Synthesis of Enantiomerically Pure Thiocrown Ethers Derived from 1,1'-Binaphthalene-2,2'-dial

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Synthetic methodology is given for the preparation of two different types of thiocrown ethers from optically pure 1,1'-binaphthalene-2,2'-dial (10). The conceptually simplest approach starts from optically pure 10 itself, which is alkylated (4 equiv of K₂CO₃ in DMF at 110°C) with 2-chloroethanol followed by mesylation to provide 2,2'-bis(2-(mesyloxy)ethoxy)-1,1'-binaphthyl (14). When allowed to react with ethane-1,2-dithiol, propane-1,3-dithiol, 1,4,7-trithiaoctane, 1,4,8,11-tetrathiaundecane, 2,2-dimethylpropane-1,3-dithiol, 2-(mercaptomethyl)-1-propene-3-thiol, and 1,2-benzenedithiol in the presence of Cs₂CO₃ in DMF at 60 °C the corresponding thiocrown ethers 22-25, 28, 30, and 32 are formed in 30-54% yields. Test reactions were carried out to establish that no racemization occurs during alklylation under these conditions. Reaction of optically pure 10 with tetrahydro-pyran (THP)-protected 3-chloropropanol under similar conditions for the preparation of 14 proceeded more sluggishly but cleanly. Removal of the THP protecting groups afforded 2,2'-bis-(3-bromopropoxo)-1,1'-binaphthyl (20), which on reaction with propane-1,3-dithiol, 1,5,9-trithiaoctane, 2,2-dimethylpropane-1,3-dithiol, 2-(mercaptomethyl)-1-propene-3-thiol, and 1,2-bis(mercaptomethyl)benzene provided the respective thiocrown ethers 26, 27, 29, 31, and 33 in 24-68% yields. Another class of thiocrown ethers was prepared from optically active 10, which was converted via ortholithiation to 3,3'-bis(bromomethyl)-2,2'-dithiophenyl ether followed by DMF and H₂O workup) followed by reduction (NaBH₄) followed by bromination (PBr₃ in C₅H₅N). Reaction (Cs₂CO₃ in DMF at 60 °C) with 1,4,7-trithiaoctane, 1,4,8,11-tetrathiaundecane, and 1,5,10,14-tetrathiatetradecane afforded the corresponding thiocrown ethers 40-44 in 40-75% yields. Despite repeated attempts using a wide range of reagents, demethylation of the methoxy ether functionalities failed. Attempts to prepare the free phenol derivatives of the latter type of crown ethers by oxidative coupling of two naphthol units failed.

Introduction

Investigations of crown ethers have been biased toward oxygen (ether) and nitrogen (amine) linkages at the cost of other heteroatoms like sulfur (sulfide). In large part this state of affairs comes about from the lack, at least until fairly recently, of generally applicable and high yield syntheses for thiocrown ethers. The templated cyclizations of α-substituted alcohols and amines that work so well for the preparation of oxo- and azacrown ethers generally fail when thiocate is the nucleophile and the intermediate chain contains sulfide linkages. Attempts to use transition metals as synthetic templates for obtaining of thiocrown ethers have in general not been too successful. In our hands, however, the use of Cs₂CO₃ in dimethylformamide (DMF) to generate cesium thiolates, which carry out nucleophilic substitutions on an appropriate chloride, bromide, mesylate, or other leaving group, has provided a satisfactory solution to the synthesis of many thiocrown ethers. The method is illustrated in eq 1 for the synthesis of thio-18-crown-6 (3).

![Chemical Structure](image)

Thiocrown ethers have been studied chiefly for their capacity to ligate transition metal ions. They bind second- and third-row transition metal ions and generally stabilize the lower oxidation states of these ions. Although sulfide linkages should have a significant affinity


(4) For a review on early thiocrown ether syntheses see: Bradshaw, J. S.; Hui, Y. K. J. Heterocycl. Chem. 1974, 11, 640.


for such transition metal ions, the observed stability constants are often disappointingly small.\(^\text{9}\) In general, thiocrown ethers show smaller macrocyclic effects than their corresponding oxo- and aza-analogs.\(^\text{10,11}\) This is chiefly due to the tendency of the sulfide linkages to arrange themselves outside (exodentate) of the cavity.\(^\text{12}\) The unit \(-\text{SCH}_2\text{CH}_2\text{S}-\) tends toward an anticonformation rather than the gauche conformation favored by \(-\text{N} (\text{R})\text{CH}_2\text{CH}_2\text{N} (\text{R})-\) and \(-\text{OCH}_2\text{CH}_2\text{O}-\) segments.

Despite these conformational problems and their effect on complexation behavior, thiocrown ethers remain an interesting class of ligands. Both the capacity of sulfides to stabilize lower oxidation states of transition metal ions as well as the relative stability of sulfides compared to the more often used phosphines toward oxidation are obvious plus points. Moreover, sulfide linkages do not readily participate in protic equilibria as do amines. The possibility of “tuning” the coordination chemistry of thiocrown ethers by varying the ring size and the number of complexation sites is well within synthetic reach.\(^\text{13}\)

Application of chiral nonracemic thiocrown ethers as ligands for asymmetric syntheses catalyzed by a transition metal is also a potent area for application of these compounds, and the present work is intended as a step toward that goal.

At the time this work was initiated (1990) the only chiral nonracemic thiocrown ethers known were 4–6 (Figure 1).

Compounds 4 and 5 had been applied as ligands in the Ni(II)-catalyzed cross-coupling reaction of Grignard reagent 7 with vinyl bromide 8 (eq 2).\(^\text{14}\) Although the chemical yields of 9 in this reaction were good to excellent, the asymmetric induction was only moderate. In the presence of 0.3 mol % thiocrown ether 5 the enantiomeric excess (ee) of 9 was 46%.

Chiral nonracemic thiocrown ethers have also been applied in the Zn(II)-catalyzed conjugate addition of isopropyl magnesium bromide to cyclohexenone (not illustrated).\(^\text{15}\) In this reaction 4b and 6 were applied as ligands resulting in asymmetric inductions of 16 and 17% ee, respectively. These results are promising in terms of chemical reactivity but the challenge of obtaining high ee's is at the same time dear.

We describe here the syntheses of two new families of chiral nonracemic thiocrown ethers derived from 1,1'-binaphthalene-2,2'-diol.

Results

Axially dissymmetric 1,1'-binaphthalene-2,2'-diol (10) has been used as the chiral component for the preparation of all the compounds described here. There are two obvious retrosynthetic approaches to simple thiocrown ethers derived from 10 (Scheme 1, eq 3).

Path A is less attractive because of the need for \(\beta\)-chloro sulfides as the chain components; such compounds are powerful vesicants and in our experience dangerous. In our experience the use of leaving groups other than chloride does not provide a viable remedy to this problem. Attachment of two functionalized arms as shown in path B allows one to avoid this complication. Path B requires that bis-alkylation of 10 be achieved. We wanted to use commercially available enantiomerically pure 10, rather than to synthesize racemic thiocrown ethers followed by optical resolution. For this reason racemization during the synthetic steps must be avoided. We noted, however, the report by Cram that enantiomerically pure 10 is 69% racemized when it is stirred for 23 h in a 0.67 M KOH solution in n-butanol at 118 °C and 72% racemized in a 1:1 mixture of dioxane and 20% aqueous HCl at 100 °C, but is optically stable under neutral conditions in dioxane–water at 100 °C.\(^\text{16}\) Under sufficiently acidic or basic conditions the phenolic groups in 10 are charged, resulting in elongation of the biaryl bond, thereby diminishing the rotational barrier along this axis, making the molecule more prone to racemization. The possibility of racemization of 10 during alkylation (under basic conditions) obviously has to be checked.

Enantiomerically pure 10 (ee >99.9%, determined by HPLC) was alkylated by stirring a mixture of 1 equiv of 10 (0.067 M) and 4 equiv of ethyl bromide in the presence of 3 equiv of base at various temperatures in THF, DMF, acetonitrile, and DMF as solvents. Potassium tert-butoxide, NaH, and K\(\text{CO}_3\) were used as bases. Both the ratio of monoalkylated product 11 to dialkylated 12 and the ee of 12 were examined (eq 4).

Under several conditions conversion to 12 was incomplete. However, to our relief, under none of the applied conditions was there more than 2% racemization. Even application of basic conditions at elevated temperatures did not result in substantial racemization. Under all investigated reaction conditions the first alkylation step, to give 11, proceeds rapidly, whereas the second alkylation...
tion step, giving 12, is much slower. Thus, during the reaction there is a high concentration of 11. Apparently, the rate of racemization of mono-alkylated 11 under basic conditions at elevated temperatures is very low and the rate of mono-alkylation of 10 is much higher than its rate of racemization. After considerable experimentation it was found that the optimized reaction conditions for bis-ethylation of 10 are the use of K$_2$CO$_3$ as base in DMF at a temperature of 110°C. Under these conditions 12 was obtained in 100% yield and 99.6% ee.

On applying these reaction conditions to the reaction of 10 with 2-chloroethanol as alkylating agent 13 was obtained in 77% yield (eq 5).

A somewhat higher yield (89%) of bis-alkylated product was obtained by using THP-protected 2-chloroethanol as alkylating agent, but after deprotection with HCl the total yield of 13 was not higher than the single step shown in eq 5. Bis-mesylation of 13 was achieved by reaction with mesyl chloride and triethylamine in the presence of 4-(N,N-dimethylamino)pyridine (DMAP) as nucleophilic catalyst.

The ligating properties of thiocrown ether ligands can be tuned by varying both the ring-size and the positioning of the heteroatoms within the crown ether. To prepare more flexible thiocrown ethers dibromide 20, a homologue of 14 with a chain length of three carbon atoms instead of two was required. The synthesis of 20 turned out to be troublesome. The routes examined are summarized in eq 6 (Scheme 2).

Alkylation of 10 was carried out with 3-chloro-1-propanol in DMF at 110°C. Although 4 equiv of chloride and of base was used, considerable amounts of mono-alkylated product 16 were obtained. The yield of bis-alkylated 15 after purification could not be raised above 59%. The problem was traced to the competitive formation of 7-chloro-4-oxaheptanol (17). This complication was avoided by use of THP-protected 18; bis-alkylated product 19 was obtained as a mixture of diastereomers in 89% yield and the deprotection step delivered 15 in 95% yield. Bromination of 15 with PBr$_3$/pyridine was, however, unsatisfactory and provided 20 in only 19% yield. Reaction of THP ethers with LiBr/BF$_3$·Et$_2$O or LiBr/ClSiMe$_3$ are reported to provide directly the halides; however, with 19 only undefinable products were found. An excellent solution to this problem was found in the method of Schwarz et al., whereby THP ether 19 was brominated directly with triphenylphosphonium bromide; the dibromide 20 was isolated in 73% yield. A disadvantage of this reaction, especially when performed on larger scale, is the huge amount of triphenylphosphine oxide produced. This byproduct can be removed, however, by crystallization from toluene/n-octane. The triphenylphosphine oxide is washed thoroughly with n-hexane to recover any remaining 20, which is then purified by column chromatography.

The procedure used for ring-closure is illustrated for the preparation of 22 in eq 7. Cyclization of 14 with 1,3-

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(17) Full details of the investigated procedures can be found in: Stock, H. T. Ph.D. Thesis, University of Groningen, the Netherlands, 1994.
propanedithiol by use of the Cs₂CO₃/DMF method⁷,⁸ afforded thiocrown ether 22 in 30% yield. Ring strain in 22 is probably the reason for the only moderate yield. Change of leaving group did not help; analogous cyclization of dibromide 21, obtained from 14 by reaction with LiBr in DMSO at 60 °C, gave 22 in essentially the same yield (eq 7).

The thiocrown ethers 23–25 were synthesized in an analogous manner by cyclization of bis-mesylate 14. Isolated yields are given in parentheses. The propylene bridged thiocrown ethers 26 and 27 were prepared from 20. The appropriate dithiols were either commercially available or were prepared by routes well described in the literature (Figure 2).

Desper and Gellman have used gem-dimethyl units in the backbone of thiocrown ethers to achieve rigidity and preorganization for complexation of metal ions.⁹ Analogously, we prepared 28 and 29. Compound 29 complexed 1 equiv of ethanol on recrystallization from that solvent. The structure of the complex is not known. The ethanol could be removed by column chromatography over silica gel using toluene/n-hexane as eluent. Macrocycles 30–33, with other incorporated units, were prepared starting from either 14 or 20.

In order to check whether racemization had occurred during any of the synthetic steps used in preparation of the thiocrown ethers the ee of 24 was determined. HPLC analysis on a Daicel O'T column showed the ee be 99.5%, so no racemization had occurred. We assume this to be general for all thiocrown ether syntheses described here, especially since the conditions for alkylation have been shown not to lead to racemization.

With the intention of maintaining the phenolic groups of 10 for binding, the synthesis from 10 of 3,3'-substituted bis-naphthol systems 34 was examined. A simple retrosynthesis is given in eq 8.

Cram has described the synthesis of racemic 3,3' disubstituted 35 (X = morpholine, R = H) by a Mannich reaction, but the prolonged high temperatures required (5 days at 160 °C) would lead to racemization of optically active 10. Cram has also reported the preparation of enantiomerically pure 35 (X = OH, R = H) via an oxidative coupling of 2-hydroxynaphthalene-3-carboxylic acid followed by resolution and reduction. The overall yield (21%) is low, however, and we sought an alternative approach to enantiomerically pure 35.

In initial attempts to achieve 3,3' functionalization of 10 Vilsmeier–Haack conditions (POCl₃/DMF), the Reimer–Tiemann reaction (75% NaOH/CHCl₃), reaction with paraformaldehyde, SnCl₄, and 2,6-lutidine, and the Fries rearrangement of the bis-benzoate of 10 were tried. All these approaches in our hands failed. More


success was obtained via an ortho-lithiation route as illustrated in eq 9. To achieve lithiation O-methylation (96%) of 10 was necessary. Ortho-lithiation of 36 with n-BuLi in the presence of N,N,N',N'-tetramethylethlenediamine (TMEDA) in THF at 0 °C led to the desired product 37, but the yield was only 24%. Contemporary with our work Naruta and co-workers27 described the synthesis of the 3,3′-bis-carboxylate of 36 via ortho-lithiation of 36 in refluxing diethyl ether as solvent. When these conditions were applied and the bis-lithiated 36 was allowed to react with DMF, bis-aldehyde 37 was obtained in 76% yield. HPLC analysis established that 37 was enantiomerically pure. Reduction to 38 (95%) and bromination (91%) (eq 10) provided dibromide 39 in 63% overall yield starting from 10.

Figure 2.

The thiocrown ethers 40-44 were prepared in 40-76% yield using the cesium thiolate approach described previously (Figure 3). Unfortunately, we were completely stymied in our attempts to demethylate these thiocrown ethers. A brief description is given of the attempts that have been made following many of the known protocols for demethylating

any reaction. The same is true of \((\text{CH}_3)_2\text{SiI}\) (Table 1, entries 8 and 9). Attempted reactions using other nucleophiles (Table 1, entries 10–13) either led to destruction of the ring system or no reaction. McKervey et al. found that oxocrown ethers are readily demethylated by LiI in what appears to be an example of catalysis by a crown ether. Reinhoudt et al. report, however, that larger ring crown ethers fail to demethylate under these conditions. When these conditions were applied to thioether crown ethers no reaction took place (Table 1, entry 14). Attempts to use cations other than lithium (Table 1, entries 15–17) were to no avail. Bartsh et al. have reported the use of LiAlH\(_4\) in refluxing THF for deprotection of aryl methyl ethers incorporated in oxocrown ethers. Unfortunately, no reaction was obtained using these conditions (Table 1, entries 18 and 19).

In view of these failures we turned to routes whereby methyl ethers are not used for protection of the phenolic groups. To check whether it is necessary to protect the phenolic groups 45 was prepared by deprotection of 39 with BBr\(_3\) (eq 11). Not unsurprisingly, attempts to cyclize 45 to 46 failed. Reaction took place readily, but a complex mixture was obtained, from which no products could be characterized.

The MOM protective group was next investigated as summarized in eq 12. Preparation of the bromide 50 (other leaving groups were also examined) fails undoubtedly because of its intrinsic instability due to intramolecular participation.

![Figure 3](image-url)

**Figure 3.**

**Table 1. Attempted Demethylation of Intraannular Methoxy Groups**

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>conditions</th>
<th>product(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>48% HBr, AcOH, reflux, 1 h</td>
<td>complex mixture</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>48% HBr, AcOH, 50 °C, 6 h</td>
<td>starting material</td>
</tr>
<tr>
<td>3</td>
<td>42</td>
<td>48% HBr, AcOH, 100 °C, 1 h</td>
<td>complex mixture</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>2 equiv of BBr(_3), CH(_2)Cl(_2), 0 °C, 4 h</td>
<td>starting material</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>12 equiv of BBr(_3), CH(_2)Cl(_2), reflux, 18 h</td>
<td>starting material</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>12 equiv of BBr(_3), CCl(_4), reflux, 18 h</td>
<td>starting material</td>
</tr>
<tr>
<td>7</td>
<td>42</td>
<td>12 equiv of BBr(_3), CH(_2)Cl(_2), reflux, 18 h</td>
<td>starting material</td>
</tr>
<tr>
<td>8</td>
<td>40</td>
<td>KI, Me(_3)SiCl, CH(_3)CN, reflux, 44 h</td>
<td>starting material</td>
</tr>
<tr>
<td>9</td>
<td>42</td>
<td>KI, Me(_3)SiCl, CH(_3)CN, reflux, 20 h</td>
<td>starting material</td>
</tr>
<tr>
<td>10</td>
<td>42</td>
<td>pyridine-HCl, reflux, 3 h</td>
<td>complex mixture</td>
</tr>
<tr>
<td>11</td>
<td>40</td>
<td>EtSNa, DMF, reflux, 2 h</td>
<td>complex mixture</td>
</tr>
<tr>
<td>12</td>
<td>43</td>
<td>EtSNa, DMF, 100 °C, 2 h</td>
<td>starting material</td>
</tr>
<tr>
<td>13</td>
<td>40</td>
<td>NaN(_3), DMSO, 180 °C, 16 h</td>
<td>starting material</td>
</tr>
<tr>
<td>14</td>
<td>42</td>
<td>LiI, pyridine, reflux, 3 d</td>
<td>starting material</td>
</tr>
<tr>
<td>15</td>
<td>42</td>
<td>Ag(_2)I, pyridine, reflux, 24 h</td>
<td>starting material</td>
</tr>
<tr>
<td>16</td>
<td>40</td>
<td>AgCN, DMSO, 100 °C, 48 h</td>
<td>starting material</td>
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<tr>
<td>17</td>
<td>40</td>
<td>AgCN, DMSO, reflux, 72 h</td>
<td>complex mixture, containing 37</td>
</tr>
<tr>
<td>18</td>
<td>40</td>
<td>LiAlH(_4), THF, reflux, 20 h</td>
<td>starting material</td>
</tr>
<tr>
<td>19</td>
<td>42</td>
<td>LiAlH(_4), THF, reflux, 20 h</td>
<td>starting material</td>
</tr>
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</table>


Methylene-protected derivative 51 is known, but ortho-lithiation of this material turned out to be very difficult. The best result obtained even under forcing conditions was a mixture of monosubstituted 52 in 18% yield and the desired disubstituted 53 in 29% yield, which had to be separated by tedious column chromatography. The approach was abandoned. Apparently, the oxygen atoms in 51 are improperly oriented for stabilization of o-lithiums. Various attempts to prepare acetonides (acetone/acid, trimethyl orthoformate/acid) of 10 also failed.40–42

Several other protecting groups for 10 were examined. Protection of 10 with dichlorodimethylsilane13,44 did not result in formation of the desired 54, but of 56 (eq 14). Owing to the low yield of 56 together with the large size of its protective group45 this compound was considered to be unsuitable for further exploration in the synthesis of thiocrown ethers of type 34.

Application of phosphane 57 (eq 15) and bis-allyl ether 59 (eq 16) as protected derivatives of 10 failed since both compounds were unstable under ortho-lithiation conditions. Bis-allyl derivative 59 seemed most promising since allyl groups have been successfully applied for protection of intraannular phenolic groups in oxocrown ethers.36 Unfortunately, under the strongly basic conditions required for ortho-lithiation of 59 extensive rearrangement (not investigated further) occurs.

An alternative approach to thiocrown ethers bearing intraannular phenolic groups is by oxidative coupling of

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(45) We anticipated difficulties in the ring closing reaction when large substituents on the phenolic groups are present.
Oxidation in Organic Chemistry


**Scheme 3**

![Scheme 3](image)

**Table 2. Attempted Oxidative Phenol Coupling of 63**

<table>
<thead>
<tr>
<th>entry</th>
<th>oxidant</th>
<th>solvent</th>
<th>T (°C)</th>
<th>product(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FeCl₃&lt;sup&gt;a&lt;/sup&gt;</td>
<td>water</td>
<td>100</td>
<td>starting material</td>
</tr>
<tr>
<td>2</td>
<td>FeCl₃&lt;sup&gt;a&lt;/sup&gt;</td>
<td>MeOH/EtOH 1:2</td>
<td>reflux</td>
<td>starting material</td>
</tr>
<tr>
<td>3</td>
<td>FeCl₃&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td>50</td>
<td>starting material</td>
</tr>
<tr>
<td>4</td>
<td>K₃Fe(CN)₆&lt;sup&gt;a&lt;/sup&gt;</td>
<td>MeOH</td>
<td>reflux</td>
<td>starting material</td>
</tr>
<tr>
<td>5</td>
<td>Cu(II)(RNH₂)₄&lt;sup&gt;b&lt;/sup&gt;</td>
<td>MeOH</td>
<td>reflux</td>
<td>starting material</td>
</tr>
<tr>
<td>6</td>
<td>e⁻, 6.0 V</td>
<td>Bu₄Ni/CH₃CN</td>
<td>16</td>
<td>polymeric material</td>
</tr>
<tr>
<td>7</td>
<td>e⁻, 3.5 V</td>
<td>KOH/water</td>
<td>19</td>
<td>polymeric material</td>
</tr>
<tr>
<td>8</td>
<td>e⁻, 4.0 V</td>
<td>KOH/MeOH</td>
<td>18</td>
<td>polymeric material</td>
</tr>
<tr>
<td>9</td>
<td>e⁻, 7.5 V</td>
<td>NiCl₂/MeOH</td>
<td>23</td>
<td>polymeric material</td>
</tr>
</tbody>
</table>

<sup>a</sup> 1.1 equiv of oxidant. <sup>b</sup> 2 equiv of oxidant.

two naphthol units already bearing the thioether chain. One such attempt is outlined in eq 17 (Scheme 3).

Starting material 61 was prepared by known procedures<sup>47</sup> and was readily converted to 63 in two steps. Oxidative cyclization of 63 to (racemic) 64 failed under all conditions examined. The results are summarized in Table 2.

Reaction of 63 with oxidants, like FeCl₃<sup>48</sup>, K₃Fe(CN)₆<sup>49</sup>, and Cu(II)(RNH₂)<sub>4</sub><sup>50</sup> known to couple efficiently 2-naphthol to 1,1′-binaphthalene-2,2′-diol, failed to effect coupling to give 64 (Table 2, entries 1–5). In all these attempts only starting material was recovered. Our hopes that transition metals like Fe(II) would act both as oxidant and template were unfortunately not rewarded. Attempts to accomplish coupling via electro-chemical oxidation<sup>51</sup> also failed; all attempts resulted in formation of polymeric material (Table 2, entries 6–9). In view of the number of unsuccessful efforts to synthesize thiocrown ethers containing intraannular phenolic groups we gave up further attempts to prepare these compounds.

**Conclusion**

The syntheses of two types of new and enantiomerically pure thiocrown ethers derived from 1,1′-binaphthalene-2,2′-diol have been achieved. These enantiomerically pure thiocrown ethers are being investigated as ligands in asymmetric catalysis.<sup>17,52</sup> This work will be reported in due course.

**Experimental Section**

**General Remarks.** All reactions were performed in a nitrogen atmosphere, unless otherwise stated. Melting points are uncorrected. Optical rotations were measured at room temperature (20 °C) at the sodium D line (589 nm) and at the mercury lines (578, 546, 436, 365 nm).<sup>14</sup>H NMR spectra were recorded at 60, 200, or 300 MHz. <sup>13</sup>C NMR spectra were recorded at 50.3 or 75.4 MHz. Mass spectra were recorded by Mr. A. Kiewiet. Elemental analyses were performed in the Microanalytical Department of this laboratory by Mr. H. Draayer, J. Ebel, J. Hommes, and J. E. Vos. All solvents and reagents were purified and dried, following standard procedures.<sup>53</sup> Reagents were purchased from Janssen Chimica, Aldrich Chemical Co., and Fluka. 1,1′-Binaphthalene-2,2′-diol (10) was purchased from Syndom BV. 1,4,7-Trithiaheptane was purchased from Aldrich Chemical Co. Compounds 36,<sup>39,57</sup> 51, 61, 41, and dithiols 1,5,9-trithianonane, 54, 1,4,7,10-tetraiodiacene, 55 1,4,8,11-tetraiodiacyciane, 56 1,5,10,14-tetrathialtetradecane, 57 2-(mercaptomethyl)-1-propene-3-thiol, 58 1,2-benzendithiol, 59 1,2-bis(thioamide)benzene, 58 and 2,2-dimethyl-1,3-propanedithiol<sup>46,59</sup> were prepared according to literature procedures. Compound 57<sup>56</sup> was kindly donated by Dr. R. Hulst. In some substitution reactions 4-(N,N-
dimethylamino)pyridine (DMAP) was added as hypernucleophilic catalyst.

Optimized Reaction Conditions.22 A solution of (R)-10 (286 mg, 1.00 mmol), K₂CO₃ (0.41 g, 3.00 mmol), and ethyl bromide (0.30 mL, 4.0 mmol) in DMF (15 ml) was stirred at 110 °C for 24 h. The reaction mixture was cooled to rt, filtered, and concentrated under reduced pressure to give a white solid (330 mg). The crude product was filtered over a short silica gel column (CH₂Cl₂) to give 12 (100%): mp 135.1–136.2 °C; ¹H NMR (CDCl₃, 200 MHz) δ 1.10 (t, J = 7.0 Hz, 6 H), 4.09 (q, J = 7.0 Hz, 4 H), 7.17–7.49 (m, 8 H), 7.90 (d, J = 7.9 Hz, 2 H); ¹C NMR (CDCl₃, 50.3 MHz) δ 15.0 (q), 65.2 (t), 115.9 (d), 120.7 (s), 123.4 (d), 125.5 (d), 126.1 (d), 127.8 (d), 129.1 (d), 132.4 (s), 154.3 (s); ee 99.6%, as determined by HPLC.62

(R)-(−)−2,2'-Bis(2-hydroxyethoxy)-1,1'-binaphthyl (13). The literature procedure for preparation of the (S)-enantiomer62 was improved and applied for preparation of both (R)- and (S)-13: (R)-(−)−10 (8.62 g, 30.1 mmol), 2-chloroethanol (8.0 ml, 119 mmol), and K₂CO₃ (16.6 g, 120 mmol) were dissolved in DMF (250 mL) and stirred at 110 °C for 17 h. The reaction mixture was filtered and concentrated under reduced pressure. The residue was taken up in CH₂Cl₂ (150 mL) and washed with water (2 × 100 mL) and 2 N NaOH (100 mL). The organic layer was dried (MgSO₄) and concentrated under reduced pressure. The residue was obtained: mp 142–143 °C; [α]₂₅₂ = +34.9 (c = 2.90, THF); [α]₂₆₅ = −22.0 (c = 1.00, THF); [α]₂₇₅ = −41.4 (c = 1.00, THF); [α]₂₈₂ = −55.2. The crude product was used for the preparation of the (R)-enantiomer.

To a solution of (R)-13 (1.07 g, 5.00 mmol), triethylamine (1.5 ml, 11 mmol), and DMAP (20 mg, 0.16 mmol) in CH₂Cl₂ (75 mL) was dropwise added methanesulfonyl chloride (0.85 mL, 11.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 17 h and subsequently washed with water (2 × 100 mL) and H₂O/CH₂Cl₂ (1:1, 150 mL). The organic layer was dried (MgSO₄) and concentrated under reduced pressure to give a viscous, slightly yellow oil (2.80 g). The crude product was crystallized from toluene/n-hexane to give 14 (95% as white crystals: mp 143–144 °C; [α]₂₅₂ = −30.5 (c = 0.650, THF); [α]₂₆₅ = −32.8; [α]₂₇₅ = −24.3; [α]₂₈₂ = +237; ¹H NMR (CDCl₃, 300 MHz) δ 1.83 (s, 6 H), 3.93–4.11 (m, 8 H), 6.09–7.25 (m, 8 H), 7.66–7.71 (m, 2 H), 7.77–7.82 (m, 2 H); ¹C NMR (CDCl₃, 75.4 MHz) δ 35.9 (q), 67.0 (t), 68.7 (t), 114.8 (d), 119.7 (s), 124.1 (d), 125.0 (d), 126.7 (d), 127.8 (d), 129.3 (d), 129.6 (d), 133.7 (s), 153.2 (s); HRMS m/e (M+ Calcd 530.107, obsd 530.106). Also, the Calculded (found) for C₂₀H₁₇O₃S: C, 58.58 (58.67); H, 4.94 (5.03); S, 12.09 (11.98).

(S)-(−)-2,2'-Bis(3-hydroxypropoxy)-1,1'-binaphthyl (15) (R)-(−)-2,2'-Bis(3-hydroxypropoxy)-1,1'-binaphthyl (15). (S)-(−)-10 (5.72 g, 20.0 mmol), 2-(3-chloro-1-propoxy)pyran63 (7.50 g, 42.0 mmol), and K₂CO₃ (5.80 g, 42 mmol) were dissolved in DMF (150 mL) and stirred at 110 °C for 4 h. The reaction mixture was concentrated under reduced pressure and the residue was taken up in CH₂Cl₂ (200 mL) and washed with water (2 × 150 mL), 2 N NaOH (150 mL), and brine (150 mL). The organic layer was dried (MgSO₄) and concentrated under reduced pressure to give a brown oil (16.1 g). The crude product was purified by column chromatography (silica gel, EtOAc) to give 15 (95%) as a white foam: mp 57.8–58.6 °C; [α]₂₅₂ = −40.8 (c = 0.526, THF), [α]₂₆₅ = −49.7; [α]₂₇₅ = −60.4; [α]₂₈₂ = −170.7; [α]₂₉₂ = −709.2. The NMR data were in accord with the data for the product obtained from 10 (wide supra).

2,2'-Bis(3-pyran-2-oxo)propoxy)-1,1'-binaphthyl (19). (S)-(−)-10 (5.72 g, 20.0 mmol), 2-(3-chloro-1-propoxy)pyran63 (7.50 g, 42.0 mmol), and K₂CO₃ (5.80 g, 42 mmol) were dissolved in DMF (150 mL) and stirred at 110 °C for 4 h. The reaction mixture was concentrated under reduced pressure and the residue was taken up in CH₂Cl₂ (200 mL) and washed with water (2 × 150 mL), 2 N NaOH (150 mL), and brine (150 mL). The organic layer was dried (MgSO₄) and concentrated under reduced pressure to give a brown oil (16.1 g). The crude product was purified by column chromatography (silica gel, EtOAc) to give 19 (89%) as a yellow oil: ¹H NMR (CDCl₃, 300 MHz) δ 1.38–1.78 (m, 16 H), 2.87–3.06 (m, 2 H), 3.33–3.45 (m, 4 H), 3.65–3.75 (m, 2 H), 4.03–4.16 (m, 6 H), 4.28–4.31 (m, 1 H), 7.15–7.47 (m, 8 H), 7.88 (d, J = 8.1 Hz, 2 H), 7.96 (d, J = 9.2 Hz, 2 H); ¹C NMR (CDCl₃, 75.4 MHz) δ 19.4 (t), 19.6 (t), 25.3 (t), 29.5 (t), 29.6 (t), 30.4 (t), 61.9 (t), 62.0 (t), 62.1 (t), 63.6 (t), 63.7 (t), 63.8 (t), 66.2 (t), 66.3 (t), 66.4 (t), 98.6 (d), 98.7 (d), 115.4 (d), 120.2 (s), 120.3 (s), 123.2 (d), 123.7 (d), 125.2 (d), 125.9 (d), 126.7 (d), 126.8 (d), 129.0 (s), 133.9 (s), 154.0 (s), 154.1 (s); HRMS m/e (M+ Calcd 570.298, obsd 570.298.

2,2'-Bis(3-methoxypropoxy)-1,1'-binaphthyl (20). (S)-(−)-10 (21.2 g, 81 mmol) was dissolved in CH₂Cl₂ (150 mL) and cooled to 0 °C. Bromine (4.14 mL, 81 mmol) was slowly added, initially forming a white precipitate that turns orange upon further adding. After all the bromine had been added the reaction mixture was stirred at 0 °C for


(62) A water-cooled 250 × 4.6 mm (5-µl) triphenylmethyl methacrylate column (DACELP ON) was used, with n-hexane/2-propanol 100:1 as eluent (flow 0.5 mL/min); retention times: (S)-22, 34.76 min; (R)-22, 42.95 min. (a) Okamoto, Y.; Honda, S.; Okamoto, I.; Yuki, K.; Murata, S.; Noyori, R.; Takaya, H. J. Am. Chem. Soc. 1981, 103, 6971. (b) Okamoto, Y.; Hatada, K.; Li, Q. J. Chromatogr. 1986, 369, 487.
45 min. A solution of 19 (6.6 g, 15.1 mmol) in CHCl₃ (30 mL) was added in 15 min at 0 °C, and the reaction mixture was stirred at room temperature for 17 h. CH₂Cl₂ (100 mL) was added, and the reaction mixture was washed twice with water. The organic layer was dried (MgSO₄) and concentrated under reduced pressure to give a light brown solid (22.3 g). The solid was recrystallized from toluene/acetone to give white crystals (7.28 g, triphenylamine oxime). The mother liquor was concentrated under reduced pressure and purified by column chromatography (silica gel, CH₂Cl₂/n-hexane 1:1) to give a yellowish brown oil (7.00 g). This oil was bailed in methanol and stirred at room temperature for 30 min, and CH₂Cl₂ (250 mL) was added dropwise to stir the mixture. The reaction mixture was washed twice with water (2 x 100 mL) and concentrated under reduced pressure to give 20 (73%) as a yellow oil. Analytically pure material was obtained by additional column chromatography (silica gel, CH₂Cl₂/n-hexane 1:20) to give 20 (2.27 g, 50.3, [α]D₂0 = 193.8, [β]D₂0 = 1.054, THF) as colorless crystals.

As a solution of 20 (2.27 g, 50.3 mmol) in THF (150 mL) was stirred at room temperature for 17 h. CH₂Cl₂ (100 mL) was added, and the reaction mixture was washed twice with water (2 x 100 mL) and concentrated under reduced pressure to give 20 (73%) as a yellow oil. Analytically pure material was obtained by additional column chromatography (silica gel, CH₂Cl₂/n-hexane 1:1) to give a yellow oil (2.25 g, 50.3%). The combined organic layers were washed with brine (75 mL), dried (MgSO₄), and concentrated under reduced pressure to give a yellow oil (16.7 g). The crude product was purified by column chromatography (silica gel, CH₂Cl₂/n-hexane 1:1) (19%) as a colorless oil: [α]D₂0 = +46.0 (c = 0.544, THF), [α]D₂9 = +49.0, [α]D₂5 = −130.3 (c = 0.284, THF). 1H NMR (CDCl₃, 300 MHz) δ 4.34 (m, 4 H), 7.16–7.50 (m, 8 H), 7.90 (d, J = 7.8 Hz, 2 H). 

Spectral data for 20: 1H NMR (CDCl₃, 300 MHz) δ 4.34 (m, 4 H), 7.16–7.50 (m, 8 H), 7.90 (d, J = 7.8 Hz, 2 H). 

Spectral data for 20: 1H NMR (CDCl₃, 300 MHz) δ 4.34 (m, 4 H), 7.16–7.50 (m, 8 H), 7.90 (d, J = 7.8 Hz, 2 H).
(S)-(−)-2,3,4,5-Di(1,2-naphtho)-1,6-dioxo-10,15-dithia-12,12,12-dimethylcycloheptadeca-2,4-diene (28). According to the procedure described for the synthesis of 22, from (R)-14, 1,2,12,12-dimethylcycloheptadeca-2,4-diene (29). According to the procedure described for the synthesis of 22, from (S)-20 and 1,2-bis(mercaptomethyl)benzene: yield 61%; mp 75.9–77.8°C; [α]D 28.5 (c = 0.306, THF), [α]D 29.2 = −210.8, [α]D 36.2 = −1158; 1H NMR (CDCl3, 200 MHz) δ 1.85–2.02 (m, 4 H), 2.44–2.67 (m, 4 H), 3.98 (AB system, J = 12.0 Hz, 2 H); 13C NMR (CDCl3, 50.3 MHz) δ 23.9 (t), 23.6 (t), 31.5 (t), 67.8 (t), 115.2 (d), 120.4 (d), 120.7 (d), 120.9 (d), 121.1 (d), 121.4 (d), 123.6 (d), 125.9 (d), 129.4 (d), 130.7 (d), 131.0 (s), 131.4 (s), 134.1 (s), 153.6 (s); HRMS m/e (M+) calcd 536.184, obsd 536.184.

(R)-(−)-2,2-Dimethoxy-1,1-biphenyl-3,3-dicarbalddehyde (37). A solution of (S)-36 (12.56 g, 40.0 mmol) and TMEDA (31.4 mL, 209 mmol) in Et2O (600 mL) was cooled to 0°C. A 2.0 M solution of n-BuLi in hexanes (87 mL, 174 mmol) was added dropwise over a period of 30 min. The mixture was stirred at 0°C for 1 h and then was slowly warmed to reflux. After being refluxed for 16 h the resulting pale brown suspension was cooled to 0°C and DMF (25 mL, 320 mmol) was added dropwise. The mixture was stirred at 0°C for 5 h, and then 4 N HCl (120 mL, 480 mmol) was added slowly under vigorous stirring. The resulting two-phase system was stirred for 30 min. The organic layer was washed, washed with 0.5 N HCl (200 mL), a saturated NaHCO3 solution (200 mL), and brine (200 mL), dried (Na2SO4), and concentrated under reduced pressure to give a yellow solid (14.36 g). The crude product was filtered over a short column (silica gel, EtOAc) and then re-distilled from 96% EtOH to yield 76% as pale yellow crystals: mp 156.5–158.3°C (lit.65) 156.3–157.7°C; [α]D 29.3 = −37.9, [α]D 36.2 = −83.2; 1H NMR (CDCl3, 200 MHz) δ 3.52 (s, 6 H), 7.17–7.55 (m, 6 H), 8.08 (d, J = 7.3 Hz, 2 H), 8.64 (s, 2 H), 10.58 (s, 2 H); 13C NMR (CDCl3, 50.3 MHz) δ 63.1 (q), 124.9 (d), 125.5 (d), 126.1 (d), 128.5 (s), 129.6 (d), 129.9 (s), 130.5 (s), 132.3 (d), 137.0 (s), 156.5 (s), 190.3 (s).

(S)-(−)-37. By the same procedure (S)-37 (75%) was obtained: mp 156.3–157.7°C; [α]D 29.3 = −37.9, [α]D 36.2 = +38.1, [α]D 49.1 = +79.9.

Determination of the Extent of Racemization in the Synthesis of 37. (R)-37 (5 mg) and (S)-37 (9 mg) were dissolved in n-hexane/2-propanol 9:1 (2 mL). A sample of this mixture was analyzed by HPLC on an OT-column (eluuent n-hexanex/2-propanol 9:1, flow 0.5 mL/min). The retention times of the enantiomers were (R) 34.39 min, (S) 36.83 min. From analogus HPLC-analysis of (S)-37, purified by column chromatography, but not crystallized, it was observed that this material was enantiomerically pure.

(R)-(−)-3,3-Bis(hydroxymethyl)-2,2-dimethoxy-1,1-biphenyl (38). (R)-38 was prepared by a modified procedure as described for the synthesis of (S)-38. To a solution of (R)-37 (61.5 g, 16.6 mmol) in a mixture of absolute ethanol (130 mL) and THF (20 mL) was added NaBH4 (1.25 g, 33.0 mmol) at room temperature. After being stirred for 4 h the reaction mixture was concentrated under reduced pressure. The residue was taken up in CH2Cl2 (200 mL) and 3 N HCl (200 mL) and was vigorously stirred until all solid material was dissolved. The organic layer was separated, and the aqueous layer was extracted with CH2Cl2 (2×150 mL). The combined organic layers were dried (MgSO4) and concentrated under reduced pressure to give 38 (95%) as a white foam: mp 182.6–184.2°C; [α]D 29.3 = +68.6 (c = 0.620, THF), [α]D 36.2 = +53.8, [α]D 49.1 = −63.1, [α]D 58.2 = −182.2; 1H NMR (CDCl3, 200 MHz) δ 2.79 (s, br, 2 H), 3.03 (s, 6 H), 4.97 (AB system, J = 28.2 Hz, 2 H), 13.9–14.4 (m, 6 H), 7.89 (d, J = 88.3 Hz, 2 H), 8.03 (s, 2 H); 1H NMR (CDCl3, 50.3 MHz) δ 60.8 (q), 62.0 (t), 124.0 (s), 125.0 (d), 125.6 (d), 126.5 (d), 128.1 (d), 129.3 (d), 130.8 (s), 134.0 (s), 154.7 (s).

(S)-(−)-38. By the same procedure (S)-38 (91%) was obtained: mp 181.8–183.9°C (lit.27 mp 183–185°C; [α]D 3103

+47.4 (c = 0.814, THF) (lit.(22) \( \delta_{13}C = +53.4, \delta_{13}B = +55.0, \delta_{13}S = +65.6, \delta_{13}N = -127.4, \delta_{13}O = -195.3. \)

1,4,8-Triphthalyl-2,3-Bis(bromomethyl)-1,1-dinaphthyl (45). To a cooled (0 °C) solution of 39 (0.75 g, 1.50 mmol) in CHCl₃ (50 mL) was added dropwise BBr₃ (1.0 M in CH₂Cl₂, 4.0 mL, 4.0 mmol). After the mixture was stirred at room temperature for 4 h a saturated NaHCO₃ solution (10 mL) was added. The mixture was poured into water (100 mL) and was extracted with CHCl₃ (3 x 75 mL). The combined organic layers were washed with 2 N HCl (100 mL), dried (MgSO₄), and concentrated under reduced pressure to give 45 (95%) as a pale yellow foam: mp 186–188.6 °C; \( \delta_{13}C = -165.9 (c = 0.340, \text{THF}), \delta_{13}B = -175.3, \delta_{13}S = -207.6, \delta_{13}N = -474.4; \)

According to the procedure described for the synthesis of 22, from (S)-39 and 1,4,8-trithiacyclohexadeca-3,5-diene (41). According to the procedure described for the synthesis of 22, from (R)-39 and 1,4,8-trithiacyclohexadeca-3,5-diene (41). According to the procedure described for the synthesis of 22, from (R)-39 and 1,4,7,10-tetradeca-3,5-diene yield 40% as a white solid; mp 182.2–183.5 °C; \( \delta_{13}C = -590.6 (c = 0.384, \text{THF}), \delta_{13}B = -642.7, \delta_{13}S = -750.5, \delta_{13}N = -1618.7; \)


According to the procedure described for the synthesis of 22, from (R)-39 and 1,4,7,10-tetradeca-3,5-diene yield 44% as a white solid; mp 186–188.6 °C; \( \delta_{13}C = -165.9 (c = 0.340, \text{THF}), \delta_{13}B = -175.3, \delta_{13}S = -207.6, \delta_{13}N = -474.4; \)

According to the procedure described for the synthesis of 22, from (S)-39 and 1,4,8-trithiacyclohexadeca-3,5-diene (41). According to the procedure described for the synthesis of 22, from (R)-39 and 1,4,7,10-tetradeca-3,5-diene yield 40% as a white solid; mp 182.2–183.5 °C; \( \delta_{13}C = -590.6 (c = 0.384, \text{THF}), \delta_{13}B = -642.7, \delta_{13}S = -750.5, \delta_{13}N = -1618.7; \)


According to the procedure described for the synthesis of 22, from (R)-39 and 1,4,7,10-tetradeca-3,5-diene yield 40% as a white solid; mp 182.2–183.5 °C; \( \delta_{13}C = -590.6 (c = 0.384, \text{THF}), \delta_{13}B = -642.7, \delta_{13}S = -750.5, \delta_{13}N = -1618.7; \)
g, 6.3 mmol). After being stirred at room temperature for 17 h the mixture was concentrated under reduced pressure to give yellow crystals (1.82 g). The crude product was purified by column chromatography (silica gel, CH₂Cl₂) to give S9 (99%) as white crystals: mp 110.1–111.1 °C; [α]_D + 29.3 (c = 0.382, THF).

As a pale yellow foam (lit. 23b racemate is a colorless oil): mp 68.6–69.2 °C; [α]_D + 66.4 (c = 0.256, THF); [α]_B + 69.9, [α]_B + 80.9, [α]_B + 151.6; 1H NMR (CDCl₃, 200 MHz) δ 3.20 (6, H), 3.54 (s, 2, H), 4.47 (AB-system, J = 8.3 Hz), J = 6.1 Hz, 4 H), 4.93 (AB-system, br, J = 30.5 Hz, H), 7.18 (4, 4 H), 7.26 (4, 4 H), 7.90 (2, 2 H), 8.11 (J = 1.9 Hz, 2 H), 8.36 (s, 1, H), 8.60 (s, 1, H); 13C NMR (CDCl₃, 125 MHz) δ 30.6 (t), 30.9 (t), 31.8 (t), 32.6 (t), 111.7 (d), 124.0 (d), 125.3 (d), 126.3 (d), 129.2 (d), 132.8 (d), 134.0 (d), 135.2 (s), 138.6 (s), 139.4 (s), 139.1 (d), 143.1 (s), 143.5 (s), 145.2 (s); MS m/e (M+) ca. 534.173, obsd 534.173.

2,3-[1,2-naphtho][4,5-[1,2-3-formyl-naphtho]]-1,6-dioxacyclohepta-2,4-diene (52) and 2,3,4,5-Bis[1,2-3-formyl-naphtho]-1,6-dioxacyclohepta-2,4-diene (53). To a cooled (0 °C) solution of S1 (2.00 g, 6.71 mmol) and TMEDA (5.2 mL, 35 mmol) in Et₂O (150 mL) was added dropwise s-BuLi (0.8 M in cyclohexane/ponentane, 34 mL, 27 mmol) over a period of 15 min. The resulting dark green solution was allowed to warm to room temperature. After being stirred at ambient temperature for 17 h the mixture was cooled to 0 °C and DMF (4.2 mL, 53 mmol) was added. After the mixture was stirred at 0 °C for 2 h, 4 N HCl (20 mL, 80 mmol) was added dropwise. The organic layer was washed with water (150 mL), a saturated NaHCO₃ solution (150 mL), and brine (150 mL), dried (MgSO₄), and concentrated under reduced pressure to give a pale yellow solid (1.82 g). The crude product was purified by column chromatography over a 30 cm silica gel column (100 g silica gel, CH₂Cl₂) to give S18 (18%) as a first fraction (R_f = 0.52) and S3 (29%) as a second fraction (R_f = 0.22). Analytically pure S3 was obtained by recrystallization from CHCl₃/n-hexane.

S2: mp 182.1–184.0 °C; 1H NMR (CDCl₃, 200 MHz) δ 5.81 (J = 7.2 Hz, J = 3.4 Hz, 2 H), 7.40–7.58 (m, 7 H), 7.95–8.10 (m, 3 H), 8.06 (s, 1 H), 10.62 (s, 1 H); 13C NMR (CDCl₃, 125 MHz) δ 103.4 (t), 121.1 (d), 124.5 (d), 125.2 (d), 125.6 (d), 125.9 (d), 126.1 (d), 126.6 (d), 126.8 (s), 127.5 (s), 128.7 (d), 129.1 (d), 130.2 (s), 130.8 (d), 131.0 (d), 131.1 (d), 131.3 (s), 131.4 (s), 140.3 (s), 150.8 (s), 151.2 (s), 189.9 (d); HRMS m/e (M+) calc 326.094, obsd 326.094.

S3: mp 238.9–240.7 °C; 1H NMR (CDCl₃, 200 MHz) δ 6.04 (s, 2 H), 7.30 (d, J = 8.1 Hz, 2 H), 7.47–7.64 (m, 4 H), 8.32 (d, J = 8.1 Hz, 2 H), 8.71 (s, 1 H), 10.51 (s, 2 H); 13C NMR (CDCl₃, 125 MHz) δ 104.3 (t), 30.5 (d), 121.3 (d), 127.3 (d), 129.3 (d), 130.3 (s), 130.8 (d), 131.5 (d), 133.9 (s), 150.9 (s), 189.8 (d); HRMS m/e (M+) calc 354.089, obsd 354.089. Anal. Calcd (found) for C₂₃H₂₂O₃Cl₂HCl: C, 60.73 (60.70); H, 3.19 (3.24); Cl, 22.41 (21.03).

7,7,9-Tetramethyl-2,3,4,5-di(2,1-naphtho)-1,6,8-trioxo-7,9-disilacyclohexa-2,4-diene (56). To a solution of S10 (2.38 g, 8.32 mmol) in CH₂Cl₂ (50 mL) were added Et₂N (3.5 mL, 25 mmol) and dichloromethylsilane (0.93 mmol, 7.7 mL). After being refluxed for 18 h the reaction mixture was washed with water (2 × 50 mL), a saturated NH₄Cl solution (50 mL), and 2 N NaOH (2 × 50 mL), dried (MgSO₄), and concentrated under reduced pressure to give a brown solid (0.7 g). The crude product was purified by column chromatography (silica gel, CH₂Cl₂) to give S56 (17%) as a pale yellow powder: mp 172.2–174.6 °C; 1H NMR (CDCl₃, 200 MHz) δ −0.55 (s, 6 H), 0.27 (s, 6 H), 7.19–7.43 (m, 8 H), 7.89–7.97 (m, 4 H); 13C NMR (CDCl₃, 200 MHz) δ −1.33 (t), 127.9 (d), 129.0 (d), 129.4 (d), 125.2 (d), 126.6 (d), 127.8 (d), 129.6 (d), 130.0 (d) (1.82 g). 1H NMR (CDCl₃, 200 MHz) δ 4.60–4.62 (m, 4 H), 5.06–5.16 (m, 4 H), 5.75–5.94 (m, 2 H), 7.27–7.45 (m, 8 H), 7.49 (d, J = 9.0 Hz, 2 H), 7.96 (d, J = 8.0 Hz, 2 H), 8.02 (d, J = 9.0 Hz, 2 H); 13C NMR (CDCl₃, 50 MHz) δ 70.0 (t), 115.7 (d), 116.5 (t), 120.4 (s), 123.7 (d), 125.6 (d), 126.3 (d), 128.0 (d), 129.2 (d), 129.4 (s), 133.8 (d), 134.2 (s), 154.1 (s); HRMS m/e (M+) calc 366.162, obsd 366.162.

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Supporting Information Available: 1H and 13C NMR spectra of thio crown ethers 22–33 and 40–44; descriptions of attempts to demethylate 40, 42, and 43; attempts to brominate 49 and to cyclize 45; attempted synthesis of 58; attempts to prepare 64 by oxidative coupling (75 pages). This manuscript contains material from libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS for the current masthead page for ordering information.

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