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SUPPORTING INFORMATION

Title: A Highly Enantioselective and Catalytic Aryl Transfer Reaction Using Mixed Triarylbismuthane and Dialkylzinc Reagents

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General procedure for asymmetric aryl transfer reaction to aldehydes using triarylbismuthane/Me_2Zn reagents

Under a nitrogen atmosphere, triarylbismuthane (2.4 mmol) was dissolved in dry toluene (7 ml). Dimethylzinc (7.2 mmol, 1.0 M in hexane) was added to the solution, and the reaction mixture was refluxed for 10 h. After the mixture was cooled to 0 °C, a solution of the chiral catalyst (0.10 mmol) in toluene (1 ml) was added to the mixture. After 15 min of stirring, the aldehyde (1.00 mmol) was added to the mixture, and the mixture was stirred for 16 h at 0 °C. The reaction was quenched by the addition of 1 M hydrochloric acid (10 ml). After the addition of sat. aq. $NaHCO_3$ (15 ml), the mixture was filtered through celite, and extracted with AcOEt. The extract was dried with Na_2SO_4 and concentrated under reduced pressure. Purification of the residue by preparative silica gel TLC (develpoping solvent: benzene/AcOEt = 15/1) produced the optically active secondary alcohol. The ee value was determined by HPLC analysis on a column fitted with a chiral stationary phase. Racemic samples for HPLC analyses were synthesized by standard Grignard conditions.

(*S*)-(-)-(*p*-Tolyl)phenylmethanol (2a).[1] Yield 88%. 97% ee. Colorless needles; m.p. 54-55 °C (hexane); $[\alpha]_D^{26}$ -8.8 (*c* 1.00, benzene) [lit[1]. $[\alpha]_D^{22}$ +8.71 (*c* 0.4, benzene) for (*R*)-**2a** with 84.6% ee]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15 (d, *J* = 3.8 Hz, 1H, OH), 2.33 (s, 3H), 5.82 (d, *J* = 3.8 Hz, 1H), 7.1-7.4 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 21.1, 76.1, 126.4, 126.5, 127.4, 128.4, 129.2, 137.3, 140.9, 143.9; IR (KBr) ν 3360, 2920, 1600, 1490 cm^{-1}; HPLC conditions: Daicel Chiralpak AD-H, eluent: 2% 2-propanol in hexane, flow set: 1.00 ml/ min, r.t., retention time (min): 31.6 (*R*-isomer), 34.6 (*S*-isomer); HRMS (ESI) calcd for $C_{14}H_{14}O$ ($M+Na^+$) 221.0942, found 221.0934.

(*S*)-(+)-(4-Chlorophenyl)phenylmethanol (2b).[2,3] Yield 96%. 96% ee. Colorless needles; m.p. 60-61 °C (hexane); $[\alpha]_D^{29}$ +20.7 (*c* 1.00, $CHCl_3$) [lit[2]. $[\alpha]_D^{25}$ +18 (*c* 1.08, benzene) for sample with 94% ee]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.20 (d, *J* = 3.5 Hz, 1H, OH), 5.82 (d, *J* = 3.5 Hz, 1H),

7.2-7.4 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 75.6, 126.5, 127.8, 128.6, 133.2, 142.2, 143.4; IR (KBr) ν 3330, 2910, 1600, 1490 cm^{-1}; HPLC conditions: Daicel Chiralcel OB-H, eluent: 10% 2-propanol in hexane, flow set: 0.65 ml/ min, r.t., retention time (min): 26.0 (*R*-isomer), 37.7 (*S*-isomer); HRMS (ESI) calcd for $C_{13}H_{11}{}^{35}ClO$ ($M-H^+$) 217.0420, found 217.0423.

(*S*)-(+)-(4-Bromophenyl)phenylmethanol (2c).[4] Yield 76%. 97% ee. Colorless needles; m.p. 81-82 °C (hexane); $[\alpha]_D^{28}$ +19.2 (*c* 1.00, benzene) [lit[4]. $[\alpha]_D^{22}$ +19.8 (*c* 5, benzene)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.28 (d, *J* = 3.4 Hz, 1H, OH), 5.78 (d, *J* = 3.4 Hz, 1H), 7.2-7.4 (m, 7H), 7.4-7.5 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 75.6, 121.4, 126.5, 127.8, 128.6, 131.5, 142.7, 143.3; IR (KBr) ν 3230, 2910, 1590, 1490 cm^{-1}; HPLC conditions: Daicel Chiralcel OB-H, eluent: 10% 2-propanol in hexane, flow set: 0.50 ml/ min, r.t., retention time (min): 33.1 (*R*-isomer), 44.6 (*S*-isomer); HRMS (ESI) calcd for $C_{13}H_{11}{}^{79}BrO$ ($M-H^+$) 260.9915, found 260.9923.

(*S*)-(-)-(2-Methoxyphenyl)phenylmethanol (2d).[2] Yield 99%. 84% ee. Colorless oil; $[\alpha]_D^{29}$ -33.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.01 (d, *J* = 5.3 Hz, 1H, OH), 3.81 (s, 3H), 6.06 (d, *J* = 5.3 Hz, 1H), 6.8-7.0 (m, 2H), 7.2-7.4 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 55.4, 72.3, 110.7, 120.8, 126.5, 127.1, 127.8, 128.1, 128.7, 131.9, 143.2, 156.7; IR (neat) ν 3400, 2940, 1600, 1490, 1240, 1030 cm^{-1}; HPLC conditions: Daicel Chiralcel OD-H, eluent: 3% 2-propanol in hexane, flow set: 1.00 ml/ min, r.t., retention time (min): 27.6 (*S*-isomer), 34.5 (*R*-isomer); HRMS (ESI) calcd for $C_{14}H_{14}O_2$ ($M+Na^+$) 237.0891, found 237.0893.

(*S*)-(+)-(3-Methoxyphenyl)phenylmethanol (2e).[5] Yield 93%. 96% ee. Colorless oil; $[\alpha]_D^{29}$ +17.2 (*c* 1.00, $CHCl_3$) [lit[2]. $[\alpha]_D^{23}$ +16.6 (*c* 2.82, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.20 (d, *J* = 3.4 Hz, 1H, OH), 3.79 (s, 3H), 5.82 (d, *J* = 3.4 Hz, 1H), 6.80 (m, 1H), 6.9-7.0 (m, 2H), 7.2-7.4 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 55.2, 76.1, 112.0, 112.9, 118.9, 126.5, 127.6, 128.5, 129.5, 143.6, 145.4, 159.7; IR (neat) ν 3430, 2940, 1600, 1490, 1260, 1040 cm^{-1}; HPLC conditions: Daicel

Chiralpak AD-H, eluent: 5% 2-propanol in hexane, flow set: 0.50 ml/ min, r.t., retention time (min): 43.7 (*S*-isomer), 46.0 (*R*-isomer); HRMS (ESI) calcd for $C_{14}H_{14}O_2$ ($M+Na^+$) 237.0891, found 237.0879.

(*S*)-(-)-(4-Methoxyphenyl)phenylmethanol (2f).[2] Yield 94%. 97% ee. Colorless oil; $[\alpha]_D^{25}$ -13.9 (*c* 1.00, benzene) [lit[2]. $[\alpha]_D^{25}$ -14 (*c* 0.627, benzene) for a sample with 91% ee]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.16 (d, *J* = 3.5 Hz, 1H, OH), 3.79 (s, 3H), 5.81 (d, *J* = 3.5 Hz, 1H), 6.8-6.9 (m, 2H), 7.2-7.4 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 55.2, 75.8, 113.8, 126.4, 127.4, 127.9, 128.4, 136.1, 144.0, 159.0; IR (neat) ν 3400, 2910, 1610, 1490, 1250, 1030 cm^{-1}; HPLC conditions: Daicel Chiralpak AD-H, eluent: 5% 2-propanol in hexane, flow set: 0.70 ml/ min, r.t., retention time (min): 32.6 (*R*-isomer), 35.6 (*S*-isomer); HRMS (ESI) calcd for $C_{14}H_{14}O_2$ ($M+Na^+$) 237.0891, found 237.0884.

(*S*)-(+)-(4-Chlorophenyl)(*p*-tolyl)methanol (2g)[1] Yield 88%, 97% ee. Colorless needles; m.p. 70-71 °C (hexane); $[\alpha]_D^{27}$ + 27.7 (*c* 1.00, $CHCl_3$) [lit[1]. $[\alpha]_D^{22}$ +19.96 (*c* 0.27, benzene) for a sample with 84.6% ee]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.31 (d, *J* = 3.1 Hz, 1H, OH), 2.32 (s, 3H), 5.73 (d, *J* = 3.1 Hz, 1H), 7.1-7.4 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 21.1, 75.4, 126.5, 127.8, 128.5, 129.3, 133.1, 137.6, 140.5, 142.3; IR (KBr) ν 3310, 2920, 1600, 1490 cm^{-1}; HPLC conditions: Daicel Chiralcel OD-H, eluent: 3% 2-propanol in hexane, flow set: 0.80 ml/ min, r.t., retention time (min): 25.3 (*R*-isomer), 27.5 (*S*-isomer); HRMS (ESI) calcd for $C_{14}H_{13}{}^{35}ClO$ ($M-H^+$) 231.0577, found 231.0583.

(*S*)-(+)-(4-Bromophenyl)(*p*-tolyl)methanol (2h).[6] Yield 93%, 97% ee. Colorless needles; m.p. 89-90 °C (hexane); $[\alpha]_D^{28}$ +25.0 (*c* 1.00, $CDCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.25 (d, *J* = 3.4 Hz, 1H, OH), 2.32 (s, 3H), 5.73 (d, *J* = 3.4 Hz, 1H), 7.1-7.3 (m, 6H), 7.4-7.5 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 21.1, 75.5, 121.2, 126.5, 128.1, 129.3, 131.4, 137.6, 140.5, 142.9; IR (KBr) ν

3290, 2920, 1590, 1490 cm^{-1}; HPLC conditions: Daicel Chiralcel OD-H, eluent: 3% 2-propanol in hexane, flow set: 0.80 ml/ min, r.t., retention time (min): 27.5 (*R*-isomer), 29.9 (*S*-isomer); HRMS (ESI) calcd for $C_{14}H_{13}{}^{79}BrO$ ($M-H^+$) 275.0072, found 275.0065.

(*S*)-(-)-(2-Methoxyphenyl)(*p*-tolyl)methanol (2i).[7] Yield 89%, 90% ee. Colorless oil; $[\alpha]_D{}^{28}$ -34.4 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.97 (d, *J* = 5.5 Hz, 1H, OH), 3.80 (s, 3H), 6.02 (d, *J* = 5.5 Hz, 1H), 6.8-7.0 (m, 2H), 7.1-7.3 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 21.1, 55.4, 72.1, 110.7, 120.7, 126.5, 127.7, 128.6, 128.8, 132.1, 136.7, 140.3, 156.7; IR (neat) ν 3390, 2920, 1600, 1490, 1240, 1030 cm^{-1}; HPLC conditions: Daicel Chiralcel OD-H, eluent: 3% 2-propanol in hexane, flow set: 0.80 ml/ min, r.t., retention time (min): 29.1 (*R*-isomer), 31.8 (*S*-isomer); HRMS (ESI) calcd for $C_{15}H_{16}O_2$ ($M+Na^+$) 251.1048, found 251.1048.

(*S*)-(+)-(3-Methoxyphenyl)(*p*-tolyl)methanol (2j) Yield 89%, 96% ee. Colorless oil; $[\alpha]_D{}^{29}$ +24.7 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 2.21 (d, *J* = 3.5 Hz, 1H, OH), 2.32 (s, 3H), 3.78 (s, 3H), 5.77 (d, *J* = 3.5 Hz, 1H), 6.79 (m, 1H), 6.9-7.0 (m, 2H), 7.1-7.23 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 21.1, 55.2, 75.9, 111.9, 112.8, 118.8, 126.5, 129.1, 129.4, 137.3, 140.8, 145.6, 159.7; IR (neat) ν 3410, 2920, 1600, 1490, 1260, 1040 cm^{-1}; HPLC conditions: Daicel Chiralcel OD-H, eluent: 5% 2-propanol in hexane, flow set: 1.00 ml/ min, r.t., retention time (min): 22.2 (*S*-isomer), 29.0 (*R*-isomer); HRMS (ESI) calcd for $C_{15}H_{16}O_2$ ($M+Na^+$) 251.1048, found 251.1053.

(*S*)-(-)-(4-Methoxyphenyl)(*p*-tolyl)methanol (2k).[5] Yield 91%, 96% ee. Colorless needles; 79-80 °C (hexane); $[\alpha]_D{}^{29}$ -6.5 (*c* 1.00, $CHCl_3$), [lit.[5] $[\alpha]_D{}^{24}$ +5.9 (*c* 2.28, $CHCl_3$) for (*R*)-**2k**]; ^1H NMR (300 MHz, $CDCl_3$) δ 2.10 (d, *J* = 3.4 Hz, 1H, OH), 2.33(s, 3H), 3.78 (s, 3H), 5.78 (d, *J* = 3.4 Hz, 1H), 6.8-6.9 (m, 2H), 7.1-7.2 (m, 2H), 7.2-7.3 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 21.1, 55.2, 75.6, 113.8, 126.4, 127.8, 129.1, 136.3, 137.1, 141.1, 159.0; IR (KBr) ν 3400, 2910, 1610, 1490, 1250, 1030 cm^{-1}; HPLC conditions: Daicel Chiralcel OD-H, eluent: 3% 2-propanol in hexane,

flow set: 1.00 ml/ min, r.t., retention time (min): 28.6 (*R*-isomer), 32.9 (*S*-isomer); HRMS (ESI) calcd for $C_{15}H_{16}O_2$ ($M+Na^+$) 251.1048, found 251.1055.

(*R*)-(-)-(4-Fluorophenyl)phenylmethanol (2l).[5] Yield 92%, 94% ee. Colorless oil; $[\alpha]_D^{25}$ -6.0 (*c* 0.76, $CHCl_3$)[lit.[5] $[\alpha]_D^{26}$ +6.7 (*c* 0.51, $CHCl_3$)]; ^1H NMR (300 MHz, $CDCl_3$) δ 2.29 (s, 1H, OH), 5.82 (s, 1H), 7.02 (m, 2H), 7.2-7.4 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 75.6, 115.3 (d, J_{CF} = 21.0 Hz), 126.4, 127.8, 128.2 (d, J_{CF} = 8.7 Hz), 128.6, 139.5 (d, J_{CF} = 3.6 Hz), 143.6, 162.1 (d, J_{CF} = 245.6 Hz); IR (neat) ν 3400, 2890, 1600, 1510 cm^{-1}; HPLC conditions: Daicel Chiralcel OB-H, eluent: 20% 2-propanol in hexane, flow set: 0.75 ml/ min, r.t., retention time (min): 21.1 (*R*-isomer), 27.2 (*S*-isomer); HRMS (ESI) calcd for $C_{13}H_{11}FO$ ($M-H^+$) 201.0716, found 201.0721.

(*S*)-(+)-(4-Chlorophenyl)(4-fluorophenyl)methanol (2m).[8] Yield 75%, 83% ee. Colorless oil; $[\alpha]_D^{26}$ +12.1 (*c* 1.00, $CHCl_3$) for a sample with 78% ee; ^1H NMR (300 MHz, $CDCl_3$) δ 5.79 (s, 1H), 7.02 (m, 2H), 7.2-7.4 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 74.9, 115.4 (d, J_{CF} = 21.7 Hz), 127.8, 128.2 (d, J_{CF} = 8.0 Hz), 128.7, 133.4, 139.2 (d, J_{CF} = 2.9 Hz), 142.0, 162.2 (d, J_{CF} = 246.5 Hz); IR (neat) ν 3360, 2880, 1600, 1490 cm^{-1}; HPLC conditions: Daicel Chiralcel OB-H, eluent: 20% 2-propanol in hexane, flow set: 0.75 ml/ min, r.t., retention time (min): 14.1 (*R*-isomer), 17.5 (*S*-isomer); HRMS (ESI) calcd for $C_{13}H_{10}{}^{35}ClFO$ ($M-H^+$) 235.0326, found 235.0320.

(*S*)-(+)-(4-Bromophenyl)(4-fluorophenyl)methanol (2n).[9] Yield 86%, 86% ee. Colorless oil; $[\alpha]_D^{26}$ +12.1 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 2.28 (d, *J* = 3.5 Hz, 1H, OH), 5.77 (d, *J* = 3.5 Hz, 1H), 7.02 (m, 2H), 7.2-7.4 (m, 4H) 7.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 74.9, 115.4 (d, J_{CF} = 21.5 Hz), 121.6, 128.1 (d, J_{CF} = 7.9 Hz), 128.3, 131.6, 139.1 (d, J_{CF} = 2.9 Hz), 142.5 162.3 (d, J_{CF} = 244.5 Hz); IR (neat) ν 3320, 2910, 1600, 1500 cm^{-1}; HPLC conditions: Daicel Chiralcel OB-H, eluent: 20% 2-propanol in hexane, flow set: 0.75 ml/ min, r.t., retention time

(min): 14.2 (*R*-isomer), 18.5 (*S*-isomer); HRMS (ESI) calcd for $C_{13}H_{10}{}^{79}BrFO$ ($M-H^+$) 278.9821, found 278.9810.

Asymmetric aryl transfer reaction to *p*-bromobenzaldehyde (1c) using a mixed reagent of (*Z*)-2-phenyl-1,3,2-dioxabismepin-4,7-dione and Me_2Zn.

Under a nitrogen atmosphere, diethylzinc (2.7 mmol, 1.0 M in hexane) was added to the suspension of (*Z*)-2-phenyl-1,3,2-dioxabismepin-4,7-dione (360 mg, 0.90 mmol) in dry toluene (2.7 ml). The mixture was refluxed for 6 h. After the mixture was cooled to 0 °C, a solution of (*R*)-DPMPM (24.1 mg, 0.0900 mmol) and aldehyde **1c** (55.5 mg, 0.30 mmol) in toluene (2.7 ml) was added. The mixture was stirred for 14 h at 0 °C. The reaction was quenched by the addition of 1 M hydrochloric acid. After the addition of sat. aq. $NaHCO_3$, the mixture was filtered through celite, and extracted with AcOEt. The extract was dried with $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by preparative silica gel TLC (develpoping solvent: benzene/AcOEt = 20/1) produced (*R*)-(4-bromophenyl)phenyl alcohol (57.3 mg, 0.22 mmol). The yield was 73%, with an estimated *ee* value of 92%.

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