Functionalization of 2,2′-Bipyridines in Their 4 and 5 Positions. Synthesis of 5-Ethynyl-2,2′-bipyridine

Johann Polin,*[a] Erich Schmohel, Vincenzo Balzani
Dip. di Chimica "G. Ciamician" Universitá degli Studi di Bologna, Via Selmi 2, I-40126 Bologna, Italy
Fax +39 51 259456; E-mail: photochem@ciam01.ciam.unibo.it
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Abstract: The synthesis of 5-ethynyl-2,2′-bipyridine (**9**) from 5-methyl-2,2′-bipyridine (**5**) is reported. The conversion of the methyl derivative, which is the most common starting material to further substitution, involves the preparation of 2,2′-bipyridine-5-carbaldehyde (**6**). Corey–Fuchs olefination and subsequent hydrolysis yields the target compound **9**. The multistep synthesis is discussed with respect to alternative routes and compared with those of related 4-substituted 2,2′-bipyridines.

Key words: 2,2′-bipyridines, Corey–Fuchs alkenation, carboxy-ethyne conversion, [Pd]-catalyzed coupling

The outstanding properties of metal 2,2′-bipyridine (bpy) metal complexes as building blocks for supramolecular species[1] and polymers[2] is a driving force to novel derivatives with applications in electrochemistry,[3] photochemistry[1, 4] and nonlinear optics.[5] In the last few years the increasing interest in these fields has evidenced the importance of availability of a variety of bpy-type ligands. New strategies for the synthesis of bpy derivatives are therefore needed.

In order to obtain vinyl-2,2′-bipyridine derivatives the most commonly used precursors have been 5-methyl-2,2′-bipyridine,[6] 4,4′-dimethyl-2,2′-bipyridine,[7] and 4-methyl-2,2′-bipyridylene-4′-carbaldehyde.[8] The Wadsworth–Emmons reaction,[9] or its modifications, has proved very successful in the synthesis of 1,2-bifunctional ethenes.

Building blocks with considerable synthetic potential are arylethyne derivatives of bpy.[10] Therefore, the preparation of ethynyl-2,2′-bipyridine, as well as of ethyne substituted 2,2′:6′,2″-terpyridyls[11] or 1,10-phenanthroline,[12, 13a] is an important goal. In this article we describe attempts to obtain 4-ethynyl and 5-ethynyl-2,2'-bipyridines.

2,2′-Bipyridine Precursors

It is well known that the chemical reactivity at the 3, 4, 5 and 6 positions of 2,2′-bipyridine differs remarkably. Unfortunately this restricts the range of functionalized bipyridine to a limited series of starting materials.

Relatively easily accessible are 6-substituted and 6,6′-disubstituted bipyridines.[2c, 13] However the steric hindrance, caused by the vicinity of the substituents to the nitrogens, limits the use of these derivatives as far as octahedral complexes are concerned. Nevertheless 6-substituted ethynyl bridged 2,2′-bipyridine macrosystems from bromo-precursors find an increasing interest, due to the convenience of the Hagihara coupling.[13, 14]

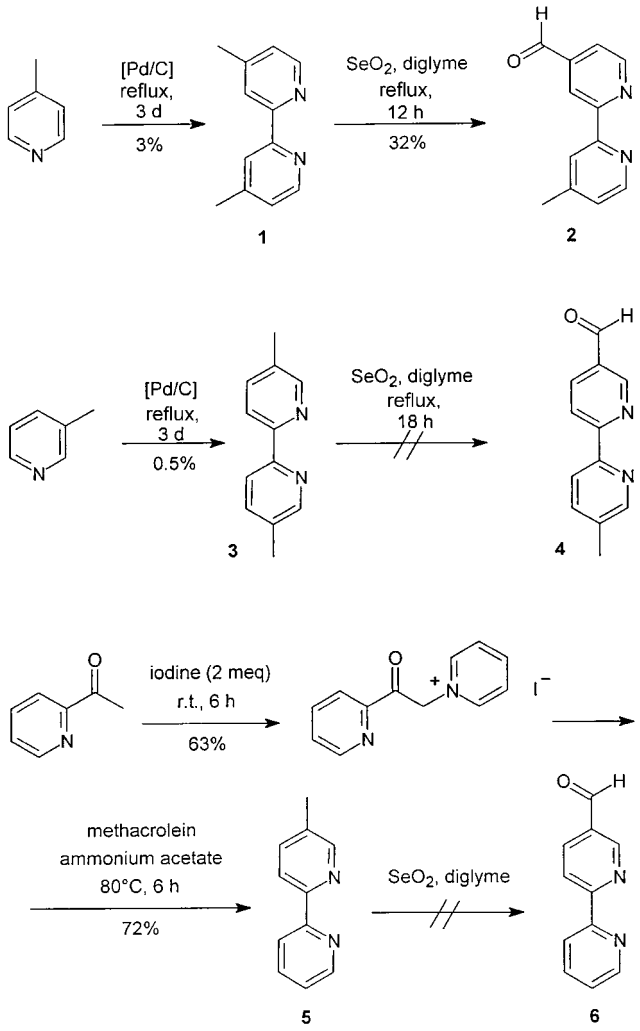
Several 4- and 5-substituted 2,2′-bipyridine precursors are easily accessible.[15] Useful starting materials are 5-methyl-2,2′-bipyridine,[6,16] 5-bromomethyl-2,2′-bipyridine,[6b,17] 2,2′-bipyridine-5-carboxylic acid and its acid chloride,[4b,d] as well as 4-methyl-[18] and 4,4′-dimethyl-2,2′-bipyridine.[4c, 7, 19] Other starting materials like 4-bromo- and 4,4′-dibromo-2,2′-bipyridine undergo Pd-catalyzed coupling reactions according to Hagihara,[14a, 20] Heck,[21] or Stille,[22] and are suitable intermediates to monosubstituted and symmetrically disubstituted vinyl- and ethynyl-2,2′-bipyridine derivatives. It must be pointed out that in this way it is possible to obtain compounds exhibiting rigidity and extended π-conjugation.

Finally, it should be noted that there are comparatively few examples of 3-substituted bpy derivatives.[23]

Synthesis of Ethynyl-2,2′-bipyridines

The first ethynylbipyridine derivatives were synthesized by Pd-catalyzed coupling of 4,4′-dibromo-2,2′-bipyridine with ethynylbenzo[15]crown ether by Beer et al.,[19d, 24] and also by ethynylation of the dibromo compound with trimethylsilylacetylene (TMSA) by Suffert and Ziessel.[13a] These derivatives result from symmetric functionalization of 4,4′dibromo-2,2′-bipyridine, which is available from 2,2′-bipyridine via 4,4′-dinitro-2,2′-bipyridyl 1,1′-dioxide.[25] The preparation of the key intermediate requires rather harsh treatment of 2,2′-bipyridine which is oxidized in a hydrogen peroxide/acetic acid mixture and nitrated by means of a fuming nitric acid/concentrated sulfuric acid mixture at high temperature. Successive bromination with acetyl bromide/phosphorus tribromide yields 4,4′-dibromo-2,2′-bipyridine. 4-Bromo-2,2′-bipyridine[26] was isolated as a side product in the aforementioned preparation and has been used as starting material for the synthesis of 4-ethynyl-2,2′-bipyridine.[11c, 13b] We tried carefully to improve the yield of 4-bromo-2,2′-bipyridine, but only a small increase was obtained.

While there are several coupling reactions based on 4-bromo-2,2′-bipyridine, there is, to our knowledge, only one paper that refers to 5-bromo-2,2′-bipyridine and 5,5′-dibromo-2,2′-bipyridine.[11b] In that paper the authors reported formation of 5-ethynyl-2,2′-bipyridine (**9**) and 5,5′-diethynyl-2,2′-bipyridine as products from Pd-catalyzed ethynylation with TMSA. The bromo compounds were prepared from 2,2′-bipyridine in constant boiling hydrobromic acid and subsequent bromination of the intermediate 2,2′-bipyridyl hydrobromide at 250 °C, according to Burstall.[27] After the removal of unreacted 2,2′-bipyridine, the remaining product was treated with an excess of picric acid and the intermediate pure picrate decomposed yielding *"5(?)-bromo-2:2-dipyridy1"*.[28] The residue insoluble in acid yielded *"5,5′(?)-dibromo-2:2-dipyridyl "*.[28] The reliability and effectiveness of this procedure seems somewhat questionable, but improved methods have re-

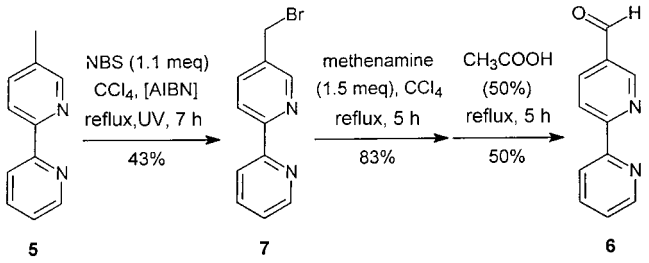


cently been reported.[29] Vögtle and co-workers, on the other hand, were able to circumvent these difficulties in the preparation of a substituted 5-ethynyl-2,2′-bipyridine by conversion of the corresponding vinylidene-bipyridine by means of an addition-elimination sequence.[14b, 17]

In the search of suitable alternatives we thought that 2,2′-bipyridine-carbaldehydes could be ideal starting materials to ethynyl-2,2′-bipyridine. Useful precursors to carbaldehydes are potentially the corresponding methyl derivatives. In order to obtain the conversion of methyl compounds into the corresponding carbaldehydes, two methods were compared. First, we checked the oxidation with selenium dioxide in diglyme, in analogy to the procedure used for the 4,4′-dimethyl-bipyridine conversion to give **2**.[19a, c]

Unfortunately, under such conditions both oxidation and partial oxidation of 5,5′-dimethyl-2,2′-bipyridine (**3**), prepared from 3-picoline,[19b] failed. We also tried the oxidation of 5-methyl-2,2′-bipyridine (**5**),[16a] obtained from 2-acetylpyridine via 1-(2-pyridylacetyl)pyridinium iodide,[30] with selenium dioxide, but even using an excess of the oxidant the reaction failed. These results strongly confirm the chemical differences at the 4 and 5 positions of bpy.

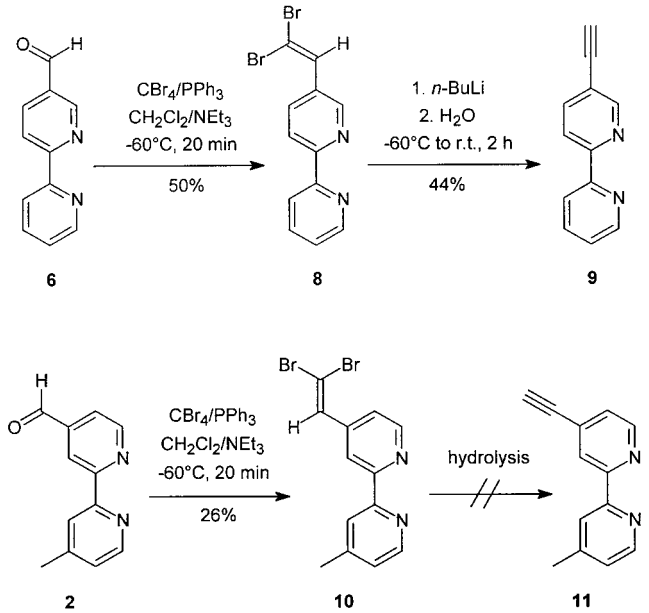
We then tried an alternative strategy to obtain 2,2′-bipyridine-5-carbaldehyde (**6**) via the corresponding methenamine salt in a large-scale synthesis.[15]



Treatment of 5-bromomethyl-2,2′-bipyridine (**7**), available from the methyl precursor **5** by NBS bromination,[31] with methenamine (hexamethylenetetraamine) gave [*N*-(5-methyl-2,2′-bipyridyl)]hexamethylenetetraammonium bromide, which was converted in boiling acetic acid into 2,2′-bipyridine-5-carbaldehyde (**6**) in 50% yield.

Carbaldehydes **2** and **6** undergo formyl-ethynyl conversion according to Corey,[32] a strategy which has recently been applied to various systems by Neidlein and co-workers[10b, 33] and others.[34] Such formyl conversion by bromination, using the carbon tetrabromide/triphenylphosphine/triethylamine system,[32] gave white needles of 5-(2,2-dibromovinyl)-2,2′-bipyridine (**8**) in satisfactory yield. The same procedure was successfully used to obtain the geminal dibromovinyl derivative **10.**

The ethynyl derivative **9** was then obtained from the hydrolysis of **8**. In contrast, the hydrolysis of **10** failed.



Standard reactions were carried out under ambient conditions. Schlenk technique was used when indicated. Solvents were dried over appropriate reagents (THF over sodium/benzophenone; CH_2Cl_2 over $CaCl_2$) and distilled before use. Reagent grade amine was dried over molecular sieve. Analytical equipment comprises: Hewlett-Packard 5971 (GC-MS), MS-50 A.E.I. Manchester (FAB), Nicolet 510M FT-

IR [KBr, ν (cm^{-1})], Varian Gemini 300 and 200 MHz [^1H NMR, δ (ppm) *vs.* TMS, r.t.].

4,4′-Dimethyl-2,2′-bipyridine (1):[19b]
Freshly distilled 4-picoline (250 mL) and 10% Pd/C (10.4 g) were refluxed for 3 d. After addition of hot benzene (100 mL) reflux was continued for 45 min. The crude product was filtered from the catalyst, concentrated and recrystallized (EtOAc); yield: 7.0 g (3%).
MS: calcd. for $C_{12}H_{12}N_2$ 184.24, found *m/z* 184 (M^+, 100%).

4-Methyl-2,2′-bipyridine-4′-carbaldehyde (2):[19c]
A mixture of4,4′-dimethyl-2,2′-bipyridine (2.6 g, 14 mmol) and SeO_2 (1.55 g, 14 mmol) in diglyme (100 mL) was refluxed for 12 h. After adjusting the pH with NaOH to pH 9–10 and extraction with CH_2Cl_2 a yellow-brownish mixture of 4,4′-dimethyl-2,2′-bipyridine and 4-methyl-2,2′-bipyridine-4′-carbaldehyde was obtained. The carbaldehyde was isolated by column chromatography (silica gel, 220-440 mesh, 4 × 40 cm, petroleum ether/CH_2Cl_2 90:10); yield: 0.9 g (32%).
MS: calcd. for $C_{12}H_{10}N_2O$ 198.22, found *m/z* 199, 198 (M^+, 100%).

5,5′-Dimethyl-2,2′-bipyridine (3):
Freshly distilled 3-picoline (250 mL, 2.57 mol) and 10% Pd/C (10.6 g, 10 mmol) were refluxed for 3 d. After addition ofhot benzene (100 mL) reflux was continued for a further 45 min. The hot product was filtered from the catalyst, concentrated and recrystallized (EtOAc); yield: 2.2 g (0.5%).

Remark: This strategy which required considerable amounts of costly Pd/C seems inappropriate, since it was impossible to increase the yield of pure product to reasonable quantities.
IR: ν = 3035 w, 3012 w, 2956 w, 2921 w, 2863 w, 1949 w, 1858 w, 1802 w, 1762 w, 1713 w, 1686 w, 1600 m, 1553 m, 1524 m, 1470 s, 1372 m, 1289 w, 1273 m, 1245 m, 1221 m, 1208 m, 1171 w, 1129 m, 1096 w, 1055 m, 1046 m, 1032 m, 1015 m, 986 m, 974 m, 930 m, 828 s, 795 s, 737 s, 652 s, 538 s, 467 cm^{-1} vs.
MS: calcd. for $C_{12}H_{12}N_2$ 184.24, found *m/z* 184.12 (M^+, 100%).

1-(2-Pyridylacetyl)pyridinium Iodide:[30]
2-Acetylpyridine (12.0 g, 0.1 mol) and I_2 (50.8 g, 0.2 mol) were dissolved in excess of freshly distilled pyridine and refluxed for 6 h. The reaction mixture was cooled to r.t. and the product collected by suction, washed with little pyridine and recrystallized (charcoal/EtOH) to give crystals which were dried in vacuo; yield: 20.5 g (63%); mp 199 °C.
^1H NMR (DMSO-d_6): δ = 9.02 (dd, 1 H, ^3J = 6.7 Hz, ^4J = 1.7 Hz), 8.88 (dd, 2 H, ^3J = 4.8 Hz, ^4J = 1.7 Hz), 8.75 (tt, 1 H, ^3J = 7.8 Hz, ^4J = 1.4 Hz), 8.29 (dd, 1 H, ^3J = 6.7 Hz,^3J = 7.8 Hz), 8.15 (ddd, 1 H, ^3J = 7.9 Hz, ^3J = 7.7 Hz, ^4J = 1.7 Hz), 8.08 (dd, 2 H, ^3J = 7.9 Hz, ^4J = 1.5 Hz), 7.85 (ddd, 1 H, ^3J = 7.7 Hz, ^3J = 4.8 Hz, ^4J = 1.5 Hz), 6.53 (s, 2 H, $–CH_2–$).
MS: calcd. for $C_{12}H_{11}N_2OI$ 326.14, found *m/z* 326 (M^+).

5-Methyl-2,2′-bipyridine (5):[16a]
1-(2-Pyridylacetyl)pyridinium iodide (16.3 g, 50 mmol), freshly distilled methacrolein (3.86 g, 55 mmol) and NH_4OAc (1.56 g, 0.15 mol) were dissolved in formamide and stirred for 6 h at 80°C under argon. The system was cooled to r.t., water was added and the mixture carefully extracted with Et_2O and CH_2Cl_2. The combined organic phases were dried and filtered and the solvent was removed. The residue was purified by column chromatography (silica gel, 220-440 mesh, CH_2Cl_2/MeOH 95:5) to give a brownish oil; yield: 6.1 g (72%).
^1H NMR ($CDCl_3$): δ = 8.73 (m, 1 H), 8.50–8.25 (m, 3 H), 7.80 (t, 1 H, ^3J = 7.9 Hz), 7.65 (dd, 1 H, ^3J = 7.7 Hz, ^4J = 1.6 Hz), 7.30 (m, 1 H), 2.4 (s, 3 H, $–CH_3$).
MS: calcd. for $C_{11}H_{10}N_2$ 170.21, found *m/z* 170 (M^+, 100%), 155 ($M^+–CH_3$, 8%).

2,2′-Bipyridine-5-carbaldehyde (6):[15]
[N-(5-methyl-2,2′-bipyridyl)]hexamethylenetetraammonium Bromide:
5-Bromomethyl-2,2′-bipyridine (4.24 g, 17 mmol) and methenamine (3.64 g, 26 mmol) were refluxed in anhyd CCl_4 for 5 h. The colorless precipitate was separated by filtration, washed with CCl_4 and dried in vacuo; yield: 5.5 g (83%).

2,2′-Bipyridine-5-carbaldehyde (**6**):
The intermediate methenammonium bromide was refluxed in 50% HOAc for 5 h. After cooling to r.t. and addition of water, the mixture was extracted with Et_2O. The organic phase was dried ($MgSO_4$), concentrated and the product recrystallized (water); yield: 1.3 g (50%).

Alternative: The oxidation of 5-methyl-2,2′-bipyridine with SeO_2 (stoichiometric or in excess) in constant boiling diglyme failed.
^1H NMR ($CDCl_3$): δ = 10.08 (s, 1 H, -CHO), 9.02 (dd, 1 H,^3J = 8.0 Hz, ^4J = 2.0 Hz), 8.65 (dm, 1 H, ^3J = 8.0 Hz), 8.52 (dd, 1 H, ^3J = 8.0 Hz, ^4J = 0.4 Hz), 8.42 (dt, 1 H, ^3J = 8.0 Hz, ^4J = 1.6 Hz), 8.19 (dd, 1 H, ^3J = 8.0 Hz, ^4J = 2.0 Hz), 7.78 (td, 1 H, ^3J = 8.0 Hz, ^4J = 1.6 Hz), 7.30 (dd, 1 H, ^3J = 8.0 Hz, ^4J = 1.6 Hz).
MS: calcd. for $C_{11}H_8N_2O$ 184.20, found *m/z* 184 (M^+, 100%).

5-Bromomethyl-2,2′-bipyridine (7):[31]
5-Methyl-2,2′-bipyridine (4.26 g, 25 mmol), NBS (4.89 g, 27.5 mmol) and catalytic amounts of AIBN were dissolved in CCl_4 and refluxed for 7 h under irradiation with a UV photolamp. The hot solution was filtered and the filtrate concentrated. The residue was dissolved in CH_2Cl_2 and extracted. The product was recrystallized (cyclohexane); yield: 2.68 g (43%); mp 70–72 °C.
^1H NMR ($CDCl_3$): δ = 8.7 (d, 2 H), 8.40 (d, 2 H), 7.85 (m, 2 H), 7.34 (m, 1 H), 4.52 (s, 2 H, $–CH_2Br$).
MS: calcd. for $C_{11}H_9N_2Br$ 249.13, found *m/z* 250 (M^+, 6%), 169 (100%).

5-(2,2-Dibromovinyl)-2,2′-bipyridine (8):
2,2′-Bipyridine-5-carbaldehyde (1.0 g, 5.4 mmol), CBr_4 (3.6 g, 11 mmol), PPh_3 (2.9 g, 11 mmol) and NEt_3 (0.8 mL, 5.5 mmol) were stirred under argon in CH_2Cl_2 for 20 min at –60°C. The temperature was allowed to rise to r.t., the product separated by filtration and dried in vacuo, and then recrystallized (EtOH); yield: 0.96 g (50%).
IR: ν = 1588 m, 1545 m, 1461 s, 1434 m, 1387 m, 1291 w, 1248 m, 1225 w, 1191 m, 1146 m, 1121 m, 1092 m, 1061 m, 1040 w, 1023 m, 994 m, 932 m, 878 s, 861 s, 841 w, 803 s, 787 s, 722 s, 697 s, 654 s, 606 w, 581 w, 538 cm^{-1} s.
^1H NMR ($CDCl_3$): δ = 8.80 (d, 1 H), 8.72 (d, 1 H), 8.44 (m, 1 H), 8.16 (m, 1 H), 7.90-7.45 (m, 2 H), 7.55 (s, 1 H, –CH=), 7.37 (m, 1 H).
MS: calcd. for $C_{12}H_8Br_2N_2$ 340,02, found *m/z* 339.92 (M^+, 100%).

5-Ethynyl-2,2′-bipyridine (9):
5-(2,2-Dibromovinyl)-2,2′-bipyridine (0.96 g, 2.8 mmol) was treated with 2.0 M BuLi in hexane (2.8 mL, 5.6 mmol) in anhyd THF under inert conditions for 2 h at –60°C. The mixture was quenched at r.t. with water and concentrated at a high vacuum pump. The residue was extracted with CH_2Cl_2, dried (Na_2SO_4) and again concentrated. The yellow-brownish raw-material was purified by column chromatography (silica gel, 220–440 mesh, 4 × 40 cm, petroleum ether) to give a product which solidified after several weeks; yield: 0.12 g (44%).
IR: ν = 3301 m, 3193 m, 2958 m, 2927 m, 2858 m, 2112 vw (C≡C), 1588 s, 1573 s, 1547 s, 1484 s, 1459 s, 1436 s, 1420 w, 1378 w, 1368 m, 1245 w, 1023 m, 859 m, 814 s, 797 m, 760 s, 714 s, 677 m, 650 m, 619 m, 523 cm^{-1} s.
^1H NMR ($CDCl_3$): δ = 8.78 (d, 1 H), 8.70 (d, 1 H), 8.40 (m, 2 H), 7.88 (m, 2 H), 7.34 (m, 1 H), 3.31 (s, 1 H, C≡C–H).
MS: calcd. for $C_{12}H_8N_2$ 180.21, found *m/z* 180.07 (M^+, 100%).

4-(2,2-Dibromovinyl)-4′-methyl-2,2′-bipyridine (10):
4-Methyl-2,2′-bipyridylene-4′-carbaldehyde (1.68g, 8.5 mmol) was treated under argon with CBr_4 (5.62 g, 17 mmol), PPh_3 (4.45 g, 17 mmol), and NEt_3 (1.2 mL) in CH_2Cl_2 for 20 min at –60 °C. The temperature was then allowed to rise to r.t. and the product separated by filtration. Recrystallization (petroleum ether) gave the product; yield: 0.78 g (26%).
MS: calcd. for $C_{13}H_{10}Br_2N_2$ 354.04, found *m/z* 354 (M^+, 56%).

4-Bromo-2,2′-bipyridine:[27]

4-Nitro-2,2′-bipyridyl 1-Oxide:

2,2′-Bipyridine (15.6 g, 0.1 mol) was oxidized in a mixture of 30% H_2O_2 (75 mL) and HOAc (75 mL) by stirring at 60 °C for 12 h. After the distillation of volatile compounds on a high vacuum pump, the system was cooled to –4 °C and the residue cautiously dissolved in concd H_2SO_4 (40 mL) and nitrated by means of fuming HNO_3/concd H_2SO_4 (60 mL/40 mL). The product was isolated after 3 h at 100 °C by precipitation from the neutralized solution (using NaOH pellets) and recrystallization (EtOH); yield: 6.1 g (28%).

IR: ν = 3051 w, 1924 w, 1590 m, 1576 s, 1565 s, 1546 s, 1532 s, 1482 m, 1453 s, 1385 s, 1356 s, 1314 m, 1279 s, 1268 m, 1248 m, 1227 m, 1152 m, 1115 m, 1081 m, 1067 s, 996 s, 884 m, 832 s, 741 s, 726 s, 689 vs, 660 m, 617 s, 587 cm^{-1} s.

MS: calcd. for $C_{10}H_7N_3O_3$ 217.18, found *m/z* 217 ($M^{+\cdot}$ 22%),

4-Bromo-2,2′-bipyridine:

4-Nitro-2,2′-bipyridyl 1-oxide (2.17 g, 10 mmol) was treated under reflux with AcBr (40 mL) and PBr_3 (10 mL) for 2 h. Neutralization (using NaOH pellets) and extraction with CH_2Cl_2 gave the crude product. The product was isolated after recrystallization (EtOH) as a white solid; yield: 0.84 g (36%).

MS: calcd. for $C_{10}H_7BrN_2$ 235.08, found *m/z* 236, 234 (M^+, 100%).

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[a] Present Address: KLEMA Dentalprodukte GmbH, Koblacherstr. 3a, A-6812 Meiningen, Austria

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