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Manganese-catalyzed enantioselective oxidation of C–H bonds of alkanes and silyl ethers to optically active ketones

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Abstract—The (salen)manganese(III) complex-catalyzed oxidation of C–H bonds of symmetrical alkanes and symmetrical 1,3- and 1,4-disilyl ethers with iodosylbenzene gave the corresponding optically active ketones (up to 70% ee) and β- and γ-siloxyketones (up to 93% ee).

1. Introduction

The catalytic oxidation of C–H bonds under mild conditions is an important reaction with respect to synthetic and industrial chemistry;[1] however, the catalytic oxidation of C–H bonds of alkanes is extremely difficult because of the lack of the reactivity of alkanes. Therefore, the catalytic oxidation, and in particular asymmetric oxidation of alkanes remains a challenging target. A few examples of the enantioselective hydroxylation of alkanes have already been reported;[2,3] however, there is no method for the enantioselective oxidative transformation of alkanes to optically active ketones.

During the course of our systematic study on biomimetic catalytic oxidations,[4] we found that ruthenium-catalyzed oxidation of alkanes can be carried out under mild conditions by two catalytic systems, $RuCl_2(PPh_3)_3$/^{t}BuOOH and Ru–C (ruthenium on charcoal)/CH_3CO_3H, to give the corresponding alcohols and ketones highly efficiently.[5] These systems can be extended to aerobic oxidations, in which peracetic acid can be generated in situ from acetaldehyde and molecular oxygen.[6] These catalytic systems are effective in the oxidation of alkanes to give the corresponding ketones.

It was expected that the catalytic systems could be applied to the asymmetric oxidation of symmetrical alkanes to give optically active ketones, where desymmetrization of the substrates takes place. For asymmetric oxidation, the ligand of the catalyst must be robust under oxidation conditions. Phosphine ligands cannot be used, and hence hydrocarbon ligands, nitrogen, and oxygen ligands were explored and used for asymmetric Wacker-type oxidation,[7] epoxidations, and dihydroxylations.[8] With the results of this systematic study, we found that the oxidative desymmetrization of symmetrical alkanes can be carried out upon treatment with iodosylbenzene in the presence of chiral Mn(salen)[9] catalysts to give the corresponding optically active ketones (Eq. 1, Scheme 1).[10] This was the first report on the enantioselective, direct, oxidation of alkanes to give optically active ketones bearing an asymmetric center at the α-position. Furthermore, this catalytic oxidation can be applied to the α-C–H oxidation of disilyl ethers, and hence the enantioselective oxidation of symmetrical 1,3- and 1,4-disilyl ethers gives the corresponding optically active β- and γ-siloxyketones, respectively (Eq. 2, Scheme 1).[11]

Oxidative desymmetrization reactions of symmetrical substrates are highly useful and enantioselective, catalytic oxidations of *meso*-tetrahydrofuran,[12] *meso*-pyrrolidine,[13] symmetrical 1,3-diols,[14] and 1,4-diols[15] have been explored.

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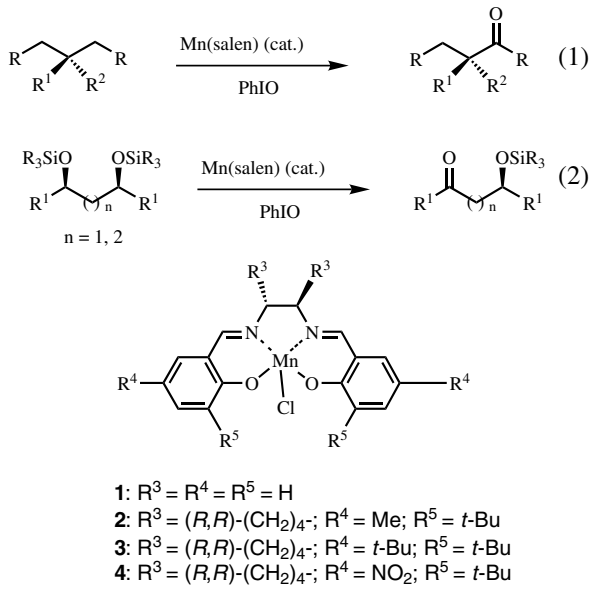


Scheme 1.

Herein, we report in full detail the enantioselective oxidations of C–H bonds of symmetrical alkanes[10] and symmetrical 1,3- and 1,4-disilyl ethers[11] with respect to scope, limitation, and mechanism.

2. Results and discussion

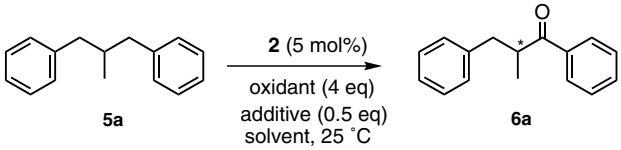
2.1. Enantioselective oxidation of alkanes

As a model for the oxidative desymmetrization of symmetrical C–H bonds of alkanes, we examined 2-methyl-1,3-diphenylpropane **5a** bearing a *C*s symmetry and a prochiral carbon at the center of the molecule. Enantioselective oxidative desymmetrization of **5a**, bearing two symmetrical benzylic positions, gives optically active 2-methyl-1,3-diphenyl-1-propanone **6a** (Eq. 3). Treatment of **5a** with PhIO in the presence of Mn(salen) **2** and 4-phenylpyridine-*N*-oxide (4-PPN) in chlorobenzene at room temperature under argon gave **6a**. The enantiomeric excess of **6a** was determined to be 22% by HPLC analysis using a chiral column (CHIRALCEL OB–H, hexane/2-propanol = 10:1). The effect of the oxidants is shown in Table 1. When CH_3CO_3H and ^{t}BuOOH were used in the oxidation of **5a**, the enantioselectivities obtained were low (entries 1 and 2). Sodium hypochlorite resulted in a slight improvement of enantioselectivity for **6a**, although the reaction was slow (entry 3). When iodosylbenzene was used, the enantioselectivity was improved to 22% ee (entry 4). A solvent effect was also observed. Better results were obtained in chlorobenzene in comparison to other solvents such as CH_2Cl_2, CH_3CN, and EtOAc (entries 5–7). The addition of 4-phenylpyridine *N*-oxide[16] gave higher enantioselectivities, which increased from 12% ee to 22% ee (entries 4 and 8).

Representative results for the asymmetric oxidation of alkanes with iodosylbenzene in the presence of the catalyst **2** to give the corresponding optically active ketones are shown in Table 2. The electronic effect at the *para*-position of **5** is not important for these enantioselective oxidation reactions (entries 1–3). The oxidation of cyclic substrate, 2-methyl-2-phenylindane **7** afforded ketone **8** in 14% ee (entry 4). This is the first example of a catalytic asymmetric oxidation of alkanes to the optically active ketones, although the enantioselectivities are still low. The product ketones were isolated in 20–28% yields along with trace amounts of the corresponding alcohols. This is due to dimerization of the salen catalysts and oxidation of the ligands occur under the reaction conditions.[17]

Asymmetric oxidation of the C–H bonds of alkanes bearing a functional group is particularly important in organic synthesis. The present asymmetric oxidation can be applied to the oxidation of alkanes bearing an oxygen functional group such as a siloxy group. Thus,

Table 1. Mn(salen)-catalyzed asymmetric oxidation of **5a**[a]

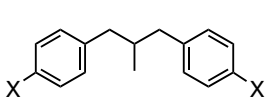
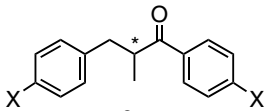
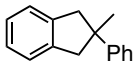
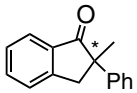


(3)

Entry	Oxidant	Solvent	Additive	Yield (%)[b]	ee (%)[c]
1	CH_3CO_3H	C_6H_5Cl	4-PPN[d]	14	12 (−)
2	^{t}BuOOH	C_6H_5Cl	4-PPN	12	2 (−)
3	NaClO	C_6H_5Cl	4-PPN	2	18 (−)
4	PhIO	C_6H_5Cl	4-PPN	24	22 (−)
5	PhIO	CH_2Cl_2	4-PPN	9	10 (−)
6	PhIO	CH_3CN	4-PPN	4	13 (−)
7	PhIO	EtOAc	4-PPN	0	0 (−)
8[e]	PhIO	C_6H_5Cl	—	14	12 (−)

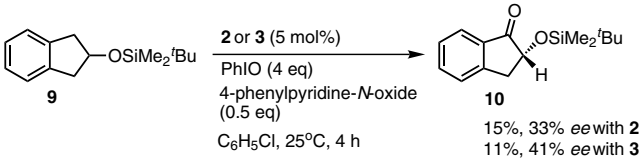
[a] A mixture of **5a** (0.48 mmol), **2** (0.024 mmol), additive (0.24 mmol), oxidant (1.92 mmol), and solvent (3 mL) was stirred for 1 h.
[b] Isolated yield.
[c] Determined by HPLC analysis using a chiral column (CHIRALCEL OB-H, hexane/2-propanol = 10:1).
[d] 4-Phenylpyridine *N*-oxide.
[e] In the absence of 4-phenylpyridine *N*-oxide.

Table 2. Mn(salen)-catalyzed asymmetric oxidation of alkanes[a]

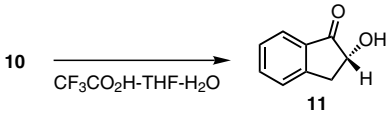
Entry	Substrate	Product	Yield (%)[b]	ee (%)[c]
		 **6a-c**		
1	X = H (**5a**)		24	22
2	X = CH_3 (**5b**)		20	15
3	X = Cl (**5c**)		20	9
4	 **7**	 **8**	28	14

[a] A mixture of alkane (0.48 mmol), **2** (0.024 mmol), 4-phenylpyridine *N*-oxide (0.24 mmol), PhIO (1.92 mmol), and C_6H_5Cl (3.0 mL) was stirred for 24 h.
[b] Isolated yield.
[c] Determined by HPLC analysis using chiral columns. See the Section 4.

the oxidation of 2-(*tert*-butyldimethylsiloxy)indane **9** with iodosylbenzene in the presence of the catalyst **2** gave (*R*)-(−)-2-*tert*-butyldimethylsiloxy-1-indanone **10** (33% ee) (Eq. 4). Ketone **10** was isolated with PTLC (SiO_2, hexane/ethyl acetate = 3:1). The enantiomeric excess of **10** was determined by HPLC analysis using a chiral column (CHIRALPAK AS, hexane/2-propanol = 500:1). The absolute configuration of **10** was determined by comparison with the specific rotation after conversion to 2-hydroxy-1-indanone **11** (Eq. 5).[18] When (*R*,*R*)-**3** complex catalyst bearing *tert*-butyl groups at the C5 and C5′ positions was used for the oxidation of **9**, the enantioselectivity of product **10** was improved to 41% ee.



(4)



(5)

A remarkable temperature effect was observed for the oxidation of **9** as shown in Table 3 and Figure 1. Generally, enantioselectivity is improved by lowering the temperature; however, the present oxidation gave a maximum enantioselectivity (70% ee) at 40 °C. Such a nonlinear relationship was also observed when using the manganese complex catalyst with other substituents (R^4 = Me **2**, NO_2 **4**). The maximum enantioselectivity (42% ee) was observed at 40 °C using catalyst **2**, and 56% ee at −10 °C with catalyst **4**. The nonlinear relationship between reaction temperature and enantioselectivity may be due to two factors: steric repulsion and chelation effects between the manganese catalyst and 2-siloxyindane. The reactions, which involve the reversible formation of diastereomeric intermediates and the irreversible transformation of the intermediates to products or other intermediates have a possibility of showing a nonlinear relationship between reaction temperature and enantioselectivity (Scheme 2).[19]

Table 3. Asymmetric oxidation of **9** with catalyst **3**[a]

Entry	Temp (°C)	Yield (%)[b]	ee (%)[c]	Config.
1	10	2	2	(*R*)
2	25	11	41	(*R*)
3	30	10	43	(*R*)
4	40	13	70	(*R*)
5	50	12	59	(*R*)
6	60	8	39	(*R*)
7	70	11	22	(*R*)
8[d]	40	8	67	(*S*)

[a] A mixture of **9** (0.21 mmol), **3** (0.011 mmol), 4-phenylpyridine *N*-oxide (0.11 mmol), PhIO (0.84 mmol), and C_6H_5Cl (1.5 mL) was stirred for 4 h.
[b] Isolated yield.
[c] Determined by HPLC analysis using a chiral column (CHIRALPAK AS, hexane/2-propanol = 500:1).
[d] (*S*,*S*)-**3** was used.

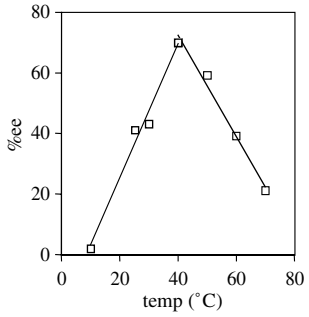
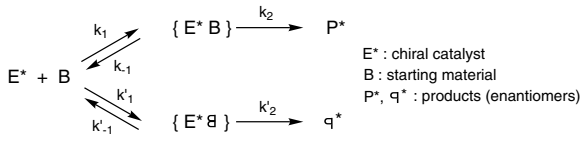


Figure 1. Temperature effect for asymmetric oxidation of **9** in the presence of Mn(salen) catalyst **3**.

The optically active ketone **10** can be easily converted to optically active *cis*-(1*S*,2*R*)-1-amino-2-indanol stereoselectively by protonation, oximation, and palladium catalyzed hydrogenation.[20] This type of asymmetric oxidation reaction could be a future method for the



Scheme 2.

short step synthesis of *cis*-1-amino-2-indanol, which is a key intermediate for the synthesis of chiral auxiliaries[21] and various biologically active compounds, such as HIV protease inhibitor components.[22]

2.2. Enantioselective oxidation of 1,3- and 1,4-disilyl ethers

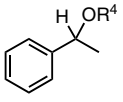
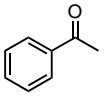
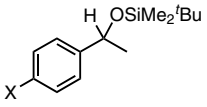
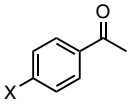
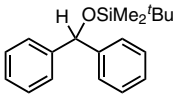
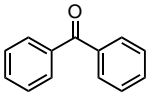
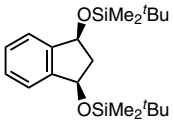
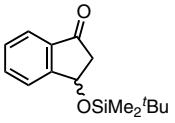
The direct catalytic oxidative transformation of silyl ethers to carbonyl compounds is highly useful because the conversion of silyl ethers to the corresponding carbonyl compounds is often used in organic synthesis and is usually carried out by two steps, that is, deprotection and oxidation.[23] Stoichiometric methods have been reported,[24] however, the chromiun-catalyzed oxidation of silyl ethers with ^{t}BuOOH is the only catalytic method reported.[25] This method can only be used for less hindered substrates.[25]

In order to carry out the enantioselective oxidation of silyl ethers, it is necessary to oxidize the α-C–H bond of silyl ethers. We found that (salen)Mn(III) is an efficient catalyst for the oxidative transformation of silyl ethers to ketones. Treatment of silyl ethers with iodosylbenzene in the presence of achiral (salen)Mn(III) complex **1** in acetonitrile at 25 °C under argon gave the corresponding ketones efficiently. The representative results of the oxidation of silyl ethers are summarized in Table 4. Importantly, the oxidation of the hindered *tert*-butyldimethylsilyl (TBDMS) ether proceeds with high conversion as well as the TMS ether (entries 1 and 2), while the chromium-catalyzed oxidation is not effective for the oxidation of the TBDMS ether.[25] The oxidations, of the substituted benzylic silyl ethers (*p*-methoxy, *p*-methyl, and *p*-chloro) gave the corresponding ketones in high yields (entries 3–5). Diphenylmethyl silyl ether was efficiently converted to benzophenone (entry 6). The oxidation of disilyl ether, *meso*-1,3-bis (*tert*-butyldimethylsilylsiloxy)-indane, gave the monooxidized product (entry 7).

The enantioselective oxidation of symmetrical disilyl ethers with a chiral (salen)Mn catalyst was next examined. Asymmetric oxidative desymmetrization of *cis*-1,3-disiloxyindane **12** bearing two silyl ethers, in the presence of the chiral (salen)Mn complex catalyst **3**, gave the corresponding optically active 3-siloxy-1-indanones **13** (Eq. 6). The representative results of the enantioselective oxidation of **12** are shown in Table 5.

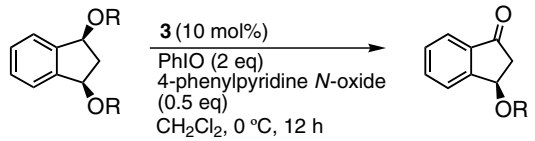
The oxidation of *cis*-1,3-di(*tert*-butyldimethylsiloxy)indane **12a** with iodosylbenzene in the presence of (*R*,*R*)-**3** catalyst gave siloxyketone **13a** with 57% ee (*R*) (entry 1). The absolute configuration of **13a** was

Table 4. Catalytic oxidation of silyl ethers using (salen)Mn(III) (**1**)[a]

Entry	Substrate	Product	Conv (%)[b]	Yield (%)[c]
				
1	$R^4 = SiMe_3$		84	81
2	$R^4 = SiMe_2{}^tBu$		80	81
				
3	X = OMe		91	71
4	X = Me		87	61
5	X = Cl		78	85
6			83	91
7			nd[d]	57[b]

[a] A mixture of substrate (0.10 mmol), (salen)Mn(III) **1** (0.005 mmol), PhIO (0.20 mmol), and CH_3CN (1.0 mL) was stirred at room temperature for 6 h.
[b] Determined by GLC analysis based on the starting substrate using an internal standard.
[c] Determined by GLC analysis based on the converted substrate.
[d] Not determined.

Table 5. Enantioselective oxidation of 1,3-disiloxyindanes using (*R*,*R*)-**3** catalyst[a]



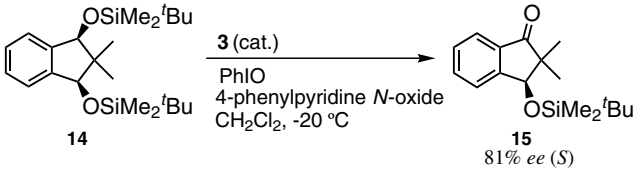
R = $SiMe_2{}^tBu$ **12a**
= $SiMe_3$ **12b**
= $Si(^iPr)_3$ **12c**
= $SiPh_2{}^tBu$ **12d**
= H **12e**

13a-e (6)

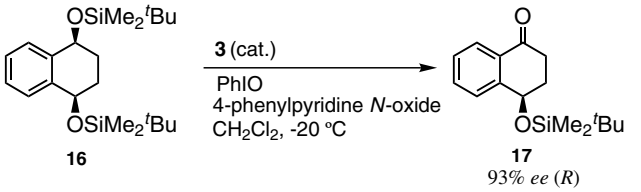
Entry	Substrate	Additive[b]	Temp (°C)	Conv[c] (%)	ee[d] (%)
1	**12a**	None	25	13	57 (*R*)
2	**12a**	4-PPN	25	24	66 (*R*)
3	**12a**	4-PPN	0	5	78 (*R*)
4[e]	**12a**	4-PPN	0	17	78 (*R*)
5[e]	**12a**	4-PPN	−20	8	89 (*R*)
6	**12b**	4-PPN	0	30	49[f] (*R*)
7	**12c**	4-PPN	0	3	48 (*R*)
8	**12d**	4-PPN	0	Trace	16[f] (*R*)
9	**12e**	4-PPN	0	19	51[g] (*R*)

[a] To a mixture of 1,3-disiloxyindane **12** (0.050 mmol), 4-phenylpyridine *N*-oxide (0.025 mmol), and (*R*,*R*)-**3** (0.0025 mmol) in CH_2Cl_2 (1.0 mL) was added PhIO (0.10 mmol). The mixture was stirred for 12 h.
[b] 4-PPN = 4-phenylpyridine *N*-oxide.
[c] Determined by GLC analysis based on the starting substrate using an internal standard.
[d] Determined by HPLC analysis using a chiral column (CHIRALPAK AD, hexane/2-propanol = 500:1).
[e] Reaction was carried out for 72 h.
[f] Determined by HPLC analysis using a chiral column (CHIRALPAK AS, hexane/2-propanol = 20:1).
[g] Determined by HPLC analysis using a chiral column (CHIRALPAK OB-H, hexane/2-propanol = 10:1).

assigned by comparison with the reported specific rotation value after converting to 3-hydroxy-1-indanone.[26] The addition of 4-phenylpyridine *N*-oxide as an axial ligand and the catalyst improved both the conversion and enantioselectivity (entry 2).[16] When the reaction was carried out at lower temperatures, 0 °C and −20 °C, the enantioselectivity of **13a** was improved to 78% ee and 89% ee, respectively (entries 3–5). The effect of the silyl group is remarkable. The asymmetric oxidation of the less hindered trimethylsilyl (TMS) derivative **12b** gave product **13b** with lower enantioselectivity (49% ee) (entry 6). On the other hand, the oxidation of substrates bearing sterically bulky triisopropylsilyl (TIPS) **12c** and *tert*-butyldiphenylsilyl (TBDPS) **12d** groups are not effective (entries 7 and 8). The oxidation of non-protected *cis*-1,3-indandiol **12e** was examined using (*R*,*R*)-**3** catalyst at 0 °C (entry 9). The enantioselectivity of 3-hydroxyindane-1-one **13e** was 51% ee, which is lower than that of **13a** (78% ee) (entry 4). The siloxy groups and their size have considerable influence on the improvement of the enantioselectivity, while *tert*-butyldimethylsiloxy group is the most suitable for the present asymmetric oxidation reaction. The oxidative desymmetrization of other substrates also proceeds with high enantioselectivity. The oxidation of *cis*-1,3-di(*tert*-butyldimethylsiloxy)-2,2-dimethylindane **14** at −20 °C gave siloxyketone **15** with 81% ee (*S*) (conv 9%) (Eq. 7). The absolute configuration of **15** was determined after conversion to the corresponding (*R*)- and (*S*)-α-methoxy-α-(trifluoromethyl)phenylacetic acid esters (MTPA esters). Furthermore, the oxidation of *cis*-1,4-di(*tert*-butyldimethylsiloxy)tetraline **16** gave **17** with 93% ee (*R*) (conv 15%) (Eq. 8). The absolute configuration of **17** was assigned in comparison with the reported specific rotation value after conversion to 4-hydroxytetralone.[26]



14 **15** 81% *ee* (*S*) (7)



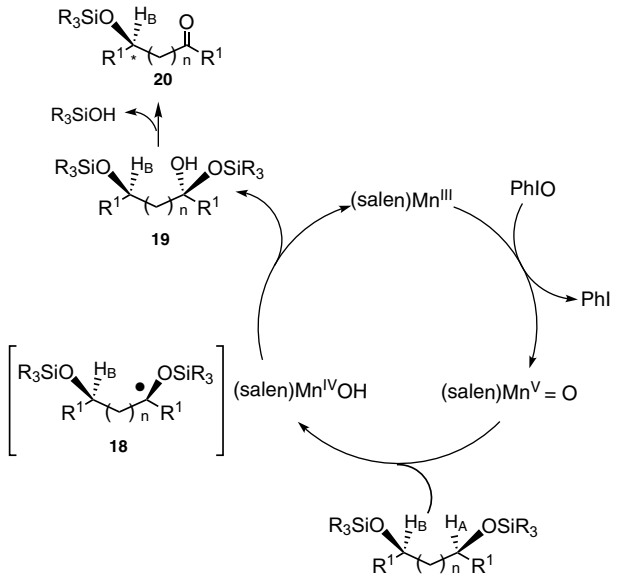
16 **17** 93% *ee* (*R*) (8)

Chiral 3-siloxyindanone **15** and 4-siloxytetralone **17** thus obtained can be readily converted to the corresponding chiral 3-hydroxyindanone and 4-hydroxytetralone, respectively. The chiral 3-hydroxyindanone unit can be found in natural products such as indatraline,[27] while the chiral 4-hydroxytetralone unit is present in biologically active compounds such as catalponol,[28] isoshinanolone,[29] and palmarumycin CP_4.[30]

Substrate **12a** has two symmetric benzylic positions, while the oxidized product **13a** has one benzylic position. There is a possibility of Mn(salen)-catalyzed

kinetic resolution of ketone **13a** in the oxidation of **12a**. The kinetic resolution of (±)-**13a** using (*S*,*S*)-**3** was examined. We found that the oxidation of (±)-**13a** with 2 equiv of iodosylbenzene in the presence of (*S*,*S*)-**3** catalyst and 4-phenylpyridine *N*-oxide (0.5 equiv) at 25 °C under an argon atmosphere proceeded slowly. Thus, the conversion of (±)-**13a** is low (5%), while the enantioselectivity of the remaining **13a** is <2% ee (*S*). This experiment indicates that the kinetic resolution of **13a** does not occur in the oxidation of **12a**.

To determine the rate-determining step of the reaction, the deuterium isotope effect was examined. The reaction rates were determined for the **1**-catalyzed oxidations of 1-phenylethyl *tert*-butyldimethylsilyl ether ($k_H = 1.2 \times 10^{-6}\ M^{-1}\ s^{-1}$) and 1-deuterio-1-phenylethyl *tert*-butyldimethylsilyl ether ($k_D = 1.7 \times 10^{-7}\ M^{-1}\ s^{-1}$) with PhIO in dichloromethane at 10 °C under pseudo-first-order reaction conditions (solvent, CH_2Cl_2, 10 °C; [silyl ether] = 2.0×10^{-1} M; [**1**] = 1.0×10^{-3} M; [PhIO] = 2.0×10^{-2} M). The kinetic isotope effect ($k_H/k_D = 7.1$) obtained indicates that C–H bond cleavage occurs in the transition state. The present oxidation can be rationalized by assuming the following mechanism (Scheme 3). The (salen)Mn(III) complex reacts with iodosylbenzene to give a (salen)Mn(V)=O species,[16] which undergoes rate-determining α-C–H abstraction from the substrate to generate α-siloxybenzyl radical intermediate **18** bearing (salen)Mn(IV)OH. Rebounding of the hydroxy ligand to the carbon radical gives the corresponding α-siloxyalcohol **19** and (salen)-Mn(III) to complete the catalytic cycle. The α-siloxyalcohol **19** is rapidly converted to the corresponding ketone **20** by elimination of the corresponding silanol under the reaction conditions. This was confirmed by the detection of *tert*-butyldimethylsilanol, which is identified by comparison with an authentic sample. The siloxy group plays an important role to improve the enantioselectivity.



Scheme 3.

3. Conclusion

In conclusion, we have found that the direct oxidation of symmetrical alkanes with iodosylbenzene to give optically active ketones can be carried out in the presence of chiral Mn(salen) complex catalysts. The catalytic system can be applied to the enantioselective oxidative transformation of 1,3- and 1,4-disilyl ethers to the corresponding optically active β- and γ-siloxy ketones, respectively, with high enantioselectivity (up to 93% ee). These methods could be useful in future methods in the synthesis of optically active ketones, which are key intermediates for the synthesis of chiral auxiliaries and various biologically active compounds.

4. Experimental

4.1. General

All melting points were determined in capillary tubes and are uncorrected. IR spectra were measured by a Shimadzu FTIR-4100 spectrometer. NMR spectra were recorded on a Varian Unity-Inova 500 spectrometer. Analytical GLC evaluations of product mixtures were carried out on a Shimadzu GC-17A gas chromatograph. GC–MS analyses were performed on a Shimadzu GC–MS QP5000 mass spectrometer. Analytical HPLC was carried out on a JASCO UVIDEC-100-VI (UV spectrophotometer), a DG-3510 (degasser), a PU-980 (intelligent HPLC Pump), a LG-980-02 (ternary gradient unit), and a MULTI 340 (UV detector). Optical rotations were measured by a JASCO DIP-370 polarimeter.

4.2. Materials

All Mn(salen) complexes were prepared by the literature procedure.[9]

4.3. General procedure for the Mn(salen)(2)-catalyzed enantioselective oxidation of 2-methyl-1,3-diphenylpropane 5a

To a mixture of 2-methyl-1,3-diphenylpropane **5a** (100 mg, 0.480 mmol), **2** (3.10 mg, 0.0240 mmol), 4-phenylpyridine *N*-oxide (41.1 mg, 0.240 mmol), and solvent (3 mL) was added oxidant (1.92 mmol) at room temperature under an argon atmosphere. After the mixture was stirred for 1 h, a 5% Na_2SO_3 aqueous solution (10 mL) was added to the mixture. The mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with a saturated $NaHCO_3$ aqueous solution (25 mL × 3) and brine (25 mL), and dried over Na_2SO_4. After evaporation of the filtrate, the residue was subjected to PTLC (SiO_2, hexane/ethyl acetate = 5:1) to give 2-methyl-1,3-diphenylpropan-1-one **6a** as a colorless oil: IR (neat): 3029, 1730 (C=O), 1684, 1403, 974, 741, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz): δ 1.20 (d, $J = 6.8$ Hz, 3H, CH_3), 2.69 (dd, $J = 13.8$ and 7.8 Hz, 1H, CH_2), 3.14 (dd, $J = 13.8$ and 6.3 Hz, 1H, CH_2), 3.75 (ddq, $J = 7.8$, 6.8, and 6.3 Hz, 1H, CH), 7.13–7.29 (m, 5H, ArH), 7.43 (ddd, $J = 6.7$, 6.7, and 1.4 Hz, 2H, ArH), 7.53 (dddd, $J = 6.7$, 6.7, 1.8, and

1.8 Hz, 1H, ArH), 7.91 (dd, $J = 6.7$ and 1.7 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$, 68 MHz): δ 203.7 (C=O), 140.0, 136.6, 132.9, 128.6, 128.4, 128.3, 128.2, 126.2, 42.8, 39.4, 17.4; HRMS (EI) calcd for $C_{16}H_{16}O$ 224.1201, found 224.1193. The enantiomeric excess was determined by HPLC analysis using a chiral column (CHIRALCEL OB-H, hexane/2-propanol = 10:1, 0.5 mL/min). The results are shown in Table 1.

4.4. General procedure for the Mn(salen)(2)-catalyzed enantioselective oxidation of various alkanes with Iodosylbenzene

To a mixture of substrate (0.48 mmol), Mn(salen) **2** (3.1 mg, 0.024 mmol), 4-phenylpyridine *N*-oxide (41.1 mg, 0.240 mmol), and C_6H_5Cl (3 mL) was added iodosylbenzene (1.92 mmol) at 25 °C. After the mixture was stirred for 1 h, a 5% Na_2SO_3 aqueous solution (10 mL) was added to the mixture. The mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with a saturated $NaHCO_3$ aqueous solution (25 mL × 3) and brine (25 mL) and dried over Na_2SO_4. After evaporation of the filtrate, the residue was subject to PTLC (SiO_2, hexane/ethyl acetate = 5:1) to give the corresponding ketone. The enantiomeric excess was determined by HPLC analyses using chiral columns. The results are shown in Table 2.

4.4.1. 2-Methyl-1,3-di(4′-methylphenyl)-1-propanone 6b. Colorless oil; ^1H NMR ($CDCl_3$, 270 MHz): δ 1.17 (d, $J = 6.4$ Hz, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.63 (dd, $J = 13.7$ and 7.9 Hz, 1H, CH_2), 3.11 (dd, $J = 13.7$ and 6.1 Hz, 1H, CH_2), 3.68 (ddd, $J = 7.9$, 6.4, and 6.1 Hz, 1H, CH), 7.06 (m, 4H, ArH), 7.21–7.24 (m, 2H, ArH), 7.81–7.84 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 68 MHz): δ 203.3 (C=O), 143.6, 136.9, 135.6, 134.0, 129.3, 129.0, 128.4, 128.3, 42.6, 39.0, 21.5, 20.9, 17.3. The enantiomeric excess was determined by HPLC analysis using a chiral column (CHIRALCEL OJ, hexane/2-propanol = 10:1, 0.5 mL/min).

4.4.2. 2-Methyl-1,3-di(4′-chlorophenyl)-1-propanone 6c. Colorless oil; ^1H NMR ($CDCl_3$, 270 MHz): δ 1.19 (d, $J = 7.1$ Hz, 3H, CH_3), 2.69 (dd, $J = 13.8$ and 7.2 Hz, 1H, CH_2), 3.11 (dd, $J = 13.8$ and 7.0 Hz, 1H, CH_2), 3.63 (ddq, $J = 7.2$, 7.1, and 7.0 Hz, 1H, CH), 7.09–7.84 (m, 8H, ArH). The enantiomeric excess was determined by HPLC analysis using a chiral column (CHIRALCEL OJ, hexane/2-propanol = 20:1, 0.5 mL/min).

4.4.3. 2-Methyl-2-phenyl-1-indanone 8. Colorless oil; IR (neat): 2965, 1713 (C=O), 1607, 1470, 1464, 1373, 1325, 1289, 1208, 1154, 1030, 970, 911, 760, 731, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz): δ 1.66 (s, 3H, CH_3), 3.30 (d, $J = 17.5$ Hz, 1H, CH_2), 3.60 (d, $J = 17.5$ Hz, 1H, CH_2), 7.25–7.30 (m, 5H, ArH), 7.42 (dt, $J = 7.1$ and 0.9 Hz, 1H, ArH), 7.49 (d, $J = 7.6$ Hz, 1H, ArH), 7.63 (dd, $J = 6.2$ and 1.1 Hz, 1H, ArH), 7.82 (d, $J = 7.8$ Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 68 MHz): δ 208.7 (C=O), 152.6, 143.8, 135.5, 135.1, 128.5, 127.7, 126.6, 126.3, 126.1, 124.9, 53.1, 44.8, 24.4; HRMS (EI) calcd for $C_{16}H_{14}O$ *m/z* 222.1045, found *m/z* 222.1025. The enantiomeric excess was determined by HPLC analysis using a chiral column (CHIRALCEL OB-H, hexane/2-propanol = 10:1, 0.5 mL/min).

4.5. Mn(salen)-catalyzed enantioselective oxidation of 2-(*tert*-butyldimethylsiloxy)indane 9 with iodosylbenzene

To a mixture of **9** (52 mg, 0.21 mmol), Mn(salen) (5 mol %), 4-phenylpyridine *N*-oxide (18.2 mg, 0.11 mmol), and C_6H_5Cl (1.5 mL) was added iodosylbenzene (0.84 mmol) at the appropriate temperature. After the mixture was stirred for 4 h, a 5% Na_2SO_3 aqueous solution (10 mL) was added to the mixture. The mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with H_2O (25 mL × 1) and dried over Na_2SO_4. After evaporation of the filtrate, the residue was subject to PTLC (SiO_2, hexane/ethyl acetate = 3:1) to give 2-*tert*-butyldimethylsiloxy-1-indanone **10** as a colorless solid; mp = 67–69 °C; $[\alpha]_D^{27} = -3.6$ (*c* 0.20, $CHCl_3$) (42% ee (*R*)); IR (KBr): 2953, 1730 (C=O), 1611, 1256, 1206, 1156, 1107, 967, 837, 781, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz): δ 0.19 (s, 3H, CH_3), 0.22 (s, 3H, CH_3), 0.97 (s, 9H, ^{t}Bu), 2.98 (dd, $J = 16.4$ and 4.9 Hz, 1H, CH_2), 3.49 (dd, $J = 16.4$ and 7.8 Hz, 1H, CH_2), 4.52 (dd, $J = 7.8$ and 4.9 Hz, 1H, CH), 7.34–7.41 (m, 2H, ArH), 7.56–7.62 (m, 1H, ArH), 7.72–7.75 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 68 MHz): δ 203.1 (C=O), 156.0, 136.2, 135.0, 129.0, 125.8, 123.0, 68.9, 47.9, 25.8, 18.2, −4.4, −4.7; GC–MS (EI): *m/z* 247 ($M^+ - CH_3$) 205, 203, 175, 161, 147, 131, 115, 103, 91, 73, 59. Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found: C, 68.68; H, 8.26. The enantiomeric excess was determined by HPLC analysis using a chiral column (CHIRALPAK AS, hexane/2-propanol = 500:1, 0.5 mL/min).

4.6. Deprotection of (*R*)-2-*tert*-butyldimethylsiloxy-1-indanone 10 to (*R*)-2-hydroxy-1-indanone 11

A 25 mL round-bottomed flask equipped with a magnetic stirring bar was charged with **10** (10 mg, 0.044 mmol), CF_3CO_2H (1.0 mL), THF (0.1 mL), and H_2O (0.1 mL). The mixture was stirred for 24 h. After evaporation of the solvent, the residue was subject to PTLC (SiO_2, hexane/ethyl acetate = 1:1) to give **11** (3.5 mg, 60%) as a colorless solid: IR (KBr): 3434 (OH), 2851, 1789 (C=O), 1611, 1468, 1300, 1252, 1206, 1113, 752 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz): δ 3.01 (dd, $J = 16.8$ and 4.9 Hz, 1H, CH_2), 3.42 (br, 1H, OH), 3.57 (dd, $J = 16.8$ and 7.8 Hz, 1H, CH_2), 4.54 (dd, $J = 7.8$ and 4.9 Hz, 1H, CH), 7.37–7.48 (m, 2H, ArH), 7.61–7.67 (m, 1H, ArH), 7.75–7.78 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 68 MHz): δ 206.5 (C=O), 150.9, 135.8, 134.1, 128.0, 126.7, 124.4, 74.2, 35.2; GC–MS (EI) *m/z* (relative intensity) 148 (M^+), 147 (31), 131 (18), 119 (67), 105 (33). The absolute configuration of **11** was determined by comparison of the retention time of HPLC analysis with the authentic sample; (Ref. 18: HPLC data as follows, (*R*)-**11**: CHIRALCEL OB-H, hexane/2-propanol = 10:1, 0.5 mL/min, retention time: 26 min, $[\alpha]_D^{21} = -11.2$ (*c* 1.0, $CHCl_3$) (99% ee). (*S*)-**11**: CHIRALCEL OB-H,

hexane/2-propanol = 10:1, 0.5 mL/min, retention time: 33 min, $[\alpha]_D^{21} = +10.0$ (*c* 1.1, $CHCl_3$) (99% ee)).

4.7. General procedure for the Mn(salen) (1)-catalyzed oxidation of silyl ethers with iodosylbenzene

To a mixture of silyl ether (0.10 mmol), **1** (1.8 mg, 0.0050 mmol), and CH_3CN (1.0 mL) was added iodosylbenzene (44 mg, 0.20 mmol) at room temperature. The mixture was stirred under an argon atmosphere for 6 h. The conversion of the starting substrate and the yield of product were determined by GLC analysis using an internal standard. The product ketone was isolated by column chromatography (SiO_2, hexane/ethyl acetate). The results are shown in Table 4.

4.8. General procedure for the Mn(salen) 3-catalyzed enantioselective oxidation of 1,3- and 1,4-disilyl ethers to optically active β- and γ-siloxyketones with iodosylbenzene

A 25 mL Schlenk flask equipped with a magnetic stirring bar was charged with a substrate (0.050 mmol), Mn(salen) **3** (0.0025 mmol), 4-phenylpyridine *N*-oxide (4.3 mg, 0.025 mmol), and CH_2Cl_2 (1.0 mL). To the mixture was added iodosylbenzene (22.0 mg, 0.10 mmol) at the appropriate temperature. The mixture was stirred for 17 h. After the mixture was poured into a 0.2 M solution of triphenylphosphine in CH_2Cl_2 (0.2 mL), the mixture was analyzed by GLC to determine the conversion of starting materials and the yield of products using an internal standard (*n*-pentadecane). The product siloxyketone was isolated by column chromatography (SiO_2, hexane/ethyl acetate = 5:1). The results are shown in Table 5 and Eqs. 7 and 8. The spectral data of the products and the conditions for the determination of enantiomeric excess are shown below.

4.8.1. (*R*)-3-*tert*-Butyldimethylsilyloxy-1-indanone 13a. Colorless solid; mp 51.2–52.0 °C; IR (neat): 3072, 3036, 2955, 2930, 1722 (C=O), 1604, 1471, 1464, 1361, 1278, 1217, 1161, 1107, 1080, 1047, 1006, 933, 777 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 0.19 (s, 3H, CH_3), 0.23 (s, 3H, CH_3), 0.96 (s, 9H, ^{t}Bu), 2.60 (dd, $J = 18.5$ and 3.4 Hz, 1H, CH_2), 3.07 (dd, $J = 18.3$ and 6.6 Hz, 1H, CH_2), 5.39 (dd $J = 6.8$ and 3.5 Hz, 1H, CH), 7.74 (d, $J = 7.6$ Hz, 1H, ArH), 7.26–7.75 (m, 3H, ArH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 203.1 (C=O), 156.0, 136.2, 135.0, 129.0, 125.8, 123.0, 68.9, 47.9, 25.8, 18.2, −4.4, −4.7. Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found; C, 68.50; H, 8.54. MS (EI): *m*/*z* 205 ($M^+ - {}^t$Bu), 163, 147, 131, 103, 75, 59, 45; HPLC data as follows, (*R*)-**13a** isomer: CHIRALPAK AD, hexane/2-propanol = 500:1, 0.5 mL/min, retention time: 22 min. (*S*)-**13a** isomer: CHIRALPAK AD, hexane/2-propanol = 500:1, 0.5 mL/min, retention time: 27 min.

4.8.2. (*R*)-3-Trimethylsilyloxy-1-indanone 13b. Colorless oil; IR (neat): 2959, 1721, 1604, 1464, 1350, 1261, 1252, 1105, 1073, 934, 874, 845, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 0.25 (s, 9H, $Si(CH_3)_3$), 2.60 (dd, $J = 18.4$ and 3.3 Hz, 1H, CH_2), 3.06 (dd, $J = 18.5$ and 6.6 Hz, 1H, CH_2), 4.92 (dd $J = 6.6$ and 3.3 Hz, 1H, CH), 7.44–7.74 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 203.1 (C=O), 155.6, 136.3, 135.1, 129.1, 125.9, 123.0, 68.4, 47.6, 0.1. HRMS (EI) Calcd for $C_{12}H_{16}O_2Si$ *m*/*z* 220.0920, found *m*/*z* 220.0949. The enantiomeric excess was determined by HPLC analysis using a chiral column (CHIRALPAK AS, hexane/2-propanol = 20:1, 0.5 mL/min).

4.8.3. (*R*)-3-Triisopropylsiloxy-1-indanone 13c. Colorless solid; mp = 41.4–42.8 °C; IR (KBr): 2944, 1715 (C=O), 1603, 1462, 1281, 1237, 1215, 1105, 1084, 1047, 932, 882, 837, 799, 762 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 1.14–1.22 (m, 21H, $Si(^iPr)_3$), 2.67 (dd, $J = 18.1$ and 3.7 Hz, 1H, CH_2), 3.11 (dd, $J = 18.1$ and 6.4 Hz, 1H, CH_2), 5.52 (dd, $J = 6.6$ and 3.7 Hz, 1H, CH), 7.45–7.48 (m, 1H, ArH), 7.66–7.75 (m, 3H, ArH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 203.3 (C=O), 156.5, 136.4, 135.3, 129.2, 126.0, 123.2, 69.3, 48.7, 18.3, 18.2, 12.5. The enantiomeric excess was determined by HPLC analysis using a chiral column (CHIRALPAK AD, hexane/2-propanol = 500:1, 0.5 mL/min).

4.8.4. (*R*)-3-*tert*-Butyldiphenylsiloxy-1-indanone 13d. Colorless oil; IR (neat): 2959, 2859, 1721 (C=O), 1605, 1427, 1362, 1281, 1242, 1215, 1159, 1113, 1078, 1047, 943, 822, 762, 741, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 1.12 (s, 9H, ^{t}Bu), 2.63 (dd, $J = 18.5$ and 3.4 Hz, 1H, CH_2), 2.75 (dd, $J = 18.5$ and 6.4 Hz, 1H, CH_2), 5.40 (dd, $J = 6.4$ and 3.4 Hz, 1H, CH), 7.38–7.49 (m, 8H, ArH), 7.58–7.61 (m, 1H, ArH), 7.69–7.71 (m, 3H, ArH), 7.75–7.76 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 203.0 (C=O), 157.7, 135.9, 135.8, 134.9, 133.5, 133.4, 130.1, 130.0, 128.9, 127.9, 126.0, 122.9, 69.7, 47.7, 27.0, 19.2. The enantiomeric excess was determined by HPLC analysis using a chiral column (CHIRALPAK As, hexane/2-propanol = 20:1, 0.5 mL/min).

4.8.5. (*R*)-3-Hydroxy-1-indanone 13e. Colorless oil; $[\alpha]_D^{23} = -87.5$ (*c* 2.0, $CHCl_3$) for **13e** with 62% ee (*R*); IR (neat): 3416 (OH), 1712 (C=O), 1606, 1466, 1397, 1333, 1283, 1244, 1213, 1099, 1049, 765 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 2.61 (ddd, $J = 18.8$, 2.1, and 0.9 Hz, 1H, CH_2), 2.87 (s, 1H, OH), 3.11 (ddd, $J = 18.9$, 6.8, and 0.9 Hz, 1H, CH_2, 5.43 (dd, $J = 6.6$ and 2.5 Hz, 1H, CH), 7.47–7.34 (m, 4H, ArH); ^{13}C NMR ($CDCl^3$, 125 MHz): δ 203.5 (C=O), 155.1, 136.3, 135.3, 129.5, 125.9, 123.2, 68.4, 47.1; HRMS (EI) calcd for $C_9H_8O_2$ *m*/*z* 148.0524, found *m*/*z* 148.0508; HPLC data as follows, (*R*)-**13e** isomer: CHIRALCEL OB-H, hexane/2-propanol = 10:1, 0.5 mL/min, retention time: 24 min. (*S*)-**13e** isomer: CHIRALCEL OB-H, hexane/2-propanol = 10:1, 0.5 mL/min, retention time: 28 min.

4.8.6. (*S*)-3-*tert*-Butyldimethylsiloxy-2,2-dimethyl-1-indanone (15). Colorless solid; mp 42.2–43.3 °C; $[\alpha]_D^{23} = -9.2$ (*c* 0.07, $CHCl_3$) for **15** with 80% ee (*S*); IR (KBr): 2959, 2859, 1712 (C=O), 1607, 1468, 1379, 1217, 1111, 1082, 1007, 876, 775, 754 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 0.21 (s, 3H, CH_3), 0.28 (s, 3H, CH_3), 0.98 (s, 9H, ^{t}Bu), 1.07 (s, 3H, CH_3), 1.28 (s, 3H,

CH_3), 4.92 (s, 1H, CH), 7.45 (t, $J = 7.4$ Hz, 1H, ArH), 7.56 (dd, $J = 8.2$ and 0.7 Hz, 1H, ArH), 7.66 (dt, $J = 7.5$ and 1.1 Hz, 1H, ArH), 7.75 (d, $J = 7.5$ Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 208.2 (C=O), 153.8, 134.9, 134.3, 128.8, 125.5, 123.6, 78.4, 51.8, 25.9, 22.4, 21.0, 18.2, −4.1, −4.3; HRMS (EI) calcd for $C_{17}H_{26}O_2Si$ m/z 290.1702, found m/z 290.1741. The enantiomeric excess was determined by HPLC analysis using a chiral column (CHIRALPAK AD, hexane/2-propanol = 500:1, 0.5 mL/min).

4.8.7. (*R*)-4-*tert*-Butyldimethylsiloxy-1,2,3,4-tetrahydronaphthalene-1-one 17. Colorless solid; mp 50.2–51.5 °C; IR (KBr): 2959, 2857, 1682 (C=O), 1597, 1460, 1368, 1327, 1289, 1090, 1057, 943, 891, 837, 775 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 0.16 (s, 3H, CH_3), 0.19 (s, 3H, CH_3), 0.95 (s, 9H, $SiCH_3$), 2.12–2.19 (m, 1H, CH_2), 2.28–2.33 (m, 1H, CH_2), 2.59 (ddd, $J = 12.7$, 10.6 and 4.7 Hz, 1H, CH_2), 2.92 (ddd, $J = 13.0$, 6.4 and 4.4 Hz, 1H, CH_2), 4.96 (dd, $J = 8.7$ and 3.9 Hz, 1H, CH), 7.37–7.41 (m, 1H, ArH), 7.51–7.52 (m, 1H, ArH), 7.56–7.60 (m, 1H, ArH), 7.99–8.02 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 197.6 (C=O), 146.4, 133.8, 131.1, 127.8, 127.0, 126.7, 68.8, 35.6, 32.8, 25.8, 18.2, −4.4, −4.7. The enantiomeric excess was determined by HPLC analysis using a chiral column (CHIRALPAK AS, hexane/2-propanol = 20:1, 0.5 mL/min).

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