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Enantioselective Synthesis of Alkylidene Cyclohexanes by an Asymmetric Olefination/Cross-Coupling Sequence

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ABSTRACT

A general method for the preparation of dissymmetric olefins has been developed. The anion derived from an enantiomerically enriched P-(phenylthiomethyl)phosphonamidate(1,3,2-oxazaphosphorinane 2-oxide) was added to 4-tert-butylcyclohexanone with excellent diastereoselectivity. The β-hydroxyphosphonamidate was converted into a (phenylthio)methylidene with excellent stereospecificity using a novel electrophile-promoted olefination that employed trityl triflate and 2,6-lutidine in warm acetonitrile. The vinyl sulfide underwent nickel-catalyzed coupling with Grignard and dialkylzinc reagents to produce (S)-4-(tert-butyl)alkylidenecyclohexanes with moderate to high stereospecificity.

INTRODUCTION

Enantiomerically enriched, dissymmetric olefins are of synthetic value due to their unique chiroptical properties. In addition, their utility has recently been extended to serve as potential triggers for physical amplification of a photo response in liquid crystalline materials [1]. The conventional method for providing enantiomerically enriched cycloalkylidenes is by resolution of racemic materials [2]. However, this method is highly restricted to the preparation of alkylidenecarboxylic acids. Despite efforts toward further functional group manipulations [3] and coupling reactions of the related bromoalkylidenes [4], difficulties associated with the preparation of highly enantiomerically enriched parent compounds and serious problems of stereomutation in the coupling of bromoalkenes significantly hinder the application of this approach.

Over the last decade, reports describing enantiocontrolled synthesis of dissymmetric olefins have appeared. Synthesis of optically active bromoalkylidenes and α,β-unsaturated carboxylic acids can be accomplished by dehydrohalogenation of β-halo carboxylic acids with chiral bases [5] and elimination of chiral sulfoxides [6] and selenoxides [7]. Approaches by means of palladium-catalyzed asymmetric substitutions of allyl alkanoates [8] and chiral titanium (IV)-catalyzed isomerization of a terminal alkene [9] allow access to various alkylidenecyclohexane derivatives. Further, Sharpless and co-workers have reported highly enantioselective syntheses of dissymmetric olefins by the utilization of asymmetric dihydroxylation of racemic substrates with concomitant kinetic resolution [10].

The Wittig olefination reaction has risen to prominence as the preeminent method for alkene construction in organic synthesis [11]. Its versatility, together with its potential for high stereocontrol, attests to the venerable popularity of this transformation. In addition, the carbonyl olefination reaction utilizing phosphoryl-stabilized carbanions (Horner–Wadsworth–Emmons (HWE)) has served as a useful and complementary alternative to the Wittig olefination [12]. On the basis of this type of approach, the employment of phosphorus-based reagents has been developed to provide dissymmetric olefins [13]. As part of our general program on establishing the structure [14] and utility

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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[15] of auxiliary-based, chiral *P=O* stabilized anions, we have recently reported the use of phosphonamidate (2*R*,6*S*)-**1a** (*R* = Ph) for the synthesis of dissymmetric alkylidenes [16]. The success of this method hinges on the sequential, highly diastereoselective addition of oxazaphosphorinane 2-oxide Li^+(2*R*,6*S*)-**1a**$^-$ to prochiral 4-substituted cyclohexanones and stereospecific trityl triflate-activated elimination. Highly selective syntheses of benzylidene 4-substituted cyclohexanes **3a** (86–99% ee) can be accomplished in good yields (68–77%) and with essentially complete stereospecificity (Scheme 1).

To generalize this two-step olefination process and to access a variety of alkylidene 4-substituted cyclohexanes, incorporation of an appropriate group into the *P*-alkyl chain was considered. A synthetically efficient approach requires the selection of a functional group that can allow for further manipulations and transformations to a diverse array of organic groups. Herein, we describe a general entry toward the synthesis of dissymmetric olefins by incorporation of a phenylthio unit into the alkylidene (*R* = SPh) and subsequent, nickel-catalyzed, cross-coupling reactions.

RESULTS AND DISCUSSION

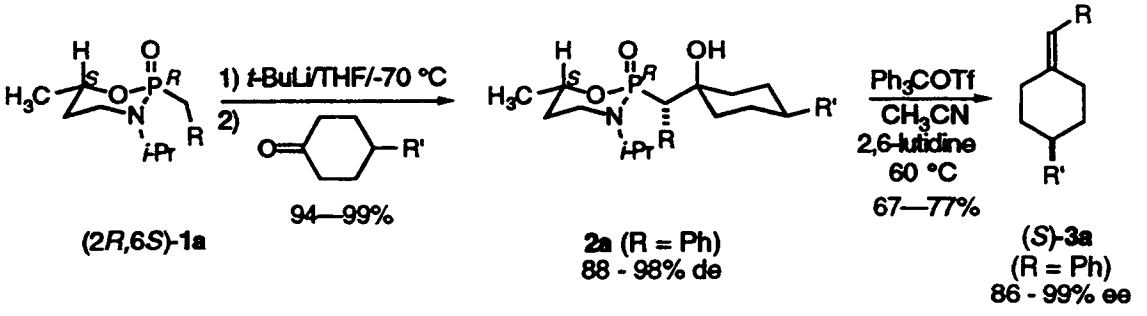
Synthesis of P-(Phenylthio)methyloxazaphosphorinane 2-Oxide (2*R*,6*S*)-**1b**

Among the various approaches for the synthesis of (phenylthio)methyl phosphonates [17], the Arbuzov protocol was viewed as most promising. Treatment of ethyl phosphite **4** [16] with chloromethyl phenyl sulfide in hot acetonitrile (80°C) for 16 hours furnished a 6/1 mixture of diastereomeric *P*-(phenylthio)methyloxazaphosphorinane 2-oxides **1b** in 29% overall yield (Table 1). Addition of tetrabutylammonium bromide (1 equiv) enhanced only the reaction rate. The Arbuzov reaction of **4** with the in-situ-generated iodomethyl phenyl sulfide led to a cleaner and more efficient conversion by the addition of tetrabutylammonium iodide. The diastereomer (2*R*,6*S*)-**1b** was isolated in 48% yield. Final improvements in both diastereoselectivity (2*R*/2*S* = 8/1) and the chemical yield (66% of pure (2*R*,6*S*)-**1b**) were attained by the employment of freshly prepared electrophile [18] and milder reaction conditions (room temperature).

Sequential Addition and Olefination Reactions with (2*R*,6*S*)-**1b**

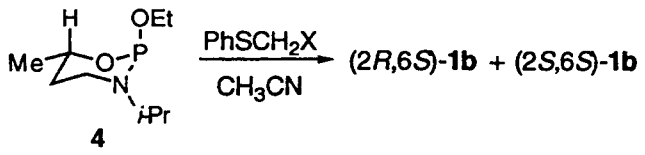
Initial studies on the addition of (2*R*,6*S*)-**1b** to 4-*tert*-butylcyclohexanone under the standard reaction conditions were disappointing. A mixture of two diastereomeric β-hydroxyphosphonamidates **2b/2b′** was obtained in 82% yield and in a ratio of 77/23, (entry 1, Table 2). The use of LDA as the base led to similar results. The upfield shift ($\Delta\delta$ = −1.7 ppm) of the ^{31}P resonance and a smaller $^2J_{HP}$ (Δ^2J_{HP} = −3.4 Hz) in the major diastereomer (2*R*,6*S*,1′*S*)-**2b** led us to assign their diastereomeric relationship as differing at the C(1′) stereocenter. This marked erosion of facial selectivity in the addition is reminiscent of the poor alkylation selectivity observed in the *P*-methoxymethyl analog, presumably due to the competing pathway arising from a chelated anion [19]. If this mechanistic assumption is correct, the erosion of diastereoselection in the addition may be avoided by judicious choice of solvent and additive. Extensive surveys of solvents (THF, DME, ether, and toluene) and additives ($MgBr_2$, HMPA, TMEDA, and PMDTA [20]) with varying coordinating ability strongly supported this contention. Significant enhancement in the diastereoselectivity of addition was observed when the reaction was carried out in toluene or ether solution in the presence of PMDTA (2 equiv). The diastereomeric β-hydroxyphosphonamidates **2b/2b′** were produced in greater than 90/10 selectivity (entries 2 and 3). However, due to the more nucleophilic nature of the resultant alkoxide Li^+**2b**$^-$ in the presence of PMDTA, direct olefination took place to some extent at −70°C.

To hinder the direct olefination, the addition reaction was conducted at lower temperature (−90°C) leading to β-hydroxyphosphonamidates **2b/2b′** with higher 95/5 diastereoselectivity in 74%



SCHEME 1

TABLE 1 Arbuzov Reaction of Oxazaphosphorinane 4 with Halomethyl Phenyl Sulfides

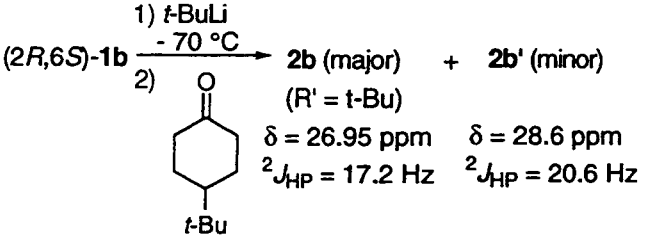


X (equiv)	T, °C (time, hour)	Ratio (2R:2S)[a]	Yield (2R:2S), %
Cl (2)	80 (16)	6:1	24:5
Cl (2)[b]	80 (8)	6.4:1	24:5
Cl (1.3)[c]	80 (8)	6:1	48:—[d]
I (2)	20 (14)	8:1	66:—[d]

[a]Determined by ^{31}P NMR.
[b]Tetrabutylammonium bromide (1 equiv) was added.
[c]Tetrabutylammonium iodide (1 equiv) was added.
[d]Not isolated.

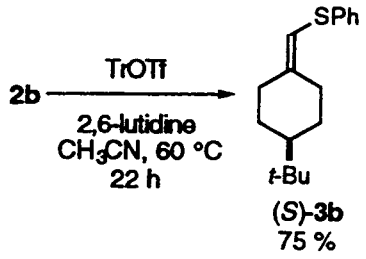
yield, but still with formation of olefin **3b** in 17% yield. The enantiomeric purity of (phenylthio)methylidene **3b** was determined to be 87% after conversion to the corresponding benzylidene 4-*tert*-butylcyclohexane **3a**. Attempts to enhance the

TABLE 2 Survey of Solvents and Additives in the Addition Reactions of (2*R*, 6*S*)-**1b**



Entry	Solvent	Additive (equiv)	Temperature (°C)	Ratio (2b/2b')[a]	Yield, %[b]
1	THF	—	−70	77:23	82
2	toluene	PMDTA (2)	−70	90:10	86[c]
3	ether	PMDTA (2)	−70	92:8	61
4	ether	PMDTA (2)	−90	95:5	74
5	ether	PMDTA (2)	−90 → rt	94:6	13
6	ether	PMDTA (1.1)	−90	94:6	84–96

[a]Determined by ^{31}P NMR.
[b]Isolated yield.
[c]Percent conversion based on ^{31}P NMR.



SCHEME 2

olefin production by gradual warming of the initially generated lithium alkoxide to ambient temperature for 36 hours afforded olefin **3b** in 54% yield with 11% erosion of enantioselectivity (76% ee) and recovered **2b** (13%) with unchanged diastereoselectivity. Further optimization to maximize the chemical yield of **2b** was achieved by reducing the amount of PMDTA (1.1 equiv). The adducts were obtained in up to 94% yield and without significant erosion of the high diastereoselection.

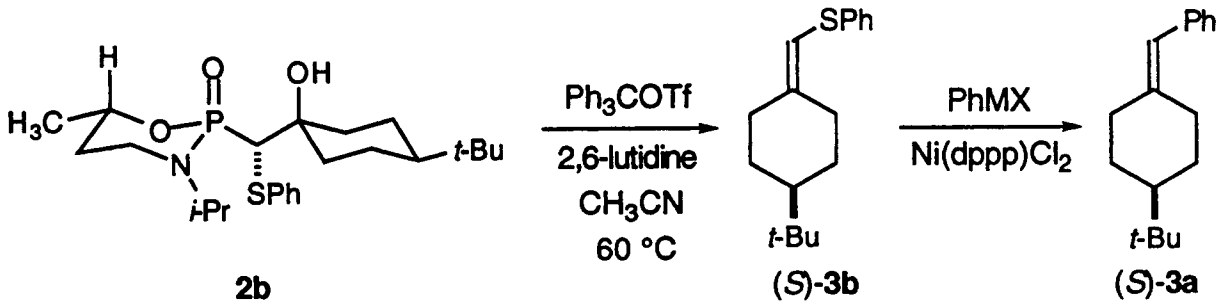
The trityl triflate-activated olefination of **2b** was conducted with 100% excess of reagents relative to the previously optimized reaction stoichiometry. Longer reaction time (22 vs. 5 hours) was also found to be necessary to effect complete conversion, presumably due to the competitive, reversible coordination of TrOTf at the sulfur center. Nevertheless, transformation of **2b** cleanly afforded the (phenylthio)methylidene **3b** in 75% yield without formation of epoxide by-products [21] (Scheme 2).

Coupling Reactions with (Phenylthio)methylidene **3b**

The Stereochemical Course of Olefination with (2*R*,6*S*)-**1b**. To establish the overall stereochemical course of olefination, the phenylthio group in **3b** was displaced in a nickel-catalyzed, cross-coupling reaction, with phenylmagnesium bromide [22]. This reaction proceeded readily at ambient temperature to afford benzylidene **3a** in moderate (51%) to good yield (80%) (Table 3). The absolute configuration of olefin **3a** was shown to be *S*. Therefore, we can infer the stereostructure of **2b** by assuming a *syn*-cycloelimination of **2b** to the (phenylthio)methylidene **3b** [23]. Since the dissymmetric olefins synthesized thus far are all of the *S* configuration, this reduces to a stereostructure for the major adduct (2*R*,6*S*,1′*S*)-**2b** that likewise arises from equatorial attack on the pro-*R* face of the anion Li^+(2*R*,6*S*)-$\mathbf{1b}^-$. Thus, the ability of PMDTA to interrupt the chelation of the lithium in Li^+(2*R*,6*S*)-$\mathbf{1b}^-$ was substantiated by these results. Furthermore, the sense of asymmetric induction in the addition was, as expected, found to be independent of the substituent at the C(1′) position.

It is important to note that the coupling re-

TABLE 3 Nickel-Catalyzed Coupling of (Phenylthio)methylidene **3b**



2b (*S*)-**3b** (*S*)-**3a**

de, %[a]	*Solvent*	*Catalyst*[b]	*Reagent*[c]	*T*, °C (*time*, *hour*)	*Yield*,[d] %	*ee*,[e] %	*Specificity*,[f] %
89	THF	A	I	20 (44)	51	71	80
80	Et_2O	A	I	20 (44)	76	67	84
90	Et_2O	A	II	40 (11)	84	68	76
82	Et_2O	B	I	20 (48)	70	77	94
87	Et_2O	B	I	20 (48)	80	82	94

[a]Diastereomeric excess of **2b** by ^{31}P NMR.
[b]A: commercial; B: analytically pure.
[c]I: PhMgBr; II: $Ph_2Zn \cdot MgX_2$.
[d]Yield of isolated, purified product.
[e]ee of **3** by chiral GC.
[f](ee of **3a**)/(de of **2b**) × 100.

action is extremely sensitive to the nature of the solvent and the purity of (phenylthio)methylidene **3b** and Ni(dppp)Cl_2 catalyst. Stereochemical erosion occurred to a greater extent when the coupling reaction was performed in THF solution. The reaction proceeded with retention of configuration and 84% stereospecificity by the use of the commercially available nickel catalyst when performed in ether solution (Table 3).

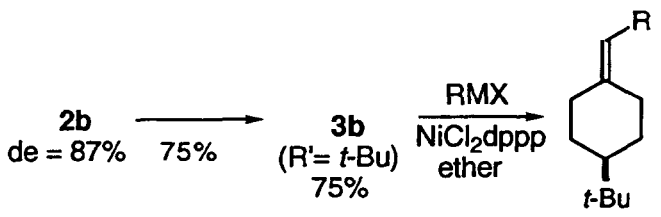
It has been well documented that the stereospecificity associated with the nickel-catalyzed coupling reactions is highly substrate dependent [24]. Particularly in the cases of trisubstituted olefins, considerable loss (up to 26%) of stereospecificity has been observed. Nevertheless, the stereochemical integrity in the coupling was preserved when the reaction was conducted under similar reaction conditions, but with the employment of analytically pure catalyst. The dissymmetric olefin (*S*)-**3a** was obtained in 70% yield and with 94% stereospecificity. Moreover, cleaner and more effective olefin conversion was accomplished by the use of analytically pure (*S*)-**3b**, leading to benzylidene (*S*)-**3a** in 80% yield. The exploitation of Ph_2Zn [25] in the presence of magnesium (II) salts increased the yield but afforded (*S*)-**3a** in lower ee (76% stereospecificity).

Asymmetric Synthesis of Alkylidene 4-tert-Butylcyclohexanes. Given the preliminary success in the highly stereospecific, nickel-catalyzed, cross-coupling of olefin (*S*)-**3b** with PhMgBr, further extensions toward the introduction of alkyl, aryl, and α-branched alkyl groups with suitable Grignard and dialkylzinc reagents were carried out. As summarized in Table 4, a variety of dissymmetric alkylidenes, **3a** and **3c–f**, can be synthesized in moderate to good yields (55–87%), and the coupling reactions proceeded with retention of configuration and with stereospecificity in the range of 74 to 94%.

The coupling protocol was also amenable to other arylmagnesium bromides, e.g., 1-naphthyl and 2-naphthyl Grignard reagents. Due to their intrinsically larger steric demands in these two cases, a higher reaction temperature was necessary to effect complete coupling transformations. The resulting (1-naphthyl)- and (2-naphthyl)methylidenes, **3c** and **3d**, were produced in 65 and 87% yield, respectively. Their stereospecificities are of similar magnitude but 10% lower than that for the corresponding coupling with PhMgBr.

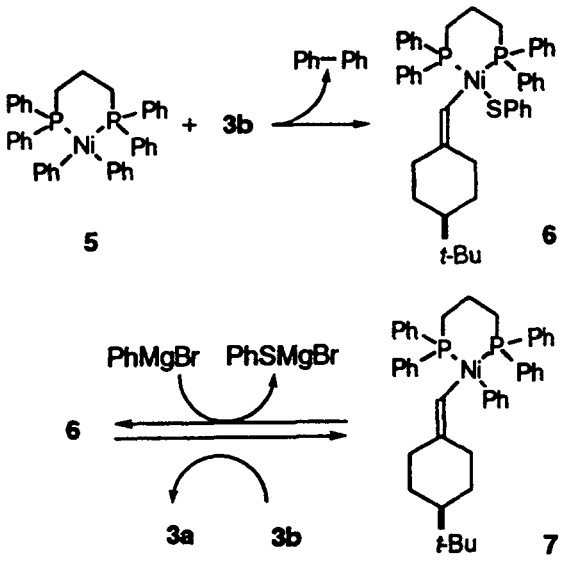
Attempts to couple (phenylthio)methylidene **3b** with methyl or vinylmagnesium bromide led to the complete recovery of the starting material. However, incorporation of an ethyl group into the olefinic moiety was readily achieved by the employment of Et_2Zn. The propylidene 4-*tert*-butylcyclohexane **3e** was synthesized in 55% yield, albeit with considerable erosion of stereospecificity (64–77%). The direct reduction of **3b** to generate achiral methylidene 4-*tert*-butylcyclohexane

TABLE 4 Nickel-Catalyzed Coupling with (Phenylthio)methylidene **3b**



R'MX	T, °C	Product	Yield, %[a]	ee, %[b]	Specificity, %
PhMgBr	20	**3a**	80	82	94
1-(Naph)MgBr[c,d]	40	**3c**	65	72	83
2-(Naph)MgBr[d]	40	**3d**	87	70	80
$Et_2Zn \cdot MgBr_2$	40	**3e**	55	56–67	64–77
$c\text{-}Hex_2Zn \cdot MgX_2$	40	**3f**	73	78	90

[a]Isolated yield.
[b]Determined by chiral GC analyses of the corresponding epoxides **8**.
[c]Prepared as a solution of ether/benzene (8/3).
[d]PhCHO was added to quench the remaining Grignard reagent.



SCHEME 3

appeared to be the major competing side reaction in the coupling reaction with Et_2Zn. These two drawbacks were significantly alleviated by the employment of the sterically bulkier dicyclohexylzinc (c-Hex_2Zn) reagent [26]. The corresponding (cyclohexyl)methylidene **3f** was obtained in 73% yield and 90% specificity.

It should be noted that the addition of magnesium salts can facilitate the weakening of the C–S bond by their Lewis acidic coordination at sulfur [25]. Similar reaction conditions without MgX_2 led to dramatic attenuation of both yield and enantioselectivity. Unfortunately, these types of coupling reactions are amenable only to Ph_2Zn. Similar couplings with divinyl, diallyl, and di-*tert*-butylzinc reagents failed.

Although the stereospecific couplings of (phenylthio)methylidenes were somewhat problematic, especially in the asymmetric synthesis of propylidene 4-*tert*-butylcyclohexane (*S*)-**3e**, combining the unique two-step olefination methodology with the nickel-catalyzed cross-coupling reaction truly provides an efficacious and general entry for the preparation of a diverse array of optically active alkylidene 4-substituted cyclohexanes.

On the basis of the commonly accepted mechanism for the similar transformations with organic halides [27], the nickel-catalyzed coupling of (phenylthio)methylidene **3b** with aryl Grignard reagents is believed to proceed via initial formation of diarylnickel complex **5** by the displacement reaction of $NiCl_2$dppp with the arylmagnesium bromide [22] (Scheme 3). Subsequent coupling of **5** with **3b** would lead to the (phenylthio)alkenylnickel complex **6** with release of a biaryl. Further reaction of **6** with the Grignard reagent provides an (aryl)(alkenyl)nickel complex **7**, from which the cross-coupling product, **3a** is extruded by its concurrent coupling with (phenylthio)methylidene **3b**. Thereby, the original complex **6** is regenerated to complete the catalytic cycle. Since varying degrees of stereochemical erosion were observed in these types of coupling reactions as well as in the related coupling of bromoalkylidenes to form dissymmetric olefins [28], possible intervention of an electron-transfer-type mechanism cannot be overlooked [29]. Another potential factor for the loss of stereospecificity stems from the deprotonation of (phenylthio)methylidene **3b** by a Grignard reagent to form the corresponding alkenyl anion [25,30]. Due to the carbenoid nature of this type of anion [30,31], the loss of geometric integrity may be expected. Similar mechanistic scenarios can also be applied to the coupling reactions with diorganozinc reagents.

CONCLUSION

A general method for the preparation of dissymmetric olefins has been developed. The phenylthio substituent was selected on the basis of mechanistic and chemical reactivity considerations and was found to be compatible with the olefination process. A thorough survey of solvents and additives of the first stage led to the use of PMDTA in Et_2O at −90°C to maximize the diastereoselectivity of addition. The asymmetric phenylthiomethylidenation can thus proceed with high overall selectivity. The dissymmetric alkylidene sulfide underwent nickel-catalyzed coupling with various

arylmagnesium bromides and diorganozinc reagents, providing an easy entry to a diverse array of dissymmetric alkylidenes with moderate to high stereospecificity.

EXPERIMENTAL

General Procedures

Nuclear magnetic resonance spectra were recorded on General Electric QE-300, General Electric GN-300NB, or Varian Unity-400 spectrometers in deuterochloroform with tetramethylsilane (TMS) or deuterochloroform as an internal reference. Phosphorus-31 spectra were referenced to external 85% H_3PO_4 (δ = 0.00 ppm). In carbon spectra, all peaks for which coupling constants are reported are doublets due to phosphorus coupling unless otherwise stated. Infrared spectra were recorded on an IBM FTIR-32 or a Mattson FTIR spectrometer. Mass spectra were recorded on a Varian MAT CH-5 spectrometer with ionization voltages of 70 or 10 eV. Combustion analyses were performed by the University of Illinois Microanalytical Laboratory. Bulb-to-bulb distillations were performed on a Buchi GKR-50 Kugelrohr apparatus; boiling points refer to air bath temperatures and are uncorrected. Melting points were determined on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Radial chromatography was performed on a Harrison Research Chromatotron using either 1, 2, or 4 mm rotors. All solvents utilized in reactions were distilled from appropriate drying agents before use. Analytical high pressure liquid chromatography (HPLC) was performed on a Hewlett-Packard 1090 Liquid Chromatograph with a Perkin-Elmer LC-75 spectrophotometric detector. Analytical gas chromatography was performed on a Hewlett-Packard 5890 Series II Gas Chromatograph fitted with a flame ionization detector (H_2 carrier gas, 1 mL/min). Retention times (t_R) and integrated ratios were obtained from a Hewlett-Packard 3390 integrator. Optical rotations were obtained on a Jasco DIP-360 Digital Polarimeter at room temperature. *t*-Butyllithium was titrated according to the method of Gilman and Schulze [32]. All reactions were run under a nitrogen atmosphere.

(2*R*,6*S*)-6-Methyl-3-(1-methylethyl)-2-(phenylthio)methyl-1,3,2-oxazaphosphorinane 2-oxide ((2*R*,6*S*)-**1b**)

Freshly distilled ethyl dichlorophosphite (915 μL, 8.0 mmol, 1.05 equiv) was introduced to an oven-dried 250 mL, 3-necked flask equipped with a reflux condenser, stirring bar, septum, and N_2-inlet. Anhydrous CH_2Cl_2 (52 mL) was added followed by addition of anhydrous triethylamine (2.23 mL, 16.0 mmol, 2.1 equiv). The solution was heated at reflux and treated dropwise with (*S*)-N-(1-methylethyl)-4-amino-2-butanol (1000.9 mg, 7.63 mmol) in anhydrous CH_2Cl_2 (10 mL) over 20 minutes. The reaction mixture was refluxed for 9 hours. The reaction mixture was cooled to room temperature, and anhydrous hexane (120 mL) was added. The solution was filtered through a Schlenk tube and the solvent removed under reduced pressure. The intermediate phosphite **4** was purified by Kugelrohr distillation (95°C, 10 torr) to afford 1.382 g (88.4%) of a colorless oil with a diastereoselectivity of 22.2:1 (EtO_{ax}:EtO_{eq}) as determined by ^{31}P NMR spectroscopy.

A 25 mL 3-necked flask was charged with phosphite **4** (691.4 mg, 3.37 mmol) and 10 mL of anhydrous CH_3CN in the presence of 4 Å molecular sieves. To this solution was added freshly prepared iodomethyl phenyl sulfide (1705 mg, 6.82 mmol, 2.0 equiv). The reaction mixture was stirred at ambient temperature for 14 hours. The crude reaction mixture was filtered through a short plug of Celite and concentrated. Aqueous $NaHCO_3$ (10%, 10 mL) was added. The aqueous layer was separated and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were dried (K_2CO_3), filtered, and evaporated. The mixture was analyzed by HPLC, which showed a diastereomeric ratio of 7.9:1 (*u*:*l*). Column chromatographic purification (EtOAc/hexane, 4/1, neutral alumina) [33] of the crude oil afforded 662.4 mg (66%) of (2*R*,6*S*)-**1b** as a white solid: bp 160°C (0.3 torr/air bath); ^1H NMR (300 MHz) 7.37–7.15 (m, 5H, Ph), 4.55–4.48 (m, 1H, HC(6)), 3.90–3.78 (m, 1H, $(CH_3)_2CHN$), 3.33 (dd, J_{HP} = 19.4, J_{HH} = 14.9, 1H, $H_aH_bC(1')$), 3.28 (dd, J_{HP} = 17.9, J_{HH} = 14.9, 1H, $H_aH_bC(1')$), 3.16–3.09 (m, 2H, $H_2C(4)$), 2.02–1.82 (m, 2H, $H_2C(5)$), 1.25 (d, J = 6.5, 3H, $(CH_3)_a(CH_3)_bCHN$)), 1.23 (dd, J_{HH} = 5.7, J_{HP} = 1.3, 3H, $CH_3C(6)$), 1.13 (d, J = 6.8, 3H, $(CH_3)_a(CH_3)_bCHN$)); ^{13}C NMR (75.5 MHz) 136.25 (J = 6.7, C_{ipso}), 128.78 (C_{ortho}), 128.16 (C_{meta}), 125.91 (C_{para}), 73.40 (J = 7.9, C(6)), 46.37 (J = 4.8, $(CH_3)_2CHN$), 37.49 (C(4)), 32.45 (J = 3.4, C(5)), 29.96 (J = 137.9, C(1')), 21.85 (J = 8.0, $CH_3C(6)$), 20.61 ($(CH_3)_a(CH_3)_bCHN$)), 20.09 (J = 4.3, $(CH_3)_a(CH_3)_bCHN$)); ^{31}P NMR (121.65 MHz) 21.50; IR (CCl_4) 3080 (w), 2975 (s), 2934 (m), 1482 (m), 1439 (m), 1408 (m), 1385 (m), 1246 (s, P=O), 1192 (s), 1175 (s), 1103 (s), 1032 (s), 994 (s), 893 (m), 866 (m), 857 (m); MS (70 eV) 299 (M^+, 51), 285 (13), 284 (85), 252 (12), 242 (19), 230 (12), 176 (100), 161 (12), 134 (79), 123 (79), 121 (11), 112 (22), 98 (20), 92 (12), 84 (13), 77 (21), 75 (14), 72 (14), 70 (29), 58 (16), 56 (50), 55 (37), 51 (14), 45 (65), 44 (21), 43 (36), 42 (32), 40 (15); TLC R_f 0.28 (EtOAc/hexane, 4/1); $[\alpha]_D$ 50.4 (c = 0.71, CH_2Cl_2). Anal. calcd for $C_{14}H_{22}NO_2PS$ (299.37): C, 56.17; H, 7.41; N, 4.68; P, 10.35; S: 10.71. Found: C, 56.18; H, 7.43; N, 4.66; P, 10.32; S, 10.61.

(2R,6S,1'S)-2-[1'-(4''-(1,1-Dimethylethyl)-1''-hydroxy)cyclohexyl-1'-phenylthiomethyl]-6-methyl-3-(1-methylethyl)-1,3,2-oxazaphosphorinane 2-oxide (**2b**)

In an oven-dried, 50 mL, 3-necked, round-bottomed, flask equipped with a thermometer, N_2-inlet, and septum was placed a solution of (2*R*,6*S*)-**1b** (222.0 mg, 0.74 mmol) and PMDTA (173 μL, 0.83 mmol, 1.1 equiv) in anhydrous ether (25 mL). The solution was cooled to an internal temperature of −68°C and *t*-butyllithium (1.81 M in pentane, 458 μL, 0.83 mmol, 1.1 equiv) was added with the appearance of a yellow color. The resulting reaction mixture was stirred at this temperature for 30 minutes. 4-*t*-Butylcyclohexanone (174.3 mg, 1.13 mmol, 1.5 equiv) in anhydrous ether (2 mL) was added via a cannula at −90°C over a period of 1 minute, and the reaction mixture was stirred for an additional 3.5 hours. A solution of HOAc/CH_3OH (226 mg/53 μL, 3.77 mmol, 5.1 equiv) in ether (0.5 mL) was added, followed by pH 7 buffer, and the slurried mixture was allowed to warm to room temperature. The aqueous layer was separated and extracted with *t*-butyl methyl ether (4 × 30 mL). The combined organic layers were dried (Na_2SO_4), filtered, and evaporated. ^{31}P NMR spectroscopic analysis of the crude product showed a diastereomeric ratio of 95:5. Flash chromatography of the crude product (neutral alumina) yielded 281.1 mg (84%) of **2b** as a white solid along with 33.1 mg (10%) of starting material: mp 113–115°C (CH_2Cl_2/pentane); ^1H NMR (300 MHz) 7.45–7.15 (m, 5H, Ph), 5.53 (s, 1H, OH), 4.59–4.54 (m, 1H, HC(6)), 3.85–3.78 (m, 1H, $(CH_3)_2CHN$), 3.53 (d, J = 20.6, $HC(1')_{minor}$), 3.28 (d, J = 17.2, 1H, $HC(1')_{major}$), 3.11–3.03 (m, 2H, $H_2C(4)$), 2.43–2.29 (m, 1H, $H_{eq}C(5)$), 2.10–1.84 (m, 3H, $H_{ax}C(5)$, 2 × $H_{ax}C(''))$, 1.71–1.39 (m, 7H, 2 × $H_2C(3'')$, 2 × $H_{eq}C(2'')$, HC(4'')), 1.40 (dd, J = 5.9, 1.2, 3H, $H_3CC(6)$), 1.20 (d, J = 6.7, 3H, $(CH_3)_a(CH_3)_bCHN$), 0.85 (s, 9H, $(H_3C)_3CC(4'')$), 0.77 (d, J = 6.8, 3H, $(CH_3)_a(CH_3)_bCHN$); ^{13}C NMR (75.5 MHz) 137.50 (J = 5.4, C_{ipso}), 129.01 (C_{ortho}), 128.93 (C_{meta}), 126.40 (C_{para}), 74.32 (C(1'')), 73.92 (J = 8.8, C(6)), 55.46 (J = 128.3, C(1')), 47.33 (C(4'')), 46.31 (J = 5.0 $(CH_3)_2CHN$), 37.39 (C(4)), 36.82 (J = 12.8, C(5)), 33.71 (J = 1.9, C(2a'')), 32.32 ($(H_3C)_3CC(4'')$), 31.69 (J = 3.4, C(2b'')), 27.56 ($(H_3C)_3CC(4'')$), 22.50 (J = 1.5, C(3a'')), 22.36 (C(3b'')), 21.95 (J = 8.1, $CH_3C(6)$), 20.87 ($(CH_3)_a(CH_3)_bCHN$), 19.59 (J = 4.6, $(CH_3)_a(CH_3)_bCHN$); ^{31}P NMR (121.65 MHz) 27.09 (major), 28.73 (minor); IR (CCl_4) 3351 (m), 2955 (s), 1584 (m), 1480 (s), 1439 (s), 1412 (s), 1366 (s), 1210 (P=O), 1100 (s), 1030 (s), 997 (s), 932 (s); MS (70 eV) 435 (M^+ − 18, 2), 299 (48), 284 (21), 177 (11), 176 (100), 162 (10), 134 (28), 123 (27), 112 (14), 98 (30), 72 (26), 70 (19), 69 (11), 58 (13), 57 (72), 56 (23), 55 (31), 45 (18), 44 (10), 43 (24), 42 (45), 40 (13); TLC R_f 0.58 (EtOAc/hexane, 1/2, basic alumina); $[\alpha]_D$ − 14.6 (c = 0.33; CH_2Cl_2). Anal. calcd for $C_{24}H_{40}NO_3PS$ (453.61): C, 63.55; H, 8.89; N, 3.09; P, 6.83; S, 7.07. Found: C, 63.65; H, 9.08; N, 3.01; P, 6.75; S, 6.98.

[*S*]-(+)-(*4-tert-Butylcyclohexylidene)phenylthiomethane* (**3b**)

In an oven-dried 25 mL, 3-necked, round-bottomed, flask fitted with a glass stopper, reflux condenser topped with a N_2-inlet, and septum was placed a suspension of **2b** (141.2 mg, 0.31 mmol) in CH_3CN (2.4 mL). The heterogeneous mixture was heated at 60°C to become partially homogeneous and anhydrous 2,6-lutidine (72.5 μL, 0.62 mmol, 2.0 equiv) was added. With this solution was added trityl triflate (195.4 mg, 0.50 mmol, 1.6 equiv) in anhydrous CH_3CN (1.2 mL) over a period of 2 minutes. The resulting brown solution, which became homogeneous, was allowed to stir at this temperature for 14.5 hours. Additional 2,6-lutidine (72.5 μL, 0.62 mmol, 2 equiv) and trityl triflate (195.4 mg, 0.50 mmol, 1.6 equiv) in CH_3CN (1.2 mL) were added. The reaction mixture was stirred for an additional 22 hours. The concentrated reaction mixture was purified by column chromatography (pentane/petroleum ether, 1/1) to yield 53.8 mg (72%) of olefin (*S*)-**3b**. An analytical sample was obtained by Kugelrohr distillation: bp 90°C (0.45 torr/air bath); ^1H NMR (400 MHz) 7.31–7.25 (m, 4H, Ar (2 × H_{para} + 2 × H_{meta})), 7.17–7.13 (m, 2H, Ar (2 × H_{ortho})), 5.87 (t, J = 1.6, 1H, C*H*SPh), 3.02–2.97 (m, 1H, $H_{eq}C(6)$), 2.47–2.42 (m, 1H, $H_{eq}C(2)$), 2.18–2.10 (m, 1H, $H_{ax}C(2)$), 1.93–1.79 (m, 3H, $H_{ax}C(6)$, $H_{eq}C(3)$, $H_{eq}C(5)$), 1.21 (tt, J = 12.0, 2.7, 1H, HC(4)), 1.11 (dq, J = 12.2, 3.9, 1H, $H_{ax}C(5)$), 1.05 (dq, J = 11.5, 3.9, 1H, $H_{ax}C(3)$), 0.87 (s, 9H, 3 × $H_3C(8)$); ^{13}C NMR (100 MHz) 148.03 (C(1)), 137.62 (C(1')), 128.79 (C(2')), 127.67 (C(3')), 125.41 (C(4')), 111.45 (*C*HSPh), 48.01 (C(4)), 36.51 (C(6)), 32.45 (C(7)), 30.25 (C(2)), 28.99 (C(5)), 28.04 (C(3)), 27.59 (C(8)); IR (CCl_4) 3078 (w), 2948 (s), 2867 (m), 2838 (m), 1584 (w), 1480 (s), 1441 (m), 1395 (w), 1366 (m), 1296 (w), 1240 (w), 1173 (w), 1090 (w), 1026 (w), 988 (w), 930 (w), 851 (w); MS (70 eV) 261 (M^+ + 1, 14), 260 (M^+, 76), 135 (24), 123 (13), 110 (11), 107 (16), 95 (39), 94 (28), 93 (36), 91 (27), 81 (21), 79 (17), 77 (21), 69 (10), 67 (11), 65 (10), 57 (100), 55 (13), 45 (11), 43 (12), 42 (38), 40 (10); TLC R_f 0.43 (petroleum ether/pentane, 1/1); $[\alpha]_D$ − 103.2 (c = 0.5, CH_3OH). Anal. calcd for $C_{17}H_{24}S$ (260.42): C, 78.40; H, 9.29; S: 12.31. Found: C, 78.47; H, 9.31; S, 12.24.

[*S*]-(+)-(*4-tert-Butylcyclohexylidene)phenylmethane* (**3a**)

In a 100 mL, 3-necked, round-bottomed, flask equipped with a glass stopper, reflux condenser topped with a N_2-inlet, and septum was placed a

suspension of alkenyl sulfide (*S*)-**3b** (141.9 mg, 0.54 mmol) and $NiCl_2$dppp (59 mg, 0.11 mmol, 20 mol %) in anhydrous ether (27 mL). The heterogeneous mixture was cooled on ice, and phenylmagnesium bromide (3.0 M in ether, 545 μL, 1.63 mmol, 3 equiv) was added via a 1 mL, gas-tight syringe over 2 minutes. The solution turned homogeneous and brown gradually, upon warming to ambient temperature. The resulting reaction mixture was stirred for 28 hours. To the mixture was added dropwise saturated aqueous NH_4Cl (20 mL) at 0°C, followed by addition of H_2O (17 mL). The heterogeneous mixture was passed through a short plug of Celite, and the plug was washed with pentane (3 × 10 mL). The aqueous layer was separated and extracted with ether (3 × 45 mL). The combined organic layers were washed with brine (1 × 10 mL) and dried (MgSO4), filtered, and evaporated. Column and radial chromatographic purification (petroleum ether) of the crude oil afforded 99.8 mg (80.2 %) of (*S*)-**3a** as a colorless oil. GC analysis (J&W cyclodex-B, 145°C isothermal) of the corresponding epoxides **8a** showed an enantiomeric excess of 82.4%: bp 150°C (10 torr/air bath); ^{1}H NMR (300 MHz) 7.33–7.15 (m, 5H, Ph), 6.22 (s, 1H, C*H*Ph), 2.99–2.94 (m, 1H, H_{eq}C(6)), 2.43–2.37 (m, 1H, H_{eq}C(2)), 2.24–2.16 (m, 1H, H_{ax}C(2)), 1.95–1.80 (m, 3H, H_{ax}C(6), H_{eq}C(5), H_{eq}C(3)), 1.28–0.93 (m, 3H, H_{ax}C(3), H_{ax}C(5), HC(4)), 0.86 (s, 9H, $(CH_3)_3$CC(4)); ^{13}C NMR (75.5 MHz) 143.35 (C(1)), 138.38 (C(1')), 128.90 (C(3')), 127.97 (C(4')), 125.74 (C(2)), 121.59 (*C*HPh), 48.21 (C(4)), 37.57 (C(6)), 32.47 ($(CH_3)_3C$), 29.26 (C(2)), 29.21 (C(5)), 28.52 (C(3)), 27.62 ($(CH_3)_3C$); IR (CCl_4) 3079 (w), 3023 (w), 2955 (s), 2865 (s), 2838 (m), 1653 (w), 1597 (w), 1480 (m), 1445 (m), 1393 (w), 1364 (m), 1240 (w), 988 (w), 932 (w), 912 (w), 853 (w); MS (70 eV) 228 (M^+, 55), 171 (12), 143 (11), 137 (11), 130 (16), 129 (45), 128 (16), 123 (11), 117 (17), 115 (21), 104 (31), 92 (13), 91 (56), 81 (25), 80 (17), 79 (11), 67 (21), 57 (100), 41 (32); TLC R_f 0.68 (pentane).

(*S*)-(+)-(*4-tert-Butylcyclohexylidene-1'-naphthyl*)*methane* (**3c**)

In a 50 mL, 3-necked, round-bottomed, flask equipped with a glass stopper, reflux condenser topped with a N_2-inlet, and septum was placed a suspension of alkenyl sulfide (*S*)-**3b** (152.5 mg, 0.59 mmol) and $NiCl_2$dppp (63.49 mg, 0.117 mmol, 20 mol %) in anhydrous ether (20 mL). The heterogeneous mixture was cooled on ice, and 1-naphthylmagnesium bromide (0.73 M in ether/benzene: 8/3, 4.0 mL, 2.93 mmol, 5 equiv) was added via a 5 mL, gas-tight syringe over 2 minutes. The solution turned brown gradually, upon warming to ambient temperature. The resulting reaction mixture was stirred at reflux for 48 hours. The reaction mixture was cooled to 0°C and the excess of 1-naphthylmagnesium bromide was treated with anhydrous benzaldehyde (298 μL, 2.93 mmol, 5 equiv). To the mixture was added dropwise saturated aqueous NH_4Cl (30 mL), followed by addition of H_2O (10 mL). The heterogeneous mixture was passed through a short plug of Celite, and the plug was washed with ether (3 × 10 mL). The aqueous layer was separated and extracted with ether (3 × 40 mL). The combined organic layers were washed with brine (1 × 10 mL) and dried (MgSO4), filtered, and evaporated. Column and radial chromatographic purification (hexane) of the crude oil afforded 106.4 mg (65%) of (*S*)-**3c** as a colorless oil. An analytical sample was obtained by Kugelrohr distillation. GC analysis (G-TA γ-cyclodextrin, 180°C isothermal) of the corresponding epoxides **8c** showed an enantiomeric ratio of 72%: bp 110°C (0.05 torr/air bath); ^{1}H NMR (400 MHz) 8.05–7.28 (m, 7H, ArH), 6.60 (s, 1H, ArHC=C(1)), 2.69–2.55 (m, 2H, H_{eq}C(2), H_{eq}C(6)), 2.35–2.25 (m, 1H, H_{ax}C(2)), 2.04–1.98 (m, 1H, H_{eq}C(3)), 1.87–1.77 (m, 2H, H_{ax}C(6), H_{ax}C(3)), 1.33–1.18 (m, 2H, H_{eq}C(5), H_{ax}C(4)), 1.10–0.97 (m, 1H, H_{ax}C(5)), 0.88 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100.6 MHz) 144.52 (C(1)), 135.54 (C(1')), 133.53 (C(10')), 132.35 (C(9')), 128.24 (C(2')), 126.67 (C(4')), 126.60 (C(7')), 125.52 (C(6')), 125.50 (C(5')), 125.29 (C(8')), 125.25 (C(3')), 119.37 (ArCH), 48.23 (C(4)), 37.29 (C(2)), 32.41 ($C(CH_3)_3$), 29.85 (C(6)), 29.42 (C(3)), 28.66 (C(5)), 27.65 ($C(CH_3)_3$); IR (neat) 3058 (m), 2948 (s), 2865 (s), 2836 (s), 1653 (m), 1590 (m), 1507 (m), 1478 (m), 1441 (m), 1393 (s), 1364 (s), 1240 (m), 1175 (w), 1015 (w), 984 (m), 930 (w), 880 (w), 864 (w); MS (70 eV) 279 (M^+ + 1, 22), 178 (M^+, 100), 221 (14), 193 (13), 180 (24), 179 (57), 178 (26), 167 (21), 166 (18), 165 (62), 154 (30), 153 (16), 152 (11), 142 (22), 141 (55), 57 (60), 55 (10), 41 (22); TLC R_f 0.48 (hexane); $[\alpha]_D$ −3.7° ($CHCl_3$, c = 0.57); $[\alpha]_{405}$ −43.5° ($CHCl_3$, c = 0.57). Anal. calcd for $C_{21}H_{26}$ (278.44): C, 90.59; H, 9.41. Found: C, 90.62; H, 9.37.

(*S*)-(+)-(*4-tert-Butylcyclohexylidene-2'-naphthyl*)*methane* (**3d**)

In a 50 mL, 3-necked, round-bottomed, flask equipped with a glass stopper, reflux condenser topped with a N_2-inlet, and septum was placed a suspension of alkenyl sulfide (*S*)-**3b** (170.6 mg, 0.66 mmol) and $NiCl_2$dppp (71.02 mg, 0.13 mmol, 20 mol %) in anhydrous ether (22 mL). The heterogeneous mixture was cooled on ice, and 2-naphthylmagnesium bromide (1.18 M in ether, 1.7 mL, 1.97 mmol, 3 equiv) was added via a 5 mL, gas-tight syringe over 2 minutes. The solution turned brown gradually and became homogeneous upon warming to ambient temperature. The resulting reaction mixture was stirred at reflux for 24 hours. The reaction mixture was cooled to 0°C, and the excess of 2-naphthylmagnesium bromide was treated with anhydrous benzaldehyde (200 μL, 1.97 mmol, 3 equiv). To the mixture was added dropwise saturated aqueous NH_4Cl (30 mL), followed by addition of H_2O (10 mL). The heterogeneous mixture

was passed through a short plug of Celite, and the plug was washed with ether (3 × 10 mL). The aqueous layer was separated and extracted with ether (3 × 40 mL). The combined organic layers were washed with brine (1 × 15 mL) and dried (MgSO4), filtered, and evaporated. Column and radial chromatographic purification (hexane) of the crude oil afforded 158.3 mg (87%) of (*S*)-**162** as a colorless oil. An analytical sample was obtained by Kugelrohr distillation. GC analysis (G-TA γ-cyclodextrin, 185°C isothermal) of the corresponding epoxides **8d** showed an enantiomeric ratio of 70%: bp 150°C (0.05 torr/air bath); ^{1}H NMR (300 MHz) 7.81–7.35 (m, 6H, Ar), 7.65 (s, 1H, HC(1')), 6.38 (s, 1H, ArHC=C(1)), 3.09–3.02 (m, 1H, H_{eq}C(2)), 2.50–2.44 (m, 1H, H_{eq}C(6)), 2.31–2.22 (m, 1H, H_{ax}C(2)), 1.99–1.85 (m, 3H, H_{eq}C(3), H_{ax}C(6), H_{ax}C(3)), 1.32–1.02 (m, 3H, H_{eq}C(5), H_{ax}C(4), HC(4)), 0.88 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (75.5 MHz) 143.94 (C(1)), 135.90 (C(9')), 133.38 (C(2')), 131.79 (C(10')), 127.75 (C(1')), 127.69 (C(8')), 127.53 (C(6')), 127.36 (C(4')), 127.15 (C(5')), 125.84 (C(7')), 125.84 (C(7')), 125.27 (C(3')), 121.64 (ArCH), 48.21 (C(4)), 37.64 (C(2)), 32.49 ($C(CH_3)_3$), 29.41 (C(6)), 29.22 (C(3)), 28.52 (C(5)), 27.62 ($C(CH_3)_3$); IR (CCl_4) 3019 (s), 2957 (s), 2867 (m), 1505 (w), 1478 (w), 1429 (w), 1393 (w), 1366 (m), 1215 (s), 1044 (w), 930 (w), 901 (w), 876 (w), 816 (s); MS (70 eV) 279 (M^+ + 1, 23), 278 (M^+, 100), 221 (15), 194 (10), 193 (13), 180 (21), 179 (49), 178 (24), 167 (19), 166 (12), 165 (35), 154 (38), 142 (50), 141 (78), 136 (11), 128 (11), 93 (12), 67 (11), 57 (66), 55 (10), 41 (25); TLC R_f 0.45 (hexane); $[\alpha]_D$ +32.3° ($CHCl_3$, c = 0.61). Anal. calcd for $C_{21}H_{26}$ (278.44): C, 90.59; H, 9.41. Found: C, 90.64; H, 9.38.

(*S*)-(+)-(*4-tert-Butylcyclohexylidene*)*ethylmethane* (**3e**)

In a 50 mL, 3-necked, round-bottomed, flask equipped with a glass stopper, reflux condenser topped with a N_2-inlet, and septum was placed a suspension of alkenyl sulfide (*S*)-**3b** (148.8 mg, 0.57 mmol) and $NiCl_2$dppp (61.9 mg, 0.114 mmol, 20 mol %) in anhydrous ether (14 mL). The heterogeneous mixture was cooled on ice, and neat Et_2Zn (234 μL, 2.29 mmol, 4 equiv) was added via a gas-tight syringe over 1 minute. The solution became homogeneous and greenish brown. A solution of $MgBr_2$ in ether (2.0 M, 2.3 mL, 4.57 mmol, 8 equiv) was added. The reaction mixture became bilayered with a brownish color in the bottom layer. The solution turned brown gradually upon warming to ambient temperature. The resulting reaction mixture was stirred at reflux for 20 hours. The reaction mixture was cooled to 0°C, and saturated aqueous NH_4Cl (20 mL) was added dropwise, followed by addition of H_2O (7 mL). The heterogeneous mixture was passed through a short plug of Celite, and the plug was washed with pentane (3 × 10 mL). The aqueous layer was separated and extracted with pentane (3 × 40 mL). The combined organic layers were dried (MgSO4), filtered, and evaporated. Column and radial chromatographic purification (hexane) of the crude oil afforded 56.2 mg (55%) of (*S*)-**3e** as a colorless oil. An analytical sample was obtained by Kugelrohr distillation. GC analysis (B-PH β-cyclodextrin, 100°C isothermal) of the corresponding epoxides **8e** showed an enantiomeric excess of 56%: bp 45°C (0.1 torr/air bath); ^{1}H NMR (300 MHz) 5.06 (t, J = 7.1, 1H, EtCH=C(1)), 2.63 (ddd, J = 13.4, 5.5, 3.0, 1H, H_{eq}C(2)), 2.23–2.15 (m, 1H, H_{eq}(6)), 1.99 (quintet, J = 7.2, 2H, CH_2CH_3), 2.04–1.94 (m, 1H, H_{ax}C(2), 1.89–1.78 (m, 2H, H_{eq}C(3), H_{ax}C(6)), 1.71–1.61 (m, 1H, H_{ax}(C(3)), 1.15 (tt, J = 11.9, 2.8, 1H, HC(4)), 1.07–0.91 (m, 2H, H_2C(5)), 0.93 (t, J = 7.5, 3H, CH_2CH_3), 0.85 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100.6 MHz) 138.81 (C(1)), 122.83 (EtCH=C(1)), 48.55 (C(4)), 36.95 (C(2)), 32.46 ($C(CH_3)_3$), 29.26 (C(6)), 28.51 (C(3)), 28.38 (C(5)), 27.65 ($C(CH_3)_3$), 20.46 (CH_2CH_3), 14.89 (CH_2CH_3); IR (neat) 2959 (s), 2869 (s), 2838 (s), 1653 (w), 1559 (w), 1507 (w), 1478 (m), 1456 (m), 1443 (m), 1393 (m), 1369 (s), 1304 (w), 1240 (m), 1223 (w), 1169 (w), 1067 (w), 1032 (w), 982 (w), 928 (w), 901 (w), 845 (m); MS (70 eV) 180 (M^+, 12), 124 (11), 123 (12), 109 (14), 95 (18), 82 (31), 81 (61), 79 (15), 69 (11), 68 (12), 67 (33), 57 (100), 55 (21), 41 (45), 39 (12); TLC R_f 0.68 (hexane); $[\alpha]_D$ +5.9° ($CHCl_3$, c = 0.575); +7.4° (CH_3OH, c = 0.84). Anal. calcd for $C_{13}H_{24}$ (180.34): C, 86.59; H, 13.41. Found: C, 86.51; H, 13.41.

(*S*)-(+)-(*4-tert-Butylcyclohexylidene*)*cyclohexylmethane* (**3f**)

In a 50 mL, 3-necked, round-bottomed, flask equipped with a glass stopper, reflux condenser topped with a N_2-inlet, and septum was placed a suspension of alkenyl sulfide (*S*)-**3b** (148.3 mg, 0.57 mmol) and $NiCl_2$dppp (61.7 mg, 0.114 mmol, 20 mol %) in anhydrous ether (14 mL). The heterogeneous mixture was cooled on ice, and a freshly prepared dicyclohexylzinc-2 · $MgCl_2$ mixture (0.28 M in ether, 8.1 mL, 2.28 mmol, 4 equiv) was added via a 10-mL, gas-tight syringe over 3 minutes. A solution of $MgBr_2$ in ether (2.0 M, 2.3 mL, 4.56 mmol, 8 equiv) was added. The reaction mixture became bilayered with a brownish color in the bottom layer. The solution turned dark brown gradually upon warming to ambient temperature. The resulting reaction mixture was stirred at reflux for 20 hours. The reaction mixture was cooled to 0°C, and saturated aqueous NH_4Cl (20 mL) was added dropwise, followed by addition of H_2O (7 mL). The heterogeneous mixture was passed through a short plug of Celite, and the plug was washed with pentane (3 × 10 mL). The aqueous layer was separated and extracted with pentane (3 × 50 mL). The combined organic layers were dried (MgSO4), filtered, and evaporated. Column and radial chromatographic purification (hexane) of the crude oil afforded 97.1

mg (73%) of (*S*)-**3f** as a colorless oil. An analytical sample was obtained by Kugelrohr distillation. GC analysis (J&W β-cyclodextrin, 135°C isothermal) of the corresponding epoxides **8f** showed an enantiomeric excess of 78%: bp 80°C (0.1 torr/air bath); ^{1}H NMR (400 MHz) 4.89 (d, J = 8.8, 1H, CH=C(1)), 2.62 (ddd, J = 13.4, 5.6, 3.2, 1H, $H_{eq}C(2)$), 2.21–2.11 (m, 2H, HC(1'), $H_{eq}C(6)$), 1.98 (dt, J = 12.9, 4.2, 1H, $H_{ax}C(2)$), 1.88–1.79 (m, 2H, $H_{ax}C(6)$, $H_{eq}C(6')$), 1.75–1.55 (m, 6H, cyclohexane Hs), 1.33–0.88 (m, 8H, cyclohexane Hs), 0.84 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100.6 MHz) 137.76 (C(1)), 127.55 (C=*C*H), 48.51 (C(4)), 36.97 (C(2)), 36.14 (C(1')), 34.13 (C(6)), 33.62 (C(6')), 32.44 ($C(CH_3)_3$), 29.33 (C(2')), 28.88 (C(3)), 28.78 (C(5)), 27.64 ($C(CH_3)_3$), 26.89 (C(4')), 26.14 (C(5')), 26.11 (C(3')); IR (neat) 2921 (s), 2851 (s), 1653 (w), 1559 (w), 1539 (w), 1447 (m), 1478 (w), 1393 (w), 1364 (m), 1240 (m), 990 (w), 891 (w), 843 (w); MS (70 eV) 234 (M^+, 10), 135 (15), 109 (16), 97 (28), 96 (35), 95 (42), 94 (10), 93 (16), 91 (10), 83 (46), 82 (81), 81 (54), 80 (23), 79 (24), 69 (14), 67 (66), 57 (100), 55 (66), 54 (12), 53 (11), 43 (12), 41 (64), 39 (13); TLC R_f 0.86 (hexane); $[\alpha]_D$ +6.3° ($CHCl_3$, c = 0.59); +14.5° (CH_3OH, c = 0.455). Anal. calcd for $C_{17}H_{30}$ (234.43): C, 86.81; H, 12.90. Found: C, 87.06; H, 12.93.

6-(1,1-Dimethylethyl)-2-(1'-naphthyl)-1-oxaspiro[2.5]octane (**8c**)

In a 25 mL, 2-necked, round-bottomed, flask fitted with a N_2-inlet and septum was placed a solution of olefin **3c** (404.1 mg, 1.45 mmol) in anhydrous CH_2Cl_2 (10 mL). The solution was cooled in an ice-water bath, and *m*CPBA (275.5 mg, 16.0 mmol, 1.1 equiv) in anhydrous CH_2Cl_2 (7 mL) was added via a cannula over a 2 minute period. The reaction mixture was stirred at this temperature for 30 minutes and then at room temperature for 9 hours. Aqueous $NaHCO_3$ (10%, 10 mL) was added, followed by H_2O (5 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were dried (K_2CO_3), filtered, and evaporated. Column chromatographic purification (pentane/ether, 20/1) of the crude solid afforded epoxides **8c** (351.4 mg, 82%) as a white solid. An analytical sample was obtained by Kugelrohr distillation: bp 150°C (0.1 torr/air bath); ^{1}H NMR (300 MHz) 8.12–8.09, 7.93–7.74, and 7.55–7.43 (m, 7H, Ar), 4.33 (s, 1H, HC(2)), 2.19 (dt, J = 13.5, 4.4, 1H, $H_{ax}C(4)$), 2.17–2.04 (m, 1H, $H_{eq}C(4)_{minor}$), 1.96–1.87 (m, 1H, $H_{eq}C(4)_{major}$), 1.77–1.23 (m, 6H, $H_2C(8)$, $H_2C(5)$, $H_2C(7)$), 1.10 (m, 1H, HC(6)), 0.88 (s, 9H, $(CH_3)_3C_{major}$), 0.81 (s, 9H, $(CH_3)_3C_{minor}$); ^{13}C NMR (75.5 MHz) major: 133.06 (C(1')), 132.55 (C(10')), 130.97 (C(9')), 128.59 (C(3')), 127.39 (C(4')); aromatic carbons: 126.04, 125.68, 125.24, 124.04, 123.03 (C(8')); 64.84 (C(3)), 63.00 (C(2)), 47.55 (C(6)), 34.73 (C(4)), 32.44 ($C(CH_3)_3$), 28.64 (C(8)), 27.55 ($C(CH_3)_3$), 24.94 (C(5)), 24.73 (C(7)); minor: 133.10 (C(1')), 132.21 (C(10')), 130.97 (C(9')), 128.66 (C(3')), 127.52 (C(4')); aromatic carbons: 126.04, 125.73, 125.24, 123.94, 123.21 (C(8')); 66.28 (C(3)), 63.71 (C(2)), 46.96 (C(6)), 35.32 (C(4)), 32.15 ($C(CH_3)_3$), 28.64 (C(8)), 27.48 ($C(CH_3)_3$), 26.70 (C(5)), 26.00 (C(7)); IR (CCl_4) 3061 (m), 2948 (s), 2867 (s), 1597 (w), 1511 (m), 1480 (m), 1447 (m), 1395 (m), 1366 (s), 1343 (w), 1312 (w), 1260 (w), 1242 (w), 1211 (m), 1173 (w), 1040 (m), 1021 (w), 984 (m), 936 (m), 926 (m), 880 (w), 816 (m); MS (70 eV) 295 (M^+ + 1, 14), 294 (M^+, 63), 276 (10), 219 (22), 195 (13), 192 (13), 179 (11), 178 (10), 167 (13), 165 (14), 157 (21), 156 (46), 155 (41), 142 (14), 141 (100), 140 (85), 139 (43), 129 (19), 128 (31), 127 (20), 95 (12), 81 (15), 67 (12), 57 (52), 55 (16), 42 (35); TLC R_f 0.58, 0.50 (pentane/ether, 20/1); GC t_R 42.48 minutes, 43.15 minutes; 54.99 minutes (G-TA γ-cyclodextrin, 30 m × 0.2 mm, 180°C isothermal). Anal. calcd for $C_{21}H_{26}O$ (294.42): C, 85.67; H, 8.90. Found: C, 85.69; H, 8.90.

6-(1,1-Dimethylethyl)-2-(2'-naphthyl)-1-oxaspiro[2.5]octane (**8d**)

Data for **8d** (yield 81%): bp 160°C (0.1 torr/air bath); ^{1}H NMR (400 MHz) 7.86–7.75 and 7.51–7.41 (m, 7H, Ar), 4.07 (s, 1H, $HC(2)_{major}$), 4.02 (s, 1H, $HC(2)_{minor}$), 2.04 (dt, J = 13.9, 4.2, 1H, $H_{ax}C(4)_{minor}$), 2.01 (dt, J = 13.4, 4.2, 1H, $H_{ax}C(4)_{major}$), 1.90–1.83 (m, 1H, $H_{eq}C(4)_{major}$), 1.78–1.74 (m, 1H, $H_{eq}C(8)_{major}$), 1.66–1.27 (m, 5H, $H_{ax}C(8)$, $H_2C(5)$, $H_2C(7)$), 1.12–1.05 (m, 1H, HC(6)), 0.89 (s, 9H, $(CH_3)_3C_{major}$), 0.83 (s, 9H, $(CH_3)_3C_{minor}$); ^{13}C NMR (75.5 MHz) major: 133.89 (C(2')), 132.89 (C(9')), 132.64 (C(10')), 127.69 (C(5')), 127.61 (C(4')), 127.52 (C(8')), 126.07 (C(7')), 125.62 (C(6')), 124.98 (C(1')), 124.31 (C(3')), 65.27 (C(3)), 64.22 (C(2)), 47.53 (C(6)), 35.01 (C(4)), 32.40 ($C(CH_3)_3$), 28.22 (C(8)), 27.52 ($C(CH_3)_3$), 24.92 (C(5)), 24.79 (C(7)); minor: 133.77 (C(2')), 132.89 (C(9')), 132.64 (C(10')), 127.69 (C(5')), 127.61 (C(4')), 127.52 (C(8')), 126.07 (C(7')), 125.62 (C(6')), 124.98 (C(1')), 124.31 (C(3')), 66.27 (C(3)), 64.73 (C(2)), 46.91 (C(6)), 35.45 (C(4)), 32.18 ($C(CH_3)_3$), 28.09 (C(8)), 27.52 ($C(CH_3)_3$), 26.85 (C(5)), 25.66 (C(7)); IR (CCl_4) 3056 (m), 2895 (s), 2867 (m), 1653 (w), 1509 (w), 1478 (w), 1447 (w), 1395 (w), 1366 (w), 926 (w); MS (70 eV) 294 (M^+, 29), 157 (32), 156 (100), 155 (30), 142 (12), 141 (78), 140 (29), 139 (21), 129 (14), 127 (13), 81 (10), 57 (37), 55 (10), 41 (26); TLC R_f 0.5, 0.43 (pentane/ether, 20/1); GC t_R 47.80 minutes, 49.36 minutes; 61.73 minutes (G-TA γ-cyclodextrin, 30 m × 0.2 mm, 185°C isothermal). Anal. calcd for $C_{21}H_{26}O$ (294.42): C, 85.67; H, 8.90. Found: C, 85.64; H, 8.93.

(1,1-Dimethylethyl)-2-Ethyl-6-1-oxaspiro[2.5]octane (**8e**)

Data for **8e** (yield 97%): bp 55°C (0.15 torr/air bath); ^{1}H NMR (300 MHz) 2.72 (t, J = 6.5, 1H, $HC(2)_{major}$), 2.67 (t, J = 6.6, 1H, $HC(2)_{minor}$), 1.91–1.46 (m, 8H,

$H_2C(4)$, $H_2C(8)$, $C(2)CH_2CH_3$, $H_2C(5)$), 1.41–1.22 (m, 2H, $H_2C(7)$), 1.13–1.06 (m, 1H, HC(6)), 1.07 (t, J = 7.6, 3H, $CH_2CH_3C(2)_{minor}$), 1.02 (t, J = 7.5, 3H, $CH_2CH_3C(2)_{major}$), 0.88 (s, 9H, $(CH_3)_3C_{major}$), 0.87 (s, 9H, $(CH_3)_3C_{minor}$); ^{13}C NMR (75.5 MHz) major: 65.40 (C(2)), 62.01 (C(3)), 47.64 (C(6)), 35.09 (C(4)), 32.34 ($C(CH_3)_3$), 28.74 (C(8)), 27.41 ($C(CH_3)_3$), 24.56 (C(5)), 24.50 (C(7)), 21.15 ($C(2)CH_2CH_3$), 10.45 ($C(2)CH_2CH_3$); minor: 66.01 (C(2)), 63.31 (C(3)), 47.21 (C(6)), 35.82 (C(4)), 32.14 ($C(CH_3)_3$), 29.12 (C(8)), 27.48 ($C(CH_3)_3$), 26.62 (C(5)), 26.45 (C(7)), 21.62 ($C(2)CH_2CH_3$), 10.63 ($C(2)CH_2CH_3$); IR (neat) 2969 (s), 2868 (m), 2842 (m), 1456 (m), 1395 (w), 1366 (m), 1222 (w), 986 (w), 924 (w), 903 (w); MS (70 eV) 196 (M^+, 7), 181 (33), 167 (10), 139 (22), 112 (10), 111 (19), 98 (19), 97 (38), 95 (11), 85 (11), 83 (30), 81 (23), 79 (15), 71 (50), 70 (14), 69 (26), 67 (20), 62 (31), 57 (100), 55 (30); TLC R_f 0.48, 0.35 (pentane/ether, 20/1); GC t_R 20.26 minutes; 25.03 minutes, 27.05 minutes (B-PH β-cyclodextrin, 30 m × 0.2 mm, 100°C isothermal). Anal. calcd for $C_{13}H_{24}O$ (196.32): C, 79.58; H, 12.32. Found: C, 79.83; H, 12.48.

2-Cyclohexyl-6-(1,1-dimethylethyl)-1-oxaspiro[2.5]octane (**8f**)

Data for **8f** (yield 93%): bp 70°C (0.1 torr/air bath); ^1H NMR (300 MHz) 2.45 (d, J = 9.0, 1H, $HC(2)_{major}$), 2.41 (d, J = 8.4, 1H, $HC(2)_{minor}$), 1.93–1.48 and 1.41–0.93 (m, 20H, cyclohexane Hs), 0.86 (s, 9H, $(CH_3)_3C_{major}$), 0.86 (s, 9H, $(CH_3)_3C_{minor}$); ^{13}C NMR (75.5 MHz); major: 68.93 (C(2)), 62.09 (C(3)), 47.70 (C(6)), 36.83 (C(1')), 35.35 (C(4)), 32.43 ($C(CH_3)_3$), 30.52 (C(2a')), 29.06 (C(2b')), 28.91 (C(8)), 27.48 ($C(CH_3)_3$), 26.18 (C(4')), 25.53 (C(5)), 24.38 (C(7)), 24.57 (C3')); minor: 69.93 (C(2)), 63.56 (C(3)), 47.26 (C(6)), 37.03 (C(1')), 36.04 (C(4)), 32.22 ($C(CH_3)_3$), 30.39 (C(2a')), 29.52 (C(2b')), 29.38 (C(8)), 27.56 ($C(CH_3)_3$), 26.77 (C(5)), 26.63 (C(7)), 26.23 (C(4')), 24.65 (C(3')); IR (neat) 2928 (s), 2853 (s), 1449 (m), 1393 (w), 1366 (m), 1242 (w), 1219 (w), 1184 (w), 992 (w), 924 (w), 887 (m), 857 (w); 250 (M^+, 6), 167 (13), 155 (52), 151 (20), 149 (10), 139 (34), 137 (11), 98 (30), 97 (32), 96 (44), 95 (29), 93 (17), 84 (13), 83 (36), 82 (10), 81 (63), 80 (16), 79 (17), 70 (24), 69 (22), 68 (11), 67 (41), 57 (100), 55 (62), 54 (11), 53 (12), 43 (14), 41 (55), 39 (10); TLC R_f 0.48, 0.33 (pentane/ether, 8/1); GC t_R 44.34 minutes, 45.33 minutes; 51.39 minutes, 52.57 minutes (J&W β-cyclodextrin, 30 m × 0.2 mm, 135°C isothermal). Anal. calcd for $C_{17}H_{30}O$ (250.43): C, 81.54; H, 12.07. Found: C, 81.55; H, 12.07.

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