2,3,6,7-Tetrasubstituted Decalins: Biconformational Transducers for Molecular Signal Transduction

Ulrich Koert,*[a] Rolf Krauss,[a] Hans-Georg Weinig,[a] Carola Heumann,[a] Burkhard Ziemer,[a] Clemens Mügge,[a] Matthias Seydack,[a] and Jürgen Bendig[a]

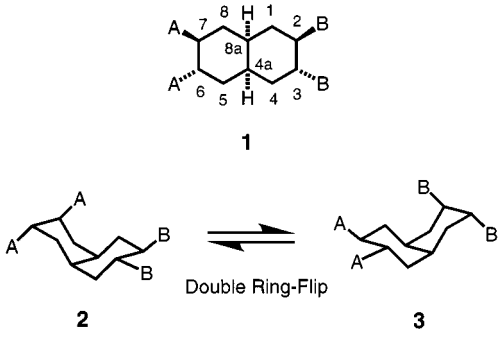
Keywords: Biconformational double ring flip / Conformation analysis / Decalin / Signal transduction / Synthesis design

2,3,6,7-Tetrasubstituted decalins of relative configuration (2β,3α,4aα,6α,7β,8aα) have been synthesized. If substituents as in **6** are chosen, the equilibrium of the biconformational system **2/3** is shifted towards conformer **2**. Conversion into the bis(acetal) **16** resulted in a covalently induced double ring flip **17** → **18**. A chelation-induced double ring flip (**21** → **22**) was achieved when 2,2′-bipyridyl substituents were attached by ether linkages at the receptor positions 6 and 7 of the decalin system. Effector groups were introduced by adding pyrene groups, through an (*E*)-olefin linker, in positions 2 and 3. The resulting compound **25** proved to be an effective device for molecular signal transduction over a signal distance of 1.5 nm. A zinc signal caused a conformational axial-to-equatorial change at the receptor site, which was transduced by a double ring flip of the decalin moiety (**28** → **29**) to the pyrene effector site, where the induced equatorial-to-axial flip induced a characteristic fluorescence peak.

Introduction

The generation and transduction of signals in molecular systems is a key goal for chemical design.[1] Potential applications lie in the fields of information storage[2] and of synthetic implants into biological signal-transduction chains.[3] Molecular signal transduction by conformational transmission is the product of a conformational change, upon a signal stimulus, at the receptor site.[4] The associated motion is transmitted by the transducer to the effector site, where a second conformational change gives some kind of measurable effect, such as a new signal, a chemical reaction, or a mechanical change.[5] The two-state behavior of biconformational *cis*-*anti*-*cis*-perhydroanthracenes[6] is suited for this purpose. Here, a triple ring flip of one all-chair conformer to the other all-chair conformer has been used to bridge a signal distance of 2 nm. With the goal of varying this signal distance, we investigated the shorter *cis*-decalin system. Here we show that 2,3,6,7-tetrasubstituted *cis*-decalins of type **1** show two-state conformational behavior and are well suited as transducers for molecular signal transduction by conformational transmission.

The decalin **1** has the relative configuration (2β,3α,4aα,6α,7β,8aα) resulting in its adopting the biconformational system **2/3** (assuming that the all-chair ground state conformation of the *cis*-decalin[7] is not significantly changed by tetrasubstitution) (Figure 1). Conformer **2** has axial A substituents and equatorial B substituents, while in conformer **3** the A substituents are now equatorial and the B substituents have changed to axial positions.



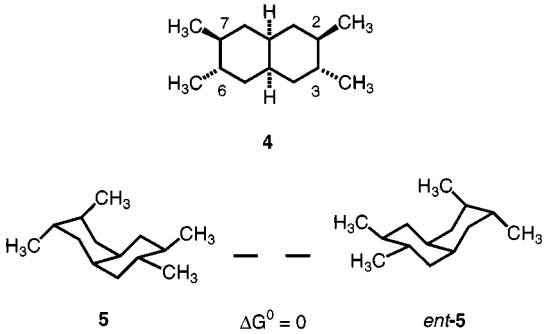
1 **2** **3**

Figure 1. Biconformational (2β,3α,4aα,6α,7β,8aα)-tetrasubstituted decalin **1** in the two all-chair conformations **2** and **3**

Results and Discussion

Choice of Substituents A and B

The position of the equilibrium between **2** and **3** will depend on the choice of substituents A and B. In the case of A = B, compounds like **4** result, and the two conformers **5** and *ent*-**5** are isoenergetic and, in an achiral environment, populated equally (Figure 2).



4 **5** **ent-5**

Figure 2. 2,3,6,7-Tetramethyl-*cis*-decalin (**4**) in the two isoenergetic conformers **5** and *ent*-**5**

[a] Institut für Chemie, Humboldt Universität zu Berlin, Hessische Straße 1−2, 10115 Berlin, Germany
Fax: (internat.) + 49-30/2093-7266
E-mail: koert@chemie.hu-berlin.de

  1434−193X/01/0203−0575 $ 17.50+.50/0

A predictable switch from **2** to **3** needs prior fixing of the equilibrium on the left-hand side. This might be accomplished by choosing a decalin substitution pattern such as that in **6**. Here, oxygen is situated at the 6 and 7 positions, while carbon is used in the 2 and 3 positions (Figure 3). From a synthetic point of view, the tetraol **6a** offers the opportunity to differentiate between the A site and the B site through selective addressing of primary or secondary hydroxy functions.

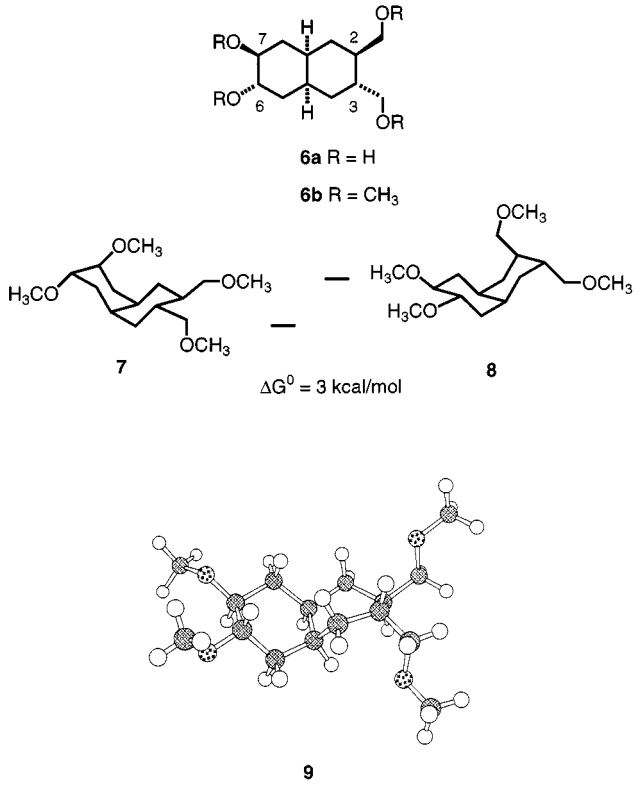
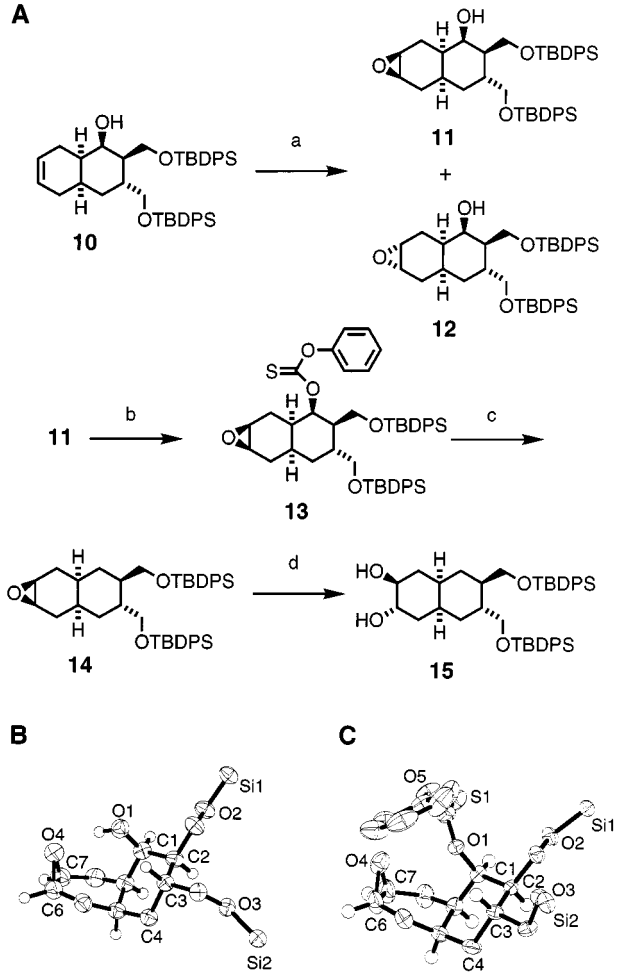


Figure 3. Structures of 2,3-C-6,7-O-tetrasubstituted *cis*-decalins **6a** and **6b** in the two low-energy all-chair conformations **7** and **8** of tetramethyl ether **6b** and one high-energy non-all-chair conformer **9**

The tetramethyl ether **6b** was chosen as a model for conformational study. In conformer **7**, the most unfavorable interaction is an O−C-1,3-diaxial interaction. In conformer **8**, the most unfavorable interaction is a C−C-1,3-diaxial one. The latter is disfavored relative to the former by 1 kcal/mol.[7] Molecular dynamics calculations for **6b** (INSIGHT/DISCOVER, cvff, 200 cycles, 300−1000 K) found only the two conformers **7** and **8** within 0−3 kcal/mol. Conformer **8** is 3 kcal/mol higher in energy than **7**. Therefore, at 298 K, **7** is the predominating species, at more than 99% of the total. Inspection of the conformational space revealed that other non all-chair conformers, such as **9**, are much higher in energy than **7** (8 kcal/mol for **9**).

Synthesis of the Tetrasubstituted Decalins

The synthesis of decalins with a substitution pattern of type **6** was carried out on the racemic series (Scheme 1). The alcohol **10**, which is accessible from a cyclohexenone precursor by means of a Diels−Alder reaction with 1,3-butadiene,[6] was allowed to react with *m*-chloroperbenzoic acid (MCPBA). The two diasteromeric epoxides **11** and **12** were obtained as a 4.3:1 mixture in 80% yield, and could be separated by chromatography. The main isomer **11** is probably formed in a hydroxy-directed attack by the peracid from the sterically shielded concave site of the molecule. An X-ray crystal structure of **11** verified the correct stereochemical assignment of the epoxides **11** and **12**. As a preliminary to a Barton-McCombie deoxygenation,[8] the epoxy alcohol **11** was converted into the thiocarbonate **13**, the structure of which we were able to confirm by an X-ray crystal structure analysis. Treatment of **13** with Bu_3SnH gave the epoxydecalin **14** in 82% yield. Stereoselective[9] opening of the epoxide functionality to afford the *trans*-diaxial diol **15** was achieved in 95% yield using catalytic amounts of $HClO_4$ in an acetone/water solvent system.

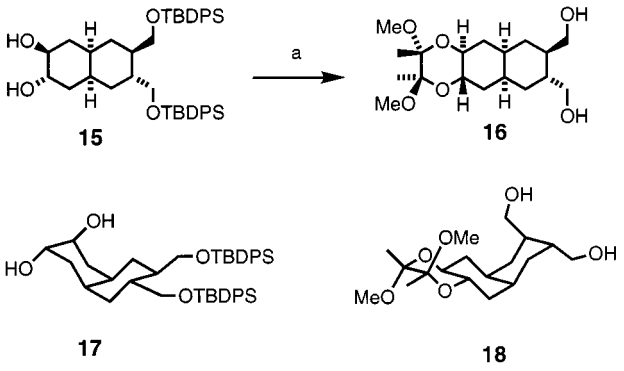


Scheme 1. A: Synthesis of *trans*-diol **15**: a) MCPBA, CH_2Cl_2, 0 °C, 2 h, 80%, ratio **11/12** (4.3:1); b) *n*BuLi, PhOCSCl, THF, 0 °C → room temp., 9 h, 82%; c) Bu_3SnH, AIBN, toluene, 90 °C, 1 h, 82%; d) $HClO_4$, acetone/H_2O, 0 °C, 3 h, 95%; B: X-ray crystal structure of **11**; C: X-ray crystal structure of **13**. MCPBA = *m*-chloroperbenzoic acid, AIBN = azobis(isobutyronitrile)

Covalently Induced Double Ring Flip

Taking into account the X-ray crystal structures of **11** and **13**, as well as NMR studies on **15**, we are able to state that the diol **15** has the preferred conformation **17**, with axial OH groups in the 6 and 7 positions and equatorial

$CH_2OTBDPS$ groups in the 2 and 3 positions. A covalent clamp using a Ley bisacetal[10] (**15** → **16**) should anchor the O-substituents at positions 6 and 7 in the equatorial orientation, with the consequences of double ring flip induction (**17** → **18**) and hence a diaxial arrangement of the CH_2OH groups at positions 2 and 3 (Scheme 2).



Scheme 2. Covalently induced double ring flip **17** → **18** by conversion of **15** into **16**: a) 2,2′,3,3′-tetramethoxybutane, camphorsulfonic acid, trimethyl orthoformate, MeOH, 50 °C, 48 h, 99%

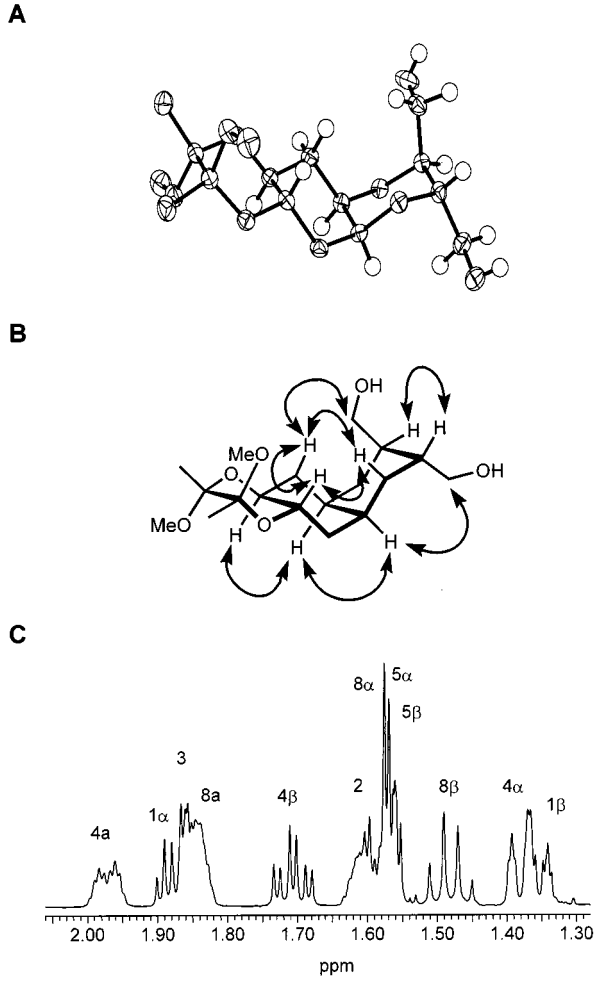
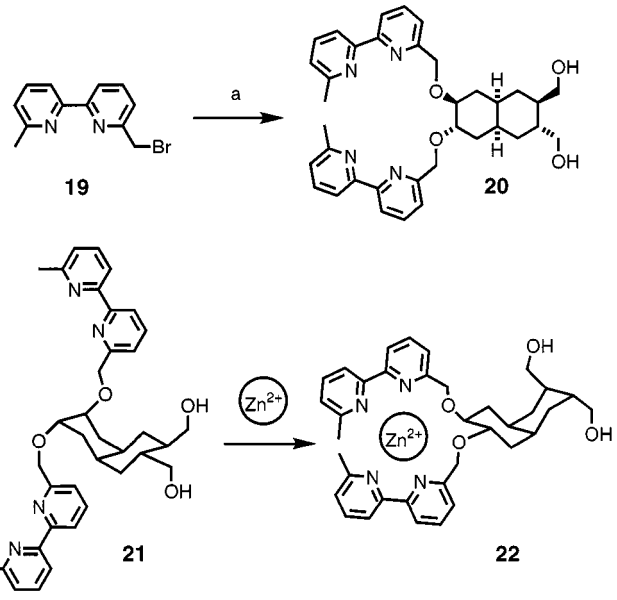


Figure 4. A: X-ray crystal structure of **16**; B: preferred conformation of **16** in solution ([D_4]MeOH), based on NOESY data; selected NOESY cross signals are marked by double arrows; C: ^{1}H NMR spectrum of **16** (600 MHz, [D_4]MeOH)

Indeed, treatment of **15** with 2,2,3,3-tetramethoxybutane and camphorsulfonic acid gave the bis(acetal) **16** in 99% yield. The X-ray crystal structure of **16** showed the predicted conformation **18** (Figure 4, a). The 1,3-diaxial repulsive interaction (2 ⇄ 8a) resulted in an expansion of the C(1)−C(2)−CH_2OH angle to 115.1° and of the C(8)−C(8a)−C(1) angle to 114.4°. The C−C bond lengths in the right-hand chair of the decalin system were not affected to any significant extent by the induced strain. Analysis of NOESY data from **16** in [D_4]MeOH proved the presence of conformation **18** in solution. Figure 4, b summarizes the NOE contacts found for **16**. Of particular importance are the contacts between the three axial protons H_β-(4), H-(6), and H_β-(8), as well as the contact between H_β-(8) and CH_2OH-(2). H_β-(8) (δ = 1.48), is the only signal with three large J coupling constants of 12 Hz [^2J and two ^3J (*trans*-diaxial)]. The characteristic ^{1}H signals of the decalin skeleton of **16** are displayed in a section of the ^{1}H NMR spectrum shown in Figure 4, c. On the basis of these ^{1}H NMR spectra, it can be stated that **18** is the only observable conformation at 25 °C.

Chelation-Induced Double Ring Flip

2,2′-Bipyridine groups were attached by ether linkages as receptor substituents in positions 6 and 7 of the decalin system. Williamson reaction between the diol **15** and an excess of the bipyridine bromide **19**,[11] with subsequent fluoride-mediated cleavage of the TBDPS ethers, gave compound **20** in 72% overall yield (Scheme 3).



Scheme 3. Synthesis of **20** and chelation-induced double ring flip **21** → **22**: a) 1. **15**, NaH, nBu$_4$NI, THF, 3 d, room temp., 83%; 2. TBAF, THF, 40 °C, 4 h, 87%; TBAF = tetrabutylammonium fluoride

Harding et al. have shown that zinc(II) ions and bis(2,2′-bipyridyl) ether ligands can form chelation-mode complexes, with the zinc(II) ion hexacoordinated to two bipyridyl groups and two ether linker oxygen atoms.[12] Addition of $Zn(OTf)_2$ to **20** in CD_3CN gave the complex Zn^{II}-**20**-

$(OTf)_2$. NMR analysis of the zinc(II) complex of **20** established complete conformational switching from **21** to **22**. Figure 5, a shows two regions of the NOESY spectrum of Zn^{II}-**20**-$(OTf)_2$ in CD_3CN. The diagnostic NOE contacts determined from this spectrum are summarized in Figure 5, b.

Characteristic for conformation **22** are the contacts between the three axial protons H_β-(4), H-(6), and H_β-(8), as well as the contact between H_β-(8) and CH_2OH-(2). H_β-(8) (δ = 1.09), is the only proton of the decalin skeleton of **22** with three large J coupling constants of 12 Hz. The two axial protons − **22**: H-(6) (δ = 3.16) and H-(7) (δ =2.97) − show two large coupling constants and one small one. These results confirm the ability of the bis(2,2′-bipyridyl) ether ligands, in the case of decalins, to act as a receptor unit for inducing the double ring flip.

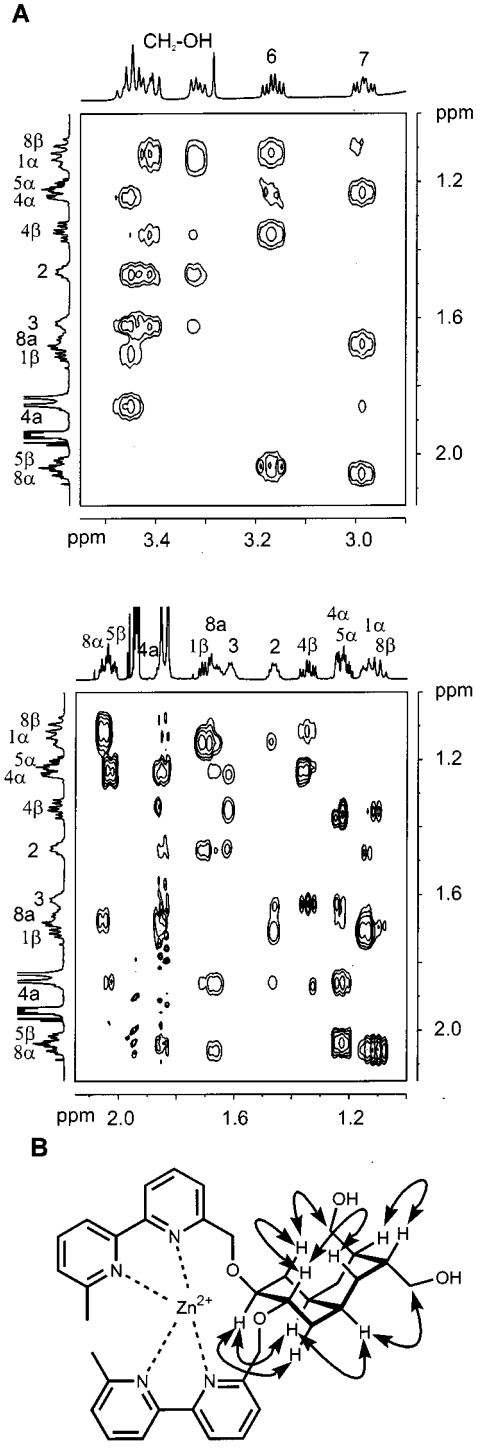
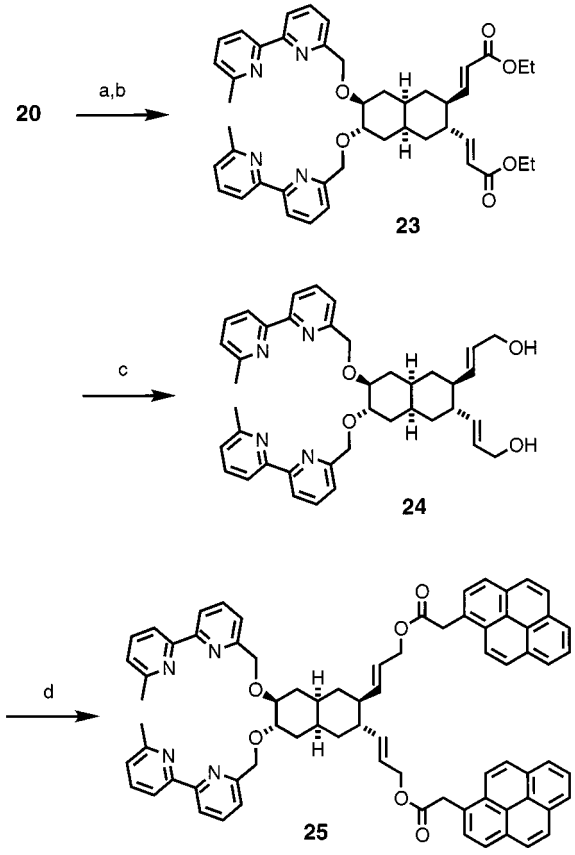


Figure 5. A: Regions of the NOESY spectrum of **22** (600 MHz, CD_3CN); B: preferred solution conformation of **22**, based on NOESY data; selected NOESY cross signals are marked by double arrows

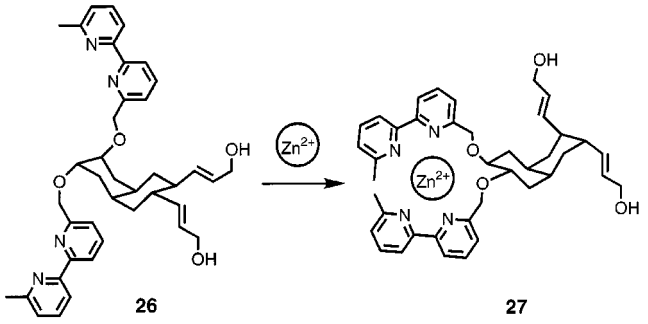
The decalindiol **20** was oxidized under Swern conditions to the corresponding dialdehyde. This was converted by means of an (*E*)-selective Wittig reaction into the α,β-unsaturated ester **23** (72% overall yield) (Scheme 4). A DIBAH reduction of **23** gave the diol **24** in 71% yield.



Scheme 4. Synthesis of **25**: a) oxalyl chloride, DMSO, iPr$_2$NEt, CH_2Cl_2, −78 → 0 °C, 90 min; b) Ph_3P=CHCOOEt, toluene, 90 °C, 15 h, 72% (two steps); c) DIBAH, CH_2Cl_2, −78 → 0 °C, 6 h, 71%; d) DMAP, EDC, pyren-1-ylacetic acid, CH_2Cl_2, room temp., 2 h, 77%; DMSO = dimethyl sulfoxide, DIBAH = diisobutylaluminium hydride, DMAP = 4-(dimethylamino)pyridine, EDC = *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide

With compound **24** in hand, the chelation-induced double ring flip (**26** → **27**) was next examined (Scheme 5).

Without any chelating metal ion present, the only observable conformation of compound **24** is **26**. Figure 6, a shows two regions of the NOESY spectrum of **24** in $CDCl_3$. The diagnostic NOE contacts determined from this spectrum are summarized in Figure 6, b. Characteristic for the conformation **26** are the contacts between the three axial protons H_β-(1), H-(3), and H_β-(5), as well as the contact between H-(6) and H-(7). The signals of the two equatorial protons of **26** − H-(6) (δ = 3.91) and H-(7) (δ = 3.79) −



Scheme 5. Chelation-induced double ring flip **26** → **27**

are the product of three small coupling constants. The signals for the methylene protons of the ether linkages at δ = 4.7−4.8 are split into A,B systems. The only proton of the decalin skeleton of **26** with three large *J* coupling constants of 12.9 Hz is $H_β$-(1) (δ = 2.02).

Addition of $Zn(OTf)_2$ to **24** in CD_3CN solution gave the complex Zn^{II}-**24**-$(OTf)_2$. Analysis of the NMR spectrum of Zn^{II}-**24**-$(OTf)_2$ confirmed a successful chelation-induced double ring flip (**26** → **27**). Figure 7, a shows part of the NOESY spectrum of **27**. The diagnostic NOE contacts determined from this spectrum are summarized in Figure 7, b. The ^1H NMR signals for the equatorial protons − H-(2) (δ = 2.1) and H-(3) (δ = 2.2) − in Zn^{II}-**24**-$(OTf)_2$ are the product of three small *J* coupling constants, while the signals for the two axial protons − H-(6) (δ = 3.17) and H-(7) (δ = 2.96) − display two large *J* coupling constants and a small one. The observed contacts between the three axial protons $H_β$-(4), H-(6), and $H_β$-(8), as well as the contact between $H_β$-(8) and the olefinic CH, corroborate the presence of the conformation **27**.

A UV titration[13] (Figure 8) was used to determine the receptor binding energy necessary for inducing the double ring flip **26** → **27**. A binding energy in acetonitrile/choroform of ΔG = 6.8 kcal mol^{-1} was derived[13] for the complex Zn^{II}-**24**-$(OTf)_2$. This value is comparable with the related binding energy for inducing the triple ring flip in the perhydroanthracene series (ΔG = 7.1 kcal mol^{-1}).[4]

Molecular Signal Transduction

With a functional decalin transducer in hand and the bipyridine receptors in place, the next thing to do was to choose an effector. Our goal was to effect a photosignal upon equatorial-to-axial change of the positions 2 and 3. From experience of the perhydroanthracene series,[4] we decided to use pyrene groups[14] at the effector site. The idea behind this was that, in the fluorescence spectrum of the conformer with bis(equatorial) pyrene groups, an excimer signal at 480 nm would primarily be observed, while the decalin conformer with axially linked pyrenes should show a monomer fluorescence at 380 nm as the dominant photosignal. It was found that an (*E*)-olefin spacer and an ester group were suited to suppress excimer formation in the bis(axial) conformer to a large extent.[4] To this end, the decalindiol **24** was allowed to react with pyren-1-ylacetic acid to form the diester **25** (Scheme 4).

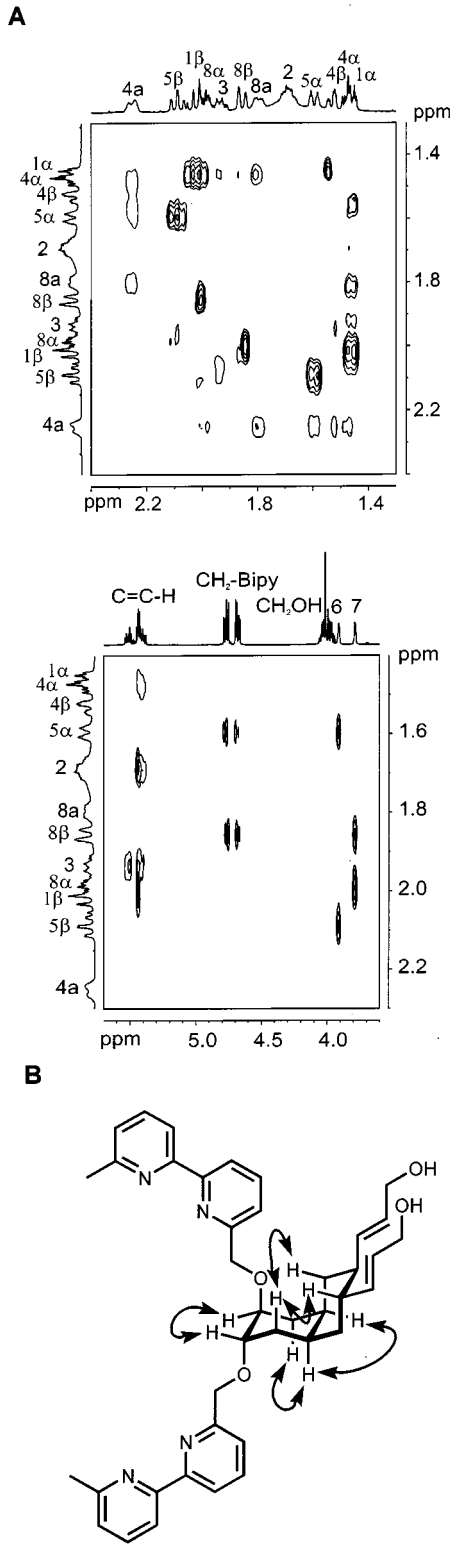


Figure 6. A: Regions of the NOESY spectra of **24** (600 MHz, $CDCl_3$); B: preferred solution conformation **26** of compound **24**, based on NOESY data; selected NOESY cross signals are marked by double arrows

The emission fluorescence spectrum of uncomplexed **25** displayed the expected strong excimer band at 480 nm and a weak monomer band at around 380 nm (Figure 9). Addition of $Zn(OTf)_2$ to a solution of **25** in $CHCl_3/CH_3CN$ (1:1)

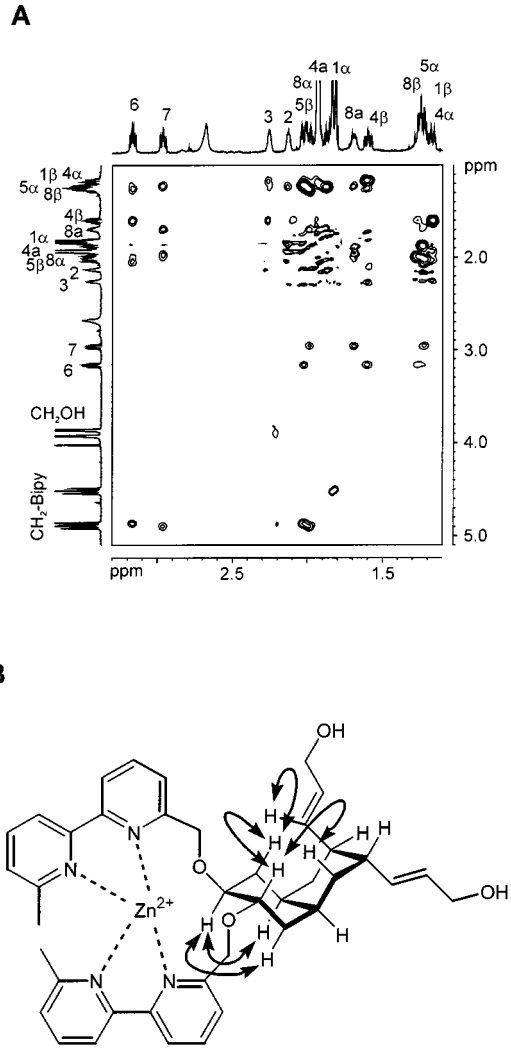


Figure 7. A: Part of the NOESY spectra of **27** (600 MHz, CD_3CN); B: preferred solution conformation of **27**, based on NOESY data; selected NOESY cross signals are marked by double arrows

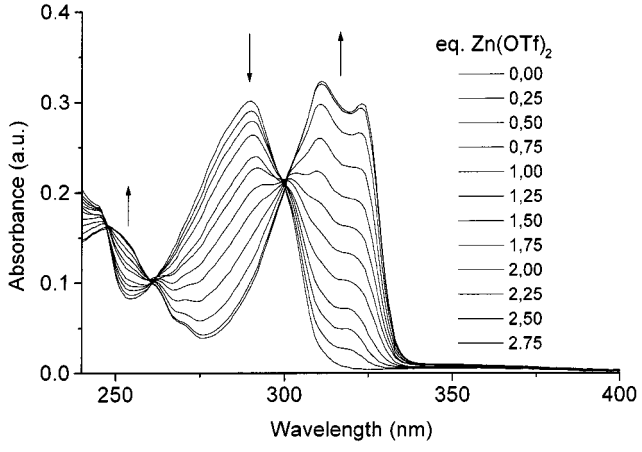


Figure 8. UV/Vis titration of **24** with $Zn(OTf)_2$ (acetonitrile/chloroform, 1:1, $c = 7.7 \times 10^{-6}$ mol L^{-1}, $T = 298$ K)

resulted in a distinct decrease of the excimer band relative to the pyrene monomer fluorescence band (Figure 9, Scheme 6). On binding to the bipyridine ligands in a chela-

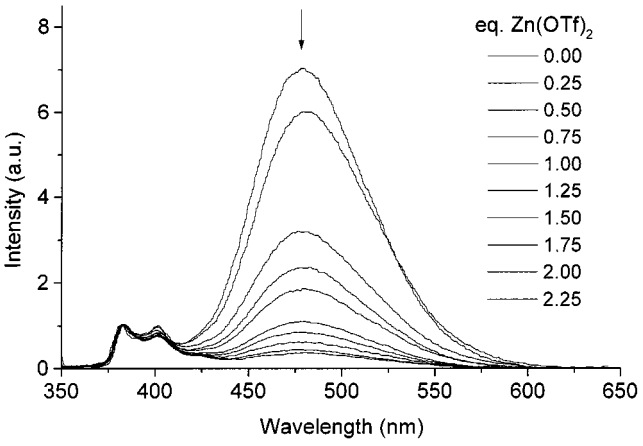
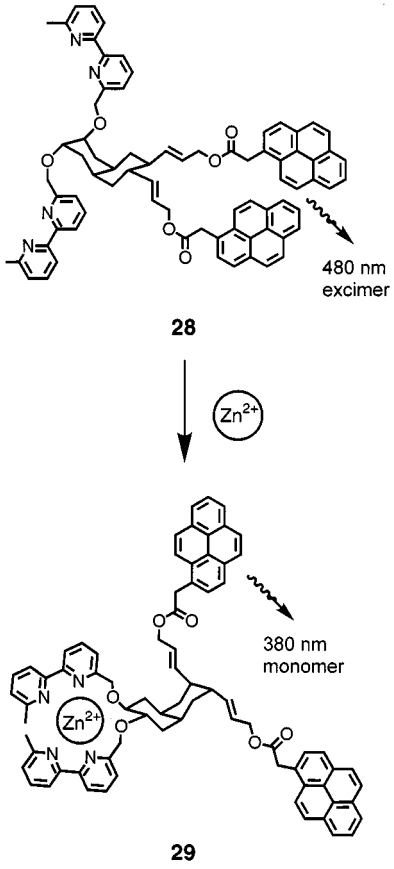


Figure 9. Photoresponse of **25** to a zinc(II) signal; fluorescence spectrum of **25** in $CH_3CN/CHCl_3$ (1:1) as a function of added $Zn(OTf)_2$ (excitation at 343 nm, $c = 4.9 \times 10^{-6}$ mol L^{-1}, $T = 298$ K); fluorescence spectra were normalized to the monomer peak at 380 nm



Scheme 6. Chelation-induced double ring flip **28** → **29**

tion mode, the zinc cation acts as an incoming signal. This is accompanied with an axial-to-equatorial change of the bipyridine substituents, which in turn causes a double ring flip of the decalin system (**28** → **29**). This conformational switch transduces the signal to the effector site. Here, an equatorial-to-axial change of the pyrene substituents results, and this produces a new signal: in this case a change in the fluorescence emission. Inspection of molecular models showed that the signal distance defined by the

length between the center of the receptor and the center of the effector of the decalin system was 1.5 nm.

The double ring flip **28** → **29** could be confirmed by NMR spectroscopy. Figure 10 (A) shows the ^{1}H NMR spectrum of the conformer **28** and Figure 10 (B) displays the ^{1}H NMR spectrum of **29**. Only one preferred conformer could be detected in either spectrum. The conformational switch of the system upon addition of the Zn^{II} signal is a complete one.

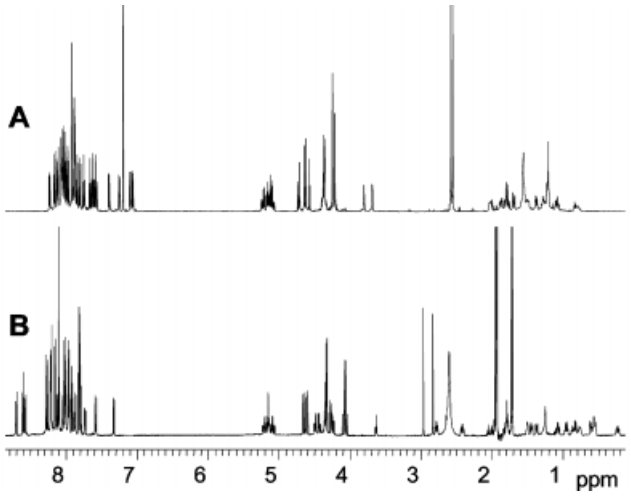


Figure 10. ^{1}H NMR spectra of A: **25**, showing the conformation **28** (600 MHz, $CDCl_3$); B: the Zn-**25**-$(OTf)_2$ complex, showing the conformation **29** (600 MHz, CD_3CN)

Conclusion

This study proves the ability of 2,3-C-6,7-O-tetrasubstituted decalins of type **6** and of (2β,3α,4aα,6α,7β,8aα) relative configuration to act as transducers for molecular signal transduction by conformational transmission. With the decalin system, it is possible to transmit a signal over a distance of 1.5 nm. In combination with their perhydroanthracene relatives, these biconformational compounds show great potential as molecular devices. Other stimuli at the receptor site (redox process or photoisomerization) and other signals at the effector site (dissociation of an ion or ligand) are possible extensions worthy of investigation in the future.

Experimental Section

General Remarks: All boiling and melting points are uncorrected values. − IR: Bruker IFS 88. − NMR: Bruker AM-300, DPX-300, and AMX-600. For ^{1}H NMR, $CDCl_3$ as solvent (δ_H = 7.25), [D_8]toluene as solvent (δ_H = 2.09), [D_4]MeOH as solvent (δ_H = 4.78), [D_3]acetonitrile as solvent (δ_H = 1.93); for ^{13}C NMR, $CDCl_3$ as solvent (δ_C = 77.0), [D_8]toluene as solvent (δ_C = 20.4), [D_4]MeOH as solvent (δ_C = 49.0), [D_3]acetonitrile as solvent (δ_C = 1.3). − Elemental analysis: CHN Rapid (Heraeus), CHNS-932 Analysator (Leco). − HRMS: Finnigan MAT 95. − All reactions were performed under argon in oven- or flame-dried glassware. Dry solvents: THF, benzene, and toluene were distilled from sodium/benzophenone, CH_2Cl_2 was distilled from calcium hydride. All commercially available reagents were used without purification unless otherwise noted. All reactions were monitored by thin layer chromatography (TLC) carried out on Merck F-254 silica glass plates viewed with the aid of UV light and/or heat-gun treatment with 5% phosphomolybdic acid in ethanol. Column chromatography (CC) was performed with Merck silica gel 60 (70−200 mesh and 230−400 mesh). PE: light petroleum ether, b.p. 40−60 °C.

(1*R,2*R**,3*R**,4a*R**,6*R**,7*S**,8a*S**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)-6,7-epoxydecalin-1-ol (11) and (1*R**,2*R**,3*R**,4a*R**,6*S**,7*R**,8a*S**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)-6,7-epoxydecalin-1-ol (12):** Alkene **10** (3.00 g, 4.35 mmol) was dissolved in CH_2Cl_2 (150 mL). At 0 °C, a solution of MCPBA (1.50 g, 8.71 mmol) in CH_2Cl_2 (20 mL) was added. The mixture was stirred for 2 h, and then saturated, aqueous Na_2SO_3 (50 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with saturated, aqueous $NaHCO_3$ (100 mL) and with saturated, aqueous NaCl (100 mL), and dried with Na_2SO_4. The solvent was removed in vacuo and the residue purified by CC (100 g SiO_2, PE/AcOEt, 6:1) to afford 1.98 g of β-epoxide **11** (2.82 mmol, 65%) as a colorless solid, and 446 mg of α-epoxide **12** (0.63 mmol, 15%) as a colorless oil. The overall yield was 80%, in a ratio of 4.3:1 (**11/12**). − **β-Epoxide:** M.p. 48 °C. − R_f = 0.28 (PE/AcOEt, 6:1). − IR (KBr): $\tilde{\nu}$ = 3404 cm^{-1} (OH), 3068, 2929, 2859, 1592, 1467, 1428, 1256, 1108, 1004, 821, 736, 703, 613. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 [s, 9 H, TBDPS, $(CH_3)_3$], 0.98 [s, 9 H, TBDPS, $(CH_3)_3$], 1.37−2.50 (m, 10 H, 2,3,4,4a,5,8,8a-H), 3.21−3.26 (m, 1 H, 7-H), 3.33−3.36 (m, 1 H, 6-H), 3.39 (dd, *J* = 9.8 and 6.7 Hz, 1 H), 3.66 (dd, *J* = 6.7 and 3.2 Hz, 1 H) (CH_2 at C-3), 3.71−3.74 (m, 1 H), 3.79 (dd, *J* = 13.5 and 7.9 Hz, 1 H) (CH_2 at C-2), 3.97 (br. s, 1 H, 1−H), 4.39 (br. s, 1 H, OH), 7.23−7.41 (m, 12 H), 7.53−7.67 (m, 8 H) (TBDPS, phenyl). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 [$C(CH_3)_3$-TBDPS], 19.3 [$C(CH_3)_3$-TBDPS], 26.4 (C-5), 26.9 [$C(CH_3)_3$-TBDPS], 28.6 (C-3), 29.0 (C-8), 31.5 (C-4a), 34.5 (C-4), 38.1 (C-8a), 47.4 (C-2), 51.9 (C-7), 53.4 (C-6), 64.0, 66.6 (C at C-2,3), 69.4 (C-1), 127.5, 127.6, 129.3, 129.4, 129.5, 133.9, 134.0, 134.3, 135.5, 135.6, 135.7 (TPDPS, phenyl). − $C_{48}H_{62}O_5Si_2$ (775.2): calcd. C 74.37, H 8.06; found C 74.11, H 7.88. − **α-Epoxide:** R_f = 0.13 (PE/EtOAc, 6:1). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02 [s, 9 H, $C(CH_3)_3$-TBDPS], 1.10 [s, 9 H, $C(CH_3)_3$-TBDPS], 1.49−1.59 (m, 2 H), 1.61−1.72 (m, 2 H), 1.84−1.92 (m, 1 H), 2.02−2.16 (m, 3 H), 2.21−2.39 (m, 2 H) (2,3,4,4a,5,8,8a-H), 2.98 (br. s, 1 H, OH), 3.29−3.38 (m, 2 H, 6,7-H), 3.48−3.58 (m, 2 H), 3.79−3.87 (m, 1 H), 3.97−4.05 (m, 1 H) (CH_2 at C-2,3), 4.18 (br. s, 1 H, 1-H), 7.28−7.49 (m, 12 H), 7.52−7.70 (m, 8 H), (TBDPS, phenyl). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1 [TBDPS, $C(CH_3)_3$], 19.2 [TBDPS, $C(CH_3)_3$], 26.2, 30.0, 35.0 (C-3,4a,8a), 26.8 [TBDPS, $C(CH_3)_3$], 26.9 [TBDPS, $C(CH_3)_3$], 27.9, 28.1 34.3 (C−4,5,8), 44.1 (C-2), 51.7, 55.1 (C-6,7), 64.8, 65.6 (CH_2 at C-2,3), 75.8 (C-1), 127.5, 127.6, 127.7, 129.3, 129.4, 129.6, 129.7, 129.8, 132.6, 132.8, 133.6, 135.4, 135.5, 135.6 (TBDPS, phenyl).

(1*R,2*R**,3*R**,4a*S**,6*R**,7*S**,8a*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)-6,7-epoxy-1-[(phenyloxy)thiocarbonyloxy]decalin (13):** To a solution of alcohol **11** (985 mg, 1.40 mmol) in THF (120 mL) was added dropwise *n*BuLi (1.29 mL, 1.68 mmol, 1.3 M in hexane) at 0 °C. The mixture turned yellow and was stirred for 30 min. At the same temperature, PhOCSCl (0.23 mL, 1.68 mmol) was added. The mixture was allowed to reach room temp. and was stirred for 9 h. The reaction was quenched by adding saturated, aqueous NH_4Cl (30 mL) and Et_2O (30 mL). The aqueous layer was extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with saturated, aqueous NaCl (50 mL) and dried with

Na_2SO_4. After evaporation of the solvent in vacuo, the residue was purified by flash chromatography (30 g SiO_2, PE/AcOEt, 10:1) to give 967 mg thiocarbonate **13** (1.15 mmol, 82%) as a colorless oil, which crystallized after storage at 0 °C. – R_f = 0.24 (PE/AcOEt, 10:1). – IR (neat): $\tilde{\nu}$ = 3070 cm^{-1}, 2930, 2857 (CH), 2361, 1591 (C=S), 1488, 1427, 1289, 1202, 1109, 1086, 1008, 822, 735, 702, 614, 505. – ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 [s, 9 H, $C(CH_3)_3$-TBDPS], 1.07 [s, 9 H, $(CH_3)_3$-TBDPS], 1.47–1.60 (m, 3 H), 1.66–1.97 (m, 7 H) (2,3,4,4a,5,8,8a-H), 2.79–2.80 (m, 1 H), 3.01–3.08 (m, 1 H) (6,7-H), 3.20 (t, *J* = 4.2 Hz, 1 H), 3.96 (dd, *J* = 10.0 and 5.2 Hz, 1 H), 3.40–3.58 (m, 1 H), 3.86 (dd, *J* = 12.5 and 3.5 Hz, 1 H) (CH_2 at C-2,3), 6.06 (br. s, 1 H, 1-H), 7.00–7.44 (m, 18 H), 7.49–7.55 (m, 3 H), 7.61–7.72 (m, 4 H) (aromat.-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1 [*C*$(CH_3)_3$-TBDPS], 19.2 [*C*$(CH_3)_3$-TBDPS], 26.9 [C(*C*$H_3)_3$-TBDPS], 27.0 [C(*C*$H_3)_3$-TBDPS], 22.6, 26.8, 29.0, 33.0 (C-1,4,5,8), 29.4, 32.9, 37.2 (C-3,4a,8a), 46.1 (C-2), 49.9, 50.9 (C-6,7), 62.4, 66.2 (C at C-2,3), 82.5 (C-1), 122.5, 126.0, 127.6, 127.7, 129.2, 129.5, 129.6, 134.6, 134.8, 134.9, 135.5, 135.6, 153.8 (C-aromat.), 195.9 (C=S). – $C_{51}H_{60}O_5SSi_2$ (841.3): calcd. C 72.93, H 7.30; found C 72.92, H 7.59.

(2*R,3*R**,4a*S**,6*R**,7*S**,8a*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)-6,7-epoxydecalin (14):** Thiocarbonate **13** (960 mg, 1.17 mmol) was dissolved in toluene (50 mL). At −78 °C, the solution was degassed in vacuo. The mixture was heated to 90 °C and then *n*Bu_3SnH (1.0 mL, 3.72 mmol) and AIBN (2 mg) were added. The reaction mixture was stirred for 1 h at 90 °C. After cooling to room temp., the solvent was removed in vacuo and the resulting residue was purified by CC (20 g SiO_2, PE/AcOEt, 10:1) to yield 664 mg of epoxide **14** (964 μmol, 82%) as a colorless oil. – R_f = 0.56 (PE/AcOEt, 6:1). – IR (neat): $\tilde{\nu}$ = 3070 cm^{-1}, 2927, 2854, 1427, 1180, 1112, 1008, 823, 700. – ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 [s, 9 H, $(CH_3)_3$-TBDPS], 0.88 [s, 9 H, $(CH_3)_3$-TBDPS], 1.10–1.87 (m, 12 H, 1,2,3,4,4a,5,8,8a-H), 3.00–3.08 (m, 1 H, 7-H), 3.10–3.15 (m, 1 H, 6-H), 3.34–3.36 (m, 2 H), 3.40–3.52 (m, 2 H) (CH_2 at C-2,3), 7.13–7.29 (m, 12 H), 7.44–7.50 (m, 8 H) (TBDPS, phenyl). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 [*C*$(CH_3)_3$-TBDPS], 19.3 [*C*$(CH_3)_3$-TBDPS], 26.9 [C(*C*$H_3)_3$-TBDPS], 24.6, 30.2, 31.8, 34.4 (C-1,4,5,8), 30.4, 33.4, 35.2 (C-3,4a,8a), 42.3 (C-2), 52.1, 52.2 (C-6,7), 66.3, 66.4 (CH_2 at C-2,3), 127.5, 129.3, 129.4, 133.9, 134.0, 135.5, 135.6, 135.7 (TPDPS, phenyl). – HRMS [M^+ − *tert*-butyl]: calcd. 631.3063; found 631.3035.

(2*R,3*R**,4a*S**,6*S**,7*S**,8a*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)decalin-6,7-diol (15):** To a solution of epoxide **14** (937 mg, 1.36 mmol) in acetone (80 mL) was added a 3% $HClO_4$ solution (0.9 mL) at 0 °C. After 3 h at 0 °C, the reaction was quenched with saturated, aqueous Na_2SO_3 (10 mL). Saturated, aqueous NH_4Cl (10 mL) was added and the mixture was concentrated in vacuo. After addition of AcOEt (50 mL) and H_2O (50 mL), the layers were separated. The aqueous layer was extracted with AcOEt (3 × 30 mL). The combined organic layers were washed with saturated, aqueous NaCl (50 mL) and dried with Na_2SO_4. The solvent was removed in vacuo and the residue purified by CC (20 g SiO_2, PE/AcOEt, 1:1) to afford 910 mg of diol **15** (1.29 mmol, 95%) as a colorless solid. – R_f = 0.31 (*n*-hexane/AcOEt, 1:1). – IR (KBr): $\tilde{\nu}$ = 3441 cm^{-1} (OH), 2929, 2856, 1635, 1399, 1112, 739, 701, 613, 504. – ^1H NMR (300 MHz, [D_8]toluene): δ = 1.03–1.22 (m, 3 H), 1.15 [s, 9 H, $C(CH_3)_3$-TBDPS], 1.16 [s, 9 H, $C(CH_3)_3$-TBDPS], 1.26 (dt, *J* = 13.9 and 5.7 Hz, 1 H), 1.45–1.59 (m, 5 H), 1.73–1.84 (m, 3 H), 1.84–1.93 (m, 2 H) (1,2,3,4,4a,5,8,8a-H, OH), 3.28 (q, *J* = 4.6 Hz, 1 H, 7-H), 3.40–3.46 (m, 1 H, 6-H), 3.57–3.62 (m, 2 H), 3.66–3.74 (m, 2 H) (CH_2 at C-2,3), 7.18–7.26 (m, 12 H), 7.71–7.77 (m, 8 H) (TBDPS, phenyl). – ^{13}C NMR (75 MHz, [D_8]toluene): δ = 19.6 [*C*$(CH_3)_3$-TBDPS], 27.2 [C(*C*$H_3)_3$-TBDPS], 29.2, 34.4 (C-4a,8a), 31.3, 32.1, 32.1, 34.6 (C-1,4,5,8), 36.8 (C-3), 40.4 (C-2), 66.5, 67.3 (CH_2 at C-2,3), 71.4, 72.3 (C-6,7), 128.0, 129.8, 129.9, 134.3, 134.3, 134.4, 134.4, 136.0, 136.0, 136.1 (TBDPS, phenyl). – $C_{44}H_{58}O_4Si_2$ (707.1): calcd. C 74.47, H 8.26; found C 74.16, H 8.10.

(2*R,3*R**,4a*S**,6*S**,7*S**,8a*R**)-2,3-Bis(hydroxymethyl)-6,7-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)decalin-6,7-diol (16):** Diol **15** (175 mg, 247 μmol) was dissolved in MeOH (5 mL), and 2,2′,3,3′-tetramethoxybutane (88 mg, 0.50 mmol), trimethyl orthoformate (105 mg, 990 μmol), and camphorsulfonic acid (2 mg, 9 μmol) were added. The mixture was stirred for 48 h at 50 °C. After it had cooled to room temp., solid $NaHCO_3$ (20 mg) was added and the solvent was removed in vacuo. The resulting crude product was purified by CC (5 g SiO_2, PE/AcOEt, 1:1) to afford 85 mg bis(acetal) **16** (0.25 mmol, 99%) as a colorless solid. – M.p. 175 °C (MeOH). – R_f = 0.09 (PE/AcOEt, 1:1). – IR (KBr): $\tilde{\nu}$ = 3378 cm^{-1} (OH), 2929, 2888, 1451, 1373, 1218, 1132, 1038, 932, 856, 755. ^1H NMR (600 MHz, [D_4]MeOH): δ = 1.23 (s, 3 H), 1.24 (s, 3 H) (1′,4′-H), 1.33–1.38 (m, 1 H, 1β-H), 1.38 (dt, *J* = 13.8 and 2.6 Hz, 1 H, 4α-H), 1.48 (q, *J* = 12.0 Hz, 1 H, 8β-H), 1.54–1.64 (m, 4 H, 2,5,8α-H), 1.71 (dt, *J* = 13.8 and 5.6 Hz, 1 H, 4β-H), 1.82–1.91 (m, 3 H, 1α,3,8a-H), 1.94–2.01 (m, 1 H, 4a-H), 3.21 (s, 6 H, 2 × OCH_3), 3.38 (ddd, *J* = 11.6, 9.7 and 4.3 Hz, 1 H, 7-H), 3.46 (dd, *J* = 10.6 and 6.1 Hz, 1 H, CH_2 at C-2), 3.53–3.66 (m, 4 H, 6-H, CH_2 at C-2,3), 4.84 (s, 2 H, OH). – ^{13}C NMR (75 MHz, [D_4]MeOH): δ = 18.6 (C-1′,4′), 25.8 (C-4), 30.8 (C-1), 31.4 (C-4a), 34.5 (C-8), 35.2 (C-8a), 36.1 (C-5), 38.2 (C-2), 39.2 (C-3), 48.5 (2 × OCH_3), 65.2 (C at C-3), 67.7 (C at C-2), 69.5 (C-6), 73.5 (C-7), 101.1 (C-2′,3′). – HRMS [M^+ − OCH_3]: calcd. 313.2015; found 313.2013.

(2*R,3*R**,4a*S**,6*S**,7*S**,8a*R**)-2,3-Bis(hydroxymethyl)-6,7-bis[(6′-methyl-2,2′-bipyridin-6-yl)methyloxy]decalin (20). – 1. Williamson Reaction: (2*R**,3*R**,4a*S**,6*S**,7*S**,8a*R**)-2,3-Bis(*tert*-butyldiphenylsiloxymethyl)-6,7-bis[(6′-methyl-2,2′-bipyridin-6-yl)methyloxy]decalin:** To a solution of the diol **15** (164 mg, 232 μmol) in THF (2 mL) at 0 °C were added NaH (17 mg, 0.70 mmol) and one drop of DMSO. After 30 min., BipyBr (**19**) (244 mg, 0.93 mmol) and a catalytic amount of *n*Bu_4NI were added. After 3 d, the reaction mixture was quenched by addition of saturated, aqueous $NaHCO_3$ (5 mL) and CH_2Cl_2 (5 mL). The aqueous layer was extracted with CH_2Cl_2 (5 × 5 mL) and the combined organic layers were dried with $MgSO_4$. After removal of the solvent in vacuo, the remaining crude product was purified by CC on silica (7 g, PE/AcOEt, 4:1) to yield the corresponding ether as a colorless oil (206 mg, 192 μmol, 83%). – R_f = 0.22 (SiO_2, hexane/AcOEt, 4:1). – IR (neat): $\tilde{\nu}$ = 3067 cm^{-1}, 3051, 2956, 2928, 2857, 1574, 1463, 1471, 1440, 1428, 1391, 1361, 1254, 1195, 1113, 1084, 1008, 823, 785, 740, 702, 635, 613, 505. – ^1H NMR (300 MHz, $CDCl_3$): δ = 0.65–2.28 (m, 30 H, 1,2,3,4,4a,5,8,8a-H TBDPS-CH_3), 2.54 (s, 6 H, CH_3-bipy), 3.39–3.63 (m, 4 H, CH_2–OSi), 3.73 (s, 1 H), 3.86 (s, 1 H) (6,7-H), 4.80–4.82 (m, 4 H, CH_2-bipy), 7.01–7.10 (m, 2 H, bipy-H), 7.12–7.63 (m, 25 H, bipy-H, TBDPS-Ph), 7.67–7.76 (m, 1 H, bipy-H), 8.04–8.23 (m, 4 H, bipy-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 (TBDPS-$C(CH_3)_3$), 19.3 (TBDPS-$C(CH_3)_3$), 26.8 (TBDPS-CH_3), 26.9 (TBDPS-CH_3), 26.3, 28.9, 30.6, 31.2, 34.4, 35.1, 35.9 (C-1,3,4,4a,5,8,8a), 41.9 (C-2), 66.3, 66.5 (CH_2 at C-2,3), 71.7 and 72.0 (CH_2-bipy), 76.0 and 76.6 (C-6,7), 118.1, 118.1, 119.4, 119.6, 120.6, 120.8, 123.1, 123.1, 127.5, 127.5, 129.3, 129.4, 133.9, 133.9, 134.0, 135.5, 135.5, 135.6, 136.9, 137.3, 155.5, 155.6,

155.7, 157.8, 157.8, 158.7, 158.8 (C-Ar). − **2. Deprotection: (2*R**,3*R**,4a*S**,6*S**,7*S**,8a*R**)-2,3-Bis(hydroxymethyl)-6,7-bis[(6′-methyl-2,2′-bipyridin-6-yl)methyloxy]decalin (20):** To a solution of the silyl ether (50 mg, 47 μmol) in THF (2 mL) was added tetrabutylammonium fluoride (59 mg, 0.19 mmol). After 4 h at 40 °C, the solvent was removed in vacuo. The residue was purified by CC on silica (6 g, PE/AcOEt/MeOH, 10:10:1) to yield 24 mg (40 mmol, 87%) of **20** as a colorless oil. − R_f = 0.18 (SiO_2, hexane/AcOEt/MeOH, 10:10:1). − IR (neat): $\tilde{\nu}$ = 3357 cm^{-1} (OH), 3061, 2914, 2872, 1574, 1441, 1385, 1250, 1150, 1113, 1081, 1063, 785, 754, 669, 635. − ^{1}H NMR (300 MHz, CD_3CN): δ = 1.06−2.23 (m, 12 H, 1,2,3,4,4a,5,8,8a-H), 2.53 (s, 6 H, CH_3-bipy), 3.23 (br. s, 2 H, OH), 3.40 (br. s, 4 H, CH_2 at C-2,3), 3.70−3.74 (m, 1 H), 3.81−3.89 (m, 1 H) (6,7-H), 4.54−4.75 (m, 4 H, CH_2-bipy), 7.19 (bd, *J* = 7.7 Hz, 2 H), 7.40−7.46 (m, 2 H), 7.65−7.73 (m, 2 H), 7.77−7.84 (m, 2 H), 8.13 (d, *J* = 8.1 Hz, 2 H), 8.24 (d, *J* = 7.9 Hz, 2 H) (bipy(6)- and bipy(7)-H). − ^{13}C NMR (75 MHz, CD_3CN): δ = 24.7 (CH_3-bipy), 27.0, 31.1, 32.2, 36.0 (C-1,4,5,8), 29.8, 35.4 (C-4a,8a), 38.8 (C-3), 45.3 (C-2), 67.0, 67.0 (C at C-2.3), 72.6 (CH_2-bipy), 72.7 (CH_2-bipy), 76.5, 77.2 (C-6,7), 118.6, 118.6, 120.0, 120.1, 122.2, 122.3, 124.2, 138.2, 138.5, 156.1, 156.3, 158.9, 159.7, 159.7 (C-bipy). − HRMS [M^+]: calcd. 594.3206; found 594.3213.

(2*R,3*R**,4a*S**,6*S**,7*S**,8a*R**)-2,3-Bis(hydroxymethyl)-6,7-bis[(6′-methyl-2,2′-bipyridin-6-yl)methyloxy]decalin Zinc Bistriflate Complex (22):** A solution of $Zn(OTf)_2$ (7.3 mg, 20 μmol) in CD_3CN (0.7 mL) was added to compound **20** (12 mg, 20 μmol) and the mixture was heated to 50 °C for 2 min. Removal of the solvent gave the Zn^{II} complex as a glassy oil in quantitative yield. − IR (neat): $\tilde{\nu}$ = 3061 cm^{-1}, 2941, 2911, 2872, 2849, 1600, 1579, 1440, 1253, 1229, 1179, 1031, 789, 716, 639, 579, 522. − ^{1}H NMR (600 MHz, CD_3CN): δ = 1.09 (q, *J* = 11.9 Hz, 1 H, 8β-H), 1.09−1.16 (m, 1 H, 1α-H), 1.18−1.25 (m, 2 H, 4α,5α-H), 1.33 (td, *J* = 13.2 and *J* = 5.7 Hz, 1 H, 4β-H), 1.42−1.48 (m, 1 H, 2-H), 1.57−1.63 (m, 1 H, 3-H), 1.63−1.72 (m, 2 H, 1β,8a-H), 1.80−1.87 (m, 1 H, 4a-H), 1.82 (s, 3 H, CH_3-bipy), 1.84 (s, 3 H, CH_3-bipy), 2.02 (dt, *J* = 13.2 and *J* = 4.4 Hz, 1 H, 5β-H), 2.04 (dt, *J* = 12.7 and *J* = 4.9 Hz, 1 H, 8α-H), 2.82 (br. s, 2 H, OH), 2.97 (ddd, *J* = 11.1, *J* = 9.6 and *J* = 4.3 Hz, 1 H, 7-H), 3.16 (td, *J* = 10.1 and *J* = 4.9 Hz, 1 H, 6-H), 3.31 (dd, *J* = 10.5 and *J* = 5.7 Hz, 1 H, CH_2 at C-2), 3.37−3.48 (m, 3 H, CH_2 at C-2,3), 4.50 (d, *J* = 16.0 Hz, 1 H), 4.53 (d, *J* = 16.2 Hz, 1 H), 4.89 (d, *J* = 15.7 Hz, 1 H), 4.91 (d, *J* = 15.7 Hz, 1 H) (AB systems, CH_2-bipy), 7.59 (d, *J* = 7.6 Hz, 1 H) and 7.61 (d, *J* = 7.6 Hz, 1 H) [bipy(6)- and bipy(7)-5′-H], 7.87 (d, *J* = 7.8 Hz, 1 H) and 7.89 (d, *J* = 7.9 Hz, 1 H) [bipy(6)- and bipy(7)-5-H], 8.24 (t, *J* = 7.8 Hz, 1 H) and 8.26 (t, *J* = 7.8 Hz, 1 H) [bipy(6)- and bipy(7)-4′-H], 8.46 (t, *J* = 7.9 Hz, 1 H) and 8.47 (t, *J* = 7.9 Hz, 1 H) [bipy(6)- and bipy(7)-4-H], 8.52 (d, *J* = 7.8 Hz, 1 H) and 8.53 (d, *J* = 7.8 Hz, 1 H) [bipy(6)- and bipy(7)-3′-H], 8.61 (d, *J* = 7.7 Hz, 1 H) and 8.62 (d, *J* = 7.7 Hz, 1 H) [bipy(6)- and bipy(7)-3-H]. − ^{13}C NMR (75 MHz, CD_3CN): δ = 23.7 (CH_3-bipy), 23.8 (CH_3-bipy), 25.4 (C-4), 29.9 (C-4a), 30.1 (C-1), 32.1 (C-8), 33.2 (C-8a), 33.5 (C-5), 37.9 (C-2), 38.4 (C-3), 65.0 (C at C-3), 67.0 (C at C-2), 67.1 (CH_2-bipy), 77.6 (C-6), 80.8 (C-7), 122.5 [bipy(6)- and bipy(7)-C-3′], 124.3 and 124.3 [bipy(6)- and bipy(7)-C-3], 128.3 and 128.6 [bipy(6)- and bipy(7)-C-5], 130.5 [bipy(6)- and bipy(7)-C-5′], 143.7 and 143.8 [bipy(6)- and bipy(7)-C-4′], 145.1 and 145.3 [bipy(6)- and bipy(7)-C-4], 149.1, 149.1, 150.1, 150.2, 156.9, 157.0, 161.7 and 161.7 [bipy(6)- and bipy(7)-C-2,2′,6,6′]. − FAB-MS [Zn-**20**-OTf^+]: calcd. 807; found 807.

(2*R,3*R**,4a*S**,6*S**,7*S**,8a*R**)-2,3-Bis[(*E*)-2-(ethoxycarbonyl)-vinyl]-6,7-bis[(6′-methyl-2,2′-bipyridin-6-yl)methyloxy]decalin (23): − 1. Swern Oxidation:** Oxalyl chloride (34 μL, 0.39 mmol) was dissolved in CH_2Cl_2 (2 mL) and the solution cooled to −78 °C. DMSO (55 mL, 0.79 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise. Over 15 min the temperature was allowed to rise to −50 °C. After cooling to −78 °C, the diol **20** (78 mg, 131 mmol) in CH_2Cl_2 (1.5 mL) was added. Again the temperature was allowed to warm to −50 °C over 15 min. After cooling to −78 °C, Et*N*i*Pr*$_2$ (0.32 mL, 1.83 mmol) was added. The temperature of the cooling bath was allowed to rise to −40 °C (30 min) and then the reaction mixture was kept for an additional 30 min at 0 °C. The reaction was quenched by addition of saturated, aqueous $NaHCO_3$ (10 mL). The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (5 × 5 mL), and the combined organic layers were washed with saturated, aqueous NaCl (10 mL) and dried with Na_2SO_4. The solvent was removed in vacuo. Traces of water were azeotropically distilled with toluene (2 × 5 mL). The aldehyde was used in the next step without further purification. − **2. Wittig Reaction:** The aldehyde and Ph_3P=CHCOOEt (365 mg, 1.05 mmol) were dissolved in toluene (5 mL) and heated to 90 °C. After 15 h, the solvent was removed in vacuo and the residue purified by flash chromatography on silica (8 g, PE/AcOEt/MeOH, 20:20:1) to yield the ester **23** (69 mg, 94 μmol, 72%) as a colorless oil. − R_f = 0.47 (SiO_2, hexane/AcOEt/MeOH, 10:10:1). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08−1.21 (m, 6 H, CH_3-Et), 1.35−2.30 (m, 12 H, 1,2,3,4,4a,5,8,8a-H), 2.49 (s, 6 H, CH_3), 3.68 (q, *J* = 2.5 Hz, 1 H, 7-H), 3.81 (br. s, 1 H, 6-H), 3.96−4.10 (m, 4 H, CH_2-Et), 4.50−4.79 (m, 4 H, CH_2-bipy), 5.58−5.69 (m, 2 H, C=CH−COO), 6.55−6.73 (m, 2 H, HC=C−COO), 6.96−8.20 (m, 12 H, bipy-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (CH_3-Et), 24.7, 25.8, 28.3, 30.1, 32.9, 33.6, 37.4 (C-1,4,4a,5,8,8a and CH_3-bipy), 60.2 and 60.2 (CH_2-Et), 71.9 and 72.1 (CH_2-bipy), 75.2 (C-7), 76.1 (C-6), 118.1, 119.7, 120.7, 120.8, 121.0, 121.3, 123.2, 123.2, 125.3, 128.2, 129.0, 137.0, 137.4, 137.4, 151.7, 151.8, 155.6, 155.6, 155.7, 155.7, 157.9, 157.9, 158.4 and 158.4 (C=C, C-bipy), 166.5 and 166.6 (COO). − HRMS [M^+]: calcd. 730.3730; found 730.3736.

(2*R,3*R**,4a*S**,6*S**,7*S**,8a*R**)-2,3-Bis[(*E*)-2-(hydroxymethyl)vinyl]-6,7-bis[(6′-methyl-2,2′-bipyridin-6-yl)methyloxy]decalin (24):** The ester **23** (65 mg, 89 μmol) was dissolved in CH_2Cl_2 (5 mL) and the solution cooled to −78 °C. DIBAH (1 M in CH_2Cl_2, 0.73 mL, 0.73 mmol) was added. Over 4 h, the temperature of the cooling bath was allowed to rise to −40 °C. For an additional 2 h, the reaction mixture was kept at 0 °C, during which it turned from yellow to orange. The reaction was quenched by addition of Rochelle's salt solution (3 mL, 1 M in water). Stirring was continued overnight in order to destroy the aluminium complex of the product. The aqueous layer was extracted with CH_2Cl_2 (5 × 5 mL) and AcOEt (2 × 5 mL). The combined organic layers were dried with Na_2SO_4. After removal of the solvent in vacuo and CC on silica (8 g, PE/AcOEt/MeOH, 10:10:1), the diol **24** was obtained in 71% yield (41 mg, 63 μmol) as a colorless oil. − R_f = 0.14 (hexane/AcOEt/MeOH, 10:10:1). − IR (neat): $\tilde{\nu}$ = 3450 cm^{-1} (OH), 2959, 2923, 2861, 1726, 1600, 1574, 1441, 1258, 1171, 1117, 1081, 1033, 974, 788, 640, 521. − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.42−1.50 (m, 2 H, 1α,4α-H), 1.51−1.56 (m, 1 H, 4β-H), 1.62−1.76 (m, 3 H, 2-H, OH), 1.77−1.83 (m, 1 H, 8a-H), 1.85 (d, *J* = 14.6 Hz, 1 H, 8β-H), 1.90−1.97 (m, 1 H, 3-H), 1.97−2.01 (m, 1 H, 8α-H), 2.02 (q, *J* = 12.9 Hz, 1 H, 1β-H), 2.09 (td, *J* = 13.8 and *J* = 2.2 Hz, 1 H, 5β-H), 2.22−2.28 (m, 1 H, 4a-H), 2.61 (s, 6 H, CH_3), 3.77−3.81 (m, 1 H, 7-H), 3.89−3.93 (m, 1 H, 6-H), 3.93−4.07 (m, 4 H, CH_2−OH), 4.68 (d, *J* = 13.5 Hz, 1 H), 4.68 (d, *J* = 13.5 Hz, 1 H), 4.76 (d, *J* = 13.5 Hz, 1 H), 4.78 (d, *J* = 13.5 Hz, 1 H) (AB system, CH_2-bipy), 5.37−5.55 (m, 4 H, C=C-H), 7.13 [d, *J* = 7.6 Hz, 2 H, bipy(6)- and bipy(7)-5′-H], 7.42 (d, *J* = 7.6 Hz, 1 H) and 7.44 (d, *J* = 7.6 Hz, 1 H) [bipy(6)- and bipy(7)-5-H], 7.65 [t, *J* = 7.7 Hz, 2

H, bipy(6)- and bipy(7)-4′-H], 7.77 (t, J = 7.7 Hz, 1 H) and 7.78 (t, J = 7.7 Hz, 1 H) [bipy(6)- and bipy(7)-4-H], 8.12 (d, J = 7.9 Hz, 1 H) and 8.13 (d, J = 7.9 Hz, 1 H) [bipy(6)- and bipy(7)-3′-H], 8.24 (d, J = 7.5 Hz, 1 H) and 8.25 (d, J = 7.6 Hz, 1 H) [bipy(6)- and bipy(7)-3-H]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.6 (CH_3), 24.6 (CH_3), 26.0 (C-5), 28.6 (C-4a), 30.0 (C-8), 33.9 (C-1), 34.0 (C-8a), 38.2 (C-4), 40.2 (C-3), 46.5 (C-2), 63.7 (CH_2−OH), 71.7 and 71.9 (CH_2-bipy), 75.4 (C-7), 76.4 (C-6), 118.2, 118.3 [bipy(6)- and bipy(7)-C-3′], 119.7 [bipy(6)- and bipy(7)-C-3], 120.8 [bipy(6)- and bipy(7)-C-5], 123.2 [bipy(6)- and bipy(7)-C-5′], 128.4, 128.7 (C=C), 137.0, 137.4, 137.6, 137.6 [bipy(6)- and bipy(7)-C-4,4′, C=C], 155.6, 155.6, 157.9, 158.6 [bipy(6)- and bipy(7)-C-2,2′,6,6′]. − HRMS [M^+]: calcd. 646.3519; found 646.3527.

(2*R,3*R**,4a*S**,6*S**,7*S**,8a*R**)-2,3-Bis[(*E*)-2-(hydroxymethyl)vinyl]-6,7-bis[(6′-methyl-2,2′-bipyridin-6-yl)methyloxy]decalin Zinc Bistriflate Complex (27):** A solution of $Zn(OTf)_2$ (3.4 mg, 9.4 μmol) in CD_3CN (0.7 mL) was added to compound **24** (5.5 mg, 8.5 μmol) and the mixture was heated for 2 min at ca. 50 °C. Removal of the solvent gave the Zn^{II} complex as a glassy oil in quantitative yield. − IR (neat): $\tilde{\nu}$ = 3378 cm^{-1} (br., OH), 3062, 3000, 2915, 2866, 1679, 1574, 1441, 1341, 1245, 1116, 1083, 994, 971, 785, 755, 635. − ^{1}H NMR (600 MHz, CD_3CN): δ = 1.17 (dt, J = 13.5 and J = 3.9 Hz, 1 H, 4α-H), 1.19−1.27 (m, 2 H, 1β,5α-H), 1.26 (q, J = 11.8 Hz, 1 H, 8β-H), 1.60 (td, J = 13.0 and J = 5.0 Hz, 1 H, 4β-H), 1.66−1.74 (m, 1 H, 8a-H), 1.78−2.05 (m, 10 H, 1α,4a,5β,8α-H, CH_3), 2.10−2.33 (m, 2 H, 2,3-H), 2.63 (br. s, 1 H, OH), 2.69 (br. s, 1 H, OH), 2.96 (ddd, J = 11.1, J = 9.6 and J = 4.2 Hz, 1 H, 7-H), 3.17 (td, J = 10.0 and J = 5.1 Hz, 1 H, 6-H), 3.84−3.95 (m, 4 H, CH_2−OH), 4.50 (d, J = 16.2 Hz, 1 H), 4.53 (d, J = 15.9 Hz, 1 H), 4.87 (d, J = 15.8 Hz, 1 H) and 4.90 (d, J = 15.8 Hz, 1 H) (AB systems, CH_2-bipy), 5.39−5.71 (m, 4 H, C=C-H), 7.59 (d, J = 7.6 Hz, 1 H) and 7.60 (d, J = 7.6 Hz, 1 H) [bipy(6)- and bipy(7)-5′-H], 7.87 (d, J = 7.6 Hz, 1 H) and 7.88 (d, J = 7.6 Hz, 1 H) [bipy(6)- and bipy(7)-5-H], 8.24 (t, J = 7.9 Hz, 1 H) and 8.25 (t, J = 7.9 Hz, 1 H) [bipy(6)- and bipy(7)-4′-H], 8.46 (t, J = 8.1 Hz, 1 H) and 8.47 (t, J = 8.1 Hz, 1 H) [bipy(6)- and bipy(7)-4-H], 8.51 (d, J = 7.9 Hz, 1 H) and 8.53 (d, J = 7.9 Hz, 1 H) [bipy(6)- and bipy(7)-3′-H], 8.60 (d, J = 8.1 Hz, 1 H) and 8.62 (d, J = 8.1 Hz, 1 H) [bipy(6)- and bipy(7)-3-H]. − ^{13}C NMR (75 MHz, CD_3CN): δ = 23.7 (CH_3), 23.8 (CH_3), 29.1 (C-4), 30.0 (C-4a), 31.7 (C-8), 33.6 and 33.6 (C-1,5), 33.8 (C-8a), 40.1 (C-2), 40.6 (C-3), 63.2 and 63.3 (CH_2−OH), 67.1 and 67.2 (CH_2-bipy), 77.7 (C-6), 81.0 (C-7), 122.5 [bipy(6)- and bipy(7)-C-3′], 124.3 and 124.4 [bipy(6)- and bipy(7)-C-3], 128.3 and 128.6 [bipy(6)- and bipy(7)-C-5], 129.6 and 130.5 (C=C), 130.4 and 130.5 [bipy(6)- and bipy(7)-C-5′], 135.2 and 136.8 (C=C), 143.8 and 143.8 [bipy(6)- and bipy(7)-C-4′], 145.1 and 145.3 [bipy(6)- and bipy(7)-C-4], 149.1, 149.1, 150.1, 150.2, 157.0, 157.0, 161.7, 161.8 [bipy(6)- and bipy(7)-C-2,2′,6,6′]. − FAB-MS [Zn-**24**-OTf^+]: calcd. 859; found 859.

(2*R,3*R**,4a*S**,6*S**,7*S**,8a*R**)-2,3-Bis[(*E*)-2-(pyren-1-ylmethylcarbonyloxymethyl)vinyl]-6,7-bis[(6′-methyl-2,2′-bipyridin-6-yl)methyloxy]decalin (25):** The diol **24** (20 mg, 31 μmol) was dissolved in CH_2Cl_2 (1 mL). *N*,*N*-Dimethylaminopyridine (DMAP) (57 mg, 0.46 mmol), *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC) (59 mg, 0.31 mmol), and pyrene-1-yl-acetic acid (80 mg, 0.31 mmol) were added. After 2 h at room temp., the reaction was quenched by addition of saturated, aqueous $NaHCO_3$ (5 mL) and CH_2Cl_2 (5 mL). The layers were separated. The aqueous layer was extracted with CH_2Cl_2 (5 × 5 mL). The combined organic layers were washed with saturated, aqueous NaCl and dried with Na_2SO_4. The solvent was removed in vacuo. The residue was purified by CC on silica (25 g, PE/AcOEt, 4:1 → PE/AcOEt/MeOH, 10:10:1) to yield 27 mg (24 mmol, 77%) of the ester **25** as a yellow oil. − R_f = 0.24 (hexane/AcOEt/MeOH, 10:10:1). − IR (neat): $\tilde{\nu}$ = 3042 cm^{-1}, 2918, 1731 (C=O), 1574, 1440, 1376, 1313, 1252, 1148, 1116, 1097, 968, 845, 785, 756, 712, 667, 635, 516. − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.12 (td, J = 12.9 and J = 5.1 Hz, 1 H, 4α-H), 1.19−1.35 (m, 3 H, 1α,4β,2-H), 1.41 (dt, J = 14.0 and J = 2.8 Hz, 1 H, 5α-H), 1.49−1.66 (m, 2 H, 8a,3-H), 1.72 (d, J = 14.7 Hz, 1 H, 8-H), 1.82 (q, J = 13.1 Hz, 1 H, 1β-H), 1.84 (td, J = 13.9 and J = 2.1 Hz, 1 H, 5β-H), 1.91 (dddd, J = 15.0, J = 5.6, J = 3.4 and J = 0.7 Hz, 1 H, 8-H), 2.07 (bd, J = 12.4 Hz, 1 H, 4a-H), 3.74 (dt, J = 2.6 and J = 2.5 Hz, 1 H, 7-H), 3.85 (td, J = 2.3 and J = 2.2 Hz, 1 H, 6-H), 4.25 (s, 1 H), 4.25 (s, 1 H), 4.28 (s, 2 H) (CH_2-pyr), 4.34−4.44 (m, 4 H, CH_2-bipy), 4.62 (d, J = 13.6 Hz, 1 H), 4.68 (d, J = 13.9 Hz, 2 H), 4.77 (d, J = 13.6 Hz, 1 H) (AB systems, CH_2−OOC), 5.10−5.29 (m, 4 H, C=C-H), 7.11 (d, J = 7.5 Hz, 1 H), 7.15 (d, J = 7.6 Hz, 1 H) [bipy(6)- and bipy(7)-5′-H], 7.30 (d, J = 7.6 Hz, 1 H) and 7.45 (d, J = 7.7 Hz, 1 H) [bipy(6)- and bipy(7)-5-H], 7.63 (t, J = 7.7 Hz, 1 H) and 7.67 (t, J = 7.7 Hz, 1 H) [bipy(6)- and bipy(7)-4′-H], 7.71 (t, J = 7.7 Hz, 1 H) and 7.80 (t, J = 7.7 Hz, 1 H) [bipy(6)- and bipy(7)-4-H], 7.86 (d, J = 7.7 Hz, 1 H, pyr-H), 7.89 (d, J = 7.7 Hz, 1 H, pyr-H), 7.90−8.18 [m, 17 H, pyr-H and bipy(6)- and bipy(7)-3′-H], 8.20 (d, J = 9.2 Hz, 1 H, pyr-H), 8.21 (d, J = 7.6 Hz, 1 H) and 8.29 (d, J = 7.7 Hz, 1 H) [bipy(6)- and bipy(7)-3-H]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.7 (CH_3), 25.8 (C-5), 28.4 (C-4a), 30.0 (C-8), 33.4 (C-1), 33.7 (C-8a), 37.7 (C-4), 39.5 and 39.6 (CH_2-pyr), 39.7 (C-3), 45.8 (C-2), 65.3 and 65.5 (CH_2−OOC), 71.7 and 71.9 (CH_2-bipy), 75.3 (C-7), 76.2 (C-6), 118.1 and 118.1 [bipy(6)- and bipy(7)-C-3′], 119.6 and 119.7 [bipy(6)- and bipy(7)-C-3], 120.7 and 120.8 [bipy(6)- and bipy(7)-C-5], 122.6 and 122.9 (C=C), 123.1 and 123.2 [bipy(6)- and bipy(7)-C-5′], 123.3, 123.3, 124.6, 124.7, 124.8, 124.8, 124.9, 125.0, 125.0, 125.0, 125.1, 125.2, 125.9, 125.9, 127.1, 127.2, 127.3, 127.8, 127.8, 128.2, 128.2, 128.3, 128.4, 129.4, 129.4, 130.7, 130.7, 130.7, 130.7, 131.2 and 131.2 (C-pyr), 136.9 and 137.0 [bipy(6)- and bipy(7)-C-4′], 137.3 and 137.4 [bipy(6)- and bipy(7)-C-4], 139.6 and 139.8 (C=C), 155.6, 155.7, 157.7, 157.9, 158.5 and 158.6 [bipy(6)- and bipy(7)-C-2,2′,6,6′], 171.2 (COO). − HRMS [M^+]: calcd. 1130.4982; found 1130.5013.

(2*R,3*R**,4a*S**,6*S**,7*S**,8a*R**)-2,3-Bis[(*E*)-2-(pyren-1-ylmethylcarbonyloxymethyl)vinyl]-6,7-bis[(6′-methyl-2,2′-bipyridin-6-yl)methyloxy]decalin Zinc Bistriflate Complex (29):** A solution of $Zn(OTf)_2$ (4.7 mg, 12.8 μmol) in CD_3CN (0.7 mL) was added to compound **25** (14.5 mg, 12.8 μmol) and the mixture was heated for 2 min at ca. 50 °C. Removal of the solvent gave the Zn^{II} complex **29** as a glassy oil in quantitative yield. − IR (neat): $\tilde{\nu}$ = 3042 cm^{-1}, 2945, 2887, 1713 (C=O), 1660, 1600, 1574, 1439, 1308, 1251, 1171, 1092, 1032, 969, 848, 788, 761, 710, 638, 521. − ^{1}H NMR (600 MHz, CD_3CN): δ = 0.22 (ddd, J = 13.3, J = 10.9 and J = 5.4 Hz, 1 H, 5α-H), 0.52−0.58 (m, 2 H, 1,8a-H), 0.61 (dt, J = 13.6 and J = 3.4 Hz, 1 H, 4α-H), 0.73−0.80 (m, 1 H, 4a-H), 0.82 (q, J = 12.6 Hz, 1 H, 8β-H), 0.95 (dt, J = 14.2 and J = 5.9 Hz, 1 H, 1-H), 1.07 (td, J = 13.4 and J = 4.9 Hz, 1 H, 4β-H), 1.37 (ddd, J = 13.5, J = 4.6 and J = 3.4 Hz, 1 H, 5β-H), 1.45 (dt, J = 13.2 and J = 4.1 Hz, 1 H, 8α-H), 1.50 (br. s, 1 H, 2-H), 1.71 (s, 3 H, CH_3), 1.72 (s, 3 H, CH_3), 1.76−1.83 (m, 1 H, 3-H), 2.42 (ddd, J = 11.1, J = 9.7 and J = 4.3 Hz, 1 H, 7-H), 2.78 (ddd, J = 10.2, J = 9.9 and J = 4.8 Hz), 4.05 (d, J = 16.0 Hz, 1 H), 4.09 (d, J = 15.9 Hz, 1 H) (AB system, CH_2-pyr), 4.24 (ddt, J = 12.9, J = 5.7 and J = 0.6 Hz, 1 H, CH_2−OOC), 4.27 (d, J = 15.7 Hz, 1 H, CH_2-bipy), 4.29−4.38 (m, 4 H, CH_2−OOC, CH_2-bipy and CH_2-pyr), 4.43 (ddt, J = 13.7, J = 5.2 and J = 0.8 Hz, 1 H, CH_2−OOC), 4.49 (ddt, J = 13.7, J = 5.2 and J = 0.8 Hz, 1 H, CH_2−OOC), 4.61 (d, J = 16.0 Hz, 1 H, CH_2-bipy), 4.65 (d, J = 15.8 Hz, 1 H,

Table 1. X-ray crystallographic data for compounds **11**, **13**, and **16**

Compound	**11**	**13**	**16**
Empirical formula, Z	$C_{44}H_{56}O_4Si_2$, 2	$C_{51}H_{60}O_5SSi_2$, 4	$C_{18}H_{32}O_6$, 2
Molecular mass, D_x [g/cm^3]	705.07, 1.190	841.23, 1.172	344.44, 1.280
Temperature [K]	150(2)	180(2)	180(2)
Crystal system, space group	triclinic, $P\bar{1}$	monoclinic, $P21/c$	triclinic, $P\bar{1}$
Radiation [pm]	Mo-K_α (71.073)	Mo-K_α (71.073)	Mo-K_α (71.073)
Crystal size [mm]	0.44 × 0.32 × 0.28	0.76 × 0.76 × 0.28	0.73 × 0.60 × 0.11
a [pm]	948.68(16)	1381.3(2)	760.7(2)
b [pm]	1309.20(3)	2231.5(4)	1117.0(4)
c [pm]	1629.80(3)	1546.1(3)	1131.6(4)
α [°]	101.66(2)		91.07(4)
β [°]	91.56(2)	90.19(2)	104.16(4)
γ [°]	96.22(2)		105.69(4)
Volume [10^6 pm^3]	1968.2(6)	4765.6(15)	893.9(5)
F_{000}	760	1800	376
θ range [°]	2.24 < Θ < 25.25	1.60 < Θ < 25.06	2.54 < Θ < 25.25
h, k, l range	h: −11/11, k: −15/15, l: −19/19	h: −16/16, k: 0/26, l: 0/18	h: −9/9, k: −13/13, l: −13/13
Data, restraints, parameters	6721, 0, 629	8445, 0, 539	3009, 0, 346
Absorption coefficient [mm^{-1}]	0.131	0.163	0.094
Atom form factors	International Tables for Crystallography, vol. C, Tab. 4.2.6.8 and Tab. 6.1.1.4, Kluwer Academic Press, Dordrecht, Boston, London, **1995**		
Refinement	Full-matrix least squares based on F^2		
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0733	$R1$ = 0.0661	$R1$ = 0.0472
Final R indices [all data]	$wR2$ = 0.1854	$wR2$ = 0.1868	$wR2$ = 0.127
GoF	0.910	1.076	1.004
Final difmap (min/max) e [10^{-6} pm^{-3}]	−0.508/0.469	−0.555/0.665	−0.234/0.310

CH_2-bipy), 5.05−5.24 (m, 4 H, C=C-H), 7.33 (d, J = 7.7 Hz, 1 H) and 7.59 (d, J = 7.7 Hz, 1 H) [bipy(6)- and bipy(7)-5′-H], 7.74 (dd, J = 6.2 and J = 2.2 Hz, 1 H, Ar-H), 7.80 [t, J = 7.6 Hz, 1 H, bipy(6)- or bipy(7)-4′-H], 7.79−7.83 (m, 2 H, Ar-H), 7.87 [d, J = 7.7 Hz, 1 H, bipy(6)- or bipy(7)-5-H], 7.92 (d, J = 8.9 Hz, 1 H, Ar-H), 7.94−8.13 (m, 11 H, Ar-H), 8.16 (d, J = 7.8 Hz, 2 H, Ar-H), 8.20−8.23 [m, 4 H, Ar-H and bipy(6)- or bipy(7)-4-H], 8.27 (d, J = 6.2 Hz, 1 H, Ar-H), 8.28 [d, J = 7.6 Hz, 1 H, bipy(6)- or bipy(7)-4′-H], 8.58 [d, J = 7.9 Hz, 1 H, bipy(6)- or bipy(7)-3′-H], 8.60 [t, J = 8.0 Hz, 1 H, bipy(6)- or bipy(7)-4-H], 8.70 [d, J = 8.2 Hz, 1 H, bipy(6)- or bipy(7)-3-H]. − ^{13}C NMR (75 MHz, CD_3CN): δ = 23.6 and 23.7 (CH_3), 27.9 (C-4), 29.6 (C-4a), 31.1 (C-8), 32.4 (C-1), 33.0 (C-8a), 33.1 (C-5), 38.8 (C-2), 39.6 (C-3), 39.7 and 40.2 (CH_2-pyr), 65.0, 65.6, 66.8 and 66.9 (CH_2-bipy and CH_2−OOC), 77.3 (C-6), 80.7 (C-7), 122.1 and 122.6 [bipy(6)- and bipy(7)-C-3′], 123.1 (C=C), 124.0 (Ar-C), 124.4 (C=C), 124.4, 124.6, 125.5, 125.9, 125.9, 126.1, 126.1, 126.3, 126.4, 127.1, 127.4, 128.0, 128.1, 128.3, 128.4, 128.5, 128.6, 129.7, 129.8, 130.0, 130.2, 130.3 (Ar-C), 130.2 and 130.5 [bipy(6)- and bipy(7)-C-5′], 131.6, 131.6 (Ar-C), 136.9 and 140.9 (C=C), 143.4 and 143.8 [bipy(6)- and bipy(7)-C-4′], 145.1 and 145.3 [bipy(6)- and bipy(7)-C-4], 148.6, 149.0, 149.8, 150.2 and 156.8 [bipy(6)- and bipy(7)-C-2,2′,6,6′], 161.5 and 161.7 (COO). − FAB-MS [Zn-**25**-OTf$^+$]: calcd. 1343; found 1343.

UV/Vis Titration and Fluorescence Study: All compounds were used as solutions in $CH_3CN/CHCl_3$ (UVASOL, Merck), 1:1. The titrations were performed by adding increasing amounts (up to 25 μL) of dissolved $Zn(OTf)_2$ to solutions (3.0 mL) of **24** and **25**. The samples were contained in 1×1 cm quartz cuvettes, which were purged for 10 min with argon and air-sealed in the case of the fluorescence titration. The absorption spectra were recorded with a HITACHI U-3410 spectrophotometer, while the fluorescence spectra were taken using a HITACHI-PERKIN ELMER MPF-2A spectrometer at an excitation wavelength of 343 nm and a bandpass of 5 nm.

X-ray Crystallographic Study. − X-ray Structure Determination of 11, 13, and 16: Intensity data collection for **11**, **13**, and **16** was performed with an IPDS one-circle diffractometer (Stoe, Darmstadt). The crystal structure analyses were performed with the SHELX-97 program package;[15] for details see Table 1. Further crystallographic data, excluding structure factor listings, have been deposited at the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-143391 (**11**), -143390 (**13**), -143389 (**16**). Copies of the data can be obtained free of charge on application to CCCD, 12 Union Road, Cambridge CB21EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Dr. G. Höhne (TU Berlin) for MS analysis.

[1] [1a] J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**. − [1b] T. Shimidzu, K. Honda in *Functionality of Molecular Systems*, vol. 2 (Ed.: K. Honda), p. 1−4, Springer, Tokyo, **1999**.

[2] V. Balzani, M. Gomez-Lopez, J. F. Stoddart, *Acc. Chem. Res.* **1998**, *31*, 405−414.

[3] [3a] G. Krauss, *Biochemie der Regulation und Signaltransduktion*, Wiley-VCH, Weinheim, **1997**. − [3b] K. Hinterding, D. Alonso-Díaz, H. Waldmann, Angew. *Chem.* **1998**, *110*, 716−780; *Angew. Chem. Int. Ed.* **1998**, *37*, 688−749.

[4] R. Krauss, H.-G. Weinig, M. Seydack, J. Bendig, U. Koert, *Angew. Chem.* **2000**, *112*, 1905−1908; *Angew. Chem. Int. Ed.* **2000**, *39*, 1835−1837.

[5] For leading references on conformational switching: [5a] H. Yuasa, H. Hashimoto, *J. Am. Chem. Soc.* **1999**, *121*, 5089−5090. − [5b] S. E. O'Connor, B. Imperiali, *J. Am. Chem. Soc.* **1997**, *119*, 2296−2296. − [5c] M. Raban, D. L. Burch, E. R. Hortelano, D. Durocher, D. Kost, *J. Org. Chem.* **1994**, *59*, 1283−1287.

[6] J. Berninger, R. Krauss, H.-G. Weinig, U. Koert, B. Ziemer, K. Harms, *Eur. J. Org. Chem.* **1999**, 875−884.
[7] E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, Wiley, New York, **1994**, p. 686 ff.
[8] D. H. R. Barton, S. W. McCombie, *J. Chem. Soc., Perkin I* **1975**, 1574−1585.
[9] A. Fürst, P. A. Plattner, *Helv. Chim. Acta* **1949**, *32*, 275−283.
[10] [10a] S. V. Ley, H. W. M. Priepke, S. L. Warriner, *Angew. Chem.* **1994**, *106*, 2410−2412. − [10b] J.-L. Montchamp, F. Tian, M. E. Hart, J. W. Frost, *J. Org. Chem.* **1996**, *61*, 3897−3899.
[11] M. M. Harding, U. Koert, J.-M. Lehn, C. Piguet, A. Marquis-Rigault, J. Siegel, *Helv. Chim. Acta* **1991**, *74*, 594−610.
[12] A. Bilyk, M. M. Harding, P. Turner, T. W. Hambley, *J. Chem. Soc., Dalton Trans.* **1994**, 2783−2790.
[13] Details for the use of UV titration for the determination of ΔG: [13a] R. Foster, R. *Organic Charge-Transfer Complexes*, Academic Press, London, **1969**, p. 128. − [13b]H. Braatz, S. Hecht, H. Seifert, S. Helm, J. Bendig, W. Rettig, J. Photochem. Photobiol. A: *Chem.* **1999**, *123*, 99−108.
[14] [14a] I. Aoki, T. Harada, T. Sakaki, Y. Kawahara, S. Shinkai, *J. Chem. Soc., Chem. Commun.* **1992**, 1341−1345. − [14b] A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice; *Chem. Rev.* **1997**, *97*, 1515−1566. − [14c] L. Fabbrizzi, M. Licchelli, P. Pallavivini, *Acc. Chem. Res.* **1999**, *32*, 846−853.
[15] G. M. Sheldrick, *SHELXS-97.2, a program for crystal structure solution*, Universität Göttingen, **1998**. G. M. Sheldrick, *SHELXL-97.2, a program for crystal structure refinement*, Universität Göttingen, **1998**.

Received May 31, 2000
[O00276]