5,5″-Disubstituted 2,2′:6′,2″-Terpyridines through and for Metal-Mediated Cross-Coupling Chemistry

Uwe Lehmann, Oliver Henze, and A. Dieter Schlüter*[a]

Abstract: The 0.3 – 5 g scale syntheses of the 2,2′:6′,2″-terpyridines **3**, **6**, **9**, and **10** are described. The pyridine units are connected to one another by Pd-catalyzed cross-coupling reactions. This method allows the easy introduction of halogen, stannyl, and boronic ester functionalities at positions C-5 and C-5″; this results in a novel functionality pattern for terpyridines that considerably widens the applicability of this class of tridentate ligands for supra- and macromolecular applications. The feasibility of growth reactions with these novel terpyridines was demonstrated by the synthesis of compounds **12a – c**.

Keywords: cross-coupling · modular chemistry · supramolecular chemistry · terpyridines

Introduction

We have recently reported on repetitive syntheses of oligophenylene hexagons with up to 24[1] phenylene rings that make these compounds available at a reasonable quantity/effort relationship. The main motivation for this research is a) to approach extended honeycomblike, two-dimensional networks for which these shape persistent, geometrically regular molecules may serve as constituents,[2] and b) to apply the developed methodology to the synthesis of shape-persistent macrocycles with integral donor moieties like 2,2′:6′,2″-terpyridine for subsequent transition metal complexation and supramolecular assembly.[3] The present contribution describes the synthesis of a number of terpyridine building blocks that carry chloro-, bromo-, trimethylstannyl- (in situ), and boronic acid ester functions at C-5 and C-5″ and some of them hexoxymethyl or methoxy(ethoxy)methoxymethyl [(MEM)OCH_2] substituents at C-4′. Some further growth reactions with these terpyridines that lead to immediate starting materials for ring closure reactions are also reported.

Results and Discussion

Terpyridines to be used for the outlined project need a) to be functionalized in a way that they can be used as building blocks in Stille[4] and Suzuki-type transition metal catalyzed cross-coupling reactions,[5] b) to open up the possibility to construct a variety of differently sized rings, c) to allow for optimum complexation with transition metals, d) to be soluble also when integrated into larger structures, and (e) to have the potential to decorate the targeted rings in their periphery with some relevant groups. To meet these criteria the following measures seemed appropriate: For a) dihalo, distannyl (in situ), and diboronic functionalities, for b) and c) attachment of these functionalities at C-5 and C-5″, for d) flexible chains at C-4′,[6] and for e) the selection of such chains at C-4′ that allow them to be used as anchor groups after modification (deprotection).

The incorporation of the coupling functionalities at C-5 and C-5″ (point b and c) should be addressed because of the many terpyridines known,[7] those with a C-5, C-5″ substitution pattern are the least common ones. Additionally, neither of the present functionality patterns has ever been realized at these positions. Two important reasons, nevertheless, led us to undertake the considerable synthetic effort: First, to allow for a variable linear extension of the two outer pyridine units of the terpyridine into what later will become the side of an hexagonal cycle, and, second, to account for the observation[8] that complexation of terminally substituted terpyridines in some cases proceed better if their substitutents are at C-5 and C-5″ and not at C-6 and C-6″.[9]

The synthetic routes are summarized in Schemes 1 – 4. Scheme 1 describes the syntheses of the central dibromo pyridines **1e** and **1f** and the coupling of **1a** and **1e** with the tin component **2b** to give dichloroterpyridines **3a** and **3e**. Scheme 2 describes the opposite approach, which involves the synthesis of the central pyridine unit **4a**, **e**, and **f** with two trimethyltin (TMSn) groups (**4e** and **4f** in situ) and their coupling with bromochloropyridine **2a** (done for **4a** only) to

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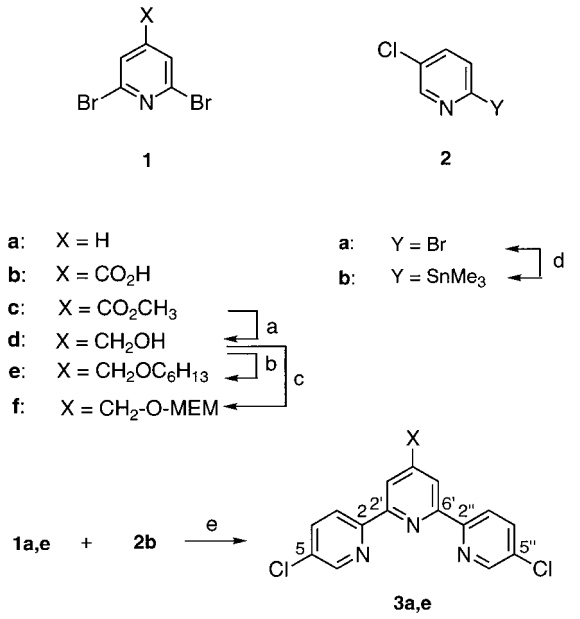
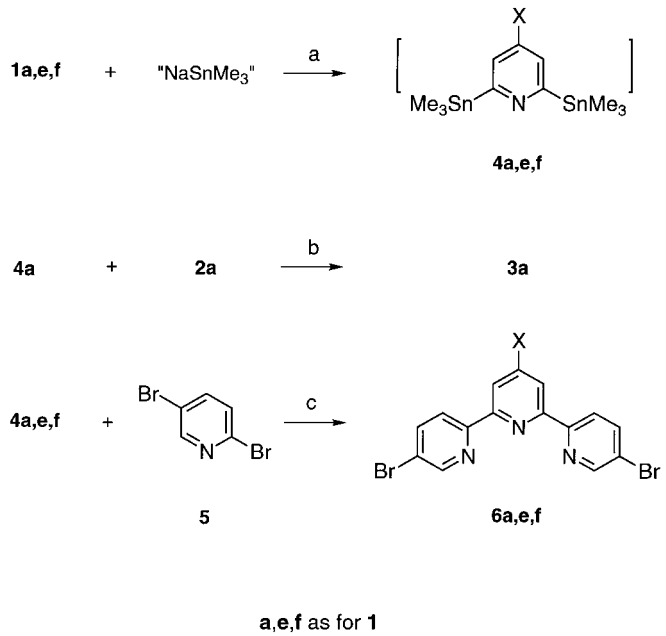


Scheme 1. a) LAH, THF, −20 °C, 58.1 %; b) TfOTf, NEt_3, CH_2Cl_2, 0 °C, then: $C_6H_{13}OH$, 20 °C, 78.7 %; c) MEMCl, $N(iPr)_2Et$, CH_2Cl_2, 20 °C, 69.9 %; d) BuLi, Me_3SnCl, −78 °C, Et_2O, 47.7 %; e) $Pd(PPh_3)_4$, toluene, reflux, **3a**: 65.1 %, **3e**: 68.6 %.



a,**e**,**f** as for **1**

Scheme 2. a) $NaSnMe_3$, 0 °C, DME; b) $Pd(PPh_3)_4$, toluene, reflux, 44.4 %; c) $Pd(PPh_3)_4$, toluene, reflux, **6a**: 26.5 %, **6e**: 13.8 %, **6f**: 26.4 %.

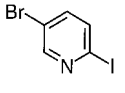
give dichloroterpyridine **3a** and with 2,5-dibromo pyridine **5** to give dibromoterpyridines **6a**, **e**, and **f**. The sequence in Scheme 3 also uses the distannyl pyridine **4a**, but converts this now into terpyridine **9** which carries two boronic acid ester functions, and Scheme 4 provides an example in which two of the novel terpyridines, **9** and **10**, are used for further extension.

The syntheses of **1e** and **1f** (Scheme 1) starts from 2,6-dibromopyridine-4-carboxylic acid (**1b**)[10], which was esterified to give **1c**[11], which in turn was reduced with LAH to afford **1d.**[12] Whereas the conversion of **1d** into **1f** could easily be achieved by normal protecting-group chemistry, the conversion into **1e** had to be done via the corresponding triflate intermediate (not shown). The presence of free alkoxide otherwise led to an effective competition for the nucleophiles by the reactive C-2 position of **1d**. The tin component **2b**, prepared by electrophilic stannylation via the corresponding bromochloropyridine (**2a**), was lithiated at C-2.[13, 14] The coupling between the central pyridines **1a** and **1e** and tin compound **2b** was achieved by the normal Stille procedure with 4 mol % of $Pd[(PPh_3)_4]$.[15]

The central pyridines **4e** and **4f** with two TMSn groups were synthesized by nucleophilic stannylation (Scheme 2) in analogy to the known synthesis of **4a**.[16, 17] Except for **4a** the distannyls **4** were not isolated, but rather used in situ.[18] The coupling of **4a** with **2a** to give **3a** (method B, see Experimental Section) proceeded in yields comparable with the opposite reaction between **1a** and **2b** (method A) leading to the same compound (Scheme 1). Judged by the overall synthetic effort, the latter route (method A) is somewhat more convenient. Dibromoterpyridines **6a**, **e**, and **f** were obtained by Stille coupling between 2,5-dibromopyridine (**5**) and **4a**, **4e**, and **4f**, respectively; these reactions proceeded with yields of 22.8–32.6 % from the stannyl compounds and more accurately 15.5–26.4 % for the two steps from the corresponding pyridines **1**. The coupling of **4e** with **5** was difficult to reproduce for unknown reasons. In the worst case, the yield of the corresponding terpyridine **6e** is only 8 %. It could nevertheless be obtained in amounts of 150–300 mg per run. Terpyridines **6a** and **6f** were obtained on the 2.5–5 g scale. A reason for the moderate coupling yields may be the occurance of some homocoupling of **5**. This took place at C-2 and gave 5,5′-dibromo-2,2′-bipyridine (see below).

The proposed regiochemical course of the coupling of **4e** and **5** (with its two bromo functions) was verified by a control experiment to make sure that the terpyridine obtained had the proposed 2,2′:6′,2″ and not 3,2′:6′,3″ connectivity. Pyridine **4e** was coupled with compound **7**,[19] which should have a much higher reactivity at C-2 than **5**. The only isolable product was identical with the one obtained in the above reaction. Though its yield was only 8 %, this finding nevertheless establishes the proposed structure of **6e**. Additional evidence comes from NMR heternuclear correlation experiments with **6f** in which the coupling between H-3′ and C-2 can be unequivocally established. For a related experiment also supporting the proposed structure, see compound **12c**. Kumada-type coupling reactions of **5** also proceeded at C-2.[20]

The coupling of **4a** with **8** (Scheme 3) uses the fact that boronic esters (apart from boronic acids[21]) do not get involved into cross-couplings under Stille conditions, because no base is present that could saponify the ester. It proceeds with higher yields (approx. 50 %) than the couplings in Scheme 2. The synthesis of compound **8** involves the known regiospecific lithiation of **5** at C-5[22] followed by the standard procedure for the introduction of boronic acid esters.[23]



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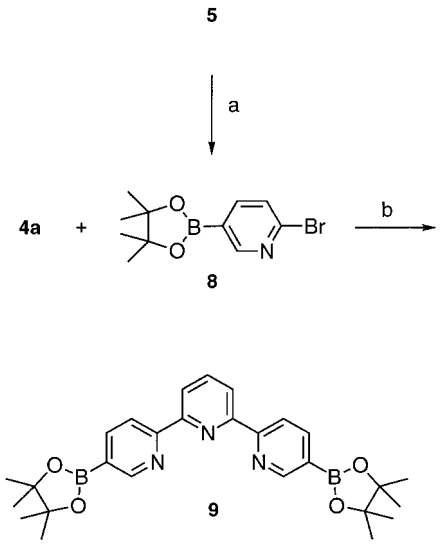
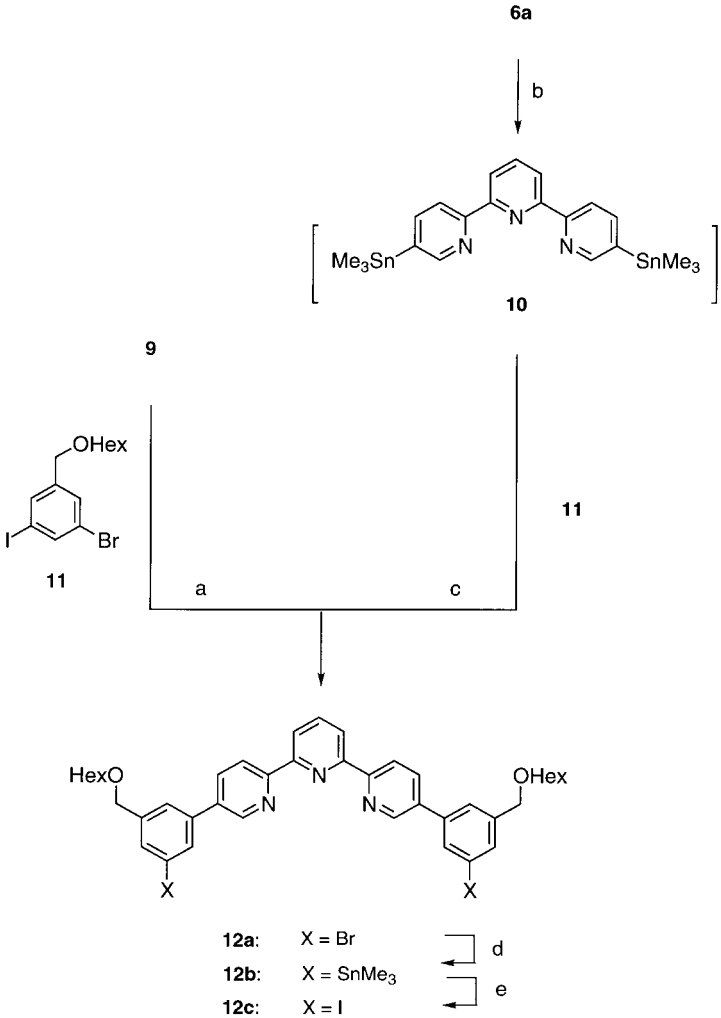
Scheme 4 shows the in situ synthesis of building block **10**, the linear extension of terpyr-



Scheme 3. a) BuLi, $B(O\text{-}iPr)_3$, Et_2O, $-78\,^{\circ}C$, then: pinacole, dioxane, 45.6%; b) $Pd(PPh_3)_4$, toluene, reflux, 55%.



Scheme 4. a) $Pd(PPh_3)_4$, toluene, 1M Na_2CO_3, reflux, 41.1%; b) $NaSnMe_3$, DME, $0\,^{\circ}C$; c) $Pd(PPh_3)_4$, toluene, reflux, 26.7%; d) $NaSnMe_3$, DME, $0\,^{\circ}C$, 61.4%; e) I_2, CH_2Cl_2, $20\,^{\circ}C$, 97.8%.

idines **9** and **10** with iodobenzene **11** to give the identical product **12a**, and, finally, the conversion of **12a** into the new building blocks **12b** and **12c**. Compound **11**[24] was selected for these couplings because it carries a flexible chain and two functional groups with a known coupling selectivity ($I \gg Br$).[25] Considering the respective synthetic effort associated with these different routes to **12a**, the coupling of **9** and **11** is to be favored. For example,the total sequence via **9** requires only one nucleophilic stannylation,[26] whereas that via **10** requires two. Furthermore compound **9** is an easy to recrystallize solid, whereas **10** is prepared and used in situ.

The conversion of building block **12a** into the others, **12b** and **12c**, went smoothly either by nucleophilic stannylation or nucleophlic stannylation followed by iododestannylation. Compounds **12** are available in amounts of 3.2 g (**12a**), 2.5 g (**12b**), and 1.2 g (**12c**). The TMSn group in **12b** serves two important functions, it can act as both a coupling functionality and a place holder for iodide.

Some further comments may be useful:

a) All Stille-type couplings to terpyridines involving C-2-substituted pyridines **2a**, **5**, and **8** were accompanied by some homocoupling of the respective pyridines to give the corresponding 2,2′-bipyridines. This unusual homocoupling, whose mechanism is not yet clear, could be substantiated by experiments in which compounds **2a**, **5**, and **8** were subjected to coupling conditions without a coupling partner present. This also led to the same homocoupling products.

b) The stannyl compounds **2b**, **4e**, **4f**, and **10**, in which the TMSn group is located at a pyridine nucleus, cannot be chromatographed through silica or alumina without at least substantial decomposition. Compound **12b**, however, which carries stannyl at phenyl, can be easily purified this way (alumina).

c) Whereas pyridine boronic ester **8** can be chromatographed, the diboronic ester tpy **9** decomposes on both silica and alumina. Fortunately it could be recrystallized from toluene.

d) NMR heternuclear correlation experiments with compound **12c** proved the coupling between H-3 and C-2′ as well as H-3′ and C-2 and thus establish the proposed regiochemical course of the reaction between **4a** and **5** (Scheme 2)

The terpyridine syntheses presented in this paper start from properly substituted pyridines that are connected to one another. In this regard our approach differs from the known syntheses[7] in which the central pyridine is built-up during the sequence by some condensation chemistry. The terminal pyridines are usually introduced starting from 2-acetylpyridines. In order to obtain the C-5, 5″ substitution pattern described here, these aldehydes would have to have a halogen function at C-5, which may be difficult to synthesize. In this regard the present strategy widens the substitution patterns available for terpyridines and complements to the known syntheses.

Experimental

General: Compounds **1a** and **5** were purchased from Aldrich or Acros. Compounds **1c**[11] and **1d**[12] are known, but were prepared alternatively. Compounds **1b**,[10] **2a**,[13] **4a**, [16] and **11**[24] were prepared according to the literature. For compounds **2b** and **7**, see references [14] and [19]. All other compounds are new.[26] $NaSnMe_3$ was prepared according to the literature.[16] All other reagents were purchased from Aldrich or Acros and used without further purification. All chromatographic separations were done

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with methylene chloride as eluent if not otherwise stated. Prior to combustion microanalysis, the terpyridines were dried in high vacuum at 20 °C for 6 h to avoid eventual problems with hydrate formation.

5-Chloro-2-trimethylstannylpyridine (**2b**): BuLi (1.6 M, 34 mL) in hexane was added dropwise to a solution of 5-bromo-2-chloropyridine (**2a**; 10.0 g, 52.0 mmol) in Et_2O (200 mL), while the temperature was kept at −78 °C. After stirring at −78 °C for 2 h a solution of trimethystannylchloride 12.42 g (62.3 mmol) in Et_2O (50 mL) was added dropwise. Then the mixture was allowed to warm up to room temperature overnight. The insoluble inorganic precipitate was removed by filtration, and the solvent was evaporated under reduced pressure. The residue was distilled to afford 6.84 g (24.79 mmol) of **2b** (47.7 %) as a colourless oil. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.32$ [s, 3H; $Sn(CH_3)$] 7.37 (d, $J_{H\text{-}3,H\text{-}4} = 8.2$ Hz, 1H; H-3), 7.49 (dd, $J_{H\text{-}4,H\text{-}6} = 2.2$ Hz, $J_{H\text{-}4,H\text{-}3} = 8.2$ Hz, 1H; H-4), 8.69 (d, $J_{H\text{-}6,H\text{-}4} = 2.2$ Hz, 1H; H-6); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 131.30$, 131.64, 133.05, 149.16, 171.02; MS (70 eV, EI): *m/z* (%): 281 (4.96), 279 (10.28), 278 (6.19), 277 (26.99), 276 (13.42), 275 (21.45), 274 (9.96), 273 (11.22) [M^+], 265 (4.28), 264 (36.82), 263 (16.75), 262 (100.00), 261 (34.75), 260 (72.85), 259 (24.09), 258 (36.83) [$M^+ - CH_3$], 234 (19.55), 233 (7.86), 232 (50.71), 231 (17.57), 230 (36.45), 229 (12.65) [$M^+ - 2CH_3$]; HRMS: *m/z* calcd for $C_8H_{12}ClNSn$ 276.96802; found 276.96832.

5,5″-Dichloro-2,2′:6′,2″-terpyridine (**3a**)

Method A: 2,6-Dibromopyridine (**1a**; 1.09 g, 4.60 mmol) and **2b** (3 g, 10.85 mmol) were dissolved in toluene (70 mL). The solution was degassed twice. Then $(Ph_3P)_4Pd$ (0.228 g, 0.197 mmol) was added and the mixture was degassed again. After the mixture was refluxed for 41 h, a saturated solution of KF (50 mL) was added, and the inorganic precipitate was filtered. The organic phase was separated, and the solvent was evaporated. The aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL). The residue and the organic layers were combined and diluted with 15 % HCl (30 mL). The solution was warmed and stirred for 5 min. The aqueos layer was separated, made alkaline with Na_2CO_3, and washed with CH_2Cl_2 (2 × 50 mL). The organic phases were combined, dried over $MgSO_4$, and evaporated to give 0.905 g of **3a** (65.1 %) as a white solid.

Method B: Compound **2a** (19.9 g, 103.3 mmol) and 2,6-bis(trimethylstannyl)pyridine (**4a**; 19.01 g, 47.0 mmol) were dissolved in toluene (400 mL). The solution was degassed twice. Then $(Ph_3P)_4Pd$ (2.17 g, 1.87 mmol) was added, and the mixture was degassed again. After the mixture was heated under reflux for 60 h, a saturated solution of KF (150 mL) was added, and the inorganic precipitate removed by filtration. The organic phase was separated, and the solvent was evaporated. The aqueous layer was extracted with CH_2Cl_2 (2 × 200 mL). The residue and the organic layers were combined and diluted with 15 % HCl (280 mL). The solution was warmed and stirred for 5 min. The aqueous layer was separated, made alkaline with Na_2CO_3, and washed with CH_2Cl_2 (300 mL). The organic phases were combined, dried over $MgSO_4$, and evaporated to give 6.3 g of **3a** (44.4 %) as a white solid, m.p. 195 °C. The same experiment was also carried out at a much smaller scale (0.457 g **4a**) and gave **3a** with higher yield (66.1 %). ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.79$ (dd, $J_{H\text{-}4,H\text{-}6} = 2.4$ Hz, $J_{H\text{-}4,H\text{-}3} = 8.6$ Hz, 2H; H-4), 7.93 (t, $J_{H\text{-}4',H\text{-}3'} = 7.8$ Hz, 1H; H-4′), 8.40 (d, $J_{H\text{-}3'H\text{-}4'} = 7.8$ Hz, 2H; H-3′), 8.52 (d, $J_{H\text{-}3,H\text{-}4} = 8.6$ Hz, 2H; H-3), 8.62 (d, $J_{H\text{-}6,H\text{-}4} = 2.4$ Hz, 2H; H-6); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 121.13$, 121.85, 132.33, 136.55, 138.08, 148.00, 154.16, 154.40; MS (80 eV, EI): *m/z* (%): 305 (10.98), 303 (64.46), 301 (100), [M^+], 268 (6.71), 266 (13.08) [$M^+ - Cl$]; HMRS: *m/z* calcd for $C_{15}H_9N_3Cl_2$ 301.017353; found 301.01809; $C_{15}H_9Cl_2N_3$ (302.15): calcd C 59.62, H 3.00, N 13.90; found C 59.79, H 3.16, N 13.34.

5,5″-Dibromo-2,2′:6′,2″-terpyridine (**6a**): Terpyridine **6a** (5.7 g, 26.5 %) was obtained from **4a** (22.24 g, 54.95 mmol), **5** (31.24 g, 131.9 mmol), and $(Ph_3P)_4Pd$ (2.53 g, 2.19 mmol) with the procedure described in method B for **3a** as a white solid, m.p. 197 °C. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.93$ (t, $J_{H\text{-}4'H\text{-}3'} = 7.8$ Hz, 1H; H-4′), 7.95 (dd, $J_{H\text{-}4,H\text{-}6} = 2.2$ Hz, $J_{H\text{-}4,H\text{-}3} = 8.4$ Hz, 2H; H-4), 8.41 (d, $J_{H\text{-}3',H\text{-}4'} = 7.8$ Hz, 2H; H-3′), 8.47 (d, $J_{H\text{-}3,H\text{-}4} = 8.4$ Hz, 2H; H-3), 8.72 (d, $J_{H\text{-}6,H\text{-}4} = 2.2$ Hz, 2H; H-6); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 121.17$, 121.23, 122.33, 138.10, 139.43, 150.18, 154.47; MS (80 eV, EI): *m/z* (%): 393 (51.13), 391 (100), 389 (53.41) [M^+], 312 (10.72), 310 (10.84), [$M^+ - Br$]; $C_{15}H_9Br_2N_3$ (391.06): calcd C 46.07, H 2.31, N 10.74; found C 45.85, H 2.40, N 10.74.

2,6-Dibromo-4-methoxycarbonylpyridine (**1c**): A solution of **1b** (53.4 g, 190.2 mmol) in MeOH (300 mL) was treated with conc. H_2SO_4 (2.4 mL) and refluxed for 16 h. After the mixture was cooled to RT, a white solid precipated. The crude product was filtered and chromatographed on silica gel with CH_2Cl_2 to afford 42.3 g of **1c** (75.4 %) as a white solid, m.p. 88–89 °C. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 3.94$ (s, 3H), 7.96 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 53.29$, 126.67, 141.42, 141.50, 162.94; MS (80 eV, EI): *m/z* (%): 297 (49.73), 295 (100.00), 294 (7.53) [M^+], 266 (16.19), 264 (30.01), 262 (15.50) [$M^+ - OCH_3$], 238 (7.24), 236 (14.58), 234 (7.56) [$M^+ - CO_2CH_3$], 216 (23.20), 214 (23.42) [$M^+ - Br$]; $C_7H_5Br_2NO_2$ (294.93): calcd C 28.50, H 1.70, N 4.74; found C 28.49, H 1.71, N 4.59.

2,6-Dibromo-4-hydroxymethylpyridine (**1d**): A suspension of $LiALH_4$ (8.13 g, 214.4 mmol) in dry THF (50 mL) was added dropwise to a solution of **1c** (97.3 g, 329.9 mmol) in THF (500 mL) over a period of 30 min at −20 °C. The mixture was allowed to warm to RT within 2 h and brine (200 mL) was added carefully. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (150 mL). The combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated in vacuum. Chromatographic separation on silica with hexane/ethyl ether (1:1) as eluent gave 51.2 g of **1d** (58.1 %) as a white solid, m.p. 110–111 °C. ^{1}H NMR (270 MHz, [D_6]DMSO): $\delta = 4.54$ (brs, 2H) 5.68 (brs, 1H), 7.60 (s, 2H); ^{13}C NMR (68 MHz, [D_6]DMSO): $\delta = 60.53$, 124.53, 139.76, 158.82; MS (80 eV, EI): *m/z* (%): 269 (48.28), 267 (100.00), 265 (50.97) [M^+], 188 (46.41), 186 (51.24) [$M^+ - Br$]; $C_6H_5Br_2NO$ (266.91): calcd C 27.00, H 1.88, N 5.24; found C 27.16, H 1.82, N 5.07.

2,6-Dibromo-4-hexoxymethylpyridine (**1e**): A mixture of **1d** (4.73 g, 17.72 mmol) and NEt_3 (2.47 mL, 17.72 mmol) in CH_2Cl_2 (40 mL) was slowly added to a solution of triflate anhydride (2.98 mL, 17.72 mmol) in dry CH_2Cl_2 (20 mL), within 45 min at 0 °C. After 15 min the mixture was treated with hexanol (50 mL) and stirred at RT for 1 h. Solvent and excess hexanol were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL) and washed with H_2O (20 mL). The organic phase was separated, dried over $MgSO_4$, and evaporated. Chromatography of the compound on silica gel gave 4.9 g of **1e** (78.7 %) as a colourless oil. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.82$ (t, $J = 6.6$ Hz, 3H), 1.24–1.35 (m, 6H), 1.56 (q, $J = 6.6$ Hz, 2H), 3.43 (t, $J = 6.6$ Hz, 2H), 4.38 (s, 2H), 7.34 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 13.92$, 22.45, 25.62, 29.37, 31.46, 69.54, 71.41, 124.68, 140.55, 153.58; MS (70 eV, EI): *m/z* (%): 353 (0.5), 351 (0.98), 349 (0.53) [M^+], 269 (2.89), 267 (5.83), 265 (3.34) [$M^+ - C_6H_{13}$+H], 253 (49.32), 251 (100.00), 249 (51.93) [$M^+ - OC_6H_{13}$+H]; $C_{12}H_{17}Br_2NO$ (351.08): calcd C 41.05, H 4.88, N 3.98; found C 40.83, H 4.74, N 3.87.

4-Hexoxymethyl-2,6-bis(trimethylstannyl)pyridine (**4e**): Compound **1e** (1.45 g, 4.13 mmol) dissolved in DME (10 mL) was added to a solution of $NaSn(CH_3)_3$ in DME (20 mL), prepared from Na (0.842 g, 36.62 mmol) and $ClSn(CH_3)_3$ (2.43 g, 12.19 mmol), over a period of 20 min at 0 °C. After 2 h the solution was allowed to warm and stirred for 2 h at RT. The inorganic precipitate was filtered and the solvent removed under reduced pressure to give 1.46 g of **4e** as crude product, which was used without further purification. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.30$ (s, 18H; $Sn(CH_3)_3$), 0.88 (t, $J = 6.4$, 3H), 1.28–1.42 (m, 6H), 1.63 (q, $J = 6.4$ Hz, 2H), 3.48 (t, $J = 6.4$ Hz, 2H), 4.41 (s, 2H), 7.28 (s, 2H). ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = -9.42$ (s, $Sn(CH_3)_3$), 14.04, 22.60, 25.89, 29.68, 31.67, 70.99, 71.73, 128.18, 141.87, 173.63; MS (80 eV, EI): *m/z* (%): 508 (31.59), 507 (25.65), 506 (79.48), 505 (52.54), 504 (100), 503 (65.01), 502 (92.10), 501 (43.77), 500 (45.31), 499 (18.15) [$M^+ - CH_3$], 476 (6.94), 475 (4.61), 474 (8.42), 473 (5.69), 472 (7.39), 471 (3.84), 470 (4.11), 469 (4.66), 468 (3.30) [$M^+ - 3\,CH_3$]; HRMS: *m/z* calcd for [$M^+ - CH_3$] 504.052196; found 504.05481.

5,5″-Dibromo-4′-hexoxymethyl-2,2′:6′,2″-terpyridine (**6e**): A solution of crude **4e** and **5** (1.48 g, 6.24 mmol) in toluene (50 mL) was degassed twice. Then $(Ph_3P)_4Pd$ (0.065 g, 0.056 mmol) was added, and the system was degassed again. The solution was refluxed and stirrred vigorously for 60 h, then allowed to cool to RT and extracted with a saturated solution of KF (20 mL). Removal of the solvent and chromatographic separation on silica gel afforded 0.324 g of **6e** (15.5 % with reference to **1e**) as a white solid, m.p. 90 °C. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.86$ (t, $J = 6.9$, 3H), 1.22–1.43 (m, 6H), 1.64 (q, $J = 6.7$ Hz, 2H), 3.52 (t, $J = 6.7$ Hz, 2H), 4.61 (s, 2H), 7.90 (dd, $J_{H\text{-}4,H\text{-}6} = 1.8$ Hz, $J_{H\text{-}4,H\text{-}3} = 8.8$ Hz, 2H; H-4), 8.35 (s, 2H; H-3′), 8.40 (d, $J_{H\text{-}3,H\text{-}4} = 8.8$ Hz, 2H; H-3), 8.69 (d, $J_{H\text{-}6,H\text{-}4} = 1.8$ Hz, 2H; H-6); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 13.94$, 22.52, 25.74, 29.55, 31.57, 71.19, 71.28, 119.19, 121.03, 122.21, 139.11, 149.92, 150.14, 154.20, 154.33; MS (80 eV, EI): *m/z* (%): 507 (1.09), 505 (2.20), 503 (1.13) [M^+], 422 (8.10), 420 (15.09), 418 (7.60) [$M^+ - C_6H_{13}$], 407 (52.10), 405 (100), 403 (53.80) [$M^+ - OC_6H_{13}$+H]; $C_{22}H_{23}Br_2N_3O$ (505.25): calcd C 52.29, H 4.58, N 8.31; found C 52.19, H 4.41, N 8.21.

5,5″-Dichloro-4′-hexoxymethyl-2,2′:6′,2″-terpyridine (**3e**): Terpyridine **3e** was obtained from **1e** (1.73 g, 4.92 mmol), **2b** (3.00 g, 10.84 mmol), and $(Ph_3P)_4Pd$ (0.228 g, 0.197 mmol) in 70 mL toluene with the procedure described for **6e**. The crude product was chromatographed on silica gel to afford 1.40 g of **3e** (68.6 %) as a white solid, m.p. 88 °C. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.83$ (t, $J = 7.0$ Hz, 3H), 1.17 – 1.37 (m, 6H), 1.60 (q, $J = 6.7$ Hz, 2H), 3.46 (t, $J = 6.7$ Hz, 2H), 4.52 (s, 2H), 7.64 (dd, $J_{H\text{-}4,H\text{-}6} = 2.4$ Hz, $J_{H\text{-}4,H\text{-}3} = 8.6$ Hz, 2H; H-4), 8.25 (s, 2H; H-3′), 8.33 (d, $J_{H\text{-}3,H\text{-}4} = 8.6$ Hz, 2H; H-3), 8.52 (d, $J_{H\text{-}6,H\text{-}4} = 2.4$ Hz, 2H; H-6); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta =$ 13.90, 22.49, 25.72, 29.52, 31.55, 71.14, 71.26, 119.08, 121.64, 132.02, 136.15, 147.67, 150.07, 153.86, 154.18; MS (80 eV, EI): *m/z* (%): 419 (0.59), 417 (2.61), 415 (4.06) [M^+], 334 (1.89), 332 (8.24), 330 (11.73) [$M^+ - C_6H_{13}$], 319 (11.40), 317 (64.52), 315 (100) [$M^+ - OC_6H_{13}$]; $C_{22}H_{23}Cl_2N_3O$ (416.34): calcd C 63.46, H 5.56, N 10.09; found C 63.31, H 5.62, N 9.92.

2,6-Dibromo-4-methoxyethoxymethoxymethylpyridine (**1f**): A suspension of **1d** (4.70 g, 17.6 mmol) in CH_2Cl_2 (30 mL) was added to a solution of MEM chloride (3.29 g, 3.00 mL, 26.4 mmol) and diisopropylethylamine (3.41 g, 4.50 mL, 26.4 mmol) in CH_2Cl_2 (100 mL) at RT. The mixture was stirred for 3 h, and then H_2O (50 mL) was added. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2×60 mL). After the combined organic phases were dried over $MgSO_4$, and evaporated, chromatography on silica gel gave 4.37 g of **1f** (69.9 %) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$): 3.09 (s, 3H), 3.25 – 3.31 (m, 2H), 3.43 – 3.48 (m, 2H), 4.23 (s, 2H), 4.51 (s, 2H), 7.17 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 58.52$, 65.77, 66.56, 71.31, 94.92, 124.26, 140.00, 152.62; MS (70 eV, EI): *m/z* (%): 357 (1.05), 355 (2.18), 353 (1.09) [M^+], 282 (7.83), 280 (15.93), 278 (8.36) [$M^+ - O{-}CH_2{-}CH_2{-}OCH_3$], 252 (40.66), 250 (75.80), 248 (37.63) [$M^+ -$ OMEM], 171 (15.70), 169 (14.57) [$M^+ -$ OMEM – Br], 45 (100) [$CH_2{-}OCH_3^+$]; $C_{10}H_{13}Br_2NO_3$ (355.02): calcd C 33.83, H 3.69, N 3.94; found C 33.64, H 3.50, N 3.87.

4-Methoxyethoxymethoxymethyl-2,6-bis(trimethylstannyl)pyridine (**4f**): Compound **4f** was obtained from **1f** (1.50 g, 4.22 mmol) with the procedure described for **4e** to give 1.79 g as crude product, which was used without further purification. ^{1}H NMR (270 MHz, $CDCl_3$): 0.28 [s, 18H; $Sn(CH_3)_3$], 3.32 (s, 3H), 3.43 – 3.56 (m, 2H), 3.60 – 3.76 (m, 2H), 4.52 (s, 2H), 4.78 (s, 2H), 7.25 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = -9.62$ (s, $Sn(CH_3)_3$), 58.67, 66.77, 67.95, 71.51, 94.86, 128.01, 140.97, 173.39; MS (70 eV, EI): *m/z* (%): 514 (50.90), 512 (57.96), 511 (53.73), 510 (87.30), 509 (70.26), 508 (100.00), 507 (78.94), 506 (94.23), 505 (65.32), 504 (66.41), 503 (47.23), 502 (49.11) [M^+], 465 (48.18), 463 (51.07), 462 (46.50), 461 (50.15) [$M^+ - CH_2{-}OCH_3$], 404 (47.71) [$M^+ -$ OMEM].

5,5″-Dibromo-4′-methoxyethoxymethoxymethyl-2,2′:6′,2″-terpyridine (**6f**): Terpyridine **6f** was prepared from **4f** (1.79 g), **5** (1.78 g, 7.55 mmol), and $(Ph_3P)_4Pd$ (0.040 g, 0.034 mmol) in toluene (70 mL) with the procedure desribed for **6e**. Chromatographic separation on silica gel afforded 0.57 g of **6f** (26.4 % with reference to **1f**) as a white solid. The same experiment was also done on a larger scale starting from 7.42 g of **1f** to give 2.63 g of **6f** (24.7 %), m.p. 134 °C. ^{1}H NMR (270 MHz, $CDCl_3$): 3.38 (s, 3H), 3.54 – 3.57 (m, 2H), 3.75 – 3.79 (m, 2H), 4.77 (s, 2H), 4.88 (s, 2H), 7.94 (dd, $J_{H\text{-}4,H\text{-}6} =$ 2.3 Hz, $J_{H\text{-}4,H\text{-}3} = 8.6$ Hz, 2H; H-4), 8.40 (s, 2H; H-3′), 8.46 (d, $J_{H\text{-}3,H\text{-}4} =$ 8.6 Hz, 2H; H-3), 8.72 (d, $J_{H\text{-}6,H\text{-}4} = 2.3$ Hz, 2H; H-6); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 58.90$, 67.00, 67.90, 71.59, 95.27, 119.13, 121.10, 122.25, 139.19, 149.46, 149.95, 154.14, 154.43; MS (80 eV, EI): *m/z* (%): 511 (1.01), 509 (3.09), 507 (1.61) [M^+], 452 (7.48), 450 (14.44), 448 (7.85) [$M^+ - CH_2{-}CH_2{-}OCH_3$], 422 (14.87), 420 (27.44), 418 (15.36) [$M^+ -$ MEM], 407 (50.43), 405 (100.00), 403 (53.33) [$M^+ -$ OMEM+H]; $C_{20}H_{19}Br_2N_3O_3$ (509.19): calcd C 47.17, H 3.76, N 8.25; found C 47.08, H 3.60, N 7.91.

2-Bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**8**): BuLi (1.6 M, 69 mL) in hexane was added dropwise to a solution of compound **5** (25 g, 105.5 mmol) in Et_2O (800 mL), while the temperature was kept at – 78 °C. After stirring at – 78 °C for 6 h, a solution of triisopropyl borate (41.67 g, 221.6 mmol) in Et_2O (50 mL) was added dropwise. Then the mixture was allowed to warm to room temperature overnight. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel first with EtOAc as eluent to remove impurities and second with MeOH to wash the product off the column to give 21.26 g of crude 2-bromopyridyl-5-boronic acid, which was used for the subsequent esterification without further purification. ^{1}H NMR (270 MHz, [D$_6$]DMSO): $\delta = 7.59$ (d, $J_{H\text{-}3,H\text{-}4} = 8.2$ Hz, 1H; H-3), 7.99 (dd, $J_{H\text{-}4,H\text{-}6} =$ 2.0 Hz, $J_{H\text{-}4,H\text{-}3} = 8.2$ Hz, H-4), 8.44 [br s, $B(OH)_2$], 8.62 (d, $J_{H\text{-}6,H\text{-}4} = 2.0$ Hz, 1H; H-6); ^{13}C NMR (68 MHz, [D$_6$]DMSO): $\delta = 127.48$, 128.41, 143.79, 144.84, 155.95; MS (80 eV, EI): *m/z* (%): 555 (7.10), 554 (8.49), 553 (23.37), 552 (18.92), 551 (25.11), 550 (16.94), 549 (12.35), 548 (5.72) [M^+] (trimeric anhydride), 474 (13.81), 473 (13.24), 472 (28.18), 471 (20.42), 470 (19.16), 469 (11.43) [$M^+ -$ Br] (trimeric anhydride), 212 (21.41), 210 (24.48) [$M^+ -$ 2H+B] (monomer), 186 (19.78), 184 (26.07) [$M^+ -$ OH] (monomer), 159 (77.05), 157 (100,00) [$M^+ - BO_2H$] (monomer), 104 (49.03) [$M^+ - H_2O -$ Br] (monomer), 78 (64.20) [$M^+ - BO_2H -$ Br] (monomer); HRMS: *m/z* calcd for $C_{15}H_9B_3Br_3N_3O_3$ (trimeric anhydride) 550.845269; found 550.84564. The crude boronic acid and 2,3-dimethylbutane-2,3-diol (12.44 g, 105.25 mmol) were dissolved in 1,4-dioxane (400 mL). The solvent was evaporated under normal pressure, and the residue was chromatographed on silica gel to give 13.66-17.04 g of **8** (45.6 – 56.8 % with reference to **5**) as white solid, m.p. 94 °C. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.43$ (d, $J_{H\text{-}3,H\text{-}4} = 7.7$ Hz,1H; H-3), 7.83 (dd, $J_{H\text{-}4,H\text{-}6} = 1.2$ Hz, $J_{H\text{-}4,H\text{-}3} = 7.7$ Hz, 1H; H-4), 8.62 (d, $J_{H\text{-}6,H\text{-}4} = 1.2$ Hz, 1H; H-6); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta =$ 24.77, 84.44, 127.55, 144.33, 145.39, 156.00; MS (80 eV, EI): *m/z* (%): 286 (7.20), 285 (53.22), 284 (25.70) 283 (55.89), 282 (23.45) [M^+], 271 (12.88), 270 (98.25), 269 (38.25), 268 (100), 267 (27.32) [$M^+ - CH_3$], 229 (3.18), 228 (34.99), 227 (13.60), 226 (38.95), 225 (11.61) [$M^+ - CH_3 - C_3H_6$], 187 (4.30), 186 (57.80), 185 (22.56), 184 (57.01), 183 (19.58) [$M^+ - CH_3{-}C_3H_6{-}CH_2CO$], 104 (29.62) [$M^+ - C_6H_{12}O -$ Br]; $C_{11}H_{15}BBrNO_2$ (283.94) calcd C 46.52, H 5.32, N 4.93; found C 46.57, H 5.20, N 4.84.

5,5″-Bis[4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl]-2,2′: 6′,2″-terpyridine (**9**): Boronic ester **8** (6.76 g, 23.80 mmol) and **4a** (4.37 g, 10.79 mmol) were dissolved in toluene (70 mL). The mixture was degassed twice. Then $(Ph_3P)_4Pd$ (0.249 g, 0.215 mmol) was added, and the system was degassed again. After the mixture was refluxed for 15 h, a saturated solution of KF (30 mL) was added, and the inorganic precipate was removed by filtration. The layers were separated and the aqueous layer was washed with toluene (2×20 mL). The combined organic layers were dried over $MgSO_4$ and filtered, and the solvent was removed. Recrystallization from toluene afforded 2.87 g of **9** (55.0 %) as a white solid, m.p. 251 °C. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.36$ (s, 12H), 7.93 (t, $J_{H\text{-}4',H\text{-}3'} = 7.8$ Hz, 1H; H-4′), 8.20 (dd, $J_{H\text{-}4,H\text{-}6} = 1.5$ Hz, $J_{H\text{-}4,H\text{-}3} = 7.8$ Hz, 2H; H-4), 8.48 (d, $J = 7.8$ Hz, 2H), 8.56 (d, $J = 7.8$ Hz, 2H), 9.00 (d, $J_{H\text{-}6,H\text{-}4} = 1.5$ Hz, 2H; H-6); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 24.86$, 84.17, 120.24, 121.70, 137.81, 143.12, 155.05, 155.41, 158.08; MS (80 eV, EI): *m/z* (%): 487 (6.54), 486 (31.69), 485 (100.00), 484 (48.89), 483 (8.68) [M^+], 470 (6.13) [$M^+ - CH_3$], 428 (2.61) [$M^+ - CH_3 - C_3H_6$], 386 (16.04) [$M^+ - CH_3{-}C_3H_6{-}CH_2CO$]; HRMS: *m/z* calcd for $C_{27}H_{33}B_2N_3O_4$ 485.26518; found 485.26312.

5,5″-Bis[5-bromo-3-hexoxymethylphenyl]-2,2′:6′,2″-terpyridine (**12a**)

Method A: A suspension of **6a** (6.2 g, 15.85 mmol) in DME (50 mL) was added to a solution of $NaSn(CH_3)_3$ in 60 mL DME, prepared as described in the literature from Na (3.29 g, 143.3 mmol) and $ClSn(CH_3)_3$ (9.53 g, 47.82 mmol), over a period of 20 min at 0 °C. After 2 h the solution was allowed to warm and was stirred for 2 h at RT. The inorganic precipate was filtered off, and the solvent removed under reduced pressure to give crude **10**. This material and **11** (13.84 g, 34.85 mmol) were dissolved in toluene (150 mL). The mixture was degassed twice, then $(Ph_3P)_4Pd$ (0.732 g, 0.634 mmol) was added, and the system was degassed again. After the mixture was refluxed for 39 h, a saturated solution of KF (50 mL) was added, and the inorganic precipate was removed by filtration. The layers were separated, and the aqueous layer was washed with CH_2Cl_2 (30 mL). The combined organic layers were dried over $MgSO_4$ and filtered, and the solvent removed. Chromatographic separation on aluminium oxide with hexane/CH_2Cl_2 as eluent afforded 3.26 g of **12a** (26.7 % with reference to **6a**) as white solid.

Method B: Compounds **9** (2.0 g, 4.12 mmol) and **11** (3.6, 9.06 mmol) were dissolved in toluene (40 mL) and a sodium carbonate solution (1 M, 40 mL) was added. The mixture was degassed twice. Then $(Ph_3P)_4Pd$ (0.047 g, 0.041 mmol) was added, and the system was degassed again. The solution was refluxed for 72 h with vigorous stirring. The mixture was allowed to cool to RT, the layers were separated, and the aqueous layer was washed with CH_2Cl_2 (2×40 mL). The combined organic layers were dried over $MgSO_4$ and filtered, and the solvent removed. Chromatographic separation on aluminium oxide with hexane/CH_2Cl_2 (3:2) as eluent afforded 1.30 g of **12a** (41.1 %) as white solid, m.p. 85 °C. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta =$ 0.86 (t, $J = 6.5$ Hz, 6H), 1.20 – 1.39 (m, 12H), 1.60 (q, $J = 6.7$ Hz, 4H), 3.45 (t, $J = 6.7$ Hz, 4H), 4.45 (s, 4H), 7.45 (s, 4H), 7.60 (s, 2H), 7.88 (t, $J_{H\text{-}4',H\text{-}3'} =$ 7.8 Hz, 1H; H-4′), 7.91 (dd, $J_{H\text{-}4,H\text{-}6} = 2.3$ Hz, $J_{H\text{-}4,H\text{-}3} = 8.3$ Hz, 2H; H-4), 8.41 (d, $J_{H\text{-}3',H\text{-}4'} = 7.8$ Hz, 2H; H-3′), 8.55 (d, $J_{H\text{-}3,H\text{-}4} = 8.3$ Hz, 2H; H-3), 8.79 (d,

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$J_{H\text{-}6,H\text{-}4} = 2.3$ Hz, 2H; H-6); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 13.93$, 22.47, 25.72, 29.53, 31.51, 70.85, 71.63, 120.70, 120.95, 123.04, 124.24, 128.66, 129.70, 134.61, 134.72, 137.54, 139.41, 141.78, 147.21, 154.60, 155.19; MS (70 eV, EI): *m/z* (%): 774 (22.23), 773 (54.89), 772 (45.56), 771 (100), 770 (24.34), 769 (48.05) [M^+], 688 (16.24), 687 (41.96), 686 (33.51), 685 (78.08), 684 (20.44), 683 (40.73) [$M^+ - C_6H_{13} - H$], 673 (14.66), 672 (41.68), 671 (36.01), 670 (79.52), 669 (32.04), 668 (41.67) [$M^+ - OC_6H_{13} - H$], 572 (11.54), 571 (28.25), 570 (13.11), 569 (48.77), 568 (17.04), 567 (22.57) [$M^+ - 2OC_6H_{13}$], 493 (13.71), 492 (38.66), 491 (24.32), 490 (43.64), 489 (16.49) [$M^+ - 2OC_6H_{13} - Br + H$]; $C_{41}H_{45}Br_2N_3O_2$ (771.63): calcd C 63.81, H 587, N 5.44; found C 63.71, H 5.74, N 5.48.

5,5″-Bis[5-trimethylstannyl-3-hexoxymethylphenyl]-2,2′:6′,2″-terpyridine (**12b**): A solution of **12a** (3.37 g, 4.36 mmol) in DME (10 mL) was added to a solution of $NaSn(CH_3)_3$ in DME (60 mL), prepared as described in the literature from Na (2.40 g, 104.6 mmol) and $ClSn(CH_3)_3$ (6.94 g, 34.88 mmol), over a period of 20 min at 0 °C. After 2 h the solution was allowed to warm to RT and stirred for 2 h at this temperature. The inorganic precipitate was filtered off, and the solvent was removed under reduced pressure. The residue was chromatographed on aluminium oxide with hexane/CH_2Cl_2 (3:2) as eluent to give 2.52 g of **12b** (61.4%) as a white solid, m.p. 98–99 °C. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.35$ (s,18H), 0.88 (t, $J = 6.5$ Hz, 6H), 1.27–1.45 (m, 12H), 1.65 (q, $J = 6.6$ Hz, 4H), 3.53 (t, $J = 6.6$ Hz, 4H), 4.59 (s, 4H), 7.52 (s, 2H), 7.58 (s, 2H), 7.76 (s, 2H), 7.98 (t, $J_{H\text{-}4',H\text{-}3'} = 7.9$ Hz, 1H; H-4′), 8.07 (dd, $J_{H\text{-}4,H\text{-}6} = 2.3$ Hz, $J_{H\text{-}4,H\text{-}3} = 8.2$ Hz, 2H; H-4), 8.50 (d, $J_{H\text{-}3',H\text{-}4'} = 7.9$ Hz, 2H; H-3′), 8.71 (d, $J_{H\text{-}3,H\text{-}4} = 8.2$ Hz, 2H; H-3), 8.95 (d, $J_{H\text{-}6,H\text{-}4} = 2.3$ Hz, 2H; H-6); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta =$ 14.01, 22.56, 25.87, 29.70, 31.64, 70.74, 72.76, 120.83, 120.91, 126.33, 133.47, 134.72, 135.18, 136.75, 137.25, 137.78, 138.85, 143.51, 147.67, 154.91, 155.12; MS (70 eV, EI): *m/z* (%): 942 (6.74), 941 (12.25), 940 (10.97), 939 (14.79), 938 (7.71), 937 (12.21), 936 (7.40), 935 (6.65) [M^+], 928 (23.49), 927 (33.93), 926 (70.20), 925 (68.67), 924 (100), 923 (51.32), 922 (70.03), 921 (35.13) [$M^+ - CH_3$]; $C_{47}H_{63}N_3O_2Sn_2$ (939.45) calcd C 60.09, H 6.75, N 4.47; found C 59.87, H 6.59, N 4.30.

5,5″-Bis[5-iodo-3-hexoxymethylphenyl]-2,2′:6′,2″-terpyridine (**12c**): A solution of I_2 (0.767 g, 3.02 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **12b** (1.42 g, 1.51 mmol) in CH_2Cl_2 (20 mL) over a period of 15 min at RT. The reaction mixture was stirred for 1 h at this temperature, and then a saturated solution of KF (10 mL) was added. The resulting mixture was made alkaline with potassium carbonate and subsequently extracted with CH_2Cl_2 (2×20 mL). The combined organic layers were washed with a saturated solution of KF and a saturated sodium thiosulfate solution, dried over $MgSO_4$, and concentrated under reduced pressure. Some impurities were separated by chromatography on silica gel with hexane/CH_2Cl_2 (3:2) as eluent. The product was eluted by CH_2Cl_2 affording 1.28 g of **12c** (97.8%) as a white solid, m.p. 71 °C. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.87$ (t, $J = 6.7$ Hz, 6H), 1.25–1.40 (m, 12H), 1.60 (q, $J = 6.6$ Hz, 4H), 3.49 (t, $J = 6.6$ Hz, 4H), 4.49 (s, 4H), 7.55 (s, 2H), 7.71 (s, 2H), 7.87 (s, 2H), 7.93 (t, $J_{H\text{-}4',H\text{-}3'} = 7.8$ Hz, 1H; H-4′), 7.97 (dd, $J_{H\text{-}4,H\text{-}6} = 2.4$ Hz, $J_{H\text{-}4,H\text{-}3} = 8.3$ Hz, 2H; H-4), 8.46 (d, $J_{H\text{-}3',H\text{-}4'} = 7.8$ Hz, 2H; H-3′), 8.64 (d, $J_{H\text{-}3,H\text{-}4} = 8.3$ Hz, 2H; H-3), 8.85 (d, $J_{H\text{-}6,H\text{-}4} = 2.4$ Hz, 2H; H-6); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta =$ 14.04, 22.60, 25.85, 29.67, 31.65, 71.03, 71.75, 95.02, 121.03, 121.20, 125.39, 134.98, 135.16, 136.00, 137.97, 139.84, 141.91, 147.52, 154.99, 155.50; MS (70 eV, EI): *m/z* (%): 866 (42.61), 865 (100.00) [M^+], 781 (17.66), 780 (36.31) [$M^+ - C_6H_{13}$], 766 (14.04), 765 (39.65) [$M^+ - OC_6H_{13}$], 739 (14.04) [$M^+ - I + H$]; $C_{41}H_{45}I_2N_3O_2$ (865.63) calcd C 56.88, H 5.24, N 4.85; found C 57.05, H 5.30, N 4.70.

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