A Short Synthetic Route to 4,7-Dihalogenated 1,10-Phenanthrolines with Additional Groups in 3,8-Position: Soluble Precursors for Macrocyclic Oligophenanthrolines

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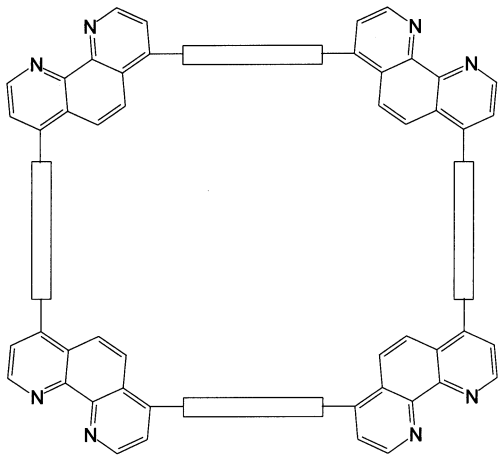
A short and efficient preparation of 3,8-dialkylated or 3,8-diarylated 1,10-phenanthrolines-4,7-diones is described. Their chlorination or bromination furnishes the corresponding, highly soluble 4,7-dichloro- or 4,7-dibromo phenanthrolines that constitute versatile precursors to macrocyclic oligophenanthrolines with *exo*-coordination sites. They can be further reacted by nucleophilic aromatic substitution or Heck-coupling reactions.

Introduction

Over many decades 1,10-phenanthrolines have been used as important ligands for a vast amount of metal complexes[1] that play an important role in many fields of chemistry, e.g. in analytical chemistry,[2] in homogenous catalysis,[3] as chemical nucleases[4] and as versatile electron transfer reagents.[5] Moreover, phenanthrolines, as well as bipyridines, occupy an increasingly important part in supramolecular coordination chemistry,[6][7] which has stimulated the preparation of phenanthroline ligands with different substitution patterns. A comprehensive analysis of the phenanthroline literature, however, reveals that most phenanthroline derivatives carry substituents in the 2,9-position because such compounds are easily accessible from the parent phenanthroline itself. On the contrary, much less is known about 4,7- or 3,8-disubstituted[8][9] compounds although they may serve as versatile building blocks for the construction of linear or macrocyclic oligophenanthrolines.

We have recently become interested in the coordination chemistry of macrocyclic oligophenanthroline ligands **A** with *exo*-coordination sites because of their potential for the convergent construction of redoxactive cubes and channel structures. Herefore, rigid and planar oligophenanthrolines would be most interesting.[10][11]

Our first approach to the macrocyclic oligophenanthrolines **A**[11] commenced from 4,7-dichloro- and 4,7-dibromophenanthroline.[12][13] After Heck coupling of various bisalkynes to the 4,7-position of phenanthroline the subsequent oxidative coupling led to macrocyclic oligophenanthrolines of type **A** with *exo*-coordination sites that however exhibited such a low solubility thus preventing any further work. This frustrating finding propelled our search[14] for an efficient synthetic route to novel phenanthroline building blocks with chloro- and bromo substituents in 4,7-position and appropriate alkyl groups in 3,8-position to increase solubility. Such substrates should be reactive in nucleophilic aromatic substitution reactions[15] as well as in Heck or Kumada[16] couplings thus leading to a large number of 4,7-disubstituted phenanthrolines.



A

Results and Discussion

For devising an efficient preparation of soluble phenanthrolines particular attention had to be paid to the fact that separation of 4,7-disubstituted phenanthrolines by column chromatography is in general quite difficult because of their poor eluation behavior. Therefore, high yield reactions and simple work-up schemes are highly desirable. To minimize the number of transformations with phenanthrolines the substituents in 3,8-position should be attached with the construction of the phenanthroline itself. In addition, a double-cyclization-strategy starting from 1,2-diaminobenzene derivatives instead of using a mono-cyclization-strat-

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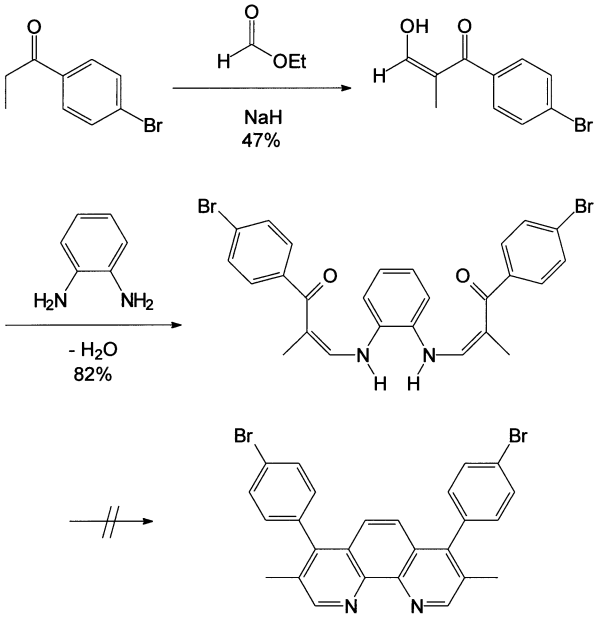
egy commencing from the corresponding quinoline system appeared more rewarding.[17]

While the preparation of such compounds seemed to be trivial in the beginning in light of several strategies to prepare phenanthrolines and quinolines[18] we rapidly learned that the modification of many literature approaches failed in providing the substitution pattern as desired by us. For example, to avoid halogenation directly at the heterocycle we wanted to prepare a phenanthroline system with *p*-bromophenyl substituents in 4,7-position by following a procedure of Cook and Thomson.[17] They had used this approach to synthesize 4,7-diphenylphenanthrolines without substituents in positions 3 and 8. Although using different temperatures and various acids, such as concentrated H_2SO_4, polyphosphoric acid or Lewis acids as $AlCl_3$, $SnCl_4$, or $TiCl_4$, the cyclization of 1,2-bis(β-4-bromobenzoyl-α-methylvinylamino)benzene could not be effected (Scheme 1). After workup the only product that could be isolated was 4-bromopropiophenone.

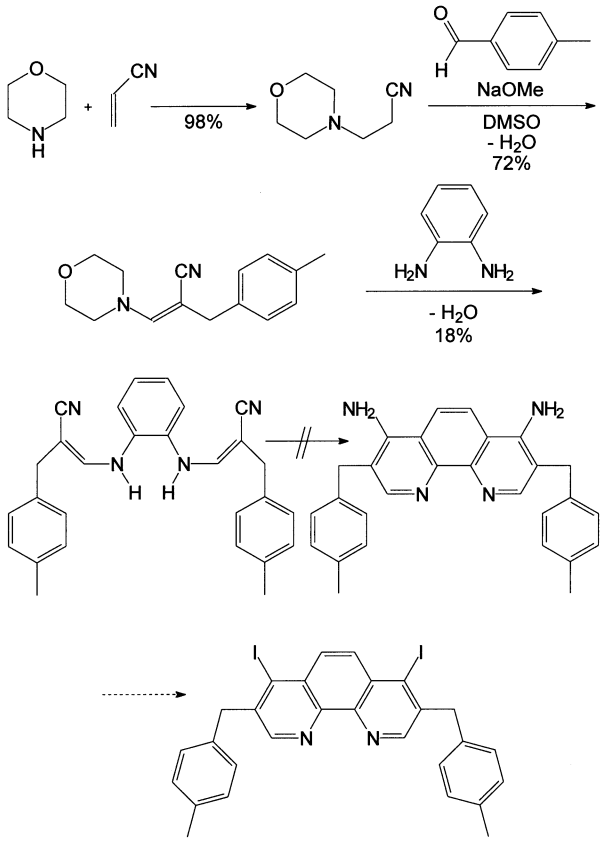
Scheme 1



Likewise, the final cyclization failed in a second synthetic approach which was designed along a preparation of aminoquinolines devised by Lamant and Le Moine[18] and also used by Schäfer and Gewald.[19] We were not able to detect any traces of a phenanthroline product after treatment of the bisenamine with Lewis acids such as $AlCl_3$ or $SnCl_4$ in refluxing chlorobenzene. Heating the reactants without solvent at 140−160°C did not reveal the desired products as judged by usual spectroscopic methods (Scheme 2). Presumably, the nitrile reacts after activation by the Lewis acid with the amino functionality, a process that has been described by Okamoto and Ueda.[20]

Much more successful was our last attempt. Inspired by a synthetic approach to 3,8-diaryl-4,7-dihydroxyphenanthroline by Case[21] and to 1,2,3,4,9,10,11,12,13,14-decahydrodibenzo[*b*,*j*]-1,10-phenanthroline-5,8-dione (**4g**) by

Scheme 2



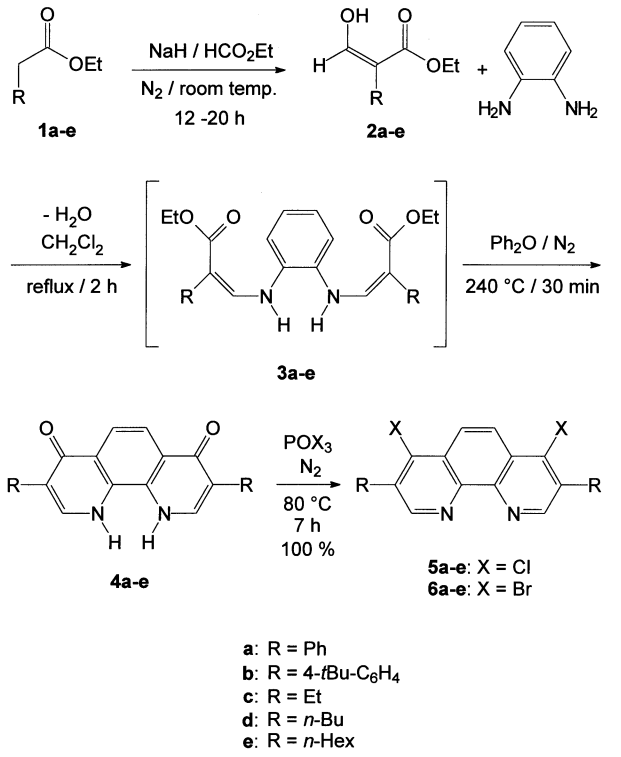
Bell[16] which included several low yield and time-consuming steps (up to 3 months) we succeeded to develop an efficient procedure to the new desired 3,8-dialkyl-4,7-dihalogeno-phenanthrolines. By this route, 10 g of phenanthrolines **5c−e** and **6c−e** can be readily prepared within 3 days.

We first prepared the α-formylacetic esters **2a** and **2b** as described by Marchesini[22] and the α-formylacetic esters **2c−2e** by the method of Spengler.[23] After hydrolysis and an acid/base separation the crude products could be used without further purification.

While Case[13] had to react the neat starting materials over phosphorous pentoxide for several days in a desiccator, it was found that the transformation of **2a−e** with 1,2-diaminobenzene in dichloromethane at reflux temperature in a Dean-Stark apparatus afforded the corresponding 1,2-bis(β-ethoxycarbonyl-α-alkyl/aryl-vinylamino)benzene **3a−3e** after a few hours in nearly quantitative yield (as detected by ^{1}H-NMR spectroscopy).

However, this method failed for the preparation of **3f** and **3g**. After several hours of refluxing **2f** or **2g** with 1,2-diaminobenzene in dichloromethane, only the mono condensation product and the 2-methylbenzimidazole could be detected. In no case the desired compounds were observed. Since for the latter two systems, the intramolecular cyclization to 2-methylbenzimidazole proved obviously to be faster at higher temperature than the second condensation, it was necessary to use the established procedure as proposed by Bell.[16] After mixing the reactants, adding catalytic

Scheme 3



Scheme 4

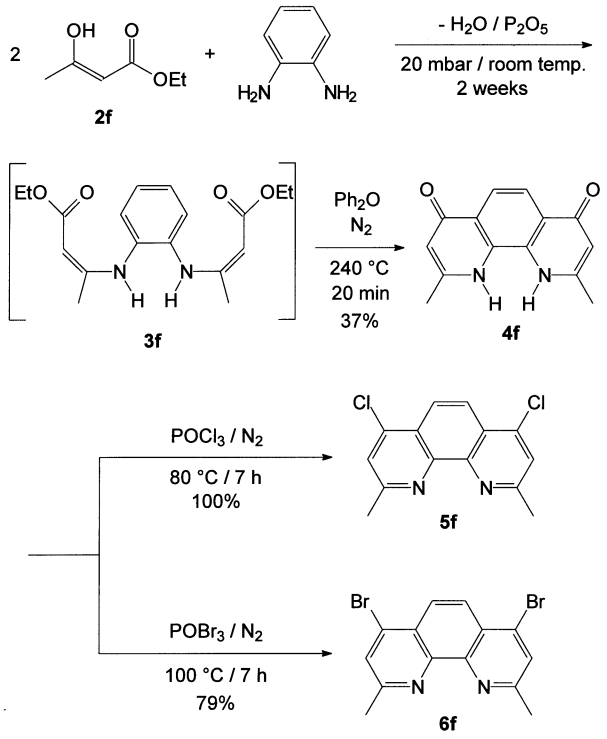
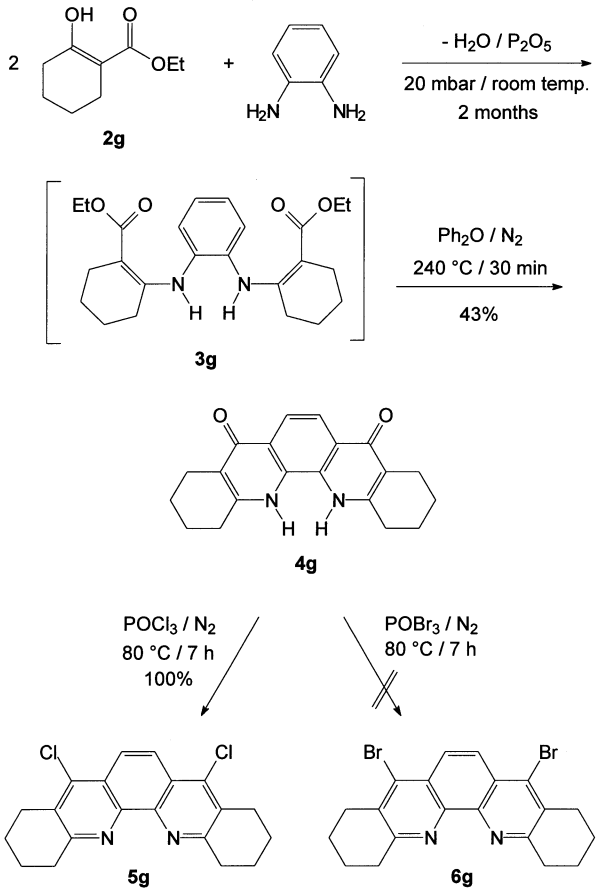


Table 1. Reaction times and yields of α-formylacetic esters **2** and phenanthroline-4,7-diones **4** (see Scheme 3)

Product	R	Reaction time	Yield [%]
2a	Ph	18 h	44
2b	4-*t*Bu-C_6H_4	12 h	67
2c	Et	20 h	27
2d	*n*Bu	20 h	31
2e	*n*Hex	20 h	28
4a	Ph	30 min	71[a]
4b	4-*t*Bu-C_6H_4	30 min	61[a]
4c	Et	30 min	38[a]
4d	*n*Bu	30 min	69[a]
4e	*n*Hex	30 min	56[a]

[a] Based on 1,2-diaminobenzene.

Scheme 5



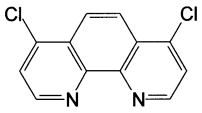
amounts of HCl gas and storage over phosphorous pentoxide at room temperature and at reduced pressure **3f** or **3g** slowly formed (2 weeks to 2 months).

Compounds **3a**−**3g** were all cyclized without any purification in diphenylether at 240°C to furnish the corresponding 1,10-phenanthroline-4,7-diones **4a**−**4g** in satisfactory yield (Table 1). This reaction is very sensitive towards reaction times longer than 30 minutes and to high concentrations, resulting in lower product yields, a behaviour which was also described by Bell.[16] As all compounds **4a**−**4g** proved to be highly insoluble in organic solvents, all impurities could readily removed by extraction with acetone. To obtain the corresponding 4,7-dichloro-1,10-phenanthrolines **5a**−**g** phosphoryl chloride at 80°C proved to be the reagent of choice.[16] The yields were much higher than when using PCl_3/PCl_5 as described by Case[21] for the prep-

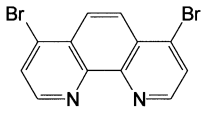
aration of 4,7-dichloro-3,8-diphenyl-1,10-phenanthroline (**5d**) in 27% yield. Quantitative yields of **5a–g** were obtained when the reactants completely dissolved in phosphoryl chloride during heating.

Inspired by this discovery we prepared the analogous 4,7-dibromo-1,10-phenanthrolines equally by applying a great excess of phosphoryl bromide (instead of using the typical mixture of phosphorous pentabromide in phosphorous tribromide[13][21]). In all cases the reactants dissolved completely during heating to finally afford quantitatively compounds **6a–e**. With **4f** a clear solution was obtained at the beginning of the reaction, but after several minutes a voluminous solid precipitated. Only 79 % of **6f** were obtained. Surprisingly, the conversion of **4g** to **6g** by the analogous method failed absolutely although **5g** was readily obtained. Only insoluble products resulted.

After we had developed a successful preparation route to 3,8-dialkyl-4,7-dibromo-1,10-phenanthrolines **6c–f**, we were interested how the solubility of the compounds depended on the length of the attached alkyl chains.



5h



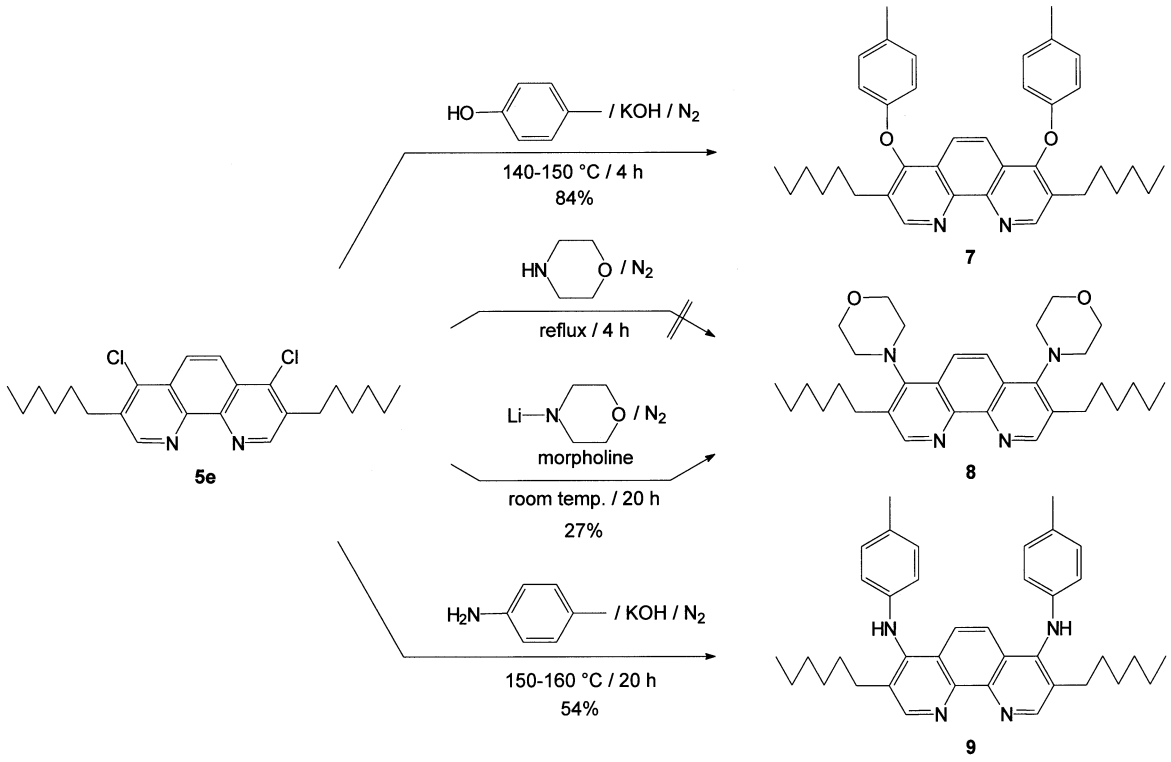
6h

Table 2. Solubility of 4,7-dibromophenanthroline (**6h**) and 3,8-alkylated 4,7-dibromophenanthrolines (**6c–e**) in chloroform at 20°C

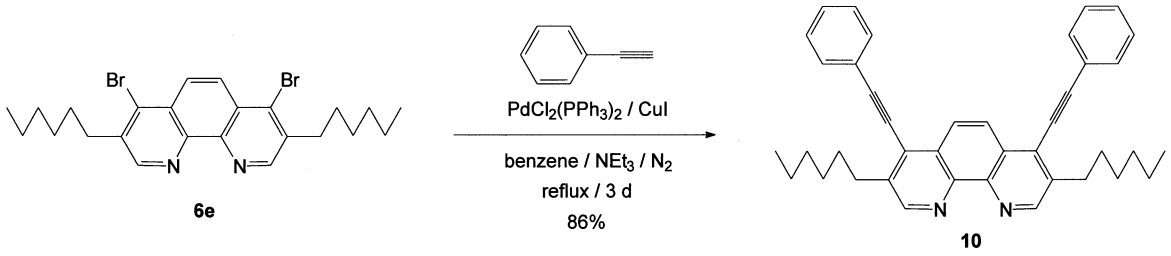
Compound	[g·l^{-1}]	[mol·l^{-1}]
4,7-dibromo-1,10-phenanthroline (**6h**)	3.889	0.012
4,7-dibromo-3,8-diethyl-1,10-phenanthroline (**6c**)	241.3	0.612
4,7-dibromo-3,8-di-*n*-butyl-1,10-phenanthroline (**6d**)	415.3	0.922
4,7-dibromo-3,8-di-*n*-hexyl-1,10-phenanthroline (**6e**)	1079	2.131

We found that the solubility of the phenanthrolines increased drastically by adding ethyl groups in 3,8-position

Scheme 6



Scheme 7



and augmented even further in presence of longer alkyl chains (see Table 2). With 4,7-dibromo-3,8-di-*n*-hexyl-1,10-phenanthroline (**6e**) we have prepared a phenanthroline building block the solubility of which reaches nearly 200-fold the value of the 4,7-dibromo-1,10-phenanthroline (**6h**). This observation proposes that macrocyclic systems incorporating the 3,8-di-*n*-hexylphenanthroline units should equally exhibit increased solubility.[24]

With the 4,7-dichloro- and dibromophenanthrolines **5** and **6** at hand, it became important to test whether the presence of the 3,8-dialkyl groups would severely change their chemical reactivity towards nucleophilic aromatic substitution and Heck coupling reactions. As a reference point we chose the analogous reactions with 4,7-dichlorophenanthroline (**5h**) and 4,7-dibromophenanthroline (**6h**).

We observed that there was no or little difference for nucleophilic substitution with phenolates or primary amines as probed with 4,7-dichlorophenanthroline **5e**.[5][15] After stirring **5e** for several hours in a large excess of *p*-cresole and KOH or with *p*-toluidine at a temperature of 140−160°C a quantitative conversion was registered. After purification we were able to isolate **7** in 84% and **9** in 54% yield. However, a different behavior is observed with secondary amines. While morpholine reacted nearly quantitatively with 4,7-dichloro-1,10-phenanthroline (**5h**) after several hours at reflux temperature, no reaction was observed after treatment of **5e** with morpholine under the same reaction conditions. To accomplish disubstitution by morpholine it was necessary to react lithium morpholinide, generated by treatment of dry morpholine with *n*-butyllithium, with **5e** for several hours at room temperature. The low yield (27%) of **8** is caused by incomplete conversion.

In addition, one may worry about the utility of phenanthroline **6e** in Heck-coupling reactions because of the alkyl substituents in 3,8-position. However, when **6e** was treated with an excess of phenylacetylene in the presence of catalytic amounts of $PdCl_2(PPh_3)_2$ and CuI the bisalkynylated phenanthroline **10** was afforded in 86% yield. This yield is close to that of the analogous Heck-coupling of the parent compound 4,7-dibromo-1,10-phenanthroline (95%).[11]

In conclusion, we have developed a fast and efficient synthetic route to highly soluble 3,8-disubstituted 4,7-dichloro- and 4,7-dibromophenanthrolines. Despite the presence of alkyl groups in position 3 and 8, nucleophilic aromatic substitution reactions and Heck couplings are still possible with high yields.

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Experimental Section

Commercial reagents were purchased from standard chemical suppliers and were used without further purification. − Melting points: Measured by DSC; Dupont 910. − IR: Perkin-Elmer 1605 FT-IR. − NMR: Bruker AC 200 (200 MHz and 50 MHz, for ^1H and ^{13}C, respectively). For ^1H NMR and ^{13}C NMR, $CDCl_3$ was used as solvent, TMS as internal standard.

4-tert-Butylphenylacetic Ester (**1b**) was prepared as described in ref.[25]. The *α-formylacetic esters* **2a−e** were prepared according to literature procedures[22][23] and used as crude products.

General Procedure for the Preparation of 1,2-Bis(β-ethoxycarbonyl-α-alkyl/aryl-vinylamino)benzene **3a−e**: 1,2-diaminobenzene (33 mmol) was added to a solution of **2a−e** (75 mmol) in 100 ml of dichlormethane. After heating to reflux for 2 h in a Dean-Stark apparatus, the solvent was evaporated off. The oily brown residue could be used in the following reactions without purification.

1,2-Bis(β-ethoxycarbonyl-β-methylvinylamino)benzene (**3f**) and **3g** were prepared according to the literature[16] and used without any purification.

2-Methylbenzimidazol (**3i**)[26]: A mixture of ethyl 2-acetyl heptanoate (10.0 g, 50.0 mmol), 1,2-diaminobenzene (2.60 g, 24.0 mmol), and $CaSO_4$ Φ 1/2 H_2O (12.3 g, 84.7 mmol) in 35 ml of ethanol was refluxed for 17 h under nitrogen. After filtering the hot reaction mixture over celite the solvent was evaporated. The residue was washed twice with 15 ml of petroleum ether 50−70 and dried in vacuo to furnish **3i** in nearly quantitative yield. m.p. 176°C. − IR (KBr): $\tilde{\nu}$ = 3097 cm^{-1}, 3063, 2995, 2917, 2848, 2786, 2678, 2541, 1623, 1557, 1450, 1417, 1386, 1361, 1271, 1219, 1027, 834, 733. − ^1H NMR ($CDCl_3$): δ = 2.66 (s, 3 H, Me), 7.18−7.27 (m, 2 H, 4-, 7-H), 7.52−7.61 (m, 2 H, 5-, 6-H), 10.20 (s, 1 H, N-H). − ^{13}C NMR ($CDCl_3$): δ = 14.9 (q, Me), 114.5 (d, C-5, -6), 122.1 (d, C-4, -7), 138.7 (s, C-3a, -7a), 151.3 (s, C-2).

General Procedure for the Preparation of 3,8-Dialkyl/diaryl-1,10-phenanthroline-4,7-diones (**4a−g**): 8−12 g of the crude oil (**3a−e**) or solid (**3f**, **g**) was added under nitrogen to diphenylether (300 ml) at a temperature of 200°C. The temperature was raised to 240−250°C for 30 min while a vigorous stream of nitrogen was bubbled through the mixture. The reaction solution was allowed to cool down thus furnishing a colorless precipitate. Petroleum ether 50−70 (200 ml) was added, the precipitate filtered off and washed twice with 100 ml of diethylether. The colorless residue was suspended in acetone (100 ml) and heated to reflux for 15 min. The precipitate was again filtered off, washed with acetone and dried in vacuo to yield **4a−f** as a highly unsoluble colorless solid in 37−71% (Table 1).

3,8-Diphenyl-1,10-phenanthroline-4,7-dione (**4a**)[21]: m.p. >300°C. − IR (KBr): $\tilde{\nu}$ = 3343 cm^{-1} (NH), 3052, 1630, 1577, 1518, 1444, 1341, 1297, 1222, 1087, 1028, 1005, 899, 884, 778, 756, 696.

3,8-Di-(4-tert-butylphenyl)-1,10-phenanthroline-4,7-dione (**4b**): m.p. >300°C. − IR (KBr): $\tilde{\nu}$ = 3338 cm^{-1} (NH), 3241, 3185, 3132, 3049, 2959, 2896, 1664, 1631, 1598, 1549, 1486, 1455, 1396, 1366, 1304, 1232, 1212, 1119, 1081, 901, 831, 766, 684, 645. − $C_{32}H_{32}N_2O_2$ (476.62): calcd. C 80.64, H 6.77, N 5.88; found C 80.36, H 6.65, N 5.95.

3,8-Diethyl-1,10-phenanthroline-4,7-dione (**4c**): m.p. >300°C. − IR (KBr): $\tilde{\nu}$ = 3352 cm^{-1} (NH), 3248, 3186, 3049, 2960, 1675, 1625, 1590, 1502, 1299, 1199, 1079, 1014, 898, 844, 736, 687. − $C_{16}H_{16}N_2O_2$ (268.32): calcd. C 71.62, H 6.01, N 10.44; found C 71.36, H 5.86, N 10.34.

3,8-Di-n-butyl-1,10-phenanthroline-4,7-dione (**4d**): m.p. 221°C. − IR (KBr): $\tilde{\nu}$ = 3340 cm^{-1} (NH), 3252, 3181, 3063, 2957, 2861, 1670, 1588, 1543, 1499, 1409, 1200, 907, 750, 730. − $C_{20}H_{24}N_2O_2$ (324.42): calcd. C 74.05, H 7.46, N 8.63; found C 73.82, H 7.48, N 8.56.

3,8-Di-n-hexyl-1,10-phenanthroline-4,7-dione (**4e**): m.p. 195°C. − IR (KBr): $\tilde{\nu}$ = 3344 cm^{-1} (NH), 3253, 3184, 3063, 2956, 2923, 2853, 1670, 1609, 1558, 1491, 1409, 1218, 1201, 908, 835, 751, 722.

− $C_{24}H_{32}N_2O_2$ (380.53): calcd. C 75.75, H 8.48, N 7.36; found C 75.68, H 8.80, N 7.30.

2,9-Dimethyl-1,10-phenanthroline-4,7-dione (**4f**)[27]: m.p. >300°C. − IR (KBr): $\tilde{\nu}$ = 3368 cm^{-1} (NH), 3244, 3083, 2982, 1679, 1596, 1560, 1508, 1431, 1375, 1321, 1234, 1039, 833, 728, 692. − ^1H NMR (NaOD/D_2O): δ = 1.63 (s, 6 H, Me), 5.59 (s, 2 H, 3-, 8-H), 7.01 (s, 2 H, 5-, 6-H). − ^{13}C NMR (NaOD/D_2O): δ = 25.7 (q, Me), 111.6 (d, C-5, -6), 118.7 (d, C-3, -8), 125.2 (s, C-4a, -6a), 147.3 (s, C-4, -7), 160.5 (s, C-1a, -10a), 174.4 (s, C-2, -9). − $C_{14}H_{12}N_2O_2 \cdot 2\ H_2O$ (276.29): calcd. C 60.86, H 5.84, N 10.14; found C 60.99, H 5.45, N 10.10.

1,2,3,4,9,10,11,12,13,14-Decahydrodibenzo[b,j]-1,10-phenanthroline-5,8-dione (**4g**)[16]: m.p. >300°C. − IR (KBr): $\tilde{\nu}$ = 3342 cm^{-1} (NH), 3239, 3069, 1671, 1578, 1546, 1524, 1492, 1449, 1394, 1316, 1216, 1162, 1069, 814, 750, 704.

General Procedure for the Preparation of 4,7-Dichloro-3,8-dialkyl/diaryl-1,10-phenanthrolines (**5a−5e**), *4,7-Dichloro-2,9-dimethyl-1,10-phenanthrolines* (**5f**) *and 5,8-Dichloro-1,2,3,4,9,10,11,12-octahydrodibenzo[b,j]-1,10-phenanthroline* (**5g**): 3,8-Dialkyl/diaryl-1,10-phenanthroline-4,7-dione **4a−g** (4.00 mmol) was added under nitrogen to phosphoryl chloride (30 ml) and the resulting solution was stirred at 80°C for 7 h. The hot solution was then slowly added to a well stirred mixture of ice (100 g) in 200 ml of water. After stirring for 15 min, chloroform (50 ml) was added and the resulting two-layer-system was carefully brought to pH 13−14 by adding concentrated KOH solution. The organic layer was separated and the residue was extracted twice with 50 ml of chloroform. The combined organic layers were washed with 100 ml of concentrated KOH solution and dried with $MgSO_4$. After evaporation of the solvent the 4,7-dichloro-3,8-dialkyl/diaryl-1,10-phenanthrolines were isolated as colorless solids in quantitative yield.

4,7-Dichloro-3,8-diphenyl-1,10-phenanthroline (**5a**): m.p. 235°C. − IR (KBr): $\tilde{\nu}$ = 3039 cm^{-1}, 2960, 1604, 1540, 1470, 1415, 1357, 816, 761, 698, 594, 560. − ^1H NMR ($CDCl_3$): δ = 7.51−7.61 (m, 10 H, Ph), 8.67 (s, 2 H, 5-, 6-H), 9.14 (s, 2 H, 2-, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 124.1 (d, C-4′), 126.5 (s, C-1′), 128.5 (d, C-3′, -5′), 128.6 (d, C-5, -6), 129.8 (d, C-2′, -6′), 135.6 (s, C-3, -8), 135.8 (s, C-4a, -6a), 140.2 (s, C-4, -7), 145.6 (s, C-1a, -10a), 151.6 (d, C-2, -9).

4,7-Dichloro-3,8-di(4-tert-butylphenyl)-1,10-phenanthroline (**5b**): m.p. 304°C. − IR (KBr): $\tilde{\nu}$ = 3025 cm^{-1}, 2960, 2904, 2865, 1609, 1542, 1473, 1412, 1362, 1268, 1125, 1017, 837, 817, 766, 746, 699. − ^1H NMR ($CDCl_3$): δ = 1.42 (s, 18 H, Me), 7.58 (s, 8 H, Ph), 8.50 (s, 2 H, 5-, 6-H), 9.15 (s, 2 H, 2-, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 31.3 (q, Me), 34.8 [s, $C(CH_3)_3$], 124.1 (s, C-1′), 125.5 (d, C-3′, -5′), 126.7 (d, C-4′), 129.6 (d, C-5, -6), 132.9 (d, C-2′, -6′), 135.6 (s, C-3, -8), 140.2 (s, C-4a, -6a), 145.5 (s, C-4, -7), 151.8 (s, C-1a, -10a), 151.9 (d, C-2, -9). − $C_{32}H_{30}Cl_2N_2 \cdot 0.5\ H_2O$ (522.52): calcd. C 73.56, H 5.98, N 5.36; found C 73.70, H 5.96, N 5.53.

4,7-Dichloro-3,8-diethyl-1,10-phenanthroline (**5c**): m.p. 209°C. − IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1}, 2869, 1581, 1546, 1485, 1455, 1420, 1365, 1271, 1223, 1053, 815, 736. − ^1H NMR ($CDCl_3$): δ = 1.37 (t, J = 7.5 Hz, 6 H, CH_3), 3.04 (q, J = 7.5 Hz, 4 H, CH_2), 8.31 (s, 2 H, 5-, 6-H), 8.99 (s, 2 H, 2-, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (q, CH_3), 25.0 (t, CH_2), 123.3 (d, C-5, -6), 126.1 (s, C-3, -8), 136.7 (s, C-4a, -6a), 140.9 (s, C-4, -7), 145.2 (s, C-1a, -10a), 151.3 (d, C-2, -9). $C_{16}H_{14}Cl_2N_2$ (305.21): calcd. C 62.97, H 4.62, N 9.18; found C 62.73, H 4.47, N 9.14.

4,7-Dichloro-3,8-di-n-butyl-1,10-phenanthroline (**5d**): m.p. 174°C. − IR (KBr): $\tilde{\nu}$ = 2948 cm^{-1}, 2859, 1607, 1544, 1480, 1362, 1221, 1079, 921, 814, 776, 736. − ^1H NMR ($CDCl_3$): δ = 0.96 (t, J = 7.2 Hz, 6 H, 4′-H), 1.35−1.53 (m, 4 H, 3′-H), 1.63−1.81 (m, 4 H, 2′-H), 2.99 (t, J = 7.5 Hz, 4 H, 1′-H), 8.28 (s, 2 H, 5-, 6-H), 8.96 (s, 2 H, 2-, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 13.8 (q, C-4′), 22.4 (t, C-3′), 31.3 (t, C-2′), 31.7 (t, C-1′), 123.3 (d, C-5, -6), 126.1 (s, C-3, -8), 135.5 (s, C-4a, -6a), 141.0 (s, C-4, -7), 145.2 (s, C-1a, -10a), 151.7 (d, C-2, -9). $C_{20}H_{22}Cl_2N_2$ (361.31): calcd. C 66.49, H 6.14, N 7.75; found C 66.18, H 6.12, N 7.71.

4,7-Dichloro-3,8-di-n-hexyl-1,10-phenanthroline (**5e**): m.p. 132°C. − IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1}, 2953, 2852, 1547, 1482, 1457, 1418, 1366, 1069, 836, 814, 777, 738. − ^1H NMR ($CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 6 H, 6′-H), 1.34−1.51 (m, 12 H, 3′-, 4′-, 5′-H), 1.63−1.84 (m, 4 H, 2′-H), 3.01 (t, J = 7.7 Hz, 4 H, 1′-H), 8.33 (s, 2 H, 5-, 6-H), 8.98 (s, 2 H, 2-, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (q, C-6′), 22.5 (t, C-5′), 29.0 (t, C-4′), 29.5 (t, C-3′), 31.5 (t, C-2′), 31.6 (t, C-1′), 123.3 (d, C-5, -6), 126.2 (s, C-3, -8), 135.6 (s, C-4a, -6a), 141.1 (s, C-4, -7), 145.0 (s, C-1a, -10a), 151.7 (d, C-2, -9). − $C_{24}H_{30}Cl_2N_2$ (417.42): calcd. C 69.06, H 7.24, N 6.71; found C 68.78, H 7.43, N 6.64.

4,7-Dichloro-2,9-dimethyl-1,10-phenanthroline (**5f**): m.p. 202°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3460 cm^{-1}, 3365, 3213, 2966, 2920, 1579, 1530, 1444, 1372, 1342, 1238, 1170, 1102, 1027, 901, 860, 833, 810, 713. − ^1H NMR ($CDCl_3$): δ = 2.91 (s, 6 H, Me), 7.61 (s, 2 H, 3-, 8-H), 8.21 (s, 2 H, 5-, 6-H). − ^{13}C NMR ($CDCl_3$): δ = 25.7 (q, Me), 122.0 (d, C-5, -6), 124.0 (d, C-3, -8), 124.9 (s, C-4a, -6a), 142.7 (s, C-4, -7), 146.0 (s, C-1a, -10a), 159.8 (s, C-2, -9). − $C_{14}H_{10}Cl_2N_2$ (277.15): calcd. C 60.67, H 3.64, N 10.11; found C 60.23, H 3.70, N 9.92.

5,8-Dichloro-1,2,3,4,9,10,11,12-octahydrodibenzo[b,j]-1,10-phenanthroline[16] (**5g**): m.p. 325°C. − IR (KBr): $\tilde{\nu}$ = 2933 cm^{-1}, 2857, 1570, 1526, 1459, 1421, 1376, 1339, 1245, 1164, 860, 826, 808, 722. − ^1H NMR ($CDCl_3$): δ = 1.94−1.96 (m, 8 H, 2-, 3-, 10-, 11-H), 3.00−3.10 (m, 4 H, 4-, 9-H), 3.30−3.40 (m, 4 H, 1-, 12-H), 8.18 (s, 2 H, 6-, 7-H). − ^{13}C NMR ($CDCl_3$): δ = 21.4 (t, C-3, -10), 21.6 (t, C-2, -11), 27.7 (t, C-4, -9), 31.7 (t, C-1, -12), 123.0 (d, C-6, -7), 125.6 (s, C-4a, -8a), 134.1 (s, C-5a, -7a), 136.5 (s, C-5, -8), 146.2 (s, C-13a, -14a), 160.6 (s, C-1a, -12a).

General Procedure for the Preparation of 4,7-dibromo-3,8-dialkyl/diaryl-1,10-phenanthrolines (**6a−6e**): 3,8-Dialkyl/diaryl-1,10-phenanthroline-4,7-dione **4a−e** (3.00 mmol) was added under nitrogen to melted phosphoryl bromide (30 ml). After stirring the resulting solution at 80°C for 7 h, the hot solution was then slowly added to a well-stirred mixture of ice (100 g) in 200 ml of water. After 15 min, chloroform (50 ml) was added and the resulting two-layer-system was carefully brought to pH 13−14 by adding concentrated KOH solution. The organic layer was separated and the residue extracted twice with 50 ml of chloroform. The combined organic layers were washed with 100 ml of concentrated KOH solution and dried with $MgSO_4$. After evaporation of the solvent in vacuo the 4,7-dibromo-3,8-dialkyl/diaryl-1,10-phenanthrolines were obtained as colorless solids in quantitative yield.

4,7-Dibromo-3,8-diphenyl-1,10-phenanthrolin (**6a**): m.p. 236°C. − IR (KBr): $\tilde{\nu}$ = 3052 cm^{-1}, 1601, 1540, 1464, 1441, 1410, 1356, 1306, 918, 810, 780, 765, 731, 699, 586, 557. − ^1H NMR ($CDCl_3$): δ = 7.45−7.54 (m, 10 H, Ph), 8.39 (s, 2 H, 5-, 6-H), 9.04 (s, 2 H, 2-, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 127.1 (d, C-4′), 127.8 (s, C-1′), 128.3 (d, C-3′, -5′), 128.4 (d, C-5, -6), 129.6 (d, C-2′, -6′), 133.5 (s, C-3, -8), 137.6 (s, C-4a, -6a), 138.4 (s, C-4, -7), 145.2 (s, C-1a, -10a), 151.1 (s, C-2, -9).

4,7-Dibromo-3,8-di-(4-tert-butylphenyl)-1,10-phenanthroline (**6b**): m.p. 307°C. − IR (KBr): $\tilde{\nu}$ = 3025 cm^{-1}, 2961, 2905, 2867, 1610, 1541, 1467, 1414, 1361, 1268, 1124, 1016, 836, 821, 791, 757, 746,

666, 578. − ^{1}H NMR ($CDCl_3$): δ = 1.42 (s, 18 H, Me), 7.53 (d, *J* = 8.9 Hz, 4 H, 3′-, 5′-H), 7.58 (d, *J* = 8.9 Hz, 4 H, 2′-, 6′-H), 8.49 (s, 2 H, 5-, 6-H), 9.08 (s, 2 H, 2-, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 31.3 (q, Me), 34.7 [s, $C(CH_3)_3$], 125.3 (d, C-2′, -3′, -5′, -6′), 127.2 (d, C-4′), 128.0 (s, C-1′), 129.4 (d, C-5, -6), 133.6 (s, C-3, -8), 134.7 (s, C-4a, -6a), 138.5 (s, C-4, -7), 151.4 (s, C-1a, -10a), 151.7 (d, C-2, -9). − $C_{32}H_{31}Br_3N_2$ (683.32): calcd. C 56.25, H 4.57, N 4.10, found C 56.82, H 4.48, N 4.27.

4,7-Dibromo-3,8-diethyl-1,10-phenanthroline (**6c**): m.p. 215°C. − IR (KBr): $\tilde{\nu}$ = 3036 cm^{-1}, 2968, 2938, 2868, 1544, 1480, 1457, 1421, 1363, 1050, 812, 785, 747, 734. − ^{1}H NMR ($CDCl_3$): δ = 1.35 (t, *J* = 7.5 Hz, 6 H, CH_3), 3.04 (q, *J* = 7.5 Hz, 4 H, CH_2), 8.27 (s, 2 H, 5-, 6-H), 8.93 (s, 2 H, 2-, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 14.1 (q, CH_3), 27.8 (t, CH_2), 126.3 (d, C-5, -6), 127.5 (s, C-3, -8), 134.4 (s, C-4a, -6a), 139.0 (s, C-4, -7), 144.9 (s, C-1a, -10a), 150.9 (d, C-2, -9). − $C_{16}H_{14}Br_2N_2$ (394.11): calcd. C 48.76, H 3.58, N 7.11; found C 48.47, H 3.35, N 7.41.

4,7-Dibromo-3,8-di-n-butyl-1,10-phenanthroline (**6d**): m.p. 188°C. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 2926, 2857, 1600, 1548, 1478, 1414, 1364, 1230, 1160, 1083, 1056, 963, 923, 812, 786, 755, 734. − ^{1}H NMR ($CDCl_3$): δ = 0.96 (t, *J* = 7.1 Hz, 6 H, 4′-H), 1.35−1.53 (m, 4 H, 3′-H), 1.63−1.78 (m, 4 H, 2′-H), 3.00 (t, *J* = 7.7 Hz, 4 H, 1′-H), 8.25 (s, 2 H, 5-, 6-H), 8.89 (s, 2 H, 2-, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 13.7 (q, C-4′), 22.4 (t, C-3′), 31.8 (t, C-2′), 34.1 (t, C-1′), 126.3 (d, C-5, -6), 127.6 (s, C-3, -8), 134.6 (s, C-4a, -6a), 138.0 (s, C-4, -7), 144.9 (s, C-1a, -10a), 151.4 (d, C-2, -9). − $C_{20}H_{22}Br_2N_2$ (450.22): calcd. C 53.36, H 4.93, N 6.22; found C 53.09, H 5.19, N 6.02.

4,7-Dibromo-3,8-di-n-hexyl-1,10-phenanthroline (**6e**): m.p. 141°C. − IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1}, 2923, 2853, 1602, 1546, 1475, 1413, 1086, 1058, 812, 785, 756, 734. − ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, *J* = 6.9 Hz, 6 H, 6′-H), 1.24−1.51 (m, 12 H, 3′-, 4′-, 5′-H), 1.63−1.84 (m, 4 H, 2′-H), 2.99 (t, *J* = 7.5 Hz, 4 H, 1′-H), 8.24 (s, 2 H, 5-, 6-H), 8.89 (s, 2 H, 2-, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (q, C-6′), 22.5 (t, C-5′), 29.0 (t, C-4′), 29.7 (t, C-3′), 31.5 (t, C-2′), 34.4 (t, C-1′), 126.3 (d, C-5, -6), 127.6 (s, C-3, -8), 134.6 (s, C-4a, -6a), 138.0 (s, C-4, -7), 144.8 (s, C-1a, -10a), 151.4 (d, C-2, -9). − $C_{24}H_{30}Br_2N_2$ (506.32): calcd. C 56.93, H 5.97, N 5.53; found C 56.65, H 6.29, N 5.50.

4,7-Dibromo-2,9-dimethyl-1,10-phenanthroline (**6f**): 2,9-Dimethyl-1,10-phenanthroline-4,7-dione (**4f**) (3.00 mmol) was added under nitrogen to melted phosphoryl bromide (30 ml). The resulting solution was then stirred at 100°C for 7 h, whereafter it was added dropwise to a well-stirred mixture of ice (100 g) in 200 ml of water. After 15 minutes chloroform (50 ml) was added and the resulting two-layer-system was carefully brought to pH 13−14 by adding concentrated KOH-solution. The organic layer was separated and the residue twice extracted with 50 ml of chloroform. The combined organic layers were washed with 100 ml of concentrated KOH solution and then dried over $MgSO_4$. After evaporation of the solvent in vacuo and purification of the residue by column chromatography (CH_2Cl_2/MeOH/conc. NH_3, 300:15:2) analytically pure **6f** (79%) was obtained. m.p. >160°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3462 cm^{-1}, 3391, 3359, 3210, 2965, 2918, 1764, 1605, 1581, 1526, 1467, 1445, 1373, 1264, 1171, 1100, 1027, 862, 804, 716, 698. − ^{1}H NMR ($CDCl_3$): δ = 2.90 (s, 6 H, Me), 7.80 (s, 2 H, 3-, 8-H), 8.15 (s, 2 H, 5-, 6-H). − ^{13}C NMR ($CDCl_3$): δ = 25.6 (q, Me), 124.9 (d, C-5, -6), 126.3 (s, C-4a, -6a), 127.8 (d, C-3, -8), 134.6 (s, C-4, -7), 145.8 (s, C-1a, -10a), 159.8 (s, C-2, -9). − $C_{14}H_{10}Br_2N_2$ (366.05): calcd. C 45.94, H 2.75, N 7.65; found C 45.73, H 2.64, N 7.61.

3,8-Di-n-hexyl-4,7-bis(4-methylphenoxy)-1,10-phenanthroline (**7**): At 140°C KOH (0.55 g, 9.80 mmol) was added to a molten mixture of **5e** (0.30 g, 0.72 mmol) and of *p*-cresol (6.00 g, 55.5 mmol) kept under nitrogen. After stirring for 4 h at 140°C the black mixture was taken up in 150 ml of a KOH-solution (10%) and 50 ml of chloroform. The organic layer was separated and dried over $MgSO_4$. After evaporation of the solvent in vacuo the residue was purified by column chromatography (SiO_2, ethyl acetate) to afford 0.34 g of **7** (84 %): m.p. 95°C. − IR (KBr): $\tilde{\nu}$ = 3033 cm^{-1}, 2927, 2858, 1607, 1591, 1504, 1420, 1375, 1209, 1174, 908, 818, 770. − ^{1}H NMR ($CDCl_3$): δ = 0.83 (t, *J* = 6.9 Hz, 6 H, 6′-H), 1.14−1.39 (m, 12 H, 3′-, 4′-, 5′-H), 1.55−1.77 (m, 4 H, 2′-H), 2.26 (s, 6 H, 7′′-H), 2.72 (t, *J* = 7.5 Hz, 4 H, 1′-H), 6.66 (d, *J* = 8.6 Hz, 4 H, 2′′-, 6′′-H), 7.02 (d, *J* = 8.6 Hz, 4 H, 3′′-, 6′′-H), 7.75 (s, 2 H, 5-, 6-H), 9.07 (s, 2 H, 2-, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (q, C-6′), 20.5(q, C-7′′), 22.5 (t, C-5′), 27.9 (t, C-4′), 28.9 (t, C-3′), 29.8 (t, C-2′), 31.4 (t, C-1′), 115.0 (d, C-3′′, -5′′), 120.8 (s, C-4′′), 123.4 (d, C-5, -6), 129.9 (s, C-3, -8), 130.2 (d, C-2′′, -6′′), 131.7 (s, C-4a, -6a), 146.9 (s, C-1a, -10a), 153.5 (d, C-2, -9), 155.7 (s, C-1′′), 156.2 (s, C-4, -7). − $C_{38}H_{44}N_2O_2$ (560.78): calcd. C 81.39, H 7.91, N 5.00; found C 81.09, H 7.75, N 4.78.

3,8-Di-n-hexyl-4,7-di-N-morpholino-1,10-phenanthroline (**8**): At room temperature a 1.4 M BuLi solution (5.40 ml, 7.56 mmol) was added slowly to dry morpholine (25.0 ml, 287 mmol) under nitrogen. After stirring the mixture for 45 min at room temperature, **5e** (0.20 g, 0.48 mmol) was added. The deep redbrown mixture was then stirred for 18 h. After quenching the reaction by adding 50 ml of water, the mixture was extracted twice with 50 ml of chloroform. After drying the organic layer over $MgSO_4$ and evaporation of the solvent in vacuo, the colorless residue was purified by column chromatography (SiO_2, ethyl acetate) to yield 0.07 g of **8** (27 %): m.p. 152°C dec. − IR (KBr): $\tilde{\nu}$ = 3027 cm^{-1}, 2956, 2921, 2852, 1670, 1565, 1504, 1425, 1390, 1258, 1116, 952, 844, 8.06, 763. − ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, *J* = 6.9 Hz, 6 H, 6′-H), 1.35−1.50 (m, 12 H, 3′-, 4′-, 5′-H), 1.55−1.65 (m, 4 H, 2′-H), 2.91 (t, *J* = 7.5 Hz, 4 H, 1′-H), 3.27−3.42 (m, 8 H, 2′′-H), 3.87−4.05 (m, 8 H, 3′′-H), 8.21 (s, 2 H, 5-, 6-H), 8.88 (s, 2 H, 2-, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (q, C-6′), 22.6 (t, C-5′), 29.4 (t, C-4′), 30.6 (t, C-3′), 31.7 (t, C-2′), 32.0 (t, C-1′), 51.5 (t, C-2′′), 67.8 (t, C-3′′), 122.0 (d, C-5, -6), 126.5 (s, C-3, -8), 133.5 (s, C-4a, -6a), 144.5 (s, C-1a, -10a), 146.9 (s, C-4, -7), 153.8 (d, C-2, -9). − $C_{32}H_{46}N_4O_2 \cdot 0.5\,H_2O$ (527.75): calcd. C 72.83, H 8.98, N 10.62, found C 72.56, H 9.20, N 10.23.

3,8-Di-n-hexyl-4,7-di[N-(4-methylphenyl)amino]-1,10-phenanthroline (**9**): A mixture of **5e** (0.20 g, 0.72 mmol) and *p*-toluidine (6.00 g, 56.0 mmol) was stirred under nitrogen at 160°C for 20 h. After distilling off the excess of *p*-toluidine under reduced pressure the black residue was taken up in 50 ml of a KOH solution (10%) and 50 ml of chloroform. The organic layer was separated and dried over $MgSO_4$. After evaporation of the solvent in vacuo the residue was purified by column chromatography (SiO_2, 1. dichloromethane, 2. ethyl acetate) to yield 0.14 g of **9** (54 %): m.p. 76−78°C. − IR (KBr): $\tilde{\nu}$ = 3222 cm^{-1}, 3025, 2922, 2854, 1611, 1566, 1507, 1422, 1377, 1312, 1234, 1110, 914, 808. − ^{1}H NMR ($CDCl_3$): δ = 0.83 (t, *J* = 6.9 Hz, 6 H, 6′-H), 1.14−1.45 (m, 12 H, 3′-, 4′-, 5′-H), 1.55−1.75 (m, 4 H, 2′-H), 2.24 (s, 6 H, 7′′-H), 2.77 (t, *J* = 7.5 Hz, 4 H, 1′-H), 5.82 (s, 2 H, N-H), 6.59 (d, *J* = 8.4 Hz, 4 H, 2′′-, 6′′-H), 6.96 (d, *J* = 8.4 Hz, 4 H, 3′′-, 5′′-H), 7.57 (s, 2 H, 5-, 6-H), 8.94 (s, 2 H, 2-, 9-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (q, C-6′), 20.5(q, C-7′′), 22.5 (t, C-5′), 28.9 (t, C-4′), 29.5 (t, C-3′), 29.9 (t, C-2′), 31.5 (t, C-1′), 116.8 (d, C-3′′,-5′′), 121.5 (d, C-5, -6), 123.2 (s, C-4′′), 129.1 (s, C-3, -8), 129.7 (d, C-2′′, -6′′), 130.4 (s, C-4a, -6a), 142.6 (s, C-1a, -10a), 143.8 (s, C-4, -7), 146.7 (s, C-

1′′), 152.3 (d, C-2, -9). – $C_{38}H_{46}N_4 \cdot 0.5\ H_2O$ (567.82): calcd. C 80.38, H 8.34, N 9.87, found C 80.75, H 8.40, N 9.97.

4,7-Diethynylphenyl-3,8-di-n-hexyl-1,10-phenanthroline (**10**): To a solution of **6e** (1.00 g, 1.95 mmol), phenylacetylene (0.67 ml, 6.12 mmol), and 10 ml of dry triethylamine in benzene (20 ml) a mixture of $PdCl_2(PPh_3)_2$ (0.15 g) and CuI (0.30 g) was added. After refluxing the mixture for three days under nitrogen the solvent was evaporated. The black residue was dissolved in 100 ml of dichloromethane, washed with 100 ml of 2% KCN solution, 100 ml of water, and dried over $MgSO_4$. The residue was purified by column chromatography (SiO_2, 1. CH_2Cl_2, 2. ethyl acetate) to furnish 0.94 g of **10** (86%): m.p. 136°C. – IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1}, 2917, 2852, 2205, 1598, 1559, 1499, 1467, 1421, 753, 686, 522. – ^1H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 6.9 Hz, 6 H, 6′-H), 1.24–1.59 (m, 12 H, 3′-, 4′-, 5′-H), 1.73–1.94 (m, 4 H, 2′-H), 3.11 (t, *J* = 7.5 Hz, 4 H, 1′-H), 7.43–7.46 (m, 6 H, H-Ph), 7.66–7.71 (m, 4 H, H-Ph), 8.43 (s, 2 H, 5-, 6-H), 9.05 (s, 2 H, 2-, 9-H). – ^{13}C NMR ($CDCl_3$): δ = 14.0 (q, C-6′), 22.5 (t, C-5′), 29.1 (t, C-4′), 30.5 (t, C-3′), 31.6 (t, C-2′), 34.6 (t, C-1′), 84.0 (s, C-2′′), 102.3 (s, C-1′′), 122.5 (s, C-3′′), 125.0 (d, C-6′′), 127.6 (d, C-5, -6), 127.9 (s, C-3, -8), 128.6 (d, C-4′′, -8′′), 129.2 (d, C-5′′, -7′′), 131.8 (s, C-4a, -6a), 138.8 (s, C-4, -7), 144.4 (s, C-1a, -10a), 151.1 (d, C-2, -9). – $C_{40}H_{40}N_2 \cdot 0.66\ H_2O$ (560.78): calcd. C 85.67, H 7.43, N 5.00, found C 85.54, H 7.10, N 4.71.

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