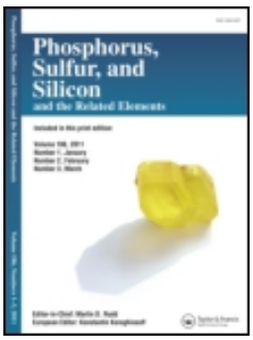

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(Diphenoxyphosphoryl)methyl *p*-tolyl sulfoxide: A new reagent for *Z*-selective synthesis of racemic and optically active vinyl sulfoxides

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ABSTRACT

Racemic and optically active (+)-(*S*)-(diphenoxyphosphoryl)methyl *p*-tolyl sulfoxide were prepared and used as Horner olefination reagents. Their reaction with aromatic and aliphatic aldehydes afforded the corresponding racemic and enantiomeric α,β-unsaturated sulfoxides with moderate to high *Z*-selectivity. The *E*/*Z* ratio was found to be dependent on the structure of aldehyde, nature of base, reaction conditions, and addition of 18-crown-6.

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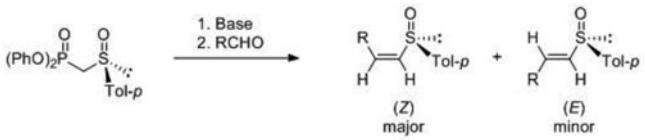
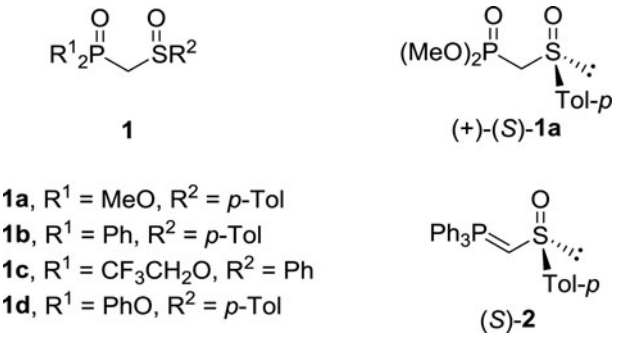
Chiral (diphenoxyphosphoryl)methyl *p*-tolyl sulfoxide; vinyl sulfoxides; Horner reaction; *Z*-selectivity

GRAPHICAL ABSTRACT



Introduction

α,β-Unsaturated sulfoxides (vinyl sulfoxides), both in racemic and enantiomeric forms, received a considerable attention as useful building blocks in the synthesis of diverse biologically active compounds and as valuable intermediates in a variety synthetic transformations and asymmetric reactions.[1] Among many methods and reagents used for the synthesis of vinyl sulfoxides, α-phosphoryl sulfoxides **1** (Scheme 1), first synthesized in racemic[2,3] and optically active forms[4] in our laboratory, turned out to be the best reagents in the Horner olefination reaction that afforded in good to high yields vinyl sulfoxides. Interestingly, racemic and (+)-(*S*)-(dimethoxyphosphoryl) methyl *p*-tolyl sulfoxide **1a** has become a reagent of choice for the synthesis of variously substituted vinyl sulfoxides, which were usually formed as separable mixtures of (*E*)- and (*Z*)-isomers. The Horner olefination reaction with racemic and (+)-(*S*)-(diphenylphosphinoyl)methyl *p*-tolyl sulfoxide **1b** gave almost pure (*E*)-vinyl sulfoxides, as reported later by van Steenis and his coworkers.[5] In an extension of our studies on the synthesis of vinyl sulfoxides, it has been found that the Wittig reaction of the in situ generated α-sulfinylphosphonium ylide **2** with carbonyl compounds results in the formation of racemic and optically active vinyl sulfoxides as almost pure (*E*)-isomers.[6]



Scheme 1. Structure of α-phosphoryl sulfoxide **1** and reagents used for the synthesis of vinyl sulfoxides.

Recently, extensive effort has been devoted to the synthesis of (*Z*)-α,β-unsaturated esters using α-phosphoryl acetates **3** as the Horner olefination reagents. These studies have indicated that (*Z*)-selectivity depends essentially on the structure of phosphonate moiety. Thus, a high (*Z*)-selectivity may be achieved with cyclic five-membered phosphonates,[7] cyclic five-membered diamidophosphonates,[8] di(2,2,2-trifluoroethoxy)phosphonates,[9] and di(aryloxy)-phosphonates[10,11] (Scheme 2).

Based on the above observations on the synthesis of (*Z*)-vinylic esters, Kokin et al.[12] prepared racemic (di-2,2,2-trifluoroethoxyphosphoryl)methyl *p*-tolyl sulfoxide **1c** and found that (*Z*)-vinyl sulfoxides were predominantly formed in its reaction with aldehydes. In our independent studies aimed at the synthesis of racemic and optically active (*Z*)-vinyl sulfoxides, we decided to prepare both racemic and optically active

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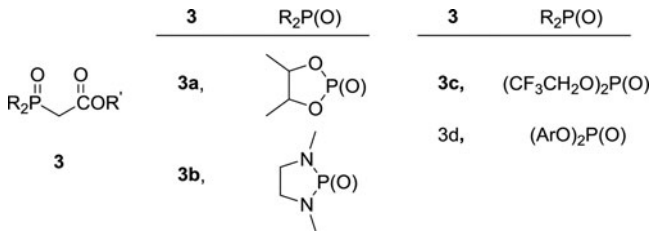
This paper is dedicated to late Professor Reinhard Schmutzler–founder of the phosphorus-fluorine chemistry.
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gpss.



Scheme 2. α-Phosphoryl acetates **3** used in the synthesis of (*Z*)-α,β-unsaturated esters.

(diphenoxyphosphoryl)methyl *p*-tolyl sulfoxide **1d** and investigate (*Z*)-selectivity of its reaction with aldehydes. The results obtained[13] are reported herein.

Results and discussion

Synthesis of racemic and optically active sulfoxide 1d

The racemic sulfoxide (±)-**1d** was easily and efficiently prepared in two steps (Scheme 3). At first, the Arbuzov reaction of diphenylmethyl phosphite with chloromethyl *p*-tolyl sulfide gave upon heating the corresponding (diphenoxyphosphoryl)methyl *p*-tolyl sulfide **4** in 81% yield. This, in turn, was selectively oxidized to (±)-**1d** by hydrogen peroxide in methanol in the presence of a H_2SO_4/*i*-PrOH mixture as a catalyst.[14] This procedure afforded the desired sulfoxide (±)-**1d** in 83% yield as a white solid. For comparison purposes, the corresponding sulfone **5** was synthesized by oxidation of (±)-**1d** with hydrogen peroxide using selenium dioxide as a catalyst.

The synthesis of optically active sulfoxide **1d** turned out to be somewhat complicated and less effective. Our standard procedure [4] for the synthesis of optically active α-phosphoryl sulfoxides **1** involving at first generation of α-phosphonate carbanion and subsequent addition of (-)-(*S*)-menthyl *p*-toluenesulfinate failed. It was found (^{31}P NMR assay) that the generated (diphenoxyphosphoryl)methyl carbanion reacts at once with diphenyl methanephosphonate to form the corresponding bis-phosphonate **A** (Scheme 4, reaction a). This nucleophilic substitution reaction at *P* occurs due to a good leaving group ability of the *P*-phenoxy substituent. Therefore, in a modified procedure both diphenyl methanephosphonate and (-)-(*S*)-menthyl *p*-toluenesulfinate were placed in the reaction vessel and then potassium hexamethyldisilazane (KHMDS) was added to this mixture under standard conditions (tetrahydrofuran (THF), −78°C). Analysis of the crude reaction product by ^{1}H NMR and ^{31}P NMR spectra revealed that it consisted of the starting phosphonate (50%), expected sulfoxide **1d** (30%), and menthylphenyl methanephosphonate **B** as a side reaction product (Scheme 4, reaction b). The pure optically active sulfoxide (+)-(*S*)-**1d** was obtained by flash chromatography.

Synthesis of vinyl sulfoxides by the Horner reaction of (diphenoxyphosphoryl)methyl p-tolyl sulfoxide with aldehydes and (Z/E)-selectivity

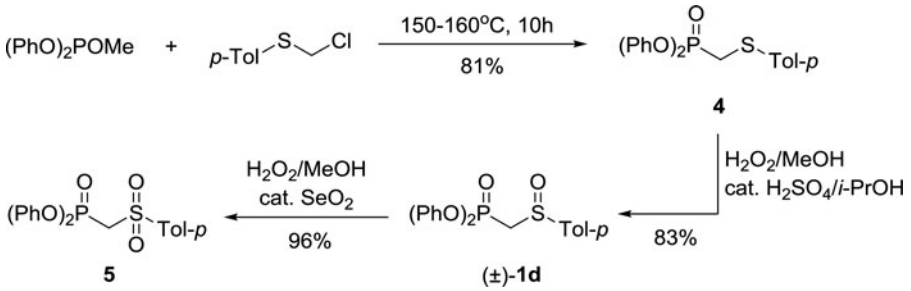
Having a new Horner olefination reagent **1d** in hand, we could use it for the synthesis of vinyl sulfoxides **6** and investigate the (*Z*/*E*)-selectivity of this reaction (Scheme 5). Generally, the Horner reaction of **1d** with aldehydes was performed in a THF solution at low temperature (−78°C) using different strong bases (NaH, *n*-BuLi, *t*-BuOK, KH, KHMDS, and Triton B) for the α-phosphonate carbanion generation. After addition of an aldehyde at −78°C and stirring for a proper time (see Tables 1 and 2), the reaction mixture was warmed to proper temperature and quenched. The usual work-up procedure afforded the crude sulfoxides **6**. After the determination of (*Z*/*E*)-ratio by gas chromatography (GC), the crude **6** were separated into pure (*Z*)- and (*E*)-isomers by column chromatography.

To begin with, the reaction of **1d** with benzaldehyde was investigated. This model reaction resulted in the formation of the already known (*Z*)- and (*E*)-sulfoxides **6a**[4] and allowed us to determine the effect of various factors on the (*Z*/*E*)-selectivity. The results obtained are summarized in Table 1.

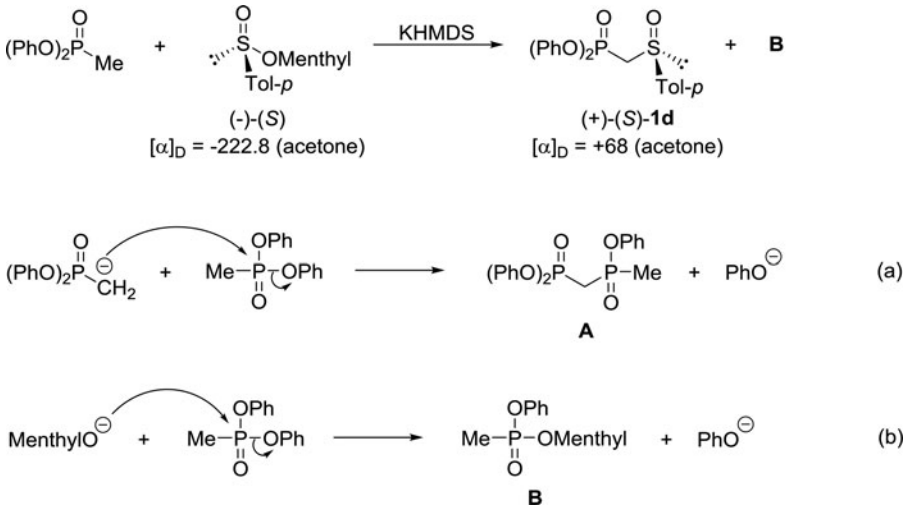
An inspection of the results in Table 1 revealed that in almost all cases investigated the reaction gave quantitatively 2-phenylvinyl *p*-tolylsulfoxide **6a**. The (*Z*)-selective Horner reaction was observed with all bases used for the α-phosphonate carbanion generation with the exception of *n*-butyllithium (*n*-BuLi). The use of the latter base preferred the formation of the (*E*)-isomer of **6a** (from 58 to 61%). Moderate (*Z*)-selectivity around 60% was observed with NaH, *t*-BuOK, KH, and KHMDS. A sharp increase in (*Z*)-selectivity (78%) was attained when KHMDS/18-crown-6 (5 eq) was applied as a basic system (Table 1, entry 12). However, it should be noted that the presence of such a big amount of crown ether in the reaction mixture makes the isolation and purification of **6a** less effective. An important effect of 18-crown-6 on the (*E*/*Z*)-selectivity of the Horner reaction under discussion was additionally demonstrated by carrying out the reaction of racemic α-phosphoryl sulfoxide **1a** with benzaldehyde using *n*-BuLi on the one hand, and KHMDS/18-crown-6 as a basic system on the other. Whereas in the former case the (*E*/*Z*)-ratio of sulfoxide **6a** was 2:1, the reverse relationship was observed in the latter case (Scheme 6).

Having established the most favorable conditions for the synthesis of (*Z*)-sulfoxide **6a** (Table 1, entries 10–12), the effect of the structure of an aldehyde on (*E*/*Z*)-selectivity in the Horner reaction of **1d** was examined as the second step of the present study. Thus, the following aldehydes were used as the Horner reaction partners with α-phosphoryl sulfoxide **1d**: *para*-bromobenzaldehyde, *ortho*-bromobenzaldehyde, acetaldehyde, and 4-pyridylcarboxyaldehyde. As in the case of benzaldehyde, the corresponding vinyl sulfoxides **6b–e** were obtained in high yields (85–94%). Some experimental data (base, conditions, *Z*/*E*-ratio) are collected in Table 2.

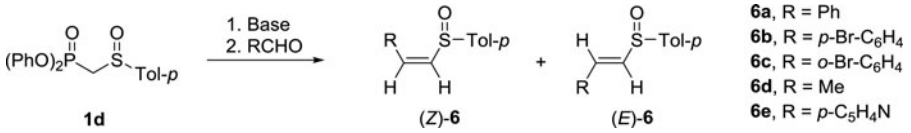
It was found that the reaction of **1d** with bromo-substituted benzaldehydes was highly *Z*-selective. The highest (*Z*/*E*)-ratio (93/7) was obtained with *ortho*-bromobenzaldehyde, suggesting that steric hindrance in the *ortho* position of the aromatic ring may play essential role in controlling selectivity. Unexpectedly, 4-pyridinecarboxyaldehyde afforded under the same experimental conditions an inseparable mixture of *Z* and *E* vinyl sulfoxides **6e**, the latter being the major one (Table 2, entry 5).



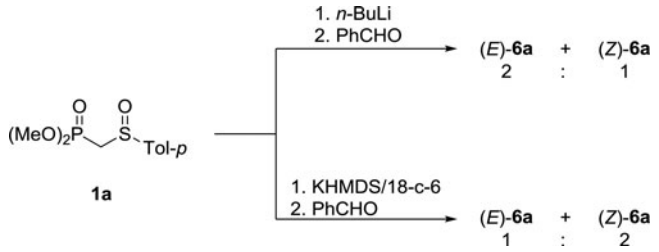
Scheme 3. Synthesis of racemic olefination reagent **1d**.



Scheme 4. Synthesis of optically active α-phosphoryl sulfoxide **1d** and accompanying side reactions.



Scheme 5. Vinyl sulfoxides **6** from the Horner reaction of **1d** with aldehydes.

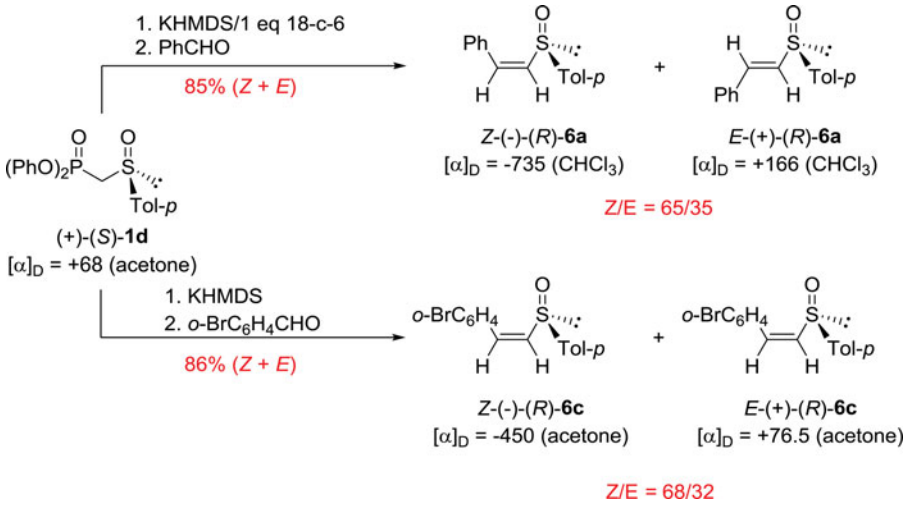


Scheme 6. Dependence of (*E*/*Z*)-selectivity on the nature of base in the Horner reaction of **1a**.

As vinyl sulfoxides **6b**, **6c**, and **6e** are new compounds, their *Z*- and *E*-isomers were characterized by ^{1}H NMR spectroscopy. Assignment of configurations *Z* and *E* to the respective isomers of the above-mentioned sulfoxides was based on the well-known geometrical dependence of vicinal proton coupling constants in olefins. The ^{1}H NMR spectra of these three sulfoxides reveal AB systems for *trans* and *cis* vinyl protons with $^3J_{H-H}$ of ca. 15.5 and 10.5 Hz, respectively.

Finally, the synthesis of optically active vinyl sulfoxides using (+)-(*S*)-**1d** as a new chiral Horner olefination reagent was briefly examined. Although the reaction of racemic sulfoxide (±)-**1d** with aromatic aldehydes showed the highest *Z*-selectivity in the presence of KHMDS/5 eq 18-c-6 as a basic system (Table 1, entry 12), the reaction of (+)-**1d** with benzaldehyde was performed with 1 equivalent of crown ether and that with *o*-bromobenzaldehyde in its absence to avoid some problems connected with isolation of products and separation of pure (*Z*)- and (*E*)-isomers. In Scheme 7, some experimental data for these two reactions performed according to a general procedure are given.

Since the synthesis of optically active α-phosphoryl sulfoxide (+)-(*S*)-**1d** described above was not efficient, the (*Z*)- and (*E*)-isomers of both optically active sulfoxides **6a** and **6c** were also prepared by a one-pot procedure described by Craig et al.[15] from three components: diphenyl methanephosphonate, (-)-(*S*)-menthyl *p*-toluenesulfinate, and benzaldehyde in the presence of KHMDS as a base. In this procedure, α-phosphoryl sulfoxide **1d** is not isolated since its carbanion generated from phosphonate and sulfinate reacts in situ with aldehyde. In our hands, this one-pot procedure gave the desired optically active vinylic sulfoxides **6a** and **6c**, however, with lower (*Z*/*E*)-selectivity (ca. 1:1) and lower yields of the isolated products (ca. 40%).



Scheme 7. Synthesis of optically active vinyl sulfoxides **6**.

Table 1. Reaction of α-phosphoryl sulfoxide **1d** with benzaldehyde.

Entry	Base	Reaction conditions	(*Z*/*E*)-ratio[b]	Conversion (%)[a]
1	*n*-BuLi	−78°C, 30 min	42/58	25
2	*n*-BuLi	−78°C, 15 min → −20°C	39/61	100
3	NaH	−78°C, 1 h → −20°C	66/34	100
4	NaH	−40°C, 1 h	55/45	100
5	NaH	−100°C → rt	62/38	100
6	*t*-BuOK	−78°C, 30 min → −30°C	60/40	50
7	*t*-BuOK	−78°C, 15 min → −20°C	60/40	100
8	KH	−78°C, 15 min → −30°C	57/43	100
9	KHMDS	−78°C, 1 h	58/42	15
10	KHMDS	−78°C → -30°C, 1 h	60/40	100
11	KHMDS	−78°C → rt, 1 eq 18-crown-6	64/36	100
12	KHMDS	−78°C → rt, 5 eq 18-crown-6	78/22	100
13	Triton B	−78°C → −20°C	-	0[c]

[a] Determined by ^{1}H NMR spectra of the crude reaction product.
[b] Determined by gas chromatography.
[c] Starting sulfoxide **1d** was recovered.

Experimental

General experimental details

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DRX 500, Bruker MSL 300, and Bruker AC 200 spectrometers using deuterochloroform as a solvent. ^{31}P NMR spectra were recorded on a Jeol JNM-FX 60 spectrometer. Mass spectra were recorded on Finnigan MAT95. The optical rotations were measured on a Perkin-Elmer 241 MC photopolarimeter at 20°C. The microanalyses were performed on an Elemental Analyzer EA 1108. Thin-layer chromatography (TLC) was carried out on silica gel plates (Merck F254). Silica Gel 60 (70-230 ASTM) was used for chromatography, and visualization was achieved by ultraviolet (UV) light. THF was freshly distilled over potassium/benzophenone.

Table 2. Reaction of α-phosphoryl sulfoxide **1d** with aldehydes, RCHO.

Entry	R	Base	Conditions	**6**/y (%)	*Z*/*E*-ratio
1	C_6H_5	KHMDS/18-c-6	−78°C → rt, overnight	**6a**/87	64/36
2	*p*-BrC_6H_4	KHMDS/18-c-6	−78°C → rt, overnight	**6b**/94	76/24
3	*o*-BrC_6H_4	KHMDS	−78°C → rt, overnight	**6c**/85	70/30
4	*o*-BrC_6H_4	KHMDS/18-c-6	−78°C → rt, overnight	**6c**/87	93/7
5	Me	KHMDS	−78°C → rt, overnight	**6d**/88	60/40
6	4-C_5H_4N	KHMDS	−78°C → rt, overnight	**6e**/85	34/66

Diphenoxyphosphoryl)methyl p-tolyl sulfide (4)

A mixture of diphenylmethyl phosphite (12.4 g, 0.05 mol) and chloromethyl *p*-tolyl sulfide (8.5 g, 0.05 mol) was heated at 150–160°C for 10 h. The crude α-phosphoryl sulfide **4** formed was purified by column chromatography to give sulfide **4** (15.2 g) in 82% yield as a semi-solid, m.p. 21°C, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.32 (s, 3H, CH_3), 3.40 (d, 2H, J = 13.4 Hz, CH_2P), 7.1–7.4 (m, 14H, HAr); ^{31}P NMR (24.3 MHz, $CDCl_3$) δ: 17.3; ^{13}C NMR (80 MHz, $CDCl_3$) δ: 20.6, 29.1 (d, J = 148 Hz, CH_2P), 115.9, 120.2, 120.3, 125.1, 128.9, 129.4, 129.6, 131.1, 137.4, 149.6, 149.8, 156.6; MS (EI, 70 eV) *m*/*z*: 370.0 (M^+, 100%), 247.8 (M^+-STol, 8.3%), 137.0 [M^+-$(PhO)_2P(O)$, 83%]; Anal. calc for $C_{20}H_{19}O_3PS$ (370.4): C 64.85, H 5.17, S 8.65; Found: C 64.79, H 5.20, S 8.68.

(Diphenoxyphosphoryl)methyl p-tolyl sulfoxide (1d)

To a solution of **4** (1.85 g, 0.05 mol) and catalyst (1.2 g, prepared from 1.38 g of 96% H_2SO_4 and 30 g of isopropanol) in MeOH (10 mL), 30% hydrogen peroxide (1.2 g, 0.011 mol) was added at once to the stirred reaction mixture. The progress of oxidation was followed by TLC (silica gel, benzene/methanol (10:1), iodine vapors as developer). After 10 h, oxidation was complete and water (150 mL) was added to the reaction mixture. Aqueous phase was extracted with $CHCl_3$ (3 × 30 mL) and combined chloroform extracts were dried over anhydrous $MgSO_4$ and evaporated to give crude α-phosphoryl sulfoxide **1d**. Purification by column chromatography provided sulfoxide **1d** (1.6 g, 83%) as a white solid, m.p. 57°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.40 (s, 3H, CH_3), 3.50–3.65 (d, 2H, CH_2, AB part of ABX system), 7.10–7.35 (m, 12H, HAr), 7.64–7.68 (d, 2H, J = 8.2 Hz, part of $[AB]_2$ system); ^{31}P NMR (24.3 MHz, $CDCl_3$) δ: 9.7; ^{13}C NMR (80 MHz, $CDCl_3$) δ: 21.4, 54.1 (d, J = 140.4 Hz, CH_2P), 115.3, 119.9, 120.4, 120.5, 124.3, 125.7, 129.3, 129.8, 130.2; MS (EI, 70eV) *m*/*z*: 386 (M^+, 8.3%), 247 [M^+-S(O)Tol, 16.6%], 293

(M^+-PhO, 100%); Anal. calc. for $C_{20}H_{19}O_4PS$ (386.4): C 62.17, H 4.95, S 8.29; Found: C 62.20, H 4.91, S 8.28.

(Diphenoxyphosphoryl)methyl p-tolyl sulfone (5)

To a solution of sulfoxide **4** (1.93 g, 0.005 mol) and SeO_2 (0.06 g) in methanol (15 mL), hydrogen peroxide (0.25 mL) was added. The progress of oxidation was followed by TLC (silica gel, petroleum ether–acetone, 2:1). After completion of oxidation (15 h), water (50 mL) was added to the reaction mixture. Aqueous phase was extracted with $CHCl_3$ (3 × 15 mL) and the extract was dried over anhydrous $MgSO_4$. Removal of chloroform gave α-phosphoryl sulfone **5** (1.93 g, 96%) as a white solid, m.p. 62°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.40 (s, 3H, CH_3), 4.01 (d, 2H, J_{HP} = 16.9 Hz, CH_2P), 7.10–7.30 (m, 12H, HAr), 7.69–7.80 (d, 2H, $[AB]_2$ system, J = 8.3 Hz); ^{31}P NMR (24.3 MHz, $CDCl_3$) δ: 4.9; ^{13}C NMR (80 MHz, $CDCl_3$) δ: 21.1, 53.0 (d, J = 139.8 Hz, CH_2P), 120.4, 120.5, 125.3, 128.1, 129.4, 129.5, 137.1, 144.8, 149.6; MS (EI, 70eV) *m/z*: 402 (M^+, 16%), 247 [M^+-S(O)$_2$Tol, 100%], 309 (M^+-PhO, 8.4%); Anal. calc. for $C_{20}H_{19}O_5PS$ (402.4): C 59.69, H 4.76, S 7.96; Found: C 59.66, H 4.79, S 7.94.

(+)-(S)-(Diphenoxyphosphoryl)metyl p-tolyl sulfoxide (1d)

To a solution of diphenyl methanephosphonate (0.55 g, 0.0022 mol) and (-)-(*S*)-menthyl *p*-toluenesulfinate (0.56 g, 0.002 mol) in THF (50 mL), KHDMS (4.84 mL) was added dropwise at −78°C. The reaction mixture was stirred at −78°C for 1 h and then allowed to warm up to −40°C. The reaction was quenched at this temperature with aqueous NH_4Cl solution. The aqueous phase was extracted with $CHCl_3$ (3 × 100 mL), and chloroform extract was dried over anhydrous $MgSO_4$ and evaporated. The residue containing unreacted diphenyl phosphonate (ca. 50%, δ_P = 24 ppm), desired sulfoxide **1d** (ca. 30%, δ_P = 9.7 ppm), and menthylphenyl phosphonate **B** (ca. 20%, δ_P = 27.2–26.6 ppm) was purified by flash chromatography (petroleum ether/acetone). The separated sulfoxide (+)-(*S*)-**1d**, $[\alpha]_D$ = +68.0 (c 1.2, Me_2CO), (0.22 g, 28%) exhibited the same spectral properties as (±)-**1d**.

General procedure for synthesis of vinyl sulfoxides 6a–e

To a solution of α-phosphoryl sulfoxide **1d** (0.193 g, 0.5 mmol) in THF (15 mL), solution of a base (0.6 mmol) in THF was added at −78°C. After 30 min, the reaction solution became yellow. Then a solution of an aldehyde (0.05 mmol) in THF (5 mL) was added dropwise at −78°C and the reaction mixture was stirred for 30 min at this temperature. After warming the reaction solution to a desired temperature it was quenched with aqueous NH_4Cl. Aqueous phase was extracted with $CHCl_3$ (3 × 25 mL), and organic phase was dried over anhydrous $MgSO_4$ and evaporated. The crude sulfoxides **6** obtained were purified by flash chromatography (petroleum ether) and separated into corresponding *Z*- and *E*-isomers.

2-Phenylvinyl p-tolyl sulfoxide (6a)

The crude product (0.05 g, 87%) obtained from benzaldehyde (0.03 g, 0.23 mmol) consisted of *Z*- and *E*-isomers in a ratio 78:22 (^{1}H NMR assay), which were separated by column chromatography.

Z-**6a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.40 (s, 3H, CH_3), 6.40 (AB system, 1H, J_{AB} = 10.6 Hz, Hvinyl), 7.01 (AB system, 1H, J_{HH} = 10.5 Hz, Hvinyl), 7.10–7.50 (m, 9H, HAr); Anal. calc. for $C_{15}H_{14}OS$ (242.3) C 74.35, H 5.82, Found: C 74.39, H 5.78.

E-**6a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.40 (s, 3H, CH_3), 6.80 (AB system, 1H, J_{AB} = 15.5 Hz, Hvinyl), 7.10–7.50 (m, 9H, HAr + 1H, part of AB system, Hvinyl); Anal. calc. for $C_{15}H_{14}OS$ (242.3) C 74.35, H 5.82, Found: C 74.32 H 5.85.

2-(4-Bromophenyl)vinyl p-tolyl sulfoxide (6b)

The crude product (0.15 g, 94%) obtained from *p*-bromobenzaldehyde (0.1 g, 0.5 mmol) was a mixture of *Z*- and *E*-isomers in a ratio 76:24. These were separated by column chromatography (petroleum ether–acetone (100:2)) and obtained in analytically pure state.

Z-**6b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.40 (s, 3H, CH_3), 6.40 (d, 1H, J_{AB} = 10.6 Hz, Hvinyl), 6.90 (d, 1H, J = 10.5 Hz, Hvinyl), 7.20–7.50 (m, 8H, HAr); Anal. calc. for $C_{15}H_{13}OSBr$ (321.2): C 56.09, H 4.08; Found: C 56.04, H 4.20.

E-**6b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.40 (s, 3H, CH_3), 6.80 (d, 1H, J_{AB} = 15.3 Hz, Hvinyl), 7.10–7.50 (m, 8H, HAr + 1H, Hvinyl); Anal. calc. for $C_{15}H_{14}OS$ (321.2): C 56.09, H 4.08; Found: C 56.12 H 4.04.

2-(2-Bromophenyl)vinyl p-tolyl sulfoxide (6c)

The crude product (0.14 g, 87.5%) obtained from *o*-bromobenzaldehyde (0.11 g, 0.5 mmol) and comprising *Z*- and *E*-isomers in a ratio of 93:7 gave after column chromatography (petroleum ether–acetone (100:2)) both pure isomers.

Z-**6c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.90 (s, 3H, CH_3), 6.20 (d, 1H, J_{AB} = 10.3 Hz, Hvinyl), 6.60 (d, 1H, J_{AB} = 10.4 Hz, Hvinyl), 6.90–7.80 (m, 8H, HAr); Anal. calc. for $C_{15}H_{13}OSBr$ (321.2): C 56.09, H 4.08; Found: C 56.05, H 4.12.

E-**6c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.90 (s, 3H, CH_3), 6.50 (d, 1H, J_{AB} = 15.3 Hz, Hvinyl), 6.90–7.80 (m, 8H, HAr + 1H, Hvinyl); Anal. calc. for $C_{15}H_{14}OS$ (321.2): C 56.09, H 4.08; Found: C 56.14 H 4.03.

2-(4-Pyridyl)vinyl p-tolyl sulfoxide (6e)

The crude product (0.1 g, 85%) arising from the reaction with 4-pyridinecarboxyaldehyde (0.03 mL, 0.3 mmol) comprised *Z*- and *E*-isomers in a ratio 34:66. This mixture was purified by flash chromatography. Analysis of ^{1}H NMR spectrum of the above *Z*/*E* mixture allowed to assign proton resonances to the corresponding isomers.

Z-**6e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.42 (s, 3H, CH_3), 6.60 (d, 1H, J_{AB} = 10.6 Hz, Hvinyl), 7.15 (d, 1H, J_{AB} = 10.5 Hz, Hvinyl), 7.20–7.70 (m, 8H, HAr).

E-**6e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.42 (s, 3H, CH_3), 7.00 (d, 1H, J_{AB} = 15.5 Hz, Hvinyl), 7.20–7.80 (m, 8H, HAr + 1H, Hvinyl);

Anal. calc. for $C_{14}H_{13}ONS$ (243.3): C 69.11, H 5.38; Found: C 69.14 H 5.35.

One-pot synthesis of (S)-2-phenylvinyl p-tolyl sulfoxide (6a)

A solution of KHMDS (2 mmol) in THF was added dropwise to a solution of diphenyl methanephosphonate (0.26 g, 1 mmol), (-)-(*S*)-menthyl *p*-toluenesulfinate (0.29 g, 1 mmol), and 18-crown-6 (1.9 g, 1 mmol) in THF (30 mL) at −78°C. The resulting reaction mixture was stirred for 1 h. A solution of benzaldehyde (0.2 mL, 2 mmol) in THF was then added. The reaction mixture was warmed slowly to room temperature and stirred overnight. The reaction was quenched with saturated aqueous NH_4Cl (10 mL). The water phase was extracted with diethyl ether (3 × 30 mL). Organic phase was dried over anhydrous $MgSO_4$, filtered off, and evaporated. The residue was purified by column chromatography (benzene–acetone), and *Z*- and *E*-isomers of **6a** formed in equal amounts were separated.

Z-(*R*)-**6a**: $[\alpha]_D$ = −735.0 (c 1.4, $CHCl_3$); *E*-(*R*)-**6a**: $[\alpha]_D$ = +166.0 (c 1.1, $CHCl_3$).

One-pot synthesis of 2-(2-bromophenyl)winyl p-tolyl sulfoxide (6c)

The same procedure as described above with 2-bromobenzaldehyde (0.4 mL, 2 mmol) gave the crude vinyl sulfoxide **6c**, which upon column chromatography was separated into *Z*-(-)-(*R*)-**6c**: $[\alpha]_D$ = −450.0 (c 1.1, Me_2CO) and *E*-(+)-(*R*)-**6c**: $[\alpha]_D$ = +76.5 (c 1.4, Me_2CO) in almost equal amounts.

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