Supporting Information for:

A Highly Efficient Asymmetric Synthesis of Optically Active α,γ-Substituted γ-Butyrolactones Using Chiral Auxiliary Derived from Isosorbide

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General procedure of the SmI_2 mediated asymmetric reductive coupling reaction: To samarium metal powder 230mg(1.5mmol) in a Schlenk flask was added a solution of diiodomethane(freshly distilled, 0.081ml, 1.0mmol) in THF(5ml) at room temperature under nitrogen. After approximately one hour, the color of the mixture solution turned to deep blue, indicating the formation of samarium diiodide. The solution was then cooled to –78^{o}C, and then a mixture of methacrylate(0.5mmol), ketone(0.5mmol),and chiral proton source(0.5mmol) in THF(5ml) was added. The resulting mixture was stirred for 2h at the same temperature and then allowed to warm slowly, the reaction was subsequently quenched at -10^{o}C with 5% aqueous HCl, extracted with diethyl ether, washed with aqueous $NaHCO_3$, brine, dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The resulting residue was finally purified by flash-column chromatography on silica gel to afford the optically active γ-butyrolactones.

Determination of the enantiomeric excess:
The enantiomeric excess was determined by HPLC analysis using a chiralcel OJ or AD column with *n*-hexane/*iso*-propyl alcohol (80/20) as eluent (UV detected at 254nm). For comparison, racemic γ-butyrolactones were prepared by the reaction of methyl methacrylate with corresponding ketones in the presence of t-butyl alcohol.

1: m. p. : 118-120^{o}C; $[\alpha]_D^{20}$ +26.0°(c 0.495, $CHCl_3$) for 97%ee; FT-IR(KBr): ν 1774, 1451, 1304, 1230, 1191, 1167, 1039, 987, 935, 749, 707 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$): δ 1.27(d, J=7.0Hz, CH_3, 3H), 2.47(t, J=12.1Hz, 1H), 2.61-2.72(m, 1H), 3.23(dd, J_1=7.6Hz, J_2=12.3Hz, 1H), 7.26-7.46(m, PhH, 10H)ppm; EIMS (m/z, %): 252(M^+, 47.47), 224(1.65), 183(65.03), 175(33.28), 115(15.06), 105(100.00), 77(34.11), 42(12.81); Elemental analysis: Calcd for $C_{17}H_{16}O_2$, C 80.93%, H 6.39%, Found C 80.73%, H 6.50%.

trans-**8**: $[\alpha]_D^{20}$ +39.0^o (c 0.32, $CHCl_3$) for >99%*ee*; FT-IR(film): ν 2980, 1771, 1448, 1228, 1142, 1047, 953, 768, 701 cm^{-1}; ^{1}H NMR(400 MHz, $CDCl_3$): δ 1.25(d, 7.1Hz, C-2 CH_3, 3H), 1.73(s, C-4 CH_3, 3H), 2.04(dd, J_1=10.1Hz, J_2=12.2Hz, H_3, 1H), 2.46-2.54(m, H_2, 1H), 2.78(dd, J_1=8.1Hz, J_2=12.2Hz, $H_{3'}$, 1H), 7.28-7.37(m, PhH, 5H)ppm; ^{13}C NMR(75.5 MHz, $CDCl_3$): δ 14.73, 30.34, 35.02, 45.07, 84.52, 124.24, 127.60, 128.61,

143.94, 179.20ppm; EIMS (m/z, %): 190(M^+, 2.15), 175(71.94), 145(2.25), 131(27.06), 105(100.00), 91(16.04), 77(26.88), 43(31.11); HRMS for $C_{12}H_{14}O_2$: Calcd. 190.0994, Found 190.1008

cis-**8**: FT-IR(film): ν 2976, 1772, 1448, 1308, 1219, 1155, 1110, 953, 765, 702 cm^{-1}; ^1H NMR(400 MHz, $CDCl_3$): δ 1.25(d, J=7.1Hz, C-2 CH_3, 3H), 1.67(s, C-4 CH_3, 3H), 2.04-2.12(dd, J_1=10.8Hz, J_2=12.5Hz, H_3, 1H), 2.71(dd, J_1=8.8Hz, J_2=12.6Hz, $H_{3'}$, 1H), 2.89-2.97(m, H_2, 1H), 7.29-7.40(m, PhH, 5H)ppm; ^{13}C NMR(75.5 MHz, $CDCl_3$): δ 15.43, 28.80, 35.29, 44.00, 84.45, 123.91, 127.52, 128.57, 145.39, 178.82ppm; EIMS (m/z, %): 190(M^+, 2.91), 175(100.00), 145(5.08), 105(85.88), 91(18.27), 77(30.93), 51(13.92), 43(16.74); HRMS for $C_{12}H_{14}O_2$: Calcd. 190.0994, Found 190.1010.

trans-**9**: FT-IR(film): ν 2974, 1776, 1450, 1205, 965, 930, 762, 708 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$): δ 0.81(t, J=7.4Hz, $CH_2C\underline{H}_3$, 3H), 1.25(d, 7.0Hz, C-2 CH_3, 3H), 1.90-2.10(m, CH_2, H_3, 3H), 2.43-2.57(m, H_2, 1H) , 2.72(dd, J_1=8.2Hz, J_2=12.2Hz, $H_{3'}$, 1H), 7.25-7.47(m, PhH, 5H)ppm; ^{13}C NMR(75.5 MHz, $CDCl_3$): δ 8.30, 14.73, 34.70, 35.73, 43.40, 87.48, 124.99, 127.58, 128.52, 142.27, 179.41ppm EIMS (m/z, %): 205(M^++1, 0.19), 204(M^+, 0.10), 175(49.21), 131(8.62), 105(100.00), 91(12.06), 77(32.43), 51(13.21);

cis-**9**: FT-IR(film): ν 2974, 1774, 1450, 1198, 1114, 967, 937, 761, 703 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$): δ 0.81(t, J=7.4Hz, CH_2CH_3, 3H), 1.23(d, J=7.1Hz, CH_3, 3H), 1.86-2.12(m, CH_2, H_3, 3H), 2.76(dd, J_1=9.2Hz, J_2=12.5Hz, $H_{3'}$, 1H), 2.84-2.97(m, H_2, 1H), 7.26-7.41(m, PhH, 5H)ppm; EIMS (m/z, %): 205(M^++1, 10.29), 187(4.46), 175(51.15), 159(5.01), 105(100.00), 91(14.47), 77(29.81), 51(12.47)

trans-**10:** $[\alpha]_D^{20}$ +17.6° (c 0.55, $CHCl_3$) for 95%*ee*; FT-IR(KBr): ν 1769, 1512, 1257, 1228, 1140, 1030, 953, 832 cm^{-1}; ^1H NMR(400 MHz, $CDCl_3$): δ 1.25(d, 7.1Hz, C-2 CH_3, 3H), 1.70(s, CH_3, 3H), 2.00(dd, J_1=J_2=12.2Hz, , H_3, 1H) , 2.47-2.56(m, H_2, 1H), 2.74(dd, J_1=8.2Hz, J_2=12.4Hz, $H_{3'}$, 1H), 6.89(m, PhH, 2H), 7.28(m, PhH, 2H)ppm; ^{13}C NMR(75.5 MHz, $CDCl_3$): δ 14.71, 30.51, 35.11, 44.96, 55.33, 84.48, 113.89, 125.49, 130.62, 135.89, 158.96, 179.36ppm; EIMS (m/z, %): 220(M^+, 19.76), 205(66.92), 175(3.40), 161(15.43), 151(16.85), 135(100.00), 77(19.29), 41(17.30)

cis-**10**: FT-IR(KBr): ν 1770, 1614, 1515, 1322, 1250, 1035, 948, 915, 828 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$): δ 1.27(d, 7.1Hz, C-2 CH_3, 3H), 1.66(s, CH_3, 3H), 2.08(dd, J_1=11.0Hz, J_2=12.4Hz, , H_3, 1H) , 2.68(dd, J_1=8.8Hz, J_2=12.5Hz, $H_{3'}$, 1H), 2.90-2.98(m, H_2, 1H), 6.88-6.93(m, PhH, 2H), 7.27-7.35(m, PhH, 2H)ppm; EIMS (m/z, %): 220(M^+, 15.87), 205(72.28), 175(2.09), 161(11.31), 151(14.43), 135(100.00), 77(16.60), 43(22.10)

trans-**11:** $[\alpha]_D^{20}$ +19.2° (c 0.49, $CHCl_3$) for 96%*ee*; FT-IR(KBr): ν 1771, 1484, 1449, 1228, 1142, 1087, 1009, 957, 823 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$): δ 1.26(d, 7.0Hz, C-2 CH_3, 3H), 1.71(s, C-4 CH_3, 3H), 2.04(dd, J_1=J_2=12.2Hz, , H_3, 1H) , 2.43-2.57(m, H_2, 1H), 2.73(dd, J_1=8.2Hz, J_2=12.3Hz, $H_{3'}$, 1H), 7.26(m, PhH, 2H), 7.50(m, PhH, 2H)ppm; ^{13}C NMR(75.5 MHz, $CDCl_3$): δ 14.71, 30.23, 34.94, 44.87, 84.07, 121.65, 126.10,

131.74, 143.01, 178.88ppm; EIMS (m/z, %): 271(M^++2, 27.38), 269(M^+, 31.09), 255(87.54), 253(89.43), 185(69.67), 183(74.58), 130(54.98), 76(33.02), 42(100.00)

cis-**11**: FT-IR(film): ν 2972, 1769, 1488, 1378, 1316, 1224, 1206, 1158, 1057, 1009, 953, 916, 822 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$): δ 1.26(d, 7.1Hz, C-2 CH_3, 3H), 1.65(s, C-4 CH_3, 3H), 2.04(dd, J_1=11.0Hz, J_2=9.0Hz, , H_3, 1H) , 2.70(dd, J_1=8.8Hz, J_2=12.6Hz, $H_{3'}$, 1H), 2.87-2.99(m, H_2, 1H), 7.26(m, PhH, 2H), 7.50(m, PhH, 2H)ppm; EIMS (m/z, %): 270(M^++1, 12.31), 269(M^+, 6.08), 268(M^+-1, 12.85), 255(100.00), 185(79.40), 183(80.29), 130(37.17), 42(61.34)

trans-**12**: $[\alpha]_D^{20}$ -6.0°(c 0.725, $CHCl_3$) for 98%*ee*; FT-IR (KBr): ν 2979, 1768, 1460, 1381, 1228, 1137, 1030, 952, 822, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.27 (d, 7.0Hz, C-2 CH_3, 3H), 1.81(s, C-4 CH_3, 3H), 2.10 (t, 12.2Hz, H_3, 1H), 2.51-2.63 (m , H_2, 1H), 2.88 (dd, J_1=12.4Hz, J_2=8.1Hz, H_3, 1H), 7.41-7.51(m, ArH, 3H),7.81-7.87(m, ArH, 4H)ppm; ^{13}C NMR (75.5MHz, $CDCl_3$): δ 14.74, 30.21, 35.03, 44.87, 84.52, 122.59, 122.81, 126.34, 126.63, 127.54, 128.20, 128.65, 132.60, 132.96, 141.06, 179.32ppm; EI-MS (m/z, %): 241(M^++1, 25.17), 240(M^+, 63.51), 225(91.57), 181(26.18), 166(15.97), 165(21.66), 155(100.00), 127(38.02); HRMS for $C_{16}H_{15}O_2$: Calcd. 240.1151, Found 240.1163

cis-**12**: $[\alpha]_D^{20}$ +10.2°(c 0.50, $CHCl_3$) for 52%*ee*; FT-IR (KBr): ν 2976, 1772, 1455, 1380, 1306, 1219, 1154, 1105, 1054, 954, 821, 751cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.27(d, 7.1Hz, C-2 CH_3, 3H), 1.76(s, C-4 CH_3, 3H), 2.18(dd, J_1=12.3Hz, J_2=10.8Hz, H_3, 1H), 2.78(dd, J_1=12.5Hz, J_2=8.8Hz, H_3, 1H), 2.92-3.03(m, H_2, 1H), 7.43-7.51(m, ArH, 3H), 7.82-7.88(m, ArH, 4H)ppm; ^{13}C NMR (75.5MHz, $CDCl_3$): δ 15.53, 28.77, 35.36, 44.01, 84.59, 122.32, 122.42, 126.23, 126.52, 127.59, 128.20, 128.55, 132.59, 133.07, 142.59, 178.89ppm; EI-MS (m/z, %): 241(M^++1, 36.95), 240(M^+, 70.24), 225(100.00), 195(17.54), 181(21.94), 165(19.53), 155(99.38), 127(30.87); HRMS for $C_{16}H_{15}O_2$: Calcd. 240.1151, Found 240.1160

trans-**13**: $[\alpha]_D^{20}$ -12.0°(c 1.00, $CHCl_3$) for 97%*ee*; FT-IR (KBr): ν 2938, 1768, 1492, 1454, 1279, 1227, 1161, 1065, 999, 879, 764, 727 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.36 (d, 7.2Hz, C-2 CH_3, 3H), 1.93-2.03(m, H_3, $H_{2'}$, $H_{3'}$, 3H), 2.18-2.26(m, $H_{2'}$, 1H), 2.69(dd, J_1=13.1Hz, J_2=9.9Hz, H_3, 1H), 2.82-2.88 (m, $H_{4'}$, 2H), 3.06(m, H_2, 1H), 7.11-7.26(m, ArH, 4H)ppm; ^{13}C NMR (75.5MHz, $CDCl_3$): δ 16.81, 19.27, 28.61, 35.19, 38.05, 44.75, 83.44, 124.75, 126.37, 127.98, 129.33, 136.49, 138.94, 179.78ppm; EI-MS (m/z, %): 216(M^+, 37.20), 147(87.73), 146(62.45), 129(100.00), 128(75.67), 118(92.53), 115(59.08), 90(55.94); HRMS for $C_{14}H_{16}O_2$: Calcd. 216.1151, Found 216.1176

cis-**13**: $[\alpha]_D^{20}$ -17°(c 0.25, $CHCl_3$) for 75%*ee*; FT-IR (KBr): ν 2949, 1760, 1494, 1454, 1322, 1227, 1168, 1091, 977, 933, 767 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.37(d, 7.1Hz, C-2 CH_3, 3H), 1.80-1.89(m, $H_{2'}$, 1H), 1.98-2.09(m, H_3, $H_{2'}$, $H_{3'}$, 4H), 2.66(dd, J_1=13.1Hz, J_2=8.9Hz, H_3, 1H), 2.80-2.87(m, $H_{4'}$, 2H), 2.90-2.96(m, H_2, 1H), 7.08-7.36(m, ArH, 4H)ppm; ^{13}C NMR (75.5MHz, $CDCl_3$): δ 15.52, 20.40, 29.09, 34.26,

35.12, 44.93, 83.64, 126.54, 126.63, 127.98, 128.79, 137.32, 138.38, 179.28ppm; EI-MS (m/z, %): 216(M^+, 35.01), 147(80.01), 146(62.13), 129(100.00), 128(80.32), 118(83.17), 115(55.35), 90(52.00); HRMS for $C_{14}H_{16}O_2$: Calcd. 216.1151, Found 216.1155