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Synthesis of (R)-4,5-Dihydro-3H-Dinaphtho-[2,1-c:1′,2′-e]Selenepin Oxide and Preliminary Studies on Its Use in the Oxidation of Sulfides

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SYNTHESIS OF (*R*)-4,5-DIHYDRO-3*H*-DINAPHTHO-[2,1-*c*:1',2'-*e*]SELENEPIN OXIDE AND PRELIMINARY STUDIES ON ITS USE IN THE OXIDATION OF SULFIDES

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Abstract: The first synthesis (*R*)-4,5-dihydro-3*H*-dinaphtho-[2,1-*c*:1',2'-*e*]-selenepin oxide **1** has been achieved from (*R*)-(+)-1,1'-bi-2-naphthol, which in turn was obtained by resolution of *rac*-1,1'-bi-2-naphthol. Palladium catalyzed alkoxy-carbonylation of ditriflate **4** gave dimethyl ester **5** which was then reduced and the resultant diol converted to key intermediate chloride **8**. Cyclization with sodium selenolate gave novel enantiomerically pure selenide **9**, which upon oxidation yielded the desired selenoxide (*R*)-**1**. Preliminary studies on the oxidation of sulfides to sulfoxides using **1** and 2,2,2-trifluoroethane sulfonic acid are also described.

In recent years binaphthyl-containing compounds have been used extensively as chiral auxiliaries and enantiomerically pure ligands in asymmetric synthesis.[2] A limited number of heterocyclic derivatives are now beginning to appear and are being investigated as new reagents in a variety of asymmetric processes. For example, binaphthyl-based oxaziridinium salts have been used for the asymmetric oxidation of unfunctionalized alkenes;[3] a cyclic binaphthyl-based tin hydride reagent has been used in asymmetric radical chemistry;[4] and sulfur based reagents containing a binapthyl group have also been reported.[5]

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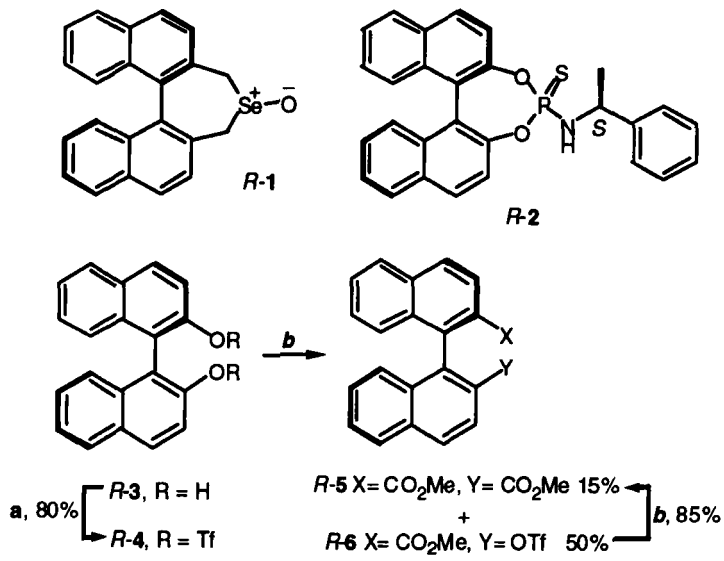
Our interest in the chemistry of selenoxides coupled with our work in other areas of sulfur and selenium mediated asymmetric synthesis,[6] has led us to examine new routes to enantiomerically pure selenides and sulfides.[7] As part of this study we wished to prepare novel binaphthyl-based selenoxide (*R*)-**1**. Due to the C_2-symmetry in the precursor selenide **9**, simple oxidation with an achiral oxidant was expected to give a single, enantiomerically pure selenoxide with no complications arising from prochirality at the selenium atom. To date, to the best of our knowledge, only one selenium-containing binaphthyl compound has been used in asymmetric synthesis.[8,9]

Rac-1,1'-bi-2-naphthol was resolved using a literature procedure involving the formation of diastereomeric thiophosphoramidate esters using (*S*)-(-)-α-methylbenzylamine and thiophosphoryl chloride.[10] Fractional recrystallization allowed (*R*)-(-)-1,1'-binaphthyl-2,2'-diyl N-((*S*)-α-methylbenzyl) thiophosphoramidate **2** to be isolated and subsequent reduction gave (*R*)-1,1'-bi-2-naphthol **3**. Isolation of the other thiophosphoramidate ester diastereoisomer, leading to (*S*)-1,1'-bi-2-naphthol, was less successful in our hands.

(*R*)-Bi-2-naphthol was then converted to the corresponding ditriflate **4** with trifluoromethanesulfonic anhydride, 2,6-lutidine and N,N-dimethylaminopyridine (scheme 1).[11] Palladium catalyzed methoxycarbonylation[11] with $Pd(OAc)_2$, diphenylphosphinopropane and N,N-diisopropylethylamine in methanol and DMSO gave a mixture of the monomethyl ester **6** and the desired diester **5**[12]. In accord with the literature, increasing the carbon monoxide pressure gave improved yields of **5**, however, on the relatively large scales involved, it proved more convenient to simply expose the monoester **6** to the reaction conditions for a second time. In this way a satisfactory yield of diester **5** was obtained.

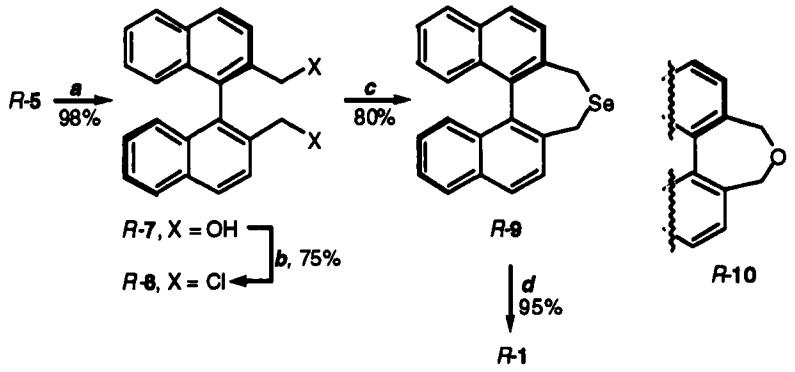


a Tf_2O, 2,6-lutidine, DMAP, CH_2Cl_2, -30°C-rt; *b* $Pd(OAc)_2$ 15mol%, dppp, CO, MeOH, DMSO, 80°C, 72h.
Scheme 1

Reduction of **5** with $LiAlH_4$ then gave diol **7**.[13] Our original strategy to form the selenium-containing ring involved the nucleophilic reaction of Na_2Se with the ditosylate derived from diol **7**. In an attempt to form the ditosylate, diol **7** was treated with TsCl in pyridine, however, known cyclic ether **10**[14] and dichloride **8**[15] were formed in approximately equal amounts as the only products. It was recognised however that dichloride **8** was an equally suitable substrate for selenide anion-mediated cyclization and we found it could be conveniently prepared from diol **7** by treatment with N-chlorosuccinimide and triphenylphosphine (scheme 2). Subsequent addition of dichloride **8** to a freshly prepared solution of Na_2Se in EtOH[16] gave novel C_2-symmetrical selenide **9** in excellent yield. Oxidation with *m*CPBA then gave the desired selenoxide (*R*)-**1**.

Our approach to enantiomerically pure 2,2'-hydroxymethyl and chloromethyl compounds, *ie.* **7** and **8**, and to cyclic systems like selenide **9**, is

particularly attractive as it involves resolution at an early stage in the synthesis unlike previous routes which carry out resolutions on advanced intermediates using chiral columns,[17,9] or *via* the formation of diastereomeric quaternary ammonium salts.[18]

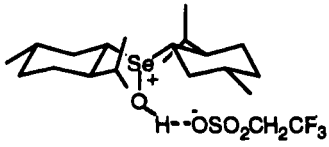


a $LiAlH_4$, THF, 0°C, 30min; *b* NCS, PPh_3, THF, rt, 5h; *c* Se, $NaBH_4$, EtOH, 0°C-rt; *d* *m*CPBA, K_2CO_3, CH_2Cl_2, rt, 10min.
Scheme 2

Our interest in the development of selenoxides as oxidising agents has led to the discovery of novel selenoxide-sulfonic salts, and subsequently to a new, selective oxidation of sulfides using these salts.[6a] We have previously reported the preparation of the first enantiomerically pure selenoxide-sulfonic acid salt **11** derived from menthol. An analogous enantiomerically pure salt ***R*-12** is the expected intermediate in the oxidation of dialkyl sulfides with selenoxide **1** in the presence of a stoichiometric amount of 2,2,2-trifluoroethanesulfonic acid.

Oxidation of dialkyl sulfides with ***R*-1** and 2,2,2-trifluoroethanesulfonic acid were found to proceed efficiently but with low enantioselectivity. For example, methyl ^{n}octyl sulfide, and cyclohexyl methyl sulfide, were oxidized to the corresponding sulfoxides in 90% and 80% yield respectively.[19] Importantly,

selenide **9** was recovered from the oxidation in near quantitative yield and could be reused.



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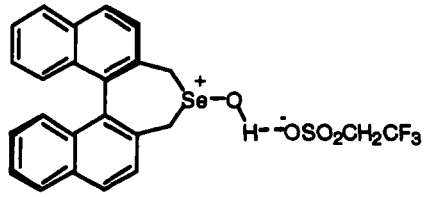

***R*-12**

In summary, an efficient synthesis of novel (*R*)-4,5-dihydro-3*H*-dinaphtho-[2,1-*c*:1',2'-*e*]-selenepin oxide **1** has been achieved *via* oxidation of the novel C_2-symmetrical selenide **9**. The route utilizes the previously reported palladium catalyzed alkoxy-carbonylation of (*R*)-1,1'-binaphthalene-2,2'-ditrifluoromethane sulfonate **4** to introduce the necessary single carbon units at the 2 and 2' positions. In the presence of 2,2,2-trifuoroethane sulfonic acid, selenoxide **1** was found to oxidize dialkyl sulfides to the corresponding sulfoxides in good yield and with clean regeneration of selenide **9**. Further studies on the oxidation of a variety of substrates using selenoxide **1** are currently under investigation in our laboratories, along with other applications of **9** in asymmetric synthesis.

Experimental Section.

Melting points were determined on a Reichert Hot Stage apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded on a General Electric QE 300 spectrometer or a Bruker AM400 spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield of tetramethylsilane for ^1H resonances, and referenced to the central peak of the deuterated chloroform triplet

for ^{13}C resonances. Infrared spectra were recorded on a Philips PU 8706 infrared spectrophotometer and signals were referenced to the polystyrene 1601 cm^{-1} absorbtion. Mass spectra were recorded on a VG Autospec mass spectrometer. Optical rotations were measured on an Optical Activity AA-1000 polarimeter and calibrated using a solution of camphor in ethanol of known rotation, $[\alpha]_D^{20}$ +44.1 (*c* 10, ethanol). Microanalyses were carried out at the University of Leeds Microanalytical Laboratory. All C, H, N, and S analytical figures are percentage values. Flash chromatography signifies column chromatography on Merck silica gel (230-400) or equivalent according to the method of Still.[20] Thin layer chromatography was carried out using precoated aluminium (or plastic) backed silica plates which were visualised using either ultraviolet light, permanganate or anisaldehyde stain. All glassware was washed with acetone, oven dried overnight at 125°C and allowed to cool under a stream of dry nitrogen prior to use. Reactions were carried out under a positive pressure of dry oxygen - free nitrogen. Solvents were removed under reduced pressure using a Buchi rotary evaporator at water aspirator pressure, followed by drying under high vacuum at 0.5 mm Hg. Solvents were purified prior to use by established procedures[21] and other reagents used as received. Petroleum ether refers to petroleum ether (bp 40-60°C) unless otherwise stated. *Rac*-1,1'-bi-2-naphthol was resolved using a literature procedure via diastereomeric thiophosphoramidate esters using (*S*)-(-)-α-methylbenzylamine and thiophosphoryl chloride.[10]

(*R*)-1,1'-Binaphthalene-2,2'-dimethyl dicarboxylate[12] **5** and **(*R*)-1,1'-binaphthalene-2-methyl carboxylate-2'-trifluoromethane sulfonate 6**

Methanol (18.9ml) and N,N-diisopropylethylamine (7.40ml) were added to a solution of (*R*)-1,1'-binaphthalene-2,2'-ditriflate **4** (5.30g, 9.64mmol, 1eq) in dimethylsulfoxide (50ml). The above solution was then transfered to a reaction

vessel containing $Pd(OAc)_2$ (325mg, 1.45mmol, 0.15eq) and diphenylphosphinopropane (596mg, 1.45mmol, 0.15eq), flushed out with carbon monoxide and fitted with a condenser. The solution was then heated under reflux under an atmosphere of carbon monoxide (balloon pressure) at 80°C for 72h. Saturated aqueous NaCl (70ml) was then added and the aqueous layer separated and extracted with diethyl ether (4x30ml). The combined organic extracts were then dried ($MgSO_4$) and concentrated *in vacuo*. Purification by column chromatography [silica gel, 20% ethyl acetate, petroleum ether (bp 40-60°C) eluant] gave diester **5** (0.54g, 1.45mmol, 15%) as a colourless crystalline solid, mp 157-158°C [*cf.* 156.5-157.5°C][12], which was used without further purification; δ_H (300 MHz; $CDCl_3$) 3.49 (6H, s, MeCO), 7.07 (2H, d, J 9.0Hz), 7.23 (2H, t, J 6.0Hz), 7.51 (2H, t, 6.0Hz), 7.95 (2H, t, J 9.0Hz), 8.02 (2H, s) and 8.18 (2H, d, J 6.0Hz); ν_{max} (KBr)/cm^{-1} 3060-2940m (C-H), 1725s (C=O), 1620w, 1600w (C=C), 1460m (C=C), 1435m, 1335w, 1285s, 1245m, 1190s, 1140s, 1070m, 835m and 770m; MS (EI) *m/z* 370 (M^+, 100%), 339(32), 311(35), 295(24), 280(29), 268(16), 252(52), 239(26), 213(7.6), 163(7) and 125(15); $[\alpha]_D$ +21.6 (c 1.0, MeOH) [*cf.* +22.4 (c 1.0, MeOH)][12]. **(*R*)-1,1'-binaphthalene-2-methyl carboxylate-2'-trifluoromethane sulfonate 6** was also isolated (2.22g, 4.82mmol, 50%). Recrystallisation ($CHCl_3$, hexane) gave **6** as pale yellow needles; δ_H (400 MHz; $CDCl_3$) 3.60 (3H, s, MeCO), 7.21 (2H, t, J 8.5 Hz), 7.36 (2H, br.s), 7.54-7.63 (4H, m), 8.01 (2H, t, J 6.9 Hz), 8.11 (1H, t, J 8.6 Hz) and 8.29 (1H, d, J 8.7 Hz); δ_C (400 MHz; $CDCl_3$) 52.12 (*Me*CO), 118.13 (CF_3, q, ^1J (^{13}C-^{19}F) 318 Hz), 119.29 (CH), 126.14 (CH), 126.45 (CH), 126.87 (CH), 127.17 (CH), 127.35 (CH), 127.59 (CH), 128.11 (CH), 128.14 (CH), 128.24 (CH), 128.66 (C), 129.39 (CH), 129.66 (C), 130.28 (CH), 132.11 (C), 132.56 (C), 133.41 (C), 133.78 (C), 135.14 (C), 144.36 (C) and 166.62 (C); ν_{max} (neat)/cm^{-1} 3050-2940m (C-H), 1720s (C=O), 1615m, 1590m (C=C), 1500m

(C=C), 1450s, 1410s (SO_2-O), 1360m, 1325s, 1270s, 1220s (SO_2-O), 1130s, 1060s, 990m, 950s and 930s; MS (EI) *m/z* 460 (M^+, 14%), 327(13), 311(68), 295(12), 283(16), 268(100), 239(42), 120(8) and 69(11) ; $[\alpha]_D^{20}$ -45.2 (c 2.9, $CHCl_3$); (Found: C, 60.20; H, 3.0; S, 7.0. Calc. for $C_{23}F_3H_{15}O_5S$: C, 60.00; H, 3.28; S, 6.96%). Ditriflate starting material **4** (0.63g, 1.45mmol, 15%) was also recovered and recycled.

(R)-2,2'-bis hydroxymethyl-1,1'-binaphthyl **7**[22]

$LiAlH_4$ (107mg, 1.08mmol, 1.0eq) was added cautiously to a solution of 1,1'-binaphthalene-2,2'-dimethyl dicarboxylate **5** (400mg, 1.08mmol, 1eq) in THF (20ml) at 0°C. After addition, the solution was stirred at room temperature for 30min. H_2O (20ml) and aqueous HCl (2M, 20ml) were added and the aqueous layer separated and extracted with CH_2Cl_2 (4x30ml). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to give diol **7** as a white solid (333mg, 1.06mmol, 98%). Recrystallisation gave a microcrystalline solid, mp 191.4-192.6°C (ethyl acetate, petroleum ether (bp 60-80°C)); δ_H (400 MHz; $CDCl_3$) 2.86 (2H, br.s, OH), 4.16 (2H, d, J 11.6 Hz, CH_2OH), 4.39 (2H, d, J 11.6 Hz, CH_2OH), 7.04 (2H, d, J 8.4 Hz, ArH), 7.24 (2H, t, J 8.0 Hz, ArH-7,7' or ArH-8,8'), 7.46 (2H, t, J 7.1 Hz, ArH-7,7' or ArH-8,8'), 7.72 (d, J 8.4 Hz, 2H), 7.93 (d, J 8.2 Hz, 2H) and 7.99 (d, J 8.4 Hz, 2H); δ_C (400 MHz: $CDCl_3$) 63.23 (CH_2OH), 126.09 (ArCH), 126.30 (ArCH), 126.56 (ArCH), 127.33 (ArCH), 128.08 (ArCH), 128.72 (ArCH), 133.11 (ArC), 133.22 (ArC), 134.35 (ArC) and 137.20 (ArC); ν_{max} (CH_2Cl_2)/cm^{-1} 3450br (OH), 3100-3050m (C-H), 1470m (C=C), 1380m, 1320m, 1270s, 1230s, 1180m and 1080; MS (EI) *m/z* 314 (M^+, 12%), 296(M-H_2O, 72), 277(M-2H_2O, 100), 265(52), 252(56), 239(18), 226(7), 139(20), 126(22), 120(11) and 113(7); $[\alpha]_D^{20}$ +53.0 (c 1.2, acetone) [*cf.* +110°

(dioxane)][22]; (Found: C, 83.90; H, 5.65. Calc. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77%).

(R)-2,2'-bis chloromethyl-1,1'-binaphthyl **8**[15]

Triphenylphosphine (2.01g, 7.66mmol, 2.4eq) and N-chlorosuccinimide (1.18g, 8.84mmol, 2.8eq) were dissolved in THF (75ml) and stirred at room temperature for 15min. To the resulting white suspension was added (*R*)-2,2'-*bis*hydroxymethyl-1,1'-binaphthyl **7** (0.99g, 3.15mmol, 1eq) and the solution stirred for 5h. Diethyl ether (100ml) and H_2O (75ml) were added and the aqueous layer extracted with diethyl ether (60ml). The combined organic extracts were washed with saturated aqueous NaCl (50ml), dried ($MgSO_4$) and concentrated *in vacuo* . Chromatography [silica gel, 10% ethyl acetate, petroleum ether (bp 40-60°C) eluant] gave dichloride **8** (829mg, 2.36mmol, 75%) as a white solid which was used without further purification; δ_H (300 MHz; $CDCl_3$) 4.32 (4H, s, CH_2Cl), 7.07 (2H, d, J 8.4Hz, ArH), 7.26 (2H, t, J 8.1 Hz, ArH-7,7' or ArH-8,8'), 7.48 (2H, t, 7.8Hz, ArH-7,7' or ArH-8,8'), 7.93 (2H, d, J 8.4 Hz, ArH) and 8.03 (2H, d, J 8.4Hz, ArH); ν_{max} (CH_2Cl_2)/cm^{-1} 3050-2950m (C-H), 1600w (C=C), 1500m (C=C), 1440w, 1350w, 1320w, 1250s, 1215s, 1150m, 1050m, 1020m, 900m and 810s; MS (EI) *m/z* 351 (M^+, 43%), 350(63), 315(9), 279(60), 266(100) and 138(30); $[\alpha]_D^{20}$ +155.1 (c 1.2, $CHCl_3$) [*cf.* +145°][15].

(*R*)-4,5-Dihydro-3*H*-dinaphtho-[2,1-*c*:1',2'-*e*]-selenepin 9

Ethanol (40ml) was added with stirring to selenium (0.24g, 2.99mmol, 3eq) and $NaBH_4$ (0.12g, 3.29mmol, 3.3eq) at 0°C. After 15min, (*R*)-2,2'-*bis*chloromethyl-1,1'-binaphthyl **8** (350mg, 1.00mmol, 1eq) was added and the solution heated under reflux for 30min. Aqueous dilute HCl (50ml) and H_2O (20ml) were added and the aqueous layer separated and extracted with CH_2Cl_2

(3x40ml). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* . Recrystallisation gave selenide **9** as a pale yellow microcrystalline solid (286mg, 0.80mmol, 80%), mp 241.8-243.9°C ($CHCl_3$, ethanol); δ_H (400 MHz; $CDCl_3$) 3.48 (2H, d, J 11.2 Hz, CH_2Se), 3.53 (2H, d, J 11.2 Hz, CH_2Se), 7.22-7.28 (4H, m, ArH), 7.43-7.47 (2H, m, ArH), 7.57 (2H, d, J 8.4 Hz, ArH), 7.93 (2H, d, J 8.2 Hz, ArH) and 7.97 (2H, d, J 8.4 Hz, ArH); δ_C (400 MHz; $CDCl_3$) 24.71 (CH_2Se, t, $^1J(^{13}C\text{-}^{77}Se)$ 144.0 Hz), 125.38 (ArCH), 126.07 (ArCH), 126.31 (ArCH), 126.56 (ArCH), 128.19 (ArCH), 129.12 (ArCH). 131.93 (ArC), 132.76 (ArC), 133.35 (ArC) and 134.45 (ArC); ν_{max} (CH_2Cl_2)/cm^{-1} 3000-2900m (C-H), 1600w (C=C), 1500m (C=C), 1400s, 1340w, 1320w, 1220s, 1160m, 1000w and 800s; MS (EI) *m/z* 359 (M^+, 5%), 316(16), 291(11), 281(69), 266(40), 239(9), 137(11), 109(25), 95(48), 81(56), 69(86) and 55(100); $[\alpha]_D^{20}$ -198.7 (c 0.6, $CHCl_3$); (Found: C, 73.55; H, 4.40. $C_{22}H_{16}Se$ requires C, 73.54; H, 4.49%).

(*R*)-4,5-Dihydro-3*H*-dinaphtho-[2,1-*c*:1',2'-*e*]-selenepin oxide 1

*m*CPBA (55% H_2O, 60.0mg, 0.18mmol, 1.1eq) and saturated aqueous K_2CO_3 (1ml) were added to a solution of (*R*)-binaphthyl derived selenide **9** (60.0mg, 0.17mmol, 1eq) in CH_2Cl_2 (4ml) and the solution stirred at room temperature for 10min. Saturated aqueous Na_2CO_3 (2ml) was added and the aqueous layer separated and extracted with CH_2Cl_2 (4x4ml). The combined organic extracts were then dried ($MgSO_4$) and concentrated *in vacuo* to give selenoxide **1** (60.0mg, 0.16mmol, 95%) as a white solid which was used without further purification; δ_H (300 MHz; $CDCl_3$) 3.19 (1H, d, J 10.8 Hz, CH_2Se), 3.56 (1H, d, J 12.3 Hz, CH_2Se), 3.82 (1H, d, J 12.3 Hz, CH_2Se), 4.38 (1H, d, J 10.8 Hz, CH_2Se), 7.25-7.33 (4H, m, ArH), 7.50-7.53 (3H, m, ArH), 7.65 (1H, dd, J 8.4, 2.7 Hz, ArH) and 7.94-8.05 (4H, m, ArH); ν_{max} (thin film)/cm^{-1} 3020-2900s

(C-H), 1580m (C=C), 1500m (C=C), 1400m, 1350m, 1310m, 1250m, 1215m, 1020m and 810s (Se=O); MS (EI) *m/z* no M^+ detected, 360(M-O, 69%), 310(34), 295(32), 281(71), 265(100), 252(66), 239(12), 167(10), 149(34), 138(33), 126(32), 113(12), 71(11) and 57(18).

Oxidation of methyl ^{n}octyl sulfide with (*R*)-1 and 2,2,2-trifluoroethane sulfonic acid

To a solution of (*R*)-**1** (50mg, 0.13mmol, 1.2eq) in CH_2Cl_2 (2ml) at room temperature was added 2,2,2-trifluoroethane sulfonic acid (0.02ml, 0.13mmol, 1.2eq). After 10min, methyl ^{n}octyl sulfide (0.02ml, 0.11mmol, 1eq) was added and the reaction mixture stirred at room temperature for 1.5h. Saturated aqueous Na_2CO_3 (1ml) was then added and the aqueous layer separated and extracted with CH_2Cl_2 (4x1ml). The combined organic extracts were then dried ($MgSO_4$) and concentrated *in vacuo* to give a pale yellow oil. Purification by column chromatography [silica gel, petroleum ether (bp 40-60°C) eluant] gave recovered selenide (*R*)-**9** (47mg, 0.13mmol, 94%). Increasing the solvent polarity (30% petroleum ether (bp 40-60°C), 50% ethyl acetate, 20% ethanol) gave methyl ^{n}octyl sulfoxide (17mg, 0.10mmol, 90%) as colourless crystals [mp 36.5-38.1°C (^{n}pentane) *cf.* 37-38°C[23]]

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References

1. Current address: Department of Chemistry, The Joseph Black Building, University of Glasgow, G12 8QQ
2. Pu, L. *Chem. Rev.*, 1998, **98**, 2405.

3. Aggarwal, V.K. and Wang, M.F. *J. Chem. Soc., Chem. Commun.*, 1996, 191.

4. Blumenstein, M.; Schwarzkopf, K. and Metzger, J. O. *Angew. Chem., Int. Ed. Engl.*, 1998, **36**, 235.

5. De Lucchi, O. *Pure Appl. Chem.*, 1996, **68**, 945; Cossu, S.; DeLucchi, O.; Fabbri, D.; Valle, G.; Painter, G.F. and Smith, R.A.J. *Tetrahedron*, 1997, **53**, 6073.

6. a) Procter, D.J. and Rayner, C.M. *Tetrahedron Lett.*,1994, **35**, 1449: Procter, D.J.; Lovell, S.J. and Rayner, C.M. *Synthesis*, 1994, 20: Procter, D.J.; Thornton-Pett, M. and Rayner, C.M. *Tetrahedron*, 1996, **52**, 1841. b) Archer, N.J.; Rayner, C.M.; Bell, D. and Miller, D. *Synlett*, 1994, 617;

7. Procter, D.J.; Archer, N.J.; Needham, R.A.; Bell, D.; Marchington, A.P. and Rayner, C.M. *Tetrahedron*, 1999, **55**, 9611.

8. Tomoda, S. and Iwaoka, M. *J. Chem. Soc., Chem. Commun.*, 1988, 1283.

9. Since the synthesis of (*R*)-**1** reported herein, an account describing the preparation by a literature route of the corresponding racemic sulfoxide has appeared, see: Curtis, A.D.M.; McCague, R.; Ramsden, C.A. and Raza, M.R. *Chem. Commun.*, 1999, 189.

10. Fabbri, D.; Delogu, G. and De Lucchi, O. *J. Org. Chem.*, 1993, **58**, 1748.

11. Ohta, T.; Ito, M.; Inagaki, K. and Takaya, H. *Tetrahedron Lett.*, 1993, **34**, 1615.

12. Kanoh, S.; Hongoh, Y.; Motoi, M. and Suda, H. *Bull. Chem. Soc. Jpn.*, 1988, **61**, 1032.

13. Hall, D.M. and Turner, E.E. *J. Chem. Soc., Chem. Commun.*, 1955, 1242.

14. Gottarello, G.; Hibert, M.; Samori, B.; Solladie, G.; Spada, G.P. and Zimmerman, R. *J. Am. Chem. Soc.*, 1983, **105**, 7318.

15. Chong, M.J.; MacDonald, G.K.; Park, S.B. and Wilkinson, S.H. *J. Org. Chem.*, 1993, **58**, 1266.

16. Klayman, D.L. and Griffin, T.S. *J. Am. Chem. Soc.*, 1973, **95**, 197.

17. Stara, I.G.; Stary, I.; Tichy, M.; Zavada, J. and Fiedler, P. *J. Org. Chem.*, 1994, **59**, 1326.

18. Mazaleyrat, J-P. *Tetrahedron Lett.*, 1983, **24**, 1243: Maigrot, N. and Mazaleyrat, J-P. *Synthesis*, 1985, 317 and references cited therein.

19. Enantiomeric excesses of <10% have so far been observed.

17. Still, W.C.; Khan, M. and Mitra, A; *J. Org. Chem.*, 1978, *43*, 2923; see also: Leonard, J.; Lygo, B. and Procter, G. *Advanced Practical Chemistry*, Blackie, 1990.

21. Perrin, D.D.; Armarego, W.L.F. and Perrin, D.R. *Purification of Laboratory Chemicals*, Pergamon, 1980.

22. Mislow, K.; Glass, M.A.W.; O'Brien, R.E.; Rutkin, P.; Steinberg, D.H.; Weiss, J. and Djerrassi, C. *J. Am. Chem. Soc.*, 1962, **84**, 1455.

23. Katritzky, A.R.; Takahashi, I. and Marson, C.M. *J. Org. Chem.*, 1986, **51**, 4914.

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