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Concave Annelated Terpyridines[‡]

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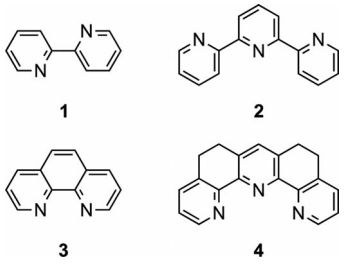
Bimacrocyclic concave annelated terpyridines were generated from a U-shaped nonmacrocyclic tetraalkene precursor by ring closing metathesis followed by hydrogenation. The U-shaped precursor was synthesized by condensing two aryltetrahydroquinolones with Eschenmoser's salt. The quinolones themselves were accessible by coupling a 2-chloroquinolone with a bis-alkenyloxy-substituted boronic acid. The concave terpyridine was tested for reactivity and stereoselectivity in a copper(I)-catalyzed cyclopropanation.

Introduction

N-Heterocyclic compounds play an important role as ligands for metal ions, especially transition metal species. The resulting complexes serve in a multitude of ways, for example as catalysts,[1,2] but also in supramolecular chemistry for self assembly.[3–6] When more than one nitrogen atom is suitably positioned, the ligands are even more powerful due to the chelate effect. Thus 2,2′-bipyridine (**1**) and 1,10-phenanthroline (**3**) are widely used two-site chelates, and 2,2′:6′,2"-terpyridine (**2**) is the most prominent chelating ligand with three coordinating nitrogen atoms (Scheme 1).[7–10] Whereas the pyridine–pyridine dihedral angles may vary in bi- and ter-pyridines **1** and **2** – with the *anti* orientation usually being favored – the two nitrogen atoms of 1,10-phenanthroline (**3**) are fixed in a *syn* orientation due to the annelated benzene ring. Therefore, the 1,10-phenanthroline unit has been used in concave bases,[11] rather than the 2,2′-bipyridine moiety to ensure the concave positioning of the lone pairs of the nitrogen atoms (Figure 1).



Scheme 1. Chelating N-heterocycles.

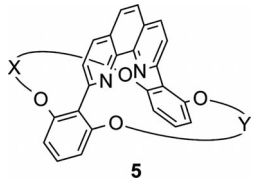


Figure 1. General structure for a concave 1,10-phenanthroline **5**.[11–14] X and Y may be polymethylene or oligoethylene glycol chains.

It is therefore clear that the use of bridged terpyridines **4** as concave bases and ligands would also be suitable.[15] In the 1980's, Thummel and Jahng presented the synthesis of annelated 2,2′:6′,2"-terpyridines **4**,[16] and Zimmerman et al. developed a route to such terpyridines with additional functionalities in the α-position relative to the outer nitrogen atoms, eventually leading to the construction of partially shielded systems such as molecular pincers,[17] which were also found to act as host systems for organic guests and transition-metal ions.[18]

At present, the most effective way of synthesizing bimacrocyclic concave reagents such as concave 1,10-phenanthrolines starts from a 2,9-dihalogeno-1,10-phenanthroline.[13] The halogen atoms are then exchanged by aryl bridgeheads that carry alkenyloxy chains in their *ortho* positions. Ring-closing metathesis then generates the concave bimacrocycles. For a similar approach in the case of terpyridines, the bis-α-disubstituted terpyridines described above seemed suitable.

Results and Discussion

Suitably substituted terpyridines (**12** and **13**) were first required. For their syntheses, a literature approach[17] was adopted. In the central step, two tetrahydroquinolone units

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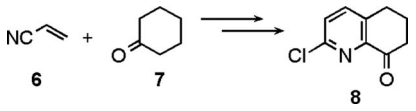
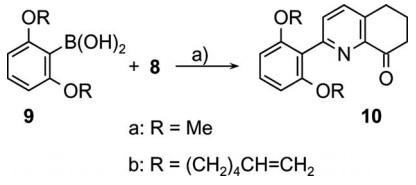
such as **8** were to be submitted to a condensation reaction with a carbonyl compound (or an equivalent) in the presence of a nitrogen source (see below). Therefore, suitable tetrahydroquinolone compounds had to be synthesized first. Chlorotetrahydroquinolone **8** (Scheme 2) was synthesized in a multistep reaction starting from acrylonitrile (**6**) and cyclohexanone (**7**), as described in the literature.[17,19,20]



Scheme 2. Synthetic route to chlorotetrahydroquinolone **8**.

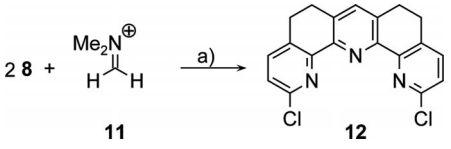
The last step of the reaction sequence was the oxidation of an alcoholic precursor to ketone **8**. Swern oxidation is critical for larger amounts of substrate, but the reaction was quick and smooth. Several batch reactions were carried out in parallel, which allowed a larger scale (20 g) synthesis of **8**.

At this stage in the route to concave terpyridines, the bridgehead moieties were introduced. Suzuki–Miyaura cross-coupling between chloride **8** and boronic acid **9b** gave the arylated tetrahydroquinolone **10b** as the precursor to the concave terpyridines **14** and **15**. For comparison, a dimethoxy derivative **10a** was also synthesized. Both compounds were isolated in acceptable yields of 72% for building block **10b** and 59% for the methyoxy analogue **10a** (Scheme 3).



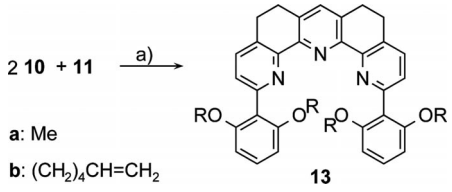
Scheme 3. Synthesis of aryl-substituted quinolones **10**. Reagents and conditions: a) $[Pd(PPh_3)_4]$, $Ba(OH)_2$, dimethoxyethane, H_2O.

The condensation of two tetrahydroquinolones with a C_1 unit and a nitrogen source was tested first with chloride **8**. Whereas Knoevenagel reactions with, for instance, benzaldehyde, only yielded products that were difficult to purify, a variant, described by Risch,[21–23] was more successful. In a one-pot reaction, tetrahydroquinolone **8** was treated with Eschenmoser's salt (**11**; *N*,*N*-dimethylmethylene iminium iodide). In principle, S- and U-shaped annealed terpyridines may form in this reaction, however, suitable reaction conditions and substitution can direct the reaction to give the U-shaped products.[24] Indeed, U-shaped dichloroterpyridine **12** was formed exclusively in the test reaction (Scheme 4).



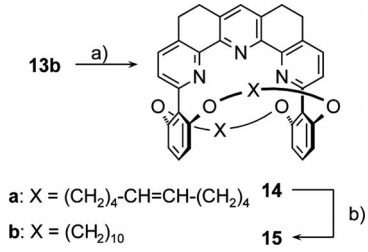
Scheme 4. Synthesis of rigid dichloroterpyridine **12**. Reagents and conditions: a) NH_4OAc, DMSO.

The aryl-substituted tetrahydroquinolones **10** were then condensed with Eschenmoser's salt **11**. The U-shaped products were formed when the reaction was carried out under suitable conditions involving the following steps: first, one equivalent of the quinolone **10** was mixed with Eschenmoser's salt **11**, and, in parallel, a second equivalent of **10** was mixed with ammonium acetate. The two batches were mixed, and the reaction proceeded with the desired regiochemistry; the methoxy derivative **13a** (Scheme 5) was isolated in 25% yield, and the tetraalkenyloxy derivative **13b** in 48% yield, both were obtained as U-isomers exclusively.



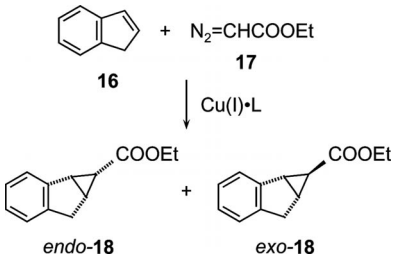
Scheme 5. Synthesis of diaryl-substituted terpyridines **13**. Reagents and conditions: a) NH_4OAc, DMSO.

In tetraalkene **13b**, four vinyl groups are suitably positioned for macrocyclization by ring-closing metathesis. It is well-established in the synthesis of other bimacrocyclic concave reagents[13,25] that a double macrocyclization can be carried out in moderate dilution in dichloromethane using Grubbs' catalyst. The resulting concave terpyridine **14**, as a diene, was found to form as a mixture of diastereoisomers (*E*,*E*; *E*,*Z*; *Z*,*Z*). As established for other concave reagents,[13,25] the mixture could be simplified to only one saturated product by hydrogenation. The double ring-closure gave **14** in 74% isolated yield, the hydrogenated product **15** was isolated in 90% yield (Scheme 6).



Scheme 6. Synthesis of concave terpyridines **14** and **15**. Reagents and conditions: a) Grubbs' catalyst, dichloromethane; b) H_2, Pd/C, MeOH.

With compounds **14** and **15**, the first two concave terpyridines have been manufactured. As a first test to investigate whether the active site in the bimacrocyclic system is still sufficiently accessible to allow catalysis and to determine the influence of the concave shielding, the copper(I)-catalyzed cyclopropanation of alkenes with ethyl diazoacetate (**17**) was studied. Indene (**16**) was chosen as the substrate so that the results could be compared with those of other (concave) ligands (Scheme 7).[26] The cyclopropanation product **18** was formed as a mixture of *endo*- and *exo*-cyclopropanes. An analysis of the stereoselectivity of the reaction was conducted using gas chromatography (Table 1).[26–28]



Scheme 7. Copper(I)-catalyzed cyclopropanation of indene (**16**) with ethyl diazoacetate (**17**). For the nature of ligands L, see Table 1.

Table 1. Stereoselectivity of the copper(I)-catalyzed cyclopropanation of indene (**16**) with ethyl diazoacetate (**17**) in the presence (and absence) of ligands.

Ligand (L)	*endo*-**18**/*exo*-**18**
None	31:69
2,9-Dimethyl-1,10-phenanthroline	29:71
12	32:68
13a	32:68
15	12:88

In all reactions, the expected cyclopropanes **18** were formed, and, in all cases, the *exo*-product (*exo*-**18**) predominated. The nonmacrocyclic ligands **12** and **13a** showed no influence on the stereochemistry when compared to neocuproine (2,9-dimethyl-1,10-phenanthroline) or copper(I) catalysis in the absence of ligands. When bimacrocycle **15** was employed, a shift of the selectivity towards the *exo*-product was found.

Conclusions

As a new class of concave bases and concave ligands, terpyridines **14** and **15** have been synthesized. The saturated bimacrocycle **15** has been used as a ligand for copper(I) ions and the resulting complex has successfully been used in a cyclopropanation reaction. The stereoselectivity of the cyclopropanation of indene **16** was studied and the results were compared to those obtain with analogous terpyridine ligands **12**, **13a**, and with 2,9-dimethyl-1,10-phenanthroline. The concave shielding enhances the *endo*/*exo* selectivity from ca. 30:70 to 12:88 in favor of the *exo* form. Thus, concave terpyridine **15** is indeed a promising concave ligand. The catalytic center remained active, and the concave part of the ligand enhances selectivity. In this test reaction, however, **15** did not reach the results[27] achieved by tailored concave 1,10-phenanthrolines (up to 1:99) but its potential has nevertheless been demonstrated.

Experimental Section

General Remarks: The following chemicals were obtained commercially and used without further purification: acetic anhydride (Aldrich), acrylonitrile (Acros), ammonia solution (25%) (Riedel-de Haën), ammonium acetate (Merck), barium hydroxide octahydrate (Merck), benzylidenebis(tricyclohexylphosphane)dichlororuthenium (Fluka), cyclohexanone (Merck), cyclohexylamine (Aldrich), 1,2-dimethoxyethane (Acros), dimethyl sulfoxide (Merck), Eschenmoser's salt (*N*,*N*-dimethylmethyleneiminium iodide; Acros), glacial acetic acid (Merck), hydrogen peroxide (30%; Merck), 4-methoxyphenol (Aldrich), oxalyl chloride (Fluka), Pd/C (10%) (Merck), phosphoroxy chloride (Merck), sulfuric acid (96%) (Riedel-de Haën), tetrakis(triphenylphosphane)palladium(0) (Aldrich), triethylamine (Merck). [2,6-Bis(hex-5-enyloxy)phenyl]boronic acid[14] and (2,6-dimethoxyphenyl)boronic acid[14] were prepared according to literature procedures. Anhydrous solvents were obtained by using suitable desiccants: ethyl acetate, cyclohexane, and chloroform were distilled from calcium chloride, and dichloromethane was distilled from calcium hydride. Column chromatography was carried out on silica gel (Macherey–Nagel, activity I) and neutral alumina (Merck, activity II). Preparative, centrifugally accelerated, thin-layer chromatograph (Chromatotron) was performed with a model 7924 T instrument from Harrison Research. ^{1}H and ^{13}C NMR spectra were recorded with Bruker AC 200 (200 MHz or 50 MHz), ARX 300 (300 MHz or 75 MHz), DRX 500 (500 MHz or 125 MHz), or Avance 600 (600 MHz or 150 MHz) spectrometers. Assignments are supported by COSY, HSQC, HMBC, and NOESY experiments; the type of ^{13}C NMR signal is always listed (singlet, doublet, etc). All chemical shifts are referenced to either TMS or to the residual proton or carbon signal of the solvent. If not stated otherwise, coupling constants are ^{3}J. Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded with Finnigan MAT 8200 or 8230 spectrometers, or with an ESI mass spectrometer Mariner (Applied Biosystems, using methanol/dichloromethane, 1:1, as solvent). IR spectra were measured with a Perkin–Elmer 1600 Series spectrometer. Elemental analyses were carried out with an Euro EA3000 CHNS instrument (HEKAtech). Gas chromatography was performed with an 6890 N instrument (Agilent; split/splitless injector, split ratio 11:1; injector temp. 250 °C; FID detector temp. 300 °C).

General Procedure for the Synthesis of Substituted U-Shaped Terpyridines:[24] A solution of 2-substituted 5,6,7,8-tetrahydroquinolinone and ammonium acetate (1.1 equiv.) in anhydrous DMSO was heated at 85 °C for 5 min. In a second flask, 2-substituted 5,6,7,8-tetrahydroquinolinone and Eschenmoser's salt (*N*,*N*-dimethylmethyleneiminium iodide, 1.1 equiv.) were dissolved in anhydrous DMSO. The homogeneous solution of the iminium salt and 2-substituted 5,6,7,8-tetrahydroquinolinone was added to the mixture of warm (85 °C) 2-substituted 5,6,7,8-tetrahydroquinolinone and ammonium acetate in DMSO. The combined mixture was heated for an additional 16–48 h at 130 °C. The reaction mixture was cooled to room temp., water (50 mL) and dichloromethane (50 mL) were added, the layers were separated, and the aqueous layer was extracted with dichloromethane (4–6 × 40 mL). The combined organic layer was washed with water (3 × 20 mL) and brine (3 × 20 mL) and dried with magnesium sulfate. After removal of the solvent in vacuo, the residue was purified as detailed below.

2-(2,6-Dimethoxyphenyl)-5,6,7,8-tetrahydro-8-quinolone (10a): (2,6-Dimethoxyphenyl)boronic acid[14] (**9a**; 5.64 g, 31.1 mmol), tetrakis-(triphenylphosphane)palladium(0) (1.43 g, 1.24 mmol), barium hydroxide (3.12 g, 18.2 mmol), and water (30.0 mL) were added to a solution of 2-chloro-5,6,7,8-tetrahydro-8-quinolone (**8**; 4.51 g, 24.8 mmol) in 1,2-dimethoxyethane (300 mL). The reaction mixture was heated to reflux temperature for 45 h. After the addition of water (50 mL) and chloroform (50 mL), the aqueous layer was extracted with chloroform (3 × 50 mL) and the combined organic layer was washed with brine (20 mL). The solvent was removed in vacuo and the residue was purified by chromatography (silica gel; cyclohexane/ethyl acetate, 1:1), yielding **10a** (4.10 g, 59%). IR

(KBr): $\tilde{\nu}$ = 2934, 1697, 1598, 1471, 1241, 1090 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, J = 8.0 Hz, 1 H, 4-*H*), 7.38 (d, J = 8.0 Hz, 1 H, 3-*H*), 7.29 (t, J = 8.4 Hz, 1 H, 4′-*H*), 6.61 (m_c, 2 H, 3′-*H*, 5′-*H*), 3.69 (s, 6 H, OCH_3), 3.06 (t, J = 6.1 Hz, 2 H, 7-*H*), 2.81 (t, J = 6.1 Hz, 2 H, 5-*H*), 2.21 (quint, J = 6.4 Hz, 2 H, 6-*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.6 (s, C-8), 158.3 (s, C-2′, C-6′), 154.3 (s, C-2), 148.1 (s, C-1′), 138.9 (s, C-8a), 137.2 (d, C-4), 129.8 (d, C-3, C-4′), 118.8 (s, C-4a), 104.2 (d, C-3′, C-5′), 55.9 (q, CH_3), 39.9 (t, C-7), 29.2 (t, C-5), 22.7 (t, C-6) ppm. MS (ESI): m/z (%) = 306 (100) [M + Na^+]. HRMS: calcd. for $C_{17}H_{17}NO_3$ 283.12085; found 283.12304 (7.7 ppm); calcd. for $C_{16}{}^{13}CH_{17}NO_3$ 284.12421; found 284.12462 (1.4 ppm). $C_{17}H_{17}NO_3$ (283.32): calcd. C 72.07, H 6.05, N 4.94; found C 71.90, H 6.23, N 4.94.

2-[2,6-Bis(hex-5-enyloxy)phenyl]-5,6,7,8-tetrahydro-8-quinolone (10b): [2,6-Bis(hex-5-enyloxy)phenyl]boronic acid[14] (**9b**; 1.25 g, 3.93 mmol), tetrakis(triphenylphosphane)palladium(0) (186 mg, 161 μmol), barium hydroxide (390 mg, 2.28 mmol), and water (15 mL) were added to a solution of 2-chloro-5,6,7,8-tetrahydro-8-quinolone (**8**; 584 mg, 3.22 mmol) in 1,2-dimethoxyethane (90 mL). The reaction mixture was heated to reflux temperature for 48 h. After addition of water (50 mL) and chloroform (50 mL), the aqueous layer was extracted with chloroform (3 × 50 mL) and the combined organic layer was washed with brine (20 mL). The solvent was removed in vacuo and the residue was purified by chromatography (silica gel; cyclohexane/ethyl acetate, 1:1), yielding **10b** (973 mg, 72%). IR (KBr): $\tilde{\nu}$ = 2934, 1697, 1639, 1598, 1471, 1241, 1090 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.61 (d, J = 8.0 Hz, 1 H, 4-*H*), 7.37 (d, J = 8.0 Hz, 1 H, 3-*H*), 7.22 (t, J = 8.3 Hz, 1 H, 4′-*H*), 6.57 (d, J = 8.3 Hz, 2 H, 3′-*H*, 5′-*H*), 5.69 (tdd, J = 6.8, 10.9, 17.8 Hz, 2 H, C*H*=), 4.96–4.82 (m, 4 H, =CH_2), 3.90 (t, J = 6.2 Hz, 4 H, OCH_2), 3.04 (t, J = 6.1 Hz, 2 H, 7-*H*), 2.80 (t, J = 6.1 Hz, 2 H, 5-*H*), 2.21 (quint, J = 6.4 Hz, 2 H, 6-*H*), 1.98–1.84 (m, 4 H, =CHCH_2), 1.66–1.48 (m, 4 H, OCH_2CH_2), 1.38–1.22 (m, 4 H, $OCH_2CH_2CH_2$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 196.3 (s, C-8), 157.9 (s, C-2′, C-6′), 154.4 (s, C-2), 147.8 (s, C-1′), 138.8 (d, CH_2CH=CH_2), 138.5 (s, C-8a), 136.7 (d, C-4), 129.9 (d, C-3), 129.6 (d, C-4′), 119.8 (s, C-4a), 114.3 (t, CH_2CH=CH_2), 105.6 (d, C-3′, C-5′), 68.7 (t, OCH_2CH_2), 39.9 (t, C-7), 33.2 (t, CH_2CH=CH_2), 29.2 (t, C-5), 28.8 (t, OCH_2CH_2), 28.5 (t, $CH_2CH_2CH_2$), 22.8 (t, C-6) ppm. MS (ESI): m/z (%) = 861 (17) [2M + Na^+], 442 (16) [M + Na^+], 420 (100) [M + H^+]. $C_{27}H_{33}NO_3$ (419.56): calcd. C 77.29, H 7.93, N 3.34; found C 77.54, H 8.05, N 3.35.

2,12-Dichloro-5,6,8,9-tetrahydroquino[8,7-*b*]-1,10-phenanthroline (12): Synthesized according to the general procedure: 2-chloro-5,6,7,8-tetrahydro-8-quinolone (**8**; 1.22 g, 6.60 mmol), ammonium acetate (255 mg, 3.30 mmol), Eschenmoser's salt (648 mg, 3.50 mmol), DMSO (50 mL). Purified by column chromatography on neutral alumina (activity II–III) eluting with dichloromethane/ethyl acetate (4:1); yield 322 mg (26%). IR (KBr): $\tilde{\nu}$ = 2927, 1654, 1543, 1457, 1403 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, J = 7.9 Hz, 2 H, 4-*H*, 10-*H*), 7.46 (s, 1 H, 7-*H*), 7.23 (d, J = 7.9 Hz, 2 H, 3-*H*, 11-*H*), 3.06–2.92 (m, 8 H, 5-*H*, 6-*H*, 8-*H*, 9-*H*) ppm. ^1H NMR (200 MHz, CD_2Cl_2): δ = 7.56 (d, J = 7.9 Hz, 2 H, 4-*H*, 10-*H*), 7.46 (s, 1 H, 7-*H*), 7.27 (d, J = 7.9 Hz, 2 H, 3-*H*, 11-*H*), 3.03–2.96 (m, 8 H, 5-*H*, 6-*H*, 8-*H*, 9-*H*) ppm. ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 152.7 (s, C-2, C-12), 150.5 (s, C-13a, C-14b), 150.1 (s, C-13b, C-14a), 139.1 (d, C-4, C-10), 136.1 (d, C-7), 135.5 (s, C-6a, C-7a), 133.2 (s, C-4a, C-9a), 124.2 (d, C-3, C-11), 27.6 (t, C-6, C-8), 27.1 (t, C-5, C-9) ppm. MS (ESI): m/z (%) = 731 (45) [2M + Na^+], 376 (100) [M + Na^+]. MS (EI, 70 eV): m/z (%) = 355 (13), 353 (21) [M^+]. MS (CI, isobutane): m/z (%) = 356 (26), 354 (31) [M + H^+]. $C_{19}H_{13}Cl_2N_3$ (354.23): calcd. C 64.42, H 3.70, N 11.86; $C_{19}H_{13}Cl_2N_3 \cdot 0.2\ CH_2Cl_2$: calcd. C 62.12, H 3.64, N 11.32; found C 62.11, H 3.77, N 11.25.

2,12-Bis(2,6-dimethoxyphenyl)-5,6,8,9-tetrahydroquino[8,7-*b*]-1,10-phenanthroline (13a): Synthesized according to the general procedure: 2-(2,6-dimethoxyphenyl)-5,6,7,8-tetrahydro-8-quinolone (**10a**; 0.48 g, 1.66 mmol), ammonium acetate (64.0 mg, 0.83 mmol), Eschenmoser's salt (155 mg, 0.83 mmol), DMSO (25 mL). Purified by column chromatography on neutral alumina (activity II–III) eluting with dichloromethane/ethyl acetate (4:1); yield 139 mg (25%). IR (KBr): $\tilde{\nu}$ = 2928, 1601, 1473, 1430, 1251, 1109 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, J = 7.7 Hz, 2 H, 4-*H*, 10-*H*), 7.40 (s, 1 H, 7-*H*), 7.27 (t, J = 8.3 Hz, 2 H, 4′-*H*, 4′′-*H*), 7.22 (d, J = 7.7 Hz, 2 H, 3-*H*, 11-*H*), 6.59 (d, J = 8.3 Hz, 4 H, 3′-*H*, 3′′-*H*, 5′-*H*, 5′′-*H*), 3.66 (s, 12 H, OCH_3), 2.99 (m, 8 H, 5-*H*, 6-*H*, 8-*H*, 9-*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.5 (s, C-2′, C-2′′, C-6′, C-6′′), 153.3 (s, C-2, C-12), 151.8 (s, C-13a, C-14b), 151.1 (s, C-13b, C-14a), 135.3 (d, C-4, C-10), 135.0 (d, C-7), 133.8 (s, C-6a, C-7a), 131.6 (s, C-4a, C-9a), 129.3 (d, C-4′, C-4′′), 125.9 (d, C-3, C-11), 119.6 (s, C-1′, C-1′′), 104.6 (d, C-3′, C-3′′, C-5′, C-5′′), 56.3 (q, OCH_3), 27.7 (t, C-6, C-8), 27.6 (t, C-5, C-9) ppm. MS (ESI): m/z (%) = 1115 (4) [$2M^+$], 558 (100) [M + H^+]. $C_{35}H_{31}N_3O_4$ (557.64): calcd. C 75.38, H 5.60, N 7.54; found C 75.24, H 5.51, N 7.35.

2,12-Bis[2,6-bis(hex-5-enyloxy)phenyl]-5,6,8,9-tetrahydroquino[8,7-*b*]-1,10-phenanthroline (13b): Synthesized according to the general procedure: 2-[2,6-Bis(hex-5-enyloxy)phenyl]-5,6,7,8-tetrahydro-8-quinolone (**10b**; 2.02 g, 4.76 mmol), ammonium acetate (185 mg, 2.40 mmol), Eschenmoser's salt (450 mg, 2.43 mmol), DMSO (30 mL). Purified by column chromatography on neutral alumina (activity II–III) eluting with dichloromethane/ethyl acetate (4:1) and chromatotron on neutral alumina eluting with dichloromethane/ethyl acetate (10:1 to 4:1); yield 946 mg (48%). IR (Film): $\tilde{\nu}$ = 2928, 1639, 1600, 1244, 1099 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, J = 7.7 Hz, 2 H, 4-*H*, 10-*H*), 7.40 (s, 1 H, 7-*H*), 7.22 (t, J = 8.3 Hz, 2 H, 4′-*H*, 4′′-*H*), 7.19 (d, J = 7.7 Hz, 2 H, 3-*H*, 11-*H*), 6.57 (d, J = 8.3 Hz, 4 H, 3′-*H*, 5′-*H*, 3′′-*H*, 5′′-*H*), 5.58 (tdd, J = 6.6, J = 10.3, J = 16.9 Hz, 4 H, C*H*=), 4.84–4.76 (m, 8 H, =CH_2), 3.87 (t, J = 6.3 Hz, 8 H, OCH_2), 2.98 (br. s, 8 H, 5-*H*, 6-*H*, 8-*H*, 9-*H*), 1.85–1.79 (m, 8 H, =CHCH_2), 1.53–1.45 (m, 8 H, OCH_2CH_2), 1.28–1.21 (m, 8 H, $OCH_2CH_2CH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.9 (s, C-2′, C-2′′, C-6′, C-6′′), 153.5 (s, C-2, C-12), 151.6 (s, C-13a, C-14b), 151.1 (s, C-13b, C-14a), 139.1 (d, *C*H=), 134.9 (d, C-4, C-7, C-10), 133.8 (s, C-6a, C-7a), 131.6 (s, C-4a, C-9a), 129.2 (d, C-4′, C-4′′), 126.0 (d, C-3, C-11), 120.4 (s, C-1′, C-1′′), 113.9 (t, =CH_2), 105.9 (d, C-3′, C-3′′, C-5′, C-5′′), 68.8 (t, OCH_2), 33.4 (t, CH_2CH=), 28.6 (t, OCH_2CH_2), 27.9 (t, C-6, C-8), 27.7 (t, C-5, C-9), 25.2 (t, CH_2) ppm. MS (ESI): m/z (%) = 830 (100) [M + H^+]. $C_{55}H_{63}N_3O_4$ (830.11): calcd. C 79.58, H 7.65, N 5.06; found C 79.38, H 7.60, N 5.10.

27^5,27^6,27^8,27^9-Tetrahydro-2,13,15,26-tetraoxa-1,14(1,3,2)-dibenzena-27(2,12)-{quino[8,7-*b*]-1,10-phenanthrolina}bicyclo[12.12.1]-heptacosaphane-7,20-diene (14): 2,12-Bis-[2,6-bis(hex-5-enyloxy)-phenyl]-5,6,8,9-tetrahydroquino[8,7-*b*]-1,10-phenanthroline (**13b**; 950 mg, 1.14 mmol) was dissolved in dichloromethane (600 mL) and benzylidenebis(tricyclohexylphosphane)dichlororuthenium (84.0 mg, 102 μmol, 9 mol-%) was added. After stirring for 19 h at room temp., the solvent was removed in vacuo and the residue was filtered two times through neutral alumina (activity II–III) eluting with dichloromethane/ethyl acetate (4:1). Finally, the residue was purified with a chromatotron (neutral alumina) eluting with dichloromethane/ethyl acetate (10:1 to 4:1); yield 670 mg (74%). IR

(Film): $\tilde{\nu}$ = 2929, 1599, 1458, 1245, 1099 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.51, 7.50 (3d, J = 7.7 Hz, 2 H, 27^4-*H*, 27^{10}-*H*), 7.38, 7.37, 7.36 (3× s, 1 H, 27^7-*H*), 7.31, 7.29, 7.27 (3× d, J = 7.7 Hz, 2 H, 27^3-*H*, 27^{11}-*H*), 7.24, 7.23, 7.22 (3× t, J = 8.3 Hz, 2 H, 1^4-*H*, 14^4-*H*), 6.66, 6.65, 6.50 (3× d, J = 8.3 Hz, 4 H, 1^3-*H*, 1^5-*H*, 14^3-*H*, 14^5-*H*), 4.95–4.79 (m, 2 H, C*H*=), 4.25–4.04, 3.84–3.69 (m, 8 H, OCH_2), 3.00, 2.99 (2× s, 8 H, 27^5-*H*, 27^6-*H*, 27^8-*H*, 27^9-*H*), 1.64–0.88 (m, 32 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.4, 158. 3, 158.2 (3× s, C-1^2, C-1^6, C-14^2, C-14^6), 153.2, 153.1 (2× s, C-27^2, C-27^{12}), 151.4, 151.3 (4× s, C-27^{13a}, C-27^{13b}, C-27^{14a}, C-27^{14b}), 134.6 (2× d, C-27^4, C-27^{10}), 134.4 (2× d, C-27^7), 133.2, 132.9 (2× s, C-27^{6a}, C-27^{7a}), 131.0, 130.7 (2× s, C-27^{4a}, C-27^{9a}), 130.3, 129.8, 128.9 (3× d, C-1^4, C-14^4), 125.9, 125.7 (2× d, C-27^3, C-27^{11}), 124.2, 123.4 (2× s, C-1^1, C-14^1), 109.1, 108.7, 108.4 (3× d, C-1^3, C-1^5, C-14^3, C-14^5), 70.9, 70.7, 70.3 (3× t, OCH_2), 31.8, 31.7, 28.7, 28.3, 28.0, 27.9, 27.8, 27.6, 25.9, 25.7, 25.3, 24.5, 24.3 (13× t, C-27^5, C-27^6, C-27^8, C-27^9, CH_2) ppm. MS (ESI): *m*/*z* (%) = 774 (100) [M + H^+]. $C_{51}H_{57}N_3O_4$ (776.02): calcd. C 78.93, H 7.40, N 5.41; found C 78.67, H 7.51, N 5.25.

2,13,15,26-Tetraoxa-1,14(1,3,2)-dibenzena-27(2,12)-{quino[8,7-*b*]-1,10-phenanthrolina}bicyclo[12.12.1]heptacosaphane (15): Palladium on charcoal (10%, 210 mg) was mixed with methanol (140 mL) and hydrogen was bubbled through the mixture for 30 min. This activated mixture was then mixed with a solution of **14** (510 mg, 659 μmol) in chloroform (10 mL), and hydrogen was bubbled through the solution for 3 h, while stirring at room temp. The solution was stirred under a hydrogen atmosphere for 18 h at room temp., then the solvent was evaporated in vacuo and the residue was purified by chromatography on neutral alumina (activity II–III) eluting with dichloromethane/ethyl acetate (4:1) and by using a chromatotron (neutral alumina) eluting with dichloromethane/ethyl acetate (10:1 to 4:1); yield 460 mg (90%). IR (Film): $\tilde{\nu}$ = 2929, 1599, 1458, 1245, 1099 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, J = 7.7 Hz, 2 H, 27^4-*H*, 27^{10}-*H*), 7.38 (s, 1 H, 27^7-*H*), 7.29 (d, J = 7.7 Hz, 2 H, 27^3-*H*, 27^{11}-*H*), 7.20 (t, J = 8.3 Hz, 2 H, 1^4-*H*, 14^4-*H*), 6.63 (d, J = 8.3 Hz, 4 H, 1^3-*H*, 1^5-*H*, 14^3-*H*, 14^5-*H*), 3.99–3.96, 3.92–3.87 (m, 8 H, OCH_2), 2.97 (s, 8 H, 27^5-*H*, 27^6-*H*, 27^8-*H*, 27^9-*H*), 1.54–1.46, 1.40–1.32, 1.15–1.04, 0.99–0.91, 0.88–0.72 (m, 32 H, CH_2) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.1 (s, C-1^2, C-1^6, C-14^2, C-14^6), 153.1 (s, C-27^2, C-27^{12}), 151.6 (s, C-27^{13a}, C-27^{14b}), 151.5 (s, C-27^{13b}, C-27^{14a}), 134.6 (d, C-27^4, C-27^{10}), 134.4 (d, C-27^7), 133.5 (s, C-27^{6a}, C-27^{7a}), 131.2 (s, C-27^{4a}, C-27^{9a}), 129.1 (d, C-1^4, C-14^4), 126.3 (d, C-27^3, C-27^{11}), 122.1 (s, C-1^1, C-14^1), 107.8 (d, C-1^3, C-1^5, C-14^3, C-14^5), 69.7 (t, OCH_2), 28.6, 28.2, 28.0, 27.6, 27.1, 24.7 (6t, C-27^5, C-27^6, C-27^8, C-27^9, CH_2) ppm. MS (ESI): *m*/*z* (%) = 678 (100) [M + H^+]. HRMS: calcd. for $C_{51}H_{59}N_3O_4$ 777.45056; found 777.45012 (0.6 ppm); calcd. for $C_{50}{}^{13}CH_{59}N_3O_4$ 778.45392; found 778.45483 (–1.2 ppm). $C_{51}H_{59}N_3O_4$ (778.03): calcd. C 78.73, H 7.64, N 5.40, $C_{51}H_{59}N_3O_4 \cdot H_2O$: calcd. C 76.95, H 7.72, N 5.28; found C 76.93, H 7.89, N 5.25.

Cyclopropanation: Under argon, copper(I) triflate hemi-benzene complex [Aldrich; 4.0–12.0 mg (±0.01 mg)] was placed in a vial, and indene **16** [350 equiv. based on copper(I)] and ligands 2,9-dimethyl-1,10-phenanthroline **12**, **13a**, or **15** (1.2–2.4 equiv.) dissolved in 1,2-dichloroethane (c = 0.01 mol L^{-1}), were added. After addition of diazoacetate **17** (50 equiv.), the mixture was stirred at room temp. for 24 h. At the beginning of the reaction, rapid development of gas was frequently noted. 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 *n*-hexadecane [ca. 25 mg (±0.01 mg)] as GC standard, the products were analyzed by GC (HP-5/30 m; 80 °C for 5 min, 2 °C/min until 140 °C, 1 min, 1 °C/min until 160 °C, 1 min, 20 °C/min until 240 °C, 20 min).

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