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New Chiral Calixsalen Chromium Complexes: Recyclable Asymmetric Catalysts**

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Abstract: A chiral *N*,*N*′-bis(salicylidene)ethylenediamine (salen) polymer has been prepared by a condensation reaction between a thiophenedisalicyladehyde derivative and (*S*,*S*)-cyclohexane-1,2-diamine. This polymeric compound was demonstrated to possess a cyclic structure with two to five repetitive units. The addition of chromium(II) salts led to the generation of a chiral catalyst that could be recovered as an insoluble powder. The performance of this new calixsalen-type catalyst was examined in various transformations, particularly in its ability to promote nucleophilic epoxide ring opening under heterogeneous conditions. The target products were obtained in high yields and with improved selectivity compared with those obtained by using analogous linear polymers. The arrangement of the catalytic sites in the cyclic structure is probably more suitable for the necessary cooperative bimetallic pathway of this demanding reaction. The catalyst could be successfully recycled. This approach represents the first use of calixsalen complexes under heterogeneous catalytic conditions.

Keywords: asymmetric catalysis · catalyst recycling · heterogeneous catalysis · N,O ligands · ring opening

Introduction

Chiral *N*,*N*′-bis(salicylidene)ethylenediamine (salen) complexes have been intensively studied because they constitute one of the main catalyst families that can be used to prepare valuable, highly enantioenriched synthons.[1] Associated with numerous metals, they promote the catalytic enantioselective formation of carbon–carbon[2] or carbon–heteroatom[3] bonds with high efficiencies in terms of both activity and selectivity. Following the principles of green chemistry,[4] one major goal is now to establish efficient procedures for the recovery and reuse of such catalysts. However, although many studies have already been directed towards the fine-tuning of new methods for catalyst recycling,[5] no satisfactory global solution exists that affords the targeted enantiopure product in high yield, free of metal traces, in an economic and environmentally friendly process. Various heterogenization procedures have been described that involve the modification of the salen structure through covalent grafting of organic[6] or inorganic supports.[7] Other methodologies involve noncovalent interactions with different supports based on, for instance, electrostatic exchanges.[8] Whereas the first method involves expensive, time-consuming organic syntheses, the second can suffer from low recyclability due to significant catalyst leaching. Procedures that combine the advantages of both homo- and heterogeneous catalyses often come from modifications of the ligand at some distance from the metallic coordinating sites, leading to a monomer that is suitable for polymerization within the main chain. Some very recent examples have been described dealing with coordination polymers.[9] The most developed procedure, however, involves polycondensation reactions between suitably modified diamine and disalicyladehyde derivatives. For instance, Kureshy and co-workers described the synthesis of salen oligomers by polycondensation, and prepared the corresponding chromium and manganese complexes.[10,11] These catalysts were soluble in the reaction media and were active for kinetic aminolytic epoxide resolution[10] and for kinetic oxidative resolution of secondary alcohols.[11] The complexes were used as homogeneous catalysts and could be recovered and efficiently reused after precipitation in a suitable solvent. In other examples, however, a new class of compound was obtained in which the targeted polymer was not linear, but possessed a macrocyclic structure, named calixsalen. Jablonski and Li prepared such macrocycles with the help of barium salts as templates and ob-

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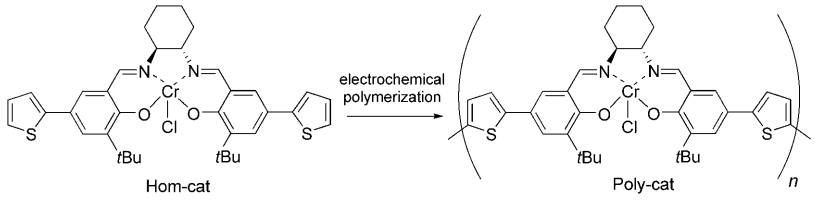
[**] Salen = *N*,*N*′-bis(salicylidene)ethylenediamine.

tained the corresponding manganese complexes, which proved to be active, soluble catalysts that promoted alkene epoxidation reactions.[12] Some reports describe the synthesis of a range of bridged calixsalens,[13] and a number of them were driven towards the selective formation of macrocycles with defined size.[14] Jacobsen et al. reported the synthesis of cobalt–calixsalen complexes, which were obtained as a mixture of different oligomers.[15,16] These catalysts were used for epoxide kinetic resolution under homogeneous conditions to yield the targeted products with excellent enantioselectivities.[15] This mixture was also recently used to mediate intramolecular oxetane ring opening.[16] However, to the best of our knowledge, no complexes involving calixsalen-type structures have yet been used as asymmetric heterogeneous catalysts.

We have previously described the synthesis of chiral thiophene salen chromium monomers and their efficient polymerization by electrochemical anodic oxidation.[17] The monomers (for instance, see Hom-cat in Scheme 1) proved to be suitable catalysts for the promotion of diverse, well-known chromium-driven reactions, and the corresponding insoluble complexes (Poly-cat) were efficiently used for the same transformations as heterogeneous and reusable chiral catalysts.[18] Comparable results in terms of activity and selectivity could be obtained from the homo- and heterogeneous catalyses of hetero-Diels–Alder and Henry reactions.[18a–c] When applied to epoxide ring opening, however, Poly-cat led to a dramatic decrease in the enantioselectivity values relative to its homogeneous counterpart, Hom-cat.[18d] An explanation for these results may possibly be found in the mechanistic pathway proposed to describe the ring opening of epoxides.[3b,19] Indeed, a bimolecular mechanism has now been confirmed that involves two catalytic species acting in a cooperative way to activate both the epoxide ring and the nucleophile. The arrangement of the catalytic sites in the electrogenerated Poly-cat complex in a 'pearl necklace' manner is probably not favorable for this specific optimal positioning of the catalytic sites. Taking these results into account, we report herein our efforts to gain deeper insights into the course of the epoxide ring-opening reaction in the presence of the electrogenerated heterogeneous salen complexes. Furthermore, we have prepared structurally distinct polysalen chromium derivatives through a chemical polycondensation reaction that has led to the generation of new chiral calixsalen–thiophen compounds. These derivatives were also tested as promoters for heterogeneous asymmetric catalysis and the results were compared with those obtained with their linear homologues.



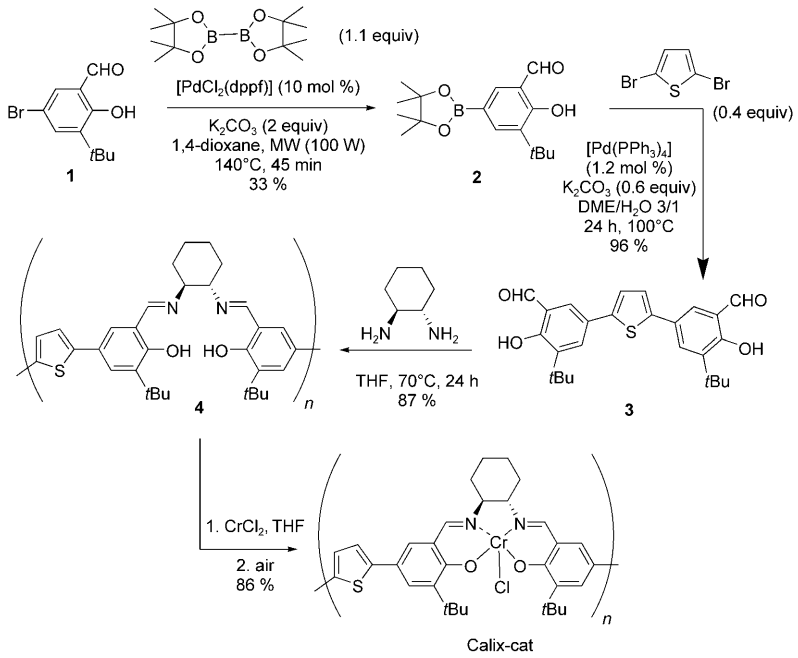
Scheme 1. Electrosynthesis of an insoluble chromium thiophene–salen complex.

Results and Discussion

Synthesis of new polysalen complexes by polycondensation: Aiming to at least match the performance of the best of the electrogenerated Poly-cat complexes, we prepared the new disalicylaldehyde compound **3** as a monomer to be introduced into the polycondensation reaction with well-known (*S*,*S*)-cyclohexane-1,2-diamine. The first route was based on a Suzuki-type coupling reaction between 5-bromo-3-*tert*-butyl-2-hydroxybenzaldehyde (**1**) and commercially available thiophene-2,5-diboronic acid. Such coupling with a diboronic derivative is, however, not a straightforward procedure.[20] Although this strategy was recently reported with analogous compounds,[21] it did not lead to reproducible results in our hands. The opposite approach, however, afforded the expected product **3** (see Scheme 2). The preparation of boronic ester **2** could be fine-tuned by combining the procedures described by Nocera and Yang[22] and DiMauro and Vitullo[23] through the use of bis-(pinacolato)diboron and diphenylphosphinoferrocene (dppf) palladium dichloride as a catalyst under microwave activation. Compound **2** was isolated in a low but constant yield of 33%.

Starting from boronic ester **2** and 2,5-dibromothiophene, a double Suzuki coupling was successfully performed with potassium carbonate as base and palladium tetrakisdiphenylphosphane as catalyst, which was used in a very low ratio.[24] Dimer **3** was isolated in nearly quantitative yield after purification by silica gel chromatography. Subsequent condensation with (*S*,*S*)-cyclohexane-1,2-diamine was performed in THF, in which both compounds were soluble. At the end of the transformation, anhydrous methanol was added, leading to the precipitation of a yellow powder, which was recovered by filtration. The ^{1}H NMR spectrum in $CDCl_3$ revealed a number of similar signals in very close proximity, which was clearly indicative of a mixture of different compounds possessing similar structures. This mixture was further analyzed by MALDI-TOF spectroscopy, and the results indeed indicated the presence of different macrocycles possessing two to five salen units, with each repetitive unit (with the loss of a water molecule) having a molecular mass of 514 g mol^{-1}, thus confirming the presence of cyclic structures **4**.

Attempts were made to separate the macrocycles to obtain well-defined molecules. However, neither silica gel chromatography nor separation by steric exclusion on type LH-20 material led to satisfactory results; NMR spectrosco-



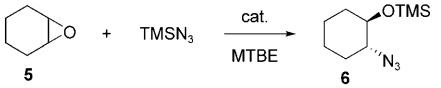
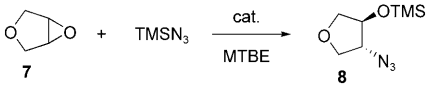
Scheme 2. Synthesis of a new thiophene–salen chromium Calix-cat.

py analysis always indicated mixtures of compounds. This mixture was therefore dissolved in THF and stirred with chromium chloride salts, first under an argon atmosphere and then in the presence of air, following a procedure described by Jacobsen et al. for the preparation of salen–chromium complexes.[25] Calix-cat complexes could thus be isolated in high yield as a brown powder, for which the elemental analysis revealed a slight deficit in the chromium content compared with the total number of possible anchoring sites. These new chiral complexes were then tested, as a mixture, for their ability to promote a number of asymmetric catalytic reactions and, particularly, the asymmetric ring opening of epoxides.

Catalytic tests under homogeneous and heterogeneous conditions: In 1995 Jacobsen and co-workers discovered the ability of chromium–salen complexes to very efficiently promote the ring opening of epoxides with trimethylsilylazide as a nucleophile.[26] They reported high activity and enantioselectivity values of up to 98%. Because mechanistic studies revealed a cooperative bimetallic pathway involving the simultaneous activation of both species,[19] some articles have reported the preparation of chromium dimers to favor this cooperativity.[8a,10a,27] We thus aimed to test our catalysts under both homo- and heterogeneous conditions in epoxide ring-opening reactions using commercially available 7-oxa-bicyclo[4.1.0]heptane (**5**) and 3,6-dioxa-bicyclo[3.1.0]hexane (**7**; prepared according to a reported procedure from dihydrofuran)[28] as substrates. The reactions proceeded in methyl *tert*-butyl ether (MTBE) in the presence of Hom-cat, and led to the expected products in satisfactory to high yields at room temperature (Table 1, entries 1 and 6). The reactions were quite slow, but increasing the temperature to 50°C afforded the products **6** or **8** with shorter reaction times (Table 1, entries 2 and 7). The enantioselectivity values for both compounds nevertheless remained less impressive than the results reported by Jacobsen et al.,[26] clearly indicating that replacement of the sterically hindered donating *tert*-butyl group by a thiophene moiety is accompanied by a distinct reduction of catalyst selectivity. These values are, however, significant enough to be compared to those arising from the use of their heterogeneous counterparts, Poly-cat and Calix-cat.

Poly-cat was then used as an insoluble complex in MTBE and introduced into the transformation of **5**; the reaction was performed at 50°C to favor mass transfer under the heterogeneous conditions. The expected product **6** could be satisfactorily isolated in a very good 85% yield, however, in nearly racemic form (Table 1, entry 3). The complex Poly-cat could be recovered as an insoluble powder in the following way: After complete conversion of the substrate, the solution was removed from the Schlenk tube through a filtration syringe and the remaining powdered catalyst was washed thoroughly with MTBE and then dried. New substrates were then added to the same catalyst to evaluate its recyclability. This complex showed high stability for two further reuses (Table 1, entries 4 and 5) and allowed the prepa-

Table 1. Homogeneous and heterogeneous thiophene–salen chromium complexes in the epoxide ring-opening reactions.

Entry	Catalyst	T [°C]	t [h]	Yield [%][a]	*ee* [%][b]
					
	5			**6**	
1	Hom-cat[c]	20	72	98	49
2		50	24	70	59
3	Poly-cat[d]	50	24	85	5
4[e]		50	24	90	5
5[f]		50	24	97	6
					
	7			**8**	
6	Hom-cat[c]	20	72	40	88
7		50	24	63	70
8	Poly-cat[d]	50	24	95	24

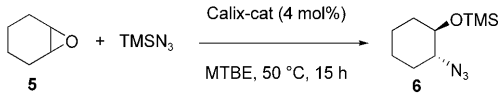
[a] Isolated yield. [b] Enantiomeric excess determined by chiral GC analyses. [c] 2 mol%. [d] 4 mol%. [e] 1st reuse of Poly-cat. [f] 2nd reuse of Poly-cat.

ration of compound **6** with continued high yields. Similarly, Poly-cat catalyzed the ring opening of epoxides **7** at a much lower level of enantioselectivity than its homogeneous counterpart (Table 1, entry 8). We assume that this significant decrease in the selectivity for the transformations that are run under heterogeneous conditions is due to the structure of the polymeric catalyst itself, with the chromium coordinating sites arranged in a pearl necklace manner. The position of the catalytic sites, which is critical for the cooperative bimetallic pathway, is probably not optimal in this case.

To gain more insight into this phenomenon, we then tested the new Calix-cat complexes. Analogously to Poly-cat, these new complexes also lack the important *tert*-butyl groups in the 5- and 5′-positions of the phenol rings, however, they possess a cyclic structure that possibly allows a better arrangement of the catalytic sites for this demanding epoxide ring-opening reaction.

Calix-cat, as a complex oligomeric mixture, was initially used in the transformation of compound **5**. The complex was insoluble in MTBE, the reaction solvent, which allowed the reaction to be run under heterogeneous conditions. To our delight, this new chiral catalyst provided the expected product after 15 h reaction time at 50 °C with a high isolated yield (Table 2, entry 1) and 42 % *ee*. This value is not as high as that obtained with Hom-cat under homogeneous conditions, but it is much improved compared with the same catalytic reaction run with Poly-cat. We assume that this improvement is due to the ability of the cyclic calix structure to arrange the position of the catalytic sites in a favorable manner.

Table 2. Use of Calix-cat in the ring-opening reaction of **5**.



5 **6**

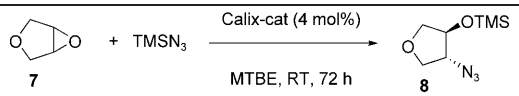
Run	Yield [%][a]	*ee* [%][b]
1	90	42
2	87	36
3	91	41
4	84	36
5	94	22
6	87	27

[a] Isolated yield. [b] Enantiomeric excess determined by chiral GC analyses.

Calix-cat, as an insoluble powder, could also be recovered and reused in successive catalytic runs as reported in Table 2. This catalytic species showed a high stability in respect to its activity, and product **6** could be isolated in consistently high yield for six cycles. This recycling was, however, accompanied by a significant decrease in the selectivity value achieved after each progressive run. This example nevertheless represents, as far as we know, the first use of calixsalen complexes in asymmetric catalytic heterogeneous transformations.

The results could be further improved when the ring-opening reaction of epoxide **7** was performed with trimethylsilylazide at room temperature (see Table 3). The first use of Calix-cat in this transformation allowed the preparation of the target product **8** in 73 % isolated yield with 62 % *ee*, which is a value approaching that obtained with the corresponding homogeneous catalyst (compare Table 3, entry 1, with Table 1, entry 6). With respect to selectivity, Calix-cat is thus confirmed to be a superior catalyst to its equivalent linear analogue, Poly-cat, probably because of its cyclic structure, which facilitates bimolecular catalysis. The enantioselectivity value obtained with this heterogeneous catalyst did not reach the maximal value obtained with the homogeneous species (i.e., 88 %), probably because Calix-cat is a mixture of differently sized macrocycles, which leads to an average, not optimized, value. Work is in progress to separate these macrocycles so that the optimal ring size for this challenging transformation can be found.

Table 3. Use of Calix-cat in the ring-opening reaction of **7**.



7 **8**

Run	Yield [%][a]	*ee* [%][b]
1	73	62
2	47	64
3	66	64
4	62	67
5	64	66

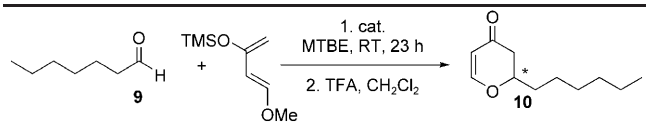
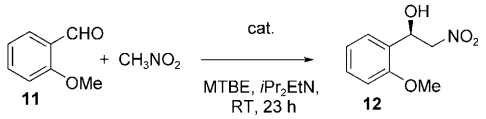
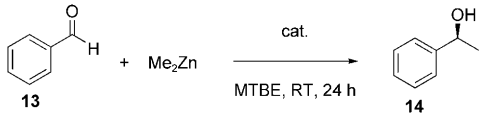
[a] Isolated yield. [b] Enantiomeric excess determined by chiral GC analyses.

Calix-cat could also be recovered after the first run of the reaction and new substrates added for its reuse in four new consecutive runs. To our delight, under these optimized reaction conditions, compound **8** could be isolated with a remarkably stable enantioselectivity and in satisfying yields. Calix-cat derived from chromium thiophene–salen complexes are thus good candidates for the efficient promotion of epoxide ring-opening reactions, as new chiral heterogeneous recyclable catalysts.

We have previously reported[18] the efficient use of the electrogenerated polymer Poly-cat to catalyze the hetero Diels–Alder reaction,[25,29] the Henry reaction,[30] and the addition of dimethylzinc to aldehydes.[31] Corresponding Calix-cat salen was also applied to these transformations to test its suitability as an asymmetric catalyst. The first reaction involved the hetero-Diels–Alder reaction between heptanal **9** and Danishefsky's diene at room temperature in MTBE. 2-Hexyl-2,3-dihydropyran-4-one (**10**) was isolated with an enantioselectivity value similar to that obtained by using Poly-cat and in a similar yield (Table 4, entries 1–3). It is known that, for this transformation, no bimolecular mechanism is required for efficient catalysis and, although they possess clearly different macrostructures, both heterogene-

ous catalysts led to the same activity, probably due to a similar arrangement of catalytic sites. We then tested a different transformation: the nitroaldol reaction between 2-methoxybenzaldehyde (**11**) and nitromethane, to afford 1-(2-methoxyphenyl)-2-nitroethanol (**12**; Table 4, entries 4–6). In this case, again, Calix-cat was found to be an efficient catalyst, affording the expected product in satisfactory yield and enantioselectivity. Under these heterogeneous conditions, the transfer of chirality occurred smoothly from both insoluble polymers. Finally, the addition of dimethylzinc to aldehydes, recently described by Cozzi and Kotrusz,[31] was also attempted in the presence of Calix-cat. The monomeric chromium thiophene–salen species Hom-cat showed high activity and enantioselectivity for this transformation, providing compound **14** from benzaldehyde with 93% *ee* (Table 4, entry 7). Surprisingly, we found that the electrogenerated complex Poly-cat was almost inactive for this transformation (Table 4, entry 8), whereas Calix-cat afforded 1-phenylethanol with 60% *ee*, albeit in low yield (Table 4, entry 9). The mechanism of this reaction is not well understood, but the increase in enantioselectivity obtained through the use of cyclic structures may indicate a possible bimetallic intermediate.

Table 4. Monomeric and polymeric chromium thiophen–salen complexes as chiral catalysts.

Entry	Catalyst	Yield [%][a]	*ee* [%][b]
			
1	Hom-cat[c]	53	72
2	Poly-cat[d]	63	63
3	Calix-cat[d]	58	61
			
4	Hom-cat[c]	88	74
5	Poly-cat[d]	92	54
6	Calix-cat[d]	77	65
			
7	Hom-cat[c]	79	93
8	Poly-cat[d]	5	20
9	Calix-cat[d]	30	60

[a] Isolated yield. [b] Enantiomeric excess determined by chiral GC or HPLC analyses. [c] 2 mol%. [d] 4 mol%.

Conclusion

An efficient synthetic procedure for the preparation of new chiral calixsalen-type chromium complexes has been described. These compounds were tested as heterogeneous catalysts in different transformations and, particularly, in enantioselective epoxide ring opening. They compared well with the homogeneous monomer counterparts in terms of activity, and allowed the preparation of target products with satisfactory levels of enantioselectivity. Furthermore, they proved to be much more selective than analogous catalysts possessing a linear polymeric structure, thus confirming that their cyclic structure was more suitable for transformations involving a bimolecular activation mechanism. Interestingly, these macrocyclic chiral chromium complexes were insoluble in the reaction mixture, thus, they act as heterogeneous catalysts. They could be recovered by filtration and efficiently reused to promote the transformation of a new substrate batch. As far as we know, this report represents the first use and recycling of calixsalen complexes under heterogeneous catalytic conditions. Work is underway to evaluate the ability of these new structures to promote other asymmetric catalytic transformations, either as a mixture or as isolated species.

Experimental Section

General methods: All reactions were carried out under an argon atmosphere in oven-dried glassware with magnetic stirring. Solvents were distilled before use: THF from sodium metal/benzophenone, and MTBE, DME, 1,4-dioxane, and CH_2Cl_2 from calcium hydride. 7-Oxa-bicyclo-[4.1.0]heptane (**5**) was purchased from Aldrich and 3,6-dioxa-bicyclo-[3.1.0]hexane (**7**) was prepared according to a reported procedure from dihydrofuran.[28] The epoxides were distilled before use and trimethylsilylazide was used as received from commercial sources. The synthesis of Hom-cat and Poly-cat were performed as previously described, as were the hetero Diels–Alder, the Henry reaction, and the addition of dimethylzinc to benzaldehyde.[18] ^1H and ^{13}C NMR spectra were recorded with either Bruker AM 360 (360 MHz), AM 300 (300 MHz), or AM 250 (250 MHz) instruments with samples dissolved in $CDCl_3$; data are reported in ppm with the solvent signal as reference ($\delta = 7.27$ ppm for ^1H NMR and $\delta = 77$ ppm for ^{13}C NMR). Optical rotations were measured at the sodium D-line for solutions in 10 cm cells with a Perkin–Elmer 241 polarimeter. IR spectra were recorded as KBr disks with a Perkin–Elmer spectrometer. Mass spectra were recorded with a Finnigan MAT 95 S spectrometer. UV/Vis experiments were performed with a Uvikon polarimeter from Bio-tek instruments. GC analyses were carried out with a GC430 Varian instrument equipped with a FID detector and a split/splitless injector.

3-*tert*-Butyl-2-hydroxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (2): 3-*tert*-Butyl-5-bromo-2-hydroxybenzaldehyde (500 mg, 1.94 mmol), bis(pinacolato)diborane (543 mg, 2.14 mmol), potassium carbonate (538 mg, 3.89 mmol), and [$PdCl_2$(dppf)] (159 mg, 0.19 mmol) were introduced into a 10 mL microwave reaction vessel, and 1,4-dioxane (2.5 mL) was added. The vessel was sealed and the mixture was heated in the microwave for 45 min at 140 °C (100 W) then allowed to cool to RT. The mixture was filtered through Celite and the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel (heptane/diethyl ether 90:10) to afford **2** as a yellow solid (175 mg, 33%). M.p. 86–88 °C; ^1H NMR (250 MHz, $CDCl_3$): $\delta =$ 12.00 (s, 1H), 9.91 (s, 1H), 7.93–7.89 (m, 2H), 1.44 (s, 9H), 1.36 ppm (s, 12H); ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 197.5$, 163.6, 140.0, 139.9, 137.4, 120.4, 83.9, 34.8, 29.2, 24.8 ppm; MS (EI): *m/z* (%): 304 (20), 290 (17), 289 (100), 288 (26).

2,5-Di[5-(3-*tert*-butyl-2-hydroxybenzaldehyde)]thiophene (3): A Schlenk tube was charged with **2** (175 mg, 0.58 mmol), 2,5-dibromothiophene (26 μL, 0.23 mmol), [$Pd(PPh_3)_4$] (8 mg, 0.007 mmol), and K_2CO_3 (48 mg, 0.35 mmol) and the mixture was placed under argon by successive

vacuum–argon cycles (3 h). Thoroughly degassed DME (460 μL) and degassed water (154 μL) were introduced into the Schlenk tube by using a cannula. The mixture was heated at 100 °C for 24 h, then water (10 mL) was added and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel (cyclohexane/ethyl acetate, 90:10) to afford **3** as a yellow solid (112 mg, 96 %). M.p. 135 °C; ^{1}H NMR (360 MHz, $CDCl_3$): $\delta = 11.86$ (s, 2H), 9.95 (s, 2H), 7.81 (d, $J = 2.2$ Hz, 2H), 7.64 (d, $J = 2.2$ Hz, 2H), 7.23 (s, 2H), 1.52 ppm (s, 18H); ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 197.0$, 160.7, 142.1, 139.1, 131.6, 128.5, 125.8, 123.4, 120.6, 35.0, 29.3 ppm. HRMS (ESI): m/z: calcd for $C_{26}H_{27}O_4S$ [M – H]: 435.1630; found: 435.1637.

Calixsalen ligand 4: (*S*,*S*)-Cyclohexane-1,2-diamine (145 mg, 1.27 mmol) was added to a solution of dialdehyde **3** (553 mg, 1.27 mmol) in THF (18 mL) with continuous stirring, and the mixture was heated at 70 °C for 24 h. The reaction was cooled to RT, THF was partially evaporated and methanol was added. The solid was filtered and washed with cold methanol to afford **4** as a yellow powder (538 mg, 83 %). M.p. 173–177 °C; ^{1}H NMR (360 MHz, $CDCl_3$): $\delta = 14.40$–13.72 (m, 2H), 8.65–8.28 (m, 2H), 7.68–6.72 (m, 6H), 3.48–3.05 (m, 2H), 2.18–1.62 (m, 8H), 1.48 ppm (s, 18H); ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 213.8$, 165.4, 160,2, 160.1, 160.0, 142.5, 142.4, 137.8, 137.7, 127.4, 127.2, 126.6, 126.4, 124.6, 124.5, 122.5, 122.4, 118.6, 118.5, 118.4, 34.9, 29.5 ppm. IR (KBr): $\tilde{\nu} = 2936$, 2862, 1629, 1439 cm^{-1}; $[\alpha]_D^{20} = -33$ (c 1.0, $CHCl_3$); UV/Vis (CH_3CN): λ_{max} (ε) = 221, 250, 347 nm.

Calix-cat: Chiral ligand **4** (150 mg, 0.29 mmol) in anhydrous, degassed THF (5 mL) was added to a solution of anhydrous $CrCl_2$ (39.4 mg, 0.32 mmol) in anhydrous, degassed THF (5 mL). The resulting brown solution was stirred for 2 h under argon and then exposed to air. Stirring was continued overnight to give a dark-brown solution, which was diluted with CH_2Cl_2 and washed with sat. NH_4Cl and brine. The organic layer was dried over $MgSO_4$ and solvents were removed under reduced pressure to afford the expected complex (130 mg, 74 %). IR (KBr): $\tilde{\nu} = 2939$, 2862, 1622 cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{36}ClCrN_2O_2S_2$ (632): C 64.04, H 6.05, N 4.67, S 5.34, Cl 5.91, Cr 8.66; found: C 59.70, H 6.82, N 3.76, S 3.99, Cl 4.63, Cr 4.95; $[\alpha]_D^{20} = +371$ (c 0.18, $CHCl_3$); UV/Vis (CH_3CN) : λ_{max} (ε) = 226, 359 nm.

Epoxide ring-opening reaction under homogeneous conditions: A Schlenk tube was charged with Hom-cat (2 mol %) and placed under an argon atmosphere by three successive vacuum–argon cycles. MTBE (330 μL) and the epoxide (1 mmol) were introduced by using a syringe. The resulting solution was stirred at the given temperature and then trimethylsilylazide (197 μL, 1.5 mmol) was introduced. The mixture was stirred for the specified amount of time. The mixture was purified by filtration through Celite and the solvents were removed under reduced pressure, to give the product, which was used to determine the yield of the reaction and the enantiomeric excess.

Heterogeneous conditions: A Schlenk tube was charged with Poly-cat or Calix-cat (4 mol %) and placed under an argon atmosphere by three successive vacuum–argon cycles. MTBE (330 μL) and the epoxide (1 mmol) were introduced by using a syringe. The resulting solution was stirred at the given temperature and then trimethylsilylazide (197 μL, 1.5 mmol) was introduced. The mixture was stirred for the specified amount of time, then filtered with a filtering syringe. The solution was purified by filtration through Celite and the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel to give the product, which was used to determine the yield of the reaction and the enantiomeric excess. In the Schlenk tube, the catalyst was dried under vacuum and new substrates and solvents were added for reuse.

(1*R*,2*R*)-1-Azido-2-trimethylsiloxycyclohexane (6): Colorless oil; $[\alpha]_D^{20} = +18.5$ (c 0.99, $CHCl_3$) for 58 % *ee*, Lit.[26]: $[\alpha]_D^{23} = -22.4$ (c 2.87, $CHCl_3$) for 88 % *ee* material. The absolute stereochemistry was assigned as (1*R*,2*R*) based on comparison of the measured rotation with the literature value.[26] The *ee* was determined by GC analysis using a chiraldex column (50 m × 0.25 mm × 0.25 μm, 120 °C), which resolved both enantiomers [t_R(major) = 9.82 min, t_R(minor) = 10.17 min]. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.49$–3.37 (m, 1H), 3.21–3.08 (m, 1H), 1.96–1.81 (m, 2H), 1.71–1.57 (m, 2H), 1.41–1.02 (m, 4H), 0.14 ppm (s, 9H); ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 75.1$, 66.6, 34.5, 30.4, 24.0, 23.8, −0.1 ppm. MS (IE): m/z (%): 170 (32), 143 (21), 142 (69), 129 (26), 118 (29), 75 (86), 73 (100), 45 (15).

(3*R*,4*S*)-3-Azido-4-trimethylsiloxytetrahydrofurane (8): Colorless oil; $[\alpha]_D^{20} = -20.8$ (c 1.02, $CHCl_3$) for 36 % *ee*, Lit.[26]: $[\alpha]_D^{23} = +64.0$ (c 2.35, $CHCl_3$) for 98 % *ee* material. The absolute stereochemistry was assigned as (3*R*,4*S*) based on comparison of the measured rotation with the literature value.[26] The *ee* was determined by GC analysis using a chiraldex column (50 m × 0.25 mm × 0.25 μm, 120 °C), which resolved both enantiomers [t_R(major) = 7.73 min, t_R(minor) = 7.86 min]. ^{1}H NMR (360 MHz, $CDCl_3$): $\delta = 4.25$–4.21 (m, 1H), 3.99 (ddd, $J = 4.6$, 9.4, 19.7 Hz, 2H), 3.83–3.74 (m, 2H), 3.6 (dd, $J = 2.7$, 9.4 Hz, 1H), 0.15 ppm (s, 9H); ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 76.2$, 74.1, 70.2, 67.6, −0.3 ppm; MS (EI): m/z (%): 144 (14), 117 (26), 102 (51), 101 (73), 75 (30), 73 (100), 59 (24), 45 (20).

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