2O$ (302.38): C, 79.44; H, 6.00; N, 9.26. Found: C, 79.44; H, 5.94; N, 9.40.

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Supporting Information Available: ^{1}H NMR spectra of compound **2c** and **3b** in DMSO-d_6; structure of complex **14b** in the crystal. This material is available free of charge via the Internet at http://pubs.acs.org.

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