A Synthesis of Conjugatively Bridged Bis- and Tris-5-(2,2′-Bipyridines): Multitopic Metal Ion-Binding Modules for Supramolecular Nanoengineering

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An efficient preparation of linear and curved bis- and branched tris-5-(2,2′-bipyridines) of nanoscopic dimensions possessing rigid conjugated bridges is presented. The synthesis, which avoids the need of protection/deprotection methodology, utilizes central bridge precursors which are outwardly di- and trifunctionalized with a 5-(2-chloropyridine) synthon via a chemoselective palladium-catalyzed Sonogashira or Negishi cross-coupling protocol to yield the bridged linear (**5a**−**c**, **5f**,**g**) and curved (**6**, **7**) bis- and branched (**8**) tris-5-(2-chloropyridines). Under more forcing conditions, the ethyne-bridged 5-(2-chloropyridines) undergo the Stille cross-coupling reacton with 2-trimethylstannylpyridines to afford the conjugatively bridged linear (**1a**,**b**, **1g**−**j**) and curved (**2a**,**b**, **3a**,**b**) bis- and branched, (**4a**,**b**) tris-5-(2,2′-bipyridines) in good overall yields. The phenyl- and biphenyl-bridged linear bis-5-(2,2′-bipyridines) (**1c**−**f**) were best prepared from the bis-5-(2-bromopyridines) (**5d**,**e**) to ensure completion of the Stille cross-coupling reactions. The Stille cross-couplings showed a marked substituent effect in which the terminally phenylated bis- and tris-5-(2,2′-bipyridines) were formed in higher yields than the methyl-substituted analogues with the same bridge. The advantages of the methodology lie in its synthetic convenience and adaptibility for creating multitopic metal ion-binding scaffolds with a potentially very large variety of bridging units and substituents on the terminal pyridine rings. The bridged 5-(2-chloropyridines) may also serve as precursors for the fabrication of metal ion-coordinated conjugated polymers.

Introduction

Organic polymers and oligomers which possess electronically conjugated backbones currently fulfill a pivotal role in the design and generation of new materials.[1a−e] The unique physicochemical properties exhibited by such systems have encouraged the development of a cornucopia of technologically diverse and industrially important applications. For example, oligo- and polythiophenes, pyrroles, pyridines, quinolines, benzobisthiazoles, phenylenes, and similar substrates incorporating alternate ethene or ethyne groups have been demonstrated to function as organic electronic conductors and photoconductors,[1a−e,2a,b] electroluminescent materials for light-emitting diodes,[3] field-effect transistors,[4] laser emitters,[5a−c] NLO substrates,[6a,b] and materials with high tensile strength and heat resistance.[7] Within the field of nanoengineering, the structural rigidity of phenylacetylene oligomers has been successfully exploited for the construction of a range of nanosized hydrocarbon molecular architectures such as rings, cages, and dendritic macromolecules.[8] These have also enjoyed uses as modules for crystal engineering,[9] liquid crystals,[10] and organic antenna arrays.[11]

In light of the aforementioned considerations, conjugated organic polymers and oligomers which incorporate metal ions as integral structural units would represent especially interesting synthetic targets with respect to materials science applications. Substrates of this type would be expected to display a rich variety of physicochemical properties in addition to those discussed above, such as, for example, multiple redox behavior and optical, magnetic, mechanical, sensing, and catalytic activity. Other possibilities concern the unique characteristics of particular metal ions, which may be harnessed to fine-tune the electronic properties of the conjugated organic component in order to perform a desired function.

The preparation of conjugated organic structures comprising electronically communicating metal ions therefore requires the prior incorporation of metal ion-binding sites, which cause minimum disruption of the conjugation pathway and which are able to function as ligands to a wide variety of metal cations. An ideal candidate for this purpose is the 2,2′-bipyridine moiety which adopts a rigid,

(1) (a) *Handbook of conducting polymers*, 2nd ed.; Skotheim, T. A., Ed.; Dekker: New York, 1997. (b) *Conjugated Conducting Polymers*; Kies, H., Ed.; Springer Series in Solid-State Physics; Springer: Berlin, 1992; Vol. 102. (c) *Conjugated polymers*; Brédas, J. L., Sylbey, R., Eds.; Kluwer: Dordrecht, The Netherlands, 1991. (d) Miller, J. S. *Adv. Mater.* **1993**, *5*, 671. (e) Yamamoto, T. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 999.

(2) (a) Kanatzidis, M. G. *Chem. Eng. News*, **1990**, 36. (b) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

(3) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402.

(4) Horowitz, G. *Adv. Mater.* **1998**, *10*, 365.

(5) (a) Berggren, M.; Dodabalapur, A.; Bao, Z.; Slusher, R. E. *Adv. Mater.* **1997**, *9*, 968. (b) Kallinger, C.; Hilmer, M.; Haugeneder, A.; Perner, M.; Spirkl, W.; Lemmer, U.; Feldmann, J.; Scherf, U.; Müllen, K.; Gombert, A.; Wittwer, V. *Adv. Mater.* **1998**, *10*, 920. (c) Johansson, N.; Salbeck, J.; Bauer, J.; Weissörtel, F.; Bröms, P.; Andersson, A.; Salaneck, W. R. *Adv. Mater.* **1998**, *10*, 1136.

(6) (a) Nalwa, H. S. *Adv. Mater.* **1993**, *5*, 341. (b) Brédas, J. L.; Adant, C.; Tackx, P.; Persoons, A.; Pierce, B. M. *Chem. Rev.* **1994**, *94*, 243.

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(8) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402.

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(10) Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 2655.

(11) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635.

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conjugated planar conformation when complexed.[12] It is characterized by an extensive coordination chemistry and a rich electro- and photophysical behavior of its metal complexes.[12,13a,b] A limited number of recent reports describing the preparation of conjugated organic polymers incorporating the 2,2′-bipyridine ligand and some of its metal complexes have shown that materials of this type do indeed display interesting properties such as unusual photophysics,[14] redox activity,[15] metal ion-sensing,[16a−c] and photocatalytic,[17] photoconductive,[18] and photorefractive[19] behavior. However, despite such promising investigative potential, a study of the properties of conjugated oligomeric architectures of nanometric dimensions, possessing spatially precisely defined arrays of metal ions other than short, linear binuclear complexes, has received little attention.[20a−e] This may in part result from the circuitous synthetic procedures and solubility problems associated with the preparation of oligomeric structures of appropriate geometries with the inclusion of large numbers of metal ion-binding sites.

Synthesis

Ligand Design. High molecular weight organic oligomeric and dendritic materials are most frequently constructed using two main design strategies, i.e., that of convergent and divergent syntheses which may be used separately or in combination. In the convergent approach, a section or segments of the desired architecture are prepared initially and then connected together to a central core unit in the final step of the synthesis. In the divergent approach, the target molecule is built outwardly in sequence from a difunctionalized or multiply functionalized core. A combination of the two strategies results in molecular doubling at each iteration, enabling the creation of very high molecular weight oligomers and normally requires extensive use of protection/deprotection methodology.

As a first step toward the creation of nanosized coordination arrays based upon rigid, conjugated organic frameworks possessing multitopic metal ion-binding domains, the divergent approach[21] was envisioned as providing the shortest preparative pathway to materials of this type. Structurally simple ethyne, phenyl, biphenyl, and aryldi- and -triethyne-bridged bis- and tris-5-(2,2′-bipyridines) were selected as model targets for this study owing to their ease of construction, enhanced conjugation, and the favorable solubility characteristics of the smaller ligand architectures.[22a−e] Specifically, the construction sequence starts with a central bridging scaffold or core which is outwardly chemoselectively functionalized with 2-chloropyridine units. These are then reacted further with appropriately substituteded pyridine derivatives to form the metal ion-binding 2,2′-bipyridine moieties in the last step of the synthesis.

This method of preparation of bridged 5-(2,2′-bipyridines) has many advantages in terms of brevity and adaptibility which are detailed as follows: (i) Temperature-controllable chemoselective reactions are used for ligand construction, which avoid the need for protection/deprotection steps. In principle, the reaction sequence could be iterated through multiple cycles to generate larger multitopic oligomers if, for example, trialkylsilylethyne-substituted pyridines were used to form the bipyridine units. (ii) The methodology avoids the need for the prior syntheses of unsymmetrically functionalized 2,2′-bipyridines. In the case where differing combinations of bridging groups and terminal pyridine functionalities are required, a new bipyridine synthesis would have to be accomplished for each bridge/terminal functionality combinaton. This would involve time-consuming and repetitive multistep syntheses. (iii) Formation of the bipyridine units in the final step of the synthesis permits direct incorporation of a wide variety of terminal substituents into the bridged 5-(2,2′-bipyridine) products by way of readily accessible and appropriately functionalized pyridine synthons. Solubilizing substituents may thus be readily introduced, thereby avoiding the solubility problems which are frequently encountered with higher molecular weight oligomers incorporating aromatic and heterocyclic rings.[23] Also, in cases where terminal substituents may complicate workup conditions, this problem will only be encountered in the last synthetic step. (iv) The halopyridyl-functionalized bridging units will serve as monomers for the generation of 2,2′-bipyridine-incorporated polymers, thereby maximizing the synthetic utility of the bridged 5-(2,2′-bipyridine) precursors.

Subsequent experimental investigations fully justified the above considerations and showed that the bridged bis- and tris-5-(2,2′-bipyridines) **1a**−**j**, **2a**,**b**, **3a**,**b**, and

(12) Constable, E. C. *Adv. Inorg. Chem.* **1989**, *34*, 1.

(13) (a) Kalyanasundaram, K. *Photochemistry of polypyridine and porphyrin complexes;* Academic Press: London, 1992. (b) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759.

(14) Ley, K. D.; Whittle, C. E.; Bartberger, M. D.; Schanze, K. S. *J. Am. Chem. Soc.* **1997**, *119*, 3423.

(15) Grosshenny, V.; Harriman, A.; Gisselbrecht, J.-P.; Ziessel, R. *J. Am. Chem. Soc.* **1996**, *118*, 10315.

(16) (a) Swager, T. M.; Zhu, S. S. *J. Am. Chem. Soc.* **1997**, *119*, 12568. (b) Wang, B.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1997**, *119*, 12. (c) Kimura, M.; Horai, T.; Hanabusa, K.; Shirai, H. *Adv. Mater.* **1998**, *10*, 459.

(17) Yamamoto, T.; Maruyama, T.; Zhou, Z.-hua.; Ito, T., Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J. Am. Chem. Soc.* **1994**, *116*, 4832.

(18) Peng, Z.; Yu, L.; *J. Am. Chem. Soc.* **1996**, *118*, 3777.

(19) Peng, Z.; Gharavi, A. R.; Yu, L.; *J. Am. Chem. Soc.* **1997**, *119*, 4622.

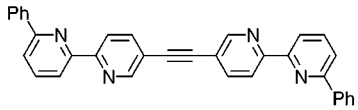
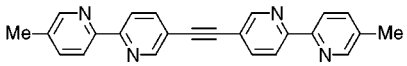
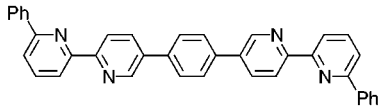
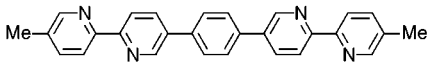
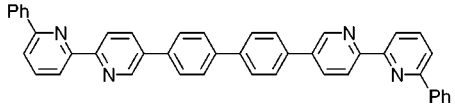
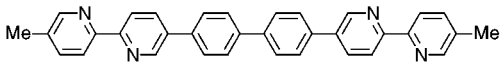
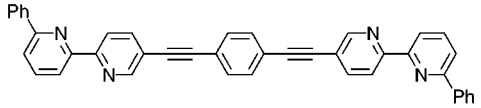
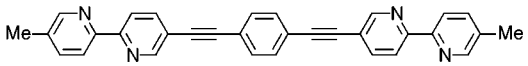
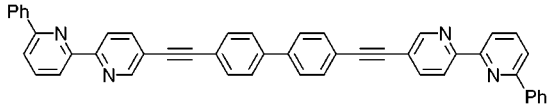
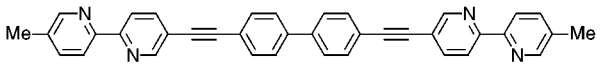
(20) For reports on the syntheses of bis-2,2′-bipyridines with short conjugated bridges, and the properties of their dinuclear metal complexes see; (a) Kocian, O.; Mortimer, R. J.; Beer, P. D. *Tetrahedron Lett.* **1990**, *31*, 5069. (b) Benniston, A. C.; Goulle, V.; Harriman, A.; Lehn, J.-M.; Marczinke, B. *J. Phys. Chem.* **1994**, *98*, 7798. (c) Baba, A. I.; Ensley, H. E.; Schmehl, R. H. *Inorg. Chem.* **1995**, *34*, 1198. (d) Strouse, G. F.; Schoonover, J. R.; Duesing, R.; Boyde, S.; Jones, Jr. W. E.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 473. (e) Harriman, A.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1996**, 1707 and references therein.

(21) For a discussion concerning generalized strategies for oligomer synthesis, see for example: Moore, J. S.; Prince, R. B. In *Materials Science and Technology, A Comprehensive Treatment; Synthesis of Polymers;* Cahn, R. W., Haasen, P., Kramer, E. J., Eds.; Schlüter, A.-D., Vol. Ed.; Wiley-VCH: 1999, pp 13−36.

(22) For early reports on the direct ethynylation of brominated 2,2′-bipyridines using the Sonogashira protocol, see: (a) Butler, I. R.; Soucy-Breau, C. *Can. J. Chem.* **1991**, *69*, 1117. (b) Suffert, J.; Ziessel, R. *Tetrahedron Lett.* **1991**, *32*, 757. This methodology has been extended to the syntheses of linear, terminally *unfunctionalized* bis-(2,2′-bipyridine) ligands bearing ethyne and diethyne bridges via a more convergent approach. (c) Ziessel, R. Suffert, J.; Youinou, M.-T. *J. Org. Chem.* **1996**, *61*, 6535. (d) Grosshenny, V.; Romero, F. M.; Ziessel, R. *J. Org. Chem.* **1997**, *62*, 1491. An identical methodology has been communicated to yield terminally unfunctionalized aryldiethyne-bridged bis(2,2′-bipyridines), but full product characterization and experimental details were not reported. (e) El-Ghayoury, A.; Ziessel, R. *Tetrahedron Lett.* **1997**, *38*, 2471.

(23) It must be emphasized that the poor solubility expected of larger ligand architectures may not necessarily hamper the processibility and usefulness of the resulting metal complexes. In the case of ligand scaffolds coordinated by charge−neutral metal complexes, ancillary metal-bound ligands may act as the solubilizing components. For ionic complexes, the couterions may endow solubility-enhancing properties to the resulting superstructure.

Table 1. Synthesis and Structure of Conjugatively Bridged Linear Bis-5-(2,2′-bipyridines)

Reactants	Product no.	Product	Length (Å)[a]
5a + 18a	**1a**		25.8 (10.9)
5a + 18b	**1b**		23.7 (10.9)
5d + 18a	**1c**		28.0 (13.0)
5d + 18b	**1d**		25.9 (13.0)
5e + 18a	**1e**		32.0 (17.3)
5e + 18b	**1f**		30.3 (17.3)
5f + 18a	**1g**		32.2 (17.5)
5f + 18b	**1h**		30.6 (17.5)
5g + 18a	**1i**		36.8 (21.8)
5g + 18b	**1j**		34.9 (21.8)

[a] The length (including van der Waals surfaces) is defined as the Me−Me distance for **1b**, **1d**, **1f**, **1h**, and **1j**, and the distance between the *para* hydrogens of the terminal phenyl substituents in **1a**, **1c**, **1e**, **1g**, and **1i**. Distances between the metal ion-binding sites are included in parentheses. The lengths were calculated for the linear bridged bis-5-(2,2′-bipyridines) with the all-planar, all-transoid conformations shown above, in the gas phase, using the MM3 force field with MacroModel version 5.5 (Columbia University, New York).

4a,**b** could be rapidly constructed in relatively few steps starting from the common building block, 2-chloro-5-iodopyridine (**9**) (Table 1, Schemes 1−3). Pyridine **9** was selected for two reasons. First, the 5-iodo substituent is more reactive toward palladium-catalyzed organometallic cross-coupling reactions than the 2-chloro group. This ensures preferential chemoselective reactivity at the 5-position rather than the normally more reactive 2-position to yield the bridged bis-2-chloropyridine precursors **5a**−**c**, **5f**,**g**, and **6**−**8**.[24] These can be further homologated to the desired bridged bis-5-(2,2′-bipyridines) via a Stille cross-coupling reaction with 2-trialkylstannylpyridines under more forcing conditions in the last step of the synthesis.[25a,b] Second, **9** could be prepared in two steps from 2-aminopyridine on a 50−100 g scale and in high overall yield by electrophilic iodination followed by a diazotization−chlorination protocol.[26a−c] The bridged bis-5-(2,2′-bipyridine) terminal pyridine ring substituents chosen for this study were 5′-methyl and 6′-phenyl groups. These were selected to investigate the influence of widely differing steric and electronic substituent effects upon the Stille cross-coupling reactions.

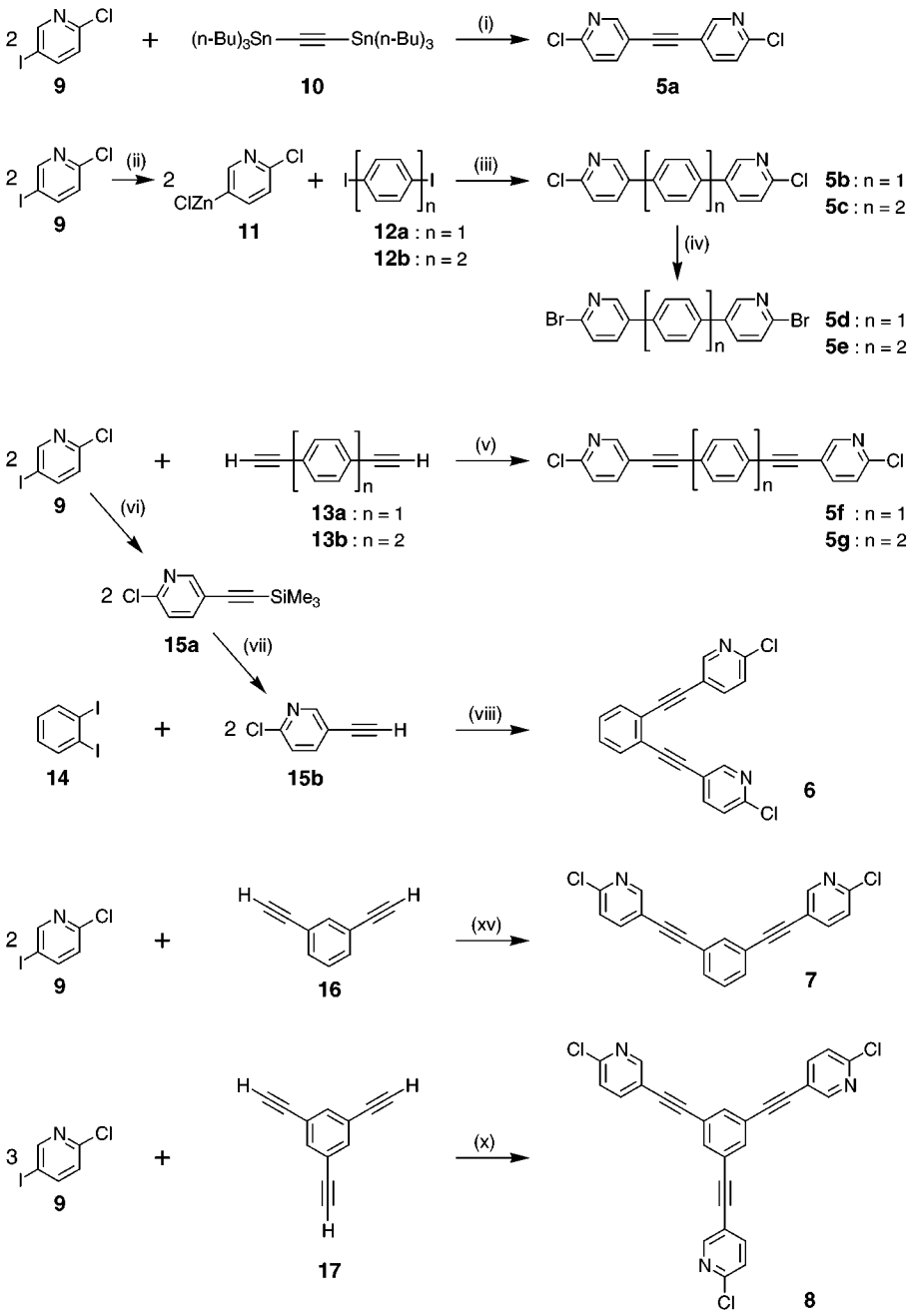
Synthesis of Conjugatively Bridged Bis- and Tris-5-(2-chloropyridines). 1, 2-bis[5-(2-chloropyridyl)]ethyne (**5a**) comprises a single acetylene connecting the pyridine rings and therefore represents the shortest bridged bischloropyridine prepared in this study. Previous reports on the syntheses of dibromo-, dimethoxy-, and dithiomethoxy-substituted analogues of **5a** employed Wadsworth−Emmons and McMurry methodology to give first the corresponding 1,2-bis[5-(2-bromopyridyl)], 1, 2-bis-[5-(2-methoxypyridyl)]- and 1,2-bis[5-(2-thiomethoxypyridyl)]ethenes. This required the initial preparation of the appropriately substituted pyridine-5-carboxaldehydes and diethyl [5-methyl-(2-bromopyridyl)]phosphonate. Treatment of the ethenes with bromine followed by dehydrobromination with potassium *tert*-butoxide afforded the 1,2-bis[5-(2-bromopyridyl)]-, 1,2-bis[5-(2-methoxypyridyl)]-, and 1,2-bis[5-(2-thiomethoxypyridyl)]ethynes

(24) 2-Chloro-3-iodopyridine and 2,6-dimethyl-3-iodo-4-chloropyridine are both reported to undergo selective palladium-catalyzed ethynylation at the 3-iodo substituent: Sakamoto, T.; Kondo, Y.; Watanabe, R.; Yamanaka, H. *Chem. Pharm. Bull.* **1986**, *34*, 2719.

(25) For examples of 2,2′-bipyridine syntheses via Stille cross-couplings with 2-chloropyridines, see for example: (a) Ghadiri, M. R.; Soares, C.; Choi, C. *J. Am. Chem. Soc.* **1992**, *114*, 825. (b) Zhang, B.; Breslow, R. *J. Am. Chem. Soc.* **1997**, *119*, 1676.

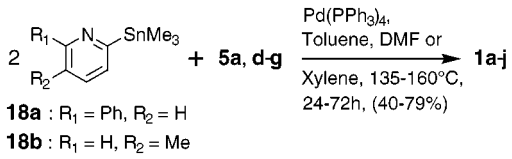
(26) (a) Clayton, S. C.; Regan, A. C. *Tetrahedron Lett.* **1993**, *34*, 7493. (b) Hama, Y.; Nobuhara, Y.; Aso, Y.; Otsubo, T.; Ogura, F. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1683. (c) Magidson, O.; Menschikoff, G. *Chem. Ber.* **1925**, *58*, 113.

Scheme 1[a]



[a] Reaction conditions and yields: (i) $Pd(PPh_3)_4$, DMF, 105 °C, 24 h (77%); (ii) 1 equiv of *n*-BuLi, THF, −90 °C, then $ZnCl_2$; (iii) $PdH_2(PPh_3)_2$, THF, 20 °C (68%, **5b**; 58%, **5c**); (iv) $POBr_3$, 170 °C, 15−20 h (77%, **5d**, 90%, **5e**); (v) $PdCl_2(PPh_3)_2$, CuI, Et_3N and/or Py, 25−70 °C, 48 h (68%, **5f**; 78%, **5g**); (vi) $PdCl_2(PPh_3)_2$, CuI, Et_3N, TMS(ethyne), 20 °C, 48 h (94%); (vii) 0.01 M aqueous NaOH, THF, MeOH, 20 °C, 24 h (82−95%); (viii) $Pd_2(dba)_3$, CuI, PPh_3, Et_3N, 40 °C, 14 h (75%); (xv) $PdCl_2(PPh_3)_2$, CuI, Et_3N, 20−75 °C, 48 h (59%); (x) see (xv) (94%).

Scheme 2

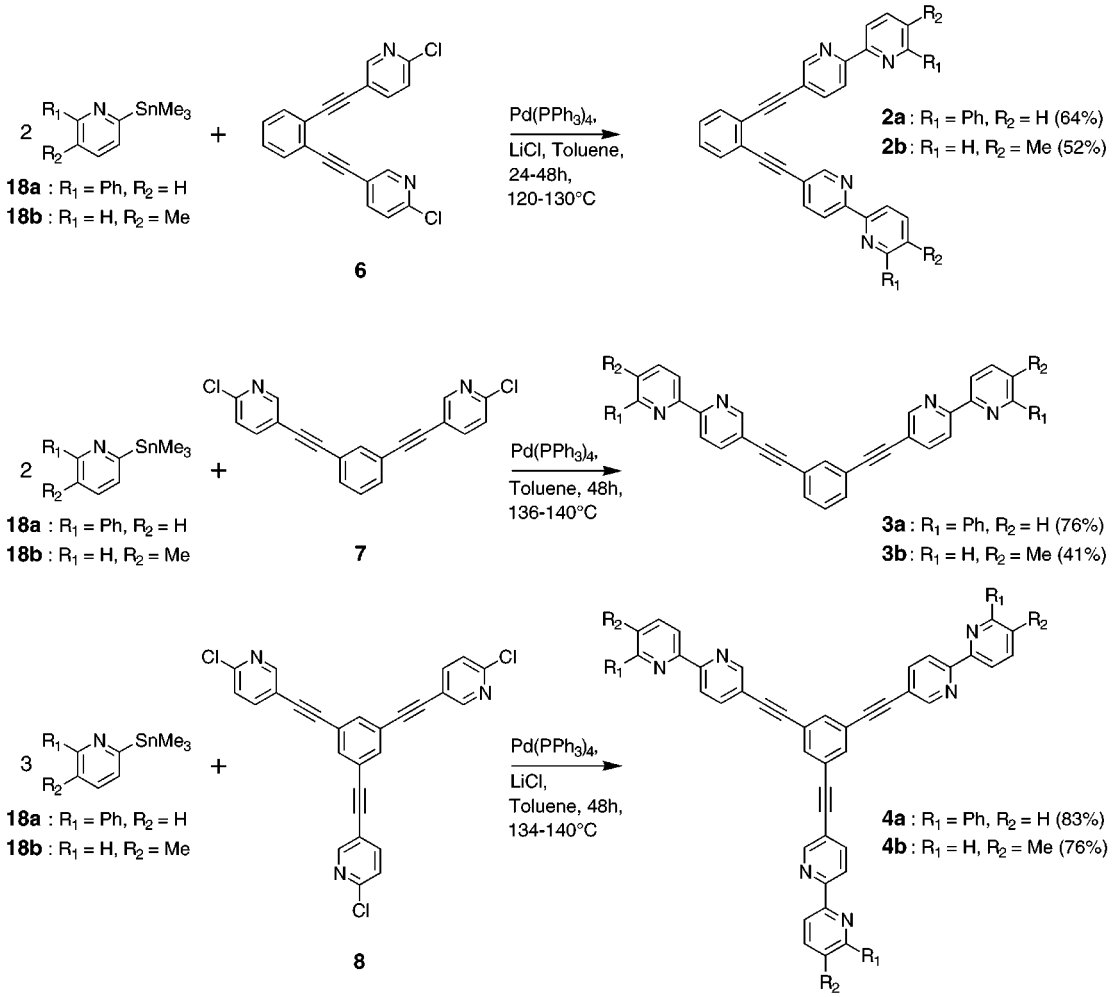


in moderate overall yields.[27] However, the circuitous routes to the substituted pyridine precursors and lack of adaptability for variation in structure of the bridging unit suggested the necessity of a more general approach from readily accessible starting materials. 1,2-Bis(tributylstannyl)ethyne (**10**) has been demonstrated to function as an acetylene synthon for the generation of a range of symmetrically substituted diphenylethynes via the Stille cross-coupling protocol.[28] Using this methodology, reaction of ≥2 equiv of **9** with **10** in the presence of a catalytic amount of $Pd(PPh_3)_4$ in toluene solution gave a 63% isolated yield of **5a**. Changing the solvent to DMF resulted in an increase in yield to 77% after an identical workup procedure. Product **5a** can therefore be prepared in three steps from commercially available materials in high overall yield. This result represents a considerable

(27) Windscheif, P.-M.; Vögtle, F. *Synthesis* **1994**, 87.

(28) Cummins, C. H. *Tetrahedron Lett.* **1994**, *35*, 857.

Scheme 3



synthetic improvement over the previously reported methodology for the generation of substituted bis(pyridyl)ethynes and may provide a general method of access to functionalized bisheterocyclic ethynes.

The Sonogashira cross-coupling protocol was found to provide the shortest and most convenient route to the linear 1,4-diethynylphenyl- and 4,4′-diethynyl-1,1′-biphenyl-bridged bis-5-(2-chloropyridines) **5f** and **5g**, and the curved 1,3-diethynylphenyl-bridged bis-5-(2-chloropyridine) **7**.[29] Thus, reaction of ≥2 equiv of **9** with the readily accessible terminal diethynes **13a**,**b** and **16** in the presence of catalytic quantities of $PdCl_2(PPh_3)_2$ and CuI afforded the bridged bis-5-(2-chloropyridines) **5f**, **5g**, and **7** in 68%, 78%, and 59% isolated yields, respectively. The reactions yielding **5f** and **7** were conducted in triethylamine and that of **5g** was conducted in pyridine−triethylamine (1:4.5) to avoid precipitation of semireacted species. The yields were unoptimized and the products easily purified by recrystallization from the appropriate solvent. Interestingly, the Sonogashira methodology could also be successfully applied to the synthesis of the branched species 1,3,5-tris(5-ethynyl-2-chloropyridyl)-benzene (**8**). Reaction of 1,3,5-triethynylbenzene (**17**) with ≥3 equiv of **9** under conditions identical to those used for the preparation of **5f** and **7** afforded **8** in 94% isolated yield.[30]

Parallel experimental investigations showed 2-chloro-5-ethynylpyridine (**15b**) to be an excellent synthon for introducing the 5-ethynyl-2-chloropyridyl group into halogenated aromatic substrates via the Sonogashira protocol.[31] **15b** could be conveniently prepared in two steps from **9**, first upon reaction of a 1:1 ratio of (trimethylsilyl)ethyne and **9** with catalytic quantities of $PdCl_2(PPh_3)_2$ and CuI in triethylamine to yield 2-chloro-(5-trimethylsilylethynyl)pyridine (**15a**). Second, aqueous hydroxide mediated hydrolytic deprotection of **15a** afforded **15b** in 77−89% overall yield from **9**. Therefore, to explore the possible advantages of using **15b** in place of the dialkynyl precursors for the syntheses of bridged 5-(2-chloropyridines), it was decided to prepare the acutely bent bridged bis-5-(2-chloropyridine) **6** via **15b**. However, the reaction between 1,2-dibromobenzene and ≥2 equiv of **15b** at 70 °C using conditions similar to those used for the preparation of **5f**, **7**, and **8** above provided only a poor (<20%) yield of **6** after workup. A significant improvement in the isolated yield of **6** to 75% was finally

(29) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467.

(30) Syntheses of 1,3,5-tris(pyridylethynyl)benzenes appear to be rare in the literature. For a preparation of 1,3,5-tris(4-pyridylethynyl)-benzene, see: Anderson, H. L.; Walter, C. J.; Vidal-Ferran, A.; Hay, R. A.; Lowden, P. A.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2275.

(31) The reaction of **15b** with iodobenzene and 1-bromo-4-(trimethylsilylethynyl)benzene under Sonogashira conditions provided the respective 2-chloro-5-(ethynylphenyl)pyridine and 2-chloro-5-(1-ethynyl-4-trimethylsilylethynylphenyl)pyridine in >70% isolated yields: P. N. W. Baxter, unpublished results.

obtained upon using 1,2-diiodobenzene (**14**) in place of the dibromo analogue, changing the catalyst system to a 1:4.6:1 ratio of $Pd_2(dba)_3/PPh_3/CuI$, reducing the reaction temperature to 40 °C, and reducing the reaction time from 48 to 14 h.

The syntheses of the 1,4-phenyl- and 4,4′-(1,1′-biphenyl) bridged bis-5-(2-chloropyridines) **5b** and **5c** relied upon the utilization of an efficient chemoselective heteroaryl−aryl cross-coupling strategy. The three currently most widely used methods for sp^2-sp^2 carbon−carbon bond formation between unsymmetrically substituted aromatic substrates comprise the palladium-catalyzed Stille,[32a−d] Suzuki,[32b−d, 33] and transmetalation cross-coupling protocols.[32b−d] The latter transmetalation methodology was selected as the preferred route to **5b** and **5c** as it avoids the need for prior isolation and purification of the metalated aromatic component. The metalated entity is normally generated in situ upon reaction between an initially formed aryllithium species and a zinc, magnesium, or copper salt. The metalate is then added directly to the aryl or heteroaryl halide and palladium catalyst to give finally the cross-coupled product in the same pot. An experimental investigation into the reactivity of metalated **9** with aryl iodides showed the organozincate (Negishi) adaptation to be the most superior transmetalation methodology owing to its mild reaction conditions and freedom from side reactions.[34] Thus, the iodine substituent of **9** can be cleanly chemoselectively lithiated at low temperature with 1 equiv of *n*-butyllithium to give 2-chloro-5-lithiopyridine, and this can be converted to 2-chloro-5-chlorozincatopyridine (**11**) upon addition of 1 equiv of $ZnCl_2$ in Et_2O solution. The zincate **11**, which is stable at ambient temperature, then underwent a palladium-catalyzed double cross-coupling reaction with 0.5 equiv of the diiodides **12a** and **12b** to afford **5b** and **5c** in 68% and 58% isolated yields, respectively. The reaction proceeds efficiently without the need for external heating and appears to be unreactive toward the 2-chloro substituents of **11**, **5b**, and **5c**.[35]

Having defined optimal reaction pathways for the syntheses of the bridged bis- and tris-5-(2-chloropyridines) **5a**−**c**, **5f**,**g**, and **6**−**8**, an exploration into their use as precursor substrates for the preparation of terminally substituted bridged bis-5-(2,2′-bipyridines) was next undertaken.

Synthesis of Symmetrically Substituted Conjugatively Bridged Bis- and Tris-5-(2,2′-bipyridines). The successful synthesis of the bridged bis- and tris-5-(2-chloropyridines) relies upon the fact that the 2-chloro substituent of **9** and its bridged derivatives is relatively unreactive toward cross-coupling chemistry at temperatures between 20 and 70 °C, in the presence of the conventional triphenylphosphine-ligated palladium catalysts.[24] At higher temperatures, the unactivated 2-chloropyridyl group can be induced to undergo the Stille cross-coupling reaction with 2-trialkylstannylpyridines to give substituted 2,2′-bipyridines.[25a,b] The temperature-dependent reactivity of the 2-chloropyridyl group therefore allows the sequential homologative construction of oligopyridyl structures while avoiding the need for introducing additional functional group protection/deprotection steps. The synthetic economy of this approach provided a rapid and efficient method of access to a wide range of conjugatively bridged 5-(2,2′-bipyridines) via multiple Stille cross-couplings with the bridged 5-(2-chloropyridine) precursors.

Thus, reaction between the ethyne-containing bridged bis-5-(2-chloropyridines) **5a**, **5f**,**g**, and **7** and an excess of 2-trimethylstannyl-6-phenylpyridine (**18a**) or 2-trimethylstannyl-5-methylpyridine (**18b**) with $Pd(PPh_3)_4$ as catalyst and at a temperature of greater than 120 °C afforded the linearly bridged bis-5-(2,2′-bipyridines) **1a**,**b** and **1g**−**j**, and curved **3a** and **3b** in good yields. The products were obtained in higher purity and about 10% higher yields when trimethylstannylpyridines were used in place of their tri-*n*-butylstannyl analogues. In the majority of examples investigated, the use of toluene as reaction solvent provided products of higher purity than DMF, although the yields were unaffected. In cases where the limited solubility of the product precluded purification by column chromatography, solvent washing and recrystallizations sufficed to yield material of analytical purity. During the course of each reaction, color darkening and sometimes palladium mirror formation occurred. Catalyst decomposition was therefore taking place, and resulted in part from the relatively high temperatures employed. However, the product yields remained unchanged upon adding extra catalyst or by continual infusion of the catalyst into the reaction mixture over a 24 h period. Changing the catalyst from $Pd(PPh_3)_4$ to $PdCl_2(PPh_3)_2$ or $Pd_2(dba)_3/AsPh_3$ (1:8) also had no affect upon the product yield, although the latter system exhibited marked reaction rate enhancements.[36]

Studies concerning the influence of additives on the Stille cross-coupling reaction have demonstrated that the presence of LiCl,[37a,b] transition metal salts,[38] and oxides[39] can cause significant increases in product yields. In an attempt to improve the yields of **2b** and **3b**, the reactions were therefore repeated under identical conditions in the presence of excess LiCl. However, after identical workup procedures the reactions conducted with added LiCl did not show any significant increase in the isolated yield of the respective bridged bis-5-(2,2′-bipyridines). The origin of the moderate yield of **2b** may derive in part from the enhanced reactivity of aryl-1,2-diethynes toward thermally induced cyclizations and polymerizations.[40a−c] However, the presence of LiCl did influence the yield of **2a**, which increased from 46% to 64% when excess LiCl was added to the reaction mixture. The yields of **4a** and **4b** were also sensitive to the presence of LiCl, and increased

(32) (a) Mitchell, T. N. *Synthesis* **1992**, 803. (b) Kalinin, V. N. *Synthesis*, **1992**, 413. (c) Undheim, K.; Benneche, T. *Adv. Heterocycl. Chem.* **1995**, *62*, 305. (d) Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263.

(33) Yang, Y.; Martin, A. R. *Acta Chem. Scand.* **1993**, *47*, 221.

(34) Negishi, E.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, *42*, 1821.

(35) If the Sonogashira and Negishi cross-coupling reactions with **13a** and **12a**, respectively, are performed using 2-bromo-5-iodopyridine in place of **9**, then chemoselectivity is lost and product mixtures are obtained, which arise from reaction at both the 2- and 5-pyridine ring positions.

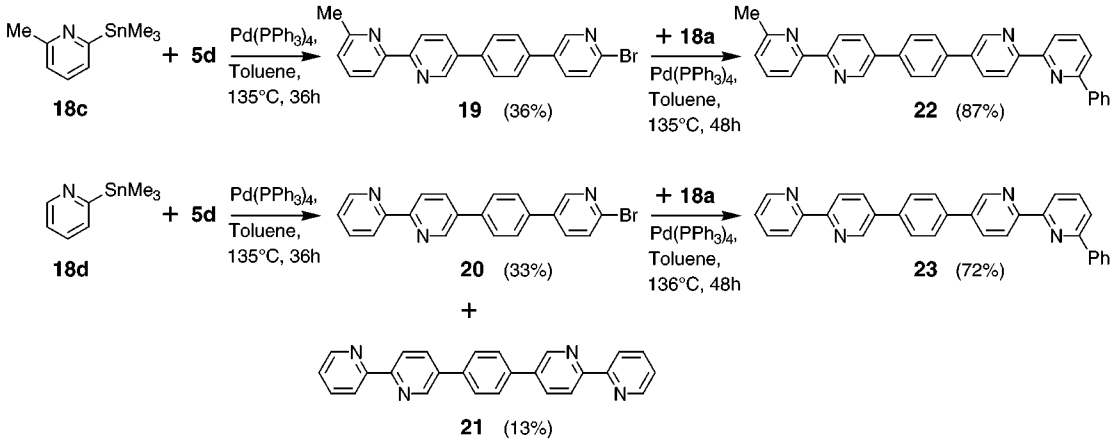
(36) For a detailed investigation into the influence of the catalyst upon the rate, yield, and temperature dependence of the Stille cross-coupling reaction, see: Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585.

(37) (a) Fujita, M.; Oka, H.; Ogura, K. *Tetrahedron Lett.* **1995**, *36*, 5247. (b) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478 and references therein.

(38) Evans, D. A.; Black, W. C. *J. Am. Chem. Soc.* **1993**, *115*, 4497.

(39) Gronowitz, S.; Björk, P.; Malm, J.; Hörnfeldt, A.-B. *J. Organomet. Chem.* **1993**, *460*, 127.

Scheme 4



from, respectively, 73% and 64% to 83% and 76% when repeated with added LiCl.

Initial investigations into the syntheses of the bis-5-(2,2′-bipyridines) with 1,4-phenyl and 4,4′-biphenyl bridges revealed that the Stille cross-coupling reactions between **5b**, **5c**, and **18b** afforded the methyl-substituted **1d** and **1f** in only ≤20% yields. The crude reaction products comprised mainly of unreacted **5b**, **5c**, and bridged 5-(2-chloropyridine)-5-(2,2′-bipyridyl) species arising from reactions of 1:1 stoichiometry between **18b** and the bridged bis-2-chloropyridines **5b** and **5c**. It was therefore decided to prepare all the 1,4-phenyl- and 4,4′-biphenyl bridged bis-5-(2,2′-bipyridines) from the more reactive dibromo-substituted analogues **5d** and **5e**. Thus, heating **5b** and **5c** in excess $POBr_3$ resulted in efficient halogen metathesis to give the dibromo adducts **5d** and **5e**. Finally, reaction of **5d** and **5e** with more than 2 equiv of **18a** and **18b** in the presence of catalytic quantities of $Pd(PPh_3)_4$ afforded **1c**−**f** in 63−71% isolated yields. DMF and xylene were used as solvents in these examples to achieve higher reflux temperatures and thereby drive the reactions to completion. The lower reactivity of **5b**,**c** toward the Stille cross-coupling reaction with **18a** compared to the bis- and tris-5-(2-chloropyridines) incorporating ethyne moieties in their bridges (**5a**, **5f**,**g**, **6**−**8**) is currently unclear, but may result from insufficient electronic activation of the 2-chloropyridyl groups.[41]

Particularly noteworthy is that a correlation exists between the position and identity of the substituent on the 2-trimethylstannylpyridine and yield of bridged bis-5-(2,2′-bipyridine) in all cases studied. For a given bridging unit, Stille cross-couplings with **18a** gave consistently higher yields of bis-2,2′-bipyridines with 6-phenyl substituents on the terminal pyridine rings, compared to the analogous reactions with **18b**. The origin of this phenomenon may be related to the rate of catalyst destruction via coordination to the product as it is formed during the course of the reaction. In the case of reactions with **18a**, the *o*-phenyl substituent may sterically disfavor binding of the product to the catalyst. This would result in an increased catalyst lifetime, thereby allowing the formation of larger amounts of product. Electronic factors may also be operative.

Synthesis of Unsymmetrically Substituted 1,4-Phenyl-Bridged Bis-5-(2,2′-bipyridines). The marked reluctance of **5b** and **5c** to undergo Stille cross-couplings at both chlorine substituents suggested that the conditions of this reaction may possibly be adjusted to provide access to 1,4-phenylene-bridged 5-(2-chloropyridine)-5-(2,2′-bipyridyl) species in synthetically useful yields. The remaining halogen would then be available for further homologations to unsymmetrically substituted bridged bis-2,2′-bipyridines or longer entities. The 2-trimethylstannylpyridines **18c** and **18d** and bis-2-chloropyridine **5b** were chosen for this investigation because they afforded reaction products of sufficient solubility to be separated by column chromatography. However, only low yields (≤15%) of monocoupled products were obtained from the $Pd(PPh_3)_4$-catalyzed reaction between 1:1 equiv of **18c**, **18d**, and **5b**. The yields of monocoupled products increased to 30% when an excess of **18c** and **18d** and 30−50 mol % $Pd(PPh_3)_4$ were used, but this was clearly wasteful in 2-trimethylstannylpyridines and catalyst. When the 1:1 stoichiometric reactions were repeated using **5d** in place of **5b**, slightly higher yields of monocoupled products **19** (36%) and **20** (33%) resulted (Scheme 4). Although the yield enhancement of **19** and **20** originated directly from the greater reactivity of **5d**, the product distributions showed no preferential selectivity for monocoupling. The monocoupled products **19** and **20** underwent clean $Pd(PPh_3)_4$-catalyzed reactions with **18a** in refluxing toluene to give, respectively, the unsymmetrically substituted **22** and **23** in high yield.

Characterization and Properties

Spectroscopic Characterization of the Conjugatively Bridged Bis- and Tris-5-(2,2′-bipyridines). The

(40) Yield reductions have also been observed in the Sonogashira-type synthesis of a phenyl-1,2-bis(*meso*-ethynylporphyrin) system: (a) Arnold, D. P.; Nitschinsk, L. J. *Tetrahedron Lett.* **1993**, *34*, 693. For investigations on the thermal rearrangements of phenyl-1,2-ethynes, see: (b) Semmelhack, M. F.; Neu, T.; Foubelo, F. *Tetrahedron Lett.* **1992**, *33*, 3277. (c) John, J. A.; Tour, J. M. *Tetrahedron* **1997**, *53*, 15515.

(41) The bis- and tris-5-(2-chloropyridines) incorporating ethyne moieties in their bridges will be expected to experience an increased electronic communication between the 2-chloro groups of the terminal pyridine rings in the case of **5a** and **5f**, and to a lesser extent **6**−**8**. The 2-chloro groups of the 5-(2-chloropyridines) **5f**,**g**, and **6**−**8** would also be strongly electronically linked to the bridging phenyl and biphenyl rings. Both situations would result in a net electron-withdrawing effect upon the 2-chloro substituents of **5a**, **5f**,**g**, and **6**−**8**. It is well documented that the rates and yields of Stille cross-coupling reactions with aryl- and vinyltrialkyltin reagents are enhanced by the presence of electron-withdrawing substituents on the aryl−halide component. See for example: (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 516. (b) McKean, D. R.; Parrinello, G.; Renaldo, A. F.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 422. The lower reactivity of **5b** and **5c** toward double Stille cross-couplings with **18b** may therefore result from a lack of reactivity enhancement of the chlorine groups, due to poorer electronic communication through the phenyl and biphenyl bridges. In this case, catalyst decomposition effectively competes with bis-5-(2,2′-bipyridine) formation.

^{1}H NMR spectra of all the bridged 2,2′-bipyridines were in accordance with their proposed structures and were assigned on the basis of COSY, ROESY, and/or NOESY measurements and spectral comparisons. The ^{13}C NMR spectra of the majority of compounds studied were free from overlapping resonances and exhibited the expected number of bands. The resonances due to the ethyne bridging carbons were also clearly identifyable in **1a**,**b** as a single band, and as two bands of low-medium intensity in **1g**−**j**, **2a**,**b**, **3a**,**b**, and **4a**,**b** between 82 and 103 ppm. The determination of NMR spectra of the higher molecular weight linear bridged bis-5-(2,2′-bipyridines) was impeded by the poor solubility of these substrates in most organic solvents. However, the use of $CDCl_2CDCl_2$ at elevated temperatures and/or CF_3COOD at ambient temperature caused rapid solubilization of the products and enabled the recording of clean NMR spectra. Comparison of the ^{1}H NMR spectra of the terminally substituted bridged bis-5-(2,2′-bipyridines) revealed some general, solvent-independent correlations which aided spectral interpretations and assignments. These are briefly discussed below.

In the ^{1}H NMR spectra of the terminally phenyl-substituted bridged bis-2,2′-bipyridines **1a**, **1c**, **1e**, **1g**, **1i**, **2a**, **3a**, **4a**, **22**, and **23**, the *ortho*, *meta*, and *para* protons of the phenyl substituent invariably appeared as a well-separated group of signals comprising a doublet and two triplets in a 2:2:1 ratio. The bands also exhibited the characteristic fine-structured splitting patterns resulting from second-order $>^3J$ couplings. The doublet corresponding to the *ortho* protons was always situated further downfield than the two triplets arising from the *meta* and *para* protons. The stronger deshielding experienced by the *ortho* protons evidenced their close proximity to the adjacent terminal pyridine ring nitrogen lone pair. In the ^{1}H NMR spectra of all 2,2′-bipyridines studied, the H6′ (**1a**−**j**, **2a**,**b**, **3a**,**b**, **4a**,**b**, **19**−**21**) and H6′/6‴ (**22**, **23**) protons of the inner pyridine rings were the most deshielded and gave the furthest downfield situated signals. The inner pyridine H4′ of **1a**−**i**, **2a**,**b**, **3a**,**b**, **4a**,**b**, and **19**−**21** and H4′/4‴ of **22** and **23** also followed a similar trend in that they were more deshielded than the corresponding terminal pyridine H4 and H4/4⁗ protons. In **1j** the H4 and H4′ signals were overlapping. In contrast, the bands assigned to the terminal pyridine ring H5 protons of **1a**, **1c**, **1e**, **1g**, **1i**, **2a**, **3a**, **4a**, and **19**−**21** and H5/5⁗ protons of **22** and **23** were always the most upfield positioned and shielded of the pyridine ring signals.

Compounds **19**, **20**, **22**, and **23** afforded the most complex ^{1}H NMR spectra of the 2,2′-bipyridines investigated. In the case of **19**, **20**, and **23**, a completely unambiguous assignment was not possible owing to an absence of interpyridine ring proton cross-peaks in their ROESY and NOESY spectra. Assignments of the inner pyridine and bromopyridine ring protons of **19** and **20** were therefore made instead by comparison with the ^{1}H NMR spectrum of **5d**. In the spectra of **19** and **20**, three relatively upfield shifted signals from protons of the same ring at 8.65, 7.79, and 7.58−7.59 ppm occurred at chemical shifts similar to those of the H6, H4, and H3 bromopyridine ring protons of **5d** at 8.66, 7.87, and 7.66 ppm, respectively. These were therefore assigned to the H6‴, H4‴, and H3‴ protons of the bromopyridine ring of **19** and **20**, and the remaining peaks to H6′, H4′, and H3′ of the inner pyridine rings. The ^{1}H NMR of **23** would be expected to comprise a total of 18 magnetically and chemically inequivalent resonances. In $CDCl_3$ solution, 14 bands are observed, 3 of which consist of overlapping multiplets assigned to the inner pyridine H6′/6‴ and H4′/4‴pairs, and the terminal phenylpyridine H5/bridging phenyl H2″,6″;3″,5″ protons. The H3⁗,4⁗,5⁗,6⁗ protons of the terminal unsubstituted pyridine ring were readily assignable through COSY cross-peaks and their characteristic splitting patterns, comprising a doublet of triplets, a triplet, a quartet, and a doublet of doublets, respectively. The terminal phenylpyridine H4 was also identifiable as the typically simple triplet at 7.92 ppm, and H5 and H3 through COSY cross-peaks with H4. The remaining doublets corresponding to the inner pyridine H3′ and H3‴ protons were identified on the basis of the presence of COSY cross-peaks with the H6′/6‴ and H4′/4‴ multiplets. However, these two signals could not be unambiguously assigned for the above-mentioned reasons. A tentative assignment was made possible through comparison with the ^{1}H NMR spectrum of **21**. The chemical shifts of the terminal unsubstituted pyridine ring protons, the inner pyridine H6′/6‴ and H4′/4‴pairs, and the more upfield of the pair of bands corresponding to the H3′ and H3‴ protons were virtually identical to those of the terminal and inner pyridine ring protons of **21** in $CDCl_3$ solution. The identical values of the chemical shifts of the inner pyridine H3′ (8.52 ppm) of **21** and the band at 8.52 ppm in the spectrum of **23** suggested that the latter band originated from H3‴ and the resonance at 8.75 ppm from H3′ of the inner pyridine ring adjacent to the terminal phenylpyridine. In the ^{1}H NMR spectra of **2a**,**b**, an unambiguous assignment of the bridging phenyl H3″,6″ and H4″,5″ protons was not possible owing to a lack of ROESY and COSY cross-peaks with the inner pyridine H4′ and H6′ protons. The more downfield of the bridging phenyl multiplets was therefore assigned to the H3″,6″ protons adjacent to the ethyne groups, as these would be expected to be the most sensitive to the inductive electron-withdrawing influence of the 2,2′-bipyridine moieties.

The EI and FAB mass spectra were also in agreement with the proposed structural formulas of all compounds investigated. In the case of the less soluble bridged 5-(2,2′-bipyridines), optimal conditions for recording mass spectra were afforded by FAB using CF_3COOH as matrix. The bridged 5-(2,2′-bipyridines) proved to be particularly stable materials under mass-spectral conditions, giving predominantly M and M + 1 clusters with little or no fragmentation.

The solid-state infrared spectra of the bridged 5-(2,2′-bipyridines) studied exhibited a considerable variation in complexity throughout the fingerprint region, and were characteristic for each compound. The vibrational modes of the pyridine ring CC, CN, and CH bonds were clearly distinguishable as medium to very strong intensity bands in all cases. However, the stretching vibrational mode of the ethynyl bridge was only observed in **1h**−**j**, at 2215−2213 cm^{-1}, and **4a,b** at 2207 and 2208 cm^{-1}, respectively, as bands of weak intensity.

The UV/vis spectra of the bridged 5-(2,2′-bipyridines) all display intense absorption envelopes between 258 and 373 nm, which arise predominantly from $\pi \rightarrow \pi^*$ electronic transitions originating from the pyridyl and phenyl

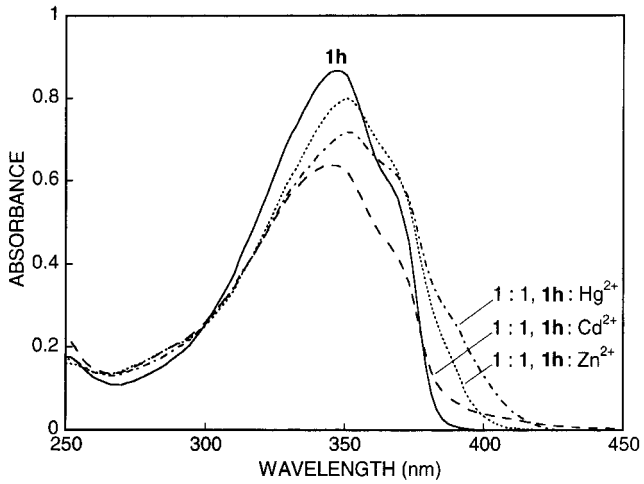


Figure 1. UV/vis spectra of 1:1 stoichiometric mixtures of 9.1 × 10^{-6} mol dm^{-3} solutions of **1h** with, respectively, $Zn(CF_3SO_3)_2$, $Cd(CF_3SO_3)_2$, and $Hg(CF_3SO_3)_2$ in 1:2 $CHCl_3$/MeOH.

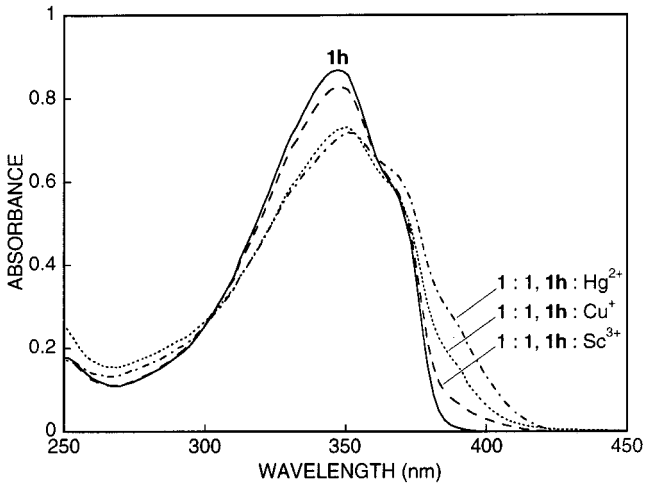


Figure 2. UV/vis spectra of 1:1 stoichiometric mixtures of 9.1 × 10^{-6} mol dm^{-3} solutions of **1h** with, respectively, $Sc(CF_3SO_3)_3$, $[Cu(MeCN)_4](CF_3SO_3)$, and $Hg(CF_3SO_3)_2$ in 1:2 $CHCl_3$/MeOH.

rings.[42a,b] In particular, a band associated with the presence of a terminal phenyl substituent is always present in the spectra of **1a**, **1c**, **1e**, **1g**, **1i**, **2a**, **3a**, **4a**, **22**, and **23**, at 262−270 nm. The lowest energy absorbances of all compounds investigated are exhibited by **1g** and **1h** at 373 and 371 nm, respectively, indicating that they possess bridging units with the most extended electronic delocalization.

Metal Ion Complexation Behavior of 1h. Ligands incorporating bridging units with maximal conjugation are expected to exhibit the most interesting physicochemical properties with respect to metal ion coordination. In the case of **1 g**,**h**, it was suspected that metal ion-binding would cause shifts in the absorption envelopes to values characteristic of the electronic and coordination preferences of particular classes of metal cations. An investigation into the complexation behavior of **1h** was therefore undertaken to evaluate its potential for the spectroscopic sensing of colorless metal ions.

The results of this study are summarized in Figures 1 and 2, and show that the absorption maxima of **1h** shift to lower energy in the event of metal ion complexation, and exhibit the greatest changes in the presence of Sc^{3+}, Cu^{+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}. Stoichiometric 1:1 mixtures of **1h** with the triflate salts of Na^{+}, Mg^{2+}, Ba^{2+}, Ag^{+}, Mn^{2+}, Tl^{+}, Pb^{2+}, La^{3+}, and Eu^{3+} at equivalent concentrations yielded spectra which were essentially identical to that of the free, uncomplexed ligand. This suggests that either a negligible or zero degree of binding between **1h** and the latter cations was operative at high dilution in 1:2 $CHCl_3$/MeOH.

Of particular interest is that the greatest complexation-induced spectral shift for all cations investigated occurs in the presence of Hg^{2+}. The incremental addition of Hg^{2+} into solutions of **1h** (Figure 3) resulted in the progressive disappearance of the free ligand absorption at 350 nm, and an increase in intensity and a shift to lower energy of the band at 371 nm. Increasing the relative [Hg^{2+}] to greater than 2 equiv with respect to the [**1h**] resulted in a continued shift of the latter absorption maximum to

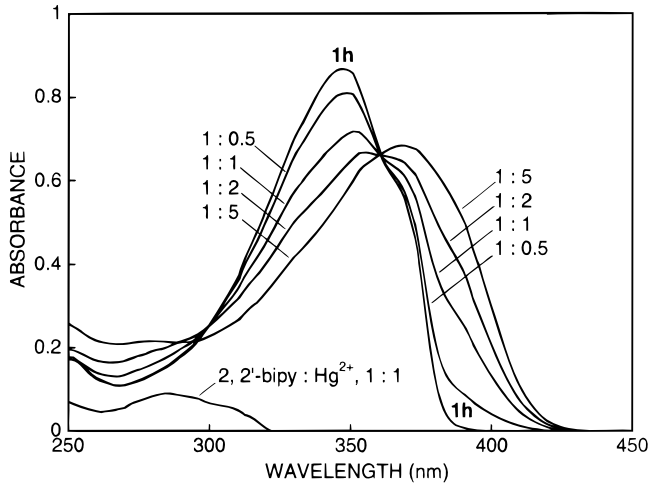


Figure 3. Titration comprising incremental additions of $Hg(CF_3SO_3)_2$ into 9.1 × 10^{-6} mol dm^{-3} solutions of **1h** in 1:2 $CHCl_3$/MeOH. The **1h**:Hg^{2+} stoichiometric ratio is indicated for each curve. The UV/vis spectrum of an equivalent concentration of a 1:1 stoichiometric mixture of 2,2′-bipyridine:Hg^{2+} in 1:2 $CHCl_3$/MeOH is also included for comparison.

lower energy and the concomitant development of a pale yellow coloration. This behavior may originate from incomplete coordination of both the 2,2′-bipyridine moieties of **1h** at a 1:2 ratio of **1h**:Hg^{2+}. The presence of an excess of Hg^{2+} may thus be necessary to saturate all the metal ion-binding sites of **1h** in a dilute environment. Interactions between the Hg^{2+} cations and the 1, 4-diethynylphenyl bridge of **1h** may also possibly contribute to the observed spectral shifts at higher [Hg^{2+}]. From the titration, the lower limit for the detection of Hg^{2+} was estimated to be at a [Hg^{2+}] of 5 × 10^{-6} mol dm^{-3}.

Comparison of the spectra obtained from 1:1 stoichiometric mixtures of **1h**:Hg^{2+} and 2,2′-bipyridine:Hg^{2+} at identical concentrations strikingly demonstrated the effect of conjugation enhancement on the spectroscopic properties of metal ion complexes of **1h**. The 1:1 mixture of 2,2′-bipyridine:Hg^{2+} yielded a spectrum with only a weak and poorly defined absorption envelope at 285 nm. The conjugated 1,4-diethynylphenyl bridge has therefore completely transformed the electronic nature of the

(42) For an assignment of the UV absorption spectrum of 2,2′-bipyridine, see: (a) Gondo, Y.; Kanda, Y. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1187. (b) *Supramolekulare Chemie;* Vögtle, F., Ed.; B. G. Teubner: Stuttgart, 1989, Chapter 2, p 33 and references therein.

appended 2,2′-bipyridine units and significantly contributes to the spectroscopic behavior of **1h**.

Ligand **1h** therefore possesses potential for the spectrophotometric detection of Zn^{2+}, Cd^{2+}, and Hg^{2+} in the presence of group 1 and 2, lanthanides, main group, and specific "colorless" transition metal ions. The introduction of further structural modifications into **1h** and related ligands may be expected to maximize the selectivity and sensitivity toward specific metal ions, and thereby afford a new class of sensing materials for metallic environmental toxins.

Conclusion

In conclusion, the work presented above describes a convenient synthesis of linear (**1a**−**j**, **21**−**23**) and curved (**2a**,**b**, **3a**,**b**) bis-5-(2,2′-bipyridines) and branched tris-5-(2,2′-bipyridines) (**4a**,**b**) incorporating rigid conjugated bridging units, which avoids the use of protection/deprotection steps. The ligands **1a**−**j**, **3a**,**b**, **4a**,**b**, and **21**−**23** are of nanoscopic dimensions and lie within the size range of 20−35 Å (including van der Waals surfaces). In the initial stage of the syntheses, a central preformed bridging module with $n \geq 2$ outwardly positioned reactive sites is functionalized with pyridine synthon **9** to yield the bridged bis-5-(2-chloropyridine) precursors **5a**−**c**, **5f**,**g**, and **6**−**8**. The success of this methodology relies upon the fact that the 2-chloro substituent of **9** is unreactive to ambient temperature organometallic cross-coupling protocols such as the Sonogashira and Negishi reactions. This enabled a facile regioselective reaction at the 5-position of **9**, and its chlorozincate **11** with ethynyl- and diiodoaryl-functionalized bridging units. The reactivity of the 2-chloropyridyl group can then be "switched on" at higher temperatures, and thereby induced to participate in the Stille cross-coupling reaction with trialkylstannylpyridines to afford the desired bridged 5-(2,2′-bipyridines). The 1,4-phenyl- and 4,4′-(1,1′-biphenyl)-bridged bis-5-(2,2′-bipyridines), on the other hand, were best prepared from the bis-5-(2-bromopyridines) **5d**,**e**, owing to the lower reactivity of the corresponding bis-2-chloropyridines **5b**,**c**. The Stille cross-coupling yields also showed a marked sensitivity to the type of substituent on the trimethylstannylpyridine, and in some cases to the presence of additives such as LiCl. In all cases investigated, reactions with identical bridging units gave higher Stille cross-coupling product yields with the phenyl-substituted **18a**.

The economy and adaptability of the synthetic procedures detailed above make possible the formation of bis- and tris-5-(2-chloropyridines) and 5-(2,2′-bipyridines) incorporating a potentially very large variety of bridging moieties in addition to those already investigated. In particular, the synthesis provides a convenient method of access to conjugatively bridged 5-(2,2′-bipyridines) possessing substituents on the outer pyridine rings. This option is important for the additional modulation and control of the physicochemical properties of these materials, and also for synthetic elaboration and incorporation into larger architectures.

The conjugatively bridged 5-(2-halopyridines) and 5-(2,2′-bipyridines) constitute a reservoir of structural building blocks which can be expected to find many uses in materials science and nanotechnology. For example, the bridged 5-(2-halopyridines) **5a**−**g** and **6**−**8** may function as substrates for the tailored engineering of metal ion-coordinating polymers and copolymers with unusual and intriguing optical, sensing, mechanical, and electronically conducting properties. The bridged 5-(2,2′-bipyridines) will be capable of forming an extensive range of multinuclear transition metal complexes, such as, for example, unusual cyclometalated species with **1a**, **1c**, **1e**, **1g**, **1i**, **2a**, **3a**, and **4a**, metalloclefts with **2a**,**b**, metallomacrocycles with **3a**,**b**, and dendritic entities in the case of **4a**,**b**. A multitude of functions may be envisioned for these materials, especially within the supramolecular arena, such as electronically controllable catalysts, molecular electronics device components, and precursors to metallo-assembled nanoarchitectures. Many of these ligands may also display metal ion-sensing capabilities, as in the case of **1h**. Optimization of these properties via additional structural refinements may afford a potentially new class of analytical reagents for the spectrophotometric detection of toxic metals.

The synthetic methodology described above therefore provides a platform for the future construction of rigid nanosized and polymeric organic scaffolds with metal ion-binding capabilities, for which many diverse materials applications await discovery in the 21st century.

Experimental Section

General Methods and Starting Materials. Standard inert atmosphere and Schlenk techniques were employed for reactions conducted under dinitrogen and argon. All solvents used for the palladium-catalyzed coupling reactions were freshly redistilled under dry, oxygen-free argon over the appropriate drying agent before use. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, Université Louis Pasteur. The ^{1}H and ^{13}C NMR spectra of **1h**, recorded in 20% D_2O/CF_3COOD, were referenced to the trimethylsilyl peak of added sodium 3-(trimethylsilyl)-1-propanesulfonate (TSPSA). 1,4-Diethynylbenzene,[43] 4,4′-bisethynyl-1,1′-biphenyl,[43] 1,2-diiodobenzene,[44] 1,3-diethynylbenzene,[45] 1,3,5-trisethynylbenzene,[46] $Pd(PPh_3)_4$,[47] $Pd_2(dba)_3$,[48] and 2-trimethylstannylpyridine (**18d**)[49] were prepared according to published procedures. 2-Trimethylstannyl-6-phenylpyridine (**18a**), 2-trimethylstannyl-5-methylpyridine (**18b**), and 2-trimethylstannyl-6-methylpyridine (**18c**) were prepared in the same way as **18d**.

1,2-Bis[5-(2-chloropyridyl)]ethyne (5a). To a mixture of 2-chloro-5-iodopyridine (**9**) (1.004 g, 4.19×10^{-3} mol), 1,2-bis(tri-*n*-butyltin)ethyne (**10**) (1.27 g, 2.10×10^{-3} mol), and 0.38 g of $Pd(PPh_3)_4$ under an atmosphere of argon was added via syringe 15 mL of dry dimethylformamide. The mixture was then heated and stirred in a bath at 105 °C for 24 h, during which time the reaction mixture became dark-brown in color. After heating, all solvent was removed under reduced pressure and the residue column chromatographed on alumina (standardized activity II−III), using 75:25 CH_2Cl_2/hexane as eluant. The product **5a** thus obtained was further purified by suspension in 5 mL of MeOH followed by brief ultrasonication, filtration under vacuum, washing of the isolated solid with MeOH, and finally air-drying to yield 0.402 g (77%) of **5a** as a cream-colored microcrystalline solid. Analytically pure **5a** (mp 229−230 °C) could be obtained upon sublimation under

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(44) Shuttleworth, R. G.; Rapson, W. S.; Stewart, E. T. *J. Chem. Soc.* **1944**, 71.
(45) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988**, *53*, 2489.
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(48) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.
(49) Jutzi, P.; Gilge, U. *J. Organomet. Chem.* **1983**, *246*, 163.

vacuum at 110−130 °C/5 × 10^{-7} mmHg. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ (ppm) 8.55 (dd, $^4J_{6,4}$ = 2.3 Hz, $^5J_{6,3}$ = 0.7 Hz, 2H; H6), 7.77 (dd, $^3J_{4,3}$ = 8.3 Hz, $^4J_{4,6}$ = 2.4 Hz, 2H; H4), 7.36 (dd, $^3J_{3,4}$ = 8.3 Hz, $^5J_{3,6}$ = 0.7 Hz, 2H; H3). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 152.1, 151.3, 140.9, 124.1, 118.3, 89.0 (C≡C). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 276sh (22 374), 285sh (25 522), 294 (27 951), 302 (25 896), 312 (26 643). EIMS: *m*/*z* 248 (M^+, 100). Anal. Calcd for $C_{12}H_6Cl_2N_2$: C, 57.86; H, 2.43; N, 11.25. Found: C, 58.01; H, 2.49; N, 11.31.

1,4-Bis[5-(2-chloropyridyl)]benzene (5b). To **9** (2.5 g, 1.04 × 10^{-2} mol) in a dried argon-filled flask equipped with an alcohol thermometer and argon/vacuum septum inlet adaptor was added 37 mL of THF via syringe. The solution was cooled to an internal temperature of −95 °C (liquid N_2/hexane bath), and then 1.6 M *n*-BuLi (6.51 mL, 1.04 × 10^{-2} mol) was added by syringe to the stirred solution of **9** at such a rate as to maintain the reaction temperature below −90 °C. During addition, the reaction solution became dark brown in color, and a suspended brown solid formed. The stirred mixture was subsequently allowed to warm to −83 °C over 0.75 h and then recooled to −96 °C. A solution of $ZnCl_2$ (1.0 M in Et_2O; 11 mL, 1.10 × 10^{-2} mol) was then syringed into the reaction solution at such a rate as to maintain the temperature at ≤−80 °C. The resulting pale brown solution of **11** was allowed to warm to ambient temperature with stirring over 1.5 h. To $PdCl_2(PPh_3)_2$ (0.24 g, 3.42 × 10^{-4} mol) in a dried, argon-filled flask were added 38 mL of THF and $(n\text{-Bu})_2$AlH (1.0 M in hexane; 0.7 mL, 7.0 × 10^{-4} mol) by syringe, and the resulting dark brown-green mixture was stirred for 0.25 h. 1,4-Diiodobenzene (**12a**; 1.70 g, 5.15 × 10^{-3} mol) was then added to the catalyst mixture, and after being stirred for 0.1 h the solution of **11** was cannulated into the reaction flask. The mixture was stirred for 48 h at ambient temperature. During this time, a faun-colored suspended solid developed. All solvent was then distilled off under reduced pressure, 100 mL of a saturated aqueous disodium−EDTA solution added to the residue, and the mixture vigorously stirred for 3 h. The suspended solid was collected by filtration under vacuum, washed with distilled water, and air-dried. The solid was then suspended in Et_2O (20 mL), briefly ultrasonicated, isolated by vacuum filtration, washed with Et_2O, and air-dried. After the Et_2O washing, the product was sublimed under vacuum at 210−240 °C/1 × 10^{-6} mmHg to yield 1.069 g (68%) of **5b**. Analytically pure product could be obtained upon boiling the sublimate in 20 mL of MeOH, isolation of the solid by vacuum filtration followed by washing with MeOH, and then finally recrystallization from 2-methoxyethanol to yield **5b** (mp 261−264 °C) as colorless microcrystals. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ (ppm) 8.65 (dd, $^4J_{6,4}$ = 2.6 Hz, $^5J_{6,3}$ = 0.7 Hz, 2H; H6), 7.89 (dd, $^3J_{4,3}$ = 8.3 Hz, $^4J_{4,6}$ = 2.6 Hz, 2H; H4), 7.68 (s, 4H; phenyl H2′,3′,5′,6′), 7.44 (dd, $^3J_{3,4}$ = 8.3 Hz, $^5J_{3,6}$ = 0.7 Hz, 2H; H3). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ (ppm) 150.7, 147.9, 137.0, 136.6, 134.7, 127.8, 124.4. UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 273sh (27 525), 291 (34 140). EIMS: *m*/*z* 300 (M^+, 100). Anal. Calcd for $C_{16}H_{10}Cl_2N_2$: C, 63.81; H, 3.35; N, 9.30. Found: C, 63.84; H, 3.30; N, 9.10.

4,4′-Bis[5-(2-chloropyridyl)]-1,1′-biphenyl (5c). This compound was prepared in a manner identical to that of **5b**. Thus, **11** was generated from **9** (2.0 g, 8.35 × 10^{-3} mol), *n*-BuLi (1.6 M; 5.3 mL, 8.48 × 10^{-3} mol), and $ZnCl_2$ (1.0 M in Et_2O; 8.5 mL, 8.5 × 10^{-3} mol) in 50 mL of anhydrous THF. The catalyst mixture was prepared from $PdCl_2(PPh_3)_2$ (0.20 g, 2.85 × 10^{-4} mol) and $(n\text{-Bu})_2$AlH (1.0 M; 0.58 mL, 5.8 × 10^{-4} mol) in 20 mL of THF. 4,4′-Diiodo-1,1′-biphenyl (**12b**; 1.6 g, 3.94 × 10^{-3} mol) was then added to the catalyst followed by **11**. The suspended solid from the Na_2EDTA treatment was filtered off, washed with distilled water and MeOH, and air-dried. Final purification was achieved by boiling the product in 150 mL of $CHCl_3$, filtering the cooled mixture under vacuum, washing with $CHCl_3$, and sublimation under vacuum at 218 °C/2 × 10^{-6} mmHg to yield 0.862 g (58%) of analytically pure **5c** as a white powder (mp 285−302 °C, continual softening to an opaque melt). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ (ppm) 8.68 (dd, $^4J_{6,4}$ = 2.6 Hz, $^5J_{6,3}$ = 0.7 Hz, 2H; H6), 7.91 (dd, $^3J_{4,3}$ = 8.3 Hz, $^4J_{4,6}$ = 2.6 Hz, 2H; H4), 7.76 (d, $^3J_{2',3';6',5'}$ = 8.5 Hz, 4H; biphenyl (inner) H2′,6′), 7.67 (d, $^3J_{3',2';5',6'}$ = 8.5 Hz, 4H; biphenyl (outer) H3′,5′), 7.44 (dd, $^3J_{3,4}$ = 8.2 Hz, $^5J_{3,6}$ = 0.7 Hz, 2H; H3). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 150.5, 147.9, 140.3, 137.0, 135.8, 135.0, 127.8, 127.6, 124.3. UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 303 (51 868). EIMS: *m*/*z* 376 (M^+, 100). Anal. Calcd for $C_{22}H_{14}Cl_2N_2$: C, 70.04; H, 3.74; N, 7.43. Found: C, 69.88; H, 3.80; N, 7.24.

1,4-Bis[5-(2-bromopyridyl)]benzene (5d). An intimate mixture of **5b** (0.255 g, 8.47 × 10^{-4} mol) and $POBr_3$ (9.0 g) in a flask fitted with a $CaCl_2$ drying tube was heated in a bath at 170 °C with stirring for 20 h. After the mixture was cooled to ambient temperature, the resulting black solid was broken up, added to excess crushed ice/water, and vigorously stirred until all the ice had melted and the suspended solid homogenized. More ice was added and the mixture adjusted to pH 14 by the dropwise addition of 10% aqueous NaOH. The mixture was stirred for a further 6 h, and then the suspended solid isolated by filtration under vacuum, washed with distilled water, and air-dried. The solid was then Soxhlet extracted with boiling $CHCl_3$ for 48 h. Removal of the solvent from the extract on a water bath yielded 0.246 g of crude **5d** as a khaki solid. The product was purified by sublimation under vacuum at 150 °C/2 × 10^{-6} mmHg, and finally by boiling the sublimate in MeOH, isolating the solid by vacuum filtration, washing with MeOH, and drying under dynamic vacuum to yield 0.224 g (77%) of **5d** (mp 291−293 °C) as a white amorphous solid. ^{1}H NMR ($CDCl_2CDCl_2$, 300 MHz, 25 °C): δ (ppm) 8.66 (d, $^4J_{6,4}$ = 2.3 Hz, 2H; H6), 7.87 (dd, $^3J_{4,3}$ = 8.3 Hz, $^4J_{4,6}$ = 2.6 Hz, 2H; H4), 7.70 (s, 4H; phenyl H2′,3′,5′,6′), 7.66 (d, $^3J_{3,4}$ = 8.4 Hz, 2H; H3). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 275sh (35 421), 293 (44 797). EIMS: *m*/*z* 390 (M^+, 100). HRMS (FAB+, $CHCl_3$): calcd for $C_{16}H_{10}Br_2N_2$ 388.9262, found 388.9274.

4,4′-Bis[5-(2-bromopyridyl)]-1,1′-biphenyl (5e). Compound **5e** was prepared as described for **5d** above from **5c** (0.322 g, 8.53 × 10^{-4} mol) and 11.2 g of $POBr_3$. After workup, the solid isolated from the $CHCl_3$ Soxhlet extraction was washed with CH_2Cl_2 and sublimed under vacuum at 265 °C/2 × 10^{-6} mmHg to yield 0.360 g (90%) of **5e** as a white powder (mp > 320 °C). ^{1}H NMR ($CDCl_2CDCl_2$, 500 MHz, 100 °C): δ (ppm) 8.69 (dd, $^4J_{6,4}$ = 2.6 Hz, $^5J_{6,3}$ = 0.7 Hz, 2H; H6), 7.82 (dd, $^3J_{4,3}$ = 8.2 Hz, $^4J_{4,6}$ = 2.6 Hz, 2H; H4), 7.81 (d, $^3J_{2',3';\ 6',5'}$ = 8.2 Hz, 4H; biphenyl (inner) H2′,6′), 7.70 (d, $^3J_{3',2';5',6'}$ = 8.1 Hz, 4H; biphenyl outer) H3′,5′), 7.61 (dd, $^3J_{3,4}$ = 8.2 Hz, $^5J_{3,6}$ = 0.7 Hz, 2H; H3). ^{13}C NMR ($CDCl_2CDCl_2$, 125.8 MHz, 100 °C): δ (ppm) 148.4, 141.3, 140.5, 136.7, 136.0, 135.5, 128.1, 127.9, 127.6. UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 304 (60 118). FABMS: *m*/*z* 466 (M^+, 100). Anal. Calcd for $C_{22}H_{14}Br_2N_2$: C, 56.68; H, 3.03; N, 6.01. Found: C, 56.95; H, 3.06; N, 5.93.

1,4-Bis(5-ethynyl-2-chloropyridyl)benzene (5f). To a mixture of **9** (1.223 g, 5.11 × 10^{-3} mol), 1,4-diethynylbenzene (**13a**; 0.320 g, 2.54 × 10^{-3} mol), and $PdCl_2(PPh_3)_2$ (0.073 g, 1.04 × 10^{-4} mol) under an argon atmosphere was added 50 mL of Et_3N via syringe, and the mixture was stirred for 0.2 h. A solution of CuI (0.040 g, 2.10 × 10^{-4} mol) in 10 mL of Et_3N was then added via syringe and the mixture stirred at 25−30 °C for 24 h and finally at 70 °C for 24 h. During the course of the reaction a flocculent dark-brown solid formed which changed in color to pale yellow-brown. After heating, all solvent was removed under reduced pressure, and the remaining solid suspended in 50 mL of acetone, followed by brief ultrasonication, reisolation by vacuum filtration, washing with acetone, and air-drying. Further purification was achieved upon recrystallization first from 70 mL of pyridine and then toluene to which 0.266 g of decolorizing charcoal had been added. The product **5f**, 0.600 g (68%), was isolated after washing with toluene and air-drying as pale yellow flakes. Analytically pure **5f** (mp 281−283 °C) could be obtained upon sublimation under vacuum at 207 °C/1 × 10^{-6} mmHg. ^{1}H NMR ($CDCl_2CDCl_2$, 500 MHz, 100 °C): δ (ppm) 8.58 (d, $^4J_{6,4}$ = 2.2 Hz, 2H; H6), 7.80 (dd, $^3J_{4,3}$ = 8.2 Hz, $^4J_{4,6}$ = 2.4 Hz, 2H; H4), 7.60 (s, 4H; phenyl H2′,3′,5′,6′), 7.37 (d, $^3J_{3,4}$ = 8.2 Hz, 2H; H3). ^{13}C NMR ($CDCl_2CDCl_2$, 125.8 MHz, 100 °C): δ (ppm) 152.1, 150.9, 140.8, 131.8, 123.9, 123.0, 119.1, 93.3 (C≡C), 87.1 (C≡C). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}): 312sh (62 089),

326 (77 989), 346 (51 727), 371 (4256). EIMS: *m/z* 348 (M^+, 100). Anal. Calcd for $C_{20}H_{10}Cl_2N_2$: C, 68.79; H, 2.89; N, 8.02. Found: C, 68.89; H, 2.88; N, 7.91.

4,4′-Bis(5-ethynyl-2-chloropyridyl)-1,1′-biphenyl (5g). Compound **5g** was prepared in the same way as **5f**, from **9** (0.355 g, 1.48×10^{-3} mol), **13b**, (0.15 g, 7.42×10^{-4} mol), $PdCl_2(PPh_3)_2$ (0.020 g, 2.85×10^{-5} mol) in 9 mL of pyridine, and CuI (0.013 g, 6.83×10^{-5} mol) in 2 mL of Et_3N. The solid isolated by filtration of the cooled reaction mixture was washed with pyridine and recrystallized from toluene to which 0.15 g of decolorizing charcoal had been added. The crystals thus obtained were isolated by vacuum filtration, washed with toluene, and dried under vacuum to yield 0.245 g (78%) of **5g** as lemon-yellow needles. Analytically pure **5g** (mp 302−304 °C) could be obtained by further recrystallization from $CHCl_3$ followed by sublimation under vacuum at 230 °C/2 × 10^{-6} mmHg. ^{1}H NMR ($CDCl_2CDCl_2$, 500 MHz, 100 °C): δ (ppm) 8.59 (d, $^4J_{6,4} = 2.2$ Hz, 2H; H6), 7.82 (dd, $^3J_{4,3} = 8.2$ Hz, $^4J_{4,6} = 2.3$ Hz, 2H; H4), 7.69 (d, $^3J_{2',3';6',5'} = 8.7$ Hz, 4H; biphenyl (inner) H2′,6′), 7.67 (d, $^3J_{3',2';5',6'} = 8.8$ Hz, 4H; biphenyl (outer) H3′,5′), 7.37 (d, $^3J_{3,4} = 8.3$ Hz, 2H; H3). ^{13}C NMR ($CDCl_2CDCl_2$, 125.8 MHz, 100 °C): δ (ppm) 152.1, 150.7, 140.8, 140.7, 132.4, 127.0, 123.8, 121.9, 119.0, 93.7 (C≡C), 86.0 (C≡C). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 330 (86 211). EIMS: *m/z* 424 (M^+, 100). Anal. Calcd for $C_{26}H_{14}Cl_2N_2$: C, 73.42; H, 3.32; N, 6.59. Found: C, 73.39; H, 3.34; N, 6.75.

1,2-Bis(5-ethynyl-2-chloropyridyl)benzene (6). Compound **6** was prepared in the same way as **5f** from 1, 2-diiodobenzene (**14**; 0.236 g, 7.15×10^{-4} mol), **15b** (0.197 g, 1.43×10^{-3} mol), $Pd_2(dba)_3$ (0.028 g, 3.06×10^{-5} mol), PPh_3 (0.037 g, 1.41×10^{-4} mol), and CuI (0.006 g, 3.15×10^{-5} mol) in 7 mL of Et_3N at 40 °C for 14 h. After removal of solvent, the residue was dissolved in 25 mL of CH_2Cl_2 and extracted twice with distilled water. The organic layer was subsequently dried ($MgSO_4$) and filtered, and the solvent reduced in volume to 8 mL on a water bath. The CH_2Cl_2 solution was then flash chromatographed on a column of silica, eluting with CH_2Cl_2, and the isolated product boiled in 5 mL of hexane, filtered under vacuum, washed with 2 mL of hexane, and air-dried. Final purification was achieved upon sublimation under vacuum (135 °C/2 × 10^{-6} mmHg), to yield 0.187 g (75%) of **6** (mp 153−154 °C) as a cream-colored solid. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ (ppm) 8.54 (dd, $^4J_{6,4} = 2.3$ Hz, $^5J_{6,3} = 0.7$ Hz, 2H; H6), 7.74 (dd, $^3J_{4,3} = 8.2$ Hz, $^4J_{4,6} = 2.3$ Hz, 2H, H4), 7.59 (m, 2H; phenyl H6′,3′), 7.39 (m, 2H; phenyl H4′,5′), 7.34 (dd, $^3J_{3,4} = 8.3$ Hz, $^5J_{3,6} = 0.7$ Hz, 2H; H3). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 152.0, 150.8, 140.7, 132.1, 128.9, 124.8, 124.1, 119.1, 92.1 (C≡C), 88.9 (C≡C). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 275 (44 049), 301 (27 472), 318 (24 287), 339sh (9615). EIMS: *m/z* 348 (M^+, 100). Anal. Calcd for $C_{20}H_{10}Cl_2N_2$: C, 68.79; H, 2.89; N, 8.02. Found: C, 68.96; H, 3.04; N, 8.24.

1, 3-Bis(5-ethynyl-2-chloropyridyl)benzene (7). Compound **7** was prepared in the same way as **5f**, from **9** (1.14 g, 4.76×10^{-3} mol), **16** (0.30 g, 2.38×10^{-3} mol), $PdCl_2(PPh_3)_2$ (0.100 g, 1.42×10^{-4} mol) in 45 mL of Et_3N, and CuI (0.070 g, 3.67×10^{-4} mol) in 3 mL of Et_3N. After removal of solvent, the product was briefly ultrasonicated in 60 mL of acetone, stirred for 5 h, and then filtered under vacuum and the solid collected, washed with acetone, and air-dried. The khaki solid was then recrystallized from 25 mL of boiling toluene to which 0.20 g of decolorizing charcoal had been added. The product was isolated by vacuum filtration, washed with cold toluene, and dried under vacuum to yield 0.489 g (59%) of **7** (mp 215−217 °C) as golden needles. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ (ppm) 8.54 (d, $^4J_{6,4} = 2.2$ Hz, 2H; H6), 7.76 (dd, $^3J_{4,3} = 8.2$ Hz, $^4J_{4,6} = 2.4$ Hz, 2H; H4), 7.72 (t, 1H; phenyl H2′), 7.54 (m, $^3J_{4',5';6',5'} = 7.8$ Hz, 2H; phenyl H4′,6′), 7.39 (t, $^3J_{5',4';5',6'} = 7.8$ Hz, 1H; phenyl H5′), 7.34 (d, $^3J_{3,4} = 8.2$ Hz, 2H; H3). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 152.1, 150.7, 140.9, 134.7, 132.0, 128.8, 124.0, 122.8, 119.0, 92.5 (C≡C), 85.5 (C≡C). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 273 (50 756), 289 (66 065), 301 (59 860), 309 (61 856), 333 (6966), 345 (4540). EIMS: *m/z* 348 (M^+, 100). Anal. Calcd for $C_{20}H_{10}Cl_2N_2$: C, 68.79; H, 2.89; N, 8.02. Found: C, 68.88; H, 2.86; N, 8.08.

1,3,5-Tris(5-ethynyl-2-chloropyridyl)benzene (8). Compound **8** was prepared in the same way as **5f**, from **9** (1.440 g, 6.01×10^{-3} mol), **17** (0.300 g, 2.0×10^{-3} mol), $PdCl_2(PPh_3)_2$ (0.100 g, 1.42×10^{-4} mol) in 45 mL of Et_3N, and CuI (0.070 g, 3.67×10^{-4} mol) in 3 mL of Et_3N. All solvent was removed from the completed reaction under reduced pressure and the remaining khaki solid dissolved in 40 mL of CH_2Cl_2 and flash column chromatographed on silica, eluting with CH_2Cl_2, to yield 0.913 g (94%) of **8** as a pale yellow solid. Analytically pure **8** (mp 243−245 °C) could be obtained upon further recrystallization from MeCN followed by sublimation under vacuum. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ (ppm) 8.55 (dd, $^4J_{6,4} = 2.3$ Hz, $^5J_{6,3} = 0.7$ Hz, 3H; H6), 7.76 (dd, $^3J_{4,3} = 8.3$ Hz, $^4J_{4,6} = 2.4$ Hz, 3H; H4), 7.70 (s, 3H; phenyl H2′,4′,6′), 7.36 (dd, $^3J_{3,4} = 8.3$ Hz, $^5J_{3,6} = 0.7$ Hz, 3H; H3). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 152.2, 151.1, 140.9, 134.7, 124.1, 123.4, 118.6, 91.5 (C≡C), 86.4 (C≡C). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 276 (63 766), 293 (93 458), 302 (87 660), 311 (96 982), 337 (2591). EIMS: *m/z* 483 (M^+, 100). Anal. Calcd for $C_{27}H_{12}Cl_3N_3$: C, 66.90; H, 2.50; N, 8.67. Found: C, 66.86; H, 2.77; N, 8.69.

General Procedure for Stille Coupling Reactions. The appropriate quantities of bis- and tris-5-(2-halopyridines) **5a**,**d**−**g** and **6**−**8**), bromopyridines **19** and **20**, trimethylstannylpyridine **18a**−**d**, $Pd(PPh_3)_4$, and LiCl in the case of **2a** and **4a**,**b** were refluxed in toluene, xylene, or DMF at 120−160 °C for 24−72 h under an atmosphere of argon. The solvent was then removed under reduced pressure on a water bath, and unless otherwise stated, MeOH was added to the residue, the suspension briefly ultrasonicated and filtered under vacuum, and the isolated solid washed with excess MeOH and air-dried. Further purifications are described for each compound.

1,2-Bis[5-(6′-phenyl-2,2′-bipyridyl)]ethyne (1a). 5a (0.111 g, 4.46×10^{-4} mol), **18a** (0.510 g, 1.60×10^{-3} mol), and $Pd(PPh_3)_4$ (0.035 g, 3.03×10^{-5} mol) in 13 mL of toluene were refluxed for 48 h at 135 °C. After removal of solvent, the residue was dissolved in 25 mL of hot $CHCl_3$ and chromatographed on a column of alumina (standardized activity II−III), using $CHCl_3$ as eluant. The product thus obtained was suspended in 30 mL of Et_2O, briefly ultrasonicated, isolated by filtration under vacuum, washed with Et_2O, and dried under vacuum to yield 0.172 g (79%) of **1a** (mp 260−261 °C) as a cream-colored microcrystalline solid. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ (ppm) 8.88 (dd, $^4J_{6',4'} = 2.1$ Hz, $^5J_{6',3'} = 0.8$ Hz, 2H; H6′), 8.69 (dd, $^3J_{3',4'} = 8.2$ Hz, $^5J_{3',6'} = 0.8$ Hz, 2H; H3′), 8.42 (dd, $^3J_{3,4} = 7.8$ Hz, $^4J_{3,5} = 0.9$ Hz, 2H; terminal pyridine H3), 8.16 (dm, $^3J_{o,m} = 7.1$ Hz, 4H; phenyl H-*ortho*), 8.01 (dd, $^3J_{4',3'} = 8.2$ Hz, $^4J_{4',6'} = 2.1$ Hz, 2H; H4′), 7.91 (t, $^3J_{4,3;4,5} = 7.8$ Hz, 2H; terminal pyridine H4), 7.80 (dd, $^3J_{5,4} = 7.8$ Hz, $^4J_{5,3} = 0.9$ Hz, 2H; terminal pyridine H5), 7.53 (tm, $^3J_{m,o;m,p} = 7.4$ Hz, 4H; phenyl H-*meta*), 7.46 (tt, $^3J_{p,m} = 7.3$ Hz, 2H; phenyl H-*para*). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 156.6, 155.5, 155.0, 151.6, 139.4, 139.2, 137.8, 129.1, 128.8, 127.0, 120.6, 119.7, 90.5 (C≡C). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 267 (37 214), 340 (66 832), 359 (52 514). FABMS: *m/z* 487 ([M + H]$^+$, 100). Anal. Calcd for $C_{34}H_{22}N_4$: C, 83.93; H, 4.56; N, 11.51. Found: C, 83.78; H, 4.63; N, 11.53.

1,2-Bis[5-(5′-methyl-2,2′-bipyridyl)]ethyne (1b). 5a (0.151 g, 6.06×10^{-4} mol), **18b** (0.398 g, 1.56×10^{-3} mol), and $Pd(PPh_3)_4$ (0.030 g, 2.59×10^{-5} mol) in 7 mL of toluene were refluxed for 24 h at 140 °C. After removal of solvent, the residue was dissolved in $CHCl_3$ and twice column chromatographed on alumina (basic, activity IV), using $CHCl_3$ as eluant. The product thus obtained was suspended in Et_2O, briefly ultrasonicated, and filtered under vacuum and the isolated solid washed with Et_2O and dried under vacuum to yield 0.139 g (63%) of **1b** (mp 279−281 °C) as colorless needles. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ (ppm) 8.82 (dd, $^4J_{6',4'} = 2.1$ Hz, $^5J_{6',3'} = 0.8$ Hz, 2H; H6′), 8.51 (d, $^4J_{6,4} = 2.2$ Hz, 2H; methylpyridine H6), 8.40 (dd, $^3J_{3',4'} = 8.3$ Hz, $^5J_{3',6'} = 0.8$ Hz, 2H; H3′), 8.32 (d, $^3J_{3,4} = 8.1$ Hz, 2H; methylpyridine H3), 7.95 (dd, $^3J_{4',3'} = 8.2$ Hz, $^4J_{4',6'} = 2.1$ Hz, 2H; H4′), 7.64 (dd, $^3J_{4,3} = 8.1$ Hz, $^4J_{4,6} = 2.2$ Hz, 2H; methylpyridine H4), 2.41 (s, 6H; CH_3). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 155.4, 152.8, 151.6, 149.8, 139.4, 137.5, 133.9, 121.0, 120.1, 119.3,

90.3 (C≡C), 18.4 (CH_3). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 326sh (63 594), 336 (69 272), 355 (52 365). FABMS: *m/z* 363 ($[M + H]^+$, 100). Anal. Calcd for $C_{24}H_{18}N_4$: C, 79.54; H, 5.01; N, 15.46. Found: C, 79.63; H, 4.92; N, 15.41.

1,4-Bis[5-(6′-phenyl-2,2′-bipyridyl)]benzene (1c). 5d (0.160 g, 4.10×10^{-4} mol), **18a** (0.524 g, 1.65×10^{-3} mol), and $Pd(PPh_3)_4$ (0.033 g, 2.86×10^{-5} mol) in 15 mL of toluene were refluxed at 136 °C for 48 h. After removal of solvent and treatment with MeOH, the product was recrystallized from 100 mL of boiling toluene and dried under vacuum to yield 0.158 g (71%) of **1c** (mp 312−314 °C) as cream-colored flakes. ^{1}H NMR (CF_3COOD), 500 MHz, 25 °C): δ (ppm) 9.63 (d, $^4J_{6',4'}$ = 1.8 Hz, 2H; H6′ inner pyridine), 9.20 (dd, $^3J_{4',3'}$ = 8.4 Hz, $^4J_{4',6'}$ = 2.1 Hz, 2H; H4′ inner pyridine), 9.01 (t, $^3J_{4,3;4,5}$ = 8.1 Hz, 2H; phenylpyridine H4), 8.93 (d, $^3J_{3',4'}$ = 8.4 Hz, 2H; H3′ inner pyridine), 8.74 (dd, $^3J_{3,4}$ = 7.9 Hz, $^4J_{3,5}$ = 0.9 Hz, 2H; phenylpyridine H3), 8.67 (dd, $^3J_{5,4}$ = 8.3 Hz, $^4J_{5,3}$ = 0.9 Hz, 2H; phenylpyridine H5), 8.26 (s, 4H; central phenyl H2″,3″, 5″,6″), 8.14 (dm, $^3J_{o,m}$ = 7.2 Hz, 4H; terminal phenyl H-*ortho*), 7.99 (tt, $^3J_{p,m}$ = 7.5 Hz, 2H; terminal phenyl H-*para*), 7.91 (t, $^3J_{m,o;m,p}$ = 7.7 Hz, 4H; terminal phenyl H-*meta*). ^{13}C NMR (CF_3-COOD, 125.8 MHz, 25 °C): δ (ppm) 157.6, 148.3, 144.4, 144.0, 143.7, 142.8, 142.2, 136.0, 134.7, 130.8, 130.1, 129.5, 128.6, 128.4, 128.1, 125.7. UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 265 (44 852), 332 (89 654). FABMS: *m/z* 539 ($[M + H]^+$, 100). Anal. Calcd for $C_{38}H_{26}N_4$: C, 84.73; H, 4.87; N, 10.40. Found: C, 84.95; H, 5.00; N, 10.43.

1,4-Bis[5-(5′-methyl-2,2′-bipyridyl)]benzene (1d). 5d (0.152 g, 3.90×10^{-4} mol), **18b** (0.390 g, 1.52×10^{-3} mol), and $Pd(PPh_3)_4$ (0.032 g, 2.77×10^{-5} mol) in 18 mL of xylene were refluxed at 160 °C for 48 h. After removal of solvent and treatment with MeOH, the product was recrystallized from boiling pyridine, washed with CH_2Cl_2, and dried under vacuum to yield 0.104 g (64%) of **1d** (mp > 320 °C) as a cream-colored microcrystalline solid. ^{1}H NMR (CF_3COOD), 500 MHz, 25 °C): δ (ppm) 9.34 (dd, $^4J_{6',4'}$ = 2.2 Hz, $^5J_{6',3'}$ = 0.4 Hz, 2H; H6′), 8.96 (dd, $^3J_{4',3'}$ = 8.4 Hz, $^4J_{4',6'}$ = 2.2 Hz, 2H; H4′), 8.87 (m, $^4J_{6,4}$ = 1.9 Hz, 2H; methylpyridine H6), 8.63 (m, $^3J_{4,3}$ and $^3J_{3',4'}$ = 8.2 Hz, 4H; methylpyridine H4, inner pyridine H3′), 8.55 (d, $^3J_{3,4}$ = 8.3 Hz, 2H; H3), 7.99 (s, 4H; phenyl H2″,3″,5″,6″), 2.70 (s, 6H; CH_3). ^{13}C NMR (CF_3COOD, 125.8 MHz, 25 °C): δ (ppm) 149.5, 145.0, 144.1, 144.0, 143.7, 142.8, 141.8, 140.8, 135.9, 129.5, 128.1, 127.7, 17.6 (CH_3). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 326 (67 198). FABMS: *m/z* 415 ($[M + H]^+$, 100). Anal. Calcd for $C_{28}H_{22}N_4$: C, 81.13; H, 5.35; N, 13.52. Found: C, 81.16; H, 5.40; N, 13.59.

4,4′-Bis[5-(6′-phenyl-2,2′-bipyridyl)]-1,1′-biphenyl (1e). 5e (0.100 g, 2.15×10^{-4} mol), **18a** (0.300 g, 9.43×10^{-4} mol), and $Pd(PPh_3)_4$ (0.021 g, 1.82×10^{-5} mol) in 9 mL of DMF were heated at 150 °C for 72 h. After cooling, the mixture was filtered under vacuum and the solid collected, washed with MeOH, and air-dried. The solid was then Soxhlet extracted with 400 mL of boiling pyridine for 48 h, and the extract twice gravity filtered, boiled down to 190 mL, and left to stand for 24 h. The solid which formed was isolated by filtration under vacuum, washed with pyridine, and dried under vacuum to yield 0.086 g (65%) of **1e** as pale yellow microcrystals. Analytically pure **1e** was obtained by dissolving the product in 8 mL of concentrated aqueous HCl to which 0.40 g of decolorizing charcoal had been added and briefly boiling the mixture followed by filtration through a G3 glass frit. The filtrate was then diluted with distilled water until precipitation ceased, adjusted to pH 7 with dilute aqueous NaOH, and boiled for 0.5 h. The product was isolated by filtration under vacuum, washed with distilled water, and dried under vacuum at 100 °C/2 × 10^{-6} mmHg to yield **1e** (mp > 320 °C) as a white amorphous solid. ^{1}H NMR (CF_3COOD), 500 MHz, 25 °C): δ (ppm) 9.52 (s, 2H; H6′), 9.17 (dd, $^3J_{4',3'}$ = 8.4 Hz, $^4J_{4',6'}$ = 1.5 Hz, 2H; H4′), 8.92 (t, $^3J_{4,3;4,5}$ = 8.1 Hz, 2H; terminal pyridine H4), 8.84 (d, $^3J_{3',4'}$ = 8.4 Hz, 2H; H3′), 8.62 (d, $^3J_{3,4}$ = 7.7 Hz, 2H; terminal pyridine H3), 8.58 (d, $^3J_{5,4}$ = 8.3 Hz, 2H; terminal pyridine H5), 8.08−8.02 (m, 12H; central biphenyl H2″,6″;3″,5″, and terminal phenyl H-*ortho*), 7.89 (t, $^3J_{p,m}$ = 7.5 Hz, 2H; terminal phenyl H-*para*), 7.80 (t, $^3J_{m,o;m,p}$ = 7.8 Hz, 4H; terminal phenyl H-*meta*). ^{13}C NMR (CF_3COOD, 125.8 MHz, 25 °C): δ (ppm) 158.0, 148.4, 144.9, 144.3, 143.7, 143.1, 142.7, 140.7, 134.7, 132.1, 130.8, 130.1, 129.3, 128.9 (two bands), 128.5, 128.4, 126.3. UV/vis ($CHCl_3$, [**1e**] ≤ 5×10^{-6} mol dm^{-3}): λ (nm) (ϵ, M^{-1} cm^{-1}) 268 (30 672), 334 (49 509). FABMS: *m/z* 615 ($[M + H]^+$, 100). Anal. Calcd for $C_{44}H_{30}N_4$: C, 85.97; H, 4.92; N, 9.11. Found: C, 86.03; H, 5.09; N, 9.29.

4,4′-Bis[5-(5′-methyl-2,2′-bipyridyl)]-1,1′-biphenyl (1f). 5e (0.118 g, 2.53×10^{-4} mol), **18b** (0.260 g, 1.02×10^{-3} mol), and $Pd(PPh_3)_4$ (0.030 g, 2.60×10^{-5} mol) in 10 mL of xylene were heated for 72 h at 150 °C. After removal of solvent and treatment with MeOH, the product was recrystallized from 90 mL of boiling pyridine to yield 0.078 g (63%) of **1f** (mp > 320 °C) as a cream-colored solid. ^{1}H NMR (CF_3COOD), 500 MHz, 60 °C): δ (ppm) 9.75 (d, $^4J_{6',4'}$ = 2.2 Hz, 2H; H6′), 9.39 (dd, $^3J_{4',3'}$ = 8.5 Hz, $^4J_{4',6'}$ = 2.2 Hz, 2H; H4′), 9.31 (dd, $^4J_{6,4}$ = 1.3 Hz, $^5J_{6,3}$ = 0.6 Hz, 2H; methylpyridine H6), 9.05 (m, 4H; methylpyridine H3, inner pyridine H3′), 8.98 (d, $^3J_{4,3}$ = 8.3 Hz, 2H; methylpyridine H4), 8.37 (d, $^3J_{2'',3'';6'',5''}$ = 8.6 Hz, 4H; biphenyl (inner) H2″,6″), 8.32 (d, $^3J_{3'',2'';5'',6''}$ = 8.6 Hz, 4H; biphenyl (outer) H3″,5″), 3.16 (s, 6H; CH_3). ^{13}C NMR (CF_3-COOD, 125.8 MHz, 60 °C): δ (ppm) 149.1, 144.3, 144.2, 144.0, 143.7, 143.5, 143.4, 141.1, 141.0, 132.4, 129.2, 128.3, 127.6, 127.3, 17.5 (CH_3). UV/vis ($CHCl_3$, [**1f**] < 2×10^{-6} mol dm^{-3}): λ (nm) (ϵ, M^{-1} cm^{-1}) 330 (78 909). FABMS: *m/z* 491 ($[M + H]^+$, 100). Anal. Calcd for $C_{34}H_{26}N_4$: C, 83.24; H, 5.34; N, 11.42. Found: C, 83.09; H, 5.32; N, 11.41.

1,4-Bis[5-ethynyl(6′-phenyl-2,2′-bipyridyl)]benzene (1g). 5f (0.152 g, 4.35×10^{-4} mol), **18a** (0.520 g, 1.64×10^{-3} mol), and $Pd(PPh_3)_4$ (0.046 g, 3.98×10^{-5} mol) in 17 mL of toluene were refluxed at 136 °C for 48 h. After cooling, the reaction mixture was filtered under vacuum, washed with toluene, and air-dried. The product was then dissolved in 80 mL of boiling toluene to which 0.1 g of decolorizing charcoal had been added, gravity filtered, and left to cool. The crystalline solid which formed on standing was isolated by filtration under vacuum, washed with toluene, and dried under vacuum to yield 0.164 g (64%) of **1g** (mp 285−286 °C) as slightly green flourescent plates. ^{1}H NMR ($CDCl_2CDCl_2$, 500 MHz, 70 °C): δ (ppm) 8.91 (dd, $^4J_{6',4'}$ = 2.2 Hz, $^5J_{6',3'}$ = 0.9 Hz, 2H; H6′), 8.68 (dd, $^3J_{3',4'}$ = 8.2 Hz, $^5J_{3',6'}$ = 0.9 Hz, 2H; H3′), 8.48 (dd, $^3J_{3,4}$ = 7.8 Hz, $^4J_{3,5}$ = 0.9 Hz, 2H; terminal pyridine H3), 8.20 (dm, $^3J_{o,m}$ = 7.7 Hz, 4H; terminal phenyl H-*ortho*), 8.03 (dd, $^3J_{4',3'}$ = 8.2 Hz, $^4J_{4',6'}$ = 2.1 Hz, 2H; H4′), 7.94 (t, $^3J_{4,3;4,5}$ = 7.8 Hz, 2H; terminal pyridine H4), 7.83 (dd, $^3J_{5,4}$ = 7.8 Hz, $^4J_{5,3}$ = 1.0 Hz, 2H; terminal pyridine H5), 7.65 (s, 4H; central phenyl H2″,3″,5″,6″), 7.57 (tm, $^3J_{m,o;m,p}$ = 7.4 Hz, 4H; terminal phenyl H-*meta*), 7.50 (tt, $^3J_{p,m}$ = 7.3 Hz, 2H; terminal phenyl H-*para*). ^{13}C NMR ($CDCl_2CDCl_2$, 125.8 MHz, 70 °C): δ (ppm) 156.8, 155.5, 155.2, 151.7, 139.4, 139.3, 137.6, 131.8, 129.1, 128.8, 127.1, 123.2, 120.6, 120.5, 120.1, 119.9, 93.2 (C≡C), 88.9 (C≡C). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}): 266 (32 749), 353 (84 595), 373 (59 344). FABMS: *m/z* 587 ($[M + H]^+$, 100%). Anal. Calcd for $C_{42}H_{26}N_4$: C, 85.98; H, 4.47; N, 9.55. Found: C, 85.89; H, 4.64; N, 9.54.

1,4-Bis[5-ethynyl(5′-methyl-2,2′-bipyridyl)]benzene (1h). 5f (0.127 g, 3.64×10^{-4} mol), **18b** (0.344 g, 1.34×10^{-3} mol), and $Pd(PPh_3)_4$ (0.032 g, 2.77×10^{-5} mol) in 16 mL of toluene were refluxed at 140 °C for 48 h. After removal of solvent and treatment with MeOH, the product was recrystallized from 50 mL of toluene to which 0.15 g of decolorizing charcoal had been added. The solid thus obtained was finally sublimed under vacuum at 250 °C/2 × 10^{-6} mmHg and the sublimate suspended in acetone, briefly ultrasonicated, isolated by filtration under vacuum, washed with acetone, and dried under vacuum to yield 0.093 g (55%) of **1h** (mp 295−297 °C) as a light-sensitive pale yellow-green solid. ^{1}H NMR ($CDCl_2CDCl_2$, 500 MHz, 100 °C): δ (ppm) 8.87 (d, 2H; inner pyridine H6′), 8.59 (s, 2H; methylpyridine H6), 8.50 (d, $^3J_{3',4'}$ = 8.2 Hz, 2H; inner pyridine H3′), 8.41 (d, $^3J_{3,4}$ = 8.0 Hz, 2H; methylpyridine H3), 7.97 (dd, $^3J_{4',3'}$ = 8.2 Hz, $^4J_{4',6'}$ = 2.1 Hz, 2H; inner pyridine H4′), 7.70 (dd, $^3J_{4,3}$ = 8.1 Hz, $^4J_{4,6}$ = 2.1 Hz, 2H; methylpyridine H4), 7.63 (s, 4H; phenyl H2″,3″,5″,6″), 2.46 (s, 6H; CH_3). ^{1}H NMR (CF_3COOD/20% D_2O, 500 MHz, 25 °C): δ (ppm) 9.00 (dd, $^4J_{6',4'}$ = 1.9 Hz, $^5J_{6',3'}$ = 0.7 Hz, 2H; inner pyridine H6′), 8.74 (dm, $^4J_{6,4}$ = 1.2 Hz, 2H; methylpyridine H6), 8.57 (dd,

$^3J_{4,3}$ = 8.4 Hz, $^4J_{4,6}$ = 1.3 Hz, 2H; methylpyridine H4), 8.49 (d, $^3J_{3,4}$ = 8.4 Hz, 2H; methylpyridine H3), 8.36 (dd, $^3J_{4',3'}$ = 8.3 Hz, $^4J_{4',6'}$ = 2.0 Hz, 2H; inner pyridine H4′), 8.30 (dd, $^3J_{3',4'}$ = 8.4 Hz, $^5J_{3',6'}$ = 0.6 Hz, 2H; inner pyridine H3′), 7.67 (s, 4H; phenyl H2″,3″,5″,6″), 2.70 (s, 6H; CH_3). ^{13}C NMR (CF_3COOD/20% D_2O, 125.8 MHz, 25 °C): δ (ppm) 154.7, 152.4, 147.6, 146.9, 146.1, 145.5, 144.7, 135.8, 129.5, 128.0, 126.7, 126.6, 101.2 (C≡C), 89.1 (C≡C). 20.7 (CH_3). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 350 (98 621), 371 (64 037). FABMS: *m*/*z* 463 ([M + H]$^+$, 100). Anal. Calcd for $C_{32}H_{22}N_4$: C, 83.09; H, 4.79; N, 12.11. Found: C, 83.17; H, 5.07; N, 12.19.

4,4′-Bis[5-ethynyl(6′-phenyl-2,2′-bipyridyl)]-1, 1′-biphenyl (1i). 5g (0.100 g, 2.35 × 10^{-4} mol), **18a** (0.400 g, 1.26 × 10^{-3} mol), and $Pd(PPh_3)_4$ (0.035 g, 3.03 × 10^{-5} mol) in 10 mL of toluene were refluxed at 135 °C for 60 h. A suspended solid remained present throughout the reaction period. After removal of solvent, the residue was worked up as described for **1d**, with the exception that the boiling pyridine solution prior to gravity filtration contained 0.1 g of decolorizing charcoal. The product **1i** (0.112 g, 72%) was isolated as lemon-yellow microcrystalline flakes, pure by ^{1}H NMR. Analytically pure material was obtained upon boiling in 25 mL of concentrated aqueous HCl and adding 125 mL of distilled water. Boiling was continued for 0.1 h and the mixture allowed to cool to ambient temperature. The suspended solid was then isolated by filtration under vacuum, washed with distilled water, air-dried, and finally recrystallized from boiling pyridine (mp 313−316 °C). ^{1}H NMR ($CDCl_2CDCl_2$, 500 MHz, 120 °C): δ (ppm) 8.94 (dd, $^4J_{6',4'}$ = 2.1 Hz, $^5J_{6',3'}$ = 0.8 Hz, 2H; H6′), 8.69 (dd, $^3J_{3',4'}$ = 8.2 Hz, $^5J_{3',6'}$ = 0.8 Hz, 2H; H3′), 8.51 (dd, $^3J_{3,4}$ = 7.8 Hz, $^4J_{3,5}$ = 0.9 Hz, 2H; phenylpyridine H3), 8.20 (dm, $^3J_{o,m}$ = 7.1 Hz, 4H; terminal phenyl H-*ortho*), 8.06 (dd, $^3J_{4',3'}$ = 8.2 Hz, $^4J_{4',6'}$ = 2.1 Hz, 2H; H4′), 7.95 (t, $^3J_{4,3;4,5}$ = 7.8 Hz, 2H; phenylpyridine H4), 7.84 (dd, $^3J_{5,4}$ = 7.8 Hz, $^4J_{5,3}$ = 0.9 Hz, 2H; phenylpyridine H5), {7.74 (dm, ^3J = 8.6 Hz, 4H) and 7.70 (dm, ^3J = 8.6 Hz, 4H), biphenyl H2″,6″;3″,5″}, 7.57 (tm, $^3J_{m,o;m,p}$ = 7.4 Hz, 4H; terminal phenyl H-*meta*), 7.51 (tt, $^3J_{p,m}$ = 7.5 Hz, 2H; terminal phenyl H-*para*). ^{13}C NMR ($CDCl_2CDCl_2$, 125.8 MHz, 120 °C): δ (ppm) 156.8, 155.3, 151.6, 140.6, 139.5, 139.1, 137.4, 132.3, 129.0, 128.6, 127.0, 126.9, 122.4, 120.5, 120.3, 119.9, 93.5 (C≡C), 87.8 (C≡C). UV/vis ($CHCl_3$, [**1i**] ≤ 5 × 10^{-6} mol dm^{-3}), λ (nm) (ϵ, M^{-1} cm^{-1}) 263 (41 931), 351 (91 836). FABMS: *m*/*z* 663 ([M + H]$^+$, 100). Anal. Calcd for $C_{48}H_{30}N_4$: C, 86.98; H, 4.56; N, 8.45. Found: C, 86.91; H, 4.58; N, 8.53.

4,4′-bis[5-ethynyl(5′-methyl-2,2′-bipyridyl)]-1,1′-biphenyl (1j). 5g (0.080 g, 1.88 × 10^{-4} mol), **18b** (0.270 g, 1.05 × 10^{-3} mol), and $Pd(PPh_3)_4$ (0.023 g, 1.99 × 10^{-5} mol) in 8 mL of DMF were heated at 150 °C for 48 h. Upon cooling to ambient temperature, a solid formed which was isolated by fitration under vacuum, washed with DMF, and twice recrystallized from 4 mL portions of boiling DMF to yield 0.04 g (40%) of **1j** (mp > 320 °C) after drying under vacuum as a khaki-yellow powder. ^{1}H NMR (CF_3COOD), 500 MHz, 25 °C): δ (ppm) 9.19 (d, $^4J_{6',4'}$ = 1.5 Hz, 2H; H6′), 8.98 (s, 2H; methylpyridine H6), 8.75 (dd, $^3J_{4,3}$ and $^3J_{4',3'}$ = 8.4 Hz, $^4J_{4',6'}$ = 1.5 Hz, 4H; methylpyridine H4, inner pyridine H4′), 8.66 (d, $^3J_{3,4}$ = 8.3 Hz, 2H; methylpyridine H3), 8.61 (d, $^3J_{3',4'}$ = 8.4 Hz, 2H; inner pyridine H3′), 7.81 (s, 8H; biphenyl H2″,6″;3″,5″), 2.83 (s, 6H; CH_3). ^{13}C NMR (CF_3COOD, 125.8 MHz, 25 °C): δ (ppm) 149.5, 148.2, 147.3, 143.6, 143.1, 142.9, 141.5, 140.7, 133.3, 128.4, 127.6, 127.1, 126.6, 120.6, 102.2 (C≡C), 82.6 (C≡C), 17.6 (CH_3). UV/vis ($CHCl_3$, [**1j**] ≤ 5 × 10^{-6} mol dm^{-3}), λ nm (ϵ, M^{-1} cm^{-1}) 350 (85 954). FABMS: *m*/*z* 539 ([M + H]$^+$, 100). Anal. Calcd for $C_{38}H_{26}N_4$: C, 84.73; H, 4.86; N, 10.40. Found: C, 84.91; H, 4.87; N, 10.22.

1,2-Bis[5-ethynyl(6′-phenyl-2,2′-bipyridyl)]benzene (2a). 6 (0.100 g, 2.86 × 10^{-4} mol), **18a** (0.329 g, 1.03 × 10^{-3} mol), LiCl (0.380 g, 8.96 × 10^{-3} mol), and $Pd(PPh_3)_4$ (0.020 g, 1.73 × 10^{-5} mol) in 10 mL of toluene were refluxed at 130 °C for 48 h. After removal of solvent, the residue was briefly ultrasonicated in 20 mL of Et_2O and filtered under vacuum and the collected solid resuspended in 15 mL of MeOH and refiltered under vacuum. The isolated solid was washed with MeOH and then acetone and recrystallized from boiling methylcyclohexane to which 0.09 g of decolorizing charcoal had been added prior to filtration, to yield 0.107 g (64%) of **2a** (mp 230−231 °C) as fibrous cream-colored needles. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ (ppm) 8.89 (dd, $^4J_{6',4'}$ = 2.1 Hz, $^5J_{6',3'}$ = 0.9 Hz, 2H; H6′), 8.69 (dd, $^3J_{3',4'}$ = 8.2 Hz, $^5J_{3',6'}$ = 0.8 Hz, 2H; H3′), 8.41 (dd, $^3J_{3,4}$ = 7.8 Hz, $^4J_{3,5}$ = 0.9 Hz, 2H; phenylpyridine H3), 8.16 (dm, $^3J_{o,m}$ = 7.0 Hz, 4H; terminal phenyl H-*ortho*), 8.01 (dd, $^3J_{4',3'}$ = 8.2 Hz, $^4J_{4',6'}$ = 2.1 Hz, 2H; H4′), 7.90 (t, $^3J_{4,3;4,5}$ = 7.8 Hz, 2H; phenylpyridine H4), 7.79 (dd, $^3J_{5,4}$ = 7.8 Hz, $^4J_{5,3}$ = 0.9 Hz, 2H; phenylpyridine H5), 7.66 (m, 2H; central phenyl H3″,6″), 7.51 (tm, $^3J_{m,o;m,p}$ = 7.4 Hz, 4H; terminal phenyl H-*meta*), 7.44 (tt, $^3J_{p,m}$ = 7.3 Hz, 2H; terminal phenyl H-*para*), 7.40 (m, 2H; central phenyl H4″,5″). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 156.6, 155.4, 155.0, 151.5, 139.3, 139.2, 137.8, 132.1, 129.1, 128.7, 128.6, 127.0, 125.3, 120.7, 120.6, 120.1, 119.7, 92.0 (C≡C), 90.8 (C≡C). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 262sh (50 536), 270 (51 046), 322 (76 097), 350sh (41 926). FABMS *m*/*z* 587 ([M + H]$^+$, 100). Anal. Calcd for $C_{42}H_{26}N_4$: C, 85.98; H, 4.47; N, 9.55. Found: C, 85.80; H, 4.61; N, 9.61.

1,2-Bis[5-ethynyl(5′-methyl-2,2′-bipyridyl)]benzene (2b). 6 (0.100 g, 2.86 × 10^{-4} mol), **18b** (0.232 g, 9.06 × 10^{-4} mol), and $Pd(PPh_3)_4$ (0.020 g, 1.73 × 10^{-5} mol) in 5.5 mL of toluene were refluxed at 120 °C for 24 h. After removal of solvent and treatment with MeOH, the brown solid was chromatographed on alumina (standardized activity II−III), using CH_2Cl_2 as eluant, and the isolated product suspended in 3 mL of acetone. The mixture was briefly ultrasonicated, filtered under vacuum, washed with acetone, and air-dried to yield 0.070 g (52%) of **2b** as a pale-yellow microcrystalline solid. Analytically pure product was obtained upon sublimation under vacuum (2 × 10^{-4} mmHg/220 °C, with some decomposition), and brief ultrasonication of the sublimate in acetone followed by filtration under vacuum, washing with acetone, and drying under vacuum to yield **2b** (mp 246−247 °C) as a cream-colored powder. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ (ppm) 8.84 (dd, $^4J_{6',4'}$ = 2.1 Hz, $^5J_{6',3'}$ = 0.9 Hz, 2H; inner pyridine H6′), 8.51 (m, 2H; methylpyridine H6), 8.39 (dd, $^3J_{3',4'}$ = 8.2 Hz, $^5J_{3',6'}$ = 0.9 Hz, 2H; inner pyridine H3′), 8.31 (dd, $^3J_{3,4}$ = 8.0 Hz, $^5J_{3,5}$ = 0.2 Hz, 2H; methylpyridine H3), 7.95 (dd, $^3J_{4',3'}$ = 8.2 Hz, $^4J_{4',6'}$ = 2.1 Hz, 2H; inner pyridine H4′), 7.63 (dm, $^3J_{4,3}$ = 8.1 Hz, 2H; methylpyridine H4), 7.62 (m, 2H; central phenyl H3″,6″), 7.38 (m, 2H; central phenyl H4″,5″), 2.40 (s, 6H; CH_3). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 155.3, 152.9, 151.5, 149.8, 139.3, 137.5, 133.8, 132.1, 128.6, 125.3, 121.0, 120.2, 119.7, 91.9 (C≡C), 90.8 (C≡C), 18.3 (CH_3). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 258 (26 445), 274 (27 773), 315 (78 492), 348 (37 154). FABMS: *m*/*z* 463 ([M + H]$^+$, 100). Anal. Calcd for $C_{32}H_{22}N_4$: C, 83.09; H, 4.79; N, 12.11. Found: C, 83.26; H, 4.75; N, 12.21.

1,3-Bis[5-ethynyl(6′-phenyl-2,2′-bipyridyl)]benzene (3a). 7 (0.140 g, 4.01 × 10^{-4} mol), **18a** (0.365 g, 1.15 × 10^{-3} mol), and $Pd(PPh_3)_4$ (0.036 g, 3.12 × 10^{-5} mol) in 10 mL of toluene were refluxed at 136 °C for 48 h. After removal of solvent and treatment with MeOH, the solid was chromatographed on silica, eluting first with $CHCl_3$ and then 1% MeOH/$CHCl_3$, and the product collected in a single fraction (200 mL). Decolorizing charcoal (0.1 g) was added, the mixture stirred and refluxed for 0.25 h and then gravity filtered, and all solvent removed from the filtrate by distillation on a water bath. The remaining buff-colored solid was then dissolved in 220 mL of boiling acetone and gravity filtered and the solvent reduced in volume to 12 mL by rotary evaporation on a water bath. The product was isolated by filtration under vaccum, washed with acetone, and dried under vacuum to yield 0.178 g (76%) of **3a** (mp 228−230 °C) as a cream-colored microcrystalline solid. A product of microanalytical purity was obtained upon recrystallization from toluene. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ (ppm) 8.86 (d, $^4J_{6',4'}$ = 2.1 Hz, 2H; H6′), 8.67 (d, $^3J_{3',4'}$ = 8.2 Hz, 2H; H3′), 8.40 (d, $^3J_{3,4}$ = 7.7 Hz, 2H; phenylpyridine H3), 8.16 (dm, $^3J_{o,m}$ = 7.2 Hz, 4H; terminal phenyl H-*ortho*), 7.99 (dd, $^3J_{4',3'}$ = 8.2 Hz, $^4J_{4',6'}$ = 2.1 Hz, 2H; H4′), 7.91 (t, $^3J_{4,3;4,5}$ = 7.8 Hz, 2H; phenylpyridine H4), 7.83 (m, 1H; central phenyl H2″), 7.80 (d, $^3J_{5,4}$ = 7.8 Hz, 2H; phenylpyridine H5), 7.59 (dd, $^3J_{4'',5'';6'',5''}$ = 7.7 Hz, $^4J_{4'',2'';6'',2''}$ = 1.6 Hz, 2H; central phenyl H4″,6″), 7.53

(tm, $^3J_{m,o;m,p}$ = 7.4 Hz, 4H; terminal phenyl H-*meta*), 7.46 (tt, $^3J_{p,m}$ = 7.3 Hz, 2H; terminal phenyl H-*para*), 7.42 (t, $^3J_{5'',4'';5'',6''}$ = 7.6 Hz, 1H; central phenyl H5″). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 156.7, 155.0, 154.6, 151.3, 139.7, 139.1, 137.8, 134.8, 131.9, 131.8, 129.2, 128.8, 127.0, 123.1, 120.9, 120.7, 120.1, 119.8, 92.6 (C≡C), 87.1(C≡C). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 269 (64 264), 330 (122 284), 343 (109 094). FABMS: *m*/*z* 587 ([M + H]$^+$, 100). Anal. Calcd for $C_{42}H_{26}N_4$: C, 85.98; H, 4.47; N, 9.55. Found: C, 86.09; H, 4.39; N, 9.49.

1,3-Bis[5-ethynyl(5′-methyl-2,2′-bipyridyl)]benzene (3b). **7** (0.141 g, 4.04 × 10^{-4} mol), **18b** (0.300 g, 1.17 × 10^{-3} mol), and $Pd(PPh_3)_4$ (0.018 g, 1.56 × 10^{-5} mol) in 7 mL of toluene were refluxed at 140 °C for 48 h. After removal of solvent, the residue was chromatographed on alumina (basic, activity IV), eluting with $CHCl_3$. The product was then sublimed under vacuum at 230 °C/6 × 10^{-6} mmHg and the sublimate suspended in acetone, briefly ultrasonicated, isolated by filtration under vacuum, washed with acetone, and dried under vacuum to yield **3b** (0.077 g, 41%) as a white solid. Analytically pure **3b** could be obtained by boiling in excess MeCN, isolation by vacuum filtration, followed by recrystallization from 4 mL of toluene, and drying under vacuum to yield **3b** (mp 287−288 °C) as colorless microcrystals. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ (ppm) 8.80 (dd, $^4J_{6',4'}$ = 2.1 Hz, $^5J_{6',3'}$ = 0.9 Hz, 2H; H6′), 8.52 (m, $^4J_{6,4}$ = 2.2 Hz, $^5J_{6,3}$ = 0.8 Hz, 2H; methylpyridine H6), 8.38 (dd, $^3J_{3',4'}$ = 8.3 Hz, $^5J_{3',6'}$ = 0.9 Hz, 2H; H3′), 8.31 (d, $^3J_{3,4}$ = 8.1 Hz, 2H; methylpyridine H3), 7.93 (dd, $^3J_{4',3'}$ = 8.2 Hz, $^4J_{4',6'}$ = 2.1 Hz, 2H; H4′), 7.79 (td, $^4J_{2'',4'';\ 2'',6''}$ = 1.6 Hz, $^5J_{2'',5''}$ = 0.5 Hz, 1H; phenyl H2″), 7.64 (dd, $^3J_{4,3}$ = 8.1 Hz, $^4J_{4,6}$ = 2.3 Hz, 2H; methylpyridine H4), 7.56 (m, $^3J_{4'',5'';\ 6'',5''}$ = 7.7 Hz, $^4J_{4'',2'';\ 6'',2''}$ = 1.7 Hz, 2H; phenyl H4″,6″), 7.40 (td, $^3J_{5'',4'';\ 5'',6''}$ = 7.8 Hz, $^5J_{5'',2''}$ = 0.6 Hz, 1H; phenyl H5″), 2.41 (s, 6H; CH_3). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 155.1, 152.8, 151.6, 149.6, 139.4, 137.6, 134.8, 133.9, 131.7, 128.7, 123.2, 121.0, 120.1, 119.6, 92.3 (C≡C), 87.2 (C≡C), 18.4 (CH_3). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 323 (10 1580), 339 (85 044). FABMS: *m*/*z* 463 ([M + H]$^+$, 100). Anal. Calcd for $C_{32}H_{22}N_4$: C, 83.09; H, 4.79; N, 12.11. Found: C, 83.23; H, 5.01; N, 11.91.

1,3,5-Tris[5-ethynyl(6′-phenyl-2,2′-bipyridyl)]benzene (4a). **8** (0.100 g, 2.08 × 10^{-4} mol), **18a** (0.366 g, 1.15 × 10^{-3} mol), LiCl (0.736 g, 1.74 × 10^{-2} mol), and $Pd(PPh_3)_4$ (0.031 g, 2.68 × 10^{-5} mol) in 10 mL of toluene were refluxed at 134 °C for 48 h. The product precipitated from solution during reflux. After removal of solvent and treatment with MeOH, the solid was recrystallized from toluene containing 0.1 g of decolorizing charcoal, washed with acetone, and air-dried to yield **4a** (0.146 g, 83%) as a cream-colored powder (mp ≥ 292 °C with gradual decomposition). A product of microanalytical purity was obtained upon further recrystallization from toluene. ^{1}H NMR ($CDCl_2CDCl_2$, 500 MHz, 25 °C): δ (ppm) 8.91 (dd, $^4J_{6',4'}$ = 1.9 Hz, $^5J_{6',3'}$ = 0.5 Hz, 3H; inner pyridine H6′), 8.69 (dd, $^3J_{3',4'}$ = 8.4 Hz, $^5J_{3',6'}$ = 0.5 Hz, 3H; inner pyridine H3′), 8.44 (d, $^3J_{3,4}$ = 7.6 Hz, 3H; phenylpyridine H3), 8.18 (dm, $^3J_{o,m}$ = 7.1 Hz, 6H; terminal phenyl H-*ortho*), 8.06 (dd, $^3J_{4',3'}$ = 8.2 Hz, $^4J_{4',6'}$ = 2.1 Hz, 3H; inner pyridine H4′), 7.95 (t, $^3J_{4,3;4,5}$ = 7.8 Hz, 3H; phenylpyridine H4), 7.87 (s, 3H; central phenyl H2″,4″,6″), 7.83 (dd, $^3J_{5,4}$ = 7.9 Hz, $^4J_{5,3}$ = 0.7 Hz, 3H; phenylpyridine H5), 7.56 (tm, $^3J_{m,o;m,p}$ = 7.4 Hz, 6H; terminal phenyl H-*meta*), 7.50 (tm, $^3J_{p,m}$ = 7.3 Hz, 3H; terminal phenyl H-*para*). ^{13}C NMR ($CDCl_2CDCl_2$, 125.8 MHz, 25 °C): δ (ppm) 156.6, 155.4, 154.9, 151.8, 139.7, 139.1, 138.0, 134.9, 129.4, 129.0, 127.1, 123.7, 120.9, 120.7, 120.0, 119.7, 91.8 (C≡C), 88.2 (C≡C). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 270 (65 152), 290 (57 976), 332 (118 375), 346 (108 621). FABMS: *m*/*z* 841 ([M + H]$^+$, 100). Anal. Calcd for $C_{60}H_{36}N_6$: C, 85.69; H, 4.31; N, 9.99. Found: C, 85.75; H, 4.54; N, 10.16.

1,3,5-Tris[5-ethynyl(5′-methyl-2,2′-bipyridyl)]benzene (4b). **8** (0.052 g, 1.08 × 10^{-4} mol), **18b** (0.220 g, 8.60 × 10^{-4} mol), LiCl (0.140 g, 3.30 × 10^{-3} mol), and $Pd(PPh_3)_4$ (0.018 g, 1.56 × 10^{-5} mol) in 8 mL of toluene were refluxed at 140 °C for 24 h. Further portions of **18b** (0.150 g, 5.86 × 10^{-4} mol) and $Pd(PPh_3)_4$ (0.018 g, 1.56 × 10^{-5} mol) were added, and stirring was continued at 140 °C for an additional 24 h. After removal of solvent and treatment with MeOH, the product was chromatographed on alumina (standardized activity II−III), eluting with $CHCl_3$. The product thus obtained was briefly ultrasonicated in 3 mL of cold 1,4-dioxane, filtered under vacuum, washed with ice cold 1,4-dioxane, and dried under vacuum to yield 0.054 g (76%) of **4b** (mp 302−303 °C) as a cream-colored powder. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ (ppm) 8.81(dd, $^4J_{6',4'}$ = 2.1 Hz, $^5J_{6',3'}$ = 0.8 Hz, 3H; H6′), 8.52 (dd, $^4J_{6,4}$ = 1.4 Hz, $^5J_{6,3}$ = 0.8 Hz, 3H; methylpyridine H6), 8.40 (dd, $^3J_{3',4'}$ = 8.2 Hz, $^5J_{3',6'}$ = 0.8 Hz, 3H; H3′), 8.32 (d, $^3J_{3,4}$ = 8.2 Hz, 3H; methylpyridine H3), 7.93 (dd, $^3J_{4',3'}$ = 8.2 Hz, $^4J_{4',6'}$ = 2.1 Hz, 3H; H4′), 7.75 (s, 3H; phenyl H2″,4″,6″), 7.64 (m, $^3J_{4,3}$ = 8.1 Hz, $^4J_{4,6}$ = 2.2 Hz, 3H; methylpyridine H4), 2.41 (s, 9H; CH_3). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 155.4, 152.8, 151.7, 149.8, 139.4, 137.5, 134.5, 133.9, 123.7, 120.9, 120.1, 119.3, 91.3 (C≡C), 88.0 (C≡C), 18.4 (CH_3). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 325 (179 505), 342 (146 303). EIMS: *m*/*z* 654 (M^+, 100). Anal. Calcd for $C_{45}H_{30}N_6$: C, 82.55; H, 4.62; N, 12.84. Found: C, 82.60; H, 4.84; N, 12.87.

2-Chloro-5-(trimethylsilylethynyl)pyridine (15a). To a mixture of **9** (1.703 g, 7.11 × 10^{-3} mol), $PdCl_2(PPh_3)_2$ (0.040 g, 5.70 × 10^{-5} mol), and CuI (0.036 g, 1.89 × 10^{-4} mol) were added consecutively 25 mL of Et_3N and (trimethylsilyl)ethyne (0.700 g, 7.13 × 10^{-3} mol), and the reaction was stirred at ambient temperature for 48 h. After removal of solvent, the residue was boiled in 25 mL of hexane. The hexane extract was flash chromatographed on a column of silica, eluting with 5% Et_2O/hexane, to yield an oil which solidified upon cooling after removal of solvent by distillation on a water bath. The solid was subsequently dried under vacuum (20 °C/0.1 mmHg) to yield 1.400 g (94%) of **15a** (mp 58−59 °C) as volatile colorless crystals. The product could also be readily sublimed under vacuum (50 °C/0.1 mmHg). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ (ppm) 8.45 (d, $^4J_{6,4}$ = 2.3 Hz, 1H; H6), 7.67 (dd, $^3J_{4,3}$ = 8.3 Hz, $^4J_{4,6}$ = 2.3 Hz, 1H; H4), 7.26 (d, $^3J_{3,4}$ = 8.3 Hz, 1H; H3), 0.25 (s, 9H; CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ (ppm) 152.4, 150.6, 141.2, 123.7, 119.2, 100.0 (C≡C), 99.6 (C≡C), −0.3 (CH_3). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 255 (20 368), 259sh (19 222), 278 (6227), 285 (6621), 294sh (4821). EIMS: *m*/*z* 209 (M^+, 15). Anal. Calcd for $C_{10}H_{12}ClNSi$: C, 57.26; H, 5.77; N, 6.68. Found: C, 57.27; H, 5.73; N, 6.72.

2-Chloro-5-ethynylpyridine (15b). To a solution of **15a** (0.400 g, 1.91 × 10^{-3} mol) in THF (20 mL) and MeOH (15 mL) was added a solution of NaOH (0.430 g, 1.08 × 10^{-2} mol) in distilled water (2 mL), and the reaction was stirred at ambient temperature for no longer than 24 h. Saturated aqueous NaCl (30 mL) was then added and the mixture extracted with 3 × 60 mL portions of Et_2O. The organic extracts were combined, dried ($MgSO_4$), and filtered and the solvent distilled off at atmospheric pressure on a water bath at 55 °C. The remaining solid was sublimed under vacuum at 52 °C/0.1 mmHg to yield **15b** (82−95%) as volatile, pungent-smelling colorless crystals (mp 81−82 °C). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ (ppm) 8.48 (d, $^4J_{6,4}$ = 2.2 Hz, 1H; H6), 7.70 (dd, $^3J_{4,3}$ = 8.3 Hz, $^4J_{4,6}$ = 2.3 Hz, 1H; H4), 7.29 (d, $^3J_{3,4}$ = 8.3 Hz, 1H; H3), 3.25 (s, 1H; HC≡C). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ (ppm) 152.6, 151.1, 141.4, 123.8, 118.1, 81.7 (C≡C), 79.1 (C≡C). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 275sh (3860), 281 (4509), 289 (3480). EIMS: *m*/*z* 137 (M^+, 100). Anal. Calcd for C_7H_4ClN: C, 61.12; H, 2.93; N, 10.18. Found: C, 61.36; H, 2.94; N, 10.17.

1-[5-(6′-Methyl-2,2′-bipyridyl)]-4-[5-(2-bromopyridyl)]-benzene (19). **5d** (0.233 g, 5.97 × 10^{-4} mol), **18c** (0.195 g, 7.62 × 10^{-4} mol), and $Pd(PPh_3)_4$ (0.040 g, 3.46 × 10^{-5} mol) in 20 mL of toluene were refluxed at 135 °C for 36 h. After removal of solvent, the residue was chromatographed on alumina (standardized activity II−III), eluting with CH_2Cl_2. Unreacted **5d** eluted first followed by **19**. After removal of solvent by distillation on a water bath, the **5d** and **19** thus obtained were separately suspended in 20 mL of MeOH, briefly ultrasonicated, isolated by vacuum filtration, washed with MeOH, and air-dried to yield **5d** (0.027 g) and **19** (0.077 g, 36% based on reacted **5d**) (mp 237−240 °C) as white solids. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ (ppm) 8.95 (dd, $^4J_{6',4'}$ = 2.4 Hz, $^5J_{6',3'}$ = 0.8 Hz, 1H; inner pyridine H6′), 8.65 (dd, $^4J_{6''',4'''}$ = 2.6 Hz, $^5J_{6''',3'''}$ = 0.6 Hz, 1H; bromopyridine H6‴), 8.52 (dd, $^3J_{3',4'}$ = 8.2 Hz, $^5J_{3',6'}$ = 0.8 Hz, 1H; inner pyridine H3′), 8.22 (d, $^3J_{3,4}$ = 7.8 Hz, 1H; methylpyridine H3), 8.04 (dd, $^3J_{4',3'}$ =

8.2 Hz, $^4J_{4',6'} = 2.4$ Hz, 1H; inner pyridine H4′), 7.79 (dd, $^3J_{4''',3'''} = 8.2$ Hz, $^4J_{4''',6'''} = 2.6$ Hz, 1H; bromopyridine H4‴), 7.77 (dm, $^3J_{2'',3'';6'',5''} = 8.4$ Hz, 2H; phenyl (inner) H2″,6″), 7.73 (t, $^3J_{4,3;4,5} = 7.7$ Hz, 1H; methylpyridine H4), 7.68 (dm, $^3J_{3'',2'';5'',6''} = 8.5$ Hz, 2H, phenyl (outer) H3″,5″), 7.58 (dd, $^3J_{3''',4'''} = 8.2$ Hz, $^5J_{3''',6'''} = 0.7$ Hz, 1H; bromopyridine H3‴), 7.20 (d, $^3J_{5,4} = 7.6$ Hz, 1H; methylpyridine H5), 2.66 (s, 3H; CH_3). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 158.1, 155.8, 155.2, 148.4, 147.5, 141.2, 138.0, 137.1, 136.8, 136.2, 135.3 (2 peaks), 135.0, 128.1, 127.9, 127.7, 123.4, 121.2, 118.1, 24.7 (CH_3). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 314 (58 056). EIMS: *m*/*z* 401 (M^+, 100). Anal. Calcd for $C_{22}H_{16}BrN_3$: C, 65.68; H, 4.01; N, 10.45. Found: C, 65.62; H, 3.97; N, 10.24.

1-[5-(2,2′-Bipyridyl)]-4-[5-(2-bromopyridyl)]benzene (20) and 1,4-Bis-5-(2,2′-bipyridyl)benzene (21). 5d (0.305 g, 7.82 × 10^{-4} mol), **18d** (0.224 g, 9.26 × 10^{-4} mol), and $Pd(PPh_3)_4$ (0.054 g, 4.67 × 10^{-5} mol) in 25 mL of toluene were refluxed at 135 °C for 36 h. After removal of solvent, 25 mL of Et_2O was added and the mixture briefly ultrasonicated, filtered under vacuum, washed with Et_2O, and air-dried. The solid was then chromatographed on alumina (basic, activity IV), eluting with CH_2Cl_2. Unreacted **5d** eluted first followed by **20** and finally **21**. **5d** was further purified by brief ultrasonication in Et_2O, isolation by suction filtration, and drying under vacuum to yield 0.043 g of **5d**. Pure **20** (0.087 g, 33% based on reacted **5d**) was obtained in a manner identical to that described for **5d**, and **21** (0.033 g, 13% based on reacted **5d**) (mp 299−303 °C) after washing with acetone and drying under vacuum. Microanalytically pure **20** (mp 217−219 °C) was obtained upon recrystallization from toluene and drying under vacuum at 120 °C/2 × 10^{-6} mmHg.

Data for 20. ^{1}H NMR ($CDCl_3$), 500 MHz, 25 °C): δ (ppm) 8.96 (dd, $^4J_{6',4'} = 2.4$ Hz, $^5J_{6',3'} = 0.8$ Hz, 1H; inner pyridine H6′), 8.71 (dq, $^3J_{6,5} = 4.8$ Hz, $^4J_{6,4} = 1.8$ Hz, $^5J_{6,3} = 0.9$ Hz, 1H; terminal pyridine H6), 8.65 (dd, $^4J_{6''',4'''} = 2.6$ Hz, $^5J_{6''',3'''} = 0.7$ Hz, 1H; bromopyridine H6‴), 8.51 (dd, $^3J_{3',4'} = 8.2$ Hz, $^5J_{3',6'} = 0.8$ Hz, 1H; H3′), 8.45 (dt, $^3J_{3,4} = 7.9$ Hz, $^4J_{3,5;}$ $^5J_{3,6} = 1.1$ Hz, 1H; terminal pyridine H3), 8.07 (dd, $^3J_{4',3'} = 8.3$ Hz, $^4J_{4',6'} = 2.4$ Hz, 1H; inner pyridine H4′), 7.85 (qd, $^3J_{4,3} = 7.9$ Hz, $^3J_{4,5} = 7.6$ Hz, $^4J_{4,6} = 1.8$ Hz, 1H; terminal pyridine H4), 7.79 (dd, $^3J_{4''',3'''} = 8.3$ Hz, $^4J_{4''',6'''} = 2.6$ Hz, 1H; bromopyridine H4‴), 7.78 (d, $^3J_{2'',3'';6'',5''} = 8.6$ Hz, 2H; phenyl inner H2″,6″), 7.69 (d, $^3J_{3'',2'';5'',6''} = 8.6$ Hz, 2H; phenyl outer H3″,5″), 7.59 (dd, $^3J_{3''',4'''} = 8.2$ Hz, $^5J_{3''',6'''} = 0.7$ Hz, 1H; bromopyridine H3‴), 7.34 (qd, $^3J_{5,4} = 7.5$ Hz, $^3J_{5,6} = 4.8$ Hz, $^4J_{5,3} = 1.2$ Hz, 1H; terminal pyridine H5). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 155.7, 155.3, 149.3, 148.4, 147.5, 141.2, 137.8, 137.0, 136.8, 136.3, 135.5, 135.3, 135.1, 128.1, 127.9, 127.7, 123.8, 121.1. UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}): 312 (48 369). EIMS: *m*/*z* 389 (M^+, 100). Anal. Calcd for $C_{21}H_{14}BrN_3$: C, 64.96; H, 3.63; N, 10.82. Found: C, 64.94; H, 3.84; N, 10.62.

Data for 21. ^{1}H NMR ($CDCl_3$), 500 MHz, 25 °C): δ (ppm) 8.99 (s, 2H; inner pyridine H6′), 8.72 (m, $^3J_{6,5} = 4.0$ Hz, 2H; terminal pyridine H6), 8.52 (d, $^3J_{3',4'} = 8.2$ Hz, 2H; inner pyridine H3′), 8.46 (d, $^3J_{3,4} = 7.9$ Hz, 2H; terminal pyridine H3), 8.09 (dd, $^3J_{4',3'} = 8.2$ Hz, $^4J_{4',6'} = 2.3$ Hz, 2H; inner pyridine H4′), 7.85 (td, $^3J_{4,3;4,5} = 7.7$ Hz, $^4J_{4,6} = 1.7$ Hz, 2H; terminal pyridine H4), 7.80 (s, 4H; phenyl H2″,3″,5″,6″), 7.34 (dd, $^3J_{5,4} = 6.7$ Hz, $^3J_{5,6} = 5.1$ Hz, 2H; terminal pyridine H5). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 155.8, 155.2, 149.3, 147.5, 137.4, 137.0, 135.7, 135.1, 127.8, 127.7, 123.8, 121.1. UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 323 (67 088). EIMS: *m*/*z* 386 (M^+, 100). Anal. Calcd for $C_{26}H_{18}N_4$: C, 80.81; H, 4.69; N, 14.50. Found: C, 80.54; H, 4.93; N, 14.60.

1-[5-(6′-Phenyl-2,2′-bipyridyl)]4-[5-(6′-methyl-2,2′-bipyridyl)]benzene (22). 19 (0.077 g, 1.91 × 10^{-4} mol), **18a** (0.228 g, 7.17 × 10^{-4} mol), and $Pd(PPh_3)_4$ (0.026 g, 2.25 × 10^{-5} mol) in 12 mL of toluene were refluxed at 135 °C for 48 h. After removal of solvent and treatment with MeOH, the solid was washed with MeOH and air-dried. The product was then recrystallized from 23 mL of boiling toluene to yield 0.079 g (87%) of **22** (mp 275−276 °C) as a hard white solid. ^{1}H NMR (CF_3COOD, 500 MHz, 25 °C): δ (ppm) 9.53 (d, $^4J_{6',4';6''',4'''} = 2.1$ Hz, 2H; H6′,6‴), 9.14 (dd, $^3J_{4''',3'''} = 8.4$ Hz, $^4J_{4''',6'''} = 2.2$ Hz, 1H; H4‴), 9.09 (dd, $^3J_{4',3'} = 8.4$ Hz, $^4J_{4',6'} = 2.2$ Hz, 1H; H4′), 8.91 (t, $^3J_{4,3;4,5} = 8.1$ Hz, 1H; phenylpyridine H4), 8.84 (t, $^3J_{4'''',3'''';4'''',5''''} = 8.1$ Hz, 1H; methylpyridine H4⁗), 8.83 (dd, $^3J_{3',4'} = 8.4$ Hz, $^5J_{3',6'} = 0.5$ Hz, 1H: H3′), 8.80 (dd, $^3J_{3''',4'''} = 8.4$ Hz, $^5J_{3''',6'''} = 0.4$ Hz, 1H; H3‴), 8.65 (dd, $^3J_{3,4} = 7.9$ Hz, $^4J_{3,5} = 1.0$ Hz, 1H; phenylpyridine H3), 8.61 (d, $^3J_{3'''',4''''} = 7.9$ Hz, 1H; methylpyridine H3⁗), 8.57 (dd, $^3J_{5,4} = 8.3$ Hz, $^4J_{5,3} = 1.0$ Hz, 1H; phenylpyridine H5), 8.24 (d, $^3J_{5'''',4''''} = 7.8$ Hz, 1H; methylpyridine H5⁗), 8.17 (s, 4H; central phenyl H2″,6″;3″,5″), 8.06 (dd, $^3J_{o,m} = 8.4$ Hz, 2H; terminal phenyl H-*ortho*), 7.91 (tt, $^3J_{p,m} = 7.5$ Hz, 1H; terminal phenyl H-*para*), 7.83 (t, $^3J_{m,o;m,p} = 7.7$ Hz, 2H; terminal phenyl H-*meta*), 3.17 (s, 3H; CH_3). ^{13}C NMR (CF_3COOD, 125.8 MHz, 25 °C): δ (ppm) 158.8, 157.5, 148.6, 148.3, 144.9, 144.2, 144.1, 143.9, 143.1, 143.0, 142.6, 142.3, 141.7, 136.3, 135.7, 134.7, 130.9, 130.8, 130.2, 129.5 (two bands), 128.4, 128.3 (two bands), 127.9, 125.8, 125.5, 19.6 (CH_3). UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}) 266 (32 301), 329 (99 214). EIMS: *m*/*z* 476 (M^+, 100). Anal. Calcd for $C_{33}H_{24}N_4$: C, 83.17; H, 5.08; N, 11.76. Found: C, 83.34; H, 5.00; N, 11.82.

1-[5-(6′-Phenyl-2,2′-bipyridyl)]-4-[5-(2,2′-bipyridyl)]benzene (23). 20 (0.070 g, 1.80 × 10^{-4} mol), **18a** (0.240 g, 7.55 × 10^{-4} mol), and $Pd(PPh_3)_4$ (0.030 g, 2.60 × 10^{-5} mol) in 12 mL of toluene were refluxed at 136 °C for 48 h. After removal of solvent and treatment with MeOH, the solid was recrystallized from 5 mL of boiling toluene. Upon cooling, 10 mL of hexane was added to complete crystallization. The product was isolated by filtration under vacuum, washed with 1:1 toluene/hexane, and dried under vacuum to yield 0.060 g (72%) of **23** as cream-colored microcrystals. Microanalytically pure **23** (mp 277−278 °C) was obtained upon further recrystallization from toluene and drying under vacuum at 120 °C/2 × 10^{-6}mmHg. ^{1}H NMR ($CDCl_3$), 500 MHz, 25 °C): δ (ppm) 9.00 (m, 2H; inner pyridines H6′, H6‴), 8.75 (dd, $^3J_{3',4'} = 8.2$ Hz, $^5J_{3',6'} = 0.7$ Hz, 1H; inner pyridine H3′), 8.72 (dq, $^3J_{6'''',5''''} = 4.8$ Hz, $^4J_{6'''',4''''} = 1.7$ Hz, $^5J_{6'''',3''''} = 0.9$ Hz, 1H; terminal unsubstituted pyridine H6⁗), 8.52 (dd, $^3J_{3''',4'''} = 8.2$ Hz, $^5J_{3''',6'''} = 0.6$ Hz, 1H; inner pyridine H3‴), 8.46 (dt, $^3J_{3'''',4''''} = 7.9$ Hz, $^4J_{3'''',5'''';}$ $^5J_{3'''',6''''} = 0.9$ Hz, 1H; terminal unsubstd. pyridine H3⁗), 8.43 (dd, $^3J_{3,4} = 7.8$ Hz, $^4J_{3,\ 5} = 0.9$ Hz, 1H; terminal phenylpyridine H3), 8.18 (d, $^3J_{o,m} = 7.6$ Hz, 2H; terminal phenyl H-ortho), 8.10 (m, 2H; inner pyridines H4′, H4‴), 7.92 (t, $^3J_{4,3;4,5} = 7.8$ Hz, 1H; terminal phenylpyridine H4), 7.86 (td, $^3J_{4'''',3'''';4'''',5''''} = 7.7$ Hz, $^4J_{4'''',6''''} = 1.8$ Hz, 1H; terminal unsubstituted pyridine H4⁗), 7.82−7.79 (m, 5H; terminal phenylpyridine H5 and central phenyl H2″,6″;3″,5″), 7.53 (t, $^3J_{m,o;m,p} = 7.5$ Hz, 2H; terminal phenyl H-*meta*), 7.46 (tt, $^3J_{p,m} = 7.3$ Hz, 1H; terminal phenyl H-*para*), 7.34 (qd, $^3J_{5'''',4''''} = 7.5$ Hz, $^3J_{5'''',6''''} = 4.8$ Hz, $^4J_{5'''',3''''} = 1.2$ Hz, 1H; terminal unsubstituted pyridine H5⁗). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 25 °C): δ (ppm) 156.5, 155.8, 155.5, 155.4, 155.2, 149.3, 147.6, 147.4, 139.3, 137.7, 137.6, 137.4, 137.0, 135.7, 135.13, 135.06, 129.1, 128.7, 127.8, 127.0, 123.8, 121.3, 121.1, 120.4, 119.3. UV/vis ($CHCl_3$): λ (nm) (ϵ, M^{-1} cm^{-1}): 267 (22 174), 328 (64 079). FABMS *m*/*z*: 463 ($[M + H]^+$, 100). Anal. Calcd for $C_{32}H_{22}N_4$: C, 83.09; H, 4.79; N, 12.11. Found: C, 83.10; H, 4.66; N, 12.18.

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Supporting Information Available: Full experimental details and complete product infrared and mass spectral data. This material is available free of charge via the Internet at http://pubs/acs/org.

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