Facile Synthesis of Polypyridine Esters: A Route to Functionalized Aldehydes

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A wide range of ester-substituted oligopyridines, based on pyridine, 1,8-naphthyridine, 1,10-phenanthroline, 2,2′-bipyridine, and 2,2′:6′,6″-terpyridine units, has been synthesized and fully characterized. The principal reaction involves the palladium(0)-catalyzed carboalkoxylation of the bromo-, chloro- or triflate-substituted pyridine unit with carbon monoxide in the presence of a primary alcohol as nucleophile and a tertiary amine as base. Monofunctionalization of disubstituted compounds is realized by reaction in ethanol under mild conditions (70 °C, 1 atm CO). Stepwise reduction of selected esters with sodium borohydride, followed by Swern oxidation, affords the corresponding carbaldehydes in good yield. Several products are reported for the first time. The synthetic methods reported herein represent a valuable approach to the large-scale preparation of ester-functionalized oligopyridines that can be subsequently transformed to the corresponding alcohols or acids. These procedures also provide a practical methodology to the rational design of ligands bearing different kinds of functionalities.

Introduction

Polypyridine-based dicarbaldehydes are frequently prepared by formylation of the metalated derivatives[1], by SeO_2[2] or tertiobutyliodine[3] oxidation of the methyl-substituted compounds, by hydrolysis of dibromomethyl-substituted products[4] or, more recently, by enamine oxidation.[5] These procedures usually begin with the readily available halogeno- or methyl-substituted derivatives but are prone to modest yields. Additional drawbacks concern the difficulty in obtaining monofunctionalized derivatives, contamination by selenium, and [to a lesser extent] the relatively high cost of the reagents. In certain cases, such as 6,6″-disubstituted 2,6:6′,6″-terpyridine, it has not been possible to prepare the target biscarbaldehyde by these classical routes. Furthermore, monofunctionalization of symmetrical or disymmetrical oligopyridines is highly desirable because of their potential use as synthons in the fabrication of magnetic,[6] optical[7] or mesomorphic materials.[8] In searching for alternative routes to oligopyridine-substituted aldehydes, we have explored the use of carboalkoxylation reactions that utilize halogeno- or pseudo-halogeno-substituted pyridine derivatives as precursors. This is a particularly convenient procedure when promoted by low-valent palladium(0) that facilitates the isolation of di- and mono-substituted esters. Many of these activated esters can be reduced to the corresponding alcohols and subsequently oxidized under mild conditions to the analogous aldehydes.

Results and Discussion

The carboalkoxylation of aryl halides, mediated by low-valent palladium(0), was pioneered by Heck,[9,10] but to date it has not been applied to the functionalization of oligopyridines.[11] We have, however, described the preparation of ethynyl-grafted polypyridine building blocks using a Pd-catalyzed process.[12] Because carboalkoxylation reactions are known to proceed smoothly with a variety of aromatic compounds and because Sonogashira cross-coupling reactions are very effective with alkynes, it seems reasonable to suppose that such reactions might afford ester-functionalized oligopyridines in good yield. Consequently, we began a detailed investigation of the best conditions for preparation of suitable esters equipped with ancillary oligopyridine-based coordination sites.

It was soon established that halogeno- or pseudo-halogeno-substituted polypyridines react readily with carbon monoxide on a 1-g scale when the reaction

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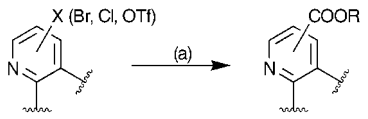
Scheme 1[a]



[a] Key: (a) CO (1 atm), ROH (excess), R′$_3$N (excess), Pd^0(PPh$_3$)$_4$ (2% mol), 70−120 °C.

mixture contains a primary alcohol, a tertiary amine, and catalytic amounts of $Pd(PPh_3)_2Cl_2$ (2 mol %) (Scheme 1). This strategy provides easy access to a large variety of useful esters (Chart 1), with isolated yields ranging from 40 to 98%. The halogenated precursors are conveniently prepared by conventional procedures (see Experimental Section).

Initial experiments were carried out with *n*-butanol as the nucleophile and with tri-*n*-butylamine as the base, since their boiling points exceed the required reaction temperature. In general, reactions run at 120 °C in the presence of 2 mol % of catalyst required 20−96 h to reach completion. This temperature ensures that all the starting materials are properly dissolved. When the starting compounds are highly soluble (e.g., 2,6-dibromopyridine, 6,6′-dibromo-2,2′-bipyridine, or methyl-substituted bpys), it is possible to replace *n*-butanol with ethanol and operate at much lower temperature (70 °C) and for shorter reaction times (8−12h). Under these conditions, the products are readily isolated by column chromatography after evaporation of the solvent. It is noteworthy that carboethoxylation proceeds much faster and gives far higher yields than the corresponding carbobutoxylation, and examples are gathered in Table 1. It is surmised that the catalyst is less prone to thermal breakdown under milder conditions appropriate for carboethoxylation. Thus, in the case of **4a**, it was found that addition of an extra aliquot of 6,6′-dibromo-bpy (0.5 g) to the reaction mixture at the end of the first run allowed isolation of an equivalent amount of product after the same reaction time (compare entries 3 and 4, Table 1). In contrast, it was not possible to achieve even modest conversion of additional precursor in the case of carbobutoxylation, despite higher temperature and longer reaction times (compare entries 1 and 2, Table 1).

Although significant differences in rate and stereospecificity have been noted for the carboalkoxylation of vinylic halides with $Pd(PPh_3)_2X_2$ where X = Cl, Br to I,[13] surprisingly, no obvious differences were found for either rate or yield when the palladium precursor was initially present as the chloro or bromo forms (entries 1 and 5, Table 1). Furthermore, similar rates of carbobutoxylation were found for bromo- or chloro-disubstituted 1,10-phenanthrolines (entries 6 and 7, Table 1) and for bromo- or triflato-substituted 2,2′:6′,6″-terpyridines (entries 8 and 9, Table 1). Both sets of experiments support the idea that coordination of the anion to the palladium center does not play a significant role, as recently highlighted in classical Heck-type coupling reactions.[14] Oxidative addition of the halogenopyridine is unlikely to be the rate-limiting step in the overall process.

In an attempt to identify those parameters that most markedly influence the course of these carboalkoxylation reactions, we studied the relative reactivity of compounds **10a** and **11a** (Chart 2) toward carboethoxylation (Table 1). It was found that the formation of the less hindered ethyl ester **11b** is about 12 times faster than derivative **10c** (entries 11 and 12, Table 1). It is likely that either the oxidative addition of Py-X to the palladium center or nucleophilic attack of the primary alcohol on the acylated intermediate becomes less effective when a methyl substituent is located near the activated Py-X bond. It is further surmised that the presence of bulky substituents will decrease the efficiency of the catalytic process and might seriously limit the scope of these reactions. Our results are in line with the sequence of consecutive steps involved in the catalytic cycle.[9]

The success achieved in the palladium-catalyzed carboalkoxylations prompted us to investigate the monofunctionalization of dibromo-substituted oligopyridines. This is an important issue for the chemistry community since these ligands are promising building blocks for construction of hybrid molecules (from the corresponding carbaldehyde and bromide substituted compounds) bearing for example a stable radical and a C≡C−H crystal director.[15] Mono-carboethoxylation could be achieved with modest yield (40 to 50%) under a continuous flow of CO at atmospheric pressure and in refluxing ethanol with tri-*n*-butylamine as base (Scheme 2). Surprisingly, when tri-*n*-butylamine is replaced with triethylamine difunctionalization takes place in good yield, as described above. For the moment, the nature of this effect remains unclear. Furthermore, this practice suffers from several disadvantages associated with the poor solubility of the starting material. In the case of the weakly soluble compounds, such as 2,2′:6′,6″-terpyridine derivatives, the more soluble mono-ester could not be isolated due to its increased reactivity toward further carboethoxylation. Reduction of the catalyst concentration to 0.2 mol % substantially improves the percentage of the monoester but not to an attractive overall yield. In general, difunctionalization occurs when the ester is much more soluble than the precursor but monocarboalkoxylation is achieved if the precursor is sufficiently soluble. This assignment is supported by the observation that the sparingly soluble naphthyridine and phenanthroline derivatives do not react under these conditions.

Polypyridine ligands bearing ester groups are useful starting materials for the preparation of the carbaldehyde derivatives. These esters were readily converted to the respective methyl alcohols (Scheme 3). Swern oxidation[16] provides a simple means by which to synthesize novel bipyridine **4f** and **10e** and terpyridine **9d** based compounds. The terpyridine target was used subsequently to prepared imino-based ligands[17,18] and nitronyl-nitroxide based free radicals.[19] Some interesting applications pertaining to the field of liquid crystals and molecular magnetism have recently emerged with these scaffolds.[20,21]

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Chart 1

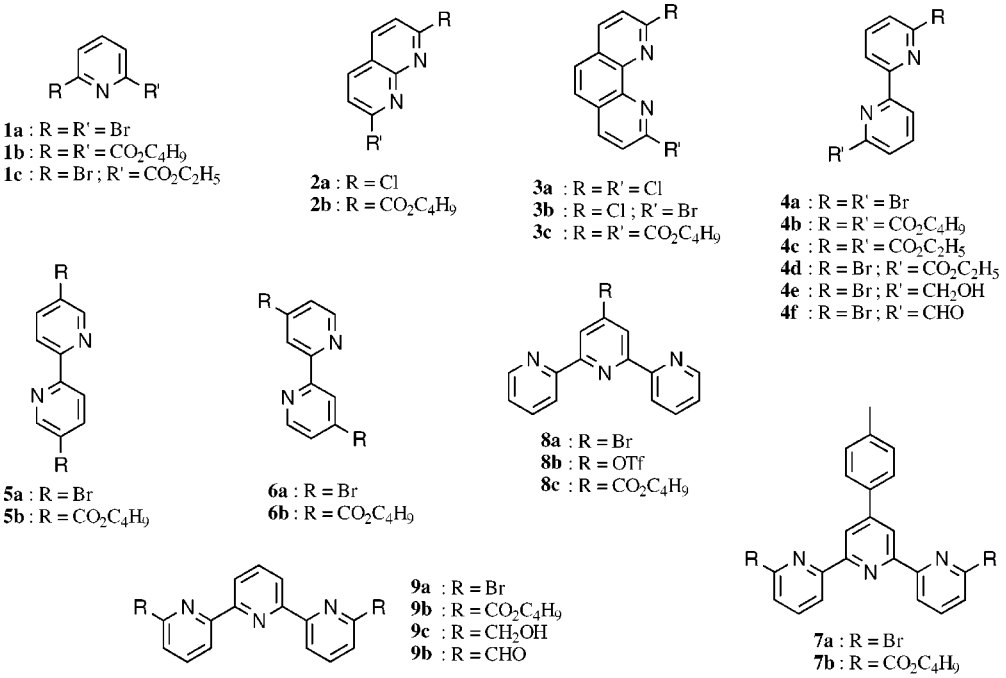
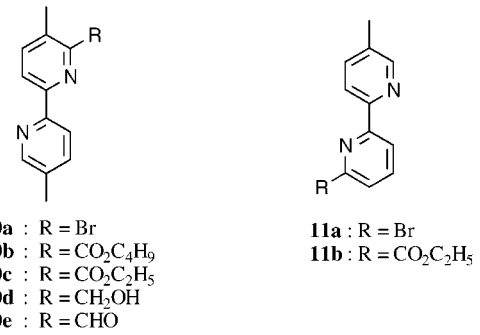


Table 1. Palladium-Catalyzed Carboalkoxylation[a]

entry	starting compd	product	solvent	*T* (°C)	reaction time (h)	% yield
1	**4a**	**4b**	^{n}BuOH/^{n}Bu$_3$N	120	96	72
2[b]	**4a**	**4b**	^{n}BuOH/^{n}Bu$_3$N	120	120	30
3	**4a**	**4c**	EtOH/Et$_3$N	70	12	85
4[c]	**4a**	**4c**	EtOH/Et$_3$N	70	12	82
5	**4a**	**4b**	^{n}BuOH/^{n}Bu$_3$N	120	96	70
6	**3a**	**3c**	^{n}BuOH/^{n}Bu$_3$N	120	72	60
7	**3b**	**3c**	^{n}BuOH/^{n}Bu$_3$N	120	72	62
8	**8a**	**8c**	^{n}BuOH/^{n}Bu$_3$N	120	72	74
9	**8b**	**8c**	^{n}BuOH/^{n}Bu$_3$N	120	72	76
10	**10a**	**10b**	^{n}BuOH/^{n}Bu$_3$N	120	96	75
11	**10a**	**10c**	EtOH/Et$_3$N	70	96	97
12	**11a**	**11b**	EtOH/Et$_3$N	70	8	98

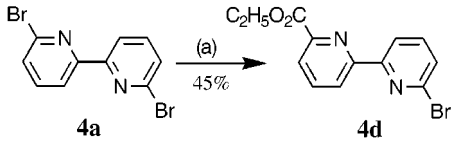
[a] Carried out under a continuous flow of CO at atmospheric pressure with $Pd(PPh_3)_2Cl_2$. For entry 5, $Pd(PPh_3)_2Br_2$ was used as catalyst. [b] After 96 h of reaction, 0.5 g of **4a** was added as a solid. [c] After 12 h of reaction, 0.5 g of **4a** was added as a solid.

Chart 2



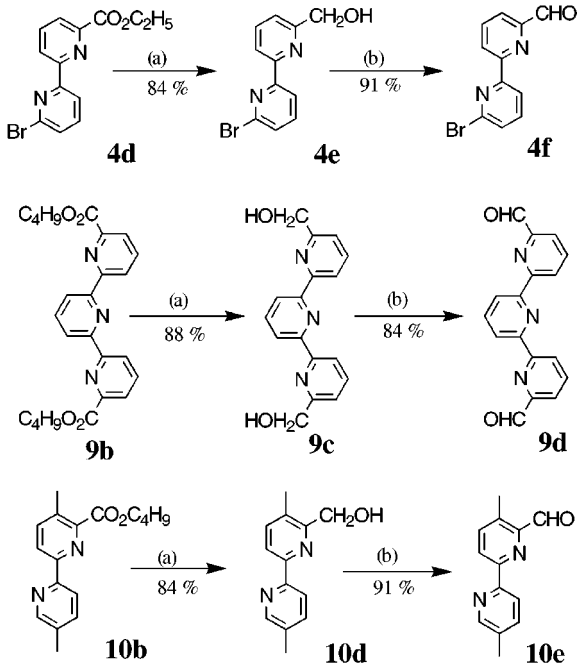
In conclusion, we have developed a practical and general protocol for the synthesis of ester-substituted polypyridines. The ready availability of the reagents, the overall simplicity of the procedure, the use of mild reaction conditions, and the reasonable yields obtained suggest that this methodology is a useful entry for the preparation of the corresponding carbaldehydes and carboxylates. These acids are promising synthons for the preparation of luminescent lanthanide probes.[22] The selected procedure is based on a carboalkoxylation reac-

Scheme 2[a]



[a] Key: (a) CO (1 atm), EtOH, *n*-Bu$_3$N, $Pd^0(PPh_3)_4$ (2% mol), 70 °C.

Scheme 3[a]



[a] Key: (a) $NaBH_4$; EtOH; (b) $(COCl)_2$, DMSO, CH_2Cl_2, Et_3N, −60 °C.

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tion promoted by low-valent palladium(0). It was found that monoalkoxylation does not always work but becomes possible when the solubility of the starting material is at least comparable to that of the intermediate monosubstituted compound. Otherwise, the monoester reacts faster than the starting compound and only difunctionalized products are isolated. Reduction of certain esters with sodium borohydride leads to the corresponding alcohols while oxidation gives the corresponding carbaldehydes, some of which have been prepared for the first time.

Experimental Section

General Methods. The 200.1 (^{1}H) and 50.3 MHz (^{13}C) NMR spectra were recorded at room temperature, unless otherwise specified, using perdeuterated solvent as internal standard: δ (H) in ppm relative to residual protiated solvent in $CDCl_3$ (7.26) or d_6-DMSO (2.60); δ (C) in ppm relative to the solvent in $CDCl_3$ (77.0), all carbon signals were detected as singlets. Melting points were obtained on a capillary melting point apparatus in open-ended capillaries and are uncorrected. FT-IR spectra were measured in KBr pellets. UV−vis spectra were measured in CH_2Cl_2 at room temperature. Fast-atom bombardment (FAB, positive mode) mass spectra were obtained using *m*-nitrobenzyl alcohol (*m*-NBA) as the matrix, and EI-MS were measured by direct introduction with a LKB-9000S apparatus.

Materials. 2,6-Dibromopyridine (**1a**), trimethylsilylacetylene, and $NaIO_4$ are commercially available. 2,7-Dichloro-1,8-naphthyridine (**2a**)[23] and 2-chloro-9-bromo-1,10-phenanthroline (**3b**) were synthesized from *N*-methyl-2-chloro-1,10-phenanthroline-9-one, using PBr_5.[24] 2,9-Dichloro-1,10-phenanthroline (**3b**) was synthesized from *N*-methyl-2-chloro-1,-10-phenanthroline-9-one using PCl_5.[25] 6,6′-Dibromo-2,2′-bipyridine (**4a**),[1] 5,5′-dibromo-2,2′-bipyridine (**5a**),[26,27] 4,4′-dibromo-2,2′-bipyridine (**6a**),[28] 6,6″-dibromo-4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine (**7a**),[29] 4′-bromo-2,2′:6′,2″-terpyridine (**8a**),[30] 4′-[[(trifluoromethylsulfonyl]oxy]-2,2′:6′,2″-terpyridine (**8b**),[31] 6,6″-dibromo-2,2′:6′,2″-terpyridine (**9a**),[32] 6-bromo-5,5′-dimethyl-2,2′-bipyridine (**10a**),[33] 6-bromo-5-methyl-2,2′-bipyridine (**11a**),[34] and $Pd(PPh_3)_2Cl_2$[35] were prepared and purified according to the literature procedures. All reactions were carried out under dry argon using Schlenk-tube techniques. Solvents were used as purchased expect for tri-*n*-butylamine and triethylamine which were dried over solid KOH pellets and freshly distilled under argon before use. Compound **6b** has previously been prepared by esterification of the acid chloride and display identical spectroscopic characteristics.[36]

Careful! Carbon monoxide is harmful and must be used exclusively in a well-ventilated fumehood.

General Procedure for the Preparation of the Carbobutoxy Derivatives, Following Experimental Conditions 1. In a 100 mL two-neck flask, equipped with a reflux condenser, a gas bubbler, and a magnetic stirring bar, $Pd(PPh_3)Cl_2$ (2 mol %) was added to a solution or a suspension of the substrate (1.0 g scale), in *n*-BuOH and *n*-Bu_3N. The reaction mixture was degassed under a continuous flow of CO at atmospheric pressure and stirred along with heating. During the reaction, a homogeneous light-yellow solution was formed. After complete comsumption of the starting material (determined by TLC) the solution turned black. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was dissolved in a mixture of dichloromethane and water and extracted with dichloromethane. The combined organic phases were washed with 20% hydrochloric acid solution, water, saturated aqueous solution of sodium bicarbonate, and finally with water. The organic phase was dried over $MgSO_4$ and filtered through paper, and the solvent was evaporated under vacuum. The resulting crude brown residue was purified by flash chromatography on NEt_3 deactivated SiO_2 as solid phase and eluted with a gradient of hexane/CH_2Cl_2. The analytically pure compounds were obtained as white powders or as colorless oils.

General Procedure for the Preparation of the Carboethoxy Derivatives, Following Experimental Conditions 2. In a 100 mL two-neck flask, equipped with a reflux condenser, a gas bubbler, and a magnetic stirring bar, $Pd(PPh_3)Cl_2$ (2 mol %) was added to a solution of the substrate (1.0 g scale), in a mixture of EtOH and Et_3N (2/1 v/v). The reaction mixture was degassed with a continuous flow of CO at atmospheric pressure and heated. After complete comsumption of the starting material (determined by TLC), the homogeneous solution turned black. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography column using NEt_3 deactivated SiO_2 as solid support and eluted with a gradient of hexane/CH_2Cl_2 to give the analytically pure compounds as white crystalline products or colorless oils.

General Procedure for the Preparation of the Hydroxymethyl Derivatives, Following Experimental Conditions 3. To a solution of the butoxy or ethoxy esters in EtOH was added $NaBH_4$ (20 equiv) stepwise as solid. The white suspension was stirred at room temperature for 2 d, and then water was slowly added and the solvent was evaporated under vacuum. The residue was dissolved in water and dichloromethane. The organic phase separated, and the aqueous phase was extracted with dichloromethane. The combined organic extracts were dried over $MgSO_4$, and the solvent was reduced by evaporation. The product was precipitated by addition of hexane and recovered by filtration and yielded the desired hydroxymethyl derivatives as white powders. No further purification of the hydroxymethyl compounds is required before oxidation to the aldehyde and generally analytically pure compounds were isolated.

General Procedure for the Preparation of the Carbaldehyde Derivatives, Following Experimental Conditions 4. Into a dry 100 mL two-neck flask cooled below −60 °C were sucessively added oxalyl chloride dissolved in freshly distilled dichloromethane. Then, a solution of dry dimethyl sulfoxide diluted with dichloromethane was dropwise added over 20 min. After 10 min, a cold solution of the hydroxymethyl derivative dissolved in a mixture of dimethyl sulfoxide (5 mL) and dichloromethane (5 mL) was dropwise added. The mixture was stirred below −60 °C for 3 h. After the mixture was cooled to −30 °C, triethylamine (10 mL) was dropwise added. The cooling bath was then removed, the reaction mixture was allowed to warm to room temperature (ca. 30 min), and water (30 mL) was added. The aqueous phase was extracted with dichloromethane, the combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated to the minimum. The product was precipitated by addition of hexane. The resulting precipitate was filtered to afford the desired compounds as pale-yellow powders. No additional purification of the carbaldehyde compound is required at this stage and give analytically pure products.

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2,6-Dicarbobutoxypyridine (1b). This compound was prepared according to experimental condition 1, from 1.00 g (4.22 mmol) of **1a** and 0.046 g (0.066 mmol) of $Pd(PPh_3)_2Cl_2$, in *n*-BuOH (20 mL) and *n*-Bu_3N (2 mL). The reaction mixture was heated at 120 °C for 20 h. Purification was performed by a NEt_3-deactivated SiO_2 flash chromatography column eluted with a gradient of hexane/CH_2Cl_2 (95/5 to 70/30, v/v) and afforded ligand **1b** as a white powder (0.940 g, 80%): mp 63−64 °C; UV/Vis (CH_2Cl_2) λ_{max} (ϵ) 224 nm (4600 M^{-1} cm^{-1}), 264 (3200); ^1H NMR ($CDCl_3$) δ 0.98 (t, J = 7.4 Hz, 6H), 1.49 (m, 4H), 1.82 (m, 4H), 4.42 (t, J = 6.9 Hz, 4H), 7.98 (t, J = 7.3 Hz, 1H), 8.25 (d, J = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.8, 19.2, 30.6, 65.1, 127.7, 139.2, 148.7, 164.6; IR (KBr, cm^{-1}) 2959 (s), 2873 (m), 1741 (ν_{COO}, s), 1576 (m), 1464 (m), 1382 (m), 1296 (s), 1245 (s), 1165 (m), 1060 (m); EI/MS (*m*/*z*) 279 (M^+, 100), 178 (M − $CO_2C_4H_9$, 47), 77 (M − $2CO_2C_4H_9$, 25). Anal. Calcd for $C_{15}H_{21}NO_4$: C, 64.50; H, 7.58; N, 5.01. Found: C, 64.38; H, 7.32; N, 4.75.

2-Bromo-6-carboethoxypyridine (1c). This compound was prepared according to experimental condition 2, from 0.600 g (2.52 mmol) of **1a** and 0.035 g (0.049 mmol) of $Pd(PPh_3)_2Cl_2$, in EtOH (20 mL) and Et_3N (2 mL). The reaction mixture was heated at 70 °C for 40 h. Purification was performed by a chromatography column on alumina eluted with a mixture of hexane/CH_2Cl_2 (50/50, v/v) and afforded ligand **1c** as a white powder (0.24 g, 41%): mp 40−41 °C; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 222 nm (7600 M^{-1} cm^{-1}), 271 (4600); ^1H NMR ($CDCl_3$) δ 1.43 (t, J = 7.1 Hz, 3H), 4.47 (m, 2H), 7.68 (*p*t, J = 6.2, 3.1 Hz, 2H), 8.07 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.2, 62.3, 123.9, 131.6, 139.1, 142.1, 149.0, 163.8; IR (KBr, cm^{-1}) 3049 (w), 2981 (w), 1723 (ν_{COO}, s), 1560 (m), 1433 (m), 1405 (m), 1301 (s), 1247 (s), 1166 (m), 1122 (s); EI/MS (*m*/*z*) 229/231 (M^+, 100), 156/158 (M − $CO_2C_2H_5$, 53), 150 (M − Br, 26). Anal. Calcd for $C_8H_8NBrO_2$: C, 41.77; H, 3.51; N, 6.09. Found: C, 41.51; H, 3.26; N, 5.74.

2,7-Dicarbobutoxy-1,8-naphthyridine (2b). This compound was prepared according to experimental condition 1, from 0.45 g (2.26 mmol) of **2a** and 0.024 g (0.034 mmol) of $Pd(PPh_3)_2Cl_2$, in *n*-BuOH (15 mL) and *n*-Bu_3N (3 mL). The reaction mixture was heated at 120 °C during 40 h. Purification was performed by a NEt_3-deactivated SiO_2 flash chromatography column eluted with a gradient of hexane/CH_2Cl_2 (90/10 to 70/30, v/v) and afforded ligand **2b** as a colorless oil (0.298 g, 40%): UV/vis (CH_2Cl_2) λ_{max} (ϵ) 222 nm (15 000 M^{-1} cm^{-1}), 298 (13 600), 305 (22 800), 312 (20 800), 319 (30 600); ^1H NMR ($CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 6H), 1.48 (m, 4H), 1.77 (m, 4H), 4.50 (t, J = 6.6 Hz, 4H), 6.75 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 19.3, 31.1, 66.3, 110.8, 114.7, 138.5, 154.8, 165.2; IR (KBr, cm^{-1}) 2958 (m), 2874 (w), 1745 (ν_{COO}, s), 1610 (s), 1503 (m), 1443 (s), 1324 (s), 1260 (s), 1126 (m); EI/MS (*m*/*z*) 330 (M^+, 100), 229 (M − $CO_2C_4H_9$, 20), 128 (M − 2 $CO_2C_4H_9$, 52). Anal. Calcd for $C_{18}H_{22}N_2O_4$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.31; H, 6.62; N, 8.23.

2,9-Dicarbobutoxy-1,10-phenanthroline (3c). This compound was prepared according to experimental condition 1, from 1.128 g (4.53 mmol) of **3a** and 0.042 g (0.060 mmol) of $Pd(PPh_3)_2Cl_2$, in *n*-BuOH (30 mL) and *n*-Bu_3N (3 mL). The reaction mixture was heated at 120 °C during 72 h. Purification was performed by a chromatography column on alumina, eluted with a mixture of hexane/CH_2Cl_2 (50/50, v/v), and afforded ligand **3c** as a pale yellow oil (1.032 g, 60%): UV/vis (CH_2Cl_2) λ_{max} (ϵ) 222 nm (73 400 M^{-1} cm^{-1}), 279 (40 800), 291 (31 300); ^1H NMR ($CDCl_3$) δ 1.03 (t, J = 7.3 Hz, 6H), 1.58 (m, 4H), 1.93 (m, 4H), 4.73 (t, J = 6.6 Hz, 4H), 7.03 (d, J = 8.8 Hz, 2H), 7.51 (s, 2H), 8.00 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 19.5, 31.2, 65.8, 113.5, 123.1, 125.0, 138.8, 143.2, 162.6; IR (KBr, cm^{-1}) 2957 (s), 2870 (m), 1743 (ν_{COO}, s), 1609 (s), 1561 (m), 1501 (m), 1468 (s), 1340 (s), 1281 (s), 1225 (m); EI/MS (*m*/*z*) 380 (M^+, 100), 279 (M − $CO_2C_4H_9$, 37). Anal. Calcd for $C_{22}H_{24}N_2O_4$: C, 69.46; H, 6.36; N, 7.36. Found: C, 69.36; H, 6.28; N, 7.29.

6,6′-Dicarbobutoxy-2,2′-bipyridine (4b). This compound was prepared according to experimental condition 1, from 0.804 g (2.56 mmol) of **4a** and 0.030 g (0.043 mmol) of $Pd(PPh_3)_2Cl_2$, in *n*-BuOH (20 mL) and *n*-Bu_3N (2 mL). The reaction mixture was heated at 120 °C for 4 d. Purification was performed by a NEt_3 deactivated SiO_2 flash chromatography column eluted with a gradient of hexane/CH_2Cl_2 (90/10 to 70/30, v/v) and afforded ligand **4b** as a white powder (0.650 g, 72%): mp 92−93 °C; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 241 nm (16 400 M^{-1} cm^{-1}), 278 (18 200); ^1H NMR ($CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 6H), 1.44 (m, 4H), 1.75 (q, J = 7.3, 6.7 Hz, 4H), 4.36 (t, J = 6.6 Hz, 4H), 7.91 (ddd, J = 7.8, 6.7, 1.1 Hz, 2H), 8.06 (dd, J = 7.8, 1.1 Hz, 2H), 8.69 (dd, J = 7.8, 1.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.7, 19.2, 30.7, 65.6, 124.5, 125.3, 137.7, 147.8, 155.4, 165.1; IR (KBr, cm^{-1}) 3083 (m), 2957 (s), 2868 (m), 1731 (ν_{COO}, s), 1571 (m), 1299 (s), 1252 (s), 1161 (s); EI/MS (*m*/*z*) 356 (M^+, 100), 255 (M − $CO_2C_4H_9$, 29), 154 (M − 2 $CO_2C_4H_9$, 5). Anal. Calcd for $C_{20}H_{24}N_2O_4$: C, 67.40; H, 6.79; N, 7.86. Found: C, 67.27; H, 6.62; N, 7.75.

6,6′-Dicarboethoxy-2,2′-bipyridine (4c). This compound was prepared according to experimental condition 2, from 1.206 g (3.84 mmol) of **4a** and 0.040 g (0.057 mmol) of $Pd(PPh_3)_2Cl_2$, in EtOH (30 mL) and Et_3N (3 mL). The reaction mixture was heated at 70 °C during 12 h. Purification was performed by a NEt_3-deactivated SiO_2 flash chromatography column eluted with a gradient of hexane/CH_2Cl_2 (90/10 to 70/30, v/v) and afforded ligand **4c** as a white powder (0.980 g, 85%): mp 82−83 °C; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 240 nm (16 800 M^{-1} cm^{-1}), 280 (18 900); ^1H NMR ($CDCl_3$) δ 1.45 (t, J = 7.1 Hz, 6H), 4.49 (q, J = 7.2 Hz, 4H), 7.91 (ddd, J = 7.8, 6.7, 1.1 Hz, 2H), 8.25 (dd, J = 7.8, 1.1 Hz, 2H), 8.72 (dd, J = 7.8, 1.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.8, 62.6, 124.9, 126.2, 138.8, 148.8, 156.7, 166.0; IR (KBr, cm^{-1}) 3085 (m), 2960 (s), 1735 (ν_{COO}, s), 1573 (m), 1302 (s), 1255 (s), 1160 (s); EI/MS (*m*/*z*) 300 (M^+, 100), 199 (M − $CO_2C_4H_9$, 12); Anal. Calcd for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33. Found C, 63.69; H, 5.12; N, 9.06.

6-Bromo-6′-carboethoxy-2,2′-bipyridine (4d). This compound was prepared according to experimental condition 2, from 7.236 g (23.04 mmol) of **4a** and 0.252 g (0.359 mmol) of $Pd(PPh_3)_2Cl_2$, in EtOH (200 mL) and Et_3N (20 mL). The reaction mixture was heated at 70 °C during 40 h. Purification was performed by a NEt_3-deactivated SiO_2 flash chromatography column eluted with a gradient of hexane/CH_2Cl_2 (90/10 to 70/30, v/v) and afforded ligand **4d** as a white powder (3.18 g, 45%): mp 106−107 °C; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 236 nm (17 200 M^{-1} cm^{-1}), 286 (23 800), ^1H NMR ($CDCl_3$) δ 1.42 (t, J = 7.1 Hz, 3H), 4.45 (q, J = 7.2 Hz, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.65 (t, J = 7.9 Hz, 1H), 7.90 (t, J = 7.9 Hz, 1H), 8.08 (d, J = 7.3 Hz, 1H), 8.50 (t, J = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.3, 61.9, 120.3, 124.3, 125.3, 128.5, 137.9, 139.3, 141.5, 147.9, 154.6, 156.3, 165.0; IR (KBr, cm^{-1}) 3049 (w), 2979 (w), 1739 (ν_{COO}, s), 1577 (m), 1543 (m), 1421 (m), 1228 (m), 1138 (s), 1083 (s); EI/MS (*m*/*z*) 306/308 (M^+, 100), 235/233 (M − $CO_2C_2H_5$, 70), 154 (M − $CO_2C_2H_5$ − Br, 50). Anal. Calcd for $C_{13}H_{11}N_2O_2$-Br: C, 50.84; H, 3.61; N, 9.12. Found: C, 50.74; H, 3.53; N, 9.02.

6-Bromo-6′-hydroxymethyl-2,2′-bipyridine (4e). This compound was prepared according to experimental condition 3, from 2.880 g (9.36 mmol) of **4d** and 7.080 g (0.186 mol) of $NaBH_4$, in EtOH (95 mL). The reaction mixture was stirred at room temperature during 48 h. Purification was performed by recrystallization of the crude product from a mixture of dichloromethane/hexane and afforded ligand **4e** as a white powder (2.280 g, 92%): mp 158−159 °C; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 245 nm (6300 $M^{-1}cm^{-1}$), 293 (16 300); ^1H NMR ($CDCl_3$) δ 3.88 (t, J = 4.7 Hz, 1H), 4.83 (d, J = 4.3 Hz, 2H), 7.27 (d, J = 7.8 Hz, 1H), 7.50 (dd, J = 7.8, 0.8 Hz, 1H), 7.68 (t, J = 7.8, 1H), 7.83 (t, J = 7.8 Hz, 1H), 8.34 (d, J = 7.8 Hz, 1H)), 8.39 (dd, J = 7.8, 0.8 Hz, 1H); IR (KBr, cm^{-1}) 3412 (s), 3304 (w), 2896 (w), 1576 (s), 1549 (s), 1420 (s); EI/MS (*m*/*z*) 264/266 (M^+, 100), 185 (M − Br, 60). Anal. Calcd for $C_{11}H_9N_2OBr$: C, 49.84; H, 3.42; N, 10.57. Found: C, 49.53; H, 3.01; N, 10.24.

6-Bromo-6′-formyl-2,2′-bipyridine (4f). This compound was prepared according to experimental condition 4, from 1.950 g (7.35 mmol) of **4e**, 0.700 mL (8.00 mmol) of oxalyl chloride in dichloromethane (45 mL), and 0.600 mL (8.45 mmol) of DMSO in dichloromethane (15 mL). Purification was performed by an aqueous workup and by recrystallization of

the crude product from a mixture of dichloromethane and hexane and afforded ligand **4f** as a cream powder (1.610 g, 83%): mp 192−193 °C; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 256 nm (7500 M^{-1} cm^{-1}), 291 (15 700); ^1H NMR ($CDCl_3$) δ 7.55 (dd, J = 7.8, 1.1 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 8.01 (m, 2H), 8.54 (dd, J = 7.8, 1.1 Hz, 1H), 8.66 (m, 1H), 10.15 (s, 1H); IR (KBr, cm^{-1}) 2930 (w), 2821 (w), 1715 (ν_{CHO}, s), 1575 (m), 1549 (m), 1424 (m), 1116 (s); EI/MS (*m*/*z*) 262/264 (M^+, 100), 183 (M − Br, 10). Anal. Calcd for $C_{11}H_7N_2OBr$: C, 50.22; H, 2.68; N, 10.65. Found: C, 50.09; H, 2.40; N, 10.35.

5,5′-Dicarbobutoxy-2,2′-bipyridine (5b). This compound was prepared according to experimental condition 1, from 0.804 g (2.56 mmol) of **5a** and 0.030 g (0.043 mmol) of $Pd(PPh_3)_2Cl_2$, in *n*-BuOH (20 mL) and *n*-Bu_3N (2 mL). The reaction mixture was heated at 120 °C during 40 h. Purification was performed by a NEt_3-deactivated SiO_2 flash chromatography column eluted with a gradient of hexane/CH_2Cl_2 (90/10 to 70/30, v/v) and afforded ligand **5b** as a white powder (0.820 g, 90%): mp 131−132 °C; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 244 nm (11 000 M^{-1} cm^{-1}), 251 (11 800), 294 (18 200); ^1H NMR ($CDCl_3$) δ 1.03 (t, J = 7.3 Hz, 6H), 1.5 (m, 4H), 1.78 (m, 4H), 4.36 (t, J = 6.6 Hz, 4H), 8.38 (dd, J = 8.3, 2.2 Hz, 2H), 8.54 (dd, J = 8.3, 0.8 Hz, 2H), 9.25 (dd, J = 2.2, 0.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.7, 19.2, 30.7, 65.3, 121.2, 126.5, 138.0, 150.5, 158.2, 165.1; IR (KBr, cm^{-1}) 2959 (s), 2870 (m), 1713 (ν_{COO}, s), 1461 (s), 1369 (m), 1285 (s), 1114 (s), 1019 (m); EI/MS (*m*/*z*) 356 (M^+, 100), 255 (M − $CO_2C_4H_9$, 7). Anal. Calcd for $C_{20}H_{24}N_2O_4$: C, 67.40; H, 6.79; N, 7.86. Found: C, 67.19; H, 6.67; N, 7.80.

6,6″-Dicarbobutoxy-4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine (7b). This compound was prepared according to experimental condition 1, from 0.900 g (1.87 mmol) of **7a** and 0.030 g (0.043 mmol) of $Pd(PPh_3)_2Cl_2$, in *n*-BuOH (50 mL) and *n*-Bu_3N (10 mL). The reaction mixture was heated at 120 °C during 20 h. Purification was performed by a NEt_3-deactivated SiO_2 flash chromatography column eluted with a gradient of hexane/CH_2Cl_2 (90/10 to 70/30, v/v) and afforded ligand **7b** as a white powder (0.510 g, 52%): mp 90−91 °C; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 221 nm (24 500 M^{-1} cm^{-1}), 256 (35 300), 276 (30 900); ^1H NMR ($CDCl_3$) δ 1.05 (t, J = 7.3 Hz, 6H), 1.58 (m, 4H), 1.87 (m, 4H), 2.45 (s, 3H), 4.47 (t, J = 6.6 Hz, 4H), 7.34 (d, J = 7.8 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 8.02 (t, J = 7.8 Hz, 2H), 8.16 (dd, J = 7.0, 1.2 Hz, 2H), 8.84 (dd, J = 7.3, 1.1 Hz, 2H), 8.89 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 19.4, 21.3, 30.7, 65.7, 119.5, 124.2, 124.9, 127.1, 129.7, 135.2, 137.7, 139.2, 147.9, 150.3, 155.0, 156.4, 165.4; IR (KBr, cm^{-1}) 2958 (m), 2924 (w), 2868 (w), 1715 (ν_{COO}, s), 1581 (m), 1457 (m), 1314 (s), 1265 (m), 1228 (m), 1152 (s); FAB$^+$/MS (*m*/*z*) 524 ([M + H]$^+$, 100), 422 (M − $CO_2C_4H_9$, 37), 321 (M − 2 $CO_2C_4H_9$, 17). Anal. Calcd for $C_{32}H_{33}N_3O_4$: C, 73.40; H, 6.35; N, 8.02. Found: C, 73.11; H, 6.02; N, 7.72.

4′-Carbobutoxy-2,2′:6′,2″-terpyridine (8c). This compound was prepared according to experimental condition 1, from 0.900 g (2.37 mmol) of **8b** and 0.027 g (0.038 mmol) of $Pd(PPh_3)_2Cl_2$, in *n*-BuOH (30 mL) and *n*-Bu_3N (3 mL). The reaction mixture was heated at 120 °C for 3 d. Purification was performed by a chromatography column on alumina eluted with CH_2Cl_2 and afforded ligand **8c** as a white powder (0.600 g, 76%): mp 68−69 °C; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 229 nm (25 300 M^{-1} cm^{-1}), 271 (21 400), 314 (10 500); ^1H NMR ($CDCl_3$) δ 1.00 (t, J = 7.6 Hz, 3H), 1.51 (m, 2H), 1.83 (m, 2H), 4.43 (t, J = 6.7 Hz, 2H), 7.37 (ddd, J = 7.5, 2.7, 1.1 Hz, 2H), 7.88 (td, J = 7.8, 1.9 Hz, 2H), 8.62 (dd, J = 7.8, 0.8 Hz, 2H), 8.76 (dq, J = 4.8, 1.9, 0.8 Hz, 2H), 8.99 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 19.3, 30.8, 65.7, 120.4, 121.3, 124.2, 136.9, 140.1, 149.3, 155.5, 156.5, 165.5; IR (KBr, cm^{-1}) 2959 (m), 2868 (w), 1716 (ν_{COO}, s), 1558 (m), 1466 (m), 1393 (s), 1351 (m), 1257 (s), 1112 (m); EI/MS (*m*/*z*) 333 (M^+, 100), 232 (M − $CO_2C_4H_9$, 42). Anal. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.60. Found: C, 71.98; H, 5.62; N, 12.48.

6,6″-Dicarbobutoxy-2,2′:6′,2″-terpyridine (9b). Prepared according to experimental condition 1, from 2.0 g (5.12 mmol) of **9a** and 0.072 g (0.102 mmol) of $Pd(PPh_3)_2Cl_2$, in *n*-BuOH (60 mL) and *n*-Bu_3N (6 mL). The reaction mixture was heated at 120 °C during 4 d. Purification was performed by a NEt_3-deactivated SiO_2 flash chromatography column eluted with a gradient of hexane/CH_2Cl_2 (90/10 to 70/30, v/v) and afforded ligand **9b** as a white powder (1.100 g, 50%): mp 121−122 °C; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 221 nm (23 100 M^{-1} cm^{-1}), 243 (23 900), 282 (26 000); ^1H NMR ($CDCl_3$) δ 1.02 (t, J = 7.3 Hz, 6H), 1.51 (m, 4H), 1.85 (t, J = 6.8 Hz, 4H), 4.44 (t, J = 6.8 Hz, 4H), 8.02 (m, 3H), 8.14 (dd, J = 7.7, 1.1 Hz, 2H), 8.64 (d, J = 7.7 Hz, 2H), 8.8 (dd, J = 7.7, 1.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.6, 19.2, 30.7, 65.6, 122.0, 124.0, 124.7, 137.7, 138.0, 147.8, 154.4, 156.2, 165.3; FT-IR (KBr, cm^{-1}) 2960 (m), 2871 (w), 1738 (ν_{COO}, s), 1575 (m), 1463 (w), 1431 (m), 1301 (m), 1255 (s), 1156 (s); FAB$^+$/MS (*m*/*z*) 434 ([M + H]$^+$, 100), 332 (M − $CO_2C_4H_9$, 54), 231 (M − $2CO_2C_4H_9$, 12). Anal. Calcd for $C_{25}H_{27}N_3O_4$: C, 69.27; H, 6.28; N, 9.69. Found: C, 68.93; H, 5.94; N, 9.44.

6,6″-Dihydroxymethyl-2,2′:6′,2″-terpyridine (9c). This compound was prepared according to experimental condition 3, from 0.750 g (1.73 mmol) of **9b** and 1.300 g (0.034 mol) of $NaBH_4$, in EtOH (150 mL). The reaction mixture was stirred at room temperature for 2 d. Purification was performed by recrystallization of the crude product from a mixture of dichloromethane and hexane and afforded ligand **9c** as a white powder (0.450 g, 88%): mp 142−143 °C; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 238 nm (16 300 M^{-1} cm^{-1}), 284 (28 300); ^1H NMR ($CDCl_3$) δ 3.98 (t, J = 4.6 Hz, 2H), 4.96 (d, J = 4.3 Hz, 4H), 7.30 (s, 1H), 7.87 (t, J = 7.7 Hz, 2H), 7.98 (m, 3H), 8.49 (d, J = 7.8 Hz, 2H), 8.55 ppm (d, J = 7.7 Hz, 2H); IR (KBr, cm^{-1}) 3542 (w), 2853 (w), 1576 (m), 804 (s); EI/MS (*m*/*z*) 293 (M^+, 100), 276 (M − OH, 20), 262 (M − CH_2OH, 5). Anal. Calcd for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33. Found: C, 69.54; H, 5.03; N, 14.22.

6,6″-Diformyl-2,2′:6′,2″-terpyridine (9d). This compound was prepared according to experimental condition 4, from 0.445 g (1.52 mmol) of **9c** and 0.330 mL (3.46 mmol) of oxalyl chloride in dichloromethane (15 mL), 0.500 mL (3.67 mmol) of DMSO in dichloromethane (5 mL). Purification was performed by recrystallization of the crude product from a mixture of dichloromethane and hexane and afforded ligand **9d** as a cream powder (0.380 g, 86%): mp >230 °C dec; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 222 nm (32 400 M^{-1} cm^{-1}), 260 (14 400), 285 (17 200); ^1H NMR ($CDCl_3$) δ 8.06 (m, 5H), 8.67 (d, J = 8.0 Hz, 2H), 8.87 (dd, J = 6.6, 2.2 Hz, 2H), 10.21 (s, 2H); IR (KBr, cm^{-1}) 3082 (w), 2849 (w), 1721 (ν_{COH}, s), 1576 (m), 793 (s); FAB$^+$/MS (*m*/*z*) 290 ([M + H]$^+$, 100), 260 (M − CHO, 28). Anal. Calcd for $C_{17}H_{11}N_3O_2$: C, 70.58; H, 3.83; N, 14.52. Found: C, 70.36; H, 3.54; N, 14.28.

6-Carbobutoxy-5,5′-dimethyl-2,2′-bipyridine (10b). Prepared according to experimental condition 1, from 0.900 g (3.42 mmol) of **10a** and 0.039 g (0.056 mmol) of $Pd(PPh_3)_2Cl_2$, in *n*-BuOH (20 mL) and *n*-Bu_3N (2 mL). The reaction mixture was heated at 120 °C for 4 d. Purification was performed by a NEt_3-deactivated SiO_2 flash chromatography column eluted with a gradient of hexane/CH_2Cl_2 (90/10 to 70/30, v/v) and afforded ligand **10b** as a colorless oil (0.730 g, 75%): UV/vis (CH_2Cl_2) λ_{max} (ϵ) 221 nm (13 600 M^{-1} cm^{-1}), 246 (24 100), 281 (30 300); ^1H NMR ($CDCl_3$) δ 1.00 (t, J = 7.3 Hz, 3H), 1.54 (m, 2H), 1.82 (m, 2H), 2.38 (s, 3H), 2.57 (s, 3H), 4.42 (t, J = 6.6 Hz, 2H), 7.60 (ddd, J = 8.0, 2.2, 0.7 Hz, 1H), 7.69 (dd, J = 8.0, 0.7 Hz, 1H), 8.37 (m, 2H), 8.48 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.9, 18.4, 19.4, 20.8, 30.8, 65.4, 121.0, 123.0, 133.8, 133.9, 137.9, 140.5, 147.8, 149.5, 153.0, 153.7, 166.9; IR (KBr, cm^{-1}) 2961 (m), 2872 (w), 1725 (ν_{COO}, s), 1455 (s), 1216 (s), 1137 (s), 1098 (s); EI/MS (*m*/*z*) 284 (M^+, 100), 183 (M − $CO_2C_4H_9$, 57). Anal. Calcd for $C_{17}H_{20}N_2O_2$: C, 71.81; H, 7.09; N, 9.85. Found: C, 71.55; H, 6.89; N, 9.79.

6-Carboethoxy-5,5′-dimethyl-2,2′-bipyridine (10c). Prepared according to experimental condition 2, from 1.800 g (6.84 mmol) of **10a** and 0.060 g (0.086 mmol) of $Pd(PPh_3)_2Cl_2$, in EtOH (30 mL) and Et_3N (4 mL). The reaction mixture was heated at 70 °C for 4 d. Purification was performed by a NEt_3-deactivated SiO_2 flash chromatography column eluted with a gradient of hexane/CH_2Cl_2 (90/10 to 70/30, v/v) and afforded ligand **10c** as a colorless oil (1.700 g, 97%): UV/vis (CH_2Cl_2) λ_{max} (ϵ) 222 nm (13 800 $M^{-1}cm^{-1}$), 244 (23 800), 280 (30 000); ^1H NMR ($CDCl_3$) δ 1.45 (t, J = 7.1 Hz, 3H), 2.30 (s, 3H), 2.52 (s, 3H), 4.45 (q, J = 7.1 Hz, 2H), 7.59 (ddd, J = 8.0, 2.0, 0.8

Hz, 1H), 7.67 (dd, J = 8.0, 0.8 Hz, 1H), 8.34 (m, 2H), 8.49 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.9, 18.6, 20.9, 64.0, 121.3, 123.5, 132.9, 134.8, 138.7, 139.9, 148.9, 149.0, 152.5, 152.9, 165.9; IR (KBr, cm^{-1}) 2966 (m), 2875 (w), 1737 (ν_{COO}, s), 1455 (s), 1223 (s), 1142 (s), 1098 (s); FAB$^+$/MS (m/z) 257 ([M + H]$^+$, 100), 183 (M − $CO_2C_2H_5$, 28). Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.05; H, 6.02; N, 10.65.

6-Hydroxymethyl-5,5′-dimethyl-2,2′-bipyridine (10d). This compound was prepared according to experimental condition 3, from 1.100 g (3.86 mmol) of **10c** and 2.920 g (77.2 mmol) of $NaBH_4$, in EtOH (200 mL). The reaction mixture was stirred at room temperature for 4 d. Purification was performed by recrystallization of the crude product from a mixture of dichloromethane and hexane and afforded ligand **10d** as a white powder (0.700 g, 84%): mp 97−98 °C; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 266 nm (10 400 M^{-1} cm^{-1}), 307 (16 200), 318 (16 900); ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3H), 2.40 (s, 3H), 4.75 (d, J = 3.0 Hz, 2H), 5.02 (t, J = 4.00 Hz, 1H), 7.62 (m, 2H), 8.26 (m, 2H), 8.49 (m, 1H); IR (KBr, cm^{-1}) 3342 (s), 2923 (w), 2887 (w), 1557 (m), 1459 (s), 1399 (m), 1305 (m), 1047 (s), 828 (m); EI/MS (m/z) 214 (M$^+$, 100), 197 (M − OH, 32). Anal. Calcd for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.72; H, 6.42; N, 12.82.

6-Formyl-5,5′-dimethyl-2,2′-bipyridine (10e). This compound was prepared according to experimental condition 4, from 0.400 g (1.86 mmol) of **10d**, 0.164 mL (1.88 mmol) of oxalyl chloride in dichloromethane (8 mL), and 0.140 mL (1.97 mmol) of DMSO in dichloromethane (3 mL). Purification was performed by recrystallization of the crude product from a mixture of dichloromethane and hexane and afforded ligand **10e** as a cream powder (0.360 g, 91%): mp 96−97 °C; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 265 nm (9200 M^{-1} cm^{-1}), 287 (14 400); ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H), 2.69 (s, 3H), 7.65 (m, 1H), 7.71 (d, J = 8.2 Hz, 1H), 8.47 (m, 3H), 10.26 (s, 1H); IR (KBr, cm^{-1}) 2926 (w), 2819 (w), 1708 (ν_{CHO}, s), 1454 (m), 1107 (m), 830 (m); EI/MS (m/z) 212 (M$^+$, 100). Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.57; H, 5.70; N, 13.20. Found: C, 73.32; H, 5.45; N, 13.11.

6-Carboethoxy-5′-methyl-2,2′-bipyridine (11b). Prepared according to experimental condition 2, from 0.500 g (2.00 mmol) of **11a** and 0.050 g (0.071 mmol) of $Pd(PPh_3)_2Cl_2$, in EtOH (10 mL) and Et_3N (3 mL). The reaction mixture was heated at 70 °C for 8 h. Purification was performed by a NEt_3-deactivated SiO_2 flash chromatography column eluted with a gradient of hexane/CH_2Cl_2 (90/10 to 70/30, v/v) and afforded ligand **11b** as a white powder (0.475 g, 98%): UV/vis (CH_2Cl_2) λ_{max} (ϵ) 230 nm (14 300 $M^{-1}cm^{-1}$), 256 (24 500), 283 (35 000); ^{1}H NMR ($CDCl_3$) δ 1.38 (t, J = 7.1 Hz, 3H), 2.35 (s, 3H) 4.43 (q, J = 7.1 Hz, 2H), 7.55 (ddd, J = 8.0, 2.0, 0.8 Hz, 1H), 7.84 (t, J = 7.9 Hz, 1H), 8.22 (dd, J = 7.9, 0.8 Hz, 1H), 8.37 (m, 2H), 8.49 (dd, J = 7.9, 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 20.6 61.6, 121.0, 123.6, 124.4, 133.7, 137.5, 137.3, 147.5, 149.4, 152.5, 156.3, 165.1; IR (KBr, cm^{-1}) 2958 (m), 2876 (w), 1739 (ν_{COO}, s), 1443 (s), 1228 (s), 1145 (s), 1100 (s); EI/MS (m/z) 242 (M$^+$, 100), 169 (M − $CO_2C_2H_5$, 28). Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.26; H, 5.72; N, 11.38.

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