General Method for the Preparation of Alkyne-Functionalized Oligopyridine Building Blocks

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A large series of alkyne-substituted oligopyridines based on 2,2′-bipyridine, 1,10-phenanthroline, 2,2′:6′,2″-terpyridine, or 1,8-naphthyridine substrates has been synthesized and fully characterized. The palladium(0)-catalyzed coupling of bromo- or chloro-substituted derivatives with (trimethylsilyl)-acetylene proceeds readily in diisopropylamine under ambient conditions giving good yields of the corresponding alkyne-substituted substrates oligoPy(C≡C)$SiMe_3$. The terminal monoynes oligoPyC≡CH become available upon treatment with K_2CO_3 in methanol. Stepwise homologation of the acetylene function by Cadiot-Chodkiewicz coupling of oligoPyC≡CH with (bromoethynyl)-triethylsilane (BrC≡C$SiEt_3$) affords, in good yield, the silylated diynes oligoPy(C≡C)$_2SiEt_3$, from which the terminal diynes oligoPy(C≡C)$_2$H are formed by treatment with aqueous methanolic alkali. Reaction of oligoPy(C≡C)$_2$H with BrC≡C$SiEt_3$ yields the silylated triynes oligoPy(C≡C)$_3SiEt_3$ in modest yield. Further homologation is limited by nucleophilic attack of *n*-propylamine at the C-2 carbon of the alkyne chain, giving rise to a mixture of *cis*/*cis* (48%), *cis*/*trans* (33%), and *trans*/*trans* (19%) enaminediyne compounds **21a**−**c**. Glaser oxidative self-coupling of the terminal diynes provides access to ditopic bipyridine or terpyridine ligands oligoPy(C≡C)$_4$oligoPy comprising a tetrayne spacer. Quantitative formation of air-stable copper(I) complexes is described for the 6,6′-substituted ligands. A single crystal X-ray structure of complex **22a** shows that the two ligands are interlocked around the copper(I) center in a pseudotetrahedral arrangement, similar to the structure deduced from NMR and FAB^+ data. The synthetic methods reported herein represent a valuable approach to the large-scale preparation of alkyne-functionalized oligopyridines.

Introduction

The field of *molecular electronics* involves the search for new materials that favor long-range vectorial electron or energy transfer and/or exhibit nonlinear optical properties.[1,2] Recently, interesting results have been obtained using polyene,[3] phenyl,[4] and alkyne[5,6] groups as spacers between metal centers. Among the many criteria for obtaining efficient information transfer across spacer subunits, the most important are (i) rigidity of the molecular structure, (ii) the presence of extended π^* orbitals, (iii) a well-defined separation between interacting termini, and (iv) excellent photochemical stability. Good examples of such molecules are metal complexes formed from alkyne-substituted oligopyridines, these complexes might also be expected to possess important applications in material, molecular, and polymer science.[6]

We have demonstrated recently that alkyne spacers are effective promoters of light-induced electron- and energy-transfer processes in heterotrinuclear metal complexes.[7−9] We also note that π-conjugated organic materials often exhibit large third-order nonlinear optical properties[10] and recent results suggest that triple-bond alternation could be a useful approach for achieving increased third-order nonlinearity.[11]

Despite the important opportunities available by metal complexation of properly functionalized oligopyridine ligands, the synthesis of only a few such alkyne-substituted *N*-heteroarenes (e.g., pyridine, quinoline, pyrimidine, pyrazine, and pyridazine) has been reported

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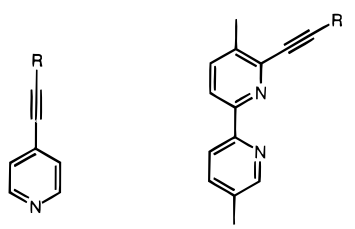
Chart 1



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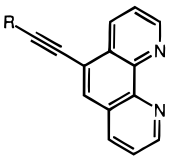
1b R = H

2a R = $Si(CH_3)_3$
2b R = H



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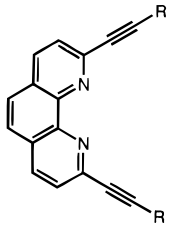

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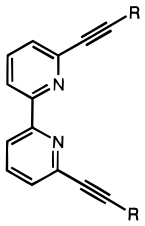

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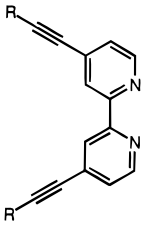
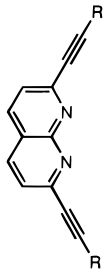
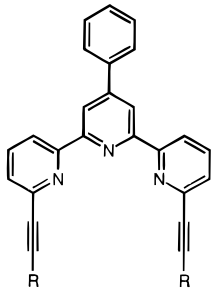
5b R = H



6a R = $Si(CH_3)_3$
6b R = H



7a R = $Si(CH_3)_3$
7b R = H



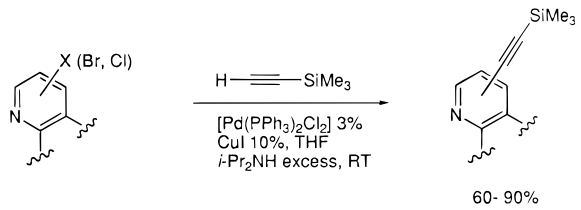
8a R = $Si(CH_3)_3$
8b R = H

in the literature.[12−15] We now descibe a general procedure for the synthesis of substituted oligopyridines bearing a single alkyne chain comprising one, two, or three ethynyl groups. This study complements an earlier report of the synthesis of aromatic polyimine chelates substituted with one or two monoalkyne groups.[16] The resultant molecular-scale building blocks have been used for the synthesis of novel ditopic ligands by means of an oxidative homo-coupling reaction. Furthermore, air-stable copper(I) complexes have been prepared from the 6,6′-dialkyne-functionalized 2,2′-bipyridine chelates.

Results and Discussion

Synthesis of the Monoethynylated Compounds. Synthesis of acetylene-substituted 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 2,2′:6′,2″-terpyridine (terpy), or 1,8-naphthyridine (naphty) substrates had not been reported in the literature when this work was initiated. Consequently, we began a detailed investigation of possible synthetic routes based on palladium-catalyzed cross-coupling reactions involving (trimethylsilyl)acetylene and halide-substituted oligopyridines (Scheme 1). Our reasoning was that since such procedures were well established for functionalization of a variety of aromatic compounds[12,17−20] it should be possible to employ similar conditions for the preparation of alkyne-substituted oligopyridines. It was found that (trimethylsilyl)acetylene reacts smoothly, on a multigram scale, with the monobromo-, dibromo-, or dichloro-substituted oligopyridine compounds in the presence of $[Pd(PPh_3)_2Cl_2]$ as catalyst precursor (3−14 mol % with respect to the substrate), CuI (10 to 14 mol %) as reducing agent, and diisopropylamine as base. This strategy provides easy access to a variety of useful substrates (Chart 1). By way of such palladium(0)-catalyzed reactions we were able to isolate the first known oligopyridines functionalized by one or two alkyne substituents. The isolated yields are in the range 60−90%. The halogenated precursors are conveniently prepared by a multistep sequence of reactions using adapted synthetic procedures.

Scheme 1



Selected spectroscopic and related data collected for the monoethynyl-containing compounds depicted in Chart 1 are collected in Table 1 and some general comments are as follows. Phenanthroline derivatives are formed in significantly lower yields than are the other oligopyridines. During cross-coupling under standardized conditions, formation of $[Cu(phenRR')_2]^+$ complexes (phenRR′ = 2,9-substituted-1,10-phenanthroline derivatives) was evidenced by transient development of a deep-red coloration (λ_{max} ca. 490 nm). These complexes are likely to be more stable than the bpy analogues.[21] Decomplexation of copper with KCN in water and subsequent sonication was necessary in order to increase the isolated yields from about 7% to 60% for **3a** and **4a**. Recently, the synthesis of 2,9-bis(trimethylsilyl)acetylene-1,10-phenanthroline has also been achieved using more polar

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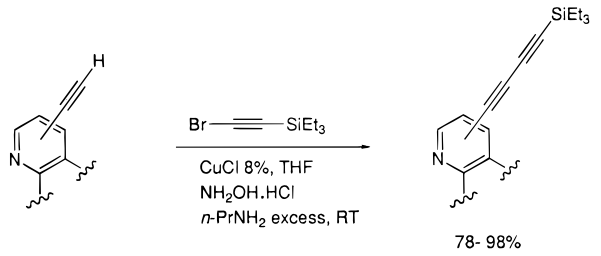
Table 1. Selected Data for Compounds 1a,b to 8a,b

entry	starting compd	product	isolated yield, %	IR[a] $\nu_{C\equiv C}$ (cm^{-1})	^{13}C NMR[b] $\delta_{C\equiv C}$ (ppm)	^{1}H NMR[c] (ppm)	mass[d] spectrum
1	4-bromopyridine	1a	84	2165	81.03, 81.95	0.26	175
		1b	68	3300, 2120	99.95, 102.02	3.29	103
2	6-bromo-5,5′-dimethyl-2,2′−bipyridine	2a	53	2155	80.45, 82.21	0.30	280
		2b	97	3305, 2110	98.30, 102.84	3.43	208
3	5-bromo-1,10-phenanthroline	3a	60[e]	2170	77.35, 83.48	0.29	276
		3b	85	3310, 2120	97.48, 101.26	3.63	204
4	2-chloro-9-bromo-1,10-phenanthroline	4a	60[e]	2160	78.16, 83.67	0.30	372
		4b	93	3300, 2115	96.71, 104.56	3.29	228
5	6,6′-dibromo-2,2′−bipyridine	5a	87	2140	77.01, 83.17	0.30	348
		5b	98	3295, 2110	94.53, 103.93	3.24	204
6	4,4′-dibromo-2,2′−bipyridine	6a	70	2220	83.33, 85.22	0.26	348
		6b	98	3200, 2090	99.97, 102.15	3.40	204
7	2,7-dichloro-1,8-naphtyridine	7a	69	2180	79.71, 82.87	0.28	322
		7b	82	3300, 2112	97.87, 103.74	3.34	178
8	6,6″-dibromo-4′-phenyl- 2,2′:6′,2″−terpyridine	8a	76	2150	76.88, 83.09	0.33	501
		8b	81	3308, 2105	94.56, 104.05	3.22	357

[a] $\nu_{C\equiv C}$ for species **a** and **b**, and $\nu_{C\equiv CH}$ for species **b**, measured in $CHCl_3$, THF, or CCl_4 solutions. [b] Chemical shifts for the C≡C (species **a** and **b**) and for the C≡CH (species **b**) are reported relative to the solvent $CDCl_3$ (77.0 ppm), or THF-d_8 (68.6 and 26.7 ppm), or CD_2Cl_2 (53.84). [c] Chemical shifts for the TMS (species **a**) and for the terminal alkynes (species **b**) are reported relative to residual protiated solvent in $CDCl_3$ (7.25) or THF-d_8 (3.70 and 1.80). [d] Value obtained by electron impact and corresponding to the molecular peak of the ligands (*m/e*). [e] Obtained by aqueous KCN treatment and sonication; yield dropped to 5% (**3a**) and 9% (**4a**) without decomplexation.

Scheme 2



conditions combined with a higher temperature.[22] Surprisingly, we found no difference of reactivity between dibromo-, dichloro-, or monobromo/monochloro-substituted phenanthroline precursors.

Deprotection of the TMS group using K_2CO_3 as base afforded the corresponding terminal alkyne derivatives in good yield (Table 1). In most cases, it was not necessary to isolate the intermediate silylated derivative in order to obtain the terminal acetylenic compound. Instead, in-situ deprotection with K_2CO_3 in methanol after the coupling reaction was found to give adequate yields.

The observed ethynyl carbon chemical shifts in the oligoPy(C≡C)$SiMe_3$ compounds (77.0 to 85.2 ppm) lie, as expected, at a frequency higher than that found for the related oligoPyC≡CH compounds (94.5 to 104.6 ppm).[19,20] The characteristic stretching vibration of the C≡C bonds falls within the range of 2220−2140 cm^{-1} for the (trimethylsilyl)acetylene derivatives and 2120−2090 cm^{-1} for the terminal acetylenic compounds.

Synthesis of the Diethynylated Compounds. In seeking to extend the above work a strategy was sought that enables construction of oligopyridine substrates each bearing two extended alkyne chains, such compounds being useful for the subsequent construction of oligomeric metal complexes. Reaction of the substrate (1 equiv) with bromo(triethylsilyl)acetylene (2.4 equiv) was carried out in the presence of CuCl (8−15 mol %), hydroxylamine hydrochloride (27−60 mol %), and *n*-propylamine (40 equiv), in THF (Scheme 2).

It was found that by using Cadiot−Chodkiewicz conditions with the bpy-based diyne compounds **1b**−**8b** one of the two ethynyl functions reacted rapidly with a molecule of (triethylsilyl)acetylene to produce the corresponding bpy-based monoyne-diyne compound. This latter species reacts slowly with a second molecule of (triethylsilyl)acetylene to give the desired bis-diyne products (Chart 2 and 3). The reaction proceeded at 0 °C, or even rt, yielding the corresponding homologous series of compounds **9a**, **11a**, **13a**, **15a** and **17a** in good yield (see Table 2).

Optimum yields were obtained in CH_2Cl_2 for the bis-diyne compound **13a** (84%) using a large excess (i.e., 40 equiv) of *n*-propylamine as base. When coupling was performed in the presence of amines such as DABCO, *t*-$BuNH_2$, *i*-Pr_2NH, *i*-$BuNH_2$, *i*-$PrNH_2$ instead of *n*-$PrNH_2$, lower yields, or in the case of **4b**, **7b**, and **8b** no reactions at all, were observed. Where reaction was very inefficient it proved possible to use a palladium-catalyzed Stille-coupling reaction on 1-(tributylstannyl)-4-(trimethylsilyl)-butadiyne so as to generate, in low yield, the 2,9-dibutadiynyl-1,10-phenanthroline compound.[22]

The new triethylsilane protected bis-diynes **9a**, **11a**, **13a**, **15a**, and **17a** were then treated with sodium hydroxide in methanol[24] to afford the corresponding terminal alkynes in good yield. Compounds **9b**, **11b**, **13c**, **15b**, and **17b** must be stored at 4 °C to avoid their slow polymerization. Alternatively, they can be used rapidly in the next step of a protracted synthesis. Four ethynyl carbon chemical shifts were observed in the ^{13}C NMR spectra in the range of 73 to 93 ppm for the TES protected compound and 64 to 100 ppm for the terminal diynes. The strong (i.e. >20 ppm) shielding observed for the diynes *versus* the monoyne compounds is consistent with a delocalized $\pi-\pi^*$ framework.[25] A similar effect is found for the stretching vibrations of the C≡C bonds which show a decrease of about 60 cm^{-1} upon extension of the chain.

Oxidative coupling reactions in the presence of Cu(II) under Glaser conditions (Scheme 3)[26] afforded, in high

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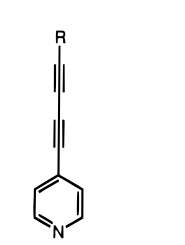
Chart 2



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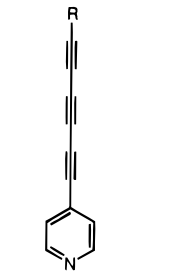
9b R = H



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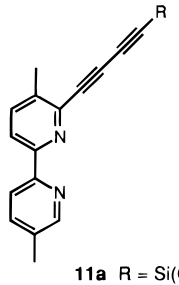
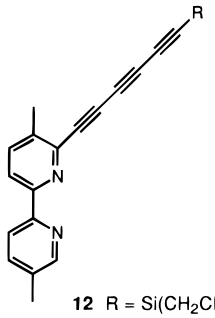
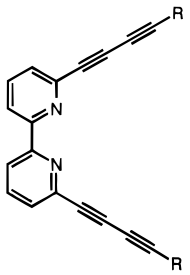


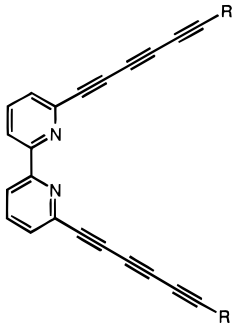
11a R = $Si(CH_2CH_3)_3$
11b R = H



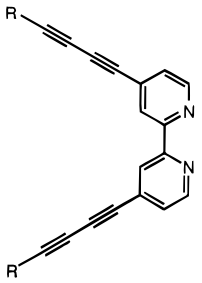
12 R = $Si(CH_2CH_3)_3$



13a R = $Si(CH_2CH_3)_3$
13b R = C_5H_{11}
13c R = H

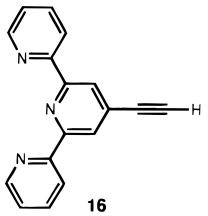


14 R = $Si(CH_2CH_3)_3$



15a R = $Si(CH_2CH_3)_3$
15b R = H

Chart 3



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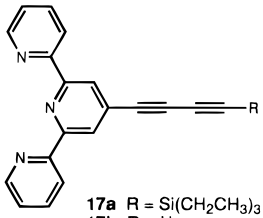
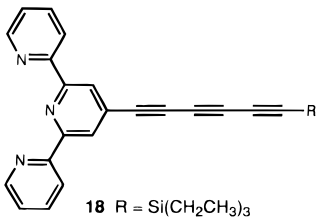
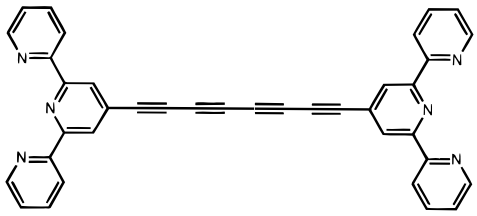


17a R = $Si(CH_2CH_3)_3$
17b R = H



18 R = $Si(CH_2CH_3)_3$



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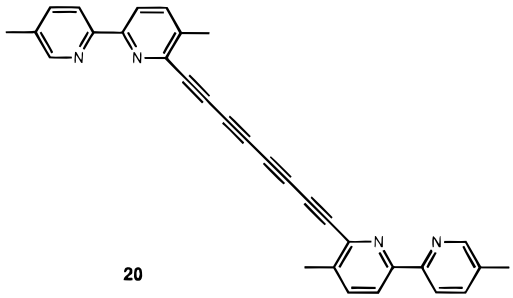

20

yield, the ditopic ligands **19** and **20** bearing four triple bonds as molecular spacers (Chart 3).

Synthesis of the Triethynylated Compounds. The diethynylated compounds **9b**, **11b**, **13c**, **15b**, and **17b** were treated as previously with (triethylsilyl)acetylene bromide in the presence of CuCl, hydroxylamine hydrochloride, and *n*-propylamine (Scheme 4).

Reaction proceeded slowly and after workup the corresponding bis-triethynylated products **10**, **12**, **14**, and **18** were isolated in modest yield (entries 11, 14, 19, and 24, Table 2). Interestingly, no reaction occurred in the case of **15b**, presumably due to its low solubility in THF. Attempts to improve the yield of the reaction in the case of **13c**, using solvents such as CH_2Cl_2, DMF, and Et_2O, were unsuccessful. Our tentative understanding of these reactions is that the initially-formed hexatriyne **14** reacts rapidly with excess *n*-propylamine present in the reaction mixture (Scheme 5).

Thus, *n*-propylamine attacks the two triple bonds located in the α position of the pyridine rings, yielding a mixture of three products **21a**−**c** (Chart 4). When secondary (*i*-Pr_2NH, Et_2NH) or tertiary amines (Et_3N, *n*-Bu_3N) are used as proton scavenger in place of *n*-propylamine, no reaction occurs and the starting compound **13c** is recovered almost quantitatively. Although the crude yellow reaction mixture obtained in the presence of *n*-propylamine exhibits an NMR spectrum indica-

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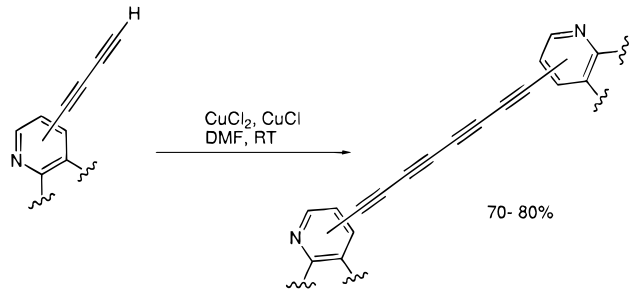
Table 2. Selected Data for Compounds 9a–b to 15b

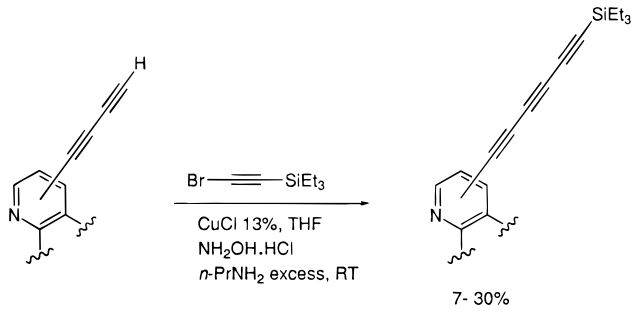
entry	starting compd	product	isolated yield, %	reaction time	IR[a] $\nu_{C\equiv C}$ cm^{-1}	^{13}C NMR[b] $\delta_{C\equiv C}$ (ppm)	^{1}H NMR[c] (ppm)	mass[d] spectrum
9	1b	9a	82	14 h	2103	73.21, 78.54, 88.24, 92.09	0.69	241 [M]
10	9a	9b	78	15 min	3290, 2080	67.36, 72.58, 73.76, 77.38	2.69	127 [M]
11	9b	10	29	4.5 h	2110	60.01, 69.01, 73.79 78.17, 88.63, 89.75	0.63	265 [M]
12	2b	11a	84	10 h	2110	74.53, 76.95, 88.75, 90.97	0.66	346 [M]
13	11a	11b	90	2 h	3167, 2053	67.83, 73.01, 73.79, 75.80	2.69	233 $[M + H]^+$
14	11b	12	30	2 h	2063	61.04, 68.12, 74.71 77.02, 88.93, 90.81	0.55	371 $[M + H]^+$
15	5b	13a	78[e]	2 h	2100	73.82, 74.75, 88.38, 90.34	0.71	480 [M]
16	5b	13a	87[f]	3 h	2100	73.82, 74.75, 88.38, 90.34	0.71	480 [M]
17	5b	13b	85	6 h	2240	73.69, 74.14, 84.83, 86.12	2.38	392 [M]
18	13a	13c	98	5 min	3244, 2059	73.73, 77.60, 79.37 [g]	3.60	252 [M]
19	13c	14	7	10 min	3244, 2059	60.39, 67.81, 73.77 75.14, 88.25, 88.71	0.69	529 $[M + H]^+$
20	6b	15a	80	6 h	2100	72.97, 78.60, 87.98, 91.64	0.65	480 [M]
21	15a	15b	70	30 min	3196, 2059	73.73, 77.60, 79.38 [g]	2.73	252 [M]
22	16	17a	54	18 h	2102	74.12, 78.29 88.56, 91.77	0.72, 1.07	396 $[M + H]^+$
23	17a	17b	93	2 h	3210, 2065	64.90, 72.06 78.56, 99.95	2.58	282 $[M + H]^+$
24	17b	18	25	2 h	2110	60.27, 68.36, 73.46 78.33, 88.93, 90.22	0.75, 1.10	420 $[M + H]^+$

[a] $\nu_{C\equiv C}$ for species **a** and **b,** and $\nu_{C\equiv CH}$ for species **b**, measured in $CHCl_3$, or CCl_4 solutions or KBr pellets. [b] Chemical shifts for the C≡C (species **a** and **b**) and for the C≡CH (species **b**) are reported relative to the solvent $CDCl_3$ (77.0 ppm) or THF-d_8 (68.6 and 26.7 ppm), CD_2Cl_2 (53.84 ppm) or DMSO-d_6 (39.50 ppm). [c] Chemical shifts for the TMS (species **a**) and for the terminal alkynes (species **b**) are reported relative to residual protiated solvent in $CDCl_3$ (7.25) or THF-d_8 (3.70 and 1.80) or CD_2Cl_2 (5.32 ppm). [d] Value obtained by electron impact and corresponding to the molecular peak of the ligands (*m*/*e*). [e] In THF. [f] In CH_2Cl_2. [g] One signal is missing due to its superposition with THF-d_8 solvent.

Scheme 3



Scheme 4



tive of a mixture of three species in the ratio 48:33:19 (Figure 1), their separation could not be achieved due to its rapid decomposition on conventional chromatographic supports. For example, decomposition was apparent by the appearance of a deep red coloration during chromatographic separation on silica. Extensive NMR studies (NOE, COSY, ^{13}C) confirmed the presence of **21a** (*cis-cis*), **21b** (*cis-trans*), and **21c** (*trans-trans*). It is noteworthy that these products are stereoisomers in that attack of *n*-propylamine on the triple bond gives rise to a mixture of *E* and *Z* isomers.

A better understanding of the detailed molecular structures **21a–c** was obtained from NOE experiments, aided by IR spectroscopy. When irradiating proton H^{1a}, a strong (i.e., 12%) NOE effect on proton H^5 was observed (Chart 4). This result can only be interpreted in terms of a locked (or closed) conformation of the molecule in **21a** and **21b** that allows close proximity of the two protons. As evidenced by IR spectroscopy carried out with the mixture, two NH stretching vibrations were observed, one at 3155 cm^{-1} being typical of a hydrogen-bonded NH group and the other one at 3379 cm^{-1} being due to free NH.[27] Such hydrogen bonding between the nitrogen of the pyridine moiety and the NH of the enamine might also be responsible for the above-mentioned NMR observations. Irradiation of the second vinyl proton $H^{1a'}$ allowed detection of a weaker (i.e., 6%) NOE effect on the methylene protons of the added *n*-propylamine subunit (Chart 4).

The lack of an observable NOE effect between the pyridine proton $H^{5'}$ in **21b** and/or H^5 in **21c** and, respectively, the vinyl $H^{1a'}$ and H^{1a} protons is considered to be a consequence of electronic repulsion between the nitrogen lone pairs and the π-electrons of the triple bonds. This repulsion would impose the conformation shown for **21b** and **21c** in Chart 4. In the ^{1}H NMR spectrum the downfield shift of H^5 at 7.6 ppm in **21a** as opposed to 8.3 ppm in **21c** can be explained by its interaction with one of the triple bonds of the side chain. FAB measurement is in agreement with the postulated formula of the three stereoisomers (647.3 $[M + H]^+$). Nucleophilic attack by amines on triple bonds is rare.[28]

Synthesis of the Copper(I) Complexes 22a/b to 25. The copper(I) complexes were conveniently prepared from reaction of ligands **5a**, **5b**, **13a**, **13b**, and **14** with $[Cu(CH_3CN)_4](ClO_4)$ using the appropriate stoichiometry. The tetrafluoroborate or hexafluorophosphate complexes were subsequently obtained either by anion-exchange of the perchlorate complexes with $NaBF_4$ or KPF_6 or by using the appropriate copper(I) precursor. As expected, subtle modifications of the ethynyl chemical shifts and stretching vibrations were observed in the ^{13}C NMR and IR spectra (Table 3), indicating weak interaction between metal center and triple bonds. This observation was further confirmed by an X-ray structure determination (Figure 1).[49] The deep-red complexes are stable in air and in solution as a result of the fully-interlocked ligands around the copper cation.[29] The absorption spectrum of

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Scheme 5

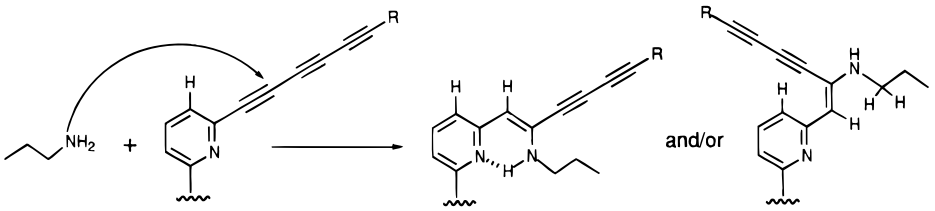


Chart 4

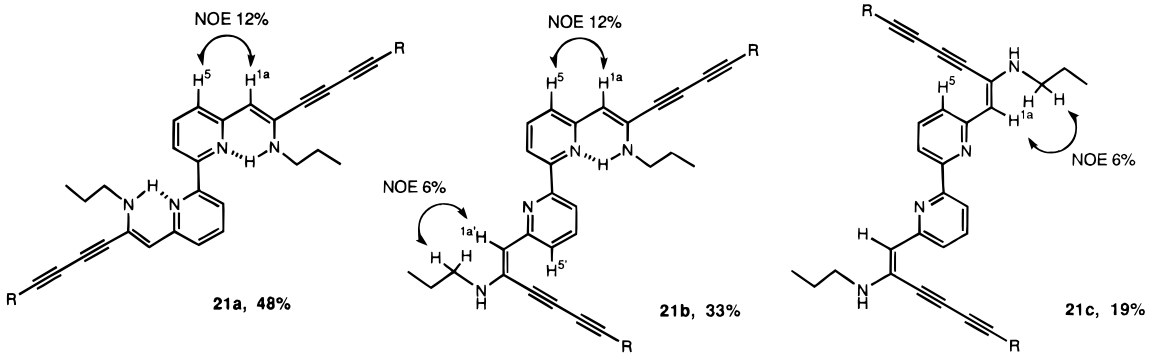
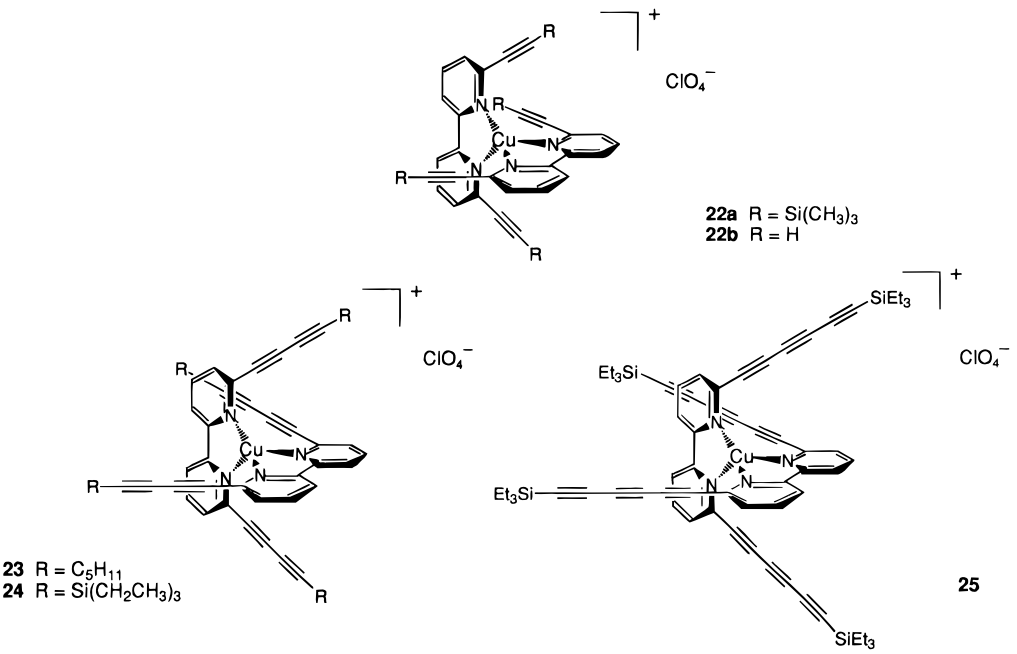


Chart 5



the complexes exhibit intense bands in the range 210−350 nm reminiscent of the respective free ligands. Small absorption changes apparent between free ligand and complex[30] are attributed to intraligand transitions. The weaker absorption band observed in the visible region (467− 493 nm) is assigned as metal-to-ligand-charge-transfer (MLCT) transitions, as typically observed in Cu(I)−polypyridine complexes.[31,32] The significative bathochromic shift (ca. 40 nm) observed relative to analogous $[Cu(dmphen)_2]^+$ (λ_{max} 454 nm) and $[Cu(tmbpy)_2]^+$ (λ_{max} 454 nm)[33] complexes might be indicative of electronic delocalization arising from the presence of extended π^* orbitals on the chelating ligand.[34]

Concluding Remarks

In conclusion, we have applied the palladium-catalyzed coupling of terminal acetylenes to the preparation of a large number of 2,2′-bipyridines, phenanthrolines, naphthyridine, and terpyridine derivatives containing one or two reactive halogen atoms. Stepwise extension of the terminal alkyne function using a series of successive Cadiot−Chodkiewicz reactions, in conjunction with alkali-methanolic deprotection, leads to the isolation of a family of novel dibutadiynyl- and hexadiynyl-oligopyridine compounds. In turn, these materials are versatile intermedi-

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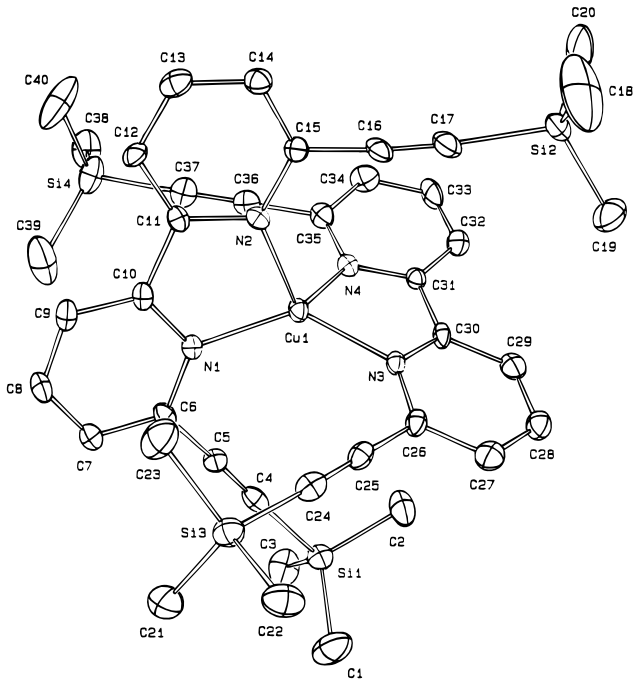

Figure 1. ORTEP diagram of $[Cu(\mathbf{5a})_2]^+$ showing 50% probability ellipsoids. Hydrogen atoms were omitted for clarity. Selected distances are Cu(1)−N(1) 1.984 (6), Cu(1)−N(2) 2.041 (6), Cu(1)−N(3) 1.992 (7), Cu(1)−N(4) 2.021 (7), C(24)−C(25) 1.20 (1), C(4)−C(5) 1.17 (1), C(16)−C(17) 1.20 (1), C(36)−C(37) 1.21 (1). Selected angles are N(1)−Cu(1)−N(2) 81.6 (3), N(1)−Cu(1)−N(3) 131.3 (3), N(1)−Cu(1)−N(4) 132.4 (3), N(2)−Cu-(1)−N(3) 126.9(3), C(24)−C(25)−C(26) 178 (1), Si(3)−C(24)−C(25) 178.0 (8), Si(4)−C(37)−C(36) 177.1 (9), C(35)−C(36)−C(37) 177 (1), C(15)−C(16)−C(17) 172(1), Si(2)−C(17)−C(16) 169(1), C(4)−C(5)−C(6) 178 (1), Si(1)−C(4)−C(5) 177.1 (8).

ates for the subsequent synthesis of homoditopic ligands bearing spacer groups comprising four triple bonds. Extension of the alkyne chain is restricted to three triple bonds because of nucleophilic addition of *n*-propylamine, this reactant being crucial for the Cadiot−Chodkiewicz coupling reactions. A mixture of three enaminediyne isomers is formed by addition of the primary amine to the alkyne chain. Stable copper(I) complexes, having two ligands coordinated to a copper center, are formed with the 6,6′-substituted set of 2,2′-bipyridine ligands. These unusual complexes contain four, eight, or twelve alkyne functions. The synthetic procedure reported in this paper is of particular importance in that it represents a facile but direct route to a wide variety of substituted-oligopyridines using readily available starting materials. Some of these ligands have valuable complexation properties and can be used, for example, for the selective stabilization of *anti*-isomer of (η^3-allyl)palladium complexes, which are key intermediates in the stereoselective preparation of *Z*-alkenes.[22]

Experimental Section

General Methods. 200.1 (^{1}H) and 50.3 MHz (^{13}C{^{1}H}) NMR) spectra were recorded at rt, unless otherwise specified, using perdeuterated solvents as internal standard: δ (H) in ppm relative to residual protiated solvent in $CDCl_3$ (7.26), CD_2Cl_2 (5.32), DMF-d_7 (8.00, 3.07 and 2.90), THF-d_8 (1.8 and 3.7); δ (C) in ppm relative to $CDCl_3$ (77.03), CD_2Cl_2 (53.84), THF-d_8 (26.7 and 68.6) or DMSO-d_6 (39.5). Carbon signals were detected as singlets and chemical shifts are quoted in ppm on the δ scale with coupling constants expressed in hertz (Hz). THF and *n*-propylamine were distilled prior to use.

Materials. 4-Bromopyridine was prepared from 4-bromopyridine hydrochloride. Deprotonation was performed on a Dowex column (1 × 8 resin in the basic form), but special care should be taken when handling pure 4-bromopyridine because of **its high tendency to polymerize with an exothermic reaction** as previously observed.[35] 6-Bromo-5,5′-dimethyl-2,2′-bipyridine[36] and 5-bromo-1,10-phenanthroline[37] were synthesized according to literature procedures. 2-Chloro-9-bromo-1,10-phenanthroline was synthesized from *N*-methyl-2-chloro-1,10-phenanthrolin-9-one, using PBr_5 and $POBr_3$ as described for the synthesis of 2-chloro-1,10-phenanthroline.[38,39] 2,9-Dichloro-1,10-phenanthroline was synthesized from *N*-methyl-2-chloro-1,10-phenanthrolin-9-one using PCl_5 as described for the synthesis of 2-chloro-1,10-phenanthroline.[38,39] 6,6′-Dibromo-2,2′-bipyridine,[40] 4,4′-dibromo-2,2′-bipyridine,[41] 2,7-dichloro-1,8-naphthyridine,[42] 6,6″-dibromo-4′-phenyl-2,2′:6′,2″-terpyridine,[43] 4′-ethynyl-2,2′:6′,2″-terpyridine,[34] $[Pd(PPh_3)_2Cl_2]$,[44] $[Pd(PPh_3)_4]$,[45] $[Cu(CH_3CN)_4](ClO_4)$,[46] 1-bromo-2-(triethylsilyl)-acetylene,[47] and 1-iodohept-1-yne[48] were prepared and purified according to the literature procedures. (Trimethylsilyl)acetylene, CuI, diisopropylamine, *n*-propylamine, hydroxylamine hydrochloride, CuCl, and $CuCl_2 \cdot 2H_2O$ are commercially available.

Preparation of the (Trimethylsilyl)alkyne Derivatives 1a−8a (Chart 1). General Procedure. To an argon degassed solution of the substrate (bromo or chloro derivative, 1−5 g scale) in THF (50 mL) were added as solids bis-(triphenylphosphine)palladium(II) dichloride (3−14 mol %) and CuI (10−14 mol %). Then, (trimethylsilyl)acetylene (1.2 equiv per bromo or chloro function) and diisopropylamine (20 mL) were added slowly *via* a syringe. The solution turned black instantaneously. After stirring 4 to 16 h at rt, the reaction mixture was quenched with water (50 mL) and the product extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude material was chromatographed on flash silica gel to give the analytically pure derivatives in good yields.

4-[2-(Trimethysilyl)-1-ethynyl]pyridine (1a): 4-bromopyridine hydrochloride (5.700 g, 29.1 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.200 g, 0.28 mmol), CuI (0.600 g, 3.15 mmol**)**, (trimethylsilyl)acetylene (5.560 g, or 8 mL, 56.6 mmol), diisopropylamine (20 mL). Chromatography on flash silica gel previously deactivated with triethylamine (CH_2Cl_2/hexane 80/20) to give 4.300 g of a colorless liquid (84%): R_f 0.19 (CH_2Cl_2/hexane 80/20), IR ($CHCl_3$, cm^{-1}) 2960 (br), 2165 (m), 1595 (s), 1408 (s), 1252 (s); ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 9H), 7.31 (d, 2H, J = 4.3 Hz), 8.55 (d, 2H, J = 4.3 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$) δ −0.3, 99.9, 102.0, 125.8, 131.2, 149.7; EI/MS *m*/*z* (%) 175 (M^+, 38), 160 ($M^+ - CH_3$, 100). Anal. Calcd for $C_{10}H_{13}NSi$: C, 68.51; H, 7.28; N, 7.74. Found: C, 68.35; H, 6.93; N, 7.52.

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Table 3. Selected Data for Copper(I) Complexes 22a/b to 25

entry	complex	isolated yield (%)	IR ($\nu_{C\equiv C}$, cm^{-1})[a]	$^{13}C\{^1H\}NMR$[b] δ	λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)[c]	FAB^+ [d]
25	**22a**	86	2159	99.54, 102.32	493 (2640)	759.0
26	**22b**	89	3248/2109	81.38, 82.05	470 (2000)	471.0
27	**23**	93	2235	63.80, 72.52, 78.33, 89.65	467 (1620)	847.2
28	**24**	89	2100	77.61, 81.73, 91.61, 98.46	493 (1850)	1023.2
29	**25**	65	2080	64.29, 71.01, 75.02, 79.54, 93.01, 93.21	493 (1270)	1121.3

[a] Measured in KBr pellets. [b] Measured in CH_3CN-d_3, δ (C≡C) or δ (C≡CH) in ppm. [c] In CH_3CN. [d] Value obtained by fast atom bombardment spectroscopy in *m*-nitrobenzyl alcohol and corresponding to $[M - ClO_4]^+$.

6-[2-(Trimethysilyl)-1-ethynyl]-5,5′-dimethyl-2,2′-bipyridine (2a): 6-bromo-5,5′-dimethyl-2,2′-bipyridine (2.000 g, 7.6 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.200 g, 0.28 mmol), CuI (0.200 g, 1.05 mmol), (trimethylsilyl)-acetylene (0.970 g, or 1.4 mL, 9.88 mmol), diisopropylamine (8 mL). Chromatography on silica gel (diethylether/hexane 30/70) to give 1.140 g of a white crystalline product (53%): mp 92/3 °C, R_f 0.40, (ether/hexane 30/70), IR ($CHCl_3$, cm^{-1}) 3000 (w), 2955 (br), 2155 (s), 1480 (s), 1443 (vs), 1370 (s), 1248 (vs), 1180 (s), 1130 (s), 1115 (s); ^1H NMR ($CDCl_3$) δ 0.30 (s, 9 H), 2.35 (s, 3 H), 2.46 (s, 3 H), 7.57 (dd, 1 H, J = 8.0, 2.2 Hz), 7.60 (d, 1 H, J = 8.0 Hz), 8.21 (d, 1 H, J = 8.0 Hz), 8.32 (d, 1 H, J = 8.0 Hz), 8.44 (s, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ −0.2, 18.2, 19.2, 98.3, 102.8, 120.1, 120.7, 133.17, 136.1, 137.2, 141.9, 149.2, 149.3, 152.9, 154.0; EI/MS *m/z* (%) 280 (M^+, 85), 265 ($M^+ - CH_3$, 100), 250 ($M^+ - 2CH_3$), 235 ($M^+ - 3CH_3$). Anal. Calcd for $C_{17}H_{20}N_2Si$: C, 72.81; H, 7.19; N, 9.99. Found: C, 72.74; H, 7.08; N, 9.89.

5-[2-(Trimethysilyl)-1-ethynyl]-1,10-phenanthroline (3a): 5-bromo-1,10-phenanthroline (1.000 g, 3.9 mmol), bis-(triphenylphosphine)palladium(II) dichloride (0.250 g, 0.39 mmol), CuI (0.083 g, 0.43 mmol), (trimethylsilyl)acetylene (0.590 g, or 0.85 mL, 6.0 mmol), diisopropylamine (10 mL). After 4 h, the solvent was distillated under vacuum and the residue dissolved in methanol (50 mL). Addition of KCN (0.200 g, 3.1 mmol) in water (20 mL) followed by sonication (1 h) resulted in copper decomplexation. Chromatographed on silica gel (CH_2Cl_2/methanol 95/5) to give 0.650 g of a white crystalline product (60%): R_f 0.51 (CH_2Cl_2); mp 126/8 °C; IR ($CHCl_3$, cm^{-1}) 2980 (br), 2170 (w), 1590 (s), 1505 (vs), 1495 (vs), 1270 (s), 1260 (s); ^1H NMR ($CDCl_3$) δ 0.29 (s, 9 H), 7.68 (m, 2 H), 8.04 (s, 1 H), 8.19 (dd, 1 H, J = 8.2, 1.6 Hz), 8.71 (dd, 1 H, J = 8.2, 1.6 Hz), 9.19 (m, 2 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ −0.1, 97.5, 101.3, 119.9, 123.4, 128.0, 131.1, 131.3, 134.7, 135.0, 135.8, 146.0, 146.2, 150.9, 151.0; EI/MS *m/z* (%) 276 (M^+, 85), 261 ($M^+ - CH_3$, 100), 246 ($M^+ - 2CH_3$, 7), 231 ($M^+ - 3CH_3$, 3). Anal. Calcd for $C_{17}H_{16}N_2Si$: C, 73.87; H, 5.83; N, 10.14. Found: C, 73.69; H, 5.82; N, 10.09.

2,9-Bis[2-(trimethysilyl)-1-ethynyl]-1,10-phenanthroline (4a): 2-chloro-9-bromo-1,10-phenanthroline (1.100 g, 3.7 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.360 g, 0.51 mmol), CuI (0.720 g, 3.78 mmol), (trimethylsilyl)-acetylene (1.390 g, or 2 mL, 14.15 mmol), diisopropylamine (20 mL). After 15 h the deep-red reaction mixture was quenched with water (20 mL) and evaporated to dryness and the residue dissolved in CH_3OH (50 mL). Addition of KCN (2.000 g, 31.0 mmol) in water (20 mL) followed by sonication (1 h) resulted in copper decomplexation. Chromatographed on silica gel (CH_2Cl_2) to give 1.120 g of a white crystalline product (80%): R_f 0.42 (CH_2Cl_2); mp 267/8 °C; IR ($CHCl_3$, cm^{-1}) 2970 (br), 2160 (w), 1585 (s), 1500 (vs), 1490 (vs), 1270 (s), 1255 (s); ^1H NMR (CD_2Cl_2) δ 0.30 (s, 18 H), 7.74 (d, 2 H, J = 8.3 Hz), 7.77 (s, 2 H), 8.20 (d, 2 H, J = 8.3 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ −0.3, 96.7, 104.6, 124.7, 126.8, 128.7, 136.5, 142.6, 144.9; EI/MS *m/z* (%) 372 (M^+, 100), 367 ($M^+ - CH_3$, 65). Anal. Calcd for $C_{22}H_{24}N_2Si_2$: C, 70.92; H, 6.49; N, 7.52. Found: C, 70.69; H, 6.22; N, 7.38.

6,6′-Bis[2-(trimethysilyl)-1-ethynyl]-2,2′-bipyridine (5a): 6,6′-dibromo-2,2′-bipyridine (5.000 g, 16.13 mmol), bis-(triphenylphosphine)palladium (II) dichloride (0.320 g, 0.46 mmol), CuI (0.320 g, 1.68 mmol), (trimethylsilyl)acetylene (4.030 g, or 5.8 mL, 41.03 mmol), diisopropylamine (20 mL). Chromatographed on silica gel (CH_2Cl_2/hexane 80/20) to give 4.890 g (87%) of a white crystalline product: mp 227/8 °C; R_f 0.52 (CH_2Cl_2/hexane 9/1); IR (CCl_4, cm^{-1}) 2960 (br), 2140 (w), 1605 (vs), 1495 (vs), 1420 (s), 1130 (s); ^1H NMR ($CDCl_3$) δ 0.30 (s, 18H), 7.48 (dd, 2H, J = 7.9, 1.0 Hz), 7.76 (dt, 2H, J = 7.9, 1.0 Hz); 8.42 (dd, 2H, J = 7.9, 1.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ −0.3, 94.5, 103.9, 121.1, 127.8, 136.9, 142.3, 155.7; EI/MS *m/z* (%) 348 (M^+, 98), 333 ($M^+ - CH_3$, 100). Anal. Calcd for $C_{20}H_{24}N_2Si_2$: C, 68.91; H, 6.94; N, 8.04. Found: C, 68.89; H, 6.92; N, 7.85.

4,4′-Bis[2-(trimethysilyl)-1-ethynyl]-2,2′-bipyridine (6a): 4,4′-dibromo-2,2′-bipyridine (2.000 g, 6.45 mmol), bis-(triphenylphosphine)palladium(II) dichloride (0.150 g, 0.213 mmol), CuI (0.150 g, 0.79 mmol), (trimethylsilyl)acetylene (1.570 g or 2.26 mL, 15.98 mmol), diisopropylamine (10 mL). Chromatographed on silica gel using a CH_2Cl_2/hexane 30/70 mixture to give 1.570 g (70%) of the pure product as a white crystalline powder: mp 113/4 °C, R_f 0.18 (CH_2Cl_2/hexane 80/20); IR (CCl_4, cm^{-1}) 2950 (br), 2220 (s), 1588 (vs), 1533 (s), 1360 (s), 1250 (vs); ^1H NMR ($CDCl_3$) δ 0.26 (s, 18H), 7.32 (dd, 2H, J = 5.0, 1.5 Hz); 8.42 (d, 2H, J = 1.5 Hz), 8.61 (dd, 2H, J = 5.0, 1.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ −0.3, 99.9, 102.0, 125.8, 126.7, 131.2, 148.8, 149.7; EI/MS *m/z* (%) 348 (M^+, 88), 333 ($M^+ - CH_3$, 100), 318 ($M^+ - 2CH_3$, 20), 303 ($M^+ - 3CH_3$). Anal. Calcd for $C_{20}H_{24}N_2Si_2$: C, 68.91; H, 6.94; N, 8.04. Found C, 69.15; H, 6.99; N, 8.17.

2,7-Bis[2-(trimethylsilyl)-1-ethynyl]-1,8-naphthyridine (7a): 2,7-dichloro-1,8-naphthyridine (0.500 g, 2.5 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.050 g, 0.07 mmol**)**, CuI (0.050 g, 0.26 mmol), (trimethylsilyl)acetylene (0.610 g or 0.88 mL, 6.21 mmol), diisopropylamine (3 mL). Chromatographed on silica gel using a mixture of CH_2Cl_2/hexane (50/50) to give **7a** as a pale brown crystalline powder (69%); R_f 0.51 (CH_2Cl_2/hexane/methanol 3/6.8/0.2); mp 278/9 °C; IR ($CHCl_3$, cm^{-1}) 2950 (br), 2180 (w), 1605 (vs), 1520 (s), 1495 (vs), 1225 (s), 1210 (vs), 1130 (vs); ^1H NMR ($CDCl_3$) δ 0.28 (s, 18 H), 7.52 (d, 2 H, J = 8.3 Hz), 8.08 (d, 2 H, J = 8.3 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ −0.5, 97.9, 103.7, 121.2, 125.4, 136.6, 146.9, 155.4; EI/MS *m/z* (%) 322 (M^+, 63), 307 ($M^+ - CH_3$, 100). Anal. Calcd for $C_{18}H_{22}N_2Si_2$: C, 67.02; H, 6.87; N, 8.68. Found: C, 66.92; H, 6.62; N, 8.48.

6,6″-Bis[2-(trimethylsilyl)-1-ethynyl]-4′-phenyl-2,2′:6′,2″-terpyridine (8a): 6,6″-dibromo-4′-phenyl-2,2′:6′,2″-terpyridine (0.500 g, 1.07 mmol), bis(triphenylphosphine)palladium-(II) chloride (0.020 g, 0.028 mmol), CuI (0.020 g, 0.1 mmol), (trimethylsilyl)acetylene (0.222 g or 0.380 mL, 2.26 mmol), diisopropylamine (2 mL). Chromatographed on silica gel using a mixture of CH_2Cl_2/hexane (30/70) to give a clear brownish crystalline powder (75%); mp 203/4 °C, R_f 0.75 (CH_2Cl_2/hexane 3/2); IR (CCl_4, cm^{-1}) 2950 (br), 2150 (w), 1455 (s), 1440 (s), 1400 (vs), 1250 (s); ^1H NMR ($CDCl_3$) δ 0.33 (s, 18 H), 7.50−7.55 (m, 5H), 7.83 (t, 2 H, J = 7.8 Hz), 7.88−7.93 (dd, 2 H, J = 8.2, 1.0 Hz), 8.59 (dd, 2 H, J = 8.2, 1.0 Hz), 8.77 (s, 2 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ −0.2, 94.6, 104.1, 119.8, 120.8, 127.4, 127.7, 128.8, 128.9, 136.8, 138.5, 142.4, 150.5, 155.1, 156.5; EI/MS *m/z* (%) 501 (M^+, 100), 487 ($M^+ - CH_3$, 18), 472 ($M^+ - 2CH_3$, 16), 457 ($M^+ - 3CH_3$, 10), 428 ($M^+ - Si(CH_3)_3$, 30). Anal. Calcd for $C_{31}H_{30}N_3Si_2$: C, 74.20; H, 6.22; N, 8.37. Found: C, 73.94; H, 6.20; N, 8.33.

Preparation of the Terminal Alkyne Derivatives 1b−8b (Chart 1). General Procedure. A solution of the trimethylsilyl protected derivatives in CH_3OH (20 mL) was treated, at rt, with K_2CO_3 (1.1−1.4 equiv). After 15 h, the reaction mixture was quenched with H_2O (50 mL) and the organic solvent evaporated under *vacuum*. The product was extracted with CH_2Cl_2 (3 × 50 mL) and the organic layer dried over $MgSO_4$. After filtration and evaporation of the solvent

the crude product was chromatographed on flash silica gel to give the analytically pure derivatives in excellent yields.

4-Ethynylpyridine (1b): 4-[2-(trimethylsilyl)-1-ethynyl]-pyridine (1.000 g, 5.7 mmol), K_2CO_3 (0.898 g, 6.5 mmol). Chromatographed, in the dark, on silica gel (CH_2Cl_2/methanol 98/2) affording a colorless, light-sensitive oil (0.460 g, 79%): R_f 0.23 (CH_2Cl_2/methanol 98/2); IR ($CHCl_3$, cm^{-1}) 3300(s), 2120(w), 1600(vs), 1408(s); ^1H NMR ($CDCl_3$) δ 3.29 (s, 1H), 7.32 (d, 2H, J = 5.6 Hz), 8.57 (d, 2H, J = 5.6 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 81.0, 81.9, 126.1, 130.4, 149.9; EI/MS m/z (%) 103 (M^+, 100), 75($M^+ - C{\equiv}CH$). Anal. Calcd for C_7H_5N: C, 81.53, N, 4.89, H, 13.58. Found: C, 81.45; H, 4.75; N, 13.23.

6-Ethynyl-5,5′-dimethyl-2,2′-bipyridine (2b): 6-[2-(trimethysilyl)-1-ethynyl]-5,5′-dimethyl-2,2′-bipyridine (1.000 g, 3.6 mmol), K_2CO_3 (0.600 g, 4.35 mmol). Chromatographed, in the dark, on silica gel (CH_2Cl_2/CH_3OH 98/2) affording 0.720 g of a white crystalline solid (97%): R_f 0.30 CH_2Cl_2/CH_3OH 98/2); mp 128/9 °C; IR ($CHCl_3$, cm^{-1}) 3310 (vs), 2990 (br), 2115 (w), 1625 (w), 1500 (s); ^1H NMR (CD_2Cl_2) δ 2.36 (s, 3H), 2.47 (s, 3H), 3.43 (s, 1H), 7.61 (dd, 1H, J = 7.3, 0.9 Hz), 7.64 (d, 1H, J = 8.1 Hz), 8.18 (d, 1H, J = 8.1 Hz), 8.29 (d, 1H, J = 8.1 Hz), 8.46 (d, 1H, J = 0.9 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 18.4, 19.3, 80.5, 82.2, 120.5, 120.7, 134.0, 136.7, 137.7, 138.3, 141.4, 149.8, 153.1, 154.5; EI/MS m/z (%) 208 (M^+, 100), 193 ($M^+ - CH_3$, 12), 183 ($M^+ - CCH$, 8). Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74, 5.81, 13.45. Found: C, 80.69; H, 5.73; N, 13.36.

5-Ethynyl-1,10-phenanthroline (3b): 5-[2-(trimethylsilyl)-1-ethynyl]-1,10-phenanthroline (1.000 g, 3.62 mmol), K_2CO_3 (0.600 g, 4.35 mmol). Chromatographed on silica gel (CH_2Cl_2/CH_3OH 95/5) to give 0.630 g of a beige crystalline product (85%): R_f 0.23 (CH_2Cl_2/CH_3OH 95/5); mp 163 °C dec; IR ($CHCl_3$, cm^{-1}) 3305 (vs), 2980 (br), 2110 (w), 1550 (s), 1450 (vs), 1250 (br), 1130 (s), 1115 (s); ^1H NMR (CD_2Cl_2) δ 3.63 (s, 1 H), 7.69 (m, 2 H), 8.10 (s, 1 H), 8.24 (dd, 1 H, J = 8.2, 1.6 Hz), 8.76 (dd, 1 H, J = 8.2, 1.6 Hz), 9.15 (m, 2 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ 83.5, 77.4, 123.9, 128.3, 128.8, 132.4, 134.8, 136.3, 146.4, 146.8, 151.0, 151.5; EI/MS m/z (%) 204 (M^+, 100). Anal. Calcd for $C_{14}H_8N_2$: C, 82.34; H, 3.95; N, 13.72. Found: C, 82.17; H, 3.82; N, 13.58.

2,9-Diethynyl-1,10-phenanthroline (4b): 2,9-bis[2-(trimethylsilyl)-1-ethynyl]-1,10-phenanthroline (1.100 g, 2.95 mmol), K_2CO_3 (0.483 g, 3.50 mmol). Chromatographed on silica gel (CH_2Cl_2/CH_3OH 99/1) to give 0.630 g of a beige crystalline solid (93%): R_f 0.33 (CH_2Cl_2/CH_3OH 95/5); mp 237 °C dec; IR ($CHCl_3$, cm^{-1}) 3300 (s), 2980 (br), 2115 (w), 1620 (w), 1585 (w), 1492 (vs); ^1H NMR (CD_2Cl_2) δ 3.29 (s, 2 H), 7.75 (s, 2 H), 7.76 (d, 2 H, J = 8.2 Hz), 8.18 (d, 2 H, J = 8.2 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ 78.2, 83.7, 127.0, 127.4, 128.7, 136.7, 142.6, 146.0; EI/MS m/z (%) 228 (M^+, 100). Anal. Calcd for $C_{16}H_8N_2$: C, 84.19; H, 3.53; N, 12.27. Found: C, 83.93; H,3.28; N, 12.07.

6,6′-Diethynyl-2,2′-bipyridine (5b): 6,6′-bis(2-trimethysilyl-1-ethynyl)-2,2′-bipyridine (3.000 g, 8.60 mmol), K_2CO_3 (1.500 g, 10.85 mmol). A considerable amount of precipitate formed. The product was filtered and washed with CH_3OH (3 × 50 mL) to give the desired compound as a beige crystalline powder 98%: R_f 0.40 (CH_2Cl_2); mp 170 °C dec; IR(CCl_4, cm^{-1}) 3270 (s), 2101 (w), 1573 (s), 1556(s), 1435 (s); ^1H NMR (CD_2Cl_2) δ 3.24 (s, 2H), 7.53 (dd, 2H, J = 7.7, 1.0 Hz); 7.83 (t, 2H, J = 7.7 Hz); 8.44 (dd, 2H, ^3J = 7.7, 1.0 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 77.0, 83.2, 121.4, 128.2, 137.66, 141.9, 155.9; EI/MS m/z (%) 204 (M^+, 100). Anal. Calcd for $C_{14}H_8N_2$: C, 82.34; H, 3.95; N, 13.72. Found: C, 82.30; H, 3.95; N, 13.94.

4,4′-Diethynyl-2,2′-bipyridine (6b): 4,4′-bis[2-(trimethysilyl)-1-ethynyl]-2,2′-bipyridine (3.000 g, 8.60 mmol), K_2CO_3 (1.600 g, 11.58 mmol). A considerable amount of precipitate formed. The product was filtered and washed with CH_3OH (3 × 60 mL) to give the desired compound as a beige crystalline powder 98%: R_f 0.23 (CH_2Cl_2); mp 192/3 °C; IR (THF, cm^{-1}) 3200 (s), 2090 (w), 1575 (s), 1525 (w); ^1H NMR (THF-d_8) δ 4.12 (s, 2H), 7.53 (dd, 2H, J = 4.8, 1.6 Hz), 8.63 (br s, 2H), 8.75 (dd, 2H, J = 4.8, 1.6 Hz); $^{13}C\{^1H\}$ NMR (THF-d_8) 83.3, 85.2, 125.2, 128.3, 133.7, 151.7, 157.0 (CC); EI/MS m/z (%); 204 (M^+, 100). Anal. Calcd for $C_{14}H_8N_2$: C, 82.34; H, 3.95; N, 13.72. Found: C, 82.18; H, 3.74; N, 13.53.

2,7-Diethynyl-1,8-naphtyridine (7b): 2,7-bis[2-(trimethylsilyl)-1-ethynyl]-1,8-naphthyridine (0.453 g, 1.40 mmol), K_2CO_3 (0.249 g, 1.80 mmol). Reaction time: 5 min, 82%: R_f 0.49 (CH_2Cl_2/ether 9/1); mp 140 °C dec; IR (CCl_4, cm^{-1}) 3300 (s), 2965 (br), 2112 (s), 1600 (vs), 1520 (s), 1495 (vs), 1290 (s), 1220 (s), 1130 (s); ^1H NMR ($CDCl_3$) δ 3.34 (s, 2 H), 7.62 (d, 2H, J = 8.3 Hz), 8.16 (d, 2H, J = 8.3 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 82.9, 79.7, 121.7, 125.8, 136.93, 145.6, 146.6; EI/MS m/z (%) 178 (M, 100). Anal. Calcd for $C_{12}H_6N_2$ (M_r = 178.195) C, 80.89; H, 3.39; N, 15.72. Found: C, 80.62; H, 3.25; N, 15.49.

6,6″-Diethynyl-4′-phenyl-2,2′,6′,2″-terpyridine (8b): 6,6″-bis[2-(trimethylsilyl)-1-ethynyl]-4′-phenyl-2,2′:6′,2″-terpyridine (0.204 g, 0.407 mmol), K_2CO_3 (0.077 g, 0.56 mmol). Reaction time 1 h, yield 82%: R_f 0.20 (CH_2Cl_2/hexane 1/1); mp 220/1 °C. IR (CCl_4, cm^{-1}) 3308 (s), 2950 (br), 2105 (w), 1555 (br), 1440 (s), 1399 (vs), 1258 (s); ^1H NMR ($CDCl_3$) δ 3.23 (s, 2H), 7.52 (m, 5H), 7.85 (m, 4H), 8.64 (dd, 2H, J = 8.0, 1.0 Hz), 8.77 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 76.9, 83.1, 119.7, 121.2, 127.4, 127.6, 128.8, 129.0, 137.0, 138.3, 141.6, 150.6, 155.0, 156.6; EI/MS m/z (%) 357 (M^+, 100). Anal. Calcd for $C_{12}H_6N_2$: C, 84.01; H, 4.23; N, 11.76. Found: C, 83.82; H, 4.11; N, 11.59.

Preparation of the Triethylsilyl Protected Diyne Derivatives 9a, 11a, 13a, 15a, 17a (Charts 2 and 3). General Procedure. A solution of the monoethynyl derivatives (1 g scale) in THF (20 mL) was cooled down to 0 °C. After addition of CuCl (8−15 mol %) and hydroxylamine hydrochloride (27−60 mol %), *n*-propylamine (ca. 40 equiv) was slowly added *via* a syringe. After 15 min, 1-bromo-2-(triethylsilyl)-acetylene (1.0−1.9 equiv) in THF (10 mL) was added dropwise over a period of 15 min. After stirring during 4 h at 0 °C, the temperature was allowed to rise to 20 °C. After an additional stirring time of 10 h, the reaction mixture was quenched with H_2O (50 mL) and the organic product extracted with CH_2Cl_2 (3 × 75 mL). The organic layer was dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude material was chromatographed on flash silica gel to give the analytically pure derivatives in excellent yields.

4-[4-(Triethylsilyl)-1,3-butadiynyl]pyridine (9a): 4-ethynylpyridine (1.100 g, 10.6 mmol), CuCl (0.080 g, 0.8 mmol), hydroxylamine hydrochloride (0.200 g, 2.9 mmol), *n*-propylamine (17 mL), 1-bromo-2-(triethylsilyl)acetylene (3.250 g, 14.81 mmol). Chromatographed on flash silica gel (hexane/CH_2Cl_2 20/80−0/100) to give 2.100 g of a colorless liquid, 82%: R_f 0.42 (CH_2Cl_2/hexane 1/1, silica TLC sheets treated with triethylamine); IR (CCl_4, cm^{-1}) 2980 (s), 2920 (m), 2960 (s), 2103 (s), 1580 (vs); ^1H NMR (CD_2Cl_2) δ 0.69 (q, 6H, J = 8.0 Hz), 1.02 (t, 9H, J = 8.0 Hz), 7.33 (d, 2H, J = 4.5 Hz), 8.57 (d, 2H, J = 4.5 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 4.5, 7.6, 73.2, 78.5, 88.2, 92.1, 126.6, 129.9, 150.3; EI/MS m/z (%) 241 (M^+, 20), 212 ($M^+ - C_2H_5$, 100), 184 ($M^+ - 2C_2H_5 + H$, 65), 156 ($M^+ - 3C_2H_5 + 2H$, 55). Anal. Calcd for $C_{15}H_{19}NSi$: C, 74.63; H, 7.93; N, 5.80. Found: C, 74.50; H, 7.85; N, 5.64.

6-[4-(Triethylsilyl)-1,3-butadiynyl]-5,5′-dimethyl-2,2′-bipyridine (11a): 6-ethynyl-5,5′-dimethyl-2,2′-bipyridine (1.000 g, 4.80 mmol), CuCl (0.066 g, 0.66 mmol), hydroxylamine hydrochloride (0.100 g, 1.44 mmol), *n*-propylamine (6.8 mL), 1-bromo-2-(triethylsilyl)acetylene (1.560 g, 7.11 mmol). Chromatographed on flash silica gel (hexane/CH_2Cl_2 70/30) to give 1.120 g of a white crystalline product (84%): R_f 0.47 (CH_2Cl_2/hexane 70/30); mp 58/9 °C; IR (CCl_4, cm^{-1}) 2960 (s), 2878 (m), 2100 (s), 1540 (br), 1445 (s); ^1H NMR ($CDCl_3$) δ 0.66 (q, 6H, J = 8.0 Hz), 1.00 (t, 9H, J = 8.0 Hz), 2.35 (s, 3H), 2.47 (s, 3H), 7.58 (m, 2H arom.), 8.23 (d, 1H, J = 7.9 Hz), 8.28 (d, 1H, J = 7.9 Hz), 8.43 (s, 1H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 4.6, 7.6, 18.5, 19.2, 74.5, 76.9, 88.7, 91.0, 120.6, 121.1, 134.1, 137.7 (CH), 137.9, 138.4, 140.9, 149.9, 153.0, 154.9; EI/MS m/z (%) 346 (M^+, 100), 317 ($M^+ - C_2H_5$, 98), 290 ($M^+ - 2C_2H_5 + 2H$, 52), 260 ($M^+ - 3C_2H_5 + 2H$, 38). Anal. Calcd for $C_{22}H_{26}N_2Si$: C, 76.25; H, 7.56; N, 8.08. Found: C, 76.10; H, 7.45; N, 8.04.

6,6′-Bis[4-(triethylsilyl)-1,3-butadiynyl]-2,2′-bipyridine (13a): 6,6′-diethynyl-2,2′-bipyridine (0.100 g, 0.489 mmol), CuCl (0.006 g, 0.06 mmol), hydroxylamine hydrochloride (0.009 g, 0.13 mmol), *n*-propylamine (1.5 mL), 1-bromo-2-(triethylsilyl)acetylene (0.200 g, 0.91 mmol). Chromatographed on flash silica gel (hexane/CH_2Cl_2 80/20) to give 0.150

g of a clear brown crystalline material, 87%: mp 168/9 °C; IR (CCl_4, cm^{-1}) 2960 (s), 2905 (s), 2870 (s), 2100 (s), 1445 (s), 1425 (s), 1040 (s), 1015 (s); ^1H NMR ($CDCl_3$) δ 0.71 (q, 6H, $J = 8.0$ Hz), 1.03 (t, 9H, $J = 8.0$ Hz), 7.51 (dd, 1H, $J = 7.6$, 0.9 Hz); 7.78 (t, 1H, $J = 7.6$ Hz), 8.43 (dd, 1H, $J = 7.6$, 0.9 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 4.1, 7.3, 73.8, 74.8, 88.4, 90.3, 121.4, 128.5, 137.1, 141.2, 155.7; EI/MS *m/z* (%) 480 (M^+, 85), 451 ($M^+ - C_2H_5$, 100), 422 ($M^+ - 2C_2H_5$, 15). Anal. Calcd for $C_{30}H_{36}N_2Si_2$: C, 74.94; H, 7.55; N, 5.83. Found: C, 74.77; H, 7.32; N, 5.76.

6,6′-Bis(1,3-nonadiynyl)-2,2′-bipyridine (13b): 6,6′-diethynyl-2,2′-bipyridine (0.200 g, 0.98 mmol), CuCl (0.010 g, 0.1 mmol), hydroxylamine hydrochloride (0.036 g, 0.52 mmol), *n*-propylamine (1.5 mL), 1-iodohept-1-yne (0.544 g, 2.45 mmol). Chromatographed on flash silica gel (hexane/CH_2Cl_2 30/70) to give 0.326 g of a white crystalline compound, 85%: mp 162/3 °C; R_f 0.65 (hexane/CH_2Cl_2 50/50); IR (CCl_4, cm^{-1}) 2960 (s), 2930 (s), 2240 (s), 1555 (br), 1435 (s), 1150 (w); ^1H NMR ($CDCl_3$), δ 0.92 (t, 3H, $J = 6.8$ Hz), 1.26−1.64 (m, 6H), 2.38 (t, 2H, $J = 6.7$ Hz), 7.49 (dd, 1H, $J = 7.7$, 1.0 Hz), 7.76 (t, 1H, $J = 7.7$ Hz), 8.42 (dd, 1H, $J = 7.7$, 1.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 13.9, 19.5, 22.1, 27.8, 30.9, 84.8, 73.7, 74.1, 86.1, 121.0, 128.2, 197.0, 141.7, 155.7; EI/MS *m/z* (%) 392 (M^+, 100), 377 ($M^+ - CH_3$, 25), 363 ($M^+ - CH_2CH_3$, 10), 349 ($M^+ - (CH_2)_2CH_3$, 8), 335 ($M^+ - (CH_2)_3CH_3$, 6), 321 ($M^+ - (CH_2{}_4CH_3$, 6). Anal. Calcd for $C_{28}H_{28}N_2Si$: C, 85.67; H, 7.19; N, 7.14. Found: C, 85.49; H, 7.02; N, 7.03.

4,4′-Bis[4-(triethylsilyl)-1,3-butadiynyl]-2,2′-bipyridine (15a): 4,4′-diethynyl-2,2′-bipyridine (0.300 g, 1.46 mmol), CuCl (0.022 g, 0.22 mmol), hydroxylamine hydrochloride (0.056 g, 0.8 mmol), *n*-propylamine (2.5 mL), 1-bromo-2-(triethylsilyl)-acetylene (0.490 g, 2.23 mmol). Chromatographed on flash silica gel (hexane/ethylacetate 95/5) to give 0.567 g of a yellow crystalline powder, 80%: mp 63/4 °C; IR (CCl_4, cm^{-1}) 2957 (s), 2872 (s), 2100 (s), 1581 (br), 1452 (s), 1358 (s); ^1H NMR ($CDCl_3$) δ 0.65 (q, 6H, $J = 8.0$ Hz), 1.03 (t, 9H, $J = 8.0$ Hz), 7.34 (dd, 1H, $J = 5.0$, 1.6 Hz), 8.45 (d, 1H, $J = 1.6$ Hz), 8.61 (d, 1H, $J = 5.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 4.1, 7.3, 73.0, 78.6, 88.0, 91.6, 123.9, 126.2, 130.8, 149.2, 155.4; EI/MS *m/z* (%) 180 (M^+, 90), 451 ($M^+ - C_2H_5$, 100), 422 ($M^+ - 2C_2H_5$, 50), 403 ($M^+ - 3C_2H_5$, 20), 374 ($M^+ - 4C_2H_5$, 18). Anal. Calcd for $C_{30}H_{36}N_2Si_2$: C, 74.94; H, 7.55; N, 5.83. Found: C, 74.82; H, 7.48; N, 5.74.

4′-[4-(Triethylsilyl)-1,3-butadiynyl]-2,2′:6′,2″-terpyridine (17a): 4′-ethynyl-2,2′:6′,2″-terpyridine (1.340 g, 5.21 mmol), CuCl (0.060 g, 0.606 mmol), hydroxylamine hydrochloride (0.220 g, 3.16 mmol), *n*-propylamine (20mL), 1-bromo-2-(triethylsilyl)acetylene (2.200 g, 10 mmol). Chromatographed on alumina (CH_2Cl_2/hexane 40/60) to give 1.100 g of a white crystalline powder, 54%: mp 65/6 °C; R_f 0.74 (alumina, CH_2Cl_2); IR ($CHCl_3$, cm^{-1}) 2959 (s), 2876 (s), 2102 (s), 1583 (br), 1467 (s), 1391 (s); ^1H NMR (CD_2Cl_2) δ 0.72 (q, 6H, $J = 8.0$ Hz), 1.07 (t, 9H, $J = 8.0$ Hz), 7.34 (ddd, 2H, $J = 7.5$, 4.8, 1.0 Hz), 7.84 (td, 2H, $J = 7.7$, 1.7 Hz), 8.51 (s, 2H), 8.56 (d, 2H, $J = 8.0$ Hz), 8.69 (d, 2H, $J = 4.8$ Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 4.6, 7.6, 74.1, 78.3, 88.6, 91.8, 121.4, 123.7, 124.6, 131.8, 137.2, 149.6, 155.6, 156.1; FAB^+ (*m*-NBA) *m/z* (%) 396 ($[M + H]^+$, 100), 281 ($[M - Si(C_2H_5)_3 + H]$, 15). Anal. Calcd for $C_{25}H_{25}N_3Si$: C, 75.91; H, 6.37; N, 10.62. Found: C, 75.77; H, 6.09; N, 10.48.

Preparation of the Diyne Derivatives 9b, 11b, 13c, 15b, 17b (Chart 2 and 3). General Procedure. To a solution of the (triethylsilyl)-1,3-butadiyne derivatives (1.000 g scale) in CH_3OH/CH_2Cl_2 4/1, an aqueous solution of NaOH (5 M, 4 mL) was added. After a 15 min of stirring, the organic product was extracted with CH_2Cl_2 (3 × 75 mL), and the organic layer was dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude material was chromatographed on flash silica gel to give the analytically pure derivative **9b** in good yield. For other compounds after stirring for 2 h, the organic solvent was evaporated by rotary evaporation resulting in the precipitation of a white product. The pure compound was filtered and washed with cold CH_3OH (2 × 50 mL) and ether (3 × 50 mL) and dried under *vacuum* leading to the analytically pure derivative in fair yield.

Preparation of 4-(1,3-butadiynyl)pyridine (9b): 4-[4-(triethylsilyl)-1,3-butadiynyl]pyridine (1.000 g, 4.1 mmol). Chromatographed on flash silica gel (hexane/$CH_2Cl_2$90 to 80/10 to 20) to give 0.410 g of a colorless liquid (78%): $R_f = 0.34$ (CH_2Cl_2/hexane 1/1, silica TLC sheet treated with triethylamine); IR ($CHCl_3$, cm^{-1}) 3290 (s), 2970 (br), 1585 (vs); ^1H NMR (CD_2Cl_2) δ 2.69 (s, 1H), 7.36 (d, 2H, $J = 4.5$ Hz), 8.59 (d, 2H, $J = 4.5$ Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 67.4, 72.6, 73.8, 77.4, 126.6, 129.3, 150.3; EI/MS *m/z* (%) 127 (M^+, 100); Anal. Calcd for C_9H_5N: C, 85.02; H, 3.96; N, 11.02. Found: C, 84.87; H, 3.95; N, 10.94.

6-(1,3-Butadiynyl)-5,5′-dimethyl-2,2′-bipyridine (11b): 6-[4-(triethylsilyl)-1,3-butadiyne]-5,5′-dimethyl-2,2′-bipyridine (1.000 g, 2.88 mmol). A 0.602 g amount of **11b** was obtained, 90%: mp 87 °C dec; R_f 0.30 (CH_2Cl_2, silica); IR (KBr, cm^{-1}) 3167 (s), 2965 (s), 2053 (s), 1547 (s), 1491 (s), 1439 (vs), 1262 (s); ^1H NMR (CD_2Cl_2) δ 2.37 (s, 3H), 2.48 (s, 3H), 2.69 (s, 1H), 7.62 (dd, 1H, $J = 8.1$, 0.6 Hz), 7.65 (d, 1H, $J = 8.2$ Hz), 8.27 (d, 1H, $J = 7.8$ Hz), 8.30 (d, 1H, $J = 7.8$ Hz), 8.45 (d, 1H, $J = 0.6$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 18.4, 19.1, 67.8, 73.0, 73.8, 75.8, 120.6, 121.3, 134.2, 137.7, 138.1, 138.5, 140.4, 149.9, 152.9, 154.9; FAB^+ (*m*-NBA) *m/z* (%) 233 ($[M + H]^+$, 100). Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.51; H, 5.00; N, 11.83.

6,6′-Bis(1,3-butadiynyl)-2,2′-bipyridine (13c): 6,6′-bis-[4-(triethylsilyl)-1,3-butadiynyl]-2,2′-bipyridine (0.500 g, 1.04 mmol). The pure product (0.248 g) changed color very rapidly from white to grey and must be used soon after its isolation, 98%: mp 130 °C dec; R_f 0.65 (CH_2Cl_2/hexane 7/3); IR (KBr, cm^{-1}) 3244 (s), 2059 (w), 1561 (s), 1436 (s); ^1H NMR (DMSO-d_6) δ 3.17 (s, 2H), 7.80 (d, 2H, $J = 7.5$ Hz), 8.04 (t, 2H, $J = 7.5$ Hz), 8.40 (d, 2H, $J = 7.5$ Hz). Its very poor solubility in common solvents prevented the obtention of a ^{13}C NMR spectrum. EI/MS *m/z* (%) 252 (M^+, 100). Anal. Calcd for $C_{18}H_8N_2$: C, 85.70; H, 3.19; N, 11.10. Found: C, 85.52; H, 3.01; N, 10.97.

4,4′-Bis(1,3-butadiynyl)-2,2′-bipyridine (15b): 4,4′-bis-[4-(triethylsilyl)-1,3-butadiynyl]-2,2′ bipyridine (0.480 g, 1 mmol). The pure product (0.177 g) changed color very rapidly from white to grey and must be used soon after its isolation, 70%: mp 140 °C dec; IR (KBr, cm^{-1}) 3196 (s), 2059 (m), 1587 (s), 1457 (m), 1359 (m); ^1H NMR (THF-d_8) δ 2.73 (s, 2H), 7.56 (d, 1H, $J = 5.0$ Hz), 8.61 (s, 1H) 8.75 (d, 1H, $J = 5.0$ Hz); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 73.7, 77.6, 79.4, 125.4, 128.5, 132.3, 151.8, 157.6; EI/MS *m/z* (%) 252 (M^+, 100). Anal. Calcd for $C_{18}H_8N_2$: C, 85.70; H, 3.19; N, 11.10. Found: C, 85.61; H, 3.02; N, 10.98.

4′-(1,3-Butadiynyl)-2,2′:6′,2″-terpyridine (17b): 4′-[4-(triethylsilyl)-1,3-butadiynyl]-2,2′:6′,2″-terpyridine (0.300 g, 0.7 mmol), 93%: R_f 0.60 (alumina, CH_2Cl_2/CH_3OH 99/1); mp 110 °C dec; IR ($CHCl_3$, cm^{-1}) 3210 (s), 2925 (br), 2065 (w), 1584 (s), 1565 (s), 1463 (br), 1388 (br); ^1H NMR ($CDCl_3$) δ 2.58 (s, 1H) 7.36 (ddd, 2H, $J = 7.5$, 4.8, 1.0 Hz), 7.87 (td, 2H, $J = 7.7$, $J = 1.7$ Hz), 8.55 (s, 2H), 8.58 (d, 2H, $J = 8.0$ Hz), 8.70 (d, 2H, $J = 4.7$ Hz); $^{13}C\{^1H\}$ NMR (DMSO-d_6) δ 64.9, 72.1, 78.6, 99.9, 120.9, 121.2, 122.7, 124.9, 130.4, 137.6, 153.9, 155.5; FAB^+ (*m*-NBA) *m/z* (%) 282 ($[M + H]^+$, 100). Anal. Calcd for $C_{19}H_{11}N_3$: C, 81.12; H, 3.94; N, 14.94. Found: C, 81.03; H, 3.72; N, 14.73.

Preparation of the Triethylsilyl Protected Triyne Derivatives 10, 12, 14, 19 (Charts 2 and 3). 4-[6-(Triethylsilyl)-1,3,5-hexatriynyl]pyridine (10). 4-(1,3-Butadiyne)-pyridine (0.400 g, 3.15 mmol) was dissolved in THF (40 mL). After addition of CuCl (0.040 g, 0.4 mmol) and hydroxylamine hydrochloride (0.080 g, 1.15 mmol), *n*-propylamine (4 mL) was slowly added *via* a syringe. After a 5 min stirring, 1-bromo-2-(triethylsilyl)acetylene (1.040 g, 4.74 mmol) in THF (5 mL) was added dropwise. After a 4.5 h stirring, the reaction mixture was quenched with H_2O (25 mL) and the organic product extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude material was chromatographed on flash silica gel (CH_2Cl_2) to give 0.240 g of a yellowish liquid, 29%: R_f 0.42 (CH_2Cl_2); IR (CCl_4, cm^{-1}) 2930 (br), 2110 (s), 1590 (vs); ^1H NMR (CD_2Cl_2) δ 0.63 (q, 6H, $J = 7.9$ Hz), 0.98 (t, 9H, $J = 7.9$ Hz), 7.28 (d, 2H, $J = 4.7$ Hz), 8.54 (d, 2H, $J = 4.7$ Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 4.4, 7.5, 60.0, 69.0, 73.8, 78.2, 88.6,

89.7, 126.7, 129.2, 150.3; EI/MS *m/z* (%) 265 (M^+, 35), 236 ($M^+ - C_2H_5$, 100), 208 ($M^+ - 2C_2H_5 + H$, 70), 180 ($M^+ - 3C_2H_5 + 2H$, 78). Anal. Calcd for $C_{17}H_{19}NSi$: C, 76.93; H, 7.22; N, 5.28. Found: C, 76.59; H, 7.15; N, 4.96.

6-[6-(Triethylsilyl)-1,3,5-hexatriynyl]-5,5′-dimethyl-2,2′-bipyridine (12). 6-(1,3-Butadiynyl)-5,5′-dimethyl-2,2′-bipyridine (0.400 g, 1.72 mmol) was dissolved in THF (100 mL). After addition of CuCl (0.070 g, 0.707 mmol) and hydroxylamine hydrochloride (0.120 g, 1.72 mmol), *n*-propylamine (10 mL) was added slowly *via* a syringe. 1-Bromo-2-(triethylsilyl)-acetylene (0.750 g, 3.42 mmol) in THF (20 mL) was then added dropwise over a period of 30 min. After a 2 h stirring, the solvent was removed and the crude residue was chromatographed on alumina (hexane/CH_2Cl_2 50/50) to give a yellowish oil, 30%: R_f 0.7 (alumina, CH_2Cl_2/hexane 50/50); IR (KBr, cm^{-1}) 3170 (s), 2968 (s), 2063 (s), 1550 (s), 1498 (s), 1441 (vs); ^1H NMR (CD_2Cl_2) δ 0.55 (q, 6H, J = 8.0 Hz), 0.92 (t, 9H, J = 8.0 Hz), 2.37 (s, 3H), 2.47 (s, 3H), 7.56 (dd, 1H, J = 8.0, 0.8 Hz), 7.64 (d, 1H, J = 8.1 Hz), 8.23 (d, 1H, J = 7.9 Hz), 8.27 (d, 1H, J = 7.9 Hz), 8.46 (d, 1H, J = 0.8 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 4.3, 7.3, 18.5, 21.8, 61.0, 68.1, 74.7, 77.0, 88.9, 90.8, 120.6, 121.8, 133.1, 137.3, 137.4, 139.4, 141.2, 149.4, 153.4, 155.7; FAB^+ (*m*-NBA) *m/z* (%) 371 ([M + H]$^+$, 100), 255 ([M − Si(C_2H_5)$_3$], 10). Anal. Calcd for $C_{24}H_{26}N_2Si$: C, 77.29; H, 7.07; N, 7.56. Found: C, 76.97; H, 6.81; N, 7.30.

6,6′-Bis[6-(trimethylsilyl)-1,3,5-hexatriynyl]-2,2′-bipyridine (14). 6,6′-Bis(1,3-butadiynyl)-2,2′-bipyridine (0.259 g, 1.02 mmol) was suspended in CH_2Cl_2 (10 mL). After addition of CuCl (0.016 g, 0.16 mmol) and hydroxylamine hydrochloride (0.038 g, 0.55 mmol), *n*-propylamine (3 mL) was slowly added *via* a syringe. Then, 1-bromo-2-(triethylsilyl)acetylene (0.890 g, 4.05 mmol) in CH_2Cl_2 (2 mL) was added dropwise at rt. After a 10 min stirring, the reaction was quenched with CH_3OH. Two new products were observed by TLC (silica). The major one became rapidly red on contact with silica plates. The less polar one corresponded to the expected compound. The reaction mixture was powered into H_2O (100 mL) and the organic product extracted with CH_2Cl_2 (3 × 30 mL). The yellow organic layer was dried over Na_2SO_4. After filtration on Celite and evaporation of the solvent, the crude product was chromatographed on flash silica gel (hexane/CH_2Cl_2 10/90) to give 0.027 g of a clear brown solid, 5%: mp 136/7 °C; IR (KBr, cm^{-1}) 2957 (s), 2876 (s), 2074 (w), 1569 (s), 1438 (s); ^1H-NMR ($CDCl_3$) δ 0.69 (q, 6H, J = 8.0 Hz), 1.02 (t, 9H, J = 8.0 Hz), 7.55 (dd, 1H, J = 6.7, 1.0 Hz), 7.80 (t, 1H, J = 6.7 Hz), 8.46 (dd, 1H, J = 6.7, 1.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 4.0, 7.3, 60.4, 67.8, 73.8, 75.1, 88.2, 88.7, 121.8, 129.1, 137.2, 140.7, 155.7; EI/MS *m/z* (%) 528 (M^+, 76), 499 ($M^+ - C_2H_5$, 100), 470 ($M^+ - 2C_2H_5$, 35), 441 ($M^+ - 3C_2H_5$, 7). Anal. Calcd for $C_{34}H_{36}N_2Si_2$: C, 77.22; H, 6.86; N, 5.30. Found: C, 77.07; H, 6.63; N, 5.09.

4′-[6-(Triethylsilyl)-1,3,5-hexatriynyl]-2,2′:6′,2″-terpyridine (18). 4′-(1,3-Butadiynyl)-2,2′:6′,2″-terpyridine (0.585 g, 2.07 mmol) was dissolved in THF (100 mL). After addition of CuCl (0.082 g, 0.83 mmol) and hydroxylamine hydrochloride (0.145 g, 2.09 mmol), *n*-propylamine (10 mL) was added *via* a syringe. Then, 1-bromo-2-(triethysilyl)acetylene (0.910 g, 4.15 mmol) in THF (50 mL) was added dropwise at rt. After a 2 h stirring, the solvent was evaporated by rotary evaporation. The crude product was chromatographed on alumina (CH_2Cl_2/hexane 1/1) to give 0.287 g of a yellowish oil, 25%: R_f 0.46 (alumina, CH_2Cl_2/hexane 1/1); IR ($CHCl_3$, cm^{-1}) 2962 (s), 2880 (s), 2110 (s), 1585 (br), 1470 (s), 1391 (s); ^1H NMR (CD_2Cl_2) δ 0.75 (q, 6H, J = 8.0 Hz), 1.10 (t, 9H, J = 8.0 Hz), 7.52 (ddd, 2H, J = 7.6, 4.7, 1.1 Hz), 7.96 (td, 2H, J = 7.8, 1.8 Hz), 8.64 (s, 2H), 8.73 (d, 2H, J = 8.2 Hz), 8.69 (d, 2H, J = 4.7 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 4.5, 7.5, 60.3, 68.4, 73.5, 78.3, 88.9, 90.2, 121.4, 123.9, 124.1, 136.9, 147.1, 149.2, 155.8, 155.9; FAB^+ (*m*-NBA) *m/z* (%) 420 ([M + H]$^+$, 100), 304 ([M − Si(C_2H_5)$_3$], 25). Anal. Calcd for $C_{27}H_{25}N_3Si$: C, 77.29; H, 6.01; N, 10.01. Found: C, 77.01; H, 5.83; N, 9.71.

Preparation of the Ditopic Tetrayne Ligands 19, 20 (Chart 3). Bis(2,2′:6′,2″-terpyridin-4′-yl)octatetrayne (19). 4′-(1,3-Butadiynyl)-2,2′: 6′,2″-terpyridine (0.300 g, 1.07 mmol) was dissolved in anhydrous DMF (60 mL). Then $CuCl_2$ (1.000 g, 7.44 mol) and CuCl (2.000 g, 20.20 mmol) were added as solid. O_2 was bubbled into the suspension for 1 h and allowed to react during 2 days at rt. After disappearance of the starting compound by TLC, the reaction mixture was poured into H_2O (100 mL), and KCN (7.000 g, 112 mmol) was used to remove copper from the deep-green complexes. The precipitate was recovered by centrifugation, washed with H_2O (3 × 50 mL) and ether (3 × 50 mL), and dried under vacuum. Ditopic ligand **19** was obtained as a grey solid (0.270 g, 80%): mp > 270 °C. IR (KBr, cm^{-1}) 2965 (s), 1592 (s), 1468 (s), 1395 (s), 1120 (br); ^1H NMR (DMF-d_7, 120 °C) δ 7.43 (ddd, 2H, J = 7.6, 4.9, 1.0 Hz), 7.93 (td, 2H, J = 7.9, 1.7 Hz), 8.64 (s, 2H), 8.66 (d, 2H, J = 7.9 Hz), 8.79 (d, 2H, J = 4.9 Hz). Its very poor solubility in common solvents prevented the obtention of a ^{13}C NMR spectrum. FAB^+ (*m*-NBA + 10% TfA) *m/z* (%) 561 ([M + H]$^+$, 100). Anal. Calcd for $C_{38}H_{20}N_6$: C, 81.41; H, 3.60; N, 14.99. Found: C, 81.18; H, 3.43; N, 14.63.

Bis(5,5′-dimethyl-2,2′-bipyridin-6-yl)octatetrayne (20). In a similar manner to **19**, compound **20** was prepared from 6-(1,3-butadiynyl)-5,5′-dimethyl-2,2′-bipyridine (0.450 g, 1.937 mmol), $CuCl_2$ (1.823 g, 13.56 mmol), CuCl (3.835 g, 38.74 mmol). An identical workup gave 0.309 g (69%) of ligand **20**: mp > 270 °C; IR (KBr, cm^{-1}) 2963 (s), 1637 (s), 1553 (s), 1450 (s), 1235 (s), 1135 (m), 1052 (br); ^1H NMR (DMF-d_7, 100 °C) δ 2.56 (s, 6H), 2.73 (s, 6H), 7.89 (dd, 2H, J = 8.2, 2.1 Hz), 7.95 (dd, 2H, J = 8.2, 0.8 Hz), 8.29 (d, 2H, J = 8.3 Hz), 8.34 (d, 2H, J = 8.3 Hz), 8.54 (d, 2H, J = 0.8 Hz). Its very poor solubility in common solvents prevented the obtention of a ^{13}C NMR spectrum. FAB^+ (*m*-NBA + 10% TFA) *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, 82.79; H, 4.41; N, 11.97.

6,6′-Bis[2-(aminopropyl)-6-(trimethylsilyl)-1-hexene-3,5-diynyl]-2,2′-bipyridine (mixture of three *Z* and *E* stereoisomers 21a, 21b, 21c). 6,6′-Bis(1,3-butadiynyl)-2,2′-bipyridine (0.105 g, 0.416 mmol) was suspended in THF (4 mL). After addition of CuCl (0.006 g, 0.06 mmol) and hydroxylamine hydrochloride (0.015 g, 0.22 mmol), *n*-propylamine (1 mL) was slowly added *via* a syringe. Then, 1-bromo-2-(triethylsilyl)acetylene (0.200 g, 0.91 mmol) in THF (1 mL) was added dropwise at rt. After a 4 h stirring, the crude product was poured into a saturated solution of NH_4Cl and extracted with Et_2O (2 × 10 mL). The organic phase was dried over $NaSO_4$, and after filtration on Celite the solvent was evaporated under vacuum to give 0.269 g of a yellow oil (100%) corresponding to the mixture of the three stereoisomers **21a**, **21b**, and **21c**: R_f (decomposition and appearance of a red spot on silica plates); IR (KBr, cm^{-1}) 3379 (NH, m), 3155 (NH, m), 2960 (vs), 2876 (vs), 2253 (s), 2166 (s), 1593 (s), 1564 (s), 1469 (s), 1437 (s), 1381 (m), 197 (s), 1011 (s); ^1H NMR (500 MHz, $CDCl_3$) δ 0.62−0.68 (m, 36 H, CH_2Si, isomers **21a**, **21b**, **21c**); 0.99−1.06 (m, 72 H, C*H*$_3$CH$_2$Si, C*H*$_3$CH$_2$CH$_2$NH, isomers **21a**, **21b**, **21c**); 1.75−1.82 (m, 12H, NCH$_2$C*H*$_2$CH$_3$, isomers **21a**, **21b**, **21c**); 3.11−3.13 (m, 6H, NCH_2 in the *trans* part of the isomers **21b** and **21c**); 3.75−3.79 (m, 6H, CH_2N in the *cis* part of the isomers **21a** and **21b**); 4.70 (s, 3H, vinylic H in the *trans* part of isomers **21b** and **21c**); 5.01 (s, 3H, vinylic H in the *cis* part of isomers **21a** and **21b**); 6.03−6.10 (m, 3H, NH in the *trans* part of isomers **21b** and **21c**, exchanged with D_2O); 6.45−6.55 (m, 3H, NH in the *cis* part of isomers **21a** and **21b**, exchanged with D_2O); 7.66 (d, 3H, ^3J = 7.8 Hz, H^5 of the *cis* part of isomers **21a** and **21b**); 7.81 (t, 1H, ^3J = 7.8 Hz, H_4 or H_4' of the isomer **21b**); 7.82 (t, 2H, ^3J = 7.8 Hz, H^4 and $H^{4'}$ of the isomer **21c**); 7.92 (t, 2H, ^3J = 7.8 Hz, H^4 and $H^{4'}$ of the isomer **21a**); 7.93 (t, 1H, ^3J = 7.8 Hz, $H^{4'}$ or H^4 of isomer **21b**); 8.29 (dd, 2H, ^3J = 7.8, ^4J = 0.8 Hz, H^5 and $H^{5'}$ or H^3 and $H^{3'}$ of the isomer **21c**); 8.31 (dd, 1H, ^3J = 7.8, ^4J = 0.8 Hz, H^5 or H^3 or $H^{5'}$ or $H^{3'}$ of the isomer **21b**); 8.33 (dd, 1H, ^3J = 7.8, ^4J = 0.8 Hz, $H^{3'}$ or $H^{5'}$ of the isomer **21b**); 8.35 (dd, 2H, ^3J = 7.8, ^4J = 0.8 Hz, H^3 and $H^{3'}$ or H^5 and $H^{5'}$ of the isomer **21c**); 8.64 (overlapping dd, 3H, ^3J = 7.8 Hz, ^4J = 0.8 Hz, H^3, $H^{3'}$ of the isomer **21a,** H^3 of the isomer **21b**). Proton integration given above has been normalized for an equimolar concentration of compounds **21a**, **21b**, and **21c**. The relative proportion of compounds is 48% of **21a**, 33% of **21b**, and 19% of **21c** and has been obtained by integration of the corresponding signals in the aromatic part of the spectrum: $^{13}C\{^1H\}$ NMR (250 MHz, $CDCl_3$) δ 154.2, 154.1, 154.0, 154.0, 153.9, 153.9, 152.4, 152.4,

152.4, 152.3, 151.1, 151.1, 137.8, 137.7, 137.7, 137.6, 123.8, 123.7, 121.2, 120.8, 120.1, 120.0, 90.7, 90.7, 90.6, 88.2, 88.2, 87.9, 87.8, 78.9, 78.8, 78.0, 77.9, 77.9, 77.1, 72.21 (C═C), 72.1 (C═C), 72.0 (C═C), 46.5 (NCH_2), 45.3 (NCH_2), 23.8 (NCH_2CH_2), 21.9 (NCH_2CH_2), 11.8 ($NCH_2CH_2CH_3$), 11.3 ($NCH_2CH_2CH_3$), 7.5 ($SiCH_2CH_3$), 4.4 ($SiCH_2$). FAB^+ (*m*-NBA) *m/z* (%) 677 ([M + H]$^+$,100), 604.2 ([M − C_3H_7 + H], 18), 532.2 ([M − $C_6H_{15}Si$ + H], 17), 489.2 [M − $C_9H_{22}Si$ + H], 16).

Preparation of the Copper(I) Complexes 22a/b, 23, 24, 25 (Chart 5). General Procedure. To an argon degassed solution of the chelating ligand (100 mg scale, 1 equiv) in CH_2Cl_2 (10 mL) was added dropwise, over a period of 15 min, an argon degassed solution of $[Cu(CH_3CN)_4](ClO_4)$ (0.5 equiv) in CH_3CN (10 mL). The solution turned immediately deep-red, showing fast copper(I) complexation. After a 3 h stirring at rt, the solution was filtered over Celite and the solution concentrated under *vacuum* to ca. 5 mL. Addition of ether caused the precipitation of the desired product. Complexes were recrystallized from acetone/hexane 1/1 mixture, affording analytical pure samples in good yields.

[Cu(**5a**)$_2$](ClO$_4$) (**22a**):[49] 86%; IR (KBr, cm^{-1}) 2972 (s), 2159 (s), 1646 (m), 1589 (m), 1560 (m), 1452 (s), 1251 (s), 1093 (vs, ClO_4); UV-vis [CH_3CN, λ_{max} nm, (ϵ M^{-1} cm^{-1})]; 493 (2640), 294 (32000), 245 (43600), 218 (76400); ^{1}H NMR (CD_3COCD_3) δ −0.21 (s, 36H), 7.92 (d, 4H, J = 7.8 Hz), 8.34 (t, 4H, J = 7.8 Hz), 8.82 (d, 4H, J = 7.8 Hz); $^{13}C\{^1H\}$ (CD_3COCD_3) δ −0.8, 99.5, 102.3, 123.2, 130.9, 139.3, 141.9, 152.4; FAB^+ (*m*-NBA, rel %) 759.0 ([M − ClO_4]$^+$, 100), 687.0 ([M − ClO_4 − $Si(CH_3)_3$ + H], 7), 411.0 ([M − ClO_4 − L], 95). Anal. Calcd for $C_{40}H_{48}ClN_4O_4Si_4Cu$: C, 55.85; H, 5.62; N, 6.51. Found: C, 55.78; H, 5.48; N, 6.35.

[Cu(**5b**)$_2$](ClO$_4$) (**22b**): 89%; IR (KBr, cm^{-1}) 3248 (s), 2109 (s), 1591 (m), 1562 (m), 1450 (s), 1251 (s), 1171 (m), 1092 (vs); UV-vis [CH_3CN, λ_{max} nm, (ϵ M^{-1} cm^{-1})]; 470 (2000), 362 (1600), 289 (32400); ^{1}H NMR (CD_3CN) δ 3.17 (s, 4H), 7.76 (dd, 2 H, J = 8.0, 0.9 Hz), 7.76 (t, 4H, J = 8.0 Hz), 8.42 (dd, 4 H, J = 8.0, 0.9 Hz); $^{13}C\{^1H\}$ NMR (CD_3CN), δ 81.4, 82.1, 123.2, 130.2, 139.2, 141.1, 152.8; FAB^+ (*m*-NBA, rel %) 471.0 ([M − ClO_4]$^+$, 100), 267.0 ([M − ClO_4 − L], 83). Anal. Calcd for $C_{28}H_{16}ClN_4O_4Cu$: C, 58.85; H, 2.82; N, 9.80. Found: C, 58.76; H, 2.69; N, 9.77.

[Cu(**13b**)$_2$](ClO$_4$) (**23**): 93%; IR (KBr, cm^{-1}) 2932 (s), 2235 (s), 1591 (m), 1559 (m), 1560 (m), 1457 (s), 1094 (vs); UV-vis [CH_3CN, λ_{max} nm, (ϵ M^{-1} cm^{-1})]; 467 (1620), 301 (44600), 275 (41700), 250 (29200); ^{1}H NMR (CD_3CN) δ −0.89 (t, 12H, J = 7.0 Hz), 1.32 (m, 24H), 2.12 (m, 8H), 7.74 (d, 4H, J = 7.9 Hz), 8.17 (t, 4H, J = 7.9 Hz), 8.40 (d, 4H, J = 7.9 Hz); $^{13}C\{^1H\}$ (CD_3CN) δ 14.0, 19.6, 27.8, 31.4, 22.5, 63.8, 72.5, 78.3, 89.7, 122.5, 129.3, 138.9, 140.1, 151.8; FAB^+ (*m*-NBA, rel %) 847.2 ([M − ClO_4]$^+$, 100), 455.1 ([M − ClO_4 − L], 53). Anal. Calcd for $C_{56}H_{56}ClN_4O_4Cu$: C, 70.94; H, 5.95; N, 5.91. Found: C, 70.92; H, 5.87; N, 5.85.

[Cu(**13a**)$_2$](ClO$_4$) (**24**): 89%; IR (KBr, cm^{-1}) 2956 (s), 2874 (s), 2100 (s), 1652 (m), 1588 (m), 1558 (m), 1455 (s), 1091 (vs); UV-vis [CH_3CN, λ_{max} nm, (ϵ M^{-1} cm^{-1})]; 493 (1850), 302 (69400), 277 (57900), 259 (39800), 216 (199300); ^{1}H NMR (CD_3CN) δ 0.59 (q, 24H, J = 7.3 Hz), 0.90 (t, 36H, J = 7.3 Hz), 7.84 (d, 4H, J = 7.8 Hz), 8.18 (t, 4H, J = 7.8 Hz), 8.46 (d, 4H, J = 7.8 Hz); $^{13}C\{^1H\}$ (CD_3CN) δ 8.8, 12.2, 77.6, 81.7, 91.6, 98.5, 128.3, 135.5, 144.2, 144.7, 157.1; FAB^+ (*m*-NBA, rel %) 1023.2 ([M − ClO_4]$^+$, 100), 543.1 ([M − ClO_4 − L], 71). Anal. Calcd for $C_{60}H_{72}ClN_4O_4Si_4Cu$: C, 64.08; H, 6.45; N, 4.98. Found: C, 63.82; H, 6.18; N, 4.89.

[Cu(**14**)$_2$](ClO$_4$) (**25**): 65%; IR (KBr, cm^{-1}) 2960 (s), 2879 (s), 2080 (s), 1648 (m), 1583 (m), 1565 (m), 1239 (m), 1092 (vs), 1056 (s); UV-vis [CH_3CN, λ_{max} nm, (ϵ M^{-1} cm^{-1})]; 493 (1270), 339 (88700), 317 (101000), 299 (51800), 276 (27200), 251 (157400), 231 (145200); ^{1}H-NMR (CD_3CN) δ 0.52 (q, 4H, J = 7.8 Hz); 0.98 (t, 12H, J = 7.8 Hz); 7.85 (dd, 4H, J = 6.5, J = 1.0 Hz), 7.96 (t, 4H, J = 6.5 Hz), 8.73 (dd, 4H, J = 6.5, J = 1.2 Hz). $^{13}C\{^1H\}$ NMR (CD_3CN) δ 9.0, 10.1, 64.3, 71.0, 75.0, 79.5, 93.0, 93.2, 123.6, 130.7, 141.2, 143.8, 156.8; FAB^+ (*m*-NBA, rel %) 1121.3 ([M − ClO_4]$^+$, 100), 591.3.([M − ClO_4 − L], 67). Anal. Calcd for $C_{68}H_{72}ClN_4O_4Si_4Cu \cdot 0.5\ CH_3CN$: C, 66.76; H, 5.97; N, 5.08. Found: C, 66.62; H, 5.68; N, 4.98.

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Supporting Information Available: X-ray experimental section, discussion of the molecular structure of complex **22a**, and related references (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(49) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.