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An Easy Synthesis of Chiral Sulfinyl Allylic Bromides and their Use in the Preparation of $(R)_S$- and $(S)_S$-2-p-Tolylsulfinyl-1,3-alkadienes

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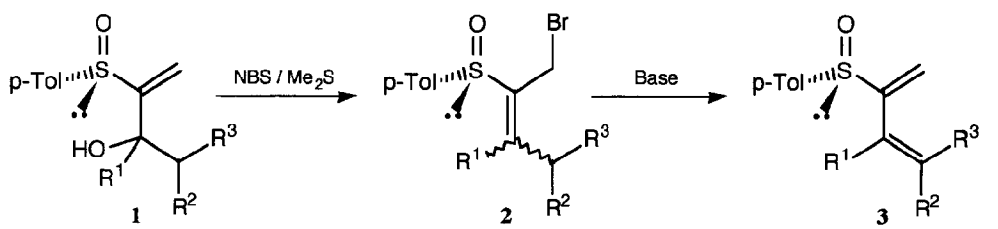
Abstract: Condensation of (R)-vinyl-p-tolylsulfoxide anion on carbonyl compounds led directly to chiral allylic sulfinylalcohols **1**. By treatment with NBS/Me_2S, these alcohols **1** were converted into the rearranged primary allylic bromides **2** *via* SN_2' displacement. Optically pure (R)- and (S)-2-p-tolylsulfinyl-1,3-alkadienes **3** resulted from the action of KOH/ROH upon these bromides **2** *via* E_2' eliminations.

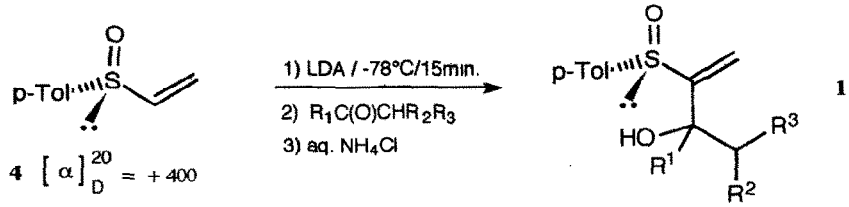
Stereoselective reactions using chiral sulfoxides have provided useful new methods for synthetic organic chemistry [1] and thus, their preparation with high enantiomeric excess is still of great interest.

In particular, optically active sulfinyldienophiles have been used in many asymmetric Diels-Alder reactions.[2] However, it is worthy to note that only few chiral sulfinyldienes have been described, where the sulfoxide group is on the first carbon atom of the dienic system.[3] Recently, we published the first synthesis of chiral (R)- and (S)-2-p-tolylsulfinyl-1,3-butadiene **3a**.[4] Unfortunately, generalization of the synthetic scheme used for the synthesis, *via* mesylate elimination, of the parent compound **3a** proved to be unsuccessfull.[5] We wish to report here a general synthesis of 2-sulfinylbutadienes, which is based on elimination reactions from chiral sulfinyl allylic bromides.



I - PREPARATION OF SULFINYL ALLYLIC ALCOHOLS 1

Allylic alcohols **1** appeared to be interesting precursors to dienes **3**. Until now, preparation of these alcohols required a preliminary protection of the double bond of the starting vinylsulfoxide **4**.[6] We describe here a direct access to alcohols **1** starting from (R)-(+)-p-tolylvinylsulfoxide **4**. The treatment of **4** with 1.1 equiv. of LDA in THF at -78°C, followed by the addition of various aldehydes and ketones (cf Table I), afforded after usual workup the desired compounds **1**.



4 $[\alpha]_D^{20} = +400$

1

Table I. Preparation of Alcohols 1

1	R^1	R^2	R^3	Yield (%)	D.e. (%)[a]	M.p. (°C)
a	H	H	H	61	20	oil
b	H	Me	H	58	20	oil
c	H	Me	Me	49	20	oil
d	Me	H	H	59	b	78,5
e	iPr	H	H	59	0	oil
f	$-(CH_2)_4-$		H	58[c]	c	105
g	Ph	H	H	45	20	134 and 182[d]

[a] Determined by 400 MHz ^1H NMR

[b] $[\alpha]_D^{25} = +227$ ($c = 2.0$ in ethanol)

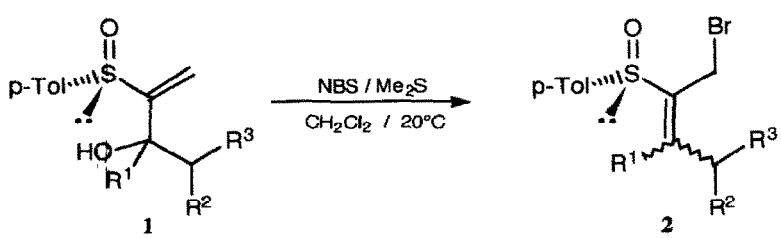
[c] The alcohol **1f** was prepared according our previous method.[6] $[\alpha]_D^{25} = +126$ ($c = 0.59$ in acetone).

[d] Melting points for each diastereoisomer

This new synthesis using vinylsulfoxide anion allowed the preparation of alcohols **1** in fair yields, comparable to those obtained by our previously reported method,[6] but in a single step.

II - SN_2' REARRANGEMENT OF ALCOHOLS 1. PREPARATION OF ALLYLIC BROMIDES 2

The alcohols **1** could be converted into the allylic rearranged bromides **2** (1.5 equiv. of N-bromosuccinimide : 1.8 equiv. of Me_2S in CH_2Cl_2 at 20°C)[7] in high yields (Table II). Such a rearrangement has been studied in the case of sulfonylalcohols.[8]



1 2

Table II. Preparation of Bromides 2

2	R^1	R^2	R^3	Reaction time (h)	Yield (%)	E/Z	$[\alpha]_D^{25}$ [a]	M.p. (°C)[a]
a	H	H	H	17	80	91/9	+67 (E)	57 (E)
b	H	Me	H	14	77	90/10	b	b
c	H	Me	Me	25	78	90/10	+79 (E)	87 (E)
d	Me	H	H	60	80		-142	73,5
e	iPr	H	H	60	47	50/50	b	b
f	$-(CH_2)_4-$		H	24	80		-157	oil
g	Ph	H	H	60	c			

[a] Optical rotations and melting points are only reported for pure isomers

[b] Separation of E and Z isomers was not achieved

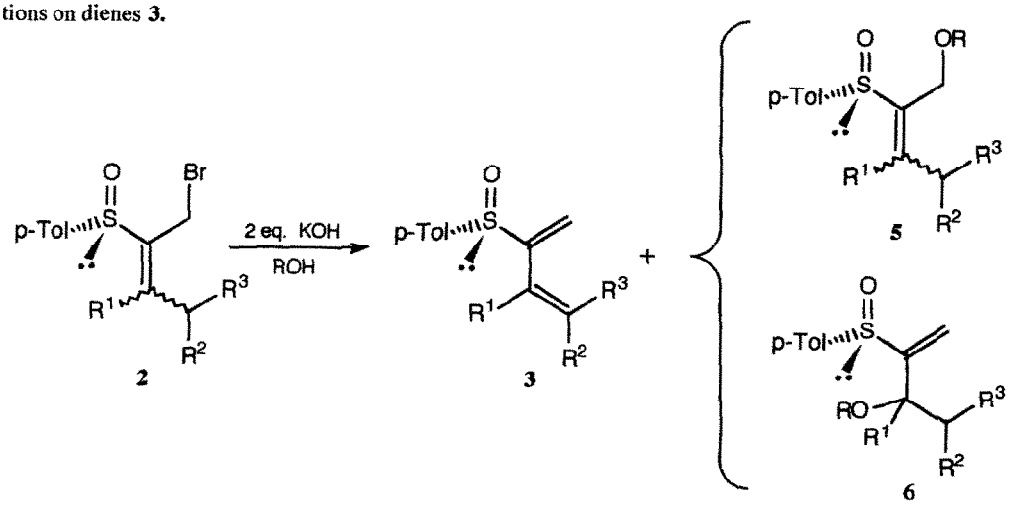
[c] Owing to its instability, **2g** could not be characterized

These SN_2' displacements of allylic alcohols **1** proceeded generally with high E selectivity. The stereochemistry of **2a** was shown to be E by NMR : a 8,7% NOE enhancement was observed for the methyl group by irradiating the methylene protons.

III - E_2' REACTIONS OF BROMIDES 2
PREPARATION OF $(R)_S$- and $(S)_S$-2-p-TOLYLSULFINYLALKADIENES 3

Among the various possibilities offered by these new chiral sulfinyl bromides **2** we decided, in connection with our interest in sulfinylalkadienes **3**,[4] to study the transformation of **2** into **3** by E_2' reaction.

Various basic media have been tested on the bromide **2a**. $NaHCO_3$/MeOH left the starting bromide unchanged. Traces of diene **3a** were detected by ^{1}H-NMR when K_2CO_3/MeOH or Et_3N/Et_2O were used instead. A 50% yield of **3a** was obtained by treatment with LDA/THF. KOH/MeOH led to the exclusive formation of allylic ethers **5a** and **6a**, resulting either from nucleophilic substitutions on bromides **2** or additions on dienes **3**.



But, in contrast, the best result was obtained when iPrOH was used in place of MeOH, and a 81% yield of pure **3a** was achieved after easy separation of some ether **5a**.

By varying the reaction time, the temperature and the alcoholic solvent, the formation of undesired ethers **5** and **6** could be limited in each case. This allowed the synthesis of sulfinylalkadienes **3** in good yield (Table III).

Table III - Elimination of Bromides **2**

3	R^1	R^2	R^3	R	Reaction time (h) / Temperature (°C)	Yield of **3** (%) (a)	$[\alpha]_D^{25}$ (a)	M.p. (°C)	Mol % (b) of **3** **2** **5** **6**
a	H	H	H	Me	0.25/20				0 0 61 39
				iPr	0.33/0				39 0 61 0
				iPr	0.17/-20	81	+174 (c)	39-40	90 0 10 0
b	H	Me	H	iPr	0.33/0				70 19 11 0
				iPr	0.58/-20				28 66 6 0
				iPr	0.50/0	70	(d)	(oil)	81 7 12 0
c	H	Me	Me	iPr	1.00/10				4 84 12 0
				tBu	2.5/25	22	(e)	(oil)	(e)
d	Me	H	H	Me	4.50/20				13 0 75 12
				Me	4.00/0				78 0 5 17
				iPr	0.50/0	85	+252	48.5	100 0 0 0
e	iPr	H	H	Me	18.0/20	11			
				Me	1.00/20	71			75 22 3 0
				iPr	0.67/20	76	+234	44	88 0 12 0
f	$-(CH_2)_4-$		H	iPr	0.42/0				56 37 7 0
				iPr	2.00/0				85 0 15 0
				iPr	0.67/20	68	+152	oil	88 0 12 0

(a) Yields and optical rotations refer to pure isolated products.

(b) Determined by 400 MHz ^{1}H-NMR of the crude product.

(c) The optical purity of dienes **3** was ≥ 99% as determined by HPLC analysis (Chiralcel OB, hexane/2-propanol 9/1). Excellent resolution (α = 1.41) of racemic **3a** was achieved on this column.

(d) Product **3b** was contaminated by traces of ether **5b**. Only one isomer, E, detected by ^{1}H-NMR (J_{HH} = 16 Hz, $R_1 = R_3 = H$).

(e) Performed under ultrasonic irradiation; Diene **3c** was contaminated by unseparable minor impurities.

In summary, we have shown that chiral sulfinyl allylic bromides, obtained from the corresponding alcohols by SN_2' displacement, are easily converted into (R)- and (S)-2-p-tolylsulfinyl-1,3-alkadienes of high enantiomeric purity. We are currently evaluating the reactivity of these new chiral bromides and dienes.

EXPERIMENTAL

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AC 400 instrument in $CDCl_3$ using TMS for ^1H spectra and the solvent for ^{13}C spectra as internal reference. Chemical shifts are expressed in ppm (abbreviations used : s singulet, d doublet, q quadruplet, m multiplet, b broad). J values are given in Hz. Multiplicities in the ^{13}C spectra were determined by DEPT experiments. IR spectra were recorded on a Nicolet 5DX spectrometer. Melting points were determined on a Reichert apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer Model 241 polarimeter. Elemental analyses were performed at the Service de Microanalyse du CNRS (Gif sur Yvette). UV spectrum was recorded on a Varian DMS 100 spectrophotometer. High resolution mass measurements were performed at the C.R.M.P.O. (Rennes). Liquid chromatography were carried out on SDS silica gel 60 A C.C. (230-400 mesh).

Preparation of alcohols **1**[9]

$(S)_S$-3-p-Tolylsulfinyl-3-buten-2-ol **1a:** To a stirred solution of LDA (11 mmol) in dry THF (30 mL) under a nitrogen atmosphere was slowly added at -78°C distilled (R)-(+)-p-tolylvinylsulfoxyde[10] (1.66 g ; 10 mmol) in THF (15 mL). After 30 min at -78°C, freshly distilled ethanal (1.69 mL ; 30 mmol) was added dropwise. The reaction mixture was maintained at -78°C for 15 min, then allowed to reach -30°C. A half-saturated aqueous NH_4Cl solution (20 mL) was added at this temperature and most of the THF was removed under reduced pressure. The residue was finally extracted with CH_2Cl_2. After drying over $MgSO_4$ and evaporation of the solvent, the crude oil was purified by column chromatography on 40 g of silica gel (eluent : ether/cyclohexane 7/3 then ether) to give the diastereomeric sulfinylallylic alcohols **1a** (1.29 g ; 61%) as a colorless oil. IR (neat) : 3323, 1590, 1025, 919, 806 cm^{-1}. ^1H-NMR : δ = 1.23 and 1.35 (d, J = 6.4, 3H, $C\underline{H}_3CH$) ; 2.41 and 2.42 (s, 3H, $C\underline{H}_3Ar$) ; 4.29 and 4.41 (q, J = 6.4, 1H, $C\underline{H}OH$) ; 5.85 and 5.87 (s, 1H, H *trans*) ; 6.03 (s, 1H, H *cis*) ; 7.30, 7.56 and 7.32, 7.52 (AA'BB' system, J = 8.2, 4H arom.). ^{13}C-NMR : δ= 21.4 (q, $\underline{C}H_3Ar$) ; 21.8 and 22.8 (q, $\underline{C}H_3CH$) ; 64.4 and 65.1 (d, $CH_3\underline{C}H$) ; 115.9 and 117.5 (t, CH_2=) ; 124.7 and 125.0 (d) ; 130.0 and 130.1 (d) ; 138.7 and 139.5 (s) ; 141.9 (s) ; 156.9 and 158.3 (s).

$(S)_S$-2-p-Tolylsulfinyl-1-penten-3-ol **1b:** The reaction was performed using the same conditions described for **1a**. Starting from 1.66 g (10 mmol) of (R)-(+)-p-tolylvinylsulfoxide and 2.16 mL (30 mmol) of freshly distilled propanal, 1.25 g (58%) of alcohol **1b** were obtained after chromatography on 60 g of silica gel (eluent : cyclohexane/ether : 3/7 then ether). IR (neat) : 3356, 2964, 2925, 1590, 1079, 1032, 932, 813 cm^{-1}. ^1H-NMR : δ = 0.81 and 0.87 (t, J = 7.4, 3H, $CH_2C\underline{H}_3$) ; 1.57 and 1.65 (m, 2H, $C\underline{H}_2CH_3$) ; 2.41 and 2.42 (s, 3H, $C\underline{H}_3Ar$) ; 4.08 (m, 1H, $C\underline{H}OH$) ; 5.84 and 5.86 (s, 1H, H *trans*) ; 6.06 and 6.07 (s, 1H, H *cis*) ; 7.30, 7.56 and 7.32, 7.52 (AA'BB' system, J = 8.2, 4H arom.). ^{13}C-NMR : δ = 9.5 and 9.6 (q, $\underline{C}H_3CH_2$) ; 21.4 ($\underline{C}H_3Ar$) ; 28.5 and 29.3 (t, $\underline{C}H_2CH_3$) ; 69.6 and 70.6 (d, CHOH) ; 117.1 and 117.5 (t, =CH_2) ; 125.2 and 125.5 (d) ; 130.0 and 130.1 (d) ; 138.8 and 139.6 (s) ; 141.9 and 142.0 (s) ; 156.1 and 156.9 (s, $\underline{C}$=CH_2).

$(S)_S$-4-Methyl-2-p-tolylsulfinyl-1-penten-3-ol **1c**: The reaction was performed in the same way as for **1a**. Starting from 1.66 g (10 mmol) of (R)-(+)-p-tolylvinylsulfoxide and 2.70 mL (30 mmol) of 2-methylpropanal, 1.17 g (49%) of **1c** were obtained after chromatography on 60 g of silica gel (eluent : cyclohexane/ether : 4/6 then ether). IR (neat) : 3356, 2958, 1596, 1025, 806 cm^{-1}. ^{1}H-NMR : δ = 0.77 and 0.80 (d, J = 6.7, 3H, C$\underline{H}_3$CH) ; 0.91 and 0.93 (d, J = 6.7, 3H, C$\underline{H}_3$CH) ; 1.84 and 1.95 (dqq, J = 6.7, 6.7, 6.7, 1H, C$\underline{H}$(CH$_3$)$_2$) ; 2.40 and 2.41 (s, 3H, C$\underline{H}_3$Ar) ; 3.76 and 3.94 (bt, J = 5.7, 1H, C$\underline{H}$OH) ; 5.82 and 5.88 (s, 1H, H *trans*) ; 6.11 and 6.13 (s, 1H, H *cis*) ; 7.30, 7.56 and 7.31, 7.53 (AA'BB' system, J = 8.2, 4H arom.). Analysis : Calculated for $C_{13}H_{18}O_2S$: 65.50% C 7.63% H 13.44% O 13.44% S, found 65.46% C 7.38% H 13.52% O 13.29% S.

$(S)_S$-2-Methyl-3-p-tolylsulfinyl-3-buten-2-ol **1d:** Following the same procedure as for **1a** from 1.66 g (10 mmol) of (R)-(+)-p-tolylvinylsulfoxide and 2.25 mL (30 mmol) of freshly distilled propanone, 1.32 g (59%) of alcohol **1d** were obtained after chromatography on 45 g of silica gel (eluent : ether/cyclohexane : 7/3 then ether). White crystals ; m.p. = 78,5°C (petroleum ether). $[\alpha]_D^{25}$ +227 (c = 2.0, EtOH) [Litt[6] : $[\alpha]_D^{25}$ =+277 (c = 0,72 ; acetone)]. IR (neat) : 3343, 2971, 1590, 1025, 813 cm^{-1}. ^{1}H-NMR : δ = 1.31 (s, 3H, C$\underline{H}_3$C) ; 1.38 (s, 3H, C$\underline{H}_3$C) ; 2.40 (s, 3H, C$\underline{H}_3$Ar) ; 5.77 (d, J = 1.0, 1H, H *trans*) ; 6.00 (d, J = 1.0, 1H, H *cis*) ; 7.28, 7.59 (AA'BB' system, J = 8.2, 4H arom.). ^{13}C-NMR : δ = 21.4 (q, $\underline{C}$H$_3$Ar) ; 31.1 (q, $\underline{C}$H$_3$C) ; 31,4 (q, $\underline{C}$H$_3$C) ; 73.6 (s, $\underline{C}$(CH$_3$)$_2$) ; 115.1 (t, CH$_2$=) ; 126.1 (d) ; 129.8 (d) ; 141.0 (s) ; 141.7 (s) ; 161.3 (s, $\underline{C}$=CH$_2$).

$(S)_S$-3,4-Dimethyl-2-p-tolylsulfinyl-1-penten-3-ol **1e:** The reaction was performed using the same conditions described for **1a**. Starting from 5 g (30 mmol) of (R)-(+)-p-tolylvinylsulfoxide and 6.42 mL (60 mmol) of 3-methylbutanone, 4.48 g (59%) of **1e** were obtained after chromatography through 180 g of silica gel (eluent : cyclohexane/ethylacetate : 6/4). IR (neat) : 3358, 2984, 1490, 1025, 806 cm^{-1}. ^{1}H-NMR : δ = 0.80, 0.85 and 0.87, 0.93 (2d, J = 6.8, 6H, (C$\underline{H}_3$)$_2$CH) ; 1.18 and 1.20 (s, 3H, C$\underline{H}_3$COH) ; 1.85 and 1.90 (qq, J = 6.8, 6.8, 1H, C$\underline{H}$(CH$_3$)$_2$) ; 2.38 and 2.39 (s, 3H, C$\underline{H}_3$Ar) ; 5.66 and 5.67 (d, J = 1.2, 1H, H *trans*) ; 5.98 and 6.21 (d, J = 1.2, 1H, H *cis*) ; 7.25, 7.60 and 7.27, 7.57 (AA'BB' system, J = 8.2, 4H arom.). ^{13}C-NMR : δ = 16.5 (q, $\underline{C}$H$_3$CH) ; 16.7 (q, $\underline{C}$H$_3$CH) ; 21.4 (q, $\underline{C}$H$_3$Ar) ; 26.7 (q, $\underline{C}$H$_3$C) ; 37.0 and 38.0 (d, $\underline{C}$H(CH$_3$)$_2$) ; 78.3 and 79.3 (s, C-OH) ; 114.9 and 116.4 (t, =CH$_2$) ; 125.9 and 126.1 (d) ; 129.7 (d) ; 140.4 and 141.8 (s) ; 141.6 (s) ; 160.1 and 160.4 (s, $\underline{C}$=CH$_2$). Analysis : Calculated for $C_{14}H_{20}O_2S$ 66,62% C 8,00% H 12,70% S, found 66,44% C 8,04% H 12,78% S.

$(S)_S$-2-Phenyl-2-p-tolylsulfinyl-3-buten-2-ol **1g:** The reaction was performed using the same conditions described for **1a**. Starting from 1.66 g (10 mmol) of (R)-(+)-p-tolylvinylsulfoxide and 2.0 mL (17 mmol) of acetophenone, 1.29 g (45%) of alcohol **1g** were obtained after chromatography on 80 g of silica gel (eluent : ether/cyclohexane : 7/3) as a mixture of readily separable diastereoisomers. Less polar diastereoisomer : White crystals ; m.p. = 134°C (ether). ^{1}H-NMR : δ = 1.68 (s, 3H, CH$_3$) ; 2.34 (s, 3H, C$\underline{H}_3$Ar) ; 4.04 (s, 1H, OH) ; 5.88 (s, 1H, H *trans*) ; 6.14 (s, 1H, H *cis*) ; 7.09, 7.27 (AA'BB' system, J = 8.1, 4H arom.) ; 7.13 (m, 3H, H$_m$ and H$_p$) ; 7.22 (m, 2H, H$_o$). ^{13}C-NMR : δ = 21.3 (q, $\underline{C}$H$_3$Ar) ; 31.3 (q, CH$_3$) ; 77.7 (s, C-OH) ; 117,6 (t, CH$_2$=) ; 125.0 (d) ; 125.2 (d) ; 127.0 (d) ; 128.0 (d) ; 129.5 (d) ; 140.0 (s) ; 141.1 (s) ; 144.4 (s) ; 159.1 (s, $\underline{C}$=CH$_2$). Most polar diastereoisomer : White crystals ; m.p. = 182°C (dichlorome-

thane). IR (nujol) : 3280, 1032, 1020, 923, 806 cm^{-1}. ^{1}H-NMR: δ = 1.71 (s, 3H, CH_3) ; 2.37 (s, 3H, $C\underline{H}_3Ar$) ; 4.11 (s, 1H, OH) ; 5.72 (d, J = 1.3, 1H, H *trans*) ; 5.76 (d, J = 1.3 , 1H, H *cis*) ; 7.19, 7.47 (AA'BB' system, J = 8.1, 4H arom.) ; 7.23 (m, 3H, H_m and H_p) ; 7.31 (m, 2H, H_o). ^{13}C-NMR : δ = 21.4 (q, $\underline{C}H_3Ar$) ; 31.3 (q, CH_3) ; 77.1 (s, C-OH) ; 116.7 (t, CH_2=) ; 125.1 (d) ; 126.3 (d) ; 127.0 (d) ; 128.0 (d) ; 129.6 (d) ; 140.0 (s) ; 141.8 (s) ; 144.7 (s) ; 160.2 (s, $\underline{C}$=CH_2).

General procedure for the preparation of bromides **2**

To a stirred solution containing 540 mg (3.0 mmol) of N-bromosuccinimide in 10 mL of anhydrous methylene chloride under a nitrogen atmosphere was added dropwise at 0°C over a few minutes, 0.264 mL (3.6 mmol) of methylsulfide, followed by 2 mmol of the p-tolylsulfinyl allylic alcohol **1** in 3 mL of methylene chloride. Then the reaction mixture was stirred at ambient temperature for the indicated time (Table II), and poured into 10 mL of water. The aqueous layer was extracted with ether (3 x 7 mL). The combined organic layer was washed with brine (7 mL) and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the resulting brown residue was purified by silica gel column chromatography (eluent : cyclohexane/ether : 7/3).

(S)-1-Bromo-2-p-tolylsulfinyl-2-butene **2a** : Yield = 80%. IR (neat) : 1081, 1045, 809 cm^{-1}. *E isomer* : White crystals : m.p. = 57°C (ether/petroleum ether) ; $[\alpha]_D^{25}$ = +67 (c = 1.25, EtOH). ^{1}H-NMR : δ = 1.95 (d, J = 7.2, 3H, $C\underline{H}_3CH$=) ; 2.41 (s, 3H, $C\underline{H}_3Ar$) ; 3.87, 3.95 (AB system, J = 11.6, 2H, CH_2Br) ; 6.75 (q, J = 7.2, 1H, $CH_3C\underline{H}$=) ; 7.30, 7.53 (AA'BB' system, J = 8.2, 4H arom.). ^{13}C-NMR : δ = 14.4 (q, $\underline{C}H_3CH$=) ; 19.2 (t , CH_2Br) ; 21.4 (q, $\underline{C}H_3Ar$) ; 125.3 (d) ; 129.9 (d) ; 135.8 (d, =$\underline{C}HCH_3$) ; 138.8 (s) ; 141.9 (s) ; 142.3 (s). Analysis : Calculated for $C_{11}H_{13}OSBr$ 48.35% C 4.81% H 5.86% O 1.72% S 29.26% Br, found 48.52% C 4.70% H 5.84% O 11.63% S 29.21% Br. *Z isomer* : ^{1}H-NMR : δ = 2.21 (d, J = 7.2, 3H, $C\underline{H}_3CH$=) ; 2.41 (s, 3H, $C\underline{H}_3Ar$) ; 4.00, 4.10 (AB system, J = 12.4, 2H, CH_2Br) ; 6.59 (q, J = 7.2, 1H, $CH_3C\underline{H}$=) ; 7.31, 7.47 (AA'BB' system, J = 8.2, 4H arom.).

(S)-1-Bromo-2-p-tolylsulfinyl-2-pentene **2b** : Yield : 77%. IR (neat) : 2964, 1079, 1052, 806 cm^{-1}. *E isomer* : ^{1}H-NMR : δ = 1.16 (t, J = 7.5, 3H, $C\underline{H}_3CH_2$) ; 2.35 (dq, J = 7.5, 7.5, 2H, $CH_3C\underline{H}_2CH$=) ; 2.41 (s, 3H, $C\underline{H}_3Ar$) ; 3.84, 3.94 (AB system, J = 11.6, 2H, CH_2Br) ; 6.66 (t, J = 7.5, 1H, =$C\underline{H}CH_2$) ; 7.31, 7.53 (AA'BB' system, J = 8.1, 4H arom.). Analysis : Calculated for $C_{12}H_{15}SOBr$ 50.16% C 5.28% H 11.15% S, found 49.67% C 5.66% H 11.21% S.

(S)-1-Bromo-4-methyl-2-p-tolylsulfinyl-2-pentene **2c** : Yield = 78%. IR (nujol) : 2950, 1590, 1455, 1070, 1045, 815 cm^{-1}. *E isomer* : White crystals ; m.p. = 87°C (ether/petroleum ether) ; $[\alpha]_D^{25}$ = +79 (c 1.5, EtOH). ^{1}H-NMR : δ = 1.13 (d, J = 6.6, 6H, $(C\underline{H}_3)_2CH$) ; 2.41 (s, 3H, $C\underline{H}_3Ar$) ; 2.82 (dqq, J = 10.4, 6.6, 6.6, 1H, $C\underline{H}(CH_3)_2$) ; 3.83, 3.95 (AB system, J = 11.6, 2H, CH_2Br) ; 6.48 (d, J = 10.4, 1H, CH=) ; 7.30, 7.52 (AA'BB' system, J = 8.1, 4H arom.). ^{13}C-NMR : δ = 19.4 (t, CH_2Br) ; 21.4 (q, $\underline{C}H_3Ar$) ; 21.5 (q, CH_3) ; 21.8 (q, CH_3) ; 28.6 (d, $\underline{C}H(CH_3)_2$; 125.4 (d) ; 130.0 (d) ; 139.0 (s) ; 139.2 (s) ; 141.9 (s) ; 146.7 (d, =$\underline{C}$HiPr). Analysis : Calculated for $C_{13}H_{17}OSBr$ 51.82% C 5.70% H 5.31% O 10.63% S 26.54% Br,

found 52.10% C 5.60% H 5.09% O 10.76% S 26.60% Br. *Z isomer* : ^{13}C-NMR : δ = 21.4 (q, $\underline{C}H_3Ar$) ; 22.4 (q, CH_3) ; 22.6 (q, CH_3) ; 24.5 (t, CH_2Br) ; 28.4 (d, $\underline{C}H(CH_3)_2$) ; 124.3 (d) ; 130.0 (d) ; 138.2 (s) ; 138.4 (s) ; 141.2 (s) ; 150.2 (d, =$\underline{C}$HiPr).

(S)-1-Bromo-3-methyl-2-p-tolylsulfinyl-2-butene **2d** : Yield : 80%. White crystals ; m.p. =73.5°C (petroleum ether). $[\alpha]_D^{25}$ = -142 (c = 1.0, EtOH). IR (nujol) : 1610, 1087, 1027, 801 cm^{-1}. ^{1}H-NMR : δ = 2.00 (s, 3H, CH_3) ; 2.30 (s, 3H, CH_3) ; 2.41 (s, 3H, $C\underline{H}_3Ar$) ; 3.96, 4.29 (AB system, J = 11.6, 2H, CH_2Br) ; 7.30, 7.47 (AA'BB' system, J = 8.2, 4H arom.). ^{13}C-NMR : δ = 20.1 (t, CH_2Br) ; 21.4 (q, $\underline{C}H_3Ar$) ; 22.1 (q, CH_3) ; 22.6 (q, CH_3) ; 124.4 (d) ; 129.8 (d) ; 135.9 (s) ; 139.1 (s) ; 141.0 (s) ; 149.6 (s). Analysis : Calculated for $C_{12}H_{15}OSBr$ 50,19% C 5.28% H 5.58% O 11.15% S 27.85% Br, found 50.01% C 5.04% H 5.32% O 11.09% S 27.58% Br.

(S)-1-Bromo-3,4-dimethyl-2-p-tolylsulfinyl-2-pentene **2e** : Yield : 47%. Colorless oil. IR (neat) : 2964, 1616, 1079, 1045, 806 cm^{-1}. *E isomer* : ^{1}H-NMR : δ = 1.10 (d, J = 6.8, 3H, CH_3CH) ; 1.14 (d, J = 6.8, $C\underline{H}_3CH$) ; 2.16 (s, 3H, CH_3C=) ; 2.40 (s, 3H, CH_3Ar) ; 3.07 (qq, J = 6.8, 6.8, 1H, $C\underline{H}(CH_3)_2$) ; 3.99, 4.31 (AB system, J = 11.6, 2H, CH_2Br) ; 7.29, 7.46 (AA'BB' system, J = 8.2, 4H arom.). *Z isomer* : ^{1}H-NMR : δ = 1.16 (d, J = 6.8, 3H, $C\underline{H}_3CH$) ; 1.17 (d, J = 6.8, 3H, $C\underline{H}_3CH$) ; 1.90 (s, 3H, CH_3C=) ; 3.40 (s, 3H, $C\underline{H}_3Ar$) ; 3.80 (qq, J = 6.8, 6.8, 1H, $C\underline{H}(CH_3)_2$) ; 3.93, 4.28 (AB system, J = 11.5, 2H, CH_2Br) ; 7.30, 7.48 (AA'BB' system, J = 8.2, 4H arom.)

(S)-2-Bromo-1-cyclohexylidene-1-p-tolylsulfinyl ethane **2f** : Yield : 80%. Colorless oil. $[\alpha]_D^{25}$ = -157 (c = 1, EtOH). IR (neat) : 2925, 2852, 1623, 1490, 1444, 1079, 1039, 806 cm^{-1}. ^{1}H-NMR : δ = 1.60-1.90 (m, 6H, -(CH_2)-$_3$) ; 2.40 (m, 2H, CH_2C=) ; 2.41 (s, 3H, $C\underline{H}_3Ar$) ; 2.82 (bt, J = 5.6, 2H, CH_2C=) ; 3.99, 4.27 (AB sytem, J = 11.6, 2H, CH_2Br) ; 7.30, 7.47 (AA'BB' system, J = 8.0, 4H arom.). ^{13}C-NMR : δ = 19.6 (t, CH_2Br) ; 21.4 (q, $\underline{C}H_3Ar$) ; 26.1 (t) ; 27.3 (t) ; 28.2 (t) ; 31.9 (t) ; 33.0 (t) ; 124.4 (d) ; 129.8 (d) ; 133.1 (s) ; 139.0 (s) ; 140.9 (s) ; 157.1 (s).

General procedure for the preparation of $(R)_S$-and $(S)_S$-2-p-tolylsulfinyl-1,3-alkadienes **3**

To a stirred solution of bromide **2** (1 mmol) in 1mL of alcoholic solvent (cf Table III) at the indicated temperature (cf Table III) under a nitrogen atmosphere was added dropwise a 2M alcoholic solution of KOH (1 mL). After the indicated time (cf Table III), water (3 mL) was added and most solvents were removed under reduced pressure. The residue was extracted with ether. The combined organic layer was washed with brine and dried over $MgSO_4$. After solvent evaporation, the crude product was purified by silica gel chromatography (eluent : ether/cyclohexane 2/8).

(+)-(R)-2-p-tolylsulfinyl-1,3-butadiene **3a** : Yield : 81%. White crystals ; m.p. = 39-40°C (ether/pentane). $[\alpha]_D^{25}$ = +174 (c = 2.0, EtOH). UV : λ_{max} (EtOH) = 231 nm (ε 14200). ^{1}H-NMR : δ = 2.39 (s, 3H, $C\underline{H}_3$ Ar) ; 5.22 (d, J_{AX} = 11.3, J_{MX} = 0, 1H, part X of AMX system) ; 5.48 (d, J_{AM} = 17.7, J_{MX} = 0, 1H, part M of AMX system) ; 5.66 (s, 1H, H *trans*) ; 6.14 (s, 1H, H *cis*) ; 6.24 (dd, J_{AX} = 11.3, J_{AM} = 17.7, 1H,

part A of AMX system) ; 7.26, 7.56 (AA'BB' system, J = 8.2, 4H arom). ^{13}C-NMR : δ = 21.4 (q, $\underline{C}H_3$ Ar) ; 117.1 (t) ; 119.0 (t) ; 125.7 (d) ; 129.4 (d, $\underline{C}H$ = CH_2 ; 129.9 (d) ; 140.0 (s) ; 141.9 (s) ; 151.4 (s). MS : m/z (rel. intensity) : 192 (30, M^+) ; 140 (100) ; 139 (18) ; 137 (23) ; 123 (32) ; 92 (96) ; 91 (45) ; 65 (17) ; 53 (33) ; 27 (17). HR-MS : Calculated for $C_{11}H_{12}OS$: 192.0609, found : 192.0599.

(E)-(+)-(R)-2-p-tolylsulfinyl-1,3-pentadiene **3b** : Yield : 70%. Colorless oil. IR (neat) : 1590, 1079, 1052, 959, 813 cm^{-1}. ^{1}H-NMR : δ = 1.69 (dd, J_{AX} = 6.4, J_{BX} = 0.6, 3H, part X of ABX_3 system, $C\underline{H}_3CH$ = CH) ; 2.38 (s, 3H, $C\underline{H}_3Ar$) ; 5.71 (s, 1H, H *trans*) ; 5.91 (bd, J_{AB} = 16.0, 1H, part B of ABX_3 system, $C\underline{H}$= $CHCH_3$) ; 5.97 (s, 1H, H *cis*) ; 6.01 (dq, J_{AB} = 16.0, J_{AX} = 6.4, 1H, part A of ABX_3 system, CH =$C\underline{H}CH_3$) ; 7.27, 7.53 (AA'BB' system, J = 8.1, 4H arom.). ^{13}C-NMR : δ = 18.7 (q, $\underline{C}H_3CH$=) ; 21.4 (q, $\underline{C}H_3Ar$) ; 114.9 (t, CH_2=) ; 123.5 (d) ; 125.7 (d) ; 129.9 (d) ; 131.4 (d) ; 140.1 (s) ; 141.8 (s) ; 151.0 (s). MS : m/z (rel. intensity) : 206 (3, M^+) ; 140 (100) ; 139 (14) ; 92 (82) ; 91 (45) ; 69 (16) ; 67 (63) ; 65 (27) ; 41 (45) ; 39 (25). HR-MS : Calculated for $C_{12}H_{14}OS$: 206.0765, found : 206.0770.

(+)-(R)-4-methyl-2-p-tolylsulfinyl-1,3-pentadiene **3c** : In this case, the reaction was performed in *ter*-butanol with sonication. Yield : 22%. Colorless oil. The following analyses were obtained on a product contaminated by traces of impurities. ^{1}H-NMR : δ = 1.60 (d, J = 1.1, 3H) ; 1.73 (d, J = 1.2, 3H) ; 2.39 (s, 3H, $C\underline{H}_3Ar$) ; 5.38 (bd, J = 1.3, 1H, $C\underline{H}$ = $C(CH_3)_2$) ; 5.57 (d, J = 1.3, 1H, H *trans*) ; 6.15 (s, 1H, H *cis*) ; 7.26, 7.48 (AA'BB' system, J = 8.3, 4H arom.). MS : m/z (rel. intensity) : 220 (2, M^+) ; 140 (44) ; 92 (21) ; 91 (14) ; 81 (100) ; 79 (25) ; 57 (14) ; 53 (25) ; 41 (26) ; 39 (16). HR-MS : Calculated for $C_{13}H_{16}OS$: 220.0922, found : 220.0932.

(+)-(S)-3-methyl-2-p-tolylsulfinyl-1,3-butadiene **3d** : Yield : 85%. White crystals ; m.p. = 48.5°C (ether/pentane) $[\alpha]_D^{25}$ = +252 (c = 0.75, EtOH). IR (nujol) : 1582, 1297, 1025, 900, 809 cm^{-1}. ^{1}H-NMR : δ = 1.82 (s, 3H, CH_3C=) ; 2.38 (s, 3H, CH_3Ar) ; 5.06 (s, 1H) ; 5.20 (s, 1H) ; 5.84 (s, 1H, H *trans*) ; 6.21 (s, 1H, H *cis*) ; 7.24, 7.53 (AA'BB' system, J = 8.2, 4H arom.). ^{13}C-NMR : δ = 21.4 (q, $\underline{C}H_3Ar$) ; 22.2 (q, $\underline{C}H_3C$=) ; 114.8 (t) ; 116.2 (t) ; 126.0 (d) ; 129.8 (d) ; 137.6 (s, =$\underline{C}CH_3$) ; 140.07 (s) ; 141.9 (s) ; 153.8 (s). Analysis : Calculated for $C_{12}H_{14}OS$ 69.86% C 6.86% H 7.76% O 15.52% S, found 69.73% C 7.05% H 7.92% O 15.27% S. MS = m/z (rel. intensity) : 206 (14, M^+) ; 140 (100) ; 123 (8) ; 92 (78) ; 91 (28) ; 67 (24) ; 65 (17) ; 45 (7) ; 41 (37) ; 39 (17). HR-MS : Calculated for $C_{12}H_{14}OS$: 206.0765, found : 206.0760.

(+)-(S)-3-Isopropyl-2-p-tolylsulfinyl-1,3-butadiene **3e** : Yield : 71%. White crystals ; m.p. = 44°C (ether/petroleum ether). $[\alpha]_D^{25}$ = +234 (c = 2.0, EtOH). IR (neat) : 2963, 1083, 1045, 908, 806 cm^{-1}. ^{1}H-NMR : δ = 0.64 (d, J = 6.8, 3H, $C\underline{H}_3CH$) ; 0.99 (d, J = 6.8, 3H, $C\underline{H}_3CH$) ; 2.34 (s, 3H, $C\underline{H}_3Ar$) ; 2.41 (qq, J = 6.8, 6.8, 1H, $C\underline{H}(CH_3)_2$) ; 5.02 (s, 1H) ; 5.11 (s, 1H) ; 5.74 (s, 1H, H *trans*) ; 6.15 (s, 1H, H *cis*) ; 7.21, 7.49 (AA'BB' system, J = 8.1, 4H arom.). ^{13}C-NMR : δ = 20.7 (q, $\underline{C}H_3CH$) ; 21.2 (q, $\underline{C}H_3CH$) ; 21.4 (q, $\underline{C}H_3Ar$) ; 113.3 (t) ; 113.6 (t) ; 125.8 (d) ; 129.5 (d) ; 140.0 (s) ; 141.7 (s) ; 148.3 (s, $\underline{C}iPr$) ; 154.6 (s). MS : m/z (rel. intensity) : 234 (2, M^+) ; 140 (100) ; 95 (50) ; 92 (54) ; 91 (24) ; 79 (11) ; 67 (17) ; 55 (17) ; 43 (18) ; 41 (17). HR-MS : Calculated for $C_{14}H_{18}OS$: 234.1078, found : 234.1085.

(+)-(S)-1-(1-cyclohexenyl)-1-p-tolylsulfinyl ethene **3f** : Yield : 68%. Colorless oil. $[\alpha]_D^{25}$ = +152 (c = 1.5, EtOH). IR (neat) : 2910, 1590, 1485, 1070, 1040, 910, 800 cm^{-1}. ^{1}H-NMR : δ = 1.38-1.63 (m, 4H) ; 1.72 (m, 1H) ; 2.04 (m, 2H) ; 2.19 (m, 1H) ; 2.38 (s, 3H, C$\underline{H}_3$Ar) ; 5.67 (s, 1H, H *trans*) ; 5.98 (m, 1H, =C$\underline{H}$CH$_2$-) ; 6.03 (s, 1H, H *cis*) ; 7.23, 7.50 (AA'BB' system, J = 8.2, 4H arom.). ^{13}C-NMR : δ = 21.4 (q, $\underline{C}$H$_3$Ar) ; 21.7 (t) ; 22.3 (t) ; 25.4 (t) ; 27.6 (t) ; 112.0 (t) ; 125.7 (d) ; 129.0 (d) ; 129.7 (d) ; 131.5 (s) ; 140.9 (s) ; 141.6 (s) ; 154.3 (s). MS : m/z (rel. intensity) : 246 (3, M^+) ; 140 (50) ; 107 (73) ; 92 (44) ; 91 (100) ; 79 (89) ; 77 (33) ; 65 (27) ; 41 (30) ; 39 (28) . HR-MS : Calculated for $C_{15}H_{18}OS$: 246.1078, found : 246.1085.

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