A Facile Route to Aryl-Substituted 1,10-Phenanthrolines by Means of Suzuki Coupling Reactions between Substituted Areneboronic Acids and Halogeno-1,10-phenanthrolines[‡]

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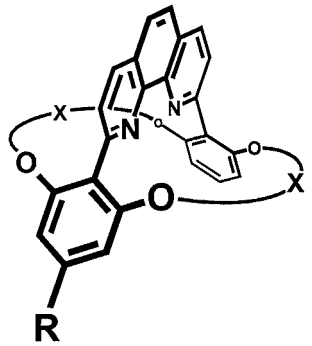
Twelve new mono- or diaryl-substituted 1,10-phenanthrolines (**17** and **18**) have been synthesized. The key step is a Suzuki coupling reaction between the substituted areneboronic acids **6**, **11**, and **15** and the mono- and dihalo-1,10-phenanthrolines **16**. The syntheses of bis-*ortho*-substituted boronic acids **6**, **11**, and **15** from substituted arenes **5** or substituted bromoarenes **10** and **14** by lithiation and subsequent treatment with trimethyl borate is described. Not only 2,9-diiodo- (**16c**) but also 2,9-dichloro-1,10-phenanthroline (**16b**) can be used with good yields (65–92%) in the described Suzuki coupling. For the syntheses of unsymmetrically substituted 1,10-phenanthrolines **18b**, **18i**, and **18j**, the use of 2-chloro-9-iodo-1,10-phenanthroline is not necessary; two different bis-*ortho*-substituted arene rings can be introduced stepwise in 46 to 64% total yield.

Introduction

The high selectivity of enzymes is largely caused by the concave environment of the active site.[1] Geometrically related molecules such as macrocycles, clefts, or pincers have therefore also found wide interest in supramolecular chemistry.[2–5] Concave reagents have been developed to increase the selectivity of reactions or catalyses by a corresponding shielding of the reaction site. In particular, the concave 1,10-phenanthrolines **1a** have shown good selectivities in a number of reactions.[6–10] The active and selective catalysts in most of these cases are transition metal ion complexes of these ligands, such as copper(I) complexes in the stereoselective cyclopropanation of alkenes by diazoacetates.[7,10]



1 X = polymethylene or polyether
1a R = H

Concave 1,10-phenanthrolines **1a** have, since 1990, commonly been synthesized in a kinetically controlled double macrocyclization[11] starting from a tetraphenol **2**, which is only accessible under rather extreme reaction conditions.[12–14] By separation of the macrocyclization from the ether synthesis, followed by a ring-closing metathesis and hydrogenolysis [see Scheme 1, PCy_3 = tris(cyclohexyl)phosphane], the yields have been improved considerably (for instance, from 19 to 79%[14]).

For better manipulability of the selectivity of catalysis by metal ion complexes of these concave ligands **1a**, the introduction of additional functional groups into the 1,10-phenanthroline ligands **1** would be desirable. These additional functional groups can either be connected to the aryl bridgeheads (as substituents R) or they can be part of the bridges X. However, the harsh reaction conditions used during the synthesis of the tetraphenol **2** (lithium powder, MnO_2, molten pyridinium chloride) are not compatible with a broad variety of functional groups, and so another method for the introduction of aryl rings into the 1,10-phenanthroline system was necessary. Negishi and Suzuki couplings[15–17] for the synthesis of diaryl-1,10-phenanthrolines have been described by Parker et al.[18] and Siegel et al.[19,20]

This publication shows how the addition of aryllithium compounds to 1,10-phenanthroline can be substituted by a Suzuki coupling[18,21] between benzeneboronic acids **6**, **11**,

[‡] Concave Reagents, 37. Part 36: M. Gelbert, C. Körber, O. Friedrich, F. Fahrenkrug, M. Keller, U. Lüning, *Supramol. Chem.* **2002**, *14*, 199–210.

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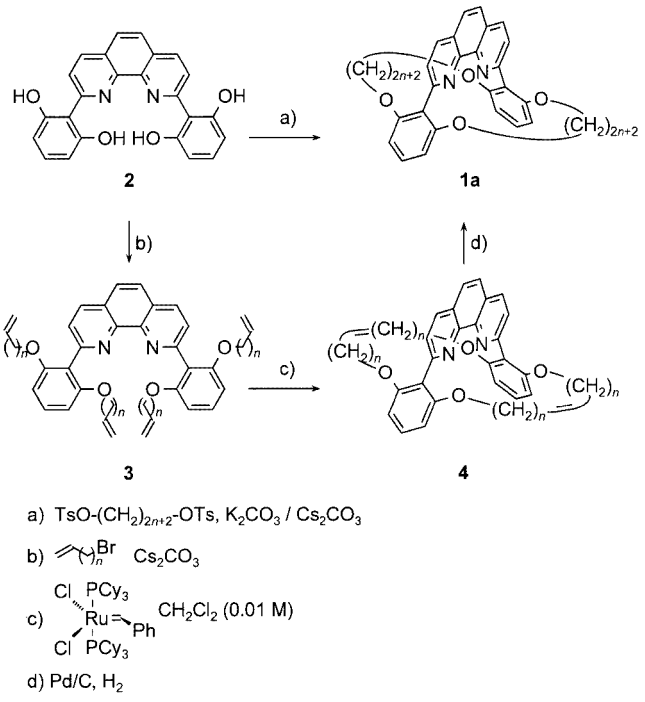


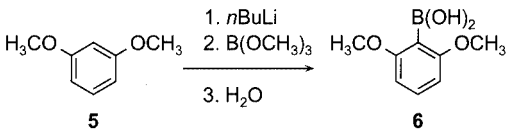
Scheme 1

or **15** and the halogenated 1,10-phenanthrolines **16**. We present a number of new 2-aryl- and 2,9-diaryl-1,10-phenanthrolines **17** and **18** in which the aryl rings are always doubly substituted in their *ortho* positions. In addition, the resulting diaryl-1,10-phenanthrolines either carry functional groups in the *para* position of a bridgehead or the bridgeheads are alkylated with alkenyl groups at the four oxygen atoms, ready for metathesis.[14]

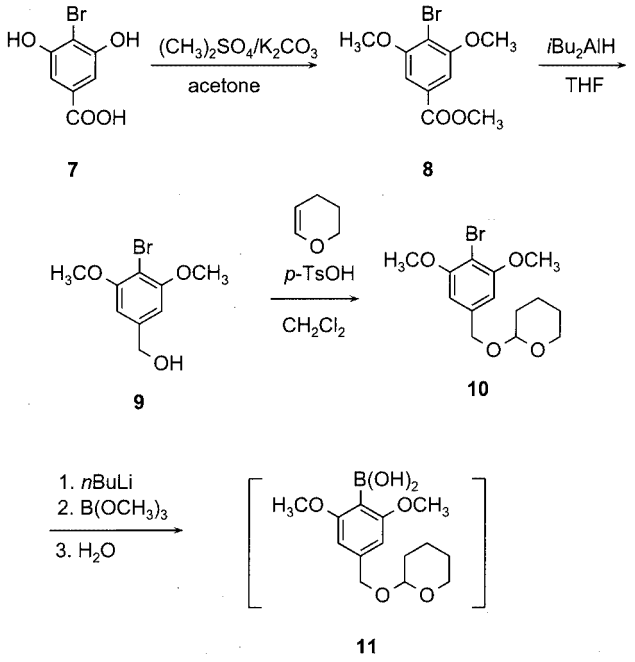
Results

Syntheses of Starting Materials

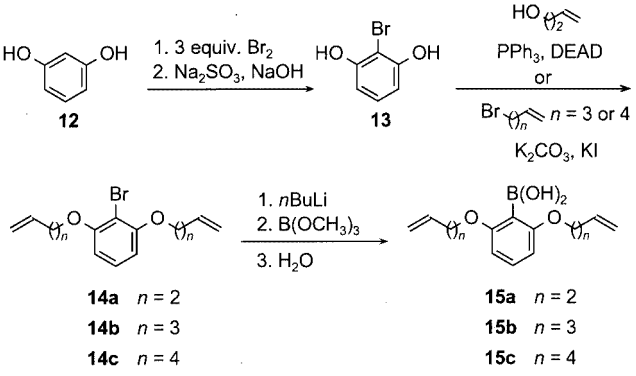
Schemes 2 to 4 summarize the syntheses of the benzeneboronic acids **6**, **11**, and **15**. All syntheses have in common that a lithium aryl compound is treated with trimethyl borate with subsequent hydrolysis. However, the lithium aryl compound can either be obtained by lithiation of an unsubstituted position activated by neighboring oxygen atoms (Scheme 2), or it can be generated by bromine/lithium exchange (Schemes 3 and 4). The boronic acids **6** and **15** have been isolated and characterized. In the case of the boronic acid **11**, crude **11** was used for the Suzuki coupling and gave excellent overall yields of **17b** and **18b** (91 and 88%, respectively).



Scheme 2



Scheme 3



Scheme 4

While the synthesis of the boronic acid **6** was straightforward,[22] the synthesis of the analogous, *para*-substituted boronic acid **11** needed several steps, starting from the commercially available carboxylic acid **7**. From **7**, the tetrahydropyran-protected aryl bromide **10** was synthesized in 47% total yield. From **10**, the boronic acid was obtained by lithiation, treatment with trimethylborate, and subsequent hydrolysis, and was then used in the coupling reactions without isolation.

The alkenyl-substituted boronic acids **15** were synthesized from the corresponding bromides **14** in 83 to 86% yield. While the alkenylation of the diphenol **13** with 1-bromo-4-pentene or 1-bromo-5-hexene was possible in 93 and 87% yields, respectively, the synthesis of the homoallylic bromo compound **14a** could only be performed in 41% yield, even when a large excess of the respective bromide was used. Presumably, the small alkylation yield is caused by competing HBr elimination from the homoallyl bromide.

Table 1. Yields and reaction conditions for the coupling products **17** and **18** from Suzuki coupling between the boronic acids **6**, **11**, and **15** and the halogenated 1,10-phenanthrolines **16** and **17**; the equivalents of catalyst were calculated from the amount of halo-1,10-phenanthroline used, while the equivalents of base are relative to the amount of boronic acid

Product	Boronic acid	Halogenated 1,10-phenanthroline	Reaction conditions[a]	Base	Yield (%)
17a	**6**	**16a**	5 mol %, DME, reflux 20 h	2 N Na_2CO_3	73
17b	**11**	**16a**	5 mol %, DME, reflux 20 h	2 N Na_2CO_3	91
17f	**6**	**16b**	5 mol %, DME, reflux 20 h	2 N Na_2CO_3	73
17g	**15b**	**16b**	10 mol %, DME, reflux 16 h	2 N Na_2CO_3	71
18a	**6**	**16b**	10 mol %, DME, reflux 2 d	2 N Na_2CO_3	83
18b	**11**	**17f**	5 mol %, DME, reflux 2 d	2 N Na_2CO_3	88
18f	**15a**	**16b**	10 mol %, DME, reflux 16 h	1.5 equiv. $Ba(OH)_2$	78
18g	**15b**	**16b**	10 mol %, DME/H_2O, reflux 16 h	1.5 equiv. $Ba(OH)_2$	92
18g	**15b**	**16c**	10 mol %, DME, reflux 16 h	2 equiv. $(n\text{Bu})_4\text{NF}$	88
18h	**15c**	**16b**	10 mol %, DME/H_2O, reflux 16 h	1.5 equiv. $Ba(OH)_2$	73
18h	**15c**	**16c**	10 mol %, DME, reflux 16 h	2 equiv. $(n\text{Bu})_4\text{NF}$	88
18i	**15a**	**17g**	10 mol %, DME/H_2O, reflux 16 h	1.5 equiv. $Ba(OH)_2$	65
18j	**15c**	**17g**	10 mol %, DME/H_2O, reflux 16 h	1.5 equiv. $Ba(OH)_2$	88

[a] DME = 1,2-dimethoxyethane, $Pd(PPh_3)_4$ was used as catalyst

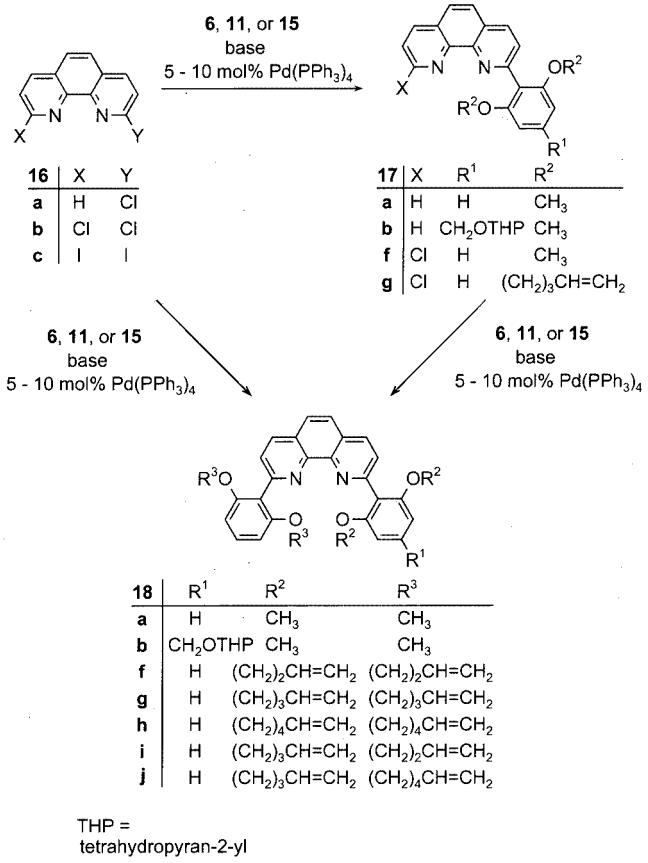
When, however, the alkylation was carried out under Mitsunobu conditions[23] with homoallylic alcohol, diethyl azodicarboxylate (DEAD), and triphenylphosphane, bromo compound **14a** was obtained in 69% yield. All three bromides **14** − even the homoallyl compound − gave the corresponding boronic acids **15** in good yields (83 to 86%).

Suzuki Couplings

As already described by Parker et al.[18] and Siegel et al.,[19,20] halo-substituted 1,10-phenanthrolines can be coupled with boronic acids under palladium catalysis conditions.[24] Therefore, some boronic acids were first coupled with 2,9-diiodo-1,10-phenanthroline (**16c**). When using the alkene-substituted boronic acids **15** we feared that the Heck reaction[15,25,26] might act as a competition reaction. We therefore first checked Suzuki couplings in the absence of strong bases. Fluoride ions[27] can also be used in Suzuki reactions to activate the boronic acid, and good yields have been found for fluoride-promoted Suzuki coupling when aryl iodides have been used as reaction partners (Table 1, compounds **18g** and **18h**).

With stronger bases, chloro-1,10-phenanthrolines[18] can also be employed in Suzuki coupling, and − despite the possibility of potentially competing Heck reactions − identical or sometimes even better coupling yields were achieved with the chloro-1,10-phenanthrolines **16a** and **16b** in combination with sodium carbonate solution or barium hydroxide[24,28] (Table 1, compounds **18g** and **18h**). This method has the advantage that it avoids the reaction step from the dichloro-1,10-phenanthroline **16a** to the diiodo analogue **16c**.

Unsymmetrically substituted 2,9-diaryl-1,10-phenanthrolines have previously been synthesized by traditional Sauvage chemistry;[29] unsymmetrical Suzuki coupling products have also been obtained but only when starting from 2-chloro-9-iodo-1,10-phenanthroline.[30] In those cases, prior to a second coupling, the remaining chlorine atom first had to be substituted by iodide.[19] With the boronic acids **6** and **15b**, however, 2,9-dichloro-1,10-phenanthroline (**16b**) could be selectively coupled with only *one* aryl unit to give 2-aryl-9-chloro-1,10-phenanthrolines **17f** and **17g** in very good yields (Scheme 5). Thus, there was no need to synthesize 2-chloro-9-iodo-1,10-phenanthroline.[19]



Scheme 5

The yields and reaction conditions for all the Suzuki couplings carried out in this work are summarized in Table 1. The monoaryl coupling products **17** were obtained in 71 to 91% yields. In the case of the diaryl-1,10-phenanthrolines **18**, simultaneous coupling in the 2- and 9-positions yielded the symmetrical compounds **18a** and **18f−h** in 73 to 92% yields. The unsymmetrically substituted diaryl-1,10-phenanthrolines **18b**, **18i**, and **18j** were obtained in overall yields of 64, 46, and 63%, respectively.

The resulting 2-aryl and 2,9-diaryl-substituted 1,10-phenanthrolines **17** and **18** are new, interesting intermediates for the synthesis of concave 1,10-phenanthrolines **1**. However, these nonmacrocyclic precursors are also often already sufficiently shielded to allow remarkable increases in selectivity.[9]

The synthesis of bimacrocycles **1** from the symmetrically alkenylated intermediates **18g** and **18h** (although obtained by a different route) by ring-closing metathesis has already been described.[14]

The conversion of the group R^1 at the bridgehead and an illustrative connection with a carbon nucleophile (here malonate) is shown in Figure 1.

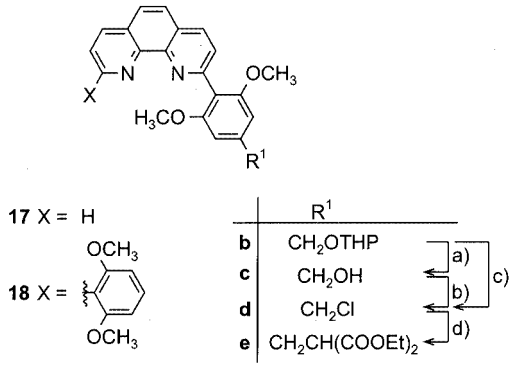


Figure 1. a) *p*TsOH, EtOH; b) conc. HCl; c) conc. HCl; d) $CH_2(COOEt)_2$, NaH, DMF; THP = tetrahydropyran-2-yl

In the *para*-substituted mono- or diaryl-1,10-phenanthrolines **17b** and **18b**, one aryl ring possesses an additional functional group R^1 in the *para* position. The benzylic alcohol **17c** can be liberated from the tetrahydropyranyl ether **17b** by acidic hydrolysis in 73% yield. Subsequent treatment of **17c** with concentrated hydrochloric acid yields the benzyl chloride **17d** in 83% yield. However, **17d** could also be generated in one step from the THP ether **17b** in 64% yield when concentrated hydrochloric acid was used for the cleavage. Analogously the chloride **18d** could be obtained in one step from **18b** in 82% yield. As a first example of further functionalization, both chlorides **17d** and **18d** were substituted with diethyl malonate nucleophile to give the diesters **17e** and **18e** in 52 and 48% yields, respectively. One potential application of such a "malonated" ligand **17e** or **18e** is the amidation of the ester groups with oligopeptides, which would allow the production of "libraries"[31] of substituted diaryl 1,10-phenanthrolines.

Experimental Section

General Remarks: The following chemicals were obtained commercially and were used without further purification: 3,4-dihydro-2*H*-pyran (Fluka), diisopropylaluminium hydride (1.0 M in hexanes, Aldrich), 4-bromo-3,5-dihydroxybenzoic acid (Aldrich, Lancaster), diethyl malonate (Janssen), *N*,*N*-dimethylformamide (Fluka, ≥99.8%), dimethyl sulfate (Merck), resorcinol (Riedel de Haën), tetrakis(triphenylphospane)palladium(0) (Aldrich), dimethoxyethane (Aldrich), 3-buten-1-ol (Fluka), 5-bromo-1-pentene (Fluka), 6-bromo-1-hexene (Fluka), diethyl azodicarboxylate (Fluka), triphenylphosphane (Aldrich), trimethyl borate (Fluka), *n*-butyllithium (2.5 M in hexanes, Aldrich).

2-Chloro-1,10-phenanthroline (**16a**), 2,9-dichloro-1,10-phenanthroline (**16b**), and 2,9-diiodo-1,10-phenanthroline (**16c**) were prepared according to literature procedures.[19,32]

Dry solvents were obtained with suitable desiccants: ethanol was distilled from sodium, tetrahydrofuran from lithium aluminium hydride, and ethyl acetate and acetone were distilled from calcium chloride. Column chromatography was carried out on basic alumina (Fluka, activity I) or silica gel (Macherey−Nagel, activity 1). The ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AC 200 (200 MHz), AM 300 (300 MHz or 75 MHz) or DRX 500 (500 MHz or 125 MHz) instruments, with tetramethylsilane as internal standard. IR spectra were measured on a Perkin−Elmer 1600 Series machine, MS spectra were recorded on a Finnigan MAT 8230, and elemental analyses were carried out on a VarioEl (Elementaranalysensysteme GmbH) instrument. Gas chromatography was performed with a Varian 3400 gas chromatograph equipped with a Macherey−Nagel SE30/25 m column.

2,6-Dimethoxybenzeneboronic Acid (6): The synthesis was carried in analogy to the procedure of Kuivila and Nahabedian,[22] starting from 80 mmol and giving 2.6 g of **6** (18%). M.p. 105−113 °C. IR (KBr): $\tilde{\nu}$ = 3332 (O−H), 2993, 2926, 2832 (aliph. C−H), 1598, 1466 (arom.) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.92 (s, 6 H, $ArOCH_3$), 6.64 (d, *J* = 8.4 Hz, 2 H, 3,5-H), 7.24 (s, 2 H, OH), 7.40 (t, *J* = 8.4 Hz, 1 H, 4-H) ppm. MS (EI, 70 eV): *m*/*z* (%) = 182, 181 (100, 28) [M^+]; 164, 163 (34, 10) [$M^+ - H_2O$]; 137 (14) [$M^+ - B(OH)_2$].

Methyl 4-Bromo-3,5-dimethoxybenzoate (8): 4-Bromo-3,5-dihydroxybenzoic acid (**7**, 4.74 g, 20.3 mmol) was dissolved in acetone (100 mL). After addition of potassium carbonate (8.71 g, 63.0 mmol) and dimethyl sulfate (6.0 mL, 63 mmol), the mixture was heated under reflux for 4 h. The solvent was removed in vacuo and the residue was dissolved in water and diethyl ether (100 mL each). The water layer was extracted with diethyl ether (3 times, 50 mL each) and the combined organic layer was dried with magnesium sulfate. The solvent was evaporated in vacuo and the residue was purified by recrystallization from methanol, yielding 4.23 g (76%) of **8**. M.p. 114−116 °C. IR[33] (KBr): $\tilde{\nu}$ = 3001 (arom. C−H), 2955 (aliph. C−H), 1717 (C=O), 1587, 1458 (arom.) cm^{-1}. ^1H NMR[33] (300 MHz, $CDCl_3$): δ = 3.90 (s, 3 H, $ArCOOCH_3$), 3.93 (s, 6 H, $ArOCH_3$), 7.25 (s, 2 H, ArH) ppm. MS (EI, 70 eV): *m*/*z* (%) = 276, 274 (98, 100) [M^+]; 245, 243 (54, 56) [$M^+ - CH_3O$].

4-Bromo-3,5-dimethoxyphenylmethanol (9):[33] Methyl 4-bromo-3,5-dimethoxybenzoate (**8**, 11 g, 40 mmol) was dissolved in tetrahydrofuran (50 mL). After the addition of a solution of diisopropylaluminium hydride (1.0 M in hexanes, 100 mL, 100 mmol), the reaction mixture was stirred for 2 h at room temperature. Water (15 mL) was added. The precipitated solid was filtered off and washed

several times with ethyl acetate. The filtrate was evaporated, and 8.1 g (33 mmol, 81%) of **9** precipitated, m.p. 119−121 °C. IR (KBr): $\tilde{\nu}$ = 3247 (O−H), 2955 (aliph. C−H), 1591, 1454 (arom.), 1245, 1127 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.88 (s, 1 H, OH), 3.90 (s, 6 H, $ArOCH_3$), 4.67 (s, 2 H, $ArCH_2OH$), 6.59 (s, 2 H, ArH) ppm. MS: (EI, 70 eV): *m/z* (%) = 248, 246 (96, 100) [M^+]; 233, 231 (7, 11) [$M^+ - CH_3$]; 217, 215 (7, 11) [$M^+ - CH_3O$].

2-[(4-Bromo-3,5-dimethoxybenzyl)oxy]tetrahydro-2*H*-pyran (10): 4-Bromo-3,5-dimethoxyphenylmethanol (**9**, 8.03 g, 32.5 mmol) was dissolved in dry dichloromethane (200 mL). After the addition of 3,4-dihydro-2*H*-pyran (7.4 mL, 81 mmol) and *p*-toluenesulfonic acid (108 mg, 568 μmol), the reaction mixture was stirred for 16 h at room temperature. The solvent was removed and the residue was purified by chromatography (silica gel, dichloromethane), yielding 8.30 g (77%) of **10** as a colorless solid. IR (KBr): $\tilde{\nu}$ = 2971, 2835 (aliph. C−H), 1588, 1464 (arom.), 1234, 1123 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.4−1.9 (m, 6 H, CH_2), 3.5−3.6 (m, 1 H, CH_2O), 3.9−4.0, 3.91 (m, CH_2O, s, $ArOCH_3$; 7 H), 4.49 (d, *J* = 12.3 Hz, 1 H, $ArCH_2O$), 4.7 (m, 1 H, OCHO), 4.75 (d, *J* = 12.3 Hz, 1 H, $ArCH_2O$), 6.60 (s, 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.5 (t, CH_2), 25.4 (t, CH_2), 30.6 (t, CH_2), 56.4 (q, $ArOCH_3$), 62.4 (t, $ArCH_2O$), 68.6 (t, CH_2O), 97.8 (d, OCHO), 99.6 (s, 4-C), 104.0 (d, 2,6-C), 139.1 (s, 1-C), 157.0 (s, 3,5-C) ppm. MS (EI, 70 eV): *m/z* (%) = 332, 330 (3, 4) [M^+]; 232, 230 (62, 60) [$M^+ - C_5H_8O_2$]; 231, 229 (62, 60) [$M^+ - C_5H_9O_2$]. $C_{14}H_{19}BrO_4$ (331.21), calcd. C 50.77, H 5.78; found C 50.44, H 5.56.

2-Bromo-1,3-dihydroxybenzene (13):[34] Sodium hydroxide (20.0 g, 500 mmol) and sodium sulfite (63.0 g, 500 mmol) were dissolved in water (625 mL) and methanol (125 mL). After addition of 2,4,6-tribromoresorcinol (86.7 g, 250 mmol), the reaction mixture was stirred for 15 min at room temperature. The mixture was then acidified with 2 N hydrochloric acid, and most of the methanol was removed in vacuo. After extraction with diethyl ether (6 times, 100 mL each), the solvent was removed in vacuo and the residue was recrystallized from chloroform, yielding 30.7 g (65%) of **13**. M.p. 101−102 °C. GC (SE30/25 m, temp. program[35]): t_{Ret} = 6.44 min, purity: 99%. IR (KBr): $\tilde{\nu}$ = 3330 (O−H), 1600, 1585, 1467 (arom.), 1296 (O−H), 1234, 1188 (C−OH), 1035 (arom. C−Br) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 5.42 (s, 2 H, OH), 6.60 (d (AB_2), *J* ≈ 8.2 Hz, 2 H, 4,6-H), 7.11 (dd (AB_2), *J* ≈ 7.8 Hz, *J* ≈ 8.5 Hz, 1 H, 5-H) ppm. MS (EI, 70 eV): *m/z* (%) = 190, 188 (98, 100) [M^+]; 172, 170 (37, 38) [$M^+ - H_2O$].

2-Bromo-1,3-bis(but-3-enoxy)benzene (14a): A solution of diethyl azodicarboxylate (4.86 mL, 24.9 mmol) in tetrahydrofuran (6 mL) was added at 0 °C to a solution of 2-bromo-1,3-dihydroxybenzene (**13**, 1.47 g, 7.78 mmol), triphenylphosphane (4.91 g, 18.7 mmol), and 3-butene-1-ol (2.00 mL, 24.9 mmol) in tetrahydrofuran (20 mL). After the mixture had been stirred for 2 h at room temperature, water (20 mL) was added. The water layer was extracted with diethyl ether (3 times, 20 mL each), and the combined organic layer was washed with aqueous sodium hydroxide (2 N, 3 times, 20 mL each) and with saturated sodium chloride solution and was then dried with magnesium sulfate. The solvent was evaporated and the residue was filtered through silica gel (cyclohexane/ethyl acetate, 95:5) and purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 90:10), yielding 1.57 g (69%) of **14a**. M.p. 31 °C. GC (SE30/25 m, temp. program[35]): t_{Ret} = 16.32 min, purity: 97%. IR (KBr): $\tilde{\nu}$ = 2926 (aliph. C−H), 1643 (aliph. C=C), 1593 (arom.), 1095 (C−O−C), 1034 (arom. C-Br) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.60 (qt, J_q = 6.8 Hz, J_t = 1.4 Hz, 4 H, OCH_2CH_2), 4.07 (t, *J* = 6.8 Hz, 4 H, OCH_2), 5.12, 5.19 (tdd, J_t ≈ 1.1 Hz, J_d = 1.9 Hz, J_d = 10.2 Hz, $=CH_{cis}$; tdd, J_t ≈ 1.8 Hz, J_d ≈ 1.9 Hz, J_d = 17.2 Hz, $=CH_{trans}$, 4 H), 5.96 (tdd, J_t = 6.8 Hz, J_d = 10.2 Hz, J_d = 17.2 Hz, 2 H, CH=), 6.54 (d, *J* = 8.3 Hz, 2 H, 4,6-H), 7.17 (t, *J* = 8.3 Hz, 1 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.6 (t, OCH_2CH_2), 68.6 (t, OCH_2), 102.3 (s, 2-C), 106.0 (d, 4,6-C), 117.3 (t, $=CH_2$), 128.0 (d, 5-C), 134.2 (d, CH=), 156.6 (s, 1,3-C) ppm. MS: (EI, 70 eV): *m/z* (%) = 298, 296 (32, 31) [M^+]; 217 (99) [M^+ − Br]; 190, 188 (78, 89) [$M^+ - C_8H_{12}$]. $C_{14}H_{17}BrO_2$ (297.19), calcd. C 56.58, H 5.77; found C 56.57, H 5.60.

2-Bromo-1,3-bis(pent-4-enoxy)benzene (14b): 2-Bromo-1,3-dihydroxybenzene (**13**, 1.60 g, 8.47 mmol) was dissolved in dry *N,N*-dimethylformamide. After the addition of potassium carbonate (7.00 g, 50.6 mmol), potassium iodide (500 mg, 3.01 mmol), and 5-bromo-1-pentene (2.50 mL, 21.1 mmol), the reaction mixture was stirred for 16 h at 60 °C. The solvent was removed in vacuo and the residue was dissolved in water and diethyl ether (20 mL each). The water layer was extracted with diethyl ether (3 times, 20 mL each), and the combined organic layer was washed with sodium hydroxide (2 N, 3 times, 20 mL each) and saturated aqueous sodium chloride and dried with magnesium sulfate. The solvent was evaporated in vacuo and the residue was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 90:10), yielding 2.56 g (93%) of **14b** as a colorless oil. GC (SE30/25 m, temp. program[35]): t_{Ret} = 18.32 min, purity: 99%. IR (film): $\tilde{\nu}$ = 3076 (arom. C−H), 2940, 2876 (aliph. C−H), 1640 (aliph. C=C), 1591, 1459 (arom.), 1097 (C−O−C), 1036 (arom. C-Br) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.93 (m_c, 4 H, OCH_2CH_2), 2.30 (m_c, 4 H, $CH_2CH=$), 4.03 (t, *J* = 6.3 Hz, 4 H, OCH_2), 5.00, 5.07 (tdd, J_t = 1.2 Hz, J_d = 2.0 Hz, J_d = 10.2 Hz, $=CH_{cis}$; tdd, J_t = 1.5 Hz, J_d = 2.0 Hz, J_d = 17.1 Hz, $=CH_{trans}$; 4 H), 5.86 (tdd, J_t = 6.7 Hz, J_d = 10.2 Hz, J_d = 17.1 Hz, 2 H, CH=), 6.53 (d, *J* = 8.3 Hz, 2 H, 4,6-H), 7.16 (t, *J* = 8.3 Hz, 1 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.3 (t, $CH_2CH=$), 30.1 (t, OCH_2CH_2), 68.4 (t, OCH_2), 102.1 (s, 2-C), 105.7 (d, 4,6-C), 115.3 (t, $=CH_2$), 128.0 (d, 5-C), 137.8 (d, CH=), 156.7 (s, 1,3-C) ppm. MS (CI, 70 eV): *m/z* (%) = 327, 325 (26, 25) [M^+ + H]. MS (EI, 70 eV): *m/z* (%) = 245 (100) [M^+ − Br]; 190, 188 (84, 88) [$M^+ - C_{10}H_{16}$]. $C_{16}H_{21}BrO_2$ (325.24), calcd. C 59.09, H 6.51; found C 58.97, H 6.37.

2-Bromo-1,3-bis(hex-5-enoxy)benzene (14c): As described for **14b**, **13** (7.46 mmol) was treated with excess 6-bromo-1-hexene, giving 2.30 g (87%) of **14c** as a colorless oil. GC (SE30/25 m, temp. program[35]): t_{Ret} = 20.51 min, purity: 93%. IR (film): $\tilde{\nu}$ = 2935 (aliph. C−H), 1592, 1460 (arom.), 1097 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.62 (m_c, 4 H, $OCH_2CH_2CH_2$), 1.85 (m_c, 4 H, OCH_2CH_2), 2.14 (m_c, 4 H, $CH_2CH=$), 4.03 (t, *J* = 6.4 Hz, 4 H, OCH_2), 4.97, 5.04 (tdd, J_t = 1.2 Hz, J_d = 2.1 Hz, J_d = 10.2 Hz, $=CH_{cis}$; tdd, J_t = 1.5 Hz, J_d = 2.1 Hz, J_d = 17.1 Hz, $=CH_{trans}$; 4 H), 5.84 (tdd, J_t = 6.7 Hz, J_d = 10.2 Hz, J_d = 17.1 Hz, 2 H, CH=), 6.53 (d, *J* = 8.3 Hz, 2 H, 4,6-H), 7.16 (t, *J* = 8.3 Hz, 1 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.3 (t, $OCH_2CH_2CH_2$), 28.6 (t, OCH_2CH_2), 33.4 (t, $CH_2CH=$), 69.1 (t, OCH_2), 102.1 (s, 2-C), 105.7 (d, 4,6-C), 114.7 (t, $=CH_2$), 128.0 (d, 5-C), 138.6 (d, CH=), 156.7 (s, 1,3-C) ppm. MS (CI, 70 eV): *m/z* (%) = 355, 353 (100, 98) [M^+ + H]. MS (EI, 70 eV): *m/z* (%) = 273 (90) [M^+ − Br]; 190, 188 (100, 99) [$M^+ - C_{12}H_{20}$]. $C_{18}H_{25}BrO_2$ (353.30), calcd. C 61.19, H 7.13; found C 61.03, H 7.39.

2,6-Bis(but-3-enoxy)benzeneboronic Acid (15a): 2-Bromo-1,3-bis(but-3-enoxy)benzene (**14a**, 1.30 g, 4.42 mmol) was dissolved in tetrahydrofuran (20 mL). At -78 °C, *n*-butyllithium (2.5 M in hexanes, 1.90 mL, 4.80 mmol) was added and the reaction mixture was

stirred at −78 °C for 1 h. After the addition of trimethyl borate (1.60 mL, 14.4 mmol), stirring was continued for 2 h while the reaction mixture was allowed to warm up to room temperature. Water (20 mL) was added, the water layer was extracted with diethyl ether (3 times, 20 mL each), and the combined organic layer was washed with saturated aqueous sodium chloride and dried with magnesium sulfate. After evaporation of the solvent in vacuo, the residue was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 85:15, until all starting material was collected, then 50:50), yielding 956 mg (83%) of **15a**. M.p. 78−79 °C. IR (KBr): $\tilde{\nu}$ = 3489 (O−H), 2947, 2878 (aliph. C−H), 1645 (aliph. C=C), 1598, 1574 (arom.), 1101 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.61 (qt, $J_q \approx 6.4$ Hz, $J_t \approx 1.4$ Hz, 4 H, OCH_2CH_2), 4.12 (t, J = 6.3 Hz, 4 H, OCH_2) 5.19, 5.24 (tdd, $J_t \approx 1.5$ Hz, $J_d \approx 1.6$ Hz, J_d = 10.2 Hz, $=CH_{cis}$; tdd, $J_d \approx 1.5$ Hz, $J_d \approx 1.6$ Hz, J_d = 17.1 Hz, $=CH_{trans}$; 4 H), 5.86 (tdd, J_t = 6.8 Hz, J_d = 10.2 Hz, J_d = 17.1 Hz, 2 H, CH=), 6.60 (d, J = 8.4 Hz, 2 H, 3,5-H), 7.21 (s, 2 H, OH), 7.35 (t, J = 8.4 Hz, 1 H, 4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.6 (t, OCH_2CH_2), 67.7 (t, OCH_2), 105.0 (d, 3,5-C), 118.3 (t, $=CH_2$), 132.8 (d, 4-C), 133.6 (d, CH=), 164.7 (s, 2,6-C). Because of relaxation effects with ^{11}B-isotopes the signal for 1-C is not detectable. MS (EI, 70 eV): m/z (%) = 262 (52) [M^+]; 208 (32) [$M^+ - C_4H_6$]; 154 (83) [$M^+ - C_8H_{12}$]. $C_{14}H_{19}BO_4$ (262.11) calcd. C 64.15, H 7.31; found C 63.88, H 7.15.

2,6-Bis(pent-4-enoxy)benzeneboronic Acid (15b): The synthesis was carried out analogously to that of **15a**, on a 5−10 mmol scale. Column chromatography was performed on silica gel (cyclohexane/ethyl acetate, 85:15). A 7.46 mmol batch gave 1.91 g (86%) of **15b**. M.p. 37−37.5 °C. IR (KBr): $\tilde{\nu}$ = 3510 (O−H), 3080 (arom. C−H), 2945 (aliph. C−H), 1644 (aliph. C=C), 1595, 1573 (arom.), 1099 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.96 (m_c, 4 H, OCH_2CH_2), 2.25 (m_c, 4 H, CH_2CH=), 4.09 (t, J = 6.5 Hz, 4 H, OCH_2), 5.03, 5.08 (tdd, $J_t \approx 1.5$ Hz, $J_d \approx 1.9$ Hz, J_d = 10.2 Hz, $=CH_{cis}$; tdd, $J_t \approx 1.5$ Hz, $J_d \approx 1.9$ Hz, J_d = 17.2 Hz, $=CH_{trans}$; 4 H), 5.82 (tdd, J_t = 6.7 Hz, J_d = 10.2 Hz, J_d = 17.2 Hz, 2 H, CH=), 6.60 (d, J = 8.4 Hz, 2 H, 3,5-H), 7.35 (t, J = 8.4 Hz, 1 H, 4-H), 7.35 (s, 2 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.3 (t, CH_2CH=), 30.0 (t, OCH_2CH_2), 68.3 (t, OCH_2), 105.2 (d, 3,5-C), 106.4 (s, 1-C)*, 115.2 (t, $=CH_2$), 132.9 (d, 4-C), 137.0 (d, CH=), 164.7 (s, 2,6-C). * Intensity of the signal is very low (see above). MS (EI, 70 eV): m/z (%) = 290 (28) [M^+]; 154 (73) [$M^+ - C_{10}H_{16}$]. $C_{16}H_{23}BO_4$ (290.17), calcd. C 66.23, H 7.99; found C 66.37, H 7.78.

2,6-Bis(hex-5-enoxy)benzeneboronic acid (15c): The synthesis was carried out analogously to that of **15a**, on a 5−10 mmol scale. Column chromatography was performed on silica gel (cyclohexane/ethyl acetate, 85:15). A 5.66 mmol batch gave 1.54 g (86%) of **15c**. M.p: 58−59 °C. IR (KBr): $\tilde{\nu}$ = 3504 (O−H), 3072 (arom. C−H), 2944 (aliph. C−H), 1640 (aliph. C=C), 1595 (arom.), 1103 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.60 (m_c, 4 H, $OCH_2CH_2CH_2$), 1.88 (m_c, 4 H, OCH_2CH_2), 2.13 (m_c, 4 H, CH_2CH_2=), 4.08 (t, J = 6.5 Hz, 4 H, OCH_2), 4.99, 5.03 (tdd, $J_t \approx 1.5$ Hz, J_d = 2.0 Hz, J_d = 10.2 Hz, $=CH_{cis}$; tdd, $J_t \approx 1.5$ Hz, J_d = 2.0 Hz, J_d = 17.1 Hz, $=CH_{trans}$; 4 H), 5.81 (tdd, J_t = 6.7 Hz, J_d = 10.2 Hz, J_d = 17.1 Hz, 2 H, CH=), 6.60 (d, J = 8.4 Hz, 2 H, 3,5-H), 7.34 (t, J = 8.4 Hz, 1 H, 4-H), 7.36 (s, 2 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.1 (t, $OCH_2CH_2CH_2$), 28.5 (t, OCH_2CH_2), 33.2 (t, CH_2CH=), 68.8 (t, OCH_2), 105.0 (d, 3,5-C), 105.0 (s, 1-C)*, 115.1 (t, $=CH_2$), 132.8 (d, 4-C), 137.5 (d, CH=), 164.9 (s, 2,6-C). * Intensity of the signal is very low (see above). MS (CI, 70 eV): m/z (%) = 319 (100) [M^+ + H]. MS (EI, 70 eV): m/z (%) = 318 (6) [M^+]; 236 (5) [$M^+ - C_6H_{10}$]; 154 (16) [$M^+ - C_{12}H_{20}$]. $C_{18}H_{27}BO_4$ (318.22), calcd. C 67.94, H 8.55; found C 68.11, H 8.74.

2-(2,6-Dimethoxyphenyl)-1,10-phenanthroline (17a): 2-Chloro-1,10-phenanthroline (**16a**, 373 mg, 1.74 mmol), 2,6-dimethoxybenzeneboronic acid (**3**, 317 mg, 1.74 mmol), and tetrakis(triphenylphosphane)palladium(0) (100 mg, 87.0 μmol) were dissolved in dimethoxyethane (10 mL). After addition of aqueous sodium carbonate (2 N, 1.8 mL), the reaction mixture was heated under reflux for 20 h. Water and dichloromethane (10 mL each) were added, the water layer was extracted with dichloromethane (3 times, 15 mL each), and the combined organic layer was washed with saturated aqueous sodium chloride and dried with magnesium sulfate. The solvent was evaporated in vacuo and the residue was purified by recrystallization from chloroform/methanol, yielding 398 mg (72%) of **17a**. The spectroscopic data were in accordance with the literature.[11]

2-{2,6-Dimethoxy-4-[(2-tetrahydropyranyloxy)methyl]phenyl}-1,10-phenanthroline (17b): 2-Bromo-1,3-dimethoxy-5-[(2-tetrahydropyranyloxy)methyl]benzene (**10**, 2.000 g, 6.039 mmol) was dissolved in tetrahydrofuran (40 mL). At −70 °C, *n*-butyllithium (2.5 M in hexanes, 2.70 mL, 6.75 mmol) was added and the reaction mixture was stirred for 30 min at −70 °C. After the addition of trimethyl borate (2.1 mL, 19 mmol), stirring was continued for 1 h, during which the reaction mixture was allowed to warm up to room temperature. Water (40 mL) was added, the water layer was extracted with diethyl ether (3 times, 40 mL each), and the combined organic layer was washed with saturated aqueous sodium chloride and was dried with magnesium sulfate. After evaporation of the solvent in vacuo, the residue, 2-chloro-1,10-phenanthroline (**16a**, 1.166 g, 5.435 mmol), and tetrakis(triphenylphosphane)palladium(0) (360 mg, 313 μmol) were dissolved in dimethoxyethane (60 mL). After the addition of aqueous sodium carbonate (2 N, 6 mL), the reaction mixture was heated under reflux for 20 h. Water and dichloromethane (60 mL each) were added, the water layer was extracted with dichloromethane (3 times, 60 mL each), and the combined organic layer was washed with saturated aqueous sodium chloride and dried with magnesium sulfate. The solvent was evaporated in vacuo and the residue was purified by recrystallization from chloroform/*n*-pentane, yielding 2.14 g (91%) of **17b**. M.p. 155 °C. IR (KBr): $\tilde{\nu}$ = 2932, 2864 (aliph. C−H), 1582, 1455 (arom.), 1228, 1127 (C−O−C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.7−1.9 (m, 6 H, CH_2), 2.28 (H_2O, ca. 0.5 H), 3.5−3.6 (m, 1 H, CH_2O), 3.70 (s, 6 H, $ArOCH_3$), 3.9−4.0 (m, 1 H, CH_2O), 4.60 (d, J = 12.3 Hz, 1 H, $ArCH_2O$), 4.74 (dd, J = 2.9 Hz, J = 4.5 Hz, 1 H, OCHO), 4.82 (d, J = 12.3 Hz, 1 H, $ArCH_2O$), 6.68 (s, 2 H, ArH), 7.26 (s, 1 H, $CHCl_3$), 7.56 (dd, J = 4.3 Hz, J = 8.0, 1 H, 8-H), 7.61 (d, J = 8.1 Hz, 1 H, 3-H), 7.77 (m_c, 2 H, 5,6-H), 8.20 (dd, J = 1.8 Hz, J = 8.1 Hz, 1 H, 7-H), 8.23 (d, J = 8.2 Hz, 1 H, 4-H), 9.18 (dd, J = 1.8 Hz, J = 4.3 Hz, 1 H, 9-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.6, 25.5, 30.7 (3 t, CH_2), 56.0 (q, $ArOCH_3$), 62.5 (t, $ArCH_2O$), 68.9 (t, CH_2O), 97.4 (d, OCHO), 103.9 (d, 3′,5′-C), 119.4 (s, 1′-C), 122.6 (d, 8-C), 126.1, 126.1, 126.6 (3 d, 3,5,6-C), 127.4, 128.7 (2 s, 4a,6a-C), 135.5, 135.8 (2 d, 4,7-C), 140.2 (s, 4′-C), 146.3, 146.6 (2 s, 10a,10b-C), 150.2 (d, 9-C), 155.7 (s, 2-C), 158.5 (s, 2′,6′-C) ppm. MS: (EI, 70 eV): m/z (%) = 430 (87) [M^+]; 429 (100) [$M^+ - H$]; 412 (25) [$M^+ - H_2O$]; 345 (10) [$M^+ - C_5H_9O$]; 330 (10) [$M^+ - C_6H_{12}O$]; 329 (16) [$M^+ - C_6H_{13}O$]; 312 [$M^+ - C_6H_{14}O_2$]. $C_{26}H_{26}N_2O_4$ (430.50): calcd. C 72.54, H 6.09, N 6.51, $C_{48}H_{56}N_2O_4 \cdot 0.9CHCl_3 \cdot 0.1H_2O$, calcd. C 59.86, H 5.06, N 5.19, found C 59.60, H 4.69, N 5.03.

2-[2,6-Dimethoxy-4-(hydroxymethyl)phenyl]-1,10-phenanthroline (17c): A solution of *p*-toluenesulfonic acid (133 mg, 699 μmol) in

dry ethanol (5 mL) was added dropwise over 30 min to a refluxing solution of compound **17b** (200 mg, 0.465 mmol) in dry ethanol (50 mL). Heating was continued for 4 h. The volume was reduced to 5 mL and addition of water and neutralization with 2 N aqueous sodium hydroxide precipitated the product. The beige solid was filtered off and dried in vacuo (< 1 mbar) in the presence of P_2O_5 to yield pure compound **17c** as a beige powder, in 73% yield (118 mg). M.p. >250 °C. IR (KBr): $\tilde{\nu}$ = 3363 (O−H), 2935 (aliph. C−H), 1581, 1450 (arom.), 1222, 1122 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, [D_6]DMSO): δ = 3.64 (s, 6 H, $ArOCH_3$), 4.62 (d, *J* = 5.8 Hz, 2 H, $ArCH_2OH$), 5.41 (t, *J* = 5.8 Hz, 1 H, $ArCH_2OH$), 6.79 (s, 2 H, ArH), 7.59 (d, *J* = 8.2 Hz, 1 H, 3-H), 7.75 (dd, *J* = 4.3 Hz, *J* = 8.1 Hz, 1 H, 8-H), 8.01 (m_c, 2 H, 5,6-H), 8.45 (d, *J* = 8.2 Hz, 1 H, 4-H), 8.50 (dd, *J* = 1.8 Hz, *J* = 8.1 Hz, 1 H, 7-H), 9.03 (dd, *J* = 1.8 Hz, *J* = 4.3 Hz, 1 H, 9-H) ppm. MS: (EI, 70 eV): *m*/*z* (%) = 346 (48) [M^+]; 345 (100) [M^+ − H]; 328 (62) [M^+ − H_2O]; 315 (17) [M^+ − CH_3O].

2-[4-(Chloromethyl)-2,6-dimethoxyphenyl]-1,10-phenanthroline (17d): 2-[2,6-Dimethoxy-4-(hydroxymethyl)phenyl]-1,10-phenanthroline (**17c**, 100 mg, 289 μmol) was dissolved in conc. hydrochloric acid (4 mL). The yellow solution was stirred for 16 h at 100 °C. After neutralization with solid sodium carbonate, the product precipitated. The solid was filtered off, dissolved in 10 mL of dichloromethane, and dried with magnesium sulfate. The solvent was removed in vacuo and the residue was purified by filtration through basic aluminium oxide (dichloromethane), yielding 87.0 mg (83%) of **17d**.

The reaction was also carried out with 2-{2,6-dimethoxy-4-[(2-tetrahydropyranyloxy)methyl]phenyl}-1,10-phenanthroline (**17b**, 100 mg, 232 μmol) instead of compound **17c**, yielding 54 mg (64%) of **17d**. M.p. 189 °C. IR (KBr): $\tilde{\nu}$ = 2934 (aliph. C−H), 1585, 1456 (arom.), 1235, 1126 (C−O−C) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.70 (s, 6 H, $ArOCH_3$), 4.63 (s, 2 H, $ArCH_2Cl$), 6.68 (s, 2 H, ArH), 7.58 (dd, *J* = 4.4 Hz, *J* = 8.0 Hz, 1 H, 8-H), 7.60 (d, *J* = 8.2 Hz, 1 H, 3-H), 7.80 (m_c, 2 H, 5,6-H), 8.23 (dd, *J* = 1.7 Hz, *J* = 8.0 Hz, 1 H, 7-H), 8.25 (d, *J* = 8.2 Hz, 1 H, 4-H), 9.18 (dd, *J* = 1.7 Hz, *J* = 4.4 Hz, 1 H, 9-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.8 (t, $ArCH_2Cl$), 55.9 (q, $ArOCH_3$), 104.5 (d, 3′,5′-C), 119.2 (s, 1′-C), 122.8 (d, 8-C), 126.2, 126.3, 126.8 (3 d, 3,5,6-C), 127.5, 128.8 (2 s, 4a,6a-C), 135.8, 137.1 (2 d, 4,7-C), 139.4 (s, 4′-C), 145.2 (s, 10a,10b-C), 149.3 (d, 9-C), 154.9 (s, 2-C), 158.3 (s, 2′,6′-C) ppm. MS: (EI, 70 eV): *m*/*z* (%) = 366, 364 (27, 62) [M^+]; 365, 363 (49, 100) [M^+ − H]; 348, 346 (31, 66) [M^+ − H_2O]; 335, 333 (12, 18) [M^+ − CH_3O]; 329 (10) [M^+ − Cl].

2-{2,6-Dimethoxy-4-[(2,2-bis(ethoxycarbonyl)ethyl]phenyl}-1,10-phenanthroline (17e): Sodium hydride (60% dispersion in mineral oil, 49.0 mg, 1.23 mmol, washed with *n*-pentane) was added to diethyl malonate (10 mL). After the mixture had been stirred for 30 min, a solution of compound **17d** (300 mg, 822 μmol) in dry *N*,*N*-dimethylformamide (5 mL) was added. The reaction mixture was stirred for 16 h at 100 °C. The solvents were removed in vacuo, and the residue was dissolved in dichloromethane and water (10 mL each). The water layer was extracted with dichloromethane (3 times, 10 mL each) and the combined organic layer was dried with magnesium sulfate. The solvent was evaporated in vacuo, and the residue was purified by column chromatography (basic aluminium oxide, dichloromethane) and recrystallization from cyclohexane/ethyl acetate, yielding 209 mg (52%). M.p. 136 °C. IR (KBr): $\tilde{\nu}$ = 2936 (aliph. C−H), 1721 (C=O), 1581, 1456 (arom.), 1242, 1126 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.1 Hz, 6 H, OCH_2CH_3), 2.20 (H_2O, ca. 1 H), 3.28 (d, *J* = 7.7 Hz, 2 H, $ArCH_2$), 3.68 (s, 6 H, $ArOCH_3$), 3.71 [t, *J* = 7.7 Hz, 1 H, $ArCH_2CH(COOEt)_2$], 4.24 (m_c, 4 H, OCH_2CH_3), 6.53 (s, 2 H, ArH), 7.58, 7.59 (dd, *J* = 4.4 Hz, *J* = 8.1 Hz, 8-H; d, *J* = 8.2 Hz, 3-H; 2 H), 7.79 (m_c, 2 H, 5,6-H), 8.22, 8.24 (dd, *J* = 1.8 Hz, *J* = 8.1 Hz, 7-H; d, *J* = 8.2 Hz, 4-H; 2 H), 9.18 (dd, *J* = 1.8 Hz, *J* = 4.4 Hz, 1 H, 9-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (q, OCH_2CH_3), 35.3 (t, $ArCH_2$), 54.0 [d, $ArCH_2CH(COOEt)_2$], 56.0 (q, $ArOCH_3$), 61.7 (t, OCH_2CH_3), 104.9 (d, 3′,5′-C), 118.6 (s, 1′-C), 122.6 (d, 8-C), 126.1, 126.2, 126.6 (3 d, 3,5,6-C), 127.4, 128.7 (2 s, 4a,6a-C), 135.5, 135.9 (2 d, 4,7-C), 140.1 (s, 4′-C), 146.2, 146.5 (2 s, 10a,10b-C), 150.2 (d, 9-C), 155.5 (s, 2-C), 158.4 (s, 2′,6′-C), 168.9 (s, COOEt) ppm. MS: (EI, 70 eV): *m*/*z* (%) = 488 (78) [M^+]; 487 (100) [M^+ − H]; 470 (78) [M^+ − H_2O]; 459 (5) [M^+ − C_2H_5]; 443 (14) [M^+ − C_2H_5O]. $C_{28}H_{28}N_2O_6$ (488.54): calcd. C 68.84, H 8.78, N 5.73, $C_{48}H_{56}N_2O_4 \cdot 0.2H_2O$, calcd. C 68.34, H 5.82, N 5.69, found C 68.35, H 5.91, N 5.53.

2-Chloro-9-(2,6-dimethoxyphenyl)-1,10-phenanthroline (17f): The synthesis of compound **17f** was carried out analogously to the synthesis of **17a**, starting from 803 μmol of 2,9-dichloro-1,10-phenanthroline (**16b**) and yielding 207 mg (73%) of **17f**. M.p. > 250 °C. IR (KBr): $\tilde{\nu}$ = 2837 (aliph. C−H), 1590, 1471 (arom.), 1248, 1111 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.67 (H_2O, ca. 1 H), 3.75 (s, 6 H, $ArOCH_3$), 6.70 (d, *J* = 8.3 Hz, 2 H, 3′,5′-H), 7.36 (t, *J* = 8.3 Hz, 1 H, 4′-H), 7.55 [d, *J* = 8.4 Hz, 1 H, 8-H (or 3-H)]; 7.67 [d, *J* = 8.3 Hz, 1 H, 3−H (or 8-H)]; 7.77 (m_c, 2 H, 5,6-H), 8.15 [d, *J* = 8.4 Hz, 1 H, 7-H (or 4-H)]; 8.23 [d, *J* = 8.4 Hz, 1 H, 4-H (or 7-H)] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.4 (q, $ArOCH_3$), 104.9 (d, 3′,5′-C), 120.2 (s, 1′-C), 123.9, 125.3, 126.8, 127.0 (4 d, 3,5,6,8-C), 127.3, 128.8 (2 s, 4a,6a-C), 129.9 (d, 4′-C), 135.3, 138.6 (2 d, 4,7-C), 145.1, 146.4 (2 s, 10a,10b-C), 151.0 (s, 2-C), 155.8 (s, 9-C), 158.5 (s, 2′,6′-C) ppm. MS: (EI, 70 eV): *m*/*z* (%) = 352, 350 (23, 53) [M^+]; 351, 349 (40, 100) [M^+ − H]; 334, 332 (32, 46) [M^+ − H_2O]; 321, 319 (9, 18) [M^+ − CH_3O]. $C_{20}H_{15}ClN_2O_2$ (350.80): calcd. C 68.48, H 4.31, N 7.99, $C_{48}H_{56}N_2O_4 \cdot 0.3\ H_2O$, calcd. C 67.44, H 4.41, N 7.86, found C 67.43, H 4.34, N 7.91.

2-Chloro-9-[2,6-bis(pent-4-enoxy)phenyl]-1,10-phenanthroline (17g): 2,6-Bis(pent-4-enoxy)benzeneboronic acid (**15b**, 96.0 mg, 331 mmol), tetrakis(triphenylphosphane)palladium(0) (35.0 mg, 30.0 μmol), and aqueous sodium carbonate (2 N, 0.3 mL) were added to a solution of 2,9-dichloro-1,10-phenanthroline (**16b**, 75.0 mg, 301 μmol) in dimethoxyethane (20 mL). The reaction mixture was heated under reflux for 16 h. After addition of water and dichloromethane (20 mL each), the water layer was extracted with dichloromethane (3 times, 30 mL each) and the combined organic layer was washed with saturated aqueous sodium chloride. The solvent was removed in vacuo, and the residue was purified by filtration through basic aluminium oxide (dichloromethane) and by column chromatography (silica gel, dichloromethane/0.5% methanol), and was then recrystallized from dichloromethane/*n*-hexane to yield 98 mg (71%) of **17g**. M.p. 85−87 °C. IR (KBr): $\tilde{\nu}$ = 2932 (aliph. C−H), 1641 (aliph. C=C), 1592, 1479, 1456 (arom.), 1107 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.66 (m_c, 4 H, OCH_2CH_2), 2.03 (m_c, 4 H, $CH_2CH=$), 4.01 (t, *J* = 6.3 Hz, 4 H, OCH_2), 4.7−4.9 (m, 4 H, $=CH_2$), 5.63 (tdd, J_t = 6.6 Hz, J_d = 9.6 Hz, J_d = 17.7 Hz, 2 H, CH=), 6.68 (d, *J* = 8.4 Hz, 4 H, 3′,5′-H), 7.31 (t, *J* = 8.4 Hz, 2 H, 4′-H), 7.56, 7.75 (2 d, *J* = 8.4 Hz, 2 H, 3,8-H), 7.76, 7.84 (2 d, *J* = 8.8 Hz, 2 H, 5,6-H), 8.17, 8.22 (2 d, *J* = 8.4 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.4 (t, $CH_2CH=$), 30.0 (t, OCH_2CH_2), 68.4 (t, OCH_2), 106.1 (d, 3′,5′-C), 114.5 (t, $=CH_2$), 120.7 (s, 1′-C), 123.8, 125.1, 127.0, 127.1, 130.0, 134.6, 138.5 (7 d, 4′,3,4,5,6,7,8-C), 127.2, 127.5 (2 s, 4a,6a-C), 138.2 (d, CH=), 144.8, 146.3 (2 s, 10a,10b-C), 150.9, 155.7 (2 s,

2,9-C), 158.1 (2′,6′-C) ppm. MS: (EI, 70 eV): *m/z* (%) = 460, 458 (26, 63) [M^+]; 419, 417 (34, 100) [$M^+ - C_3H_5$]; 405, 403 (29, 77) [$M^+ - C_4H_7$]; 391, 389 (7, 18) [$M^+ - C_5H_9$]. $C_{28}H_{27}ClN_2O_2$ (458.99): calcd. C 73.27, H 5.93, N 6.10; found C 73.19, H 6.09, N 5.98.

2,9-Bis(2,6-dimethoxyphenyl)-1,10-phenanthroline (18a): The synthesis of compound **18a** was carried out analogously to the synthesis of **17a**, with 2,9-dichloro-1,10-phenanthroline (**16b**, 803 μmol) and 2 equiv. of compound **3**. Refluxing for 2 days gave 300 mg (83%) of **18a**. The spectroscopic data were in accordance with ref.[11]

9-(2,6-Dimethoxyphenyl)-2-{2,6-dimethoxy-4-[(2-tetrahydropyranyloxy)methyl]phenyl}-1,10-phenanthroline (18b): The synthesis of compound **18b** was carried out analogously to the synthesis of **17b**, with 2-chloro-9-(2,6-dimethoxyphenyl)-1,10-phenanthroline (854 μmol, **17f**). Refluxing for 2 days gave 283 mg (88%) of **18b**. M.p. > 250 °C. IR (KBr): $\tilde{\nu}$ = 2939 (aliph. C−H), 1582, 1472 (arom.), 1247, 1108 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.5−1.9 (m, 6 H, CH_2), 3.5−3.6 (m, 1 H, CH_2O), 3.72 (s, 6 H, $ArOCH_3$), 3.73 (s, 6 H, $ArOCH_3$), 3.9−4.0 (m, 1 H, CH_2O), 4.55 (d, *J* = 12.3 Hz, 1 H, $ArCH_2O$), 4.72 (dd, *J* = 2.9 Hz, *J* = 4.4 Hz, 1 H, OCHO), 4.79 (d, *J* = 12.3 Hz, 1 H, $ArCH_2O$), 6.65 (d, *J* = 8.4 Hz, 2 H, 3′′,5′′-H), 6.67 (s, 2 H, 3′,5′-H), 7.25 (s, 1 H, $CHCl_3$), 7.30 (t, *J* = 8.4 Hz, 1 H, 4′′-H), 7.61, 7.62 (2 d, *J* = 8.2 Hz, 2 H, 3,8-H), 7.80 (m_c, 2 H, 5,6-H), 8.23, 8.23 (2 d, *J* = 8.2 Hz, 2 H, 4,7-H) ppm. MS: (EI, 70 eV): *m/z* (%) = 566 (100) [M^+]; 565 (96) [$M^+ - H$]; 548 (49) [$M^+ - H_2O$]; 535 (17) [$M^+ - CH_3O$]; 481 (13) [$M^+ - C_5H_9O$]; 465 (17) [$M^+ - C_5H_9O_2$]. $C_{34}H_{34}N_2O_6$ (566.65): calcd. C 72.07, H 6.05, N 4.94, $C_{34}H_{34}N_2O_6 \cdot 0.75\ CHCl_3$, calcd. C 63.61, H 5.34, N 4.27, found C 63.85, H 4.98, N 4.14.

2-(4-Chloromethyl-2,6-dimethoxyphenyl)-9-(2,6-dimethoxyphenyl)-1,10-phenanthroline (18d): The synthesis of compound **18d** was carried out analogously to the synthesis of **17d**, with 9-(2,6-dimethoxyphenyl)-2-{2,6-dimethoxy-5-[(2-tetrahydropyranyloxy)methyl]phenyl}-1,10-phenanthroline (**18b**, 176 μmol) and yielding 72 mg (82%) of **18c**. M.p. > 250 °C. IR (KBr): $\tilde{\nu}$ = 2935 (aliph. C−H), 1585, 1470 (arom.), 1248, 1110 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.72, 3.73 (2 s, 12 H, $ArOCH_3$), 6.65 (d, *J* = 8.4 Hz, 2 H, 3′′,5′′-H), 6.67 (s, 2 H, 3′,5′-H), 7.24 (s, ca. 0.5 H, $CHCl_3$), 7.30 (t, *J* = 8.4 Hz, 1 H, 4′′-H), 7.60, 7.63 (2 d, *J* = 8.2 Hz, 2 H, 3,8-H), 7.81 (s, 2 H, 5,6-H), 8.24 (d, *J* = 8.2 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.7 (t, $ArCH_2Cl$), 56.0 (2 q, $ArOCH_3$), 104.5, 104.8 (2 d, 3′,5′,3′′,5′′-C), 119.5, 119.6 (2 s, 1′,1′′-C), 125.9, 126.1, 126.2, 126.4 (4 d, 3,5,6,8-C), 127.6 (2 s, 4a,6a-C), 129.9 (d, 4′′-C), 135.7, 135.8 (2 d, 4,7-C), 139.3 (s, 4′-C), 145.9 (2 s, 10a,10b-C), 154.3, 154.7 (2 s, 2,9-C), 158.2, 158.3 (2 s, 2′,6′,2′′,6′′-C) ppm. MS: (EI, 70 eV): *m/z* (%) = 500, 502 (53, 23) [M^+]; 499, 501 (100, 44) [$M^+ - H$]; 482, 484 (28, 16) [$M^+ - H_2O$]; 481, 483 (28, 12) [$M^+ - H - H_2O$]; 465 (8) [$M^+ - Cl$]. $C_{29}H_{25}ClN_2O_4$ (500.98): calcd. C 69.53, H 5.03, N 5.59, $C_{29}H_{25}ClN_2O_4 \cdot 0.5\ CHCl_3$, calcd. C 63.20, H 4.58, N 5.00, found C 63.53, H 4.62, N 4.84.

2-{2,6-Dimethoxy-4-[(2,2-bis(ethoxycarbonyl)ethyl]phenyl}-9-(2,6-dimethoxyphenyl)-1,10-phenanthroline (18e): The synthesis of compound **18e** was carried out analogously to the synthesis of **17e**, with 2-(4-chloromethyl-2,6-dimethoxyphenyl)-9-(2,6-dimethoxyphenyl)-1,10-phenanthroline (**18d**, 299 μmol). The product was purified by chromatography (silica gel, dichloromethane/2% methanol) and filtration through basic aluminium oxide (dichloromethane), yielding 89 mg (48%) of **18e**. M.p. > 250 °C. IR (KBr): $\tilde{\nu}$ = 2936 (aliph. C−H), 1746 (C=O), 1579, 1472 (arom.), 1249, 1112 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.1 Hz, 6 H, OCH_2CH_3), 2.41 (H_2O, ca. 1 H), 3.24 (d, *J* = 7.7 Hz, 2 H, $ArCH_2$), 3.69 (t, *J* = 7.7 Hz, 1 H, $ArCH_2CH(COOEt)_2$], 3.70, 3.72 (2 s, 12 H, $ArOCH_3$), 4.21 (m_c, 4 H, OCH_2CH_3), 6.51 (s, 2 H, 3′,5′-H), 6.65 (d, *J* = 8.4 Hz, 2 H, 3′′,5′′-H), 7.30 (t, *J* = 8.4 Hz, 1 H, 4′′-H), 7.59, 7.62 (2 d, *J* = 8.2 Hz, 2 H, 3,8-H), 7.79 (s, 2 H, 5,6-H), 8.22, 8.23 (2 d, *J* = 8.2 Hz, 1 H, 4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (q, OCH_2CH_3), 35.2 (t, $ArCH_2$), 53.9 [d, $ArCH_2CH(COOEt)_2$], 56.4, 56.4 (2 q, $ArOCH_3$), 61.6 (t, OCH_2CH_3), 105.0, 105.7 (2 d, 3′,5′,3′′,5′′-C), 119.2, 120.7 (2 s, 1′,1′′-C), 125.9, 126.0, 126.2 (3 d, 3,5,6,8-C), 127.5 (s, 4a,6a-C), 129.7 (d, 4′′-C), 135.3, 135.4 (2 d, 4,7-C), 140.1 (s, 4′-C), 146.3 (s, 10a,10b-C), 154.7, 154.9 (2 s, 2,9-C), 158.4, 158.5 (2 s, 2′,6′,2′′,6′′-C), 168.9 (s, COOEt) ppm. MS: (EI, 70 eV): *m/z* (%) = 642 (92) [M^+]; 623 (100) [$M^+ - H$]; 606 (45) [$M^+ - H_2O$]; 593 (12) [$M^+ - CH_3O$]; 579 (11) [$M^+ - CHO_2$]. $C_{36}H_{36}N_2O_8$ (624.69): calcd. C 69.22, H 5.81, N 4.48, $C_{29}H_{25}N_2O_4 \cdot 0.5\ H_2O$, calcd. C 68.23, H 5.89, N 4.42, found C 68.24, H 6.01, N 4.30.

2,9-Bis[2,6-bis(but-3-enoxy)phenyl]-1,10-phenanthroline (18f): 2,9-Bis(but-4-enoxy)benzeneboronic acid (**15a**, 263 mg, 1.00 mmol), tetrakis(triphenylphosphane)palladium(0) (46.0 mg, 40.0 μmol), barium hydroxide (258 mg, 1.51 mmol), and water (2 mL) were added to a solution of 2,9-dichloro-1,10-phenanthroline (**16b**, 100 mg, 402 μmol) in dimethoxyethane (20 mL). The reaction mixture was heated under reflux for 16 h. After the addition of water and dichloromethane (20 mL each), the water layer was extracted with dichloromethane (3 times, 30 mL each) and the combined organic layer was washed with saturated aqueous sodium chloride. The solvent was removed in vacuo, and the residue was purified by filtration through basic aluminium oxide (dichloromethane) and recrystallized from dichloromethane/*n*-hexane, yielding 191 mg (78%) of **18f**. M.p. 142-143 °C. IR (KBr): $\tilde{\nu}$ = 3448 (O−H, moisture), 3070 (arom. C−H), 2938, 2872 (aliph. C−H), 1642 (aliph. C=C), 1593, 1459 (arom.), 1102 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.25 (qt, J_q = 6.8 Hz, $J_t \approx$ 1.3 Hz, 8 H, OCH_2CH_2), 3.96 (t, *J* = 6.8 Hz, 8 H, OCH_2), 4.7−4.9, (m, 8 H, $=CH_2$), 5.60 (tdd, J_t = 6.8 Hz, J_d = 10.2 Hz, J_d = 17.2 Hz, 4 H, CH=), 6.63 (d, *J* = 8.4 Hz, 4 H, 3′,3′′,5′,5′′-H), 7.25 (t, *J* = 8.4 Hz, 2 H, 4′,4′′-H), 7.62 (d, *J* = 8.2 Hz, 2 H, 3,8-H), 7.81 (s, 2 H, 5,6-H), 8.20 (d, *J* = 8.2 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 33.5 (t, OCH_2CH_2), 68.5 (t, OCH_2), 106.3 (d, 3′,3′′,5′,5′′-C), 116.4 (t, $=CH_2$), 121.4 (s, 1′,1′′-C), 126.0, 126.1 (2 d, 3,5,6,8-C), 127.2 (s, 4a,6a-C), 129.5 (d, 4′,4′′-C), 134.7, 134.8 (2 d, 4,7-C, CH=), 146.2 (s, 10a,10b-C), 154.8 (s, 2,9-C), 157.8 (s, 2′,2′′,6′,6′′-C). Assignment was confirmed by HMBC and HSQC. MS: (EI, 70 eV): *m/z* (%) = 612 (100) [M^+]; 571 (88) [$M^+ - C_3H_5$]; 557 (26) [$M^+ - C_4H_7$]. $C_{40}H_{40}N_2O_4$ (612.77), calcd. C 78.41, H 6.58, N 4.57, $C_{40}H_{40}N_2O_4 \cdot 0.2\ H_2O$, calcd. C 77.95, H 6.61, N 4.55, found C 77.87, H 6.68, N 4.48.

2,9-Bis[2,6-bis(pent-4-enoxy)phenyl]-1,10-phenanthroline (18g): 2,9-Diiodo-1,10-phenanthroline (**16c**, 200 mg, 462 μmol) was dissolved in dimethoxyethane (40 mL). After addition of 2,9-bis(pent-4-enoxy)-benzeneboronic acid (**15b**, 336 mg, 1.16 mmol), tetrabutylammonium fluoride (732 mg, 2.32 mmol), and tetrakis(triphenylphosphane)palladium(0) (54.0 mg, 46.0 μmol), the reaction mixture was heated under reflux for 16 h. After the addition of water and dichloromethane (20 mL each), the water layer was extracted with dichloromethane (3 times, 30 mL each) and the combined organic layer was washed with saturated aqueous sodium chloride. The solvent was removed in vacuo and the residue was purified by filtration through basic aluminium oxide (dichloromethane) and recrystallized from dichloromethane/*n*-hexane, yielding 273 mg

(88%) of **18g**. − The reaction analogous to that used for the preparation of **18f**, but with 2,9-dichloro-1,10-phenanthroline (1.61 mmol) and barium hydroxide as the base, gave 988 mg (92%) of **18g**. M.p. 111 °C. IR (KBr): $\tilde{\nu}$ = 3072 (arom. C−H), 2936, 2871 (aliph. C−H), 1638 (aliph. C=C), 1596, 1459 (arom.), 1102 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.58 (m_c, 8 H, OCH_2CH_2), 1.87 (m_c, 8 H, CH_2CH=), 3.92 (t, J = 6.4 Hz, 8 H, OCH_2), 4.7−4.8 (m, 8 H, $=CH_2$), 5.57 (tdd, J_t = 6.7 Hz, J_d = 10.3 Hz, J_d = 17.0 Hz, 4 H, CH=), 6.61 (d, J = 8.4 Hz, 4 H, 3′,3′′,5′,5′′-H), 7.23 (t, J = 8.4 Hz, 2 H, 4′,4′′-H), 7.61 (d, J = 8.2 Hz, 2 H, 3,8-H), 7.80 (s, 2 H, 5,6-H), 8.21 (d, J = 8.2 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.2 (t, CH_2CH=), 29.9 (t, OCH_2CH_2), 68.5 (t, OCH_2), 106.3 (d, 3′,3′′,5′,5′′-C), 114.6 (t, $=CH_2$), 121.9 (s, 1′,1′′), 125.9, 126.0 (2 d, 3,5,6,8-C), 127.2 (s, 4a,6a-C), 129.3 (d, 4′,4′′-C), 134.7 (d, 4,7-C), 138.1 (d, CH=), 146.4 (s, 10a,10b-C), 155.0 (s, 2,9-C), 158.0 (2′,2′′,6′,6′′-C) ppm. MS: (EI, 70 eV): *m/z* (%) = 668 (100) [M^+]; 627 (97) [$M^+ - C_3H_5$]; 613 (74) [$M^+ - C_4H_7$]; 599 (20) [$M^+ - C_5H_9$]. $C_{44}H_{48}N_2O_4$ (668.36): calcd. C 79.01, H 7.23, N 4.19; found C 78.88, H 7.06, N 4.09.

2,9-Bis[2,6-bis(hex-5-enoxy)phenyl]-1,10-phenanthroline (18h): The synthesis of compound **18h** was carried out analogously to that of **18g**, with 2,6-bis(hex-5-enoxy)benzeneboronic acid (**15c**, 254 µmol), yielding 162 mg (88%) of **18h**. − The reaction analogous to that used for the preparation of **18f**, but with 2,9-dichloro-1,10-phenanthroline (1.61 mmol) and barium hydroxide as the base, gave 1.17 g (73%) of **18h**. M.p. 108−109 °C. IR (KBr): $\tilde{\nu}$ = 3072 (arom. C−H), 2934 (aliph. C−H), 1639 (aliph. C=C), 1596, 1458 (arom.), 1104 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.21 (m_c, 8 H, $OCH_2CH_2CH_2$), 1.49 (m_c, 8 H, OCH_2CH_2), 1.80 (m_c, 8 H, CH_2CH=), 3.91 (t, J = 6.4 Hz, 8 H, OCH_2), 4.7−4.8 (m, 8 H, $=CH_2$), 5.30 (s, 0.10 H, CH_2Cl_2), 5.53 (tdd, J_t = 6.6 Hz, J_d = 10.4 Hz, J_d = 16.9 Hz, 4 H, CH=), 6.61 (d, J = 8.4 Hz, 4 H, 3′,3′′,5′,5′′-H), 7.24 (t, J = 8.4 Hz, 2 H, 4′,4′′-H), 7.60 (d, J = 8.2 Hz, 2 H, 3,8-H), 7.80 (s, 2 H, 5,6-H), 8.19 (d, J = 8.2 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.0 (t, $OCH_2CH_2CH_2$), 28.4 (t, OCH_2CH_2), 33.1 (t, CH_2CH=), 69.0 (t, OCH_2), 106.2 (d, 3′,3′′,5′,5′′-C), 114.2 (t, $=CH_2$), 121.8 (s, 1′,1′′-C), 125.9, 126.0 (2 d, 3,5,6,8-C), 127.3 (s, 4a,6a-C), 129.3 (d, 4′,4′′-C), 134.7 (d, 4,7-C), 138.6 (d, CH=), 146.4 (s, 10a,10b-C), 155.1 (s, 2,9-C), 158.1 (2′,2′′,6′,6′′-C) ppm. MS: (EI, 70 eV): *m/z* (%) = 724 (100) [M^+]; 669 (12) [$M^+ - C_4H_7$]; 655 (58) [$M^+ - C_5H_9$]; 641 (81) [$M^+ - C_6H_{11}$]. $C_{48}H_{56}N_2O_4$ (724.99): calcd. C 79.52, H 7.79, N 3.86, $C_{48}H_{56}N_2O_4 \cdot 0.1CH_2Cl_2$, calcd. C 78.77, H 7.72, N 3.82, found C 78.68, H 7.72, N 3.70.

2-[2,6-Bis(but-3-enoxy)phenyl]-9-[2,6-bis(pent-4-enoxy)phenyl]-1,10-phenanthroline (18i): 2,9-Bis(but-3-enoxy)benzeneboronic acid (**15a**, 357 mg, 1.36 mmol), tetrakis(triphenylphosphane)palladium(0) (126 mg, 109 µmol), barium hydroxide (350 mg, 2.04 mmol), and water (12.5 mL) were added to a solution of 2-chloro-9-[2,6-bis(pent-4-enoxy)phenyl]-1,10-phenanthroline (**17g**, 500 mg, 1.09 mmol) in dimethoxyethane (50 mL). The reaction mixture was heated under reflux for 16 h. After the addition of water and dichloromethane (50 mL each), the water layer was extracted with dichloromethane (3 times, 50 mL each) and the combined organic layer was washed with saturated aqueous sodium chloride solution. The solvent was removed in vacuo and the residue was purified by filtration through basic aluminium oxide (dichloromethane) and was recrystallized from dichloromethane/*n*-hexane yielding 456 mg (65%) of **18i**. M.p. 96−98 °C. IR (KBr): $\tilde{\nu}$ = 3476 (O−H, moisture), 3075 (arom. C−H), 2938, 2871 (aliph. C−H), 1640, 1620 (aliph. C=C), 1593, 1458 (arom.), 1101 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.56 (m_c, 4 H, $OCH_2CH_2CH_2CH$=), 1.85 (m_c, 4 H, $O(CH_2)_2CH_2CH$=), 2.25 (qt, J_q = 6.8 Hz, $J_t \approx$ 1.3 Hz, 4 H, OCH_2CH_2CH=), 3.35 (br. s, 0.6 H, OH), 3.91, 3.97 (2 t, J = 6.4, J = 6.7, 8 H, OCH_2), 4.7−4.9 (m, 8 H, $=CH_2$), 5.5−5.7 (m, 4 H, CH=), 6.61, 6.63 (2 d, J = 8.4, J = 8.4, 4 H, 3′,3′′,5′,5′′-H), 7.25, 7.26 (2 t, J = 8.4 Hz, 2 H, 4′,4′′-H), 7.61, 7.62 (2 d, J = 8.2 Hz, 2 H, 3,8-H), 7.80 (s, 2 H, 5,6-H), 8.19, 8.22 (2 d, J = 8.2 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.2 [t, $O(CH_2)_2CH_2CH$=], 29.9 (t, $OCH_2CH_2CH_2CH$=), 33.5 (t, OCH_2CH_2CH=), 68.1, 68.4 (2 t, OCH_2), 105.2, 106.2 (2 d, 3′,3′′,5′,5′′-C), 114.6, 116.4 (2 t, $=CH_2$), 121.0, 121.0 (2 s, 1′,1′′-C), 125.9, 126.1, 126.1, 126.2 (4 d, 3,5,6,8-C), 127.3, 127.3 (2 s, 4a,6a-C), 129.6, 129.6 (2 d, 4′,4′′-C), 134.7, 138.0 (2 d, CH=), 134.9, 135.0 (2 d, 4,7-C), 146.0, 146.1 (2 s, 10a,10b-C), 154.8, 155.1 (2 s, 2,9-C), 157.7, 157.8 (2 s, 2′,2′′,6′,6′′-C) ppm. MS: (EI, 70 eV): *m/z* (%) = 640 (100) [M^+]; 599 (78) [$M^+ - C_3H_5$]; 585 (47) [$M^+ - C_4H_7$]; 532 (11) [$M^+ - C_8H_{14}$]. $C_{42}H_{44}N_2O_4$ (640.82), calcd. C 78.72, H 6.92, N 4.37, $C_{42}H_{44}N_2O_4 \cdot 0.3\,H_2O$, calcd. C 78.06, H 6.96, N 4.34; found C 78.12, H 7.05, N 4.20.

2-[2,6-Bis(hex-5-enoxy)phenyl]-9-[2,6-bis(pent-4-enoxy)phenyl]-1,10-phenanthroline (18j): The synthesis of compound **18j** was carried out analogously to that of **18i**, with 2,6-bis(hex-5-enoxy)benzeneboronic acid (**15c**, 736 µmol), yielding 450 mg (88%) of **18j**. M.p. 110−111 °C. IR (KBr): $\tilde{\nu}$ = 3429 (O−H, moisture), 2934 (aliph. C−H), 1639 (aliph. C=C), 1596, 1460 (arom.), 1104 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.1−1.3 [m, 4 H, $O(CH_2)_2CH_2CH_2CH$=), 1.4−1.65 (m, 8 H, OCH_2CH_2), 1.75−1.95 (m, 8 H, CH_2CH=), 3.35 (br. s, 0.4 H, OH), 3.92 (m_c, 8 H, OCH_2), 4.7−4.9 (m, 8 H, $=CH_2$), 5.55 (m_c, 4 H, CH=), 6.60, 6.61 (2 d, J = 8.4, J = 8.4, 4 H, 3′,3′′,5′,5′′-H), 7.24 (t, J = 8.4 Hz, 2 H, 4′,4′′-H), 7.59, 7.62 (2 d, J = 8.2 Hz, 2 H, 3,8-H), 7.80 (s, 2 H, 5,6-H), 8.19, 8.21 (2 d, J = 8.2 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.0 [t, $O(CH_2)_2CH_2CH_2CH$=], 28.2, 28.4 [2 t, $O(CH_2)_2CH_2CH$=, $OCH_2CH_2(CH_2)_2CH$=], 29.9 (t, $OCH_2CH_2CH_2CH$=), 33.1 [t, $O(CH_2)_3CH_2CH$=], 68.4, 68.9 (2 t, OCH_2), 106.1, 106.1 (2 d, 3′,3′′,5′,5′′-C), 114.1, 114.6 (2 t, $=CH_2$), 121.6 (s, 1′,1′′-C), 125.9, 126.0, 126.1 (3 d, 3,5,6,8-C), 127.2 (s, 4a,6a-C), 129.4, 129.4 (2 d, 4′,4′′-C), 134.7, 134.8 (2 d, 4,7-C), 138.1, 138.6 (2 d, CH=), 146.4 (s, 10a,10b-C), 155.0, 155.1 (2 s, 2,9-C), 158.0, 158.0 (2 s, 2′,2′′,6′,6′′-C) ppm. MS: (EI, 70 eV): *m/z* (%) = 696 (100) [M^+]; 655 (52) [$M^+ - C_3H_5$]; 641 (47) [$M^+ - C_4H_7$]; 627 (40) [$M^+ - C_5H_9$]; 613 (43) [$M^+ - C_6H_{11}$]. $C_{46}H_{52}N_2O_4$ (696.93), calcd. C 79.28, H 7.52, N 4.02, $C_{46}H_{52}N_2O_4 \cdot 0.2H_2O$, calcd. C 78.87, H 7.54, N 4.00; found C 78.89, H 7.43, N 3.84.

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