Phenanthroline ligands with divergent pyridine units

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2-Mono- and 2,9-di-substituted 1,10-phenanthrolines with 4-pyridine units attached either *via* 1,4-phenylene- or 4-ethynyl-phenyl spacers, have been synthesised. The strategy is based on the introduction of 4-trimethylsilylphenyl group(s) at the phenanthroline core with the subsequent *ipso*-substitution of TMS groups by bromine or iodine and successive Suzuki or Sonogashira reactions with 4-pyridineboronic acid or 4-ethynylpyridine, respectively.

Keywords: phenanthroline, pyridine, TMS-protection, Sonogashira, Suzuki

1,10-Phenanthrolines are known first for their ability to form stable complexes with transition metal cations.[1,2] Depending on the nature of metal, such complexes demonstrate rich photochemical properties,[3] that are successfully used in analytical and various biochemical applications.[4,5] Homo- and hetero-leptic complexes of 2,9-disubstituted derivatives of this heterocycle with copper(I) in the ratio 2:1, have been efficiently used in templated syntheses of such mechanically interlocked molecules as rotaxanes,[6] catenanes,[7] doubly braded [2]-catenanes[8] and knots.[9] Introduction of additional complexation units (*e.g.* bi-pyridines) enabled the possibility of the use of these building blocks in assemblies of large structures on the nanometre scale.[10-12] The use of 2,9-disubstituted 1,10-phenanthrolines has inspired the formulation of the appealing concept of concave reagents.[13]

Obviously, realisation of different goals including the self-assembled structures needs different derivatives of 1,10-phenanthroline. In this article are described convenient syntheses of various ligands containing one or two 4-pyridyl units rigidly coupled to the positions 2,9- of the 1,10-phenanthroline core either via 1,4-phenylene or via 4-ethynyl-phenyl (–C_6H_4–C≡C–) spacers, which have not been described previously to the best of my knowledge. Such molecules might be used in self-assembly of new structures on the nanometre scale.[14] The analogous compounds with pyridine units attached *via* longer spacers have been already described. The difference in the length is one diphenyloxide unit, which also possesses a kink. The self-assembly of these compounds *via* copper (I) and palladium (II) cations leads to the formation of [2]-catenanes.[15]

The strategy proposed is based on the introduction of one or two 4-trimethylsilyl-phenyl group(s) at the positions 2- and 9- of the phenanthroline core, subsequent *ipso*-substitution of the TMS-groups by halogens (bromine or iodine) and successive C–C coupling using either Suzuki[16] or Sonogashira[17] reactions. The synthesis of the phenanthroline derivatives having either one or two 4-bromo-phenyl groups, has been already described.[15] The preparation of these compounds proposed in here, is simply the alternative to the already method described and allows the formation of much more soluble trimethylsilyl intermediates. On the other hand, the latter can be used for synthesis of even more reactive iodo- derivatives (see later) and potentially for the introduction of other electrophiles *via* the analogous *ipso*-substitution of the TMS groups.[18]

The typical addition of lithium-*para*-trimethylsilyl-benzene (readily obtained from 1-bromo-4-trimethylsilylbenzene[19]) to the phenanthroline with successive rearomatisation[20] leads to the formation of the expected compound **1** with the yields of 75–80% (Scheme 1). The introduction of the second 4-TMS-phenyl group also goes smoothly with the lower but still acceptable yield of 63%.

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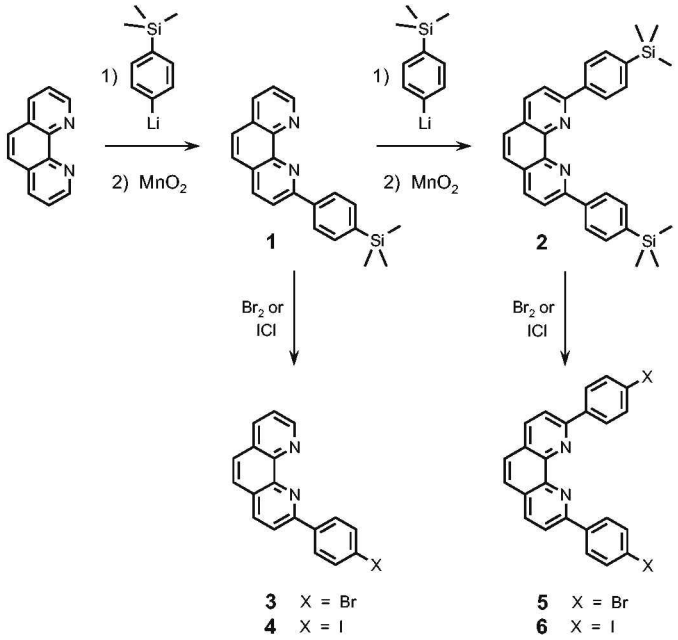
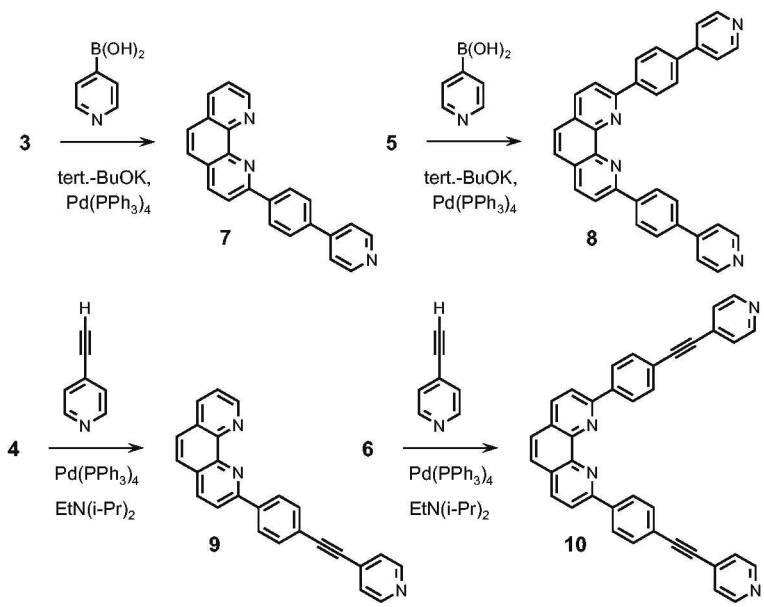
Addition of halogen to a pre-cooled solution of the TMS derivatives(s) in dichloromethane, leads to the nearly immediate formation of a precipitate in all cases. However, using stoichiometric amounts of halogenating agents did not lead to complete reactions. This was proved by the presence of the residual signal at δ 0.37 ppm of the Ar-Si($C\underline{H}_3$)$_3$ group (in DMSO-D_6) and a double set of some signals in the aromatic region of the ^{1}H NMR spectrum of a crude product (after evaporation of the solvent).

An elemental analysis of the precipitate formed during the bromination reaction of **2** with 3.3 mole-equivalents of bromine (found: C 36.93, H 2.01, N 4.75) is much different from the expected one for **5** (calculated: C 58.81, H 2.88, N 5.71). This sample had been dried carefully under high vacuum for 24 h without heating before it was submitted to elemental analysis and a mixture of the complexed bromonium salts with two different counter-anions (for the complex (**5**·Br^+)Br^- calculated: C 44.35, H 2.17, N 4.31; and (**5**·Br^+)Br_3^- calculated: C 35.60, H 1.74, N 3.46) is suggested with the prevalence of the latter, rather than either the presence of traces of the solvent (for **5**·(CH_2Cl_2) calculated: C 52.21, H 2.80, N 4.89) or salt (for (**5**·H^+)Br^- calculated: C 50.47, H 2.65, N 4.90). Such complexation obviously reduces the reactivity 1) of the aromatic system itself; 2) of a halogenating agent (Hal^+) due to the surprisingly strong complexation occurring. This explains the need for one additional mole-equivalent of the halogen to complete the reaction. To destroy an excess of halogen, bromotrimethylsilane and complexes of phenanthroline with Hal^+ at the end of the reaction, the solvent is removed under reduced pressure and the crude product is solubilised under a short reflux in a mixture of ethyl acetate, methanol and triethylamine. The crude product is then pre-adsorbed on silica and purified using column chromatography. The yields of these reactions are within 70–91%, which is quite acceptable.

After a period of trial and error it became clear that bromo derivatives are better suited for Suzuki reaction than iodo ones in the conditions used, since in the former case the lower amounts of by-products are formed (due to the lower reactivity). The reaction of mono bromo derivative **3** (Scheme 2), has been carried out in a mixture of 1,2-dimethoxyethane and water, giving the desired product **7** in 77% yield. The small amount of by-products formed in this reaction and the not too complicated purification makes this reaction easy even in unexperienced hands. However, the solvent mixture used here is not suited for reaction with the dibromo derivative **5** due to solubility problems. Unfortunately, the formation of a mixture of at least four compounds due to the side reactions is observed. 4,4'-Bipyridyl (due to the homo-coupling of 4-pyridineboronic acid) was identified among the products of this reactions. In all cases, the purification is very inconvenient and never led to an analytically pure product. Although changing the solvent mixture to DMSO containing 10% water, increases the yields of **8** up to 86% after column chromatography (assuming



Scheme 1



Scheme 2

only the formation of this product), its purity remains no higher than 85% on the basis of ^{1}H NMR spectra. Neither crystallisation of this product nor flash chromatography led to the higher purity.

On the other hand, the Sonogashira reaction (Scheme 2) always gives reproducible and very satisfactory results. This reaction has always been carried out in the absence of copper(I) halides, since in this case one avoids the destruction of the copper complexes with phenanthrolines or their removal from the crude product.[21] Di-*iso*-propylamine is used as a base. All in all, the crude products after this reaction are much easier to purify than the ones after Suzuki reaction with **5**. The yields are moderate (60–66%), but there are no experimental difficulties in the synthesis of **9** and **10**. As in the case of **7**, this pair of compounds can be also synthesised in less experienced hands.

In conclusion, the syntheses of phenanthroline derivatives containing one or two pyridine units attached to the 1,10-phenanthroline core at the second and ninth positions via 1,4-phenylene or 4-ethynyl-phenyl spacers, are described. The trimethylsilyl protection strategy has been chosen to prepare 4-bromo- and 4-iodo-phenyl precursors, which have been then converted into the desired products either *via* Suzuki or Sonogashira reactions. The compounds of this type might be interesting for the self-assembly of large structures.

Experimental

All chemicals have been purchased from Acros and Aldrich if not stated otherwise, and used without further purification. All solvents used, were of p.a. grade (99.5+%) while the ones used for purifications (>99%) were additionally distilled. Melting points were determined with a MEL TEMP 2 capillary melting point apparatus and are not corrected. ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance DRX400 spectrometer at 25 °C at 400 MHz and 100 MHz working frequencies, respectively. The chemical shifts are given in respect to the positions of the residual solvent signals. FD and ESI mass spectra were measured on a Finnigan MAT 8230 and Micromass QTOF Ultima 3 instruments. 1-bromo-4-trimethylsilylbenzene was readily obtained from 1,4-dibromobenzene in 90-95% yields.[19] All reactions were carried out under an inert atmosphere if not stated otherwise. The work with all compounds (especially with the new ones) requires the maintenance of all necessary safety rules.

2-(4-Trimethylsilylphenyl)-1,10-phenanthroline (**1**): A solution of 1-bromo-4-trimethylsilyl-benzene (6.67 g, 29.1 mmol) in THF (130 mL) was cooled to ~ –85 °C (acetone–dry ice bath, additionally cooled *via* the addition of liquid nitrogen) with stirring and 2.5 M solution of *n*-butyllithium in hexane (11.8 mL, 29.40 mmol) was added dropwise. The reaction mixture was stirred at –85 to 80 °C for 30 minutes and then the cooling bath was removed and phenanthroline (3.93 g, 21.8 mmol) was added in one portion. The reaction mixture was stirred on an ice bath during 6 h (the temperature should not be higher than 10 °C) and then a concentrated solution of ammonium chloride (60 mL) was added. The organic layer was separated and the aqueous layer was extracted with ether (4 × 40 mL). The combined organic layers were dried over magnesium sulfate, filtered and evaporated under reduced pressure. The residue was dissolved in dichloromethane (30 mL) and magnesium (IV) oxide (22.76 g, 0.267 mol) was added in one portion. The reaction mixture was stirred overnight in an open flask and then filtered through a short plug of silica and evaporated. The oily residue was treated with hot petroleum ether, which was allowed to cool slowly to room temperature and decanted. The residue was washed with petroleum ether (3 × 20 mL) and dried yielding 5.94 g (83%) of the desired product as a yellow viscous oil. ^{1}H NMR ($CDCl_3$) δ: 0.32 (s, 9H), 7.62 (dd, J_1 = 8.0 Hz, J_2 = 4.4 Hz, 1H), 7.68 (d, J = 8.1 Hz, 2H), 7.75 and 7.80 (two d of AB system, J = 8.8 Hz, 2H), 8.09 (d, J = 8.4 Hz, 1H), 8.23 (dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, 1H), 8.27 (d, J = 8.2 Hz, 1H), 8.29 (d, J = 8.1 Hz, 2H), 9.22 (dd, J_1 = 4.1 Hz, J_2 = 1.7 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: –1.16, 120.6, 122.8, 126.2, 126.3, 127.1, 127.5, 129.0, 133.7, 136.0, 136.7, 139.9, 141.8, 146.1, 146.4, 150.4, 157.6. MS (FD): *m/z* Calcd for $C_{21}H_{20}N_2Si$ M^+: 328.5. Found 328.3. Calcd for $C_{21}H_{20}N_2S{\cdot}0.5H_2O$: C, 74.75; H, 6.27; N, 8.30. Found: C, 75.16; H, 6.31; N, 8.27%.

2,9-Bis(4-trimethylsilylphenyl)-1,10-phenanthroline (**2**): This compound was obtained analogously to **1**. After the oxidation step with manganese (IV) oxide, the crude product was purified on a silica column using ethyl acetate: petroleum ether (1 : 1 v/v) mixture as an eluant giving the desired compound in 63% yield (yellowish crystals). M.p. 282 °C. ^{1}H NMR ($CDCl_3$) δ: 0.35 (s, 18H), 7.75 (d, J = 7.9 Hz, 4H), 7.77 (s, 2H), 8.14 (d, J = 8.2 Hz, 2H), 8.29 (d, J = 8.2 Hz, 2H), 8.44 (d, J = 7.9 Hz, 4H). ^{13}C NMR ($CDCl_3$) δ: –1.07, 120.0, 126.0, 126.8, 128.0, 133.9, 136.8, 139.8, 141.9, 146.2, 156.9. MS (FD): *m/z* Calcd for $C_{30}H_{32}N_2Si_2$ M^+: 476.7. Found: 476.4. Anal. Calcd for $C_{30}H_{32}N_2Si_2$: C, 75.57; H, 6.77; N, 5.87. Found: C, 75.56; H, 6.87; N, 5.86%.

2-(4-Bromophenyl)-1,10-phenanthroline (**3**): A solution of **1** (0.184 g, 0.56 mmol) in dichloromethane (12 mL) was first pre-cooled to ~10 °C on an ice/water bath and bromine (0.296 g, 1.85 mmol) was added in one portion. The cooling bath was removed and the reaction mixture was stirred at room temperature for 6 h. During this period of time a yellow precipitate was formed. The reaction mixture was evaporated and dried under reduced pressure. The residue was dissolved in a mixture of ethyl acetate (30 mL), methanol (15 mL) and triethylamine (3 mL). The silica (~3 g) was added and the mixture was evaporated gently under reduced pressure and dried. The column chromatography (ethyl acetate and petroleum ether (2 : 1 v/v)) gave 0.131 g (70%) of **3** (white crystals). M.p. 179–180 °C (lit.[15] 187–189 °C). ^{1}H NMR (DMSO-D_6) δ: 7.80 (dd, *J*s can not be found due to the overlap with the next signal, 1H), 7.81 (d, J = 8.5 Hz, 2H), 8.00 and 8.03 (two d of AB system, J = 8.8 Hz, 2H), 8.42 (d, J = 8.5 Hz, 3H), 8.52 (dd, J_1 = 8.2 Hz, J_2 = 1.4 Hz, 1H), 8.60 (d, J = 8.5 Hz, 1H), 9.17 (dd, J_1 = 4.1 Hz, J_2 = 1.5 Hz, 1H). ^{13}C NMR (DMSO-D_6) δ: 120.2, 123.0, 123.9, 126.3, 126.5, 127.7, 129.1, 129.5, 131.9, 136.2, 137.0, 138.4, 146.1, 146.3, 150.4, 156.2.

2-(4-Iodophenyl)-1,10-phenanthroline (**4**): A 1M solution of iodochlorine (2.50 mL, 2.50 mmol) was added in one portion to a solution of **1** (0.275 g, 0.837 mmol) in dichloromethane (20 mL). A white precipitate was formed nearly immediately. The reaction mixture was stirred for 1.5 days. The reaction mixture was evaporated under reduced pressure to dryness. A mixture of ethyl acetate (40 mL), methanol (20 mL) and triethylamine (6 mL) was added and the residue was dissolved on gentle heating. The mixture was evaporated under reduced pressure. THF (30 mL) was added and the solution was filtered from the precipitate (triethylammonium chloride and iodide) then pre-adsorption on silica (1 g) was carried out. The column chromatography on silica using a mixture of ethyl acetate and petroleum ether (2 : 1 v/v) yielded 240 mg (75%) of **4** (yellowish crystals). M.p. 172–173 °C. ^{1}H NMR (DMSO-D_6) δ: 7.80 (dd, J_1 = 8.2 Hz, J_2 = 4.0 Hz, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.99 and 8.03 (two d of AB system, J = 8.8 Hz, 2H), 8.25 (d, J = 8.2 Hz, 2H), 8.40 (d, J = 8.5 Hz, 1H), 8.51 (dd, J_1 = 8.2 Hz, J_2 = 1.2 Hz, 1H), 8.59 (d, J = 8.5 Hz, 1H), 9.17 (dd, J_1 = 4.1 Hz, J_2 = 1.5 Hz, 1H). ^{1}H NMR ($CDCl_3$) δ: 7.70 (dd, J_1 = 8.2 Hz, J_2 = 4.1 Hz, 1H), 7.84 and 7.87 (two d of AB system, J = 8.8 Hz, 2H), 7.93 (d, J = 8.2 Hz, 2H), 8.12 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 8.5 Hz, 2H), 8.32 (dd, J_1 = 8.2 Hz, J_2 = 1.2 Hz, 1H), 8.36 (d, J = 8.4 Hz, 1H), 9.29 (dd, J_1 = 4.4 Hz, J_2 = 1.7 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 96.0, 120.2, 123.0, 126.4, 126.5, 127.7, 129.1, 129.6, 136.3, 137.0, 137.9, 138.9, 145.9, 146.0, 150.3, 156.3. MS (FD): *m/z* Calcd for $C_{18}H_{11}N_2I$ M^+: 382.2. Found: 382.0. Anal. Calcd for $C_{18}H_{11}N_2I$: C, 56.57; H, 2.90; N, 7.33. Found: C, 56.74; H, 2.89; N, 7.33%.

2,9-Bis(4-bromophenyl)-1,10-phenanthroline (**5**): The compound was obtained analogously to **3** using the same ratio of bromine to **2**, with the yield of 83% (yellowish crystals). M.p. 222–223 °C (lit.[15] 219–221 °C). ^{1}H NMR (DMSO-D_6) δ: 7.83 (d, J = 8.5 Hz, 4H), 8.02 (s, 2H), 8.43 (d, J = 8.4 Hz, 2H), 8.48 (d, J = 8.5 Hz, 4H), 8.60 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 119. 8, 124.1, 126.2, 128.1, 129.1, 132.0, 137.1, 138.2, 146.9, 155.7.

2,9-Bis(4-iodophenyl)-1,10-phenanthroline (**6**): The compound was obtained analogously to **4** using 3.6 equivalents of iodochlorine. The crude product was purified on silica column using a mixture of ethyl acetate and petroleum ether (1 : 1 v/v) giving a yellowish crystalline compound with the yield of 91%. M.p. 233–235 °C (with decomp.). ^{1}H NMR (DMSO-D_6) δ: 8.00 (d, J = 9.1 Hz, 4H), 8.01 (s, 2H), 8.30 (d, J = 8.2 Hz, 4H), 8.41 (d, J = 8.2 Hz, 2H), 8.60 (d, J = 8.2 Hz, 2H). ^{13}C NMR (DMSO-D_6) δ: 96.9, 119.9, 126.3, 128.0, 129.3, 137.7, 138.0, 144.7, 154.3. MS (FD): *m/z* Calcd for $C_{24}H_{14}N_2I_2$ M^+: 584.2. Found: 584.3. Anal. Calcd for $C_{24}H_{14}N_2I_2$: C, 49.34, H, 2.42; N, 4.80. Found: C, 49.42; H, 2.42; N, 4.80%.

2-(4'-(4''-Pyridyl)phenyl)-1,10-phenanthroline (**7**): A solution of potassium *tert*-butoxide (0.728 g, 6.50 mmol) in water (3 mL) was added in one portion to a solution of **3** (0.234 g, 0.698 mmol) and tetrakis(triphenylphosphine) palladium(0) (81 mg, 69.8 μmol) in 1,2-dimethoxyethane (8 mL) and the mixture was purged with nitrogen for 10 min. The reaction mixture was stirred at 84 °C for 12 h under a nitrogen atmosphere. Then water (50 mL) was added. The precipitate was filtered off, washed with water (3 × 10 mL) and dried. The residue was pre-adsorbed on silica (6 g) and eluted using mixture of tetrahydrofuran and methanol (1 : 1 v/v). 180 mg (77% yield) of the desired product were obtained. M.p. 221–223 °C. ^{1}H NMR (DMSO-D_6) δ: 7.80 (dd, J_1 = 8.2 Hz, J_2 = 4.4 Hz, 1H), 7.81 (d, J = 6.2 Hz, 2H), 7.99 and 8.02 (two d of AB system, J = 8.8 Hz, 2H), 8.04 (d, J = 8.2 Hz, 2H), 8.45 (d, J = 8.5 Hz, 1H), 8.50 (dd, J_1 = 8.2 Hz, J_2 = 1.5 Hz, 1H), 8.59 (d, J = 8.2 Hz, 3H), 8.68 (d, J = 6.2 Hz, 2H), 9.19 (dd, J_1 = 4.1 Hz, J_2 = 1.8 Hz, 1H). ^{13}C NMR (DMSO-D_6) δ: 120.4, 121.4, 123.7, 126.7, 127.0, 127.5, 128.0, 128.3, 129.2, 136.6, 137.7, 138.2, 139.8, 145.6, 145.9, 146.6, 150.3, 150.6, 155.0. HRMS (ESI): *m/z* Calcd for $C_{23}H_{16}N_3$ $[M + H]^+$: 334.1341, Calcd for $C_{23}H_{15}N_3Na$ $[M + Na]^+$: 356.1161, Found: 334.1363 (14%), 356.1176 (100%). Anal. Calcd for $C_{23}H_{16}N_3{\cdot}0.25H_2O$: C, 81.75; H, 4.62; N, 12.43. Found: C, 81.98; H, 4.72; N, 12.23%.

2,9-Bis(4'-(4''-pyridyl)phenyl)-1,10-phenanthroline (**8**): A mixture of **5** (85 mg, 0.173 mmol), 4-pyridineboronic acid (64 mg, 0.520 mmol) and potassium hydroxide (57 mg, 0.867 mmol) in a mixture of dimethylsulfoxide (12 mL) and water (1.2 mL) had been first heated gently until all reagents were dissolved. The mixture was cooled to room temperature, purged with nitrogen and tetrakis (triphenylphosphine)palladium(0) (20 mg, 17.3 μmol) was added and the reaction mixture was stirred at 45 °C for 2 h under a nitrogen atmosphere. Then water (50 mL) was added and the precipitate formed was filtered off and dried. Then the residue was dissolved in a mixture of THF and methanol (1:1, v/v), silica (5 g) was added and the solvent was carefully evaporated under reduced pressure.

After the solid was dried, column chromatography on silica using first a mixture of THF: petroleum ether (2:1, v/v) and then THF, gave 72 mg (86%) of **8** (~85% purity, that could not be improved under the conditions applied). M.p. >245 °C (decomposition). ^{1}H NMR (DMSO-D_6) δ: 7.87 (d, J = 5.8 Hz, 4H), 8.05 (s, 2H), 8.11 (d, J = 8.3 Hz, 4H), 8.53 and 8.64 (two d of AB system, J = 8.4 Hz, 4H), 8.71 (d, J = 5.8 Hz, 4H), 8.72 (d, J = 8.3 Hz, 4H). ^{1}H NMR (THF-D_8) δ: 7.72 (d, J = 4.6 Hz, 4H), 7.88 (s, 2H), 7.99 (d, J = 7.4 Hz, 4H), 8.36 (d, J = 8.4 Hz, 2H), 8.44 (d, J = 8.4 Hz, 2H), 8.66 (d, J = 4.6 Hz, 4H), 8.75 (d, J = 7.4 Hz, 4H). ^{13}C NMR (DMSO-D_6) δ: 120.1, 121.1, 126.3, 127.3, 127.9, 128.0, 137.5, 137.9, 139.5, 145.3, 146.3, 150.2, 154.5. ^{13}C NMR (THF-D_8) δ: 120.4, 121.9, 127.0, 128.0, 129.0, 129.2, 137.6, 139.8, 141.2, 147.4, 148.0, 151.3, 156.1. HRMS (ESI): *m/z* Calcd for $C_{34}H_{23}N_4$ $[M + H]^+$: 487.1918, Calcd for $C_{34}H_{22}N_4Na$ $[M + Na]^+$: 509.1738. Found: 487.1945 (10%), 509.1741 (100%).

2-(4'-(4''-Pyridyl-ethynyl)phenyl)-1,10-phenanthroline (**9**): A mixture of mono iodo derivative **4** (266 mg, 0.696 mmol), 4-ethynylpyridine (106 mg, 1.03 mmol) [the commercially available hydrochloride can be used instead] in DMF (2 mL) and di-*iso*-propylamine (1 mL) was purged with nitrogen for 10 min, then tetrakis (triphenylphosphine)palladium(0) (82.4 mg, 70.0 μmol) was added and the reaction mixture was stirred at 60 °C (temperature of the oil bath) for 3 h and then cooled to the room temperature. Water (20 mL) was added and the precipitate formed was filtered off, pre-adsorbed on silica and purified on a silica column (THF : petroleum ether 3 : 2 v/v mixture to wash first by-products, then pure THF), that gave 150 mg (60%) of the desired product. M.p. 241–243 °C. ^{1}H NMR (DMSO-D_6) δ: 7.59 (d, J = 6.0 Hz, 2H), 7.82 (dd, J_1 = 8.0 Hz, J_2 = 4.3 Hz, 1H), 7.86 (d, J = 8.4 Hz, 2H), 8.01 and 8.05 (two d of AB system, J = 8.8 Hz, 2H), 8.48 (d, J = 8.5 Hz, 1H), 8.52 (dd, J_1 = 8.1 Hz, J_2 = 1.7 Hz, 1H), 8.57 (d, J = 8.4 Hz, 2H), 8.62 (d, J = 8.5 Hz, 1H), 8.66 (d, J = 6.0 Hz, 2H), 9.19 (dd, J_1 = 4.3 Hz, J_2 = 1.7 Hz, 1H). ^{1}H NMR ($CDCl_3$) δ: 7.41 (d, J = 6.0 Hz, 2H), 7.64 (dd, J_1 = 8.0 Hz, J_2 = 4.4 Hz, 1H), 7.72 (d, J = 8.2 Hz, 2H), 7.78 and 7.81 (two d of AB system, J = 8.8 Hz, 2H), 8.11 (d, J = 8.4 Hz, 1H), 8.25 (dd, J_1 = 8.0 Hz, J_2 = 1.7 Hz, 1H), 8.32 (d, J = 8.4 Hz, 2H), 8.61 (d, J = 8.5 Hz, 1H), 9.24 (dd, J_1 = 4.4 Hz, J_2 = 1.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 88.0, 94.0, 120.5, 122.9, 123.0, 125.5, 126.3, 126.7, 127.8, 127.9, 129.1, 131.4, 132.3, 136.1, 137.0, 140.1, 146.2, 146.4, 149.8, 150.5, 156.2. MS (FD): *m/z* Calcd for $C_{25}H_{15}N_3$ M^+: 357.4. Found: 357.2. Anal. Calcd for $C_{25}H_{15}N_3$: C, 84.01; H, 4.23; N, 11.76. Found: C, 83.97; H, 4.28; N, 11.68%.

2,9-Bis(4'-(4''-pyridyl-ethynyl)phenyl)-1,10-phenanthroline (**10**). A mixture of **6** (159 mg, 0.272 mmol), 4-ethynylpyridine (70.2 mg, 0.68 mmol) [the commercially available hydrochloride can be used instead] in DMF (2 mL) and di-*iso*-propylamine (4 mL), was purged with nitrogen during 10 minutes, then tetrakis(triphenylphosphine) palladium(0) (31.5 mg, 27.2 μmol) was added and the reaction mixture was stirred at 60 °C (temp. of the oil bath) for 3 h and then cooled to the room temperature. Diethyl ether (25 mL) was added and the precipitate formed was filtered off, washed with ether (3 × 3 mL), dried and washed with water. After drying, 100 mg (66%) of **10** were obtained. M.p. >220 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ: 7.42 (d, J = 6.0 Hz, 4H), 7.77 (d, J = 8.3 Hz, 4H), 7.81 (s, 2H), 8.16 (d, J = 6.0 Hz, 2H), 8.33 (d, J = 8.4 Hz, 2H), 8.49 (d, J = 8.3 Hz, 4H), 8.63 (d, J = 6.0 Hz, 4H). ^{1}H NMR (DMSO-D_6) δ: 7.59 (d, J = 5.8 Hz, 4H), 7.89 (d, J = 8.5 Hz, 4H), 8.06 (s, 2H), 8.50 (d, J = 8.5 Hz, 2H), 8.60–8.70 (m, 10H). ^{1}H NMR (THF-D_8) δ: 7.43 (d, J = 5.8 Hz, 4H), 7.78 (d, J = 8.2 Hz, 4H), 7.89 (s, 2H), 8.33 (d, J = 8.4 Hz, 2H), 8.43 (d, J = 8.4 Hz, 2H), 8.59 (d, J = 5.8 Hz, 4H), 8.66 (d, J = 8.2 Hz, 4H). ^{13}C NMR ($CDCl_3$) δ : 88.1, 94.0, 120.1, 123.1, 125.6, 126.4, 127.6, 128.2, 131.5, 132.4, 137.1, 140.0, 146.1, 149.8, 155.7. HRMS (ESI): *m/z* Calcd for $C_{38}H_{23}N_4$ $[M + H]^+$: 535.1918. Found: 535.1921. Anal. Calcd for $C_{38}H_{22}N_4 \cdot 0.5H_2O$: C, 83.96; H, 4.17; N, 10.30. Found: C, 83.53; H, 4.56; N, 9.18%.

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