Supporting Information
for
Palladium-Catalyzed Diastereoselective
Coupling of Propargylic Oxiranes
with Terminal Alkynes

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General. All nonaqueous reactions were carried out under a positive atmosphere of argon in dried glassware unless otherwise indicated. Materials were obtained from commercial suppliers and used without further purification except when otherwise noted. Solvents were dried and distilled according to standard protocol. The phrase ‘residue upon workup’ refers to the residue obtained when the organic layer was separated and dried over anhydrous MgSO_4 and the solvent was evaporated under reduced pressure. Alkynes **2c**,¹ **2d**,² **2f**³ and alkynylmetal reagents **2g**,⁴ **2h**,⁵ **2i**,⁴ **2j**⁶ were prepared according to the procedures described in the literature.

Preparation of Propargylic Oxiranes

Scheme S-1

General procedure for the synthesis of propargylic oxiranes **1a–1e** (Scheme S-1).

Synthesis of alkynylalcohol S-2a. To a stirred solution of phenylacetylene (**S-1a**) (6.5 mL, 59 mmol) in THF (150 mL) were added 1.54 M hexane solution of *n*-BuLi (40.5 mL, 64 mmol) and TMEDA (9.7 mL, 59 mmol) at $-78\text{ }^{\circ}\text{C}$. After stirring was continued for 1 h, cyclohexanone (4.8 g, 49 mmol) was added dropwise to the reaction mixture at the same temperature, and stirring was continued for 2 h at the same temperature. The reaction mixture was diluted with water and then extracted with AcOEt. The combined

extracts were washed with brine. The residue upon workup was chromatographed on silica gel with hexane-AcOEt (90 : 10 v/v) as eluent to give alkynylalcohol **S-2a** (9.8 g, quant.) as a colorless oil.

Synthesis of eneyne S-3a. To a stirred solution of alkynylalcohol **S-2a** (9.8 g, 49 mmol) in pyridine (200 mL) was added POCl₃ (13.8 mL, 148 mmol) at 0 °C, and the stirring was continued for 2 h at rt. The reaction mixture was diluted with water at 0 °C and extracted with AcOEt. The combined extracts were washed with brine, and the residue upon workup was chromatographed on silica gel with hexane-AcOEt (97 : 3 v/v) as eluent to give enyne **S-3a** (5.10 g, 57%) as a colorless oil.

Synthesis of propargylic oxirane 1a. To a stirred solution of enyne **S-3a** (1.50 g, 8.2 mmol) in CH₂Cl₂ (60 mL) was added *m*-CPBA (1.63 g, 15.9 mol) at rt, and stirring was continued for 2 h at rt. The reaction mixture was diluted with saturated aqueous solution of NaHCO₃ and extracted with AcOEt. The combined extracts were washed with brine. After filtration of the reaction mixture using small amount of base Al₂O₃, the residue upon workup was chromatographed on silica gel with hexane-AcOEt (95 : 5 v/v) as eluent to give alkynylepoxy **1a** (1.02 g, 63%) as a colorless oil.

The spectrum data of **1a** and **1c** were in complete agreement with that of the literature.⁷

(1*R, 2*R**)-1-[2-(*tert*-Butyldimethylsilyl)ethynyl]-7-oxabicyclo[4.1.0]heptane (1b)**

Colorless oil; IR (neat): 2952, 2171, 834 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.095 (s, 3H), 0.098 (s, 3H), 0.93 (s, 9H), 1.20–1.35 (m, 2H), 1.36–1.45 (m, 2H), 1.89–1.92 (m, 2H), 1.97–2.04 (m, 1H), 2.11–2.18 (m, 1H), 3.33 (t, *J* = 0.8 Hz, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ -4.7×2 (CH₃), 16.5 (Cq), 18.8 (CH₂), 19.4 (CH₂), 24.1 (CH₂), 26.0×3 (CH₃), 29.7 (CH₂), 50.4 (Cq), 60.2 (CH), 85.3 (Cq), 106.6 (Cq); HRMS (ESI) *m/z* calcd for C₁₄H₂₅OSi [M+H]⁺ 237.1675, found 237.1684.

(1*R, 2*R**)-1-(3-Phenylpropynyl)-7-oxabicyclo[4.1.0]heptane (1d)**

Colorless oil; IR (neat) 2206, 1648, 1603, 1495 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 1.22–1.26 (m, 1H),

1.30–1.35 (m, 1H), 1.38–1.44 (m, 2H), 1.89–1.93 (m, 2H), 1.99–2.05 (m, 1H), 2.14–2.20 (m, 1H), 3.34–3.35 (m, 1H), 3.62 (s, 2H), 7.22–7.25 (m, 1H), 7.31–7.32 (m, 4H); ^{13}C -NMR (100 MHz, CDCl_3) δ 18.9 (CH_2), 19.4 (CH_2), 24.1 (CH_2), 25.0 (CH_2), 29.9 (CH_2), 50.5 (Cq), 60.0 (CH), 80.3 (Cq), 82.8 (Cq), 126.6 (CH), 127.8 $\times$ 2 (CH), 128.5 $\times$ 2 (CH), 136.3 (Cq); HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{17}\text{O}$ $[\text{M}+\text{H}]^+$ 213.1279, found 213.1289.

(1*R, 2*R**)-1-Hexynyl-7-oxabicyclo[4.1.0]heptane (1e)**

Colorless oil; IR (neat): 2936, 2245 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 0.90 (t, $J = 7.2$ Hz, 3H), 1.19–1.32 (m, 2H), 1.33–1.43 (m, 4H), 1.46–1.51 (m, 2H), 1.88–1.91 (m, 2H), 1.93–2.00 (m, 1H), 2.09–2.16 (m, 1H), 2.19 (t, $J = 7.2$ Hz, 2H), 3.28–3.29 (m, 1H); ^{13}C -NMR (100 MHz, CDCl_3) δ 13.5 (CH_3), 18.3 (CH_2), 18.9 (CH_2), 19.4 (CH_2), 21.9 (CH_2), 24.1 (CH_2), 30.1 (CH_2), 30.5 (CH_2), 50.5 (Cq), 60.0 (CH), 80.6 (Cq), 82.9 (Cq); MS (EI) m/z 95 (100%), 178 $[\text{M}^+]$; HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{18}\text{O}$ $[\text{M}^+]$ 178.1358, found 178.1348.

Scheme S-2

Synthesis of propargylic oxirane 1f (Scheme S-2). To a stirred solution of propargylic oxirane **1c** (725 mg, 3.73 mmol) in MeOH (37 mL) was added K_2CO_3 (1.03 g, 7.46 mmol) at rt, and stirring was continued for 20 min at the same temperature. The reaction mixture was quenched with saturated NH_4Cl aq. and extracted with CH_2Cl_2 . The combined extracts were washed with brine, and the residue upon workup was distilled as eluent to give propargylic oxirane **1f** (313 mg, 69%) as a colorless oil. The spectrum data of prepared propargylic oxiranes **1f** were in complete agreement with that of the literature.⁷

Scheme S-3

Synthesis of optically active propargylic oxirane (*1R,2R*)-1a** (Scheme S-3).**

Optically active propargylic oxiranes (*1R, 2R*)-**1a** was prepared from **S-3a** by following the procedure for Shi's asymmetric epoxidation.⁸

(1*R*, 2*R*)-1-Phenylethynyl-7-oxabicyclo[4.1.0]heptane [(*1R,2R*)-1a**]**

To a stirred solution of enyne **S-3a** (272 mg, 1.49 mmol) and the chiral ketone **S-4** (385 mg, 1.49 mmol) in dimethoxymethane-CH₃CN (45 mL, 2 : 1 v/v) were added aqueous K₂CO₃-AcOH solution (prepared by adding 1.0 mL AcOH to 200 mL of 0.1 M aqueous K₂CO₃, pH 9.1) (30 mL) and a catalytic amount of Bu₄NHSO₄. After the mixture was cooled to -15 °C, a solution of Oxone[®] (2.75 g, 4.48 mmol) in 4 × 10⁻³ M aqueous solution of Na₂(EDTA) (10 mL) and a solution of 1.5 M aqueous KOH (12 mL) were added dropwise simultaneously from separate syringes over 3 h. The reaction mixture was stirred for an additional 1 h at the same temperature, and then quenched with water. The aqueous layer was extracted with hexane. The organic layers were washed with brine, and the residue upon workup was chromatographed on silica gel with hexane-NEt₃ (99 : 1 v/v) as eluent to give propargylic oxirane (*1R, 2R*)-**1a** (238 mg, 1.20 mmol, 81%, 91% ee) as a colorless oil. $[\alpha]_D^{23} = +22^\circ$ (*c* 1.00, CHCl₃); enantiomeric excess was determined by HPLC chiral column [DAICEL CHIRALCEL OD-H, 250 × 4.6 mm (i.d.), flow rate 0.5 mL/min, hexane-*i*-PrOH = 95:5, detection UV at 254 nm, (*1R, 2R*) 13 min, (*1S, 2S*) 25 min]. Other spectral data coincides with those of racemic propargylic oxiranes **1a**.

General procedure for the palladium-catalyzed reaction of propargylic oxiranes with alkynes.

Reaction of **1a** with **2a**.

Condition A (entry 5 in Table 1). To a stirred solution of propargylic oxirane **1a** (26.7 mg, 0.130 mmol) in 1,4-dioxane (2 mL) were added alkyne **2a** (19.1 mg, 0.194 mmol), CuI (5.0 mg, 26.0 μ mol), *i*Pr₂NEt (0.11 mL, 0.650 mmol) and Pd(PPh₃)₄ (15.0 mg, 13.0 μ mol) at rt, and stirring was continued for 12 h at the same temperature. After filtration of the reaction mixture using small amount of silica gel, the mass was concentrated. The residue was chromatographed on silica gel with hexane-AcOEt-Et₃N (88 : 11 : 1 v/v/v) as eluent to give diastereomeric mixture of alkynylallenes *syn*-**3aa** and *anti*-**3aa** (27.9 mg, 72%, *anti* : *syn* = 1 : 2) as a colorless oil.

Condition B (entry 9 in Table 1). To a stirred solution of propargylic oxirane **1a** (84.0 mg, 0.424 mmol) in 1,4-dioxane (5 mL) were added alkyne **2a** (62.5 mg, 0.636 mmol), CuI (16.2 mg, 84.8 μ mol), *i*Pr₂NEt (0.37 mL, 2.12 mmol), Pd₂(dba)₃·CHCl₃ (21.9 mg, 21.2 μ mol) and dppe (33.8 mg, 84.8 μ mol) at rt, and the stirring was continued for 6 h at the same temperature. After filtration of the reaction mixture using small amount of silica gel, the mass was concentrated. The residue was chromatographed on silica gel with hexane-AcOEt-Et₃N (89 : 10 : 1 v/v/v) as eluent to give *anti*-alkynylallene *anti*-**3aa** (118 mg, 94%) as a colorless oil.

(**1R***, **2R***)-2-(2-Phenyl-4-trimetylsilyl-1-buten-3-ynylidene)cyclohexanol (*anti*-**3aa**)

Colorless oil; IR (neat) 3401, 2148, 1940, 1597, 1492 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.26 (s, 9H), 1.45–1.62 (m, 2H), 1.83–1.91 (m, 3H), 2.12–2.24 (m, 2H), 2.54–2.57 (m, 1H), 4.19–4.22 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ 0.0×3 (CH₃), 23.8 (CH₂), 26.8 (CH₂), 29.8 (CH₂), 36.1 (CH₂), 69.7 (CH), 96.3 (Cq), 98.2 (Cq), 98.6 (Cq), 113.8 (Cq), 125.8×2 (CH), 127.3 (CH), 128.2×2 (CH), 134.1 (Cq), 201.6 (Cq); MS (EI) *m/z* 73 (100%), 296 [M⁺]; HRMS (EI) *m/z* calcd for C₁₉H₂₄OSi [M⁺] 296.1596, found 296.1573.

(1*R, 2*S**)-2-(2-Phenyl-4-trimetylsilyl-1-buten-3-ynylidene)cyclohexanol (*syn*-3aa)**

Colorless oil; IR (neat) 3410, 2150, 1939, 1597 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 0.26 (s, 9H), 1.49–1.55 (m, 2H), 1.81–1.88 (m, 2H), 1.99–2.07 (m, 2H), 2.15–2.22 (m, 1H), 2.55–2.60 (m, 1H), 4.27–4.30 (m, 1H), 7.22 (d, $J = 7.4$ Hz, 1H), 7.32 (t, $J = 7.4$ Hz, 2H), 7.51 (d, $J = 7.4$ Hz, 2H); ^{13}C -NMR (100 MHz, CDCl_3) δ 0.0 $\times$ 3 (CH_3), 22.9 (CH_2), 26.6 (CH_2), 28.9 (CH_2), 35.8 (CH_2), 69.4 (CH), 90.0 (Cq), 98.0 (Cq), 105.4 (Cq), 112.6 (Cq), 125.9 $\times$ 2 (CH), 127.2 (CH), 128.2 $\times$ 2 (CH), 134.2 (Cq), 202.2 (Cq); MS (EI) m/z 73 (100%), 296 [M^+]; HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{24}\text{OSi}$ [M^+] 296.1596, found 296.1602.

(1*R, 2*R**)-2-[4-(*tert*-Butyldimethylsilyl)-2-phenyl-1-buten-3-ynylidene]cyclohexanol (*anti*-3ab)**

Colorless oil; IR (neat) 3407, 2148, 1941, 1598 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 0.19 (s, 6H), 1.00 (s, 9H), 1.47–1.52 (m, 2H), 1.83–1.92 (m, 3H), 2.12–2.23 (m, 2H), 2.55–2.58 (m, 1H), 4.20–4.24 (m, 1H), 7.22–7.26 (m, 1H), 7.30–7.35 (m, 2H), 7.56–7.59 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3) δ -4.4 $\times$ 2 (CH_3), 16.9 (Cq), 23.8 (CH_2), 26.3 $\times$ 3 (CH_3), 26.9 (CH_2), 29.8 (CH_2), 36.2 (CH_2), 69.7 (CH), 96.4 (Cq), 96.5 (Cq), 99.2 (Cq), 113.7 (Cq), 125.9 $\times$ 2 (CH), 127.4 (CH), 128.3 $\times$ 2 (CH), 134.3 (Cq), 201.9 (Cq); HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{31}\text{OSi}$ [$\text{M}+\text{H}]^+$ 339.2144, found 339.2131.

[(1*R, 2*R**) and (1*R**, 2*S**)]-2-[4-(*tert*-Butyldimethylsilyl)-2-phenyl-buten-3-ynylidene]-cyclohexanol (*syn*-3ab + *anti*-3ab) (ratio of 3 : 7)**

Colorless oil; IR (neat) 3414, 2151, 1940, 1598 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 0.19 (s, 6H), 1.00 (s, 9H), 1.49–1.52 (m, 2H), 1.82–1.92 (m, 3H), 2.13–2.23 (m, 2H), 2.55–2.58 (m, 1H), 4.21–4.26 (m, 0.7H), 4.26–4.28 (m, 0.3H), 7.22–7.24 (m, 1H), 7.31–7.35 (m, 2H), 7.53–7.58 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3) δ -4.6 $\times$ 2 (-4.4 $\times$ 2) (CH_3), 14.2 (16.9) (Cq), 23.0 (23.8) (CH_2), 26.2 $\times$ 3 (26.3 $\times$ 3) (CH_3), 26.7 (26.9) (CH_2), 29.1 (29.8) (CH_2), 36.0 (36.2) (CH_2), 69.5 (69.7) (CH), 95.7 (96.4) (Cq), 96.3 (96.5) (Cq), 99.4 (99.2) (Cq), 112.9 (113.7) (Cq), 126.1 $\times$ 2 (125.9 $\times$ 2) (CH), 127.4 (127.4) (CH), 128.4 $\times$ 2 (128.3 $\times$ 2) (CH), 134.4 (134.3) (Cq), 202.6 (201.9) (Cq), signals for the *anti* diastereomer are given in parentheses;

HRMS (ESI) calcd for $C_{22}H_{31}OSi$ ($M^+ + H$): 339.2144, found 339.2162.

(1*R, 2*R**)-2-[5-(*tert*-Butyldiphenylsiloxy)-2-phenyl-1-penten-3-ynylidene]cyclohexanol (*anti*-3ac)**

Colorless oil; IR (neat) 3399, 2246, 1941, 1590 cm^{-1} ; 1H -NMR (400 MHz, $CDCl_3$) δ 1.08 (s, 9H), 1.46–1.57 (m, 3H), 1.82–1.91 (m, 2H), 2.07–2.10 (m, 1H), 2.13–2.22 (m, 1H), 2.52–2.55 (m, 1H), 4.16–4.20 (m, 1H), 4.57 (s, 2H), 7.21–7.25 (m, 1H), 7.29–7.33 (m, 2H), 7.36–7.45 (m, 6H), 7.50–7.53 (m, 2H), 7.74–7.76 (m, 4H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ 19.2 (Cq), 23.8 (CH_2), 26.7 $\times$ 3 (CH_3), 26.9 (CH_2), 29.8 (CH_2), 36.2 (CH_2), 53.4 (CH_2), 69.7 (CH), 79.0 (Cq), 91.2 (Cq), 96.0 (Cq), 113.7 (Cq), 126.0 $\times$ 2 (CH), 127.4 (CH), 127.7 $\times$ 4 (CH), 128.4 $\times$ 2 (CH), 129.8 $\times$ 2 (CH), 133.2 $\times$ 2 (Cq), 134.4 (Cq), 135.7 $\times$ 4 (CH), 201.6 (Cq); HRMS (ESI) m/z calcd for $C_{33}H_{37}O_2Si$ [$M+H$] $^+$ 493.2563, found 493.2554.

(1*R, 2*S**)-2-[5-(*tert*-Butyldiphenylsiloxy)-2-phenyl-1-penten-3-ynylidene]cyclohexanol (*syn*-3ac)**

Colorless oil; IR (neat) 3429, 2247, 1941, 1590 cm^{-1} ; 1H -NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 9H), 1.45–1.67 (m, 2H), 1.74–1.75 (m, 2H), 1.87–1.90 (m, 1H), 2.05–2.11 (m, 1H), 2.14–2.21 (m, 1H), 2.52–2.58 (m, 1H), 4.24–4.26 (m, 1H), 4.57 (s, 2H), 7.21–7.25 (m, 1H), 7.29–7.33 (m, 2H), 7.36–7.45 (m, 6H), 7.46–7.49 (m, 2H), 7.74–7.76 (m, 4H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ 19.3 (Cq), 23.1 (CH_2), 26.6 (CH_2), 26.7 $\times$ 3 (CH_3), 29.1 (CH_2), 35.9 (CH_2), 53.4 (CH_2), 69.5 (CH), 79.2 (Cq), 91.0 (Cq), 95.2 (Cq), 112.8 (Cq), 126.1 $\times$ 2 (CH), 127.4 (CH), 127.7 $\times$ 4 (CH), 128.3 $\times$ 2 (CH), 129.8 $\times$ 2 (CH), 133.2 (Cq), 134.5 $\times$ 2 (Cq), 135.7 $\times$ 4 (CH), 202.1 (Cq); HRMS (ESI) m/z calcd for $C_{33}H_{37}O_2Si$ [$M+H$] $^+$ 493.2563, found 493.2567.

(1*R, 2*R**)-2-[6-(*tert*-Butyldiphenylsiloxy)-2-phenyl-1-hexen-3-ynylidene]cyclohexanol (*anti*-3ad)**

Colorless oil; IR (neat) 3436, 2224, 1944, 1596 cm^{-1} ; 1H -NMR (400 MHz, $CDCl_3$) δ 1.07 (s, 9H), 1.44–1.55 (m, 3H), 1.82–1.90 (m, 2H), 2.07–2.14 (m, 1H), 2.19–2.22 (m, 1H), 2.51–2.54 (m, 1H), 2.71 (t, $J = 6.8$ Hz, 2H), 3.87 (t, $J = 6.8$ Hz, 2H), 4.14–4.16 (m, 1H), 7.20–7.23 (m, 1H), 7.28–7.31 (m, 2H),

7.35–7.42 (m, 6H), 7.57–7.63 (m, 2H), 7.69–7.73 (m, 4H); ^{13}C -NMR (100 MHz, CDCl_3) δ 19.2 (Cq), 23.9 (CH_2), 26.7 $\times$ 3 (CH_3), 26.8 (CH_2), 30.0 (CH_2), 36.2 (CH_2), 62.3 (CH_2), 67.0 (CH_2), 69.7 (CH), 75.1 (Cq), 91.1 (Cq), 96.5 (Cq), 113.5 (Cq), 125.4 (CH), 126.0 $\times$ 2 (CH), 127.3 (CH), 127.7 $\times$ 2 (CH), 128.3 $\times$ 2 (CH), 128.9 (CH), 129.6 $\times$ 2 (CH), 130.5 (CH), 133.5 $\times$ 2 (Cq), 134.7 (Cq), 135.5 $\times$ 2 (CH), 143.3 (CH), 201.2 (Cq); HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{39}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 507.2719, found 507.2728.

(1*R, 2*S**)-2-[6-(*tert*-Butyldiphenylsiloxy)-2-phenyl-1-hexen-3-ynylidene]cyclohexanol (*syn*-3ad)**

Colorless oil; IR (neat) 3426, 2227, 1942, 1590 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 1.07 (s, 9H), 1.46–1.52 (m, 1H), 1.56–1.64 (m, 1H), 1.67–1.74 (m, 1H), 1.81–1.88 (m, 2H), 2.02–2.04 (m, 1H), 2.13–2.20 (m, 1H), 2.52–2.55 (m, 1H), 2.70 (t, J = 6.8 Hz, 2H), 3.87 (t, J = 6.8 Hz, 2H), 4.23–4.26 (m, 1H), 7.19–7.22 (m, 1H), 7.27–7.30 (m, 2H), 7.35–7.42 (m, 6H), 7.53–7.54 (m, 2H), 7.70–7.71 (m, 4H); ^{13}C -NMR (100 MHz, CDCl_3) δ 19.2 (Cq), 23.0 (CH_2), 23.9 (CH_2), 26.6 (CH_2), 26.8 $\times$ 3 (CH_3), 29.1 (CH_2), 35.8 (CH_2), 62.4 (CH_2), 69.5 (CH), 75.3 (Cq), 90.9 (Cq), 95.5 (Cq), 112.4 (Cq), 126.1 $\times$ 2 (CH), 127.3 (CH), 127.7 $\times$ 4 (CH), 128.3 $\times$ 2 (CH), 129.7 $\times$ 2 (CH), 133.6 $\times$ 2 (Cq), 134.9 (Cq), 135.6 $\times$ 4 (CH), 201.9 (Cq); HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{39}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 507.2719, found 507.2739.

(1*R, 2*R**)-2-(2-Phenyl-1-octen-3-ynylidene)cyclohexanol (*anti*-3ae)**

Colorless oil; IR (neat) 3411, 2221, 1943, 1597 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 0.95 (t, J = 7.4 Hz, 3H), 1.44–1.52 (m, 6H), 1.85–1.91 (m, 1H), 1.91–1.92 (m, 2H), 2.10–2.18 (m, 1H), 2.21–2.24 (m, 1H), 2.44 (t, J = 7.2 Hz, 2H), 2.53–2.57 (m, 1H), 4.17–4.19 (m, 1H), 7.30–7.35 (m, 3H), 7.57–7.59 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3) δ 13.7 (CH_3), 19.5 (CH_2), 22.2 (CH_2), 23.9 (CH_2), 27.0 (CH_2), 30.1 (CH_2), 30.9 (CH_2), 36.4 (CH_2), 69.7 (CH), 74.0 (Cq), 94.3 (Cq), 96.7 (Cq), 113.3 (Cq), 125.9 $\times$ 2 (CH), 127.2 (CH), 128.3 $\times$ 2 (CH), 134.9 (Cq), 200.8 (Cq); HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{25}\text{O}$ $[\text{M}+\text{H}]^+$ 281.1905, found 281.1923.

[(1*R, 2*R**) and (1*R**, 2*S**)]-2-(2-Phenyl-1-octen-3-ynylidene)cyclohexanol (*syn*-3ae + *anti*-3ae)**

Colorless oil; IR (neat) 3412, 2222, 1941, 1597 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 0.95 (t, $J = 7.4$ Hz, 1.8H), 0.96 (t, $J = 7.2$, 1.2H), 1.44–1.53 (m, 3H), 1.58–1.65 (m, 4H), 1.83–1.94 (m, 2H), 2.04–2.11 (m, 1H), 2.14–2.23 (m, 1H), 2.44 (t, $J = 7.2$ Hz, 2H), 2.53–2.59 (m, 1H), 4.17–4.19 (m, 0.4H), 4.23–4.29 (m, 0.6H), 7.20–7.25 (m, 1H), 7.30–7.35 (m, 2H), 7.52–7.59 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3) δ 13.6 (13.7) (CH_3), 19.4 (19.5) (CH_2), 22.1 (22.2) (CH_2), 23.1 (23.9) (CH_2), 26.7 (27.0) (CH_2), 29.2 (30.1) (CH_2), 30.9 (30.9) (CH_2), 35.9 (36.4) (CH_2), 69.5 (69.7) (CH), 74.2 (74.0) (Cq), 94.1 (94.3) (Cq), 95.9 (96.7) (Cq), 112.4 (113.3) (Cq) 126.1 $\times$ 2 (125.9 $\times$ 2) (CH), 127.3 (127.2) (CH), 128.3 $\times$ 2 (128.3 $\times$ 2) (CH), 135.2 (134.9) (Cq), 201.7 (200.8) (Cq), signals for the *anti* diastereomer are given in parentheses; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{25}\text{O}$ $[\text{M}+\text{H}]^+$ 281.1905, found 281.1919.

(1*R, 2*R**)-2-(2,6-Diphenyl-1,5-hexadien-3-ynylidene)cyclohexanol (*anti*-3af)**

Colorless oil; IR (neat) 3425, 2247, 1947, 1599 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 1.22–1.30 (m, 2H), 1.86–1.93 (m, 3H), 2.15–2.26 (m, 2H), 2.58–2.6 (m, 1H), 4.21–4.25 (m, 1H), 6.41 (d, $J = 16.4$ Hz, 1H), 7.05 (d, $J = 16.4$ Hz, 1H), 7.28–7.61 (m, 8H), 7.62–7.63 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3) δ 23.8 (CH_2), 26.9 (CH_2), 30.0 (CH_2), 36.3 (CH_2), 58.4 (Cq), 67.1 (Cq), 68.9 (CH), 76.7 (CH), 92.4 (Cq), 96.8 (Cq), 108.2 (CH), 113.9 (Cq), 126.1 $\times$ 2 (CH), 126.3 $\times$ 2 (CH), 127.6 (CH), 128.5 $\times$ 2 (CH), 128.7 (CH), 128.8 $\times$ 2 (CH), 141.2 (Cq), 201.8 (Cq); HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$ 327.1749, found 327.1741.

(1*R, 2*S**)-2-(2,6-Diphenyl-1,5-hexadien-3-ynylidene)cyclohexanol (*syn*-3af)**

Colorless oil; IR (neat) 3425, 2926, 2251, 1947 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 1.24–1.28 (m, 2H), 1.61–1.70 (m, 1H), 1.76–1.84 (m, 1H), 1.88–1.94 (m, 1H), 2.07–2.13 (m, 1H), 2.17–2.25 (m, 1H), 2.56–2.63 (m, 1H), 4.29–4.32 (m, 1H), 6.41 (d, $J = 16.0$ Hz, 1H), 7.05 (d, $J = 16.0$ Hz, 1H), 7.26–7.31 (m, 2H), 7.33–7.38 (m, 5H), 7.42–7.44 (m, 2H), 7.57–7.58 (m, 1H); ^{13}C -NMR (100 MHz, CDCl_3) δ 23.0

(CH₂), 26.6 (CH₂), 29.2 (CH₂), 35.9 (CH₂), 69.6 (CH), 85.8 (Cq), 92.2 (Cq), 95.9 (Cq), 108.3 (CH), 112.9 (Cq), 126.1×2 (CH), 126.3×2 (CH), 127.5 (CH), 128.4×2 (CH), 128.6 (CH), 128.7×2 (CH), 134.6 (Cq), 136.4 (Cq), 141.1 (CH), 202.3 (Cq); HRMS (ESI) m/z Calcd for C₂₄H₂₃O [M+H]⁺ 327.1749, found 327.1744.

(1*R, 2*S**)-2-[2-(*tert*-Butyldimethylsilyl)-4-trimethylsilyl-1-buten-3-ynylidene]cyclohexanol**
(*anti*-3ba)

Colorless oil; IR (0.1 mm KBr, CHCl₃) 3585, 2127, 1933 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.13 (s, 3H), 0.15 (s, 3H), 0.16 (s, 9H), 0.97 (s, 9H), 1.34–1.42 (m, 2H), 1.69–1.74 (m, 2H), 1.80–1.82 (m, 1H), 2.02–2.10 (m, 2H), 2.36–2.41 (m, 1H), 4.08–4.11 (m, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ -6.3 (CH₃), -6.0 (CH₃), 0.0×3 (CH₃), 17.8 (Cq), 23.7 (CH₂), 26.1 (CH₂), 26.5×3 (CH₃), 29.3 (CH₂), 35.3 (CH₂), 68.7 (CH), 85.8 (Cq), 96.3 (Cq), 101.0 (Cq), 103.3 (Cq), 206.9 (Cq); MS (EI) m/z 73 (100%), 277(M⁺-57), 334 [M⁺]; HRMS (ESI) m/z calcd for C₁₉H₃₅OSi₂ [M⁺+H] 335.2226, found 335.2237.

(1*R, 2*S**)-2-[2,4-Bis(trimethylsilyl)-1-buten-3-ynylidene]cyclohexanol (*anti*-3ca)**

Colorless oil; IR (neat) 3433, 2127, 1936 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.18 (s, 9H)×2, 1.33–1.40 (m, 2H), 1.72–1.75 (m, 2H), 1.81–1.83 (m, 1H), 2.00–2.12 (m, 2H), 2.37–2.41 (m, 1H), 4.07–4.10 (m, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ -1.9×3 (CH₃), 0.0×3 (CH₃), 23.7 (CH₂), 26.3 (CH₂), 29.1 (CH₂), 35.3 (CH₂), 68.5 (CH), 88.3 (Cq), 96.2 (Cq), 99.9 (Cq), 104.0 (Cq), 205.4 (Cq); HRMS (ESI) m/z calcd for C₁₆H₂₉OSi₂ [M+H]⁺ 293.1757, found 293.1786.

[(1*R, 2*R**) and (1*R**, 2*S**)]-[2,4-Bis(trimethylsilyl)-1-buten-3-ynylidene]cyclohexanol**
(*syn*-3ca + *anti*-3ca) (ratio of 3 : 7)

Colorless oil; IR (neat) 3419, 2128, 1935 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.18 (s, 9H)×2, 1.25–1.40 (m, 2H), 1.67–1.84 (m, 3H), 1.99–2.12 (m, 2H), 2.37–2.46 (m, 1H), 4.07–4.10 (m, 0.7H), 4.17–4.20 (m,

0.3H); ^{13}C -NMR (100 MHz, CDCl_3) δ -1.9 (-1.9) $\times$ 3 (CH_3), -0.3 (0.0) $\times$ 3 (CH_3), 21.9 (23.7) (CH_2), 26.4 (26.3) (CH_2), 27.4 (29.1) (CH_2), 34.9 (35.3) (CH_2), 68.8 (68.5) (CH), 84.1 (88.3) (Cq), 95.9 (96.2) (Cq), 102.2 (99.9) (Cq), 110.9 (104.0) (Cq), 206.4 (205.4) (Cq), signals for the *anti* diastereomer are given in parentheses; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{29}\text{OSi}_2$ $[\text{M}+\text{H}]^+$ 293.1757, found 293.1786.

[(1*R, 2*S**) and (1*R**, 2*R**)]-2-(2-Benzyl-4-trimethylsilyl-1-buten-3-ynylidene)cyclohexanol**

(*anti*-3da + *syn*-3da) (ratio of 7 : 3)

Colorless oil; IR (neat) 3419, 2143, 1954, 1603 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 0.17 (s, 3H), 0.18 (s, 6H), 0.90–1.02 (m, 1H), 1.20–1.33 (m, 1H), 1.36–1.49 (m, 1H), 1.51–1.64 (m, 2H), 1.67–1.71 (m, 1H), 1.84–1.93 (m, 2H), 2.18–2.23 (m, 0.7H), 2.30–2.36 (m, 0.3H), 3.41–3.42 (m, 0.3H), 3.45–3.49 (m, 0.7H), 3.87–3.91 (m, 0.7H), 3.92–3.95 (m, 0.3H), 7.19–7.23 (m, 3H), 7.26–7.31 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3) δ *anti* [0.0 $\times$ 3 (CH_3), 23.4 (CH_2), 26.1 (CH_2), 29.4 (CH_2), 35.3 (CH_2), 41.0 (CH_2), 69.1 (CH), 94.5 (Cq), 95.8 (Cq), 101.1 (Cq), 111.5 (Cq), 126.5 (CH), 128.3 $\times$ 2 (CH), 129.5 $\times$ 2 (CH), 138.6 (Cq), 201.6 (Cq).] *syn* [-0.03 $\times$ 3 (CH_3), 22.5 (CH_2), 26.3 (CH_2), 28.6 (CH_2), 35.1 (CH_2), 41.1 (CH_2), 69.3 (CH), 92.9 (Cq), 95.9 (Cq), 101.3 (Cq), 110.0 (Cq), 126.4 (CH), 128.2 $\times$ 2 (CH), 129.1 $\times$ 2 (CH), 138.7 (Cq), 202.1 (Cq).]; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{27}\text{OSi}$ $[\text{M}+\text{H}]^+$ 311.1831, found 311.1830.

[(1*R, 2*S**) and (1*R**, 2*R**)]-2-(2-butyl-4-trimethylsilyl-1-buten-3-ynylidene)cyclohexanol**

(*anti*-3ea + *syn*-3ea) (ratio of 8 : 2)

Colorless oil; IR (neat) 3411, 2143, 1952 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 0.00 (s, 9H), 0.85–0.90 (m, 3H), 1.29–1.45 (m, 6H), 1.46–1.59 (m, 1H), 1.71–1.80 (m, 1H), 1.95–2.03 (m, 2H), 2.07–2.13 (m, 3H), 2.35–2.43 (m, 1H), 4.01–4.07 (m, 0.8H), 4.06–4.10 (m, 0.2H); ^{13}C -NMR (100 MHz, CDCl_3) δ *anti* [0.0 $\times$ 3 (CH_3), 13.9 (CH_3), 21.9 (CH_2), 23.8 (CH_2), 26.6 (CH_2), 29.8 (CH_2), 29.9 (CH_2), 34.0 (CH_2), 35.7 (CH_2), 69.2 (CH), 93.9 (Cq), 95.0 (Cq), 101.4 (Cq), 110.3 (Cq), 200.3 (Cq).] *syn* [0.0 $\times$ 3 (CH_3), 13.9 (CH_3), 21.9 (CH_2), 22.9 (CH_2), 26.5 (CH_2), 29.1 (CH_2), 29.9 (CH_2), 34.0 (CH_2), 35.7 (CH_2), 69.3 (CH),

92.8 (Cq), 94.9 (Cq), 101.6 (Cq), 109.1 (Cq), 201.0 (Cq).]; HRMS (ESI) m/z Calcd for $C_{17}H_{29}OSi$ $[M+H]^+$ 277.1988, found 277.1973.

(1*R, 2*R**)-2-(4-Trimetylsilyl-1-buten-3-ynylidene)cyclohexanol (*anti*-3fa)**

Colorless oil; IR (neat) 3388, 2153, 1954 cm^{-1} ; 1H -NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 9H), 1.36–1.49 (m, 1H), 1.56–1.64 (m, 1H), 1.70–1.76 (m, 1H), 1.81–1.83 (m, 2H), 2.04–2.10 (m, 2H), 2.42–2.46 (m, 1H), 4.11–4.14 (m, 1H), 5.58–5.60 (m, 1H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ 0.0 $\times$ 3 (CH_3), 23.6 (CH_2), 26.2 (CH_2), 29.4 (CH_2), 35.4 (CH_2), 69.0 (CH), 79.0 (CH), 95.2 (Cq), 98.5 (Cq), 110.1 (Cq), 205.0 (Cq); MS (EI) m/z 73 (100%), 220 $[M^+]$; HRMS (ESI) m/z calcd for $C_{13}H_{20}OSi$ $[M^+]$ 220.1283, found 220.1285.

(1*R, 2*S**)-2-(4-Trimetylsilyl-1-buten-3-ynylidene)cyclohexanol (*syn*-3fa)**

Colorless oil; IR (neat) 339, 2152, 1953 cm^{-1} ; 1H -NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 9H), 1.38–1.48 (m, 1H), 1.65–1.69 (m, 2H), 1.76–1.78 (m, 1H), 1.83–1.86 (m, 1H), 1.98–2.07 (m, 2H), 2.44–2.50 (m, 1H), 4.08–4.13 (m, 1H), 5.53–5.54 (m, 1H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ 0.0 $\times$ 3 (CH_3), 23.1 (CH_2), 26.3 (CH_2), 28.9 (CH_2), 35.6 (CH_2), 69.2 (CH), 78.4 (CH), 95.1 (Cq), 98.5 (Cq), 109.6 (Cq), 205.2 (Cq); MS (EI) m/z 73 (100%), 220 $[M^+]$; HRMS (ESI) m/z calcd for $C_{13}H_{20}OSi$ $[M^+]$ 220.1283, found 220.1299.

Procedure for the reaction of optically active propargylic oxirane (*1*R*,2*R)-1a with 2a (Scheme 2).**

(1*R*, 2*R*)-2-(2-Phenyl-4-trimetylsilyl-1-buten-3-ynylidene)cyclohexanol [(1*R*,2*R*)-*anti*-3aa]

By following the same procedure described for *anti*-3aa, optically active alkynylallene (*1*R*,2*R**)-*anti*-3aa was prepared from (*1*R*,2*R**)-1a with 2a. Yield 94%; 91% ee; colorless oil; $[\alpha]_D^{26} = +28.4$ (c 1.06 in $CHCl_3$); enantiomeric excess was determined by HPLC analysis [CHIRALCEL OD-H column, hexane-*i*-PrOH = 95 : 5, 0.5 mL/min, $\lambda = 254$ nm, retention time 13.0 min (*1*R*, 2*R**) and 15.7 (*1*S*, 2*S**)]. Other spectral data coincides with those of the racemic *anti*-3aa.

General procedure for the palladium-catalyzed reaction of propargylic oxiranes with alkynylmetal reagents (Table 4). Reaction of 1a with alkynylborate 2j (entry 4 in Table 4)

To a stirred solution of alkynylborate **2j** (103 mg, 0.353 mmol) in 1,4-dioxane (2 mL) were added CuI (5.39 mg, 28.3 μ mol), Pd₂(dba)₃·CHCl₃ (7.32 mg, 7.07 μ mol) and dppe (11.3 mg, 28.3 μ mol) at rt, and the stirring was continued for 5 min at the same temperature. Then the reaction mixture was added propargylic oxirane **1e** (25.2 mg, 0.141 mmol) at rt, and the stirring was continued for 3.5 h at the same temperature. After filtration of the reaction mixture using small amount of silica gel, the mass was concentrated. The residue was chromatographed on silica gel with hexane-AcOEt-Et₃N (88 : 11 : 1 v/v/v) as eluent to give 4-alkynyl-2,3-allenylalcohol **3ea** (31.0 mg, 80%, *anti* : *syn* = 3.9 : 1) as a yellow oil.

Procedure for the conversion of *anti*-3aa to vinylidihydrofuran 5aa (Scheme 1).

(2*R, 7*aR**)-2-(2-Trimethylsilyl)ethynyl-3-iodo-2-phenyl-2,4,5,6,7,7a-hexahydrobenzofuran (4aa)**

To a stirred solution of allenylalcohol *anti*-**3aa** (35.9 mg, 0.121 mmol) in CH₂Cl₂/MeOH (2.5 mL, 1 : 4 v/v) were added NaI (20.0 mg, 0.133 mmol) and NCS (16.2 mg, 0.121 mmol) at 0 °C, and stirring was continued for 1 h at the same temperature. The reaction mixture was diluted with water at 0 °C and extracted with AcOEt. The combined extracts were washed with brine, and the residue upon workup was chromatographed on silica gel with hexane as eluent to give dihydrofuran **4aa** (39.9 mg, 78%) as a yellow oil. IR (neat) 2167, 1600 1123 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.24 (s, 9H), 1.26–1.35 (m, 1H), 1.41–1.47 (m, 2H), 1.89–1.91 (m, 2H), 2.07–2.15 (m, 1H), 2.23–2.25 (m, 1H), 2.52–2.56 (m, 1H), 4.77–4.81 (m, 1H), 7.30–7.39 (m, 3H), 7.61–7.63 (m, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ 0.0×3 (CH₃), 23.5 (CH₂), 25.8 (CH₂), 29.2 (CH₂), 34.9 (CH₂), 85.2 (CH), 89.6 (Cq), 91.0 (Cq), 93.6 (Cq), 102.8 (Cq), 127.3×2 (CH), 127.9×2 (CH), 128.3 (CH), 140.1 (Cq), 147.3 (Cq); MS (EI) *m/z* 295 (100%), 422 [M⁺] HRMS (EI) *m/z* calcd for C₁₉H₂₃OISi [M⁺] 422.0563, found 422.0571.

(2*S, 7*aR**)-3-Iodo-2-phenyl-2-vinyl-2,4,5,6,7,7a-hexahydrobenzofuran (5aa)**

To a stirred solution of hexahydrobenzofuran **4aa** (31.6 mg, 0.0748 mmol) in MeOH (2 mL) was added K_2CO_3 (20.7 mg, 0.150 mmol) at rt, and the stirred was continued for 0.5 h at the same temperature. The reaction mixture was quenched with sat. NH_4Cl aq. at rt and extracted with AcOEt. The combined extracts were washed with brine, and the residue upon workup was chromatographed on silica gel with hexane-AcOEt (95:5 v/v) as eluent to give alkyne (27.1 mg, quant.) as a colorless oil. IR (neat) 2945, 1602 cm^{-1} ; 1H -NMR (400 MHz, $CDCl_3$) δ 1.29–1.35 (m, 1H), 1.42–1.48 (m, 2H), 1.90–1.93 (m, 2H), 2.06–2.14 (m, 1H), 2.25–2.26 (m, 1H), 2.53–2.57 (m, 1H), 2.87 (s, 1H), 4.78–4.82 (m, 1H), 7.33–7.39 (m, 3H), 7.62–7.64 (m, 2H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ 23.4 (CH_2), 25.8 (CH_2), 29.1 (CH_2), 34.9 (CH_2), 76.5 (CH), 81.7 (Cq), 85.3 (CH), 89.3 (Cq), 90.4 (Cq), 127.3 $\times$ 2 (CH), 128.0 $\times$ 2 (CH), 128.6 (CH), 139.5 (Cq), 147.8 (Cq); MS (EI) m/z 165 (100%), 350 [M^+] HRMS (EI) m/z calcd for $C_{16}H_{15}OI$ [M^+] 350.0168, found 350.0157.

To a stirred solution of the alkyne described above (5.9 mg, 0.017 mmol) in EtOH (2 mL) was added Lindlar catalyst (6.9 mg, 117 wt%) at rt, and the stirred was continued for 28 h at the same temperature under H_2 atmosphere. After filtration of the reaction mixture through a Celite pad, the residue upon concentration of the solvent was chromatographed on silica gel with hexane-AcOEt (9 : 1 v/v) as eluent to give vinyl dihydrofuran **5aa** (3.7 mg, 63%) as a colorless oil. IR (neat) 2945, 1659, 1601 cm^{-1} ; 1H -NMR (400 MHz, $CDCl_3$) δ 1.19–1.22 (m, 1H), 1.32–1.49 (m, 2H), 1.81–1.84 (m, 2H), 1.94–2.01 (m, 1H), 2.16–2.18 (m, 1H), 2.47–2.52 (m, 1H), 4.52–4.55 (m, 1H), 5.28 (dd, J = 1.6, 10.8 Hz, 1H), 5.50 (dd, J = 1.6, 17.4 Hz, 1H), 6.27 (dd, J = 10.8, 17.4 Hz, 1H), 7.21–7.23 (m, 1H), 7.24–7.30 (m, 2H), 7.36–7.39 (m, 2H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ 23.5 (CH_2), 25.9 (CH_2), 29.2 (CH_2), 35.1 (CH_2), 77.2 (Cq), 84.8 (CH), 90.6 (Cq), 114.6 (Cq), 127.6 $\times$ 2 (CH), 127.9 (CH), 128.0 $\times$ 2 (CH), 135.8 (Cq), 137.2 (CH), 146.7 (Cq); HRMS (ESI) m/z calcd for $C_{16}H_{18}OI$ [$M+H$] $^+$ 53.0402, found 53.0405.

Scheme S-4

Procedure for the conversion of **3da** to vinyl dihydrofuran **5da** (Scheme S-4).

[(**2R***, **7aR***) and (**2S***, **7aR***)]-2-Benzyl-2-ethynyl-3-iodo-2,4,5,6,7,7a-hexahydrobenzofuran (*trans*-**4da** + *cis*-**4da**) (ratio of 8 : 2)

By following the same procedure described for **4aa**, dihydrofuran *trans*- and *cis*-**4da** (4 : 1 diastereomeric mixture) **4da** were prepared from allenylalcohols *anti*- and *syn*-**3da** (*anti*: *syn* = 4 : 1) and NaI, NCS; quantitative yield. Colorless oil; IR (neat) 2939, 1662, 1604 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.17–0.18 (m, 9H), 0.31–0.44 (m, 1H), 0.81–0.93 (m, 1H), 1.14–1.31 (m, 2H), 1.68–1.71 (m, 1H), 1.84–2.01 (m, 2H), 2.40–2.44 (m, 1H), 3.07–3.24 (m, 2H), 3.89–3.93 (m, 0.2H), 4.53–4.57 (m, 0.8H), 7.18–7.25 (m, 3H), 7.29–7.31 (m, 2H); HRMS (ESI) *m/z* calcd for C₁₉H₂₃OISi [M+H]⁺ 437.0798, found 437.0788.

(**2R***, **7aR***)-2-Benzyl-3-iodo-2-vinyl-2,4,5,6,7,7a-hexahydrobenzofuran (**5da**)

By following the same procedure described for alkyne **5aa**, vinyl dihydrofuran **5da** was prepared from dihydrofurans **4da** (*trans* : *cis* = 4 : 1) in 2 steps 65% yield (from *trans*-**4da**). Colorless oil; IR (neat) 2936, 1663, 1636, 1604 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.17–0.27 (m, 1H), 0.78–0.86 (m, 1H), 1.10–1.18 (m, 2H), 1.62–1.65 (m, 1H), 1.78–1.88 (m, 2H), 2.37–2.41 (m, 1H), 2.87 (d, *J* = 13.8 Hz, 1H), 3.19 (d, *J* = 13.8 Hz, 1H), 4.44–4.48 (m, 1H), 5.13 (dd, *J* = 1.6, 10.8 Hz, 1H), 5.36 (dd, *J* = 1.6, 17.2 Hz, 1H), 6.06–6.13 (m, 1H), 7.16–7.24 (m, 3H), 7.26–7.30 (m, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ 23.4 (CH₂), 25.5 (CH₂), 29.3 (CH₂), 34.3 (CH₂), 43.4 (CH₂), 85.7 (CH), 92.6 (Cq), 113.4 (CH₂), 126.3 (CH), 127.4×2

(CH), 130.8 (CH), 131.4×2 (CH), 136.7 (Cq), 139.9 (CH), 146.6 (Cq); HRMS (ESI) m/z calcd for $C_{17}H_{20}OI$ $[M+H]^+$ 367.0559, found 367.0569.

Procedure for the palladium-catalyzed isomerization of 4-alkynyl-substituted 2,3-allenol *anti*-**3aa** (Scheme 4)

To a stirred solution of 4-alkynyl-2,3-allenylalcohol *anti*-**3aa** (25.8 mg, 0.0870 mmol) in 1,4-dioxane (2 mL) were added CuI (3.3 mg, 17.4 μ mol), i Pr₂NEt (0.076 mL, 0.435 mmol), PPh₃ (9.1 mg, 34.8 μ mol) and Pd(OAc)₂ (2.0 mg, 8.70 μ mol) at rt, and the stirring was continued for 40 h at the same temperature. After filtration of the reaction mixture using small amount of silica gel, the mass was concentrated. The residue was chromatographed on silica gel with hexane-AcOEt-Et₃N (89 : 10 : 1 v/v/v) as eluent to give 4-alkynyl-2,3-allenylalcohol *anti*- and *syn*-**3aa** (21.8 mg, 85%) as a colorless oil.

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818

6.1056

9.0636

1d

1d

syn-3ad

syn-3af

2.6180
1.0438
1.9121
2.1214
1.0035

1.0000

17.7996

anti-3ca

anti-3ca

3.0000
2.2511

0.2583
0.7168

0.5807
1.4234

0.2254

0.7284

1.8753

2.2246

1.1808

1.3616

1.5416

2.9031

6.1712

anti-3fa

syn-3fa

trans-4da + *cis*-4da

8.6002

trans-4da + cis-4da

5aa

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 PC 1.00
 F1 - Processing parameters
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 GB 0

5da

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 MCWRR 1.0000000 sec
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 FIDRES 26.537024 Hz
 SWH 8.469 ppm
 FMODE States-TPPI
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 SF 400.1300156 MHz
 WDW QSI
 SSB 2
 LB 0.00 Hz
 GB 0
 PC 1.00
 F1 - Processing parameters
 SI 1024
 MC2 States-TPPI
 SF 400.1300126 MHz
 WDW QSI
 SSB 2
 LB 0.00 Hz
 GB 0

060422
 hayashi003
 CDCl3
 noesy