SUPPORTING INFORMATION

Reversal of Stereoselectivity in [5+2] Pyrone-Alkene Cycloadditions using a Sulfoxide to Sulfoximine switch. Enantiodivergent Synthesis of 8-Oxabicyclo[3.2.1]octane Systems

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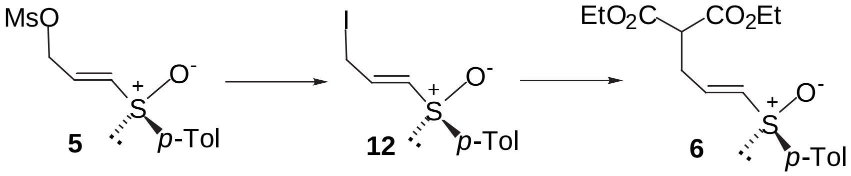
General Procedures. All dry solvents were freshly distilled under argon from the appropriate drying agent before use. Toluene and THF were distilled from sodium/benzophenone. CH_2Cl_2 was distilled from P_2O_5. MeOH was distilled from Mg/I_2. All reactions were conducted in dry solvents under argon atmosphere unless otherwise stated. Melting points (open capillary tubes) are uncorrected. Thin-layer chromatography (TLC) was performed on silica gel plates and components were visualized by observation under UV light, or by treating the plates with a phosphomolybdic reagent followed by heating. Flash chromatography was performed on silica gel, unless otherwise stated. Dryings were performed with anhydrous Na_2SO_4. Concentrations were carried out in a rotary evaporator. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, at 250 MHz and 62.9 MHz, respectively, and in some cases at 300 or 500 MHz (75.4 or 125.7 for ^{13}C NMR). Carbon types were determined from DEPT ^{13}C NMR experiments. The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. $[\alpha]_D$ were measured at rt (20 °C) in $CHCl_3$. $Eu(hfc)_3$ refers to tris[heptafluoropropyl-hydroxymethylene)-(-) camphorate]europium (III).

Diethyl-(2*E*, *R*$_S$)-3-*p*-Tolylsulfinyl-2-propenylmalonate (6).



Potasium iodide (0.33 g, 2.01 mmol) was added to a solution of mesylate **5**[1](0.55 g, 2.01 mmol) in acetone (40 ml). After stirring for 3 h at rt the reaction mixture was poured into water, extracted with Et_2O, dried, filtered and concentrated. The crude residue was used without further purification in the next reaction. ^1H NMR δ 7.42 (2H, d, *J* = 8.1 Hz), 7.25 (2H, d, *J* = 8.1 Hz), 6.64 (1H, m), 6.29 (1H, d, *J* = 14.8 Hz), 3.85 (2H, d, *J* = 8.1 Hz), 2.33 (3H, s).

Diethylmalonate (0.65 g, 4.03 mmol) was added to a cooled (-78 ºC) suspension of NaH (0.16 g, 60% mineral oil, 4.03 mmol) in THF (25 ml). After being stirred for 20 min at rt, a solution of allyl iodide **12** (2.01 mmol) in THF (3 ml) was added. The reaction mixture was stirred for 20 min at rt, poured into brine, extracted with Et_2O, dried, filtered and concentrated. The crude residue was flash chromatographed on silica gel (30-40% EtOAc/Hexanes) to afford 537 mg of **6** as a colorless oil [79%, Rf 0.65

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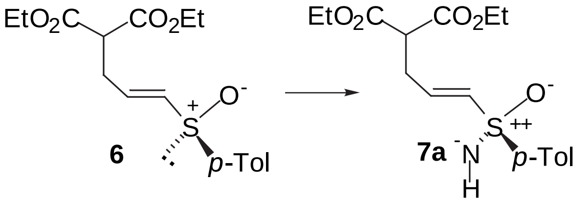
[1] For the synthesis of **5** see: López. F.; Castedo. L.; Mascareñas. J. L. *Org. Lett.* **2000**, *2*, 1005.

(40% EtOAc/Hexanes)]. $[\alpha]_D^{21}$ = +112 (*c*=0.77); ^{1}H NMR δ 7.31 (2H, d, *J* = 7.9 Hz), 7.11 (2H, d, *J* = 7.9 Hz), 6.31 (1H, m), 6.09 (1H, d, *J* = 15.1 Hz), 3.92 (4H, m), 3.27 (1H, t, *J* = 7.3 Hz), 2.58 (2H, m), 2.16 (3H, s), 0.99 (6H, m); ^{13}C NMR δ 168.5 (C), 141.9 (C), 140.8 (C), 138.0 (CH), 134.6 (CH), 130.4 (CH), 125.0 (CH), 62.0 (CH_2), 51.0 (CH), 31.1 (CH_2), 21.7 (CH_3), 14.3 (CH_3); LRMS *m/z* 338 (M^+, 2.42), 321 (15), 293 (9), 290 (31), 216 (56), 143 (100); HRMS calcd. for $C_{17}H_{22}O_5S$ 338.1188, found 338.1193.

Amination of alkenylsulfoxide 6 with O-mesitylsulfonylhydroxylamine (MSH)[2]



MSH (412 mg, 1.92 mmol) was added to a 0 ºC cooled solution of alkenylsulfoxide **6** (405 mg, 1.20 mmol) in acetonitrile (7 ml). After being stirred at 0 ºC for 2 h the reaction was slowly allowed to reach rt and further stirred at that temperature for 18 h. The reaction mixture was diluted in CH_2Cl_2 (5 ml), poured into a cold (0ºC) aqueous solution of NaOH (10%, 10 ml), stirred for 15 min, and extracted with CH_2Cl_2. The organic phases were dried, filtered, and concentrated. The crude residue **7a** was used for the next step without further purification. [ee ≥ 96%][3]; ^{1}H NMR δ 7.83 (2H, d, *J* = 8.3 Hz), 7.32 (2H, d, *J* = 8.0 Hz), 6.85 (1H, m), 6.50 (1H, d, *J* = 14.9 Hz), 4.15 (4H, m), 3.47 (1H, t, *J* = 7.3 Hz), 2.80 (2H, m), 2.40 (3H, s), 2.29 (1H, s), 1.18 (6H, m).

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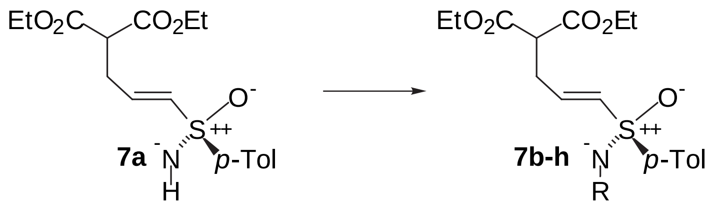
[2] **Caution**: It is documented that MSH cristals may cause explotions: Johnson, C.R.; Kirchhoff, R.A.; Corkins, H.G. *J. Org. Chem*. **1974**, *39*, 2458. and refernces cited therein.

[3] The enantiomeric excess of **7a** was determined by derivatization with both (+) and (±)-Methoxyphenyl acetic acid and comparation of the integrated signals of the vinylic protons in the ^{1}H NMR spectrums of the crude reaction mixtures. For more details see : Yabuuchi, T.; Kusumi, T. *J. Am. Chem. Soc.* **1999**, *121*, 10646.

Preparation of N-substituted sulfoximine derivatives 7b-7i.



b, R = $COCH_3$ **f**, R = SO_2CH_3
c, R = $COCF_3$ **g**, R = SO_2CF_3
d, R = COPh **h**, R = SO_2*p*Tol
e, R = CO*p*NO_2Ph **i**, R = MPA

7b: Acetyl chloride (44 mg, 0.57 mmol) was added dropwise to a stirred solution of the crude alkenylsulfoximine **7a** (0.28 mmol) and Et_3N (57 mg, 0.57 mmol) in CH_2Cl_2 (5 ml) at 0 ºC. After being stirred for 30 min at 0 ºC the mixture was poured into brine, extracted with CH_2Cl_2, dried, filtered and concentrated. The crude was flash chromatographed on silica gel (30-40% EtOAc/hexanes) to afford 93 mg of **7b** as a colorless oil [82% two steps, Rf 0.15 (40% EtOAc/hexanes)]. $[\alpha]_D^{18} = +15$ (c=0.85); ^1H NMR δ 7.77 (2H, d, J = 8.3 Hz), 7.31 (2H, d, J = 8.2 Hz), 6.90 (1H, m), 6.51 (1H, d, J = 15.0 Hz), 4.13 (4H, m), 3.49 (1H, t, J = 7.3 Hz), 2.83 (2H, m), 2.43 (3H, s), 2.14 (3H, s), 1.23 (6H, m); ^{13}C NMR δ 179.6 (C), 167.8 (C), 144.5 (C), 142.2 (CH), 134.9 (C), 131.1 (CH), 130.0 (CH), 127.3 (CH), 61.8 (CH_2), 50.0 (CH), 30.2 (CH_2), 26.7 (CH_3), 21.5 (CH_3), 13.8 (CH_3); LRMS *m/z* 350 (M^+ - C_2H_5O, 8.1), 308 (5), 247 (39), 215 (10), 201 (14), 139 (100); HRMS calcd. for $C_{17}H_{20}NO_5S$ 350.1062, found 350.1066.

7c: Trifluoroacetic anhydride (196 mg, 0.93 mmol), was added dropwise to a stirred solution of the crude alkenylsulfoximine **7a** (0.47 mmol) and Et_3N (95 mg, 0.93 mmol) in CH_2Cl_2 (8 ml) at 0 ºC. After being stirred for 30 min at 0 ºC the mixture was poured into brine, extracted with CH_2Cl_2, dried, filtered and concentrated. The crude was flash chromatographed on silica gel (20-40% EtOAc/Hexanes) to afford 151 mg of **7c** as a colorless oil [72% two steps, Rf 0.56 (40% EtOAc/hexanes)]. $[\alpha]_D^{18} = +14$ (c=1.6); ^1H NMR δ 7.79 (2H, d, J = 8.4 Hz), 7.40 (2H, d, J = 8.1 Hz), 7.06 (1H, m), 6.52 (1H, d, J = 14.0 Hz), 4.15 (4H, m), 3.53 (1H, t, J = 7.2 Hz), 2.89 (2H, m), 2.46 (3H, s), 1.22 (6H, m); ^{13}C NMR δ 167.7 (C), 145.9 (C), 144.8 (CH), 133.0 (C), 130.5 (CH), 129.3 (CH), 127.4 (CH), 62.0 (CH_2), 49.9 (CH), 30.4 (CH_3), 21.6 (CH_3), 13.9 (CH_3); LRMS *m/z* 404 (M^+ - C_2H_5O, 9.1), 380 (40), 262 (4), 247 (18), 201 (16), 139 (100); HRMS calcd. for $C_{17}H_{17}NO_5F_3S$ 404.0780, found 404.0789.

7d: Benzoyl chloride (160 mg, 1.13 mmol) was added dropwise to a stirred solution of the crude alkenylsulfoximine **7a** (0.57 mmol), Et_3N (115 mg, 1.13 mmol) and DMAP (14mg, 0.2 .mmol) in CH_2Cl_2 (10 ml) at 0 ºC. After being stirred for 10 h at rt the mixture was poured into brine, extracted with CH_2Cl_2, dried, filtered and concentrated. The crude was flash chromatographed on silica gel (20-35% EtOAc/hexanes) to afford 155 mg of **7d** as a colorless oil [60% two steps, Rf 0.15 (30% EtOAc/hexanes)]. $[\alpha]_D^{18}$ = +6 (*c*=2.1); ^1H NMR δ 8.20 (2H, m), 7.81 (2H, m), 7.45 (5H, m), 7.12 (1H, m), 6.65 (1H, d, J = 15.0 Hz), 4.15 (4H, m), 3.52 (1H, t, J = 7.4 Hz), 2.87 (2H, m), 2.44 (3H, s), 1.15 (6H, m); ^{13}C NMR δ 192.5 (C), 175 (C), 167.6 (C), 145 (C), 143.6 (CH), 136 (C), 134.3 (CH), 133.1 (CH), 131.0 (CH), 134.3 (CH), 129.3 (CH), 127.2 (CH), 61.7 (CH_2), 49.8 (CH), 30.2 (CH_2), 21.3 (CH_3), 13.7 (CH_3); LRMS *m/z* 412 (M^+ - C_2H_5O, 16), 380 (2), 351 (8), 258 (6), 247 (100), 201 (17), 173 (19), 139 (62); HRMS calcd. for $C_{22}H_{22}NO_5S$ 412.1218, found 412.1229.

Procedure for the synthesis of 7e and 7i (exemplified for **7e**): A solution of the crude alkenylsulfoximine **7a** (0.620 mmol) in CH_2Cl_2 (5 ml) was added to a stirred solution of *p*-nitrobenzoic acid (130 mg, 0.78 mmol), EDC (179 mg, 0.94 mmol) and DMAP (15 mg, 0.12 mmol) in CH_2Cl_2 (10 ml) at rt. After being stirred at rt for 12 h the reaction was poured into brine, extracted with CH_2Cl_2 , dried, filtered and concentrated. The crude was flash chromatographed on silica gel (20% EtOAc/Hexanes) to afford 252 mg of **7e** as a colorless oil [81% two steps, Rf 0.15 (30% EtOAc/hexanes)]. $[\alpha]_D^{18}$ = +11 (*c*=1.6); ^1H NMR δ 8.20 (2H, d, *J* = 8.7 Hz), 8.12 (2H, d, *J* = 8.6 Hz), 7.75 (2H, d, *J* = 8.4 Hz), 7.29 (2H, d, *J* = 8.4 Hz), 6.97 (1H, m), 6.57 (1H, d, *J* = 15.0 Hz), 4.05 (4H, m), 3.48 (1H, t, *J* = 7.4 Hz), 2.82 (2H, m), 2.34 (3H, s), 1.12 (6H, m); ^{13}C NMR δ 171.3 (C), 167.6 (C), 149.6 (C), 144.9 (C), 143.1 (CH), 141.0 (C), 134.3 (C), 130.7 (CH), 130.5 (CH), 130.1 (CH), 127.2 (CH), 122.9 (CH), 61.7 (CH_2), 49.8 (CH), 30.2 (CH_2), 21.3 (CH_3), 13.7 (CH_3); LRMS *m/z* 457 (M^+ - C_2H_5O, 6.2), 380 (2), 288 (3), 247 (55), 201 (18), 139 (100); HRMS calcd. for $C_{22}H_{21}N_2O_7S$ 457.1069, found 457.1080.

7i: ^1H NMR δ 7.52-7.08 (9H, m), 6.76 (1H, m), 6.31 (1H, s), 4.73 (1H, s), 4.09 (4H, m), 3.42 (3H, s), 3.38 (1H, m), 2.73 (2H, m), 2.31 (3H, s), 1.18 (6H, m); ^{13}C NMR δ 178.7 (C), 167.8 (C), 144.6 (C), 142.7 (C), 138.0 (CH), 134.7 (CH), 130.7 (CH), 130.0 (CH), 128.3 (CH), 128.1 (C), 127.2 (CH), 125.0 (CH), 85.9 (CH), 61.9 (CH_2), 57.4 (CH_3), 50.0 (CH), 30.3 (CH_2), 21.5 (CH_3), 13.9 (CH_3); LRMS *m/z* 456 (M^+ - C_2H_5O, 1.2), 380 (100), 290 (1), 234 (5), 121 (32); HRMS calcd. for $C_{26}H_{31}NO_7S$ 501.1821, found 501.1826.

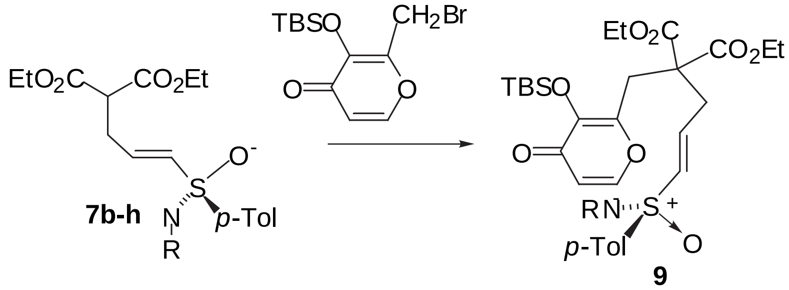
7f: Methanesulfonyl chloride (122 mg, 0.1.08 mmol) was added dropwise to an ice-water cooled solution of the crude alkenylsulfoximine **7a** (0.71 mmol) and Et_3N (110 mg, 1.08 mmol) in CH_2Cl_2 (10 ml) at 0 ºC. After being stirred for 30 min at 0 ºC the mixture was poured into brine, extracted with CH_2Cl_2, dried, filtered and concentrated. The crude was flash chromatographed on silica gel (30-70% EtOAc/Hexanes) to afford 230 mg of **7f** as a colorless oil [75% two steps, Rf 0.56 (60% EtOAc/hexanes)]. $[\alpha]_D^{18}$ =

+ 17 (*c*=1.5); ^{1}H NMR δ 7.79 (2H, d, *J* = 8.3 Hz), 7.35 (2H, d, *J* = 8.3 Hz), 6.92 (1H, m), 6.50 (1H, d, *J* = 14.9 Hz), 4.14 (4H, m), 3.48 (1H, t, *J* = 7.2 Hz), 3.10 (3H, s), 2.82 (2H, m), 2.42 (3H, s), 1.19 (6H, m); ^{13}C NMR δ 167.7 (C), 145.4 (C), 143.2 (CH), 134.4 (C), 131.5 (CH), 130.2 (CH), 127.6 (CH), 61.8 (CH_2), 49.8 (CH), 45.2 (CH_3), 30.2 (CH_2), 21.5 (CH_3), 13.8 (CH_3); LRMS *m/z* 386 (M^+ - C_2H_5O, 27), 337 (3), 247 (50), 215 (100), 201 (19), 139 (98).

7g: Triflic anhydride (450 mg, 1.60 mmol) was added dropwise to a stirred solution of the crude alkenylsulfoximine **7a** (1.06 mmol) and pyridine (241 mg, 3.05 mmol) in CH_2Cl_2 (12 ml) at 0 ºC. The resultant bright yellow solution was stirred for 10 min at 0 ºC and poured into water (10 ml). The organic layer was extracted with CH_2Cl_2, dried, filtered and concentrated. The crude was flash chromatographed on silica gel (25-40% EtOAc/Hexanes) to afford 334 mg of **7g** as a colorless oil [65% two steps, Rf 0.76 (40% EtOAc/hexanes)]. $[\alpha]_D^{21}$ = +16 (*c*=1.6); ^{1}H NMR δ 7.79 (2H, d, *J* = 8.3 Hz), 7.39 (2H, d, *J* = 8.3 Hz), 7.05 (1H, m), 6.57 (1H, d, *J* = 14.9 Hz), 4.10 (4H, m), 3.52 (1H, t, *J* = 7.2 Hz), 2.86 (2H, m), 2.43 (3H, s), 1.18 (6H, m); ^{13}C NMR δ 168.1 (C), 147.1 (C), 146.0 (CH), 134.0 (C), 131.0 (CH), 130.7 (CH), 127.9 (CH), 62.4 (CH_2), 50.2 (CH), 30.7 (CH_2), 22.0 (CH_3), 14.2 (CH_3); LRMS *m/z* 486 (M^+ +1, 100), 470 (22), 440 (37), 339 (74), 215 (72), 199 (94); HRMS calcd. for $C_{18}H_{23}NO_7$ F_3S_2 486.0868, found 486.0876.

7h: *p*-Tolylsulfonyl chloride (78 mg, 0.41 mmol) was added to a stirred solution of the crude alkenylsulfoximine **7a** (0.34 mmol) in dry pyridine at 0 ºC. After being stirred at rt for 12 h the mixture was concentrated. The crude residue was flash chromatographed on silica gel (15-30% EtOAc/Hexanes) to afford 123 mg of **7h** as a colorless oil [71% two steps, Rf 0.55 (35% EtOAc/hexanes)]. $[\alpha]_D^{21}$ = +1 (*c*=1.6); ^{1}H NMR δ 7.68 (4H, m), 7.21 (2H, d, *J* = 8.3 Hz), 7.12 (2H, d, *J* = 8.1 Hz), 6.78 (1H, m), 6.39 (1H, d, *J* = 14.9 Hz), 4.02 (4H, m), 3.36 (1H, t, *J* = 7.3 Hz), 2.70 (2H, m), 2.31 (3H, s), 2.27 (3H, s), 1.09 (6H, m); ^{13}C NMR δ 168.2 (C), 145.8 (C), 143.6 (CH), 143.1 (C), 142.2 (C), 135.2 (C), 132.1 (CH), 130.6 (CH), 129.6 (CH), 128.2 (CH), 127.0 (CH), 62.3 (CH_2), 50.3 (CH), 30.7 (CH_2), 22.0 (CH_3), 21.9 (CH_3), 14.3 (CH_3); LRMS *m/z* 462 (M^+ - C_2H_5O, 2.08), 434 (0.5), 352 (0.5), 292 (9), 247 (19), 139 (100); HRMS calcd. for $C_{24}H_{29}O_7S_2N$ - C_2H_5O 462.1045, found 462.1040.

General procedure for the synthesis of pyrones 9b-9h (exemplified for substrate **7h**).



b, R = $COCH_3$
c, R = $COCF_3$
d, R = COPh
e, R = CO*p*NO_2Ph
f, R = SO_2CH_3
g, R = SO_2CF_3
h, R = SO_2*p*Tol

A solution of compound **7h** (105 mg, 0.21 mmol) in THF (2ml) was added to an ice-cooled suspension of NaH (8.5 mg, 60% mineral oil, 0.21 mmol) in THF (5ml). After stirring for 20 min at rt a solution of bromide **8** (167 mg, 0.52 mmol) in THF (2ml) was added. The reaction mixture was stirred at rt for 1h and quenched by adding 3 ml of water. The mixture was poured into brine, extracted with Et_2O, dried, filtered and concentrated. The crude was flash chromatographed on silica gel (30-50% EtOAc/hexanes) to afford 142 mg of pyrone **9h** as a colorless oil [91%, Rf 0.10 (30% EtOAc/hexanes)]. $[\alpha]_D^{21}$ = -9 (*c*=1.6); ^{1}H NMR δ 7.81 (4H, m), 7.53 (1H, d, *J* = 5.5 Hz), 7.34 (2H, d, *J* = 8.3 Hz), 7.23 (2H, d, *J* = 8.3 Hz), 6.93 (1H, m), 6.57 (1H, d, *J* = 14.8 Hz), 6.28 (1H, d, *J* = 5.5 Hz), 4.07 (4H, m), 3.44 (2H, s), 2.75 (2H, d, *J* = 7.5 Hz), 2.43 (3H, s), 2.38 (3H,s), 1.16 (6H, m), 0.97 (9H, s), 0.26 (6H); ^{13}C NMR δ 173.7 (C), 169.0 (C), 152.9 (CH), 151.8 (C), 145.2 (C), 144.3 (C), 142.6 (C), 142.0 (CH), 140.7 (C), 134.9 (C), 132.6 (CH), 130.1 (CH), 129.1 (CH), 127.7 (CH), 126.5 (CH), 115.6 (CH), 62.1 (CH_2), 56.2 (C), 35.2 (CH_2), 31.5 (CH_2), 25.9 (CH_3), 21.5 (CH_3), 21.4 (CH_3), 18.7 (C), 13.8 (CH_3), -3.8 (CH_3); LRMS *m/z* 688 (M^+ - C_4H_9, 20.3), 550 (2), 460 (1), 379 (18), 305 (11), 233 (29), 173 (19), 139 (58), 91 (100); HRMS calcd. for $C_{32}H_{38}NO_{10}S_2Si$ 688.1706, found 688.1728.

9b: [77 %, colorless oil, Rf 0.23 (40% EtOAc/hexanes)]. $[\alpha]_D^{18}$ = +5 (*c*=1.3); ^{1}H NMR δ 7.75 (2H, d, *J* = 8.3 Hz), 7.53 (1H, d, *J* = 5.6 Hz), 7.33 (2H, d, *J* = 8.3 Hz), 6.90 (1H, m), 6.45 (1H, d, *J* = 14.9 Hz), 6.29 (1H, d, *J* = 5.6 Hz), 4.12 (4H, m), 3.43 (2H, s), 2.76 (2H, d, *J* = 7.6 Hz), 2.42 (3H, s), 2.12 (3H, s), 1.20 (6H, m), 0.97 (9H, s), 0.26 (6H); ^{13}C NMR δ 179.6 (C), 173.8 (C), 169.1 (C), 169.0 (C), 152.9 (CH), 151.9 (C), 144.3 (C), 141.2 (CH), 135.1 (C), 132.1 (CH), 130.1 (CH), 127.3 (CH), 115.6 (CH), 62.1

(CH_2), 56.3 (C), 35.3 (CH_2), 31.6 (CH_2), 26.7 (CH_3), 25.9 (CH_3), 21.5 (CH_3), 18.7 (C), 13.8 (CH_3), -3.8 (CH_3); LRMS *m/z* 576 (M^+ - C_4H_9, 100), 534 (19), 428 (2), 379 (12), 339 (36), 277 (13), 233 (37), 182 (59), 139 (57), 107 (31); HRMS calcd. for $C_{27}H_{34}NO_9SiS$ 576.1723, found 576.1701.

9c: [93 %, colorless oil, Rf 0.31 (40% EtOAc/Hexanes)]. $[\alpha]_D^{18}$ = -14 (*c*=0.5); ^1H NMR δ 7.80 (2H, d, *J* = 8.4 Hz), 7.55 (1H, d, *J* = 5.5 Hz), 7.41 (2H, d, *J* = 8.2 Hz), 7.15 (1H, m), 6.49 (1H, d, *J* = 14.9 Hz), 6.32 (1H, d, *J* = 5.5 Hz), 4.17 (4H, m), 3.48 (2H, s), 2.81 (2H, d, *J* = 7.5 Hz), 2.47 (3H, s), 1.25 (6H, m), 0.99 (9H, s), 0.28 (6H); ^{13}C NMR δ 173.8 (C), 169.1 (C), 152.9 (CH), 151.9 (C), 145.8 (C), 144.4 (CH), 144.1 (C), 133.1 (C), 130.5 (CH), 130.1 (CH), 129.0 (C), 128.2 (C), 127.4 (CH), 115.7 (CH), 62.3 (CH_2), 56.4 (C), 35.4 (CH_2), 31.9 (CH_2), 26.0 (CH_3), 21.6 (CH_3), 18.8 (C), 13.9 (CH_3), -3.7 (CH_3); LRMS *m/z* 630 (M^+ - C_4H_9, 85), 573 (4), 492 (4), 379 (26), 305 (23), 278 (6), 233 (51), 182 (100), 139 (72), 91 (38); HRMS calcd. for $C_{27}H_{31}NO_9F_3SiS$ 630.1441, found 630.1463.

9d: [78 %, colorless oil, Rf 0.21 (40% EtOAc/hexanes)]. $[\alpha]_D^{18}$ = +5 (*c*=1.5); ^1H NMR δ 8.17 (2H, d, *J* = 8.1 Hz), 7.86 (2H, d, *J* = 8.3 Hz), 7.47 (1H, d, *J* = 5.5 Hz), 7.35-7.45 (5H, m), 7.05 (1H, m), 6.58 (1H, d, *J* = 14.9 Hz), 6.31 (1H, d, *J* = 5.5 Hz), 4.15 (4H, m), 3.45 (2H, s), 2.82 (2H, d, *J* = 7.6 Hz), 2.42 (3H, s), 1.23 (6H, m), 0.99 (9H, s), 0.28 (6H); ^{13}C NMR δ 173.8 (C), 173.6 (C), 169.2 (C), 152.9 (CH), 152.0 (C), 144.0 (C), 141.5 (CH), 135.7 (C), 135.3 (C), 132.3 (CH), 132.0 (CH), 130.2 (CH), 129.4 (CH), 127.9 (CH), 127.5 (CH), 115.7 (CH), 62.2 (CH_2), 56.5 (C), 35.5 (CH_2), 31.7 (CH_2), 26.0 (CH_3), 21.5 (CH_3), 18.8 (C), 13.9 (CH_3), -3.7 (CH_3); LRMS *m/z* 695 (M^+, 3.5), 650 (10), 639 (42), 638 (100), 379 (28), 316 (29), 278 (10), 233 (60), 182 (98), 139 (56), 105 (99), 77 (16); HRMS calcd. for $C_{36}H_{45}NO_9SiS$ 695.2539, found 695.2563

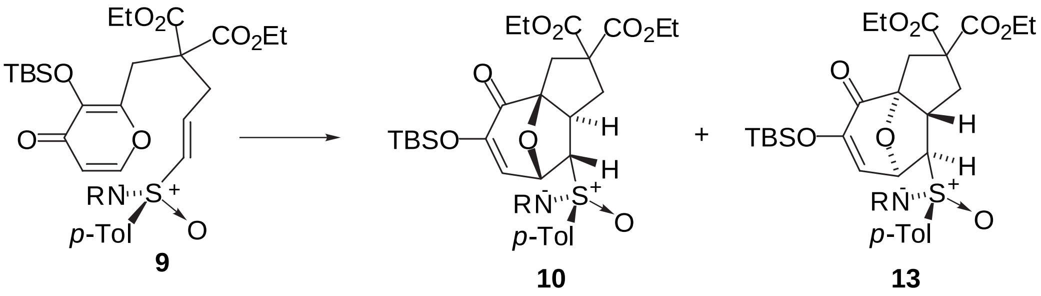
9e: [77 %, colorless oil, Rf 0.27 (40% EtOAc/hexanes)]. $[\alpha]_D^{18}$ = +5 (*c*=0.9); ^1H NMR δ 8.27 (4H, m), 7.84 (2H, d, *J* = 8.3 Hz), 7.56 (1H, d, *J* = 5.5 Hz), 7.40 (2H, d, *J* = 8.2 Hz), 7.15 (1H, m), 6.60 (1H, d, *J* = 14.9 Hz), 6.32 (1H, d, *J* = 5.5 Hz), 4.17 (4H, m), 3.50 (2H, s), 2.84 (2H, d, *J* = 7.6 Hz), 2.46 (3H, s), 1.23 (6H, m), 0.99 (9H, s), 0.28 (6H); ^{13}C NMR δ 173.7 (C), 171.4 (C), 169.1 (C), 152.9 (CH), 151.9 (C), 149.8 (C), 145.0 (C), 144.3 (C), 142.4 (CH), 141.1 (C), 134.6 (C), 131.5 (CH), 130.3 (CH), 128.9 (CH), 127.3 (CH), 123.1 (CH), 115.7 (CH), 62.1 (CH_2), 56.3 (C), 35.4 (CH_2), 31.7 (CH_2), 25.9 (CH_3), 21.5 (CH_3), 18.7 (C), 13.8 (CH_3), -3.8 (CH_3); LRMS *m/z* 683 (M^+ - C_4H_9, 33), 575 (1), 428 (4), 379 (17), 305 (26), 278 (10), 233 (64), 182 (74), 139 (85), 73 (100); HRMS calcd. for $C_{32}H_{35}N_2O_{11}SiS$ 683.1730, found 683.1729.

9f: [80 %, colorless oil, Rf 0.23 (40% EtOAc/hexanes)]. $[\alpha]_D^{18}$ = -5 (*c*=2.2); ^1H NMR δ 7.78 (2H, d, *J* = 8.3 Hz), 7.51 (1H, d, *J* = 5.6 Hz), 7.33 (2H, d, *J* = 8.2 Hz), 6.93 (1H, m), 6.45 (1H, d, *J* = 14.9 Hz), 6.27 (1H, d, *J* = 5.5 Hz), 4.12 (4H, m), 3.41 (2H, s), 3.08

(3H, s), 2.75 (2H, d, *J* = 7.5 Hz), 2.41 (3H, s), 1.21 (6H, m), 0.95 (9H, s), 0.24 (6H); ^{13}C NMR δ 173.7 (C), 168.9 (C), 152.9 (C), 151.8 (CH), 145.4 (C), 144.3 (C), 142.1 (CH), 134.6 (C), 132.5 (CH), 130.2 (CH), 127.7 (CH), 115.6 (CH), 62.1 (CH_2), 56.2 (C), 35.2 (CH_2), 31.4 (CH_2), 25.9 (CH_3), 21.5 (CH_3), 18.7 (C), 14.1 (CH_3), 13.8 (CH_3), -3.8 (CH_3); LRMS *m/z* 612 (M^+ - C_4H_9, 96), 520 (3), 474 (15), 379 (39), 339 (7), 288 (27), 233 (76), 182 (100), 139 (85), 57 (68).

9g: [76%, colorless oil, Rf 0.40 (50% EtOAc/Hexanes)]. $[\alpha]_D^{21}$ = -8 (*c*=2.2); ^{1}H NMR δ 7.81 (2H, d, *J* = 8.3 Hz), 7.54 (1H, d, *J* = 5.5 Hz), 7.42 (2H, d, *J* = 8.4 Hz), 7.10 (1H, m), 6.48 (1H, d, *J* = 14.9 Hz), 6.29 (1H, d, *J* = 5.5 Hz), 4.17 (4H, m), 3.47 (2H, s), 2.79 (2H, d, *J* = 6.5 Hz), 2.46 (3H, s), 1.22 (6H, m), 0.98 (9H, s), 0.26 (6H); ^{13}C NMR δ 174.2 (C), 169.4 (C), 153.5 (CH), 152.2 (C), 147.0 (C), 144.9 (CH), 144.8 (C), 134.2 (C), 131.4 (CH), 131.1 (CH), 128.0 (CH), 120.1 (CF_3), 116.1 (CH), 62.8 (CH_2), 56.7 (C), 35.7 (CH_2), 32.2 (CH_2), 26.4 (CH_3), 22.4 (CH_3), 19.2 (C), 14.2 (CH_3), -3.3 (CH_3); LRMS *m/z* 666 (M^+ - C_4H_9, 9.6), 577 (1), 528 (2), 379 (11), 305 (11), 278 (79), 231 (21), 182 (59), 139 (100), 91 (74); HRMS calcd. for $C_{26}H_{31}NO_{10}F_3SiS_2$ 666.1111, found 666.1131.

General procedure for the thermal cycloadditions (exemplified for substrate **9h**).



a, R = H
b, R = COCH$_3$
c, R = COCF$_3$
d, R = COPh
e, R = CO*p*NO$_2$Ph
f, R = SO$_2$CH$_3$
g, R = SO$_2$CF$_3$
h, R = SO$_2$*p*Tol

A solution of pyrone **9h** (130 mg, 0.17 mmol) in toluene (7 ml) was heated under reflux for 1 h. The solvent was evaporated and the crude purified by flash chromatography (20-30% EtOAc/hexanes) to afford a 90:10 ratio of an inseparable mixture of diastereoisomers **10h** and **13h** as a colorless oil [88%, Rf 0.62 (30% EtOAc/hexanes)]. $[\alpha]_D^{21}$ = -170 (*c*=0.6). The diastereomeric ratio was determined integrating the signals of the H-7 (t) of the two isomers in the ^{1}H NMR spectrum of the crude reaction mixture.

10h: ^{1}H NMR δ 7.87 (2H, d, *J* = 8.2 Hz), 7.79 (2H, d, *J* = 8.2 Hz), 7.43 (2H, d, *J* = 8.2 Hz), 7.24 (2H, d, *J* = 8.1 Hz), 5.98 (1H, d, *J* = 4.8 Hz), 5.16 (1H, t, *J* = 5.2 Hz), 4.44 (1H, t, *J* = 6.1 Hz), 4.11 (4H, m), 2.97 (1H, d, *J* = 14.9 Hz), 2.73 (1H, m), 2.48 (3H, s), 2.45 (1H, m), 2.40 (3H, s), 1.69 (2H, m), 1.18 (6H, m), 0.91 (9H, s), 0.07 (3H, s), 0.06 (3H, s); ^{13}C NMR δ 191.0 (C), 170.7 (C), 169.7 (C), 147.1 (C), 146.0 (C), 142.8 (C), 140.7 (C), 134.2 (C), 130.8 (CH), 129.3 (CH), 128.1 (CH), 126.5 (CH), 122.5 (CH), 97.9 (C), 75.4 (CH), 73.1 (CH), 62.0 (CH$_2$), 61.0 (C), 44.0 (CH), 36.8 (CH$_2$), 35.7 (CH$_2$), 25.4 (CH$_3$), 21.7 (CH$_3$), 21.5 (CH$_3$), 18.1 (C), 13.9 (CH$_3$), 1.0 (CH$_3$), -4.9 (CH$_3$); LRMS *m/z* 688 (M$^+$ - C$_4$H$_9$, 30.4), 379 (30), 333 (12), 305 (19), 233 (38), 205 (27), 182 (36), 173 (14), 139 (64), 91 (100); HRMS calcd. for C$_{32}$H$_{38}$NO$_{10}$S$_2$Si 688.1706, found 688.1720.

The cycloaddition of **9a** affords a 50:50 mixture of diastereoisomers **10a** and **13a** as colorless oils [86%, Rfs (40% EtOAc/Hexanes): **10a**=0.48, **13a**=0.54]. The diastereomeric ratio was determined integrating the signals of the vinylic hydrogen of the two isomers in the ^{1}H NMR spectrum of the crude reaction mixture.

10a: $[\alpha]_D^{18}$ = -67 (*c*=0.45); ^{1}H NMR δ 7.81 (2H, d, *J* = 8.3 Hz), 7.34 (2H, d, *J* = 8.3 Hz), 6.50 (1H, d, *J* = 4.9 Hz), 5.13 (1H, m), 4.23 (1H, m), 4.13 (4H, m), 3.01 (1H, d, *J* = 14.9 Hz), 2.89 (1H, m), 2.49 (1H, m), 2.43 (3H, s), 2.25 (1H, m), 1.81 (1H, m), 1.23 (6H, m), 0.97 (9H, s), 0.23 (6H, s); LRMS *m/z* 591 (M$^+$, 33.0), 534 (76), 381 (7), 339

(85), 204 (54), 139 (100), 91 (27); HRMS calcd. for $C_{29}H_{41}NO_8SiS$ 591.2322, found 591.2329.

13a: $[\alpha]_D^{18}$ = 38 (*c*=0.35); ^1H NMR δ 7.85 (2H, d, *J* = 8.3 Hz), 7.37 (2H, d, *J* = 8.3 Hz), 6.40 (1H, d, *J* = 4.9 Hz), 4.93 (1H, m), 4.25 (1H, m), 4.15 (4H, m), 3.09 (1H, d, *J* = 14.9 Hz), 3.04 (1H, m), 2.51 (1H, m), 2.47 (3H, s), 2.15 (1H, m), 2.03 (1H, m), 1.23 (6H, m), 0.97 (9H, s), 0.23 (6H, s).

The cycloaddition of **9b** affords a 65:35 mixture of diastereoisomers **10b** and **13b** as a colorless oil [86%, Rf 0.23 (30% EtOAc/Hexanes)]. $[\alpha]_D^{18}$ = -31 (*c*=1.1). The diastereomeric ratio was determined integrating the signals of the vinylic hydrogen of the two isomers in the ^1H NMR spectrum of the crude reaction mixture.

10b: ^1H NMR δ 7.76 (2H, d, *J* = 8.3 Hz), 7.39 (2H, d, *J* = 8.1 Hz), 6.49 (1H, d, *J* = 4.9 Hz), 5.22 (1H, m), 4.32 (1H, m), 4.06 (4H, m), 3.02 (1H, d, *J* = 15.0 Hz), 2.85 (1H, m), 2.51 (1H, m), 2.46 (3H, s), 2.17 (3H, s), 1.65 (2H, m), 1.23 (6H, m), 0.94 (9H, s), 0.19 (3H, s); ^{13}C NMR δ 191.3 (C), 179.8 (C), 171.1 (C), 171.0 (C), 146.9 (C), 145.0 (C), 134.1 (C), 130.7 (CH), 127.5 (CH), 124.0 (CH), 97.6 (C), 75.9 (CH), 72.5 (CH), 62.0 (CH_2), 61.0 (C), 44.5 (CH), 36.8 (CH_2), 35.8 (CH_2), 26.6 (CH_3), 25.5 (CH_3), 21.6 (CH_3), 18.3 (C), 13.8 (CH_3), -4.7 (CH_3); LRMS *m/z* 576 (M^+ - C_4H_9, 100), 534 (39), 516 (7), 428 (3), 379 (16), 339 (39), 305 (30), 277 (25), 233 (76), 182 (68), 139 (88), 107 (45); HRMS calcd. for $C_{27}H_{34}NO_9SiS$ 576.1723, found 576.1729.

The cycloaddition of **9c** affords a 86:14 mixture of diastereoisomers **10c** and **13c** as colorless oils [85%, Rfs (30% EtOAc/Hexanes): **10c**=0.60, **13c**=0.54]. The diastereomeric ratio was determined integrating the signals of the the H-7 (t) of the two isomers in the ^1H NMR spectrum of the crude reaction mixture.

10c: $[\alpha]_D^{18}$ = -115 (*c*=2.5); ^1H NMR δ 7.78 (2H, d, *J* = 8.3 Hz), 7.47 (2H, d, *J* = 8.2 Hz), 6.42 (1H, d, *J* = 4.9 Hz), 5.27 (1H, t, *J* = 5.2 Hz), 4.42 (1H, t, *J* = 6.3 Hz), 4.12 (4H, m), 3.05 (1H, d, *J* = 15.0 Hz), 2.87 (1H, m), 2.49 (1H, m), 2.48 (3H, s), 1.77 (2H, m), 1.26 (6H, m), 0.96 (9H, s), 0.20 (3H, s); ^{13}C NMR δ 190.9 (C), 171.1 (C), 169.7 (C), 164.1 (C), 147.3 (C), 146.5 (C), 131.8 (C), 131.2 (CH), 127.4 (CH), 122.8 (CH), 117.1 (C), 97.9 (C), 75.8 (CH), 72.8 (CH), 62.1 (CH_2), 61.1 (C), 44.1 (CH), 36.9 (CH_2), 35.8 (CH_2), 25.5 (CH_3), 21.8 (CH_3), 18.3 (C), 13.9 (CH_3), -4.8 (CH_3); LRMS *m/z* 630 (M^+ - C_4H_9, 91), 612 (7), 492 (13), 399 (3), 379 (51), 305 (48), 277 (26), 259 (15), 233 (99), 182 (89), 139 (92), 91 (48), 73 (100); HRMS calcd. for $C_{27}H_{31}NO_9F_3SiS$ 630.1441, found 630.1434.

13c: $[\alpha]_D^{18}$ = +65 (*c*=0.50); ^1H NMR δ 7.78 (2H, d, *J* = 8.3 Hz), 7.47 (2H, d, *J* = 8.2 Hz), 6.07 (1H, d, *J* = 4.9 Hz), 4.59 (1H, t, *J* = 5.2 Hz), 4.44 (1H, m), 4.12 (4H, m), 3.27

(1H, m), 3.11 (1H, d, *J* = 15.0 Hz), 2.57 (1H, m), 2.48 (3H, s), 2.18 (2H, m), 1.26 (6H, m), 0.96 (9H, s), 0.20 (3H, s).

The cycloaddition of **9d** affords a 76:24 mixture of diastereoisomers **10d** and **13d** as colorless oils [95%, Rfs (30% EtOAc/Hexanes): **10d**=0.62, **13d**=0.58]. The diastereomeric ratio was determined integrating the signals of the the H-7 (t) of the two isomers in the ^{1}H NMR spectrum of the crude reaction mixture.

10d: $[\alpha]_D^{18}$ = -106 (*c*=1.5); ^{1}H NMR δ 8.15 (2H, d, *J* = 8.0 Hz), 7.83 (2H, d, *J* = 8.1 Hz), 7.47 (5H, m), 6.56 (1H, d, *J* = 4.9 Hz), 5.38 (1H, t, *J* = 5.3 Hz), 4.41 (1H, t, *J* = 6.3 Hz), 4.15 (4H, m), 3.07 (1H, d, *J* = 15.0 Hz), 2.93 (1H, m), 2.51 (1H, d, *J* = 15.0 Hz), 2.45 (3H, s), 1.79 (2H, m), 1.24 (6H, m), 0.95 (9H, s), 0.20 (3H, s); ^{13}C NMR δ 191.4 (C), 173.8 (C), 171.1 (C), 169.9 (C), 147.0 (C), 145.1 (C), 135.3 (C), 134.1 (C), 132.3 (CH), 130.8 (CH), 129.4 (CH), 128.1 (CH), 127.5 (CH), 123.8 (CH), 97.8 (C), 76.0 (CH), 72.8 (CH), 62.0 (CH_2), 61.1 (C), 44.4 (CH), 36.9 (CH_2), 36.0 (CH_2), 25.5 (CH_3), 21.7 (CH_3), 18.3 (C), 13.9 (CH_3), -4.7 (CH_3); LRMS *m/z* 638 (M^+ - C_4H_9, 84), 379 (20), 316 (53), 278 (12), 233 (68), 182 (59), 139 (51), 105 (100), 77 (11); HRMS calcd. for $C_{32}H_{36}NO_9SiS$ 638.1880, found 638.1870.

13d: $[\alpha]_D^{18}$ = +94 (*c*=0.5); ^{1}H NMR δ 8.06 (2H, d, *J* = 8.3 Hz), 7.80 (2H, d, *J* = 8.2 Hz), 7.42 (5H, m), 6.28 (1H, d, *J* = 4.9 Hz), 4.79 (1H, t, *J* = 5.3 Hz), 4.41 (1H, t, *J* = 6.3 Hz), 4.15 (4H, m), 3.32 (1H, m), 3.17 (1H, d, *J* = 15.0 Hz), 2.48 (1H, d, *J* = 14.7 Hz), 2.46 (3H, s), 2.25 (2H, m), 1.26 (6H, m), 0.95 (9H, s), 0.23 (3H, s).

The cycloaddition of **9e** affords a 58:42 mixture of diastereoisomers **10e** and **13e** as colorless oils [91%, Rfs (40% EtOAc/Hexanes): **10e**=0.70, **13e**=0.65]. The diastereomeric ratio was determined integrating the signals of the vinylic hydrogen of the two isomers in the ^{1}H NMR spectrum of the crude reaction mixture.

10e: $[\alpha]_D^{18}$ = -108 (*c*=3.5); ^{1}H NMR δ 8.23 (4H, m), 7.79 (2H, d, *J* = 8.3 Hz), 7.43 (2H, d, *J* = 8.2 Hz), 6.50 (1H, d, *J* = 4.9 Hz), 5.36 (1H, t, *J* = 5.3 Hz), 4.47 (1H, t, *J* = 6.5 Hz), 4.16 (4H, m), 3.06 (1H, d, *J* = 15.0 Hz), 2.91 (1H, m), 2.50 (1H, d, *J* = 15.2 Hz), 2.46 (3H, s), 1.78 (2H, m), 1.22 (6H, m), 0.94 (9H, s), 0.19 (3H, s); ^{13}C NMR δ 191.1 (C), 171.7 (C), 171.1 (C), 169.7 (C), 150.1 (C), 147.2 (C), 145.6 (C), 140.7 (C), 133.4 (C), 130.9 (CH), 130.4 (CH), 127.4 (CH), 123.4 (CH), 123.3 (CH), 97.7 (C), 76.0 (CH), 72.8 (CH), 62.0 (CH_2), 61.1 (C), 44.5 (CH), 36.9 (CH_2), 35.9 (CH_2), 25.5 (CH_3), 21.7 (CH_3), 18.3 (C), 13.9 (CH_3), -4.7 (CH_3); LRMS *m/z* 683 (M^+ - C_4H_9, 98), 525 (1), 428 (6), 396 (11), 380 (17), 379 (31), 305 (46), 277 (28), 233 (80), 182 (67), 150 (70), 57 (100); HRMS calcd. for $C_{32}H_{35}N_2O_{11}SiS$ 683.1730, found 683.1737.

13e: $[\alpha]_D^{18}$ = +82 (*c*=3.2); ^{1}H NMR δ 8.27 (4H, s), 7.81 (2H, d, *J* = 8.3 Hz), 7.44 (2H, d, *J* = 8.2 Hz), 6.23 (1H, d, *J* = 5.0 Hz), 4.80 (1H, t, *J* = 5.2 Hz), 4.46 (1H, t, *J* = 6.1 Hz), 4.25 (4H, m), 3.35 (1H, m), 3.17 (1H, d, *J* = 15.0 Hz), 2.54 (1H, d, *J* = 16.1 Hz), 2.47 (3H, s), 2.26 (2H, m), 1.26 (6H, m), 0.94 (9H, s), 0.24 (3H, s).

The cycloaddition of **9f** affords a 77:23 mixture of diastereoisomers **10f** and **13f** as a colorless oil [88%, Rf 0.41 (40% EtOAc/Hexanes)]. $[\alpha]_D^{21}$ = -95 (*c*=1.1). The diastereomeric ratio was determined integrating the signals of the vinylic hydrogen of the two isomers in the ^{1}H NMR spectrum of the crude reaction mixture.

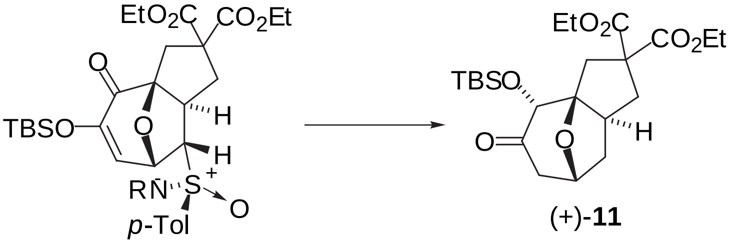
10f: ^{1}H NMR δ 7.86 (2H, d, *J* = 8.3 Hz), 7.43 (2H, d, *J* = 8.2 Hz), 6.38 (1H, d, *J* = 4.9 Hz), 5.23 (1H, t, *J* = 5.2 Hz), 4.45 (1H, m), 4.14 (4H, m), 3.08 (3H, s), 3.05 (1H, m), 2.78 (1H, m), 2.47 (3H, s), 2.44 (1H, m), 1.72 (2H, m), 1.20 (6H, m), 0.95 (9H, s), 0.19 (3H, s), 0.18 (3H, s). ^{13}C NMR δ 191.4 (C), 171.3 (C), 170.2 (C), 147.8 (C), 146.7 (C), 134.1 (C), 131.3 (CH), 128.7 (CH), 122.9 (CH), 98.4 (C), 75.7 (CH), 74.9 (CH), 62.5 (CH_2), 61.6 (C), 45.5 (CH), 37.2 (CH_2), 36.2 (CH_2), 25.9 (CH_3), 22.2 (CH_3), 18.7 (C), 14.4 (CH_3), 14.1 (CH_3), -4.4 (CH_3), -4.9 (CH_3); LRMS *m/z* 612 (M^+ - C_4H_9, 100), 520 (7), 474 (26), 379 (79), 339 (8), 288 (38), 233 (97), 182 (46), 139 (60), 57 (99).

The cycloaddition of **9g** affords a 87:13 mixture of diastereoisomers **10g** and **13g** as colorless oils [80%, Rfs (30% EtOAc/hexanes): **10g**=0.65, **13g**=0.58]. The diastereomeric ratio was determined integrating the signals of the vinylic hydrogen of the two isomers in the ^{1}H NMR spectrum of the crude reaction mixture.

10g: $[\alpha]_D^{21}$ = -123 (*c*=1.0); ^{1}H NMR δ 7.90 (2H, d, *J* = 8.4 Hz), 7.52 (2H, d, *J* = 8.2 Hz), 6.35 (1H, d, *J* = 4.9 Hz), 5.24 (1H, t, *J* = 5.2 Hz), 4.57 (1H, m), 4.12 (4H, m), 3.03 (1H, d, *J* = 15.0 Hz), 2.83 (1H, m), 2.52 (3H, s), 2.46 (1H, m), 1.75 (2H, m), 1.21 (6H, m), 0.97 (9H, s), 0.24 (3H, s), 0.20 (3H, s); ^{13}C NMR δ 190.7 (C), 170.9 (C), 169.5 (C), 147.6 (C), 147.4 (C), 133.1 (C), 131.2 (CH), 127.8 (CH), 121.5 (CH), 98.2 (C), 75.4 (CH), 73.7 (CH), 62.2 (CH_2), 61.0 (C), 44.0 (CH), 36.8 (CH_2), 35.6 (CH_2), 25.4 (CH_3), 21.9 (CH_3), 18.2 (C), 13.8 (CH_3), -4.8 (CH_3), -4.9 (CH_3); LRMS *m/z* 666 (M^+ - C_4H_9, 44.9), 648 (1), 528 (8), 380 (12) 379 (31), 305 (25), 278 (6), 233 (65), 182 (78), 139 (67), 73 (100); HRMS calcd. for $C_{26}H_{31}NO_{10}F_3SiS_2$ 666.1111, found 666.1117.

13g: $[\alpha]_D^{18}$ = +80 (*c*=0.50); ^{1}H NMR δ 7.90 (2H, d, *J* = 8.4 Hz), 7.52 (2H, d, *J* = 8.2 Hz), 6.07 (1H, d, *J* = 4.9 Hz), 4.67 (1H, t, *J* = 5.2 Hz), 4.57 (1H, m), 4.12 (4H, m), 3.20 (1H, m), 3.12 (1H, d, *J* = 15.0 Hz), 2.59 (1H, m), 2.52 (3H, s), 2.20 (2H, m), 1.21 (6H, m), 0.97 (9H, s), 0.24 (3H, s), 0.20 (3H, s).

General procedure for the desulfurization of cycloadducts 10. (exemplified for **10c**).



10

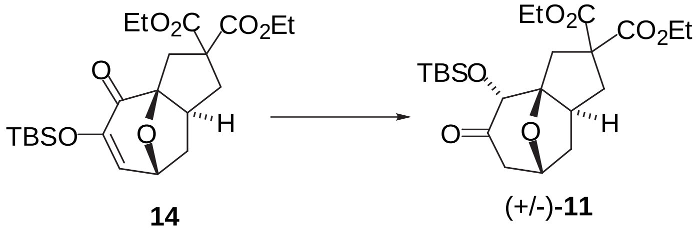
(+)-11

b, R = $COCH_3$
c, R = $COCF_3$
d, R = COPh
e, R = CO*p*NO_2Ph
f, R = SO_2CH_3
g, R = SO_2CF_3
h, R = SO_2*p*Tol

A solution of compound **10c** (60 mg, 0.14 mmol) in THF (2 mL) was added to a suspension of activated Raney nickel (1.2 g) in THF (8 mL). The reaction mixture was refluxed for 2 h, allowed to come to rt, filtered, and poured into water. Extraction with Et_2O, drying and concentration gave a residue which was purified by flash chromatography (3-20% EtOAc/hexanes) to afford 29 mg of **(+)-11** [76%, ≥ 96% ee, Rf 0.23 (15% EtOAc/hexanes), colorless oil]. Enantiomeric excess was determined by ^1H NMR in presence of $Eu(hfc)_3$ (0.3 equiv) by comparation of the split signals of the TBS methyl protons with those of racemic **11**. $[\alpha]_D^{18} = +19$ (c=1.1); ^1H NMR δ 4.39 (1H, d, J = 6.1 Hz), 4.02 (5H, m), 2.63 (1H, d, J = 14.0 Hz), 2.51 (3H, m), 2.28 (1H, d, J = 13.7 Hz), 2.12 (1H, d, J = 15.2 Hz), 2.01 (2H, m), 1.84 (1H, m), 1.12 (6H, m), 0.80 (9H, s), 0.00 (3H, s), -0.11 (3H, s); ^{13}C NMR δ 205.1 (C), 171.1 (C), 95.7 (C), 78.0 (CH), 76.0 (CH), 61.4 (CH_2), 61.2 (CH_2), 48.2 (CH_2), 41.0 (CH_2), 40.6 (CH), 39.5 (CH_2), 39.3 (CH_2), 25.6 (CH_3), 18.3 (C), 13.8 (CH_3), -4.4 (CH_3), -5.8 (CH_3); LRMS m/z 383 (M^+ - C_4H_9, 100), 365 (21), 355 (14), 339 (12), 337 (14), 291 (30), 263 (14), 235 (6), 155 (16), 129 (6), 139 (88), 57 (4); HRMS calcd. for $C_{18}H_{27}O_7Si$ 383.1526, found 383.1535.

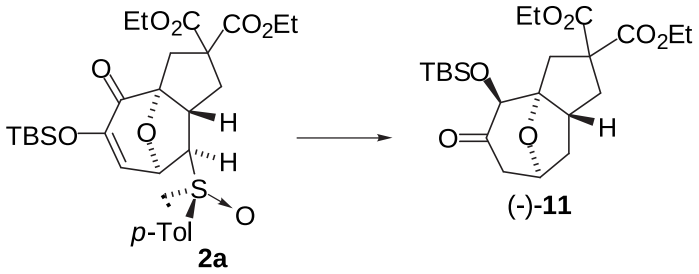
The desulfurization of the other sulfoximines **10** was achieved in similar yields (71-83%) using the same conditions. In the case of the *N*-acetyl, Mesyl and Tosyl derivatives the desulfurization was carried out on the mixture of the cycloadduct **10** and the diastereoisomers **13**, thereby yielding **11** with smaller optical rotation.

Synthesis of (±)-11 by desulfurization of (±)-14.



A solution of the racemic compound **14**[1] (150 mg, 0.34 mmol) in THF (2 mL) was added to a suspension of activated Raney nickel (2.2 g) in THF (12 mL). The reaction mixture was refluxed for 2 h, allowed to come to rt, filtered, and poured into water. Extraction with Et_2O, drying and concentration gave a residue which was purified by flash chromatography (3-20% EtOAc/hexanes) to afford 107 mg of **(±)-11** [72 %, Rf 0.23 (15% EtOAc/hexanes), colorless oil].

Synthesis of (-)-11 by desulfurization of 2a.



A solution of compound **2a** (60 mg, 0.10 mmol) in THF (2 mL) was added to a suspension of activated Raney nickel (1.0 g) in THF (12 mL). The reaction mixture was refluxed for 1 h, allowed to come to rt, filtered, and poured into water. Extraction with Et_2O, drying and concentration gave a residue which was purified by flash chromatography (3-20% EtOAc/hexanes) to afford 107 mg of **(-)-11**. $[\alpha]_D^{18}$ = -19 (c=1.2); [66 %, Rf 0.23 (15% EtOAc/hexanes), colorless oil].