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-Tetrahydronaphtho-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. ¹H NMR data were recorded on a Bruker AMX-300 spectrometer with chemical shifts referenced to SiMe₄ 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: GaMe₃ (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 °C. After the solution was stirred for 1h at room temperature, a solution of Ti(O*i*Pr)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 °C. 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 NH₄Cl solution and extracted with ether. The organic phase was dried over Na₂SO₄, and removed the solvent. After being separated by preparative silica gel TLC, the β-arylseleno alcohol was obtained.

2-Phenylseleno-1-cyclohexanol³

Yellow oil, $^1\text{H NMR}$ $\square$ CDCl_3 , 300M $\square$ δ 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). $[\alpha]_{\text{D}}^{20} + 48.7^\circ$ ($c = 1.1$, 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, $^1\text{H NMR}$ $\square$ CDCl_3 , 300M $\square$ δ 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 $\text{C}_{11}\text{H}_{14}\text{OSe}$ (%): C, 54.78; H, 5.85; Found : C, 54.50; H, 5.77. $[\alpha]_{\text{D}}^{20} + 2.1^\circ$ ($c = 0.7$, 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, $^1\text{H NMR}$ $\square$ CDCl_3 , 300M $\square$ δ 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)

$\nu = 3428, 3061, 3021, 2924, 1580, 1493, 1477, 1454, 1437 \text{ cm}^{-1}$. 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. $[\alpha]^{20}_D + 55.1^\circ$ ($c = 1.9, CHCl_3$). 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, 1H NMR ($CDCl_3$, 300M) δ 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, $J = 5.3 \text{ Hz}$, 3H), 1.24 (d, $J = 5.2 \text{ Hz}$, 3H); IR (KBr) $\nu = 3417, 3071, 2973, 2926, 1579, 1476, 1438, 1377 \text{ cm}^{-1}$. 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. $[\alpha]^{20}_D + 34.2^\circ$ ($c = 1.1, CHCl_3$). 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, 1H NMR ($CDCl_3$, 300M) δ 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, $J = 8.6 \text{ Hz}$, 1H), 4.55 (d, $J = 8.6 \text{ Hz}$, 1H), 3.42 (m, br, 1H). IR (KBr) $\nu = 3434, 3031, 2925, 1601, 1493, 1453 \text{ cm}^{-1}$; 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. $[\alpha]^{20}_D + 17.3^\circ$ ($c = 1.6, CHCl_3$). 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, $^1\text{H NMR}$ $\square$ CDCl_3 , 300M $\square$ δ 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), 1.15-1.71 (m, 6H). IR (KBr) ν = 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 $\text{C}_{16}\text{H}_{18}\text{OSe}$ (%): C, 62.95; H, 5.94; Found: C, 63.11; H, 5.98. $[\alpha]_{\text{D}}^{20} + 101.2^\circ$ ($c = 0.8$, 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, $^1\text{H NMR}$ $\square$ CDCl_3 , 300M $\square$ δ 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) ν = 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 $\text{C}_{15}\text{H}_{16}\text{OSe}$ (%): C, 61.86; H, 5.54; Found: C, 61.95; H, 5.61. $[\alpha]_{\text{D}}^{20} + 4.1^\circ$ ($c = 1.1$, 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-Naphthylseleno)-2-butanol

Yellow oil, $^1\text{H NMR}$ $\square$ CDCl_3 , 300M $\square$ δ 8.50-8.53 (d, $J = 8.2\text{ Hz}$, 1H), 7.48-7.93(m, 5H), 7.37-7.42 (m, 1 H), 3.72-3.81 (m, 1H), 3.28-3.32 (m, 1H), 2.46 (s, br, 1H), 1.40-1.42 (d, $J = 6.9\text{ Hz}$, 3H), 1.27-1.29 (d, $J = 6.1\text{ Hz}$, 3H). IR (KBr) $\nu = 3414, 3052, 2968, 1560, 1501, 1447\text{ cm}^{-1}$. MS (EI) m/z (%) = 280 (M^+ , 7), 208 (15), 128 (44), 73 (100). Anal. calcd. for $\text{C}_{14}\text{H}_{16}\text{OSe}$ (%): C, 60.22; H, 5.78; Found: C, 60.48; H, 5.64. $[\alpha]_{\text{D}}^{20} + 50.6^\circ$ ($c = 1.3, \text{CHCl}_3$). 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, $^1\text{H NMR}$ $\square$ CDCl_3 , 300M $\square$ δ 8.23-8.26 (d, $J = 8.6\text{ Hz}$, 1H), 7.80-7.82 (m, 2H), 6.97-7.36 (m, 14H), 5.15-5.17(d, $J = 8.1\text{ Hz}$, 1H), 5.03-5.06 (d, $J = 8.1\text{ Hz}$, 1H), 3.26 (s, br, 1H). IR (KBr) $\nu = 3436, 3029, 2973, 1600, 1493, 1452\text{ cm}^{-1}$. MS (EI) m/z (%) = 404 (M^+ , 10), 208 (11), 178 (51), 107 (100). Anal. calcd. for $\text{C}_{24}\text{H}_{20}\text{OSe}$ (%): C, 71.46; H, 5.00; Found: C, 71.21; H, 4.87. $[\alpha]_{\text{D}}^{20} + 2.9^\circ$ ($c = 0.4, \text{CHCl}_3$). 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

- 1 Cook, E. S.; Hill, A. J. *J. Am. Chem. Soc.* **1940**, 62, 1995.
- 2 *Org. Syntheses Coll.* **1955**, 3, 777.
- 3 Dowsland, J.; Mckerlie, F.; Procter, D. J. *Tetrahedron Lett.* **2000**, 41, 4923.

HPLC analysis

HPLC report

ymh

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Cal. Range	Volt Range	BL	Raw Amount	Adjusted Amount
1		11.332	8297562.65	524575.74	49.85	49.85			MM	8.2976	8.2976
2		14.538	8346023.92	410067.20	50.15	50.15			MM	8.3460	8.3460
			16643586.57	934642.94	100.00	100.00				16.6436	16.6436

Racemic 2-(phenylseleno)-1-cyclohexanol

色谱分析报告

分析结果

Peak #	Time [min]	Area [uV*s]	Height [uV]	Area [%]	Norm. Area [%]	Area/Height [s]
1	11.352	121237.53	8671.21	1.30	1.30	13.9816
2	14.560	9228933.75	453655.74	98.70	98.70	20.3435
		9350171.28	462326.96	100.00	100.00

Optical active 2-(phenylseleno)-1-cyclohexanol resulted from
the reaction catalyzed by **3b**

HPLC REPORT

HPLC REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Raw Amount	Adjusted Amount
1		11.212	42151536.08	2.87e+06	50.36	50.36		
2		14.363	41548208.30	2.12e+06	49.64	49.64	41.5482	41.5482
			83699744.37	4.99e+06	100.00	100.00	41.5482	41.5482

Racemic 2-(phenylseleno)-1-cyclopentanol

HPLC REPORT

HPLC REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Raw Amount	Adjusted Amount
1		11.250	877878.92	61487.10	3.24	3.24	0.8779	0.8779
2		14.323	26255303.28	1.29e+06	96.76	96.76	26.2553	26.2553
			27133182.20	1.35e+06	100.00	100.00	27.1332	27.1332

Optical active 2-(phenylseleno)-1-cyclopentanol resulted from
the reaction catalyzed by **3b**

HPLC REPORT

HPLC REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Raw Amount	Adjusted Amount
1		17.580	6537618.62	260132.71	50.28	50.28	6.5376	6.5376
2		19.509	6466003.85	230433.25	49.72	49.72	6.4660	6.4660
			13003622.47	490565.96	100.00	100.00	13.0036	13.0036

Racemic 3-(phenylseleno)-1,2,3,4-tetrahydro-2-naphthalenol

HPLC REPORT

HPLC REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Raw Amount	Adjusted Amount
1		5.825	4969.84	374.18	0.03	0.03	0.0050	0.0050
2		8.111	5347.11	756.12	0.04	0.04	0.0053	0.0053
3		13.906	9673.71	545.67	0.07	0.07	0.0097	0.0097
4		17.528	774488.28	33780.68	5.25	5.25	0.7745	0.7745
5		19.339	13961547.85	510981.77	94.62	94.62	13.9615	13.9615
			14756026.80	546438.43	100.00	100.00	14.7560	14.7560

Optical active 3-(phenylseleno)-1,2,3,4-tetrahydro-2-naphthalenol

resulted from the reaction catalyzed by **3b**