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Modular chiral polyether podands and their lanthanide complexes

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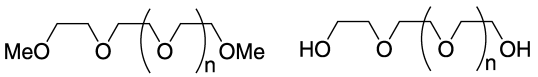
Abstract—A novel series of modular chiral polyether podands derived from enantiomerically pure hydrobenzoin and binaphthol has been prepared using a NaH/15-crown-5 mediated Williamson ether synthesis. These new homochiral ligands form catalytically active complexes with lanthanide triflates, two of which have been characterised by X-ray diffraction.

1. Introduction

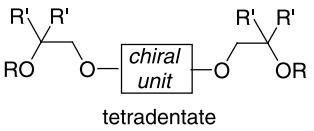
Polyether ionophore antibiotics are a class of complex naturally occurring chiral compounds containing several oxygen atoms which act as ligands for the complexation of inorganic cations.[1,2] Coordination of the metal cations by the ionophores facilitates transport across membrane barriers resulting in a range of important biological activity. The similarity between alkali metal cations, which are the guests for ionophore antibiotics, and may be thought of as featureless charged spheres and lanthanide 3+ cations, which lack any directional preference for ligand binding, led us to consider simpler chiral polyether podands as potential ligands for lanthanide catalysis. They should have sufficient flexibility[3] to accept a range of lanthanide cations and yet be conformationally biased by the chiral backbone.[4] Functionalised oligoethylene glycols are also important intermediates for the preparation of crown ethers and cryptands[5] and show enantiomeric recognition of secondary amines.[6,7]

Earlier work from our laboratories has shown that the use of polyether or polyethylene glycol ligands can enhance the catalytic properties of lanthanide triflates by increasing their solubility in organic solvents and by making them easier to obtain in anhydrous form. Polyether ligands **1** worked well for the Diels–Alder reaction, when activity was enhanced compared with that of uncomplexed $Ln(OTf)_3$, whereas the polyethylene glycol ligands **2** worked well for the carbonyl allylation reaction.[8]

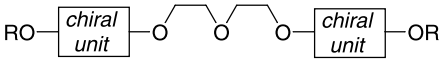


1 **2**

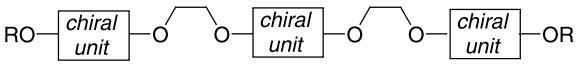
Having demonstrated the utility of the achiral ligands **1** and **2** in catalysis we then set out to prepare C_2 symmetric tetra- and penta- and hexadentate versions of these ligands and investigate their utility in catalysis. It was essential to prepare ligands with both ether and alcohol end groups so that they would be compatible with both Diels–Alder and carbonyl allylation reactions.



tetradentate

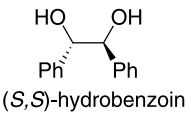


pentadentate

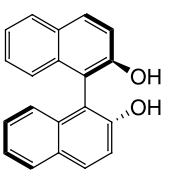


hexadentate

The chiral units we chose for our ligands were hydrobenzoin **3** and binaphthol **4**, both of which are readily available in enantiomerically pure form.[9,10]



(*S,S*)-hydrobenzoin
3



R-binaphthol
4

Keywords: polyether podand; lanthanide complex; Williamson ether synthesis; c_2-symmetric; chiral.
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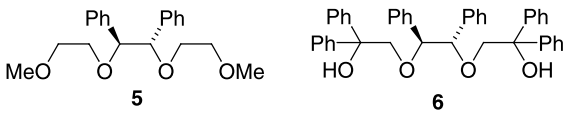
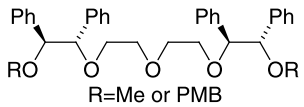
2. Results and discussion

2.1. Hydrobenzoin derived ligands

We prepared a series of tetra-, penta- and hexadentate ligands **5**–**8** based on the hydrobenzoin chiral unit as shown below. In this series of ligands we have a variety of end-groups (ether or alcohol) and varying degrees of steric bulk along the ligand backbone. Ligand **9** is a very bulky 1-naphthyl substituted analogue of **8**.



5 **6**



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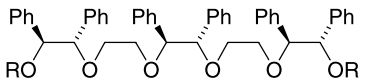

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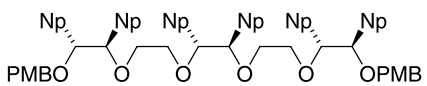


9

The tetradentate polyether ligand **5** was synthesised straightforwardly in high yield as shown in Scheme 1, utilising our 15-crown-5 mediated etherification procedure.[11]

The tetradentate diol ligand **6** was prepared according to Scheme 2.

Our retrosynthetic strategy for the synthesis of the pentadentate polyether ligand **7** is shown in Scheme 3.

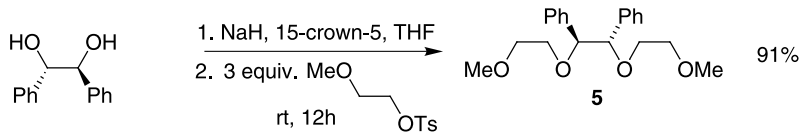
This scheme required efficient routes to singly protected 1,2-diols which can itself be problematic since many methods give statistical mixtures of mono-, di- and unalkylated material.[12]

2.2. Alkyl ether strategy

This strategy required the selective monoalkylation of diol **3** followed by coupling to ditosylate **12**. We aimed to synthesise both Me and PMB ethers. In addition to being a useful ligand in its own right, it was hoped that the PMB ether could be converted into a chiral tetraethylene glycol (R=H), by selective removal of the PMB-groups. Mono-alkylations of **3** were accomplished using a modified procedure reported by Ohno et al. as shown in Scheme 4.[13]

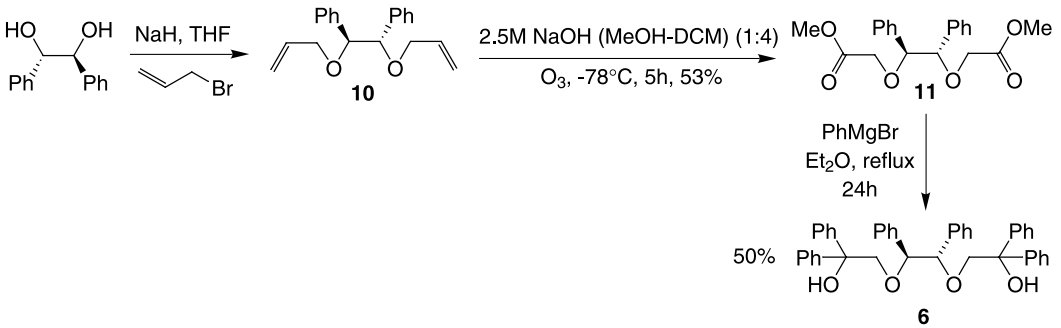
Hydrobenzoin **3** was converted to tin acetal **14** by reaction with 1 equiv. of dibutyltin oxide in refluxing toluene: the water was removed by azeotropic distillation into a Dean–Stark head. Concentration under reduced pressure yielded acetal **14** which was used in the subsequent step without purification.

The tin acetal **14** was opened with CsF in DMF solvent, and the resulting caesium alkoxide was trapped with either MeI, or PMB chloride. As chloride is an inferior leaving group to



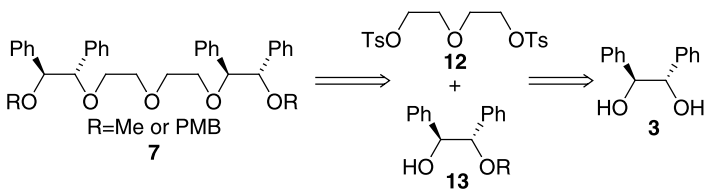
5

Scheme 1.

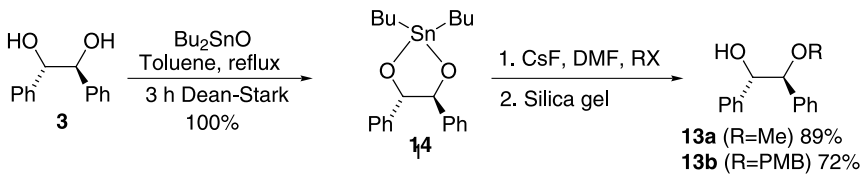


10 **11** **6**

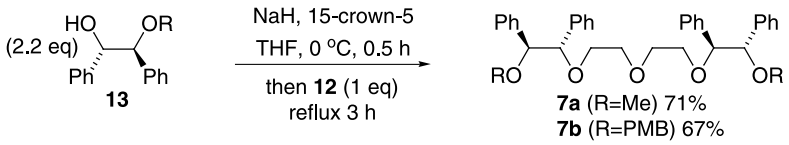
Scheme 2.



Scheme 3.



Scheme 4.



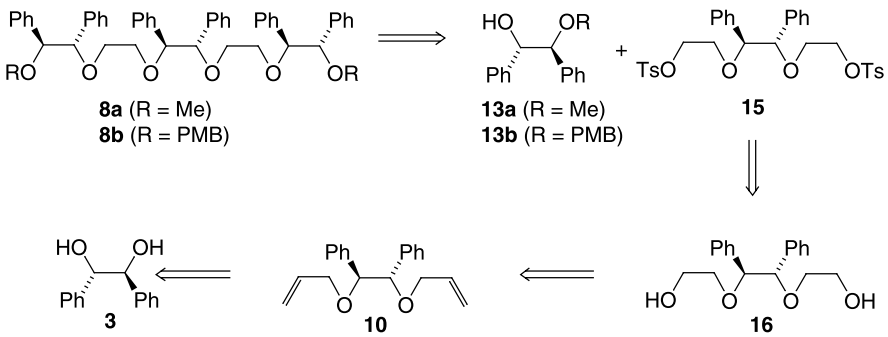
Scheme 5.

iodide, conversion to alcohol **13** had to be carried out in the presence of KI catalyst: thus the PMB chloride probably undergoes an in situ Finkelstein reaction, generating the much more reactive alkyl iodide. The method of work-up and purification turned out to be crucial. Quenching with dilute HCl (aq.) resulted in product which was very difficult to separate from the residual tin compounds. Non-aqueous work-up on silica gel proved much more satisfactory, giving high yields of tin-free material after chromatography.

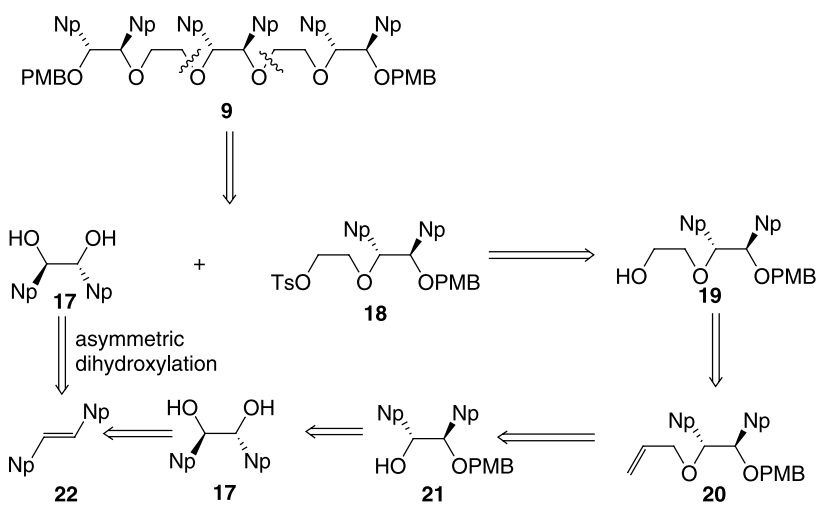
Early attempts at the etherification were unsuccessful. When alcohol **13** was deprotonated by sodium hydride followed by treatment with ditosylate **12** in refluxing THF, only starting materials could be isolated. Repetition of this reaction in DMF and DMSO solvent in the presence of a KI catalyst produced unacceptably low yields of polyether **7**. However use of our 15-crown-5 etherification procedure[11] as shown in Scheme 5 gave good results.

Our retrosynthetic analysis for the hexadentate hydrobenzoin derived ligand **8** is shown in Scheme 6. We proposed that ligands **8a** and **8b** could be prepared by treatment of ditosylate **15** with the appropriate alcohol **13a** or **13b**.

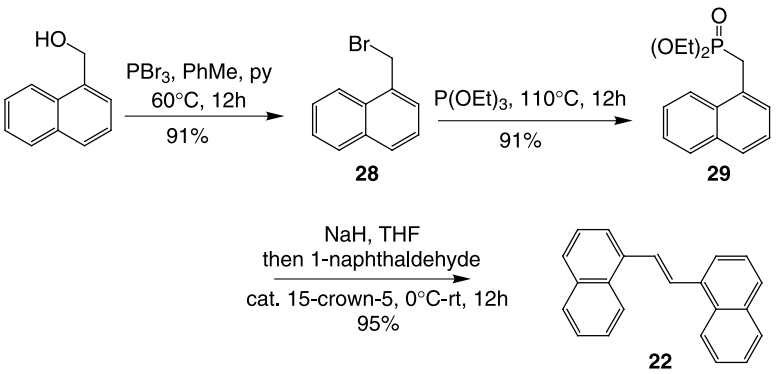
We prepared diol **16** in 60% yield by ozonolysis of diene **10** followed by $NaBH_4$ work-up.[14,15] This procedure had previously not been applied to dienes. Ligands **8a** and **8b** were prepared in modest yield using our NaH/15-crown-5 methodology.



Scheme 6.



Scheme 7.



Scheme 8.

Our strategy for the synthesis of the naphthyl substituted hexadentate ligand **9** is outlined in Scheme 7.

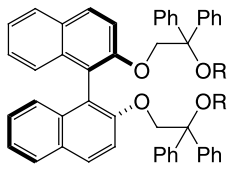
Geometrically pure olefin **22** is not commercially available, but several procedures involving a simple Wittig reaction have been reported. However, the highest yield recorded for the Wittig procedure was only 31%.[16] Our revised route to this olefin is shown in Scheme 8, with the key step being a Wadsworth–Emmons reaction. Commercially available 1-naphthylene methanol was treated with PBr_3, to give bromide **28** in 91% yield. Subsequent Arbuzov reaction with triethyl phosphite yielded the phosphonate ester **29**.[17] Conversion of phosphonate **29** to the alkene was achieved by deprotonation with NaH, followed by reaction with 1-naphthaldehyde in the presence of a catalytic quantity of 15-crown-5.[18] Work-up and purification of this reaction was very simple, and yields of up to 95% of olefin **22** were isolated, by simply washing the crude material with chilled methanol. Comparison of the melting point and ^{1}H NMR spectrum with the literature[16] indicated that the *E*-alkene had been formed exclusively.

This procedure compares favourably with other routes to this compound: it is high yielding, and the work-up and purification is much easier than simple Wittig reactions, as triphenylphosphine oxide can be difficult to remove. Separation of water-soluble sodium diethyl phosphate from this hydrophobic olefin occurs in the aqueous work-up.

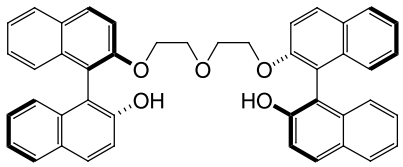
Synthesis of the chiral diol **17** was achieved by the published procedure using a 'classical' Sharpless AD reaction.[16]

2.3. Binaphthol derived ligands

Binaphthol has been the most successful ligand in enantioselective lanthanide catalysis and so we have investigated its use as a chiral unit in polyether ligands. The range of ligands we investigated are shown below:



R=H or Me
23



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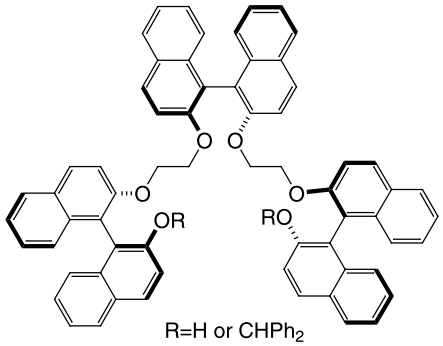
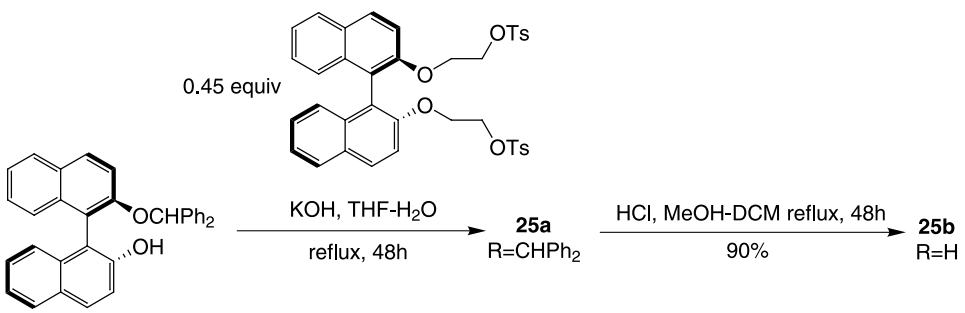


R=H or $CHPh_2$
25

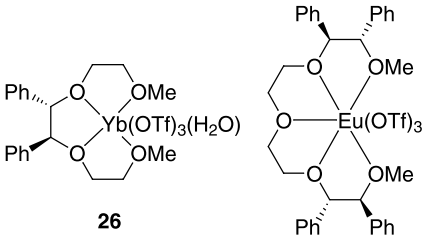


Scheme 9.

Ligand **23** was prepared by the published method.[11] Ligand **24** had been prepared by Cram[19] as an intermediate to chiral crown ethers, but had not been purified or characterised. Ligand **25** was prepared according to Scheme 9 by a similar method to that used for the hydrobenzoin derived ligands **8**.

2.4. Complexation

Preparation of complexes for in situ catalytic studies was achieved by addition of a CH_2Cl_2 solution of an excess of ligand to dried $Ln(OTf)_3$. After brief sonication a homogeneous solution was obtained and in all cases we found the complexes prepared in this way to be extremely soluble even in hydrocarbon solvents. Complexes of ligands **6**, **23** and **24** were of poor quality, but in two cases (complexes **26** and **27** below) we were able to isolate crystals of a sufficient quality for X-ray diffraction. The structures of these complexes are shown in Figures 1 and 2.



Complex **26** is eight-coordinate, with one molecule of coordinated H_2O, and Yb and the four O atoms of the polyether ligand are close to coplanar. The chelate rings adopt λδλ conformations dictated by the chiral substitution pattern of the ligand. The only other published example of a lanthanide complex with a triglyme ligand shows δδλ conformations.[20] In other respects the coordination of the polyether ligand in **26** is very similar to that of its achiral analogue triglyme.

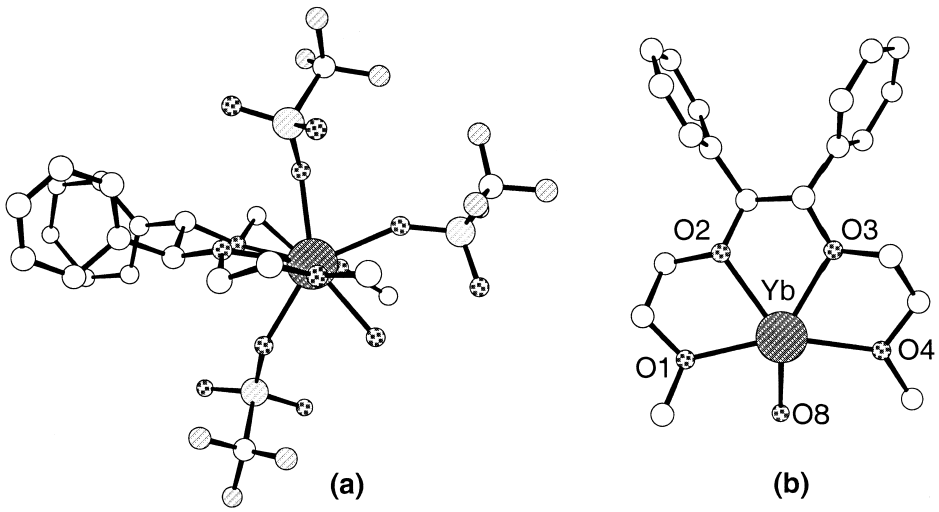


Figure 1. (a) Structure of complex **26** (b) OTf omitted for clarity. Selected distances (Å) and angles (°): Yb–O1, 2.325(7); Yb–O2, 2.440(5); Yb–O3, 2.375(9); Yb–O4, 2.353(6); Yb–O8, 2.306(7); O1–Yb–O2, 67.4(3); O2–Yb–O3, 66.2(3); O3–Yb–O4, 67.2(3).

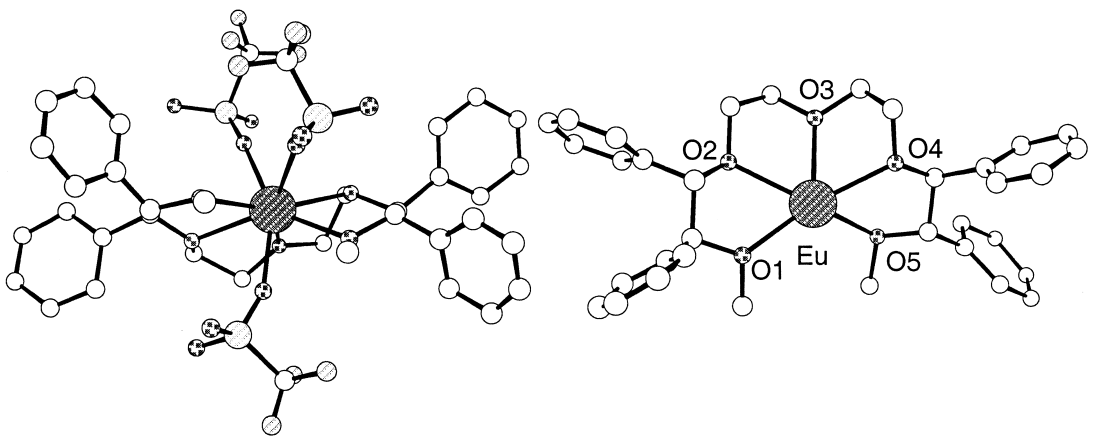


Figure 2. (a) Structure of complex **27** (b) OTf omitted for clarity. Selected distances (Å) and angles (°): Eu–O1, 2.420(19); Eu–O2, 2.550(13); Eu–O3, 2.39(2); Eu–O4, 2.487(16); Eu–O5, 2.444(17); O1–Eu–O2, 63.2(8); O2–Eu–O3, 65.7(8); O3–Eu–O4, 64.0(6); O4–Eu–O5, 62.8(5).

There are several examples of lanthanide complexes with achiral tetraglyme ligands, but complex **27** is the first published example of a chiral version of these complexes. In achiral complexes the conformations of chelate rings are essentially random; in complex **27** (as in complex **26**) the chiral substituents dictate that the hydrobenzoin derived chelate rings adopt a δ conformation. The Eu atom and O1, O2, O3, O4 are almost to coplanar; O5 is significantly displaced from this plane and the Eu–O5 distance is somewhat longer than the Eu–O1 distance. Similar distortions from planarity have been observed in complexes of lanthanides with tetraglyme, and probably arise in order to minimise steric interactions between the terminal OMe groups of the ligand.[8,21–23] These steric interactions are expected to be greater for the smaller, later lanthanides and indeed measurement of stability constants for lanthanide tetraglyme complexes has shown a significant decrease in stability from Tb–Lu.[24]

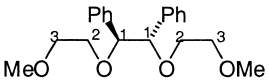
3. Conclusions

We set out to prepare a series of modular chiral polyether podands which would be capable of forming complexes with lanthanide triflates of a range of sizes from La to Yb. The ligand synthesis has been achieved and we have shown that these ligands will indeed coordinate to a range of $Ln(OTf)_3$. Crystal structures have been determined for a $Yb(OTf)_3$ complex with a tetradentate podand and a $Eu(OTf)_3$ complex with a pentadentate podand. We have found $Ln(OTf)_3$ complexes with all of these ligands show Lewis acidity, but enantioselectivities in the Diels–Alder and carbonyl allylation reactions were very poor (generally <5%). Although a degree of preorganisation has been achieved in these ligands via the chiral substituents, the flexibility required to allow coordination to the full range of Ln^{3+} ions means that chiral binding sites are not sufficiently well-defined to achieve good enantioselectivities in catalytic reactions. The necessary degree of structural rigidity can be achieved using macrocyclic ligands,[25] although such ligands may be applicable only to a limited range of metal radii. Although our new chiral podands have not been effective in enantioselective Lewis acid catalysis it is worth noting that complexes of Sm(III) with chiral diols related to **6**, **7** and **23** have been used as chiral proton sources resulting in ees of up to 93%.[26–28] The very properties that make lanthanides attractive for catalytic applications (e.g. labile Ln–ligand bonds, flexible coordination geometry) make it extremely difficult to define an effective chiral binding site for substrates in catalytic reactions.[29] The most effective and versatile ligands for enantioselective lanthanide catalysis have so far been pybox and binaphthol which are both rather more rigid than our chiral podands. The unique coordination chemistry of the lanthanides means that structural rigidity in ligands will generally be required in order to define effective chiral binding sites.

4. Experimental

4.1. General

4.1.1. (4*S*,5*S*)-4,5-Diphenyl-1,8-dimethoxy-3-5-dioxa-octane 5.



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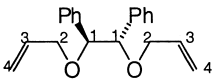
Sodium hydride (60% dispersion in mineral oil, 0.50 g, 12.61 mmol, 2.7 equiv.) was weighed into a 50 ml Schlenk flask containing a magnetic stirrer bar, and washed repeatedly with *n*-hexane. To a stirred suspension of the base in anhydrous THF (15 ml) at 0°C was slowly added (via cannula) a solution of (*S*,*S*)-hydrobenzoin **3** (1.0 g, 4.67 mmol, 1 equiv.) in anhydrous THF (4 ml). After the effervescence had subsided the flask was fitted with a reflux condenser before adding 15-crown-5 (2.28 ml, 9.34 mmol, 2 equiv.) followed by 1-methoxy-2-(toluene-4-sulfonyloxy)ethane[30] (3.28 g, 14.24 mmol, 3 equiv.). The mixture was allowed to warm to room temperature over 2 h, before refluxing for a further 12 h. Most of the THF was removed under reduced pressure, before cooling the flask in ice and quenching the excess sodium hydride with brine (10 ml) [CARE!]. The residue was extracted into Et_2O (4×15 ml) and the combined ethereal extracts were washed (brine), dried ($MgSO_4$), filtered and concentrated on the rotary evaporator to give a yellow oil. Purification by flash chromatography (eluent: petroleum ether–Et_2O 4:1) yielded a colourless oil (1.40 g, 91%); $[\alpha]_D^{17}=+27°$ (c=1.70, $CHCl_3$); $C_{20}H_{30}O_4N$ $[M+NH_4]^+$ requires 348.21748, found 348.21723; R_f (petroleum ether–EtOAc 4:6) 0.30; ν_{max}/cm^{-1} (neat) 3200–2900 (C–H); δ_H ($CDCl_3$) 7.18–6.99 (10H, m, aromatic), 4.50 (2H, s, H-1), 3.58–3.47 (8H, m, H-2 and 3), 3.33 (6H, s, CH_3×2); δ_C ($CDCl_3$) 138.46, 127.54, 127.32 and 127.06 (aromatic), 85.91 (C-1), 71.59 and 68.495 (C-2 and 3), 58.45 (CH_3×2); *m*/*z* (CI) 348.2 (26%, $[M+NH_4]^+$), 272.2 (30%, $[M-CH_2CH_2OCH_3+H]^+$), 255.2 (100%, $[M-OCH_2CH_2OCH_3-H]^+$).

4.1.2. (5*S*,6*S*)-5,6-Diphenyl-4-7-dioxa-1,9-decadiene 10.

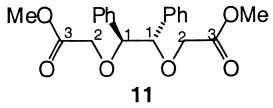


10

Sodium hydride (60% dispersion in mineral oil, 2.80 g, 70.05 mmol, 3 equiv.) was placed in a 250 ml round bottomed flask containing a magnetic stirrer, and repeatedly washed with, and then suspended in anhydrous THF (100 ml). The reaction vessel was cooled in an ice–water bath whilst (*S*,*S*)-hydrobenzoin **3** (5.00 g, 23.35 mmol, 1 equiv.) in THF (50 ml) was carefully added. After the initial effervescence had ceased, a reflux condenser was fitted and allyl bromide (7.05 ml, 81.75 mmol, 3.5 equiv.) was introduced. After refluxing for 2 h, the mixture was cooled to room temperature, the solvent was removed under reduced pressure and the residue was quenched with water (50 ml) [CARE!]. The mixture was extracted with Et_2O (3×50 ml), and the combined ethereal extracts were washed (brine), dried ($MgSO_4$), filtered and concentrated on a rotary evaporator to give a pale yellow oil. Purification by flash chromatography (eluent petroleum ether–Et_2O 9:1) gave a colourless oil, (6.7 g, 98%). Data is consistent with literature for racemate:[31] $[\alpha]_D^{21}=+6.7°$ (c=2.23, DCM); R_f (petroleum ether–Et_2O 9:1) 0.31; δ_H ($CDCl_3$) 7.19–7.00

(10H, m, aromatic), 5.86 (2H, ddt, J=17.6, 10.5, 5.5 Hz, H-3), 5.22 (2H, ddt, J=17.6, 1.7, 1.7 Hz, H-4_{trans}), 5.11 (2H, ddt, J=10.5, 1.7, 1.7 Hz, H-4_{cis}), 4.53 (2H, s, H-1), 4.06–3.81 (4H, m, H-2); δ_C ($CDCl_3$) 138.8, 135.1, 128.0 and 127.7 (aromatic), 127.5 (C-3), 116.4 (C-4), 85.0 (C-1), 70.2 (C-2); m/z (CI) 312 (1%, $[M+NH_4]^+$), 237 (100%, $[M-OCH_2CH{=}CH_2]^+$).

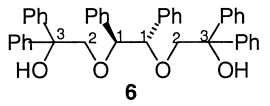
4.1.3. (4*S*,5*S*)-4,5-Diphenyl-3-6-dioxaoctane-1,8-dimethylester 11.



11

A 100 ml round bottomed flask charged with 2.5 M methanolic NaOH solution (9.5 ml), DCM (38 ml) and diene **10** (0.50 g, 1.70 mmol) was cooled to −78°C in an acetone–dry ice bath. Ozone was passed through the solution for 5 h until the bright yellow solution changed to pale blue, then the excess ozone was displaced by bubbling argon through the solution for 5 min. The mixture was neutralised with dilute hydrochloric acid before partitioning between water (50 ml) and DCM (50 ml). After extraction of the aqueous phase with DCM (3×50 ml) the combined organic extracts were washed (brine), dried (Na_2SO_4), filtered and concentrated under reduced pressure. The translucent white paste was purified by flash chromatography (gradient elution with petroleum ether–Et_2O from 8:2 to 1:1) to yield a colourless oil, (0.33 g, 53%); $[\alpha]_D^{19}$=+39.0° (c=1.7, DCM); (found: C, 67.24; H, 6.25%. $C_{20}H_{22}O_6$ requires C, 67.03; H, 6.19%); R_f (petroleum ether–Et_2O 3:2) 0.22; ν_{max}/cm^{-1} (neat) 3064–2911 (C–H), 1757 (C=O); δ_H ($CDCl_3$) 7.27–6.91 (10H, m, aromatic), 4.73 (2H, s, H-1), 4.19 and 4.08 (4H, AB system J=16.5 Hz, H-2), 3.70 (6H, s, OCH_3); δ_C ($CDCl_3$) 170.8 (C=O), 137.2 and 128.1–127.9 (m, aromatic), 86.2 (C-1), 66.9 (C-2), 51.7 (OCH_3); m/z (CI) 376.2 (100%, $[M+NH_4]^+$), 269 (45%, $[M-OCH_2CO_2CH_3]^+$).

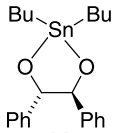
4.1.4. (4*S*,5*S*)-1,1,4,5,8,8-Hexaphenyl-3,6-dioxa-1.8-octanediol 6.



6

A 50 ml three-necked flask charged with magnesium turnings (0.73 g, 29.9 mmol, 10 equiv.), anhydrous Et_2O (10 ml), a crystal of I_2 and a magnetic stirrer bar was equipped with a stopper, a rubber septa and a reflux condenser. Bromobenzene (2.52 ml, 23.92 mmol, 8 equiv.) in anhydrous ether (10 ml) was carefully added by syringe at such a rate to maintain a gentle reflux. After addition was complete the mixture was heated under reflux for a further 40 min. The reaction vessel was cooled in ice as diester **11** (1.07 g, 2.99 mmol, 1 equiv.) in Et_2O (10 ml) was slowly added by syringe. After heating under reflux for 17 h, the flask was transferred to an ice bath and the excess Grignard reagent was quenched with saturated ammonium chloride solution (10 ml) [CARE!]. The mixture was partitioned between Et_2O (50 ml) and 2 M aqueous hydrochloric acid (50 ml). Upon dissolution of the gummy residues, the aqueous layer was extracted into Et_2O (4×30 ml), and the combined organic extracts were washed (brine), dried ($MgSO_4$), filtered and concentrated under reduced pressure. Purification of the thick yellow syrup by flash chromatography (eluent: petroleum ether–Et_2O 4:1) followed by recrystallisation from n-hexane–EtOAc yielded a white crystalline solid, (0.91 g, 50%); mp 157–159°C; $[\alpha]_D^{19}$=−27.5° (c=1.85, DCM); (found: C, 83.18; H, 6.35%. $C_{42}H_{38}O_4$ requires C, 83.14; H, 6.31%); R_f (petroleum ether–EtOAc 1:4) 0.38; ν_{max}/cm^{-1} (nujol) 3550 (O–H), 3245–2825 (C–H); δ_H ($CDCl_3$) 7.36–6.86 (30H, m, aromatic), 4.45 (2H, s, H-1), 4.06–3.58 (4H, AB-system, J=9.9 Hz, H-2) and 3.50 (2H, s, OH); δ_C ($CDCl_3$) 144.6, 144.5, 128.1, 127.8, 127.1, 126.9 and 126.3 (aromatic), 87.4, 78.0 and 76.0; m/z (FAB) 629.1 (0.1%, $[M+Na]^+$), 393.1 (2%, $[M-OCH_2C(OH)(Ph)_2]^+$), 197 (89%, $[M-CH_2C(OH)(Ph)_2]^+$).

4.2. General procedure for tin acetals 14



14

A 250 ml round bottomed flask charged with dibutyltin oxide (26.46 mmol), the appropriate diol (26.46 mmol), toluene (ca. 125 ml) and a magnetic stirrer bar was fitted with a Dean–Stark head. The mixture was refluxed at ca. 125°C under argon until all of the water had been removed azeotropically (typically 3 h). Solvent removal under reduced pressure gave a solid, which was dried under vacuum for 12 h at 85°C. The tin acetals, obtained in quantitative yield, were used in the subsequent step without further purification.

4.3. General procedure for monoalkylation of aryl diols

Tin acetal (11.22 mmol, 1 equiv.), caesium fluoride and potassium iodide were weighed into a 100 ml Schlenk flask containing a magnetic stirrer bar, and dried under vacuum for 2 h at room temperature. Dry DMF (40 ml) followed the alkyl halide were added and the mixture was stirred under nitrogen at room temperature for a further 19 h. The gelatinous suspension was concentrated under reduced pressure to give a yellow solid, which was extracted into hot EtOAc (50 ml), and filtered through a sintered glass funnel, thoroughly washing the white residue with a further 50 ml of hot EtOAc. The filtrate was concentrated onto silica gel and subjected to flash chromatography (eluent: petroleum ether–EtOAc).

Quantities and chromatography eluent for each alcohol are shown below:

Alcohol	CsF (equiv.)	KI (equiv.)	Alkyl halide (equiv.)	Eluent ratio
13a	1.26	None	MeI (4)	4:1
13b	1.19	1.33	PMBCl (1.33)	9:1
21	1.19	1.33	PMBCl (1.33)	3:1

4.3.1. (1*S*,2*S*)-1,2-Diphenyl-2-methoxyethanol 13a. White solid (2.27 g, 89%). Data consistent with literature.[32]

4.3.2. (1*S*,2*S*)-1,2-Diphenyl-2-(4-methoxybenzyl)ethanol 13b. Cream solid (2.71 g, 72%); mp 85–87°C; $[\alpha]_D^{20}$=+18.7° (*c*=1.24, DCM); (found: C, 78.83; H, 6.61%. $C_{22}H_{22}O_3$ requires C, 79.02; H, 6.63%); R_f (petroleum ether–Et_2O 3:2) 0.31; ν_{max}/cm^{-1} (nujol) 3524 (O–H), 3032–2925 (C–H); δ_H ($CDCl_3$) 6.84–7.24 (14H, m, aromatic), 4.69 (1H, dd, *J*=8.24, 1.65 Hz, H-1), 4.46 and 4.25 (2H, AB system, *J*=11.0 Hz, $OCH_2C_6H_4OMe$), 4.32 (1H, d, *J*=8.24 Hz, H-2), 3.80 (3H, s, CH_3), 3.52 (1H, d, *J*=1.65 Hz, OH); δ_C ($CDCl_3$) 159.5, 139.4, 137.8, 129.9, 129.7, 128.2, 128.1, 128.0, 127.9, 127.7, 127.4 and 114.0 (aromatic), 86.7 (C-2), 78.6 (C-1), 70.6 ($OCH_2C_6H_4OMe$) and 55.3 (OCH_3); *m*/*z* (CI) 352.1 (3%, $[M+NH_4]^+$), 214 (25%, $[M-CH_2(C_6H_4OMe)+H]^+$).

4.3.3. (1*R*,2*R*)-1,2-(1-Naphthyl)-2-(4-methoxybenzyl)-ethanol 21. Pale yellow oil, (3.70 g, 76%); $[\alpha]_D^{19}$=+11° (*c*=1.91, DCM); $C_{30}H_{30}NO_3$ $[M+NH_4]^+$ requires 452.22257, found 452.22289; R_f (petroleum ether–EtOAc 1:1) 0.69; ν/cm^{-1} (neat) 3549 (OH), 3052–2838 (CH), 1613, 1597, 1586, 1513; δ_H ($CDCl_3$) 7.95–6.83 (18H, m, aromatic), 5.74 (1H, dd, *J*=8.3, 1.65 Hz, H-1), 5.33 (1H, d, *J*=8.3 Hz, H-2), 4.56–4.30 (2H, AB system *J*=11 Hz, $-OCH_2C_6H_4OCH_3$), 3.84 (3H, s, OCH_3) and 3.81 (1H, d, *J*=1.65 Hz,O*H*); δ_C ($CDCl_3$) 159.4, 135.9–123.4 (m) and 114.0 (aromatic), 83.8 (C-2), 75.2 (C-3), 70.8 ($-OCH_2C_6H_4OCH_3$), 55.4 (CH_3); *m*/*z* (CI) 452.3 (4%, $[M+NH_4]^+$), 434.3 (3%, M^+), 314.2 (77%, $[M-CH_2C_6H_4OCH_3+H]^+$).

4.3.4. (1*S*,2*S*,10*S*,11*S*)-1,2,10,11-Tetraphenyl-1,11-dimethoxy-3,5,9-trioxaundecane 7a. Sodium hydride (60% dispersion in mineral oil, 0.36 g, 9.00 mmol, 3 equiv.) was weighed into a 25 ml Schlenk flask containing a magnetic stirrer and repeatedly washed with hexane. To a stirred suspension of the base in dry THF (2 ml) at 0°C was slowly added (via cannula) a solution of alcohol **13a** (1.50 g, 6.58 mmol, 2.2 equiv.) in dry THF (1 ml). 15-Crown-5 (1.52 ml, 7.5 mmol, 2.5 equiv.) was slowly added, and after the mild effervescence had subsided, diethyleneglycol ditosylate (1.26 g, 2.96 mmol, 1 equiv.) was added to the alkoxide solution. The flask was fitted with a reflux condenser, and reaction mixture was heated to 80°C for 5 h. On allowing the mixture to cool to room temperature the solvent was removed under reduced pressure, before quenching with brine (10 ml) [CARE!] and extracting into Et_2O (3×15 ml). The combined ethereal extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to give a yellow gel. Purification by flash chromatography (eluent petroleum ether–Et_2O 4:1) yielded a colourless oil (1.26 g, 73%); $[\alpha]_D^{25}$=+34° (*c*=1.44, $CHCl_3$); $C_{34}H_{42}O_5N$ $[M+NH_4]^+$ requires 544.30630, found 544.30707; R_f (petroleum ether–Et_2O 1:1) 0.52; ν_{max}/cm^{-1} (neat) 2900–3200 (C–H); δ_H ($CDCl_3$) 7.14–7.01 (20H, m, aromatic), 4.48–4.30 (4H, AB system, *J*=6.6 Hz, H-1 and 2), 3.51 (8H, m, H-3 and 4), 3.25 (6H, s, CH_3×2); δ_C ($CDCl_3$) 138.9, 138.6 and 127.9–127.4 (m, aromatic), 87.5 and 86.2 (C-1 and 2), 70.4 and 68.7 (C-3 and 4), 57.3 (CH_3×2); *m*/*z* (CI) 544.4 (100%, $[M+NH_4]^+$).

4.3.5. (1*S*,2*S*,10*S*,11*S*)-1,2,10,11-Tetraphenyl-1,15-di(4-methoxybenzyloxy)-3,5,7-trioxaundecane 7b. Prepared by reaction of alcohol **13b** (1.6 g, 4.8 mmol, 2.2 equiv.) with diethyleneglycol ditosylate (0.9 g, 2.16 mmol, 1 equiv.) as outlined for polyether **7a**. Reaction time: 6 h at room temperature. Purification by flash chromatography (eluent: petroleum ether–Et_2O 3:1) yielded a colourless syrup (1.07 g, 67%); $[\alpha]_D^{20}$=+32.7° (*c*=1.27, DCM); (found: C, 77.74; H, 6.86%. $C_{43}H_{50}O_7$ requires C, 78.24; H, 6.82%); R_f (petroleum ether–EtOAc 1:1) 0.70; ν_{max}/cm^{-1} (neat) 3105–2822 (C–H); δ_H ($CDCl_3$) 7.18–6.76 (28H, m, aromatic), 4.49 (4H, s, H-1 and 2), 4.46 and 4.27 (4H, AB system, J_{AB}=12.1 Hz, CH_2Ar×2), 3.77 (6H, s, OCH_3×2), 3.48 (8H, m, H-3 and 4); δ_C ($CDCl_3$) 159.2, 139.0, 138.9, 130.8, 129.1, 128.1, 127.9, 127.75, 127.7, 127.5, 127.4 and 113.7 (aromatic), 86.3 and 84.7 (C-1 and 2), 70.6 and 69.2 (C-3, 4, and 55.3; *m*/*z* (FAB) 761.2 (0.5%, $[M+Na]^+$), 739.3 (0.2%, $[M+H]^+$).

4.3.6. (4*S*,5*S*)-4,5-Diphenyl-3,6-dioxa-1,8-octanediol 16. Diene **10** (5.89 g, 20.0 mmol) was placed in a 100 ml round bottomed flask containing a magnetic stirrer bar and dissolved in methanol (60 ml). After cooling to −78°C, ozone was bubbled through the solution for 2.5 h, until a permanent blue colour had developed. The excess ozone was displaced by passing argon through the solution for 10 min, before warming to 0°C. Sodium borohydride (0.77 g, 20.0 mmol) was carefully added in portions and the resulting mixture was stirred for 2 h. After quenching with 2 M HCl (20 ml) and the solvents were removed under reduced pressure to give a white residue which was extracted with hot chloroform (3×50 ml). The organic solution was dried ($MgSO_4$), and concentrated under reduced pressure gave a thick white paste. Purification by flash chromatography (eluent: EtOAc), gave a colourless oil, (3.64 g, 60%). Data are consistent with literature for racemate:[31] $[\alpha]_D^{21}$=+28° (*c*=0.5, $CHCl_3$); (lit. for (4*R*,5*R*)-**16**: $[\alpha]_D$=−19° (*c*=0.8, $CHCl_3$)); $C_{18}H_{26}O_4N$ requires 320.18618, found 320.18662; R_f (Et_2O) 0.21; ν_{max}/cm^{-1} (neat) 3410 (OH) and 3087–2871 (C–H); δ_H ($CDCl_3$) 7.20–7.01 (10H, m, aromatic), 4.48 (2H, s, H-1), 3.78–3.41 (8H, m, H-2 and 3), 3.00 (2H, br s, OH×2); δ_C ($CDCl_3$) 138.3, 128.1, 128.0 and 127.6 (aromatic), 86.9 (C-1), 71.1 (C-2), 61.8 (C-3); *m*/*z* (CI) 320.1 (100%, $[M+NH_4]^+$), 258.1 (68%, $[M-CH_2CH_2O]^+$), 241.1 (58%, $[M-OCH_2CH_2OH]^+$).

4.3.7. (4*S*,5*S*)-4,5-Diphenyl-1,8-bis(*p*-toluenesulfonyloxy)-3,6-dioxaoctane 15. To a solution of diol **16** (0.80 g, 2.64 mmol, 1 equiv.) in DCM (25 ml) was added toluene-*p*-sulfonyl chloride (2.5 equiv.), triethylamine (2.2 equiv.) and DMAP (0.1 equiv.). The mixture was stirred at room temperature for 48 h and was then quenched with saturated aqueous NH_4Cl (25 ml). After extraction of the aqueous layer with DCM (3×25 ml), the combined organic extracts were washed (brine), dried ($MgSO_4$), filtered and concentrated under reduced pressure to give a brown oily solid. Purification by flash chromatography (eluent EtOAc–petroleum ether 1:4) yielded a colourless oil (1.48 g, 91%). Data are consistent with literature for racemate:[31] $[\alpha]_D^{21}$=+6.6° (*c*=1.06, Me_2CO), lit. $[\alpha]_D^{21}$ for (*R*,*R*)-**61** −4.6° (*c*=0.5, Me_2CO); (found: C, 62.95; H, 5.63%. $C_{32}H_{34}O_8S_2$ requires C, 62.93; H, 5.61%); R_f (petroleum ether–EtOAc 1:1) 0.73; δ_H ($CDCl_3$) 7.75 and 7.31 (8H, AA′BB′ system, *J*=8.24, 2.2 Hz, (p-$MeC_6H_4SO_3^-$)×2),

7.14–6.84 (10H, m, Ph×2), 4.35 (2H, s, H-1), 4.14–4.09 (4H, m, H-3), 3.59–3.55 (4H, m, H-2) and 2.45 (6H, s, OCH×2); *m/z* (FAB) 632.9 (0.1%, $[M+Na]^+$), 394.9 (6%, $[M-OCH_2CH_2OTs]^+$).

4.3.8. (1*S*,2*S*,7*S*,8*S*,13*S*,14*S*)-1,2,7,8,13,14-Hexaphenyl-1,14-dimethoxy-3,6,9,12-tetraoxatetradecane 8a. Ditosylate **15** (2.09 g, 3.27 mmol, 1 equiv.) was coupled to alcohol **13a** (1.71 g, 7.20 mmol, 2.2 equiv.) as outlined for polyether **7a**. Reaction time 18 h under reflux. Purification by flash chromatography (eluent: petroleum ether–EtOAc 9:1) yielded a colourless oil, (1.26 g, 51%); $[\alpha]_D^{20}=+32.4°$ (c=0.56, $CHCl_3$); (found: C, 79.34; H, 7.08%. $C_{48}H_{50}O_6$ requires C, 79.75; H, 6.97%); R_f (petroleum ether–EtOAc 1:1) 0.69; ν_{max}/cm^{-1} (neat) 3089–2870 (C–H), 1493, 1453; δ_H (400 MHz, $CDCl_3$) 7.16–7.09 and 7.01–6.94 (30H, m, aromatic), 4.49 (2H, s, H-1), 4.47 and 4.29 (4H, AB system J_{AB}=6.59 Hz, H-4 and 5), 3.56–3.43 (8H, m, H-2 and 3), 3.27 (6H, s, CH_3×2); δ_C ($CDCl_3$) 138.8–138.6 (m) and 128.1–127.3 (m, aromatic), 87.6, 85.8 and 85.6 (C-1,4 and 5), 68.8 (C-2 and 3), 57.3 (OMe); *m/z* (FAB) 745.4 (1%, $[M+Na]^+$).

4.3.9. (1*S*,2*S*,7*S*,8*S*,13*S*,14*S*)-1,2,7,8,13,14-Hexaphenyl-1,14-di(4-methoxybenzyloxy)-3,6,9,12-tetraoxatetradecane 8b. Ditosylate **15** (1.29 g, 2.15 mmol, 1 equiv.) was coupled to alcohol **13b** (1.49 g, 4.65 mmol, 2.2 equiv.) as outlined for polyether **7a**. Reaction time 67 h under reflux. Purification by flash chromatography (eluent: petroleum ether–EtOAc 9:1) gave a colourless oil, (0.64 g, 33%); $[\alpha]_D^{21}=+20.7°$ (c=1.3, DCM); (found: C, 79.24; H, 6.65%. $C_{62}H_{62}O_8$ requires C, 79.63; H, 6.68%); R_f (petroleum ether–EtOAc 1:1) 0.69; ν/cm^{-1} (neat) 3080–2875 (C–H), 1483, 1456, 1114 (C–O); δ_H (400 MHz, $CDCl_3$) 7.20–7.06 (26H, m), 6.99–6.94 (8H, m) and 6.81–6.78 (4H, m, aromatic) 4.52 and 4.29 (4H, AB system, J=11.6 Hz, OCH_2Ar×2), 4.46 (2H, s, H-1), 4.43 and 4.48 (4H, AB system, H-4 and 5), 3.77 (6H, s, OCH_3×2), 3.56–3.42 (8H, m, H-2 and 3); δ_C ($CDCl_3$) 159.1, 139.0, 138.8, 129.1, 128.2–127.2 (m) and 113.7 (aromatic), 85.9, 85.7 and 84.7 (C-1,4 and 5), 70.6 ($OCH_2C_6H_4OCH_3$), 69.0 (C-2 and 3) and 55.3 (OCH_3); *m/z* (FAB) 957.3 (0.1%, $[M+Na]^+$).

4.3.10. (*E*)-1,2-Di(1-naphthyl)ethylene 22. Sodium hydride (60% dispersion in mineral oil, 2.12 g, 53.06 mmol, 1.2 equiv.) was weighed into 250 ml round bottomed flask and repeatedly washed with, and then suspended in, anhydrous THF (50 ml) under argon. To a stirred suspension of the base at 0°C, a solution of 1-naphthylmethylphosphonic acid diethyl ester[17] (12.31 g, 44.22 mmol, 1 equiv.) in THF (50 ml), followed by 1-naphthaldehyde (6.17 ml, 44.22 mmol, 1 equiv.) was slowly added. 15-Crown-5 (2 ml, 0.01 mmol, 0.23 equiv.) was introduced, which resulted in rapid evolution of H_2 and the formation of a gelatinous precipitate. The reaction was allowed to warm to room temperature, and stirred for a further 12 h. The solvent was removed on the rotary evaporator before quenching the excess sodium hydride with brine (20 ml) [CARE!]. After partitioning the mixture between DCM (100 ml) and water (100 ml), the aqueous layer was extracted with DCM (2×100 ml) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting solid was repeatedly washed with chilled MeOH and dried under vacuum to give a pale yellow UV-fluorescent solid, (11.38 g, 95%). Data are consistent with literature:[16] mp 158–161°C (found: C, 93.97; H, 5.75%. $C_{22}H_{16}$ requires C, 94.25; H, 5.75%); δ_H ($CDCl_3$) 8.30–8.23 (2H, m), 7.93–7.82 (8H, m) and 7.59–7.49 (6H, m); *m/z* (EI) 280 (100%, M^+).

4.3.11. (5*R*,6*R*)-5,6-Di(1-naphthyl)-4-oxa-6-(*p*-methoxybenzyloxy)hex-1-ene 20. Sodium hydride (60% dispersion in mineral oil, 0.31 g, 7.02 mmol, 2 equiv.) was placed in a 100 ml round bottomed flask containing a magnetic stirrer bar, and repeatedly washed with, and suspended in anhydrous THF (10 ml). The reaction vessel was cooled in an ice–water bath as alcohol **21** (1.7 g, 3.91 mmol, 1 equiv.) in THF (20 ml) was carefully added. After the initial effervescence had ceased, a reflux condenser was fitted and allyl bromide (500 ml, 5.86 mmol, 1.5 equiv.) was added. The mixture was heated under reflux for 2 h and then stirred at room temperature overnight. After solvent removal under reduced pressure the residue was quenched with water (50 ml) [CARE!]. The mixture was extracted with Et_2O (3×50 ml), and the combined ethereal extracts washed (brine), dried ($MgSO_4$), filtered and concentrated on a rotary evaporator to give a colourless oil which was found to be analytically pure, (1.85 g, 100%); $C_{33}H_{34}NO_4$ ($[M+NH_4]^+$) requires 492.25387, found 492.25385; R_f (petroleum ether–Et_2O 9:1) 0.20; ν_{max}/cm^{-1} (neat) 3051–2860 (C–H), 1644 (C=C) and 1513; δ_H ($CDCl_3$) 8.25–8.05 (2H, m), 7.74–7.57 (4H, m), 7.45–7.15 (8H, m), 7.04 (2H, m) and 6.74–6.70 (2H, m, aromatic), 5.89–5.70 (1H, ddt, J=17.0, 10.5, 5.5 Hz, H-3), 5.50 (2H, s, H-1 and 2), 5.13 (1H, ddt, J=17.0, 1.7, 1.6 Hz, H-5_{trans}), 5.04 (1H, ddt, J=10.5, 1.7, 1.5 Hz, H-5_{cis}), 4.53–4.24 (2H, AB system, J=11.55 Hz, $-OCH_2Ar$), 4.05–3.81 (2H, m, H-3), 3.76 (3H, s, OCH_3); δ_C ($CDCl_3$) 159.0, and 135.1–124.0 (m, aromatic), 126.8 (C-4), 116.4 (C-5), 113.6 (aromatic), 82.6 and 81.0 (C-1 and 2), 70.8 and 70.5 (C-3 and $-OCH_2Ar$) and 55.3 (OCH_3); *m/z* (CI) 492.3 (2%, $[M+NH_4]^+$), 434.4 (2%, $[M-CH_2{=}CHCH_2+H]^+$), 354.2 (4%, $[M-CH_2C_6H_4OCH_3+H]^+$).

4.3.12. (4*R*,5*R*)-4,5-Di(1-naphthyl)-3-oxa-5-(*p*-methoxybenzyloxy)pentan-1-ol 19. Olefin **20** (1.3 g, 2.71 mmol, 1 equiv.) was dissolved in THF (130 ml) and water (30 ml) in a 250 ml round bottomed flask. The mixture was stirred at room temperature whilst OsO_4 solution (2.5% in *t*-BuOH, 520 ml, 50.7 mmol) was added, and stirred for a further 30 min, during which time the solution turned dark brown. $NaIO_4$ (1.47 g, 6.87 mmol, 2.5 equiv.) was slowly added over 20 min, and the mixture was stirred for a further 24 h at room temperature. The flask was chilled to 0°C prior to addition of $NaBH_4$ (0.62 g, 16.26 mmol, 6 equiv.) [CARE!]. After stirring at room temperature for a further 48 h, sodium sulfite (0.34 g, 2.71 mmol, 1 equiv.) was added and the solvent was removed under reduced pressure. The residue was partitioned between 1 M HCl (30 ml) and DCM (50 ml), and the aqueous phase was extracted with DCM (4×50 ml).The combined organic extracts were washed with water (2×100 ml), dried ($MgSO_4$), filtered and concentrated under reduced pressure to give a red–brown oil. Purification by flash chromatography (eluent: petroleum ether–EtOAc 7:3) to give a colourless syrup, (0.91 g, 70%); $[\alpha]_D^{17}=-8.9°$ (c=0.73, $CHCl_3$); $C_{32}H_{34}NO_4$ $[M+NH_4]^+$ requires

496.24878, found 496.24864; R_f (petroleum ether–EtOAc 7:3) 0.13; ν/cm^{-1} (neat) 3454 (O–H), 3052–2838 (C–H), 1613 and 1513; δ_H ($CDCl_3$) 8.25–8.00 (2H, m), 7.76–7.59 (4H, m), 7.29–7.18 (8H, m), 7.05 (2H, m) and 6.75 (2H, m, aromatic), 5.52–5.43 (2H, AB system J=6.6 Hz, H-1 and 2), 4.52–4.21 (2H, AB system, J=11.55 Hz, $-OCH_2Ar$), 3.76 (3H, s, OCH_3), 3.74–3.59 (3H, m, H-3×2 and H-4×1), 3.47–3.35 (1H, m, 1H-5) and 2.76 (1H, br s, O*H*); δ_C ($CDCl_3$) 159.3, 134.6–123.9 (m), and 113.8 (aromatic), 84.0 and 82.4 (C-1 and 2), 71.3 and 70.9 (C-3 and $-OCH_2OC_6H_4OCH_3$), 61.9 (C-1) and 55.3 (OCH_3); *m/z* (CI) 496.2 (8%, $[M-NH_4]^+$), 358.1 (15%, $[M-CH_2C_6H_4OCH_3+H]^+$), 341.1 (27%, $[M-OCH_2C_6H_4-OCH_3]^+$), 314.1 (95%, $[(Ar(CHOH))_2]^+$).

4.3.13. (4*R*,5*R*)-4,5-Di(1-naphthyl)-5-(*p*-methoxybenzyloxy)-1-(*p*-toluenesulphonyloxy)-3-oxapentane 18. Alcohol **19** (0.88 g, 1.84 mmol) was tosylated according to the procedure reported for 1-methoxy-2-(toluene-4-sulfonyloxy)ethane.[30] Reaction time: 38 h. Purification by flash chromatography (eluent: petroleum ether–Et_2O 1:1) gave a white foam, (0.75 g, 64%); $[\alpha]_D^{20}$=+21.5° (c=1.03, DCM); (found: C, 73.66; H, 5.71%. $C_{39}H_{36}O_6S$ requires C, 74.03; H, 5.73%); R_f (petroleum ether–EtO 1:1) 0.39; ν_{max}/cm^{-1} (nujol) 2926–2855 (C–H), 1377 and 1174 (SO); δ_H ($CDCl_3$) 8.15–7.88 (2H, m), 7.74–7.56 (6H, m), 7.40–7.03 (12H, m), and 6.78–6.74 (2H, m, aromatic), 5.47–5.34 (2H, AB system, J=6.1 Hz, H-3 and 4), 4.51–4.22 (2H, AB system, J=11.5 Hz, OCH_2Ar), 4.19–4.07 (2H, m, H-1), 3.79 (3H, s, $-OCH_3$), 3.59–3.52 (2H, m, H-2) and 2.38 (3H, s, $ArCH_3$); δ_C ($CDCl_3$) 159.1, 144.5, 134.4, 134.0, 133.2–123.9 (m) and 113.7 (aromatic), 84.3 and 82.0 (C-3 and 4), 70.9 ($-OCH_2Ar$), 69.3 and 67.3 (C-1 and 2), 55.3 (OCH_3) and 21.6 ($ArCH_3$); *m/z* (FAB) 655.2 (0.5%, $[M+Na]^+$), 633.2 (0.2%, $[M+H]^+$) and 495.1 (1.5%, $[M-OCH_2C_6H_4OCH_3]^+$).

4.3.14. (1*R*,2*R*,7*R*,8*R*,13*R*,14*R*)-1,2,7,8,13,14-Hexa(1-naphthyl)-1,14-di(4-methoxy-benzyloxy)-3,6,9,12-tetraoxatetradecane 9. Tosylate **18** (0.60 g, 0.949 mmol, 2.1 equiv.) was coupled to diol **17**[16] (0.135 g, 0.431 mmol, 1 equiv.) as for polyether **5**. The reaction was heated under reflux for 44 h. Purification by flash chromatography gave a white solid, (0.44 g, 83%); mp 91–96°C; $[\alpha]_D^{21}$=+32.7° (c=1.14, DCM); (found: C, 83.57; H, 6.22%. $C_{86}H_{24}O_8$ requires C, 83.6; H, 6.04%); R_f (petroleum ether–EtOAc 1:1) 0.67; ν_{max}/cm^{-1} (nujol) 2938–2855 (CH); δ_H (400 MHz, $CDCl_3$) 8.15–7.90 (4H, m), 7.68–7.51 (12H, m), 7.32–6.93 (30H, m) and 6.67–6.61 (4H, m, aromatic), 5.41–5.29 (6H, m, H-1,4 and 5), 4.13–4.15 (4H, AB system, J=11.5 Hz, OCH_2Ar×2), 3.71 (6H, s, OCH_3×2), 3.52–3.35 (8H, m, H-2 and 3); δ_C ($CDCl_3$) 158.92, 135.4–124.1 (m) and 113.5 (aromatic), 83.8–82.6 (m, C-1,3 and 4), 70.8 and 69.4 (C-2,3 and $-OCH_2OC_6H_4OCH_3$), 55.2 ($-OCH_3$); *m/z* (FAB) 1257.7 (0.8%, $[M+Na]^+$).

4.3.15. *R*,*R*-1,15-Dihydroxy-1,2:3,4:12,13:14,15-tetra(1,2-naphtho)-5,8,11-triaoxa-1,3,12,14-pentadecatetraene 24. Ligand **24** was prepared according to the published procedure.[19] It was purified by flash chromatography (gradient elution with petroleum ether–DCM from 9:1 to 4:1) to give a pale pink foam (0.34 g, 66%); $[\alpha]_D^{19}$=−25.0° (c=1.205); $C_{44}H_{34}O_5$ requires 642.24063, found 642.24121; R_f (petroleum ether–EtOAc 1:1) 0.53; ν_{max}/cm^{-1} (nujol) 3510–3490 (OH), 2950–2850 (CH); δ_H ($CDCl_3$) 7.98–6.74 (24H, m, aromatic), 5.17 (2H, s, OH), 3.79 (4H, m, H-1), 3.11 (4H, m, H-2); δ_C ($CDCl_3$) 155.3, 151.4, 134.1, 134.0, 130.8, 129.7, 129.6, 129.2, 128.2, 128.0, 127.2, 126.4, 125.2, 125.0, 124.3, 123.2, 117.9, 116.8, 115.7 and 115.6 (aromatic), 69.5 and 69.2 (C-1 and 2); *m/z* (FAB) 642.1 (24%, M^+), 313.0 (21%), 286.0 (10%).

4.3.16. (*SSS*)-1,20-Dihydroxy-1,2:3,4:9,10:11,12:17,18:19,20-hexa(1,2-naphthio)-5,8,13,16-tetraoxa-1,3,9,11,17,19-icosahexaene 25b. A 50 ml round bottomed flask was charged with potassium hydroxide pellets (85%, 0.91 g, 16.25 mmol), THF (19.5 ml), water (0.5 ml), (*S*)-2-benzhydryloxy-2′-hydroxyl-1,1′-binaphthyl[19] (3.40 g, 7.52 mmol, 2.2 equiv.) and (*S*)-1,10-di(*p*-toluenesulphonyloxy)-4,5:6,7-di(1,2-naphtho)-3,8-dioxa-4,6-decadiene (2.33 g, 3.42 mmol, 1 equiv.). After refluxing for 48 h, the mixture was evaporated to dryness under reduced pressure and the residue was partitioned between water (50 ml) and DCM (50 ml). The aqueous phase was further extracted with DCM (2×50 ml) and the combined organic extracts were washed (brine), dried ($MgSO_4$), filtered and concentrated to about 100 ml. Methanol (30 ml) followed by concentrated HCl (5 ml) was added, and the solution was refluxed for 48 h. After treatment with 10% aqueous NaOH (50 ml), the aqueous layer was extracted with DCM (2×100 ml), and the combined organic extracts were dried, ($MgSO_4$). Concentration under reduced pressure produced a yellow solid which was purified by flash chromatography (gradient elution with petroleum ether–DCM from 9:1 to 1:1) to give a white foam, (3.11 g, 90%); mp 119.2°C; $[\alpha]_D^{18}$=−43.3° (c=1.09, DCM); $C_{64}H_{46}O_6$ requires 910.32944, found 910.32970; R_f (petroleum ether–EtOAc 1:1) 0.61; ν_{max}/cm^{-1} (nujol) 3500 (OH), 2927–2856 (CH); δ_H ($CDCl_3$) 7.83–6.71 (36H, m, aromatic), 5.03 (2H, s, OH×2) and 3.82–3.62 (8H, m, OCH_2CH_2O×2); δ_C ($CDCl_3$) 155.5, 154.2, 151.4, 133.9–123.2 (m), 123.2, 120.5, 117.7, 116.6, 116.2 and 115.3 (aromatic), 69.2 and 68.8 ($-OCH_2CH_2O$); *m/z* (FAB) 910.2 (20%, M^+), 313.0 (60%), 268.0 (75%). 239.0 (100%).

4.4. General procedure for preparation of Ln(OTf)$_3$ complexes

The appropriate rare earth triflate (0.098 mmol, 0.1 equiv.) was dried in vacuo at 140°C for 4–16 h in a 25 ml Schlenk flask. After cooling to room temperature the flask was filled with nitrogen and a solution of ligand (0.147 mmol, 0.15 equiv.) in dry DCM (2 ml) was added by cannula. The mixture was subjected to ultrasound for 2 min. Complexes prepared in this way were used in situ for catalytic studies.

4.4.1. Europium(III) (1*S*,2*S*,10*S*,11*S*)-1,2,10,11-tetraphenyl-1,11-dimethoxy-3,5,9-trioxaundecane trifluoromethanesulphonate 27. A 50 ml Schlenk flask was charged with europium(III) triflate nonahydrate (0.85 g, 1.1 mmol, 1 equiv.), ligand **7a** (0.58 g, 1.1 mmol, 1 equiv.), activated 4 Å MS (ca. 1 g) and DCM (25 ml). The mixture was stirred vigorously under nitrogen for 4 h, before decanting the solution into another 50 ml Schlenk flask via cannula. The solvent was removed under vacuum to give

a residue which was dried under vacuum at 80°C for 4 h to give a cream solid. This material was recrystallised by dissolving this material in dry toluene (2 ml) in a Schlenk tube under nitrogen. Dry petroleum ether (5 ml) was carefully layered onto the toluene phase, and the mixture was allowed to stand at room temperature. After about 5 weeks a cream crystalline solid had settled to the bottom of the tube, (1.12 g, 90%); (found: C, 40.51; H, 3.57%. $C_{37}H_{38}O_{14}F_9S_3Eu$ requires C, 39.47; H, 3.4%); δ_H ($CDCl_3$) 14.78 (4H, br s), 8.34 (2H, br s), 7.51–6.85 (20H, br m, aromatic), 5.94 (6H, br s, CH×2), 4.16 (4H, br s), −3.02 (2H, br s); *m/z* (FAB) 977.0 (100%, $[M-OTf]^+$), 828 (20%, $[M-2OTf]^+$).

4.5. X-ray crystallography

Crystals were coated in nujol oil and frozen onto glass fibres under a stream of N_2 gas at −120°C. Data were collected on a Rigaku AFC6S diffractometer using graphite-monochromated Mo Kα radiation (λ=0.71073 Å). Structures were solved using direct methods. CIF files have been deposited with the Cambridge Crystallographic Data Base.

5. Supplementary data

Crystallographic data for complexes **26** and **27** have been deposited with the Cambridge Crystallographic Data Centre (Deposition numbers CCDC 209355 and 209356). Copies of this data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam).

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