From 1,2,4-Triazines and Tributyl(ethynyl)tin to Stannylated Bi- and Terpyridines: The Cycloaddition Pathway

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Dedicated to Professor Dr. Reinhard W. Hoffmann on the occasion of his 65th birthday

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Recently, we reported on cycloadditions between electron-deficient heterodienes and tributyl(ethynyl)tin, which provide a new pathway to stannylated pyridazines and, in one special case, pyridines. In order to broaden the synthetic scope of these reactions, we have developed hetero [4+2] cycloaddition reactions between a number of tailor-made 1,2,4-triazines **5**–**9** (acting as heterodienes), and tributyl(ethynyl)tin (acting as dienophile). The desired 1,2,4-triazines are readily available, in moderate to very good yields, by the condensation reactions of appropiate carbamidrazones and glyoxals. These cycloadditions open up a novel route to regiospecifically stannylated 2,2′-bi- and 2,2′,6′,2′′-terpyridines **1**–**4**, **11** in good yields. The stannanes **1**–**4**, **11** are versatile synthetic intermediates, and with this strategy various substituents can be incorporated directly by substitution of the stannyl group, as was shown for halogens and carbon electrophiles under Stille conditions.

In the last few years numerous 2,2′-bi- and 2,2′,6′,2′′-terpyridines have been used as encapsulating ligands for the complexation of various metal ions. A large variety of possible applications for these metal complexes have been described, including molecular electronics and self-assembly of double-helical and triple-helical metal complexes.[1][2] However, the synthetic methodology is still in its infancy, particularly in the case of the preparation of unsymmetrically substituted bipyridines. Most papers concerned with 4-substituted 2,2′-bipyridines still use the procedure reported by Jones et al. in 1967, which is based on the *N*-oxidation of 2,2′-bipyridine followed by nitration.[3] The resulting complex mixture of unchanged, *N*-oxidized and/or nitrated bipyridines has to be separated, and, after successful isolation, the desired 4-nitro-2,2′-bipyridine *N*-oxide functionalized by nucleophilic substitution reactions or by hydrogenation, followed by diazotation and subsequent reactions of the diazonium compound.[4] To the best of our knowledge, other synthetic approaches, which have been reported in the literature,[5] have not found further applications. Therefore, it is of no surprise that most authors focus their interest on the use of the more readily accessible 4,4′-disubstituted 2,2′-bipyridines and 4′-substituted 2,2′,6′,2′′-terpyridines.[6]

The synthetic applications of [4+2] cycloaddition reactions of electron-deficient dienes, such as 1,2,4,5-tetrazines or 1,2,4-triazines, are limited by the demand for dienophiles of complementary electronic character, such as ynamines, which guarantee sufficient overlap of the frontier orbitals.[7] However, we have recently found that simple organotin alkynes offer good reactivity as electron-rich dienophiles towards electron-deficient heterodienes, such as those mentioned above. Originally, the application of this method was restricted to the use of highly electron-deficient tetrazines,[8] but in the course of these studies it was recognized that tributyl(ethynyl)tin can also be used as a dienophile in [4+2] cycloadditions with less electron-deficient heterodienes, such as the 1,2,4-triazines, at higher reaction temperatures.[9] Thus, because the stannanes obtained can serve as synthetic intermediates for a vast number of transformations provided by organotin chemistry,[10] [4+2] cycloadditions with tributyl(ethynyl)tin are a promising tool for organic synthesis.

Based on this work, we report here on thermically induced [4+2] cycloaddition reactions between tailor-made 1,2,4-triazines and tributyl(ethynyl)tin, which open up a new and very efficient route to regioselectively stannylated 2,2′-bi- and 2,2′,6′,2′′-terpyridines **1**−**4** (Figure 1). This method gives rapid access to a variety of stannylated oligopyridines, all of which are interesting starting compounds for supramolecular chemistry.

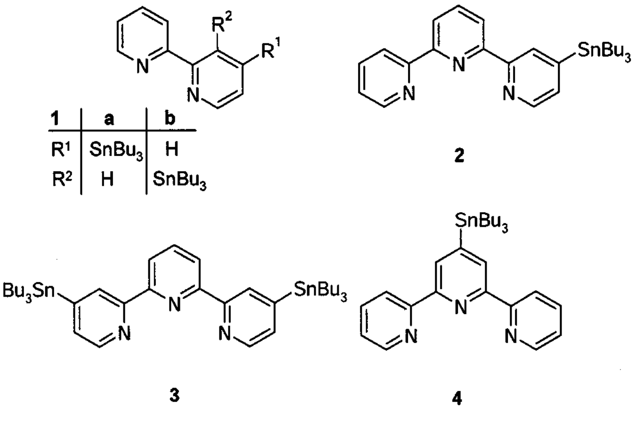

Figure 1. Stannylated 2,2′-bi- and 2,2′,6′,2′′-terpyridines available by the cycloaddition route from 1,2,4-triazines

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Results and Discussion

The key idea behind our concept was as follows: If suitable 2-pyridyl-substituted 1,2,4-triazines were readily accessible starting materials, the cycloaddition reaction with tributyl(ethynyl)tin would accomplish two ends. First, the triazine nucleus would be transformed into the desired pyridine core. Secondly, the tributyltin group would also be incorporated as a substituent into the bipyridine ring system. Furthermore, it has been shown previously that the regiochemistry of the cycloaddition reaction between unsymmetrically substituted heterodienes like 3-aryl-1,2,4,5-tetrazines and tributyl(ethynyl)tin is controlled only by steric interactions, giving rise to a marked (> 95%) preference for *meta*-substituted pyridazines.[8b] Therefore, the use of suitably substituted 1,2,4-triazines should also lead to only one regioisomer. For example, the synthesis of bipyridine **1** was planned as shown in Figure 2.

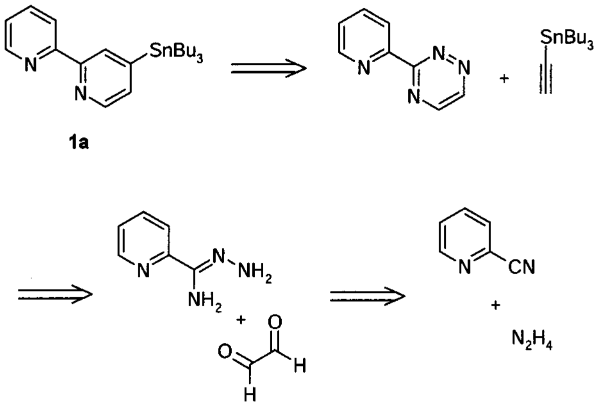
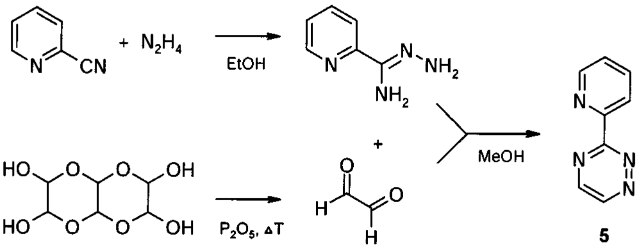


Figure 2. Retrosynthetic considerations for the synthesis of bipyridine **1**

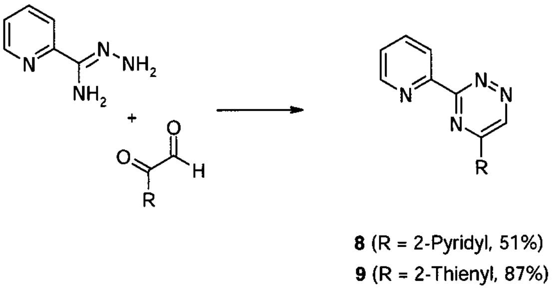
Retrosynthetic considerations led to the choice of the triazines **5**−**9** as suitable precursors for the projected reactions (Table 1). With the exception of **5**, none of them could be found in the Beilstein database. Usually, 1,2,4-triazine cores are synthesized by condensation reactions starting from the appropriate carbamidrazones and glyoxals.[11] Unfortunately, according to the literature, the desired triazine derivative **5** is obtained from 2-pyridylcarbamidrazone and glyoxal sodium bisulfite in a yield of only 15%,[12] and, even more unsatisfactorarily, in our hands this procedure gave yields that did not exceed 2%. Thus, we decided to use monomeric glyoxal in the condensation reaction as reported by Neunhoeffer et al.[13] Monomeric glyoxal was prepared by the method of Harries and Temme.[14] The yellow needles of the monomeric glyoxal, which had been collected in a cold trap at −78°C, were dissolved in anhydrous methanol and added rapidly to a solution of 2-pyridylcarbamidrazone in the same solvent at room temp. After condensation and sublimation, the desired triazine **5** was obtained in a very good yield of 81−89% (Scheme 1).

By following an identical procedure with suitably substituted, literature-known carbamidrazones, the triazines **6** and **7** were obtained in moderate to good yields (Table 1). The units from which the 1,2,4-triazine core was constructed are shown by the dotted lines in Table 1.



Scheme 1. Synthesis of 3-(2-pyridyl)-1,2,4-triazine **5**

A further complication arose from the synthesis of the triazine **8**, which should be accessible by the condensation of 2-pyridylcarbamidrazone and 2-pyridylglyoxal. According to a procedure given by Schank,[15] the desired 2-pyridylglyoxal was prepared by the acid hydrolysis of the corresponding acetal and used at once in aqueous solution without isolation. The subsequent condensation step furnished triazine **8** in a yield of 51% over two steps. The condensation reaction to form 1,2,4-triazines generally gives very good yields of about 85−90%. For example, the analogous reaction with the stable 2-thienylglyoxal in ethanol afforded the triazine **9** in a yield of 87%. In both cases, only one of two possible regioisomeric condensation products was obtained (Scheme 2). Needless to say, this procedure can be extended to other known glyoxals, thus giving rapid access to a large variety of 1,2,4-triazines with aliphatic, aromatic and heterocyclic substituents, instead of the thiophene or pyridine ring.



8 (R = 2-Pyridyl, 51%)
9 (R = 2-Thienyl, 87%)

Scheme 2. Synthesis of 3,5-disubstituted triazines **8** and **9**

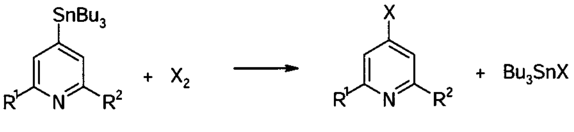
As has been already observed in earlier reports,[11] if monosubstituted glyoxals are used in the condensation reaction, the formation of 3,5-disubstituted 1,2,4-triazines is strongly favoured in comparison to the formation of 3,6-disubstituted 1,2,4-triazine derivatives. Fortunately, this selectivity seems to also be quite high for the desired triazines. The ^{1}H-NMR spectrum of crude **8** showed the resonance signal of the triazine proton strongly deshielded as a sharp singlet at $\delta = 10.31$. Further resonances in this part of the spectrum indicating the formation of a second triazine isomer could not be detected. The ^{13}C-NMR spectrum of **8** also confirmed the formation of only one isomer.

With the desired heterodienes now readily available, the [4+2] cycloadditions planned with tributyl(ethynyl)tin (**10**) were carried out under strong conditions (16 h reflux in 1,2-dichlorobenzene) to furnish the projected bi- and terpyridines **1−4**, **11** in yields ranging from 47 to 95% (Table 1).

The reaction with the triazine derivative **5** afforded two regioisomers **1a** and **1b**, which could be separated by flash column chromatography, again showing a strong preference for the 4-substituted regioisomer (isolated yield 86% for **1a** and 5% for **1b**). The steric course of the reactions between the triazines and tributyl(ethynyl)tin can be understood assuming that the reaction partners adopt an orientation in the transition state in order to minimize unfavourable steric interactions between the bulky tributyltin group and the pyridine substituent. Extrusion of nitrogen leads to the desired pyridine core as final stable reaction product. The substitution patterns were unambiguously assigned to **1a** and **1b** by the typical ^{1}H-NMR coupling constant sets for 2,4- and 2,3-disubstituted pyridine ring systems, respectively.

In all other cases separation of the minor regioisomer was not possible by means of standard flash column chromatographic techniques. However, the content of this minor isomer was always less than 5% (as determined by ^{1}H and ^{13}C NMR under the assumption that the additional small resonance signals belong to the regioisomer; mass spectra and elemental analyses support this assumption) and can be neglected for further preparative purposes. Yields of the stannylated 2,2′,6′,2′′-terpyridines obtained are summarized in Table 1.

The pyridine−Sn bond can be cleaved by electrophiles much more readily than the pyridine−H bond, and the stannylated pyridines therefore react by *ipso* substitution with electrophilic reagents such as halogens. These substitution reactions make it possible to introduce an electrophilic group X (X = Br, I) under mild conditions, regiospecifically overruling the normal directive effect of the pyridine nitrogen atom, as well as the lack of reactivity towards electrophilic reagents of the electron-deficient pyridine moiety. Smooth displacement of the stannyl group at low (−60°C, Br$_2$) or room temp. (I$_2$) was achieved for all the compounds described above.



1a-4 **12-15**

Scheme 3. Synthesis of halogenated oligopyridines by substitution of the stannyl group with elemental halogens

The halogenations are also responsible for a clean-up of the compounds. Whereas for **1a** a clean substitution of the tributyltin group is observed, **1b** reacts by substitution of a butyl group at the tin atom, thus giving rise to a much more soluble species, because of the remaining two butyl groups at the tin atom. This effect has already been reported in the literature.[16] For this reason traces of regioisomers for **2−4** diminish during further synthetic transformations.

Table 1. Triazines **5**−**9** as precursors for the pyridines **1**−**4**, **11**

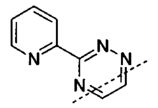
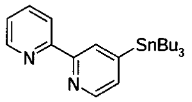
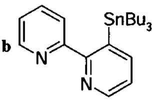
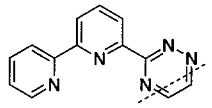
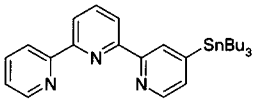
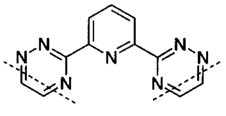
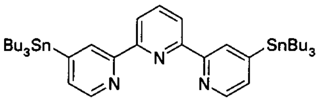
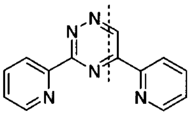
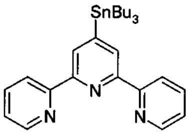
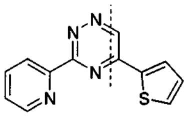
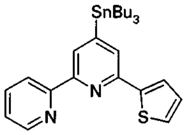
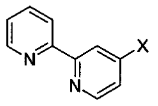
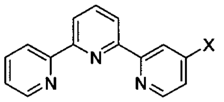
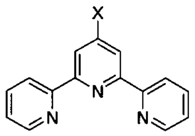
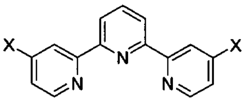
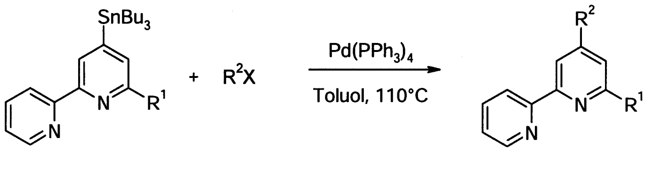
	Triazine	Yield [%]	Method		Product(s)	Yield [%]
5		89	$\xrightarrow[\Delta T,\ -\mathrm{N_2}]{+\ \equiv\!-\mathrm{SnBu_3}\ \ \mathbf{10}}$	**1a**	 **1b** 	86 (**1a**) 5 (**1b**)
6		54	“	**2**		54
7		67	“	**3**		47
8		51	“	**4**		73
9		87	“	**11**		95

Table 2. Yields of the halogenated pyridines **12−15**

Starting material	Pyridine		X	Yield [%]
1a	**12a** **12b**		–Br –I	57 68
2	**13a** **13b**		–Br –I	69 61
4	**14a** **14b**		–Br –I	54 48
3	**15a** **15b**		–Br –I	79 53

The synthesized pyridine−tin compounds also readily take part in the Stille cross-coupling reaction, with $Pd(PPh_3)_4$ as catalyst, to form aryl-substituted oligopyridine compounds. This was demonstrated for some examples as shown in Scheme 4 and Table 3.



1a, 4, 11 **16-18**

Scheme 4. Displacement of the stannyl group by aromatic substituents (Stille cross-coupling)

Table 3. Yields of the cross-coupling products **16−18**

Starting compound	R^1	R^2X	Product	Yield [%]
1a	H	5-bromopyrimidine	**16a**	72
1a	H	2-bromothiophene	**16b**	52
4	2-pyridyl	5-bromopyrimidine	**17a**	53
4	2-pyridyl	2-bromothiophene	**17b**	43
11	2-thienyl	2-bromothiophene	**18**	42

Conclusion

These cross-coupling reactions should be of great synthetic importance as they allow the direct introduction of an oligopyridine fragment to various substrates. In this context, we particularly consider a combination with fluorophores or other molecules with material properties.[17] The bi- or terpyridine unit serves as complexing molecular agent for many metal ions, and, on the basis of the complexed metal ion, changes the photophysical properties (e.g. absorbance and emission maxima) of the fluorophore. This should be an interesting application of the molecules now readily available by our new cycloaddition pathway, not forgetting that the halogenated pyridines should also be versatile starting compounds for similar purposes.

Experimental Section

General Remarks: IR: Beckmann Acculab 1. − NMR: Bruker AC250 (250 MHz for ^1H and 63 MHz for ^{13}C), $CDCl_3$ with TMS as an internal standard, δ values reported in ppm downfield from internal TMS (δ = 0.00). The degree of substitution of the C atoms was determined by the DEPT-135 method. − UV/Vis: Zeiss Specord M 500. − MS: ionizing voltage of 70 eV by electron impact with a Varian MAT311A instrument. − M.p.: Büchi melting point apparatus, uncorrected values. − Elemental analyses: Microanalytical Laboratory of the Chemical Institute of the University of Regensburg with Heraeus Mikro U/E and CHN-Rapid instruments. − Analytical TLC: Performed on precoated plastic sheets (POLYGRAM SIL G/UV254, Macherey-Nagel), visualized by UV light. Silica gel 60 (230−400 mesh, 0.040−0.063 mm, Merck) was used for flash column chromatography. Reactions were carried out under nitrogen, and solvents for reactions were dried according to standard procedures.[18] Pyridine-2-carbamidrazone,[19] 2,2′-bipyridyl-6-carbamidrazone,[20] pyridine-2,6-biscarbamidrazone[21] were prepared according to literature procedures from the corresponding nitriles. Monomeric glyoxal,[14] 2-thienylglyoxal[22] and tributyl(ethynyl)tin[23] were also prepared according to published procedures. 2-Bromothiophene and 5-bromopyrimidine are commercially available (Aldrich).

3-(2-Pyridyl)-1,2,4-triazine (5): Monomeric glyoxal (2.30 g, 39.7 mmol) was trapped at −78°C, dissolved in dry methanol (50 mL, at room temp.) and added to a stirred solution of 2-pyridylcarbamidrazone (4.86 g, 35.7 mmol) in dry methanol (150 mL) at room temp. The colour of the combined solutions changed slowly from colourless to bright yellow. After stirring at room temp. for 10 min, the reaction mixture was heated to reflux for further 3 h. After cooling to room temp., the solvent was removed in a rotary evaporator at reduced pressure. The orange-brown semisolid residue was dissolved in dichloromethane. A small amount of an unsoluble yellow precipitate was removed by filtration chromatography (approx. 2 × 2 cm, kieselgel 60, eluent: ethyl acetate). Evaporation of the solvent at reduced pressure gave crude yellow crystals (5.64 g, 99%, m.p. 77−79°C). Sublimation (70−75°C/0.05 Torr) yielded triazine **5** (5.07 g, 89%) as analytically pure, bright yellow crystals, m.p. 85−86°C. − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3010, (=C−H); 1585, 1535, 1520 (C=C); 1395, 1355, 1120, 1045, 980, 770, 740. − ^1H NMR (250 MHz, $CDCl_3$): δ = 7.51 (ddd, ^3J = 4.8 and 7.6 Hz, ^4J = 1.2 Hz, 1 H, 5-H), 7.95 (ddd, ^3J = 7.6 and 8.0 Hz, ^4J = 1.8 Hz, 1 H, 4-H), 8.70 (ddd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, ^5J = 0.95 Hz, 1 H, 3-H), 8.84 (d, ^3J = 2.4 Hz, 1 H, 5-H, triazine), 8.90 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.95 Hz, 1 H, 6-H), 9.30 (d, ^3J = 2.4 Hz, 1 H, 6-H, triazine). − UV/Vis (1,4-dioxane): λ_{max} (ε) = 238 nm (11370), 270 (8500), 396 (360). − $C_8H_6N_4$ (158.2): calcd. C 60.75, H 3.82, N 35.42; found C 60.53, H 3.96, N 35.50.

3-(2,2′-Bipyridin-6-yl)-1,2,4-triazine (6): Monomeric glyoxal (ca. 160 mg, 2.76 mmol) was trapped at −78°C, dissolved in dry methanol (5 mL, at room temp.) and immediately added to a stirred solution of 2,2′-bipyridyl-6-carbamidrazone (405 mg, 1.90 mmol) in dry methanol (25 mL) at room temp. The colourless mixture turned slowly yellow. After 5 min at room temp., the reaction mixture was heated to reflux for 3 h. After cooling to room temp., the solvent was removed in a rotary evaporator under reduced pressure. The orange residue was dissolved in a small amount of dichloromethane. Slow evaporation in a hood for about 14 h yielded crude orange crystals which were transferred to a sublimation apparatus. Sublimation (130°C/0.05 Torr) yielded triazine **2** as pale yellow crystals (239 mg, 54%), m.p. 160−162°C. − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} (=C−H); 1580, 1560, 1525 (C=C); 1430, 1390, 1265, 1080, 1045, 990, 835, 770, 740. − ^1H NMR (250 MHz, $CDCl_3$): δ = 7.36 (ddd, ^3J = 4.8 and 7.5 Hz, ^4J = 1.2 Hz, 1 H, 5′-H), 7.87 (ddd, ^3J = 7.5 and 8.0 Hz, ^4J = 1.8 Hz, 1 H, 4′-H), 8.07 (t, ^3J = 7.9 Hz, 1 H, 4-H), 8.61−8.73 (m, 4 H), 8.87 (d, ^3J = 2.4 Hz, 1 H, 5-H, triazine), 9.33 (d, ^3J = 2.4 Hz, 1 H, 6-H, triazine). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 121.81, 123.16, 124.05, 124.15, 137.00, 138.04, 148.56, 149.17 (2 C), 152.11, 155.68, 157.06, 163.82. − UV/Vis (1,4-dioxane): λ_{max} (ε) = 234 nm (24420), 277 (15550), 397 (335). − MS (70eV); *m/z* (%): 235 (30) [M^+], 207 (39) [$M^+ - N_2$], 181 (100) [$M^+ - N_2 - C_2H_2$], 155 (15), 128 (8), 103 (7), 78 (17), 51 (12). − $C_{13}H_9N_5$ (235.3): calcd. C 66.37, H 3.86, N 29.77; found C 66.23, H 4.02, N 30.01.

2,6-Bis(1,2,4-triazin-3-yl)pyridine (7): Monomeric glyoxal (350 mg, 12.0 mmol) was trapped at −78°C, dissolved in dry methanol (5 mL, at room temp.) and added rapidly to a stirred suspension of pyridine-2,6-biscarbamidrazone (580 mg, 3.00 mmol) in dry methanol (30 mL) at room temp. The colour of the stirred suspension turned yellow within 3 h at room temp. The reaction mixture was then heated to reflux for a further 2 h. The suspension was then allowed to reach room temp. The yellow precipitate was filtered off with suction and transferred to an extraction thimble. The crude, deep yellow product was purified by extraction with dichloromethane in a hot vapour extractor. Removal of the solvent yielded triazine **7** as a yellow powder (474 mg, 2.00 mmol, 67%). Sublimation (190°C/0.05 Torr) led to extensive losses by thermal decomposition; m.p. 252°C (dec., above 220°C shrinking and discolouration from yellow to brown). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3010 (=C−H); 1595, 1550, 1510 (C=C); 1370, 1325, 1250, 1035, 980, 820, 775. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 8.21 (t, *J* = 7.9 Hz, 1 H, 4-H), 8.87 (d, *J* = 7.9 Hz, 2 H, 3/5-H), 8.91 (d, *J* = 2.4 Hz, 2 H, 5′/5′′-H), 9.34 (d, *J* = 2.4 Hz, 2 H, 6′/6′′-H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 126.00 (2 C), 138.53, 148.77 (2 C), 149.53 (2 C), 153.44 (2 C), 163.42 (2 C). − UV/Vis (1,4-dioxane): λ_{max} (ε) = 229 nm (27810), 290 (sh, 9160), 393 (sh, 806). − MS (70eV); *m/z* (%): 237 (69) [M^+], 209 (53) [$M^+ - N_2$], 155 (81) [$M^+ - 2\ N_2 - C_2H_2$], 129 (100) [155 − C_2H_2, ≡ 2,6-dicyanopyridine], 103 (16), 76 (16), 77 (16), 50 (11). − $C_{11}H_7N_7$ (237.2): calcd. C 55.69, H 2.97, N 41.33; found C 55.24, H 3.54, N 40.98.

3,5-Bis(2-pyridyl)-1,2,4-triazine (8): 2-Pyridylcarbamidrazone (1.54 g, 11.3 mmol) was dissolved in ethanol (200 mL). The aqueous solution of 2-pyridylglyoxal (1.53 g, 11.3 mmol in approx. 50 mL of H_2O under the assumption of an 80% yield, as described in the original literature[14]) was added with magnetic stirring. A colourless precipitate formed (Na_2SO_4) immediately and the colour of the reaction mixture changed from colourless to yellow. The reaction mixture was stirred at ambient temperature for 6 h, then the precipitate filtered off and the yellow filtrate heated at 60°C for 2 h. Most of the solvent was removed in a rotary evaporator to furnish a brown solution (approx. 10−15 mL). Upon standing overnight, triazine **8** separated as yellow crystals, which were filtered off with suction and dried (1.35 g, 51%), m.p. 163−165°C. − IR (KBr): $\tilde{\nu}$ = 3070, 3040 (=C−H); 1575, 1560, 1525, 1500 (C=C); 1455, 1235, 1120, 1035, 980, 970, 745, 725 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 7.51 (ddd, ^3J = 4.8 and 7.6 Hz, ^4J = 1.2 Hz, 1 H, 5-H or 5′-H), 7.52 (ddd, ^3J = 4.8 and 7.6 Hz, ^4J = 1.2 Hz, 1 H, 5′-H or 5-H), 7.94 (ddd, ^3J = 7.6 and 7.9 Hz, ^4J = 1.8 Hz, 1 H, 4-H or 4′-H), 7.96 (ddd, ^3J = 7.6 and 7.9 Hz, ^4J = 1.8 Hz, 1 H, 4′-H or 4-H), 8.70 (ddd, ^3J = 7.9 Hz, ^4J = 1.2 Hz, ^4J = 1.0 Hz, 1 H, 3-H or 3′-H), 8.77 (ddd, ^3J = 7.9 Hz, ^4J = 1.2 Hz, ^4J = 1.0 Hz, 1 H, 3′-H or 3-H), 8.81 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 1.0 Hz, 1 H, 6-H or 6′-H), 8.94 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 1.0 Hz, 1 H, 6′-H or 6-H, all pyridine protons), 10.31 (s, 1 H, 6-H, triazine). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 123.37, 124.25, 125.58, 126.55, 137.14, 137.32, 145.93, 150.01, 150.49, 151.99, 153.11, 154.4, 162.72. − UV/Vis (1,4-dioxane): λ_{max} (ε) = 237 nm (14230), 277 (16470), 382 (sh, 870). − MS (70eV); *m/z* (%): 235 (17) [M^+], 207 (42) [$M^+ - N_2$], 103 (100) [207 − C_5H_4NCN], 76 (49) [103 − HCN], 50 (18). − $C_{13}H_9N_5$ (235.3): calcd. C 66.37, H 3.86, N 29.77; found C 66.35, H 4.26, N 29.73.

3-(2-Pyridyl)-5-(2-thienyl)-1,2,4-triazine (9): 2-Thienylglyoxal (3.65 g, 26.0 mmol) was dissolved in ethanol (25 mL). 2-Pyridylcarbamidrazone (3.54 g, 26.0 mmol) in ethanol (25 mL) was added to the stirred yellow solution of the glyoxal. The dark yellow reaction mixture was heated to reflux for 2 h. Yellow crystals separated upon cooling from the clear orange reaction mixture, which were collected on a Büchner funnel and washed with cold ethanol to give triazine **9** (5.43 g, 87%), m.p. 175°C. − IR (KBr): $\tilde{\nu}$ = 3120 cm^{-1}, 3100, 3060, 3020 (=C−H); 1585, 1550 (C=C); 1495, 1430, 1350, 1250, 1140, 1060,1020, 975, 865, 825, 775, 730, 670. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.27 (dd, ^3J = 3.8 and 5.0 Hz, 1 H, 4′′-H), 7.50 (ddd, ^3J = 4.8 and 7.6 Hz, ^4J = 1.2 Hz, 1 H, 5′-H), 7.73 (dd, ^3J = 5.0 Hz, ^4J = 1.1 Hz, 1 H, 5′′-H), 7.94 (ddd, ^3J = 7.6 und 7.9 Hz, ^4J = 1.8 Hz, 1 H, 4′-H), 8.05 (dd, ^3J = 3.8 Hz, ^4J = 1.1 Hz, 1 H, 3′′-H), 8.60 (ddd, ^3J = 7.9 Hz, ^4J = 1.2 Hz, ^5J = 0.9 Hz, 1 H, 3′-H), 8.94 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.9 Hz, 1 H, 6′-H), 9.54 (s, 1 H, 6-H). − UV/Vis (1,4-dioxane): λ_{max} (ε) = 237 nm (16270), 271 (15800), 327 (18920), 391 (542). − MS (70eV); *m/z* (%): 240 (54) [M^+], 212 (3) [$M^+ - N_2$], 108 (100) [$C_4H_3S-C\equiv C-H$], 104 (1) [C_5H_4N-CN]. − $C_{12}H_8N_4S$ (240.3): calcd. C 59.99, H 3.36, N 23.32; found C 59.98, H 3.42, N 23.34.

3- and 4-Tributylstannyl-2,2′-bipyridine: 3-(2-Pyridyl)-1,2,4-triazine (**5**, 2.00 g, 12.64 mmol), dissolved in dry 1,2-dichlorobenzene (15 mL), and tributyl(ethynyl)tin (5.30 mL, 18.33 mmol) were heated under dry nitrogen to light reflux (180°C) for 16 h. After cooling to room temp., the solvent was removed under reduced pressure (0.1 Torr). The resulting yellow-brownish oil was purified by FCC [kieselgel 60, 95 g, petroleum ether (40/60)/ethyl acetate 97:3 → 90:10, after elution of the first isomer].

3-Tributylstannyl-2,2′-bipyridine (1b, First Fraction): Obtained as colourless liquid (328 mg, 5%). − IR (film): $\tilde{\nu}$ = 3050 cm^{-1} (=C−H); 2980, 2940, 2890, 2870 (−C−H); 1595, 1580, 1550 (C=C); 1470, 1405, 1110, 1050, 795, 760. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.81 (t, *J* = 7.2 Hz, 9 H, $-CH_3$), 0.95−1.02 (m, 6 H, $-CH_2-$), 1.21−1.33 (m, 6 H, $-CH_2-$), 1.36−1.49 (m, 6 H, $-CH_2-$), 7.26 (dd, ^3J = 4.7 and 7.4 Hz, 1 H, 5-H, Sn satellites), 7.29 (ddd, ^3J = 4.8 and 7.5 Hz, ^4J = 1.2 Hz, 1 H, 5′-H), 7.82 (ddd, ^3J = 7.5 and 8.0 Hz, ^4J = 1.8 Hz, 1 H, 4′-H), 8.02 (dd, ^3J = 7.4 Hz, ^4J = 1.9 Hz, 1 H, 4-H, Sn satellites), 8.50−8.57 (m, 2 H, 6′-H/3′-H), 8.62 (dd, ^3J = 4.7 Hz, ^4J = 1.9 Hz, 1 H, 6-H, Sn satellites). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 12.77 (3 C), 13.61 (3 C), 27.44 (3 C), 29.22 (3 C), 121.36, 123.39, 123.43, 136.54, 137.18, 145.80, 146.76, 148.56, 157.01, 159.18. − $C_{22}H_{34}N_2Sn$ (445.2): calcd. C 59.35, H 7.70, N 6.29; found C 59.74, H 8.03, N 6.26.

4-Tributylstannyl-2,2′-bipyridine (1a, Second Fraction): Obtained after removal of the eluent as colourless liquid (4.83 g, 86%). − IR (film): $\tilde{\nu}$ = 3060 cm^{-1}, 3040 (=C−H); 2970, 2940, 2890, 2870 (−C−H); 1575, 1560, 1530 (C=C); 1460, 1375, 1095, 800, 750. −

^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.89 (t, J = 7.2 Hz, 9 H, $-$CH$_3$), 1.10−1.20 (m, 6 H, $-$CH$_2-$), 1.25−1.43 (m, 6 H, $-$CH$_2-$), 1.50−1.75 (m, 6 H, $-$CH$_2-$), 7.30 (ddd, ^3J = 4.8 and 7.5 Hz, ^4J = 1.2 Hz, 1 H, 5′-H), 7.40 (dd, ^3J = 4.5 Hz, ^4J = 1.0 Hz, 1 H, 5-H, Sn-satellites), 7.81 (ddd, ^3J = 7.5 and 7.9 Hz, ^4J = 1.8 Hz, 1 H, 4′-H), 8.37 (ddd, ^3J = 7.9 Hz, ^4J = ^5J ≈ 1.0 Hz, 1 H, 3′-H), 8.47 (dd, ^4J = ^5J ≈ 1.0 Hz, 1 H, 3-H, Sn satellites), 8.56 (dd, ^3J = 4.5 Hz, ^4J = 1.0 Hz, 1 H, 6-H, Sn satellites), 8.70 (ddd, ^3J = 4.7 Hz, ^4J = 1.8 Hz, ^5J = 1.0 Hz, 1 H, 6′-H). − ^{13}C NMR (CDCl$_3$, 63 MHz): δ = 9.71 (3 C), 13.57 (3 C), 27.26 (3 C), 29.00 (3 C), 121.30, 123.32, 129.00, 131.93, 136.72, 147.56, 149.13, 154.12, 154.29, 156.94. − MS (70eV); *m/z* (%): 446 (1) [M$^+$], 389 (62) [M$^+$ − C$_4$H$_9$], 333 (24) [389 − C$_4$H$_9$+H], 157 (100) [bpy + H$^+$]. − C$_{22}$H$_{34}$N$_2$Sn (445.2): calcd. C 59.35, H 7.70, N 6.29; found C 59.40, H 7.54, N 6.28.

4-Tributylstannyl-2,2′,6′,2′′-terpyridine (2): 3-(2,2′-Bipyridin-6-yl)-1,2,4-triazine (**6**, 201 mg, 0.85 mmol) and tributyl(ethynyl)tin (450 μL, 1.56 mmol) were heated in dry 1,2-dichlorobenzene (2 mL) under an inert atmosphere for 16 h at 180°C. The clear yellow-brownish reaction mixture was concentrated under reduced pressure and purified by FCC [kieselgel 60, 15 g, petroleum ether (40/60)/ethyl acetate, 90:10] to yield pyridine **2** (280 mg, 63%) as a colourless liquid. − IR (film): ṽ = 3050 cm^{-1}, 3020 (=C−H); 2950, 2920, 2860, 2840 (−C−H); 1575, 1555, 1520 (C=C); 1445, 1420, 1365, 815, 775. − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.92 (t, J = 7.2 Hz, 9 H, $-$CH$_3$), 1.15−1.21 (m, 6 H, $-$CH$_2-$), 1.32−1.46 (m, 6 H, $-$CH$_2-$), 1.56−1.69 (m, 6 H, $-$CH$_2-$), 7.32 (ddd, ^3J = 4.8 and 7.5 Hz , ^4J = 1.2 Hz, 1 H), 7.42 (dd, J = 0.9 and 4.6 Hz, 1 H), 7.84 (ddd, ^3J ≈ ^3J ≈ 7.6 Hz, ^4J = 1.8 Hz, 1 H), 7.95 (t, J = 7.8 Hz, 1 H), 8.44 (dd, ^3J = 7.8 Hz, ^4J = 1.0 Hz, 1 H), 8.46 (dd, ^3J = 7.8 Hz, ^4J = 1.0 Hz, 1 H), 8.58−8.64 (m, 2 H), 8.70 (ddd, ^3J = 4.8 Hz, ^4J = 1.7 Hz, ^5J = 1.0 Hz, 1 H), 8.74−8.75 (m, 1 H). − ^{13}C NMR (CDCl$_3$, 63 MHz): δ = 9.79 (3 C), 13.61 (3 C), 27.33 (3 C), 29.07 (3 C), 120.70, 120.99, 121.20, 123.62, 129.15, 131.99, 136.67, 137.78, 147.59, 149.13, 153.88, 154.29, 155.28, 156.03, 156.46. − MS (70eV); *m/z* (%): 466 (85) [M$^+$ − C$_4$H$_9$], 410 (22) [466 − C$_4$H$_8$], 352 (28) [M$^+$ − 3 C$_4$H$_9$], 234 (100) [M$^+$ − SnBu$_3$ + 4 H], 205 (14), 176 (11) [SnBu$^+$ − H], 155 (9). − C$_{27}$H$_{37}$N$_3$Sn (522.3): calcd. C 62.09, H 7.14, N 8.05; found C 61.79, H 7.29, N 8.27.

4,4′′-Bis(tributylstannyl)-2,2′,6′,2′′-terpyridine (3): 2,6-Bis(1,2,4-triazin-3-yl)pyridine (**7**, 142 mg, 0.52 mmol) was suspended in dry 1,2-dichlorobenzene (2 mL). Tributyl(ethynyl)tin (723 μL, 2.50 mmol) was added under an inert atmosphere and the reaction mixture was heated to 180°C for 18 h. The triazine dissolved within 3 h, the colour of the reaction mixture changed from yellow to dark brown during this period. After removal of the solvent under reduced pressure the resulting black oil was subjected to FCC [kieselgel 60, 30 g, petroleum ether (40/60)/EtOAc, 95:5] to yield terpyridine **3** (199 mg, 47%) as pale yellow oil. − IR (film): ṽ = 3070 cm^{-1}, 3050 (=C−H); 2970, 2920, 2880, 2860 (−C−H); 1580, 1565, 1530 (C=C); 1460, 1375, 820. − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.89 (t, J = 7.2 Hz, 18 H, $-$CH$_3$), 1.06−1.23 (m, 12 H, $-$CH$_2-$), 1.26−1.43 (m, 12 H, $-$CH$_2-$), 1.50−1.67 (m, 12 H, $-$CH$_2-$), 7.43 (dd, ^3J = 4.6 Hz, ^4J = 1.0 Hz, 2 H, 5/5′′-H, Sn satellites), 7.94 (t, J = 7.8 Hz, 1 H, 4′-H), 8.43 (d, J = 7.8 Hz, 2 H, 3′/5′-H), 8.60 (dd, ^3J = 4.6 Hz, ^4J = 1.0 Hz, 2 H, 6/6′′-H), 8.66 (dd, ^4J = ^5J ≈ 1.0 Hz, 2 H, 3/3′′-H, Sn satellites). − ^{13}C NMR (CDCl$_3$, 63 MHz): δ = 9.74 (6 C), 13.63 (6 C), 27.27 (6 C), 29.04 (6 C), 121.17 (2 C), 128.88 (2 C), 131.89 (2 C), 137.62, 147.52 (2 C), 153.83 (2 C), 154.51 (2 C), 156.16 (2 C). − MS (70eV); *m/z* (%): 813 (1) [M$^+$], 755 (100) [M$^+$ − C$_4$H$_9$], 699 (42) [M$^+$ − 2 C$_4$H$_9$], 642 (87) [M$^+$ − 3 C$_4$H$_9$], 586 (44) [M$^+$ − 4 C$_4$H$_9$], 528 (29) [M$^+$ − 5 C$_4$H$_9$], 471 (15) [M$^+$ − 6 C$_4$H$_9$], 466 (28), 352 (35), 234 (18) [M$^+$ − 2 SnBu$_3$ + 4 H], 57 (19) [C$_4$H$_9$$^+$], 41 (37), 39 (16). − C$_{39}H_{63}N_3Sn_2$ (811.3): calcd. C 57.74, H 7.83, N 5.18; found C 58.05, H 7.74, N 5.29.

4′-Tributylstannyl-2,2′,6′,2′′-terpyridine (4): 3,5-Bis(2-pyridyl)-1,2,4-triazine (**8**, 243 mg, 1.03 mmol) was dissolved in dry 1,2-dichlorobenzene (2 mL), tributyl(ethynyl)tin (580 μL, 2.00 mmol) was added and the reaction mixture was heated to reflux (180°C) for 15 h under nitrogen. The orange-brown reaction mixture was concentrated under reduced pressure and purified by FCC [kieselgel 60, 15 g, petroleum ether (40/60)/ethyl acetate, 90:10] to furnish terpyridine **4** (348 mg, 73%) as a pale yellow liquid. − IR (film): ṽ = 3070 cm^{-1}, 3030 (=C−H); 2975, 2950, 2890, 2875 (−C−H); 1580, 1570, 1560, 1535 (C=C); 1470, 1380, 790, 740. − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.90 (t, J = 7.2 Hz, 9 H, $-$CH$_3$), 1.10−1.25 (m, 6 H, $-$CH$_2-$), 1.29−1.43 (m, 6 H, $-$CH$_2-$), 1.53−1.70 (m, 6 H, $-$CH$_2-$), 7.31 (ddd, ^3J = 4.8 and 7.5 Hz, ^4J = 1.2 Hz, 2 H, 5/5′′-H), 7.84 (ddd, ^3J = 7.5 and 8.0 Hz , ^4J = 1.8 Hz, 2 H, 4/4′′-H), 8.56 (s, $J_{\mathrm{Sn-H}}$ = 38.0 Hz, 2 H, 3′/5′-H, Sn satellites), 8.61 (ddd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, ^5J = 0.9 Hz, 2 H, 3/3′′-H), 8.72 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.9 Hz, 2 H, 6/6′′-H). − ^{13}C NMR (CDCl$_3$, 63 MHz): δ = 9.80 (3 C), 13.60 (3 C), 27.29 (3 C), 29.06 (3 C), 121.37 (2 C), 123.37 (2 C), 128.97 (2 C), 136.67 (2 C), 149.10 (2 C), 153.31 (2 C), 155.20 (1 C), 157.03 (2 C). − MS (70eV); *m/z* (%): 523 (1) [M$^+$], 466 (91) [M$^+$ − C$_4$H$_9$], 410 (22) [M$^+$ − 2 C$_4$H$_9$ + H], 352 (28) [M$^+$ − 3 C$_4$H$_9$], 234 (100) [M$^+$ − SnBu$_3$ + 4 H]. − C$_{27}$H$_{37}$N$_3$Sn (522.3): calcd. C 62.09, H 7.14, N 8.05; found C 61.87, H 7.30, N 8.00.

6-(2-Thienyl)-4-tributylstannyl-2,2′-bipyridine (11): 3-(2-Pyridyl)-5-(2-thienyl)-1,2,4-triazine (**9**, 200 mg, 0.85 mmol) and tributyl(ethynyl)tin (370 μL, 1.28 mmol) were heated in dry 1,2-dichlorobenzene (2 mL) for 15 h at 180°C under an inert atmosphere. The solvent was removed under reduced pressure, precipitated unreacted starting material was removed by filtration with suction. The filtered triazine (34 mg, 0.14 mmol, 3%) was washed with petroleum ether 40/60 (5 × 2 mL). The filtrate and the washings were combined and concentrated. The resulting orange oil was purified by FCC [kieselgel 60, 30 g, petroleum ether (40/60)/ethyl acetate, 95:5] to give bipyridine **11** (2.18 g, 95%) as a pale yellow liquid. A small amount (^{1}H NMR: < 5%) of 6-(2-thienyl)-3-tributylstannyl-2,2′-bipyridine could not be separated from the major isomer by means of chromatographic techniques. − IR (film): ṽ = 3060 cm^{-1} (=C−H); 2950, 2920, 2870, 2850 (−C−H); 1580, 1570, 1550, 1520 (C=C); 1460, 1425, 1370, 1235, 1115, 1000, 860, 850, 785, 690. − ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.90 (t, J = 7.2 Hz, 9 H, $-$CH$_3$), 1.11−1.21 (m, 6 H, $-$CH$_2-$), 1.25−1.43 (m, 6 H, $-$CH$_2-$), 1.47−1.66 (m, 6 H, $-$CH$_2-$), 7.13 (dd, ^3J = 3.7 and 5.1 Hz, 1 H, 4-H, thienyl), 7.28 (ddd, ^3J = 4.8 and 7.4 Hz, ^4J = 1.2 Hz, 1 H, 5′-H), 7.40 (dd, ^3J = 5.1 Hz, ^4J = 1.1 Hz, 1 H, 5-H, thienyl), 7.65 (dd, ^3J = 3.7 Hz, ^4J = 1.1 Hz, 1 H, 3-H, thienyl), 7.76 (d, ^4J = 0.6 Hz, 1 H, 5-H, Sn satellites), 7.82 (ddd, ^3J = 7.4 and 8.0 Hz, ^4J = 1.8 Hz, 1 H, 4′-H), 8.39 (d, ^4J = 0.6 Hz, 3-H, 1 H, Sn satellites), 8.58 (ddd, ^3J = 8.0 Hz, ^4J = ^5J ≈ 1.1 Hz, 3′-H, 1 H), 8.69 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 1.1 Hz, 1 H, 6′-H). − ^{13}C NMR (CDCl$_3$, 63 MHz): δ = 9.81 (3 C), 13.62 (3 C), 27.29 (3 C), 29.05 (3 C), 121.56, 123.46, 124.21, 126.62, 126.99, 127.26, 127.91, 136.74, 145.92, 148.98, 150.14, 153.58, 154.79, 156.65. − MS (70eV); *m/z* (%): 528 (4) [M$^+$], 471 (71) [M$^+$ − C$_4$H$_9$], 415 (20), [471 − C$_4$H$_8$], 357 (24) [M$^+$ − 3 × C$_4$H$_9$], 259 (19), 239 (100) [M$^+$ − SnBu$_3$ + 2 H], 203 (8), 179 (6), 145 (7), 57 (6), 41 (9). − C$_{26}$H$_{36}$N$_2$SSn (527.3): calcd. C 59.22, H 6.88, N 5.31; found C 59.19, H 7.05, N 5.16.

General Procedure for the Bromination: The organotin compound was dissolved in dry chloroform and cooled to −60°C. A solution of bromine in dry chloroform was added dropwise. The brown colour of the bromine disappeared immediately at the beginning of the addition. After completion of the addition, a clear bright yellow solution was obtained. The cooling bath was removed and the reaction mixture allowed to reach room temp. The solvent was removed under reduced pressure and the residue purified and separated by FCC.

4-Bromo-2,2′-bipyridine (12a): Pyridine **1a** (1.21 g, 2.72 mmol) and bromine (145 μL, 2.80 mmol) in chloroform (15 mL each) yielded, after FCC [kieselgel 60, 30 g, petroleum ether (40/60)/ethyl acetate, 98:2], **12a** (670 mg), which still contained a small amount of tributyltin bromide (5%). Due to the good solubility of **12a**, recrystallization from petroleum ether is tedious but unavoidable to remove the tributyltin bromide. Yield 363 mg (57%), m.p. 52°C. − IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (=C−H); 1560, 1540 (C=C), 1440, 1450, 1380, 1280, 1065, 995, 830, 785, 740, 685. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.34 (ddd, ^3J = 4.8 and 7.5 Hz, ^4J = 1.2 Hz, 1 H, 5′-H), 7.48 (dd, ^3J = 5.2 Hz, ^4J = 1.9 Hz, 1 H, 5-H), 7.83 (ddd, ^3J = 7.5 and 8.0 Hz, ^4J = 1.8 Hz, 1 H, 4′-H), 8.39 (ddd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, ^5J = 0.9 Hz, 1 H, 3′-H), 8.49 (dd, ^3J = 5.2 Hz, ^5J = 0.6 Hz, 1 H, 6-H), 8.63 (dd, ^4J = 1.9 Hz, ^5J = 0.6 Hz, 1 H, 3-H), 8.69 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.9 Hz, 1 H, 6′-H).

4-Bromo-2,2′,6′,2′′-terpyridine (13a): Pyridine **2** (122 mg, 0.23 mmol) and bromine (12 μL, 0.23 mmol) in chloroform (3 mL each) yielded, after FCC [kieselgel 60, 15 g, petroleum ether (40/60)/ethyl acetate, 97:3 → 90:10] and recrystallization from petroleum ether (40/60)/ethyl acetate (25:1), terpyridine **13a** (50 mg, 69%) as colourless needles, m.p. 105−106°C. − IR (KBr): $\tilde{\nu}$ = 3090 cm^{-1}, 3060, 3020 (=C−H); 1565, 1550 (C=C); 1455, 1430, 1385, 1080, 995, 900, 830, 820, 790, 750, 685. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.34 (ddd, ^3J = 4.8 and 7.5 Hz , ^4J = 1.2 Hz, 1 H), 7.49 (dd, J = 0.9 and 4.6 Hz, 1 H), 7.88 (ddd, $^3J \approx {}^3J \approx$ 7.5 Hz, ^4J = 1.7 Hz, 1 H), 7.95 (t, J = 7.8 Hz, 1 H), 8.41−8.52 (m, 3 H), 8.58−8.62 (m, 1 H), 8.70 (ddd, ^3J = 4.8 Hz, ^4J = 1.7 Hz, ^5J = 1.0 Hz, 1 H), 8.78−8.79 (m, 1 H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 121.22, 121.34, 121.63, 123.86, 124.52, 126.85, 133.83, 136.88, 137.96, 149.20, 149.86, 154.06, 155.63, 156.03, 157.65. − MS (70eV); *m/z* (%): 311 (78) [M^+], 232 (100) [M^+ − Br], 205 (19), 155 (13), 78 (16). − $C_{15}H_{10}BrN_3$ (312.2): calcd. C 57.71, H 3.23, N 13.46; found C 57.62, H 3.22, N 13.33.

4′-Bromo-2,2′,6′,2′′-terpyridine (14a): Pyridine **4** (229 mg, 0.44 mmol) and bromine (23 μL, 0.45 mmol) in chloroform (5 mL each) yielded, after FCC [kieselgel 60, 10 g, petroleum ether (40/60)/ethyl acetate, 90:10] and recrystallization from petroleum ether (40/60), terpyridine **14a** (74 mg, 54%) as colourless needles, m.p. 135°C. − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3050 (=C−H); 1580, 1545 (C=C); 1460, 1390, 1320, 1260, 1165, 990, 880, 885, 740, 730, 670. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.36 (ddd, ^3J = 4.8 and 7.5 Hz, ^4J = 1.2 Hz, 2 H, 5-H, 5′′-H), 7.87 (dd, $^3J \approx$ 7.5 and 7.5 Hz, ^4J = 1.8 Hz, 2 H, 4-H, 4′′-H), 8.59 (ddd, $^4J \approx$ 1.0 and 1.0 Hz, ^3J = 8.0 Hz, 2 H, 3-H, 3′′-H), 8.65 (s, 2 H, 3′-H, 5′-H), 8.70 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.9 Hz, 2 H, 6-H, 6′′-H). − $C_{15}H_{10}BrN_3$ (312.2): calcd. C 57.71, H 3.23, N 13.46; C 57.71, H 3.45, N 13.29.

4,4′′-Dibromo-2,2′,6′,2′′-terpyridine (15a): Pyridine **3** (81 mg, 0.10 mmol) and bromine (10 μL, 0.20 mmol) in chloroform (2 mL each) yielded, after FCC [kieselgel 60, 15 g, petroleum ether (40/60)/ethyl acetate, 95:5 → 90:10] and recrystallization from petroleum ether (40/60)/ethyl acetate (10:1), terpyridine **15a** (31 mg, 79%) as colourless needles, m.p. 203°C. − IR (KBr): $\tilde{\nu}$ = 3090 cm^{-1}, 3060 (=C−H); 1565, 1550 (C=C); 1450, 1375, 1270, 1075, 995, 885, 815, 760, 740, 680, 660. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.51 (dd, ^3J = 5.1 Hz, ^4J = 2.0 Hz, 2 H, 5/5′′′-H), 7.96 (t, J = 7.9 Hz, 1 H, 4′-H), 8.45 (d, J = 7.9 Hz, 2 H, 3′/5′-H), 8.50 (d, ^3J = 5.1 Hz, 2 H, 6/6′′-H), 8.74 (d, ^4J = 2.0 Hz, 2 H, 3/3′′-H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 121.99 (2 C), 124.52 (2 C), 127.02 (2 C), 133.91 (2 C), 138.06, 149.87 (2 C), 154.31 (2 C), 157.32 (2 C). − MS (70eV); *m/z* (%): 391 (100) [M^+], 310 (80) [M^+ − Br], 283 (10) [310 − HCN], 231 (23) [310 − Br], 230 (21) [310 − HBr], 203 (13), 154 (15). − $C_{15}H_9Br_2N_3$ (391.1): calcd. C 46.07, H 2.32, N 10.75; found C 45.82, H 2.55, N 10.63.

General Procedure for the Iodination: A solution of iodine (in dry chloroform or dry THF) was added dropwise to the stirred solution of the organotin compound in the same solvent at room temp. After stirring at room temp. for some hours, a yellow solution was obtained, and the workup was carried out as described above for the bromination.

4-Iodo-2,2′-bipyridine (12b): Pyridine **1a** (196 mg, 0.44 mmol) and iodine (112 mg, 0.44 mmol) in chloroform (3 resp. 8 mL) yielded, after FCC [kieselgel 60, 30 g, petroleum ether (40/60)/ethyl acetate, 95:5] and recrystallization, bipyridine **12b** (84 mg, 68%), m.p. 88.5−89.5°C. − IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1}, 3060 (=C−H); 1590, 1560, 1540 (C=C); 1455, 1380, 1280, 1070, 1000, 830, 790, 750, 675. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.33 (ddd, ^3J = 4.8 and 7.5 Hz, ^4J = 1.2 Hz, 1 H, 5′-H), 7.69 (dd, ^3J = 5.1 Hz, ^4J = 1.7 Hz, 1 H, 5-H), 7.82 (ddd, ^3J = 7.5 and 8.0 Hz, ^4J = 1.8 Hz, 1 H, 4′-H), 8.32 (dd, ^3J = 5.1 Hz, ^5J = 0.6 Hz, 1 H, 6-H), 8.38 (ddd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, ^5J = 0.9 Hz, 1 H, 3′-H), 8.68 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.9 Hz, 1 H, 6′-H), 8.83 (dd, ^4J = 1.7 Hz, ^5J = 0.6 Hz, 1 H, 3-H). − $C_{10}H_7IN_2$ (282.1): calcd. C 42.58, H 2.50, N 9.93; found C 42.64, H 2.76, N 9.78.

4-Iodo-2,2′,6′,2′′-terpyridine (13b): Pyridine **2** (100 mg, 0.19 mmol) and iodine (48 mg, 0.19 mmol) in THF (3 mL each) yielded, after FCC [kieselgel 60, 15 g, petroleum ether (40/60)/ethyl acetate, 95:5 → 90:10] and recrystallization from petroleum ether (40/60)/ethyl acetate (20:1), terpyridine **13b** (42 mg, 61%) as colourless needles, m.p. 128.5°C. − IR (KBr): $\tilde{\nu}$ = 3090 cm^{-1}, 3060, 3020 (=C−H); 1565, 1550 (C=C); 1455, 1430, 1385, 1080, 995, 900, 830, 820, 790, 750, 685. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.34 (ddd, ^3J = 4.8 and 7.5 Hz , ^4J = 1.2 Hz, 1 H, 5′′-H), 7.70 (dd, ^4J = 1.7 Hz, ^3J = 5.0 Hz, 1 H, 5-H), 7.88 (ddd, ^3J = 7.5 and 8.0 Hz, ^4J = 1.8 Hz, 1 H, 4′′-H), 7.95 (t, ^3J = 7.8 Hz, 1 H, 4′-H), 8.33 (d, ^3J = 5.0 Hz, 1 H, 6-H), 8.41 (dd, ^4J = 1.0 Hz, ^3J = 7.8 Hz, 1 H, 5′-H), 8.47 (dd, ^4J = 1.0 Hz, ^3J = 7.8 Hz, 1 H, 3′-H), 8.59 (ddd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, ^5J = 0.9 Hz, 1 H, 3′′-H), 8.70 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.9 Hz, 1 H, 6′′-H), 8.98 (d, ^4J = 1.7 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 106.37, 121.22, 121.31, 121.56, 123.83, 130.53, 132.77, 136.88, 137.93, 149.20, 149.39, 153.98, 155.61, 156.03, 156.93. − MS (70eV); *m/z* (%): 359 (69) [M^+], 232 (100) [M^+], 205 (13) [232 − HCN], 155 (9) [M^+ − C_5H_3NI], 78 (9) [C_5H_4N]. − $C_{15}H_{10}IN_3$ (359.2): calcd. 50.16, H 2.81, N 11.70; found C 49.74, H 2.92, N 11.56.

4′-Iodo-2,2′,6′,2′′-terpyridine (14b): Pyridine **4** (295 mg, 0.57 mmol) and iodine (143 mg, 0.56 mmol) in chloroform (3 resp. 5 mL) yielded, after FCC [kieselgel 60, 10 g, petroleum ether (40/60)/ethyl acetate, 90:10] and recrystallization from petroleum ether (40/60)/ethyl acetate (10:1), the terpyridine **14b** (97 mg, 48%) as colourless needles, m.p. 147°C. − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3020 (=C−H); 1585, 1570, 1545 (C=C); 1465, 1385, 1260, 1070, 995, 890, 790, 760, 730, 665. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.33 (ddd, ^3J = 4.8 and 7.5 Hz, ^4J = 1.2 Hz, 2 H, 5/5′′-H), 7.84 (ddd, ^3J = 7.5 and 8.0 Hz, ^4J = 1.8 Hz, 2 H, 4/4′′-H), 8.55 (ddd, ^4J = 1.2 and 0.9 Hz, ^3J = 8.0 Hz, 2 H, 3/3′′-H), 8.68 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.9 Hz, 2 H, 6/6′′-H), 8.84 (s, 2 H, 3′-H, 5′-H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 107.58, 121.35 (2 C), 124.14

(2 C), 130.16 (2 C), 136.87 (2 C), 149.20 (2 C), 154.91 (2 C), 155.79 (2 C). − MS (70eV); *m/z* (%): 359 (85) [M$^+$], 232 (100) [M$^+$ − I], 128 (57) [HI$^+$], 78 (49) [$C_5H_5N^+$]. − $C_{15}H_{10}IN_3$ (359.2): calcd. C 50.16, H 2.81, N 11.70; found C 50.05, H 2.79, N 11.48.

4,4′′-Diiodo-2,2′,6′,2′′-terpyridine (15b): Pyridine **3** (90 mg, 0.11 mmol) and iodine (57 mg, 0.22 mmol) in dry THF (1.5 mL each) yielded, after FCC [kieselgel 60, 15 g, petroleum ether (40/60)/ethyl acetate, 95:5 → 85:15] and recrystallization from petroleum ether (40/60)/ethyl acetate (3:1), the terpyridine **15b** (28 mg, 0.06 mmol, 53%) as colourless needles, m.p. 204−205°C. − IR (KBr): ṽ = 3080 cm^{-1}, 3040 (=C−H); 1550, 1535 (C=C); 1440, 1370, 1110, 1075, 1060, 995, 900, 815, 750, 670. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.73 (dd, ^3J = 5.1 Hz, ^4J = 1.7 Hz, 2 H, 5/5′′-H), 7.95 (t, ^3J = 7.8 Hz, 1 H, 4′-H), 8.34 (d, ^3J = 5.1 Hz, 2 H, 6/6′′-H), 8.43 (d, ^3J = 7.8 Hz, 2 H, 3′/5′-H), 8.93 (d, ^4J = 1.7 Hz, 2 H, 3/3′′-H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 106.42 (2 C), 121.92 (2 C), 130.56 (2 C), 132.97 (2 C), 138.02, 149.42 (2 C), 154.27 (2 C), 156.65 (2 C). − MS (70 eV); *m/z* (%): 485 (85) [M$^+$], 358 (100) [M$^+$ − I], 231 (53) [358 − I], 204 (21) [231 − HCN], 154 (14), 128 (14) [HI$^+$], 127 (14) [I$^+$], 102 (11), 77 (10), 51 (13). − $C_{15}H_9I_2N_3$ (485.1): calcd. C 37.14, H 1.87, N 8.66; found C 37.03, H 1.85, N 8.51.

General Procedure for the Cross-Coupling Reactions: $Pd(PPh_3)_4$ was dissolved in toluene. The aryl halide (solid: dissolved in toluene, liquid: neat) was added and the reaction mixture stirred for 5 min at room temp. After this period, the solution of the organotin compound in toluene was added and the mixture heated to reflux for the indicated time. After cooling, the reaction mixture was worked up by FCC (except for **16a** and **17a**) and recrystallization.

4-(5-Pyrimidinyl)-2,2′-bipyridine (16a): Reaction mixture: $Pd(PPh_3)_4$ (15 mg, 0.014 mmol, 3 mol-%) in toluene (3 mL), 5-bromopyridine (105 mg, 0.66 mmol) in toluene (1 mL), pyridine **1a** (195 mg, 0.44 mmol) in toluene (2 mL). Reaction time: 24 h. The product separated from the reaction mixture as colourless crystals upon cooling. After storage at +4°C (1 h) and −20°C (1 h), **16a** was filtered off with suction. Recrystallization from toluene gave colourless needles (74 mg, 72%), m.p. 171−172°C. − IR (KBr): ṽ = 3040 cm^{-1}, 3020 (=C−H); 1590, 1570, 1545 (C=C); 1450, 1395, 1370, 1340, 1170, 975, 875, 825, 780, 735, 700, 620, 610. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.37 (ddd, ^3J = 4.8 and 7.5 Hz, ^4J = 1.2 Hz, 1 H, 5′-H), 7.54 (dd, ^3J = 5.0 Hz, ^4J = 1.8 Hz, 1 H, 5-H), 7.87 (ddd, ^3J = 7.5 and 7.8 Hz, ^4J = 1.8 Hz, 1 H, 4′-H), 8.49 (ddd, ^3J = 7.8 Hz, ^4J = ^5J ≈ 1.0 Hz, 1 H, 3′-H), 8.71−8.74 (m, 2 H, 6′-H, 3-H), 8.83 (dd, ^3J = 5.0 Hz, ^4J = 0.7 Hz, 1 H, 6-H), 9.13 (s, 2 H, 4-H, 6-H, pyrimidyl), 9.32 (s, 1 H, 2-H, pyrimidyl). − MS (70eV); *m/z* (%): 234 (100) [M$^+$], 233 (47) [M$^+$ − H], 207 (39), 206 (41), 156 (39) [M$^+$ − C_5H_4N], 78 (9) [$C_5H_4N^+$]. − $C_{14}H_{10}N_4$ (234.3): calcd. C 71.78, H 4.30, N 23.92; found C 71.31, H 4.55, N 23.69.

4-(2-Thienyl)-2,2′-bipyridine (16b): Reaction mixture: $Pd(PPh_3)_4$ (15 mg, 0.014 mmol, 3 mol-%) in toluene (3 mL), 2-bromothiophene (64 μL, 109 mg, 0.67 mmol), pyridine **1a** (200 mg, 0.45 mmol) in toluene (3 mL). Reaction time: 20 h. Purification by FCC [kieselgel 60, 15 g, petroleum ether (40/60)/ethyl acetate, 90:10] and recrystallization from petroleum ether yielded off-white crystals (56 mg, 52%), m.p. 106°C. − IR (KBr): ṽ = 3120 cm^{-1}, 3080, 3040 (=C−H); 1595, 1580, 1545 (C=C); 1450, 1395, 1100, 990, 860, 825, 795, 700. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.15 (dd, ^3J = 3.7 and 5.1 Hz, 1 H, 4-H, thienyl), 7.33 (ddd, ^3J = 4.8 and 7.5 Hz, ^4J = 1.2 Hz, 1 H, 5′-H), 7.42 (dd, ^4J = 1.1 Hz, ^3J = 5.1 Hz, 1 H, 5-H, thienyl), 7.50 (dd, ^3J = 5.0 Hz, ^4J = 2.0 Hz, 1 H, 5-H), 7.64 (dd, ^4J = 1.1 Hz, ^3J = 3.7 Hz, 1 H, 3-H, thienyl), 7.83 (ddd, ^3J = 7.5 and 7.8 Hz, ^4J = 1.8 Hz, 1 H, 4′-H), 8.42 (ddd, ^3J = 7.8 Hz, ^4J = ^5J ≈ 1.0 Hz, 1 H, 3′-H), 8.62−8.68 (m, 2 H, 6-H, 3-H), 8.72 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 1.0 Hz, 1 H, 6′-H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 117.31, 119.92, 121.26, 123.82, 125.59, 127.11, 128.34, 136.86, 141.60, 142.45, 149.18, 149.77, 156.03, 156.92. − MS (70eV); *m/z* (%): 238 (100) [M$^+$], 237 (43) [M$^+$ − H], 210 (10) [237 − HCN], 119 (5) [M^{2+}]. − $C_{14}H_{10}N_2S$ (238.3): calcd. C 70.56, H 4.23, N 11.76; found C 70.74, H 4.37, N 11.71.

4′-(5-Pyrimidinyl)-2,2′,6′,2′′-terpyridine (17a): Reaction mixture: $Pd(PPh_3)_4$ (8 mg, 0.007 mmol, 3 mol-%) in toluene (1 mL), 5-bromopyrimidine (56 mg, 0.35 mmol) in toluene (1 mL), pyridine **4** (120 mg, 0.23 mmol) in toluene (1 mL). Reaction time: 20 h. The product separated from the reaction mixture as colourless crystals upon cooling. After storage for 1 h at +4°C, **17a** was filtered off with suction. Recrystallization from toluene gave colourless crystals (38 mg, 53%), m.p. 255°C. − IR (KBr): ṽ = 3040 cm^{-1}, 3020 (=C−H); 1590, 1570, 1545 (C=C); 1450, 1395, 1370, 1340, 1170, 975, 875, 825, 780, 735, 700, 620, 610. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.39 (ddd, ^3J = 4.8 and 7.5 Hz, ^4J = 1.2 Hz, 2 H, 5/5′′-H), 7.83 (ddd, ^3J = 7.5 and 8.0 Hz, ^4J = 1.8 Hz, 2 H, 4/4′′-H), 8.69 (ddd, ^3J = 8.0 Hz, ^4J = ^5J ≈ 1.0 Hz, 2 H, 3/3′′-H), 8.74 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 1.0 Hz, 2 H, 6/6′′-H), 8.75 (s, 2 H, 3′-H, 5′-H), 9.23 (s, 2 H, 4-H, 6-H, pyrimidyl), 9.33 (s, 1 H, 2-H, pyrimidyl). − MS (70eV); *m/z* (%): 311 (100) [M$^+$], 284 (31) [M$^+$ − HCN], 283 (25) [M$^+$ − N_2], 258 (7), 233 (26) [M$^+$ − C_5H_4N], 155.4 (8) [M^{2+}], 78 (6) [$C_5H_4N^+$]. − $C_{19}H_{13}N_5$ (311.4): calcd. C 73.30, H 4.21, N 22.49; found C 72.39, H 4.42, N 22.36.

4′-(2-Thienyl)-2,2′,6′,2′′-terpyridine (17b): Reaction mixture: $Pd(PPh_3)_4$ (10 mg, 0.009 mmol, 3 mol-%) in toluene (2 mL), 5-bromothiophene (50 μL, 86 mg, 0.51 mmol), pyridine **4** (180 mg, 0.35 mmol) in toluene (2 mL). Reaction time: 20 h. **17b** was isolated by FCC [kieselgel 60, 15 g, CH_2Cl_2/Et_2O, 100:0 → 50:50] and recrystallized from ethyl acetate to give colourless crystals (47 mg, 43%), m.p. 211°C. − IR (KBr): ṽ = 3060 cm^{-1}, 3020 (=C−H); 1600, 1580, 1570, 1550, 1535 (C=C); 1465, 1395, 1270, 1010, 990, 890, 790, 770, 710, 620. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.17 (dd, ^3J = 3.7 and 5.1 Hz, 1 H, 4-H, thienyl), 7.36 (ddd, ^3J = 4.8 and 7.5 Hz, ^4J = 1.2 Hz, 2 H, 5/5′′-H), 7.45 (dd, ^3J = 5.1 Hz, ^4J = 1.2 Hz, 1 H, 5-H, thienyl), 7.78 (dd, ^3J = 3.7 Hz, ^4J = 1.2 Hz, 1 H, 3-H, thienyl), 7.87 (ddd, ^3J = 7.5 and 8.0 Hz, ^4J = 1.8 Hz, 2 H, 4/4′′-H), 8.64 (ddd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, ^5J = 0.9 Hz, 2 H, 3/3′′-H), 8.69 (s, 2 H, 3′-H, 5′-H), 8.74 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.9 Hz, 2 H, 6/6′′-H). − MS (70eV); *m/z* (%): 315 (100) [M$^+$], 309 (8), 287 (7) [M$^+$ − N_2], 237 (4) [M$^+$ − C_5H_4N], 157.4 (8) [M^{2+}]. − $C_{19}H_{13}N_3S$ (315.4): calcd. C 72.36, H 4.15, N 13.32; found C 72.69, H 4.53, N 13.23.

2,4-Bis(2-thienyl)-2,2′-bipyridine (18): Reaction mixture: $Pd(PPh_3)_4$ (33 mg, 0.028 mmol, 3 mol-%) in toluene (8 mL), 5-bromothiophene (145 μL, 248 mg, 1.52 mmol), pyridine **11** (526 mg, 1.00 mmol) in toluene (4 mL). Reaction time: 22 h. **18** was isolated by FCC [kieselgel 60, 15 g, petroleum ether (40/60)/ethyl acetate, 95:5] and recrystallized from methanol/toluene (5:1) to give yellow needles (134 mg, 42%), m.p. 172−173°C. − IR (KBr): ṽ = 3080 cm^{-1}, 3040 (=C−H); 1585, 1570, 1555, 1535 (C=C); 1455, 1415, 1385, 1225, 985, 975, 840, 815, 780, 730, 690. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.146 (dd, ^3J = 3.6 and 5.1 Hz, 1 H, 4-H, thienyl), 7.153 (dd, ^3J = 3.7 and 5.1 Hz, 1 H, 4-H, thienyl), 7.33 (ddd, ^3J = 4.8 and 7.5 Hz, ^4J = 1.2 Hz, 1 H, 5′-H), 7.425 (dd, ^4J = 1.1 Hz, ^3J = 5.1 Hz, 1 H, 5-H, thienyl), 7.435 (dd, ^4J = 1.1 Hz, ^3J = 5.1 Hz, 1 H, 5-H, thienyl), 7.67 (dd, ^4J = 1.1 Hz, ^3J = 3.6 Hz, 1 H, 3-H, thienyl), 7.71 (dd, ^4J = 1.1 Hz, ^3J = 3.7 Hz, 1 H, 3-H, thienyl), 7.82 (d, ^4J = 1.6 Hz, 1 H, 5-H), 7.85 (ddd, ^3J = 7.5 and 8.0 Hz,

^4J = 1.8 Hz, 1 H, 4′-H), 8.52 (d, ^4J = 1.6 Hz, 1 H, 3-H), 8.42 (ddd, ^3J = 8.0 Hz, ^4J = ^5J ≈ 1.0 Hz, 1 H, 3′-H), 8.72 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 1.0 Hz, 1 H, 6′-H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 114.91, 115.58, 121.53, 123.92, 124.75, 125.66, 127.04, 127.70, 127.99, 128.32, 136.85, 141.69, 143.25, 145.15, 149.03, 152.59, 155.77, 156.36. − MS (70eV); *m/z* (%): 320 (100) [M^+], 287 (6) [M^+ − SH], 160 (5) [M^{2+}]. − $C_{18}H_{12}N_2S_2$ (320.4): calcd. C 67.47, H 3.77, N 8.74; found C 67.46, H 3.97, N 8.63.

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[1] [1a] J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelleti, L. De Cola, L. Flamingi, *Chem. Rev.* **1994**, *94*, 993−1020. − [1b] V. Balzani, L. Moggi, F. Scandola in *Supramolecular Photochemistry* (Ed.: V. Balzani), Reidel, Dordrecht, The Netherlands, **1987**. − [1c] R. F. Ziessel, *J. Chem. Educ.* **1997**, *74*, 673−679.

[2] [2a] J. M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, **1995**. − [2b] F. Vögtle, *Supramolekulare Chemie*, B. G. Teubner, Stuttgart, **1992**. − [2c] E. C. Constable, *Metals and Ligand Reactivity*, VCH, Weinheim, **1996**. − [2d] E. C. Constable, A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.* **1995**, 1615−1627.

[3] R. A. Jones, B. D. Roney, W. H. F. Sasse, K. O. Wade, *J. Chem. Soc. B* **1967**, 106−111.

[4] M. Sprecher, R. Breslow, O. Uziel, T. M. Link, *Org. Prep. Proced. Int.* **1994**, *26*, 696−701.

[5] [5a] K. T. Potts, P. A. Winslow, *J. Org. Chem.* **1985**, *50*, 5405−5409. − [5b] B. M. Kelly-Basetti, I. Krodkiewska, W. H. F. Sasse, G. P. Savage, G. W. Simpson, *Tetrahedron Lett.* **1995**, *36*, 327−330.

[6] For example: D. Armspach, E. C. Constable, F. Diederich, C. E. Housecroft, J.-F. Nierengarten, *Chem. Eur. J.* **1998**, *4*, 723−733.

[7] J. Sauer, R. Sustmann, *Angew. Chem.* **1980**, *92*, 773−801; *Angew. Chem. Int. Ed.* **1980**, *19*, 779−807.

[8] [8a] D. K. Heldmann, J. Sauer, *Tetrahedron Lett.* **1997**, *38*, 5791−5794. − [8b] J. Sauer, D. K. Heldmann, *Tetrahedron* **1998**, *54*, 4297−4312.

[9] J. Sauer, D. K. Heldmann, *Tetrahedron Lett.* **1998**, *39*, 2549−2552.

[10] [10a] M. Pereyre, J.-P. Quintard, A. Rahm, *Tin in Organic Synthesis*, Butterworths, London, **1987**. − [10b] A. G. Davies, *Organotin Chemistry*, VCH, Weinheim, **1997**.

[11] H. Neunhoeffer, "1,2,4-Triazines" in *Comprehensive Heterocyclic Chemistry I* (Eds.: A. R. Katritzky, C. W. Rees), Pergamon Press, Oxford, **1984**, vol. 3, p. 385−456.

[12] F. H. Case, *J. Heterocycl. Chem.* **1970**, *7*, 1001−1005.

[13] H. Neunhoeffer, F. Weischedel, *Liebigs Ann. Chem.* **1971**, 16−23.

[14] C. Harries, P. Temme, *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 165−172.

[15] K. Schank, *Chem. Ber.* **1969**, *102*, 383−387.

[16] B. Jousseaume, P. Villeneuve, *J. Chem. Soc., Chem. Commun.* **1987**, 513−514.

[17] [17a] Y. Shen, B. P. Sullivan, *J. Chem. Educ.* **1997**, *74*, 685−689. − [17b] J. N. Demas, B. A. DeGraff, *J. Chem. Educ.* **1997**, *74*, 690−695.

[18] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon Press, Oxford, **1988**.

[19] R. Hage, R. Prins, J. G. Haasnoot, J. Reedijk, J. G. Vos, *J. Chem. Soc., Dalton Trans.* **1987**, 1389−1396.

[20] F. H. Case, *J. Org. Chem.* **1966**, *31*, 2398−2400.

[21] F. H. Case, *J. Heterocycl. Chem.* **1971**, 1043−1046.

[22] F. Kipnis, J. Ornfelt, *J. Am. Chem. Soc.* **1946**, *68*, 2734.

[23] A. F. Renaldo, J. W. Labadie, J. K. Stille, *Org. Synth. Coll. Vol. VIII*, **1993**, 268−274.

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