Supporting Information for

Sulfur-Directed Enantioselective Synthesis of Functionalized Dihydropyrans

Roberto Fernández de la Pradilla, Mariola Tortosa, Nadia Lwoff, Miguel A. del Águila, Alma Viso.*

Instituto de Química Orgánica General, CSIC, Juan de la Cierva, 3, 28006 Madrid, Spain.

Fax: (+34) 915644853

E-mail: iqofp19@iqog.csic.es

Table of Contents

Materials and methods S6

1.Synthesis of sulfinyl vinyl stannanes S6

1.1. General procedure for the synthesis of 1-sulfinyl alkenyl tributylstannanes S6

1.2. Synthesis of (–)-(*S*)-[(*E*)-2-Phenyl-1-(*p*-tolylsulfinyl)vinyl]tributylstannane, **3a** S7

1.3. Synthesis of (–)-(*S*)-[(*Z*)-2-Phenyl-1-(*p*-tolylsulfinyl)vinyl]tributylstannane, **4a** S7

2. Synthesis of iodo vinyl sulfoxides S8

2.1. General procedure for the synthesis of 1-iodo-1-sulfinyl alkenes S8

2.2. Synthesis of (+)-(*S*)-(*Z*)-2-Phenyl-1-(*p*-tolylsulfinyl)-1-iodoethene, **6a** S8

2.3. Synthesis of (–)-(*S*)-(*E*)-2-Phenyl-1-(*p*-tolylsulfinyl)-1-iodoethene, **5a** S9

3. Synthesis of hydroxyl sulfinyl dienes S9

3.1. General method for the preparation of hydroxy 4-sulfinyl dienes S9

3.2. Synthesis of (–)-(*S*)-2-(*Z*)-4-(*Z*)-5-Phenyl-4-(*p*-tolylsulfinyl)penta-2,4-dien-1-ol, **8a** S10

3.3. Synthesis of (–)-(*R*)-2-(*Z*)-4-(*Z*)-4-(*p*-Tolylsulfinyl)nona-2,4-dien-1-ol, **8b** S10

3.4. Synthesis of (–)-(*R*)-3-(*Z*)-5-(*Z*)-5-(*p*-Tolylsulfinyl)deca-3,5-dien-1-ol, **8c** S11

3.5. Synthesis of 4-(*Z*)-6-(*Z*)-(*p*-Tolylsulfinyl)undeca-4,6-dien-1-ol, **8d** S12

3.6. Synthesis of (–)-(2*S*,S_S)-3-(*Z*)-5-(*Z*)-6-Phenyl-5-(*p*-tolylsulfinyl)hexa-3,5-dien -2-ol, **8e**, and (2*R*,S_S)-3-(*Z*)-5-(*Z*)-6-Phenyl-5-(*p*-tolylsulfinyl)hexa-3,5-dien-2-ol, **8f** S12

3.7. Synthesis of (–)-(*S*)-2-(*Z*)-4-(*Z*)-3-Methyl-5-phenyl-4-(*p*-tolylsulfinyl)penta-2,4 -dien-1-ol, **8g** S13

3.8. Synthesis of (–)-(*S*)-2-(*Z*)-4-(*Z*)-3-Methyl-4-(*p*-tolylsulfinyl)nona-2,4-dien-1-ol, **8h** S14

3.9. Synthesis of (+)-(*S*)-2-(*Z*)-4-(*E*)-5-Phenyl-4-(*p*-tolylsulfinyl)penta-2,4-dien-1-ol, **9a** S15

3.10. Synthesis of (+)-(*R*)-2-(*Z*)-4-(*E*)-4-(*p*-Tolylsulfinyl)nona-2,4-dien-1-ol, **9b** S15

4. Synthesis of sulfinyl dihydropyrans and oxepines S16

4.1. General procedures for the synthesis of 3-sulfinyl-3,6-dihydro-2*H*-pyrans S16

4.2. Synthesis of (–)-(2*S*,3*R*,R_S)-2-Phenyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, **10a** S17

4.3. Synthesis of (–)-(2*S*,3*R*,R_S)-2-*n*-Butyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, **10b** S18

4.4. Attempts to capture the intermediate anion formed in cyclization reactions S19

4.5. Synthesis of (+)-(2*S*,3*S*,R_S)-2-Phenyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2H-pyran, **11a** S20

4.6. Synthesis of (2*S*,3*S*,R_S)-2-*n*-Butyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, **11b** and (–)-(3*R*,6*S*)-6-*n*-Butyl-3,6-dihydro-2*H*-pyran-3-ol, **14b** S21

4.7. Synthesis of (–)-(2*S*,3*R*,6*S*,R_S)-6-Methyl-2-phenyl-3-(*p*-tolylsulfinyl)-3,6-

dihydro-2*H*-pyran, **10e** S22
4.8. Synthesis of (2*S*,3*R*,6*R*,R_S)-6-Methyl-2-phenyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, **10f** S23
4.9. Synthesis of (2*S*,3*R*)-4-Methyl-2-phenyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, **10g** S23
4.10. Synthesis of (2*S*,3*R*)-2-*n*-Butyl-4-methyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, **10h** S24
4.11. Synthesis of (+)-(2*R*,3*S*,R_S)-2-Phenyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, **16a** S25
4.12. Synthesis of (–)-(2*R*,3*R*,R_S)-2-*n*-Butyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, **15b** S25
4.13. Synthesis of (–)-(2*S*,3*R*)-2-*n*-Butyl-3-(*p*-tolylsulfinyl)-2,3,6,7-tetrahydrooxepine, **17c** S27
5. Synthesis of allylic sulfones S28
5.1. General procedure for the oxidation of allylic sulfoxides S28
5.2. Synthesis of (–)-(2*S*,3*R*)-2-Phenyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, **20a** S29
5.3. Synthesis of (–)-(2*R*,3*S*)-2-Phenyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, ***ent*-20a** S29
5.4. Synthesis de (–)-(2*S*,3*R*)-2-*n*-Butyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, **20b** S30
5.5. Synthesis of (+)-(2*S*,3*S*)-2-Phenyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, **21a** S30
5.6. Synthesis of (–)-(2*R*,3*R*)-2-*n*-Butyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, ***ent*-21b** S31
5.7. Synthesis of (+)-(2*S*,3*S*)-2-*n*-Butyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, **21b** S31
5.8. Synthesis of (–)-(2*S*,3*R*,6*R*)-6-Methyl-2-phenyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, **20f** S32
5.9. Synthesis of (–)-(2*S*,3*R*)-4-Methyl-2-phenyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, **20g** S32
5.10. Synthesis of (–)-(2*R*,3*R*)-2-*n*-Butyl-4-methyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, **20h** S33
5.11. Synthesis of 2-*n*-Butyl-3-(*p*-tolylsulfonyl)-2,3,6,7-tetrahydro-oxepines, **22c**, **23c** S34
6. Synthesis of tetrahydropyranyl diols S34
6.1. General procedure for the dihydroxylation of dihydropyrans S34
6.2. Synthesis of (+)-(3*S*,4*S*,5*S*,6*S*)-4-Methyl-6-phenyl-5-(*p*-tolylsulfonyl)tetrahydro-2*H*-

pyran-3,4-diol, **24g** S35
6.3. Synthesis of (+)-(3*S*,4*S*,5*R*,6*S*)-6-Phenyl-5-(*p*-tolylsulfonyl)tetrahydro-2*H*-pyran-3,4-diol, **24a** S35
6.4. Synthesis of (−)-(3*S*,4*S*,5*R*,6*S*)-6-*n*-Butyl-5-(*p*-tolylsulfonyl)tetrahydro-2*H*-pyran-3,4-diol, **24b** S37
7. Exploratory transformations of sulfonyl diols S37
7.1. Synthesis of (−)-(3*R*,6*S*)-6-Phenyl-5-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran-3-ol, **25** S38
7.2. Synthesis of (−)-(2*S*,3*R*,4*R*,5*S*)-2-Phenyl-3-(*p*-tolylsulfonyl)-3,4-epoxytetrahydro-2*H*-pyran-5-ol, **26** S39
7.3. Synthesis of (−)-(2*S*)-[(2*S*,3*R*,4*R*,5*S*)-2-Phenyl-3-(*p*-tolylsulfonyl)-3,4-epoxytetrahydro-2*H*-pyran-5-yl]-2-methoxy-2-phenylacetate **28**, and (2*R*)-[(2*S*,3*R*,4*R*,5*S*)-2-Phenyl-3-(*p*-tolylsulfonyl)-3,4-epoxytetrahydro-2*H*-pyran-5-yl]-2-methoxy-2-phenylacetate, **29** S40
7.4. Synthesis of (2*S*,4*S*,5*S*)-4-Bromo-5-hydroxy-2-phenyldihydro-2*H*-pyran-3(4*H*)-one, **(*S*)-30**, and (2*S*,4*R*,5*S*)-4-Bromo-5-hydroxy-2-phenyldihydro-2*H*-pyran-3(4*H*)-one, **(*R*)-30** S41
7.5. Synthesis of (2*S*,5*R*)-5-Hydroxy-2-phenyldihydro-2*H*-pyran-3(4*H*)-one, **31**, and (*R*)-4,5-dihydroxy-1-phenylpentan-2-one, **32** S42
7.6. Synthesis of (+)-(2*S*,3*S*,5*R*)-2-Phenyltetrahydro-2*H*-pyran-3,5-diol, **33** S42
8. Synthesis of vinyl, dienyl and allyl sulfoximines S43
8.1. General procedure for the imination of sulfoxides S43
8.2. Synthesis of (−)-(*S*)-[(*E*)-1-(*S*-*p*-Tolyl-*N*-tosylsulfoximinoyl)hex-1-enyl] tributylstannane, **35** S43
8.3. Synthesis of (−)-(*S*)-[(*Z*)-1-(*S*-*p*-Tolyl-*N*-tosylsulfoximinoyl)hex-1-enyl] tributylstannane, **36** S44
8.4. Synthesis of (+)-(*S*)-[(*E*)-1-Phenyl-1-(*S*-*p*-tolyl-*N*-tosylsulfoximinoyl)]hex-1-ene, **38**, and (−)-(*R*)-[(*E*)-1-(*S*-*p*-tolyl-*N*-tosylsulfoximinoyl)]hex-1-ene, **39** S45
8.5. Synthesis of (+)-(*S*)-(*Z*)-1-(*S*-*p*-Tolyl-*N*-tosylsulfoximinoyl)-1-iodohex-1-ene, **37** S46
8.6. Synthesis of (+)-(*R*)-2-(*Z*)-4-(*Z*)-4-(*S*-*p*-Tolyl-*N*-tosylsulfoximinoyl)nona-2,4-dien-1-ol, **41** S46
8.7. Synthesis of (+)-(*R*)-2-(*Z*)-4-(*E*)-4-(*S*-*p*-Tolyl-*N*-tosylsulfoximinoyl)nona-2,4-dien-1-ol, **40** S47

8.8. Synthesis of (–)-(2*S*,3*R*,R_S)-2-*n*-Butyl-3-(*S*-*p*-tolyl-*N*-tosylsulfoximinoyl)-3,6-dihydro-2*H*-pyran, **42** and (+)-(2*R*,3*S*,R_S)-2-*n*-Butyl-3-(*S*-*p*-tolyl-*N*-tosylsulfoximinoyl) -3,6-dihydro-2*H*-pyran, **43** S48
8.9. Synthesis of (–)-(2*S*,3*R*,R_S)-2-*n*-Butyl-3-(*S*-*p*-tolyl-*N*-tosylsulfoximinoyl)-3,6-dihydro-2*H*-pyran, **42** S49
8.10. Synthesis of (+)-(2*S*,3*S*,R_S)-2-*n*-Butyl-3-(*S*-*p*-tolyl-*N*-tosylsulfoximinoyl)-3,6-dihydro-2*H*-pyran, **44** S50
8.11. Synthesis of (–)-(2R*S*,3*R*,R_S)-2-*n*-Butyl-3-(*S*-*p*-tolyl-*N*-tosylsulfoximinoyl)-3,6-dihydro-2*H*-pyran, **45** S50
9. Allylic displacements of sulfones and sulfoximines with organocuprates S51
9.1. General procedure for S_N2' alkylation of allylic sulfones and allylic sulfoximines S51
9.2. S_N2' alkylation of allylic sulfones S52
9.2.1. Synthesis of (–)-(3*R*,6*R*)-3,6-Di-*n*-butyl-3,6-dihydro-2*H*-pyran, **46a** S52
9.2.2. Synthesis of (2*Z*,4*Z*)-4-(*p*-Tolylsulfonyl)nona-2,4-dien-1-ol, **49** S53
9.2.3. Synthesis of (±)-2-*n*-Butyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, **20b** S53
9.2.4. Synthesis of (–)-(3*R*,6*S*)-6-*n*-Butyl-3-methyl-3,6-dihydro-2*H*-pyran, **46c** and (2*Z*,4*E*)-4-(*p*-Tolylsulfonyl)nona-2,4-dien-1-ol, **47** S54
9.2.5. Synthesis of (–)-(3*S*,6*S*)-6-*n*-Butyl-3-phenyl-3,6-dihydro-2*H*-pyran, **46d** S54
9.2.6. Synthesis of (3*S*,6*R*)-3-*n*-Butyl-6-phenyl-3,6-dihydro-2H-pyran, **48e** S55
9.3. S_N2' alkylation of allylic sulfoximines S55
9.3.1. Synthesis of (–)-(3*R*,6*R*)-3,6-Di-*n*-butyl-3,6-dihydro-2*H*-pyran, **46a** S55
9.3.2. Synthesis of (–)-(3*R*,6*S*)-6-*n*-Butyl-3-methyl-3,6-dihydro-2*H*-pyran, **46c** S56
9.3.3. Synthesis of (3*R*,6*R*)-3,6-Di-*n*-butyl-3,6-dihydro-2*H*-pyran, ***ent*-48a** S56
10. Dihydroxylation and epoxidation of S_N2' products S57
10.1. Synthesis of (–)-(2*S*,3*R*,4*R*,5*R*)-2,5-Di-*n*-butyltetrahydro-2*H*-pyran-3,4-diol, **50a** S57
10.2. Synthesis of (–)-(2*S*,3*R*,4*R*,5*R*)-2-*n*-Butyl-5-phenyltetrahydro-2*H*-pyran-3,4-diol, **50d** S57
10.3. Synthesis of the diacetate of (–)-(2*S*,3*S*,4*R*,5*S*)-2,5-Di-*n*-butyltetrahydro-2*H*-pyran-3,4-diol, **51a** S58
10.4. General procedure for the epoxidation of dihydropyrans S58
10.5. Synthesis of (–)-(1*S*,2*S*,5*S*,6*R*)-2,5-Di-*n*-butyl-3,7-dioxabicyclo[4.1.0]heptane, **52**, and (–)-(1*R*,2*S*,5*S*,6*S*)-2,5-di-*n*-butyl-3,7-dioxabicyclo[4.1.0]heptane, **53** S59

Materials and methods

Reagents and solvents were handled using standard syringe techniques. All reactions were carried out under an argon atmosphere. Hexane, toluene, CH_3CN and CH_2Cl_2 were distilled from CaH_2, and THF and Et_2O from sodium. 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 and 0.3% ninhydrin solution with 3% AcOH. All reagents were commercial products. Through this section, the volume of solvents is reported in mL/mmol of starting material. ^{1}H and ^{13}C NMR spectra were recorded at 200, 300, 400 or 500 MHz (^{1}H) using $CDCl_3$ as solvent and with the residual solvent signal as internal reference ($CDCl_3$, 7.24 and 77.0 ppm) unless otherwise noted. The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), ap (apparent). Melting points are uncorrected. Optical rotations were measured at 20 ºC 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. Alkynyl sulfoxides **1a-b**,[1] sulfinyl alkenyl tributylstannanes **3b** and **4b**,[2] iodo vinyl sulfoxides **5b** and **6b**,[2] and hydroxy vinyl stannanes **7a-e**,[3] were prepared as described in the literature.

1. Synthesis of sulfinyl vinyl stannanes.

1.1. General procedure for the synthesis of 1-sulfinyl alkenyl tributylstannanes.

To a solution of alkynyl sulfoxide in anhydrous toluene (6 mL/mmol sulfoxide) at rt under argon, $Pd(Ph_3P)_4$ (0.02 equiv) was added. The mixture was cooled to −78 ºC and a solution of 1.1 equiv of freshly distilled Bu_3SnH in toluene (1 mL/mmol sulfoxide) was added. The mixture was stirred and warmed up to room temperature until disappearance of starting material was observed (TLC). Solvent was removed and the crude product was purified by column chromatography on silica gel with the appropriate combination of solvents. Alternatively, the uncatalyzed protocol entailed the addition of a solution of 1.1 equiv of freshly distilled Bu_3SnH in toluene (3 mL/ mmol sulfoxide) to a solution of alkynyl sulfoxide in toluene (5 mL/mmol) at rt, under argon. The mixture was stirred at rt until

---

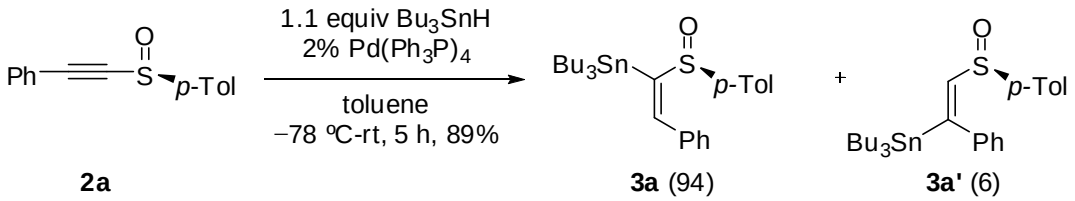
[1] (a) Louis, C.; Mill, S.; Mancuso, V.; Hootelé, C. *Can. J. Chem.* **1994**, *72*, 1347-1350. (b) Kosugi, H.; Kitaoka, M.; Tagami, K.; Takahashi, A.; Uda, H. *J. Org. Chem.* **1987**, *52*, 1078-1082.

[2] Paley, R. S.; de Dios, A.; Estroff, L. A.; Lafontaine, J. A.; Montero, C.; McCulley, D. J.; Rubio, M. B.; Ventura, M. P.; Weers, H. L.; Fernández de la Pradilla, R.; Castro, S.; Dorado, R.; Morente, M. *J. Org. Chem.* **1997**, *62*, 6326-6343.

[3] (a) Jung, M. E.; Light, L. A. *Tetrahedron Lett.* **1982**, *23*, 3851-3854. (b) Havránek, M.; Dvorák, D. *Synthesis* **1998**, 1264-1268. (c) Miura, K.; Wang, D.; Matsumoto, Y.; Hosomi, A. *Org. Lett.* **2005**, *7*, 503-505.

disappearance of starting material was observed (TLC). The solvent was removed and the crude product was purified by column chromatography on silica gel with the appropriate combination of solvents.

1.2. Synthesis of (–)-(*S*)-[(*E*)-2-Phenyl-1-(*p*-tolylsulfinyl)vinyl]tributylstannane, 3a.

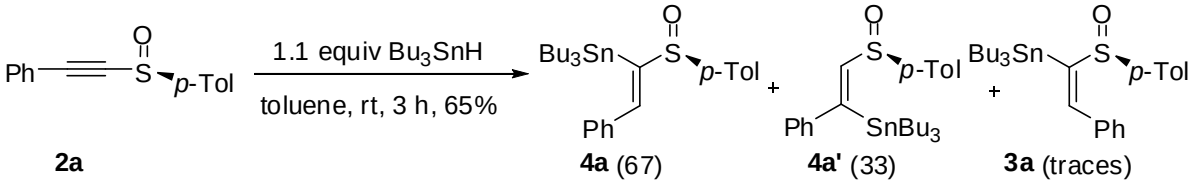


From alkynyl sulfoxide **2a** (4.55 g, 18.93 mmol), Bu_3SnH (6.52 mL, 20.82 mmol) and $Pd(Ph_3P)_4$ (437 mg, 0.38 mmol), according to the general procedure (5 h) a 94:6 mixture of stannanes **3a** and **3a'** was obtained. Purification by chromatography (2-50% EtOAc-hexane) afforded **3a** (8.25 g, 16.00 mmol, 84%) and **3a'** (488 mg, 0.95 mmol, 5%), as colorless oils.

Data for **3a**: R_f = 0.45 (30% EtOAc-hexane). $[\alpha]^{20}_D$ = –280.0 (*c* = 1.10). **^{1}H NMR (300 MHz)** δ 0.83 (t, 9 H, *J* = 7.1 Hz, Me-*n*-Bu), 0.86-1.00 (m, 6 H, *n*-Bu), 1.16-1.28 (m, 6 H, *n*-Bu), 1.29-1.48 (m, 6 H, *n*-Bu), 2.37 (s, 3 H, Me-*p*-Tol), 7.16 (s, 1 H, H-2), 7.22 (d, 2 H, *J* = 7.8 Hz), 7.32-7.42 (m, 5 H), 7.47 (d, 2 H, *J* = 7.8 Hz). **^{13}C NMR (50 MHz)** δ 11.9 (3 C), 13.6 (3 C), 21.2 (Me-*p*-Tol), 27.3 (3 C), 28.8 (3 C), 124.8 (2 C), 128.6 (2 C), 128.7, 129.6 (4 C), 136.3, 140.1, 141.7, 144.8, 159.8. **IR** (film): 3054, 3021, 2955, 2922, 2870, 2852, 1585, 1565, 1490, 1463, 1376, 1179, 1076, 1038, 922, 877, 807, 748 cm^{-1}. **MS** (ES): 475 $[(M–Bu)+1]^+$ (100%).

Data for (–)-(*R*)-[(*E*)-1-Phenyl-2-(*p*-tolylsulfinyl)vinyl]tributylstannane, **3a'**: R_f = 0.15 (10% EtOAc-hexane). $[\alpha]^{20}_D$ = –169.9 (*c* = 1.10). **^{1}H NMR (200 MHz)** δ 0.79 (t, 9 H, *J* = 7.0 Hz, Me-*n*-Bu), 0.86-0.92 (m, 6 H, *n*-Bu), 1.10-1.46 (m, 12 H, *n*-Bu), 2.37 (s, 3 H, Me-*p*-Tol), 6.43 (s, 1 H, H-2), 7.06 (m, 2 H), 7.22-7.42 (m, 7 H). **^{13}C NMR (50 MHz)** δ 10.5 (3 C), 13.5 (3 C), 21.3 (Me-*p*-Tol), 27.1 (3 C), 28.6 (3 C), 124.3 (2 C), 126.3 (2 C), 126.6, 128.4 (2 C), 129.8 (2 C), 140.7, 141.9, 142.1, 144.2, 159.5. **IR** (film): 3050, 3014, 2949, 2925, 2869, 2847, 1596, 1491, 1463, 1079, 1041, 807, 739 cm^{-1}. **MS** (ES): 1085 $[2M+Na]^+$, 1063 $[2M+1]^+$ (100%).

1.3. Synthesis of (–)-(*S*)-[(*Z*)-2-Phenyl-1-(*p*-tolylsulfinyl)vinyl]tributylstannane, 4a.



From alkynyl sulfoxide **2a** (514 mg, 2.14 mmol) and Bu_3SnH (0.74 mL, 2.35 mmol, 1.1 equiv), according to the general procedure (3 h) a 67:33 mixture of stannanes **4a** and **4a'** and traces of **3a** was obtained. Purification by chromatography (2-15% EtOAc-hexane) afforded **3a** (10 mg, 0.02 mmol, 1%), **4a'** (277 mg, 0.52 mmol, 24%) and **4a** (454 mg, 0.85 mmol, 40%) all as colorless oils.

Data for **4a**: R_f = 0.45 (30% EtOAc-hexane). $[\alpha]^{20}_D$ = −72.0 (*c* = 1.30). **^{1}H NMR (300 MHz)** δ 0.63-0.67 (m, 6 H), 0.74 (t, 9 H, *J* = 7.0 Hz), 1.05-1.16 (m, 12 H), 2.38 (s, 3 H, Me-*p*-Tol), 7.25-7.38 (m, 7 H), 7.53 (d, 2 H, *J* = 8.3 Hz), 8.22 (s, 1 H). **^{13}C NMR (75 MHz)** δ 11.6 (3 C), 13.5 (3 C), 21.4 (Me-*p*-Tol), 27.1 (3 C), 28.6 (3 C), 127.0 (2 C), 128.0 (2 C), 128.3 (2 C), 128.4, 129.9 (2 C), 138.1, 141.2, 141.7, 143.1, 151.1. **IR** (film): 2955, 2922, 2870, 2853, 1596, 1491, 1463, 1376, 1081, 1050, 808, 746 cm^{-1}. **MS** (ES): 533 $[M+1]^+$ (100%).

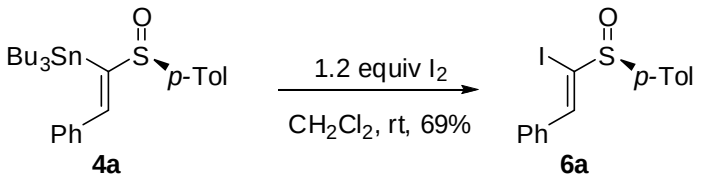
Data for (*R*)-[(*Z*)-1-Phenyl-2-(*p*-tolylsulfinyl)vinyl]tributylstannane, **4a'**: R_f = 0.22 (10% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 0.84 (t, 9 H, *J* = 7.0 Hz, Me), 1.06-1.52 (m, 18 H), 2.38 (s, 1 H, Me-*p*-Tol), 6.88 (s, 1 H, H-2), 7.01 (m, 2 H), 7.16-7.30 (m, 5 H), 7.52 (d, 2 H, *J* = 8.1 Hz).

2. Synthesis of iodo vinyl sulfoxides.

2.1. General procedure for the synthesis of 1-iodo-1-sulfinyl alkenes.

To a solution of 1.0 equiv of sulfinyl vinyl stannane in CH_2Cl_2 (5 mL/mmol sulfoxide) at rt under argon, a solution of 1.2 equiv of I_2 in CH_2Cl_2 (6 mL/mmol sulfoxide) was added. The mixture was stirred at rt until disappearance of starting material (TLC), and then it was quenched with a $Na_2S_2O_4$ solution (2 mL/mmol, 1 M) and diluted with EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (2 x 4 mL/mmol sulfoxide). The combined organic layers were washed with brine, dried under $MgSO_4$, filtered and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel.

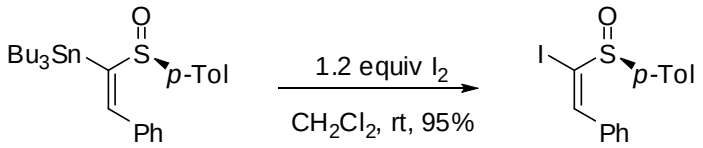
2.2. Synthesis of (+)-(*S*)-(*Z*)-2-Phenyl-1-(*p*-tolylsulfinyl)-1-iodoethene, 6a.



From stannane **4a** (431 mg, 0.81 mmol) and iodine (247 mg, 0.97 mmol), according to the general procedure (20 min), iodide **6a** was obtained. Purification by chromatography (5-30% EtOAc-hexane) afforded **6a** (205 mg, 0.56 mmol, 69%) as a white solid that was recrystallized from EtOAc-hexane.

Data for **6a**: R_f = 0.33 (30% EtOAc-hexane). **mp**: 89-90 ºC. $[\alpha]^{20}_D$ = +40.9 (*c* = 1.10). **^{1}H NMR (300 MHz)** δ 2.39 (s, 3 H, Me-*p*-Tol), 7.29 (d, 2 H, *J* = 8.1 Hz), 7.38-7.42 (m, 3 H), 7.58 (d, 2 H, *J* = 8.3 Hz), 7.74-7.78 (m, 2 H), 8.14 (s, 1 H, H-2). **^{13}C NMR (75 MHz)** δ 21.5 (Me-*p*-Tol), 110.3, 126.0 (2 C), 128.4 (2 C), 129.2 (2 C), 129.9 (2 C), 130.0, 134.1, 138.9, 139.9, 142.3. **IR** (KBr): 3065, 2912, 1632, 1591, 1443, 1336, 1267, 1082, 1045, 1014, 921, 861, 809, 751 cm^{-1}. **MS** (ES): 369 $[M+1]^+$ (100%). **Anal. calcd for** $C_{15}H_{13}IOS$: C, 48.93; H, 3.56; I, 34.46; S, 8.71. **Found**: C, 49.12; H, 3.67; I, 34.64; S, 8.82.

2.3. Synthesis of (–)-(*S*)-(*E*)-2-Phenyl-1-(*p*-tolylsulfinyl)-1-iodoethene, 5a.



3a **5a**

From stannane **3a** (1.31 g, 2.47 mmol) and iodine (751 mg, 2.96 mmol), according to the general procedure (2 h), iodide **5a** was obtained. Purification by chromatography (5-30% EtOAc-hexane) afforded **5a** (863 g, 2.34 mmol, 95%) as a white solid that was recrystallized from EtOAc-hexane.

Data for **5a**: R_f = 0.40 (30% EtOAc-hexane). **mp**: 59-61 ºC. $[\alpha]^{20}_D$ = –400.9 (*c* = 2.10). **^{1}H NMR (300 MHz)** δ 2.37 (s, 3 H, Me-*p*-Tol), 7.27 (d, 2 H, *J* = 8.3 Hz), 7.35-7.44 (m, 5 H), 7.48-7.53 (m, 2 H), 7.88 (s, 1 H, H-1). **^{13}C NMR (75 MHz)** δ 21.5 (Me-*p*-Tol), 118.4, 124.5 (2 C), 128.8 (2 C), 129.3 (2 C), 129.6, 129.9 (2 C), 135.5, 140.2, 141.8, 149.5. **IR** (KBr): 3020, 1632, 1568, 1487, 1443, 1394, 1375, 1301, 1179, 1083, 1052, 1016, 929, 887, 872, 804, 749 cm^{-1}. **MS** (ES): 759 $[2M+Na]^+$, 391 $[M+Na]^+$, 369 $[M+1]^+$ (100%). **Anal. calcd for** $C_{15}H_{13}IOS$: C, 48.93; H, 3.56; I, 34.46; S, 8.71. **Found**: C, 49.06; H, 3.75; I, 34.52; S, 8.62.

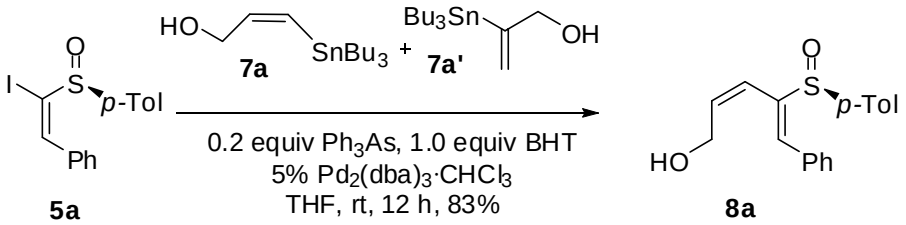
3. Synthesis of hydroxyl sulfinyl dienes.

3.1. General method for the preparation of hydroxy 4-sulfinyl dienes.

To a solution of sulfinyl vinyl iodide in THF (10 mL/mmol sulfoxide) at rt 1.0 equiv of 2,6-di-*tert*-butyl-4-methyphenol (BHT), 0.2 equiv of Ph_3As and 1.2-1.5 equiv of the corresponding hydroxy vinyl stannane were added. Argon was bubbled through the solution for 10 min and 0.05-0.10 equiv of $Pd_2(dba)_3{\cdot}CHCl_3$ was added. The mixture was stirred at room temperature until disappearance of starting

material. The solvent was then evaporated and the crude was purified by column chromatography on silica gel.

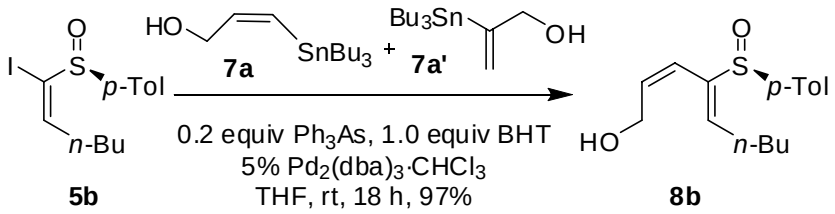
3.2. Synthesis of (−)-(*S*)-2-(*Z*)-4-(*Z*)-5-Phenyl-4-(*p*-tolylsulfinyl)penta-2,4-dien-1-ol, 8a.



From iodide **5a** (295 mg, 0.80 mmol, 1.0 equiv) a 62:38 mixture of (*Z*)-3-(tributylstannyl)prop-2-en-1-ol, **7a**, and 2-(tributylstannyl)prop-2-en-1-ol, **7a'** (1.09 g, 3.14 mmol, 1.5 equiv of **7a**), BHT (176 mg, 0.80 mmol, 1.0 equiv), Ph_3As (50 mg, 0.16 mmol, 0.2 equiv) and $Pd_2(dba)_3{\cdot}CHCl_3$ (42 mg, 0.04 mmol, 0.05 equiv), according to the general procedure (12 h), diene **8a** was obtained as a single isomer. Purification by chromatography (5-80% EtOAc-hexane) afforded 229 mg of **8a** as a brown solid. A second purification (10-50% EtOAc-CH_2Cl_2) afforded **8a** (200 mg, 0.67 mmol, 83%) as a pale brown solid that was recrystallized from EtOAc-hexane.

Data for **8a**: R_f = 0.14 (50% EtOAc-hexane). **mp**: 135-137 ºC. $[\alpha]^{20}_{D}$ = –162.2 (*c* = 1.00). **^{1}H NMR (300 MHz)** δ 2.38 (s, 3 H, Me-*p*-Tol), 2.67 (br s, 1 H, OH), 3.97 (dddd, 1 H, *J* = 12.7, 8.3, 6.1, 0.7 Hz, H-1), 4.18 (dddd, 1 H, *J* = 12.7, 8.1, 4.7, 1.2 Hz, H-1), 5.76 (ddd, 1 H, *J* = 11.2, 2.8, 1.1 Hz, H-3), 6.12 (ddd, 1 H, *J* = 11.2, 8.3, 6.1 Hz, H-2), 6.98 (d, 1 H, *J* = 1.5 Hz, H-5), 7.26 (d, 2 H, *J* = 8.1 Hz), 7.36-7.46 (m, 5 H), 7.52-7.57 (m, 2 H). **^{13}C NMR (75 MHz)** δ 21.4 (Me-*p*-Tol), 58.3 (C-1), 121.8, 124.5 (2 C), 128.6 (2 C), 129.1, 129.8 (4 C), 133.6, 138.1, 138.2, 139.1, 141.2, 141.8. **IR** (KBr): 3401, 3021, 1630, 1490, 1445, 1318, 1230, 1183, 1079, 1042, 1017, 1003, 806, 759, 700 cm^{-1}. **MS** (ES): 619 $[2M+Na]^+$, 321 $[M+Na]^+$, 299 $[M+1]^+$ (100%). **Anal. calcd for** $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08; S, 10.75. **Found**: C, 72.24; H, 6.12; S, 10.70.

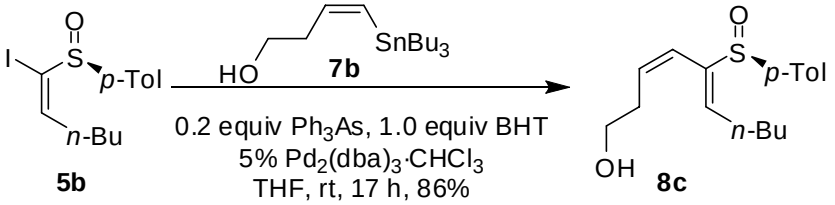
3.3. Synthesis of (−)-(*R*)-2-(*Z*)-4-(*Z*)-4-(*p*-Tolylsulfinyl)nona-2,4-dien-1-ol, 8b.



From iodide **5b** (986 mg, 2.83 mmol), stannane **7a** (1.2 equiv, 1.64 g of 72:28 mixture **7a** and **7a'**, 3.40 mmol **7a**), BHT (624 mg, 2.83 mmol), Ph_3As (175 mg, 0.57 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (151 mg, 0.14 mmol), according to the general procedure (18 h), diene **8b** was obtained as a single isomer. Purification by chromatography (10-50% EtOAc-hexane) afforded **8b** (768 mg, 2.76 mmol, 97%) as a colorless oil.

Data for **8b**: R_f = 0.20 (75% EtOAc-hexane). $[\alpha]^{20}_D$ = –29.6 (*c* = 2.44). **^{1}H NMR (200 MHz)** δ 0.97 (t, 3 H, *J* = 7.1 Hz, Me-*n*-Bu), 1.24-1.64 (m, 4 H, *n*-Bu), 2.39 (s, 3 H, Me-*p*-Tol), 2.40-2.79 (m, 2 H, H-6), 3.02 (br s, 1 H, OH), 3.83 (dd, 1 H, *J* = 12.6, 6.0 Hz, H-1), 4.05 (ddd, 1 H, *J* = 12.5, 8.2, 1.1 Hz, H-1), 5.60 (dd, 1 H, *J* = 11.2, 1.0 Hz, H-3), 5.92-6.11 (m, 2 H, H-2, H-5), 7.26 (d, 2 H, *J* = 8.1 Hz), 7.38 (d, 2 H, *J* = 8.3 Hz). **^{13}C NMR (50 MHz)** δ 13.8, 21.3, 22.3, 28.5, 31.5, 58.0, 121.5, 124.2 (2 C), 129.6 (2 C), 137.6, 138.5, 140.7, 140.9, 141.6. **IR** (film): 3400 (br), 2960, 2930, 2870, 1600, 1490, 1460, 1380, 1300, 1240, 1210, 1180, 1080, 1060, 940, 810, 760 cm^{-1}. **MS** (EI): 279 $[M+1]^+$, 278 $[M]^+$.

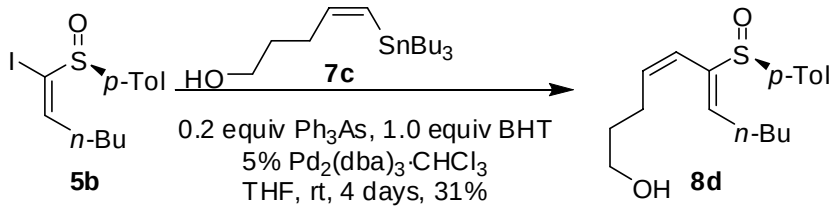
3.4. Synthesis of (–)-(*R*)-3-(*Z*)-5-(*Z*)-5-(*p*-Tolylsulfinyl)deca-3,5-dien-1-ol, 8c.



From iodide **5b** (130 mg, 0.373 mmol), stannane **7b** (1.3 equiv, 175 mg, 0.485 mmol), BHT (82 mg, 0.373 mmol), Ph_3As (23 mg, 0.075 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (20 mg, 0.019 mmol), according to the general procedure (17 h), diene **8c** was obtained. Purification by chromatography (10-50% EtOAc-hexane) gave **8c** (94 mg, 0.321 mmol, 86%) as a yellow oil.

Data for **8c**: R_f = 0.11 (50% EtOAc-hexane). $[\alpha]^{20}_D$ = –12.5 (*c* = 0.40). **^{1}H NMR (300 MHz)** δ 0.95 (t, 3 H, *J* = 7.2 Hz, Me-*n*-Bu), 1.36-1.61 (m, 4 H, *n*-Bu), 2.08-2.16 (m, 1 H, H-7), 2.36 (s, 3 H, Me-*p*-Tol), 2.38-2.48 (m, 1 H, H-7), 2.56 (m, 1 H, H-2), 2.74 (m, 1 H, H-2), 2.92 (br s, 1 H, OH), 3.60 (quint, 1 H, *J* = 5.2 Hz, H-1), 3.52 (td, 1 H, *J* = 9.8, 4.5 Hz, H-1), 5.62 (d, 1 H, *J* = 11.3 Hz, H-4), 5.76 (ddd, 1 H, *J* = 11.2, 9.1, 5.8 Hz, H-3), 5.99 (td, 1 H, *J* = 8.5, 1.3 Hz, H-6), 7.24 (d, 2 H, *J* = 8.6 Hz, *p*-Tol), 7.38 (d, 2 H, *J* = 8.1 Hz, *p*-Tol). **^{13}C NMR (75 MHz), HSQC** δ 13.8 (Me), 21.3 (Me-*p*-Tol), 22.4 (CH_2), 28.6 (CH_2), 31.6 (2 CH_2), 61.1 (C-1), 121.6 (C-4), 124.2 (2 C), 129.6 (2 C), 136.1 (C-3), 138.6 (C-5), 140.7, 140.8, 141.1 (C-6). **IR** (film): 3429, 2956, 2927, 2869, 1627, 1464, 1082, 1045, 808 cm^{-1}. **MS** (ES): 315 $[M+Na]^+$ (100%), 293 $[M+1]^+$.

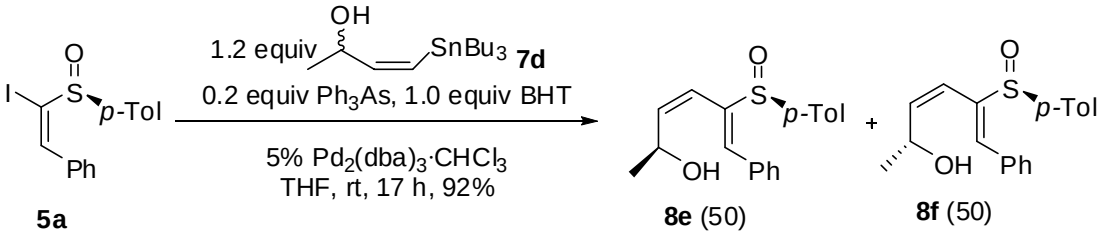
3.5. Synthesis of 4-(*Z*)-6-(*Z*)-(*p*-Tolylsulfinyl)undeca-4,6-dien-1-ol, 8d.



From iodide **5b** (204 mg, 0.586 mmol), stannane **7c** (1.4 equiv, 307 mg, 0.818 mmol), BHT (129 mg, 0.586 mmol), Ph_3As (36 mg, 0.117 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (30 mg, 0.029 mmol), according to the general procedure (4 days), diene **8d** was obtained. Purification by chromatography (10-50% EtOAc-hexane) afforded **8d** (56 mg, 0.183 mmol, 31%) as an orange oil and 182 mg of a 62:38 mixture of stannane and iodide **5b**.

Data for **8d**: R_f = 0.13 (50% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 0.96 (t, 3 H, *J* = 7.2 Hz, Me-*n*-Bu), 1.25-1.59 (m, 6 H, *n*-Bu, H-2), 1.97 (dtd, 1 H, *J* = 14.4, 5.6, 2.0 Hz, H-8), 2.35 (m, 1 H, H-8), 2.38 (s, 3 H, Me-*p*-Tol), 2.59 (dtd, 1 H, *J* = 14.9, 7.5, 1.2 Hz, H-3), 2.75 (dt, 2 H, *J* = 15.0, 7.7 Hz, H-3, OH), 3.51 (dd, 1 H, *J* = 11.0, 5.6 Hz, H-1), 3.56 (ddd, 1 H, *J* = 11.2, 8.1, 4.6 Hz, H-1), 5.52 (d, 1 H, *J* = 11.7 Hz, H-5), 5.70 (ddd, 1 H, *J* = 11.2, 9.2, 5.2 Hz, H-4), 5.98 (td, 1 H, *J* = 7.3, 1.2 Hz, H-7), 7.26 (d, 2 H, *J* = 8.3 Hz, *p*-Tol), 7.39 (d, 2 H, *J* = 8.1 Hz, *p*-Tol). **^{13}C NMR (75 MHz), DEPT** δ 13.9 (Me), 21.3 (Me-*p*-Tol), 22.4 (CH_2), 24.5 (C-2), 28.6 (C-3), 31.7 (C-8), 60.7 (C-1), 120.0 (C-5), 124.2 (2 C), 129.6 (2 C), 138.7 (C-4), 139.0 (C-6), 140.7, 141.2, 141.4 (C-7). **IR** (film): 3411, 3007, 2949, 2928, 2869, 1620, 1490, 1454, 1078, 1041, 1013, 808 cm^{-1}. **MS** (ES): 329 $[M+Na]^+$ (100%), 307 $[M+1]^+$.

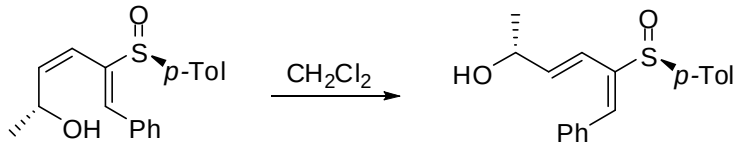
3.6. Synthesis of (–)-(2*S*,*S*$_S$)-3-(*Z*)-5-(*Z*)-6-Phenyl-5-(*p*-tolylsulfinyl)hexa-3,5-dien-2-ol, 8e, and (2*R*,*S*$_S$)-3-(*Z*)-5-(*Z*)-6-Phenyl-5-(*p*-tolylsulfinyl)hexa-3,5-dien-2-ol, 8f.



From iodide **5a** (147 mg, 0.4 mmol), stannane **7d** (173 mg, 0.48 mmol), BHT (88 mg, 0.40 mmol), Ph_3As (25 mg, 0.08 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (21 mg, 0.02 mmol), according to the general procedure (17 h), a 50:50 mixture of **8e** and **8f** was obtained. Purification by chromatography (5-30% EtOAc-CH_2Cl_2) afforded **8e** (27 mg, 0.086 mmol, 22%) as a white solid that was recrystallized from

EtOAc-hexane, a 62:38 mixture of **8e** and **8f** (47 mg, 0.15 mmol, 37%) and **8f** (41 mg, 0.13 mmol, 33%) as a colorless oil.

Diene **8f** was unstable and had to be used rapidly. Deactivated silica gel (2% Et_3N) was used for the purification and it was observed that in CH_2Cl_2 solution it was transformed into *E*,*E* diene **8f'**. This low stability prevented the complete characterization of **8f**.



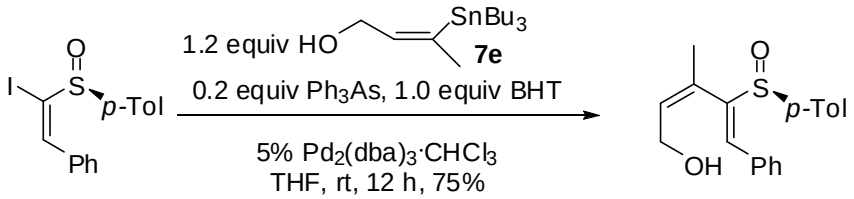
8f **8f'**

Data for **8e**: R_f = 0.17 (20% EtOAc-CH_2Cl_2). **mp**: 108-109 ºC. $[\alpha]^{20}_D$ = –386.3 (*c* = 1.47). **^{1}H NMR (300 MHz)** δ 1.25 (d, 3 H, *J* = 6.3 Hz, Me-1), 1.59 (br s, 1 H, OH), 2.37 (s, 3 H, Me-*p*-Tol), 4.39 (quint, 1 H, *J* = 7.1 Hz, H-2), 5.75 (dd, 1 H, *J* = 11.5, 8.3 Hz, H-3), 6.00 (d, 1 H, *J* = 11.5 Hz, H-4), 7.00 (s, 1 H, H-6), 7.27 (d, 2 H, *J* = 8.1 Hz), 7.30-7.45 (m, 5 H), 7.54 (d, 2 H, *J* = 7.1 Hz). **^{13}C NMR (75 MHz)** δ 21.3 (Me-*p*-Tol), 23.1 (Me-1), 64.5 (C-2), 120.5, 124.4 (2 C), 128.6 (2 C), 129.1, 129.7 (2 C), 129.8 (2 C), 133.8, 138.3, 139.5, 141.1, 141.6, 142.4. **IR** (KBr): 3422, 3014, 2971, 2927, 2862, 1490, 1442, 1369, 1106, 1081, 1023, 1012, 929, 895, 808, 764, 702 cm^{-1}. **MS** (ES): 625 $[2M+1]^+$ (100%), 313 $[M+1]^+$, 295 $[(M–18)+1]^+$. **Anal. calcd for** $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45; S, 10.26. **Found**: C, 73.26; H, 6.34; S, 10.47.

Data for **8f**: R_f = 0.12 (20% EtOAc-CH_2Cl_2). **^{1}H NMR (300 MHz)** δ 1.22 (t, 3 H, *J* = 6.3 Hz, Me-1), 2.38 (s, 3 H, Me-*p*-Tol), 4.18 (m, 1 H, H-2), 5.47 (d, 1 H, *J* = 11.0 Hz, H-4), 5.92 (dd, 1 H, *J* = 10.7, 9.3 Hz, H-3), 7.01 (s, 1 H, H-6), 7.21-7.46 (m, 7 H), 7.55 (d, 2 H, *J* = 7.8 Hz).

Data for **8f'**: R_f = 0.24 (50% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 1.17 (t, 3 H, *J* = 6.2 Hz, Me-1), 1.64 (br s, 1 H, OH), 2.35 (s, 3 H, Me-*p*-Tol), 4.29 (m, 1 H, H-2), 6.09 (dd, 1H, *J* = 16.5, 5.7 Hz, H-3), 6.33 (d, 1 H, *J* = 16.3 Hz, H-4), 7.20-7.57 (m, 10 H).

3.7. Synthesis of (–)-(*S*)-2-(*Z*)-4-(*Z*)-3-Methyl-5-phenyl-4-(*p*-tolylsulfinyl)penta-2,4-dien-1-ol, 8g.



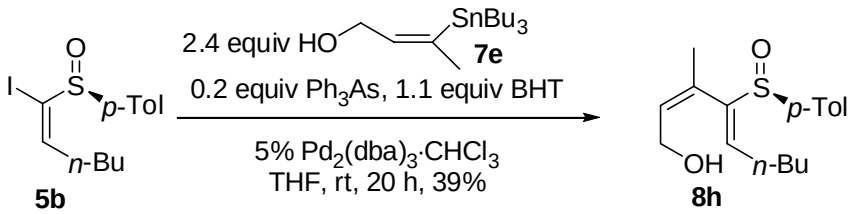
5a **8g**

From iodide **5a** (147 mg, 0.4 mmol), stannane **7e** (174 mg, 0.48 mmol), BHT (88 mg, 0.40 mmol), Ph_3As (25 mg, 0.08 mmol) and $Pd_2(dba)_3·CHCl_3$ (21 mg, 0.02 mmol), according to the general

procedure (12 h), diene **8g** was obtained. Purification by chromatography (1-20% EtOAc-CH_2Cl_2, silica gel deactivated with 2% Et_3N) afforded **8g** (94 mg, 0.30 mmol, 75%) as a colorless oil.

Data for **8g**: R_f = 0.18 (50% EtOAc-hexane). $[\alpha]^{20}_D$ = –233.7 (*c* = 0.74). **^{1}H NMR (300 MHz)** δ 1.20 (s, 3 H, Me-3), 2.38 (s, 3 H, Me-*p*-Tol), 3.60 (br s, 1 H, OH), 3.80 (m, 1 H, H-1), 3.91 (t, 1 H, *J* = 10.0 Hz, H-1), 5.94 (ddd, 1 H, *J* = 9.8, 6.1, 1.5 Hz, H-2), 6.98 (s, 1 H, H-5), 7.25 (d, 2 H, *J* = 8.3 Hz), 7.30-7.60 (m, 7 H). **^{13}C NMR (75 MHz)** δ 21.4 (Me-*p*-Tol), 26.1 (Me-3), 58.9 (C-1), 124.7 (2 C), 128.7 (2 C), 128.8, 129.1, 129.6 (2 C), 129.7 (2 C), 131.1, 133.1, 133.6, 137.9, 139.6, 141.6. **IR** (film): 3413, 2923, 2855, 1486, 1446, 1082, 1013, 808, 752 cm^{-1}. **MS** (ES): 313 $[M+1]^+$ (100%).

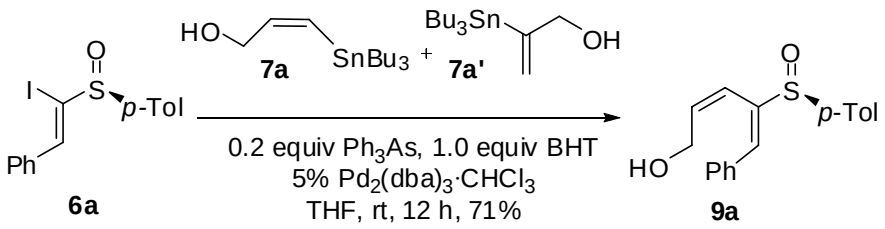
3.8. Synthesis of (–)-(*S*)-2-(*Z*)-4-(*Z*)-3-Methyl-4-(*p*-tolylsulfinyl)nona-2,4-dien-1-ol, 8h.



From iodide **5b** (875 mg, 2.51 mmol), stannane **7e** (2.17 g, 6.35 mmol), BHT (609 mg, 2.77 mmol), Ph_3As (154 mg, 0.503 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (132 mg, 0.128 mmol), according to the general procedure (20 h), diene **8h** was obtained. Purification by chromatography (1-20% EtOAc-hexane, silica gel deactivated with 2% Et_3N) afforded **8h** (286 mg, 0.979 mmol, 39%) as a colorless oil along with iodide **8h** (540 mg, 1.55 mmol, 61%).

Data for **8h**: R_f = 0.39 (50% EtOAc-hexane). $[\alpha]^{20}_D$ = –38.6 (*c* = 1.46). **^{1}H NMR (300 MHz)** δ 0.96 (t, 3 H, *J* = 7.2 Hz, CH_3), 1.10 (s, 3 H, Me-3), 1.36-1.57 (m, 4 H, 2 CH_2), 2.37 (s, 3 H, Me-*p*-Tol), 2.58 (hept, 1 H, *J* = 7.2 Hz, H-6), 2.78 (hept, 1 H, *J* = 7.2 Hz, H-6), 3.55 (dd, 1 H, *J* = 9.8, 3.8 Hz, H-1), 3.62-3.80 (m, 2 H, H-1, OH), 5.85 (ddd, 1 H, *J* = 9.6, 6.2, 1.5 Hz, H-2), 5.95 (dd, 1 H, *J* = 8.6, 7.1 Hz, H-5), 7.25 (d, 2 H, *J* = 7.9 Hz, Ar-H), 7.41 (d, 2 H, *J* = 8.3 Hz, Ar-H). **^{13}C NMR (75 MHz)** δ 13.8, 21.3 (Me-*p*-Tol), 22.3, 26.2 (Me-3), 28.3, 31.5, 58.7 (C-1), 124.3 (2 C), 129.6 (2 C), 131.2, 132.5, 138.1, 141.2, 142.0 (2 C), 145.0. **IR** (film): 3413, 2926, 2855, 1656, 1491, 1447, 1083, 1037, 1012, 809, 703 cm^{-1}. **MS** (ES): 315 $[M+Na]^+$ (100%).

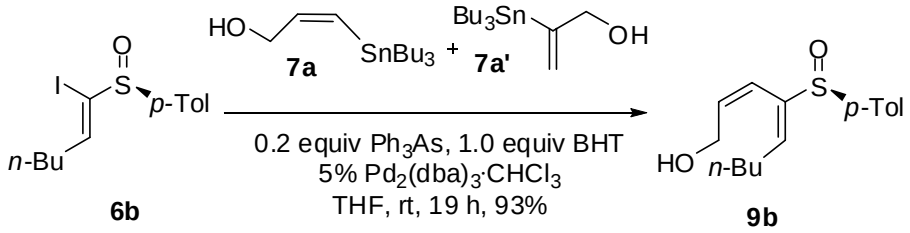
3.9. Synthesis of (+)-(*S*)-2-(*Z*)-4-(*E*)-5-Phenyl-4-(*p*-tolylsulfinyl)penta-2,4-dien-1-ol, 9a.



From iodide **6a** (258 mg, 0.70 mmol), a 74:26 mixture of **7a** and **7a'**, (427 mg, 1.23 mmol, 1.3 equiv of **7a**), BHT (154 mg, 0.70 mmol), Ph_3As (43 mg, 0.14 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (36 mg, 0.035 mmol), according to the general procedure (12 h), diene **9a** was obtained as a single isomer. Purification by chromatography (10-50% EtOAc-hexane) afforded **9a** (150 mg, 0.50 mmol, 71%) as a yellow oil.

Data for **9a**: R_f = 0.18 (50% EtOAc-hexane). $[\alpha]^{20}_D$ = +19.5 (*c* = 0.41). **^{1}H NMR (300 MHz)** δ 2.37 (s, 3 H, Me-*p*-Tol), 2.89 (dd, 1 H, *J* = 8.1, 5.4 Hz, OH), 3.74-3.89 (m, 2 H, H-1), 5.62 (dt, 1 H, *J* = 11.2, 1.0 Hz, H-3), 6.17 (ddd, 1 H, *J* = 11.0, 8.3, 6.3 Hz, H-2), 7.25 (d, 2 H, *J* = 8.5 Hz), 7.30-7.36 (m, 3 H), 7.46 (d, 2 H, *J* = 8.1 Hz), 7.51-7.54 (m, 2 H). **^{13}C NMR (75 MHz)** δ 21.4 (Me-*p*-Tol), 58.9 (C-1), 119.6, 124.8 (2 C), 128.7 (2 C), 129.6, 129.7 (2 C), 129.9 (2 C), 134.0, 135.6, 138.5, 138.7, 141.5, 141.8. **IR** (film): 3400, 3053, 3023, 2922, 2867, 1595, 1491, 1449, 1398, 1303, 1209, 1179, 1082, 1037, 930, 809, 756 cm^{-1}. **MS** (ES): 619 $[2M+Na]^+$, 321 $[M+Na]^+$, 299 $[M+1]^+$ (100%), 281 $[(M-18)+1]^+$.

3.10. Synthesis of (+)-(*R*)-2-(*Z*)-4-(*E*)-4-(*p*-Tolylsulfinyl)nona-2,4-dien-1-ol, 9b.



From iodide **6b** (665 mg, 1.90 mmol), a 50:50 mixture of **7a** and **7a'**, (1.86 g, 2.68 mmol, 1.41 equiv of **7a**), BHT (421 mg, 1.90 mmol), Ph_3As (113 mg, 0.37 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (96 mg, 0.093 mmol), according to the general procedure (19 h), diene **9b** was obtained as a single isomer. Purification by chromatography (10-50% EtOAc-hexane) afforded **9b** (490 mg, 1.75 mmol, 93%) as a colorless oil.

Data for **9b**: R_f = 0.25 (50% EtOAc-hexane). $[\alpha]^{20}_D$ = +92.8 (*c* = 1.02). **^{1}H NMR (300 MHz)** δ 0.87 (t, 3 H, *J* = 7.2 Hz, H-9), 1.24-1.47 (m, 4 H, H-7, H-8), 2.10 (m, 2 H, H-6), 2.38 (s, 3 H, Me-*p*-Tol), 3.19 (dd, 1 H, *J* = 8.5, 4.9 Hz, OH), 3.80 (m, 2 H, H-1), 5.36 (d, 1 H, *J* = 10.5 Hz, H-3), 6.11 (ddd, 1 H,

J = 11.0, 8.5, 6.1 Hz, H-2), 6.56 (td, 1 H, *J* = 7.4, 1.7 Hz, H-5), 7.26 (d, 2 H, *J* = 8.5 Hz, *p*-Tol), 7.40 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **^{13}C NMR (75 MHz)** δ 13.7, 21.3 (Me-*p*-Tol), 22.2, 29.0, 30.3, 58.3 (C-1), 118.6, 124.5 (2 C), 129.6 (2 C), 138.2, 138.7, 140.7, 141.2, 141.8. **IR** (film): 3391, 2957, 2928, 2859, 1596, 1493, 1455, 1379, 1303, 1209, 1178, 1083, 1046, 915, 810, 704 cm^{-1}. **MS** (ES): 579 [2M+Na]$^+$, 301 [M+Na]$^+$, 279 [M+1]$^+$ (100%).

4. Synthesis of sulfinyl dihydropyrans and oxepines.

4.1. General procedures for the synthesis of 3-sulfinyl-3,6-dihydro-2*H*-pyrans.

Method A: To a cold solution (–78 ºC) of dienyl sulfoxide in THF (10 mL/mmol sulfoxide), was added a freshly prepared solution of LDA (1.2 equiv, 0.5 M in THF) and the mixture was stirred and warmed up to rt. When disappearance of starting material was observed (TLC, 2-4 h) the reaction was quenched with saturated NH_4Cl solution (3 mL/mmol sulfoxide) and H_2O (3 mL/mmol sulfoxide) and the layers were separated. The aqueous layer was extracted with EtOAc (3 x 5 mL/mmol) and the combined organic layers were washed with saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated under vacuum to obtain a crude product that was purified by chromatography on silica gel.

Method B: To a cold suspension (–30 ºC) of 1.1-1.3 equiv of NaH or KH in THF (5 mL/mmol sulfoxide) was added a solution of dienyl sulfoxide in THF (5 mL/mmol sulfoxide). The mixture was stirred and warmed up to rt. When disappearance of starting material was observed (TLC, 2-4 h) the reaction was quenched and isolated according to Method A.

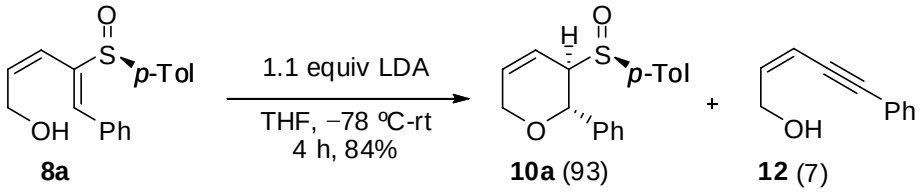
Method C: To a solution of dienyl sulfoxide in CH_2Cl_2 (10 mL/mmol sulfoxide) at 0 ºC, 1.1 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added. The mixture was stirred and warmed up to rt. When no more evolution was observed (TLC, 5 days) the reaction was quenched and isolated according to Method A.

Method D: To a solution of dienyl sulfoxide in CH_2Cl_2 (10 mL/mmol sulfoxide) at 0 ºC, 1.3 equiv of 2-*tert*-butylimino-2-diethylamino-1,3-dimethyl-perhydro-1,3,2-diazaphosphorine (BEMP) was added. The mixture was stirred and warmed up to rt. When disappearance of starting material was observed (TLC), the reaction was quenched and isolated according to Method A.

Method E: To a solution of dienyl sulfoxide in CH_2Cl_2 (10 mL/mmol sulfoxide) at −78 ºC, 1.1 equiv of 1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2^5,4^5-catenadi(phosphazene) (P_2-^{t}Bu) was added, stirring at low temperature. When disappearance of starting material was observed (TLC), the reaction was quenched and isolated according to Method A.

Method F: To a solution of dienyl sulfoxide in CH_2Cl_2 (10 mL/mmol sulfoxide) at −78 ºC, 1.1 equiv of 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2^5,4^5-catenadi(phosphazene) (P_4-^{t}Bu) was added, stirring at low temperature. When disappearance of starting material was observed (TLC), the cold reaction mixture was filtered through a pad of silica gel. The solvent was evaporated and the crude product was purified by chromatography on silica gel.

4.2. Synthesis of (–)-(2*S*,3*R*,*R*$_S$)-2-Phenyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, 10a.

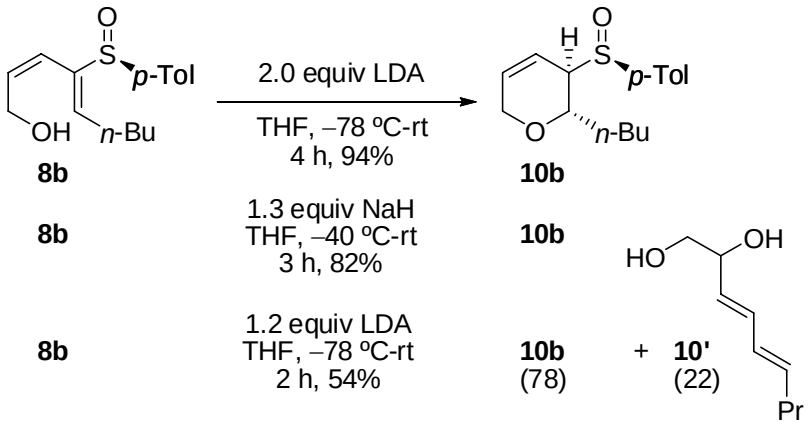


From dienyl sulfoxide **8a** (597 mg, 2 mmol) and LDA (4.4 mL, 2.2 mmol) according to the general procedure (Method A, 4 h), dihydropyran **10a** was obtained. Chromatography (15-50% EtOAc-hexane) afforded **12** (35 mg, 0.11 mmol, 5%) as a colorless oil and **10a** (500 mg, 1.67 mmol, 84%), as a white solid that was recrystallized from hexane.

Data for **10a**: R_f = 0.34 (50% EtOAc-hexane). **mp**: 87-89 ºC. $[\alpha]^{20}_D$ = –291.7 (*c* = 0.82). **^{1}H NMR (300 MHz), COSY** δ 2.44 (s, 3 H, Me-*p*-Tol), 3.78 (m, 1 H, H-3), 3.91 (dq, 1 H, *J* = 17.6, 2.4 Hz, H-6), 4.14 (dm, 1 H, *J* = 17.6 Hz, H-6), 5.33 (d, 1 H, *J* = 2.9 Hz, H-2), 5.51 (ddtd, 1 H, *J* = 10.2, 4.9, 2.2, 0.5 Hz, H-4), 6.00 (dtd, 1 H, *J* = 10.2, 3.2, 1.0 Hz, H-5), 7.30-7.40 (m, 7 H), 7.59 (d, 2 H, *J* = 8.3 Hz). **NOESY-1D** H-2/*p*-Tol: 0.6%; H-2/Ph: 1.9%; H-2/H-3: 1.0%; H-3/H-2: 1.3%; H-3/H-4: 1.6%; H-3/*p*-Tol: 1.3%; H-3/Ph: 3.2%; H-4/H-5: 2.2%; H-4/*p*-Tol: 1.1%; H-4/H-3: 1.5%; H-5/H-4: 1.3%; H-5/H-6%: 1.1%; H-5/H-6 (4.14 ppm): 1.1%; H-5/H-6 (3.91 ppm): 1.9%; H-6/H-5: 2.1%. **^{13}C NMR (75 MHz), HSQC** δ 21.5 (Me-*p*-Tol), 61.6 (C-6), 64.3 (C-3), 71.5 (C-2), 117.1 (C-4), 125.6 (2 C), 127.9 (2 C), 128.3, 128.5 (2 C), 129.7 (2 C), 133.2 (C-5), 137.3, 138.4, 142.2. **IR** (KBr): 2945, 2829, 1632, 1490, 1449, 1304, 1198, 1074, 1041, 1015, 960, 897, 821, 807, 752, 700 cm^{-1}. **MS** (ES): 619 $[2M+Na]^+$, 321 $[M+Na]^+$, 299 $[M+1]^+$ (100%). **Anal. calcd for** $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08; S, 10.75. **Found**: C, 72.60; H, 6.26; S, 10.38.

Data for **12**: R_f = 0.45 (50% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 1.61 (br s, 1 H, OH), 4.49 (t, 2 H, *J* = 4.6 Hz, H-1), 5.80 (dt, 1 H, *J* = 11.0, 1.5 Hz, H-3), 6.13 (dt, 1 H, *J* = 11.0, 6.3 Hz, H-2), 7.28-7.32 (m, 3 H, Ph), 7.40-7.43 (m, 2 H, Ph). **MS** (ES): 159 $[M+1]^+$ (100%), 141 $[(M–18)+1]^+$.

4.3. Synthesis of (–)-(2*S*,3*R*,*R*$_S$)-2-*n*-Butyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, 10b.



From dienyl sulfoxide **8b** (20 mg, 0.070 mmol) and LDA (0.28 mL, 0.14 mmol) according to the general procedure (Method A, 4 h), dihydropyran **10b** was obtained. Purification by chromatography (10-50% EtOAc-hexane) afforded **10b** (18 mg, 0.066 mmol, 94%) as a colorless oil.

From dienyl sulfoxide **8b** (2.02 g, 7.26 mmol) and NaH (227 mg, 9.44 mmol) according to the general procedure (Method B, 3 h), dihydropyran **10b** was obtained. Purification by chromatography (10-50% EtOAc-hexane) afforded **10b** (1.66 g, 5.96 mmol, 82%) as a colorless oil.

In a few instances, if warming of the reaction from –78 ºC to 0 ºC was slow, undesired by-products were obtained for this substrate using LDA. Thus from dienyl sulfoxide **8b** (128 mg, 0.46 mmol) and LDA (1.1 mL, 0.55 mmol) according to the general procedure (Method A, 2 h), a 78:22 mixture of dihydropyran **10b** and diol **10'** was obtained. Purification by chromatography (10-50% EtOAc-hexane) afforded **10b** (70 mg, 0.25 mmol, 54%) and diol **10'** (20 mg, 0.12 mmol, 28%) as colorless oils.

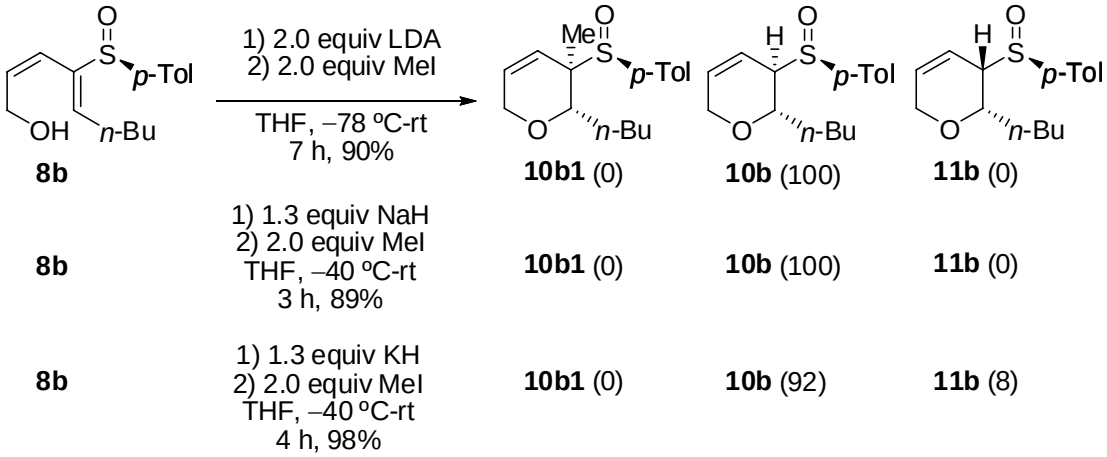
Data for **10b**: R_f = 0.34 (50% EtOAc-hexane). $[\alpha]^{20}_D$ = –218.8 (*c* = 0.75). **^{1}H NMR (300 MHz), COSY** δ 0.88 (t, 3 H, *J* = 7.1 Hz, Me-*n*-Bu), 1.25-1.54 (m, 5 H), 1.74 (m, 1 H), 2.39 (s, 3 H, Me-*p*-Tol), 3.07 (m, 1 H, H-3), 4.09 (m, 2 H, H-6), 4.32 (dm, 1 H, *J* = 9.5 Hz, H-2), 5.14 (ddd, 1 H, *J* = 10.2, 4.9, 2.5 Hz, H-4), 5.95 (dtd, 1 H, *J* = 10.2, 2.5, 1.0 Hz, H-5), 7.29 (d, 2 H, *J* = 7.8 Hz, *p*-Tol), 7.53 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **NOESY-1D** H-2/CH_2-*n*-Bu: 0.8%; H-2/*p*-Tol: 0.8%; H-2/H-3: 1.5%; H-3/*p*-Tol: 1.6%; H-3/H-4: 1.4 %; H-5/H-4: 1.5%; H-5/H-6: 2.6%; H-6/H-5: 2.3 %; H-6/CH_2-*n*-Bu: 1.0%. **^{13}C NMR (50 MHz), HSQC** δ 14.0 (Me-*n*-Bu), 21.5 (Me-*p*-Tol), 22.5, 27.9, 30.7, 60.8 (C-6), 66.1 (C-3), 69.9 (C-2), 116.6 (C-4), 125.5 (2 C), 129.7 (2 C), 132.6 (C-5), 138.9, 142.0. **IR** (film): 3038, 2932, 2857, 1651, 1596, 1493, 1462, 1380, 1302, 1210, 1182, 1082, 1037, 1016, 812 cm^{-1}. **MS** (ES): 579 $[2M+Na]^+$, 301 $[M+Na]^+$, 279 $[M+1]^+$ (100%).

Data for **10'**: R_f = 0.13 (50% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 0.88 (t, 3 H, *J* = 7.3 Hz, H-9), 1.39 (ap hept, 2 H, *J* = 7.4 Hz, H-8), 2.04 (q, 2 H, *J* = 7.3 Hz, H-7), 2.09 (m, 1 H, OH), 2.38 (br s, 1 H, OH), 3.49 (dd, 1 H, *J* = 11.0, 7.3 Hz, H-1), 3.64 (dd, 1 H, *J* = 11.2, 3.7 Hz, H-1) 4.26 (m, 1 H, H-2),

5.53 (dd, 1 H, J = 15.1, 6.5 Hz, H-5), 5.71 (ddd, 1 H, J = 14.5, 7.5, 7.0 Hz, H-6), 6.00 (dd, 1 H, J = 15.1, 10.3 Hz, H-3), 6.27 (dd, 1 H, J = 15.2, 10.4 Hz, H-4). **^{13}C NMR (75 MHz)** δ 13.7 (Me), 22.3 (CH_2), 34.7 (CH_2), 66.5 (C-1), 73.0 (C-2), 128.6, 129.3, 132.9, 136.3. **IR** (film): 3368, 2957, 2927, 2869, 1656, 1454, 1071, 1024, 989, 807 cm^{-1}. **MS** (ES): 179 [M+Na]$^+$ (100%).

4.4. Attempts to capture the intermediate anion formed in cyclization reactions.

Several attempts to capture the intermediate anion were made using different conditions.

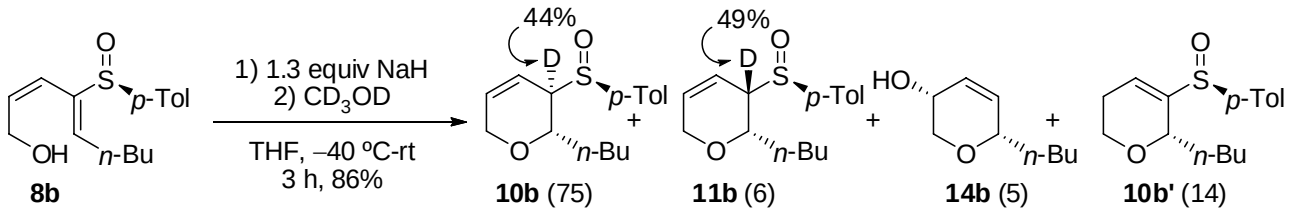


To a cold solution (–78 ºC) of dienyl sulfoxide **8b** (60 mg, 0.172 mmol) in THF (10 mL/mmol sulfoxide), was added a freshly prepared solution of LDA (0.4 mL, 1.2 equiv, 0.5 M in THF) and the mixture was stirred and warmed up to rt (5 h). After 30 min, it was cooled to 0 ºC and 2 equiv of MeI (21 µL, 0.344 mmol) were added. When disappearance of starting material was observed (TLC, 2 h) the reaction was quenched and isolated according to Method A. Purification by chromatography on silica gel (15-30% EtOAc-hexane) afforded **10b** (43 mg, 0.154 mmol, 90%) as a colorless oil.

To a cold suspension (–40 ºC) of 1.3 equiv of NaH (6 mg, 0.235 mmol) in THF (5 mL/mmol sulfoxide) was added a solution of dienyl sulfoxide **8b** (63 mg, 0.181 mmol) in THF (5 mL/mmol sulfoxide). The mixture was stirred for 1 h 10 min from –40 ºC to –25 ºC and MeI (23 µL, 0.362 mmol, 2 equiv) was added. The reaction was warmed up to rt. When disappearance of starting material was observed (TLC, 2 h) the reaction was quenched and isolated according to Method A. The crude product was purified by chromatography (15-30% EtOAc-hexane) to afford **10b** (56 mg, 0.161 mmol, 89%) as a colorless oil.

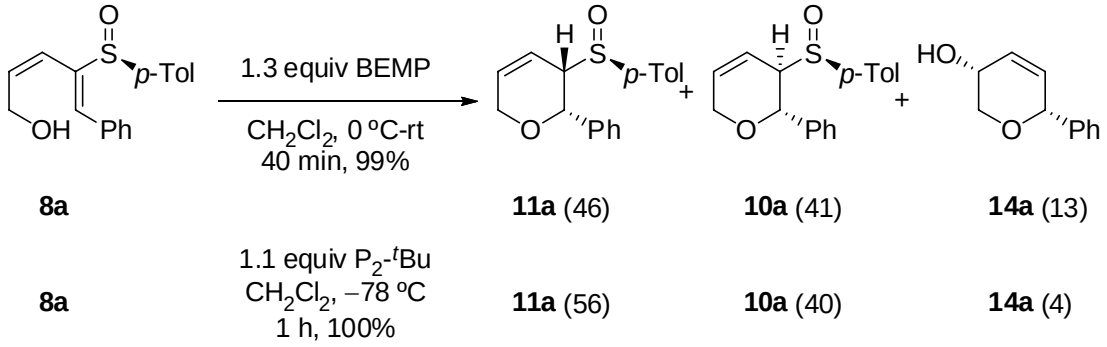
To a cold suspension (–40 ºC) of 1.3 equiv of KH (7 mg, 0.176 mmol) in THF (5 mL/mmol sulfoxide) was added a solution of dienyl sulfoxide **8b** (38 mg, 0.135 mmol) in THF (5 mL/mmol sulfoxide). The mixture was stirred for 30 min at –40 ºC and MeI (17 µL, 0.27 mmol, 2 equiv) was added. The reaction was warmed up to rt. When disappearance of starting material was observed (TLC, 4 h) the reaction was

quenched and isolated according to Method A. The crude product was purified by chromatography (15-30% EtOAc-hexane) to afford **10b** (34 mg, 0.122 mmol, 90%) and **11b** (3 mg, 0.011 mmol, 8%) as colorless oils.



To a cold suspension (–40 ºC) of 1.3 equiv of NaH (5 mg, 0.20 mmol) in THF (5 mL/mmol sulfoxide) was added a solution of dienyl sulfoxide **8b** (43 mg, 0.154 mmol) in THF (5 mL/mmol sulfoxide). The mixture was stirred for 50 min from –40 ºC to –10 ºC and a few drops of CD_3OD were added. The reaction was warmed up to rt. When disappearance of starting material was observed (TLC, 3 h) the reaction was quenched and isolated according to Method A. The crude product was a 75:14:6:5 mixture of **10b**, **10b'**, **11b** and **14b** that was purified by chromatography (10-30% EtOAc-hexane) to afford a 80:14:6 mixture of **10b** (44% deuterated), **10b'** and **14b** (32 mg) and **11b** (5 mg, 49% deuterated, 0.018 mmol, 12%) as colorless oils.

4.5. Synthesis of (+)-(2*S*,3*S*,*R*$_S$)-2-Phenyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2H-pyran, 11a.

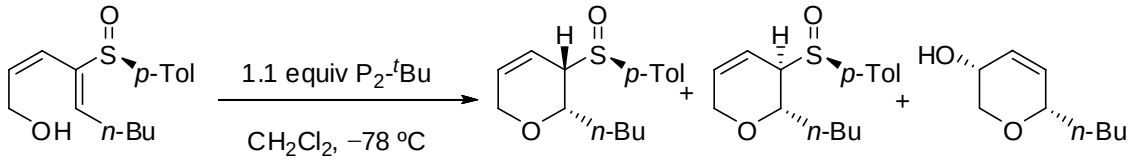


From dienyl sulfoxide **8a** (40 mg, 0.134 mmol) and BEMP (1.3 equiv, 51 µL, 0.174 mmol) according to the general procedure (Method D, 40 min) a 46:41:13 mixture of **11a**, **10a** and **14a** was obtained. Purification by chromatography (0-20% EtOAc-CH_2Cl_2) afforded **11a** (17 mg, 0.056 mmol, 41%) as a white solid and a 75:25 mixture of **10a** and **14a** (18 mg) as a colorless oil.

From dienyl sulfoxide **8a** (25 mg, 0.084 mmol) and P_2-^{t}Bu (1.1 equiv, 46 µL, 0.092 mmol) according to the general procedure (Method E, 1 h), a 56:40:4 mixture of **11a**, **10a** and **14a** was obtained. Column chromatography (0-30% EtOAc-CH_2Cl_2) afforded a 93:7 mixture of **10a** and alcohol **14a** (10 mg) and **11a** (14 mg, 0.047 mmol, 56%) as an off-white solid that was readily transformed upon standing in solution into alcohol **14a**.

Data for **11a**: R_f = 0.27 (30% EtOAc-CH_2Cl_2). **mp**: 108-110 ºC. $[\alpha]^{20}_D$ = +566.0 (*c* = 0.70). **^{1}H NMR (400 MHz), COSY** δ 2.35 (s, 3 H, CH_3 *p*-Tol), 3.33 (ap dt, 1 H, *J* = 5.7, 2.7 Hz, H-3), 4.40 (dq, 1 H, *J* = 17.4, 2.4 Hz, H-6), 4.62 (dt, 1 H, *J* = 17.2, 2.6 Hz, H-6), 5.07 (d, 1 H, *J* = 2.9 Hz, H-2), 5.50 (ddt, 1 H, *J* = 8.0, 5.8, 2.8 Hz, H-4), 6.34 (m, 1 H, H-5), 7.15 (d, 2 H, *J* = 8.2 Hz, H_m *p*-Tol), 7.19 (d, 2 H, *J* = 8.4 Hz, H_o *p*-Tol), 7.35 (d, 1 H, *J* = 7.1 Hz, H_p Ph), 7.42 (t, 2 H, *J* = 7.5 Hz, H_m Ph), 7.50 (d, 2 H, *J* = 7.5 Hz, H_o Ph). **NOESY-1D** H-2/H-6 (4.40 ppm): 2.7%; H-2/H-3: 6.5%; H-2/Ph: 3.3%. **^{13}C NMR (100 MHz), HSQC** δ 21.4 (Me *p*-Tol), 66.7 (C-3), 66.9 (C-6), 76.4 (C-2), 116.3 (C-4), 123.9 (2 C, Ar), 126.1 (2 C Ar), 128.0 (Ar-C), 128.6 (2 C Ar), 129.6 (2 C Ar), 134.7 (C-5), 138.7, 140.4, 140.6. **IR** (KBr): 3435, 3028, 2921, 2833, 1635, 1490, 1452, 1183, 1101, 1049, 805, 752, 727, 705, 670 cm^{-1}. **MS** (ES): 619 $[2M+Na]^+$ (100%), 321 $[M+Na]^+$, 299 $[M+1]^+$.

4.6. Synthesis of (2*S*,3*S*,*R*$_S$)-2-*n*-Butyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, 11b, and (–)-(3*R*,6*S*)-6-*n*-Butyl-3,6-dihydro-2*H*-pyran-3-ol, 14b.



8b	1.1 equiv P_2-^{t}Bu, CH_2Cl_2, −78 ºC, 1 h, 81%	**11b** (52)	**10b** (44)	**14b** (4)
8b	1.3 equiv P_2-^{t}Bu, CH_2Cl_2, 0 ºC-rt, 5 min, 100%	**11b** (22)	**10b** (78)	**14b** (0)
8b	0.5 equiv P_2-^{t}Bu, CH_2Cl_2, −78 ºC, 30 min, 49%	**11b** (45)	**10b** (14)	**14b** (40)
8b	1.1 equiv P_2-^{t}Bu, CH_2Cl_2, −78 ºC, 5 min, 86%	**11b** (58)	**10b** (22)	**14b** (20)[a]
8b	1.1 equiv P_2-^{t}Bu, Toluene, −78 ºC, 17 h, 60%	**11b** (11)	**10b** (89)	**14b** (0)

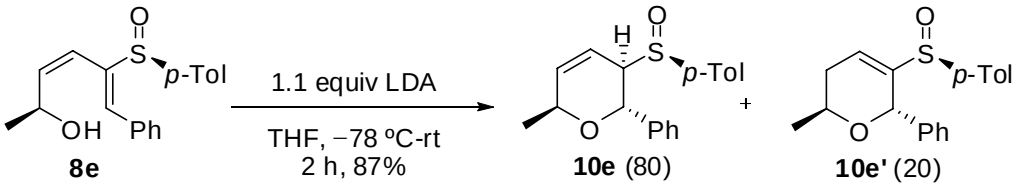
[a]Reaction mixture was filtered through silica gel, without quenching.

From dienyl sulfoxide **8b** (32 mg, 0.115 mmol) and P_2-^{t}Bu (1.1 equiv, 63 µL, 0.127 mmol) according to the general procedure (Method E, 1 h), a 52:44:4 mixture of **11b**, **10b** and **14b** was obtained. Column chromatography (0-30% EtOAc-CH_2Cl_2) afforded a 92:8 mixture of **10b** and alcohol **14b** (12 mg) and **11b** (15 mg, 0.054 mmol, 47%) as an off-white solid that was readily transformed upon standing in solution into alcohol **14b**.

Partial data for **11b**: R_f = 0.20 (20% EtOAc-CH_2Cl_2). **^{1}H NMR (300 MHz)** δ 0.94 (t, 3 H, *J* = 7.1 Hz, CH_3), 1.34-1.57 (m, 4 H, 2 CH_2), 1.83-2.35 (m, 2 H, CH_2), 2.39 (s, 3 H, CH_3 *p*-Tol), 3.04 (dt, 1 H, *J* = 5.8, 2.9 Hz, H-3), 3.82 (ddd, 1 H, *J* = 8.2, 5.5, 2.8 Hz, H-2), 4.17 (dq, 1 H, *J* = 17.3, 2.5 Hz, H-6), 4.38 (dt, 1 H, *J* = 17.4, 2.5 Hz, H-6), 5.33 (ddt, 1 H, *J* = 10.1, 5.0, 2.2 Hz, H-4), 6.24 (ap ddt, 1 H, *J* = 10.3, 3.1, 1.7 Hz, H-5), 7.27 (d, 2 H, *J* = 8.6 Hz, H_m *p*-Tol), 7.43 (d, 2 H, *J* = 8.2 Hz, H_o *p*-Tol). **^{13}C NMR (75 MHz), HSQC** δ 14.1 (Me *p*-Tol), 21.4, 22.6, 28.2, 32.9, 64.0, 66.4, 75.3, 115.6, 124.1 (2 C Ar), 129.7 (2 C Ar), 135.1, 139.7, 140.8. **MS** (ES): 579 $[2M+Na]^+$ (100%), 301 $[M+Na]^+$, 279 $[M+1]^+$.

Data for **14b**: R_f = 0.27 (15% EtOAc-CH_2Cl_2). **$[\alpha]^{20}_D$** = –18.7 (*c* = 0.30). **^{1}H NMR (300 MHz)** δ 0.89 (t, 3 H, *J* = 7.1 Hz, CH_3-Bu), 1.27-1.58 (m, 6 H, 3 CH_2), 1.82 (br s, 1 H, OH), 3.66 (dd, 1 H, *J* = 12.0, 2.4 Hz, H-2), 3.84 (ddd, 1 H, *J* = 5.3, 3.7, 1.7 Hz, H-3), 3.95 (m, 1 H, H-6), 3.96 (dt, 2 H, *J* = 12.1, 1.5 Hz, H-2), 5.81 (dd, 1 H, *J* = 10.1, 1.3 Hz, H-5), 5.97 (ddt, 1 H, *J* = 8.6, 5.0, 1.9 Hz, H-4). **^{13}C NMR (75 MHz), HMQC** δ 14.0 (Me), 22.7 (CH_2), 27.2 (CH_2), 34.7 (CH_2), 62.7 (C-3), 70.8 (C-2), 74.4 (C-6), 126.4 (C-5), 134.4 (C-4). **IR** (film): 3400, 3028, 2958, 2927, 2855, 1466, 1378, 1261, 1183, 1092, 949, 820 cm^{-1}. **MS** (ES): 212 $[M+Na+MeOH]^+$, 190 $[M+2+MeOH]^+$ (100%), 179 $[M+Na]^+$.

4.7. Synthesis of (–)-(2*S*,3*R*,6*S*,R_S)-6-Methyl-2-phenyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, 10e.



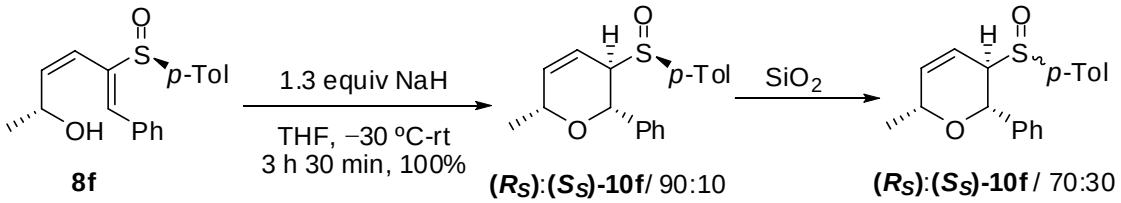
From dienyl sulfoxide **8e** (18 mg, 0.060 mmol) and LDA (0.13 mL, 0.066 mmol) according to the general procedure (Method A, 2 h), an 80:20 mixture of **10e** and **10e'** was obtained. Purification by chromatography (10-50% EtOAc-hexane) afforded **10e** (13 mg, 0.042 mmol, 70%) and **10e'** (3 mg, 0.010 mmol, 17%) as white solids that were recrystallized from hexane.

Data for **10e**: R_f = 0.21 (30% EtOAc-hexane). **mp**: 128-130 ºC. **$[\alpha]^{20}_D$** = –237.1 (*c* = 0.73). **^{1}H NMR (400 MHz), COSY** δ 1.19 (d, 3 H, *J* = 6.8 Hz, Me-6), 2.42 (s, 3 H, Me-*p*-Tol), 3.66 (m, 1 H, H-3), 3.88 (m, 1 H, H-6), 5.30 (dddd, 1 H, *J* = 10.4, 5.5, 2.2, 1.1 Hz, H-4), 5.58 (s, 1 H, H-2), 5.84 (dm, 1 H, *J* = 10.2 Hz, H-5), 7.27-7.37 (m, 7 H), 7.61 (d, 2 H, *J* = 8.2 Hz). **NOESY-1D** H-3/H-2: 1.5%; H-3/H-4: 1.6%; H-3/Ph: 3.5%; H-3/*p*-Tol; H-6/H-5: 1.6%; H-6/Me: 2.5%; H-6/Ph: 1.0%; Me/H-6: 1.2%; Me/H-5: 0.5%. **^{13}C NMR (75 MHz), HSQC** δ 20.3 (Me-6), 21.5 (Me-*p*-Tol), 64.3 (C-3), 65.1 (C-6), 70.9 (C-2), 116.3 (C-4), 125.5 (2 C), 127.8 (2 C), 128.1, 128.3 (2 C), 129.7 (2 C), 137.6, 138.1 (C-5), 138.9, 142.1. **IR** (KBr): 3057, 2971, 2920, 2833, 1635, 1595, 1490, 1452, 1085, 1068, 1049, 806, 747,

710 cm^{-1}. **MS** (ES): 647 $[2M+Na]^+$ (100%), 335 $[M+Na]^+$, 313 $[M+1]^+$. **Anal. calcd for** $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45; S, 10.26. **Found**: C, 73.18; H, 6.37; S, 10.50.

Data for **10e'**: R_f = 0.16 (30% EtOAc-hexane). **^{1}H NMR (200 MHz)** δ 1.08 (t, 3 H, *J* = 6.2 Hz, Me-6), 2.17 (ddm, 1 H, *J* = 18.1, 9.1 Hz, H-5), 2.36 (s, 3 H, Me-*p*-Tol), 2.46 (dm, 1 H, *J* = 18.1 Hz, H-5), 3.70 (m, 1 H, H-6), 4.71 (s, 1 H, H-2), 7.01 (m, 1 H, H-4), 7.19-7.59 (m, 9 H).

4.8. Synthesis of (2*S*,3*R*,6*R*,*R*$_S$)-6-Methyl-2-phenyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, 10f.



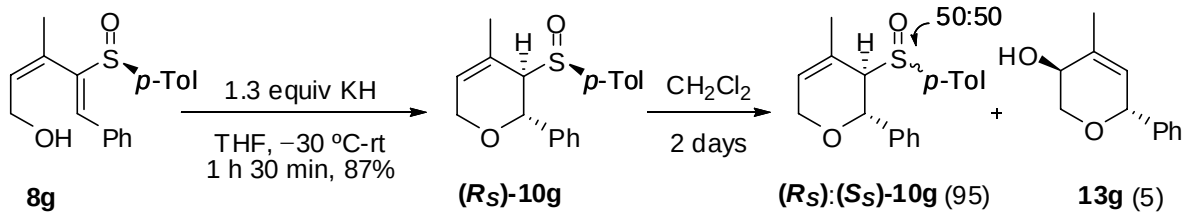
From dienyl sulfoxide **8f** (29 mg, 0.093 mmol) and NaH (3 mg, 0.121 mmol, 1.3 equiv) according to the general procedure (Method B, 3 h 30 min), a 90:10 mixture of **(R_S)-10f** and **(S_S)-10f** was obtained. Purification by chromatography (0-15% EtOAc-CH_2Cl_2) afforded a 90:10 mixture of **(R_S)** and **(S_S)-10f** (29 mg, 0.093, 100%).

When the mixture was in the presence of SiO_2 for longer times the ratio changed to 70:30.

Data for **(R_S)-10f** (from the mixture): R_f = 0.36 (50% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 1.17 (d, 3 H, *J* = 6.6 Hz, Me-6), 2.38 (s, 3 H, Me-*p*-Tol), 4.10 (m, 2 H, H-3, H-6), 4.24 (d, 1 H, *J* = 9.3 Hz, H-2), 5.95 (d, 1 H, *J* = 10.2 Hz), 6.12 (d, 1 H, *J* = 10.2 Hz), 7.21-7.43 (m, 9 H). **^{13}C NMR (50 MHz, partial data)** δ 20.9, 21.5, 63.6, 71.3, 75.7, 118.0, 125.8, 127.9, 128.8, 129.4.

Data for **(S_S)-10f** (from the mixture): R_f = 0.33 (50% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 1.26 (d, 3 H, *J* = 6.8 Hz, Me-6), 2.38 (s, 3 H, Me-*p*-Tol), 3.35 (m, 1 H, H-3), 4.45 (m, 1 H, H-6), 4.92 (d, 1 H, *J* = 10.0 Hz, H-2), 5.44 (dm, 1 H, *J* = 10.5 Hz, H-4), 6.09 (dm, 1 H, *J* = 10.2 Hz, H-5), 7.20-7.46 (m, 7 H), 7.55 (d, 1 H, *J* = 6.6 Hz).

4.9. Synthesis of (2*S*,3*R*)-4-Methyl-2-phenyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, 10g.



From dienyl sulfoxide **8g** (15 mg, 0.048 mmol) and KH (2.5 mg, 0.062 mmol, 1.3 equiv) according to the general procedure (Method B, 1 h 30 min), dihydropyran **(R_S)-10g** was obtained. The crude product

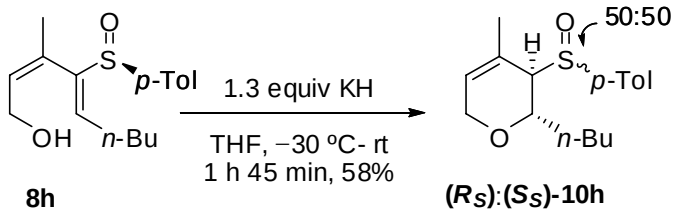
was rapidly filtered through silica gel (20% EtOAc-CH_2Cl_2) to afford **10g** (13 mg, 0.042 mmol, 87%) as a colorless oil that crystallized at 4 ºC. After 2 days at rt diastereomerization of the sulfur center was observed, to give a 50:50 mixture of R_S:S_S dihydropyrans, along with a small amount of **13g**.

Data for **(R_S)-10g**: R_f = 0.32 (20% EtOAc-CH_2Cl_2). **mp**: 91-93 ºC. **^{1}H NMR (300 MHz)** δ 1.39 (q, 3 H, *J* = 1.9 Hz, Me-4), 2.39 (s, 3 H, Me-*p*-Tol), 3.61 (m, 1 H, H-3), 3.89 (dsext, 1 H, *J* = 17.1, 2.2 Hz, H-6), 4.17 (dm, 1 H, *J* = 17.3 Hz, H-6), 5.55 (d, 1 H, *J* = 2.2 Hz, H-2), 5.63 (oct, 1 H, *J* = 1.5 Hz, H-5), 7.18-7.30 (m, 7 H), 7.58 (d, 2 H, *J* = 8.3 Hz). **MS** (ES): 647 $[2M+Na]^+$, 335 $[M+Na]^+$, 313 $[M+1]^+$ (100%). **Anal. calcd for** $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45; S, 10.26. **Found**: C, 73.12; H, 6.27; S, 10.35.

Data for **(S_S)-10g** (from the mixture): R_f = 0.34 (20% EtOAc-CH_2Cl_2). **^{1}H NMR (300 MHz)** δ 2.05 (s, 3 H, Me-4), 2.39 (s, 3 H, Me-*p*-Tol), 3.64 (m, 1 H, H-3), 3.84 (m, 2 H, H-6), 5.22 (s, 1 H, H-2), 5.70 (m, 1 H, H-5), 7.20-7.30 (m, 7 H), 7.51 (dm, 2 H, *J* = 8.3 Hz).

Partial data for **13g** (from the mixture): R_f = 0.17 (20% EtOAc-CH_2Cl_2). **^{1}H NMR (300 MHz)** δ 1.91 (t, 3 H, *J* = 1.7 Hz, Me-4), 3.63 (dd, 1 H, *J* = 12.4, 5.1 Hz, H-2), 3.88 (dd, 1 H, *J* = 12.7, 3.7 Hz, H-2), 3.90 (m, 1 H, *J* = 12.7, 3.7 Hz, H-2), 5.15 (m, 1 H, H-6), 5.74 (m, 1 H, H-5).

4.10. Synthesis of (2*S*,3*R*)-2-*n*-Butyl-4-methyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, 10h.

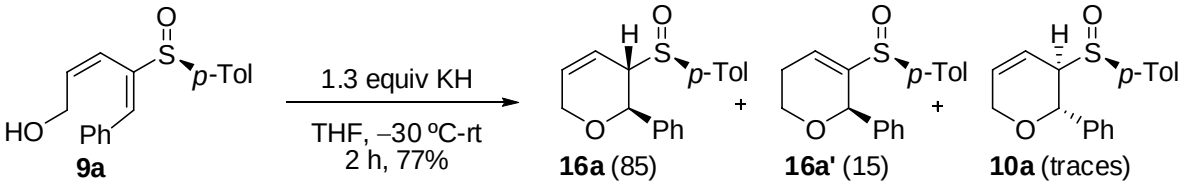


From dienyl sulfoxide **8h** (43 mg, 0.147 mmol) and KH (1.3 equiv, 8 mg, 0.191 mmol) according to the general procedure (Method B, 1 h 45 min), an 89:11 mixture of dihydropyrans **(R_s):(S_s) 10h** was obtained. Column chromatography (15-40% EtOAc-hexane) afforded a 50:50 mixture of **(R_s):(S_s) 10h** (25 mg, 0.086 mmol, 58%) as a colorless oil.

Data for **10h** (50:50 mixture): R_f = 0.40 (50% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 0.83 (t, 6 H, *J* = 7.0 Hz, 2 CH_3), 1.18-1.40 (m, 11 H, 4 CH_2, Me-4 isom B), 1.56-1.67 (m, 4 H, 2 CH_2 isom A), 1.96 (s, 3 H, Me-4 isom A), 2.37 (s, 3 H, Me-*p*-Tol isom B), 2.39 (s, 3 H, Me-*p*-Tol isom A), 2.95 (s, 1 H, H-3 isom A), 3.20 (s, 1 H, H-3 isom B), 3.48 (d, 1 H, *J* = 17.3 Hz, H-6 isom B), 3.84 (dd, 1 H, *J* = 17.3, 2.3 Hz, H-6 isom B) 3.98-4.14 (m, 3 H, H-2 isom B, 2 x H-6 isom A), 4.44 (m, 1 H, H-2 isom A), 5.65 (d, 1 H, *J* = 1.5 Hz, H-5 isom A), 5.67 (s, 1 H, H-5 isom B), 7.23-7.57 (m, 8 H, Ar-H). **^{13}C NMR (75 MHz)** δ 13.9 (2 Me), 21.4 (2 C), 22.4 (2 C), 22.8, 23.1, 27.8, 27.9, 30.4, 31.1, 59.7, 60.8, 66.9, 68.1, 69.3, 71.3, 116.1 (2 C), 123.9, 124.3, 124.8 (3 C), 125.5 (3 C), 126.5, 126.7, 129.1 (3 C), 129.7 (3 C),

141.1, 141.9. **IR** (film): 3021, 2950, 2930, 2855, 2826, 1594, 1493, 1454, 1382, 1271, 1147, 1100, 1084, 1044, 1015, 809 cm^{-1}. **MS** (EI): 292 $[M]^+$, 153 $[M–p\text{-Tol}]^+$.

4.11. Synthesis of (+)-(2*R*,3*S*,*R*$_S$)-2-Phenyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, 16a.

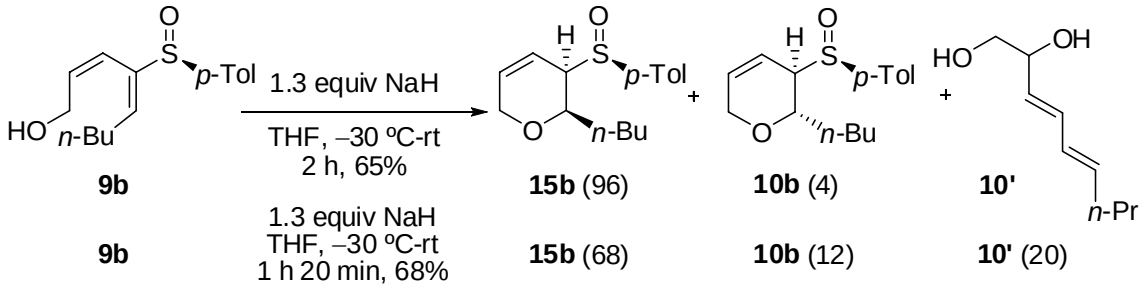


From dienyl sulfoxide **9a** (30 mg, 0.100 mmol) and KH (5.2 mg, 0.130 mmol, 1.3 equiv) according to the general procedure (Method B, 2 h), an 85:15 mixture of **16a** and **16a'** was obtained. Purification by chromatography (20-50% EtOAc-hexane) afforded **16a** (20 mg, 0.067 mmol, 67%) and **16a'** impure with traces of **10a** (3 mg, 0.010 mmol, 10%) as colorless oils.

Data for **16a**: R_f = 0.29 (50% EtOAc-hexane). $[\alpha]^{20}_D$ = +248.2 (*c* = 0.50). **^{1}H NMR (300 MHz), COSY** δ 2.37 (s, 3 H, Me-*p*-Tol), 3.45 (ap dquint, 1 H, *J* = 8.3, 2.7 Hz, H-3), 4.19 (ddd, 1 H, *J* = 17.1, 5.6, 2.5 Hz, H-6), 4.32 (ddd, 1 H, *J* = 17.1, 5.5, 2.3 Hz, H-6), 4.90 (d, 1 H, *J* = 8.5 Hz, H-2), 5.59 (dq, 1 H, *J* = 10.5, 2.3 Hz, H-4), 6.20 (ddt, 1 H, *J* = 10.5, 3.4, 2.1 Hz, H-5), 7.26-7.45 (m, 7 H), 7.50 (dm, 2 H, *J* = 8.3 Hz). **NOESY-1D** H-2/*p*-Tol: 2.3%; H-3/H-4: 2.3%; H-3/*p*-Tol: 1.8%; H-3/Ph: 2%; H-6/H-5: 5.7%; H-6/H-5: 2%; H-6/H-2: 2.9%. **^{13}C NMR (75 MHz), HSQC** δ 21.4 (Me-*p*-Tol), 65.3 (C-6), 65.7 (C-3), 75.7 (C-2), 117.3 (C-4), 124.3 (2 C), 127.6 (2 C), 128.8 (3 C), 129.8 (2 C), 134.2 (C-5), 137.6, 138.8, 141.2. **IR** (film): 3028, 2923, 2855, 1596, 1492, 1453, 1177, 1084, 1045, 910, 809, 757 cm^{-1}. **MS** (ES): 619 $[2M+Na]^+$ (100%), 321 $[M+Na]^+$, 299 $[M+1]^+$.

Partial data for **16a'**: R_f = 0.16 (10% EtOAc-CH_2Cl_2). **^{1}H NMR (300 MHz)** δ 2.33 (s, 3 H, Me-*p*-Tol), 2.45 (m, 2 H, H-5), 3.67 (ddd, 1 H, *J* = 11.6, 6.3, 5.1 Hz, H-6), 3.87 (dt, 1 H, *J* = 11.7, 5.6 Hz, H-6), 5.20 (ap dd, 1 H, *J* = 3.9, 2.2 Hz, H-2), 6.85 (ddd, 1 H, *J* = 4.6, 3.4, 1.5 Hz, H-4), 7.08-7.22 (m, 9 H).

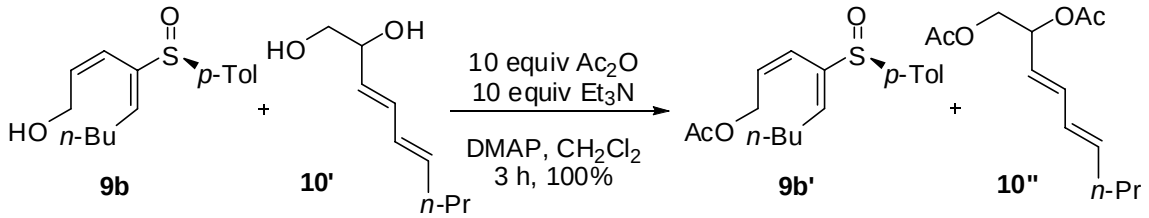
4.12. Synthesis of (–)-(2*R*,3*R*,*R*$_S$)-2-*n*-Butyl-3-(*p*-tolylsulfinyl)-3,6-dihydro-2*H*-pyran, 15b.



From dienyl sulfoxide **9b** (20 mg, 0.070 mmol) and NaH (2.2 mg, 0.090 mmol) according to the general procedure (Method B, 2 h), a 65:3:16:16 mixture of **15b**, **10b**, **10'** and starting material was obtained. Column chromatography (10-50% EtOAc-hexane) afforded **15b** (13 mg, 0.048 mmol, 65%) as a white solid that was recrystallized from Et_2O-hexane and 6 mg of an inseparable mixture of diol **10'** and diene **9b**.

The cyclization of **9b** occasionally displayed lower selectivities.

From dienyl sulfoxide **9b** (98 mg, 0.352 mmol) and NaH (11 mg, 0.458 mmol) according to the general procedure (Method B, 1 h 20 min), a 68:12:20 mixture of **15b**, **10b** and **10'** was obtained. Column chromatography (10-50% EtOAc-hexane) afforded **15b** (59 mg, 0.213 mmol, 61%) as a white solid, **10b** (7 mg, 0.025 mmol, 7%) and **10'** (16 mg, 0.102 mmol, 29%) as colorless oils.



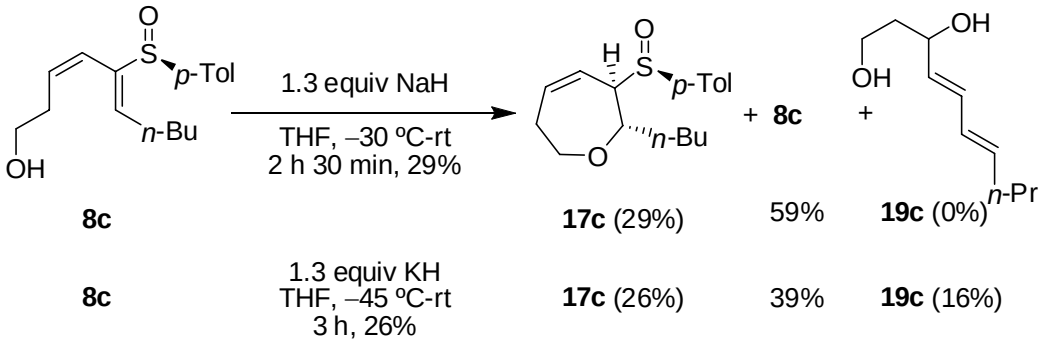
To a solution of 5 mg of a 50:50 mixture of **9b** and **10'** in 0.5 mL of CH_2Cl_2, was added acetic anhydride (30 μL, 0.32 mmol, 10 equiv), Et_3N (50 μL, 0.32 mmol, 10 equiv) and catalytic DMAP. The mixture was stirred at rt for 3 h and quenched by addition of a saturated solution of NH_4Cl and H_2O and diluted with CH_2Cl_2. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification by chromatography (5-50% EtOAc-hexane) afforded **9b'** (5 mg, 0.016 mmol, 50%) and **10''** (4 mg, 0.016 mmol, 50%), as colorless oils.

Data for **15b**: R_f = 0.33 (50% EtOAc-hexane). **mp**: 80-82 ºC. $[\alpha]^{20}_D$ = –334.1 (*c* = 0.91). **^{1}H NMR (300 MHz), COSY** δ 0.93 (t, 3 H, *J* = 7.1 Hz, Me-*n*-Bu), 1.33-1.64 (m, 4 H), 1.99-2.07 (m, 2 H), 2.39 (s, 3 H, Me-*p*-Tol), 3.30 (dqd, 1 H, *J* = 5.9, 2.2, 1.0 Hz, H-3), 3.83 (ddd, 1 H, *J* = 6.8, 5.8, 2.2 Hz, H-2), 4.15 (dd, 2 H, *J* = 4.6, 2.3 Hz, H-6), 5.02 (ddt, 1 H, *J* = 10.2, 5.9, 2.2, H-4), 5.76 (dtd, 1 H, *J* = 10.0, 2.5, 1.0 Hz, H-5), 7.26 (d, 2 H, *J* = 8.5 Hz, *p*-Tol), 7.53 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **NOESY-1D** H-2/H-3: 2.2%; H-2/H-6: 1.9%; H-3/H-2: 2.3%; H-3/H-4: 2.0%; H-3/CH_2-*n*-Bu: 1.6%; CH_2-*n*-Bu/H-3: 0.9%; CH_2-*n*-Bu/H-2: 1.2%; CH_2-*n*-Bu/*p*-Tol: 0.3%. **^{13}C NMR (75 MHz), HSQC** δ 14.0 (Me-*n*-Bu), 21.4 (Me-*p*-Tol), 22.5 (CH_2 *n*-Bu), 28.7 (CH_2 *n*-Bu), 32.8 (CH_2 *n*-Bu), 66.6 (C-3), 66.8 (C-6), 75.8 (C-2), 120.1 (C-4), 126.0 (2 C), 129.4 (2 C), 131.4 (C-5), 139.1, 141.6. **IR** (KBr): 3043, 2956, 2927, 2847, 1631, 1261, 1184, 1091, 1042, 812 cm^{-1}. **MS** (ES): 579 $[2M+Na]^+$, 301 $[M+Na]^+$, 279 $[M+1]^+$ (100%). **Anal. calcd for** $C_{16}H_{22}O_2S$: C, 69.02; H, 7.96; S, 11.52. **Found**: C, 69.14; H, 7.73; S, 11.66.

Data for diacetate **10''**: R_f = 0.18 (15% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 0.88 (t, 3 H, *J* = 7.3 Hz, Me-*n*-Pr), 1.39 (sext, 2 H, *J* = 7.3 Hz, H-8), 2.04 (s, 3 H, Me-CO), 2.05 (m, 2 H, H-7), 2.07 (s, 3 H, Me-CO), 4.07 (dd, 1 H, *J* = 11.7, 7.1 Hz, H-1), 4.21 (dd, 1 H, *J* = 11.7, 3.4 Hz, H-1), 5.41-5.52 (m, 2 H, H-3, H-2), 5.75 (dt, 1 H, *J* = 15.1, 7.1 Hz, H-6), 5.99 (ddt, 1 H, *J* = 15.1, 10.3, 1.2 Hz, H-5), 6.28 (dd, 1 H, *J* = 14.2, 10.4 Hz, H-4).

Partial data for acetate **9b'**: R_f = 0.42 (50% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 0.87 (t, 3 H, *J* = 6.6 Hz, Me-*n*-Bu), 1.30 (m, 2 H), 1.45 (m, 2 H), 1.99 (s, 3 H, Me-CO), 2.10 (m, 2 H), 2.39 (s, 3 H, Me-*p*-Tol), 4.22 (m, 2 H, H-1), 5.73 (dm, 1 H, *J* = 13.1 Hz, H-3), 5.85 (dt, 1 H, *J* = 13.1, 6.5 Hz, H-2), 6.53 (td, 1 H, *J* = 7.6, 1.2 Hz, H-5).

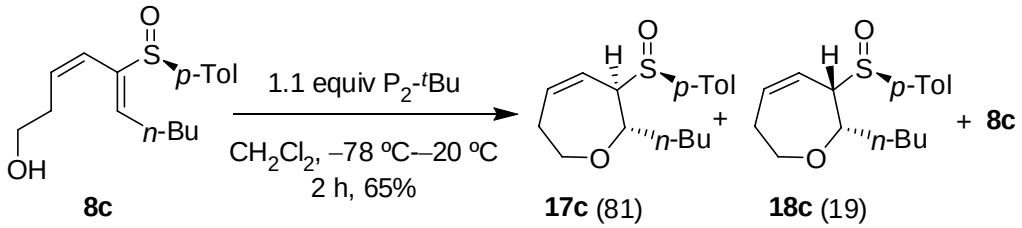
4.13. Synthesis of (−)-(2*S*,3*R*)-2-*n*-Butyl-3-(*p*-tolylsulfinyl)-2,3,6,7-tetrahydrooxepine, 17c.



From dienyl sulfoxide **8c** (34 mg, 0.116 mmol), 1.3 equiv de NaH (4 mg, 0.151 mmol), according to the general procedure (Method B, 2 h 30 min), a 31:69 mixture of oxepine **17c** and starting material was obtained. Purification by chromatography (0-30% EtOAc-CH_2Cl_2) afforded oxepine **17c** (10 mg, 0.034 mmol, 29%) and starting material (20 mg, 0.068 mmol, 59%) as yellow oils.

When the reaction is carried out using KH and following the same procedure, **17c** is obtained in 26% yield along with dienyl sulfoxide **8c** (39%) and diol **19c** (16%).

Partial data for diol **19c**: **^{1}H NMR (200 MHz)** δ 2.08 (dd, 1 H, *J* = 15.0, 6.3 Hz), 2.30-2.51 (m, 2 H), 3.67 (t, 1 H, *J* = 6.4 Hz), 5.69 (m, 1 H), 6.14 (m, 1 H). **MS** (ES): 171 $[M+1]^+$ (100%).



From dienyl sulfoxide **8c** (17 mg, 0.058 mmol), P_2-^{t}Bu (1.1 equiv, 32 μL, 0.064 mmol), according to the general procedure (Method E, 2 h), a 65:16:19 mixture of oxepines **17c**, **18c** and starting material

was obtained. Purification by chromatography (0-30% EtOAc-CH_2Cl_2) afforded an 81:19 mixture of oxepines **17c** and **18c** (11 mg, 0.038 mmol, 65%) and starting material (3 mg, 0.010 mmol, 18%) as yellow oils.

Data for **17c**: R_f = 0.39 (30% EtOAc-CH_2Cl_2). $[\alpha]^{20}_D$ = –196.8 (*c* = 0.50). **^{1}H NMR (300 MHz), COSY** δ 0.88 (t, 3 H, *J* = 7.1 Hz, CH_3-Bu), 1.24-1.36 (m, 5 H), 1.84 (m, 1 H), 2.20 (ddt, 1 H, *J* = 17.1, 7.7, 3.8 Hz, H-6), 2.39 (s, 3 H, CH_3 *p*-Tol), 2.70 (m, 1 H, H-6), 3.23 (dd, 1 H, *J* = 7.8, 3.4 Hz, H-3), 3.77 (dd, 1 H, *J* = 6.4, 3.9 Hz, H-7), 3.78 (dd, 1 H, *J* = 7.9, 3.6 Hz, H-7), 4.43 (dt, 1 H, *J* = 9.5, 3.7 Hz, H-2), 5.03 (ddd, 1 H, *J* = 11.0, 7.9, 2.9 Hz, H-4), 6.01 (ddd, 1 H, *J* = 11.3, 7.6, 3.7 Hz, H-5), 7.26 (d, 2 H, *J* = 8.8 Hz, H_m *p*-Tol), 7.53 (d, 1 H, *J* = 8.1 Hz, H_o *p*-Tol). **NOESY-1D** H-2/*p*-Tol: 0.5%; H-2/H-7 (3.78 ppm): 1.2%; H-2/H-3: 2.6%; H-6 (2.70 ppm)/H-5: 1.0%; H-6 (2.70 ppm)/H-7 (3.77 ppm): 3.0%. **^{13}C NMR (75 MHz)** δ 14.0 (Me-Bu), 21.5 (Me *p*-Tol), 22.5, 27.8, 31.3, 31.8, 61.5, 72.8, 73.4, 121.9, 124.0, 125.5 (2 C, Ar), 129.5 (2 C, Ar), 136.0. **IR** (film): 3401, 3021, 2949, 2930, 2860, 1595, 1492, 1456, 1378, 1288, 1208, 1096, 1048, 809 cm^{-1}. **MS** (ES): 607 $[2M+Na]^+$ (100%), 315 $[M+Na]^+$, 293 $[M+1]^+$.

Partial data for **18c**: R_f = 0.39 (30% EtOAc-CH_2Cl_2). **^{1}H NMR (300 MHz)** δ 3.47 (td, 1 H, *J* = 10.5, 1.8 Hz), 4.17 (dt, 1 H, *J* = 12.0, 3.9 Hz, H-2), 5.22 (ddd, 1 H, *J* = 11.0, 8.0, 2.9 Hz, H-4), 6.30 (ddd, 1 H, *J* = 11.2, 8.0, 3.2 Hz, H-5).

5. Synthesis of allylic sulfones.

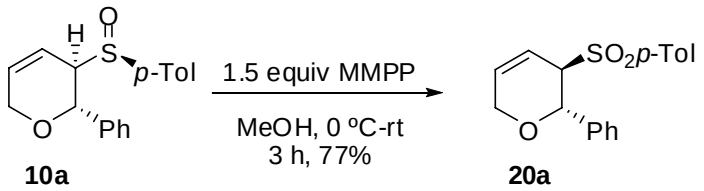
5.1. General procedure for the oxidation of allylic sulfoxides.

Method G: To a cold (0 ºC) solution of 1.0 equiv of sulfoxide in MeOH (10 mL/mmol) under an argon atmosphere, 1.5 equiv of magnesium bis(monoperoxyphthalate) hexahydrate (MMPP) was added. The reaction was warmed to rt and stirred until disappearance of starting material was observed (TLC). The mixture was quenched with saturated $NaHCO_3$ solution (4 mL/mmol) and MeOH was eliminated under reduced pressure. The residue was diluted with EtOAc and H_2O and the layers were separated. The aqueous layer was extracted with EtOAc (3 x 4 mL/mmol) and the combined organic layers were washed with brine (1 mL/mmol), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with the appropriate combination of solvents.

Method H: To a cold (–40 ºC) solution of sulfoxide in CH_2Cl_2 (8 mL/mmol), 1.5 equiv of *meta*-chloroperbenzoic acid (*m*-CPBA) was added. The reaction was warmed to rt and stirred until disappearance of starting material was observed (TLC). The mixture was quenched with 1 M $Na_2S_2O_4$

solution (3 mL/mmol), saturated $NaHCO_3$ solution (2 mL/mmol) and H_2O (3 mL/mmol). The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (2 x 4 mL/mmol) and the combined organic layers were washed with saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel with the appropriate combination of solvents.

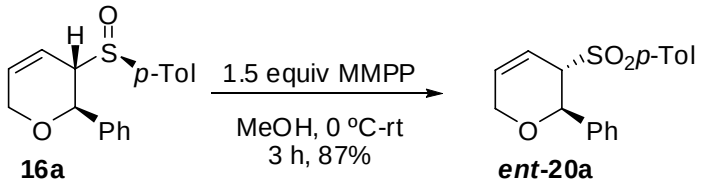
5.2. Synthesis of (–)-(2*S*,3*R*)-2-Phenyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, 20a.



From sulfoxide **10a** (10 mg, 0.033 mmol) and MMPP [31 mg (80%), 0.049 mmol] according to the general procedure (Method G, 3 h) sulfone **20a** was obtained. Purification by chromatography (10-30% EtOAc-hexane) afforded sulfone **20a** (8 mg, 0.025 mmol, 77%) as a white solid that was recrystallized from Et_2O-hexane.

Data for **20a**: R_f = 0.47 (50% EtOAc-hexane). **mp**: 173-175 ºC. $[\alpha]^{20}_D$ = –205.1 (*c* = 0.67). **^{1}H NMR (300 MHz)** δ 2.39 (s, 3 H, Me-*p*-Tol), 3.83 (ap q, 2 H, *J* = 2.3 Hz, H-6), 4.17 (m, 1 H, H-3), 5.20 (d, 1 H, *J* = 4.1 Hz, H-2), 6.08 (dtd, 1 H, *J* = 10.5, 2.4, 1.5 Hz, H-5), 6.16 (dquint, 1 H, *J* = 10.2, 1.9 Hz, H-4), 7.19-7.27 (m, 7 H), 7.66 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **^{13}C NMR (50 MHz)** δ 21.6 (Me-*p*-Tol), 61.8, 63.4, 73.2, 117.2, 127.6 (2 C), 128.5 (2 C), 129.2 (2 C), 129.3 (2 C), 133.6, 134.4, 137.4, 144.5. **IR** (KBr): 3028, 2898, 2833, 1631, 1595, 1299, 1134, 1084, 810, 748, 708 cm^{-1}. **MS** (ES): 651 $[2M+Na]^+$ (100%), 337 $[M+Na]^+$, 315 $[M+1]^+$. **Anal. calcd for** $C_{18}H_{18}O_3S$: C, 68.76; H, 5.77; S, 10.20. **Found**: C, 68.98; H, 5.59; S, 10.47.

5.3. Synthesis of (–)-(2*R*,3*S*)-2-Phenyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, *ent*-20a.

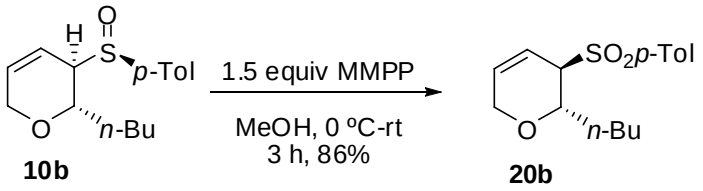


From sulfoxide **16a** (10 mg, 0.033 mmol) and MMPP [31 mg (80%), 0.049 mmol], according to the general procedure (Method G, 3 h) sulfone ***ent*-20a** was obtained. Purification by chromatography (10-

30% EtOAc-hexane) afforded sulfone ***ent*-20a** (9 mg, 0.028 mmol, 87%) as a white solid that was recrystallized from Et_2O-hexane.

The data for ***ent*-20a** was identical to that of **20a** except for the optical rotation: $[\alpha]^{20}_{D}$ = +196.4 (*c* = 0.83).

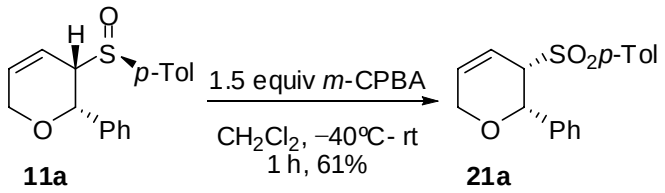
5.4. Synthesis de (–)-(2*S*,3*R*)-2-*n*-Butyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, 20b.



From sulfoxide **10b** (569 mg, 2.04 mmol) and MMPP [1.9 g (80%), 3.06 mmol], according to the general procedure (Method G, 3 h) sulfone **20b** was obtained. Purification by chromatography (10-30% EtOAc-hexane) afforded **20b** (517 mg, 1.76 mmol, 86%) as a colorless oil.

Data for **20b**: R_f = 0.38 (30% EtOAc-hexane). $[\alpha]^{20}_{D}$ = –150.6 (*c* = 0.59). **^{1}H NMR (300 MHz)** δ 0.87 (t, 3 H, *J* = 7.1 Hz, Me-*n*-Bu), 1.20-1.40 (m, 4 H), 1.62 (m, 2 H), 2.42 (s, 3 H, Me-*p*-Tol), 3.51 (m, 1 H, H-3), 3.63 (ddd, 1 H, *J* = 17.6, 4.6, 2.4 Hz, H-6), 3.93 (ddd, 1 H, *J* = 17.6, 4.8, 2.7 Hz, H-6), 4.13 (ddd, 1 H, *J* = 8.7, 5.4, 3.7 Hz, H-2), 5.87 (ddt, 1 H, *J* = 10.2, 3.7, 2.2 Hz), 6.00 (dtd, 1 H, *J* = 10.2, 2.7, 1.5 Hz), 7.30 (d, 2 H, *J* = 8.1 Hz, *p*-Tol), 7.71 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **^{13}C NMR (75 MHz)** δ 14.0, 21.7, 22.4, 27.6, 32.0, 60.8, 64.6, 70.8, 117.0, 129.3, 129.6, 133.0, 134.1, 144.6. **IR** (film): 3022, 2949, 2928, 2859, 1597, 1493, 1456, 1380, 1309, 1301, 1284, 1216, 1182, 1132, 1084, 1019, 814, 758, 708 cm^{-1}. **MS** (ES): 611 $[2M+Na]^+$, 317 $[M+Na]^+$, 295 $[M+1]^+$ (100%).

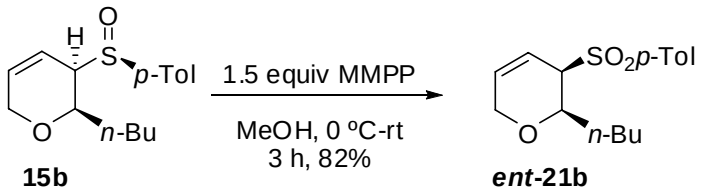
5.5. Synthesis of (+)-(2*S*,3*S*)-2-Phenyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, 21a.



From sulfoxide **11a** (14 mg, 0.047 mmol, 1.0 equiv) and *m*-CPBA (70%, 1.5 equiv, 18 mg, 0.071 mmol) according to the general procedure (Method H, 1 h) sulfone **21a** was obtained. Purification by chromatography (0-5% EtOAc-CH_2Cl_2) afforded sulfone **21a** (9 mg, 0.029 mmol, 61%) as white solid that was recrystallized from Et_2O-hexane.

Data for **21a**: R_f = 0.33 (50% EtOAc-hexane). **mp**: 121-123 ºC. $[\alpha]^{20}_D$ = +262.9 (*c* = 0.88). **^{1}H NMR (300 MHz)** δ 2.36 (s, 3 H, CH_3 *p*-Tol), 4.13 (ddt, 1 H, *J* = 6.0, 4.3, 3.0 Hz, H-3), 4.27 (m, 2 H, H-6), 4.95 (d, 1 H, *J* = 3.2 Hz, H-2), 6.10-6.20 (m, 2 H, H-4, H-5), 7.09 (d, 2 H, *J* = 8.5 Hz, H_m *p*-Tol), 7.20-7.26 (m, 5 H, Ar-H), 7.35 (d, 1 H, *J* = 8.3 Hz, H_o *p*-Tol). **NOESY-1D** H-2/Ph: 4.5%; H-2/H-6 (4.26): 2.0%; H-2/H-3: 2.9%. **^{13}C NMR (75 MHz), HMQC** δ 21.6 (Me *p*-Tol), 64.2 (C-3), 66.7 (C-6), 75.0 (C-2), 119.3 (C-4), 125.8 (2 C, Ar), 127.4, 127.8 (2 C, Ar), 128.9 (2 C, Ar), 129.0 (2 C, Ar), 133.4 (C-5), 136.7, 137.1, 143.7. **IR** ($CHCl_3$): 3449, 3028, 2920, 2847, 1595, 1490, 1450, 1315, 1299, 1179, 1179, 1143, 1082, 811 cm^{-1}. **MS** (ES): 337 $[M+Na]^+$ (100%).

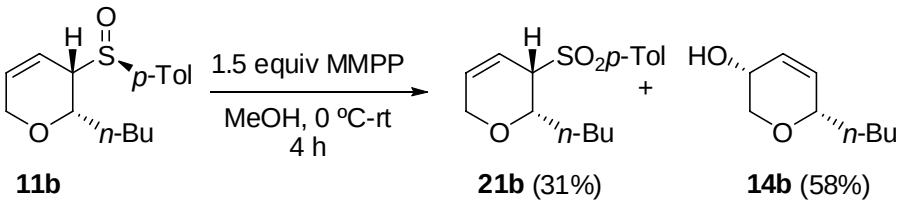
5.6. Synthesis of (–)-(2*R*,3*R*)-2-*n*-Butyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, *ent*-21b.



From sulfoxide **15b** (6 mg, 0.022 mmol) and MMPP [20 mg (80%), 0.033 mmol], according to the general procedure G (3 h) sulfone ***ent*-21b** was obtained. Purification by chromatography (10-30% EtOAc-hexane) afforded sulfone ***ent*-21b** (5 mg, 0.018 mmol, 82%) as a colorless oil.

Data for ***ent*-21b**: R_f = 0.36 (30% EtOAc-hexane). $[\alpha]^{20}_D$ = –208.5 (*c* = 0.47). **^{1}H NMR (300 MHz)** δ 0.90 (t, 3 H, *J* = 7.1 Hz, Me-*n*-Bu), 1.31-1.50 (m, 4 H), 1.98 (m, 2 H), 2.41 (s, 3 H, Me-*p*-Tol), 3.67 (m, 2 H, H-2, H-3), 3.78 (dm, 1 H, *J* = 17.1 Hz, H-6), 4.03 (dm, 1 H, *J* = 17.1 Hz, H-6), 5.88 (ddt, 1 H, *J* = 10.2, 4.9, 1.9 Hz), 5.95 (dm, 1 H, *J* = 10.2 Hz), 7.27 (d, 2 H, *J* = 8.1 Hz, *p*-Tol), 7.72 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **^{13}C NMR (75 MHz)** δ 14.0, 21.6, 22.5, 28.8, 29.7, 32.2, 63.7, 66.0, 75.1, 120.0, 129.1, 129.6, 132.9, 136.2, 144.2. **IR** (film): 3043, 3014, 2925, 2855, 2826, 1596, 1466, 1450, 1385, 1371, 1313, 1286, 1182, 1136, 1083, 1035, 1013, 962, 854, 826, 752, 712 cm^{-1}. **MS** (ES): 611 $[2M+Na]^+$ (100%), 317 $[M+Na]^+$, 295 $[M+1]^+$.

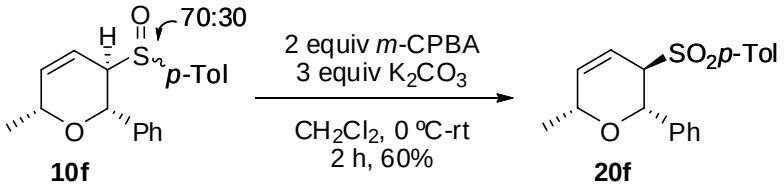
5.7. Synthesis of (+)-(2*S*,3*S*)-2-*n*-Butyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, 21b.



From sulfoxide **11b** (6 mg, 0.022 mmol) and MMPP [1.5 equiv, 20 mg, (80%) 0.033 mmol] according to the general procedure (Method G, 4 h) sulfone **21b** was obtained, along with alcohol **14b**. Purification by chromatography (5-30% EtOAc-hexane) afforded sulfone **21b** (2 mg, 0.007 mmol, 31%) and alcohol **14b** (2 mg, 0.013 mmol, 58%) as colorless oils.

The data for **21b** was identical to that of ***ent*-21b** except for the optical rotation. $[\alpha]^{20}_{D}$ = +201.6 (*c* = 0.38).

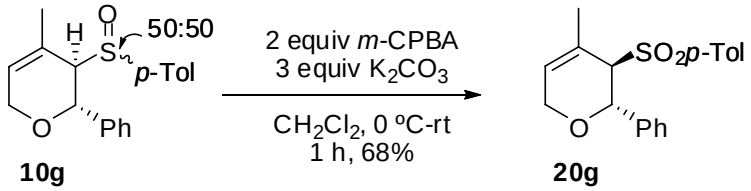
5.8. Synthesis of (−)-(2*S*,3*R*,6*R*)-6-Methyl-2-phenyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, 20f.



From a 70:30 mixture of sulfoxides **(R_S):(S_S)-10f** (3 mg, 0.010 mmol), K_2CO_3 (4 mg, 0.030 mmol) and *m*-CPBA [4 mg (70%), 0.015 mmol], according to the general procedure (Method H, 2 h), sulfone **20f** was obtained. Purification by chromatography (10-30% EtOAc-hexane) afforded sulfone **20f** (2 mg, 0.006 mmol, 60%) as a colorless oil.

Data for **20f**: R_f = 0.38 (30% EtOAc-hexane). $[\alpha]^{20}_{D}$ = −53.0 (*c* = 0.16). **^{1}H NMR (400 MHz)** δ 1.20 (d, 3 H, *J* = 6.8 Hz, Me-6), 2.34 (s, 3 H, Me-*p*-Tol), 4.25 (m, 2 H, H-3, H-6), 6.09 (d, 1 H, *J* = 11.2 Hz), 6.13 (d, 1 H, *J* = 11.2 Hz), 7.09 (d, 2 H, *J* = 8.1 Hz), 7.17-7.22 (m, 5 H), 7.45 (d, 2 H, *J* = 8.2 Hz). **^{13}C NMR (100 MHz, partial data)** δ 20.8 (Me-6), 21.5 (Me-*p*-Tol), 65.2, 71.1, 118.1 (C-4), 128.0 (2 C), 128.4 (2 C), 128.7, 129.3 (2 C), 137.9 (C-5). **IR** (film): 3021, 2926, 2855, 1595, 1494, 1456, 1374, 1313, 1303, 1215, 1144, 1085, 1042, 758 cm^{-1}. **MS** (ES): 679 $[2M+Na]^+$ (100%), 351 $[M+Na]^+$, 329 $[M+1]^+$.

5.9. Synthesis of (−)-(2*S*,3*R*)-4-Methyl-2-phenyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, 20g.

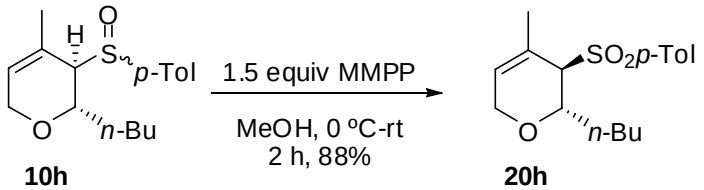


From a 50:50 mixture of sulfoxides **(R_S):(S_S)-10g** (7 mg, 0.022 mmol), K_2CO_3 (9 mg, 0.066 mmol) and *m*-CPBA [8 mg (70%), 0.034 mmol], according to the general procedure (Method H, 1 h), sulfone

20g was obtained. Purification by chromatography (10-30% EtOAc-hexane) afforded sulfone **20g** (5 mg, 0.015 mmol, 68%) as a white solid that was recrystallized from EtOAc-hexane.

Data for **20g**: R_f = 0.42 (30% EtOAc-hexane). **mp**: 107-109 ºC. $[\alpha]^{20}_D$ = –233.3 (*c* = 0.45). **^{1}H NMR (300 MHz)** δ 2.12 (d, 3 H, *J* = 1.7 Hz, Me-4), 2.42 (s, 3 H, Me-*p*-Tol), 3.34 (dm, 1 H, *J* = 17.6 Hz, H-6), 3.56 (dd, 1 H, *J* = 17.6, 1.7 Hz, H-6), 3.99 (s, 1 H, H-3), 5.48 (br s, 1 H, H-2), 5.66 (s, 1 H, H-5), 7.19-7.22 (m, 2 H), 7.26-7.32 (m, 5 H), 7.81 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **^{13}C NMR (75 MHz)** δ 21.7, 23.3, 60.2, 67.7, 71.7, 124.1, 126.9 (2 C), 128.1, 128.5 (3 C), 129.0 (2 C), 129.8 (2 C), 134.6, 137.3, 144.4. **IR** (KBr): 3028, 2920, 2826, 1630, 1285, 1131, 1084, 694 cm^{-1}. **MS** (ES): 679 [2M+Na]$^+$ (100%), 351 [M+Na]$^+$, 329 [M+1]$^+$. **Anal. calcd for** $C_{19}H_{20}O_3S$: C, 69.48; H, 6.14; S, 9.76. **Found**: C, 69.25; H, 6.43; S, 9.52.

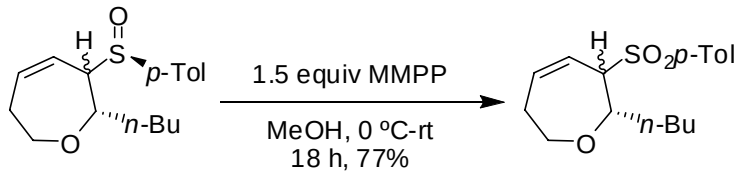
5.10. Synthesis of (–)-(2*R*,3*R*)-2-*n*-Butyl-4-methyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, 20h.



From a 50:50 mixture of sulfoxides **(R_S):(S_S)-10h** (27 mg, 0.092 mmol), and MMPP [68 mg (80%), 0.138 mmol], according to the general procedure (Method G, 20 h) sulfone **20h** was obtained. Purification by chromatography (10-20% EtOAc-hexane) afforded sulfone **20h** (25 mg, 0.081 mmol, 88%) as a colorless oil.

Data for **20h**: R_f = 0.40 (20% EtOAc-hexane). $[\alpha]^{20}_D$ = –122.3 (*c* = 1.36). **^{1}H NMR (300 MHz)** δ 0.86 (t, 3 H, *J* = 6.5 Hz, Me-*n*-Bu), 1.21-1.33 (m, 4 H, 2 CH_2), 1.43-1.60 (m, 2 H, CH_2), 2.01 (3 H, d, *J* = 1.7 Hz, Me-4), 2.40 (s, 3 H, Me-*p*-Tol), 3.28 (d, 1 H, *J* = 1.7 Hz, H-3), 3.29 (dt, 1 H, *J* = 17.4, 2.4 Hz, H-6), 3.78 (dq, 1 H, *J* = 17.7, 2.4 Hz, H-6), 4.52 (dd, 1 H, *J* = 9.3, 3.6 Hz, H-2), 5.51 (d, 1 H, *J* = 1.2 Hz, H-5), 7.25 (d, 2 H, *J* = 8.5 Hz, *p*-Tol), 7.70 (d, 2 H, *J* = 8.3 Hz, *p*-Tol). **^{13}C NMR (75 MHz)** δ 13.9, 21.6, 22.4, 23.4, 27.9, 30.5, 59.6 (C-6), 69.5 (C-2), 70.5 (C-3), 123.7, 127.2 (C-5), 128.8 (2 C), 129.7 (2 C), 134.5, 144.2. **IR** (film): 2926, 2855, 1652, 1594, 1453, 1300, 1129, 1082, 812, 765 cm^{-1}. **MS** (ES): 331 [M+Na]$^+$ (100%).

5.11. Synthesis of 2-*n*-Butyl-3-(*p*-tolylsulfonyl)-2,3,6,7-tetrahydro-oxepines, 22c, 23c.



17c:18c [81:19] **22c:23c** [83:17]

From an 81:19 mixture of sulfoxides **17c** and **18c** (6 mg, 0.021 mmol), and MMPP [1.5 equiv, 20 mg, (80%), 0.032 mmol] according to the general procedure (Method G, 18 h) a mixture of sulfones **22c**, **23c** was obtained. Purification by chromatography (0-30% EtOAc-hexane) afforded an 83:17 mixture of sulfones **22c**, **23c** (5 mg, 0.016 mmol, 77%) as a colorless oil.

Partial data for **22c** (from the mixture): R_f = 0.25 (20% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 0.87 (t, 3 H, *J* = 7.1 Hz, CH_3-Bu), 1.24-1.43 (m, 4 H), 1.65 (ap q, 2 H, *J* = 6.8 Hz, CH_2), 1.99 (ddt, 1 H, *J* = 16.6, 7.2, 4.6 Hz, H-6), 2.06-2.16 (m, 1 H, H-6), 2.43 (s, 3 H, CH_3 *p*-Tol), 3.54-3.72 (m, 3 H, H-3, H-7), 4.30 (q ap, 1 H, *J* = 6.3 Hz, H-2), 5.43 (ddd, 1 H, *J* = 11.3, 7.3, 2.5 Hz, H-4), 5.93 (ddd, 1 H, *J* = 11.5, 7.3, 4.1 Hz, H-5), 7.31 (d, 2 H, *J* = 8.6 Hz, H_m *p*-Tol), 7.53 (d, 1 H, *J* = 8.3 Hz, H_o *p*-Tol). **^{13}C NMR (75 MHz), HSQC** δ 14.0 (Me-Bu), 21.7 (Me *p*-Tol), 22.4 (CH_2), 27.9 (CH_2), 29.6 (C-6), 35.1 (CH_2), 64.3 (C-7), 73.0 (C-3), 74.5 (C-2), 120.6 (C-4), 124.3, 129.4 (2 C, Ar), 129.7 (2 C, Ar), 135.2 (C-5), 144.7 (Ar-C). **MS** (ES): 331 $[M+Na]^+$ (100%).

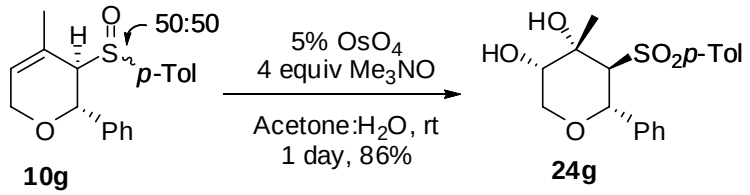
Partial data for **23c** (from the mixture): **^{1}H NMR (300 MHz)** δ 2.42 (s, 3 H, CH_3 *p*-Tol), 3.27 (td, 1 H, *J* = 10.0, 2.1 Hz), 5.75 (td, 1 H, *J* = 9.4, 2.1 Hz).

6. Synthesis of tetrahydropyranyl diols.

6.1. General procedure for the dihydroxylation of dihydropyrans.

To a solution of allylic sulfoxide in acetone-H_2O (9:1) (10 mL/mmol of sulfoxide) 2.5 equiv of $Me_3NO{\cdot}2H_2O$, and 5% mol of OsO_4 solution (2.5%) were added. The reaction was stirred at rt for 1 day and then quenched with 1 M solution of $Na_2S_2O_4$. The solvent was evaporated and the residue was dissolved in EtOAc and filtered through a pad of silica gel. The filtrate was concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel with the appropriate combination of solvents.

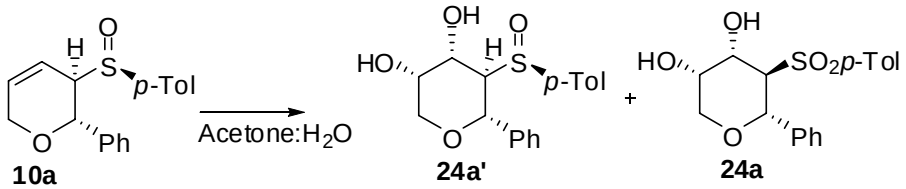
6.2. Synthesis of (+)-(3*S*,4*S*,5*S*,6*S*)-4-Methyl-6-phenyl-5-(*p*-tolylsulfonyl)tetrahydro-2*H*-pyran-3,4-diol, 24g.



From sulfoxide **10g** (9 mg, 0.029 mmol), Me_3NO (13 mg, 0.116 mmol) and OsO_4 [25 μL (2.5%), 0.002 mmol], according to the general procedure (1 day), diol **24g** was obtained. Purification by chromatography (50% EtOAc-hexane) afforded **24g** (9 mg, 0.025 mmol, 86%) as a white solid that was recrystallized from EtOAc-hexane.

Data for **24g**: R_f = 0.10 (80% EtOAc-hexane). **mp**: 188-190 ºC. $[\alpha]^{20}_D$ = +45.4 (*c* = 0.32). **^{1}H NMR (300 MHz)** δ 1.89 (s, 3 H, Me-4), 2.28 (s, 3 H, Me-*p*-Tol), 3.27 (m, 1 H, H-3), 3.60 (s, 1 H, OH), 3.85 (ddd, 1 H, *J* = 12.9, 2.3, 1.3 Hz, H-2), 4.05 (dd, 1 H, *J* = 12.9, 1.9 Hz, H-2), 4.13 (d, 2 H, *J* = 10.2 Hz, H-5), 4.58 (d, 2 H, *J* = 10.2 Hz, H-6), 6.88 (d, 2 H, *J* = 8.1 Hz), 6.93-7.00 (m, 4 H), 7.04-7.10 (m, 3 H). **^{13}C NMR (50 MHz)** δ 21.4, 21.8, 67.5, 70.0, 72.9, 74.1, 78.0, 126.9 (2 C), 128.0 (2 C), 128.7, 128.9 (2 C), 129.1 (2 C), 136.3, 137.6, 143.5. **IR** (KBr): 3513, 3434, 2920, 1285, 1133, 1017, 717 cm^{-1}. **MS** (ES): 747 $[2M+Na]^+$ (100%), 385 $[M+Na]^+$. **Anal. calcd for** $C_{19}H_{22}O_5S$: C, 62.96; H, 6.12; S, 8.85. **Found**: C, 62.78; H, 6.42; S, 8.64.

6.3. Synthesis of (+)-(3*S*,4*S*,5*R*,6*S*)-6-Phenyl-5-(*p*-tolylsulfonyl)tetrahydro-2*H*-pyran-3,4-diol, 24a.



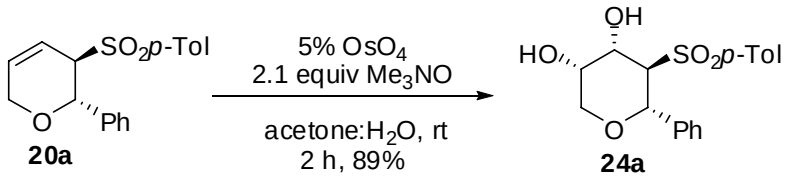
2.1 equiv Me_3NO 5% OsO_4, rt, 3 h 30 min	(35)	(65)	79%
1.2 equiv Me_3NO 8% OsO_4, rt, 7 h	(57)	(43)	70%
1.2 equiv Me_3NO 12% OsO_4, 4 ºC, 3 days	(43)	(57)	—
4 equiv Me_3NO 5% OsO_4, rt, 1 day	(0)	(100)	70%

From sulfoxide **10a** (90 mg, 0.300 mmol), Me_3NO (133 mg, 1.200 mmol) and OsO_4 [0.19 mL (2.5%), 0.015 mmol], according to the general procedure (1 day), diol **24a** was obtained. Purification by chromatography (30-80% EtOAc-hexane) afforded **24a** (74 mg, 0.21 mmol, 70%) as a white solid that was recrystallized from EtOAc-hexane.

Data for **24a**: R_f = 0.32 (80% EtOAc-hexane). **mp**: 133-135 ºC. $[\alpha]^{20}_D$ = +35.0 (*c* = 0.48). **^{1}H NMR (300 MHz), COSY** δ 2.29 (s, 3 H, Me-*p*-Tol), 2.88 (s, 1 H, OH), 3.71 (dm, 1 H, *J* = 12.7 Hz, H-2), 3.93 (t, 1 H, *J* = 10.1 Hz, H-5), 4.08 (m, 1 H, H-3), 4.14 (dd, 1 H, *J* = 12.7, 2.2 Hz, H-2), 4.45 (d, 1 H, *J* = 10.0 Hz, H-6), 4.57 (ddd, 1 H, *J* = 10.2, 3.4, 1.6 Hz, H-4), 5.15 (dd, 1 H, *J* = 1.5, 0.5 Hz, OH), 6.92 (d, 2 H, *J* = 8.5 Hz), 6.98-7.12 (m, 7 H). **^{13}C NMR (75 MHz), HSQC** δ 21.5 (Me-*p*-Tol), 67.3 (C-3), 67.6 (C-5), 67.9 (C-4), 69.5 (C-6), 78.7 (C-2), 127.4 (2 C), 128.2 (2 C), 128.8 (2 C), 129.2 (2 C), 136.1, 136.2, 144.1. **IR** (KBr): 3503, 3065, 2913, 2876, 1627, 1595, 1288, 1230, 1138, 1097, 882, 813, 768, 724 cm^{-1}. **MS** (ES): 719 $[2M+Na]^+$ (100%), 371 $[M+Na]^+$, 349 $[M+1]^+$. **Anal. calcd for** $C_{18}H_{20}O_5S$: C, 62.05; H, 5.79; S, 9.20. **Found**: C, 62.36; H, 5.47; S, 9.31.

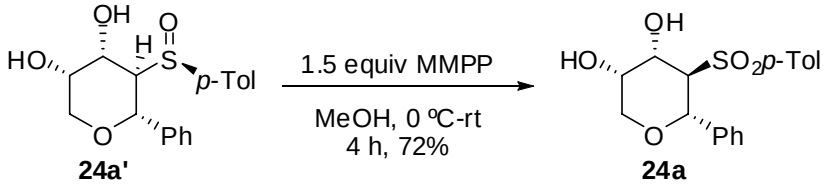
Different experiments were carried out trying to control the oxidation of the sulfoxide to sulfone. Using 5% OsO_4 and 2.1 equiv of Me_3NO, after 3 h 30 min, a 35:65 mixture of **24a'** and **24a** was obtained. With 8% OsO_4 and 1.2 equiv of Me_3NO the ratio of **24a'** and **24a** was 57:43, after 7 h at rt. Finally, from 1.2 equiv of Me_3NO and 12% OsO_4, at 4 ºC for 3 days, a 43:57 mixture of diol sulfoxide and sulfone was obtained.

Data for **24a'**: R_f = 0.14 (EtOAc). **mp**: 102-103 ºC. $[\alpha]^{20}_D$ = +92.6 (*c* = 0.50). **^{1}H NMR (300 MHz)** δ 2.45 (s, 3 H, Me-*p*-Tol), 2.99 (br s, 1 H, OH), 3.40 (d, 1 H, *J* = 12.7 Hz, H-2), 3.55 (d, 1 H, *J* = 10.2, H-6), 3.80 (ap t, 1 H, *J* = 1.6 Hz, H-3), 4.05 (dd, 1 H, *J* = 12.9, 1.9 Hz, H-2), 4.15 (t, 1 H, *J* = 10.1 Hz, H-5), 4.28 (dd, 1 H, *J* = 10.0, 3.4 Hz, H-4), 6.21 (s, 1 H, OH), 7.34-7.45 (m, 9 H). **^{13}C NMR (75 MHz)** δ 21.6 (Me-*p*-Tol), 60.7, 68.5, 69.6, 70.7, 77.1, 126.1 (2 C), 128.5 (2 C), 129.1 (2 C), 129.7, 130.1 (2 C), 133.6, 136.2, 143.2. **IR** (KBr): 3435, 2963, 2913, 1632, 1074, 1009, 802, 759 cm^{-1}. **MS** (ES): 687 $[2M+Na]^+$, 355 $[M+Na]^+$, 333 $[M+1]^+$ (100%). **Anal. calcd for** $C_{18}H_{20}O_4S$: C, 65.04; H, 6.06; S, 9.65. **Found**: C, 65.36; H, 5.98; S, 9.42.



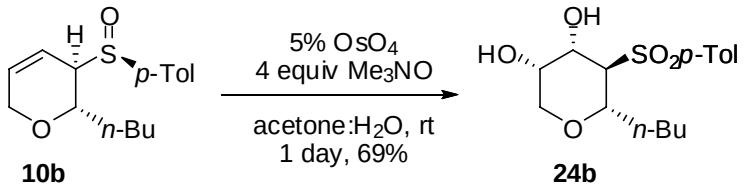
From sulfone **20a** (20 mg, 0.064 mmol), Me_3NO (14 mg, 0.13 mmol) and OsO_4 [41 μL (2.5%), 0.0032 mmol], according to the general procedure (2 h), diol **24a** was obtained. Purification by

chromatography (30-80% EtOAc-hexane) afforded **24a** (20 mg, 0.057 mmol, 89%) as a white solid that was recrystallized from EtOAc-hexane.



From diol **24a'** (4 mg, 0.012 mmol) and MMPP [7 mg (80%), 0.018 mmol], according to the general procedure (Method G, 3 h), sulfone **24a** was obtained. Purification by chromatography (10-30% EtOAc-hexane) afforded **24a** (3 mg, 0.0086 mmol, 72%) as a white solid.

6.4. Synthesis of (–)-(3*S*,4*S*,5*R*,6*S*)-6-*n*-Butyl-5-(*p*-tolylsulfonyl)tetrahydro-2*H*-pyran-3,4-diol, 24b.

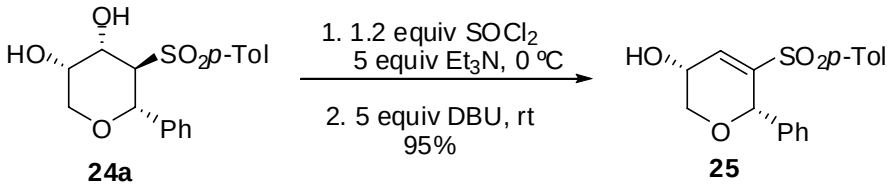


From sulfoxide **10b** (43 mg, 0.154 mmol), Me_3NO (70 mg, 0.616 mmol) and OsO_4 [0.1 mL (2.5%), 0.008 mmol], according to the general procedure (1 day), diol **24b** was obtained. Purification by chromatography (0-20% EtOAc-CH_2Cl_2) afforded **24b** (35 mg, 0.107 mmol, 69%) as a colorless oil.

Data for **24b**: R_f = 0.16 (20% EtOAc-CH_2Cl_2). $[\alpha]^{20}_D$ = –6.3 (*c* = 1.04). **^{1}H NMR (300 MHz), COSY** δ 0.76 (t, 3 H, *J* = 7.1 Hz, CH_3), 1.05-1.44 (m, 5 H), 1.69-1.80 (m, 1 H), 2.46 (s, 3 H, CH_3 *p*-Tol), 2.79 (br s, 1 H, OH), 3.26 (ddd, 1 H, *J* = 10.0, 8.1, 2.4 Hz, H-6), 3.37 (dd, 1 H, *J* = 12.7, 1.0 Hz, H-2), 3.46 (t, 1 H, *J* = 9.8 Hz, H-5), 3.92 (dd, 1 H, *J* = 3.4, 2.2 Hz, H-3), 3.99 (dd, 1 H, *J* = 12.7, 2.2 Hz, H-2), 4.14 (dd, 1 H, *J* = 9.8, 3.4 Hz, H-4), 4.90 (s, 1 H, OH), 7.38 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.75 (d, 2 H, *J* = 8.3 Hz, Ar-H). **^{13}C NMR (75 MHz)** δ 13.9 (CH_3), 21.7 (CH_2), 22.3 (CH_2), 26.8 (CH_2), 32.7, 67.3, 67.4, 67.7, 68.5, 75.0, 128.3 (2 C), 130.1 (2 C), 136.0, 145.6. **IR** (film): 3468, 2956, 2929, 2873, 1597, 1453, 1286, 1136, 1085, 858, 815 cm^{-1}. **MS** (ES): 351 $[M+Na]^+$ (100%), 329 $[M+1]^+$.

7. Exploratory transformations of sulfonyl diols.

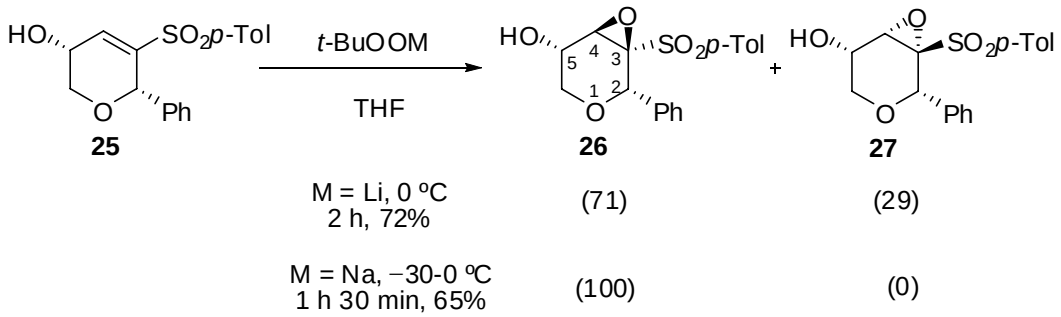
7.1. Synthesis of (–)-(3*R*,6*S*)-6-Phenyl-5-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran-3-ol, 25.[4]



To a cold (0 ºC) solution of diol **24a** (70 mg, 0.20 mmol) in CH_2Cl_2, under an argon atmosphere, was added Et_3N (0.14 mL, 1.00 mmol, 5.0 equiv) followed by $SOCl_2$ (18 μL, 0.24 mmol, 1.2 equiv). The reaction mixture was stirred for 30 min at 0 ºC and then concentrated under reduced pressure for 15 min. The residue was dissolved in CH_2Cl_2 (2 mL) under argon, and DBU (0.15 mL, 1.00 mmol, 5.0 equiv) was added. The mixture was stirred at rt until completion (30 min) and quenched with a saturated solution of NH_4Cl (2 mL/mmol) and water (2 mL/mmol). The layers were separated and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic extracts were washed with a saturated solution of NaCl, dried over anhydrous $MgSO_4$ and concentrated. Purification by chromatography (30-80% EtOAc-hexane) afforded 63 mg (0.19 mmol, 95%) of **25** as a white solid that was recrystallized from EtOAc-hexane.

Data for **25**: R_f = 0.32 (50% EtOAc-hexane). **mp**: 126-128 ºC. $[\alpha]^{20}_{D}$ = –37.0 (*c* = 0.50). **^{1}H NMR (300 MHz), COSY** δ 2.06 (d, 1 H, *J* = 8.8 Hz, OH), 2.31 (s, 3 H, Me-*p*-Tol), 3.75 (dd, 1 H, *J* = 12.0, 3.5 Hz, H-2), 3.84 (dd, 1 H, *J* = 12.0, 3.5 Hz, H-2), 4.38 (m, 1 H, H-3), 5.40 (t, 1 H, *J* = 1.6 Hz, H-6), 6.96 (d, 2 H, *J* = 7.8 Hz), 7.01-7.04 (m, 5 H), 7.14 (d, 2 H, *J* = 8.3 Hz), 7.37 (ddd, 1 H, *J* = 4.9, 1.7, 0.5 Hz, H-4). **NOESY-1D** H-2 (3.84 ppm)/H-3: 3.4%; H-2 (3.75 ppm)/H-6: 5.4%; H-2 (3.75 ppm)/H-3: 6.2%; H-3/H-2 (3.84 ppm): 1.9%; H-3/H-2 (3.75 ppm): 2.4%; H-3/H-4: 4.6%; H-4/H-3: 4.5%; H-6/H-2: 2.7%. **^{13}C NMR (75 MHz)** δ 21.5 (Me-*p*-Tol), 62.5 (C-2), 67.2, 76.2, 127.7 (2 C), 128.1 (2 C), 128.7, 129.2 (2 C), 129.3 (2 C), 135.4, 136.3, 137.7, 143.8, 145.4. **IR** (KBr): 3484, 2971, 2913, 2855, 1631, 1302, 1142, 1086, 1056, 829, 761, 702 cm^{-1}. **MS** (ES): 683 $[2M+Na]^+$, 353 $[M+Na]^+$ (100%), 331 $[M+1]^+$. **Anal. calcd for** $C_{18}H_{18}O_4S$: C, 65.43; H, 5.49; S, 9.70. **Found**: C, 65.67; H, 5.24; S, 9.56.

7.2. Synthesis of (–)-(2*S*,3*R*,4*R*,5*S*)-2-Phenyl-3-(*p*-tolylsulfonyl)-3,4-epoxytetrahydro-2*H*-pyran-5-ol, 26.



A two-necked round-bottomed flask fitted with a tube in T for entrance and exit of argon and a polyethylene stopper, was charged with anhydrous THF (10 mL/mmol) and 4.0 equiv of oil free NaH (9 mg, 0.36 mmol). The mixture was cooled to 0 ºC and then 4.5 equiv of *t*-BuOOH (51 μL, 0.40 mmol, 80% in *t*-BuOO-*t*-Bu) was added. After stirring at rt for 30 min, the resulting mixture was cooled to –30 ºC and a solution of sulfone **25** (30 mg, 0.09 mmol) in THF (10 mL/mmol), was added dropwise. The reaction mixture was allowed to warm to rt until completion (1 h 30 min) then quenched with a 1 M solution of $Na_2S_2O_4$ (4 mL/mmol), diluted with EtOAc and the layers were separated. The aqueous phase was extracted with EtOAc (3 times, 10 mL/mmol) and the combined organic extracts were washed with a saturated solution of NaCl (4 mL/mmol), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by chromatography (30-50% EtOAc-hexane) afforded **26** (20 mg, 0.058 mmol, 65%) as a white solid that was recrystallized from Et_2O-hexane.

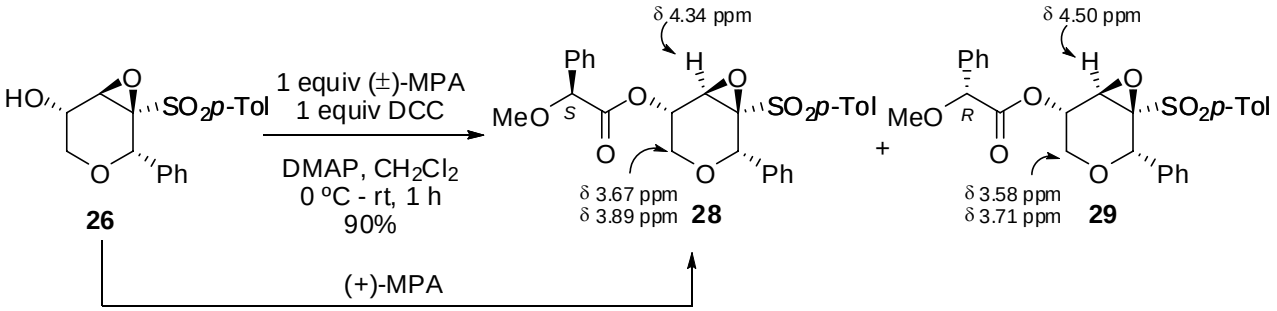
Data for **26**: R_f = 0.30 (50% EtOAc-hexane). **mp**: 58-60 ºC. $[\alpha]^{20}_{D}$ = –90.0 (*c* = 0.10). **^{1}H NMR (300 MHz)** δ 2.28 (s, 3 H, Me-*p*-Tol), 2.54 (d, 1 H, *J* = 11.7 Hz, OH), 3.62 (dd, 1 H, *J* = 12.7, 2.93 Hz, H-6), 3.89 (dt, 1 H, *J* = 12.7, 1.2 Hz, H-6), 4.13 (m, 1 H, H-5), 4.42 (dd, 1 H, *J* = 5.1, 1.0 Hz, H-4), 5.21 (s, 1 H, H-2), 6.91 (d, 2 H, *J* = 8.5 Hz), 7.05 (m, 2 H), 7.13-7.21 (m, 5 H). **^{13}C NMR (50 MHz)** δ 21.5, 57.8, 61.6, 71.0, 73.0, 75.2, 128.3 (2 C), 129.0 (5 C), 129.2 (2 C), 132.8, 135.1, 144.8. **IR** (KBr): 3479, 3021, 2925, 2855, 1597, 1494, 1456, 1403, 1324, 1299, 1215, 1149, 1096, 1049, 989, 899, 812, 763 cm^{-1}. **MS** (ES): 715 $[2M+Na]^+$, 369 $[M+Na]^+$ (100%), 347 $[M+1]^+$. **Anal. calcd for** $C_{18}H_{18}O_5S$: C, 62.41; H, 5.24; S, 9.26. **Found**: C, 62.75; H, 5.09; S, 9.13.

In a related experiment, a system like the one described above was charged with THF (10 mL/mmol) and 4 equiv of *t*-BuOOH (18 μL, 0.1 mmol, 5.5 M in decane) was added. The mixture was cooled to 0 ºC and *n*-BuLi (63 μL, 0.1 mmol, 1.6 M in hexane) was added. After 10 min a solution of **25** (8 mg, 0.024 mmol) in THF (10 mL/mmol) was added. The mixture was stirred at 0 ºC until disappearance of starting material was observed (TLC, 2 h) and it was quenched and isolated according to the procedure

described above. Purification by chromatography (10-30% EtOAc-hexane) afforded **26** (3 mg, 0.0086 mmol, 36%), a mixture of **26** and **27** (1 mg, 0.0029 mmol, 12%) and **27** (2 mg, 0.0057 mmol, 24%).

Data for **27**: R_f = 0.27 (50% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 2.32 (d, 1 H, *J* = 9.0 Hz, OH), 2.40 (s, 3 H, Me-*p*-Tol), 3.73 (m, 2 H, H-6), 3.90 (dm, 1 H, *J* = 2.2 Hz, H-4), 4.20 (m, 1 H, H-5), 4.87 (d, 1 H, *J* = 1.0 Hz, H-2), 7.16 (d, 2 H, *J* = 8.1 Hz), 7.23-7.33 (m, 7 H).

7.3. Synthesis of (−)-(2*S*)-[(2*S*,3*R*,4*R*,5*S*)-2-Phenyl-3-(*p*-tolylsulfonyl)-3,4-epoxytetrahydro-2*H*-pyran-5-yl]-2-methoxy-2-phenylacetate, 28, and (2*R*)-[(2*S*,3*R*,4*R*,5*S*)-2-Phenyl-3-(*p*-tolylsulfonyl)-3,4-epoxytetrahydro-2*H*-pyran-5-yl]-2-methoxy-2-phenylacetate, 29.

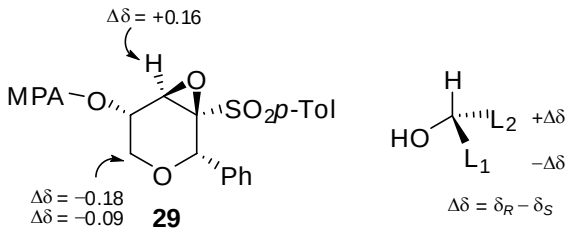


To a solution of sulfone **26** (3 mg, 0.009 mmol) and 1.1 equiv of (±)-2-methoxy-2-phenylacetic acid (1.7 mg, 0.010 mmol) in CH_2Cl_2 (10 mL/mmol) at 0 ºC, was added dicyclohexylcarbodiimide (1.1 equiv, 2 mg, 0.010 mmol) and a catalytic amount of DMAP. The mixture was allowed to warm to room temperature and monitored by TLC until starting material disappearance (3 h). The reaction mixture was filtered to remove dicyclohexylurea and the ester was purified by chromatography (20% EtOAc-hexane) to give 4 mg (0.008 mmol, 90%) of a 50:50 mixture of **28** and **29**.

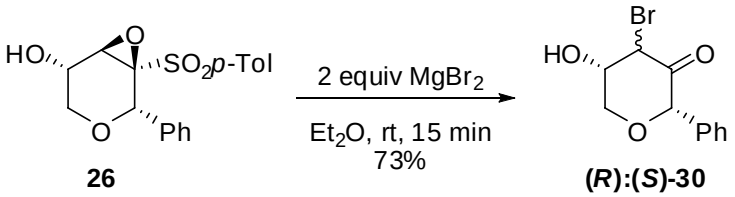
In an identical experiment with (+)-2-methoxy-2-phenylacetic acid, 4 mg (0.008 mmol, 90%) of **28** was obtained as a white solid. The ^{1}H NMR of the crude product did not show any signal of compound **29** and thus the optical purity of **26** was established.

Data for **28**: R_f = 0.15 (30% EtOAc-hexane). **$[\alpha]^{20}_D$** = −44.1 (*c* = 0.17). **^{1}H NMR (300 MHz)** δ 2.29 (s, 3 H, Me-*p*-Tol), 3.44 (s, 3 H, MeO), 3.67 (dd, 1 H, *J* =13.2, 3.8 Hz, H-6), 3.89 (dd, 1 H, *J* = 13.2, 2.4 Hz, H-6), 4.34 (d, 1 H, *J* = 4.6 Hz, H-4), 4.86 (s, 1 H, Hα), 5.11 (m, 1 H, H-5), 5.24 (s, 1 H, H-2), 6.91 (d, 2 H, *J* = 8.3 Hz), 7.02 (m, 1 H), 7.03 (d, 2 H, *J* = 7.3 Hz), 7.10-7.17 (m, 4 H), 7.31-7.39 (m, 3 H), 7.47-7.51 (m, 2 H). **IR** (film): 3065, 2963, 2927, 1750, 1591, 1494, 1455, 1320, 1260, 1111, 801 cm^{-1}. **MS** (ES): 517 $[M+Na]^+$ (100%), 495 $[M+1]^+$.

Partial data for **29** (from the mixture): R_f = 0.22 (30% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 2.29 (s, 3 H, Me-*p*-Tol), 3.44 (s, 3 H, MeO), 3.58 (dd, 1 H, *J* =13.2, 3.8 Hz, H-6), 3.71 (dd, 1 H, *J* = 13.2, 2.4 Hz, H-6), 4.50 (d, 1 H, *J* = 4.4 Hz, H-4), 4.88 (s, 1 H, Hα), 5.11 (m, 1 H, H-5), 5.26 (s, 1 H, H-2).



7.4. Synthesis of (2*S*,4*S*,5*S*)-4-Bromo-5-hydroxy-2-phenyldihydro-2*H*-pyran-3(4*H*)-one, (*S*)-30, and (2*S*,4*R*,5*S*)-4-Bromo-5-hydroxy-2-phenyldihydro-2*H*-pyran-3(4*H*)-one, (*R*)-30.

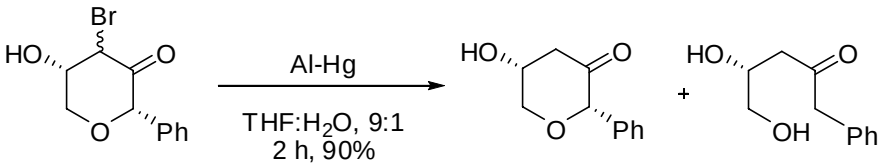


To a solution of sulfone **26** (10 mg, 0.03 mmol) in Et_2O at rt, under an argon atmosphere, was added a freshly prepared 0.3 M solution of $MgBr_2$ (0.5 mL, 0.50 mmol, 5.0 equiv) in Et_2O. The mixture was stirred at rt, monitored by TLC until completion (15 min) and then quenched with a saturated solution of NH_4Cl (3 mL/mmol) and water (3 mL/mmol). The layers were separated and the aqueous phase was extracted with EtOAc (5 mL/mmol, 3 times). The combined organic extracts were washed with a saturated solution of NaCl, dried over anhydrous $MgSO_4$, filtered and concentrated. The ^{1}H NMR spectra of the crude product showed a 70:30 mixture of **(4*S*)-30** and **(4*R*)-30**. Purification by chromatography (20-50% EtOAc-hexane) afforded 6 mg (0.022 mmol, 73%) of a 60:40 mixture of **(4*S*)-30** and **(4*R*)-30**. Recrystallization of the crude product from EtOAc-Et_2O gave 3 mg of **(4*S*)-30** as a white solid. After 2 days in $CDCl_3$ epimerization at C-4 took place affording a 60:40 mixture of diastereomers.

Data for **(4*S*)-30**: R_f = 0.30 (40% EtOAc-hexane). **^{1}H NMR (200 MHz)** δ 2.61 (br s, 1 H, OH), 4.15 (dd, 1 H, *J* = 12.6, 1.6 Hz, H-2), 4.36 (dd, 1 H, *J* = 12.6, 2.7 Hz, H-2), 4.56 (m, 1 H, H-3), 5.05 (s, 1 H, H-6), 5.11 (d, 1 H, *J* = 3.3 Hz, H-4), 7.26-7.38 (m, 5 H).

Partial data of **(4*R*)-30** (from the mixture): R_f = 0.28 (40% EtOAc-hexane). **^{1}H NMR (200 MHz)** δ 2.70 (br s, 1 H, OH), 5.44 (s, 1 H, H-6), 5.11 (d, 1 H, *J* = 3.3 Hz, H-4), 7.26-7.38 (m, 5 H). **IR** (film): 3369, 3057, 3021, 2924, 2847, 1740, 1700, 1606, 1494, 1447, 1125, 1095, 1028, 751, 698 cm^{-1}.

7.5. Synthesis of (2*S*,5*R*)-5-Hydroxy-2-phenyldihydro-2*H*-pyran-3(4*H*)-one, 31, and (*R*)-4,5-dihydroxy-1-phenylpentan-2-one, 32.



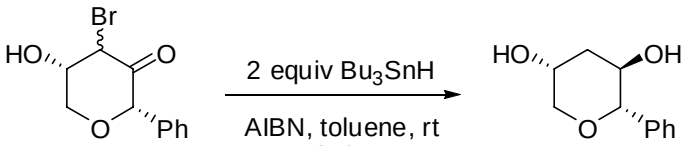
(*R*):(*S*)-30 **31** (50) **32** (50)

To prepare Al-Hg, aluminum foil (6 mg) was introduced in a solution of 2% $HgCl_2$ in H_2O for 20-30 seconds. The strip was washed with EtOH, then with Et_2O and added to a solution of **(*R*):(*S*)-30** (6 mg, 0.022 mmol) in 0.5 mL of THF:H_2O (9:1). The mixture was stirred at rt for 2 h monitoring the disappearance of starting material by TLC. The crude product was filtered through celite and the solvent was evaporated under reduced pressure. Purification by chromatography (20-80% EtOAc-hexane) afforded **31** (2 mg, 0.01 mmol, 45%) and **32** (2 mg, 0.01 mmol, 45%), both as colorless oils.

Data for **31**: R_f = 0.14 (50% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 2.05 (d, 1 H, *J* = 6.6 Hz, OH), 2.76 (ddd, 1 H, *J* = 15.9, 4.9, 1.7 Hz, H-4), 2.87 (dd, 1 H, *J* = 15.9, 4.9 Hz, H-4), 4.00 (dd, 1 H, *J* = 12.2, 2.5 Hz, H-6), 4.06 (ddd, 1 H, *J* = 12.2, 3.4, 1.7 Hz, H-6), 4.40 (m, 1 H, H-5), 4.91 (s, 1 H, H-2), 7.30-7.36 (m, 5 H, Ph). **IR** (film): 3405, 2449, 2926, 1717, 1450, 1275, 1071, 1024 cm^{-1}.

Data for **32**: R_f = 0.07 (50% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 1.90 (t, 1 H, *J* = 6.1 Hz), 2.65 (m, 2 H), 3.13 (d, 1 H, *J* = 3.4 Hz), 3.43 (dt, 1 H, *J* = 11.7, 6.1 Hz), 3.59 (ddd, 1 H, *J* = 11.2, 6.7, 3.8 Hz), 3.71 (s, 2 H, H-1), 4.10 (m, 1 H, H-5), 7.23-7.40 (m, 5 H, Ph).

7.6. Synthesis of (+)-(2*S*,3*S*,5*R*)-2-Phenyltetrahydro-2*H*-pyran-3,5-diol, 33.



(*R*):(*S*)-30 **33**

To a solution of a 60:40 mixture of **(4*S*)** and **(4*R*)-30** (6 mg, 0.022 mmol) in toluene (10 mL/mmol) at rt, under an argon atmosphere, 2 equiv of freshly distilled tributyltin hydride (14 μL, 0.044 mmol) and a catalytic amount of AIBN were added. The mixture was stirred at rt and monitored by TLC until completion (2 h) and the solvent was removed under reduced pressure. Purification by chromatography (50-80% EtOAc-hexane) afforded 4 mg (0.021 mmol, 95%) of diol **33** as a colorless oil.

Data for **33**: R_f = 0.18 (80% EtOAc-hexane). $[\alpha]^{20}_D$ = +28.7 (*c* = 0.18). **^{1}H NMR (300 MHz)** δ 1.50 (d, 1 H, *J* = 2.9 Hz, OH), 1.73 (ddd, 1 H, *J* = 13.5, 10.7, 3.2 Hz, H-4), 1.98 (d, 1 H, *J* = 6.8 Hz,

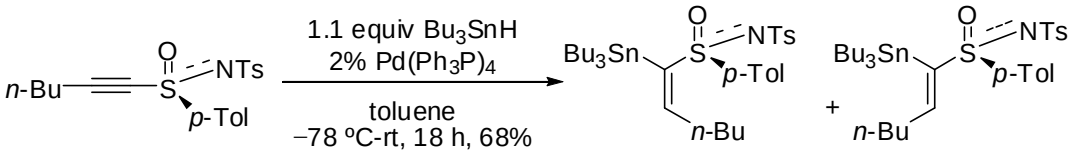
OH), 2.39 (ddt, 1 H, J = 13.2, 4.6, 2.9 Hz, H-4), 3.71 (dd, 1 H, J = 12.2, 1.2 Hz, H-6), 3.94 (m, 1 H, H-3), 3.98 (s, 1 H, H-2), 4.00 (m, 1 H, H-6), 4.10 (m, 1 H, H-5), 7.30-7.44 (m, 5 H). **^{13}C NMR (50 MHz)** δ 38.6 (C-4), 67.3, 67.8, 72.8, 85.6, 127.4 (2 C), 128.7, 128.8 (2 C). **IR** (film): 3338, 2956, 2925, 2847, 1450, 1346, 1261, 1107, 1048, 987, 903, 757, 700 cm^{-1}. **MS** (ES): 217 $[M+Na]^+$ (100%), 177 $[(M-18)+1]^+$.

8. Synthesis of vinyl, dienyl and allyl sulfoximines.

8.1. General procedure for the imination of sulfoxides.[5]

To a solution of sulfoxide (1 equiv) in acetonitrile (6 mL/mmol sulfoxide) under argon at rt, $Cu(OTf)_2$ (10-20 mol%) was added. Then, PhI=NTs (1.1-3.0 equiv) was added in one portion. The reaction was monitored by the rapid disappearance of the yellowish powder from the reaction mixture, which turned homogeneous and green generally after a few minutes. Acetonitrile was removed in vacuo and the crude material was purified by flash chromatography on silica gel with the appropriate combination of solvents.

8.2. Synthesis of (–)-(*S*)-[(*E*)-1-(*S*-*p*-Tolyl-*N*-tosylsulfoximinoyl)hex-1-enyl]tributylstannane, 35.

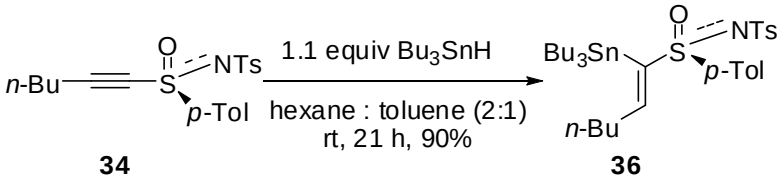


34		**35** (50)	**36** (50)
34	1.1 equiv Bu_3SnH 5% $Pd(dba)_3{\cdot}CHCl_3$ toluene, –78 ºC-rt 22 h, 0%	**35** (0)	**36** (0)
34	1.1 equiv Bu_3SnH 5% $PdCl_2(PPh_3)_2$ toluene, –78 ºC-rt 17 h, 74%	**35** (22)	**36** (78)

From alkynyl sulfoximine **34**[5] (82 mg, 0.211 mmol), Bu_3SnH (62 µl, 0.232 mmol) and $PdP(Ph_3)_4$ (5 mg, 0.004 mmol), according to the general procedure (18 h), stannanes **35** and **36** were obtained. Purification by chromatography (2-20% EtOAc-hexane) afforded stannane **35** (48 mg, 0.071 mmol, 33%) and **36** (42 mg, 0.062 mmol, 29%) along with a 13:87 mixture of **35** and **36** (8 mg, 0.012 mmol, 6%) as colorless oils.

Data for **35**: R_f = 0.27 (20% EtOAc-hexane). $[\alpha]^{20}_D$ = –92.1 (*c* = 1.90). **^{1}H NMR (300 MHz)** δ 0.71 (t, 3 H, *J* = 7.1 Hz, CH_3), 0.86 (t, 9 H, *J* = 7.3 Hz, 3 CH_3), 1.02-1.56 (m, 22 H, 11 CH_2), 2.02-2.13 (m, 1 H, CH_2), 2.25-2.32 (m, 1 H, CH_2), 2.35 (s, 3 H, CH_3 *p*-Tol), 2.41 (s, 3 H, CH_3-Ts), 6.30 (t, 1 H, *J* = 7.3 Hz, H-2), 7.16 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.29 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.72 (d, 2 H, *J* = 7.8 Hz, Ar-H), 7.75 (d, 2 H, *J* = 8.1 Hz, Ar-H). **^{13}C NMR (75 MHz)** δ 12.3 (3 CH_3), 13.6 (3 CH_2), 21.4 (CH_3 *p*-Tol), 21.6 (CH_3-Ts), 22.1 (CH_3), 27.2 (3 CH_2), 28.7 (3 CH_2), 28.9 (CH_2), 30.2 (CH_2), 31.0 (CH_2), 126.8 (2 C), 127.9 (2 C), 128.9 (2 C), 129.7 (2 C), 138.6, 141.1, 142.1, 143.9, 149.1, 159.8. **IR** (film): 2957, 2920, 2867, 2855, 1594, 1522, 1455, 1364, 1235, 1154, 1088, 1066, 1014, 873, 811, 741 cm^{-1}. **MS** (ES): 704 [M+Na]$^+$, 682 [M+1]$^+$.

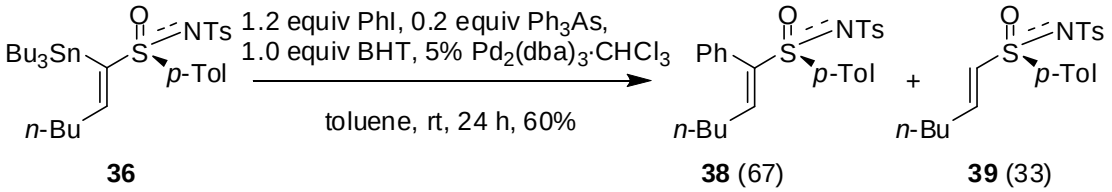
8.3. Synthesis of (–)-(*S*)-[(Z)-1-(*S*-*p*-Tolyl-*N*-tosylsulfoximinoyl)hex-1-enyl]tributylstannane, 36.



To a solution of **34** (144 mg, 0.37 mmol) in 2 mL of hexane:toluene (2:1) (5 mL/mmol sulfoximine), at rt under argon, a solution of freshly distilled Bu_3SnH (0.11 ml, 0.407 mmol, 1.1 equiv), in 1 mL of hexane (3 mL/mmol sulfoximine) was added. The mixture was stirred at rt for 21 h, and the solvent was evaporated to obtain **36**. Purification by chromatography (5-30% EtOAc-hexane) afforded stannane **36** (226 mg, 0.332 mmol, 90%) as a colorless oil.

Data for **36**: R_f = 0.20 (20% EtOAc-hexane). $[\alpha]^{20}_D$ = –41.2 (*c* = 1.20). **^{1}H NMR (300 MHz)** δ 0.82 (t, 9 H, *J* = 7.2 Hz, 3 CH_3), 0.87 (t, 3 H, *J* = 7.1 Hz, CH_3), 0.98 (m, 2 H, CH_2), 1.16-1.38 (m, 20 H, 10 CH_2), 2.17 (q, 2 H, *J* = 7.5 Hz, CH_2), 2.35 (s, 3 H, CH_3 *p*-Tol), 2.41 (s, 3 H, CH_3-Ts), 7.01 (t, 1 H, *J* = 7.5 Hz, H-2), 7.17 (d, 2 H, *J* = 8.1 Hz, Ar-H), 7.28 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.70 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.76 (d, 2 H, *J* = 8.3 Hz, Ar-H). **^{13}C NMR (75 MHz)** δ 12.6 (3 CH_3), 13.6 (3 CH_2), 21.4 (CH_3 *p*-Tol), 21.6 (CH_3-Ts), 22.5 (CH_3), 27.0 (4 CH_2), 28.6 (3 CH_2), 30.8 (CH_2), 33.3 (CH_2), 126.7 (2 C), 128.5 (2 C), 128.9 (2 C), 129.7 (2 C), 135.7, 141.5, 142.0, 144.2, 145.7, 156.4. **IR** (film): 2957, 2926, 2867, 1595, 1522, 1456, 1367, 1318, 1236, 1154, 1089, 1064, 1015, 813, 744, 668 cm^{-1}. **MS** (ES): 704 [M+Na]$^+$, 682 [M+1]$^+$.

8.4. Synthesis of (+)-(*S*)-[(*E*)-1-Phenyl-1-(*S*-*p*-tolyl-*N*-tosylsulfoximinoyl)]hex-1-ene, 38, and (–)-(*R*)-[(*E*)-1-(*S*-*p*-tolyl-*N*-tosylsulfoximinoyl)]hex-1-ene, 39.

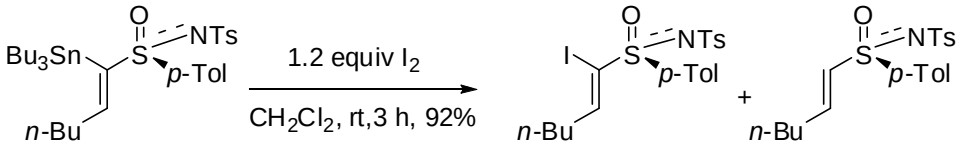


From stannane **36** (87 mg, 0.128 mmol), iodobenzene (1.2 equiv, 16 μL, 0.148 mmol), BHT (28 mg, 0.128 mmol), and $Pd_2(dba)_3{\cdot}CHCl_3$ (7 mg, 0.006 mmol) in toluene, according to the general procedure (24 h), a 67:33 mixture of **38** and **39** was obtained. Purification by chromatography (30-60% Et_2O-hexane) afforded **38** (24 mg, 0.051 mmol, 40%) and **39** (10 mg, 0.026 mmol, 20%) as colorless oils.

Data for **38**: R_f = 0.28 (60% Et_2O-hexane). **$[\alpha]^{20}_D$** = +3.9 (*c* = 0.76). **^{1}H NMR (300 MHz), COSY** δ 0.80 (t, 3 H, *J* = 7.4 Hz, CH_3), 1.24 (m, 2 H, CH_2), 1.40 (m, 2 H, CH_2), 1.39 (q, 2 H, *J* = 7.7 Hz, CH_2), 1.98 (q, 2 H, *J* = 7.4 Hz, CH_2), 2.36 (s, 6 H, 2 CH_3 *p*-Tol and Ts), 6.97 (d, 2 H, *J* = 7.1 Hz, Ar-H), 7.14-7.30 (m, 8 H, H-2, Ar-H), 7.47 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.84 (d, 2 H, *J* = 8.1 Hz, Ar-H). **^{13}C NMR (75 MHz), HSQC** δ 13.7 (CH_3), 21.5 (CH_3 *p*-Tol), 21.6 (CH_3-Ts), 22.2 (CH_2), 29.2 (CH_2), 30.3 (CH_2), 126.6 (2 C), 128.2 (2 C), 128.6 (2 C), 129.1 (2 C), 129.2, 129.5 (2 C), 131.4 (2 C), 133.7, 141.0, 141.5, 142.4, 144.7, 144.8 (2 C). **IR** (film): 2955, 2926, 2867, 1594, 1444, 1318, 1233, 1153, 1089, 813, 752, 700 cm^{-1}. **MS** (ES): 490 $[M+Na]^+$, 468 $[M+1]^+$.

Data for **39**: R_f = 0.44 (50% EtOAc-hexane). **$[\alpha]^{20}_D$** = –19.5 (*c* = 1.09). **^{1}H NMR (300 MHz)** δ 0.88 (t, 3 H, *J* = 7.2 Hz, CH_3), 1.21-1.43 (m, 4 H, 2 CH_2), 2.22 (q, 2 H, *J* = 6.8 Hz, CH_2), 2.37 (s, 3 H, CH_3 *p*-Tol), 2.41 (s, 3 H, CH_3-Ts), 6.37 (dt, 1 H, *J* = 14.9, 1.6 Hz, H-1), 6.93 (dt, 1 H, *J* = 14.9, 6.8 Hz, H-2), 7.21 (d, 2 H, *J* = 8.1 Hz, Ar-H), 7.32 (d, 2 H, *J* = 8.1 Hz, Ar-H), 7.80 (d, 4 H, 2 H, *J* = 8.3 Hz, Ar-H), 7.81 (d, 2 H, *J* = 8.1 Hz, Ar-H). **^{13}C NMR (75 MHz), HSQC** δ 13.7 (CH_3), 21.5 (CH_3 *p*-Tol), 21.6 (CH_3-Ts), 22.1 (CH_2), 29.4 (CH_2), 31.3 (CH_2), 126.7 (2 x CH Ar), 127.7 (2 x CH Ar), 129.0 (CH=CH), 129.2 (2 x CH Ar), 130.2 (2 x CH Ar), 135.6 (C), 141.0 (C), 142.6 (C), 145.1 (C), 148.5 (CH). **IR** (film): 3052, 2958, 2929, 2872, 1678, 1626, 1596, 1494, 1455, 1403, 1381, 1318, 1236, 1184, 1153, 1063, 1015, 974, 924, 813, 745, 702, 667 cm^{-1}. **MS** (ES): 414 $[M+Na]^+$, 392 $[M+1]^+$.

8.5. Synthesis of (+)-(*S*)-(*Z*)-1-(*S*-*p*-Tolyl-*N*-tosylsulfoximinoyl)-1-iodohex-1-ene, 37.

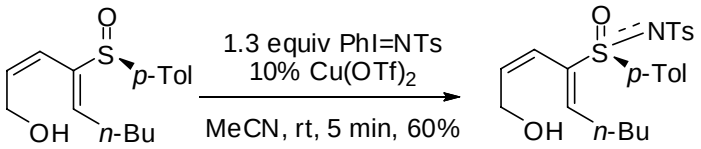


36 **37** (91) **39** (9)

From stannane **36** (155 mg, 0.228 mmol) and I_2 (70 ml, 0.274 mmol), according to the general procedure, iodide **37** was obtained. Purification by chromatography (5-30% EtOAc-hexane) afforded iodide **37** (94 mg, 0.20 mmol, 88%) and vinyl sulfoximine **39** (3 mg, 0.009 mmol, 4%) as colorless oils.

Data for **37**: R_f = 0.31 (30% EtOAc-hexane). **$[\alpha]^{20}_D$** = +41.2 (*c* = 0.77). **^{1}H NMR (300 MHz), COSY** δ 0.90 (t, 3 H, *J* = 7.3 Hz, CH_3), 1.22-1.67 (m, 4 H, 2 CH_2), 2.29 (q, 2 H, *J* = 7.1 Hz, CH_2), 2.37 (s, 3 H, CH_3 *p*-Tol), 2.42 (s, 3 H, CH_3-Ts), 7.22 (d, 2 H, *J* = 8.8 Hz, Ar-H), 7.47 (t, 1 H, *J* = 7.1 Hz, CH), 7.32 (d, 2 H, *J* = 8.6 Hz, Ar-H), 7.82 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.85 (d, 2 H, *J* = 8.3 Hz, Ar-H). **^{13}C NMR (75 MHz), HSQC** δ 13.8 (CH_3), 21.5 (CH_3 *p*-Tol), 21.7 (CH_3-Ts), 22.3 (CH_2), 29.3 (CH_2), 36.0 (CH_2), 100.6, 126.8 (2 C), 129.0 (2 C), 129.2 (2 C), 129.9 (2 C), 132.7, 140.8, 142.7, 145.6, 153.8. **IR** (film): 3026, 2955, 2927, 2867, 1595, 1455, 1320, 1236, 1154, 1088, 1064, 812, 748 cm^{-1}. **MS** (ES): 540 $[M+Na]^+$, 518 $[M+1]^+$.

8.6. Synthesis of (+)-(*R*)-2-(*Z*)-4-(*Z*)-4-(*S*-*p*-Tolyl-*N*-tosylsulfoximinoyl)nona-2,4-dien-1-ol, 41.



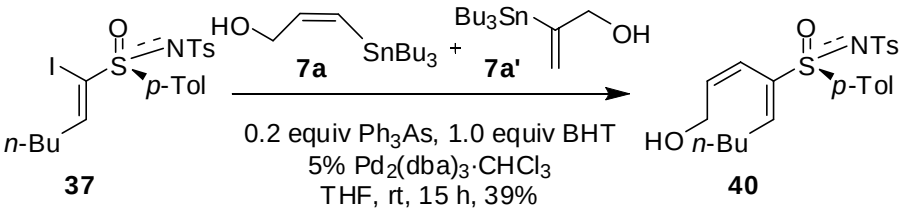
8b **41**

From dienyl sulfoxide **8b** (27 mg, 0.097 mmol), *N*-tosyl phenyliminoiodinane (47 mg, 0.126 mmol, 1.3 equiv) and $Cu(OTf)_2$ (4 mg, 0.010 mmol, 0.10 equiv), according to the general procedure (5 min) sulfoximine **41** was obtained. Purification by chromatography (0-10% EtOAc-CH_2Cl_2) afforded dienyl sulfoximine **41** (26 mg, 0.058 mmol, 60%) as a colorless oil.

Data for **41**: R_f = 0.14 (10% EtOAc-CH_2Cl_2). **$[\alpha]^{20}_D$** = +73.6 (*c* = 0.92). **^{1}H NMR (300 MHz), COSY** δ 0.86 (t, 3 H, *J* =7.1 Hz, CH_3), 1.23-1.43 (m, 4 H, 2 CH_2), 2.36 (s, 3 H, Me-*p*-Tol), 2.41 (s, 3 H, Me-Ts), 2.65-2.74 (m, 2 H, CH_2), 3.99 (dd, 1 H, *J* = 13.4, 3.4 Hz, H-1), 4.26 (dd, 1 H, *J* = 13.4, 3.9 Hz, H-1), 5.98 (ap t, 2 H, *J* = 4.0 Hz, H-2, H-3), 6.08 (t, 1 H, *J* = 7.7 Hz, H-5), 7.23 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.32 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.82 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.85 (d, 2 H, *J* = 8.3 Hz, Ar-H).

^{13}C NMR (75 MHz), HSQC δ 13.8 (CH_3-Bu), 21.5 (Me), 21.6 (Me), 22.4 (CH_2), 28.2 (CH_2), 31.0 (CH_2), 58.4 (C-1), 124.3, 126.5 (2 C), 127.9 (2 C), 129.2 (2 C), 129.9 (2 C), 135.2, 135.6, 137.4, 141.0, 142.7, 145.4, 148.5 (C-5). **IR** (film): 3499, 2956, 2928, 2867, 1735, 1596, 1454, 1316, 1303, 1233, 1153, 1088, 1065, 1013, 814 cm^{-1}. **MS** (ES): 917 $[2M+Na]^+$, 470 $[M+Na]^+$ (100%), 448 $[M+1]^+$.

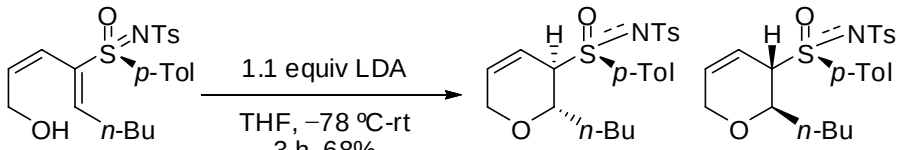
8.7. Synthesis of (+)-(*R*)-2-(*Z*)-4-(*E*)-4-(*S*-*p*-Tolyl-*N*-tosylsulfoximinoyl)nona-2,4-dien-1-ol, 40.



From iodide **37** (986 mg, 2.83 mmol), stannane **7a** (1.2 equiv, 110 mg of a 76:24 mixture **7a** and **7a'**, 0.24 mmol **7a**), BHT (44 mg, 0.20 mmol), Ph_3As (12 mg, 0.04 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (10 mg, 0.01 mmol), according to the general procedure (15 h), diene **40** was obtained as a single isomer. Purification by chromatography (10-50% EtOAc-hexane) afforded **40** (35 mg, 0.078 mmol, 39%) as a colorless oil.

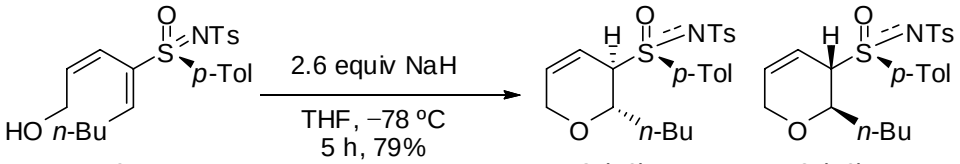
Data for **40**: R_f = 0.37 (20% EtOAc-CH_2Cl_2). $[\alpha]^{20}_D$ = +55.5 (*c* = 0.71). **^{1}H NMR (300 MHz), COSY** δ 0.88 (t, 3 H, *J* = 7.1 Hz, CH_3), 1.30 (sext, 2 H, *J* = 7.1 Hz, CH_2), 1.45 (q, 2 H, *J* = 7.1 Hz, CH_2), 1.50-1.80 (br, s, 1 H, OH), 2.10 (m, 2 H, CH_2), 2.39 (s, 3 H, CH_3 *p*-Tol) 2.44 (s, 3 H, CH_3-Ts), 3.68 (ddd, 1 H, *J* = 13.4, 5.6, 1.2 Hz, H-1), 4.05 (dd, 1 H, *J* = 13.4, 7.8 Hz, H-1'), 5.69 (dm, 1 H, *J* = 11.2 Hz, H-3), 6.11 (ddd, 1 H, *J* = 11.2, 7.8, 5.6 Hz, H-2), 7.11 (t, 1 H, *J* = 7.1 Hz, H-5), 7.23 (d, 2 H, *J* = 8.8 Hz, Ar-H), 7.31 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.79 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.84 (d, 2 H, *J* = 8.3 Hz, Ar-H). **^{13}C NMR (75 MHz), HSQC** δ 13.7 (CH_3), 21.5 (CH_3 *p*-Tol), 21.6 (CH_3-Ts), 22.3 (CH_2), 29.4 (CH_2), 30.0 (CH_2), 59.3 (C-1), 117.9 (C-3), 126.5 (2 C), 128.4 (2 C), 129.2 (2 C), 129.9 (2 C), 133.7, 136.4, 140.4 (C-2), 141.0, 142.7, 145.0 (C-5), 145.3. **IR** (film): 3512, 2958, 2928, 2872, 1596, 1455, 1314, 1303, 1234, 1152, 1089, 1064, 814, 755, 702, 657 cm^{-1}. **MS** (ES): 470 $[M+Na]^+$, 448 $[M+1]^+$.

8.8. Synthesis of (−)-(2*S*,3*R*,*R*$_S$)-2-*n*-Butyl-3-(*S*-*p*-tolyl-*N*-tosylsulfoximinoyl)-3,6-dihydro-2*H*-pyran, 42, and (+)-(2*R*,3*S*,*R*$_S$)-2-*n*-Butyl-3-(*S*-*p*-tolyl-*N*-tosylsulfoximinoyl)-3,6-dihydro-2*H*-pyran, 43.



41	1.1 equiv LDA, THF, −78 ºC-rt, 3 h, 68%	**42** (20)	**43** (80)
41	1.3 equiv NaH, THF, −78 ºC-rt, 1 h 30 min, 54%	**42** (17)	**43** (83)
41	1.3 equiv KH, THF, −78 ºC-rt, 1 h 30 min, 68%	**42** (15)	**43** (85)

From dienyl sulfoximine **41** (24 mg, 0.054 mmol) and NaH (2 mg, 0.07 mmol, 1.3 equiv) according to the general procedure (Method B, 1 h 30 min), an 83:17 mixture of **43** and **42** was obtained. Purification by chromatography (10-30% EtOAc-hexane) afforded an 83:17 mixture of **43** and **42** (13 mg, 0.029 mmol, 54%) as a colorless oil.



40 → **42** (50), **43** (50)

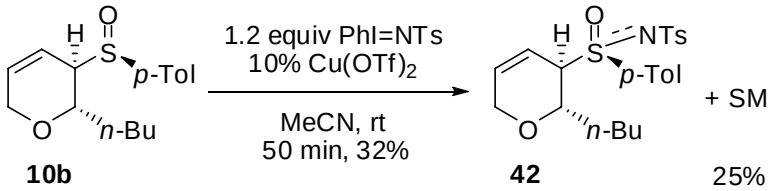
From dienyl sulfoximine **40** (23 mg, 0.051 mmol) and NaH (4 mg, 0.133 mmol, 2.6 equiv) according to the general procedure (Method B, 5 h), a 50:50 mixture of **43** and **42** was obtained. Purification by chromatography (10-50% EtOAc-hexane) afforded a 50:50 mixture of **43** and **42** (18 mg, 0.040 mmol, 79%) as a colorless oil.

Subsequent chromatographies (30-50% Et_2O-hexane) allowed for the separation and characterization of both isomers.

Data for **43**: R_f = 0.26 (50% EtOAc-hexane). $[\alpha]^{20}_D$ = +146.0 (*c* = 0.86). **^{1}H NMR (300 MHz, C_6D_6)** δ 0.75 (t, 3 H, *J* = 7.0 Hz, CH_3), 1.05-1.78 (m, 6 H, 3 CH_2), 1.80 (s, 3 H, Me-*p*-Tol), 1.81 (s, 3 H, Me-Ts), 2.87 (ddd, 1 H, *J* = 17.8, 3.2, 2.1 Hz, H-6), 3.27 (ddd, 1 H, *J* = 17.9, 5.1, 2.1 Hz, H-6), 4.45 (ddd, 1 H, *J* = 9.5, 4.2, 2.0 Hz, H-2), 4.69 (ap td, 1 H, *J* = 3.3, 1.5 Hz, H-3), 5.28 (d, 1 H, *J* = 10.3 Hz, H-5), 6.20 (dddd, 1 H, *J* = 10.3, 5.4, 3.2, 1.0 Hz, H-4), 6.74 (d, 2 H, *J* = 8.1 Hz, Ar-H), 6.77 (d, 2 H, *J* = 8.1 Hz, Ar-H), 7.84 (d, 2 H, *J* = 8.3 Hz, Ar-H), 8.30 (d, 2 H, *J* = 8.3 Hz, Ar-H). **NOESY-1D** H-2/H-3: 3%; H-2/CH_2 (Bu): 3%; H-2/Ar-H: 2%; H-3/Bu: 1.4%; H-3/H-4: 1.4%; H-6 (3.27 ppm)/H-5: 5%, H-6

(3.27 ppm)/CH_2 (Bu): 2%; H-6 (2.87 ppm)/H-5: 2.4%; H-6 (2.87 ppm)/H-3: 0.4%. **^{13}C NMR (75 MHz, $CDCl_3$), HSQC** δ 13.9 (CH_3-Bu), 21.5 (Me-*p*-Tol), 21.7 (Me-Ts), 22.3 (CH_2), 27.7 (CH_2), 31.0 (CH_2), 59.3 (CH_2), 65.9 (C-3), 69.2 (C-2), 116.2 (C-4), 126.6 (2 C), 129.2 (4 C), 129.9 (2 C), 130.8, 134.4 (C-5), 140.8, 142.8, 145.3. **IR** (film): 3392, 2956, 2929, 2867, 1596, 1454, 1316, 1237, 1152, 1088, 1065, 1016, 814, 753, 704 cm^{-1}. **MS** (ES): 917 $[2M+Na]^+$ (100%), 470 $[M+Na]^+$.

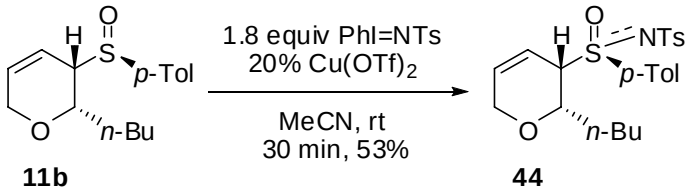
8.9. Synthesis of (–)-(2*S*,3*R*,*R*$_S$)-2-*n*-Butyl-3-(*S*-*p*-tolyl-*N*-tosylsulfoximinoyl)-3,6-dihydro-2*H*-pyran, 42.



From dihydropyran **10b** (158 mg, 0.568 mmol), *N*-tosyl phenyliminoiodinane (254 mg, 0.682 mmol) and $Cu(OTf)_2$ (21 mg, 0.057 mmol), according to the general procedure (50 min) sulfoximine **42** was obtained. Purification by chromatography (10-50% EtOAc-hexane) afforded sulfoximine **42** (80 mg, 0.179 mmol, 32%) as a white solid along with recovered starting material (40 mg, 0.144 mmol, 25%).

Data for **42**: R_f = 0.26 (50% EtOAc-hexane). **mp**: 89-91 ºC. $[\alpha]^{20}_D$ = –142.5 (*c* = 0.71). **^{1}H NMR (300 MHz)** δ 0.87 (t, 3 H, *J* = 7.1 Hz, CH_3), 1.24-1.36 (m, 4 H, 2 CH_2), 1.37-1.68 (m, 2 H, CH_2), 2.36 (s, 3 H, Me-*p*-Tol), 2.40 (s, 3 H, Me-Ts), 3.38 (d, 1 H, *J* = 18.1 Hz, H-6), 3.84 (ddd, 1 H, *J* = 18.1, 4.9, 2.0 Hz, H-6), 4.43 (m, 1 H, H-3), 4.48 (dd, 1 H, *J* = 9.8, 4.8 Hz, H-2), 5.94 (ddd, 1 H, *J* = 10.3, 2.1, 1.0 Hz, H-4), 6.02 (d, 1 H, *J* = 10.5 Hz, H-5), 7.23 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.28 (d, 2 H, *J* = 8.1 Hz, Ar-H), 7.76 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.86 (d, 2 H, *J* = 8.5 Hz, Ar-H). **^{1}H NMR (300 MHz, C_6D_6)** δ 0.84 (t, 3 H, *J* = 7.2 Hz, CH_3), 1.19-1.39 (m, 4 H, 2 CH_2), 1.40-1.56 (m, 2 H, CH_2), 1.80 (s, 3 H, Me-*p*-Tol), 1.82 (s, 3 H, Me-Ts), 2.97 (dt, 1 H, *J* = 17.8, 2.2 Hz, H-6), 3.34 (dq, 1 H, *J* = 18.1, 2.4 Hz, H-6), 4.66 (hept, 1 H, *J* = 1.5 Hz, H-3), 4.83 (ap t, 1 H, *J* = 7.1 Hz, H-2), 5.27 (dq, 1 H, *J* = 10.2, 1.5 Hz, H-5), 5.77 (dddd, 1 H, *J* = 10.3, 5.4, 3.2, 1.0 Hz, H-4), 6.74 (d, 2 H, *J* = 9.7 Hz, Ar-H), 6.77 (d, 2 H, *J* = 7.8 Hz, Ar-H), 7.85 (d, 2 H, *J* = 8.3 Hz, Ar-H), 8.28 (d, 2 H, *J* = 8.3 Hz, Ar-H). **^{13}C NMR (75 MHz)** δ 13.9 (CH_3-Bu), 21.5 (Me-*p*-Tol), 21.7, 22.3, 27.6, 30.6, 59.2, 65.8, 70.1, 115.1, 126.6 (2 C), 129.2 (4 C), 130.0 (2 C), 130.8, 134.8, 141.1, 142.6, 145.4. **IR** (film): 2950, 2926, 2867, 1594, 1451, 1316, 1152, 1088, 1062, 1015, 940, 812, 753 cm^{-1}. **MS** (ES): 917 $[2M+Na]^+$ (100%), 470 $[M+Na]^+$. **Anal. calcd for** $C_{23}H_{29}NO_4S_2$: C, 61.72; H, 6.53; N, 3.13; S, 14.33. **Found**: C, 61.53; H, 6.40; N, 3.20; S, 14.24.

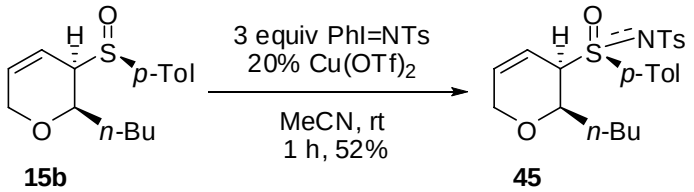
8.10. Synthesis of (+)-(2*S*,3*S*,*R*$_S$)-2-*n*-Butyl-3-(*S*-*p*-tolyl-*N*-tosylsulfoximinoyl)-3,6-dihydro-2*H*-pyran, 44.



From dihydropyran **11b** (13 mg, 0.047 mmol), *N*-tosyl phenyliminoiodinane (21 mg, 0.056 mmol) and $Cu(OTf)_2$ (4 mg, 0.01 mmol), according to the general procedure (30 min) sulfoximine **44** was obtained. Purification by chromatography (10-30% EtOAc-hexane) afforded sulfoximine **44** (11 mg, 0.025 mmol, 53%) as a white solid that was recrystallized from CH_2Cl_2-hexane.

Data for **44**: R_f = 0.24 (30% EtOAc-hexane). **mp**: 102-104 ºC. $[\alpha]^{20}_D$ = +131.6 (*c* = 1.12). **^{1}H NMR (300 MHz, C_6D_6), COSY** δ 0.87 (t, 3 H, *J* = 6.9 Hz, CH_3), 1.17-1.46 (m, 4 H, 2 CH_2), 1.79 (s, 3 H, Me-*p*-Tol), 1.81 (s, 3 H, Me-Ts), 1.90-2.06 (m, 2 H, CH_2), 3.06 (d, 1 H, *J* = 17.3 Hz, H-6), 3.24 (ddd, 1 H, *J* = 8.3, 5.4, 3.0 Hz, H-2), 3.36 (dd, 1 H, *J* = 17.6, 2.2 Hz, H-6), 4.91 (ap q, 1 H, *J* = 2.7 Hz, H-3), 5.29 (dd, 1 H, *J* = 10.2, 1.1 Hz, H-5), 6.38 (ddt, 1 H, *J* = 10.2, 5.7, 2.2 Hz, H-4), 6.69 (d, 2 H, *J* = 8.5 Hz, Ar-H), 6.77 (dd, 2 H, *J* = 8.0, 0.6 Hz, Ar-H), 7.81 (d, 2 H, *J* = 8.3 Hz, Ar-H), 8.29 (d, 2 H, *J* = 8.3 Hz, Ar-H). **^{13}C NMR (75 MHz, C_6D_6)** δ 14.2 (CH_3-Bu), 21.0, 21.1, 22.8, 29.2, 32.7, 66.0, 66.1, 75.7, 120.7, 127.2 (2 C), 129.0 (2 C), 129.3 (2 C), 130.4 (2 C), 133.5, 134.0, 142.0, 142.8, 144.4. **IR** (KBr): 2956, 2927, 2855, 1597, 1313, 1228, 1200, 1155, 1088, 1058, 1014, 812, 751, 686, 659 cm^{-1}. **MS** (ES): 917 $[2M+Na]^+$ (100%), 470 $[M+Na]^+$. **Anal. calcd for** $C_{23}H_{29}NO_4S_2$: C, 61.72; H, 6.53; N, 3.13; S, 14.33. **Found**: C, 62.01; H, 6.39; N, 3.09; S, 14.51.

8.11. Synthesis of (−)-(2R*S*,3*R*,*R*$_S$)-2-*n*-Butyl-3-(*S*-*p*-tolyl-*N*-tosylsulfoximinoyl)-3,6-dihydro-2*H*-pyran, 45.



From dihydropyran **15b** (12 mg, 0.043 mmol), *N*-tosyl phenyliminoiodinane (48 mg, 0.129 mmol) and $Cu(OTf)_2$ (4 mg, 0.008 mmol), according to the general procedure (1 h) sulfoximine **45** was obtained. Purification by chromatography (10-30% EtOAc-hexane) afforded sulfoximine **45** (10 mg, 0.022 mmol, 52%) as a colorless oil.

Data for **45**: R_f = 0.22 (30% EtOAc-hexane). $[\alpha]^{20}_D$ = –63.8 (*c* = 0.26). **^{1}H NMR (300 MHz, C_6D_6)** δ 0.99 (t, 3 H, *J* = 7.1 Hz, CH_3), 1.19-1.54 (m, 4 H, 2 CH_2), 1.77 (s, 3 H, Me-*p*-Tol), 1.81 (s, 3 H, Me-Ts), 2.16 (m, 1 H, CH_2), 2.45 (m, 1 H, CH_2), 3.13 (ap d, 1 H, *J* = 17.3 Hz, H-6), 3.25 (dt, 1 H, *J* = 10.3, 2.9 Hz, H-2), 3.36 (dq, 1 H, *J* = 17.1, 2.4 Hz, H-6), 4.80 (m, 1 H, H-3), 5.27 (dq, 1 H, *J* = 10.3, 1.5 Hz, H-5), 5.94 (ddt, 1 H, *J* = 10.2, 5.7, 2.2 Hz, H-4), 6.67 (d, 2 H, *J* = 8.3 Hz, Ar-H), 6.77 (d, 2 H, *J* = 8.1 Hz, Ar-H), 7.84 (d, 2 H, *J* = 8.5 Hz, Ar-H), 8.32 (d, 2 H, *J* = 8.3 Hz, Ar-H). **^{13}C NMR (75 MHz, C_6D_6)** δ 14.3 (CH_3-Bu), 21.0 (2 C), 22.8, 29.4, 32.5, 66.1 (2 C), 75.3, 113.7, 120.0, 127.1, 127.2, 127.3, 129.1 (2 C), 129.3 (2 C), 130.4 (2 C), 134.0, 142.0, 144.6. **IR** (film): 3016, 2961, 2926, 2854, 1596, 1456, 1378, 1302, 1263, 1183, 1149, 1088, 1064, 1015, 814, 761, 703, 681, 660 cm^{-1}. **MS** (ES): 917 $[2M+Na]^+$ (100%), 470 $[M+Na]^+$, 448 $[M+1]^+$.

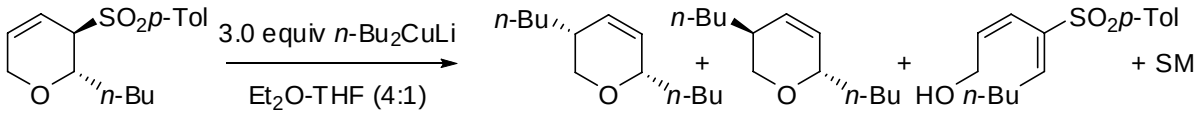
9. Allylic displacements of sulfones and sulfoximines with organocuprates.

9.1. General procedure for S_N2' alkylation of allylic sulfones and allylic sulfoximines.

In a round-bottomed flask a suspension of the copper salt [CuI, CuCN, CuBr·(Me_2S) (3 equiv)] in anhydrous Et_2O (10 mL/mmol of sulfone) was deoxygenated with argon for 5-10 minutes. The suspension was then cooled to –78 ºC and 3-6 equiv of the corresponding organometallic solution was added. The mixture was stirred from –78 to 0 ºC and then a solution of sulfone in (4:1) Et_2O-THF (5 mL/mmol) was added. The reaction was warmed to room temperature and stirred until disappearance of starting material was observed (TLC). The mixture was quenched with saturated NH_4Cl solution (4 mL/mmol) and H_2O (4 mL/mmol) and diluted with Et_2O. The layers were separated and the aqueous layer was extracted with Et_2O (3 x 4 mL/mmol). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with the appropriate combination of solvents.

9.2. S_N2' alkylation of allylic sulfones.

9.2.1. Synthesis of (–)-(3*R*,6*R*)-3,6-Di-*n*-butyl-3,6-dihydro-2*H*-pyran, 46a.



20b		**46a** (91)	**48a** (9)	**47** (0)	**20b** (0)
20b	3.0 equiv *n*-Bu_2CuLi Et_2O-THF (4:1) 0 ºC to rt, 15 h, 100%	**46a** (42)	**48a** (4)	**47** (54)	**20b** (0)
20b	4.0 equiv *n*-Bu_2CuLi Et_2O-THF (4:1) 0 ºC to rt, 19 h, 67%	**46a** (43)	**48a** (4)	**47** (10)	**20b** (19)
20b	4.0 equiv *n*-BuCNCuLi Et_2O-THF (4:1) 0 ºC to rt, 40 h, 100%	**46a** (0)	**48a** (0)	**47** (0)	**20b** (100)
20b	4.0 equiv *n*-$Bu_2CuLi{\cdot}(Me_2S)$ Et_2O-THF (4:1) 0 ºC to rt, 19 h, 67%	**46a** (0)	**48a** (0)	**47** (0)	**20b** (100)
20b	3.0 equiv *n*-$Bu_2CuMgBr$ Et_2O-THF (4:1) 0 ºC to rt, 21 h, 100%	**46a** (66)	**48a** (0)	**47** (0)	**20b** (34)

From sulfone **20b** (23 mg, 0.078 mmol), CuI (45 mg, 0.234 mmol), butyllithium (0.3 mL, 1.6 M, 0.468 mmol), according to the general procedure (40 h) dihydropyran **46a** was obtained. Purification by chromatography (2-5% EtOAc-hexane) afforded a 91:9 mixture of **46a** and **48a** (12 mg, 0.061 mmol, 78%) as a colorless oil. This experiment was difficult to reproduce using the conditions described above.

From sulfone **20b** (27 mg, 0.092 mmol), CuI (54 mg, 0.276 mmol), butylmagnesium bromide (0.68 mL, 0.81 M, 0.552 mmol, prepared form magnesium turnings and *n*-BuBr in Et_2O), according to the general procedure (21 h) dihydropyran **46a** was obtained. Purification by chromatography (2-5%-EtOAc-hexane) afforded **46a** (12 mg, 0.061 mmol, 66%) as a colorless oil, along with recovered starting material (9 mg, 0.031 mmol, 34%).

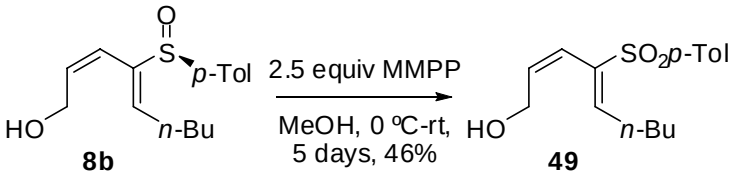
Data for **46a**: R_f = 0.48 (10% EtOAc-hexane). $[\alpha]^{20}_D$ = –11.1 (*c* = 0.75). **^{1}H NMR (500 MHz), COSY** δ 0.88 (t, 3 H, *J* = 7.1 Hz, CH_3), 0.88 (t, 3 H, *J* = 7.2 Hz, CH_3), 1.21-1.52 (m, 12 H, 6 CH_2), 1.92 (m, 1 H, H-3), 3.67 (ap d, 2 H, *J* = 3.9 Hz, H-2), 4.02 (hept, 1 H, *J* = 2.5 Hz, H-6), 5.59 (dt, 1 H, *J* = 10.3, 1.7 Hz, H-5), 5.78 (ddd, 1 H, *J* = 10.3, 4.5, 2.1 Hz, H-4). **^{13}C NMR (125 MHz), HSQC** δ 14.0 (CH_3), 14.1 (CH_3), 22.8 (CH_2), 22.9 (CH_2), 27.4 (CH_2), 29.4 (CH_2), 33.1 (CH_2), 34.8 (CH_2), 34.9 (C-3),

67.2 (C-2), 74.1 (C-6), 129.3 (C-5), 129.7 (C-4). **IR** (film): 2962, 2920, 2850, 1650, 1459, 1376, 1261, 1091, 1020, 800 cm^{-1}. **MS** (ES): 219 $[M+Na]^+$, 197 $[M+1]^+$.

Partial data for **48a**: R_f = 0.48 (10% EtOAc-hexane) **^{1}H NMR (500 MHz)** δ 4.14 (dd, 1 H, *J* = 4.5, 2.3 Hz, H-6).

Data for **47**: R_f = 0.12 (30% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 0.86 (t, 3 H, *J* = 7.2 Hz, CH_3), 1.21-1.45 (m, 4 H), 2.04 (qd, 2 H, *J* = 7.5, 1.1 Hz, CH_2), 2.41 (s, 3 H, CH_3 *p*-Tol), 3.75 (dd, 2 H, *J* = 6.9, 1.1 Hz, H-1), 5.75 (dq, 1 H, *J* = 11.1, 1.2 Hz, H-3), 6.01 (dt, 1 H, *J* = 11.1, 6.9 Hz, H-2), 6.94 (td, 1 H, *J* = 7.6, 1.4 Hz, H-5), 7.29 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.68 (d, 2 H, *J* = 8.4 Hz, Ar-H). **^{13}C NMR (75 MHz), HSQC** δ 13.7 (CH_3), 21.6 (CH_3 *p*-Tol), 22.3 (CH_2), 28.9 (CH_2), 30.1 (CH_2), 59.1 (C-1), 119.8 (C-3), 128.4 (2 C), 129.6 (2 C), 136.2, 137.6, 138.6 (C-2), 143.0 (C-5), 144.4. **IR** (film): 3479, 2956, 2930, 2872, 1688, 1597, 1457, 1400, 1312, 1301, 1288, 1139, 1088, 1036, 815 cm^{-1}. **MS** (ES): 317 $[M+Na]^+$ (100%).

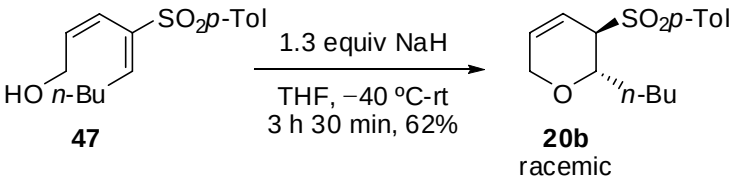
9.2.2. Synthesis of (2*Z*,4*Z*)-4-(*p*-Tolylsulfonyl)nona-2,4-dien-1-ol, 49.



From diene **8b** (6 mg, 0.022 mmol) and MMPP (34 mg, 0.055 mmol) according to the general procedure of oxidation (Method G, 5 days) sulfone **49** was obtained. Purification by chromatography (10-50% EtOAc-hexane) afforded sulfone **49** (3 mg, 0.01 mmol, 46%) as a colorless oil, along with recovered starting material (2 mg, 0.007 mmol, 33%).

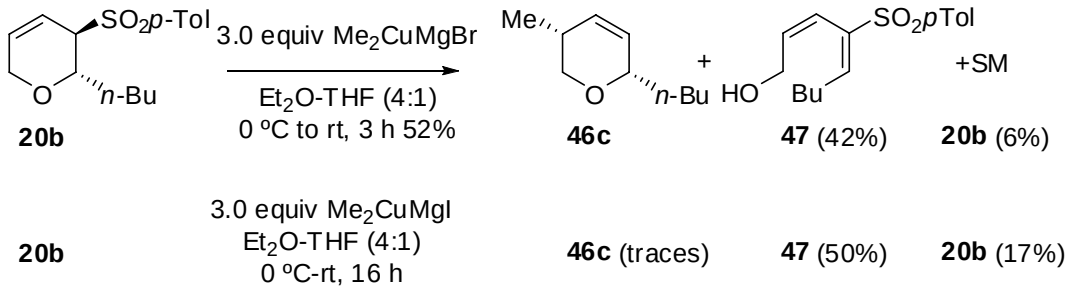
Data for **49**: R_f = 0.30 (50% EtOAc-hexane). **^{1}H NMR (300 MHz)** δ 0.90 (t, 3 H, *J* = 7.1 Hz, CH_3), 1.23-1.45 (m, 4 H, 2 CH_2), 2.42 (s, 3 H, CH_3 *p*-Tol), 2.74 (q, 2 H, *J* = 7.2 CH_2), 3.95 (dd, 2 H, *J* = 6.7, 1.2 Hz, H-1), 5.88 (dt, 1 H, *J* = 11.3, 6.7 Hz, H-2), 5.94 (dd, 1 H, *J* = 8.0, 1.3 Hz, H-5), 6.14 (dq, 1 H, *J* = 11.3, 1.5 Hz, H-3), 7.30 (d, 2 H, *J* = 8.1 Hz, Ar-H), 7.72 (d, 2 H, *J* = 8.2 Hz, Ar-H).

9.2.3. Synthesis of (±)-2-*n*-Butyl-3-(*p*-tolylsulfonyl)-3,6-dihydro-2*H*-pyran, 20b.



From diene **47** (32 mg, 0.109 mmol) and NaH (3 mg, 0.142 mmol) according to the general procedure (Method B, 3 h 30 min) racemic sulfone **20b** was obtained. Purification by chromatography (10-50% EtOAc-hexane) afforded racemic sulfone **20b** (20 mg, 0.068 mmol, 62%) as a colorless oil.

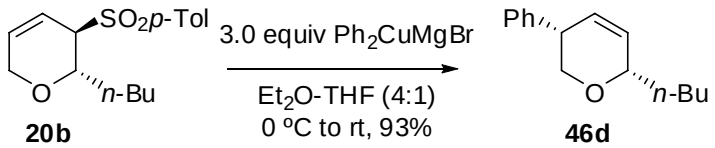
9.2.4. Synthesis of (–)-(3*R*,6*S*)-6-*n*-Butyl-3-methyl-3,6-dihydro-2*H*-pyran, 46c, and (2*Z*,4*E*)-4-(*p*-Tolylsulfonyl)nona-2,4-dien-1-ol, 47.



From sulfone **20b** (33 mg, 0.112 mmol), CuI (65 mg, 0.336 mmol), methylmagnesium bromide (0.32 mL, 2.13 M), according to the general procedure (3 h) dihydropyran **46c** was obtained. Purification by chromatography (5-30% CH_2Cl_2-hexane) afforded **46c** (9 mg, 0.058 mmol, 52%) as a colorless oil, along with *Z,E* sulfonyl diene **47** (14 mg, 0.048 mmol, 42%), and starting material (2 mg, 0.007 mmol, 6%).

Data for **46c**: R_f = 0.23 (30% CH_2Cl_2-hexane). $[\alpha]^{20}_D$ = –6.7 (*c* = 0.15). **^{1}H NMR (300 MHz), COSY** δ 0.88 (t, 3 H, *J* = 7.2 Hz, CH_3 Bu), 1.03 (d, 3 H, *J* = 7.1 Hz, CH_3), 1.23-1.52 (m, 6 H, 3 CH_2), 2.12 (m, 1 H, H-3), 3.54 (ddd, 2 H, *J* = 11.2, 2.5, 0.7 Hz, H-2), 3.71 (dd, 1 H, *J* = 11.1, 4.0 Hz, H-2), 4.02 (quint, 1 H, *J* = 2.3 Hz, H-6), 5.57 (dt, 1 H, *J* = 10.3, 1.7 Hz, H-5), 5.73 (dddd, 1 H, *J* = 10.3, 4.4, 2.2, 0.7 Hz, H-4). **^{13}C NMR (75 MHz)** δ 14.0 (CH_3), 18.6, 22.8 (CH_2), 27.5 (CH_2), 29.7 (CH_2), 34.8 (CH_2), 68.8, 73.8, 129.5, 130.5. **IR** (film): 2963, 2925, 2854, 1414, 1262, 1100, 1021, 865, 800, 661 cm^{-1}. **MS** (ES): 269 $[2M+H_2O–Bu]^+$, 187 $[M+1+MeOH]^+$.

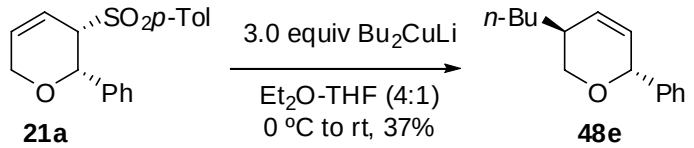
9.2.5. Synthesis of (–)-(3*S*,6*S*)-6-*n*-Butyl-3-phenyl-3,6-dihydro-2*H*-pyran, 46d.



From sulfone **20b** (41 mg, 0.139 mmol), CuI (81 mg, 0.417 mmol), phenylmagnesium bromide (1.3 mL, 0.65 M, 0.834 mmol, prepared from magnesium turnings and PhBr in Et_2O), according to the general procedure (40 min) dihydropyran **46d** was obtained. Purification by chromatography (5-10% CH_2Cl_2-hexane) afforded **46d** (21 mg, 0.129 mmol, 93%) as a colorless oil.

Data for **46d**: R_f = 0.24 (30% CH_2Cl_2-hexane). $[\alpha]^{20}_D$ = –75.1 (*c* = 0.87). **^{1}H NMR (300 MHz), COSY** δ 0.91 (t, 3 H, *J* = 7.1 Hz, CH_3), 1.24-1.69 (m, 6 H, 3 CH_2), 3.30 (quint, 1 H, *J* = 3.5 Hz, H-3), 3.82 (dd, 1 H, *J* = 11.2, 3.2 Hz, H-2), 3.94 (dd, 1 H, *J* = 11.2, 4.4 Hz, H-2), 4.11 (m, 1 H, H-6), 5.82-5.92 (m, 2 H, H-4, H-5), 7.18-7.35 (m, 5 H, Ar-H). **^{13}C NMR (125 MHz)** δ 14.0 (CH_3), 22.8 (CH_2), 27.7 (CH_2), 34.8 (CH_2), 41.2 (C-3), 69.2 (C-2), 73.8 (C-6), 126.5, 127.2, 128.2 (2 C), 128.4, (2 C), 131.0, 142.9. **IR** (film): 3028, 2959, 2926, 2859, 1491, 1453, 1262, 1086, 1021, 799, 757, 699 cm^{-1}. **MS** (ES): 239 $[M+Na]^+$ (100%), 217 $[M+1]^+$.

9.2.6. Synthesis of (3*S*,6*R*)-3-*n*-Butyl-6-phenyl-3,6-dihydro-2H-pyran, 48e.

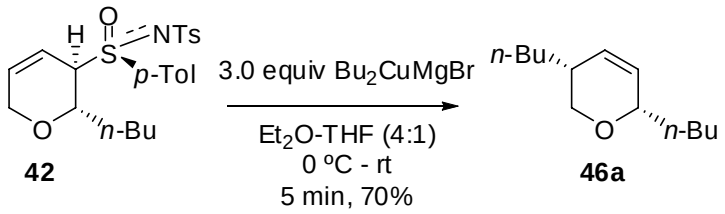


From sulfone **21a** (8 mg, 0.025 mmol), CuI (14 mg, 0.075 mmol), butyllithium (0.1 mL, 1.6 M, 0.15 mmol), according to the general procedure (1 h) dihydropyran **48e** was obtained. Purification by chromatography (2-20% EtOAc-hexane) afforded slightly impure **48e** (2 mg, 0.009 mmol, 37%) as a colorless oil.

Partial data for **48e**: R_f = 0.40 (20% EtOAc-hexane). **^{1}H NMR (500 MHz), COSY** δ 0.90 (t, 3 H, *J* = 6.8 Hz, CH_3), 1.20-1.35 (m, 6 H, 3 CH_2), 2.35 (m, 1 H, H-3), 3.42 (dd, 1 H, *J* = 11.0, 8.8 Hz, H-2), 4.04 (ddd, 1 H, *J* = 11.2, 5.1, 1.0 Hz, H-2), 5.06 (ap q, 1 H, *J* = 2.5 Hz, H-6), 5.75 (dt, 1 H, *J* = 10.3, 2.2 Hz, H-5), 5.87 (dtd, 1 H, *J* = 10.2, 2.3, 1.2 Hz, H-4), 7.25-7.45 (m, 5 H, Ar-H). **^{13}C NMR (125 MHz), HSQC** δ 14.0 (CH_3), 22.9 (CH_2), 28.8 (CH_2), 31.9 (CH_2), 34.3 (C-3), 69.3 (C-2), 76.6 (C-6), 127.4 (2 C), 127.8, 128.5 (2 C), 128.8 (C-5), 130.2 (C-4), 141.3. **MS** (ES): 239 $[M+Na]^+$, 218 $[M+2]^+$.

9.3. S_N2' alkylation of allylic sulfoximines.

9.3.1. Synthesis of (–)-(3*R*,6*R*)-3,6-Di-*n*-butyl-3,6-dihydro-2*H*-pyran, 46a.

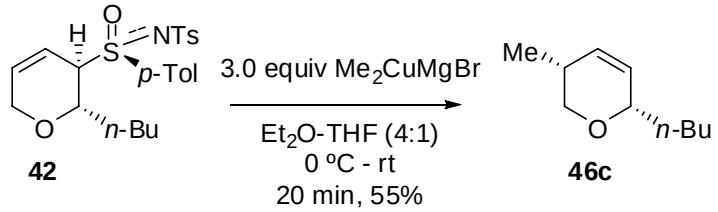


From sulfoximine **42** (20 mg, 0.045 mmol), CuI (26 mg, 0.135 mmol), butylmagnesium bromide (0.39 mL, 0.72 M, 0.27 mmol, prepared form magnesium turnings and *n*-BuBr in Et_2O), according to the

general procedure (5 min) dihydropyran **46a** was obtained. Purification by chromatography (5-30% CH_2Cl_2-hexane) afforded **46a** (6 mg, 0.031 mmol, 70%) as a colorless oil.

The data measured was identical to that obtained in the reaction from sulfone **20b**.

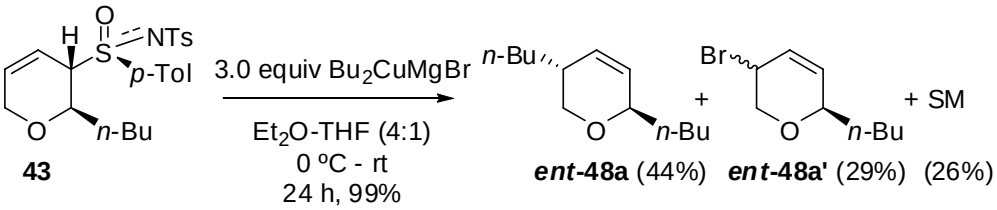
9.3.2. Synthesis of (–)-(3*R*,6*S*)-6-*n*-Butyl-3-methyl-3,6-dihydro-2*H*-pyran, 46c.



From sulfoximine **42** (32 mg, 0.071 mmol), CuI (41 mg, 0.213 mmol), methylmagnesium bromide (0.20 mL, 2.13 M, 0.426 mmol), according to the general procedure (20 min) dihydropyran **46c** was obtained. Purification by chromatography (2-10% EtOAc-hexane) afforded **46c** (6 mg, 0.039 mmol, 55%) as a colorless oil.

The data measured was identical to that obtained in the reaction from sulfone **20b**.

9.3.3. Synthesis of (3*R*,6*R*)-3,6-Di-*n*-butyl-3,6-dihydro-2*H*-pyran, *ent*-48a.



From sulfoximine **43** (15 mg, 0.034 mmol), CuI (20 mg, 0.102 mmol), butylmagnesium bromide (0.28 mL, 0.72 M, 0.204 mmol, prepared form magnesium turnings and *n*-BuBr in Et_2O), according to the general procedure (24 h) dihydropyran ***ent*-48a** was obtained. Purification by chromatography (5-30% CH_2Cl_2-hexane) afforded impure ***ent*-48a** (4 mg, 0.015 mmol, 44%) as a colorless oil along with a mixture of brominated products (4 mg, 0.01 mmol, 29%) and recovered starting material (4 mg, 0.009 mmol, 26%).

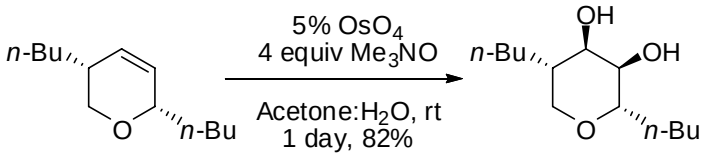
Partial data for ***ent*-48a**: R_f = 0.23 (30% CH_2Cl_2-hexane). **^{1}H NMR (500 MHz)** δ 0.88 (t, 3 H, *J* = 6.8 Hz, CH_3), 0.90 (t, 3 H, *J* = 6.7 Hz, CH_3), 1.14-1.41 (m, 12 H, 6 CH_2), 1.94 (m, 1 H, H-3), 3.72 (dd, 1 H, *J* = 11.5, 8.3 Hz, H-2), 4.09-4.27 (m, 2 H, H-6, H-2), 5.73 (ap d, 1 H, *J* = 10.5 Hz, H-5), 5.96 (ap d, 1 H, *J* = 10.3 Hz, H-4). **MS** (ES): 219 $[M+Na]^+$.

Data for ***ent*-48a'** (major isomer): R_f = 0.47 (30% Et_2O-hexane). **^{1}H NMR (300 MHz)** δ 0.89 (t, 3 H, *J* = 7.1 Hz, CH_3 Bu), 1.26-1.49 (m, 4 H, 2 CH_2), 1.55-1.70 (m, 2 H, CH_2), 3.97 (dd, 1 H, *J* = 12.9, 2.7 Hz, H-2), 4.15 (dt, 1 H, *J* = 12.9, 1.5 Hz, H-2), 4.20 (m, 1 H, H-6), 4.53 (ap q, 1 H, *J* = 2.4 Hz, H-3),

5.75 (ddd, 1 H, J = 10.1, 1.6, 0.7 Hz, H-5), 6.00 (dddd, 1 H, J = 10.0, 4.9, 2.2, 1.2 Hz, H-4). **^{13}C NMR (75 MHz)** δ 14.0, 22.7, 27.2, 34.4, 43.8, 69.8, 74.1, 126.4, 133.6. **IR** (film): 2956, 2920, 2850, 1732, 1441, 1259, 1071, 1029, 874 cm^{-1}. **MS** (ES): 283 [M+2MeOH]$^+$ (100%), 241 [M+Na]$^+$.

10. Dihydroxylation and epoxidation of S_N2' products.

10.1. Synthesis of (–)-(2*S*,3*R*,4*R*,5*R*)-2,5-Di-*n*-butyltetrahydro-2*H*-pyran-3,4-diol, 50a.

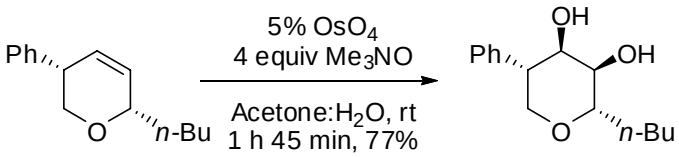


46a **50a**

From dihydropyran **46a** (25 mg, 0.127 mmol), Me_3NO (36 mg, 0.318 mmol) and OsO_4 [75 μL (2.5%), 0.006 mmol], according to the general procedure (1 h 40 min), diol **50a** was obtained. Purification by chromatography (0-20% EtOAc-CH_2Cl_2) afforded **50a** (24 mg, 0.104 mmol, 82%) as a white solid.

Data for **50a**: R_f = 0.35 (20% EtOAc-CH_2Cl_2). **mp**: 57-59 ºC. $[\alpha]^{20}_D$ = –2.8 (c = 1.23). **^{1}H NMR (300 MHz), COSY** δ 0.87 (t, 3 H, J = 6.9 Hz, CH_3), 0.88 (t, 3 H, J = 7.0 Hz, CH_3), 1.23-1.51 (m, 12 H, 6 CH_2), 1.65-1.72 (m, 1 H, H-5), 2.10 (br s, 2 H, 2 OH), 3.45 (m, 2 H, H-2, H-4), 3.50 (dd, 1 H, J = 11.8, 2.5 Hz, H-6), 3.77 (dd, 1 H, J = 11.7, 3.2 Hz, H-6), 3.81 (t, 1 H, J = 2.7 Hz, H-3). **^{13}C NMR (75 MHz)** δ 14.0 (2 C, 2 CH_3), 22.8 (2 C, 2 CH_2), 27.7 (CH_2), 28.5 (CH_2), 29.8 (CH_2), 31.2 (CH_2), 41.8, 64.6, 69.6, 71.3, 76.6. **IR** (KBr): 3339, 2958, 2926, 2857, 1465, 1291, 1262, 1082, 1020, 801, 760 cm^{-1}. **MS** (ES): 253 [M+Na]$^+$, 198 [M+2-2OH]$^+$ (100%). **Anal. calcd for** $C_{13}H_{26}O_3$: C, 67.79; H, 11.38. **Found**: C, 67.72; H, 11.21.

10.2. Synthesis of (–)-(2*S*,3*R*,4*R*,5*R*)-2-*n*-Butyl-5-phenyltetrahydro-2*H*-pyran-3,4-diol, 50d.

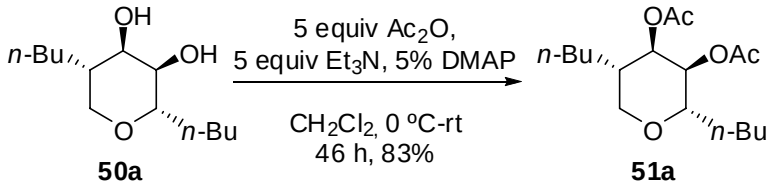


46d **50d**

From dihydropyran **46d** (18 mg, 0.083 mmol), Me_3NO (23 mg, 0.208 mmol) and OsO_4 [50 μL (2.5%), 0.004 mmol], according to the general procedure (1 h 45 min), diol **50d** was obtained. Purification by chromatography (0-20% EtOAc-CH_2Cl_2) afforded **50d** (16 mg, 0.064 mmol, 77%) as a white solid.

Data for **50d**: R_f = 0.18 (20% EtOAc-CH_2Cl_2). **mp**: 49-51 ºC. $[\alpha]^{20}_D$ = –4.2 (*c* = 0.52). **^{1}H NMR (300 MHz), COSY** δ 0.91 (t, 3 H, *J* = 7.1 Hz, CH_3), 1.29-1.54 (m, 4 H, 2 CH_2), 1.60-1.68 (m, 2 H, CH_2), 2.23 (br s, 1 H, OH), 2.32 (br s, 1 H, OH), 3.08 (td, 1 H, *J* = 6.3, 4.4 Hz, H-5), 3.64 (m, 1 H, H-3), 3.79 (dd, 1 H, *J* = 12.6, 6.0 Hz, H-2), 3.84 (dd, 1 H, *J* = 12.1, 6.0 Hz, H-6), 3.91 (dd, 1 H, *J* =12.0, 4.4 Hz, H-6), 4.09 (dd, 1 H, *J* = 6.8, 2.9 Hz, H-4), 7.21-7.40 (m, 5 H, Ar-H). **^{13}C NMR (75 MHz)** δ 14.0 (CH_3), 22.7 (CH_2), 27.8 (CH_2), 29.8 (CH_2), 46.4, 64.7, 69.5, 71.5, 76.8, 127.0, 128.5 (2 C), 128.7 (2 C), 139.6. **IR** ($CHCl_3$): 3369, 2950, 2932, 2861, 1495, 1454, 1376, 1215, 1106, 1080, 1006, 754, 700 cm^{-1}. **MS** (ES): 273 $[M+Na]^+$ (100%). **Anal. calcd for** $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. **Found**: C, 71.85; H, 8.93.

10.3. Synthesis of the diacetate of (–)-(2*S*,3*S*,4*R*,5*S*)-2,5-Di-*n*-butyltetrahydro-2*H*-pyran-3,4-diol, 51a.



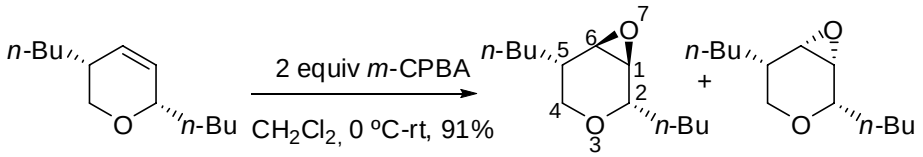
To a cold solution (0 ºC) of diol **50a** (16 mg, 0.069 mmol) in CH_2Cl_2 (0.7 mL, 10 mL/mmol), was added Ac_2O (33 μL, 0.345 mmol), Et_3N (48 μL, 0.345 mmol) and DMAP (1 crystal). The reaction mixture was stirred for 15 min at 0 ºC and then warmed to room temperature. When disappearance of starting material was observed (46 h) the reaction was quenched with saturated NH_4Cl solution (3 mL/mmol) and H_2O (3 mL/mmol). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 4 mL/mmol). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (5-10% EtOAc-hexane) to afford diacetate **51a** (18 mg, 0.057 mmol, 83%) as a colorless oil.

Data for **51a**: R_f = 0.24 (10% EtOAc-hexane). $[\alpha]^{20}_D$ = –9.4 (*c* = 1.42). **^{1}H NMR (300 MHz)** δ 0.87 (t, 6 H, *J* = 7.1 Hz, 2 CH_3), 1.25-1.52 (m, 12 H, 6 CH_2), 1.73 (m, 1 H, H-5), 2.00 (s, 3 H, CH_3CO), 2.07 (s, 3 H, CH_3CO), 3.58 (dd, 1 H, *J* = 11.7, 2.2 Hz, H-6), 3.61 (m, 1 H, H-2), 3.77 (dd, 1 H, *J* = 11.7, 2.9 Hz, H-6), 4.78 (dd, 1 H, *J* = 8.8, 2.9 Hz, H-3), 5.17 (t, 1 H, *J* = 3.5 Hz, H-4). **^{13}C NMR (75 MHz)** δ 13.9, 14.0, 20.9, 21.1, 22.6, 22.7, 27.4, 28.5, 29.5, 31.0, 40.0, 65.4, 69.5, 70.9, 74.8, 170.1 (C=O), 170.2 (C=O). **IR** (film): 2956, 2932, 2864, 1747, 1467, 1371, 1246, 1224, 1050, 944 cm^{-1}. **MS** (ES): 337 $[M+Na]^+$ (100%).

10.4. General procedure for the epoxidation of dihydropyrans.

To a cold solution (0 ºC) of the dihydropyran in anhydrous CH_2Cl_2 (4 mL/mmol), *m*-CPBA (2 equiv) was added. The mixture was allowed to warm to room temperature and stirred until disappearance of starting material was observed (TLC). The reaction was quenched with 1 M solution of $Na_2S_2O_4$ and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 4 mL/mmol) and the combined organic layers were washed with saturated $NaHCO_3$ solution (4 mL/mmol) and brine. The resulting organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with the appropriate combination of solvents.

10.5. Synthesis of (–)-(1*S*,2*S*,5*S*,6*R*)-2,5-Di-*n*-butyl-3,7-dioxabicyclo[4.1.0]heptane, 52, and (–)-(1*R*,2*S*,5*S*,6*S*)-2,5-di-*n*-butyl-3,7-dioxabicyclo[4.1.0]heptane, 53.



46a **52** (57) **53** (43)

From dihydropyran **46a** (6 mg, 0.031 mmol) and *m*-CPBA (15 mg, 0.062 mmol), according to the general procedure (18 h), a 57:43 mixture of epoxides **52** and **53** was obtained. Purification by chromatography (0-10% EtOAc-hexane) afforded **52** (3.5 mg, 0.016 mmol, 52%) and **53** (2.5 mg, 0.012 mmol, 39%) as colorless oils.

Data for **52**: R_f = 0.37 (10% EtOAc-hexane). $[\alpha]^{20}_D$ = –15.3 (*c* = 0.19). **^{1}H NMR (300 MHz), COSY** δ 0.90 (t, 6 H, *J* = 7.1 Hz, 2 CH_3), 1.26-1.47 (m, 8 H, 4 CH_2), 1.50-1.68 (m, 4 H, 2 CH_2), 1.85 (m, 1 H, H-5), 2.95 (d, 1 H, *J* = 4.4 Hz, H-6), 3.10 (ap dd, 1 H, *J* = 3.4, 0.7 Hz, H-1), 3.37 (dq, 1 H, *J* = 11.7, 1.0 Hz, H-4), 3.48 (dd, 1 H, *J* = 11.6, 3.3 Hz, H-4), 3.74 (t, 1 H, *J* = 6.3 Hz, H-2). **^{13}C NMR (75 MHz)** δ 14.0 (2 CH_3), 22.7 (CH_2), 22.8 (CH_2), 27.3 (CH_2), 28.6 (CH_2), 29.7 (CH_2), 33.3 (CH_2), 34.2, 54.3, 54.7, 63.1, 74.1. **IR** (film): 2959, 2928, 2860, 1460, 1429, 1376, 1262, 1135, 1108, 1029, 800 cm^{-1}. **MS** (ES): 235 $[M+Na]^+$ (100%).

Data for **53**: R_f = 0.29 (10% EtOAc-hexane). $[\alpha]^{20}_D$ = –21.7 (*c* = 0.12). **^{1}H NMR (300 MHz), COSY** δ 0.89 (t, 3 H, *J* = 6.8 Hz, CH_3), 0.90 (t, 3 H, *J* = 7.1 Hz, CH_3), 1.26-1.43 (m, 8 H, 4 CH_2), 1.57-1.69 (m, 4 H, 2 CH_2), 1.85-1.93 (m, 1 H, H-5), 3.13 (dd, 1 H, *J* = 4.4, 2.2 Hz, H-1), 3.30 (dd, 1 H, *J* = 11.3, 5.0 Hz, H-4), 3.32 (m, 1 H, H-6), 3.36 (dd, 1 H, *J* = 11.5, 5.9 Hz, H-4), 3.78 (ddd, 1 H, *J* = 7.6, 6.5, 2.4 Hz, H-2). **^{13}C NMR (75 MHz)** δ 14.0 (2 CH_3), 22.7 (CH_2), 22.9 (CH_2), 27.7 (CH_2), 29.0

(CH_2), 29.2 (CH_2), 30.5 (CH_2), 33.7, 53.7, 53.8, 64.4, 72.3. **IR** (film): 2956, 2927, 2855, 1460, 1379, 1261, 1121, 1099, 1071, 906, 874, 800, 789 cm^{-1}. **MS** (ES): 230 $[M+H_2O]^+$ (100%).