Synthesis of Substituted 2,2′-Bipyridines from 2-Bromo- or 2-Chloropyridines Using Tetrakis(triphenylphosphine)palladium(0) as a Catalyst in a Modified Negishi Cross-Coupling Reaction

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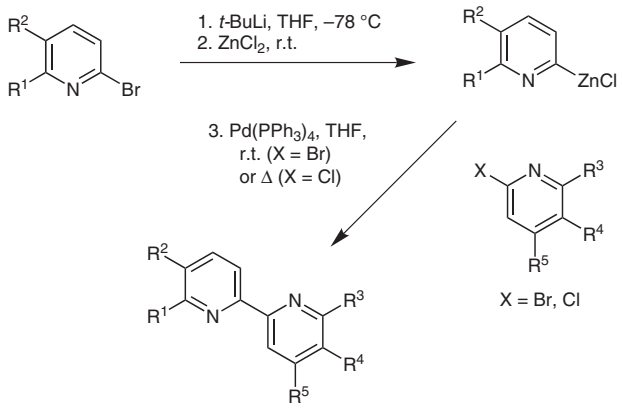
Abstract: A protocol for an efficient, modified Negishi cross-coupling strategy for substituted 2,2′-bipyridines employing tetrakis(triphenylphosphine)palladium(0) as a simple, commercially available, and relatively inexpensive catalyst for both 2-bromo- and 2-chloropyridines has been developed. Further transformations were carried out yielding some new valuable functionalized 2,2′-bipyridines.

Key words: Negishi reaction, 2,2′-bipyridines, cross-coupling reactions, organozinc compounds, palladium

The 2,2′-bipyridine moiety is among the most widely used ligand structure motifs in metal coordination chemistry and its complexes with various transition metal ions have been extensively studied.[1] Ligands containing two or more 2,2′-bipyridine units can serve as precursors for supramolecular self-assembled helicates,[2] macromolecular devices[3] or can be used in asymmetric homogenous catalysis.[4] Several methods have been applied to the synthesis of mono- and disubstituted bipyridines. Among them are the homocoupling of halogenated pyridine precursors, which gives access to symmetrically substituted bipyridines,[5] the Kröhnke reaction,[6] or the modification of an existing bipyridine core, which often involves multistep procedures and/or requires harsh reaction conditions.[7] With the advance of cross-coupling reactions over the last thirty years, an increasing number of methods has been established for the formation of aryl–aryl, and also heteroaryl–heteroaryl, bonds.[8] The coupling of two different pyridine components using palladium-catalyzed cross-coupling procedures such as the Stille, Suzuki, or Negishi reactions has proved to be very efficient and it has been applied to the synthesis of a variety of mono- and disubstituted 2,2′-bipyridines. However, the use of organozinc compounds provides better transmetalation activity than that obtained by the use of organotin and organoboron reagents and with good chemoselectivity, as most common functional groups are not attacked by organozinc species.[9] One example of a very powerful catalyst in Negishi cross-coupling reactions is bis(tri-*tert*-butylphosphine)palladium(0), established by Fu and co-workers.[10] During the course of our studies toward the formation of self-assembled supramolecular aggregates,[11] the synthesis of substituted 2,2′-bipyridines as ligand units was essential. Therefore, we developed a general method for the synthesis of 5-monosubstituted, as well as variously disubstituted 2,2′-bipyridines, in a one-pot procedure from an organozinc pyridyl reagent and chloropyridines by a palladium-catalyzed, modified Negishi cross-coupling strategy using bis(tri-*tert*-butylphosphine)palladium(0) as a catalyst.[12] This catalyst is commercially available, but relatively expensive, and can also be synthesized,[13] or prepared in situ, from tris(dibenzylideneacetone)dipalladium(0)–chloroform adduct; this synthesis involves the use of tri-*tert*-butylphosphine (t-Bu_3P), which is also expensive and not easily handled. Since we often perform the Negishi reaction on a large-scale basis, due to our increased demand for starting materials for the design of 2,2′-bipyridine-based ligands, we were looking for an inexpensive and simple, but equally efficient, catalytic system. In 2003, Hanan reported the synthesis of some, mostly methyl-substituted, 2,2′-bipyridines from 1.5 equivalents of 2-pyridylzinc bromide using tetrakis(triphenylphosphine)palladium(0) as the catalyst.[14] We now wish to report a general procedure for the synthesis of various mono- and disubstituted 2,2′-bipyridines using a modified Negishi cross-coupling strategy starting from both 2-bromo- and 2-chloropyridines that is catalyzed by the relatively inexpensive, commercially available catalyst tetrakis(triphenylphosphine)palladium(0) (Scheme 1).



Scheme 1 Synthesis of various mono- and disubstituted 2,2′-bipyridines.

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Table 1 Mono- and Disubstituted 2,2′-Bipyridines Synthesized from Variously Substituted 2-Bromopyridines[a]

Entry	Product	R^1	R^2	R^3	R^4	R^5	Yield (%)
1	**1**	H	H	H	Me	H	quant.
2	**2**	H	H	H	OMe	H	98
3	**3**	H	H	H	2,5-dimethylpyrrol-1-yl	H	73
4	**4**	H	Me	H	C≡CTMS	H	84
5	**5**	H	*n*-heptyl	H	Br	H	85
6	**6**	2,5-dimethylpyrrol-1-yl	H	CO_2Me	H	H	50
7	**7**	2,5-dimethylpyrrol-1-yl	H	H	H	CO_2Me	55

[a] $Pd(PPh_3)_4$ (1.5–3 mol%) was used.

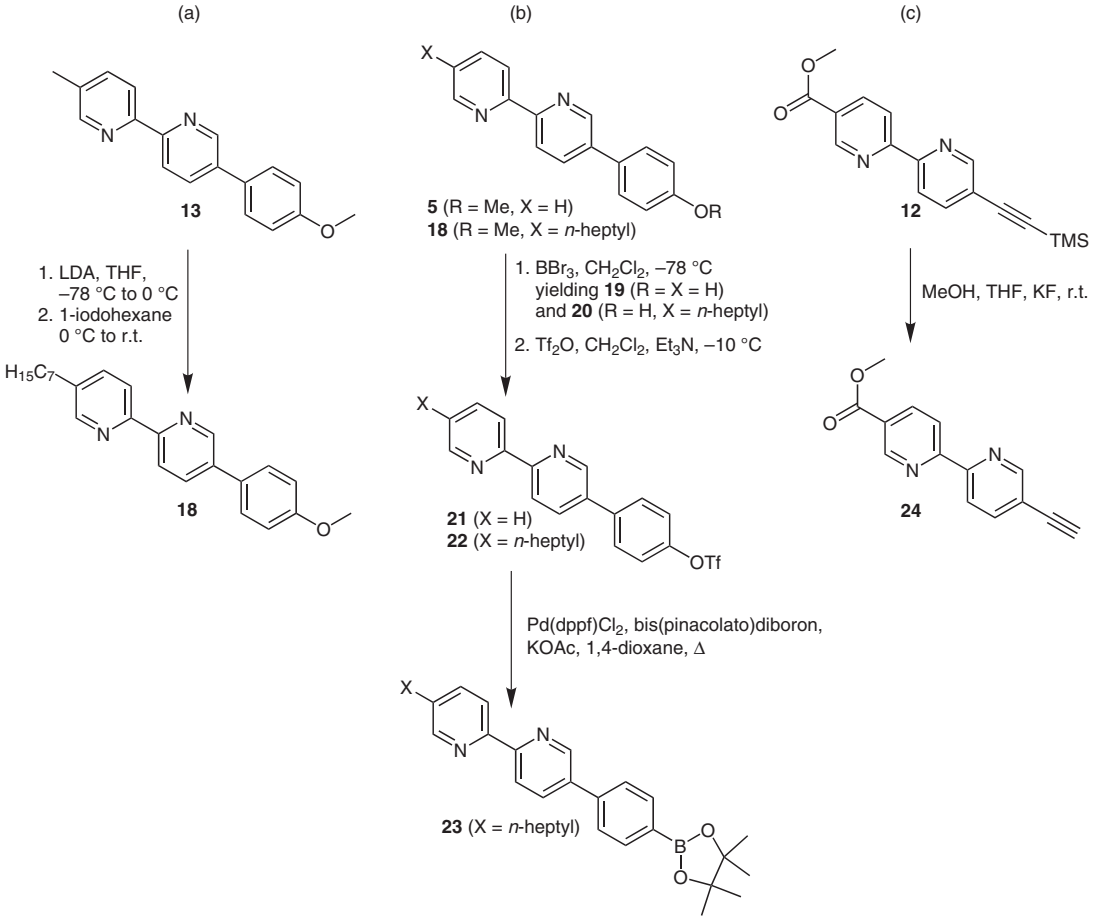
The bromine–lithium exchange of 2-bromopyridine or substituted 2-bromopyridines was achieved with *tert*-butyllithium at –78 °C in tetrahydrofuran according to our previously published procedure.[12] The preparation of the organozinc species in situ proved to be more efficient than using commercially available 2-pyridylzinc bromide solution in our hands and it is necessary for the synthesis of disubstituted bipyridines. Various ratios of 2-pyridylzinc bromide/halo-substituted pyridine (from 1.5 to 1.1 equiv) were used and it could be shown that this variation appears to have no effect on the yield of the corresponding 2,2′-bipyridines. Bromo-substituted pyridines are by far more reactive in cross-coupling reactions than chloro-substituted pyridines[15] and for this reason they were initially used as substrates. A variety of 2,2′-bipyridines were synthesized in this manner and the reaction occurred smoothly at room temperature (Table 1).

These results encouraged us to also use the inexpensive and more easily available chloropyridines in the same way. Due to the fact, that chloropyridines are relatively inactive compared to the corresponding bromopyridines, no reaction occurred after addition of the solution of the chloropyridine to the 2-pyridylzinc species and stirring the resulting mixture at room temperature. However, refluxing this mixture yielded the desired 2,2′-bipyridines in good to excellent yields. It should be noted that this method is also successful for the notoriously difficult-to-synthesize bipyridines bearing ester functions. This is also the case when the organozinc species is generated from a pyridine moiety bearing a labile (trimethylsilyl)ethynyl function, which is robust enough to overcome lithiation (Table 2, entry 5).

Table 2 Mono- and Disubstituted 2,2′-Bipyridines Synthesized from Variously Substituted 2-Chloropyridines[a]

Entry	Product	R^1	R^2	R^3	R^4	R^5	Yield (%)
1	**8**	H	H	H	CO_2Me	H	80
2	**9**	H	H	H	4-$MeOC_6H_4$	H	76
3	**10**	H	H	H	C≡CTMS	H	90
4	**11**	H	*n*-heptyl	H	CO_2Me	H	51
5	**12**	H	C≡CTMS	H	CO_2Me	H	70
6	**13**	H	Me	H	4-$MeOC_6H_4$	H	66
7	**14**	Me	H	H	H	Me	84
8	**15**	OMe	H	H	H	OMe	71
9	**16**	OMe	H	H	H	2,5-dimethylpyrrol-1-yl	88
10	**17**	2,5-dimethylpyrrol-1-yl	H	H	H	OMe	74

[a] $Pd(PPh_3)_4$ (1.5–3 mol%) was used.



Scheme 2 Further transformations: (a) elongation of the alkyl chain of **13**; (b) demethylation of **9** and **18**, triflation of **21** and **22**, and borylation of **22**; (c) deprotection of **12**.

Some of the 2,2′-bipyridines were further functionalized, for example an *n*-heptyl chain was generated from the methyl-substituted derivative **13** to yield **18** (Scheme 2). Bipyridines **9** and **18** were transformed via two steps into valuable triflates **21** and **22**, which are precursors for further cross-coupling reactions as well as the boronic acid ester derivative **23**, which was synthesized from **22** via palladium-catalyzed borylation. Finally, the (trimethylsilyl)ethynyl group of **12** could be deprotected to yield **24**, which is a building block for Sonogashira reactions. We are currently using all these substituted 2,2′-bipyridines to construct larger ligand structures.

In conclusion, we have demonstrated that simple tetrakis(triphenylphosphine)palladium(0) is a powerful catalyst in the Negishi cross coupling of different monosubstituted and unsymmetrically disubstituted 2,2′-bipyridines **1**–**17** starting from both 2-bromo- and 2-chloropyridines. Furthermore we showed that some of the cross-coupling products could be used for further transformations involving, for example, the formation of valuable triflates **21** and **22**.

All reactions except the synthesis of **24** were performed under an argon atmosphere using standard Schlenk techniques and oven-dried glassware prior to use. TLC was performed on aluminum TLC plates silica gel 60 F_{254} from Merck; detection: UV light (254 and 366 nm). Products were purified by column chromatography (silica gel 60, 70–230 mesh, Merck). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 spectrometer at 300 K at 500.1 and 125.8 MHz, a Bruker AM 400 at 298 K at 400.1 MHz and 100.6 MHz, or an Bruker DPX 300 at 298 K at 300.1 MHz and 75.5 MHz, respectively. ^{19}F NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300 K at 282.4 MHz. NMR chemical shifts are reported relative to the following standards: ^{1}H NMR, residual non-deuterated solvent, internal standard; ^{13}C NMR, deuterated solvent, internal standard; ^{19}F NMR: $CFCl_3$, external standard. Signals were assigned on the basis of ^{1}H, ^{13}C, H,H-COSY, HMQC, and HMBC NMR experiments. Numbering of the ^{1}H and ^{13}C nuclei is according to Figure 1.

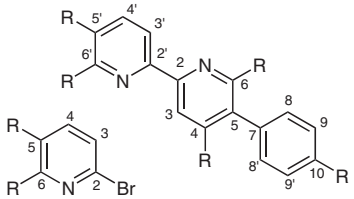


Figure 1 Numbering of the pyridine and bipyridine core for NMR peak assignments.

MS spectra were taken on a Finnigan MAT 212 with data system MMS–ICIS (EI, CI, isobutane, NH_3), a Finnigan MAT 95 with data system DEC-Station 5000 (CI, isobutane or NH_3; HiRes-CI, isobutane or NH_3; FD), or an A.E.I. MS-50 (EI; HiRes-EI). Melting points were measured with a hot-stage microscope SM-Lux from Leitz or a SMP-20 from Büchi and are not corrected. Elemental analyses were carried out with a Fisons Instrument EA1108 or a Heraeus Vario EL.

Most solvents were dried, distilled, and stored under argon according to standard procedures. *t*-BuLi solutions were purchased from Aldrich and were titrated prior to use against *N*-pivaloyl-*o*-toluidine.[16] All chemicals were used as received from commercial sources. $Pd(PPh_3)_4$ was purchased from ABCR.

2-Bromo-5-methoxypyridine,[17] 2-bromo-5-[(trimethylsilyl)ethynyl]pyridine,[18] 2-chloro-4-(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridine,[12b] 2-chloro-5-(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridine,[12a] 2-chloro-5-(4-methoxyphenyl)pyridine,[12b] 2-chloro-5-[(trimethylsilyl)ethynyl]pyridine[19] were prepared according to published procedures.

3-Heptylpyridine

A soln of *i*-Pr_2NH (1.66 mL, 11.8 mmol, 1.05 equiv) and THF (60 mL) was cooled to –78 °C. 1.6 M *n*-BuLi in hexanes (7.36 mL, 11.8 mmol, 1.05 equiv) and 3-methylpyridine (1.09 mL, 11.2 mmol, 1 equiv) were subsequently added via syringe. The acetone–N_2 cooling bath was replaced by an ice-water bath. After 5 min, 1-iodohexane (1.75 mL, 11.8 mmol, 1.05 equiv) was added via syringe. The soln was stirred at this temperature for 5 min, then it was allowed to warm to r.t., stirred for a further 36 h, and concentrated. The crude product was dissolved in CH_2Cl_2 and washed with H_2O. The aqueous layer was extracted with CH_2Cl_2 (4 × 25 mL) and the combined organic layers were dried (Na_2SO_4). Purification by flash column chromatography (silica gel, *n*-hexane–EtOAc, 1:1 + 0.5% Et_3N, R_f = 0.65) gave the product a yellow oil; yield: 1.516 g (76%).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.9 Hz, 3 H, CH_3), 1.22–1.36 (m, 8 H, 4 × CH_2), 1.57–1.65 (m, 2 H, CH_2), 2.59 (t, ^3J = 7.7 Hz, 2 H, CH_2), 7.17 (m, 1 H, H5), 7.69 (ddd, ^3J = 7.69 Hz, 2 × ^4J not resolved, 1 H, H4), 8.40–8.45 (m, 2 H, H2, H6).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6, 29.04, 29.09, 31.1, 31.7, 33.0 (6 × CH_2), 123.2 (C5), 135.7 (C4), 137.9 (C3), 147.2 (C6), 150.0 (C2).

MS (EI): *m*/*z* = 177.1 ($[C_{12}H_{19}N]^+$ = $[M]^+$, 14), 93.0 ($[M - C_6H_{12}]^+$, 100).

HRMS (EI): *m*/*z* (M – H]$^+$ calcd for $C_{12}H_{18}N$: 176.1445; found: 176.1442.

Anal. Calcd for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 79.54; H, 10.33; N, 7.60.

2-Bromo-5-heptylpyridine

A soln of 2-(dimethylamino)ethanol (0.63 mL, 6 mmol, 3 equiv) in *n*-hexane (2.6 mL) was cooled to 0 °C. At this temperature 1.6 M *n*-BuLi in *n*-hexane (7.5 mL, 12 mmol, 6 equiv) was added. The soln was stirred at 0 °C for 30 min. 3-Heptylpyridine (363 mg, 2.04 mmol, 1 equiv) dissolved in *n*-hexane (2.61 mL) was added via syringe and the soln was stirred at 0 °C for 1 h and then quenched by the addition of CBr_4 (2.436 g, 7.344 mmol, 3.6 equiv) in THF (10 mL). The soln was stirred at r.t. for 72 h, hydrolyzed and then CH_2Cl_2 (25 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (5 × 25 mL) and the combined organic layers were dried (Na_2SO_4). Purification of the crude product by flash column chromatography (silica gel, *n*-hexane–EtOAc, 20:1, R_f = 0.48) gave the product as a yellow oil. The regioisomer 2-bromo-3-heptylpyridine could also be isolated as a yellow oil (*n*-hexane–EtOAc 20:1, R_f = 0.35).

2-Bromo-5-heptylpyridine

Yield: 200 mg (38%).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.8 Hz, 3 H, CH_3), 1.20–1.37 (m, 8 H, 4 × CH_2), 1.54–1.66 (m, 2 H, CH_2), 2.65 (t, ^3J = 7.7 Hz, 2 H, CH_2), 7.33–7.39 (m, 2H, H3, H4), 7.91 (s, 1 H, H6).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.2 (CH_3), 22.7, 29.1, 31.1, 31.8, 32.4 (6 × CH_2), 127.7 (C3), 137.5 (C5), 138.7 (C4), 139.4 (C2), 150.3 (C6).

MS (CI, isobutane): *m*/*z* = 255.9 ($[C_{12}H_{18}{}^{79}BrN]^+$ = $[M]^+$, 100), 257.9 ($[C_{12}H_{18}{}^{81}BrN]^+$ = $[M]^+$, 95).

HRMS (EI): *m*/*z* [M – H]$^+$ calcd for $C_{12}H_{17}BrN$: 254.0550; found: 254.0545.

Anal. Calcd for $C_{12}H_{18}BrN$: C, 56.26; H, 7.08; N, 5.47. Found: C, 56.98; H, 7.06; N, 5.54.

2-Bromo-3-heptylpyridine

Yield: 40 mg (8%).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.8 Hz, 3 H, CH_3), 1.21–1.41 (m, 8 H, 4 × CH_2), 1.57–1.66 (m, 2 H, CH_2), 2.69 (t, ^3J = 7.9 Hz, 2 H, CH_2), 7.16 (dd, ^3J = 7.4 Hz, ^3J = 7.5 Hz, 1 H, H5), 7.47 (dd, ^3J = 7.4 Hz, ^4J = 1.6 Hz, 1 H, H4), 8.18 (dd, ^3J = 7.5 Hz, ^4J = 1.6 Hz, 1 H, H6).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.2 (CH_3), 22.8, 29.2, 29.4, 29.5, 31.9, 35.4 (6 × CH_2), 122.9 (C5), 138.2 (C4), 139.4 (C3), 144.5 (C2), 147.6 (C6).

MS (EI): *m*/*z* = 255.0 ($[C_{12}H_{18}{}^{79}BrN]^+$ = $[M]^+$, 28), 257.0 ($[C_{12}H_{18}{}^{81}BrN]^+$ = $[M]^+$, 26), 171.0 ($[M(^{79}Br) - C_6H_{12}]^+$, 100), 173.0 ($[M(^{81}Br) - C_6H_{12}]^+$, 95).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{12}H_{18}BrN$: 255.0623; found: 255.0622.

Anal. Calcd for $C_{12}H_{18}BrN$: C, 56.26; H, 7.08; N, 5.47. Found: C, 56.41; H, 7.02; N, 5.34.

2-Bromo-6-(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridine

2-Amino-6-bromopyridine (5 g, 28.90 mmol, 1 equiv), hexane-2,5-dione (4.1 mL, 34.68 mmol, 1.2 equiv), and PTSA (50 mg, 0.28 mmol, 1 mol%) were dissolved in toluene (30 mL) and heated in a Dean–Stark apparatus for 2 h. After cooling to r.t., the mixture was washed with sat. aq $NaHCO_3$, H_2O (5 × 25 mL), and brine (25 mL). The organic layer was dried ($MgSO_4$). Purification of the crude product by column chromatography (*n*-hexane–EtOAc, 5:1 + 0.5% Et_3N, R_f = 0.5) gave the product as a pale yellow solid; yield: 6.83 g (94%); mp 104 °C.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.15 (s, 6 H, CH_3), 5.88 (s, 2 H, CH-pyrrole), 7.16 (d, ^3J = 8.2 Hz, 1 H, H5), 7.47 (d, ^3J = 8.2 Hz, 1 H, H3), 7.60 (dd, ^3J = 8.2 Hz, ^3J = 8.2 Hz, 1 H, H4).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.3 (CH_3), 107.7 (2 C, CH-pyrrole), 120.2 (C5), 126.4 (C3), 128.7 (2 C, CMe-pyrrole), 139.8 (C4), 140.6 (C2), 151.8 (C6).

MS (EI): *m*/*z* = 251.1 ($[C_{11}H_{12}N_2Br^{79}]^+$ = $[M]^+$, 100), 253.1 ($[C_{11}H_{12}N_2Br^{81}]^+$ = $[M]^+$, 96), 173.1 ($[C_{11}H_{12}N_2]^+$, 15).

HRMS (EI): *m*/*z* M – H]$^+$ calcd for $C_{11}H_{10}BrN_2$: 249.0022; found: 249.0023.

Anal. Calcd for $C_{11}H_{11}BrN_2$: C, 52.61; H, 4.42; N, 11.16. Found: C, 52.65; H, 4.45; N, 11.05.

2,2′-Bipyridines from Substituted 2-Bromopyridines: General Procedure 1

A two-necked, 250-mL round-bottomed flask equipped with a stirring bar, an argon inlet, and a rubber septum was charged with THF (50 mL) and cooled to –78 °C. 1.6 M *t*-BuLi in *n*-pentane (8.01 mL, 12.82 mmol) was added via syringe resulting in a pale-yellow soln.

To this mixture the first 2-bromopyridine (8.25 mmol, 1.5 equiv) was slowly added via syringe [solid pyridines were dissolved in THF (6 mL)] and stirred at the same temperature for 30 min. After that time a soln of $ZnCl_2$ (2.68 g, 19.68 mmol, 3.6 equiv) in THF (40 mL) was added. The resulting soln was allowed to warm to r.t. and stirred for 2.5 h (soln 1).

A two-necked, 25-mL round-bottomed flask equipped with an argon inlet, and a rubber septum was charged with the second 2-bromopyridine (5.5 mmol, 1 equiv) and $Pd(PPh_3)_4$ (127 mg, 0.11 mmol, 2 mol%). The mixture was evacuated and flushed with argon (2 ×) and dissolved in THF (10 mL) (soln 2).

Soln 2 was slowly added to soln 1 and the resulting mixture was stirred at r.t. for 18 h. When TLC monitoring revealed complete consumption of the starting material the mixture was quenched with sat. aq EDTA soln (60 mL) and stirred at r.t. for 15 min. After that time sat. aq Na_2CO_3 soln was added until pH 8. The product was extracted with CH_2Cl_2 (3 × 25 mL) and the combined organic layers were dried (Na_2SO_4), concentrated in vacuo, and purified by flash chromatography (silica gel).

5-Methyl-2,2′-bipyridine (1)[20]

2-Bromopyridine (648 mg, 4.1 mmol, 1.5 equiv), 1.6 M *t*-BuLi in *n*-pentane (4.13 mL, 6.6 mmol, 2.4 equiv), $ZnCl_2$ (1.35 g, 9.9 mmol, 3.6 equiv), 2-bromo-5-methylpyridine (473 mg, 2.75 mmol, 1 equiv), and $Pd(PPh_3)_4$ (95 mg, 82.5 μmol, 3 mol%) were reacted according to general procedure 1 to give **1** as a pale yellow oil after flash column chromatography (*n*-hexane–EtOAc, 5:1 + 0.5% Et_3N, R_f = 0.20); yield: 467 mg (quant.).

Analytical data were in accordance with those previously published.[20]

5-Methoxy-2,2′-bipyridine (2)[12a]

Treatment of 2-bromopyridine (1.66 g, 10.56 mmol, 1.5 equiv), 1.6 M *t*-BuLi in *n*-pentane (10.56 mL, 16.9 mmol, 2.4 equiv), $ZnCl_2$ (3.45 g, 25.34 mmol, 3.6 equiv), 2-bromo-5-methoxypyridine (1.32 g, 7.04 mmol, 1 equiv), and $Pd(PPh_3)_4$ (244 mg, 211.2 μmol, 3 mol%) according to general procedure 1 gave **2** as an amorphous solid after flash column chromatography (EtOAc + 5% Et_3N, R_f = 0.20); yield: 1.28 g (98%).

Analytical data were in accordance with those previously published.[12a]

5-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-2,2′-bipyridine (3)[12b]

Treatment of 2-bromopyridine (1.6 g, 10.16 mmol, 1.5 equiv), 1.6 M *t*-BuLi in *n*-pentane (10.16 mL, 16.25 mmol, 2.4 equiv), $ZnCl_2$ (3.32 g, 24.37 mmol, 3.6 equiv), 2-bromo-5-(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridine (1.7 g, 6.77 mmol, 1 equiv), and $Pd(PPh_3)_4$ (157 mg, 135.4 μmol, 2 mol%) according to general procedure 1 gave **3** as a brown solid after flash column chromatography (*n*-hexane–EtOAc, 1:1 + 0.5% Et_3N, R_f = 0.67); yield: 1.23 g (73%).

Analytical data were in accordance with those previously published.[12a]

5-Methyl-5′-[(trimethylsilyl)ethynyl]-2,2′-bipyridine (4)[12b]

Treatment of 2-bromo-5-methylpyridine (1.13 g, 6.56 mmol, 1.12 equiv), 1.65 M *t*-BuLi in *n*-pentane (8.35 mL, 13.78 mmol, 2.36 equiv), $ZnCl_2$ (2.24 g, 16.44 mmol, 2.8 equiv), 2-bromo-5-[(trimethylsilyl)ethynyl]pyridine (1.485 g, 5.84 mmol, 1 equiv), and $Pd(PPh_3)_4$ (135 mg, 117 μmol, 2 mol%) according to general procedure 1 gave **4** as a yellow solid after flash column chromatography (*n*-hexane–EtOAc, 5:1 + 5% Et_3N, R_f = 0.62); yield: 1.304 g (84%).

Analytical data were in accordance with those previously published.[12b]

5-Bromo-5′-heptyl-2,2′-bipyridine (5)

Treatment of 2-bromo-5-heptylpyridine (336 mg, 1.31 mmol, 1.2 equiv), 1.6 M *t*-BuLi in *n*-pentane (1.65 mL, 2.64 mmol, 2.4 equiv), $ZnCl_2$ (540 mg, 3.96 mmol, 3.6 equiv), 2,5-dibromopyridine (258 mg, 1.1 mmol, 1 equiv), and $Pd(PPh_3)_4$ (38 mg, 33 μmol, 3 mol%) according to general procedure 1 gave **5** as a yellow solid after flash column chromatography (*n*-hexane–EtOAc, 10:1 + 0.5% Et_3N, R_f = 0.5); yield: 310 mg (85%); mp 42–46 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.9 Hz, 3 H, CH_3), 1.20–1.38 (m, 8 H, 4 × CH_2), 1.60–1.69 (m, 2 H, CH_2), 2.65 (t, ^3J = 7.6 Hz, 2 H, CH_2), 7.62 (dd, ^3J = 8.1 Hz, ^4J = 2.3 Hz, 1 H, H4′), 7.91 (dd, ^3J = 8.5 Hz, ^4J = 2.4 Hz, 1 H, H4), 8.27 (m, 2 H, H3, H3′), 8.48 (d, ^4J = 2.3 Hz, 1 H, H6′), 8.69 (d, ^4J = 2.4 Hz, 1 H, H6).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 29.11, 29.13, 31.1, 31.8, 32.9 (6 × CH_2), 120.65 (C3′), 120.73 (C5), 122.1 (C3), 136.9 (C4′), 138.8 (C5′), 139.5 (C4), 149.4 (C6′), 150.1 (C6), 152.9 (C2′), 154.8 (C2).

MS (EI): *m*/*z* = 332.1 ($[C_{17}H_{21}{}^{79}BrN_2]^+$ = $[M]^+$, 8), 334.1 ($[C_{17}H_{21}{}^{81}BrN_2]^+$ = $[M]^+$, 7), 170.9 ($[M(^{79}Br) - C_{11}H_{15}N]^+$, 98), 172.9 ($[M(^{81}Br) - C_{11}H_{15}N]^+$, 100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{21}BrN_2$: 332.0888; found: 332.0891.

Anal. Calcd for $C_{17}H_{21}BrN_2$·0.25 EtOAc: C, 60.85; H, 6.52; N, 7.88. Found: C, 62.06; H, 6.67; N, 7.88.

Methyl 6′-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-2,2′-bipyridine-6-carboxylate (6)

2-Bromo-6-(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridine (767 mg, 3.05 mmol, 1.2 equiv), 1.5 M *t*-BuLi in *n*-pentane (3.65 mL, 5.47 mmol, 2.15 equiv), $ZnCl_2$ (954 mg, 7.00 mmol, 2.75 equiv), methyl 8-bromopyridine-2-carboxylate (550 mg, 2.55 mmol, 1 equiv), and $Pd(PPh_3)_4$ (88 mg, 76.5 μmol, 3 mol%) were used. Purification by flash column chromatography (*n*-hexane–EtOAc, 5:1 + 5% Et_3N, R_f = 0.6) gave **6** as a yellow solid; yield: 394 mg (50%); mp 102 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.19 (s, 6 H, CH_3), 4.04 (s, 3 H, OCH_3), 5.94 (s, 2 H, CH-pyrrole), 7.26 (dd, ^3J = 7.8 Hz, ^4J = 0.9 Hz, 1 H, H5′), 7.94 (dd, ^3J = 7.9 Hz, ^3J = 7.8 Hz, 1 H, H4), 7.97 (dd, ^3J = 7.8 Hz, ^3J = 7.8 Hz, 1 H, H4′), 8.13 (dd, ^3J = 7.7 Hz, ^4J = 1.0 Hz, 1 H, H5), 8.56 (dd, ^3J = 7.8 Hz, ^4J = 0.9 Hz, 1 H, H3′), 8.59 (dd, ^3J = 7.9 Hz, ^4J = 1.0 Hz, 1 H, H3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.4 (2 C, CH_3), 52.9 (OCH_3), 107.1 (2 C, CH-pyrrole), 119.1 (C3′), 122.1 (C5′), 124.6 (C3), 125.3 (C5), 128.7 (2 C, CMe-pyrrole), 138.0 (C4), 139.1 (C4′), 147.6 (C6), 151.4 (C6′), 155.1 (C2), 155.8 (C2′), 165.8 (COO).

MS (EI): *m*/*z* = 307.1 ($[C_{18}H_{17}N_3O_2]^+$ = $[M]^+$, 100).

HRMS (EI): *m*/*z* $[M - H]^+$ calcd for $C_{18}H_{16}N_3O_2$: 306.1237; found: 306.1244.

Anal. Calcd for $C_{18}H_{17}N_3O_2$·0.2 EtOAc·0.2 CH_2Cl_2: C, 66.74; H, 5.60; N, 12.29. Found: C, 66.67; H, 5.77; N, 11.82.

Methyl 6′-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-2,2′-bipyridine-4-carboxylate (7)

2-Bromo-6-(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridine (1.00 g, 4.00 mmol, 1.2 equiv), 1.55 M *t*-BuLi in *n*-pentane (4.62 mL, 7.17 mmol, 2.15 equiv), $ZnCl_2$ (1.25 g, 9.16 mmol, 2.75 equiv), methyl 2-bromopyridine-6-carboxylate (720 mg, 3.33 mmol, 1 equiv), and $Pd(PPh_3)_4$ (116 mg, 100 μmol, 3 mol%) were used. Purification by flash column chromatography (*n*-hexane–EtOAc, 5:1 + 5% Et_3N, R_f = 0.5) gave **7** as a yellow solid; yield: 564 mg (55%); mp 113 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.22 (s, 6 H, CH_3), 3.97 (s, 3 H, OCH_3), 5.96 (s, 2 H, CH-pyrrole), 7.26 (dd, ^3J = 7.8 Hz, ^4J = 0.9 Hz, 1 H, H5′), 7.88 (dd, ^3J = 5.0 Hz, ^4J = 1.6 Hz, 1 H, H5), 7.96 (dd, ^3J = 7.8, ^3J = 7.8 Hz, 1 H, H4′), 8.46 (dd, ^3J = 7.8 Hz, ^4J = 0.9 Hz, 1

H, H3′), 8.82 (dd, ^3J = 5.0 Hz, ^5J = 0.9 Hz, 1 H, H6), 8.94 (dd, ^4J = 1.6 Hz, ^5J = 0.9 Hz, 1 H, H3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.5 (2 C, CH_3), 52.8 (OCH_3), 107.1 (2 C, CH-pyrrole), 119.4 (C3′), 120.7 (C3), 122.1 (C5′), 123.2 (C5), 128.8 (2 C, CMe-pyrrole), 138.6 (C4), 139.0 (C4′), 150.0 (C6), 151.5 (C6′), 155.1 (C2), 156.6 (C2′), 165.7 (*C*OO).

MS (EI): *m/z* = 307.1 ($[C_{18}H_{17}N_3O_2]^+$ = $[M]^+$, 100).

HRMS (EI): *m/z* $[M - H]^+$ calcd for $C_{18}H_{16}N_3O_2$: 307.1321; found: 307.1317.

Anal Calcd for $C_{18}H_{17}N_3O_2$·0.33 EtOAc: C, 68.96; H, 5.89; N, 12.48. Found: C, 68.71; H, 5.47; N, 12.74.

2,2′-Bipyridines from Substituted 2-Chloropyridines; General Procedure 2

The same procedure was used as applied for the substituted 2-bromopyridines except for the fact that a 2-chloropyridine was used to prepare soln 2 and that the resulting mixture obtained upon adding soln 2 to soln 1 was refluxed instead of stirred at r.t.

Methyl 2,2′-Bipyridine-5-carboxylate (8)[21]

Treatment of 2-bromopyridine (1.81 g, 11.45 mmol, 1.2 equiv), 1.5 M *t*-BuLi in *n*-pentane (13.67 mL, 20.51 mmol, 2.15 equiv), $ZnCl_2$ (3.58 g, 26.24 mmol, 2.75 equiv), methyl 6-chloronicotinate (1.64 g, 9.54 mmol, 1 equiv), and $Pd(PPh_3)_4$ (331 mg, 287 μmol, 3 mol%) according to general procedure 2 gave **8** as a white solid after flash column chromatography (*n*-hexane–EtOAc, 3:1 + 5% Et_3N, R_f = 0.48); yield: 1.626 g (80%).

Analytical data were in accordance with those previously published.[21]

5-(4-Methoxyphenyl)-2,2′-bipyridine (9)[22]

Treatment of 2-bromopyridine (216 mg, 1.37 mmol, 1.5 equiv), 1.6 M *t*-BuLi in *n*-pentane (1.37 mL, 2.18 mmol, 2.4 equiv), $ZnCl_2$ (447 mg, 3.28 mmol, 3.6 equiv), 2-chloro-5-(4-methoxyphenyl)pyridine (200 mg, 0.91 mmol, 1 equiv), and $Pd(PPh_3)_4$ (21 mg, 18.2 μmol, 2 mol%) according to general procedure 2 gave **9** as a yellow solid after flash column chromatography (*n*-hexane–EtOAc, 1:1 + 0.5% Et_3N, R_f = 0.38); yield: 181 mg (76%); mp 131–133 °C.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.87 (s, 3 H, OCH_3), 7.03 (d, ^3J = 8.7 Hz, 2 H, H9, H9′), 7.33 (ddd, ^3J = 4.5 Hz, ^4J = 1.6 Hz, 1 H, H5′, ^3J = 6.6 Hz), 7.60 (d ,^3J = 8.7 Hz, 2 H, H8, H8′), 7.85 (ddd, ^3J = 7.7 Hz, ^3J = 6.6 Hz, ^4J = 1.6 Hz, 1 H, H4′), 8.00 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 1 H, H4), 8.48 (dd, ^3J = 8.5 Hz, ^3J = 7.7 Hz, 2 H, H3, H3′), 8.70 (d, ^3J = 4.5 Hz, 1 H, H6′), 8.90 (d, ^4J = 2.2 Hz, 1 H, H6).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 55.4 (C11), 114.6 (2 C, C9, C9′), 121.3 (2 C, C3, C3′), 123.7 (C5′), 128.2 (2 C, C8, C8′), 129.7 (C7), 135.0 (C4), 136.4 (C5), 137.3 (C4′), 146.9 (C6), 148.9 (C6′),153.6 (C2), 155.4 (C2′), 160.0 (C10).

MS (EI): *m/z* = 262.1 ($[C_{17}H_{14}N_2O]^+$ = $[M]^+$, 100).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{17}H_{14}N_2O$: 262.1106; found: 262.1105.

Anal. Calcd for $C_{17}H_{14}N_2O$·0.2 THF: C, 77.26; H, 5.68; N, 10.12. Found: C, 77.07; H, 5.52; N, 9.92.

5-[(Trimethylsilyl)ethynyl]-2,2′-bipyridine (10)[23]

Treatment of 2-bromopyridine (567 mg, 3.59 mmol, 1.5 equiv), 1.6 M *t*-BuLi in *n*-pentane (4.63 mL, 7.41 mmol, 3.1 equiv), $ZnCl_2$ (1.08 g, 7.89 mmol, 3.3 equiv), 2-chloro-5-[(trimethylsilyl)ethynyl]pyridine (500 mg, 2.39 mmol, 1 equiv), and $Pd(PPh_3)_4$ (55 mg, 48 μmol, 2 mol%) according to general procedure 2 gave **10** as a yellow solid after flash column chromatography (*n*-hexane–EtOAc 5:1, + 5% Et_3N, R_f = 0.75); yield: 540 mg (90%).

Analytical data were in accordance with those previously published.[23]

Methyl 5′-Heptyl-2,2′-bipyridine-5-carboxylate (11)

Treatment of 2-bromo-5-heptylpyridine (200 mg, 0.78 mmol, 1.2 equiv), 1.5 M *t*-BuLi in *n*-pentane (0.929 mL, 1.4 mmol, 2.15 equiv), $ZnCl_2$ (244 mg, 1.79 mmol, 2.75 equiv), methyl 6-chloronicotinate (112 mg, 0.65 mmol, 1 equiv), and $Pd(PPh_3)_4$ (15 mg, 13.1 μmol, 2 mol%) according to general procedure 2 gave **11** as a yellow solid after flash column chromatography (*n*-hexane–EtOAc, 5:1 + 5% Et_3N, R_f = 0.58); yield: 103 mg (51%); mp 76–80 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.87 (t, ^3J = 6.9 Hz, 3 H, CH_3), 1.20–1.38 (m, 8 H, 4 × CH_2), 1.59–1.68 (m, 2 H, CH_2), 2.66 (t, ^3J = 7.7 Hz, 2 H, CH_2), 3.96 (s, 3 H, CO_2CH_3), 7.64 (dd, ^3J = 8.1 Hz, ^4J = 2.2 Hz, 1 H, H4′), 8.37 (m, 2 H, H3′, H4), 8.46 (dd, ^3J = 8.3 Hz, ^5J = 0.8 Hz, 1 H, H3), 8.51 (d, ^4J = 2.2 Hz, 1 H, H6′), 9.23 (dd, ^4J = 2.1 Hz, ^5J = 0.8 Hz, 1 H, H6).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 29.10, 29.12, 31.1, 31.8, 32.9 (6 × CH_2), 52.4 (OCH_3), 120.2 (C3), 121.6 (C3′), 125.3 (C5), 136.9 (C4′), 138.0 (C4), 139.3 (C5′), 149.6 (C6′), 150.5 (C6), 152.8 (C2′), 159.7 (C2), 165.9 (CO_2Me).

MS (EI): *m/z* (%) = 312.8 ($[C_{19}H_{24}N_2O_2$ (M)$]^+$, 56), 227.1 ($[M - C_6H_{13}]^+$,100).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{19}H_{24}N_2O_2$: 312.1838; found: 312.1836.

Anal. Calcd for $C_{19}H_{24}N_2O_2$·0.5 EtOAc: C, 71.05; H, 8.04; N, 7.71. Found: C, 70.39; H, 8.04; N, 7.76.

Methyl 5′-[(Trimethylsilyl)ethynyl]-2,2′-bipyridine-5-carboxylate (12)

Treatment of 2-bromo-5-[(trimethylsilyl)ethynyl]pyridine (400 mg, 1.57 mmol, 1.2 equiv), 1.6 M *t*-BuLi in *n*-pentane (1.97 mL, 3.14 mmol, 2.4 equiv, lithiation time reduced to 5 min), $ZnCl_2$ (500 mg, 3.67 mmol, 2.8 equiv), methyl 6-chloronicotinate (225 mg, 1.31 mmol, 1 equiv), and $Pd(PPh_3)_4$ (46 mg, 40 μmol, 3 mol%) according to general procedure 2 gave **12** as a yellow solid after flash column chromatography (*n*-hexane–EtOAc, 5:1 + 5% Et_3N, R_f = 0.58); yield: 284 mg (70%); mp 152–154 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.27 [s, 9 H, $Si(CH_3)_3$], 3.95 (s, 3 H, OCH_3), 7.86 (dd, ^3J = 8.2 Hz, ^4J = 2.1 Hz, 1 H, H4′), 8.36 (dd, ^3J = 8.3 Hz, ^4J = 2.2 Hz, 1 H, H4), 8.40 (dd, ^3J = 8.2 Hz, ^5J = 0.8 Hz, 1 H, H3′), 8.46 (dd, ^3J = 8.3 Hz, ^5J = 0.8 Hz, 1 H, H3), 8.72 (dd, ^4J = 2.1 Hz, ^5J = 0.8 Hz, 1 H, H6′), 9.22 (dd, ^4J = 2.1 Hz, ^5J = 0.8 Hz, 1 H, H6).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –0.3 [$Si(CH_3)_3$], 52.6 (OCH_3), 100.1 (*C*≡CTMS), 101.8 (C≡*C*TMS), 121.0 (C3), 121.1 (C3′), 125.9 (C5), 138.2 (C4), 140.0 (C4′), 150.7 (C6), 152.3 (C6′), 153.9 (C2′), 158.9 (C2), 165.9 (CO_2Me); (C5′) not found.

MS (EI): *m/z* (%) = 310.1 ($[C_{17}H_{18}N_2O_2Si]^+$ = $[M]^+$, 44), 295.1 ($[M - CH_3]^+$, 100).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{17}H_{18}N_2O_2Si$: 310.1138; found: 310.1138.

Anal. Calcd for $C_{17}H_{18}N_2O_2Si$·0.2 EtOAc·.02 C_6H_{14}: C, 66.09; H, 6.54; N, 8.11. Found: C, 65.35; H, 6.65; N, 8.08.

5-(4-Methoxyphenyl)-5′-methyl-2,2′-bipyridine (13)[12b]

Treatment of 2-bromo-5-methylpyridine (1.40 g, 8.16 mmol, 1.5 equiv), 1.6 M *t*-BuLi in *n*-pentane (10.54 mL, 16.86 mmol, 3.1 equiv), $ZnCl_2$ (2.7 g, 19.58 mmol, 3.6 equiv), 2-chloro-5-(4-methoxyphenyl)pyridine (1.2 g, 5.44 mmol, 1 equiv), and $Pd(PPh_3)_4$ (189 mg, 163.2 μmol, 3 mol%) according to general procedure 2 gave **13** as a yellow solid after flash column chromatography (*n*-hexane–EtOAc, 3:1 + 5% Et_3N, R_f = 0.45); yield: 990 mg (66%).

Analytical data were in accordance with those previously published.[12b]

4,6′-Dimethyl-2,2′-bipyridine (14)[24]

2-Bromo-6-methylpyridine (2.5 g, 14.53 mmol, 1.2 equiv), 1.5 M *t*-BuLi in *n*-pentane (17.36 mL, 26.04 mmol, 2.15 equiv), $ZnCl_2$ (4.54 g, 33.31 mmol, 2.75 equiv), 2-chloro-4-methylpyridine (1.55 g, 12.11 mmol, 1 equiv), and $Pd(PPh_3)_4$ (420 mg, 363 μmol, 3 mol%) were used. Purification by flash column chromatography (*n*-hexane–EtOAc, 5:1 + 5% Et_3N, R_f = 0.6) gave **14** as a colorless oil; yield: 1.88 g (84%).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, 4-CH_3), 2.63 (s, 3 H, 6′-CH_3), 7.10 (d, ^3J = 4.9 Hz, 1 H, H5), 7.14 (d, ^3J = 7.7 Hz, 1 H, H5′), 7.67 (dd, ^3J = 7.7 Hz, ^3J = 7.7 Hz, 1 H, H4′), 8.15 (d, ^3J = 7.7 Hz, 1 H, H3′), 8.22 (s, 1 H, H3), 8.51 (d, ^3J = 4.9 Hz, 1 H, H6).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 21.2 (4-CH_3), 24.6 (6′-CH_3), 118.2 (C3′), 121.9 (C3), 123.1 (C5′), 124.5 (C5), 137.0 (C4′), 148.0 (C4), 148.9 (C6), 155.7 (C2), 156.2 (C2′), 157.8 (C6′).

MS (EI): *m*/*z* (%) = 184.1 ($[C_{12}H_{12}N_2]^+$ = $[M]^+$, 100).

HRMS (EI): *m*/*z* $[M - H]^+$ calcd for $C_{12}H_{11}N_2$: 183.0917; found: 183.0923.

Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 77.13; H, 7.13; N, 14.64.

4,6′-Dimethoxy-2,2′-bipyridine (15)

2-Bromo-6-methoxypyridine (1.09 g, 5.8 mmol, 1.2 equiv), 1.5 M *t*-BuLi in *n*-pentane (7.57 mL, 11.36 mmol, 2.15 equiv), $ZnCl_2$ (1.98 g, 14.53 mmol, 2.75 equiv), 2-chloro-4-methoxypyridine (759 mg, 5.28 mmol, 1 equiv), and $Pd(PPh_3)_4$ (184 mg, 159 μmol, 3 mol%) were used. Purification by flash column chromatography (*n*-hexane–EtOAc, 2:1 + 5% Et_3N, R_f = 0.58) gave **15** as a colorless oil; yield: 811 mg (71%).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.92 (s, 3 H, 4-OCH_3), 4.03 (s, 3 H, 6′-OCH_3), 6.76 (d, ^3J = 7.7 Hz, 1 H, H5′), 6.81 (dd, ^3J = 5.5 Hz, ^4J = 2.2 Hz, 1 H, H5), 7.68 (dd, ^3J = 7.7 Hz, ^3J = 7.7 Hz, 1 H, H4′), 7.95 (d, ^3J = 2.2 Hz, 1 H, H3), 8.00 (d, ^3J = 7.7 Hz, 1 H, H3′), 8.48 (d, ^3J = 5.5 Hz, 1 H, H6).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 53.2 (4-OCH_3), 55.2 (6′-OCH_3), 106.9 (C3), 109.6 (C5), 111.2 (C5′), 114.0 (C3′), 139.4 (C4′), 150.2 (C6), 153.0 (C2′), 157.7 (C2), 163.5 (C6′), 166.7 (C4).

MS (EI): *m*/*z* (%) = 215.1 ($[C_{12}H_{11}N_2O_2]^+$, 100), 216.1 ($[C_{12}H_{12}N_2O_2]^+$ = $[M]^+$, 96), 186.1 ($[C_{11}H_{10}N_2O]^+$, 52).

HRMS (EI): *m*/*z* $[M - H]^+$ calcd for $C_{12}H_{11}N_2O_2$: 215.0815; found: 215.0820.

Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 65.65; H, 5.73; N, 12.32.

4-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-6′-methoxy-2,2′-bipyridine (16)

2-Bromo-6-methoxypyridine (1.00 g, 5.32 mmol, 1.2 equiv), 1.5 M *t*-BuLi in *n*-pentane (6.37 mL, 9.56 mmol, 2.15 equiv), $ZnCl_2$ (1.67 g, 12.22 mmol, 2.75 equiv), 2-chloro-4-(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridine (916 mg, 4.45 mmol, 1 equiv), and $Pd(PPh_3)_4$ (154 mg, 133 μmol, 3 mol%) were used. Purification by flash column chromatography (*n*-hexane–EtOAc, 5:1 + 5% Et_3N, R_f = 0.6) gave **16** as a colorless solid; yield: 1.094 g (88%); mp 84 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.15 (s, 6 H, CH_3), 3.99 (s, 3 H, OCH_3), 5.98 (s, 2 H, H7, H7′), 6.81 (d, ^3J = 8.2 Hz, 1 H, H5), 7.16 (dd, ^3J = 5.5 Hz, ^4J = 1.7 Hz, 1 H, H5′), 7.73 (dd, ^3J = 7.7 Hz, ^3J = 8.2 Hz, 1 H, H4), 8.10 (d, ^3J = 7.7 Hz, 1 H, H3), 8.31 (d, ^3J = 1.7 Hz, 1 H, H3′), 8.75 (d, ^3J = 5.5 Hz, 1 H, H6′).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.2 (2 C, CH_3), 53.3 (OCH_3), 107.4 (2 C, C7, C7′), 112.0 (C5), 114.1 (C3), 120.0 (C3′), 122.2 (C5′), 128.5 (2 C, C8, C8′), 139.5 (C4), 147.5 (C4′), 149.8 (C6), 152.2 (C2), 157.5 (C2′), 163.6 (C6′).

MS (EI): *m*/*z* (%) = 279.2 ($[C_{17}H_{17}N_3O]^+$ = $[M]^+$, 100), 186.1 ($[C_{11}H_{10}N_2O]^+$, 42).

HRMS (EI): *m*/*z* $[M - H]^+$ calcd for $C_{18}H_{16}N_3O$: 278.1288; found: 278.1298.

Anal. Calcd for $C_{17}H_{17}N_3O$: C, 73.10; H, 6.13; N, 15.04. Found: C, 72.52; H, 6.32; N, 14.64.

6′-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-4-methoxy-2,2′-bipyridine (17)

2-Bromo-6-(2,5-dimethyl-1*H*-pyrrol-1-yl)pyridine (1.09 g, 4.34 mmol, 1.2 equiv), 1.5 M *t*-BuLi in *n*-pentane (5.02 mL, 7.78 mmol, 2.15 equiv), $ZnCl_2$ (1.36 g, 9.96 mmol, 2.75 equiv), 2-chloro-4-methoxypyridine (520 mg, 3.62 mmol, 1 equiv), and $Pd(PPh_3)_4$ (126 mg, 108.6 μmol, 3 mol%) were used. Purification by flash column chromatography (*n*-hexane–EtOAc, 5:1 + 5% Et_3N, R_f = 0.43) gave **17** as a yellow oil; yield: 684 mg (68%).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.21 (s, 6 H, CH_3), 3.91 (s, 3 H, OCH_3), 5.95 (s, 2 H, CH-pyrrole), 6.85 (dd, ^3J = 5.7 Hz, ^4J = 2.7 Hz, 1 H, H5), 7.22 (dd, ^3J = 7.8 Hz, ^4J = 0.9 Hz, 1 H, H5′), 7.93 (dd, ^3J = 7.8, ^3J = 7.8 Hz, 1 H, H4′), 7.99 (d, ^4J = 2.7 Hz, 1 H, H5), 8.43 (dd, ^3J = 7.8 Hz, ^4J = 0.9 Hz, 1 H, H3′), 8.49 (d, ^3J = 5.7 Hz, 1 H, H6).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.5 (2 C, CH_3), 55.4 (OCH_3), 106.5 (C3), 107.0 (2 C, CH-pyrrole), 111.1 (C5), 119.4 (C3′), 121.7 (C5′), 128.8 (2 C, CMe-pyrrole), 138.8 (C4′), 150.3 (C6), 151.2 (C6′), 155.7 (C2′), 157.3 (C2), 166.8 (C4).

MS (EI): *m*/*z* (%) = 279.1 ($[C_{17}H_{17}N_3O]^+$ = $[M]^+$, 100).

HRMS (EI): *m*/*z* $[M - H]^+$ calcd for $C_{17}H_{16}N_3O$: 278.1288; found: 278.1295.

Anal. Calcd for $C_{17}H_{16}N_3O \cdot 0.166\ CH_2Cl_2$: C, 70.25; H, 5.95; N, 14.32. Found: C, 70.87; H, 6.07; N, 14.42.

5-Heptyl-5′-(4-methoxyphenyl)-2,2′-bipyridine (18)

i-Pr_2NH (0.610 mL, 4.31 mmol, 1.05 equiv) and anhyd THF (38 mL) were cooled to –78 °C and 1.6 M *n*-BuLi in *n*-hexane (2.70 mL, 4.31 mmol, 1.05 equiv) was added. A soln of **13** (1.125 g, 4.08 mmol, 1 equiv) in anhyd THF (10 mL) was added via syringe. The soln became dark red immediately. The acetone–nitrogen cooling bath was replaced by an ice-water bath. After 5 min, 1-iodohexane (0.633 mL, 4.31 mmol, 1.05 equiv) was added via syringe. The soln was allowed to warm to r.t., stirred for 3 h, concentrated, and the crude product was dissolved in CH_2Cl_2 (25 mL) and washed with H_2O (25 mL). After extraction of the aqueous layer with CH_2Cl_2 (3 × 25 mL) the combined organic layers were dried (Na_2SO_4) and the solvent was removed. Purification by flash column chromatography (*n*-hexane–EtOAc, 2:1 + 5% Et_3N, R_f = 0.3–0.65) gave **18** as a yellow solid; yield: 1.059 g (72%); mp 75–76 °C.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.81 (t, ^3J = 6.9 Hz, 3 H, CH_3), 1.20–1.28 (m, 8 H, 4 × CH_2), 1.59 (m, 2 H, CH_2), 2.58 (t, ^3J = 7.7 Hz, 2 H, CH_2), 3.79 (s, 3 H, OCH_3), 6.95 (m, 2 H, H9), 7.52 (m, 2 H, H8), 7.57 (dd, ^3J = 8.1 Hz, ^4J = 2.0 Hz, 1 H, H4′), 7.89 (dd, ^3J = 8.3 Hz, ^4J = 2.2 Hz, 1 H, H4), 8.27 (d, ^3J = 8.1 Hz, 1 H, H3′), 8.35 (d, ^3J = 8.3 Hz, 1 H, H3), 8.44 (d, ^4J = 2.0 Hz, 1 H, H6′), 8.80 (d, ^4J = 2.2 Hz, 1 H, H6).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6, 29.0, 29.1, 31.1, 31.7, 32.9 (6 × CH_2), 55.4 (OCH_3), 114.6 (C9), 120.6 (C3′), 120.7 (C3), 128.1 (C8), 130.0 (C7), 134.7 (C4), 135.8 (C5), 136.9 (C4′), 138.2 (C5′), 147.1 (C6), 149.2 (C6′), 153.5 (C2′), 154.3 (C2), 159.8 (C10).

MS (CI, isobutane): *m*/*z* (%) = 361.3 ($[C_{24}H_{29}N_2O]^+$ = $[M]^+$, 100).

HRMS (CI, isobutane): *m/z* [M + H]$^+$ calcd for $C_{24}H_{29}N_2O$: 361.2279; found: 361.2274.

Anal. Calcd for $C_{24}H_{28}N_2O$: C, 79.96; H, 7.83; N, 7.77. Found: C, 80.75; H, 8.00; N, 7.64.

5-(4-Hydroxyphenyl)-2,2′-bipyridine (19)

5-(4-Methoxyphenyl)-2,2′-bipyridine (**9**, 600 mg, 2.29 mmol, 1 equiv) was dissolved in CH_2Cl_2 (15 mL) and cooled to –78 °C. 1 M BBr_3 in CH_2Cl_2 (6.78 mL, 6.78 mmol) was slowly added. The mixture was allowed to warm up to r.t. and stirred for 7 h. After a short time an orange-brown precipitate formed. H_2O (50 mL) was carefully added in order to hydrolyze excessive BBr_3. EtOAc (50 mL) was added and the soln was neutralized with 6 M aq NaOH. The orange precipitate was filtered off and dried in vacuo. The neutralized soln was extracted with EtOAc (5 × 25 mL) and dried (Na_2SO_4). The solvents were removed and then, the product fractions were combined and **19** was obtained as an orange-brown solid; yield: 506 mg (89%); mp 146–148 °C.

^{1}H NMR (500.1 MHz, DMSO-d_6): δ = 6.91 (d, H9′, ^3J = 8.8 Hz, 2 H, H9), 7.44 (ddd, ^3J = 6.9 Hz, ^3J = 4.9 Hz, ^4J = 1.1 Hz, 1 H, H5′), 7.64 (d, ^3J = 8.8 Hz, 2 H, H8, H8′), 7.95 (ddd, ^3J = 7.7 Hz, ^3J = 6.9 Hz, ^4J = 1.6 Hz, 1 H, H4′), 8.14 (dd, ^3J = 8.2 Hz, ^4J = 2.2 Hz, 1 H, H4), 8.40 (dd, ^3J = 7.7 Hz, ^3J = 8.2 Hz, 2 H, H3, H3′), 8.68 (dd, ^3J = 4.9 Hz, ^4J = 1.6 Hz, 1 H, H6′), 8.93 (d, ^4J = 2.2 Hz, 1 H, H6), 9.79 (s, 1 H, OH).

^{13}C NMR (125.8 MHz, DMSO-d_6): δ = 116.1 (2 C, C9, C9′), 120.4, 120.6 (C3, C3′), 124.1 (C5′), 127.3 (C7), 128.1 (2 C, C8, C8′), 134.3 (C4), 135.8 (C5), 137.5 (C4′), 146.6 (C6), 149.3 (C6′), 153.1 (C2), 155.0 (C2′), 158.0 (C10).

MS (EI): *m/z* (%) = 248.0 ([$C_{16}H_{12}N_2O$]$^+$ = [M]$^+$, 100).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{16}H_{12}N_2O$: 248.0950; found: 248.0950.

Anal. Calcd for $C_{16}H_{12}N_2O$·0.166 EtOAc: C, 76.12; H, 5.11; N, 10.65. Found: C, 76.71; H, 5.18; N, 10.42.

5-Heptyl-5′-(4-hydroxyphenyl)-2,2′-bipyridine (20)

Bipyridine **18** (180 mg, 0.49 mmol, 1 equiv) was dissolved in CH_2Cl_2 (5 mL) and the soln was cooled to –78 °C. 1 M BBr_3 in CH_2Cl_2 (2.2 mL, 2.2 mmol, 4.4 equiv) was slowly added. The mixture was allowed to warm up to r.t. and stirred for 10 h. Aq 2 M NaOH was carefully added in order to hydrolyze excessive BBr_3. EtOAc (25 mL) was added and the soln was neutralized with aq 6 M HCl. The orange precipitate was filtered off and dried in vacuo. The neutralized soln was extracted with EtOAc (5 × 25 mL) and dried (Na_2SO_4). Solvent was removed and the product fractions were combined to give **20** as an orange-brown solid; yield: 171 mg (quant); mp 90–92 °C.

R_f = 0.05 (*n*-hexane–EtOAc, 2:1 + 5% Et_3N).

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.86 (t, ^3J = 6.9 Hz, 3 H, CH_3), 1.23–1.34 (m, 8 H, 4 × CH_2), 1.64 (m, 2 H, CH_2), 2.65 (t, ^3J = 7.3 Hz, 2 H, CH_2), 6.93 (m, 2 H, H9), 7.44 (m, 2 H, H8), 7.66 (d, ^3J = 7.6 Hz, 1 H, H4′), 7.91 (d, ^3J = 7.9 Hz, 1 H, H4), 8.29 (d, ^3J = 7.6 Hz, 1 H, H3′), 8.34 (d, ^3J = 7.9 Hz, 1 H, H3), 8.51 (s, 1 H, H6′), 8.81 (s, 1 H, H6); O*H* not found.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6, 29.0, 29.1, 31.0, 31.7, 32.8 (6 × CH_2), 116.3 (C9), 121.1 (C3/C3′), 128.2 (C8), 129.2 (C7), 134.9 (C4), 136.2 (C5), 137.4 (C4′), 138.6 (C5′), 146.9 (C6), 149.0 (C6′), 153.2 (C2′), 153.7 (C2), 157.0 (C10).

MS (CI, isobutane): *m/z*& nbsp;(%) = 347.3 ([$C_{23}H_{27}N_2O$]$^+$ = [M + H]$^+$, 100).

HRMS (CI, isobutane): *m/z* [M + H]$^+$ calcd for $C_{23}H_{27}N_2O$: 347.2123; found: 347.2122.

Anal. Calcd for $C_{23}H_{26}N_2O$·0.33 CH_2Cl_2: C, 74.78; H, 7.17; N, 7.47. Found: C, 74.78; H, 7.49; N, 7.40.

5-[4-(Trifluoromethylsulfonyl)phenyl]-2,2′-bipyridine (21)

Bipyridine **19** (300 mg, 1.21 mmol, 1 equiv) was dissolved in Et_3N (2 mL) and CH_2Cl_2 (30 mL) and the soln was cooled to –30 °C. At this temperature, Tf_2O (0.41 mL, 682 mg, 2.42 mmol, 2 equiv) in CH_2Cl_2 (10 mL) was slowly added to the mixture. The cooling bath was removed and the soln was stirred at r.t. for 13 h. The mixture was then poured into cold H_2O (50 mL) and extracted with CH_2Cl_2 (5 × 25 mL). The combined organic layers were washed with sat. aq $NaHCO_3$ (50 mL) and with brine (50 mL). The organic layer was dried (Na_2SO_4) and the solvents were removed. Purification by flash column chromatography (*n*-hexane–EtOAc, 1:1 + 0.5% Et_3N, R_f = 0.66) gave **21** as a yellow solid; yield: 184 mg (40%); mp 109–111 °C.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 7.36 (ddd, ^3J = 6.3 Hz, ^3J = 3.9 Hz, ^4J = 1.1 Hz, 1 H, H5′), 7.41 (d, ^3J = 8.6 Hz, 2 H, H9, H9′), 7.72 (d, ^3J = 8.6 Hz, 2 H, H8, H8′), 7.87 (ddd, ^3J = 7.7 Hz, ^3J = 6.3 Hz, ^4J = 1.6 Hz, 1 H, H4′), 8.01 (dd, ^3J = 8.2 Hz, ^4J = 2.2 Hz, 1 H, H4), 8.47 (d, ^3J = 7.7 Hz, 1 H, H3′), 8.54 (d, ^3J = 8.2 Hz, 1 H, H3), 8.72 (d, ^3J = 3.9 Hz, 1 H, H6′), 8.90 (d, ^4J = 2.2 Hz, 1 H, H6).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 118.8 (CF_3, $^1J_{C\text{-}F}$ = 321 Hz), 121.2 (C3), 121.3 (C3′), 122.1 (2 C, C9, C9′), 124.0 (C5′), 128.9 (2 C, C8, C8′), 134.7 (C5), 135.4 (C4), 137.3 (C4′), 138.1 (C7), 147.5 (C6), 149.1 (C6′), 149.5 (C10), 155.3, 155.4 (C2, C2′).

^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –72.7 (CF_3).

MS (EI): *m/z* (%) = 380.0 ([$C_{17}H_{11}F_3N_2O_3S$]$^+$ = [M]$^+$, 100).

HRMS (EI): *m/z* calcd for $C_{17}H_{11}F_3N_2O_3S$: 380.0442; found: 380.0447.

Anal. Calcd for $C_{17}H_{11}F_3N_2O_3S$·0.33 $C_6H_5CH_3$: C, 56.49; H, 3.35; N, 6.82. Found: C, 56.92; H, 2.92; N, 6.52.

5-Heptyl-5′-[4-(trifluoromethylsulfonyl)phenyl]-2,2′-bipyridine (22)

Bipyridine **20** (150 mg, 0.43 mmol, 1 equiv) was dissolved in Et_3N (0.2 mL) and CH_2Cl_2 (10 mL) and the soln was cooled to –30 °C. At this temperature Tf_2O (110 μL, 182 mg, 0.65 mmol, 1.5 equiv) was slowly added to the mixture. The cooling bath was removed and the mixture was stirred at r.t. for 15 h. TLC monitoring still revealed some starting material, hence additional Tf_2O (20 μL) was added at r.t. and the mixture was stirred for an additional 3 h. The mixture was then poured into cold H_2O (25 mL) and extracted with CH_2Cl_2 (5 × 15 mL). The combined organic layers were washed with sat. aq $NaHCO_3$ (25 mL) and with brine (25 mL). The organic layer was dried (Na_2SO_4) and the solvents were removed. Purification by flash column chromatography (*n*-hexane–EtOAc, 5:1 + 5% Et_3N, R_f = 0.6) gave **22** as a yellow solid; yield: 152 mg (74%); mp 112–114 °C.

^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.9 Hz, 3 H, CH_3), 1.25–1.39 (m, 8 H, 4 × CH_2), 1.67 (m, 2 H, CH_2), 2.69 (t, ^3J = 7.7 Hz, 2 H, CH_2), 7.40 (m, 2 H, H9), 7.70 (m, 3 H, H4′, H8), 7.99 (dd, ^3J = 8.3 Hz, ^4J = 2.2 Hz, 1 H, H4), 8.38 (d, ^3J = 7.9 Hz, 1 H, H3′), 8.52 (m, 2 H, H3, H6′), 8.87 (s, 1 H, H6).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6, 29.0, 29.1, 31.0, 31.7, 32.9 (6 × CH_2), 118.8 (CF_3, $^1J_{C\text{-}F}$ = 321 Hz), 121.1 (C3, C3′), 122.1 (C9), 128.9 (C8), 134.5 (C5), 135.4 (C4), 137.4 (C4′), 138.1 (C7), 139.0 (C5′), 147.5 (C6), 148.8 (C6′), 149.5 (C10), 152.6 (C2′), 155.3 (C2).

^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –72.73 (CF_3).

MS (CI, NH_3): *m/z* (%) = 479.2 ([$C_{24}H_{26}F_3N_2O_3S$]$^+$ = [M + H]$^+$, 100).

HRMS (CI, NH_3): *m/z* $[M + H]^+$ calcd for $C_{24}H_{26}F_3N_2O_3S$: 479.1616; found: 479.1622.

Anal. Calcd for $C_{24}H_{25}F_3N_2O_3S$: C, 60.24; H, 5.27; N, 5.85; S 6.70. Found: C, 60.96; H, 5.57; N, 5.81; S 6.23.

5-Heptyl-5′-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-2,2′-bipyridine (23)

KOAc (246 mg, 2.508 mmol, 3 equiv), **22** (400 mg, 0.84 mmol, 1 equiv), bis(pinacolato)diboron (255 mg, 1.003 mmol, 1.2 equiv), $[PdCl_2(dppf)]$ (61 mg, 84 μmol, 10 mol% Pd), and 1,1′-bis(diphenylphosphino)ferrocene (dppf) (47 mg, 84 μmol, 10 mol%) were dissolved in 1,4-dioxane (12 mL) and the resulting soln was heated to 120 °C and stirred at this temperature for 18 h. When TLC monitoring revealed complete consumption of the starting material H_2O (25 mL) and CH_2Cl_2 (25 mL) were added. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried (Na_2SO_4) and the solvents were removed. Purification by flash column chromatography (*n*-hexane–EtOAc, 5:1, R_f = 0.6) gave **23** as a brown solid; yield: 343 mg (90%); mp 158–162 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.9 Hz, 3 H, CH_3), 1.22–1.41 (m, 8 H, 4 × CH_2), 1.37 (s, 12 H, 4 × CH_3), 1.61–1.71 (m, 2 H, CH_2), 2.67 (t, ^3J = 7.7 Hz, 2 H, CH_2), 7.62–7.68 (m, 3 H, H4′, H8), 7.93 (d, ^3J = 8.3 Hz, 2 H, H9), 8.03 (dd, ^3J = 8.3 Hz, ^4J = 2.4 Hz, 1 H, H4), 8.34 (dd, ^3J = 8.1 Hz, ^5J = 0.7 Hz, 1 H, H3′), 8.44 (dd, ^3J = 8.3 Hz, ^5J = 0.8 Hz, 1 H, H3), 8.51 (dd, ^4J = 2.2 Hz, ^5J = 0.7 Hz, 1 H, H6′), 8.92 (dd, ^4J = 2.4 Hz, ^5J = 0.8 Hz, 1 H, H6).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7 (CH_2), 24.9 (4 × CH_3), 29.13, 29.15, 31.1, 31.8, 32.9 (5 × CH_2), 84.0 (2 C, CMe_2), 120.71 (C3)*, 120.76 (C3′)*, 126.3 (2 C, C8), 135.3 (C4), 135.6 (2 C, C9), 136.0 (C5), 136.8 (C4′), 138.4 (C5′), 140.4 (C7), 147.7 (C6), 149.4 (C6′), 153.6 (C2′), 155.4 (C2), C10 not found; * interchangeable assignments.

MS (EI): *m/z* (%) = 456.3 ($[C_{29}H_{37}BN_2O_2]^+$ = $[M]^+$, 100).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{29}H_{37}{}^{10}BN_2O_2$: 455.2984; found: 455.2977.

Anal. Calcd for $C_{29}H_{37}BN_2O_2$·0.2 EtOAc: C, 75.50; H, 8.21; N, 5.91. Found: C, 76.31; H, 8.06; N, 5.89.

Methyl 5′-Ethynyl-2,2′-bipyridine-5-carboxylate (24)

Bipyridine **12** (284 mg, 0.91 mmol, 1 equiv) was dissolved in THF (25 mL) and MeOH (25 mL). KF (64 mg, 1.10 mmol, 1.2 equiv) was added and the resulting mixture stirred for 24 h. The solvents were removed and the resulting crude product subjected to flash column chromatography (*n*-hexane–EtOAc, 5:1 + 5% Et_3N, R_f = 0.69) to give **24** as a yellow solid; yield: 155 mg (71%); mp 180–182 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.32 (s, 1 H, C≡CH), 3.97 (s, 3 H, OCH_3), 7.91 (dd, ^3J = 8.3 Hz, ^4J = 2.0 Hz, 1 H, H4′), 8.38 (dd, ^3J = 8.4 Hz, ^4J = 2.1 Hz, 1 H, H4), 8.40 (m, ^3J = 8.2 Hz, 1 H, H3′), 8.46 (m, ^3J = 8.4 Hz, 1 H, H3), 8.72 (dd, ^4J = 2.0 Hz, ^5J = 0.9 Hz, 1 H, H6′), 9.22 (dd, ^4J = 2.1 Hz, ^5J = 0.9 Hz, 1 H, H6).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 52.5 (OCH_3), 80.5 (*C*≡CH), 82.0 (C≡*C*H), 120.0 (C5′), 120.9 (C3), 121.1 (C3′), 125.9 (C5), 138.1 (C4), 140.1 (C4′), 150.6 (C6), 152.4 (C6′), 154.3 (C2′), 158.6 (C2), 165.7 (C7).

MS (EI): *m/z* (%) = 238.0 ($[C_{14}H_{10}N_2O_2]^+$ = $[M]^+$, 100).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{14}H_{10}N_2O_2$: 238.0742; found: 238.0746.

Anal. Calcd for $C_{14}H_{10}N_2O_2$·0.25 EtOAc·0.25 C_6H_{14}: C, 70.32; H, 5.54; N, 9.94. Found: C, 69.71; H, 5.55; N, 9.78.

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