Preparative Bioorganic Chemistry; XIV.[1] Preparation of (2*S*,3*S*)-1-Phenylthio-2,3-pentanediol and (2*S*,3*S*)-1-Phenylsulfonyl-2,3-pentanediol by Yeast Reduction of the Corresponding Diketones, and Conversion of the Former to (+)-*endo*-Brevicomin

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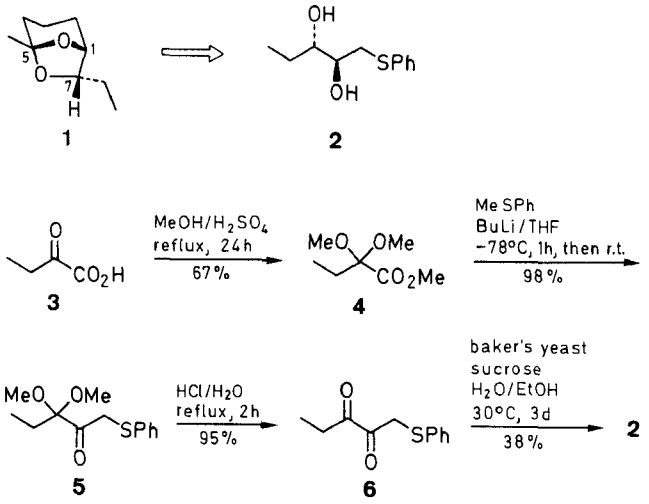
(2*S*,3*S*)-1-Phenylthio-2,3-pentanediol (**2**) and (2*S*,3*S*)-1-phenylsulfonyl-2,3-pentanediol (**16**) were prepared by reducing the corresponding diketones, **6** and **15**, with baker's yeast. Conversion of **2** to (3*S*,4*R*)-8-nonene-3,4-diol (**13**), the key intermediate for the synthesis of (+)-*endo*-brevicomin [*endo*-7-ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]octane, (1*R*,5*S*,7*S*)-**1**], is also described.

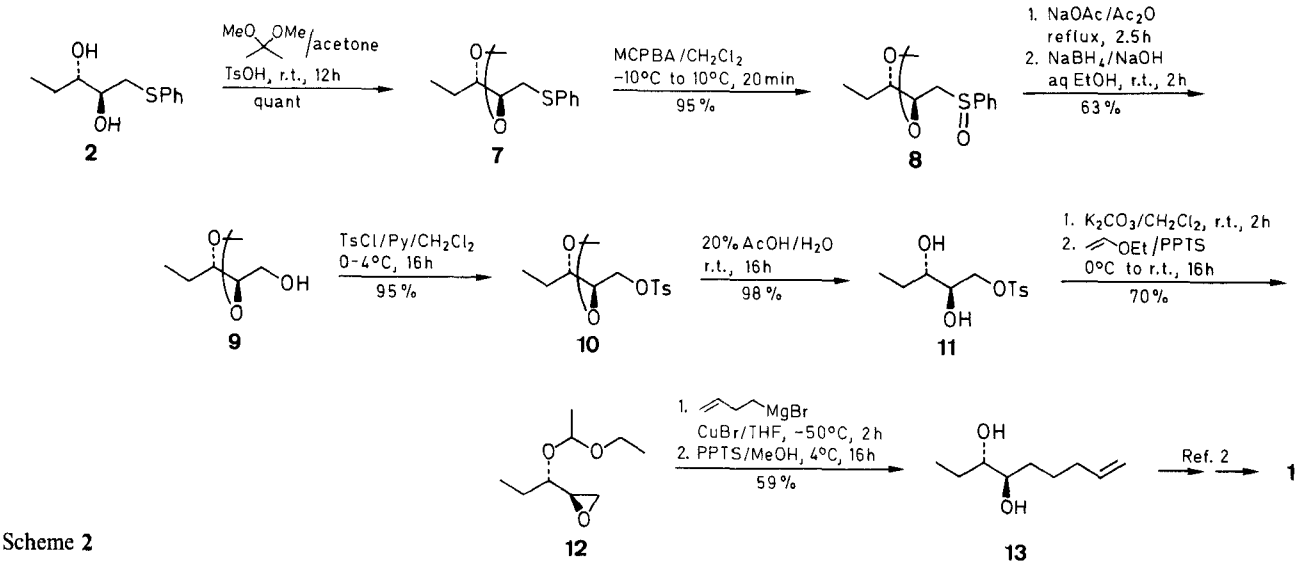
(+)-*endo*-Brevicomin (*endo*-7-ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]octane [(1*R*,5*S*,7*S*)-**1**]) is the pheromone of the bark beetles, *Dendroctonus frontalis* and *Dryocetes autographus*. Its enantioselective synthesis was previously reported by us by means of the Sharpless asymmetric epoxidation as the key step.[2] It occurred to us that a diol like **2** might be a useful building block for the synthesis of **1**. The diol **2** seemed readily available by reducing the corresponding diketone with baker's yeast.[3] There is a report by Fujisawa et al. on the similar reduction of a diketone with baker's yeast.[4]



Scheme 1

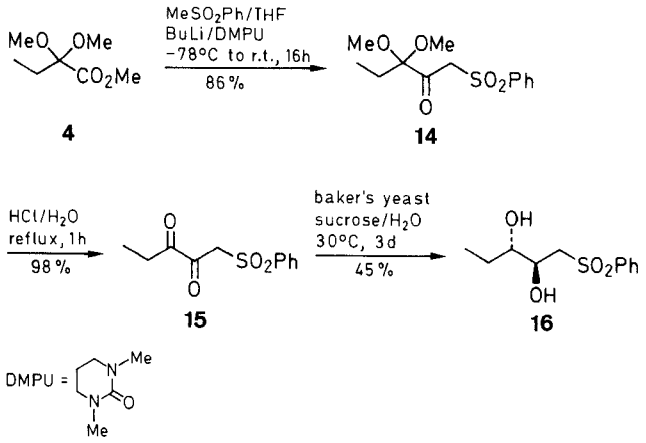
2-Oxobutanoic acid (**3**) was treated with methanol and sulfuric acid to give **4**. (Scheme **1**). Addition of the anion derived from thioanisole[5] to **4** yielded **5**, acid hydrolysis of which furnished the desired but unstable diketone **6**. Reduction of **6** with baker's yeast gave crude **2** in 64% yield, which was recrystallized to afford pure **2** in 38% yield from **6**. The absolute configuration of **2** was deduced to be 2*S*, 3*S* by its later conversion to the known (3*S*,4*R*)-**13**.[2]

Conversion of **2** to **13** was carried out as shown in Scheme **2**. The diol **2** gave acetonide **7** upon treatment with acetone and 2,2-dimethoxypropane in the presence of *p*-toluenesulfonic acid. Oxidation of **7** with 3-chloroperoxybenzoic acid furnished sulfoxide **8** as a diastereoisomeric mixture. This was submitted to the Pummerer rearrangement followed by reduction with sodium borohydride to give alcohol **9**, which was tosylated in the usual manner to furnish **10**. The acetonide protective group of **10** was removed to give a triol monotosylate **11**. Potassium carbonate converted it to an epoxy alcohol, whose hydroxy group was protected as 1-ethoxyethyl ether **12**. Treatment of **12** with 3-butenylmagnesium bromide in the presence of copper(I) bromide effected the coupling, and the 1-ethoxyethyl protective group of the product was removed to afford (3*S*,4*R*)-**13**. This was identical with an authentic sample of **13** on the basis of the IR and ^{1}H-NMR comparison.[2] The enantiomeric purity of **13** was estimated to be 99.7% by the HPLC analysis of the corresponding bis-(*R*)-MTPA [α-methoxy-α-(trifluoromethyl)phenylacetic acid] ester.[6] Conversion of **13** to (+)-*endo*-brevicomin (**1**) is a known process.[2]



Scheme 2

In a similar fashion, a sulfone **15** was prepared from **4** via **14**. (Scheme **3**). Reduction of **15** with baker's yeast gave crude (2*S*,3*S*)-diol **16**. After recrystallization, pure **16** could be secured. The absolute configuration of **16** was determined by its derivation from **2** through oxidation with 3-chloroperoxybenzoic acid. Diol **16** may also serve as a useful chiral building block. In conclusion, (2*S*,3*S*)-diols **2** and **16** were obtained by the yeast reduction of **6** and **15**, respectively.



Scheme 3

All boiling and melting points are uncorrected. ^{1}H-NMR spectra were recorded on Jeol JNM EX-90 or Jeol JNM FX-100 spectrometer using TMS as an internal standard. IR spectra were recorded on Jasco A-102 spectrometer. Optical rotations were measured on Jasco DIP 140 polarimeter. Column chromatography was carried out on columns packed with Merck Kieselgel 60, Art. 7734.

Methyl 2,2-Dimethoxybutanoate (4):
A mixture of **3** (13.2 g, 129 mmol) and H_2SO_4 (2 mL) in MeOH (700 mL) is heated under reflux for 24 h. Then $NaHCO_3$ (7.6 g) is added, and the mixture is stirred for a few minutes. The mixture is filtered and concentrated *in vacuo*. The residue is distilled to give **4**; yield: 14.0 g (67%); bp 81–82°C/20 Torr; n_D^{16} 1.4169.

$C_7H_{14}O_4$ (162.2) calc. C 51.84 H 8.70 found 51.68 8.61

IR (film): ν = 1750, 1130, 1050 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.80 (t, 3H, J = 7.0 Hz, 4-H), 1.88 (q, 2H, J = 7.0 Hz, 3-H), 3.10 (s, 6H, OCH_3), 3.35 (s, 3H, CO_2CH_3).

3,3-Dimethoxy-1-phenylthio-2-pentanone (5):
To a solution of **4** (10.0 g, 61.7 mmol) in dry THF (180 mL) is added dropwise a solution of $PhSCH_2Li$ (185 mmol) in dry THF (180 mL), which is prepared by Corey's method[5] at −78°C under Argon. After stirring for 1 h, the temperature is allowed to rise gradually to r.t. The mixture is poured into sat. aq NH_4Cl (200 mL) and extracted with Et_2O (3 × 300 mL). The ether solution is washed with sat. aq $NaHCO_3$ (150 mL), brine (150 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The residue is chromatographed on silica gel (600 g). Elution with hexane/EtOAc (25:1) affords **5**. An analytical sample is obtained by distillation; yield: 15.4 g (98%); bp 157–158°C/6 Torr; $n_D^{17.5}$ 1.5369.

$C_{13}H_{18}O_3S$ (254.3) calc. C 61.39 H 7.13 found 61.18 7.04

IR (film): ν = 3080, 3000, 1735, 1585, 1050 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.75 (t, 3H, J = 6.0 Hz, 5-H), 1.83 (q, 2H, J = 6.0 Hz, 4-H), 3.22 (s, 6H, OCH_3), 4.03 (s, 2H, 1-H), 7.15–7.60 (m, 5 H_{arom}).

1-Phenylthio-2,3-pentanedione (6):
A mixture of **5** (6.24 g, 24.6 mmol) and 6N aq HCl (5 mL) in H_2O (150 mL) is stirred and heated under reflux for 2 h. Then it is cooled to r.t. and extracted with Et_2O (4 × 200 mL). The ether solution is washed with H_2O (150 mL), sat. aq $NaHCO_3$ (150 mL), brine (150 mL), dried ($MgSO_4$), and concentrated *in vacuo* to give **6**; yield 12.5 g (95%). This is used for the next reaction without purification.

IR (film): ν = 3400, 1720, 1705, 1650, 1370 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.10, 1.18 (each t, 3H, J = 7.2 Hz, 5-H), 2.68, 2.77 (each q, 2H, J = 7.2 Hz, 4-H), 4.00 (s, 1.1H, 1-H), 6.71 (m, 0.45H, 1-H enol form), 7.15–7.60 (m, 5 H_{arom}).

(2*S*,3*S*)-1-Phenylthio-2,3-pentanediol (2):
To a stirred solution of sucrose (80 g) in H_2O (1 L) is added baker's yeast (80 g) and the suspension is stirred for 30 min at 30°C. Then an EtOH (50 mL) solution of **6** [prepared from 6.24 g (24.6 mmol) of **5**] is added. After 30 h, baker's yeast (40 g) and sucrose (40 g) are added to the mixture. The mixture is stirred at 30°C for 2 days. EtOAc (200 mL) and CH_2Cl_2 (200 mL) are then added to the mixture, which is filtered through a Celite pad. The filtrate is saturated with NaCl, and extracted with EtOAc (7 × 1 L). The extract is washed with sat. aq $NaHCO_3$ (1 L), brine (1 L), dried ($MgSO_4$), and concentrated *in vacuo*. The residue is chromatographed on silica gel (300 g). Elution with hexane/EtOAc (20:1) affords 2.32 g of **2** and half-reduced material (1.7 g). The latter is reduced again in the same manner as described above giving 3.34 g (64%) of **2** in sum total. This is recrystallized four times from *i*-Pr_2O to give **2** as white plates; yield: 2.00 g (38.4%); mp 92–93°C; $[\alpha]_D^{22}$ + 56.8° (c = 0.97, $CHCl_3$).

$C_{11}H_{16}O_2S$ (212.3) calc. C 62.23 H 7.60 found 62.63 7.69

IR (KBr): ν = 3250, 1580, 1070, 665 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.99 (t, 3H, J = 7.2 Hz, 5-H), 1.30–1.65 (m, 2H, 4-H), 2.95 (dd, 1H, J = 9.0, 14.5 Hz, 1-H) 3.26 (dd, 1H, J = 4.5, 14.5 Hz, 1-H), 3.42–3.80 (m, 2H, 2, 3-H), 7.15–7.70 (m, 5 H_{arom}).

(2*S*,3*S*)-1-Phenylthio-2,3-(isopropylidenedioxy)pentane (7):
A mixture of **2** (1.90 g, 9.00 mmol), 2,2-dimethoxypropane (50 mL) and a catalytic amount of TsOH · H_2O in acetone (50 mL) is stirred at r.t. for 12 h. Et_2O (50 mL) is added to the mixture, which is neutralized with $NaHCO_3$. After filtration, the filtrate is concentrated *in vacuo*, and the residue is chromatographed on silica gel (60 g). Elution with hexane/EtOAc (40:1) affords **7**; yield: quantitative; $[\alpha]_D^{22}$ + 9.64° (c = 1.12, $CHCl_3$); n_D^{22} 1.5279.

$C_{14}H_{20}O_2S$ (252.4) calc. C 66.63 H 7.99 found 66.57 7.96

IR (film): ν = 1375, 1365, 1220, 1165, 1090, 1040 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.03 (t, 3H, J = 7.4 Hz, 5-H), 1.20–1.80 (m, 2H, 4-H), 1.35 (s, 3H, CH_3C), 1.45 (s, 3H, CH_3C), 2.95 (dd, 1H, J = 6.4, 13.0 Hz, 1-H), 3.08 (dd, 1H, J = 6.7, 13.0 Hz, 1-H), 4.09 (ddd, 1H, J = 6.4, 6.7, 12.4 Hz, 2-H), 4.24 (dt, 1H, J = 6.2, 12.4 Hz, 3-H), 7.15–7.60 (m, 5 H_{arom}).

(2*S*,3*S*)-1-Phenylsulfinyl-2,3-(isopropylidenedioxy)pentane (8):
MCPBA (80%, 1.9 g, 1.05 eq) is added to a stirred and cooled solution of **7** (2.20 g, 8.7 mmol) in CH_2Cl_2 (50 mL) at −10°C. The mixture is stirred for 20 min at 10°C. It is then poured into 5% aq $NaHSO_3$ (50 mL), and extracted with Et_2O (4 × 60 mL). The ether solution is washed with H_2O (50 mL), sat. aq $NaHCO_3$ (50 mL), brine (50 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The residue is chromatographed on silica gel (25 g). Elution with hexane/EtOAc (10:1) gives **8** as an oil; yield: 2.22 g (95%); $[\alpha]_D^{21.5}$ + 132° (c = 0.97, $CHCl_3$); $n_D^{21.4}$ 1.5257.

$C_{14}H_{20}O_3S$ (268.3) calc. C 62.66 H 7.51 found 62.81 7.57

IR (film): ν = 1590, 1200, 1095, 1080, 1050, 880, 760 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.95, 0.98 (each t, total 3H, J = 7 Hz, 5-H), 1.08–1.70 (m, 2H, 4-H), 1.30, 1.43, 1.45, 1.53, (each s,

total 6H, CH_3C), 2.65–3.52 (m, 2H), 3.80–4.90 (m, 2H), 7.40–7.85 (m, 5 H_{arom}).

(2*R*,3*S*)-2,3-(Isopropylidenedioxy)-1-pentanol (9):
A mixture of **8** (2.20 g, 8.20 mmol) and NaOAc (0.77 g, 9.4 mmol) in Ac_2O (40 mL) is stirred and heated under reflux for 2.5 h. The mixture is cooled to r.t., diluted with benzene (200 mL) and concentrated *in vacuo*. The residue is dissolved in benzene (200 mL) and passed through a silica gel pad. The solution is concentrated *in vacuo* again. To a solution of this residue in EtOH (40 mL) is added $NaBH_4$ (1.32 g, 34.9 mmol) in N NaOH (50 mL). After 2 h, the mixture is extracted with Et_2O (3 × 100 mL). The ether solution is washed with H_2O (50 mL), sat. aq $NaHCO_3$ (50 mL), brine (50 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The residue is distilled to give **9**; yield: 820 mg (63%); bp 74–75.5 °C/25 Torr; $[\alpha]_D^{20.9}$ + 40.1° (*c* = 1.00, $CHCl_3$); $n_D^{20.9}$ 1.4384.

$C_8H_{16}O_3$ (160.2) calc. C 59.98 H 10.07
found 59.84 10.01

IR (film): ν = 3450, 1240, 1220, 1045 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.00 (t, 3H, *J* = 7.2 Hz, 5-H), 1.36 (s, 3H, CH_3C), 1.47 (s, 3H, CH_3C), 1.20–1.83 (m, 2H, 4-H), 2.00 (1H, s, OH), 3.60 (d, 2H, *J* = 6.7 Hz, 1-H), 3.90–4.25 (m, 2H, 2, 3-H).

[(2*R*,3*S*)-2,3-(Isopropylidenedioxy)pentyl] *p*-Toluenesulfonate (10):
A mixture of **9** (780 mg, 4.90 mmol) and pyridine (2 mL) in CH_2Cl_2 (20 mL) is stirred and cooled at 0 °C. To the mixture is added *p*-toluenesulfonyl chloride (1.94 g, 10.2 mmol) at 0 °C and stirring is continued at 4 °C for 16 h. To the mixture is added H_2O (30 mL), and the mixture is stirred for 10 min. This is extracted with Et_2O (3 × 50 mL). The ether solution is washed with sat. aq $CuSO_4$ (30 mL), H_2O (30 mL), sat. aq $NaHCO_3$ (30 mL), and brine (30 mL). The solution is dried ($MgSO_4$), and concentrated *in vacuo*. The residue is chromatographed on silica gel (20 g). Elution with hexane/EtOAc (15:1) gives **10**. This is recrystallized from hexane to give an analytical sample as white needles; yield: 1.53 g (95%); mp 45.0–45.5 °C; $[\alpha]_D^{22}$ + 28.5° (*c* = 1.13, $CHCl_3$).

$C_{15}H_{22}O_5S$ (314.4) calc. C 57.30 H 7.05
found 57.55 6.98

IR (KBr): ν = 3020, 3000, 1600, 1175, 975 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.01 (t, 3H, *J* = 7.3 Hz, 5-H), 1.15–1.75 (m, 2H, 4-H), 1.31 [s, 6H, $(CH_3)_2C$], 2.46 (s, 3H, $ArCH_3$), 3.78–4.35 (m, 4H), 7.25–7.90 (m, 5 H_{arom}).

(2*R*,3*S*)-1-Tosyloxy-2,3-pentanediol (11):
A solution of **10** (850 mg, 2.71 mmol) in 20% AcOH (50 mL) is stirred at r.t. for 16 h. To the mixture is added $NaHCO_3$ to neutralize it. It is extracted with Et_2O (5 × 50 mL). The ether solution is washed with brine (50 mL), and concentrated *in vacuo*. The residue is diluted with benzene (150 mL) and concentrated *in vacuo* to remove AcOH. The crude **11** [730 mg (98%)] thus obtained is used for the next reaction without purification.

IR (KBr): ν = 3450, 1595, 1360, 1180, 970 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.98 (t, 3H, *J* = 7.9 Hz, 5-H), 1.15–1.80 (m, 4H), 2.47 (s, 3H, $ArCH_3$), 3.45–3.90 (m, 2H), 4.15 (d, 1H, *J* = 1.4 Hz, 1-H), 4.21 (s, 1H, 1-H), 7.18–7.90 (m, 4 H_{arom}).

(2*R*,3*S*)-1,2-Epoxy-3-pentanol 1-Ethoxyethyl Ether (12):
To a solution of **11** [prepared from **10** (850 mg, 2.71 mmol)] in CH_2Cl_2 (15 mL) is added K_2CO_3 (380 mg, 2.74 mmol), and the mixture is stirred for 2 h at r.t. After filtration, the filtrate is cooled to 0 °C. To this are added ethyl vinyl ether (5 mL) and a catalytic amount of pyridinium *p*-toluenesulfonate at 0 °C and the mixture is stirred at r.t. overnight. The mixture is poured into H_2O (30 mL) and extracted with Et_2O (3 × 50 mL). The ether solution is washed with brine (30 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The residue is chromatographed on silica gel (50 g). Elution with pentane/Et_2O (20:1) gives **12**. An analytical sample is prepared by distillation; yield: 330 mg (70%); bp 115–116 °C/67 Torr; $[\alpha]_D^{20.6}$ − 5.40° (*c* = 1.43, $CHCl_3$); $n_D^{20.6}$ 1.4173.

IR (film): ν = 1390, 1345, 1320, 1140, 1090, 1065, 1045, 1000 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.85–1.37 (m, 9H), 1.40–1.90 (m, 2H), 2.65–3.02 (m, 3H), 3.10–3.90 (m, 3H), 4.60–4.92 (m, 1H).

(3*S*,4*R*)-8-Nonene-3,4-diol (13):
A solution of 3-butenylmagnesium bromide in dry THF is prepared from 4-bromo-1-butene (2.36 g, 17.5 mmol) and Mg (510 mg, 21.0 mmol) in dry THF (17 mL). This is added dropwise to a stirred and cooled suspension of CuBr (1.17 g, 8.14 mmol) in THF (5 mL) at − 15 °C under Ar. The stirring is continued for 15 min. A solution of **12** (280 mg, 1.62 mmol) in dry THF (5 mL) is added to the stirred and cooled mixture of the organocopper reagent at − 50 °C. After 2 h at − 50 °C the mixture is poured into sat. aq NH_4Cl (30 mL) and extracted with Et_2O (5 × 50 mL). The ether solution is washed with sat. aq $NaHCO_3$ (50 mL), brine (50 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The residue is diluted with MeOH (20 mL) and to this is added a catalytic amount of pyridinium *p*-toluenesulfonate at 0 °C. The mixture is stirred at 4 °C for 16 h. The mixture is concentrated *in vacuo* and the residue is recrystallized from hexane to afford **13**; yield: 150 mg (59%); mp 81–82 °C; $[\alpha]_D^{20}$ + 10.1° (*c* = 0.99, $CHCl_3$) [Lit.[2] mp 81–82 °C; $[\alpha]_D^{21}$ + 11.6° (*c* = 1.00, $CHCl_3$)].

$C_9H_{18}O_2$ (244.3) calc. C 54.07 H 6.60
found 53.93 6.51

IR (KBr): ν = 3440, 3080, 1635, 1100, 1070, 1030, 990, 965, 910 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.00 (t, 3H, *J* = 6.8 Hz, 1-H), 1.20–1.80 (m, 6H), 1.80–2.25 (m, 2H, 7-H), 4.85–5.20 (m, 2H, 9-H), 5.55–6.15 (m, 1H, 8-H). These spectral data are identical with those reported.[2]

The enantiomeric purity of **13** is estimated to be 99.7% by HPLC analysis of the corresponding (*R*)-MTPA ester [column: Senshu Pak silica-1251-N, 25 cm × 4.6 mm; solvent; hexane/$ClCH_2CH_2Cl$ (4:1); flow rate; 1.0 mL/min.]: T_r = 61.4 min (99.85%).

3,3-Dimethoxy-1-phenylsulfonyl-2-pentanone (14):
To a stirred solution of methyl phenyl sulfone (6.13 g, 39.3 mmol, 1.1 eq) in dry THF (170 mL) is added BuLi (49.7 mL, 1.58 mol/l, 78.5 mmol, 2.2 eq) at 5–10 °C under Ar and the stirring is continued for 2 h. To the mixture is added **4** (5.78 g, 35.7 mmol) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU, 5 mL) in dry THF (50 mL) at − 78 °C. The temperature is allowed to rise gradually to r.t. and the mixture is stirred for 16 h at r.t. The mixture is poured into sat. aq NH_4Cl (200 mL) and extracted with Et_2O (3 × 300 mL). The ether solution is washed with sat. aq $NaHCO_3$ (100 mL), brine (100 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The residue is recrystallized from *i*-Pr_2O to give **14**; yield: 8.79 g (86%); mp 95–96 °C.

$C_{13}H_{18}O_5S$ (286.3) calc. C 54.23 H 6.33
found 54.44 6.24

IR (KBr): ν = 3080, 3000, 1735, 1585, 1370, 1320, 1310, 1270, 1170, 1095, 1050, 1025, 870 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.67 (t, 3H, *J* = 7.2 Hz, 5-H), 1.75 (q, 2H, *J* = 7.2 Hz, 4-H), 3.19 (s, 6H, OCH_3), 4.48 (s, 2H, 1-H), 7.45–7.80 (m, 3 H_{arom}), 8.00 (dd, 2 H_{arom}, *J* = 2.0, 7.8 Hz).

1-Phenylsulfonyl-2,3-pentanedione (15):
A mixture of **14** (11.5 g, 40.2 mmol) and 6N aq HCl (5 mL) in H_2O (500 mL) is stirred and heated under reflux for 1.5 h. Then the mixture is cooled to r.t. and extracted with Et_2O (4 × 200 mL). The ether solution is washed with H_2O (100 mL), sat. aq $NaHCO_3$ (100 mL), brine (100 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The residue is recrystallized from benzene/hexane (1:1) to afford **15** as yellow plates; yield: 9.5 g (98%); mp 97–98 °C.

$C_{11}H_{12}O_4S$ (240.3) calc. C 54.99 H 5.03
found 54.73 5.07

IR (KBr): ν = 3450, 1735, 1585, 1450, 1310, 1150, 915 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.10 (t, 3H, *J* = 6.7 Hz, 5-H), 2.78 (q, 2H, *J* = 6.7 Hz, 4-H), 4.67 (s, 2H, 1-H), 7.45–7.75 (m, 3 H_{arom}), 7.75–8.05 (m, 2 H_{arom}).

(2*S*,3*S*)-1-Phenylsulfonyl-2,3-pentanediol (16):
To a stirred solution of sucrose (60 g) in H_2O (500 mL) is added baker's yeast (60 g) and the suspension is stirred for 30 min at 30 °C. Then EtOH (30 mL) solution of **15** (3.2 g, 13.3 mmol) is added. After 24 h, baker's yeast (30 g) and sucrose (30 g) are added to the mixture. It is stirred at 30 °C for 2 d. EtOAc (100 mL) and CH_2Cl_2 (100 mL) are added to the mixture, and it is then filtered through a Celite pad. The filtrate is saturated with NaCl, and extracted with EtOAc (7 × 500 mL). The extract is washed with sat. aq $NaHCO_3$ (500 mL), brine (500 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The residue is chromatographed on silica gel (100 g). Elution with CH_2Cl_2/Et_2O (7:1) gives 2.09 g (64%) of **16**. This is recrystallized three times from benzene to give **16** as white needles; yield: 1.46 g (45%); mp 100.0–101.5 °C; $[\alpha]_D^{21.5}$ + 16.6° (*c* = 0.965, EtOH).

$C_{11}H_{16}O_4S$	calc.	C 54.07	H 6.60
(244.3)	found	53.93	6.51

IR (KBr): ν = 3400, 3310, 2990, 1585, 1310, 1140, 1070, 975, 750 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.92 (t, 3H, J = 7.0 Hz, 5-H), 1.23–1.65 (m, 2H), 1.60 (s, 2H, OH), 3.30 (d, 2H, J = 5.8 Hz, 1-H), 3.62 (m, 1H, 3-H), 4.06 (m, 1H, 2-H), 7.55–8.05 (m, 5 H_{arom})

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