Synthesis of Bis(BINOL) Substituted 2,2′-Bipyridines and their Late Transition Metal Complexes

Arne Lützen,* Marko Hapke, Sven Meyer

University of Oldenburg, Department of Chemistry, P. O. Box 2503, 26111 Oldenburg, Germany
E-mail: arne.luetzen@uni-oldenburg.de

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Abstract: Bis(BINOL) substituted 2,2′-bipyridines (**1a** and **1b**) have been prepared via a twofold Sonogashira cross-coupling reaction from 3-iodo-2,2′-di(methoxymethoxy)-1,1′-binaphthyl (**4**) and 5,5′-diethynyl-2,2′-bipyridine (**2**), which could be synthesised through a palladium mediated homodimerisation using zinc powder as a reducing agent. **1a** and **1b** form well defined silver(I), copper(I) or zinc(II) complexes $[M\mathbf{1}_2]^+$ and $[Zn\mathbf{1a}_2]^{2+}$ thereby orienting the BINOL groups in a fashion potentially useful for molecular recognition of chiral substrates.

Key words: cross-coupling reactions, palladium, ligands, complexes, supramolecular chemistry

2,2′-Dihydroxy-1,1′-binaphthyl (BINOL) and its derivatives certainly belong to the most important components of catalysts that are routinely used in asymmetric synthesis[1] and they have also been used very successfully in the recognition of chiral substrates both in solid phase and solution phase supramolecular chemistry.[2,3] This outstanding performance in not only asymmetric catalysis but also as receptors could often even be increased through the use of compounds containing multiple BINOL units.[4] Recently, we were able to synthesise an example where four BINOL units are covalently linked to a central spirobifluorene.[5] However, the synthesis and isolation of this compound as of some others of these oligo(BINOL) compounds proved to be quite tedious although convergent strategies have been used. Therefore, we were looking for an alternative way to build up such an oligo(BINOL) and we decided to make use of self-assembly processes of metal complexes[6] to build up self-assembled analogues.

Herein, we would like to report on our design and synthesis concept based on a homofunctionalised central 2,2′-bipyridine as the central ligand unit for co-ordinating to an appropriate transition metal ion which is linked to two BINOLs via ethynyl bridges (Figure 1).[7]

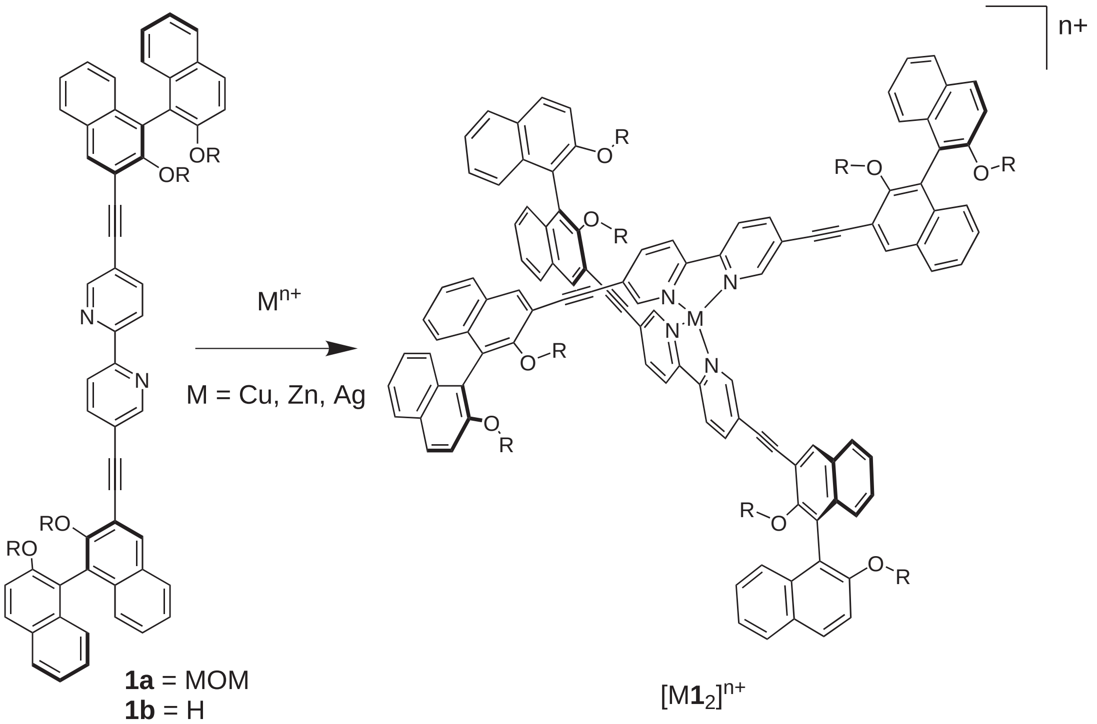

Figure 1 Bis(BINOL) substituted 2,2′-bipyridine (**1**) and its dimeric metal complex.

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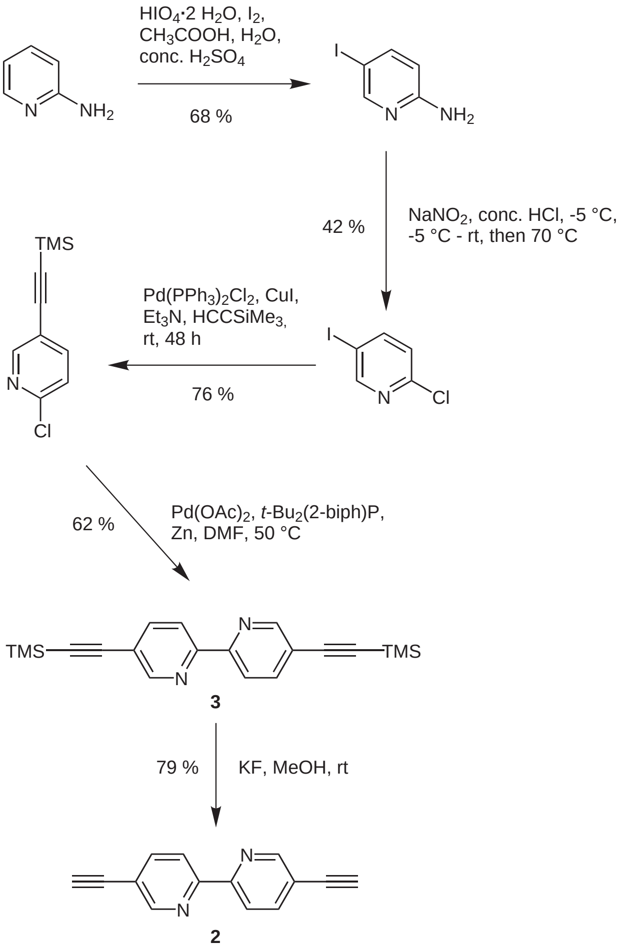
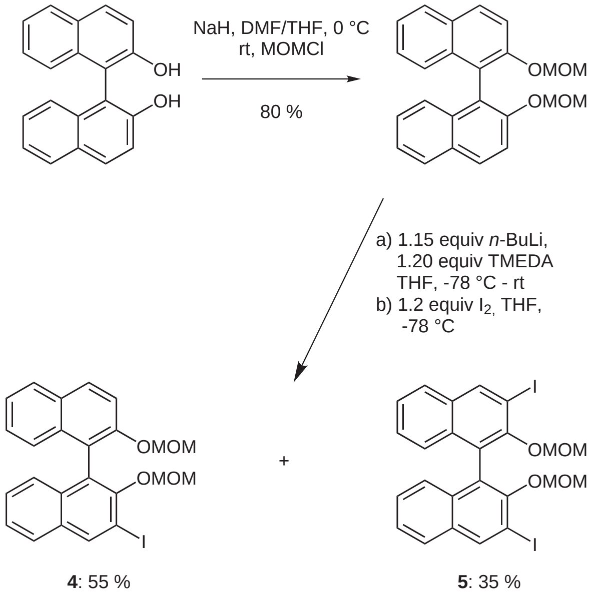
The central 5,5′-diethynyl-2,2′-bipyridine (**2**) core has already been prepared earlier by Ziessel and co-workers.[8] However, the initial bromination of 2,2′-bipyridine to the mono- and the dibrominated product needs relatively harsh conditions and some further problems with this procedure have been reported.[9,10] As an alternative to this direct functionalisation of 2,2′-bipyridines cross- and homocoupling reactions have been employed. Only recently, e.g., Michl et al. described a synthesis of the dibrominated compound based on a Stille reaction.[10] During our efforts in developing a new approach to monofunctionalised 5-substituted 2,2′-bipyridines through a modified Negishi cross-coupling reaction[11] we thought to use a palladium mediated reaction also for the homodimerisation of 2-chloropyridines with zinc powder as a reducing agent. Hence, 5,5′-bis[(trimethylsilyl)ethynyl]-2,2′-bipyridine (**3**) was prepared in a four step synthesis starting from commercially available 2-aminopyridine (Scheme 1). The first steps were conducted following published procedures. Initial electrophilic iodination[12] and subsequent Sandmeyer analogous reaction[13] was followed by a first palladium catalysed Sonogashira coupling with trimethylsilylacetylene to give 2-chloro-5-[(trimethylsilyl)ethynyl]-pyridine[14] in an overall yield of 22%. The homodimerisation of this compound in a one-pot-synthesis could be accomplished using palladium(II) acetate, Buchwald's ligand 2-(di-*tert*-butylphosphanyl)biphenyl [*t*-Bu$_2$(2-biph)P],[15] and zinc powder in DMF at 50-60 °C.[16] The product **3** could be isolated in 62% yield. Finally, pure **2** was obtained after complete desilylation with potassium fluoride in methanol in 79% yield.[8]

It should be noted that the often used nickel mediated homodimerisation procedures[17]could not be used in this case because the ethynyl groups were not tolerated by this metal under our conditions. Although there are existing procedures using palladium as a catalyst and an electrochemical or chemical method of reduction[17a,18] our approach seems to be an efficient and mild method for performing homocoupling reactions. Thus, further studies concerning the scope and limitations of this catalytic system are currently underway.

Enantiopure (*S$_a$*)- and (*R$_a$*)-3-iodo-2,2′-di(methoxymethoxy)-1,1′-binaphthyl (**4**) were prepared in two steps from enantiopure BINOL as shown in Scheme 2.[5,19,20] After standard methoxymethyl ether protection of the hydroxyl functions in 80% yield, *ortho*-lithiation facilitated by the protecting groups followed by quenching with iodine furnished the desired monoiodinated BINOL **4** together with diiodinated BINOL derivative **5** which could be separated by column chromatography on silica gel. It should be mentioned that we were able to shift the ratio of the products in favour of the monoiodinated compound compared to our earlier results through the addition of *N*,*N*,*N*′,*N*′-tetramethylethylendiamine (TMEDA), however, **5** is also a versatile building block for the synthesis of interesting BINOL-derivatives.[5,21]

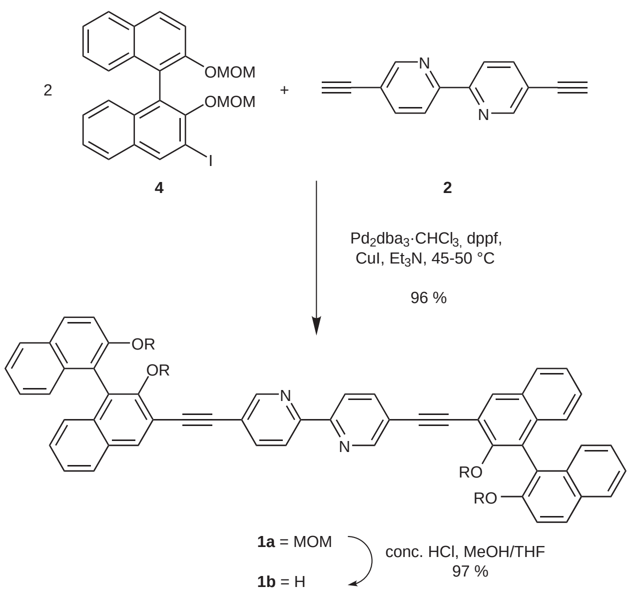


Scheme 1



Scheme 2

Finally, twofold Sonogashira cross-coupling reaction of **2** and **4** using tris(dibenzylideneacetone)dipalladium(0) ($Pd_2dba_3{\cdot}CHCl_3$),[22] 1,1′-bis(diphenylphosphanyl)-ferrocene (dppf),[23] and copper(I) iodide as catalytic system gave tetra-MOM protected bis(BINOL) substituted 2,2′-bipyridine **1a** in excellent yield of 96% and the corresponding tetrol **1b** was obtained in almost quantitative yield after acidic hydrolysis as depicted in Scheme 3.



Scheme 3

Addition of previously prepared or commercially available $Zn(BF_4)_2{\cdot}6{-}7\ H_2O$, $Zn(ClO_4)_2{\cdot}6\ H_2O$, $AgClO_4$, $[Ag(CH_3CN)_2]BF_4$, or $[Cu(CH_3CN)_4]BF_4$ to solutions of (*all*-S_a)-**1a** or (*all*-R_a)-**1a** in dichloromethane–acetonitrile resulted in instant colour changes to intensive red-brown in case of the copper(I) salt and intensive yellow in case of the silver(I) and zinc(II) salt, indicating the formation of metal complexes.

This was confirmed by NMR experiments of solutions in deuterated solvents where significant shifts in the ^1H and ^{13}C NMR spectra were observed (Figure 2). Copper(I) complexes show essentially the same spectroscopic behaviour as the silver(I) complexes.

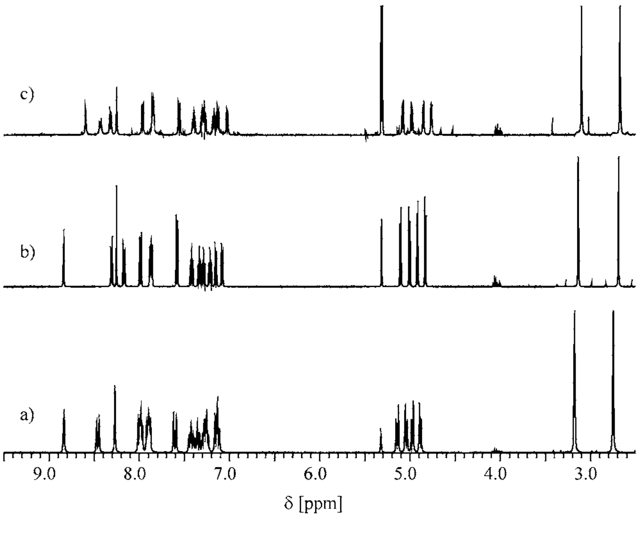


Figure 2 ^1H NMR spectra (500.1 MHz, $[\mathbf{1a}]_0 = 8{-}11\ mmolL^{-1}$ in $CD_2Cl_2{-}CD_3CN$ at 300 K) (a) (*all*-S_a)-**1a** (b) (*all*-S_a)-**1a** + 0.5 equiv $[Ag(CH_3CN)_4]BF_4$ (c) (*all*-S_a)-**1a** + 0.5 equiv $Zn(ClO_4)_2{\cdot}6\ H_2O$.

These complexes could also be characterised by ESI-MS where we only found signals with the expected isotope patterns arising from the desired complexes and their frag-

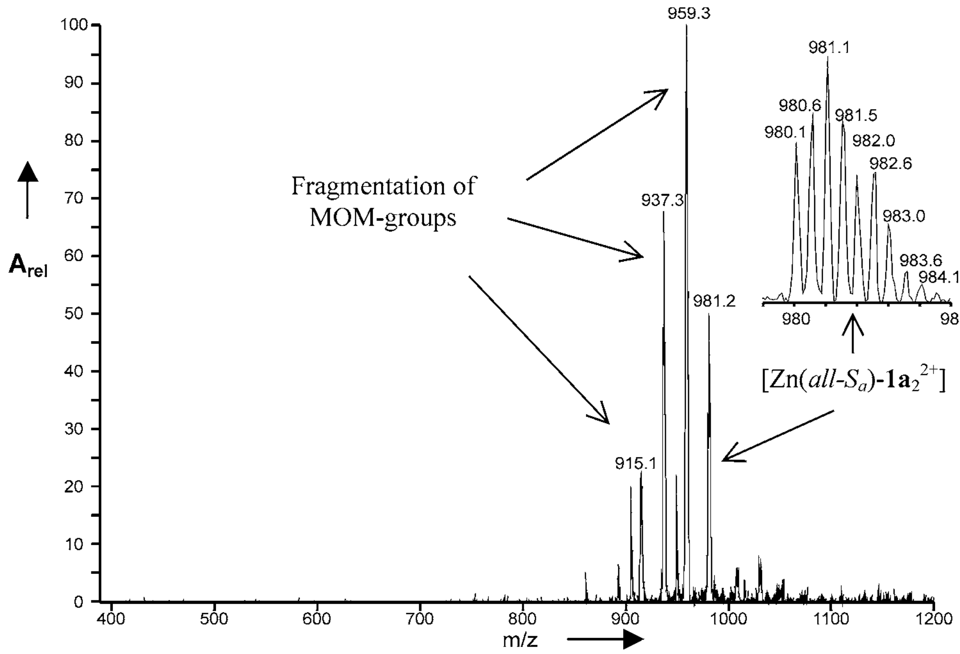


Figure 3 Positive ESI-MS of a $5 \times 10^{-4}\ mol\ L^{-1}$ soln of $[Zn(\textit{all-}S_a)\text{-}\mathbf{1a}_2](BF_4)_2$ complex in $CH_2Cl_2{-}CH_3CN$.

mentation products, respectively, as shown for the zinc complex in Figure 3.

We were also able to prepare metal complexes with the deprotected ligand **1b**. The formation of coloured metal complexes could again be observed by significant shifts in the ^{1}H and the ^{13}C NMR spectra as well as by ESI-MS.

The zinc(II) metal ions showed an interesting behaviour. Whereas zinc(II) ions and **1a** form exclusively well defined [Zn**1a**$_2$]$^{2+}$complexes, a different behaviour was found for ligand **1b**. When we mixed zinc(II) ions and **1b** in a 1:2 ratio we observed the formation of two different metal complexes, most probably a mixture of a [Zn**1b**$_2$]$^{2+}$ and a [Zn**1b**$_3$]$^{2+}$ complex, as indicated by respective signals in the ESI-MS. The latter coordination complex seems now possible because of less steric repulsion due to the lack of the MOM groups compared to **1a**. However, most of the ^{1}H NMR signals were very broad when we recorded spectra at room temperature indicating that these complexes are in a fast equilibrium. This could, however, be considerably slowed down by lowering the temperature to 0 °C where sharp signals were observed. Both species, although in slightly different ratio, were still present in a mixture together with free ligand when we increased the amount of **1b** to a sixfold excess. Although this is a very nice example for the tremendous effects of small structural changes on self-assembly processes in supramolecular chemistry we did not investigate this phenomenon any further because a fast equilibrating system like this would not be effective or at least very difficult to rationalise in the sense of an application of these complexes in catalysis or molecular recognition.

However, silver(I) and copper(I) ions again formed well defined [M**1b**$_2$]$^{+}$ complexes (Figures 4 and 5) which may be suitable compounds for recognition studies on chiral substrates.

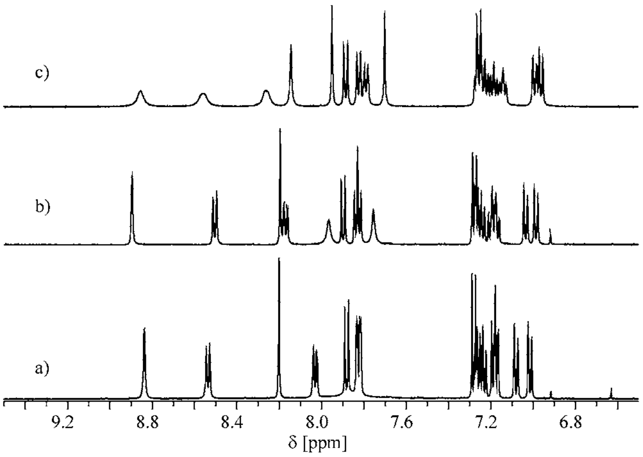


Figure 4 ^{1}H NMR spectra (500.1 MHz, [**1b**]$_0$ = ca. 10 mmolL^{-1} in THF-d_8–CD$_3$CN at 300 K) (a) (*all*-S_a)-**1b** (b) (*all*-S_a)-**1b** + 0.5 equiv [Ag(CH$_3$CN)$_2$]BF$_4$ (c) (*all*-S_a)-**1b** + 0.5 equiv [Cu(CH$_3$CN)$_4$]BF$_4$.

In conclusion, we have presented the synthesis and self-assembly behaviour of bis(BINOL) substituted 2,2′-bipyridines **1**. These form well defined dimeric complexes upon coordination to silver(I) or copper(I) ions. This is also true for the zinc(II) complex of the fully MOM-protected ligand **1a**. Unprotected tetrol **1b** was found to behave differently when coordinated to zinc(II) ions because in this case a fast equilibrium of dimeric and trimeric [Zn**1b**$_2$]$^{2+}$ and [Zn**1b**$_3$]$^{2+}$ complexes was observed. The dimeric complexes give rise to supramolecular structures that closely reassemble a covalently linked tetra(BINOL) substituted spirobifluorene derivative. We are currently

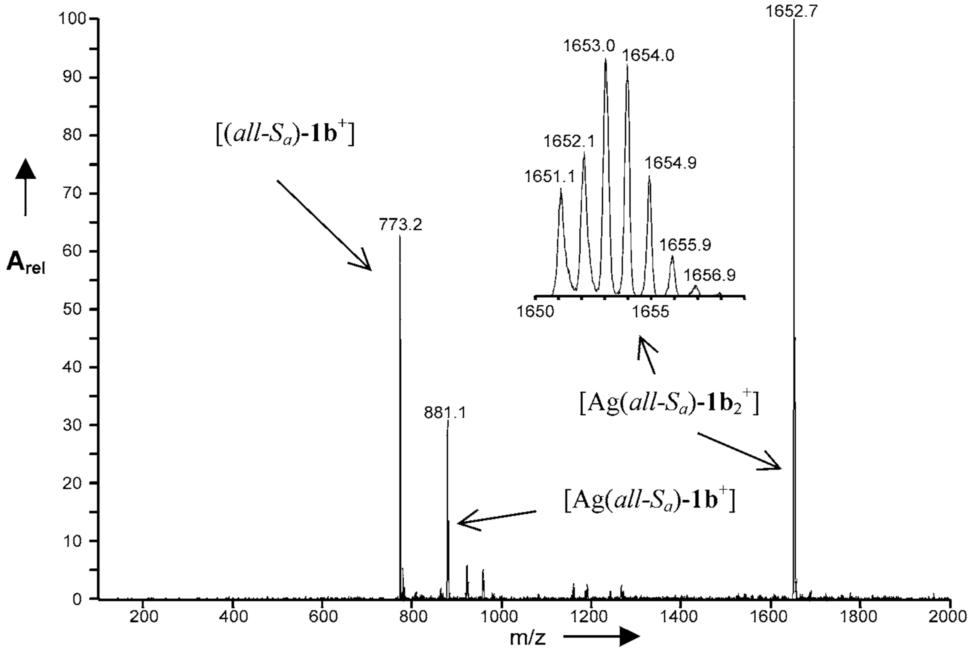


Figure 5 Positive ESI-MS of a ca. 5 × 10^{-4} mol L^{-1} soln of [Ag(*all*-S_a)-**1b**$_2$]BF$_4$ complex in CH$_2$Cl$_2$–CH$_3$CN.

investigating the recognition behaviour of both species in the binding of chiral substrates like monosaccharides.

2-Aminopyridine was purchased from Sigma-Aldrich Chemie GmbH and used as received. Trimethylsilylacetylene was a generous gift from Wacker-Chemie GmbH. THF was dried over and distilled from sodium benzophenone ketyl. DMF and Et_3N were dried over calcium hydride. Tris(dibenzylideneacetone)dipalladium(0) ($Pd_2dba_3\cdot CHCl_3$),[21] 1,1′-bis(diphenylphosphanyl)-ferrocene (dppf),[22] and *t*-Bu_2(2-biph)P[15] were prepared following published procedures. *n*-BuLi solutions were purchased from Merck and were titrated prior to use against *N*-pivaloyl-*o*-toluidine.[24] Sensitive reactions were performed under an argon atmosphere in oven-dried glassware using standard Schlenk techniques.

Thin-layer chromatography was performed on aluminum TLC-layers Silica gel 60 F_{254} from Merck. Detection was done by UV-light (254 and 366 nm). Products were purified by column chromatography on silica gel (0.063–0.2 or 0.004–0.063 mm) from Merck. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 spectrometer at 500.1 and 125.8 MHz, respectively. ^1H NMR chemical shifts are reported on the δ-scale (ppm) relative to residual nondeuterated solvent as internal standard. ^{13}C NMR chemical shifts are reported on the δ-scale relative to deuterated solvent as internal standard. Signals were assigned on the basis of ^1H, ^{13}C, H,H-COSY, HMQC, and (in some cases) HMBC NMR experiments. Mass spectra were taken on a Finnegan-MAT 212 instrument with data system MMS and processing system ISIS or on a Finnigan MAT 95 with data system DEC-Station 5000 in CI mode with *i*-butane as reactant gas. ESI-MS measurements were conducted with a Thermoquest Finnigan LCQ with processing software Xcalibur. Melting points were measured with a hot-stage microscope SM-Lux from Leitz and are not corrected. Elemental analyses were carried out with a EA 1108 Fisons Instruments. Specific optical rotations were measured on a Perkin Elmer Polarimeter 343 in a 10 cm cuvette**.** Petroleum ether (PE) used had a bp range of 40−60 °C. All washing and extraction steps were performed according to standard procedures.[25]

5,5′-Bis[(trimethylsilyl)ethynyl]-2,2′-bipyridine (3)[8]

In a Schlenk flask $Pd(OAc)_2$ (81 mg, 0.36 mmol), *t*-Bu_2(2-biph)P (215 mg, 0.72 mmol), 2-chloro-5-[(trimethylsilyl)ethynyl]-pyridine (1.5 g, 7.2 mmol), and zinc powder (804 mg, 12.3 mmol) were twice evacuated and flushed with argon. Anhyd DMF (20 mL) was added and the mixture heated to 50–55 °C. After TLC indicated the complete consumption of 2-chloro-5-[(trimethylsilyl)ethynyl]-pyridine, the mixture was cooled to r.t. A suspension of EDTA (10 g, 34 mmol) in H_2O (100 mL) was added and the mixture stirred for 15–30 min. Neutralisation with sat. aq Na_2CO_3 soln to pH 8–9 was followed by extraction with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and the solvent removed in vacuo. The residue was subjected to column chromatography on silica using PE−EtOAc−Et_3N (75:25:0.5) as eluent. The product was dried in high vacuum and used for the desilylation procedure.

Slightly brownish-yellow solid; yield: 780 mg (62%).

^1H NMR and ^{13}C NMR spectroscopical data recorded in $CDCl_3$ were in agreement with the ones reported by Ziessel.[8]

5,5′-Diethynyl-2,2′-bipyridine (2)[8]

Compound **3** (740 mg, 2.12 mg) and potassium fluoride (738 mg, 12.7 mmol) were dissolved in MeOH (200 mL) and stirred for 15 h according to the procedure published by Ziessel et al.[8] The solvent was evaporated and the residue subjected to column chromatography on silica using PE–EtOAc–Et_3N (75:25:0.5) as eluent.

Reddish solid; yield: 342 mg (79%); mp 130 °C (decomp.) (Lit.[8] 130 °C).

^1H NMR and ^{13}C NMR spectroscopic data recorded in $CDCl_3$ were in agreement with the ones reported by Ziessel.[8]

3-Iodo-2,2′-di(methoxymethoxy)-1,1′-binaphthyl (4)[5]

A soln of 2,2′-di(methoxymethoxy)-1,1′-binaphthyl (1 g, 2.67 mmol) in anhyd THF (10 mL) was cooled to -78 °C, treated with TMEDA (0.48 mL, 3.21 mmol) and subsequently with *n*-BuLi (2.2 mL of a 1.38 $molL^{-1}$ soln in hexane, 3.02 mmol). The soln was allowed to warm up to 0 °C and stirred at that temperature for 30 min. After cooling to –78 °C again iodine (805 mg, 3.18 mmol) dissolved in anhyd THF (10 mL) was added dropwise. After stirring for another 30 min the mixture was allowed to warm up to r.t., quenched with 10% aq sodium dithionite soln (20 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with H_2O and brine and dried over Na_2SO_4. After removing the solvents the residue was subjected to column chromatography on silica gel using PE–EtOAc (5:1 containing 0.5% of Et_3N) as eluent to give the desired product together with the diiodinated BINOL **5**.

White solid; yield: 700 mg (52%) together with 580 mg (32%) 3,3′-diiodo-2,2′-di(methoxymethoxy)-1,1′-binaphthyl; mp 114 °C.

(*R*$_a$)-4

$[\alpha]_D^{20}$ +99.5 (*c* = 0.99, THF).

(*S*$_a$)-4

$[\alpha]_D^{20}$ –100.1 (*c* = 0.99, THF).

^1H NMR and ^{13}C NMR spectroscopical data recorded in $CDCl_3$ have been previously reported.[5,21b]

(*all-S*$_a$)-5,5′-Di[2,2′-di(methoxymethoxy)-3-ethyndiyl-1,1′-binaphthyl]-2,2′-bipyridine (1a)

(*S*$_a$)-3-Iodo-2,2′-di(methoxymethoxy)-1,1′-binaphthyl (**4**) (541 mg, 1.08 mmol), 5,5′-diethynyl-2,2′-bipyridine (**2**) (96 mg, 0.47 mmol), $Pd_2dba_3\cdot CHCl_3$ (7.4 mg, 3 mol% Pd), dppf (7.9 mg, 3 mol%), and copper(I) iodide (5.4 mg, 6 mol%) were evacuated and flushed with argon two times in a Schlenk flask. Anhyd Et_3N (35 mL) was added and the mixture heated to 45–50 °C. After some time a bright beige precipitate formed and after 24 h the reaction was completed. After cooling to r.t., the mixture was diluted with brine (10 mL) and CH_2Cl_2 (40 mL). After stirring for a short period of time the solids were removed by filtration over celite. The precipitate was washed with CH_2Cl_2. The filtrate was extracted several times with CH_2Cl_2 and the combined organic layers were washed with sat. aq $NaHCO_3$ soln and dried over Na_2SO_4. Evaporation of the solvents and twofold column chromatography on silica using PE–EtOAc (2:1 containing 5% Et_3N) as eluent gave the pure product.

Yellow solid; yield 430 mg (96%); mp 210–212 °C.

(*all-S*$_a$)-1a

$[\alpha]_D^{20}$ –204.5 (*c* = 1.0, THF).

(*all-R*$_a$)-1a

$[\alpha]_D^{20}$ +191.4 (*c* = 0.93, THF).

^1H NMR (CD_2Cl_2–CD_3CN 6:1): δ = 2.79 (s, 6 H), 3.23 (s, 6 H), 4.93 (d, 2 H, *J* = –5.8 Hz), 5.02 (d, 2 H, *J* = –5.8 Hz), 5.09 (d, 2 H, *J* = –6.9 Hz), 5.19 (d, 2 H, *J* = –6.9 Hz), 7.15–7.21 (m, 4 H), 7.29-7.35 (m, 4 H), 7.41 (ddd, 2 H, *J* = 7.3, 7.3, 0.9 Hz), 7.48 (ddd, 2 H, *J* = 7.3, 7.3, 0.9 Hz), 7.65 (d, 2 H, *J* = 9.2 Hz), 7.92–7.98 (m, 4 H), 8.03 (dd, 2 H, *J* = 8.3, 2.2 Hz), 8.05 (d, 2 H, *J* = 9.2 Hz), 8.32 (s, 2 H), 8.51 (d, 2 H, *J* = 8.3 Hz), 8.89 (d, 2 H, *J* = 2.2 Hz).

^{13}C NMR (CD_2Cl_2–CD_3CN, 6:1): δ = 55.7, 56.2, 90.2, 91.0, 95.0, 98.9, 116.3, 116.9, 119.6, 120.4, 120.5, 124.1, 125.2, 125.6, 125.8, 126.4, 126.5, 127.4, 127.9, 127.9, 129.6, 129.9, 130.4, 133.8, 134.0, 134.1, 139.2, 151.6, 152.5, 153.0, 154.2.

ESI-MS: *m*/*z* (%) = 949.4 (100) (MH^+).

Anal. Calcd for $C_{62}H_{48}N_2O_8$·THF: C, 77.63; H, 5.53; N, 2.74. Found: C, 77.78; H, 5.59; N, 2.83.

(all-S_a)-5,5′-Di[3-ethyndiyl-2,2′-di(hydroxyl)-1,1′-binaphthyl]-2,2′-bipyridine (1b)

(*all*-S_a)-5,5′-Di(2,2′-di(methoxymethoxy)-3-ethyndiyl-1,1′-binaphthyl)-2,2′-bipyridine **1a** (100 mg, 0.105 mmol) was dissolved in a mixture of MeOH (50 mL) and THF (50 mL). Concd HCl (37%, 2 mL) was added and the reaction mixture stirred for 20 h. After that time a small amount of H_2O was added and the organic solvents were removed. The precipitate formed was filtered off, thoroughly washed with H_2O and small amounts of cold MeOH, and dried in high vacuum.

Intensive yellow solid; yield: 79 mg (97%); mp 208–210 °C.

(*all*-S_a)-1b
$[\alpha]_D^{20}$ –304.6 (*c* = 0.91, THF).

(*all*-R_a)-1b
$[\alpha]_D^{20}$ +310.7 (*c* = 0.85, THF).

^{1}H NMR (THF-d_8): δ = 7.02 (d, 2 H, *J* = 8.4 Hz), 7.08 (d, 2 H, *J* = 8.4 Hz), 7.16–7.20 (m, 4 H), 7.22–7.26 (m, 2 H), 7.26–7.28 (m, 2 H), 7.28 (d, 2 H, *J* = 8.8 Hz), 7.83 (dd, 4 H, *J* = 2.6, 8.1 Hz), 7.88 (d, 2 H, *J* = 8.8 Hz), 8.03 (dd, 2 H, *J* = 8.1, 1.8 Hz), 8.20 (s, 2 H), 8.54 (d, 2 H, *J* = 8.1 Hz), 8.84 (d, 2 H, *J* = 1.8 Hz). Resonances of the free OH protons could only be observed as a broad H_2O peak.

^{13}C NMR (THF-d_8): δ = 91.0, 92.0, 114.0, 114.0, 116.0, 119.6, 121.2, 122.0, 123.6, 124.3, 125.3, 125.6, 127.1, 128.7, 128.7, 129.6, 130.1, 130.8, 134.6, 135.5, 135.8, 139.9, 152.4, 154.1, 154.9, 155.0.

ESI-MS: *m*/*z* (%) = 773.3 (100) (MH^+).

Anal. Calcd for $C_{54}H_{32}N_2O_4$·2 MeOH: C, 80.37; H, 4.82; N, 3.35. Found: C, 80.45; H, 4.88; N, 3.44.

Silver(I) Complex of 1a [Ag1a$_2$]BF$_4$

A soln of **1a** (15.0 mg, 15.8 μmol) in 0.6 mL THF-d_8 was added to a soln of $Ag(CH_3CN)_2BF_4$ (2.2 mg, 7.9 μmol) in 0.1 mL CD_3CN. The resulting yellow soln was subjected to NMR analysis. The complex could be isolated as solid by removing of the solvents and washing with MeOH.

Solid; yield 16.5 mg (quant.); mp >210 °C (dec.).

(*all*-S_a)-1a
$[\alpha]_D^{20}$ –401.6 (*c* = 0.5, THF−CH_3CN, 9:1).

(*all*-R_a)-1a
$[\alpha]_D^{20}$ +390.0 (*c* = 0.50, THF−CH_3CN, 9:1).

^{1}H NMR (CD_2Cl_2−CD_3CN, 6:1): δ = 2.69 (s, 12 H), 3.14 (s, 12 H), 4.84 (d, 4 H, *J* = –5.7 Hz), 4.92 (d, 4 H, *J* = –5.7 Hz), 5.01 (d, 4 H, *J* = –7.0 Hz), 5.11 (d, 4 H, *J* = –7.0 Hz), 7.09 (d, 4 H, *J* = 8.2 Hz), 7.16 (d, 4 H, *J* = 8.5 Hz), 7.22 (ddd, 8 H, *J* = 8.2, 6.7, 1.2 Hz), 7.34 (ddd, 4 H, *J* = 8.2, 6.7, 1.2 Hz), 7.43 (ddd, 4 H, *J* = 8.2, 6.7, 1.2 Hz), 7.59 (d, 4 H, *J* = 9.1 Hz), 7.87 (d, 4 H, *J* = 8.2 Hz), 7.88 (d, 4 H, *J* = 8.2 Hz), 7.99 (d, 4 H, *J* = 9.1 Hz), 8.18 (dd, 4 H, *J* = 8.2, 2.1 Hz), 8.26 (s, 4 H), 8.31 (d, 4 H, *J* = 8.2 Hz), 8.84 (d, 4 H, *J* = 2.1 Hz).

^{13}C NMR (CD_2Cl_2−CD_3CN, 6:1): δ = 56.0, 56.5, 88.8, 93.6, 95.2, 99.3, 116.5, 116.6, 119.6, 122.6, 122.8, 124.3, 125.3, 126.1, 126.1, 126.8, 126.8, 128.1, 128.2, 129.9, 130.3, 130.6, 134.0, 134.5, 134.8, 141.3, 150.1, 152.6, 153.1, 153.2.

ESI-MS: *m*/*z* (%) = 2004.5 (100) [Ag**1a**$_2$]$^+$, 951.4 (54) [**1a**+H]$^+$.

Anal. Calcd for perchlorate $C_{124}H_{96}AgClN_4O_{20}$·$CH_2Cl_2$·$CH_3OH$: C, 68.10; H, 4.63; N, 2.52. Found: C, 68.30; H, 4.67; N, 2.97.

Zinc(II) Complex of 1a [Zn1a$_2$(ClO$_4$)$_2$]

The zinc(II) complex was prepared following the same procedure as described for [Ag**1a**$_2$]BF$_4$.

Solid; mp >180 °C (dec.).

(*all*-R_a)-1a
$[\alpha]_D^{20}$ +426.4 (*c* = 0.31, THF−CH_3CN, 9:1).

(*all*-S_a)-1a
$[\alpha]_D^{20}$ –418.2 (*c* = 0.30, THF−CH_3CN, 9:1).

^{1}H NMR (CD_2Cl_2−CD_3CN, 6:1): δ = 2.68 (s, 12 H), 3.11 (s, 12 H), 4.77 (d, 4 H, *J* = –4.9 Hz), 4.86 (d, 4 H, *J* = –4.9 Hz), 4.99 (d, 4 H, *J* = –6.9 Hz), 5.09 (d, 4 H, *J* = –6.9 Hz), 7.05 (d, 4 H, *J* = 8.6 Hz), 7.16 (d, 4 H, *J* = 8.2 Hz), 7.18–7.21 (m, 4 H), 7.28–7.32 (m, 4 H), 7.29–7.34 (m, 4 H), 7.39–7.43 (m, 4 H), 7.57 (d, 4 H, *J* = 9.2 Hz), 7.84–7.88 (m, 8 H), 7.98 (d, 4 H, *J* = 9.2 Hz), 8.26 (s, 4 H), 8.31–8.35 (m, 4 H), 8.40-8.46 (m, 4 H), 8.59-8.65 (m, 4 H).

^{13}C NMR (CD_2Cl_2−CD_3CN, 6:1): δ = 55.9, 56.5, 88.1, 95.2, 95.3, 99.3, 116.1, 116.5, 119.4, 123.2, 124.3, 124.4, 125.3, 126.0, 126.1, 126.8, 126.8, 128.2, 128.2, 128.3, 129.8, 130.3, 130.6, 133.9, 134.6, 135.0, 143.7, 147.1, 150.6, 152.6, 153.2.

ESI-MS: *m*/*z* (%) = 981.1 (49) [Zn**1a**$_2$]$^{2+}$, 959.3 (100) [Zn**1a**$_2$]$^{2+}$ − C_2H_5O, 936.7 (79) [Zn**1a**$_2$]$^{2+}$ − 2 C_2H_5O.

Anal. Calcd for the perchlorate $C_{124}H_{96}Cl_2N_4O_{24}Zn$·3 H_2O: C, 67.19; H, 4.64; N, 2.53. Found: C, 67.21; H, 4.64; N, 2.44.

Silver(I) Complex of 1b [Ag1b$_2$]BF$_4$

The silver(I) complex was prepared following the same procedure as described for [Ag**1a**$_2$]BF$_4$.

Solid, mp >200 °C (dec.).

(*all*-S_a)-1b
$[\alpha]_D^{20}$ –523.8 (*c* = 0.515, THF−CH_3CN, 9:1).

(*all*-R_a)-1b
$[\alpha]_D^{20}$ +534.4 (*c* = 0.605, THF−CH_3CN, 9:1).

^{1}H NMR (THF-d_8−CD_3CN, 7:1): δ = 6.99 (d, 4 H, *J* = 8.6 Hz), 7.03 (d, 4 H, *J* = 8.5 Hz), 7.16–7.21 (m, 8 H), 7.23–7.28 (m, 8 H), 7.28 (d, 4 H, *J* = 8.9 Hz), 7.75 (br s, 4 H), 7.81–7.85 (m, 8 H), 7.90 (d, 4 H *J* = 8.9 Hz), 7.97 (br s, 4 H), 8.17 (dd, 4 H, *J* = 8.6, 1.8 Hz), 8.20 (s, 4 H), 8.50 (d, 4 H, *J* = 8.6 Hz), 8.90 (d, 4 H, *J* = 1.8 Hz).

^{13}C NMR (THF-d_8−CD_3CN, 7:1): δ = 90.3, 93.1, 113.5, 113.8, 116.3, 119.5, 122.5, 122.9, 123.7, 124.5, 125.1, 125.6, 127.2, 128.3, 128.8, 128.9, 129.5, 130.1, 131.0, 134.8, 135.4, 135.8, 141.1, 152.6, 153.2, 153.7, 154.9.

ESI-MS: *m*/*z* (%) = 1653.0 (100) [Ag**1b**$_2$]$^+$, 881.0 (30) [Ag**1b**]$^+$, 773.2 (63) (**1b**H$^+$).

Anal. Calcd for the perchlorate $C_{108}H_{64}AgClN_4O_{12}$·3$CH_3OH$: C, 72.10; H, 4.14; N, 3.03. Found: C, 71.70; H, 3.84; N, 2.90.

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