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Highly Active 3-Oxobutylideneaminatocobalt Complex Catalysts for an Enantioselective Hetero Diels–Alder Reaction

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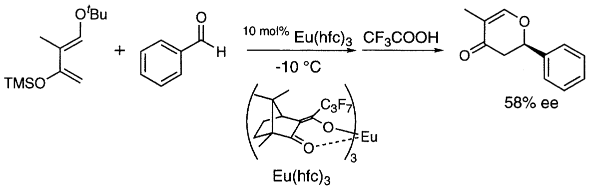
Optically active 3-oxobutylideneaminatocobalt(III) complexes were developed as effective catalysts for the enantioselective hetero Diels–Alder reaction of aromatic and aliphatic aldehydes with 3-(*t*-butyldimethylsilyloxy)-1-methoxy-1,3-butadiene. In the presence of the highly active cationic cobalt(III) complex, the hetero Diels–Alder reactions proceeded to afford the corresponding dihydropyran-4-ones with high performance and high enantioselectivities. The reaction with aromatic aldehydes substituted by a coordinating group at the ortho position proceeded more smoothly.

Among the various carbon–carbon bond-forming reactions, the enantioselective hetero Diels–Alder reaction has emerged as an important method in synthetic organic chemistry,[1] because carbon–carbon and carbon–oxygen bonds are both formed to stereoselectively afford six-membered pyran derivatives. Lewis acids have been versatile catalysts for the Diels–Alder reaction; therefore, much effort has been made to develop efficient organometallic complex catalysts for the enantioselective hetero Diels–Alder reaction. The first report on an enantioselective catalytic hetero Diels–Alder reaction was attempted by Danishefsky[2] et al. The available chiral lanthanide β-diketonato complex Eu(hfc)$_3$ was employed as a Lewis acid to achieve 58% ee in the hetero Diels–Alder reaction of benzaldehyde with 1-*t*-butoxy-2-methyl-3-(trimethylsilyloxy)-1,3-butadiene (Eq. 1).



(1)

Recently, several groups have reported promising Lewis acid catalysts for catalytic enantioselective versions of this reaction. For instance, as typical Lewis acids, high performance was achieved by chiral (acyloxy)borane catalysts,[3] optically pure binaphthol (BINOL) aluminum catalysts,[4] and chiral BINOL titanium catalysts.[5] Rare earth metal catalysts, such as chiral yttrium bis-trifluoromethanesulfonylamides[6] and chiral ytterbium(III) phosphate,[7] were also proposed for use as effective Lewis acids. Remarkable development was recently reported for the chiral transition-metal-based Lewis acid catalysts; e.g., the chiral salen chromium(III)[8] complex, the corresponding cobalt[9] and ruthenium[10] complexes, bis(3-acylcamphorato)oxovanadium,[11] bis(oxazoline)copper[12] and zinc[13] complexes, and the BINAP-palladium(II)[14] complex were employed as a chiral Lewis acid. In order to achieve a high ability and selectivity as a catalyst, the choice of the center metal, the design of the chiral ligand, and the combination of the ligand with the metal are essential.

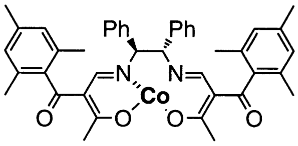


Fig. 1. (*S*)-MPAC (**1a**).

Optically active 3-oxobutylideneaminato ligands derived from the corresponding 3-oxoalkanals and optically active 1,2-diarylethylenediamines were also employed as effective catalysts in various enantioselective reactions. Their manganese(III) complexes catalyzed the aerobic enantioselective oxidation of alkenes[15] and sulfides,[16] and their corresponding cobalt(II) complexes (Fig. 1) effectively catalyzed the enantioselective borohydride (tetrahydroborate) reductions of ketones,[17] imines,[18] and α,β-unsaturated carboxamides,[19] and the enantioselective cyclopropanation of styrene derivatives with diazoacetate.[20] In our previous paper, it was observed that the corresponding cobalt(II) complexes employed as a chiral Lewis acid catalyst for the hetero Diels-Alder reactions of aromatic[21] and aliphatic aldehydes with electron-rich diene (Danishefsky's diene) afforded the corresponding dihydropyran-4-ones with high yields and high enantioselectivities.[22] By designing optically active 3-oxobutylideneaminato cationic cobalt(III) complex catalysts, high performance was achieved for the catalytic enantioselective reaction. In this paper, we disclose the detailed results of a highly enantioselective hetero Diels–Alder reaction of aromatic and aliphatic aldehydes with electron-rich dienes catalyzed by optically active 3-oxobutylideneaminatocobalt(III) complexes.

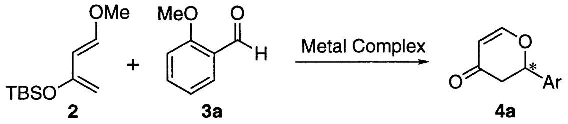
Results and Discussion

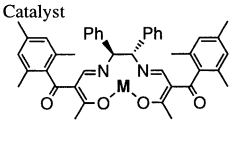
Various Metal Complexes with the Optically Active 3-Oxobutylideneaminato Ligand. Various metal complexes with the optically active 3-oxobutylideneaminato ligand were prepared and their catalytic activities for the hetero Diels–Alder reaction were examined. In the presence of 5.0 mol% of each complex catalyst, the hetero Diels–Alder reaction of *o*-methoxybenzaldehyde (**3a**) with 3-(*t*-butyldimethylsilyloxy)-1-methoxy-1,3-butadiene (**2**)[23] was tried in dichloromethane solution at −20 °C (Table 1). After the treatment of the crude product with trifluoroacetic acid, the optical yield of the obtained dihydropyran-4-one derivative was determined by HPLC analysis (Chiralpak AD). Although titanium[5] and aluminum[4] complexes were often employed as effective Lewis acid catalysts, their optically active 3-oxobutylideneaminato complexes were not efficient catalysts for the present hetero Diels-Alder reaction (Entries 1 and 2). The copper(II) complexes with the bis(oxazoline) ligands[12] and the chromium(III) complexes with salen-type ligands[8] were reported to be effective as Lewis acid catalysts for the hetero Diels-Alder reaction; however, the corresponding 3-oxobutylideneaminato complexes were not employed (Entries 3 and 4). When the 3-oxobutylideneaminatomanganese(III), nickel(II), or oxovanadium(IV) complex catalyst was subjected to the reaction, the racemic product was only obtained in low yield (Entries 5, 6, and 7). On the contrary, in the presence of a catalytic amount of the optically active 3-oxobutylideneaminatocobalt(II) complex catalyst ((*S*)-MPAC), the hetero Diels–Alder reaction smoothly proceeded to afford the corresponding dihydropyran-4-one with moderate enantioselectivity (Entry 8).

Enantioselective Hetero Diels–Alder Reaction in Various Solvents. Solvation influences the steric factor of the Lewis acid catalysts and the stereochemistry. A nonpolar solvent was conventionally used for Lewis acid catalyzed reactions, while the coordination of the solvent would be sometimes effective for the stereoselectivities.[3a,12f,24] As shown in Table 2, the product yields and enantiomer excesses were quite dependent on the solvent used. In dichloromethane, fluorobenzene, and toluene, a more than 95% yield of the product was obtained and the optical yields were 62%, 57%, and 50%, respectively (Entries 2–4). The solvents, such as acetonitrile, diethyl ether, and tetrahydrofuran, however, decreased the catalytic activity, since their coordination to the cobalt complexes changed the stereochemical configuration in the intermediate (Entries 5–7). The 3-oxobutylideneaminatocobalt catalysts were not dissolved in hexane and afforded the products in low yield with low enantioselectivities (Entry 8). In order to avoid lowering the yield and the enantiomer excess, a halogenated or aromatic solvent was utilized. Dichloromethane was chosen as the reaction solvent due to its high yield and high enantioselectivity.

Temperature Effect in Enantioselective Hetero Diels–Alder Reaction. The reaction temperature dependence was examined for the hetero Diels-Alder reaction using *o*-methoxybenzaldehyde (**3a**) (Table 3). At room temperature, 80% of

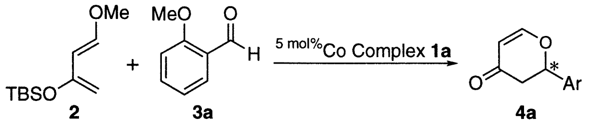
Table 1. Various Metal Complex Catalysts with Optically Active 3-Oxobutylideneaminato Ligand for Asymmetric Hetero Diels–Alder Reaction



Entry[a)]	Catalyst 	Time/h	Yield/ %[b)]	Ee/ %[c)]
1	Ti(IV)Cl_2	92	23	4
2	Al(III)Cl	92	23	1
3	Cu(II)	30	trace	—
4	Cr(III)Cl	30	10	0
5	Mn(III)Cl	30	15	0
6	Ni(II)	41	41	0
7	V(IV)=O	92	32	6
8	Co(II)	55	96	62

a) Reaction conditions: metal complex catalyst 0.025 mmol (5.0 mol%), dienophile 0.5 mmol, and diene 1.0 mmol at −20 °C in CH_2Cl_2. b) Isolated yield after the treatment with CF_3COOH. c) Determined by HPLC analysis using Chiralpak AD (0.5% 2-propanal in hexane).

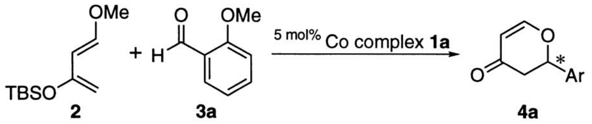
Table 2. Various Solvents for Asymmetric Hetero Diels–Alder Reaction



Entry[a)]	Solvent	Time/h	Yield/%[b)]	Ee/%[c)]
1	—	24	89	51
2	CH_2Cl_2	55	96	62
3	PhF	72	96	57
4	Toluene	47	quant	50
5	CH_3CN	95	44	59
6	Et_2O	47	32	56
7	THF	70	trace	—
8	Hexane	98	28	46

a) Reaction conditions: Co(II) complex catalyst 0.025 mmol (5.0 mol%), dienophile 0.5 mmol, and diene 1.0 mmol at −20 °C. b) Isolated yield after the treatment with CF_3COOH. c) Determined by HPLC analysis using Chiralpak AD (0.5% 2-propanol in hexane).

Table 3. Temperature Effect for Asymmetric Hetero Diels–Alder Reaction *o*-Methoxybenzaldehyde



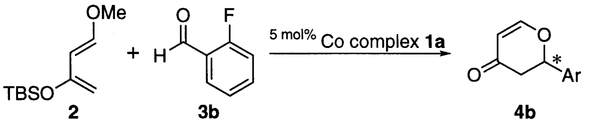
Entry[a)]	Temp/°C	Time/h	Yield/%[b)]	Ee/%[c)]
1	r.t.	30	80	25
2	−20	55	96	62
3	−40	55	85	60
4	−78	77	23	38

a) Reaction conditions: Co(II) complex catalyst 0.025 mmol (5.0 mol%), dienophile 0.5 mmol, and diene 1.0 mmol in CH_2Cl_2. b) Isolated yield after the treatment with CF_3COOH. c) Determined by HPLC analysis using Chiralpak AD (0.5% 2-propanol in hexane).

the products were obtained and the optical yield was 25% (Entry 1). In order to enhance the stereoselectivity of the pyranone derivatives, the reaction was tried at −20 °C and −40 °C (Entries 2 and 3), and the optical yields increased to 62 and 60%, respectively. However, both the yield and the ee decreased at −78 °C after a long reaction (Entry 4). In the reaction of *o*-fluorobenzaldehyde (**3b**), more than 70% of the products were obtained, and the optical yield was 40% at room temperature (Table 4, Entry 1). Then, the reaction was tried at −50 °C and −78 °C (Entries 2 and 3), and the optical yields increased to 70 and 78%, respectively.

Various Optically Active 3-Oxobutylideneaminatocobalt(II) Complexes and Effective Axial Ligands. A variety of optically active 3-oxobutylideneaminatocobalt complexes (Fig. 2) were examined for the asymmetric hetero Diels–Alder reaction of *o*-fluorobenzaldehyde (Table 5). These complexes (**1a**, **5a**, and **6a**) were respectively prepared from the corresponding optically active 1,2-diarylethylenediamines and 1,3-dicarbonyl compounds. When the optically active cobalt(II) complex **5a** was employed as the catalyst, the yield and the optical yield of the product were slightly improved compared with complex **1a** (Entries 1 and 2). On the contrary, both the activity and enantioselectivity unexpectedly decreased when complex **6a** was used. A variety of axial ligands were next examined to enhance the Lewis acidity. The cobalt(III) complexes, **1b** and **1c**,[25] were obtained by the oxidation of the cobalt(II) complex **1a** with Br_2 and I_2, respectively. In the presence of complexes **1b**, though the optical yield of the product significantly decreased, the reaction smoothly proceeded (Entry 4). When the cobalt(III) complex **1c** was employed, the reaction time was shortened and the optical yield of the product was maintained (Entry 5). Furthermore, the cationic cobalt(III) complex **1d**, obtained by treating the corresponding cobalt(III) iodide **1c** with silver trifluoromethanesulfonate (AgOTf) (Eq. 2), was proved to be a highly active catalyst for the hetero Diels-Alder reaction. In the presence of the 5 mol% complex catalyst **1d**, the reaction was completed in 12 h to give pyranone **4b** with 85% ee (Entry 6). The addition of MS 4A[26] to the reaction mixture improved both the yield and the optical yield of the product, and the cationic cobalt(III) triflate complex **5d**, prepared from complex **5c**, significantly accelerated the hetero Diels–Alder reaction to produce the corresponding dihydropyran-4-one with high enantioselectivity (Entries 7,8, and 9).

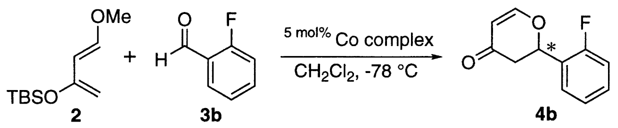
Table 4. Temperature Effect for Asymmetric Hetero Diels–Alder Reaction of *o*-Fluorobenzaldehyde



Entry[a]	Temp/°C	Time/h	Yield/%[b]	Ee/%[c]
1	r.t.	22	76	40
2	−50	48	68	70
3	−78	50	62	78

a) Reaction conditions: Co(II) complex catalyst 0.025 mmol (5.0 mol%), dienophile 0.5 mmol, and diene 1.0 mmol in CH_2Cl_2. b) Isolated yield after the treatment with CF_3COOH. c) Determined by HPLC analysis using Chiralpak AD (1.0% 2-propanol in hexane).

Table 5. Various Cobalt Complex Catalysts for Asymmetric Hetero Diels–Alder Reaction of *o*-Fluorobenzaldehyde



Entry[a]	Catalysts	Time/h	Yield/%[b]	Ee/%[c]
1	**1a**	50	62	78
2	**5a**	72	71	83
3	**6a**	31	9	14
4	**1b**	36	84	73
5	**1c**	36	87	78
6	**1d**	12	89	85
7	**5c**	24	83	81
8[d]		24	91	86
9[d]	**5d**	3	89	87

a) Reaction conditions: 0.025 mmol (5.0 mol%) cobalt catalyst, 0.5 mmol dienophile (*o*-fluorobenzaldehyde), and 1.0 mmol diene in CH_2Cl_2 (2.5 mL). b) Isolated yield after the treatment with CF_3COOH. c) Determined by HPLC analysis using Chiralpak AD (1.0% 2-propanol in hexane). d) Powdered 4 Å molecular sieves (MS 4A) were added.

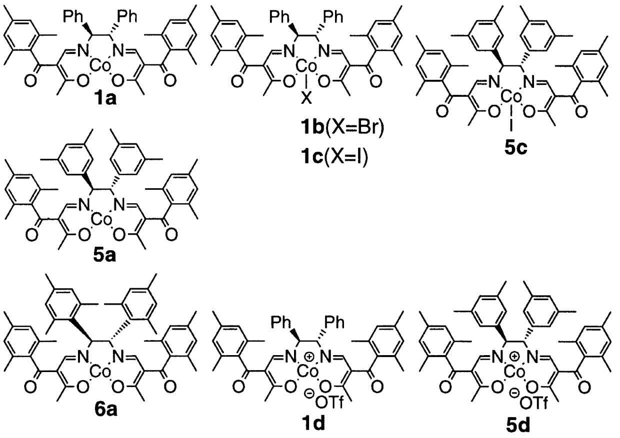
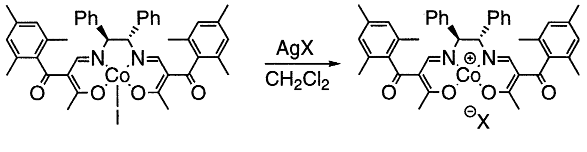


Fig. 2. Various 3-oxobutylideneaminato cobalt(II) and cobalt(III) complexes.

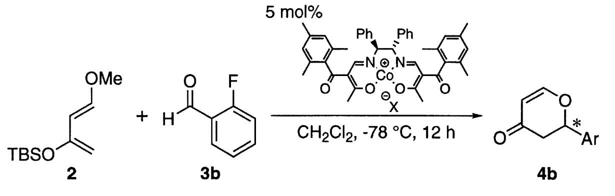


(2)

Various Counter Anions of the Cationic Cobalt(III) Complexes. In the previous section, it was mentioned that the hetero Diels–Alder reaction proceeded smoothly in the presence of the cationic cobalt(III) trifluoromethanesulfonate complex catalyst. Other counter anions have also been screened to achieve high reactivities and high selectivities (Table 6). The cationic cobalt(III) complexes (**1e**, **1f**, **1g**, **1h**, and **1d**) were synthesized by the treating the cobalt(III) complex **1c** with the corresponding silver salts. The yield of 2,3-dihydro-4*H*-pyran-

4-one was higher than 90% when complexes **1e** and **1f** were used as catalysts (Entries 1 and 2). On the other hand, the product was obtained with about an 80% yield when **1g**, **1d**, and **1h** were employed. As a result of these experiments, the cationic cobalt(III) complexes catalyzed the hetero Diels–Alder reaction more effectively than the corresponding cobalt(III) iodide, and little difference in the catalytic activity was found among the cationic cobalt(III) complexes.

Table 6. Various Cationic Cobalt Complex Catalysts for Asymmetric Hetero Diels–Alder Reaction



Entry[a)]	Catalysts	Yield/%[b)]	Ee/%[c)]
1	**1e**(SbF_6)	90	82
2	**1f**(PF_6)	98	85
3	**1g**(BF_4)	77	82
4	**1d**(OTf)	89	85
5	**1h**(OTs)	81	80

a) Reaction conditions: 0.025 mmol (5.0 mol%) cobalt catalyst, 0.5 mmol dienophile (*o*-fluorobenzaldehyde), and 1.0 mmol diene in CH_2Cl_2 (2.5 mL). b) Isolated yield after the treatment with CF_3COOH. c) Determined by HPLC analysis using Chiralpak AD (1.0% 2-propanol in hexane). d) Powdered 4 Å molecular sieves (MS 4A) were added.

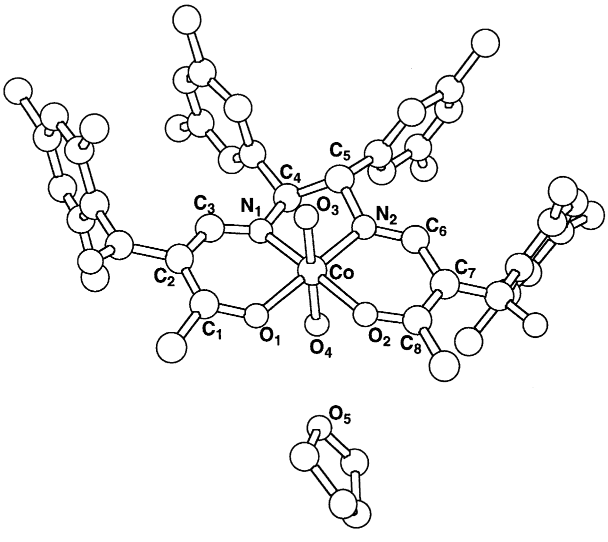
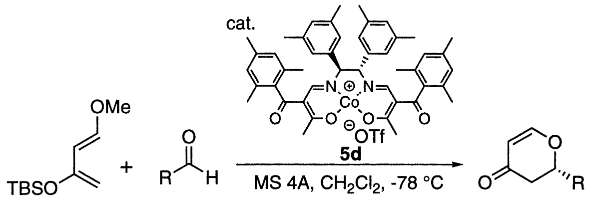
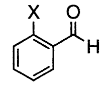
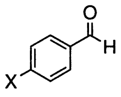
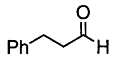
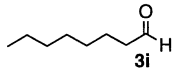


Fig. 3. Crystal structure of {(1*S*,2*S*)-1,2-bis(3,5-dimethylphenyl)-*N*,*N*′-bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]ethylenediaminato}cobalt(III) trifluoromethanesulfonate dihydrate (**5d**): Selected bond lengths (Å) and bond angles (°) are as follows: Co–O1, 1.899(7); Co–O2, 1.912(8); Co–N1, 1.864(8); Co–N2, 1.853(8); Co–O3, 1.939(8); Co–O4, 1.931(8); O1-Co-N2, 179.1(3); O2-Co-N1, 178.8(4); O1-Co-O2, 86.0(3); O1-Co-N1, 93.3(3); O2-Co-N2, 94.8(4); N1-Co-N2, 85.8(4); O1-Co-O4, 89.4(3); O2-Co-O4, 88.6(3); O4-Co-N1, 90.5(3); O4-Co-N2, 90.2(4); (Two molecules exist in each unit cell, and one of them and $^{-}OSO_2CF_3$ ion were omitted for clarity).

X-ray Analysis of the Cationic Cobalt(III) Complex. An X-ray analysis of the cationic cobalt(III) complex was carried out. Screening of the various combinations of the cobalt(III) complexes and solvent for the formation of single crystals revealed that when the cationic cobalt(III) **5d** was recrystallized from a mixed solvent of tetrahydrofuran–hexane, single crystals of sufficient size were obtained for a structural analysis. Figure 3 shows the crystal structure of cobalt(III) trifluoromethanesulfonate **5d**. The structure of the optically active 3-oxobutylideneaminato cationic cobalt(III) trifluoromethanesulfonate **5d** was found to be very similar to that of the corresponding cobalt(III) iodide complex previously reported.[27] Two oxygen atoms and two nitrogen atoms coordinating to the central cobalt atoms are on the same plane. This is evidence in support of similar transition states to the corresponding cobalt(III) iodide. Two water molecules occupy each of the opposite axial positions perpendicular to the coplanar formed by the oxygen and nitrogen atoms on the cobalt complex. Tetrahydrofuran, a solvent for recrystallization, was 2.58 Å (2.61 Å for another independent cobalt complex in a unit cell) from the water oxygen and trifluoromethanesulfonate ion was 2.67 Å (2.86 Å) from the water oxygen. As compared with the length of the cobalt–iodine bond of **1c** (2.57 Å),[27] it is reasonable to consider that the 3-oxobutylideneaminatocobalt(III) cation was completely separated from the trifluoromethanesulfonate ion; therefore, its Lewis acidity was enhanced. The FAB mass-

Table 7. The Asymmetric Hetero Diels–Alder Reaction of Various Dienophiles



Entry[a)]	R-CHO		Time/h	Yield/%[b)]	Ee/%
1		**3b** (X=F)	3	89	87
2		**3c** (X=Cl)	3	81	81
3		**3d** (X=NO_2)	7	94	94
4		**3e** (X=CF_3)	7	88	91
5		**3f** (X=Cl)	24	81	91
6		**3g** (X=H)	59	83	90
7		**3h**	96[c)]	69	90
8	 **3i**		96[d)]	89	88

a) Reaction conditions: 0.025 mmol (5.0 mol%) cobalt(III)-OTf catalyst **5d**, 0.5 mmol dienophile (aldehyde), 150 mg MS 4A, and 1.0 mmol diene in CH_2Cl_2 (2.5 mL). b) Isolated yield after the treatment with CF_3COOH. c) 9.0 mol% cobalt(III)-OTf complex **1d** and 200 mg MS 4A was employed. d) 8.0 mol% complex **1d** was employed.

spectra data also indicated that cobalt(III) iodide and cobalt(III) bromide provided their own molecular weight, while the cationic cobalt(III) complex showed their cationic cobalt species and their anions.

Enantioselective Hetero Diels–Alder Reaction of Various Aldehydes. The highly active cationic cobalt(III) triflate complexes **1d** and **5d** were successfully applied as effective chiral catalysts for the enantioselective hetero Diels–Alder reaction of various aldehydes with the electron-rich diene. As shown in Table 7, the hetero Diels–Alder reactions of the *o*-fluoro- and *o*-chlorobenzaldehydes (**3b** and **3c**) smoothly proceeded to afford the corresponding dihydropyran-4-ones in high yield with high enantioselectivity (Entries 1 and 2). By using the cationic cobalt(III) complex **5d** as a Lewis acid catalyst, aromatic aldehydes substituted by an electron-withdrawing group at the para position reacted with Danishefsky's diene, and was completely consumed in 7–24 h. The enantioselectivities in these reactions of the *p*-nitro-, *p*-trifluoromethyl-, and *p*-chlorobenzaldehydes (**3d**, **3e**, and **3f**) were 94, 91, and 91% ee, respectively (Entries 3–5). The hetero Diels–Alder reaction of benzaldehyde (**3g**) also proceeded to afford the corresponding pyranone derivative in 83% yield with 90% ee (Entry 6). In the presence of a catalytic amount of the cationic cobalt(III) triflate complex **1d**, the hetero Diels–Alder reaction of 3-phenylpropionaldehyde (**3h**) and octanal (**3i**) smoothly proceeded to afford the corresponding dihydropyran-4-ones with high enantioselectivity (90 and 88% ee, Entries 7 and 8, respectively).

Acceleration of the Reaction for the Ortho Substituted Aromatic Aldehydes. The reaction proceeded rapidly when a methoxy group or halogen atom was substituted at the ortho position of the aromatic aldehyde. For instance, the 2-(2-chlorophenyl)-2,3-dihydro-4*H*-pyran-4-one was obtained in 81% within 3 h, whereas the 2-(4-chlorophenyl)-2,3-dihydro-4*H*-pyran-4-one was obtained in 81% yield after 24 h.[28] These results suggest that the hetero Diels–Alder reaction was accelerated due to the coordination of the cobalt complex by a substituent group at the ortho position. The time-course of the products' yields was then investigated (Fig. 4). The cobalt complex **1a** was employed in the reaction. For the ortho-chloro substituted aromatic aldehyde, the reaction was completed in 24 h and the optical yield was 75% ee. On the contrary, when para-chloro derivatives were used, the reactions proceeded slower and did not finish even after 48 h, but the optical yields were 83% ee.

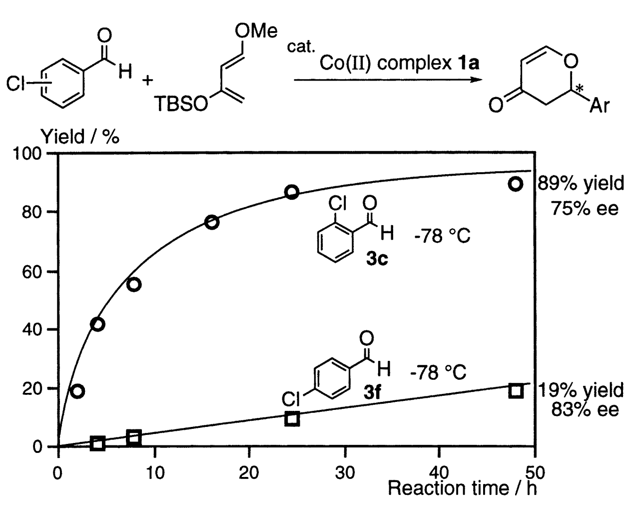


Fig. 4. Time-course of hetero Diels–Aider reaction for *o*- and *p*-cholorobenzaldehydes.

Absolute Configuration of Optically Active Pyranone Derivatives. In the previous section, it was mentioned that the reaction proceeded rapidly when a methoxy or halogen substituent was at the ortho position of the aromatic aldehyde. These phenomena made us suspect that the stereocourses were different for the ortho and para substituted aromatic aldehydes. The absolute configurations of the hetero Diels-Alder adducts were then determined (Fig. 5). The absolute configurations of the hetero Diels–Alder adducts, 2-(4-nitrophenyl)-2,3-dihydro-4*H*-pyran-4-one (**4d**) and 2-phenyl-2,3-dihydro-4*H*-pyran-4-one (**4g**), were determined by comparing their optical rotations with the reported values.[29] For 2-(2-bromophenyl)-2,3-dihydro-4*H*-pyran-4-one (**4j**), the optical rotation was compared after conversion by a dehalogenation reaction to 2-phenyl-2,3-dihydro-4*H*-pyran-4-one. The value of the enantiomer excess calculated from the specific rotation agreed with that by the high-performance liquid chromatography (HPLC) method. These observations indicated that a pyranone derivative of (*S*)-configuration was obtained from either the ortho-substituted, para-substituted or non-substituted aromatic aldehyde in the presence of the (*S*,*S*)-cobalt complex catalysts. Therefore, it is possible to assume that similar stereocourses occurred for each aldehyde except for the reaction rate.

It is presumed that both the *o*- and *p*-substituted aldehydes were activated by the coordination of the cobalt atom to form a similar intermediate. The computational experiment on the structure of the (*S*,*S*)-cobalt complex with benzaldehyde was then attempted by a semi-empirical method with a Mac Spartan Pro (PM3(tm)). After examining the energy surface and the optimization of the structure, it was revealed that the lone pair of oxygen atoms *anti* to the phenyl group in the aldehyde contributed to coordinate the cobalt atom, and that the phenyl group was oriented between two coordinating oxygen atoms, O^1 and O^2, on the planar 3-oxobutylideneaminato ligand (Fig. 6). The diene should approach the *si*-face of the activated dienophile mentioned above to afford the (*S*)-endo adduct in high selectivities because the *re*-face is blocked by the aryl group of the chiral diamine and the bulky alkyl or aryl group

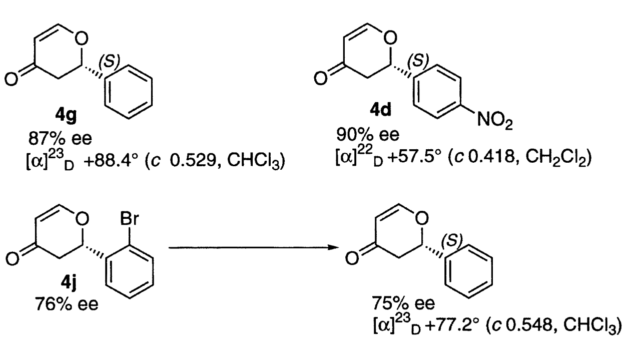


Fig. 5. Absolute configurations of hetero Diels–Alder products.

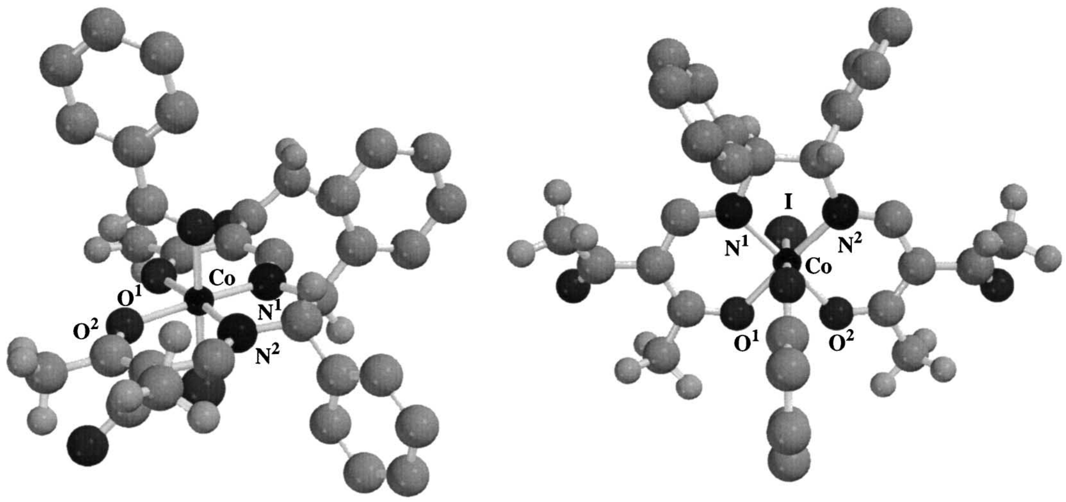


Fig. 6. The optimized structure of (*S*,*S*)-cobalt/PhCHO complex by semi-empirical method with Mac Spartan Pro (PM3(tm)). Side view (left) and top view (right).

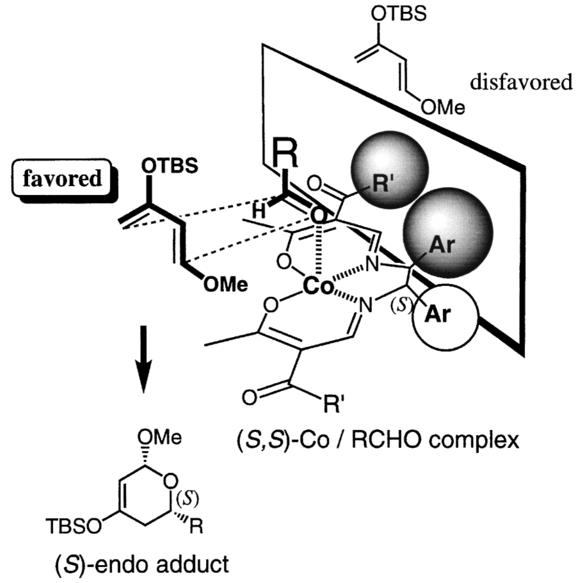


Fig. 7. Reasonable explanation for the endo-selection and the enantioselection in the hetero Diels–Alder reaction catalyzed by (*S*,*S*)-cobalt complex.

on the side chain of the 3-oxobutylideneaminato ligand. These explanations are in full accord with the enantioselection of the present hetero Diels–Alder reaction (Fig. 7).

Conclusion

The cationic cobalt(III) complexes with optically active 3-oxobutylideneaminato ligands effectively catalyzed the hetero Diels–Alder reaction of various aromatic and aliphatic aldehydes with Danishefsky's diene to afford the corresponding dihydropyran-4-one derivatives in high yield with high enantioselectivity.

The authors thank Professor Shigeru Ohba and Dr. Masanobu Tsuchimoto, Keio University, for X-ray analysis of cobalt complex **5d**.

Experimental

General: The melting points were measured on an Electrothermal IA9100 apparatus or a Rigaku DSC-8230 apparatus and were uncorrected.

(a) Spectrometers: Infrared (IR) spectra were recorded on a JASCO Model FT/IR-410 infrared spectrometer on KBr pellets or liquid film on NaCl. ^{1}H NMR spectra and ^{13}C NMR spectra were measured on a JEOL Model GX-400 spectrometer using $CDCl_3$ or C_6D_6 as a solvent and with tetramethylsilane as an internal standard. High-resolution mass spectra were obtained with a HITACHI M-8013. FAB mass spectra were recorded with a JEOL MStation JMS-700 spectrometer using 3-nitrobenzyl alcohol (NBA) as a matrix agent.

(b) Chromatography: For the thin-layer chromatography (TLC) analysis used throughout this work, Merck precoated TLC plates (silica gel 60 F254, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel (silica gel 60 N). High-performance liquid chromatography (HPLC) analyses were performed with a Shimadzu LC-6A chromatograph using an optically active column (Chiralcel OD-H, and Chiralpak AD columns, Daicel Ltd., Co.); the peak areas were obtained with a Shimadzu chromatopack CR-4A or Varian Dynamax MacIntegrator.

(c) Optical Rotations: Optical rotations were measured with a JASCO DIP-370 digital polarimeter.

Aldehydes: *o*-Methoxybenzaldehyde (**3a**), *o*-chlorobenzaldehyde (**3c**), *p*-nitrobenzaldehyde (**3d**), *p*-trifluoromethylbenzaldehyde (**3e**), *p*-chlorobenzaldehyde (**3f**), 3-phenylpropionaldehyde (**3h**), octanal (**3i**) were purchased from Tokyo Kasei Kogyo (TCI) Co., Ltd., respectively. *o*-Fluorobenzaldehyde (**3b**) was purchased from ACROS Organics. Benzaldehyde (**3g**) was purchased from Kanto Chemical Co., Inc. *o*-Bromobenzaldehyde (**3j**) was purchased from Wako Pure Chemical Industries, Ltd.

Diene: 3-(*t*-Butyldimethylsilyloxy)-1-methoxy-1,3-butadiene (**2**) was prepared by a reported method.[23]

Tetrakis(triphenylphosphine)palladium(0) was purchased from Kanto Chemical Co., Inc.

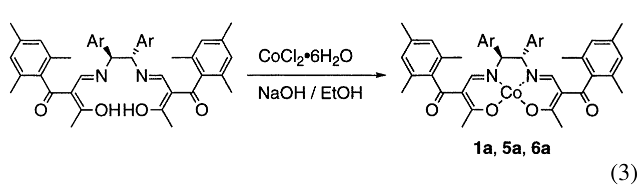
Preparation of Optically Active 3-Oxobutylideneaminato Ligands: Ligands **1**, **5**, and **6** were prepared by a reported method[15] from 3-oxo-2-(2,4,6-trimethylbenzoyl)butanal and optically active 1,2-diarylethylenediamines.

(1*S*,2*S*)-*N*,*N*′-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-diphenylethylenediamine (1): ^{1}H NMR (400 MHz) δ 1.92 (6H, s), 1.98 (6H, s), 2.26 (6H, s), 2.63 (6H, brs), 4.41 (2H, d, J = 7.2 Hz), 6.72–6.74 (4H, m), 6.98–7.00 (6H, m), 7.24–7.26 (6H, m), 11.98 (2H, brs); ^{13}C NMR (100 MHz) δ 19.1, 21.1, 31.8, 69.4, 112.6, 126.5, 128.0, 128.2, 128.6, 128.9, 133.3, 133.4, 135.4, 137.4, 161.0, 196.2, 201.1; IR (KBr) 2971, 2917, 1615, 1454, 1405, 1353, 1299, 1252, 1200, 981, 849, 697 cm^{-1}. Found: C, 78.55; H, 6.91; N, 4.39%. Calcd for $C_{42}H_{44}N_2O_4$: C, 78.72; H, 6.92; N, 4.37%. Mp 210.4–211.2 °C. $[\alpha]_D^{28}$ +72.3° (c 0.507, $CHCl_3$).

(1*S*,2*S*)-1,2-Bis(3,5-dimethylphenyl)-*N*,*N*′-bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]ethylenediamine (5): ^{1}H NMR (400 MHz) δ 1.82 (6H, s), 1.99 (6H, s), 2.23–2.25 (18H, m), 2.66 (6H, brs), 4.34 (2H, d, J = 6.8 Hz), 6.63 (4H, s), 6.70 (4H, s), 6.83–6.95 (4H, m), 11.91 (2H, br); ^{13}C NMR (100 MHz) δ 19.0, 19.2, 21.1, 21.3, 31.8, 69.5, 112.5, 124.1, 128.0, 130.2, 133.3, 133.4, 135.4, 137.3, 138.6, 161.3, 196.2, 200.9; IR (KBr) 2921, 2860, 1620, 1407, 1352, 1307, 1257, 1200, 1169, 980, 849, 802 cm^{-1}. HRMS: Calcd for $C_{46}H_{52}N_2O_4$: (M$^+$), 696.3927. Found: m/z 696.3914. Mp 211.3–213.3 °C. $[\alpha]_D^{22}$ +106.3° (c 1.006, $CHCl_3$).

(1*S*,2*S*)-*N*,*N*′-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-bis(2,4,6-trimethylphenyl)ethylenediamine (6): ^{1}H NMR (400 MHz) δ 1.42 (6H, s), 2.02 (6H, s), 2.10 (6H, s), 2.18 (6H, s), 2.23 (6H, brs), 2.28 (6H, s), 2.64 (6H, brs), 4.84 (2H, brs), 6.54 (2H, s), 6.73 (2H, s), 6.79 (4H, s), 7.07 (2H, brs), 11.52 (2H, brs); ^{13}C NMR (100 MHz) δ 19.01, 19.05, 19.9, 20.4, 20.8, 21.2, 31.6, 61.6, 112.7, 127.7, 128.1, 129.38, 129.44, 131.4, 133.0, 133.6, 134.8, 136.7, 137.5, 138.3, 140.7, 161.2, 196.3, 200.2; IR (KBr) 2921, 1624, 1404, 1350, 1305, 1257, 1200, 1171, 983, 849, 820 cm^{-1}. Found: C, 79.27; H, 7.70; N, 3.83%. Calcd for $C_{48}H_{56}N_2O_4$: C, 79.52; H, 7.79; N, 3.86%. Mp 171.4–173.2 °C. $[\alpha]_D^{24}$ +27.5° (c 1.019, $CHCl_3$).[30]

Preparation of Optically Active 3-Oxobutylideneaminatocobalt(II) Complexes: Catalysts **1a**, **5a**, and **6a** were prepared by a reported method.[27]



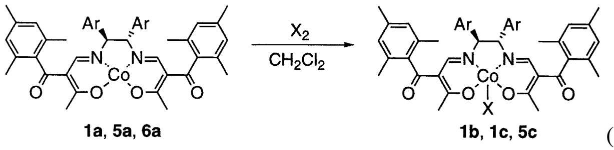
(3)

(1*S*,2*S*)-*N*,*N*′-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-diphenylethylenediaminatocobalt(II) (1a): IR (KBr) 2919, 1640, 1571, 1454, 1397, 1354, 1284, 1267, 993, 880, 847, 700, 593 cm^{-1}. MS (FAB) m/z 698 (M+H)$^+$. Mp 299.2 °C (DSC).

(1*S*,2*S*)-1,2-Bis(3,5-dimethylphenyl)-*N*,*N*′-bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]ethylenediaminatocobalt(II) (5a): IR (KBr) 2917, 1644, 1610, 1572, 1428, 1388, 1354, 1275, 1256, 995, 873, 845, 802 cm^{-1}. MS (FAB) m/z 754 (M+H)$^+$. Mp 334.1 °C (DSC).

(1*S*,2*S*)-*N*,*N*′-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-bis(2,4,6-trimethylphenyl)ethylenediaminatocobalt(II) (6a): IR (KBr) 2921, 1623, 1587, 1398, 1353, 1261, 849 cm^{-1}. MS (FAB) m/z 782 (M+H)$^+$. Mp 248.8 °C (DSC).

Preparation of Optically Active 3-Oxobutylideneaminatocobalt(III) Complexes: Cobalt(III) complexes type-**A** **1b**, **1c**, and **5c** were prepared by a reported method.[27]



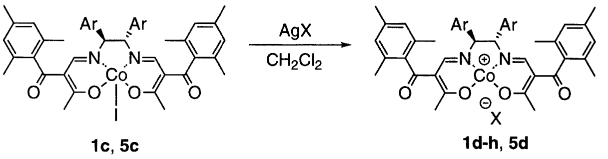
(4)

Bromo{*N*,*N*′-bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-(1*S*,2*S*)-1,2-diphenylethylenediaminato}cobalt(III) (1b): IR (KBr) 2917, 1591, 1496, 1398, 1352, 1298, 1268, 1199, 994, 879, 847, 701, 592 cm^{-1}. MS (FAB) m/z 777 (M+H)$^+$.

Iodo{*N*,*N*′-bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-(1*S*,2*S*)-1,2-diphenylethylenediaminato}cobalt(III) (1c): IR (KBr) 2919, 1588, 1398, 1353, 1268, 994, 880, 848, 701, 592 cm^{-1}. MS (FAB) m/z 825 (M+H)$^+$.

Iodo{(1*S*,2*S*)-1,2-bis(3,5-dimethylphenyl)-*N*,*N*′-bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]ethylenediaminato}cobalt(III) (5c): IR (KBr) 2918, 1590, 1398, 1352, 1285, 1199, 1125, 996, 872, 849, 745, 723, 600 cm^{-1}. MS (FAB) m/z 881 (M+H)$^+$.

Cobalt(III) complexes type-**B** 1d–h and 5d were prepared as follows.



(5)

(1*S*,2*S*)-1,2-Bis(3,5-dimethylphenyl)-*N*,*N*′-bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]ethylenediaminatocobalt(III) trifluoromethanesulfonate (5d): To a solution of the cobalt complex **5c** (259.9 mg, 0.295 mmol) in dichloromethane (10.0 mL) was added AgOTf (84.4 mg, 0.329 mmol) in dichloromethane (1.0 mL). The mixture was stirred for 1.5 h, and the resulting AgI and excess AgOTf were filtered off. The solvent were removed under reduced pressure and the crude product was purified by reprecipitation from dichloromethane/hexane to afford the cationic cobalt(III) complex **5d** (231.4 mg) in 87% yield as a green solid. IR (KBr) 2921, 1592, 1472, 1399, 1355, 1290, 1171, 1030, 997, 874, 849, 640, 601 cm^{-1}. MS (FAB(positive)) m/z 754 (M−OTf+H)$^+$, (FAB (negative)) m/z 149 (OTf)$^-$.

(1*S*,2*S*)-*N*,*N*′-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-diphenylethylenediaminatocobalt(III) trifluoromethanesulfonate (1d): IR (KBr) 2921, 1589, 1399, 1355, 1271, 1171, 1031, 995, 881, 849, 701, 639, 593 cm^{-1}. MS (FAB(positive)) m/z 698 (M−OTf+H)$^+$, (FAB(negative)) m/z 149 (OTf)$^-$.

(1*S*,2*S*)-*N*,*N*′-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-diphenylethylenediaminatocobalt(III) hexafluoroantimonate (1e): IR (KBr) 2922, 1583, 1456, 1398, 1355, 1301, 1270, 1200, 994, 882, 849, 701, 669, 593 cm^{-1}. MS (FAB(positive)) m/z 698 (M−SbF_6+H)$^+$, (FAB(negative)) m/z 235 $(SbF_6)^-$.

(1*S*,2*S*)-*N*,*N*′-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-diphenylethylenediaminatocobalt(III) hexafluorophosphate (1f): IR (KBr) 2922, 1587, 1456, 1399, 1355, 1296, 1271, 995, 880, 702, 593, 558 cm^{-1}. MS (FAB(positive)) m/z 698 (M−PF_6+H)$^+$, (FAB(negative)) m/z 145 $(PF_6)^-$.

(1*S*,2*S*)-*N*,*N*′-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-diphenylethylenediaminatocobalt(III) tetrafluoroborate (1g): IR (KBr) 2921, 1587, 1455, 1399, 1355, 1299, 1270, 1124, 1084, 994, 881, 847, 701, 593 cm^{-1}. MS (FAB(positive)) *m/z* 698 $(M-BF_4+H)^+$, (FAB(negative)) *m/z* 87 $(BF_4)^-$.

(1*S*,2*S*)-*N*,*N*′-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-diphenylethylenediaminatocobalt(Ⅲ) *p*-toluenesulfonate (1h): IR (KBr) 2919, 1592, 1455, 1398, 1353, 1269, 1158, 1123, 1035, 1010, 880, 847, 701, 682, 639, 592, 567 cm^{-1}. MS (FAB(positive)) *m/z* 698 $(M-OTs+H)^+$, (FAB(negative)) *m/z* 171 $(OTs)^-$.

General Procedure for the Enantioselective Hetero Diels–Alder Reaction of 2-(4-Nitrophenyl)-2,3-dihydro-4*H*-pyran-4-one (4d): To a solution of the cobalt complex **5d** (22.9 mg, 5.0 mol%) in dichloromethane (0.5 mL) in the presence of molecular sieves 4A was added *p*-nitrobenzaldehyde (75.4 mg, 0.50 mmol) in dichloromethane (1.0 mL). A solution of the 3-(*t*-butyldimethylsilyloxy)-1-methoxy-1,3-butadiene (200 μL, 0.97 mmol) in dichloromethane (1.0 mL) was then added at −78 °C. The mixture was stirred for 7 h at −78 °C, followed by a treatment with trifluoroacetic acid (0.2 mL) at rt for 5 h. After neutralization with a sat. $NaHCO_3$ solution, a standard workup and chromatography on silica gel afforded 2,3-dihydro-2-(4-nitrophenyl)-4*H*-pyran-4-one (102.5 mg) in 94% yield. The optical yield of the product was determined by an HPLC analysis (Chiralcel OD-H, 10% 2-propanol in hexane, Flow 1.0 mL/min, 35.3 min (major), 49.0 min (minor)) to be 94% ee.

The products 2-(4-nitrophenyl)-2,3-dihydro-4*H*-pyran-4-one (**4d**)[29b,31] and 2-phenyl-2,3-dihydro-4*H*-pyran-4-one (**4g**)[3b,8a,29a] were identified with the corresponding material reported previously.

2-(2-Methoxyphenyl)-2,3-dihydro-4*H*-pyran-4-one (4a): ^{1}H NMR (400 MHz) δ 2.71–2.81 (2H, m), 3.84 (3H, s), 5.52 (1H, d, J = 6.4 Hz), 5.81 (1H, dd, J = 5.9, 11.7 Hz), 6.92 (1H, d, J = 7.8 Hz), 7.01–7.05 (1H, m), 7.32–7.37 (1H, m), 7.48 (1H, dd, J = 2.0, 7.6 Hz), 7.52 (1H, d, J = 6.4 Hz); ^{13}C NMR (100 MHz) δ 42.4, 55.4, 76.4, 107.1, 110.4, 120.7, 126.2, 126.4, 129.5, 155.7, 163.4, 192.7; IR (neat) 3071, 2940, 2840, 1678, 1595, 1496, 1464, 1404, 1273, 1226, 1040, 756 cm^{-1}. HRMS: Calcd for $C_{12}H_{12}O_3$: (M^+), 204.0786. Found: *m/z* 204.0801. $[\alpha]_D^{26}$ −48.1° (*c* 0.883, $CHCl_3$). Optical yield was determined by Chiralpak AD (0.5% 2-propanol in hexane, Flow 1.0 mL/min), 45.8 min (minor), 57.9 min (major).

2-(2-Fluorophenyl)-2,3-dihydro-4*H*-pyran-4-one (4b): ^{1}H NMR (400 MHz) δ 2.70 (1H, ddd, J = 1.0, 3.4, 16.7 Hz), 2.90 (1H, dd, J = 14.2, 16.7 Hz), 5.55 (1H, dd, J = 1.0, 6.1 Hz), 5.73 (1H, dd, J = 3.4, 14.2 Hz), 7.09–7.14 (1H, m), 7.20–7.24 (1H, m), 7.35–7.40 (1H, m), 7.49–7.53 (2H, m); ^{13}C NMR (100 MHz) δ 42.4, 75.5 (d, J_{CF} = 3 Hz), 107.4, 115.7 (d, J_{CF} = 21 Hz), 124.5 (d, J_{CF} = 4 Hz), 125.1 (d, J_{CF} = 13 Hz), 127.3 (d, J_{CF} = 3 Hz), 130.4 (d, J_{CF} = 8 Hz), 159.5(d, J_{CF} = 248 Hz), 162.9, 191.5; IR (neat) 3070, 2920, 1681, 1619, 1597, 1496, 1272, 1224, 1038, 761 cm^{-1}. HRMS: Calcd for $C_{11}H_9O_2F$: (M^+), 192.0587. Found: *m/z* 192.0557. $[\alpha]_D^{29}$ +52.4° (*c* 0.887, $CHCl_3$). Optical yield was determined by Chiralpak AD (1.0% 2-propanol in hexane, Flow 1.0 mL/min), 32.7 min (minor), 41.4 min (major).

2-(2-Chlorophenyl)-2,3-dihydro-4*H*-pyran-4-one (4c): ^{1}H NMR (400 MHz) δ 2.72 (1H, dd, J = 13.7, 16.8 Hz), 2.81 (1H, ddd, J = 1.0, 3.9, 16.8 Hz), 5.56 (1H, dd, J = 1.0, 5.9 Hz), 5.83 (1H, dd, J = 3.9, 13.7 Hz), 7.30–7.42 (3H, m), 7.52 (1H, d, J = 5.9 Hz), 7.58–7.61 (1H, m); ^{13}C NMR (100 MHz; C_6D_6) δ 42.2, 78.1, 107.7, 127.3, 127.5, 129.7, 129.8, 132.0, 136.2, 162.3, 190.4; IR (neat) 3069, 2905, 1683, 1598, 1402, 1273, 1227, 1038, 932, 758 cm^{-1}. HRMS: Calcd for $C_{11}H_9O_2Cl$: (M^+), 208.0291. Found: *m/z* 208.0282. $[\alpha]_D^{28}$ −95.6° (*c* 0.812, $CHCl_3$). Optical yield was determined by Chiralpak AD (1.0% 2-propanol in hexane, Flow 1.0mL / min), 23.2 min (minor), 25.7 min (major).

2-(4-Trifluoromethylphenyl)-2,3-dihydro-4*H*-pyran-4-one (4e): ^{1}H NMR (400 MHz) δ 2.70 (1H, ddd, J = 1.0, 3.4, 17.0 Hz), 2.86 (1H, dd, J = 14.2, 17.0 Hz), 5.50 (1H, dd, J = 3.4, 14.2 Hz), 5.56 (1H, dd, J = 1.0, 6.1 Hz), 7.51 (1H, d, J = 6.1 Hz), 7.54 (2H, d, J = 8.3 Hz), 7.69 (2H, d, J = 8.3 Hz); ^{13}C NMR (100 MHz) δ 43.4, 80.1, 107.6, 123.7 (q, J_{CF} = 272 Hz), 125.7 (q, J_{CF} = 4 Hz), 126.1, 130.8 (q, J_{CF} = 33 Hz), 141.6, 162.6, 191.0; IR (KBr) 3060, 2896, 1665, 1623, 1597, 1411, 1326, 1285, 1178, 1127, 843 cm^{-1}. HRMS: Calcd for $C_{12}H_9O_2F_3$: (M^+), 242.0555. Found: *m/z* 242.0544. Mp 72.2–74.4 °C. $[\alpha]_D^{24}$ +44.4° (*c* 0.630, $CHCl_3$). Optical yield was determined by Chiralpak AD (1.0% 2-propanol in hexane, Flow 1.0 mL/min), 36.1 min (minor), 51.1 min (major).

2-(4-Chlorophenyl)-2,3-dihydro-4*H*-pyran-4-one (4f): ^{1}H NMR (400 MHz) δ 2.65 (1H, ddd, J = 1.2, 3.4, 16.6 Hz), 2.86 (1H, dd, J = 14.2, 16.6 Hz), 5.41 (1H, dd, J = 3.4, 14.2 Hz), 5.54 (1H, dd, J = 1.2, 5.9 Hz), 7.33–7.35 (2H, m), 7.39–7.41 (2H, m), 7.47 (1H, d, J = 5.9 Hz); ^{13}C NMR (100 MHz) δ 43.4, 80.3, 107.4, 127.3, 128.9, 134.6, 136.2, 162.8, 191.4; IR (neat) 3068, 2901, 1682, 1596, 1495, 1402, 1272, 1227, 1039, 933, 834 cm^{-1}. Found: C, 63.05; H, 4.48%. Calcd for $C_{11}H_9O_2Cl$: C, 63.32; H, 4.35%. $[\alpha]_D^{27}$ +91.2° (*c* 0.548, $CHCl_3$). Optical yield was determined by Chiralcel OD-H (1.0% 2-propanol in hexane, Flow 1.0 mL/min), 43.9 min (major), 58.1 min (minor).

2-(2-Phenylethyl)-2,3-dihydro-4*H*-pyran-4-one (4h): ^{1}H NMR (400 MHz) δ 1.84–1.92 (1H, m), 2.04–2.13 (1H, m), 2.36 (1H, ddd, J = 1.0, 3.9, 16.6 Hz), 2.48 (1H, dd, J = 13.7, 16.6 Hz), 2.64–2.80 (2H, m), 4.29–4.36 (1H, m), 5.34 (1H, dd, J = 1.0, 6.4 Hz), 7.11–7.16 (3H, m), 7.21–7.25 (2H, m), 7.31 (1H, d, J = 6.4 Hz); ^{13}C NMR (100 MHz) δ 31.0, 36.1, 41.8, 78.4, 107.0, 126.1, 128.2, 128.4, 140.5, 162.9, 192.2; IR (neat) 3025, 2952, 1673, 1591, 1414, 1271, 1228, 1045, 726, 699 cm^{-1}. HRMS: Calcd for $C_{13}H_{14}O_2$: (M^+), 202.0994. Found: *m/z* 202.1000. $[\alpha]_D^{27}$ +97.0° (*c* 1.021, $CHCl_3$).[28a] Optical yield was determined by Chiralpak AD (1.0% 2-propanol in hexane, Flow 1.0 mL/min), 23.1 min (minor), 30.9 min (major).

2-Heptyl-2,3-dihydro-4*H*-pyran-4-one (4i): ^{1}H NMR (400 MHz) δ 0.80–0.94 (3H, m), 1.19–1.57 (10H, m), 1.60–1.72 (1H, m), 1.75–1.89 (1H, m), 2.43 (1H, dd, J = 3.9, 16.6 Hz), 2.52 (1H, dd, J = 13.7, 16.6 Hz), 4.32–4.48 (1H, m), 5.40 (1H, d, J = 5.9 Hz), 7.37 (1H, d, J = 5.9 Hz); ^{13}C NMR (100 MHz) δ 14.2, 22.7, 24.8, 29.2, 29.3, 31.8, 34.4, 41.9, 79.6, 106.8, 163.2, 192.7; IR (neat) 2927, 2857, 1684, 1597, 1466, 1406, 1275, 1227, 1040, 791 cm^{-1}. HRMS: Calcd for $C_{12}H_{20}O_2$: (M^+), 196.1463. Found: *m/z* 196.1446. $[\alpha]_D^{25}$ +105.5° (*c* 0.727, $CHCl_3$). Optical yield was determined by Chiralpak AD (0.5% 2-propanol in hexane, Flow 1.0 mL/min), 19.6 min (minor), 28.6 min (major).

2-(2-Bromophenyl)-2,3-dihydro-4*H*-pyran-4-one (4j): ^{1}H NMR (400 MHz) δ 2.59 (1H, dd, J = 14.2, 16.8 Hz), 2.73 (1H, dd, J = 3.4, 16.8 Hz), 5.47 (1H, d, J = 5.9 Hz), 5.69 (1H, dd, J = 3.4, 14.2 Hz), 7.12–7.17 (1H, m), 7.30–7.33 (1H, m), 7.43 (1H, d, J = 5.9 Hz), 7.48–7.51 (2H, m); ^{13}C NMR (100 MHz) δ 42.2, 80.1, 107.4, 121.2, 127.1, 127.8, 129.9, 132.8, 137.2, 162.8, 191.2; IR (neat) 3068, 2905, 1680, 1597, 1401, 1272, 1226, 1038, 995, 932, 757 cm^{-1}. HRMS: Calcd for $C_{11}H_9O_2Br$: (M^+), 251.9786. Found: *m/z* 251.9767. $[\alpha]_D^{23}$ −116.8° (*c* 1.147, $CHCl_3$). Optical yield was determined by Chiralcel OD-H (2.0% 2-propanol in hexane, Flow 1.0 mL/min), 19.2 min (major), 22.5 min (minor).

Debromination[32] of 2-(2-Bromophenyl)-2,3-dihydro-4*H*-py-

ran-4-one (4j) to 2-Phenyl-2,3-dihydro-4*H*-pyran-4-one (4g): A mixture of the 2-(2-bromophenyl)-2,3-dihydro-4*H*-pyran-4-one (113.1 mg, 0.45 mmol), sodium formate (67.0 mg, 0.99 mmol), tetrakis(triphenylphosphine)palladium(0) (51.7 mg, 44.7 μmol) in DMF (3.0 mL). The mixture was stirred for 1.5 h at 100 °C. A standard workup and chromatography on silica gel afforded 2,3-dihydro-2-phenyl-4*H*-pyran-4-one (54.8 mg) in 70% yield. The optical yield of the product was determined by an HPLC analysis (Chiralcel OD-H, 2.0% 2-propanol in hexane, 28.0 min (major), 34.6 min (minor)) to be 75% ee. $[\alpha]_D^{23}$ +77.2° (c 0.548, $CHCl_3$).

X-ray Crystallography of Cobalt(III) Trifluoromethanesulfonate (5d): The crystals were grown from a THF solution by diffusion of a small amount of hexane. A crystal specimen was sealed in a capillary with the mother liquor to avoid efflorescence. The X-ray intensities were measured on a Rigaku AFC-7R diffractometer with Mo $K\alpha$ radiation. The structure was refined by full-matrix least-squares calculations.[33] The crystal structure had a pseudo center of symmetry and the space group was approximately $P2_1/a$. There was an orientational disorder of the trifluoromethanesulfonates, although one of the oxygen atoms was established. It was assumed that the sulfur atom has two possible positions and two oxygen atoms are four disordered sites with 50% probability each; also the positional disorder was modeled only tentatively. Crystal data for $[Co(C_{46}H_{50}N_2O_4)\cdot(H_2O)_2]\cdot CF_3SO_3\cdot C_4H_8O$: $C_{51}H_{62}CoF_3N_2O_{10}S$, Formula weight = 1011.05, monoclinic, space group $P2_1$, a = 14.521(2), b = 19.263(2), c = 19.285(2) Å, β = 97.619(10)°, V = 5346.7(11) Å^3, Z = 4, D_{calc} = 1.256 g cm^{-3}, T = 296(1) K, μ (Mo $K\alpha$) = 0.425 mm^{-1}, no. of data collected 13145, no. of independent data 12648, no. of parameters 547, $R(F)$ = 0.116, $R_w(F^2)$ = 0.313, Flack parameter = −0.01(3).

Computational Details: The computations were performed using the GAUSSIAN-98 package[34] and Mac Spartan Pro (PM3(tm)).[35] Iodo[*N*,*N*′-bis(3-oxo-2-formylpropylidene)-ethylenediaminato]cobalt(III) (**7**) (Fig. 8) was chosen as the prototypal molecule and the following basis sets were chosen for the geometry optimization by the Gaussian 98 suite of programs: LANL2DZ (cobalt atom), 3-21G (ethylenediamine bridge, formyl groups of side chains, iodide on cobalt, and hydrogens), and 6-31G for the other atoms. To the optimized complex, the benzaldehyde molecule was attached at the axial position. The distance between the cobalt atom and the carbonyl oxygen was optimized by a semi-empirical method. The ethylenediamine part was then replaced with 1,2-diphenylethylenediamine and the terminal methyl groups were attached based on the result by an X-ray analysis of a similar cobalt complex. The thus-obtained cobalt complex with benzaldehyde was subjected to geometry optimization by the semi-empirical method with Mac Spartan Pro (PM3(tm)). After searching for the energy minimum with a rotating benzaldehyde molecule around the cobalt-oxygen bond as an axis per ten degrees and with optimizing each geometry, it was found that the phenyl group of the benzaldehyde is located over the ligand plane between the two coordinating oxygen atoms.

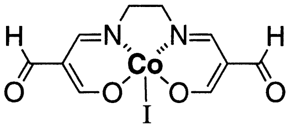


Fig. 8. The prototypal molecule for computations; iodo[*N*,*N*′-bis(3-oxo-2-formylpropylidene)-ethylenediaminato]cobalt(III) (**7**).

References

1 K. Maruoka and H. Yamamoto, "Catalytic Asymmetric Synthesis," ed by I. Ojima, VCH, Weinheim (1993), p. 413; M. D. Bednarski and J. P. Lyssikatos, "Comprehensive Organic Synthesis," ed by B. M. Trost and I. Fleming, Pergamon Press, Oxford (1991), vol. 2, p. 661; D. L. Boger, "Comprehensive Organic Synthesis," ed by B. M. Trost and I. Fleming, Pergamon Press, Oxford (1991), vol. 5, p. 451; D. L. Boger and S. M. Weinreb, "Hetero Diels–Alder Methodology in Organic Synthesis," Academic Press, San Diego (1987); T. Ooi and K. Maruoka, "Comprehensive Asymmetric Catalysis," ed by E. N. Jacobsen, A. Pfaltz, and H. Yamamoto, Springer-Verlag, Berlin and Heiderberg (1999), vol. 3, p. 1237; L. C. Dias, *J. Braz. Chem. Soc.*, **8**, 289 (1997); K. A. Jørgensen, *Angew. Chem., Int. Ed. Engl.*, **39**, 3558 (2000).

2 M. Bednarski, C. Maring, and S. Danishefsky, *Tetrahedron Lett.*, **24**, 3451 (1983); M. Bednarski and S. Danishefsky, *J. Am. Chem. Soc.*, **105**, 6968 (1983); M. Bednarski and S. Danishefsky, *J. Am. Chem. Soc.*, **108**, 7060 (1986); S. Danishefsky, *Aldrichimica Acta*, **19**, 59 (1986).

3 a) Q. Gao, T. Maruyama, M. Mouri, and H. Yamamoto, *J. Org. Chem.*, **57**, 1951 (1992). b) Q. Gao, K. Ishihara, T. Maruyama, M. Mouri, and H. Yamamoto, *Tetrahedron*, **50**, 979 (1994). c) Y. Motoyama and K. Mikami, *J. Chem. Soc., Chem. Commun.*, **1994**, 1563.

4 a) K. Maruoka, T. Itoh, T. Shirasaka, and H. Yamamoto, *J. Am. Chem. Soc.*, **110**, 310 (1988). b) K. Maruoka and H. Yamamoto, *J. Am. Chem. Soc.*, **111**, 789 (1989). c) A. Graven, M. Johannsen, and K. A. Jørgensen, *J. Chem. Soc., Chem. Commun.*, **1996**, 2373. d) K. B. Simonsen, N. Svenstrup, M. Roberson, and K. A. Jørgensen, *Chem. Eur. J.*, **6**, 123 (2000).

5 M. Terada, K. Mikami, and T. Nakai, *Tetrahedron Lett.*, **32**, 935 (1991); K. Mikami, M. Terada, S. Narisawa, and T. Nakai, *Synlett*, **1992**, 255; K. Mikami and M. Shimizu, *Chem. Rev.*, **92**, 1021 (1992); K. Mikami, Y. Motoyama, and M. Terada, *J. Am. Chem. Soc.*, **116**, 2812 (1994); Y. Motoyama, M. Terada, and K. Mikami, *Synlett*, **1995**, 967; K. Mikami and S. Matsukawa, *Nature*, **385**, 613 (1997); S. Matsukawa and K. Mikami, *Tetrahedron: Asymmetry*, **8**, 815 (1997); G. E. Keck, X.-Y. Li, and D. Krishnamurthy, *J. Org. Chem.*, **60**, 5998 (1995).

6 K. Mikami, O. Kotera, Y. Motoyama, and H. Sakaguchi, *Synlett*, **1995**, 975.

7 J. Inanaga, Y. Sugimoto, and T. Hanamoto, *New J. Chem.*, **19**, 707 (1995); T. Hamamoto, H. Furuno, Y. Sugimoto, and J. Inanaga, *Synlett*, **1997**, 79; H. Furuno, T. Hanamoto, Y. Sugimoto, and J. Inanaga, *Org. Lett.*, **2**, 49 (2000).

8 a) S. E. Schaus, J. Brånalt, and E. N. Jacobsen, *J. Org. Chem.*, **63**, 403 (1998). b) A. G. Dossetter, T. F. Jamison, and E. N. Jacobsen, *Angew. Chem., Int. Ed.*, **38**, 2398 (1999).

9 L.-S. Li, Y. Wu, Y.-J. Hu, L.-J. Xia, and Y.-L. Wu, *Tetrahedron: Asymmetry*, **9**, 2271 (1998).

10 J. Mihara, T. Hamada, T. Takeda, R. Irie, and T. Katsuki, *Synlett*, **1999**, 1160.

11 A. Togni, *Organometallics*, **9**, 3106 (1990).

12 a) A. K. Ghosh, P. Mathivanan, J. Cappiello, and K. Krishnan, *Tetrahedron: Asymmetry*, **7**, 2165 (1996). b) A. K. Ghosh, P. Mathivanan, and J. Cappiello, *Tetrahedron Lett.*, **38**, 2427 (1997). c) M. Johannsen and K. A. Jørgensen, *J. Org. Chem.*, **60**, 5757 (1995). d) M. Johannsen and K. A. Jørgensen, *Tetrahedron*, **52**, 7321 (1996). e) M. Johannsen and K. A. Jørgensen, *J.*

Chem. Soc., Perkin Trans. 2, **1997**, 1183. f) M. Johannsen, S. Yao, and K. A. Jørgensen, *Chem. Commun.*, **1997**, 2169. g) S. Yao, M. Johannsen, R. G. Hazell, and K. A. Jørgensen, *J. Org. Chem.*, **63**, 118 (1998). h) S. Yao, M. Johannsen, H. Audrain, R. G. Hazell, and K. A. Jørgensen, *J. Am. Chem. Soc.*, **120**, 8599 (1998).

13 S. Yao, M. Johannsen, and K. A. Jørgensen, *J. Chem. Soc., Perkin Trans. 1*, **1997**, 2345.

14 S. Oi, E. Terada, K. Ohuchi, T. Kato, Y. Tachibana, and Y. Inoue, *J. Org. Chem.*, **64**, 8660 (1999).

15 T. Nagata, K. Imagawa, T. Yamada, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **68**, 1455 (1995).

16 T. Nagata, K. Imagawa, T. Yamada, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **68**, 3241 (1995).

17 T. Nagata, K. Yorozu, T. Yamada, and T. Mukaiyama, *Angew. Chem., Int. Ed. Engl.*, **34**, 2145 (1995).

18 K. D. Sugi, T. Nagata, T. Yamada, and T. Mukaiyama, *Chem. Lett.*, **1997**, 493.

19 T. Yamada, Y. Ohtsuka, and T. Ikeno, *Chem. Lett.*, **1998**, 1129.

20 T. Yamada, T. Ikeno, H. Sekino, and M. Sato, *Chem. Lett.*, **1999**, 719; T. Ikeno, M. Sato, and T. Yamada, *Chem. Lett.*, **1999**, 1345.

21 T. Yamada, S. Kezuka, T. Mita, and T. Ikeno, *Heterocycles*, **52**, 1041 (2000).

22 S. Kezuka, T. Mita, N. Ohtsuki, T. Ikeno, and T. Yamada, *Chem. Lett.*, **2000**, 824.

23 S. Danishefsky and T. Kitahara, *J. Am. Chem. Soc.*, **96**, 7807 (1974); R. E. Ireland, P. A. Aristoff, and C. F. Hoyng, *J. Org. Chem.*, **44**, 4318 (1979).

24 P. C. B. Page and J. C. Prodger, *Synlett*, **1991**, 84; Y. Arai, T. Masuda, Y. Masaki, and M. Shiro, *Tetrahedron: Asymmetry*, **7**, 1199 (1996); T. A. Adams, M. E. Welker, and C. S. Day, *J. Org. Chem.*, **63**, 3683 (1998).

25 It was reported that the cobalt(II) complexes with salen-type ligands showed better enantioselectivity in the hetero-DA reaction than the corresponding cobalt(III) complexes; See Ref. 9.

26 R. M. Hanson and K. B. Sharpless, *J. Org. Chem.*, **51**, 1922 (1986); K. Narasaka, M. Inoue, and T. Yamada, *Chem. Lett.*, **1986**, 1967; K. Mikami, M. Terada, and T. Nakai, *J. Am. Chem. Soc.*, **112**, 3949 (1990); K. V. Gothelf, R. G. Hazell, and K. A. Jørgensen, *J. Org. Chem.*, **63**, 5483 (1998).

27 T. Yamada, T. Nagata, T. Ikeno, Y. Ohtsuka, A. Sagara, and T. Mukaiyama, *Inorg. Chim. Acta*, **296**, 86 (1999).

28 The difference of the reaction rate was also observed in the reactions of fluorobenzaldehyde and methoxybenzaldehyde. The 2-(2-fluorophenyl)-2,3-dihydro-4*H*-pyran-4-one was obtained in 62% within 50 h, whereas the 2-(4-fluorophenyl)-2,3-dihydro-4*H*-pyran-4-one was obtained in 13% yield after 45 h. Similarly the 2-(2-methoxyphenyl)-2,3-dihydro-4*H*-pyran-4-one was obtained in 96% within 55 h at −20 °C, whereas the 2-(4-methoxyphenyl)-2,3-dihydro-4*H*-pyran-4-one was obtained in 49% yield after 97 h at room temperature.

29 a) E. J. Corey, C. L. Cywin, and T. D. Roper, *Tetrahedron Lett.*, **33**, 6907 (1992). b) R. F. Lowe and R. J. Stoodley, *Tetrahedron Lett.*, **35**, 6351 (1994).

30 Absolute configuration of the corresponding diamines were determined; S. Ohba, T. Nagata, and T. Yamada, *Acta Crystallogr. Sect. E*, **E57**, m124 (2001).

31 G. A. Molander and R. M. Rzasa, *J. Org. Chem.*, **65**, 1215 (2000).

32 P. Helquist, *Tetrahedron Lett.*, **1978**, 1913.

33 G. M. Sheldrick, SHELXL 97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany (1997).

34 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

35 Mac Spartan Pro Ver 1.0.1 was released from Wavefunction, Inc., 18401, Von Karman Avenue, Suite 370 Irvine, CA 92612 U.S.A.