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Oxidation of Alkenes and Sulfides with Transition Metal Catalysts

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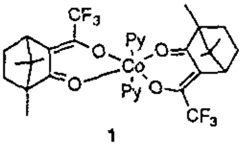
Alkenes and sulfides were oxidized with transition-metal catalysts. The oxidant sources include molecular dioxygen, air and iodosylbenzene. The metal ions Mn(III), Fe(III), Co(II) and Ni(II) were used. The catalysts **1-18** of 1,3-dioxo-, β-ketoimine- or salen-types were prepared and their efficacy was examined. 1,2-Dihydronaphthalene is most efficiently epoxidized with O_2/Me_2CHCHO or PhIO in the presence of Mn(III)-salen catalysts. The Ni(II)-, Co(II)- and Fe(III)-catalysts of either β-ketoimine- or salen-types are useful for epoxidation of styrene, (*E*)-stilbene and (*E*)-benzalacetone in the O_2/Me_2CHCHO system; these epoxidations are stereospecific without formation of corresponding diastereomeric epoxides. Oxidation of methyl *p*-tolyl sulfide with O_2/Me_2CHCHO is facilitated by the 1,3-dioxo-catalyst Co(II)-**1**. Monooxidation is achieved with Me_2CHCHO in equimolar proportions to give the corresponding sulfoxide, whereas overoxidation is realized with excess Me_2CHCHO to give the sulfone. These epoxidation and sulfide oxidations all occur at 25 °C and are complete in less than a day.

INTRODUCTION

Oxidation, especially stereoselective oxidation of alkenes, is an important organic reaction and is practiced extensively in the laboratory. Untilization of biological catalysts such as monooxygenase[1] or chloroperoxidase[2] is exploited for expoxidation of unactivated alkenes and derivatives of allylic alcohols. These oxidations are generally mediated with metalloenzymes with iron-oxo species for reaction with substrates. Non-biological catalytic asymmetric epoxidation of alkenes is reported.[3] Many metalloporphyrin analogues are synthesized and used for epoxidation of simple alkenes.[4] With the assistance of a hydroxyl group, epoxidation of C=C double bonds of allylic alcohols, for example, is achieved with the Katsuki-Sharpless method that employs dialkyl tartrates as catalysts.[5] Jacobsen's[6] and Katsuki's[7] groups demonstrate a method using Mn(III)-salen type catalysts, which are especially useful for asymmetric epoxidation of *cis* aryl-substituted alkenes. In these two methods, oxidants such as *t*-BuOOH, NaOCl and PhIO are generally utilized to transfer one oxygen atom to the alkene substrate. Mukaiyama's group[8] uses molecular dioxygen and metal catalysts to effect epoxidation of certain cycloalkenes with modest asymmetric induction.

Oxidation of sulfides to chiral sulfoxides by biological and chemical methods is reviewed.[9] Optically active sulfoxides, such as methyl *p*-tolyl sulfoxides, are versatile substrates for synthesis of many natural products. We report here our results of oxidation of alkenes and sulfides with



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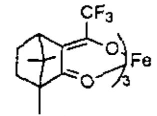

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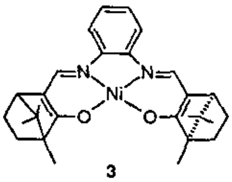

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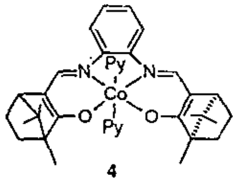

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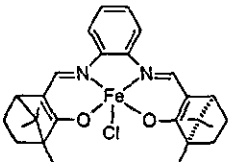

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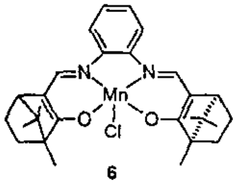

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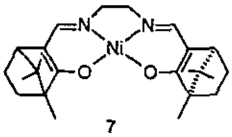

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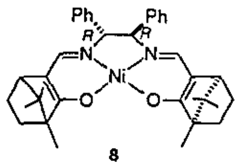

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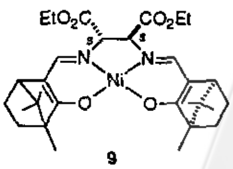

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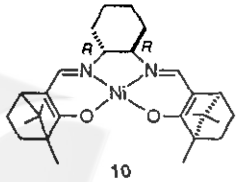

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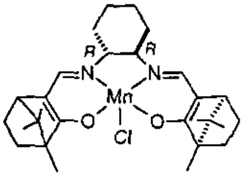
Dedicated to Professor Koji Nakanishi on the occasion of his seventieth birthday.



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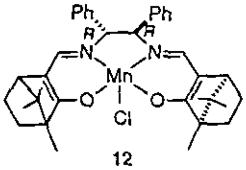

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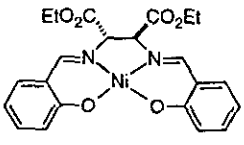

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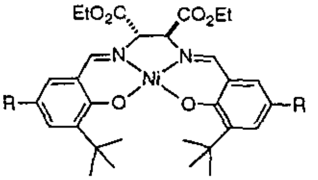

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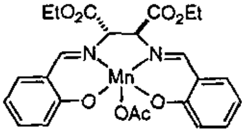
15 R = *t*-Bu



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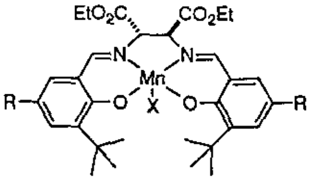
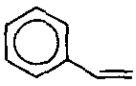


17 R = MeO, X = OAc
18 R = *t*-Bu, X = Cl



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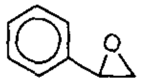

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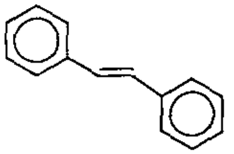

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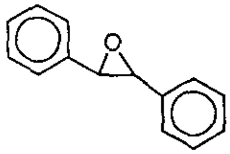

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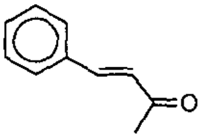

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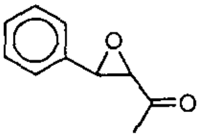

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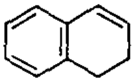

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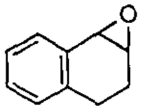

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transition-metal catalysts. Oxidant sources include molecular oxygen, air and iodosylbenzene. Metal ions Mn(III), Fe(III), Co(II) and Ni(II) were used. Catalysts **1-18** of 1,3-dioxo-, β-ketoimine- or salen-types were prepared and their efficacy was examined.

RESULTS AND DISCUSSION

Epoxidation

The results of epoxidation of alkenes with transition-metal catalysts are listed in Table 1. When PhIO served as the oxidant, 1,2-dihydronaphthalene was most effectively epoxidized (≥91% conversion at 25 °C in one day) with salen-type catalyst Mn(III)-**16** or Mn(III)-**17** (entries 38, 39 and 41). Epoxidation with Ni-salen or Ni-ketoimine catalysts, such as Ni(II)-**8**, Ni(II)-**9**, Ni(II)-**10**, Ni(II)-**13** and Ni(II)-**14**, were less efficient (entries 27-29, 34 and 35). Contrary to previous reports,[7,10] epoxidation was somewhat inhibited on addition of *N*-methylimidazole, regardless of Ni(II)-, Co(II)-, Fe(III)- or Mn(III)-catalysts (entries 22-26, 36, 37 and 42). The conversion of styrene and stilbene (an *E*-alkene) to their corresponding epoxides with oxidant PhIO was small (32-55%, entries 6, 9, 14 and 15), even though Mn(III)-**16** or Mn(III)-**17** served as catalyst.

By using molecular dioxygen (or air) and 2-methylpropanal (or 2,2-dimethylpropanal) as co-oxidant, metal catalyzed epoxidation of alkenes proceeded smoothly. In most cases, Ni(II), Co(II), Fe(II) and Mn(III) were active catalysts; over 90% conversion of alkenes was complete at 25 °C in one day. Both salen- and ketoimine-ligands were suitable for preparation of catalysts. Epoxidation was conducted in a non-polar (PhH, CH_2Cl_2 or $ClCH_2CH_2Cl$) or polar solvent CH_3CN. Epoxidation conditions were suitable for styrene (monosubstituted alkene), stilbene (*E*-alkene) and benzalacetone (alkene conjugated with ketone). For epoxidation of dihydronaphthalene (a *Z*-cycloalkene), Mn(III) is the catalyst of choice (entries 21 and 40), whereas Ni(II), Co(II) or Fe(III) was less active. An additive (pyridine or 4-*t*-butylpyridine *N*-oxide)[7b] showed no significant effect on epoxidation of stilbene using Fe(III)-**2** catalyst (compared entries 10-12). Planar Ni(salen) complex is reported to be inactive for aerobic epoxidation,[8b,8d] we showed that salen catalyst Ni(II)-**13** was active for epoxidation of stilbene and dihydronaphthalene with O_2/Me_2CHCHO in CH_3CN (entries 13 and 33).[11]

Mechanism

When iodosylbenzene serves the terminal oxidant, epoxidation is believed to proceed with high-valent metal-oxo intermediates such as $Mn^V = O$.[6e,7c] In aerobic epoxida-

Table 1. Oxidation of Alkenes with Catalysis of Transition Metals at 25 °C

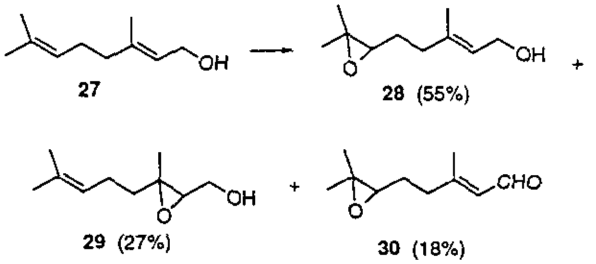
Entry	Substrate	Catalyst/mol %	Oxidant/molar proportions	Solvent	Reaction time/h	Conversion/%	Product (yield/%)
1	**19** (stryrene)	Co(II)-**1** (2)	air/Me_2CHCHO (2)	$ClCH_2CH_2Cl$	17	50	**23** (63)
2	**19**	Fe(III)-**2** (2.5)	air/Me_2CHCHO (2)	$ClCH_2CH_2Cl$	36	100	**23** (77)
3	**19**	Mn(III)-**11s** (10)	O_2/Me_3CCHO (2)	PhH	24	75	**23** (80)
4	**19**	Mn(III)-**11r** (10)	O_2/Me_3CCHO (2)	PhH	24	63	**23** (73)
5	**19**	Mn(III)-**12** (10)	O_2/Me_3CCHO (2)	PhH	48	47	**23** (77)
6	**19**	Mn(III)-**16** (3.5)	PhIO (2)[a]	CH_2Cl_2	14	32	**23** (71)
7	**20** (stilbene)	Co(II)-**1** (2)	air/Me_2CHCHO (2)	$ClCH_2CH_2Cl$	18	100	**24** (87)
8	**20**	Co(II)-**1** (2)	air/Me_2CHCHO (2)	CH_3CN	3.5	50	**24** (92)
9	**20**	Co(II)-**1** (5)	PhIO (1.27)	CH_2Cl_2	24	30	**24** (68)
10	**20**	Fe(III)-**2** (5)	air/Me_2CHCHO (2)	$ClCH_2CH_2Cl$	12	100	**24** (100)
11	**20**	Fe(III)-**2** (2.5)	air/Me_2CHCHO (2)[b]	$ClCH_2CH_2Cl$	17	100	**24** (92)
12	**20**	Fe(III)-**2** (5)	air/Me_2CHCHO (2)[c]	$ClCH_2CH_2Cl$	20	100	**24** (89)
13	**20**	Ni(II)-**11** (3)	O_2/Me_2CHCHO (2)	CH_3CN	14	100	**24** (92)
14	**20**	Mn(III)-**16** (3.5)	PhIO (2)	CH_3CN	13	55	**24** (83)
15	**20**	Mn(III)-**17** (2)	PhIO (2)	CH_2Cl_2	24	33	**24** (77)
16	**21** (benzalacetone)	Co(II)-**1** (2)	air/Me_2CHCHO (2)	$ClCH_2CH_2Cl$	15	85	**25** (96)
17	**21**	Fe(III)-**2** (2.5)	air/Me_2CHCHO (2)	$ClCH_2CH_2Cl$	16	48	**25** (96)
18	**22** (dihydronaphthalene)	Ni(II)-**3** (10)	O_2/Me_2CHCHO (2)[d]	C_6H_6	24	9	**26** (52)
19	**22**	Co(II)-**4** (10)	O_2/Me_2CHCHO (2)[d]	C_6H_6	24	15	**26** (70)
20	**22**	Fe(III)-**5** (10)	O_2/Me_2CHCHO (2)[d]	C_6H_6	24	22	**26** (72)
21	**22**	Mn(III)-**6** (10)	O_2/Me_2CHCHO (2)[d]	C_6H_6	24	96	**26** (78)
22	**22**	Ni(II)-**3** (3)	PhIO (2)[e]	CH_2Cl_2	3	0	
23	**22**	Co(II)-**4** (3)	PhIO (2)[e]	CH_2Cl_2	3	17	**26** (59)
24	**22**	Fe(III)-**5** (3)	PhIO (2)[e]	CH_2Cl_2	3	19	**26** (62)
25	**22**	Mn(III)-**6** (3)	PhIO (2)[e]	CH_2Cl_2	3	35	**26** (77)
26	**22**	Ni(II)-**7** (3)	PhIO (2)[e]	CH_2Cl_2	24	57	**26**
27	**22**	Ni(II)-**8** (3)	PhIO (2)	CH_2Cl_2	24	26	**26** (76)
28	**22**	Ni(II)-**9** (3)	PhIO (2)	CH_2Cl_2	24	17	**26** (89)
29	**22**	Ni(II)-**10** (3)	PhIO (2)	CH_2Cl_2	24	55	**26** (72)
30	**22**	Mn(III)-**11s** (10)	O_2/Me_3CCHO (2)	PhH	24	68	**26** (82)
31	**22**	Mn(III)-**11r** (10)	O_2/Me_3CCHO (2)	PhH	24	60	**26** (71)
32	**22**	Mn(III)-**12** (10)	O_2/Me_3CCHO (2)	PhH	48	40	**26** (76)
33	**22**	Ni(II)-**13** (3)	O_2/Me_2CHCHO (2)[f]	CH_3CN	4	77	**26** (73)
34	**22**	Ni(II)-**13** (2.5)	PhIO (2)	CH_2Cl_2	14	72	**26** (72)
35	**22**	Ni(II)-**14** (2)	PhIO (2)	CH_2Cl_2	72	65	**26** (73)
36	**22**	Ni(II)-**14** (2)	PhIO (2)[g]	CH_2Cl_2	72	23	**26** (81)
37	**22**	Ni(II)-**15** (2)	PhIO (2)[g]	CH_2Cl_2	72	23	**26** (89)
38	**22**	Mn(III)-**16** (3.5)	PhIO (2)	CH_2Cl_2	4	100	**26** (85)
39	**22**	Mn(III)-**16** (3.5)	PhIO (2)[h]	CH_2Cl_2	12	97	**26** (76)
40	**22**	Mn(III)-**17** (1.25)	O_2/Me_2CHCHO (2)	$ClCH_2CH_2Cl$	23	94	**26** (86)
41	**22**	Mn(III)-**17** (2)	PhIO (2)	CH_2Cl_2	24	91	**26** (78)
42	**22**	Mn(III)-**18** (2)	PhIO (2)[g]	CH_2Cl_2	16	60	**26** (86)

[a] 4-*t*-Butylpyridine *N*-oxide (0.33 molar proportions) was added. [b] Pyridine (0.4 mL, 5 mmol) was added and the reaction was conducted at 0 °C. [c] 4-*t*-Butylpyridine *N*-oxide (0.25 molar proportions) was added. [d] *N*-Methylimidazole (0.5 molar proportions) was added. [e] *N*-Methylimidazole (equimloar proportions) was added. [f] The reaction was conducted at 60 °C. [g] *N*-Methylimidazole (double molar proportions) was added. [h] The reaction was conducted at 0 °C.

tion, the aldehyde was considered to behave as a reductant to accept one oxygen atom from molecular oxygen. In the *absence* of metal catalyst, the active epoxidation agent is proposed to be a peracid generated from autoxidation of the aldehyde.[12] The reacting species in aerobic epoxidation with a metal-ion catalyst was not fully characterized.[13] For example, geraniol is known to undergo metal-catalyzed epoxidation selectively at the $C_{2,3}$-double bond,[5,14] giving **29**, by assistance of the adjacent hydroxyl group to coordinate with the reacting metal peroxide species, whereas oxidation of geraniol (Scheme I) with O_2/Me_2CHCHO and Ni(II)-**13** proceeded differently, giving epoxides **28** (55%),

29 (27%), and **30** (18%). The epoxidation occurred preferentially at the $C_{6,7}$-double bond to give **28**, of which the allylic alcohol moiety might be further oxidized to give the aldehyde **30**.[15]

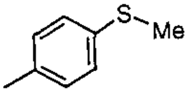
Scheme I



Reagents and conditions: O_2/isobutanal (triple molar proportions), cat. *Ni(II)-13 (2.5 mol %)*, $ClCH_2CH_2Cl$, 50 °C, 14 h; 100% conversion.

Sulfur Oxidation

Investigation of oxidation of methyl *p*-tolyl sulfide (Table 2) with molecular dioxygen (or air) showed that 1,3-dioxo catalyst Co(II)-**1** is most efficient (entries 1 and 2). The reaction with dioxygen and Me_2CHCHO in equimolar proportions in CH_3CN gave exclusively sulfoxide **32**, whereas corresponding sulfone **33** was obtained in the presence of Me_2CHCHO (double molar proportions). The present oxidation of methyl *p*-tolyl sulfide appears superior to previously reported methods[9] in trems of economy, efficacy and selectivity. β-Ketoimine catalyst Co(II)-**4** was less selective (entry 4) for oxidation of methyl *p*-tolyl sulfide with O_2/Me_2CHCHO (triple molar proportions); it took 24 h in benzene to afford both sulfoxide **32** and sulfone **33**. Salen catalyst Ni(II)-**13** was suitable for oxidation of sulfide, although a greater reaction temperature (60-80 °C) was required. A large yield (94%) of sulfone **33** was thus obtained in an oxidation with such a Ni(II)-**13** catalyst (entry 9). Catalysts Fe(III)-**5** and Mn(III)-**6** were inferior to Co(II)-catalyst for oxidation of methyl *p*-tolyl sulfide. In the presence of *N*-methylimidazole (entries 3-6), aerobic oxidation was either slow or non-selective with ketoimine catalysts Ni(II)-**3**, Fe(III)-**5** or Mn(III)-**6**.



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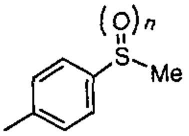
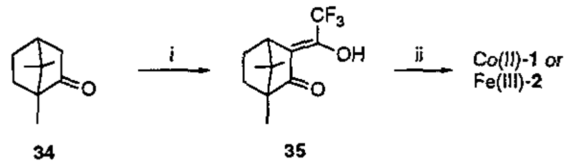


32 *n* = 1
33 *n* = 2

Preparation of Catalysts

Lithiation of (1*R*)-(+)-camphor with LDA (Scheme II), followed by acylation with CF_3CO_2Et, gave β-hydroxyenone **35** in 74% yield.[16] Treatment of **35** with $CoCl_2$ in the presence of pyridine gave bis-ligated complex Co(II)-**1**, whereas complexation of **35** with $FeCl_3$ under similar conditions gave tris-ligated complex Fe(III)-**2**. The exact mass measurement of Fe(III)-**2** indicated $[M]^+$ at *m/z* 797.218 attributable to a molecular formula $C_{36}H_{42}O_6F_9Fe$. X-ray analysis of single crystal showed that complex Co(II)-**1** had two pyridines on axial positions. (1*R*)-(+)-Camphor was formylated, giving **36**, and treated with 1,2-phenylenediamine to give enolimine ligand **37** (Scheme III), that complexed with $Ni(OAc)_2$, $CoCl_2$ and $FeCl_3$, respectively, to give Ni(II)-**3**, Co(II)-**4** and Fe(III)-**5**.[17] Treatment of **37** with $Mn(OAc)_2$ in EtOH, followed by addition of LiCl, yielded Mn(III)-**6**. According to similar procedures, complexes Ni(II)-**7**, Ni(II)-**8**, Ni(II)-**9** and Ni(II)-**10** were prepared from formylcamphor **36**, $Ni(OAc)_2$ and appropriate 1,2-diamines (Scheme IV). Replacing **36** with salicylaldehydes **43-45**, the salen complexes Ni(II)-**13**, Ni(II)-**14**, Ni(II)-**15**, Mn(III)-**16**, Mn(III)-**17** and Mn(III)-**18** were prepared (Scheme V). The synthesized complexes had elemental analyses and spectral properties compatible with their assigned structures. Structures of Ni(II)-**9** and Ni(II)-**13** were confirmed on X-ray analyses.

Scheme II



Reagents and conditions. (i) LDA, THF, -35 °C, 20 min; CF_3CO_2Et, -70 °C to -20 °C, 45 min; 74%. (ii) For Co(II)-1: anhydrous $CoCl_2$, MeOH, KOH, pyridine, 25 °C, 10 min; 68%. For Fe(III)-2: anhydrous $FeCl_3$, MeOH, pyridine, 25 °C, 30 min; 74%.

Commercially available 1,2-diamines used in this work included 1,2-phenylenediamine, 1,2-ethylenediamine, (1*R*,2*R*)-1,2-diphenylethylenediamine and (1*R*,2*R*)-1,2-diaminocyclohexane. (±)-2,3-Diaminosuccinic acid diethyl ester **42** was prepared from *meso*-2,3-dibromosuccinic acid **49** (Scheme VI).[18] The sequence involved conversion of *meso*-2,3-diaminosuccinic acid **50** to its anhydride **51**, which epimerized *in situ* to give racemic mixture. Hydrolysis of (±)-**51** gave diacid (±)-**52**, which was subjected to esterification ($SOCl_2$, EtOH) and hydrogenolysis to give the desired (±)-2,3-diaminosuccinic acid diethyl ester **42**.

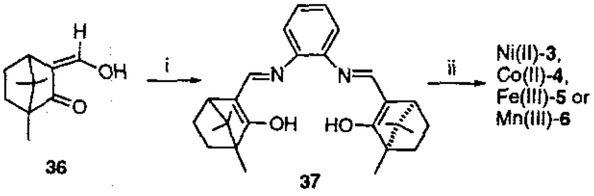
Table 2. Oxidation of Methyl *p*-Tolyl Sulfide **31** with Catalysis of Transition Metals, Giving Sulfoxide **32** and Sulfone **33**

Entry	Catalyst/mol %	Oxidant/molar proportions)	Solvent	Reaction temp./°C	Reaction time/h	Conversion/%	Product (yield/%)
1	Co(II)-**1** (1.4)	air/Me_2CHCHO (1)	CH_3CN	25	4	100	**32** (88)
2	Co(II)-**1** (1.4)	air/Me_2CHCHO (2)	CH_3CN	25	8	88	**33** (80)
3	Ni(II)-**3** (3)	O_2/Me_2CHCHO (3)[a]	C_6H_6	25	24	25	**32** (98)
4	Co(II)-**4** (3)	O_2/Me_2CHCHO (3)[a]	C_6H_6	25	24	97	**32** (30) + **33** (50)
5	Fe(III)-**5** (3)	O_2/Me_2CHCHO (3)[a]	C_6H_6	25	24	27	**32** (98)
6	Mn(III)-**6** (3)	O_2/Me_2CHCHO (3)[a]	C_6H_6	25	24	61	**32** (40) + **33** (58)
7	Ni(II)-**13** (1.25)	O_2/Me_2CHCHO (1)	$ClCH_2CH_2Cl$	25	96	43	**32** (72)
8	Ni(II)-**13** (5.8)	O_2/Me_2CHCHO (2)	CH_3CN	60	12	57	**32** (82) + **33** (11)
9	Ni(II)-**13** (1.25)	O_2/Me_2CHCHO (2)	$ClCH_2CH_2Cl$	80	6	100	**33** (94)

[a] *N*-Methylimidazole (0.48 molar proportions) was added.

Resolution of (±)-**52** was achieved on crystallization of its brucine salt from Me_2CO-H_2O (10:1, v/v). Crystals of (2*S*,3*S*)-**52** showed dextrorotation, whereas the (2*R*,3*R*)-enantiomer was obtained from the mother liquor. The optical isomers were respectively converted to enantiomerically pure 2,3-diaminosuccinic acids (2*S*,3*S*)-**42** and (2*R*,3*R*)-**42**.

Scheme III

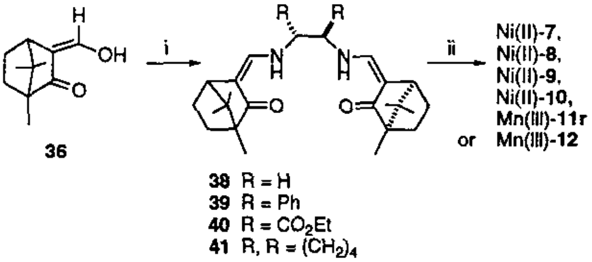


Reagents and conditions. (i) 1,2-phenylenediamine, EtOH, 25 °C, 30 min; 97%. (ii) For Ni(II)-**3**: $Ni(OAc)_2 \cdot 4H_2O$, MeOH, 25 °C, 15 min; 90%. For Co(II)-**4**: $CoCl_2 \cdot 6H_2O$, MeOH, 25 °C, 1.5 h; pyridine, 20 min; 93%. For Fe(III)-**5**: anhydrous $FeCl_3$, EtOH, 25 °C, 1 h; pyridine, 20 min; 81%. For Mn(III)-**6**: $Mn(OAc)_2 \cdot 4H_2O$, EtOH, 25 °C, 12 h; LiCl, H_2O, 25 °C, 10 min; 69%.

Crystal Data

Crystal and molecular structures of Co(II)-**1**, Ni(II)-**9** and Ni(II)-**13** are analyzed from X-ray diffraction data of single crystals. Essential crystal data of these three compounds appear in Table 3. Their molecular structures are displayed in Figs. 1-3.

Scheme IV



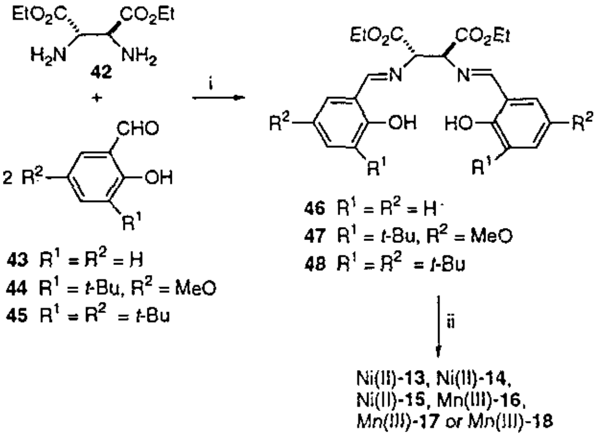
Reagents and conditions. For Ni(II)-**7**: (i) **36**,1,2-ethylenediamine, MeOH, 25 °C, 10 min; giving **38** (63%). (ii) $Ni(OAc)_2 \cdot 4H_2O$, MeOH, 25 °C, 3 h; 65%. For Ni(II)-**8**: (i) **36**, 1,2-diphenylethylenediamine, EtOH, 25 °C, 1 h; (ii) $Ni(OAc)_2 \cdot 4H_2O$, MeOH, 25 °C, 45 min; 42%. For Ni(II)-**9**: (i) **36**, $H_2NCH(CO_2Et)CH(CO_2Et)NH_2$, EtOH, 25 °C, 1 h; (ii) $Ni(OAc)_2 \cdot 4H_2O$, MeOH, 25 °C, 30 min; 43%. For Ni(II)-**10**: (i) **36**, 1,2-diaminocyclohexane, EtOH, 25 °C, 1 h; (ii) $Ni(OAc)_2 \cdot 4H_2O$, MeOH, 25 °C, 2.5 h; 30%. For Mn(III)-**11r**: (i) **36**, (1*R*,2*R*)-diaminocyclohexane, EtOH, 25 °C, 4 h; (ii) $Mn(OAc)_2 \cdot 4H_2O$, EtOH, reflux, 2 h; LiCl, H_2O, reflux, 30 min; 30%. For Mn(III)-**12**: (i) **36**, (1*R*,2*R*)-diphenylethylenediamine, EtOH, 25 °C, 12 h; (ii) $Mn(OAc)_2 \cdot 4H_2O$, EtOH, reflux, 3 h; LiCl, H_2O, reflux, 30 min; 20%.

CONCLUSION

1,2-Dihydronaphthalene is most efficiently epoxidized with O_2/Me_2CHCHO or PhIO in the presence of Mn(III)-salen catalysts. Ni(II)-, Co(II)- and Fe(III)-catalysts of either β-ketoimine- or salen-types are useful for epoxidation of styrene, (*E*)-stilbene and (*E*)-benzalacetone in the O_2/Me_2CHCHO system. Epoxidations of (*E*)-stilbene and (*E*)-benzalacetone are stereospecific, no corresponding diastereomeric epoxides are formed. Oxidation of methyl *p*-tolyl sulfide with O_2/Me_2CHCHO is facilitated by 1,3-dioxo-catalyst Co(II)-**1**. Monooxidation is achieved with Me_2CHCHO in equimolar proportions to give the corresponding sulfoxide, whereas overoxidation is realized with excess Me_2CHCHO to give the sulfone. These epoxidation and sulfide oxidations all occur at 25 °C and are complete in less than a day.

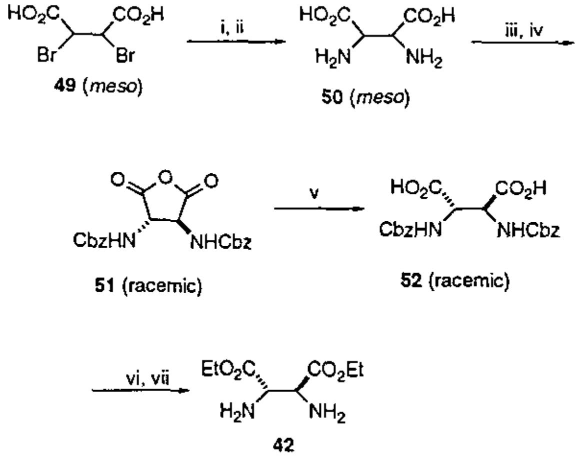
The metal catalyzed oxidation of alkenes and sulfides can occur in enantiotopic manners with chiral metal catalysts. Although these catalysts are chiral, they induce enantioselectivity in only small fractions (< 10%). Greater enantioselectivity may be obtained on using the camphor ligand having bulky substituents. We are investigating this subject.

Scheme V



Reagents and conditions. (*i*) For **46**: **42**, **43** (2 molar proportions), EtOH, 25 °C, 1 h; 99%. For **47**: **42**, **44** (2 molar proportions), EtOH, 50 °C, 8 h; 79%. For **48**: **42**, **45** (2 molar proportions), EtOH, 25 °C, 2 h; 93%. (*ii*) For *Ni(II)-**13***: **44**, $Ni(OAc)_2 \cdot 4\ H_2O$, MeOH, 25 °C, 1 h; 79%. For Ni(II)-**14**: **47**, $Ni(OAc)_2 \cdot 4\ H_2O$,EtOH, 50 °C, 8 h; 99%. For Ni(II)-**15**: **48**, $Ni(OAc)_2 \cdot 4\ H_2O$, MeOH, 25 °C, 15 min; 61%. For *Mn(III)-**16***: **46**, $Mn(OAc)_2 \cdot 4\ H_2O$, EtOH, 25 °C, 1.5 h; 69%. For Mn(III)-**17**: **47**, $Mn(OAc)_2 \cdot 4\ H_2O$, EtOH, 25 °C, 50 min; 79%. For Mn(III)-**18**: **48**, $Mn(OAc)_2 \cdot 4\ H_2O$, EtOH, KOH, 78 °C, 1 h; LiCl, H_2O, 25 °C, 30 min; 48%.

Scheme VI



Reagents and conditions. (i) $PhCH_2NH_2$, EtOH, reflux, 5 h; 81%. (ii) H_2 (3 atm), 10% Pd/C cat., HOAc, HCl, 25 °C, 20 h; 84%. (iii) $ClCO_2CH_2Ph$, NaOH, 1,4-dioxane, 55 °C, 5 h; 64%. (iv) Ac_2O, reflux, 20 min; recrystallization from $CHCl_3$-hexane. (v) KOH (2 M) Me_2CO, 25 °C, 30 min; HCl (12 M); 96%. (vi) $SOCl_2$, EtOH, 60 °C, 5 h; 99%. (vii) H_2 (1 atm), 10% Pd/C cat., EtOAc, 25 °C, 14 h ; 99%.

EXPERIMENTAL SECTION

Elemental analysis was carried out on a Perkin-Elmer 2400 C or a Heraeus CHN-O-RAPID analyzer. Infrared spectra were measured on a Perkin-Elmer 983G infrared spectrophotometer. Ultraviolet spectra were measured on a Perkin-Elmer 555 UV/Vis spectrophotometer; a quartz cell (length 1 cm) was used. ^1H NMR spectra were recorded at 200 or 300 MHz (Bruker AC-200 or AM-300WB spectrometer); tetramethylsilane served as internal standard. ^{13}C NMR spectra were recorded at 50 or 75 MHz. Mass spectra were recorded (Finnigan TSQ46c spectrometer) at an ionizing voltage 70 eV or 20 eV. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-HX 110 spectrometer. X-ray diffraction data were collected on a CAD-4 diffractometer; analyses were made with a micro VAX III com-

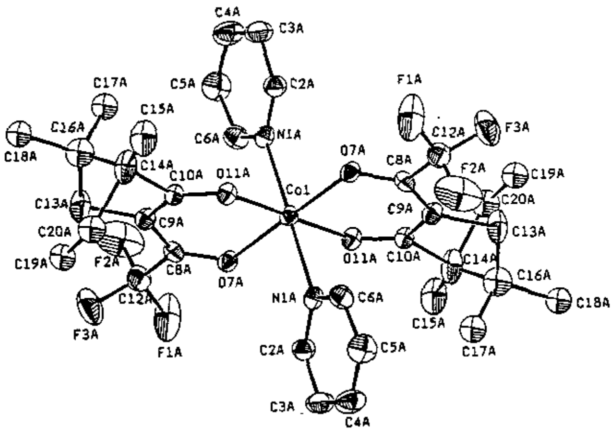


Fig. 1. ORTEP Drawing of Compound **1**.

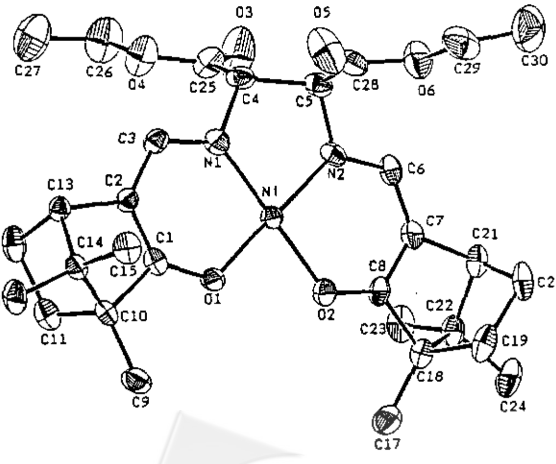


Fig. 2. ORTEP Drawing of Compound **9**.

Table 3. Crystal Data of Compounds **1**, **9** and **13**

Compound	**1**$^+$	**9**	**13**
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_{1/c}$
a, Å	9.283(1)	11.218(4)	10.780(4)
b, Å	14.255(7)	12.204(3)	21.19(1)
c, Å	14.281(5)	22.325(4)	11.93(1)
α, °	111.91(3)		
β, °	102.40(2)		108.10(6)
γ, °	81.24(2)		
V, Å^3	1707(1)	3056(1)	2589(3)
Z	2	4	4
D(calc), g·cm^{-3}	1.427	1.272	1.510
λ(Mo Kα), Å	0.7107	0.7107	0.7107
F(000)	734	1250	1211
unit cell detn; #; 2θ range	24,(18.92-24.24)	25,(19.20-28.68)	24,(18.84-24.32)
scan type	θ/2θ	θ/2θ	θ/2θ
2θ scan width, deg	2(0.7+0.35 tanθ)	2(0.85+0.35 tanθ)	2(0.7+0.35 tanθ)
2θ max, deg	50°	50°	45°
μ(Mo Kα), cm^{-1}	5.664	6.768	7.839
Crystal size, mm	0.25 × 0.30 × 0.30	0.45 × 0.50 × 0.15	0.20 × 0.30 × 0.30
Temperature, K	298	298	298
No. of unique reflns	5964	3036	3377
No. of obs reflns ($I > 2\sigma(I)$)	4412	2272	1876
R, R$_w$*	0.096, 0.111	0.040; 0.039	0.064; 0.053
GoF	2.09	1.69	2.69
Minimized function	$\Sigma w\|Fo-Fc\|^2$	$\Sigma w\|Fo-Fc\|^2$	$\Sigma w\|Fo-Fc\|^2$
Weighting scheme	$1/\sigma^2(Fo)$	$1/\sigma^2(Fo)$	$1/\sigma^2(Fo)$
g(second.ext.coeff.) × 10^4	2.61(0)	0.6(1)	-
$(\Delta/\sigma)_{max}$	0.1406	0.6167	0.05
$(\Delta\rho)_{max,min}$ eÅ^{-3}	0.930, -0.560	0.410; -0.330	0.500; -0.630

* $R = [\Sigma|Fo-Fc|/Fo]$

$R_w = [\Sigma w|Fo-Fc|^2/\Sigma w|Fo|^2]^{1/2}$; $\sigma^2(Fo)$ from counting statistics

$^+$ Part of the ligand are in disorder

puter using NRC VAX software.[24] Optical rotation measurements were conducted on JASCO Dip-360 or Schmidt/Haensh polarimeter; a quartz cuvette (length 10 cm) was used. Silica gel sheets (Merck 60F) were used for analytical TLC. A column chromatograph contained silica gel 60 (Merck, 70-230 mesh ASTM). GC was run on a Hitachi gas chromatograph with an OV-1 column (2% on Chromosorb WHP/80-100 mesh, 2 m × 3 mm ID). (1*R*)-(+)-Camphor, mp 176-178 °C, $[\alpha]_D^{25}$ +44.1° (*c* = 10, EtOH) was obtained from China Camphor Company (Taipei) as a gift.

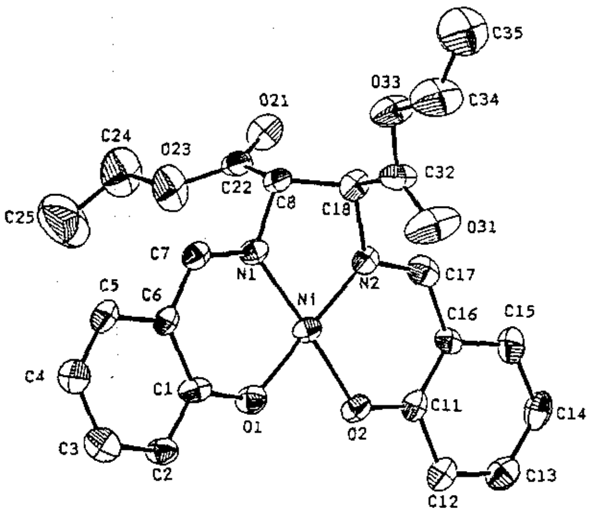


Fig. 3. ORTEP Drawing of Compound **11**.

Bis-[3-(trifluoromethylhydroxymethylene)camphorato]-dipyridinocobalt(II) 1

Under N$_2$, BuLi (27 mmol, 27 mL of 1.0 M solution in hexane) was added dropwise to a solution of diisopropylamine (3.5 mL, 27 mmol) in Et$_2$O (15 mL) at -60 °C. The LDA solution was stirred for 30 min at -35 °C, (1*R*)-camphor (3.8 g, 25 mmol) in Et$_2$O (50 mL) was added in one portion. The mixture was stirred for 20 min, cooled to -70 °C, and ethyl trifluoroacetate (3.55 mL, 25 mmol) in Et$_2$O (40 mL) was added in one portion. The mixture was warmed from -60 °C to -20 °C for 45 min, and added via syringe to a mixture of HCl solution (1 M, 40 mL) and ice (38 g). The mixture was extracted twice with Et_2O, the combined organic phase was dried over Na_2SO_4 and filtered. The filtrate was concentrated and distilled, bp 64-68 °C/1 mmHg, to give 3-(trifluoromethylhydroxymethylene)camphor **35** as colorless liquid (4.65 g, 74%).[16b] ^{13}C NMR ($CDCl_3$, 50 MHz) δ 8.5 (q), 18.2 (q), 20.4 (q), 26.6 (t), 30.1 (t), 43.0 (d), 47.0 (s), 58.0 (s), 117.7 (s), 121.2 (s), 148.0 (s), 214.2 (s).

To a solution of **35** (0.15 g, 1.15 mmol) in MeOH (3 mL) was added a solution of anhydrous $CoCl_2$ (0.15 g, 1.15 mmol) in MeOH at 25 °C, followed by addition of KOH (0.06 g, 2 mmol) and pyridine (0.3 mL). After stirring for 10 min, the formed orange solids were filtered, rinsed with hexane, and dried in vacuo to give Co(II)-**1** (0.37 g). Another crop of Co(II)-**1** (0.15 g) was obtained from the mother liquor. Total yield 68%. Co(II)-**1** was purified on recrystallization from hexane or on a silica-gel column chromatograph. mp 137-139 °C; TLC (10% Et_2O in hexane) $R_f = 0.20$; IR (KBr) 2955, 2925, 1639, 1598, 1526, 1123, 700 cm^{-1}; UV λ_{max} (EtOH) 309 (ε 14480 L mol^{-1} cm^{-1}), 257 (ε 6589); CD(EtOH)/nm $[\theta]_{380}$ +2551, $[\theta]_{322}$ +22530, $[\theta]_{294}$ +10580; MS *m/z* (relative int.) 553 (36, M^+-2Py), 525 (20), 248 (13), 79 (100). A sample for X-ray analysis was obtained on recrystallization from Me_2CO containing water in a small proportions.

Tris-[3-(trifluoromethylhydroxymethylene)camphonato]iron(III) 2

To a solution of **35** (0.25 g, 1 mmol) in MeOH (2 mL) was added a solution of anhydrous $FeCl_3$ (0.08 g, 1 mmol) in MeOH (1 mL) at 25 °C. The mixture was stirred for 10 min, pyridine (1 mL) was added. The mixture was stirred for 30 min, concentrated and taken up with EtOAc. The solution was washed twice with water. The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated to give dark brown solid Fe(III)-**2**. Recrystallization from Me_2CO-H_2O at 0 °C gave pure sample (0.20 g, 74%). Dark red crystal; mp 138 °C; IR (KBr) 2959, 1635, 1533, 1128, 1079, 649 cm^{-1}; UV λ_{max} ($CHCl_3$) 505 (ε 3200 L mol^{-1} cm^{-1}), 406 (ε 2400), 291 (ε 16600), 248 (ε 15200); MS *m/z* (relative int.) 796 (18, M^+-1), 550 (72), 284 (100). HRMS calcd for $C_{36}H_{42}F_9FeO_6$: 797.2187; found *m/z* 797.2184.

N,N'-Bis(camphormethylene)-1,2-phenylenediaminatonickel(II) 3

(1*R*)-3-Formyl-camphor **36**,[19] mp 71-73 °C, was prepared from (1*R*)-camphor and HCO_2Me by a procedure similar to that for **35**. A mixture of 1,2-phenylenediamine (0.108 g, 1 mmol) and **36** (0.36 g, 2 mmol) in EtOH (10 mL) was stirred at 25 °C for 30 min and concentrated on rotary evaporation to give crude *N,N'*-bis-(camphormethylene)-1,2-phenylenediamine **37** (0.42 g, 97%) as a yellow solid, mp 93-98 °C; TLC (10% EtOAC in hexane) $R_f = 0.31$; MS *m/z* (relative int.) 432 (M^+, 100). HRMS Calcd for $C_{28}H_{36}N_2O_2$: 432.2777; found: *m/z* 432.2769.

A mixture of $Ni(OAc)_2{\cdot}4H_2O$ (0.08 g, 0.33 mmol) and **37** (0.11 g, 0.25 mmol) in MeOH (7 mL) was stirred at 25 °C for 15 min, and concentrated on rotary evaporation. The residue was chromatographed on a silica-gel column by elution with EtOAc/hexane (10:90) to give Ni(II)-**3** (0.11 g, 90%) as a dark red solid, mp 173-174 °C (recrystallized from EtOH-$CHCl_3$). TLC (10% EtOAc in hexane) R_f = 0.54; IR (KBr), 1599, 1511 cm^{-1}; UV λ_{max} ($CHCl_3$) 411 (ε 17600 L mol^{-1} cm^{-1}), 296 (ε 7800), 256 (ε 16800); ^1H NMR ($CDCl_3$) δ 0.78 (6 H, s), 0.84 (6 H, s), 1.05 (6 H, s), 1.17-1.44 (4 H, m), 1.51-1.64 (2 H, m), 2.00 (2 H, m), 2.54 (2 H, d, J = 3.3 Hz), 6.82 (2 H, dd, J = 6.2, 3.3 Hz), 7.15 (2 H, br s), 7.35 (2 H, dd, J = 6.2, 3.4 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 9.5 (q), 19.4 (q), 20.5 (q), 28.3 (t), 30.7 (t), 49.0 (d), 53.6 (s), 57.0 (s), 112.5 (d), 115.8 (s), 122.2 (d), 140.0 (d), 143.0 (s), 194.2 (s); MS *m/z* (relative int.) 488 (100, M^+), 460 (7), 445 (8), 76 (6). HRMS calcd for $C_{28}H_{34}N_2NiO_2$: 488.1974; found: *m/z* 488.1944. Anal. Calcd. for $C_{28}H_{34}N_2NiO_2$: C, 68.74%; H, 7.00%; N, 5.73%; found: C, 68.44%; H, 7.06%; N, 5.68%.

N,N'-Bis(camphormethylene)-1,2-phenylenediaminato]-bis(pyridino)cobalt(II) 4

A mixture of $CoCl_2{\cdot}6H_2O$ (0.077 g, 0.325 mmol) and **37** (0.11 g, 0.25 mmol) in MeOH (8 mL) was stirred at 25 °C for 1.5 h, followed by addition of pyridine (0.5 mL). After 20 min, the mixture was concentrated on rotary evaporation. The residue was dissolved in CH_2Cl_2 and washed twice with water. The organic phase was dried (Na_2SO_4) and filtered, and the filtrate was concentrated on rotary evaporation to give Co(II)-**4** (0.15 g, 93%) as a dark green solid mp > 295 °C; IR (KBr) 2951, 1597, 1462, 1335, 1278, 750; UV ($CHCl_3$) 438 (ε 5248 L mol^{-1} cm^{-1}), 421 (ε 4800), 258 (ε 13951); FAB-MS *m/z* (relative int.) 647 (1, M^+), 568 (10, M^+-Py), 489 (100), M^+-2Py. HRMS calcd for $C_{28}H_{34}CoN_2O_2$: 489.1952; found: *m/z* 489.1929.

N,N'-Bis(camphormethylene)-1,2-phenylenediaminato-iron(III) chloride 5

According to a procedure similar to that for Co(II)-**4**, treatment of **37** (0.21 g, 0.5 mmol) with anhydrous $FeCl_3$ (0.09 g, 0.55 mmol) in EtOH (10 mL), followed by addition of pyridine (1 mL), gave Fe(III)-**5** as a dark red solid (0.2 g, 81%). mp 136-138 °C; IR (KBr) 2952, 1682, 1589, 1449, 1295, 1276, 745; UV ($CHCl_3$) 494 (ε 2688 L mol^{-1} cm^{-1}), 422 (ε 4608), 350 (ε 14080), 240 (ε 11136); MS *m/z* (relative int.) 521 (100, M$^+$), 486 (20), 432 (88), 281 (71), 268 (16). HRMS calcd for $C_{28}H_{34}{}^{35}ClFeN_2O_2$: 521.1658; found: *m/z* 521.1671.

N,N′-Bis(camphormethylene)-1,2-phenylenediaminatomanganese(III) chloride 6

A mixture of $Mn(OAc)_2{\cdot}4H_2{}^{\circ}$ (0.135 g, 0.55 mmol) and **37** (0.21 g, 0.55 mmol) in EtOH (8 mL) was stirred at 25 °C for 1 h. The mixture was concentrated to about two thirds the volume; a solution of LiCl (0.132 g, 3 mmol) in water (1 mL) was added. After 10 min, the mixture was concentrated to about half the volume. Water was added; precipitates were filtered and dissolved in CH_2Cl_2. The organic phase was washed twice with water, dried (Na_2SO_4) and filtered. The filtrate was concentrated on rotary evaporation to give Mn(III)-**6** (0.18 g, 69%) as a black solid. mp 167-169 °C; IR (KBr) 2947, 1678, 1585, 1458, 1303, 743; UV λ_{max} ($CHCl_3$) 470 (ε 1632 L mol^{1-} cm^{-1}), 346 (ε 3968), 241 (ε 5376); MS *m/z* (relative int.) 520 (8, M$^+$), 432 (61), 281 (100), 266 (21), 95 (5).

N,N′-Bis(camphormethylene)ethylenediaminatonickel(II) 7

A solution of **36** (0.72 g, 4 mmol) and ethylenediamine (0.132 g, 2.2 mmol) in MeOH (10 mL) was stirred at 25 °C for 10 min. Water was added, the turbid mixture was kept at 0 °C for 1 day. The precipitates were filtered and rinsed with Et_2O to give *N,N′*-bis(camphormethylene)ethylenediamine **38** (0.48 g, 63%) as a white solid. mp 210-212 °C (lit. 212-213 °C); IR (KBr) 3272, 2945, 1683, 1604, 1114, 945 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.81 (6 H, s), 0.90 (6 H, s), 0.93 (6 H, s), 1.18-1.39 (4 H, m), 1.59-1.66 (2 H, m), 1.80-1.95 (2 H, m), 2.44 (2 H, d, *J* = 3.6 Hz), 3.30 (4 H, s), 4.40 (2 H, br d, N-H *J* = 13 Hz), 6.95 (2 H, d, *J* = 13 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.4 (q), 18.9 (q), 20.3 (q), 26.8 (t), 31.5 (t), 46.3 (d), 48.0 (s), 48.7 (t), 57.6 (s), 114.1 (s), 137.0 (s), 206.5 (s); MS *m/z* (relative int.) 384 (M$^+$, 25), 341 (30), 205 (98), 192 (100). HRMS calcd for $C_{24}H_{36}N_2O_2$: 384.2777; found: *m/z* 384.2789.

By a procedure similar to that for Ni(II)-**3**, treatment of **38** (0.21 g, 0.55 mmol) with $Ni(OAc)_2{\cdot}4H_2O$ (0.11 g, 0.6 mmol) in MeOH (14 mL) gave Ni(II)-**7** (0.17 g, 65%). Green crystal; mp 248 °C; TLC (10% EtOAc in hexane) R_f = 0.40; IR (KBr) 2948, 1685, 1603, 1498, 1367, 1105, 1075 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.73 (6 H, s), 0.75 (6 H, s), 0.91 (6 H, s), 1.05-1.13 (2 H, m), 1.23-1.45 (4 H, m), 1.83-2.02 (2 H, m), 2.26 (2 H, d, *J* = 3.3 Hz), 2.91 (4 H, s), 6.25 (2 H, s); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 9.5 (q), 19.6 (q), 20.4 (q), 28.5 (t), 30.7 (t), 48.6 (d), 53.6 (s), 56.1 (s), 57.8 (t), 111.3 (s), 150.2 (d), 189.5 (s); UV ($CHCl_3$) λ_{max} 438 (ε 3400 L mol^{-1} cm^{-1}), 398 (ε 11800), 320 (ε 10000), 287 (ε 17600), 257 (ε 38800); MS *m/z* (relative int.) 440 (45, M$^+$), 384 (22), 341 (26), 205 (93), 192 (100). HRMS calcd for $C_{24}H_{34}N_2NiO_2$: 440.1974. found: *m/z* 440.1963.

N,N′-Bis(camphormethylene)-1,2-diphenylethylenediaminatonickel(II) 8

Ligand **39** was prepared from (1*R*,2*R*)-1,2-diphenylenediamine (21.1 mg, 0.1 mmol) and **36** (40 mg, 0.22 mmol) in EtOH (5 mL). Treatment of **39** with $Ni(OAc)_2{\cdot}4H_2O$ (37.2 mg) in MeOH (4 mL) yielded Ni(II)-**8** (25 mg, 42%), which was purified on a silica-gel column chromatograph with elution of EtOAc/hexane (20:80). Yellow-green crystal; mp > 285 °C; TLC (30% EtOAc in hexane) R_f = 0.67; IR (neat) 2946, 1600, 1490, 1354, 909, 732 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.72 (6 H, s), 0.79 (6 H, s), 0.98 (6 H, s), 1.02 (2 H, m), 1.23-1.62 (6 H, m), 1.79 (2 H, m), 2.17 (2 H, d, *J* = 3.1 Hz), 3.91 (2 H, s), 3.91 (2 H, s), 5.97 (2 H, s), 7.27 (2 H, s), 7.38 (2 H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.5 (q), 19.5 (q), 20.5 (q), 28.5 (t), 30.6 (t), 48.6 (d), 53.5 (s), 56.3 (s), 79.0 (d), 112.7 (s), 127.3 (d), 127.4 (d), 128.5 (d), 143.5 (s), 151.3 (d), 190.6 (s); FAB-MS *m/z* (relative int.) 592 (100, M$^+$), 325 (67), 289 (13). HRMS calcd forr $C_{36}H_{42}N_2O_2Ni$: 592.2600; found: *m/z* 592.2612.

N,N′-Bis(camphormethylene)-1,2-di(ethoxycarbonyl)-ethylenediaminatonickel(II) 9

By a procedure similar to that for Ni(II)-**8**, Ni(II)-**9** (25 mg, 43%) was prepared from (1*S*,2*S*)-1,2-di(ethoxycarbonyl)ethylenediamine (20 mg, 0.1 mmol), **36** (45 mg, 0.25 mmol) and $Ni(OAc)_2{\cdot}4H_2O$ (37.2 mg, 1.5 mmol), and purified on a silica-gel column chromatograph with elution of EtOAc/hexane (20:80). Yellow-green crystal; mp 179 °C; TLC (20% EtOAc in hexane) R_f = 0.44; IR (KBr) 2927, 1732, 1600, 1484, 1247, 1196, 1013 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.75 (6 H, s), 0.79 (6 H, s), 0.90 (6 H, s), 1.04-1.11 (2 H, m), 1.21-1.37 (2 H, m), 1.30 (6 H, t, *J* = 4.3 Hz), 1.39-1.60 (2 H, m), 1.84-1.88 (2 H, m), 2.31 (2 H, d, *J* = 7.1 Hz), 3.75 (2 H, s), 4.23 (4 H, qd, *J* = 7.1, 1.5 Hz), 6.24 (2 H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.4 (q), 14.1 (q), 19.5 (q), 20.5 (q), 28.7 (t), 30.5 (t), 48.6 (d), 53.3 (s), 56.4 (s), 61.9 (t), 71.4 (d), 112.8 (s), 152.5 (d), 170.6 (s), 191.9 (s); MS *m/z* (relative int.) 584 (100, M$^+$), 512 (12), 361 (5), 106 (6). HRMS calcd for $C_{30}H_{42}N_2O_6Ni$: 584.2896; found: *m/z* 584.2891.

***N,N′*-Bis(camphormethylene)-1,2-cyclohexylenediaminatonickel(II) 10**

By a procedure similar to that for Ni(II)-**8**, Ni(II)-**10** (74 mg, 30%) was prepared from (1*R*,2*R*)-1,2-diaminocyclohexane (57 mg, 0.5 mmol), **36** (0.18 mg, 1 mmol) and $Ni(OAc)_2\cdot 4H_2O$ (37.2 mg, 1.5 mmol), and purified on a silica-gel column chromatograph with elution of EtOAc/hexane (10:90). Green crystal; TLC (5% EtOAc in hexane) R_f = 0.30; IR (KBr) 2944, 1600, 1496, 1361, 1302, 1113 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.68 (6 H, s), 0.73 (6 H, s), 0.84 (6 H, s), 1.06-1.27 (8 H, m), 1.44 (2 H, m), 1.71 (2 H, br d, *J* = 7.3 Hz), 1.89 (2 H, m), 2.20 (2 H, br s), 2.26 (2 H, d, *J* = 3.3 Hz), 2.59 (2 H, dd, *J* = 4.0, 4.0 Hz), 6.31 (2 H, s); ^{13}C NMR (Acetone-d^6, 50 MHz) δ 8.3 (q), 18.3 (q), 19.0 (q), 23.9 (t), 28.1 (t), 28.9 (t), 29.8 (t), 48.0 (d), 52.7 (s), 54.7 (s), 68.7 (d), 109.7 (s), 144.6 (d), 187.3 (s); FAB-MS *m/z* (relative int.) 494 (100, M$^+$), 466 (13), 281 (22), 221 (21). HRMS calcd for $C_{28}H_{40}N_2O_2Ni$: 4942443; found: *m/z* 494.2432.

***N,N′*-Bis(camphormethylene)-1,2-cyclohexylenediaminatomanganese(III) chloride 11**

By a procedure similar to that for Mn(III)-**6**, Mn(III)-**11s** (132 mg, 25%) or Mn(III)-**11r** (160 mg, 30%) was prepared from (1*S*,2*S*)- or (1*R*,2*R*)-1,2-diaminocyclohexane (114 mg, 1 mmol), **36** (360 mg, 2 mmol), $Mn(OAc)_2\cdot 4H_2O$ (37.2 mg, 2 mmol) and LiCl (132 mg, 3 mmol), purified on a silica-gel column chromatograph with elution of acetone/CH_2Cl_2 (1:1) and crystallized from $CHCl_3$-hexane. **11r**: IR (KBr) 2947, 1685, 1496, 1592, 1104, 1073 cm^{-1}; MS *m/z* (relative int.) 491 (29, M$^+$-Cl), 438 (26), 396 (31), 260 (57), 259 (100). **11s**: IR (KBr) 2940, 1693, 1598, 1121, 1094 cm^{-1}; MS *m/z* (relative int.) 491 (30, M$^+$-Cl), 438 (37), 396 (40), 260 (68), 259 (100).

***N,N′*-Bis(camphormethylene)-1,2-diphenylethylenediaminatomanganese(III) chloride 12**

By a procedure similar to that for Mn(III)-**6**, Mn(III)-**12** (63 mg, 20%) was prepared from (1*R*,2*R*)-1,2-diphenylethylenediamine (106 mg, 0.5 mmol), **36** (180 mg, 1 mmol), $Mn(OAc)_2\cdot 4H_2O$ (129 mg, 1 mmol) and LiCl (66 mg, 1.5 mmole), purified on a silica-gel column chromatograph with elution of acetone/CH_2Cl_2 (1:1) and crystallized from $CHCl_3$-hexane. Brown crystal; IR (KBr) 2956, 1686, 1589, 1070, 699 cm^{-1}; MS *m/z* (relative int.) 589 (20, M$^+$-Cl), 536 (20), 268 (29), 267 (100).

***N,N′*-Bis(salicylidene)-1,2-di(ethoxycarbonyl)ethylenediaminatonickel(II) 13**

Reaction of (±)-1,2-di(ethoxycarbonyl)ethylenediamine (0.34 g, 1.67 mmol) **42** with salicylaldehyde (408 mg, 3.34 mmol) in EtOH gave *N,N′*-bis(salicylidene)-1,2-di(ethoxycarbonyl)ethylenediamine (±)-**46** (0.32 g, 99%). Yellow crystal; mp 118-119 °C; TLC (30% EtOAc in hexane) R_f = 0.39; IR (KBr) 3430, 2976, 1730, 1620, 1573, 1274, 1182 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.23 (6 H, t, *J* = 7 Hz), 4.20 (4 H, q, *J* = 7 Hz), 4.63 (2 H, s), 6.83 (2 H, t, *J* = 7.7 Hz), 6.92 (2 H, d, *J* = 8.3 Hz), 7.23 (2 H, dd, *J* = 7.8, 1.6 Hz), 7.29 (2 H, td, *J* = 8, 1.8 Hz), 8.40 (2 H, s), 12.47 (2 H, br s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.0 (q), 62.0 (t), 72.6 (d), 117.2 (d), 118.3 (s), 118.9 (s), 132.2 (d), 133.2 (d), 161.0 (s), 168.7 (s), 169.8 (s); MS *m/z* (relative int.) 412 (8, M$^+$), 339 (5), 220 (26), 172 (33), 132 (100), 1211, 91 (11). HRMS calcd for $C_{22}H_{24}N_2O_6$: 412.1634; found: *m/z* 412.1629; Anal. calcd for $C_{22}H_{24}N_2O_6$: C, 64.05%; H, 5.87%; N, 6.79%. found: C, 63.74%; H, 5.87%; N, 6.89%. (*R*)-**46** was prepared similarly from (1*R*,2*R*)-**42** and salicylaldehyde.

A solution of $Ni(OAc)_2\cdot 4H_2O$ (65 mg, 0.26 mmol) and **46** (120 mg, 0.26 mmol) in MeOH (10 mL) was stirred at 25 °C for 1.5 h, and concentrated on rotary evaporation to give a dark red oil. Crystallization from EtOH-hexane (1:3) at 0 °C gave Ni(II)-**13** (0.1 g, 73%) as an orange-red solid. mp 195 °C; TLC (80% EtOAc in hexane) R_f = 0.52; IR (KBr) 3423, 2974, 1731, 1608, 1527, 1445, 1203 cm^{-1}; UV λ_{max} ($CHCl_3$) 460 (ε 2501 L mol^{-1} cm^{-1}), 421 (ε 5814), 399 (ε 3469), 349 (ε 6711), 332 (ε 7139), 258 (ε 36364); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.29 (6 H, t, *J* = 7.2 Hz), 4.28 (2 H, s), 4.31 (4 H, q, *J* = 7.1 Hz), 6.55 (2 H, m), 7.01 (2 H, d, *J* = 8.6 Hz) 7.13 (2 H, dd, *J* = 8, 1.7 Hz), 7.21 (2 H, m), 7.59 (2 H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.1 (q), 63.3 (t), 71.9 (d), 115.5 (d), 119.9 (s), 122.0 (d), 132.7 (d), 134.8 (d), 165.3 (d), 165.7 (s), 167.4 (s); MS *m/z* (relative int.) 468 (69, M$^+$), 395 (21), 322 (100), 177, (40), 132 (58). HRMS calcd for $C_{22}H_{22}N_2O_6Ni$: 468.0831; found: *m/z* 468.0815. Anal. calcd for $C_{22}H_{22}N_2O_6Ni$: C, 56.40%; H, 4.74%; N, 5.98%. found: C, 55.57%; H, 4.75%; N, 5.97%. A sample for X-ray analysis was obtained on recrystallization from $CHCl_3$-hexane.

***N,N′*-Bis(3-*t*-butyl-5-methoxysalicylidene)-1,2-di(ethoxycarbonyl)ethylenediaminatonickel(II) 14**

By a procedure similar to that for **46**. treatment of (1*S*,2*S*)-1,2-di(ethoxycarbonyl)ethylenediamine with 3-*t*-butyl-5-methoxysalicylaldehyde in EtOH gave bis(3-*t*-butyl-5-methoxysalicylidene)-(1*S*,2*S*)-1,2-di(ethoxycarbonyl) ethylenediamine (*S*)-**47** (79%). Yellow oil; TLC (20% EtOAc in hexane) R_f= 0.38; $[\alpha]_D^{23}$ = -282° ($CHCl_3$; *c* = 1); IR (neat) 2955, 1734, 1626, 1592, 1427, 1332, 1057 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.27 (6 H, t, *J* = 7.1 Hz), 3.70 (6 H, s), 4.23 (4 H, q, *J* = 7.1 Hz), 4.62 (2 H, s), 6.55 (2 H, d, *J* = 3.1 Hz), 6.94 (2 H, d, J = 3.1 Hz), 8.38 (2 H, s), 12.63 (2 H, br s); ^{13}C NMR (CDCl$_3$) δ 14.0 (q), 29.1 (q), 55.6 (q), 61.9 (t), 72.3 (d), 111.6 (d), 117.4 (s), 119.5 (d), 139.1 (s), 151.3 (s), 154.9 (s), 168.9 (s), 170.3 (d); MS *m/z* (relative int.) 584 (99, M$^+$), 377 (100), 292 (76), 208, (88), 193 (52); HRMS calcd for $C_{32}H_{44}N_2O_8$: 584.3098; found: *m/z* 584.3094.

By a procedure similar to that for Ni(II)-**13**, treatment of (*S*)-**47** (0.12 g, 0.21 mmol) with Ni(OAc)$_2$·4H$_2$O (0.054 g, 0.22 mmol), followed by purification on a silica-gel column with elution of EtOAc/hexane (50:50), gave Ni(II)-**14** (0.13 g, 99%). Golden-yellow powder; mp 117-118 °C; TLC (50% EtOAc in hexane) R_f = 0.21; IR (KBr) 2945, 1733, 1603, 1531, 1460, 1357, 1059 cm^{-1}; UV λ_{max} (CH$_3$OH) 446 (ε 11942 L mol^{-1} cm^{-1}), 338 (ε 11731), 262 (ε 63456), 237 (ε 44442), 225 (ε 49357); ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.32 (6 H, t, J = 7.2 Hz), 1.37 (18 H, s), 3.73 (6 H, s), 4.21 (2 H, s), 4.34 (4 H, m), 6.40 (2 H, d, J = 3.2 Hz), 6.97 (2 H, d, J = 3.2 Hz), 7.54 (2 H, s); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 13.2 (q), 28.6 (q), 34.8 (s), 54.7 (q), 62.2 (t), 70.7 (d), 108.1 (d), 117.9 (s), 122.4 (d), 141.7 (s), 147.5 (s), 160.9 (s), 163.8 (d), 166.9 (s); CD(CH$_3$OH)/nm $[\theta]_{651}$ -39450, $[\theta]_{499}$ +29420, $[\theta]_{433}$ +27710, $[\theta]_{364}$ +20660. FAB-MS *m/z* (relative int.) 640 (100, M$^+$), 625 (16), 567 (13), 479 (12), 218 (11), 154 (32), 136 (24). HRMS calcd for $C_{32}H_{42}N_2O_8Ni$: 640.2295; found: *m/z* 640.2297.

N,N′-Bis(3,5-di-*t*-butylsalicylidene)-1,2-di(ethoxycarbonyl)ethylenediaminatonickel(II) 15

By a procedure similar to that for **46**, treatment of (1*R*,2*R*)-1,2-di(ethoxycarbonyl)ethylenediamine with 3,5-di-*t*-butylsalicylaldehyde in EtOH gave bis(3,5-di-*t*-butyl-5-methoxysalicylidene)-1,2-di(ethoxycarbonyl)ethylenediamine (*R*)-**48** (93%). Yellow crystal; mp = 136-137 °C; TLC (10% EtOAc in hexane) R_f = 0.22; $[\alpha]_D^{25}$ = +130° (acetone; c = 0.5); IR (KBr) 3430, 2951, 1737, 1622, 1436, 1028 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.25 (18 H, s), 1.28 (6 H, t, J = 7.3 Hz), 1.43 (18 H, s), 4.23 (4 H, m), 4.62 (2 H, s), 7.07 (2 H, d, J = 2.5 Hz), 7.36 (2 H, d, J = 2.5 Hz), 8.45 (2 H, s), 12.87 (2 H, br s); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 14.0 (q), 29.3 (q), 31.4 (s), 35.0 (s), 61.8 (t), 72.4 (d), 117.6 (s), 126.7 (d), 128.0 (d), 136.7 (s), 140.3 (s), 158.1 (s), 169.0 (s), 170.9 (d); FAB-MS *m/z* (relative int.) 637 (100, M$^+$+1).

By a procedure similar to that for Ni(II)-**13**, Ni(II)-**15** (0.04 g, 61%) was prepared from (*R*)-**48** (0.06 g, 0.09 mmol) and Ni(OAc)$_2$·4H$_2$O (0.028 g, 0.11 mmol) in MeOH (2 mL), and purified on a silica-gel column chromatograph with elution of EtOAe/hexane (10:90). Red crystal; mp = 78 °C; TLC (10% EtOAc in hexane) R_f = 0.16; IR (KBr) 3437, 1733, 1603, 1521, 1385, 1174 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.25 (18 H, s), 1.31 (6 H, t, J = 7 Hz), 1.37 (18 H, s), 4.18 (2 H, s), 4.32 (4 H, m), 6.90 (2 H, d, J = 2.6 Hz), 7.31 (2 H, d, J = 2.6 Hz), 7.55 (2 H, s); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 14.2 (q), 29.6 (q), 31.2 (q), 35.8 (s), 37.8 (s), 63.1 (t), 71.7 (d), 119.5 (s), 126.2 (d), 129.9 (d), 136.1 (s), 140.4 (s), 163.9 (s), 165.4 (d), 167.9 (s); UV (CHCl$_3$) 470 (ε 5400 L mol^{-1} cm^{-1}), 436 (ε 10200), 407 (ε 5200), 342 (ε 12000), 270 (ε 62200); FAB-MS *m/z* (relative int.) 692 (100, M$^+$), 619 (13), 533 (8), 388 (6), 244 (16), 154 (8). HRMS calcd for $C_{83}H_{54}N_2O_6Ni$: 692.3335; found: *m/z* 692.3335.

N,N′-Bis(salicylidene)-1,2-di(ethoxycarbonyl)ethylenediaminatomanganese(III) acetate 16

By a procedure similar to that for Ni(II)-**13**, Mn(III)-**16** (0.07 g, 69%) was prepared from (±)-**46** (0.08 g, 0.2 mmol) and Mn(OAc)$_2$·4H$_2$O (0.05 g, 0.2 mmol) in EtOH (5 mL), and crystallized from CHCl$_3$-hexane. Brown powder; IR (KBr) 3443, 2977, 1731, 1694, 1604, 1531, 1111 cm^{-1}; UV λ_{max} (CHCl$_3$) 315 (ε 9332 L mol^{-1} cm^{-1}), 279 (ε 13541); MS $_{m/z}$ (relative int.) 524 (8, M$^+$), 307 (11), 161 (84), 133 (56), 119 (90), 94 (67), 44 (100). The sample prepared from (*R*)-**46** and Mn(OAc)$_2$·4H$_2$O showed CD (CHCl$_3$)/nm $[\theta]_{249.5}$ -152, $[\theta]_{242.5}$ -8211, $[\theta]_{233}$ +17820, $[\theta]_{226}$ +3069.

N,N′-Bis(3-*t*-butyl-5-methoxysalicylidene)-1,2-di(ethoxycarbonyl)ethylenediaminatomanganese(III) acetate 17

By a procedure similar to that for Ni(II)-**13**, Mn(III)-**17** (0.19 g, 79%) was prepared from (*S*)-**47** (0.2 g, 0.34 mmol) and Mn(OAc)$_2$·4H$_2$O (0.14 g, 0.34 mmol) in EtOH (9 mL), and crystallized from CH$_2$Cl$_2$-hexane. Brown powder; IR (KBr) 2949, 1733, 1595, 1532, 1423, 1209, 1057 cm^{-1}; UV (MeOH) 364 (ε 14070 L mol^{-1} cm^{-1}), 310.8 (ε 12594), 258.8 (ε 27636), 220 (ε 57126); CD (CHCl$_3$) $[\theta]_{652}$ -39200, $[\theta]_{399}$ -3235, $[\theta]_{253}$ -4130; FAB-MS *m/z* (relative int.) 635 (92), 583 (68), 290 (100), 218 (44), 154 (43).

N,N′-Bis(3,5-di-*t*-butylsalicylidene)-1,2-di(ethoxycarbonyl)ethylenediaminatomanganese(III) chloride 18

Mn(III)-**18** (0.06 g, 48%) was prepared from **48** (0.11 g, 0.173 mmol), Mn(OAc)$_2$·4H$_2$O (0.106 g, 0.43 mmol) and LiCl (0.022 g, 0.52 mmol) in EtOH (95%, 3.5 mL) in the presence of KOH (0.7 mL of 0.5 M aqueous solution), by a procedure similar to that for Mn(III)-**6**. Brown powder; IR (KBr) 2955, 1643, 1607, 1358, 1249, 1168 cm^{-1}; FAB-MS *m/z* (relative int.) 689 (3, M$^+$-Cl), 587 (27), 543 (100).

Diethyl 2,3-diamino-1,4-butanedioate 42

The following procedures are modified from previous reports.[18] A mixture of *meso*-2,3-dibromosuccinic acid **49** (5 g, 18.2 mmol) and benzylamine (17.1 mL, 163 mmol) in EtOH (95%, 20 mL) was stirred at 25 °C for 10 min, heated under reflux for 5 h and cooled. The formed white solids were filtered, rinsed with EtOH (95%) and dissolved in aqueous KOH (1 M). The mixture was extracted twice with Et_2O. The aqueous phase was treated with charcoal and filtered; acetic acid was added until pH 4-5 to give white precipitates. The precipitates were filtered, rinsed with water and dried (100 °C in oven, then 50 °C *in vacuo*) to give *meso*-2,3-bis-(benzylamino)succinic acid (5.25 g, 81%). Benzylamino acid (4 g, 12.2 mmol) was hydrogenolyzed (3 atm H_2) over Pd/C (10%, 0.4 g) in HOAc (20 mL)-HCl (12 N, 16.8 mL) at 25 °C for 20 h. The mixture was dissolved in water (40 mL), filtered and concentrated on rotary evaporation. The residue was dissolved in aqueous NaOH (1 M), and adjusted to pH 5-6 with HOAc. The formed white solids were filtered and dried in vacuo to give *meso*-2,3-di(carbobenzoxylamino)-1,4-butanedioic acid **50** (1.52 g, 84%). White solids; mp > 295 °C; ^{1}H NMR (4.5% KOH in D_2O) δ 3.13 (s).

Diacid **50** (0.297 g, 2 mmol) was dissolved in aqueous NaOH (4 M, 2.05 mL) and 1,4-dioxane (2 mL). Benzyl chloroformate (0.65 mL, 3.2 mmol) was added dropwise at 0 °C; the mixture was stirred, heated at 50-60 °C for 5 h, and cooled. Water (20 mL) was added, and the mixture was extracted twice with Et_2O. The aqueous phase was acidified to pH 2-3 with HCl (12 M), kept at 0-5 °C overnight, and filtered. The white solids were dried in vacuo to give *meso*-2,3-bis-(carbobenzyloxylamino)succinic acid (0.53 g, 64%). The resulting Cbz-amino diacid (1.05 g, 2.64 mmol) in Ac_2O (10 mL) was refluxed for 20 min, cooled and concentrated to give 2,3-di(carbobenzoxylamino)-1,4-butanedioic anhydride **51** (0.9 g, 86%; racemic/*meso* = 4:1). The diastereomeric mixture was treated with $CHCl_3$, the insoluble *meso*-isomer was filtered, the filtrate was treated with appropriate volume of hexane to give crystals of (±)-**51** after standing at 0 °C. White crystal; mp 151-153 °C; IR (KBr) 3394, 3100, 1866, 1792, 1518, 1267 cm^{-1}; ^{1}H NMR (Acetone-d^6) δ 5.05 (2 H, dd, *J* = 5.4, 1.9 Hz), 5.14 (4 H, s), 7.35 (10 H, m), 7.48 (2 H, br d, *J* = 4.3 Hz); ^{13}C NMR (Acetone-d^6) δ 56.3 (d), 67.5 (t), 128.6 (d), 128.7 (d), 129.0 (d), 137.0 (s), 156.8 (s), 168.0 (s).

A solution of (±)-**51** (0.1 g, 0.25 mmol) in Me_2CO (1 mL) was added dropwise KOH (2 M, 0.3 mL) at 25 °C. The mixture stood for 30 min, Me_2CO was removed on rotary evaporation, and the aqueous phase was acidified with HCl (12 M). The mixture was diluted with water (2 mL) and extracted twice with EtOAc. The combined extracts were washed with water, dried (Na_2SO_4) and filtered. The filtrate was concentrated on rotary evaporation to give diacid (±)-**52** (0.1 g, 96%) as white solids. mp 175-176 °C; IR (KBr) 3317, 2951, 1721, 1514, 1254, 1065 cm^{-1}; ^{1}H NMR (Acetone-d^6) δ 5.03 (2 H, dd, *J* = 9.5, 2.3 Hz), 5.07 (4 H, s), 6.78 (2 H, br d, *J* = 8.8 Hz), 7.32 (10 H, m), 9.12 (1 H, br s); ^{13}C NMR (Acetone-d^6) δ 55.7 (d), 66 5 (t), 127.9 (d), 128.0 (d), 128.5 (d), 137.1 (s), 156.5 (s), 170.3 (s).

Resolution of (±)-**52**. A solution of (±)-**52** (1.9 g, 4.57 mmol) in Me_2CO (38 mL) and water (3.8 mL) was heated under reflux, and brucine·$2H_2O$ (3.93 g, 9.14 mmol) was added. The mixture was heated for 5 min and then cooled to 0 °C for 18 h. The formed white solids (3.4 g) were filtered and dissolved in Me_2CO/water (38 mL/38 mL). The mixture was heated under reflux for 5 min, and cooled to 0 °C for 6 h. The collected white solids (2.8 g, 97%) of (2*S*,3*S*)-**52** brucine salt was teated with HCl (1 M, 30 mL) and extracted with EtOAc to give pure acid (2*S*,3*S*)-**52** (0.72 g, 76%). The mother liquor was concentrated to 4 mL, treated with HCl (30 mL, 1 M) and extracted with EtOAc to give (2*R*,3*R*)-**52** (0.84 g, 88%). Brucine $2H_2O$ was recovered on treating aqueous phase with NaOH (4 M).

A solution of (±)-**52** (0.72 g, 1.73 mmol) in EtOH (14.5 mL) was treated with $SOCl_2$ (0.48 mL, 2.47 mmol) at 25 °C. The mixture was heated at 60 °C for 5 h, cooled and concentrated on rotary evaporation. The residue was purified on a silica-gel column chromatograph with elution of EtOAc/hexane (50:50) to give the diethyl ester (0.81 g, 99%) as a colorless oil. Crystallization from EtOH-hexane (1:5) at 0 °C gave white solids. mp 62 °C; TLC (50% EtOAc in hexane) R_f = 0.69; IR (KBr) 3299, 2979, 1742, 1724, 1681, 1531, 1247 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.27 (6 H, br t, *J* = 6.8 Hz), 4.20 (4 H, br d, *J* = 2.7 Hz), 4.84 (2 H, br d, *J* = 8 Hz), 5.06 (4 H, s), 5.61 (2 H, br d, *J* = 7.4 Hz), 7.32 (10 H, m); ^{13}C NMR ($CDCl_3$) δ 13.9 (q), 55.7 (d), 62.4 (t), 67.2 (t), 128.0 (d), 128.2 (d), 128.5 (d), 135.9 (s), 155.7 (s), 169.3 (s); FAB-MS *m/z* (relative int.) 473 (44, M$^+$), 429 (35), 307 (21), 154 (100), 136 (70). (2*S*,3*S*)-Diethyl 2,3-di(carbobenzoxylamino)-1,4-butanedioate, white crystal $[\alpha]_D^{20}$ = +31° (acetone; *c* = 1), and the (2*R*,3*R*)-isomer, white crystal, $[\alpha]_D^{20}$ = -30° (acetone; *c* = 1), were similarly prepared from the corresponding optically pure acids **52**.

The diethyl ester (0.8 g, 1.69 mmol) was dissolved in EtOAc (20 mL), and hydrogenolyzed (1 atm H_2) over Pd/C (10%, 0.08 g) at 25 °C. Hydrogenation was complete after 12 h as monitored by TLC. The mixture was filtered and rinsed with EtOAc. The filtrate was concentrated on rotary evaporation to give (±)-**42** (0.35 g, 99%) as pale yellow oil. IR (neat) 3371, 2966, 1733, 1244 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.20 (6 H, t, *J* = 7.9 Hz), 1.65 (4 H, br s), 3.85 (2 H, d, *J* = 0.9 Hz), 4.15 (4 H, qd, *J* = 7.1, 0.7 Hz,); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.0 (q), 56.8 (d), 61.2 (t), 173.3 (s); MS *m/z* (relative int.) 205 (100, M$^+$+1), 131 (38), 103 (68), 74 (82), 58 (64), 46 (22).

The optical isomers were prepared, respectively, from hydrogenolyses of the corresponding (2*S*,3*S*)- or (2*R*,3*R*)-enantiomers of diethyl 2,3-di(carbobenzoxylamino)-1,4-butanedioate. (2*S*,3*S*)-**42**: yellow oil; $[\alpha]_D^{25} = +17°$ ($CHCl_3$; *c* = 1). (2*R*,3*R*)-**42**: yellow oil; $[\alpha]_D^{25} = +16°$ ($CHCl_3$; *c* = 1).

General Procedure for Epoxidations (Table 1 and Scheme I)

A mixture of metallo-catalyst (**1-18**, 1.25-10 mol%), alkene (**19-22** or geraniol, equimolar proportions), oxidizing agents [PhIO (double molar proportions), O_2/Me_2CHCHO (double molar proportions), O_2/Me_3CCHO (double molar proportions) or air/Me_2CHCHO (double molar proportions)] in an appropriate solvent (1,2-dichloroethane, dichloromethane, acetonitrile or benzene, *ca.* 2-7 mL for 1 mmol of alkene) was stirred at 25 °C (or other indicated temperatures) for a period shown in Table 1. Pyridine (5 molar proportions), *N*-methylimidazole (0.5-2 molar proportions) or 4-*t*-butylpyridine *N*-oxide (0.25 molar proportions) may be added in certain cases as mentioned in Table 1. The conversion was determined on analysis of the crude product with GC or of the ^1H NMR spectrum. The mixture was concentrated on rotary evaporation and chromatographed on a silica-gel column to give epoxidation[20] products (52-100% yields). The physical and spectral properties of epoxides **23**,[4b,6b] **24**,[20] **25**,[21] **26**,[22] **28**,[14] **29**,[14] and **30**[23] are reported.

General Procedure for Sulfide Oxidations (Table 2)

A mixture of metallo-catalyst (**1-6** or **13**, 1.4-5.8 mol%), methyl *p*-tolyl sulfide (**31**, equimolar proportions), oxidizing agents (O_2/Me_2CHCHO or air/Me_2CHCHO, 1-3 molar proportions) in an appropriate solvent (1,2-dichloroethane, acetonitrile or benzene, *ca.* 3-6 mL for 1 mmol of sulfide) was stirred at 25 °C (or other indicated temperatures) for a period shown in Table 2. The conversion was determined on analysis of the crude product with GC or of the ^1H NMR spectrum. The mixture was concentrated on rotary evaporation and chromatographed on a silica-gel column to give corresponding sulfoxide **32** and sulfone **33** (72-98% total yields).[9]

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Key Words

Oxidation; Transition metals; Alkenes; Sulfides; 1,3-Diketone; β-Ketoimine; Salen.

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