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Concave Reagents

Enantiopure Chiral Concave 1,10-Phenanthrolines[‡]

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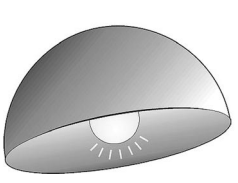
Abstract: Chiral information has been introduced into concave 1,10-phenanthrolines of different ring sizes by using a 2,7-disubstituted naphthalene bridgehead, which causes axial chirality. A tetraphenolic 2-(dihydroxynaphthyl)-9-(dihydroxyphenyl)-1,10-phenanthroline was synthesized as a key intermediate. Two strategies were followed to obtain the bimacrocyclic chiral concave 1,10-phenanthrolines: quadruple Williamson ether synthesis or alkenylation of the OH groups and subsequent ring-closing metathesis followed by hydrogenation. The overall yields of bimacrocyles **19** were 10 to 17 % starting from the respective Suzuki coupling of the substituted arenes **11** and **13** to 2,9-dichloro-1,10-phenanthroline (**5**). Racemic mixtures of the three concave 1,10-phenanthrolines **19** were separated by using chiral high-performance liquid chromatography (HPLC) techniques, and their absolute stereochemistry was assigned by comparison of simulated and experimental circular dichroism (CD) spectra. The enantiopure concave 1,10-phenanthrolines were used as ligands in a copper-catalysed cyclopropanation, and their selectivity was determined by chiral gas chromatography (GC).

Introduction

Numerous chemical transformations are carried out selectively with the help of enzymes in the living cell.[1] An important feature for this selectivity is geometry. The catalytic functionalities are embedded in a specially shielded area of the respective protein: the active site. Concave reagents (see Figure 1) copy this geometry by incorporating a catalytic centre into a bimacrocycle.[2–4] Previous work has shown that the chemo-,[5] regio-[6] and stereoselectivity[7] of catalytic reactions can be controlled by using bimacrocyclic concave reagents.

To also control enantioselectivity[9] – as enzymes do due to their chiral structure – concave reagents have to be enantiomerically pure. There are several ways of introducing chiral information into a catalyst. Often, chiral substituents are attached; however, a problem emerges in the case of concave reagents. If a chiral substituent was attached to these usually bimacrocyclic reagents, an attachment at the outside of the bimacrocycle would normally have little influence on the active site in the interior. However, if a substituent was attached on the inside, the cavity would be filled and the substrates would no longer be able to approach the catalytic site.

Therefore, we have chosen a different approach and have designed the whole molecule asymmetrically. This can be performed by introducing axial chirality by using nonsymmetric bridgeheads in the bimacrocycle. This approach has been successful for concave N-heterocyclic carbenes (NHC).[10] By exchanging one of the usual phenyl bridgeheads for a naphthalene, a chiral NHC precursor (Figure 2) was synthesized. By chromatography,[11,12] separation of the enantiomers was possible.[13]



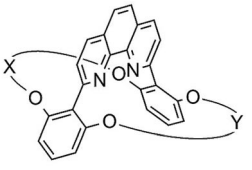


Figure 1. The geometry of a concave reagent resembles that of a light bulb in a lampshade with the light bulb being the active centre and the shade being the concave shielding. One class of such concave reagents are the concave 1,10-phenanthrolines. They are built up by attaching two bridgeheads to positions 2 and 9 of 1,10-phenanthroline and then connecting the *ortho*-positions of the bridgeheads to yield a bimacrocyclic concave 1,10-phenanthroline (X, Y = polymethylene or polyethylene glycol).[8]

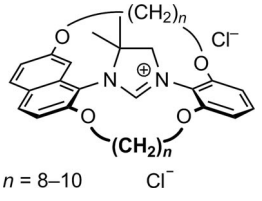


Figure 2. Configurationally stable chiral concave NHC precursor.[13]

In this work, we have adopted this strategy for the synthesis of chiral concave 1,10-phenanthrolines, which contain two nitrogen atoms. A concave 1,10-phenanthroline may react as a base or a base catalyst but even more as a chelating ligand for transition-metal ions. There are numerous reactions that may

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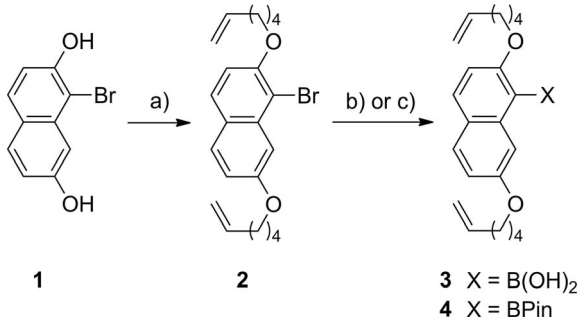
be catalyzed by complexes of 1,10-phenanthrolines. In the past, we have been able to improve the diastereoselectivity of cyclopropanations up to >99:1 by the concave shielding in concave 1,10-phenanthrolines.[7] In addition, with enantiomerically pure concave 1,10-phenanthrolines, enantioselectivity can be expected in these catalyses.

Results and Discussion

Two slightly different pathways have previously been developed to synthesize concave 1,10-phenanthrolines: the first involves a tetraphenol as intermediate and uses a quadruple Williamson ether synthesis to build up the macrocycle.[8] The second approach connects bridgeheads carrying alkenyl substituents to the phenanthroline by Suzuki couplings first, followed by ring-closing metathesis and hydrogenation. Although the second route requires more steps, the overall yields were better.[14]

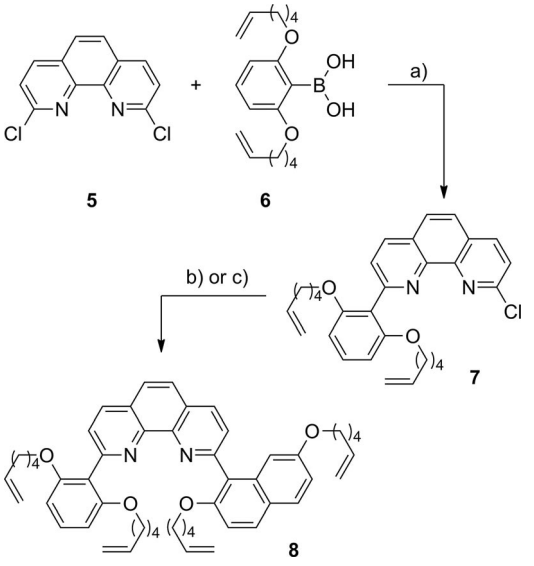
To transfer this second approach to chiral concave 1,10-phenanthrolines, a 2,7-dialkenylated naphthaleneboronic acid **3** or the respective pinacol ester of the boronic acid **4**, needed to be synthesized (Scheme 1).



Scheme 1. Synthesis of the 2,7-dialkenylated naphthalene building blocks **3** and **4** (Pin = $OCMe_2CMe_2O$). Reagents and conditions: (a) 5-hexen-1-ol, PPh_3, diisopropyl azodicarboxylate (DIAD), THF, 74 %; (b) 1. *n*BuLi, THF; 2. $B(OMe)_3$; 3. H_2O, crude product; (c) 1. *n*BuLi, THF; 2. $B(OMe)_3$; 3. pinacol, 79 %.

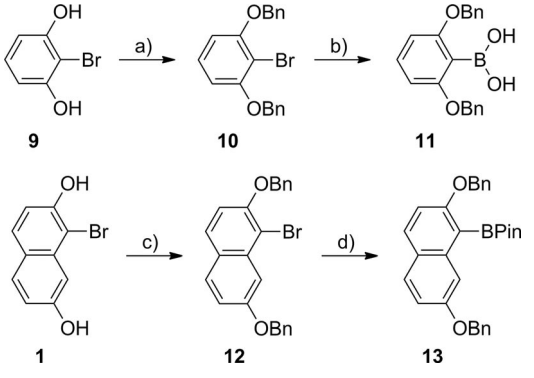
Respective boronic acids or esters can be coupled with 2,9-dihalogeno-1,10-phenanthrolines.[15,16] By using one equivalent of phenylboronic acid **6** (accessed through the Mitsunobu reaction; see the Supporting Information) first and subsequently one equivalent of a respective naphthalene derivative **3** or **4**, the tetraalkenylated 1,10-phenanthroline **8** was synthesized in 43 or 42 % overall yield, respectively (Scheme 2).

After isolation of product **8**, NMR spectroscopic data showed that an isomerization of the terminal alkenyl groups from terminal to internal alkenes (10–20 %) had occurred during the Suzuki coupling reaction of the naphthyl building block. This was confirmed by subsequent ring-closing metathesis, after which MS spectroscopy showed additional smaller bimacrocycles. Considering that a mixture of bimacrocycles of different ring sizes would be an obstacle to the enantioseparation of the final products and, moreover, because the stereoselective effect of the macrocycles in the cyclopropanation reaction was to be examined in relation to their ring sizes, alkene isomerization had to be avoided. Therefore, we decided to introduce the alkene moieties later in the synthesis by alkylation of a tetra-



Scheme 2. Synthesis of tetraalkenylated 1,10-phenanthroline **8** by Suzuki couplings. Reagents and conditions: (a) synthesized according to a reported procedure,[15] 66 %; (b) Method A: **3**, $Pd(PPh_3)_4$, $Ba(OH)_2$, 1,2-dimethoxyethane, H_2O, 65 %; (c) Method B: **4**, $Pd(OAc)_2$, 1,3-bis(diphenylphosphanyl)propane (dppp), $Ba(OH)_2$, 1,2-dimethoxyethane, H_2O, 64 %.

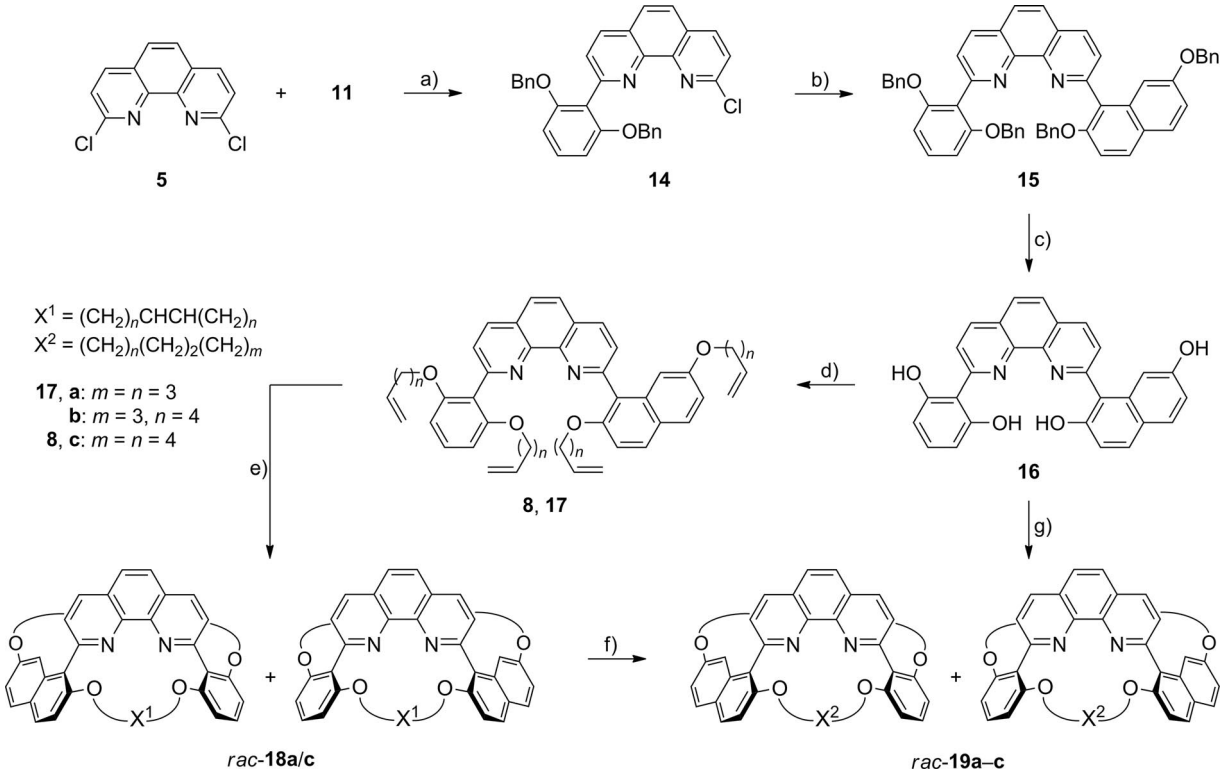
phenolic naphthyl-phenyl-1,10-phenanthroline **16**. Benzyl groups were chosen as protecting groups for the phenolic OH groups. Scheme 3 summarises the syntheses of benzyl protected phenylboronic acid **11** and naphthylboronic ester **13**, which were synthesized from the respective bromides **10** and **12**.



Scheme 3. Generation of aryl boronic acid **11** and boronic ester **13** (Pin = $OCMe_2CMe_2O$), precursors of the bridgeheads in the concave 1,10-phenanthrolines: Reagents and conditions: (a) benzyl bromide, K_2CO_3, acetone, 92 %; (b) 1. *n*BuLi, THF; 2. $B(OMe)_3$; 3. H_2O, 54 %; (c) benzyl bromide, K_2CO_3, acetone, 72 %; (d) 1. *n*BuLi, THF; 2. isopropoxyboronic acid pinacol ester, 51 %.

Using building blocks **11** and **13**, tetrabenzyl ether **15** could be synthesized by first coupling the phenyl moiety to position 2 (**14**, 59 %) and then the naphthyl unit to position 9 of 1,10-phenanthroline (**15**, 57 %; Scheme 4). Hydrogenation with palladium as catalyst gave tetraphenol **16** in 94 % yield.

Quadruple Williamson ether syntheses with 5-bromo-1-pentene or 6-bromo-1-hexene gave the respective precursors **17** and **8** (81 % each) for ring-closing metatheses. Double ring-closure was performed with Grubbs' catalyst I in dichloro-



Scheme 4. Concave 1,10-phenanthrolines **19** can be prepared from tetraphenol **16**. Reagents and conditions: (a) $Pd(PPh_3)_4$, Na_2CO_3, 1,2-dimethoxyethane, H_2O, 59 %; (b) **13**, $Pd(dppf)Cl_2$, $Ba(OH)_2$, 1,2-dimethoxyethane, H_2O, 57 %; (c) H_2, $Pd(OH)_2$/C, Pd/C, EtOAc, 94 %; (d) 5-bromo-1-pentene or 6-bromo-1-hexene, Cs_2CO_3, DMSO, 81 %; (e) Grubbs type I catalyst, CH_2Cl_2, *rac*-**18a** 78 %, *rac*-**18c** 84 %; (f) H_2, Pd/C, EtOAc, CH_2Cl_2, *rac*-**19a** 76 %, *rac*-**19c** 80 %; (g) 1,9-dibromononane, Cs_2CO_3, K_2CO_3, DMF, *rac*-**19b** 31 %.

methane, and bimacrocyclic 1,10-phenanthrolines *rac*-**18a** and *rac*-**18c** were obtained as *E*/*Z* mixtures in 78 and 84 % yield, respectively. The final step of the synthetic sequence (Scheme 4) was the hydrogenation of the double bonds, in which all *E* or *Z* isomers were transformed into the same saturated products *rac*-**19a** (76 %) or *rac*-**19c** (80 %).

With this approach, homolog free bimacrocycles with an even number of CH_2 groups in the alkylene chains (*rac*-**19a**: n = 8, *rac*-**19c**: n = 10) could be synthesized in 100–200 mg amounts. For *rac*-**19b**, with an odd number of CH_2 groups (n = 9), a different route had to be chosen. Nonamethylene chains were directly introduced by Williamson ether syntheses using 1,9-dibromononane as bridging reagent under high dilution conditions. *rac*-**19b** was isolated in 31 % yield.

The racemic mixtures of the three bimacrocycles *rac*-**19** were then separated by chiral HPLC to give the enantiopure compounds (Figure 3).

For characterization and determination of the absolute configuration of the enantiopure bimacrocycles **19**, circular dichroism (CD) spectra were recorded. Figure 4 shows the CD spectra of the smallest bimacrocycles **19a**. Between 200 and 350 nm, four Cotton effects could be observed. The largest Cotton effect was measured at 230 nm with a negative maximal polarization of –169 mol^{-1} dm cm^{-1} for enantiomer (*M*)-**19a** and a positive maximal polarization of +156 mol^{-1} dm^3 cm^{-1} for enantiomer (*P*)-**19a**.[17] Thus, the expected mirrored shape of the polarization of the two enantiomers could be observed.

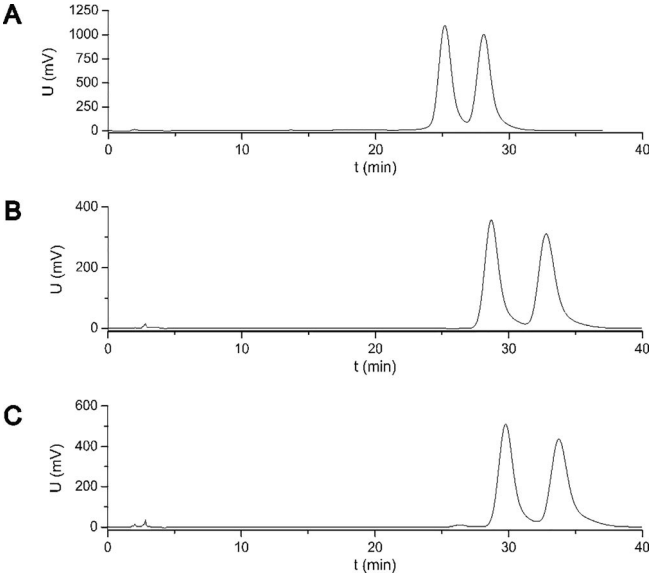


Figure 3. Chiral HPLC chromatograms of (A) *rac*-**19a** [t_R = 25.3 (*M*), 28.1 (*P*) min]; (B) *rac*-**19b** [t_R = 28.7 (*M*), 32.8 (*P*) min]; (C) *rac*-**19c** [t_R = 29.8 (*M*), 33.8 (*P*) min]. For experimental details, see experimental section.

The absolute configuration could be determined by comparing the recorded spectra of the bicyclic 1,10-phenanthrolines **19a** with the calculated CD spectrum of the *M*-isomer of **19a**. For this purpose, the structure of (*M*)-**19a** was optimized by

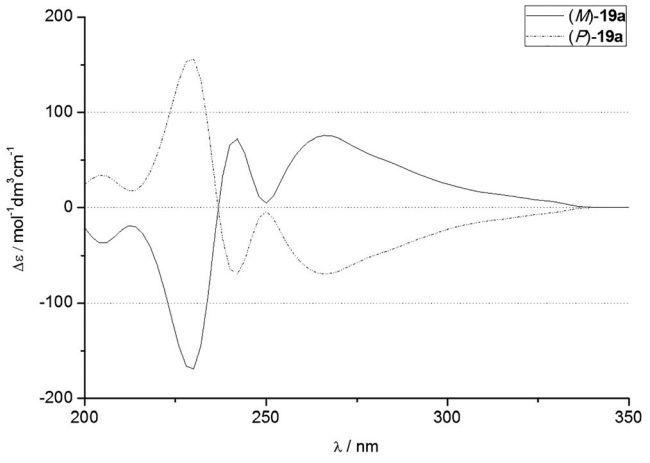


Figure 4. Recorded CD spectra of **19a** in MeCN [*c*((*M*)-**19a**) = 0.451 mM, *c*((*P*)-**19a**) = 0.378 mM].

means of B3LYP-D3[18,19] calculations using the 6-31G*[20] basis set. Subsequently, the CD spectrum of (*M*)-**19a** was simulated with the time-dependent density functional theory (TD-DFT) using the B3LYP functional and the 6-31G* basis set. No solvent model was taken into account for the calculation of the spectrum. A comparison of the simulated CD spectrum of (*M*)-**19a** (Figure 5) with the measured CD spectrum of **19a** (Figure 4), which shows a minimum at 230 nm and maxima at 242 and 266 nm, reveals that the corresponding compound represents the *M*-isomer.

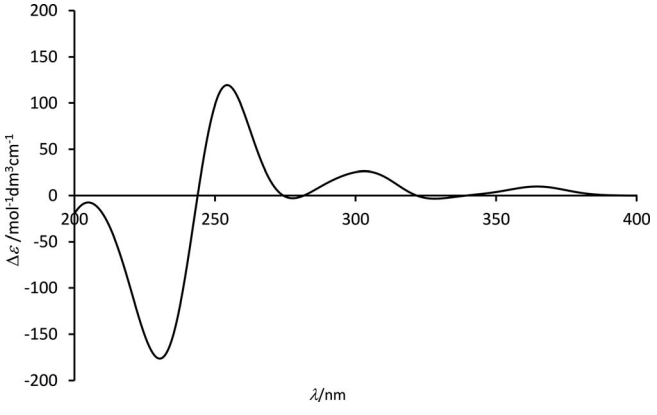


Figure 5. Simulated CD spectrum of (*M*)-**19a** using TD-DFT-B3LYP/6-31G*.

The recorded CD spectra of the larger bicyclic 1,10-phenanthrolines **19b** and **19c** are very similar to those of **19a**. As their structures only differ in length changes of the oligomethylene chains by one or two methylene groups, the assignment of the enantiomers can be executed in analogy to **19a** (Figure 6 and Figure 7).

For complete characterization, the specific optical rotations of all enantiomers were determined as listed in Table 1.

Finally, the stereoselective effect of the enantiopure concave 1,10-phenanthrolines **19** as ligands in the copper(I) catalyzed cyclopropanation reaction of indene[21] (**21**) with ethyl diazoacetate (EDA, **20**) was examined.[22] In this reaction, four stereoisomers of cyclopropane **22** (Scheme 5) can be formed (the

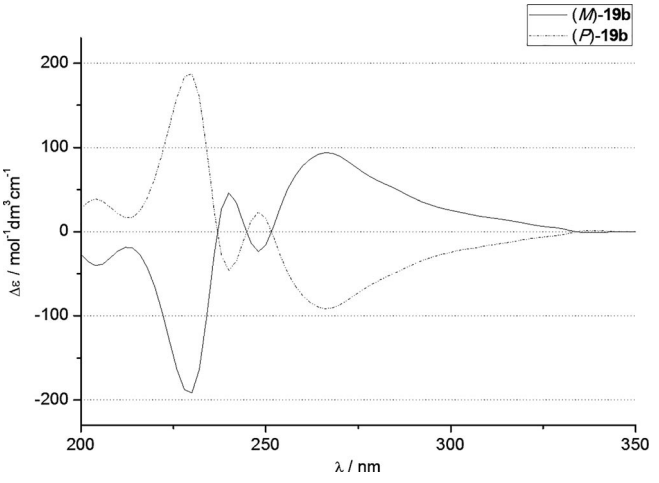


Figure 6. Recorded CD spectra of **19b** in MeCN [*c*((*M*)-**19b**) = 0.334 mM, *c*((*P*)-**19b**) = 0.371 mM].

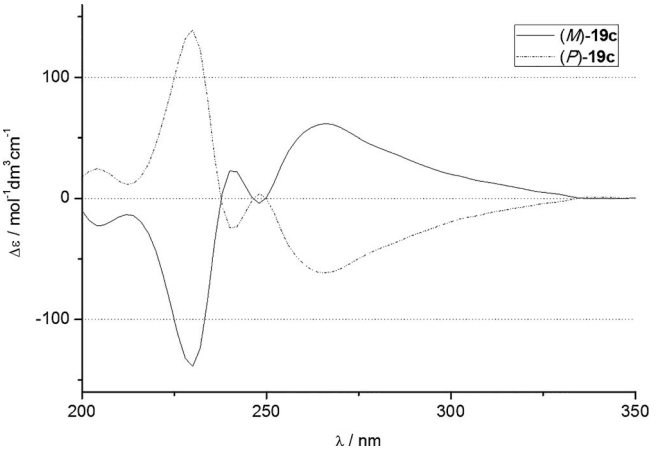


Figure 7. Recorded CD spectra of **19c** in MeCN [*c*((*M*)-**19c**) = 0.398 mM, *c*((*P*)-**19c**) = 0.300 mM].

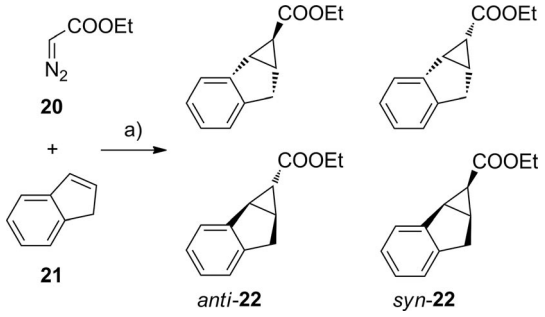
Table 1. Optical rotations of the different concave enantiomers measured in acetonitrile.

	19a	**19b**	**19c**
$[\alpha]_D^{20}$(*M*)-isomer [°mL dm^{-1} g^{-1}]	+495°	+466°	+320°
Concentration [mM]	0.43	0.54	0.52
$[\alpha]_D^{20}$ (*P*)-isomer [°mL dm^{-1} g^{-1}]	–500°	–434°	–314°
Concentration [mM]	0.45	0.37	0.42

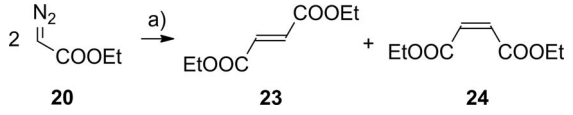
diastereomeric cyclopropanes *anti*-**22** and *syn*-**22** with their respective enantiomers).

In addition to the cyclopropanation, a side reaction between two molecules of EDA **20** can occur, which leads to the formation of the diastereomers diethyl fumarate (**23**) and diethyl maleate (**24**) (Scheme 6).

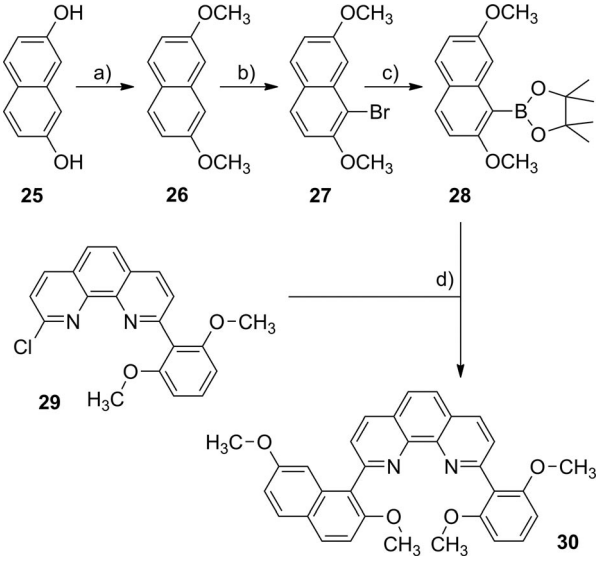
The reaction was carried out with the respective *M*-enantiomers of the bicyclic 1,10-phenanthrolines **19**. The results were compared to the cyclopropanations without any ligand and in the presence of the acyclic 1,10-phenanthroline **30**, which was synthesized in analogy to 1,10-phenanthroline **15** (Scheme 7).



Scheme 5. Cyclopropanation of indene (**21**) by ethyl diazoacetate (**20**) yields four products, two diastereomeric pairs of enantiomers *anti*-**22** and *syn*-**22**. (a) Copper(I) triflate, ligands.



Scheme 6. Side reaction of the cyclopropanation of alkenes by ethyl diazoacetate (**20**): dimerization of the carbene subunit to give diethyl fumarate (**23**) and diethyl maleate (**24**). (a) Copper(I) triflate, ligand.



Scheme 7. Synthesis of reference substance **30**: Reagents and conditions: (a) Me_2SO_4, KOH, H_2O, 53 %; (b) NBS, $LiClO_4$•SiO_2, CH_2Cl_2, 81 %; (c) 1. *n*BuLi, THF, 2. isopropoxyboronic acid pinacol ester, 74 %; (d) $Pd(dppf)Cl_2$, $Ba(OH)_2$, 1,2-dimethoxyethane, H_2O, 42 %.

The results of the cyclopropanation reactions, which were carried out as batch reactions, are shown in Table 2 and Table 3.

Concerning *syn*/*anti*-diastereoselectivity for the formation of the cyclopropanes **22**, the nonchiral, acyclic ligand **30** showed the best selectivity in favor of the *anti*-cyclopropane *anti*-**22**. By comparison with experiments in which nonchiral concave 1,10-phenanthrolines were used,[7] *anti*-selectivity was expected (*syn*-/*anti*-ratios up to <1:99). But the chiral concave 1,10-phenanthrolines **19** showed less pronounced diastereoselectivities. In contrast, only the largest bimacrocycle **19c** led to a preferred formation of the *anti*-cyclopropane *anti*-**22** with an *syn*/*anti*-diastereoselectivity similar to the cyclopropanation

Table 2. Diastereomeric and enantiomeric ratios and overall yields of the cyclopropanes **22** measured by chiral GC. The absolute configuration of the enantiomers was not assigned. E1 and E2 correlate with the respective retention times in the gas chromatograms.

Ligand	*syn*/*anti*	*syn*-*E*1/*E*2	*anti*-*E*1/*E*2	Yield (%)
–	26:74	48:52	50:50	39
30	15:85	50:50	50:50	25
19a	54:46	53:47	55:45	19
19b	61:39	47:53	60:40	26
19c	28:72	37:63	77:23	37

Table 3. Ratios and overall yields of the side products diethyl fumarate (**23**) and diethyl maleate (**24**) observed in the cyclopropanation of indene (**21**) with EDA (**20**), measured by GC.

Ligand	**23**/**24**	Yield (%)
–	59:41	10
30	66:34	9
19a	31:69	10
19b	29:71	8
19c	35:65	9

without any ligand present. The smaller ligands **19a** and **19b** even favored the *syn*-product (*syn*-**22**), albeit with little selectivity.

Concerning enantioselectivity, the largest chiral phenanthroline **19c** performed best, with ratios of enantiomers of approximately 1:2 (*syn*-**22** *E*1/*E*2) and 1:3 (*anti*-**22** *E*1/*E*2). The other ligands **19a**, **19b** and of course **30** did not influence the enantioselectivity of *syn*-**22** *E*1/E2 in a significant way (*ee* determinations possess an error of at least 2–3 %). However, for *anti*-**22** *E*1/*E*2, an increasing enantioselectivity could be observed with increasing ring size.

The side reaction in copper(I) catalyzed cyclopropanations is the reaction of the copper carbenoid – formed by reaction of a first molecule of diazoacetate with the copper(I) ion followed by expulsion of nitrogen – with a second molecule of diazoacetate instead of the alkene, leading to the formation of diastereomeric fumarates (**23**) and maleates (**24**) (Scheme 6). The *E*/*Z* selectivity of the formation of these two alkenes **23** and **24** is also influenced by the nature of the ligands bound to the copper(I) ions. Without any ligand or in the presence of non-macrocyclic ligand **30**, *E*-selectivity (i.e., the preferred formation of fumarate **23**) was found. Previously, a preference for the *E*-isomer was found for most concave 1,10-phenanthrolines.[7] Only a calixarene-based 1,10-phenanthroline[23] showed reversed selectivities,[7] both for the formation of maleate and fumarate but also in the cyclopropanations themselves. A combined experimental and theoretical investigation suggested a different orientation of the reaction partners in symmetric concave 1,10-phenanthrolines and in distorted bridged calixarenes.[24] The reversed *E*/*Z*-selectivities for the fumarate/maleate formation and the small *anti*-selectivity (smaller than in the absence of any ligand) in the cyclopropanation of indene in the reactions with chiral concave 1,10-phenanthrolines **19** as ligands suggest distorted transition states, which may resemble those in the calixarene case, especially for the smaller chiral concave 1,10-phenanthrolines **19a** and **19b**.

Conclusions

Chiral concave 1,10-phenanthrolines **19a**–**c** of different ring sizes have been synthesized. First, two bridgeheads were added to 2,9-dichloro-1,10-phenanthroline (**5**) by Suzuki couplings with bis(benzyloxy)phenylboronic acid **11** and bis(benzyloxy)naphthyl boronic acid pinacol ester **13**. Next, the oxygen substituents were deprotected. Double ring-closure formed the bimacrocycles **19a**–**c** either by fourfold Williamson ether synthesis or by attaching alkenyl groups, followed by double ring-closing metathesis and hydrogenation of the remaining double bonds. The overall yields of *rac*-**19a**–**c** were 10–17 %. The enantioseparation of the racemic mixtures was possible using chiral HPLC. Absolute configuration could be determined by comparing experimental and simulated CD spectra of (*M*)-**19a**. First investigations of the stereoselective influence of (*M*)-**19a**–**c** as ligands in the copper(I)-catalyzed cyclopropanation reaction of indene (**21**) with ethyl diazoacetate (EDA, **20**) were carried out. The use of the largest chiral concave 1,10-phenanthroline **19c** led to the highest diastereo- and enantioselectivities. Further investigations have to be made to fully understand the observed selectivities.

Experimental Section

General Remarks: The following chemicals were obtained commercially and used without further purification: basic aluminium oxide (Macherey–Nagel), benzyl bromide (ABCR), benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (Grubbs type I catalyst; Aldrich), [1,1′-bis(diphenylphosphanyl)ferrocene]dichloropalladium(II) (ABCR), 1,3-bis(diphenylphosphanyl)propane (Aldrich), 6-bromo-1-hexene (Matrix Scientific), 5-bromo-1-pentene (Matrix Scientific), *n*-butyllithium (Aldrich), Celite (Sigma–Aldrich), copper(I) triflate benzene complex (Aldrich), 1,9-dibromononane (ABCR), 2,7-dihydroxynaphthalene (**25**, Merck), diisopropyl azodicarboxylate (Alfa Aesar), dimethyl sulfate (Sigma–Aldrich), dimethyl sulfoxide (anhydrous, Sigma–Aldrich), ethyl diazoacetate (Aldrich, contains ≥ 13 wt.-% dichloromethane), 5-hexen-1-ol (Alfa Aesar), indene (Aldrich), isopropoxyboronic acid pinacol ester (ABCR), lithium perchlorate (Sigma–Aldrich), *N*-bromosuccinimide (Merck), *N*,*N*-dimethylformamide (anhydrous; Sigma–Aldrich), palladium diacetate (in-house chemical supply), palladium on charcoal (10 %; ABCR), Pearlmans catalyst [20 % $Pd(OH)_2$ on charcoal (50 % water); Alfa Aesar], pinacol (Alfa Aesar), tetrakis(triphenylphosphine)palladium(0) (ABCR), trimethyl borate (Fluka), triphenylphosphine (in-house chemical supply). 1-Bromo-2,7-dihydroxynaphthalene (**1**),[25] 2,9-dichloro-1,10-phenanthroline (**5**),[26,27] 2,6-bis(hex-5-enyloxy)phenylboronic acid (**6**),[16] 2-[2,6-bis(hex-5-enyloxy)phenyl]-9-chloro-1,10-phenanthroline (**7**),[15] 2-bromoresorcinol (**9**)[28,29] and 2-chloro-9-(2,6-dimethoxyphenyl)-1,10-phenanthroline (**29**)[16] were synthesized according to reported procedures. Anhydrous solvents were obtained with suitable desiccants. Other solvents were distilled before use. Column chromatography was carried out with silica gel (Macherey–Nagel, particle size 0.04–0.063 mm). Melting points were measured with a Gallenkamp MPD350.BM2.5 instrument or a Electrothermal Melting Point Apparatus. NMR spectra were recorded with a Bruker DRX 500 or Avance 600 instrument. Assignments are supported by COSY, HSQC, and HMBC. Even when obtained by DEPT, the type of ^{13}C signal is always listed as singlet, doublet, etc. All chemical shifts are referenced to tetramethylsilane or the residual proton or carbon of the solvent. Signal assignment in NMR spectra: for assignment of the signals, "phen" for phenanthroline, "naph" for naphthyl, "ar" for phenyl, and "bn" for benzyl are used. In the case of the bimacrocyclic 1,10-phenanthrolines **18** and **19**, aromatic signals were assigned in analogy to the acyclic precursors, to allow better comparison. EI/CI mass spectra were recorded with a Finnigan MAT 8200 and MAT 8230. ESI mass spectra were recorded with an Applied Biosystems Mariner Spectrometry Workstation. MALDI-TOF mass spectra were recorded with a Bruker-Daltronics Biflex III with CI-CCA (4-chloro-α-cyano-cinnamic acid) as matrix. HRMS were recorded with a Bruker-Daltronics APEX 3 FT-ICR mass spectrometer (7.05 T, ESI, CH_2Cl_2/MeOH/HCOOH). IR spectra were recorded with a Perkin–Elmer Spectrum 100 spectrometer equipped with an MKII Golden GateTM Single Reflection ATR unit. Elemental analyses were carried out with a Euro EA 3000 Elemental Analyzer from Euro Vector. Preparative separation of the enantiomers of **19** was conducted with a VWR-Hitachi HPLC-system Elite LaChrom (L-2130 pump system, L-2400 UV-detector) connected to a Waters In-Line degasser AF, a Waters 717plus autosampler and a Foxy R1 fraction collector. A 8 × 250 mm DELTA-RP S column (Macherey–Nagel) protected by a 8 × 10 mm guard column of the same material was used. The chiral separation was achieved by elution with acetonitrile/water/triethylamine (80:20:0.1) with a flow rate of 3 mL/min. The CD Spectra of **19** were recorded with a Jasco J-720 CD spectrometer. The specific optical rotation was measured with a Perkin–Elmer Polarimeter 241 at 589.3 nm. The analyses of the cyclopropanation reactions were conducted with a Varian 3400 gas chromatograph using a 25.0 m × 250 µm Hydrodex-β-PM column (Macherey–Nagel, T_{column} = 120 °C), helium as carrier gas (10 psi), and a Varian 4290 Integrator.

1-Bromo-2,7-bis(hex-5-enyloxy)naphthalene (2): Under nitrogen, 1-bromo-2,7-dihydroxynaphthalene (**1**; 2.54 g, 10.6 mmol), 5-hexen-1-ol (3.83 mL, 3.19 g, 31.9 mmol) and triphenylphosphine (5.58 g, 21.3 mmol) were dissolved in anhydrous tetrahydrofuran (55 mL). The solution was cooled to 0 °C and diisopropyl azodicarboxylate (6.70 mL, 6.43 g, 31.9 mmol) was added slowly. The solution was then stirred at room temp. for 19 h. The reaction mixture was hydrolyzed with water (31 mL), then sodium hydroxide solution (2 M, 8 mL) was added. After stirring for 30 min and separation of the layers, the aqueous layer was extracted twice with diethyl ether. The combined organic layer was washed with brine and dried with magnesium sulfate. The solvents were evaporated and the residue was dissolved in dichloromethane (15 mL). Cyclohexane (200 mL) was added and the mixture was cooled to 1 °C overnight. The precipitated triphenylphosphine oxide was filtered off and washed with cyclohexane. The solvent of the filtrate was evaporated and the crude product was purified by column chromatography (silica gel; cyclohexane/ethyl acetate, 9:1; R_f = 0.54) to obtain **2** (3.19 g, 7.91 mmol, 74 %) as a slightly yellow solid, m.p. 26–27 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, ^3J = 8.9 Hz, 1 H, 4-$C_{naph}H$), 7.65 (d, ^3J = 8.9 Hz, 1 H, 5-$C_{naph}H$), 7.48 (d, ^4J = 2.4 Hz, 1 H, 8-$C_{naph}H$), 7.07 (d, ^3J = 8.9 Hz, 1 H, 3-$C_{naph}H$), 7.03 (dd, ^3J = 8.9 Hz, ^4J = 2.4 Hz, 1 H, 6-$C_{naph}H$), 5.85 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.6 Hz, 2 H, CH=CH_2), 5.05 (ddt, ^3J = 17.0 Hz, ^2J = 2.0 Hz, ^4J = 1.7 Hz, 2 H, CH=$CH H_{trans}$), 4.98 (ddt, ^3J = 10.2 Hz, ^2J = 2.0 Hz, ^4J = 1.2 Hz, 2 H, CH=$CH H_{cis}$), 4.15 (m_c, 4 H, OCH_2), 2.16 (m_c, 4 H, CH_2CH=), 1.89 (m_c, 4 H, OCH_2 CH_2), 1.65 (m, 4 H, $OCH_2CH_2CH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.8 (s, 7-C_{naph}), 153.9 (s, 2-C_{naph}), 138.6, 138.7 (2d, CH=CH_2), 134.7 (s, 8a-C_{naph}), 129.7 (d, 5-C_{naph}), 128.4 (d, 4-C_{naph}), 125.2 (s, 4a-C_{naph}), 117.5 (d, 6-C_{naph}), 114.8 (t, CH=CH_2), 112.3 (d, 3-C_{naph}), 108.3 (s, 1-C_{naph}), 105.4 (d, 8-C_{naph}), 69.9 (t, 2-C_{naph}-OCH_2), 67.9 (t, 7-C_{naph}-OCH_2), 33.4, 33.5 (2t, CH_2CH=), 28.7, 28.9 (2t, OCH_2CH_2), 25.3, 25.4 (2t, $OCH_2CH_2CH_2$) ppm. IR (ATR): $\tilde{\nu}$ = 3069 (arom. C–H), 2943, 2917, 2864 (aliph. C–H), 1624, 1508 (arom. C–C),

1261, 1213, 1072 (C–O–C), 1001, 907, 828, 787 (arom. C–H) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 404, 402 (15, 13) $[M]^{+\cdot}$, 240, 238 (100, 98) $[M - C_{12}H_{20}]^{+\cdot}$. MS (CI, isobutane): *m/z* (%) = 405, 403 (99, 100) $[M + H]^+$. $C_{22}H_{27}BrO_2$ (402.12): calcd. C 65.51, H 6.75; found C 65.69, H 6.81.

2,7-Bis(hex-5-enyloxy)naphthylboronic Acid (3): Under nitrogen, 1-bromo-2,7-bis(hex-5-enyloxy)naphthalene (**2**; 1.00 g, 2.48 mmol) was dissolved in anhydrous tetrahydrofuran (16 mL) and cooled to –78 °C. *n*-Butyllithium (2.5 M in hexanes, 1.10 mL, 2.75 mmol) was added slowly and the mixture was stirred at –78 °C for 1 h. Trimethyl borate (830 µL, 770 mg, 7.40 mmol) was then added and the mixture was stirred for 2 h while warming to room temp. After the addition of water (7 mL), the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 10 mL) and the combined organic layer was washed with brine and dried with magnesium sulfate. The solvent was evaporated to give the crude product **3** (976 mg) as a slightly yellow, oily solid. The product could be confirmed by mass spectra: MS (ESI, MeOH, measured as dimethyl ester): *m/z* = 815 $[2M + Na]^+$, 419 $[M + Na]^+$. Further spectroscopic data could not be obtained due to the instability of the product, e.g., with NMR spectroscopy only the decomposition product 2,7-bis(hex-5-enyloxy)naphthalene could be observed.

Pinacol 2,7-Bis(hex-5-enyloxy)naphthylboronate (4): Under nitrogen, 1-bromo-2,7-bis(hex-5-enyloxy)naphthalene (**2**; 2.00 g, 4.96 mmol) was dissolved in anhydrous tetrahydrofuran (50 mL) and cooled to –78 °C. *n*-Butyllithium (2.5 M in hexanes, 2.2 mL, 5.5 mmol) was added slowly and the mixture was stirred at –78 °C for 1 h. Trimethyl borate (700 µL, 644 mg, 6.20 mmol) was then added and the mixture was stirred for 2 h while warming to room temp. Pinacol (876 mg, 7.43 mmol) was added and the reaction mixture was heated to 60 °C for 1 h. After cooling to room temp., the suspension was filtered through Celite before the solvent was evaporated. The crude product was purified by column chromatography (silica gel; cyclohexane/ethyl acetate, 19:1; R_f = 0.29) to give **4** (1.77 g, 3.93 mmol, 79 %) as a yellow liquid. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, ^3J = 8.9 Hz, 1 H, 4-C_{naph}H), 7.61 (d, ^3J = 8.9 Hz, 1 H, 5-C_{naph}H), 7.31 (d, ^4J = 2.4 Hz, 1 H, 8-C_{naph}H), 7.01 (d, ^3J = 8.9 Hz, 1 H, 3-C_{naph}H), 6.94 (dd, ^3J = 8.9 Hz, ^4J = 2.4 Hz, 1 H, 6-C_{naph}H), 5.84 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.6 Hz, 2 H, C*H*=CH_2), 5.04 (m_c, 2 H, CH=CHH_{trans}), 4.97 (m_c, 2 H, CH=CHH_{cis}), 4.06 (m_c, 4 H, OCH_2), 2.13 (m_c, 4 H, CH_2CH=), 1.84 (m_c, 4 H, OCH$_2$CH_2), 1.61 (m_c, 4 H, OCH$_2$CH$_2$CH_2), 1.46 (s, 12 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.9 (s, 2-C_{naph}), 157.6 (s, 7-C_{naph}), 138.8 (s, 8a-C_{naph}), 138.60, 138.62 (2d, *C*H=CH_2), 131.4 (d, 4-C_{naph}), 129.5 (d, 5-C_{naph}), 124.3 (s, 4a-C_{naph}), 116.4 (d, 6-C_{naph}), 114.65, 114.74 (2t, CH=CH_2), 111.1 (d, 3-C_{naph}), 105.9 (d, 8-C_{naph}), 83.7 [s, O*C*(CH$_3$)$_2$], 68.8 (t, 2-C_{naph}-OCH$_2$), 67.5 (t, 7-C_{naph}-OCH$_2$), 33.5, 33.6 (2t, CH_2CH=), 28.7, 29.2 (2t, OCH$_2$CH), 25.41, 25.49 (2t, OCH$_2$CH$_2$CH$_2$), 25.0 (q, CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3076 (arom. C–H), 2976, 2932, 2866 (aliph. C–H), 1622, 1509 (arom. C–C), 1445 (aliph. C–H), 1236, 1211, 1142, 1070 (C–O–C), 994, 907, 849, 826 (arom. C–H) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 450 (100) $[M]^{+\cdot}$, 368 (10) $[M - C_6H_{10}]^{+\cdot}$, 324 $[M - C_6H_{12}BO_2]^{+\cdot}$. MS (CI, isobutane): *m/z* (%) = 451 (100) $[M + H]^+$. $C_{28}H_{39}BO_4$ (450.29): calcd. C 74.66, H 8.73; found C 74.82, H 9.12.

2-[2,7-Bis(hex-5-enyloxy)naphthyl]-9-[2,6-bis(hex-5-enyloxy)-phenyl]-1,10-phenanthroline (8). Method A: Under nitrogen, 2-[2,6-bis(hex-5-enyloxy)phenyl]-9-chloro-1,10-phenanthroline (**7**; 208 mg, 427 µmol), the crude product of 2,7-bis(hex-5-enyloxy)naphthylboronic acid (**3**; 303 mg, ≤ 770 µmol), tetrakis(triphenylphosphine)palladium(0) (47 mg, 41 µmol) and barium hydroxide octahydrate (201 mg, 637 µmol) were dissolved in 1,2-dimethoxyethane (12 mL) and water (3 mL). The mixture was heated to 80 °C for 40 h. After cooling to room temp., dichloromethane and water (20 mL each) were added to the solution and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 20 mL) and the combined organic layer was washed with half conc. aqueous sodium chloride solution, dried with magnesium sulphate, and the solvent was evaporated. The residue was filtered through basic aluminium oxide with dichloromethane. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel; dichloromethane/methanol, 98:2; R_f = 0.05) to give **8** (215 mg, 277 µmol, 65 %) as a slightly yellow solid. The product contained isomers with migrated double bonds (see main text).

Method B: Under nitrogen, **7** (63.0 mg, 129 µmol), 2,7-bis(hex-5-enyloxy)naphthylboronic acid pinacol ester (**4**; 70.0 mg, 155 µmol), palladium diacetate (3.0 mg, 13 µmol), 1,3-bis(diphenylphosphanyl)propane (dppp, 11 mg, 26 µmol) and barium hydroxide octahydrate (63.0 mg, 200 µmol) were dissolved in 1,2-dimethoxyethane (4 mL) and water (1 mL). The mixture was heated to 60 °C for 24 h. After cooling to room temp., dichloromethane and water (10 mL each) were added to the solution and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 10 mL) and the combined organic layer was washed with half conc. aqueous sodium chloride solution, dried with magnesium sulfate and the solvent was evaporated. The residue was filtered through basic aluminium oxide with dichloromethane. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel; dichloromethane/methanol, 98:2; R_f = 0.05) to give **8** (64 mg, 83 µmol, 64 %) as a slightly yellow solid. The product contained isomers with migrated double bonds (see main text).

Method C: Under nitrogen, **16** (250 mg, 560 µmol) and cesium carbonate (2.40 g, 7.38 mmol) were dissolved in anhydrous dimethyl sulfoxide (11 mL). After adding 6-bromo-1-hexene (980 µL, 1.19 g, 7.28 mmol) the solution was stirred at room temp. for 3 d. The solvent was then distilled off in vacuo and the light-brown residue was dissolved in water and dichloromethane (20 mL each), the layers were separated and the aqueous layer was extracted with dichloromethane (4 × 5 mL). The combined organic layer was washed with aqueous sodium hydroxide solution (2 M, 20 mL), dried with magnesium sulfate and the solvent was evaporated. The yellow-brown crude product was purified by column chromatography (silica gel; dichloromethane/methanol, 98:2; R_f = 0.05) to give **8** (350 mg, 452 µmol, 81 %) as a yellow solid, m.p. 143–144 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.31 (d, ^3J = 8.2 Hz, 1 H, 4-C_{phen}H), 8.23 (d, ^3J = 8.2 Hz, 1 H, 7-C_{phen}H), 7.87 (s, 2 H, 5,6-C_{phen}H), 7.78 (d, ^3J = 9.0 Hz, 1 H, 4-C_{naph}H), 7.73 (d, ^3J = 8.2 Hz, 1 H, 3-C_{phen}H), 7.68 (d, ^3J = 8.9 Hz, 1 H, 5-C_{naph}H), 7.65 (d, ^3J = 8.2 Hz, 1 H, 8-C_{phen}H), 7.21 (t, ^3J = 8.4 Hz, 1 H, 4-C_{ar}H), 7.16 (d, ^3J = 9.0 Hz, 1 H, 3-C_{naph}H), 6.95 (dd, ^3J = 8.9 Hz, ^4J = 2.4 Hz, 1 H, 6-C_{naph}H), 6.91 (d, ^4J = 2.4 Hz, 1 H, 8-C_{naph}H), 6.59 (d, ^3J = 8.4 Hz, 2 H, 3,5-C_{ar}H), 5.68 [ddt, ^3J = 17.1 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 1 H, 7-C_{naph}O(CH$_2$)$_4$C*H*=], 5.59–5.47 [m, 3 H, 2-C_{naph}O(CH$_2$)$_4$C*H*=, C_{ar}O(CH$_2$)$_4$C*H*=], 4.90 [ddt, ^3J = 17.1 Hz, ^2J = 2.0 Hz, ^4J = 1.6 Hz, 1 H, 7-C_{naph}O(CH$_2$)$_4$CH=CHH_{trans}], 4.86 [ddt, ^3J = 10.2 Hz, ^2J = 2.0 Hz, ^4J = 1.2 Hz, 1 H, 7-C_{naph}-O(CH$_2$)$_4$CH=CHH_{cis}], 4.81–4.73 [m, 6 H, 2-C_{naph}O(CH$_2$)$_3$CH=CH_2, C_{ar}O(CH$_2$)$_3$CH=CH_2], 4.02 (t, ^3J = 6.4 Hz, 2 H, 2-C_{naph}OCH_2), 3.89 (t, ^3J = 6.5 Hz, 4 H, C_{ar}OCH_2), 3.70 (t, ^3J = 6.4 Hz, 2 H, 7-C_{naph}OCH_2), 1.93 [tdt, ^3J = 7.4 Hz, ^3J = 6.7 Hz, ^4J = 1.3 Hz, 2 H, 7-C_{naph}-O(CH$_2$)$_3$CH_2], 1.86–1.80 [m, 2 H, 2-C_{naph}O(CH$_2$)$_3$CH_2], 1.80–1.73 [m, 4 H, C_{ar}O(CH$_2$)$_3$CH_2], 1.60–1.50 (m, 4 H, C_{naph}OCH$_2$CH_2), 1.50–1.43 (m, 4 H, C_{ar}OCH$_2$CH_2), 1.39–1.31 [m, 2 H, 7-C_{naph}O(CH$_2$)$_2$CH_2], 1.28–1.20 [m, 2 H, 2-C_{naph}O(CH$_2$)$_2$CH_2], 1.20–1.13 [m, 4 H, C_{ar}O(CH$_2$)$_2$CH_2] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.1 (s, 2,6-C_{ar}), 157.8 (s, 7-C_{naph}), 157.0 (s, 2-C_{phen}), 155.4 (s, 9-C_{phen}), 155.0 (s, 2-C_{naph}), 146.7 (s, 10b-C_{phen}), 146.3 (s, 10a-C_{Phen}), 138.8, 138.7 (2d, *C*H=CH_2), 135.6 (d, 4-

C_{Phen}), 135.0 (s, 8a-C_{naph}), 134.9 (d, 7-C_{phen}), 129.9 (d, 4-C_{naph}), 129.7 (d, 4-C_{ar}), 129.4 (d, 5-C_{naph}), 127.54 (s, 6a-C_{phen}), 127.48 (s, 4a-C_{phen}), 126.6 (d, 6-C_{phen}), 126.5 (d, 8-C_{phen}*), 126.4 (d, 3-C_{phen}*), 126.1 (d, 5-C_{phen}), 124.9 (s, 4a-C_{naph}), 124.7 (s, 1-C_{naph}), 121.6 (s, 1-C_{ar}), 116.5 (d, 6-C_{naph}), 114.6 [t, 7-$C_{naph}O(CH_2)_4CH{=}CH_2$], 114.3 [t, 2-$C_{naph}O(CH_2)_4CH{=}CH_2$], 114.2 [t, $C_{ar}O(CH_2)_4CH{=}CH_2$], 112.8 (d, 3-C_{naph}), 106.6 (d, 3,5-C_{ar}), 105.0 (d, 8-C_{naph}), 69.7 (t, 2-$C_{naph}OCH_2$), 69.3 (t, $C_{ar}OCH_2$), 67.6 (t, 7-$C_{naph}OCH_2$), 33.6 [t, 7-$C_{naph}O(CH_2)_3CH_2$], 33.3 [t, 2-$C_{naph}O(CH_2)_3CH_2$], 33.2 [t, $C_{ar}O(CH_2)_3CH_2$], 28.9 (t, 2-$C_{naph}OCH_2CH_2$), 28.7 (t, 7-$C_{naph}OCH_2CH_2$), 28.5 (t, $C_{ar}OCH_2CH_2$), 25.4 [t, 7-$C_{naph}O(CH_2)_2CH_2$], 25.2 [t, 2-$C_{naph}O(CH_2)_2CH_2$], 25.1 [t, $C_{ar}O(CH_2)_2CH_2$] ppm. * Assignment may be reversed. IR (ATR): $\tilde{\nu}$ = 3074 (arom. C–H), 2936, 2862 (aliph. C–H), 1622, 1588 (arom. C–C), 1455 (aliph. C–H), 1237, 1223, 1209, 1090, 1070 (C–O–C), 992, 906, 856, 826 (arom. C–H) cm^{-1}. MS (ESI, $CHCl_3$/MeOH): *m/z* = 797 $[M + Na]^+$, 775 $[M + H]^+$. $C_{52}H_{58}N_2O_4$ (744.44): calcd. C 80.59, H 7.54, N 3.61; found C 80.51, H 7.75, N 3.70.

1,3-Bis(benzyloxy)-2-bromobenzene (10): Under nitrogen, 2-bromoresorcinol (**9**; 10.0 g, 52.9 mmol) and anhydrous potassium carbonate (16.1 g, 116 mmol) were suspended in anhydrous acetone (120 mL). After addition of benzyl bromide (14.0 mL, 20.2 g, 118 mmol), the mixture was heated to reflux for 6.5 h. After cooling, dichloromethane (100 mL) was added and the salt was filtered off and washed with additional dichloromethane (150 mL). The solvent was evaporated and the residue was recrystallized from cyclohexane (70 mL) to give **10** (17.9 g, 48.5 mmol, 92 %) as a white solid, m.p. 96–97 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50–7.46 (m, 4 H, 2,6-C_{bn}H), 7.40–7.36 (m, 4 H, 3,5-C_{bn}H), 7.33–7.29 (m, 2 H, 4-C_{bn}H), 7.14 (t, ^3J = 8.3 Hz, 1 H, 4-C_{ar}H), 6.60 (d, ^3J = 8.3 Hz, 2 H, 3,5-C_{ar}H), 5.16 (s, 4 H, OCH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.6 (s, 2,6-C_{ar}), 136.8 (s, 1-C_{bn}), 128.7 (d, 3,5-C_{bn}), 128.2 (d, 4-C_{ar}), 128.0 (d, 4-C_{bn}), 127.1 (d, 2,6-C_{bn}), 106.9 (d, 3,5-C_{ar}), 102.9 (s, 1-C_{ar}), 71.1 (t, OCH_2) ppm. IR (ATR): $\tilde{\nu}$ = 3065, 3032 (arom. C–H), 2907, 2862 (aliph. C–H), 1606, 1593, 1571 (arom. C–C), 1474, 1449 (aliph. C–H), 1257 (C–O–C), 1035 (C–Br), 760, 727, 692 (arom. C–H) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 370, 368 (14, 16) $[M]^{+\cdot}$, 289 (3) $[M - Br]^+$, 181 (100) $[M - C_7H_8BrO]^+$. MS (CI, isobutane): *m/z* (%) = 371, 369 (100, 99) $[M + H]^+$. $C_{20}H_{17}BrO_2$ (368.04): calcd. C 65.05, H 4.64; found C 65.26, H 4.62.

2,6-Bis(benzyloxy)phenylboronic Acid (11): Under nitrogen, 1,3-bis(benzyloxy)-2-bromobenzene (**10**; 10.0 g, 27.1 mmol) was dissolved in anhydrous tetrahydrofuran (65 mL) and cooled to –78 °C. Slowly, *n*-butyllithium (2.5 M in hexanes, 11.9 mL, 29.8 mmol) was added over a period of 1 h and the mixture was stirred at –78 °C for another 40 min. Trimethyl borate (6.0 mL, 5.6 g, 54 mmol) was then added and the mixture was stirred for 16 h while warming to room temp. After the addition of water and diethyl ether (50 mL each), the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 30 mL) and the combined organic layer was washed with brine (30 mL) and dried with magnesium sulfate. Approximately 25 g of silica gel was added, and the solvent was evaporated in vacuo. The resulting product was loaded on silica gel and transferred to the top of a silica gel filled column. Subsequent column chromatography (silica gel; cyclohexane/ethyl acetate, 3:1; R_f = 0.30) gave **11** (4.91 g, 14.7 mmol, 54 %) as a yellow solid, m.p. 127 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.33 (m, 11 H, C_{bn}H, 4-C_{Ar}H), 7.20 (s, 2 H, O*H*), 6.71 (d, ^3J = 8.4 Hz, 2 H, 3,5-C_{ar}H), 5.14 (s, 4 H, OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.9 (s, 2,6-C_{ar}), 135.7 (s, 1-C_{bn}), 133.1 (d, 4-C_{ar}), 129.1 (d, 3,5-C_{bn}), 128.8 (d, 4-C_{bn}), 127.9 (d, 2,6-C_{bn}), 106.1 (d, 3,5-C_{ar}), 71.4 (t, OCH_2) ppm. IR (ATR): $\tilde{\nu}$ = 3499 (OH), 3030 (arom. C–H), 2954, 2889 (aliph. C–H), 1590, 1574 (arom. C–C), 1474, 1454, 1317 (aliph. C–H), 1233, 1091, 1058 (C–O–C), 789, 744, 692 (arom. C–H) cm^{-1}. MS (ESI, MeOH, measured as dimethyl ester): *m/z* = 385 $[M + Na]^+$. $C_{20}H_{19}BO_4$ (334.14): calcd. C 71.88, H 5.73; found C 71.81, H 5.81.

2,7-Bis(benzyloxy)-1-bromonaphthalene (12): Under nitrogen, 1-bromo-2,7-dihydroxynaphthalene (**1**; 7.00 g, 29.3 mmol) and anhydrous potassium carbonate (9.70 g, 70.3 mmol) were suspended in anhydrous acetone (80 mL) and heated to 60 °C for 1 h. After addition of benzyl bromide (8.40 mL, 12.0 g, 70.3 mmol), the black mixture was heated to 60 °C for 2 h. After cooling, dichloromethane (120 mL) was added and the salt was filtered off. The solvent was evaporated and the black, oily residue was recrystallized first from *n*-hexane/dichloromethane (6:1) and then from *n*-hexane/dichloromethane (4:1). The still black crude product was purified by column chromatography (silica gel; cyclohexane/ethyl acetate, 19:1; R_f = 0.27) to give **12** (8.80 g, 21.0 mmol, 72 %) as a slightly yellow solid, m.p. 103 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67 (d, ^3J = 8.8 Hz, 1 H, 4-C_{naph}H), 7.66 (d, ^3J = 8.9 Hz, 1 H, 5-C_{naph}H), 7.63 (d, ^4J = 2.4 Hz, 1 H, 8-C_{naph}H), 7.54–7.50 (m, 4 H, 2,6-C_{bn}H), 7.43–7.37 (m, 4 H, 3,5-C_{bn}H), 7.37–7.30 (m, 2 H, 4-C_{bn}H), 7.11 (dd, ^3J = 8.9 Hz, ^4J = 2.4 Hz, 1 H, 6-C_{naph}H), 7.11 (d, ^3J = 8.8 Hz, 1 H, 3-C_{naph}H), 5.28 (s, 2 H, 2-$C_{naph}OCH_2$), 5.23 (s, 2 H, 7-$C_{naph}OCH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.6 (s, 7-C_{naph}), 153.7 (s, 2-C_{naph}), 136.9, 136.8 (2s, 1-C_{bn}), 134.8 (s, 8a-C_{naph}), 129.9 (d, 5-C_{naph}), 128.8, 128.7 (2d, 3,5-C_{bn}), 128.6 (d, 4-C_{naph}), 128.3, 128.1 (2d, 4-C_{bn}), 128.0 (d, 7-$C_{naph}OCH_2$-2,6-C_{bn}), 127.3 (d, 2-$C_{naph}OCH_2$-2,6-C_{bn}), 125.7 (s, 4a-C_{naph}), 117.9 (d, 6-C_{naph}), 113.0 (d, 3-C_{naph}), 109.0 (s, 1-C_{naph}), 106.2 (d, 8-C_{naph}), 71.8 (t, 2-$C_{naph}OCH_2$), 70.3 (t, 7-$C_{naph}OCH_2$) ppm. IR (ATR): $\tilde{\nu}$ = 3063, 3031 (arom. C–H), 2871 (aliph. C–H), 1626, 1603, 1509 (arom. C–C), 1453, 1379, 1346 (aliph. C–H), 1264, 1244, 1220, 1202, 1004 (C–O–C), 818, 727, 719, 692 (arom. C–H) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 420, 418 (100, 91) $[M]^{+\cdot}$, 339 (34) $[M - Br]^+$. MS (CI, isobutane): *m/z* (%) = 421, 419 (100, 94) $[M + H]^+$. $C_{24}H_{19}BrO_2$ (418.06): calcd. C 68.75, H 4.57; found C 68.69, H 4.55.

Pinacol 2,7-Bis(benzyloxy)naphthylboronate (13): Under nitrogen, 2,7-bis(benzyloxy)-1-bromonaphthalene (**12**; 2.00 g, 4.77 mmol) was dissolved in anhydrous tetrahydrofuran (90 mL) and cooled to –78 °C. *n*-Butyllithium (2.5 M in hexanes, 2.00 mL, 5.01 mmol) was added and the mixture was stirred at –78 °C for 1 h. Isopropoxyboronic acid pinacol ester (1.95 mL, 1.78 g, 9.54 mmol) was added and the mixture was stirred for 1.5 h while warming to room temp., followed by heating the mixture to 60 °C for 2.5 h. After cooling to room temp., water and diethyl ether (50 mL each) were added to the suspension and the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 30 mL) and the combined organic layer was washed with brine and dried with magnesium sulfate. The solvent was evaporated and the orange-brown residue was purified by column chromatography (silica gel; cyclohexane/ethyl acetate, 14:1; R_f = 0.19) to give **13** (1.13 g, 2.42 mmol, 51 %) as a white solid, m.p. 112 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (d, ^3J = 8.9 Hz, 1 H, 4-C_{naph}H), 7.66 (d, ^3J = 8.9 Hz, 1 H, 5-C_{naph}H), 7.55–7.52 (m, 2 H, 2-$C_{naph}OCH_2$-2,6-C_{bn}*H*), 7.51–7.46 (m, 3 H, 8-C_{naph}H, 7-$C_{naph}OCH_2$-2,6-C_{bn}*H*), 7.43–7.29 (m, 6 H, 3,4,5-C_{bn}H), 7.11 (d, ^3J = 8.9 Hz, 1 H, 3-C_{naph}H), 7.07 (dd, ^3J = 8.9 Hz, ^4J = 2.5 Hz, 1 H, 6-C_{naph}H), 5.20 (s, 2 H, 2-$C_{naph}OCH_2$), 5.17 (s, 2 H, 7-$C_{naph}OCH_2$), 1.38 (s, 12 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.7 (s, 2-C_{naph}), 157.5 (7-C_{naph}), 138.8 (s, 8a-C_{naph}), 137.5 (s, 2-C_{naph}-OCH_2-1-C_{bn}), 137.0 (s, 7-C_{naph}-OCH_2-1-C_{bn}), 131.6 (d, 4-C_{naph}), 129.6 (d, 5-C_{naph}), 128.6 (d, 2-C_{naph}-OCH_2-3,5-C_{bn}*[1]), 128.2 (d, 7-C_{naph}-OCH_2-3,5-C_{bn}*[1]), 127.9 (d, 2-C_{naph}-OCH_2-4-C_{bn}*[2]), 127.64 (d, 7-C_{naph}-OCH_2-4-C_{bn}*[2]), 127.57 (d, 2,6-C_{bn}), 124.8 (s, 4a-C_{naph}), 116.7 (d, 6-C_{naph}), 111.8 (d, 3-C_{naph}), 106.6 (d, 8-C_{naph}), 83.7 [s, $OC(CH_3)_2$], 71.2 (t, 2-C_{naph}-OCH_2), 69.8 (t, 7-C_{naph}-OCH_2), 25.0 (q, CH_3) ppm. *[1,*2] Assignments may be reversed, respectively. IR (ATR): $\tilde{\nu}$ = 3068 (arom. C–H), 2974, 2908, 2863 (aliph. C–H), 1621, 1595, 1575, 1511 (arom.

C–C), 1434, 1372, 1334, 1311 (aliph. C–H), 1238, 1207, 1139, 1064 (C–O–C), 1006, 833, 760, 734, 699 (arom. C–H) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 466 (100) $[M]^{+\cdot}$. MS (CI, isobutane): *m/z* (%) = 467 (100) $[M + H]^+$. $C_{30}H_{31}BO_4$ (466.23): calcd. C 77.26, H 6.70; found C 77.45, H 6.75.

2-[2,6-Bis(benzyloxy)phenyl]-9-chloro-1,10-phenanthroline (14): Under nitrogen, 2,9-dichloro-1,10-phenanthroline (**5**; 884 mg, 3.55 mmol), 2,6-bis(benzyloxy)phenylboronic acid (**11**; 1.30 g, 3.89 mmol), tetrakis(triphenylphosphine)palladium(0) (415 mg, 359 µmol) and sodium carbonate (1.13 g, 10.7 mmol) were dissolved in 1,2-dimethoxyethane (72 mL) and water (18 mL). The mixture was heated to 80 °C for 19 h. After cooling to room temp., dichloromethane and water were added and the layers were separated. The aqueous layer was extracted with dichloromethane three times, and the combined organic layer was washed with brine, dried with magnesium sulfate and the solvent was evaporated. The residue was filtered through basic aluminium oxide with dichloromethane. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel; dichloromethane/methanol, 199:1; R_f = 0.11) to give **14** (1.05 g, 2.09 mmol, 59 %) as a yellow solid, m.p. 169 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19 (d, ^3J = 8.4 Hz, 1 H, 7-C_{phen}H), 8.18 (d, ^3J = 8.2 Hz, 1 H, 4-C_{phen}H), 7.81 (d, ^3J = 8.2 Hz, 1 H, 3-C_{phen}H), 7.80 (d, ^3J = 8.7 Hz, 1 H, 5-C_{phen}H), 7.74 (d, ^3J = 8.7 Hz, 1 H, 6-C_{phen}H), 7.62 (d, ^3J = 8.4 Hz, 1 H, 8-C_{phen}H), 7.42–7.38 (m, 4 H, 2,6-C_{bn}H), 7.32 (t, ^3J = 8.4 Hz, 1 H, 4-C_{ar}H), 7.18–7.13 (m, 6 H, 3,4,5-C_{bn}H), 6.77 (d, ^3J = 8.4 Hz, 2 H, 3,5-C_{ar}H), 5.13 (s, 4 H, OCH_2) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.0 (s, 2,6-C_{ar}), 155.5 (s, 2-C_{phen}), 151.1 (s, 9-C_{phen}), 146.6 (s, 10a-C_{phen}), 145.0 (s, 10b-C_{phen}), 138.7 (d, 7-C_{phen}), 137.5 (s, 1-C_{bn}), 135.0 (d, 4-C_{phen}), 130.3 (d, 4-C_{ar}), 128.3, 127.9, 127.51, 127.46, 127.29, 127.25 (s, 5d, 3,4a,6a,5-C_{phen}, 2,3,4,5,6-C_{bn}), 125.3 (d, 6-C_{phen}), 123.9 (d, 8-C_{phen}), 121.1 (s, 1-C_{ar}), 106.9 (d, 3,5-C_{ar}), 71.1 (t, OCH_2) ppm. IR (ATR): $\tilde{\nu}$ = 3027 (arom. C–H), 2869 (aliph. C–H), 1580 (arom. C–C), 1480, 1450 (aliph. C–H), 1247, 1100, 1075 (C–O–C), 891, 848, 743, 697 (arom. C–H) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 502 (74) $[M]^{+\cdot}$, 395 (88) $[M - C_7H_7O]^+$, 290 (100) $[M - C_{14}H_{14}O_2]^{+\cdot}$. MS (CI, isobutane): *m/z* (%) = 503 (100) $[M + H]^+$. $C_{32}H_{23}ClN_2O_2$ (502.14): calcd. C 76.41, H 4.61, N 5.57; found C 76.21, H 4.73, N 5.53.

2-[2,7-Bis(benzyloxy)naphthyl]-9-[2,6-bis(benzyloxy)phenyl]-1,10-phenanthroline (15): Under nitrogen, **14** (270 mg, 536 µmol), 2,7-bis(benzyloxy)naphthylboronic acid pinacol ester (**13**; 375 mg, 804 µmol), [1,1′-bis(diphenylphosphanyl)ferrocene]dichloropalladium(II) (60 mg, 73 µmol) and barium hydroxide octahydrate (470 mg, 149 mmol) were dissolved in 1,2-dimethoxyethane (32 mL) and water (8 mL). The mixture was heated to 70 °C for 20 h. After cooling to room temp., dichloromethane and water (50 mL each) were added to the dark-green solution and the layers were separated. The aqueous layer was extracted with dichloromethane (5 × 50 mL) and the combined organic layer was washed with half conc. aqueous sodium chloride solution, dried with magnesium sulfate and the solvent was evaporated. The dark-green residue was filtered through basic aluminium oxide with dichloromethane. After evaporation of the solvent, the yellow crude product was purified by column chromatography (silica gel; dichloromethane/methanol, 98:2; R_f = 0.15) to give **15** (246 mg, 305 µmol, 57 %) as a slightly yellow solid, m.p. 188 °C. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 8.57 (d, ^3J = 8.2 Hz, 1 H, 4-C_{phen}H), 8.53 (d, ^3J = 8.2 Hz, 1 H, 7-C_{phen}H), 8.09 (m_c, 2 H, 5,6-C_{phen}H), 7.94 (d, ^3J = 9.1 Hz, 1 H, 4-C_{naph}H), 7.84 (d, ^3J = 9.0 Hz, 1 H, 5-C_{naph}H), 7.755 (d, ^3J = 8.2 Hz, 1 H, 8-C_{phen}H), 7.750 (d, ^3J = 8.2 Hz, 1 H, 3-C_{phen}H), 7.41 (d, ^3J = 9.1 Hz, 1 H, 3-C_{naph}H), 7.28 (t, ^3J = 8.5 Hz, 1 H, 4-C_{ar}H), 7.28–7.26 (m, 2 H, 2-C_{naph}OCH_2-2,6-$C_{bn}H$), 7.20–7.17 (m, 4 H, C_{ar}OCH_2-2,6-$C_{bn}H$), 7.09–7.04 (m, 4 H, 6-C_{naph}H, 2-C_{naph}OCH_2-3,4,5-$C_{bn}H$), 7.04–6.91 (m, 11 H, C_{ar}OCH_2-3,4,5-$C_{bn}H$, 7-C_{naph}OCH_2-$C_{bn}H$), 6.85 (d, ^4J = 2.3 Hz, 1 H, 8-C_{naph}H), 6.77 (d, ^3J = 8.5 Hz, 2 H, 3,5-C_{ar}H), 5.12 (s, 2 H, 2-C_{naph}OCH_2), 4.97 (s, 4 H, C_{ar}OCH_2), 4.72 (s, 2 H, 7-C_{naph}OCH_2) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 156.8 (s, 7-C_{naph}), 156.7 (s, 2,6-C_{ar}), 156.0 (s, 2-C_{phen}), 154.8 (s, 9-C_{phen}), 153.9 (s, 2-C_{naph}), 145.8 (s, 10b-C_{phen}), 145.6 (s, 10a-C_{phen}), 137.2 (s, 2-C_{naph}OCH_2-1-C_{bn}), 137.1 (s, C_{Ar}OCH_2-1-C_{bn}), 136.5 (s, 7-C_{naph}OCH_2-1-C_{bn}), 136.1 (d, 4-C_{phen}), 135.6 (d, 7-C_{phen}), 134.0 (s, 8a-C_{naph}), 129.7 (d, 4-C_{naph}), 129.64 (d, 4-C_{ar}), 129.60 (d, 5-C_{naph}), 128.1 (d, 2-C_{naph}OCH_2-3,5-C_{bn}), 127.98 (d, 7-C_{naph}OCH_2-3,5-C_{bn}), 127.96 (d, C_{ar}OCH_2-3,5-C_{bn}), 127.4 (d, 7-C_{naph}OCH_2-4-C_{bn}), 127.29 (br. d, 2-C_{naph}OCH_2-4-C_{bn}, 7-C_{naph}OCH_2-2,6-C_{bn}), 127.23 (s, 6a-C_{phen}), 127.17 (s, 4a-C_{phen}), 127.10 (d, C_{ar}OCH_2-4-C_{bn}), 127.07 (d, 2-C_{naph}OCH_2-2,6-C_{bn}), 126.8 (d, C_{ar}OCH_2-2,6-C_{bn}), 126.5 (d, 6-C_{phen}), 126.3 (d, 5-C_{phen}), 126.0 (d, 3-C_{phen}*), 125.8 (d, 8-C_{phen}*), 124.3 (s, 4a-C_{naph}), 123.8 (s, 1-C_{naph}), 120.5 (s, 1-C_{ar}), 116.1 (d, 6-C_{naph}), 112.8 (d, 3-C_{naph}), 106.2 (d, 3,5-C_{ar}), 105.2 (d, 8-C_{naph}), 70.0 (t, 2-C_{naph}-OCH_2), 69.4 (t, C_{ar}OCH_2), 69.2 (t, 7-C_{naph}OCH_2) ppm. * Assignment may be reversed. IR (ATR): $\tilde{\nu}$ = 3031 (arom. C–H), 2862 (aliph. C–H), 1621, 1591 (arom. C–C), 1510, 1496, 1447 (aliph. C–H), 1249, 1111 (C–O–C), 851, 826, 730, 694 (arom. C–H) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 806 (80) $[M]^{+\cdot}$, 715 (100) $[M - C_7H_7]^+$, 533 (33) $[M - C_{21}H_{21}]^+$. MS (CI, isobutane): *m/z* (%) = 807 (52) $[M + H]^+$. MS (ESI, $CHCl_3$/MeOH): *m/z* = 807 $[M + H]^+$. $C_{56}H_{42}N_2O_4$ (806.31): calcd. C 83.35, H 5.25, N 3.47; found C 83.64, H 5.20, N 3.42.

2-(2,7-Dihydroxynaphthyl)-9-(2,6-dihydroxyphenyl)-1,10-phenanthroline (16): In ethyl acetate (45 mL), most of **15** (601 mg, 745 µmol) was dissolved by heating. Nitrogen was then bubbled through the solution for 10 min while cooling to room temp. Pearlman's catalyst [20 % $Pd(OH)_2$ on charcoal (50 % water), 205 mg, 146 µmol] and palladium on charcoal (10 %, 146 mg, 149 µmol) were added and nitrogen was bubbled through the suspension for another 10 min. Hydrogen was then bubbled through the suspension for 2 h. The suspension was stirred under hydrogen for 20 h, then the catalyst was removed by centrifugation, and the catalyst was heated again with hot ethyl acetate/methanol (1:1, 6 × 20 mL), followed by additional centrifugation. The solvent of the combined organic layer was evaporated to give **16** (311 mg, 697 µmol, 94 %) as an orange-red solid, m.p. 230 °C (decomposition). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 13.21 (s, 2 H, C_{ar}O*H*), 10.12 (s, 1 H, 2-C_{naph}O*H*), 9.36 (s, 1 H, 7-C_{naph}O*H*), 9.03 (d, ^3J = 8.9 Hz, 1 H, 8-C_{phen}H), 8.67 (d, ^3J = 8.9 Hz, 1 H, 7-C_{phen}H), 8.64 (d, ^3J = 8.3 Hz, 1 H, 4-C_{phen}H), 8.12 (d, ^3J = 8.8 Hz, 1 H, 5-C_{phen}H), 8.09 (d, ^3J = 8.8 Hz, 1 H, 6-C_{phen}H), 7.88 (d, ^3J = 8.2 Hz, 1 H, 3-C_{phen}H), 7.79 (d, ^3J = 8.8 Hz, 1 H, 4-C_{naph}H), 7.73 (d, ^3J = 8.8 Hz, 1 H, 5-C_{naph}H), 7.11 (d, ^3J = 8.8 Hz, 1 H, 3-C_{naph}H), 7.07 (t, ^3J = 8.1 Hz, 1 H, 4-C_{ar}H), 6.86 (dd, ^3J = 8.8 Hz, ^4J = 2.1 Hz, 1 H, 6-C_{naph}H), 6.76 (d, ^4J = 2.1 Hz, 1 H, 8-C_{naph}H), 6.40 (d, ^3J = 8.1 Hz, 2 H, 3,5-C_{ar}H) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 159.9 (s, 2,6-C_{ar}), 157.5 (s, 2-C_{phen}), 156.4 (s, 9-C_{phen}), 156.1 (s, 7-C_{naph}), 153.3 (s, 2-C_{naph}), 143.5 (s, 10b-C_{phen}), 141.3 (s, 10a-C_{phen}), 137.4 (d, 7-C_{phen}), 136.7 (d, 4-C_{phen}), 134.7 (s, 8a-C_{naph}), 131.4 (d, 4-C_{ar}), 130.0 (d, 4-C_{naph}), 129.7 (d, 5-C_{naph}), 127.2 (s, 4a-C_{phen}), 127.0 (d, 3-C_{phen}), 126.3 (d, 5-C_{phen}), 126.2 (s, 6a-C_{phen}), 125.7 (d, 6-C_{phen}), 124.5 (d, 8-C_{phen}), 122.8 (s, 4a-C_{naph}), 118.7 (s, 1-C_{naph}), 115.3 (d, 6-C_{naph}), 115.1 (d, 3-C_{naph}), 107.9 (s, 1-C_{ar}), 107.5 (d, 3,5-C_{ar}), 105.6 (d, 8-C_{naph}) ppm. IR (ATR): $\tilde{\nu}$ = 3307 (O–H), 1621, 1604, 1576 (arom. C-C), 1496, 1470 (O-H), 1348, 1227, 1197 (arom.), 852, 787, 734 (arom. C-H) cm^{-1}. MS (MALDI, Cl-CCA): *m/z* = 447 $[M + H]^+$. $C_{28}H_{18}N_2O_4$ (446.13): calcd. C 75.33, H 4.06, N 6.27; found C 74.84, H 4.30, N 5.92.

2-[2,7-Bis(pent-4-enyloxy)naphthyl]-9-[2,6-bis(pent-4-enyloxy)phenyl]-1,10-phenanthroline (17): Under nitrogen, **16** (401 mg, 889 µmol) and cesium carbonate (3.80 g, 11.7 mmol) were dissolved in anhydrous dimethyl sulfoxide (18 mL). After adding 5-

bromo-1-pentene (1.40 mL, 1.74 g, 11.7 mmol), the solution was stirred at room temp. for 4 d, then the solvent was distilled off in vacuo. The light-brown residue was dissolved in water and dichloromethane (50 mL each), the layers were separated and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layer was washed with aqueous sodium hydroxide solution (2 M, 20 mL), dried with magnesium sulfate, and the solvent was evaporated. The orange-brown crude product was purified by column chromatography (silica gel; dichloromethane/methanol, 98:2; R_f = 0.07) to give **17** (521 mg, 725 µmol, 81 %) as a yellow solid, m.p. 151–153 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.58 (d, ^3J = 8.2 Hz, 1 H, 4-C$_{phen}$H), 8.48 (d, ^3J = 8.3 Hz, 1 H, 7-C$_{phen}$H), 8.08 (d, ^3J = 8.8 Hz, 1 H, 5-C$_{phen}$H*), 8.06 (d, ^3J = 8.8 Hz, 1 H, 6-C$_{phen}$H*), 7.94 (d, ^3J = 9.0 Hz, 1 H, 4-C$_{naph}$H), 7.84 (d, ^3J = 9.0 Hz, 1 H, 5-C$_{naph}$H), 7.76 (d, ^3J = 8.2 Hz, 1 H, 3-C$_{phen}$H), 7.60 (d, ^3J = 8.3 Hz, 1 H, 8-C$_{phen}$H), 7.35 (d, ^3J = 9.0 Hz, 1 H, 3-C$_{naph}$H), 7.28 (t, ^3J = 8.4 Hz, 1 H, 4-C$_{ar}$H), 7.01 (dd, ^3J = 9.0 Hz, ^4J = 2.5 Hz, 1 H, 6-C$_{naph}$H), 6.69 (d, ^3J = 8.4 Hz, 2 H, 3,5-C$_{ar}$H), 6.69 (d, ^4J = 2.5 Hz, 1 H, 8-C$_{naph}$H), 5.61–5.51 [m, 2 H, C$_{naph}$O(CH$_2$)$_3$C*H*=], 5.47 [ddt, ^3J = 18.2 Hz, ^3J = 9.2 Hz, ^3J = 6.6 Hz, 2 H, C$_{ar}$O(CH$_2$)$_3$C*H*=], 4.78 [ddt, ^3J = 17.2 Hz, ^2J = 2.0 Hz, ^4J = 1.6 Hz, 1 H, 7-C$_{naph}$O(CH$_2$)$_3$CH=CH*H$_{trans}$*], 4.76–4.70 [m, 3 H, 7-C$_{naph}$O(CH$_2$)$_3$CH=CH*H$_{cis}$*, 2-C$_{naph}$O(CH$_2$)$_3$CH=C*H*$_2$], 4.66–4.60 [m, 4 H, C$_{ar}$O(CH$_2$)$_3$CH=C*H*$_2$], 4.03 (t, ^3J = 6.3 Hz, 2 H, 2-C$_{naph}$OC*H*$_2$), 3.84 (t, ^3J = 6.3 Hz, 4 H, C$_{ar}$OC*H*$_2$), 3.64 (t, ^3J = 6.4 Hz, 2 H, 7-C$_{naph}$OC*H*$_2$), 1.90 [m$_c$, 2 H, 7-C$_{naph}$O(CH$_2$)$_2$C*H*$_2$], 1.83 [m$_c$, 2 H, 2-C$_{naph}$O(CH$_2$)$_2$C*H*$_2$], 1.73 [m$_c$, 4 H, C$_{ar}$O(CH$_2$)$_2$C*H*$_2$], 1.54 (m$_c$, 4 H, C$_{naph}$OCH$_2$C*H*$_2$), 1.43 (m$_c$, 4 H, C$_{ar}$OCH$_2$C*H*$_2$) ppm. * Assignment may be reversed. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 157.1 (s, 2,6-C$_{ar}$), 156.9 (s, 7-C$_{naph}$), 156.2 (s, 2-C$_{phen}$), 154.9 (s, 9-C$_{phen}$), 154.2 (2-C$_{naph}$), 145.7 (s, 10b-C$_{phen}$), 145.5 (s, 10a-C$_{phen}$), 137.8 [d, C$_{ar}$O(CH$_2$)$_3$*C*H=, 2-C$_{naph}$O(CH$_2$)$_3$*C*H=*^{1}], 137.6 [d, 7-C$_{naph}$O(CH$_2$)$_3$*C*H=*^{1}], 135.9 (d, 4-C$_{phen}$), 135.2 (d, 7-C$_{phen}$), 134.2 (s, 8a-C$_{naph}$), 129.7 (d, 4-C$_{naph}$), 129.64 (d, 4-C$_{ar}$), 129.57 (d, 5-C$_{naph}$), 127.05 (s, 6a-C$_{phen}$), 127.01 (s, 4a-C$_{phen}$), 126.4 (d, 6-C$_{phen}$), 126.1 (d, 5-C$_{phen}$), 125.9 (d, 3-C$_{phen}$), 125.6 (d, 8-C$_{phen}$), 124.2 (s, 4a-C$_{naph}$), 123.7 (s, 1-C$_{naph}$), 120.6 (s, 1-C$_{ar}$), 115.7 (d, 6-C$_{naph}$), 114.9 [t, 7-C$_{naph}$O(CH$_2$)$_3$CH=*C*H$_2$], 114.8 [t, 2-C$_{naph}$O(CH$_2$)$_3$CH=*C*H$_2$], 114.6 [t, C$_{ar}$O(CH$_2$)$_3$CH=*C*H$_2$], 112.7 (d, 3-C$_{naph}$), 105.8 (d, 3,5-C$_{ar}$), 104.5 (d, 8-C$_{naph}$), 68.1 (t, 2-C$_{naph}$O*C*H$_2$), 67.5 (t, C$_{ar}$O*C*H$_2$), 66.4 (t, 7-C$_{naph}$O*C*H$_2$), 29.39 [t, 7-C$_{naph}$O(CH$_2$)$_2$*C*H$_2$], 29.36 [t, 2-C$_{naph}$O(CH$_2$)$_2$*C*H$_2$], 29.27 [t, C$_{ar}$O(CH$_2$)$_2$*C*H$_2$], 27.9 (t, 7-C$_{naph}$OCH$_2$*C*H$_2$*^{2}), 27.6 (t, C$_{ar}$OCH$_2$*C*H$_2$), 27.3 (t, 2-C$_{naph}$OCH$_2$-*C*H$_2$*^{2}) ppm. *^{1}, *^{2} Assignments may be reversed, respectively. IR (ATR): $\tilde{\nu}$ = 3073 (arom. C–H), 2939, 2873 (aliph. C–H), 1622, 1590 (arom. C–C), 1510, 1455 (aliph. C–H), 1250, 1209, 1093, 1067 (C–O–C), 991, 909, 855, 827 (arom. C–H) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 718 (100) [M]$^{+\cdot}$, 677 (46) [M – C$_3$H$_5$]$^+$, 663 (52) [M – C$_4$H$_7$]$^+$, 649 (33) [M – C$_5$H$_9$]$^+$. MS (CI, isobutane): *m/z* (%) = 719 (17) [M + H]$^+$. MS (MALDI, Cl-CCA): *m/z* = 719 [M + H]$^+$. C$_{48}$H$_{50}$N$_2$O$_4$ (718.38): calcd. C 80.19, H 7.01, N 3.90; found C 80.22, H 6.96, N 3.97.

2,11,13,22-Tetraoxa-1(1,3,2)-benzena-12(2,7,1)-naphthalina-23(2,9)-1,10-phenanthrolinabicyclo[10.10.1]tricosaphane-6,17-diene (*rac*-18a): Under nitrogen, **17** (260 mg, 362 µmol) and benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (Grubbs type I catalyst, 30 mg, 37 µmol) were dissolved in anhydrous dichloromethane (360 mL). The solution was stirred at room temp. for 24 h, then the mixture was filtered through basic aluminium oxide (dichloromethane/methanol, 98:2). Ethyl vinyl ether (15 mL) was added, the mixture was stirred at room temp. for 10 min, and the solvent was evaporated. The yellow-brown crude product was purified by column chromatography (silica gel; dichloromethane/methanol, 98:2; R_f = 0.15–0.02) to give *rac*-**18a** (188 mg, 284 µmol, 78 %) as a yellow solid, m.p. 148–152 °C. NMR spectra were measured (see the Supporting Information); however, due to signal overlaps of the four diastereomers generated by ring closing metathesis, complete determination of the signals was not possible. IR (ATR): $\tilde{\nu}$ = 2929, 2864 (aliph. C–H), 1621, 1585 (arom. C–C), 1510, 1494, 1455 (aliph. C–H), 1227, 1208, 1096 (C–O–C), 968, 855, 827, 720 (arom. C–C) cm^{-1}. MS (ESI, CHCl$_3$/MeOH): *m/z* = 685 [M + Na]$^+$, 663 [M + H]$^+$. MS (MALDI, Cl-CCA): *m/z* = 663, [M + H]$^+$. HRMS (FT-ICR): *m/z* calcd. For C$_{44}$H$_{43}$N$_2$O$_4^+$ [M + H]$^+$: 663.321; found: 663.322 (Δ = 2 ppm).

2,13,15,26-Tetraoxa-1(1,3,2)-benzena-14(2,7,1)-naphthalina-27(2,9)-1,10-phenanthrolina-bicyclo[12.12.1]heptacosaphane-7,20-diene (*rac*-18c): Under nitrogen, **8** (338 mg, 436 µmol) and benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (Grubbs type I catalyst, 36 mg, 44 µmol) were dissolved in anhydrous dichloromethane (440 mL). The solution was stirred at room temp. for 18 h, then ethyl vinyl ether (20 mL) was added and the mixture was stirred at room temp. for 1 h. The mixture was filtered through basic aluminium oxide (dichloromethane) before the solvent was evaporated. The beige crude product was purified by column chromatography (silica gel; dichloromethane/methanol, 98:2; R_f = 0.19–0.04) to give *rac*-**18c** (263 mg, 366 µmol, 84 %) as a light-yellow solid, m.p. 247–249 °C. NMR spectra were measured (see the Supporting Information); however, due to signal overlaps of the four diastereomers generated by ring closing metathesis, complete determination of the signals was not possible. IR (ATR): $\tilde{\nu}$ = 2922, 2871 (aliph. C–H), 1622, 1590 (arom. C–C), 1513, 1455 (aliph. C–H), 1245, 1093 (C–O–C), 970, 826, 720 (arom. C–H) cm^{-1}. MS (ESI, CHCl$_3$/MeOH): *m/z* = 741 [M + Na]$^+$, 719 [M + H]$^+$. MS (MALDI, Cl-CCA): *m/z* = 719 [M + H]$^+$. C$_{48}$H$_{50}$N$_2$O$_4$ (718.38): calcd. C 80.19, H 7.01, N 3.90; found C 80.27, H 7.26, N 3.73.

2,11,13,22-Tetraoxa-1(1,3,2)-benzena-12(2,7,1)-naphthalina-23(2,9)-1,10-phenanthrolina-bicyclo[10.10.1]tricosaphane (*rac*-19a): First nitrogen, then hydrogen were bubbled through a suspension of palladium on charcoal (10 %, 29 mg, 27 µmol) in acid-free dichloromethane/ethyl acetate (1:1, 15 mL) for 15 min each. A solution of *rac*-**18a** (180 mg, 272 µmol) in acid-free dichloromethane/methanol (1:1, 10 mL) was added, and the mixture was flushed with hydrogen for 1 h followed by stirring at room temp. for 20 h under hydrogen. The suspension was filtered through basic aluminium oxide (dichloromethane) and the solvent was evaporated. The residue was filtered through a little magnesium sulfate (dichloromethane) and the solvent was removed again to give *rac*-**19a** (138 mg, 207 µmol, 76 %) as a yellow solid, m.p. 247–249 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 8.33 (d, ^3J = 8.1 Hz, 1 H, 4-C$_{phen}$H), 8.25 (d, ^3J = 8.2 Hz, 1 H, 7-C$_{phen}$H), 7.89 (s, 2 H, 5,6-C$_{phen}$H), 7.78 (d, ^3J = 9.0 Hz, 1 H, 4-C$_{naph}$H), 7.69 (d, ^3J = 8.1 Hz, 1 H, 3-C$_{phen}$H), 7.67 (d, ^3J = 9.0 Hz, 1 H, 5-C$_{naph}$H), 7.60 (d, ^3J = 8.2 Hz, 1 H, 8-C$_{phen}$H), 7.20 (t, ^3J = 8.3 Hz, 1 H, 4-C$_{ar}$H), 7.15 (d, ^3J = 9.0 Hz, 1 H, 3-C$_{naph}$H), 6.94 (dd, ^3J = 9.0 Hz, ^2J = 2.4 Hz, 1 H, 6-C$_{naph}$H), 6.67 (d, ^2J = 2.4 Hz, 1 H, 8-C$_{naph}$H), 6.59 (d, ^3J = 8.3 Hz, 1 H, 3-C$_{ar}$H*), 6.53 (d, ^3J = 8.3 Hz, 1 H, 5-C$_{ar}$H*), 4.15 (m$_c$, 1 H, 2-C$_{naph}$OCH*H$_a$*), 3.93–3.70 (m, 6 H, 2-C$_{naph}$-OCH*H$_b$*, C$_{ar}$OC*H*$_2$, 7-C$_{naph}$OCH*H$_a$*), 3.62–3.57 (m, 1 H, 7-C$_{naph}$OCH*H$_b$*), 1.70–0.51 (m, 24 H, CH$_2$C*H*$_2$CH$_2$) ppm. * Assignment may be reversed. ^{13}C NMR (151 MHz, CDCl$_3$): δ = 158.4 (s, 2-C$_{ar}$*^{1}), 157.8 (s, 7-C$_{naph}$), 157.7 (s, 2-C$_{phen}$), 157.4 (s, 6-C$_{ar}$*^{1}), 155.8 (s, 9-C$_{phen}$), 154.9 (s, 2-C$_{naph}$), 146.5 (s, 10b-C$_{phen}$), 146.2 (s, 10a-C$_{phen}$), 135.8 (d, 4-C$_{phen}$), 135.2 (d, 7-C$_{phen}$), 134.9 (s, 8a-C$_{naph}$), 129.8 (d, 4-C$_{naph}$), 129.7 (d, 4-C$_{ar}$), 129.3 (d, 5-C$_{naph}$), 127.5 (s, 4a-C$_{phen}$), 127.4 (s, 6a-C$_{phen}$), 126.7 (d, 6-C$_{phen}$*^{2}), 126.6 (d, 3-C$_{phen}$*^{2}), 126.3 (d, 8-C$_{phen}$*^{3}), 126.1 (d, 5-C$_{phen}$*^{3}), 124.8 (s, 1-C$_{naph}$), 124.7 (s, 4a-C$_{naph}$), 120.9 (s, 1-C$_{ar}$), 116.5 (d, 6-C$_{naph}$), 112.5 (d, 3-C$_{naph}$), 106.1 (d, 5-C$_{ar}$*^{4}), 105.6 (d, 3-C$_{ar}$*^{4}), 105.0 (d, 8-C$_{naph}$), 69.7 (t, 2-C$_{naph}$OCH$_2$), 69.3, 67.9 (2t, C$_{ar}$-OCH$_2$), 67.2 (t, 7-C$_{naph}$OCH$_2$), 29.3, 28.8, 28.2, 27.8, 27.7, 27.4, 25.85, 25.80, 24.9, 24.8 (10t, CH$_2$CH$_2$CH$_2$) ppm. *^{1}, *^{2}, *^{3}, *^{4} Assignments

may be reversed, respectively. IR (ATR): $\tilde{\nu}$ = 2925, 2855 (aliph. C–H), 1623, 1589 (arom. C–C), 1510, 1456 (aliph. C–H), 1238, 1096 (C–O–C), 854, 825, 719 (arom. C–H) cm^{-1}. MS (ESI, $CHCl_3$/MeOH): *m/z* = 689 $[M + Na]^+$, 667 $[M + H]^+$. MS (MALDI, Cl-CCA): *m/z* = 667 $[M + H]^+$. $C_{44}H_{46}N_2O_4$ (666.35): calcd. C 79.25, H 6.95, N 4.20; found C 78.99, H 7.01, N 4.07.

2,12,14,24-Tetraoxa-1(1,3,2)-benzena-13(2,7,1)-naphthalina-25(2,9)-1,10-phenanthrolina-bicyclo[11.11.1]pentacosaphane (*rac*-19b): Under nitrogen, cesium carbonate (707 mg, 2.17 mmol) and anhydrous potassium carbonate (391 mg, 2.83 mmol) were suspended in anhydrous *N*,*N*-dimethylformamide (86 mL). A solution of **16** (250 mg, 560 µmol) and 1,9-dibromononane (228 µL, 320 mg, 1.12 mmol) in anhydrous *N*,*N*-dimethylformamide (40 mL) were added dropwise by using a syringe driver at 65 °C over 15 h. The suspension was then stirred at 65 °C for 1.5 h. After cooling to room temp., the solid was filtered off and the solvent was evaporated. The brown residue was dissolved in dichloromethane (40 mL) and water (20 mL), the layers were separated and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layer was dried with magnesium sulfate and the solvent was evaporated. The red-brown crude product was purified by column chromatography (silica gel; dichloromethane/ethyl acetate, 9:1; R_f = 0.29) to give *rac*-**19b** (121 mg, 174 µmol, 31 %) as a yellow solid, m.p. 247–249 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.34 (d, ^3J = 8.1 Hz, 1 H, 4-C_{phen}H), 8.26 (d, ^3J = 8.2 Hz, 1 H, 7-C_{phen}H), 7.89 (s, 2 H, 5,6-C_{phen}H), 7.77 (d, ^3J = 8.9 Hz, 1 H, 4-C_{naph}H), 7.69 (d, ^3J = 8.1 Hz, 1 H, 3-C_{phen}H), 7.68 (d, ^3J = 9.0 Hz, 1 H, 5-C_{naph}H), 7.62 (d, ^3J = 8.2 Hz, 1 H, 8-C_{phen}H), 7.19 (t, ^3J = 8.3 Hz, 1 H, 4-C_{ar}H), 7.17 (d, ^3J = 8.9 Hz, 1 H, 3-C_{naph}H), 6.95 (dd, ^3J = 9.0 Hz, ^4J = 2.4 Hz, 1 H, 6-C_{naph}H), 6.58 (d, ^4J = 2.4 Hz, 1 H, 8-C_{naph}H), 6.56 (d, ^3J = 8.3 Hz, 2 H, 3,5-C_{ar}H), 4.17–3.67 (m, 8 H, OCH_2), 1.70–0.50 (m, 28 H, $CH_2CH_2CH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.1 (s, 2-C_{ar}*1), 157.9 (s, 6-C_{ar}*1), 157.5 (s, 2-C_{phen}, 7-C_{naph}), 155.9 (s, 9-C_{phen}), 154.9 (s, 2-C_{naph}), 146.7 (10b-C_{phen}), 146.3 (10a-C_{phen}), 135.9 (d, 4-C_{phen}), 135.2 (d, 7-C_{phen}), 135.0 (s, 8a-C_{naph}), 129.7 (2d, 4-C_{ar}, 4-C_{naph}), 129.4 (d, 5-C_{naph}), 127.53 (s, 4a-C_{phen}), 127.49 (s, 6a-C_{phen}), 126.6 (d, 6-C_{phen}), 126.31 (d, 5-C_{phen}*2), 126.28 (d, 8-C_{phen}*2), 126.1 (d, 3-C_{phen}), 125.2 (s, 1-C_{naph}), 124.9 (s, 4a-C_{naph}), 121.0 (s, 1-C_{ar}), 116.5 (d, 6-C_{naph}), 113.0 (d, 3-C_{naph}), 105.9 (d, 3-C_{ar}*3), 105.8 (d, 5-C_{ar}*3), 104.6 (d, 8-C_{naph}), 69.12, 69.06, 68.4, 66.6 (4t, OCH_2), 28.9, 28.82, 28.75, 28.6, 27.9, 27.3, 27.19, 27.15, 26.8, 26.5, 25.3, 25.1, 24.4, 24.2 (14t, $CH_2CH_2CH_2$) ppm. *1, *2, *3 Assignments may be reversed, respectively. IR (ATR): $\tilde{\nu}$ = 3957, 3028 (arom. C–H), 2926, 2854 (aliph. C–H), 1622, 1587 (arom. C–C), 1511, 1456 (aliph. C–H), 1245, 1099 (C–O–C), 854, 824, 720 (arom. C–H) cm^{-1}. MS (MALDI, Cl-CCA): *m/z* = 695 $[M + H]^+$. HRMS (FT-ICR): calcd. for $C_{46}H_{51}N_2O_4^+$ $[M + H]^+$: 695.384; found: 695.384 (Δ = 2 ppm).

2,13,15,26-Tetraoxa-1(1,3,2)-benzena-14(2,7,1)-naphthalina-27(2,9)-1,10-phenanthrolina-bicyclo[12.12.1]heptacosaphane (*rac*-19c): First nitrogen, then hydrogen were bubbled through a suspension of palladium on charcoal (10 %, 35 mg, 33 µmol) in acid-free dichloromethane/ethyl acetate (1:1, 15 mL) for 15 min each. A solution of *rac*-**18c** (233 mg, 324 µmol) in acid-free dichloromethane/methanol (1:1, 20 mL) was added, and the mixture was flushed with hydrogen for 1 h followed by stirring at room temp. for 20 h under hydrogen. The suspension was filtered through basic aluminium oxide (dichloromethane) and the solvent was evaporated. The residue was filtered through a little magnesium sulfate (dichloromethane) and the solvent was removed again. The crude product was purified by column chromatography (silica gel; dichloromethane/ethyl acetate, 9:1; R_f = 0.39) to give *rac*-**19c** (188 mg, 260 µmol, 80 %) as a white solid, m.p. 259–261 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.32 (d, ^3J = 8.2 Hz, 1 H, 4-C_{phen}H), 8.24 (d, ^3J = 8.2 Hz, 1 H, 7-C_{phen}H), 7.88 (s, 2 H, 5,6-C_{phen}H), 7.77 (d, ^3J = 9.0 Hz, 1 H, 4-C_{naph}H), 7.68 (d, ^3J = 8.9 Hz, 1 H, 5-C_{naph}H), 7.66 (d, ^3J = 8.2 Hz, 1 H, 3-C_{phen}H), 7.60 (d, ^3J = 8.2 Hz, 1 H, 8-C_{phen}H), 7.19 (t, ^3J = 8.3 Hz, 1 H, 4-C_{ar}H), 7.16 (d, ^3J = 9.0 Hz, 1 H, 3-C_{naph}H), 6.96 (dd, ^3J = 8.9 Hz, ^2J = 2.4 Hz, 1 H, 6-C_{naph}H), 6.70 (d, ^2J = 2.4 Hz, 1 H, 8-C_{naph}H), 6.57 (d, ^3J = 8.3 Hz, 1 H, 3-C_{ar}H*), 6.56 (d, ^3J = 8.3 Hz, 1 H, 5-C_{ar}H*), 4.04–3.94 (m, 2 H, 2-$C_{naph}OCH_2$), 3.93–3.72 (m, 6 H, $C_{ar}OCH_2$, 7-$C_{naph}OCH_2$), 1.68–1.31 (m, 8 H, OCH_2CH_2), 1.13–0.40 (m, 24 H, $CH_2CH_2CH_2$) ppm. * Assignment may be reversed. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.2 (s, 2-C_{ar}*1), 158.0 (s, 6-C_{ar}*1), 157.8 (s, 7-C_{naph}), 157.5 (s, 2-C_{phen}), 155.9 (s, 9-C_{phen}), 155.2 (s, 2-C_{naph}), 146.8 (s, 10b-C_{phen}), 146.4 (s, 10a-C_{phen}), 135.9 (d, 4-C_{phen}), 135.1 (d, 7-C_{phen}), 135.0 (s, 8a-C_{naph}), 129.7 (d, 4-C_{naph}), 129.6 (d, 4-C_{ar}), 129.4 (d, 5-C_{naph}), 127.65 (s, 6a-C_{phen}*2), 127.60 (s, 4a-C_{phen}*2), 126.6 (d, 6-C_{phen}), 126.45 (d, 8-C_{phen}*3), 126.36 (d, 3-C_{phen}*3), 126.1 (d, 5-C_{phen}), 125.0 (s, 4a-C_{naph}*4), 124.9 (s, 1-C_{naph}*4), 121.3 (s, 1-C_{ar}), 115.9 (d, 6-C_{naph}), 113.0 (d, 3-C_{naph}), 106.1 (d, 3-C_{ar}*5), 106.0 (d, 5-C_{ar}*5), 105.5 (d, 8-C_{naph}), 70.0 (t, 2-$C_{naph}OCH_2$), 69.4, 69.0, 67.8 (3t, OCH_2), 29.0, 28.60, 28.56, 28.3, 27.6, 27.4, 27.33, 27.25, 27.24, 26.8, 26.6, 25.0, 24.8, 24.71, 24.69 (15t, $CH_2CH_2CH_2$) ppm. *1, *2, *3, *4, *5 Assignments may be reversed, respectively. IR (ATR): $\tilde{\nu}$ = 3061, 3037 (arom. C–H), 2923, 2854 (aliph. C–H), 1622, 1588 (arom. C–C), 1455 (aliph. C–H), 1243, 1230, 1213 (C–O–C), 852, 823 (arom. C–H) cm^{-1}. MS (ESI, $CHCl_3$/MeOH): *m/z* = 745 $[M + Na]^+$, 723 $[M + H]^+$. $C_{48}H_{54}N_2O_4$ (722.41): calcd. C 79.74, H 7.53, N 3.87; found: C 79.39, H 7.77, N 4.02.

2,7-Dimethoxynaphthalene (26):[30] In a flow of nitrogen, 2,7-dihydroxynaphthalene (**25**; 10.0 g, 62.5 mmol) was added to a 15 °C solution of potassium hydroxide (8.72 g, 156 mmol) in water (88 mL). Then dimethyl sulfate (12.5 mL, 132 mmol) was added to the brown solution, while keeping the temperature under 20 °C. The mixture was heated to 100 °C for 1 h. After cooling to room temp., the precipitate was washed with potassium hydroxide solution (2 M, 30 mL) and water (30 mL). Then the solid was dissolved in dichloromethane, washed with brine and dried with magnesium sulfate. The solvent was evaporated and the crude product was recrystallized from ethyl acetate to give **26** (6.17 g, 32.8 mmol, 53 %) as a slightly brown solid, m.p. 138 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, ^3J = 9.0 Hz, 2 H, 4,6-C_{naph}H), 7.06 (d, ^4J = 2.5 Hz, 2 H, 1,8-C_{naph}H), 6.99 (dd, ^3J = 9.0 Hz, ^4J = 2.5 Hz, 2 H, 3,5-C_{naph}H), 3.90 (s, 6 H, OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.4 (s, 2,7-C_{naph}), 136.1 (s, 8a-C_{naph}), 129.3 (d, 4,5-C_{naph}), 124.4 (s, 4a-C_{naph}), 116.2 (d, 3,6-C_{naph}), 105.4 (d, 1,8-C_{naph}), 55.4 (q, OCH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3010 (arom. C–H), 2965, 2936 (aliph. C–H), 2836 (O–CH_3), 1625, 1605, 1510 (arom. C–C), 1469, 1459, 1384 (aliph. C–H), 1230, 1211, 1025 (C–O–C), 863, 835, 777 (arom. C–H) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 188 (100) $[M]^{+\cdot}$, 159 (4) $[M - C_2H_6]^+$, 145 (46) $[M - C_2H_6O]^+$, 130 (8) $[M - C_3H_7]^{+\cdot}$, 115 (8) $[M - C_3H_6O_2]^+$. MS (CI, isobutane): *m/z* (%) = 189 (100) $[M + H]^+$. $C_{12}H_{12}O_2$ (188.08): calcd. C 76.57, H 6.43; found: C 76.79, H 6.41.

1-Bromo-2,7-dimethoxynaphthalene (27): The synthesis was carried out in analogy to the procedure of Bagheri, Azizi and Saidi.[25] Lithium perchlorate on silica gel (1:4, 4.26 g) and 2,7-dimethoxynaphthalene (**26**; 4.00 g, 21.3 mmol) were suspended in dichloromethane (250 mL). *N*-Bromosuccinimide (3.80 g, 21.4 mmol) was added and the suspension was stirred at room temp. for 18 h. The remaining solid was filtered off and washed with dichloromethane. The solvent of the organic layer was then evaporated. The residue was dissolved in acetonitrile and water was added. The yellow precipitate was filtered off and dissolved in dichloromethane. After separation from remaining water, the organic layer was dried with magnesium sulfate. The solvent was evaporated and the brown crude product was purified by column chromatography (silica gel; cyclo-

hexane/ethyl acetate, 6:1; R_f = 0.36) and subsequent recrystallization from methanol to give **27** (4.58 g, 17.2 mmol, 81 %) as colourless needles, m.p. 80 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, ^3J = 8.9 Hz, 1 H, 4-C_{naph}H), 7.67 (d, ^3J = 8.9 Hz, 1 H, 5-C_{naph}H), 7.50 (d, ^4J = 2.4 Hz, 1 H, 8-C_{naph}H), 7.11 (d, ^3J = 8.9 Hz, 1 H, 3-C_{naph}H), 7.04 (dd, ^3J = 8.9 Hz, ^4J = 2.4 Hz, 1 H, 6-C_{naph}H), 4.02 (s, 3 H, 2-$C_{naph}OCH_3$), 3.97 (s, 3 H, 7-$C_{naph}OCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.4 (s, 7-C_{naph}), 154.4 (s, 2-C_{naph}), 134.6 (s, 8a-C_{naph}), 129.8 (d, 5-C_{naph}), 128.6 (d, 4-C_{naph}), 125.2 (s, 4a-C_{naph}), 117.3 (d, 6-C_{naph}), 110.9 (d, 3-C_{naph}), 107.6 (s, 1-C_{naph}), 104.5 (d, 8-C_{naph}), 57.0 (q, 2-$C_{naph}OCH_3$), 55.4 (q, 7-$C_{naph}OCH_3$) ppm. IR (ATR): $\tilde{\nu}$ = 3003 (arom. C–H), 2965, 2935 (aliph. C–H), 2842 (O–CH_3), 1621, 1598, 1508 (arom. C–C), 1459, 1447, 1381 (aliph. C–H), 1263, 1219 (C–O–C), 1066 (C–Br), 1027 (C–O–C), 830, 772 (arom. C–H) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 268, 266 (97, 100) $[M]^{+\cdot}$, 225, 223 (45, 46) $[M - CH_3O]^+$, 172 (12) $[M - CH_3Br]^{+\cdot}$, 157 (13) $[M - C_2H_5Br]^+$. MS (CI, isobutane): *m/z* (%) = 269, 267 (100, 97) $[M + H]^+$. $C_{12}H_{11}BrO_2$ (265.99): calcd. C 53.96, H 4.15; found C 54.31, H 4.08.

Pinacol 2,7-Dimethoxynaphthylboronate (28): Under nitrogen, 1-bromo-2,7-dimethoxynaphthalene (**27**; 1.0 g, 3.7 mmol) was dissolved in anhydrous tetrahydrofuran (25 mL) and cooled to –78 °C. *n*-Butyllithium (2.5 M in hexanes, 1.65 mL, 4.12 mmol) was added and the mixture was stirred at –78 °C for 1 h. Isopropoxyboronic acid pinacol ester (1.53 mL, 1.40 g, 7.52 mmol) was then added and the mixture was stirred for 15 h while warming slowly to room temp. Water was added, the layers were separated, and the aqueous layer was extracted with diethyl ether (4 × 15 mL). The combined organic layer was washed with brine and dried with magnesium sulfate. The solvent was evaporated and the slightly orange residue was purified by column chromatography (silica gel; cyclohexane/ethyl acetate, 6:1; R_f = 0.29) to give **28** (871 mg, 2.77 mmol, 74 %) as a white solid, m.p. 131 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, ^3J = 9.0 Hz, 1 H, 4-C_{naph}H), 7.63 (d, ^3J = 9.0 Hz, 1 H, 5-C_{naph}H), 7.31 (d, ^4J = 2.5 Hz, 1 H, 8-C_{naph}H), 7.04 (d, ^3J = 9.0 Hz, 1 H, 3-C_{naph}H), 6.96 (dd, ^3J = 9.0 Hz, ^4J = 2.5 Hz, 1 H, 6-C_{naph}H), 3.90 (s, 3 H, 2-$C_{naph}OCH_3$), 3.88 (s, 3 H, 7-$C_{naph}OCH_3$), 1.47 (s, 12 H, CCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.5 (s, 2-C_{naph}), 158.3 (s, 7-C_{naph}), 138.8 (s, 8a-C_{naph}), 131.6 (d, 4-C_{naph}), 129.7 (d, 5-C_{naph}), 124.6 (s, 4a-C_{naph}), 116.3 (d, 6-C_{naph}), 110.5 (d, 3-C_{naph}), 105.4 (d, 8-C_{naph}), 83.9 (s, CCH_3), 56.7 (q, 2-$C_{naph}OCH_3$), 55.1 (q, 7-$C_{naph}OCH_3$), 25.1 (q, CCH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2976, 2836 (aliph. C–H), 1629, 1581 (arom. C–C), 1505, 1460, 1430, 1335, 1314 (aliph. C–H), 1243, 1221, 1140, 1127, 1072 (C–O–C), 845, 830, 775 (arom. C–H) cm^{-1}. MS (ESI, $CHCl_3$/MeOH): *m/z* = 337 $[M + Na]^+$, 314 $[M]^{+\cdot}$, 300 $[M - CH_2]^{+\cdot}$. $C_{18}H_{23}BO_4$ (314.17): calcd. C 68.81, H 7.38; found C 68.89, H 7.37.

2-(2,7-Dimethoxynaphthyl)-9-(2,6-dimethoxyphenyl)1,10-phenanthroline (30): Under nitrogen, 2-chloro-9-(dimethoxyphenyl)-1,10-phenanthroline (**29**; 351 mg, 1.00 mmol), 2,7-dimethoxynaphthylboronic acid pinacol ester (**28**; 471 mg, 1.50 mmol), [1,1′-bis(diphenylphosphanyl)ferrocene]dichloropalladium(II) (122 mg, 150 µmol) and barium hydroxide octahydrate (877 mg, 2.78 mmol) were dissolved in 1,2-dimethoxyethane (60 mL) and water (15 mL). The suspension was heated to 70 °C for 21 h. After cooling to room temp., dichloromethane and water (50 mL each) were added and the layers were separated. The aqueous layer was extracted with dichloromethane (5 × 50 mL) and the combined organic layer was washed with half conc. aqueous sodium chloride solution, dried with magnesium sulfate and the solvent was evaporated. The dark-brown residue was filtered through basic aluminium oxide with dichloromethane. After evaporation of the solvent, the yellow crude product was purified by column chromatography (silica gel; dichloromethane/methanol, 98:2; R_f = 0.07) to give **30** (211 mg, 429 µmol, 42 %) as a yellow-brown solid, m.p. 259 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.32 (d, ^3J = 8.2 Hz, 1 H, 4-C_{phen}H), 8.26 (d, ^3J = 8.1 Hz, 1 H, 7-C_{phen}H), 7.86 (s, 2 H, 5,6-C_{phen}H), 7.81 (d, ^3J = 8.9 Hz, 1 H, 4-C_{naph}H), 7.78 (d, ^3J = 8.2 Hz, 1 H, 3-C_{phen}H), 7.68 (d, ^3J = 9.0 Hz, 1 H, 5-C_{naph}H), 7.63 (d, ^3J = 8.1 Hz, 1 H, 8-C_{phen}H), 7.26 (t, ^3J = 8.4 Hz, 1 H, 4-C_{ar}H), 7.19 (d, ^3J = 8.9 Hz, 1 H, 3-C_{naph}H), 7.12 (d, ^4J = 2.4 Hz, 1 H, 8-C_{naph}H), 6.96 (dd, ^3J = 9.0 Hz, ^4J = 2.4 Hz, 1 H, 6-C_{naph}H), 6.61 (d, ^3J = 8.4 Hz, 2 H, 3,5-C_{ar}H), 3.84 (s, 3 H, 2-$C_{phen}OCH_3$), 3.67 (s, 6 H, $C_{ar}OCH_3$), 3.56 (s, 3 H, 7-$C_{phen}OCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.7 (s, 2,6-C_{ar}), 158.3 (s, 7-C_{naph}), 156.8 (s, 2-C_{phen}), 155.8 (s, 2-C_{naph}), 155.3 (s, 9-C_{phen}), 146.65 (s, 10a-C_{phen}*1), 146.61 (s, 10b-C_{phen}*1), 135.7 (d, 4-C_{phen}), 135.4 (d, 7-C_{phen}), 135.0 (s, 8a-C_{naph}), 130.1 (d, 4-C_{naph}), 129.8 (d, 4-C_{ar}), 129.4 (d, 5-C_{naph}), 127.7 (s, 4a-C_{phen}*2), 127.5 (s, 6a-C_{phen}*2), 126.71, 126.66 (2d, 3-C_{phen}, 6-C_{phen}*3), 126.26, 126.25 (2d, 5-C_{phen}*3, 8-C_{phen}), 125.1 (s, 4a-C_{naph}), 124.4 (s, 1-C_{naph}), 120.9 (s, 1-C_{ar}), 116.3 (d, 6-C_{naph}), 111.7 (d, 3-C_{naph}), 105.2 (d, 3,5-C_{ar}), 104.2 (d, 8-C_{naph}), 57.2 (q, 2-$C_{naph}OCH_3$), 56.5 (q, $C_{ar}OCH_3$), 55.2 (q, 7-$C_{naph}OCH_3$) ppm. *1,*,2*3 Assignments may be reversed, respectively. IR (ATR): $\tilde{\nu}$ = 3051 (arom. C–H),2953(aliph.C–H),2833(O–CH_3),1622,1587,1496(arom.C–C),1470 (aliph. C–H), 1249, 1225, 1214, 1106, 1070, 1028 (C–O–C), 854, 825, 779 (arom. C–H) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 502 (100) $[M]^{+\cdot}$, 487 (50) $[M - CH_3]^+$. MS (CI, isobutane): *m/z* (%) = 503 (100) $[M + H]^+$. $C_{32}H_{26}N_2O_4$ (502.57): calcd. C 76.48, H 5.21, N 5.57; found C 76.59, H 5.25, N 5.62.

Calculations: All calculations were performed using the program TURBOMOLE.[31] The geometry of (*M*)-**19a** was fully optimized in the gas phase using the DFT potential B3LYP-D3,[18] which includes an additional dispersion correction.[19] As basis set, 6-31G*[20] was employed. For all calculations, the default thresholds implemented in TURBOMOLE were used. The obtained geometry of (*M*)-**19a** was characterized as minimum by a subsequent frequency calculation using B3LYP-D3/6-31G*. The CD spectrum of (*M*)-**19a** was simulated with the time-dependent density functional theory (TD-DFT), using the B3LYP functional and the 6-31G* basis set. The TD-DFT calculation was performed at the optimized ground-state geometry of (*M*)-**19a**, and the energy, oscillator strength, and rotatory strength were calculated for each of the 100 lowest singlet excitations. The CD spectrum was simulated by overlapping Gaussian functions for each transition, for which the width of the Gaussian function was fixed at 10 nm. The intensity of the simulated CD spectrum was scaled to the experimental values.

General Procedure for Cyclopropanation: Under nitrogen, copper(I) triflate benzene complex [ca. 0.2 to 0.8 mg (± 0.01 mg)] was placed in a vial. One of the ligands **19a**–**c** or **30** [2.1 equiv.; based on copper(I)] and indene (**21**, 350 equiv.) dissolved in degassed, anhydrous 1,2-dichloroethane (0.8 mL) were then added. After addition of ethyl diazoacetate (**20**, 50 equiv.), the mixture was stirred at room temp. for 20 h. The mixture was then filtered through silica gel with dichloromethane as eluent. Most of the solvent was evaporated in vacuo until ca. 1.5 mL remained. After addition of *n*-hexadecane [ca. 1 to 1.5 mg/mL (± 0.01 mg)] as GC standard, the products were analyzed by GC.

Keywords: Macrocycles · Chiral resolution · Circular dichroism · Stereoselectivity · Cyclopropanation

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