Supporting Information for

Nucleophilic Epoxidation of α' -Hydroxy Dienyl Sulfoxides

Roberto Fernández de la Pradilla,^{,†} Pilar Manzano,[†] Carlos Montero,[†] Julián Priego,[†] Martín Martínez-Ripoll,[‡] and Luis A. Martínez-Cruz.[‡]*

[†] Instituto de Química Orgánica, CSIC, Juan de la Cierva, 3, 28006 Madrid, Spain.

Fax: 34-91-564-4853 ; 34-91-562-1829

E-mail: iqofp19@iqog.csic.es

[‡] Departamento de Cristalografía, Instituto de Química-Física Rocasolano, CSIC, Serrano 119, 28006 Madrid, Spain.

Table of Contents

Materials and Methods	S8
1. Preparation of Starting Materials	S8
1.1. General Procedure for Synthesis of Hydroxy Dienyl Sulfoxides	S8
1.2. Synthesis of (+)-(4 <i>E</i>)-(3 <i>R</i> , <i>S_s</i>)-4-(<i>p</i> -Tolylsulfinyl)hepta-1,4,6-trien-3-ol, 3a, and (-)-(4 <i>E</i>)-(3 <i>S</i> , <i>S_s</i>)-4-(<i>p</i> -Tolylsulfinyl)hepta-1,4,6-trien-3-ol, 4a.	S8
1.3. Synthesis of (+)-(2 <i>E</i> ,5 <i>E</i>)-(4 <i>R</i> , <i>S_s</i>)-5-(<i>p</i> -Tolylsulfinyl)octa-2,5,7-trien-4-ol, 3b, and (-)-(2 <i>E</i> ,5 <i>E</i>)-(4 <i>S</i> , <i>S_s</i>)-5-(<i>p</i> -Tolylsulfinyl)octa-2,5,7-trien-4-ol, 4b.	S9
1.4. Synthesis of (+)-(3 <i>R</i> , <i>S_s</i>)-(4 <i>E</i>)-4-(<i>p</i> -Tolylsulfinyl)hepta-4,6-dien-3-ol, 3c, and (+)-(3 <i>S</i> , <i>S_s</i>)-(4 <i>E</i>)-4-(<i>p</i> -Tolylsulfinyl)hepta-4,6-dien-3-ol, 4c.	S10
1.5. Synthesis of (+)-(3 <i>R</i> , <i>S_s</i>)-(4 <i>E</i>)-2-Methyl-4-(<i>p</i> -tolylsulfinyl)hepta-4,6-dien-3-ol, 3d, and (+)-(3 <i>S</i> , <i>S_s</i>)-(4 <i>E</i>)-2-Methyl-4-(<i>p</i> -tolylsulfinyl)hepta-4,6-dien-3-ol, 4d.	S11
1.6. Synthesis of (+)-(2 <i>E</i>)-(1 <i>R</i> , <i>S_s</i>)-1-Phenyl-2-(<i>p</i> -tolylsulfinyl)penta-2,4-dien-1-ol, 3e, and (-)-(2 <i>E</i>)-(1 <i>S</i> , <i>S_s</i>)-1-Phenyl-2-(<i>p</i> -tolylsulfinyl)penta-2,4-dien-1-ol, 4e.	S12
1.7. Synthesis of (+)-(1 <i>R</i> , <i>S_s</i>)-(2 <i>E</i>)-1-(3-Pyridyl)-2-(<i>p</i> -tolylsulfinyl)penta-2,4-dien-1-ol, 3f, and (-)-(1 <i>S</i> , <i>S_s</i>)-(2 <i>E</i>)-1-(3-Pyridyl)-2-(<i>p</i> -tolylsulfinyl)penta-2,4-dien-1-ol, 4f.	S12
1.8. Synthesis of (±)-(1 <i>R</i> , <i>S_s</i>)-(2 <i>E</i>)-1-(<i>p</i> -Fluorophenyl)-2-(<i>p</i> -tolylsulfinyl)penta-2,4-dien- 1-ol, 3g, and (±)-(1 <i>S</i> , <i>S_s</i>)-(2 <i>E</i>)-1-(<i>p</i> -Fluorophenyl)-2-(<i>p</i> -tolylsulfinyl)penta-2,4-dien-1-ol, 4g.	S13
1.9. Synthesis of (±)-2-Methyl-3-(<i>p</i> -tolylsulfinyl)hexa-3,5-dien-2-ol, 5.	S14
1.10. General Procedure for Oxidation of Sulfoxides with MMPP	S14
1.11. Synthesis of (-)-(4 <i>E</i>)-(3 <i>S</i>)-4-(<i>p</i> -Tolylsulfonyl)hepta-1,4,6-trien-3-ol, 6a.	S15
1.12. Synthesis of (±)-(2 <i>E</i>)-1-Phenyl-2-(<i>p</i> -tolylsulfonyl)penta-2,4-dien-1-ol, 6e.	S15
1.13. Synthesis of (±)-(2 <i>E</i>)-1-(3-Pyridyl)-2-(<i>p</i> -tolylsulfonyl)penta-2,4-dien-1-ol, 6f, and <i>N</i> -oxide of (±)-(2 <i>E</i>)-1-(3-Pyridyl)-2-(<i>p</i> -tolylsulfonyl)penta-2,4-dien-1-ol, 6f'.	S16

1.14. General Procedure for Mitsunobu Inversion/Deprotection Protocol

S17

1.15. Transformation of 3a into 4a.

S17

1.16. Transformation of 3e into 4e.

S18

2. Epoxidation of Dienyl Sulfoxides

S18

2.1. General Procedure for Nucleophilic Epoxidation of Vinyl and Dienyl Sulfoxides and Sulfones

S18

2.2. Synthesis of (+)-(2*R*,3*S*,*S_s*)-2-(*p*-Tolylsulfinyl)-3-vinyl oxirane, 8a,(+)-(2*R*,3*S*,*S_s*)-3-[(2'*R*)-Epoxy]-2-(*p*-tolylsulfinyl)oxirane, 9a, and(+)-(2*R*,3*S*,*S_s*)-3-[(2'*S*)-Epoxy]-2-(*p*-tolylsulfinyl)oxirane, 10a.

S19

2.3. Synthesis of (2*R*,3*S*,*S_s*)-3-[(2'*R*,3'*S*)-3'-Methyl-2'-oxiranyl]-2-(*p*-tolylsulfinyl)oxirane, 9b, and (2*R*,3*S*)-3-[(2'*R*,3'*S*)-3'-Methyl-2'-oxiranyl]-2-(*p*-tolylsulfonyl)oxirane, 11b.

S19

2.4. Synthesis of (–)-(2*R*,3*S*,*S_s*)-3-(2'-Propenyl)-2-(*p*-tolylsulfinyl)oxirane, 8c.

S20

2.5. Synthesis of (+)-(2*R*,3*R*,4*R*,5*S*,*S_s*)-3,4-Epoxy-4-(*p*-tolylsulfinyl)-5-vinyl-tetrahydrofuran-2-methanol, 18a, (+)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-4--(*p*-tolylsulfonyl)-5-vinyl-tetrahydrofuran-2-methanol, 22a, and (+)-(2*R*,5*S*,*S_s*)-4-(*p*-tolylsulfinyl)-5-vinyl-2,5-dihydrofuran-2-methanol, 16a.

S20

2.6. Nucleophilic Epoxidation of (+)-(2*R*,5*S*,*S_s*)-4-(*p*-Tolylsulfinyl)-5-vinyl-

2,5-dihydrofuran-2-methanol, 16a.

S23

2.7. Synthesis of (2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-2-(*p*-tolylsulfonyl)-5-vinyl-

tetrahydrofuran-2-methanol, (major isomer), 22a.

S23

2.8. Synthesis of (+)-(2*R*,3*R*,4*R*,5*S*,*S_s*)-3,4-Epoxy-5-(1'-propenyl)-4-(*p*-tolylsulfinyl)tetrahydrofuran-2-methanol, 18b, and3,4-Epoxy-5-(1'-propenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22b.

S24

2.9. Synthesis of (±)-(2*R*,3*R*,4*R*,5*S*,*S_s*)-3,4-Epoxy-5-ethyl-4-(*p*-tolylsulfinyl)tetrahydrofuran-2-methanol, 18c, (±)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-ethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22c, and (±)-(2*R*,5*S*,*S_s*)-4-(*p*-Tolylsulfinyl)-5-ethyl-2,5-dihydrofuran-

2-methanol, 16c.

S25

2.10. Synthesis of (±)-(2*R*,3*R*,4*R*,5*S*,*S_s*)-3,4-Epoxy-5-isopropyl-4-

(*p*-tolylsulfinyl)tetrahydrofuran-2-methanol, 18d, ($\pm$)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-isopropyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22d, and ($\pm$)-(2*R*,5*S*,*S_s*)-4-(*p*-Tolylsulfinyl)-5-isopropyl-2,5-dihydrofuran-2-methanol, 16d. S27

2.11. Nucleophilic epoxidation of ($\pm$)-(2*R*,5*S*,*S_s*)-5-Isopropyl-4-(*p*-tolylsulfinyl)-2,5-dihydrofuran-2-methanol, 16d, and oxidation of the crude mixture. S29

2.12. Synthesis of (+)-(2*R*,3*R*,4*R*,5*S*,*S_s*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfinyl)tetrahydrofuran-2-methanol, 18e, (+)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22e, and (+)-(2*R*,5*S*,*S_s*)-4-(*p*-Tolylsulfinyl)-5-phenyl-2,5-dihydrofuran-2-methanol, 16e. S29

2.13. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22e.

S30

2.14. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22e.

S30

2.15. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,5*S*,*S_s*)-3,4-Epoxy-5-(3-pyridyl)-4-(*p*-tolylsulfinyl)tetrahydrofuran-2-methanol, 18f, ($\pm$)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-(3-pyridyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22f, and ($\pm$)-(2*R*,5*S*,*S_s*)-4-(*p*-Tolylsulfinyl)-5-(3-pyridyl)-2,5-dihydrofuran-2-methanol, 16f. S31

2.16. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-(3-pyridyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22f. S32

2.17. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,5*S*,*S_s*)-3,4-Epoxy-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfinyl)tetrahydrofuran-2-methanol, 18g, ($\pm$)-(2*S*,3*R*,4*R*,5*S*,*S_s*)-3,4-Epoxy-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22g, ($\pm$)-(2*S*,3*R*,4*R*,5*S*,*S_s*)-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfinyl)-2,5-dihydrofuran-2-methanol, 16g.

S34

2.18. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,*S_s*)-5,5-Dimethyl-3,4-epoxy-4-(*p*-tolylsulfinyl)tetrahydrofuran-2-methanol, 18h, ($\pm$)-(2*R*,3*R*,4*R*)-5,5-Dimethyl-3,4-epoxy-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22h, ($\pm$)-(2*R*,*S_s*)-5,5-Dimethyl-4-(*p*-tolylsulfinyl)-2,5-dihydrofuran-2-methanol, 16h. S36

3. Synthesis and Epoxidation of Sulfonyl Dihydrofurans. S37

3.1. General Procedure for Oxidation/Epoxidation of Hydroxy Dienyl

Sulfoxides with <i>m</i> -CPBA	S37
3.2. Synthesis of (±)-(1 <i>S</i> ,4 <i>S</i>)-(2 <i>E</i>)-4,5-Epoxy-1-phenyl-2-(<i>p</i> -tolylsulfonyl)pent-2-en-1-ol, 26e, and (±)-(1 <i>S</i> ,4 <i>R</i>)-(2 <i>E</i>)-4,5-Epoxy-1-phenyl-2-(<i>p</i> -tolylsulfonyl)pent-2-en-1-ol, 27e.	S37
3.3. Synthesis of (±)-(1 <i>S</i> ,4 <i>S</i>)-(2 <i>E</i>)-4,5-Epoxy-1-ethyl-2-(<i>p</i> -tolylsulfonyl)pent-2-en-1-ol, 26c, and (±)-(1 <i>S</i> ,4 <i>R</i>)-(2 <i>E</i>)-4,5-Epoxy-1-ethyl-2-(<i>p</i> -tolylsulfonyl)pent-2-en-1-ol, 27c.	
S38	
3.4. Synthesis of (±)-(1 <i>S</i> ,4 <i>S</i>)-(2 <i>E</i>)-4,5-Epoxy-1-isopropyl-2-(<i>p</i> -tolylsulfonyl)pent-2-en-1-ol, 26d, and (±)-(1 <i>S</i> ,4 <i>R</i>)-(2 <i>E</i>)-4,5-Epoxy-1-isopropyl-2-(<i>p</i> -tolylsulfonyl)pent-2-en-1-ol, 27d.	S39
3.5. Synthesis of (±)-(1 <i>S</i> ,4 <i>S</i>)-(2 <i>E</i>)-4,5-Epoxy-1-(<i>p</i> -fluorophenyl)-2-(<i>p</i> -tolylsulfonyl)pent-2-en-1-ol, 26g, and (±)-(1 <i>S</i> ,4 <i>R</i>)-(2 <i>E</i>)-4,5-Epoxy-1-(<i>p</i> -fluorophenyl)-2-(<i>p</i> -tolylsulfonyl)pent-2-en-1-ol, 27g.	S40
3.6. General Procedure for Cyclization of Monoepoxides with CSA	S40
3.7. Synthesis of (±)-(2 <i>R</i> ,5 <i>S</i>)-5-Phenyl-4-(<i>p</i> -tolylsulfonyl)-2,5-dihydrofuran-2-methanol, 28e.	S41
3.8. Synthesis of (±)-(2 <i>S</i> ,5 <i>S</i>)-5-Phenyl-4-(<i>p</i> -tolylsulfonyl)-2,5-dihydrofuran-2-methanol, 29e.	S41
3.9. Synthesis of (±)-(2 <i>R</i> ,5 <i>S</i>)-5-Ethyl-4-(<i>p</i> -tolylsulfonyl)-2,5-dihydrofuran-2-methanol, 28c.	S41
3.10. Synthesis of (±)-(2 <i>S</i> ,5 <i>S</i>)-5-Ethyl-4-(<i>p</i> -tolylsulfonyl)-2,5-dihydrofuran-2-methanol, 29c.	S41
3.11. Synthesis of (±)-(2 <i>R</i> ,5 <i>S</i>)-5-Isopropyl-4-(<i>p</i> -tolylsulfonyl)-2,5-dihydrofuran-2-methanol, 28d.	S42
3.12. Synthesis of (±)-(2 <i>S</i> ,5 <i>S</i>)-5-Isopropyl-4-(<i>p</i> -tolylsulfonyl)-2,5-dihydrofuran-2-methanol, 29d.	S42
3.13. Synthesis of (±)-(2 <i>R</i> ,5 <i>S</i>)-5-(<i>p</i> -Fluorophenyl)-4-(<i>p</i> -tolylsulfonyl)-2,5-dihydrofuran-2-methanol, 28g.	S43
3.14. Synthesis of (±)-(2 <i>S</i> ,5 <i>S</i>)-5-(<i>p</i> -Fluorophenyl)-4-(<i>p</i> -tolylsulfonyl)-2,5-dihydrofuran-2-methanol, 29g.	S44
3.15. Synthesis of (±)-(2 <i>R</i> ,5 <i>S</i>)-5-(<i>p</i> -Fluorophenyl)-4-(<i>p</i> -tolylsulfonyl)-2,5-	

- dihydrofuran-2-methanol, 28g, and ($\pm$)-(2*S*,5*S*)-5-(*p*-Fluorophenyl)-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, 29g. S44
- 3.16. Synthesis of ($\pm$)-(2*R*,5*S*)-5-(*p*-Fluorophenyl)-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, 28g, ($\pm$)-(2*S*,5*S*)-5-(*p*-Fluorophenyl)-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, 29g, and (2*E*)-1-(*p*-Fluorophenyl)-2-(*p*-tolylsulfonyl)penta-2,4-dien-1-ol, 6g. S45
- 3.17. Synthesis of ($\pm$)-5,5-Dimethyl-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, 30. S45
- 3.18. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22e, and ($\pm$)-(2*R*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 23e. S46
- 3.19. Synthesis of ($\pm$)-(2*S*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 24e, and ($\pm$)-(2*S*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 25e. S46
- 3.20. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-ethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22c, and ($\pm$)-(2*R*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-ethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 23c. S47
- 3.21. Synthesis of ($\pm$)-(2*S*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-ethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 25c, and 5-Ethyl-4-(*p*-tolylsulfonyl)furan-2-methanol, 31c. S48
- 3.22. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-isopropyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22d, ($\pm$)-(2*R*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-isopropyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 23d, and 5-Isopropyl-4-(*p*-tolylsulfonyl)furan-2-methanol, 31d. S48
- 3.23. Synthesis of ($\pm$)-(2*S*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-isopropyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 24d, and ($\pm$)-(2*S*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-isopropyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 25d. S49
- 3.24. Synthesis of ($\pm$)-(2*S*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22g, and ($\pm$)-(2*S*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 23g. S50
- 3.25. Synthesis of ($\pm$)-(2*S*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 24g, and ($\pm$)-(2*S*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 25g. S51
- 3.26. Synthesis of ($\pm$)-(2*S*,3*R*,4*R*)-3,4-Epoxy-5,5-dimethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22h, and ($\pm$)-(2*S*,3*S*,4*S*)-3,4-Epoxy-

5,5-dimethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 23h.

S52

4. Oxidations and Derivatizations S52

4.1. Synthesis of (2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-4-(*p*-tolylsulfonyl)-5-vinyl-tetrahydrofuran-2-methanol, 22a. S52

4.2. Synthesis of the *p*-nitrobenzoate of (+)-(2*R*,3*R*,4*R*,5*S*,*S*₅)-3,4-Epoxy-4-(*p*-tolylsulfinyl)-5-vinyl-tetrahydrofuran-2-methanol, 34. S53

4.3. General Procedure for Oxidation of Sulfoxides to Sulfones with *m*-CPBA S53

4.4. Synthesis of (–)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-(1'-propenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22b.

S54

4.5. Synthesis of (±)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-ethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22c.

S54

4.6. Synthesis of (±)-(2*R*,5*S*,*S*₅)-5-Isopropyl-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, 28d. S55

4.7. Synthesis of (±)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-isopropyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22d.

S55

4.8. Synthesis of (±)-(2*R*,5*S*)-4-(*p*-Tolylsulfonyl)-5-phenyl-2,5-dihydrofuran-2-methanol, 28e. S55

4.9. Synthesis of (2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22e. S56

4.10. Synthesis of (±)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22g. S56

4.11. Synthesis of (±)-(2*S*,3*R*,4*R*)-5,5-Dimethyl-3,4-epoxy-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, 22h.

S57

Materials and Methods

Reagents and solvents were handled by using standard syringe techniques. All reactions were carried out under an argon atmosphere. Hexane, toluene and CH_2Cl_2 were distilled from CaH_2 , and THF and Et_2O from sodium. $(\text{MeO})_2\text{P}(\text{O})\text{Me}$, Et_3N , and $i\text{-Pr}_2\text{NH}$ were distilled from CaH_2 . Crude products were purified by flash chromatography on 230-400 mesh silica gel with distilled solvents. Analytical TLC was carried out on silica gel plates with detection by UV light, iodine, acidic vanillin solution, 10% phosphomolybdic acid solution in ethanol. All reagents were commercial products. Organolithium reagents were titrated prior to use.¹ NaH and KH (60% in mineral oil) were washed repeatedly with dry hexane and dried prior to use. Through this section, the volume of solvents is reported in mL/mmol of starting material. ^1H and ^{13}C NMR spectra were recorded at 200, 300 or 400 MHz (^1H) using CDCl_3 as solvent and with the residual solvent signal as internal reference (CDCl_3 , 7.24 and 77.0 ppm). The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Melting points are uncorrected. Optical rotations were measured at 20 °C using a sodium lamp and in CHCl_3 solution. Low resolution mass spectra were recorded using the electronic impact technique with an ionization energy of 70 eV or using the atmospheric pressure chemical ionization (APCI) or electrospray (ES) chemical ionization techniques in its positive or negative modes.

1. Preparation of Starting Materials

1.1. General Procedure for Synthesis of Hydroxy Dienyl Sulfoxides

See printed version of the paper.

1.2. Synthesis of (+)-(4*E*)-(3*R*,*S*₅)-4-(*p*-Tolylsulfinyl)hepta-1,4,6-trien-3-ol, **3a**, and (–)-(4*E*)-(3*S*,*S*₅)-4-(*p*-Tolylsulfinyl)hepta-1,4,6-trien-3-ol, **4a**.

From *i*-Pr₂NH (0.70 mL, 540 mg, 5.28 mmol) in 18 mL of anhydrous THF, with *n*-BuLi (1.6 M, 3.17 mL, 5.08 mmol), a solution of dienyl sulfoxides **1a,2a** (389 mg, 2.03 mmol) in 5 mL of THF, and acrolein (0.68 mL, 570 mg, 10.15 mmol) according to the general procedure, a 42:58 mixture of hydroxy trienyl sulfoxides **3a** and **4a** was obtained. Chromatographic purification (20-50% EtOAc-hexane and CH₂Cl₂-20% EtOAc-CH₂Cl₂), gave **3a** (133 mg, 26%) as a white solid recrystallized from CH₂Cl₂-hexane and **4a** (180 mg, 36%) as a white solid recrystallized from Et₂O-hexane.

Data of **3a**: mp: 100-101 °C. *R_f* = 0.29 (15% EtOAc-CH₂Cl₂). [α]_D²⁰ = +179.7 (*c* = 0.80). ¹H NMR (300 MHz) δ 2.38 (d, 1 H, *J* = 5.4 Hz), 2.38 (s, 3 H), 5.04-5.20 (m, 3 H), 5.49 (dd, 1 H, *J* = 9.8, 1.7 Hz), 5.59 (dd, 1 H, *J* = 16.6, 1.7 Hz), 5.71 (m, 1 H), 6.78 (ddd, 1 H, *J* = 16.6, 11.3, 9.8 Hz), 6.95 (d, 1 H, *J* = 11.3 Hz), 7.27 (d, 2 H, *J* = 8.1 Hz), 7.52 (d, 2 H, *J* = 8.1 Hz). ¹³C NMR (50 MHz) δ 21.4, 69.4, 115.6, 125.4, 125.7 (2 C), 129.9 (2 C), 130.5, 134.1, 137.4, 140.0, 141.8, 144.6. IR (film): 3350, 2940, 1640, 1600, 1500, 1420, 1400, 1300, 1130, 1080, 1040, 1015, 1000, 930, 810 cm⁻¹. MS (EI): 248 [M]⁺, 246, 231, 218, 204, 200, 175, 143, 140, 123, 92 (100%), 91, 79, 65, 53, 41, 39. Anal. calcd for C₁₄H₁₆O₂S: C, 67.71; H, 6.49; S, 12.91. Found: C, 67.94; H, 6.32; S, 12.80.

Data of **4a**: mp: 67-71 °C. *R_f* = 0.20 (15% EtOAc-CH₂Cl₂). [α]_D²⁰ = -76.2 (*c* = 1.60). ¹H NMR (300 MHz) δ 2.38 (s, 3 H), 2.76 (d, 1 H, *J* = 3.5 Hz), 4.94 (dt, 1 H, *J* = 10.3, 1.3 Hz), 4.99-5.03 (m, 1 H), 5.05 (dt, 1 H, *J* = 17.1, 1.4 Hz), 5.41-5.61 (m, 3 H), 6.75-6.90 (m, 2 H, H-5), 7.26 (d, 2 H, *J* = 8.0 Hz), 7.50 (d, 2 H, *J* = 8.2 Hz). ¹³C NMR (50 MHz) δ 21.4, 68.4, 115.4, 125.1, 125.5 (2 C), 129.9 (2 C), 130.9, 134.3, 137.5, 139.5, 141.7, 145.6. IR (film): 3350, 3100, 2940, 1600, 1500, 1420, 1400, 1305, 1180, 1130, 1080, 1040, 1010, 930, 810 cm⁻¹. MS (EI): 248 [M]⁺, 246, 218, 175, 140, 123, 92 (100%), 91, 79, 65, 53, 39. Anal. calcd for C₁₄H₁₆O₂S: C, 67.71; H, 6.49; S, 12.91. Found: C, 67.85; H, 6.64; S, 13.05.

1.3. Synthesis of (+)-(2*E*,5*E*)-(4*R*,*S_s*)-5-(*p*-Tolylsulfinyl)octa-2,5,7-trien-4-ol, **3b**, and (-)-(2*E*,5*E*)-(4*S*,*S_s*)-5-(*p*-Tolylsulfinyl)octa-2,5,7-trien-4-ol, **4b**.

From *i*-Pr₂NH (0.97 mL, 749 mg, 7.44 mmol) in 25.8 mL of anhydrous THF, with *n*-BuLi (1.46 M, 4.91 mL, 7.17 mmol), a solution of dienyl sulfoxides **1a,2a** (551 mg, 2.86 mmol) in 7.3 mL of THF, and crotonaldehyde (1.11 mL, 1007 mg, 14.31 mmol) according to the general procedure, a 43:57

mixture of hydroxy trienyl sulfoxides **3b** and **4b** was obtained. Chromatographic purification (5-100% EtOAc-hexane and CH₂Cl₂-20% EtOAc-CH₂Cl₂), gave **3b** (226 mg, 31%) and **4b** (304 mg, 40%) as a white solids recrystallized from Et₂O-hexane (1:2 and 1:1.5 respectively) and 41 mg (5.5%) of a mixture of hydroxy dienes.

Data of **3b**: mp: 93-94 °C. R_f = 0.34 (50% EtOAc-hexane), 0.28 (15% EtOAc-CH₂Cl₂). $[\alpha]_D^{20} = +134.0$ ($c = 1.80$). ¹H NMR (300 MHz) δ 1.55 (dd, 3 H, $J = 4.9, 1.0$ Hz), 2.39 (s, 3 H), 2.41 (d, 1 H, $J = 4.2$ Hz), 5.00 (m, 1 H), 5.41-5.64 (m, 4 H, H-2, H-3), 6.80 (ddd, 1 H, $J = 15.9, 11.2, 9.4$ Hz), 6.94 (d, 1 H, $J = 11.2$ Hz), 7.27 (d, 2 H, $J = 8.0$ Hz), 7.53 (d, 2 H, $J = 8.3$ Hz). ¹³C NMR (50 MHz) δ 17.2, 21.2, 69.6, 124.7, 125.6 (2 C), 127.7, 129.6 (2 C), 130.4, 133.0 (2 C), 140.2, 141.5, 145.2. IR (film): 3350, 3005, 1600, 1500, 1220, 1085, 1040, 810, 760, 670 cm⁻¹. MS (EI): 262 [M]⁺, 245, 218, 185, 140, 123, 95, 91 (100%), 77, 65, 53, 41, 39. Anal. calcd for C₁₅H₁₈O₂S: C, 68.67; H, 6.92; S, 12.22. Found: C, 68.32; H, 6.83; S, 11.92.

Data of **4b**: mp: 107-109 °C. R_f = 0.24 (50% EtOAc-hexane), 0.16 (15% EtOAc-CH₂Cl₂). $[\alpha]_D^{20} = -33.2$ ($c = 3.50$). ¹H NMR (300 MHz) δ 1.46 (dt, 3 H, $J = 6.3, 1.0$ Hz), 2.37 (s, 3 H), 2.76 (br s, 1 H), 4.94 (br d, 1 H, $J = 6.5$ Hz), 5.11 (ddq, 1 H, $J = 15.1, 6.2, 1.5$ Hz), 5.30-5.37 (m, 1 H), 5.45-5.60 (m, 2 H), 6.78-6.92 (m, 2 H, H-6), 7.26 (d, 2 H, $J = 6.5$ Hz), 7.49 (d, 2 H, $J = 8.3$ Hz). ¹³C NMR (50 MHz) δ 17.3, 21.3, 68.7, 124.6, 125.7 (2 C), 127.8, 129.7 (2 C), 130.6, 131.1, 133.3, 139.6, 141.5, 146.4. IR (film): 3350, 3005, 2910, 1600, 1495, 1450, 1220, 1090, 1040, 1020, 970, 815, 760, 620 cm⁻¹. MS (EI): 262 [M]⁺, 245, 185, 140, 123, 95, 91 (100%), 77, 53. Anal. calcd for C₁₅H₁₈O₂S: C, 68.67; H, 6.92; S, 12.22. Found: C, 68.29; H, 6.57; S, 11.98.

1.4. Synthesis of (+)-(3*R*,*S*_s)-(4*E*)-4-(*p*-Tolylsulfinyl)hepta-4,6-dien-3-ol, **3c**, and (+)-(3*S*,*S*_s)-(4*E*)-4-(*p*-Tolylsulfinyl)hepta-4,6-dien-3-ol, **4c**.

From dienyl sulfoxides **1a,2a** (577 mg, 3 mmol), 2.5 equiv of LDA and propionaldehyde (0.65 mL, 9 mmol) according to the general procedure, a 47:53 mixture of hydroxy dienyl sulfoxides **3c** and **4c** was obtained. Chromatographic purification (0-40% EtOAc-CH₂Cl₂), gave **3c** (341 mg, 36%) and **4c** (384 mg, 41%) as colorless oils. Racemic material was obtained similarly on a 30 mmol scale (70%).

Data of **3c**: $R_f = 0.32$ (15% EtOAc-CH₂Cl₂). $[\alpha]_D^{20} = +107.1$ ($c = 1.21$). **¹H NMR (200 MHz)** δ 0.82 (t, 3 H, $J = 7.4$ Hz), 1.41-1.77 (m, 2 H), 2.24 (d, 1 H, $J = 4.2$ Hz), 2.37 (s, 3 H), 4.43-4.52 (m, 1 H), 5.47 (dd, 1 H, $J = 9.5$ Hz, 1.6 Hz), 5.58 (dd, 1 H, $J = 16.2$ Hz, 1.6 Hz), 6.72 (ddd, 1 H, $J = 16.2$ Hz, 11.3 Hz, 9.6 Hz), 6.92 (d, 1 H, $J = 11.3$ Hz), 7.25 (d, 2 H, $J = 8.2$ Hz), 7.52 (d, 2 H, $J = 8.2$ Hz). **¹³C NMR (50 MHz)** δ 10.1, 21.2, 30.3, 70.2, 124.2, 125.3 (2 C), 129.6 (2 C), 130.5, 132.2, 140.6, 141.3, 146.9. **IR** (film): 3300, 2940, 2900, 1580, 1450, 1290, 1060, 1010, 900, 795, 715 cm⁻¹. **MS** (EI): 250 [M]⁺, 233, 202, 175, 140, 92 (100%), 77, 65, 55, 43. **Anal. calcd for C₁₄H₁₈O₂S**: C, 67.16; H, 7.25; S, 12.81. **Found**: C, 67.42; H, 7.46; S, 12.76.

Data of **4c**: $R_f = 0.19$ (15% EtOAc-CH₂Cl₂). $[\alpha]_D^{20} = +45.1$ ($c = 0.62$). **¹H NMR (200 MHz)** δ 0.76 (t, 3 H, $J = 7.3$ Hz), 1.11-1.24 (m, 1 H), 1.37-1.55 (m, 1 H), 2.37 (s, 3 H), 2.94 (d, 1 H, $J = 4.4$ Hz), 4.37 (quint, 1 H, $J = 4.5$ Hz), 5.41-5.61 (m, 2 H), 6.71-6.92 (m, 2 H), 7.26 (d, 2 H, $J = 8.2$ Hz), 7.50 (d, 2 H, $J = 8.2$ Hz). **¹³C NMR (50 MHz)** δ 10.4, 21.4, 30.5, 69.7, 125.6, 128.2, 129.8 (2 C), 131.0, 132.5, 139.7, 141.7, 147.7. **IR** (film): 3300, 2940, 2900, 1580, 1475, 1445, 1060, 1010, 900, 790, 715 cm⁻¹. **MS** (EI): 250 [M]⁺, 233, 221, 202, 175, 140, 92 (100%), 77, 65, 55, 43. **Anal. calcd for C₁₄H₁₈O₂S**: C, 67.16; H, 7.25; S, 12.81. **Found**: C, 67.33; H, 7.04; S, 12.97.

1.5. Synthesis of (+)-(3*R*,*S*_s)-(4*E*)-2-Methyl-4-(*p*-tolylsulfinyl)hepta-4,6-dien-3-ol, **3d, and (+)-(3*S*,*S*_s)-(4*E*)-2-Methyl-4-(*p*-tolylsulfinyl)hepta-4,6-dien-3-ol, **4d**.**

From dienyl sulfoxides **1a,2a** (577 mg, 3 mmol), 2.5 equiv of LDA and isobutyraldehyde (1.36 mL, 15 mmol) according to the general procedure, a 36:64 mixture of hydroxy dienyl sulfoxides **3d** and **4d** was obtained. Chromatographic purification (0-40% EtOAc-CH₂Cl₂), gave **3d** (354 mg, 33%) as a colorless oil and **4d** (632 mg, 60%) as a white solid that was recrystallized from EtOAc-hexane. Racemic material was obtained similarly on a 30 mmol scale (83%).

Data of **3d**: $R_f = 0.32$ (15% EtOAc-CH₂Cl₂). $[\alpha]_D^{20} = +83.2$ ($c = 1.06$). **¹H NMR (200 MHz)** δ 0.74 (d, 3 H, $J = 6.8$ Hz), 0.99 (d, 3 H, $J = 6.5$ Hz), 1.90-2.00 (m, 2 H), 2.37 (s, 3 H), 4.27 (dd, 1 H, $J = 8.3$, 4.7 Hz), 5.47 (dd, 1 H, $J = 9.9$, 1.6 Hz), 5.59 (dd, 1 H, $J = 16.6$, 1.6 Hz), 6.70 (ddd, 1 H, $J = 16.6$, 11.2, 9.9 Hz), 6.99 (d, 1 H, $J = 11.2$ Hz), 7.26 (d, 2 H, $J = 8.1$ Hz), 7.54 (d, 2 H, $J = 8.2$ Hz). **¹³C NMR (50 MHz)** δ 18.4, 19.0, 21.2, 34.0, 74.4, 124.4, 125.2 (2 C), 129.7 (2 C), 130.5, 132.7, 141.2, 141.3,

146.7. **IR** (CCl_4): 3300, 2940, 1585, 1485, 1460, 1170, 1070, 1000, 915, 800 cm^{-1} . **MS** (EI): 265 $[\text{M}+1]^+$, 247, 221, 140, 123, 107, 92 (100%), 79, 65, 55, 43. **Anal. calcd for** $\text{C}_{15}\text{H}_{20}\text{O}_2\text{S}$: C, 68.14; H, 7.62; S, 12.13. **Found**: C, 68.37; H, 7.83; S, 12.37.

Data of **4d**: **mp** (racemic): 73-74 $^{\circ}\text{C}$. $R_f = 0.17$ (15% EtOAc- CH_2Cl_2). $[\alpha]_D^{20} = +180.7$ ($c = 1.06$). **^1H NMR (200 MHz)** δ 0.71 (d, 3 H, $J = 6.8$ Hz), 0.93 (d, 3 H, $J = 6.5$ Hz), 1.75-1.86 (m, 1 H), 2.37 (s, 3 H), 2.54 (d, 1 H, $J = 4.9$ Hz), 3.93 (dd, 1 H, $J = 8.3$ Hz, 4.7 Hz), 5.40-5.60 (m, 2 H), 6.72-6.93 (m, 2 H), 7.26 (d, 2 H, $J = 8.6$ Hz), 7.53 (d, 2 H, $J = 8.2$ Hz). **^{13}C NMR (50 MHz)** δ 18.8, 19.0, 21.4, 34.1, 74.8, 123.9, 126.0 (2 C), 129.9 (2 C), 131.2, 132.1, 139.9, 142.0, 146.5. **IR** (CCl_4): 3300, 2940, 1580, 1480, 1455, 1065, 1015, 1000, 910, 800 cm^{-1} . **MS** (EI): 221, 140, 105, 91, 57, 43 (100%). **Anal. calcd for** $\text{C}_{15}\text{H}_{20}\text{O}_2\text{S}$: C, 68.14; H, 7.62; S, 12.13. **Found**: C, 68.06; H, 7.48; S, 12.31.

1.6. Synthesis of (+)-(2E)-(1R, S_s)-1-Phenyl-2-(p-tolylsulfinyl)penta-2,4-dien-1-ol, 3e, and (-)-(2E)-(1S, S_s)-1-Phenyl-2-(p-tolylsulfinyl)penta-2,4-dien-1-ol, 4e.

See printed version of the paper.

1.7. Synthesis of (+)-(1R, S_s)-(2E)-1-(3-Pyridyl)-2-(p-tolylsulfinyl)penta-2,4-dien-1-ol, 3f, and (-)-(1S, S_s)-(2E)-1-(3-Pyridyl)-2-(p-tolylsulfinyl)penta-2,4-dien-1-ol, 4f.

From diethyl sulfoxides **1a,2a** (385 mg, 2 mmol), 2.5 equiv of LDA and 3-pyridylcarboxaldehyde (0.57 mL, 6 mmol) according to the general procedure, a 47:53 mixture of hydroxy diethyl sulfoxides **3f** and **4f** was obtained. Chromatographic purification (10-15% EtOH-toluene), gave **3f** (86 mg, 14%) as a yellowish solid contaminated with *ca.* 5% of **4f**, mixture of isomers (137 mg, 23%) and **4f** (97 mg, 16%) as a yellow solid that was recrystallized from EtOAc-hexane. Racemic material was obtained similarly on a 16 mmol scale (53%).

Data of **3f**: $R_f = 0.31$ (15% EtOH-toluene). $[\alpha]_D^{20} = +23.8$ ($c = 0.31$). $^1\text{H NMR}$ (200 MHz) δ 2.34 (s, 3 H), 3.39 (br s, 1 H), 5.52 (d, 1 H, $J = 10.0$ Hz), 5.65 (d, 1 H, $J = 16.6$ Hz), 5.81 (br s, 1 H), 6.63 (m, 1 H), 7.02 (d, 1 H, $J = 11.3$ Hz), 7.08-7.15 (m, 1 H), 7.22 (d, 2 H, $J = 8.3$ Hz), 7.39 (d, 2 H, $J = 8.1$ Hz), 7.54 (d, 1 H, $J = 8.1$ Hz), 8.36 (br d, 1 H, $J = 4.1$ Hz), 8.44 (br s, 1 H). $^{13}\text{C NMR}$ (50 MHz) δ 21.3, 67.3, 123.0, 125.1 (2 C), 126.3, 129.8 (2 C), 130.2, 134.0, 135.1, 137.4, 139.4, 141.6, 145.7, 147.1, 147.9. IR (KBr): 3300, 1580, 1480, 1460, 1410, 1060, 1030, 910, 790, 730, 690, 640 cm^{-1} . MS (EI): 299 $[\text{M}]^+$, 282, 160 (100%), 140, 130, 117, 108, 92, 84, 78, 65, 39.

Data of **4f**: mp: 115-116 °C (60% EtOAc-hexane). mp (racemic): 127-128 °C (70% EtOAc-hexane). $R_f = 0.28$ (15% EtOH-toluene). $[\alpha]_D^{20} = -31.2$ ($c = 1.76$). $^1\text{H NMR}$ (200 MHz) δ 2.29 (s, 3 H), 4.59 (br s, 1 H), 5.45 (dd, 1 H, $J = 9.9, 1.4$ Hz), 5.58 (dd, 1 H, $J = 16.7, 1.3$ Hz), 5.74 (s, 1 H), 6.58 (ddd, 1 H, $J = 16.7, 11.2, 9.9$ Hz), 6.96 (d, 1 H, $J = 11.3$ Hz), 7.02 (dd, 1 H, $J = 7.9, 4.8$ Hz), 7.12 (d, 2 H, $J = 8.1$ Hz), 7.36 (m, 1 H), 7.38 (d, 2 H, $J = 8.2$ Hz), 8.17 (d, 1 H, $J = 2.3$ Hz), 8.31 (dd, 1 H, $J = 4.8, 1.6$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ 21.3, 66.8, 122.9, 125.4 (2 C), 126.1, 129.8 (2 C), 130.5, 133.7, 134.4, 136.6, 138.7, 141.9, 146.3, 147.7, 148. IR (KBr): 3400, 2940, 3000, 2800, 1580, 1460, 1400, 1170, 1060, 1020, 900, 890, 780, 770, 690, 660, 610 cm^{-1} . MS (EI): 299 $[\text{M}]^+$, 282, 160 (100%), 140, 130, 117, 108, 92, 78, 65, 53, 39. Anal. calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_2\text{S}$: C, 68.20; H, 5.72; N, 4.68; S, 10.70. Found: C, 68.27; H, 5.83; N, 4.73; S, 10.63.

1.8. Synthesis of ($\pm$)-(1*R*,*S*_s)-(2*E*)-1-(*p*-Fluorophenyl)-2-(*p*-tolylsulfinyl)penta-2,4-dien-1-ol, **3g**, and ($\pm$)-(1*S*,*S*_s)-(2*E*)-1-(*p*-Fluorophenyl)-2-(*p*-tolylsulfinyl)penta-2,4-dien-1-ol, **4g**.

From racemic dienyl sulfoxides **1a,2a** (5.19 g, 27 mmol), 2.5 equiv of LDA and 4-fluorobenzaldehyde (7.24 mL, 67.5 mmol) according to the general procedure, a 48:52 mixture of hydroxy dienyl sulfoxides **3g** and **4g** was obtained. Chromatographic purification (5-30% EtOAc- CH_2Cl_2), gave **3g** (3.21 g, 34%) as a white solid recrystallized from EtOAc-hexane, and **4g** (3.48 g, 37%) as a white solid that was recrystallized from EtOAc.

Data of **3g**: mp: 145-146 °C. $R_f = 0.21$ (10% EtOAc- CH_2Cl_2). $^1\text{H NMR}$ (200 MHz) δ 2.35 (s, 3 H), 2.80 (dd, 1 H, $J = 5.2, 1.7$ Hz), 5.48 (ddd, 1 H, $J = 9.9, 1.5, 0.6$ Hz), 5.62 (ddd, 1 H, $J = 16.7, 1.5, 0.7$ Hz), 5.74 (d, 1 H, $J = 4.2$ Hz), 6.60 (ddd, 1 H, $J = 16.7, 11.3, 10.0$ Hz), 6.87 (t, 2 H, $J = 8.8$ Hz),

6.99 (d, 1 H, $J = 11.2$ Hz), 7.16-7.23 (m, 4 H), 7.40 (d, 2 H, $J = 8.2$ Hz). ^{13}C NMR (50 MHz) δ 21.3, 69.2, 115.0 (2 C, $p\text{-F-C}_6\text{H}_4$, $J_{\text{C-F}} = 21.7$ Hz), 125.0 (2 C), 126.1, 126.5 (2 C, $p\text{-F-C}_6\text{H}_4$, $J_{\text{C-F}} = 8.4$ Hz), 129.8 (2 C), 130.2, 134.9, 136.7, 139.7, 141.5, 146.0, 162.0 (C $p\text{-F-C}_6\text{H}_4$, $J_{\text{C-F}} = 246.1$ Hz). IR (KBr): 3435, 1507, 1057, 817 cm^{-1} . MS (ES): 665 $[\text{2M+Na}]^+$ (100%), 339 $[\text{M+Na}]^+$, 317 $[\text{M+1}]^+$. Anal. calcd for $\text{C}_{18}\text{H}_{17}\text{FO}_2\text{S}$: C, 68.33; H, 5.42; S, 10.13. Found: C, 68.07; H, 5.36; S, 9.89.

Data of **4g**: mp: 175-176 $^{\circ}\text{C}$. $R_f = 0.09$ (10% EtOAc- CH_2Cl_2). ^1H NMR (200 MHz) δ 2.34 (s, 3 H), 3.64 (d, 1 H, $J = 4.4$ Hz), 5.40 (dd, 1 H, $J = 9.9, 1.6$ Hz), 5.53 (dd, 1 H, $J = 16.8, 1.6$ Hz), 5.64 (d, 1 H, $J = 4.2$ Hz), 6.49 (ddd, 1 H, $J = 16.7, 11.2, 10.0$ Hz), 6.80 (d, 2 H, $J = 8.8$ Hz), 6.89 (d, 1 H, $J = 11.0$ Hz), 7.00 (dd, 2 H, $J = 8.9, 5.4$ Hz), 7.18 (d, 2 H, $J = 8.4$ Hz), 7.41 (d, 2 H, $J = 8.3$ Hz). ^{13}C NMR (75 MHz) δ 21.3, 68.8, 115.0 (2 C, $p\text{-F-C}_6\text{H}_4$, $J_{\text{C-F}} = 21.7$ Hz), 125.4 (2 C), 125.8, 127.8 (2 C, $p\text{-F-C}_6\text{H}_4$, $J_{\text{C-F}} = 8.1$ Hz), 129.9 (2 C), 130.7, 134.5, 136.5, 139.2, 141.9, 146.8, 162.0 (C $p\text{-F-C}_6\text{H}_4$, $J_{\text{C-F}} = 246.3$ Hz). IR (KBr): 3282, 1603, 1506, 1215, 1054, 1020, 999, 936, 872, 843, 805, 674, 510 cm^{-1} . MS (ES): 665 $[\text{2M+Na}]^+$ (100%), 339 $[\text{M+Na}]^+$. Anal. calcd for $\text{C}_{18}\text{H}_{17}\text{FO}_2\text{S}$: C, 68.33; H, 5.42; S, 10.13. Found: C, 68.23; H, 5.60; S, 10.41.

1.9. Synthesis of ($\pm$)-2-Methyl-3-(p -tolylsulfinyl)hexa-3,5-dien-2-ol, **5**.

From racemic dieny sulfoxides **1a,2a** (8.17 g, 48.49 mmol), 2.5 equiv of LDA and acetone (9.37 mL, 127.47 mmol) according to the general procedure, dieny sulfoxide **5** was obtained. Chromatographic purification (10-100% EtOAc- CH_2Cl_2), gave **5** (8.32 g, 78%) as a white solid recrystallized from EtOAc-hexane.

Data of **5**: mp: 145-147 $^{\circ}\text{C}$. $R_f = 0.25$ (40% EtOAc-hexane). ^1H NMR (200 MHz) δ 1.28 (s, 3 H), 1.43 (s, 3 H), 2.36 (s, 3 H), 2.66 (br s, 1 H), 5.48 (d, 1 H, $J = 9.6$ Hz), 5.59 (d, 1 H, $J = 15.9$ Hz), 6.70-6.93 (m, 2 H), 7.24 (d, 2 H, $J = 8.2$ Hz), 7.54 (d, 2 H, $J = 8.2$ Hz). ^{13}C NMR (50 MHz) δ 21.3, 30.7, 31.3, 73.4, 124.1, 126.4 (2 C), 128.8, 129.6 (2 C), 130.7, 141.4, 141.5, 150.8. IR (KBr): 3329, 2970, 1172, 1077, 1024, 1014, 921, 810 cm^{-1} . MS (ES): 523 $[\text{2M+Na}]^+$ (100%), 273 $[\text{M+Na}]^+$. Anal. calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{S}$: C, 67.16; H, 7.25; S, 12.81. Found: C, 67.43; H, 7.50; S, 12.68.

1.10. General Procedure for Oxidation of Sulfoxides with MMPP

To a cold ($-30/0\text{ }^{\circ}\text{C}$) solution of sulfoxide in MeOH (10 mL/mmol) was added 1.7-2.0 equiv of magnesium monoperoxyphthalate hexahydrate (MMPP). The mixture was allowed to warm up to rt, monitored by TLC until completion and then quenched with a saturated solution of NaHCO_3 (5 mL/mmol). After removal of MeOH under reduced pressure, the mixture was diluted with EtOAc (10 mL/mmol), the layers were separated and the aqueous phase was extracted with EtOAc (2 times, 4 mL/mmol). The combined organic layers were washed with a saturated solution of NaCl (4 mL/mmol), dried over MgSO_4 , filtered and concentrated under reduced pressure to give a crude product that was purified by gradient column chromatography using the appropriate mixture of solvents.

1.11. Synthesis of (–)-(4E)-(3S)-4-(*p*-Tolylsulfonyl)hepta-1,4,6-trien-3-ol, **6a**.

From hydroxy dienyl sulfoxide **4a** (35 mg, 0.14 mmol) in MeOH (1.40 mL) and MMPP (87 mg, 0.21 mmol), according to the general procedure (3 h), after chromatography (5-30% EtOAc-hexane), dienyl sulfone **6a** (29 mg, 78%) was obtained as a colorless oil.

Data of **6a**: $R_f = 0.30$ (30% EtOAc-hexane). $[\alpha]_D^{20} = -50.9$ ($c = 0.90$). $^1\text{H NMR}$ (300 MHz) δ 2.41 (s, 3 H), 2.69 (d, 1 H, $J = 5.5$ Hz), 5.05 (dt, 1 H, $J = 10.4, 1.4$ Hz), 5.12 (ddd, 1 H, $J = 5.0, 3.2, 1.8$ Hz), 5.18 (dt, 1 H, $J = 17.0, 1.4$ Hz), 5.63 (dd, 1 H, $J = 9.9, 1.7$ Hz), 5.70 (dd, 1 H, $J = 16.9, 1.4$ Hz), 5.71 (ddd, 1 H, $J = 17.0, 10.4, 3.4$ Hz), 6.85 (ddd, 1 H, $J = 16.8, 11.3, 9.9$ Hz), 7.30 (d, 2 H, $J = 8.1$ Hz), 7.32 (d, 1 H, $J = 11.3$ Hz), 7.72 (d, 2 H, $J = 8.3$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ 21.6, 68.9, 115.8, 128.1 (2 C), 128.8, 129.8 (2 C), 130.4, 136.9, 137.2, 140.3, 141.2, 144.4. IR (KBr): 3500, 3100, 2930, 1635, 1600, 1500, 1405, 1320, 1300, 1290, 1145, 1090, 1000, 940, 815, 675 cm^{-1} . MS (EI): 211, 155, 139, 115, 104, 92, 91 (100%), 77, 65, 43, 39. Anal. calcd for $\text{C}_{14}\text{H}_{16}\text{O}_3\text{S}$: C, 63.61; H, 6.10; S, 12.13. Found: C, 63.94; H, 6.23; S, 12.50.

1.12. Synthesis of (±)-(2E)-1-Phenyl-2-(*p*-tolylsulfonyl)penta-2,4-dien-1-ol, **6e**.

From hydroxy dienyl sulfoxides **3e** and **4e** (100 mg, 0.34 mmol) in MeOH (1.70 mL) and MMPP (336 mg, 0.68 mmol), according to the general procedure (45 min), after chromatography (5-50% EtOAc-hexane), dienyl sulfone **6e** (81 mg, 76%) was obtained as a white solid that was recrystallized from EtOAc-hexane.

Data of **6e**: mp: 94-95 °C (50% EtOAc-hexane). R_f = 0.22 (30% EtOAc-hexane). $^1\text{H NMR}$ (200 MHz) δ 2.35 (s, 3 H), 3.83 (d, 1 H, J = 7.2 Hz), 5.60 (dd, 1 H, J = 9.9, 1.7 Hz), 5.74 (dd, 1 H, J = 16.7 Hz, 1.5 Hz), 5.83 (d, 1 H, J = 7.2 Hz), 6.62 (ddd, 1 H, J = 16.7, 11.3, 9.9 Hz), 7.14 (d, 2 H, J = 8.2 Hz), 7.14 (s, 5 H), 7.43 (d, 1 H, J = 11.4, Hz), 7.49 (d, 2 H, J = 8.4 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 21.4, 69.2, 125.6, 127.3, 127.8 (2 C), 128.1 (2 C), 129.3, 129.6 (2 C), 130.2, 137.1, 140.0, 140.8, 142.4, 144.0. IR (KBr): 3400, 1600, 1565, 1460, 1420, 1250, 1110, 1050, 1010, 920, 780, 705, 650, cm^{-1} . MS (ES): 337 $[\text{M}+\text{Na}]^+$. Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{O}_3\text{S}$: C, 68.76; H, 5.77; S, 10.20. Found: C, 68.45; H, 6.02; S, 10.31.

1.13. Synthesis of ($\pm$)-(2E)-1-(3-Pyridyl)-2-(*p*-tolylsulfonyl)penta-2,4-dien-1-ol, **6f, and *N*-oxide of ($\pm$)-(2E)-1-(3-Pyridyl)-2-(*p*-tolylsulfonyl)penta-2,4-dien-1-ol, **6f'**.**

From a mixture of hydroxy dienyl sulfoxides **3f** and **4f** (659 mg, 2.20 mmol) in MeOH (33 mL) and MMPP (2.31 g, 3.74 mmol), according to the general procedure (1 h), an 89:11 mixture of **6f** and **6f'** was obtained. Column chromatography (0-20% MeOH-EtOAc), gave dienyl sulfone **6f** (513 mg, 74%) as a white solid that was recrystallized from EtOAc-hexane and *N*-oxide **6f'** (44 mg, 6%) as a white solid that was recrystallized from EtOH.

In a separate experiment, to a solution of dienyl sulfoxides **3f** and **4f** (60 mg, 0.2 mmol) in toluene (0.4 mL) and CH_2Cl_2 (0.4 mL) at rt was added VO(acac)₂ (2.65 mg, 0.01 mmol, 0.05 equiv). After 15 min, a solution of *t*-BuOOH (91 μL , 0.5 mmol, 2.5 equiv, 5-6 M in decane) in toluene (0.25 mL) was added and the reaction mixture turned red. After 40 min, the reaction was quenched with 1 M solution of $\text{Na}_2\text{S}_2\text{O}_4$ and diluted with EtOAc (8 mL). The layers were separated, the aqueous phase was

extracted with EtOAc (3 x 8 mL) and the combined organic layers were washed with saturated NaCl solution (8 mL), dried over Na₂SO₄ and concentrated to give a crude product that was purified by chromatography on silica gel (0-10% MeOH-EtOAc) to give **6f** (20 mg, 30%) as a white solid.

Data of **6f**: mp: 138-140 °C (60% EtOAc-hexane). R_f = 0.48 (20% MeOH-EtOAc). ¹H NMR (300 MHz) δ 2.36 (s, 3 H), 3.83 (br s, 1 H), 5.63 (dd, 1 H, J = 10.0, 1.5 Hz), 5.76 (dd, 1 H, J = 16.0, 0.7 Hz), 5.86 (br s, 1 H), 6.66 (ddd, 1 H, J = 16.7, 11.4, 9.8 Hz), 7.08 (dd, 1 H, J = 7.9, 4.9 Hz), 7.17 (d, 2 H, J = 8.5 Hz), 7.46 (dd, 1 H, J = 11.4, 0.5 Hz), 7.50-7.56 (m, 1 H), 7.55 (d, 2 H, J = 8.4 Hz), 8.32-8.36 (m, 2 H). ¹³C NMR (50 MHz) δ 21.4, 67.0, 123.0, 127.8 (2 C), 129.6, 129.7 (2 C), 130.3, 134.1, 136.5, 137.1, 140.9, 142.0, 144.3, 147.1, 147.7. IR (KBr): 3434, 1628, 1594, 1422, 1316, 1304, 1143, 1087, 949, 822, 675, 577 cm⁻¹. MS (ES): 338 [M+Na]⁺ (100%), 316 [M+1]⁺. Anal. calcd for C₁₇H₁₇NO₃S: 64.74; H, 5.43; N, 4.44; S, 10.17. Found: C, 64.53; H, 5.53; N, 4.50; S, 10.40.

Data of **6f'**: mp: 194-196 °C (EtOH). R_f = 0.25 (20% MeOH-EtOAc). ¹H NMR (CD₃OD, 300 MHz) δ 2.40 (s, 3 H), 4.08 (d, 1 H, J = 6.0 Hz), 5.67 (d, 1 H, J = 10.1 Hz), 5.75-5.80 (m, 2 H), 6.63 (ddd, 1 H, J = 16.6, 10.1, 10.0 Hz), 7.02-7.13 (m, 2 H), 7.26 (d, 2 H, J = 8.1 Hz), 7.44 (d, 1 H, J = 11.4 Hz), 7.63 (d, 2 H, J = 8.3 Hz), 7.95 (d, 1 H, J = 6.2 Hz), 8.09 (s, 1 H). ¹³C NMR (CD₃OD, 50 MHz) δ 21.8, 67.4, 127.8, 129.1, 129.8 (2 C), 130.9, 131.4 (2 C), 132.1, 138.7, 138.8, 139.2, 143.0, 143.5, 144.7, 146.6. IR (KBr): 3400, 3040, 1610, 1580, 1465, 1425, 1290, 1275, 1125, 1070, 765, 650 cm⁻¹. MS (ES): 354 [M+Na]⁺ (100%), 332 [M+1]⁺. Anal. calcd for C₁₇H₁₇NO₄S: 61.61; H, 5.17; N, 4.23; S, 9.68. Found: C, 61.87; H, 5.42; N, 4.55; S, 9.43.

1.14. General Procedure for Mitsunobu Inversion/Deprotection Protocol

To a solution of 1 equiv of alcohol in the appropriate solvent (THF, benzene, toluene, 10 mL/mmol) was added at rt Ph₃P (3 equiv, recrystallized recently), followed by the carboxylic acid (*p*-NO₂C₆H₄CO₂H or C₆H₅CO₂H, 3 equiv) and diisopropyl azodicarboxylate (DIAD, 3 equiv). The reaction was stirred at rt until disappearance of starting material (TLC) and then quenched with a saturated solution of NaHCO₃ (15 mL/mmol) and diluted with EtOAc (30 mL/mmol). The layers were separated, the organic layer was washed with a saturated solution of NaCl (15 mL/mmol), dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to give a crude product that was partially purified by chromatography on a short column of silica gel using the appropriate mixture of solvents. The product was dissolved in MeOH (4 mL/mmol) and treated with K₂CO₃ or NaOMe (generated before by addition of Na) until disappearance of starting material (TLC). Usual extractive work-up (H₂O, EtOAc) gave a crude product that was purified by chromatography on silica gel.

1.15. Transformation of 3a into 4a.

From hydroxy sulfinyl diene **3a** (20 mg, 0.080 mmol) in 5:1 benzene:THF mixture (1.2 mL), with Ph_3P , p -nitrobenzoic acid and DIAD (3 equiv each), according to the general procedure (20 min), followed by deprotection with K_2CO_3 in MeOH (0.3 mL, 1 h), a 64:36 mixture of alcohols resulting from inversion and $\text{S}_{\text{N}}2'$ displacement **4a** and **7**, respectively, was obtained. Purification by chromatography (1-50% EtOAc-hexane) gave **4a** (7 mg, 35%) and conjugated trienol **7** (4 mg, 11%).

Partial data of (S_s)-(2*E*,4*E*)-4-(p -Tolylsulfinyl)hepta-2,4,6-trien-1-ol, **7**: $R_f = 0.11$ (3 x 5% EtOAc- CH_2Cl_2). $^1\text{H NMR}$ (300 MHz) δ 1.51 (t, 1 H, $J = 6.0$ Hz, OH), 2.36 (s, 3 H, CH_3 p -Tol), 4.14 (td, 2 H, $J = 5.4, 1.7$ Hz, H-1), 5.47 (dm, 1 H, $J = 10.0$ Hz, H-7), 5.63 (dm, 1 H, $J = 16.6$ Hz, H-7), 6.07 (dt, 1 H, $J = 16.2, 5.0$ Hz, H-2), 6.35 (dt, 1 H, $J = 16.1, 1.8$ Hz, H-3), 6.72 (ddd, 1 H, $J = 16.7, 11.2, 10.0$ Hz, H-6), 6.95 (d, 1 H, $J = 11.2$ Hz, H-5), 7.23 (d, 2 H, $J = 7.9$ Hz), 7.49 (d, 2 H, $J = 8.0$ Hz).

1.16. Transformation of 3e into 4e.

From hydroxy sulfinyl diene **3e** (34 mg, 0.114 mmol) in toluene (1.2 mL), with Ph_3P , benzoic acid and DIAD (3 equiv each), according to the general procedure (1 h), followed by deprotection with catalytic NaOMe in MeOH (0.3 mL, 1 h), an 86:14 mixture of alcohols resulting from inversion and retention **4e** and **3e**, respectively, was obtained. Purification by chromatography (1-50% EtOAc- CH_2Cl_2) gave **4e** (20 mg, 59%) and **3e** (4 mg, 11%).

2. Epoxidation of Dienyl Sulfoxides

2.1. General Procedure for Nucleophilic Epoxidation of Vinyl and Dienyl Sulfoxides and Sulfones

See printed version of the paper.

2.2. Synthesis of (+)-(2*R*,3*S*,*S*₃)-2-(*p*-Tolylsulfinyl)-3-vinyl oxirane, **8a, (+)-(2*R*,3*S*,*S*₃)-3-[(2'*R*)-Epoxy]-2-(*p*-tolylsulfinyl)oxirane, **9a**, and (+)-(2*R*,3*S*,*S*₃)-3-[(2'*S*)-Epoxy]-2-(*p*-tolylsulfinyl)oxirane, **10a**.**

See printed version of the paper.

2.3. Synthesis of (2*R*,3*S*,*S*₃)-3-[(2'*R*,3'*S*)-3'-Methyl-2'-oxiranyl]-2-(*p*-tolylsulfinyl)oxirane, **9b, and (2*R*,3*S*)-3-[(2'*R*,3'*S*)-3'-Methyl-2'-oxiranyl]-2-(*p*-tolylsulfonyl)oxirane, **11b**.**

From a solution of sulfinyl diene **2b** (30 mg, 0.145 mmol), in THF (1.0 mL) and a cold (-20 to 0 °C) 0.2 M THF solution of KOO-*t*-Bu (2 equiv), (2 h 15 min), according to the general procedure, a 70:30 mixture of bisepoxides **9b** and **11b** was obtained at 51% conversion. Purification by chromatography (5-30% EtOAc-hexane) gave sulfonyl bisepoxide **11b** and sulfinyl bisepoxide **9b** as colorless oils and both as practically single isomers. The yield was not determined. Structural assignments are tentative

Data of **9b**: $R_f = 0.17$ (2x20% EtOAc-hexane). $[\alpha]_D^{20} = +10.0$ ($c = 0.19$). **¹H NMR (300 MHz)** δ 1.40 (d, 3 H, $J = 5.0$ Hz), 2.42 (s, 3 H), 3.00-3.08 (m, 3 H), 4.00 (d, 1 H, $J = 3.3$ Hz), 7.36 (d, 2 H, $J = 7.8$ Hz), 7.60 (d, 2 H, $J = 8.2$ Hz). **¹³C NMR (50 MHz)** δ 17.0, 21.5, 52.2, 54.7, 57.8, 75.2, 124.6 (2 C), 130.4 (2 C), 137.6, 142.4. **MS (APCI)**: 239 $[M+1]^+$ (100%), 139, 123.

Data of **11b**: $R_f = 0.23$ (2x20% EtOAc-hexane). **¹H NMR (200 MHz)** δ 1.40 (d, 3 H, $J = 5.2$ Hz), 2.46 (s, 3 H), 3.00 (dd, 1 H, $J = 6.9, 3.9$ Hz), 3.08 (qd, 1 H, $J = 5.2, 2.9$ Hz), 3.47 (dd, 1 H, $J = 6.8, 2.2$ Hz), 4.02 (d, 1 H, $J = 3.8$ Hz), 7.40 (d, 2 H, $J = 8.0$ Hz), 7.83 (d, 2 H, $J = 8.4$ Hz).

2.4. Synthesis of (-)-(2*R*,3*S*,*S_s*)-3-(2'-Propenyl)-2-(*p*-tolylsulfinyl)oxirane, **8c**.

From a solution of sulfynyl diene **2c** (18 mg, 0.087 mmol), in THF (1.0 mL) and a cold (−10 to 0 °C) 0.2 M THF solution of KOO-*t*-Bu (3 equiv), (1 h 30 min), according to the general procedure, sulfynyl oxirane **8c** was obtained. Purification by chromatography (5-30% EtOAc-hexane) gave sulfynyl oxirane **8c** (11 mg, 56%) as a colorless oil. The configuration of the oxirane was assigned tentatively.

Data of **8c**: $R_f = 0.26$ (2x30% EtOAc-hexane). $[\alpha]_D^{20} = -28.4$ ($c = 0.93$). $^1\text{H NMR}$ (300 MHz) δ 1.76 (s, 3 H), 2.41 (s, 3 H), 3.55 (dd, 1 H, $J = 3.9, 0.5$ Hz), 4.05 (d, 1 H, $J = 3.9$ Hz), 5.20 (s, 1 H), 5.31 (s, 1 H), 7.33 (d, 2 H, $J = 8.5$ Hz), 7.51 (d, 2 H, $J = 8.3$ Hz). $^{13}\text{C NMR}$ (75 MHz) δ 19.7, 21.5, 58.5, 77.4, 115.5, 124.5 (2 C), 130.2 (2 C), 136.2, 137.8, 142.6. IR (film): 2980, 2920, 1660, 1490, 1450, 1380, 1290, 1220, 1090, 1050, 1020, 910, 810 cm^{-1} . MS (APCI): 223 $[\text{M}+1]^+$, 205, 139 (100%).

2.5. Synthesis of (+)-(2*R*,3*R*,4*R*,5*S*,*S_s*)-3,4-Epoxy-4-(*p*-tolylsulfinyl)-5-vinyl-tetrahydrofuran-2-methanol, **18a**, (+)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-4-(*p*-tolylsulfonyl)-5-vinyl-tetrahydrofuran-2-methanol, **22a**, and (+)-(2*R*,5*S*,*S_s*)-4-(*p*-tolylsulfinyl)-5-vinyl-2,5-dihydrofuran-2-methanol, **16a**.

a) With 2 equiv de KOO-*t*-Bu from **4a.** From a solution of hydroxy sulfynyl diene **4a** (62 mg, 0.250 mmol), in THF (2.5 mL) and a cold (−20 to 0 °C) 0.2 M THF solution of KOO-*t*-Bu (2 equiv), (50 min), according to the general procedure, an 87:13 mixture of sulfynyl and sulfonyl tetrahydrofurans **18a** and **22a** was obtained. Purification by chromatography (15-100% EtOAc-hexane) gave sulfynyl oxirane **18a** (29 mg, 41%, practically a single isomer) as a white solid that was recrystallized from CH_2Cl_2 -hexane and **22a** (5 mg, 7%, inseparable 90:10 mixture) as a colorless oil.

b) With 2.2 equiv of KOO-*t*-Bu from 4a. From a solution of hydroxy sulfinyl diene **4a** (41 mg, 0.165 mmol), in THF (1.2 mL) and a cold (−20 to 0 °C) 0.2 M THF solution of KOO-*t*-Bu (2 equiv), (40 min), according to the general procedure, an 80:20 mixture of sulfinyl and sulfonyl tetrahydrofurans **18a** and **22a** was obtained along with a relatively important amount of monoepoxide **12a**. Careful purification by chromatography (10-100% EtOAc-hexane) gave sulfinyl monoepoxide **12a** (3 mg, 7.3%, single isomer) as a colorless oil. Stereochemical assignment is tentative

c) With 0.85 equiv of KOO-*t*-Bu from 4a. From a solution of hydroxy sulfinyl diene **4a** (58 mg, 0.234), in THF (2.0 mL) and a cold (−78 to 4 °C, refrigerator) 0.2 M THF solution of KOO-*t*-Bu (0.85 equiv), (18 h), according to the general procedure, a 38:54:8 mixture of sulfinyl dihydrofuran, sulfinyl and sulfonyl tetrahydrofurans **16a:18a:22a** was obtained with 65% conversion. Purification by chromatography (10-100% EtOAc-hexane) gave sulfinyl dihydrofuran **16a** (6 mg, 10%) as a white solid that was recrystallized from CH₂Cl₂-hexane.

d) With 3 equiv of KOO-*t*-Bu from 4a. From a solution of hydroxy sulfinyl diene **4a** (45 mg, 0.181 mmol), in THF (1.2 mL) and a cold (−20 to 0 °C) 0.2 M THF solution of KOO-*t*-Bu (3 equiv), (4 h 50 min), according to the general procedure, a 18:82 mixture of sulfinyl and sulfonyl tetrahydrofurans **18a** and **22a** was obtained. Purification by chromatography (15-100% EtOAc-hexane) gave sulfonyl oxirane **22a** (18 mg, 15%) as a colorless oil.

Data of **18a**: mp: 149-152 °C. $[\alpha]_D^{20} = +123.5$ ($c = 1.30$). $R_f = 0.20$ (40% EtOAc-CH₂Cl₂). $R_f = 0.10$ (50% EtOAc-hexane). ¹H NMR (300 MHz) δ 2.09 (br s, 1 H), 2.41 (s, 3 H), 3.76 (br t, 2 H, $J = 4.3$ Hz), 4.13 (d, 1 H, $J = 8.9$ Hz), 4.22 (t, 1 H, $J = 4.8$ Hz), 4.25 (s, 1 H), 5.25 (dt, 1 H, $J = 16.9, 1.2$ Hz), 5.38 (dt, 1 H, $J = 10.2, 1.1$ Hz), 6.08 (ddd, 1 H, $J = 16.9, 10.2, 8.8$ Hz), 7.31 (d, 2 H, $J = 7.9$ Hz), 7.60 (d, 2 H, $J = 8.3$ Hz). ¹H NMR (C₆D₆, 300 MHz) δ 1.95 (s, 3 H), 3.29 (dd, 1 H, $J = 11.9, 3.9$ Hz), 3.37 (dd, 1 H, $J = 12.0, 4.5$ Hz), 3.93 (t, 1 H, $J = 4.2$ Hz), 4.12 (d, 1 H, $J = 9.1$ Hz), 4.32 (s, 1 H), 4.91 (d, 1 H, $J = 17.0$ Hz), 5.02 (d, 1 H, $J = 10.1$ Hz), 6.15 (ddd, 1 H, $J = 17.0, 10.1, 8.2$ Hz), 6.85 (d, 2 H, $J = 8.1$ Hz), 7.58 (d, 2 H, $J = 8.2$ Hz). DNOE (C₆D₆): between H-5 and H-vinyl: 3.9%; between H-5 and H-vinyl: 1.7%; between H-5 and H-ArH: 1.3%; between H-ArH (7.60) and H-ArH (6.85): 8.5%. ¹³C NMR (50 MHz) δ 21.6, 62.9, 65.1, 78.9, 79.8, 81.5, 121.8, 126.3 (2 C), 130.1 (2 C), 133.4, 135.9, 143.4. IR (KBr): 3380, 2930, 1090, 1050, 1000, 930, 850, 810 cm^{−1}. MS (EI): 280 [M]⁺, 264, 250, 232, 217, 185, 139 (100%), 123, 111, 192, 77, 65, 39. Anal calcd for C₁₄H₁₆O₄S: C, 59.98; H, 5.75; S, 11.44. Found: C, 60.15; H, 5.97; S, 11.23.

Data of **22a** (major isomer, from a 90:10 mixture): $R_f = 0.30$ (15% EtOAc-CH₂Cl₂). $[\alpha]_D^{20} = +17.6$ ($c = 0.54$). $^1\text{H NMR}$ (300 MHz) δ 2.45 (s, 3 H), 3.74 (d, 2 H, $J = 5.4$ Hz), 4.17 (t, 1 H, $J = 5.1$ Hz), 4.27 (s, 1 H), 4.36 (d, 1 H, $J = 8.3$ Hz), 5.25 (dt, 1 H, $J = 16.7, 1.2$ Hz), 5.34 (dt, 1 H, $J = 10.2, 1.1$ Hz), 6.22 (ddd, 1 H, $J = 16.8, 10.1, 8.4$ Hz), 7.35 (d, 2 H, $J = 8.2$ Hz), 7.77 (d, 2 H, $J = 8.4$ Hz). $^1\text{H NMR}$ (C₆D₆, 300 MHz) δ 1.79 (s, 3 H), 3.08 (dd, 1 H, $J = 11.6, 4.7$ Hz), 3.18 (dd, 1 H, $J = 11.6, 5.1$ Hz), 3.78 (t, 1 H, $J = 4.9$ Hz), 4.14 (s, 1 H), 4.40 (d, 1 H, $J = 8.4$ Hz), 5.00 (dm, 1 H, $J = 16.8$ Hz), 5.09 (dm, 1 H, $J = 10.8$ Hz), 6.47 (ddd, 1 H, $J = 16.8, 10.0, 8.4$ Hz), 6.66 (d, 1 H, $J = 8.1$ Hz), 7.83 (d, 2 H, $J = 8.3$ Hz). **DNOE** between H-5/H-2: 1.0%. $^{13}\text{C NMR}$ (50 MHz) δ 21.7, 62.9, 65.1, 78.1, 79.7, 120.1, 129.2 (2 C), 129.9 (2 C), 133.6, 133.8, 134.2, 146.0. **IR** (CCl₄): 3440, 2980, 2820, 1580, 1400, 1310, 1200, 1150, 1220, 1470, 1030, 910, 790, 680, 600 cm⁻¹.

Partial data of **22a'** (minor isomer, from a 90:10 mixture): $^1\text{H NMR}$ (300 MHz) δ 2.44 (s, 3 H), 3.78 (d, 2 H, $J = 5.1$ Hz), 4.11 (t, 1 H, $J = 5.0$ Hz), 4.24 (s, 1 H).

Data of **16a**: $R_f = 0.06$ (50% EtOAc-hexane). **mp**: 91-93 °C. $[\alpha]_D^{20} = +112.8$ ($c = 0.44$). $^1\text{H NMR}$ (300 MHz) δ 2.40 (s, 3 H), 3.64 (dd, 1 H, $J = 11.7, 5.3$ Hz), 3.73 (d, 1 H, $J = 6.6$ Hz), 3.78 (dd, 1 H, $J = 11.5, 6.3$ Hz), 4.74 (dm, 1 H, $J = 7.6$ Hz), 4.97 (m, 1 H), 5.14 (d, 1 H, $J = 17.6$ Hz), 5.17 (d, 1 H, $J = 10.1$ Hz), 5.73 (ddd, 1 H, $J = 17.4, 10.2, 7.4$ Hz), 6.55 (t, 1 H, $J = 1.7$ Hz), 7.30 (d, 2 H, $J = 8.1$ Hz), 7.51 (d, 2 H, $J = 8.1$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ 21.5, 64.8, 85.5, 87.5, 119.2, 125.7 (2 C), 130.2 (2 C), 130.9, 136.1, 138.1, 142.9, 149.0. **IR** (KBr): 3420, 2920, 2860, 1590, 1490, 1420, 1110, 1080, 1060, 1030, 1010, 930, 860, 820 cm⁻¹.

Data of **(3S,6S,S_e)-(4E)-6,7-Epoxy-4-(p-tolylsulfinyl)hepta-1,4-dien-3-ol, 12a**: $R_f = 0.28$ (EtOAc). $^1\text{H NMR}$ (300 MHz) δ 2.39 (s, 3 H), 2.74 (dd, 1 H, $J = 5.4, 2.6$ Hz), 2.78 (br s, 1 H), 3.04 (dd, 1 H, $J = 5.4, 4.3$ Hz), 3.96 (ddd, 1 H, $J = 7.7, 4.1, 2.6$ Hz), 4.86 (dm, 1 H, $J = 5.2$ Hz), 5.02 (ddd, 1 H, $J = 10.4, 1.7, 1.2$ Hz), 5.12 (ddd, 1 H, $J = 17.1, 1.7, 1.2$ Hz), 5.57 (ddd, 1 H, $J = 17.1, 10.4, 5.2$ Hz), 6.11 (d, 1 H, $J = 7.7$ Hz), 7.28 (d, 2 H, $J = 7.9$ Hz), 7.50 (d, 2 H, $J = 8.2$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ 21.4, 48.1, 48.6, 68.2, 115.8, 125.8 (2 C), 130.1 (2 C), 132.9, 133.4, 142.3, 150.9.

2.6. Nucleophilic Epoxidation of (+)-(2*R*,5*S*,*S_s*)-4-(*p*-Tolylsulfinyl)-5-vinyl-2,5-dihydrofuran-2-methanol, **16a**.

From a solution of sulfinyl dihydrofuran **16a** (14 mg, 0.053 mmol), in THF (1.0 mL) and a cold (−20 to 0 °C) 0.2 M THF solution of KOO-*t*-Bu (4 equiv), (1 h), according to the general procedure, an 85:15 mixture of sulfinyl and sulfonyl tetrahydrofurans **18a** and **22a** was obtained with 85% conversion. Purification by chromatography (30-50% EtOAc-hexane) gave sulfinyl oxirane **18a** (7 mg, 47%).

2.7. Synthesis of (2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-2-(*p*-tolylsulfonyl)-5-vinyl-tetrahydrofuran-2-methanol, (major isomer), **22a**.

From a solution of hydroxy sulfonyl diene **6a** (34 mg, 0.129 mmol), in THF (2.4 mL) and a cold (−20 to 0 °C) 0.2 M THF solution of KOO-*t*-Bu (2 equiv), (30 min), according to the general procedure, an inseparable 62:29:9 mixture of sulfonyl tetrahydrofurans **22a** was obtained. Purification by chromatography (10-50% EtOAc-hexane) gave sulfinyl oxirane **22a** (11 mg, 29%).

Data of **22a** (major isomer): Identical to that described above.

Partial data of **22a'** (first minor isomer): ¹H NMR (300 MHz) δ 2.44 (s, 3 H), 3.78 (d, 2 H, *J* = 5.1 Hz), 4.11 (t, 1 H, *J* = 5.0 Hz), 4.24 (s, 1 H), 4.86 (dd, 1 H, *J* = 4.4, 2.5 Hz), 5.60 (dd, 1 H, *J* = 6.7, 5.0 Hz), 5.29 (m, 2 H). ¹H NMR (C₆D₆, 300 MHz) δ 3.77 (d, 2 H, *J* = 5.0 Hz), 3.99 (s, 1 H), 4.82 (d, 1 H, *J* = 10.1 Hz), 4.88 (d, 1 H, *J* = 7.6 Hz), 5.22 (d, 1 H, *J* = 17.8 Hz), 5.46 (ddd, 1 H, *J* = 17.7, 10.2, 7.6 Hz). **DNOE** between H-2/H-3: 1.4%; between H-2/H-5: 1.0%; between H-3/H-2: 3.7%.

Partial data of **22a''** (second minor isomer): ^1H NMR (300 MHz) δ 3.77 (d, 2 H, $J = 5.2$ Hz), 4.23 (s, 1 H), 4.40 (d, 1 H, $J = 8.2$ Hz), 6.14 (m, 1 H). ^1H NMR (C_6D_6 , 300 MHz) δ 3.51 (t, 1 H, $J = 4.5$ Hz), 3.92 (s, 1 H), 4.35 (dm, 1 H, $J = 6.1$ Hz), 6.30 (m, 1 H)

2.8. Synthesis of (+)-(2*R*,3*R*,4*R*,5*S*,*S*₅)-3,4-Epoxy-5-(1'-propenyl)-4-(*p*-tolylsulfinyl)tetrahydrofuran-2-methanol, **18b, and 3,4-Epoxy-5-(1'-propenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22b**.**

From a solution of hydroxy sulfinyl diene **4b** (40 mg, 0.15 mmol), in THF (1.0 mL) and a cold (-20 to 0 $^\circ\text{C}$) 0.2 M THF solution of KOO-*t*-Bu (4 equiv), (2 h), according to the general procedure, a 93:7 mixture of sulfenyl tetrahydrofurans **18b** and **18b'** was obtained, along with traces of sulfenyl tetrahydrofuran. Purification by chromatography (0-30% EtOAc- CH_2Cl_2) gave a 93:7 mixture of sulfenyl oxiranes **18b/18b'** (16 mg, 36%).

Data of **18b** (from the 93:7 mixture): $R_f = 0.23$ (40% EtOAc- CH_2Cl_2). $[\alpha]_D^{20} = +35.9$ ($c = 1.35$). ^1H NMR (300 MHz) δ 1.77 (d, 3 H, $J = 5.1$ Hz), 2.40 (s, 3 H), 2.60 (br s, 1 H), 3.73 (d, 2 H, $J = 4.8$ Hz), 4.09 (d, 1 H, $J = 8.8$ Hz), 4.17 (td, 1 H, $J = 4.8, 1.3$ Hz), 4.26 (s, 1 H), 5.50-5.79 (m, 2 H), 7.30 (d, 2 H, $J = 8.0$ Hz), 7.56 (d, 2 H, $J = 8.2$ Hz). ^{13}C NMR (50 MHz) δ 17.9, 21.6, 62.9, 65.2, 78.7, 79.6, 81.4, 126.3 (2 C), 126.4, 130.0 (2 C), 134.2, 143.3, 147.9. IR (CHCl_3): 3400, 3050, 2950, 1600, 1500, 1450, 1240, 1080, 1060, 1040, 980, 910, 850, 810 cm^{-1} . MS (EI): 294 $[\text{M}]^+$, 246, 190, 140, 139 (100%), 91, 77, 65, 39.

Partial data of **18b'** (minor, from the 93:7 mixture): ^1H NMR (300 MHz) δ 3.68 (m, 2 H), 4.00 (td, 1 H, $J = 4.8, 1.3$ Hz), 4.25 (s, 1 H).

2.9. Synthesis of (±)-(2*R*,3*R*,4*R*,5*S*,*S*_s)-3,4-Epoxy-5-ethyl-4-(*p*-tolylsulfinyl)tetrahydrofuran-2-methanol, **18c, (±)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-ethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22c**, and (±)-(2*R*,5*S*,*S*_s)-4-(*p*-Tolylsulfinyl)-5-ethyl-2,5-dihydrofuran-2-methanol, **16c**.**

a) With 1 mmol of dienyl sulfoxide. From a solution of hydroxy sulfinyl diene **4c** (250 mg, 1 mmol), in THF (11.0 mL) and a cold (−25 to 0 °C) 0.2 M THF solution of KOO-*t*-Bu (1.5 equiv), (1 h 30 min), according to the general procedure, a 27:47:26 mixture of sulfinyl dihydrofuran and sulfinyl and sulfonyl tetrahydrofurans was obtained. Purification by chromatography (20-100% EtOAc-hexane) gave **22c** and **23c** (39 mg, 13%, 70:30 mixture of diastereomers) as a white solid, **18c** and **19c** (68 mg, 24%, 73:27 mixture) as a white solid that was recrystallized from EtOAc-hexane to give pure **18c** and **16c** (36 mg, 13%, single isomer) as a colorless oil.

b) With 4 mmol of dienyl sulfoxide. From a solution of hydroxy sulfinyl diene **4c** (1001 mg, 4 mmol), in THF (41.0 mL) and a cold (−25 to 0 °C) 0.2 M THF solution of KOO-*t*-Bu (1.5 equiv) that had been "aged" for 1 h and 30 min, (1 h), according to the general procedure, a 19:37:19:25 mixture of sulfenate, sulfinyl dihydrofuran and sulfinyl and sulfonyl tetrahydrofurans was obtained. Purification by chromatography (20-100% EtOAc-hexane) gave **22c** and **23c** (143 mg, 12%, 70:30 mixture of diastereomers) as a white solid, **XX** (88 mg, 9%, single isomer), **18c** and **19c** (113 mg, 10%, 70:30 mixture) as a white solid that was recrystallized from EtOAc-hexane to give pure **18c** and **16c** (139 mg, 13%, single isomer) as a colorless oil.

c) With 3 equiv of KOO-*t*-Bu.

From a solution of hydroxy sulfinyl diene **4c** (148 mg, 0.6 mmol), in THF (11.0 mL) and a cold (–20 to 0 °C) 0.2 M THF solution of KOO-*t*-Bu (3.0 equiv), (35 min), according to the general procedure, a 17:83 mixture of sulfenyl and sulfonyl tetrahydrofurans was obtained. Purification by chromatography (5-100% EtOAc-hexane) gave **22c** and **23c** (68 mg, 39%, 77:23 mixture of diastereomers) and **18c** and **19c** (19 mg, 11%,).

Data of **16c**: R_f = 0.15 (80% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.90 (t, 3 H, J = 7.4 Hz), 1.46 (m, 1 H), 1.66 (m, 1 H), 1.81 (t, 1 H), 2.40 (s, 3 H), 3.65 (m, 1 H), 3.75 (ddd, 1 H, J = 11.1, 6.8, 3.8 Hz), 4.40 (ddm, 1 H, J = 3.8, 2.0 Hz), 4.94 (ddm, 1 H, J = 3.8, 1.7 Hz), 6.50 (ap. t, 1 H, J = 1.7 Hz), 7.31 (d, 2 H, J = 8.2 Hz), 7.53 (d, 2 H, J = 8.2 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 9.0, 21.4, 27.9, 64.9, 85.2, 86.4, 125.6 (2 C), 130.3 (2 C), 130.8, 138.2, 142.9, 148.9. IR (film): 3400, 2925, 2875, 1596, 1491, 1455, 1047, 810 cm^{-1} . MS (ES): 533 $[2\text{M}+1]^+$, 267 $[\text{M}+1]^+$ (100%).

Data of **18c** (major isomer): mp: 101-102 °C. R_f = 0.13 (40% EtOAc-hexane). $^1\text{H NMR}$ (200 MHz) δ 0.99 (t, 3 H, J = 7.3 Hz), 1.63-1.81 (m, 3 H), 2.41 (s, 3 H), 3.63-3.74 (m, 3 H), 4.17 (s, 1 H), 4.20 (t, 1 H, J = 5.6 Hz), 7.34 (d, 2 H, J = 8.0 Hz), 7.63 (d, 2 H, J = 8.2 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 10.4, 21.6, 26.3, 63.0, 64.4, 78.6, 79.4, 82.1, 126.1 (2 C), 130.3 (2 C), 136.3, 143.4. IR (KBr): 3401, 2968, 1596, 1461, 1086, 1053, 811, 755 cm^{-1} . MS (ES): 305.2 $[\text{M}+\text{Na}]^+$ (100%), 283.3 $[\text{M}+1]^+$. Anal. calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4\text{S}$: C, 59.55; H, 6.43, S, 11.36. Found: C, 59.54; H, 6.21; S, 10.98.

Partial data of **19c** (minor isomer, from a 45:55 mixture of **18c** and **19c**): R_f = 0.13 (40% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.85 (t, 3 H, J = 7.5 Hz), 2.41 (s, 3 H), 3.77 (d, 2 H, J = 5.1 Hz), 3.95 (t, 1 H, J = 5.1 Hz), 4.02 (t, 1 H, J = 6.0 Hz), 4.06 (s, 1 H).

Data of (±)-(2*R*,5*S*)-5-ethyl-4-oxo-3-(*p*-tolylsulfonyloxy)-tetrahydrofuran-2-methanol, **XX**: R_f = 0.16 (50% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.86 (t, 3 H, J = 7.4 Hz), 1.52 (m, 1 H), 1.65 (m, 1 H), 2.40 (s, 3 H), 2.60 (br s, 1 H),

3.20 (dd, 1 H, $J = 7.0, 4.5$ Hz), 3.79 (dd, 1 H, $J = 11.8, 3.8$ Hz), 3.85 (dd, 1 H, $J = 11.8, 4.8$ Hz), 4.06 (d, 1 H, $J = 8.2$ Hz), 4.39 (ddd, 1 H, $J = 8.3, 4.8, 3.8$ Hz), 7.32 (d, 2 H, $J = 8.1$ Hz), 7.45 (d, 2 H, $J = 8.3$ Hz). ^{13}C NMR (50 MHz) δ 9.2, 21.4, 23.5, 63.8, 69.5, 75.4, 82.9, 125.3 (2 C), 130.1 (2 C), 135.3, 142.8, 206.5. IR (film): 3400, 2928, 1755 (strong), 1596, 1493, 1456, 1083, 1043, 812, 755 cm^{-1} . MS (ES): 587 $[2\text{M}+\text{Na}]^+$ (100%), 305 $[\text{M}+\text{Na}]^+$, 283 $[\text{M}+1]^+$.

The data for sulfonyl tetrahydrofurans **22c** and **23c** is described below.

2.10. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,5*S*,*S*_s)-3,4-Epoxy-5-isopropyl-4-(*p*-tolylsulfinyl)tetrahydrofuran-2-methanol, **18d, ($\pm$)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-isopropyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22d**, and ($\pm$)-(2*R*,5*S*,*S*_s)-4-(*p*-Tolylsulfinyl)-5-isopropyl-2,5-dihydrofuran-2-methanol, **16d**.**

a) With 1 mmol of dienyl sulfoxide. From a solution of hydroxy sulfinyl diene **4d** (264 mg, 1 mmol), in THF (11.0 mL) and a cold (-30 to -5 °C) 0.2 M THF solution of KOO-*t*-Bu (1.6 equiv), (25 min), according to the general procedure, a 35:40:25 mixture of sulfinyl dihydrofuran and sulfinyl and sulfonyl tetrahydrofurans was obtained. Purification by chromatography (15-100% EtOAc-hexane) gave **22d-25d** (62 mg, 20%, 53:13:11:13 mixture of diastereomers) as a white solid, **18d-20d** (74 mg, 25%, 73:12:15 mixture) as a white solid that was recrystallized from EtOAc-hexane to give pure **18d** and **16d-17d** (39 mg, 14%, 77:33 mixture of diastereomers) as a colorless oil.

b) With 4 mmol of dienyl sulfoxide. From a solution of hydroxy sulfinyl diene **4d** (1058 mg, 4 mmol), in THF (41.0 mL) and a cold (-30 to -5 °C) 0.2 M THF solution of KOO-*t*-Bu (1.5 equiv), (1 h 25 min), according to the general procedure, a 38:29:33 mixture of sulfinyl dihydrofuran and sulfinyl and sulfonyl tetrahydrofurans was obtained. Purification by chromatography (15-100% EtOAc-hexane) gave sulfonyl tetrahydrofurans (250 mg, 20%, mixture of diastereomers), sulfinyl tetrahydrofurans (298 mg, 25%, mixture of isomers) and sulfinyl dihydrofurans (157 mg, 14%, mixture of diastereomers). A second chromatography of the dihydrofurans gave pure **16d** (16 mg) and a mixture of isomers (95 mg).

Data of **16d** (major isomer): $R_f = 0.08$ (50% EtOAc-hexane). ^1H NMR (300 MHz) δ 0.85 (d, 3 H, $J = 6.8$ Hz), 0.92 (d, 3 H, $J = 7.0$ Hz), 1.76 (sept d, 1 H, $J = 6.8, 3.1$ Hz), 2.02 (br s, 1 H), 2.40 (s, 3 H), 3.63-3.75 (m, 2 H), 4.28 (ddd, 1 H, $J = 4.3, 3.1, 2.1$ Hz), 4.92 (ddd, 1 H, $J = 10.6, 4.3, 1.6$ Hz), 6.59 (dd, 1 H, $J = 2.0, 1.6$ Hz), 7.30 (d, 2 H, $J = 8.4$ Hz), 7.53 (d, 2 H, $J = 8.2$ Hz). ^{13}C NMR (50 MHz) δ 16.1, 19.3, 21.5, 31.4, 65.0, 86.1, 89.1, 126.0 (2 C), 130.4 (2 C), 130.7, 138.3, 143.1, 149.0. IR (film): 3399, 2964, 2874, 1596, 1466, 1387, 1084, 1046, 810, 755, 623 cm^{-1} . MS (ES): 303 $[\text{M}+\text{Na}]^+$, 281 $[\text{M}+1]^+$ (100%).

Partial data of **17d** (minor isomer, from an 80:20 mixture of **16d** and **17d**): $R_f = 0.08$ (50% EtOAc-hexane). ^1H NMR (200 MHz) δ 0.80 (d, 3 H, $J = 6.8$ Hz), 0.89 (d, 3 H, $J = 6.8$ Hz), 4.31 (m, 1 H), 5.01 (m, 1 H).

Data of **18d** (major isomer): mp: 83-84 $^{\circ}\text{C}$. $R_f = 0.13$ (50% EtOAc-hexane). ^1H NMR (300 MHz) δ 0.97 (d, 3 H, $J = 6.8$ Hz), 1.09 (d, 3 H, $J = 6.7$ Hz), 1.83 (t, 1 H, $J = 5.9$ Hz), 1.96 (sept d, 1 H, $J = 6.8, 3.1$ Hz), 2.42 (s, 3 H), 3.73 (d, 1 H, $J = 3.3$ Hz), 3.74 (t, 2 H, $J = 6.3$ Hz), 4.16 (t, 1 H, $J = 6.6$ Hz), 4.19 (s, 1 H), 7.34 (d, 2 H, $J = 7.9$ Hz), 7.65 (d, 2 H, $J = 8.3$ Hz). ^{13}C NMR (50 MHz) δ 17.0, 20.7, 21.5, 29.5, 61.9, 66.0, 78.5, 78.6, 83.4, 126.4 (2 C), 130.2 (2 C), 136.4, 143.4. IR (film): 3411, 2964, 2932, 2876, 1724, 1651, 1596, 1468, 1388, 1086, 1047, 920, 810, 624 cm^{-1} . MS (ES): 593 $[2\text{M}+1]^+$, 337, 297 $[\text{M}+1]^+$ (100%). Anal. calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4\text{S}$: C, 60.79; H, 6.80, S, 10.82. Found: C, 60.35; H, 6.52; S, 10.54.

Partial data of **19d** (first minor isomer, from a 73:12:15 mixture of **18d**, **19d** and **20d**): $R_f = 0.13$ (50% EtOAc-hexane). ^1H NMR (200 MHz) δ 1.01 (d, 3 H, $J = 6.8$ Hz), 1.10 (d, 3 H, $J = 6.7$ Hz), 4.23 (ap.t, 1 H), 4.28 (s, 1 H).

Partial data of **20d** (second minor isomer, from a 73:12:15 mixture of **18d**, **19d** and **20d**): $R_f = 0.13$ (50% EtOAc-hexane). ^1H NMR (200 MHz) δ 0.76 (d, 3 H, $J = 6.7$ Hz), 0.96 (d, 3 H, $J = 6.9$ Hz), 3.89 (ap.t, 1 H), 4.13 (s, 1 H).

The data for sulfonyl tetrahydrofurans **22d-25d** is described below.

2.11. Nucleophilic epoxidation of ($\pm$)-(2*R*,5*S*,*S_s*)-5-Isopropyl-4-(*p*-tolylsulfinyl)-2,5-dihydrofuran-2-methanol, **16d, and oxidation of the crude mixture.**

From a solution of hydroxy sulfinyl dihydrofuran **16d** (42 mg, 0.15 mmol), in THF (4.0 mL) and a cold (-20 to 0 °C) 0.2 M THF solution of KOO-*t*-Bu (4 equiv), (4 h min), according to the general procedure, followed by oxidation of the crude reaction mixture with *m*-CPBA (52 mg, 0.3 mmol, 2 equiv) in CH₂Cl₂, according to the general procedure, a 66:8:16:10 mixture of sulfonyl tetrahydrofurans **22d-25d** was obtained. Purification by chromatography (30-50% EtOAc-hexane) gave the mixture of sulfones (36 mg, 77%).

2.12. Synthesis of (+)-(2*R*,3*R*,4*R*,5*S*,*S_s*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfinyl)tetrahydrofuran-2-methanol, **18e, (+)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22e**, and (+)-(2*R*,5*S*,*S_s*)-4-(*p*-Tolylsulfinyl)-5-phenyl-2,5-dihydrofuran-2-methanol, **16e**.**

See printed version of the paper.

2.13. Synthesis of (±)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22e.**

From a solution of hydroxy sulfonyle diene **6e** (31 mg, 0.10 mmol), in THF (1.5 mL) and a cold (-10 to 0 °C) 0.2 M THF solution of KOO-*t*-Bu (1.8 equiv), (30 min), according to the general procedure, a 69:18:11:2 mixture of sulfonyl tetrahydrofurans **22e-25e** was obtained. The yield was not determined.

2.14. Synthesis of (±)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22e.**

From a solution of hydroxy sulfinyle diene **4e** (60 mg, 0.2 mmol), in THF (3.0 mL) and a cold (0 °C) 0.2 M THF solution of KOO-*t*-Bu (1.8 equiv), (1 h 10 min), according to the general procedure, and treatment of the crude reaction product with *m*-CPBA (98 mg, 0.4 mmol, 2 equiv) in CH₂Cl₂, according to the general procedure (4 h), a 76:7:4:13 mixture of sulfonyl tetrahydrofurans **22e-25e** was obtained. Purification by chromatography gave the mixture of sulfonyl tetrahydrofurans (21 mg, 30%) as a white solid.

2.15. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,5*S*,*S*₅)-3,4-Epoxy-5-(3-pyridyl)-4-(*p*-tolylsulfinyl)tetrahydrofuran-2-methanol, **18f, ($\pm$)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-(3-pyridyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22f**, and ($\pm$)-(2*R*,5*S*,*S*₅)-4-(*p*-Tolylsulfinyl)-5-(3-pyridyl)-2,5-dihydrofuran-2-methanol, **16f**.**

From a solution of hydroxy sulfinyl diene **4f** (130 mg, 0.43 mmol), in THF (6.5 mL) and a cold (-20 to -5 °C) 0.2 M THF solution of KOO-*t*-Bu (2.0 equiv), (1 h 15 min), according to the general procedure, a 20:76:4 mixture of sulfinyl dihydrofuran and sulfinyl and sulfonyl tetrahydrofurans was obtained. Purification by chromatography (5-15% EtOH-toluene) gave a mixture of these products (79 mg, 39%) as a yellow solid. A second careful chromatography (5-15% EtOH-toluene) gave sulfonyl tetrahydrofurans **22f-24f**, a 90:5:5 mixture of **18f-20f** that was recrystallized from *i*-PrOH to give pure **18f** and a 90:10 mixture of dihydrofurans **16f** and **17f**.

Data of **16f** (major isomer, from a 90:10 mixture of **16f** and **17f**): R_f = 0.20 (20% EtOH-toluene). $^1\text{H NMR}$ (300 MHz) δ 1.80 (br s, 1 H), 2.38 (s, 3 H), 3.84 (m, 2 H), 5.07 (m, 1 H), 5.32 (dd, 1 H, J = 4.5, 2.2 Hz), 6.79 (dd, 1 H, J = 2.1, 1.6 Hz), 7.21-7.38 (m, 5 H), 7.63 (ddd, 1 H, J = 7.9, 2.1, 1.9 Hz), 8.31 (d, 1 H, J = 1.6 Hz), 8.52 (ddd, 1 H, J = 4.9, 2.4, 1.5 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 21.5, 64.3, 83.8, 87.3, 123.7, 125.4 (2 C), 128.2, 130.3 (2 C), 132.6, 135.7, 137.4, 143.0, 148.6, 148.8, 150.3. IR (CHCl₃): 3400, 2900, 2850, 1590, 1410, 1330, 1120, 1090, 1050, 1010, 800, 740, 700 cm⁻¹. MS (ES): 338 [M+Na]⁺ (100%), 316 [M+1]⁺.

Partial data of **17f** (minor isomer, from a 90:10 mixture of **16f** and **17f**): R_f = 0.20 (20% EtOH-toluene). $^1\text{H NMR}$ (200 MHz) δ 4.20 (ap t, 1 H), 5.40 (m, 1 H), 6.78 (t, 1 H, J = 1.8 Hz).

Data of **18f** (major isomer): **mp**: 65-66 °C. R_f = 0.25 (20% EtOH-toluene). ^1H NMR (200 MHz) δ 2.39 (s, 3 H), 3.60 (br s, 1 H), 3.92 (d, 2 H, J = 3.9 Hz), 4.33 (t, 1 H, J = 3.9 Hz), 4.53 (s, 1 H), 4.65 (s, 1 H), 7.24-7.25 (m, 4 H), 7.33 (dd, 1 H, J = 7.9, 4.8 Hz), 7.94 (dd, 1 H, J = 8.0, 2.0 Hz), 8.40 (d, 1 H, J = 2.2 Hz), 8.60 (dd, 1 H, J = 4.9, 1.7 Hz). ^{13}C NMR (50 MHz) δ 21.5, 62.4, 67.4, 77.1, 79.5, 80.4, 83.3, 123.6, 126.8 (2 C), 130.1 (2 C), 131.7, 135.3, 137.1, 143.9, 150.3, 150.6. IR (KBr): 3400, 2960, 1590, 1480, 1420, 1080, 1045, 800, 705, 645, 610 cm^{-1} . MS (ES): 685 $[2\text{M}+\text{Na}]^+$ (100%), 354 $[\text{M}+\text{Na}]^+$, 332 $[\text{M}+1]^+$. **Anal. calcd for** $\text{C}_{17}\text{H}_{17}\text{NO}_4\text{S}$: C, 61.62; H, 5.17, N, 4.23; S, 9.68. **Found**: C, 61.53; H, 5.52; N, 4.02; S, 9.81.

Partial data of **19f** (first minor isomer, from a 78:14:8 mixture of **18f-20f**): R_f = 0.25 (20% EtOH-toluene). ^1H NMR (200 MHz) δ 4.76 (s, 1 H), 5.12 (s, 1 H).

Partial data of **20f** (second minor isomer, from a 78:14:8 mixture of **18f-20f**): R_f = 0.25 (20% EtOH-toluene). ^1H NMR (200 MHz) δ 4.20 (m, 2 H), 4.52 (s, 1 H), 4.60 (s, 1 H).

2.16. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-(3-pyridyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22f**.

From a solution of hydroxy sulfonyl diene **6f** (530 mg, 1.68 mmol), in THF (25.0 mL) and a cold (–30 to –5 °C) 0.2 M THF solution of KOO-*t*-Bu (2.0 equiv), (1 h 30 min), according to the general procedure, a 74:11:11:4 mixture of sulfonyl tetrahydrofurans **22f-25f** was obtained. Purification by chromatography (0-6% MeOH-EtOAc) gave **23f** (10 mg, 2%) and a mixture of **22f-25f** (153 mg, 26%) that was recrystallized from EtOAc to give pure **22f**.

Data of **22f** (major isomer): **mp**: 147-148 °C. $R_f = 0.32$ (20% EtOH-toluene), 0.13 (100% EtOAc). **^1H NMR (200 MHz)** δ 2.05 (br s, 1 H), 2.43 (s, 3 H), 3.97 (d, 2 H, $J = 4.5$ Hz), 4.29 (t, 1 H, $J = 4.6$ Hz), 4.48 (s, 1 H), 5.05 (s, 1 H), 7.25 (d, 2 H, $J = 8.1$ Hz), 7.40 (dd, 1 H, $J = 8.5, 3.8$ Hz), 7.40 (d, 2 H, $J = 8.4$ Hz), 7.88 (dt, 1 H, $J = 7.9, 2.0$ Hz), 8.40 (d, 1 H, $J = 2.3$ Hz), 8.57 (dd, 1 H, $J = 4.8, 1.6$ Hz). **^{13}C NMR (50 MHz)** δ 21.6, 61.9, 67.8, 77.8, 79.4, 79.7, 79.7, 123.2, 128.8 (2 C), 129.7 (2 C), 132.1, 133.2, 137.5, 146.0, 149.3. **IR** (KBr): 3434, 1595, 1332, 1163, 1098, 1049, 814, 664, 587, 543 cm^{-1} . **MS** (ES): 348 $[\text{M}+1]^+$.

Data of **23f** (first minor isomer): $R_f = 0.15$ (100% EtOAc). **^1H NMR (200 MHz)** δ 2.30 (s, 3 H), 2.60 (br s, 1 H), 3.89 (d, 2 H, $J = 5.5$ Hz), 4.15 (t, 1 H, $J = 5.4$ Hz), 4.45 (s, 1 H), 5.37 (s, 1 H), 6.95-8.42 (m, 8 H). **^{13}C NMR (50 MHz)** δ 21.6, 61.2, 64.0, 75.0, 76.9, 77.2, 123.2, 128.7 (2 C), 129.5 (2 C), 129.8, 132.6, 136.1, 145.7, 149.3, 149.9. **IR** (film): 3390, 2971, 1639, 1380, 1124, 1034, 1010, 951, 816, 684 cm^{-1} . **MS** (ES): 348 $[\text{M}+1]^+$.

Partial data of **24f** (second minor isomer, from a 75:10:10:5 mixture of **22f-25f**): $R_f = 0.15$ (100% EtOAc). **^1H NMR (200 MHz)** δ 2.44 (s, 3 H), 3.82 (d, 2 H, $J = 5.4$ Hz), 4.54 (t, 1 H, $J = 5.4$ Hz), 5.00 (s, 1 H).

Partial data of **25f** (third minor isomer, from a 75:10:10:5 mixture of **22f-25f**): $R_f = 0.15$ (100% EtOAc). **^1H NMR (200 MHz)** δ 2.30 (s, 3 H), 3.99 (d, 2 H, $J = 5.4$ Hz), 4.34 (t, 1 H, $J = 5.4$ Hz), 4.40 (s, 1 H), 5.54 (s, 1 H).

2.17. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,5*S*,*S_s*)-3,4-Epoxy-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfinyl)tetrahydrofuran-2-methanol, **18g, ($\pm$)-(2*S*,3*R*,4*R*,5*S*,*S_s*)-3,4-Epoxy-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22g**, ($\pm$)-(2*S*,3*R*,4*R*,5*S*,*S_s*)-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfinyl)-2,5-dihydrofuran-2-methanol, **16g**.**

a) In THF. From a solution of hydroxy sulfinyl diene **4g** (158 mg, 0.50 mmol), in THF (7.0 mL) and a cold (-30 to -5 °C) 0.22 M THF solution of KOO-*t*-Bu (2.0 equiv), (1 h 10 min), according to the general procedure, a 9:78:13 mixture of sulfinyl dihydrofuran, sulfinyl and sulfonyl tetrahydrofurans was obtained. Purification by chromatography (15-100% EtOAc-hexane) gave **22g-25g** (9 mg, 5%, 61:21:11:7 mixture of diastereomers), **18g-20g** (56 mg, 32%, 62:21:17 mixture of diastereomers that gave pure **18g** by recrystallization from EtOAc-hexane) and **16g** and **17g** (7 mg, 4%, 89:11 mixture of diastereomers), all as white solids.

From a solution of hydroxy sulfinyl diene **4g** (316 mg, 1 mmol), in THF (14.0 mL) and a cold (-40 to -5 °C) 0.22 M THF solution of KOO-*t*-Bu (2.0 equiv), (40 min), according to the general procedure, a 47:20:23 mixture of sulfinyl and sulfonyl tetrahydrofurans and bisepoxide **12g'** was obtained. Purification by chromatography (20-100% EtOAc-hexane) gave sulfonyl tetrahydrofurans (40 mg, 11%), sulfinyl tetrahydrofurans (59 mg, 16%) and **12g'** (27 mg, 10% as a single isomer).

b) In CH₂Cl₂. From a solution of hydroxy sulfinyl diene **4g** (253 mg, 0.80 mmol), in CH₂Cl₂ (12.0 mL) and a cold (0 °C) 0.3 M CH₂Cl₂ solution of KOO-*t*-Bu (3.0 equiv), (1 h 10 min), according to the general procedure, a 40:50:10 mixture of sulfinyl dihydrofuran, sulfinyl and sulfonyl tetrahydrofurans was obtained. Purification by chromatography (10-100% EtOAc-hexane) gave sulfonyl tetrahydrofurans **22g-25g** (29 mg, 13%, 52:32:10:6 mixture of diastereomers), sulfinyl tetrahydrofurans **18g-20g** (41 mg, 15%, 75:15:10 mixture of diastereomers; pure major isomer was obtained by recrystallization from EtOAc-hexane) and dihydrofurans **16g** and **17g** (24 mg, 9%, 90:10 mixture of diastereomers), all obtained as white solids.

c) In CH₂Cl₂, short reaction time. From a solution of hydroxy sulfinyl diene **4g** (475 mg, 1.50 mmol), in CH₂Cl₂ (12.0 mL) and a cold (0 °C) 0.2 M CH₂Cl₂ solution of KOO-*t*-Bu (2.0 equiv), (40 min), according to the general procedure, a mixture of sulfinyl dihydrofuran, sulfinyl and sulfonyl tetrahydrofurans was obtained. Purification by chromatography (10-100% EtOAc-hexane) gave sulfonyl tetrahydrofurans **22g-25g** (25 mg, 4%), sulfinyl tetrahydrofurans **18g-20g** (129 mg, 21%), dihydrofurans **16g** and **17g** (129 mg, 22%,) and recovered starting material (138 mg, 20%), all obtained as white solids.

d) In toluene. From a solution of hydroxy sulfinyl diene **4g** (63 mg, 0.2 mmol), in toluene and a cold (0 °C) 0.2 M toluene solution of KOO-*t*-Bu (3.0 equiv), (24 h), according to the general procedure, a 67:20:13 mixture of sulfinyl dihydrofuran, sulfinyl and sulfonyl tetrahydrofurans and *ca.* 40% recovered starting material was obtained.

Data of **16g** (major isomer, from an 88:12 mixture of **16g** and **17g**): R_f = 0.14 (30% EtOAc-hexane). **¹H NMR (200 MHz)** δ 2.38 (s, 3 H), 2.80 (br s, 1 H), 3.76 (d, 2 H, J = 4.2 Hz), 5.00 (ddd, 1 H, J = 8.6, 4.2, 1.5 Hz), 5.19 (dd, 1 H, J = 4.4, 2.0 Hz), 6.75 (dd, 1 H, J = 2.1, 1.5 Hz), 6.90-7.34 (m, 8 H). **¹³C NMR (50 MHz)** δ 21.5, 64.4, 85.4, 87.0, 115.6 (J_{C-F} = 21.7 Hz, 2 CH-3'), 125.6 (2 C), 130.0 (J_{C-F} = 8.7 Hz, 2 CH-2'), 130.2 (2 C), 132.2, 133.8, 137.3, 142.9, 148.9 (C *p*-Tol), 160.3 (J_{C-F} = 248.1 Hz, C-4'). **IR** (KBr): 3428, 1604, 1509, 1227, 1157, 1051, 811, 519 cm⁻¹. **MS** (ES): 333 [M+1]⁺ (100%), 139, 102.

Partial data of **17g** (minor isomer, from an 88:12 mixture of **16g** and **17g**): R_f = 0.14 (30% EtOAc-hexane). **¹H NMR (200 MHz)** δ 2.28 (s, 3 H), 5.29 (dd, 1 H, J = 5.5, 1.7 Hz), 6.70 (m, 1 H). **¹³C NMR (75 MHz)** δ 21.5 (CH₃ *p*-Tol), 63.7 (CH₂-OH), 85.6 (CH-5), 87.3 (CH-2), 115.5 (J_{C-F} = 22.0 Hz, 2 CH-3').

Data of **18g** (major isomer): **mp**: 153-154 °C. R_f = 0.18 (30% EtOAc-hexane). **¹H NMR (300 MHz)** δ 2.02 (br s, 1 H), 2.40 (s, 3 H), 3.90 (ap. t, 2 H, J = 5.0 Hz), 4.29 (t, 1 H, J = 4.7 Hz), 4.46 (s, 1 H), 4.61 (s, 1 H), 7.04-7.34 (m, 8 H). **¹³C NMR (75 MHz)** δ 21.5, 62.1, 67.2, 80.1, 80.8, 82.9, 115.6 (J_{C-F} = 21.7 Hz, 2 CH-3'), 126.7 (2 C), 129.8 (2 C), 131.1 (J_{C-F} = 8.1 Hz, 2 CH-2'), 131.2, 134.9, 143.7, 163.2 (J_{C-F} = 249.3 Hz, C-4'). **IR** (KBr): 3420, 2945, 1600, 1510, 1220, 1052 cm⁻¹. **MS** (ES): 719 [2M+Na]⁺ (100%), 349 [M+1]⁺. **Anal. calcd for C₁₈H₁₇FO₄S**: C, 62.02; H, 4.92; S, 9.20. **Found**: C, 61.74; H, 4.96; S, 9.18.

Partial data of **19g** (first minor isomer, from a 92:8 mixture of **19g** and **18g**): $R_f = 0.18$ (30% EtOAc-hexane). $^1\text{H NMR}$ (200 MHz) δ 2.30 (s, 3 H), 3.89 (d, 2 H, $J = 5.5$ Hz), 4.15 (t, 1 H, $J = 5.5$ Hz), 4.32 (s, 1 H), 5.10 (s, 1 H).

Partial data of **20g** (second minor isomer, from an 86:14 mixture of **18g** and **20g**): $R_f = 0.18$ (30% EtOAc-hexane). $^1\text{H NMR}$ (200 MHz) δ 2.42 (s, 3 H), 3.81 (m, 2 H), 4.51 (s, 1 H), 4.55 (s, 1 H).

Partial data of **12g'** (from a complex mixture): $R_f = 0.18$ (30% EtOAc-hexane). $^1\text{H NMR}$ (200 MHz) δ 2.40 (s, 3 H), 2.77 (dd, 1 H, $J = 5.0, 2.6$ Hz), 2.87 (t, 1 H, $J = 5.0$ Hz), 3.22 (m, 1 H), 3.32 (d, 1 H, $J = 4.9$ Hz), 5.17 (s, 1 H).

The data of sulfonyl tetrahydrofurans **22g-25g** is described below.

2.18. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,*S*_s)-5,5-Dimethyl-3,4-epoxy-4-(*p*-tolylsulfinyl)tetrahydrofuran-2-methanol, **18h, ($\pm$)-(2*R*,3*R*,4*R*)-5,5-Dimethyl-3,4-epoxy-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22h**, ($\pm$)-(2*R*,*S*_s)-5,5-Dimethyl-4-(*p*-tolylsulfinyl)-2,5-dihydrofuran-2-methanol, **16h**.**

From a solution of hydroxy sulfinyl diene **5** (50 mg, 0.20 mmol), in THF (2.4 mL) and a cold (4 °C) 0.22 M THF solution of KOO-*t*-Bu (1.8 equiv), (3.5 days), according to the general procedure, a 20:50:30 mixture of sulfinyl dihydrofuran, sulfinyl and sulfonyl tetrahydrofurans was obtained. Purification by chromatography (5-80% EtOAc-hexane) gave **22h** and **23h** (4 mg, 7%, 77:23 mixture of diastereomers), **20h** and **21h** (2 mg, 4%, 59:41 mixture of diastereomers), **18h**, **16h** and **17h** (6 mg, 10%, 64:26:9 mixture of diastereomers), and recovered starting material (20 mg, 40%).

Data of **16h** (major isomer, from a 64:26:9 mixture of **18h**, **16h** and **17h**): $R_f = 0.15$ (80% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 1.11 (s, 3 H), 1.26 (s, 3 H), 2.40 (s, 3 H), 3.70 (m, 2 H), 4.92 (m, 1 H), 6.33 (s, 1 H), 7.30 (d, 2 H, $J = 8.1$ Hz), 7.55 (d, 2 H, $J = 8.2$ Hz).

Data of **17h** (minor isomer, from a 64:26:9 mixture of **18h**, **16h** and **17h**): $R_f = 0.15$ (80% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 4.92 (m, 1 H), 6.28 (s, 1 H).

Data of **18h** (major isomer, from a 64:26:9 mixture of **18h**, **16h** and **17h**): $R_f = 0.15$ (80% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.70 (s, 3 H), 1.46 (s, 3 H), 1.95 (br s, 1 H), 2.41 (s, 3 H), 3.69 (ap. d, 2 H, $J = 5.6$ Hz), 4.15 (ap. t, 1 H, $J = 5.6$ Hz), 4.16 (s, 1 H), 7.33 (d, 2 H, $J = 8.1$ Hz), 7.66 (d, 2 H, $J = 8.1$ Hz).

Data of **20h** (first minor isomer, from a 59:41 mixture of **20h** and **21h**): $R_f = 0.27$ (80% EtOAc-hexane). $^1\text{H RMN}$ (300 MHz) δ 1.10 (s, 3 H), 1.54 (s, 3 H), 1.77 (br s, 1 H), 2.41 (s, 3 H), 3.49 (s, 1 H), 3.72 (ap. d, 2 H, $J = 5.0$ Hz), 4.01 (ap. t, 1 H, $J = 5.1$ Hz), 7.33 (d, 2 H, $J = 7.9$ Hz), 7.58 (d, $J = 8.3$ Hz).

Data of **21h** (second minor isomer, from a 59:41 mixture of **20h** and **21h**): $R_f = 0.27$ (80% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 1.11 (s, 3 H), 1.62 (s, 3 H), 1.77 (br s, 1 H), 2.41 (s, 3 H), 3.49 (s, 1 H), 3.64 (ap. d, 2 H, $J = 5.9$ Hz), 4.08 (ap. t, 1 H, $J = 5.8$ Hz), 7.33 (d, 2 H, $J = 7.9$ Hz), 7.58 (d, $J = 8.3$ Hz).

The data of sulfonyl tetrahydrofurans **22h** and **23h** is described below.

3. Synthesis and Epoxidation of Sulfonyl Dihydrofurans.

3.1. General Procedure for Oxidation/Epoxidation of Hydroxy Dienyl Sulfoxides with *m*-CPBA

See printed version of the paper.

3.2. Synthesis of (±)-(1*S*,4*S*)-(2*E*)-4,5-Epoxy-1-phenyl-2-(*p*-tolylsulfonyl)pent-2-en-1-ol, **26e**, and (±)-(1*S*,4*R*)-(2*E*)-4,5-Epoxy-1-phenyl-2-(*p*-tolylsulfonyl)pent-2-en-1-ol, **27e**.

See printed version of the paper.

3.3. Synthesis of (±)-(1*S*,4*S*)-(2*E*)-4,5-Epoxy-1-ethyl-2-(*p*-tolylsulfonyl)pent-2-en-1-ol, **26c, and (±)-(1*S*,4*R*)-(2*E*)-4,5-Epoxy-1-ethyl-2-(*p*-tolylsulfonyl)pent-2-en-1-ol, **27c**.**

From a mixture of sulfenyl dienes **3c** and **4c** (444 mg, 1.77 mmol), with *m*-CPBA (1.75 g, 7.09 mmol, 4 equiv), according to the general procedure, a mixture of monoepoxides (**26c** and **27c**) and sulfenyl diene (**6c**) was obtained. Purification by chromatography (10-60% EtOAc-hexane) gave sulfenyl diene **6c** (38 mg), **26c** (227 mg, 45%) as a colorless oil and **27c** (138 mg, 28%) as a colorless oil.

Data of **6c**: R_f = 0.33 (40% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.82 (t, 3 H, J = 7.4 Hz), 1.47-1.61 (m, 1 H), 1.63-1.80 (m, 1 H), 2.37 (br s, 1 H), 2.40 (s, 3 H), 4.50 (m, 1 H), 5.60 (d, 1 H, J = 11.5 Hz), 5.67 (d, 1 H, J = 16.7 Hz), 6.86 (ddd, 1 H, J = 16.8, 11.4, 10.0 Hz), 7.29 (d, 2 H, J = 8.7 Hz), 7.73 (d, 2 H, J = 8.2 Hz). $^{13}\text{C NMR}$ (75 MHz) δ 10.5, 21.6, 30.4, 70.6, 127.9 (2 C), 128.4, 129.1, 129.6, 129.8 (2 C), 130.4, 139.7, 144.3.

Data of **26c**: R_f = 0.25 (40% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.89 (t, 3 H, J = 7.4 Hz), 1.62-1.79 (m, 2 H), 2.36 (d, 1 H, J = 5.6 Hz), 2.43 (s, 3 H), 2.78 (dd, 1 H, J = 5.4, 2.6 Hz), 3.09 (dd, 1 H, J = 5.4, 4.3 Hz), 4.06 (ddd, 1 H, J = 7.9, 4.3, 2.6 Hz), 4.46 (dt, 1 H, J = 8.3, 5.4 Hz), 6.49 (d, 1 H, J = 8.1 Hz), 7.32 (d, 2 H, J = 7.9 Hz), 7.73 (d, 2 H, J = 8.4 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 10.2, 21.5, 30.8, 47.4, 48.5, 70.1, 128.1 (2 C), 129.9 (2 C), 136.1, 140.3, 144.7, 148.6. IR (film): 3499, 3062, 2971, 2933, 2878, 1643, 1597, 1494, 1462, 1380, 1314, 1146, 1086, 985, 933, 832, 815, 669 cm^{-1} . MS (ES): 305 $[\text{M}+\text{Na}]^+$. Anal. calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4\text{S}$: C, 59.55; H, 6.43, S, 11.36. Found: C, 59.73; H, 6.32; S, 11.54.

Data of **27c**: R_f = 0.21 (40% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.86 (t, 3 H, J = 7.4 Hz), 1.53 (m, 1 H), 1.73 (m, 1 H), 2.41 (s, 3 H), 2.59 (d, 1 H, J = 5.4 Hz), 2.77 (dd, 1 H, J = 5.4, 2.4 Hz), 3.09 (ap. t, 1 H, J = 5.4 Hz), 3.94 (ddd, 1 H, J = 8.7, 5.4, 2.4 Hz), 4.51 (m, 1 H), 6.39 (d, 1 H, J = 8.7 Hz), 7.31 (d, 2 H, J = 8.4 Hz), 7.71 (d, 2 H, J = 8.2 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 10.3, 21.5, 30.2, 47.0, 48.6, 70.1, 128.0 (2 C), 129.8 (2 C), 136.2, 140.3, 144.7, 148.9. IR (film): 3496, 2971, 2932, 2878, 1644, 1597, 1457, 1381, 1315, 1241, 1085, 987, 835, 815, 669 cm^{-1} . MS (ES): 305 $[\text{M}+\text{Na}]^+$. Anal. calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4\text{S}$: C, 59.55; H, 6.43, S, 11.36. Found: C, 59.34; H, 6.77; S, 11.17.

3.4. Synthesis of (±)-(1*S*,4*S*)-(2*E*)-4,5-Epoxy-1-isopropyl-2-(*p*-tolylsulfonyl)pent-2-en-1-ol, **26d, and (±)-(1*S*,4*R*)-(2*E*)-4,5-Epoxy-1-isopropyl-2-(*p*-tolylsulfonyl)pent-2-en-1-ol, **27d**.**

From a mixture of sulfynyl dienes **3d** and **4d** (264 mg, 1 mmol), with *m*-CPBA (986 mg, 4 mmol, 4 equiv), according to the general procedure, a 70:30 mixture of monoepoxides (**26d** and **27d**) and dihydrofurans (**28d** and **29d**) was obtained. Purification by chromatography (5-50% EtOAc-hexane) gave **26d** (101 mg, 34%) as a white solid that was recrystallized from EtOAc-hexane, **27d** (73 mg, 25%) as a white solid that was recrystallized from EtOAc-hexane and a 75:25 mixture of dihydrofurans **28d** and **29d** (75 mg, 25%).

Data of **26d**: R_f = 0.34 (40% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.76 (d, 3 H, J = 6.8 Hz), 0.98 (d, 3 H, J = 6.7 Hz), 2.01 (ap sext, 1 H), 2.42 (s, 3 H), 2.45 (br m, 1 H), 2.76 (dd, 1 H, J = 5.4, 2.6 Hz), 3.07 (dd, 1 H, J = 5.4, 4.3 Hz), 3.99-4.04 (m, 1 H), 4.22 (dd, 1 H, J = 7.7, 6.1 Hz), 6.49 (d, 1 H, J = 7.9 Hz), 7.31 (d, 2 H, J = 8.0 Hz), 7.73 (d, 2 H, J = 8.2 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 18.1, 19.2, 21.6, 34.1, 47.6, 48.5, 74.4, 128.2 (2 C), 130.0 (2 C), 136.5, 141.2, 144.7, 148.0. IR (KBr): 3490, 2963, 1639, 1469, 1286, 1141, 1084, 1052, 933, 835, 818, 730, 563 cm^{-1} . MS (ES): 319 $[\text{M}+\text{Na}]^+$. Anal. calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4\text{S}$: C, 60.79; H, 6.80; S, 10.82. Found: C, 60.76; H, 6.87; S, 10.76.

Data of **27d**: mp: 85-86 °C. R_f = 0.29 (40% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.73 (d, 3 H, J = 6.8 Hz), 1.00 (d, 3 H, J = 6.6 Hz), 2.04 (m, 1 H), 2.41 (s, 3 H), 2.52 (d, 1 H, J = 6.3 Hz), 2.76 (dd, 1 H, J = 5.5, 2.4 Hz), 3.08 (dd, 1 H, J = 5.4, 4.1 Hz), 3.86 (ddd, 1 H, J = 8.7, 4.1, 2.4 Hz), 4.30 (dd, 1 H, J = 7.9, 6.2 Hz), 6.38 (d, 1 H, J = 8.7 Hz), 7.30 (d, 2 H, J = 7.9 Hz), 7.73 (d, 2 H, J = 8.4 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 18.3, 19.3, 21.6, 33.6, 47.5, 48.7, 74.7, 128.2 (2 C), 129.9 (2 C), 136.9, 141.3, 144.7, 148.3. IR (KBr): 3472, 2972, 1641, 1366, 1299, 1282, 1137, 1084, 1010, 839, 673, 571 cm^{-1} . MS (ES): 319 $[\text{M}+\text{Na}]^+$. Anal. calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4\text{S}$: C, 60.79; H, 6.80; S, 10.82. Found: C, 60.60; H, 6.90; S, 10.71.

3.5. Synthesis of (±)-(1*S*,4*S*)-(2*E*)-4,5-Epoxy-1-(*p*-fluorophenyl)-2-(*p*-tolylsulfonyl)pent-2-en-1-ol, **26g, and (±)-(1*S*,4*R*)-(2*E*)-4,5-Epoxy-1-(*p*-fluorophenyl)-2-(*p*-tolylsulfonyl)pent-2-en-1-ol, **27g**.**

From a mixture of sulfenyl dienes **3g** and **4g** (316 mg, 1 mmol), with *m*-CPBA (1.23 g, 5 mmol, 5 equiv), according to the general procedure, an 83:17 mixture of monoepoxides (**26g** and **27g**) and dihydrofurans (**28g** and **29g**) was obtained. Purification by chromatography (10-60% EtOAc-hexane) gave **26g** (161 mg, 46%) as a white solid that was recrystallized from EtOAc-hexane, **27g** (112 mg, 32%) as a white solid that was recrystallized from EtOAc-hexane and a 75:25 mixture of dihydrofurans **28g** and **29g** (56 mg, 16%).

Data of **26g**: mp: 121-122 °C. $R_f = 0.40$ (10% EtOAc-CH₂Cl₂). ¹H NMR (300 MHz) δ 2.39 (s, 3 H), 2.71 (dd, 1 H, *J* = 5.4, 2.5 Hz), 2.92 (dd, 1 H, *J* = 5.2, 4.2 Hz), 3.28 (d, 1 H, *J* = 6.2 Hz), 3.70 (ddd, 1 H, *J* = 7.8, 4.3, 2.6 Hz), 5.80 (d, 1 H, *J* = 5.5 Hz), 6.64 (d, 1 H, *J* = 7.9 Hz), 6.87 (t, 2 H, *J* = 8.7 Hz), 7.17-7.23 (m, 4 H), 7.52 (d, 2 H, *J* = 8.3 Hz). ¹³C NMR (50 MHz) δ 21.6, 47.4, 48.0, 68.7, 115.2 (2 CH-3', *J*_{C-F} = 21.7 Hz), 127.4 (2 CH-4', *J*_{C-F} = 8.4 Hz), 128.0 (2 C), 129.9 (2 C), 135.7, 136.1, 141.8, 144.8, 148.1, 162.2 (C-4', *J*_{C-F} = 246.8 Hz). IR (KBr): 3481, 1603, 1508, 1411, 1305, 1220, 1142, 1086, 835, 814, 734, 557 cm⁻¹. EM (ES): 719 [2M+Na]⁺, 371 [M+Na]⁺, 366 [M+NH₄]⁺ (100%), 175. Anal. calcd for C₁₈H₁₇FO₄S: C, 62.05; H, 4.92; S, 9.20. Found: C, 62.25; H, 4.77; S, 8.98.

Data of **27g**: mp: 113-114 °C. $R_f = 0.37$ (10% EtOAc-CH₂Cl₂). ¹H NMR (300 MHz) δ 2.39 (s, 3 H), 2.74 (dd, 1 H, *J* = 5.5, 2.4 Hz), 3.01 (dd, 1 H, *J* = 5.5, 4.3 Hz), 3.17 (d, 1 H, *J* = 5.7 Hz), 3.59 (ddd, 1 H, *J* = 8.3, 4.3, 2.4 Hz), 5.79 (d, 1 H, *J* = 5.4 Hz), 6.59 (d, 1 H, *J* = 8.3 Hz), 6.88 (t, 2 H, *J* = 8.7 Hz), 7.15 (dd, 2 H, *J* = 8.9, 5.3 Hz), 7.22 (d, 2 H, *J* = 7.9 Hz), 7.59 (d, 2 H, *J* = 8.3 Hz). ¹³C NMR (50 MHz) δ 21.5, 47.3, 48.6, 69.1, 115.4 (2 CH-3', *J*_{C-F} = 21.7 Hz), 127.9 (2 CH-4', *J*_{C-F} = 8.1 Hz), 128.2 (2 C), 129.9 (2 C), 135.4, 136.0, 141.9, 144.8, 148.3, 162.3 (C-4', *J*_{C-F} = 247.2 Hz). IR (KBr): 3478, 1508, 1296, 1226, 1145, 1063, 814, 674, 595, 554 cm⁻¹. MS (ES): 719 [2M+Na]⁺, 371 [M+Na]⁺, 175 (100%). Anal. calcd for C₁₈H₁₇FO₄S: C, 62.05; H, 4.92; S, 9.20. Found: C, 62.21; H, 5.04; S, 8.98.

3.6. General Procedure for Cyclization of Monoepoxides with CSA

See printed version of the paper.

3.7. Synthesis of (±)-(2*R*,5*S*)-5-Phenyl-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, **28e**.

See printed version of the paper.

3.8. Synthesis of (±)-(2*S*,5*S*)-5-Phenyl-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, **29e**.

See printed version of the paper.

3.9. Synthesis of (±)-(2*R*,5*S*)-5-Ethyl-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, **28c**.

From monoepoxide **26c** (180 mg, 0.64 mmol), with CSA (30 mg, 0.13 mmol, 0.2 equiv), according to the general procedure (1 h 45 min), sulfonyl dihydrofuran **28c** (176 mg, 98%) was obtained after purification by chromatography (10-80% EtOAc-hexane) as a colorless oil.

Data of **28c**: R_f = 0.13 (40% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.86 (t, 3 H, J = 7.3 Hz), 1.53 (m, 1 H), 1.79 (t, 1 H, J = 6.4 Hz), 1.87 (m, 1 H), 2.44 (s, 3 H), 3.68 (m, 2 H), 4.82-4.92 (m, 2 H), 6.62 (ap t, 1 H, J = 1.6 Hz), 7.34 (d, 2 H, J = 8.4 Hz), 7.76 (d, 2 H, J = 8.3 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 8.9, 21.4, 27.5, 64.1, 85.1, 85.2, 127.8 (2 C), 129.9 (2 C), 136.3, 139.1, 145.0, 145.1. IR (film): 3514, 2969, 2929, 2876, 1624, 1596, 1455, 1317, 1156, 1084, 960, 815, 666, 591 cm^{-1} . MS (ES): 305 $[\text{M}+\text{Na}]^+$. Anal. calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4\text{S}$: C, 59.55; H, 6.43, S, 11.36. Found: C, 59.40; H, 6.64; S, 11.59.

3.10. Synthesis of (±)-(2*S*,5*S*)-5-Ethyl-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, **29c**.

From monoepoxide **27c** (83 mg, 0.29 mmol), with CSA (14 mg, 0.06 mmol, 0.2 equiv), according to the general procedure (1 h 30 min), sulfonyl dihydrofuran **29c** (80 mg, 96%) was obtained after purification by chromatography (10-80% EtOAc-hexane) as a colorless oil.

Data of **29c**: R_f = 0.13 (40% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.83 (t, 3 H, J = 7.3 Hz), 1.52-1.66 (m, 1 H), 1.75-1.89 (m, 2 H), 2.43 (s, 3 H), 3.58-3.72 (m, 2 H), 4.86-4.98 (m, 1 H), 6.65 (br s, 1 H), 7.33 (d, 2 H, J = 8.5 Hz), 7.76 (d, 2 H, J = 8.4 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 8.3, 21.6, 27.5, 64.0, 85.4, 85.6, 127.9 (2 C), 130.0 (2 C), 136.3, 138.9, 145.1 (2 C). IR (film): 3495, 2969, 1596, 1456, 1317, 1155, 1086, 956, 736, 706 cm^{-1} . MS (ES): 305 $[\text{M}+\text{Na}]^+$. Anal. calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4\text{S}$: C, 59.55; H, 6.43, S, 11.36. Found: C, 59.33; H, 6.59; S, 11.19.

3.11. Synthesis of (±)-(2*R*,5*S*)-5-Isopropyl-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, **28d**.

From monoepoxide **26d** (325 mg, 1.10 mmol), with CSA (51 mg, 0.22 mmol, 0.2 equiv), according to the general procedure (25 min), sulfonyl dihydrofuran **28d** (314 mg, 97%) was obtained after purification by chromatography (20-60% EtOAc-hexane) as a colorless oil.

Data of **28d**: R_f = 0.17 (40% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.68 (d, 3 H, J = 6.7 Hz), 1.00 (d, 3 H, J = 7.0 Hz), 1.75 (t, 1 H, J = 6.4 Hz), 2.15 (ap hept d, 1 H, J = 7.0, 1.8 Hz), 2.44 (s, 3 H), 3.63-3.70 (m, 2 H), 4.83-4.91 (m, 2 H), 6.60 (ap t, 1 H, J = 1.7 Hz), 7.35 (d, 2 H, J = 8.4 Hz), 7.77 (d, 2 H, J = 8.4 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 14.2, 19.8, 21.6, 31.9, 64.1, 86.3, 89.3, 128.0 (2 C), 130.0 (2 C), 136.2, 139.2, 144.6, 145.1. IR (film): 3513, 2968, 2932, 2874, 1785, 1622, 1596, 1558, 1466, 1387, 1318, 1154, 1130, 1085, 814, 706, 668, 584 cm^{-1} . EM (ES): 319 $[\text{M}+\text{Na}]^+$. Anal. calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4\text{S}$: C, 60.79; H, 6.80, S, 10.82. Found: C, 60.45; H, 6.61; S, 10.93.

3.12. Synthesis of (±)-(2*S*,5*S*)-5-Isopropyl-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, **29d**.

From monoepoxide **27d** (260 mg, 0.88 mmol), with CSA (41 mg, 0.17 mmol, 0.2 equiv), according to the general procedure (1 h), sulfonfyl dihydrofuran **29d** (258 mg, 99%) was obtained after purification by chromatography (20-60% EtOAc-hexane) as a colorless oil.

Data of **29d**: R_f = 0.17 (40% EtOAc-hexane). $^1\text{H NMR}$ (300 MHz) δ 0.71 (d, 3 H, J = 6.7 Hz), 0.99 (d, 3 H, J = 7.0 Hz), 1.79 (ap t, 1 H, J = 6.4 Hz), 2.07 (m, 1 H), 2.43 (s, 3 H), 3.59 (ddd, 1 H, J = 11.7, 6.9, 4.5 Hz), 3.71 (ddd, 1 H, J = 11.7, 5.9, 3.8 Hz), 4.80-4.87 (m, 1 H), 4.89-4.95 (m, 1 H), 6.65 (ap t, 1 H, J = 1.6 Hz), 7.33 (d, 2 H, J = 8.5 Hz), 7.77 (d, 2 H, J = 8.3 Hz). $^{13}\text{C NMR}$ (50 MHz) δ 14.2, 19.8, 21.6, 31.9, 64.1, 86.3, 89.4, 128.0 (2 C), 130.0 (2 C), 136.2, 139.1, 144.7, 145.1. IR (film): 3495, 2971, 2932, 2878, 1644, 1597, 1457, 1381, 1315, 1146, 1085, 987, 835, 669, 587 cm^{-1} . MS (ES): 319 $[\text{M}+\text{Na}]^+$. Anal. calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4\text{S}$: C, 60.79; H, 6.80, S, 10.82. Found: C, 60.82; H, 6.93; S, 10.71.

3.13. Synthesis of (±)-(2*R*,5*S*)-5-(*p*-Fluorophenyl)-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, **28g**.

From monoepoxide **26g** (350 mg, 1 mmol), with CSA (46 mg, 0.2 mmol, 0.2 equiv), according to the general procedure (30 min), sulfonfyl dihydrofuran **28g** (347 mg, 99%) was obtained after purification by chromatography (10-80% EtOAc-hexane) as a white solid that was recrystallized from EtOAc-hexane.

Data of **28g**: mp: 104-105 °C. R_f = 0.14 (10% EtOAc- CH_2Cl_2). $^1\text{H NMR}$ (200 MHz) δ 1.89 (t, 1 H, J = 6.2 Hz), 2.34 (s, 3 H), 3.79 (ddd, 1 H, J = 14.2, 6.4, 4.0 Hz), 3.85 (ddd, 1 H, J = 14.2, 6.2, 3.8 Hz), 5.04 (ddd, 1 H, J = 5.1, 3.8, 1.6 Hz), 5.84 (dd, 1 H, J = 5.0, 2.1 Hz), 6.74 (t, 2 H, J = 8.8 Hz), 6.99-7.11 (m, 5 H), 7.22-7.28 (m, 2 H). $^{13}\text{C NMR}$ (50 MHz) δ 21.5, 63.7, 85.6, 85.7, 115.1 (2 CH-3', $J_{\text{C-F}}$ = 21.7 Hz), 128.0 (2 C), 129.4 (2 C), 131.7 (2 CH-2', $J_{\text{C-F}}$ = 8.4 Hz), 133.3 (C-1' $J_{\text{C-F}}$ = 3.1 Hz), 136.0, 139.9, 144.6, 145.5, 163.0 (C-4', $J_{\text{C-F}}$ = 248.0 Hz). IR (KBr): 3498, 3066, 1603, 1507, 1323,

1221, 1152, 1123, 1084, 832, 812, 682, 588 cm^{-1} . **MS** (ES): 719 $[\text{2M+Na}]^+$, 371 $[\text{M+Na}]^+$ (100%), 366 $[\text{M+NH}_4]^+$. **Anal. calcd for** $\text{C}_{18}\text{H}_{17}\text{FO}_4\text{S}$: C, 62.05; H, 4.92, S, 9.20. **Found:** C, 61.76; H, 4.78; S, 8.97.

3.14. Synthesis of (±)-(2*S*,5*S*)-5-(*p*-Fluorophenyl)-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, **29g**.

From monoepoxide **27g** (530 mg, 1.52 mmol), with CSA (71 mg, 0.30 mmol, 0.2 equiv), according to the general procedure (1 h), sulfonyl dihydrofuran **29g** (523 mg, 99%) was obtained after purification by chromatography (20-80% EtOAc-hexane) as a white solid that was recrystallized from EtOAc.

Data of **29g**: mp: 173-174 °C. $R_f = 0.12$ (10% EtOAc-CH₂Cl₂). ¹H NMR (200 MHz) δ 1.91 (t, 1 H, $J = 6.4$ Hz), 2.34 (s, 3 H), 3.77 (m, 2 H), 5.21 (m, 1 H), 5.92 (dd, 1 H, $J = 6.0, 1.8$ Hz), 6.78 (t, 2 H, $J = 8.7$ Hz), 6.95-7.07 (m, 4 H), 6.97 (s, 1 H), 7.30 (d, 2 H, $J = 8.7$ Hz). ¹³C NMR (50 MHz) δ 21.5, 64.3, 86.1, 86.4, 115.3 (2 CH-3', $J_{C-F} = 21.8$ Hz), 128.0 (2 C), 129.2, 129.5 (2 C), 133.7, 136.2, 138.9, 144.7, 146.7, 163.1 (C-4', $J_{C-F} = 247.8$ Hz). IR (KBr): 3533, 1603, 1508, 1304, 1222, 1154, 1119, 1057, 823, 678, 594, 529 cm⁻¹. MS (ES): 719 [2M+Na]⁺ (100%), 371 [M+Na]⁺, 366 [M+NH₄]⁺. Anal. calcd for C₁₈H₁₇FO₄S: C, 62.05; H, 4.92, S, 9.20. Found: C, 62.23; H, 5.03; S, 9.05.

3.15. Synthesis of (±)-(2*R*,5*S*)-5-(*p*-Fluorophenyl)-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, **28g**, and (±)-(2*S*,5*S*)-5-(*p*-Fluorophenyl)-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, **29g**.

From a mixture of sulfonyl dienes **3g** and **4g** (316 mg, 1 mmol), with *m*-CPBA (1.23 g, 5 mmol, 5 equiv), according to the general procedure, after 3 days (disappearance of sulfonyl diene, TLC), CSA (46 mg, 0.2 mmol, 0.2 equiv) was added and the mixture was stirred until disappearance of monoepoxides (22 h). Purification by chromatography (10-80% EtOAc-hexane) of the crude product gave a 60:40 mixture of sulfonyl dihydrofurans **28g** and **29g** (293 mg, 84%) as a white solid.

3.16. Synthesis of (±)-(2*R*,5*S*)-5-(*p*-Fluorophenyl)-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, **28g, (±)-(2*S*,5*S*)-5-(*p*-Fluorophenyl)-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, **29g**, and (2*E*)-1-(*p*-Fluorophenyl)-2-(*p*-tolylsulfonyl)penta-2,4-dien-1-ol, **6g**.**

From a mixture of sulfinyl dienes **3g** and **4g** (8.86 g, 28 mmol), with *m*-CPBA ((27.61 g, 112 mmol, 4 equiv), according to the general procedure, after 3 days (disappearance of sulfonyl diene, ¹H NMR of an aliquot). The crude product was dissolved in CH₂Cl₂, CSA (1.3 g, 5.6 mmol, 0.2 equiv) was added and according to the general procedure (1 h) a 60:40 mixture of sulfonyl dihydrofurans **28g** and **29g** and traces of sulfonyl diene **6g** was obtained. Recrystallization of the crude gave pure **29g** (2.89 g, 30%) as a white solid. Purification by chromatography (10-80% EtOAc-hexane) of the mother liquors gave **6g** (42 mg, 0.4%) as a white solid that was recrystallized from EtOAc-hexane, **28g** (2.67 g, 27%) as a white solid and a mixture of **28g** and **29g** (2.83 g, 29%) .

Data of **6g**: mp: 100-101 °C. *R_f* = 0.43 (10% EtOAc-CH₂Cl₂). ¹H NMR (200 MHz) δ 2.37 (s, 3 H), 3.35 (d, 1 H, *J* = 7.3 Hz), 5.63 (d, 1 H, *J* = 10.1 Hz), 5.76 (d, 1 H, *J* = 16.8 Hz), 5.81 (d, 1 H, *J* = 7.3 Hz), 6.63 (ddd, 1 H, *J* = 16.7, 11.3, 9.9 Hz), 6.81 (t, 2 H, *J* = 8.8 Hz), 7.09 (m, 2 H), 7.16 (d, 2 H, *J* = 8.6 Hz), 7.43 (d, 1 H, *J* = 11.4 Hz), 7.48 (d, 2 H, *J* = 8.2 Hz). ¹³C NMR (50 MHz) δ 21.5, 68.7, 115.0 (2 CH *p*-F-C₆H₄, *J*_{C-F} = 21.7 Hz), 127.4 (2 CH *p*-F-C₆H₄, *J*_{C-F} = 8.0 Hz), 127.7 (2 C), 129.6 (2 C), 129.8, 129.9, 135.7, 137.1, 141.0, 142.0, 144.3, 162.0 (C *p*-F-C₆H₄, *J*_{C-F} = 246.1 Hz). IR (CCl₄): 3480, 3066, 2924, 1894, 1628, 1601, 1508, 1412, 1287, 1224, 1142, 1086, 1054, 945, 815, 673 cm⁻¹. MS (ES): 687 [2M+Na]⁺, 350 [M+NH₄]⁺ (100%). Anal. calcd for C₁₈H₁₇FO₃S: C, 65.04; H, 5.16; S, 9.65. Found: C, 65.04; H, 5.44; S, 9.86.

3.17. Synthesis of (±)-5,5-Dimethyl-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, **30.**

From sulfinyl diene **5** (410 mg, 1.64 mmol) and *m*-CPBA (1.62 g, 6.56 mmol, 4 equiv), according to the general procedure, after purification by chromatography (10-80% EtOAc-hexane), **30** (394 mg, 85%) was obtained as a pale yellow solid that was recrystallized from EtOAc-hexane.

Data of **30**: R_f = 0.19 (50% EtOAc-hexane). $^1\text{H NMR}$ (200 MHz) δ 1.32 (s, 3 H), 1.35 (s, 3 H), 2.01 (br s, 1 H), 2.42 (s, 3 H), 3.61 (dd, 1 H, J = 11.7, 4.6 Hz), 3.69 (dd, 1 H, J = 11.7, 4.0 Hz), 4.87 (dt, 1 H, J = 4.0, 1.5 Hz), 6.58 (d, 1 H, J = 1.5 Hz), 7.31 (d, 2 H, J = 8.1 Hz), 7.77 (d, 2 H, J = 8.4 Hz). $^{13}\text{C NMR}$ (75 MHz) δ 21.5, 27.5, 28.2, 63.9, 82.7, 88.1, 128.0 (2 C), 129.8 (2 C), 136.9, 138.7, 144.9, 149.4. IR (film): 3486, 2980, 2932, 2872, 1623, 1597, 1460, 1401, 1365, 1317, 1245, 1158, 816 cm^{-1} . MS (ES): 283 $[\text{M}+1]^+$, 265 $[\text{M}-\text{H}_2\text{O}+1]^+$ (100%).

3.18. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22e, and ($\pm$)-(2*R*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **23e**.**

See printed version of the paper.

3.19. Synthesis of ($\pm$)-(2*S*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **24e, and ($\pm$)-(2*S*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **25e**.**

See printed version of the paper.

3.20. Synthesis of (±)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-ethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22c, and (±)-(2*R*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-ethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **23c**.**

Conditions	22c:23c ratio	Yield (THF)
LiOO- <i>t</i> -Bu, -20 to 0 °C, 24 h	71:29	72%
KOO- <i>t</i> -Bu, -40 to 0 °C, 45 min	72:28	88%

From a solution of sulfonylethyl tetrahydrofuran **28c** (28 mg, 0.1 mmol), in THF (0.7 mL) and a cold (−65 to 0 °C) 0.2 M THF solution of LiOO-*t*-Bu (2 equiv), (24 h), according to the general procedure, a 71:29 mixture of sulfonylethyl tetrahydrofurans **22c** and **23c** was obtained. Purification by chromatography (20-60% EtOAc-hexane) gave a mixture of **22c** and **23c** (21 mg, 72%) as a colorless oil.

From a solution of sulfonylethyl tetrahydrofuran **28c** (166 mg, 0.59 mmol) in THF (6.0 mL) and a cold (−40 to 0 °C) 0.2 M THF solution of KOO-*t*-Bu (2 equiv), (45 min), according to the general procedure, a 72:28 mixture of sulfonylethyl tetrahydrofurans **22c** and **23c** was obtained. Purification by chromatography (15-30% EtOAc-hexane) gave mixture of **22c** and **23c** (154 mg, 88%) as a white solid that was recrystallized from 40% EtOAc-hexane to produce pure **22c** (78 mg, 45%).

Data of **22c**: R_f = 0.20 (15% EtOAc-CH₂Cl₂). ¹H NMR (300 MHz) δ 0.99 (t, 3 H, J = 7.4 Hz), 1.65-1.81 (m, 2 H), 1.98-2.12 (m, 1 H), 2.46 (s, 3 H), 3.68 (t, 2 H, J = 5.6 Hz), 3.96 (dd, 1 H, J = 11.5, 3.0 Hz), 4.08 (s, 1 H), 4.11 (t, 1 H, J = 5.9 Hz), 7.37 (d, 2 H, J = 8.1 Hz), 7.80 (d, 2 H, J = 8.3 Hz). ¹³C NMR (50 MHz) δ 10.6, 21.7, 26.3, 62.8, 64.4, 77.7, 77.8, 79.6, 128.9 (2 C), 130.0 (2 C), 133.5, 146.0. IR (KBr): 3513, 2981, 1561, 1305, 1151, 1021, 667, 592 cm^{−1}. MS (ES): 321 [M+Na]⁺. Anal. calcd for C₁₄H₁₈O₅S: C, 56.36; H, 6.08, S, 10.75. Found: C, 56.53; H, 6.39; S, 10.53.

Partial data of **23c** (from a 71:29 mixture of **22c** and **23c**): R_f = 0.20 (15% EtOAc-CH₂Cl₂). ¹H NMR (200 MHz) δ 3.74 (d, 2 H, J = 5.1 Hz), 3.98 (s, 1 H), 4.00 (t, 1 H, J = 5.1 Hz), 4.40 (dd, 1 H, J = 11.4, 2.9 Hz).

3.21. Synthesis of (±)-(2*S*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-ethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **25c, and 5-Ethyl-4-(*p*-tolylsulfonyl)furan-2-methanol, **31c**.**

From a solution of sulfonyl dihydrofuran **29c** (100 mg, 0.35 mmol) in THF (2.5 mL) and a cold (-60 to -20 °C) 0.2 M THF solution of $\text{KOO-}t\text{-Bu}$ (2 equiv), (2 h 10 min), according to the general procedure, a mixture of sulfonyl tetrahydrofuran **25c** and sulfonyl furan **31c** was obtained. Purification by chromatography (0-20% EtOAc- CH_2Cl_2) gave **31c** (4 mg, 4%) as a white solid and **25c** (59 mg, 56%) as a colorless oil.

Data of **25c**: $R_f = 0.19$ (15% EtOAc- CH_2Cl_2). $^1\text{H NMR}$ (300 MHz) δ 0.85 (t, 3 H, $J = 7.4$ Hz), 1.37-1.47 (m, 2 H), 1.66 (dd, 1 H, $J = 6.3, 5.0$ Hz), 2.46 (s, 3 H), 3.64-3.77 (m, 2 H), 3.95 (s, 1 H), 4.09 (dd, 1 H, $J = 5.1, 4.6$ Hz), 4.50 (dd, 1 H, $J = 7.4, 4.3$ Hz), 7.37 (d, 2 H, $J = 8.2$ Hz), 7.81 (d, 2 H, $J = 8.4$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ 9.8, 21.7, 23.1, 62.2, 64.7, 74.1, 77.7, 77.8, 129.0 (2 C), 129.9 (2 C), 133.5, 146.0. IR (film): 3445, 2934, 1596, 1456, 1327, 1148, 1102, 1050, 955, 815, 669, 592, 538 cm^{-1} . MS (ES): 321 $[\text{M}+\text{Na}]^+$. Anal. calcd for $\text{C}_{14}\text{H}_{18}\text{O}_5\text{S}$: C, 56.36; H, 6.08, S, 10.75. Found: C, 56.61; H, 6.27; S, 10.62.

Data of **31c**: $R_f = 0.25$ (15% EtOAc- CH_2Cl_2). $^1\text{H NMR}$ (300 MHz) δ 1.20 (t, 3 H, $J = 7.6$ Hz), 1.94 (br t, 1 H), 2.39 (s, 3 H), 2.96 (q, 2 H, $J = 7.6$ Hz), 4.49 (d, 2 H, $J = 5.0$ Hz), 6.42 (s, 1 H), 7.28 (d, 2 H, $J = 8.5$ Hz), 7.76 (d, 2 H, $J = 8.4$ Hz). $^{13}\text{C NMR}$ (50 MHz) δ 12.2, 20.5, 21.5, 57.1, 107.6, 122.5, 126.9 (2 C), 129.8 (2 C), 139.7, 144.1, 152.9, 160.9. IR (KBr): 3505, 2917, 1598, 1561, 1400, 1294, 1153, 1106, 1019, 970, 821, 756, 671, 596, 548 cm^{-1} . MS (ES): 303 $[\text{M}+\text{Na}]^+$.

3.22. Synthesis of (±)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-isopropyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22d, (±)-(2*R*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-isopropyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **23d**, and 5-Isopropyl-4-(*p*-tolylsulfonyl)furan-2-methanol, **31d**.**

From a solution of sulfonyl dihydrofuran **28d** (160 mg, 0.54 mmol), in THF (4.0 mL) and a cold (–20 to 0 °C) 0.2 M THF solution of LiOO-*t*-Bu (2 equiv), (6 h), according to the general procedure, a 83:17 mixture of sulfonyl tetrahydrofurans **22d** and **23d** and some sulfonyl furan **31d** was obtained. Purification by chromatography (5-20% EtOAc-CH₂Cl₂) gave **31d** (12 mg, 8%) as a white solid that was recrystallized from EtOAc-hexane and a mixture of **22d** and **23d** (130 mg, 78%) as a white solid that was recrystallized from 40% EtOAc-hexane to give a 93:7 mixture of **22d** and **23d** (93 mg, 56%).

Data of **22d**: R_f = 0.32 (15% EtOAc-CH₂Cl₂). ¹H NMR (300 MHz) δ 1.02 (d, 3 H, J = 7.0 Hz), 1.06 (d, 3 H, J = 6.6 Hz), 1.69 (dd, 1 H, J = 6.6, 5.1 Hz), 2.40 (m, 1 H), 2.45 (s, 3 H), 3.67-3.78 (m, 2 H), 3.97 (s, 1 H), 4.06 (d, 1 H, J = 2.8 Hz), 4.07 (t, 1 H, J = 6.7 Hz), 7.36 (d, 2 H, J = 8.1 Hz), 7.81 (d, 2 H, J = 8.3 Hz). ¹³C NMR (50 MHz) δ 17.6, 21.3, 21.7, 29.3, 62.0, 66.2, 77.8, 78.1, 84.5, 129.2 (2 C), 129.9 (2 C), 133.3, 146.0. IR (KBr): 3436, 2967, 1596, 1468, 1328, 1149, 1043, 815, 664, 582, 540 cm⁻¹. MS (ES): 335 [M+Na]⁺. Anal. calcd for C₁₅H₂₀O₅S: C, 57.67; H, 6.45, S, 10.26. Found: C, 57.92; H, 6.27; S, 10.49.

Partial data of **23d** (from an 83:17 mixture of **22d** and **23d**): R_f = 0.32 (15% EtOAc-CH₂Cl₂). ¹H NMR (200 MHz) δ 0.60 (d, 3 H, J = 6.8 Hz), 2.38 (s, 3 H), 3.88 (s, 1 H), 4.36 (d, 1 H, J = 2.8 Hz).

Data of **31d**: mp: 132-133 °C. R_f = 0.25 (10% EtOAc-CH₂Cl₂). ¹H NMR (300 MHz) δ 1.20 (d, 6 H, J = 7.0 Hz), 1.76 (br s, 1 H), 2.39 (s, 3 H), 3.72 (hept, 1 H, J = 7.0 Hz), 4.50 (d, 2 H, J = 6.0 Hz), 6.42 (s, 1 H), 7.28 (d, 2 H, J = 8.1 Hz), 7.77 (d, 2 H, J = 8.4 Hz). ¹³C NMR (75 MHz) δ 20.8 (2 C), 21.5, 26.6, 57.0, 107.5, 126.9 (2 C), 129.2, 129.8 (2 C), 139.6, 144.1, 152.7, 163.9. IR (KBr): 3514, 2981, 1596, 1561, 1319, 1305, 1296, 1151, 1108, 1064, 1021, 1014, 668, 592 cm⁻¹. MS (ES): 317 [M+Na]⁺. Anal. calcd for C₁₅H₁₈O₄S: C, 61.20; H, 6.16; S, 10.89. Found: C, 60.98; H, 6.09; S, 10.91.

3.23. Synthesis of (±)-(2*S*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-isopropyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **24d, and (±)-(2*S*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-isopropyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **25d**.**

From a solution of sulfonyl dihydrofuran **29d** (190 mg, 0.64 mmol), in THF (4.5 mL) and a cold (–60 to –20 °C) 0.2 M THF solution of KOO-*t*-Bu (2 equiv), (1 h 45 min), according to the general procedure, a 96:4 mixture of sulfonyl tetrahydrofurans **25d** and **24d** and some sulfonyl furan **31d** was

obtained. Purification by chromatography (0-15% EtOAc-CH₂Cl₂) gave **31d** (16 mg, 8%) as a white solid that was recrystallized from EtOAc-hexane and a 96:4 mixture of **25d** and **24d** (146 mg, 73%) as a colorless oil.

Partial data of **24d** (from a 96:4 mixture of **25d** and **24d**): $R_f = 0.25$ (10% EtOAc-CH₂Cl₂). ¹H NMR (200 MHz) δ 4.14 (s, 1 H), 4.18 (t, 1 H, $J = 5.1$ Hz), 4.37 (d, 1 H, $J = 2.9$ Hz).

Data of **25d** (from a 96:4 mixture of **25d** and **24d**): $R_f = 0.25$ (10% EtOAc-CH₂Cl₂). ¹H NMR (300 MHz) δ 0.68 (d, 3 H, $J = 6.8$ Hz), 0.96 (d, 3 H, $J = 7.1$ Hz), 1.80 (dd, 1 H, $J = 6.4, 4.9$ Hz), 1.87 (dhept, 1 H, $J = 6.9, 3.1$ Hz), 2.45 (s, 3 H), 3.63-3.76 (m, 2 H, CH₂-OH), 3.83 (s, 1 H), 4.04 (t, 1 H, $J = 5.1$ Hz), 4.47 (d, 1 H, $J = 3.0$ Hz), 7.36 (d, 2 H, $J = 7.9$ Hz), 7.81 (d, 2 H, $J = 8.4$ Hz). ¹³C NMR (50 MHz) δ 15.9, 20.2, 21.7, 29.4, 62.0, 64.0, 76.4, 77.1, 78.1, 129.1 (2 C), 129.8 (2 C), 133.5, 146.0. IR (film): 3534, 2967, 1596, 1467, 1327, 1158, 1091, 1050, 815, 706, 667, 586 cm⁻¹. MS (ES): 335 [M+Na]⁺. Anal. calcd for C₁₅H₂₀O₅S: C, 57.67; H, 6.45, S, 10.26. Found: C, 57.96; H, 6.66; S, 10.50.

3.24. Synthesis of (±)-(2*S*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22g**, and (±)-(2*S*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **23g**.

From a solution of sulfonylepoxide **28g** (530 mg, 1.52 mmol), in THF (11.0 mL) and a cold (0 °C) 0.2 M THF solution of LiOO-*t*-Bu (2 equiv), (2.5 h), according to the general procedure, an 87:13 mixture of sulfonylepoxide **22g** and **23g** and some sulfonylepoxide **31g** was obtained. Purification by chromatography (20-50% EtOAc-hexane) gave a mixture of **22g** and **23g** (454 mg, 82%) as a white solid that was recrystallized from 60% EtOAc-hexane to give pure **22g** (276 mg, 56%).

Data of **22g**: mp: 133-134 °C. $R_f = 0.20$ (50% EtOAc-hexane). ¹H NMR (200 MHz) δ 1.94 (br t, 1 H, $J = 5.0$ Hz), 2.42 (s, 3 H), 3.92 (t, 2 H, $J = 5.0$ Hz), 4.25 (t, 1 H, $J = 5.0$ Hz), 4.43 (s, 1 H), 5.05 (s, 1 H), 6.95 (t, 2 H, $J = 8.7$ Hz), 7.19-7.40 (m, 6 H). ¹³C NMR (50 MHz) δ 21.6, 62.5, 67.5, 78.8, 81.8, 115.0 (2 CH-3', $J_{C-F} = 21.7$ Hz), 129.0 (2 C), 129.6 (2 C), 130.8 (2 CH-2', $J_{C-F} = 8.4$ Hz), 131.0, 134.0, 145.7, 163.3 (C-4', $J_{C-F} = 248.4$ Hz). IR (KBr): 3515, 1511, 1326, 1221, 1161, 1139, 1059, 847, 668,

598, 544 cm^{-1} . **MS** (ES): 751 $[\text{2M}+\text{Na}]^+$ (100%), 387 $[\text{M}+\text{Na}]^+$, 365 $[\text{M}+1]^+$. **Anal. calcd for** $\text{C}_{18}\text{H}_{17}\text{FO}_5\text{S}$: C, 59.33; H, 4.70; S, 8.80. **Found**: C, 59.61; H, 4.83; S, 8.69.

Data of **23g** (from a 67:33 mixture of **22g** and **23g**): $R_f = 0.20$ (50% EtOAc-hexane). **^1H NMR (200 MHz)** δ 1.90 (br s, 1 H), 2.30 (s, 3 H), 3.85 (d, 2 H, $J = 5.5$ Hz), 4.17 (t, 1 H, $J = 5.5$ Hz), 4.41 (s, 1 H), 5.31 (s, 1 H), 6.76 (t, 2 H, $J = 8.8$ Hz), 7.00 (d, 2 H, $J = 8.4$ Hz), 7.14-7.39 (m, 4 H).

3.25. Synthesis of ($\pm$)-(2*S*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **24g, and ($\pm$)-(2*S*,3*S*,4*S*,5*S*)-3,4-Epoxy-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **25g**.**

From a solution of sulfonyl dihydrofuran **29g** (348 mg, 1 mmol), in THF (7.0 mL) and a cold (-50 to -15 $^\circ\text{C}$) 0.2 M THF solution of KOO-*t*-Bu (2 equiv), (25 min), according to the general procedure, a 93:7 mixture of sulfonyl tetrahydrofurans **25g** and **24g** was obtained. Purification by chromatography (20-60% EtOAc-hexane) gave **25g** (92 mg, 25%) as a white solid and a mixture of **25g** and **24g** (247 mg, 68%) that was recrystallized from 60% EtOAc-hexane. Thus, pure **25g** (185 mg, 50%) was isolated.

Partial data of **24g** (from a 93:7 mixture of **25g** and **24g**): $R_f = 0.21$ (50% EtOAc-hexane). **^1H NMR (200 MHz)** δ 2.41 (s, 3 H), 5.03 (s, 1 H).

Data of **25g**: mp: 142-143 $^\circ\text{C}$. $R_f = 0.23$ (50% EtOAc-hexane). **^1H NMR (200 MHz)** δ 1.96 (t, 1 H, $J = 5.3$ Hz), 2.32 (s, 3 H), 3.87 (ap t, 2 H, $J = 4.8$ Hz), 4.32 (t, 1 H, $J = 4.6$ Hz), 4.36 (s, 1 H), 5.51 (s, 1 H), 6.78 (t, 2 H, $J = 8.7$ Hz), 7.03 (d, 2 H, $J = 7.9$ Hz), 7.17-7.21 (m, 2 H), 7.36 (d, 2 H, $J = 8.2$ Hz). **^{13}C NMR (50 MHz)** δ 21.5, 62.4, 64.8, 76.3, 77.0, 77.5, 114.5 (2 CH-3', $J_{\text{C-F}} = 21.6$ Hz), 128.8 (2 C), 129.3 (2 C), 130.1, 130.3 (2 CH-2', $J_{\text{C-F}} = 8.4$ Hz), 133.4, 145.5, 163.3 (C-4', $J_{\text{C-F}} = 247.9$ Hz). **IR** (KBr): 3572, 3434, 2927, 1602, 1513, 1319, 1159, 668 cm^{-1} . **MS** (ES): 751 $[\text{2M}+\text{Na}]^+$ (100%), 387 $[\text{M}+\text{Na}]^+$. **Anal. calcd for** $\text{C}_{18}\text{H}_{17}\text{FO}_5\text{S}$: C, 59.33; H, 4.70; S, 8.80. **Found**: C, 59.70; H, 4.73; S, 8.52.

3.26. Synthesis of (±)-(2*S*,3*R*,4*R*)-3,4-Epoxy-5,5-dimethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22h, and (±)-(2*S*,3*S*,4*S*)-3,4-Epoxy-5,5-dimethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **23h**.**

From a solution of sulfonyl dihydrofuran **30** (56 mg, 0.2 mmol), in THF (1.4 mL) and a cold (0 °C) 0.2 M THF solution of KOO-*t*-Bu (2 equiv), (2 h), according to the general procedure, a 82:18 mixture of sulfonyl tetrahydrofurans **22h** and **23h** was obtained. Purification by chromatography (0-20% EtOAc-CH₂Cl₂) gave a mixture of **22h** and **23h** (50 mg, 84%) as a white solid that was recrystallized from EtOAc-hexane. Thus, a 95:5 mixture of **22h** and **23h** (36 mg, 60%) was obtained.

Data of **22h**: R_f = 0.21 (20% EtOAc-CH₂Cl₂). ¹H NMR (300 MHz) δ 1.05 (s, 3 H), 1.60 (s, 3 H), 1.76 (br s, 1 H), 2.45 (s, 1 H), 3.68 (d, 1 H, J = 5.9 Hz), 3.70 (d, 1 H, J = 6.1 Hz), 4.04 (s, 1 H), 4.09 (ap t, 1 H, J = 6.4 Hz), 7.36 (d, 2 H, J = 8.31 Hz), 7.81 (d, 2 H, J = 8.3 Hz). NOESY between: CH₂-OH/H-3 and CH₃ α /CH₂-OH. ¹³C NMR (75 MHz) δ 21.7, 23.2, 26.7, 62.7, 65.1, 76.7, 79.2, 80.2, 129.2 (2 C), 129.9 (2 C), 133.4, 146.0. MS (ES): 619 [2M+Na]⁺, 321 [M+Na]⁺, 316 [M+H₂O]⁺ (100%), 299 [M+1]⁺.

Partial data of **23h**: R_f = 0.21 (20% EtOAc-CH₂Cl₂). ¹H NMR (300 MHz) δ 1.25 (s, 3 H), 1.56 (s, 3 H), 2.44 (s, 1 H), 3.99 (s, 1 H).

4. Oxidations and Derivatizations

4.1. Synthesis of (2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-4-(*p*-tolylsulfonyl)-5-vinyl-tetrahydrofuran-2-methanol, **22a.**

From sulfynyl tetrahydrofuran **18a** (11 mg, 0.039 mmol) with MMPP (36 mg, 0.058 mmol, 1.5 equiv) in MeOH (1.5 mL), according to the general procedure, sulfonyl tetrahydrofuran **22a** (8 mg, 71%) was obtained after purification by chromatography (CH₂Cl₂-hexane) as a colorless oil.

4.2. Synthesis of the *p*-nitrobenzoate of (+)-(2*R*,3*R*,4*R*,5*S*,*S*_s)-3,4-Epoxy-4-(*p*-tolylsulfinyl)-5-vinyl-tetrahydrofuran-2-methanol, **32.**

From a solution of **18a** (14 mg, 0.05 mmol) in THF (0.5 mL) with Et₃N (14 μ L, 10 mg, 0.10 mmol), a catalytic amount of DMAP and *p*-nitrobenzoyl chloride (14 mg, 0.07 mmol) after 2 h from 0 $^\circ$ C to rt, *p*-nitrobenzoate **32** (14 mg, 65%) was obtained after standard extractive isolation and chromatography (CH₂Cl₂-50% EtOAc-CH₂Cl₂) as a white solid that was recrystallized from Et₂O.

Data of **32**: mp: 105-110 $^\circ$ C. R_f = 0.36 (15% EtOAc-CH₂Cl₂). $[\alpha]_D^{20}$ = +22.3 (c = 0.30) ¹H NMR (300 MHz) δ 2.42 (s, 3 H), 4.22 (d, 1 H, J = 8.3 Hz), 4.33 (s, 1 H), 4.43-4.47 (m, 3 H), 5.30 (d, 1 H, J = 16.9 Hz), 5.36 (d, 1 H, J = 10.2 Hz), 5.93 (ddd, 1 H, J = 16.9, 10.3, 8.3 Hz), 7.34 (d, 2 H, J = 8.2 Hz), 7.61 (d, 2 H, J = 8.2 Hz), 8.24 (d, 2 H, J = 8.9 Hz), 8.32 (d, 2 H, J = 8.9 Hz) ¹³C NMR (50 MHz) δ 21.6, 64.8, 65.3, 75.8, 79.9, 81.8, 121.9, 123.8 (2 C), 126.2 (2 C), 130.2 (2 C), 130.9 (2 C), 132.5, 134.7, 135.7, 143.6, 164.1. IR (CHCl₃): 3010, 2960, 1730, 1600, 1530, 1350, 1270, 1210, 1080, 1060, 1010, 750 cm⁻¹. MS (EI): 290, 150, 139, 120, 104, 91, 76, 65.

4.3. General Procedure for Oxidation of Sulfoxides to Sulfones with *m*-CPBA

To a solution of the sulfoxide in CH₂Cl₂ or acetone (10 mL/mmol), 3.0-6.0 equiv of K₂CO₃ was added. The mixture was cooled to 0 $^\circ$ C, 2.0 equiv of 70% *m*-CPBA was added and the reaction mixture was allowed to warm up slowly to rt and monitored by TLC. The reaction was quenched with 1 M aqueous Na₂S₂O₄ (3 mL/mmol) and a saturated solution of NaHCO₃ (3 mL/mmol) and water (3 mL/mmol). The layers were separated and the aqueous phase was extracted with CH₂Cl₂ (2 times, 5 mL/mmol). The organic layer was washed with a saturated solution of NaCl (4 mL/mmol), dried over MgSO₄, filtered and concentrated under reduced pressure to give a crude product that was purified by column chromatography.

4.4. Synthesis of (-)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-(1'-propenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22b.**

From sulfinyl tetrahydrofuran **18b** (6 mg, 0.020 mmol, 90:10 mixture), with *m*-CPBA (6 mg, 0.024 mmol, 1.2 equiv) in CH_2Cl_2 (0.4 mL), according to the general procedure (5 h 30 min), sulfonyl tetrahydrofuran **22b** (90:10 mixture) was obtained as a colorless oil after chromatography (20-50% EtOAc-hexane). The yield was not determined.

Data of **22b** (major isomer, from the 90:10 mixture): $R_f = 0.34$ (50% EtOAc- CH_2Cl_2). $[\alpha]_D^{20} = -68.9$ ($c = 0.29$). **^1H NMR (400 MHz)** δ 1.76 (dd, 3 H, $J = 6.4, 1.4$ Hz), 2.45 (s, 3 H), 3.73 (m, 2 H), 3.78 (br s, 1 H), 4.14 (t, 1 H, $J = 5.3$ Hz), 4.28 (s, 1 H), 4.31 (d, 1 H, $J = 9.2$ Hz), 5.59 (dq, 1 H, $J = 15.1, 6.4$ Hz), 5.74 (dd, 1 H, $J = 15.1, 9.3, 1.6$ Hz), 7.35 (d, 2 H, $J = 8.3$ Hz), 7.73 (d, 2 H, $J = 8.3$ Hz). **^{13}C NMR (50 MHz)** δ 17.8, 21.8, 62.9, 65.1, 78.7, 79.7, 126.7, 129.2 (2 C), 129.8 (2 C), 132.8, 145.9, 153.4. **IR** (CHCl_3): 3460, 2920, 2880, 2820, 1580, 1420, 1310, 1240, 1130, 1020 cm^{-1} .

Partial data of **22b'** (minor isomer, from the 90:10 mixture): **^1H NMR (400 MHz)** δ 4.07 (t, 1 H, $J = 5.2$ Hz), 4.10 (d, 1 H, $J = 7.2$ Hz).

4.5. Synthesis of ($\pm$)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-ethyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22c.**

From sulfinyl tetrahydrofuran **18c** (14 mg, 0.05 mmol) in MeOH (0.5 mL) and MMPP (62 mg, 0.1 mmol), according to the general procedure (3 h), after chromatography (5-40% EtOAc-hexane), sulfonyl tetrahydrofuran **22c** (12 mg, 80%) was obtained as a colorless oil.

4.6. Synthesis of (±)-(2*R*,5*S*,*S_S*)-5-Isopropyl-4-(*p*-tolylsulfonyl)-2,5-dihydrofuran-2-methanol, **28d**.

From a mixture of sulfinyl dihydrofurans **16d** and **17d** (14 mg, 0.05 mmol) in MeOH (0.5 mL) and MMPP (62 mg, 0.1 mmol), according to the general procedure (2 h), after chromatography (10-60% EtOAc-hexane), an 80:20 mixture of sulfonyl dihydrofurans **28d** and **29d** (11 mg, 74%) was obtained as a colorless oil.

4.7. Synthesis of (±)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-isopropyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22d**.

From an 84:8:8 mixture of sulfinyl tetrahydrofurans **18d-20d** (32 mg, 0.11 mmol) in CH₂Cl₂ (1.1 mL) and *m*-CPBA (53 mg, 0.22 mmol), according to the general procedure (3 h), after chromatography (5-50% EtOAc-hexane), sulfonyl tetrahydrofurans **22d-24d** (29 mg, 84%, 84:8:8 mixture) was obtained as a colorless oil.

4.8. Synthesis of (±)-(2*R*,5*S*)-4-(*p*-Tolylsulfonyl)-5-phenyl-2,5-dihydrofuran-2-methanol, **28e**.

From sulfinyl dihydrofurans **16e** and **17e** (40 mg, 0.13 mmol, 71:29 mixture of isomers) in MeOH (1.3 mL) and MMPP (126 mg, 0.26 mmol), according to the general procedure (45 min), after

chromatography (10-60% EtOAc-hexane), sulfonyl tetrahydrofuran **28e** and **29e** (15 mg, 65%, 69:31 mixture) was obtained as a white solid.

4.9. Synthesis of (2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-phenyl-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22e.**

From sulfinyl tetrahydrofurans **18e-20e** (22 mg, 0.066 mmol, 74:14:12 mixture of isomers) in MeOH (0.8 mL) and MMPP (41 mg, 0.099 mmol), according to the general procedure (1 h), after chromatography (10-30% EtOAc-hexane) and recrystallization of the 74:14:12 mixture (CH₂Cl₂-hexane), sulfonyl tetrahydrofuran **22e** (15 mg, 65%, 88:6:6 mixture) was obtained as a white solid.

Data of **22e** (from the 88:6:6 mixture): **mp**: 135-140 °C. *R_f* = 0.26 (50% EtOAc-hexane). $[\alpha]_D^{20} = -52.8$ (*c* = 0.46). Additional data for **22e**, as well as for **23e** and **24e** was identical to that described before.

4.10. Synthesis of (±)-(2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-(*p*-fluorophenyl)-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22g.**

From a 67:33 mixture of sulfinyl tetrahydrofurans **18g** and **19g** (5 mg, 0.014 mmol) in CH₂Cl₂ (0.5 mL) and *m*-CPBA (7 mg, 0.028 mmol), according to the general procedure (4 h), a 67:33 mixture of sulfonyl tetrahydrofurans **22g** and **23g** was obtained.

4.11. Synthesis of (±)-(2*S*,3*R*,4*R*)-5,5-Dimethyl-3,4-epoxy-4-(*p*-tolylsulfonyl)tetrahydrofuran-2-methanol, **22h.**

From a 59:41 mixture of sulfinyl tetrahydrofurans **18h** and **19h** (3 mg, 0.011 mmol) in CH_2Cl_2 (0.5 mL) and *m*-CPBA (6 mg, 0.022 mmol), according to the general procedure (2 h), a 59:41 mixture of sulfonyl tetrahydrofurans **22h** and **23h** was obtained.

1. Watson, S. C.; Eastham, J. E. *J. Organomet. Chem.* **1967**, 9, 165-168.