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The New and Simple 'LEGO' System: Its Application to the Synthesis of 4-Stannyl-, 4-Bromo- and Branched Oligopyridines

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Dedicated to Prof. Dr. Reiner Sustmann on the occassion of his 60th birthday.

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Abstract

3,5-Di-(pyridin-2-yl)-[1,2,4]-triazines **3** are converted to 4-tributylstannyl-2,6-oligopyridines **5** regioselectively via [4+2] cycloadditions with ethynyltributyltin. Bromination of the tin compounds **5** leads to 4-bromo-2,6-oligopyridines **7**. Cross-coupling reactions of compounds **5** and **7** under Stille conditions yield branched oligopyridines **8** containing 8 to 14 pyridine units.

Keywords: *Triazines; Pyridines; Tin and compounds; Coupling reactions*

INTRODUCTION

In the foregoing paper [1] we reported on the synthesis and reactions of 4-tributylstannyl-2,6-oligopyridines as a part of our new and simple 'LEGO' system [2-8]. In this communication we extend our 'LEGO' System to the generation of branched oligopyridines **8**.

The regiospecific cyclocondensation of carboxamidrazones **1** (Scheme 1, Table 1) with α-pyridylglyoxal **2** leads to 3,5-di-(pyridin-2-yl)-[1,2,4]-triazines **3** (Table 1) [2]. These triazines **3** are the central point of our 'LEGO' system, because they are able to undergo inverse-type Diels-Alder reactions either with norborna-2,5-diene as a synthetic equivalent for acetylene in 1,2-dichlorobenzene (1,2-DCB) to form 2,6-oligopyridines **4**, as we have already described [2], or with ethynyltributyltin to form 4-tributylstannyl-2,6-oligopyridines **5** (Scheme 1, Table 2) [1,7,8].

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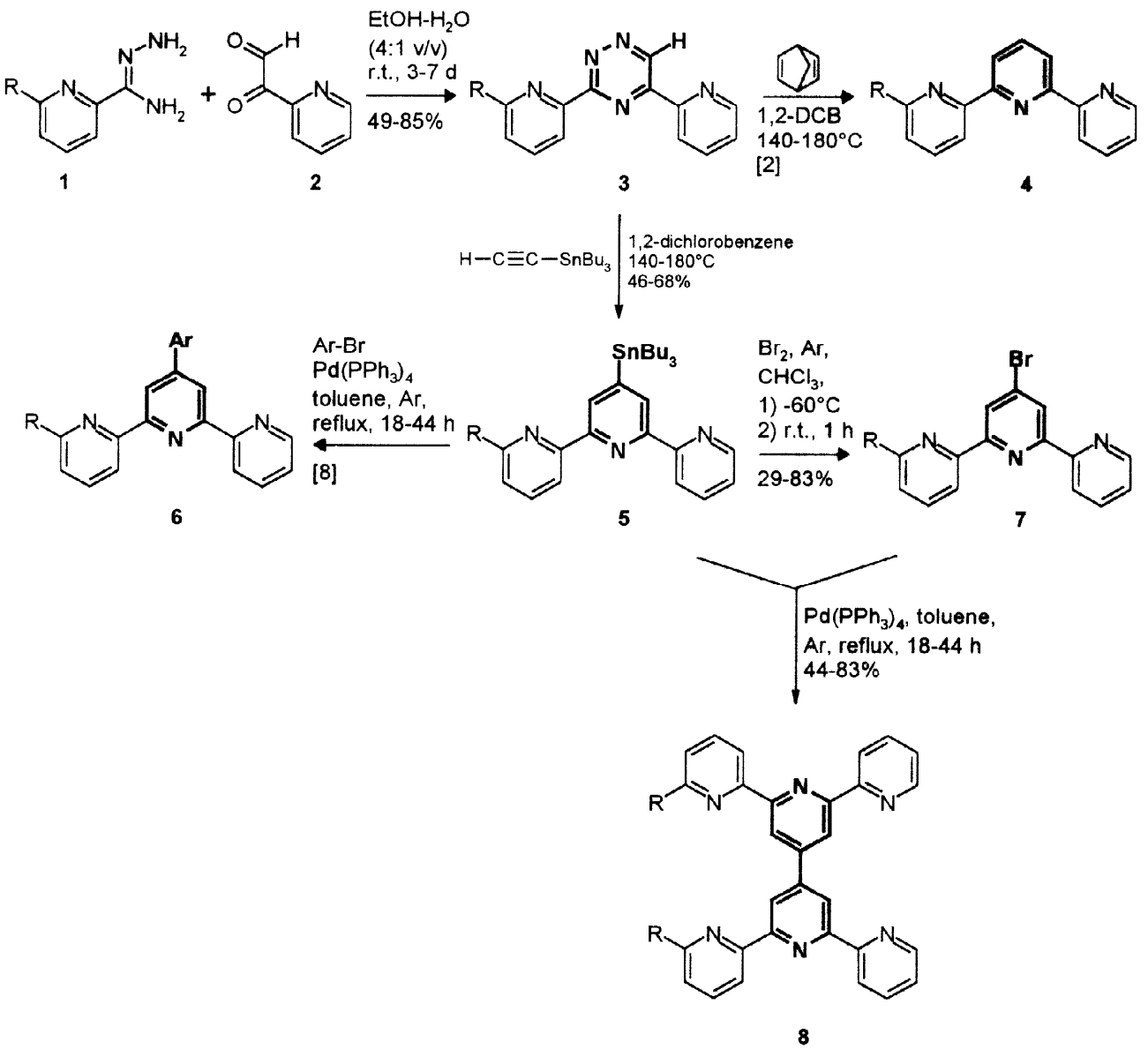
The stannanes **5** are versatile synthetic intermediates. Various substituents can be incorporated directly substituting the stannyl group by electrophiles, as it was shown recently for halogens and carbon electrophiles under Stille conditions [9,10,11,12]. As we have also shown recently stannanes **5** can be either arylated to compounds **6** or brominated to compounds **7** [8]. Complex structures **8**, highly branched oligopyridines, can be obtained by coupling the brominated compounds **7** with stannanes **5** [7] (Scheme 1, rings formed in extrabold print). In this contribution we report on the synthesis of 2,6-oligopyridines **5**, **7** and **8**.



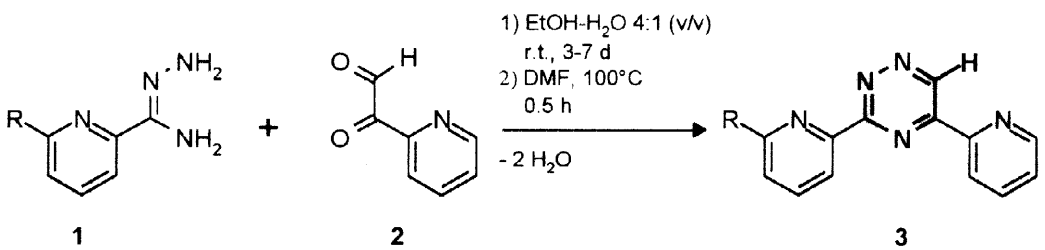
Scheme 1. The new and simple 'LEGO' system for the synthesis of 4-substituted 2,6-oligopyridines.

Taking all into account, this part of our 'LEGO' system means a new and rapid access to a variety of stannylated oligopyridines, all of them being interesting starting compounds for supramolecular chemistry [13,14].

RESULTS AND DISCUSSION

Synthesis of 1,2,4-triazines 3: Heating of carboxamidrazones with 1,2-dicarbonyl compounds in ethanol under reflux is the easiest method to form 1,2,4-triazines [15]. Using α-arylglyoxals as unsymmetrically substituted 1,2-diones, 3,5-disubstituted 1,2,4-triazines are formed regioselectively [1,2,5,16,17], a fact which considerably simplifies workup procedures and raises yields.

Unfortunately these reaction conditions fail for the synthesis of 3,5-di-(2-pyridyl)-1,2,4-triazines because of the thermolability of 2-pyridylglyoxal, which is only available in aqueous solution [18]. Therefore, we have treated 2-pyridylglyoxal with the corresponding carboxamidrazone in ethanol-water (4:1 v/v) for 3-9 days at ambient temperature with eventually heating of the isolated precipitate in *N,N*-dimethylformamide at 100°C for 0.5 hours to complete condensation (Table 1, Scheme 2). The concentration of 2-pyridylglyoxal was determined by ^{1}H NMR spectroscopy of its aqueous solution with 3-trimethylsilyl-(2,2,3,3-d_4)-propionic acid sodium salt as internal and integral standard.

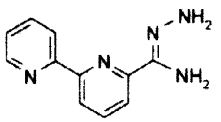
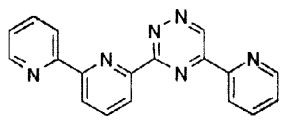
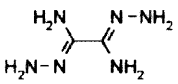
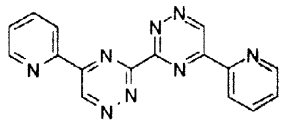
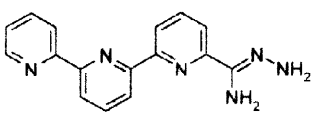
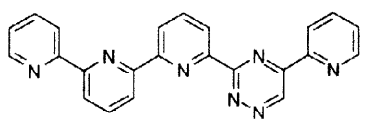
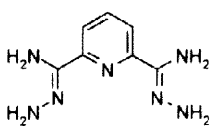
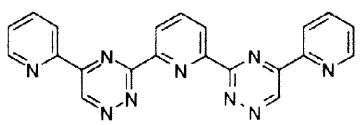
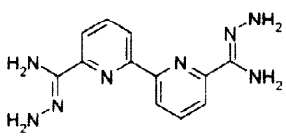
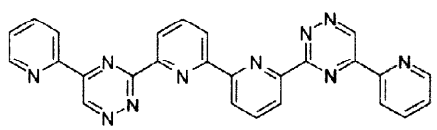


Scheme 2. Synthesis of 3,5-di-(pyridin-2-yl)-[1,2,4]-triazines **3**

The regioselectivity of the cyclocondensation can be proved by the ^{1}H NMR spectra of 1,2,4-triazines **3**, exhibiting in each case just one singlet for the expected triazine H^6. Furthermore, the structure of the corresponding pyridines **4** - **8** is confirmed by the expected coupling constants for 2,6-oligopyridines and 4-substituted 2,6-oligopyridines.

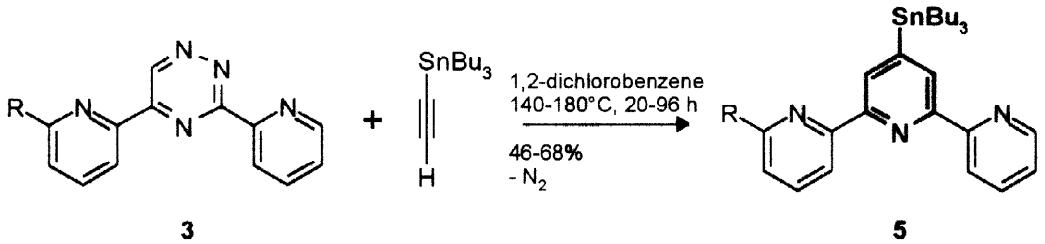
In this communication we restricted our synthetic investigations on using α-pyridylglyoxal as 1,2-dione, although all combinations of carboxamidrazones **1** with monomeric glyoxal should be possible, too. Some examples for the condensation of monomeric glyoxal, prepared in our laboratories, have been reported recently [8].

Table 1. Mono-, bi- and bis-[1,2,4]-triazines **3** synthesized according to Scheme 2.

Carboxmidrazone [Ref.]		Triazine [Ref.]		Reaction Conditions	Yield [%]	M.P. [°C]
1a [19]		**3a** [2]		2 d, r.t.	85	220-222
1b [20]		**3b**		3 d, r.t.; 2 h 100°C in DMF	82	336-339
1c		**3c**		2 d, r.t.	72	246-248
1d [21]		**3d**		3 d, r.t.	67	293-298
1e [1]		**3e**		9 d, r.t.; 2 h 100°C in DMF	71	395-398

The solubility of the yellow 1,2,4-triazines **3** in all common solvents decreases from **3a**, **3c**, **3b**, **3d** to **3e**. The last one is soluble only in refluxing *N,N*-dimethyl-formamide and refluxing 1,2-dichlorobenzene, therefore no ^{1}H NMR spectra could be recorded.

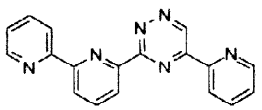
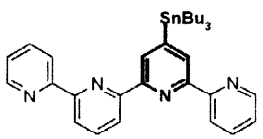
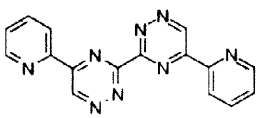
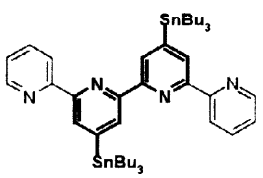
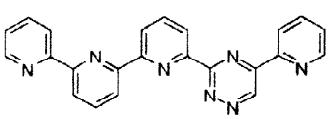
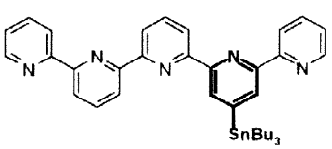
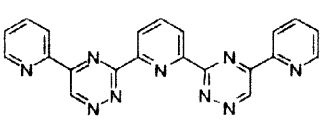
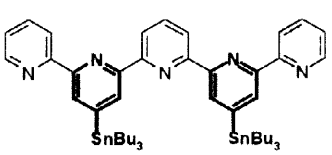
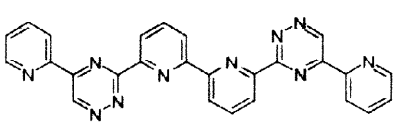
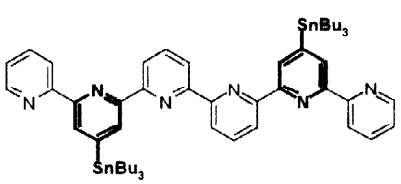
Synthesis of stannylated pyridines ***5*** *from 1,2,4-triazines* ***3****:* 1,2,4-Triazines act as dienes in inverse type Diels-Alder reactions with various electron-rich or angle strained dienophiles to yield dihydropyridines and pyridines after extrusion of nitrogen [1-8,15]. The first systematical investigations with ethynyltributyltin as dienophile affording 4-stannylated pyridines were started in our laboratories [1,7,8]. On account of the lower reactivity of 1,2,4-triazines compared to 1,2,4,5-tetrazines, [4+2] cycloaddition reactions with 1,2,4-triazines afford high reaction temperatures to supply the necessary energy of activation [22]. The 4-stannylated pyridines **5** were formed as major isomers because of steric reasons (Scheme 3, Table 2) [1,7,8].



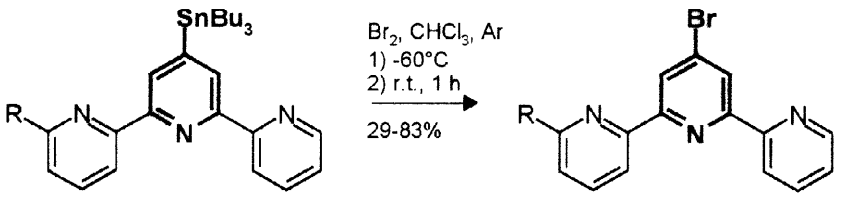
Scheme 3. Synthesis of 4-stannylated pyridines 5

The melting points of the colourless compounds **5** depend on symmetry and the number of tributyl groups.

Table 2. Synthesis of 4-tributylstannyl-2,6-oligopyridines **5** according to Scheme 3.

Triazine		4-Tributylstannyl-2,6-oligopyridine		Reaction Conditions	Yield [%]	M.P. [°C]
3a		**5a**		180°C, 23 h	68	61
3b		**5b**		180°C, 23 h	64	58-59
3c		**5c**		180°C, 20 h	57	124-125
3d		**5d**		180°C, 23h	46	73-75
3e		**5e**		180°C, 96 h	57	143-146

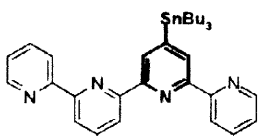
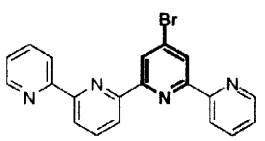
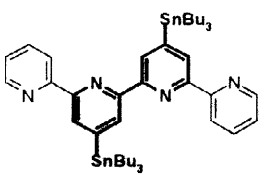
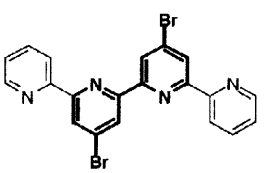
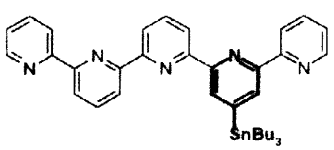
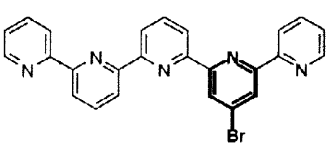
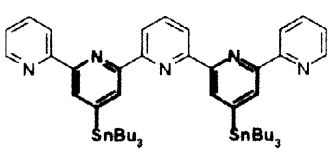
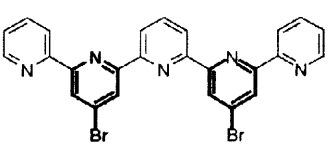
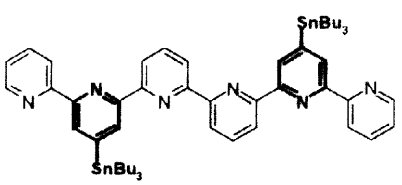
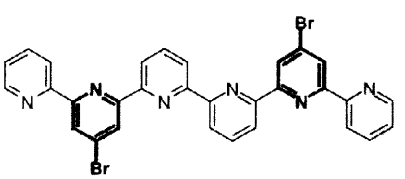
Synthesis of 4-bromo-2,6-oligopyridines 7: The pyridine-Sn bond can be cleaved by electrophiles much more rapidly than the pyridine-H bond, and therefore, the stannylated pyridines react easily by ipso substitution with electrophilic reagents like halogens. These substitution reactions make it possible to introduce an electrophilic group under mild conditions regiospecifically [8]. Smooth displacement of the stannyl group at low temperature (-60°C,Br_2) was achieved for all tin-compounds described above to yield mono- and dibrominated 2,6-oligopyridines **7** (Scheme 4, Table 3).



5 **7**

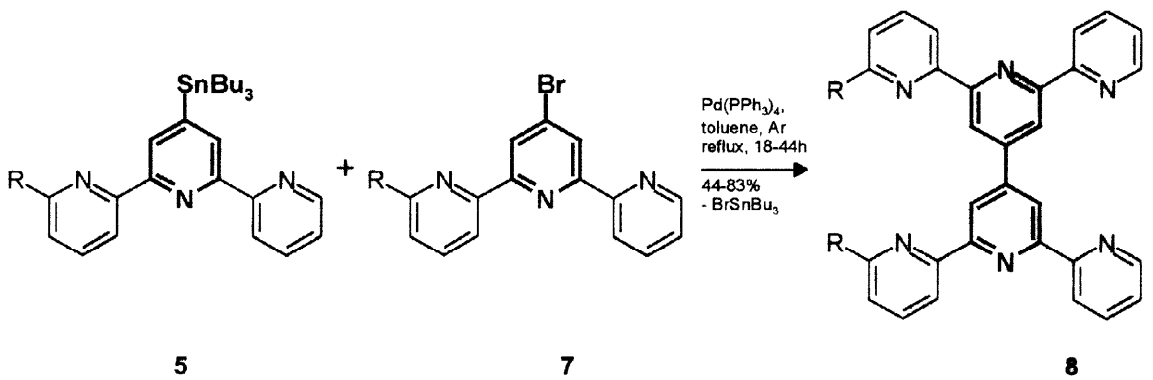
Scheme 4. Synthesis of 4-bromo-2,6-oligopyridines 7

Table 3. Synthesis of 4-bromo-2,6-oligopyridines 7 according to Scheme 4.

4-Tributylstannyl-2,6-oligopyridine		4-Bromo-2,6-oligopyridine		Reaction Conditions	Yield [%]	M.P. [°C]
5a		7a		1) -60°C, 0.5 h 2) r.t., 1 h	56	198-199
5b		7b		1) -60°C, 0.5 h 2) r.t., 1 h	29	317-321
5c		7c		1) -60°C, 0.5 h 2) r.t., 1 h	55	213-214
5d		7d		1) -60°C, 0.5 h 2) r.t., 1 h	62	320-323
5e		7e		1) -60°C, 0.5 h 2) r.t., 1 h	83	374-378

The solubility of the 4-bromo-2,6-oligopyridines **7** decreases in analogy to triazines **3**. Compound **7e** is soluble only in refluxing 1,2-dichlorobenzene.

Pd-catalyzed cross-coupling reactions: The pyridine-tin compounds **5** also take part in the Stille cross-coupling reaction with the brominated compounds **7** and $Pd(PPh_3)_4$ as catalyst to form highly branched oligopyridines **8** containing 8 to 14 pyridine units. This was demonstrated for some examples as shown in Scheme 5 and Table 4. On account of their symmetry compounds **8b** to **8e** are soluble only in CF_3CO_2H at r.t. and in 1,2-dichlorobenzene at high temperature.



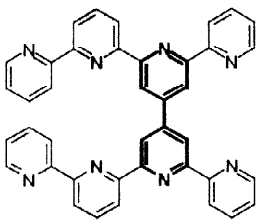
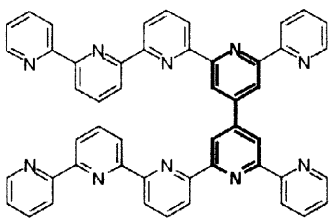
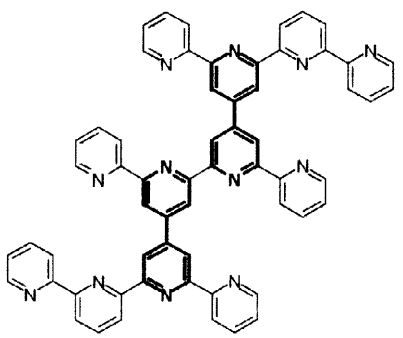
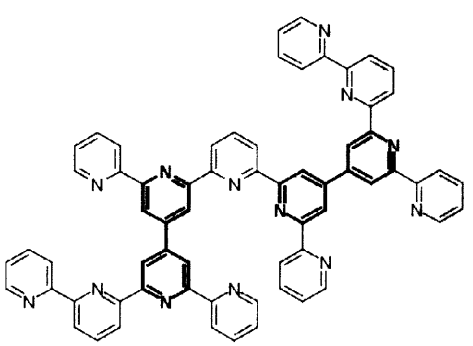
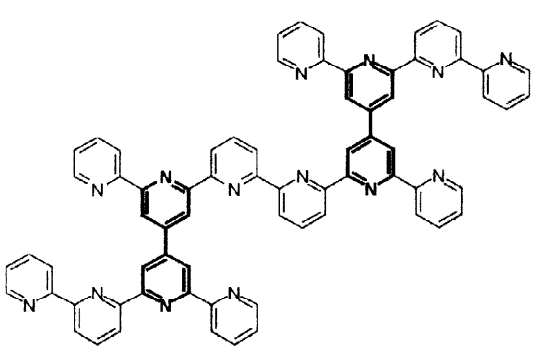
5 **7** **8**

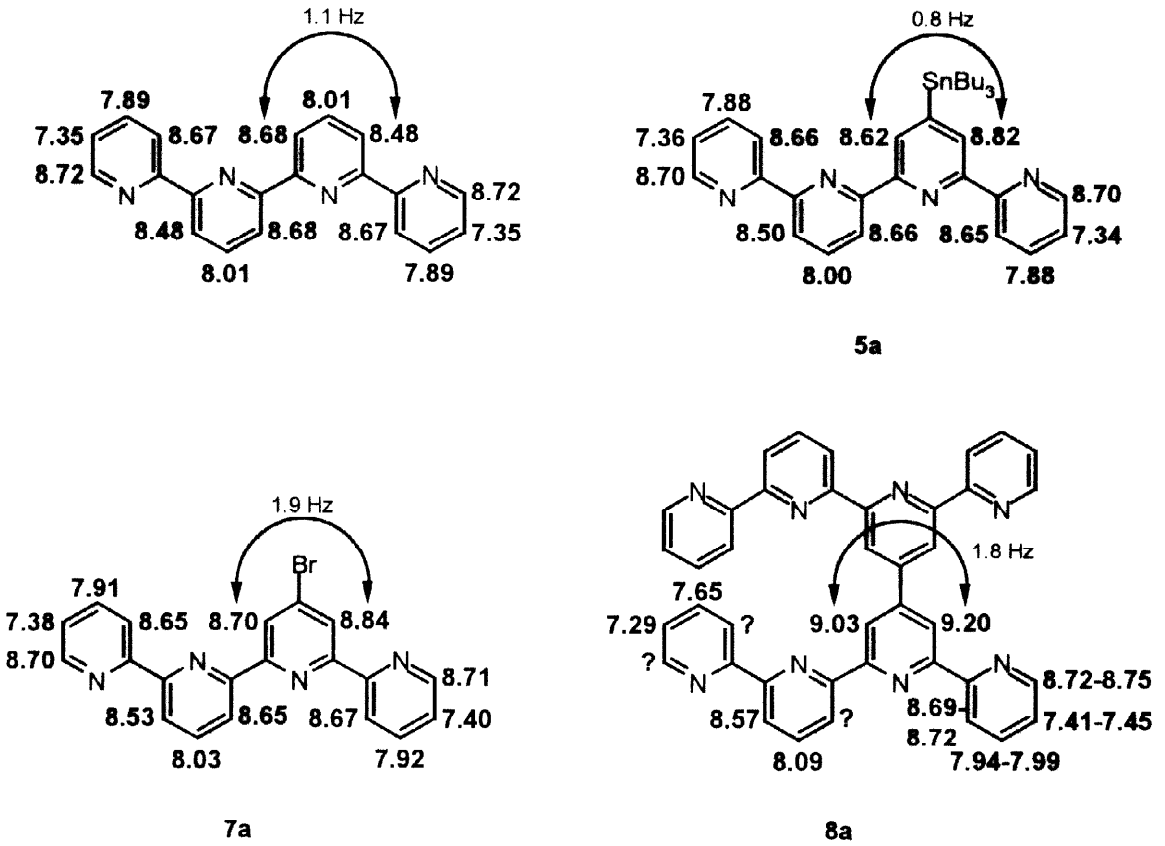
Scheme 5. Cross-coupling reactions forming branched oligopyridines **8**

Comparison of ^1H NMR data: In Scheme 6 the ^1H NMR data of different oligopyridines are listed. The meta-coupling of the substituted pyridine ring depends on the different substituents. All other coupling constants do not change significally. The ^1H NMR spectra of the 4-4'-branched octapyridine **8a** is not resolved completely because of the hindrance of rotation of the pyridine rings.

The assignment of the ppm-values results on comparison of the spectra in a series of compounds and on comparison with those of literature data [23].

Table 4. Synthesis of 4-4'-branched oligopyridines **8** according to Scheme 5.

Tin compound	4-Bromo-2,6-oligopyridine	Branched oligopyridine (number of pyridine rings)	Reaction conditions	Yield [%]	M.P. [°C]
5a	**7a**	**8a** (8)		$Pd(PPh_3)_4$, 13 mol%, 180°C, 20 h	83	324-327
5c	**7c**	**8b** (10)		$Pd(PPh_3)_4$, 15 mol%, 180°C, 18 h	66	381-385
5b	**7a**	**8c** (12)		$Pd(PPh_3)_4$, 21 mol%, 180°C, 20 h	66	352-355
5d	**7a**	**8d** (13)		$Pd(PPh_3)_4$, 23 mol%, 180°C, 20 h	44	290-294
5e	**7a**	**8e** (14)		$Pd(PPh_3)_4$, 23 mol%, 180°C, 19 h	47	425-430



Scheme 6. Comparison of ^{1}H NMR data of different oligopyridines (400 MHz, $CDCl_3$ as solvent)

CONCLUSION

Our 'LEGO' system offers a new and simple approach to 4-stannylated 2,6-oligopyridines, the corresponding bromo derivatives and their coupling products. The 4-stannylated compounds are easily obtained by [4+2] cycloaddition of 1,2,4-triazines with ethynyltributyltin in 1,2-dichlorobenzene. Replacement of the tributyltin group leads to novel 4-substituted 2,6-oligopyridines [24,25]. 4-Bromo-oligopyridines are versatile intermediates in these transformations.

EXPERIMENTAL SECTION

General: IR spectra were recorded with a Beckmann Acculab I. NMR spectra were obtained with a Bruker AC250 and ARX400 (250 MHz / 400 MHz for ^{1}H and 63 MHz / 100 MHz for ^{13}C). The degree of substitution of the C atoms was determined by the DEPT-135 method. Mass spectra were recorded either with an ionizing voltage of 70 eV by electron impact with a Varian CH90 instrument or by field desorption or secondary ion (Cs^{+}) with a Varian 311A instrument. Melting points were determined either with a Büchi melting point apparatus (<280°C) or with a copper block (>280°C) and are uncorrected. Elemental analysis were performed in the microanalytical laboratory of the University of Regensburg. For analytical thin layer chromatography precoated plastic sheets (POLYGRAM SIL G/UV254, Macherey-Nagel) were used. Silica gel 60 (particle size 0.040 - 0.063 mm, Merck) was used for flash column chromatography (fcc). Cycloaddition and coupling reactions were carried out under an atmosphere of argon in solvents dried according to standard procedures. UV/visible spectra were recorded with a Karl Zeiss Specord M500. Cyclovoltametry was carried out with a voltage-scan-generator (Bank Wenking VSG 72), a potentiostat (Metrawatt Lerrayer XY 733), a Ag/0.1 N $AgNO_3$ reference electrode and a Hg electrode with acetonitrile als solvent and 0.1 N tributyl ammoniumtetrafluoroborate as conducting salt.
α-Pyridylglyoxal [18], 6-bromo-[2,2';6',2'']terpyridine [26], ethynyltributyltin [27], tetrakis(triphenylphosphine)-palladium(0) [28] and benzylchlorobis(triphenylphosphine)-palladium(II) [29] were prepared according to literature procedures.

Determination of the concentration of α-pyridylglyoxal 2 by ^{1}H NMR: Following the procedure by Schank [18] the volume of the aqueous solution of α-pyridylglyoxal was measured (80 ml). For ^{1}H NMR 0.5 ml of the aqueous solution was mixed with 0.3 ml D_2O and 1.05 mg 3-trimethylsilyl-(2,2,3,3-d_4)-propionic acid sodium salt (TSP) was added. After integration the concentration was determined to 156 µmol/l. Then the aqueous solution was diluted with 320 ml reagent grade ethanol (1:4 v/v) to give a final volume of 375 ml and a final concentration of 33.3 µmol/ml. The aqueous solution contains an equilibrum mixture of the free glyoxal and its hydrate (4 : 9). For ^{1}H NMR determination the hydrogens of the hydrate are set equal one. - ^{1}H NMR (0.5 ml H_2O, 0.3 ml D_2O, 400 MHz): δ = 0.00 (s, 0.95 H, TSP), 5.23 (s, 1 H, hydrate), 6.34 (s, 0.45 H, free glyoxal), 7.48 (ddd, 1 H, J=7.6 Hz, J=4.9 Hz, J=1.2 Hz, hydrate), 7.69-7.77 (m, 0.45 H, free glyoxal), 7.77 (ddd, 1 H, J=8.0 Hz, J=1.1 Hz, J=0.9 Hz, hydrate), 7.95 (ddd, 1 H, J=8.0 Hz, J=7.6 Hz, J=1.8 Hz), 8.05-8.14 (m, 0.45 H, free glyoxal), 8.15-8.22 (m, 0.45 H, free glyoxal), 8.57 (ddd, 1 H, J=4.9 Hz, J=1.7 Hz, J=0.9 Hz, hydrate), 8.68-8.75 (m, 0.45 H, free glyoxal) ppm.

6-Cyano-[2,2';6',2'']terpyridine: 1.50 g (4.81 mmol) of 6-bromo-[2,2';6',2'']terpyridine, 489 mg (5.46 mmol) of copper(I)-cyanide and 4.5 ml of absolute pyridine were heated at 140-150°C for 8 h. After cooling the still warm solution was poured into a cold saturated solution of potassium cyanide (40 ml) and stirred magnetically at r.t. over night. Then the mixture was diluted with 250 ml of distilled water and the resulting precipitate was isolated by suction filtration and washed with 50 ml of distilled water. Sublimation of the precipitate at 130°C/0.001 Torr yielded 871 mg (3.37 mmol, 70%) of colourless crystals, m.p. 141-143°C. - IR (KBr): $\tilde{\nu}$ = 3090, 3040, 2020, 1570, 1550, 1425, 1410, 975, 800, 760, 740 cm^{-1}. - ^1H NMR (CD_2Cl_2, 250 MHz): δ = 7.37 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.75 (dd, 1 H, J=7.6 Hz, J=1.1 Hz), 7.88 (ddd, 1 H, J=8.0 Hz, J=7.5 Hz, J=1.8 Hz), 8.01 (dd, 1 H, J=7.8 Hz, J=7.8 Hz), 8.02 (dd, 1 H, J=8.2 Hz, J=7.6), 8.48 (dd, 1 H, J=7.8 Hz, J=1.1 Hz), 8.54 (dd, 1 H, J=7.8 Hz, J=1.1 Hz), 8.60 (ddd, 1 H, J=8.0 Hz, J=1.2 Hz, J=0.9 Hz), 8.70 (ddd, 1 H, J=4.8 Hz, J=1.8 Hz, J=0.9 Hz), 8.87 (dd, 1 H, J=8.2 Hz, J=1.1) ppm. This compound was identified by the successful preparation of **1c** and **3c**.

[2,2';6',2'']Terpyridine-6-carboxamidrazone (**1c**): 1.00 g (3.87 mmol) of 6-cyano-[2,2';6',2'']terpyridine, suspended in 25 ml of reagent grade ethanol, was treated with 2.08 ml (2.14 g, 22.8 mmol) of hydrazine hydrate (100%). After stirring at r.t. for 24 h the same amount of hydrazine hydrate (100%) was added. After another 7 d stirring at r.t. the solution was diluted with 80 ml of distilled water and the resulting precipitate was isolated by suction filtration, washed with 50 ml of distilled water and dried at 30°C/0.01 Torr, yielded 1.07 g (3.67 mmol, 95%) of **1c**, colourless needles, m.p. 272-274°C (beginning decomp. at 240°C). **1c** was used without any further purification. - IR (KBr): $\tilde{\nu}$ = 3440, 3290, 3190, 3050, 3020, 3000, 1645, 1605, 1565, 1555, 1440, 1420, 1060, 980, 895, 855, 805, 795, 760 cm^{-1}. - ^1H NMR ($CDCl_3$, 250 MHz): δ = 5.50 (s, br, 2 H), 6.10 (s, br, 2 H), 7.71 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.96 (dd, 1 H, J=8.0 Hz, J=7.2 Hz), 8.02 (ddd, 1 H, J=8.0 Hz, J=7.5 Hz, J=1.8 Hz), 8.02 (dd, 1 H, J=8.0 Hz, J=1.6 Hz), 8.12 (dd, 1 H, J=7.8 Hz, J=7.8), 8.46 (dd, 1 H, J=7.8 Hz, J=1.1 Hz), 8.57 (dd, 1 H, J=7.2 Hz, J=1.6 Hz), 8.65 (ddd, 1 H, J=8.0 Hz, J=1.2 Hz, J=0.9 Hz), 8.74 (ddd, 1 H, J=4.8 Hz, J=1.8 Hz, J=0.9 Hz), 8.77 (dd, 1 H, J=7.8 Hz, J=1.1) ppm. **1c** was identified by the successful preparation of **3c**.

General procedure for the synthesis of 1,2,4-triazines **3a-e**: A mixture of carboxamidrazone **1** and α-pyridylglyoxal **2** (1 eq.) in ethanol-water (4 :1, v/v) was stirred magnetically at r.t. for several days. For reaction times and temperature see Table 1. The yellow precipitate formed was separated by suction filtration, washed well with water and ethanol, recrystallized and dried at 60°C/0.01 Torr.

3-([2,2']Bipyridin-6-yl)-5-(pyridin-2-yl)-[1,2,4]triazine (**3a**) [2]: Following the *general procedure* **1a** (1.58 g, 7.40 mmol) and **2** (1.00 g, 7.40 mmol, c = 33.3 µmol/l) yielded after stirring at r.t. for 2 d 1.97 g (6.29 mmol, 85%) of **3a**, yellow crystals, m.p. 220-222°C. No further purification was necessary. - IR (KBr): $\tilde{\nu}$ = 3080, 3060, 3000, 1570, 1550, 1505, 1460, 1420, 1350, 1235, 1030, 980, 755, 725 cm^{-1}. - ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.37 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.53 (ddd, 1 H, J=7.6 Hz, J=4.7 Hz, J=1.2 Hz), 7.90 (ddd, 1 H, J=8.0 Hz, J=7.5 Hz, J=1.8 Hz), 7.98 (ddd, 1 H, J=7.8 Hz, J=7.6 Hz, J=1.8 Hz), 8.09 (dd, 1 H, J=7.8 Hz, J=7.8 Hz), 8.66 (dd, 1 H, J=7.9 Hz, J=1.1 Hz), 8.70 (dd, 1 H, J=7.8 Hz, J=1.1 Hz), 8.73 (ddd, 1 H, J=4.8 Hz, J=1.8 Hz, J=0.9 Hz), 8.77 (ddd, 1 H, J=8.0 Hz, J=1.2 Hz, J=0.9 Hz), 8.81 (ddd, 1 H, J=7.8 Hz, J=1.2 Hz, J=0.9 Hz), 8.83 (ddd, 1 H, J=4.7 Hz, J=1.8 Hz, J=0.9 Hz), 10.34 (s, 1 H) ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 121.70 (1C, +), 122.89 (1C, +), 123.09 (1C, +), 124.08 (1C, +), 1124.17 (1C, +), 126.55 (1C, +), 137.02 (1C, +), 137.33 (1C, +), 138.02 (1C, +), 145.72 (1C, +), 149.11 (1C, +), 149.96 (1C, +), 151.95 (1C, 0), 152.34 (1C, 0), 154.17 (1C, 0), 155.67 (1C, 0), 156.75 (1C, 0), 162.73 (1C, 0). - UV/Vis (CH_2Cl_2): 236 nm (26370 $lmol^{-1}cm^{-1}$, lg ε 4.421), 286 nm (27730 $lmol^{-1}cm^{-1}$, lg ε 4.440), 400 (405 $lmol^{-1}cm^{-1}$, lg ε 2.607). - $E_{1/2}$ = -1.67 V. - EI MS (70 eV); m/z (%): 312 (35) [M^+], 284 (78) [M^+ - N_2], 236 (4) [M^+ + 2 H - C_5H_4N], 206 (5) [M^+ - N_2 - C_5H_4N], 181 (100) [M^+ - N_2 - C_7H_5N], 155 (15) [$C_{10}H_7N_2^+$], 128 (11) [$C_{10}H_7N_2^+$ - HCN], 103 (95) [$C_7H_5N^+$], 77.9 (20) [$C_5H_4N^+$], 51.1 (9) [$C_5H_4N^+$ - HCN]. - $C_{18}H_{12}N_6$ (312.3): calcd. C 69.22, H 3.87, N 26.91; found C 69.13, H 4.01, N 26.80.

5,5'-Di-(pyridin-2-yl)-bi-[1,2,4]triazine (**3b**) [2]: Following the *general procedure* **1b** (0.43 g, 3.70 mmol) and **2** (1.00 g, 7.40 mmol, c = 33.3 µmol/l) yielded after stirring at r.t. for 3 d and heating of the precipitate in *N,N*-dimethylformamide (50 ml) at 100°C for 2 h, 948 mg (3.02 mmol, 82%) of **3b**, yellow crystals, m.p. 336-339°C (beginning decomp. at 310°C). No further purification was necessary. - IR (KBr): $\tilde{\nu}$ = 3070, 3040, 1575, 1560, 1525, 1500, 1460, 1310, 1225, 1135, 1035, 985, 970 cm^{-1}. - ^1H NMR (DMSO-D_6, 100°C, 400 MHz): δ = 7.70 (ddd, 2 H, J=7.6 Hz, J=4.8 Hz, J=1.2 Hz), 8.13 (ddd, 2 H, J=7.9 Hz, J=7.6 Hz, J=1.7 Hz), 8.72 (ddd, 2 H, J=7.9 Hz, J=1.2 Hz, J=0.9 Hz), 8.89 (ddd, 2 H, J=4.8 Hz, J=1.7 Hz, J=0.9 Hz), 10.40 (s, 2 H) ppm.). - UV/Vis: too insoluble. - $E_{1/2}$: too insoluble. - EI MS (70 eV); m/z (%): 314 (36) [M^+], 286 (27) [M^+ - N_2], 103 (100) [$C_7H_5N^+$], 75.9 (33) [$C_7H_5N^+$ - HCN], 50.1 (14) [$C_7H_5N^+$ - HCN - C_2H_2]. - $C_{16}H_{10}N_8$ (314.3): calcd. C 61.14, H 3.21, N 35.65; found C 60.94, H 3.64, N 35.68.

3-([2,2';6',2'']Terpyridin-6-yl)-5-(pyridin-2-yl)-[1,2,4]triazine (**3c**) [2]: Following the *general procedure* **1c** (0.71 g, 2.45 mmol) and **2** (0.33 g, 2.45 mmol, c = 33.3 µmol/l) yielded after stirring at r.t. for 2 d and recrystallization from dichloromethane 684 mg (1.76 mmol, 72%) of **3c**, yellow crystals, m.p. 246-248°C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3080, 3050, 3000, 1570, 1550, 1520, 1500, 1455, 1430, 1410, 1345, 1255, 1230, 1100, 1065, 1030, 980, 760 cm^{-1}. - ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.36 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.54 (ddd, 1 H, J=7.6 Hz, J=4.7 Hz, J=1.2 Hz), 7.89 (ddd, 1 H, J=8.0 Hz, J=7.5 Hz, J=1.8 Hz), 8.00 (ddd, 1 H, J=8.1 Hz, J=7.5 Hz, J=1.6 Hz), 8.05 (dd, 1 H, J=7.8 Hz, J=7.8 Hz), 8.13 (dd, 1 H, J=7.8 Hz, J=7.8 Hz), 8.52 (dd, 1 H, J=7.8 Hz, J=1.1 Hz), 8.67 (ddd, 1 H, J=8.0 Hz, J=1.2 Hz, J=0.9 Hz), 8.73 (ddd, 1 H, J=4.8 Hz, J=1.8 Hz, J=0.9 Hz), 8.73 (dd, 1 H, J=7.8 Hz, J=1.1 Hz), 8.82 (dd, 1 H, J=7.8 Hz, J=1.1 Hz), 8.88 (dd, 1 H, J=7.9 Hz, J=1.1 Hz), 8.80-8.85 (m, 2 H), 10.35 (s, 1 H) ppm.). - UV/Vis (CH_2Cl_2): 290 nm (35830 $lmol^{-1}cm^{-1}$, lg ε 4.554), 400 (413 $lmol^{-1}cm^{-1}$, lg ε 2.616). - $E_{1/2}$ = -1.67 V. - EI MS (70 eV); m/z (%): 389 (25) [M^+], 361 (38) [M^+ - N_2], 311 (1) [M^+ - C_5H_4N], 258 (100) [M^+ - N_2 - C_7H_5N], 230 (11) [M^+ - 2 N_2 - C_7H_5N], 180 (3) [$C_{10}H_7N_2$-CN^+], 155 (12) [$C_{10}H_7N_2^+$], 103 (25) [$C_7H_5N^+$], 78.0 (6) [$C_5H_4N^+$]. - $C_{23}H_{15}N_7$ (389.4): calcd. C 70.94, H 3.88, N 25.18; found C 70.71, H 4.05, N 24.94.

2,6-Bis-(5-(pyridin-2-yl)-[1,2,4]triazin-3-yl)-pyridine (**3d**) [2]: Following the *general procedure* **1d** (0.72 g, 3.70 mmol) and **2** (1.00 g, 7.40 mmol, c = 33.3 µmol/l) yielded after stirring at r.t. for 3 d and recrystallization from trichloromethane 972 mg (2.48 mmol, 67%) of **3d**, yellow crystals, m.p. 293-298°C (beginning decomp. at 285°C). - IR (KBr): $\tilde{\nu}$ = 3080, 3050, 1575, 1525, 1505, 1460, 1445, 1340, 1240, 985, 770 cm^{-1}. - ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.54 (ddd, 2 H, J=7.6 Hz, J=4.8 Hz, J=1.2 Hz), 7.98 (ddd, 2 H, J=7.9 Hz, J=7.6 Hz, J=1.8 Hz), 8.25 (dd, 1 H, J=7.9 Hz, J=7.7 Hz), 8.84 (ddd, 2 H, J=4.7 Hz, J=1.8 Hz, J=0.9 Hz), 8.91 (ddd, 2 H, J=7.9 Hz, J=1.2 Hz, J=0.9 Hz), 8.93 (d, 2 H, J=7.8 Hz), 10.37 (s, 2 H) ppm.). - UV/Vis ($CHCl_3$): 237 nm (32410 $lmol^{-1}cm^{-1}$, lg ε 4.511), 289 nm (34050 $lmol^{-1}cm^{-1}$, lg ε 4.532), 396 (911 $lmol^{-1}cm^{-1}$, lg ε 2.959). - $E_{1/2}$ = -1.55 V. - EI MS (70 eV); m/z (%): 391 (8) [M^+], 363 (19) [M^+ - N_2], 260 (6) [M^+ - N_2 - C_7H_5N], 232 (12) [M^+ - 2 N_2 - C_7H_5N], 103 (100) [$C_7H_5N^+$], 76.0 (39) [$C_7H_5N^+$ - HCN], 50.1 (10) [$C_7H_5N^+$ - HCN - C_2H_2]. - $C_{21}H_{13}N_9$ (391.4): calcd. C 64.44, H 3.35, N 32.22; found C 63.29, H 3.85, N 31.79.

6,6'-Bis-(5-(pyridin-2-yl)-[1,2,4]triazin-3-yl)-2,2'-bipyridine (**3e**) [2]: Following the *general procedure* **1e** (0.75 g, 2.77 mmol) and **2** (0.75 g, 5.55 mmol, c = 31.5 µmol/l) yielded after stirring at r.t. for 9 d, heating of the precipitate in *N,N*-dimethylformamide (50 ml) at 100°C for 2 h, 927 mg (1.97 mmol, 71%) of **3e**, yellow crystals, m.p. 395-398°C (beginning decomp. at 335°C). - IR (KBr): $\tilde{\nu}$ = 3080, 3050, 1575, 1555, 1525, 1505, 1465, 1435, 1350, 1240, 1110, 1040, 985, 770 cm^{-1}. - EI MS (70 eV); m/z (%): 468 (2) [M^+], 440 (12) [$M^+ - N_2$], 337 (1) [$M^+ - N_2 - C_7H_5N$], 309 (8) [$M^+ - 2\ N_2 - C_7H_5N$], 206 (4) [$C_{12}H_6N_4^+$], 180 (4) [$C_{12}H_6N_4^+ - CN$], 103 (100) [$C_7H_5N^+$], 75.9 (40) [$C_7H_5N^+ - HCN$], 50.1 (10) [$C_7H_5N^+ - HCN - C_2H_2$]. - $C_{26}H_{16}N_{10}$ (468.5): calcd. C 66.65, H 3.44, N 29.91; found C 65.48, H 3.66, N 29.11. Compound **3e** is too insoluble for ^{1}H-NMR, UV and $E_{1/2}$.

General procedure for the synthesis of tributyltin-pyridines **5a-e**: The appropriate 1,2,4-triazine **3** and a 2 fold molar excess (per triazine ring) of ethynyltributyltin were heated in 1,2-dichlorobenzene under an atmosphere of argon. For reaction times and temperatures see Table 2. The solvent was stripped off and the residue was either purified by fcc on silica gel or recrystallized.

4'-Tributylstannyl-[2,2';6',2'';6'',2''']quaterpyridine (**5a**): Following the *general procedure* **3a** (1.91 g, 6.12 mmol) and ethynyltributyltin (2.50 g, 12.4 mmol) in 13 ml 1,2-dichlorobenzene yielded after evaporating of the solvent, treating of the residue with methanol, cooling of the solution over solid carbon dioxide and suction filtration of the precipitate which was formed, 2.48 g (4.14 mmol, 68%) of **5a**, colourless crystals, m.p. 61°C. - IR (KBr): $\tilde{\nu}$ = 3050, 2920, 2860, 2840, 1580, 1550, 1540, 1520, 1460, 1440, 1420, 1410, 1370, 1260, 1110, 1060, 780, 740, 650 cm^{-1}. - ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 0.93 (t, 9 H, J=7.3 Hz), 1.12 - 1.32 (m, 6 H), 1.34 - 1.52 (m, 6 H), 1.54 - 1.85 (m, 6 H), 7.34 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.36 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.87 (ddd, 1 H, J=8.0 Hz, J=7.5 Hz, J= 1.8 Hz), 7.88 (ddd, 1 H, J=8.0 Hz J=7.5 Hz, J=1.8 Hz), 8.00 (dd, 1 H, J=7.8 Hz, J=7.8 Hz), 8.50 (dd, 1 H, J=7.8 Hz, J=1.1 Hz), 8.62 (d, 1 H, J=0.8 Hz), 8.65 (ddd, 1 H, J=8.0 Hz, J=1.2 Hz, J=0.9 Hz), 8.66 (dd, 1 H, J=7.8 Hz, J=1.1 Hz), 8.67 (ddd, 1 H, J=8.0 Hz, J=1.2 Hz, J=1.0 Hz), 8.70 (ddd, 1 H, J=4.8 Hz, J=1.8 Hz, 0.9 Hz), 8.71 (ddd, 1 H, J=4.8 Hz, J=1.8 Hz, J=1.0 Hz), 8.82 (d, 1 H, J=0.6 Hz) ppm. - ^{13}C NMR (CD_2Cl_2, 100 MHz, DEPT): δ = 10.15 (3 C, -), 13.84 (3 C, +), 27.79 (3 C, -), 29.49 (3 C, -), 120.98 (1 C, +), 121.15 (1 C, +), 121.44 (1 C, +), 121.46 (1 C, +), 123.91 (1 C, +), 124.15 (1 C, +), 129.32 (1 C, +), 129.39 (1 C, +), 137.11 (1 C, +), 137.13 (1 C, +), 138.14 (1 C, +), 149.46 (1 C, +), 149.54 (1 C, +), 153.51 (1 C, 0), 153.65 (1 C, 0), 155.47 (1 C, 0), 155.62 (1 C, 0), 156.34 (1 C, 0), 156.56 (1 C, 0), 157.12 (1 C, 0). - FD MS (CH_2Cl_2); m/z (%): 1200 (<35) [M_2^+], 1141 (100) [$M_2^+ - C_4H_9$], 1085 (<5) [$M_2^+ - 2\ C_4H_9$], 657 (<5) [M^+ +

C_4H_9], 601 (<80) [M^+ + H], 543 (<95) [M^+ + H - C_4H_9]. - $C_{32}H_{40}N_4Sn$ (599.4): calcd. C 64.12, H 6.73, N 9.35; found C 64.13, H 6.87, N 9.25.

4',4''-Bis-tributylstannyl-[2,2';6',2'';6'',2''']quaterpyridine (**5b**): Following the *general procedure* **3b** (1.66 g, 5.28 mmol) and ethynyltributyltin (4.30 g, 21.4 mmol) in 20 ml 1,2-dichlorobenzene yielded after fcc (petroleum ether 40/60 : ethyl acetate = 4 : 1) 2.98 g (3.36 mmol, 64%) of **5b**, colourless crystals, m.p. 58-59°C. - IR (KBr): $\tilde{\nu}$ = 3040, 2940, 2900, 2860, 2840, 1570, 1560, 1540, 1450, 1340, 1260, 1120, 1100, 870, 780, 730 cm^{-1}. - ^1H NMR (CD_2Cl_2, 250 MHz): δ = 0.93 (t, 18 H, J=7.4 Hz), 1.12 - 1.32 (m, 12 H), 1.34 - 1.52 (m, 12 H), 1.54 - 1.85 (m, 12 H), 7.34 (ddd, 2 H, J=7.5 Hz, J=4.8 Hz, J=1.3 Hz), 7.86 (ddd, 2 H, J=8.0 Hz, J=7.5 Hz, J= 1.8 Hz), 8.61 (d, 2 H, J=0.8 Hz), 8.65 (ddd, 2 H, J=8.0 Hz, J=1.3 Hz, J=0.9 Hz), 8.70 (ddd, 2 H, J=4.8 Hz, J=1.8 Hz, 0.9 Hz), 8.80 (d, 2 H, J=0.8 Hz) ppm. - ^{13}C NMR (CD_2Cl_2, 63 MHz, DEPT): δ = 10.27 (6 C, -), 13.83 (6 C, +), 27.81 (6 C, -), 29.55 (6 C, -), 121.42 (2 C, +), 123.67 (2 C, +), 129.09 (2 C, +), 129.68 (2 C, +), 137.05 (2 C, +), 149.51 (2 C, +), 153.67 (2 C, 0), 154.27 (2 C, 0), 155.37 (2 C, 0), 157.38 (2 C, 0). - FD MS (CH_2Cl_2); m/z (%): 1779 (<5) [M_2^+ + 2 H], 1719 (<25) [M_2^+ - C_4H_9], 1662 (<5) [M_2^+ - 2 C_4H_9], 947 (<5) [M^+ + H + C_4H_9], 889 (100) [M^+], 832 (<15) [M^+ - C_4H_9]. - $C_{44}H_{66}N_4Sn_2$ (888.5): calcd. C 59.48, H 7.48, N 6.31; found C 59.51, H 7.53, N 6.31.

4'-Tributylstannyl-[2,2';6',2'';6'',2''';6''',2'''']quinquepyridine (**5c**): Following the *general procedure* **3c** (0.56 g, 1.44 mmol) and ethynyltributyltin (0.91 g, 2.88 mmol) in 10 ml 1,2-dichlorobenzene yielded after evaporating of the solvent, treating of the residue with methanol, cooling of the solution over solid carbon dioxide, suction filtration of the precipitate which was formed and recrystallization from methanol, 559 mg (827 µmol, 57%) of **5c**, colourless needles, m.p. 124-125°C. - IR (KBr): $\tilde{\nu}$ = 3080, 3040, 2950, 2910, 2860, 2840, 1575, 1555, 1520, 1460, 1440, 1415, 1260, 770 cm^{-1}. - ^1H NMR (CD_2Cl_2, 400 MHz): δ = 0.94 (t, 9 H, J=7.3 Hz), 1.22 - 1.32 (m, 6 H), 1.34 - 1.50 (m, 6 H), 1.65 - 1.80 (m, 6 H), 7.34 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.36 (ddd, 1 H, J=7.5 Hz, J=4.7 Hz, J=1.3 Hz), 7.88 (ddd, 1 H, J=8.0 Hz, J=7.5 Hz, J=1.8 Hz), 7.90 (ddd, 1 H, J=8.0 Hz J=7.5 Hz, J=1.8 Hz), 8.02 (dd, 1 H, J=7.8 Hz, J=7.8 Hz), 8.05 (dd, 1 H, J=7.8 Hz, J=7.8 Hz), 8.51 (dd, 1 H, J=7.8 Hz, J=1.1 Hz), 8.62 (d, 1 H, J=0.8 Hz), 8.65 - 8.72 (m, 7 H), 8.86 (d, 1 H, J=0.8 Hz) ppm. - ^{13}C NMR (CD_2Cl_2, 100 MHz, DEPT): δ = 10.16 (3 C, -), 13.84 (3 C, +), 27.80 (3 C, -), 29.50 (3 C, -), 121.06 (1 C, +), 121.19 (1 C, +), 121.27 (1 C, +), 121.29 (1 C, +), 121.46 (1 C, +), 121.52 (1 C, +), 123.91 (1 C, +), 124.19 (1 C, +), 129.35 (1 C, +), 129.43 (1 C, +), 137.17 (1 C, +), 137.19 (1 C, +), 138.12 (1 C, +), 138.16 (1 C, +), 149.47 (1 C, +), 149.55 (1 C, +), 153.50 (1 C, 0), 153.65 (1 C, 0), 155.51 (1 C, 0), 155.63 (1 C, 0), 155.78 (1 C, 0), 155.83 (1 C, 0), 156.38 (1 C, 0), 156.50 (1 C, 0), 157.12 (1

C, 0). - EI MS (70 eV); m/z (%): 620 (44) [M^+ - C_4H_9], 507 (22) [M^+ - 2 C_4H_9 - C_4H_8], 388 (44) [M^+ - $Sn(C_4H_9)_3$ + 2 H], 386 (13) [M^+ - $Sn(C_4H_9)_3$], 361 (10) [M^+ - $Sn(C_4H_9)_3$ - HCN + 2 H], 258 (26) [$C_{17}H_{11}N_3^+$], 254 (6), 232 (4) [$C_{15}H_{10}N_3^+$], 205 (3) [$C_{15}H_{10}N_3^+$ - HCN], 155 (5) [$C_{10}H_7N_2^+$], 128 (2) [$C_{10}H_7N_2^+$ - HCN], 103 (7) [$C_6H_4N_2^+$], 78 (3) [$C_5H_4N^+$], 41.1 (8). - $C_{37}H_{43}N_5Sn$ (676.4): calcd. C 65.69, H 6.41, N 10.36; found C 65.86, H 6.32, N 10.88.

4',4'''-Bis-tributylstannyl-[2,2';6',2'';6'',2''';6''',2'''']quinquepyridine (**5d**): Following the *general procedure* **3d** (1.03 g, 2.63 mmol) and ethinyltributyltin (2.32 g, 11.6 mmol) in 8 ml 1,2-dichlorobenzene yielded after fcc (dichloromethane : ethyl acetate = 1 : 1) 1.16 g (1.20 mmol, 46%) of **5d**, colourless crystals, m.p. 73-75°C. - IR (KBr): $\tilde{\nu}$ = 3050, 2950, 2900, 2860, 2840, 1580, 1560, 1540, 1520, 1460, 1450, 1360, 1260, 1110, 1100, 810, 780, 730, 650 cm^{-1}. - ^1H NMR (CD_2Cl_2, 400 MHz): δ = 0.90 (t, 18 H, J=7.2 Hz), 1.12 - 1.32 (m, 12 H), 1.34 - 1.52 (m, 12 H), 1.54 - 1.80 (m, 12 H), 7.35 (ddd, 2 H, J=7.5 Hz, J=4.8 Hz, J=1.3 Hz), 7.89 (ddd, 2 H, J=8.0 Hz, J=7.5 Hz, J= 1.8 Hz), 8.04 (dd, 1 H, J=7.9 Hz, J=7.7 Hz), 8.63 (d, 2 H, J=0.8 Hz), 8.67 (ddd, 2 H, J=8.0 Hz, J=1.3 Hz, J=0.9 Hz), 8.67 (d, 2 H, J=7.8 Hz), 8.71 (ddd, 2 H, J=4.8 Hz, J=1.8 Hz, 0.9 Hz), 8.77 (d, 2 H, J=0.8 Hz) ppm. - ^{13}C NMR (CD_2Cl_2, 100 MHz, DEPT): δ = 10.20 (6 C, -), 13.89 (6 C, +), 27.75 (6 C, -), 29.52 (6 C, -), 121.50 (2 C, +), 121.52 (2 C, +), 123.87 (2 C, +), 129.18 (2 C, +), 129.33 (2 C, +), 137.07 (2 C, +), 137.93 (1 C, +), 149.50 (2 C, +), 153.73 (2 C, 0), 153.83 (2 C, 0), 156.48 (2 C, 0), 156.62 (2 C, 0), 157.29 (2 C, 0). - FD MS (CH_2Cl_2); m/z (%): 1022 (<5) [M^+ - H + C_4H_9], 966 (<40) [M^+], 908 (100) [M^+ - C_4H_9], 599 (<5) [(M + 2 $Sn(C_4H_9)_2)^{2+}$], 455 (<5) [(M - $C_4H_9)^{2+}$], 425 (<15) [(M + H - 2 $C_4H_9)^{2+}$]. - $C_{49}H_{69}N_5Sn_2$ (965.5): calcd. C 60.95, H 7.20, N 7.25; found C 61.05, H 7.34, N 7.29.

4',4''''-Bis-tributylstannyl-[2,2';6',2'';6'',2''';6''',2'''';6'''',2''''']sexipyridine (**5e**): Following the *general procedure* **3e** (1.50 g, 3.20 mmol) and ethynyltributyltin (4.04 g, 12.8 mmol) in 30 ml 1,2-dichlorobenzene were heated at 180°C for 24 h. After suction filtration 1.19 g (2.54 mmol) of **3e** were recovered. The recovered **3e** was again treated with 3.20 g (10.2 mmol) of ethynyltributyltin for 72 h. After suction filtration, evaporating of the solvent, dissolving of the residue in dichloromethane and treating of the solution with methanol until it became cloudy, cooling over solid carbon dioxide yielded 1.91 g (1.83 mmol) of **5e**, colourless crystals, m.p. 143-146°C. - IR (KBr): $\tilde{\nu}$ = 3050, 2960, 2930, 2860, 1585, 1560, 1550, 1525, 1465, 1440, 1370, 1270, 1115, 805, 790, 735, 655 cm^{-1}. - ^1H NMR (CD_2Cl_2, 400 MHz): δ = 0.95 (t, 18 H, J=7.2 Hz), 1.12 - 1.32 (m, 12 H), 1.34 - 1.52 (m, 12 H), 1.54 - 1.80 (m, 12 H), 7.35 (ddd, 2 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.89 (ddd, 2 H, J=8.0 Hz, J=7.5 Hz, J= 1.9 Hz), 8.06 (dd, 1 H, J=7.8 Hz, J=7.8 Hz), 8.63 (d, 2 H, J=0.8 Hz), 8.67 (ddd, 2 H, J=8.0 Hz, J=1.2 Hz, J=0.9 Hz), 8.70 (dd, 2 H, J=7.8 Hz, J=1.1 Hz), 8.71 (ddd, 2 H, J=4.8 Hz, J=1.9 Hz, 0.9 Hz), 8.73 (dd, 2 H, J=7.8 Hz, J=1.1 Hz), 8.88 (d, 2 H, J=0.8 Hz) ppm. - ^{13}C NMR (CD_2Cl_2, 100

MHz, DEPT): δ = 10.31 (6 C, -), 13.85 (6 C, +), 27.83 (6 C, -), 29.57 (6 C, -), 121.06 (2 C, +), 121.56 (2 C, +), 121.58 (2 C, +), 123.92 (2 C, +), 129.46 (2 C, +), 129.55 (2 C, +), 137.11 (2 C, +), 138.11 (2 C, +), 149.54 (2 C, +), 153.72 (2 C, 0), 153.85 (2 C, 0), 155.55 (2 C, 0), 155.90 (2 C, 0), 156.57 (2 C, 0), 157.34 (2 C, 0). - FD MS (CH_2Cl_2); m/z (%): 1099 (<5) [M^+ + C_4H_9], 1044 (<5) [M^+], 986 (100) [M^+ + H], 639 (<5) [M^+ - $Sn(C_4H_9)_3$ - C_4H_9], 465 (<5) [M^+ - 2 $Sn(C_4H_9)_3$]. - $C_{54}H_{72}N_6Sn_2$ (1042.6): calcd. C 62.20, H 6.96, N 8.06; found C 61.88, H 6.93, N 7.90.

General procedure for the bromination to ***7a-e****:* The organotin compound **5** 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 r.t.. The solvent was removed under reduced pressure and the residue purified as described. Reaction conditions are described in Table 3.

4'-Bromo-[2,2';6',2'';6'',2'''}quaterpyridine (**7a**)*:* Following the *general procedure* **5a** (957 mg, 1.60 mmol) and bromine (98.0 µl, 306 mg, 1.93 mmol) in chloroform (10 ml each) yielded after evaporation of the solvent and recrystallization from methanol 346 mg (888 µmol, 56%) of **7a**, colourless crystals, m.p. 198-199°C. - IR (KBr): $\tilde{\nu}$ = 3080, 3060, 1580, 1550, 1540, 1460, 1425, 1380, 1370, 1260, 1070, 980, 870, 770 cm^{-1}. - ^1H NMR (CD_2Cl_2, 400 MHz): δ = 7.38 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.40 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.91 (ddd, 1 H, J=8.0 Hz, J=7.5 Hz, J= 1.8 Hz), 7.92 (ddd, 1 H, J=8.0 Hz J=7.5 Hz, J=1.8 Hz), 8.03 (dd, 1 H, J=7.8 Hz, J=7.8 Hz), 8.53 (dd, 1 H, J=7.8 Hz, J=1.1 Hz), 8.64 (ddd, 1 H, J=8.0 Hz, J=1.2 Hz, J=0.9 Hz), 8.65 (dd, 1 H, J=7.8 Hz, J=1.1 Hz), 8.67 (ddd, 1 H, J=8.0 Hz, J=1.2 Hz, J=1.0 Hz), 8.70 (ddd, 1 H, J=4.8 Hz, J=1.8 Hz, 0.9 Hz), 8.70 (d, 1 H, J=1.9 Hz), 8.71 (ddd, 1 H, J=4.8 Hz, J=1.8 Hz, J=1.0 Hz), 8.84 (d, 1 H, J=1.9 Hz) ppm. - EI MS (70 eV); m/z (%): 388 (100) [M^+], 360 (7) [M^+ - N_2], 309 (66) [M^+ - Br], 280 (3) [M^+ - N_2 -Br], 230 (10) [M^+ - Br - C_5H_4N - H], 205 (28) [M^+ - Br - $C_6H_4N_2$], 194 (7) [M^{2+}], 155 (25) [$C_{10}H_7N_2^+$], 154.5 (2) [(M - Br)$^{2+}$], 128 (22) [$C_{10}H_7N_2^+$ - HCN], 78 (38) [$C_5H_4N^+$], 51.1 (7) [$C_5H_4N^+$ - HCN]. - $C_{20}H_{13}N_4Br$ (389.3): calcd. C 61.71, H 3.37, N 14.39; found C 61.49, H 3.38, N 14.15.

4',4''-Dibromo-[2,2';6',2'';6'',2'''}quaterpyridine (**7b**)*:* Following the *general procedure* **5b** (0.52 g, 0.59 mmol) and bromine (80.0 µl, 0.25 g, 1.56 mmol) in chloroform (10 ml each) yielded after evaporation of the solvent and recrystallization from DMSO 80.4 mg (172 µmol, 29%) of **7b**, colourless needles, m.p. 317-321°C. - IR (KBr): $\tilde{\nu}$ = 3060, 3040, 1580, 1540,

1460, 1370, 1360, 1260, 1060, 980, 860, 780, 730, 680 cm^{-1}. - ^1H NMR (DMSO-d_6, 400 MHz, 120°C): δ = 7.50 (ddd, 2 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 8.02 (ddd, 2 H, J=8.0 Hz, J=7.5 Hz, J= 1.8 Hz), 8.58 (ddd, 2 H, J=8.0 Hz, J=1.2 Hz, J=1.0 Hz), 8.64 (d, 2 H, J=1.9 Hz), 8.72 (ddd, 2 H, J=4.8 Hz, J=1.8 Hz, 1.0 Hz), 8.73 (d, 2 H, J=1.9 Hz) ppm. - EI MS (70 eV); m/z (%): 468 (100) [M^+], 440 (5) [M^+ - N_2], 387 (42) [M^+ - Br], 308 (8) [M^+ - 2 Br], 283 (19) [M^+ - Br - $C_6H_4N_2$], 260 (5) [$C_{11}H_6BrN_3$ + H], 234 (8) [M^{2+}], 233 (9) [$C_{10}H_6BrN_2^+$], 203 (12) [M^+ - 2 Br - $C_6H_4N_2$], 193.5 (2) [(M - Br)$^{2+}$], 154 (14) [$C_{10}H_6N_2^+$], 128 (36) [$C_{10}H_7N_2^+$ - HCN], 104 (2) [$C_6H_4N_2^+$], 78 (53) [$C_5H_4N^+$], 51.1 (9) [$C_5H_4N^+$ - HCN]. - $C_{20}H_{12}Br_2N_4$ (468.2): calcd. C 51.31, H 2.58, N 11.97; found C 51.11, H 2.76, N 11.81.

4'-Bromo-[2,2';6',2'';6'',2''';6''',2''''']quinquepyridine (**7c**): Following the *general procedure* **5c** (399 mg, 590 µmol) and bromine (36.0 µl, 112 mg, 708 µmol) in chloroform (10 ml each) yielded after evaporation of the solvent and recrystallization from methanol 152 mg (327 µmol, 55%) of **7c**, colourless crystals, m.p. 213-214°C. - IR (KBr): ν = 3080, 3050, 3000, 1555, 1545, 1460, 1420, 1385, 1265, 1070, 805, 770, 735 cm^{-1}. - ^1H NMR (CD_2Cl_2, 400 MHz): δ = 7.37 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.40 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.91 (ddd, 1 H, J=8.0 Hz, J=7.5 Hz, J=1.8 Hz), 7.92 (ddd, 1 H, J=8.0 Hz J=7.5 Hz, J=1.8 Hz), 8.06 (dd, 1 H, J=7.8 Hz, J=7.8 Hz), 8.09 (dd, 1 H, J=7.8 Hz, J=7.8 Hz), 8.52 (dd, 1 H, J=7.8 Hz, J=1.1 Hz), 8.66 (ddd, 1 H, J=8.0 Hz, J=1.2 Hz, J= 1.0 Hz), 8.68 (ddd, 1 H, J=8.0 Hz, J=1.2 Hz, J= 1.0 Hz), 8.69 (dd, 1 H, J=7.8 Hz, J=1.1 Hz), 8.71 (ddd, 1 H, J=4.8 Hz, J=1.8 Hz, J=1.0 Hz), 8.71 (ddd, 1 H, J=4.8 Hz, J=1.8 Hz, J=1.0 Hz), 8.72 (dd, 1 H, J=7.8 Hz, J=1.1 Hz), 8.72 (d, 1 H, J=1.8 Hz), 8.74 (dd, J=7.8 Hz, J=1.1 Hz), 8.88 (d, 1 H, J=1.8 Hz) ppm. - EI MS (70 eV); m/z (%): 466 (100) [M^+], 437 (4) [M^+ - N_2], 386 (36) [M^+ - Br], 282 (20) [M^+ - Br - $C_6H_4N_2$], 233 (5) [M^{2+}], 232 (13) [$C_{15}H_{10}N_3^+$], 205 (7) [$C_{15}H_{10}N_3^+$ - HCN], 193 (3) [(M - Br)$^{2+}$], 155 (15) [$C_{10}H_7N_2^+$], 128 (14) [$C_{10}H_7N_2^+$ - HCN], 78 (19) [$C_5H_4N^+$], 51.1 (2) [$C_5H_4N^+$ - HCN]. - $C_{25}H_{16}BrN_5$ (465.8): calcd. C 64.46, H 3.46, N 15.04; found C 64.13, H 3.62, N 14.91.

4',4'''-Dibromo-[2,2';6',2'';6'',2''';6''',2''''']quinquepyridine (**7d**): Following the *general procedure* **5d** (285 mg, 296 µmol) and bromine (40.0 µl, 125 mg, 781 µmol) in chloroform (5 ml each) yielded after evaporation of the solvent and recrystallization from DMSO 99.6 mg (183 µmol, 62%) of **7d**, colourless crystals, m.p. 320-323°C. - IR (KBr): ν = 3060, 3010, 1580, 1540, 1470, 1380, 1320, 1270, 1100, 1070, 1050, 990, 870, 810, 780, 750, 730, 650 cm^{-1}. - ^1H NMR (DMSO-d_6, 120°C, 400 MHz): δ = 7.50 (ddd, 2 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 8.00 (ddd, 2 H, J=8.0 Hz, J=7.5 Hz, J= 1.8 Hz), 8.21 (dd, 1 H, J=8.0 Hz, J=7.6 Hz), 8.58 (ddd, 2 H, J=8.0 Hz, J=1.2 Hz, J=1.0 Hz), 8.61 (d, 2 H, J=1.8 Hz), 8.66 (d, 2 H, J=7.8 Hz), 8.73 (ddd, 2 H, J=4.8 Hz, J=1.8 Hz, 1.0 Hz), 8.75 (d, 2 H, J=1.8 Hz) ppm. - EI MS (70 eV); m/z (%): 545 (100) [M^+], 517 (3) [M^+ - N_2], 464 (22) [M^+ - Br], 388 (2) [M^+ - Br - C_5H_4N], 387 (5) [M^+ - 2 Br], 360 (12)

[M^+ - Br - $C_6H_4N_2$], 310 (9) [M^+ - Br - $C_{10}H_7N_2$], 272 (2) [M^{2+}], 233 (7) [$C_{10}H_6BrN_2^+$], 232 (5) [(M - Br)$^{2+}$], 180 (1) [$C_{11}H_6N_3^+$], 154 (9) [$C_{10}H_6N_2^+$], 128 (30) [$C_{10}H_7N_2^+$ - HCN], 104 (2) [$C_6H_4N_2^+$], 78 (34) [$C_5H_4N^+$], 51.1 (4) [$C_5H_4N^+$ - HCN]. - $C_{25}H_{15}Br_2N_5$ (545.2): calcd. C 55.07, H 2.77, N 12.84; found C 54.78, H 2.92, N 12.67.

4',4''''-Dibromo-[2,2';6',2'';6'',2''';6''',2'''';6'''',2''''']sexipyridine (**7e**): Following the *general procedure* **5e** (521 mg, 500 µmol) and bromine (56.3 µl, 176 mg, 1.10 mmol) in chloroform (10 ml each) yielded after evaporation of the solvent and recrystallization from DMSO 285 mg (415 µmol, 83%) of **7e**, colourless needles, m.p. 374-378°C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3080, 3050, 1550, 1475, 1445, 1390, 1275, 1075, 810, 790, 780 cm^{-1}. - EI MS (70 eV); m/z (%): 622 (100) [M^+], 543 (68) [M^+ - Br], 465 (5) [M^+ - Br - C_5H_4N], 462 (5) [M^+ - 2 Br], 437 (7) [M^+ - Br - C_5H_4N - N_2], 387 (6) [M^+ - Br - 2 C_5H_4N], 311 (21) [M^{2+}], 272 (4) [(M - Br)$^{2+}$], 230 (5) [$C_{15}H_8N_3^+$], 203 (3) [$C_{15}H_8N_3^+$ - HCN], 155 (4) [$C_{10}H_7N_2^+$], 128 (30) [$C_{10}H_7N_2^+$ - HCN], 78 (12) [$C_5H_4N^+$]. - $C_{30}H_{18}Br_2N_6$ (622.3): calcd. C 57.90, H 2.92, N 13.50; found C 57.71, H 3.06, N 13.44. Compound **7e** is too insoluble for ^{1}H NMR spectroscopy.

General procedure for the synthesis of branched oligopyridines ***8a-e***: $Pd(PPh_3)_4$ (13-23 mol%) was dissolved in 5 ml toluene. The 4-bromo-oligopyridine **7** was added and the reaction mixture stirred for 5 min. After this period the tributyltin compound **5** (60 mmol) in 5 ml toluene was added and the reaction mixture heated to reflux for the time indicated in Table 4. In most cases the precipitation of palladium indicated the end of the reaction. After filtration and stripping off the solvent the residue was purified by recrystallization.

6'',6'''-Di-pyridin-2-yl-[2,2';6',2'';4'',4''';2''',2'''';6'''',2''''']sexipyridine (**8a**): Following the *general procedure* **5a** (111 mg, 186 µmol), **7a** (68.4 mg, 176 µmol) and $Pd(PPh_3)_4$ (27.3 mg, 24.0 µmol) yielded after suction filtration of the precipitate and recrystallization from chloroform (hot filtration to separate from precipitated palladium) 90.9 mg (147 µmol, 83%) of **8a**, colourless crystals, m.p. 324-327°C (decomp). - IR (KBr): $\tilde{\nu}$ = 3050, 3000, 1570, 1550, 1530, 1470, 1450, 1420, 1380, 1270, 1070, 780, 730 cm^{-1}. - ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 7.30 (ddd, 2 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.41 - 7.45 (m, 2 H), 7.65 (ddd, 2 H, J=7.9 Hz, J=7.5 Hz, J= 1.8 Hz), 7.94 - 7.99 (m, 2 H), 8.09 (dd, 2 H, J=7.8 Hz, J=7.8 Hz), 8.57 (dd, 2 H, J=7.8 Hz, J=1.1 Hz), 8.69 - 8.81 (m, 10 H), 9.03 (d, 2 H, J=1.8 Hz), 9.20 (d, 2 H, J=1.8 Hz) ppm. - PI SIMS (Cs^+, CH_2Cl_2, NBA); m/z (%): 620 (100) [MH^+]. - $C_{40}H_{26}N_8$ (618.7): calcd. C 77.65, H 4.24, N 18.11. found C 77.46, H 4.51, N 17.84.

6''',6''''-Di-pyridin-2-yl-[2,2';6',2'';6'',2''';4''',4'''';2'''',2''''';6''''',2'''''';6'''''',2''''''']octapyridine (**8b**): Following the *general procedure* **5c** (116 mg, 172 µmol), **7c** (79.9 mg, 172 µmol) and $Pd(PPh_3)_4$ (29.6 mg, 25.6 µmol) yielded after suction filtration of the precipitate and recrystallization from 1,2-dichlorobenzene 87.3 mg (113 µmol, 66%) of **8b**, colourless crystals, m.p. 381-385°C (decomp). - IR (KBr): $\tilde{\nu}$ = 3050, 3000, 1565, 1550, 1525, 1460, 1440, 1430, 1415, 1375, 1270, 1065, 800, 775, 765, 740, 730 cm^{-1}. - ^1H NMR (CF_3CO_2D, 400 MHz): δ = 8.20 - 8.27 (m, 2 H), 8.30 - 8.36 (m, 2 H), 8.57 - 8.64 (m, 2 H), 8.69 - 8.77 (m, 4 H), 8.86 - 8.91 (m, 4 H), 8.93 - 9.03 (m, 6 H), 9.05 - 9.17 (m, 8 H), 9.19 - 9.26 (m, 4 H) ppm. - PI SIMS (Cs^+, CF_3CO_2H, glycerine); m/z (%): 775 (100) [MH_2^+], 774 (<95) [MH^+]. - $C_{50}H_{32}N_{10}$ (772.9): calcd. C 77.70, H 4.17, N 18.13. found C 77.42, H 4.23, N 17.89.

6'',6''',6'''',6'''''-Tetra-pyridin-2-yl-[2,2';6',2'';4'',4''';2''',2'''';4'''',4''''';2'''''2''''''; 6'''''',2''''''']octapyridine (**8c**): Following the *general procedure* **5b** (158 mg, 178 µmol), **7a** (141 mg, 363 µmol) and $Pd(PPh_3)_4$ (43.2 mg, 37.0 µmol) yielded after suction filtration of the precipitate and recrystallization from 1,2-dichlorobenzene (hot filtration to separate from precipitated palladium) 109 mg (118 µmol, 66%) of **8c**, colourless crystals, m.p. 352-355°C (decomp). - IR (KBr): $\tilde{\nu}$ = 3040, 3000, 1570, 1550, 1530, 1460, 1450, 1370, 770, 730 cm^{-1}. - ^1H NMR (CF_3CO_2D, 400 MHz): δ = 8.12 - 8.23 (m, 4 H), 8.26 - 8.32 (m, 2 H), 8.47 - 8.58 (m, 4 H), 8.78 - 9.04 (m, 20 H), 9.05 - 9.11 (m, 2 H), 9.11 - 9.17 (m, 2 H), 9.25 -9.33 (m, 2 H), 9.33 - 9.42 (m, 2 H) ppm. - PI SIMS (Cs^+, CF_3CO_2H, glycerine); m/z (%): 929 (100) [MH_2^+], 928 (<90) [MH^+]. - $C_{60}H_{38}N_{12}$ (927.0): calcd. C 77.74, H 4.13, N 18.13. found C 77.52, H 4.19, N 17.97.

6'',6''',6''''',6''''''-Tetra-pyridin-2-yl-[2,2';6',2'';4'',4''';2''',2'''';6'''',2''''';4''''', 4'''''';2''''''',2'''''''',6'''''''',2''''''''']nonapyridine (**8d**): Following the *general procedure* **5d** (74.1 mg, 77.0 µmol), **7a** (59.1 mg, 152 µmol) and $Pd(PPh_3)_4$ (21.1 mg, 18.0 µmol) yielded after suction filtration of the precipitate and recrystallization from 1,2-dichlorobenzene (hot filtration to separate from precipitated palladium) 34.2 mg (34.1 µmol, 44%) of **8d**, colourless crystals, m.p. 290-294°C (decomp). - IR (KBr): $\tilde{\nu}$ = 3110, 3040, 1570, 1555, 1525, 1460, 1370, 775, 730, 625 cm^{-1}. - ^1H NMR (CF_3CO_2D, 400 MHz): δ = 8.14 - 8.21 (m, 2 H), 8.26 - 8.34 (m, 4 H), 8.46 - 8.57 (m, 4 H), 8.78 - 8.87 (m, 4 H), 8.88 - 9.19 (m, 25 H), 9.29 - 9.32 (m, 2 H) ppm. - PI SIMS (Cs^+, CF_3CO_2H, glycerine); m/z (%): 1006 (100) [MH_2^+], 1005 (<80) [MH^+]. - $C_{65}H_{41}N_{13}$ (1004.1): calcd. C 77.75, H 4.12, N 18.13. found C 77.48, H 4.42, N 17.94.

6'',6''',6'''''',6''''''',6'''''''-Tetra-pyridin-2-yl-[2,2';6',2'';4'',4''';2''',2'''';6'''',2''''';6''''',2''''''';4''''''',4'''''''',2'''''''',2'''''''';6'''''''',2''''''''']decapyridine (**8e**): Following the *general procedure* **5e** (134 mg, 129 µmol), **7a** (100 mg, 257 µmol) and $Pd(PPh_3)_4$ (34.2 mg, 29.6 µmol) yielded after suction filtration of the precipitate and recrystallization from 1,2-dichlorobenzene (hot filtration to separate from precipitated palladium) 66.0 mg (61.0 µmol, 47%) of **8e**, colourless crystals, m.p. 425-430°C (decomp). - IR (KBr): $\tilde{\nu}$ = 3060, 3000, 1580, 1560, 1540, 1470, 1450, 1430, 1385, 1080, 815, 790, 750, 740, 665, 635 cm^{-1}. - ^1H NMR (CF_3CO_2D, 400 MHz): δ = 8.12 - 8.19 (m, 2 H), 8.24 - 8.32 (m, 4 H), 8.43 - 8.50 (m, 2 H), 8.51 - 8.56 (m, 2 H), 8.75 - 9.05 (m, 24 H), 9.07 - 9.20 (m, 8 H), 9.24 -9.28 (m, 2H) ppm. - PI SIMS (Cs^+, CF_3CO_2H, glycerine); m/z (%): 1083 (100) [MH_2^+], 1082 (<70) [MH^+]. - $C_{70}H_{50}N_{14}$ (1081.2): calcd. C 77.76, H 4.10, N 18.14. found C 76.98, H 4.22, N 17.95.

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REFERENCES

[1] Pabst GR, Pfüller OC, Sauer J. Tetrahedron 1999; **preceding paper.**
[2] Pabst GR, Sauer J. Tetrahedron Lett. 1998; 39: 6687-6690.
[3] Pabst GR, Schmid K, Sauer J. Tetrahedron Lett. 1998; 39: 6691-6694.
[4] Pabst GR, Sauer J. Tetrahedron Lett. 1998; 39: 8817-8820.
[5] Pfüller OC, Sauer J. Tetrahedron Lett. 1998; 39: 8821-8824.
[6] Pabst GR, Pfüller OC, Sauer J. Tetrahedron Lett. 1998; 39: 8825-8828.
[7] Sauer J, Heldmann DK, Tetrahedron Lett. 1998; 39: 2549-2552.
[8] Sauer J, Heldmann DK, Pabst GR. Eur. J. Org. Chem. 1999: 313-321.
[9] Pereyre M, Quintard JP, Rahm A. Tin in Organic Synthesis, Butterworths: London, 1987.
[10] Davies AG. Organotin Chemistry, Weinheim: VCH, 1997.
[11] Stille JK, Angew. Chem. 1986; 98: 504-519. Angew. Chem. Int. Ed. Engl. 1986; 25: 508-523.
[12] Farina V, Krishnamurthy V, Scott WJ. The Stille Reaction, New York: John Wiley & Sons, 1998.
[13] Constable EC. Metals and Ligands, Weinheim: VCH, 1996.
[14] Lehn JM. Supramolecular Chemistry - Concepts and Perspectives, Weinheim: VCH, 1995.
[15] Neunhoeffer H. 1,2,4-Triazines and their Benzo-Derivatives, Comprehensive Heterocyclic Chemistry II, Katritzky AR, Rees CW, Scriven EFV, editors, Oxford: Pergamon Press, 1996; 6: 507-574.
[16] Culbertson BM, Parr GR. J. Heterocyclic Chem. 1967, 4: 422-424.
[17] Neunhoeffer H, Motitschke L, Henning H, Ostheimer K. Liebigs Ann. Chem. 1972; 760: 88-101.
[18] Schank K. Chem. Ber. 1969; 102: 383-387.
[19] Case FH. J. Org. Chem. 1966; 31: 2398-2400
[20] Dedichen G. Avhandl. Norske Videnkaps-Akad. Oslo, I, Mat-Naturv. Klasse 1936, No. 5.

[21] Case FH. J. Heterocyclic Chem. 1971; 8: 1043-1046.
[22] Sauer J. 1,2,4,5-Tetrazines, Comprehensive Heterocyclic Chemistry II, Katritzky AR, Rees CW, Scriven EFV, editors, Oxford: Pergamon Press, 1996; 6: 901-957.
[23] Constable EC, Heirtzler F, Neuburger M, Zehnder M. J. Am. Chem. Soc., 1997; 119: 5606-5517.
[24] For a general survey over the 'LEGO' System see: Pabst GR. Das neue und einfache 'LEGO'-System zur Synthese von Oligopyridinen, Ph.D. Thesis, University of Regensburg 1999.
[25] Pfüller OC. Ein neues 'LEGO' System zur Darstellung von Oligopyridinen, Ph.D. Thesis, University of Regensburg 1999.
[26] Newcome GR, Hager DC, Kiefer GE. J. Org. Chem. 1986; 51: 850-853.
[27] Renaldo AF, Labadie JW, Stille JK. Org. Synth. Coll. Vol. VIII, John Wiley & Sons, New York, 1993: 268-274.
[28] Coulson DR. Inorg. Synth. XIII, McGraw-Hill, New York, 1972: 121-124.
[29] Lau SKY, Wang PK, Stille JK. J. Am. Chem. Soc., 1976; 98: 5832-5849.