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New Chiral Thiophene−Salen Chromium Complexes for the Asymmetric Henry Reaction

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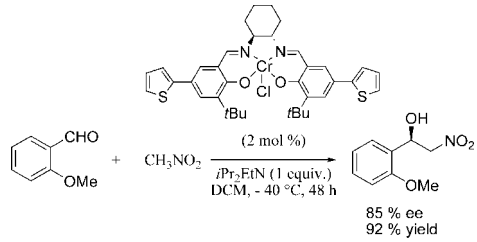

Chiral thiophene−salen chromium complexes were investigated in their monomeric form as soluble catalysts in the enantioselective Henry reaction of several aldehydes. The anodic polymerization of one complex led to an insoluble powder that was successfully used as a heterogeneous catalyst for the transformation of 2-methoxybenzaldehyde with enantiomeric excesses up to 77%. The polymerized catalyst was recovered and also recycled in an original multisubstrate procedure.

The nitroaldol reaction (or Henry reaction, discovered in 1895)[1] is an efficient method for the formation of a C−C bond between a nucleophile coming from a nitroalkane with a carbonyl electrophile from an aldehyde or a more challenging ketone. The first asymmetric catalytic version of this transformation was reported by Shibasaki et al.,[2] nearly one century later. An optically active lanthanum alkoxide from binaphthol was used, exhibiting a sufficient basic character for the in situ generation of a nitronate species and leading to high enantiomeric excesses for the targeted nitroaldol derivatives. Since this first issue, numerous successful catalytic asymmetric Henry reactions have been described in the literature, and these results have been discussed in recent exhaustive reviews.[3,4] Apart from the early rare-earth-based asymmetric catalysis developed and optimized by Shibasaki's group,[5] zinc(II)-based catalysts have also proved their efficiency in the enantioselective Henry reaction.[6] Copper-based catalysis has been also intensively studied by different groups, leading to high levels of enantiocontrol with a wide variety of ligands.[7] More recently, other metals such as cobalt[8] or chromium[9] associated with chiral salen derivatives afforded β-nitroalcohol in satisfactory yields and enantioselectivities. By fine-tuning the synthesis of the salen ligands, up to 94% ee was recently reached with chromium complexes.[9b] The Henry reaction has also been successfully performed by using organocatalysts[10] or enzymes.[11] The products of the enantioselective Henry reaction are highly valuable synthons for the preparation of useful chiral intermediates in synthetic organic chemistry, and their preparation in high yield and selectivity following a safe and economic procedure is still challenging. In such a context and for matching at best the "principles in green chemistry",[12] some examples have been reported in which the asymmetric catalytic Henry reaction was performed under heterogeneous conditions as an attempt to improve the procedures by the efficient recovery and recycling of the chiral catalysts. By immobilizing (*S*)-(−)-binol onto nanocrystalline magnesium oxide, Choudary, Kantam, and coworkers were able to carry out efficiently the asymmetric nitroaldol reaction using five times the same batch of catalyst without noting any loss in activity nor in enantioselectivity.[13] Chiral lanthanum−lithium−binaphthol complexes were also bonded to silica and MCM-41, and they proved to be as efficient as their homogeneous counterparts in terms of enantioselectivity.[14] A chiral copper acetate complex tethered to poly(ethylene glycol) was also used in a recycling procedure, demonstrating a high activity and stability.[15]

We have recently proposed a method for the polymerization of new chiral thiophene-containing salen ligands via the

(1) Henry, L. *C. R. Hebd. Seances Acad. Sci.* **1895**, *120*, 1265–1267.
(2) Sasai, H.; Suzuki, T.; Arai, S.; Arai, T.; Shibasaki, M. *J. Am. Chem. Soc.* **1992**, *114*, 4418–4420.
(3) Boruwa, J.; Gogoi, N.; Saikia, P. P.; Barua, N. C. *Tetrahedron: Asymmetry* **2006**, *17*, 3315–3326.
(4) Palomo, C.; Oiarbide, M.; Laso, A. *Eur. J. Org. Chem.* **2007**, 2561–274.
(5) (a) Shibasaki, M.; Sasai, H.; Arai, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1236–1256, and literature cited therein. See also: (b) Sohtome, Y.; Kato, Y.; Handa, S.; Aoyama, N.; Nagawa, K.; Matsunaga, S.; Shibasaki, M. *Org. Lett.* **2008**, *10*, 2231–2234. (c) Tosaki, S. Y.; Hara, K.; Gnanadesikan, V.; Morimoto, H.; Harada, S.; Sugita, M.; Yamagiwa, N.; Matsunaga, S.; Shibasaki, M. *J. Am. Chem. Soc.* **2006**, *128*, 11776–11777. (d) Saa, J. M.; Tur, F.; Gonzalez, J.; Vega, M. *Tetrahedron: Asymmetry* **2006**, *17*, 99–106.
(6) (a) Trost, B. M.; Yeh, V. S. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 861–863. (b) Trost, B. M.; Yeh, V. S. C.; Ito, H.; Bremeyer, N. *Org. Lett.* **2002**, *4*, 2621–2623. (c) Gao, J.; Martell, A. E. *Org. Biomol. Chem.* **2003**, *1*, 2801–2806. (d) Palomo, C.; Oiarbide, M.; Laso, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 3881–3884. (e) Liu, S.; Wolf, C. *Org. Lett.* **2008**, *10*, 1831–1834.
(7) (a) Christensen, C.; Juhl, K.; Hazell, R. G.; Jørgensen, K. A. *J. Org. Chem.* **2002**, *67*, 4875–4881. (b) Xiong, Y.; Wang, F.; Huang, X.; Wen, Y.; Feng, X. *Chem.−Eur. J.* **2007**, *13*, 829–833. (c) Bandini, M.; Piccinelli, F.; Tommasi, S.; Umani-Ronchi, A.; Ventrici, C. *Chem. Commun.* **2007**, 616–618. (d) Arai, T.; Takashita, R.; Endo, Y.; Watanabe, M.; Yanagisawa, A. *J. Org. Chem.* **2008**, *73*, 4903–4906. (e) Ma, K.; You, J. *Chem.−Eur. J.* **2007**, *13*, 1863–1871.
(8) Kogami, Y.; Nakajima, T.; Ikeno, T.; Yamada, T. *Synthesis* **2004**, 1947–1950.
(9) (a) Kowalczyk, R.; Sidorowicz, Ł.; Skarżewski, J. *Tetrahedron: Asymmetry* **2007**, *18*, 2581–2586. (b) Kowalczyk, R.; Kwiatkowski, P.; Skarżewski, J.; Jurczak, J. *J. Org. Chem.* **2009**, *74*, 753–756.
(10) (a) Chinchilla, R.; Nájera, C.; Sánchez-Agulló, P. *Tetrahedron: Asymmetry* **1994**, *5*, 1393–1402. (b) Sohtome, Y.; Hashimoto, Y.; Nagasawa, K. *Eur. J. Org. Chem.* **2006**, 2894–2897. (c) Marcelli, T.; van der Haas, R. N. S.; van Maarseveen, J. H.; Hiemstra, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 929–931.
(11) Gruber-Khadjawi, M.; Purkarthofer, T.; Skrane, W.; Griengl, H. *Adv. Synth. Catal.* **2007**, *349*, 1445–1450.
(12) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, 1988; p 30.
(13) Choudary, B. M.; Ranganath, K. V. S.; Pal, U.; Kantam, M. L.; Sreedhar, B. *J. Am. Chem. Soc.* **2005**, *127*, 13167–13171.
(14) Bhatt, A. P.; Pathak, K.; Jasra, R. V.; Kureshy, R. I.; Khan, N.-u. H.; Abdi, S. H. R. *J. Mol. Catal. A: Chem.* **2006**, *244*, 110–117.
(15) Bandini, M.; Benaglia, M.; Sinisi, R.; Tommasi, S.; Umani-Ronchi, A. *Org. Lett.* **2007**, *9*, 2151–2153.

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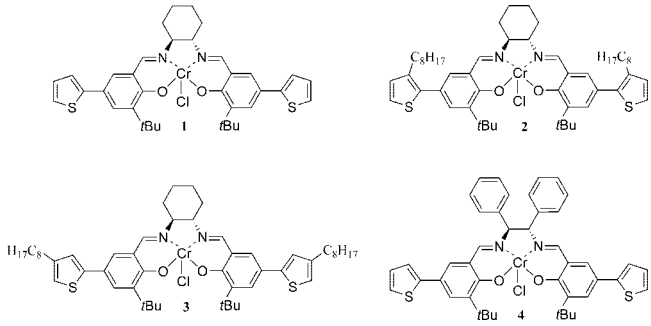
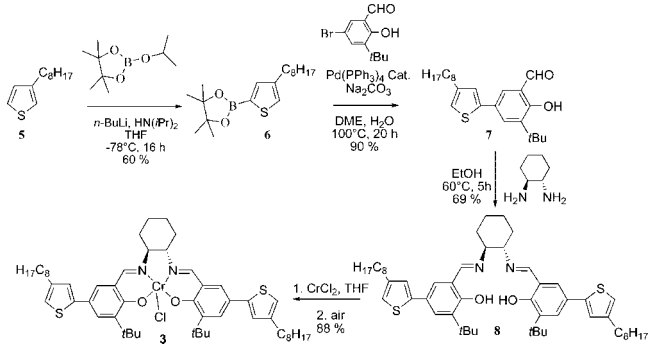


FIGURE 1. Structures of thiophene salen complexes **1**−**4**.

SCHEME 1. Synthetic Pathway for the Preparation of Chromium Complex 3

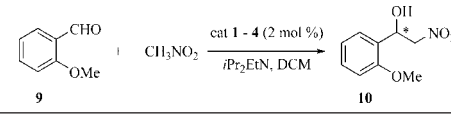


electrochemical oxidation of their metal complexes (Co, Cu, Cr, and Ni).[16] Various chromium-containing polymers were thus prepared and used to promote the asymmetric Diels−Alder reaction between Danishefsky's diene and different aldehydes.[17] A procedure for the reuse of these heterogeneous catalysts was optimized, and they gratifyingly exhibited a very high stability, allowing their recycling in an original multisubstrate process.[18] We report here the efficient use of monomeric chiral thiophene−salen chromium complexes as soluble catalysts in the Henry reaction under homogeneous conditions. After anodic polymerization, one complex was engaged as insoluble powder to catalyze the asymmetric nitroaldol reaction under heterogeneous conditions. The reuse of this catalyst is also described.

Thiophene−salen chromium complexes **1**, **2**, and **4** were synthesized as we previously reported.[18] Another new complex was prepared, compound **3**, in which the alkyl groups on the thiophene rings are placed in the fourth position for an evaluation of steric effects on the enantioselectivity of the catalytic transformation compared to complex **2** (Figure 1).

Starting from octylthiophene **5**, 4,4,5,5-tetramethyl-2-(4-octylthiophen-2-yl)-[1,3,2]dioxaborolane **6** was almost selectively prepared in the presence of LDA as base[19] with 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane at low temperature (Scheme 1). Compound **6** was isolated with 60% yield and then treated in a Suzuki−Miyaura coupling[20] with 5-bromo-3-*tert*-butyl-2-hydroxybenzaldehyde to yield **7** in a high yield after purification. A condensation reaction with (*S*,*S*)-cyclohexane-1,2-diamine yielded the new chiral ligand **8** that was readily transformed in the corresponding chromium complex **3**, following a procedure described by Jacobsen.[21]

TABLE 1. Asymmetric Henry Reaction Catalyzed by Complexes 1−4



entry	cat	*i*Pr$_2$EtN (equiv)[a]	time (h)	*T* (°C)	yield **10** (%)[b]	ee **10** (%)[c]
1	**1**	1	24	20	74	34
2	**1**	0.5	24	20	83	47
3	**1**	0.05	24	20	61	69
4	**1**	1	48	−20	77	74
5	**1**	1	48	−40	92	85
6	**1**	1	72	−78	74	79
7	**1**	0.5	48	−40	79	82
8	**2**	1	24	20	70	54
9	**2**	1	48	−40	91	81
10	**2**	0.5	48	−40	75	81
11	**3**	1	24	20	86	49
12	**4**	1	24	20	74	32
13[d]	**1**	1	24	20	88	74
14[d]	**1**	1	48	−40	82	73

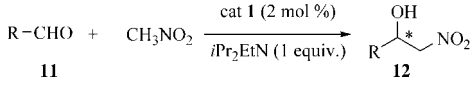
[a] The amount of base is calculated according to the quantity of aldehyde. [b] Isolated yield. [c] Enantiomeric excesses are determined by chiral HPLC analyses (see Supporting Information). [d] Reaction run in MTBE.

All chromium complexes were then evaluated in their capacity to promote the enantioselective nitroaldol reaction. Complex **1** was first tested for the transformation of 2-methoxybenzaldehyde **9** with nitromethane into 1-(2-methoxyphenyl)-2-nitroethanol **10** in dichloromethane (DCM). Catalyst **1** afforded the desired compound **10** with 34% ee in 74% isolated yield when the reaction was performed at room temperature in the presence of 1 equiv of diisopropylethylamine (Table 1, entry 1). A similar result was obtained when triethylamine was used as the base, whereas K_3PO_4 led to a much less efficient catalytic system (19% yield and 9% ee). The decrease of the amount of base allowed interestingly an enhancement in the reaction selectivity (Table 1, entries 2 and 3), albeit accompanied by a loss of activity if 5 mol % of base was used. The reaction temperature had an important effect on both the activity and enantioselectivity of the transformation (Table 1, entries 4−7). The best compromise was obtained by working at −40 °C using 1 equiv of base. Product **10** was indeed obtained with a very high isolated yield and 85% ee after 48 h reaction time (Table 1, entry 5). A further decrease in the temperature (Table 1, entry 6) or using a lower amount of base (entry 7) did not improve the results.

Complex **2**, bearing sterically hindered alkyl-donating groups on the third positions of the thiophene ring proved to be a more enantioselective catalyst for the preparation of compound **10** at ambient temperature than complex **1** (Table 1, compare entries 1 and 8). Unfortunately, these results were not improved by lowering the temperature (Table 1, compare entries 5 and 7 to entries 9 and 10). Complexes **3** and **4** promoted also efficiently the Henry reaction of 2-methoxybenzaldehyde with nitromethane, albeit without leading to enhanced enantioselectivities. Different solvents were then investigated for performing this transformation. Similar reactions were run with complex **1** in methyl *tert*-

(16) Voituriez, A.; Mellah, M.; Schulz, E. *Synth. Met.* **2006**, *156*, 166–175.
(17) Mellah, M.; Ansel, B.; Patureau, F.; Voituriez, A.; Schulz, E. *J. Mol. Catal. A: Chem.* **2007**, *272*, 20–25.
(18) Zulauf, A.; Mellah, M.; Guillot, R.; Schulz, E. *Eur. J. Org. Chem.* **2008**, 2118–2129.
(19) Jayakannan, M.; Van Hal, P. A.; Janssen, R. A. J. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 251–261.
(20) Mohanakrishnan, A. K.; Hucke, A.; Lyon, M. A.; Lakshmikantham, M. V.; Cava, M. P. *Tetrahedron* **1999**, *55*, 11745–11754.
(21) Schaus, S. E.; Branålt, J.; Jacobsen, E. N. *J. Org. Chem.* **1998**, *63*, 403–405.

TABLE 2. Asymmetric Henry Reaction with Different Aldehydes Catalyzed by Thiophene−Salen Complex 1



11 12

entry		aldehyde R =	solvent	time (h)		T (°C)	yield 12 (%)[a]	ee 12 (%)[b]
1			DCM	24		20	39	25
2	**11a**	Ph	MTBE	24	**12a**	20	37	34
3			DCM	48		−40	62	62
4			DCM	24		20	42	25
5	**11b**	*p*-Cl-C_6H_4	MTBE	24	**12b**	20	62	36
6			DCM	48		−40	43	64
7			DCM	24		20	66	<5
8	**11c**	*p*-NO_2-C_6H_4	MTBE	24	**12c**	20	77	36
9			DCM	48		−40	87	15
10			MTBE	48		−40	81	40
11			DCM	24		20	13	18
12	**11d**	*p*-MeO-C_6H_4	MTBE	24	**12d**	20	34	48
13			DCM	48		−40	29	65
14			DCM	24		20	92	64
15	**11e**	cyclohexyl	MTBE	24	**12e**	20	79	69
16			DCM	48		−40	59	80
17			DCM	24		20	63	59
18	**11f**	C_6H_{13}	MTBE	24	**12f**	20	33	69
19			DCM	48		−40	72	83

[a] Isolated yield. [b] Enantiomeric excesses are determined by chiral HPLC analyses (see Supporting Information).

butyl ether (MTBE), and a highly improved enantioselectivity, at least at room temperature (up to 74% ee), was obtained, compared to the reaction in DCM (Table 1, compare entries 1 and 13). In this case, however, the temperature showed no influence on the enantioselectivity (Table 1, compare entries 13 and 14). We further demonstrated that the uncatalyzed nitroaldol reaction between nitromethane and **9** occurred at room temperature. Racemic product **10** was indeed isolated with 37% yield when the reaction was run in DCM, whereas less than 5% was produced in MTBE. These control experiments are thus in total accordance with the results of the catalyzed transformations and can explain the low enantioselectivity observed in DCM. Indeed, the competitive noncatalyzed racemic reaction is probably favored in this more polar solvent. The reaction was also conducted in ethanol, and the targeted product **10** was isolated in poor yield (33%) and enantioselectivity (23%) together with the important formation of the corresponding acetal 1-(1,1-diethoxyethyl)-2-methoxybenzene.

Complex **1** was thus chosen as the best catalyst of the series, considering its easy synthesis and its efficiency and further involved in the transformation of various substrates for widening the scope of its application. The transformation of various aldehydes with nitromethane in the presence of 2 mol % of catalyst **1** was investigated, and the reactivity and enantioselectivity of the catalyst were compared at different temperatures in DCM or in MTBE. In each case, the catalyst proved to be active for promoting the transformations, which led in general to better enantioselectivities at room temperature in MTBE compared to those obtained in DCM.

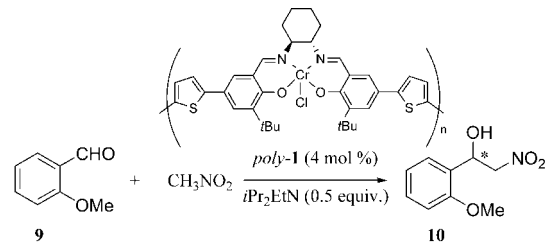
Aromatic aldehydes were fairly transformed, but the corresponding products were isolated in only modest yields, except for 2-nitro-1-(4-nitrophenyl)ethanol (Table 2, entries 7 and 10). Aliphatic aldehydes proved to be more reactive substrates, and the corresponding nitroalcohols were isolated in up to 92% yield (Table 2, entry 14). In each case, higher enantioselectivities were observed when the reaction was performed in MTBE instead of DCM at room temperature, indicating probably a faster competitive racemic reaction in this latter solvent. However, running the reaction in DCM at −40 °C allowed the preparation of the targeted products with the highest enantioselectivities (up to 83% for the preparation of 1-hexyl-2-nitroethanol **12f**) as the best conditions for this homogeneous reaction. Substrate **11c** was an exception since better results were obtained in MTBE (Table 2, entry 10).

Taking into account these results, we attempted to perform the Henry reaction under heterogeneous conditions, in the presence of a polymerized catalyst, poly-**1**.[22] This insoluble complex was prepared by electrochemical oxidative polymerization of monomer **1** in an undivided cell in the presence of nBu$_4$NBF$_4$ as supporting electrolyte at a fixed intensity. We have already reported this procedure in a previous paper.[18] Poly-**1** was recovered as an insoluble powder from the electrode surface and used as catalyst to promote the Henry reaction of 2-methoxybenzaldehyde **9** with nitromethane under heterogeneous conditions. Reactions were performed either in dichloromethane at −40 °C or in MTBE at room temperature. After complete conversion of the substrate, the solution was removed from the Schlenk tube through a filtration syringe, and the remaining powdered catalyst was washed successively with DCM or MTBE, water and then dried. New substrates were then added to the same set of catalyst to evaluate its recycling ability. The polymerized catalyst promoted satisfyingly the Henry reaction in both solvents, and the expected products were recovered with yields similar to those observed under homogeneous conditions. It is noticeable that the polymerized catalyst does not show any loss in activity compared to its homogeneous counterpart, as is often the case for heterogeneous catalysts. Following experiments were then performed to confirm that the transformation was promoted by the catalyst under heterogeneous conditions. Samples of poly-**1** were stirred for 16 h in DCM and in MTBE in the presence of the base and nitromethane. The solutions were then removed from the insoluble powder by filtration. 2-Methoxybenzaldehyde was added to these solutions that were further stirred for an additional 24 h at room temperature. After classical workup, only traces of alcohol **10** were obtained from the MTBE solution. Accordingly, **10** was isolated in 33% yield as racemic compound from the DCM solution. These results indicate that no chiral complex was leaching from the polymer into the solution as asymmetric catalyst for the transformation. The first use of poly-**1** in both solvents afforded thus the expected products with high enantioselectivity values, showing however a slight decrease compared to the results obtained under homogeneous conditions. These polymers were reused four times, but each recycling was accompanied with a diminution of the yield and of the enantioselectivity (see Scheme 2).

The versatility of poly-**1** as catalyst was demonstrated in a multisubstrate procedure. New structurally different aldehydes were introduced at each recycling of the polymer catalyst (see Table 3) since the efficiency of the corresponding monomer complex **1** was previously evaluated with different substrates in homogeneous conditions.

(22) For a recent review on heterogeneous asymmetric catalysis promoted by salen complexes, see: Baleizão, C.; Garcia, H. *Chem. Rev.* **2006**, *106*, 3987–4043.

SCHEME 2. Asymmetric Henry Reaction with 2-Methoxybenzaldehyde Catalyzed by poly-1 under Heterogeneous Conditions—Recycling of the Catalyst



DCM 48 h, - 40°C	isolated yield (%)	ee (%)	MTBE 24 h, 20°C	isolated yield (%)	ee (%)
1st run	93	77	1st run	100	65
2nd run	60	75	2nd run	83	63
3rd run	36	64	3rd run	45	60
4th run	33	60	4th run	24	32
5th run	10	34	5th run	22	27

TABLE 3. Asymmetric Heterogeneous Henry Reaction with Different Aldehydes Catalyzed by poly-1—Multisubstrate Procedure[a]

product	cycle	yield (%)[b]	ee (%)[c]	cycle	yield (%)[b]	ee (%)[c]
10	1st	92	54	4th	77	62
12e	2nd	66	51	5th	27	52
12f	3rd	13	38	6th	11	47

[a] Reaction run in MTBE, 4 mol % of poly-**1**, 20 °C, 24 h. [b] Isolated yield. [c] Enantiomeric excesses are determined by chiral HPLC analyses.

The recycling procedure under these conditions afforded all expected products with satisfying yields (except for compound **12f** as volatile species) that were interestingly easily isolated without contamination with any product traces from the preceding run at each cycle. The enantioselectivity values were similar to that obtained under homogeneous conditions and remained remarkably stable by comparing each entry and the corresponding run of the preceding sequence.

New chiral chromium Schiff base complexes substituted by thiophene units at the 5,5′-positions of the phenolic rings were thus efficiently used as enantioselective catalysts for the Henry reaction between nitromethane and various aldehydes. The desired nitroaldols were produced with enantiomeric excesses up to 83% ee. These results compare well in terms of enantioselectivity with those obtained by the best complexes described in the literature for this transformation. A corresponding electrogenerated polymer, poly-**1**, promoted also successfully the heterogeneous Henry reaction, and this catalyst was recycled four times, albeit with a slight loss in efficiency. The same catalyst batch was engaged in an original multisubstrate procedure and used also many times by adding a structurally different aldehyde at each recycling. As far as we know, this report is the first use of a chiral heterogenized salen complex active in the Henry reaction.

Experimental Section

Representative Procedure for Henry Reactions. Homogeneous Conditions. A Schlenk tube was charged with the catalyst (2 mol %) and maintained under an argon atmosphere by three successive vacuo-argon cycles. DCM or MTBE (4 mL), the aldehyde (1 mmol), and nitromethane (2 mL, 37.5 mmol) were introduced. In the case of reactions performed at low temperature, the mixture was first cooled to the desired temperature, then followed by the addition of a solution of diisopropylethylamine (1 or 0.5 equiv) in DCM or MTBE (4 mL). The resulting solution was stirred for the specified amount of time. The solvents were then removed under reduced pressure, and the residue was purified by flash chromatography on silica gel for the determination of the yield of the reaction and the enantiomeric excess of the product.

Heterogeneous Conditions. A Schlenk tube was charged with the catalyst poly-**1** (27.4 mg, 4 mol %), and the procedure is analogous to that described above. After the resulting suspension was stirred for the specified amount of time, it was then filtered with a filtering syringe and the precipitate was thoroughly washed twice with DCM or MTBE. The solvents of the combined filtrates were removed under reduced pressure, and the residue was purified by flash chromatography on silica gel for the determination of the yield of the reaction and the enantiomeric excess of the product. In the Schlenk tube, the powdered catalyst was washed with water and THF or MTBE then dried under vacuum, and new substrates and solvents were added for its recycling.

Preparation of (*R*)-1-(2-Methoxyphenyl)-2-nitroethanol 10. Solvent for flash chromatography: pentane/diethyl ether 4/1. Yellowish oil, $[\alpha]^{20}_D$ −36.2 (*c* 1.01, $CHCl_3$) for 74% ee, lit[9] $[\alpha]_D$ +42.3 (*c* 1.1, CH_2Cl_2) for 73% ee material. The ee was determined by HPLC analysis using an IB column (flow rate = 1.0 mL·min^{-1}; 90% hexane, 10% isopropanol, λ = 254 nm), which resolved both enantiomers (t_R = 9.3 min, t_S = 10.2 min). The absolute stereochemistry was assigned as *R* based on comparison of the measured rotation with the literature value: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (dd, J = 1.5, 7.5 Hz, 1H), 7.32 (ddd, J = 1.5, 7.9, 9.4 Hz, 1H), 7.00 (dd, J = 0.9, 7.5 Hz, 1H), 6.91 (dd, J = 0.9, 8.1 Hz, 1H), 5.62 (dd, J = 3.2, 9.2 Hz, 1H), 4.63 (dd, J = 3.2, 13.0 Hz, 1H), 4.55 (dd, J = 9.2, 13.0 Hz, 1H), 3.88 (s, 3H), 3.47 (br s, 1H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 155.8, 129.6, 127.0, 126.0, 120.9, 110.4, 79.7, 67.5, 55.2; MS (CI) 215 [MNH_4^+] (100), 197 (14), 137 (14).

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Supporting Information Available: Complete experimental procedures, characterization, and ee determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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