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Enantiopure alkylidene-1,1-bis-*p*-tolylsulfoxides as new partners in diastereoselective radical cyclizations

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Abstract—Enantiopure alkylidene-1,1-bis-*p*-tolylsulfoxides have been used as new partners in diastereoselective radical cyclizations. An efficient and highly diastereoselective 6-*exo*-*trig* cyclization was observed.

1. Introduction

Radical processes hold nowadays an important position in the realm of asymmetric synthesis.[1,2] This is due in part to the high compatibility of radical reactions with a large number of interesting functionalities, notably present on chiral auxiliaries, and to the possibility of optimizing the stereoselectivities on using Lewis acids.[3] For instance, the addition of a carbon-centered (alkyl or vinyl) radical to an alkene moiety bearing a chiral auxiliary has been well-studied (Fig. 1).[4] Generally higher diastereoselectivities are obtained when the addition occurs α to the chiral auxiliary. Good to excellent β-diastereoselectivities could also be observed,[5] the use of Lewis acids being critical in the case of chiral acrylates[6] and *N*-enoyloxazolidinones.[7]

We have focused for some years on the use of chiral sulfur-based auxiliaries, mainly sulfoxides, because of their easy introduction, their low cost and their versatile final functionalization. Our initial approach, based on the Michael addition of a vinyl radical onto vinyl sulfoxides gave mixed results. High diastereoselectivities were obtained for β-alkoxy vinyl sulfoxides,[8] while the pure carbon systems have so far led to poor results, even in the case of *N*-sulfinimines.[9] A rationale for this is the likely absence of control of the s-*cis* or s-*trans* vinyl sulfoxide conformation.[10]

We have proposed two solutions: The first one was based on a 5-*exo*-*trig* cyclization of a prochiral radical in an anti-Michael orientation, followed by the well-established β-elimination of the sulfinyl radical.[11] Implying an a priori quite favorable α-selectivity, this radical addition was highly diastereoselective. Moreover, the presence of bulky Lewis acid MAD could reverse the stereochemical outcome of the reaction.[12] The second solution consists of the implementation of a second Lewis base on the vinylsulfoxide moiety which could set the stage for chelation and thus enhance the diastereoselection by locking the reacting conformations. This was for instance achieved by Toru who concentrated on the diastereoselective addition of alkyl radicals on 2-arylsulfinyl-2-cyclopentenones.[13] Our own approach has focused on enantiopure alkylidene-1,1-bis-*p*-tolylsulfoxides as radical acceptors which in addition to displaying two Lewis basic sites offer the

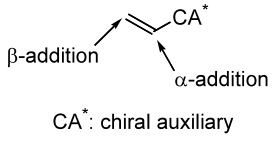
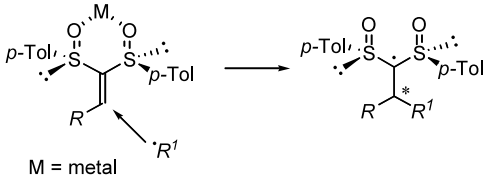


Figure 1.



Scheme 1.

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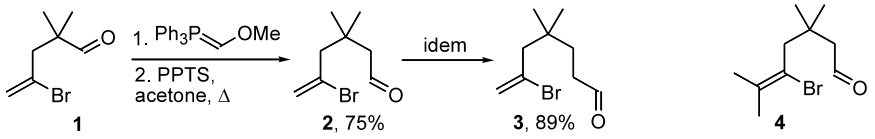
advantage of presenting a C_2-symmetry environment (Scheme 1), and serving as masked chiral ketene equivalents.[14] Preliminary results of radical additions are described herein.

2. Results and discussions

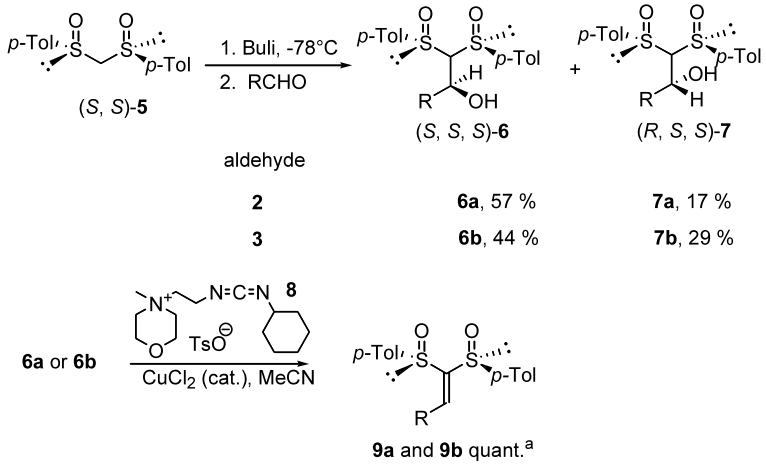
Radical cyclization precursors were synthesized in a two-step sequence, as previously described,[15] from aldehydes **2** and **3** that were obtained, respectively, after simple and double homologation of the known aldehyde **1**[16] (Scheme 2). Aldehyde **4** was prepared following the same type of chemistry.

The first step involves the alkylation of the lithium anion of (*S*,*S*)-bis-*p*-tolylsulfinylmethane **5**[17] with the aforementioned aldehydes.[15] This proceeded uneventfully to provide satisfactory yields of diastereomeric alcohols **6** and **7**, but with moderate diastereoselectivity (Scheme 3). The second one consists of a mild dehydration of the sulfinyl alcohols with the morpho CDI reagent.[18] Because the two diastereomeric alcohols **6** and **7** do not react at the same rate in the dehydration reaction which generates separation problems, we preferred running this step on the separate diastereomers. Similarly, precursor **9c** was obtained in 44% overall yield from aldehyde **4**.

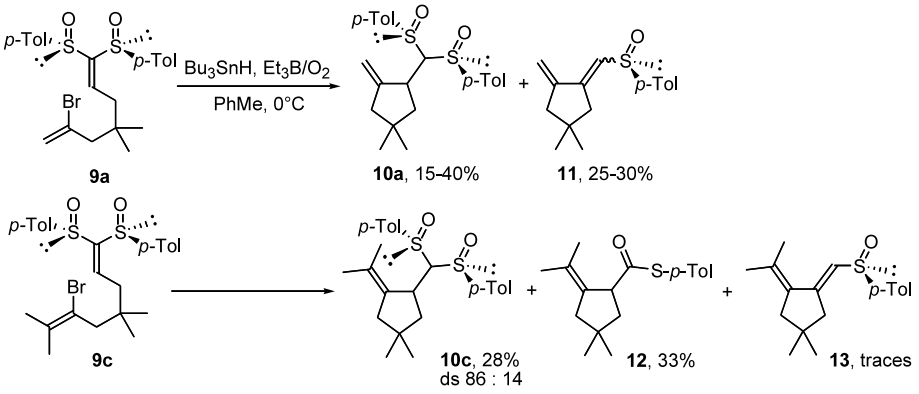
We next examined the radical behavior of these new partners and radical cyclizations were conducted under the usual conditions using triethylborane as an initiator.[19] Initial results with 5-*exo* precursors **9a** were rather frustrating (Scheme 4). Although complete consumption of the starting material was observed, isolation by chromatography of cyclization product **10a** proved to be difficult because of its instability. This resulted in variable yields of isolated compounds. ^{1}H



Scheme 2.



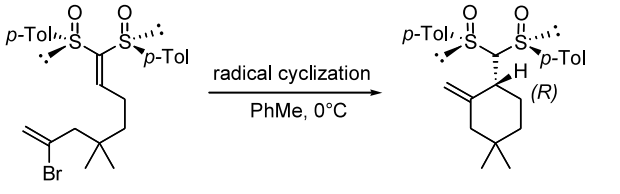
Scheme 3.



Scheme 4.

NMR of the crude cyclization products suggested a high diastereoselectivity in the cyclization process, and among the minor side products that could be observed we could not ascertain that a minor diastereomer was formed. The major adduct rapidly decomposed into dienes **11** as a 1.3:1 mixture of diastereomers,[20] presumably due to spontaneous loss of arylsulfenic acid, a previously reported phenomenon on some alkylidene bis-sulfoxides.[21] Precursor **9c** gave a more stable cyclization adduct **10c**, clearly present as two diastereomers in a 86:14 ratio. Only traces of diene **13** were observed. A major side product in this reaction was the Pummerer adduct[15] **12** whose mechanism of formation remains to be clarified.

More fruitful results were obtained with precursor **9b**, since cyclization adducts **10b** were stable and could be fully characterized (Scheme 5). Once again, full consumption of starting material **9b** was obtained and reasonable diastereomeric excesses up to 76% could be reached. Major diastereomer **10bM** gave suitable crystals for an X-ray diffraction analysis which allowed us to determine the (*R*) absolute configuration at the newly formed stereogenic center (Fig. 2).



9b **10bM**

conditions	yield (%)of **10b**	ds **10bM** : **10bm**
Bu_3SnH, 2 equiv. Et_3B/O_2, 10 equiv.	60[a]	81 : 19
Bu_3SnH, 2 equiv. Et_3B/O_2, 10 equiv.	72	79 : 21
Bu_3SnH, 1.5 equiv. AIBN, hν, 0°C	41	88 : 12

[a] A KF/MeOH treatment was run.

Scheme 5.

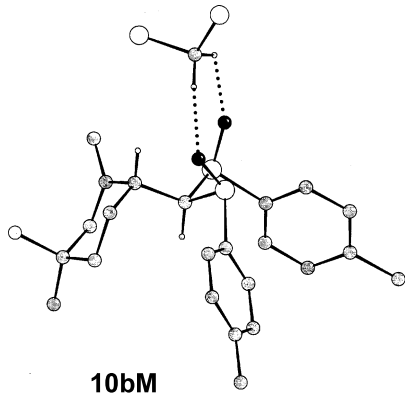
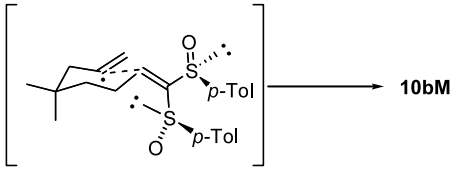


Figure 2.

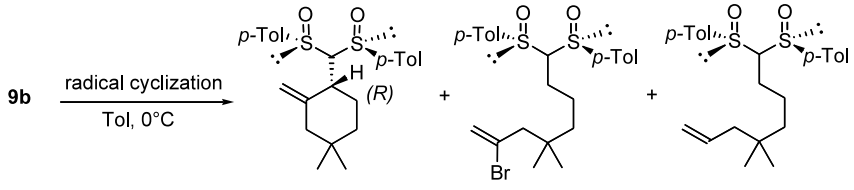
The X-ray[22] view of **10bM** shows an additional intriguing feature of the molecular system: a guest CH_2Cl_2 is chelated through double hydrogen bonds (2.1–2.4 Å) from the sulfinyl oxygens.[23]

To rationalize this finding, we propose the following transition state based on several criteria (Scheme 6). The crucial one is the conformation of the two sulfinyl groups of the alkylidene compounds **9b**. Based on our previous findings on vinylsulfoxides,[8,12] calculations by Tietze,[10] and minimization of allylic strain,[24] we propose an eclipsed lone pair conformation of the sulfinyl group *cis* to the alkyl chain, and a *s-cis* conformation for the *trans* sulfinyl group. Attack of the incoming radical would then take place *anti* to the *p*-tolyl group.



Scheme 6.

We next sought to operate the radical cyclizations in the chelation mode as in Scheme 1. For this purpose, we added to the reaction mixture one equivalent of a bidentate Lewis acid such as $ZnBr_2$ or Et_2AlCl. In both cases, a complex reaction mixture was obtained (Scheme 7). Three main products were isolated, the



Lewis acid	**10bM**	**14**	**15**
$ZnBr_2$	15% ds 83 : 17	33%	16%
Et_2AlCl	18% ds 82 : 18	44%	14%

Scheme 7.

expected cyclization adduct **10bM** with a similar diastereoselectivity, accompanied by the reduction adducts **14** and **15**. These compounds presumably originate from polar reduction by the hydride due to over-activation of the substrate from the Lewis acids.[7] This complicated reactivity, and the non-alteration of the diastereoselection in these reactions were not particularly encouraging and no other attempts were made on these precursors.

In conclusion, alkylidene-1,1-bis-*p*-tolylsulfoxides have been used for the first time in radical cyclizations. Although, some of the cyclization reactions were plagued by the instability of the cyclization products or side processes, the efficiency of these new partners as radical acceptor was demonstrated. Moreover, high diastereoselectivities could be observed in the 6-*exo*-*trig* case. The application of Lewis acids on other substrates in order to reach a highly organized chelated transition state is now in progress and will be reported in due course.

3. Experimental

3.1. General

All reactions were run under an argon or nitrogen atmosphere in anhydrous solvents and dried flasks. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F 254 and revealed with either an ultraviolet lamp ($\lambda = 254$ nm) or a *p*-anisaldehyde solution. Flash column chromatography has been performed with silica gel Merck Geduran SI (40–63 nm). Solvents were systematically distilled prior to be used. EA refers to ethyl acetate, PE to petroleum ethers. The aldehydes were dried over $CaSO_4$ and distilled. IR spectra were recorded on a Perkin–Elmer 1420 spectrometer and on a Bruker Tensor 27. ^1H and ^{13}C NMR spectra were recorded at room temperature, either at 200 MHz and 50 MHz on a AC200 Bruker spectrometer, or at 250 MHz and 63 MHz on a AC250 Bruker, or at 400 MHz and 100 MHz respectively on an ARX400 Bruker spectrometer. Shifts are given in ppm and referenced from the solvent residual signal (7.26 ppm for $CDCl_3$) for proton NMR. For carbon NMR, shifts are referenced from the solvent central peak (77.3 ppm for $CDCl_3$). Coupling constants (J) are given in hertz (Hz). The letters m, s, d, t, q, hept mean, respectively, multiplet, singulet, doublet, triplet, quadruplet, heptuplet. Optical rotations were measured on a Perkin Elmer 343 polarimeter. Elemental analysis were performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie. Melting points were obtained on a Reichert apparatus and are uncorrected.

3.1.1. 3,3-Dimethyl-5-bromo-hex-5-en-1-al 2. To a THF solution (25 mL) of di-isopropylamine (3.5 mL, 25 mmol, 2.5 equiv.) at 0°C, was added 16.7 mL of *n*-butyllithium (1.5 M in hexanes, 25 mmol, 2.5 equiv.). After 5 min of stirring at 0°C, this mixture was cannulated into a 25 mL THF solution of (methoxymethyl)triphenylphosphonium chloride (8.84 g, 25 mmol, 2.5 equiv.). After stirring for 30 min at 0°C, 30 min at rt, the reaction mixture was cooled to −78°C and a 10 mL THF solution of aldehyde **1**[16] (1.91 g, 10 mmol, 1 equiv.) was added. After 30 min of stirring at rt, the reaction was complete and usual aqueous work-up (sat. NH_4Cl, NaCl washings, drying over $MgSO_4$) was operated. Chromatography (PE/EA: 95/5) afforded 3.30 g of an oil (quantitative yield) as a 50:50, *E*:*Z* mixture of diastereomers. This mixture was treated with pyridinium-*p*-toluenesulfonate (258 mg, 0.5 mmol, 0.05 equiv.) in 100 mL of refluxing acetone overnight, then hydrolized with water. After extraction with ether and drying with $MgSO_4$, chromatography (PE/Et_2O: 95/5) afforded 1.54 g (75%) of **2** as an oil. IR (neat): 2980, 1720, 1620 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 1.18 (s, 6H, CH_3-C-CH_3), 2.46 (d, $J = 2.6$ Hz, 2H, CH_2CHO), 2.59 (s, 2H, CH_2-CBr), 5.58 (d, $J = 1.2$ Hz, 1H, $=CHH$), 5.61 (d, $J = 1.2$ Hz, 1H, $=CHH$), 9.88 (t, $J = 2.6$ Hz, 1H, CHO). ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.8 (CH_3-C-CH_3), 34.3 (CH_3-C-CH_3), 52.7 (CH_2), 54.1 (CH_2), 121.5 ($=CH_2$), 129.1 (CBr), 202.8 (CHO). Anal. calcd for $C_8H_{13}BrO$: C, 46.85; H, 6.39. Found: C, 46.70; H, 6.59.

3.1.2. 4,4-Dimethyl-6-bromo-hept-6-en-1-al 3. Following the same procedure from **2** (1.82 g, 8.9 mmol), chromatography (PE/Et_2O: 95/5) afforded 1.72 g (89%) of **3** as an oil. IR (neat): 2960, 1730, 1620 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 1.00 (s, 6H, CH_3-C-CH_3), 1.68 (t, $J = 6.5$ Hz, 2H, CH_2CH_2CHO), 2.44 (s, 2H, CH_2-CBr), 2.47 (m, 2H, CH_2CHO), 5.55 (d, $J = 1.3$ Hz, 1H, $=CHH$), 5.58 (d, $J = 1.3$ Hz, 1H, $=CHH$), 9.81 (t, $J = 1.6$ Hz, 1H, CHO). ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.1 (CH_3-C-CH_3), 33.4 (CH_2), 33.8 (CH_3-C-CH_3), 39.4 (CH_2), 52.4 (CH_2), 120.9 ($=CH_2$), 129.7 (CBr), 202.7 (CHO). Anal. calcd for $C_9H_{15}BrO$: C, 49.33; H, 6.90. Found: C, 49.28; H, 7.09.

3.1.3. 3,3-Dimethyl-5-bromo-6-methyl-hept-5-en-1-al 4. IR (neat): 2960, 2930, 1860, 1720, 1600, 1380, 1150 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 1.15 (s, 6H, CH_3-C-CH_3), 1.77 (s, 3H, $=C(CH_3)_2$), 1.90 (s, 3H, $=C(CH_3)_2$), 2.42 (d, $J = 2.7$ Hz, 2H, CH_2CHO), 2.68 (s, 2H, CH_2-CBr), 9.87 (t, $J = 2.7$ Hz, 1H, CHO). ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.9 (CH_3-C-CH_3), 28.2 ($=C(CH_3)_2$), 35.4 (CH_3-C-CH_3), 48.8 (CH_2), 54.9 (CH_2), 114.1 (CBr), 128.2 ($=C(CH_3)_2$), 203.2 (CHO).

3.2. General procedure for the synthesis of bis-sulfinyl alcohols 6 and 7

To a solution of (*S*,*S*)-bis-*p*-tolylsulfinylmethane **5** (1 equiv.) in THF (0.025 M) were added, at −40°C, *n*-BuLi in hexanes (1.2 equiv.) and the solution was stirred at −40°C for 1 h. Then, the reaction mixture was cooled to −78°C and the freshly distilled aldehyde was added neat (1.5 equiv.). The reaction was stirred at this temperature for 0.5 h and at −40°C for 1 h (only 1 h at −78°C in the case of **6a** and **6b**). Then, it was quenched at this temperature with an aqueous saturated NH_4Cl solution. The THF was evaporated and then extracted twice with CH_2Cl_2 and the combined organic layers were washed with brine and dried over $MgSO_4$. The

residue was purified by flash chromatography to give by order of elution the two diastereomeric alcohols **7** then **6**.

3.2.1. (S_S,S_S,2*S*)-1,1-Di-*p*-tolylsulfinyl-4,4-dimethyl-6-bromo-hept-6-en-2-ol 6a. Using the general procedure from **5** (195 mg, 0.66 mmol) and aldehyde **2** (205 mg, 1 mmol), chromatography (pentane/EA, from 75/25 to 50/50) afforded 189 mg (57%) of **6a** as a slightly yellow gum; $[\alpha]_D^{20}$ +60.0 (*c* 1.05, $CHCl_3$). IR (neat): 3405, 3011, 2960, 2926, 1622, 1492, 1083, 1050, 811, 755 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (s, 3H, CH_3-C-CH_3), 0.92 (s, 3H, CH_3-C-CH_3), 1.20 (d, J=14.4 Hz, 1H, C*H*H-CHOH), 1.94 (dd, J=14.4, 8.8 Hz, 1H, CH*H*-CHOH), 2.35 (s, 3H, *p*-Tol), 2.36–2.39 (m_{AB}, 2H, =CBr-CH_2), 2.47 (s, 3H, *p*-Tol), 3.32 (s, 1H, C*H*(SO*p*-Tol)$_2$), 4.76 (d, J=8.8 Hz, 1H, C*H*-OH), 5.39 (s, 1H, =C*H*H), 5.42 (s, 1H, =CH*H*), 7.01 (d, J=8.3 Hz, 2H, arom), 7.22 (d, J=7.8 Hz, 2H, arom), 7.40 (d, J=7.8 Hz, 2H, arom), 7.63 (d, J=8.3 Hz, 2H, arom). ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.5 (*p*-Tol), 21.7 (*p*-Tol), 27.9, 28.1 (*C*H_3-C-*C*H_3), 34.7 (CH_3-*C*-CH_3), 46.3 (CH_2), 52.3 (CH_2), 64.8 (CH-OH), 93.2 (*C*H(SO*p*-Tol)$_2$), 121.1 (=CH_2), 123.8 (2 CH arom), 124.7 (2 CH arom), 129.7 (=CBr), 130.5 (4 CH arom), 138.2, 139.8, 142.0, 142.4 (4 C arom). Anal. calcd for $C_{23}H_{29}BrO_3S_2$: C, 55.53; H, 5.88. Found: C, 55.42; H, 5.88.

3.2.2. (S_S,S_S,2*R*)-1,1-Di-*p*-tolylsulfinyl-4,4-dimethyl-6-bromo-hept-6-en-2-ol 7a. The second minor fraction consisted of 57 mg (17%) of **7a** as a colorless oil; $[\alpha]_D^{20}$ +35.0 (*c* 0.8, $CHCl_3$). IR (neat): 3380, 3039, 2961, 2927, 1713, 1623, 1493, 1084, 1040, 892, 811, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.08 (s, 3H, CH_3-C-CH_3), 1.09 (s, 3H, CH_3-C-CH_3), 1.77 (dd, J=14.4, 9.4 Hz, 1H, C*H*H-CHOH), 1.94 (d, J=14.4 Hz, 1H, CH*H*-CHOH), 2.29 (s, 3H, *p*-Tol), 2.45 (s, 3H, *p*-Tol), 2.52 (s, 2H, =CBr-CH_2), 3.57 (d, J=8.8 Hz, 1H, C*H*(SO*p*-Tol)$_2$), 4.76 (m, 1H, C*H*-OH), 5.51 (s, 1H, =C*H*H), 5.53 (s, 1H, =CH*H*), 6.71 (d, J=8.1 Hz, 2H, arom), 7.08 (d, J=8.1 Hz, 2H, arom), 7.36 (d, J=8.1 Hz, 2H, arom), 7.50 (d, J=8.1 Hz, 2H, arom). ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.5 (*p*-Tol), 21.7 (*p*-Tol), 27.6, 27.9 (*C*H_3-C-*C*H_3), 34.8 (CH_3-*C*-CH_3), 46.2 (CH_2), 53.3 (CH_2), 68.3 (CH-OH), 90.8 (*C*H(SO*p*-Tol)$_2$), 121.2 (=CH_2), 124.3 (2 CH arom), 125.1 (2 CH arom), 130.1 (=CBr), 130.2 (2 CH arom), 130.5 (2 CH arom), 136.9, 141.0, 141.8, 142.8 (4 C arom).

3.2.3. (S_S,S_S,2*S*)-1,1-Di-*p*-tolylsulfinyl-5,5-dimethyl-7-bromo-oct-7-en-2-ol 6b. Using general procedure from **5** (940 mg, 3.2 mmol) and aldehyde **3** (1.05 g, 4.8 mmol), chromatography (pentane/EA, from 80/20 to 50/50) afforded 719 mg (44%) of **6b** as a white gum; $[\alpha]_D^{20}$ +107.5 (*c* 1.0, $CHCl_3$). IR (neat): 3400, 3000, 2980, 1625, 1600, 1490, 1100, 1070, 910, 830 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 0.83 (s, 3H, CH_3-C-CH_3), 0.84 (s, 3H, CH_3-C-CH_3), 1.01 (m, 1H, CH_2), 1.24 (m, 1H, CH_2), 1.69 (m, 1H, CH_2), 2.25 (s, 2H, =CBr-CH_2), 2.34 (m, 1H, CH_2), 2.34 (s, 3H, *p*-Tol), 2.46 (s, 3H, *p*-Tol), 3.34 (s, 1H, C*H*(SO*p*-Tol)$_2$), 4.40 (m, 1H, C*H*-OH), 5.40 (s, 1H, =C*H*H), 5.45 (s, 1H, =CH*H*), 7.03 (d, J=8.4 Hz, 2H, arom), 7.22 (d, J=8.4 Hz, 2H, arom), 7.40 (d, J=8.4 Hz, 2H, arom), 7.66 (d, J=8.4 Hz, 2H, arom). ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.3 (*p*-Tol), 21.5 (*p*-Tol), 26.9, 27.1 (*C*H_3-C-*C*H_3), 29.7 (CH_2), 33.7 (CH_3-*C*-CH_3), 36.9 (CH_2), 52.1 (CH_2), 67.6 (CH-OH), 92.2 (*C*H(SO*p*-Tol)$_2$), 120.5 (=CH_2), 123.7 (2 CH arom), 124.7 (2 CH arom), 130.2 (4 CH arom), 129.7, 136.6, 139.5, 141.7, 142.3 (4 C arom+=CBr). Anal. calcd for $C_{24}H_{31}BrO_3S_2$: C, 56.35; H, 6.11. Found: C, 56.24; H, 6.22.

3.2.4. (S_S,S_S,2*R*)-1,1-Di-*p*-tolylsulfinyl-5,5-dimethyl-7-bromo-oct-7-en-2-ol 7b. The second minor fraction consisted of 474 mg (29%) of **7b** as an oil. ^1H NMR (250 MHz, $CDCl_3$) δ 0.95 (s, 3H, CH_3-C-CH_3), 0.96 (s, 3H, CH_3-C-CH_3), 1.33 (m, 1H, CH_2), 1.61 (m, 1H, CH_2), 1.75 (m, 1H, CH_2), 1.99 (m, 1H, CH_2), 2.32 (s, 3H, *p*-Tol), 2.39 (s, 2H, =CBr-CH_2), 2.47 (s, 3H, *p*-Tol), 3.64 (d, J=8.3 Hz, 1H, C*H*(SO*p*-Tol)$_2$), 4.50 (m, 1H, C*H*-OH), 5.52 (bs, 1H, =C*H*H), 5.54 (d, J=1.5 Hz, 1H, =CH*H*), 6.77 (d, J=8.2 Hz, 2H, arom), 7.10 (d, J=8.2 Hz, 2H, arom), 7.37 (d, J=8.2 Hz, 2H, arom), 7.52 (d, J=8.2 Hz, 2H, arom). ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.6 (*p*-Tol), 21.8 (*p*-Tol), 27.3 (*C*H_3-C-*C*H_3), 29.4 (CH_2), 34.2 (CH_3-*C*-CH_3), 37.5 (CH_2), 51.8 (CH_2), 70.8 (CH-OH), 90.0 (*C*H(SO*p*-Tol)$_2$), 120.8 (=CH_2), 124.4 (2 CH arom), 125.2 (2 CH arom), 130.3 (2 CH arom+=CBr), 130.5 (2 CH arom), 136.9, 141.2, 141.9, 142.9 (4 C arom).

3.3. General procedure for the dehydration of bis-sulfinyl alcohols 6 and 7

To a solution of alcohol **6** or **7** (1 equiv.) in CH_3CN (0.1 M) were added (1.5–2.0 equiv.) of 1-cyclohexyl-3-(2-morpholinoethyl)-carbodiimide metho-*p*-toluenesulfonate (**8**) and a catalytic amount of $CuCl_2$ (0.1 equiv.). The reaction was monitored by TLC and was generally over after 2–3 h between 40 and 70°C. After cooling, the reaction mixture was diluted in CH_2Cl_2 and filtered over a short pad of Celite and silica and concentrated in vacuo.

3.3.1. (S_S,S_S)-1,1-Di-*p*-tolylsulfinyl-4,4-dimethyl-6-bromo-1,6-heptadiene 9a. Using the general procedure from **6a** (135 mg, 0.27 mmol), filtration afforded 130 mg (quantitative yield) of **9a** as a white solid: mp 75–77°C; $[\alpha]_D^{20}$ −2.6 (*c* 1.05, $CHCl_3$). IR (neat): 3060, 2970, 2930, 1620, 1590, 1480, 1080, 1050, 895 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.13 (s, 3H, CH_3-C-CH_3), 1.14 (s, 3H, CH_3-C-CH_3), 2.30 (s, 3H, *p*-Tol), 2.31 (s, 3H, *p*-Tol), 2.50–2.59 (m_{AB}, 2H, =CBr-CH_2), 2.60 (dd, J=15.2, 6.1 Hz, 1H, C*H*H-CH=C(SO*p*-Tol)$_2$), 2.84 (dd, J=15.2, 9.6 Hz, 1H, CH*H*-CH=C(SO*p*-Tol)$_2$), 5.59 (d, J=1.5 Hz, 1H, =C*H*H), 5.61 (d, J=1.5 Hz, 1H, =CH*H*), 6.96 (d, J=8.1 Hz, 2H, arom), 6.99 (s, 4H, arom), 7.20 (d, J=8.1 Hz, 2H, arom), 7.23 (dd, J=9.6, 6.1 Hz, 1H, C*H*=C(SO*p*-Tol)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3 (*p*-Tol), 21.5 (*p*-Tol), 27.2 (*C*H_3-C-*C*H_3), 35.6 (CH_3-*C*-CH_3), 40.9 (CH_2), 52.5 (CH_2), 121.5 (=CH_2), 124.2 (2 CH arom), 126.3 (2 CH arom), 129.0 (=CBr), 129.5 (2 CH arom), 129.6 (2 CH arom), 139.9 (*C*H=C(SO*p*-Tol)$_2$), 137.6, 139.6, 141.1, 142.4 (4 C arom), 150.2 (CH=*C*(SO*p*-Tol)$_2$).

3.3.2. (S_S,S_S)-1,1-Di-*p*-tolylsulfinyl-5,5-dimethyl-7-bromo-1,7-octadiene 9b. Using the general procedure from **6b** (717 mg, 1.4 mmol), filtration afforded 690 mg (quantitative yield) of **9b** as a white solid: mp 103–105°C; $[\alpha]_D^{20}$ −3.7 (*c* 1.06, $CHCl_3$). IR (neat): 3040, 2965, 2922, 1622, 1594, 1492, 1450, 1393, 1082, 1044, 1015, 803, 622 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.02 (s, 6H, CH_3-C-CH_3), 1.58 (m, 2H, CH_2), 2.30 (s, 3H, *p*-Tol), 2.32 (s, 3H, *p*-Tol), 2.55 (s, 2H, =CBr-CH_2), 2.56 (m, 1H, C*H*H-CH=C(SO*p*-Tol)$_2$), 2.79 (m, 1H, CH*H*-CH=C(SO*p*-Tol)$_2$), 5.54 (s, 1H, =C*H*H), 5.57 (s, 1H, =CH*H*), 6.96–7.00 (m, 6H, arom), 7.08 (dd, *J*=8.8, 6.9 Hz, 1H, C*H*=C(SO*p*-Tol)$_2$), 7.21 (d, *J*=8.1 Hz, 2H, arom). ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.4 (*p*-Tol), 21.6 (*p*-Tol), 24.9 (CH_2), 27.2, 27.3 (*C*H_3-C-*C*H_3), 34.4 (CH_3-*C*-CH_3), 40.5 (CH_2), 52.3 (CH_2), 121.0 (=CH_2), 124.2 (2 CH arom), 126.3 (2 CH arom), 129.6 (2 CH arom+=CBr), 129.7 (2 CH arom), 143.7 (*C*H=C(SO*p*-Tol)$_2$), 137.8, 139.5, 141.1, 142.5 (4 C arom), 144.9 (CH=*C*(SO*p*-Tol)$_2$). Anal. calcd for $C_{24}H_{29}BrO_2S_2$: C, 58.41; H, 5.91. Found: C, 58.30; H, 5.95.

3.3.3. (S_S,S_S)-1,1-Di-*p*-tolylsulfinyl-4,4-dimethyl-6-bromo-7-methyl-1,6-octadiene 9c. Orange oil; $[\alpha]_D^{20}$ −15.0 (*c* 0.7, $CHCl_3$). IR (neat): 3052, 2959, 2918, 1595, 1491, 1468, 1449, 1082, 1045, 1014, 803, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.03 (s, 3H, CH_3-C-CH_3), 1.05 (s, 3H, CH_3-C-CH_3), 1.71 (s, 3H, =C(CH_3)$_2$), 1.85 (s, 3H, =C(CH_3)$_2$), 2.22 (s, 3H, *p*-Tol), 2.23 (s, 3H, *p*-Tol), 2.57 (dd, *J*=14.9, 6.3 Hz, 1H, C*H*H-CH=C(SO*p*-Tol)$_2$), 2.60 (s, 2H, =CBr-CH_2), 2.79 (dd, *J*=14.9, 9.4 Hz, 1H, CH*H*-CH=C(SO*p*-Tol)$_2$), 6.87–6.94 (m, 6H, arom), 7.11 (d, *J*=8.1 Hz, 2H, arom), 7.20 (dd, *J*=9.4, 6.3 Hz, 1H, C*H*=C(SO*p*-Tol)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 21.4, 21.9, 26.0, 27.3, 27.5 (6 CH_3), 37.3 (CH_3-*C*-CH_3), 41.5 (CH_2), 48.7 (CH_2), 117.1 (=*C*(CH_3)$_2$), 124.1 (2 CH arom), 126.2 (2 CH arom), 129.4 (2 CH arom), 129.5 (2 CH arom), 140.5 (*C*H=C(SO*p*-Tol)$_2$), 134.4, 137.6, 139.7, 141.0, 142.3 (4 C arom+=CBr), 149.8 (CH=*C*(SO*p*-Tol)$_2$).

3.4. General procedure for the radical cyclization of compounds 9

Et_3B/O_2 induced radical cyclizations: To a solution of alkylidene bis-sulfoxide (1 equiv.) in toluene (0.02 M) were added, at 0°C, 10 equiv. of Et_3B (1 M in hexane), *n*-Bu_3SnH (2 equiv.) and the radical process was initiated by addition of air (10 mL). The solution was stirred at 0°C and air (10 mL) was added every hour until completion (4–9 h). The reaction mixture was concentrated in vacuo and the residue purified by flash chromatography.

Photochemically induced radical cyclizations: To a solution of alkylidene bis-sulfoxide (1 equiv.) in degassed toluene (0.02 M) were added AIBN (0.3 equiv.) and *n*-Bu_3SnH (1.5 equiv.). The solution was cooled to 0°C and irradiated with a sunlamp (Osram Ultra-Vitalux®) until completion (4 hours). The reaction mixture was concentrated in vacuo and the residue purified by flash chromatography.

3.4.1. (S_S,S_S)-1-(Di-*p*-tolylsulfinylmethyl)-2-methylene-4,4-dimethyl-cyclopentane 10a. Chromatography (pentane/EA, from 100/0 to 70/30) afforded **10a** as a white solid which decomposes into dienes **11**: mp 92–93°C; $[\alpha]_D^{20}$ 36.1 (*c* 1.35, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$) δ 0.83 (s, 3H, CH_3-C-CH_3), 0.86 (s, 3H, CH_3-C-CH_3), 2.02 (s, 2H, =C-CH_2), 2.36 (s, 3H, *p*-Tol), 2.42 (s, 3H, *p*-Tol), 2.60 (dd, *J*=15.0, 6.2 Hz, 1H, C*H*H-CH-CH(SO*p*-Tol)$_2$), 2.84 (dd, *J*=15.0, 9.6 Hz, 1H, CH*H*-CH-CH(SO*p*-Tol)$_2$), 3.56 (m, 1H, C*H*-CH(SO*p*-Tol)$_2$), 3.72 (d, *J*=4.9 Hz, 1H, C*H*(SO*p*-Tol)$_2$), 5.21 (d, *J*=2.0 Hz, 1H, =C*H*H), 5.57 (d, *J*=2.0 Hz, 1H, =CH*H*), 7.19 (m, 4H, arom), 7.29 (d, *J*=7.9 Hz, 2H, arom), 7.47 (d, *J*=7.9 Hz, 2H, arom).

3.4.2. (S_S,S_S,1*R*)-1-(Di-*p*-tolylsulfinylmethyl)-2-methylene-4,4-dimethyl-cyclohexane 10bM. Chromatography (pentane/EA, from 95/5 to 70/30) afforded **10bM** as a white solid: mp 104–106°C; $[\alpha]_D^{20}$ −58.5 (*c* 1.0, $CHCl_3$). IR (neat): 3036, 2970, 1640, 1453, 1210, 1070, 1040, 810 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.68 (m, 1H, C*H*H-CH_2-CH-CH(SO*p*-Tol)$_2$), 0.83 (s, 3H, CH_3-C-CH_3), 0.86 (s, 3H, CH_3-C-CH_3), 0.95 (m, 1H, CH*H*-CH_2-CH-CH(SO*p*-Tol)$_2$), 1.56 (m, 1H, C*H*H-CH-CH(SO*p*-Tol)$_2$), 1.74 (m, 1H, CH*H*-CH-CH(SO*p*-Tol)$_2$), 1.87 (d, *J*=13.3 Hz, 1H, =C-C*H*H), 2.01 (d, *J*=13.3 Hz, 1H, =C-CH*H*), 2.31 (s, 3H, *p*-Tol), 2.46 (s, 3H, *p*-Tol), 3.52 (m, 1H, C*H*-CH(SO*p*-Tol)$_2$), 3.67 (d, *J*=10.9 Hz, 1H, C*H*(SO*p*-Tol)$_2$), 5.03 (s, 1H, =C*H*H), 5.32 (s, 1H, =CH*H*), 6.65 (d, *J*=8.1 Hz, 2H, arom), 7.08 (d, *J*=8.1 Hz, 2H, arom), 7.41 (d, *J*=8.1 Hz, 2H, arom), 7.53 (d, *J*=8.1 Hz, 2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3 (*p*-Tol), 21.6 (*p*-Tol), 25.4 (*C*H_3-C-CH_3), 25.6 (*C*H_2-CH-CH(SO*p*-Tol)$_2$), 31.6 (CH_3-C-*C*H_3), 32.6 (CH_3-*C*-CH_3), 33.8 (*C*H_2-CH_2-CH-CH(SO*p*-Tol)$_2$), 38.2 (*C*H-CH(SO*p*-Tol)$_2$), 46.9 (=C-*C*H_2), 85.2 (*C*H(SO*p*-Tol)$_2$), 115.2 (=CH_2), 123.3 (2 CH arom), 125.0 (2 CH arom), 130.0 (2 CH arom), 130.3 (2 CH arom), 138.9, 140.7, 141.6, 142.1, 143.4 (4 C arom+*C*=CH_2).

3.4.3. Characteristic signals for (S_S,S_S,1*S*)-1-(di-*p*-tolylsulfinylmethyl)-2-methylene-4,4-dimethyl-cyclohexane 10bm. ^1H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H, *p*-Tol), 2.46 (s, 3H, *p*-Tol), 3.07 (m, 1H, C*H*-CH(SO*p*-Tol)$_2$), 3.77 (d, *J*=5.6 Hz, 1H, C*H*(SO*p*-Tol)$_2$), 4.48 (s, 1H, =CH*H*), 4.64 (s, 1H, =CH*H*), 6.75 (d, *J*=8.2 Hz, 2H, arom), 7.05 (d, *J*=8.2 Hz, 2H, arom), 7.38 (d, *J*=8.2 Hz, 2H, arom), 7.59 (d, *J*=8.2 Hz, 2H, arom).

3.4.4. (S_S,S_S)-1-(Di-*p*-tolylsulfinylmethyl)-2-isopropylidene-4,4-dimethyl-cyclopentane 10c. Chromatography (pentane/EA, from 95/5 to 70/30) afforded **10c** (mixture of two diastereoisomers in a 86: 14 ratio) as a white solid: IR of both dias. (neat): 2955, 2921, 2861, 1595, 1492, 1464, 1118, 1081, 1049, 808 cm^{-1}. ^1H NMR of major dias. (400 MHz, $CDCl_3$) δ 0.70 (s, 3H, CH_3-C-CH_3), 0.86 (s, 3H, CH_3-C-CH_3), 1.47 (m, 2H, CH_2-CH-CH(SO*p*-Tol)$_2$), 1.57 (s, 3H, =C(CH_3)$_2$), 1.66 (s, 3H, =C(CH_3)$_2$), 1.87 (d, *J*=13.9 Hz, 1H, =C-CH*H*), 2.00 (d, *J*=13.9 Hz, 1H, =C-C*H*H), 2.37 (s, 3H, *p*-Tol), 2.44 (s, 3H, *p*-Tol), 3.46 (m, 1H, C*H*-CH(SO*p*-Tol)$_2$), 3.84 (d, *J*=6.3 Hz, 1H, C*H*(SO*p*-Tol)$_2$), 7.16 (d, *J*=8.4

Hz, 2H, arom), 7.23 (d, $J=8.4$ Hz, 2H, arom), 7.38 (d, $J=8.1$ Hz, 2H, arom), 7.59 (d, $J=8.1$ Hz, 2H, arom). ^{13}C NMR of major dias. (100 MHz, $CDCl_3$) δ 21.4, 21.6 (2C), 21.8 (2 *p*-Tol+=C(CH_3)$_2$), 28.4, 29.4 (CH_3-C-CH_3), 37.3 (CH-CH(SO*p*-Tol)$_2$), 37.9 (CH_3-C-CH_3), 46.0, 46.1 (CH_2), 93.7 (CH(SO*p*-Tol)$_2$), 124.1 (2 CH arom), 125.7 (2 CH arom), 129.9 (2 CH arom), 130.3 (2 CH arom), 127.2, 134.3, 139.7, 141.0 (2C), 142.7 (4 C arom+2 vinyl).

3.4.5. Characteristic signals for minor diastereomer of 10c. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (m, 1H, CH-CH(SO*p*-Tol)$_2$), 4.05 (d, $J=3.0$ Hz, 1H, CH(SO*p*-Tol)$_2$).

3.4.6. (R_S)-1-(2-Methylene-4,4-dimethyl-cyclopentylidene-methanesulfinyl)-4-methyl-benzene 11. Chromatography (pentane/EA, from 100/0 to 70/30) afforded **11** (two diastereomers majo:mino, 1.3:1) as an orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 3H, CH_3-C-CH_3 of majo), 1.04 (s, 3H, CH_3-C-CH_3 of majo), 1.05 (s, 3H, CH_3-C-CH_3 of mino), 1.08 (s, 3H, CH_3-C-CH_3 of mino), 2.27–2.40 (m, 6H, CH_2=C-CH_2 of majo+CH_2-C=CH(SO*p*-Tol) of majo and mino), 2.40 (s, 3H, *p*-Tol of majo), 2.40 (s, 3H, *p*-Tol of mino), 2.53 (dd, $J=16.4$, 2.2 Hz, 1H, CH_2=C-CH of mino), 2.80 (dd, $J=16.4$, 2.0 Hz, 1H, CH_2=C-CH of mino), 5.09 (s, 1H, =CH of mino), 5.42 (s, 1H, =CH of majo), 5.46 (t, $J=2.2$ Hz, 1H, =CH of mino), 5.92 (s, 1H, =CH of majo), 6.16 (s, 1H, =CH(SO*p*-Tol) of majo), 6.46 (t, $J=2.0$ Hz, 1H, =CH(SO*p*-Tol) of mino), 7.30 (d, $J=8.1$ Hz, 2H, arom of majo), 7.31 (d, $J=8.4$ Hz, 2H, arom of mino), 7.50 (d, $J=8.4$ Hz, 2H, arom of mino), 7.53 (d, $J=8.1$ Hz, 2H, arom of majo). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4 (2 *p*-Tol), 27.7, 27.8, 27.9 (2C) (CH_3-C-CH_3), 37.0, 37.5 (CH_3-C-CH_3), 46.7 (CH_2-C=CH(SO*p*-Tol) of mino), 48.0, 49.8, 50.8 (CH_2), 110.4 (=CH_2 of mino), 117.2 (=CH_2 of majo), 124.3 (2$_*$2 CH arom), 124.4 (2$_*$2 CH arom), 126.3 (=CH(SO*p*-Tol) of mino), 130.3 (=CH(SO*p*-Tol) of majo), 130.3 (2$_*$2 CH arom), 141.3 (2C), 141.9, 142.1, 146.1, 147.2, 151.9, 152.6 (2$_*$2 C arom+2$_*$2 vinyl).

3.4.7. 2-Isopropylidene-4,4-dimethyl-cyclopentane carbothioic acid S-*p*-tolyl ester 12. Chromatography (pentane/Et_2O, from 100/0 to 95/5) afforded **12** as a colorless oil: $[\alpha]_D^{20}$ −51.0 (*c* 1.1, $CHCl_3$). IR (neat): 2953, 2925, 2864, 1696, 1493, 1462, 1367, 1070, 1002, 886, 806, 776 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 3H, CH_3-C-CH_3), 1.16 (s, 3H, CH_3-C-CH_3), 1.71 (s, 3H, =C(CH_3)$_2$), 1.72 (s, 3H, =C(CH_3)$_2$), 1.85 (dd, $J=12.6$, 8.8 Hz, 1H, CH-CH-CO), 2.00 (dd, $J=12.6$, 8.8 Hz, 1H, CH-CH-CO), 2.25 (bs, 2H, =C-CH_2), 2.37 (s, 3H, *p*-Tol), 3.80 (t, $J=8.8$ Hz, 1H, CH-CO), 7.20 (d, $J=8.1$ Hz, 2H, arom), 7.28 (d, $J=8.1$ Hz, 2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6 (*p*-Tol), 21.9, 22.1 (=C(CH_3)$_2$), 27.5, 28.6 (CH_3-C-CH_3), 38.8 (CH_3-C-CH_3), 46.6, 47.1 (CH_2), 56.2 (CH-CO), 130.1 (2 CH arom), 134.8 (2 CH arom), 125.3, 129.1, 133.6, 139.4 (2 C arom+2 vinyl), 201.6 (CO). MS (CI NH_3) *m*/*z*: 289 (MH^+, 100).

3.4.8. (R_S)-1-(2-Isopropylidene-4,4-dimethyl-cyclopentyl-idenemethanemethyl)-*p*-tolylsulfoxide 13. Colorless oil; $[\alpha]_D^{20}$ −274.0 (*c* 1.3, $CHCl_3$). IR (neat): 3036, 2953, 2921, 2864, 1647, 1597, 1492, 1463, 1366, 1081, 1037, 1013, 804, 758 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 3H, CH_3-C-CH_3), 1.07 (s, 3H, CH_3-C-CH_3), 1.77 (s, 3H, =C(CH_3)$_2$), 2.06 (s, 3H, =C(CH_3)$_2$), 2.17–2.32 (2 m_{AB}, 4H, =C-CH_2), 2.39 (s, 3H, *p*-Tol), 5.93 (s, 1H, =CH(SO*p*-Tol)), 7.26 (d, $J=8.1$ Hz, 2H, arom), 7.53 (d, $J=8.1$ Hz, 2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6 (*p*-Tol), 22.8, 25.2 (=C(CH_3)$_2$), 29.5, 29.7 (CH_3-C-CH_3), 35.6 (CH_3-C-CH_3), 46.1 (CH_2), 50.8 (CH_2), 124.7 (2 CH arom), 127.4 (=CH(SO*p*-Tol)), 130.1 (2 CH arom), 134.2, 133.8, 141.1, 142.6, 153.9 (2 C arom+3 vinyl).

3.4.9. (S_S,S_S)-1,1-Di-*p*-tolylsulfinyl-5,5-dimethyl-7-bromo-oct-7-ene 14. Chromatography (pentane/EA, from 95/5 to 75/25) afforded **14** as a white solid: mp 107–109°C; $[\alpha]_D^{20}$ +106.0 (*c* 1.0, $CHCl_3$). IR (neat): 3040, 2922, 1620, 1493, 1083, 1053, 905, 810 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.68 (s, 3H, CH_3-C-CH_3), 0.69 (s, 3H, CH_3-C-CH_3), 0.80–0.95 (m, 4H, CH_2-CH_2-C(CH_3)$_2$), 1.53 (m, 1H, CH-CH(SO*p*-Tol)$_2$), 1.95 (m, 1H, CH-CH(SO*p*-Tol)$_2$), 2.11 (s, 2H, =CH-CH_2), 2.36 (s, 3H, *p*-Tol), 2.43 (s, 3H, *p*-Tol), 3.39 (t, $J=5.0$ Hz, 1H, CH(SO*p*-Tol)$_2$), 5.33 (s, 1H, =CH), 5.44 (s, 1H, =CH), 7.25 (s, 4H, arom), 7.36 (d, $J=8.1$ Hz, 2H, arom), 7.63 (d, $J=8.1$ Hz, 2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4 (CH_2), 20.6 (*p*-Tol), 20.8 (*p*-Tol), 21.5 (CH_2), 27.3 (CH_3-C-CH_3), 34.0 (CH_3-C-CH_3), 41.1 (CH_2), 52.0 (CH_2), 89.2 (CH(SO*p*-Tol)$_2$), 120.5 (=CH_2), 124.1 (2 CH arom), 125.7 (2 CH arom), 130.2 (=CBr), 130.3 (2 CH arom), 130.4 (2 CH arom), 138.1, 139.4, 141.8, 143.1 (4 C arom).

3.4.10. (S_S,S_S)-1,1-Di-*p*-tolylsulfinyl-5,5-dimethyl-oct-7-ene 15. Chromatography (pentane/EA, from 95/5 to 75/25) afforded **15** as a colorless oil: $[\alpha]_D^{20}$ +115.0 (*c* 1.0, $CHCl_3$). IR (neat): 3053, 2956, 2924, 1595, 1492, 1469, 1083, 1056, 911, 810, 731 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.58 (s, 6H, CH_3-C-CH_3), 0.65–0.80 (m, 4H, CH_2-CH_2-C(CH_3)$_2$), 1.51 (m, 1H, CH-CH(SO*p*-Tol)$_2$), 1.65–1.66 (m_{AB}, 2H, =CH-CH_2), 1.92 (m, 1H, CH-CH(SO*p*-Tol)$_2$), 2.36 (s, 3H, *p*-Tol), 2.43 (s, 3H, *p*-Tol), 3.34 (dd, $J=6.3$, 5.0 Hz, 1H, CH(SO*p*-Tol)$_2$), 4.83 (td, $J=16.9$, 1.0 Hz, 1H, =CH), 4.92 (dd, $J=10.1$, 2.3 Hz, 1H, =CH), 5.58 (tdd, $J=16.9$, 10.1, 7.6 Hz, 1H, CH=CH_2), 7.25 (s, 4H, arom), 7.36 (d, $J=8.1$ Hz, 2H, arom), 7.62 (d, $J=8.1$ Hz, 2H, arom). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4 (CH_2), 21.6 (*p*-Tol), 21.8 (*p*-Tol), 22.4 (CH_2), 26.9 (CH_3-C-CH_3), 33.0 (CH_3-C-CH_3), 41.0 (CH_2), 46.2 (CH_2), 89.3 (CH(SO*p*-Tol)$_2$), 117.0 (=CH_2), 124.1 (2 CH arom), 125.7 (2 CH arom), 130.3 (2 CH arom), 130.4 (2 CH arom), 135.5 (CH=CH_2), 138.1, 139.4, 141.8, 143.1 (4 C arom). MS (CI NH_3) *m*/*z*: 417 (MH^+, 60), 277 (M−*p*-TolSO, 100).

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