New Asymmetric Catalysis by (Salen)cobalt(III) Complexes (Salen = [Bis(salicylidene)ethylenediaminato] = {{2,2′-[ethane-1,2-diyl]bis[(nitrilo-κ*N*)methylidyne]bis[phenolato-κ*O*]}(2−)}) of *cis*-β-Structure: Enantioselective *Baeyer-Villiger* Oxidation of Prochiral Cyclobutanones

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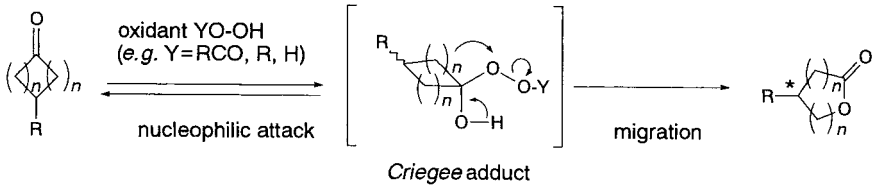
This paper is dedicated with admiration and respect to Professor *Dieter Seebach* on the occasion of his sixty-fifth birthday

A series of chiral (salen)cobalt(III) complexes (salen = [bis(salicylidene)ethylenediaminato] = {{2,2′-[(ethane-1,2-diyl)bis[(nitrilo-κ*N*)methylidyne]bis[phenolato-κ*O*]}(2−)}) of *cis*-β structure were prepared and used for the enantioselective *Baeyer-Villiger* oxidation of prochiral cyclobutanones with hydrogen peroxide as terminal oxidant. Both cationic (salen)cobalt(III) and neutral iodo(salen)cobalt(III) complexes **3**–**5** and **7**–**12**, respectively, all having a chiral binaphthalenediamine unit, were found to be effective catalysts for the enantioselective *Baeyer-Villiger* oxidation (*Tables 1*, *3*, and *4*). In particular, complex **8** bearing electron-withdrawing F-atoms showed a good level of enantioselectivity (75–79% ee) in the reactions of 3-arylcyclobutanones (*Scheme 4*). On the other hand, complex **12** bearing *t*Bu groups at C(3) and C(3′) and electron-withdrawing NO_2 groups at C(5) and C(5′) (trivial numbering) exhibited a high enantioselectivity of 98% ee in the reaction of a tricyclic cyclobutanone (*Table 4*).

Introduction. – In the last two decades, enantioface-selective oxidation of alkenes has been remarkably improved by introducing well-designed chiral catalysts. Furthermore, C−H oxidation has also been achieved in a highly enantiotopos-selective manner, though asymmetric oxidation of non-activated C−H bonds remains unsettled [1]. On the other hand, asymmetric *Baeyer-Villiger* (*B.-V.*) oxidation of prochiral ketones, another enantiotopos-selective reaction, still remains on a unsatisfactory level, except for a few examples [2], despite of its high synthetic utility [3]. In contrast, biological *B.-V.* oxidation is well known to proceed with excellent enantioselectivity by the aid of so-called Baeyer-Villigerases [4]. *B.-V.* oxidation consists of two steps: nucleophilic attack of an oxidant to give the *Criegee* adduct intermediate and subsequent migration of a C−C bond to the proximal O-atom to give a lactone or ester (*Scheme 1*). Enzymes are considered to promote the face-selective addition of hydroperoxide to a carbonyl compound and the enantiotopos-selective rearrangement of the resulting *Criegee* adduct to a lactone in their highly sophisticated reaction sites, in

Scheme 1



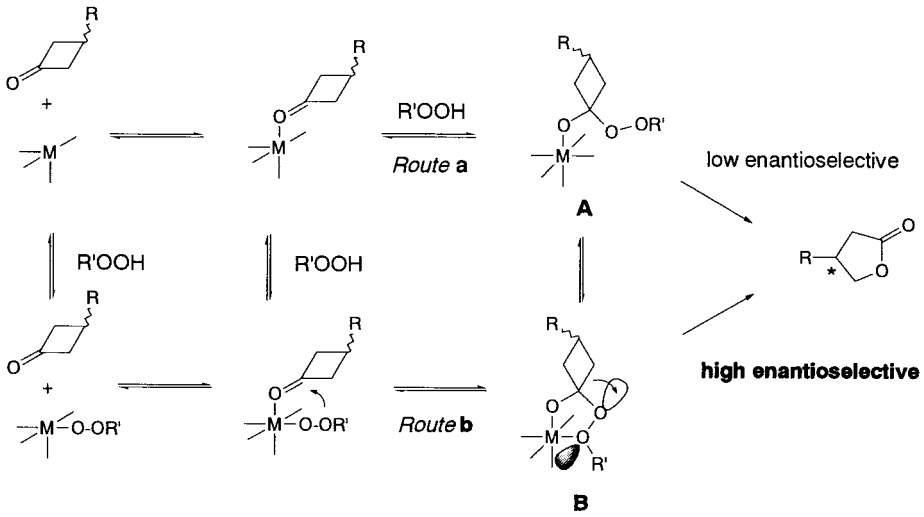
which the conformation of the *Criegee* adduct is appropriately regulated to allow the topos-selective migration of the C–C bond [4].

A *Lewis* acid can activate both carbonyl and peroxide groups and, therefore, the nucleophilic attack and the migration steps in the *B.-V.* oxidation are considered to be accelerated by *Lewis* acid catalysts. Thus, the stereochemistry of the *B.-V.* oxidation can be regulated with a suitable chiral *Lewis* acid catalyst. If the substrate is racemic, enantiomer differentiation is also expected. Indeed, *Bolm et al.* [5] reported the enantiomer-differentiating *B.-V.* oxidation of racemic 2-arylcyclohexanones with a combination of O_2 and aldehyde (*Mukaiyama* condition) [6] (for other *B.-V.* oxidations with O_2, see [7]) in the presence of a chiral bis(dihydrooxazolylphenolato)-copper(II) complex as the catalyst. *Strukul* and co-workers [8] also independently reported the enantiomer-differentiating reaction of racemic 2-substituted cyclohexanones with H_2O_2 in the presence of a chiral [pt^{II}(binap)] complex as the catalyst. The copper catalysts were further applied to the enantioselective *B.-V.* oxidation of prochiral cyclobutanone derivatives, but moderate enantioselectivities of 47% ee were obtained, except for the reaction of some tricyclic cyclobutanones, which showed high enantioselectivity [9a–e]. Quite recently, it was reported that (binaphthalenolato)magnesium(II) and (6,6′-dibromobinaphthalenolato)aluminium(III) complexes showed good enantioselectivity of 65 and 77% ee, respectively, in the reaction of 3-phenylcyclobutanone [9f,g]. *B.-V.* oxidation of 3-substituted cyclobutanones in the presence of stoichiometric amounts of chiral complexes such as titanium(IV) complexes [10a,b], zinc(II) complexes [10c], and zirconium(IV) complexes [10d] has also been reported, but they also exhibit moderate enantioselectivities (< 50% ee).

As discussed above, two factors, *i.e.*, face-selection in the formation of the *Criegee* adduct and enantiotopos-selection in the C–C bond migration, are related to the stereochemistry of the *B.-V.* oxidation of prochiral ketones. However, the *Criegee* adduct formation is reversible, and the migration of the C–C bond is irreversible. Thus, the topos-selection in the migration is considered to have a main influence on the stereochemistry of the *B.-V.* reaction (*Scheme 2*). This topos-selection is considered to be mainly governed by stereoelectronic factors, because orbital interaction between the σ-orbital of the migrating C–C bond and the σ^*-orbital of the O–O bond is indispensable for the migration [4b]. Therefore, to achieve high enantioselectivity, the σ^*-orbital of the O–O bond must overlap selectively with one of the σ-orbitals of the two C–C bonds prone to migration. The peroxy unit of the *Criegee* adduct **A**, generated by addition of a hydroperoxide, has high conformational freedom, and either

of the two σ-orbitals can overlap with the σ^*-orbital. Thus, the rearrangement of **A** to the lactone is considered to be a low-enantioselective process. On the other hand, it was expected that the migration of the C–C bond would be enhanced by coordination of the distal O-atom of the peroxide unit to the metal center due to activation of the O–O bond. Furthermore, if the conformation of the resulting chelate **B** is regulated to allow the topos-selective σ,σ^* interaction, high enantioselectivity is expected. Of course, the formation of **B** must be faster than the rearrangement of **A** to the lactone. Although there are two possible routes (*Routes a* and *b*) for the formation of the chelated *Criegee* adduct **B**, use of the oxidant carrying a sterically less-demanding R′ group such as the H-atom (R′=H) is highly recommended to meet the above condition. It is apparent that a metal complex possessing two vacant coordinating sites *cis*-positioned to each other is requested for the chelate formation. Use of a metal complex, the metal center of which is stereogenic, is also considered to be desirable for achieving high enantioselectivity.

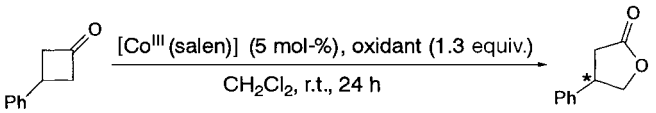
Scheme 2



Results and Discussion. – With these considerations in mind, we examined the *B.-V.* oxidation of 3-phenylcyclobutanone in the presence of two types of cationic (salen)-cobalt complexes (salen = [bis(salicylidene)ethylenediaminato] = {{2,2′-[(ethane-1,2-diyl)bis[(nitrilo-κN)methylidyne]]bis[phenolato-κO]}(2–)}) as catalyst in CH_2Cl_2 at room temperature (*Table 1*) (for a preliminary communication, see [11]). (Salen)-cobalt complexes **1** and **2** (hereafter denoted as [Co(salen)]s) bearing a chiral ethane-1,2-diamine moiety are considered to take a square planar geometry (*SP-4*) and to have two apical vacant coordination sites *trans* to each other (for X-ray analyses of [Co^{III}(salen)]s bearing an ethane-1,2-diamine moiety as their diamine unit, see [12]). On the other hand, *Che* and co-workers have reported that [Mn(salen)] and [Fe(salen)] bearing a binaphthalenediamine moiety as their diamine unit take a *cis*-β

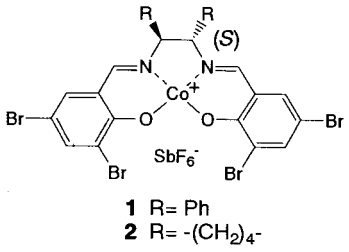
structure [13]. Although the structures of complexes **3**–**6** have not been determined, we expected that they also adopt the *cis-β* structure and have two vacant coordination sites *cis* to each other. Except for complex **6** bearing an electron-donating MeO group, all complexes catalyzed the *B.-V.* oxidation (see *Table 1*), but enantioselectivity was observed only when the complexes **3**–**5** of *cis-β* structure were used as the catalyst and H_2O_2 or its urea adduct (UHP) was used as the oxidant (*Entries 7*, *8*, *11*, and *12*). This observation completely agrees with the above-discussed analysis. Among the reactions examined, the one performed with a combination of complex **4** bearing F-substituents and UHP showed the best enantioselectivity (*Entry 11*).

Table 1. *Asymmetric* B.-V. *Oxidation of 3-Phenylcyclobutanone by Different Oxidants in the Presence of (Salen)cobalt Complexes* **1**–**6** *as Catalyst*

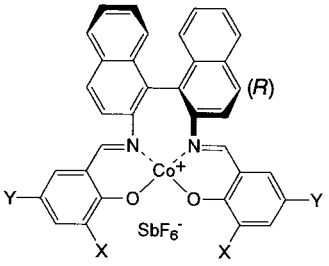


Entry	Catalyst	Oxidant[a])	Yield [%]	% ee[b])	Configuration[c])
1	**1**	H_2O_2	29	0	–
2	**1**	TBHP	72	0	–
3[d])	**1**	*m*CPBA	75	0	–
4	**2**	H_2O_2	20	0	–
5	**2**	TBHP	62	0	–
6[d])	**2**	*m*CPBA	80	0	–
7	**3**	H_2O_2	30	20	(*S*)
8	**3**	UHP	31	53	(*S*)
9	**3**	TBHP	27	0	–
10[d])	**3**	*m*CPBA	78	0	–
11	**4**	UHP	30	57	(*S*)
12	**5**	UHP	10	55	(*S*)
13	**6**	UHP	0	–	–

[a]) TBHP = *tert*-butyl hydroperoxide; *m*CPBA = 3-chloroperbenzoic acid; UHP = urea · H_2O_2 adduct. [b]) Determined by HPLC analysis with a chiral-stationary-phase column (*Daicel Chiralpak AD-H*, hexane/^{i}PrOH 49 : 1). [c]) The absolute configuration was determined by chiroptical comparison [10c]. [d]) The reaction was carried out at −78° in the presence of 1 equiv. of *N*-methylmorpholine *N*-oxide.



1 R= Ph
2 R= -$(CH_2)_4$-



3 X=Y= Br
4 X=Y= F
5 X=Y= H
6 X= MeO, Y= H

We next attempted the optimization of the reaction conditions involving complex **4** as the catalyst (*Table 2*). Although no clear relationship between solvent polarity and enantioselectivity was observed, the reactions in polar solvents such as EtOH and THF proceeded with better enantioselectivity than those in nonpolar solvent such as hexane and benzene. It is noteworthy that an aqueous H_2O_2 solution could be employed as the stoichiometric oxidant as efficiently as UHP when EtOH was used as solvent (*Entries 4–7*). Lowering the reaction temperature to $-20°$ improved enantioselectivity up to 77% ee (*Entry 8*). Further lowering the temperature, however, reduced enantioselectivity to some extent (*Entry 9*).

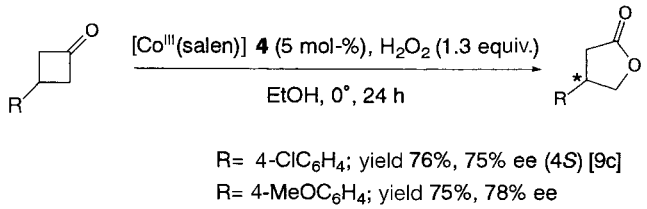
Table 2. *Asymmetric* B.-V. *Oxidation of 3-Phenylcyclobutanone by UHP in the Presence of (Salen)cobalt Complex* **4** as *Catalyst*

Entry	Solvent	Temp.	Yield [%]	% ee[a])	Configuration[b])
1	CH_2Cl_2	r.t.	30	57	(*S*)
2	THF	r.t.	69	70	(*S*)
3	MeCN	r.t.	93	67	(*S*)
4	EtOH	r.t.	87	71	(*S*)
5	EtOH[c])	r.t.	92	69	(*S*)
6	EtOH	0°	90	75	(*S*)
7	EtOH[c])	0°	85	75	(*S*)
8	EtOH[c])	−20°	72	77	(*S*)
9	EtOH	−78°	86	69	(*S*)
10	MeOH	r.t.	84	70	(*S*)
11	^{i}PrOH	r.t.	92	71	(*S*)
12	AcOEt	r.t.	87	60	(*S*)
13	Et_2O	r.t.	83	69	(*S*)
14	hexane	r.t.	78	50	(*S*)
15	benzene	r.t.	22	55	(*S*)
16	toluene	r.t.	25	55	(*S*)

[a]) Determined by HPLC analysis with a chiral-stationary-phase column (*Daicel Chiralpak AD-H*, hexane/^{i}PrOH 49 : 1).[b]) The absolute configuration was determined by chiroptical comparison [10c]. [c]) Aqueous H_2O_2 solution (30%) was used as terminal oxidant.

The reactions of 3-(4-chlorophenyl)- and 3-(4-methoxyphenyl)cyclobutanones were also performed at 0° in the presence of **4** with aqueous H_2O_2 solution as the terminal oxidant and showed good enantioselectivity of 75 and 78% ee, respectively (*Scheme 3*). The reactions at −78° exhibited a somewhat reduced enantioselectivity (72 and 76% ee, resp.).

Scheme 3

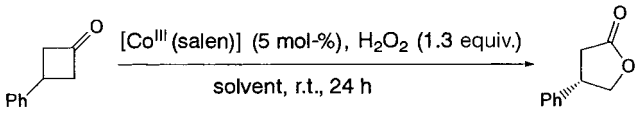


R= 4-ClC_6H_4; yield 76%, 75% ee (4*S*) [9c]
R= 4-MeOC_6H_4; yield 75%, 78% ee

Thus far, we used cationic [Co(salen)] **4** as the catalyst. However, neutral bromo- and iodo(salen)cobalt(III) complexes **7** and **8**, which are the synthetic precursors of **4**, were also found to serve as catalyst for the *B.-V.* oxidation. Therefore, we examined the *B.-V.* oxidation of 3-phenylcyclobutanone at room temperature in the presence of the neutral [Co(salen)]s as catalyst and H_2O_2 as oxidant (*Table 3*). Complex **7** bearing a bromo ligand showed poor enantioselectivity, suggesting that the chelate formation was not fast enough (*Entry 2*). On the other hand, complex **8** possessing a iodo ligand exhibited catalytic activity and enantioselectivity almost identical with cationic complex **4** (*Entry 3*). We next examined the solvent effects on the enantioselectivity. Both the reactions with **4** and **8** showed a similar trend: the reactions in polar solvents exhibited a slightly better enantioselectivity than those in less polar solvents.

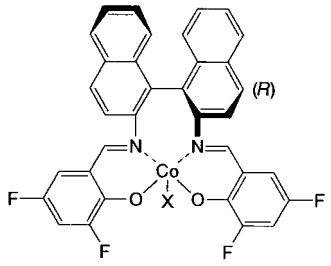
The reactions of several 3-substituted cyclobutanones in the presence of complex **8** were examined in EtOH at 0° (*Scheme 4*). For the 3-(4-chlorophenyl)- and 3-(4-

Table 3. *Asymmetric* B.-V. *Oxidation of 3-Phenylcyclobutanone by Aqueous H_2O_2 Solution in the Presence of [Co(salen)]s* **8** *and* **9** *as Catalyst*



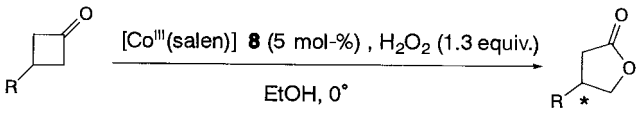
Entry	Catalyst	Solvent	Yield [%]	% ee[a])	Configuration[b])
1	**4**	EtOH	87	71	(*S*)
2	**7**	EtOH	70	26	(*S*)
3	**8**	EtOH	97	72	(*S*)
4	**8**	THF	52	71	(*S*)
5	**8**	MeCN	62	65	(*S*)
6	**8**	AcOEt	75	71	(*S*)
7	**8**	Et_2O	71	69	(*S*)
8	**8**	hexane	45	54	(*S*)
9	**8**	benzene	21	66	(*S*)
10	**8**	toluene	25	64	(*S*)
11	**8**	CH_2Cl_2	43	69	(*S*)

[a]) Determined by HPLC analysis with a chiral-stationary-phase column (*Daicel Chiralpak AD-H*, hexane/^{i}PrOH 49 : 1). [b]) The absolute configuration was determined by chiroptical comparison [10c].



7 X= Br
8 X= I

Scheme 4



R = Ph; yield 96%, 79% ee (4*S*)
R = 4-ClC$_6$H$_4$; yield 82%, 75% ee (4*S*)
R = 4-MeOC$_6$H$_4$; yield 99%, 75% ee
R = Me(CH$_2$)$_7$; yield 89%, 69% ee

methoxyphenyl)cyclobutanones, a similar level of enantioselectivity to that of 3-phenylcyclobutanone was observed, while it was somewhat lower for 3-octylcyclobutanone.

B.-V. oxidation of a prochiral tricyclic cyclobutanone at room temperature in the presence of **8** was next examined (*Table 4*). *Bolm et al.* have achieved high enantioselectivity (91% ee) in its reaction in the presence of their bis(dihydrooxazolylphenolato)copper(II) complex as catalyst [9d]. The reaction with the H_2O_2/complex **8** system, however, showed modest enantioselectivity (*Entry 1*). Use of the UHP adduct instead of 30% aqueous H_2O_2 solution slightly improved the enantioselectivity (*Entry 2*). We also examined the reaction in other polar solvents, and enantioselectivity was improved to 60% ee in AcOEt (*Entry 6*). No more improvement could, however, be achieved by modification of the reaction conditions. The reaction of the bulky tricyclic ketone was considered to proceed through a sterically congested transition state, and the transition-state conformation for the migration step was expected to be strongly affected by the substituent of the salen ligand. Therefore, we examined the *B.-V.* oxidation of the tricyclic ketone in the presence of complexes **9**–**12** bearing substituents different from those of **8**. The reaction in the presence of complex **10** showed high enantioselectivity of 86% ee, but the chemical yield was low (*Entry 8*). However, with complex **12** as catalyst, an excellent enantioselectivity of 98% ee as well as a good chemical yield were achieved (*Entry 10*).

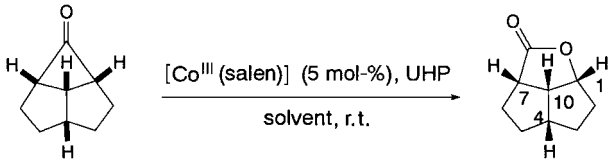
Finally, we also examined the oxidation of 3-phenylcyclobutanone in the presence of **12** as catalyst, but enantioselectivity was moderate though chemical yield was good (*Scheme 5*).

Conclusions. – We were able to demonstrate that topos-selective σ(C–C),σ^*(O–O) interaction in the migration step required for a highly enantioselective *Baeyer-Villiger* oxidation of prochiral cyclic ketones could be realized with (salen)cobalt(III) complexes of *cis-β* structure as catalyst. Further studies on asymmetric *Baeyer-Villiger* oxidations are underway in our laboratory.

Experimental Part

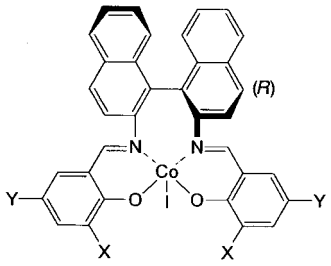
1. *General.* Solvents were dried and distilled shortly before use. Reactions were carried out under N_2 if necessary. Column chromatography (CC): silica gel *60N* (spherical, neutral), 63–210 mm, from *Kanto Chemical*

Table 4. *Asymmetric* B.-V. *Oxidation of Tricyclic Cyclobutanone by UHP in the Presence of [Co(salen)]s* **8**–**12** *as Catalyst*



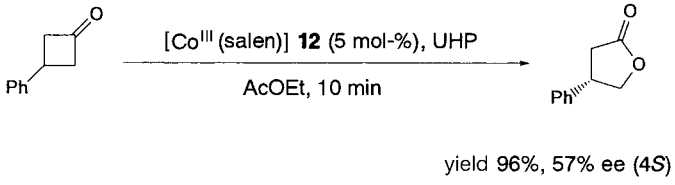
Entry	Catalyst	Solvent	Time [h]	Yield [%]	% ee[a])	Configuration[b])
1[c])	**8**	EtOH	24	31	36	(1*R*,4*S*,7*S*,10*R*)
2	**8**	EtOH	24	38	43	(1*R*,4*S*,7*S*,10*R*)
3	**8**	MeCN	24	15	55	(1*R*,4*S*,7*S*,10*R*)
4	**8**	Et_2O	24	15	56	(1*R*,4*S*,7*S*,10*R*)
5	**8**	AcOEt	24	21	59	(1*R*,4*S*,7*S*,10*R*)
6	**8**	AcOEt	48	42	60	(1*R*,4*S*,7*S*,10*R*)
7	**9**	AcOEt	48	36	76	(1*R*,4*S*,7*S*,10*R*)
8	**10**	AcOEt	48	26	86	(1*R*,4*S*,7*S*,10*R*)
9	**11**	AcOEt	48	49	64	(1*R*,4*S*,7*S*,10*R*)
10	**12**	AcOEt	48	92	98	(1*R*,4*S*,7*S*,10*R*)

[a]) Determined by HPLC analysis with a chiral-stationary-phase column (*Daicel Chiralcel OB-H*, hexane/^{i}PrOH 9 : 1) after conversion to the corresponding γ-hydroxy-*N*-benzylamide (see *Exper. Part*). [b]) The absolute configuration was determined by chiroptical comparison [4]. [c]) Aqueous H_2O_2 solution (30%) was used as terminal oxidant.



9 X=Y= Cl
10 X=Y= Br
11 X=Y= I
12 X= ^{t}Bu, Y= NO_2

Scheme 5



yield 96%, 57% ee (4*S*)

Co. Inc. Prep. TLC: 0.5 mm × 20 cm × 20 cm *E. Merck* silica gel plate (*60 F-254*). Enantiomer excesses (ee): by HPLC (*Shimadzu LC-10AT-VP*) on chiral-stationary-phase column (see *Tables 1–4* and *Exper. Part*). Optical rotations: *Jasco P-1020* polarimeter. IR Spectra: *Shimadzu FTIR-8400* instrument; in cm^{-1}. ^{1}H-NMR Spectra (400 MHz): *Jeol JNM-AL-400* instrument; δ in ppm rel. to Me_4Si internal standard (= 0 ppm), *J* in Hz; $CDCl_3$ solns. HR-MS: *Jeol JMS-SX/SX-102A* instrument; in *m/z*.

2. *Substrates.* The 3-substituted cyclobutanones [13][14], the tricyclic cyclobutanone [15] (tricyclo[4.2.1.$0^{3,9}$]nonan-2-one = octahydro-1,6-methanopentalen-7-one), and 3-(*tert*-butyl)-5-nitrosalicylaldehyde (= 3-(*tert*-butyl)-2-hydroxy-4-nitrobenzaldehyde) [16] were prepared according to the literature procedures.

3. *Chiral [Co^{II}(salen)] Complexes. [(1*S*,2*S*)-*N*,*N*′-Bis(3,5-dibromosalicylidene)cyclohexane-1,2[diaminato]cobalt(II)* (*={{2,2′-{[(1*S*,2*S*)-Cyclohexane-1,2-diyl]bis[(nitrilo-κN)methylidyne]}bis[4,6-dibromophenolato-κO]}(2−)}cobalt*). To a soln. of (1*S*,2*S*)-cyclohexane-1,2-diamine (57.0 mg, 0.5 mmol) in EtOH (10 ml), 3,5-dibromosalicylaldehyde (279.0 mg, 1.0 mmol) was added, and the mixture was stirred for 6 h at r.t. The resulting light yellow precipitate was filtered off and dried *in vacuo*. This precipitate was added to a soln. of $Co(OAc)_2$ (124.5 mg, 0.5 mmol), which was obtained by heating $Co(OAc)_2 \cdot 4\,H_2O$ at 70–80° under vacuum until its color turned from pink to purple, in degassed EtOH (10 ml). The mixture was heated at 90° for 6 h and then cooled to r.t. The resulting brown precipitate was filtered off, washed with degassed EtOH under N_2, and dried *in vacuo:* brown solid (311.3 mg, 89%). IR (KBr): 3063, 2936, 2860, 1599, 1501, 1404, 1215, 1165, 1036, 943, 860, 808, 750, 718, 681, 615, 583, 552, 480, 448. Anal. calc. for $C_{20}H_{16}Br_4CoN_2O_2 \cdot 0.5\,H_2O$: C 34.13, H 2.43, N 3.98; found: C 34.05, H 2.41, N 3.80.

The chiral [Co^{II}(salen)] complexes given below were prepared in the same manner.

*[(1*S*,2*S*)-*N*,*N*′-Bis(3,5-dibromosalicylidene)-1,2-diphenylethane-1,2-diaminato]cobalt(II)* (*={{2,2′-{[(1*S*,2*S*)-1,2-Diphenylethane-1,2-diyl]bis[(nitrilo-κN)methylidyne]}bis[4,6-dibromophenolato-κO]}(2−)}cobalt*). Orange solid (84%). IR (KBr): 3061, 3030, 2914, 1589, 1499, 1433, 1373, 1315, 1271, 1215, 1165, 1003, 945, 864, 787, 754, 704, 569, 546, 515. Anal. calc. for $C_{28}H_{18}Br_4CoN_2O_2$: C 42.19, H 2.31, N 3.49; found: C 42.41, H 2.29, N 3.53.

*[(1*R*)-*N*,*N*′-Bis(salicylidene)-1,1′-binaphthalene-2,2′-diaminato]cobalt(II)* (*={{2,2′-{[(*M*)-[1,1′-Binaphthalene]-2,2′-diyl]bis[(nitrilo-κN)methylidyne]}bis[phenolato-κO]}(2−)}cobalt*). Brown solid (99%). IR (KBr): 3055, 2924, 2893, 1585, 1539, 1504, 1439, 1387, 1188, 1153, 1072, 1034, 976, 951, 910, 860, 829, 752, 679, 638, 586, 525, 482, 455, 424. Anal. calc. for $C_{34}H_{22}CoN_2O_2 \cdot H_2O$: C 71.96, H 4.26, N 4.94; found: C 71.90, H 4.37, N 4.74.

*[(1*R*)-*N*,*N*′-Bis(3,5-difluorosalicylidene)-1,1′-binaphthalene-2,2′-diaminato]cobalt(II)* (*={{2,2′-{[(*M*)-[1,1′-Binaphthalene]-2,2′-diyl]bis[(nitrilo-κN)methylidyne]}bis[4,6-difluorophenolato-κO]}(2−)}cobalt*). Prepared as described above, except for the purification. EtOH was removed by distillation, and the residue was washed with hexane and H_2O to give an orange solid (98%). IR (KBr): 3061, 3011, 2930, 1595, 1555, 1506, 1492, 1441, 1393, 1327, 1263, 1225, 1178, 1124, 1049, 991, 972, 858, 808,783, 748, 698, 617, 588, 542, 494, 432. Anal. calc. for $C_{34}H_{18}CoF_4N_2O_2 \cdot 0.5\,H_2O$: C 64.77, H 3.04, N 4.44; found: C 64.82, H 3.24, N 4.40.

*[(1*R*)-*N*,*N*′-Bis(3,5-dichlorosalicylidene)-1,1′-binaphthalene-2,2′-diaminato]cobalt(II)* (*={{2,2′-{[(*M*)-[1,1′-Binaphthalene]-2,2′-diyl]bis[(nitrilo-κN)methylidyne]}bis[4,6-dichlorophenolato-κO]}(2−)}cobalt*). Orange solid (95%). IR (KBr): 3059, 2922, 1605, 1508, 1433, 1379, 1310, 1200, 1163, 1070, 968, 864, 822, 750, 690, 536, 500, 424. Anal. calc. for $C_{34}H_{18}Cl_4CoN_2O_2 \cdot 0.5$ EtOH: C 59.18, H 2.98, N 3.94; found: C 58.97, H 2.87, N 4.01.

*[(1*R*)-*N*,*N*′-Bis(3,5-dibromosalicylidene)-1,1′-binaphthalene-2,2′-diaminato]cobalt(II)* (*={{2,2′-{[(*M*)-[1,1′-Binaphthalene]-2,2′-diyl]bis[(nitrilo-κN)methylidyne]}bis[4,6-dibromophenolato-κO]}(2−)}cobalt*). Orange solid (99%). IR (KBr): 3059, 3009, 2920, 1597, 1502, 1427, 1375, 1306, 1200, 1150, 1070, 959, 868, 920, 750, 714, 687, 532, 498. Anal. calc. for $C_{34}H_{18}Br_4CoN_2O_2 \cdot 0.5\,H_2O$: C 46.72, H 2.19, N 3.20; found: C 46.88, H 2.13, N 3.23.

*[(1*R*)-*N*,*N*′-Bis(3,5-diiodosalicylidene)-1,1′-binaphthalene-2,2′-diaminato]cobalt(II)* (*={{2,2′-{[(*M*)-[1,1′-Binaphthalene]-2,2′-diyl]bis[(nitrilo-κN)methylidyne]}bis[4,6-diiodophenolato-κO]}(2−)}cobalt*). Orange solid (92%). IR (KBr): 3053, 1597, 1489, 1419, 1371, 1302, 1205, 1146, 1113, 1070, 965, 953, 868, 816, 750, 677, 530. Anal. calc. for $C_{34}H_{18}CoI_4N_2O_2 \cdot 0.5$ EtOH: C 39.07, H 1.97, N 2.60; found: C 39.32, H 1.85, N 2.75.

*[(1*R*)-*N*,*N*′-Bis(5-methoxysalicylidene)-1,1′-binaphthalene-2,2′-diaminato]cobalt(II)* (*={{2,2′-{[(*M*)-[1,1′-Binaphthalene]-2,2′-diyl]bis[(nitrilo-κN)methylidyne]}bis[6-methoxyphenolato-κO]}(2−)}cobalt*). Orange solid (95%). IR (KBr): 3055, 2997, 2933, 2903, 2831, 1581, 1533, 1487, 1466, 1433, 1381, 1331, 1271, 1219, 1157, 1038, 949, 812, 750, 727, 530, 459, 432. HR-FAB-MS: 609.1225 ($C_{36}H_{26}CoN_2O_4^+$; calc. 609.1232).

4. *Chiral Cationic [Co^{III}salen] Complexes. [(1*S*,2*S*)-*N*,*N*′-Bis(3,5-dibromosalicylidene)cyclohexane-1,2-diaminato]cobalt(III) Hexafluoroantimonate* (*={{2,2′-{[(1*S*,2*S*)-Cyclohexane-1,2-diyl]bis[(nitrilo-κN)methylidyne]}bis[4,6-dibromophenolato-κO]}(2−)}cobalt(1+) Hexafluoroantimonate(1−)*; **2**). To the soln. of [(1*S*,2*S*)-*N*,*N*′-bis(3,5-dibromosalicylidene)cyclohexane-1,2-diaminato]cobalt(II) (69.5 mg, 0.1 mmol) in

CH_2Cl_2 (1 ml), I_2 (12.7 mg, 0.05 mmol) was added and stirred at r.t. for 1 h. Then $AgSbF_6$ (34.4 mg, 0.1 mmol) was added and stirred for another 6 h. The resulting suspension was filtered through a pad of *Celite*, the filtrate evaporated, and the residue submitted to CC (silica gel, CH_2Cl_2/MeOH 1:0 → 10:1): **2** (74.8 mg, 81%). Dark green solid. IR (KBr): 3065, 2937, 2862, 1637, 1581, 1516, 1441, 1377, 1344, 1315, 1290, 1165, 1034, 957, 868, 746, 715, 660, 586, 552, 511, 457. HR-FAB-MS: 690.7283 ($C_{20}H_{16}{}^{79}Br_4CoN_2O_2^+$, $[M-SbF_6]^+$; calc. 690.7277).

The cationic [Co^{III}(salen)] complexes **1** and **3**–**6** were prepared in the same manner.

*[(1*S*,2*S*)-*N*,*N*′-Bis(3,5-dibromosalicylidene)-1,2-diphenylethane-1,2-diaminato]cobalt(III) Hexafluoroantimonate* (=*{[2,2′-{[(1*S*,2*S*)-1,2-Diphenylethane-1,2-diyl]bis[(nitrilo-κN)methylidyne]}bis[4,6-dibromophenolato-κO]}(2−)}cobalt(1+) Hexafluoroantimonate(1−)*; **1**). Dark green solid (75%). IR (KBr): 3065, 3056, 2959, 1632, 1583, 1502, 1439, 1375, 1310, 1217, 1167, 1078, 1005, 964, 864, 789, 748, 714, 664, 550, 521. HR-FAB-MS: 788.7429 ($C_{28}H_{18}{}^{79}Br_4CoN_2O_2^+$, $[M-SbF_6]^+$; calc. 788.7434).

*[(1*R*)-*N*,*N*′-Bis(3,5-dibromosalicylidene)-1,1′-binaphthalene-2,2′-diaminato]cobalt(III) Hexafluoroantimonate* (=*{[2,2′-{[(*M*)-[1,1′-Binaphthalene]-2,2′-diyl]bis[(nitrilo-κN)methylidyne]}bis[4,6-dibromophenolato-κO]}(2−)}cobalt(1+) Hexafluoroantimonate(1−)*; **3**). Dark green solid (56%). IR (KBr): 3381, 3290, 3230, 3059, 3014, 2924, 2854, 1601, 1504, 1431, 1367, 1306, 1265, 1203, 1161, 1092, 951, 864, 820, 777, 750, 723, 662, 540, 496, 438. HR-FAB-MS: 860.7443 ($C_{34}H_{18}{}^{79}Br_4CoN_2O_2^+$, $[M-SbF_6]^+$; calc. 860.7434).

*[(1*R*)-*N*,*N*′-Bis(3,5-difluorosalicylidene)-1,1′-binaphthalene-2,2′-diaminato]cobalt(III) Hexafluoroantimonate* (=*{[2,2′-{[(*M*)-[1,1′-Binaphthalene]-2,2′-diyl]bis[(nitrilo-κN)methylidyne]}bis[4,6-difluorophenolato-κO]}(2−)}cobalt(1+) Hexafluoroantimonate(1−)*; **4**). Dark green solid (60%). IR (KBr): 3385, 3236, 3057, 2930, 1713, 1610, 1553, 1506, 1450, 1352, 1308, 1267, 1232, 1180, 1126, 1066, 989, 951, 831, 750, 694, 660, 582, 536, 488. HR-FAB-MS: 621.0641 ($C_{34}H_{18}CoF_4N_2O_2^+$, $[M-SbF_6]^+$; calc. 621.0636).

*[(1*R*)-*N*,*N*′-Bis(salicylidene)-1,1′-binaphthalene-2,2′-diaminato]cobalt(III) Hexafluoroantimonate* (=*{[2,2′-{[(*M*)-[1,1′-Binaphthalene]-2,2′-diyl]bis[(nitrilo-κN)methylidyne]}bis[phenolato-κO]}(2−)}cobalt(1+) Hexafluoroantimonate(1−)*; **5**). Dark green solid (85%). IR (KBr): 3298, 3236, 3055, 3014, 2926, 1607, 1527, 1441, 1375, 1313, 1190, 1149, 1074, 1074, 957, 910, 816, 752, 660, 492, 440. HR-FAB-MS: 549.1012 ($C_{34}H_{22}CoN_2O_2^+$, $[M-SbF_6]^+$; calc. 549.1013).

*[(1*R*)-*N*,*N*′-Bis(5-dimethoxysalicylidene)-1,1′-binaphthalene-2,2′-diaminato]cobalt(III) Hexafluoroantimonate* (=*{[2,2′-{[(*M*)-[1,1′-Binaphthalene]-2,2′-diyl]bis[(nitrilo-κN)methylidyne]}bis[6-methoxyphenolato-κO]}(2−)}cobalt(1+) Hexafluoroantimonate(1−)*; **6**). Dark green solid (53%). IR (KBr): 3385, 3302, 3238, 3055, 3001, 2937, 2837, 1593, 1533, 1510, 1462, 1431, 1356, 1302, 1267, 1219, 1155, 1076, 1036, 947, 818, 750, 660, 575, 527, 494, 440. HR-FAB-MS: 609.1225 ($C_{36}H_{26}CoN_2O_4^+$, $[M-SbF_6]^+$; calc. 609.1225).

5. *Chiral [Co^{III}I(salen)] Complexes. [(1*R*)-*N*,*N*′-Bis(3-(*tert*-butyl)-5-nitrosalicylidene)-1,1′-binaphthalene-2,2′-diaminato]cobalt(III) Iodide* (=*{[2,2′-{[(*M*)-[1,1′-Binaphthalene]-2,2′-diyl]bis[(nitrilo-κN)methylidyne]}bis[6-(*tert*-butyl)-4-nitrophenolato-κO]}(2−)}cobalt(1+) Iodide*; **12**). To a soln. of (1*R*)-1,1′-binaphthalene-2,2′-diamine (200 mg, 0.7 mmol) in EtOH (7 ml), 3-(*tert*-butyl)-5-nitrosalicylaldehyde (314 mg, 1.4 mmol) was added and the mixture was heated at 90° for 12 h. After cooling to r.t., the resulting light yellow precipitate was filtered off and dried *in vacuo*. This precipitate (139 mg, 0.2 mmol) was added to a soln. of $Co(OAc)_2$ (50 mg, 0.2 mmol), which was obtained by heating $Co(OAc)_2 \cdot 4\,H_2O$ at 70–80° under vacuum until its color turned from pink to purple, in degassed DMF (4 ml). The mixture was heated at 110° for 24 h and then evaporated and the residue dissolved in CH_2Cl_2 (4 ml). To this soln., I_2 (25.4 mg, 0.1 mmol) was added. After being stirred for 1 h, the mixture was evaporated and the residue submitted to CC (silica gel, hexane/CH_2Cl_2 1:0 → 1:1): **12** (113 mg, 64%). Brown solid. IR (KBr): 3059, 2957, 2916, 2870, 1593, 1554, 1500, 1470, 1419, 1387, 1315, 1200, 1173, 1115, 1076, 1028, 984, 922, 866, 829, 798, 739, 681, 561, 509, 484. HR-FAB-MS: 751.1971 ($C_{42}H_{36}CoN_4O_6$, $[M-I]^+$; calc. 751.1967).

The [Co^{III}I(salen)] complexes **8**–**11** were prepared *in situ* from the corresponding [Co^{II}(salen)] complex and used for *B.-V.* oxidation without isolation.

6. *Asymmetric* Baeyer-Villiger *Oxidation of 3-Substituted Cyclobutanones in the Presence of [Co^{III}(salen)] Complex* **8** *as Catalyst: General Procedure.* To a CH_2Cl_2 soln. (0.5 ml) of [(1*R*)-*N*,*N*′-bis(3,5-difluorosalicylidene)-1,1′-binaphthalene-2,2′-diaminato]cobalt(II) (3.1 mg, 5.0 mmol), I_2 (0.7 mg, 2.5 mmol) was added under N_2. After being stirred for 1 h, the mixture was evaporated, and the residue was dissolved in EtOH (0.5 ml). To this soln., 3-substituted cyclobutanone (0.1 mmol) was added and cooled to 0°. Aq. H_2O_2 soln. (30%; 15 ml, 0.13 mmol) was added to the mixture and stirred at 0° for 24 h. EtOH was evaporated and the residue submitted to CC (silica gel, hexane/AcOEt 45:7): 3-substituted butano-4-lactone.

*(3*S*)-3-Phenylbutano-4-lactone* (=*(4*S*)-4,5-Dihydro-4-phenylfuran-2(3*H*)-one*). Colorless solid. HPLC (*Daicel Chiralpak AD-H*; hexane/^{i}PrOH 49:1): 79% ee. Yield 96%. M.p. 56.1–56.2°. $[\alpha]_D^{24} = +44.4$ ($c = 0.43$,

$CHCl_3$) ([17a]: 96% ee, (*S*)-isomer; $[\alpha]_D^{20} = +46.0$ ($c = 0.95$, $CHCl_3$)). Anal. calc. for $C_{10}H_{10}O_2$: C 74.06, H 6.21; found: C 74.01, H 6.24.

*(3*S*)-3-(4-Chlorophenyl)-butano-4-lactone* (= *(4*S*)-4-(4-Chlorophenyl)-4,5-dihydrofuran-2(3*H*)-one*). Colorless solid. HPLC (*Daicel Chiralpak AD-H*, hexane/^{i}PrOH 49 : 1): 75% ee. Yield 82%. M.p. 63.5 – 63.9°. $[\alpha]_D^{24} = +39.6$ ($c = 0.43$, $CHCl_3$) ([17b]: 85% ee, (*S*)-isomer; $[\alpha]_D^{20} = +42.0$ ($c = 0.5$, $CHCl_3$)). Anal. calc. for $C_{10}H_{19}ClO_2$: C 61.08, H 4.61; found: C 61.08, H 4.68.

3-(4-Methoxyphenyl)butano-4-lactone (= *4,5-Dihydro-4-(4-methoxyphenyl)furan-2(3*H*)-one*). Colorless solid. HPLC (*Daicel Chiralpak AD-H*, hexane/^{i}PrOH 49 : 1): 75% ee. Yield 99%. M.p. 89.8 – 90.1°. $[\alpha]_D^{24} = +36.0$ ($c = 0.30$, $CHCl_3$). IR (KBr): 3527, 3454, 3014, 2962, 2904, 1774, 1483, 1356, 1300, 1167, 1092, 1011, 905, 833, 681, 590, 542, 501, 455. ^{1}H-NMR (400 MHz): 7.15 (*d*, *J* = 8.5, 2 H); 6.90 (*d*, *J* = 8.5, 2 H); 4.63 (*dd*, *J* = 7.8, 9.0, 1 H); 4.22 (*dd*, *J* = 8.3, 9.0, 1 H); 3.81 (*s*, 3 H); 3.78 – 3.69 (*m*, 1 H); 2.89 (*dd*, *J* = 8.7, 17.6, 1 H); 2.63 (*dd*, *J* = 9.3, 17.6, 1 H). Anal. calc. for $C_{11}H_{12}O_3$: C 68.74, H 6.29; found: C 68.74, H 6.29.

3-Octylbutano-4-lactone (= *4,5-Dihydro-4-octylfuran-2(3*H*)-one*). Yellow oil. Yield 89% (69% ee). $[\alpha]_D^{24} = +3.0$ ($c = 0.50$, $CHCl_3$). IR (neat): 2924, 2854, 1780, 1462, 1421, 1377, 1259, 1169, 1020, 798. ^{1}H-NMR (400 MHz): 4.41 (*dd*, *J* = 7.0, 9.0, 1 H); 3.92 (*dd*, *J* = 7.0, 9.0, 1 H); 2.62 (*dd*, *J* = 8.3, 16.8, 1 H); 2.60 – 2.48 (*m*, 1 H); 2.18 (*dd*, *J* = 7.8, 16.8, 1 H); 1.48 – 1.45 (*m*, 2 H); 1.27 – 1.26 (*m*, 12 H); 0.88 (*t*, *J* = 7.0, 3 H). Anal. calc. for $C_{11}H_{12}O_3$: C 72.68, H 11.18; found: C 72.49, H 11.14.

7. *Enantiomer Excess of 3-Octylbutano-4-lactone.* To a soln. of benzylamine (110 ml, 1.0 mmol) in CH_2Cl_2 (1.5 ml), 0.98M trimethylaluminium in hexane (1.0 ml, 1.0 mmol) was added at r.t. and stirred at r.t. for 1 h. The resulting aluminiumamide soln. (0.7 ml) was added to the 3-octylbutano-4-lactone (10.0 mg) at r.t. After being stirred for 3 h at r.t., the mixture was quenched with H_2O and extracted with CH_2Cl_2, the extract dried ($MgSO_4$) and evaporated, and the residue submitted to CC (silica gel, hexane/AcOEt 6 : 4): corresponding γ-hydroxy-*N*-benzylamide as white solid. HPLC (*Daicel Chiralcel OD-H*, hexane/^{i}PrOH 9 : 1): 69% ee.

8. *Asymmetric* Baeyer-Villiger *Oxidation of Tricyclic Cyclobutanone in the Presence of [Co^{III}(salen)] Complex* **12** *as Catalyst*. To a soln. of tricyclo[4.2.1.0^{3,9}]nonan-2-one (13.6 mg, 0.1 mmol) in AcOEt (0.5 ml), **12** (4.4 mg, 5.0 mmol) and UHP (12.2 mg, 0.13 mmol) were added successively at r.t. After being stirred at r.t. for 48 h, the mixture was evaporated and the residue submitted to CC (silica gel, hexane/AcOEt 8 : 2): *2-oxatricyclo[5.2.1.0^{4,10}]decan-3-one* (= *Octahydro-1*H*-pentaleno[6,1-*bc*]furan-1-one*; 13.9 mg, 91%). Oil. $[\alpha]_D^{23} = +82.6$ ($c = 0.27$, $CHCl_3$) ([15]: > 98% ee, (1*R*,4*S*,7*S*,10*R*)-isomer; $[\alpha]_D^{25} = +62$ ($c = 1.0$, $CHCl_3$)).

9. *Enantiomer Excess of the Tricyclic Lactone.* As described in *Exper. 7*, with benzylamine (110 ml, 1.0 mmol), CH_2Cl_2 (1.5 ml), and 0.98M trimethylaluminium in hexane (1.0 ml, 1.0 mmol); then with the resulting aluminiumamide soln. (1.0 ml) and tricyclic lactone (13.9 mg). After being stirred for 24 h at r.t., the mixture was quenched with 1M aq. HCl and extracted with CH_2Cl_2, the extract dried ($MgSO_4$) and evaporated, and the residue submitted to CC (silica gel, hexane/AcOEt 8 : 2): corresponding γ-hydroxy-*N*-benzylamide as white solid. HPLC (*Daicel Chiralcel OB-H*, hexane/^{i}PrOH 9 : 1): 98% ee.

REFERENCES

[1] 'Transition Metals for Organic Synthesis', Eds. M. Beller and C. Bolm, Wiley-VCH, Weinheim, 1998, Vol. 2.

[2] C. Bolm, O. Beckmann, in 'Comprehensive Asymmetric Catalysis', Eds. E. N. Jacobsen, A. Pfaltz, and H. Yamamoto, Springer, Berlin, 1999, Vol. 2, p. 803; G. Strukul, *Angew. Chem., Int. Ed*. **1998**, *37*, 1198.

[3] G. R. Krow, *Org. React.* **1993**, *43*, 251; U. Schwarz-Linek, A. Krödel, F.-A. Ludwig, A. Schulze, S. Rissom, U. Kragl, V. I. Tishkov, M. Vogel, *Synthesis* **2001**, 947.

[4] a) V. Alphand, R. Furstoss, in ' Handbook of Enzyme Catalysis in Organic Synthesis', Eds. K. Drauz and H. Waldmann, VCH Publishers, Weinheim, 1995, Vol. 2, p. 744; b) D. R. Kelly, *Chim. Oggi* **2000**, *18*, 33 and 52; c) V. Alphand, R. Furstoss, in 'Practical Approach in Chemistry: Asymmetric Oxidation Reactions', Ed. T. Katsuki, Oxford University Press, Oxford, 2001, p. 214.

[5] C. Bolm, G. Schlingloff, K. Weickhardt, *Angew. Chem., Int. Ed.* **1994**, *33*, 1848.

[6] T. Yamada, K. Takahashi, K. Kato, T. Takai, S. Inoki, T. Mukaiyama, *Chem. Lett*. **1991**, 641.

[7] S.-i. Murahashi, Y. Oda, T. Naota, *Tetrahedron Lett*. **1992**, *33*, 7557; M. Hamamoto, K. Nakayama, Y. Nishiyama, Y. Ishii, *J. Org. Chem*. **1993**, *58*, 6421; C. Bolm, G. Schlingloff, K. Weickhardt, *Tetrahedron Lett*. **1993**, *34*, 3405.

[8] G. Gusso, C. Baccin, F. Pinna, G. Strukul, *Organometallics* **1994**, *13*, 3442.

[9] a) C. Bolm, G. Schlingloff, *J. Chem. Soc., Chem. Commun*. **1995**, 1247; b) C. Bolm, G. Schlingloff, F. Bienewald, *J. Mol. Catal., A – Chem.* **1997**, *117*, 347; c) G. Strukul, A. Varagnolo, F. Pinna, *J. Mol. Catal., A – Chem.* **1997**, *117*, 413; d) C. Bolm, K. K. Luong, G. Schlingloff, *Synlett* **1997**, 1151; e) C. Paneghetti, R. Gavagnin, F. Pinna, G. Strukul, *Organometallics* **1999**, *18*, 5057; f) C. Bolm, O. Beckmann, A. Cosp, C. Palazzi, *Synlett* **2001**, 1461; g) C. Bolm, O. Beckmann, C. Palazzi, *Can. J. Chem*. **2001**, *79*, 1593.

[10] a) M. Lopp, A. Paju, T. Kanger, T. Pehk, *Tetrahedron Lett*. **1996**, *37*, 7583; b) T. Kanger, K. Kriis, A. Paju, T. Pehk, M. Lopp, *Tetrahedron: Asymmetry* **1988**, *9*, 4475; c) T. Shinohara, S. Fujioka, H. Kotsuki, *Heterocycles* **2001**, *55*, 237; d) C. Bolm, O. Beckmann, *Chirality* **2000**, *12*, 523

[11] T. Uchida, T. Katsuki, *Tetrahedron Lett*. **2001**, *42*, 6911.

[12] M. Calligaris, D. Minichelli, G. Nardin, L. Randacchio, *J. Chem. Soc. A* **1971**, 2720; J. M. Ready, E. N. Jacobsen, *J. Am. Chem. Soc*. **1999**, *121*, 6086; R. Blaauw, I. E. Kingma, J. H. Laan, J. L. van der Baan, S. Balt, M. W. G. de Bolster, G. W. Klumpp, W. J. J. Smeets, A. L. Spek, *J. Chem. Soc., Perkin Trans. 1* **2000**, 1199.

[13] M.-C. Cheng, M. C.-W. Chang, S.-M. Penk, K.-K. Cheung, C.-M. Che, *J. Chem. Soc., Dalton Trans*. **1997**, 3479.

[14] C. Schmit, J. B. Falmagne, J. Escudero, H. Vanlierde, L. Ghosez, *Org. Synth*. **1990**, *69*, 199.

[15] D. R. Kelly, C. J. Knowles, J. G. Mahdi, M. A. Wright, I. N. Taylor, D. E. Hibbs, M. B. Hursthouse, A. K. Mish'al, S. M. Roberts, P. W. H. Wan, G. Grogan, A. J. Willetts, *J. Chem. Soc., Perkin Trans. 1* **1995**, 2057.

[16] D. A. Cogan, G. Liu, K. Kim, B. J. Backes, J. A. Ellman, *J. Am. Chem. Soc*. **1998**, *120*, 8011.

[17] a) Y. Takaya, T. Senda, H. Kurushima, M. Ogasawara, T. Hayashi, *Tetrahedron: Asymmetry* **1999**, *10*, 4047; b) C. Mazzini, J. Lebreton, V. Alphand, R. Furstoss, *Tetrahedron Lett*. **1997**, *38*, 1195.

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