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Aluminum Oxidation Catalysis under Aqueous Conditions: Highly Enantioselective Sulfur Oxidation Catalyzed by Al(salalen) Complexes

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Dedication to Professor Teruaki Mukaiyama on the occasion of his 80th birthday

Abstract: Asymmetric oxidation catalysis with an aluminum-based complex was achieved by a combination of newly synthesized chiral aluminum(salalen) complexes (salalen = half-reduced salen = salan/salen-hybridized [ONNO]-type tetradentate ligand; salan = reduced salen, salen = *N*,*N*′-ethylenebis(salicylideneiminato)) derived from binol (1,1′-bi-2,2′-naphthol) with aqueous hydrogen peroxide as the oxidant. The combination was found to be efficient for asymmetric sulfur oxidation. Various sulfides were smoothly converted into the corresponding sulfoxides with high to excellent enantioselectivity. Thioacetals are also good substrates for the oxidation.

Keywords: aluminum · asymmetric catalysis · hydrogen peroxide · oxidation · sulfides

Introduction

Aluminum-based compounds are typical Lewis acid reagents for organic synthesis.[1] Owing to their high Lewis acidity, a variety of chiral aluminum complexes have been developed, and they are recognized as valuable catalysts for various asymmetric reactions such as carbon–carbon and carbon–heteroatom bond formations.[2] For example, Jacobsen and co-workers revealed that a chiral Al(salen) (salen = *N*,*N*′-ethylenebis(salicylideneiminato) complex is an efficient catalyst for the conjugate addition of nitrogen nucleophiles.[3] An elegant bifunctional catalyst based on aluminum and phosphine oxide was presented for the asymmetric cyanation of aldehydes by Shibasaki and co-workers.[4] Yamamoto and co-workers recently described the asymmetric conjugate addition of silyl enol ethers catalyzed by tethered bis(8-quinolinolato) aluminum complexes.[5] Despite the remarkable development of aluminum-based Lewis acid catalysts, their application to asymmetric oxidation has been rather limited.[6] Given that reagents such as titanium,[7] vanadium,[8] and molybdenum[9] complexes serve as not only Lewis acid catalysts but also oxidation catalysts, this situation is somewhat surprising. As a rare example, Bolm and co-workers reported a highly enantioselective aluminum-catalyzed Baeyer–Villiger oxidation, illustrating the potential of aluminum complexes as oxidation catalysts.[10]

On the other hand, optically active sulfoxides are of great importance as chiral auxiliaries in organic synthesis and are an important class of pharmaceuticals. Consequently, much research effort has been devoted to the development of effective catalysts for the asymmetric oxidation of sulfides, and a large number of chiral catalysts have been reported.[11] In 1984, the Kagan and Modena groups independently reported highly enantioselective sulfoxidation by using the 1:2:1 titanium/tartrate/H_2O or the 1:4 titanium/tartrate system.[12,13] Bolm and co-workers found that vanadium/Schiff base complexes efficiently catalyze the oxidation of sulfides with aqueous hydrogen peroxide as the oxidant, and they and others have further improved the catalysis.[14] Furthermore, Bolm and co-workers also developed an iron catalyst for the oxidation.[15,16] Although there are many catalysts for the asymmetric oxidation of sulfides, the development of more green, sustainable systems that realize the requirements of the use of an atom-efficient and economical stoichiometric oxidant such as aqueous hydrogen perox-

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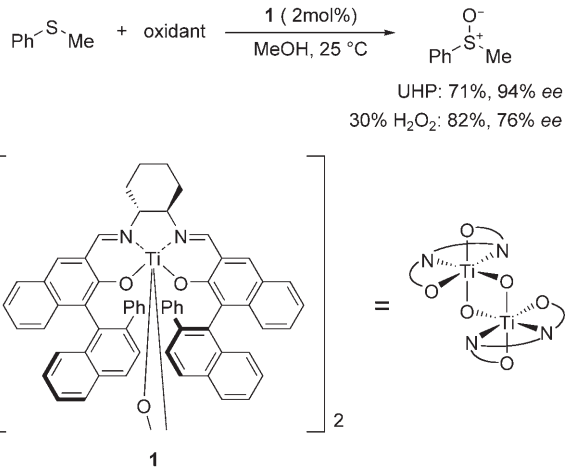
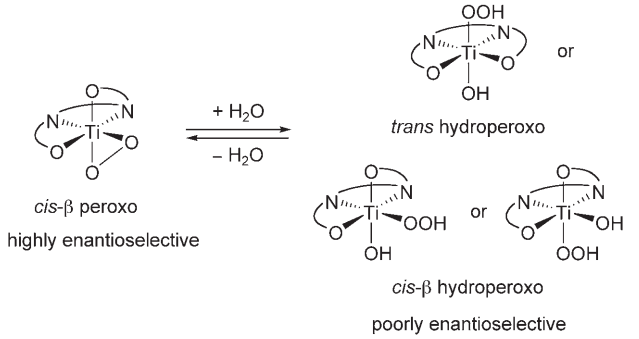
ide,[17] the employment of a nonhalogenated solvent, low catalyst loading, and ambient reaction conditions, still remain a challenge in organic chemistry.

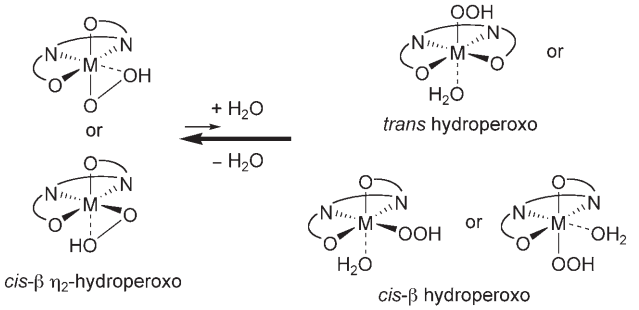
Recently, we reported that di-μ-oxo titanium(salen) complex **1** is an efficient catalyst for asymmetric sulfide oxidation in the presence of UHP (urea·hydrogen peroxide adduct) as the oxidant, and we proposed that a peroxo complex of *cis*-β structure is the active species (Scheme 1).[18] Al-



Scheme 1. Ti(salen)-catalyzed sulfide oxidation.



Scheme 2. A possible explanation of the degradation in enantioselectivity with aqueous H_2O_2.

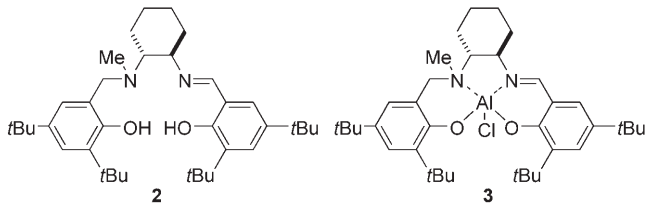


Scheme 3. Working hypothesis for an effective catalyst for oxidation with aqueous H_2O_2.

though high enantioselectivity was obtained with UHP, the employment of aqueous hydrogen peroxide as the oxidant resulted in a significant erosion of enantioselectivity. In the presence of water, the participation of poorly enantioselective hydroperoxo species in the oxidation was speculated upon (Scheme 2). This speculation led us to hypothesize that a trivalent metal complex of *cis*-β structure would be a better catalyst for oxidation with aqueous hydrogen peroxide, because the hydroperoxide species with a neutral aqua ligand should be easily transformed into an η^2-coordinated hydroperoxo species, and the participation of a monodentate hydroperoxide species should be significantly decreased (Scheme 3).

We also reported the synthesis of chiral salalen (half-reduced salen, that is, salan/salen-hybridized [ONNO]-type tetradentate ligand) ligand **2** and its aluminum complex **3**, which has a distorted trigonal-bipyramidal structure (Scheme 4); we found that complex **3** is an efficient catalyst for the hydrophosphonylation of aldehydes and imines.[19,20] To explore new catalysis with Al(salalen) complexes, we tried to modify the complex. During the course of this study, we found that treatment of an Al(salalen) complex with water yielded a new water-tolerant Al(salalen) species. Although we could not purify and fully identify the species, this finding indicated that Al(salalen) complexes might serve as catalysts for oxidation with aqueous hydrogen peroxide, as Al(salalen) complexes possibly adopt a *cis*-β structure in a six-coordinated state.

Herein, we report highly enantioselective sulfur oxidations with aqueous hydrogen peroxide as the oxidant, which were catalyzed by newly synthesized Al(salalen) complexes derived from binol (1,1′-bi-2,2′-naphthol) in methanol under ambient conditions.[21]



Scheme 4. Salalen ligand **2** and Al(salalen) complex **3**.

Abstract in Japanese:

光学活性なアルミニウム錯体は様々な不斉反応の触媒として用いられている。しかしながら、その不斉酸化触媒作用はほとんど明らかにされておらず、特に過酸化水素水を酸化剤として用いた高エナンチオ選択的酸化反応の報告例はない。今回，新たに合成したアルミニウム- サラレン錯体が、過酸化水素水を酸化剤とする不斉スルホ酸化の優れた触媒となることを見出した。種々のスルフィドを高エナンチオ選択的にスルホキシドへと変換することができ，チオアセタール類の酸化においても高い立体選択性が得られた。

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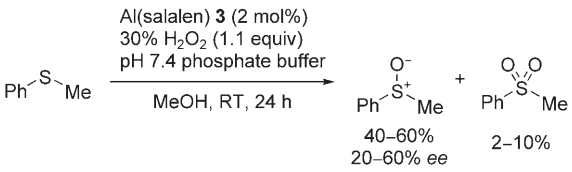
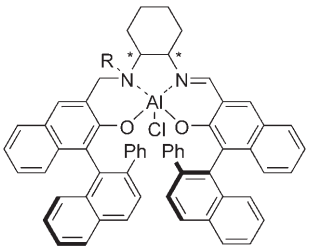
Results and Discussion

Asymmetric oxidation of thioanisole with complex **3** as the catalyst was first examined with 30% hydrogen peroxide as the oxidant in the presence of pH 7.4 phosphate buffer, and we found that the desired sulfoxide was obtained with moderate enantioselectivity, albeit with poor reproducibility (Scheme 5).



Scheme 5. Asymmetric oxidation of thioanisole with complex **3**.

Thus, we explored more-effective Al(salalen) complexes for oxidation, and found that Al(salalen) complexes **4**–**7**, which bear a binol-derived axially chiral component that was developed by our group, showed better catalysis (Scheme 6).[22]

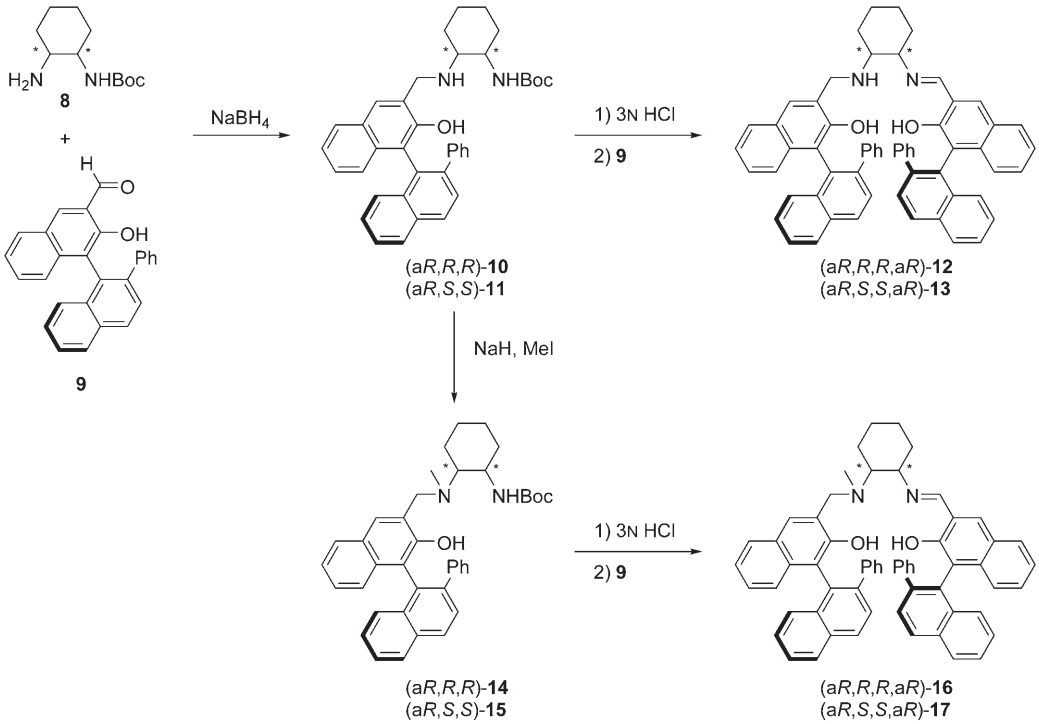


4: (a*R*,*R*,*R*,a*R*), R = H
5: (a*R*,*R*,*R*,a*R*), R = Me
6: (a*R*,*S*,*S*,a*R*), R = H
7: (a*R*,*S*,*S*,a*R*), R = Me

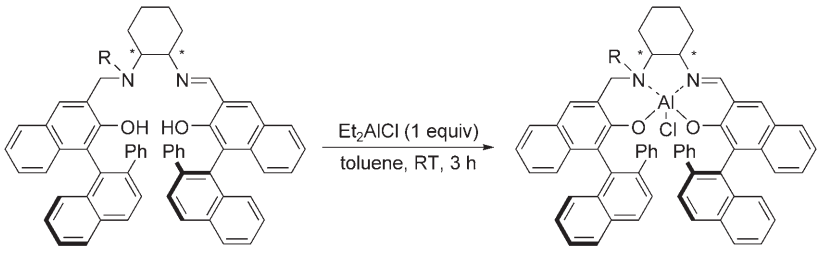
Scheme 6. Binol-derived Al(salalen) complexes **4**–**7**.

The necessary salalen ligands could not be obtained in satisfactory yields with the procedure[19] used for the preparation of salalen ligand **2**; however, they were prepared by modified routes (Scheme 7). First, synthetic intermediates **10** and **11** were prepared by reductive amination of binol-derived salicylaldehyde **9** with the corresponding Boc-protected cyclohexanediamine (*R*,*R*)- or (*S*,*S*)-**8**. Removal of the protecting group and the following condensation with salicylaldehyde **9** afforded salalen ligand **12** and its diastereomer **13** in high yields, respectively. Notably, the salalen ligands could be prepared without any purification methods such as chromatography and recrystallization, except for filtration in the last step of the synthesis. Salalen ligands **16** and **17** were prepared by N methylation of **10** and **11**, respectively, followed by deprotection and condensation. Finally, Al(salalen) complexes **4**–**7** were prepared from the corresponding salalen ligands and diethylaluminum chloride in toluene, and the desired complexes were isolated with acceptable yields and purity by filtration of the precipitates obtained by addition of hexane to the reaction mixture (Scheme 8). The complexes were used without further purification in the following asymmetric oxidation.

With these Al(salalen) complexes in hand, we examined the asymmetric oxidation of thioanisole in methanol



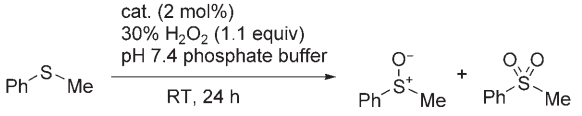
Scheme 7. Synthesis of salalen ligands. Boc = *tert*-butoxycarbonyl.



Scheme 8. Synthesis of Al(salalen) complexes **4**–**7**.

(Table 1, entries 1–4). Whereas (a*R*,*R*,*R*,a*R*)-type complexes **4** and **5** were poorly enantioselective, (a*R*,*S*,*S*,a*R*)-type complexes, especially N-methylated **7**, showed high catalytic activity with good reproducibility, and the corresponding sulfoxide was obtained in high yield with excellent enantioselectivity. With complex **7**, we further tested the effect of the solvent with ethanol, ethyl acetate, tetrahydrofuran, dichloromethane, and toluene (Table 1, entries 5–9). Although high enantioselectivity was obtained regardless of the solvent used, the reaction in methanol gave the highest yield accompanied by the smallest amount of the overoxidation product, sulfone. Although the *ee* of the desired sulfoxide was as high as 94% at the early stage of the reaction when only a trace amount of the sulfone was formed, the *ee* and the amount of sulfone increased as the reaction proceeded (Table 1, entry 10 vs. entry 4).

Table 1. Asymmetric oxidation of thioanisole.

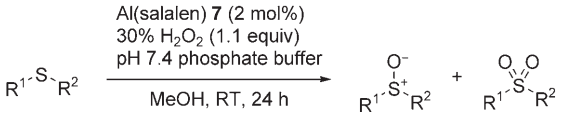


Entry	Cat.	Solvent	Conv. of sulfide[a] [%]	Yield[a] [%] sulfoxide	sulfone	*ee*[b,c] [%]
1	**4**	MeOH	70	64	6	46 (*S*)
2	**5**	MeOH	55	51	4	10 (*R*)
3	**6**	MeOH	86	78	8	89 (*S*)
4	**7**	MeOH	99	90	9	98 (*S*)
5	**7**	EtOH	92	78	14	98 (*S*)
6	**7**	AcOEt	85	68	17	97 (*S*)
7	**7**	THF	85	66	18	98 (*S*)
8	**7**	CH_2Cl_2	91	78	13	99 (*S*)
9	**7**	$PhCH_3$	84	59	25	99 (*S*)
10[d]	**7**	MeOH	33	32	<1	94 (*S*)

[a] Determined by ^{1}H NMR spectroscopic analysis (400 MHz). [b] The *ee* value was determined by chiral HPLC analysis. [c] The absolute configuration was determined by HPLC analysis by comparison of the order of elution of the enantiomers with that of an authentic sample. [d] Reaction time: 1 h.

The scope of sulfide substrates was investigated with complex **7** under the optimized conditions (Table 2). The reactions of aryl methyl sulfides proceeded smoothly to give the corresponding sulfoxides in high yields with excellent enantioselectivity, irrespective of the electronic nature and the location of the substituent on the aromatic ring (Table 2, entries 1–8). In the reaction of *ortho*-substituted aryl methyl sulfides, the formation of sulfone was significantly retarded (Table 2, entries 5–7). The oxidation could be carried out on the gram scale without any loss of enantioselectivity (Table 2, entry 6). This catalytic system was also applicable to the oxidation of sulfides other than aryl methyl sulfides. Ethyl phenyl sulfide is a good substrate for the oxidation; it gave the sulfoxide in high yield with high enantioselectivity. The oxidation of benzyl methyl sulfide was high-yielding, albeit with a slightly diminished enantioselectivity of 80% (Table 2, entries 9 and 10).

Table 2. Asymmetric oxidation of various sulfides with complex **7**.[a]



Entry	R^1	R^2	Yield [%] sulfoxide[b]	sulfone[c]	*ee*[d,e] [%]
1	Ph	Me	86	9	98 (*S*)
2	*p*-ClC_6H_4	Me	83	9	97 (*S*)
3	*p*MeC_6H_4	Me	82	9	98 (*S*)
4	*p*$MeOC_6H_4$	Me	82	8	97 (*S*)
5	*o*$MeOC_6H_4$	Me	82	1	99 (*S*)
6[f]	*o*$MeOC_6H_4$	Me	91	<1	99 (*S*)
7	*o*-$NO_2C_6H_4$	Me	84	2	99 (−)
8	*m*-BrC_6H_4	Me	81	10	99 (*S*)
9	Ph	Et	80	n.d.[g]	91 (*S*)
10	$PhCH_2$	Me	83	n.d.[g]	80 (*S*)

[a] The reaction was carried out on the 0.20-mmol scale, unless otherwise noted. [b] Yield of the isolated sulfoxide. [c] Determined by ^{1}H NMR spectroscopic analysis (400 MHz). [d] The *ee* value was determined by chiral HPLC analysis. [e] The absolute configuration was determined by HPLC analysis by comparison of the order of elution of the enantiomers with that of an authentic sample. [f] The reaction was carried out on the 10.0-mmol scale. [g] Not determined.

Asymmetric desymmetrization of thioacetals by sulfur oxidation was also examined (Scheme 9). In the reactions of 2-substituted 1,3-dithianes, there were significant amounts of overoxidation by-products, the sulfone and disulfoxide, observed at room temperature, but the formation of the by-products were effectively suppressed at 10 °C, and the monosulfoxide was obtained in high yield with high enantioselectivity. Reaction of 2-methyl-2-phenyl-1,3-dithiane also proceeded to give the sulfoxide with 99% *ee*.

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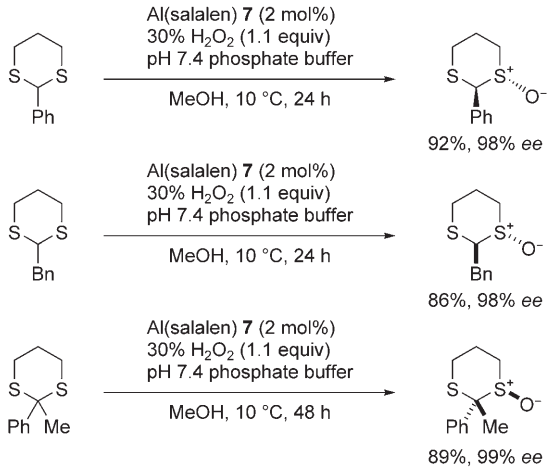
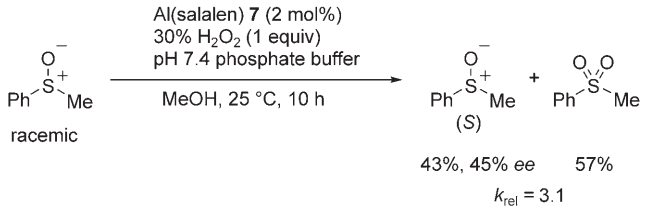


Scheme 9. Asymmetric desymmetrization of thioacetals. Bn = benzyl.

As described above, the overoxidation of the sulfoxide products to the corresponding sulfones was observed in this reaction. Thus, we examined the oxidative kinetic resolution of racemic sulfoxides with complex **7** as the catalyst (Scheme 10). When racemic methyl phenyl sulfide was exposed to the reaction conditions, methyl phenyl sulfone was obtained in 57% yield after 10 h, and the *S* sulfoxide was dominantly recovered.[23] This result shows that the *R* sulfoxide was preferentially oxidized to the sulfone. On the other hand, the *S* sulfoxide was selectively produced in the oxidation of thioanisole in the presence of complex **7**. These results explain the gradual increase in the *ee* value of the formed sulfoxide as the reaction proceeds in the oxidation of sulfides. The high enantiomeric excesses of the sulfoxides observed were achieved by cooperation of the highly enantioselective sulfide oxidation process and the following oxidative kinetic resolution process.[24]



Scheme 10. Kinetic resolution of racemic methyl phenyl sulfoxide.

Conclusions

We have developed a highly enantioselective oxidation of sulfides and thioacetals with newly synthesized binol-derived aluminum(salalen) complexes. This system employs environmentally friendly aqueous hydrogen peroxide as the oxidant and methanol as the solvent.

Experimental Section

General

All reactions were carried out in oven-dried glassware with magnetic stirring. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL AL-400 spectrometer. Tetramethylsilane (TMS) served as the internal standard (0 ppm) for ^{1}H NMR, and $CDCl_3$ was used as the internal standard (77.0 ppm) for ^{13}C NMR spectroscopy. Optical rotations were measured on a JASCO P-1020 polarimeter. Infrared spectra were recorded as KBr disks on a SHIMADZU FTIR-8600 spectrophotometer. High-performance liquid chromatography was carried out on a SHIMADZU LC-10AT-VP chromatograph equipped with a variable-wavelength detector on chiral stationary columns from DAICEL. All reagents and solvents were used as supplied commercially. Thioacetals were prepared according to published procedures. All the products in Table 2 and Scheme 8 except for (−)-*trans*-2-methyl-2-phenyl-1,3-dithiane 1-oxide gave spectroscopic data in agreement with those reported in the literature,[14e,15c,17,25–26] and only their optical rotations are given.

Syntheses

10: Aldehyde **9** (374 mg, 1.0 mmol) was added to a solution of (*R*,*R*)-**8** (214 mg, 1.0 mmol) in THF/MeOH (1:1, 4 mL) at room temperature, and the resulting solution was stirred for 1 h. Sodium borohydride (60 mg, 1.5 mmol) was then added to the mixture. After 1 h, water was added, and the mixture was extracted with Et_2O, washed with brine, and dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure to give **10**. The product was used in the following reaction without further purification. ^{1}H NMR ($CDCl_3$): δ = 11.26 (br s, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.65–7.62 (m, 2H), 7.47 (s, 1H), 7.45–7.41 (m, 1H), 7.32–6.99 (m, 10H), 4.30–4.27 (m, 2H), 4.09 (d, J = 14.2 Hz, 1H), 3.34–3.32 (m, 1H), 2.28–2.22 (m, 1H), 1.95–1.84 (m, 2H), 1.67–1.59 (m, 2H), 1.38–1.03 (m, 12H), 0.98–0.89 ppm (m, 1H).

11: Compound **11** was prepared in the same manner as described for **10**, except that (*S*,*S*)-**8** (214 mg, 1.0 mmol) was used instead of (*R*,*R*)-**8**. ^{1}H NMR ($CDCl_3$): δ = 10.98 (br s, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.49 (s, 1H), 7.44–7.41 (m, 1H), 7.29–7.11 (m, 7H), 7.07–7.03 (m, 3H), 4.24–4.08 (m, 3H), 3.29–3.20 (m, 1H), 2.14–2.12 (m, 1H), 1.91–1.81 (m, 2H), 1.67–1.64 (m, 2H), 1.34–1.18 (m, 10H), 1.07–0.92 ppm (m, 3H).

12: Aqueous HCl (3 N, 2 mL) was added to a solution of **10** in MeOH (6.0 mL), and the resulting solution was warmed to 60 °C and stirred overnight. After cooling, the mixture was neutralized with 3 N NaOH, extracted with Et_2O, washed with brine, and dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure to give the deprotected product. The product was dissolved in EtOH (10 mL). Aldehyde **9** (340 mg, 0.92 mmol) was added to the solution, and the resulting mixture was heated at reflux and stirred for 2 h. After cooling to 0 °C, the precipitate was filtered off and washed with cold ethanol to give salalen ligand **12** (690 mg, 83% from **8**). Yellow powder; FTIR (KBr): $\tilde{\nu}$ = 3053, 2928, 2855, 1628, 1502, 1439, 1344, 1256, 943, 822, 754, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 12.72 (s, 1H), 11.52 (br s, 1H), 8.48 (s, 1H), 8.03–7.90 (m, 4H), 7.71–7.68 (m, 2H), 7.66–7.62 (m, 2H), 7.54–7.52 (m, 1H), 7.43–7.37 (m, 3H), 7.29–6.98 (m, 20H), 4.28 (d, J = 14.7 Hz, 1H), 3.93 (d, J = 14.7 Hz, 1H), 3.00–2.94 (m, 1H), 2.71–2.65 (m, 1H), 1.98–1.16 (m, 8H), 0.82–0.72 ppm (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 165.4, 154.2, 153.7, 142.2, 142.0, 140.3, 139.8, 135.6, 133.9, 133.2, 132.9, 132.8, 132.7, 131.7, 130.9, 128.8, 128.5, 128.2, 128.0, 128.0, 127.8, 127.8, 127.5, 127.3, 127.0, 126.9, 126.9, 126.5, 126.4, 126.3, 126.2, 126.1, 126.1, 126.0, 125.7, 125.6, 125.5, 125.4, 124.8, 124.7, 123.1, 122.5, 120.0, 119.8, 119.3, 73.9, 61.6, 51.2, 33.6, 29.7, 24.5, 24.1 ppm; elemental analysis: calcd (%) for $C_{60}H_{48}N_2O_2$: C 86.93, H 5.84, N 3.38; found: C 86.80, H 5.81, N 3.42.

13: Salalen ligand **13** was prepared in 89% yield from **8** in the same manner as described for **12**, except that **11** was used instead of **10**. Yellow powder; FTIR (KBr): $\tilde{\nu}$ = 3053, 2928, 2856, 1628, 1502, 1439, 1348, 1256, 1113, 1076, 943, 822, 754, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 12.95 (s, 1H), 11.12 (br s, 1H), 8.33 (s, 1H), 8.04–7.92 (m, 4H), 7.66–7.61 (m, 4H), 7.47–7.39 (m, 3H), 7.33–6.99 (m, 15H), 6.62–6.54 (m, 4H), 6.42–6.35 (m, 2H), 4.16 (d, J = 14.1 Hz, 1H), 3.95 (d, J = 14.1 Hz, 1H), 2.98–2.92 (m,

1H), 2.78–2.72 (m, 1H), 2.03–2.00 (m, 1H), 1.73–1.16 ppm (m, 8H); ^{13}C NMR ($CDCl_3$): δ=165.1, 154.3, 153.7, 142.0, 141.8, 141.4, 140.0, 135.4, 133.7, 133.3, 133.0, 132.9, 132.8, 132.7, 131.7, 130.9, 128.7, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.4, 127.1, 127.0, 126.9, 126.5, 126.3, 126.1, 126.0, 125.7, 125.5, 125.4, 125.3, 124.8, 124.6, 123.1, 122.7, 120.2, 119.9, 119.7, 74.0, 61.4, 51.0, 33.8, 30.9, 24.5, 24.3 ppm; elemental analysis: calcd (%) for $C_{60}H_{48}N_2O_2$: C 86.93, H 5.84, N 3.38; found: C 86.83, H 5.87, N 3.36.

14: Sodium hydride (60% dispersion in oil, 100 mg, 2.5 mmol) was added to a solution of **10** in THF (4.0 mL) at 0°C, and the resulting solution was stirred for 30 min. Methyl iodide (100 mL, 1.6 mmol) was added to the solution. After 1 h, water was added, and the mixture was extracted with Et_2O, washed with brine, and dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The crude product was purified by silica-gel chromatography (*n*-hexane/AcOEt=4:1) to give **14** (550 mg, 94% from **8**). White solid; $[\alpha]_D=+184.2$ (c=3.02, $CHCl_3$); FTIR (KBr): $\tilde{\nu}$=3410, 3053, 2930, 2858, 1711, 1626, 1593, 1504, 1443, 1356, 1315, 1258, 1167, 1107, 1034, 945, 862, 822, 754, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=11.54 (br s, 1H), 7.97–7.92 (m, 2H), 7.64–7.58 (m, 2H), 7.46–7.42 (m, 2H), 7.37 (d, J=8.3 Hz, 1H), 7.30–7.04 (m, 6H), 7.00–6.95 (m, 3H), 4.36 (d, J=9.8 Hz, 1H), 4.08 (d, J=13.7 Hz, 1H), 3.92 (d, J=13.7 Hz, 1H), 3.63–3.54 (m, 1H), 2.46–2.39 (m, 1H), 2.09 (s, 3H), 2.06–2.03 (m, 1H), 1.95–1.92 (m, 1H), 1.83–1.80 (m, 1H), 1.71–1.68 (m, 1H), 1.40–1.03 ppm (m, 13H); ^{13}C NMR ($CDCl_3$): δ=155.2, 154.1, 142.3, 140.1, 133.7, 133.0, 132.8, 132.1, 128.6, 128.0, 127.8, 127.4, 127.3, 127.1, 126.9, 126.4, 126.1, 125.9, 125.6, 125.2, 124.7, 124.0, 122.4, 119.2, 79.2, 66.2, 59.5, 50.8, 34.6, 33.8, 28.2, 25.3, 25.1, 23.2 ppm; elemental analysis: calcd (%) for $C_{39}H_{42}N_2O_3$: C 79.83, H 7.21, N 4.77; found: C 79.79, H 7.31, N 4.71.

15: Compound **15** was prepared in 90% yield from **11** in the same manner as described for **14**. White solid; $[\alpha]_D=-158.2$ (c=3.03, $CHCl_3$); FTIR (KBr): $\tilde{\nu}$=3406, 3053, 2932, 2858, 1711, 1626, 1593, 1504, 1443, 1358, 1317, 1256, 1167, 1107, 1022, 984, 945, 862, 822, 756, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=11.11 (br s, 1H), 7.98 (d, J=8.5 Hz, 1H), 7.92 (d, J=8.1 Hz, 1H), 7.73–7.71 (m, 1H), 7.65 (d, J=8.5 Hz, 1H), 7.48 (s, 1H), 7.43–7.39 (m, 1H), 7.27–7.17 (m, 7H), 7.05–7.03 (m, 3H), 4.06–4.03 (m, 2H), 3.85 (d, J=13.7 Hz, 1H), 3.56–3.47 (m, 1H), 2.16 (s, 3H), 2.01–1.96 (m, 1H), 1.91–1.88 (m, 2H), 1.77–1.73 (m, 1H), 1.64–1.61 (m, 1H), 1.23–1.13 (m, 11H), 1.03–0.87 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ=155.2, 153.4, 142.5, 139.6, 134.8, 133.1, 132.8, 131.5, 128.9, 128.1, 127.7, 127.6, 127.3, 127.3, 127.2, 126.7, 126.2, 126.0, 126.0, 125.3, 125.0, 124.1, 122.5, 118.6, 79.1, 63.5, 57.9, 50.6, 35.5, 34.2, 28.2, 25.2, 25.0, 22.3 ppm; elemental analysis: calcd (%) for $C_{39}H_{42}N_2O_3$: C 79.83, H 7.21, N 4.77; found: C 79.83, H 7.25, N 4.59.

16: Aqueous HCl (3N 2.0 mL) was added to a solution of **14** (400 mg, 0.68 mmol) in MeOH (5.0 mL), and the resulting solution was warmed to 60°C and stirred overnight. After cooling, the mixture was neutralized with 3N NaOH, extracted with Et_2O, washed with brine, and dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure to give the deprotected product. The product was dissolved in EtOH (12 mL). Aldehyde **9** (230 mg, 0.61 mmol) was added to the solution, and the resulting mixture was heated at reflux and stirred for 3 h. After cooling to 0°C, the precipitate was filtered off and washed with cold ethanol to give salalen ligand **16** (440 mg, 76%). Yellow powder; FTIR (KBr): $\tilde{\nu}$=3051, 2928, 2856, 1630, 1501, 1437, 1344, 1319, 1256, 1111, 1024, 945, 860, 820, 754, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=13.03 (s, 1H), 10.75 (br s, 1H), 8.61 (s, 1H), 8.01 (d, J=8.5 Hz, 1H), 7.91 (d, J=8.3 Hz, 1H), 7.80–7.74 (m, 3H), 7.69–7.62 (m, 2H), 7.40–6.94 (m, 24H), 6.79–6.75 (m, 1H), 4.07 (d, J=13.7 Hz, 1H), 3.91 (d, J=13.7 Hz, 1H), 3.50–3.44 (m, 1H), 2.83–2.77 (m, 1H), 2.05 (s, 3H), 1.84–1.73 (m, 3H), 1.59–1.39 (m, 3H), 1.28–1.19 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ=164.0, 154.6, 153.6, 142.3, 142.0, 139.9, 139.6, 134.9, 134.1, 132.9, 132.7, 132.6, 131.5, 131.1, 128.7, 128.6, 128.3, 127.9, 127.9, 127.6, 127.5, 127.4, 127.3, 127.0, 126.8, 126.7, 126.4, 126.2, 126.0, 125.9, 125.7, 125.6, 125.2, 124.8, 124.7, 123.8, 123.0, 122.3, 120.0, 119.8, 118.6, 70.0, 64.8, 58.9, 35.7, 34.9, 27.3, 25.3, 24.3 ppm; elemental analysis: calcd (%) for $C_{61}H_{50}N_2O_2$: C 86.90, H 5.98, N 3.32; found: C 86.50, H 5.97, N 3.22.

17: Salalen ligand **17** was prepared in 80% yield from **15** in the same manner as described for **16**. Yellow powder; FTIR (KBr): $\tilde{\nu}$=3051, 2928, 2855, 1626, 1501, 1437, 1342, 1254, 1111, 1024, 945, 860, 820, 752, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=12.99 (s, 1H), 11.16 (br s, 1H), 8.58 (s, 1H), 8.06 (d, J=8.3 Hz, 1H), 7.99–7.91 (m, 3H), 7.76–7.74 (m, 2H), 7.69 (d, J=8.5 Hz, 1H), 7.61 (d, J=8.5 Hz, 1H), 7.51–7.41 (m, 3H), 7.35–6.91 (m, 21H), 4.08 (d, J=14.2 Hz, 1H), 3.80 (d, J=14.2 Hz, 1H), 3.50–3.45 (m, 1H), 2.91–2.85 (m, 1H), 2.10 (s, 3H), 1.79–1.69 (m, 4H), 1.53–1.44 (m, 2H), 1.26–1.18 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ=164.4, 154.2, 153.6, 142.3, 141.9, 140.3, 140.0, 135.5, 133.9, 133.0, 132.8, 132.8, 132.7, 131.8, 130.8, 128.7, 128.6, 128.5, 128.2, 128.0, 128.0, 127.9, 127.7, 127.4, 127.3, 127.1, 126.9, 126.8, 126.5, 126.3, 126.2, 126.0, 125.9, 125.6, 125.5, 125.4, 125.0, 124.7, 124.1, 123.1, 122.5, 120.1, 118.9, 70.6, 65.4, 60.1, 35.4, 35.3, 30.1, 25.3, 24.3 ppm; elemental analysis: calcd (%) for $C_{61}H_{50}N_2O_2$: C 86.90, H 5.98, N 3.32; found: C 86.68, H 6.02, N 3.32.

Typical procedure for the preparation of aluminum(salalen) complexes: Diethylaluminum chloride (217 mL, 0.92M in hexane, 0.20 mmol) was added to a solution of salalen ligand **17** (169 mg, 0.20 mmol) in toluene (1.0 mL), and the red solution was stirred at room temperature. After 3 h, hexane (500 mL) was added to the reaction mixture. The resultant yellow precipitate was filtered off and washed with hexane to give complex **7** (128 mg, 70%) as a yellow solid. The crude product was used in the following reaction without further purification.

4: 76%; ^{1}H NMR (CD_3OD): δ=8.53 (d, J=2.0 Hz, 1H), 8.23–8.08 (m, 5H), 7.81 (d, J=8.1 Hz, 1H), 7.68 (d, J=8.1 Hz, 1H), 7.62 (s, 1H), 7.56–7.52 (m, 1H), 7.51–7.47 (m, 1H), 7.41 (d, J=8.3 Hz, 1H), 7.34 (d, J=8.5 Hz, 1H) 7.21–7.01 (m, 6H), 6.92–6.89 (m, 2H), 6.83–6.74 (m, 3H), 6.69 (d, J=8.3 Hz, 1H), 6.59–6.55 (m, 2H), 6.49–6.43 (m, 4H), 6.23–6.21 (m, 2H), 4.15 (d, J=13.4 Hz, 1H), 3.82–3.73 (m, 1H), 3.14–3.05 (m, 1H), 2.65–2.55 (m, 2H), 2.43–2.31 (m, 1H), 2.09–1.91 (m, 2H), 1.52–1.15 ppm (m, 4H).

5: 71%; ^{1}H NMR (CD_3OD): δ=8.48 (d, J=1.7 Hz, 1H), 8.27 (d, J=8.5 Hz, 1H), 8.16 (d, J=8.3 Hz, 1H), 8.06–8.04 (m, 2H), 7.99 (d, J=8.1 Hz, 1H), 7.78–7.75 (m, 1H), 7.72–7.68 (m, 2H), 7.60–7.57 (m, 2H), 7.49–7.45 (m, 2H), 7.30–7.26 (m, 1H), 7.20–7.05 (m, 7H), 6.87–6.85 (m, 1H), 6.77–6.74 (m, 1H), 6.69–6.67 (m, 1H), 6.64–6.60 (m, 1H), 6.47–6.40 (m, 4H), 6.22–6.18 (m, 2H), 6.07–6.05 (m, 2H), 3.96–3.91 (m, 2H), 3.57–3.51 (m, 1H), 3.15–3.10 (m, 1H), 2.60–2.49 (m, 2H), 2.33–2.26 (m, 1H), 2.02–1.93 (m, 2H), 1.47–1.23 ppm (m, 4H).

6: 77%; ^{1}H NMR (CD_3OD): δ=8.60 (s, 1H), 8.25–8.16 (m, 4H), 8.10 (s, 1H), 7.79 (d, J=7.8 Hz, 1H), 7.70 (d, J=8.0 Hz, 1H), 7.63 (s, 1H), 7.61–7.57 (m, 1H), 7.54–7.45 (m, 2H), 7.24–6.56 (m, 19H), 6.28–6.26 (m, 2H), 4.19 (d, J=13.5 Hz, 1H), 3.93 (d, J=13.5 Hz, 1H), 3.38–3.33 (m, 1H), 2.73–2.61 (m, 2H), 2.31–2.28 (m, 1H), 2.01–1.96 (m, 5H), 1.45–1.29 ppm (m, 4H).

7: 70%; ^{1}H NMR (CD_3OD): δ=8.62 (d, J=1.7 Hz, 1H), 8.23 (d, , J=8.3 Hz, 1H), 8.14–8.10 (m, 2H), 8.01–7.97 (m, 2H), 7.79–7.75 (m, 2H), 7.70–7.67 (m, 1H), 7.60–7.54 (m, 2H), 7.47–7.43 (m, 2H), 7.31–7.07 (m, 8H), 6.88–6.86 (m, 1H), 6.82–6.78 (m, 1H), 6.68–6.60 (m, 4H), 6.53–6.49 (m, 2H), 6.19–6.10 (m, 4H), 3.98 (d, J=13.2 Hz, 1H), 3.73 (d, J=13.2 Hz, 1H), 3.51–3.41 (m, 1H), 2.73–2.54 (m, 2H), 2.25–2.22 (m, 1H), 2.04 (s, 3H), 1.98–1.96 (m, 2H), 1.50–1.25 ppm (m, 4H).

Typical procedure for the asymmetric oxidation of sulfides: Thioanisole (24.8 mg, 0.20 mmol), phosphate buffer (20.0 mL, pH 7.4, 67 mmol L^{-1}), and hydrogen peroxide (30%, 25.0 mg, 0.22 mmol) were added to a solution of Al(salalen) complex **7** (3.6 mg, 0.004 mmol) in methanol (2.0 mL), and the mixture was stirred at room temperature. After 24 h, the mixture was concentrated under reduced pressure, and the residue was subjected to chromatography on silica gel (hexane/acetone=4:1→1:1) to afford methyl phenyl sulfoxide (24.1 mg, 86%). The enantiomeric excess (98% *ee*) was determined by chiral HPLC analysis with a Daicel Chiralcel OB-H column (*n*-hexane/*i*PrOH=4:1).

(−)-(*S*)-Methyl phenyl sulfoxide: 86%, 98% *ee* (CHIRALCEL OB-H); $[\alpha]_D=-134.8$ (c=0.83, acetone) (reference [15c]: $[\alpha]_D=-130.1$ (c=1.7, acetone), 90% *ee*, *S* isomer).

(−)-(*S*)-*p*-Chlorophenyl methyl sulfoxide: 83%, 97% *ee* (CHIRALCEL OB-H); $[\alpha]_D = -115.5$ ($c = 1.78$, acetone) (reference [15c]: $[\alpha]_D = -109.7$ ($c = 2.0$, acetone), 92% *ee*, *S* isomer).

(−)-(*S*)-Methyl *p*-methylphenyl sulfoxide: 82%, 98% *ee* (CHIRALCEL OB-H); $[\alpha]_D = -144.9$ ($c = 0.87$, acetone) (reference [15c]: $[\alpha]_D = -126.9$ ($c = 2.0$, acetone), 92% *ee*, *S* isomer).

(−)-(*S*)-*p*-Methoxyphenyl methyl sulfoxide: 82%, 97% *ee* (CHIRALCEL OB-H); $[\alpha]_D = -164.2$ ($c = 1.55$, $CHCl_3$) (reference [15c]: $[\alpha]_D = -129.7$ ($c = 2.0$, $CHCl_3$), 86% *ee*, *S* isomer).

(−)-(*S*)-*o*-Methoxyphenyl methyl sulfoxide: 82%, 99% *ee* (CHIRALCEL OB-H); $[\alpha]_D = -324.7$ ($c = 1.33$, acetone) (reference [15c]: $[\alpha]_D = -36.0$ ($c = 0.9$, acetone), 70% *ee*, *S* isomer).

(−)-Methyl *o*-nitrophenyl sulfoxide: 84%, 99% *ee* (CHIRALCEL OD-H); $[\alpha]_D = -126.6$ ($c = 1.53$, $CHCl_3$).

(−)-(*S*)-*m*-Bromophenyl methyl sulfoxide: 81%, 99% *ee* (CHIRALCEL OB-H); $[\alpha]_D = -103.4$ ($c = 1.21$, acetone) (reference [25]: $[\alpha]_D = -110.4$ ($c = 1.33$, acetone), >99.9% *ee*, *S* isomer).

(−)-(*S*)-Ethyl phenyl sulfoxide: 80%, 91% *ee* (CHIRALCEL OD-H); $[\alpha]_D = -182.1$ ($c = 1.08$, EtOH) (reference [15c]: $[\alpha]_D = -169.1$ ($c = 1.4$, EtOH), 82% *ee*, *S* isomer).

(+)-(*S*)-Benzyl methyl sulfoxide: 83%, 80% *ee* (CHIRALCEL OB-H); $[\alpha]_D = +77.0$ ($c = 0.64$, EtOH) (reference [26]: $[\alpha]_D = +104$ ($c = 0.15$, EtOH), 100% *ee*, *S* isomer).

Typical procedure for the asymmetric oxidation of thioacetals: 2-Phenyl-1,3-dithiane (39.3 mg, 0.20 mmol), phosphate buffer (20.0 mL, pH 7.4, 67 mmol L^{-1}), and hydrogen peroxide (30%, 25.0 mg, 0.22 mmol) were added to a solution of Al(salalen) complex **7** (3.6 mg, 0.004 mmol) in methanol (1.0 mL) at 10 °C, and the mixture was stirred for 24 h. Aqueous sodium thiosulfate was added, the mixture was extracted with ethyl acetate, and the organic phase was dried over sodium sulfate. After filtration, the solvents were removed under reduced pressure, and the residue was subjected to chromatography on silica gel (ethyl acetate) to give the oxide (39.4 mg, 93%). The enantiomeric excess (98% *ee*) was determined by chiral HPLC analysis with a Daicel Chiralcel OD-H column (*n*-hexane/*i*PrOH = 7:3).

(+)-*trans*-(1*S*,2*S*)-2-Phenyl-1,3-dithiane 1-oxide: 92%, 98% *ee* (CHIRALCEL OD-H); $[\alpha]_D = +118.7$ ($c = 0.88$, $CHCl_3$) (reference [27]: $[\alpha]_D = +94$ ($c = 1.2$, $CHCl_3$), >98% *ee*, *S*,*S* isomer).

(−)-*trans*-2-Benzyl-1,3-dithiane 1-oxide: 86%, 98% *ee* (CHIRALPAK AD-H); $[\alpha]_D = -72.9$ ($c = 0.33$, $CHCl_3$); FTIR (KBr): $\tilde{\nu} = 3026$, 2901, 2849, 1491, 1427, 1263, 1219, 1169, 1080, 1022, 912, 867, 826, 758, 702, 594 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.36$–7.28 (m, 5H), 3.79 (dd, $J = 3.4$, 10.0 Hz, 1H), 3.71 (dd, $J = 3.4$, 14.2 Hz, 1H), 3.49–3.46 (m, 1H), 2.97 (dd, $J = 10.0$, 14.2 Hz, 1H), 2.71–2.58 (m, 2H), 2.53–2.41 (m, 2H), 2.32–2.20 ppm (m, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 135.4$, 129.5, 128.3, 127.1, 67.5, 54.0, 34.8, 30.2, 29.7 ppm; elemental analysis: calcd (%) for $C_{11}H_{14}OS_2$: C 58.37, H 6.23; found: C 58.26, H 6.16.

(−)-*trans*-2-Methyl-2-phenyl-1,3-dithiane 1-oxide: 89%, 99% *ee* (CHIRALCEL OD-H); $[\alpha]_D = -76.7$ ($c = 1.18$, $CHCl_3$).

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