Palladium-Catalyzed Enantioselective Ring-Opening of Oxabicyclic Alkenes with Organozinc Halides

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General Methods

All reactions were performed under a dry argon atmosphere. Et₂O and THF were freshly distilled from sodium. Dichloromethane was freshly distilled from calcium hydride. Benzyl bromides were used as received without further purification. CH₃I and C₂H₅I were redistilled before use. Benzylzinc bromides,¹ CH₃ZnI,² and C₂H₅ZnI,³ Pd(dppb)Cl₂,⁴ and Pd(CH₃CN)₂Cl₂,⁵ were prepared according to the literature procedures. Melting points were uncorrected. Enantiomeric excess were determined by HPLC using chiral column.

General procedure for palladium-catalyzed ring-opening of oxabicyclic alkenes with organozinc halides.

A solution of bis(acetonitrile)palladium dichloride (5 mol%), (S)-Prⁱ-PHOX **6** (5 mol%), in dichloromethane (1 mL) was stirred at room temperature for two hours. To this solution was added at 10°C *via* canula a solution of oxabenzonorbornadiene (1 mmol) in dichloromethane (15 mL), followed by a solution of organozinc halide (1.5 mmol) in THF. The resulting mixture was allowed to stir at 10°C until completion (monitored by TLC). Drops of water were added and the solution was stirred for half an hour, filtered through a short plug of celite. The solution was concentrated and the crude mixture was purified by flash chromatography on silica gel (ethyl acetate : petroleum = 1 : 7) to afford dihydronaphthol **3**. The ee value was determined by HPLC using chiral AD or OD column.

(+)-(1*S*, 2*S*)-2-Benzyl-1,2-dihydronaphth-1-ol (3aa)⁶

Yield 64%. [α]_D²⁰ = +159° (*c* = 0.59, EtOH). 90% ee (Chiralcel AD column, *n*-hexane / *i*-PrOH = 80/20, *t*_R: 10.0 min, 12.4 min). ¹H NMR (300 MHz, CDCl₃): δ 1.62(s, 1H), 2.77-

2.81(m, 1H), 2.89(dd, $J = 8.0\text{Hz}$, 12.8 Hz, 1H), 3.15 (dd, $J = 7.7\text{Hz}$, 13.0 Hz, 1H), 4.47(dd, $J = 4.1\text{Hz}$, 7.0Hz, 1H), 5.80(dd, $J = 2.5\text{Hz}$, 9.6 Hz, 1H), 6.57(dd, $J = 2.4\text{Hz}$, 9.6 Hz, 1H), 7.12-7.25(m, 3H), 7.26-7.37 (m, 6H). MS (EI) m/z (rel) 236 (M^+ , 1), 218 (47), 145 (100), 144 (46), 127 (51), 115 (34), 91 (43).

(+)-(1*S*, 2*S*)-2-(4-Bromo-benzyl)-1,2-dihydronaphth-1-ol (3ab)

Yield 70%. M.p.115-117°C. $[\alpha]_D^{20} = +182^\circ$ ($c = 0.43$, EtOH). 96% ee (Chiralcel OD column, *n*-hexane / *i*- PrOH = 85/15, t_R : 13.1min, 14.7 min). ^1H NMR (300MHz, CDCl_3): δ 2.72-2.78 (m, 1H), 2.83 (dd, $J = 7.8\text{Hz}$, 13.0 Hz, 1H), 3.10 (dd, $J = 8.4\text{Hz}$, 12.8 Hz, 1H), 4.42 (d, $J = 3.3\text{Hz}$, 1H), 5.75 (dd, $J = 2.4\text{Hz}$, 9.5 Hz, 1H), 6.57 (dd, $J = 2.5\text{Hz}$, 9.5 Hz, 1H), 7.11-7.32 (m, 6H), 7.39 -7.46 (m, 2H). ^{13}C NMR (75MHz, CDCl_3): δ 139.0, 136.2, 132.4, 131.4, 131.0, 129.8, 128.7, 127.7, 127.6, 127.3, 126.6, 120.0, 69.3, 42.3, 34.7. MS (EI) m/z (rel) 314 (M^+ , 2), 296 (7), 145 (100), 144 (16), 127 (31), 115 (19), 91 (7). IR (KBr): 3345, 3201, 2951, 1487, 1335, 1011 cm^{-1} . HRMS ($M^+ - \text{H}_2\text{O}$) calcd. for $\text{C}_{17}\text{H}_{13}\text{Br}$: 296.02006; Found: 296.02013.

(+)-(1*S*, 2*S*)-2-(4'-Fluoro-benzyl)-1,2-dihydronaphth-1-ol (3ac)

Yield 57%. M.p. 77-78°C. $[\alpha]_D^{20} = +172^\circ$ ($c = 0.47$, EtOH). 90% ee (Chiralcel OD column, *n*-hexane / *i*- PrOH = 95/5, t_R : 21.4min, 24.0 min). ^1H NMR (300MHz, CDCl_3): δ 1.66 (d, $J = 6.9\text{Hz}$, 1H), 2.68-2.76 (m, 1H), 2.82 (dd, $J = 7.8\text{Hz}$, 13.0 Hz, 1H), 3.10 (dd, $J = 8.6\text{Hz}$, 13.2 Hz, 1H), 4.41 (t, $J = 5.2\text{Hz}$, 1H), 5.75 (dd, $J = 2.4\text{Hz}$, 9.6 Hz, 1H), 6.55 (dd, $J = 2.4\text{Hz}$, 9.6 Hz, 1H), 6.95-7.10 (m, 2H), 7.13-7.30 (m, 6H). ^{13}C NMR (75MHz, CDCl_3): δ 161.4 (d, $J_{\text{C-F}} = 242.5\text{Hz}$), 136.3, 135.6 (d, $J_{\text{C-F}} = 3.5\text{Hz}$), 132.5, 130.7, 130.5, 130.0, 128.2 (d, $J_{\text{C-F}} = 70.9\text{Hz}$), 127.6, 126.9 (d, $J_{\text{C-F}} = 45.8\text{Hz}$), 115.3, 115.0, 69.3, 42.5 (d, $J_{\text{C-F}} = 1.1\text{Hz}$), 34.5. MS (EI) m/z (rel) 254 (M^+ , 7), 255 (1), 236 (7), 145 (100), 127 (49), 115 (29), 91 (9). IR (KBr): 3370, 3296, 2930, 1599, 1508, 1454, 1335, 1220, 1155, 1080 cm^{-1} . Anal. Calcd. for $\text{C}_{17}\text{H}_{15}\text{FO}$: C, 80.29; H, 5.95, Found: C, 80.33; H, 6.07.

(+)-(1*S*, 2*S*)-2-(4'-Methyl-benzyl)-1,2-dihydronaphth-1-ol (3ad)

Yield 65%. $[\alpha]_D^{20} = +21.3^\circ$ ($c = 0.80$, CHCl_3). 87% ee (Chiralcel AD column, *n*-hexane / *i*- PrOH = 80/20, t_R : 27.8min, 35.7 min). ^1H NMR (300MHz, CDCl_3): δ 2.35 (s, 3H), 2.74-2.81 (m, 1H), 2.85 (dd, $J = 8.0\text{Hz}$, 12.6 Hz, 1H), 3.11 (dd, $J = 8.0\text{Hz}$, 12.8 Hz, 1H), 4.47 (d, $J = 3.6\text{Hz}$, 1H), 5.80 (dd, $J = 2.6\text{Hz}$, 9.3 Hz, 1H), 6.56 (dd, $J = 2.5\text{Hz}$, 9.6 Hz, 1H), 7.12-7.25 (m, 6H), 7.28-7.43 (m, 2H). ^{13}C NMR (75MHz, CDCl_3): δ 136.9, 136.4, 135.5, 132.6, 130.4, 129.1,

129.0, 128.6, 127.7, 127.6, 127.0, 126.5, 69.6, 42.5, 34.8, 21.0. MS (EI) m/z (rel) 250 (M^+ , 1), 232 (49), 145 (100), 144 (74), 127 (65), 115 (65), 91 (24). IR (KBr): 3416, 2922, 1601, 1516, 1486, 1382, 1279, 1086 cm^{-1} . HRMS (M^+ -H₂O) calcd. for C₁₈H₁₆: 232.12520; Found: 232.12460.

(+)-(1*S*, 2*S*)-2-(3'-Methoxyl-benzyl)-1,2-dihydronaphth-1-ol (3ae)

Yield 44%. $[\alpha]_D^{20} = +66^\circ$ ($c = 1.02$, EtOH). 76% ee (Chiralcel AD column, *n*-hexane / *i*-PrOH = 85/15, t_R : 15.5 min, 20.7 min). ¹H NMR (300MHz, CDCl₃): δ 2.75-2.87 (m, 2H), 3.11 (dd, $J = 7.0\text{Hz}$, 12.2 Hz, 1H), 3.79 (s, 3H), 4.47 (d, $J = 3.9\text{Hz}$, 1H), 5.79 (dd, $J = 2.3\text{Hz}$, 9.6 Hz, 1H), 6.55 (dd, $J = 2.4\text{Hz}$, 9.2 Hz, 1H), 6.76-6.90 (m, 3H), 7.12 (d, $J = 7.5\text{Hz}$, 1H), 7.17-7.30 (m, 4H). ¹³C NMR (75MHz, CDCl₃): δ 159.6, 141.7, 136.4, 132.5, 130.2, 129.3, 128.6, 127.6, 127.0, 126.5, 121.6, 114.9, 111.4, 69.6, 55.1, 42.3, 35.3. MS (ESI) m/z (rel) 289.1(100), 266.1(36), 305.0(8). IR (KBr): 3368, 3296, 2945, 1600, 1593, 1488, 1266, 1238, 1162, 1039 cm^{-1} . HRMS(ESI) calcd. for C₁₈H₁₈O₂: 289.1199009; Found: 289.1185430.

(+)-(1*S*, 2*S*)-2-(3',4'-Dichloro-benzyl)-1,2-dihydronaphth-1-ol (3af)

Yield 53%. $[\alpha]_D^{20} = +112^\circ$ ($c = 1.52$, EtOH). 89% ee (Chiralcel OD column, *n*-hexane / *i*-PrOH = 95/5, t_R : 29.4 min, 33.3 min). ¹H NMR (300MHz, CDCl₃): δ 2.69-2.75 (m, 1H), 2.80 (dd, $J = 8.0\text{Hz}$, 13.0Hz, 1H), 3.09 (dd, $J = 8.3\text{Hz}$, 13.0 Hz, 1H), 4.42 (d, $J = 3.9\text{Hz}$, 1H), 5.73 (dd, $J = 1.4\text{Hz}$, 9.4 Hz, 1H), 6.57 (dd, $J = 2.4\text{Hz}$, 9.7 Hz, 1H), 7.12-7.15 (m, 2H), 7.19-7.32 (m, 3H), 7.36-7.48 (m, 3H). ¹³C NMR (75MHz, CDCl₃): 140.4, 136.1, 132.3, 131.1, 130.5, 130.2, 130.0, 129.4, 128.8, 128.7, 127.8, 127.6, 127.5, 126.7, 69.2, 42.3, 34.5. MS (EI) m/z (rel) 304 (M^+ , 2), 286 (2), 145 (100), 127 (34), 115 (26), 91 (7). IR (KBr): 3394, 2926, 1594, 1560, 1473, 1396, 1260, 1131, 1031 cm^{-1} . HRMS (M^+) calcd. for C₁₇H₁₄Cl₂O: 304.04217; Found: 304.04250.

(+)-(1*S*, 2*S*)-2-(3'-Bromobenzyl)-1,2-dihydronaphth-1-ol (3ag)

Yield: 35%. $[\alpha]_D^{20} = +147.7^\circ$ ($c = 2.265$, EtOH); 95% ee (Chiral OD, Flow rate: 0.7mL / min, *n*-hexane / *i*-PrOH = 85 / 15, 254nm, t_R 14.53 min, 15.79 min). ¹H NMR (300MHz, CDCl₃): δ 2.72-2.76(m, 2H), 2.81(dd, $J = 7.8$, 13.2Hz, 1H), 3.13(dd, $J = 7.8$, 12.6Hz, 1H), 4.44(s, 1H), 5.72-5.76(m, 1H), 6.572(dd, $J = 2.1$, 9.3Hz, 1H), 7.11-7.45(m, 8H); ¹³C NMR (75MHz, CDCl₃): δ 34.947, 42.307, 69.328, 122.436, 126.600, 127.298, 127.595, 127.738, 127.959, 128.658, 129.248, 129.714, 129.912, 132.196, 132.397, 136.226, 142.498; MS (EI) m/z (rel) 297(3.45), 296(9.90), 145(100.00), 127(42.52), 115(129.11), 91(11.70), 77(9.79), 63(9.78), 51(7.64); IR: 3411, 2852, 1595, 1567, 1474, 1453, 1021, 998, 887, 771, 706, 670, 512, 445 cm^{-1} ; Anal. Calcd for C₁₇H₁₅BrO: C, 64.78; H, 4.80. Found: C, 64.77; H, 4.77;

(+)-(1*S*, 2*S*)-2-(2'-Bromo benzyl)-1,2-dihydronaphth-1-ol (3ah)

Yield:76%. $[\alpha]_{\text{D}}^{20} = +96.4^{\circ}$ ($c = 3.700$, EtOH); 93%ee (Chiral OD, Flow rate: 0.7mL / min, *n*-hexane / *i*-PrOH = 85 / 15, 254nm, $t_{\text{R}} = 14.14\text{min}$, 15.52min). ^1H NMR (300MHz, CDCl_3): δ 2.29-2.99(m, 2H), 3.03 (dd, $J = 7.5$, 12.6Hz, 1H), 3.11-3.3-21(dd, $J = 8.1$, 12.9Hz, 1H), 4.44-4.98(m, 1H), 5.78-5.83(m, 1H), 6.57(dd, $J = 2.1$, 9.3Hz, 1H), 7.08-7.58(m, 8H); ^{13}C NMR (75MHz, CDCl_3): δ 35.680, 40.400, 69.628, 124.869, 126.618, 127.223, 127.309, 127.712, 127.724, 127.994, 128.674, 129.891, 131.943, 132.482, 132.950, 136.310, 139.257; MS (EI) m/z (rel) 316(0.15), 314(0.19), 145(100.00), 127(52.85), 115(66.98), 77(82.53), 63(82.15), 51(63.83), 39(61.93); IR (KBr): 3369, 3045, 2931, 1565, 1471, 1374, 1297, 1080, 1045, 1024, 786, 749, 667, 442 cm^{-1} ; Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{BrO}$: C, 64.78; H, 4.80. Found: C, 64.72; H, 4.85.

(+)-(1*S*, 2*S*)-2-(2'-Methoxy-benzyl)-1,2-dihydronaphth-1-ol (3ai)

Yield:49.4%; $[\alpha]_{\text{D}}^{20} = +56.6^{\circ}$ ($c = 0.795$, EtOH); 94%ee (Chiral AD; Flow rate: 0.7mL / min, *n*-hexane / *i*-PrOH = 85 / 15, 254nm, $t_{\text{R}} = 17.210\text{min}$, 21.127min). ^1H NMR (300MHz, CDCl_3): δ 2.39(d, $J = 5.4\text{Hz}$, 1H), 2.84-2.95(m, 2H), 3.11-3.18(m, 1H), 3.84(s, 3H), 4.39-4.44(m, 1H), 5.82-5.86(m, 1H), 6.56(dd, $J = 2.1$, 9.0Hz, 1H), 7.08-7.21(m, 8H); ^{13}C NMR (75MHz, CDCl_3): δ 29.922, 41.339, 55.348, 69.420, 110.319, 120.719, 126.394, 126.915, 127.408, 127.572, 127.853, 127.976, 128.431, 130.811, 131.300, 132.871, 136.247, 157.347; MS (EI) m/z (rel) 266(8.27), 145(65.98), 127(53.33), 91(100.00), 77(22.24), 65(26.06), 51(15.13); IR (KBr): 3364, 3290, 2931, 2834, 1587, 1494, 1464, 1289, 1243, 1182, 1052, 1033, 790, 782, 751, 558, 499; Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2$: C, 81.17; H, 6.81; Found: C, 81.02; H, 6.85.

(+)-(1*S*, 2*S*)-2-(2'-Methyl-benzyl)-1,2-dihydronaphth-1-ol (3ai)

Yield:20%); $[\alpha]_{\text{D}}^{20} = +159.1^{\circ}$ ($c = 1.000$, EtOH); 88%ee (Chiral AD, Flow rate: 0.7mL / min, *n*-hexane / *i*-PrOH = 80 / 20, 254nm, $t_{\text{R}} = 6.11\text{ min}$, 6.75 min). ^1H NMR (300MHz, CDCl_3): δ 2.35(s, 3H), 2.77-2.81(m, 1H), 2.89(dd, $J = 8.1$, 13.2Hz, 1H), 3.13(dd, $J = 8.1$, 13.5Hz, 1H), 4.48(s, 1H), 5.79-5.89(m, 1H), 6.56(dd, $J = 2.1$, 9.3Hz, 1H), 7.12-7.30(m, 8H); ^{13}C NMR (75MHz, CDCl_3): δ 19.506, 32.375, 40.953, 69.862, 125.839, 126.254, 126.553, 127.134, 127.573, 127.655, 128.589, 130.068, 130.374, 130.400, 132.517, 136.530, 138.097; IR : 3370, 3023, 2927, 2864, 1603, 1485, 1454, 1333, 1298, 1080, 1044, 791, 769, 741, 694, 570 cm^{-1} ; MS (EI) m/z (rel) 250(0.25), 232(44.33), 145(100.00), 127(65.64), 115(45.39), 105(43.84), 77(34.66), 65(12.45), 51(17.25), 39(20.33); HRMS for ($\text{M}^+ - \text{H}_2\text{O}$) $\text{C}_{18}\text{H}_{16}$: 232.12520; Found: 232.12124.

(+)-(1*S*, 2*S*)-2-(4'-Bromo-benzyl)-1,2-dihydro-5,8-dimethylnaphth-1-ol (3bb)

Yield 76%. $[\alpha]_{\text{D}}^{20} = +61.2^{\circ}$ ($c = 3.28$, EtOH). 95% ee (Chiralcel OD column, *n*-hexane / *i*-PrOH = 97/3, t_{R} : 18.6 min, 20.7 min). ^1H NMR (300MHz, CDCl_3): δ 2.31 (s, 3H), 2.32 (s, 3H), 2.62-2.71(m, 1H), 2.93(dd, $J = 8.0\text{Hz}$, 13.4Hz, 1H), 3.14 (dd, $J = 8.6\text{Hz}$, 13.5 Hz, 1H), 4.59 (dd, $J = 3.9\text{Hz}$, 6.9 Hz, 1H), 5.75 (dt, $J = 1.8\text{Hz}$, 9.5 Hz, 1H), 6.75 (dd, $J = 3.1\text{Hz}$, 9.8 Hz, 1H), 6.99 (dd, $J = 7.8\text{Hz}$, 16.5Hz, 2H), 7.18-7.24 (m, 2H), 7.42-7.47 (m, 2H). ^{13}C NMR (75MHz, CDCl_3): 139.1, 134.3, 133.4, 131.7, 131.5, 131.0, 130.3, 130.1, 129.7, 128.7, 124.6, 119.9, 65.3, 42.0, 35.4, 18.9, 18.3. MS (EI) m/z (rel) 342 (M^+ , 4), 343 (1), 344 (4), 324 (3), 174 (15), 173 (100), 158 (25), 91 (3). IR (KBr): 3440, 2949, 1591, 1574, 1488, 1380, 1259, 1165, 1097, 1012 cm^{-1} . HRMS (M^+) calcd. for $\text{C}_{19}\text{H}_{19}\text{BrO}$: 342.06192; Found: 342.06367.

(+)-(1*S*, 2*S*)-2-(4'-Bromo-benzyl)-1,2-dihydro-6,7-dimethylnaphth-1-ol (3cb)

Yield 72%. $[\alpha]_{\text{D}}^{20} = +32.7^{\circ}$ ($c = 1.70$, CHCl_3). 90% ee (Chiralcel OD column, *n*-hexane / *i*-PrOH = 97/3, t_{R} : 24.6 min, 29.4 min). ^1H NMR (300MHz, CDCl_3): δ 2.23 (s, 3H), 2.27 (s, 3H), 2.66-2.71(m, 1H), 2.79(dd, $J = 7.5\text{Hz}$, 13.2Hz, 1H), 3.07 (dd, $J = 8.9\text{Hz}$, 13.1Hz, 1H), 4.32 (d, $J = 4.2\text{Hz}$, 1H), 5.66 (dd, $J = 1.3\text{Hz}$, 9.6Hz, 1H), 6.50 (dd, $J = 2.6\text{Hz}$, 9.6Hz, 1H), 6.91 (s, 1H), 7.02 (s, 1H), 7.16 (d, $J = 8.6\text{Hz}$, 2H), 7.42 (d, $J = 8.4\text{Hz}$, 2H). ^{13}C NMR (75MHz, CDCl_3): 139.2, 136.9, 136.1, 133.9, 131.4, 131.0, 130.1, 129.1, 128.7, 127.9, 127.1, 119.8, 69.0, 42.6, 34.9, 19.5, 19.4. MS (EI) m/z (rel) 342 (M^+ , 5), 343 (2), 344 (5), 324 (1), 174 (14), 173 (100), 158 (25), 145 (13), 128 (6). IR (KBr): 3383, 2918, 1591, 1558, 1488, 1455, 1330, 1287, 1073, 1012 cm^{-1} . HRMS (M^+) calcd. for $\text{C}_{19}\text{H}_{19}\text{BrO}$: 342.06192; Found: 342.06122.

(+)-(1*S*, 2*S*)-2-(4'-Bromo-benzyl)-1,2-dihydro-6,7-dibromonaphth-1-ol (3db)

Yield 52%. $[\alpha]_{\text{D}}^{20} = +73.3^{\circ}$ ($c = 2.60$, CHCl_3). 81% ee(Chiralcel AD column, *n*-hexane / *i*-PrOH = 90/10, t_{R} : 15.3 min, 25.3 min). ^1H NMR (300MHz, CDCl_3): δ 1.70 (br, 1H), 2.71-2.77(m, 2H), 3.06 (dd, $J = 6.9\text{Hz}$, 11.4Hz, 1H), 4.46 (br, 1H), 5.85 (d, $J = 9.6\text{Hz}$, 1H), 6.46 (d, $J = 9.9\text{Hz}$, 1H), 7.14 (d, $J = 8.1\text{Hz}$, 2H), 7.38 (s, 1H), 7.44 (d, $J = 8.1\text{Hz}$, 2H), 7.55 (s, 1H). ^{13}C NMR (75MHz, CDCl_3): 138.4, 136.8, 133.1, 132.2, 132.0, 131.5, 131.1, 130.9, 125.4, 124.4, 123.0, 120.1, 68.4, 42.0, 34.1. MS (EI) m/z (rel) 470 (M^+ , 3), 472 (7), 473 (2), 474 (7), 475 (2), 476 (2), 454 (4), 393 (2), 224 (96), 222 (100), 171 (28), 169 (30). IR (KBr): 3316, 3042, 2915, 1651, 1589, 1542, 1487, 1470, 1343, 1110, 1072, 1049, 1010 cm^{-1} . HRMS (M^+) calcd. for $\text{C}_{17}\text{H}_{13}\text{Br}_3\text{O}$: 469.85165; Found: 469.85381.

(+)-(1*S*, 2*S*)-2-(4'-Bromo-benzyl)-1,2-dihydro-1,4-dimethylnaphth-1-ol (3eb)

Yield 52%. $[\alpha]_{\text{D}}^{20} = +179^{\circ}$ ($c = 0.36$, EtOH). 64% ee (Chiralcel AD column, *n*-hexane / *i*-PrOH = 97.5/2.5, t_{R} : 11.9 min, 21.3 min). ^1H NMR (300MHz, CDCl_3): δ 1.53 (s, 3H), 1.84 (s, 1H), 2.01 (t, $J = 1.2\text{Hz}$, 3H), 2.28 (dd, $J = 11.1\text{Hz}$, 12.5Hz, 1H), 2.48-2.54 (m, 1H), 3.03 (dd, $J = 4.6\text{Hz}$, 12.5Hz, 1H), 5.50 (dd, $J = 1.5\text{Hz}$, 5.7Hz, 1H), 6.97-7.04 (m, 2H), 7.22-7.37 (m, 5H), 7.58-7.61 (m, 1H). ^{13}C NMR (75MHz, CDCl_3): 141.3, 139.6, 133.6, 131.1, 131.0, 130.9, 127.9, 127.8, 127.3, 123.4, 123.3, 119.6, 74.4, 47.6, 34.3, 29.1, 19.1. MS (EI) m/z (rel) 342 (M^+ , 5), 344 (5), 343 (1), 174 (15), 173 (100), 158 (30), 145 (14), 128 (8), 91 (3). IR (KBr): 3465, 2970, 2922, 1643, 1592, 1488, 1363, 1072, 1012 cm^{-1} . HRMS (M^+) calcd. for $\text{C}_{19}\text{H}_{19}\text{BrO}$: 342.06192; Found: 342.06026.

(+)-2-Methyl-1,2-dihydronaphth-1-ol (10)⁷

Yield 80%. $[\alpha]_{\text{D}}^{20} = +91.1^{\circ}$ ($c = 1.21$, CHCl_3). 80% ee (Chiralcel AD column, *n*-hexane / *i*-PrOH = 97.5/2.5, t_{R} : 19.0 min, 20.4 min). ^1H NMR (300MHz, CDCl_3): δ 1.27 (d, $J = 7.7\text{Hz}$, 3H), 1.57 (d, $J = 8.0\text{Hz}$, 1H), 2.62-2.68 (m, 1H), 4.51 (dd, $J = 4.8\text{Hz}$, 7.4Hz, 1H), 5.80 (dd, $J = 3.1\text{Hz}$, 9.4Hz, 1H), 6.53 (dd, $J = 2.5\text{Hz}$, 9.5Hz, 1H), 7.10-7.14 (m, 1H), 7.21-7.45 (m, 3H). MS (EI) m/z (rel) 160 (M^+ , 64), 161 (8), 159 (13), 145 (79), 131 (100), 128 (30).

(+)-2-Ethyl-1,2-dihydronaphth-1-ol (11)⁷

Yield 81%. $[\alpha]_{\text{D}}^{20} = +47.6^{\circ}$ ($c = 1.21$, CHCl_3). 92% ee (Chiralcel OD column, *n*-hexane / *i*-PrOH = 100/1.25, t_{R} : 25.9 min, 29.2 min). ^1H NMR (300MHz, CDCl_3): δ 1.08 (t, $J = 7.5\text{Hz}$, 3H), 1.56-1.68 (m, 1H), 1.75-1.87 (m, 1H), 2.22-2.39 (m, 1H), 4.60 (d, $J = 4.8\text{Hz}$, 1H), 5.83 (dd, $J = 3.0\text{Hz}$, 9.3Hz, 1H), 6.53 (dd, $J = 2.7\text{Hz}$, 9.9Hz, 1H), 7.09-7.12 (m, 1H), 7.17-7.33 (m, 3H). MS (EI) m/z (rel) 174 (M^+ , 8), 175 (1), 157 (17), 145 (50), 144 (100), 128 (6), 116 (23).

X-ray Structure of compound **3ab**. Only one enantiomer was detected.

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