

CHIRAL BINAPHTHALENES BEARING TWO PYRIDINE LIGANDS ATTACHED VIA ACETYLENE SPACERS. SYNTHESIS AND COORDINATION STUDY

Peter KASÁK^{a,b}, Henrich BRATH^{a1}, Katarína KRASCENICSOVÁ-POLÁKOVÁ^a, Anna KICKOVÁ^{a2}, Natalia MOLDOVAN^{a3} and Martin PUTALA^{a4,*}

^a Department of Organic Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovak Republic; e-mail: ¹ henrichbrath@hotmail.com, ² kickova@fns.uniba.sk, ³ moldovan@fns.uniba.sk, ⁴ putala@fns.uniba.sk

^b Polymer Institute of the Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovak Republic; e-mail: peter.kasak@savba.sk

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Dedicated to Professor Štefan Toma on the occasion of his 70th birthday.

An effective methodology has been developed for the synthesis of enantiopure 2,2'-dialkynylated 1,1'-binaphthalene derivatives. Enantiopure 2,2'-diiodo-1,1'-binaphthalene (**10**) provided 2,2'-diethynyl-1,1'-binaphthalene (**16**) in the Negishi alkynylation supported by microwave irradiation in a very good yield with conservation of stereochemical information. The Stephen–Castro alkynylation of **10** afforded products in lower yields; however, in stereoconservative manner as well. Terminal diacetylene **16** served as precursor in the Sonogashira cross-coupling reaction to give new bispyridine derivatives **7–9** as potential ligands in moderate to high yields. Coordination of bispyridines with Zn²⁺ and Ag⁺ ions was observed by NMR and CD spectroscopy. The coordination ability of bis(2-pyridylethynyl) derivative **7** to palladium cation was determined by X-ray structure analysis.

Keywords: Sonogashira reaction; Alkynylations; Bispyridines; Binaphthalenes; C₂-Symmetric ligands; Cross-coupling reactions; Palladium; Alkynes; Helicenes; Biaryls.

Axial chirality as a unique stereochemical property of axially chiral 1,1'-binaphthalene derivatives substituted at the position 2 and 2' plays a crucial role in their broad application in stereoselective synthesis¹, in materials science², in the separation and recognition of chiral compounds³. Substitution reactions, in particular cross-coupling reactions, at both positions 2 and 2' are critical for conservation of stereochemical information in the course of preparation of such derivatives^{4–7}. Specialty of the cross-coupling reactions (or any substitutions) at the positions 2 and 2' consist in substan-

tial steric hindrance (bulky 2-substituted 1-naphthyl group in the position adjacent to the reaction center) and the risk of racemization during the reaction, since these reactions take place in the positions where mutual nonbonding interactions between groups (replaced in the course of the reaction) is decisive for configurational stability of these derivatives⁵⁻⁷.

Bidendate nonracemic C_2 -symmetric ligands with N,N -donor atoms were used successfully in stereoselective synthesis and in supramolecular chemistry as ligands (for example oxazolines **1**⁸, sermicorrines **2**⁹, bisaziridines **3**¹⁰, bipyridines **4**¹¹, including binaphthalene based ligands **5** and **6** (Fig. 1)^{12,13}. Those based on 2,2'-diaryl-1,1'-binaphthalenes have strained chiral pocket¹³. Therefore it would be interesting to move far away donor groups from binaphthalene keeping stereochemical information via linking with rigid ethynediyl spacer **7-9**.

Racemic 2,2'-bis(arylethynyl)-1,1'-binaphthalenes were prepared by alkynylation with copper acetylide¹⁴ and in nonracemic form via a multi-step synthesis including build-up of the ethynyl group starting from 1,1'-binaphthalene-2,2'-dicarbaldehyde¹⁵ followed by attachment of aryl groups via the Sonogashira reaction.

We aimed to elaborate an effective approach to nonracemic bis(arylethynyl) derivatives **7-9** with potential application either in stereoselective synthesis (as new chiral ligands), supramolecular chemistry (as chiral building blocks), or in materials science (chiral compounds with specific optical or electronic properties). Being encouraged by the efficient Negishi 2,2'-dialkylation⁵ and diarylation^{6,16} of 2,2'-disubstituted 1,1'-binaphtha-

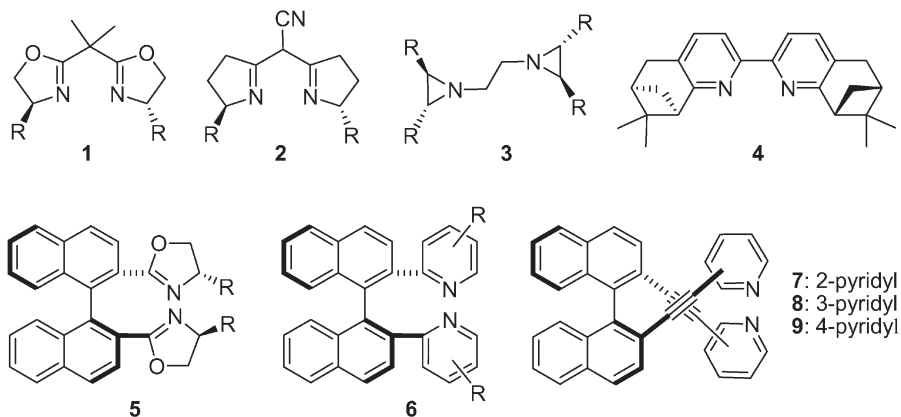


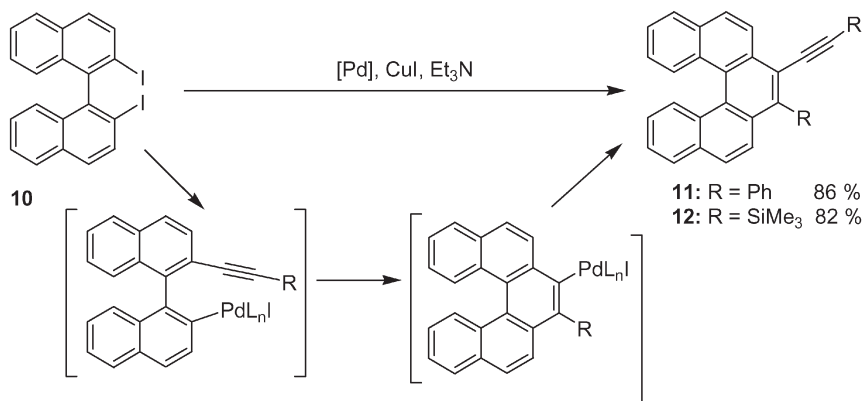
FIG. 1
Selected examples of bidendate N,N -coordinating C_2 -symmetric ligands

lenes, in particular diiodide **10**, we concentrated our effort on the use of cross-coupling reactions.

RESULTS AND DISCUSSION

Dialkynylation of 2,2'-Disubstituted 1,1'-Binaphthalenes

In agreement with the reported application of the Sonogashira reaction conditions in the reaction of racemic **10** with phenylacetylene in the presence of CuI and base, helical product **11** as an outcome of tandem reaction was formed in 86% yield¹⁴. This seems to be a general course of the reaction of diiodide **10** with terminal alkynes under the Sonogashira conditions since an analogous result was obtained also with (trimethylsilyl)ethyne; it afforded **12** in high 82% yield (Scheme 1).



SCHEME 1

Synthesis of **13** in racemic form was accomplished via the Stephen–Castro protocol in 31% yield¹⁴. Using enantiopure (*R*)-**10**, we found that this reaction proceeded stereoconservatively at 120 °C, affording the desired product in a higher, 40% yield (Table I, entry 1). With the aim to prepare universal precursor with ethynyl spacers and improve yields of the reaction, attempts to prepare copper (trimethylsilyl)acetylide were accompanied by decomposition and formation of polymerized side products (Table I, entry 2). Therefore we tried to obtain dialkynylated products via cross-coupling reaction.

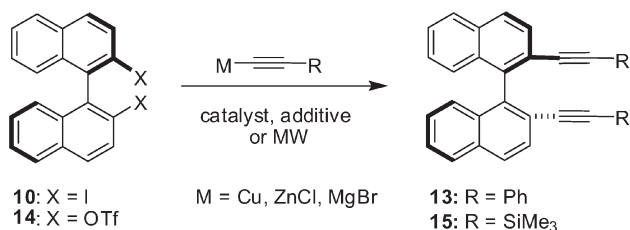
The reactions with less reactive dielectrophile, bistriflate **14**, were not successful under the Kumada or Negishi reaction conditions with various

catalytic systems (5–20 mole % of $[\text{Pd}(\text{PPh}_3)_4]$, $[\text{NiCl}_2(\text{dppe})]$, $[\text{NiCl}_2(\text{PPh}_3)_2]$, $[\text{PdCl}_2(\text{PPh}_3)_2]$) and in different solvents (diethyl ether, THF).

Then, the attempts were focused on application of more reactive diiodide **10**. No reaction was observed with the in situ formed zinc reagent from phenylacetylene, ZnCl_2 and Et_3N ¹⁷ (Table I, entry 3). The reaction with (phenylethynyl)zinc chloride, prepared via lithiation and transmetalation with zinc chloride, required excess of zinc reagent (optimally 3 equiv. for each Ar–I bond) in THF at reflux to obtain dialkynylated product **13** in

TABLE I

Preparation of nonracemic (*R*)-2,2'-dialkynyl-1,1'-binaphthalenes (**13** and **15**) from binaphthalene dielectrophiles



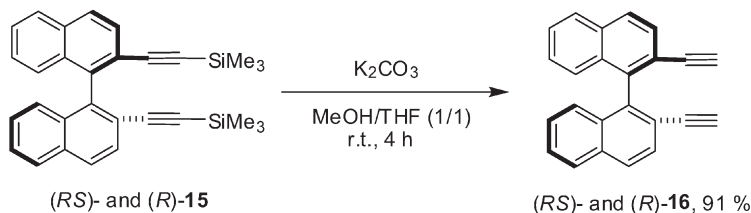
Entry	X	$\text{MC}\equiv\text{CR}$ (equivalents)	Catalyst, additive	Heating	Product	Time h	Yield ^a %
1	1	$\text{Cu}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$ (6)	pyridine	thermal	13	20	40
2	1	$\text{Cu}-\text{C}\equiv\text{C}-\text{SiMe}_3$ (6)	$[\text{Pd}(\text{PPh}_3)_4]$	thermal	15	–	–
3	1	$\text{ClZn}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$ (6) ^b	$[\text{Pd}(\text{PPh}_3)_4]$	thermal	13	72	–
4	1	$\text{ClZn}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$ (6)	$[\text{Pd}(\text{PPh}_3)_4]$	thermal	13	0.6 ^c	66
5 ^d	1	$\text{ClZn}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$ (6)	$[\text{Pd}(\text{PPh}_3)_4]$	MW	13	0.05	90
6	1	$\text{ClZn}-\text{C}\equiv\text{C}-\text{SiMe}_3$ (6)	$\text{Pd}(\text{PPh}_3)_4$	thermal	15	3 ^c	70
7 ^d	1	$\text{ClZn}-\text{C}\equiv\text{C}-\text{SiMe}_3$ (6)	$\text{Pd}(\text{PPh}_3)_4$	MW	15	0.05	81

^a Isolated yield. ^b The zinc reagent prepared in the presence of amine. ^c Time required for complete conversion of **10**. ^d Ref.¹⁶

good yield (66%, Table I, entry 4). Trimethylsilyl-protected derivative **15** was obtained according to this protocol in 70% yield (Table I, entry 6). Under the Negishi reaction conditions, helical side products **11** and **12** were formed only in small amounts (3–5%).

Considering that microwave irradiation has a positive effect on shortening the reaction time and yield of cross-coupling reactions^{16,18}, microwave irradiation was applied to the above Negishi dialkynylations. The reactions under microwave irradiation at 120 °C yielding **13** and **15** proceeded to full conversion in a shorter time (3 min compared with 40 min for **13** and 3 h for **15**) and improved yields to 90 and 81%, respectively (Table I, entries 5 and 7)¹⁶. The reaction under both the conditions (classical heating or microwave irradiation) starting from enantiomerically pure diiodide (*R*)-**10** (99% ee, HPLC) proceeded stereoconservatively (99% ee, HPLC).

The protecting trimethylsilyl group was removed with K_2CO_3 in a THF–MeOH mixture (1:1) to give (*R*)-**16** (99% ee, HPLC) in very good yield 91% (Scheme 2) as general precursor for the preparation of 2,2'-bis(arylethynyl) derivatives.

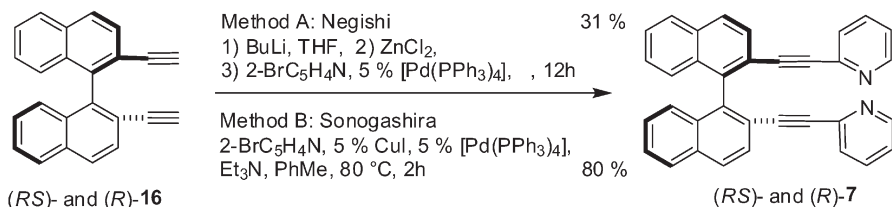


SCHEME 2

Preparation of 2,2'-Bis(pyridylethynyl)-1,1'-binaphthalenes

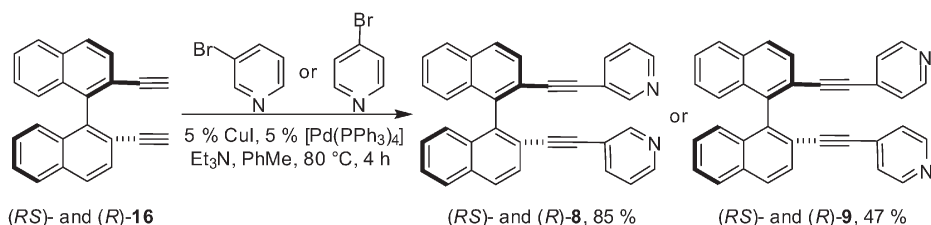
After preparation of nonracemic diethynyl derivative **16** we focused on its arylation. Bis(arylethynyl) derivatives with a donor atom in the molecule play a significant role as ligands in stereoselective synthesis and in the formation of supramolecular aggregates. Accordingly, we selected 2-, 3- and 4-pyridyl as aryl groups.

An attempt to prepare bis(2-pyridylethynyl) derivative by the Negishi reaction gave desired product **7** only in 31% yield (Scheme 3). This product was obtained under the Sonogashira reaction conditions in a significantly better yield (80%) within 2 h.



SCHEME 3

3-Pyridyl and 4-pyridyl derivatives **8** and **9** were prepared in analogous manner in 85 and 47% yield, respectively (Scheme 4). It should be noted that 4-pyridyl derivative **9** was not stable and decomposed even at low temperature and under argon atmosphere within few days.



SCHEME 4

Structure of new 2,2'-bis(pyridylethynyl)-1,1'-binaphthalenes **7–9** was confirmed by UV-VIS, IR, ¹H NMR, ¹³C NMR spectra, and elemental analysis.

Study on Coordination of 2,2'-Bis(pyridylethynyl)-1,1'-binaphthalene Derivatives

Molecular modeling (AM1 method within HyperChem) of compounds **7**, **8** and **9** in the presence of zinc chloride showed that spatial orientation of nitrogen donor atoms allows formation of bidentate chelate complex only from ligand **7**. In the case of ligands **8** and **9**, nitrogen lone electron pairs are oriented divergently, so these ligands should prefer formation of coordination dimers or oligomers (at ligand-to-metal ratio 1:1) or formation of bridged complexes M-L-M (at ligand-to-metal ratio 1:2).

Molecular structure of the chelate of (*RS*)-**7** with palladium chloride is reported in following chapter. The chelate clearly demonstrated the ability of ligand **7** to form intramolecular bidentate complex. Determination of the

exact structures of chelates of **8** and **9** would be also possible by X-ray structure analysis. Until now, we have failed to obtain crystals suitable for this purpose.

Coordination of bis(2-pyridylethynyl) **7**, bis(3-pyridylethynyl) **8** and bis(4-pyridylethynyl) **9** derivatives with Zn^{2+} ions was studied by ^1H NMR titration. Formation of white precipitate was observed in the case of **7**. We failed to crystallize or dissolve it in any common solvent. In DMSO, decomposition of the complex and formation of starting **7** were observed.

Coordination of the compound (*RS*)-**8** to the zinc cation affected proton ^1H NMR chemical shifts of **8**, which reflects different architecture of the complexes formed, keeping C_2 -symmetry of the ligand. ^1H NMR spectra (Fig. 2) obtained by successive addition of zinc chloride gave time-averaged signals, partially broadened, until whole numbers ratio of the components was reached as a result of metal–ligand exchange. Some signals (e.g. at 8.34 ppm of uncomplexed ligand) exhibited a complexation-induced shift to the lower field within the ligand-to-metal ratio ranging from 1:0 to 1:1 and then remained unchanged while increasing the zinc cation amount (up to $\Delta\delta$ 0.28 ppm). Some other signals (e.g. at 7.88 ppm) were more affected by addition of zinc cation (>1 equiv.).

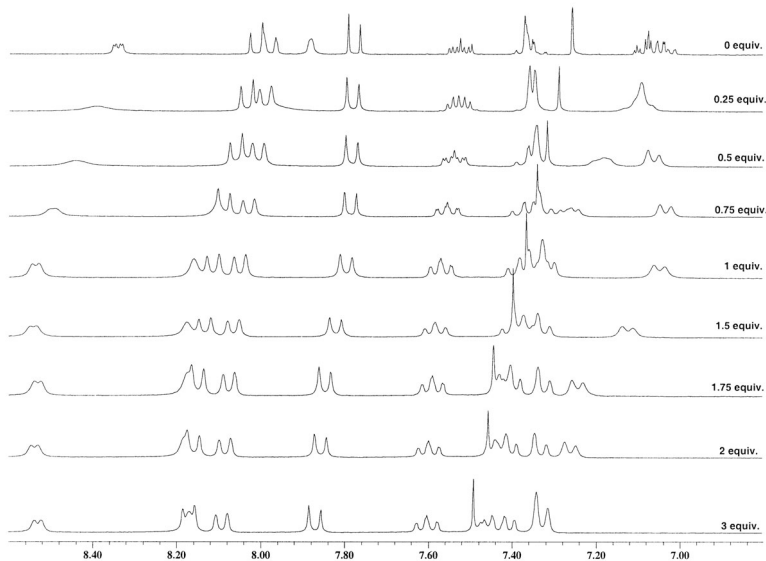


FIG. 2
 ^1H NMR spectra of (*RS*)-**8** (*c* 0.01 mol/l) after addition of corresponding amounts of ZnCl_2 , in $\text{CDCl}_3\text{--CD}_3\text{CN}$ mixture (1:1)

The same spectra were observed during the successive addition of zinc chloride to enantiopure (*R*)-**8**, reflecting the same architecture of the complexes regardless of the enantiomeric purity of ligand **8**.

Analogous changes were observed also in ^1H NMR spectra during addition of zinc chloride to ligand (*RS*)-**9** (Fig. 3). C_2 -Symmetry of the ligand was kept. However, significant changes were detected only until the addition of one equivalent of zinc chloride, which points out increased stability of the 1:1 complex. Complexation with (*R*)-**9** showed an analogous profile as in the case of (*RS*)-**9**/ ZnCl_2 .

Coordination of 2,2'-bis(2-pyridylethynyl)- (**7**) and 2,2'-bis(3-pyridylethynyl)-1,1'-binaphthalenes (**8**) to silver ions was studied by CD titration (Fig. 4). In CD spectra of ligand (*R*)-**7**, decrease in the intensity of the bisignate signal of the CD couplet was observed upon successive addition of silver ions. The intensity of the signal originating from the $^1\text{B}_b$ electronic transition of the binaphthalene moiety¹⁹, here at 307 and 335 nm, is known to decrease upon increasing the dihedral angle between two naphthalene units closer to 90° ²⁰. Formation of an intramolecular bidentate complex (analogous to that with palladium ion characterized by X-ray structure analysis; see the

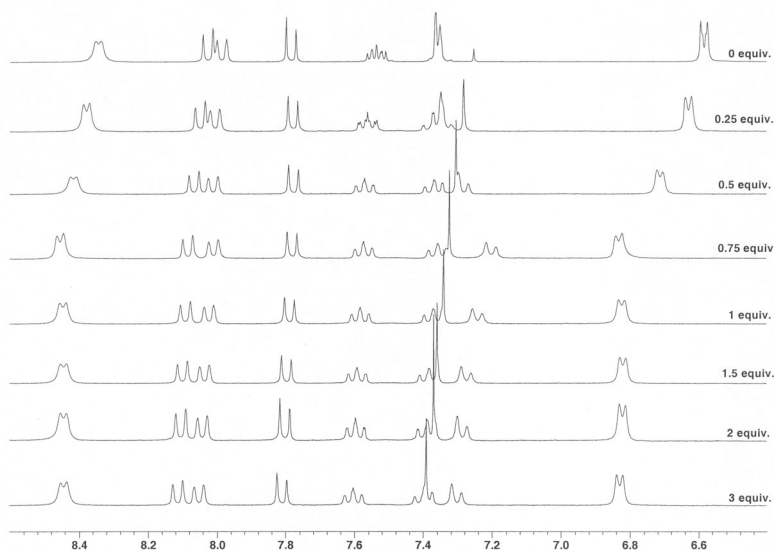


FIG. 3

^1H NMR spectra of (*RS*)-**9** (c 0.012 mol/l) after addition of corresponding amounts of ZnCl_2 , in CDCl_3 - CD_3CN mixture (1:1)

next chapter) seems to be responsible for the increase in the binaphthalene dihedral angle. In contrast, in the complexation of ligand (*R*)-**8**, where formation of an intermolecular complex is expected (dimer or oligomer), no remarkable change in CD spectra was observed, since formation of intermolecular complex does not require change in the dihedral angle of the binaphthalene moiety.

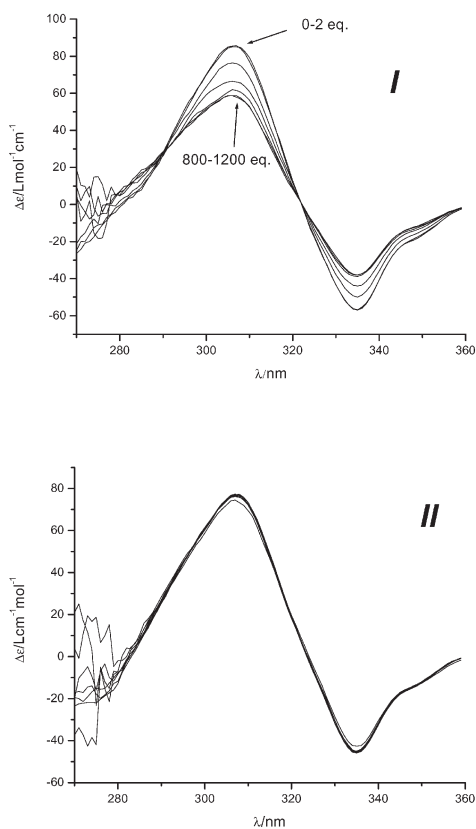


FIG. 4

CD spectra of: (*R*)-**7** ($c\ 1 \times 10^{-5}$ mol/l) after addition of 0, 1, 2, 100, 200, 400, 600, 800, 1000 and 1200 equiv. of AgOTf (a); (*R*)-**8** ($c\ 1 \times 10^{-5}$ mol/l) after addition of 0, 1, 2, 50, 250, 500, 750 and 1000 equiv. of AgOTf (b); in THF

X-ray Structure Analysis

Diffusion of a solution of $[\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2]$ in acetonitrile to a solution (*RS*)-**7** in CH_2Cl_2 yielded 77% of orange crystals of complex $[\text{PdCl}_2(\text{RS})\text{-7}]\cdot\text{CH}_3\text{CN}$ (**17**). The X-ray diffraction study showed that the crystal was composed of both enantiomers, each of them being coordinated to PdCl_2 and cocrystallizing with one molecule of acetonitrile (Fig. 5). Nitrogen atoms occupy *trans* position to the chlorine atoms bonded to palladium and gave a slightly distorted square-planar coordination geometry with typical averaged distances²¹ $\text{Pd}\text{-Cl}$ (2.31 and 2.35 Å) and $\text{Pd}\text{-N}(\text{pyridine})$ (2.04 Å), respectively. The bond angles of $\text{N}\text{-Pd}\text{-N}$, $\text{Cl}\text{-Pd}\text{-Cl}$, and $\text{N}\text{-Pd}\text{-Cl}$ are 176.5, 173.3, and 88.2, 89.3°, respectively. Torsion angles between naphthalene moieties were -73.1° for one enantiomer of **7** and -74.5° for the other one; torsion angles between pyridine planes were -32.9 and -35.3° . One of the $\text{C}\text{-C}\equiv\text{C}\text{-C}$ chains was slightly deviated from linearity, with bond angle $\text{C}(23)\text{-C}(24)\text{-C}(25)$ being 167.7° .

The supramolecular structure of complex **17** (Fig. 6) is composed of homochiral chains formed by complex molecules in a parallel orientation. The structure is directed by weak $\text{Cl}\cdots\text{H}$ intermolecular short contacts of 2.89 Å (between $\text{Cl}(2)\text{-H}(19)$ of two complex molecules from a chain) and

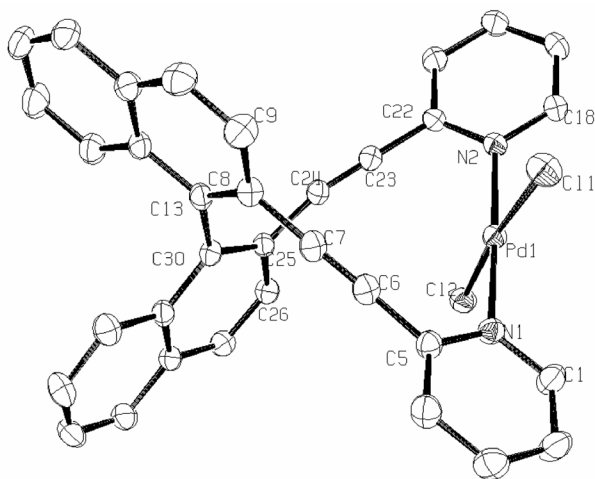


FIG. 5

ORTEP diagram of structure **17**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecule were omitted for clarity

2.80 Å (between Cl(2)–H(20) of molecules of neighboring chain), below the sum of van der Waals radii (3.45 Å). Weak Cl $\cdots$ H intermolecular short contacts (2.78 Å) between Cl(1)–H(26) of the molecules of a chain are observed in the molecular structure of **17** as well. No π – π stacking interaction of naphthalene units between complex molecules was observed since the shortest distance between centroids of naphthalene moieties was 4.39 Å.

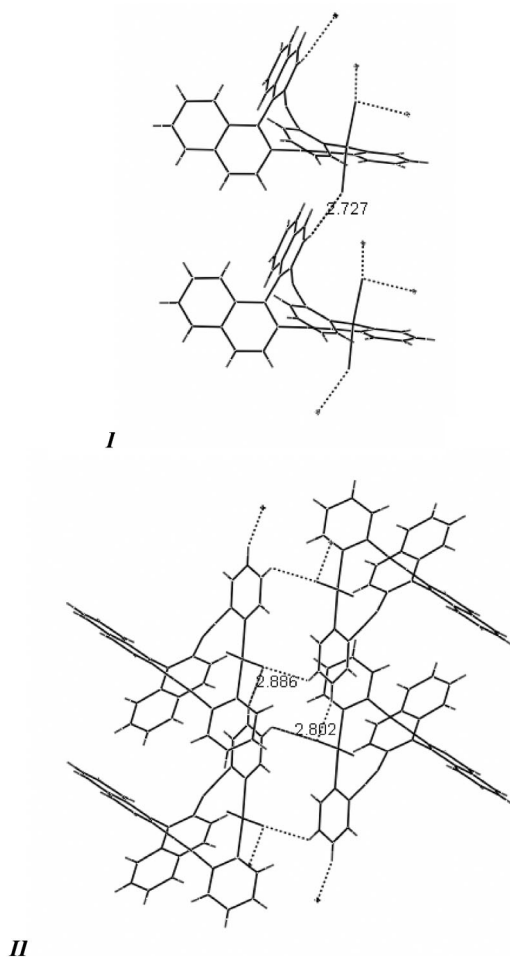


FIG. 6
Schematic representation of supramolecular structure of **17**. Intermolecular short contacts are shown by dotted lines. Solvent molecules are omitted for clarity. **I** Chain of the homochiral complexes; **II** two adjacent chains

CONCLUSION

We have developed an expedient methodology for the synthesis of enantiopure 2,2'-dialkynyl-1,1'-binaphthalene derivatives **13** and **15**. Compound **16** bearing ethynyl groups served as precursor for synthesis of bispyridine derivatives **7–9** by the Sonogashira coupling in moderate to high yield. Coordination of metal ions to the prepared bispyridines was observed by NMR and CD spectroscopy and the coordination of palladium cation was determined by X-ray structure analysis. Applications of the prepared bispyridines **7–9** as chiral ligands, supramolecular synthons or functional materials, are the subject of intensive study in our laboratory.

EXPERIMENTAL

Flash column chromatography was performed on Merck Silica Gel (60H). Merck Silica Gel F254 plates were used for thin layer chromatography and visualization was effected with UV light (254 nm). Melting points were measured on a Kofler block; the values are uncorrected. Specific optical rotations were measured on a Perkin–Elmer 241 polarimeter and are given in $\text{deg cm}^2 \text{ g}^{-1} \text{ dm}^{-1}$. IR data (in cm^{-1}) were recorded on a Specord M 80 spectrophotometer. UV-VIS spectra were measured on a Hewlett–Packard diode array 8245 spectrophotometer. CD spectra were measured on a Jasco J710 instrument. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 300 instrument at 298 K. Chemical shifts are reported in ppm (δ -scale) relative to internal standard TMS (0.00 ppm), the solvent was used as a reference. The operation frequency was 300 MHz for ^1H and 75.5 MHz for ^{13}C NMR. Coupling constants (J) are given in Hz. GC-MS spectra (70 eV, 150 μA , EI) were recorded on a Voyager GC/MS Finnigan instrument. Elemental analyses were determined with an Erba Science 1106 instrument. HPLC analysis was done on a Chiralcel Daicel OD-H column using an Agilent 1100 diode array detector (UV-VIS).

Dichloromethane, pyridine and triethylamine were dried with calcium chloride under argon atmosphere. THF, toluene and diethyl ether were dried with sodium/benzophenone. BuLi was used as 1.6 M solution in hexanes (Aldrich). All solvents for coupling reactions were degassed with a thaw-freeze pump in 3 cycles. The reactions were performed under argon atmosphere using Schlenk technique. $[\text{Pd}(\text{PPh}_3)_4]$ (ref.²²), ditriflate (*RS*)-**15** (ref.²³) were prepared according to literature procedures. All other chemicals were of analytical grade and were used without further purification.

2,2'-Diiodo-1,1'-binaphthalene (**10**)

Method A: (*R*)-1,1'-Binaphthalene-2,2'-diamine·2HCl²⁴ (5.00 g, 14 mmol, >98% ee by polarimetry) was dissolved in a H_2O – CH_3COOH – H_2SO_4 mixture (195 ml, 2:10:1, v/v) at room temperature. The solution was cooled to -5°C and NaNO_2 (4.00 g, 58 mmol) was added in three portions. The mixture was stirred at 0°C for 2 h and then carefully added to a mixture of KI (17 g, 0.104 mol) with ice (200 ml) (intensive foaming). The reaction mixture was stirred at room temperature for 12 h and then extracted with chloroform. Combined organic extracts were washed with aqueous Na_2SO_3 , dried over anhydrous Na_2SO_4 , and

solvent was evaporated. Purification through a short silica gel column (hexanes–chloroform, 10:1) gave compound (R)-**10** as a white crystalline solid (3.57 g, 50%, 99.1 ± 0.2% ee by HPLC).

Method B: Procedure according to literature²⁵, but starting from (R)-1,1'-binaphthalene-2,2'-diamine (>98% ee by polarimetry) afforded (R)-**10** (62%, 99.1 ± 0.2% ee by HPLC).

(R)-2,2'-Diiodo-1,1'-binaphthalene (**10**). M.p. 227–229 °C (hexanes), $[\alpha]_D^{23} +16.7$ (c 1.75, pyridine), >98% ee (lit.²⁴ m.p. 225–227 °C, $[\alpha]_D^{23} +16.4$ (c 1.725, pyridine), >98% ee). Spectral data were in agreement with literature values²⁵. (RS)-**10**: M.p. 205–207 °C. HPLC: Chiralcel Daicel OD-H column, heptane–DME (99:1), temperature 16 °C, flow rate 1 ml/min, pressure 31 bar, $\lambda = 280$ nm; $k = 6.52$ (S)-**10**, 7.35 (R)-**10**, $\alpha = 1.13$, $R_S = 1.42$.

Alkynylation of 2,2'-Disubstituted 1,1'-Binaphthalenes

Preparation of (Phenylethynyl)magnesium Bromide

To Mg turnings (144 mg, 6 mmol) in THF (20 ml) 2 drops of 1,2-dibromomethane were added. Then isopropyl bromide (0.28 ml, 3 mmol) was added and the mixture was heated to reflux for 2 h. The reaction mixture was cooled to –30 °C and phenylacetylene (0.34 ml, 3 mmol) was injected via syringe. The reaction mixture was then refluxed for 2 h. The filtered mixture was used in subsequent reactions.

Preparation of Alkynylzinc Chloride

To a solution of terminal acetylene (3 mmol) in THF (10 ml) was added dropwise butyllithium (2.25 ml, 3.6 mmol) solution in hexane at 0 °C. The obtained solution was stirred at this temperature for 30 min. Then a 1.5 M solution of ZnCl₂ in THF (3.6 mmol) was added and stirred at 0 °C for 30 min.

3-(Trimethylsilyl)-4-[(trimethylsilyl)ethynyl]dibenzo[c,g]phenanthrene (**12**)

A Schlenk flask containing a stirring bar, capped with a rubber septum, was flame-dried under vacuum and then filled with argon and cooled to room temperature. The flask was charged with **10** (200 mg, 0.4 mmol), [Pd(PPh₃)₄] (10 mg, 0.02 mmol, 2.5 mole %), CuI (305 mg, 1.6 mmol), and again evacuated and filled with argon. Dry Et₃N (0.9 ml, 6.4 mmol), absolute THF (10 ml) and (trimethylsilyl)acetylene (1.6 mmol) was injected into the flask and the reaction mixture was heated to reflux for 12 h under argon atmosphere. After cooling, the reaction mixture was poured into 10% aqueous HCl and extracted three times with chloroform (10-ml portions). Combined organic fractions were washed twice with water and brine, and dried over anhydrous Na₂SO₄. After filtration and evaporation of the solvent, the residue was chromatographed on silica gel (hexanes–chloroform, 10:1). 146 mg (82%) of **12** as dark red oil was obtained. R_F 0.62 (hexanes–chloroform, 4:1). ¹H NMR (300 MHz, CDCl₃): 9.33 d, 1 H, ³J = 8.4 (Ar-H); 8.46–8.23 m, 2 H (Ar-H); 8.05 d, 1 H, ³J = 8.4 (Ar-H); 7.90–7.83 m, 2 H (Ar-H); 7.80 d, 1 H, ³J = 8.2 (Ar-H); 7.73 d, 1 H, ³J = 8.2 (Ar-H); 7.80–7.38 m, 4 H (Ar-H); 0.61 s, 9 H (SiCH₃); 0.42 s, 9 H (SiCH₃). ¹³C NMR (75 MHz, CDCl₃): 139.4, 138.3, 137.0, 135.3, 135.0, 128.8, 128.6, 128.5, 128.3, 128.0, 127.9, 127.8, 127.7, 126.5, 126.1, 125.9, 125.3, 125.1, 123.2, 122.8, 116.9, 108.9, 1.4, 0.1. For C₃₀H₃₀Si₂ (446.7) calculated: 80.66% C, 6.77% H; found: 80.43% C, 6.85% H.

(RS)-, *(R)*-2,2'-Bis(phenylethynyl)-1,1'-binaphthalene (**13**) via Stephen–Castro Reaction

A dried Schlenk flask containing a stirring bar, capped with a rubber septum, was flame-dried under vacuum and then filled with argon and cooled to room temperature. The flask was charged with *(R)*-**10** (100 mg, 0.2 mmol, 99% ee) and copper(I) phenylacetylide (165 mg, 1 mmol), evacuated again and filled with argon. Dried pyridine (5 ml) was successively injected into the flask and the reaction mixture was heated to reflux for 20 h under argon atmosphere. After cooling, the reaction mixture was poured into 15% aqueous HCl and extracted three times with chloroform (10-ml portions). Combined organic fractions were washed twice with water and brine, and dried over anhydrous Na₂SO₄. After filtration and evaporation of the solvent, the residue was chromatographed on silica gel (hexanes–chloroform, 10:1; enantiomeric enriched *(R)*-**13** (28 mg, 31%, 99% ee, HPLC) as a white solid was obtained.

2,2'-Bis(phenylethynyl)- (**13**) and 2,2'-Bis[(trimethylsilyl)ethynyl]-1,1'-binaphthalene (**15**) via Negishi Reaction

Method A (under classical heating): A dried Schlenk flask containing a stirring bar, capped with a rubber septum, was flame-dried under vacuum and then filled with argon and cooled to room temperature. The flask was charged with *(R)*-**10** (100 mg, 0.2 mmol) and [Pd(PPh₃)₄] (11.5 mg, 0.01 mmol) (or another catalytic system), evacuated again and filled with argon. Dry THF (1 ml) was injected into the flask and a solution of alkynylzinc chloride was injected via cannula to the reaction mixture. The reaction mixture was heated to reflux (ca. 65 °C) for the time given in Table I. After cooling to room temperature, the mixture was quenched with 10% aqueous HCl (15 ml) and extracted three times with chloroform. Combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. Solvent was evaporated and 2,2'-diethynyl-1,1'-binaphthalenes **13** and **15** were obtained from the residue by flash chromatography on silica gel (hexanes–chloroform, 9:1).

Method B (under microwave irradiation): To a solution of *(R)*-**10** (100 mg, 0.2 mmol) and [Pd(PPh₃)₄] (11.5 mg, 0.01 mmol) (or another catalytic system) in dry THF (1 ml), a solution of alkynylzinc chloride was added. The MW reactor vessel was capped and irradiated in a Biotage Initiator microwave oven at 120 °C for the total irradiation time indicated in Table I. After cooling to room temperature, the mixture was quenched with 10% aqueous HCl (15 ml) and extracted three times with chloroform. Combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. Solvent was evaporated and 2,2'-diethynyl-1,1'-binaphthalenes **13** and **15** were obtained from the residue by flash chromatography on silica gel (hexanes–chloroform, 9:1).

(R)-2,2'-Bis(phenylethynyl)-1,1'-binaphthalene (**13**). White solid, m.p. 200–203 °C, 99% ee (determined by HPLC), [α]_D²² +6.92 (c 1, chloroform) (lit.¹⁵ [α]_D^{30.5} +6.91 (c 1.01, chloroform)), *R*_F 0.27 (chloroform–hexanes, 1:4). Spectral data were in agreement with literature values¹⁴. *(RS)*-**13**: m.p. 224–228 °C (chloroform–hexanes) (lit.¹⁴ m.p. 263–264 °C (EtOH–CH₂Cl₂)). HPLC: Chiralcel Daicel OD-H column, hexane–DME (99:1), temperature 21 °C, flow rate 1 ml/min, pressure 47 bar, λ = 280 nm; *k* = 2.32 (*S*)-**13**, 2.79 (*R*)-**13**; α = 1.20; *R*_S = 1.30.

(RS)-, *(R)*-2,2'-Bis[(trimethylsilyl)ethynyl]-1,1'-binaphthalene (**15**). Yellowish oil, *R*_F 0.52 (chloroform–hexanes, 1:4). ¹H NMR (300 MHz, CDCl₃): 7.88 d, 2 H, ³*J* = 8.4 (Ar-H); 7.86 d, 2 H, ³*J* = 8.1 (Ar-H); 7.63 d, 2 H, ³*J* = 8.7 (Ar-H); 7.46 ddd, 2 H, *J* = 3.5, 8.1, 8.2 (Ar-H); 7.29 m, 4 H (Ar-H); –0.28 s, 18 H (Si-CH₃). ¹³C NMR (75 MHz, CDCl₃): 141.8, 133.7, 133.2, 128.6, 128.5, 128.3, 127.3, 127.1, 127.0, 121.9, 105.5, 99.1, 0.03.

2,2'-Diethynyl-1,1'-binaphthalene (**16**)

Finely powdered and dried K_2CO_3 (500 mg, 3.6 mmol) was added to a solution of (*R*)-**15** (268 mg, 0.6 mmol) in MeOH–THF (10 ml, 1:1). The reaction mixture was stirred at room temperature for 4 h, and chloroform (35 ml) and water (15 ml) were added. The organic layer was separated, washed with water and brine, and dried over anhydrous Na_2SO_4 . After filtration, solvent was evaporated and the residue was purified by flash chromatography on silica gel (hexanes–chloroform, 9:1). Compound **16** (165 mg, 91%) was obtained as a white solid.

(*R*)-2,2'-Diethynyl-1,1'-binaphthalene (**16**). M.p. 190–194 °C (chloroform–hexanes), $[\alpha]_D^{23} +27.8$ (c 0.62, chloroform), >98% ee (determined by HPLC), R_F 0.37 (chloroform–hexanes, 1:4). Spectral data were in agreement with literature values¹⁵. (*RS*)-**16**: m.p. 199–205 °C. HPLC: Chiralcel Daicel OD-H column, hexane–DME (99:1), temperature 21 °C, flow rate 1 ml/min, pressure 47 bar, λ = 280 nm; k = 2.74 (*S*)-**16**, 3.05 (*R*)-**16**; α = 1.11; R_S = 0.89.

Synthesis of Bispyridines **7–9**2,2'-Bis(2-pyridylethynyl)-1,1'-binaphthalene (**7**)

Method A (Negishi reaction): A dried Schlenk flask containing a stirring bar, capped with a rubber septum, was flame-dried under vacuum, filled with argon and cooled to room temperature. The flask was charged with **15** (100 mg, 0.33 mmol), evacuated again and filled with argon. THF (1 ml) was successively injected into the flask and ice cooled. To this solution BuLi (0.53 ml, 0.79 mmol, 1.6 M solution in hexanes) was added dropwise at 0 °C. After addition, the solution was stirred at 0 °C for 1 h. Then solution of $ZnCl_2$ (162 mg, 1.18 mmol) in THF (1 ml) was added dropwise at 0 °C to it and the reaction mixture was stirred at 0 °C for 1 h. The resulting solution was added to a solution of 2-bromopyridine (0.19 ml, 1.98 mmol) and $[Pd(PPh_3)_4]$ (20 mg, 0.0165 mmol) in THF (3 ml) at room temperature and the mixture was heated to reflux for 12 h. After cooling, the mixture was quenched with water (2 ml) and extracted three times with chloroform (10 ml). Combined organic layers were dried over anhydrous Na_2SO_4 , filtered and solvent was evaporated. The residue was chromatographed on silica gel (hexanes–ethyl acetate, 1:1). Compound **7** (46 mg, 31%) as an off-white solid was obtained.

Method B (Sonogashira reaction): A dried Schlenk flask containing a stirring bar, capped with a rubber septum, was flame-dried under vacuum, filled with argon and cooled to room temperature. The flask was charged with **15** (60 mg, 0.2 mmol), 2-bromopyridine (78 mg, 0.5 mmol), CuI (2 mg, 0.01 mmol) and $[Pd(PPh_3)_4]$ (11.5 mg, 0.01 mmol), evacuated again and filled with argon. Toluene (2.5 ml) and Et_3N (1 ml) were successively injected into the flask. The dark brown reaction mixture was heated to 80 °C for 2 h. After cooling, water was added (3 ml), the mixture was poured into 10% aqueous NH_4Cl and extracted three times with ethyl acetate (10-ml portions). Combined organic fractions were dried over anhydrous Na_2SO_4 . After filtration and evaporation the solvent, the residue was chromatographed on silica gel (ethyl acetate–hexanes, gradient from 1:2 to 1:1). (*RS*)- or (*R*)-**7** (72 mg, 80%) as an off-white solid was obtained.

(*R*)-2,2'-Bis(2-pyridylethynyl)-1,1'-binaphthalene (**7**). M.p. 120–124 °C, $[\alpha]_D^{21} -75.8$ (c 1, chloroform), R_F 0.05 (ethyl acetate–hexanes, 1:1). UV–VIS (MeOH (log ϵ)): 226 (5.87), 268 (5.85), 316 (5.79). IR (chloroform): 2270 m, 2100 w, 1580 m, 1500 m, 1470 m, 1425 m, 920 m, 800 s, 695 s, 650 w. 1H NMR (300 MHz, $CDCl_3$): 8.42 d, 2 H, 3J = 4.4 (Ar-H); 8.01 d, 2 H, 3J = 8.5 (Ar-H); 7.95 d, 2 H, 3J = 8.2 (Ar-H); 7.87 d, 2 H, 3J = 8.4 (Ar-H); 7.47–7.53 m, 2 H (Ar-H);

7.32 ddd, 2 H, $J = 1.6, 7.5, 8.2$ (Ar-H); 7.32 d, 4 H, $^3J = 3.6$ (Ar-H); 7.03 ddd, 2 H, $J = 1.0, 4.9, 7.5$ (Ar-H); 6.32 d, 2 H, $^3J = 7.91$ (Ar-H). ^{13}C NMR (75 MHz, CDCl_3): 149.8, 143.5, 141.0, 135.9, 133.4, 132.7, 128.5, 128.3, 128.2, 127.6, 127.2, 127.1, 126.9, 122.5, 121.1, 92.8, 89.3. GC-MS-FAB, m/z (%): 455 (100) [$\text{M}^{++} - 1$], 378 (62), 226 (26). For $\text{C}_{34}\text{H}_{20}\text{N}_2$ (456.5) calculated: 89.45% C, 4.42% H, 6.14% N; found: 89.73% C, 4.50% H, 5.85% N. (RS)-7: m.p. 241–244 °C (chloroform–hexanes).

2,2'-Bis(3-pyridylethynyl)-1,1'-binaphthalene (**8**)

A dried Schlenk flask containing a stirring bar, capped with a rubber septum, was flame-dried under vacuum, filled with argon and cooled to room temperature. The flask was charged with **15** (100 mg, 0.33 mmol), 3-bromopyridine (128 mg, 0.825 mmol), CuI (3.3 mg, 0.0165 mmol) and $[\text{Pd}(\text{PPh}_3)_4]$ (18.1 mg, 0.0165 mmol), evacuated again and filled with argon. Toluene (4.5 ml) and Et_3N (1.7 ml) were successively injected into the flask. The dark brown reaction mixture was heated to 80 °C for 2 h. After cooling, water (3 ml) was added, the mixture was poured into 10% aqueous NH_4Cl and extracted three times with ethyl acetate (10-ml portions). Combined organic fractions were dried over Na_2SO_4 . After filtration and evaporation of the solvent, the residue was chromatographed on silica gel (hexanes–ethyl acetate, gradient from 2:1 to 1:1). (RS)- or (R)-**8** (177 mg, 85%) as an off-white solid was obtained.

(R)-2,2'-Bis(3-pyridylethynyl)-1,1'-binaphthalene (**8**). M.p. 191–193 °C, $[\alpha]_D^{21} -2.9$ (c 1, chloroform), R_F 0.10 (ethyl acetate–hexanes, 1:1). UV-VIS (MeOH (log ϵ)): 226 (6.59), 268 (6.78), 316 (6.32). IR (chloroform): 2275 m, 2095 m, 1595 m, 1530 m, 1470 m, 1420 m, 920 m, 800 s, 695 s, 650 w. ^1H NMR (300 MHz, CDCl_3): 8.33 d, 2 H, $J = 3.1$ (py-H); 8.01 d, 2 H, $^3J = 8.7$ (Ar-H); 7.98 d, 2 H, $J = 9.56$ (Ar-H); 7.88 s, 2 H (py-H); 7.78 d, 2 H, $^3J = 8.7$ (Ar-H); 7.52 ddd, 2 H, $J = 2.5, 5.5, 10.4$ (Ar-H); 7.32–7.39 m, 4 H (Ar-H); 7.01–7.11 m, 4 H (Ar-H). ^{13}C NMR (75 MHz, CDCl_3): 152.2, 148.3, 140.8, 138.1, 133.4, 132.7, 128.5, 128.3, 128.1, 127.2, 127.1, 126.8, 123.0, 122.95, 121.2, 92.6, 90.3. GC-MS-FAB: 456 (100) [M^{++}], 377 (18), 226 (16). For $\text{C}_{34}\text{H}_{20}\text{N}_2$ (456.5) calculated: 89.45% C, 4.42% H, 6.14% N; found: 89.64% C, 4.56% H, 5.83% N. (RS)-**8**: m.p. 223–225 °C (chloroform–hexanes).

2,2'-Bis(4-pyridylethynyl)-1,1'-binaphthalene (**9**)

A dried Schlenk flask containing a stirring bar, capped with a rubber septum, was flame-dried under vacuum, filled with argon and cooled to room temperature. The flask was charged with **15** (200 mg, 0.66 mmol), 4-bromopyridine (256 mg, 1.65 mmol), CuI (6.3 mg, 0.033 mmol) and $[\text{Pd}(\text{PPh}_3)_4]$ (36 mg, 0.033 mmol), evacuated again and filled with argon. Toluene (6 ml) and Et_3N (2 ml) were successively injected into the flask. The dark brown reaction mixture was heated to 80 °C for 2 h. After cooling, water (3 ml) was added, the mixture was poured into 10% aqueous NH_4Cl and extracted three times with ethyl acetate (10-ml portions). Combined organic fractions were dried over anhydrous Na_2SO_4 . After filtration and evaporation of the solvent, the residue was chromatographed on silica gel (hexanes–ethyl acetate, 2:1). (RS)- or (R)-**9** (141 mg, 47%) as an off-white solid was obtained. The product decomposes within several hours even at –30 °C under argon atmosphere.

(R)-2,2'-Bis(4-pyridylethynyl)-1,1'-binaphthalene (**9**). M.p. 240–244 °C, $[\alpha]_D^{21} -5.0$ (c 0.85, chloroform), R_F 0.06 (ethyl acetate–hexanes, 1:1). UV-VIS (MeOH (log ϵ)): 228 (5.60), 280 (5.64), 324 (5.48). IR (chloroform): 2260 m, 2100 m, 1580 s, 1500 m, 1470 m, 1410 m, 985 m, 910 m, 805 s, 680 s, 650 m. ^1H NMR (300 MHz, CDCl_3): 8.34 d, 4 H, $^3J = 4.4$ (py-H); 8.03 d, 2 H, $^3J = 8.5$ (Ar-H); 8.00 d, 2 H, $^3J = 8.2$ (Ar-H); 7.78 d, 2 H, $^3J = 8.5$ (Ar-H); 7.51–7.58 m, 2 H (Ar-H);

7.36 d, 4 H, $^3J = 3.5$ (Ar-H); 6.58 d, 4 H, $J = 4.5$ (py-H). ^{13}C NMR (75 MHz, CDCl_3): 149.5, 141.2, 133.5, 132.6, 131.3, 128.5, 128.3, 128.1, 127.4, 127.3, 126.7, 125.2, 120.7, 93.8, 90.9. GC-MS-FAB: 456 (100) $[\text{M}^{+}]$, 377 (30), 213 (13), 199 (13). For $\text{C}_{34}\text{H}_{20}\text{N}_2$ (456.5) calculated: 89.45% C, 4.42% H, 6.14% N; found: 89.85% C, 4.72% H, 5.40% N. (RS)-**9**: m.p. 222–225 °C (chloroform–hexanes).

Study on Coordination of Metal Ions to Bispyridines **7–9**

NMR titrations. NMR titrations were carried out on a Varian Gemini 300 instrument at 298 K. To a weighed amount of ca. 0.7 ml 10–20 mM stock solution of bispyridine in CDCl_3 – CD_3CN (1:1), a small amount (25–100 μl) of 100–200 mM solution of zinc chloride in the same solvent mixture was added.

CD titrations. CD titrations were carried out on a Jasco J710 spectropolarimeter at 298 K. To 10 μM stock solution of bispyridine in THF (1 ml), a small amount (10–100 μl) of 1–10 mM solution of silver triflate in the same solvent was added.

Crystal structure analysis. To a degassed solution of **7** (23 mg) in dichloromethane (2 ml) was slowly added a mixture of dichloromethane (0.3 ml) and acetonitrile (0.3 ml), and then a solution of $[\text{Pd}(\text{MeCN})_2\text{Cl}_2]$ (14 mg) in acetonitrile (2 ml). The sample was stored in the dark place at room temperature for 5 days. Compound **17** (31 mg, 77%) as orange crystals was formed. ^1H NMR (300 MHz, CDCl_3): 8.68 d, 4 H, $J = 4.9$ (Ar-H); 8.39 d, 4 H, $J = 7.2$ (Ar-H); 8.36 dd, 2 H, $J = 2.2, 3.8$ (Ar-H); 7.81 ddd, 2 H, $J = 1.6, 7.7, 8.2$ (Ar-H); 7.55–7.47 m, 4 H (Ar-H); 7.33–7.24 m, 4 H (Ar-H).

X-ray data were collected at $T = 173(2)$ K on a Stoe IPDS XRED32 diffractometer with graphite monochromatized $\text{MoK}\alpha$ radiation, $\lambda = 0.71073$ Å. The structure was solved by direct methods and refined by full-matrix least-squares techniques. The following computer programs were used: structure solution SHELXS97²⁶, refinement SHELXL97²⁷, molecular diagrams ORTEP. The non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogens were included in idealized positions. Salient crystal data are as follows: $\text{C}_{72}\text{H}_{46}\text{Cl}_4\text{N}_6\text{Pd}_2$ (1349.75), triclinic, space group $C-1$, $a = 8.7847(12)$, $b = 8.9229(9)$, $c = 22.053(3)$ Å, $\alpha = 80.470(13)$, $\beta = 80.528(12)$, $\gamma = 63.379(11)^\circ$, $V = 1516.0(3)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 1.478$ g cm⁻³. 17999 of reflections were collected in the range of θ from 2.61 to 27.98°. Final R indices: $R_1 = 0.0295$, $wR_2 = 0.0705$; R indices (all data): $R_1 = 0.0390$, $wR_2 = 0.0733$. Goodness-of-fit on F^2 : 0.943.

CCDC 647946 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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