Synthesis of Concave 1,10-Phenanthrolines by a Combination of Suzuki Coupling, Ring Closing Metathesis and Hydrogenation[‡]

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A wide variety of saturated and unsaturated concave 1,10-phenanthrolines **2** and **4** have been synthesized in good yields starting from dichloro-1,10-phenanthroline **14**. In the three step synthesis, Suzuki couplings of bis-*ortho*-substituted boronic acids were used to introduce two different or two identical aryl bridgeheads into the 2- and 9-positions of the 1,10-phenanthroline (yields ≥70%). The resulting diaryl-1,10-phenanthrolines **3**, substituted with alkenyloxy groups of different lengths, underwent ring closing metathesis reactions giving (bi)macrocyclic 1,10-phenanthrolines **4** in yields between 73 and 96%. The alkene chains of **4** were saturated using hydrogen and Pd/C giving the concave 1,10-phenanthrolines **2** in yields between 75 and 99%.

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Introduction

The high selectivity of enzymes is largely a result of the concave environment of the active site.[1] Therefore, also in supramolecular chemistry,[2−5] geometrically related molecules such as macrocycles, clefts or pincers have attracted wide interest. Concave reagents have been developed in order to increase the selectivity of reactions or catalytic processes by variation of the shielding of the reaction site. In particular, the concave 1,10-phenanthrolines **2** have shown good selectivities in a number of reactions.[6−10] In most of these cases, transition metal ion complexes of the ligands are active and selective catalysts. For example, copper(I) complexes of the ligands catalyze the stereoselective cyclopropanation of alkenes by diazoacetates.[11−21]

We have shown that concave 1,10-phenanthrolines **2** can be synthesized in good yields, not only starting from the tetraphenol **1** (see Scheme 1), but also by a combination of Suzuki coupling, ring closing metathesis and hydrogenation.[14,22] In this way, a greater variety of concave 1,10-phenanthrolines can be obtained than by the double cyclization method, which uses a fourfold Williamson ether synthesis (Scheme 1).[6] Here we report on the synthesis of both unsymmetric bi- and mono-macrocyclic 1,10-phenanthrolines.

Results and Discussion

2,9-Dihalo-1,10-phenanthrolines and areneboronic acids are the building blocks for the construction of 2,9-disubstituted 1,10-phenanthrolines using the Suzuki coupling. Synthesis of 2,9-dihalo-1,10-phenanthrolines is well established,[23,24] and it has been shown that the reactivity of 2,9-dichloro-1,10-phenanthroline (**14**) is sufficient for coupling with areneboronic acids.[22]

In order to synthesize concave 1,10-phenanthrolines with only one chain, or with two different chains X^1 and X^2 or Y^1 and Y^2, respectively (see Scheme 5, below), it was necessary to prepare the new boronic acids **8** and **13**. Their syntheses are summarized in Scheme 2 and Scheme 3.

The synthesis of both compounds is straightforward starting from the bromo-substituted resorcinol **5**.[25] Initial etherification of the phenols was followed by introduction of the boronic acid functionality. Unsymmetrical bis-*ortho*-substitution of the boronic acids **8** and **13** was achieved by a stepwise alkylation. In the preparation of the methoxy-substituted boronic acid **8**, no protecting group was used. The first alkylating step was the mono-methylation of **5** in 51% yield followed by a hexenylation of the second OH group in 94% yield. In the case of **13**, one methoxymethyl protecting group was introduced to **5** to give **9** in 31% yield, followed by hexenylation of the second phenol group to give **10** in 97% yield. Following deprotection (89% yield), the butenyl group of **12** was introduced by a Mitsunobu coupling to avoid the problem of butadiene formation which is known to occur during the butenylation of related phenols.[22] The reaction of **11** with 3-butenol, triphenylphosphane, and diethyl azodicarboxylate gave the unsymmetrically substituted phenol **12** in 64% yield.

[‡] Concave Reagents, 41. Part 40: R. Cacciapaglia, S. Di Stefano, F. Fahrenkrug, U. Lüning, L. Mandolini, *J. Phys. Org. Chem.* **2004**, *17*, 350−355.

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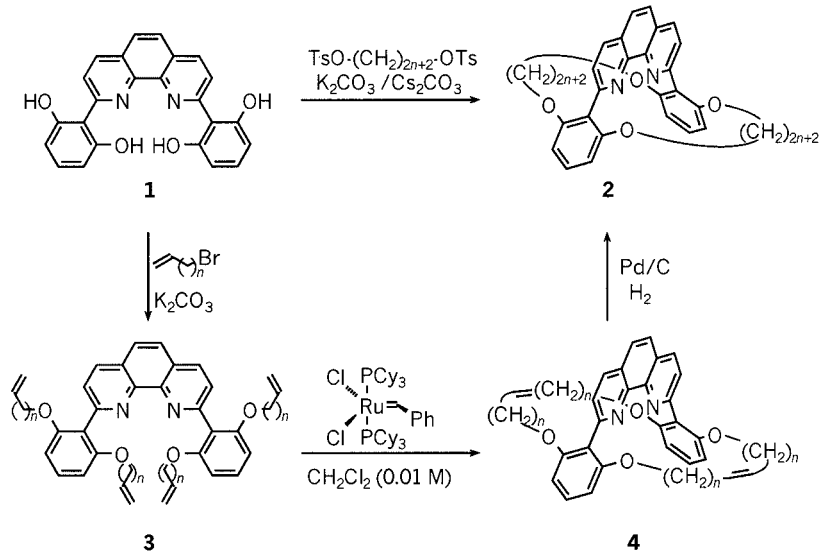
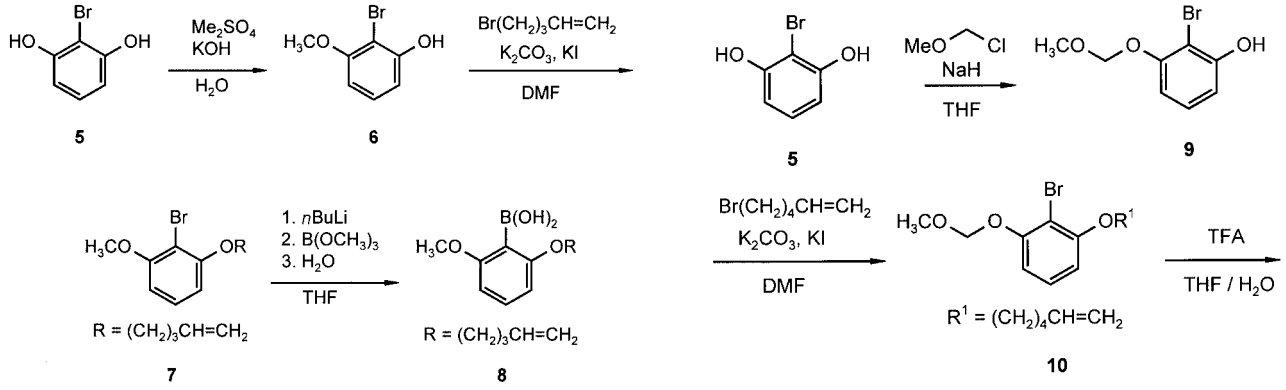


Scheme 1

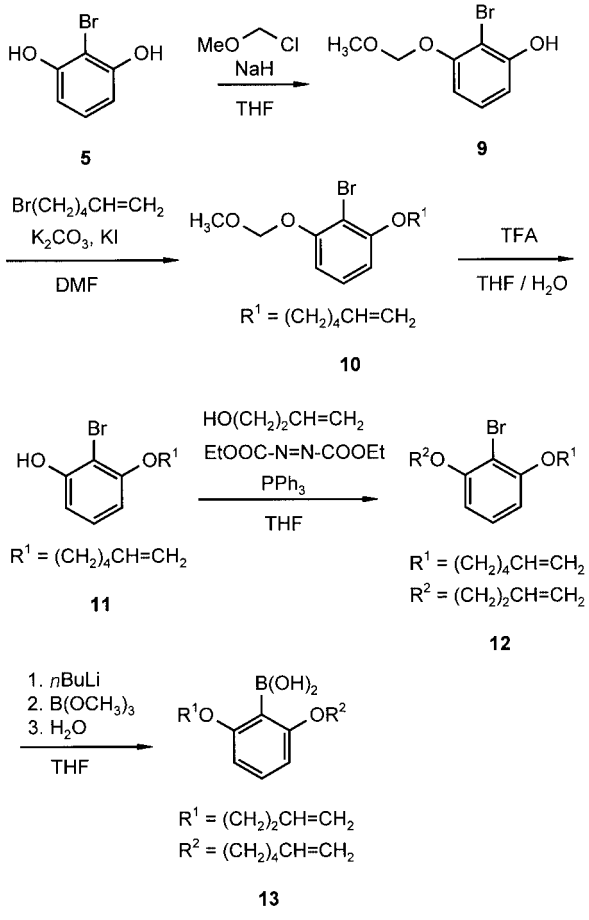


Scheme 2

The boronic acids were synthesized from the 2-bromodiethers **7** and **12** by a bromine-lithium exchange followed by reaction with trimethylborate. Aqueous workup gave the boronic acids **8** and **13** in 57% and 78% yield, respectively.

As has been demonstrated for other boronic acids that form the concave 1,10-phenanthrolines **3a**−**c**,[22] the boronic acids **8**, **13** and **15**[22] were then coupled with chloro-substituted 1,10-phenanthrolines. A one-step reaction with 2,9-dichloro-1,10-phenanthroline (**14**) yielded the 2,9-diaryl-substituted 1,10-phenanthroline **3e** with two identical aromatic rings while a two-step reaction yielded initially the mono-arylated intermediate **16** followed by the required product **3d** with two different aryl rings in the 2- and 9-positions. When performed using $Pd(PPh_3)_4$ as catalyst, barium hydroxide as base and dimethoxyethane as solvent, the Suzuki couplings gave yields of 92% (**3e**) and 78 and 76% (**3d**, first and second step) (Scheme 4).

Thus, Suzuki couplings (see also ref.[22]) provided a number of alkenyl-substituted diaryl-1,10-phenanthrolines **3**, which were then subjected to ring closing metatheses (RCM) (see Scheme 5). In all cases, the macrocycles **4** were formed in good yields (73−96%), although the reactions were carried out in only moderately dilute solutions.



Scheme 3

The RCM products **4** were mixtures of isomers (*cis*/*trans*-alkene) but simple hydrogenolyses in ethyl acetate using palladium on charcoal and hydrogen transformed these into the macrocyclic 1,10-phenanthrolines **2** containing saturated chains, Y, in good yields. Considering **2a**−**e**, only a few of these macrocyclic 1,10-phenanthrolines were access-

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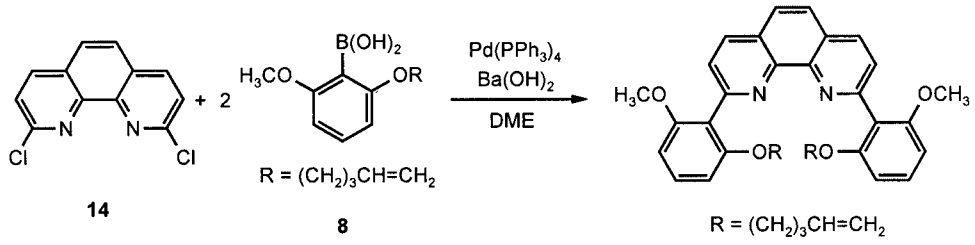
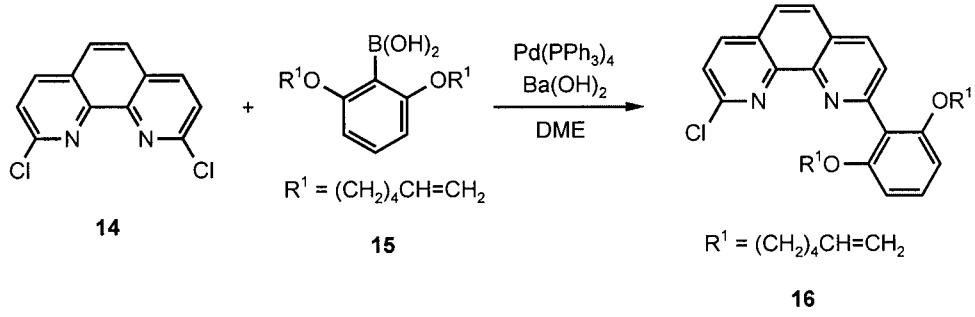
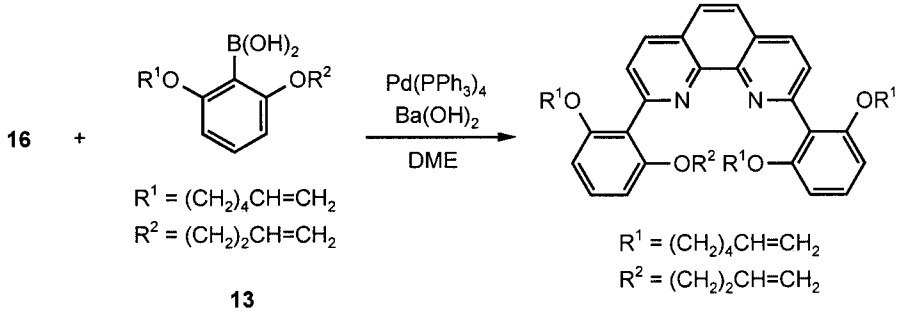
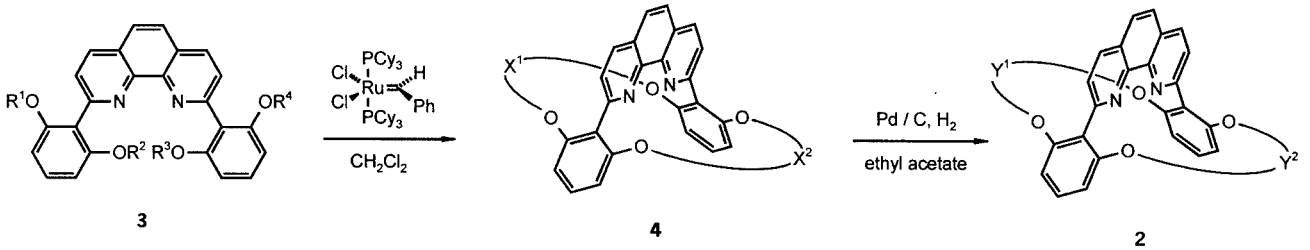






Scheme 4



	R^1	R^2	R^3	R^4	X^1	X^2	Y^1	Y^2
a	$(CH_2)_3CH=CH_2$	$(CH_2)_3CH=CH_2$	$(CH_2)_3CH=CH_2$	$(CH_2)_3CH=CH_2$	$(CH_2)_3CH=CH(CH_2)_3$	$(CH_2)_3CH=CH(CH_2)_3$	$(CH_2)_8$	$(CH_2)_8$
b	$(CH_2)_3CH=CH_2$	$(CH_2)_4CH=CH_2$	$(CH_2)_3CH=CH_2$	$(CH_2)_4CH=CH_2$	$(CH_2)_3CH=CH(CH_2)_4$	$(CH_2)_3CH=CH(CH_2)_4$	$(CH_2)_9$	$(CH_2)_9$
c	$(CH_2)_4CH=CH_2$	$(CH_2)_4CH=CH_2$	$(CH_2)_4CH=CH_2$	$(CH_2)_4CH=CH_2$	$(CH_2)_4CH=CH(CH_2)_4$	$(CH_2)_4CH=CH(CH_2)_4$	$(CH_2)_{10}$	$(CH_2)_{10}$
d	$(CH_2)_4CH=CH_2$	$(CH_2)_4CH=CH_2$	$(CH_2)_2CH=CH_2$	$(CH_2)_4CH=CH_2$	$(CH_2)_4CH=CH(CH_2)_4$	$(CH_2)_2CH=CH(CH_2)_4$	$(CH_2)_{10}$	$(CH_2)_8$
e	$(CH_2)_3CH=CH_2$	CH_3	$(CH_2)_3CH=CH_2$	CH_3	$(CH_2)_3CH=CH(CH_2)_3$	$-CH_3\ H_3C-$	$(CH_2)_8$	$-CH_3\ H_3C-$

Scheme 5

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ible by the double macrocyclization of the tetraphenol **1**. Thus, bimacrocycles containing identical chains Y^1 and Y^2, with odd or even numbers of CH_2 groups (**2a−c**), a bimacrocycle with non-identical chains Y^1 and Y^2 (**2d**), and a monomacrocycle **2e** are all readily available using the presented methodology.

Some of these compounds have been tested already as selectivity enhancing ligands in transition metal catalyses,[7,10] e.g. in the cyclopropanation of alkenes. The use of a proper concave ligand boosts the diastereoselectivity of the cyclopropanation of, for instance, indene to 140:1 (*exo*/*endo*).

Experimental Section

General Remarks: The following chemicals were obtained commercially and used without further purification: *N*,*N*-dimethylformamide (Fluka, 1, 99.8%), dimethyl sulfate (Merck), tetrakis(triphenylphosphane)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 solution in hexanes (Aldrich), benzylidene-bis(tricyclohexylphosphanyl)dichlororuthenium (Fluka). 2-Bromo-1,3-dihydroxybenzene (**5**),[25] 2,6-bis(hex-5-enyloxy)benzeneboronic acid (**15**)[22] and 2,9-dichloro-1,10-phenanthroline (**14**)[24] were prepared according to literature procedures. Dry solvents were obtained using suitable desiccants: tetrahydrofuran was distilled from lithium aluminium hydride and ethyl acetate was distilled from calcium chloride. Column chromatography was carried out on basic alumina (Fluka, activity I) or silica gel (Macherey−Nagel, activity I). 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) spectrometers, using tetramethylsilane as internal standard. IR spectra were measured on a Perkin−Elmer 1600 Series. MS spectra were recorded on a Finnigan MAT 8230. Elemental analyses were carried out on a VarioEl, Elementaranalysensysteme GmbH. Gas chromatography was performed using a Varian 3400 Gas Chromatograph equipped with a column SE30/25m from Macherey−Nagel.

General Procedure for the Williamson Synthesis of Aryl Alkenyl Ethers (7, 10): The phenolic starting material was dissolved in dry *N*,*N*-dimethylformamide. After addition of a catalytic amount of potassium iodide and ca. three equivalents of potassium carbonate per phenol function, the appropriate ω-bromo-1-alkene (1.25 equivalents) was added. After 16 h of stirring at 60 °C, the solvent was removed in vacuo and 2 N sodium hydroxide (20−30 mL) and diethyl ether (20−30 mL) were added to the residue. The aqueous layer was separated and extracted three times with diethyl ether (20−30 mL). The combined organic fractions were washed three times with 2 N sodium hydroxide (20−30 mL) and once with brine (20−30 mL). After drying with magnesium sulfate, the solvent was evaporated in vacuo and the crude product purified by filtration through silica gel after dissolving in the solvent indicated below.

General Procedure for the Synthesis of the Boronic Acids (8, 13): The aryl bromide was dissolved in tetrahydrofuran then cooled to −78 °C. *n*-Butyl lithium (1.1 equivalents, 2.5 M in hexane) was added and the mixture stirred for 1 h at −78 °C. After addition of ca. 3.3 equivalents of trimethylborate, stirring was continued for 2 h. During this period, the mixture was allowed to warm to room temp. After quenching with water (20 mL), the layers were separated and the aqueous layer was extracted three times with diethyl ether (20−30 mL). The combined organic fractions were washed with brine (20−30 mL) and dried with magnesium sulfate. After evaporation of the solvent, the crude product was purified as detailed below.

General Procedure for the Ring Closing Metathesis (RCM): The 1,10-phenanthroline **3** (di- or tetraene) was dissolved in dichloromethane (c = 0.01 mmol/L). Benzylidene-bis(tricyclohexylphosphane)dichlororuthenium (5 mol %) was added and the mixture was stirred for 16 h at room temp. After three filtrations through basic alumina using dichloromethane, the resulting isomeric mixture was analyzed. Melting points were not determined.

General Procedure for Hydrogenolysis of the Double Bonds of the RCM Products: The RCM product was dissolved in ethyl acetate ($c \approx$ 30 mmol/L). In a separate vessel, palladium on charcoal (10%) (10.0 mg per 100 μmol of starting material) was suspended in ethyl acetate (5.0 mL) and hydrogen was bubbled through the mixture for 30 min to activate the catalyst. Subsequently, the RCM product solution was added and hydrogen was bubbled through the mixture for 2 h with stirring at room temp. With the mixture remaining in a hydrogen atmosphere, stirring was continued for an additional 16 h at room temp. After evaporation of the solvent in vacuo, the crude product was dissolved in dichloromethane, filtered through basic alumina and recrystallized from dichloromethane/hexane.

2,11,13,22-Tetraoxa-1,12(1,3,2)-dibenzena-23(2,9)-1,10-phenanthrolinabicyclo[10.10.1]tricosaphane (2a): Batch size: 200 mg (326 mmol) of **4a**. Yield 201 mg (99%), ref.[14] 99%. M.p. 242−243 °C, ref.[14] 249 °C. IR (KBr): $\tilde{\nu}$ = 3039 (arom. C−H), 2929, 2854 (aliph. C−H), 1594, 1457 (arom. C=C), 1102 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.74, 0.94, 1.38 (3 m_c, 24 H, CH_2), 3.77, 3.97 (2 m_c, 8 H, OCH_2), 7.23 (t, J = 8.4 Hz, 4 H, 3′,3′′,5′,5′′-H), 7.54 (d, J = 8.4 Hz, 2 H, 4′,4′′-H), 7.54 (d, J = 8.2 Hz, 2 H, 3,8-H), 7.82 (s, 2 H, 5,6-H), 8.22 (d, J = 8.2 Hz, 2 H, 4,7-H) ppm. MS (EI, 70 eV): m/z (%) = 616 (100) [M^+], 573 (25) [$M^+ - C_3H_7$], 531 (24) [$M^+ - C_6H_{13}$].

2,12,14,24-Tetraoxa-1,13(1,3,2)-dibenzena-25(2,9)-1,10-phenanthrolinabicyclo[11.11.1]pentacosaphane (2b): Batch size: 268 mg (418 μmol) of **4b**. Yield 268 mg (99%). M.p. 206−208 °C. IR (KBr): $\tilde{\nu}$ = 3038 (arom. C−H), 2927, 2855 (aliph. C−H), 1592, 1457 (arom. C=C), 1103 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.28, 0.71, 0.85, 1.42 (4 m_c, 28 H, CH_2), 3.77, 3.97 (2 m_c, 8 H, OCH_2), 5.30 (s, 1.8 H, CH_2Cl_2), 6.60 (d, J = 8.3 Hz, 4 H, 3′,3′′,5′,5′′-H), 7.23 (t, J = 8.3 Hz, 2 H, 4′,4′′-H), 7.58 (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 = 24.8, 26.7, 28.4, 28.4 (4 t, CH_2), 53.5 (t, CH_2Cl_2), 67.9 (t, OCH_2), 105.8 (d, 3′,3′′,5′,5′′-C), 121.5 (s, 1′,1′′-C), 125.8, 126.0 (2 d, 3,5,6,8-C), 127.2 (s, 4a,4b-C), 129.4 (d, 4′,4′′-C), 135.0 (d, 4,7-C), 146.4 (s, 10a,10b-C), 155.6 (s, 2,9-C), 158.0 (s, 2′,2′′,6′,6′′-C) ppm. MS (EI, 70 eV): m/z (%) = 644 (100) [M^+], 630 (12) [$M^+ - CH_2$], 601 (20) [$M^+ - C_3H_7$]. HR-MS − $C_{42}H_{48}N_2O_4$: found 644.36030, calcd. 644.36139 (δ = 0.6 ppm); $C_{41}{}^{13}CH_{48}N_2O_4$: found 645.36460, calcd. 645.36475 (δ = 0.2 ppm). $C_{42}H_{48}N_2O_4$ (644.84): calcd. C 78.72, H 6.92, N 4.37; $C_{42}H_{44}N_2O_4 \cdot 1.3CH_2Cl_2 \cdot 1.0H_2O$ (769.24): calcd. C 67.61, H 6.37, N 3.63; found C 67.55, H 6.63, N 3.54.

2,13,15,26-Tetraoxa-1,14(1,3,2)-dibenzena-27(2,9)-1,10-phenanthrolinabicyclo[12.12.1]heptacosaphane (2c): Batch size: 109 mg (162 μmol) of **4c**. Yield 103 mg (95%), ref.[14] 95%. M.p. 182−183 °C, ref.[14] 186 °C. IR (KBr): $\tilde{\nu}$ = 2924, 2852 (aliph. C−H), 1595, 1456 (arom. C=C), 1101 (C−O−C). ^1H NMR (300 MHz, $CDCl_3$):

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δ = 0.54, 0.65−0.98, 1.41 (m_c, m, m_c, 32 H, CH_2), 3.84 (m_c, 8 H, OCH_2), 6.59 (t, J = 8.3 Hz, 4 H, 3′,3′′,5′,5′′-H), 7.23 (d, J = 8.3 Hz, 2 H, 4′,4′′-H), 7.57 (d, J = 7.5 Hz, 2 H, 3,8-H), 7.81 (s, 2 H, 5,6-H), 8.21 (d, J = 7.5 Hz, 2 H, 4,7-H) ppm. MS (EI, 70 eV): *m/z* (%) = 672 (100) [M^+], 629 (15) [$M^+ - C_3H_7$], 615 (7) [$M^+ - C_4H_9$], 601 (7) [$M^+ - C_5H_{11}$], 587 (4) [$M^+ - C_6H_{13}$], 559 (24) [$M^+ - C_8H_{17}$].

2,11,13,24-Tetraoxa-1,12(1,3,2)-dibenzena-25(2,9)-1,10-phenanthrolinabicyclo[12.10.1]pentacosaphane (2d): Batch size: 178 mg (278 μmol) of **4d**. Yield 135 mg (75%). M.p. 210−212 °C. IR (KBr): ṽ = 3032 (arom. C−H), 2924, 2860 (aliph. C−H), 1602, 1486 (arom. C=C), 1098 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.48, 0.78, 0.87, 0.97, 1.40 (5 m_c, 28 H, CH_2), 3.87 (m_c, 8 H, OCH_2), 5.29 (s, 0.11 H, CH_2Cl_2), 6.61 (m_c, 4 H, 3′,3′′,5′,5′′-H), 7.25 (t, J = 8.3 Hz, 2 H, 4′,4′′-H), 7.59 (d, J = 8.2 Hz, 2 H, 3,8-H), 7.81 (s, 2 H, 5,6-H), 8.22 (d, J = 8.2 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24−29 (16 t, CH_2), 67.9, 68.9, 68.9, 69.1 (4 t, OCH_2), 105.5, 105.6, 105.8, 105.9 (4 d, 3′,3′′,5′,5′′-C), 120.8 (s, 1′,1′′-C), 126.0, 126.0 (2 d, 3,5,6,8-C), 127.2 (s, 4a,6a-C), 129.6 (d, 4′,4′′-C), 135.0 (d, 4,7-C), 146.0 (s, 10a,10b-C), 155.4 (s, 2,9-C), 157.9, 158.1 (2 s, 2′,2′′,6′,6′′-C) ppm. MS (EI, 70 eV): *m/z* (%) = 644 (100) [M^+]. HR-MS − $C_{42}H_{48}N_2O_4$: found 644.36100, calcd. 644.36139 (δ = 0.6 ppm); $C_{41}{}^{13}CH_{48}N_2O_4$: found 645.36460, calcd. 645.36475 (δ = 0.2 ppm). $C_{42}H_{48}N_2O_4$ (644.84): calcd. C 78.23, H 7.50, N 4.34. $C_{42}H_{48}N_2O_4 \cdot 0.1CH_2Cl_2 \cdot 0.8H_2O$ (667.72): calcd. C 75.73, H 7.52, N 4.20; found C 76.00, H 7.88, N 3.73.[26]

1³,3³-Dimethoxy-4,13-dioxa-1,3(1,2)-dibenzena-2(2,9)-1,10-phenanthrolinacyclotridecaphane (2e): Batch size: 235 mg (441 μmol) of **4e**. Yield 234 mg (99%). M.p. 248 °C. IR (KBr): ṽ = 2927, 2825 (aliph. C−H), 1595, 1462 (arom. C=C), 1103 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.70, 0.88, 1.35 (3 m_c, 12 H, CH_2), 3.70 (s, 6 H, OCH_3), 3.87 (m_c, 4 H, OCH_2), 6.62 (m_c, 4 H, 3′,3′′,5′,5′′-H), 7.28 (t, J = 8.4 Hz, 2 H, 4′,4′′-H), 7.57 (d, J = 8.3 Hz, 2 H, 3,8-H), 7.81 (s, 2 H, 5,6-H), 8.23 (d, J = 8.3 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.6, 28.4, 28.8 (3 t, CH_2), 55.9 (q, OCH_3), 69.1 (t, OCH_2), 104.3, 105.9 (2 d, 3′,3′′,5′,5′′-C), 120.5 (s, 1′,1′′-C), 125.9, 126.2 (2 d, 3,5,6,8-C), 127.5 (s, 4a,6a-C), 129.7 (d, 4′,4′′-C), 135.4 (d, 4,7-C), 146.2 (s, 10a,10b-C), 155.4 (s, 2,9-C), 158.1, 158.2 (2 s, 2′,2′′,6′,6′′-C) ppm. MS (EI, 70 eV): *m/z* (%) = 534 (100) [M^+], 503 (19) [$M^+ - OCH_3$]. HR-MS − $C_{34}H_{34}N_2O_4$: found 534.25140, calcd. 534.25183 (δ = 0.8 ppm); $C_{33}{}^{13}CH_{34}N_2O_4$: found 535.25500, calcd. 535.25519 (δ = 0.4 ppm). $C_{34}H_{34}N_2O_4$ (534.65), calcd. C 76.38, H 6.41, N 5.24. $C_{34}H_{34}N_2O_4 \cdot 1.3H_2O$ (558.06): calcd. C 73.18, H 6.61, N 5.02; found C 73.08, H 6.87, N 4.77.

2-[2,6-Bis(hex-5-enyloxy)phenyl]-9-[2-(but-3-enyloxy)-6-(hex-5-enyloxy)phenyl]-1,10-phenanthroline (3d): 2-[2,6-Bis(hex-5-enyloxy)-phenyl]-9-chloro-1,10-phenanthroline (**16,** 500 mg, 1.03 mmol) was dissolved in dimethoxyethane (60 mL) and water (15 mL), then 2-(but-3-enyloxy)-6-(hex-5-enyloxy)benzeneboronic acid (**13**, 374 mg, 1.29 mmol), tetrakis(triphenylphosphane)palladium(0) (119 mg, 103μmol) and barium hydroxide (332 mg, 1.94 mmol) were added. The mixture was heated at reflux for 16 h, allowed to cool, and water (30 mL) and dichloromethane (30 mL) were added. The layers were separated and the aqueous layer was extracted three times with dichloromethane (30 mL). The combined organic fractions were washed with brine (20 mL) and dried over magnesium sulfate. After evaporation to dryness, the crude product was dissolved in dichloromethane, filtered through basic alumina and recrystallized from dichloromethane/hexane. Yield 547 mg (76%). M.p. 82−85 °C. IR (KBr): ṽ = 3073 (arom. C−H), 2935, 2868 (aliph. C−H), 1639, 1619 (aliph. C=C), 1595, 1458 (arom. C=C), 1105 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.19 (m_c, 6 H, $O(CH_2)_2CH_2CH_2CH$=), 1.48 [m_c, 6 H, $OCH_2CH_2(CH_2)_2CH$=], 1.79 [m_c, 6 H, $O(CH_2)_3CH_2CH$=], 2.25 (tq, $J_t \approx 1$, $J_q \approx 7$ Hz, 2 H, OCH_2CH_2CH=), 3.90, 3.91 [2 t, J = 6.4, J = 6.4 Hz, 6 H, $OCH_2(CH_2)_3CH$=], 3.99 (t, J = 6.8 Hz, 2 H, OCH_2CH_2CH=), 4.7−4.9 (m, 8 H, =CH_2), 5.4−5.7 (m, 4 H, CH=), 6.61 (d, J = 8.4 Hz, 2 H, 3′′,5′′-H), 6.61 (m_c, 2 H, 3′,5′-H), 7.24, 7.24 (2 t, J = 8.4, J = 8.4 Hz, 2 H, 4′,4′′-H), 7.59, 7.61 (2 d, J = 8.2, J = 8.2 Hz, 2 H, 3,8-H), 7.80 (s, 2 H, 5,6-H), 8.19, 8.19 (2 d, J = 8.2, J = 8.2 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.0, 25.1 [2 t, $O(CH_2)_2CH_2CH_2CH$=], 28.4, 28.4 (2 t, OCH_2CH_2CH=), 33.1, 33.1 [2 t, $OCH_2CH_2(CH_2)_2CH$=], 33.6 (t, OCH_2CH_2CH=), 68.8, 68.8 (2 t, OCH_2), 106.1 (d, 3′′,5′′-C), 106.2, 106.6 (2 d, 3′,5′-C), 114.1, 114.2 [2 t, $O(CH_2)_4CH$=CH_2], 116.3 [t, $O(CH_2)_2CH$=CH_2], 121.7, 121.7 (2 s, 1′,1′′-C), 125.8, 126.0 (2 d, 3,5,6,8-C), 127.2, 127.3 (2 s, 4a,6a-C), 129.4, 129.4 (2 d, 4′,4′′-C), 134.7, 134.8, 138.6 (3 d, 4,7-C, CH=), 146.3, 146.4 (2 s, 10a,10b-C), 154.9, 155.1 (2 s, 2,9-C), 157.9, 158.0, 158.0 (3 s, 2′,2′′,6′,6′′-C) ppm. MS (EI, 70 eV): *m/z* (%) = 696 (100) [M^+], 655 (26) [$M^+ - C_3H_5$], 641 (40) [$M^+ - C_4H_7$], 613 (55) [$M^+ - C_6H_{11}$]. HR-MS − $C_{46}H_{52}N_2O_4$: found 696.39240, calcd. 696.39270 (δ = 0.4 ppm); $C_{45}{}^{13}CH_{52}N_2O_4$: found 697.39590, calcd. 697.39606 (δ = 0.2 ppm). $C_{46}H_{52}N_2O_4$ (696.93): calcd. C 79.28, H 7.52, N 4.02; found C 78.98, H 7.65, N 3.77.

2,9-Bis[2-methoxy-6-(pent-4-enyloxy)phenyl]-1,10-phenanthroline (3e): 2,9-Dichloro-1,10-phenanthroline (**14**, 214 mg, 968 μmol) was dissolved in a mixture of dimethoxyethane (40 mL) and water (10 mL). After addition of 2-methoxy-6-(pent-4-enyloxy)benzeneboronic acid (**8**, 571 mg 2.42 mmol), barium hydroxide (622 mg, 3.63 mmol) and tetrakis(triphenylphosphane)palladium(0) (112 mg, 96.9 μmol), the mixture was heated at reflux for 16 h. Then, water (20 mL) and dichloromethane (20 mL) were added and the layers separated. The aqueous layer was extracted three times with dichloromethane (20 mL), and the combined organic fractions were washed with brine (20 mL) and dried with magnesium sulfate. After evaporation of the solvent in vacuo, the crude product was dissolved in dichloromethane, filtered through basic alumina and recrystallized from dichloromethane/hexane. Yield 497 mg (92%). M.p. 153 °C. IR (KBr): ṽ = 2941 (aliph. C−H), 1638 (aliph. C=C), 1591, 1465 (arom. C=C), 1104 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.58 (m_c, 4 H, OCH_2CH_2), 1.88 (m_c, 4 H, CH_2CH=), 3.72 (s, 6 H, OCH_3), 3.90 (t, J = 6.3 Hz, 4 H, OCH_2), 4.70−4.85 (m, 4 H, =CH_2), 5.59 (tdd, J_t = 6.7, J_d = 10.3, J_d = 17.0 Hz, 2 H, CH=), 6.63, 6.63 (2 t, J = 8.4, J = 8.4 Hz, 4 H, 3′,3′′,5′,5′′-H), 7.27 (t, J = 8.4 Hz, 1 H, 4′,4′′-H), 7.62 (d, J = 8.2 Hz, 2 H, 3,8-H), 7.80 (s, 2 H, 5,6-H), 8.22 (d, J = 8.2 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.2 (t, OCH_2CH_2), 29.9 (t, CH_2CH=), 56.3 (q, OCH_3), 67.9 (t, OCH_2), 104.9, 105.6 (2 d, 3′,3′′,5′,5′′-C), 114.7 (t, =CH_2), 120.6 (s, 1′,1′′-C), 126.0, 126.2 (2 d, 3,5,6,8-C), 127.4 (s, 4a,6a-C), 129.7 (d, 4′,4′′-C), 135.2 (d, 4,7-C), 138.0 (d, CH=), 146.2 (s, 10a,10b-C), 155.0 (s, 2,9-C), 157.8, 158.4 (2 d, 2′,2′′,6′,6′′-C) ppm. MS (EI, 70 eV): *m/z* (%) = 560 (100) [M^+], 519 (90) [$M^+ - C_3H_5$], 505 (63) [$M^+ - C_4H_7$]. HR-MS − $C_{36}H_{36}N_2O_4$: found 560.26740, calcd. 560.26752 (δ = 0.2 ppm); $C_{35}{}^{13}CH_{36}N_2O_4$: found 561.27080, calcd. 561.27087 (δ = 0.1 ppm). $C_{36}H_{36}N_2O_4$ (560.68): calcd. C 77.12, H 6.47, N 5.00; $C_{36}H_{36}N_2O_4 \cdot 0.7H_2O$ (573.29): calcd. C 75.19, H 6.59, N 4.87; found C 75.15, H 6.87, N 4.73.

2,11,13,22-Tetraoxa-1,12(1,3,2)-dibenzena-23(2,9)-1,10-phenanthrolinabicyclo[10.10.1]tricosaphan-6,17-diene (4a): Batch size: 200 mg (299 μmol) of tetraene **3a**. Yield 134 mg (73%), ref.[14] 73%. IR

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(KBr): $\tilde{\nu}$ = 2922 (aliph. C−H), 1596, 1581 (arom. C=C), 1246, 1091 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.3−1.8 (m, 16 H, CH_2), 3.8−4.2, 4.15 (m, m_c, 8 H, OCH_2), 4.66 (m_c, 2.1 H, *trans*-CH=CH), 4.99 (m_c, 1.9 H, *cis*-CH=CH), 5.30 (s, 0.26 H, CH_2Cl_2), 6.6−6.7 (m, 4 H, 3′,3′′,5′,5′′-H), 7.2−7.3 (m with t at 7.25, *J* = 8.3 Hz and t at 7.24, *J* = 8.3 Hz, 2 H, 4′,4′′-H), 7.60, 7.65 (2 d, *J* = 8.2, *J* = 8.2 Hz, 2 H, 3,8-H), 7.82, 7.83 (2 s, 2 H, 5,6-H), 8.22, 8.33 (2 d, *J* = 8.2, *J* = 8.2 Hz, 2 H, 4,7-H) ppm. *cis*/*trans*-ratio: 1:1.1. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.2, 28.9, 29.1, 29.4 (4 t, CH_2), 54.2 (t, CH_2Cl_2), 69.4, 69.8 (2 t, OCH_2), 107.9, 108.0 (2 d, 3′,3′′,5′,5′′-C), 123.0 (s, 1′,1′′-C), 125.9, 126.1 (2 d, 3,5,6,8-C), 127.0 (s, 4a,6a-C), 129.4, 129.6 (2 d, 4′,4′′-C, CH=CH), 134.7 (d, 4,7-C), 146.0 (s, 10a,10b-C), 155.0 (s, 2,9-C), 158.1, 158.1 (2 s, 2′,2′′,6′,6′′-C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 612 (100) [M^+], 530 (19) [$M^+ - C_6H_{10}$], 396 (6) [$C_{24}H_{16}N_2O_4$]. HR-MS − $C_{40}H_{40}N_2O_4$: found 612.29900, calcd. 612.29883 (δ = −0.3 ppm); $C_{39}{}^{13}CH_{40}N_2O_4$: found 613.30200, calcd. 613.30219 (δ = 0.3 ppm). $C_{40}H_{40}N_2O_4$ (612.77): calcd. C 78.41, H 6.58, N 4.57; $C_{40}H_{40}N_2O_4 \cdot 0.1CH_2Cl_2$ (621.25): calcd. C 77.53, H 6.52, N 4.51; found C 77.55, H 6.83, N 4.57. Using a chromatotron with neutral aluminium oxide and dichloromethane/pentane (1:1) as eluent, the isomer with a resonance at δ = 4.66 ppm could be separated from the mixture. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.8−1.3, 1.44, 1.5−1.8 (m, m_c, m, 16 H, CH_2), 3.81, 3.91 (2 m_c, 8 H, OCH_2), 4.66 (m_c, 4 H, =CH), 6.58 (d, *J* = 8.3 Hz, 4 H, 3′,3′′,5′,5′′-H), 7.19 (t, *J* = 8.3 Hz, 2 H, 4′,4′′-H), 7.60 (d, *J* = 8.2 Hz, 2 H, 3,8-H), 7.83 (s, 2 H, 5,6-H), 8.23 (d, *J* = 8.2 Hz, 2 H, 4,7-H) ppm.

2,12,14,24-Tetraoxa-1,13(1,3,2)-dibenzena-25(2,9)-1,10-phenanthrolinabicyclo[11.11.1]pentacosaphan-6,19-diene (4b): Batch size: 350 mg (502 μmol) of tetraene **3b**. Yield 308 mg (96%). IR (KBr): $\tilde{\nu}$ = 2927, 2866 (aliph. C−H), 1594, 1456 (arom. C=C), 1102 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.8−1.3, 1.44, 1.63 (m, 2 m_c, 20 H, CH_2), 3.6−4.1 (m, 8 H, OCH_2), 4.3−4.5, 4.8−5.0 (2 m, 1.3 H, 2.7 H, CH=CH), 5.30 (s, 1.64 H, CH_2Cl_2), 6.5−6.6 (m, 4 H, 3′,3′′,5′,5′′-H), 7.23 (m_c, 2 H, 4′,4′′-H), 7.63 (m_c, 2 H, 3,8-H), 7.80, 7.80, 7.81 (3 s, 2 H, 5,6-H), 8.19 (m_c, 2 H, 4,7-H) ppm. Isomer ratio (*cis* and *trans* not assignable): 1:2. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23−32 (16 t, CH_2), 53.6 (s, CH_2Cl_2), 66−70 (8 t, OCH_2), 105−108 (6 d, 3′,3′′,5′,5′′-C), 120−123 (4 s, 1′,1′′-C), 125−132 (15 signals, 4′,4′′,3,4a,5,6,6a,8-C), 134.9, 134.9, 135.1 (3 d, 4,7-C, CH=CH), 145−148 (4 s, 10a,10b-C), 155.3, 155.4, 155.6 (3 s, 2,9-C), 157−159 (5 s, 2′,2′′,6′,6′′-C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 640 (100) [M^+], 612 (44) [$M^+ - C_2H_4$], 569 (18) [$M^+ - C_5H_{11}$]. HR-MS − $C_{42}H_{44}N_2O_4$: found 640.32970, calcd. 640.33008 (δ = 0.6 ppm); $C_{41}{}^{13}CH_{44}N_2O_4$: found 641.33360, calcd. 641.33344 (δ = −0.3 ppm). $C_{42}H_{44}N_2O_4$ (640.81): calcd. C 78.72, H 6.92, N 4.37; $C_{42}H_{44}N_2O_4 \cdot 0.8CH_2Cl_2$ (708.76): calcd. C 72.53, H 6.48, N 3.95; found C 72.88, H 6.92, N 3.76.

2,13,15,26-Tetraoxa-1,14(1,3,2)-dibenzena-27(2,9)-1,10-phenanthrolinabicyclo[12.12.1]heptacosaphan-7,20-diene (4c): Batch size: 250 mg (349 μmol) of tetraene **3c**. Yield 215 mg (321 μmol) (92%), ref.[14] 92%. IR (KBr): $\tilde{\nu}$ = 2925 (aliph. C−H), 1595 (arom. C=C), 1103 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.9−1.7, 1.05, 1.35, 1.55 (m, 3 m_c, 24 H, CH_2), 3.84 (m_c, 8 H, OCH_2), 4.44 (m_c, 0.3 H, *cis*-CH=CH), 4.73 (m_c, 3.7 H, *trans*-CH=CH), 5.30 (s, 0.61 H, CH_2Cl_2), 6.5−6.7 (m with d at 6.57, *J* = 8.3 Hz, 4 H, 3′,3′′,5′,5′′-H), 7.1−7.3 (m with t at 7.22, *J* = 8.3 Hz and t at 7.24, *J* = 8.3 Hz, 2 H, 4′,4′′-H), 7.5−7.7 (m with d at *J* = 8.2 Hz, 2 H, 3,8-H), 7.8−7.9 (m with s at 7.83, 2 H, 5,6-H), 8.2−8.3 (m with d at 8.23, *J* = 8.2 Hz, 2 H, 4,7-H) ppm. *cis*/*trans*-ratio: 1:12. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.8, 25.0, 27.0, 30.5 (4 t, CH_2), 54.1 (t, CH_2Cl_2), 69.4, (t, OCH_2), 104.6 (d, 3′,3′′,5′,5′′-C), 122.0 (s, 1′,1′′-C), 124.7, 125.1 (2 d, 3,5,6,8-C), 126.4 (s, 4a,6a-C), 128.5 (d, 4′,4′′-C), 129.4 (d, CH=CH), 134.7 (d, 4,7-C), 145.6 (s, 10a,10b-C), 154.7 (s, 2,9-C), 157.2 (s, 2′,2′′,6′,6′′-C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 668 (51) [M^+], 640 (100) [$M^+ - C_2H_4$], 627 (25) [$M^+ - C_3H_5$], 597 (62) [$M^+ - C_5H_{11}$]. HR-MS − $C_{44}H_{48}N_2O_4$: found 668.36120, calcd. 668.36139 (δ = 0.3 ppm); $C_{43}{}^{13}CH_{48}N_2O_4$: found 669.36440, calcd. 669.36475 (δ = 0.5 ppm). $C_{44}H_{48}N_2O_4$ (668.86): calcd. C 79.01, H 7.23, N 4.19; $C_{44}H_{48}N_2O_4 \cdot 0.4CH_2Cl_2$ (702.84): calcd. C 75.88, H 7.00, N 3.99; found C 75.74, H 7.17, N 3.69. Using a chromatotron with neutral aluminium oxide and dichloromethane/pentane (1:1) as eluent, the isomer with a resonance at δ = 4.73 ppm could be separated from the mixture. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.03, 1.25, 1.3−1.5, 1.60 (2 m_c, m, m_c, 24 H, CH_2), 3.81, 3.88 (2 m_c, 8 H, OCH_2), 4.73 (m_c, 4 H, *trans*-CH=CH), 6.58 (d, *J* = 8.4 Hz, 4 H, 3′,3′′,5′,5′′-H), 7.22 (t, *J* = 8.4 Hz, 2 H, 4′,4′′-H), 7.56 (d, *J* = 8.1 Hz, 2 H, 3,8-H), 7.83 (s, 2 H, 5,6-H), 8.23 (d, *J* = 8.1 Hz, 2 H, 4,7-H). ^1H NMR of the mixture, selected signals (500 MHz, $CDCl_3$): δ = 4.44 (m_c, 0.62 H, *cis*-CH=CH), 4.73 (m_c, 3.38 H, *trans*-CH=CH), 8.2−8.3 (m, with d at 8.22, *J* = 8.1 Hz, 2 H, 4,7-H). *cis*/*trans*-ratio: 1:5.5.

2,11,13,24-Tetraoxa-1,12(1,3,2)-dibenzena-25(2,9)-1,10-phenanthrolinabicyclo[12.10.1]pentacosaphan-5,18-diene (4d): Batch size: 400 mg (574 μmol) of tetraene **3d**. Yield 303 mg (82%). IR (KBr): $\tilde{\nu}$ = 2932 (aliph. C−H), 1642 (aliph. C=C), 1595, 1457 (arom. C=C), 1104 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.8−1.2, 1.43, 2.09 (m with 2 m_c at 0.85 and 1.04, 2 m_c, 24 H, CH_2), 3.82, 3.90 (2 m_c, 8 H, OCH_2), 4.42, 4.70, 5.04 (3 m_c, 4 H, CH=CH), 5.30 (s, 1.75 H, CH_2Cl_2), 6.5−6.7 (m, 4 H, 3′,3′′,5′,5′′-H), 7.21 (m_c, 2 H, 4′,4′′-H), 7.48−7.65 (m, 2 H, 3,8-H), 7.76−7.82 (m with s at 7.78, 2 H, 5,6-H), 8.18−8.24 (m_c with d at 8.20, *J* = 8.2 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25−32 (17 t, CH_2), 53.5 (t, CH_2Cl_2), 68−70 (5 t, OCH_2), 104−107 (6 d, 3′,3′′,5′,5′′-C), 121.3, 121.4 (2 s, 1′,1′′-C), 125−136 (16 signals, 4′,4′′3,4,4a,5,6,6a,7,8-C, CH=CH), 146.5, 146.6 (2 s, 10a,10b-C), 155.7, 155.8 (2 s, 2,9-C), 158−159 (4 s, 2′,2′′,6′,6′′-C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 640 (100) [M^+], 612 (77) [$M^+ - C_2H_4$], 569 (43) [$M^+ - C_5H_{11}$]. HR-MS − $C_{42}H_{44}N_2O_4$: found 640.32970, calcd. 640.33008 (δ = 0.4 ppm); $C_{41}{}^{13}CH_{44}N_2O_4$: found 641.33360, calcd. 641.33344 (δ = −0.3 ppm). $C_{42}H_{44}N_2O_4$ (640.81): calcd. C 78.72, H 6.92, N 4.37; $C_{42}H_{44}N_2O_4 \cdot 0.9CH_2Cl_2$ (717.25): calcd. C 71.84, H 6.44, N 3.92; found C 71.63, H 6.33, N 3.79.

1^3,3^3-Dimethoxy-4,13-dioxa-1,3(1,2)-dibenzena-2(2,9)-1,10-phenanthrolinacyclotridecaphan-8-ene (4e): Batch size: 400 mg (713 μmol) of diene **3e**. Yield 360 mg (95%). IR (KBr): $\tilde{\nu}$ = 2925, 2869, 2840 (aliph. C−H), 1595, 1461 (arom. C=C), 1104 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.89, 1.2−1.7 (m_c, m, 8 H, CH_2), 3.67, 3.70 (2 s, 6 H, OCH_3), 3.88, 3.95 (2 m_c, 4 H, OCH_2), 4.68 (m_c, 1.15 H, *trans*-CH=CH), 5.04 (m_c, 0.85 H, *cis*-CH=CH), 6.61−6.68 (m, 4 H, 3′,3′′,5′,5′′-H), 7.27, 7.27 (2 t, *J* = 8.3, *J* = 8.3 Hz, 2 H, 4′,4′′-H), 7.58, 7.62 (2 d, *J* = 8.2, *J* = 8.2 Hz, 2 H, 3,8-H), 7.80, 7.80 (2 s, 2 H, 5,6-H), 8.22, 8.23 (2 d, *J* = 8.2, *J* = 8.2 Hz, 2 H, 4,7-H) ppm. *cis*/*trans*-ratio: 1:1.3. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.0, 28.9, 29.1, 29.4 (4 t, CH_2), 55.7, 55.9 (2 q, OCH_3), 68.4, 69.6 (2 t, OCH_2), 104.4, 104.4, 106.6, 108.0 (4 d, 3′,3′′,5′,5′′-C), 120.6, 121.9 (2 s, 1′,1′′-C), 125.7, 126.1, 126.2 (3 d, 3,5,6,8-C), 127.4, 127.4 (2 s, 4a,6a-C), 129.5, 129.6, 129.7 (3 d, 4′,4′′-C, CH=CH), 135.2, 135.3 (2 d, 4,7-C), 146.1, 146.3 (2 s, 10a,10b-C), 155.0, 155.2 (2 s, 2,9-C), 158.0, 158.1, 158.1, 158.4 (4 s, 2′,2′′,6′,6′′-C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 532 (100) [M^+], 450 (28) [$M^+ - C_6H_{10}$], 424 (17) [$C_{26}H_{20}N_2O_4$]. HR-MS − $C_{34}H_{32}N_2O_4$: found 532.23590, calcd. 532.23621 (δ = 0.6 ppm); $C_{33}{}^{13}CH_{32}N_2O_4$: found 533.23890, calcd. 533.23956 (δ = 1.2 ppm).

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$C_{34}H_{32}N_2O_4$ (532.63): calcd. C 76.67, H 6.06, N 5.26; $C_{34}H_{32}N_2O_4 \cdot 0.6H_2O$ (543.44): calcd. C 75.14, H 6.16, N 5.15; found C 75.37, H 6.35, N 4.82.

2-Bromo-3-methoxyphenol (6): 2-Bromo-1,3-dihydroxybenzene[25] (**5**, 10.0 g, 52.9 mmol) was added to a solution of potassium hydroxide (3.70 g, 66.1 mmol) in water (35 mL). Then dimethyl sulfate (5.00 mL, 52.7 mmol) was added slowly so that the temperature remained between 10 and 20 °C. After 30 min stirring at 100 °C, 2 N sodium hydroxide was added until the pH of the solution was basic. This mixture was extracted three times with dichloromethane (50 mL). The aqueous layer was then acidified with 2 N hydrochloric acid and the layers separated. The aqueous layer was extracted three times with diethyl ether (50 mL). The combined organic fractions were dried with magnesium sulfate. The solvents were evaporated in vacuo and the residue was purified by chromatography (silica gel, cyclohexane/ethyl acetate, 3:1), giving 5.48 g (51%) of **6**. M.p. 76 °C, ref.[27] 78.5−79 °C. GC (Optima 1/25 m, temp. program: 5 min at 100 °C, 10 °C/min until 250 °C, 20 min): t_{Ret} = 7.9 min, purity 89%. IR (KBr): $\tilde{\nu}$ = 3403 (O−H), 3010 (arom. C−H), 2972, 2940 (aliph. C−H), 1593, 1467 (arom. C=C), 1198 (O−H), 1080 (C−O−C), 1032 (arom. C−Br) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.89 (s, 3 H, OCH_3), 5.66 (s, 1 H, OH), 6.48 (dd, J = 1.3, J = 8.3 Hz, 1 H, 4-H), 6.58−6.70 (m, 1 H, 6-H), 7.06−7.26 (m, 1 H, 5-H) ppm. MS (EI, 70 eV): m/z (%) = 204, 202 (95, 100) [M^+], 189, 187 (10, 12) [$M^+ - CH_2$].

2-Bromo-1-methoxy-3-(pent-4-enyloxy)benzene (7): Batch size: 2-bromo-3-methoxyphenol (893 mg, 4.40 mmol, **6**) in dry *N*,*N*-dimethylformamide (20 mL), using potassium carbonate (1.82 g, 8.80 mmol), potassium iodide (500 mg, 3.01 mmol) and 5-bromo-1-pentene (650 μL, 5.50 mmol). Purification: chromatography on silica gel eluting with cyclohexane/ethyl acetate (15:1) . Yield 1.31 g (94%). GC (SE30/25 m, temp. program (5 min at 100 °C, 10 °C/min until 250 °C, 20 min at 250 °C): t_{Ret} = 14.6 min, purity: 96%. IR (film): $\tilde{\nu}$ = 3076 (arom. C−H), 2940, 2839 (aliph. C−H), 1640 (aliph. C=C), 1592, 1469 (arom. C=C), 1102 (C−O−C), 1036 (arom. C−Br) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.94 (m_c, 2 H, OCH_2CH_2), 2.30 (m_c, 2 H, CH_2CH=), 3.90 (s, 3 H, OCH_3), 4.04 (t, J = 6.3 Hz, 2 H, OCH_2), 5.00, 5.07 (tdd, J_t = 1.2, J_d = 2.0, J_d = 10.2 Hz, =CHH_{cis}, tdd, J_t = 1.5, J_d = 2.0, J_d = 17.2 Hz, =CHH_{trans}, 2 H), 5.87 (tdd, J_t = 6.7, J_d = 10.2, J_d = 17.2 Hz, 1 H, CH=), 6.56 (m_c, 2 H, 4,6-H), 7.20 (t, J = 8.3 Hz, 1 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.9 (t, OCH_2CH_2), 30.4 (t, CH_2CH=), 56.4 (q, OCH_3), 68.4 (t, OCH_2), 101.5 (s, 2-C), 104.5, 105.9 (2 d, 4,6-C), 115.3 (t, $=CH_2$), 128.1 (d, 5-C), 137.7 (d, CH=), 156.6, 157.2 (2 s, 1,3-C) ppm. MS (EI, 70 eV): m/z (%) = 272, 270 (3, 4) [M^+], 204, 202 (85, 88) [$M^+ - C_5H_8$], 191 (100) [M^+ − Br]. $C_{12}H_{18}BrO_2$ (271.15): calcd. C 53.15, H 5.58; found C 53.25, H 5.59.

2-Methoxy-6-(pent-4-enyloxy)benzeneboronic acid (8): Batch size: 2-bromo-1-methoxy-3-(pent-4-enyloxy)benzene (**7**, 1.00 g, 3.67 mmol) in tetrahydrofuran (15 mL) using *n*-butyllithium (2.5 M in *n*-hexane, 1.60 mL, 4.00 mmol) and trimethylborate (1.40 mL, 12.6 mmol). Purification: chromatography on silica gel eluting with cyclohexane/ethyl acetate (6:1). The compound was very hygroscopic. Yield 57%. M.p. 36−37 °C. IR (KBr): $\tilde{\nu}$ = 3507 (O−H), 3075 (arom. C−H), 2999, 2941, 2837 (aliph. C−H), 1640 (aliph. C=C), 1598 (arom. C=C), 1102 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.96 (m_c, 2 H, OCH_2CH_2), 2.25 (m_c, 2 H, CH_2CH=), 3.91 (s, 3 H, OCH_3), 4.09 (t, J = 6.5 Hz, 2 H, OCH_2), 4.99−5.12 (m_c, 2 H, $=CH_2$), 5.82 (tdd, J_t = 6.7, J_d = 10.2, J_d = 17.1 Hz, 1 H, CH=), 6.62 (m_c, 2 H, 3,5-H), 7.29 (s, 2 H, OH), 7.37 (t, J = 8.4 Hz, 1 H, 4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.2 (t, OCH_2CH_2), 30.0 (t, CH_2CH=), 56.0 (q, OCH_3), 68.3 (t, OCH_2), 104.2, 105.3 (2 d, 3,5-C), 115.9 (t, $=CH_2$), 133.0 (d, 4-C), 137.0 (d, CH=), 164.9, 165.5 (2 s, 2,6-C) ppm. Because of the neighbouring ^{11}B atom, the intensity of the 1-C signal was too small to be recorded. MS (CI, isobutane): m/z (%) = 237 (2) [M + H^+], 193 (100) [M + H^+ − HBO_2]. MS (EI, 70 eV): m/z (%) = 192 (27) [$M^+ - HBO_2$], 124 (100) [$M^+ - C_5H_9BO_2$]. $C_{12}H_{17}BO_4$ (236.07): calcd. C 61.05, H 7.26; $C_{12}H_{17}BO_4 \cdot 0.4H_2O$ (236.08): calcd. 59.24, H 7.37; found C 59.11, H 7.38.

2-Bromo-3-(methoxymethoxy)phenol (9): A solution of 2-bromo-1,3-dihydroxybenzene (**5**, 1.00 g, 5.29 mmol) in dry *N*,*N*-dimethylformamide (5 mL) was slowly added to a suspension of sodium hydride (212 mg, 53 mmol, 60% in mineral oil, washed three times with pentane) in dry tetrahydrofuran (10 mL) at 0 °C. After stirring for 1 h at room temp., methoxymethyl chloride (400 μL, 5.27 mmol) was added at 0 °C. After additional stirring at room temp. for 2 h, aqueous 2 N ammonium chloride (10 mL) was added, the layers were separated, and the aqueous layer was extracted three times with diethyl ether (30 mL). After drying of the combined organic layer with magnesium sulfate, the solvent was evaporated in vacuo and the crude product was purified by chromatography (silica gel, cyclohexane/ethyl acetate, 10:1) yielding 405 mg (33%) of **9**, m.p. 55−56 °C. IR (film): $\tilde{\nu}$ = 3355 (O−H), 2969, 2925 (aliph. C−H), 1594, 1580, 1477 (arom. C=C), 1148, 1087 (C−O), 1040 (arom. C-Br) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.51 (s, 3 H, OCH_3), 5.24 (s, 2 H, OCH_2O), 5.70 (s, 1 H, OH), 6.70−6.73 (m, 2 H, 4,6-H), 7.11−7.17 (m, 1 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.4 (q, OCH_3), 95.0 (t, OCH_2O), 101.3 (s, 2-C), 107.4, 109.4 (2 d, 4,6-C), 128.7 (d, 5-C), 153.5, 154.3 (2 s, 1,3-C) ppm. MS (EI, 70 eV): m/z (%) = 234, 232 (98, 100) [M^+], 204, 202 (56, 58) [$M^+ - OCH_2$], 189, 187 (9, 11) [$M^+ - OC_2H_5$], 174, 172 (16, 22) [$M^+ - O_2C_2H_4$]. HR-MS − $C_8H_9{}^{79}BrO_3$: found 231.97350, calcd. 231.97351 (δ = 0.0 ppm); $C_8H_9{}^{81}BrO_3$: found 233.97130, calcd. 233.97147 (δ = 0.7 ppm). $C_8H_9BrO_3$ (233.06): calcd. C 41.23, H 3.89; found C 41.74, H 4.18.

2-Bromo-1-(hex-5-enyloxy)-3-(methoxymethoxy)benzene (10): Batch size: 2-bromo-3-(methoxymethoxy)phenol (**9**, 254 mg, 1.09 mmol) in dry *N*,*N*-dimethylformamide (10 mL) using potassium carbonate (452 mg, 3.27 mmol), potassium iodide (166 mg, 1.00 mmol) and 6-bromo-1-hexene (182 μL, 1.36 mmol). Purification: chromatography on silica gel eluting with cyclohexane/ethyl acetate (10:1). Yield 332 mg (97%). GC (Optima 1/25 m, temp. program (5 min at 100 °C, 10 °C/min until 250 °C, 20 min at 250 °C): t_{Ret} = 17.4 min, purity: 96%. IR (film): $\tilde{\nu}$ = 2934 (aliph. C−H), 1640 (aliph. C=C), 1594, 1463 (arom. C=C), 1096, 1069 (C−O−C), 1037 (arom. C−Br) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.63 (m_c, 2 H, $OCH_2CH_2CH_2$), 1.85 (m_c, 2 H, OCH_2CH_2), 2.16 (m_c, 2 H, CH_2CH=), 3.52 (s, 3 H, OCH_3), 4.03 (t, J = 6.4 Hz, 2 H, OCH_2), 4.95−5.08 (m, 2 H, $=CH_2$), 5.25 (s, 2 H, OCH_2O), 5.84 (tdd, J_t = 6.7, J_d = 10.2, J_d = 17.1 Hz, 1 H, CH=), 6.58 (dd, J = 1.2, J = 8.3 Hz, 1 H, 6-H), 6.78 (dd, J = 1.2, J = 8.3 Hz, 1 H, 4-H), 7.17 (t, J = 8.3 Hz, 1 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.3 (t, $OCH_2CH_2CH_2$), 28.5 (t, OCH_2CH_2), 33.4 (t, CH_2CH=), 56.4 (q, OCH_3), 69.1 (t, OCH_2), 95.1 (t, OCH_2O), 103.0 (s, 2-C), 106.7 (d, 6-C), 108.3 (d, 4-H), 114.7 (t, $=CH_2$), 128.1 (d, 5-H), 138.6 (d, CH=), 155.0, 156.7 (2 s, 1,3-C) ppm. MS (EI, 70 eV): m/z (%) = 316, 314 (10, 9) [M^+], 235 (100) [M^+ − Br]. HR-MS − $C_{14}H_{19}{}^{79}BrO_3$: found 314.05160, calcd. 314.05176 (δ = 0.5 ppm); $C_{13}{}^{13}CH_{19}{}^{79}BrO_3$: found 315.05500, calcd. 315.05511 (δ = 0.4 ppm); $C_{14}H_{19}{}^{81}BrO_3$: found 316.04960, calcd. 316.04971 (δ = 0.4 ppm); $C_{13}{}^{13}CH_{19}{}^{81}BrO_3$: found 317.05300, calcd. 317.05307 (δ = 0.2 ppm). $C_{14}H_{19}BrO_3$ (315.20): calcd. C 53.35, H 6.08; found C 53.92, H 5.90.

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2-Bromo-3-(hex-5-enyloxy)phenol (11): 2-Bromo-1-(hex-5-enyloxy)-3-(methoxymethoxy)benzene (**10,** 280 mg, 892 μmol) was dissolved in tetrahydrofuran (10 mL). After addition of trifluoroacetic acid (100 μL, 1.26 mmol) and water (1.5 mL), the mixture was heated at reflux for 16 h. Following completion of the reaction, the solvent and trifluoroacetic acid were evaporated in vacuo and the crude product was purified by chromatography (silica gel, cyclohexane/ethyl acetate, 6:1). Yield 215 mg (89%). IR (film): $\tilde{\nu}$ = 3498 (O−H), 3074 (arom. C−H), 2938 (aliph. C−H), 1639 (aliph. C=C), 1594, 1461 (arom. C=C), 1200 (arom. C−OH), 1075 (C−O−C), 1031 (arom. C−Br) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.61 (m_c, 2 H, $OCH_2CH_2CH_2$), 1.84 (m_c, 2 H, OCH_2CH_2), 2.14 (m_c, 2 H, CH_2CH=), 4.01 (t, *J* = 6.3 Hz, 2 H, OCH_2), 4.95−5.08 (m, 2 H, =CH_2), 5.65 (s, 1 H, OH), 5.84 (tdd, J_t = 6.6, J_d = 10.2, J_d = 17.1 Hz, 1 H, CH=), 6.58 (dd, *J* = 1.3, *J* = 8.3 Hz, 1 H, 4-H), 6.66 (dd, *J* = 1.3, *J* = 8.3 Hz, 1 H, 6-H), 7.13 (t, J_t = 8.3 Hz, 1 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.2 (t, $OCH_2CH_2CH_2$), 28.5 (t, OCH_2CH_2), 33.3 (t, CH_2CH=), 69.0 (t, OCH_2), 100.5 (s, 2-C), 104.6 (d, 4-C), 108.3 (d, 6-H), 114.8 (t, =CH_2), 128.6 (d, 5-H), 138.5 (d, CH=), 153.5, 156.0 (2 s, 1,3-C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 272, 270 (9, 10) [M^+], 190, 188 (93, 100) [$M^+ - C_6H_{10}$]. $C_{12}H_{15}BrO_2$ (271.15): calcd. C 53.16, H 5.58; found C 52.87, H 5.73.

2-Bromo-1-(but-3-enyloxy)-3-(hex-5-enyloxy)benzene (12): 2-Bromo-3-(hex-5-enyloxy)phenol (**11**, 1.61 g, 5.95 mmol), 3-buten-1-ol (770 μL, 9.00 mmol) and triphenylphosphane (2.03 g, 7.74 mmol) were dissolved in tetrahydrofuran (20 mL). At 0 °C, diethyl azodicarboxylate (1.20 mL, 7.72 mmol) dissolved in tetrahydrofuran (5 mL) was added and the mixture was stirred for 2 h at room temp. After addition of water (20 mL), the layers were separated and the aqueous layer was extracted three times with diethyl ether (20 mL). The combined organic layer was washed three times with 2 N sodium hydroxide (20 mL) and once with brine (20 mL). After drying with magnesium sulfate, the solvent was evaporated in vacuo and the residue was purified by chromatography (cyclohexane/ethyl acetate, 9:1, silica gel). Yield 1.23 mg (64%). IR (film): $\tilde{\nu}$ = 3076 (arom. C−H), 2975, 2935 (aliph. C−H), 1640 (aliph. C=C), 1592, 1459 (arom. C=C), 1097 (C−O−C), 1036 (arom. C−Br) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.62 (m_c, 2 H, $O(CH_2)_2CH_2CH_2CH$=), 1.85 [m_c, 2 H, $OCH_2CH_2(CH_2)_2CH$=], 2.14 [m_c, 2 H, $O(CH_2)_3CH_2CH$=], 2.59 (tq, J_t = 1.3, J_q ≈ 7 Hz, 2 H, OCH_2CH_2CH=), 4.00 [t, *J* ≈ 7 Hz, 2 H, $OCH_2(CH_2)_3CH$=], 4.06 (t, *J* ≈ 7 Hz, 2 H, OCH_2CH_2CH=), 4.95−5.07 [m, 2 H, $O(CH_2)_4CH=CH_2$], 5.09−5.22 [m, 2 H, $O(CH_2)_2CH=CH_2$], 5.83 [tdd, J_t = 6.7, J_d = 10.2, J_d = 17.1 Hz, 1 H, $OCH_2(CH_2)_3CH$=], 5.95 (tdd, J_t = 6.8, J_d = 10.3, J_d = 17.1 Hz, 1 H, OCH_2CH_2CH=), 6.53 (d, *J* = 8.3 Hz, 2 H, 4,6-H), 7.16 (t, *J* = 8.3 Hz, 2 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.2 [t, $O(CH_2)_2CH_2CH_2CH$=], 28.5 [t, $OCH_2CH_2(CH_2)_2CH$=], 33.5, 33.6 (2 t, CH_2CH=), 68.6, 69.1 (2 t, OCH_2), 102.2 (s, 2-C), 105.8, 105.8 (2 d, 4,6-C), 114.7, 117.2 (2 t, =CH_2), 128.0 (d, 5-H), 134.2, 138.6 (2 d, CH=), 156.6, 156.7 (2 s, 1,3-C) ppm. MS (CI, isobutane): *m*/*z* (%) = 327, 325 (61, 61) [M + H^+]. MS (EI, 70 eV): *m*/*z* (%) = 326, 324 (3, 4) [M^+], 245 (75) [M^+ − Br], 190, 188 (100, 99) [$M^+ - C_{10}H_{16}$]. $C_{16}H_{21}BrO_2$ (325.25): calcd. C 59.09, H 6.51; found C 58.93, H 7.04.

2-(But-3-enyloxy)-6-(hex-5-enyloxy)benzeneboronic Acid (13): Batch size: 2-bromo-1-(but-3-enyloxy)-3-(hex-5-enyloxy)benzene (**12**, 1.09 g, 3.34 mmol) in tetrahydrofuran (15 mL) using *n*-butyllithium (2.5 M in hexane, 1.50 mL, 3.75 mmol) and trimethylborate (1.25 mL, 11.2 mmol). Purification: chromatography on silica gel eluting with cyclohexane/ethyl acetate (6:1). Yield 78%. M.p. 41 °C. IR (KBr): $\tilde{\nu}$ = 3504 (O−H), 3073 (arom. C−H), 2944, 2879 (aliph. C−H), 1643 (aliph. C=C), 1596, 1575 (arom. C=C), 1101 (C−O−C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.52 [m_c, 2 H, $O(CH_2)_2CH_2CH_2CH$=], 1.79 [m_c, 2 H, $OCH_2CH_2(CH_2)_2CH$=], 2.06 [m_c, 2 H, $O(CH_2)_3CH_2CH$=], 2.53 (tq, J_t = 1.4, J_q ≈ 6 Hz, 2 H, OCH_2CH_2CH=), 3.99 [t, *J* = 6.6 Hz, 2 H, $OCH_2(CH_2)_3CH$=], 4.06 (t, *J* = 6.3 Hz, 2 H, OCH_2CH_2CH=), 4.88−4.99 [m, 2 H, $O(CH_2)_4CH=CH_2$], 5.09−5.21 [m, 2 H, $O(CH_2)_2CH=CH_2$], 5.66−5.86 (m, 2 H, CH=), 6.52, 6.53 (2 d, *J* = 8.4, *J* = 8.4 Hz, 2 H, 3,5-H), 7.21 (s, 2 H, OH), 7.27 (t, *J* = 8.4 Hz, 1 H, 4-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.2 [t, $O(CH_2)_2CH_2CH_2CH$=], 27.5 [t, $OCH_2CH_2(CH_2)_2CH$=], 32.3, 32.7 (2 t, CH_2CH=), 66.7, 67.9 (2 t, OCH_2), 103.9, 104.2 (2 d, 3,5-C), 105.6 (s, 1-C), 114.1, 117.3 (2 t, =CH_2), 131.9 (d, 4-H), 132.7, 137.0 (2 d, CH=), 163.9, 163.9 (2 s, 2,6-C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 290 (28) [M^+], 246 (45) [$M^+ - HBO_2$], 207 (6) [$M^+ - C_6H_{11}$], 154 (73) [$M^+ - C_{10}H_{16}$], 83 (100) [C_6H_{11}], 69 (99) [C_5H_9]. $C_{16}H_{23}BO_4$ (290.17): calcd. C 66.23, H 7.99; found C 66.16, H 8.18.

2-[2,6-Bis(hex-5-enyloxy)phenyl]-9-chloro-1,10-phenanthroline (16): 2,9-Dichloro-1,10-phenanthroline (**14**, 564 mg, 2.30 mmol) was dissolved in dimethoxyethane (50 mL), and 2,6-bis(hex-5-enyloxy)-benzeneboronic acid **15**[22] (793 mg, 2.49 mmol), tetrakis(triphenylphosphane)palladium(0) (266 mg, 230 μmol) and 2 N aqueous sodium carbonate (2.3 mL) were added. The mixture was heated at reflux for 16 h before water (20 mL) and dichloromethane (25 mL) were added. The layers were separated and the aqueous layer was extracted three times with dichloromethane (30 mL). The combined organic layer was washed with brine (20 mL) and dried with magnesium sulfate. After evaporation to dryness, the crude product was dissolved in dichloromethane, filtered through basic alumina and purified by chromatography (dichloromethane with 0.5% of methanol, silica gel) and recrystallized from dichloromethane/hexane. Yield 878 mg (78%). M. p. 98−100 °C. IR (KBr): $\tilde{\nu}$ = 3071 (arom. C−H), 2934, 2869 (aliph. C−H), 1640 (aliph. C=C), 1582, 1477, 1456 (arom. C=C), 1096 (C−O−C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.34 (m_c, 4 H, $OCH_2CH_2CH_2$), 1.57 (m_c, 4 H, OCH_2CH_2), 1.84 (m_c, 4 H, CH_2CH=), 4.00 (t, *J* = 6.3 Hz, 4 H, OCH_2), 4.7−4.8 (m, 4 H, =CH_2), 5.51 (tdd, J_t = 6.7, J_d = 10.3, J_d = 17.1 Hz, 2 H, CH=), 6.67 (d, *J* = 8.4 Hz, 2 H, 3′,5′-H), 7.30 (t, *J* = 8.4 Hz, 1 H, 4′-H), 7.55 (d, *J* = 8.4 Hz, 1 H, 8-H), 7.73 (d, *J* = 8.3 Hz, 1 H, 3-H), 7.74 (d, *J* = 8.8 Hz, 1 H, 5-H or 6-H), 7.82 (d, *J* = 8.8 Hz, 1 H, 6-H or 5-H), 8.16 (d, *J* = 8.4 Hz, 1 H, 7-H), 8.20 (d, *J* = 8.3 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.1 (t, $OCH_2CH_2CH_2$), 28.5 (t, OCH_2CH_2), 33.2 (t, CH_2CH=), 69.0 (t, OCH_2), 106.1 (d, 3′,5′-C), 114.1 (t, =CH_2), 120.7 (s, 1′-C), 123.8, 125.0, 127.0, 127.1 (4 d, 3,5,6,8-C), 127.3, 127.6 (2 s, 4a,6a-C), 129.9 (d, 4′-C), 134.7, 138.5 (2 d, 4,7-C), 138.6 (d, CH=), 144.7, 146.3 (2 s, 10a,10b-C), 150.9, 155.7 (2 s, 2,9-C), 158.1 (s, 2′,6′-C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 488, 486 (31, 76) [M^+], 419, 417 (37, 100) [$M^+ - C_5H_9$], 405, 403 (42, 95) [$M^+ - C_6H_{11}$]. HR-MS − $C_{30}H_{31}{}^{35}ClN_2O_2$: found 486.20680; calcd. 486.20740 (δ = 1.2 ppm); $C_{30}H_{31}{}^{37}ClN_2O_2$: found 488.20340, calcd. 488.20447 (δ = 0.3 ppm). $C_{30}H_{31}ClN_2O_2$ (487.04): calcd. C 73.98, H 6.42, N 5.75; found C 73.69, H 6.57, N 5.61.

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