Catalytic Asymmetric Allylation of Unsymmetrical 1,3-Diketones Using BINAP–Palladium Catalyst

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Supporting Information

General and Materials. Specific rotations were measured with a JASCO P-1020 polarimeter. NMR spectra were measured with Varian GEMINI-2000 (7.0 T magnet) spectrometer. Flash column chromatographies and preparative TLCs were performed with silica gel 60 (230–400 mesh, Merck) and silica gel 60 PF₂₅₄ (Merck), respectively. Asymmetric allylations were carried out under nitrogen atmosphere unless otherwise noted. [Pd(η^3 -C₃H₅)Cl]₂,¹ (*E*)-3-cyclohexyl-2-propenyl acetate,² (*E*)-3-(4-methoxyphenyl)-2-propenyl acetate,³ (*E*)-3-[4-(trifluoromethyl)phenyl]-2-propenyl acetate,³ 2-acetyl-4,4-dimethylcyclohexanone,⁴ 2-acetyl-1-tetralone,^{5,6} 2-acetylcycloheptanone,^{5,6} 2-acetylcyclooctanone,^{5,6} 2-propionylcyclohexanone,⁵ 2-methyl-1-phenylbutane-1,3-dione,^{5,6} and 1-(4-methoxyphenyl)-2-methylbutane-1,3-dione⁷ were prepared according to the literatures. (*R*)-BINAP and potassium *t*-butoxide were purchased from Kanto Reagents and from Merck respectively, and were used without further purification. Other materials were purchased from commercial sources and were purified with distillation before use.

General Procedure of Catalytic Asymmetric Alkylation of 1,3-Diketones with Allylic Acetates. A mixture of [Pd(η^3 -C₃H₅)Cl]₂ (0.9 mg, 2.5 μ mol) and (*R*)-BINAP (3.3 mg, 5.3 μ mol) in toluene (0.5 ml) was stirred for 10 min at room temperature. Allylic acetate (0.50 mmol) was added to the solution. After 10 min, the solution was transferred by cannula to a suspension of 1,3-diketone (0.60 mmol) and KO(*t*-Bu) (67 mg, 0.60 mmol) in toluene (2.0 ml) at –60 °C. The resulting yellow suspension was stirred at –60 °C for 24 h, and was monitored by GC. After 1 *N* HCl aq (2.0 ml) was added, the mixture was stirred at room temperature for 5 min, was extracted twice with EtOAc. The combined organic layer was washed with brine, was dried with MgSO₄, and was evaporated under reduced pressure. The residue was purified by a preparative TLC (EtOAc/hexane), giving desired product.

(*S*)-2-Acetyl-2-(2-propenyl)cyclohexanone.⁶ The general procedure was followed with 2-acetylcyclohexanone (84 mg, 0.60 mmol) and allyl acetate (51 mg, 0.51 mmol). The residue was purified by a preparative TLC (EtOAc/hexane = 1/5) to give the desired product (75 mg, 82%) as colorless oil. The enantiomeric excess of the product was determined to be 64% ee by GLC analysis with a chiral stationary phase column, CHIRALDEX G-BP (0.25 mm ϕ $\times$ 30 m, 115 °C): [α]_D²⁰ = +179.2 (*c* 1.15, CHCl₃); ¹H NMR (300 MHz, CDCl₃, TMS) δ 1.42–1.54 (m, 1H), 1.58–1.82 (m, 3H), 1.92–2.06 (m, 1H), 2.09 (s, 3H), 2.21–2.34 (m, 1H), 2.35–2.53 (m, 3H), 2.62 (dd, *J* = 7.8, 14.4 Hz, 1H), 5.01–5.09 (m, 2H), 5.55–5.70 (m, 1H); ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 22.0, 26.3, 27.1, 34.0, 38.7, 41.7, 67.6, 118.6, 132.8, 206.2, 209.8.

(*S*)-2-Acetyl-2-[(*E*)-2-hexenyl]cyclohexanone (Table 1, entry 1). The general procedure was followed with 2-acetylcyclohexanone (84 mg, 0.60 mmol) and (*E*)-2-hexenyl acetate (70 mg, 0.50 mmol). The residue was purified by a preparative TLC (EtOAc/hexane = 1/10) to give the desired product (86 mg, 79%) as colorless oil. The enantiomeric excess of the product was determined to be 64% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OB-H (4.6 mm ϕ $\times$ 25 cm, 1% 2-propanol in hexane): [α]_D²⁰ = +158.7 (*c* 1.02, CHCl₃); ¹H NMR (300 MHz, CDCl₃, TMS) δ 0.85 (t, *J* = 7.5 Hz, 3H), 1.34 (sextet, *J* = 7.3 Hz, 2H), 1.39–1.52 (m, 1H), 1.57–1.80 (m, 3H),

1.88–2.03 (m, 3H), 2.08 (s, 3H), 2.20–2.39 (m, 2H), 2.40–2.52 (m, 2H), 2.57 (dd, $J = 7.5, 14.3$ Hz, 1H), 5.21 (dt, $J = 15.0, 7.5$ Hz, 1H), 5.45 (dt, $J = 15.0, 6.9$ Hz, 1H); ^{13}C { ^1H } NMR (75 MHz, CDCl_3) δ 13.5, 22.0, 22.4, 26.4, 27.1, 33.9, 34.5, 37.5, 41.8, 67.8, 124.0, 134.8, 206.4, 210.0; IR (neat) 1698, 1717 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_2$: C, 75.63; H, 9.97. Found: C, 75.89; H, 9.82.

(S)-2-Acetyl-2-[(E)-3-cyclohexyl-2-propenyl]cyclohexanone (Table 1, entry 2). The general procedure was followed with 2-acetylcyclohexanone (84 mg, 0.60 mmol) and (E)-3-cyclohexyl-2-propenyl acetate (91 mg, 0.50 mmol). The residue was purified by a preparative TLC (EtOAc/hexane = 1/10) to give the desired product (85 mg, 65%) as colorless oil. The enantiomeric excess of the product was determined to be 65% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OB-H (4.6 mm $\phi \times 25$ cm, 2% 2-propanol in hexane): $[\alpha]_{\text{D}}^{20} = +130.7$ (c 1.01, CHCl_3); ^1H NMR (300 MHz, CDCl_3 , TMS) δ 0.93–1.31 (m, 5H), 1.39–1.51 (m, 1H), 1.55–1.80 (m, 8H), 1.80–2.03 (m, 2H), 2.07 (s, 3H), 2.20–2.36 (m, 2H), 2.38–2.51 (m, 2H), 2.56 (dd, $J = 7.5, 14.4$ Hz, 1H), 5.17 (ddt, $J = 1.1, 15.5, 7.5$ Hz, 1H), 5.39 (dd, $J = 6.6, 15.5$ Hz, 1H); ^{13}C { ^1H } NMR (75 MHz, CDCl_3) δ 22.1, 25.9, 26.0, 26.4, 27.1, 32.9, 34.0, 37.5, 40.6, 41.8, 67.9, 121.3, 140.9, 206.4, 210.0; IR (neat) 1698, 1717 cm^{-1} ; Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_2$: C, 77.82; H, 9.99. Found: C, 77.76; H, 10.10.

(S)-2-Acetyl-2-[(E)-3-phenyl-2-propenyl]cyclohexanone (Table 1, entry 3). The general procedure was followed with 2-acetylcyclohexanone (84 mg, 0.60 mmol) and cinnamyl acetate (88 mg, 0.50 mmol). The residue was purified by a preparative TLC (EtOAc/hexane = 1/3) to give the desired product (127 mg, 99%) as colorless oil. The enantiomeric excess of the product (Table x, entry y) was determined to be 85% ee by HPLC analysis with a chiral stationary phase column, CHIRALPAK AD-H (4.6 mm $\phi \times 25$ cm, 10% 2-propanol in hexane): $[\alpha]_{\text{D}}^{20} = +174.0$ (c 1.10, CHCl_3); ^1H NMR (300 MHz, CDCl_3 , TMS) δ 1.47–1.86 (m, 4H), 1.92–2.07 (m, 1H), 2.13 (s, 3H), 2.24–2.36 (m, 1H), 2.44–2.55 (m, 2H), 2.59 (dd, $J = 7.5, 14.4$ Hz, 1H), 2.72 (dd, $J = 7.5, 14.4$ Hz, 1H), 6.02 (dt, $J = 15.9, 7.5$ Hz, 1H), 6.39 (d, $J = 15.9$ Hz, 1H), 7.17–7.34 (m, 5H); ^{13}C { ^1H } NMR (75 MHz, CDCl_3) δ 22.1, 26.3, 27.0, 34.1, 37.9, 41.8, 67.9, 124.4, 126.3, 127.4, 128.5, 133.6, 137.0, 206.3, 209.9; IR (neat) 1698, 1717 cm^{-1} ; Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_2$: C, 79.65; H, 7.86. Found: C, 79.78; H, 7.97.

2-Acetyl-2-[(E)-3-(4-methoxyphenyl)-2-propenyl]cyclohexanone (Table 1, entry 4). The general procedure was followed with 2-acetylcyclohexanone (84 mg, 0.60 mmol) and (E)-3-(4-methoxyphenyl)-2-propenyl acetate (104 mg, 0.51 mmol). The residue was purified by a preparative TLC (EtOAc/hexane = 1/3) to give the desired product (126 mg, 87%) as colorless oil. The enantiomeric excess of the product was determined to be 83% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OJ-H (4.6 mm $\phi \times 25$ cm, 30% 2-propanol in hexane): $[\alpha]_{\text{D}}^{20} = +158.3$ (c 1.06, CHCl_3); ^1H NMR (300 MHz, CDCl_3 , TMS) δ 1.47–1.83 (m, 4H), 1.92–2.06 (m, 1H), 2.12 (s, 3H), 2.23–2.36 (m, 1H), 2.44–2.55 (m, 2H), 2.57 (dd, $J = 7.8, 14.4$ Hz, 1H), 2.70 (dd, $J = 7.5, 14.4$ Hz, 1H), 3.79 (s, 3H), 5.87 (dt, $J = 15.8, 7.5$ Hz, 1H), 6.33 (d, $J = 15.8$ Hz, 1H), 6.82 (d, $J = 8.9$ Hz, 2H), 7.24 (d, $J = 8.9$ Hz, 2H); ^{13}C { ^1H } NMR (75 MHz, CDCl_3) δ 22.0, 26.3, 27.0, 34.0, 37.9, 41.8, 55.2, 67.9, 113.9, 122.1, 127.4, 129.9, 132.9, 159.1, 206.4, 209.9; IR (neat) 1032, 1246, 1696, 1717 cm^{-1} ; Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_3$: C, 75.50; H, 7.74. Found: C, 75.57; H, 7.81.

2-Acetyl-2-[(E)-3-{4-(trifluoromethyl)phenyl}-2-propenyl]cyclohexanone (Table 1, entry 5). The general procedure was followed with 2-acetylcyclohexanone (84 mg, 0.60 mmol) and (E)-3-{4-(trifluoromethyl)phenyl}-2-propenyl acetate (124 mg, 0.51 mmol). The residue was purified by a preparative TLC (EtOAc/hexane = 1/5) to give the desired product (143 mg, 87%) as colorless oil. The enantiomeric excess of the product was determined to be 84% ee by HPLC analysis with a chiral stationary phase column, CHIRALPAK AD-H (4.6 mm $\phi \times 25$ cm, 10% 2-propanol in hexane): $[\alpha]_{\text{D}}^{20} = +149.2$ (c 1.01, CHCl_3); ^1H NMR (300 MHz, CDCl_3 , TMS) δ 1.46–1.83 (m, 4H), 1.94–2.07 (m, 1H), 2.13 (s, 3H), 2.24–2.39 (m, 1H), 2.44–2.56 (m, 2H), 2.61 (dd, $J = 7.5, 14.4$ Hz, 1H), 2.74 (dd, $J = 7.5, 14.4$ Hz, 1H), 6.14 (dt, $J = 15.8, 7.5$ Hz, 1H), 6.42 (d, $J = 15.8$ Hz, 1H), 7.40 (d, $J = 8.7$ Hz, 2H), 7.53 (d, $J = 8.7$ Hz, 2H); ^{13}C { ^1H } NMR (75 MHz, CDCl_3) δ 22.1, 26.3, 27.0, 34.2, 37.8, 41.7, 67.7, 124.2 (q, $J =$

271 Hz), 125.5 (q, $J = 4$ Hz), 126.4, 127.5, 129.2 (q, $J = 11$ Hz), 132.2, 140.4, 206.2, 209.7; IR (neat) 1698, 1717 cm^{-1} ; Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{O}_2\text{F}_3$: C, 66.66; H, 5.90. Found: C, 66.61; H, 5.83.

2-Acetyl-4,4-dimethyl-2- $\{(E)\text{-3-phenyl-2-propenyl}\}$ cyclohexanone (Table 2, Entry 1). The general procedure was followed with 2-acetyl-4,4-dimethylcyclohexanone (100 mg, 0.60 mmol) and cinnamyl acetate (88 mg, 0.50 mmol). The residue was purified by a preparative TLC (EtOAc/hexane = 1/5) to give the desired product (131 mg, 92%) as colorless oil. The enantiomeric excess of the product was determined to be 89% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OF (4.6 mm $\phi \times 25$ cm, 4% 2-propanol in hexane): $[\alpha]_{\text{D}}^{20} = +99.4$ (c 1.04, CHCl_3); ^1H NMR (300 MHz, CDCl_3 , TMS) δ 1.01 (s, 3H), 1.04 (s, 3H), 1.54–1.75 (m, 3H), 2.16 (s, 3H), 2.31–2.69 (m, 5H), 6.10 (dt, $J = 15.9, 7.3$ Hz, 1H), 6.36 (d, $J = 15.9$ Hz, 1H), 7.17–7.36 (m, 5H); ^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 26.1, 26.2, 30.8, 31.8, 38.0, 39.1, 39.6, 46.5, 65.9, 124.9, 126.3, 127.4, 128.5, 133.6, 137.1, 207.7, 211.2; IR (neat) 1694, 1717 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_2$: 284.1776. Found: 284.1779.

2-Acetyl-2- $\{(E)\text{-3-phenyl-2-propenyl}\}$ -1-tetralone (Table 2, Entry 2). The general procedure was followed with 2-acetyl-1-tetralone (113 mg, 0.60 mmol) and cinnamyl acetate (88 mg, 0.50 mmol). The residue was purified by a preparative TLC (EtOAc/hexane = 1/5) to give the desired product (131 mg, 87%) as colorless oil. The enantiomeric excess of the product was determined to be 87% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OB-H (4.6 mm $\phi \times 25$ cm, 20% 2-propanol in hexane): $[\alpha]_{\text{D}}^{20} = +91.7$ (c 1.10, CHCl_3); ^1H NMR (300 MHz, CDCl_3 , TMS) δ 2.04–2.19 (m, 1H), 2.16 (s, 3H), 2.61 (dt, $J = 13.7, 4.7$ Hz, 1H), 2.78 (dd, $J = 7.7, 14.0$ Hz, 1H), 2.84–2.95 (m, 2H), 3.09 (ddd, $J = 4.8, 10.7, 17.5$ Hz, 1H), 6.12 (dt, $J = 15.8, 7.7$ Hz, 1H), 6.46 (d, $J = 15.8$ Hz, 1H), 7.16–7.36 (m, 7H), 7.49 (t, $J = 7.5$ Hz, 1H), 8.09 (d, $J = 7.8$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 25.7, 27.1, 29.4, 38.3, 64.0, 124.5, 126.3, 126.8, 127.5, 128.0, 128.5, 129.0, 132.1, 134.00, 134.03, 137.0, 143.9, 197.4, 205.7; IR (neat) 1710, 1673 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_2$: 304.1463. Found: 304.1466.

2-Acetyl-2- $\{(E)\text{-3-phenyl-2-propenyl}\}$ cyclopentanone (Table 2, Entry 3). The general procedure was followed with 2-acetylcyclopentanone (76 mg, 0.60 mmol) and cinnamyl acetate (88 mg, 0.50 mmol). The residue was purified by a preparative TLC (EtOAc/hexane = 1/5) to give the desired product (112 mg, 92%) as colorless oil. The enantiomeric excess of the product was determined to be 81% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OB-H (4.6 mm $\phi \times 25$ cm, 20% 2-propanol in hexane): $[\alpha]_{\text{D}}^{20} = +71.7$ (c 1.04, CHCl_3); ^1H NMR (300 MHz, CDCl_3 , TMS) δ 1.79–1.95 (m, 3H), 2.16–2.42 (m, 2H), 2.25 (s, 3H), 2.56–2.72 (m, 2H), 2.82 (ddd, $J = 1.2, 7.5, 14.4$ Hz, 1H), 5.95 (dt, $J = 15.6, 7.5$ Hz, 1H), 6.45 (dt, $J = 15.6, 1.2$ Hz, 1H), 7.18–7.34 (m, 5H); ^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 19.3, 26.1, 30.3, 38.3, 38.6, 68.7, 123.9, 126.3, 127.6, 128.6, 134.1, 136.8, 204.1, 215.7; IR (neat) 1704, 1737 cm^{-1} ; Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2$: C, 79.31; H, 7.49. Found: C, 79.24; H, 7.53.

2-Acetyl-2- $\{(E)\text{-3-phenyl-2-propenyl}\}$ cycloheptanone (Table 2, Entry 4). The general procedure was followed with 2-acetylcycloheptanone (92 mg, 0.60 mmol) and cinnamyl acetate (88 mg, 0.50 mmol). The residue was purified by a preparative TLC (EtOAc/hexane = 1/5) to give the desired product (127 mg, 95%) as colorless oil. The enantiomeric excess of the product was determined to be 77% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OD-H (4.6 mm $\phi \times 25$ cm, 1% 2-propanol in hexane): $[\alpha]_{\text{D}}^{20} = +151.3$ (c 1.11, CHCl_3); ^1H NMR (300 MHz, CDCl_3 , TMS) δ 1.23–1.37 (m, 1H), 1.45–1.62 (m, 2H), 1.66–1.86 (m, 3H), 1.91 (dd, $J = 9.3, 14.7$ Hz, 1H), 2.16 (s, 3H), 2.19 (dd, $J = 10.2, 14.7$ Hz, 1H), 2.44 (ddd, $J = 2.7, 7.5, 11.4$ Hz, 1H), 2.50–2.61 (m, 2H), 2.97 (dd, $J = 7.2, 14.7$ Hz, 1H), 5.99 (ddd, $J = 6.9, 7.5, 15.6$ Hz, 1H), 6.43 (dt, $J = 15.6, 1.5$ Hz, 1H), 7.17–7.37 (m, 5H); ^{13}C $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 24.1, 26.3, 26.9, 30.0, 30.2, 37.6, 42.1, 70.6, 124.6, 126.2, 127.5, 128.6, 133.9, 137.0, 206.7, 211.4; IR (neat) 1694, 1715 cm^{-1} ; Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2$: C, 79.96; H, 8.20. Found: C, 80.26; H, 8.31.

2-Acetyl-2-*[(E)-3-phenyl-2-propenyl]*cyclooctanone (Table 2, Entry 5). The general procedure was followed with 2-acetylcyclooctanone (101 mg, 0.60 mmol) and cinnamyl acetate (88 mg, 0.50 mmol). The residue was purified by a preparative TLC (EtOAc/hexane = 1/5) to give the desired product (127 mg, 90%) as a white solid. The enantiomeric excess of the product was determined to be 84% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OJ-H (4.6 mm ϕ $\times$ 25 cm, 4% 2-propanol in hexane): $[\alpha]_D^{20} = +242.9$ (*c* 1.52, CHCl₃); ¹H NMR (300 MHz, CDCl₃, TMS) δ 0.86–1.01 (m, 1H), 1.25–1.41 (m, 1H), 1.44–1.95 (m, 6H), 2.03 (dt, *J* = 15.6, 4.2 Hz, 1H), 2.10 (s, 3H), 2.12–2.22 (m, 1H), 2.47–2.62 (m, 2H), 2.68 (dt, *J* = 3.6, 12.0 Hz, 1H), 3.16 (dd, *J* = 6.9, 15.3 Hz, 1H), 5.92 (ddd, *J* = 6.9, 8.1, 15.9 Hz, 1H), 6.47 (d, *J* = 15.9 Hz, 1H), 7.18–7.37 (m, 5H); ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 23.2, 24.3, 25.5, 26.3, 26.5, 29.8, 33.5, 38.4, 70.6, 124.5, 126.2, 127.5, 128.6, 133.5, 137.0, 206.1, 214.5; IR (nujol) 1683, 1698 cm⁻¹; Anal. Calcd for C₁₉H₂₄O₂: C, 80.24; H, 8.51. Found: C, 79.97; H, 8.66.

2-Propionyl-2-*[(E)-3-phenyl-2-propenyl]*cyclohexanone (Table 2, Entry 6). The general procedure was followed with 2-propionylcyclohexanone (93 mg, 0.60 mmol) and cinnamyl acetate (88 mg, 0.50 mmol). The residue was purified by a preparative TLC (EtOAc/hexane = 1/5) to give the desired product (122 mg, 91%) as colorless oil. The enantiomeric excess of the product was determined to be 82% ee by HPLC analysis with a chiral stationary phase column, CHIRALPAK AS (4.6 mm ϕ $\times$ 25 cm, 4% 2-propanol in hexane): $[\alpha]_D^{20} = +164.3$ (*c* 1.22, CHCl₃); ¹H NMR (300 MHz, CDCl₃, TMS) δ 1.03 (t, *J* = 7.4 Hz, 3H), 1.46–1.79 (m, 4H), 1.91–2.06 (m, 1H), 2.21–2.38 (m, 2H), 2.45–2.63 (m, 4H), 2.72 (ddd, *J* = 1.2, 7.5, 14.1 Hz, 1H), 6.00 (dt, *J* = 15.6, 7.5 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 7.17–7.36 (m, 5H); ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 7.8, 22.1, 27.1, 31.8, 34.2, 38.2, 41.8, 67.6, 124.7, 126.2, 127.4, 128.5, 133.5, 137.1, 208.8, 210.0; IR (neat) 1717, 1694 cm⁻¹; HRMS (EI) Calcd for C₁₈H₂₂O₂: 270.1620. Found: 270.1629.

2-Methyl-1-phenyl-2-*[(E)-3-phenyl-2-propenyl]*butane-1,3-dione (Table 2, Entry 7). The general procedure was followed with 2-methyl-1-phenylbutane-1,3-dione (105 mg, 0.60 mmol) and cinnamyl acetate (88 mg, 0.50 mmol). The residue was purified by a preparative TLC (EtOAc/hexane = 1/5) to give the desired product (132 mg, 90%) as colorless oil. The enantiomeric excess of the product was determined to be 83% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OJ-H (4.6 mm ϕ $\times$ 25 cm, 10% 2-propanol in hexane): $[\alpha]_D^{20} = -48.1$ (*c* 1.09, CHCl₃); ¹H NMR (300 MHz, CDCl₃, TMS) δ 1.50 (s, 3H), 2.13 (s, 3H), 2.87 (dd, *J* = 7.6, 14.4 Hz, 1H), 2.96 (dd, *J* = 7.6, 14.4 Hz, 1H), 5.96 (dt, *J* = 7.6, 15.6 Hz, 1H), 6.33 (d, *J* = 15.6 Hz, 1H), 7.16–7.35 (m, 5H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.81 (d, *J* = 7.2 Hz, 2H); ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 20.2, 27.3, 39.3, 65.1, 123.9, 126.3, 127.4, 128.5, 128.8, 128.9, 133.2, 134.2, 136.0, 137.0, 199.0, 207.7; IR (neat) 1715, 1673 cm⁻¹; HRMS (EI) Calcd for C₂₀H₂₀O₂: 292.1465. Found: 292.1464.

1-(4-Methoxyphenyl)-2-methyl-2-*[(E)-3-phenyl-2-propenyl]*butane-1,3-dione (Table 2, Entry 8). The general procedure was followed with 1-(4-methoxyphenyl)-2-methylbutane-1,3-dione (124 mg, 0.60 mmol) and cinnamyl acetate (88 mg, 0.50 mmol). The residue was purified by a preparative TLC (EtOAc/hexane = 1/5) to give the desired product (154 mg, 96%) as a white solid. The enantiomeric excess of the product was determined to be 80% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OJ-H (4.6 mm ϕ $\times$ 25 cm, 20% 2-propanol in hexane): $[\alpha]_D^{20} = -82.8$ (*c* 1.09, CHCl₃); ¹H NMR (300 MHz, CDCl₃, TMS) δ 1.49 (s, 3H), 2.10 (s, 3H), 2.86 (ddd, *J* = 0.9, 7.9, 14.6 Hz, 1H), 2.95 (ddd, *J* = 0.9, 7.2, 14.6 Hz, 1H), 3.86 (s, 3H), 5.96 (dt, *J* = 15.8, 7.5 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 6.91 (d, *J* = 9.2 Hz, 2H), 7.16–7.32 (m, 5H), 7.84 (d, *J* = 9.2 Hz, 2H); ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 20.3, 27.3, 39.4, 55.5, 64.8, 114.0, 124.2, 126.3, 127.4, 128.5, 128.7, 131.4, 134.0, 137.1, 163.6, 197.0, 208.3; IR (neat) 1706, 1661 cm⁻¹; Anal. Calcd for C₂₁H₂₂O₃: C, 78.23; H, 6.88. Found: C, 77.95; H, 6.88.

Selective Protection of Cyclohexanone with Cyclic Ketal. A 20 ml two-necked round-bottomed flask was charged with (*S*)-2-acetyl-2-{(*E*)-3-phenyl-2-propenyl}cyclohexanone (79% ee, 511 mg, 2.0 mmol), *p*-toluenesulfonic acid monohydrate (7 mg, 37 μ mol), ethylene glycol (248 mg, 4.0 mmol), and benzene (4.0 ml). The flask was attached to a Dean-Stark trap filled with benzene under reflux condenser. The mixture was stirred under reflux for 8 h. After cooling to room temperature, sat Na_2CO_3 aq was added carefully to the mixture and the mixture was extracted with EtOAc twice. The combined organic layer was washed with brine, was dried with Na_2SO_4 , and was evaporated under reduced pressure. The residue was purified by a flash column chromatography on silica gel (EtOAc/hexane), giving (*S*)-6-acetyl-1,4-dioxaspiro[4,5]decane (500 mg, 84% yield): $[\alpha]_D^{20} = +17.0$ (*c* 1.08, C_6H_6); ^1H NMR (300 MHz, C_6D_6) δ 1.30–1.48 (m, 2H), 1.48–1.67 (m, 4H), 1.73–1.84 (m, 1H), 2.25 (s, 3H), 2.28–2.39 (m, 1H), 2.50 (ddd, *J* = 1.0, 8.4, 14.4 Hz, 1H), 3.08 (dd, *J* = 6.9, 14.4 Hz, 1H), 3.36–3.53 (m, 4H), 6.08 (ddd, *J* = 6.9, 8.4, 15.6 Hz, 1H), 6.41 (d, *J* = 15.6 Hz, 1H), 7.04–7.18 (m, 3H), 7.23–7.29 (m, 2H); ^{13}C { ^1H } NMR (75 MHz, C_6D_6) δ 21.1, 23.4, 29.0, 30.0, 32.3, 35.0, 59.4, 64.0, 64.4, 111.2, 125.7, 126.5, 127.4, 128.8, 133.3, 137.9, 208.4; IR (neat) 1698 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_3$: 300.1725. Found: 300.1726.

Oxidative Cleavage of C–C Double Bond in Cinnamyl Group. RuO_2 (2.6 mg, 20 μ mol) was added to a two-phase solution of (*S*)-6-acetyl-1,4-dioxaspiro[4,5]decane (295 mg, 1.0 mmol) and NaIO_4 (1.07 g, 5.0 mmol) in CCl_4 (2.0 ml), MeCN (2.0 ml), and water (3.0 ml).⁸ The mixture was vigorously stirred for 13 h at room temperature. (Trimethylsilyl)diazomethane (2.0 M solution in hexanes, 1.5 ml, 3.0 mmol) was carefully added to the mixture. After stirring for 5 min, the mixture was extracted with EtOAc twice. The combined organic layer was washed with brine, was dried with Na_2SO_4 , and was evaporated under reduced pressure. The residue was purified by a flash column chromatography on silica gel (EtOAc/hexane), giving (*S*)-6-acetyl-6-(methoxycarbonylmethyl)-1,4-dioxaspiro[4,5]decane (187 mg, 74% yield). The enantiomeric excess of the product was determined to be 79% ee by chiral GC analysis with CP-Cyclodextrin- β -2,3,6-M-19 (0.25 mm $\phi \times 50$ m, 150 $^\circ\text{C}$): ^1H NMR (300 MHz, C_6D_6) δ 1.15–1.62 (m, 6H), 2.10–2.20 (m, 1H), 2.26–2.38 (m, 1H), 2.34 (s, 3H), 2.62 (d, *J* = 16.2 Hz, 1H), 3.28 (s, 3H), 3.29–3.52 (m, 5H); ^{13}C { ^1H } NMR (75 MHz, C_6D_6) δ 21.1, 23.3, 29.0, 30.2, 32.3, 36.4, 50.9, 56.7, 64.4, 64.5, 110.9, 171.8, 208.1; IR (neat) $1737, 1710\text{ cm}^{-1}$; Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{O}_5$: C, 60.92; H, 7.87. Found: C, 60.80; H, 7.67.

Assignment of the Absolute Configuration of 2-Acetyl-2-{(E)-3-phenyl-2-propenyl}cyclohexanone. The absolute configuration of (*S*)-2-acetyl-2-{(E)-3-phenyl-2-propenyl}cyclohexanone (entry 4 in Table 1) was determined as follows: (1) An authentic *S*-rich 6-acetyl-6-(methoxycarbonylmethyl)-1,4-dioxaspiro[4,5]decane was prepared from *S*-rich 2-acetyl-2-(2-propenyl)cyclohexanone obtained from the reaction of entry 1 in Table 1 (Scheme S1). (3) The authentic sample was analyzed by a chiral GC with CP-Cyclodextrin- β -2,3,6-M-19 (0.25 mm $\phi \times 50$

Scheme S1.

m, 150 $^\circ\text{C}$). The retention time of the major isomer indicates the absolute configuration of the 2-acetyl-2-{(E)-3-phenyl-2-propenyl}cyclohexanone to be *S*.

Preparation of the Authentic Sample from 5. RuO_2 (2.7 mg, 20 μ mol) was added to a two-phase solution of (*S*)-6-acetyl-1,4-dioxaspiro[4,5]decane⁶ (225 mg, 1.0 mmol) and NaIO_4 (1.07 g, 5.0 mmol) in CCl_4 (2.0 ml), MeCN (2.0 ml), and water (3.0 ml). The mixture was vigorously stirred for 12 h at room temperature. After dilution with EtOAc (1.0 ml),

(trimethylsilyl)diazomethane (2.0 M solution in hexanes, 1.5 ml, 3.0 mmol) was carefully added to the mixture. After stirring for 5 min, the mixture was filtrated, was diluted with water, and was extracted with EtOAc three times. The combined organic layer was washed with brine, was dried with Na₂SO₄, and was evaporated under reduced pressure. The residue was purified by a flash column chromatography on silica gel (EtOAc/hexane), giving 6-acetyl-6-(methoxycarbonylmethyl)-1,4-dioxaspiro[4,5]decane (238 mg, 93% yield).

References and Notes

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