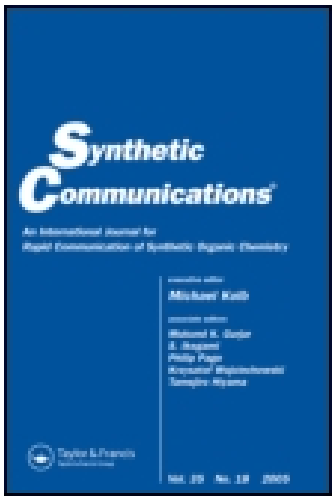

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SYNTHESIS AND X-RAY CRYSTALLOGRAPHY OF CHIRAL TROPOCORONANDS

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SYNTHESIS AND X-RAY CRYSTALLOGRAPHY OF CHIRAL TROPOCORONANDS

Philip J. Chenier,[1,*] Jason A. Halfen,[1] Tami L. Raguse,[1] Autumn E. Rich,[1] Kathryn E. Splan,[1] Kazuki Yoshioka,[1] and Thomas R. Hoye[2,*]

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ABSTRACT

The synthesis of several chiral tropocoronands (**6** and **7**) has been accomplished. These compounds have been shown to complex with various metals. Tropocoronands that have been synthesized include H_2(TC-3,cyhex) through H_2(TC-6,cyhex) (**6**) and H_2(TC-3,diphen) through H_2(TC-6,diphen) (**7**). The route is short and the tropocoronands are easily purified by chromatography or recrystallization. Two other groups have been incorporated into tropocoronands, H_2(TC-3,binap) (**9**) and H_2(TC-6,pent) (**10**).

INTRODUCTION

A very active area of organic synthetic research in the last few years has been asymmetric or enantioselective catalysis. A number of recent monographs

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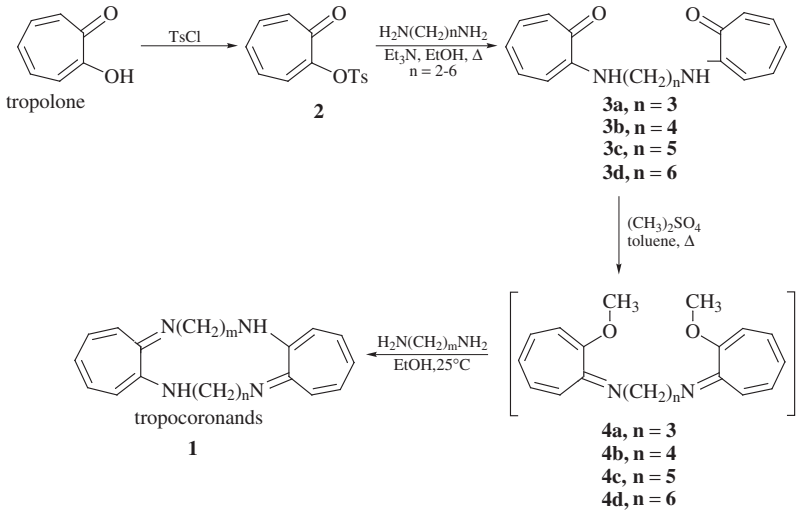

Scheme 1.

and reviews on this subject have been published (1–7). The generation of chiral molecules as single enantiomers has been the subject of intense interest for many years, but only recently have great strides been made using chiral ligands in catalysts to promote asymmetry in reactions. Tropocoronands (**1**) represent a new class of molecules with potential to be modified with a chiral moiety and applied to enantioselective reactions.

Tropocoronands (Scheme 1) are macrocycles containing two cycloheptatriene rings and four nitrogens linked by two chains. They were first synthesized by Nakanishi, Lippard, and Nozoe (8,9). Symmetrical tropocoronands where m = n = 2–6 have been made in a four-step synthesis from tropolone. Either 2-tosyloxytropone (**2**) (10–13) or 2-chlorotropone can be made from tropolone and then reacted with the appropriate diamine to give diaminodiketones **3**. These diketones then give dialkoxydiimines **4** by treatment with dimethyl sulfate in refluxing toluene, or with triethyloxonium tetrafluoroborate in refluxing chloroform/hexamethylphosphoramide. The resulting dialkoxides can then undergo amine displacement and ring closure at 25°C to the tropocoronands **1**. Reported yields in the cyclization are generally 20–40%, but only 2% when m = n = 2. However, Nozoe has demonstrated yields of 55–65% for m = n = 3 using methyl fluorosulfate in methylene chloride as the alkylating agent (14).

Recently, unsymmetrical tropocoronands have been synthesized where the number of carbons of the simple straight-chain linkages is different ($m \neq n$) (15,16). These compounds, H_2(TC-3,4) (**1**, where m = 3, n = 4) and H_2(TC-4,5) (**1**, m = 4, n = 5), were the only unsymmetrical tropocoronands reported until our work.

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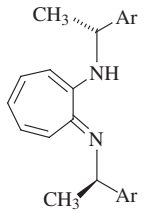
Lippard has studied tropocoronands as ligands for copper(I) and (II), rhodium(I), nickel(II), cobalt(III), and other metals (15,16). The structures of these complexes have been characterized in detail. Ethanol solutions of salts of Fe(II) through Zn(II) have been found to form intense colors with methylene chloride solutions of tropocoronands where the linker chains contain 3–6 carbons, suggesting that the complexation of these substances with transition metal ions is very general. These ligands and their complexes have contained only simple achiral linker chains. Incorporation of a chiral moiety into the tropocoronand macrocycle and subsequent study of metal complexes derived from such chiral ligands have not been reported, except for our preliminary communication (17). The only uses of a related ligand in asymmetric catalysis are those described by Brunner (18) and Lippard (19,20). Tropolone derivative **5** was shown to induce asymmetry



5

during the course of ketone hydrosilylation and 1,4-addition of cuprates to enones, respectively.

Many potential applications of chiral tropocoronand ligands to catalytic, enantioselective reactions can be envisioned. They are similar in structure to the versatile salen catalysts developed by Jacobsen, and certain porphyrins, both of which are used extensively in enantioselective processes (1–7).

RESULTS AND DISCUSSION

We now report the details of the synthesis of a number of tropocoronands that have chiral diamines incorporated into their macrocycle. These are unsymmetrical where one linker chain is chiral and the other is derived from simple straight chain α,ω-diamines with 3, 4, 5, or 6 carbons. Series **6a–d** is derived from *trans*-1,2-diaminocyclohexane and series **7a–d** from (R*,R*)-1,2-diphenylethylenediamine, both commercially available as either enantiomer. Using the synthesis as outlined in Scheme 1, but substituting *trans*-1,2-diaminocyclohexane in the final step, we have made H_2(TC-3,cyhex) (**6a**), H_2(TC-4,cyhex) (**6b**), H_2(TC-5,cyhex) (**6c**), and H_2(TC-6,cyhex) (**6d**). In analogous fashion, we have used chiral (R*,R*)-1,2-diphenylethylenediamine to synthesize H_2(TC-3,diphen) (**7a**) through H_2(TC-6,diphen) (**7d**). The syntheses proceeded well, although yields in the cyclization step

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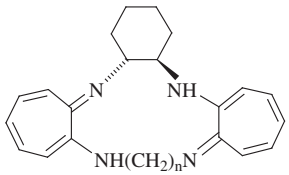
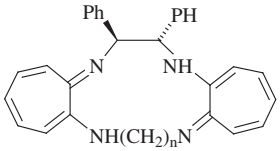
were low, as is typical for the syntheses of the simple achiral analogs such as **1**. The diaminodiketones **3** are easily prepared in large quantities and are stable.



6a, n = 3
6b, n = 4
6c, n = 5
6d, n = 6

H_2(TC-n,cyhex)

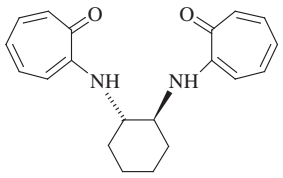


7a, n = 3
7b, n = 4
7c, n = 5
7d, n = 6

H_2(TC-n,diphen)

The dimethoxydiimines **4** were prepared and used in the cyclization step in the same day. All of the tropocoronands **6** and **7** are high melting, yellow to orange, crystalline compounds that can be isolated and purified easily by chromatography or recrystallization. Spectroscopic properties are in accord with their structure. Isolated yields of recrystallized material range from 10–39% in the cyclization.

An alternative synthesis, that of placing the chiral group in the sequence first to form a diaminoketone such as **8**, followed by cyclization with a straight chain



8

diamine in the last step, was not successful. The diaminoketone can be made, but it is difficult to purify and separate from tropolone tosylate, so the alternative order of diamine incorporation was not investigated further.

We also attempted the synthesis of smaller ring sizes, particularly H_2(TC-2,cyhex) (**6**, n = 2), but were unsuccessful in the cyclization step of the dimethoxydiimine **4** (n = 2). This is not surprising in view of the difficulty Nozoe had synthesizing smaller members of the achiral tropocoronands.

In addition to the **6** and **7** series of tropocoronands, H_2(TC-3,binap) (**9**) and H_2(TC-6,pent) (**10**), containing a binaphthyl and 2,4-pentdiyl chiral subunit, respectively, have also been prepared. 1,1′-Binaphthyl-2,2′-diamine is not sufficiently reactive with the dialkoxydiimine **4a** so a modification of the usual procedure was required to synthesize **9**. Treatment of 1,1′-binaphthyl-2,2′-diamine with two equivalents of *n*-butyllithium in tetrahydrofuran gave the dilithium salt. The

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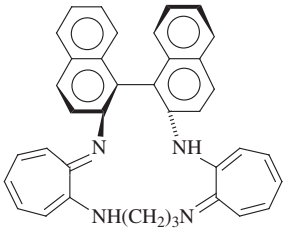

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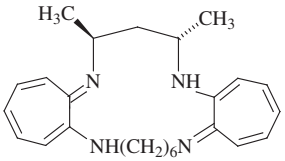

10

dialkoxydiimine **4a** was dissolved in tetrahydrofuran and added to the dilithium salt. The solution was then refluxed to complete the reaction. Both R and S enantiomers of the binaphthyldiamine were used. Very small yields of the tropocoronands were realized, but they can be isolated by chromatography.

(±)-H_2(TC-6,pent) and one optically active sample of **10** has also been prepared starting from dialkoxydiimine **4d** and 2,4-diaminopentane (21). A 9% yield of **10** was realized.

Solid state structures have been determined for three tropocoronands—(±)-**6a**, *R*-**7b**, and (±)-**10**. The x-ray crystal structure of (±)-**6a** (Fig. 1), which crystallizes in the centrosymmetric space group $P2_1/c$, reveals a structure that is entirely consistent with the proposed molecular formula. In crystals of optically pure *R*-**7b** (Fig. 2) the tropocoronand crystallizes in the chiral space group $P2_1$ and co-crystallizes with a single acetone solvate. Structural analysis of **10** indicates that, while bulk sample is racemic, the tropocoronand spontaneously resolves upon crystallization, such that the molecule crystallizes in the chiral space group $P2_12_12_1$. The absolute configuration of **10** in the sample analyzed cannot be determined, however, due to the lack of an appropriate heavy atom in the compound to

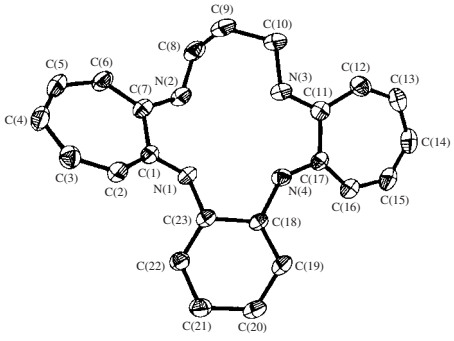

Figure 1. Thermal ellipsoid representation (35% probability ellipsoids) of the x-ray crystal structure of ±**6a**.

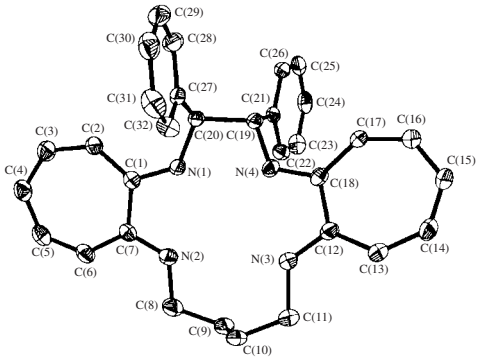

Figure 2. Thermal ellipsoid representation (35% probability ellipsoids) of the x-ray crystal structure of *R*-**7b**.

provide for anomalous dispersion of the x-ray beam. In contrast to the structures of **6a** and **7b**, the structure of **10** (Fig. 3) reveals a highly distorted macrocycle, the conformation of which may result from unfavorable intramolecular interaction between the tropylidene rings and the nearby methyl groups of the chiral spacer.

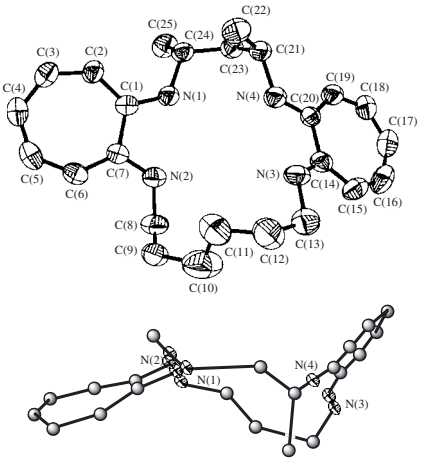

Figure 3. Top and side views of the x-ray crystal structure of **10**. Thermal ellipsoids are drawn at the 35% probability level, and only one conformation of the disordered hexyl linker is shown.

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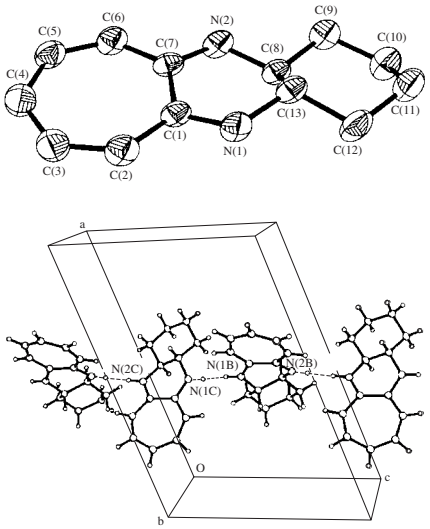
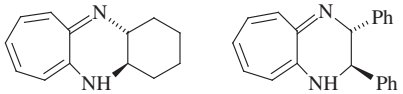


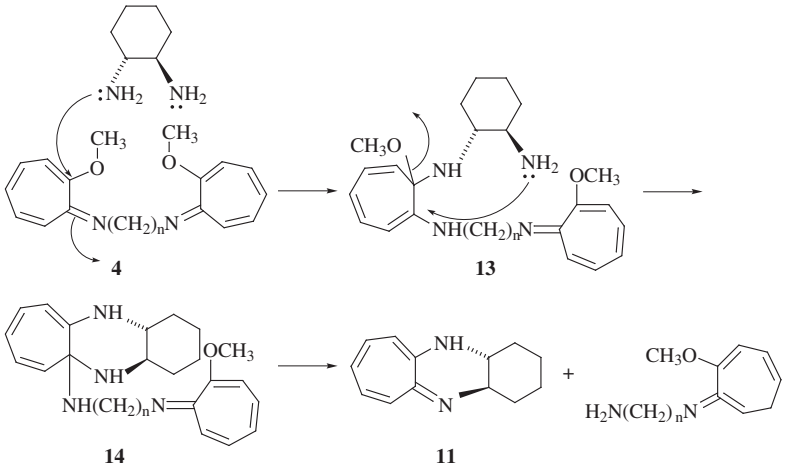
Figure 4. Thermal ellipsoid representation (35% probability ellipsoids) of the x-ray crystal structure of **11**, and view of the observed solid-state hydrogen bonding pattern.

Some interesting side products (of a type previously not reported) arise in the cyclization step to form these chiral tropocoronands. In the cyclization for both series **6** and **7**, a second major product of the reaction was either **11** or **12**. For instance, **11** was isolated from the synthesis of **6a**, **6b**, and **6d**. Proton NMR



11 **12**

and high-resolution mass spectral data are in accord with the structure of **11**, but the structure was in doubt because of the carbon NMR spectrum, which shows only four resonances. The x-ray crystal structure of **11** (Fig. 4) confirms the proposed molecular structure. The compound crystallizes in the chiral space group *C*2, and lies on a non-crystallographic two-fold symmetry axis that passes through C4 and bisects the C2-C7, C8-C13, and C10-C11 bonds, which renders the two nitrogen atoms equivalent. As a result, the single N-bound hydrogen atom is statistically disordered over both nitrogen atoms, and provides for the formation of hydrogen-bonded chains of molecules that run parallel to the crystallographic *c* axis. These chains are characterized by relatively short N···N distances of 3.014(6) Å and



Scheme 2.

3.104(6) Å. Similarly, **12** has fewer carbon resonances than expected, but other data prove its structure. These side products are no doubt caused by the ability of both nitrogens of the chiral diamine to undergo nucleophilic attack on the same tropylidene ring, eliminating the straight-chain amine, perhaps through intermediates such as **13** and **14** (Scheme 2). However, both products **11** and **12** can be separated easily from the tropocoronands and do not cause problems synthetically other than lowered yields of desired macrocycles.

In summary, we have developed a synthesis of chiral tropocoronands. Several have been examined by x-ray crystallographic studies and are found to have significantly different geometries surrounding the central array of four nitrogen atoms.

EXPERIMENTAL

Melting and boiling points are uncorrected. NMR data are given in ppm (referenced to TMS = 0 ppm). ^{1}H and ^{13}C NMR spectra were taken at various field strengths as noted. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ and Midwest Microlab, Indianapolis, IN. 2-Tosyloxytropone (**2**) (11) and diaminodiketones **3** (9) (prepared from **2**) were made by literature methods.

(±)-H_2(TC-4,cyhex) (6b)

Following the general procedure of Nozoe and Nakanishi (9), crude diaminodiketone **3b** (14.2 g, 47.9 mmol) was mixed with toluene (240 mL) at reflux and

dimethyl sulfate (13.3 g, 105.6 mmol) was added over 1 min. The mixture was refluxed for 1–2 h. A dark insoluble oil was formed, which solidified on cooling. The mixture was extracted with water (3 × 480 mL), in which the solid dissolved. The combined aqueous layers were washed with chloroform (2 × 480 mL) and then made alkaline with 5% sodium carbonate (1.2 L) to a pH of 9–10. The aqueous phase was extracted with chloroform (3 × 360 mL). The combined chloroform extracts were dried with anhydrous potassium carbonate, filtered, and concentrated to give crude dimethoxydiimine **4b** as a dark oil. The oil was dissolved in absolute ethanol (1 L) in a separatory funnel. In a second funnel, (±)-*trans*-1,2-diaminocyclohexane (6.58 g, 57.6 mmol) was also dissolved in absolute ethanol (1 L). The two solutions were added at the same rate over 3 h to a flask containing absolute ethanol (200 mL) with magnetic stirring. The solution was stirred overnight. Rotary evaporation of the ethanol yielded crude material. This was dissolved in chloroform (500 mL) and filtered through a 4-cm long column of basic alumina. The alumina was rinsed with chloroform (750 mL) and the combined eluent was rotary evaporated to give crude **6b** as an orange solid (13.66 g, 36.5 mmol, 76%). The crude tropocoronand was recrystallized from acetone to give purer product (3.82 g, 10.2 mmol, 21%), useful for further studies. Two additional recrystallizations from acetone gave pure **6b**: mp 231°–233°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (br s, 2H), 6.75 (m, 4H), 6.30 (d, J = 11.0 Hz, 2H), 6.12 (m, 4H), 3.46 (m, 2H), 3.34 (ddd, J = 13.5, 2.5, and 2.5 Hz, 2H), 3.07 (t, J = 12.4 Hz, 2H), 2.50 (br d, J = 13.2 Hz, 2H), 1.90 (m, 4H), 1.60 (m, 2H), 1.47 (m, 2H), and 1.30 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.0, 154.9, 133.3, 132.7, 117.5, 110.4, 110.2, 61.5, 46.3, 30.2, 26.5, 25.2; IR (KBr) 3436, 3248, 2929, 2857, 1587, 1546, 1513, 1463, 1381, 1271, 1212, 727 cm^{-1}. HRMS (EI) calcd for $C_{24}H_{30}N_4$ 374.2470, found 374.2471. Anal. calcd for $C_{24}H_{30}N_4$: C, 76.97; H, 8.07. Found: C, 77.13; H, 7.75.

(−)-[*R*-(*R**,*R**)]-H_2(TC-4,cyhex) (6b)

Following a similar procedure crude diaminodiketone **3b** (4.44 g, 15.0 mmol) and (*R*-*trans*)-1,2-diaminocyclohexane (1.83 g, 16.0 mmol) gave [*R*-(*R**,*R**)]-**6b** of good purity, mp 235–240°C (1.73 g, 4.63 mmol, 31%). The ^{1}H and ^{13}C NMR spectra of this compound were identical to racemic **6b**. $[\alpha]_D^{RT} = -76.7°$ (c = 0.3 in $CHCl_3$).

(±)-H_2(TC-3,cyhex) (6a)

Following the same procedure as detailed for **6b**, diaminodiketone **3a** (1.98 g, 7.00 mmol), toluene (35 mL), dimethyl sulfate (1.90 g, 15.1 mmol), (±)- *trans*-1,2-diaminocyclohexane (0.874 g, 7.66 mmol), and absolute ethanol (600 mL)

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were used and gave, after one recrystallization from acetone, (±)-**6a** (0.42 g, 1.17 mmol, 17%). Three additional recrystallizations from acetone gave pure **6a** as orange crystals: mp 218°–221°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.45 (br s, 2H), 6.75 (m, 4H), 6.37 (d, J = 11.0 Hz, 2H), 6.21 (d, J = 10.6 Hz, 2H), 6.13 (t, J = 9.2 Hz, 2H), 3.50 (m, 4H), 3.35 (m, 2H), 2.46 (d, J = 13.2 Hz, 2H), 1.92 (m, 4H), 1.59 (m, 2H), and 1.42 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.5, 155.3, 133.6, 132.9, 118.2, 111.1, 110.9, 62.9, 48.0, 31.3, 29.6, 25.3; IR (KBr) 3446, 3229, 2937, 2862, 1594, 1538, 1513, 1463, 1376, 1283, 1215, 742, 698, 661 cm^{-1}. HRMS (EI) calcd for $C_{23}H_{28}N_4$ 360.2314, found 360.2313. Anal. calcd for $C_{23}H_{28}N_4$: C, 76.63; H, 7.83. Found: C, 76.47; H, 7.66.

(−)-[*R*-(*R**,*R**)]-H_2(TC-3,cyhex) (6a)

By the same procedure, diaminoketone **3a** (3.40 g, 12.0 mmol) and (*R-trans*)-1,2-diaminocyclohexane (1.50 g, 13.2 mmol) gave [*R*-(*R**,*R**)]-**6a** of good purity, mp 200°–202°C (0.67 g, 1.90 mmol, 16%). The ^{1}H and ^{13}C NMR spectra of this compound were identical to racemic **6a**. $[\alpha]_D^{RT} = -66.7°$ (c = 0.3 in $CHCl_3$). The structure was confirmed by x-ray crystallography.

(±)-H_2(TC-5,cyhex) (6c)

Following the same procedure as detailed for **6b**, diaminodiketone **3c** (3.09 g, 10.0 mmol), toluene (50 mL), dimethyl sulfate (2.87 g, 22.8 mmol), (±)-*trans*-1,2-diaminocyclohexane (1.34 g, 11.7 mmol), and absolute ethanol (850 mL) were used and gave, after one recrystallization from acetone, (±)-**6c** (0.40 g, 1.03 mmol, 10%). Three additional recrystallizations from acetone gave pure **6c**: mp 186°–188°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.0–8.0 (br, 2H), 6.75 (m, 4H), 6.43 (d, J = 11.0 Hz, 2H), 6.23 (d, J = 10.6 Hz, 2H), 6.14 (t, J = 9.2 Hz, 2H), 3.63 (m, 2H), 3.42 (m, 2H), 3.31 (m, 2H), 2.37 (br d, J = 13.9 Hz, 2H), 1.2–1.9 (m, 12 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.2, 153.3, 132.9, 132.4, 117.7, 111.8, 109.4, 61.5, 44.5, 30.2, 27.4, 25.2, 22.8; IR (KBr) 3440, 3259, 2937, 2860, 1608, 1531, 1461, 1351, 1270, 1206, 1096, 848, 724, 636 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{32}N_4$ 388.2627, found 388.2605. An analytical sample could not be obtained because of occluded solvent.

(±)-H_2(TC-6,cyhex) (6d)

The same procedure was followed using diaminodiketone **3d** (0.150 g, 0.463 mmol), toluene (4 mL), dimethyl sulfate (0.125 g, 0.991 mmol), (±)-*trans*-1,2-diaminocyclohexane (0.0623 g, 0.546 mmol), and absolute ethanol (125 mL)

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to obtain, after one recrystallization from hexane-acetone, (±)-**6d** (0.0214 g, 0.0532 mmol, 12%). Two additional recrystallization from hexane-acetone gave pure **6d** as yellow needles, mp 221°–222°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.3–7.9 (br, 2H), 6.73 (m, 4H), 6.50 (d, J = 11.3 Hz, 2H), 6.16 (d, J = 10.6 Hz, 2H), 6.11 (t, J = 9.15 Hz, 2H), 3.67 (m, 2H), 3.50 (dt, J = 14.7 and 4.6, 2H), 3.29 (m, 2H), 2.28 (br d, J = 13.9 Hz, 2H), 1.0–1.9 (m, 14H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.1, 152.2, 132.9, 132.1, 117.3, 113.3, 107.5, 61.7, 43.4, 29.8, 26.9, 26.4, 25.3; IR (KBr) 3438, 3248, 2931, 2854, 1588, 1539, 1511, 1462, 1384, 1349, 1272, 1209, 752, 709 cm^{-1}. HRMS (FAB) calcd for $C_{26}H_{35}N_4$ $[M+1]^+$ 403.2862, found 403.2830. Anal. calcd for $C_{26}H_{34}N_4$: C, 77.57; H, 8.51. Found: C, 77.25; H, 8.79.

[*S*-(*R**,*R**)]-H$_2$(TC-6,cyhex) (6d)

By the same procedure diaminodiketone **3d** (0.450 g, 1.39 mmol) and (*S-trans*)-1,2-diaminocyclohexane (0.187 g, 1.64 mmol) gave [*S*-(*R**,*R**)]-**6d** of good purity after one recrystallization from hexane-acetone, mp 244°–248°C (0.0850 g, 0.211 mmol, 15%). The ^{1}H and ^{13}C NMR spectra of this compound were identical to racemic **6d**.

[*S*-(*R**,*R**)]-H$_2$(TC-3,diphen) (7a)

The same procedure was followed with diaminoketone **3a** (1.22 g, 4.30 mmol), toluene (20 mL), dimethyl sulfate (1.17 g, 9.28 mmol), [*S*-(*R**,*R**)]-1,2-diphenylethylenediamine (1.00 g, 4.71 mmol), and absolute ethanol (370 mL) to obtain, after chromatography on silica gel and elution with hexane:ethyl acetate mixtures containing 3% triethylamine, [*S*-(*R**,*R**)]-**7a** (0.55 g, 1.2 mmol, 28%). Recrystallization four times from hexaneethyl acetate gave pure **7a** as a yellow solid, mp 151°–154°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.12 (br s, 2H), 7.19 (m, 10H), 6.76 (t, J = 10 Hz, 2H), 6.49 (t, J = 10 Hz, 2H), 6.34 (d, J = 11.0 Hz, 2H), 6.02 (m, 4H), 4.72, (s, 2H), 3.69 (m, 4H), and 2.21 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.7, 153.4, 143.0, 133.5, 133.4, 128.4, 127.1, 127.0, 117.8, 112.6, 110.6, 66.8, 47.7 and 33.0; IR (KBr) 3435, 3268, 3195, 3058, 3024, 2913, 2854, 1590, 1544, 1507, 1462, 1385, 1259, 1124, 1020, 882, 700, and 640 cm^{-1}. HRMS (EI) calcd for $C_{31}H_{30}N_4$ 458.2470, found 458.2471. Anal. calcd for $C_{31}H_{30}N_4$: N, 12.22. Found: N, 12.06.

[*R*-(*R**,*R**)]-H$_2$(TC-3,diphen) (7a)

A procedure identical to [*S*-(*R**,*R**)]-**7a** but with [*R*-(*R**,*R**)]-1,2-diphenyle-thylenediamine gave, after chromatography, [*R*-(*R**,*R**)]-**7a** (0.45 g,

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0.98 mmol, 23%). The ^{1}H and ^{13}C spectra for this compound were identical to the spectra for the S enantiomer.

[*R*-(*R**,*R**)-H_2(TC-4,diphen) (7b)

The same procedure was followed with diaminodiketone **3b** (0.592 g, 2.00 mmol), toluene (20 mL), dimethyl sulfate (0.53 g, 4.20 mmol), [*R*-(*R*∗,*R*∗)]-1,2-diphenylethylenediamine (0.506 g, 2.38 mmol), and absolute ethanol (400 mL) to obtain, after chromatography on silica gel and elution with hexane-ethyl acetate mixtures containing 3% triethylamine, [*R*-(*R**,*R**)]-**7b** (0.171 g, 0.362 mmol, 18%). Recrystallization from hexane-acetone gave a yellow powder, mp 105°–110°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.31 (br s, 2H), 7.1–7.5 (m, 10H), 6.73 (t, J = 10.1 Hz, 2H), 6.51 (t, J = 10.1 Hz, 2H), 6.32 (d, J = 11.0 Hz, 2H), 6.03 (t, J = 9.3 Hz, 2H), 5.97 (d, J = 11.0 Hz, 2H), 4.90 (s, 2H), 3.44 (d, J = 13.9 Hz, 2H), 3.23 (t, J = 12.8 Hz, 2H), 2.22 (m, 2H), and 2.03 9m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.3, 153.0, 142.8, 133.4, 133.2, 128.7, 128.4, 127.0, 126.8, 117.5, 111.6, 110.8, 65.9, 46.4, 27.8; IR (KBr) 3442, 3222, 3063, 3022, 2925, 2853, 1583, 1542, 1506, 1460, 1388, 1276, 1112, 748, 707 cm^{-1}. HRMS (EI) calcd for $C_{32}H_{32}N_4$ 472.2627, found 472.2613. The structure was confirmed by x-ray crystallography.

[*R*-(*R**,*R**)]-H_2(TC-5,diphen) (7c)

The same procedure was followed with diaminodiketone **3c** (4.74 g, 15.3 mmol), toluene (75 mL), dimethyl sulfate (4.00 g, 31.7 mmol), [*R*-(*R**,*R**)]-1,2-diphenylethylenediamine (3.78 g, 17.8 mmol), and absolute ethanol (1.2 L) to obtain, after chromatography on silica gel and elution with hexane-ethyl acetate mixtures containing 3% triethylamine, [*R*-(*R**,*R**)]-**7c** (0.79 g, 1.93 mmol, 13%). Recrystallization four times from hexane-acetone gave a yellow solid, mp 154°–156°C; ^{1}H NMR ($CDCl_3$), 400 MHz) δ 8.95 (br s, 2H), 7.37 (d, J = 7.3 Hz, 4H), 7.22 (t, J = 7.7 Hz, 4H), 7.14 (t, J = 7.2 Hz, 2H), 6.67 (t, J = 10.1 Hz, 2H), 6.43 (t, J = 10.3 Hz, 2H), 6.31 (d, J = 11.3 Hz, 2H), 5.97 (t, J = 9.2 Hz, 2H), 5.91 (d, J = 11.0 Hz, 2H), 5.05 (s, 2H), 3.46 (m, 4H), 1.8–2.1 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.2, 142.6, 133.1, 132.8, 128.3, 127.0, 126.9, 117.6, 111.0, 110.7, 65.7, 44.0, 27.6, 22.8; IR (KBr) 3453, 3235, 3067, 3024, 2931, 2856, 1588, 1519, 1389, 1277, 1215, 749, 698, 630 cm^{-1}. HRMS (EI) calcd for $C_{33}H_{34}N_4$ 486.2783, found 486.2785. Anal calcd for $C_{33}H_{34}N_4$: N, 11.51. found: N, 11.28.

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[*S*-(*R**,*R**)]-H_2(TC-6,diphen) (7d)

The same procedure was followed with diaminodiketone **3d** (0.450 g, 1.39 mmol), toluene (10 mL), dimethyl sulfate (0.381 g, 3.02 mmol), [*S*-(*R**,*R**)]-1,2-diphenylethylenediamine (0.348 g, 1.64 mmol), and absolute ethanol (375 mL) to obtain [*S*-(*R**,*R**)]-**7d** (0.276 g, 0.552 mmol, 39%). Recrystallization from hexane-acetone gave a yellow solid, mp 178°–181°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.81 (br s, 2H), 7.1–7.4 (m, 10H), 6.67 (t, J = 10.2 Hz, 2H), 6.46 (t, J = 10.2 Hz, 2H), 6.31 (d, J = 11.0 Hz, 2H), 5.99 (t, J = 9.2 Hz, 2H), 5.93 (d, J = 11.0 Hz, 2H), 4.90 (s, 2H), 3.48 (m, 4H), 1.5–2.0 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.4, 153.1, 142.0, 133.1, 132.9, 128.2, 127.2, 126.9, 117.5, 111.6, 110.2, 66.7, 44.5, 28.6, 26.5; IR (KBr) 3436, 3023, 2928, 2854, 1590, 1539, 1513, 1500, 1464, 1386, 1274, 1265, 748, 700 cm^{-1}. HRMS (FAB) calcd for $C_{34}H_{37}N_4$ $[M+1]^+$ 501.3018, found 501.3033. Anal. calcd for $C_{34}H_{36}N_4$: N, 11.19. found: N, 10.89.

[*S*]-H_2(TC-3,binap) (9)

The usual procedure was followed to produce crude dimethoxydiimine **4a** from dimethyl sulfate (0.44 g, 3.48 mmol), diaminodiketone **3a** (0.45 g, 1.61 mmol), and toluene (10 mL). At the same time, *S*-1,1′-binaphthyl-2,2′-diamine (0.50 g, 1.76 mmol) in tetrahydrofuran (THF, 100 mL) was added to a three-neck flask equipped with a condenser and an addition funnel, and held under nitrogen. *n*-Butyllithium (2.31 mL/1.6M in hexanes, 3.70 mmol) was added over 15 min with stirring to form the dilithium salt. The dimethoxydiimine **4a** dissolved in THF (100 mL) was added to the solution over 2 h and the resulting mixture was refluxed for 1 h. It was then cooled and stirred overnight.

Water was added and the mixture was rotary evaporated. Chloroform was added (50 mL) and the solution was washed with water (5 × 50 mL), dried over anhydrous potassium carbonate, filtered, and run through a 4-cm long column of basic alumina. The alumina was rinsed with chloroform (150 mL) and the combined eluent was rotary evaporated. Chromatography on silica gel, elution with hexane-ethyl acetate mixtures containing 3% triethylamine, and recrystallization from methyl isobutyl ketone-hexane or acetone gave the pure product as an orange solid (6.6 mg, 0.012 mmol, 1%): mp 290°–294°C dec; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.29 (br s, 2H), 7.76 (d, J = 8.4 Hz, 4H), 7.25 (m, 4H), 7.12 (m, 4H), 6.73 (t, J = 11 Hz, 2H), 6.56 (d, J = 11.0 Hz, 2H), 6.37 (t, J = 11 Hz, 2H), 6.28 (d, J = 11.0 Hz, 2H), 6.08 (t, J = 9 Hz, 2H) 3.60 (m, 4H), and 2.14 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.5, 152.3, 143.6, 134.9, 133.3, 132.9, 130.4, 128.7, 127.7, 126.6, 125.8, 124.3, 123.7, 123.1, 119.8, 117.6, 110.7, 46.1, and 29.0; IR (KBr)

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3446, 3207, 3053, 2922, 2851, 1589, 1539, 1509, 1462, 1320, 1246, 1095, 1037, 940, 820, 751, and 709 cm^{-1}. HRMS (EI) calcd for $C_{37}H_{30}N_4$ 530.2470, found 530.2472.

[*R*]-H_2(TC-3,binap) (9)

A procedure similar to the one used in the synthesis of [S]-H_2(TC-3,binap) (**9**) was followed to produce the *R* enantomer. Diaminodiketone **3a** (1.13 g, 4.03 mmol) was made into dimethoxydiimine **4a**, which was reacted with the dilithium salt of *R*-1,1′-binaphthyl-2,2′-diamine (1.25 g, 4.40 mmol) to produce [*R*]-H_2(TC-3,binap) (**9**, 4.5 mg, 0.0085 mmol, 0.2%) after purification by column chromatography and recrystallization from acetone. The ^1H and ^{13}C spectra for this compound were identical to the spectra of the *S* enantomer.

(±)-H_2(TC-6,pent) (10)

Dimethoxydiimine **4d** was made by the usual procedure from dimethyl sulfate (7.69 g, 61.0 mmol), diaminodiketone **3d** (8.98 g, 27.7 mmol), and toluene (180 mL) and dissolved in absolute ethanol (1 L). (±)-2,4-Diaminopentane hydrochloride (3.40 g, 19.4 mmol) was prepared by the literature method (21) and was stirred with 50% KOH (13.5 mL) in a nitrogen atmosphere. Solid KOH was added and the liquid was decanted. The top organic layer was separated and dried with solid KOH and pipetted into absolute ethanol (1 L).

These two solutions were mixed in the usual procedure and the product was purified by chromatography on silica gel, elution with hexane-ethyl acetate mixtures containing 3% triethylamine, and recrystallization from acetone to give (±)-H_2(TC-6,pent) (**10**) as a yellow solid (0.41 g, 1.05 mmol, 5%): mp 113°–115°C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.0–8.5 (br, 2H), 6.73 (m, 4H), 6.31 (d, J = 11.0 Hz, 2H), 6.27 (d, J = 11.4 Hz, 2H), 6.09 (t, J = 9.3 Hz, 2H), 4.04 (sextet, J = 5.9 Hz, 2H), 3.35 (m, 5H), 2.13 (t, J = 5.1 Hz, 2H), 1.52–1.90 (m, 8H), 1.16 (d, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.2, 152.0, 132.8, 132.6, 117.0, 110.3, 109.4, 47.8, 46.3, 42.6, 28.8, 27.8, 19.8; IR (KBr) 3447, 3229, 2918, 2844, 1581, 1507, 1277, 705 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{34}N_4$ 390.2783, found 390.2780. Anal. calcd for $C_{25}H_{34}N_4$: N, 14.34. Found: N, 14.78. The structure was confirmed by x-ray crystallography.

(+)-H_2(TC-6,pent) (10)

(±)-2,4-Diaminopentane hydrochloride was resolved by the method of Bosnich (21) and (+)-2,4-diaminopentane hydrochloride was obtained, $[\alpha]_D^{RT} = +5.9°$ (c = 1 in 1M HCl). (+)-**10** was obtained by a procedure identical to that

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for (±)-**10** on the same scale. After chromatography, a 5% yield was obtained. Spectral properties were identical to those of (±)-**10**.

Diaminodiketone 8

2-Tosyloxytropone (10–12) (**2**, 2.76 g, 10.0 mmol), triethylamine (1.16 g, 11.5 mmol), and (±)-*trans*-1,2-diaminocyclohexane (0.64 g, 5.60 mmol) were refluxed for 5 h in absolute ethanol (30 mL). Workup according to the usual method (9) for other diaminodiketones (**3**) and chromatography and recrystallization from chloroform gave a yellow solid (0.153 g, 0.475 mmol, 8%): mp 299°– 301°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.3 (br s, 2H), 7.16 (dd, J = 9.5 and 11.3 Hz, 4H), 7.01 (d, J = 11.0 Hz, 2H), 6.68 (d, J = 10.3 Hz, 2H), 6.61 (dd, J = 8.8 and 9.9 Hz, 2H), 3.72 (m, 2H), 2.16 (m, 2H), 1.89 (m, 2H, 1.4–1.7 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.4, 154.8, 137.1, 136.1, 128.7, 122.7, 109.1, 55.8, 31.5, 24.1; IR (KBr) 3441, 3247, 3049, 2932, 2857, 1596, 1552, 1514, 1501, 1476, 1397, 1256, 1219, 754, 720, 706 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{22}N_2O_2$ 322.1681, found 322.1679. Anal. calcd for $C_{20}H_{22}N_2O_2$: N, 8.69. found: N, 9.01.

Side Product 11

A second product of the cyclizations to tropocoronands **6a**, **6b**, and **6d** was isolated and purified by chromatography and recrystallization. In one experiment, when (±)-**6b** was purified by recrystallization from acetone for a 21% yield, a second crop of crystals after concentration of the solution yielded side product **11** at 6% based on starting diaminodiketone **3b**: mp 203°–220°C dec; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.49 (t, J = 10.4 Hz, 2H), 6.24 (d, J = 10.6 Hz, 2H), 6.08 (t, J = 9.3 Hz, 1H), 4.77 (br s, 1H), 2.69 (m, 2H), 2.18 (m, 2H), 1.79 (m, 2H), 1.1–1.5 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.3, 121.4, 32.5, 24.8; HRMS (EI) calcd for $C_{13}H_{16}N_2$ 200.1313, found 200.1305. The structure was confirmed by x-ray crystallography.

Side Product 12

A second product of the cyclizations to tropocoronands 7 was isolated and purified. In one experiment, when **7d** was isolated by chromatography on silica gel with hexane ethyl acetate mixtures containing 3% triethylamine in 12% yield, later fractions yielded side product **12** at 11% based on starting diaminodiketone **3d**. Three recrystallizations from acetone gave a pure sample: mp 199°–201°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.2 (m, 8H), 6.9 (m, 4H), 6.60 (t, J = 9.7 Hz, 2H), 6.5 (br, 1H), 6.23 (t, J = 9.7 Hz, 1H), 4.1 (br, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz)

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δ 140.3, 131.3, 128.2, 127.8, 127.4, 122.6, 64 (br); IR (KBr) 3465, 3185, 3036, 2893, 2775, 1589, 1520, 1460, 1314, 760, 698, 599 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{18}N_2$ 298.1470, found 298.1471. Anal. calcd for $C_{21}H_{18}N_2$: N, 9.39. Found: N, 8.96.

X-Ray Crystallographic Data

Complete experimental details, as well as full tables of atomic positional and anisotropic displacement parameters, and tables of derived bond lengths and angles, can be provided upon request in Crystallographic Information File (CIF) format. In general, crystals of (±)-**6a**, *R*-**7b**, and (±)-**10** were analyzed using a Siemens SMART diffractometer at 173K, while **11** was analyzed using an Enraf Nonius CAD4 diffractometer at 298K. The structures were solved and refined using the SHELXTL V-5.1 crystallographic software package (Bruker AXS, Madison, WI). For **10**, there is disorder of the hexyl linker chain, which was located in two orientations of occupancies 0.71 and 0.29. Bond length and anisotropic displacement parameter restraints were applied to the carbon atoms in these disordered groups. Final *R*1 values for these compounds were 0.0529 (±**6a**), 0.0477 (*R*-**7b**), 0.0790 (±**10**), and 0.0575 (**11**). Details of the x-ray analysis in Crystallographic Information File (CIF) can be provided by writing to the author (PJC).

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