DOI: 10.1002/ejoc.200500650

Concave 1,10-Phenanthrolines as Tailored Ligands for Copper(I)-Catalyzed Diastereoselective Cyclopropanations[‡]

Ulrich Lüning*[a] and Frank Fahrenkrug[a]

Keywords: Cyclopropanation / Homogeneous catalysis / Macrocycles / Metathesis / Supramolecular chemistry

Alkenyloxy-substituted aryl bridgeheads have been connected to 2,9-dichloro-1,10-phenanthroline (**11**) either by Suzuki coupling or by nucleophilic aromatic substitution. The resulting di- or tetraalkenes **12** or **17** have been cyclized by ring-closing metathesis to give concave 1,10-phenanthrolines **14** and **19**, differing from other concave 1,10-phenanthrolines **1** in their geometries. The influence of the shapes of these ligands and those of the related concave 1,10-phenanthrolines **1a–f** and **2** on the stereochemistry of the copper(I)-catalyzed cyclopropanation of indene (**3**) and styrene (**4**) has been investigated, identifying factors that favour the formation of thermodynamically less stable *syn*-cyclopropanes **6** and **7**.

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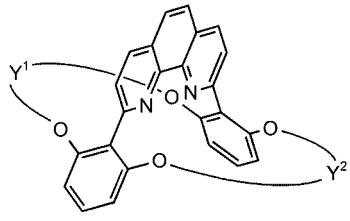
Introduction

The surprising properties of enzymes have been a stimulation for many enterprises in supramolecular chemistry.[1–5] Because the high selectivity of an enzyme is largely a product of the concave environment of the active site,[6] geometrically related molecules such as macrocycles, clefts or pincers have attracted wide interest. Concave reagents have been developed with the goal of increasing the selectivities of reactions or catalyses through the corresponding shielding of the reaction site. In particular, concave 1,10-phenanthrolines **1** and **2** (Figure 1 and Figure 2) have shown good selectivities in a number of reactions.[7–11]

The active and selective catalysts in many of these reactions are transition metal ion complexes of the ligands **1** and **2**: examples include copper(I) complexes[12] in the stereoselective cyclopropanation of alkenes such as indene (**3**) or styrene (**4**) by diazoacetates **5**.[13] The cyclopropanation of alkenes by diazoacetates has been investigated thoroughly, especially for the development of enantioselective catalysts. Styrene (**4**) is usually used as substrate, and only rarely can the *cis*/*trans* selectivity by steered in both directions in good yields.[14,15]

The concave 1,10-phenanthrolines **1** and **2** differ in their selectivities in the cyclopropanation of both alkenes **3** and **4**. While the stiff bimacrocyclic 1,10-phenanthrolines **1** with aryl bridgeheads in position 2 and 9 give *anti* products (e.g., *exo*-configured cyclopropanes of indene **6** or *trans*-configured cyclopropanes of styrene **7**; for a definition, see footnote [a] in Table 1), the 1,10-phenanthroline-bridged calix[6]arene **2** predominantly gives the complementary *syn* products (*cis* or *endo*, respectively).[11] This finding has also been investigated theoretically,[16] and the ability of **2** to adopt a bent structure seems to be the reason for the *syn* selectivity. While the complexes of the stiff concave 1,10-



1

	Y^1	Y^2
a	$(CH_2)_8$	$(CH_2)_8$
b	$(CH_2)_9$	$(CH_2)_9$
c	$(CH_2)_{10}$	$(CH_2)_{10}$
d	$(CH_2)_{10}$	$(CH_2)_8$
e	$(CH_2)_8$	$-CH_3\ H_3C-$
f	$-CH_3\ H_3C-$	$-CH_3\ H_3C-$
g	$CH_2(CH_2OCH_2)_2C\ H_2$	$CH_2(CH_2OCH_2)_2C\ H_2$

Figure 1. Concave 1,10-phenanthrolines **1a**–**1g** with direct CC-connection between the aryl bridgeheads and the 1,10-phenanthroline system.

[‡] Concave Reagents, 47. Part 46: S. Lüthje, C. Bornholdt, U. Lüning, *Eur. J. Org. Chem.*, **2006**, 909–915, preceding article.

[a] Otto Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel,
Olshausenstr. 40, 24098 Kiel, Germany
Fax: +49-431-880-1558
E-mail: luening@oc.uni-kiel.de

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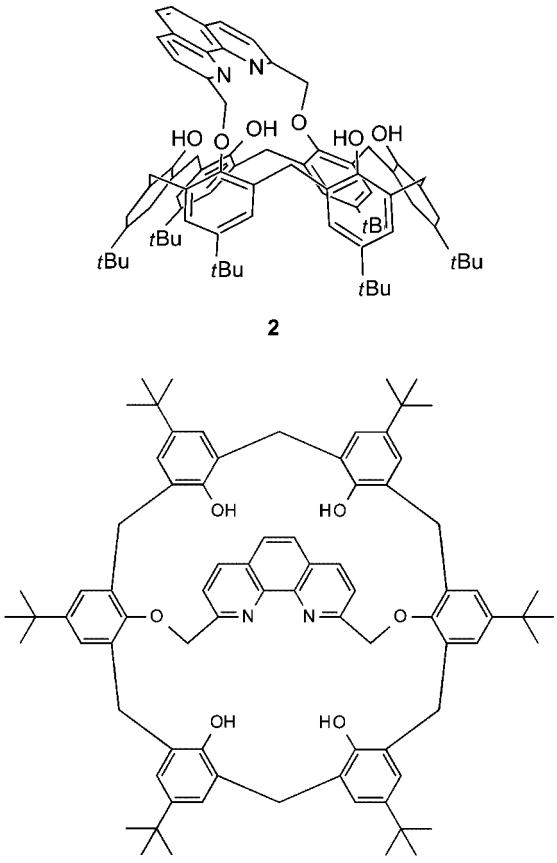
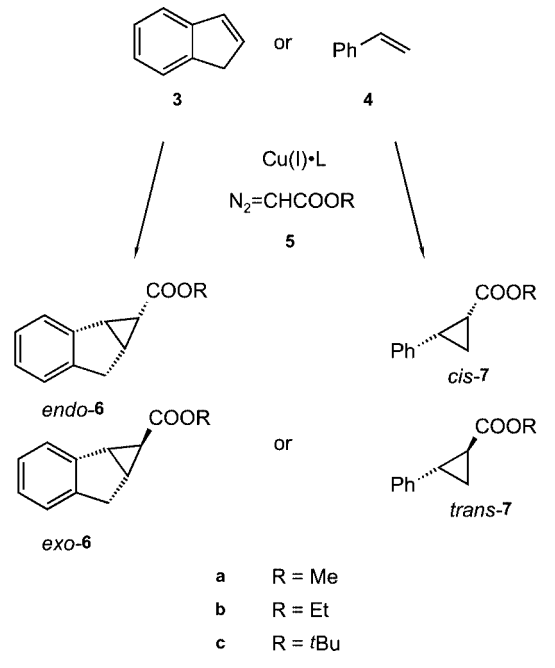


Figure 2. Calixarene-based ligand **2**, synthesized by A,D-bridging of calix[6]arene with a 2,9-bismethylene-1,10-phenanthroline unit, in two representations.



phenanthrolines **1** possess a lamp-like geometry, with the copper(I) ion being the light bulb and the bimacrocycle being the lamp shade, the bridged calixarene **2** adopts a geometry resembling a shallow bowl. In both cases, the large 1,10-phenanthroline ligand bound to the copper(I) ion determines the stereoselectivity of the cyclopropanation. According to calculations,[16] a copper carbenoid is the cyclopropanating species, but the orientations of the carbene moiety and the approaching alkene are different in the two ligands **1** and **2**.

With the stiff and symmetrical ligand **1**, the carbene sits in the cavity, presenting a hydrogen atom and an ester function towards the approaching alkene (see Figure 3). It is obvious that the alkene will approach in such a way that its substituent R will face away from the ester group, resulting in the formation of *anti* products. In the opposite orientation, R and the ester group experience steric repulsion by one another, which is increased if their mobility is reduced by the encumbering macrocycle, so the *anti* selectivity is enhanced relative to that of ligand-free catalysis. The correlation between the size of the ester group and the pro-

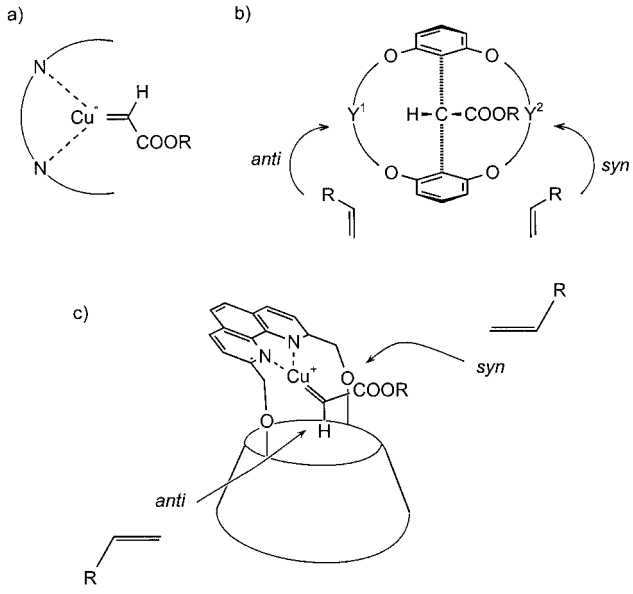


Figure 3. a) A copper carbenoid, Cu^+=CH–COOR, is the key intermediate in the copper(I)-catalyzed cyclopropanation of alkenes by diazoacetates. Concave 1,10-phenanthrolines **1** or **2** determine the *syn*/*anti* selectivity by complexing the copper(I) ion. The coordination to the nitrogen atoms and the concave shielding is indicated by the dashed bonds and the half circle. b) View onto the complex **1**·Cu^+=CH–COOR along the axis formed by the carbene carbon atom and the copper(I) ion. The macrocyclic rim consists of the two aryl bridgeheads and the two chains Y^1 and Y^2, while the bottom of the cavity is formed by the 1,10-phenanthroline, indicated by the dashed lines. The copper(I) ion is not visible: it is hidden by the carbene carbon atom connecting the ester group and the hydrogen atom. The concave shielding only allows attack from the front, but the alkene can be oriented in two fashions, providing either *anti* or *syn* products. The latter attack is more hindered because the ester group is larger than the hydrogen atom. c) In complex **2**·Cu^+=CH–COOR (for detailed structure of the ligand **2** see Figure 2), the large calixarene moiety only allows the ester group to point away from the cavity. For the attacking alkene, two sterically demanding pathways compete: either the alkene approaches from the side of the ester group, giving the *syn* product, or the alkene has to squeeze alongside the calixarene, producing the *anti* product.

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portion of the *anti* products is additional evidence of this mechanism.

In contrast to the symmetrical shielding by **1**, the shallow bowl of the calixarene derivative **2** only allows the ester group of the corresponding copper carbenoid to point in the direction of the approaching alkene. The substituents R on the alkene and the ester group therefore end up *syn* to each other in the final cyclopropane products. This suggestion is also supported by the correlation between the size of the ester group and the selectivity. With the substituents close to each other, the highest selectivity (*cis* or *endo*) is obtained with the smallest ester group. The final orientations of the substituents R depend on their interactions either with the ester group or with the large calixarene fragment.

In absolute numbers, better selectivity can be achieved for *anti* products (*anti*/*syn* value 140:1) than for *syn* products (best *syn*/*anti* value 86:14). In order to fine-tune and to optimize the *syn* selectivity, the selectivity-determining ligand **2** must be optimized. However, the calix[6]arene macrocycle in **2** cannot easily be altered[17–19] because the diameter of the calixarene is defined by the (easy) synthesis of this class of compounds.[20] Only calix[4]-, calix[6]- and calix[8]arenes are easily accessible,[21,22] and of these, only calix[6]arene[20] and calix[8]arene[23] have so far been A,D-bridged by a 1,10-phenanthroline unit.

This presents the question of whether the concave 1,10-phenanthrolines of type **1** might be altered in such a way that they would not be stiff anymore but might adopt bent structures like those of the bridged calixarenes **2**. In order to achieve a bowl-like geometry, either a joint (–CH_2–O– in **2**) would have to be incorporated between the 1,10-phenanthroline bridge and the bridgeheads, or the connection of the bridgeheads to the macrocycle chains Y^1 and Y^2 would have to be made differently (not bis-*ortho*).

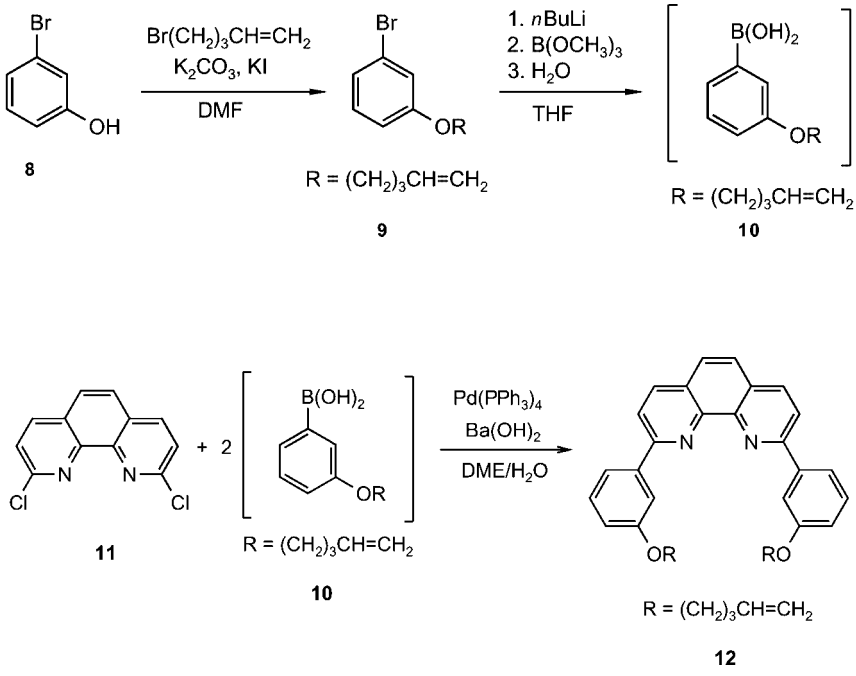
Results and Discussion

Synthesis of New Concave 1,10-Phenanthrolines

Two approaches to less symmetric and more open macrocyclic 1,10-phenanthrolines have been pursued, both trying to change the geometry of the bimacrocyclic 1,10-phenanthrolines **1** from a lamp-like cavity to a shallow pocket-like structure. The first concept leaves out one chain of the bimacrocycle, but simultaneously moves the remaining chain away from the 1,10-phenanthroline. The result is a monomacrocycle **14** (see below), with *meta*-substituted aryl rings in the 2- and 9-positions of the 1,10-phenanthroline. The construction of this macrocycle might use the well established sequence[13,24] of Suzuki coupling, ring-closing metathesis and hydrogenation.

Therefore, commercially available 3-bromophenol (**8**) was used as starting material, being alkenylated with 5-bromopent-1-ene in 95% yield in a Williamson ether synthesis. Lithiation with *n*-butyllithium, followed by treatment with trimethyl borate and hydrolysis, gave the boronic acid **10** in good yield.

However, boronic acid **10** slowly decomposes in solution; therefore, crude **10** was coupled with 2,9-dichloro-1,10-phenanthroline (**11**) under standard[25] Suzuki conditions [i.e., tetrakis(triphenylphosphane)palladium(0) as catalyst and barium hydroxide octahydrate as base in a mixture of dimethoxyethane (DME) and water]. The double-coupling product **12** was obtained in 62% yield, calculated from 2,9-



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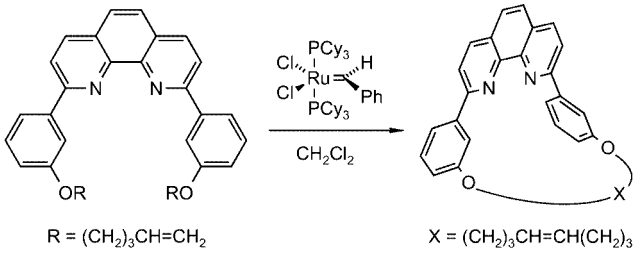
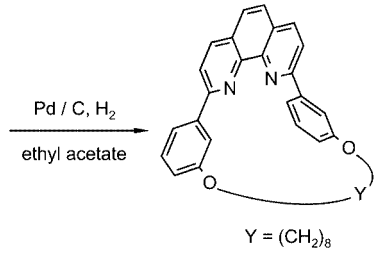
dichloro-1,10-phenanthroline (**11**) and starting from three equivalents of the bromo ether **9**.

The acyclic precursor **12** could be cyclized by ring-closing metathesis in 93% yield in the presence of the Grubbs I catalyst. The 1,2-disubstituted double bond in **13** exists as an almost 1:1 mixture of *cis*- and *trans*-configured alkene. Catalytic hydrogenation with palladium on charcoal gave the macrocyclic 1,10-phenanthroline **14**, with a saturated chain Y, in 49% yield.



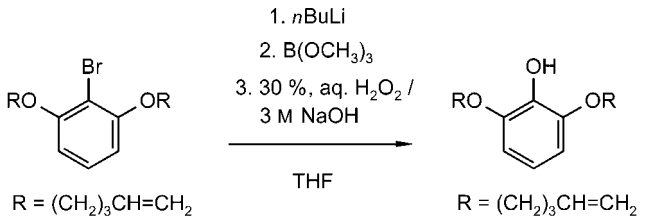
12 **13**



14

The second approach towards a concave 1,10-phenanthroline with a pocket-like structure goes back to the idea of a bimacrocyclic compound but allows the 1,10-phenanthroline bridge to flip as the bridge in the 1,10-phenanthroline-bridged calix[6]arene **2** does. The idea was to introduce two joints between the bridgeheads and the bridge. If 2,9-dichloro-1,10-phenanthroline (**11**) were again chosen as starting material, phenols instead of boronic acids would have to be coupled with **11**.

The synthesis of an appropriate phenol is straightforward because boron derivatives can easily be cleaved oxidatively. A precursor for the Suzuki coupling, the bis-pentenylated 2-bromoresorcinol **15**, was thus lithiated and treated with trimethyl borate. The resulting dimethylboronate was then oxidized with hydrogen peroxide in sodium hydroxide to afford phenol **16** in 81% yield.



15 **16**

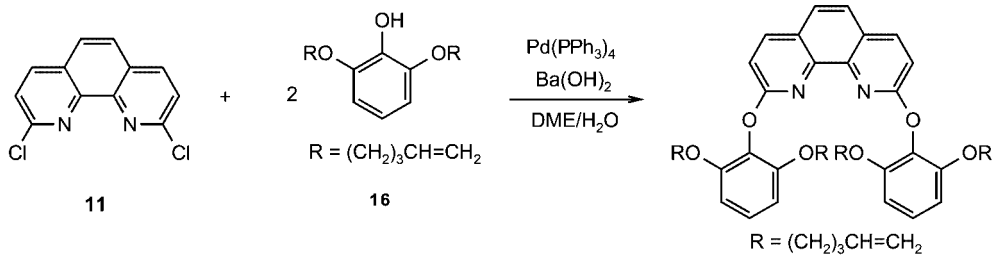
In a Pd(0)-catalyzed double nucleophilic heteroaromatic substitution, this phenol **16** reacted twice with 2,9-dichloro-1,10-phenanthroline (**11**) in 96% yield.

The resulting tetraene **17** was then cyclized to give the bimacrocyclic[26] 1,10-phenanthroline **18** in excellent yield (95%). Like all other (bi)macrocyclic 1,10-phenanthrolines obtained by ring-closing metathesis, **18** exists as a mixture with *cis* and *trans* double bonds, but hydrogenation again turns the stereoisomer into a single product and gives the bimacrocycle **19**, with saturated chains, in 98% yield.

Use of Concave 1,10-Phenanthrolines as Ligands in Copper(I)-Catalyzed Cyclopropanations

We next investigated the influence of the geometries of the two new concave 1,10-phenanthrolines **14** and **19** as ligands L on the stereochemistry of the copper(I)-catalyzed cyclopropanation of alkenes with diazoacetates **5**, in relation to other concave 1,10-phenanthrolines. The reaction conditions were chosen as in other cyclopropanations.[11,16] Indene (**3**) and styrene (**4**) were used as alkenes, with methyl, ethyl and *tert*-butyl diazoacetates (**5a**–**c**) as carbene precursors. Besides **14** and **19**, other concave 1,10-phenanthrolines **1** and **2** were also used in this reaction. Table 1 and Table 2 compare the data for these new ligands.

The concave 1,10-phenanthrolines **1**, **2**, **14** and **19** were first tested in the cyclopropanation of indene (**3**) and styrene (**4**) with ethyl diazoacetate (**5b**). Selected concave 1,10-phenanthrolines (**1a**, **1f**, **2**, **14** and **19**) were then also investigated in cyclopropanations with the smaller methyl ester **5a** or the larger *tert*-butyl ester **5c**. For better comparison, all reactions were carried out as batch reactions, still resulting in acceptable to good yields of cyclopropanes (up to 80%).



11 **16** **17**

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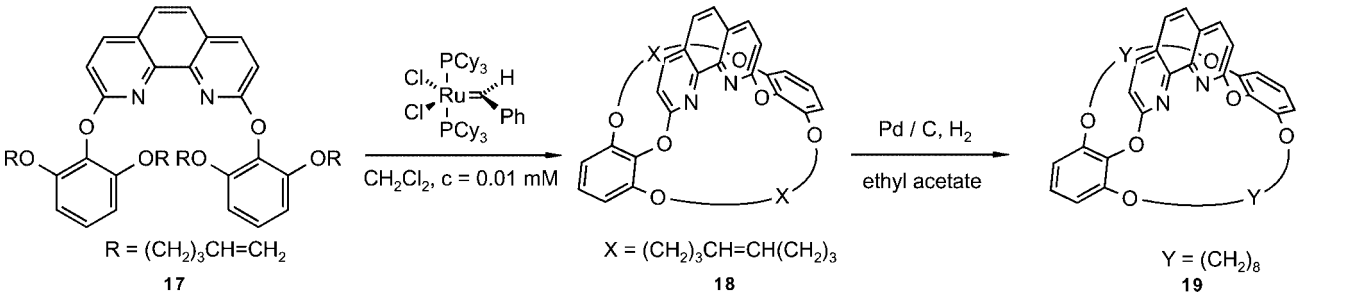

Table 1. *syn*/*anti* selectivities[a] (*endo*-**6**/*exo*-**6** or *cis*-**7**/*trans*-**7**) in the copper(I)-catalyzed cyclopropanation of indene (**3**) and styrene (**4**) with diazoacetates **5** in the presence of different concave 1,10-phenanthrolines **1**, **2**,[11,19] **14** or **19** as ligands L.

Alkene	Diazoacetate	No ligand	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**2**	**14**	**19**
3	**5a**	33:67	5:95					15:58	86:14	51:49	61:39
3	**5b**	43:57	4:96	1:99	1:99	2:98	2:98	29:71	76:24	56:44	58:42
3	**5c**	29:71	3:97					2:98	70:30	62:38	63:37
4	**5a**	43:57	24:76					62:38	74:26	60:40	48:52
4	**5b**	38:62	23:77	16:84	16:84	18:82	15:85	33:67	67:33	54:46	42:58
4	**5c**	33:67	12:88					12:88	54:46	52:48	67:33

[a] With acyclic alkenes, *cis*- and *trans*-cyclopropanes are formed, while cyclic alkenes give *exo*- and *endo*-configured bicyclic cyclopropanes. Therefore, *syn* summarizes *cis* and *endo*, *anti* summarizes *trans* and *exo*.

Table 2. Yields of the cyclopropanes **6** and **7** obtained in the copper(I)-catalyzed cyclopropanation of indene (**3**) and styrene (**4**) with diazoacetates **5** in the presence of different concave 1,10-phenanthrolines **1**, **2**, **14** or **19** as ligands L, together with yields of the side products dialkyl maleate and dialkyl fumarate when measurable (n.m. = not measurable). The yields were determined by GC with use of an internal standard.

Alkene	Diazoacetate	No ligand	**14**	**19**	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**2**
		Yield of **6** or **7** / Yield of maleate and fumarate									
3	**5a**	42 / n.m.	41 / n.m.	59 / n.m.	70 / n.m.					66 / n.m.	32 / –
3	**5b**	65 / 13	34 / 16	56 / 16	67 / 19	66 / 23	68 / 22	66 / 22	71 / 22	51 / 23	39 / 23
3	**5c**	51 / 23	34 / 9	46 / 15	55 / 26					44 / 39	35 / 14
4	**5a**	65 / 13	59 / 9	69 / 5	79 / 11					63 / 25	54 / –
4	**5b**	69 / 19	59 / 14	80 / 12	80 / 15	63 / 27	63 / 29	73 / 24	69 / 30	53 / 29	54 / 19
4	**5c**	64 / 12	47 / 11	76 / 9	72 / 15					45 / 41	45 / 16

Since it is known that the competing formation of fumarate and maleate can be reduced by slow addition of the diazo compound, these yields should be improvable.[27] In order to allow comparison of the stereochemistry of the cyclopropanation of cyclic and acyclic alkenes, the prefixes *syn* and *anti* are used. For a definition, see footnote [a] in Table 1.

As is already known from the cases of some concave 1,10-phenanthrolines, such as **1g**, with direct aryl-bridgehead 1,10-phenanthroline connections,[11] stiff concave 1,10-phenanthrolines **1** show good *syn*/*anti* selectivity, which can be enhanced by use of bulky diazoacetates (see Table 1; e.g., *endo*/*exo* ratio of <2 to >98 for addition to indene **3**).

In contrast to this large preference for the formation of the *anti* compounds, the monomacrocycle **14** is no longer *anti*-selective. With indene (**3**) and any diazoacetate **5a**–**c**, the *syn* product *endo*-**6** is the major isomer formed. Indeed, **14** is *syn*-selective, although the best selectivity is only 62:38. However, the exact *syn*/*anti* ratios should not be overinterpreted. At 50:50, 10% more or less are caused by only 1 kJ mol^{-1} energy difference for the activation barriers.

With styrene (**4**), **14** exhibits the same behaviour. Slightly more *syn* than *anti* product **7** is formed, while the bimacrocyclic concave 1,10-phenanthrolines **1** produce the *anti* product *trans*-**7** in a fourfold excess (*cis*-**7**/*trans*-**7** $\approx$ 20:80).

The second ligand with a structure fundamentally different from that of the bimacrocycles **1** is **19**, in which two oxygen atoms have been placed between the bridgeheads and the 1,10-phenanthroline moiety. This allows movement of the plains of the 1,10-phenanthroline and the macrocycle, consisting of the bridgeheads and the octamethylene chains, with respect to one another. With regard to the *syn*/*anti* selectivity, the preference of the concave 1,10-phenanthrolines **1** for the formation of the *anti* products *exo*-**6** and *trans*-**7** is also lost with **19**. In contrast, in many experiments the thermodynamically less stable *syn* products are the main compounds.

In summary, both strategies to alter the stiff bimacrocycles **1** have been successful: the less stable cyclopropanation products *endo*-**6** and *cis*-**7** are formed in (slight) excess with the new ligands, while the stiff ligands **1** showed a strong preference for the formation of the *anti* compounds. Compounds **14** and **19**, however, cannot yet compete with the calixarene derivative **2**, but the route to a *syn*-selective ligand (*endo*- or *cis*-selective) for the cyclopropanation of

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alkenes is cleared and the geometries of the new ligands **14** and **19**, unlike that of the bridged calixarene **2**, can be tailored with modified building blocks to give further concave 1,10-phenanthrolines with yet other bridgeheads and chains.

Experimental Section

General Remarks: The following chemicals were obtained commercially and were used without further purification: *N*,*N*-dimethylformamide (Fluka, ≥99.8%), dimethoxyethane (Aldrich), 3-bromophenol (Aldrich), 5-bromopent-1-ene (Fluka), trimethyl borate (Fluka), *n*-butyllithium 2.5 M in hexanes (Aldrich), tetrakis(triphenylphosphane)palladium(0) (Aldrich), barium hydroxide octahydrate (Merck), benzylidenebis(tricyclohexylphosphane)dichlororuthenium (Fluka). Pd/C (10%) (Merck). 2,9-Dichloro-1,10-phenanthroline (**11**)[28,29] and 2-bromo-1,3-bis(pent-4-enyloxy)benzene (**15**)[24] were prepared by literature procedures. Dry solvents were obtained with suitable desiccants: tetrahydrofuran was distilled from lithium aluminium hydride and ethyl acetate was distilled from calcium chloride. Column chromatography was carried out on basic alumina (Fluka, activity I) or silica gel (Macherey–Nagel, activity I). The 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), AM 300 (300 MHz or 75 MHz) or DRX 500 (500 MHz or 125 MHz) instruments, with tetramethylsilane as internal standard. IR spectra were measured on a Perkin–Elmer 1600 Series device. MS spectra were recorded on a Finnigan MAT 8230 machine. Elemental analyses were carried out on a VarioEl instrument (Elementaranalysensysteme GmbH). Gas chromatography was performed with a Varian 3400 Gas Chromatograph fitted with an Optima 1/25 m column from Macherey–Nagel. Comment: all (concave) 1,10-phenanthrolines tend to contain or absorb water.[25] The water content was calculated from the elemental analyses. As further structural corroboration, high-resolution mass spectra were recorded for all 1,10-phenanthrolines.

1-Bromo-3-(pent-4-enyloxy)benzene (9): 3-Bromophenol (**8**, 3.67 g, 21.2 mmol) was dissolved in dry *N*,*N*-dimethylformamide (40 mL), and potassium carbonate (9.00 g, 65.2 mmol), potassium iodide (500 mg, 3.01 mmol) and 5-bromopent-1-ene (2.50 mL, 16.8 mmol) were added. After the mixture had been stirred for 16 h at 60 °C, the solvent was evaporated in vacuo and the residue was dissolved in a mixture of sodium hydroxide (2 N, 30 mL) and diethyl ether (30 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic layer was washed with aqueous sodium hydroxide (2 N, 3 × 30 mL) and saturated aqueous sodium chloride solution (30 mL) and was dried with magnesium sulfate. The solvent was evaporated in vacuo and the residue was purified by filtration through silica gel with cyclohexane/ethyl acetate (10:1). Evaporation of the solvents gave 4.87 g (95%) of **9**. GC (Optima 1/25 m, temperature program: 5 min at 100 °C, 10 °C min^{-1}, 20 min at 250 °C): t_{Ret} = 12.1 min, purity: 99%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.87 (m_c, 2 H, OCH_2CH_2), 2.23 (m_c, 2 H, CH_2CH=), 3.94 (t, J = 6.4 Hz, 2 H, OCH_2), 4.99–5.10 (m, 2 H, $=CH_2$), 5.84 (tdd, J_t = 6.7, J_d = 10.2, J_d = 17.1 Hz, 1 H, CH=), 6.80–6.84 (m, 1 H, 4-H), 7.04–7.14 (m, 3 H, 2,5,6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.3 (t, OCH_2CH_2), 30.0 (t, CH_2CH=), 67.3 (t, OCH_2), 113.5 (d, 4-C), 115.4 (t, $=CH_2$), 117.7 (d, 2-C), 122.8 (s, 1-C), 123.6 (d, 6-C), 130.5 (d, 5-C), 137.6 (d, =CH), 159.8 (s, 3-C) ppm. IR (film): $\tilde{\nu}$ = 3076 (arom. C–H), 2975, 2941, 2874 (aliph. C–H), 1640 (aliph. C=C), 1590, 1573, 1468 (arom. C=C), 1064 (arom. C–Br), 1019 (C–O–C) cm^{-1}. MS (EI, 70 eV): m/z (%) = 242, 240 (13, 12) $[M]^+$, 174, 172 (38, 36) $[M - C_5H_8]^+$, 69 (100) $[C_5H_9]^+$. $C_{11}H_{13}BrO$ (241.12): calcd. C 54.79, H 5.43; found C 54.80, H 5.72.

3-(Pent-4-enyloxy)benzeneboronic Acid (10): 1-Bromo-3-(pent-4-enyloxy)benzene (**9**, 1.68 g, 6.97 mmol) was dissolved in tetrahydrofuran (25 mL). At –78 °C, *n*-butyllithium (2.5 M in hexane, 3.1 mL, 7.75 mmol) was added and the mixture was stirred for 1 h at –78 °C. After addition of trimethyl borate (2.60 mL, 23.3 mmol), stirring was continued for 2 h while the mixture was allowed to warm to room temperature. After hydrolysis with water (20 mL), the layers were separated, and the aqueous layer was extracted with diethyl ether (3 × 20–30 mL). The combined organic layer was washed with saturated aqueous sodium chloride solution (20–30 mL) and dried with magnesium sulfate, and the solvent was evaporated in vacuo. Crude yield: 1.40 g. Because of decomposition of **10** in solution, the crude product was used directly in the next synthetic step.

2,9-Bis[3-(pent-4-enyloxy)phenyl]-1,10-phenanthroline (12): Crude 3-(pent-4-enyloxy)benzeneboronic acid (**10**, 1.40 g) and 2,9-dichloro-1,10-phenanthroline (**11**, 580 mg, 2.33 mmol) were dissolved in dimethoxyethane (100 mL) and water (25 mL). After addition of barium hydroxide octahydrate (3.20 g, 10.1 mmol) and tetrakis(triphenylphosphane)palladium(0) (270 mg, 233 μmol), the mixture was heated to reflux for 16 h. Water (30 mL) and dichloromethane (30 mL) were then added, and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 30 mL), and the combined organic layer was extracted with saturated aqueous sodium chloride solution (20 mL) and dried with magnesium sulfate. The solvent was evaporated in vacuo, and the residue was purified by chromatography (silica gel, dichloromethane) and recrystallized from dichloromethane/*n*-hexane, giving 615 mg (62%) of **12**, m.p. 92–93 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.79 (m_c, 4 H, OCH_2CH_2), 2.30 (m_c, 4 H, CH_2CH=), 4.20 (t, J = 6.4 Hz, 4 H, OCH_2), 4.99–5.13 (m, 4 H, $=CH_2$), 5.90 (tdd, J_t = 6.7, J_d = 10.2, J_d = 17.1 Hz, 2 H, CH=), 7.04 (ddd, $J \approx 1$, J = 2.6, $J \approx 8$ Hz, 4 H, 4′,4′′-H), 7.45 (t, $J \approx 8$ Hz, 2 H, 5′,5′′-H), 7.76 (s, 2 H, 5,6-H), 8.03 (ddd, $J \approx 1$, $J \approx 2$, $J \approx 8$ Hz, 2 H, 6′,6′′-H), 8.09 (dd, $J \approx 2$, J = 2.6 Hz, 2 H, 2′,2′′-H), 8.12 (d, J = 8.4 Hz, 2 H, 3,8-H), 8.28 (d, J = 8.4 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.6 (t, OCH_2CH_2), 30.2 (t, CH_2CH=), 67.2 (t, OCH_2), 113.4 (d, 2′,2′′-C), 115.2 (t, $=CH_2$), 116.0 (d, 4′,4′′-C), 119.9, 120.0, (2 × d, 3,6′,6′′,8-C), 126.0 (d, 5,6-C), 127.9 (s, 4a,6a-C), 129.6 (d, 5′,5′′-C), 136.8 (d, 4,7-C), 137.9 (d, CH=), 140.8 (s, 1′,1′′-C), 145.9 (s, 10a,10b-C), 156.4 (s, 2,9-C), 159.5 (s, 3′,3′′-C) ppm. IR (KBr): $\tilde{\nu}$ = 3073, 3026 (arom. C–H), 2932, 2854 (aliph. C–H), 1640 (aliph. C=C), 1596, 1475 (arom. C=C), 1100 (C–O–C) cm^{-1}. MS (EI, 70 eV): m/z (%) = 500 (100) $[M]^+$, 459 (25) $[M - C_3H_5]^+$, 445 (38) $[M - C_4H_7]^+$, 431 (12) $[M - C_5H_9]^+$. HR-MS: $C_{34}H_{32}N_2O_2$, found 500.24640, calcd. 500.24637 (–0.1 ppm), $C_{33}{}^{13}CH_{32}N_2O_2$, found 501.24960, calcd. 501.24973 (0.3 ppm). $C_{34}H_{32}N_2O_2$ (500.63): calcd. C 81.57, H 6.44, N 5.60, $C_{34}H_{32}N_2O_2 \times 0.2\ H_2O$: calcd. C 80.99, H 6.48, N 5.56; found C 81.03, H 6.79, N 5.48.

4,13-Dioxa-1,3(1,3)-dibenzena-2(2,9)-1,10-phenanthrolinacyclotridecaphan-8-ene (13): 2,9-Bis[3-(pent-4-enyloxy)phenyl]-1,10-phenanthroline (**12**, 600 mg, 1.20 mmol) was dissolved in dichloromethane (120 mL) and benzylidenebis(tricyclohexylphosphane)dichlororuthenium (49.3 mg, 59.9 mmol, 5 mol-%) was added. After stirring for 16 h at room temperature, the mixture was filtered three times through basic aluminium oxide with dichloromethane. Evaporation of the solvent in vacuo gave 527 mg (93%) of **13**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.86, 2.34 (2 × m_c, 8 H, CH_2), 4.12, 4.18 (2 × t, $J \approx 6$, $J \approx 6$ Hz, 4 H, OCH_2), 5.47 (m_c, 1.15 H, *trans*-CH=CH)*, 5.55 (2 × m_c, 0.85 H, *cis*-CH=CH)*, 7.04 (m_c, 2 H,

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4′,4′′-H), 7.40 (t, $J \approx 8$ Hz, 2 H, 5′,5′′-H), 7.53 (m_c, 2 H, 6′,6′′-H), 7.76, 7.77 (2×s, 2 H, 5,6-H), 8.09, 8.11 (2×d, $J \approx 8$, $J \approx 8$ Hz, 2 H, 3,8-H), 8.28, 8.28 (2×d, $J \approx 8$, $J \approx 8$ Hz, 2 H, 4,7-H), 8.25, 8.44 (2×m_c, 2 H, 2′,2′′-H) ppm. * The stereoisomer ratio was 1:1.3. Because of the small difference in chemical shift, the assignment may be reversed. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.8, 27.9, 28.0, 29.3 (4×t, CH_2), 65.0, 66.9 (2×t, OCH_2), 111–121 (8×d, 2′,2′′,3,4′,4′′,6′,6′′,8-C), 126.1, 126.1 (2×d, 5,6-C), 128.0 (s, 4a,6a-C), 129.3, 129.3, 130.0, 130.5 (4×d, 5′,5′′-C, CH=CH), 136.9 (d, 4,7-C), 141.2, 141.4 (2×s, 1′,1′′-C), 146.1 (s, 10a,10b-C), 157.0, 157.4 (2×s, 2,9-C), 159.8, 160.1 (2×s, 3′,3′′-C) ppm. IR (KBr): $\tilde{\nu}$ = 2926, 2862 (aliph. C–H), 1598, 1488 (arom. C=C), 1052 (C–O–C) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 472 (100) $[M]^+$, 364 (59) $[C_{24}H_{16}O_2N_2]^+$. HR-MS: $C_{32}H_{28}N_2O_2$, found 472.21510, calcd. 472.21509 (–0.0 ppm), $C_{31}{}^{13}CH_{28}N_2O_2$, found 473.21820, calcd. 473.21844 (0.5 ppm). $C_{32}H_{28}N_2O_2$ (472.58): calcd. C 81.33, H 5.97, N 5.93, $C_{32}H_{28}N_2O_2 \times 0{\cdot}3\,H_2O$: calcd. C 80.41, H 6.03, N 5.86; found C 80.63, H 6.27, N 5.58.

4,13-Dioxa-1,3(1,3)-dibenzena-2(2,9)-1,10-phenanthrolinacyclotridecaphane (14): Palladium on charcoal (10%, 20.0 mg) was mixed with ethyl acetate (5.00 mL, filtered through basic aluminium oxide prior to use, in order to remove acid traces) and hydrogen was bubbled through the mixture for 30 min. This activated mixture was then mixed with a solution of 4,13-dioxa-1,3(1,3)-dibenzena-2(2,9)-1,10-phenanthrolinacyclotridecaphan-8-ene (**13**, 200 mg, 423 mmol) in ethyl acetate (12 mL, quality as above) and hydrogen was bubbled through the solution for 2 h while stirring at room temperature was continued. Stirring of the solution in an atmosphere of hydrogen was continued for 16 h at room temperature. The solvent was evaporated in vacuo and the residue was dissolved in dichloromethane, filtered through basic aluminium oxide, purified by chromatography with a chromatotron (neutral aluminium oxide, dichloromethane/*n*-pentane, 1:1) and recrystallized from dichloromethane/*n*-hexane, yielding 97 mg (48%) of **14**, m.p. 156–158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94, 1.23, 1.50, 1.74, 1.84 (5 m_c, 12 H, CH_2), 4.12 (t, J = 5.6 Hz, 4 H, OCH_2), 7.01 (m_c, 2 H, 4′,4′′-H), 7.40 (t, $J \approx 8$ Hz, 2 H, 5′,5′′-H), 7.45–7.50 (m, 2 H, 6′,6′′-H), 7.70 (s, 2 H, 5,6-H), 8.08 (d, J = 8.4 Hz, 2 H, 3,8-H), 8.25–8.30 (m with d at 8.28, J = 8.4 Hz, 4 H, 2′,2′′,4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.8, 26.3, 28.1 (3×t, CH_2), 67.5 (t, OCH_2), 113.9, 115.5, 120.0, 121.3 (4×d, 2′,2′′,3,4′,4′′,6′,6′′,8-C), 126.2 (d, 5,6-C), 128.1 (s, 4a,6a-C), 129.3 (d, 5′,5′′-C), 136.9 (d, 4,7-C), 141.5 (s, 1′,1′′-C), 146.3 (s, 10a,10b-C), 157.7 (s, 2,9-C), 160.0 (s, 3′,3′′-C) ppm. IR (KBr): $\tilde{\nu}$ = 3032 (arom. C–H), 2924, 2860 (aliph. C–H), 1602, 1486 (arom. C=C), 1098 (C–O–C) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 474 (100) $[M]^+$, 364 (88) $[C_{24}H_{16}N_2O_2]^+$. HR-MS: $C_{32}H_{30}N_2O_2$, found 474.23060, calcd. 474.23074 (0.3 ppm), $C_{31}{}^{13}CH_{30}N_2O_2$, found 475.23370, calcd. 475.23407 (0.8 ppm). $C_{32}H_{30}N_2O_2$ (474.59): calcd. C 80.98, H 6.37, N 5.90, $C_{32}H_{30}N_2O_2 \times 0.2\,H_2O$: calcd. C 80.37, H 6.41, N 5.86; found C 80.51, H 6.57, N 5.75.

2,6-Bis(pent-4-enyloxy)phenol (16): 2-Bromo-1,3-bis(pent-4-enyloxy)benzene (**15**, 4.93 g, 15.2 mmol) was dissolved in tetrahydrofuran (50 mL). At –78 °C, *n*-butyllithium (2.5 M in hexane, 6.80 mL, 17.0 mmol) was added and the mixture was stirred for 1 h at –78 °C. Trimethyl borate (4.90 mL, 43.9 mmol) was added and stirring was continued for 2 h, while the mixture was warmed to room temperature. After the mixture had been cooled to –78 °C, aqueous sodium hydroxide (3 M, 30 mL) and aqueous hydrogen peroxide (30%, 30 mL) were added simultaneously, and the mixture was stirred for 18 h at room temperature, after which it was extracted with diethyl ether (4×30 mL). The combined organic layer was washed with water (3×30 mL) and concentrated aqueous sodium chloride solution (30 mL). After drying with magnesium sulfate, the solvent was evaporated in vacuo and the residue was purified by chromatography (cyclohexane/ethyl acetate, 10:1) yielding 200 mg (81%) of **16**, which is partly molten at room temperature. GC (Optima 1/25 m, program: 5 min at 100 °C, 10 °C min^{-1}, 20 min at 250 °C): t_{Ret} = 17.2 min, purity: 93%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.93 (m_c, 4 H, OCH_2CH_2), 2.25 (m_c, 4 H, CH_2CH=), 4.05 (t, J = 6.6 Hz, 4 H, OCH_2), 4.99–5.09 (m, 4 H, =CH_2), 5.56 (s, 1 H, OH), 5.86 (tdd, J_t = 6.7, J_d = 10.3, J_d = 17.1 Hz, 4 H, CH=), 6.56 (d, J = 8.3 Hz, 2 H, 3,5-H), 6.75 (dd, J = 7.9, J = 8.7 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.3 (t, OCH_2CH_2), 30.1 (t, CH_2CH=), 68.6 (t, OCH_2), 106.2 (d, 3,5-C), 115.1 (t, =CH_2), 118.9 (d, 4-C), 135.5 (s, 1-C), 137.8 (d, CH=), 146.6 (s, 2,6-C) ppm. IR (KBr): $\tilde{\nu}$ = 3535 (O–H), 3075 (arom. C–H), 2974, 2941, 2874 (aliph. C–H), 1640, 1619 (aliph. C=C), 1506, 1469 (arom. C=C), 1094 (C–OH) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 262 (32) $[M]^+$, 126 (80) $[C_6H_6O_3]^+$, 69 (100) $[C_5H_9]^+$. $C_{16}H_{22}O_3$ (262.35): calcd. C 73.25, H 8.45, $C_{16}H_{22}O_3 \times 0.1\,H_2O$: calcd. C 72.75, H 8.47; found C 72.59, H 8.99.

2,9-Bis[2,6-bis(pent-4-enyloxy)phenyloxy]-1,10-phenanthroline (17): 2,9-Dichloro-1,10-phenanthroline (**11**, 43.0 mg, 173 mmol) and 2,6-bis(pent-4-enyloxy)phenol (**16**, 135 mg, 515 mmol) were dissolved in dry *N*,*N*-dimethylformamide (10 mL). After addition of caesium carbonate (300 mg, 921 μmol), the mixture was stirred for 18 h at 100 °C. After evaporation of the solvent in vacuo, the residue was dissolved in aqueous sodium hydroxide solution (2 N, 30 mL) and dichloromethane (30 mL). After separation of the layers, the aqueous layer was extracted with dichloromethane (3×40 mL). The combined organic layer was washed with aqueous sodium hydroxide solution (2 N, 3×40 mL) and concentrated aqueous sodium chloride solution (30 mL). After drying with magnesium sulfate, the solvent was evaporated in vacuo, and the residue was dissolved in dichloromethane and filtered through basic aluminium oxide. After evaporation of the solvent, the residue was recrystallized from dichloromethane/*n*-hexane, giving 116 mg (96%) of **17**, m.p. 34 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48 (m_c, 8 H, OCH_2CH_2), 1.76 (m_c, 8 H, CH_2CH=), 3.77 (t, J = 6.4 Hz, 8 H, OCH_2), 4.6–4.8 (m, 8 H, =CH_2), 5.52 (tdd, J_t = 6.6, J_d = 10.6, J_d = 16.7 Hz, 4 H, CH=), 6.56 (d, J = 8.4 Hz, 4 H, 3′,3′′,5′,5′′-H), 7.10 (t, J = 8.4 Hz, 2 H, 4′,4′′-H), 7.26 (d, J = 8.6 Hz, 2 H, 3,8-H), 7.61 (s, 2 H, 5,6-H), 8.12 (d, J = 8.6 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.5 (t, OCH_2CH_2), 29.7 (t, CH_2CH=), 68.9 (t, OCH_2), 108.3 (d, 3′,3′′,5′,5′′-C), 112.8 (d, 3,8-C), 114.4 (t, =CH_2), 123.6 (d, 5,6-C), 124.9 (d, 4′,4′′-C), 125.9 (s, 1′,1′′-C), 133.7 (s, 4a,6a-C), 138.0 (d, CH=), 139.0 (d, 4,7-C), 143.7 (s, 10a,10b), 152.6 (s, 2′,2′′,6′,6′′-C), 161.5 (s, 2,9-C) ppm. IR (KBr): $\tilde{\nu}$ = 3074 (arom. C–H), 2935, 2861 (aliph. C–H), 1640 (aliph. C=C), 1603, 1458 (arom. C=C), 1100 (C–O–C) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 700 (100) $[M]^+$, 659 (94) $[M - C_3H_5]^+$, 645 (26) $[M - C_4H_7]^+$. HR-MS: $C_{44}H_{48}N_2O_6$, found 700.35130, calcd. 700.35126 (–0.1 ppm), $C_{43}{}^{13}CH_{48}N_2O_6$, found 701.35400, calcd. 701.35461 (0.9 ppm). $C_{44}H_{48}N_2O_6$ (700.86): calcd. C 75.40, H 6.90, N 4.00; found C 75.23, H 7.01, N 3.94.

2,11,13,22,23,25-Hexaoxa-1,12(1,3,2)-dibenzena-24(2,9)-1,10-phenanthrolinabicyclo[10.10.3]pentacosaphan-6,17-diene (18): 2,9-Bis[2,6-bis(pent-4-enyloxy)phenyloxy]-1,10-phenanthroline (**17**, 410 mg, 585 mmol) was dissolved in dichloromethane (58.5 mL, c = 0.01 mmol L^{-1}). After addition of benzylidenebis(tricyclohexylphosphane)dichlororuthenium (24.1 mg, 29.3 μmol, 5 mol-%), the mixture was stirred for 16 h at room temperature and filtered three times through basic aluminium oxide with dichloromethane. Evaporation of the solvent in vacuo gave 365 mg (95%) of **18**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.0–1.9 (m with 3×m_c at 1.24, 1.45, 1.77,

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16 H, CH_2), 3.54, 3.85, 3.92 (3×m_c, 8 H, OCH_2), 4.60, 4.70, 4.94 (3×m_c, 4 H, CH=CH), 6.45–6.55 (m, with d at 6.49, J = 8.3 Hz, 4 H, 3′,3′′,5′,5′′-H), 7.07, 7.08, 7.12 (3×t, J = 8.3, J = 8.3, J = 8.3 Hz, 2 H, 4′,4′′-H), 7.37, 7.38, 7.39 (3×d, J = 8.6, J = 8.6, J = 8.6 Hz, 2 H, 3,8-H), 7.58, 7.62, 7.64 (3×s, 2 H, 5,6-H), 8.12, 8.15, 8.17 (3×d, J = 8.6, J = 8.6, J = 8.6 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.5, 26.4, 26.8, 28.6, 28.8, 29.1 (6×t, CH_2), 65.4, 66.1, 68.6 (3×t, OCH_2), 106.2, 106.8, 108.1 (3×d, 3′,3′′,5′,5′′-C), 113.0, 113.2 (2×d, 3,8-C), 123.7, 125.3, 125.3 (3×d, 4′,4′′,5,6-C), 125.9, 125.9 (2×s, 1′,1′′-C), 129.7, 130.1, 130.3 (3×d, CH=CH), 131.7 (s, 4a,6a-C), 139.1, 139.2 (2×d, 4,7-C), 143.8 (s, 10a,10b-C), 152.3, 152.3, 152.7 (3×s, 2,9-C), 161.4 (s, 2′,2′′,6′,6′′-C) ppm. IR (KBr): $\tilde{\nu}$ = 2933, 2869 (aliph. C–H), 1602 (aliph. C=C), 1458 (arom. C=C), 1103 (C–O–C) cm^{-1}. MS (EI, 70 eV): m/z (%) = 644 (100) $[M]^+$. HR-MS: $C_{40}H_{40}N_2O_6$, found 644.28850, calcd. 644.28864 (0.2 ppm), $C_{39}{}^{13}CH_{40}N_2O_6$, found 645.29150, calcd. 645.29199 (0.8 ppm). $C_{40}H_{40}N_2O_6$ (644.76): calcd. C 74.51, H 6.25, N 4.34, $C_{40}H_{40}N_2O_6\times0.5H_2O$: calcd. C 73.49, H 6.32, N 4.28; found C 73.50, H 6.40, N 4.13.

2,11,13,22,23,25-Hexaoxa-1,12(1,3,2)-dibenzena-24(2,9)-1,10-phenanthrolinabicyclo[10.10.3]pentacosaphane (19): Palladium on charcoal (10%, 40.0 mg) was mixed with ethyl acetate (5.00 mL, filtered through basic aluminium oxide prior to use, in order to remove acid traces) and hydrogen was bubbled through the mixture for 30 min, after which it was combined with a solution of 2,11,13,22,23,25-hexaoxa-1,12(1,3,2)-dibenzena-24(2,9)-1,10-phenanthrolinabicyclo[10.10.3]pentacosaphane-6,17-diene (**18**, 315 mg, 449 mmol) in ethyl acetate (20 mL, quality as above). Hydrogen was bubbled through the mixture for 2 h while stirring at room temperature was continued. Stirring of the solution in an atmosphere of hydrogen was continued for 16 h at room temperature. Total conversion was monitored by TLC. The solvent was evaporated in vacuo and the residue was dissolved in dichloromethane and filtered through basic aluminium oxide. The solvent was evaporated and the residue was recrystallized from dichloromethane/*n*-hexane, yielding 285 mg (98%) of **19**, m.p. 168 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.70, 0.76, 0.87, 1.41 (4×m_c, 24 H, CH_2), 3.87 (m_c, 8 H, OCH_2), 6.60 (d, J = 8.4 Hz, 4 H, 3′,3′′,5′,5′′-H), 7.11 (t, J = 8.4 Hz, 2 H, 4′,4′′-H), 7.22 (d, J = 8.6 Hz, 2 H, 3,8-H), 7.61 (s, 2 H, 5,6-H), 8.10 (d, J = 8.6 Hz, 2 H, 4,7-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.0, 27.4, 28.4 (3×t, CH_2), 69.0 (t, OCH_2), 108.1 (d, 3′,3′′,5′,5′′-C), 112.3 (d, 3,8-C)*, 123.7 (d, 5,6-C)*, 125.3 (d, 4′,4′′-C)*, 125.8 (s, 4a,6a-C), 133.3 (s, 10a,10b-C)°, 139.0 (d, 4,7-C), 143.8 (s, 1′,1′′-C)°, 152.6 (s, 2′,2′′,6′,6′′-C), 161.8 (s, 2,9-C) ppm. *, ° assignment may be reversed. IR (KBr): $\tilde{\nu}$ = 2929, 2855 (aliph. C–H), 1602 (aliph. C=C), 1466 (arom. C=C), 1100 (C–O–C) cm^{-1}. MS (EI, 70 eV): m/z (%) = 648 (100) $[M]^+$, 605 (7) $[M - C_3H_8]^+$. HR-MS: $C_{40}H_{44}N_2O_6$, found 648.31990, calcd. 648.31995 (0.1 ppm), $C_{39}{}^{13}CH_{44}N_2O_6$, found 649.32330, calcd. 649.32330 (0.0 ppm). $C_{40}H_{44}N_2O_6$ (648.79): calcd. C 74.05, H 6.84, N 4.32, $C_{40}H_{44}N_2O_6\times0.4\,H_2O$: calcd. C 73.24, H 6.88, N 4.27; found C 73.10, H 7.03, N 4.10.

Cyclopropanation: Under argon, ca. 2.5 to 3.5 mg (+/– 0.01 mg) of copper(I) triflate hemi-benzene complex (Aldrich) were placed in a vial, and 440 equivalents [based on copper(I)] of alkene **3** or **4**, and 1.2 equivalents of the ligands **1a**–**f**, **2**, **14** or **19**, dissolved in 1,2-dichloroethane (c = 0.01 mol L^{-1}), were added. After addition of 50 equivalents of the diazoacetate **5**, the mixture was stirred at room temp. for 24 h. At the beginning of the reaction, quick development 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-Dichloromethane was then added to give ca. 10 mL of solution. After addition of ca. 25 mg of *n*-hexadecane (+/– 0.01 mg) as GC standard, the products were analyzed by GC: Optima 1/25 m, 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, 2 min.

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Received: August 26, 2005
Published Online: December 13, 2005

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