Preparative and Mechanistic Studies Toward a Rational Development of Catalytic, Enantioselective Selenoetherification Reactions

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SUPPORTING INFORMATION

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General Experimental

All reactions were performed in oven dried (140°C) glassware. Reaction solvents tetrahydrofuran (Fisher, HPLC grade), diethyl ether (Fisher, BHT stabilized ACS grade), and CH₂Cl₂ (Fisher, unstabilized HPLC grade) were dried by passage through two columns of neutral alumina in a solvent dispensing system. Solvents for chromatography, filtration and recrystallization were CH₂Cl₂ (Aldrich, ACS grade), ethyl acetate (Fisher, ACS grade), diethyl ether (Fisher, ACS grade), *tert*-butyl methyl ether (Aldrich, ACS grade) and hexane (Fisher, Optima) and were used as received. Triethylamine (Alfa-Aesar, 99%) and pyridine (Fisher) were freshly distilled over CaH₂. Ethanol (Fisher, ACS grade) was distilled from magnesium. Acetic acid was distilled over CrO₃ and acetic anhydride prior to use. Diphenyl diselenide (Aldrich), allyl bromide (Aldrich), triphenylphosphine oxide recrystallized from ethanol (Acros), triphenylphosphine sulfide (Strem), hexamethylphosphorous triamide (Aldrich), trifluoroacetic acid (Aldrich), methanesulfonic acid (Aldrich), sodium borohydride (Aldrich), methanesulfonic acid (Aldrich), sodium borohydride (Aldrich), methanesulfonic acid (Aldrich), sodium borohydride (Aldrich), methanesulfonyl

chloride (Aldrich), 4-toluenesulfonylchloride (Aldrich), 1,3-bistrifluoromethylbenzene (TCI America), *N*-chlorosuccinimide recrystallized from acetic acid (Aldrich), morpholine distilled over KOH (Aldrich), phosphorous trichloride (Aldrich, distilled prior to use), and sodium hydride washed with hexane (Aldrich) were obtained from commercial sources. "Brine" refers to a saturated solution of sodium chloride.

Melting points were obtained in vacuum-sealed capillary tubes and are corrected. Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV (254), or potassium permanganate (KMnO₄), or ceric ammonium molybdate (CAM). Column chromatography was performed using Merck silica 60 (40-63 μ m particle size) gel purchased from Aldrich.

Analytical supercritical fluid chromatography was performed on a Berger Instruments SFC with spectrophotometric detector (220 nm) using Daicel Chiralpak OD, AD as well as a Regis Whelk-O1 column. Optical rotations were measured using a Jasco DIP-360 digital polarimeter in EtOH (ACS grade, distilled from magnesium) or Fischer ACS reagent grade CHCl₃ containing approximately 0.75% EtOH as a preservative and are reported as follows: concentration (c = g/dL), and solvent. ¹H NMR Spectra and ¹³C NMR spectra were acquired in CDCl₃ at 500 MHz or 400 MHz and referenced to residual CHCl₃ at 7.26 and 77.00 ppm respectively. Assignments were obtained by reference to COSY, HMQC and HMBC correlations. Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), hex (hextet), hep (heptet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. Mass spectroscopy was performed by the University of Illinois Mass Spectrometer Center. EI mass spectra were performed on a 70-VSE instrument. ESI mass spectra were performed on a Waters Q-Tof Ultima instrument. Data are

reported in the form of (m/z) versus intensity. Infrared spectra (IR) were recorded on a Mattson Galaxy 5020 spectrophotometer in KBr pellets or NaCl cells (film). Peaks are reported in cm⁻¹ with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%); w (weak, 0-33%). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory and Robertson Microlit Laboratories, Inc. Melting points (mp) were determined on a Thomas-Hoover capillary melting point apparatus and are corrected.

Literature Preparations

(E)-4-Phenyl-but-3-en-1-ol, ¹ (Z)- 4-phenyl-but-3-en-1-ol,² (E)-7-phenyl-hept-4-en-1-ol,³ (E)-6-methyl-hept-4-en-1-ol, ³ N-phenylselenenylsuccinimide ⁴, tris(dimethylamino) phosphine sulfide,⁵ tris(dimethylamino) phosphine selenide,⁵ tricyclohexylphosphine sulfide,⁶ 1,3dimethylhexahydropyrimidine-2-thione,⁷ 1,2-bis(4-methoxyphenyl)diselane,⁸ 1,2-bis(4trifluoromethylphenyl)diselane,⁹ 1,2-bis(2-trifluoromethylphenyl)diselane,⁹ 1,2-bis(2nitrophenyl)diselane,¹⁰ 1,2-bis(2,4,6-triisopropylphenyl)diselane,¹¹ epoxy alcohol (**23**),¹² triol (**26**, using ((DHQ)₂PHAL).¹³ (*R*)-*N*²,*N*²-dimethyl-[1,1'-binaphthalene]2,2'-diamine was synthesized via a known procedure from (*R*)-BINAM.¹⁴

Preparation of 1,2-Bis(2,6-bis-trifluoromethylphenyl)diselane



To an oven-dried, 100-mL, Schlenk flask equipped with a magnetic stir bar, was added potassium tert-butoxide (2.72 g, 24.7 mmol, 1.30 equiv), and THF (42 mL). The mixture was stirred for 5 min at room temperature and then the white suspension was cooled to -78 °C (acetone/dry ice bath temperature). 2.31 M solution of *n*-Butyl lithium in hexanes (8.1 mL, 18.7 mmol, 1.00 equiv) was added followed by 1,3-bis-(trifluoromethyl) benzene (4.00 g, 18.7 mmol) whereupon the solution turned violet. The reaction was stirred at -78 °C for 4 h after which Se (1.77 g, 22.4 mmol, 1.20 equiv) was added in one portion. The cold bath was removed and the solution was allowed to stir at room temperature for 14 h. 10% aq H₂SO₄ (67 mL) was added slowly and then air was bubbled through the mixture for 4.5 h. The mixture was filtered through a 1-inch pad of silica and eluted with TBME (100 mL). The filtrate was transferred to a 250 mL separatory funnel and the organic and aqueous layers were separated. The organics were concentrated on the rotavap (30 °C, 30 mm Hg) and the crude was filtered through a 1-inch pad of silica, which was eluted with TBME (100 mL) and the filtrate was concentrated on the rotavap (30 °C, 30 mm Hg). This procedure was repeated once more after which the crude product was recrystallized from EtOH to afford 719 mg of 1.2-bis(2,6-bis-trifluoromethylphenyl)diselane (13 %) as a yellow solid.

Data for 1,2-bis(2,6-bis-trifluoromethylphenyl)diselane:

<u>mp:</u> 178-179 °C

 1 <u>H NMR:</u> (400 MHz, CDCl₃)

7.90 (d, J = 7.6 Hz, 4 H, HC(3)), 7.62 (t, J = 8.0 Hz, 2 H, HC(4)).

 $\frac{13}{C}$ NMR: (100 MHz, CDCl₃)

137.0 (q, *J* = 29.6 Hz, C(2)), 130.3 (C(4)), 130.0 (q, *J* = 6.1 Hz, C(3)), 126.9 (C(1)), 122.9 (q, *J* = 274 Hz, C(5)).

 $\frac{77}{\text{Se NMR:}}$ (114 MHz, CDCl₃)

503 (br s)

<u>IR:</u> (thin film, CH_2Cl_2)

2920 (w), 2844 (w), 1582 (w), 1424 (w), 1333 (m), 1288 (s), 1204 (m), 1176 (s), 1145 (m), 1115 (s), 1130 (s), 1064 (w), 1028 (w), 993 (w), 815 (m), 737 (m), 674 (m), 572 (w), 508 (w).

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

585.8 (23.5, M⁺), 292.9 (100.0), 273.9 (90.6), 254.9 (18.2), 213.0 (30.6), 175.0 (10.0), 163.0 (20.0), 144.0 (28.2), 125.0 (23.5), 75.0 (12.3).

<u>HRMS:</u> calcd for $C_{16}H_6F_{12}Se_2$: 585.8608, found: 585.8608

General Procedure 1. Synthesis of Diols

Preparation of (3R,4S)-4-Phenyl-4-(phenylseleno)butane-1,3-diol (24a) (Scheme 10)



To an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added diphenyl diselenide (234 mg, 0.75 mmol, 0.75 equiv), and sodium borohydride (56.7 mg, 1.50 mmol, 1.50 equiv). The flask was cooled to 0 °C (the ice bath temperature) and 2.5 mL of EtOH was added under an atmosphere of nitrogen. The solution was stirred at 0 °C for 0.5 h and then

the ice bath was removed. After 10 min of stirring at room temperature, a solution of the epoxy alcohol (23) (164 mg, 1.00 mmol) in EtOH (2.5 mL) was added and the resulting solution was heated to 40 °C (oil bath temperature) for 14 h. The reaction mixture was allowed to cool to room temperature and then was transferred to a 125-mL separatory funnel with an additional 10 mL of CH₂Cl₂. The mixture was extracted with a sat. aq. NaHCO₃ solution (1 x 20 mL) and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (2 x 20 mL) and the combined organic extracts were washed with brine $(1 \times 25 \text{ mL})$ and dried over MgSO₄. The solution was filtered and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 3/2) to afford 250 mg of 24a (78%) as a white solid.

Data for 24a:

IR:

<u>mp:</u> 47-48 °C

¹H NMR: $(500 \text{ MHz}, \text{CDCl}_3)$

7.46 (d, J = 7.5 Hz, 2 H), 7.32-7.21 (m, 8H), 4.28 (d, J = 6.0 Hz, 1 H, HC(4)), 4.22-4.19 (m, 1 H, HC(3)), 3.76-3.74 (m, 2 H, H₂C(1)), 3.00 (d, J = 1.5 Hz, 1 H, HOC(3)), 2.57 (t, J = 4.5 Hz, 1 H, HOC(1)), 1.89-1.87 (m, 1 H, HC(2)), 1.67-1.60 (m, 1 H, HC(2)).

- ^{13}C NMR: $(125 \text{ MHz}, \text{CDCl}_3)$ 138.6, 135.0, 129.1, 128.9, 128.8, 128.5, 128.1, 127.5, 73.0 (C(3)), 61.3 (C(1)), 55.7 (C(4)), 36.3 (C(2)).
 - (NaCl plates, CH₂Cl₂) 3383 (s, br), 3058 (m), 3027 (m), 2946 (m), 2884 (m), 1951 (w), 1880 (w), 1807 (w), 1755 (w), 1600 (w), 1578 (m), 1494 (m), 1477 (s), 1452 (m), 1437 (s), 1328

(w), 1301 (w), 1266 (w), 1181 (w), 1156 (w), 1065 (s), 1052 (s), 1022 (m), 1000
(m), 988 (w), 966 (w), 897 (w), 844 (w), 740 (s), 700 (s), 670 (m), 618 (w), 554
(w), 522 (w), 507 (w)

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

322.0 (2.7, M⁺), 165.1 (44.9), 119.0 (12.5), 91.1 (100.0), 77.0 (10.3).

<u>HRMS:</u> calcd for $C_{16}H_{18}O_2$ Se: 322.0472, found: 322.0484

<u>TLC:</u> $R_f 0.18$ (hexanes/EtOAc, 3/2) [UV]

<u>Opt. Rot.:</u> $[\alpha]_{D}^{24} + 240.8 (c = 0.172, EtOH)$

Preparation of (3R,4S)-4-[(4-Methoxyphenyl)seleno]-4-phenylbutane-1,3-diol (24b)

(Scheme 10)



Following General Procedure 1, to an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added 1,2-bis(4-methoxyphenyl)diselane (186 mg, 0.50 mmol, 0.50 equiv), and sodium borohydride (45.3 mg, 1.20 mmol, 1.20 equiv). The flask was cooled to 0 °C (the ice bath temperature) and 2.5 mL of EtOH was added under an atmosphere of nitrogen. The solution was stirred at 0 °C for 0.5 h and then the ice bath was removed. After 10 min of stirring at room temperature, a solution of the epoxy alcohol (**23**) (164 mg, 1.00 mmol) in EtOH (2.5 mL) was added and the resulting solution was heated to 40 °C (oil bath temperature) for 14 h. After workup, the crude residue was purified by column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 1/1) to afford 175 mg of **24b** (50%) as a cream white solid.

Data for 24b:

<u>mp:</u> 62-63 °C

 1 <u>H NMR:</u> (500 MHz, CDCl₃)

7.36 (d, *J* = 8.5 Hz, 2 H, HC(10)), 7.26-7.20 (m, 5 H, HC(6,7,8)), 6.75 (d, *J* = 9.0 Hz, 2 H, HC(11)), 4.19-4.14 (m, 2 H, HC(3,4)), 3.77 (s, 3 H, H₃C(13)), 3.77-3.73 (m, 2 H, H₂C(1)), 3.06 (br s, 1 H, HOC(3)), 2.69 (br s, 1 H, HOC(1)), 1.89-1.86 (m, 1 H, HC(2)), 1.67-1.60 (m, 1 H, HC(2)).

 $\frac{13}{C}$ NMR: (125 MHz, CDCl₃)

159.8, 138.7, 137.4, 128.8, 128.4, 127.3, 118.8 (C(9), 114.6 (C(11)), 72.6 (C(3)), 61.2 (C(1)), 55.9 (C(4)), 55.1 (C(13)), 36.2 (C(2)).

<u>IR:</u> (NaCl plates, CH_2Cl_2)

3389 (w, br), 3060 (w), 3025 (w), 3000 (w), 2937 (w), 2836 (w), 1589 (m), 1571 (w), 1490 (s), 1461 (w), 1452 (m), 1440 (w), 1401 (w), 1285 (m), 1247 (s), 1174 (m), 1050 (m), 1029 (m), 1006 (w), 825 (m), 792 (w), 762 (w), 700 (m), 601 (w), 520 (w).

<u>MS:</u> (EI, 70 eV)

352.0 (6.6, M⁺), 190.0 (10.6), 188.0 (65.6), 187.0 (14.9), 186.0 (29.9), 185.0 (15.8), 184.0 (12.9), 135.1 (18.0), 108.1 (30.0), 107.1 (16.0), 91.1 (100.0), 79.1 (14.1), 77.0 (10.7).

- <u>HRMS:</u> calcd for $C_{17}H_{20}O_3$ Se: 352.0578, found: 352.0578
 - <u>TLC:</u> $R_f 0.22$ (hexanes/EtOAc, 1/1) [UV]
- <u>Opt. Rot.</u>: $[\alpha]_D^{24} + 222.2$ (c = 0.96, EtOH)..

Preparation of (3*R*,4*S*)-4-Phenyl-4-[[2,4,6-tri(propan-2-yl)phenyl]seleno]butane-1,3-diol (24c) (Scheme 10)



Following General Procedure 1, to an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added 1,2-bis(2,4,6-triiopropylphenyl)diselane (423 mg, 0.75 mmol, 0.75 equiv), and sodium borohydride (56.7 mg, 1.50 mmol, 1.50 equiv). The flask was cooled to 0 °C (the ice bath temperature) and 2.5 mL of EtOH was added under an atmosphere of nitrogen. After 5 min the ice bath was removed and the solution was stirred at 25 °C for 45 min. A solution of the epoxy alcohol (**23**) (164 mg, 1.00 mmol) in EtOH (2.5 mL) was added and the resulting solution was heated to 40 °C (oil bath temperature) for 14 h. After workup the crude residue was purified by column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 3/2) to afford 368 mg of **24c** (82%) as a white solid.

Data for 24c:

<u>mp:</u> 120-121 °C

<u>¹H NMR:</u> (500 MHz, $CDCl_3$)

7.26-7.19 (m, 5 H, HC(6,7,8)), 6.98 (s, 2 H, HC(11)), 4.26-4.23 (m, 1 H, HC(3)), 3.87 (d, J = 6.0 Hz, 1 H, HC(4)), 3.78-3.71 (m, 4 H, HC(1, 13)), 2.95 (br s, 1 H, HOC(3)), 2.88 (sept, J = 7.0 Hz, 1 H, HC(16)), 2.66 (t, J = 4.5 Hz, 1 H, HOC(1)), 1.89-1.87 (m, 1 H, HC(2)), 1.67-1.60 (m, 1 H, HC(2)), 1.26 (d, J = 7.0 Hz, 6 H), 1.21 (d, *J* = 6.5 Hz, 6 H), 1.11 (d, *J* = 6.5 Hz, 6 H).

 $\frac{13}{C}$ NMR: (125 MHz, CDCl₃)

153.1, 149.9, 139.0, 128.5, 128.3, 127.2, 126.7, 121.7, 73.5 (C(3)), 61.4 (C(1)), 56.5 (C(4)), 36.4 (C(2)), 34.2, 34.1, 24.5, 24.4, 23.9, 23.8.

- IR: (NaCl plates, CH₂Cl₂)
 3353 (m, br), 3195 (w), 3060 (w), 3028 (w), 2960 (s), 2927 (m), 2868 (m), 1596 (w), 1560 (w), 1493 (w), 1461 (m), 1450 (w), 1421 (w), 1382 (w), 1361 (w), 1310 (w), 1152 (w), 1068 (m), 1054 (m), 1029 (w), 876 (w), 750 (w), 698 (m), 668 (w), 556 (w).
- $\underline{MS:} \quad (EI, 70 \text{ eV})$

448.2 (4.6, M⁺), 286.1 (13.6), 285.1 (12.1), 284.1 (75.2), 282.1 (37.7), 281.1 (14.5), 280.1 (14.2), 203.2 (31.4), 119.1 (12.1), 117.1 (10.8), 91.1 (100.0).

- <u>HRMS:</u> calcd for $C_{25}H_{36}O_2Se: 448.1881$, found: 448.1874
 - <u>TLC:</u> $R_f 0.36$ (hexanes/EtOAc, 3/2) [UV]
- <u>Opt. Rot.:</u> $[\alpha]_{D}^{24} + 264.8 (c = 0.18, EtOH)$

Preparation of (3*R*,4*S*)-4-Phenyl-4-[[4-(trifluoromethyl)phenyl]seleno]butane-1,3-diol (24d) (Scheme 10)



Following General Procedure 1, to an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added 1,2-bis(4-trifluoromethylphenyl)diselane (336 mg, 0.75 mmol, 0.75

equiv), and sodium borohydride (56.7 mg, 1.50 mmol, 1.50 equiv). The flask was cooled to 0 °C (the ice bath temperature) and 2.5 mL of EtOH was added under an atmosphere of nitrogen. The solution was stirred at 0 °C for 0.5 h and then the ice bath was removed. After 10 min of stirring at room temperature, a solution of the epoxy alcohol (23) (164 mg, 1.00 mmol) in EtOH (2.5 mL) was added and the resulting solution was heated to 40 °C (oil bath temperature) for 14 h. After workup, the crude residue was purified by column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 3/2) to afford 277 mg of 24d (71%) as a white solid.

Data for 24d:

<u>mp:</u> 63.5-64.5 °C

 1 <u>H NMR:</u> (500 MHz, CDCl₃)

7.54 (d, *J* = 8.5 Hz, 2 H, HC(11)), 7.46 (d, *J* = 8.5 Hz, 2H, HC(10)), 7.37-7.25 (m, 5 H, HC(6,7,8)), 4.39 (d, *J* = 6.0 Hz, 1H, HC(4)), 4.33-4.29 (m, 1 H, HC(3)), 3.88-3.81 (m, 2H, H₂C(1)), 2.83 (d, *J* = 3.0 Hz, 1 H, HOC(3)), 2.19 (t, *J* = 5.5 Hz, 1 H, HOC(1)), 1.95-1.89 (m, 1 H, HC(2)), 1.72-1.64 (m, 1 H, HC(2)).

- ¹³<u>C NMR:</u> (125 MHz, CDCl₃) 138.6, 134.6, 134.4, 129.9 (q, J = 32 Hz, C(12)), 129.3, 128.8, 128.0, 125.9 (q, J = 3.6 Hz, C(11)), 124.2 (q, J = 270 Hz, C(13)), 73.6 (C(3)), 61.4 (C(1)), 55.9 (C(4)), 36.7 (C(2)).
- $\frac{^{19}\text{F NMR:}}{(470 \text{ MHz}, \text{CDCl}_3)}$

-63.08 (s, CF₃(13))

<u>IR:</u> (NaCl plates, CH_2Cl_2)

3371 (m, br), 3063 (w), 3028 (w), 2946 (w), 2886 (w), 1602 (m), 1494 (w), 1452 (w), 1397 (m), 1327 (s), 1165 (m), 1124 (s), 1102 (m), 1078 (s), 1057 (m), 1014

(m), 897 (w), 831 (w), 774 (w), 761 (w), 701 (m), 669 (w), 592 (w), 552 (w), 519 (w).

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 \begin{array}{lll} \underline{\text{MS:}} & (\text{EI}, 70 \text{ eV}) \\ & & 390.0 \ (2.0, \text{M}^{+}), 373.0 \ (13.6), 235.1 \ (16.9), 225.1 \ (14.5), 166.1 \ (21.3), 165.1 \ (86.3), \\ & 147.1 \ (36.7), 145.0 \ (12.3), 129.1 \ (13.3), 120.1 \ (13.7), 119.0 \ (43.6), 117.1 \ (21.5), \\ & 115.1 \ (17.1), 105.1 \ (18.4), 92.0 \ (26.9), 91.1 \ (100.0), 77.0 \ (13.9), 65.1 \ (14.0) \ . \\ \hline \underline{\text{HRMS:}} & \text{calcd for } \mathbf{C}_{17}\mathbf{H}_{17}\mathbf{F}_{3}\mathbf{O}_{2}\mathbf{Se:} \ 390.0346, \text{ found:} \ 390.0340 \\ \hline \underline{\text{TLC:}} & R_{f} \ 0.19 \ (\text{hexanes/EtOAc}, 3/2) \ [\text{UV}] \end{array}
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<u>Opt. Rot.:</u> $[\alpha]_D^{24} + 239.5 (c = 0.184, EtOH)$

Preparation of (3*R*,4*S*)-4-Phenyl-4-[[2-(trifluoromethyl)phenyl]seleno]butane-1,3-diol (24e) (Scheme 10)



Following General Procedure 1, to an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added 1,2-bis(2-trifluoromethylphenyl)diselane (336 mg, 0.75 mmol, 0.75 equiv), and sodium borohydride (56.7 mg, 1.50 mmol, 1.50 equiv). The flask was cooled to 0 °C (the ice bath temperature) and 2.5 mL of EtOH was added under an atmosphere of nitrogen. The solution was stirred at 0 °C for 0.5 h and then the ice bath was removed. After 10 min of stirring at room temperature, a solution of the epoxy alcohol (**23**) (164 mg, 1.00 mmol) in EtOH (2.5 mL) was added and the resulting solution was heated to 40 °C (oil bath temperature) for 14 h. After workup the crude residue was purified by column chromatography (silica gel, 25 mm x

21.5 cm column, hexanes/EtOAc, 1/1) to afford 289 mg of 24e (74%) as a clear viscous oil.

Data for 24e:

 1 <u>H NMR:</u> (500 MHz, CDCl₃)

7.68 (d, *J* = 7.5 Hz, 1 H), 7.55 (d, *J* = 7.0 Hz, 1 H), 7.39-7.24 (m, 7 H), 4.41 (d, *J* = 5.5 Hz, 1 H, HC(4)), 4.25-4.21 (m, 1 H, HC(3)), 3.80-3.78 (m, 2 H, HC(1)), 2.94 (d, *J* = 2.5 Hz, 1 H, HOC(3)), 2.35 (t, *J* = 4.5 Hz, 1 H, HOC(1)), 1.86-1.81 (m, 1 H, HC(2)), 1.69-1.62 (m, 1 H, HC(2)).

 $\frac{13}{C}$ NMR: (125 MHz, CDCl₃)

137.9, 137.5, 132.8 (q, *J* = 29 Hz, C(10)), 131.9, 129.2, 128.5, 127.9, 127.8, 127.7, 126.8 (q, *J* = 5.5 Hz, C(11)), 123.7 (q, *J* = 272 Hz, C(15)), 73.1 (C(3)), 61.2 (C(1)), 56.5 (C(4)), 36.3 (C(2)).

 $\frac{^{19}\text{F NMR:}}{(470 \text{ MHz, CDCl}_3)}$

-60.32 (s, CF₃(15))

<u>IR:</u> (NaCl plates, CH_2Cl_2)

3371 (w, br), 3064 (w), 3028 (w), 2916 (w), 2879 (w), 1591 (w), 1571 (w), 1493 (w), 1468 (w), 1450 (w), 1434 (w), 1312 (w), 1259 (w), 1172 (m), 1127 (m), 1109 (m), 1088 (m), 1027 (m), 765 (m), 731 (w), 701 (m), 642 (w), 527 (w), 510 (w).

MS: (ESI)

413.0 (71.4, M+Na⁺), 397.1 (17.1), 373.0 (70.2), 355.0 (55.9), 282.3 (100.0), 165.1 (15.4), 147.1 (31.4), 129.1 (18.3).

- <u>HRMS:</u> calcd for $C_{17}H_{17}F_3O_2$ SeNa: 413.0247, found: 413.0244
- <u>TLC:</u> $R_f 0.32$ (hexanes/EtOAc, 1/1) [UV]
- <u>Opt. Rot.:</u> $[\alpha]_D^{24} + 237.3 (c = 0.18, EtOH)$



Preparation of (3R,4S)-4-[(2-Nitrophenyl)seleno]-4-phenylbutane-1,3-diol (24f) (Scheme 10)

Following General Procedure 1, to an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar was added 1,2-bis(2-nitrophenyl)diselane (218 mg, 0.54 mmol, 0.62 equiv), and sodium borohydride (49.0 mg, 1.29 mmol, 1.50 equiv). The flask was cooled to 0 °C (the ice bath temperature) and 2.3 mL of EtOH was added under an atmosphere of nitrogen. The solution was stirred at 0 °C for 0.5 h and then the ice bath was removed. After 10 min of stirring at room temperature, a solution of the epoxy alcohol (23) (142 mg, 1.00 mmol) in EtOH (2.0 mL) was added and the resulting solution was heated to 40 °C (oil bath temperature) for 16 h. After workup the crude residue was purified by column chromatography (silica gel, 25 mm x 28 cm column, TBME/hexanes, 7/3) to afford 268 mg of 24f (85%) as a yellow solid.

Data for 24f:

<u>mp:</u> 49-51 °C

<u>¹H NMR:</u> (500 MHz, $CDCl_3$)

8.16 (d, J = 8.5 Hz, 1 H, HC(11)), 7.55-7.51 (m, 3H), 7.39 (t, J = 7.2 Hz, 1 H), 7.33
(t, J = 7.0 Hz, 2 H), 7.28-7.25 (m, 2 H), 4.53 (d, J = 4.5 Hz, 1 H, HC(4)), 4.38 (br s, 1 H, HC(1)), 3.80 (br s, 2 H, HC(1)), 3.06 (d, J = 3.0 Hz, 1 H, HOC(3)), 2.41 (s br, 1 H, HOC(1)), 1.89-1.86 (m, 1 H, HC(2)), 1.69-1.62 (m, 1 H, HC(2)).

 $\frac{13}{C}$ NMR: (125 MHz, CDCl₃)

147.5, 137.7, 133.4, 131.7, 130.6, 129.5, 128.8, 127.9, 126.1, 126.0, 73.7 (C(3)), 61.2 (C(1)), 53.6 (C(4)), 36.5 (C(2)).

(NaCl plates, CH₂Cl₂) 3340 (m, br), 2950 (w), 1589 (m), 1565 (w), 1510 (s), 1451 (m), 1329 (s), 1303 (s), 1253 (w), 1096 (w), 1053 (m), 1036 (m), 852 (w), 752 (w), 728 (m), 702 (s), 667 (w), 645 (w), 553 (w), 506 (w).

MS: (ESI)

IR:

390.0 (100, M + Na⁺), 201.9 (12.9).

<u>HRMS:</u> calcd for $C_{16}H_{17}NO_4SeNa: 390.0220$, found: 390.0224

<u>TLC:</u> $R_f 0.14$ (TBME/hexanes, 7/3) [UV]

<u>Opt. Rot.</u>: $[\alpha]_D^{24} + 173.8 (c = 0.355, CHCl_3)$

Preparation of (3*R*,4*S*)-4-[[2,6-Bis(trifluoromethyl)phenyl]seleno]-4-phenylbutane-1,3-diol (24g) (Scheme 10)



Following General Procedure 1, to an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added 1,2-bis(2,6-bis-trifluoromethylphenyl)diselane (438 mg, 0.75 mmol, 0.75 equiv), and sodium borohydride (56.7 mg, 1.50 mmol, 1.50 equiv). The flask was cooled to 0 °C (the ice bath temperature) and 2.5 mL of EtOH was added under an atmosphere of nitrogen. The solution was stirred at 0 °C for 0.5 h and then the ice bath was removed. After 10 min of stirring at room temperature, a solution of the epoxy alcohol (23) (164 mg, 1.00 mmol) in EtOH (2.5 mL) was added and the resulting solution was heated to 40 °C (oil bath temperature) for 13 h. After workup the crude residue was purified by column chromatography (silica gel, 25 mm x

26.5 cm column, hexanes/EtOAc, 3/2) to afford 380 mg of 24g (82%) as a white solid.

Data for 24g:

<u>mp:</u> 127-128 °C

<u>¹H NMR:</u> (500 MHz, $CDCl_3$)

7.91 (d, *J* = 8.0 Hz, 2 H, HC(11)), 7.58 (t, *J* = 8.0 Hz, 1 H, HC(12)), 7.28-7.20 (m, 5 H, HC(6,7,8)), 4.37 (d, *J* = 5.0 Hz, 1 H, HC(4)), 4.28-4.25 (m, 1 H, HC(3)), 3.72-3.69 (m, 2 H, HC(1)), 3.10 (s br, 1 H, HOC(3)), 2.48 (t, *J* = 5.5 Hz, 1 H, HOC(1)), 1.60-1.47 (m, 2 H, HC(2)).

 $\frac{^{13}\text{C NMR:}}{(125 \text{ MHz}, \text{CDCl}_3)}$

137.4 (q, *J* = 29 Hz, C(10)), 137.3, 130.5 (q, *J* = 6.4 Hz, C(11)), 129.5, 128.9, 128.3, 127.7, 126.4, 123.2 (q, *J* = 274 Hz, C(13)), 72.9 (C(3)), 61.1 (C(1)), 58.4 (C(4)), 36.5 (C(2)).

 19 F NMR: (470 MHz, CDCl₃)

-58.27 (s, CF₃(13))

- IR: (NaCl plates, CH₂Cl₂)
 3382 (w, br), 3030 (w), 2957 (w), 2929 (w), 2887 (w), 1580 (w), 1494 (w), 1454 (w), 1422 (w), 1332 (m), 1288 (s), 1199 (m), 1184 (m), 1159 (s), 1138 (s), 1116 (m), 1065 (m), 994 (w), 899 (w), 815 (m), 767 (w), 737 (w), 702(m), 675 (m), 654 (w).
- MS: (ESI)

481.0 (100, M + Na⁺), 479.0 (50), 465.0 (34), 463.0 (16), 441.0 (81), 439.0 (42), 423.0 (11), 411.0 (15), 165.1 (14), 147.1 (37), 129.1 (32).

<u>HRMS:</u> calcd for $C_{18}H_{16}F_6O_2$ SeNa: 481.0117, found: 481.0123

<u>TLC:</u> $R_f 0.35$ (hexanes/EtOAc, 3/2) [UV]

<u>Opt. Rot.:</u> $[\alpha]_D^{24} + 295.4$ (c = 0.186, EtOH)

General Procedure 2. Synthesis of Carbonates.

Preparation of (4*R*)-4-[(*S*)-Phenyl(phenylseleno)methyl]-1,3-dioxan-2-one (25a) (Scheme 10)



To an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added diol **24a** (149 mg, 0.465 mmol), and dry CH_2Cl_2 (2.3 mL). A solution of carbonyl diimidazole (113 mg, 0.698 mmol, 1.50 equiv) and 4-dimethylaminopyridine (14.2 mg, 0.116 mmol, 0.25 equiv) in CH_2Cl_2 (2.3 mL) was added under an atmosphere of nitrogen. The resulting solution was stirred at room temperature for 19 h. The reaction mixture was transferred to a 125-mL separatory funnel with an additional 10 mL of CH_2Cl_2 . The mixture was washed with H_2O (1 x 20 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organic extracts were washed with brine (1 x 25 mL) and dried over MgSO₄. The solution was filtered and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 3/2) to afford 103 mg of carbonate **25a** (64%) as a white solid.

Data for 25a:

<u>mp:</u> 120.5-121.5 °C

 1 <u>H NMR:</u> (500 MHz, CDCl₃)

7.47 (dd, *J* = 8.0, 1.0 Hz, 2 H), 7.33-7.24 (m, 8 H), 4.93 (ddd, *J* = 10.5, 6.5, 3.5 Hz, 1 H, HC(4)), 4.38.4.32 (m, 3 H, HC(6,7)), 2.31-2.26 (m, 1 H, HC(5)), 1.99-1.90 (m, 1 H, HC(5)).

- ¹³C NMR: (125 MHz, CDCl₃)
 148.2 (C(2)), 137.4, 135.3, 129.2, 128.7, 128.6, 128.5, 128.4, 127.9, 80.9 (C(4)),
 66.5 (C(6)), 51.8 (C(7)), 26.2 (C(5)).
 - <u>IR:</u> (NaCl plates, CH₂Cl₂) 3057 (w), 3021 (w), 2916 (w), 2851 (w), 1744 (m), 1578 (w), 1492 (w), 1476 (w), 1450 (w), 1436 (w), 1403 (w), 1248 (w), 1227 (w), 1116 (m), 1021 (w), 996 (w), 763 (w), 742 (w), 692 (w), 560 (w), 542 (w).
 - $\underline{MS:} \quad (EI, 70 \text{ eV})$

348.0 (5.1, M⁺), 304.0 (13.3), 198.0 (12.2), 156.9 (14.3), 147.1 (42.7), 146.1 (53.9), 118.1 (17.4), 117.1 (73.0), 115.0 (26.8), 105.0 (38.5), 91.1 (100.0), 78.0 (17.8), 77.0 (32.3), 51.0 (12.0).

- <u>HRMS:</u> calcd for $C_{17}H_{16}O_3Se: 348.0265$, found: 348.0247
 - <u>TLC:</u> $R_f 0.49$ (hexanes/EtOAc, 1/1) [UV]
- <u>Opt. Rot.</u>: $[\alpha]_D^{24} + 155.5 (c = 0.164, CHCl_3)$
- <u>Analysis:</u> $C_{17}H_{16}O_3Se(348.0265)$

Calcd: C, 58.80; H, 4.64%

Found: C, 58.67; H, 4.73%

Preparation of (4*R*)-4-[(*S*)[(4-Methoxyphenyl)seleno]phenylmethyl]-1,3-dioxan-2-one (25b)

(Scheme 10)



Following General Procedure 2, A solution of carbonyl diimidazole (83.0 mg, 0.511 mmol, 1.50 equiv) and 4-dimethylaminopyridine (10.4 mg, 0.085 mmol, 0.25 equiv) in CH_2Cl_2 (1.7 mL) was added to a solution of diol **24b** (120 mg, 0.340 mmol) in CH_2Cl_2 (1.7 mL) to yield after column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 1/1) 75.8 mg of carbonate **25b** (59%) as a light yellow solid.

Data for 25b:

<u>mp:</u> 125-126 °C

 $\frac{1}{\text{H NMR:}}$ (500 MHz, CDCl₃)

7.36 (d, *J* = 8.5 Hz, 2H, HC(13)), 7.31-7.22 (m, 5H, HC(9,10,11)), 6.78 (d, *J* = 8.5 Hz, 2H, HC(14)), 4.88 (ddd, *J* = 10.5, 6.5, 3.0 Hz, 1 H, HC(4)), 4.39-4.32 (m, 2 H, HC(6)), 4.21 (d, *J* = 6.5 Hz, 1 H, HC(7)), 3.80 (s, 3 H, HC(16)), 2.32-2.28 (m, 1 H, HC(5)), 1.99-1.91 (m, 1 H, HC(5)).

¹³C NMR: (125 MHz, CDCl₃)
160.1 (C(15)), 148.3 (C(2)), 137.7, 137.4, 128.6, 128.5, 127.7, 118.4 (C(12)), 114.8 (C(14)), 80.5 (C(4)), 66.5 (C(6)), 55.2 (C(16)), 51.9 (C(7)), 26.3 (C(5)).

<u>IR:</u> (NaCl plates, CH₂Cl₂) 3057 (w), 3028 (w), 2936 (w), 2907 (w), 28294 (w), 1747 (s), 1588 (w), 1490 (m), 1454 (w), 1405 (m), 1286 (w), 1247 (s), 1181 (m), 1118 (s), 1026 (w), 825 (w), 791 (w), 766 (w), 700 (w), 681 (w), 603 (w), 564 (w), 553 (w), 520 (w) 509 (m).

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

378.0 (3.5, M⁺), 334.0 (10.1), 226.0 (16.1), 188.0 (26.8), 187.0 (30.8), 186.0 (14.3), 185.0 (19.1), 184.0 (10.8), 171.9 (10.1), 148.1 (32.0), 147.1 (31.9), 146.1 (18.7), 145.1 (15.4), 131.1 (15.6), 130.1 (68.7), 129.1 (26.2), 118.1 (18.9), 117.1 (90.4), 116.1 (20.5), 115.1 (58.7), 108.1 (41.1), 105.0 (43.0), 93.1 (12.0), 92.0 (12.5), 91.1 (100.0), 85.9 (10.7), 84.0 (11.2), 78.1 (16.9), 77.0 (33.4), 65.1 (17.9), 63.1 (16.7), 57.1 (19.5), 55.1 (13.2), 51.0 (16.0)

- <u>HRMS:</u> calcd for $C_{18}H_{18}O_4$ Se: 378.0370, found: 378.0363
 - <u>TLC:</u> $R_f 0.42$ (hexanes/EtOAc, 1/1) [UV]
- <u>Opt. Rot.</u>: $[\alpha]_D^{24} + 154.2 (c = 0.156, CHCl_3)$
- <u>Analysis:</u> $C_{18}H_{18}O_4Se(378.0370)$

Calcd: C, 57.30; H, 4.81%

Found: C, 57.58; H, 4.91%

Preparation of (4R)-4-[(S)-Phenyl[[2,4,6-tri(propan-2-yl)phenyl]seleno]methyl]-1,3-dioxan-

2-one (25c) (Scheme 10)



Following General Procedure 2, A solution of carbonyl diimidazole (145 mg, 0.897 mmol, 1.50 equiv) and 4-dimethylaminopyridine (18.3 mg, 0.149 mmol, 0.25 equiv) in CH₂Cl₂

(3.0 mL) was added to a solution of diol **24c** (268 mg, 0.598 mmol) in CH_2Cl_2 (3.0 mL) to yield after column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 65/35) 158 mg of carbonate **25c** (56%) as a white solid.

Data for 25c:

<u>mp:</u> 178-179 °C

 1 <u>H NMR:</u> (500 MHz, CDCl₃)

7.30-7.23 (m, 5 H, HC(9,10,11)), 6.99 (s, 2 H, HC(14)), 4.85 (ddd, J = 11, 5.0, 1.5 Hz, 1 H, HC(4)), 4.33-4.31 (m, 2 H, HC(6)), 3.92 (d, J = 5.5 Hz, 1 H, HC(7)), 3.77 (sept, J = 7.0 Hz, 2 H, HC(16)), 2.89 (sept, J = 7.0 Hz, 1 H, HC(19)), 2.13-2.09 (m, 1 H, HC(5)), 1.91-1.82 (m, 1 H, HC(5)), 1.26 (d, J = 6.5 Hz, 6 H), 1.21 (d, J = 7.0 Hz, 6 H), 1.10 (d, J = 6.5 Hz, 6 H).

 $\frac{13}{C}$ NMR: (125 MHz, CDCl₃)

153.5, 150.4, 148.3, 137.2, 128.6, 128.5, 127.8, 126.5, 121.9, 80.5 (C(4)), 66.5 (C(6)), 52.0 (C(7)), 34.2, 34.1, 26.2 (C(5)), 24.6, 24.5, 23.9.

IR: (NaCl plates, CH₂Cl₂)
2960 (m), 2929 (w), 2865 (w), 1753 (s), 1595 (w), 1560 (w), 1492 (w), 1482 (w), 1461 (w), 1454 (w), 1404 (m), 1383 (w), 1362 (w), 1308 (w), 1248 (w), 1227 (w), 1181 (m), 1119 (s), 1057 (w), 940 (w), 879 (w), 766 (w), 748 (w), 700 (m), 560 (w).

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

474.2 (5.1, M⁺), 282.2 (43.7), 282.1 (31.4), 281.1 (12.0), 280.1 (14.0), 242.1 (26.4), 240.1 (14.6), 239.1 (12.2), 226.0 (16.1), 204.2 (14.8), 203.2 (90.1), 199.0 (18.4), 197.0 (22.5), 195.0 (10.9), 148.1 (15.2), 147.1 (100.0), 146.1 (27.0), 145.1 (16.1), 129.1 (15.1), 128.1 (10.3), 119.1 (12.6), 117.1 (45.5), 116.1 (10.2), 115.1 (21.1), 105.1 (53.1), 91.1 (88.1), 77.1 (17.4), 57.2 (15.2).

- <u>HRMS:</u> calcd for $C_{26}H_{34}O_3Se: 474.1673$, found: 474.1682
 - <u>TLC:</u> $R_f 0.43$ (hexanes/EtOAc, 65/35) [UV]
- <u>Opt. Rot.</u>: $[\alpha]_D^{24} + 216.6 (c = 0.178, CHCl_3)$
- <u>Analysis:</u> $C_{26}H_{34}O_3Se(474.1673)$
 - Calcd: C, 65.95; H, 7.24%
 - Found: C, 66.01; H, 7.44%

Preparation of (4*R*)-4-[(*S*)-Phenyl[[4-(trifluoromethyl)phenyl]seleno]methyl]-1,3-dioxan-2one (25d) (Scheme 10)



Following General Procedure 2, A solution of carbonyl diimidazole (109 mg, 0.674 mmol, 1.50 equiv) and 4-dimethylaminopyridine (13.7 mg, 0.112 mmol, 0.25 equiv) in CH_2Cl_2 (2.2 mL) was added to a solution of diol **24d** (175 mg, 0.449 mmol) in CH_2Cl_2 (2.2 mL) to yield after column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 1/1) 130 mg of carbonate **25d** (70%) as a white solid.

Data for 25d:

<u>mp:</u> 112.5-113.5 °C

<u>¹H NMR:</u> (500 MHz, $CDCl_3$)

7.55 (d, *J* = 8.0 Hz, 2 H, HC(14)), 7.47 (d, *J* = 8.0 Hz, 2 H, HC(13)), 7.34-7.28 (m,

5 H, HC(9,10,11)), 4.95 (ddd, *J* = 11, 5.5, 3.5 Hz, 1 H, HC(4)), 4.42 (d, *J* = 5.5 Hz, 1 H, HC(7)), 4.36-4.34 (m, 2 H, HC(6)), 2.22-2.18 (m, 1 H, HC(5)), 1.97-1.88 (m, 1 H, HC(5)).

- ¹³<u>C NMR:</u> (125 MHz, CDCl₃) 148.1 (C(2)), 136.8, 134.6, 133.6, 130.20 (q, J = 32 Hz, C(15)), 128.9, 128.8, 128.2, 125.82 (q, J = 3.6 Hz, C(14)), 123.83 (q, J = 271 Hz, C(16)), 80.9 (C(4)), 66.5 (C(6)), 51.9 (C(7)), 25.9 (C(5))
 - IR: (NaCl plates, CH₂Cl₂)
 3063 (w), 3031 (w), 2979 (w), 2920 (w), 1750 (s), 1601 (m), 1496 (w), 1480 (w), 1454 (w), 1398 (m), 1327 (s), 1251 (m), 1229 (w), 1166 (s), 1121 (s), 1078 (s), 1057 (m), 1014 (m), 831 (w), 766 (w), 702 (m), 692 (w), 593 (w), 563 (w), 540 (w).
 - <u>MS:</u> (EI)

415.9 (2.4, M⁺), 372.0 (19.0), 265.9 (39.1), 263.9 (19.7), 225.9 (10.2), 224.9 (11.7), 197.0 (11.2), 185.0 (30.1), 148.1 (10.3), 147.1 (45.7), 146.1 (82.9), 145.0 (16.8), 127.0 (10.0), 117.0 (51.6), 116.0 (17.0), 115.0 (42.1), 105.0 (51.2), 77.0 (32.5), 65.1 (10.8), 57.1 (13.2), 51.01 (12.8)

- <u>HRMS:</u> calcd for $C_{18}H_{15}F_3O_3Se: 416.0139$, found: 416.0124
 - <u>TLC:</u> $R_f 0.43$ (hexanes/EtOAc, 1/1) [UV]
- <u>Opt. Rot.</u>: $[\alpha]_D^{24} + 178.8 (c = 0.160, CHCl_3)$
- <u>Analysis:</u> $C_{18}H_{15}F_{3}O_{3}Se(416.0139)$

Calcd: C, 52.06; H, 3.64%

Found: C, 52.07; H, 3.58%

Preparation of (4*R*)-4-[(*S*)-Phenyl[[2-(trifluoromethyl)phenyl]seleno]methyl]-1,3-dioxan-2one (25e) (Scheme 10)



Following General Procedure 2, A solution of carbonyl diimidazole (142 mg, 0.877 mmol, 1.50 equiv) and 4-dimethylaminopyridine (17.9 mg, 0.146 mmol, 0.25 equiv) in CH_2Cl_2 (2.9 mL) was added to a solution of diol **24e** (228 mg, 0.585 mmol) in CH_2Cl_2 (2.9 mL) to yield after column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 3/2) 148 mg of carbonate **25e** (61%) as a white solid.

Data for 25e:

<u>mp:</u> 92-93 °C

<u>¹H NMR:</u> (500 MHz, $CDCl_3$)

7.69 (d, *J* = 7.5 Hz, 1 H, HC(14)), 7.48 (d, *J* = 7.5 Hz, 1 H), 7.39 (t, *J* = 8.0 Hz, 1 H), 7.32-7.23 (m, 6 H), 4.97-4.93 (m, 1 H, HC(4)), 4.41 (d, *J* = 6.0 Hz, 1 H, HC(7)), 4.35-4.33 (m, 2 H, HC(6)), 2.22-2.18 (m, 1 H, HC(5)), 1.96-1.87 (m, 1 H, HC(5)).

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<sup>13</sup><u>C NMR:</u> (125 MHz, CDCl<sub>3</sub>)
148.1 (C(2)), 138.3, 136.7, 133.0 (q, J = 29 Hz, C(13)), 132.0, 128.9, 128.7, 128.4,
128.1, 127.0, 126.89 (q, J = 5.5 Hz, C(14)), 123.65 (q, J = 272 Hz, C(18)), 80.9
(C(4)), 66.5 (C(6)), 52.3 (C(7)), 25.9 (C(5))
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 $\frac{^{19}\text{F NMR:}}{(376 \text{ MHz}, \text{CDCl}_3)}$

-60.15 (CF₃(13))

<u>IR:</u> (NaCl plates, CH_2Cl_2)

3057 (w), 3028 (w), 2917 (w), 2851 (w), 1751 (s), 1590 (w), 1475 (w), 1437 (w), 1405 (m), 1311 (s), 1252 (m), 1227 (w), 1173 (m), 1119 (s), 1088 (m), 1026 (m), 957 (w), 765 (m), 730 (w), 701 (m), 682 (w), 642 (w), 564 (w), 527 (w).

<u>MS:</u> (EI, 70 eV

416.0 (2.3, M⁺), 147.1 (29.4), 146.1 (16.8), 117.1 (27.4), 115.0 (19.4), 105.0 (20.3), 91.0 (100.0), 77.0 (10.2).

- <u>HRMS:</u> calcd for $C_{18}H_{15}F_3O_3Se: 416.0139$, found: 416.0125
 - <u>TLC:</u> $R_f 0.25$ (hexanes/EtOAc, 3/2) [UV]
- <u>Opt. Rot.</u>: $[\alpha]_D^{24} + 167.6 (c = 0.164, CHCl_3)$
- <u>Analysis:</u> $C_{18}H_{15}F_{3}O_{3}Se(416.0139)$

Calcd: C, 52.06; H, 3.64%

Found: C, 51.82; H, 3.49%

Preparation of (4*R*)-4-[(*S*)](2-Nitrophenyl)seleno]phenylmethyl]-1,3-dioxan-2-one (25f)

(Scheme 10)



Following General Procedure 2, A solution of carbonyl diimidazole (206 mg, 1.27 mmol, 1.50 equiv) and 4-dimethylaminopyridine (25.8 mg, 0.211 mmol, 0.25 equiv) in CH₂Cl₂ (4.2 mL)

was added to a solution of diol **24f** (310 mg, 0.850 mmol) in CH_2Cl_2 (4.2 mL) to yield after column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 1/1) 185 mg of carbonate **25f** (56%) as a yellow solid. The solid was further purified by recrystallization from CH_2Cl_2 /hexanes to obtain analytically pure product.

Data for 25f:

<u>mp:</u> 159-160 °C

<u>¹H NMR: (500 MHz, CDCl₃)</u>

8.18 (d, J = 8.5 Hz, 1H, HC(14)), 7.56-7.51 (m, 3H), 7.44 (t, J = 7.0 Hz, 1H), 7.397.30 (m, 4H), 5.05-5.01 (m, 1 H, HC(4)), 4.64 (d, J = 4.5 Hz, 1 H, HC(7)), 4.374.35 (m, 2 H, HC(6)), 2.21-2.16 (d, J = 14.5 Hz, 1 H, HC(5)), 2.04-1.96 (m, 1 H, HC(5)).

 $\frac{^{13}\text{C NMR:}}{(125 \text{ MHz}, \text{CDCl}_3)}$

147.9 (C(2)), 147.7, 136.3, 133.6, 130.7, 130.5, 129.3, 129.1, 128.4, 126.6, 126.1, 81.4 (C(4)), 66.5 (C(6)), 50.2 (C(7)), 25.7 (C(5))

- IR: (NaCl plates, CH₂Cl₂)
 3061 (w), 3028 (w), 2979 (w), 2916 (w), 1747 (s), 1589 (m), 1566 (w), 1512 (s), 1478 (w), 1451 (w), 1432 (w), 1405 (m), 1331 (s), 1305 (m), 1250 (m), 1228 (m), 1201 (m), 1184 (m), 1143 (m), 1117 (s), 1036 (w), 956 (w), 852 (w), 783 (w), 766 (w), 730 (m), 703 (m), 681 (w), 647 (w), 564 (w), 540.0 (w), 524 (w), 509 (w).
- <u>MS:</u> (ESI)

416.0 (100.0, M + Na⁺), 414.0 (56.5), 390.0 (11.4), 372.0 (11.4).

- <u>HRMS:</u> calcd for $C_{17}H_{15}NO_5SeNa: 416.0013$, found: 416.0013
 - <u>TLC:</u> $R_f 0.18$ (hexanes/EtOAc, 1/1) [UV]

<u>Opt. Rot.:</u> $[\alpha]_{D}^{24} + 175.8 (c = 0.405, CHCl_{3})$

<u>Analysis:</u> $C_{17}H_{15}NO_5Se(392.26)$

Calcd: C, 52.05; H, 3.85; N, 3.57% Found: C, 52.03; H, 3.59; N, 3.66%

Preparation of (4R)-4-[(S)[[2,6-Bis(trifluoromethyl)phenyl]seleno]phenylmethyl]-1,3-

dioxan-2-one (25g) (Scheme 10)



Following General Procedure 2, A solution of carbonyl diimidazole (121 mg, 0.749 mmol, 1.50 equiv) and 4-dimethylaminopyridine (15.2 mg, 0.125 mmol, 0.25 equiv) in CH_2Cl_2 (2.5 mL) was added to a solution of diol **24g** (228 mg, 0.499 mmol) in CH_2Cl_2 (2.5 mL) to yield after column chromatography (silica gel, 25 mm x 21.5 cm column, hexanes/EtOAc, 65/35) 168 mg of carbonate **25g** (69%) as a white solid.

Data for 25g:

<u>mp:</u> 144-145 °C

 1 <u>H NMR:</u> (500 MHz, CDCl₃)

7.94 (d, *J* = 8.0 Hz, 2 H, HC(14)), 7.63 (t, *J* = 8.0 Hz, 1 H, HC(15)), 7.29-7.20 (m, 5 H, HC(9,10,11)), 5.08 (ddd, *J* = 11, 4.0, 3.0 Hz, 1 H, HC(4)), 4.36-4.28 (m, 3 H, HC(6, 7)), 1.98-1.93 (m, 1 H, HC(5)), 1.88-1.80 (m, 1 H, HC(5)).

 $\frac{13}{C}$ NMR: (125 MHz, CDCl₃)

147.9 (C(2)), 137.4 (q, J = 29 Hz, C(13)), 135.9, 130.5 (q, J = 5.5 Hz, C(14)),

129.8, 128.8, 128.5, 128.2, 125.8, 123.1 (q, *J* = 273 Hz, C(16)), 81.0 (C(4)), 66.4 (C(6)), 53.9 (C(7)), 25.7 (C(5))

¹⁹F NMR: (376 MHz, CDCl₃)

-58.34 (CF₃(16))

- IR: (NaCl plates, CH₂Cl₂)
 3088 (w), 3032 (w), 2980 (w), 2922 (w), 1752 (m), 1582 (w), 1496 (w), 1482 (w), 1454 (w), 1406 (w), 1333 (m), 1288 (m), 1253 (w), 1228 (w), 1202 (w), 1152 (m), 1114 (m), 1066 (w), 912 (w), 814 (w), 767 (w), 737 (m), 702 (m), 675 (m), 537 (w).
- $\underline{MS:} \quad (EI, 70 \text{ eV})$

483.8 (1.5, M⁺), 147.0 (39.5), 117.0 (11.6), 115.0 (10.0), 105.0 (12.2), 91.0 (100.0).

- <u>HRMS:</u> calcd for $C_{19}H_{14}F_6O_3Se: 484.0012$, found: 483.9995
 - <u>TLC:</u> $R_f 0.26$ (hexanes/EtOAc, 65/63) [UV]
- <u>Opt. Rot.</u>: $[\alpha]_D^{24} + 203.3 (c = 0.402, CHCl_3)$
- <u>Analysis:</u> $C_{19}H_{14}F_6O_3Se(484.0012)$

Calcd: C, 47.22; H, 2.92%

Found: C, 47.49; H, 2.83%

General Procedure 3. Synthesis of Racemic Seleno Ethers.



Preparation of (+/-)-trans-3-[(4-Methoxyphenyl)seleno]-2-phenyloxolane (28b)

An oven-dried, 10-mL flask equipped with a magnetic stir bar was charged with 1,2bis(4-methoxyphenyl)diselane (94.2 mg, 0.253 mmol, 0.75 equiv). CH₂Cl₂ (0.5 mL) and SO₂Cl₂ (34.1 mg, 0.253 mmol, 0.75 equiv) were added under an atmosphere of nitrogen and the resulting solution was stirred at room temperature for 15 min. In an oven-dried, 10-mL Schlenk flask equipped with a stir bar was added olefin (*E*)-**29** (50.0 mg, 0.337 mmol) and CH_2Cl_2 (0.55 mL). The flask was cooled to -78 °C and K₂CO₃ (48.9 mg, 0.354 mmol, 1.05 equiv) was added under nitrogen. After 15 min of stirring at -78 °C, the diselenide/SO₂Cl₂ solution was added. The reaction mixture was allowed to warm to room temperature over 4 h and then was stirred for an additional 12 h. The reaction mixture was transferred to a 125-mL separatory funnel with an additional 10 mL of CH₂Cl₂. The mixture was washed with H₂O (1 x 20 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organic extracts were washed with brine (1 x 25 mL) and dried over MgSO₄. The solution was filtered and concentrated on a rotavap (30 °C, 30 mm Hg). The crude residue was purified by column chromatography (silica gel, 25 mm x 25 cm column, hexanes/EtOAc, 91/9) to afford 66.7 mg (59%) of racemic seleno ether **28b** as a clear, yellow oil.

Data for (+/-)-28b:

 $<u>^{1}H NMR</u>:$ (500 MHz, CDCl₃)

7.46 (d, *J* = 8.5 Hz, 2 H, HC(11)), 7.32-7.24 (m, 5 H, HC(7,8,9)), 6.79 (d, *J* = 8.5 Hz, 2 H, HC(12)), 4.80 (d, *J* = 6.5 Hz, 1 H, HC(2)), 4.15-4.11 (m, 1 H, HC(5)), 4.02-3.98 (m, 1 H, HC(5)), 3.82 (s, 3 H, H₃C(14)), 3.45 (dd, *J* = 14.0, 6.0 Hz, 1 H, HC(3)), 2.44-2.37 (m, 1 H, HC(4)), 2.11-2.04 (m, 1 H, HC(4)).

 $\frac{13}{C}$ NMR: (125 MHz, CDCl₃)

159.9, 141.4, 137.5, 128.3, 127.6, 125.9, 118.2 (C(10), 114.7 (C(12)), 85.9 (C(2)), 67.9 (C(5)), 55.3 (C(14)), 47.9 (C(3)), 33.9 (C(4)).

- IR: (NaCl plates, CH₂Cl₂)
 3085 (w), 3062 (w), 3030 (w), 2938 (m), 2869 (m), 2837 (m), 2361 (w), 2342 (w), 1590 (s), 1570 (m), 1490 (s), 1455 (m), 1441 (m), 1401 (w), 1362 (w), 1286 (s), 1247 (s), 1173 (s), 1102 (w), 1028 (s), 1006 (w), 969 (w), 928 (w), 908 (w), 825.5 (m), 793 (w), 756 (m), 700 (s), 600 (w), 521 (w).
- $\underline{MS:} \quad (EI, 70 \text{ eV})$

334.0 (5.9, M⁺), 226.0 (47.0), 187.0 (52.3), 171.9 (12.3), 147.1 (85.3), 117.1 (27.0), 105.0 (100.0), 91.0 (74.7), 77.0 (39.9).

- <u>HRMS:</u> calcd for $C_{17}H_{18}O_2$ Se: 334.0472, found: 334.0476
 - <u>TLC:</u> $R_f 0.34$ (hexanes/EtOAc, 91/9) [UV]



Preparation of (+/-)-trans-2-Phenyl-3-[[2,4,6-tri(propan-2-yl)phenyl]seleno]oxolane (28c)

Following General Procedure 3, a solution of 1,2-bis(2,4,6-triisopropylphenyl)diselane (286 mg, 0.506 mmol, 0.75 equiv) and SO_2Cl_2 (68.3 mg, 0.506 mmol, 0.75 equiv) in CH_2Cl_2 (1.3 mL) were added at -78 °C to a solution of olefin (*E*)-**29** (100 mg, 0.674 mmol,) and K_2CO_3 (112 mg, 0.810 mmol, 1.20 equiv) in CH_2Cl_2 (2.0 mL) to yield after column chromatography (silica gel, 25 mm x 25 cm column, hexanes/EtOAc, 97/3) 218 mg (75%) of racemic seleno ether **28c** as a clear, colorless oil.

Data for (+/-)-28c:

 1 <u>H NMR:</u> (500 MHz, CDCl₃)

7.29-7.22 (m, 3 H), 7.16 (d, J = 7.0 Hz, 2 H), 7.01 (s, 2 H, HC(11)), 4.83 (d, J = 6.0 Hz, 1 H, HC(2)), 4.20-4.12 (m, 2 H, H₂C(5)), 3.81 (sept, J = 6.5 Hz, 2 H, HC(17)), 3.35-3.31 (m, 1H, HC(3)), 2.91 (sept, J = 7.0 Hz, 1H, HC(14)), 2.43-2.35 (m, 1H, HC(4)), 2.14-2.08 (m, 1H, HC(4)), 1.28 (dd, J = 7.0, 1.0 Hz, 6H), 1.16 (d, J = 6.5 Hz, 12H).

<u>IR:</u> (NaCl plates, neat) 3062 (w), 3034 (w), 2960 (s), 2927 (s), 2868 (s), 1595 (m), 1562 (w), 1535 (w), 1494 (w), 1462 (s), 1422 (m), 1383 (m), 1362 (m), 1309 (w), 1247 (w), 1166 (m), 1101 (w), 1084 (m), 1067 (s), 1028 (m), 961 (w), 935 (w), 906 (w), 877 (m), 752 (m), 734 (m), 699 (s), 650 (w), 622 (w), 516 (w).

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

430.2 (9.6, M⁺), 284.1 (23.8), 282.1 (15.0), 242.1 (25.8), 240.1 (13.0), 226.0 (17.0), 204.2 (12.1), 203.2 (79.6), 199.0 (10.0), 197.0 (13.9), 148.1 (10.2), 147.1 (100.0), 146.1 (26.8), 145.1 (13.2), 117.1 (13.7), 105.0 (44.6), 91.1 (40.7), 77.1 (13.7).

<u>HRMS:</u> calcd for $C_{25}H_{34}OSe: 430.1775$, found: 430.1767

<u>TLC:</u> $R_f 0.41$ (hexanes/EtOAc, 97/3) [UV]

Preparation of (+/-)-trans-2-Phenyl-3-[[4-(trifluoromethyl)phenyl]seleno]oxolane (28d)



Following General Procedure 3, a solution of 1,2-bis(4-trifluoromethylphenyl)diselane (227 mg, 0.506 mmol, 0.75 equiv) and SO₂Cl₂ (68.3 mg, 0.506 mmol, 0.75 equiv) in CH₂Cl₂ (1.3 mL) were added at -78 °C to a solution of olefin (*E*)-**29** (100 mg, 0.674 mmol) and K₂CO₃ (112 mg, 0.810 mmol, 1.20 equiv) in CH₂Cl₂ (2.0 mL) to yield after column chromatography (silica gel, 25 mm x 24 cm column, hexanes/EtOAc, 95/5) 181 mg (72%) of racemic seleno ether **28d** as a clear colorless oil.

Data for (+/-)-28d:

 $\frac{1}{\text{H NMR:}}$ (500 MHz, CDCl₃)

7.46 (d, *J* = 8.5 Hz, 2 H, HC(12)), 7.41 (d, *J* = 8.5 Hz, 2 H, HC(11)), 7.32-7.26 (m, 5 H, HC(7, 8, 9)), 4.83 (d, *J* = 7.0 Hz, 1 H, HC(2)), 4.23-4.19 (m, 1 H, HC(5)), 4.08 (dd, *J* = 14.0, 6.5 Hz, 1 H, HC(5)), 3.66 (dd, *J* = 14.0, 6.5 Hz, 1 H, HC(3)), 2.60-2.53 (m, 1 H, HC(4)), 2.17-2.11 (m, 1H, HC(4)).

 $\frac{13}{C}$ NMR: (125 MHz, CDCl₃)

140.6, 134.4, 133.2, 129.3 (q, *J* = 32 Hz, C(13)), 128.4, 127.9, 125.9, 125.6 (q, *J* = 3.7 Hz, C(12)), 123.9 (q, *J* = 271 Hz, C(14)), 86.4 (C(2)), 67.8 (C(5)), 47.5 (C(3)), 34.1 (C(4)).

 $\frac{^{19}\text{F NMR:}}{(470 \text{ MHz}, \text{CDCl}_3)}$

-63.1 (F₃C(14)).

IR: (NaCl plates, neat)

3065 (w), 3033 (w), 2976 (w), 2943 (w), 2872 (m), 1602 (s), 1572 (w), 1495 (m), 1454 (m), 1398 (m), 1326 (s), 1280 (w), 1165 (s), 1123 (s), 1078 (s), 1057 (s), 1028 (m), 1014 (s), 972 (w), 929 (w), 908 (w), 826 (m), 774 (w), 756 (m), 700 (s), 689 (m), 631 (w), 592 (w), 534 (w).

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

372.0 (29.8, M⁺), 370.0 (14.8), 266.0 (56.4), 264.0 (26.9), 263.0 (10.1), 262.0 (10.1), 197.0 (12.9), 185.1 (37.4), 147.1 (33.8), 146.1 (100.0), 145.0 (11.6), 135.1 (10.3), 117.1 (21.1), 116.1 (10.6), 115.1 (25.1), 105.0 (46.4), 91.1 (38.0), 77.1 (27.3), 62.1 (32.6).

<u>HRMS:</u> calcd for $C_{17}H_{15}F_3OSe: 372.0240$, found: 372.0228

<u>TLC:</u> $R_f 0.33$ (hexanes/EtOAc, 95/5) [UV]



Preparation of (+/-)-*trans*-2-Phenyl-3-[[2-(trifluoromethyl)phenyl]seleno]oxolane (28e)

Following General Procedure 3, a solution of 1,2-bis(4-trifluoromethylphenyl)diselane (227 mg, 0.506 mmol, 0.75 equiv) and SO₂Cl₂ (68.3 mg, 0.506 mmol, 0.75 equiv) in CH₂Cl₂ (1.3 mL) were added at -78 °C to a solution of olefin (*E*)-**29** (100 mg, 0.674 mmol) and K₂CO₃ (112 mg, 0.810 mmol, 1.20 equiv) in CH₂Cl₂ (2.0 mL) to yield after column chromatography (silica gel, 25 mm x 24 cm column, hexanes/EtOAc, 95/5) 163 mg (65%) of racemic seleno ether **28e** as a clear oil.

Data for (+/-)-28e:

 1 <u>H NMR:</u> (500 MHz, CDCl₃)

7.65 (d, *J* = 8.0 Hz, 1 H, HC(12)), 7.44 (d, *J* = 7.5 Hz, 1 H), 7.32-7.24 (m, 7 H), 4.88 (d, *J* = 6.0 Hz, 1 H, HC(2)), 4.24-4.20 (m, 1 H, HC(5)), 4.14-4.09 (m, 1 H, HC(5)), 3.71 (dd, *J* = 13.5, 6.0 Hz, 1 H, HC(3)), 2.56-2.49 (m, 1 H, HC(4)), 2.16-2.10 (m, 1 H, HC(4)).

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\frac{^{13}\text{C NMR:}}{(125 \text{ MHz}, \text{CDCl}_3)}
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140.9, 135.8, 132.0 (q, *J* = 29 Hz, C(11)), 131.8, 128.5, 128.3, 127.8, 127.2, 126.7 (q, *J* = 5.5 Hz, C(12)), 125.9, 123.7 (q, *J* = 272 Hz, C(16)), 86.2 (C(2)), 67.8 (C(5)), 48.1 (C(3)), 33.8 (C(4)).

 19 F NMR: (470 MHz, CDCl₃)

 $-60.7 (F_3C(16)).$

IR: (NaCl plates, neat)

3064 (w), 3032 (w), 2977 (w), 2943 (w), 2872 (m), 1592 (m), 1571 (w), 1494 (w), 1469 (w), 1444 (m), 1312 (s), 1259 (s), 1171 (s), 1128 (s), 1110 (s), 1088 (s), 1067 (m), 1039 (m), 1027 (s), 972 (w), 929 (w), 908 (w), 761 (s), 729 (m), 699 (s), 683 (m), 642 (m), 596 (w), 571 (w).

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

372.0 (24.6, M⁺), 370.0 (12.3), 268.0 (10.7), 266.0 (62.1), 264.0 (29.4), 263.0 (10.8), 262.0 (11.2), 185.1 (26.0), 147.1 (47.9), 146.1 (100.0), 145.0 (11.9), 117.1 (19.3), 115.1 (24.5), 105.0 (48.9), 91.1 (40.8), 77.0 (27.3), 62.1 (54.5), 61.1 (12.6).

- <u>HRMS:</u> calcd for $C_{17}H_{15}F_3OSe: 372.0240$, found: 372.0242
 - <u>TLC:</u> $R_f 0.27$ (hexanes/EtOAc, 95/5) [UV]

Preparation of (+/-)-trans-2-Phenyl-3-[[2-(trifluoromethyl)phenyl]seleno]oxolane (28g)



Following General Procedure 3, a solution of 1,2-bis(2,6-ditrifluoromethylphenyl)diselane (148 mg, 0.253 mmol, 0.75 equiv) and SO_2Cl_2 (1.02 g, 7.59 mmol, 22.5 equiv) in CH_2Cl_2 (0.5 mL) were added at -78 °C to a solution of olefin (*E*)-**29** (50.0 mg, 0.337 mmol, 1.00 equiv) and K_2CO_3 (46.8 mg, 0.354 mmol, 1.05 equiv) in CH_2Cl_2 (0.26 mL) to yield after column chromatography (hexanes/EtOAc, 90/10) 40 mg (27%) of racemic
seleno ether 28g as a clear yellow oil.

Data for (+/-)-28g:

¹<u>H NMR:</u> (500 MHz, CDCl₃) 7.91 (d, J = 8.0 Hz, 2 H, HC(12)), 7.58 (t, J = 8.0 Hz, 1 H, HC(13)), 7.26-7.15 (m, 5 H), 4.94 (d, J = 5.4 Hz, 1 H, HC(2)), 4.17-4.13 (m, 1 H), 4.08 (dd, J = 15.5, 8.0 Hz, 1 H), 3.78 (dd, J = 12.5, 6.0 Hz, 1H), 2.28-2.20 (m, 1 H), 2.04-1.98 (m, 1 H).

Preparation of (2S,3S)-Tetrahydro-2-phenyl-2-furanol (27) (Scheme 11)



To an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added triol **26** (177 mg, 0.97 mmol), and pyridine (1.0 mL). The solution was cooled to -10 °C (NaCl/ice bath temperature) and a solution of *p*-toluenesulfonyl chloride (185 mg, 0.97 mmol, 1.00 equiv) in pyridine (1.71 mL) was added slowly over 45 min. The reaction mixture was stirred at -10 °C for 3h 15 min. The reaction mixture was poured onto ice and 2 N HCl (10 mL) was added. The solution was then transferred to a 125-mL separatory funnel and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4 , filtered concentrated on the rotavap (30 °C, 30 mm Hg), and dried under high vacuum. ¹H NMR spectroscopic analysis of the crude product showed complete conversion of **26** to **26-I**. The crude product was used for the next step without further purification.

To an oven-dried, 25-mL, Schlenk flask equipped with a magnetic stir bar, was added sodium hydride (58.2 mg, 2.43 mmol, 2.50 equiv) in the glove box. The flask was attached to the

manifold and THF (6 mL) was added to it. The suspension was cooled to 0 °C and a solution of **26-I** in THF (6 mL) was added to it dropwise. The resulting solution was stirred at 0 °C for 1.5 h and then stirred at room temperature for 13 h. Satd. aq. NH₄Cl (10 mL) was added and then the reaction mixture was transferred to a 125-mL separatory funnel and extracted with Et_2O (3 x 15 mL). The combined organic extracts were washed with brine (30 mL), dried over Na₂SO₄, filtered, and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by column chromatography (silica gel, 25 mm x 24 cm column, hexanes/TBME, 3/2) to afford 63.2 mg of **27** (40% over two steps) as a clear oil.

Data for 27:

<u>¹H NMR:</u> (500 MHz, $CDCl_3$)

7.38-7.26 (m, 5 H, HC(6, 7, 8)), 4.86 (d, *J* = 3.5 Hz, 1H, HC(2)), 4.37 (br s, 1 H), 4.24 (dd, *J* = 16.5, 8.5 Hz, 1 H, HC(5)), 4.03-3.99 (m, 1 H, HC(5)), 2.29-2.22 (m, 1 H, HC(4)), 2.14-2.09 (m, 1 H, HC(4)), 1.34 (br s, 1H, HOC).

 $\frac{13}{C}$ NMR: (125 MHz, CDCl₃)

136.9, 128.4, 127.8, 126.7, 84.9 (C(2)), 73.5 (C(3)), 66.9 (C(5)), 34.7 (C(4)).

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

164.1 (17.7, M⁺), 120.1 (18.4), 108.1 (12.2), 107.1 (100.0), 105.0 (15.0), 91.1 (17.1), 79.1 (45.5), 77.0 (26.3), 58.1 (12.2), 57.1 (24.9), 51.1 (11.0).

- <u>HRMS:</u> calcd for $C_{10}H_{12}O_2$: 164.0837, found: 164.0844
 - <u>TLC:</u> $R_f 0.25$ (hexanes/TBME, 3/2) [UV, KMnO₄]



Preparation of (2S, 3R)-Preparation of 2-phenyl-3-(phenylseleno)oxolane (28a) (Scheme 11)

To an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added a solution of **27** (63.2 mg, 0.38 mmol) in CH₂Cl₂ (3.8 mL), Et₃N (0.16 mL, 1.15 mmol, 3.00 equiv), and methanesulfonyl chloride (89 μ L, 1.15 mmol, 3.00 equiv). The solution was stirred at room temperature for 1h 15 min, and concentrated on the rotavap (30 °C, 30 mm Hg). ¹H NMR spectroscopic analysis of the crude product showed complete conversion of **27** to **27-I**. The crude product was used for the next step without further purification.

To an oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added diphenyl diselenide (96.1 mg, 0.31 mmol, 0.80 equiv), sodium borohydride (23.3 mg, 0.61 mmol, 1.60 equiv), and EtOH (0.5 mL) and the mixture was stirred at room temperature for 15 min. A solution of **27-I** in THF (2 mL) was added and the resulting mixture was concentrated under high vacuum. EtOH (0.1 mL) and THF (0.1 mL) were added to it and the solution was stirred at 40 °C (oil bath temperature) for 14.5 h. THF (0.1 mL) was added and the reaction was stirred at 40 °C for another 24 h. ¹H NMR spectroscopic analysis of the reaction aliquot showed 50% conversion of **27-I** to **28a**. The reaction mixture was cooled to room temperature, quenched with H₂O (10 mL), and transferred to a 125-mL separatory funnel with additional CH₂Cl₂ (15 mL). The aqueous layer was extracted with CH₂Cl₂ (2 x 15 mL) and the combined organic extracts were washed with brine (30 mL), dried over MgSO₄, filtered, and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was re-subjected to the reaction conditions as follows. To an

oven-dried, 10-mL, Schlenk flask equipped with a magnetic stir bar, was added diphenyl diselenide (60.0 mg, 0.19 mmol, 0.50 equiv), sodium borohydride (21.8 mg, 0.58 mmol, 1.50 equiv), and EtOH (0.5 mL) and the mixture was stirred at room temperature for 15 min. A solution of the crude mixture of **27-I** and **28a** in THF (0.5 mL) was added and the resulting mixture was concentrated under high vacuum. EtOH (0.1 mL) and THF (0.1 mL) were added to it and the solution was stirred at 40 °C (oil bath temperature) for 42 h. The reaction mixture was cooled to room temperature, quenched with H₂O (15 mL), and transferred to a 125-mL separatory funnel with additional CH₂Cl₂ (15 mL). The aqueous layer was extracted with CH₂Cl₂ (2 x 15 mL) and the combined organic extracts were washed with brine (30 mL), dried over MgSO₄, filtered, and concentrated on the rotavap (30 °C, 30 mm Hg). ¹H NMR spectroscopic analysis of the crude product showed complete consumption of **27-I**. The crude product was purified by column chromatography (silica gel, 25 mm x 31 cm column, hexanes/EtOAc, 96/4) to afford 48.0 mg of **28a** (41% over two steps) as a clear yellow oil.

Data for 28a:

 1 H NMR: (500 MHz, CDCl₃)

7.51 (d, *J* = 7.0 Hz, 2 H), 7.34-7.24 (m, 8 H), 4.87 (d, *J* = 6.0 Hz, 1 H, HC(2)), 4.18 (dd, *J* = 13.7, 7.2 Hz, 1 H, HC(5)), 4.07 (dd, *J* = 15.5, 7.5 Hz, 1 H, HC(5)), 3.60 (dd, *J* = 13.5, 6.0 Hz, 1 H, HC(3)), 2.53-2.46 (m, 1 H, HC(4)), 2.18-2.12 (m, 1 H, HC(4)).

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

303.9 (26.3, M⁺), 301.9 (12.9), 197.9 (23.3), 195.9 (11.3), 182.9 (17.1), 156.9 (18.8), 154.9 (10.2), 147.0 (56.9), 146.0 (100.0), 145.0 (11.4), 118.0 (22.5), 117.0 (94.1), 116.0 (13.8), 115.0 (34.6), 105.0 (67.1), 104.0 (13.3), 91.0 (68.8), 78.0

(24.4), 77.0 (55.0).

<u>HRMS:</u> calcd for $C_{16}H_{16}$ OSe: 304.0366, found: 304.0376

<u>SFC:</u> (2*R*,3*S*)-31a, t_R 6.8 min (<1%); (2*S*,3*R*)-31a, t_R 8.4 min (>99%), (Chiralpak AD, 125 bar, 3% MeOH in CO₂, 3.0 mL/min, 220 nm, 40 °C)

Configurational Stability of Seleno Ether 28a toward Brønsted Acids

Table 1, entry 1

To an HPLC vial was added a solution of ether **28a** (e.r. = 98:2) (2.60 mg, 0.009 mmol) in CH₂Cl₂ (0.9 mL). Triflic acid (0.076 μ l, 0.001 mmol, 0.1 equiv) in CH₂Cl₂ (10 μ L) was added over 1 min. After 30 minutes an aliquot of the reaction was directly analyzed on the HPLC to determine the enantiomeric ratio of the product.

<u>HPLC:</u> t_R 6.1 min (50.0%); t_R 6.7 min (50.0%), (Chiralpak OD-H, 42 bar, 95:5 hexanes/*i*-PrOH, 3.0 mL/min, 220 nm, 25 °C)

Table 1, entries 2 and 3

To an HPLC vial was added a solution of ether **28a** (e.r. = 98:2) (2.60 mg, 0.009 mmol) in CH₂Cl₂ (0.9 mL). Methanesulfonic acid (0.058 μ L, 0.001 mmol, 0.1 equiv) in CH₂Cl₂ (10 μ L) was added over 1 min. An aliquot of the reaction was directly analyzed on the HPLC to determine the enantiomeric ratio of the product.

- <u>HPLC (0.5 h)</u>: t_R 6.1 min (98.0%); t_R 6.7 min (2.0%), (Chiralpak OD-H, 42 bar, 95:5 hexanes/*i*-PrOH, 3.0 mL/min, 220 nm, 25 °C)
- <u>HPLC (3.0 h)</u>: t_R 6.1 min (87.0%); t_R 6.7 min (13.0%), (Chiralpak OD-H, 42 bar, 95:5 hexanes/*i*-PrOH, 3.0 mL/min, 220 nm, 25 °C)

Table 1, entry 4

To an HPLC vial was added a solution of ether **28a** (e.r. = 98:2) (2.60 mg, 0.009 mmol) in CH₂Cl₂ (0.9 mL). Trifluoroacetic acid (0.067 μ l, 0.001 mmol, 0.1 equiv) in CH₂Cl₂ (10 μ L) was added over 1 min. After 30 min and 24 h an aliquot of the reaction was directly analyzed on the HPLC to determine the enantiomeric ratio of the product.

- <u>HPLC (0.5 h)</u>: t_R 6.1 min (98.0%); t_R 6.7 min (2.0%), (Chiralpak OD-H, 42 bar, 95:5 hexanes/*i*-PrOH, 3.0 mL/min, 220 nm, 25 °C)
- <u>HPLC (24 h)</u>: t_R 6.1 min (98.0%); t_R 6.7 min (2.0%), (Chiralpak OD-H, 42 bar, 95:5 hexanes/*i*-PrOH, 3.0 mL/min, 220 nm, 25 °C)

Table 1 entry 5

To an oven-dried NMR tube was added trifluoroacetic acid (0.20 μ L, 0.002 mmol, 0.12 equiv), and CDCl₃ (0.1 mL). A solution of seleno ether **28a** (e.r. = >99:1) (6.80 mg, 0.022 mmol) in CDCl₃ (0.12 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. The mixture was quenched with 25 μ L of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was dissolved in hexanes/EtOAc, (9:1) (2 mL) and the solution was filtered through a 3 cm pipette column of silica gel. The column was eluted with hexanes/EtOAc, (9:1) (6 mL) and the filtrate was concentrated on the rotavap (30 °C, 30 mm Hg) to afford **28a** as a light-yellow oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

SFC: (2R,3S)-28a, t_R 6.8 min (<1%); (2S,3R)-28a, t_R 8.4 min (>99%), (Chiralpak AD, 125 bar, 3% MeOH in CO₂, 3.0 mL/min, 220 nm, 40 °C)

Table 1 entry 6

To an oven-dried NMR tube was added trifluoroacetic acid (1.70 μ L, 0.022 mmol, 1.00 equiv), and CDCl₃ (0.1 mL). A solution of seleno ether **28a** (e.r. = >99:1) (6.80 mg, 0.022 mmol) in CDCl₃ (0.12 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. The mixture was quenched with 25 μ L of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was dissolved in hexanes/EtOAc, (9:1) (2 mL) and the solution was filtered through a 3 cm pipette column of silica gel. The column was eluted with hexanes/EtOAc, (9:1) (6 mL) and the filtrate was concentrated on the rotavap (30 °C, 30 mm Hg) to afford **28a** as a light-yellow oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

<u>SFC:</u> (2*R*,3*S*)-**28a**, t_R 6.8 min (50%); (2*S*,3*R*)-**28a**, t_R 8.4 min (50%), (Chiralpak AD, 125 bar, 3% MeOH in CO₂, 3.0 mL/min, 220 nm, 40 °C)

General Procedure 4. Configurational Stability of Seleno Ethers 28d-f

Configurational Stability of Seleno Ether 28d

To an oven-dried NMR tube was added trifluoroacetic acid (2.70 μ L, 0.036 mmol, 1.00 equiv), and CDCl₃ (0.1 mL). A solution of seleno ether **28d** (e.r. = 63.2:36.8) (13.3 mg, 0.036 mmol) in CDCl₃ (0.25 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 6 h at room temperature. The mixture was quenched with 25 μ L of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was dissolved in hexanes/EtOAc, (9:1) (2 mL) and the solution was filtered through a 3 cm pipette column of silica gel. The column was eluted with hexanes/EtOAc,

(9:1) (6 mL) and the filtrate was concentrated on the rotavap (30 °C, 30 mm Hg) to afford **28d** as a clear colorless oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product. Note: The reaction of carbonate **25d** afforded the product with very similar enantiomeric ratios when conducted for 6 h (62.1:37.9) or 24 h (61.8:38.2) suggesting that seleno ether **28d** does not racemize to a significant extent even over 24 h.

SFC: (2R,3S)-28d, t_R 5.92 min (62.5%); (2S,3R)-28d, t_R 7.30 min (37.5%), (Chiralpak AD, 125 bar, 2.5% MeOH in CO₂, 3.0 mL/min, 220 nm, 40 °C)

Configurational Stability of Seleno Ether 28e

Following General Procedure 4, to an oven-dried NMR tube was added trifluoroacetic acid (2.80 μ L, 0.037 mmol, 1.00 equiv), and CDCl₃ (0.1 mL). A solution of seleno ether **28e** (e.r. = 64.5:35.5) (13.6 mg, 0.037 mmol) in CDCl₃ (0.27 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 8 h at room temperature. The mixture was quenched with 25 μ L of triethylamine and then purified to obtain **28e** as a clear colorless oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product. Note: The reaction of carbonate **25e** afforded the product with very similar enantiomeric ratios when conducted for 8 h (64.5:35.5) or 24 h (67.2:32.8) suggesting that seleno ether **28e** does not racemize to a significant extent even over 24 h.

<u>SFC:</u> (2*R*,3*S*)-**28e**, t_R 8.07 min (64.2%); (2*S*,3*R*)-**28e**, t_R 8.98 min (35.8%), (Chiralpak AD, 125 bar, 2.5% MeOH in CO₂, 2.5 mL/min, 220 nm, 40 °C)

Configurational Stability of Seleno Ether 28f toward TFA

To an oven-dried NMR tube was added trifluoroacetic acid (3.70 μ L, 0.047 mmol, 1.00

equiv), and CDCl₃ (0.1 mL). A solution of seleno ether **28f** (e.r. = 61:39) (16.6 mg, 0.047 mmol) in CDCl₃ (0.37 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. The mixture was quenched with 25 μ L of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 9 cm column, hexanes/EtOAc, 85/15) and the enantiomeric composition of the product **28f** was determined by CSP-SFC analysis of the product.

<u>SFC:</u> (2*R*,3*S*)-**28f**, t_R 8.26 min (61.0%); (2*S*,3*R*)-**28f**, t_R 11.56 min (39.0%), (Chiralpak AD, 125 bar, 12% MeOH in CO₂, 2.5 mL/min, 220 nm, 40 °C)

Configurational Stability of Seleno Ether 28f toward MsOH

To an oven-dried NMR tube was added a solution of seleno ether **28f** (e.r. = 90.4:9.6) (5.00 mg, 0.014 mmol) in CDCl₃ (0.14 mL). Methanesulfonic acid (0.95 μ L, 0.014 mmol, 1.00 equiv) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. The mixture was quenched with 25 μ L of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The mixture was quenched with 25 μ L of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The mixture was quenched with 25 μ L of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 9 cm column, hexanes/EtOAc, 85/15) and the enantiomeric composition of product **28f** was determined by CSP-SFC analysis of the product.

SFC: (2R,3S)-28f, t_R 8.26 min (90.8%); (2S,3R)-28f, t_R 11.56 min (9.2%), (Chiralpak AD, 125 bar, 12% MeOH in CO₂, 2.5 mL/min, 220 nm, 40 °C)

General Procedure 5. Carbonate Opening Experiments.

Table 2, entry 1



To an oven-dried NMR tube was added trifluoroacetic acid (0.45 μ L, 0.006 mmol, 0.1 equiv), and CDCl₃ (0.1 mL). A solution of carbonate **25a** (20.3 mg, 0.058 mmol) in CDCl₃ (0.48 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ¹H NMR spectroscopy analysis of the reaction mixture showed 19% conversion to product by comparison of the integration of protons HC(4) of the carbonate **25a** and HC(2) of ether **28a**. The mixture was quenched with 10 μ L of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was dissolved in hexanes/EtOAc, (9:1) (2 mL) and the solution was filtered through a 3 cm pipette column of silica gel. The column was eluted with hexanes/EtOAc, (9:1) (6 mL) and the filtrate was concentrated on the rotavap (30 °C, 30 mm Hg) to afford **28a** as a light-yellow oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

<u>SFC:</u> (2*R*,3*S*)-**28a**, t_R 6.8 min (57.4%); (2*S*,3*R*)-**28a**, t_R 8.4 min (42.6%), (Chiralpak AD, 125 bar, 3% MeOH in CO₂, 3.0 mL/min, 220 nm, 40 °C)

Table 2, entry 2



Following General Procedure 5, to an oven-dried NMR tube was added trifluoroacetic acid (0.40 μ L, 0.005 mmol, 0.1 equiv), and CDCl₃ (0.1 mL). A solution of carbonate **25b** (20.0 mg, 0.053 mmol) in CDCl₃ (0.43 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ¹H NMR spectroscopy analysis of the reaction mixture showed 46% conversion to product by integration of HC(5) of **25b** and **28b**. After purification, **28b** was obtained as a light-yellow oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

<u>SFC:</u> (2*R*,3*S*)-**28b**, t_R 11.33 min (52.5%); (2*S*,3*R*)-**28b**, t_R 12.82 min (47.5%), (Chiralpak AD, 125 bar, 4% MeOH in CO₂, 2.5 mL/min, 220 nm, 40 °C)

Table 2, entry 3



Following General Procedure 5, to an oven-dried NMR tube was added trifluoroacetic acid (0.38 μ L, 0.005 mmol, 0.1 equiv), and CDCl₃ (0.1 mL). A solution of carbonate **25c** (23.4

mg, 0.049 mmol) in CDCl₃ (0.39 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ¹H NMR spectroscopy analysis of the reaction mixture showed 44% conversion to product by comparison of the integrations of HC(5) in the carbonate and the ether. After purification, **28c** was obtained as a light-yellow oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

<u>SFC:</u> (2*S*,3*R*)-**28c**, t_R 11.81 min (37.2%); (2*R*,3*S*)-**28c**, t_R 14.90 min (62.8%), (Chiralpak OD, 125 bar, 2.5% MeOH in CO₂, 2.5 mL/min, 220 nm, 40 °C)

Table 2, entry 4



Following General Procedure 5, to an oven-dried NMR tube was added trifluoroacetic acid (3.7 μ L, 0.z48 mmol, 1.0 equiv), and CDCl₃ (0.1 mL). A solution of carbonate **25d** (20.0 mg, 0.048 mmol) in CDCl₃ (0.38 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ¹H NMR spectroscopy analysis of the reaction mixture showed 100% conversion to product. After purification, **28d** was obtained as a clear colorless oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

<u>SFC:</u> (2*R*,3*S*)-**28d**, t_R 5.92 min (61.8%); (2*S*,3*R*)-**28d**, t_R 7.30 min (38.2%), (Chiralpak AD, 125 bar, 2.5% MeOH in CO₂, 3.0 mL/min, 220 nm, 40 °C)

<u>Opt. Rot.:</u> $[\alpha]_D^{24} + 5.60 (c = 1.0, CHCl_3)$

Table 2, entry 5



Following General Procedure 5, to an oven-dried NMR tube was added trifluoroacetic acid (3.9 μ L, 0.051 mmol, 1.0 equiv), and CDCl₃ (0.1 mL). A solution of carbonate **25e** (20.0 mg, 0.051 mmol) in CDCl₃ (0.41 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ¹H NMR spectroscopy analysis of the reaction mixture showed 100% conversion to product. After purification, **28e** was obtained as a clear oil. The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

<u>SFC:</u> (2*R*,3*S*)-**28e**, t_R 8.07 min (67.2%); (2*S*,3*R*)-**28e**, t_R 8.98 min (32.8%), (Chiralpak AD, 125 bar, 2.5% MeOH in CO₂, 2.5 mL/min, 220 nm, 40 °C)

<u>Opt. Rot.:</u> $[\alpha]_D^{24} + 0.28 (c = 0.97, CHCl_3)$

Table 2, entry 6



Following General Procedure 4, to an oven-dried NMR tube was added trifluoroacetic acid (3.9 μ L, 0.051 mmol, 1.0 equiv), and CDCl₃ (0.1 mL). A solution of carbonate **25f** (21.3 mg, 0.051 mmol) in CDCl₃ (0.41 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ¹H NMR spectroscopy analysis of the reaction mixture showed 36% conversion to product by comparison of the integration of protons HC(4) of the carbonate **25f** and HC(2) of ether **28f**. The mixture was quenched with 10 μ L of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 11 cm column, hexanes/EtOAc, 85/15) and the enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

<u>SFC:</u> (2*R*,3*S*)-**28f**, t_R 8.26 min (93.6%); (2*S*,3*R*)-**28f**, t_R 11.56 min (6.4%), (Chiralpak AD, 125 bar, 12% MeOH in CO₂, 2.5 mL/min, 220 nm, 40 °C)

Table 2, entry 7



To an oven-dried Schlenk flask was added methanesulfonic acid (6.7 μ L, 0.103 mmol, 1.0 equiv), and CDCl₃ (0.5 mL). A solution of carbonate **25g** (50.0 mg, 0.103 mmol) in CDCl₃ (0.53 mL) was added and the flask was secured with a septum. The resulting solution was stirred for 2 h at room temperature. ¹H NMR spectroscopy analysis of the reaction mixture showed 100% conversion of **25g** to **28g**. The mixture was quenched with 14 μ L of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 9.5 cm column, hexanes/EtOAc, 95/5) and the enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

Data for 28g:

 1 <u>H NMR:</u> (500 MHz, CDCl₃)

7.91 (d, J = 8.0 Hz, 2 H, HC(12)), 7.58 (t, J = 8.0 Hz, 1 H, HC(13)), 7.26-7.15 (m, 5 H), 4.94 (d, J = 5.4 Hz, 1 H, HC(2)), 4.17-4.13 (m, 1 H), 4.08 (dd, J = 15.5, 8.0 Hz, 1 H), 3.78 (dd, J = 12.5, 6.0 Hz, 1H), 2.28-2.20 (m, 1 H), 2.04-1.98 (m, 1 H).

$$\frac{13}{C}$$
 NMR: (125 MHz, CDCl₃)

140.8, 137.9 (q, *J* = 29 Hz, C(11)), 130.3 (q, *J* = 5.9 Hz, C(12)), 129.5, 128.3, 127.7, 125.8, 125.5, 123.19 (q, *J* = 273 Hz, C(14)), 86.2 (C(2)), 67.6 (C(5)), 49.9 (C(3)), 32.9 (C(4)).

¹⁹F NMR: (470 MHz, CDCl₃)

-58.3 (F₃C(14)).

<u>IR:</u> (NaCl plates, CH_2Cl_2)

3035 (w), 2917 (w), 2872 (w), 1582 (w), 1493 (w), 1454 (w), 1423 (w), 1332 (m), 1288 (s), 1201 (m), 1142 (s), 1114 (m), 1066 (m), 1028 (w), 813 (w), 759 (w), 736 (w), 700 (w), 675 (m).

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

440.1 (15.7, M⁺), 336.0 (17.0), 335.0 (11.0), 334.0 (100.0), 332.0 (48.0), 331.0 (16.1), 330.0 (17.1), 293.0 (21.0), 291.0 (10.3), 274.0 (16.8), 147.1 (94.8), 146.1 (80.5), 121.0 (18.7), 117.1 (32.7), 116.1 (14.4), 115.1 (44.2), 105.0 (93.2), 91.1 (84.4), 86.0 (41.5), 84.0 (65.3), 77.1 (56.9), 65.0 (10.2).

- <u>HRMS:</u> calcd for $C_{18}H_{14}F_6OSe: 440.0114$, found: 440.0122
 - <u>TLC:</u> $R_f 0.30$ (hexanes/EtOAc, 95/5) [UV]
- <u>Opt. Rot.</u>: $[\alpha]_D^{24}$ 19.9 (c = 0.45, CHCl₃)
 - <u>SFC:</u> (2*R*,3*S*)-**28g**, t_R 17.06 min (93.7%); (2*S*,3*R*)-**28g**, t_R 19.57 min (6.3%), (Chiralpak Regis WhelkO1, 125 bar, 1% MeOH in CO₂, 1.5 mL/min, 220 nm, 40 °C)

Olefin Transfer Experiments

Scheme 12a



Following General Procedure 5, to an oven-dried NMR tube was added trifluoroacetic acid (3.9 μ L, 0.051 mmol, 1.0 equiv), and CDCl₃ (0.1 mL). A solution of carbonate **25f** (20.0 mg, 0.051 mmol) and olefin (*E*)-**29** (7.50 mg, 0.051 mmol, 1.0 equiv) in CDCl₃ (0.41 mL) was added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ¹H NMR spectroscopy analysis of the reaction mixture showed 21% conversion to product by comparison of the integration of protons HC(5) of the carbonate **25f** and HC(2) of ether **28f**. The mixture was quenched with 10 μ L of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 11 cm column, hexanes/EtOAc, 85/15) and the enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

<u>SFC:</u> (2*R*,3*S*)-**28f**, t_R 8.26 min (87.9%); (2*S*,3*R*)-**28f**, t_R 11.56 min (12.1%), (Chiralpak AD, 125 bar, 12% MeOH in CO₂, 2.5 mL/min, 220 nm, 40 °C)

Scheme 12b



Following General Procedure 5, to an oven-dried NMR tube was added trifluoroacetic acid (3.9 μ L, 0.051 mmol, 1.0 equiv), and CDCl₃ (0.1 mL). A solution of carbonate **25f** (20.0 mg, 0.051 mmol) in CDCl₃ (0.41 mL) followed by 1-butanol were added and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ¹H NMR spectroscopy analysis of the reaction mixture showed trace conversion to product by comparison of the integration of protons HC(4) of the carbonate **25f** and HC(2) of ether **28f**. The mixture was quenched with 10 μ L of triethylamine and then was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 11 cm column, hexanes/EtOAc, 85/15) and the enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

<u>SFC:</u> (2*R*,3*S*)-**28f**, t_R 8.26 min (94.8%); (2*S*,3*R*)-**28f**, t_R 11.56 min (5.2%), (Chiralpak AD, 125 bar, 12% MeOH in CO₂, 2.5 mL/min, 220 nm, 40 °C)

Scheme 12c



Following General Procedure 5, to an oven-dried NMR tube was added trifluoroacetic acid (3.9 μ L, 0.051 mmol, 1.0 equiv), and CDCl₃ (0.1 mL). A solution of carbonate **25f** (20.0 mg, 0.051 mmol) and olefin (*E*)-**30** (8.30 mg, 0.051 mmol, 1.0 equiv) in CDCl₃ (0.41 mL) and the tube was secured with a septum. The resulting solution was shaken and then allowed to sit for 24 h at room temperature. ¹H NMR spectroscopy analysis of the reaction mixture showed trace conversion to products **28f** and **31**. The mixture was quenched with 10 μ L of triethylamine and then was concentrated on the rotavap. The crude residue was purified by chromatography (silica gel, 25 mm x 11 cm column, hexanes/EtOAc, 85/15) and the product was isolated as a 2:1 mixture of **28f** to **31**. The enantiomeric composition of the products **28f** and **31** were determined by CSP-SFC analysis of the product.

<u>SFC:</u> (2*R*,3*S*)-**28f**, t_R 15.5 min (96.3%); (2*S*,3*R*)-**28f**, t_R 18.2 min (3.7%), (Chiralpak Regis WhelkO1, 125 bar, 10% MeOH in CO₂, 1.5 mL/min, 220 nm, 40 °C) (2*R*,3*S*)-**31**, t_R 13.7 min (50.9%); (2*S*,3*R*)-**31**, t_R 14.6 min (49.1%), (Chiralpak Regis WhelkO1, 125 bar, 10% MeOH in CO₂, 1.5 mL/min, 220 nm, 40 °C)





To an oven-dried, 100-mL, Schlenk flask equipped with a magnetic stir bar, was added 1,2-bis(2-nitrophenyl)diselane (3.71 g, 9.20 mmol) and EtOH (46 mL). The flask was cooled to 0 $^{\circ}$ C (the ice bath temperature) and sodium borohydride (869 mg, 22.9 mmol, 2.5 equiv) was added to the yellow suspension. Within 5 min the mixture turned dark brown. The solution was stirred at 0 $^{\circ}$ C for 2 h and then allyl bromide (1.7 mL, 19.3 mmol, 2.1 equiv) was added dropwise at 0 $^{\circ}$ C whereupon the reaction turned yellow. After stirring at 0 $^{\circ}$ C for 2.5 h, the ice bath was removed and the solution stirred at room temperature for 2.5 h. The reaction mixture was transferred to a 500-mL separatory funnel with hexanes 100 mL and H₂O (100 mL). The organic and the aqueous layers were separated and the aqueous layer was extracted with hexanes (3 x 150 mL). The combined organic extracts were dried over MgSO₄ filtered, concentrated on the rotavap (30 $^{\circ}$ C, 30 mm Hg) and dried under high vacuum to afford 3.0 g of **33** (67%) as a yellow solid.

Data for 33:

<u>mp:</u> 52-53 °C

 1 <u>H NMR:</u> (500 MHz, CDCl₃)

8.28 (d, *J* = 8.0 Hz, 1 H), 7.54-7.50 (m, 2 H), 7.32 (t, *J* = 8.0 Hz, 1H), 6.02-5.93 (m, 1H)), 5.33 (d, *J* = 17.0 Hz, 1H), 5.18 (d, *J* = 10.0 Hz, 1H), 3.61 (d, *J* = 7.50 Hz, 2H)

 $\frac{13}{C}$ NMR: (125 MHz, CDCl₃)

146.6, 133.5, 133.4, 132.3, 129.2, 126.3, 125.5, 119.1, 29.1.

77 SeNMR: (114 MHz, CDCl₃)

377.0

<u>IR:</u> (NaCl plates, CH_2Cl_2)

3078 (w), 2978 (w), 2929 (w), 1632 (w), 1588 (m), 1564 (m), 1503 (s), 1450 (m), 1432 (m), 1404 (w), 1328 (s), 1303 (s), 1250 (m), 1195 (w), 1167 (w), 1149 (w), 1096 (m), 1036 (m), 985 (w), 917 (w), 851 (m), 780 (m), 727 (s), 702 (w), 677 (w), 646 (w), 532 (w), 521 (w), 507 (w)

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

242.9 (31.8, M⁺), 240.9 (15.0), 203.9 (11.2), 201.9 (68.9), 199.9 (31.4), 198.9 (10.1) 197.9 (11.7), 185.9 (34.6), 183.9 (17.3), 155.9 (24.6), 153.9 (11.9), 143.9 (12.1), 115.0 (10.4), 106.0 (100.0), 78.0 (33.5), 63.1 (14.6)

<u>HRMS:</u> calcd for $C_9H_9NO_2Se: 242.9815$, found: 242.9798

<u>Analysis:</u> $C_9H_9NO_2Se(242.981)$

Calcd: C, 44.64; H, 3.75; N, 5.78%

Found: C, 44.83; H, 3.60; N, 5.78%

Preparation of *N***-(2-Nitrophenylselenenyl)succinimide (34) (Scheme 13)**



To an oven-dried, 25-mL, Schlenk flask equipped with a magnetic stir bar, was added *N*-chlorosuccinimide (689 mg, 5.20 mmol) and CH_2Cl_2 (3.4 mL) and the flask was cooled to 0 °C (the ice bath temperature). A solution of **33** (1.50 g, 6.20 mmol, 1.2 equiv) in CH_2Cl_2 (9.4 mL) was added and the solution was stirred at 0 °C for 2 h. The ice bath was removed and the

solution stirred at room temperature for 1 h. The reaction mixture was concentrated on the rotavap (30 °C, 30 mm Hg) to afford a greenish brown solid. The crude product was dissolved in 25 mL of hexanes and collected on a frit. The solid was washed with hexanes (100 mL) and anhydrous Et_2O (75 mL) to afford a yellow solid. The product was further purified by recrystallization (CH₂Cl₂/hexanes) to afford 1.25 g (81%) of analytically pure **34** as a yellow solid.

Data for 34:

<u>mp:</u> 212-214 °C (d)

- ¹<u>H NMR:</u> (500 MHz, CDCl₃) 8.37 (d, J = 8.0 Hz, 1 H), 7.63 (t, J = 7.5 Hz, 1 H), 7.45 (t, J = 7.5 Hz, 1 H), 7.07 (d, J = 8.0 Hz, 1 H), 3.04 (s, 4 H)
- $\frac{^{13}\text{C NMR:}}{(125 \text{ MHz, CDCl}_3)}$

178.6, 143.5, 135.7, 135.3, 127.3, 126.2, 125.5, 29.7.

<u>IR:</u> (NaCl plates, CH_2Cl_2)

3302 (w), 2943 (w), 1759 (w), 1706 (s), 1590 (w), 1568 (w), 1512 (m), 1452 (w), 1423 (w), 1325 (m), 1298 (s), 1240 (m), 1151 (s), 1106 (w), 1034 (w), 1006 (w), 850 (w), 819 (w), 787 (w), 732 (m), 702 (w), 670 (w), 660 (w), 642 (w), 599 (w), 568 (w), 532 (w)

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<u>MS:</u> (EI, 70 eV)
299.9 (29.0, M<sup>+</sup>), 297.9 (14.0), 253.9 (24.5), 251.9 (11.8), 201.9 (40.1), 199.9
(19.5) 185.9 (14.2), 155.9 (15.2), 143.9 (13.8), 106.0 (100.0), 78.0 (36.8), 63.1
(21.3), 56.1 (10.9), 55.1 (15.1)
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<u>HRMS:</u> calcd for $C_{10}H_8N_2O_4Se: 299.9649$, found: 299.9638

<u>Analysis:</u> $C_{10}H_8N_2O_4Se$ (299.965)

Calcd:	C, 40.15;	H, 2.70;	N, 9.36;	Se, 26.40%
Found:	C, 40.20;	H, 2.46;	N, 9.12;	Se, 24.75%

Catalytic Selenoetherification with *N*-Phenylselenenylsuccinimide (6)

Preparation of (+/-)-2-Phenyl-3-(phenylseleno)oxolane (28a)



An oven-dried, 10-mL Schlenk flask equipped with a magnetic stir bar was charged with HMPA(S) (19.5 mg, 0.100 mmol, 0.1 equiv) and (*E*)-**29** (148 mg, 1.00 mmol). *N*-Phenylselenenylsuccinimide (**6**) (279 mg, 1.10 mmol, 1.1 equiv) was added in the glove box. The flask was attached to the manifold and CH_2Cl_2 (10 mL) was added to it. AcOH (57.0 μ L, 1.00 mmol, 1.0 equiv) was added to the reaction using a syringe and the solution was stirred at room temperature for 4 h. Then the reaction mixture was quenched with Et₃N (140 μ L, 1.00 mmol, 1.0 equiv) and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was dissolved in EtOAc (20 mL) and filtered through a 1.5-inch pad of silica gel which was further eluted with EtOAc (150 mL). The filtrate was concentrated on the rotavap (30 °C, 30 mm Hg). The crude roturn, hexanes/EtOAc, 96/4) to afford 263 mg (87%) of seleno ether **28a** as a colorless clear oil.

Data for 28a:

 $\frac{1}{1}$ H NMR: (500 MHz, CDCl₃)

7.51 (d, *J* = 7.0 Hz, 2 H), 7.34-7.24 (m, 8 H), 4.87 (d, *J* = 6.0 Hz, 1H, HC(2)), 4.18 (dd, *J* = 13.7, 7.2 Hz, 1 H, HC(5)), 4.07 (dd, *J* = 15.5, 7.5 Hz, 1 H, HC(5)), 3.60 (dd, *J* = 13.5, 6.0 Hz, 1H, HC(3)), 2.53-2.46 (m, 1 H, HC(4)), 2.18-2.12 (m, 1 H, HC(4)).

- ¹³C NMR: (125 MHz, CDCl₃)
 141.2, 134.6, 129.0, 128.6, 128.3, 127.7, 127.6, 125.9, 86.0 (C(2)), 67.9 (C(5)),
 47.6 (C(3)), 34.1 (C(4)).
 - IR: (NaCl plates, neat)

3059 (s), 3031 (s), 2973 (s), 2940 (s), 2869 (s), 1951 (w), 1880 (w), 1808 (w), 1738 (w), 1603 (m), 1579 (s), 1494 (s), 1477 (s), 1453 (s), 1438 (s), 1362 (m), 1348 (m), 1327 (m), 1302 (s), 1247 (m), 1209 (m), 1175 (s), 1064 (s), 1042 (s), 1024 (s), 1000 (m), 970 (s), 909 (s), 874 (w), 844 (w), 734 (s), 691 (s), 670 (s), 624 (m), 574 (w), 531 (w).

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

304.0 (34.7, M⁺), 302.0 (16.6), 198.0 (27.5), 196.0 (13.1), 183.0 (18.5), 157.0 (20.0), 155.0 (10.0), 147.1 (60.1), 146.1 (100.0), 145.1 (11.3), 118.1 (21.6), 117.1 (84.7), 116.1 (13.2), 115.1 (31.5), 105.0 (69.1), 104.1 (13.3), 91.1 (69.5), 78.1 (18.4), 77.0 (55.2), 51.0 (17.7).

- <u>HRMS:</u> calcd for $C_{16}H_{16}$ OSe: 304.0366, found: 304.0362
 - <u>TLC:</u> $R_f 0.25$ (hexanes/EtOAc, 96/4) [UV]

General Procedure 6. Catalytic Selenoetherification with 34 and Achiral Lewis Bases.

Table 3

To an oven-dried NMR tube containing electrophile **34** (22.2 mg, 0.074 mmol, 1.10 equiv) was added a solution of olefin (*E*)-**29** (10.0 mg, 0.067 mmol), and the Lewis base (if indicated) (0.006 mmol, 0.10 equiv) in CDCl₃ (0.67 mL) under an ambient atmosphere. Acid (TFA or MsOH as indicated) (0.067 mmol, 1 equiv) was added and the tube was secured with a septum. The resulting solution was shaken and monitored periodically by ¹H NMR spectroscopy over 24 h. Note: For entries 7 and 6 in Table 3, HMPT and HMPA were added neat and not as a solution with olefin (*E*)-**29**. Additionally, the HMPT reaction was set up under an argon atmosphere. For entry 2, solution of olefin (*E*)-**29** (10.0 mg, 0.067 mmol), and the Lewis base (0.006 mmol, 0.10 equiv) in CDCl₃ (0.57 mL) was used and 100 μ L of a stock solution (39 μ L in 1 mL CDCl₃) of AcOH was added

General Procedure 7. Catalytic Selenoetherification with 34 and Chiral Lewis Bases.

Figure 2 and Figure S1

To an oven-dried NMR tube containing electrophile **34** (22.2 mg, 0.074 mmol, 1.10 equiv) was added a solution of olefin (*E*)-**29** (10.0 mg, 0.067 mmol), and the Lewis base (0.013 mmol, 0.20 equiv) in CDCl₃ (0.67 mL) under an ambient atmosphere. TFA (5.2 μ L, 0.067 mmol, 1 equiv) was added and the tube was secured with a septum. The resulting solution was shaken and monitored periodically by ¹H NMR spectroscopy over 24 h. After the time indicated in the Figure for a particular Lewis base, the reaction was quenched with Et₃N (10 μ L) and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 8 cm column, hexanes/EtOAc, 85/15). The enantiomeric



composition of the product was determined by CSP-SFC analysis of the product.

Figure S1 Chiral Lewis base survey with N-(2-nitrophenylselenenyl)succinimide.

Catalytic Selenoetherification with NPSS (6) and Chiral Lewis Base (R)-35a.

To an oven-dried NMR tube containing NPSS (18.8 mg, 0.074 mmol, 1.10 equiv) was added a solution of olefin (*E*)-**29** (10.0 mg, 0.067 mmol), and thiophosphoramide (*R*)-**35a** (6.20 mg, 0.013 mmol, 0.20 equiv) in CDCl₃ (0.57 mL) under an argon atmosphere. 100 μ L of a stock solution (39 μ L in 1 mL CDCl₃) of AcOH was added. The resulting solution was shaken and monitored periodically by ¹H NMR spectroscopy, which showed 60% conversion to product over 3 h. The reaction was quenched with Et₃N (10 μ L) and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 8 cm column, hexanes/EtOAc, 96/4). The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

<u>HPLC</u>: t_R 8.7 min (45.4%); t_R 10.4 min (54.6%), (Chiralpak Regis WhelkO1, 95:5, hexanes/*i*-PrOH, 1.0 mL/min, 220 nm, 25 °C)

Preparation of (R)-2,4-Dimethyl-3,4-dihydro-3-morpholino-dinaphthol[2,1-d:1'2'-f]-1H-

[1,3,2]diazaphosphepine 3-Sulfide ((*R*)-35m)



To an oven-dried, 25-mL, Schlenk flask equipped with a magnetic stir bar, was added (R)-N,N-dimethyl-BINAM (469 mg, 1.50 mmol), dry THF (15 mL), and Et₃N (0.52 mL, 3.75 mmol, 2.50 equiv) under an atmosphere of nitrogen and the homogeneous mixture was cooled to 0 °C (ice bath temperature). PCl₃ (0.39 mL, 4.50 mmol, 3.00 equiv) was added dropwise whereupon a colorless precipitate formed immediately. After the addition of PCl_3 , the ice bath was removed and the reaction was stirred at room temperature for 3h. The volatiles were removed under high vacuum on the manifold and anhydrous Et₂O (15 mL) was added to it and the solution stirred for a minute. The supernatant was cannula filtered into another 50-mL, ovendried Schlenk flask under nitrogen. The remaining precipitate in the reaction flask was washed with anhydrous Et₂O (6.0 mL) and was also cannula filtered into the receiver Schlenk flask. The combined filtrate was concentrated under high vacuum to afford a light yellow solid. The solid was redissolved in anhydrous Et₂O (5.0 mL) and the volatiles were again removed under high vacuum to remove any trace HCl and the light yellow foam was dried for 2.5 h. Anhydrous CH₂Cl₂ (12.5 mL) was added to it and the mixture was cooled to 0 °C (ice bath temperature). Et₃N (0.25 mL, 1.80 mmol, 1.20 equiv) and morpholine (0.14 mL, 1.65 mmol, 1.1 equiv) were added sequentially after which the ice bath was removed and the reaction mixture stirred at room temperature for 17 h. S₈ (154 mg, 4.80 mmol, 3.2 equiv) was added and the reaction was stirred at room temperature for 21 h. The solution was concentrated on the rotavap (30 °C, 30 mm Hg).

The crude residue was purified by column chromatography (silica gel, 25 mm x 22 cm column, hexanes/EtOAc, 85/15) to afford 588 mg of thiophosphoramide (*R*)-**35m** (85%) as a white solid. The e.r. (>99:1) of the (*R*)-**35m** is assumed to be the same as that of its precursor, namely the carbamate of (*R*)-BINAM precursor.

Data for (*R*)-35m:

<u>mp:</u> 255-256 °C (d)

$<u>^{1}H NMR</u>:$ (500 MHz, CDCl₃)

7.99 (d, J = 9.0 Hz, 1 H), 7.96 (d, J = 9.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1 H), 7.88 (d, J = 8.0 Hz, 1 H), 7.66 (d, J = 9.0 Hz, 1 H), 7.62 (d, J = 8.5 Hz, 1 H), 7.45 (t, J = 7.0 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.30-7.24 (m, 2 H), 7.15 (t, J = 7.5 Hz, 1 H), 7.06 (d, J = 8.5 Hz, 1H), 3.55 (br s, 4H), 3.14 (d, J = 12 Hz, 3H), 3.11 (br s, 4H), 3.01 (d, J = 12.5 Hz, 3H).

 $\frac{13}{C}$ NMR: (125 MHz, CDCl₃)

142.6 (d, ${}^{2}J_{C-P} = 4.5$ Hz), 141.4, 132.5, 132.3, 131.4, 131.3, 129.6, 129.5, 129.1, 128.1, 128.0, 127.8, 127.1 (two overlapping peaks), 126.3, 126.0, 125.5, 124.9, 123.5, 122.0 (d, ${}^{2}J_{C-P} = 2.8$ Hz), 67.4 (d, ${}^{2}J_{C-P} = 5.5$ Hz), 46.4, 37.9 (d, ${}^{2}J_{C-P} = 9.1$ Hz), 35.4 (d, ${}^{2}J_{C-P} = 4.5$ Hz).

 $\frac{^{31}P NMR:}{(202 MHz, CDCl_3)}$

87.7

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IR: (NaCl plates, CH<sub>2</sub>Cl<sub>2</sub>)
3049 (w), 2960 (w), 2894 (w), 2850 (w), 1618 (w), 1593 (w), 1506 (m), 1467 (w),
1447 (w), 1429 (w), 1360 (w), 1329 (m), 1294 (w), 1273 (m), 1255 (m), 1158 (w),
1145 (w), 1129 (m), 1114 (m), 1084 (m), 1024 (w), 964 (s), 933 (s), 866 (w), 820
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(s), 751 (m), 736 (m), 720 (s), 701 (m), 687 (w), 667 (w), 652 (w), 560 (w), 536 (w).

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

460.2 (18.3), 459.2 (63.2, M⁺), 375.1 (10.0), 374.1 (40.8), 373.1 (19.9), 342.1 (25.3), 341.1 (100.0), 311.2 (12.2), 281.1 (33.3), 280.1 (10.8), 84.0 (12.5).

<u>HRMS:</u> calcd for $C_{26}H_{26}N_3$ OPS: 459.1534, found: 459.1547

<u>TLC:</u> $R_f 0.23$ (hexanes/EtOAc, 85/15) [UV]

<u>Opt. Rot.:</u> $[\alpha]_D^{24}$ –358.6 (c = 1.15, CHCl₃)

<u>Analysis:</u> C₂₆H₂₆N₃OPS (459.1534)

Calcd: C, 67.95; H, 5.70 N, 9.14%

Found: C, 67.91; H, 5.77 N, 8.94%

Optimization of Catalytic Selenoetherification with (*R*)**-35m.**

Table 4, entry 1

To an oven-dried NMR tube containing electrophile **34** (22.2 mg, 0.074 mmol, 1.10 equiv) was added a solution of (*E*)-**29** (10.0 mg, 0.067 mmol), and (*R*)-**35m** (3.1 mg, 0.006 mmol, 0.10 equiv) in CDCl₃ (0.67 mL) under an ambient atmosphere. MsOH (4.4 μ L, 0.067 mmol, 1 equiv) was added and the tube was secured with a septum. The resulting solution was shaken and monitored periodically by ¹H NMR spectroscopy which showed complete conversion of (*E*)-**29** to **28f** in 20 min. The reaction was quenched with Et₃N (10 μ L) and concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was purified by chromatography (silica gel, 25 mm x 8 cm column, hexanes/EtOAc, 85/15). The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

<u>SFC:</u> (2*R*,3*S*)-**28f**, t_R 8.26 min (68%); (2*S*,3*R*)-**28f**, t_R 11.56 min (32%), (Chiralpak AD, 125 bar, 12% MeOH in CO₂, 2.5 mL/min, 220 nm, 40 °C

Table 4, entry 2

To an oven-dried, 10 mL, Schlenk flask was added electrophile **34** (22.2 mg, 0.074 mmol, 1.10 equiv), olefin (*E*)-**29** (10.0 mg, 0.067 mmol), thiophosphoramide (*R*)-**35m** (3.10 mg, 0.006 mmol, 0.10 equiv) and CDCl₃ (0.67 mL). The flask was cooled to -12 °C using a Cryocool, MsOH (4.4 μ L, 0.067 mmol, 1 equiv) was added and solution was stirred at -12 °C for 24 h. The reaction was quenched with Et₃N (10 μ L) at -12 °C and analyzed by ¹H NMR spectroscopy, which showed 50% conversion of (*E*)-**29** to **28f**. The reaction mixture was concentrated on the rotavap and the crude residue was purified by chromatography (silica gel, 25 mm x 8 cm column, hexanes/EtOAc, 85/15). The enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

<u>SFC:</u> (2*R*,3*S*)-**28f**, t_R 8.26 min (73%); (2*S*,3*R*)-**28f**, t_R 11.56 min (27%), (Chiralpak AD, 125 bar, 12% MeOH in CO₂, 2.5 mL/min, 220 nm, 40 °C

Table 4, entry 3

To an oven-dried, 10 mL, Schlenk flask was added electrophile **34** (44.4 mg, 0.15 mmol, 1.10 equiv), thiophosphoramide (*R*)-**35m** (12.4 mg, 0.03 mmol, 0.20 equiv) and CDCl₃ (1.34 mL). MsOH (8.8 μ L, 0.13 mmol, 1.00 equiv) was added and then a solution of olefin (*E*)-**29** (20.0 mg, 0.13 mmol) in CDCl₃ (0.67 mL) was added over 14 h using a syringe pump. The reaction was quenched with Et₃N (10 μ L), concentrated on the rotavap and the crude residue was purified by chromatography (silica gel, 25 mm x 8 cm column, hexanes/EtOAc, 85/15). The

enantiomeric composition of the product was determined by CSP-SFC analysis of the product.

General Procedure 8. Catalytic Asymmetric Selenoetherification with (*R*)-35m and 34. (2*R*,3*S*)-[3-(2-Nitrophenyl)selenenyl]-2-phenyloxolane (28f) (Table 5, entry 1)



An oven-dried, 10-mL Schlenk flask equipped with a magnetic stir bar was charged with *N*-2-nitrophenylselenenyl succinimide **34** (329 mg, 1.10 mmol, 1.1 equiv), thiophosphoramide (*R*)-**35m** (45.9 mg, 0.100 mmol, 0.1 equiv) and CHCl₃ (5 mL). A solution of olefin (*E*)-**29** (148 mg, 1.00 mmol) in CHCl₃ (5 mL) was added under an atmosphere of nitrogen. Finally MsOH (65 μ L, 1.00 mmol, 1.0 equiv) was added to the reaction using a syringe and the yellow solution was stirred at room temperature for 4 h. Then the reaction mixture was quenched with Et₃N (140 μ L, 1.00 mmol, 1.0 equiv) and was concentrated on the rotavap (30 °C, 30 mm Hg). The crude residue was dissolved in EtOAc (20 mL) and filtered through a 1.5-inch pad of silica gel which was further eluted with EtOAc (150 mL). The filtrate was concentrated on the rotavap (30 °C, 30 mm Hg). The crude product was purified by column chromatography (silica gel, 25 mm x 31 cm column, hexanes/EtOAc, 92/8) to afford 338 mg (97%) of seleno ether **28f** as a yellow oil. Note: The racemate of **28f** was prepared following General Procedure 6 with Ph₃P(S) as the catalyst and TFA as the Brønsted acid.

Data for 28f:

 1 <u>H NMR:</u> (500 MHz, CDCl₃)

8.24 (dd, J = 8.2, 2.0 Hz, 1 H, HC(11)), 7.41 (d, J = 7.0 Hz, 2 H), 7.35-7.25 (m, 6 H), 4.86 (d, J = 6.5 Hz, 1 H, HC(2)), 4.31-4.27 (m, 1 H, HC(5)), 4.09 (dd, J = 16.0, 7.5 Hz, 1 H, HC(5)), 3.72 (dd, J = 14.5, 6.5 Hz, 1 H, HC(3)), 2.79-2.72 (m, 1 H, HC(4)), 2.23-2.17 (m, 1 H, HC(4)).

- ¹³C NMR: (125 MHz, CDCl₃)
 146.9, 140.8, 133.4, 132.8, 130.0, 128.6, 128.0, 126.3, 125.9, 125.7, 85.4 (C(2)),
 67.9 (C(5)), 45.8 (C(3)), 34.0 (C(4)).
- $\frac{77}{\text{Se NMR:}}$ (114 MHz, CDCl₃)

423.9

<u>IR:</u> (NaCl plates, CH_2Cl_2)

3085 (w), 3064 (w), 3028 (w), 2972 (w), 2936 (w), 2867 (w), 1590 (m), 1566 (m), 1513 (s), 1451 (m), 1331 (s), 1304 (s), 1252 (m), 1098 (m), 1085 (w), 1067 (m), 1038 (m), 973 (w), 909 (w), 852 (w), 759 (m), 730 (s), 701 (s), 646 (w).

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

349.0 (12.9, M⁺), 243.0 (11.6), 201.9 (12.3), 186.0 (55.3), 184.0 (27.4), 182.0 (11.7), 163.1 (22.8), 156.0 (12.5), 147.1 (69.6), 146.1 (100.0), 117.1 (19.8), 116.1 (10.1), 115.1 (29.1), 106.0 (36.0), 105.0 (59.6), 91.1 (71.0), 78.0 (15.5), 77.1 (36.0).

- <u>HRMS:</u> calcd for $C_{16}H_{15}NO_3Se: 349.0217$, found: 349.0223
 - <u>TLC:</u> $R_f 0.12$ (hexanes/EtOAc, 92/8) [UV]
- <u>Opt. Rot.:</u> $[\alpha]_D^{24}$ 51.64 (c = 1.02, CHCl₃)
 - <u>SFC:</u> (2R,3S)-**28f**, t_R 8.41 min (68.9%); (2S,3R)-**28f**, t_R 11.60 min (31.1%), (Chiralpak

AD, 125 bar, 12% MeOH in CO₂, 2.5 mL/min, 220 nm, 40 °C)

<u>Analysis:</u> $C_{16}H_{15}NO_{3}Se(349.0217)$

Calcd: C, 55.18; H, 4.34; N, 4.02%

Found: C, 55.09; H, 4.32; N, 3.95%

Preparation of (2*R*,3*S*)-3-(2-Nitrophenyl)selenenyl-2-phenyloxane (31) (Table 5, entry 2)



Following General Procedure 8, **34** (329 mg, 1.10 mmol, 1.1 equiv), (*R*)-**35m** (45.9 mg, 0.100 mmol, 0.1 equiv), (*E*)-**30** (162 mg, 1.00 mmol), MsOH (65.0 μ L, 1.10 mmol, 1.0 equiv), and CHCl₃ (10 mL) were combined to yield after column chromatography (silica gel, 25 mm x 31 cm column, hexanes/EtOAc, 92/8) 312 mg (86%) of seleno ether **31** as a yellow solid. Note: The racemate of **31** was prepared following General Procedure 6 with Ph₃P(S) as the catalyst and TFA as the Brønsted acid.

Data for 31:

<u>mp:</u> 75-76 °C

<u>¹H NMR:</sub> (500 MHz, $CDCl_3$)</u>

7.94 (d, *J* = 8.0 Hz, 1 H), 7.33 (d, *J* = 7.0 Hz, 2 H), 7.18-7.08 (m, 6 H), 4.37 (d, *J* = 10.5 Hz, 1 H, HC(2)), 4.17 (dd, *J* = 11.5, 4.5 Hz, 1 H, HC(6)), 3.65 (td, *J* = 11.5, 2.0 Hz, 1 H, HC(6)), 3.58-3.52 (m, 1 H, HC(3)), 2.45-2.42 (m, 1 H, HC(4)), 2.01-1.93 (m, 1H), 1.86 (ddd, *J* = 25, 12.5, 3.5 Hz, 1 H), 1.77 (d, *J* = 13.0 Hz, 1 H).

 $\frac{13}{C}$ NMR: (125 MHz, CDCl₃)

148.2, 139.6, 132.5, 131.5, 130.1, 128.1, 128.0, 127.2, 125.7, 125.4, 85.2 (C(2)), 68.6 (C(6)), 45.7 (C(3)), 31.4 (C(4)), 27.6 (C(5)).

IR: (KBr pellets)

3092 (w), 3057 (w), 3034 (w), 2934 (m), 2851 (m), 1589 (s), 1565 (s), 1515 (s), 1452 (s), 1434 (m), 1330 (s), 1304 (s), 1248 (s), 1182 (m), 1141 (m), 1098 (s), 1076 (s), 1036 (s), 1024 (s), 962 (m), 938 (s), 910 (w), 881 (w), 852 (m), 781 (m), 758 (s), 728 (s), 701 (s), 646 (m), 533 (m).

- <u>MS:</u> (EI, 70 eV) 363.0 (8.2, M⁺), 322.3 (13.5), 162.1 (11.3), 161.1 (100.0), 105.0 (24.5), 91.1 (61.6), 77.1 (10.4), 71.1 (29.3), .
- <u>HRMS:</u> calcd for $C_{17}H_{17}NO_3Se: 363.0374$, found: 363.0360
 - <u>TLC:</u> $R_f 0.17$ (hexanes/EtOAc, 91/9) [UV]
- <u>Opt. Rot.:</u> $[\alpha]_D^{24} 62.04 (c = 1.95, CHCl_3)$
 - <u>SFC:</u> (2*S*,3*R*)-**31**, t_R 24.86 min (25.1%); (2*R*,3*S*)-**31**, t_R 26.09 min (74.9%), (Chiralpak AD, 125 bar, 10% MeOH in CO₂, 1.0 mL/min, 220 nm, 40 °C)
- <u>Analysis:</u> $C_{17}H_{17}NO_3Se(363.0374)$

Calcd: C, 56.36; H, 4.73; N, 3.87%

Found: C, 56.04; H, 4.60; N, 3.92%



Preparation of (1*S*,2*R*)-[1-[(2-Nitrophenyl)seleno]-3-phenylpropyl]oxolane (37) and

Following General Procedure 8, **34** (329 mg, 1.10 mmol, 1.1 equiv), (*R*)-**35m** (45.9 mg, 0.100 mmol, 0.1 equiv), (*E*)-**36** (190 mg, 1.00 mmol), MsOH (65.0 μ L, 1.10 mmol, 1.0 equiv), and CHCl₃ (10 mL) were combined to yield after column chromatography (silica gel, 25 mm x 30 cm column, hexanes/EtOAc, 92.5/7.5) and three sets of fractions were collected. These fractions contained pure **37** (199 mg, yellow oil), mixture of **37** and **38** (99.2 mg, yellow oil), and pure **38** (69.7 mg, yellow oil). The combined yield of the **37** and **38** was 94% (368 mg). Note: The racemates of **37** and **38** were prepared following General Procedure 6 with Ph₃P(S) as the catalyst and TFA as the Brønsted acid.

Data for 37:

8.18 (dd, J = 8.0, 1.0 Hz, 1 H), 7.68 (d, J = 7.5 Hz, 1 H), 7.39 (td, J = 8.5, 1.5 Hz, 1 H), 7.30-7.25 (m, 3 H), 7.18 (t, J = 7.0 Hz, 1 H), 7.13 (d, J = 7.0 Hz, 2 H), 4.15 (dd, J = 13.5, 7.0 Hz, 1 H), 3.85 (dd, J = 15.5, 7.0 Hz, 1 H), 3.76 (dd, J = 13.5, 7.5 Hz, 1 H), 3.57-3.53 (m, 1 H), 2.95 (ddd, J = 14.0, 9.0, 5.5 Hz, 1 H), 2.82-2.77 (m, 1 H), 2.15-2.08 (m, 1 H), 2.05-1.84 (m, 4 H), 1.78-1.70 (m, 1 H).
$\frac{13}{C}$ NMR: (125 MHz, CDCl₃)

148.1, 141.1, 133.2, 132.6, 131.4, 128.5, 128.4, 126.0, 125.9, 125.6, 81.5, 68.5, 48.7, 33.8, 33.7, 29.6, 26.0.

- IR: (NaCl plates, CH₂Cl₂)
 3085 (w), 3057 (w), 3028 (w), 2972 (w), 2943 (w), 2859 (w), 1589 (m), 1566 (m),
 1514 (s), 1454 (m), 1332 (s), 1303 (m), 1252 (w), 1096 (w), 1057 (m), 1035 (m),
 852 (w), 783 (w), 748 (w), 730 (m), 700 (m), 645 (w).
- $\underline{MS:} \quad (EI, 70 \text{ eV})$

391.1 (6.9, M⁺), 189.1 (39.5), 171.1 (12.7), 129.1 (21.2), 117.1 (13.3), 105.1 (11.6), 97.1 (15.8), 91.1 (74.2), 71.1 (100.0).

- <u>HRMS:</u> calcd for $C_{19}H_{21}NO_3Se: 391.0687$, found: 391.0699
 - <u>TLC:</u> $R_f 0.15$ (hexanes/EtOAc, 92.5/7.5) [UV]
- <u>Opt. Rot.:</u> $[\alpha]_D^{24} 85.9 (c = 2.01, CHCl_3)$
 - <u>SFC:</u> (2*R*,3*S*)-**37**, t_R 19.56 min (78.8%); (2*S*,3*R*)-**37**, t_R 20.70 min (21.2%), (Chiralpak AD, 125 bar, 10% MeOH in CO₂, 1.0 mL/min, 220 nm, 40 °C)
- <u>Analysis:</u> $C_{19}H_{21}NO_3Se$ (391.0687)

Calcd: C, 58.46; H, 5.42; N, 3.59%

Found: C, 58.55; H, 5.38; N, 3.64%

Data for 38:

<u>¹H NMR:</u> (500 MHz, $CDCl_3$)

8.19 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.61 (d, *J* = 8.5 Hz, 1 H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1 H), 7.32 (t, *J* = 8.0 Hz, 1 H), 7.27-7.24 (m, 2 H), 7.18-7.14 (m, 3 H), 4.09-4.07 (m,

1 H, HC(6)), 3.49 (td, *J* = 11.5, 2.5 Hz, 1 H, HC(6)), 3.38 (td, *J* = 8.0, 2.0 Hz, 1 H, HC(2)), 3.35-3.30 (m, 1 H, HC(3)), 2.84 (ddd, *J* = 14.0, 10.0, 4.5 Hz, 1 H, HC(8)), 2.66 (ddd, *J* = 16.5, 9.5, 7.0 Hz, 1 H, HC(8)), 2.31-2.29 (m, 1 H), 2.24-2.17 (m, 1 H), 1.85-1.66 (m, 4 H).

- ¹³C NMR: (125 MHz, CDCl₃)
 148.2, 141.7, 133.2, 130.8, 130.7, 128.5, 128.3, 126.3, 126.1, 125.7, 80.2 (C(2)),
 68.1 (C(6)), 44.1 (C(3)), 36.0, 32.0, 31.6, 27.8.
 - <u>IR:</u> (NaCl plates, CH₂Cl₂)
 3085 (w), 3057 (w), 3021 (w), 2947 (m), 2848 (w), 2859 (w), 1590 (m), 1566 (m),
 1515 (s), 1452 (m), 1331 (s), 1303 (m), 1248 (w), 1117 (w), 1098 (m), 1085 (m),
 1060 (w), 1037 (m), 852 (w), 783 (w), 730 (s), 700 (m), 645 (w).
 - $\underline{MS:} \quad (EI, 70 \text{ eV})$

391.1 (7.5, M⁺), 189.1 (72.3), 171.1 (30.1), 143.1 (13.8), 135.1 (18.0), 129.1 (31.1), 117.1 (12.8), 105.1 (23.7), 91.1 (100.0), 71.1 (41.7), 57.2 (10.9), 55.1 (19.8).

- <u>HRMS:</u> calcd for $C_{19}H_{21}NO_3Se: 391.0687$, found: 391.0682
 - <u>TLC:</u> $R_f 0.12$ (hexanes/EtOAc, 92.5/7.5) [UV]
- <u>Opt. Rot.:</u> $[\alpha]_D^{24} 23.6 (c = 0.33, CHCl_3)$
 - <u>SFC:</u> (2*S*,3*R*)-**38**, t_R 11.48 min (14.9%); (2*R*,3*S*)-**38**, t_R 18.66 min (85.1%), (Chiralpak OD, 125 bar, 12% MeOH in CO₂, 2.5 mL/min, 220 nm, 40 °C)
- <u>Analysis:</u> $C_{19}H_{21}NO_3Se$ (391.0687)

Calcd: C, 58.46; H, 5.42; N, 3.59%

Found: C, 58.35; H, 5.13; N, 3.62%

Preparation of (1*S*,2*R*)-2-[2-Methyl-1-[(2-nitrophenyl)selenenyl]propyl]oxolane (40) and (2*R*,3*S*)-3-(2-Nitrophenyl)selenenyl-2-(1-methylethyl)oxane (41) (Table 5, entry 4)



Following General Procedure 9, **34** (329 mg, 1.10 mmol, 1.1 equiv), (*R*)-**35m** (45.9 mg, 0.100 mmol, 0.1 equiv), (*E*)-**39** (128 mg, 1.00 mmol), MsOH (65.0 μ L, 1.10 mmol, 1.0 equiv), and CHCl₃ (10 mL) were combined to yield after column chromatography (silica gel, 25 mm x 31 cm column, hexanes/EtOAc, 91/9) three sets of fractions. These fractions contained pure **41** (26.4 mg, yellow oil), mixture of **40** and **41** (110 mg, yellow oil), and pure **40** (147 mg, yellow oil). The combined yield of the **40** and **41** was 86% (283 mg). Note: The racemates of **40** and **41** were prepared following General Procedure 6 with Ph₃P(S) as the catalyst and TFA as the Brønsted acid.

Data for 40:

<u>¹H NMR:</u> (500 MHz, $CDCl_3$)

8.12 (dd, J = 8.5, 1.5 Hz, 1 H), 7.86 (d, J = 7.5 Hz, 1 H), 7.47 (td, J = 8.5, 1.5 Hz, 1 H), 7.29 (td, J = 8.0, 1.0 Hz, 1 H), 4.16 (dd, J = 14.5, 7.5 Hz, 1 H), 3.85 (dd, J = 15.0, 7.0 Hz, 1 H), 3.75 (dd, J = 7.5, 6.0 Hz, 1 H), 3.43 (dd, J = 7.5, 4.5 Hz, 1 H), 2.28-2.22 (m, 1 H), 2.12-2.05 (m, 1 H), 1.90-1.83 (m, 2 H), 1.65-1.57 (m, 1H), 1.09 (d, J = 6.5 Hz, 3 H), 1.06 (d, J = 7.0 Hz, 3 H).

¹³C NMR: (125 MHz, CDCl₃)
 148.8, 133.0, 132.2, 131.8, 125.8, 125.7, 80.3, 68.2, 58.6, 30.9, 30.3, 25.9, 21.5, 19.6.

IR: (NaCl plates, CH₂Cl₂)
3085 (w), 3057 (w), 2959 (s), 2872 (s), 1589 (s), 1566 (m), 1512 (s), 1450 (m), 1383 (w), 1331 (s), 1298 (s), 1252 (m), 1181 (w), 1149 (w), 1096 (m), 1055 (s), 1053 (s), 925 (w), 851 (m), 784 (m), 729 (s), 698 (m), 645 (m).

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

329.1 (4.2, M⁺), 127.1 (15.8), 71.1 (100.0), 57.2 (11.0).

- <u>HRMS:</u> calcd for $C_{14}H_{19}NO_3Se: 329.0530$, found: 329.0528
 - <u>TLC:</u> $R_f 0.26$ (hexanes/EtOAc, 91/9) [UV]
- <u>Opt. Rot.:</u> $[\alpha]_D^{24}$ 11.70 (c = 1.80, CHCl₃)
 - <u>SFC:</u> (2*S*,3*R*)-**40**, t_R 10.47 min (17.4%); (2*R*,3*S*)-**40**, t_R 11.35 min (82.6%), (Chiralpak OD, 125 bar, 10% MeOH in CO₂, 1.0 mL/min, 220 nm, 40 °C)
- <u>Analysis:</u> $C_{14}H_{19}NO_{3}Se(329.0530)$

Calcd: C, 51.22; H, 5.83; N, 4.27%

Found: C, 51.24; H, 5.77; N, 4.28%

Data for 41:

 1 <u>H NMR:</u> (500 MHz, CDCl₃)

8.18 (dd, *J* = 8.0, 1.0 Hz, 1 H, HC(12)), 7.64 (d, *J* = 7.5 Hz, 1 H, HC(15)), 7.52 (td, *J* = 8.0, 1.0 Hz, 1 H, , HC(14)), 7.34 (td, *J* = 8.0, 1.0 Hz, 1 H, HC(13)), 4.04-4.02 (m, 1 H, HC(6)), 3.49-3.41 (m, 2 H), 3.31 (dd, *J* = 10.0, 2.5 Hz, 1 H), 2.32-2.28 (m, 1 H), 2.17 (septd, J = 6.5, 2.0 Hz, 1 H, HC(2)), 1.84-1.62 (m, 3H), 1.00 (d, J = 6.5 Hz, 3H), 0.87 (d, J = 6.5 Hz, 3H).

 $\frac{^{13}\text{C NMR:}}{(125 \text{ MHz}, \text{CDCl}_3)}$

148.6, 133.2, 130.9, 130.5, 126.2, 126.1, 84.5 (C(2)), 68.3 (C(6)), 41.9 (C(3)), 32.2, 29.9, 27.8, 20.4, 14.7.

<u>IR:</u> (NaCl plates, CH_2Cl_2)

3071 (w), 2960 (s), 2872 (m), 2851 (m), 1590 (m), 1567 (m), 1515 (s), 1464 (m), 1450 (m), 1379 (w), 1331 (s), 1302 (m), 1262 (m), 1252 (m), 1102 (s), 1081 (m), 1067 (m), 1026 (m), 999 (m), 922 (m), 872 (w), 852 (m), 805 (w), 783 (m), 730 (s), 702 (m), 645 (w).

<u>MS:</u> (EI, 70 eV)

329.1 (5.5, M⁺), 201.9 (22.9), 199.9 (11.1), 127.1 (32.2), 106.0 (14.2), 71.1 (100.0), 55.1 (18.6).

- <u>HRMS:</u> calcd for $C_{14}H_{19}NO_3Se: 329.0530$, found: 329.0525
 - <u>TLC:</u> $R_f 0.32$ (hexanes/EtOAc, 91/9) [UV]
- <u>Opt. Rot.</u>: $[\alpha]_D^{24}$ 14.3 (c = 0.80, CHCl₃)
 - <u>SFC:</u> (2*R*,3*S*)-**41**, t_R 3.27 min (83.8%); (2*S*,3*R*)-**41**, t_R 3.85 min (16.2%), (Chiralpak OD, 125 bar, 10% MeOH in CO₂, 3.0 mL/min, 220 nm, 40 °C)

5)



Preparation of *rel* (2*R*,3*R*)-3-(2-Nitrophenyl)selenenyl-2-phenyloxolane (42) (Table 5, entry

Following General Procedure 8, **34** (329 mg, 1.10 mmol, 1.1 equiv), (*R*)-**35m** (45.9 mg, 0.100 mmol, 0.1 equiv), (*Z*)-**29** (148 mg, 1.00 mmol), MsOH (65.0 μ L, 1.10 mmol, 1.0 equiv), and CHCl₃ (10 mL) were combined to yield after column chromatography (silica gel, 25 mm x 31 cm column, 91/9 then 88/12 hexanes/EtOAc) 278 mg (80%) of seleno ether **42** as a yellow solid. The product was further purified by recrystallization (EtOAc/hexanes) to obtain analytically pure material. Note: The racemate of **42** was prepared following General Procedure 6 with Ph₃P(S) as the catalyst and TFA as the Brønsted acid.

Data for 42:

<u>mp:</u> 109-110 °C

 $\frac{1}{1}$ H NMR: (500 MHz, CDCl₃)

8.13 (d, J = 8.0 Hz, 1 H, HC(11)), 7.55 (d, J = 7.5 Hz, 1 H), 7.45 (t, J = 8.0 Hz, 1 H), 7.34-7.23 (m, 6 H), 5.30 (d, J = 6.0 Hz, 1 H, HC(2)), 4.35 (dd, J = 14.0, 7.5 Hz, 1 H, HC(5)), 4.25 (dd, J = 11.0, 5.5 Hz, 1 H, HC(3)), 4.05 (dd, J = 14.0, 8.0 Hz, 1 H, HC(5)), 2.79-2.72 (m, 1 H, HC(4)), 2.30-2.23 (m, 1 H, HC(4)).

 $\frac{13}{C}$ NMR: (125 MHz, CDCl₃)

147.5, 138.6, 133.2, 132.5, 130.3, 128.0, 127.9, 126.3, 126.1, 125.5, 82.7 (C(2)), 67.3 (C(5)), 44.7 (C(3)), 33.8 (C(4)). IR: (KBr pellets)

3078 (s), 3035 (s), 2979 (m), 2950 (s), 2922 (m), 2876 (s), 1975 (w), 1948 (m), 1819 (w), 1741 (w), 1589 (s), 1563 (s), 1513 (s), 1496 (s), 1457 (s), 1369 (s), 1332 (s), 1305 (s), 1252 (s), 1223 (s), 1213 (s), 1174 (s), 1149 (s), 1099 (s), 1092 (s), 940 (s), 1055 (s), 1021 (s), 961 (s), 940 (s), 903 (s), 852 (s), 808 (m), 786 (s), 752 (s), 733 (s), 700 (s), 681 (s), 644 (s), 620 (s), 546 (m).

 $\underline{MS:} \quad (EI, 70 \text{ eV})$

349.1 (17.8, M⁺), 243.0 (12.5), 202.0 (13.1), 188.0 (10.3), 186.0 (61.5), 184.0 (29.7), 183.0 (10.3), 182.0 (12.4), 163.1 (21.0), 156.0 (11.0), 147.1 (73.0), 146.1 (100.0), 117.1 (12.2), 115.1 (19.2), 106.0 (32.8), 105.1 (73.6), 91.1 (40.1), 78.1 (12.1), 77.1 (40.2).

- <u>HRMS:</u> calcd for $C_{16}H_{15}NO_3Se: 349.0217$, found: 349.0201
 - <u>TLC:</u> $R_f 0.06$ (hexanes/EtOAc, 88/12) [UV]
 - <u>SFC:</u> (2*R*,3*R*)-**42**, t_R 12.57 min (50.9%); (2*S*,3*S*)-**42**, t_R 13.48 min (49.1%), (Chiralpak AD, 125 bar, 12% MeOH in CO₂, 2.5 mL/min, 220 nm, 40 °C)
- <u>Analysis:</u> $C_{16}H_{15}NO_{3}Se(349.0217)$

Calcd: C, 55.18; H, 4.34; N, 4.02%

Found: C, 55.10; H, 4.34; N, 3.99%



General Procedure 9. Isomerization Procedure for Seleno Ethers 37, 38, 40 and 41

To an oven-dried NMR tube containing **34** (14.9 mg, 0.049 mmol, 1.0 equiv) was added a solution of seleno ether **37** (19.5 mg, 0.049 mmol), and (*R*)-**35m** (2.3 mg, 0.005 mmol, 0.10 equiv) in CDCl₃ (0.50 mL) under an ambient atmosphere. MsOH (3.2 μ L, 0.049 mmol, 1.0 equiv) was added and the tube was secured with a septum. The resulting solution was shaken and monitored periodically by ¹H NMR spectroscopy which showed no isomerization of **37** to **38** over 4 h.



Following General Procedure 9, **34** (2.4 mg, 0.008 mmol, 1.0 equiv), seleno ether **38** (3.1 mg, 0.008 mmol), (*R*)-**35m** (0.4 mg, 0.001 mmol, 0.10 equiv) and MsOH (0.51 μ L, 0.008 mmol, 1 equiv) were combined in CDCl₃ (0.1 mL) under an ambient atmosphere. ¹H NMR spectroscopic analysis of the reaction mixture showed no isomerization of **38** to **37** over 4 h.



Following General Procedure 9, **34** (17.7 mg, 0.059 mmol, 1.0 equiv), seleno ether **40** (19.5 mg, 0.059 mmol), (*R*)-**35m** (2.7 mg, 0.006 mmol, 0.10 equiv) and MsOH (3.8 μ L, 0.059 mmol, 1.0 equiv) were combined in CDCl₃ (0.59 mL) under an ambient atmosphere. ¹H NMR spectroscopic analysis of the reaction mixture showed no isomerization of **40** to **41** over 4 h.



Following General Procedure 9, **34** (6.8 mg, 0.023 mmol, 1.0 equiv), seleno ether **41** (7.5 mg, 0.023 mmol), (*R*)-**35m** (1.0 mg, 0.002 mmol, 0.10 equiv) and MsOH (1.5 μ L, 0.023 mmol, 1.0 equiv) were combined in CDCl₃ (0.23 mL) under an ambient atmosphere. ¹H NMR spectroscopic analysis of the reaction mixture showed no isomerization of **41** to **40** over 4 h.

Mechanistic Studies. Formation of Complexes 43-45.

Formation of complex 43. Scheme 14



To an oven-dried, NMR tube containing **34** (25.0 mg, 0.083 mmol) was added a solution of HMPA(S) (16.3 mg, 0.083 mmol, 1.00 equiv) in CDCl₃ (0.83 mL). Methanesulfonic acid (5.4 μ L, 0.083 mmol, 1.00 equiv) was added and the tube was secured with a septum. The mixture was shaken and then the solution was analyzed by ¹H NMR spectroscopic analysis that showed instantaneous appearance of new peaks corresponding to **43**. The ratio of **43** to **34** equilibrated to 2:1 favoring **43** within 3 h. At room temperature ³¹P NMR spectra displayed a broad resonance at around 60 ppm, which decoalesced into two sharp peaks corresponding to **43** and **34** at room temperature. This mixture was stable in solution for 48 h after which olefin (*E*)-**29** (13.6 mg, 0.092 mmol, 1.10 equiv) was added. ¹H NMR spectroscopic analysis revealed complete conversion of the electrophile to the seleno ether after 1 h.

Data for 43:

 31 <u>P NMR:</u> (162 MHz, CDCl₃)

62.4

⁷⁷<u>Se NMR:</u> (114 MHz, $CDCl_3$)

582

Formation of Complex 44. Scheme 15



To an oven-dried, NMR tube containing **34** (25.0 mg, 0.083 mmol) was added a solution of HMPA(S) (16.35 mg, 0.083 mmol, 1.00 equiv) in CDCl₃ (0.83 mL). Trifluoroacetic acid (6.4 μ L, 0.083 mmol, 1.0 equiv) was added and the tube was secured with a septum. The mixture was shaken and then the solution was analyzed by ¹H NMR spectroscopic analysis that showed instantaneous appearance of new peaks corresponding to **44**. The ratio of **44** to **34** equilibrated to 0.9:1 within 3 h. At room temperature ³¹P NMR spectra displayed a broad resonance at around 60 ppm, which decoalesced into two sharp peaks corresponding to HMPA(S) and **44** at -50 °C. The ⁷⁷Se NMR also showed two sharp peaks corresponding to **34** and **44** at room temperature. This mixture was stable in solution for 48 h after which olefin (*E*)-**29** (13.6 mg, 0.092 mmol, 1.10 equiv) was added. ¹H NMR spectroscopic analysis revealed 77% conversion of the electrophile to the seleno ether after 1 h.

Data for 44:

³<u>P NMR:</u> (162 MHz, CDCl₃) 63.4 ⁷⁷<u>Se NMR:</u> (114 MHz, CDCl₃) 587





To an oven-dried, NMR tube containing **34** (16.3 mg, 0.054 mmol) was added a solution of (*R*)-**35m** (25.0 mg, 0.054 mmol, 1.00 equiv) in CDCl₃ (0.54 mL). Methanesulfonic acid (3.5 μ L, 0.054 mmol, 1.00 equiv) was added and the tube was secured with a septum. The mixture was shaken and then the solution was analyzed by ¹H NMR spectroscopic analysis that showed instantaneous appearance of new peaks corresponding to **45**. The ratio of (*R*)-**35m** to **45** equilibrated to 0.28:1 within 3 h. At room temperature ³¹P NMR spectra displayed a broad resonance at around 60 ppm, which decoalesced into two sharp peaks corresponding to **34** and (*R*)-**35m** and **45** at -50 °C. The ⁷⁷Se NMR also showed two sharp peaks corresponding to **34** and (*R*)-**35m** at room temperature. This mixture was stable in solution for 24 h after which olefin (*E*)-**29** (8.86 mg, 0.060 mmol, 1.1 equiv) was added. ¹H NMR spectroscopic analysis revealed 100% conversion of the electrophile to the seleno ether after 1 h.

Data for 45:

³¹<u>P NMR:</u> (500 MHz, CDCl₃)

65.1

⁷⁷<u>Se NMR:</u> (500 MHz, $CDCl_3$)

620

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absorbed DBU. # 17 date Jan 22 2010 dfr (499.693) solvent CDC13 date Jan 22 2010 dfr (499.693) solvent CDC13 data/Josoft dof aslyenid/dk-5627- dm mn 33-37.ftd dagual/dk-5627- dm nn 6536 AcquistrixToN dmf 2 at 4.665 h DEC2 sw 7024.9 dfd dom at 4.665 h DEC2 sw 7024.9 dfd dom at 4.665 hand n dfd dam2 of 1.0 gin notused PROCESSING PROCESSING FLACS Ib otf n sc 0 sc 0 sc 0 hand f bit				ېل م	·			└┬┹┯┙		Ч	4	لبا لہا
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barub Dac. # 1 date Jan 23 2010 dfrq 499.693 solvent CDC13 dn H1 file /esport/home/- dpwr 20 user14/data/us00/k- dof 0 alyanid/dt-5462 dn mn 33-37.fid dmm c AcQUISITION dnf 200 sfrq 499.693 dseq tn H1 dres 1.0 at 4.665 homo n np 65536 DEC2 sw 7024.9 dfrq2 0 fb 4000 dn2 bw 6.5 dn2 n d1 0 dmm2 c to 1 dres2 1.0 alock n homo2 n gain not used PROCESSING FLAGS 1b 0.30 i1 n wffle in n proc ft dp y fn not used hs mn math f DISPLAY sc 0 wart wp 549.66 waxp vs 194 wbs sc 0 wat wc 250 ham 21.99 is 265.47 rfl 1011.9 rfp 0 th 7 is 1.000 ai ph			1 1									
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Denmark, Kalyani and Collins

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1H-24d

expl 2 sign1 DBC. 4 VT SAMPLE DBC. 4 VT followit S00.013 dilwit S00.010 followit Gamma site Collard site S00.010 dilwit S00.010 dilwit S00.010 dilwit S00.010 dilwit S00.010 dil S00.010 dilwit S00.
expl signal EAMPLE DEC. E VT date Feb 5 2010 dfrg 500.070 solvent CDC13 dn H for feb 52010 dfrg 500.070 solvent CDC13 dn H by fellymiddle 6-73- dn mn o -59-67-5700.01d dm o at 4.096 hbmsc n np 65336 DEC2 n th H1 dres 1.0 th 4000 dd2 bs 18 dpwr2 1 typer 35 do22 0 pr 5.0 ddd n dd 0 dm 2 200 et 1 dres2 1.0 fb 4000 dd2 bs 18 dpwr2 1 typer 530 do22 n ff 400 dd2 n ff 400 dd2 bs 18 dpwr2 1 typer 530 do22 n ff 400 dd2 bs 10 0.00 dt 4 dres2 1.0 fb 4000 dd2 bs 0.00 df frg 2 00 et 1 dres2 200 et 1 dres2 1.0 fin n twist pr 5500.7 weap vs 80 dob sc 0 wnt f typer 245.1 wear vp 5500.7 weap va 80 dob sc 0 wnt f th 7 th 7 th 7 th 7 th 1.000 at 10 9 8 7 6 5 4 3 2 1 pp
expl. #2pul SAMPLE DEC. # VT date #b 50010 drq state Total dr newsel/data/ide.ef 10 bs/balyanid/dk.ef73- da cf-38-d7proton.fid dm ext 1.00 dat 4.096 homo AcQUISITION dat 4.096 tat 4.096 tat 4.096 tat 4.096 tat 4.096 date 10 fb 4000.0 date 200 et 1 date 10 gin not date 10 fb 400.0 et 1 date2 1.0 gin not point 1 fb 0.030 in n point ft db yt point 10 point 10 point 10
expl szpul SAMPLE DEC. & VT date Feb 2010 dfzq 500.070 solvent CDC13 dn flle /seport/hae/- /wr 18 userid/data/uis00m- dof 0 b/kalymid/dat-Fr3- dm nn c-38.47.proton.fid dm c ac07proton.fid dm c ac07proton.fid dm c ac000 dfcq 0 fb 4000 dba2 rev 800.0 dfcq 0 fb 4000 dba2 1 type 55 dof2 0 nt 1 desel 1.0 gain not used nexth fdp y for ant used nexth fdp y for ant used nexth fdp y for ant used nexth fdp y fa not used fsf -250.1 werp ve 80 ubs 0 se 2200 rt 1 drse2 fdp y fa fdp y fa se 250.1 vex 80 ubs se 250.0 ts 359.79 ref1 1459.6 ref5 0
expl szpul SAMFLE DZC.4 VT date Feb 5010 dfrg 500.070 solvent CCC13 dn H1 file /sep/thame/-dwr 18 user12/dats/ui500n- dof 0 b/kalyand/dx-6-75- dm nnn c-50-67-proton.fil dmm c AcQUISTION dmf 200 sfrg 500.070 dseg tn H1 dree 1.0 at 4.096 homo n np 65536 DZC2 ew 8000.0 dfrg2 0 fb 4000 dn2 bs 16 dpwr2 1 typer 55 dof2 0 pw 9.0 dm2 cc tof 0 dmf2 200 nt 1 dreg2 1.0 alock n homo.son in n proc ft dp y fn not used FDCDSING DISPLAY so 0.30 in n broused DISPLAY so 0 wat wc 250 hzmm 22.001 werr wp 5500.7 wexp vs 80 Wab sc 0 wat wc 250
expl #2pul SAMPLE DEC. 4 VT date Feb 50010 dfrg 500.070 solvent CDC13 dn H1 file /esport/home/- dpvr 18 user18/dat/ui500n- dof 0 b/kalyan(dx-6-75- dm nnn) c-58-67-proton.fild dmm c ACQUEITOR dmf 200 sfrg 500.070 dæeg tn H1 dfree DEC sforg 0 0 dfrg2 0 pv 60550 dfrg2 0 pv 55 dof2 0 nt 1 dæeg2 ct 1 dree2 1.0 alock n homo2 n put 1 dæeg2 ct 1 dree2 1.0 alock n homo2 n FLAGS 1b 0.30 il n n proc ft dp - 250.1 verr vp 550.7 vexp vs 80 vbs sc 20 vit vs 80 vbs te 220 ham ath f
expl #2pul SAMELE DEC.4 VT date Feb 5 2010 dfrq 500.070 solvent CD13 dn tile /expc Ch2ade.4 dwr 18 user1d/data/ui500n-dof 0 b/kalymid/dx-6-75- dn nn c-58-67-proton.fid dmm c at 4.096 homo np 6536 DEC2 ew 000.0 dfrq2 gb 10 dpwr2 ew 000.0 dfrq2 gb 16 dpwr2 tpwr 50 dof2 ot adm2 ct 1 dres2 ct 0 wbs gc 0 wtit wc 250
expl s2pul SAMPLE DEC. 4 VT date 7eb 5 2010 dfrq 500.070 solvent CDC13 dn H1 file /export/Ame/-4 dwr 18 user1d/data/u500 dof 0 b/kalyani/dk-6-75- dn nnn c-58-67-proton.fid dmm e ACQUISTION dmf 200 sfrq 500.070 dseq tn H1 dres 1.0 fb 4000 dn2 ew 8000.0 dfrq2 0 fb 4000 dn2 be 16 dpwr2 1 tpwr 55 dof2 0 pw 9.0 dm2 n dl 0 dm2 a tof 0 dmf2 200 nt 1 dseg2 tot 1 dres2 1.0 alook n homo2 n gain not used PROESSING FLAGS 1b 0.30 il n vtfile in n proc ft dp y fn not used processing pack 250 hzmm 22.00 is 369.75 ve 80 wba sc 0 wit
<pre>expl signl SAMPLE DEC.4 VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn E1 file /scycrithoms/- dwr 18 user1d/data/u500n- dof 0 b/kalynid/dk-6-75- dn mnn c-58-67-proton.fid dmm c AQUISTION dmf 200 sfrq 500.070 deeq tn H1 dres 1.0 dt 4.096 homo n mp 65336 DEC2 fb 4000 dn2 hs 106 dpwr2 1 thver 55 dof2 0 pw 5.0 dm2 n dl 0 dmm2 c tof 0 dmf2 200 nt 1 deeq2 ct 1 dres2 1.0 alock n homo2 n gain not used PROCESSIN0 iin n proc ft dp y fn not used hs nn math f DISFLAY gp250.1 werr wp 5500.77 wexp vs 80 Was sc 0 0 wnt vc 250 hzmm 22.00 is 359.79</pre>
expl s2pul SAMPLE DEC. 4 VT date Feb 5 2010 dfz UT solvent CDC13 df HI file /export/home/- dpvr 18 userld/data/u500n- dof 0 b/kalyand/dk-6-75- df nnn c-58-67-proton.fild dfm c tn H1 dres 1.0 at 4.096 homo n np 65336 DEC2 ft 4000 dfz bs 16 dpvr2 1 tpwr 55 dof2 0 nt 1 dres2 1 tpwr 55 dof2 0 nt 1 dres2 1.0 alock n homo2 n gain not used FPOCESSING FLAGS 1b 0.30 il n wtfile in n proc ft dp Y fn not used hs m math f DLSFLAY sp -250.1 wert we 800 wha sc 0 with vc 250
expl s2pul SAMPLE DEC.4 VT date Feb 5 2010 dirq 500.070 solvent CDC13 dn tile /export/home/- dpvr 18 userld/data/ui500n- dof 0 b/kalyani/ddk-6-75- dm nnn c-58-67-proton.fid dmm cn np 65336 DEC2 nm H1 dres 1.0 tat 4.096 hom sw 8000.0 dirg2 0 fb 4000 dn2 1 tpwr 55 dof2 0 pw 9.0 dma2 c ct 1 dseq2 c dt 0 dmm2 c dt 1 dseq2 c ct 1 dseq2 c dt n ngain not used prot pcol ft fdl 0.30 1 in n proc ft dp y fn DISPLAY math f
expl s2pul SAMPLE DEC. 4 VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn H1 file / spycot/home/- dpr 18 userid/data/ui500n- dof 0 b/kalyanid/dk-6-75- dm nnn c-58-67-proton.fid dm c AcQUISITION dmf 200 sfrq 500.070 dseq tn H1 dres 1.0 tat 4.096 homo n pp 65536 DDEC2 sw 8000.0 dfrq2 0 bs 16 dpwr2 1 tpwr 55 dof2 0 pt 41 0 dm2 c tof 0 dmf2 200 nt 1 dseq2 ct 1 dres2 1.0 gain not used FLAGS 1b 0.30 i1 n wtfile ft in n proc ft py fn not used ps -250.1 werr wp 80 whs sc 0 wtt
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn HI file /sport/hom/- dpr 18 userld/data/ui500n- dof 0 b/kalyni/ddx-6-75-fm nnn c-58-67-proton.fild dmm c nc 58-67-proton.fild dmm c ng frq 500.070 dseq tn Bil dres 1.0 nt 4.096 homo n pp 65536 DBC2 0 pw 550.00 dfrq2 0 fb 4000 dn2 bs 16 dpwr2 1 tpwr 55 dof2 0 pw 9.0 dml n dl 0 dmm2 c ct 1 dres2 1.0 alock n homo2 n gln not used FROCESSING FLAGS lb 0.0.0 il n wtfile in n proc ft dp y fn not used processing plsFLAS b 0.0.0 il n n vtfile in n proc ft dp y fn not used processing pf 5500.7 wesp vp 5500.7 wesp vp 5500.7 wesp vp 5500.7 wesp
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrg 500.070 solvent CDC13 dn H1 file/axport/hom/- dpr 18 userid/dat/ul500n- dof 0 b/kalyanid/dk-675- dn mnn c-38-67-proton.fild dm c AtQUISITION dmf 200 sfrg 500.070 dseq tn H1 dres 1.0 fb 4000 dn2 bs 16 dpwr2 1 bs 16 dpwr2 1 bs 16 dpwr2 1 bs 16 dpwr2 1 tpvr 55 dof2 0 pW 9.0 dm2 n dl 0 dm2 n dl 0 dm2 c tof 0 dmfrg 200 pt 1 dres2 1.0 gain not used PROCESSING FLAGS 1b 0.30 il n wfile in n proc ft dp y fn not used hs m math f DISPLAY sp -2850.1 werr
expl s2pul SAMFLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn H1 file /export/home/- dpwr 18 userid/dta/ui500n. dof 0 b/kalyanid/dt-6-75- dm nnn c-58-67-proton.fid dmm c AcQUISITION dmf 200 ffrq 500.070 dseq tn H1 dres 1.0 at 4.096 homo n np 65536 DEC2 sw 8000.0 dfrq2 0 fb 4000 dn2 bs 16 dpwr2 1 typer 55 dof2 0 pw 9.0 dm2 n dl 0 dmm2 c to 1 dseq2 1.0 alook n homo2 n gain not used PROCESING FLAGS 1b 0.30 il n wtfile in n proc ft dp y fn not used bs nn math ft DISPLAY pp -250.1 wer
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn HL file /export/home/- dpwr 18 userid/data/u1500n- dof 0 b/kalyanid/dk-6-75- dm nnn c-58-67-yorton.fid dmm c ACQUISITION dmf 200 sfrq 500.070 dseq tn HL dres 1.0 at 4.096 homo n np 65536 DEC2 sw 8000.0 dfrq2 0 fb 4000 dn2 bs 16 dpwr2 1 tpwr 55 dof2 0 pw 9.0 dm2 n dl 0 dmm2 c tof 0 dmf2 200 nt 1 dres2 1.0 pain not used PROCESSINO FLAGS 1b 0.30 il n wtfile in n proc ft dp y fn not used hs nn math f
expl s2pul SAMDLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDCl3 dn H1 file /export/home/- dpwr 18 userid/data/ui500n- dof 0 b/kalyanid/dk-6-75- dm nnn c-58-67-proton.fild dmm c ACQUISITION dmf 2000 sfrq 500.070 dseq tn H1 dres 1.0 at 4.096 homo n np 65336 DEC2 sw 8000.0 dfrq2 0 bb 16 dpwr2 1 tpwr 55 dof2 0 pW 9.0 dm2 n dl 0 dmm2 c tof 0 dmf2 2000 nt 1 dseq2 t.0 alock n homo2 n gain not used PROCESSING FLAS 1b 0.33 il n w tfile in n proc ft dp y fn not used
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn file /export/home/- dpwr 18 userid/data/ui500n- dof 0 b/kalyanid/dk-6-75- m c.86-67-proton.fid dmm c AcQUISITION dmf 200 sfrq 50.070 dseq tn H1 drese 1.0 at 4.096 homo n mp 65536 DEC2 sw 8000.0 dfrq2 0 ff 4000 dn2 bas bas 16 dpwr2 1 1 tpwr 55 dcf2 0 pw 9.0 dm2 n n dl 0 dmf2 cc 10 tof 0 dmf2 cc 10 alook n homo2 n n gain not used FDACESSING FLAOS 1b 0.30 i1 n tproc i11 n tproc in n tproc in n tpr
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn file /export/home/- dpwr 18 userld/data/ui500n- dof 0 b/kalyanid/dk-6-75- dn nnn c-58-67-proton.fid dnm c AcQUISITION dnf 200 sfrq 500.070 dseq tn H1 dress 1.0 np 65536 DEC2 sw 8000.0 dfrq2 0 ft 4000 dn2 0 bs 16 dpwr2 1 tpwr 9.0 dn2 n dl 0 dm2 n dl 0 dm2 n dl 0 dm2 n gain not used PROCESSING FLAGS 1b 0.30 ii n wtfile
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn file /export/home/- dpwr 18 user1d/data/ui500n- dof 0 b/kalyanid/dk-6-75- dm c-58-67-proton.fid dmm c ACQUISITION dmf 200 sfrq 500.070 dseq tn H1 dres 1.0 at 4.096 homo mp 65536 DEC2 sw 8000.0 dfrq2 bs 16 dpwr2 tpwr 5.5 dof2 pw 9.0 dm2 n tof 0 dmf2 200 nt 1 dseq2 1.0 alook n homo2 n galook n homo2 n galook n 0.30 0.30
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDCl3 dn H1 file /export/home/- dpwr 18 userld/data/ui500n- dof 0 b/kalyanid/dk-675- dm nnn c-58-67-proton.fid dmm c ACQUISITION dmf 200 sfrq 50.070 dseq tn H1 dres 1.0 at 4.096 homo n np 65536 DEC2 sw 8000.0 dfrq2 0 fb 4000 dn2 bs 16 dpwr2 1 tpwr 5.0 dof2 0 pw 9.0 dm2 n d1 0 dmm2 c ct 1 dres21 1 diat 0 dm2 n d1 0 dm2 n d1 0 ma2 n d1 0 ma2 n alock n n
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 goundary for the second
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDCl3 dn H1 file /export/home/- dpwr 18 userld/data/ui500n- dof 0 b/kalyanid/dk-6-75- dm nnn c-58-67-proton.fid dmm c ACQUISITION dmf 200 sfrq 500.070 dseq tn H1 dres 1.0 np 65536 DEC2 sw 8000.0 dfrq2 0) fb 4000 dn2 bs 16 dpwr2 1 tpwr 55 dof2 0 pw 9.0 dm2 n d1 0 dmm2 c tof 0 dmf2 200 nt 1 dseq2 ct 1 dres2 1.0
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn file /export/home/- dpwr 18 userld/data/ui500n- dof 0 b/kalyanid/dk-6-75- dm nnn c-58-67-proton.fid dmm c ACQUISITION dmf 200 sfrq 500.070 dseq tn H1 dres 1.0 at 4.096 homo n np 65536 DEC2 sw 8000.0 dfr2 0 fb 4000 dn2 bs 16 dpwr2 1 tpwr 55.0 0622 0 pw 9.0 dm2 n d1 0 dmm2 c tof 0 dmf2 2000 nt 1 dseq2
exp1 s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn H1 file /export/home/- dpwr 18 userld/data/ui500n- dof 0 b/kalyanid/dk-6-75- dm nnn c c c-58-67-proton.fid dmm c dmf 200 sfrq 500.070 dseq 1 flit tn H1 dres 1.0 flit fif at 4.096 homo n flit flit flit sw 8000.0 dfrq2 0 flit flit dpwr2 1 tpwr 55 dof2 0 pw 9.0 dm2 n d1 0 dm2 c tof 0 dmf2 200
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDCl3 dn H1 file /export/home/~ dpwr 18 userld/data/ui500n- dof 0 b/kalyanid/dk-6-75- dm nnn c-58-67-proton.fid dmm c ACQUISITION dmf 200 sfrq 500.070 dseq tn H1 dres 1.0 fb 4006 homo n np 65536 DEC2 sw 8000.0 dfrq2 0 bs 16 dpwr2 1 tpwr 55 dof2 0 pw 9.0 dm2 n d1 0 dmm2 c
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn file /export/home/- dpwr 18 userid/data/ui50n- dof 0 b/kalyanid/dk-6-75- dm nnn c-58-67-proton.fid dmm c ACQUISITION dmf 200 sfrq 500.070 dseq tn H1 dres 1.0 at 4.096 homo n np 65536 DEC2 0 sw 8000.0 dfrq2 0 fb 4000 dn2 1 bs 16 dpwr2 1 tpwr 9.0 dm2 n
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn file /export/home/~ dpwr 18 userld/data/ui500n~ dof 0 b/kalyanid/dk-6-75~ dm nnn c-58-67-proton.fid dmm c ACQUISITION dmf 200 sfrq 500.070 dseq tn H1 dres 1.0 np 65536 DEC2 sw 8000.0 dfrq2 0 fb 4000 dn2 bs 16 dpwr2 1 tpwr 55 dof2 0
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn file /export/home/~ dpwr 18 user1d/data/ui500n~ dof 0 b/kalyanid/dk-6-75~ dm nnn c-58-67-proton.fid dmm c ACQUISITION dmf 200 sfrq 500.070 dseq file tn H1 dres 1.0 at 4.096 homo n np 65536 DEC2 sw 8000.0 dfrq2 0 fb 4000 dn2 bs 16 dpwr2 1
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn H1 file /export/home/~ dpwr 18 user1d/data/ui500n~ dof 0 b/kalyanid/dk-6-75~ dm nnn c AcQUISITION dmf 200 sfrq 500.070 dseq
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDCl3 dn H1 file /export/home/~ dpwr 18 user1d/data/ui500n~ dof 0 b/kalyanid/dk-6-75~ dm nnn c-58-67-proton.fid dmm c ACQUISITION dmf 200 sfrq 500.070 dseq tn H1 dres 1.0 at 4.096 homo n np 65536 DEC2 (sw 8000.0 dfrq2 0
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn H1 file /export/home/~ dpwr 18 18 userld/data/ui500n- dof 0 0 b/kalyanid/dk-6-75- dm nnn c acQUISITION dmf 200 sfrq 500.070 dseq tn H1 dress 1.0 at 4.096 homo n np 65536 DEC2 ((((((((((((((((((((((((((((((((((((
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn file /export/home/~ dpwr 18 userld/data/ui500n~ dof 0 b/kalyanid/dk-6-75~ dm nnn c-58-67-proton.fid dmm c ACQUISITION dmf 200 sfrq 500.070 dseq (()) tn H1 dres 1.0 at 4.096 homo n
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDCl3 dn H1 file /export/home/~ dpwr 18 userld/data/ui500n~ dof 0 b/kalyanid/dk-6-75~ dm nnn c-58-67-proton.fid dmm c ACQUISITION dmf 200 sfrq 500.070 dseq tn H1 dres 1.0
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDCl3 dn H1 file /export/home/~ dpwr 18 user1d/data/ui500n~ dof 0 b/kalyanid/dk-6-75~ dm nnn c-58-67-proton.fid dmm c ACQUISITION dmf 200 sfrq 500.070 dseq ((())
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDCl3 dn H1 file /export/home/~ dpwr 18 userld/data/ui500n~ dof 0 b/kalyanid/dk-6-75~ dm nnn c-58-67-proton.fid dmm c ACQUISITION dmf 200
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDC13 dn H1 file /export/home/~ dpwr 18 user1d/data/ui500n~ dof 0 b/kalyanid/dk-6-75~ dm nnn c-58-67-proton.fid dmm c
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDCl3 dn H1 file /export/home/~ dpwr 18 user1d/data/ui500n~ dof 0 b/kalvanid/dk-6-75~ dm nnn
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDCl3 dn H1 file /export/home/~ dpwr 18 userld/data/ui500n~ dof 0
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 solvent CDCl3 dn H1 file (export/home(z dpwr 18)
expl s2pul SAMPLE DEC. & VT date Feb 5 2010 dfrq 500.070 soluent (DCl3 dp H1
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bs	16	dpwr2	1										
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pw	9.0	dm2	n										
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expl s2	2pul				(Se
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ai	0	amm2		C										
tor	2.0	ami2		200										
nt	1	dseq2												
ct	1	dres2		1.0										
alock	n	nomo2		n					1	i i				
gain	not used	PI	ROCESSING	3										
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DIS	SPLAY													
sp	-250.0	werr			'				1					
wp	5496.6	wexp												
vs	347	wbs						I A						
sc	0	wnt												
wc	250											1 I		
hzmm	21.99											N N		
is	599.95								11			M A		
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exp1 std1h



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expl s2pul



1H-44

exp1 std1h

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31P-44

exp1 s2pul



exp1 s2pul



exp1 std1h



31P-45

exp1 s2pul



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