Electronic Supplementary Information

A novel allylic transfer reaction of chirally modified 2borylbutadiene: synthesis of chiral homoallenyl alcohols

Jihoon Choi, Bobin Lee and Chan-Mo Yu*

BK-21 School of Chemical Materials Science and Department of Chemistry Sungkyunkwan University, Suwon 440-746, Korea

General. All reactions were run in flame-dried glassware under an atmosphere of nitrogen or argon. Dichloromethane and 1,4-dioxane was distilled from CaH₂ prior to use. All liquid reagents purchased from the Aldrich or TCI were distilled properly prior to use, unless otherwise indicated. Purification was conducted by flash column chromatography on silica gel (230-400 mesh), eluting with a mixture of hexanes and ethyl acetate, unless otherwise stated. The reported yields refer to chromatographically purified and isolated products. All reactions were monitored by thin layer chromatography carried out on Merck silica gel plate (60 F₂₅₄) using UV light as visualizing agent and ethanolic anisaldehyde solution and heat as developing agent. Silica gel 60 (TA792685, 230-400 mesh) from Merck was used for column chromatography. The reported yields are for chromatographically pure isolated products. FT-IR spectra were recorded on a Nicolet 320. ¹H NMR spectra were recorded on a Varian Unity Inova at 500 MHz or 300 MHz in CDCl₃ as a solvent with TMS or residual chloroform as the internal standard. ¹³C NMR spectra were measured on a Varian Unity Inova at 75 or 125 MHz in CDCl₃ as a solvent. Mass spectra were recorded on a Varian Ion Trap 4000 GC/MS and Quattro micro API. Optical rotations were measured on a JASCO P-1020 digital polarimeter at ambient temperature. Enantiomeric excesses were determined by HPLC analysis using chiral column (Chiracel OD-H and OD-RH) and/or ¹H NMR analysis of the corresponding (+)-MTPA esters in comparison with sample obtained from (1R,2R)-3a.

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(1S,2S)-1,2-N,N'-Bis[(4-toluenesulfonyl)amino]-cyclohexane (3c):

A mixture of (1*S*,2*S*)-cyclohexane-1,2-diamine (1.2 g, 10.5 mmol), DMAP (90 mg, 1.04 mmol), and CH₂Cl₂ (30 mL) was placed in flame-dried flask. The solution was cooled to 0 °C and triethylamine (4.4 mL, 3.19 g, 31.5 mmol) was added. After then, *p*-toluenesulfonyl chloride (4.6 g, 24.2 mmol) dissolved in CH₂Cl₂ (10 mL) was transferred via cannular at 0 °C. The reaction was

allowed to proceed for 3h, and then quenched by addition of aqueous buffer solution (pH 7, 10 mL). The aqueous layer was extracted with CH₂Cl₂ (ca 30 mL x 2). The combined organic extracts were washed with 10% aqueous HCl, saturated NaHCO₃, and brine and dried over MgSO₄. After filtration, the residue was concentrated under reduced pressure to give the crude product as fairly pure form. Final purification was effected by SiO₂ chromatography (EtOAc: Hexanes = 1:1) to afford **3a** (3.68 g, 8.71 mmol, 83%); $[\alpha]_D^{25} = -12.70$ (c 1.2, CHCl₃); FT-IR(film): 3281, 3059, 2941, 2861, 1598, 1305, 1259, 1161 cm⁻¹; ¹H NMR (300MHz, CDCl₃): δ 1.04-1.10 (m, 4H), 1.57-1.59 (m, 2H), 1.84-1.87 (m, 2H), 2.43 (s, 6H), 2.72 (m, 2H), 4.75 (s, 2H), 7.32 (d, J = 8.4 Hz, 4H), 7.75 (d, J = 8.1 Hz, 4H); ¹³C NMR (75MHz, CDCl₃): δ 21.7, 24.2, 33.2, 56.6, 127.3, 129.8, 137.1, 143.6.

Typical procedure for the synthesis of (-)-(S)-1-phenylhepta-5,6-dien-3-ol (2a):

A flame-dried 20 ml Schlenk flask containing **3c** (200 mg, 0.45 mmol) was charged with dry CH₂Cl₂ (7 mL). The

resulting mixture was cooled to 0 °C and treated with BBr₃ (0.6 mL, 0.6 mmol, freshly prepared 1 M solution in CH₂Cl₂). The solution was stirred at 0 °C for 1 h, warmed to 23 °C and kept for additional 3 h. The resulting solution was concentrated under vacuum (1 mmHg) through a side neck of the flask connected with three hold-cork valve. Dryness of the vacuum line was maintained with a drying tube containing anhydrous CaSO₄ and two traps (NaOH pellets and cold trap at –78 °C). Freshly distilled toluene (3 mL) was added and evaporated under vacuum as above. Freshly distilled CH₂Cl₂ (4 mL) was added and the homogeneous solution of bromoborane complex **4c** was cooled to 0 °C. After then, buta-2,3-dienyltributylstannane (**5**, 0.185 g, 0.52 mmol) in CH₂Cl₂ (1 mL) was slowly added for 10 min. After 1h at 0 °C, this solution was allowed to warm to 25 °C (rt) and was stirred for the additional 3h. After cooling to –78 °C,

hydrocinnamaldehyde (purified and distilled, 67 mg, 0.50 mmol) in CH₂Cl₂ (1 mL) was added over 10 min along the wall of the flask while keeping the temperature below -78 °C. The reaction was allowed to proceed for 2 h at -78 °C, and then guenched by addition of aqueous buffer solution (pH 7, 10 mL) followed by CH₂Cl₂ (ca 10 mL) to dissolve white precipitate (bis-sulfonamide). The aqueous layer was extracted with CH₂Cl₂ (ca 10 mL x 2). The combined organic extracts were washed with saturated NaHCO₃ (1x), brine (1x), dried over anhydrous Na₂SO₄, filtered, evaporated, and taken up ether (ca 30 mL). The solution was cooled to 0 °C for 20 min to complete precipitation of 3c. After removal of 3c by filtration through a sintered glass funnel, the filtrate was washed with cold 20 % KF (1x) and saturated aqueous NaHCO₃ (1x). The organic layer was separated, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to give the crude product. Final purification was effected by SiO₂ chromatography (Hexanes:EtOAc = 4:1) to afford 2a (66 mg, 0.35 mmol, 78%) as a colorless oil. TLC, Rf 0.37 (3:1 Hexanes/EtOAc); $[\alpha]_D^{23} = -25.1$ (c = 1.0 in CHCl₃); FT-IR (film): 3386, 3061, 3025, 2925, 1955 cm⁻¹; ¹H NMR (500MHz, CDCl₃): δ 1.69 (d, J = 4.5 Hz, 1H), 1.78-1.85 (m, 2H), 2.11-2.20 (m, 1H), 2.21-2.29 (m, 1H), 2.69 (m, 1H), 2.82 (m, 1H), 3.68-3.76 (m, 1H), 4.71 (ddt, J = 7.0, 3.0, 1.0 Hz, 2H), 5.12 (tt, J = 7.0, 7.0 Hz, 1H), 7.19 (m, 3H), 7.29 (m, 2H); ¹³C NMR (125MHz, CDCl₃): δ 32.3, 36.9, 38.6, 70.7, 75.2, 86.3, 126.1, 128.6, 128.7, 142.3, 209.7; GC/MS (EI) m/z 188 (M⁺, 4), 134 (100), 107 (65).

Chiral HPLC analysis, Chiralcel OD-H. 1 mL/min, Hexanes/i-PrOH = 97:3, t_R 14.1 min (major) : 19.4 min (minor), 91% ee

(+)-(S)-Hexa-4,5-dien-2-ol (2b):

Purified by SiO₂ column chromatography (pentane:ether = 3:2). TLC, Rf 0.42 (3:1 Hexanes/EtOAc); $[\alpha]_D^{23} = +8.8$ (c = 1.0 in CHCl₃); FT-IR (film): 3045, 2968, 2914, 2856, 1956, 1122, 844 cm⁻¹; ¹H NMR (500MHz, CDCl₃): δ 1.24 (d, J = 6.2 Hz, 3H), 1.8

(bs, 1H), 2.10-2.24 (m, 2H), 3.90 (m, 1H), 4.72 (dt, J = 6.5, 3.0 Hz, 1H), 5.13 (tt, J = 7.0, 7.0 Hz, 1H); ¹³C NMR (125MHz, CDCl₃): δ 23.2, 36.7, 67.3, 75.0, 86.4, 209.7; MS (ESI) m/z 121 (M+Na⁺, 11), 83 (22), 82 (18), 44 (100).

Chiral HPLC analysis, Chiralcel OD-H. 0.8 mL/min, Hexanes: i-PrOH = 97:3, t_R 20.1 min (minor): 23.4 min (major), 1 H NMR analysis of (+)-MTPA ester: δ 1.33 (d, minor), 1.28 (d, major), 93% ee

(+)-(S)-Undeca-1,2-dien-5-ol (2c):

TLC, Rf 0.47 (3:1 Hexanes/EtOAc); $[\alpha]_D^{25} = +9.3$ (c = 1.2 in CHCl₃); FT-IR (film): 3365, 2928, 2857, 1956, 1018, 835 em⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 0.90 (t, J = 7.0 Hz, 3H),

1.26-1.37 (m, 8H), 1.51 (m, 2H), 1.67 (d, J = 4.5 Hz, 1H), 2.08-2.16 (m, 1H), 2.21-2.29 (m, 1H), 3.70 (m, 1H), 4.73 (dd, J = 7.0, 3.1 Hz, 2H), 5.14 (tt, J = 7.0, 7.0 Hz, 1H); ¹³C NMR (125 MHz CDCl₃): δ 14.3, 22.8, 25.8, 29.5, 32.0, 36.7, 36.9, 71.4, 75.0, 86.5, 209.6; GC/MS (EI) m/z 182 (M⁺, 9), 121 (27), 129 (100), 83 (24).

Chiral HPLC analysis, Chiralcel OD-H. 1 mL/min, Hexanes:i-PrOH = 98:2, t_R 14.7 min (major) : 22.5 (minor), 93% ee

(-)-(R)-1-phenylhexa-4,5-dien-2-ol (2d):

TLC, Rf 0.38 (3:1 Hexanes/EtOAc); $[\alpha]_D^{25} = -6.35$ (c = 1.0 in CHCl₃); FT-IR (film): 3398, 3061, 3027, 2918, 1955, cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 1.75 (d, J = 4.0 Hz, 1H), 2.15-2.31 (m, 2H), 2.72 (dd, J = 13.6, 7.9 Hz, 1H), 2.86 (dd, J =

13.6, 4.9 Hz, 1H), 3.93 (m, 1H), 4.73 (dt, J = 7.0, 3.0 Hz, 2H), 5.17 (tt, J = 7.0, 7.0 Hz, 1H), 7.24 (m, 3H), 7.31 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 35.9, 43.4, 72.3, 75.2, 86.5, 126.7, 128.8, 129.7, 138.6, 209.7; GC/MS (EI) m/z 174 (M⁺, 3), 143 (32), 83 (100); Anal. Calcd for C₁₂H₁₄O: C, 82.72; H, 8.10; O, 9.18. Found: C, 82.61; H, 8.03.

Chiral HPLC analysis, Chiralcel OD-H. 0.8 mL/min, Hexanes:i-PrOH = 97:3, t_R 15.3 min (major) : 20.8 min (minor), 1 H NMR analysis of (+)-MTPA ester: δ 5.11 (minor), 4.99 (major), 86% ee

(+)-(S)-2-methylocta-6,7-dien-4-ol (2e):

TLC, Rf 0.40 (3:1 Hexanes/EtOAc); $[\alpha]_D^{22} = +10.3$ (c = 1.4 in CHCl₃); FT-IR (film): 3358, 2956, 2870, 1956 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 0.91 (d, J = 3.9 Hz, 3H),

0.93 (d, J = 3.9 Hz, 3H), 1.37 (dd, J = 14.6, 7.3 Hz, 2H), 1.61 (d, J = 2.7 Hz, 1H), 1.75-1.84 (m, 1H), 2.05-2.14 (m, 1H), 2.17-2.25 (m, 1H), 3.77 (m, 1H), 4.72 (ddt, 2H, J = 0.8, 7.0, 3.1 Hz), 5.14 (tt, 1H, J = 7.0, 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 17.8, 22.4, 37.3, 46.2, 69.5, 75.1, 86.5, 209.7. GC/MS (EI) m/z 140 (M⁺, 7), 97 (21), 87 (34), 43 (100); Anal. Calcd for C₉H₁₆O: C, 77.09; H, 11.50; O, 11.41. Found: C, 77.32; H, 10.88. Chiral HPLC analysis, Chiralcel OD-H. 0.8 mL/min, Hexanes:*i*-PrOH = 98:2, t_R 17.3 min (major): 21.4 min (minor), 91% *ee*

(-)-(*R*)-1-cyclohexylpenta-3,4-dien-1-ol (2f):

TLC, Rf 0.31 (3:1 Hexanes/EtOAc); $[\alpha]_D^{25} = -2.41$ (c = 0.9 in CHCl₃); FT-IR (film): 3435, 3031, 2926, 2855, 1954, 1290, 1242 cm⁻¹; ¹H NMR (300MHz, CDCl₃): δ 0.95-1.44 (m, 6H), 1.60-1.87 (m, 5H), 2.00-2.31 (m, 3H), 3.36-3.40 (m, 1H), 4.62-4.70 (m, 2H), 5.10 (m, 1H); ¹³C NMR (75MHz, CDCl₃):

δ 26.2, 26.3, 26.5, 28.1, 29.1, 33.5, 43.0, 74.6, 75.3, 86.8, 209.2; GC/MS (EI) m/z 180 (M⁺, 7), 127 (34), 97 (100).

Chiral HPLC analysis, Chiralcel OD-H. 0.8 mL/min, Hexanes:i-PrOH = 97:3, t_R 23.4 min (major) : 29.5 min (minor), 90% ee

(+)-(*R*)-1-phenylpenta-3,4-dien-1-ol (2g):

TLC, Rf 0.37 (3:1 Hexanes/EtOAc); $[\alpha]_D^{23} = +49.8$ (c = 1.1 in CHCl₃); FT-IR (film): 3382, 3064, 3029, 2910, 1955, 1251, 1035, 752, 688 cm⁻¹; ¹H NMR (500MHz, CDCl₃): δ 2.08 (d, J = 3.0 Hz, 1H), 2.44-2.49 (m, 2H), 4.71 (dt, J = 7.0, 3.0 Hz, 2H),

4.78 (m, 1H), 5.11 (tt, J = 7.0, 7.0 Hz, 1H), 7.26-7.29 (m, 1H), 7.32-7.36 (m, 4H); ¹³C NMR (125MHz, CDCl₃): δ 38.7, 73.9, 75.3, 86.3, 126.1, 127.9, 128.7, 143.9, 209.8; MS (ESI) m/z (rel. intensity) 183 (M+Na⁺, 20).

Chiral HPLC analysis, Chiralcel OD-H. 0.8 mL/min, Hexanes:i-PrOH = 98:2, t_R 16.4 min (major) : 22.3 min (minor), 88% ee

(+)-(*R*)-1-(4-bromophenyl)penta-3,4-dien-1-ol (2h):

TLC, Rf 0.4 (3:1 Hexanes/EtOAc); $[\alpha]_D^{22} = +31.3$ (c = 0.8 in CHCl₃); FT-IR (film): 3379, 2955, 2922, 1956, 1017, 754, cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 2.14 (d, J = 5.5 Hz, 1H), 2.37-2.47 (m, 2H), 4.71 (m, 1H), 4.73 (dd, J = 7.0, 3.0 Hz, 2H), δ 2.10, 7.48 (m, 2H), δ 2.10, 135 NMR (125 MHz, CDCl₃)

2.37-2.47 (m, 2H), 4.71 (m, 1H), 4.73 (dd, J = 7.0, 3.0 Hz, 2H), 5.10 (tt, J = 7.0, 7.0 Hz, 1H), 7.26 (m, 2H), 7.48 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 38.7, 73.2, 75.5, 86.0, 121.6, 127.9, 131.7, 142.9, 209.8; MS (ESI) m/z (rel. intensity) 261 (M+Na⁺, 11).

Chiral HPLC analysis, Chiralcel OD-H. 0.8 mL/min, Hexanes:i-PrOH = 98:2, t_R 14.9 min (major) : 22.7 min (minor), 91% ee

(+)-(R)-1-phenylhepta-1,5,6-trien-3-ol (2i):

Purified by silica gel (deactivated with 3% Et₃N in hexanes) chromatography. TLC, Rf 0.37 (3:1 Hexanes/EtOAc); $[\alpha]_D^{25} = +2.89$ (c = 1.0 in CHCl₃); FT-IR

(film): 3384, 3058, 3026, 2911, 1955, 1251, 1026, 749, 693 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 1.85 (bs, 1H), 2.29-2.43 (m, 2H), 4.40 (m,1H), 4.74 (dt, J = 2.5, 7.0 Hz, 2H), 5.12 (tt, J = 7.0, 7.0 Hz, 1H), 6.26 (dd, J = 15.7, 6.3 Hz, 1H), 6.63 (d, J = 15.7 Hz, 1H), 7.25 (m, 1H), 7.30 (m, 2H), 7.40 (m, 2H); ¹³C NMR (125 MHz CDCl₃): δ 26.9, 72.3, 75.3, 85.9, 126.7, 127.9, 128.8, 130.9, 131.6, 136.9, 209.9; MS (ESI) m/z (rel. intensity) 209 (M+Na⁺, 31).

Chiral HPLC analysis, Chiralcel OD-H. 0.8 mL/min, Hexanes:i-PrOH = 97:3, t_R 13.7 min (major) : 21.7 min (minor), 81% ee

(+)-(R)-phenylhepta-5,6-dien-1-yn-3-ol (2j):

Purified by silica gel (deactivated with 3% Et₃N in hexanes) chromatography. TLC, Rf 0.31 (5:1 Hexanes/EtOAc); [α] $_{D}^{23}$ = +9.93 (c = 0.8 in CHCl₃); FT-IR (film): 3499, 3053, 2984, 2351, 1955, 1265, 747 cm⁻¹; 1 H NMR (300MHz,

CDCl₃): δ 2.45 (m, 1H), 2.57-2.50 (m, 2H), 4.71-4.67 (m, 1H), 4.78-4.74 (m, 2H), 5.26 (m, 1H), 7.45-7.30 (m, 5H); ¹³C NMR (75MHz, CDCl₃) δ 37.2, 62.5, 75.2, 85.1, 85.3, 89.3, 122.6, 128.4, 128.5, 131.8, 209.8; MS (ESI) m/z (rel. intensity) 207 (M+Na⁺, 44); Anal. Calcd for C₁₃H₁₂O: C, 84.75; H, 6.57; O, 8.68. Found: C, 84.51; H, 6.44.

Chiralcel OD-RH. 0.8 mL/min, CH₃CN:H₂O = 7:3, t_R 14.7 min (minor) : 20.1 min (major), ¹H NMR analysis of (+)-MTPA ester: δ 5.19 (minor), 5.01 (major), 84% ee

(+)-(S)-5,6-dihydro-3-methyl-6-phenethylpyran-2-one (7a):

A dried stainless autoclave was charged with 2a (190 mg, 1.02 mmol), triethyl amine (155 mg, 1.53 mmol) and Ru₃(CO)₁₂ (6.5 mg, 0.01 mmol) in 1,4-dioxane. After the reaction system was flushed with 20 atm of CO three times, it was pressurized

to 20 atm of CO and stirred at 100 °C for 7 h. The autoclave was allowed to cool down rt and the CO was released carefully in the fume hood. The result mixture was transferred into a round bottom flask with ether and the volatiles were removed under reduced pressure. Final purification was effected by chromatography (Hexanes:EtOAc = 5:1) to afford **7a** (187 mg, 0.84 mmol, 83%) as a colorless oil: TLC, R*f* 0.32 (4:1 Hexanes/EtOAc); $[\alpha]^{25}_D = +39.1$ (c = 0.8 in CHCl₃); FT-IR (film): 3025, 2951, 1713, 1454, 756 cm⁻¹; ¹H NMR (500MHz, CDCl₃): δ 1.83-1.87 (m, 4H), 1.98-2.12 (m, 1H), 2.31-2.36 (m, 2H), 2.70 (m, 1H), 2.80 (m, 1H), 4.31 (m, 1H), 6.49 (m, 1H), 7.13 (m, 3H), 7.23 (m, 2H); ¹³C NMR (125MHz, CDCl₃): δ 17.2, 30.0, 31.2, 36.7, 77.3, 126.3, 127.8, 128.7, 128.8, 139.0, 141.2, 166.2; MS (ESI) m/z (rel. intensity) 207 (M+Na⁺, 44).

(+)-(S)-3,6-dimethyl-5,6-dihydro-2H-pyran-2-one (7b):

TLC, Rf 0.31 (3:1 Hexanes/EtOAc); $[\alpha]_D^{25} = +181.5$ (c = 1.2 in CHCl₃); FT-IR (film): 2981, 2931, 1720, 1387, 1374, 1246, 1125 cm⁻¹; ¹H NMR (500MHz, CDCl₃): δ 1.43 (d, J = 6.2 Hz, 3H), 1.93 (d, J = 1.7 Hz, 3H), 2.30 (m, 2H), 4.54 (m, 1H), 6.57 (m, 1H); ¹³C NMR (125MHz, CDCl₃): δ 17.2, 21.0, 31.8, 75.0, 128.6, 139.0, 166.3.

(-)-(3S,6R)-3,6-dimethyltetrahydro-2H-pyran-2-one (8):

A flame-dried 15ml Schlenk flask containing 5% Pd/C (10 mg) was charged with dry EtOAc (5 mL). After the reaction system was carefully flushed with H_2 gas two times, **7b** (110 mg, 0.87 mmol) in EtOAc (1 mL) was added. Reaction mixture was then

cooled to 0 °C. Reaction mixture was stirred under H_2 atmosphere (1 atm, ballon) for 5 h. After removal of catalyst by filtration on celite through a sintered glass funnel, the filtrate was concentrated under reduced pressure to afford crude product as fairly pure form. Final purification was effected by SiO_2 chromatography (Hexanes:EtOAc = 3:1) to afford **8** (98 mg, 0.76 mmol, 88%) as a white solid: TLC, Rf 0.32 (3:1 Hexanes/EtOAc); $[\alpha]_D^{23} = -97.4$ (c = 0.8 in CHCl₃); FT-IR (film): 2978, 2874, 1736 cm¹; ¹H NMR (500MHz, CDCl₃): δ 1.24 (d, J = 6.8 Hz, 3H), 1.38 (d, J = 6.2 Hz, 3H), 1.49-1.68 (m, 2H), 1.90-1.98 (m, 1H), 2.05-2.15 (m, 1H), 2.60(m, 1H), 4.48 (m, 1H); ¹³C NMR (125MHz, CDCl₃): δ 17.4, 21.4, 25.9, 28.7, 33.3, 74.7, 176.4.





























