



Enantioselective Diels-Alder Reactions Catalyzed by Chiral Magnesium Lewis Acids Prepared from Hydroxysulfoxides

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Abstract: Enantioselective Diels-Alder reactions were conducted successfully using chiral magnesium complexes prepared from magnesium iodide and chiral hydroxysulfoxides derived from (*R*)- and (*S*)-methyl 1-naphthyl sulfoxide. Convenient methods for the preparation of these chiral sulfoxides have also been developed. Hydroxysulfoxide **6** (and its enantiomer **10**) showed the highest enantioselectivity.

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The Diels-Alder reaction has long been recognized as one of the most useful processes for the construction of complex molecules, being a standard method for six-membered ring formation¹. Recently, there has been a great deal of activity in the area of asymmetric catalytic reactions, particularly enantioselective, Lewis acid-catalyzed Diels-Alder reactions². The Lewis acids employed in these processes are generally traditional ones such as titanium, boron or aluminium reagents³ and other metals such as iron⁴, copper^{5,4c,d} magnesium^{6,4c,d} and lanthanides (Sc, Yb)⁷ have also been used sporadically. In order to make chiral Lewis acids, the metals have normally been modified by chelation with non racemic diols, aminoalcohols or diamino derivatives which act as bidentate ligands². Very much less attention has been paid to bidentate sulfoxide ligands^{8,4b}.

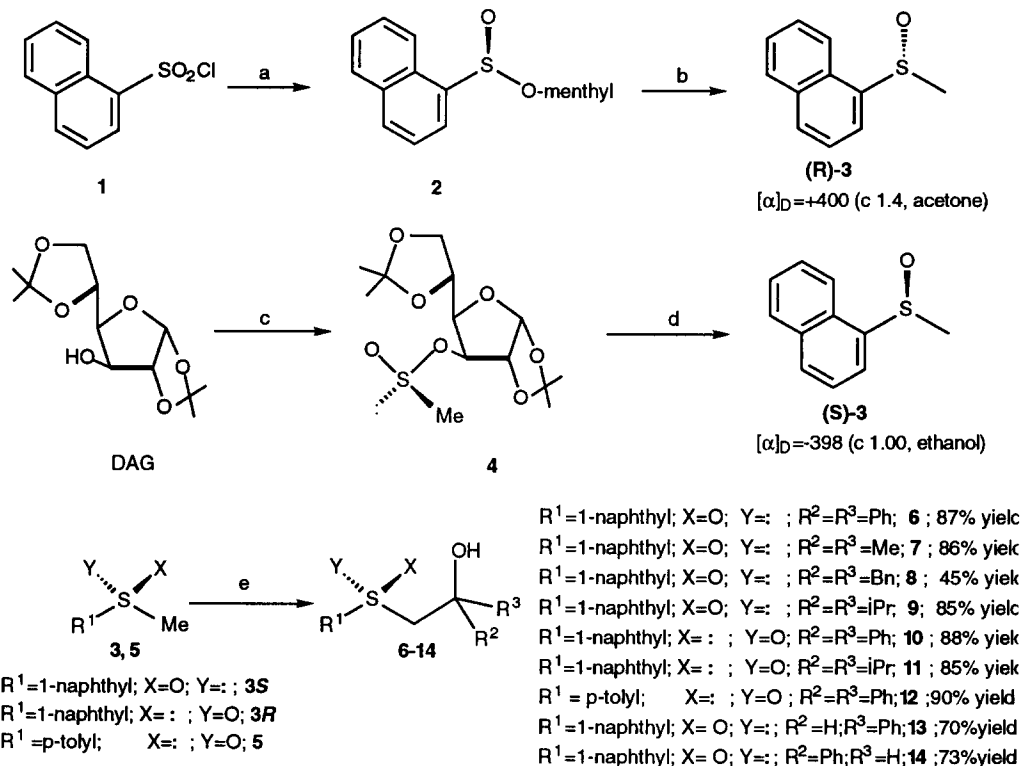
As part of our interest in chiral sulfoxides^{9,12}, we have synthesized several enantiomerically pure hydroxysulfoxides and investigated their effectiveness as chiral controller ligands in asymmetric Diels-Alder reactions. In hydroxysulfoxides **6-18**, it was hoped that the hydroxyl groups vicinal to the sulfoxide moiety would result in chelation to the Lewis acid for a better control of asymmetric catalysis.

The chiral ligands were synthesized in the following manner. The method described in the literature for the preparation of (*R*)-(+)-methyl 1-naphthyl sulfoxide (**R**)-**3** is tedious and very low yielding¹⁰ and was conveniently modified to afford the enantiomerically pure sulfoxide in 70% overall yield. Thus, sulfoxide (**R**)-**3** was readily obtained from commercially available 1-naphthalenesulfonyl chloride **1**, combining the protocol developed by Sharpless for the preparation of sulfinic esters¹¹ and classical resolution in acidic medium¹² (Scheme 1). In this way, chiral sulfinic ester **2** was obtained in 74% yield. Addition of methyl magnesium iodide to this enantiomerically pure ester afforded (**R**)-**3** in 94% chemical yield.

Its enantiomer (**S**)-**3** was prepared using our DAG methodology¹³ (Scheme 1). Thus, diacetone-*D*-glucose (DAG) was first converted to its (*S*)-methanesulfinate **4**^{13c}, which was treated with 1-naphthyl magnesium bromide to afford (**S**)-**3** in 60% overall yield.

Hydroxysulfoxides **6-11** were prepared from benzophenone, acetone, dibenzylketone or diisopropylketone and the corresponding anion of methyl sulfoxides (**S**)-**3** or (**R**)-**3** using the standard protocol for this kind of addition to carbonyl¹⁴. Hydroxysulfoxide **12** was similarly prepared¹⁵ using the anion derived

from (*R*)-(+)-methyl *p*-tolyl sulfoxide^{12,13c}. Sulfoxides **13** and **14** were synthesized through the very well-known sulfoxide monitored stereoselective carbonyl reduction^{9b,16} (using Dibal or Dibal/ZnCl₂) of the corresponding known β -ketosulfoxide¹⁷, which was obtained by condensation between ethyl benzoate and the anion of (*S*)-**3**.



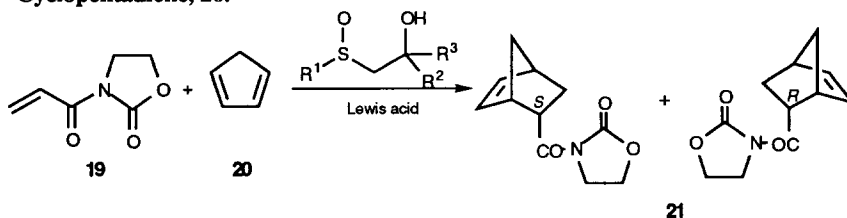
a: i) (-)-menthol / Et₃N / (MeO)₃P / Δ ; ii) crystallization (74% yield). b: MeMgI / toluene / 0°C (94% yield).
 c: MeSOCl / THF / -78°C (91% yield). d: 1-naphthylmagnesium bromide / toluene / 0°C (65% yield).
 e: For compounds **6-12**: i) LDA (1.2 equiv.) / THF / -78°C; ii) R² COR³ (1.2 equiv.). e: For compound **13**:
 i) LDA (2.2 equiv.) / THF / -78°C; ii) PhCO₂Et (1.2 equiv.); iii) Dibal / THF / -78°C. e: For derivative **14**:
 i) LDA (2.2 equiv.) / THF / -78°C; ii) PhCO₂Et (1.2 equiv.); iii) Dibal / ZnCl₂ / THF / -78°C.

Scheme 1

For catalytic studies of the Diels-Alder reaction using hydroxysulfoxides as chiral ligands, we selected the typical tandem 3-acryloyl-1,3-oxazolidin-2-one **19** as bidentate dienophile and cyclopentadiene **20** as the prochiral diene, since, in addition to the *endo:exo* ratio being easily determined by nmr, the enantioselectivity of the *endo* adduct **21** can be efficiently assessed by hplc analysis using a chiral column^{4a}. As model catalyst we first used hydroxysulfoxide **6** which was treated with EtAlCl₂, MgI₂ and FeI₃, as these Lewis acidic metals have been described to coordinate either with hydroxy or sulfinyl group and can chelate with both oxygens of hydroxysulfoxides. As shown in Table 1, chemical and stereochemical yields (entries 1, 2 and 3)

were higher when the magnesium based Lewis acid was used and, therefore, MgI_2 was the only Lewis acid used for the rest of the hydroxysulfoxides. The results are presented in Table 1.

Table 1. Asymmetric Diels–Alder Reaction of 3-Acryloyl-1,3-oxazolidin-2-one, **19** and Cyclopentadiene, **20**.



Entry	R ¹ (Conf. at Sulfur)	R ²	R ³	Comp.	Lewis acid	% yield ^a	endo:exo ^b	S:R ^{c,d}
1	1-naphthyl (<i>S</i>)	Ph	Ph	6	EtAlCl_2^e	82	90 : 10	52 : 48
2					FeI_3	74	> 98 : 2	52 : 48
3					MgI_2	95	>98 : 2	94 : 6
4	1-naphthyl (<i>S</i>)	Me	Me	7	MgI_2	92	97 : 3	55 : 45
5	1-naphthyl (<i>S</i>)	Bn	Bn	8	MgI_2	88	96 : 4	56 : 44
6	1-naphthyl (<i>S</i>)	<i>i</i> Pr	<i>i</i> Pr	9	MgI_2	89	96 : 4	60 : 40
7	1-naphthyl (<i>R</i>)	Ph	Ph	10	MgI_2	94	>98 : 2	7 : 93
8	1-naphthyl (<i>R</i>)	<i>i</i> Pr	<i>i</i> Pr	11	MgI_2	91	95 : 5	41 : 59
9	1- <i>p</i> -tolyl (<i>R</i>)	Ph	Ph	12	MgI_2	94	97 : 3	33 : 67
10	1-naphthyl (<i>S</i>)	Ph	H	13	MgI_2	94	93 : 7	47 : 53
11	1-naphthyl (<i>S</i>)	H	Ph	14	MgI_2	93	>98 : 2	64 : 36

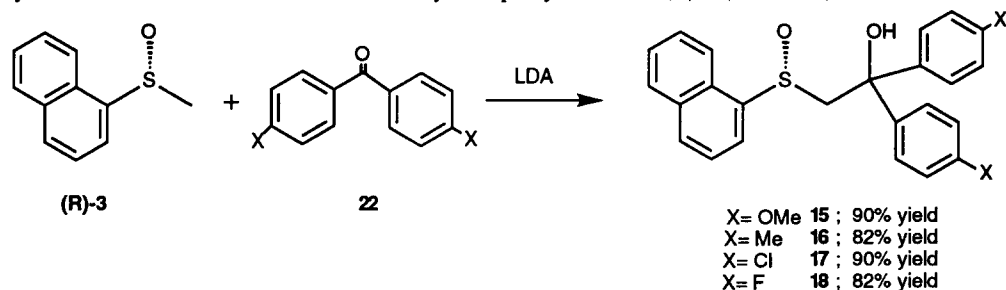
a: Chemical yield after purification by column chromatography. b: Determined by $^1\text{H-NMR}$ at 500MHz. In the *exo* isomer the olefinic protons resonate together as a multiplet at 6.18ppm and they gave two different signals at 5.88ppm (dd, $J=5.6$ and 2.8 Hz) and 6.25ppm (dd, $J=5.6$ and 3.1 Hz) in the *endo* isomer. c: The **21S** / **21R** ratio for the *endo* product was determined by HPLC analysis of the reaction mixture using a Diacel OD column with 10% isopropanol in hexane for elution. d: The absolute configuration was determined for the major isomer (*endo*) by comparison of its specific rotation with that reported in the literature^{4a,18}. e: Similar stereochemical results, although in lower chemical yield, were obtained using Me_3Al and Et_2AlCl as Lewis acid.

In all the cases studied, the chemical yield and diastereoselectivity (*endo/exo* ratio) was very high but the enantioselectivity was only good when the magnesium complexes from hydroxysulfoxide **6** (entry 3) or its enantiomer **10** (entry 7) were used as catalysts. From the comparison of the structures of the different catalysts **6-14**, it can be deduced that for a high enantioselectivity to take place, R^1 should be an 1-naphthyl group (compare entries 7 and 9) while R^2 and R^3 should both be phenyl rings (compare entry 3 with 4, 5, 6, 8, 10 or 11). When only a single phenyl ring is present at the hydroxylic carbon, as in hydroxysulfoxides **13** and **14** (entries 10 and 11), a small though significant change in the sense of stereoselectivity was observed depending on the stereochemistry at hydroxylic carbon.

Related phenomena of enhanced π -facial stereoselectivity bring about by an aromatic substituent are well documented in the literature¹⁹. As responsible for this striking effect, some property of the phenyl ring, be its size, shape, electronic character or a donor acceptor interaction (π -solvation effect) between the aromatic ring and the electron deficient double bond in the dienophile, has been suggested. Purely steric

effects can be ruled out in this case since the stereoselectivity for hydroxysulfoxide **7** ($R^2=R^3=Me$; entry 4) as compared with that for **9** ($R^2=R^3=iPr$; entry 6) decreases only slightly.

In order to investigate whether a donor-acceptor interaction (Ph/dienophile) is operating in this type of catalyzed Diels-Alder reaction, analogues of hydroxysulfoxide **10**, substituted in the *para* position of the phenyl ring with methoxy, methyl, chloro and fluoro groups were synthesized from the corresponding diarylketone derivatives **22** and the anion of methyl 1-naphthyl sulfoxide (*R*)-**3** (Scheme 2).



Scheme 2

Surprisingly, the Diels-Alder reactions using hydroxysulfoxides **15-18** as chiral catalysts afforded adducts **21** with lower enantioselectivities than that observed using *R* sulfoxide **10** (Table 2). The stereochemical result for *p*-methoxyphenyl derivative **15** (entry 1, Table 2) is comparable to that for *isopropyl* derivative **11** (entry 8, Table 1), probably due to association between *p*-MeO groups and magnesium. It can be concluded from these results that electronic π -solvation¹⁹ is not playing a significant role in this type of catalyzed Diels-Alder reaction, although the presence of both phenyl rings is absolutely required.

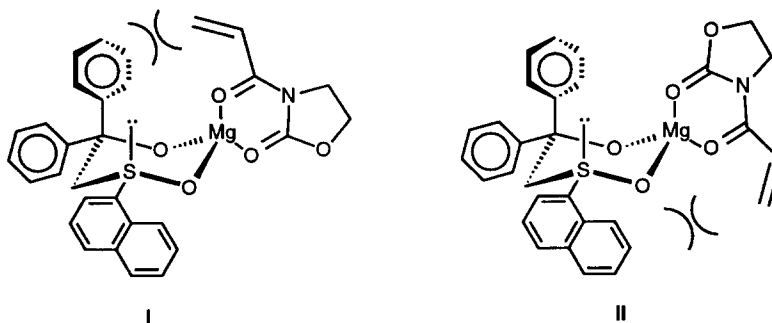
Table 2. Asymmetric Diels-Alder Reaction of 3-Acryloyl-1,3-oxazolidin-2-one **19** and cyclopentadiene **20** using hydroxysulfoxides **15-18** with a substituent in the *para* position of the phenyl ring.

Entry	Hydroxysulfoxide (X)	% yield ^a	<i>endo:exo</i> ^b	<i>S:R</i> ^b
1	15 (OMe)	74	>98 : 2	44 : 66
2	16 (Me)	95	>98 : 2	20 : 80
3	10 (H)	94	>98 : 2	7 : 93
4	17 (Cl)	94	97 : 3	25 : 75
5	18 (F)	99	97 : 3	18 : 82

a: Chemical yield after purification by column chromatography. b: See footnotes in table 1.

The sense of the asymmetric induction in the preceding reaction can be rationalized by assuming two reactive species **I** and **II**, involving a 1:1:1 complex of hydroxysulfoxide (shown in *S* configuration), Mg^{2+} and dienophile **19** with a tetrahedral arrangement of donor groups around the metal, as proposed by Corey^{6a}. Transition states **I** and **II** differ in the arrangement of the dienophile about the magnesium. In both cases, the *si* face is hindered either by the *axial* phenyl ring in **I** or by the large naphthyl group attached to sulfur in **II**. Thus, adduct (*S*)-**21** is stereoselectively formed through *endo* attack of the diene **20** on the sterically accessible dienophile *re* diastereoface. Transition state **II** could explain the decrease in stereoselectivity

observed when the naphthyl ring in *R* hydroxysulfoxide **10** is substituted by a sterically less demanding *p*-tolyl group in **12** (compare entries 7 and 9, Table 1).



As previously proposed by Evans^{19b}, the enhanced steric effect brought about by the phenyl group could be explained by dipole-dipole and van der Waals attraction between phenyl ring and dienophile double bond. The presence of both phenyl rings in the *magic diarylhydroxymethyl group*²⁰ could be important for the proper orientation of both phenyl rings (*gem* diphenyl effect²¹). In this context it should be noted that the presence of just one phenyl ring axially oriented in the transition state type **I** (compound **13**, entry 10, Table 1) is not enough to enhance stereoselectivity.

In summary, it has been shown that hydroxysulfoxide **6** and its enantiomer **10** can be easily obtained from commercially available starting materials and can be efficiently used as catalyst in asymmetric Diels–Alder reactions. The catalyst-Mg(II) complexes are made very easily and do not need co-catalyst; they are also more efficient at catalyzing the Diels Alder process than other Mg(II)-complexes published in the literature so far^{6,4c,d}. Additionally, hydroxysulfoxides can be recovered from the reaction mixture by flash chromatography without any loss of optical activity.

Experimental

Melting points were determined in open capillary tubes on a Gallenkamp apparatus and are uncorrected. ¹H-NMR (200 MHz) and ¹³C-NMR (50.3 MHz) spectra were registered on a Bruker AC-200 spectrometer. All NMR spectra were obtained using CDCl₃ as solvent and TMS as internal standard. Chemical shifts are reported in ppm, and coupling constants in Hz. Optical rotations were taken on a Perkin-Elmer 241-MC polarimeter in an 1 dm tube; concentrations are given in g/100 mL. High resolution mass measurements were performed on a Kratos MS-80-RFA spectrometer. HPLC analysis was carried out on a Waters, Millipore 6000A model using a Chiracel OD (Diacel) column. Routine monitoring of reactions was performed using Merck 60 F 254 silica gel, aluminium supported TLC plates. For flash chromatography, silica gel 60 (230-400 mesh ASTM, E.Merck) was used. All reactions were run under an atmosphere of dry argon using flame-dried glassware and freshly distilled and dried solvents. The organic extracts were dried over anhydrous sodium sulfate and concentrated *in vacuo*.

(1*R*, 2*S*, 5*R*)-Menthyl (-)-[(S) *S*]-1-Naphthalenesulfinate, 1

To a solution of 1-naphthalenesulfonyl chloride (15.0 g, 66.0 mmol) and (-)-menthol (6.9 g, 44.0 mmol) in anhydrous CH₂Cl₂ (150 mL), was added successively triethylamine (9.2 mL, 6.7 g, 66.0 mmol) and trimethyl phosphite (10.4 mL, 11 g, 88.0 mmol). After the exothermic reaction has subsided, the mixture was refluxed for 2 h. The cooled reaction mixture was washed successively with 10% hydrochloric acid solution (50 mL), saturated aqueous NaHCO₃ solution (50 mL) and saturated aqueous NaCl solution (50 mL) and dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude sulfinate was purified by flash chromatography (ethyl acetate: hexane, 1:9) to afford both possible diastereomers at sulfur (14.2 g, 95% yield). The solid was dissolved in acetone (50 mL) and treated with concentrated hydrochloric acid (5 drops). The solution was allowed to crystallize at -5°C. After filtration of the first crop, the mother liquor was concentrated, hydrochloric acid (1 drop) was added and the solution allowed once again to crystallize at -5°C. Finally the product was recrystallized from hot acetone yielding enantiomerically pure (-)-menthyl-1-naphthalenesulfinate (11 g, 73% yield); white crystals; m.p. 119-120°C (lit.¹⁰ m.p. 118-119°C); [α]_D = -444 (c 2.08, acetone); [lit.¹⁰ [α]_D = -433 (c 2.07, acetone); lit.^{14b} [α]_D = -427 (c 2.00 chloroform)].

[(S) *R*]-(+)-Methyl 1-Naphthyl sulfoxide, (R)-3

To a cooled (0°C) solution of (-)-menthyl-(*S*)-1-naphthalenesulfinate **2** (2.0 g, 6.05 mmol) in anhydrous toluene (25 mL) was added methyl magnesium bromide (5.6 mL, 1.4 M solution in toluene/THF, 7.80 mmol). The reaction mixture was stirred at 0°C for 1 h, then quenched by the addition of saturated aqueous NH₄Cl solution (10 mL), and diluted with CH₂Cl₂ (50 mL). The organic layer was removed and the aqueous phase was extracted with CH₂Cl₂ (2x25 mL). The combined organic layers were washed with saturated aqueous NaCl solution (25 mL) and dried (Na₂SO₄), and the solvent was removed under vacuum. The resultant oil was purified by flash chromatography (ethyl acetate:hexane 3:2) affording pure **3R** (1.07 g, 94% yield); m.p. 59-60°C (lit.²² m.p. 58-65°C); [α]_D = +400 (c 1.4, ethanol) [lit.^{14b} [α]_D = +399 (c 1.0, ethanol)].

[(S) *S*]-(-)-Methyl 1-Naphthyl sulfoxide, (S)-3

A solution of 1-naphthyl magnesium bromide [prepared from activated magnesium^{23,13c} (2.30 g, 94.0 mmol), 1-naphthyl bromide (12.20 mL, 18.12 g, 87.0 mmol) and ether (100 mL)] was added dropwise to a solution of 1,2:5,6-di-*O*-isopropylidene- α -*D*-glucofuranosyl-(-)-[(S) *S*]-methanesulfinate **4**^{13c} (19.0 g, 58.0 mmol) in anhydrous toluene (200 mL) at 0°C. The reaction mixture was stirred at room temperature for 2 h, then quenched by addition of saturated aqueous NH₄Cl (50 mL) and diluted with ether (50 mL). The organic layer was removed and the aqueous phase was extracted with ether (2x50 mL). The combined organic extracts were washed with saturated aqueous NaCl solution (50 mL) and dried (Na₂SO₄), and the solvent was removed under reduced pressure. The residue was dissolved in acetonitrile (200 mL) and water (75 mL) and trifluoroacetic acid (5.39 g, 3.60 mL, 29.0 mmol) were successively added. After being stirred at room temperature for 4 h, the reaction mixture was neutralized by addition of saturated aqueous NaHCO₃ solution (30 mL) and extracted with CH₂Cl₂ (2x75 mL). The organic phase was washed with saturated aqueous NaCl solution (50 mL), dried over Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by flash chromatography (ethyl acetate:hexane 3:2) affording **3S**. Recrystallization from ether-pentane (3:1) gave enantiomerically pure **3S** (7.2 g, 65% yield); m.p. 57-60°C (lit.^{14a} m.p. 55-58°C); [α]_D = -398 (c 1.0, ethanol).

General procedure for the synthesis of hydroxysulfoxides

To a cooled (-78°C) solution of diisopropylamine (0.85 mL, 6.0 mmol) in dry THF (30 mL) was added *n*-butyllithium (2.63 mL of a 2.5M solution in hexanes, 6.6 mmol). The mixture was stirred at -78°C for 30 min and a solution of methylsulfoxide **3R**, **3S** or **5** (5.0 mmol) in dry THF (30 mL) was added. The resulting pale-yellow solution was stirred for 1 h at -78°C and a solution of the appropriated ketone (6.0 mmol) in dry THF (20 mL) was added dropwise via cannula. After being stirred at -78°C for 1 h, the reaction mixture was allowed to reach room temperature and quenched by addition of saturated aqueous NH_4Cl solution (25 mL). The organic phase was separated and the aqueous layer was extracted with CH_2Cl_2 (2x75 mL). The combined organic extracts were dried over Na_2SO_4 and evaporated under reduced pressure. The crude hydroxysulfoxide was purified by flash chromatography.

[(S) S]-1,1-Diphenyl-2-(1'-naphthylsulfinyl)ethanol, 6

This hydroxysulfoxide was prepared by addition of the lithium carbanion of (*S*)-methyl 1-naphthyl sulfoxide (**S**)-**3** to benzophenone. Purified by flash chromatography (ethyl acetate:hexane 1:1). Yield 87%; m.p. 125.5 – 126°C ; $[\alpha]_{\text{D}}^{25} = -262$ (c 2.2, acetone). $^1\text{H-NMR}$, δ : 8.16 (dd, $J = 7.3$ and 1.2 Hz, 1H, aromatic), 8.01–7.87 (m, 2H, aromatics), 7.77–7.31 (m, 11H, aromatics), 7.27–7.11 (m, 3H, aromatics), 5.70 (s, 1H, OH), 3.92 (AB system, $J = -13.4$ Hz, 1H, $-\text{CH}_2-$), 3.56 (AB system, $J = -13.4$ Hz, 1H, $-\text{CH}_2-$) ppm. $^{13}\text{C-NMR}$, δ : 145.8, 144.3, 139.4, 133.4, 131.5, 129.1, 128.6, 128.3, 128.2, 127.7, 127.6, 127.5, 126.8, 126.5, 125.8, 125.7, 123.1, 121.1, 78.4, 65.8 ppm. Anal. calcd. for $\text{C}_{24}\text{H}_{20}\text{O}_2\text{S}$: C, 77.39; H, 5.41. Found: C, 77.15; H, 5.26.

[(S) S]-1,1-Dimethyl-2-(1'-naphthylsulfinyl)ethanol, 7

Obtained by addition of the lithium anion of (*S*)-**3** to acetone. Purified by flash chromatography (ethyl acetate:hexane 4:1). Yield 86%; m.p. 129.5 – 130.5°C ; $[\alpha]_{\text{D}}^{25} = -515.4$ (c 1.0, acetone). $^1\text{H-NMR}$, δ : 8.15 (dd, $J = 8.5$ and 1.3 Hz, 1H, aromatic), 7.98–7.86 (m, 3H, aromatics), 7.68–7.48 (m, 3H, aromatics), 3.98 (s, 1H, OH), 3.04 (AB system, $J = -13.5$ Hz, 1H, $-\text{CH}_2-$), 2.96 (AB system, $J = -13.5$ Hz, $-\text{CH}_2-$), 1.65 (s, 3H, Me), 1.39 (s, 3H, Me) ppm. $^{13}\text{C-NMR}$, δ : 139.6, 133.5, 131.4, 129.1, 128.3, 127.4, 126.8, 125.8, 123.0, 121.3, 70.8, 67.3, 30.4, 20.1 ppm. Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_2\text{S}$: C, 67.71; H, 6.50. Found: C, 67.56; H 6.34.

[(S) S]-1,1-Dibenzyl-2-(1'-naphthylsulfinyl)ethanol, 8

Obtained by addition of the lithium anion of (*S*)-**3** to dibenzylacetone. Purified by flash chromatography (ethyl acetate:hexane 2:3). Yield 45%; m.p. 191 – 192°C ; $[\alpha]_{\text{D}}^{25} = -365$ (c 1.3, acetone). $^1\text{H-NMR}$, δ : 8.09 (dd, $J = 7.3$ and 1.2 Hz, 1H, aromatic), 7.91–7.85 (m, 2H, aromatics), 7.65–7.19 (m, 14H, aromatics), 5.74 (s, 1H, OH), 3.40 (AB system, $J = -13.8$ Hz, 1H, $-\text{CH}_2-$), 3.26 (AB system, $J = -13.8$ Hz, $-\text{CH}_2-$), 3.10 (AB system, $J = -13.6$ Hz, $-\text{CH}_2-\text{Ph}$), 3.00 (AB system, $J = -13.6$ Hz, $-\text{CH}_2-\text{Ph}$), 2.89 (AB system, $J = -13.6$ Hz, $-\text{CH}_2-\text{Ph}$), 2.84 (AB system, $J = -13.6$ Hz, $-\text{CH}_2-\text{Ph}$) ppm. $^{13}\text{C-NMR}$, δ : 139.8, 136.4, 136.2, 133.3, 131.3, 131.1, 131.0, 128.9, 128.4, 128.2, 127.2, 126.9, 126.6, 125.8, 123.1, 121.5, 75.0, 62.0, 46.9, 46.5 ppm. Anal. Calcd. for $\text{C}_{26}\text{H}_{24}\text{O}_2\text{S}$: C, 77.97; H, 6.04. Found: C, 77.71; H, 5.86.

[(S) S]-1,1-Diisopropyl-2-(1'-naphthylsulfinyl)ethanol, 9

Obtained by addition of the lithium anion of (*S*)-**3** to 2,4-dimethyl-2-pentanone. Purified by flash chromatography (ethyl acetate:hexane 2:3). Yield 85%; oil; $[\alpha]_{\text{D}}^{25} = -324$ (c 1.2, acetone). $^1\text{H-NMR}$, δ : 8.19 (dd, $J = 7.3$ and 1.2 Hz, 1H, aromatic), 8.01–7.91 (m, 3H, aromatics), 7.72–7.51 (m, 3H, aromatics), 3.78 (s, 1H,

OH), 3.01 (AB system, $J=-14.1$ Hz, 1H, $-\text{CH}_2-$), 2.93 (AB system, $J=-14.1$ Hz, $-\text{CH}_2-$), 2.29 (septet, $J=6.9$ Hz, 1H, CHMe_2), 1.90 (septet, $J=6.9$ Hz, 1H, CHMe_2), 1.22 (d, $J=6.9$ Hz, 3H, Me), 1.11 (d, $J=6.9$ Hz, 3H, Me), 0.94 (d, $J=6.9$ Hz, 3H, Me), 0.87 (d, $J=6.9$ Hz, 3H, Me) ppm. ^{13}C -NMR, δ : 140.7, 133.4, 131.3, 129.1, 128.6, 127.4, 127.4, 126.7, 125.9, 123.2, 121.5, 78.2, 59.9, 35.9, 34.8, 18.1, 17.4, 17.0 ppm. HRMS (EI) 288.1549 M^+-16 , Calcd. for $\text{C}_{18}\text{H}_{24}\text{OS}$: 288.1542.

[(S) R]-1,1-Diphenyl-2-(1'-naphthylsulfinyl)ethanol, 10

This hydroxysulfoxide was prepared by addition of the lithium carbanion of (*R*)-methyl 1-naphthyl sulfoxide (*R*)-3 to benzophenone. Purified by flash chromatography (ethyl acetate:hexane 1:1). Yield 88%; m.p. 126–127°C; $[\alpha]_{\text{D}}^{25}+262.7$ (c 1.0, acetone). ^1H -NMR, δ : 8.16 (dd, $J=7.3$ and 1.2 Hz, 1H, aromatic), 8.01–7.87 (m, 2H, aromatics), 7.77–7.31 (m, 11H, aromatics), 7.27–7.11 (m, 3H, aromatics), 5.70 (s, 1H, OH), 3.92 (AB system, $J=-13.4$ Hz, 1H, $-\text{CH}_2-$), 3.56 (AB system, $J=-13.4$ Hz, 1H, $-\text{CH}_2-$) ppm. ^{13}C -NMR, δ : 145.8, 144.3, 139.4, 133.4, 131.5, 129.1, 128.6, 128.3, 128.2, 127.7, 127.6, 127.5, 126.8, 126.5, 125.8, 125.7, 123.1, 121.1, 78.4, 65.8 ppm. Anal. calcd. for $\text{C}_{24}\text{H}_{20}\text{O}_2\text{S}$: C, 77.39; H, 5.41. Found: C, 77.07; H, 5.41.

[(S) R]-1,1-Diisopropyl-2-(1'-naphthylsulfinyl)ethanol, 11

Obtained by addition of the lithium anion of (*R*)-3 to 2,4-dimethyl-2-pentanone. Purified by flash chromatography (ethyl acetate:hexane 2:3). Yield 84%; oil; $[\alpha]_{\text{D}}^{25}+328$ (c 1.1, acetone). ^1H -NMR, δ : 8.19 (dd, $J=7.3$ and 1.2 Hz, 1H, aromatic), 8.01–7.91 (m, 3H, aromatics), 7.72–7.51 (m, 3H, aromatics), 3.78 (s, 1H, OH), 3.01 (AB system, $J=-14.1$ Hz, 1H, $-\text{CH}_2-$), 2.93 (AB system, $J=-14.1$ Hz, $-\text{CH}_2-$), 2.29 (septet, $J=6.9$ Hz, 1H, CHMe_2), 1.90 (septet, $J=6.9$ Hz, 1H, CHMe_2), 1.22 (d, $J=6.9$ Hz, 3H, Me), 1.11 (d, $J=6.9$ Hz, 3H, Me), 0.94 (d, $J=6.9$ Hz, 3H, Me), 0.87 (d, $J=6.9$ Hz, 3H, Me) ppm. ^{13}C -NMR, δ : 140.7, 133.4, 131.3, 129.1, 128.6, 127.4, 127.4, 126.7, 125.9, 123.2, 121.5, 78.2, 59.9, 35.9, 34.8, 18.1, 17.4, 17.0. HRMS (EI) 288.1542 M^+-16 , Calcd. for $\text{C}_{18}\text{H}_{24}\text{OS}$: 288.1542.

[(S) R]-1,1-Di-(4'-methoxyphenyl)-2-(1'-naphthylsulfinyl)ethanol, 15

This hydroxysulfoxide was prepared by addition of the lithium carbanion of (*R*)-methyl 1-naphthyl sulfoxide (*R*)-3 to 4,4'-dimethoxybenzophenone. Purified by flash chromatography (ethyl acetate:hexane 1:1). Yield 90%; m.p. 104–105°C; $[\alpha]_{\text{D}}^{25}+196.6$ (c 1.2, acetone). ^1H -NMR, δ : 8.16 (dd, $J=7.3$ and 1.2 Hz, 1H, aromatic), 8.00–7.89 (m, 2H, aromatics), 7.70–7.50 (m, 4H, aromatics), 7.33 (AA'BB' system, 4H, *p*- C_6H_4 -), 6.98 (AA'BB' system, 4H, *p*- C_6H_4 -), 5.50 (s, 1H, OH), 3.87 (s, 3H, OMe), 3.83 (AB system, $J=-13.4$ Hz, 1H, $-\text{CH}_2-$), 3.69 (s, 3H, OMe), 3.53 (AB system, $J=-13.4$ Hz, 1H, $-\text{CH}_2-$) ppm. ^{13}C -NMR, δ : 159.0, 158.7, 139.5, 138.4, 136.4, 133.4, 131.4, 129.1, 128.3, 127.7, 127.5, 127.0, 126.8, 125.8, 123.1, 121.1, 113.9, 113.4, 77.9, 66.1, 55.3, 55.2 ppm. Anal. calcd. for $\text{C}_{26}\text{H}_{24}\text{O}_4\text{S}$: C, 72.19; H, 5.59. Found: C, 71.98; H, 5.61.

(*R*)-1,1-Di-(4'-methylphenyl)-2-(1'-naphthylsulfinyl)ethanol, 16

This hydroxysulfoxide was prepared by addition of the lithium carbanion of (*R*)-methyl 1-naphthyl sulfoxide (*R*)-3 to 4,4'-dimethylbenzophenone. Purified by flash chromatography (ethyl acetate:hexane 2:3). Yield 82%; m.p. 105.5–106°C; $[\alpha]_{\text{D}}^{25}+224.8$ (c 1.0, acetone). ^1H -NMR, δ : 8.18 (dd, $J=7.3$ and 1.2 Hz, 1H, aromatic), 8.01–7.89 (m, 2H, aromatics), 7.71–7.52 (m, 6H, aromatics), 7.82 (d, $J=8.1$ Hz, 2H, aromatics), 7.23 (d, $J=8.16$ Hz, 2H, aromatics), 7.02 (d, $J=8.16$ Hz, 2H, aromatics), 5.57 (s, 1H, OH), 3.88 (AB system,

$J = -13.4$ Hz, 1H, $-\text{CH}_2-$), 3.54 (AB system, $J = -13.4$ Hz, 1H, $-\text{CH}_2-$), 2.45 (s, 3H, CH_3Ph), 2.23 (s, 3H, CH_3Ph) ppm. ^{13}C -NMR, δ : 143.1, 141.4, 139.5, 137.3, 137.1, 133.4, 131.4, 129.3, 129.1, 128.9, 128.3, 127.5, 126.7, 126.3, 125.8, 125.5, 123.1, 121.2, 78.2, 65.9, 21.1, 20.9 ppm. Anal. calcd. for $\text{C}_{26}\text{H}_{24}\text{O}_2\text{S}$: C, 77.97; H, 6.04. Found: C, 77.66; H, 5.87.

[(S) R]-1,1-Di-(4'-chlorophenyl)-2-(1'-naphthylsulfinyl)ethanol, 17

This hydroxysulfoxide was prepared by addition of the lithium carbanion of (*R*)-methyl 1-naphthyl sulfoxide (*R*)-**3** to 4,4'-dichlorobenzophenone. Purified by flash chromatography (ethyl acetate:hexane 2:3). Yield 90%; m.p. 126–126.5°C; $[\alpha]_{\text{D}}^{25} = +192$ (c 1.0, acetone). ^1H -NMR, δ : 8.16 (m, 1H, aromatic), 7.98–7.95 (m, 2H, aromatics), 7.72–7.49 (m, 8H, aromatics), 7.28–7.16 (m, 4H, aromatics), 5.89 (s, 1H, OH), 3.85 (AB system, $J = -13.4$ Hz, 1H, $-\text{CH}_2-$), 3.51 (AB system, $J = -13.4$ Hz, 1H, $-\text{CH}_2-$) ppm. ^{13}C -NMR, δ : 143.4, 142.5, 138.7, 134.0, 133.6, 133.5, 131.8, 129.3, 128.9, 128.4, 128.3, 127.8, 127.7, 127.0, 126.9, 125.9, 123.2, 120.8, 113.4, 77.9, 64.6 ppm. Anal. calcd. for $\text{C}_{24}\text{H}_{18}\text{Cl}_2\text{O}_2\text{S}$: C, 71.10; H, 4.48. Found: C, 71.20; H, 4.50.

[(S) R]-1,1-Di-(4'-fluorophenyl)-2-(1'-naphthylsulfinyl)ethanol, 18

This hydroxysulfoxide was prepared by addition of the lithium carbanion of (*R*)-methyl 1-naphthyl sulfoxide (*R*)-**3** to 4,4'-difluorobenzophenone. Purified by flash chromatography (ethyl acetate:hexane 2:3). Yield 82%; m.p. 115.5–116°C; $[\alpha]_{\text{D}}^{25} = +260$ (c 1.0, acetone). ^1H -NMR, δ : 8.16 (dd, $J = 7.3$ and 1.1 Hz, 1H, aromatic), 8.03–7.94–7.95 (m, 2H, aromatics), 7.75–7.57 (m, 6H, aromatics), 7.33–7.18 (m, 4H, aromatics), 6.97–6.86 (m, 2H, aromatics), 5.87 (s, 1H, OH), 3.86 (AB system, $J = -13.4$ Hz, 1H, $-\text{CH}_2-$), 3.53 (AB system, $J = -13.4$ Hz, 1H, $-\text{CH}_2-$) ppm. ^{13}C -NMR, δ : 162.3 (d, $J = 247.1$ Hz, C_{ipso} to F), 162.0 (d, $J = 247.1$ Hz, C_{ipso} to F), 141.5 (d, $J = 2.8$ Hz, C_{para} to F), 140.0 (d, $J = 2.8$ Hz, C_{para} to F), 138.9, 133.5, 131.8, 129.2, 128.3, 128.2 (d, $J = 8.1$ Hz, C_{meta} to F), 127.7, 127.541.5 (d, $J = 8.1$ Hz, C_{meta} to F), 126.9, 125.9, 123.2, 120.9, 115.6 (d, $J = 21.0$ Hz, C_{ortho} to F), 115.1 (d, $J = 21.0$ Hz, C_{ortho} to F), 77.9, 65.3 ppm. Anal. calcd. for $\text{C}_{24}\text{H}_{18}\text{F}_2\text{O}_2\text{S}$: C, 70.57; H, 4.44. Found: C, 70.19; H, 4.27.

[1R, (S) S]-1-Phenyl-2-(1'-naphthylsulfinyl)ethanol, 13

To a cooled (-78°C) solution of (-)-[(S) S]- α -1-(Naphthylsulfinyl)acetophenone¹⁶ (250 mg, 0.85 mmol) in dry THF (10 mL) was added DIBAL-H (1.3 mL, 1.0M in THF, 1.50 mmol) and the resulting mixture was stirred at -78°C for 2 days and at room temperature for additional 3h. The reaction mixture was decomposed by addition of saturated aqueous NaHCO_3 solution (10 mL) and extracted with CH_2Cl_2 (2X25 mL). The combined organic phases were washed with 10% aqueous hydrochloric acid (50 mL), dried (Na_2SO_4) and evaporated under reduced pressure to afford hydroxysulfoxide **13** as a >99:1 mixture of diastereomers (determined by HPLC using a Chiracel OD column with 10% *i*PrOH in hexane for elution). Flash chromatography (hexane: *isopropanol* 9:1) afforded enantiomerically pure **13** (176 mg, 70% yield); m.p. 122–123.5°C, $[\alpha]_{\text{D}}^{25} = -606$ (c 1.0, acetone). ^1H -NMR, δ : 8.18 (dd, $J = 7.3$ and 1.2 Hz, 1H, aromatic), 8.02–7.83 (m, 3H, aromatics), 7.74–7.53 (m, 3H, aromatics), 7.31–7.17 (m, 5H, aromatics), 5.38 (part X of an AMX system, $J = 10.4$, 3.2 and 1.9 Hz, 1H, $\text{CH}-\text{OH}$), 4.54 (d, $J = 3.2$ Hz, 1H, OH), 3.48 (part M of an AMX system, $J = -13.5$ and 10.4 Hz, 1H, $-\text{CH}_2-$), 2.96 (part A of an AMX system, $J = -13.5$ and 1.9 Hz, 1H, $-\text{CH}_2-$) ppm. ^{13}C -NMR, δ : 142.0, 138.3, 133.5, 131.4, 129.1, 128.6, 128.4, 127.9, 127.4, 126.8, 125.6, 123.2, 121.4, 68.8, 62.4 ppm. HRMS (EI) 296.0852 M^+ , Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{S}$: 296.0871.

[1S, (S) S]-1-Phenyl-2-(1'-naphthylsulfinyl)ethanol, 14

A solution of (-)-[(S) S]- α -1-(Naphthylsulfinyl)acetophenone¹⁶ (250 mg, 0.85 mmol) and anhydrous zinc chloride (139 mg, 1.00 mmol) in dry THF (10 mL) was stirred at room temperature for 30 min and then cooled at -78°C. To the resulting solution was added DIBAL-H (1.3 mL, 1.0M in THF, 1.50 mmol) and the mixture was stirred at -78°C for 2 days and at room temperature for additional 3h. The reaction mixture was decomposed by addition of saturated aqueous NaHCO₃ solution (10 mL) and extracted with CH₂Cl₂ (2X25 mL). The combined organic phases were washed with 10% aqueous hydrochloric acid (50 mL), dried (Na₂SO₄) and evaporated under reduced pressure to afford hydroxysulfoxide **14** as a 89:11 mixture of diastereomers (determined by HPLC using a Chiracel OD column with 10% *i*PrOH in hexane for elution). Flash chromatography (hexane: isopropanol 9:1) afforded enantiomerically pure **14** (194 mg, 77% yield); m.p. 105-106°C, [α]_D = -345.5 (c 1.1, acetone). ¹H-NMR, δ : 8.12 (dd, *J* = 7.3 and 1.2 Hz, 1H, aromatic), 8.02-7.81 (m, 3H, aromatics), 7.68-7.50 (m, 3H, aromatics), 7.41-7.20 (m, 5H, aromatics), 5.52 (part X of an AMX system, *J* = 8.1, 4.4 and 1.7 Hz, 1H, CH-OH), 4.35 (d, *J* = 1.7 Hz, 1H, OH), 3.39-3.14 (m, part AM of an AMX system, 2H, -CH₂-) ppm. ¹³C-NMR, δ : 141.9, 139.5, 133.5, 131.6, 129.1, 128.7, 128.5, 128.2, 127.5, 126.8, 125.8, 122.8, 121.3, 71.5, 62.8 ppm. HRMS (EI) 296.0869, Calcd. for C₁₈H₁₆O₂S: 296.0871.

Catalysed Diels-Alder reaction using MgI₂.

To a mixture of activated magnesium^{22,13c} (1.9 mg, 0.078 mmol, 0.11 eq) and iodine (20 mg, 0.078 mmol, 0.11 eq.) was added anhydrous ether (5 mL). After stirring for 2h under reflux, the solvent was removed under reduced pressure and the residue was dissolved in anhydrous CH₂Cl₂ and a solution of hydroxysulfoxide (0.071 mmol, 0.1 eq) in anhydrous CH₂Cl₂ (2 mL) was added dropwise at room temperature. The yellow solution was stirred for 1.5 h at room temperature and treated at -78°C with 3-acryloyl-1,3-oxazolin-2-one **19** (100 mg, 0.70 mmol, 1.0 eq.) and 15 min later freshly distilled cyclopentadiene **20** (0.24 mL, 2.83 mmol, 4.0 eq.) was added. After being stirred for 4h at -78°C, the reaction was quenched with water (5 mL). The organic phase was separated and the aqueous layer was extracted with CH₂Cl₂ (2X25 mL). The combined organic extracts were washed with sodium sulfite solution, dried over Na₂SO₄ and evaporated. Cycloadduct was analyzed by ¹H-NMR (500 MHz) to determine *endo:exo* ratio.

The e.e was determined by HPLC analysis using a Diacel OD column with 10% *i*PrOH in hexane for elution (1 mL/min; retention times 21.4 min for (S)-**21** and 23.5 min for (R)-**21**.

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