Novel Chiral (Salen)Mn^{III} Complexes Containing a Calix[4]arene Unit as Catalysts for Enantioselective Epoxidation Reactions of (*Z*)-Aryl Alkenes

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Dedicated to Professor Giorgio Modena on the occasion of his 80th birthday

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New asymmetric (salen)Mn^{III} and UO_2 complexes containing a calix[4]arene unit in the ligand framework were synthesized. The UO_2 complexes were characterized by ^1H-, ^{13}C-, 2D TOCSY and T-ROESY NMR spectroscopy. Furthermore, the structure of one UO_2 complex was determined by single-crystal X-ray analysis. The data showed that UO_2 complexes, which can be considered in first approximation models of the Mn=O oxidant active species, possess a chiral pocket and adopt relevant conformations for the selectivity of the oxygen transfer process. Epoxidation data of model alkenes with the Mn^{III} complexes showed moderate *ee* values and were not conclusive in indicating that the calix[4]arene unit might be able to influence the selectivity by a molecular recognition mechanism.

Introduction

Enantioselective epoxidation reactions are of interest because chiral epoxides, owing to the presence of two contiguous stereogenic centers, are versatile intermediates to obtain biologically active compounds. Sharpless suggested a catalytic system[1] to obtain very high *ee* values for the epoxidation of functionalized alkenes. However, for unfunctionalized alkenes the achievement of high selectivity represents a challenge for asymmetric synthesis. To reach such a goal Katsuki[2] and Jacobsen[3] have followed a biomimetic strategy employing salen [*N*,*N*′-bis(salicylidene)ethylenediaminato] Mn^{III} derivatives as catalysts. The main problem in obtaining good *ee* values with unfunctionalized alkenes is the control of the alkene approach to the metal site bearing the transferable oxygen and its orientation upon approach. This control in the case of salen derivatives is performed by low energy non bonding interactions. The preferred approaching pathway of alkene is determined by the stereochemistry of the diimine bridge and by the presence of large substituents in the ligand. The presence of two stereogenic sp^3 carbon atoms in the bridge induces flexibility and the salen ligand can adopt a non planar structure.[2,3] Also the real oxidant species, supposed to be a (salen) oxo Mn^V species (oxene),[4,5] is considered to have a non planar structure. Recent theoretical studies[6] suggest that enantioselectivity depend on several factors such as the folding of the oxo species which causes the formation of a chiral pocket, the presence of bulky substituents at the 3,3′-positions of the salen ligand which regulates the alkene approaching path from the side of aromatic rings, the occurrence of π conjugation involving the olefinic double bond, which provides regioselectivity and then enantioselectivity and the electronic effects exhibited by substituents in the 5,5′ positions of the salen ligand able to tune the Mn=O bond strength, which affects the first C–O bond formation step. In this paper we report a study aimed at designing new salen catalysts containing a calix[4]arene unit, which potentially might control the alkene approach trajectory by a molecular recognition mechanism. Calixarenes[7,8] are well known macrocycles able to exert selective molecular recognition of neutral molecules by their hydrophobic cavities. The architecture of these macrocycles allows the easy chemical modification of both their upper and lower rims to achieve different spatial arrangements of the binding functionalities by the shaping of the calixarene cavity.

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Results and Discussion

Synthesis of Salen Calix[4]arene Ligands

We have synthesized four new salen ligands with a built-in calixarene cavity. The calixarene unit employed is the 5-hydroxy-25,26,27,28-tetrapropoxycalix[4]arene (**1**), with a

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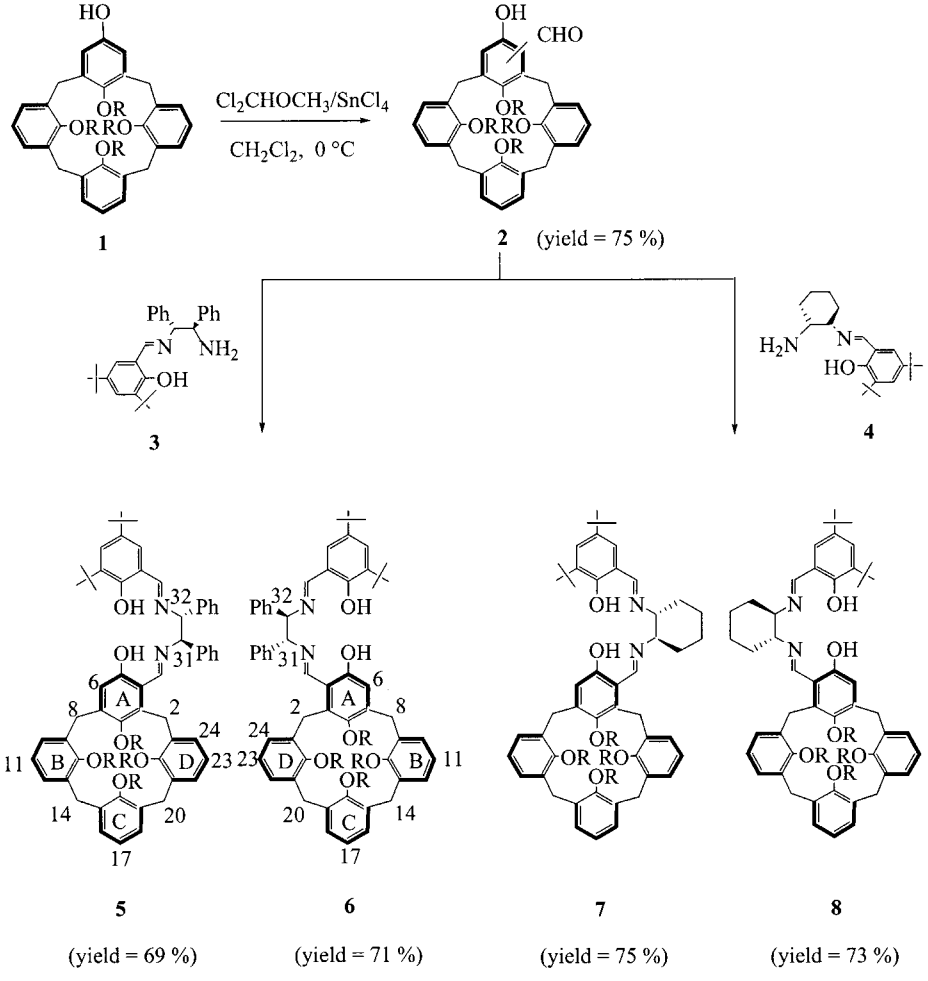
non-interconvertible cone conformation obtained by the presence of propoxy groups at the lower rim (Scheme 1).[9] Into the calixarene moiety is incorporated a salicylaldehyde functionality (OH and CHO groups *ortho* to each other) in order to build up the "teeth" of the metal binding system, through a Schiff base formation with an appropriate chiral imino-amino counterpart. Because of the inherent chirality of the resulting calix[4]arene containing the salicylaldehyde functionality **2**, upon reacting the calix[4]arene salicylaldehyde with appropriate imino-amino precursors we would expect the formation of couples of diastereomeric ligands (Schiff bases). In order to evaluate the role of the diimine bridge on the selectivity we have employed two different chiral amines, i.e. (1*R*,2*R*)-1,2-diphenylethylenediamine and (1*R*)-*trans*-1,2-cyclohexanediamine, which were condensed with 3,5-di-*tert*-butylsalicylaldehyde to yield imino-amino intermediates **3** and **4**, respectively. Therefore, starting from intermediate **1,** we have developed a two-step synthesis**,** leading to the formation of diastereomeric salen calix[4]arenes **5** and **6** with imino-amino intermediate **3,** and of **7** and **8** with imino-amino intermediate **4**.

The structural characterization of all new compounds was carried on by FAB^+ and/or ESI-MS measurements, and by NMR spectroscopy. The ^1H NMR spectra of salen calix[4]arenes **5** and **6** are characterized by the presence of four pairs of doublets for the bridged methylene protons and four resonances for the pertinent carbons in the range 31.2–31.7 ppm.[10] The high field aromatic region of the two stereoisomers shows a set of six shielded aromatic protons, which likely belong to the pair of aromatic rings (B and D) of the calixarene skeleton flanking the one (ring A) bearing the large salen-like residue. These features are suggestive of a C_{2v} cone conformation for the calix[4]arene platform for both compounds, with rings A and C pointing outwards and rings B and D inwards. This particular arrangement of the calixarene moiety, supported by the NMR-ROE data, avoids possible steric interactions of the large diimine substituent of ring A with the adjacent ring D. The ^1H NMR spectra of salen calix[4]arenes **7** and **8** are comparable to those of **5** and **6,** respectively. The protons of the 1,2-cyclohexylylene moiety resonate as sharp multiplets in the expected upfield region (1.50–1.93 ppm).



Scheme 1. Synthesis of salen ligands containing a calix[4]arene unit.

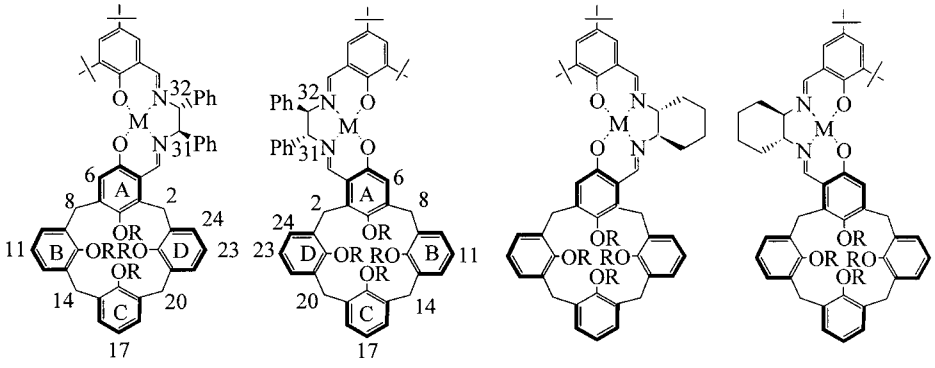
Preparation of (Salen) Mn^{III} and UO_2 Calix[4]arenes Complexes

Ligands **5**–**8** were utilized to prepare uranyl(VI) (**9**–**12**) and Mn(III) (**13**–**16**) complexes (Scheme 2), see Exp. Sect.

The extension of 2D NMR studies to the uranyl(VI) complexes **9** and **10** helped us to assign the structure of diastereoisomers **5** and **6.** Additionally, since **9** and **10** can be considered good models of the pseudo-octahedral salen Mn=O species (oxene), (thought to be the real oxidant species[2a–c,3a,6a,11] responsible for the selective oxygen transfer to the olefin), such an information is valuable in assessing possible parameters controlling the selectivity. The complete assignment of the signals, as well as the stereochemistry and conformations of **9** and **10,** were deduced on the basis of 2D TOCSY and T-ROESY experiments. In addition to the almost unbroken pattern of ROE connectivities, which was already present in the spectra of the free ligands **5** and **6**, several new cross peaks were observed in the T-ROESY spectra of the complexes. In particular for compound **9**, significant strong dipolar contacts were observed between H–24 and the aromatic protons of the phenyl ring bonded to C–31 (Ph–31) and between H–29 and H–31. The diimine protons H–31 and H–32 resonate as singlets at δ = 6.02 and 6.34 ppm, respectively, indicating that they adopt a *gauche* conformation with a dihedral angle of about 90° because of the coordination of the uranyl(VI) ion. In solution, complex **10** adopts a less hindered structure with respect to **9** as clearly indicated by the lack of dipolar correlations between the aromatic protons of Ph–31 and Ph–32 and the calix ring protons. The two diimine protons H–31 and H–32 were found arranged in an almost *anti-periplanar* conformation (AX pattern at δ = 6.2 and 5.9 ppm, ^3J = 11.5 Hz) (Figure 1).

The solid-state structure and absolute configuration of the uranyl complex **9** was established from a single-crystal X-ray analysis (Figure 2).[12]

In the case of complexes **11** and **12,** even if the signals observed in the ^{1}H NMR spectra appear quite broadened**,** a significant downfield shift (with respect to the ligands **7** and **8**) of the resonances of the protons located nearby the donor nitrogen atoms supports the presence of the bonded UO_2 group. Unfortunately, for these compounds the diimine protons H–31 and H–32 signals are buried under propoxy chain resonances, preventing a detailed conformational analysis. At any rate, the analysis of the resolved portions and comparison with the NMR spectra of **9** and **10** allowed the stereoisomer assignments, suggesting that, in solution, complexes **11** and **12** adopt conformations very similar to those of **9** and **10**, respectively.



Scheme 2. Mn^{III} and UO_2 salen calix[4]arene complexes.

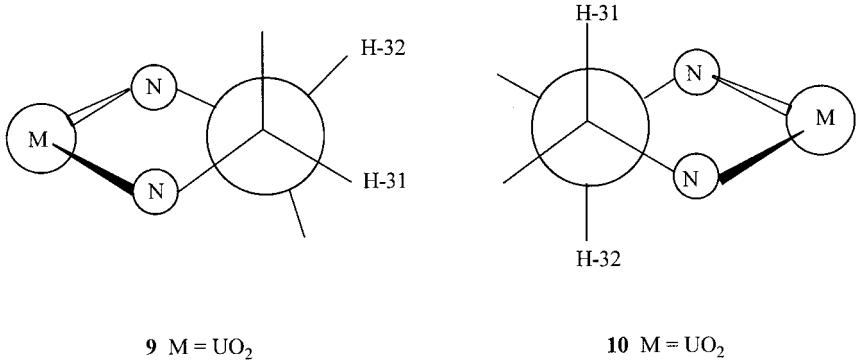


Figure 1. Newman projection of the diimine bridge.

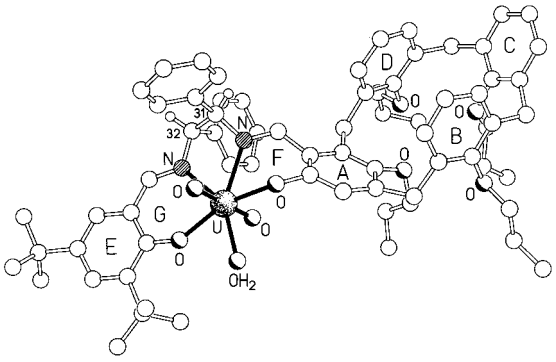


Figure 2. The molecular structure of **9**.

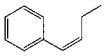
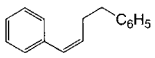
Epoxidation Reactions with (Salen)Mn^{III} Calix[4]arenes 13–16

(Salen)Mn^{III} calix[4]arene complexes were tested as catalysts in epoxidation reactions of styrene, dihydronaphtalene and of some standard *cis*-β-alkylstyrenes in order to test their oxidant abilities. The reactions were performed in CH_2Cl_2/H_2O at 25 °C using NaClO as oxygen donor and 4-phenylpyridine *N*-oxide (4-PPNO) as coligand. In the case of *cis*-β-alkylstyrenes the reaction affords mainly *cis* epoxides together with minor amounts of *trans* epoxides. Enantiomeric excess values for the formation of epoxides (*cis* epoxides in the case of β-alkylstyrenes), determined by capillary GLC analysis using chiral columns (see experimental), are reported in Table 1.

The presence of the coligand 4-PPNO helps in obtaining higher *ee* values (entry 2 in Table 1). Most reactions, under the adopted conditions, are quite fast and are completed or almost completed with reaction times going from 15 min to 4 h. However, reactions with *cis*-β-ethylstyrene (entry 3) and 1,4-diphenyl 1-butene (entry 4) are quite slow and their conversion values are nearly 30% even after 24 h. The presence of a substituent on the β carbon atom larger than the methyl group might decrease the reaction rate probably for steric reasons. *Ee* values are quite low for a terminal alkene such styrene, but are almost three times higher for all the studied β alkylstyrenes. The low *ee* values for styrene were ascribed to a special type of enantiomeric leakage pathway by Jacobsen,[13] who suggested that epoxidation proceeds via a stepwise nonstereospecific mechanism,[3d,14] leading to the irreversible formation of a radical intermediate, which can collapse or can undergo rotation followed by collapse (Scheme 3).

k_{major} and k_{minor} are related to the attack of the alkene to the favored or disfavored catalyst face respectively. In the case of terminal alkenes (R = H) the *trans* formation, due to the rotation followed by collapse of the radical intermediate, decreases the enantioselectivity because *cis* and *trans* epoxides are enantiomers.[13] The observed *ee* values for the remaining alkenes indicate that the degree of enantioselectivity displayed by the catalysts synthesized in this work is moderate. The change of diimine bridge identity upon replacing the two phenyl rings linked to the two carbon atom stereocenters 31 and 32 with a cyclohexane ring

Table 1. Enantioselective epoxidation of alkenes with NaClO catalyzed by (Salen)Mn^{III} calix[4]arenes in CH_2Cl_2/H_2O at 25 °C.[a]

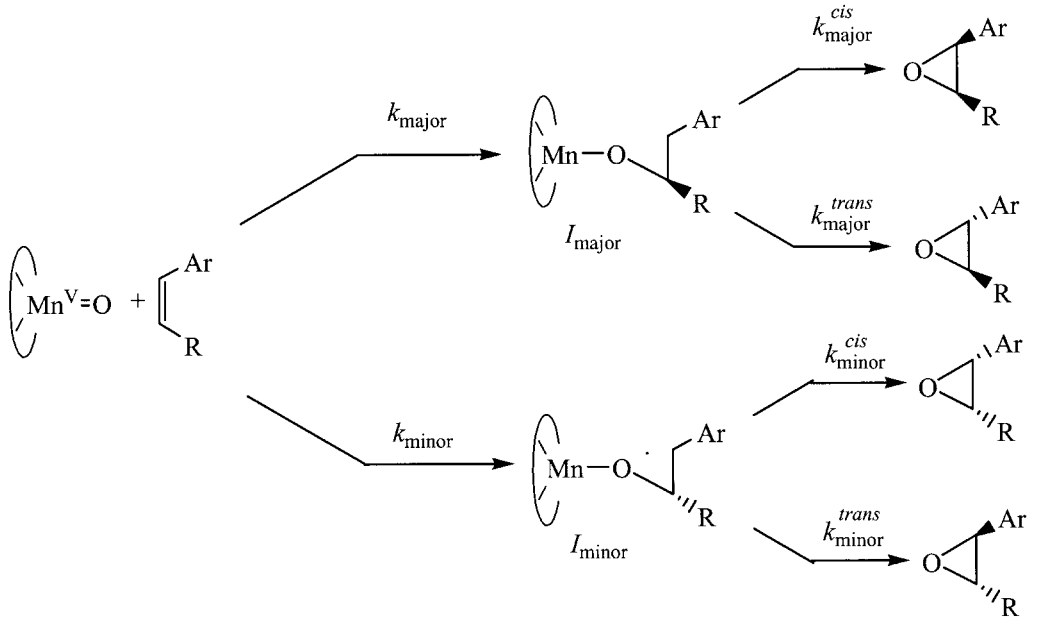
Entry	Alkene	Cat.	Conv. (%)[b]	*ee* (%)[b,c]	*cis*/*trans* ratio[b]	Conf.[d]
1		**13**	100	20	–	*R*
		14	100	22		
		15	100	20		
		16	100	20		
2		**13**	90	48	3.5	1*R*,2*S*
		14	90	61 (42)[e]	2.8	
		15	90	45	2.6	
		16	90	62 (32)[e]	3.0	
3		**13**	30	56	2.9	n.d.
		14	30	72	2.1	
		15	30	50	2.8	
		16	30	63	3.9	
4		**13**	32	57	n.d.	n.d.
		14	32	68		
		15	32	58		
		16	32	67		
5		**13**	100	40		1*R*,2*S*
		14	100	43		
		15	100	43		
		16	100	48		

[a] In all experiments [Alkene] = 0.14 M, [Catalyst] = 0.007 M, [Coligand] = [4–PPNO] = 0.07 M, [NaClO] = 0.14 M, [Na_2HPO_4] = 0.05 M at pH = 11.2 as buffer. [b] Determined by GC on chiral columns. [c] In the case of *cis*-β-alkylstyrenes *ee* values are referred to the major *cis* epoxide (ee_{cis}). [d] Determined by measuring the optical rotation. [e] No coligand added.

(catalysts **15** and **16**) does not substantially affect the *ee* values (compare catalysts **13** vs. **15** and **14** vs. **16**), according to the observations reported in previous section (NMR studies) that catalyst couples **13** and **15** or **14** and **16** should adopt similar conformations in solution.

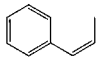
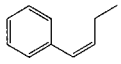
In order to try to understand the observed behavior, we determined the ee_{facial} value[14a] (the facial selectivity in the first step which depends on k_{major} vs. k_{minor}) and the relative diastereoselectivity of the ring closure step[14a] (*cis*/*trans* partitioning of intermediates I_{major} and I_{minor}[14a]) for *cis*-β-methylstyrene and *cis*-β-ethylstyrene.

The ee_{facial} values, reported in Table 2, are not very different for the different catalysts. However, only for speculation purposes, these values might be considered as indicative of a slightly better selectivity of catalysts **14** and **16** than the corresponding **13** and **15** with both *cis*-β-methylstyrene and *cis*-β-ethylstyrene. This behaviour might be ascribed to the different conformations adopted by the oxene intermediates derived from complexes **14** and **16** vs. **13** and **15**, respectively. In fact, assuming that uranyl complexes **9** and **10** represent models for oxene intermediates **13** and **14**, respectively, it is reasonable to make inferences based on the structural differences between **13** and **14**. In the gauche conformation of complex **14** the chiral pocket (generated by the distorted *R*,*R* diimine bridge) should favor the attack of alkene through the *si* enantioface (Figure 3, a), because along the attack direction of the *re* enantioface repulsive



Scheme 3. Jacobsen nonstereospecific mechanism of alkene asymmetric epoxidation.

Table 2. Enantioselectivity and diastereoselectivity factors.

Entry	Alkene[a]	Cat.	ee_{facial}[a]	$\frac{(cis/trans)_{major}}{(cis/trans)_{minor}}$[b]
6		**13**	39	1.8
		14	52	2.2
		15	37	1.8
		16	55	2.1
7		**13**	44	3.1
		14	50	4.9
		15	39	2.4
		16	58	1.9

[a] $ee_{facial} = (ee_{cis} \times \%cis) + (ee_{trans} \times \%trans)$.[14a] [b] $\frac{[cis]_{major}/[trans]_{major}}{[cis]_{minor}/[trans]_{minor}} = \frac{(1+ee_{cis})/(1-ee_{cis})}{(1+ee_{trans})/(1-ee_{trans})}$.

interactions arise between the alkene and the phenyl ring bonded to the C-32 carbon atom of the bridge (Figure 3, b). The *si* enantioface of alkene should be also favored if we assume that the calixarene cavity is able to recognize the alkene through the alkyl group.[15] Therefore, in this case, the calixarene should work in synergy with the stereochemistry of the bridge (matching) and the oxygen is transferred preferentially to the *si* face of alkene (epoxide 1*R*,2*S*), as observed.

Also in the gauche conformation of complex **13** the dissymmetry of the diimine bridge should favor the *si* enantioface of the alkene (Figure 4, a), because the attack by the *re* enantioface implies the involvement of unfavourable steric interactions between the alkene and the phenyl ring bonded to the C–31 carbon atom of the bridge (Figure 4, b).

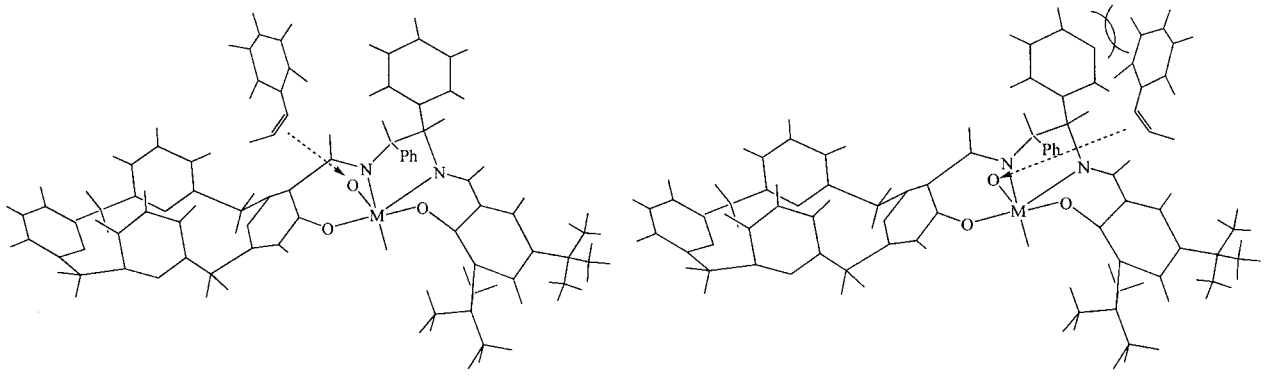


Figure 3. Approach directions for the epoxidation of *cis*-β-methylstyrene with catalyst **14**.

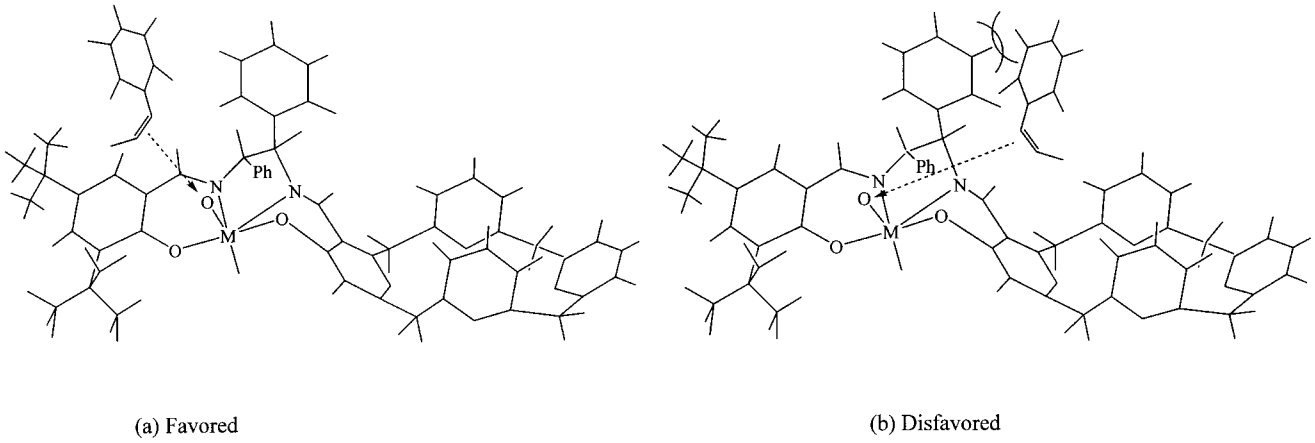


Figure 4. Approach directions for the epoxidation of *cis*-β-methylstyrene with catalyst **13**.

By way of contrast the calixarene, through the molecular recognition of the alkyl group, should favour the attack of the *re* enantioface of the alkene working thus in the opposite way to the stereochemistry of bridge (mismatching). In such a case, if the control of the calixarene on the stereochemistry of the final product were more relevant than that of the diimine bridge, the oxygen should be transferred preferentially to the *re* face of alkene (epoxide 1*S*,2*R*). At variance with these expectations we observed that the major *cis* epoxide has still the 1*R*,2*S* configuration, even though the observed ee_{cis} values (Table 1) are smaller than those observed previously with catalyst **14**. Therefore, present data do not allow to conclude that the presence of the calixarene cavity in our salen catalysts is able to induce a molecular recognition mechanism in the selective oxygen transfer to alkenes.

Conclusions

We have synthesized the first example of (salen) Mn^{III} and UO_2 complexes containing a calix[4]arene unit in the ligand framework. NMR studies and X-ray measurements of the (salen) UO_2 complexes, assumed to be structural models of oxidant active species Mn=O (oxene), indicated a good correlation between the conformations in solution and in the solid state and allowed to suggest a rationale of epoxidation enantioselectivity, based on possible relevant conformations of oxenes and on the identities of alkenes. Unfortunately, present data do not allow to indicate that the presence of the calix[4]arene unit induces a catalytic selectivity based on molecular recognition mechanism of the alkene to be oxidized. At any rate, the catalysts synthesized in this work represent the first example of salen derivatives containing a calixarene unit, and work is in progress to try to focus the relevant parameters to be controlled in order to pursue molecular recognition based catalysts to perform enantioselective epoxidations of unfunctionalized alkenes.

Experimental Section

General Remarks: Melting points were determined on a Kofler hot stage apparatus and are uncorrected. The NMR experiments were carried out at 27 °C on a 500 MHz Varian Unity Inova spectrometer (^1H at 499.88 MHz, ^{13}C NMR at 125.7 MHz) equipped with pulse field gradient module (Z axis) and a tunable 5 mm inverse detection probe. The chemical shifts (ppm) were referenced to TMS (^1H, 0.0 ppm) or $CDCl_3$ (^{13}C, 77.0 ppm). Gas chromatographic analyses of the reaction mixtures were carried out on a gas chromatograph equipped with a flame ionization detector and program capability. The *ee* values were determined employing the chiral column DMePeBETACDX (25 m × 0.25 mm ID × 0.25 μm film), for styrene (column conditions: 100 °C (5 min) to 118 °C (1 min) at 3 °C/min), for 1,2-dihydronaphthalene (isotherm 150 °C), for *cis*-β-ethylstyrene (column conditions: 50 °C (0 min) to 150 °C (1 min) at 2.5 °C/min) and for 1,4-diphenyl-1-butene (column conditions: 80 °C (3 min) to 198 °C (20 min) at 3 °C/min). For *cis*-β-methylstyrene the chiral column DMeTButiSililBETA (25 m × 0.25 mm ID x 0.25 μm film) was used (column conditions: 50 °C (0 min) to 120 °C (1 min) at 2 °C/min). The injector and detector temperatures were maintained at 250 °C for both columns. *n*-decane was used as an internal standard throughout. ESI mass spectra were obtained by employing an ES-MS spectrometer equipped with an ion trap analyzer. FAB(+) mass spectra were obtained on a MS 50 spectrometer using 3-nitrobenzyl alcohol as a matrix. GC-MS analyses of reaction mixtures were performed on a 5890 gas chromatograph (using an HP-1 dimethyl-polysiloxane 25 m capillary column) equipped with a MS computerized system. The absolute configurations of (1*R*,2*S*)-1,2-epoxy-1,2,3,4-tetrahydronaphthalene and of (1*R*,2*S*)-1,2-epoxy-1-phenylpropane were determined by measuring the optical rotations with a polarimeter. Commercial reagents were used as received without further purification unless otherwise noted. Dichloromethane was freshly distilled from calcium hydride before use.

General Procedure for Epoxidation Reactions: To a stirred solution of alkene (0.35 mmol), catalyst (0.0175 mmol) and 4-phenylpyridine *N*-oxide (4-PPNO, 0.175 mmol) in CH_2Cl_2 (2.5 mL), kept in a round-bottomed flask and maintained at 25 °C in a thermostatic bath, buffered bleach (0.35 mmol, buffered to pH = 11.2 with 0.05 M Na_2HPO_4 and 1 M NaOH) was added. The course of the reaction was monitored by GC against an internal quantitative standard (*n*-decane). Upon complete consumption of the starting olefin, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and concentrated. The crude product was purified by PLC (SiO_2).

1,2-Epoxy-1,2,3,4-tetrahydronaphthalene, 1,2-epoxy-1-phenylpropane, 1,2-epoxy-1-phenylbutane and 1,2-epoxy-1,4-diphenylbutane

were synthesized by epoxidation of the corresponding olefins with *m*-chloroperbenzoic acid in CH_2Cl_2 and characterized by comparison of their ^1H NMR spectra with those reported in literature.[16] In order to determine the absolute configuration of the major enantiomer *cis* epoxide, 1,2-epoxy-1,2,3,4-tetrahydronaphthalene and 1,2-epoxy-1-phenylpropane were isolated from the reaction mixture by preparative PLC (SiO_2) using cyclohexane/EtOAc (15:1, v/v) and cyclohexane, respectively. Measurements of optical rotation gave $[\alpha]_D^{20}$ = +17.5 (*c* = 0.20, $CHCl_3$) for 1,2-epoxy-1,2,3,4-tetrahydronaphthalene and $[\alpha]_D^{20}$ = –6.0 (*c* = 0.125, $CHCl_3$) for 1,2-epoxy-1-phenylpropane. Absolute configurations were assigned by comparison of the signs of measured $[\alpha]_D^{20}$ to the literature values.[17,18]

(3-Phenylpropyl)triphenylphosphonium Bromide (C): To a three-necked round-bottom flask equipped with a condenser and a magnetic stirrer were added triphenylphosphane (13.2 g, 50.5 mmol), 1-bromo-3-phenylpropane (10.05 g, 50.5 mmol) and 50 mL of toluene.[19] After being refluxed for 5 h, the reaction mixture was filtered to give 19.2 g (83%) of a crystalline white solid (m.p. 210–211 °C). ^1H NMR (500 MHz, $CDCl_3$): δ = 2.07 (m, 2 H), 3.13 (t, *J* = 2.5 Hz, 2 H), 3.92 (m, 2 H), 7.20–7.37 (m, 5 H), 7.77–7.91 (m, 15 H) ppm. MS (positive FAB): *m*/*z* = 381 $[M]^+$.

***cis*-1,4-Diphenyl-1-butene:** A 100-mL round-bottom flask was equipped with a condenser, additional funnel, N_2 inlet and magnetic stirrer. This flame-dried apparatus was charged with a solution of (3-phenylpropyl)triphenylphosphonium bromide (2.2 g, 4.8 mmol) in dry THF (30 mL).[20] The mixture was stirred at room temperature and 3 mL of 1.6 M *n*BuLi in hexane (4.8 mmol) was slowly added. After the solution turned dark red, benzaldehyde (0.518 g, 4.8 mmol) was added, then the color turned light orange. The resulting mixture was stirred for 20 min, poured onto ice, and diluted with diethyl ether. The aqueous phase was separated and extracted three times with diethyl ether. The combined organic extracts were dried ($MgSO_4$) and evaporated in vacuo to give a residue which was extracted with cold hexane. Evaporation of hexane solution gave 1.5 g (68%) of crude product. Chromatography on silica gel (pentane) gave 600 mg (40%) of *cis*-1,4-diphenyl-1-butene and 370 mg (25%) of *trans*-1,4-diphenyl-1-butene. The ^1H NMR and MS spectra correspond to those reported in the literature.[21]

5-Hydroxy-25,26,27,28-tetrapropoxycalix[4]arene (1): Compound **1** was prepared according to literature procedures by lithiation of cone 5-bromo-25,26,27,28-tetrapropoxycalix[4]arene[22] (1.21 g, 1.8 mmol) with *n*BuLi (10 mL of 1.6 M solution, 16 mmol) in dry THF at –78 °C followed by O_2 oxidation.[23] The yellow oil obtained was purified by column chromatography (SiO_2, eluent: hexane/$CHCl_3$, 4:1) (0.65 g, 60%). The ^1H NMR and MS spectra correspond to those reported in the literature.

5-Hydroxy-25,26,27,28-tetrapropoxycalix[4]arene-4-carbaldehyde (2): To a chilled solution of cone 5-hydroxy-25,26,27,28-tetrapropoxycalix[4]arene[24] (**1**) (0.8 g, 1.32 mmol) in dry CH_2Cl_2 (100 mL) was added Cl_2CHOCH_3 (2.34 mL, 26.4 mmol) under N_2. A 1 M solution of $SnCl_4$ in CH_2Cl_2 (1.32 mL, 1.32 mmol) was then added and after 3–4 minutes the reaction was stopped with 1 M HCl. The mixture was washed with a saturated aqueous solution of $NaHCO_3$ and then with water, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the resulting yellow oil was purified by column chromatography (SiO_2, eluent: petroleum ether/CH_2Cl_2, 4:1) to give 2 as a yellow solid. (0.62 g, 75%; m.p. 118–120 °C). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.93–1.04 (m, 12 H), 1.80–2.02 (m, 8 H), 3.15, 3.19 (d, *J* = 13.5 Hz, ratio 1:3, 4 H_{eq}), 3.70–3.92 (m, 8 H), 4.46, 4.48, 4.57 (d, *J* = 13.5 Hz, ratio 2:1:1, 4 H_{ax}), 6.38–6.80 (m, 10 H), 10.22 (s, 1 H), 11.70 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.2 (× 2), 10.3, 10.4, 23.0, 23.06, 23.1, 23.3, 31.0 (× 2), 31.2, 31.6, 76.5, 76.6, 76.94, 76.97, 117.0, 117.1, 122.0, 122.22, 122.24, 127.7, 128.1, 128.48, 128.53, 132.6, 133.5, 135.0, 135.2, 135.5, 135.7, 137.7, 147.7, 149.9, 156.2, 156.4, 156.9, 158.5, 195.1 ppm. MS (positive FAB): *m*/*z* = 637 $[M + H]^+$. $C_{41}H_{48}O_6$ (636.82): C 77.36, H 7.55; found C 77.40, H 7.53. Evidence for the racemic nature of 2 was provided by the diastereomeric interaction observed upon addition of the chiral Pirkle's reagent [(*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol] to a $CDCl_3$ solution of 2, which caused the expected doubling of most resonances.

(1*R*,2*R*)-Diphenylethylenediamine Hydrochloride (D); (1*R*)-*trans*-1,2-Cyclohexanediamine Hydrochloride (E): (1*R*,2*R*)-Diphenylethylenediamine (0.5 g, 2.36 mmol) or (1*R*)-*trans*-1,2-cyclohexanediamine (0.27 g, 2.36 mmol) was dissolved in anhydrous Et_2O (20 mL). The solution was stirred vigorously, while anhydrous HCl (1.18 mL, 2.36 mmol, 2 M Et_2O solution) was added dropwise over 10 min. After complete addition of the acid, the mixture was allowed to stir at room temperature for 16 h. The precipitate was collected by suction filtration, washed with diethyl ether and dried in vacuo (90% isolated yield).

D: ^1H NMR (500 MHz, D_2O): δ = 4.53 (s, 2 H), 7.21–7.38 (m, 10 H) ppm. MS (positive FAB): *m*/*z* 213 $[M]^+$.

E: ^1H NMR (500 MHz, D_2O): δ = 1.16 (m, 4 H), 1.60 (d, *J* = 11 Hz, 2 H_{eq}), 1,80 (d, *J* = 11 Hz, 2 H_{ax}), 2.71 (m, 2 H) ppm. MS (ESI): *m*/*z* = 115 $[M]^+$.

Condensation of Hydrochloride D or E with 3,5-Di-*tert*-butylsalicylaldehyde (3 and 4): (1*R*,2*R*)-Diphenylethylenediamine hydrochloride (0.52 g, 2.1 mmol) or (1*R*)-*trans*-1,2-cyclohexanediamine hydrochloride (0.24 g, 2.1 mmol) was dissolved in MeOH/EtOH (1:1, 25 mL). 3,5-Di-*tert*-butylsalicylaldehyde (0.49 g, 2.1 mmol) was then added, and the mixture was stirred at room temperature. After 24 h the solvent was removed under reduced pressure. The resulting solid (compound **3** or **4**) was washed with water (5 mL), diethyl ether (10 mL) and dried in vacuo. Yield 90%.

3: ^1H NMR (500 MHz, [D_6]DMSO): δ = 1.24 (s, 9 H), 1.38 (s, 9 H), 4.80–5.22 (m, 2 H), 7.02–7.42 (m, 12 H), 8.55 (br. s, 3 H), 8.78 (s, 1 H), 13.14 (s, 1 H) ppm. MS (positive FAB): *m*/*z* 429 $[M]^+$.

4: ^1H NMR (500 MHz, $CDCl_3$): δ = 1.28 (s, 9 H), 1.43 (s, 9 H), 1.20–1.72 (m, 7 H), 2.27 (m, 1 H), 3.20 (m, 1 H), 3.47 (m, 1 H), 7.10 (d, *J* = 2.5 Hz, 1 H), 7.38 (d, *J* = 2.5 Hz, 1 H), 8.29 (br. s, 3 H), 8.51 (s, 1 H), 12.82 (s, 1 H) ppm. MS (ESI): *m*/*z* = 331 $[M]^+$.

Salen Calix[4]arenes 5,6 and 7,8: The above imino-amino derivative 3 (0.29 g, 0.63 mmol) or 4 (0.23 g, 0.63 mmol) was dissolved in abs. EtOH (30 mL) and stirred over 4-Å molecular sieves. A solution of 2 (0.4 g, 0.63 mmol) and triethylamine (0.127 g, 1.26 mmol) in abs. EtOH (6 mL) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC (CH_2Cl_2/petroleum ether, 2:1). After 48–60 h the mixture was filtered and the solution was concentrated under reduced pressure. The resulting solid was washed with Et_2O and the two diastereomeric compounds of each reaction mixture were conveniently separated by preparative PLC, using CH_2Cl_2/cyclohexane (2:1, v/v) as eluent, with 70–75% recovery of each pure stereoisomer.

5: ^1H NMR (500 MHz, $CDCl_3$): δ = 0.89, 0.90, 1.02, 1.03 (t, *J* = 7.5 Hz, 3 H each), 1.26, 1.27 (s, 9 H each), 1.79–1.95 (m, 8 H), 3.09, 3.11, 3.13, 3.49 (d, *J* = 13.5 Hz, 1 H_{eq} each), 3.60–3.94 (m, 8 H), 4.29, 4.37, 4.38, 4.41 (d, *J* = 13.5 Hz, 1 H_{ax} each), 4.73, 4.78 (ABq, *J* = 9.0 Hz, 1 H each), 5.59 (d, *J* = 7.0 Hz, 1 H), 5.75 (t, *J* = 7.0 Hz, 1 H), 6.02 (d, *J* = 7.0 Hz, 1 H), 6.15 (d, *J* = 7.5 Hz, 1

H), 6.24–6.28 (m, 2 H), 6.63 (s, 1 H), 6.85 (t, *J* = 7.5 Hz, 1 H), 6.97 (d, *J* = 7.5 Hz, 1 H), 7.01 (d, *J* = 7.5 Hz, 1 H), 7.05, 7.28 (d, *J* = 2.5 Hz, 1 H each), 7.12–7.22 (m, 10 H), 8.42, 8.85 (s, 1 H each), 13.63, 14.02 (s, 1 H each) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.87, 9.89, 10.7 (× 2), 22.8, 22.9, 23.4, 24.4, 29.2 (× 3), 29.7, 30.4, 30.98 (× 2), 31.32, 31.47 (× 3), 34.1, 34.9, 38.7, 76.4, 76.63, 76.64, 76.8, 80.4, 80.7, 115.1, 116.4, 117.7, 121.6, 122.1, 122.2, 126.3, 126.7, 127.1, 127.30, 127.35 (× 2), 127.7, 127.97 (× 2), 128.0 (× 2), 128.18 (× 2), 128.22 (× 2), 128.6, 132.3, 132.5, 133.2, 133.6, 136.5, 136.74, 136.78, 136.9, 139.75, 139.88, 139.91, 142.6, 149.8, 155.29, 155.35, 157.1, 157.8, 158.1, 164.1, 167.2 ppm. MS (ESI): *m*/*z* = 1046.6 $[M + H]^+$. $C_{70}H_{82}N_2O_6$ (1047.42): C 80.31, H 7.84, N 2.68; found: C 80.27, H 7.80, N 2.65.

6: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84, 0.87, 1.04, 1.05 (t, *J* = 7.5 Hz, 3 H each), 1.25, 1.48 (s, 9 H each), 1.78–1.96 (m, 8 H), 3.06, 3.09, 3.11, 3.59 (d, *J* = 13.5 Hz, 1 H_{eq} each), 3.60–4.02 (m, 8 H), 4.39, 4.35, 4.37, 4.40 (d, *J* = 13.5 Hz, 1 H_{ax} each), 4.68, 4.66 (ABq, *J* = 9.1 Hz, 1 H each), 6.13 (t, *J* = 7.0 Hz, 1 H), 6.22 (d, *J* = 7.0 Hz, 2 H), 6.28 (d, *J* = 7.0 Hz, 1 H), 6.30 (d, *J* = 7.0 Hz, 1 H), 6.32 (d, *J* = 7.5 Hz, 1 H), 6.46 (s, 1 H), 6.68 (br. d, 1 H), 6.70 (t, *J* = 7.5 Hz, 1 H), 6.86 (d, *J* = 7.5 Hz, 1 H), 6.98, 7.34 (d, *J* = 2.5 Hz, 1 H each), 7.10–7.22 (m, 10 H), 8.34, 8.84 (s, 1 H each), 13.54, 14.00 (s, 1 H each) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.97, 10.02, 10.46, 10.57, 22.93, 22.97, 23.2, 23.4, 24.7, 29.5 (× 3), 30.9, 31.1, 31.3, 31.4 (× 3), 34.1, 35.0, 76.3, 76.5, 76.8, 79.7, 81.1, 114.9, 116.3, 117.9, 121.8, 121.9, 122.0, 125.6, 126.4, 127.0, 127.2, 127.4 (× 2), 127.6, 127.76, 127.82, 127.93, 128.1 (× 3), 128.2 (× 2), 128.3, 128.6, 128.7, 128.9, 132.9, 133.2, 134.0, 134.2, 136.1, 136.2, 136.3, 136.4, 139.5, 139.8, 140.1, 142.1, 149.5, 155.7, 155.8, 157.2, 157.3, 157.9, 164.3, 167.4 ppm. MS (ESI): *m*/*z* = 1046.6 $[M + H]^+$. $C_{70}H_{82}N_2O_6$ (1047.42): C 80.31, H 7.84, N 2.68; found: C 80.33, H 7.86, N 2.70.

7: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.5 Hz, 3 H), 0.89 (t, *J* = 7.5 Hz, 3 H), 1.03 (t, *J* = 7.5 Hz, 6 H), 1.26 (s, 9 H), 1.44 (s, 9 H), 1.75–1.93 (m, 8 H), 1.53, 1.71, 1.92 (m, 8 H), 3.04, 3.12, 3.14, 3.51 (d, *J* = 14 Hz, 1 H_{eq} each), 3.29 (m, 2 H), 3.50–4.01 (m, 8 H), 4.32, 4.34, 4.41, 4.43 (d, *J* = 14 Hz, 1 H_{ax} each), 6.15 (d, *J* = 7.0 Hz, 1 H), 6.25–6.36 (m, 5 H), 6.46 (s, 1 H), 6.78 (t, *J* = 7.0 Hz, 1 H), 6.85 (d, *J* = 7.0 Hz, 1 H), 6.91 (d, *J* = 7.0 Hz, 1 H), 7.01 (d, *J* = 2.5 Hz, 1 H), 7.33 (d, *J* = 2.5 Hz, 1 H), 8.33 (s, 1 H), 8.76 (s, 1 H), 13.70 (br. s, 1 H), 14.10 (br. s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.2, 10.75,10.85, 23.1, 23.2, 23.5, 23.6, 24.6 (× 2), 29.7 (× 3), 31.2, 31.4, 31.5, 31.7 (× 3), 33.4, 33.7, 34.3, 35.2, 72.5, 73.4, 76.6, 76.8, 77.1, 115.2, 116.6, 118.2, 122.0, 122.1, 122.2, 122.7, 124.2, 126.3, 126.9, 127.1, 127.3, 127.8, 128.0 (× 2), 128.6, 128.9, 129.7, 133.1, 133.6, 134.2, 136.3, 136.55, 136.60, 136.8, 140.2, 142.0, 149.7, 155.9, 156.1, 157.6, 157.7, 158.3, 163.4, 166.0 ppm. MS (positive FAB): *m*/*z* = 949 $[M + H]^+$. $C_{62}H_{80}N_2O_6$ (949.32): C 78.48, H 8.44, N 2.95; found: C 78.52, H 8.47, N 2.98.

8: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.5 Hz, 3 H), 0.87 (t, *J* = 7.5 Hz, 3 H), 1.04 (t, *J* = 7.5 Hz, 3 H), 1.05 (t, *J* = 7.5 Hz, 3 H), 1.14 (s, 9 H), 1.26 (s, 9 H), 1.75–1.93 (m, 8 H), 1.50, 1.71, 1,90 (m, 8 H), 3.02, 3.05, 3.09, 3.48 (d, *J* = 13.5 Hz, 1 H_{eq} each), 3.26–3.40 (m, 2 H), 3.52–3.68 (m, 8 H), 3.76–3.86 (m, 8 H), 4.28, 4.33, 4.34, 4.39 (d, 13.5 Hz, 1 H_{ax} each), 5.45 (m, 2 H), 5.84 (dd, *J* = 6.5 Hz, 2.5 Hz, 1 H), 6.10 (d, *J* = 6.5 Hz, 1 H), 6.16 (t, *J* = 6.5 Hz, 1 H), 6.22 (d, *J* = 6.5 Hz, 1 H), 6.59 (s, 1 H), 6.81 (t, *J* = 7.0 Hz, 1 H), 6.92 (d, *J* = 7.0 Hz, 1 H), 6.98 (d, *J* = 7.0 Hz, 1 H), 7.04 (d, *J* = 2.5 Hz, 1 H), 7.22 (d, *J* = 2.5 Hz, 1 H), 8.33 (s, 1 H), 8.76 (s, 1 H), 13.67 (br. s, 1 H), 14.10 (br. s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.09, 10.15, 11.0, 23.07, 23.15, 23.60, 23.69, 24.4, 24.5, 29.3 (× 3), 29.9, 31.16, 31.23, 31.5, 31.7 (× 3), 33.4, 33.7, 34.3, 34.9, 72.7, 72.9, 76.6, 76.9, 77.1, 115.3, 116.7, 117.8, 118.5, 121.8, 122.3, 122.4, 122.7, 124.2, 126.2, 126.8, 127.0 (× 2), 127.2, 127.6, 127.9, 128.4, 128.8, 128.9, 129.7, 132.46, 132.53, 133.7, 137.1, 139.9, 142.4, 150.0, 155.4 (× 2), 157.6, 158.0, 158.3, 163.0, 165.9 ppm. MS (positive FAB): *m*/*z* = 949 $[M + H]^+$. $C_{62}H_{80}N_2O_6$ (949.32): C 78.48, H 8.44, N 2.95; found: C 78.45, H 8.41, N 2.92.

Uranyl Complexes 9–12: To a stirred solution of the ligand **5** or **6** (10 mg, 0.0096 mmol) or **7** or **8** (10 mg, 0.011 mmol) in MeOH (5 mL), solid $(AcO)_2UO_2{\cdot}2H_2O$ (5.94 mg, 0.014 mmol) was added. The mixture was allowed to stir at room temperature for 1 d. The precipited complex was collected by filtration and dried (≈ 74% yield). Crystals of complex **9**, suitable for X-ray analysis, were grown from $MeOH/CH_2Cl_2$ mixture.

9: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82, 0.93, 0,98, 1.12 (t, *J* = 7.5 Hz, 3 H each), 1.29 (br. s, 18 H), 1.79–1.91 (m, 8 H), 2.85, 2.90, 3.07, 3.22 (d, *J* = 14.1 Hz, 1 H_{eq} each), 3.60–3.98 (m, 8 H), 4.23, 4.27, 4.36, 4.43 (d, *J* = 14.1 Hz, 1 H_{ax} each), 5.02 (d, *J* = 7.2 Hz, 1 H), 5.47–5.51 (m, 2 H), 5.61 (d, *J* = 7.2 Hz, 1 H), 5.69 (m, 2 H), 6.02 (s, 1 H), 6.34 (s, 1 H), 6.56–6.62 (m, 3 H), 6.95 (d, *J* = 7.5 Hz, 1 H), 6.80–7.03 (m, 2 H), 7.19, 7.65 (d, *J* = 2.5 Hz, 1 H each), 6.85–7.10 (m, 3 H), 7.46 (d, *J* = 7.5 Hz, 2 H), 7.72 (d, *J* = 7.5 Hz, 2 H), 7.91 (s, 1 H), 9.28, 9.57 (s, 1 H each) ppm. $C_{70}H_{80}N_2O_8U{\cdot}H_2O$ (1333.45): C 63.06, H 6.01, N 2.10; found: C 63.12, H 6.05, N 2.13.

10: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88, 0.92, 0.95, 1.18 (t, *J* = 7.5 Hz, 3 H each), 1.25, 1.46 (s, 9 H each), 1.78–1.96 (m, 8 H), 2.56, 2.83, 3.11, 3.35 (d, *J* = 13.5 Hz, 1 H_{eq} each), 3.64–3.90 (m, 8 H), 4.02, 4.16, 4.39, 4.52 (d, *J* = 13.5 Hz, 1 H_{ax} each), 5.9, 6.2 (ABq, *J* = 11.5 Hz, 1 H each), 5.39 (d, *J* = 7.0 Hz, 1 H), 5.44 (d, *J* = 7.0 Hz, 1 H), 5.49 (t, *J* = 7.0 Hz, 1 H), 5.85 (d, *J* = 7.6 Hz, 1 H), 5.88 (d, *J* = 7.6 Hz, 1 H), 5.96 (t, *J* = 7.6 Hz, 1 H), 6.82 (t, *J* = 7.0 Hz, 1 H), 6.94 (d, *J* = 7.0 Hz, 1 H), 7.05 (d, *J* = 7.6 Hz, 1 H), 6.97, 7.67(d, *J* = 2.75 Hz, 1 H each), 7.10–7.22 (m, 10 H), 7.55 (s, 1 H) 9.07, 9.69 (s, 1 H each) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.77, 9.84, 10.7, 10.9, 22.8, 22.9, 23.0, 23.6, 29.5, 29.7 (× 3), 30.9, 31.2, 31.3, 31.6 (× 3), 33.8, 35.0, 35.2, 75.9, 76.0, 76.6, 79.4, 79.7, 121.2, 121.4, 122.0, 122.6, 123.1, 124.4, 126.1, 126.2, 126.6, 127.1, 127.5, 127.8, 128.6, 128.7 (× 3), 128.9, 129.6 (× 2), 129.9, 130.6, 131.5, 131.7, 132.7, 133.2, 135.9, 136.6, 137.2, 138.7, 140.0, 141.3, 143.5, 151.8, 154.26, 154.32, 155.2, 158.2, 161.4, 161.9, 165.4, 166.6, 173.1 ppm. $C_{70}H_{80}N_2O_8U{\cdot}H_2O$ (1333.45): C 63.06, H 6.01, N 2.10; found: C 63.15, H 6.08, N 2.15.

11: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85–1.04 (m, 12 H), 1.28 (s, 9 H), 1.80 (s, 9 H), 1.75–1.93 (m, 8 H), 1.53–2.50 (m, 8 H), 2.80–3.07 (m, 4 H), 4.20–4.40 (m, 2 H), 3.50–4.01 (m, 8 H), 4.18–4.45 (m, 4 H), 7.75 (br. s, 1 H), 6.30–7.73 (m, 11 H), 9.43 (s, 1 H), 9.64 (s, 1 H) ppm. $C_{62}H_{78}N_2O_8U{\cdot}H_2O$ (1235.35): C 60.29, H 6.32, N 2.27; found: C 60.35, H 6.33, N 2.28.

12: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85–1.04 (m, 12 H), 1.28 (s, 9 H), 1.80 (s, 9 H), 1.77–1.96 (m, 8 H), 1.54–2.57 (m, 8 H), 2.83–3.15 (m, 4 H), 4.25–4.47 (m, 2 H), 3.50–4.05 (m, 8 H), 4.22–4.49 (m, 4 H), 5.80–7.90 (m, 12 H), 10.02 (s, 1 H), 10.20 (s, 1 H) ppm. $C_{62}H_{78}N_2O_8U{\cdot}H_2O$ (1235.35): C 60.29, H 6.32, N 2.27; found: C 60.40, H 6.35, N 2.29.

Mn^{III} Complexes 13–16: To a solution of the ligand **5** or **6** (0.065 g, 0.05 mmol) or 7 or 8 (0.047 g, 0.05 mmol) in abs. EtOH (15 mL) was added a solution of $Mn(OAc)_3{\cdot}2H_2O$ (0.020 g, 0.075 mmol) in EtOH (5 mL). The dark solution was allowed to stir overnight at room temperature and was monitored by TLC (eluent: CH_2Cl_2/cyclohexane, 2:1, v/v). Evaporation of the solvent gave a residue, which was dissolved in CH_2Cl_2, filtered and concentrated to pro-

duce the Mn^{III} catalyst (**13**–**16**) in a nearly quantitative yield. 13: MS (ESI): *m*/*z* 1099 $[LMn]^+$. $C_{72}H_{83}MnN_2O_8$ (1159.39): C 74.61, H 7.17, N 2.42; found: C 74.65, H 7.20, N 2.44.

14: MS (ESI): *m*/*z* = 1099 $[LMn]^+$. $C_{72}H_{83}MnN_2O_8$ (1159.39): C 74.61, H 7.17, N 2.42; found: C 74.69, H 7.15, N 2.40. 15: ESI-MS: *m*/*z* = 1001 $[LMn]^+$. $C_{64}H_{81}MnN_2O_8$ (1061.29): C 72.45, H 7.64, N 2.64; found: C 72.51, H 7.66, N 2.65. 16: MS (ESI) *m*/*z* = 1001 $[LMn]^+$. $C_{64}H_{81}MnN_2O_8$ (1061.20): C 72.45, H 7.64, N 2.64; found: C 72.54, H 7.68, N, 2.66.

X-ray Crystallographic Study: Suitable crystals of this compound were grown at room temperature from a solution in dichloromethane and methanol by slow concentration. Crystal data: $C_{70}H_{82}N_2O_9U{\cdot}0.65(CH_2Cl_2){\cdot}1.6(CH_3OH)$, M = 1439.88, orthorhombic, $P2_12_12_1$ (no. 19), a = 9.899(2), b = 16.956(5), c = 42.349(10) Å, V = 7108(3) Å^3, Z = 4, D_c = 1.346 g cm^{-3}, μ(Cu-$K\alpha$) = 7.329 mm^{-1}, T = 203 K, orange needles; 5833 independent measured reflections, F^2 refinement, R_1 = 0.062, wR_2 = 0.131, 3424 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 120°], 704 parameters. The absolute structure of **9** was determined by an *R*-factor test [R_1^+ = 0.0621, R_1^- = 0.0797]. CCDC-274942 contains the supplementary crystallogrtaphic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The Supporting information (see footnote on the first page of this article) section contains ^{1}H and ^{13}C NMR of reagents and products reported in this paper, APT and g-COSY NMR spectra of calix[4]-arene as well as ^{1}H,^{13}C NMR, T-ROESY, TOCSY spectra of uranyl complexes.

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[12] The tetradentate salen–like calix[4]arene ligand **5** chelates equatorially to the metal centre, which adopts a pentagonal bipyramidal coordination geometry with axial oxo groups and with the remaining equatorial site occupied by an adventitious water molecule. The equatorial atoms are coplanar to within 0.11 Å and the oxo ligands co–linear with their O···O vector inclined by ca. 87° to this plane. The pattern of bonding to the uranium centre does not differ significantly from that observed in, for example, aqua-[*N*,*N*′-ethylenebis(3-ethoxysalicyliden-iminato-*N*,*N*′,*O*,*O*′)]-dioxouranium(VI) (O. Signorini, E. R. Dockal, G. Castellano, G. Olyva, *Polyhedron* **1996**, *15*, 245–255). The two six-membered N,O chelate rings have distinctly different geometries. Ring F has an asymmetric boat conformation with C–4 and the uranium atom lying 0.34 and 1.34 Å respectively out of the plane of the remaining four atoms (which are coplanar to within 0.05 Å), whereas ring G has a much flatter envelope conformation with the metal atom lying only 0.37 Å out of plane (the remaining five atoms are coplanar to 0.03 Å). The five-membered N,N chelate ring has a δ conformation resulting in a *trans*-axial disposition of the two phenyl substituents and a *gauche* relationship for H–31 and H–32 (the H–C–C–H torsion angle is –79°), in agreement with the solution phase NMR spectroscopic data. The calix[4]arene unit has molecular C_{2v} symmetry with all four *n*-propyl groups lying on the same side of the molecule. The aromatic rings A and C are folded "outwards" and inclined by ca. 127°, whilst rings B and D are folded "inwards" and inclined by only ca. 20°. This latter arrangement effectively fills the central cavity of the calix[4]arene, the centroids of rings B and D being separated by only 4.78 Å. The folding of the N,O chelate ring F coupled with the adoption of a δ configuration for the N,N chelate ring results in the C–31 phenyl ring being angled away from the upper face of the calix[4]arene component; the distance of the *ortho* hydrogen on the C–31 phenyl ring to the hydrogen atom *para* to the oxygen on ring D (H–23) is 5.16 Å.
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