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Chromium-Thiophene-salen-Based Polymers for Heterogeneous Asymmetric Hetero-Diels–Alder Reactions

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New chiral thiophene-salen ligands have been synthesized and the corresponding chromium complexes proved to be efficient catalysts for promoting asymmetric hetero-Diels–Alder reactions with good activities and high enantioselectivities (up to 88 % *ee*). These complexes were successfully electropolymerized to give chiral polymers as insoluble powders for use in asymmetric heterogeneous catalysis. When engaged in successive hetero-Diels–Alder reactions, they afforded the expected products in high yield and enantioselectivity showing no loss of efficiency for up to 15 cycles. A chiral chromium-salen-thiophene polymer was also successfully used in a multi-substrate procedure in which a new, structurally different aldehyde was introduced for each reuse to afford the desired pyranone in its pure form.

Introduction

Tremendous work has already been carried out particularly in the academic world to perform enantioselective heterogeneous catalysis in the presence of immobilized catalysts.[1] Such procedures should be particularly outstanding for the preparation of elaborated enantiopure valuable compounds in an economic and environmentally friendly way. Indeed, asymmetric catalysis represents the best method, according to the principles of green chemistry, for synthesizing chiral enantioenriched compounds. The efficient recovery and reuse of the asymmetric catalysts would furthermore improve the procedure in terms of cost, safety and practicality. Interesting results have already been reported with well-known catalysts efficient in asymmetric C–C bond formation, such as salen derivatives[2] or bis(oxazoline) ligands.[3] Numerous strategies for their immobilization have already been reported, for example, covalent grafting onto either organic or inorganic supports. Procedures involving the polymerization of the modified ligands have also been described as well as recycling methodologies based on non-covalent interactions, filtration through membranes and biphasic separations. These methods have been applied to numerous catalytic transformations leading to some success, but they generally suffer from a too rapid loss of activity (leaching of the catalyst) and/or of enantioselectivity during the reuses. Tetradentate Schiff bases, for example, *N*,*N*′-bis(salicylidene)ethylenediamine, commonly named salen, are one of the most important classes of ligand as they are very efficient, can be complexed with different metals and perform a large variety of catalytic transformations.[4] In this context, we recently described the synthesis and the electropolymerization of new chiral thiophene-salen complexes for the preparation of insoluble organic conducting polymers.[5] The electropolymerization of metal-functionalized thiophene derivatives[6] is an original methodology for the preparation of immobilized catalysts and to the best of our knowledge only one recent example has been reported of the efficient use of the corresponding complexes as recyclable catalysts, albeit in a non-enantioselective fashion.[7] Our new enantiopure chromium polymer complexes were successfully used as efficient heterogeneous catalysts for the asymmetric hetero-Diels–Alder (HDA) reaction of various aldehydes,[8] a rare example of this reaction performed under heterogeneous conditions.[9] We were able to recycle our catalysts up to six times with stable enantiomeric excesses, but a slight decrease in the activity was observed. We report herein the synthesis of new chromium-thiophene-salen complexes together with an improved methodology for the recovery of the corresponding heterogenized complexes. Furthermore, we describe their use in an original multi-substrate procedure.

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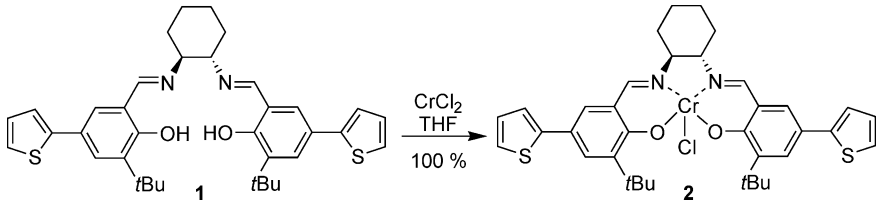
Results and Discussion

Synthesis of Ligands and the Corresponding Chromium Complexes

Salen derivatives substituted by thiophene moieties at the 5,5′-positions of the salen phenol rings were first synthesized in the study of their polymerization by electrochemical oxidation. The monomer synthesis was based on a palladium-catalyzed Suzuki coupling followed by condensation with (1*S*,2*S*)-cyclohexane-1,2-diamine which afforded the



Scheme 1. Synthesis of chromium-thiophene-salen complex **2**.

modified ligand **1** in high overall yield, as we have already reported.[5] The preparation of the corresponding chromium complex **2** (Scheme 1) was realized by reaction of the chiral ligand **1** with chromium dichloride under an inert atmosphere following the procedure described by Jacobsen and co-workers.[10a]

Dark-brown single crystals suitable for X-ray analysis were obtained by slow condensation of hexane into a concentrated THF solution of **2** at room temperature. Complex **2** crystallizes in the C_2 space group with two crystallographically independent molecules in the asymmetric unit. Complex **2** crystallizes as a THF solvate containing two molecules of THF per molecule of the complex, with one THF occupying an apical position. Figure 1 displays the thermal ellipsoid drawing of one of the two independent chromium complexes found in the unit and selected average bond lengths and angles are given in Table 1.

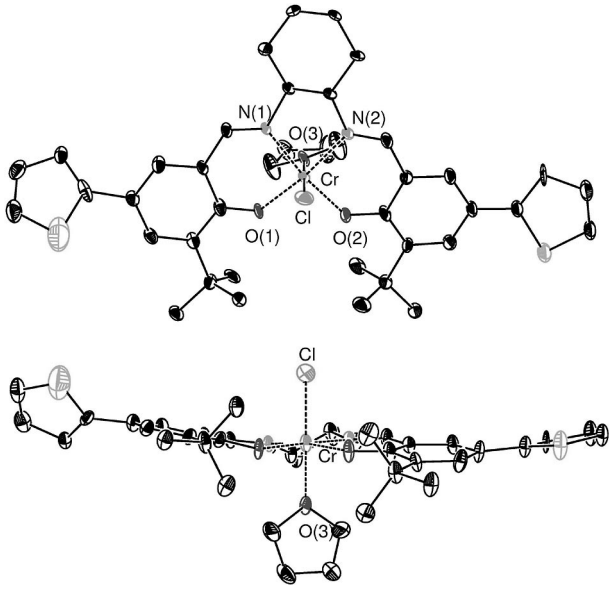


Figure 1. ORTEP drawing of complex **2** showing the atom labeling scheme. Ellipsoids are drawn at the 50% probability level. The THF solvate has been omitted. The hydrogen atoms have been omitted for the sake of clarity.

Complex **2** possesses a very similar structure to that of Jacobsen's chromium catalyst.[11] The Cr atom adopts a slightly distorted square-bipyramidal geometry with four equatorial [N(1), N(2), O(1) and O(2)] atoms and two axial [Cl and O(3)THF] atoms. The quadridentate ligand is in its stable planar conformation with the metal exactly in the plane [0.01(2) Å]. Furthermore, the absolute structure parameter (Flack) was refined to a value of 0.02(3), which is indicative of the correct stereochemistry. Compared with the analogous *t*Bu-substituted complex, the new thiophene-salen complex exhibits larger bond angles around the chromium atom. This less sterically defined environment around the catalytic centre may be responsible for the lower enantiofacial discrimination observed during the catalytic asymmetric transformations (see below). Furthermore, both thiophene rings are twisted, probably to ensure lower steric hindrance in the complex.

Table 1. Selected average bond lengths [Å] and bond angles [°] for chromium complex **2**.

Cr–Cl	2.311(2)	Cr–O(1)	1.913(4)
Cr–O(2)	1.923(4)	Cr–O(3)	2.083(6)
Cr–N(1)	2.010(5)	Cr–N(2)	2.023(5)
Cl–Cr–O(1)	92.9(2)	Cl–Cr–O(2)	94.0(2)
Cl–Cr–O(3)	178.6(2)	Cl–Cr–N(1)	93.7(2)
Cl–Cr–N(2)	90.4(2)	O(1)–Cr–O(2)	95.9(2)
O(1)–Cr–O(3)	87.3(2)	O(1)–Cr–N(1)	90.3(2)
O(1)–Cr–N(2)	172.3(2)	O(2)–Cr–O(3)	86.1(2)
O(2)–Cr–N(1)	169.0(2)	O(2)–Cr–N(2)	90.7(2)
O(3)–Cr–N(1)	85.8(3)	O(3)–Cr–N(2)	88.9(4)
N(1)–Cr–N(2)	82.5(2)		

Electrochemical Polymerization

Numerous electrochemical investigations have been performed with poly(metal–salens) owing to the easy synthesis of salen-type ligands and their ability to incorporate a wide variety of transition metals. Kingsborough and Swager prepared various monomers bearing thiophene substituents *para* to the phenolic oxygen of the salen backbone which could electropolymerize at low potentials.[12] These polymers were able to perform oxygen reduction with very high efficiency.[13] We previously reported the oxidative electropolymerization of various thiophene-salen chiral complexes under cyclic voltammetry conditions.[5] In all cases, polymerization occurred easily, typically between 0.0 and +1.25 V/SCE, leading to the formation of robust films at the platinum surface. The evolution of the current intensity when the potential was scanned several times between 0.0 and +1.25 V is shown in Figure 2 (left part) for complex **2** in dichloromethane containing nBu$_4$NBF$_4$ (0.1 M) as the electrolyte. As is typical of organic conducting polymers, the oxidation of the monomer led to the appearance of a reduction wave after the first scan which increased during successive scans, which clearly indicates the formation of a polymeric film of conducting material at the electrode

surface. The modified electrode was then washed and introduced into a new electrolytic media free of monomers. The voltammogram resulting from more than 50 cycles is represented in the right part of Figure 2. The electrochemical response is characteristic for a reversible system with no variation of the current intensity during the experiment. These observations clearly proved the formation of a very chemically and electrochemically stable film on the surface of the electrode.

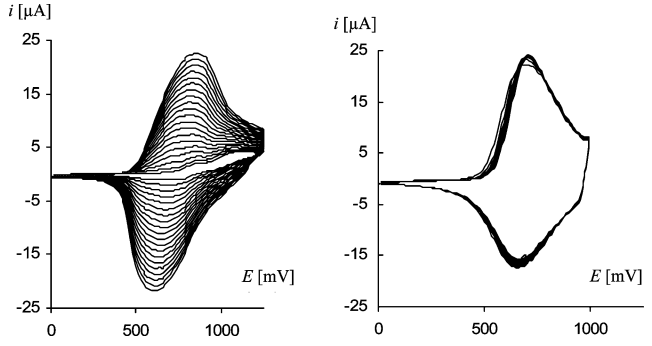


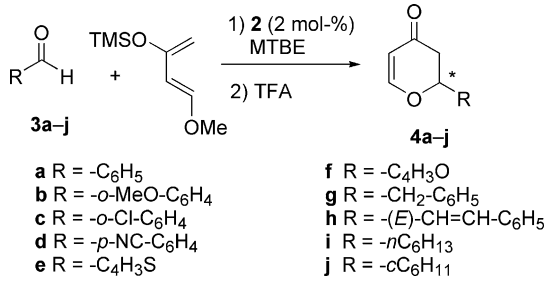
Figure 2. Left: anodic polymerization of chromium complex **2** (0.05 M) in CH_2Cl_2 with nBu_4NBF_4 (0.1 M), v = 100 mV/s. Right: analysis of the polymer-coated electrode in CH_3CN with nBu_4NBF_4 (0.1 M), v = 100 mV/s.

In order to synthesize larger quantities of polymers, various conditions were tested for preparative electropolymerization on a platinum grid (2.25 cm^2). The optimized procedure involved polymerization in dichloromethane containing nBu_4NBF_4 (0.1 M) at a controlled current of 50 mA which led to the formation of a more insoluble polymer (Scheme 2). The polymer was recovered as a dark-brown powder from the electrode in 43% yield. After several washings, the chiral chromium-thiophene-salen polymer was tested as a catalyst in the HDA reaction between various aldehydes and 1-methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene (Danishefsky's diene).

Catalytic Hetero-Diels–Alder Reactions Under Homogeneous Conditions

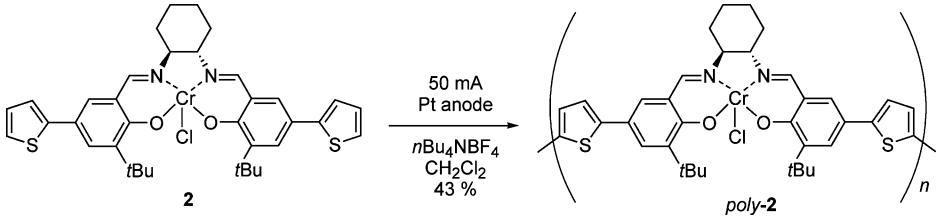
Jacobsen and co-workers[10a] described the HDA transformation of benzaldehyde to the corresponding 2-phenyl-2,3-dihydro-4*H*-pyran-4-one with an *ee* of up to 87% using the tetrafluoroborate chromium complex of (*R*,*R*)-(–)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine at –30 °C in methyl *tert*-butyl ether (MTBE). Katsuki and coworkers reported up to 97% *ee* in an analogous reaction in the presence of salen complexes bearing binaphthyl subunits as additional chiral auxiliaries.[10b] We first tested complex **2** under similar homogeneous conditions to optimize its efficiency before using *poly*-**2** as the heterogeneous catalyst in successive runs.

Various aromatic and aliphatic aldehydes were engaged at room temperature and at –40 °C as substrates for the HDA reaction (Scheme 3) in the presence of Danishefsky's diene. Subsequent treatment of the reaction mixture with trifluoroacetic acid led to the synthesis of the corresponding pyranones. A wide choice of diversely functionalized aldehydes is available and has already been used in this reaction for the preparation of various substituted pyranones. Also, some new products have been prepared in this work. In all cases, complex **2** was efficient in terms of both activity and enantioselectivity, as reported in Table 2. All the products were isolated in moderate-to-high yields (up to 98%, see entry 4).



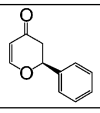
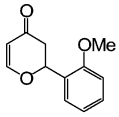
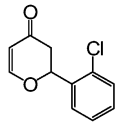
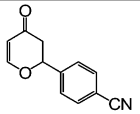
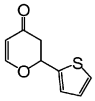
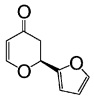
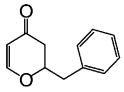
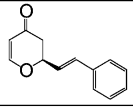
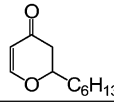
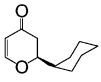
Scheme 3. HDA reaction of various aldehydes with Danishefsky's diene in the presence of chiral complex **2**.

At room temperature, complete conversion was observed in about 1 day and the reaction time was increased to 3 days for transformations conducted at –40 °C. Various aromatic aldehydes (**3a**–**f**, entries 1–6) were tested in order to evaluate the electronic effects of different substituents on the enantioselectivity of the reaction. Benzaldehydes substituted with electron-donating (*o*-MeO or *o*-Cl, entries 2–3) or -withdrawing groups (*p*-CN, entry 4) were engaged in the reaction and afforded the desired pyranones **4b**, **4c** or **4d** without significant variation of enantioselectivity according to the substituent. Thiophene-2-carbaldehyde and 2-furaldehyde were also tested in this reaction (entries 5 and 6) and gave the expected modified pyranones with up to 64% *ee*. Surprisingly, in the case of furaldehyde the reaction afforded 2-furan-2-yl-2,3-dihydro-4*H*-pyran-4-one (**4f**) but the results were irreproducible in terms of activity and enantioselectivity giving the lowest *ee* obtained in these



Scheme 2. Anodic polymerization of complex **2** in the synthesis of *poly*-**2**.

Table 2. HDA reaction between various aldehydes and Danishefsky's diene promoted by complex **2** in MTBE.

Entry	Product		T [°C]	t [h]	% Yield[a]	% *ee*[b]
1		**4a**	20	23	70	56
			– 40	68	92	54
2		**4b**	20	19	81	60
			– 40	64	70	64
3		**4c**	20	19	92	60
			– 40	65	84	67
4		**4d**	20	23	91	69
			– 40	69	98	70
5		**4e**	20	23	94	56
			– 40	69	34	64
6		**4f**	20	23	82	14
			– 40	60	65	57
7		**4g**	20	23	50	60
			– 40	66	81	78
8		**4h**	20	23	85	45
			– 40	66	19	69
9		**4i**	20	19	53	72
			– 40	65	42	82
10		**4j**	20	22	79	72
			– 40	68	58	81

[a] Isolated yields. [b] *ee* determined by chiral HPLC analyses (see Exp. Sect.).

tests at room temperature (14% *ee*, see entry 6). In addition, various aliphatic aldehydes were engaged in the HDA reaction catalyzed by **2** under the same conditions (see entries 7–10). All the pyranones were isolated in moderate-to-high yields except for the *trans*-cinnamaldehyde-substituted product at –40 °C. The enantiomeric excesses of the products obtained from the aliphatic aldehydes were slightly higher than those observed with the aromatic substrates. This was particularly true for the heptanal- and cyclohexane-derived pyranones (entries 9 and 10) and up to 82% *ee* was achieved for 2-hexyl-2,3-dihydro-4*H*-pyran-4-one (**4i**) at –40 °C.

Complex **2** thus proved to be an efficient catalyst for the formation of various scalemic pyranones although the products were generally obtained with lower enantiomeric excesses than those prepared using Jacobsen's or Katsuki's chromium-salen complexes. Replacing the *t*Bu groups on the salen core by thiophene ones had a detrimental effect in terms of enantioselectivity, probably as a result of different electronic and steric constraints, as was observed in the X-ray analysis performed on complex **2**.

HDA Reactions Under Catalytic Heterogeneous Conditions

These reactions were then studied under heterogeneous conditions in the presence of the polymerized catalyst *poly*-**2** as an insoluble, recyclable powder. The catalyst was reused by filtering it through a syringe equipped with a sintered glass, an optimized procedure for efficient recycling. The soluble part of the mixture containing the reaction products was thus removed from the reaction vessel and treated with trifluoroacetic acid before analysis. The remaining polymerized catalyst was washed several times with the reaction solvent, dried under vacuum and finally was recycled by adding new substrates and solvent to the same reaction vessel.

The ability of the polymerized catalyst *poly*-**2** to promote the HDA reaction under heterogeneous conditions was first tested in the synthesis of 2-cyclohexyl-2,3-dihydro-4*H*-pyran-4-one (**4j**) as cyclohexanecarbaldehyde had led to promising results in the presence of complex **2** as catalyst. Although we have previously reported a recycling procedure based on centrifugation that allowed the reuse of the catalyst up to six times with constant enantioselectivity values, a significant decrease in activity was observed.[8] Therefore we report in Table 3 the results obtained with the above-described optimized filtration methodology.

Table 3. Heterogeneous HDA reaction between cyclohexanecarbaldehyde (**3j**) and Danishefsky's diene promoted by 4 mol-% of *poly*-**2** at room temperature.

Entry	Cycles	t [h]	% Yield[a]	% *ee*[b]
1	1	21	27	54
2	4	21	61	60
3	7	22	49	52
4	10	18	41	55
5	15	68	68	57

[a] Isolated yield. [b] *ee* determined by chiral HPLC analysis.

The first use of *poly*-**2** (entry 1) demonstrated its ability to catalyze the reaction under heterogeneous conditions. The expected product was indeed isolated with 54% *ee* but in a modest yield (27%) in the same reaction time as that required for the homogeneous catalysis. Note the slight decrease observed in the enantioselectivity with *poly*-**2** compared with that obtained with complex **2**. We assume that the polymerization procedure probably affects the structural environment around the active chromium catalytic centre and modifies the bite angles with the decrease in enantioselectivity a consequence. The insoluble catalyst was

recovered as described above and reused up to 14 times.[14] Some activity and enantioselectivity values are reported in Table 3 and prove the high efficiency of *poly*-**2** in promoting this transformation numerous times. For example, in the fourth cycle (entry 2), the expected product was isolated in a good yield and with an enantiomeric excess that remained almost constant for all the reuses. The last cycle (entry 5) provided proof of the excellent stability of *poly*-**2** as the product **4j** was still isolated in a good yield and with the same enantioselectivity as at the beginning of the recycling procedure. Such high stability, proven with 15 efficient uses of the catalyst, has rarely been reported in the literature.

We therefore engaged our heterogeneous polymer catalyst *poly*-**2** in a multi-substrate recycling procedure (see Table 4). This approach involves introducing new structurally different aldehydes at each recycling of the polymer catalyst. As far as we know, such a procedure has rarely been described in the literature.[15] As the efficiency of the corresponding monomer catalyst **2** was previously evaluated with different substrates in homogeneous conditions, *poly*-**2** was tested and recycled in the presence of those same aldehydes (see Table 4).

The first hetero-Diels–Alder reaction was performed with 2-chlorobenzaldehyde (**3c**) in the presence of 4 mol-% of *poly*-**2** as heterogeneous catalyst at room temperature in MTBE and afforded the expected pyranone **4c** in high yield and with an enantioselectivity slightly lower than the value obtained in the homogeneous catalytic transformation (45% *ee* in Table 4 and 60% *ee* in Table 2). 2-Methoxybenzaldehyde (**3b**) was then engaged in the second run and 2-(2-methoxyphenyl)-2,3-dihydro-4*H*-pyran-4-one (**4b**) was interestingly obtained in high yield and enantioselectivity, free of any traces of the product from the preceding run. Eight different aldehydes were then successively used in the reaction with Danishefsky's diene and the corresponding pyranones were isolated in each case in their pure form with satisfactory yields and enantioselectivities. After this first reaction sequence (cycle 1 to cycle 10 in Table 4), 2-chlorobenzaldehyde was again used in the 11th run to give the pyranone **4c** with a remarkably very stable enantioselectivity compared with run 1. The recycling procedure continued under these conditions was successful as all the expected products were isolated with satisfactory yields and the same enantioselectivities as those obtained from the corresponding run of the preceding sequence. This series of experiments attests to the high stability and robustness of this new electrogenerated *poly*-**2** as an efficient reusable asymmetric catalyst. The same batch of heterogeneous catalyst *poly*-**2** can indeed promote the HDA transformation of different substrates. Moreover, and as already noted, special attention is drawn to the purity of each of the products which were easily isolated in each cycle without contamination with any traces of product from the preceding run.

Optimization of the Catalyst Structures

Although our new procedure has clearly been demonstrated by the preceding examples to be highly efficient for the recovery and reuse of hetero-Diels–Alder catalysts, lower enantiomeric excesses were generally observed compared with those reported for analogous complexes. In order to try to overcome this drawback, structurally modified ligands were prepared bearing substituents that generate a higher steric hindrance or modify the electronic character around the active metal centre.

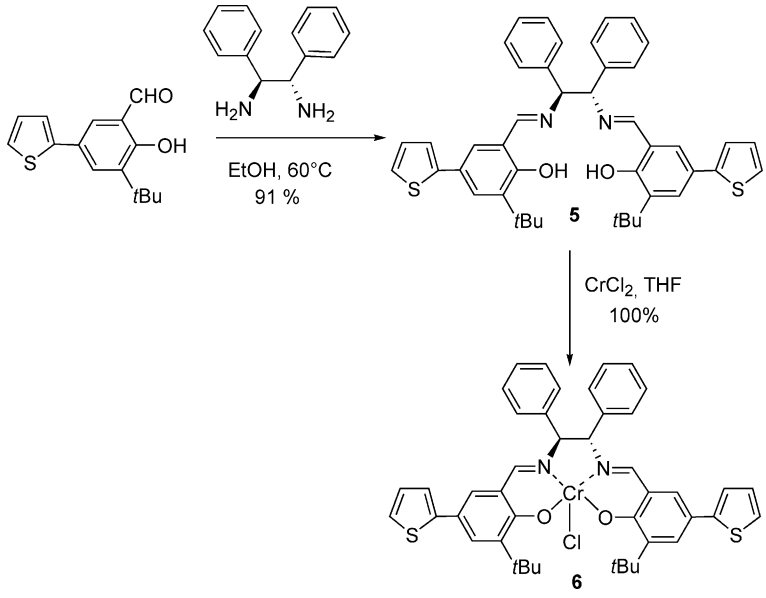
The effect of the chiral moiety of the ligand on the enantioselectivity of the transformation was first evaluated. In this context, (*S*,*S*)-1,2-diphenylethane-1,2-diamine was used as the enantiopure chiral linker instead of the previously studied cyclohexanediamine. The complete synthetic route to the new chiral complex **6** is depicted in Scheme 4 and is an analogous procedure to that described in Scheme 1. 3-*tert*-Butyl-2-hydroxy-5-(2-thienyl)benzaldehyde reacted with (*S*,*S*)-1,2-diphenylethane-1,2-diamine in ethanol to afford the desired chiral ligand **5** in 91% yield. The subsequent reaction of this new thiophene-salen derivative with chromium chloride led smoothly to the chromium(III) complex **6** in quantitative yield.

In order to evaluate the effect of electronic variations of the chiral ligand on the enantioselectivity of the catalytic transformation, the thiophene ring was also replaced by a 3,4-ethylenedioxythiophene (EDOT) moiety at the 5,5′-positions of the phenolic core. The synthesis of the new chiral complex **10a** is depicted in Scheme 5. Finally, the thiophene moiety was modified by increasing the steric bulk at the 3-position of the heteroaromatic ring with an octyl or a cyclopentenyl substituent. The preparation of the new dioxa-

Table 4. Heterogeneous HDA reaction in a multi-substrate procedure with 4 mol-% *poly*-**2** at room temperature for 23 h.

Substrate	Cycle	% Yield[a]	% *ee*[b]	Cycle	% Yield[a]	% *ee*[b]
3c	1	96	45	11	66	47
3b	2	92	52	12	72	52
3h	3	38	44	13	37	45
3g	4	46	50	14	38	50
3j	5	33	61	15	31	63
3i	6	62	59	16	63	63
3f	7	78	12	17	65	46
3e	8	64	50	18	45	55
3d	9	93	44	19	72	49
3a	10	66	50	20	51	51

[a] Isolated yield. [b] *ee* determined by chiral HPLC analyses.

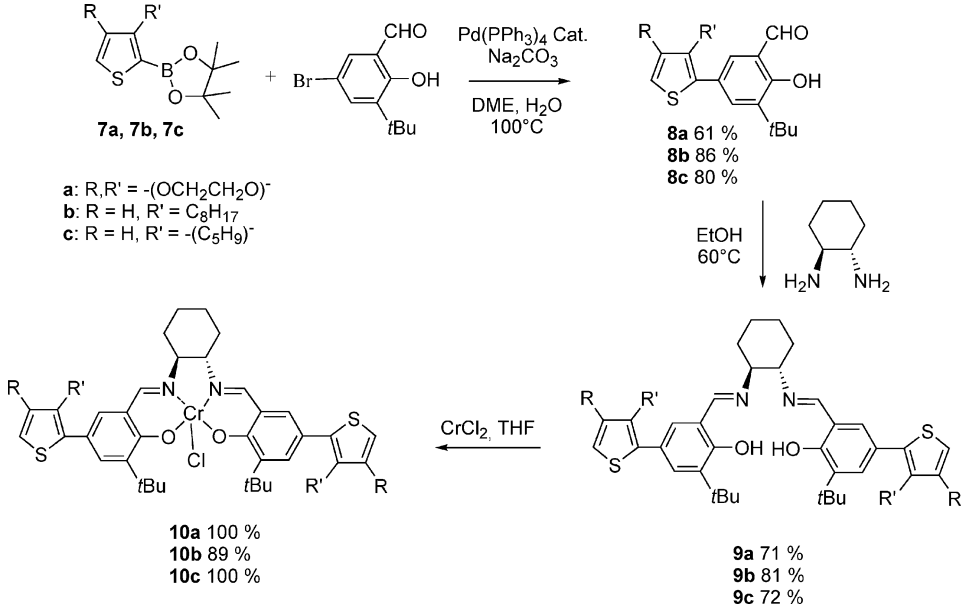


Scheme 4. Synthesis of the new chiral chromium complex **6**.

borolane **7c** starting from 3-bromothiophene is fully described in the Exp. Sect. The synthesis of the chiral ligands **9b** and **9c** and of the corresponding chromium complexes **10b** and **10c** was realized by the same procedure (Scheme 5).

Complexes **6** and **10a**–**c** were tested in the catalytic enantioselective HDA reaction under homogeneous conditions. Heptanal (**3i**) and cyclohexanecarbaldehyde (**3j**) were chosen as test substrates as they gave the best results in terms of enantioselectivity in the presence of the analogous complex **2** (see the results in Table 5).

Compared with complex **2**, use of (*S*,*S*)-1,2-diphenylethane-1,2-diamine as the chiral bridge afforded complex **6**, which led to the preparation of both **4i** and **4j** in better yields (97 and 95%, respectively, instead of 53 and 79% at 20 °C, compare entries 1 and 3). However, this improvement in activity was not accompanied by an increase in enantioselectivity. On the contrary, the structural modification of the ligand lowered quite significantly the enantiomeric excess (55% *ee* instead of 72%) for the transformation of cyclohexanecarbaldehyde (**3j**). Replacement of the



Scheme 5. Synthesis of the new chiral chromium complexes **10a**–**c**.

Table 5. HDA reactions between heptanal (**3i**) or cyclohexanecarbaldehyde (**3j**) and Danishefsky's diene promoted by various thiophene-salen complexes.

Entry	Complex	T [°C][a]	**4i**		**4j**	
			% Yield[b]	% *ee*[c]	% Yield[b]	% *ee*[c]
1	**2**	20	53	72	79	72
2	**2**	–40	42	82	58	81
3	**6**	20	97	60	95	55
4	**10a**	20	91	65	74	63
5	**10b**	20	64	70	92	78
6	**10b**	–40	100	81	54	88
7	**10c**	20	95	69	84	78

[a] Reactions run using 2 mol-% of catalyst in MTBE, 23 h reaction time at 20 °C and 64 h at –40 °C. [b] Isolated yield. [c] *ee* determined by chiral HPLC analyses.

thiophene ring by EDOT also led to the desired pyranones in good yields (entry 4) but unfortunately with a loss of enantioselectivity. Finally, increasing the steric bulk on the thiophene ring by introducing either an octyl or a cyclopentyl group was much more beneficial in terms of enantioselectivity. This was particularly true for the transformation of cyclohexanecarbaldehyde (**3j**) which afforded the desired pyranone **4j** in up to 88% *ee* by using complex **10b** at –40 °C. Complexes **10b** and **10c** are thus better candidates than complex **2** for providing the pyranones with high enantioselectivities.

Electrochemical Polymerization of the New Chromium-Thiophene-salen Complexes and Their Use in Heterogeneous Catalysis

Owing to the catalytic results obtained with the new chromium complexes in the homogeneous asymmetric hetero-Diels–Alder reaction, we studied their ability to be electropolymerized under cyclic voltammetry conditions. The preparation of *poly*-**6** has already been described[5] and *poly*-**10a**–**c** were synthesized in an analogous way to *poly*-**2** by cyclic voltammetry, typically between +0.0 and +1.2 V. In each case again, electropolymerization occurred readily in dichloromethane in the presence of nBu$_4$NBF$_4$ as electrolyte leading to the formation of polymeric materials at the platinum surface. The polymers were then analyzed in a monomer-free electrolyte and they all presented well-defined quasi-reversible redox systems, as can be concluded from the electrochemical data for these new chiral chromium-thiophene-salen polymers (see Table 6).

Table 6. Electrochemical data for the chiral chromium-thiophene-salen *poly*-**10a**–**c**.

	E_{pa} [V/SCE]	E_{pc} [V/SCE]	Q_a/Q_c
poly-**10a**	+0.56	+0.51	1.04
poly-**10b**	+0.89	+0.70	1.26
poly-**10c**	+0.95	+0.76	0.93

As the best results in terms of enantioselectivity were obtained when the asymmetric reaction was promoted by the monomer complex **10b**, *poly*-**10b** was synthesized by preparative polymerization in 45% yield using the conditions optimized for the preparation of *poly*-**2**. This new complex was also recovered as an insoluble powder and thus used as a heterogeneous catalyst in the asymmetric hetero-Diels–Alder reaction. This polymer proved efficient for promoting the transformation of cyclohexanecarbaldehyde (**3j**) with Danishefsky's diene at room temperature. The targeted pyranone **4j** was indeed isolated in 89% yield and 72% *ee*. This value is slightly higher than that obtained with the parent *poly*-**2** (see Table 3) as could be expected from the results obtained under homogeneous conditions. The recyclability of this new polymeric material was demonstrated by its efficient reuse in two subsequent runs which showed no loss in activity nor in enantioselectivity for the same catalytic transformation.

Conclusions

New chiral chromium complexes based on the *N*,*N*′-bis(salicylidene)ethylenediamine structure substituted by thiophene units at the 5,5′-positions of the phenolic rings were synthesized and efficiently used as catalysts for the hetero-Diels–Alder reaction between Danishefsky's diene and various aldehydes. The chromium complex **2** was polymerized by electrochemical oxidation and subsequent analyses indicated that the polymer formed was electrochemically and chemically stable. Preparative electropolymerization afforded the corresponding chiral polymer as a powder which was also used efficiently as a catalyst for asymmetric heterogeneous HDA transformations. Moreover, the insoluble catalyst proved to be very robust under the reaction conditions as it was recycled 15 times without showing any loss in activity or enantioselectivity. The same catalyst was engaged in a multi-substrate procedure and used 20 times by adding a structurally different aldehyde in each recycling. We assume this efficient recycling is a new and original procedure that may be used for performing heterogeneous asymmetric catalysis under the best conditions for a safer and cleaner chemistry. The results in terms of enantioselectivity were however moderate compared with those obtained by the best complexes described in the literature for these transformations. Some effort was thus devoted to improving the enantiomeric excesses by structural modification (both steric and electronic) of the ligand. In this context, increasing the steric bulk at the 3-position of the thiophene rings led to more enantioselective catalysts without modifying their activity. With complex **10b**, 2-cyclohexyl-2,3-dihydro-4*H*-pyran-4-one (**4j**) was successfully synthesized with an improved enantioselectivity of 88%. The corresponding electrogenerated complex *poly*-**10b** showed an interesting catalytic activity as it allowed the synthesis of product **4j** in high yield and with 72% *ee*, improved values compared with those obtained with *poly*-**2**. Work is in progress to further modify our polymerizable ligands to give efficient recoverable catalysts with various metals for asymmetric heterogeneous catalysis.

Experimental Section

General Methods: All reactions were carried out under argon in oven-dried glassware with magnetic stirring. Solvents were distilled before use: THF and diethyl ether from sodium metal/benzophenone, MTBE, CH_3CN and CH_2Cl_2 from calcium hydride. 4-Bromo-2-*tert*-butyl-phenol and 3-*tert*-butyl-5-bromo-2-hydroxybenzaldehyde were synthesized according to ref.[16], 2-bromo-3-octylthiophene and compound **7b** according to ref.[17] and 3-*tert*-butyl-2-hydroxy-5-(2-thienyl)benzaldehyde, **1**, **2** and **5** according to ref.[5]. Aldehydes were distilled before use. Danishefsky's diene was either prepared or used as received from commercial sources. ^1H and ^{13}C NMR spectra were recorded with either a Bruker AM 360 (360 MHz), AM 300 (300 MHz) or AM 250 (250 MHz) instrument with samples dissolved in $CDCl_3$. Data are reported in ppm with the solvent signal as reference (δ = 7.27 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR). Optical rotations were measured in solution in 10-cm cells at the sodium-D line using a Perkin–Elmer 241 polarimeter. IR spectra were recorded as KBr disks using a Perkin-Elmer spectrometer. Mass spectra were recorded with a Finnigan MAT 95 S spectrometer. HPLC analyses were carried out with a thermo separation product pump P100 chromatograph equipped with a UV100 detector using an ODH or an AD column. Electrochemical measurements were performed using a EG&G Princeton Applied Research (model 362) scanning potentiostat equipped with an IFELEC (IF 2502) recorder in an undivided three-electrode cell containing a Pt working electrode, a Pt counter-electrode and a saturated calomel electrode (SCE) as reference. The solutions were degassed by argon bubbling prior to electropolymerization. The cell was stored in a dry atmosphere and flushed with argon before the electrochemical experiments.

Synthesis of the Ligand Precursors

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrothieno-[3,4-*b*][1,4]dioxine (7a): Compound **7a** was synthesized according to ref.[18]. A solution of ethylendioxythiophene (640 μL, 6 mmol) in dry THF (12 mL) was cooled to –78 °C under argon and treated with a 2.5 M solution of *n*-butyllithium (2.64 mL). The temperature was slowly raised to 0 °C and the mixture was stirred at 0 °C for 20 min. The reaction mixture was cooled again to –78 °C and a solution of pinacolborane (2.45 mL, 12 mmol) in THF (4.6 mL) was added. Then the mixture was stirred at room temperature for 17 h and poured over crushed ice/NH_4Cl. The crude product was extracted with Et_2O and dried with $MgSO_4$. Removal of the solvent followed by trituration with methanol gave pure boronic ester **7a** (1.08 g, 67%) as a white solid; m.p. 92 °C. ^1H NMR (360 MHz, $CDCl_3$): δ = 6.64 (s, 1 H, CH), 4.33–4.30 (m, 2 H, CH_2), 4.21–4.18 (m, 2 H, CH_2), 1.36 (s, 12 H, 3 × CH_3) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 149.0 (C_q), 142.3 (2 × C_q), 107.4 (CH), 83.8 (C_q), 65.0 (CH_2), 64.2 (CH_2), 24.7 (3 × CH_3) ppm. HRMS (ESI): calcd. for $C_{12}H_{17}O_4BSNa$ 291.0833; found 291.0839.

1-(3-Thienyl)cyclopentanol: A solution of 3-bromothiophene (1.4 mL, 15 mmol) in dry diethyl ether (30 mL) was cooled to –78 °C under argon and treated with a 1.6 M solution of *n*-butyllithium (9.4 mL). The temperature was slowly raised to –20 °C and the mixture was stirred at –20 °C for 1 h. The reaction mixture was cooled again to –78 °C and a solution of cyclopentanone (1.6 mL, 18 mmol) in THF (15 mL) was added. Then the mixture was stirred at room temperature for 17 h and poured over crushed ice/NH_4Cl. The crude product was extracted with Et_2O and dried with $MgSO_4$. The solvents were removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (pentane/diethyl ether, 80:20) to afford the desired product (1.96 g, 78%) as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.29 (dd, J = 4.9, 3.0 Hz, 1 H, CH), 7.20 (dd, J = 3.0, 1.5 Hz, 1 H, CH), 7.11 (dd, J = 4.9, 1.5 Hz, 1 H, CH), 2.9 (br. s, 1 H, OH), 2.05–1.68 (m, 8 H, CH_2) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 148.8 (C_q), 125.7 (CH), 125.1 (CH), 118.8 (CH), 81.0 (C_q), 41.0 (CH_2), 23.2 (CH_2) ppm. HRMS (EI): calcd. for $C_9H_{12}OS$ 168.0603; found 168.0608.

3-Cyclopentylthiophene: The catalyst Pd/C 5% (2 g) was added to a solution of 1-(3-thienyl)cyclopentanol (1.96 g, 11.63 mmol) in dichloromethane (20 mL). The system was then subjected to a hydrogen atmosphere (P = 10 bar) whilst continuously stirring. After 2 h the mixture was filtered through Celite and the solvents were removed under reduced pressure to afford 3-cyclopentylthiophene (1.58 g, 89%) as a yellowish oil. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.28 (dd, J = 4.8, 2.8 Hz, 1 H, CH), 7.02 (dd, J = 1.3, 4.8 Hz, 1 H, CH), 6.98 (dd, J = 1.3, 2.8 Hz, 1 H, CH), 3.21–3.02 (m, 1 H, CH), 2.22–1.97 (m, 2 H, CH_2), 1.94–1.50 (m, 6 H, CH_2) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 146.8 (C_q), 127.0 (CH), 124.8 (CH), 118.3 (CH), 41.0 (CH), 33.8 (CH_2), 25.0 (CH_2) ppm. HRMS (EI): calcd. for $C_9H_{12}S$ 152.0654; found 152.0656.

2-Bromo-3-cyclopentylthiophene: 3-Cyclopentylthiophene (1.58 g, 10.38 mmol) was diluted in a mixture of chloroform/acetic acid (1:1, 10 mL/10 mL) at 0 °C and stirred in the dark. *N*-Bromosuccinimide (1.85 g, 10.38 mmol) was added portionwise. Then the mixture was stirred for 3 h at 0 °C. Water (20 mL) was added and the aqueous layer was extracted with chloroform. The combined organic layers were washed with a solution composed of $Na_2S_2O_3 \cdot 5H_2O$ and 10% KI, then with a solution of 10% $NaHCO_3$ and water. The organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (neat pentane) to afford the desired compound (1.92 g, 83%) as a colourless oil. ^1H NMR (360 MHz, $CDCl_3$): δ = 7.23 (d, J = 5.7 Hz, 1 H, CH), 6.87 (d, J = 5.7 Hz, 1 H, CH), 3.26–3.09 (m, 1 H, CH), 2.20–1.96 (m, 2 H, CH_2), 1.95–1.62 (m, 4 H, CH_2), 1.61–1.46 (m, 2 H, CH_2) ppm. ^{13}C NMR (360 MHz, $CDCl_3$): δ = 145.3 (C_q), 125.7 (CH), 125.1 (CH), 108.1 (C_q), 40.0 (CH), 33.4 (CH_2), 25.4 (CH_2) ppm. HRMS (EI): calcd. for $C_9H_{11}BrS$ 229.9759; found 229.9765.

2-(3-Cyclopentyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7c): A solution of 2-bromo-3-cyclopentylthiophene (400 mL, 1.73 mmol) in dry THF (3.5 mL) was cooled to –78 °C under argon and treated with a 2.5 M solution of *n*-butyllithium (761 μL). The temperature was slowly raised to –20 °C and the mixture was stirred at –20 °C for 1 h. The reaction mixture was cooled again to –78 °C and a solution of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (706 μL, 3.46 mmol) in THF (1.7 mL) was added. Then the mixture was stirred at room temperature for 16 h and poured over crushed ice/NH_4Cl. The aqueous layer was extracted with Et_2O and the combined organic layers were dried with $MgSO_4$. The solvents were removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (neat pentane) to afford **7c** (123.6 mg, 26%) as a colourless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, J = 4.5 Hz, 1 H, CH), 7.14 (d, J = 4.5 Hz, 1 H, CH), 3.89–3.52 (m, 1 H, CH), 2.25–1.96 (m, 2 H, CH_2), 1.94–1.51 (m, 6 H, CH_2), 1.37 (s, 12 H, CH_3) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 2 × 158.5 (C_q), 131.4 (CH), 127.4 (CH), 83.3 (C_q), 40.4 (CH), 34.9 (CH_2), 25.7 (CH_2), 24.7 (CH_3) ppm. HRMS (EI): calcd. for $C_{15}H_{23}BO_2S$ 278.1506; found 278.1507.

3-*tert*-Butyl-5-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2-hydroxybenzaldehyde (8a): A Schlenk tube was charged with 3-*tert*-butyl-5-bromo-2-hydroxybenzaldehyde (290 mg, 1.13 mmol), 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrothieno[3,4-*b*][1,4]-dioxine (**7a**) (605 mg, 2.26 mmol), $[Pd(PPh_3)_4]$ (196 mg, 0.17 mmol)

and Na_2CO_3 (180 mg, 1.69 mmol) and was maintained under argon by successive vacuum–argon cycles (3 h). Thoroughly degassed DME (2.1 mL) and degassed water (0.7 mL) were introduced through a cannula into the Schlenk tube. The mixture was heated at 100 °C for 24 h. Water (20 mL) was added and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel (pentane/diethyl ether, 4:1) to afford **8a** (218 mg, 61%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.81 (s, 1 H, OH), 9.89 (s, 1 H, CHO), 7.85 (d, J = 2.1 Hz, 1 H, CH), 7.74 (d, J = 2.1 Hz, 1 H, CH), 6.28 (s, 1 H, CH), 4.37–4.31 (m, 2 H, CH_2), 4.31–4.25 (m, 2 H, CH_2), 1.47 (s, 9 H, $3\times CH_3$) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 197.1 (CH), 159.7 (C_q), 142.1 (C_q), 138.3 (C_q), 137.5 (C_q), 132.0 (CH), 129.0 (CH), 124.5 (C_q), 120.4 (C_q), 116.1 (C_q), 96.7 (CH), 64.7 (CH_2), 64.3 (CH_2), 34.8 (C_q), 29.0 ($3\times CH_3$) ppm. HRMS (EI): calcd. for $C_{17}H_{18}O_4S$ 318.0920; found 318.0914.

3-*tert*-Butyl-2-hydroxy-5-(3-octyl-2-thienyl)benzaldehyde (8b): A Schlenk tube was charged with 3-*tert*-butyl-5-bromo-2-hydroxybenzaldehyde (281.5 mg, 1.09 mmol), 4,4,5,5-tetramethyl-2-(3-octyl-2-thienyl)-1,3,2-dioxaborolane (**7b**) (705.5 mg, 2.19 mmol), [$Pd(PPh_3)_4$] (189.8 mg, 0.16 mmol) and Na_2CO_3 (174 mg, 1.64 mmol) and was maintained under argon by successive vacuum–argon cycles (3 h). Thoroughly degassed DME (2.1 mL) and degassed water (0.7 mL) were introduced through a cannula into the Schlenk tube. The mixture was heated at 100 °C for 24 h. Water (20 mL) was added and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel (pentane/diethyl ether, 9:1) to afford **8b** (349 mg, 86%) as a yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 11.93 (s, 1 H, OH), 9.93 (s, 1 H, CHO), 7.68 (d, J = 2.3 Hz, 1 H, CH), 7.50 (d, J = 2.3 Hz, 1 H, CH), 7.26 (d, J = 5.1 Hz, 1 H, CH), 7.04 (d, J = 5.1 Hz, 1 H, CH), 2.69 (t, J = 7.9 Hz, 2 H, CH_2-C_7H_{15}), 1.83–1.62 (m, 2 H, CH_2-CH_2-C_6H_{13}), 1.53 (s, 9 H, $3\times CH_3$), 1.49–1.26 (m, 10 H, $5\times CH_2$), 1.04–0.85 (m, 3 H, CH_3) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 196.8 (CHO), 160.3 (C_q), 138.5 (C_q), 138.3 (C_q), 136.4 (C_q), 135.2 (CH), 132.2 (CH), 129.4 (CH), 125.8 (C_q), 123.3 (CH), 120.4 (C_q), 34.8 (C_q), 31.7 (CH_2), 31.1 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_3), 28.6 (CH_2), 22.5 (CH_2), 14.0 (CH_2-CH_3) ppm. HRMS (EI): calcd. for $C_{23}H_{32}O_2S$ 372.2118; found: 372.2119.

3-*tert*-Butyl-5-(3-cyclopentyl-2-thienyl)-2-hydroxybenzaldehyde (8c): A Schlenk tube was charged with 3-*tert*-butyl-5-bromo-2-hydroxybenzaldehyde (42 mg, 0.16 mmol), 2-(3-cyclopentyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7c**) (90 mg, 0.32 mmol), [$Pd(PPh_3)_4$] (28 mg, 0.02 mmol) and Na_2CO_3 (25 mg, 0.24 mmol) and was maintained under argon by successive vacuum–argon cycles (3 h). Thoroughly degassed DME (320 μL) and degassed water (110 μL) were introduced through a cannula into the Schlenk tube. The mixture was heated at 100 °C for 22 h. Water (15 mL) was added and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel (pentane/diethyl ether, 99:1) to afford **8c** (42.4 mg, 80%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.83 (s, 1 H, OH), 9.89 (s, 1 H, CHO), 7.58 (d, J = 1.9 Hz, 1 H, CH), 7.44 (d, J = 1.9 Hz, 1 H, CH), 7.22 (d, J = 5.3 Hz, 1 H, CH), 7.02 (d, J = 5.3 Hz, 1 H, CH), 3.12–2.97 (m, 1 H, CH), 2.07–1.89 (m, 2 H, CH_2), 1.89–1.72 (m, 2 H, CH_2), 1.71–1.48 (m, 4 H, CH_2), 1.44 (s, 9 H, CH_3) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 197.0 (C_q), 160.5 (C_q), 142.8 (C_q), 138.3 (C_q), 136.1 (C_q), 135.6 (CH), 132.4 (CH), 126.9 (CH), 125.8 (C_q), 123.8 (CH), 120.4 (C_q), 39.0 (CH), 35.2 (CH_2), 34.9 (C_q), 29.1 (CH_3), 25.7 (CH_2) ppm. HRMS (EI): calcd. for $C_{20}H_{24}O_2S$ 328.1492; found 328.1500.

General Procedure for the Formation of the Ligands: The diamine (0.52 equiv.) was added to a solution of the targeted aldehyde in ethanol (0.07 M) with continuous stirring, and the mixture was heated at 60 °C for 19 h. The reaction mixture was cooled to room temperature. The solvents were removed under reduced pressure and the residue was purified as described below.

(*S*,*S*)-*N*,*N*′-Bis[3-*tert*-butyl-5-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)salicylidene]cyclohexane-1,2-diamine (9a): This product was obtained using aldehyde **8a** and (*S*,*S*)-cyclohexane-1,2-diamine. The residue was recrystallized from 2-propanol to afford **9a** (71%) as a yellow powder; m.p. 148–150 °C. $[\alpha]_D^{20}$ = –28 (c = 0.99, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.97 (s, 2 H, OH), 8.35 (s, 2 H, CH), 7.57 (s, 2 H, CH), 7.38 (s, 2 H, CH), 6.20 (s, 2 H, CH), 4.40–4.18 (m, 8 H, CH_2), 3.39–3.35 (m, 2 H, CH), 2.15–1.72 (m, 6 H, CH_2), 1.70–1.35 (m, 20 H, $6\times CH_3$, CH_2) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 165.6 (CH), 159.4 (C_q), 142.1 (C_q), 137.4 (C_q), 136.9 (C_q), 127.8 (CH), 127.6 (CH), 123.0 (C_q), 118.5 (C_q), 117.6 (C_q), 96.0 (CH), 72.3 (CH), 64.7 (CH_2), 64.5 (CH_2), 34.9 (C_q), 33.1 (CH_2), 29.4 (CH_3), 24.3 (CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 2930, 2865, 1629, 1594, 1501, 1434, 1364, 1075 cm^{-1}. Probably as a result of low stability of ligand **9a**, all attempts to obtain a correct HRMS or elemental analysis failed.

(*S*,*S*)-*N*,*N*′-Bis[3-*tert*-butyl-5-(3-octyl-2-thienyl)salicylidene]cyclohexane-1,2-diamine (9b): This product was obtained using aldehyde **8b** and (*S*,*S*)-cyclohexane-1,2-diamine. The residue was purified by flash chromatography on silica gel (heptane/diethyl ether, 98:2) to afford **9b** (81%) as yellow oil. $[\alpha]_D^{20}$ = +49 (c = 0.99, $CHCl_3$). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 14.0 (s, 2 H, OH), 8.39 (s, 2 H, CH), 7.38 (d, J = 2.1 Hz, 2 H, CH), 7.18 (d, J = 5.1 Hz, 2 H, CH), 7.14 (d, J = 2.1 Hz, 2 H, CH), 6.98 (d, J = 5.1 Hz, 2 H, CH), 3.53–3.29 (m, 1 H, CH), 2.72–2.48 (m, 4 H, CH_2-C_7H_{15}), 2.05–1.85 (m, 4 H, CH_2-CH_2-C_6H_{13}), 1.80–1.06 (m, 46 H, $10\times CH_2$, $6\times CH_3$, $4\times CH_2$), 0.92 (t, J = 7 Hz, 6 H, CH_2-CH_3) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 165.4 (CH), 159.9 (C_q), 138.0 (C_q), 137.9 (C_q), 137.3 (C_q), 130.8 (CH), 130.5 (CH), 129.4 (CH), 124.3 (C_q), 122.8 (CH), 118.5 (C_q), 72.4 (CH), 34.9 (C_q), 33.2 (CH_2), 31.9 (CH_2), 31.3 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 ($4\times CH_3$), 28.7 (CH_2), 24.3 (CH_2), 22.7 (CH_2), 14.2 (CH_2-CH_3) ppm. HRMS (ESI): calcd. for $C_{52}H_{75}N_2O_2S_2$ $[M + H]^+$ 823.5264; found 823.5256. IR (KBr): $\tilde{\nu}$ = 2948, 2929, 2863, 1635, 1619, 1593, 1471, 1456, 1424 cm^{-1}.

(*S*,*S*)-*N*,*N*′-Bis[3-*tert*-butyl-5-(3-cyclopentyl-2-thienyl)salicylidene]-cyclohexane-1,2-diamine (9c): This product was obtained using aldehyde **8c** and (*S*,*S*)-cyclohexane-1,2-diamine. The residue was recrystallized from ethanol to afford **9c** (72%) as a yellow solid; m.p. 103 °C. $[\alpha]_D^{20}$ = +49 (c = 0.99, $CHCl_3$). ^{1}H NMR (360 MHz, $CDCl_3$): δ = 14.08 (br. 2 H, OH), 8.42 (s, 2 H, CH), 7.40 (s, H, CH), 7.23 (d, J = 4.8 Hz, 2 H, CH), 7.17 (s, H, CH), 7.05 (d, J = 4.8 Hz, 2 H, CH), 3.52–3.38 (m, 2 H, CH), 3.08–3.03 (m, 2 H, CH), 2.13–1.91 (m, 8 H, CH_2), 1.91–1.76 (m, 4 H, CH_2), 1.75–1.60 (m, 4 H, CH_2), 1.48 (s, 18 H, CH_3) ppm. ^{13}C NMR (360 MHz, $CDCl_3$): δ = 165.3 (CH), 159.9 (C_q), 142.2 (C_q), 137.5 (C_q), 137.2 (C_q), 131.1 (CH), 130.6 (CH), 126.8 (CH), 124.2 (C_q), 123.2 (CH), 118.4 (C_q), 72.4 (CH), 39.0 (CH), 35.3 (CH_2), 34.8 (C_q), 33.2 (CH_2), 29.3 (CH_3), 25.7 (CH_2), 24.2 (CH_2) ppm. HRMS (EI): calcd. for $C_{46}H_{58}N_2O_2S_2$ 734.3934; found 734.3892. IR (CaF_2 cell, $CHCl_3$): $\tilde{\nu}$ = 2977, 2896, 1630, 1602, 1476, 1424, 1045 cm^{-1}.

General Procedure for the Formation of the Complexes: The chiral ligand in dry, degassed THF (0.08 M) was added to a solution of anhydrous $CrCl_2$ (1.15 equiv.) in dry, degassed THF (0.04 M). 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. It was diluted with CH_2Cl_2 and washed with sat. NH_4Cl and brine. The organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure to afford the expected complex.

Chromium-Thiophene-Salen Complex 6: Starting from ligand **5** described in ref.[5], complex **6** was obtained as a brown solid in quantitative yield. IR (KBr): $\tilde{\nu}$ = 2952, 2912, 2868, 1610, 1536, 1425, 1409, 1322 cm^{-1}. $C_{44}H_{42}ClCrN_2O_2S_2 \cdot THF \cdot H_2O$ (872.52): calcd. C 66.07, H 6.01, N 3.31, S 7.35; found: C 66.52, H 6.01, N 3.22, S 7.38. LRMS: *m*/*z* (%) = 747 (61) $[M - Cl]^+$, 746 (100), 457 (14), 455 (20), 379 (17), 351 (31), 301 (36), 269 (29).

Chromium-Thiophene-Salen Complex 10a: Starting from ligand **9a**, complex **10a** was obtained as a brown solid in quantitative yield. IR (KBr): $\tilde{\nu}$ = 2943, 2874, 1627, 1535, 1499, 1430, 1365, 1175, 1074 cm^{-1}. LRMS: *m*/*z* (%) = 765 (57) $[M - Cl]^+$, 764 (100), 351 (10), 301 (20), 283 (12), 269 (17).

Chromium-Thiophene-Salen Complex 10b: Starting from ligand **9b**, complex **10b** was obtained as a brown solid in 89% yield. IR (KBr): $\tilde{\nu}$ = 2925, 2854, 1623, 1528, 1459, 1425, 1320 cm^{-1}. HRMS: calcd. for $C_{52}H_{72}CrN_2O_2S_2$ $[M - Cl]^+$ 872.4435; found 872.4427. $C_{52}H_{72}ClCrN_2O_2S_2 \cdot THF \cdot H_2O$ (998.84): calcd. C 67.34, H 8.27, N 2.80, S 6.42; found C 67.05, H 8.16, N 2.82, S 6.96.

Chromium-Thiophene-Salen Complex 10c: Starting from ligand **9c**, complex **10c** was obtained as a brown solid in quantitative yield. IR (CaF_2 cell, $CHCl_3$): $\tilde{\nu}$ = 2975, 2928, 2871, 1622, 1604, 1476, 1424, 1329, 1030 cm^{-1}. HRMS: calcd. for $C_{14}H_{56}O_2N_2ClCrS_2$ 819.2871; found 819.2866.

Electropolymerization of Complexes 2 and 10b: Complex **2** (340 mg, 0.5 mmol) was placed in an undivided electrochemical cell fitted with a platinum cathode and a platinum grid (2.25 cm^2) as anode. The anode potential was monitored versus a saturated calomel electrode (SCE) throughout the electrolysis. nBu_4NBF_4 (0.03 M in 15 mL CH_2Cl_2) was used as the supporting electrolyte and the electrolysis was performed at a constant current of 50 mA for 1 h. The platinum grid was covered with the polymerized complex. Some insoluble material also settled at the bottom of the cell. The deposited polymer was used as an insoluble catalyst after removal from the support and several washings with acetonitrile and dichloromethane. This residue was dried under vacuum and used without further purification for the asymmetric catalysis. *Poly*-**2** was isolated in 43% yield. Following the same procedure, complex **10b** (100 mg) was electropolymerized to afford *poly*-**10b** in 45% yield as a dark-green powder.

Hetero-Diels–Alder Reactions

Homogeneous Conditions: A Schlenk tube was charged with catalyst **2** (or **6**, **10a**, **10b**, **10c**) (2 mol-%) and thoroughly maintained under argon by three successive vacuum–argon cycles. MTBE (200 μL), the aldehyde (1 mmol) and Danishefsky's diene (234 μL, 1.2 mmol) were then introduced through a syringe. In the case of reactions performed at low temperature, the mixture was first cooled to –40 °C followed by the addition of the diene. The resulting solution was stirred at room temperature (or at –40 °C) for the specified amount of time. It was then diluted with CH_2Cl_2 (2 mL), treated with a drop of trifluoroacetic acid and further stirred for another 30 min. The solvents were removed under reduced pressure and the residue was purified by flash chromatography on silica gel to determine the yield of the reaction and the enantiomeric excess of the product.

Heterogeneous Conditions: A Schlenk tube was charged with catalyst *poly*-**2** (or *poly*-**10b**) (4 mol-%) and maintained under argon by three successive vacuum–argon cycles. MTBE (400 μL), the aldehyde (1 mmol) and Danishefsky's diene (1.2 mmol) were then introduced through a syringe. The resulting suspension was stirred at room temperature for the specified amount of time. It was then filtered with a filtering syringe and the residue was washed with MTBE. Then the solvents of the combined filtrates were partially removed under reduced pressure. The residue was diluted with CH_2Cl_2 (2 mL), treated with a drop of trifluoroacetic acid and stirred for another 30 min. The solvents were then removed under reduced pressure and the residue was purified by flash chromatography on silica gel to determine the yield of the reaction and the enantiomeric excess of the product.

In the Schlenk tube, catalyst *poly*-**2** (or *poly*-**10b**) was dried under vacuum for its reuse and new substrates and solvents were added.

(+)-(*S*)-2-Phenyl-2,3-dihydro-4*H*-pyran-4-one (4a): Solvent for flash chromatography: pentane/diethyl ether (1:1). Yellowish oil. $[\alpha]_D^{20}$ = +54 (*c* = 1.05, $CHCl_3$) for 56% *ee* {ref.[10a] $[\alpha]_D^{25}$ –96 (*c* = 0.6, CH_2Cl_2) for 87% *ee* material}. The *ee* was determined by HPLC analyses using an ODH column (flow rate: 0.5 mL min^{-1}; 90% hexane, 10% 2-propanol, 254 nm) which resolved both enantiomers [$t_{R(major)}$ = 29.8 min, $t_{R(minor)}$ = 35.7 min]. The absolute stereochemistry was assigned as (+)-(*S*) based on a comparison of the measured rotation with the literature value.[10a] ^1H NMR (250 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 6.1 Hz, 1 H, CH), 7.46–7.37 (m, 5 H, CH_{ar}), 5.54 (d, *J* = 6.1 Hz, 1 H, CH), 5.43 (dd, *J* = 14.4, 3.5 Hz, 1 H, CH), 2.9 [dd, *J* = 16.9, 14.4 Hz, 1 H, CH(H)], 2.68 [dd, *J* = 16.9, 3.5 Hz, 1 H, CH(H)] ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 192.2 (CO), 163.3 (CH), 137.9 (C_q), 2×128.9 (CH), 2×128.7 (CH), 126.1 (CH), 107.4 (CH), 81.1 (CH), 43.3 (CH_2) ppm. HRMS (EI): calcd. for $C_{11}H_{10}O_2$ 174.0675; found 174.0683.

2-(2-Methoxyphenyl)-2,3-dihydro-4*H*-pyran-4-one (4b): Solvent for flash chromatography: pentane/diethyl ether (7:3). Yellowish oil. $[\alpha]_D^{20}$ –32 (*c* = 1.03, $CHCl_3$) for 52% *ee* {ref.[10b] $[\alpha]_D^{25}$ –63 (*c* = 0.45, $CHCl_3$) for 96% *ee* material}. The *ee* was determined by HPLC analysis using an ODH column (flow rate: 0.5 mL min^{-1}; 95% hexane, 5% 2-propanol, 254 nm) which resolved both enantiomers [$t_{R(major)}$ = 28.0 min, $t_{R(minor)}$ = 29.9 min]. The absolute configuration was not determined. ^1H NMR (360 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 5.9 Hz, 1 H, CH), 7.47 (dd, *J* = 7.6, 1.4 Hz, 1 H, CH), 7.30 (dd, *J* = 8.1, 1.3 Hz, 1 H, CH), 7.01 (dd, *J* = 0.9, 7.7 Hz, 1 H, CH), 6.91 (d, *J* = 8.2 Hz, 1 H, CH), 5.79 (dd, *J* = 6.9, 10.8 Hz, 1 H, CH), 5.51 (d, *J* = 5.9 Hz, 1 H, CH), 3.83 (s, 3 H, CH_3), 2.77–2.72 (m, 2 H, CH_2) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 192.7 (CO), 163.5 (CH), 155.7 (C_q), 129.5 (CH), 126.3 (C_q), 126.2 (CH), 120.6 (CH), 110.4 (CH), 107.0 (CH), 76.2 (CH), 55.2 (CH_3), 42.1 (CH_2) ppm. HRMS (ESI): calcd. for $C_{12}H_{12}O_3$ 204.0781; found 204.0774.

2-(2-Chlorophenyl)-2,3-dihydro-4*H*-pyran-4-one (4c): Solvent for flash chromatography: pentane/diethyl ether (7:3). Yellowish oil. $[\alpha]_D^{20}$ –48 (*c* = 0.98, $CHCl_3$) for 45% *ee* {ref.[10b] $[\alpha]_D^{25}$ –140 (*c* = 0.82, $CHCl_3$) for 91% *ee* material}. The *ee* was determined by HPLC analysis using an ODH column (flow rate: 0.5 mL min^{-1}; 90% hexane, 10% 2-propanol, 254 nm) which resolved both enantiomers [$t_{R(major)}$ = 18.6 min, $t_{R(minor)}$ = 20.3 min]. The absolute configuration was not determined. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.61–7.51 (m, 2 H, CH), 7.42–7.30 (m, 3 H, 2×CH), 5.82 (dd, *J* = 4.4, 13.3 Hz, 1 H, CH), 5.56 (d, *J* = 4.4 Hz, 1 H, CH), 2.84–2.65 (m, 2 H, CH_2) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 191.8 (CO), 163.2 (CH), 135.9 (C_q), 131.7 (C_q), 2×129.8 (CH), 127.5 (CH),

127.2 (CH), 107.6 (CH), 78.1 (CH), 42.2 (CH_2) ppm. HRMS (ESI): calcd. for $C_{11}H_9ClO_2$ 208.0286; found 208.0287.

2-(4-Cyanophenyl)-2,3-dihydro-4*H*-pyran-4-one (4d): Solvent for flash chromatography: neat diethyl ether. Yellowish powder; m.p. 70–72 °C. $[\alpha]_D^{20}$ = +55 (*c* = 1.00, CH_2Cl_2) for 70% *ee* {ref.[19] $[\alpha]_D^{25}$ = +79 (*c* = 1.24, CH_2Cl_2) for 95% *ee* material}. The *ee* was determined by HPLC analysis using an ODH column (flow rate: 0.8 mL min^{-1}; 75% hexane, 25% 2-propanol, 254 nm) which resolved both enantiomers [$t_{R(major)}$ = 16.2 min, $t_{R(minor)}$ = 19.9 min]. The absolute configuration was not determined. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.3 Hz, 2 H, CH), 7.55 (d, *J* = 8.3 Hz, 2 H, CH), 7.51 (d, *J* = 5.1 Hz, 1 H, CH), 5.58 (d, *J* = 5.1 Hz, 1 H, CH), 5.51 (dd, *J* = 4.5, 11.6 Hz, 1 H, CH), 2.84 [dd, *J* = 11.6, 13.9 Hz, 1 H, CH(H)], 2.71 [dd, *J* = 4.5, 13.9 Hz, 1 H, CH(H)] ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 190.4 (CO), 162.6 (CH), 143.0 (C_q), 2 × 132.7 (CH), 2 × 126.6 (CH), 118.3 (C_q), 112.8 (C_q), 107.3 (CH), 79.9 (CH), 43.3 (CH_2) ppm. HRMS (EI): calcd. for $C_{12}H_9O_2N$ 199.0628; found 199.0629.

2-(2-Thienyl)-2,3-dihydro-4*H*-pyran-4-one (4e): Solvent for flash chromatography: pentane/diethyl ether (1:1). Yellowish oil. $[\alpha]_D^{20}$ = +130 (*c* = 1.03, $CHCl_3$) for 52% *ee*. The *ee* was determined by HPLC analyses using an AD column (flow rate: 0.8 mL min^{-1}; 98% hexane, 2% 2-propanol, 254 nm) which resolved both enantiomers [$t_{R(minor)}$ = 24.7 min, $t_{R(major)}$ = 27.2 min]. The absolute stereochemistry is not known. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 6.2 Hz, 1 H, CH), 7.38(dd, *J* = 1.1, 5.3 Hz, 1 H, CH), 7.11 (dd, *J* = 0.6, 3.5 Hz, 1 H, CH), 7.03 (dd, *J* = 3.5, 4.8 Hz, 1 H, CH), 5.66 (dd, *J* = 3.7, 13.1 Hz, 1 H, CH), 5.51 (d, *J* = 5.9 Hz, 1 H, CH), 3.00 [dd, *J* = 13.1, 16.7 Hz, 1 H, CH(H)], 2.81 [dd, *J* = 3.7, 16.7 Hz, 1 H, CH(H)] ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ = 191.4 (CO), 162.7 (CH), 140.3 (C_q), 126.9 (CH), 126.7 (CH), 126.2 (CH), 107.6 (CH), 76.5 (CH), 43.1 (CH_2) ppm. HRMS (EI): calcd. for $C_9H_8O_2S$ 180.0240; found 180.0238.

(+)-(*S*)-2-(Furan-2-yl)-2,3-dihydro-4*H*-pyran-4-one (4f): Solvent for flash chromatography: pentane/diethyl ether (1:1). Yellowish oil. $[\alpha]_D^{20}$ = +198 (*c* = 1, $CHCl_3$) for 57% *ee* {ref.[20,21] $[\alpha]_D^{25}$ = –310 (*c* = 1.0, $CHCl_3$) for 99% *ee* material}. The *ee* was determined by HPLC analysis using an AD column (flow rate: 0.8 mL min^{-1}; 90% hexane, 10% 2-propanol, 254 nm) which resolved both enantiomers [$t_{R(minor)}$ = 11.7 min, $t_{R(major)}$ = 17.2 min]. The absolute stereochemistry was assigned as (+)-(*S*) based on a comparison of the measured rotation with literature values.[20,21] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 1.6 Hz, 1 H, CH), 7.31 (d, *J* = 5.7 Hz, 1 H, CH), 6.41 (d, *J* = 3.4 Hz, 1 H, CH), 6.35 (dd, *J* = 1.6, 3.4 Hz, 1 H, CH), 5.47 (d, *J* = 5.7 Hz, 1 H, CH), 5.43–5.41 (m, 1 H, CH), 3.03 [dd, *J* = 12.8, 17.0 Hz, 1 H, CH(H)], 2.67 [dd, *J* = 4.4, 17.0 Hz, 1 H, CH(H)] ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 191.2 (CO), 162.4 (CH), 150.0 (C_q), 143.6 (CH), 110.6 (CH), 109.7 (CH), 107.3 (CH), 73.5 (CH), 39.5 (CH_2) ppm. HRMS (EI): calcd. for $C_9H_8O_3$ 164.0468; found 164.0568.

2-Benzyl-2,3-dihydro-4*H*-pyran-4-one (4g): Solvent for flash chromatography: pentane/diethyl ether (1:1). Yellowish oil. $[\alpha]_D^{20}$ = +45 (*c* = 0.98, CH_2Cl_2) for 50% *ee*. The *ee* was determined by HPLC analysis using an ODH column (flow rate: 0.5 mL min^{-1}; 90% hexane, 10% 2-propanol, 254 nm) which resolved both enantiomers [$t_{R(major)}$ = 18.6 min, $t_{R(minor)}$ = 20.3 min]. The absolute stereochemistry is not known. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.39–7.22 (m, 6 H, CH), 5.42 (d, *J* = 5.9 Hz, 1 H, CH), 4.68–4.62 (m, 1 H, CH), 3.13 [dd, *J* = 6.8, 14.0 Hz, 1 H, CH(H)], 3.02 [dd, *J* = 12.9, 14.0 Hz, 1 H, CH(H)], 2.55 [d, *J* = 12.9 Hz, 16.6 Hz, 1 H, CH(H)], 2.46 [dd, *J* = 4.0, 16.6 Hz, 1 H, CH(H)] ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 192.5 (CO), 163.3 (CH), 135.8 (C_q), 2 × 129.4 (CH), 2 × 128.5 (CH), 127.0 (CH), 107.0 (CH), 79.8 (CH), 41.0 (CH_2), 40.5 (CH_2) ppm. HRMS (EI): calcd. for $C_{12}H_{12}O_2$ 188.0832; found 188.0837.

(+)-(*S*)-2-Styryl-2,3-dihydro-4*H*-pyran-4-one (4h): Solvent for flash chromatography: pentane/diethyl ether (1:1). Yellowish oil. $[\alpha]_D^{20}$ = +69 (*c* = 0.95, CH_2Cl_2) for 44% *ee* {ref.[10a] $[\alpha]_D^{25}$ = –215 (*c* = 0.36, CH_2Cl_2) for 99% *ee* material}. The *ee* was determined by HPLC analysis using an ODH column (flow rate: 1 mL min^{-1}; 90% hexane, 10% 2-propanol, 254 nm) which resolved both enantiomers [$t_{R(major)}$ = 28.0 min, $t_{R(minor)}$ = 29.9 min]. The absolute stereochemistry was assigned as (+)-(*S*) based on a comparison of the measured rotation with the literature value.[10a] ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.41–7.28 (m, 6 H, CH), 6.70 (d, *J* = 16.0 Hz, 1 H, CH), 6.28 (dd, *J* = 6.4, 16.0 Hz, 1 H, CH), 5.46 (d, *J* = 5.9 Hz, 1 H, CH), 5.06–5.02 (m, 1 H, CH), 2.75–2.57 (m, 2 H, CH_2) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 191.9 (CO), 163.0 (CH), 135.5 (C_q), 133.7 (CH), 2 × 128.6 (CH), 128.5 (CH), 2 × 127.4 (CH), 124.9 (CH), 107.2 (CH), 79.6 (CH), 41.8 (CH_2) ppm. HRMS (EI): calcd. for $C_{13}H_{12}O_2$: 200.0832; found 200.0832.

2-Hexyl-2,3-dihydro-4*H*-pyran-4-one (4i): Solvent for flash chromatography: pentane/diethyl ether (1:1). Yellowish oil. $[\alpha]_D^{20}$ = +73 (*c* = 1.01, $CHCl_3$) for 59% *ee* {ref.[10b] $[\alpha]_D^{25}$ = –172 (*c* = 0.19, $CHCl_3$) for 99% *ee* material}. The *ee* was determined by HPLC analysis using an ODH column (flow rate: 0.5 mL min^{-1}; 98% hexane, 2% 2-propanol, 254 nm) which resolved both enantiomers [$t_{R(major)}$ = 19.2 min, $t_{R(minor)}$ = 21.3 min]. The absolute configuration was not determined. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 6.3 Hz, 1 H, CH), 5.39 (d, *J* = 6.3 Hz, 1 H, CH), 4.45–4.32 (m, 1 H, CH), 2.57–2.38 (m, 2 H, CH_2), 1.87–1.75 [m, 1 H, CH(H)], 1.71–1.60 [m, 1 H, CH(H)], 1.40–1.20 (m, 8 H, 4 × CH_2), 0.89 (t, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 192.8 (CO), 163.3 (CH), 106.9 (CH), 79.6 (CH), 41.8 (CH_2), 34.4 (CH_2), 31.6 (CH_2), 28.9 (CH_2), 24.7 (CH_2), 22.5 (CH_2), 14.0 (CH_3) ppm. HRMS (ESI): calcd. for $C_{11}H_{18}O_2$ 182.1301; found 182.1295.

(+)-(*S*)-2-Cyclohexyl-2,3-dihydro-4*H*-pyran-4-one (4j): Solvent for flash chromatography: pentane/diethyl ether (1:1). Yellowish oil. $[\alpha]_D^{20}$ = +105 (*c* = 1.07, CH_2Cl_2) for 72% *ee* {ref.[10a] $[\alpha]_D^{26}$ = –157 (*c* = 1.03, CH_2Cl_2) for 93% *ee* material}. The *ee* was determined by HPLC analysis using an ODH column (flow rate: 0.5 mL min^{-1}; 90% hexane, 10% 2-propanol, 254 nm) which resolved both enantiomers [$t_{R(major)}$ = 13.6 min, $t_{R(minor)}$ = 14.8 min]. The absolute stereochemistry was assigned as (+)-(*S*) based on a comparison of the measured rotation with the literature value.[10a] ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.37 (dd, *J* = 5.9, 1.1 Hz, 1 H, CH), 5.38 (dd, *J* = 5.9, 1.1 Hz, 1 H, CH), 4.17 (ddd, *J* = 14.2, 5.5, 3.3 Hz, 1 H, CH), 2.54 [dd, *J* = 16.6, 14.2 Hz, 1 H, CH(H)], 2.36 [dd, *J* = 16.6, 3.3 Hz, 1 H, CH(H)], 2.00–1.50 (m, 5 H, CH, 2 × CH_2), 1.40–1.00 (m, 6 H, 3 × CH_2) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 193.6 (CO), 163.9 (CH), 106.7 (CH), 83.6 (CH), 41.3 (CH), 38.9 (CH_2), 28.1 (CH_2), 28.0 (CH_2), 26.2 (CH_2), 25.8 (CH_2), 25.8 (CH_2) ppm. HRMS (ESI): calcd. for $C_{11}H_{16}O_2$ 180.1145; found 180.1144.

X-ray Crystallography of 2: X-ray diffraction data were collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The temperature of the crystal was maintained at the selected value (100 K) to within an accuracy of ±1 K by means of a 700 series Cryostream cooling device. The data were corrected for Lorentzian polarization and absorption effects. The structures were solved by direct methods using SHELXS-97[22] and refined against F^2 by full-matrix

least-squares techniques using SHELXL-97[23] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[24] The absolute configuration was determined by refining the Flack's[25] parameter using a large number of Friedel pairs. Crystallographic data for complex **2** are reported in Table 7.

Table 7. Crystallographic data for complex **2**.

Empirical formula	$C_{44}H_{56}ClCrN_2O_4S_2$
Formula weight [g/mol]	828.50
Temperature [K]	100(1)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	C_2
a [Å]	26.083(3)
b [Å]	8.9745(11)
c [Å]	35.900(4)
β [°]	90.749(2)
Cell volume [Å^3]	8402.8(17)
Z	8
Density (calcd.)	1.310
Absorption coefficient [mm^{-1}]	0.479
Reflections collected	44551
Independent reflections	21641, R_{int} = 4.48%
Final R indices [$I>2\sigma(I)$]	0.0869
Final wR indices [$I>2\sigma(I)$]	0.2168
Flack parameter	0.02(3)

CCDC-662070 (for **2**) contains the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

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