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Concave 1,10-Phenanthrolines as Ligands for Cyclopropanations – Towards a Deeper Understanding of the Stereoselectivity[‡]

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Four new mono- and bimacrocyclic 1,10-phenanthrolines – **3b** and **4a**–**c** – containing aryl bridgeheads have been synthesised. The etherification of the aryl bridgeheads was accomplished by Williamson or Mitsunobu reactions. A key step in the synthesis of the macrocyclic phenanthrolines **3** and **4** is the Suzuki coupling of 2,9-diiodo-1,10-phenanthroline (**12**) with the appropriately substituted boronic acids **17** and **20**. Ring-closing metathesis and hydrogenation completed the synthesis. The resulting macrocyclic 1,10-phenanthrolines **3b** and **4a**–**c** were tested as ligands in a copper(I)-catalysed stereoselective cyclopropanation.

Introduction

One of the most important goals in organic chemistry is the enhancement of selectivity in order to optimise yield, solvent requirements, catalyst loading etc. The best examples of highly selective catalysts are to be found among enzymes. Their fascinating selectivities are due to the geometries of their active sites,[1] which are often described as cleft-, cave- or hole-like. All these geometric features can be summarised in the word "concave".[2–5]

In mimicry of the geometries of enzymes, several classes of concave reagents[6] with their reactive sites shielded in varying geometries have been developed, with the goal of enhancing selectivities both in catalyses and also in stoichiometric reactions. A well investigated and successful class of ligands for catalytically active metals is the group of concave bimacrocyclic 1,10-phenanthrolines (see Figure 1), some of which show remarkable selectivities.[7–11] 1,10-Phenanthroline itself possesses two nitrogen atoms and is therefore a good chelating ligand for transition metal ions such as copper(I).

Several sub-classes of bimacrocyclic concave 1,10-phenanthrolines have been synthesised; they include bimacrocyclic bislactams,[12] bimacrocyclic cyclophanes **1** with aryl bridgeheads,[7,13] and bimacrocyclic bridged calixarenes **2**.[14,15] The last two classes have been employed as ligands in copper(I)-catalysed cyclopropanations of alkenes such as styrene or indene with diazoacetates;[8,11,16,17,18] some remarkable selectivities have been achieved. Whereas the cyclophane-derived ligands **1** exhibited strong *anti* selectivities (up to 140:1), the calixarene derivatives **2** were able to produce the *syn* products predominantly (best value: 86:14).

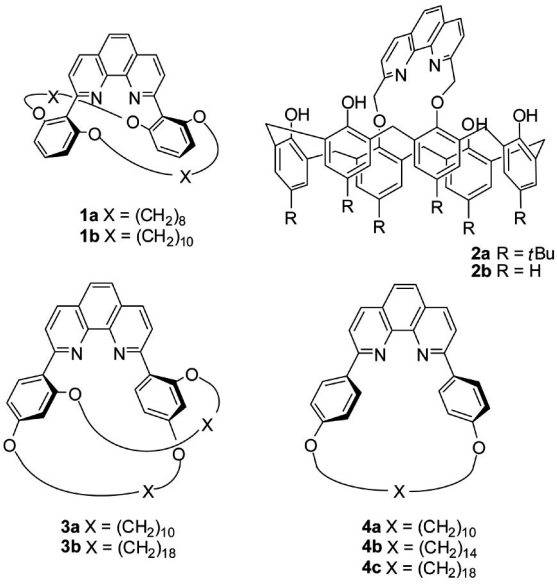

Figure 1. Classes of macrocyclic 1,10-phenanthrolines.

In a combined computational and experimental study,[16] two models that explain these *anti* and *syn* selectivities were developed. The striking differences between the two classes of catalysts were their different rigidities and their different symmetries. Figure 2 shows the different orientations of the 1,10-phenanthroline planes with respect to the macrocycles that they bridge. In the left-hand structure in Figure 2, the symmetry of the cyclophane **1b** with aryl bridgeheads becomes obvious. If a copper(I) ion were bound to the nitro-

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gen atoms of the 1,10-phenanthroline it would be located between the bridgeheads in the same way as the cyclopropanation intermediate, the copper(I) carbene complex, would have to (for details on the cyclopropanation reaction see Figure 9, below). If a diazoacetate is used for the cyclopropanation, the ester group of the carbene has to be accommodated in the complex. In the concave environment of the complex, the ester group can only stretch out of bimacrocycle **1b** to the "south" (in the orientation shown in Figure 2). An incoming alkene would have to avoid steric compression with this residue, and the resulting maximisation of distance between alkene and ester group explains the *anti* selectivity.

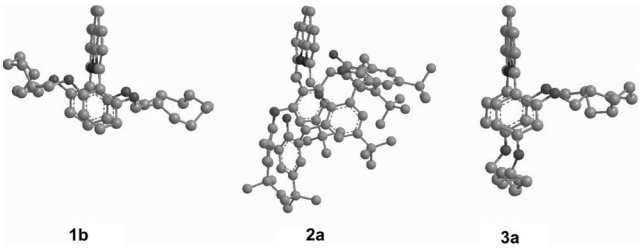

Figure 2. Geometry-optimised models of three classes of 1,10-phenanthroline-containing bimacrocycles. All bimacrocycles are oriented in the same way with respect to the 1,10-phenanthroline bridge. Whereas the bimacrocycle with *ortho*,*ortho*-disubstituted bridgeheads (**1b**, left) is symmetric, the other two classes – a 1,10-phenanthroline-bridged calix[6]arene (**2a**, middle) and a bimacrocycle with *ortho*,*para*-disubstituted bridgeheads (**3a**, right) – possess openings next to their 1,10-phenanthroline components (to the "west") but are shielded in the "south". For implications see text.

The 1,10-phenanthroline-bridged calix[6]arene **2a** is shown in the middle of Figure 2. Its geometric differences from the bimacrocyclic cyclophane **1b** on the left are obvious. Because of the O–CH_2 link between the 1,10-phenanthroline and the calixarene aryl rings, the 1,10-phenanthroline bridge can tilt to the side, thus generating an opening next to the 1,10-phenanthroline. If a copper(I) ion were bound here and were to react with a diazoacetate, the ester group would have to be accommodated in the area between the 1,10-phenanthroline and the calixarene rim. An incoming alkene would again try to avoid the ester group, but the geometry is not symmetric. The ester group would point towards the incoming alkene, but the alternative approach would be strongly shielded by the large calix[6]arene moiety. If the ester group were to carry only a small residue, the repulsion by the calixarene would dominate and this would result in the formation of a *syn* product.[16]

Unfortunately, calixarenes cannot be altered too much. The ring size, for instance, can only be changed in relatively large steps by addition or removal of one arylmethylene block. Bridging experiments have been carried out for calix[5]- and calix[8]arenes,[19] but the resulting products were not comparable with the nice bimacrocyclic calix[6]arenes **2** used so effectively in the catalyses.

We therefore thought about alteration of the cyclophane bimacrocycles **1** in such a way that their geometries would rather resemble those of the calixarene derivatives. Figure 2 shows that the *ortho*,*para*-bridged cyclophane **3** possesses such a different geometry in relation to the *ortho*,*ortho*-bridged cyclophane **1** and the calixarene derivative **2**. The goal of this work was therefore to synthesise members of this new class of unsymmetrical bimacrocyclic 1,10-phenanthroline cyclophanes.

Results and Discussion

Synthesis of the Starting Materials

The building blocks for the new macrocyclic 1,10-phenanthrolines **3** and **4** were 2,9-diiodo-1,10-phenanthroline (**12**, Figure 4, below) and the variously substituted phenylboronic acids **17** and **20** (Figure 5, below). 2,9-Diiodo-1,10-phenanthroline (**12**) was synthesised by the well known procedure described by Lewis et al.[20] and Yamada et al.[21] From 1,10-phenanthroline (**5**), chloro atoms were first introduced at the 2- and 9-positions to yield phenanthroline **10**, and then a chloro–iodo exchange was accomplished (see Figures 3 and 4).

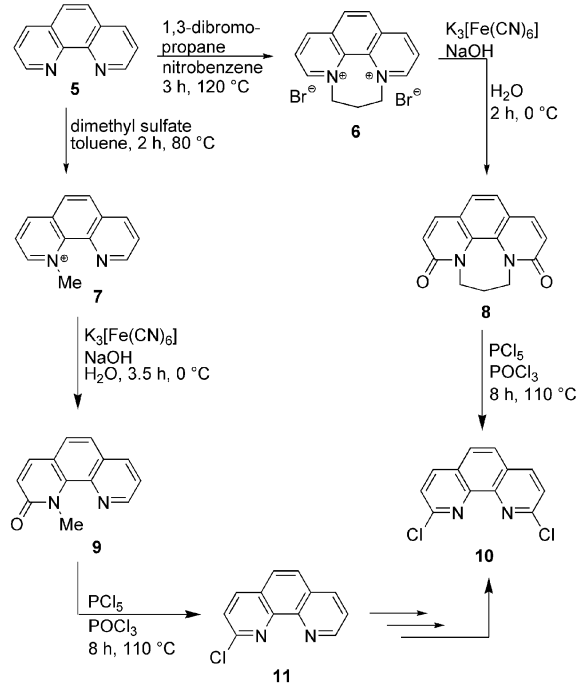

Figure 3. 2,9-Dichloro-1,10-phenanthroline (**10**) can be synthesised in two different ways starting from 1,10-phenanthroline (**5**).

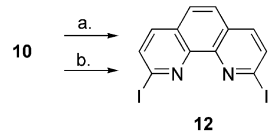

Figure 4. Transformation of 2,9-dichloro-1,10-phenanthroline (**10**) into 2,9-diiodo-1,10-phenanthroline (**12**). a) NaI, HI, 4 d, 80 °C, yield 58%; b) NaI, HI, 16 h, 100 °C, yield 48%.

The different phenylboronic acids **17** and **20** were synthesised from resorcinol (**13**) or from 4-bromophenol (**18**). Resorcinol (**13**) was first halogenated with iodine monochloride to yield the desired product, 4-iodoresorcinol (**14b**), in about 40% yield. 4-Bromoresorcinol (**14a**), which is commercially available, can also be used in the following step. The phenol groups of the halogenated aromatic compounds **14** were alkylated by the Williamson or Mitsunobu strategies. In the case of iodoarenes, Williamson alkylation is recommended because the Mitsunobu coupling of an alcohol with an iodophenol gave only a very low yield.

Figure 5 summarises the syntheses of the phenylboronic acids **17** and **20**, whereas Table 1 lists the reaction conditions and the yields corresponding to the different alkenoxyarenes **16** and **19** and Table 2 gives the workup conditions and yields for the syntheses of the different boronic acids **17** and **20**.

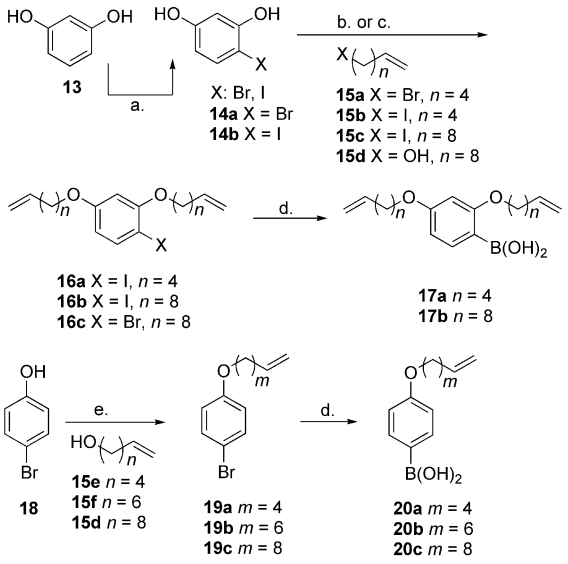

Figure 5. a) ICl, Et_2O, 1 h, 20 °C (X = I); b) 6-bromohex-1-ene (**15a**), 6-iodohex-1-ene (**15b**), or 10-iododec-1-ene (**15c**), K_2CO_3, KI, DMF, 18 h, 60 °C; c) dec-9-en-1-ol (**15d**), PPh_3, diisopropyl azodicarboxylate (DIAD), THF, 18 h, 20 °C; d) *n*-butyllithium, THF, –78 °C, 1 h, then $B(OMe)_3$, 2 h, warm to room temp., then H_2O, 10 min, e) hex-5-en-1-ol (**15e**), oct-7-en-1-ol (**15f**) or dec-9-en-1-ol (**15d**), PPh_3, diisopropyl azodicarboxylate (DIAD), THF, 18 h, 20 °C.

Table 1. Reaction conditions and yields for the ether formation to give the alkenoxyarenes **16** and **19**.

Arene	Alkene	Reaction conditions	Product	% Yield
14b	**15a**	K_2CO_3, KI, DMF, 18 h, 60 °C	**16a**	75
14b	**15b**	K_2CO_3, DMF, 18 h, 60 °C	**16a**	65
14b	**15c**	K_2CO_3, DMF, 18 h, 70 °C	**16b**	71
14b	**15d**	PPh_3, DIAD, THF, 18 h, 20 °C	**16b**	22
14a	**15c**	K_2CO_3, DMF, 18 h, 70 °C	**16c**	98
14a	**15d**	PPh_3, DIAD, THF, 18 h, 20 °C	**16c**	76
18	**15e**	PPh_3, DIAD, THF, 18 h, 20 °C	**19a**	71
18	**15f**	PPh_3, DIAD, THF, 18 h, 20 °C	**19b**	87
18	**15d**	PPh_3, DIAD, THF, 18 h, 20 °C	**19c**	79

Table 2. Workup conditions and yields for the syntheses of phenylboronic acids **17** and **20**.

Arene	Workup	Boronic acid	% Yield
16a	–	**17a**	crude product
16b	–	**17b**	crude product
16c	–	**17b**	crude product
19a	recrystallisation	**20a** [a]	84
19b	recrystallisation	**20b** [a]	90
19c	recrystallisation	**20c** [a]	78

[a] The boronic acids **19a–c** crystallise as mixtures of monomers and trimers of the boronic acids, as was shown by their mass and NMR spectra.

Suzuki Coupling and Ring-Closure

After the starting materials had been synthesised, Suzuki reactions were used to couple the boronic acids **17** and **20** to the 1,10-phenanthroline unit (Figure 6). 2,9-Diiodo-1,10-phenanthroline (**12**) was used in most couplings, because of its higher reactivity relative to 2,9-dichloro-1,10-phenanthroline (**10**). In one reaction with dichloride **10** and boronic acid **17b**, monoarylated 1,10-phenanthroline **23** could be isolated (Figure 7). In a subsequent reaction, this intermediate could also be transformed into the desired 2,9-diaryl-1,10-phenanthroline **21b** by a second Suzuki coupling with boronic acid **17b**. The Suzuki couplings[22] were carried out in mixtures of 1,2-dimethoxyethane and water (4:1). Tetrakis(triphenylphosphane)palladium(0) was chosen as catalyst, and barium hydroxide was used as base. Because of the instabilities of the disubstituted phenylboronic acids **17** during column chromatography, the crude products **17** were used in the reactions. Table 3 summarises the reaction conditions and yields for the different Suzuki couplings.

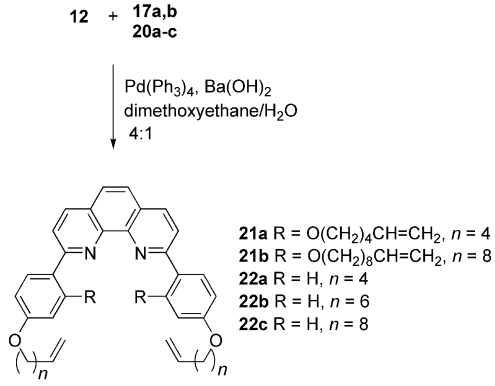

Figure 6. 2,9-Diaryl-1,10-phenanthrolines **21** and **22** were obtained by Suzuki couplings of 2,9-diiodo-1,10-phenanthroline (**12**) with phenylboronic acids **17** and **20**.

The final steps in the syntheses of the concave 1,10-phenanthrolines **3** and **4** were ring-closing metathesis and hydrogenation of the new double bonds of the ring (Figure 8). The Grubbs catalyst (first generation) was used for ring-closing metathesis, with the reactions being carried out at room temperature.

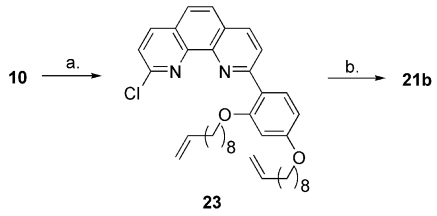

Figure 7. The monochloro-monoaryl-1,10-phenanthroline **23** could be isolated as an intermediate when 2,9-dichloro-1,10-phenanthroline (**10**) was used as starting material. In a subsequent Suzuki coupling, **23** could be coupled with boronic acid **17b** to give **21b**. a) $Pd(PPh_3)_4$, $Ba(OH)_2$, dimethoxyethane/water, **17b**, 40 h, room temp.; b) $Pd(PPh_3)_4$, $Ba(OH)_2$, dimethoxyethane/water, **17b**, 18 h, room temp.

Table 3. Yields of the Suzuki coupling reactions of 2,9-diiodo-1,10-phenanthroline (**12**) with phenylboronic acids **17** and **20** to give 2,9-diaryl-1,10-phenanthrolines **21** and **22**.

Boronic acid	*n*, R	Reaction conditions	Product	% Yield
17a	*n* = 4, R = $O(CH_2)_4CH{=}CH_2$	18 h, 60 °C	**21a**	27
17b	*n* = 8, R = $O(CH_2)_8CH{=}CH_2$	80 h, 80 °C	**21b**	10, (14[a])
20a	*n* = 4, R = H	72 h, 80 °C	**22a**	30
20b	*n* = 6, R = H	18 h, 80 °C	**22b**	46
20c	*n* = 8, R = H	18 h, 80 °C	**22c**	80

[a] Compound **21b** was synthesised in a two-step reaction starting from **10** instead of **12** with isolation of intermediate **23**.

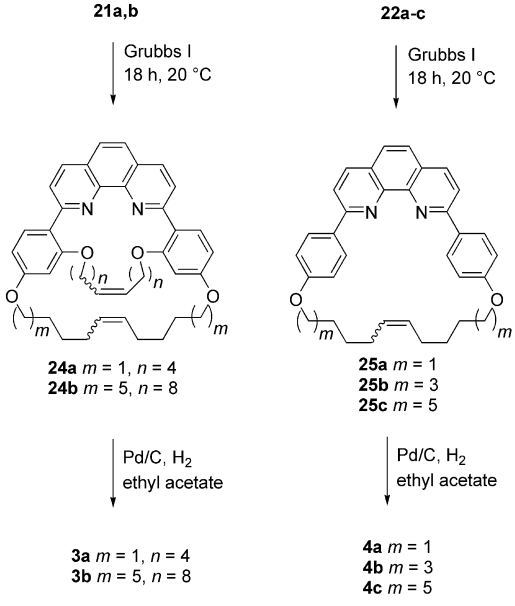

Figure 8. Syntheses of 1,10-phenanthroline macrocycles **3** and **4** from the 2,9-diaryl-1,10-phenanthrolines **21** and **22**.

After ring-closing metathesis, the new double bonds were hydrogenated under hydrogen in the presence of palladium on charcoal as heterogeneous catalyst. Table 4 summarises the yields for the ring-closing reactions and the hydrogenations.

Table 4. Yields for ring-closing metatheses (RCM) and subsequent hydrogenations in the syntheses of 1,10-phenanthroline macrocycles **3** and **4**.

21, **22**	RCM reaction time	**24**, **25**	RCM % yield	Hydrogenation reaction time	**3**, **4**	Hydrogenation % yield
21a	18 h		mixed fractions			
21b	18 h	**24b**	71	18 h	**3b**	95
22a	14 d	**25a**	53	3 d	**4a**	44
22b	48 h	**25b**	87	4 d	**4b**	60
22c	18 h	**25c**	35	18 h	**4c**	58

1,10-Phenanthroline-Based Ligands in Cyclopropanations

The copper(I)-catalysed cyclopropanation of alkenes can be carried out with different diazo compounds, of which ethyl diazoacetate (**26**) is commercially available. This diazo compound has usually been used to evaluate new catalysts. In addition to cyclopropanes, diethyl fumarate (**30**) and maleate (**31**) are usually detected as by-products (Figure 9).

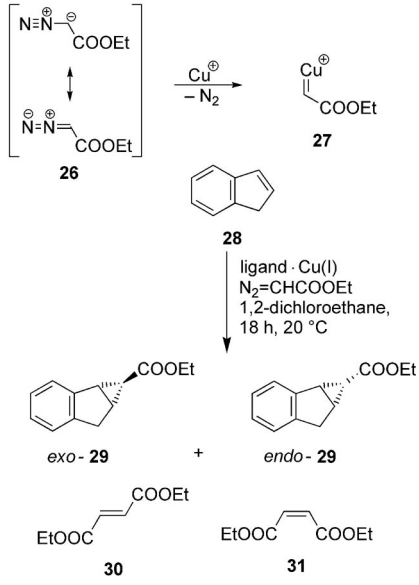

Figure 9. The copper(I) carbenoid **27** is the reactive intermediate in the cyclopropanation of indene (**28**) with ethyl diazoacetate (**26**). In addition to the cyclopropanes *exo*-**29** and *endo*-**29**, diethyl fumarate (**30**) and diethyl maleate (**31**) are always found as by-products.

The macrocyclic 1,10-phenanthrolines **3** and **4** were tested as ligands for copper(I) ions in the cyclopropanation of indene (**28**). As reference, the copper(I) trifluoromethanesulfonate/benzene complex was used in the absence of additional ligands. For this reaction, a diastereomeric ratio of 32:68 (*endo*/*exo*) is reported.[8] Through the use of 1,10-phenanthroline ligands, this diastereoselectivity can be changed[8,11,16,17,18] either towards *exo* or towards *endo* products (see Introduction). Table 5 compares the selectivities of the new ligands **3** and **4** with those of other 1,10-phenanthrolines in the copper(I)-catalysed cyclopropanation of indene (**28**). To allow better comparison of the *endo*/*exo* selectivities, all reactions were carried out as batch reactions under inert atmosphere and identical conditions.

In synthetic applications, the yields of cyclopropanes can be improved by slow addition of the diazoacetate, because the amount of by-products **30** and **31** decreases with dilution.

Table 5. Results of the copper(I)-catalysed cyclopropanations of indene (**28**) with ethyl diazoacetate (**26**) in the presence of a range of 1,10-phenanthrolines **3** and **4**. For comparison with previous results, the yields and selectivities obtained with the phenanthroline-bridged calix[6]arene **2a** and the bimacrocyclic phenanthroline **1b** with bis-*ortho*-substituted bridgeheads with chain lengths of 10 carbon atoms are shown (n.m.: not measured).

Ligand	% Yield **29**/(**30** + **31**)	*endo*-**29**/*exo*-**29**	**31**/**30**
No ligand	71/15	26:74	38:62
1b	68/22	1:99	n.m.
2a	45/n.m.	76:24	89:11
3b	46/14	32:68	44:56
4a	15/3	46:54	55:45
4b	70/16	30:70	37:63
4c	66/13	26:74	34:66

As documented in Table 5, the selectivities achieved in the cyclopropanations of indene (**28**) lie between those found for concave 2,9-diaryl-1,10-phenanthrolines (see **1b**) and for the calixarene derivatives (see **2a**). As would be expected, the *endo* fractions have increased relative to **1** with the changing of the chains from bis-*ortho* orientations to *ortho*,*para* or to *para* only. In most cases, however, the influences of the ligands on the selectivities of the cyclopropanations are small, leading to values comparable to those observed with copper(I) alone. However on comparison of compounds of varying ring size, a tendency towards greater *endo* selectivity is observed with smaller rings. Consequently, the next step in catalyst development should be to minimise the number of atoms in the chains of the macrocyclic 1,10-phenanthrolines **3** and **4** in order to enhance *endo* selectivities.

Conclusions

We have shown that different macrocyclic (**4**) and bimacrocyclic (**3**) 1,10-phenanthrolines with new geometries could be synthesised in acceptable to good yields. These 1,10-phenanthrolines **3** and **4** were used as ligands for copper(I), and the resulting complexes were tested in the cyclopropanation of indene (**28**) with ethyl diazoacetate (**26**). Unfortunately, the influences of the ligands on the *exo*/*endo* stereoselectivities were small but the ring size dependence indicates that higher selectivities might be expected for macrocycles with smaller ring sizes.

Experimental Section

General Remarks: The following chemicals were obtained commercially and were used without further purification: acetic acid (Merck), ammonia (Biesterfeld), barium hydroxide octahydrate (Merck), benzylidenebis(tricyclohexylphosphane)dichlororuthenium (Grubbs type I catalyst, Aldrich), 6-bromohex-1-ene (**15a**, Acros Organics), 4-bromophenol (**18**, Alfa Aesar), 4-bromoresorcinol (**14a**, Acros Organics), *n*-butyllithium (2.5 M in hexanes, Aldrich), copper(I) triflate hemibenzene complex (Aldrich), dec-9-en-1-ol (**15d**, Merck), ethyl diazoacetate (**26**, Aldrich), 1,3-dibromopropane (Fluka), 1,2-dichloroethane (Acros Organics), diisopropyl azodicarboxylate (DIAD, Fluka), 1,2-dimethoxyethane (Aldrich), *N*,*N*-dimethylformamide (Fluka, ≥99.8%), dimethyl sulfate (Merck), *n*-hexadecane (Aldrich), hex-5-en-1-ol (**15e**, Alfa Aesar), hypophosphoric acid (Riedel-de Haën), conc. hydroiodic acid (Merck), imidazole (Fluka), indene (**28**, Fluka), iodine (Merck), iodine monochloride (Lancaster), nitrobenzene (Merck), palladium on charcoal (10%, Fluka), 1,10-phenanthroline (**5**, Merck, ChemPur), phosphorus pentachloride (Fluka), phosphoryl chloride (Merck), potassium carbonate (Merck), potassium hexacyanoferrate(III) (Merck), potassium iodide (Merck), resorcinol (**13**, Riedel-de Haën), sodium chloride (Merck), sodium hydride (Aldrich, 60% dispersion in mineral oil), sodium hydroxide (Merck), sodium thiosulfate pentahydrate (Fluka), tetrakis(triphenylphosphane)palladium(0) (Merck, Acros Organics), trimethyl borate (Fluka), triphenylphosphane (Fluka). 2,9-Dichloro-1,10-phenanthroline (**10**) and 2,9-diiodo-1,10-phenanthroline (**12**) were prepared by literature procedures.[20,21] Oct-7-en-1-ol (**15f**) was synthesised by Dipl.-Chem. D. Stoltenberg by a literature procedure.[23] Dry solvents were obtained with suitable desiccants: tetrahydrofuran was distilled from lithium aluminium hydride, diethyl ether from sodium, and dichloromethane from calcium hydride. Column chromatography was carried out on basic alumina (Fluka, activity I) or silica gel (Macherey–Nagel, activity I). The preparative centrifugally accelerated thin-layer chromatograph (Chromatotron) was a model 7924T from Harrison Research. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AC 200 (200 MHz), ARX 300 (300 MHz or 75 MHz), DRX 500 (500 MHz or 125 MHz) or Avance 600 (600 MHz or 150 MHz) instruments, with tetramethylsilane as internal standard. IR spectra were measured on a Perkin–Elmer 1600 Series device. MS spectra were recorded on a Finnigan MAT 8230 or MAT 8200 machine or on an Applied Biosystems Mariner ESI-TOF MS 5280. Elemental analyses were carried out on a EuroVector instrument. Gas chromatography was performed with 6890 N (Agilent); split/splitless injector, split ratio 11:1, injector temp. 240 °C, FID detector temp. 250 °C.

2,21,23,42-Tetraoxa-1,22(1,3,4)-dibenzena-43(2,9)-1,10-phenanthrolina-bicyclo[20.20.1]tritetracontaphane (3b): Palladium (12 mg, 10% on activated charcoal) was suspended in acid-free ethyl acetate (2 mL). Under hydrogen, 2,21,23,42-tetraoxa-1,22(1,3,4)-dibenzena-43(2,9)-1,10-phenanthrolina-bicyclo-[20.20.1]tritetracontaphan-11,32-diene (**24b**, 23 mg, 26 μmol), dissolved in acid-free ethyl acetate (3 mL), was added. The reaction mixture was stirred under hydrogen at room temp. for 16 h. The suspension was filtered through a layer of basic aluminium oxide (dichloromethane). Evaporation of the solvent in vacuo yielded a light yellow oil (22 mg, 25 μmol, 95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82–1.15 (m, 16 H, CH_2), 1.21–1.53 (m, 40 H, CH_2), 1.84 (m_c, 8 H, OCH_2CH_2), 4.03 (t, $^3J \approx 6.9$ Hz, 4 H, OCH_2), 4.04 (t, ^3J = 6.7 Hz, 4 H, OCH_2), 6.56 (d, ^4J = 2.3 Hz, 2 H, 2-C_{Ar}H), 6.76 (dd, ^3J = 8.6, ^4J = 2.3 Hz, 2 H, 6-C_{Ar}H), 7.73 (s, 2 H, 5,6-C_{Phen}H), 8.16 (d, ^3J = 8.4 Hz, 2 H, 4,7-C_{Phen}H), 8.29 (d, ^3J = 8.4 Hz, 2 H, 3,8-C_{Phen}H), 8.35 (d, ^3J = 8.6 Hz, 2 H, 5-C_{Ar}H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.7, 25.8, 26.1, 26.2, 28.2, 28.7, 29.1, 29.4, 29.5 (d, CH_2), 68.2, 68.8 (d, OCH_2), 100.3 (d, 2-C_{Ar}), 106.5 (d, 6-C_{Ar}), 123.2 (s, 1-C_{Ar}), 124.3 (d, 3,8-C_{Phen}), 124.8 (d, 5,6-C_{Phen}), 125.5 (d, 5-C_{Ar}), 127.0 (s, 4a,6a-C_{Phen}), 133.3 (d, 4,7-C_{Phen}), 146.1 (s, 10a,10b-C_{Phen}), 156.2 (s, 2,9-C_{Phen}), 158.3 (s, 3-C_{Ar}), 161.2 (s, 4-C_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2852 (aliph. CH), 1609, 1580, 1487 (arom. C=C), 1278, 1181, 1024 (COC) cm^{-1}. MS (EI, 70 eV):

m/z (%) = 896 (28) $[M]^+$, 813 (36) $[M - C_6H_{13}]^+$, 799 (100) $[M - C_7H_{13}]^+$, 785 (97) $[M - C_8H_{15}]^+$, 771 (82) $[M - C_9H_{17}]^+$, 645 (61) $[M - C_{18}H_{35}]^+$. MS (ESI, $CHCl_3$/MeOH): *m/z* (%) = 897.6 (100) $[M + H]^+$, 883.5 (72) $[M + H - CH_2]^+$. HR-MS (ESI, $CHCl_3$/MeOH): $C_{60}H_{84}N_2O_4$ (896.64). calcd. for $C_{60}H_{84}N_2O_4 + H^+$: 897.6504; found 897.6585 (Δ = 9.0 ppm), calcd. for $C_{59}{}^{13}CH_{84}N_2O_4 + H^+$: 898.6537; found 898.6613 (Δ = 8.5 ppm).

4,15-Dioxa-1,3(1,4)-dibenzena-2(2,9)-1,10-phenanthrolina-cyclopentadecaphane (4a): Palladium on charcoal (10 mg, 10%) was suspended in acid-free ethyl acetate (2 mL) under hydrogen. 4,15-Dioxa-1,3(1,4)-dibenzena-2(2,9)-1,10-phenanthrolina-cyclopentadecaphan-7-ene (**25a**, 45 mg, 90 µmol) was dissolved in acid-free ethyl acetate (5 mL) and added to the suspension. Under hydrogen, the mixture was stirred at room temp. for 3 d before filtration through basic aluminium oxide (dichloromethane). Evaporation of the solvent in vacuo yielded colourless crystals (20 mg, 40 µmol, 44%); m.p. 234–236 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.34–1.54 (m, 12 H, CH_2), 1.84 (m_c, 4 H, $OCH_2CH_2CH_2$), 4.09 (t, ^3J = 6.6 Hz, 4 H, OCH_2), 7.09 (m_c with d, ^3J = 8.8 Hz, 4 H, 3,5-C_{Ar}H), 7.71 (s, 2 H, 5,6-C_{Phen}H), 8.03 (d, ^3J = 8.4 Hz, 2 H, 3,8-C_{Phen}H), 8.23 (d, ^3J = 8.4 Hz, 2 H, 4,7-C_{Phen}H), 8.36 (m_c, 4 H, 2,6-C_{Ar}H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.7, 27.6, 29.3 (t, CH_2), 31.6 (t, $OCH_2CH_2CH_2$), 67.4 (t, OCH_2), 114.8 (d, 3,5-C_{Ar}), 119.3 (d, 3,8-C_{Phen}), 125.5 (d, 5,6-C_{Phen}), 127.5 (s, 4a,6a-C_{Phen}), 129.0 (d, 2,6-C_{Ar}), 132.0 (s, 1-C_{Ar}), 136.6 (d, 4,7-C_{Phen}), 146.0 (s, 10a,10b-C_{Phen}), 156.5 (s, 2,9-C_{Phen}), 160.6 (s, 4-C_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 2963 (aliph. CH), 1604, 1481 (arom. C=C), 1261, 1095 (C–O–C), 802 (1,4-disubst. benzene) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 502 (100) $[M]^+$, 448 (16) $[C_{30}H_{28}N_2O_2]^+$, 364 (79) $[C_{24}H_{26}N_2O_2]^+$. MS (CI, isobutane): *m/z* (%) = 503 (100) $[M]^+$. MS (ESI, $CHCl_3$/MeOH): *m/z* (%) = 503 (100) $[M + H]^+$. HR-MS (EI, 70 eV): calcd. for $C_{34}H_{34}N_2O_2$: 502.2620; found 502.2616 (Δ = 0.9 ppm), calcd. for $C_{33}{}^{13}CH_{34}N_2O_2$: 503.2654; found 503.2653 (Δ = 0.2 ppm).

4,19-Dioxa-1,3(1,4)-dibenzena-2(2,9)-1,10-phenanthrolina-cyclononadecaphane (4b): This compound was synthesised by the procedure described above for 4,15-dioxa-1,3(1,4)-dibenzena-2(2,9)-1,10-phenanthrolina-cyclopentadecaphane (**4a**) with palladium on charcoal (10 mg, 10%) in acid-free ethyl acetate (3 mL) and 4,19-dioxa-1,3(1,4)-dibenzena-2(2,9)-1,10-phenanthrolina-cyclononadecaphan-9-ene (**25b**, 25 mg, 45 µmol) in acid-free ethyl acetate (3 mL) with stirring for 18 h to yield yellow crystals (15 mg, 27 µmol, 60%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.27–1.45 (m, 16 H, CH_2), 1.50 (m_c, 4 H, CH_2), 1.85 (m_c, 4 H, $OCH_2CH_2CH_2$), 4.15 (m_c with t, ^3J = 7.1 Hz, 4 H, OCH_2), 7.11 (m_c, 4 H, 3,5-C_{Ar}H), 7.73 (s, 2 H, 5,6-C_{Phen}H), 8.05 (d, ^3J = 8.3 Hz, 2 H, 3,8-C_{Phen}H), 8.24 (d, ^3J = 8.4 Hz, 2 H, 4,7-C_{Phen}H), 8.42 (m_c with d, ^3J = 8.8 Hz, 4 H, 2,6-C_{Ar}H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.8, 25.9, 28.5, 28.9, 29.3, 29.3, 29.7 (t, CH_2), 30.1 (t, $OCH_2CH_2CH_2$), 68.3 (t, OCH_2), 115.2 (d, 3,5-C_{Ar}), 119.3 (d, 3,8-C_{Phen}), 125.5 (d, 5,6-C_{Phen}), 127.4 (s, 4a,6a-C_{Phen}), 129.2 (d, 2,6-C_{Ar}), 130.4 (s, 1-C_{Ar}), 136.6 (d, 4,7-C_{Phen}), 146.1 (s, 10a,10b-C_{Phen}), 156.4 (s, 2,9-C_{Phen}), 160.3 (s, 4-C_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 2924 (aliph. CH), 1605, 1488 (arom. C=C), 1249, 1173 (C–O–C), 835 (1,4-disubst. benzene) cm^{-1}. MS (ESI, $CHCl_3$/MeOH): *m/z* (%) = 559 (75) $[M + H]^+$. MS (EI, 70 eV): *m/z* (%) = 558 (58) $[M]^+$, 364 (100) $[C_{24}H_{14}N_2O_2]^+$. HR-MS (EI, 70 eV): calcd. for $C_{38}H_{42}N_2O_2$: 558.3247; found 558.3246 (Δ = 0.1 ppm), calcd. for $C_{37}{}^{13}CH_{42}N_2O_2$: 559.3280; found 559.3229 (Δ = 9.2 ppm).

4,23-Dioxa-1,3(1,4)-dibenzena-2(2,9)-1,10-phenanthrolina-cyclotricosaphane (4c): This compound was synthesised by the procedure described above for 4,15-dioxa-1,3(1,4)-dibenzena-2(2,9)-1,10-phenanthrolina-cyclopentadecaphane (**4a**) with palladium on charcoal (6 mg, 10%) in acid-free ethyl acetate (2 mL) and 4,23-dioxa-1,3(1,4)-dibenzena-2(2,9)-1,10-phenanthrolina-cyclotricosaphan-11-ene (**25c**, 35 mg, 57 µmol) in acid-free ethyl acetate (3 mL) with stirring for 16 h to yield yellow crystals (20 mg, 33 µmol, 58%). ^{1}H NMR (100 MHz, $CDCl_3$): δ = 1.24–1.43 (m, 24 H, CH_2), 1.52 (m_c, 4 H, $OCH_2CH_2CH_2$), 1.86 (m_c, 4 H, OCH_2CH_2), 4.08 (t, ^3J = 6.6 Hz, 4 H, OCH_2), 7.11 (m_c with d, ^3J = 8.8 Hz, 4 H, 3,5-C_{Ar}H), 7.71 (s, 2 H, 5,6-C_{Phen}H), 8.06 (d, ^3J = 8.4 Hz, 2 H, 3,8-C_{Phen}H), 8.2 (d, ^3J = 8.4 Hz, 2 H, 4,7-C_{Phen}H), 8.43 (m_c with d, ^3J = 8.9 Hz, 4 H, 2,6-C_{Ar}H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.9, 26.1, 29.1, 29.2, 29.50, 29.55, 29.6 (t, CH_2), 29.8 (t, $OCH_2CH_2CH_2$), 68.2 (t, OCH_2), 114.8 (d, 3,5-C_{Ar}), 119.2 (d, 3,8-C_{Phen}), 125.5 (d, 5,6-C_{Phen}), 127.5 (s, 4a,6a-C_{Phen}), 129.0 (d, 2,6-C_{Ar}), 132.0 (s, 1-C_{Ar}), 136.7 (d, 4,7-C_{Phen}), 146.1 (s, 10a,10b-C_{Phen}), 156.4 (s, 2,9-C_{Phen}), 160.6 (s, 4-C_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 2928 (aliph. CH), 1607, 1583, 1491 (arom. C=C), 1250, 1024 (C–O–C), 833 (1,4-disubst. benzene) cm^{-1}. MS (ESI, $CHCl_3$/MeOH): *m/z* (%) = 615 (100) $[M + H]^+$. MS (EI, 70 eV): *m/z* (%) = 614 (71) $[M]^+$, 364 (100) $[C_{24}H_{16}N_2O_2]^+$. HR-MS (EI, 70 eV): calcd. for $C_{42}H_{50}N_2O_2$: 614.3872; found 614.3867 (Δ = 0.8 ppm), calcd. for $C_{41}{}^{13}CH_{50}N_2O_2$: 615.3906; found 615.3903 (Δ = 0.4 ppm).

4-Iodoresorcinol (14b): This compound was synthesised by a literature procedure[24] from iodine monochloride (8.00 g, 50.0 mmol) and resorcinol (**13**, 5.50 g, 50.0 mmol) in dry diethyl ether (50 mL) to yield colourless crystals (4.71 g, 19.9 mmol, 40%), ref.[24] 70%; m.p. 67–71 °C, ref.[25] 67–70 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.94 (br s, 1 H, 1-C_{Ar}OH), 5.26 (br s, 1 H, 3-C_{Ar}OH), 6.27 (dd, ^3J = 8.6, ^4J = 2.7 Hz, 1 H, 6-C_{Ar}H), 6.54 (d, ^4J = 2.9 Hz, 1 H, 2-C_{Ar}H), 7.46 (d, ^3J = 8.6 Hz, 1 H, 5-C_{Ar}H) ppm. MS (EI, 70 eV): *m/z* (%) = 236 (100) $[M]^+$, 109 (12) $[M - I]^+$. MS (CI, isobutane): *m/z* (%) = 237 (100) $[M + H]^+$, 236 (83) $[M]^+$, 110 (16) $[M - I]^+$.

1-Iodohex-5-ene (15b): This compound was synthesised by a literature procedure[26] from hex-5-en-1-ol (**15e**, 7.10 mL, 5.95 g, 59.2 mmol) with triphenylphosphane (21.7 g, 83.0 mmol), imidazole (5.65 g, 83.0 mmol), and iodine (21.0 g, 83.0 mmol) in dry dichloromethane (180 mL) to yield a colourless liquid (11.4 g, 54.5 mmol, 92%), ref.[26] 90%. n_D^{20} = 1.5105, ref.[26] 1.5106. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.52 (m_c, 2 H, CH_2CH_2CH=), 1.84 [m_c, 2 H, $CH_2(CH_2)_2I$], 2.08 (dtt, ^3J_t = 7.3, ^3J_d = 6.8, ^4J_t = 1.4 Hz, 2 H, CH_2CH=), 3.20 (t, ^3J = 7.0 Hz, 2 H, CH_2I), 4.97 (ddt, ^3J_d = 10.0, ^2J_d = 2.0, ^4J_t = 1.2 Hz, 1 H, CH=CHH_{cis}), 5.02 (ddt, ^3J_d = 17.0, ^2J_d = 2.0, ^4J_t = 1.5 Hz, 1 H, CH=CHH_{trans}), 5.79 (ddt, ^3J_t = 17.0, ^3J_t = 10.2, ^3J_t = 6.7 Hz, 1 H, =CH) ppm.

1-Iododec-9-ene (15c): This compound was synthesised by the literature procedure for 1-iodohex-5-ene[26] with triphenylphosphane (21.7 g, 83.0 mmol) and imidazole (5.65 g, 83 mmol) in dry dichloromethane (180 mL), with iodine (21.0 g, 83.0 mmol), dec-9-en-1-ol (**15d**, 10.5 mL, 9.24 g, 59.2 mmol) and sodium thiosulfate pentahydrate (18.5 g, 74.7 mmol). After workup as described for 1-iodohex-5-ene (**15b**, see above), the solvent was evaporated in vacuo and the residue was dissolved in dichloromethane (ca. 5 mL). After addition of petroleum ether (b.p. 30–60 °C, ca. 200 mL) the mixture was filtered through silica gel and the solvent was evaporated to yield a colourless liquid (10.9 g, 40.9 mmol, 69%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.24–1.42 (m, 10 H, CH_2), 1.82 (m_c, 2 H, CH_2CH_2I), 2.04 (m_c, 2 H, CH_2CH=), 3.19 (t, ^3J = 7.0 Hz, 2 H, ICH_2), 4.93 (ddt, ^3J_d = 10.2, ^2J_d = 2.2, ^4J_t = 1.2 Hz, 1 H, CH=CHH_{cis}), 5.00 (ddt, ^3J_d = 17.1, ^2J_d = 2.2, ^4J_t = 1.6 Hz, 1 H, CH=CHH_{trans}), 5.81 (ddt, ^3J_t = 17.1, ^3J_t = 10.2, ^3J_t = 6.7 Hz, 1 H, =CH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 7.3, 28.5, 28.8, 29.0, 29.3, 30.5, 33.6, 33.8 (t, CH_2), 114.2 (t, CH_2=), 139.1 (d, CH=) ppm. IR (neat): $\tilde{\nu}$ = 2925, 2852 (aliph. CH), 1640 (C=C),

1460 (arom. C=C), 994, 909 (monosubst. alkene), 599 (I–C) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 266 (100) $[M]^+$. MS (CI, isobutane): *m/z* (%) = 267 (50) $[M + H]^+$, 139 (23) $[M – I]^+$, 111 (80) $[C_8H_{15}]^+$, 99 (100) $[C_7H_{15}]^+$. HR-MS (EI, 70 eV): calcd. for $C_{10}H_{19}I$: 266.0532; found 266.0532 (Δ = 0.3 ppm), calcd. for $C_9{}^{13}CH_{19}I$: 267.0565; found 267.0536 (Δ = 10.9 ppm). $C_{10}H_{19}I$ (266.05): calcd. C 45.13, H 7.20; found C 44.83, H 7.26.

2,4-Bis(hex-5-enyloxy)-1-iodobenzene (16a). Method A: 4-Iodoresorcinol (**14b**, 1.69 g, 7.17 mmol) was dissolved in dry *N*,*N*-dimethylformamide (24 mL) and, after addition of potassium carbonate (5.96 g, 43.0 mmol), potassium iodide (480 mg, 2.90 mmol) and 6-bromohex-1-ene (**15a**, 2.44 mL, 2.92 g, 17.9 mmol), was stirred at 60 °C under nitrogen for 18 h. The solvent was evaporated in vacuo, and the residue was dissolved in sodium hydroxide solution (2 N) and diethyl ether (25 mL each). After separation of the layers, the water layer was extracted with diethyl ether (3 × 20 mL). The combined organic layer was washed with sodium hydroxide solution (2 N, 3 × 20 mL) and brine (20 mL). After drying with magnesium sulfate, the solvent was evaporated in vacuo and the crude product was purified by column chromatography (silica, cyclohexane/ethyl acetate, 15:1, R_f = 0.74) to yield a colourless liquid (2.11 g, 5.40 mmol, 75%).

Method B: 4-Iodoresorcinol (**14b**, 490 mg, 2.08 mmol) was dissolved in dry *N*,*N*-dimethylformamide (7 mL). After addition of potassium carbonate (1.72 g, 12.4 mmol) and 6-iodohex-1-ene (**15b**, 1.08 g, 5.18 mmol), the suspension was stirred at 60 °C under nitrogen for 18 h. After evaporation of the solvent in vacuo, the residue was dissolved in diethyl ether and sodium hydroxide solution (2 N, 20 mL each). The layers were separated and the water layer was extracted with diethyl ether (3 × 15 mL). The combined organic layer was washed with sodium hydroxide solution (2 N, 3 × 15 mL) and brine (15 mL) and dried with magnesium sulfate. After evaporation of the solvent in vacuo, the crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 12:1, R_f = 0.71) to yield a colourless liquid (539 mg, 1.35 mmol, 65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.56 (quin, ^3J = 7.5 Hz, 2 H, CH_2CH$_2$CH=), 1.63 (quin, ^3J = 7.5 Hz, 2 H, CH_2CH$_2$CH=), 1.78 (quin, $^3J \approx 7$ Hz, 2 H, CH_2CH$_2$O), 1.84 (quin, $^3J \approx 7$ Hz, 2 H, CH_2CH$_2$O), 2.12 (dtt, $^3J_{d,t} \approx 7$, ^4J_t = 1.3 Hz, 2 H, CH_2CH=), 2.15 (dtt, $^3J_{d,t} \approx 7$, ^4J_t = 1.3 Hz, 2 H, CH_2CH=), 3.93 (t, ^3J = 6.4 Hz, 2 H, OCH$_2$), 3.98 (t, ^3J = 6.4 Hz, 2 H, OCH$_2$), 4.98 (ddt, ^3J_d = 10.3, ^2J_d = 1.8, ^4J_t = 1.1 Hz, 2 H, =CHH_{cis}), 5.04 (ddt, ^3J_d = 17.2, ^2J_d = 2.0, ^4J_t = 1.6 Hz, 2 H, =CHH_{trans}), 5.83 (ddt, ^3J_d = 17.0, ^3J_d = 10.2, ^3J_t = 6.6 Hz, 2 H, =CH), 6.29 (dd, ^3J = 8.6, ^4J = 2.7 Hz, 1 H, 5-C_{Ar}H), 6.39 (d, ^4J = 2.7 Hz, 1 H, 3-C_{Ar}H), 7.59 (d, ^3J = 8.6 Hz, 1 H, 6-C_{Ar}H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.3, 25.4 (t, *C*H$_2$CH$_2$CH=), 28.5, 28.7 (t, OCH$_2$*C*H$_2$), 33.3, 33.4 (t, *C*H$_2$CH=), 68.0 (t, 4-C_{Ar}O*C*H$_2$), 68.9 (t, 2-C_{Ar}O*C*H$_2$), 75.3 (s, 1-C_{Ar}), 100.6 (d, 3-C_{Ar}), 107.6 (d, 5-C_{Ar}), 114.7, 114.8 (t, =CH$_2$), 138.4, 138.6 (d, =CH), 139.0 (d, 6-C_{Ar}), 158.3 (s, 4-C_{Ar}), 160.8 (s, 2-C_{Ar}) ppm. IR (neat): $\tilde{\nu}$ = 3074 (arom. CH), 2935, 2869 (aliph. CH), 1639 (C=C), 1589, 1465, (arom. C=C), 1256, 1184 (COC) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 400 (34) $[M]^+$, 273 (15) $[M – I]^+$, 236 (100) $[C_6H_5IO_2]^+$, 110 (40) $[C_6H_6O_2]^+$. MS (CI, isobutane): *m/z* (%) = 401 (100) $[M + H]^+$, 330 (25), 316 (25), 274 (19) $[M + H – I]^+$, 83 (20) $[C_6H_{11}]^+$. $C_{18}H_{25}IO_2$ (400.09): calcd. C 54.01, H 6.29. $C_{18}H_{25}IO_2 \cdot 0.15\,C_6H_{12}$ (400.09 + 12.62): calcd. C 54.97, H 6.54; found C 55.10, H 6.54.

2,4-Bis(dec-9-enyloxy)-1-iodobenzene (16b). Method A: 4-Iodoresorcinol (**14b**, 751 mg, 13.2 mmol) was dissolved in dry *N*,*N*-dimethylformamide (15 mL). After addition of potassium carbonate (2.64 g, 19.0 mmol) and 10-iododec-1-ene (**15c**, 2.11 g, 7.93 mmol), the suspension was heated to 70 °C under nitrogen for 16 h. After the system had cooled to room temp., sodium hydroxide solution (2 N) and diethyl ether (25 mL each) were added and the layers were separated. The water layer was extracted with diethyl ether (3 × 20 mL). The combined organic layer was washed twice with sodium hydroxide solution (2 N) and brine (20 mL each) and dried with magnesium sulfate. The solvent was evaporated and the crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 9:1, R_f = 0.67) to yield 1.16 g of a colourless liquid (2.27 mmol, 71%).

Method B: 4-Iodoresorcinol (**14b**, 1.50 g, 6.36 mmol), triphenylphosphane (3.34 g, 12.7 mmol), and dec-9-en-1-ol (**15d**, 3.53 mL, 2.99 g, 19.1 mmol) were dissolved in dry tetrahydrofuran (35 mL) and cooled to 0 °C. Under nitrogen, diisopropyl azodicarboxylate (DIAD, 3.74 mL, 19.1 mmol) was slowly added and the solution was afterwards stirred at room temp. for 18 h. The reaction mixture was hydrolysed with water (20 mL) and sodium hydroxide solution (2 N, 4.7 mL). After the system had been stirred for 30 min and the layers separated, the water layer was extracted with diethyl ether (3 × 20 mL). The combined organic layer was washed once with brine (20 mL) and dried with magnesium sulfate. The solvent was evaporated and the crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 9:1, $R_f \approx 0.70$) to yield a colourless liquid (705 mg, 1.38 mmol, 22%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.29–1.41 (m, 12 H, CH$_2$), 1.41–1.47 (m, 2 H, CH$_2$), 1.51 (m_c, 2 H, CH$_2$), 1.76 (m_c, 2 H, OCH$_2$CH_2), 1.82 (m_c, 2 H, OCH$_2$CH_2), 2.04 (m_c, 4 H, CH_2CH=), 3.91 (t, ^3J = 6.6 Hz, 2 H, OCH$_2$), 3.96 (t, ^3J = 6.5 Hz, 2 H, OCH$_2$), 4.93 (ddt, ^3J_d = 10.2, ^2J_d = 2.0, ^4J_t = 1.2 Hz, 2 H, CH=CHH_{cis}), 4.99 (ddt, ^3J_d = 17.1, ^2J_d = 1.9, ^4J_t = 1.6 Hz, 2 H, CH=CHH_{trans}), 5.81 (ddt, ^3J_t = 17.0, ^3J_t = 10.2, ^3J_t = 6.7 Hz, 2 H, =CH), 6.28 (dd, ^3J = 8.6, ^4J = 2.6 Hz, 1 H, 5-C_{Ar}H), 6.39 (d, ^4J = 2.6 Hz, 1 H, 3-C_{Ar}H), 7.58 (d, ^3J = 8.6 Hz, 1 H, 6-C_{Ar}H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 26.0, 28.9, 29.1, 29.2, 29.3, 29.4 (t, CH$_2$), 33.8 (t, *C*H$_2$CH=), 68.3 (t, 4-C_{Ar}O*C*H$_2$), 69.2 (t, 2-C_{Ar}O*C*H$_2$), 75.4 (s, 1-C_{Ar}), 100.7 (d, 3-C_{Ar}), 107.7 (d, 5-C_{Ar}), 114.2 (t, =CH$_2$), 139.0 (d, =CH), 139.2 (d, 6-C_{Ar}), 158.5 (s, 2-C_{Ar}), 160.9 (s, 4-C_{Ar}) ppm. IR (neat): $\tilde{\nu}$ = 3074 (arom. CH), 2936 (aliph. CH), 1576, 1464 (arom. C=C), 1302, 1186, 1041 (COC) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 512 (62) $[M]^+$, 385 (8) $[M – I]^+$, 236 (100) $[C_6H_5IO_2]^+$. MS (CI, isobutane): *m/z* (%) = 513 (100) $[M + H]^+$, 386 (41) $[M + H – I]^+$. HR-MS (EI, 70 eV): calcd. for $C_{26}H_{41}IO_2$: 512.2152; found 512.2109 (Δ = 8.4 ppm), calcd. for $C_{25}{}^{13}CH_{41}IO_2$: 513.2185; found 513.2183 (Δ = 0.5 ppm). $C_{26}H_{41}IO_2$ (512.22): calcd. C 60.93, H 8.06. $C_{26}H_{41}IO_2 \cdot 0.7\,CH_2Cl_2$ (512.22 + 67.84): calcd. C 56.07, H 7.47; found C 56.17, H 7.68.

1-Bromo-2,4-bis(dec-9-enyloxy)benzene (16c). Method A: 4-Bromoresorcinol (**14a**, 1.84 g, 9.75 mmol) was dissolved in dry *N*,*N*-dimethylformamide (40 mL). Addition of 10-iododec-1-ene (**15c**, 6.44 g, 24.2 mmol) and potassium carbonate (8.07 g, 58.1 mmol) was followed by stirring at 60 °C under nitrogen for 16 h. After the system had cooled to room temp., the residue was dissolved in sodium hydroxide solution (2 N) and diethyl ether (25 mL each). The layers were separated and the water layer was extracted with diethyl ether (3 × 20 mL). The combined organic layer was washed with sodium hydroxide solution (2 N, 2 × 20 mL) and brine (20 mL) and dried with magnesium sulfate. After evaporation of the solvent in vacuo, the crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 9:1, $R_f \approx 0.80$) to yield a colourless liquid (4.49 g, 9.68 mmol, 98%).

Method B: 4-Bromoresorcinol (**14a**, 1.80 g, 9.54 mmol), dec-9-en-1-ol (**15d**, 5.29 mL, 4.48 g, 28.6 mmol), and triphenylphosphane

(5.01 g, 19.1 mmol) were dissolved in dry tetrahydrofuran (50 mL) and cooled to 0 °C under nitrogen. Diisopropyl azodicarboxylate (5.61 mL, 28.6 mmol) was added by syringe and the mixture was stirred at room temp. for 18 h. After hydrolysis with water (30 mL) and sodium hydroxide solution (2 N, 7.0 mL) and stirring for 30 min, the layers were separated and the water layer was extracted with diethyl ether (3 × 25 mL). The combined organic layer was washed with brine (25 mL) and dried with magnesium sulfate. After evaporation of the solvent in vacuo, the crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 9:1, $R_f \approx 0.80$) to yield a colourless liquid (3.35 g, 7.22 mmol, 76%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.29–1.52 (m, 20 H, CH_2), 1.76 (m_c, 2 H, OCH_2CH_2), 1.82 (m_c, 2 H, OCH_2CH_2), 2.04 (m_c, 4 H, CH_2CH=), 3.91 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 3.98 (t, ^3J = 6.5 Hz, 2 H, OCH_2), 4.93 (ddt, ^3J_d = 10.2, ^2J_d = 2.1, ^4J_t = 1.3 Hz, 2 H, CH=CHH_{cis}), 4.99 (ddt, ^3J_d = 17.1, ^2J_d = 2.1, ^4J_t = 1.6 Hz, 2 H, CH=CHH_{trans}), 5.81 (ddt, ^3J_t = 17.0, ^3J_t = 10.2, ^3J_t = 6.7 Hz, 2 H, =CH), 6.36 (dd, ^3J = 8.7, ^4J = 2.7 Hz, 1 H, 5-C_{Ar}H), 6.46 (d, ^4J = 2.7 Hz, 1 H, 3-C_{Ar}H), 7.37 (d, ^3J = 8.7 Hz, 1 H, 6-C_{Ar}H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 26.0 (2 × t, CH_2), 28.9 (2 × t, CH_2), 29.1, 29.3 (2 × t, CH_2), 29.4 (2 × t, CH_2), 33.8 (2 × t, CH_2CH=), 68.4 (t, 4-$C_{Ar}OCH_2$), 69.2 (t, 2-$C_{Ar}OCH_2$), 101.6 (d, 3-C_{Ar}), 102.9 (s, 4-C_{Ar}), 106.6 (d, 5-C_{Ar}), 114.2 (2 × t, =CH_2), 133.0 (d, =CH), 139.2 (d, 6-C_{Ar}), 156.2 (s, 2-C_{Ar}), 159.7 (s, 1-C_{Ar}) ppm. IR (neat): $\tilde{\nu}$ = 3075 (arom. CH), 2925 (aliph. CH), 1595, 1466 (arom. C=C), 1306, 1187 (COC) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 466, 464 (64, 61) $[M]^+$, 328, 326 (10, 11) $[M - C_{10}H_{18}]^+$, 190, 188 (100, 100) $[C_6H_5BrO_2]^+$. MS (CI, isobutane): *m*/*z* (%) = 467, 465 (100, 99) $[M + H]^+$, 329, 327 (11, 11) $[M - C_{10}H_{18}]^+$, 190, 188 (51, 55) $[C_6H_5BrO_2]^+$. $C_{26}H_{41}BrO_2$ (464.23): calcd. C 67.08, H 8.88. $C_{26}H_{41}BrO_2 \cdot 0.1\,C_6H_{12}$ (464.23 + 8.41): calcd. C 67.41, H 8.98; found C 67.45, H 9.06.

2,4-Bis(hex-5-enyloxy)phenylboronic Acid (17a): 2,4-Bis(hex-5-enyloxy)-1-iodobenzene (**16a**, 200 mg, 500 μmol) was dissolved in dry tetrahydrofuran (10 mL) and cooled to –78 °C before addition of *n*-butyllithium (0.22 mL, 0.55 mmol, 2.6 M in hexanes) and stirring at –78 °C for 1 h. After addition of trimethyl borate (0.18 mL, 1.7 mmol), the solution was stirred for 2 h and warmed to room temp. The reaction was hydrolysed with water (20 mL). The layers were separated and the water layer was extracted with diethyl ether (3 × 20 mL). The combined organic layer was washed once with brine (20 mL) and dried with magnesium sulfate. The solvent was evaporated to yield a colourless liquid (153 mg) as crude product. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.58 (m_c, 4 H, CH_2CH_2CH=), 1.72–1.87 (m, 4 H, CH_2CH_2O), 2.13 (m_c, 4 H, CH_2CH=), 3.95 (t, ^3J = 6.4 Hz, 4 H, OCH_2), 4.96 (ddt, $^3J_d \approx 10.2$, ^2J_d = 2.0, ^4J_t = 1.2 Hz, 2 H, =CHH_{cis}), 5.03 (ddt, $^3J_d \approx 17$, ^4J_d = 2.0, ^2J_t = 1.6 Hz, 2 H, =CHH_{trans}), 5.83 (ddt, ^3J_d = 17.1, ^3J_d = 10.2, ^3J_t = 6.6 Hz, 2 H, CH=), 6.44 (d, ^4J = 2.1 Hz, 1 H, 3-C_{Ar}H), 6.46 (br s, 2 H, OH), 6.51 (dd, ^3J = 8.3, ^4J = 2.1 Hz, 2 H, 5-C_{Ar}H), 7.55 (t, ^3J = 8.1 Hz, 6-C_{Ar}H) ppm. IR (neat): $\tilde{\nu}$ = 3384 (OH), 2926 (aliph. CH), 1605, 1434 (arom. C=C), 1261, 1098 (COC) cm^{-1}. MS (ESI, CH_2Cl_2/MeOH): *m*/*z* = 369 (100) [M as dimethyl borate + Na]$^+$. An attempt to purify phenylboronic acid **17a** by column chromatography (silica gel, cyclohexane/ethyl acetate, 6:1, R_f = 0.57) resulted only in a colourless liquid [1,3-bis(hex-5-enyloxy)benzene]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.56 (quin, ^3J = 7.2 Hz, 4 H, CH_2CH_2CH=), 1.78 (quin, $^3J \approx 7$ Hz, 4 H, CH_2CH_2O), 2.12 (dtt, $^3J_{d,t} \approx 7$, ^4J_t = 1.3 Hz, 4 H, CH_2CH=), 3.94 (t, ^3J = 6.6 Hz, 4 H, OCH_2), 4.97 (ddt, ^3J_d = 10.2, ^2J_d = 2.0, ^4J_t = 1.3 Hz, 2 H, =CHH_{cis}), 5.03 (ddt, ^3J_d = 17.2, ^2J_d = 2.0, ^4J_t = 1.6 Hz, 2 H, =CHH_{trans}), 5.83 (ddt, ^3J_d = 17.1, ^3J_d = 10.2, ^3J_t = 6.6 Hz, 2 H, =CH), 6.46 (d, ^4J = 2.2 Hz, 1 H, 2-C_{Ar}H), 6.47 (dd, ^3J = 8.1, ^4J = 2.2 Hz, 2 H, 4,6-C_{Ar}H), 7.15 (t, ^3J = 8.0 Hz, 1 H, 5-C_{Ar}H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25 (t, CH_2CH_2CH=), 29 (t, OCH_2CH_2), 33 (t, CH_2CH=), 68 (t, OCH_2), 102 (d, 2-C_{Ar}), 107 (d, 4,6-C_{Ar}), 115 (t, =CH_2), 130 (d, 5-C_{Ar}), 139 (d, =CH), 160 (s, 1,3-C_{Ar}) ppm. IR (neat): $\tilde{\nu}$ = 3075 (arom. CH), 2937, 2868 (aliph. CH), 1640 (C=C), 1589, 1469, (arom. C=C), 1263, 1182 (COC) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 275 (6) $[M + H]^+$, 274 (28) $[M]^+$, 193 (16) $[C_{12}H_{16}O_2 + H]^+$, 110 (100) $[C_6H_6O_2]^+$. MS (CI, isobutane): *m*/*z* (%) = 275 (100) $[M + H]^+$, 274 (12) $[M]^+$. $C_{18}H_{26}O_2$ (274.19): calcd. C 78.79, H 9.55. $C_{18}H_{26}O_2 \cdot 0.2\,CH_2Cl_2$ (274.19 + 19.38): calcd. C 74.14, H 9.04; found C 73.99, H 9.28.

2,4-Bis(dec-9-enyloxy)phenylboronic Acid (17b). Method A: 2,4-Bis(dec-9-enyloxy)-1-iodobenzene (**16b**, 600 mg, 1.17 mmol) was dissolved in dry tetrahydrofuran (10 mL) and cooled to –78 °C under nitrogen. After addition of *n*-butyllithium (0.54 mL, 1.34 mmol, 2.5 M in hexanes) and stirring at –78 °C for 1 h, trimethyl borate (0.41 mL, 4.2 mmol) was added. The solution was warmed to room temp. during 2 h before hydrolysis was carried out with water (20 mL). After separation of the layers, the water layer was extracted with diethyl ether (3 × 20 mL). The combined organic layer was washed with brine (20 mL) and dried with magnesium sulfate. Evaporation of the solvents in vacuo yielded the yellow crystalline crude product (514 mg).

Method B: 1-Bromo-2,4-bis(dec-9-enyloxy)benzene (**16c**, 3.01 g, 6.50 mmol) was dissolved under nitrogen in dry tetrahydrofuran (55 mL) and cooled to –78 °C. Addition of *n*-butyllithium (3.0 mL, 7.4 mmol, 2.5 M in hexanes) was followed by stirring at –78 °C for 1 h. Trimethyl borate (2.28 mL, 23.0 mmol) was added and the solution was warmed to room temp. while stirring for 2 h. After addition of water (20 mL) and separation of the layers, the water layer was extracted with diethyl ether (3 × 25 mL). The combined organic layer was washed with brine (30 mL) and dried with magnesium sulfate. Evaporation of the solvent in vacuo yielded the colourless crystalline crude product (2.93 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22–1.50 (m, 20 H, CH_2), 1.71–1.90 (m, 4 H, OCH_2CH_2), 2.04 (m_c, 4 H, CH_2CH=), 3.97 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 4.02 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 4.93 (ddt, ^3J_d = 10.2, ^2J_d = 2.0, ^4J_t = 1.2 Hz, 2 H, CH=CHH_{cis}), 4.99 (ddt, ^3J_d = 17.1, ^2J_d = 2.1, ^4J_t = 1.6 Hz, 2 H, CH=CHH_{trans}), 5.81 (ddt, ^3J_d = 17.1, ^3J_d = 10.3, ^3J_t = 6.7 Hz, 2 H, =CH), 5.90 [s, 2 H, $B(OH)_2$], 6.43 (d, ^4J = 2.1 Hz, 1 H, 3-C_{Ar}H), 6.53 (dd, ^3J = 8.3, ^4J = 2.1 Hz, 1 H, 5-C_{Ar}H), 7.74 (d, ^3J = 8.3 Hz, 1 H, 6-C_{Ar}H) ppm. IR (KBr): $\tilde{\nu}$ = 3414 (OH), 2926 (aliph. CH), 1605, 1432 (arom. C=C), 1260, 1178, 1019 (COC) cm^{-1}.

1-Bromo-4-(hex-5-enyloxy)benzene (19a): 4-Bromophenol (**18**, 2.00 g, 11.6 mmol) was dissolved in dry tetrahydrofuran (60 mL). After addition of hex-5-en-1-ol (**15e**, 2.07 mL, 17.4 mmol) and triphenylphosphane (3.05 g, 11.6 mmol), the solution was cooled to 0 °C under nitrogen, diisopropyl azodicarboxylate (DIAD, 3.41 mL, 17.4 mmol) was added dropwise, and the solution was stirred at room temp. for 18 h. The reaction mixture was hydrolysed with water (36 mL) and sodium hydroxide solution (2 N, 8.5 mL) before separation of the layers. The water layer was extracted with diethyl ether (3 × 15 mL). The combined organic layer was washed with brine (15 mL) and dried with magnesium sulfate. The solvent was evaporated in vacuo, after which the residue was dissolved in dichloromethane (15 mL), and cyclohexane (ca. 300 mL) was added to precipitate the phosphane oxide. The precipitate was filtered off and the solvent was evaporated in vacuo. The liquid crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 6:1, R_f = 0.73) to yield a colourless liquid (2.81 g, 11.0 mmol, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50–

1.61 (m, 2 H, $OCH_2CH_2CH_2$), 1.78 (m_c, 2 H, OCH_2CH_2), 2.13 (m_c, 2 H, $=CHCH_2$), 3.91 (t, ^3J = 6.5 Hz, 2 H, OCH_2), 4.97 (ddt, ^3J_d = 10.2, ^2J_d = 2.1, ^4J_t = 1.2 Hz, 1 H, $CH=CH_{cis}$), 5.03 (ddt, ^3J_d = 17.1, ^2J_d = 2.0, ^4J_t = 1.6 Hz, 1 H, $CH=CH_{trans}$), 5.82 (ddt, ^3J_d = 17.0, ^3J_d = 10.3, ^3J_t = 6.7 Hz, 1 H, $CH=CH_2$), 6.76 (m_c with d, ^3J_d = 9.1 Hz, 2 H, 3,5-C_{Ar}H), 7.35 (m_c with d, ^3J_d = 9.1 Hz, 2 H, 2,6-C_{Ar}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, $CH_2CH=$), 68.0 (t, OCH_2), 112.6 (s, 1-C_{Ar}), 114.8 (t, $=CH_2$), 116.2 (d, 3,5-C_{Ar}), 132.2 (d, 2,6-C_{Ar}), 138.4 (d, $CH=CH_2$), 158.2 (s, 4-C_{Ar}) ppm. IR (neat): $\tilde{\nu}$ = 2933 (aliph. CH), 1594, 1489 (arom. C=C), 1243 (Ar–O–C) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 256, 254 (18, 19) $[M]^+$, 174, 172 (88, 100) $[C_6H_5BrO]^+$. MS (CI, isobutane): *m*/*z* = 257, 255 (94, 100) $[M + H]^+$, 256, 254 (35, 30) $[M]^+$, 174, 172 (30, 34) $[C_6H_5BrO]^+$. $C_{12}H_{15}BrO$ (254.03): calcd. C 56.49, H 5.93; found C 56.40, H 5.99.

1-Bromo-4-(oct-7-enyloxy)benzene (19b): This compound was synthesised by the procedure used for 1-bromo-4-(hex-5-enyloxy)benzene (**19a**), with 4-bromophenol (**18**, 1.00 g, 5.80 mmol), oct-7-en-1-ol (**15f**, 1.11 g, 8.70 mmol), triphenylphosphane (1.53 g, 5.80 mmol), and diisopropyl azodicarboxylate (DIAD, 1.71 mL, 8.70 mmol) in dry tetrahydrofuran (30 mL). The crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 6:1, $R_f \approx 0.70$) to yield a colourless liquid (1.43 g, 5.05 mmol, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32–1.51 [m, 6 H, $OCH_2CH_2(CH_2)_3$], 1.77 (m_c, 2 H, OCH_2CH_2), 2.06 (m_c, 2 H, $=CHCH_2$), 3.91 (t, ^3J = 6.5 Hz, 2 H, OCH_2), 4.94 (ddt, ^3J_d = 10.2, ^2J_d = 2.2, ^4J_t = 1.2 Hz, 1 H, $CH=CH_{cis}$), 4.99 (ddt, ^3J_d = 17.1, ^2J_d = 2.1, ^4J_t = 1.6 Hz, 1 H, $CH=CH_{trans}$), 5.81 (ddt, ^3J_d = 17.1, ^3J_d = 10.2, ^3J_t = 6.7 Hz, 1 H, $CH=CH_2$), 6.77 (m_c with d, ^3J_d = 9.0 Hz, 2 H, 3,5-CH), 7.35 (m_c with d, ^3J_d = 9.1 Hz, 2 H, 2,6-CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.9, 28.8, 29.0, 29.1, 29.2, 29.5 (t, CH_2), 33.7 (t, $CH_2CH=$), 68.3 (t, OCH_2), 112.6 (s, 1-C_{Ar}), 114.3 (t, $=CH_2$), 116.4 (d, 3,5-C_{Ar}), 132.2 (d, 2,6-C_{Ar}), 139.0 (d, $CH=CH_2$), 158.3 (s, 4-C_{Ar}) ppm. IR (neat): $\tilde{\nu}$ = 2926 (aliph. CH), 1590, 1489 (arom. C=C), 1244 (C–O–C), 821 (1,4-disubst. benzene) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 284, 282 (100, 88) $[M]^+$, 174, 172 (62, 52) $[C_6H_5BrO]^+$. MS (CI, isobutane): *m*/*z* (%) = 285, 283 (60, 58) $[M + H]^+$, 174, 172 (14, 14) $[C_6H_5BrO]^+$, 111 (100) $[C_8H_{15}]^+$. HR-MS (EI, 70 eV): calcd. for $C_{14}H_{19}{}^{79}BrO$: 282.0619; found 282.0619 (Δ = 0 ppm), calcd. for $C_{13}{}^{13}CH_{19}{}^{79}BrO$: 283.0653; found 283.0653 (Δ = 0.2 ppm), calcd. for $C_{14}H_{19}{}^{81}BrO$: 284.0599; found 284.0600 (Δ = 0.4 ppm), calcd. for $C_{13}{}^{13}CH_{19}{}^{81}BrO$: 285.0632; found 285.0631 (Δ = 0.5 ppm). $C_{14}H_{19}BrO$ (282.06): calcd. C 59.37, H 7.20. $C_{14}H_{19}BrO{\cdot}0.3\,C_6H_{12}$ (282.06 + 25.23): calcd. C 61.52, H 7.39; found C 61.18, H 7.55.

1-Bromo-4-(dec-9-enyloxy)benzene (19c): This compound was synthesised by the procedure described for 1-bromo-4-(hex-5-enyloxy)-benzene (**19a**), with 4-bromophenol (**18**, 3.00 g, 17.4 mmol), dec-9-en-1-ol (**15d**, 4.83 mL, 4.08 g, 26.1 mmol), triphenylphosphane (4.59 g, 17.4 mmol) and diisopropyl azodicarboxylate (DIAD, 5.13 mL, 26.1 mmol) in dry tetrahydrofuran (60 mL). The crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 6:1, $R_f \approx 0.80$) to yield a colourless liquid (4.27 g, 13.7 mmol, 79%); m.p. <18 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26–1.46 [m, 10 H, $OCH_2CH_2(CH_2)_5$], 1.76 (m_c, 2 H, OCH_2CH_2), 2.04 (m_c, 2 H, $=CHCH_2$), 3.90 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 4.97 (ddt, ^3J_d = 10.2, ^2J_d = 2.1, ^4J_t = 1.2 Hz, 1 H, $CH=CH_{cis}$), 5.03 (ddt, ^3J_d = 17.1, ^2J_d = 2.1, ^4J_t = 1.6 Hz, 1 H, $CH=CH_{trans}$), 5.81 (ddt, ^3J_d = 17.0, ^3J_d = 10.2, ^3J_t = 6.7 Hz, 1 H, $CH=CH_2$), 6.76 (m_c with d, ^3J_d = 9.0 Hz, 2 H, 3,5-C_{Ar}H), 7.35 (m_c with d, ^3J_d = 9.0 Hz, 2 H, 2,6-C_{Ar}H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.0 [t, $O(CH_2)_4CH_2$], 28.9, 29.1, 29.2, 29.3, 29.4 [t, $OCH_2(CH_2)_3CH_2(CH_2)_2$], 33.8 (t, $CH_2CH=$), 68.3 (t, OCH_2), 112.6 (s, 1-C_{Ar}), 114.2 (t, $=CH_2$), 116.3 (d, 3,5-C_{Ar}), 132.2 (d, 2,6-C_{Ar}), 139.2 (d, $CH=CH_2$), 158.3 (s, 4-C_{Ar}) ppm. IR (neat): $\tilde{\nu}$ = 3074 (arom. CH), 2926 (aliph. CH), 1590, 1489 (arom. C=C), 1244 (C–O–C), 821 (1,4-disubst. benzene) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 312, 310 (33, 43) $[M]^+$, 174, 172 (90, 100) $[C_6H_5BrO]^+$. MS (CI, isobutane): *m*/*z* (%) = 313, 311 (36, 51) $[M + H]^+$, 312, 310 (22, 26) $[M]^+$, 285, 283 (31, 29) $[C_{14}H_{20}BrO]^+$, 174, 172 (14, 12) $[C_6H_5BrO]^+$, 139 (16) $[C_{10}H_{19}]^+$, 111 (100) $[C_8H_{15}]^+$. HR-MS (EI, 70 eV): calcd. for $C_{16}H_{23}{}^{79}BrO$: 310.0932; found 310.0933 (Δ = 0.2 ppm), calcd. for $C_{15}{}^{13}CH_{23}{}^{79}BrO$: 311.0966; found 311.0967 (Δ = 0.3 ppm), calcd. for $C_{16}H_{23}{}^{81}BrO$: 312.0912; found 312.0912 (Δ = 0.1 ppm), calcd. for $C_{15}{}^{13}CH_{23}{}^{81}BrO$: 313.0945; found 313.0946 (Δ = 0.2 ppm). $C_{16}H_{23}BrO$ (310.09): calcd. C 61.74, H 7.45; found C 61.79, H 7.66.

4-(Hex-5-enyloxy)phenylboronic Acid (20a): 1-Bromo-4-(hex-5-enyloxy)benzene (**19a**, 1.00 g, 3.94 mmol) was dissolved in dry tetrahydrofuran (25 mL) and cooled to –78 °C under nitrogen. After addition of *n*-butyllithium (1.73 mL, 4.35 mmol, 2.5 M in hexanes), the solution was stirred at –78 °C for 1 h before addition of trimethyl borate (1.29 mL, 13.1 mmol) and was then stirred for another 2 h while warming to room temp. Water (20 mL) was then added, and the layers were separated. The water layer was extracted with diethyl ether (3 × 15 mL). The combined organic layer was washed with brine (20 mL) and dried with magnesium sulfate. Evaporation of the solvent in vacuo yielded a crystalline crude product. This crude product (300 mg) was recrystallised to yield colourless crystals (250 mg). The product crystallises as a mixture of monomer and trimer of the boronic acid, as was shown by its mass spectra and NMR spectra. Crude product: 950 mg, m.p. 93–97 °C (cyclohexane/dichloromethane), monomer/trimer. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 1.50 (m_c, 2 H, $OCH_2CH_2CH_2$), 1.72 (m_c, 2 H, OCH_2CH_2), 2.09 (m_c, 2 H, $CH_2CH=$), 3.98 (t, ^3J = 6.5 Hz, 2 H, OCH_2), 4.97 (ddt, ^3J_d = 10.2, ^2J_d = 2.2, ^4J_t = 1.2 Hz, 1 H, $CH=CH_{cis}$), 5.03 (ddt, ^3J_d = 17.2, ^2J_d = 2.1, ^4J_t = 1.6 Hz, 1 H, $CH=CH_{trans}$), 5.82 (ddt, ^3J_d = 17.1, ^3J_d = 10.3, ^3J_t = 6.7 Hz, 1 H, $CH=CH_2$), 6.87 (m_c with d, ^3J = 8.7 Hz, 2 H, 3,5-C_{Ar}H), 7.72 (m_c with d, ^3J = 8.7 Hz, 2 H, 2,6-C_{Ar}H) ppm. ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 24.7 (t, $OCH_2CH_2CH_2$), 28.1 (t, OCH_2CH_2), 32.8 (t, $CH_2CH=$), 66.9 (t, OCH_2), 113.4 (d, 3,5-C_{Ar}), 114.9 (t, $CH=CH_2$), 135.8 (d, 2,6-C_{Ar}), 138.5 (d, $CH=CH_2$), 160.3 (s, 4-C_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3220 (OH), 2943 (aliph. CH), 1602, 1415 (arom. C=C), 1351 (OH-deform.), 1245 (Ar–O–C) cm^{-1}. Because of relaxation effects with the ^{11}B isotope, the signal of 1-C_{Ar} is weak and could not be detected. MS (EI, 70 eV): *m*/*z* (%) = 606 (77) $[M(trimer)]^+$, 524 (3) $[M(trimer) - C_6H_{10}]^+$, 523 (3) $[M(trimer) - C_6H_{11}]^+$, 360 (100) $[M(trimer) - 3C_6H_{10}]^+$, 221 (3) $[M + H]^+$. $C_{36}H_{45}B_3O_6$ (trimer, 606.35): calcd. C 71.33, H 7.48; found C 71.63, H 7.76.

4-(Oct-7-enyloxy)phenylboronic Acid (20b): This compound was synthesised by the procedure used for the synthesis of 4-(hex-5-enyloxy)phenylboronic acid (**20a**), from 1-bromo-4-(oct-7-enyloxy)-benzene (**19b**, 1.00 g, 3.53 mmol), *n*-butyllithium (1.55 mL, 3.89 mmol, 2.5 M in hexanes) and trimethyl borate (1.15 mL, 11.7 mmol) in dry tetrahydrofuran (20 mL), to yield crude colourless crystals (820 mg). This crude product (200 mg) was recrystallised (cyclohexane) to yield phenylboronic acid **20b** (180 mg); m.p. 76 °C, 148 °C (monomer/trimer). The product crystallises as a mixture of monomer and trimer of the boronic acid, which was shown by its mass spectra and NMR spectra. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.55 (m, 6 H, $OCH_2CH_2CH_2$), 1.82 (m_c, 2 H, OCH_2CH_2), 2.07 (m_c, 2 H, $CH_2CH=$), 4.04 (t, ^3J = 6.5 Hz, 2 H, OCH_2), 4.95 (ddt, ^3J_d = 10.1, ^2J_d = 2.1, ^4J_t = 1.2 Hz, 1 H,

CH=CHH_{cis}), 5.01 (ddt, ^3J_d = 17.1, ^2J_d = 2.1, ^4J_t = 1.6 Hz, 1 H, CH=CHH_{trans}), 5.83 (m_c with ddt, ^3J_d = 17.1, ^3J_d = 10.2, ^3J_t = 6.7 Hz, 1 H, CH=CH$_2$), 7.00 (m_c with d, ^3J = 8.7 Hz, 3,5-C$_{Ar}$H), 8.15 (m_c with d, ^3J = 8.7 Hz, 2 H, 2,6-C$_{Ar}$H) ppm. IR (KBr): $\tilde{\nu}$ = 3400 (OH), 2927 (aliph. CH), 1602, 1412 (arom. C=C), 1350, 1246, 1171 (C–O–C) cm^{-1}. Not only could the signals of the trimer of the boronic acid be found, but also signals that probably belong to the dimer or monomer. The intensities of these signals were small in comparison to the signals of the trimer. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.9, 28.9, 29.2, 29.4, 29.5 (t, CH$_2$), 29.7 (t, OCH$_2$CH_2), 33.7 (t, CH_2CH=), 67.9 (t, OCH$_2$), 114.1 (d, 3,5-C$_{Ar}$), 114.3 (t, CH=CH_2), 137.5 (d, 2,6-C$_{Ar}$), 139.1 (d, CH=CH$_2$), 149.4 (s, 1-C$_{Ar}$), 162.8 (s, 4-C$_{Ar}$) ppm. MS (EI, 70 eV): *m*/*z* (%) = 690 (91) [M(trimer)]$^+$, 580 (6) [M(trimer) – C_8H_{14}]$^+$, 360 (100) [M(trimer) – 3C_8H_{14}]$^+$. $C_{42}H_{57}B_3O_6$ (trimer, 690.44): calcd. C 73.07, H 8.32. $C_{42}H_{57}B_3O_6$·C_6H_{12} (trimer, 690.44 + 84.10): calcd. C 74.44, H 9.98; found C 74.61, H 8.71.

4-(Dec-9-enyloxy)phenylboronic Acid (20c): This compound was synthesised by the procedure used for the synthesis of 4-(hex-5-enyloxy)phenylboronic acid (**20a**), from 1-bromo-4-(dec-9-enyloxy)benzene (**19c**, 1.21 g, 3.89 mmol), *n*-butyllithium (1.71 mL, 4.29 mmol, 2.5 M in hexanes), and trimethyl borate (1.27 mL, 12.9 mmol) in dry tetrahydrofuran (22 mL), to yield crude colourless crystals (993 mg). This crude product (250 mg) was recrystallised (cyclohexane) to yield the boronic acid (195 mg); m.p. 58–60 °C, 130 °C (monomer/trimer). The product crystallises as a mixture of monomer and trimer of the boronic acid, which was shown by its mass spectra and NMR spectra. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26–1.53 (m, 15 H, CH$_2$), 1.81 (m_c, 3 H, OCH$_2$CH_2), 2.05 (m_c, 3 H, CH_2CH=), 4.04 (t, ^3J = 6.5 Hz, 3 H, OCH$_2$), 4.96 (ddt, ^3J_d = 10.2, ^2J_d = 2.1, ^4J_t = 1.2 Hz, 1.5 H, CH=CHH_{cis}), 5.00 (ddt, ^3J_d = 17.1, ^2J_d = 2.2, ^4J_t = 1.6 Hz, 1.5 H, CH=CHH_{trans}), 5.82 (ddt, ^3J_d = 17.1, ^3J_d = 10.2, ^3J_t = 6.7 Hz, 1.5 H, CH=CH$_2$), 6.96 (d, ^3J = 8.6 Hz, 1 H, 3,5-C$_{Ar}$H$_{monomer}$), 7.00 (m_c with d, ^3J = 8.6 Hz, 2 H, 3,5-C$_{Ar}$H$_{trimer}$), 7.27 (br s, 1 H, OH), 7.75 (d, ^3J = 8.6 Hz, 1 H, 2,6-C$_{Ar}$H$_{monomer}$), 8.15 (m_c with d, ^3J = 8.7 Hz, 2 H, 2,6-C$_{Ar}$H$_{trimer}$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 26.1, 28.9, 29.1, 29.3, 29.37 (t, CH$_2$), 29.42 (t, OCH$_2$CH_2), 33.8 (t, CH_2CH=), 67.9 (t, OCH$_2$), 114.1 (t, CH=CH_2), 114.2 (d, 3,5-C$_{Ar}^{monomer}$), 116.0 (d, 3,5-C$_{Ar}^{trimer}$), 129.4 (d, 2,6-C$_{Ar}^{monomer}$), 136.6 (d, 2,6-C$_{Ar}^{trimer}$), 137.5 (d, CH=CH$_2$), 162.3 (s, 4-C$_{Ar}$) ppm. Because of relaxation effects with the ^{11}B isotope, the signal of 1-C$_{Ar}$ is weak and could not be detected. IR (KBr): $\tilde{\nu}$ = 3356 (OH), 2924 (aliph. CH), 1605, 1351 (arom. C=C), 1248 (C–O–C), 823 (1,4-disubst. benzene) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 774 (29) [M(trimer)]$^+$, 360 (100) [M(trimer) – 3$C_{10}H_{18}$]$^+$. $C_{16}H_{25}BO_3$ (monomer, 276.19): calcd. C 69.58, H 9.12; found C 69.81, H 9.08.

2,9-Bis[2,4-bis(hex-5-enyloxy)phenyl]-1,10-phenanthroline (21a): 2,9-Diiodo-1,10-phenanthroline (**12**, 300 mg, 694 μmol) was dissolved in 1,2-dimethoxyethane (21 mL) and water (5 mL). After addition of crude 2,4-bis(hex-5-enyloxy)phenylboronic acid (**17a**, 665 mg, max. 2.09 mmol), tetrakis(triphenylphosphane)palladium(0) (85.0 mg, 73.8 μmol) and barium hydroxide octahydrate (1.01 g, 3.14 mmol), the reaction mixture was heated to 60 °C under nitrogen for 16 h. After the system had cooled to room temp., water and dichloromethane (20 mL each) were added to the suspension and the layers were separated. The water layer was extracted with dichloromethane (3 × 20 mL), and the combined organic layer was washed once with brine (20 mL) and dried with magnesium sulfate. The solvent was evaporated and the residue was filtered through basic aluminium oxide (dichloromethane). Evaporation of the solvent was followed by purification of the crude product by column chromatography (Chromatotron, 2 mm, silica gel, dichloromethane to ethyl acetate, $R_f \approx 0.10$) to yield slightly yellow crystals (185 mg, 256 μmol, 27%); m.p. 193–195 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.54 [m_c, 4 H, O(CH$_2$)$_2$CH_2], 1.61 [m_c, 4 H, O(CH$_2$)$_2$CH_2], 1.83 (m_c, 8 H, OCH$_2$CH_2), 2.08 (dtt, ^3J_t = 7.3, ^3J_d = 6.9, ^4J_t = 1.3 Hz, 4 H, CH_2CH=), 2.16 (dtt, ^3J_t = 7.3, ^3J_d = 6.9, ^4J_t = 1.3 Hz, 4 H, CH_2CH=), 4.04 (t, ^3J = 6.4 Hz, 4 H, OCH$_2$), 4.05 (t, ^3J = 6.5 Hz, 4 H, OCH$_2$), 4.94 (ddt, ^3J_d = 10.2, ^2J_d = 2.0, ^4J_t = 1.3 Hz, 2 H, =CHH_{cis}), 4.99 (ddt, ^3J_d = 10.2, ^2J_d = 2.0, ^4J_t = 1.3 Hz, 2 H, =CHH_{cis}), 5.00 (ddt, ^3J_d = 17.2, ^2J_d = 2.0, ^4J_t = 1.6 Hz, 2 H, =CHH_{trans}), 5.06 (ddt, ^3J_d = 17.1, ^2J_d = 2.0, ^4J_t = 1.6 Hz, 2 H, =CHH_{trans}), 5.78 (ddt, ^3J_d = 17.0, ^3J_d = 10.3, ^3J_t = 6.7 Hz, 2 H, =CH), 5.86 (ddt, ^3J_d = 17.0, ^3J_d = 10.3, ^3J_t = 6.7 Hz, 2 H, =CH), 6.56 (d, ^4J = 2.4 Hz, 2 H, 3-C$_{Ar}$H), 6.72 (dd, ^3J = 8.6, ^4J = 2.3 Hz, 2 H, 5-C$_{Ar}$H), 7.72 (s, 2 H, 5,6-C$_{Phen}$H), 8.16 (d, ^3J = 8.5 Hz, 2 H, 3,8-C$_{Phen}$H), 8.28 (d, ^3J = 8.4 Hz, 2 H, 4,7-C$_{Phen}$H), 8.38 (d, ^3J = 8.6 Hz, 2 H, 6-C$_{Ar}$H) ppm. Assignment of the signals to the *ortho*- and *para*-side chains was not reliably possible from these data. Calculations from an increment system for NMR spectra of aromatic compounds[27] predict that the signals of a substituent in a *para* position should be shifted to higher fields than signals of the same substituent in an *ortho* position, and the signals are assigned on these grounds. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.3, 25.4 (2 × t, OCH$_2$CH_2), 28.6, 28.7 (2 × t, OCH$_2$CH_2), 33.2, 33.5 (2 × t, CH_2CH=), 67.8, 68.4 (2 × t, OCH$_2$), 100.2 (d, 3-C$_{Ar}$), 106.0 (d, 5-C$_{Ar}$), 114.8 (2 × t, =CH$_2$), 122.7 (s, 1-C$_{Ar}$), 124.6 (d, 3,8-C$_{Phen}$), 125.5 (d, 5,6-C$_{Phen}$), 127.0 (s, 4a,6a-C$_{Phen}$), 133.2 (d, 6-C$_{Ar}$), 135.0 (d, 4,7-C$_{Phen}$), 138.6 (2 × d, CH=), 146.0 (s, 10a,10b-C$_{Phen}$), 156.0 (s, 2,9-C$_{Phen}$), 158.2 (s, 4-C$_{Ar}$), 161.1 (s, 2-C$_{Ar}$) ppm. The assignment of the signals is based on the prediction that signals of a *para*-substituent are shifted to higher fields than the signals of an *ortho*-substituent. This assumption is based on calculations made with an increment system for NMR spectra of substituted aromatic compounds.[27] IR (KBr): $\tilde{\nu}$ = 2925 (aliph. CH), 1608, 1456 (arom. C=C), 1257, 1090 (COC) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 724 (100) [M]$^+$, 696 (30) [$C_{46}H_{52}N_2O_4$]$^+$, 669 (22) [$C_{44}H_{49}N_2O_4$]$^+$, 655 (62) [$C_{43}H_{47}N_2O_4$]$^+$, 641 (29) [$C_{42}H_{45}N_2O_4$]$^+$, 625 (19) [$C_{42}H_{45}N_2O_3$]$^+$, 573 (24) [$C_{37}H_{37}N_2O_4$]$^+$, 560 (27) [$C_{36}H_{36}N_2O_4$]$^+$, 379 (19) [$C_{24}H_{15}N_2O_3$]$^+$. MS (ESI, $CHCl_3$/MeOH): *m*/*z* (%) = 725 (100) [M + H]$^+$. HR-MS (EI, 70 eV): $C_{48}H_{56}N_2O_4$, calcd. 724.4240; found 724.4240 (Δ = 0 ppm), $C_{47}{}^{13}CH_{56}N_2O_4$, calcd. 725.4273; found 725.4274 (Δ = 0.1 ppm), $C_{46}{}^{13}C_2H_{56}N_2O_4$, calcd. 726.4305; found 726.4307 (Δ = 0.2 ppm). $C_{48}H_{56}N_2O_4$ (724.42): calcd. C 79.52, H 7.79, N 3.86. $C_{48}H_{56}N_2O_4$·0.3H_2O (724.42 + 5.40): calcd. C 78.93, H 7.81, N 3.84; found C 78.86, H 7.73, N 3.88.

2,9-Bis[2,4-bis(dec-9-enyloxy)phenyl]-1,10-phenanthroline (21b). Method A: 2,9-Diiodo-1,10-phenanthroline (**12**, 113 mg, 263 μmol) was dissolved in 1,2-dimethoxyethane (8 mL) and water (2 mL). After addition of crude 2,4-bis(dec-9-enyloxy)phenylboronic acid (**17b**, 510 mg, max. 1.19 mmol), tetrakis(triphenylphosphane)palladium(0) (32 mg, 26 μmol) and barium hydroxide octahydrate (384 mg, 1.19 mmol), the mixture was stirred at 80 °C under nitrogen for 40 h. To complete the reaction, the mixture was allowed to cool to room temp., additional crude 2,4-bis(dec-9-enyloxy)phenylboronic acid (**17b**, 210 mg, max. 490 μmol) and tetrakis(triphenylphosphane)palladium(0) (5.0 mg, 4.1 μmol) were then added, and stirring was continued at 80 °C under nitrogen for another 40 h. After addition of dichloromethane and water (10 mL each) and separation of the layers, the water layer was extracted with dichloromethane (3 × 10 mL). The combined organic layer was washed with brine (10 mL) and dried with magnesium sulfate. After evaporation of the solvent in vacuo, the crude product was purified by chromatography (Chromatotron, 2 mm, silica gel, dichloromethane/ethyl acetate, 4:1, $R_f \approx 0.10$) to yield a colourless oil (25 mg,

26 μmol, 10%). MS (ESI, $CHCl_3$/MeOH, crude product): *m/z* (%) = 949.7 (100) $[M + H]^+$.

Method B: 2-[2,4-Bis(dec-9-enyloxy)phenyl]-9-chloro-1,10-phenanthroline (**23**, 90.0 mg, 151 μmol) was dissolved in 1,2-dimethoxyethane (6 mL) and water (1.5 mL). After addition of tetrakis(triphenylphosphane)palladium(0) (18 mg, 15 μmol), crude 2,4-bis(dec-9-enyloxy)phenylboronic acid (**17b**, 360 mg, max. 838 μmol) and barium hydroxide octahydrate (100 mg, 341 μmol), the mixture was stirred at 80 °C under nitrogen for 18 h. Cooling down to room temp. was followed by addition of dichloromethane and water (10 mL each) and separation of the layers. The water layer was extracted with dichloromethane (3 × 10 mL). The combined organic layer was washed with brine (10 mL) and dried with magnesium sulfate. After evaporation of the solvent in vacuo, the crude product was purified by chromatography (Chromatotron, 2 mm, silica gel, dichloromethane/ethyl acetate, 4:1, $R_f \approx 0.10$) to yield a colourless oil (60 mg, 63 μmol, 42%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.21–1.49 (m, 40 H, CH_2), 1.49 (m_c, 4 H, CH_2), 1.80 (m_c, 8 H, OCH_2CH_2), 2.00 (m_c, 4 H, CH_2CH=), 2.06 (m_c, 4 H, CH_2CH=), 4.03 (t, ^3J = 6.3 Hz, 4 H, OCH_2), 4.04 (t, ^3J = 6.5 Hz, 4 H, OCH_2), 4.91 (ddt, ^3J_d = 10.2, ^2J_d = 2.2, ^4J_t = 1.2 Hz, 2 H, CH=CHH_{cis}), 4.94 (ddt, $^3J_d \approx 10.2$, ^2J_d = 2.2, ^4J_t = 1.2 Hz, 2 H, CH=CHH_{cis}), 4.97 (ddt, ^3J_d = 17.2, ^2J_d = 2.2, ^4J_t = 1.6 Hz, 2 H, CH=CHH_{trans}), 5.01 (ddt, ^3J_d = 17.1, ^2J_d = 2.2, ^4J_t = 1.6 Hz, 2 H, CH=CHH_{trans}), 5.80 (2 × ddt, ^3J_d = 17.1, ^3J_d = 10.2, ^3J_t = 6.7 Hz, 4 H, CH=CH_2), 6.57 (d, ^4J = 2.3 Hz, 2 H, 3-C_{Ar}H), 6.71 (dd, ^3J = 8.6, ^4J = 2.3 Hz, 2 H, 5-C_{Ar}H), 7.73 (s, 2 H, 5,6-C_{Phen}H), 8.16 (d, ^3J = 8.4 Hz, 2 H, 4,7-C_{Phen}H), 8.29 (d, ^3J = 8.4 Hz, 2 H, 3,8-C_{Phen}H), 8.38 (d, ^3J = 8.6 Hz, 2 H, 6-C_{Ar}H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 26.1 (d, CH_2), 26.2 (d, CH_2), 28.9 (2 × d, CH_2), 29.0 (d, CH_2), 29.1 (d, CH_2), 29.2 (d, CH_2), 29.3 (d, CH_2), 29.4 (2 × d, CH_2), 29.5 (d, CH_2), 33.8 (2 × d, CH_2CH=), 68.2 (d, OCH_2), 68.8 (d, OCH_2), 100.4 (d, 3-C_{Ar}), 106.2 (d, 5-C_{Ar}), 114.2 (2 × t, $=CH_2$), 123.7 (s, 4-C_{Ar}), 124.5 (d, 3,8-C_{Phen}), 125.5 (d, 6-C_{Ar}), 127.0 (d, 5,6-C_{Phen}), 130.8 (s, 4a,6a-C_{Phen}), 133.4 (s, 10a,10b-C_{Phen}), 134.9 (d, 4,7-C_{Phen}), 139.2 (2 × d, CH=CH_2), 156.1 (s, 2,9-C_{Phen}), 158.4 (s, 2-C_{Ar}), 161.2 (s, 1-C_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3075 (arom. CH), 2926 (aliph. CH), 1605, 1432 (arom. C=C), 1295, 1180 (COC) cm^{-1}. MS (ESI, $CHCl_3$/MeOH): *m/z* (%) = 949.7 (100) $[M + H]^+$. MS (EI, 70 eV): *m/z* (%) = 948.7 (29) $[M]^+$, 823.7 (69) $[M - C_9H_{17}]^+$, 810 (21) $[M - C_{10}H_{19}]^+$. HR-MS (EI, 70 eV): $C_{64}H_{88}N_2O_4$ (948.67), calcd. for $C_{64}H_{88}N_2O_4 + H^+$: 949.6817; found 949.6851 (Δ = 3.6 ppm), calcd. for $C_{63}{}^{13}CH_{88}N_2O_4 + H^+$: 950.6850; found 950.6866 (Δ = 1.7 ppm). $C_{64}H_{88}N_2O_4$ (948.67): calcd. C 76.16, H 7.91, N 4.67. $C_{64}H_{88}N_2O_4 \cdot 0.5\,C_6H_{12}$ (948.67 + 42.05): calcd. C 76.78, H 8.33, N 4.37; found C 76.90, H 8.34, N 4.12.

2,9-Bis[4-(hex-5-enyloxy)phenyl]-1,10-phenanthroline (22a): 2,9-Diiodo-1,10-phenanthroline (**12**) was dissolved in 1,2-dimethoxyethane (17 mL) and water (4.3 mL) before addition of 4-(hex-5-enyloxy)phenylboronic acid (**20a**, 433 mg, max. 1.97 mmol of the monomer), barium hydroxide octahydrate (958 mg, 2.97 mmol) and tetrakis(triphenylphosphane)palladium(0) (80 mg, 66 μmol). The mixture was stirred at 80 °C under nitrogen for 72 h and allowed to cool to room temp., and water and dichloromethane (20 mL each) were added. The layers were separated and the water layer was extracted with dichloromethane (3 × 20 mL). The combined organic layer was washed with brine (20 mL) and dried with magnesium sulfate. Evaporation of the solvent in vacuo was followed by purification of the crude product by column chromatography (silica gel, cyclohexane/ethyl acetate, 4:1, R_f = 0.26) to yield colourless crystals (103 mg, 195 μmol, 30%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.62 (m_c, 4 H, $OCH_2CH_2CH_2$), 1.86 (m_c, 4 H, OCH_2CH_2), 2.17 (m_c, 4 H, CH_2CH=), 4.08 (t, ^3J = 6.5 Hz, 4 H, OCH_2), 5.00 (ddt, ^3J_d = 10.2, ^2J_d = 2.0, ^4J_t = 1.2 Hz, 2 H, CH=CHH_{cis}), 5.06 (ddt, ^3J_d = 17.1, ^2J_d = 2.0, ^4J_t = 1.6 Hz, 2 H, CH=CHH_{trans}), 5.86 (ddt, ^3J_d = 17.1, ^3J_d = 10.2, ^3J_t = 6.7 Hz, 2 H, CH=CH_2), 7.09 (m_c with d, ^3J = 8.9 Hz, 4 H, 3,5-C_{Ar}H), 7.71 (s, 2 H, 5,6-C_{Phen}H), 8.06 (d, ^3J = 8.4 Hz, 2 H, 3,8-C_{Phen}H), 8.23 (d, ^3J = 8.4 Hz, 2 H, 4,7-C_{Phen}H), 8.42 (m_c with d, ^3J = 8.9 Hz, 4 H, 2,6-C_{Ar}H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.4 (t, $OCH_2CH_2CH_2$), 28.8 (t, OCH_2CH_2), 33.5 (t, CH_2CH=), 67.9 (t, OCH_2), 114.8 (t, $=CH_2$), 114.8 (d, 3,5-C_{Ar}), 119.3 (d, 3,8-C_{Phen}), 125.6 (d, 5,6-C_{Phen}), 127.5 (s, 4a,6a-C_{Phen}), 129.0 (d, 2,6-C_{Ar}), 132.1 (s, 1-C_{Ar}), 136.7 (d, 4,7-C_{Phen}), 138.6 (d, CH=CH_2), 146.1 (s, 10a,10b-C_{Phen}), 156.4 (s, 2,9-C_{Phen}), 160.5 (s, 4-C_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 2939 (aliph. CH), 1601, 1492 (arom. C=C), 1246 (Ar–O–C) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 528 (100) $[M]^+$, 446 (7) $[M - C_6H_{10}]^+$, 364 (19) $[M - 2C_6H_{10}]^+$. HR-MS (ESI, $CHCl_3$/MeOH): $C_{36}H_{36}N_2O_2$ (528.28), calcd. for $C_{36}H_{36}N_2O_2 + H^+$: 529.2850; found 529.2803 (Δ = 8.9 ppm), calcd. for $C_{35}{}^{13}CH_{36}N_2O_2 + H^+$: 530.2882; found 530.2848 (Δ = 6.4 ppm), calcd. for $2\,C_{36}H_{36}N_2O_2 + Na^+$: 1079.5446; found 1079.5354 (Δ = 8.5 ppm), calcd. for $C_{35}{}^{13}CH_{36}N_2O_2 \cdot C_{36}H_{36}N_2O_2 + Na^+$: 1080.5478; found 1080.5447 (Δ = 2.9 ppm), calcd. for $2\,C_{35}{}^{13}CH_{36}N_2O_2$: 1081.5511; found 1081.5528 (Δ = 1.6 ppm). HR-MS (EI, 70 eV): calcd. for $C_{36}H_{36}N_2O_2$: 528.2777; found 528.2778 (Δ = 0.1 ppm), calcd. for $C_{35}{}^{13}CH_{36}N_2O_2$: 529.2810; found 529.2812 (Δ = 0.2 ppm). $C_{36}H_{36}N_2O_2$ (528.28): calcd. C 81.79, H 6.86, N 5.30. $C_{36}H_{36}N_2O_2 \cdot 0.1\,H_2O$ (528.28 + 1.80): calcd. C 81.51, H 6.88, N 5.28; found C 81.36, H 6.98, N 5.14.

2,9-Bis[4-(oct-7-enyloxy)phenyl]-1,10-phenanthroline (22b): This compound was synthesised as described above by the procedure for the synthesis of 2,9-bis[4-(hex-5-enyloxy)phenyl]-1,10-phenanthroline (**22a**), from 2,9-diiodo-1,10-phenanthroline (**12**, 60.0 mg, 246 μmol), crude 4-(oct-7-enyloxy)phenylboronic acid (**20b**, 183 mg, max. 739 μmol), barium hydroxide octahydrate (359 mg, 1.11 mmol), and tetrakis(triphenylphosphane)palladium(0) (30 mg, 25 μmol) in 1,2-dimethoxyethane (8 mL) and water (2 mL). The crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 4:1, R_f = 0.75) to yield colourless crystals (66 mg, 113 μmol, 46%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.39–1.49 (m, 8 H, CH_2), 1.51 (m_c, 4 H, $OCH_2CH_2CH_2$), 1.83 (m_c, 4 H, OCH_2CH_2), 2.05 (m_c, 4 H, CH_2CH=), 4.06 (t, ^3J = 6.6 Hz, 4 H, OCH_2), 4.95 (ddt, ^3J_d = 10.2, ^2J_d = 2.1, ^4J_t = 1.1 Hz, 2 H, CH=CHH_{cis}), 5.02 (ddt, ^3J_d = 17.0, ^2J_d = 2.1, ^4J_t = 1.6 Hz, 2 H, CH=CHH_{trans}), 5.82 (ddt, ^3J_d = 17.1, ^3J_d = 10.3, ^3J_t = 6.7 Hz, 2 H, CH=CH_2), 7.08 (m_c with d, ^3J = 8.8 Hz, 4 H, 3,5-C_{Ar}H), 7.70 (s, 2 H, 5,6-C_{Phen}H), 8.04 (d, ^3J = 8.4 Hz, 2 H, 3,8-C_{Phen}H), 8.22 (d, ^3J = 8.4 Hz, 2 H, 4,7-C_{Phen}H), 8.39 (m_c with d, ^3J = 8.8 Hz, 4 H, 2,6-C_{Ar}H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.9, 28.9, 29.3, 29.4 [t, $OCH_2(CH_2)_4$], 33.7 (t, CH_2CH=), 68.1 (t, OCH_2), 114.8 (t, $=CH_2$), 115.6 (d, 3,5-C_{Ar}), 119.5 (d, 3,8-C_{Phen}), 125.6 (d, 5,6-C_{Phen}), 127.5 (s, 4a,6a-C_{Phen}), 129.1 (d, 2,6-C_{Ar}), 132.0 (s, 1-C_{Ar}), 136.8 (d, 4,7-C_{Phen}), 139.0 (d, CH=CH_2), 146.0 (s, 10a,10b-C_{Phen}), 156.6 (s, 2,9-C_{Phen}), 160.5 (s, 4-C_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 2930 (aliph. CH), 1598, 1459 (arom. C=C), 1249, 1176 (C–O–C) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 584 (100) $[M]^+$, 474 (16) $[M - C_8H_{14}]^+$, 364 (29) $[M - 2C_8H_{14}]^+$. MS (ESI, $CHCl_3$/MeOH): *m/z* (%) = 585 (100) $[M + H]^+$. HR-MS (EI, 70 eV): calcd. for $C_{40}H_{44}N_2O_2$: 584.3403; found 584.3403 ($\Delta \approx 0.1$ ppm), calcd. for $C_{39}{}^{13}CH_{44}N_2O_2$: 585.3436; found 585.3437 (Δ = 0.1 ppm).

2,9-Bis[4-(dec-9-enyloxy)phenyl]-1,10-phenanthroline (22c): This compound was synthesised as described above by the procedure used for 2,9-bis[4-(hex-5-enyloxy)phenyl]-1,10-phenanthroline (**20a**), from 2,9-diiodo-1,10-phenanthroline (**12**, 50.0 mg, 116 μmol), crude 4-(dec-9-enyloxy)phenylboronic acid (**20c**,

170 mg, max. 616 μmol of the monomer), barium hydroxide octahydrate (299 mg, 928 μmol), and tetrakis(triphenylphosphane)palladium(0) (25 mg, 21 μmol) in 1,2-dimethoxyethane (6 mL) and water (1.5 mL). The crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 4:1, R_f = 0.53) to yield yellow crystals (105 mg, 164 μmol, 80%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.30–1.47 (m, 8 H, CH_2), 1.48–1.55 (m, 8 H, CH_2), 1.84 (m_c, 4 H, OCH_2CH_2), 2.06 (m_c, 4 H, =CHCH_2), 4.07 (t, ^3J = 6.6 Hz, 4 H, OCH_2), 4.94 (ddt, ^3J_d = 10.2, ^2J_d = 2.2, ^4J_t = 1.2 Hz, 2 H, CH=CHH_{cis}), 5.01 (ddt, ^3J_d = 17.1, ^2J_d = 2.1, ^4J_t = 1.6 Hz, 2 H, CH=CHH_{trans}), 5.83 (ddt, ^3J_d = 17.1, ^3J_d = 10.2, ^3J_t = 6.7 Hz, 2 H, CH=CH$_2$), 7.10 (m_c with d, ^3J = 8.9 Hz, 4 H, 3,5-C_{Ar}H), 7.73 (s, 2 H, 5,6-C_{Phen}H), 8.08 (d, ^3J = 8.4 Hz, 2 H, 3,8-C_{Phen}H), 8.25 (d, ^3J = 8.4 Hz, 2 H, 4,7-C_{Phen}H), 8.42 (m_c with d, ^3J = 8.9 Hz, 4 H, 2,6-C_{Ar}H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 26.1, 29.0, 29.1, 29.3, 29.4, 29.5 (t, CH_2), 33.8 (t, CH_2CH=), 68.2 (t, OCH_2), 114.2 (t, =CH_2), 114.9 (d, 3,5-C_{Ar}), 119.3 (d, 3,8-C_{Phen}), 125.6 (d, 5,6-C_{Phen}), 127.5 (s, 4a,6a-C_{Phen}), 129.0 (d, 2,6-C_{Ar}), 132.0 (s, 1-C_{Ar}), 136.8 (d, 4,7-C_{Phen}), 139.2 (d, CH=CH$_2$), 146.1 (s, 10a,10b-C_{Phen}), 156.5 (s, 2,9-C_{Phen}), 160.6 (s, 4-C_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 2936 (aliph. CH), 1603, 1458 (arom. C=C), 1246, 1034 (C–O–C) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 640 (100) [M]$^+$, 515 (40) [$C_{35}H_{35}N_2O_2$]$^+$, 501 (36) [$C_{34}H_{33}N_2O_2$]$^+$, 377 (17) [$C_{25}H_{17}N_2O_2$]$^+$, 364 (72) [$C_{24}H_{15}N_2O_2$]$^+$. MS (ESI, $CHCl_3$/MeOH): *m*/*z* (%) = 641 (100) [M + H]$^+$. HR-MS (EI, 70 eV): calcd. for $C_{44}H_{52}N_2O_2$: 640.4029; found 640.4029 (Δ = 0.1 ppm), calcd. for $C_{43}{}^{13}CH_{52}N_2O_2$: 641.4063; found 641.4062 (Δ = 0.1 ppm). $C_{44}H_{52}N_2O_2$ (640.40): calcd. C 82.46, H 8.18, N 4.37. $C_{44}H_{52}N_2O_2 \cdot 0.9\,C_4H_8O_2$ (640.40 + 79.25): calcd. C 79.38, H 8.29, N 3.89; found C 79.38, H 8.21, N 3.79.

2-[2,4-Bis(dec-9-enyloxy)phenyl]-9-chloro-1,10-phenanthroline (23): In an attempt to synthesise 2,9-bis[2,4-bis(dec-9-enyloxy)phenyl]-1,10-phenanthroline (**21b**) from 2,9-dichloro-1,10-phenanthroline (**10**, 200 mg, 803 μmol) by Suzuki coupling with crude 2,4-bis(dec-9-enyloxy)phenylboronic acid (**17b**, 600 mg, ca. 1.4 mmol) in the presence of tetrakis(triphenylphosphane)palladium(0) (57 mg, 47 μmol) and barium hydroxide octahydrate (670 mg, 2.11 mmol) (reaction and workup conditions as described for the synthesis of **21b** from diiodide **12**), the monoarylated phenanthroline **23** was isolated by chromatography (Chromatotron, 2 mm, silica gel, dichloromethane/ethyl acetate, 4:1, R_f = 0.18) as a colourless oil (95 mg, 159 μmol, 34%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.21–1.52 (m, 20 H, CH_2), 1.80 (m_c, 4 H, OCH_2CH_2), 1.98 (m_c, 2 H, CH_2CH=), 2.06 (m_c, 2 H, CH_2CH=), 4.02 (t, $^3J \approx$ 6.5 Hz, 2 H, OCH_2), 4.04 (t, $^3J \approx$ 6.5 Hz, 2 H, OCH_2), 4.91 (ddt, ^3J_d = 10.2 Hz, ^2J_d = 2.2 Hz, ^4J_t = 1.1 Hz, 1 H, CH=CHH_{cis}), 4.94 (ddt, $^3J_d \approx$ 10.2 Hz, ^2J_d = 2.2 Hz, ^4J_t = 1.2 Hz, 1 H, CH=CHH_{cis}), 4.96 (ddt, ^3J_d = 17.1 Hz, ^2J_d = 2.1 Hz, ^4J_t = 1.6 Hz, 1 H, CH=CHH_{trans}), 5.01 (ddt, ^3J_d = 17.1 Hz, ^2J_d = 2.0 Hz, ^4J_t = 1.6 Hz, 1 H, CH=CHH_{trans}), 5.78 (ddt, ^3J_d = 17.0 Hz, ^3J_d = 10.2 Hz, ^3J_t = 6.7 Hz, 1 H, CH=CH$_2$), 5.82 (ddt, ^3J_d = 17.0 Hz, ^3J_d = 10.2 Hz, ^3J_t = 6.7 Hz, 1 H, CH=CH$_2$), 6.56 (t, ^4J = 2.3 Hz, 1 H, 3-C_{Ar}H), 6.71 (dd, ^3J = 8.6 Hz, ^4J = 2.3 Hz, 1 H, 5-C_{Ar}H), 7.58 (d, ^3J = 8.3 Hz, 1 H, 8-C_{Phen}H), 7.71 (d, ^3J = 8.7 Hz, 1 H, 5-C_{Phen}H), 7.80 (d, ^3J = 8.7 Hz, 1 H, 6-C_{Phen}H), 8.16 (d, ^3J = 8.4 Hz, 1 H, 7-C_{Phen}H), 8.17 (d, ^3J = 8.5 Hz, 1 H, 3-C_{Phen}H), 8.29 (d, ^3J = 8.6 Hz, 1 H, 6-C_{Ar}H), 8.30 (d, ^3J = 8.5 Hz, 1 H, 4-C_{Phen}H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 26.1 (d, CH_2), 26.2 (d, CH_2), 28.9 (d, CH_2), 28.9 (d, CH_2), 29.0 (d, CH_2), 29.1 (d, CH_2), 29.2 (d, CH_2), 29.2 (d, CH_2), 29.3 (d, CH_2), 29.4 (d, CH_2), 29.4 (d, CH_2), 29.5 (d, CH_2), 33.7 (d, CH$_2$CH=), 33.8 (d, CH$_2$CH=), 68.2 (d, OCH_2), 68.8 (d, OCH_2), 100.4 (d, 3-C_{Ar}), 106.3 (d, 5-C_{Ar}), 114.1 (2 × t, =CH_2), 122.4 (s, 4-C_{Ar}), 123.9 (d, 8-C_{Phen}), 124.7 (d, 5-C_{Phen}*), 125.5 (d, 6-C_{Ar}), 126.9 (d, 6-C_{Phen}*), 127.4 (2 × s, 10a,10b-C_{Phen}), 133.5 (d, 4-C_{Phen}), 134.9 (d, 7-C_{Phen}), 138.6 (d, 3-C_{Phen}), 139.1 (d, CH=CH$_2$), 139.2 (d, CH=CH$_2$), 144.9 (s, 4a-C_{Phen}#), 146.4 (s, 6a-C_{Phen}#), 151.2 (s, 2-C_{Phen}), 157.1 (s, 9-C_{Phen}), 158.3 (s, 2-C_{Ar}), 161.5 (s, 1-C_{Ar}) ppm. The assignments marked with #, * may be reversed. IR (KBr): $\tilde{\nu}$ = 2925 (aliph. CH), 1608, 1580, 1476 (arom. C=C), 1279, 1182 (COC) cm^{-1}. MS (EI, 70 eV): *m*/*z* = 600, 598 (7, 24) [M]$^+$, 475, 473 (34, 100) [M – C_9H_{17}]$^+$, 308, 306 (12, 40) [M + H – $C_{10}H_{18}$ – $C_{10}H_{19}O$]$^+$. MS (ESI, $CHCl_3$/MeOH): *m*/*z* (%) = 601, 599 (45, 100) [M + H]$^+$. HR-MS (EI, 70 eV): calcd. for $C_{38}H_{47}{}^{35}ClN_2O_2$: 598.3326; found 598.3360 (Δ = –5.8 ppm), calcd. for $C_{37}{}^{13}CH_{47}{}^{35}ClN_2O_2$: 599.3359; found 599.3358 (Δ = 0.3 ppm).

2,21,23,42-Tetraoxa-1,22(1,3,4)-dibenzena-43(2,9)-1,10-phenanthrolina-bicyclo[20.20.1]tritetracontaphan-11,32-diene (24b): 2,9-Bis[2,4-bis(dec-9-enyloxy)phenyl]-1,10-phenanthroline (**21b**, 30 mg, 32 μmol) was dissolved in dry dichloromethane (36 mL). After addition of benzylidene-bis(tricyclohexylphosphane)dichlororuthenium (Grubbs type I catalyst, 3 mg, 4 μmol, 12 mol-%), the solution was stirred at room temp. under nitrogen for 18 h and was then filtered through basic aluminium oxide. The solvent was evaporated in vacuo and the crude product was purified by chromatography (Chromatotron, 2 mm, silica gel, cyclohexane/ethyl acetate, 2:1, R_f = 0.58) to yield a yellow oil (20 mg, 22 μmol, 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.80–0.91 (m, 4 H, CH_2), 0.95–1.03 (m, 4 H, CH_2), 1.22–1.54 (m, 32 H, CH_2), 1.77–1.87 (m, 8 H, OCH_2CH_2), 1.94–2.09 (m, 8 H, CH_2CH=), 4.05 (m_c, 8 H, OCH_2), 4.98 (m_c, 1.46 H, CH=CHH_{cis}#), 5.06 (m_c, 0.54 H, CH=CHH_{trans}#), 5.34 (m_c, 1.2 H, CH=CHH_{cis}*), 5.42 (m_c, 0.8 H, CH=CHH_{trans}*), 6.55 (d, ^4J = 2.1 Hz, 2 H, 2-C_{Ar}H), 6.74 (dd, $^3J \approx$ 8.6, ^4J = 2.2 Hz, 2 H, 6-C_{Ar}H), 7.74 (s, 2 H, 5,6-C_{Phen}H), 8.16 (d, ^3J = 8.4 Hz, 2 H, 4,7-C_{Phen}H), 8.24 (d, ^3J = 8.4 Hz, 2 H, 3,8-C_{Phen}H), 8.28 (d, ^3J = 8.6 Hz, 2 H, 5-C_{Ar}H) ppm. The assignments marked with #, * may be reversed. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.7, 25.8, 28.2, 28.5, 28.7, 29.0, 29.1, 29.2, 29.4, 29.9 (d, CH_2), 32.2 (d, CH$_2$CH=), 32.5 (d, CH$_2$CH=), 68.0 (d, OCH_2), 68.1 (d, CH$_2$CH=), 100.6 (d, 2-C_{Ar}), 106.3 (d, 6-C_{Ar}), 123.5 (s, 1-C_{Ar}), 124.8 (d, 3,8-C_{Phen}), 125.5 (d, 5-C_{Ar}), 126.9 (s, 4a,6a-C_{Phen}), 129.7 (d, 5,6-C_{Phen}), 130.0 (d, CH=CH), 130.2 (d, CH=CH), 134.7 (d, 4,7-C_{Phen}), 146.1 (s, 10a,10b-C_{Phen}), 156.3 (s, 2,9-C_{Phen}), 158.2 (s, 3-C_{Ar}), 161.0 (s, 4-C_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2851 (aliph. CH), 1609, 1580, 1487 (arom. C=C), 1262, 1100, 1022 (COC), 801 (2 neighbouring arom. CH) cm^{-1}. MS (ESI, $CHCl_3$/MeOH): *m*/*z* (%) = 893.6 (100) [M + H]$^+$, 879.6 (40) [M + H – CH_2]$^+$. MS (EI, 70 eV): *m*/*z* (%) = 892 (11) [M]$^+$, 799 (9) [M – C_7H_{13}]$^+$, 97 (100) [C_7H_{13}]$^+$. HR-MS (ESI, $CHCl_3$/MeOH): $C_{60}H_{80}N_2O_4$ (892.61), calcd. for $C_{60}H_{80}N_2O_4$ + H$^+$: 893.6191; found 893.6249 (Δ = 6.5 ppm), calcd. for $C_{59}{}^{13}CH_{80}N_2O_4$ + H$^+$: 894.6224; found 894.6182 (Δ = 4.7 ppm).

4,15-Dioxa-1,3(1,4)-dibenzena-2(2,9)-1,10-phenanthrolina-cyclopentadecaphan-7-ene (25a): 2,9-Bis[4-(hex-5-enyloxy)phenyl]-1,10-phenanthroline (**22a**, 80.0 mg, 152 μmol) was dissolved in dry dichloromethane (160 mL) under nitrogen. After addition of benzylidene-bis(tricyclohexylphosphane)dichlororuthenium (Grubbs type I catalyst, 14.5 mg, 18.5 μmol, 12 mol-%), the solution was stirred at room temp. for 7 d. TLC still showed starting material, so benzylidene-bis(tricyclohexylphosphane)dichlororuthenium (Grubbs type I catalyst, 8.0 mg, 10 μmol, 7 mol-%) was added again and the solution was stirred at room temp. for another 4 d. The solution was filtered through basic aluminium oxide and the solvent was evaporated in vacuo. The crude product was partially purified by chromatography (Chromatotron, 2 mm, silica gel, cyclohexane/ethyl acetate, 2:1, R_f = 0.58) to yield several fractions that contained both starting material and product. The characteri-

sation of product **25a** was carried out with the purest fraction; yield 40 mg as yellow oil (mixture of starting material and product); m.p. 220–226 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.45–1.57 (m, 4 H, $OCH_2CH_2CH_2$), 1.86 (m_c, 4 H, OCH_2CH_2), 1.97–2.08 (m, 4 H, CH_2CH=), 4.09 (t, ^3J = 6.7 Hz, 4 H, OCH_2), 5.41 (t, ^3J = 4.8 Hz, 1 H, CH=CH_{cis}*), 5.50 (m_c, 1 H, CH=CH_{trans}*), 7.11 (m_c with d, ^3J = 8.9 Hz, 4 H, 3,5-C_{Ar}H), 7.73 (s, 2 H, 5,6-C_{Phen}H), 8.07 (d, ^3J = 8.5 Hz, 2 H, 3,8-C_{Phen}H), 8.25 (d, ^3J = 8.5 Hz, 2 H, 4,7-C_{Phen}H), 8.43 (m_c, 4 H, 2,6-C_{Ar}H) ppm. The assignments marked with * may be reversed. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.8 (t, CH_2), 32.8 (t, OCH_2CH_2), 33.5 (t, CH_2CH=), 67.9 (t, OCH_2), 114.9 (d, 3,5-C_{Ar}), 119.2 (d, 3,8-C_{Phen}), 125.5 (d, 5,6-C_{Phen}), 127.5 (s, 4a,6a-C_{Phen}), 129.0 (d, 2,6-C_{Ar}), 129.9 (d, CH=CH), 130.4 (d, CH=CH), 132.1 (s, 1-C_{Ar}), 136.7 (d, 4,7-C_{Phen}), 146.1 (s, 10a,10b-C_{Phen}), 156.4 (s, 2,9-C_{Phen}), 160.5 (s, 4-C_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 2919 (aliph. CH), 1599, 1488 (arom. C=C), 1249, 1176 (C–O–C), 829 (1,4-disubst. benzene) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 500 (100) $[M]^+$, 364 (21) $[M - C_{10}H_{15}]^+$. MS (ESI, $CHCl_3$/MeOH): *m*/*z* (%) = 523 (17) $[M + Na]^+$, 501 (100) $[M + H]^+$. HR-MS (EI, 70 eV): *m*/*z* (%) calcd. for $C_{34}H_{32}N_2O_2$: 500.2464; found 500.2463 (Δ = 0.1 ppm), calcd. for $C_{33}{}^{13}CH_{32}N_2O_2$: 501.2497; found 501.2495 (Δ = 0.2 ppm). $C_{34}H_{32}N_2O_2$ (500.25): calcd. C 81.57, H 6.44, N 5.11. $C_{34}H_{32}N_2O_2 \cdot 1\ H_2O \cdot 0.2\ CHCl_3$ (500.25 + 18.01 + 23.87): calcd. C 75.71, H 6.32, N 5.16; found 75.55, H 6.38, N 4.88.

4,19-Dioxa-1,3(1,4)-dibenzena-2(2,9)-1,10-phenanthrolina-cyclononadecaphan-9-ene (25b): This compound was synthesised by the procedure described above for 4,15-dioxa-1,3(1,4)-dibenzena-2(2,9)-1,10-phenanthrolina-cyclopentadecaphan-7-ene (**25a**) from 2,9-bis[4-(oct-7-enyloxy)phenyl]-1,10-phenanthroline (**22b**, 66 mg, 113 μmol) and benzylidene-bis(tricyclohexylphosphane)dichlororuthenium (Grubbs type I catalyst, 7 mg, 9 μmol, 8 mol-%) in dry dichloromethane (120 mL). After filtration through basic aluminium oxide, the crude product (30 mg, 51 μmol) was analysed by ESI-MS. The ring-closing metathesis was not fully accomplished, so the crude product was again dissolved in dichloromethane (60 mL) and, after addition of benzylidene-bis(tricyclohexylphosphane)dichlororuthenium (Grubbs type I catalyst, 4 mg, 5 μmol, 10 mol-%), stirred for 3 d. Filtration through basic aluminium oxide was followed by evaporation of the solvent in vacuo to yield yellow crystals (25 mg, 45 μmol, 87%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.36–1.54 (m, 12 H, CH_2), 1.85 (m_c, 4 H, OCH_2CH_2), 2.02–2.12 (m, 4 H, CH_2CH=), 4.15 (m_c with t, ^3J = 7.0 Hz, 4 H, OCH_2), 5.39 (m_c, 0.7 H, CH=CH_{cis}*), 5.45 (m_c, 1.3 H, CH=CH_{trans}*), 7.11 (m_c, 4 H, 3,5-C_{Ar}H), 7.71 (s, 2 H, 5,6-C_{Phen}H), 8.04 (d, ^3J = 8.3 Hz, 2 H, 3,8-C_{Phen}), 8.23 (d, ^3J = 8.4 Hz, 2 H, 4,7-C_{Phen}H), 8.39 (m_c with d, ^3J = 8.8 Hz, 4 H, 2,6-C_{Ar}H) ppm. The assignments marked with * may be reversed. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.7, 27.5, 28.3, 28.4, 29.1, 29.6 (t, CH_2), 30.1 (t, OCH_2CH_2), 32.5 (t, CH_2CH=), 68.2 (t, OCH_2), 115.3 (d, 3,5-C_{Ar}), 119.3 (d, 3,8-C_{Phen}), 125.5 (d, 5,6-C_{Phen}), 127.4 (s, 4a,6a-C_{Phen}), 129.0 (d, 2,6-C_{Ar}), 129.4 (d, CH=CH), 130.5 (s, 1-C_{Ar}), 136.6 (d, 4,7-C_{Phen}), 146.1 (s, 10a,10b-C_{Phen}), 156.4 (s, 2,9-C_{Phen}), 160.2 (s, 4-C_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 2929 (aliph. CH), 1512, 1381 (arom. C=C), 1260, 1107, 1024 (C–O–C) cm^{-1}. MS (ESI, $CHCl_3$/MeOH): *m*/*z* (%) = 557 (100) $[M + H]^+$. MS (EI, 70 eV): *m*/*z* (%) = 556 (100) $[M]^+$, 364 (99) $[C_{24}H_{14}N_2O_4]^+$. HR-MS (ESI, $CHCl_3$/MeOH): $C_{38}H_{40}N_2O_2$ (556.31) calcd. for $C_{38}H_{40}N_2O_2 + H^+$: 557.3163; found 557.3142 (Δ = 3.8 ppm), calcd. for $C_{37}{}^{13}CH_{40}N_2O_2 + H^+$: 558.3195; found 558.3191 (Δ = 0.7 ppm). HR-MS (EI, 70 eV): calcd. for $C_{38}H_{40}N_2O_2$: 556.3090; found 556.3078 (Δ = 2.2 ppm), calcd. for $C_{37}{}^{13}CH_{40}N_2O_2$: 557.3123; found 557.3117 (Δ = 1.1 ppm).

4,23-Dioxa-1,3(1,4)-dibenzena-2(2,9)-1,10-phenanthrolina-cyclotricosaphan-11-ene (25c): This compound was synthesised by the procedure described above for 4,15-dioxa-1,3(1,4)-dibenzena-2(2,9)-1,10-phenanthrolina-cyclopentadecaphan-7-ene (**25a**), from 2,9-bis[4-(dec-9-enyloxy)phenyl]-1,10-phenanthroline (**22c**, 105 mg, 164 μmol) and benzylidene-bis(tricyclohexylphosphane)dichlororuthenium (Grubbs type I catalyst, 10.2 mg, 13.0 μmol, 8 mol-%) in dry dichloromethane (175 mL). The crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 2:1, R_f = 0.26) to yield yellow crystals (35 mg, 57.2 μmol, 35%) m.p. 101 °C. ^{1}H NMR (100 MHz, $CDCl_3$): δ = 1.33–1.43 (m, 16 H, CH_2), 1.51 (m_c, 4 H, $OCH_2CH_2CH_2$), 1.82–1.88 (m, 4 H, OCH_2CH_2), 1.99–2.09 (m, 4 H, CH_2CH=), 4.09 (t, ^3J = 7.0 Hz, 4 H, OCH_2), 5.37 (m_c, 0.7 H, CH=CH_{cis}*), 5.44 (m_c, 1.3 H, CH=CH_{trans}*), 7.11 (m_c with d, ^3J = 8.7 Hz, 4 H, 3,5-C_{Ar}H), 7.71 (s, 2 H, 5,6-C_{Phen}H), 8.05 (m_c with d, ^3J = 8.3 Hz, 2 H, 3,8-C_{Phen}H), 8.22 (d, ^3J = 8.4 Hz, 2 H, 4,7-C_{Phen}H), 8.43 (m_c, 4 H, 2,6-C_{Ar}H) ppm. The assignments marked with * may be reversed. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.9, 26.0, 27.4, 28.6, 29.1, 29.3, 29.5 (t, CH_2), 30.0 (t, OCH_2CH_2), 32.5 (t, CH_2CH=), 68.1 (t, OCH_2), 114.9 (d, 3,5-C_{Ar}), 119.2 (d, 3,8-C_{Phen}), 125.5 (d, 5,6-C_{Phen}), 127.5 (s, 4a,6a-C_{Phen}), 129.0 (d, 2,6-C_{Ar}), 129.9 (d, CH=CH), 130.4 (d, CH=CH), 132.1 (s, 1-C_{Ar}), 136.7 (d, 4,7-C_{Phen}), 146.1 (s, 10a,10b-C_{Phen}), 156.4 (s, 2,9-C_{Phen}), 160.5 (s, 4-C_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 2924 (aliph. CH), 1654, 1564, 1459 (arom. C=C), 1247, 1014 (C–O–C), 834 (1,4-disubst. benzene) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 612 (94) $[M]^+$, 569 (12) $[C_{40}H_{45}N_2O_2]^+$, 515 (24) $[C_{35}H_{35}N_2O_2]^+$, 377 (42) $[C_{25}H_{17}N_2O_2]^+$, 365, 364 (51, 100) $[C_{24}H_{16}N_2O_2]^+$. HR-MS (EI, 70 eV): $C_{42}H_{48}N_2O_2$, calcd. 612.3716; found 612.3716 (Δ = 0 ppm), $C_{41}{}^{13}CH_{48}N_2O_2$, calcd. 613.3749; found 613.3746 (Δ = 0.6 ppm).

Cyclopropanation: Under argon, copper(I) triflate hemibenzene complex (ca. 2.0 to 3.5 mg, +/–0.01 mg) was placed in a vial, and indene [**28**, 440 equiv. based on copper(I)], and the ligands **1b**, **2a**, **3b** or **4a**–**c** (1.2 equiv.) dissolved in 1,2-dichloroethane (c = 0.01 mol L^{-1}) were added. After addition of ethyl diazoacetate (**26**, 50 equiv.), the mixture was stirred at room temp. for 24 h. At the beginning of the reaction, quick evolution of gas was frequently noticed. After filtration of the mixture through silica gel with diethyl ether as eluent, most of the solvent mixture was evaporated in vacuo until ca. 5 mL remained. 1,2-Dichloroethane was added to give ca. 10 mL of solution. After addition of *n*-hexadecane (ca. 25 mg, +/–0.01 mg) as GC standard, the products were analysed by GC: HP-5, 30 m × 320 μm × 0.25 μm, 80 °C for 5 min, 10 °C min^{-1} until 140 °C, 1 min, 2 °C min^{-1} until 160 °C, 1 min, 20 °C min^{-1} until 240 °C, 20 min.

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[1] See textbooks of biochemistry, e.g., D. Voet, J. G. Voet, C. W. Pratt, *Lehrbuch der Biochemie*, Wiley-VCH, Weinheim, **2002**.
[2] Concave geometry is a major factor in host–guest recognition. Most molecules are "potato shaped" and thus convex. In order to be complementary to such a molecule as a guest, host molecules have to exhibit concave areas. For references see books on supramolecular chemistry, for instance refs.[3–5]
[3] J. L. Atwood, J. W. Steed (Eds.), *Encyclopedia of Supramolecular Chemistry*, Marcel Dekker, New York, **2004**.
[4] J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, John Wiley & Sons, Chichester, New York, Weinheim, Brisbane, Singapore, Toronto, **2000**.

[5] J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, New York, Basel, Cambridge, Tokyo, **1995**.
[6] U. Lüning, *Liebigs Ann. Chem.* **1987**, 949–955.
[7] U. Lüning, M. Müller, M. Gelbert, K. Peters, H. G. v. Schnering, M. Keller, *Chem. Ber.* **1994**, *127*, 2297–2306.
[8] M. Hagen, U. Lüning, *Chem. Ber./Recueil* **1997**, *130*, 231–234.
[9] M. Gelbert, U. Lüning, *Supramol. Chem.* **2001**, *12*, 435–444.
[10] B. Meynhardt, U. Lüning, C. Wolff, C. Näther, *Eur. J. Org. Chem.* **1999**, 2327–2335.
[11] F. Löffler, M. Hagen, U. Lüning, *Synlett* **1999**, 1826–1828.
[12] U. Lüning, M. Müller, *Liebigs Ann. Chem.* **1989**, 367–374.
[13] U. Lüning, M. Müller, *Chem. Ber.* **1990**, *123*, 643–645.
[14] H. Ross, U. Lüning, *Tetrahedron Lett.* **1997**, *38*, 4539–4542.
[15] F. Löffler, U. Lüning, G. Gohar, *New J. Chem.* **2000**, *24*, 935–938.
[16] M. Bühl, F. Terstegen, F. Löffler, B. Meynhardt, S. Kierse, M. Müller, C. Näther, U. Lüning, *Eur. J. Org. Chem.* **2001**, 2151–2160.
[17] U. Lüning, F. Fahrenkrug, *Eur. J. Org. Chem.* **2006**, 916–923.
[18] S. Konrad, M. Bolte, C. Näther, U. Lüning, *Eur. J. Org. Chem.* **2006**, 4717–4730.
[19] S. Konrad, C. Näther, U. Lüning, *Eur. J. Org. Chem.* **2005**, 2330–2337.
[20] J. Lewis, T. D. O'Donoghue, *J. Chem. Soc., Dalton Trans.* **1980**, 736–742.
[21] M. Yamada, Y. Nakamura, S. Kuroda, I. Shimao, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2710–2712.
[22] U. Lüning, F. Fahrenkrug, M. Hagen, *Eur. J. Org. Chem.* **2001**, 2161–2163.
[23] P. H. Buist, J. M. Findlay, G. Leger, R. A. Pon, *Tetrahedron Lett.* **1987**, *28*, 3891–3894.
[24] K. Hiroya, N. Suzuki, A. Yahuhara, Y. Egawa, A. Kasano, T. Sakamoto, *J. Chem. Soc. Perkin Trans. 1* **2000**, 4339–4346.
[25] I. Thomsen, K. B. G. Torssell, *Acta Chem. Scand.* **1991**, *45*, 539–542.
[26] G. L. Lange, C. Gottardo, *Synth. Commun.* **1990**, *20*, 1473–1479.
[27] M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der organischen Chemie*, 5th ed., Georg Thieme Verlag, Stuttgart, New York, **1995**.

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