Synthesis of Highly Soluble Annelated Polypyridines

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Highly soluble annelated bi- and terpyridines were prepared in 46–60% yields by a two-step procedure which combines the Michael addition of an enolizable cyclic ketone with an α,β-unsaturated ketone and the cyclization of the resulting 1,5-diketone in the presence of ammonium acetate.

Annelated polypyridines constitute a class of compounds that are effective for the complexation of metals and organic guests in their preorganized clefts and cavities.[1] In order to use these structures in molecular recognition there is a strong need to develop an efficient approach for the synthesis of derivatives which are soluble in common organic solvents. However, since the initial work of Bell[2] describing the synthesis of "Torand" (Figure 1), only a few methods have been developed for the preparation of highly soluble annelated polypyridines.[3] The introduction of solubility-improving carbon fragments into the central pyridine rings can only take place in the 4-position because of to the annelated arrangement of these systems. The most important and useful approach for the preparation of these molecules are procedures involving 1,5-diketone intermediates which undergo ring closure forming the pyridines in the presence of a nitrogen-containing reagent.

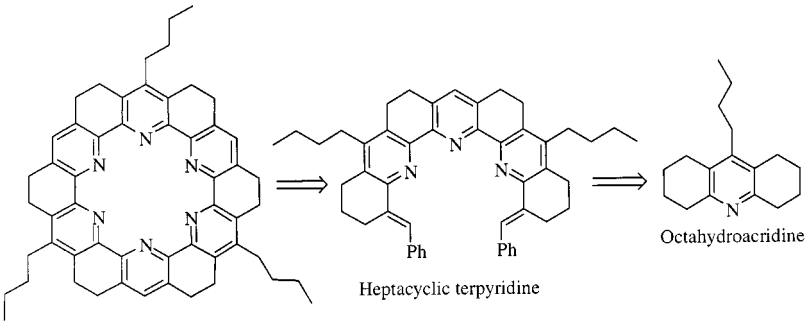

Figure 1

Recently, Bell[4] reported the syntheses of central 4-aryl-substituted annelated terpyridine derivatives by condensation of 9-butyl-2,3,5,6,7,8-hexahydro-4(1*H*)-acridinone with arylenone derivatives in anhydrous DMSO containing ammonium acetate, under modified Risch conditions.[5] The β-arylenones employed in this procedure were prepared by aldol condensation/dehydration of octahydroacridone with 4-substituted benzaldehydes. However, with aliphatic aldehydes this procedure did not lead to the desired α,β-unsaturated ketones due to their facile enolization. An alternative strategy for the preparation of substituted annelated pyridines, employing ternary iminium salts as synthetic equivalents for aliphatic and aromatic aldehydes, has been reported by Risch et al.[3e−3g] In this case, two isomers were obtained due to the competition between 1,2- and 1,4-addition. The use of an aliphatic ternary iminium gives only traces of the 1,4-addition isomer.

In order to develop an efficient approach for the synthesis of polyalkylated annelated polypyridines, we decided to investigate the Michael addition of β-alkylenones with enolizable cyclic ketones. We describe here the results, from an adaptation of this procedure, for the preparation of polyalkylated annelated bi- and terpyridines (Figure 2), which exhibit high solubility in organic solvents.

We have recently developed an efficient synthetic method based on the C-alkylation of enaminone derivatives with Grignard reagents for the preparation of β-alkylenones. Enaminones **4**−**6** were obtained in high yields by reaction of the corresponding ketones[6][7] with 2 equivalents of *N,N*-dimethylformamide dimethyl acetal[8] at 80°C for 8 h. Enaminone **7** was obtained in high yield by reaction of cyclohexanone with an equimolar ratio of *tert*-butoxybis(dimethylamino)methane at 90°C for 2 h. The reaction of these

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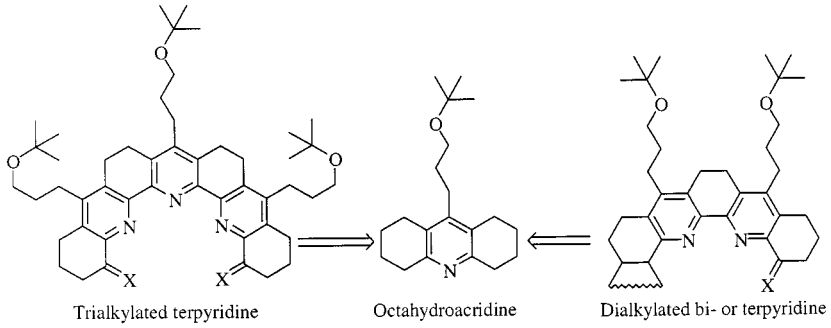
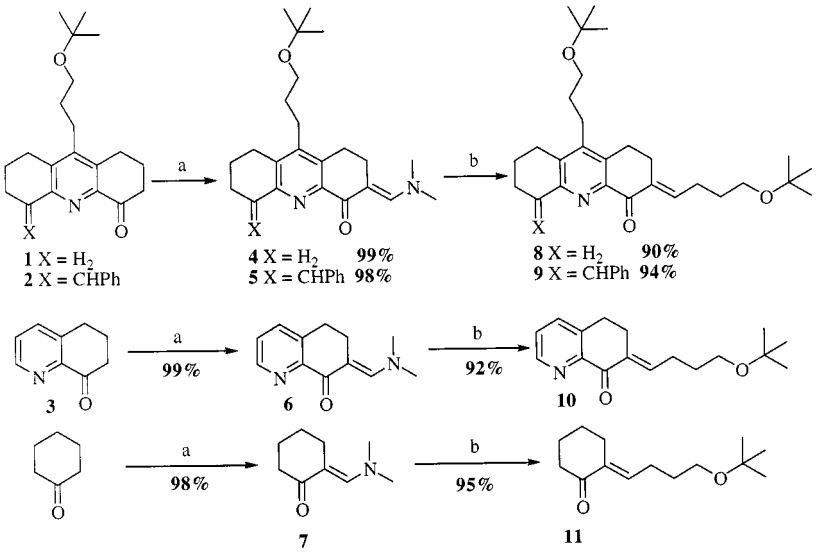


Figure 2. Synthetic strategy for the highly soluble annelated bi- and terpyridines



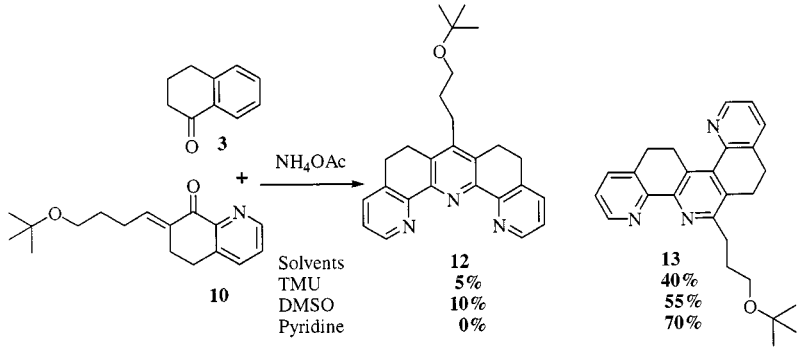
Scheme 1. a) 2 equiv. of *N,N*-dimethylformamide dimethyl acetal, 80°C for 8 h; b) 3-*tert*-butoxypropylmagnesium chloride, THF or THF/toluene, v:v, 0°C; *tert*-butoxy bis(dimethylaminomethane), 90°C, 2 h

enaminones **4**−**7** with 3-*tert*-butoxypropylmagnesium chloride under mild conditions resulted in the α,β-unsaturated ketones **8**−**11** in good to excellent yield (Scheme 1).[9]

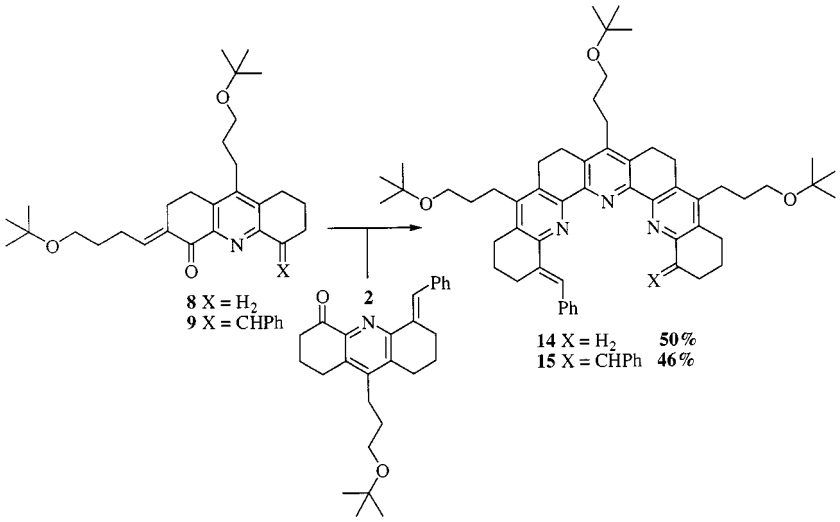
In order to optimize the experimental conditions controlling the Michael addition, the condensation of the ketone **3** with the α,β-unsaturated ketone **10**, which gave rise to the monosubstituted annelated terpyridine **12**, was selected as a reaction model (Scheme 2). The direct condensation of **3** and **10** in the presence of ammonium acetate, in pyridine, tetramethyl urea (TMU)[5] or dimethylsulfoxide (DMSO)[4] as solvent led to the formation of the 1,2-addition isomer, giving **13** as the major product. For example, the use of pyridine in this reaction led exclusively to the formation of the isomer **13** in good yield (70%).[10] However, the same reaction in acetic acid in the presence of ammonium acetate gave the 1,4-addition isomer **12** in low yield (14−16%).[11] The enamine strategy described by Thummel[3a] was also attempted. In the first step, the condensation of the enamine of **3** with **10**, followed by hydrolysis, did not show any identifiable 1,5-diketone intermediates, and in all cases the unchanged ketones **3** and **10** were recovered.[12]

An alternative two-step sequence, employing the condensation of the already generated α-ketonic carbanion with an α,β-unsaturated ketone proved to be more efficient. This procedure is based on the 1,4-addition of the carbanion generated from **3** and **10**, followed by ring closure in situ of the 1,5-diketone intermediate with ammonium acetate. Thus, the carbanion of **3**, generated in situ by treatment with *n*-butyllithium (*n*BuLi) at −20°C in tetrahydrofuran (THF), was reacted with the α,β-unsaturated ketone **10**. After stirring for 4 h at −20°C, ammonium acetate and glacial acetic acid were added to the solution, which was then heated for 5 h with continuous removal of THF.[13] This procedure led to the desired 1,4-addition product **12,** isolated in 60% yield, which represents a three- to fourfold increase over the acidic approach. The use of lithium diisopropylamide (LDA) or potassium *tert*-butoxide (*t*BuOK) as bases at −20°C gave **12** in similar yields.

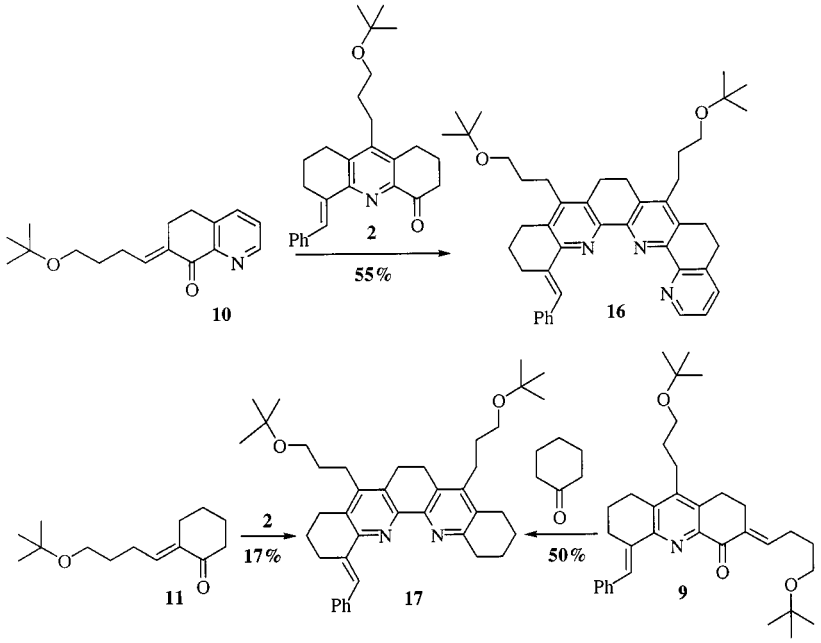
Having found favorable reaction conditions for the condensation of **10** with the carbanion generated from **3**, we turned our attention to testing the applicability of this two-step procedure to other enolizable ketones and α,β-unsaturated ketones. However, under related conditions (LDA, *t*BuOK or *n*BuLi, −20°C, NH_4OAc/AcOH) the reaction of the benzylidene ketone **2** with the α,β-unsaturated ketones **8** or **9** resulted in the trisubstituted heptacyclic terpyridines **14** and **15** in only 20% and 25% yields, respectively, without



Scheme 2. Reaction model: 1 equiv. of **3**, 1.1 equiv. of **10**, 5.5 equiv. of NH_4OAc, solvent, 90°C, 8 h



Scheme 3. The use of the benzilydene acridone **2** for the synthesis of the trialkylated annelated terpyridines **14** and **15**



Scheme 4. The use of the benzilydene acridone **2** for the preparation of the terpyridine **16** and the bipyridine **17**

the formation of the isomer derived from the 1,2-addition (Scheme 3). When the first step of this condensation was carried out at −78°C with LDA as base, the yields were 50% and 46% for **14** and **15**, respectively. It is important to

point out that the addition of oxidizing agent did not improve the yield of the desired annelated terpyridine. Furthermore, the use of *n*BuLi or *t*BuOK as bases at −78°C led to only 30% and 25% yields, respectively. We also used this procedure for the synthesis of the disubstituted annelated terpyridine **16** and bipyridine **17** (Scheme 4). The disubstituted terpyridine **16**, which contains a terminal pyridine ring, was obtained in good yield (55%) by condensation of the benzylidene ketone **2** with the α,β-unsaturated ketone **10** under the standard conditions. For the preparation of bipyridine **17**, two methods were used: i) The reaction of the α,β-unsaturated ketone **9** and the carbanion of cyclohexanone generated in situ (LDA, −78°C) resulted in the desired product in low yield (17%). It is worth pointing out that the condensation of **9** with the carbanion generated from cyclohexanone, under the conditions described for the reaction model (LDA, −20°C), was quite unsatisfactory, and only traces of the expected product were detected. ii) The reaction of the α,β-unsaturated ketone **11** with the carbanion generated from the benzylidene ketone **2** (with LDA at −78°C), under the experimental conditions described for **14** and **15**, resulted in the formation of **17**, isolated in 50% yield. It is worth noting that, except for the dialkylated terpyridine **16**, the polypyridines **14**, **15** and **17** are soluble in solvents such as hexane, diethyl ether and ethyl acetate.

In conclusion, we have demonstrated that the use of a two-step procedure employing a combination of the Michael addition of an enolizable ketone with an α,β-unsaturated ketone and the already known ring-closure method is an efficient way for the preparation of the polyalkylated annelated bi- and terpyridines, which exhibit very high solubility in organic solvents. Large helical macrostructures up to 15 annelated rings have been described.[14] Recently we have used the two procedures described here for the preparation of helical annelated polypyridines such as **18** (Figure 3) (R = H or *tert*-butoxypropyl).[15]

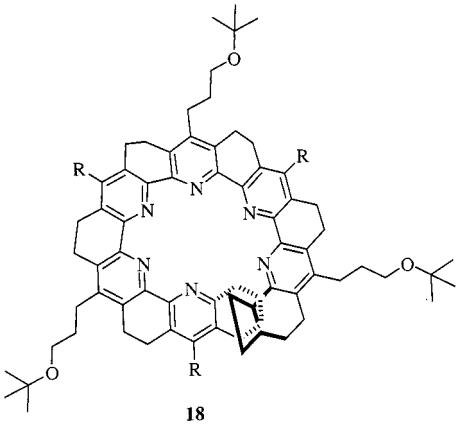


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Figure 3. Helical annelated polypyridine

Experimental Section

All reactions were carried out under an inert argon atmosphere. Nuclear magnetic resonance spectra (^{1}H,^{13}C) were recorded on Bruker AM-250 (250 MHz) or AC-200 (200 MHz) spectrometers, and chemical shifts are reported in ppm downfield from Me_4Si. IR spectra were recorded on Perkin−Elmer 883 or FT-1725X spectrometers. CI and FAB mass spectra (*m*-nitrobenzyl alcohol matrix) were recorded with a quadripolar Nermag R10−10H instrument. Elemental analysis was performed by the "Service de Microanalyse du LCC (Laboratoire de Chimie de Coordination)". Column chromatogaphy purifications were performed with Merck alumina (70−230 mesh ASTM) deactivated with 8% of water or with Merck silica gel (30−75 microns).

9-(3-*tert*-Butoxypropyl)-3-(dimethylaminomethylene)-1,2,5,6,7,8-hexahydroacridin-4-one (4): Compound **1** (3.55 g, 11.3 mmol) was added to *N,N*-dimethylformamide dimethyl acetal (3 mL,22.5 mmol, 2 eq) and the mixture was heated at 80°C for 8 h under argon. The reaction was monitored by IR spectroscopy. After checking for the absence of **1**, the solution was evaporated to dryness under reduced pressure to give 4.67 g (99%) of a brown amorphous hygroscopic solid **4**. − IR (KBr): $\tilde{\nu}$ = 1573 cm^{-1}, 1652cm^{-1}(CO). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.7 (s, 1 H), 3.4 (t, 2 H), 3.1 (s, 6 H), 2.4 (s, 2 H), 2.9−2.60 (m, 6 H), 1.8 (m, 4 H), 1.6 (m, 4 H), 1.2 (s, 9 H). − ^{13}C NMR ($CDCl_3$): δ = 184.8, 155.2, 149.5, 147.9, 146.1, 132.9, 132.0, 103.6, 72.0, 60.4, 42.9, 32.9, 29.2, 27.0, 25.6, 24.2, 24.1, 23.1, 22.4, 22.2. − $C_{23}H_{34}N_2O_2$ (370.53): calcd C 74.55, H 9.25, N 7.56; found C 74.35, H 9.61, N 7.72. − MS; *m/z* (%): 371 (100) [MH^+], 388 (25) [MNH_4^+].

9-(3-*tert*-Butoxypropyl)-3-(dimethylaminomethylene)-1,2,6,7,8-pentahydro-5-(phenylmethylene)acridin-4-one (5): This compound was prepared with the procedure described for **4**. Thus, the reaction of **2** (5.0 g, 12.4 mmol) with *N,N*-dimethylformamide dimethyl acetal (10.67 mL, 24.8 mmol, 2 eq) at 80°C for 8 h gave, after purification, 5.7 g (>99%) of a very hygroscopic brown solid **5**. − IR (KBr): $\tilde{\nu}$ = 1644 cm^{-1} (CO). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 8.17 (s, 1 H), 7.78 (s, 1 H), 7.38 (m, 4 H), 7.21 (m, 1 H), 3.41 (t, 2 H), 3.10 (s, 6 H), 2.88 (m, 8 H), 2.72 (m, 2 H), 1.84 (m, 2 H), 1.67 (m, 2 H), 1.19 (s, 9 H). − ^{13}C NMR ($CDCl_3$): δ = 185.4, 151.3, 150.0, 148.7, 146.4, 138.3, 135.7, 134.1, 132.7, 129.6, 127.7, 127.3, 126.1, 104.1, 72.5, 66.5, 60.8, 43.4, 29.7, 27.4, 26.5, 24.8, 24.7, 23.5, 22.7 − $C_{30}H_{38}N_2O_2$ (458.63): calcd C 78.56, H 8.35, N 6.11; found C 78.85, H 8.58, N 6.02. − MS; *m/z* (%): 459 (100) [MH^+].

2-(Dimethylaminomethylene)cyclohexane-1-one (7): Cyclohexanone (5.0 g, 51 mmol) and *tert*-butoxy bis(dimethylamino)methane (10.5 mL, 51 mmol) were placed in a flask fitted with a reflux condenser and heated at 90°C for 2 h. After evaporation of the solvent under reduced pressure the residue was dissolved in 50 mL of dichloromethane and washed twice with water. The aqueous layers were combined and extracted with dichloromethane. The combined organic layers were washed with saturated sodium chloride, dried over magnesium sulphate and concentrated under reduced pressure to give 7.75 g (98%) of **7** as a yellow, staining brown oil; b p: 94°C/0.005 Torr. − IR (KBr): $\tilde{\nu}$ = 3347 cm^{-1}, 1743 cm^{-1} (CO). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.5 (s, 1 H), 3.1 (s, 6 H), 2.68 (t, 2 H), 2.32 (t, 2 H), 1.75 (m, 2 H), 1.68 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 197.1, 150.5, 104.1, 43.2, 38.4, 25.9, 24.0, 22.9 − $C_9H_{15}NO$ (153.23): calcd. C 70.55, H 9.87, N 9.14; found C 70.41, H 9.61, N 9.37, O 10.75. − GC/MS; *m/z* (%):153 (50) [M^+], 82 (100).

9-(3-*tert*-Butoxypropyl)-3-(4-*tert*-butoxybutylidene)-1,2,5,6,7,8-hexahydro-4-oxoacridine (8): Compound **4** (3.83 g, 10.4 mmol) was dissolved in 50 mL of dry toluene and cooled to 0°C under argon. 4-*tert*-butoxypropylmagnesium chloride (60 mL, 30 mmol, 3 equiv., as a 0.5 M solution in THF) was then added. After the addition, the cooling bath was removed and the solution stirred overnight

at room temperature under argon. The reaction mixture was then evaporated to dryness under reduced pressure, dissolved in 150 mL of dichloromethane and hydrolyzed with 250 mL of water with vigorous stirring. Solid sodium bicarbonate was added to break the resulting emulsion and the aqueous layer was then extracted twice with 100 mL of dichloromethane. The combined organic layers were washed consecutively with saturated sodium bicarbonate, water and saturated sodium chloride before being dried over magnesium sulphate, filtered and evaporated. The resulting brown oil was purified by chromatography (silica gel, ethyl acetate) to yield 4.1 g (90%) of an analytically pure yellow oil **8**. − IR (KBr): $\tilde{\nu}$ = 1684cm^{-1}, 1622cm^{-1} (CO). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 6.95 (m, 1 H), 3.74 (t, 2 H), 3.56 (m, 2 H), 2.88 (m, 4 H), 3.04 (s, 2 H), 2.93 (t, 2 H), 2.85−2.70 (m, 4 H), 2.36 (m, 2 H), 1.80−1.60 (m, 6 H), 1.22 (s, 9 H), 1.18 (s, 9 H). − ^{13}C NMR ($CDCl_3$): δ = 186.5, 156.7, 147.6, 139.6, 135.5, 135.2, 134.3, 72.5, 72.3, 60.6, 60.3, 33.3, 29.4, 29.2, 27.3, 26.1, 24.7, 24.1, 22.5, 22.4 − $C_{28}H_{43}NO_3$ (441.66): calcd. C 76.15, H 9.81, N 3.17; found C 75.76, H 10.11, N 3.46. − MS (DCI/NH_3); *m*/*z* (%): 442(100) [MH^+].

9-(3-tert-Butoxypropyl)-1,2,6,7,8-pentahydro-3-(4-tert-butoxybutylidene)-4-oxo-5-(phenylmethylene)acridine (9): Following the same method described for **8** and after purification by chromatography (alumina, ethyl acetate) 6.8 g of **9** was obtained as a light brown oil (94%). − IR (KBr): $\tilde{\nu}$ = 1687, 1623 cm^{-1} (CO). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 8.14 (s, 1 H), 7.35 (m, 4 H), 7.28 (m, 1 H), 7.00 (t, 1 H), 3.43 (m, 4 H), 2.98 (m, 12 H), 2.34 (m, 2 H), 1.87 (m, 2 H), 1.76 (m, 2 H), 1.69 (m, 2 H), 1.24 (s, 9 H), 1.19 (s, 9 H). − ^{13}C NMR ($CDCl_3$): δ = 186.6, 152.2, 147.7, 146.8, 139.9, 137.9, 136.2, 135.3, 134.4, 129.6, 128.0, 127.8, 126.4, 72.6, 72.4, 60.7, 60.4, 29.5, 27.5, 26.6, 25.0, 24.8, 24.4, 22.5. − $C_{35}H_{47}NO_3$ (529.75): calcd C 79.35, H 8.94, N 2.64; found C 79.36, H 9.11, N 2.66. − MS; *m*/*z* (%): 530 (100) [MH^+].

7-(4-*tert*-Butoxybutylidene)-5,6,7,8-tetrahydro-8-oxoquinoline (10): A solution of 7-(dimethylaminomethylene)-5,6,7,8-tetrahydro-8-oxo-quinoline **6** (3.00 g, 19.80 mmol) in 150 mL of THF was treated with 63 mL (30.2 mmol) of a 0.48 M solution of 4-*tert*-butoxypropylmagnesium chloride in THF. After chromatography (alumina, ethyl acetate) 4.54 g of **10** was obtained as a orange oil (92%). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 8.69 (d, 1 H), 7.63 (d, 1 H),7.38 (m, 1 H), 6.98 (q, 1 H), 3.38 (t, 2 H), 3.10 (t, 2 H), 2.82 (t, 2 H), 2.38 (q, 2 H), 1.73 (m, 2 H), 1.18 (s, 9 H). − ^{13}C NMR ($CDCl_3$): δ = 185.7, 149.0, 141.3, 139.6, 136.8, 134.8, 126.3, 72.3, 60.3, 29.3, 27.8, 27.3, 24.8, 24.6. − $C_{17}H_{23}NO_2$ (273.37): calcd C 74.69, H 8.48, N 5.12; found C 75.16, H 8.34, N 5.26. − MS; *m*/*z* (%): 274 (100) [MH^+].

2-(4-*tert*-Butoxybutylidene)cyclohexane-1-one (11): To a two-necked flask was added a solution of **6** (9.42 g, 62.0 mmol) in 100 mL of dry tetrahydrofuran. 4-*tert*-butoxypropyl magnesium chloride (165 mL of a 0.47 M solution, 77.0 mmol, 1.25 equiv.) was then added slowly under an argon flow, and the mixture wasleft at 0°C for 50 min. After evaporation of the solvent under reduced pressure, the solid obtained was diluted in 200 mL of diethyl ether and hydrolyzed with a 3 M hydrochloric acid solution. The aqueous layer, after decantation, was extracted with diethyl ether (3 × 50 mL). The combined organic layers were successively washed with 50 mL of saturated sodium hydrogencarbonate, 50 mL of water and 50 mL of saturated sodium chloride, before being dried over magnesium sulphate, concentrated under reduced pressure and distilled to give 12.90 g (95%) of a pale yellow oil **11**. − b p: 96°C/0.02 Torr. − IR (KBr): $\tilde{\nu}$ = 1687 cm^{-1} (CO). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 6.65 (t, 1 H), 3.48 (t, 2 H), 2.49 (t, 2 H), 2.42 (t, 2 H), 2.18 (m, 2 H), 1.88 (m, 2 H), 1.72 (m, 2 H), 1.69 (m, 2 H),1.18 (s, 9 H). − ^{13}C NMR ($CDCl_3$): δ = 200.0, 139.1, 136.3, 72.4, 60.5, 60.2, 40.0, 29.3, 27.4, 26.5, 24.4, 23.5, 23.2, 14.0. − $C_{14}H_{24}O_2$ (224.34): calcd C 74.95, H 10.78, O 14.26; found C 74.82, H 10.57, O 14.63. − MS; *m*/*z* (%): 225 (100) [MH^+].

Preparation of the Annelated Terpyridine 12: 5,6,7,8-Tetrahydro-8-quinolinone **3** (0.4 g, 2.73 mmol) in 20 mL of THF was cooled to −20°C and, *n*BuLi (2.5 M in hexane, 1.1 mL, 2.75 mmol) was then added. The reaction was stirred for a further 2 h and **10** (0.81 g, 2.9 mmol) in 15 mL of THF was added. The mixture was stirred for 2 h at −20°C, and 1.3 g (19 mmol) of ammonium acetate and 30 mL of acetic acid were added. The reaction was then heated at reflux for 16 h. After cooling to room temperature, the solution was evaporated to dryness, the resulting solid residue was dissolved in 50 mL of dichloromethane and saponified with a saturated solution of sodium carbonate. After separation of the organic phase, the aqueous phase was extracted with dichloromethane (2 × 25 mL). The combined organic extracts were then washed with 50 mL of water and 50 mL of a saturated solution of sodium chloride, and then dried over magnesium sulphate. After evaporation, the residue was purified by column chromatography on alumina (ethyl acetate/methanol, 12:1) to give 0.6 g of **12** as a yellow oil (yield: 60%). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 8.7 (d, 2 H), 7.5 (d, 2 H), 7.2 (dd, 2 H), 3.46 (t, 2 H), 3.0 (m, 8 H), 2.8 (m, 2 H), 1.72 (m, 2 H), 1.18 (s, 9 H). − ^{13}C NMR ($CDCl_3$): δ = 152.2, 149.6, 148.3, 146.3, 135.4, 133.2, 132.7, 123.2, 72.7, 60.6, 30.3, 27.5, 27.3, 25.2, 23.7. − $C_{26}H_{29}N_3O(H_2O)$ (417.55): calcd C 74.79, H 7.48, N 10.06; found C 74.81, H 7.47, N 10.32. − MS; *m*/*z* (%): 400 (100) [MH^+].

Preparation of the Trialkylated Heptacyclic Annelated Terpyridine 14: Distilled diisopropylamine (0.14 mL, 1.0 mmol) in 5 mL of dry THF was cooled to −78°C. Then *n*BuLi (1.6 M in hexane, 0.8 mL, 1.2 mmol) was added. After stirring for 2 h at −78°C, compound **2** (0.414 g, 1.0 mmol) in 5 mL of dry THF was added and the mixture was held at −78°C for a further 2 h. To this mixture compound **8** (0.5 g, 1.2 mmol) in 5 mL of THF was added. After 16 h at −78°C, the mixture was allowed to warm to room temperature. Ammonium acetate (0.4 g, 5.0 mmol) of and 10 mL of acetic acid were then added and the mixture was refluxed for 16 h. After cooling to room temperature the solution was evaporated to dryness and the solid residue was dissolved in 50 mL of dichloromethane and basified with a saturated solution of sodium carbonate. After separation of the organic phase, the aqueous phase was extracted twice with dichloromethane. The combined organic extracts were then washed with water and a saturated solution of sodium chloride and finally dried over magnesium sulphate. After evaporation of the solvent, the residue was purified by column chromatography on alumina (ethyl acetate/pentane, 5:5) to give 0.84 g of **14** (yield: 50%). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 8.2 (s, 1 H), 7.55 (d, 2 H), 7.36 (t, 2 H), 7.2 (t, 1 H), 3.43 (m, 6 H), 3.2 (t, 2 H), 2.8 (m, 18 H), 1.8 (m, 14 H), 1.23 (s, 9 H), 1.22 (s, 9 H), 1.21 (s, 9 H). − ^{13}C NMR ($CDCl_3$): δ = 155.5, 151.7, 150.6, 150.5, 146.1, 145.9, 144.7, 135.1, 131.6, 131.5, 130.7, 130.2, 130.0, 129.8, 129.5, 128.9, 127.9, 127.5, 125.8, 72.5, 60.9, 60.8, 60.6, 32.7, 30.4, 29.8, 29.7, 27.6, 27.4, 26.3, 25.9, 24.9, 24.7, 23.9, 23.8, 23.3, 23.0, 22.8, 22.7, 20.8. − $C_{55}H_{73}N_3O_3(H_2O)$ (842.12): calcd C 78.44, H 8.98, N 4.99; found C 78.68, H 9.33, N 5.09. − MS; *m*/*z* (%): 824 (100) [MH^+].

Preparation of the Heptacyclic Annelated Terpyridine 15: This compound was obtained according to the procedure described for **14**. The reaction of **2** (0.68 g, 1.70 mmol) with **9** (0.90 g, 1.70 mmol) gave, after purification by column chromatography on alumina (ethyl acetate), compound **15** (0.7 g, 46%) as a brown oil. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.75 (s, 2 H), 7.0 (d, 4 H), 6.9 (t, 4

H), 6.6 (dd, 2 H), 3.4 (t, 6 H), 2.9−2.5 (m, 18 H), 1.7−1.5 (m, 14 H), 1.22 (s, 9 H), 1.19 (s, 9 H). − ^{13}C NMR ($CDCl_3$): δ = 157.5, 151.1, 148.6, 147.4, 146.0, 142.3, 140.9, 135.7, 132.9, 128.7, 128.0, 127.8, 126.5, 123.2, 72.8, 72.6, 62.3, 61.9, 32.3, 31.5, 30.4, 29.8, 28.6, 27.9, 27.5, 26.7, 25.1, 24.3, 22.7. − $C_{62}H_{77}N_3O_3(H_2O)$ (930.33): calcd. C 80.04, H 8.56, N 4.52; found C 80.18, H 8.33, N 4.79. − MS; *m/z* (%): 930 (100) [MH^+].

Preparation of the Hexacyclic Annelated Terpyridine 16: This compound was obtained according to the procedure described for **14**. The reaction of **10** (1.34 g, 3.33 mmol) with **2** (1.0 g, 3.66 mmol) gave, after purification by column chromatography on alumina (ethyl acetate/methanol 9:1), 1.1 g (55%) of **16** as a yellow oil. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 8.69 (d, 1 H), 8.20 (s, 1 H), 7.9 (d, 1 H), 7.52 (m, 2 H), 7.25 (m, 2 H), 7.15 (m, 2 H), 3.4 (t, 4 H), 2.9−2.75 (m, 16 H), 1.85 (m, 2 H), 1.65 (m, 4 H), 1.22 (s, 9 H), 1.19 (s, 9 H). − ^{13}C NMR ($CDCl_3$): δ = 157.5, 151.1, 148.6, 147.4, 146.0, 142.3, 140.9, 135.7, 132.9, 128.7, 128.0, 127.8, 126.5, 123.2, 72.8, 72.6, 62.3, 61.9, 32.3, 31.5, 30.4, 29.8, 28.6, 27.9, 27.5, 26.7, 25.1, 24.3, 22.7. − $C_{44}H_{53}N_3O_2$ (655.92): calcd C 80.57, H 8.14, N 6.41; found C 80.76, H 7.83, N 6.09. − MS; *m/z* (%): 656 (100) [MH^+].

Preparation of the Pentacyclic Annelated Bipyridine 17: This compound was obtained using the same procedure described for **14**. The reaction of **2** (0.68 g, 1.7 mmol) and **11** (0.38 g, 1.7 mmol) gave, after purification by column chromatography on silica gel (ethyl acetate), **17** (0.52 g, 50%). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 8.2 (s, 1 H), 7.45 (d, 2 H), 7.4 (t, 2 H), 7.2 (dd, 1 H), 3.4 (t, 4 H), 3.1 (m, 2 H), 2.9−2.6 (m, 14 H), 1.9 (t, 4 H), 1.6 (m, 6 H), 1.2 (s, 9 H), 1.19 (s, 9 H). − ^{13}C NMR ($CDCl_3$): δ = 157.9, 151.0, 148.6, 148.0, 146.3, 141.7, 138.9, 136.5, 131.5, 130.2, 130.0, 129.7, 129.1, 128.3, 126.4, 125.3, 72.7, 72.5, 61.7, 60.9, 31.7, 30.1, 29.3, 27.7, 26.6, 26.2, 25.9, 23.9, 23.3, 22.5. − $C_{41}H_{54}N_2O_2$ (606.90): calcd C 81.14, H 8.97, N 4.62; found C 81.38, H 8.63, N 4.99. − MS; *m/z* (%): 609 (100) [MH^+].

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