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Electropolymerized Cr–salen complexes for the heterogeneous asymmetric hetero Diels-Alder reaction

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Abstract

New electropolymerized chiral salen–chromium complexes have been successfully used as heterogeneous catalysts for the asymmetric hetero Diels-Alder reaction. These insoluble catalysts were reused up to six times affording the expected products with unchanged enantioselectivity along the recycling procedure. Promising attempts to use these catalysts in a multi-substrate procedure are described.
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Keywords: Heterogeneous asymmetric catalysis; Hetero Diels-Alder; Thiophene–salen complexes; Electropolymerization; Chromium

1. Introduction

Asymmetric metal-catalyzed transformations are important tools for the preparation of optically active compounds. Intensive studies, in both academic and industrial world, mainly aimed at C–H bonds formation [1] already allowed the industrialization of optimized methodologies. The formation of C–C and C-heteroatom bonds has been however less developed at a preparative scale. This can be assigned to the low substrate/catalyst ratio that is often required for a complete conversion in a reasonable time. The high costs of both precious metal and optically pure ligand required to achieve satisfactory yields of the expected products are dissuasive for an economical development of these processes. In such a context, the easy recovery of the catalyst and its efficient recycling is a solution for lowering the global cost of the process.

Tetradentate Schiff bases known as salen (*N*,*N*′-bis (salicylaldehydo)ethylenediamine) represent one of the most important class of ligand. Indeed, their chiral derivatives associated to numerous metals allow the efficient enantioselective formation of C–C, C–O and C–N bonds [2]. [V(IV)(salen)] complexes were active for the asymmetric oxidation of sulfides [3] whereas [Co(III)(salen)] complexes catalyzed enantioselective cyclopropanations [4] or Diels-Alder reactions [5]. North et al. and Belokon et al. [6] described the use of [Ti(IV)(salen)] complexes for the asymmetric trimethylsilylcyanation of aldehydes. Chiral [Mn(III)(salen)] [7] and [Cr(III)(salen)] [8] complexes were described as particularly active and enantioselective catalysts for the epoxidation of olefins [9]. Among all these efficient complexes, chromium derivatives proved to be the most useful to catalyze various transformations. Jacobsen indeed successfully described asymmetric epoxide ring-opening reactions by using [Cr(III)(salen)] complexes [10]. These catalysts allowed also the formation of new C–C bonds by asymmetric Nozaki–Hiyama–Kishi reactions [11], enantioselective addition of dimethylzinc to aldehydes [12] or alkylations of tributyltin enolates [13]. Furthermore, the simultaneous formation of C–O and C–C bonds was efficiently performed by hetero Diels-Alder (HDA) reactions catalyzed by chiral [Cr(III)(salen)] complexes [14].

Some efforts have already been devoted towards the heterogeneization of such complexes for their easy recovery and reuse. These methods are mainly based on covalent grafting on organic [15] or inorganic supports [16]. Some procedures involving the polymerization of the modified ligands [17] were also reported as well as a few papers dealing with immobilization methodologies based on non covalent interactions [18]. These procedures have been applied in numerous catalytic transformations leading to some success in terms of enantioselectivity and activity of the immobilized complexes. These results are presented in a recent

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exhaustive review [19]. One will notice that heterogenized chiral [Cr(salen)] complexes have rarely been used in asymmetric HDA reaction [20].

In other respects, an original way for the preparation of heterogenized catalysts is electropolymerization. Some metal containing organic conducting polymers have been reported as electrocatalysts for hydrogenation or epoxidation reactions [21]. Simonneaux and co-workers [22] prepared metallic complexes that were linked to the conjugated core of the polymeric material. Thus, they polymerized ruthenium complexes of chiral spirobifluorenylporphyrins by oxidative polymerization and used them as recyclable heterogeneous catalysts (seven cycles) for the cyclopropanation of olefins.

We present here our results concerning the synthesis and electropolymerization of new chiral [Cr–thiophene–(salen)] monomers with the metallic center directly incorporated into the conjugated polymer backbone. These insoluble complexes have been successfully tested in heterogeneous enantioselective HDA reactions.

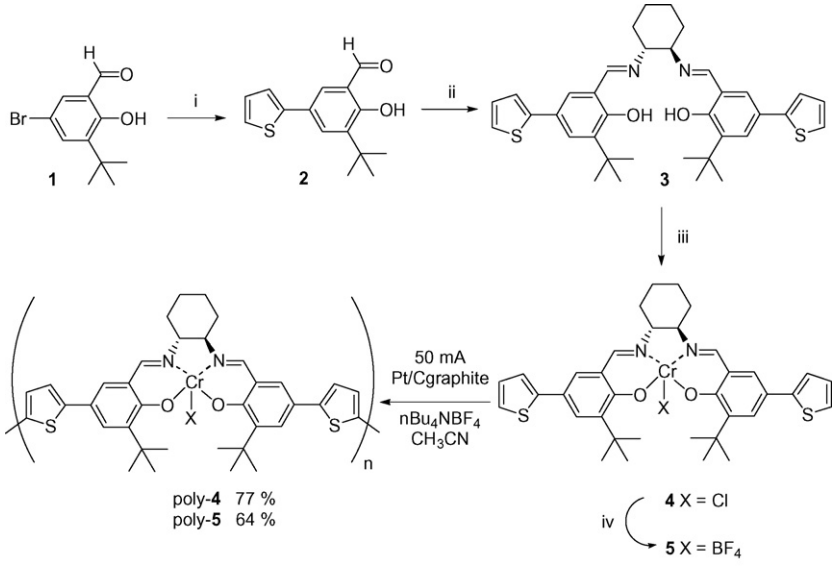
2. Results and discussion

We have prepared salen analogues, possessing thiophene moieties as electropolymerizable functionalities on the fifth positions of the phenol rings. The synthesis, based on a palladium-catalyzed Suzuki coupling followed by condensation with (1*R*, 2*R*)-cyclohexane-1,2-diamine afforded ligand **3** in good yield [23]. Complex **4** was synthesized from **3** by reaction with chromium chloride by complexation under argon atmosphere followed by a few hours of mixing under air [14]. The exchange Cl/BF_4 to yield the corresponding complex **5** was performed in the absence of light by adding $AgBF_4$ (Scheme 1).

We have previously reported the oxidative electropolymerization of various thiophene–salen chiral complexes under cyclic voltammetry conditions [23]. In all cases, polymerization occurred easily, typically between +0.0 and +1.2 V/SCE, leading to the formation of robust films at the platinum surface. This electrochemical approach to afford new organic conducting polymers for the electrocatalytic reduction of O_2 has been reported by Kingsborough and Swager [24]. Preparative electropolymerization conditions were then tested on a platinum grid (2.25 cm^2) to synthesize larger quantities of poly-**4** and poly-**5**. The polymers were recovered as dark brown powders from the electrode.

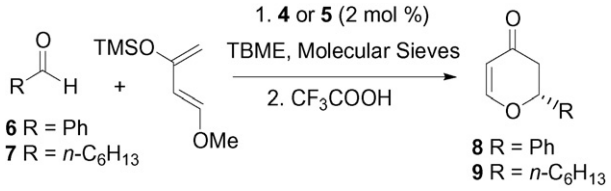
The new polymeric chiral thiophene–salen chromium complexes were tested as catalysts in the HDA reaction between various aldehydes and 1-methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene (Danishefsky's diene). Jacobsen and co-workers [14a] described the HDA transformation of benzaldehyde into the corresponding 2-phenyl-2,3-dihydro-4H-pyran-4-one **8** in up to 87% ee by using the tetrafluoroborate chromium complex of (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine at −30 °C in TBME. Katsuki reported up to 97% ee in an analogous reaction in the presence of salen complexes that bear binaphthyl subunit as a chiral auxiliary [14b]. We have firstly tested our new complexes under similar homogeneous conditions to optimize their efficiency before the use of the analogous heterogeneous catalysts in successive runs (Scheme 2).

Both complexes **4** and **5** bearing different counterion were tested for the HDA reaction in the presence of aliphatic and aromatic substrates. Several parameters were found to influence the enantioselectivity of the reaction and the results are reported in Table 1. **4** and **5** were efficient catalysts for the HDA reaction in the presence of Danishefsky's diene. Products **8** and **9** were



i. 2-thienylboronic acid, 5 mol % $PdCl_2$(dppf), Na_2CO_3, DME/H_2O = 3/1, 100°C, 76 %. ii. (1*R*, 2*R*)-1,2-diaminocyclohexane, 50 mol %, EtOH, 60°C, 2h, 50 %. iii. $CrCl_2$, THF, 75 %. iv. $AgBF_4$, TBME, 76 %.

Scheme 1. Synthesis of new Cr–thiophene–salen complexes.



Scheme 2. Homogeneous HDA reactions with **4** and **5**.

indeed isolated in moderate to high yield (up to 94%, entry 1). Catalyst **4** was found slightly more active than its tetrafluoroborate counterpart **5**. On the contrary catalyst **5** led to the expected compounds with higher enantioselectivities than **4** especially for substrate **6** (see, for example, entries 1 and 3).

The enantioselectivity of the reaction was temperature dependent only for the transformation of **7** (see entries 5 and 6, and 7 and 8). Such a marked effect was not visible with **6**. These new thiophene–salen chromium catalysts afforded products **8** and **9** albeit with lower enantioselectivities compared to the best values previously reported in the literature. The thiophene withdrawing substituent in the fifth position of the salen replacing the donating *tert*-butyl group is probably detrimental to the enantiofacial discrimination. The results are indeed quite similar to those obtained by Jacobsen with the methoxy-substituted salen ligand, indicating analogous electronic and steric effects of the methoxy and thiophene substitutents on the salen ligand for this reaction. The highest enantiomeric excess (82%) was obtained in our case for the preparation of 2-hexyl-2,3-dihydropyran-4-one **9** with catalyst **5** at −30 °C. The synthesis of **9** was also performed in THF, CH_3CN and CH_2Cl_2 leading to similar results in terms of activity and enantioselectivity, indicating that the solvent did not influence drastically the course of the transformation. These reactions in the absence of molecular sieves showed no variation in the results. For the continuation of our study under heterogeneous conditions, molecular sieves were omitted.

These reactions were then studied in the presence of the polymerized catalysts poly-**4** and poly-**5** in order to study their recycling ability. Poly-**5** was firstly used as an insoluble powder to optimize the heterogeneous procedure. Its recycling involves the centrifugation of the reaction mixture followed by the removal of the solution part and its treatment with CF_3COOH for analysis. The remaining polymerized catalyst was dried under vacuum, then substrates and solvent were added to the same reaction vessel for the catalyst recycling. Applied to the transformation of benzaldehyde **6** in TBME, this methodology afforded product **8** in 65% yield and 47% ee in the first run, with a similar activity compared to the homogeneous analogue complex. The significant decrease in the enantioselectivity (compare with Table 1, entry 3, 61% ee under homogeneous conditions) is probably due to conformational changes around the catalytic center, i.e. bite angles variation coming from the formation of the organic conducting polymers. It is indeed well-documented [25] that thiophene derivatives easily form helical structures upon polymerization. Poly-**5** was successfully used up to five times but a significant decrease of the isolated yield was observed in the following recycling. However, product **8** was each time isolated with remarkably stable enantiomeric excess around 47%.

Table 1
HDA reaction with new chiral salen complexes **4** or **5**

Entry	Substrate	X	T (°C)	t (h)	Yield (%)	ee (%) **8** or **9**
1	**6**	Cl	20	21	94	55 (*R*)
2	**6**	Cl	−30	27	92	54 (*R*)
3	**6**	BF_4	20	18	65	61 (*R*)
4	**6**	BF_4	−30	22	38	63 (*R*)
5	**7**	Cl	20	19	72	71
6	**7**	Cl	−30	69	58	81
7	**7**	BF_4	20	17	60	72
8	**7**	BF_4	−30	65	53	82

Table 2
Heterogeneous HDA reaction with heptanal in THF at room temperature in the presence of 4 mol% Poly-**4**

Recycling	t (h)	Yield (%)	ee (%) for **9**
1st use	23	74	62
2nd use	24	77	62
3rd use	22	71	64
4th use	23	60	66
5th use	24	55	63
6th use	22	56	63
7th use	23	17	63

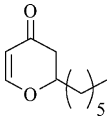
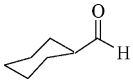
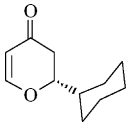
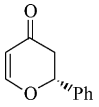
To widen the application scope of this new procedure for heterogeneous catalysis, the reaction of heptanal with Danishefsky's diene was performed in the presence of 4 mol% poly-**4** at room temperature in THF (see Table 2). Analogously, pyranone **9** was obtained with 62% ee and very good yield, in the same reaction time than under homogeneous conditions.

Following the same recycling procedure, poly-**4** was used seven times showing no decrease in the reaction selectivity. The catalyst maintained its activity for the first three runs, but the isolated yield of **9** dropped then regularly with the successive reuses, probably due to the partial loss of the insoluble catalyst during the centrifugation.

Finally, the ability of catalyst poly-**4** to perform a multi-substrate transformation was studied. Such a concept has hardly been demonstrated despite the abundant literature dealing with heterogeneization methodologies for asymmetric catalysts [26]. Poly-**4** was thus subsequently used for the transformation of three different aldehydes (see Table 3).

In the first run, heptanal afforded the targeted compound **9** with 63% ee. After removal of the reaction products, cyclohexanecarboxaldehyde was introduced in the same reaction vessel. The corresponding pyranone was isolated in 75% yield with 56% ee after 65 h reaction time. Under homogeneous conditions and in the presence of catalyst **4**, we synthesized 2-cyclohexyl-2,3-dihydro-pyran-4-one in 82% yield and 70% ee. Following the same recycling procedure, the third run was performed in the presence of benzaldehyde as substrate. This reaction was again successful since **8** was isolated in high yield and 43% ee. A same batch of our insoluble polymer was thus able to catalyze the successive transformation of various aldehy-

Table 3
Multi-substrate heterogeneous HDA reaction in TBME at room temperature in the presence of 6 mol% Poly-**4**

Recycling	Substrate	*t* (h)	Yield (%)	Product	ee (%)
1st use		23	76		63
2nd use		65	75		56 (*R*)
3rd use		42	93		43 (*R*)

des allowing the isolation of the expected pyranones in high yield.

3. Conclusion

We have developed an efficient immobilization strategy for chiral salen-based chromium catalysts by electropolymerization of the corresponding monomeric thiophene complexes. This procedure allowed the preparation of new chiral insoluble polymeric catalysts, with the active sites directly incorporated in the conjugated backbone. These materials were successfully used to perform asymmetric heterogeneous HDA reactions between several aldehydes and Danishefsky's diene. Our original procedure improved the convenience of the catalytic transformation by simple removal of the product from the reaction vessel, subsequent washing and drying of the remaining catalyst and addition of new solutions of reactants. Some decrease in enantioselectivity is observed between the results obtained from homogeneous and heterogeneous catalysis. We propose this to arise from some changes both in the electronic character of the ligand (delocalization due to the conjugation of the polymerized catalyst) and in the steric hindrance around the active metal center (different bite angle). Nevertheless, the heterogeneous catalyst was used in seven successive runs without showing any loss of enantioselectivity. Furthermore, the same batch of catalyst was used in three different consecutive reactions. Work is in progress in our laboratory to modify the structure of our insoluble chromium catalysts by co-polymerization for optimizing their enantioselectivity. Tests in other catalytic asymmetric transformations are also ongoing for widening the scope of their application.

4. Experimental

4.1. 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, TBME, CH_3CN and CH_2Cl_2 from calcium hydride. The aldehydes were distilled before use, Danishefsky's diene was engaged as received. (*R*,*R*)-(*N*,*N*′-bis(3-*tert*-butylsalicylidene-5-thiophen-2-yl)-cyclohexane-1,2-diamine **3** was prepared as reported in ref. [23]. ^{1}H NMR spectra were recorded on either a Bruker AM 200 (200 MHz) or an AM 250 (250 MHz) instrument with samples dissolved in $CDCl_3$ and data are reported in ppm with the solvent signal as reference (7.27 ppm). ^{13}C NMR spectra were recorded on a Bruker AM 250 (62.5 MHz) instrument with samples dissolved in $CDCl_3$ and data are reported in ppm with the solvent signal as reference (77.0 ppm). 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 on a Finnigan MAT 95 S spectrometer. HPLC analyses were carried out on a PERKIN-ELMER chromatograph equipped with a diode array UV detector using an ODH column. Ultraviolet–visible spectra of acetonitrile solutions were recorded on a Bio-tek instruments Uvikon XL spectrometer. 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 carbon graphite 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 dry atmosphere and flushed with argon throughout the electrochemical experiments.

4.2. (R,R)-(N,N′-bis(3-tert-butylsalicylidene-5-thiophen-2-yl)-cyclohexane-1,2-diamine 3

To a solution of 3-*tert*-butyl-2-hydroxy-5-thiophen-2-yl-benzaldehyde (2.70 mmol) in ethanol (40 mL) was added (*R*,*R*)-1,2-cyclohexanediamine (1.40 mmol) with continuous stirring, and the mixture was heated to 60 °C for 2 h. The reaction was cooled to room temperature and the resulting yellow solid was filtered, washed with ethanol, and dried to afford the desired product **3** (420 mg, 50%) as a yellow solid. m.p. = 112–114 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 14.06 (s, 2H); 8.35 (s, 2H); 7.51 (s, 2H); 7.25 (d, 2H, J = 2.4 Hz); 7.20 (dd, 2H, J = 4.9, 1.0 Hz); 7.12 (dd, 2H, J = 5.1, 1.0 Hz); 7.05 (dd, 2H, J = 5.1, 4.9 Hz); 3.40 (m, 2H); 2.05–1.65 (m, 8H); 1.47 (s, 18H). ^{13}C NMR (62,5 MHz, $CDCl_3$) δ = 165.5; 160.2; 144.6; 137.8; 127.8; 127.7; 127.2; 124.5; 123.5; 121.8; 118.6; 72.3; 34.9; 33.0; 29.4; 24.3. HRMS (EI): calcd. for $C_{36}H_{42}N_2O_2S_2$: 598.2682; found: 598.2655. IR: 3696.6 (C–OH) and 1631.7 (C=N). $[\alpha]_D^{20}$—35.4 (*c* 0.34, $CHCl_3$). UV–vis (CH_3CN) λ_{max} 218, 253, 296, 345.

4.3. Chromium–thiophene–salen complex 4

Chiral ligand **3** (385 mg, 0.64 mmol) was added to a solution of anhydrous Cr(II)Cl_2 (90.5 mg, 0.74 mmol) in dry, deoxygenated THF (18 mL) under nitrogen atmosphere. The resulting brown solution was stirred for 4 h and then exposed to air. Stirring was continued over night to give a dark brown solution. It was diluted with CH_2Cl_2 (50 mL) followed by washing with

sat. NH_4Cl (3 × 50 mL) and aq. NaCl (3 × 50 mL). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure to afford complex **4** as a brown solid (512 mg, 75%). IR (KBr, cm^{-1}): 2942, 2857, 1620, 1536, 1459, 1425, 1409, 1385, 1323, 1253, 1207, 1161, 878, 813, 689, 572. Anal. calcd. for $C_{36}H_{40}N_2O_2S_2CrClTHF$: C, 63.52; H, 6.40; N, 3.70; S, 8.48%. Found: C, 63.72; H, 6.64; N, 3.77; S, 8.43%. UV–vis (CH_3CN) λ_{max} 227, 278, 310, 445.

4.4. Chromium–thiophene–salen complex 5

Without further purification, complex **4** (100.4 mg, 0.14 mmol) was dissolved in dry TBME (2 mL) and $AgBF_4$ (30 mg, 0.15 mmol) was added to the solution. The reaction flask was wrapped with aluminum foil and stirred at room temperature for 5 h under argon atmosphere, after which it was filtered through celite and washed with TBME. Evaporation of the solvent gave complex **5** as a brown powder (82 mg, 76%), which was used without further purification. IR (KBr, cm^{-1}): 2958, 2862, 1751, 1619, 1541, 1428, 1410, 1386, 1319, 1261, 1206, 1163, 1084, 1054, 1029, 879, 813, 691, 574, 513. Anal. calcd. for $C_{36}H_{40}N_2O_2S_2CrBF_42H_2O2THF$: C, 57.70; H, 6.60; N, 3.06%. Found: C, 57.68; H, 6.61; N, 2.59%.

4.5. Procedure for the preparative electropolymerization of complexes 4 and 5

Complexes **4** (100 mg, 0.15 mmol) or **5** (103 mg, 0.14 mmol) were placed in an undivided electrochemical cell fitted with a carbon graphite cathode and a platinum grid (2.25 cm^2) as the anode. The anode potential was monitored versus a saturated calomel electrode all along the electrolysis. $n$$Bu_4NBF_4$ (0.03 M in 15 mL CH_3CN) was used as supporting electrolyte and the electrolysis was performed at a constant current of 50 mA during 0.5 h. The platinum grid was found covered with the polymerized complex. Some insoluble material also settled at the bottom of the cell. The deposited polymer was used as insoluble catalyst after removal from the support and several washings with acetonitrile. This residue was dried under vacuum and used without further purification for the asymmetric catalysis. Yield: 77% for poly-**4** and 64% for poly-**5**.

4.6. HDA reactions under homogeneous conditions

A schlenk tube was charged with 2 mol% of catalyst **4** or **5** and thoroughly maintained under an argon atmosphere by three successive vacuo-argon cycles. TBME (200 μL), the aldehyde (1 mmol) and Danishefsky's diene (195 μL, 1 mmol) were then introduced with a syringe. In the case of reactions performed at low temperature, the mixture was first cooled to −30 °C followed by the addition of the diene. The resulting solution was stirred at room temperature (or at −30 °C) for the specified amount of time. It was then diluted with 2 mL CH_2Cl_2, 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 using flash chromatography.

4.7. (R)-2-Phenyl-2,3-dihydro-pyran-4-one

Solvent for flash chromatography: heptane/EtOAc, 70:30. Yellowish oil, $[\alpha]_D^{20}$—42.8 (*c* 1, $CHCl_3$) for 43% ee, ref. [27] −83.0 (*c* 0.5, $CHCl_3$) for 82% ee material. The ee was determined by HPLC analyses using an ODH column (flow rate = 0.5 mL min^{-1}; 90% hexane, 10% isopropanol, 254 nm), which resolved both enantiomers ($t_{R(minor)}$ = 21.9 min, $t_{R(major)}$ = 25.8 min). The absolute stereochemistry was assigned as (−)-(*R*) based on comparison of the measured rotation with the literature value [27].

^1H NMR (250 MHz, $CDCl_3$) δ = 7.49 (d, J = 6.1 Hz, 1H), 7.46–7.37 (m, 5 H), 5.54 (dd, J = 6.1, 1.3 Hz, 1H), 5.43 (dd, J = 14.4, 3.5 Hz, 1H), 2.9 (dd, J = 16.9, 14.4 Hz, 1H), 2.68 (dd, J = 16.9, 3.5, Hz, 1H). ^{13}C NMR (62,5 MHz, $CDCl_3$) δ = 192.2, 163.3, 137.9, 128.9, 128.9, 126.1, 107.4, 81.1, 43.3.

4.8. 2-Hexyl-2,3-dihydro-pyran-4-one

Solvent for flash chromatography: heptane/EtOAc, 80:20. Yellowish oil, $[\alpha]_D^{20}$—78.4 (*c* 1, $CHCl_3$) for 62% ee, ref. [14b] −172.0 (*c* 0.19, $CHCl_3$) for 99% ee material. The ee was determined by HPLC analyses using an ODH column (flow rate = 0.5 mL min^{-1}; 98% hexane, 2% isopropanol, 254 nm), which resolved both enantiomers ($t_{R(minor)}$ = 19.2 min, $t_{R(major)}$ = 21.3 min). The absolute stereochemistry of this compound is not known.

^1H NMR (250 MHz, $CDCl_3$) δ = 7.35 (d, J = 5.9 Hz, 1H), 5.39 (d, J = 5.9 Hz, 1H), 4.45–4.32 (m, 1H), 2.57–2.38 (m, 2H), 1.87–1.75 (m, 1H), 1.71–1.60 (m, 1H), 1.40–1.20 (m, 8H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (62,5 MHz, $CDCl_3$) δ = 192.8, 163.3, 106.9, 79.6, 41.8, 34.4, 31.6, 28.9, 24.7, 22.5, 14.0.

4.9. (R)-2-Cyclohexyl-2,3-dihydro-pyran-4-one

Solvent for flash chromatography: heptane/EtOAc, 80:20. Yellowish oil, $[\alpha]_D^{20}$—92.7 (*c* 1, $CHCl_3$) for 56% ee, ref. [14a] −157.0 (*c* 1.03, CH_2Cl_2) for 93% ee material. The ee was determined by HPLC analyses using an ODH column (flow rate = 0.5 mL min^{-1}; 98% hexane, 2% isopropanol, 254 nm), which resolved both enantiomers ($t_{R(minor)}$ = 22.8 min, $t_{R(major)}$ = 26.0 min). The absolute stereochemistry was assigned as (−)-*R* based on comparison of the measured rotation with the literature value [27].

^1H NMR (250 MHz, $CDCl_3$) δ = 7.37 (dd, J = 5.9, 1.1 Hz, 1H), 5.38 (dd, J = 5.9, 1.1 Hz, 1H), 4.17 (ddd, J = 14.2, 5.5, 3.3 Hz, 1H), 2.54 (dd, J = 16.6, 14.2 Hz, 1H) 2.36 (ddd, J = 16.7, 3.3, 1.1 Hz, 1H), 2.00–1.50 (m, 5H) 1.40–1.00 (m, 6H). ^{13}C NMR (62,5 MHz, $CDCl_3$) δ = 193.6, 163.9, 106.7, 83.6, 41.3, 38.9, 28.1, 28.0, 26.2, 25.8, 25.8.

4.10. HDA reactions under heterogeneous conditions

A schlenk tube was charged with 4 mol% of catalyst poly-**4** or poly-**5** and thoroughly maintained under an argon atmosphere by three successive vacuo-argon cycles. TBME (or THF) (200 μL), the aldehyde (1 mmol) and Danishefsky's diene

(234 μL, 1.2 mmol) were then introduced with a syringe. The resulting solution was stirred at room temperature for the specified amount of time. It was then diluted with CH_2Cl_2 (5 mL) and the mixture was centrifuged. The solution was recovered and this procedure was repeated until the solution remained colorless. The resulting solutions were combined, treated with a drop of trifluoroacetic acid and further stirred for another 30 min. The solvents were then removed under reduced pressure and the residue was purified by using flash chromatography for the determination of the enantiomeric excess. In the schlenk tube, catalysts poly-**4** or poly-**5** were dried under vacuum and new substrates and solvent were added for their reuse.

Acknowledgments

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