Supporting information

Enantioselective ring opening reaction of meso epoxides with ArSeH catalyzed by heterometallic Ti-Ga-Salen system

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**General Procedures:** All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use according to the standard method. Unless otherwise indicated, all materials were obtained from commercial sources and were used without further purification. Trimethylgallium was provided by the National 863 Program Advanced Material MO Precursors R&D Center of China. 1,2,3,4-Tetrahedronaphtho-2,3-oxirene, phenylselenol, and 1-naphthylselenol were prepared according to literature procedures respectively,\(^1,2\) Phenylselenol and 1-naphthylselenol were stored in the argon atmosphere after purification. Elemental analyses were carried out on a Perkin-Elmer 240 C elemental analyzer in the Analysis Center of Nanjing University. \(^1\)H NMR data were recorded on a Bruker AMX-300 spectrometer with chemical shifts referenced to SiMe\(_4\) as internal standard. Infrared spectra were measured in cm\(^{-1}\), using a 5DX-FT-2 spectrometer. Mass spectra were taken using HP 5989A mass spectrometer. Ee values were determined by a Perkin-Elmer 200 HPLC on a chiral Chiralcel OD-H column with UV detection at 254 nm.

**General procedure for the ring opening of the meso epoxides by aryl selenols:** GaMe\(_3\) (0.05 mmol, 0.5 M in hexane) was added dropwise to 3 mL of hexane solution of ligand \((R,R)-1b\) (28 mg, 0.05 mmol) under argon atmosphere at \(0^\circ\). After the solution was stirred for 1h at room temperature, a solution of Ti(OiPr)\(_4\) (0.05 mmol, 0.2 M in hexane) was then added and stirred for another 1h to form the Ti–Ga-Salen complex. The result yellow solution was cooled to -40\(^\circ\). The epoxide (1.0 mmol) and arylselenol (1.2 mmol) were added successively. The mixture was stirred for 5h at the same temperature before being quenched with a saturate NH\(_4\)Cl solution and extracted with ether. The organic phase was dried over Na\(_2\)SO\(_4\), and removed the solvent. After being separated by preparative silica gel TLC, the \(\beta\)-aryl seleno alcohol was obtained.
2-Phenylseleno-1-cyclohexanol

Yellow oil, $^1$HNMR $^{13}$CDCl$_3$, 300M $^\delta$7.59-7.62 (m, 2H), 7.26-7.33 (m, 3H), 3.34-3.37 (m, 1H), 2.94 (s, br, 1H), 2.91-2.93 (m, 1H), 2.13-2.18 (m, 2H), 1.74-1.76 (m, 1H), 1.61-1.63 (m, 1H), 1.22-1.44 (m, 4H). MS (EI) $m/z$ (%) = 256 (M$^+$, 33), 158 (100), 81 (89). $\lbrack \alpha \rbrack_{20}^D +48.7^\circ$ (c = 1.1, CHCl$_3$). HPLC analysis retention time: 11.35 min (minor), 14.58 min (major) (Daicel Chiralcel OD-H, hexane/i-PrOH = 9/1, flow rate = 0.5 mL/min).

2-Phenylseleno-1-cyclopentanol

Yellow oil, $^1$HNMR $^{13}$CDCl$_3$, 300M $^\delta$7.55-7.58 (m, 2H), 7.26-7.30 (m, 3H), 4.01-4.24 (m, 2H), 3.41-3.46 (m, 1H), 1.60-2.28 (m, 6H). IR (KBr) $\nu$ = 3362, 3058, 2961, 1579, 1074 cm$^{-1}$. MS (EI) $m/z$ (%) = 256 (M$^+$, 33), 242 (15), 158 (37), 84 (39), 78(30), 67(72), 57(100). Anal. calcd. for C$_{11}$H$_{14}$OSe (%): C, 54.78; H, 5.85; Found : C, 54.50; H, 5.77. $\lbrack \alpha \rbrack_{20}^D +2.1^\circ$ (c = 0.7, CHCl$_3$). HPLC analysis retention time: 11.25 min (minor), 14.32 min (major) (Daicel Chiralcel OD-H, hexane/i-PrOH = 9/1, flow rate = 0.5 mL/min).

3-Phenylseleno-1,2,3,4-tetrahydro-2-naphthalenol

Pale yellow solid, $^1$HNMR $^{13}$CDCl$_3$, 300M $^\delta$7.66-7.70 (m, 2H), 7.31-7.37 (m, 2H), 7.05-7.20 (m, 5H), 3.87-3.9 (m, 1H), 3.29-3.44 (m, 4H), 2.87-3.16 (m, 2H ). IR (KBr)
$v = 3428, 3061, 3021, 2924, 1580, 1493, 1477, 1454, 1437 \text{ cm}^{-1}$. MS (EI) $m/z$ (%) = 304 (M+, 16), 158 (15), 147(21), 129(100), 77(24). Anal. calcd. for C$_{16}$H$_{16}$OSe (%): C, 63.37; H, 5.32; Found: C, 63.10; H, 5.47. $[\alpha]_{D}^{20} = +55.1^{\circ}$ ($c = 1.9$, CHCl$_3$). HPLC analysis retention time: 17.53 min (minor), 19.34 min (major) (Daicel Chiralcel OD-H, hexane/i-PrOH = 9/1, flow rate = 0.5 mL/min).

**3-Phenylseleno-2-butylol**

Yellow oil, $^1$HNMR (CDCl$_3$, 300M)$\delta$7.55-7.61 (m, 2H), 7.22-7.28 (m, 3H), 3.64-3.72 (m, 1H), 3.15-3.22 (s, 1H), 2.85 (m, br, 1H), 1.39 (d, J = 5.3 Hz, 3H), 1.24 (d, J = 5.2 Hz, 3H); IR (KBr) $v = 3417, 3071, 2973, 2926, 1579, 1476, 1438, 1377 \text{ cm}^{-1}$. MS (EI) $m/z = 230$ (M+, 31), 185 (10), 158 (62), 73 (97), 55 (100). Anal. calcd. for C$_{10}$H$_{14}$OSe (%): C, 52.41; H,6.16; Found: C, 52.12; H, 6.03. $[\alpha]_{D}^{20} = +34.2^{\circ}$ ($c = 1.1$, CHCl$_3$). HPLC analysis retention time: 10.73 min (minor), 11.77 min (major) (Daicel Chiralcel OD-H, hexane/i-PrOH = 9/1, flow rate = 0.5 mL/min).

**2-Phenylseleno-1,2-diphenyl-1-ethanol**

Yellow oil, $^1$HNMR (CDCl$_3$, 300M)$\delta$7.42-7.45 (m, 2H), 7.19-7.27 (m, 8H), 7.13-7.15 (m, 3H), 7.04-7.06 (m, 2H), 5.10 (d, J = 8.6 Hz, 1H), 4.55 (d, J = 8.6 Hz, 1H ), 3.42 (m, br, 1H). IR (KBr) $v = 3434, 3031, 2925, 1601, 1493, 1453 \text{ cm}^{-1}$; MS (EI) $m/z$ (%) = 354 (M+, 12), 178 (17), 107 (100), 91(37). Anal. calcd. for C$_{20}$H$_{18}$OSe (%): C, 67.99; H, 5.13; Found: C, 70.21; H, 5.25. $[\alpha]_{D}^{20} = +17.3^{\circ}$ ($c = 1.6$, CHCl$_3$). HPLC analysis retention time: 19.06 min (minor), 20.62 min (major) (Daicel Chiralcel OD-H,
hexane/i-PrOH = 9/1, flow rate = 0.5 mL/min).

2-(1-Naphthylseleno)-1-cyclohexanol

Yellow oil, $^1$HNMR $\delta$CDCl$_3$, 300M$\delta$ 8.54-8.59 (d, J=6.1 Hz, 1H), 7.84-7.94 (m, 3H), 7.42-7.59 (m, 2 H), 7.37-7.42 (m, 1H), 3.44-3.48 (m, 1H), 3.02-3.06 (m, 2H), 2.11-2.17 (m, 2H), 1.51-1.71 (m, 6H). IR (KBr) $\nu$ = 3417, 3052, 2933, 2857, 1580, 1506, 1447 cm$^{-1}$. MS (EI) $m/z$ (%) = 305.9 (M+, 11), 208 (22), 80 (37), 57 (100). Anal. calcd. for C$_{16}$H$_{18}$OSe (%): C, 62.95; H, 5.94; Found: C, 63.11; H, 5.98. $[\alpha]_{D}^{20}$ + 101.2$^\circ$ (c = 0.8, CHCl$_3$). HPLC analysis retention time: 13.32 min (minor), 22.17 min (major) (Daicel Chiralcel OD-H, hexane/i-PrOH = 9/1, flow rate = 0.5 mL/min).

2-(1-Naphthylseleno)-1-cyclopentanol

Yellow oil, $^1$HNMR $\delta$CDCl$_3$, 300M$\delta$ 8.46-8.48 (d, J = 7.7 Hz, 1H), 7.79-7.82 (m, 3H), 7.50-7.61 (m, 2H), 7.37-7.42 (m, 1H), 4.01-4.26 (m, 2H), 3.48 (s, br, 1H), 1.58-2.26 (m, 6H). IR (KBr) $\nu$ = 3397, 3053, 2961, 1588, 1560, 1501, 1445 cm$^{-1}$. MS (EI) $m/z$ (%) =292 (M$,^+$, 1), 208(2), 128 (6), 84 (50), 67(62), 57 (100). Anal. calcd. for C$_{15}$H$_{16}$OSe (%): C, 61.86; H, 5.54; Found: C, 61.95; H, 5.61. $[\alpha]_{D}^{20}$ + 4.1$^\circ$ (c = 1.1, CHCl$_3$). HPLC analysis retention time: 16.51 min (minor), 26.19min (major) (Daicel Chiralcel OD-H, hexane/i-PrOH = 9/1, flow rate = 0.5 mL/min).

3-(1-Naphthanoseleno)-2-butyline
Yellow oil, $^1$HNMR $\delta$CDCl$_3$, 300M $\delta$8.50-8.53 (d, $J$ = 8.2Hz, 1H), 7.48-7.93 (m, 5H), 7.37-7.42 (m, 1H), 3.72-3.81 (m, 1H), 2.46 (s, br, 1H), 1.40-1.42 (d, $J$ = 6.9 Hz, 3H), 1.27-1.29 (d, $J$ = 6.1 Hz, 3H). IR (KBr) $\nu$ = 3414, 3052, 2968, 1560, 1501, 1447 cm$^{-1}$. MS (EI) m/z (%) = 280 (M$^+$, 7), 208 (15), 128 (44), 73 (100). Anal. calcd. for C$_{14}$H$_{16}$OSe (%): C, 60.22; H, 5.78; Found: C, 60.48; H, 5.64. $\alpha$$_{20}$$^D$ + 50.6 ° ($c$ = 1.3, CHCl$_3$). HPLC analysis retention time: 13.43 min (minor), 16.77 min (major) (Daicel Chiralcel OD-H, hexane/i-PrOH = 9/1, flow rate = 0.5 mL/min).

2-(1-Naphthylseleno)-1, 2-diphenyl-1-ethanol

Yellow oil, $^1$HNMR $\delta$CDCl$_3$, 300M $\delta$8.23-8.26 (d, $J$ = 8.6 Hz, 1H), 7.80-7.82 (m, 2H), 6.97-7.36 (m, 14H), 5.15-5.17 (d, $J$ = 8.1 Hz, 1H), 5.03-5.06 (d, $J$ = 8.1 Hz, 1H), 3.26 (s, br, 1H). IR (KBr) $\nu$ = 3436, 3029, 2973, 1600, 1493, 1452 cm$^{-1}$. MS (EI) m/z (%) = 404 (M$^+$, 10), 208 (11), 178 (51), 107 (100). Anal. calcd. for C$_{24}$H$_{20}$OSe (%): C, 71.46; H, 5.00; Found: C, 71.21; H, 4.87. $\alpha$$_{20}$$^D$ + 2.9° ($c$ = 0.4, CHCl$_3$). HPLC analysis retention time: 31.80 min (minor), 38.74 min (major) (Daicel Chiralcel OD-H, hexane/i-PrOH = 9/1, flow rate = 0.5 mL/min).

References


HPLC analysis
Racemic 2-(phenylseleno)-1-cyclohexanol resulted from the reaction catalyzed by 3b.
Racemic 2-(phenylseleno)-1-cyclopentanol

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Optical active 2-(phenylseleno)-1-cyclopentanol resulted from the reaction catalyzed by 3b
Racemic 3-(phenylseleno)-1,2,3,4-tetrahydro-2-naphthalenol resulted from the reaction catalyzed by 3b

Optical active 3-(phenylseleno)-1,2,3,4-tetrahydro-2-naphthalenol resulted from the reaction catalyzed by 3b