Supporting Information for

**Palladium-Catalyzed Enantiospecific Reaction of Propargylic
Carbonates with Phenols: Cascade Chirality Transfer**

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General. All nonaqueous reactions were carried out under a positive atmosphere of argon or nitrogen 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 protocols. 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.

General Procedure for the Palladium-Catalyzed Cascade Reaction of 4-Substituted Propargylic Carbonates with Phenols

Reaction of 1a with 2a (entry 1 in Table 1). To a stirred solution of the propargylic carbonate **1a** (90.0 mg, 0.420 mmol) in dioxane (5 mL) were added *p*-methoxyphenol **2a** (57.0 mg, 0.460 mmol), $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (22.0 mg, 0.020 mmol) and dppe (33.0 mg, 0.080 mmol) in sealed tube at rt. After stirring was continued for 12 h at 50 °C, the reaction mixture was concentrated and the residue was chromatographed on silica gel with hexane-AcOEt (93:7 v/v) as eluent to give the (*Z*)-cyclic carbonate (*Z*)-**3aa** (78.3 mg, 60%), (*E*)-cyclic carbonate (*E*)-**3aa** (7.8 mg, 6%) as a colorless oil.

Characterization Data of the Cyclic Carbonates for Table 1

1,2-Carbonyldioxy-1,1-diethyl-2-[1-(4-methoxyphenoxy)-(2*Z*)-methylvinyl]ethane [(*Z*)-3aa**].** Yield 60%; colorless oil; IR (neat) 2975, 1801, 1504 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.87 (3H, t, $J = 7.3$ Hz), 1.02 (3H, t, $J = 7.3$ Hz), 1.59 (3H, d, $J = 6.8$ Hz), 1.71–1.87 (3H, m), 1.90–2.00 (1H, m), 3.77 (3H, s), 4.70 (1H, s), 5.58 (1H, q, $J = 6.8$ Hz), 6.81 (2H, dt, $J = 9.1$ and 2.7 Hz), 6.87 (2H, dt, $J = 9.1$ and 2.7 Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 7.2, 7.7, 10.6, 25.7, 28.8, 55.6, 80.5, 88.9, 114.8, 114.8, 115.2, 115.8, 115.8, 144.3, 149.9, 153.6, 154.7; MS m/z 306 (M^+); HRMS m/z calcd for $\text{C}_{17}\text{H}_{22}\text{O}_5$ 306.1467 (M^+), found 306.1452.

1,2-Carbonyldioxy-1,1-diethyl-2-[1-(4-methoxyphenoxy)-(2*E*)-methylvinyl]ethane [(*E*)-3aa**].** Yield 6%; colorless oil; IR (neat) 2967, 1800, 1505 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 1.02 (3H, t, $J = 7.3$ Hz), 1.03 (3H, t, $J = 7.3$ Hz), 1.62 (3H, d, $J = 7.3$ Hz), 1.82–1.92 (3H, m), 2.10–2.19 (1H, m), 3.78 (3H, s), 4.86 (1H, q, $J = 7.3$ Hz), 5.17 (1H, s), 6.84 (2H, dt, $J = 9.0$ and 3.9 Hz), 6.93 (2H, dt, $J = 9.0$ and 3.9 Hz); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 7.1, 7.8, 10.9, 24.6, 29.1, 55.5, 77.8, 88.4, 106.07, 114.8, 114.8, 121.7, 121.7, 148.3, 149.8, 154.7, 156.4; MS m/z 306 (M^+); HRMS m/z calcd for $\text{C}_{17}\text{H}_{22}\text{O}_5$ 306.1467 (M^+), found 306.1487.

1,1-Diethyl-2-[1-(4-methoxyphenoxy)-(2*Z*)-methylvinyl]epoxyde ((*Z*)-4aa**) and 1,1-Diethyl-2-[1-(4-methoxyphenoxy)-(2*E*)-methylvinyl]epoxyde [(*E*)-**4aa**] (ratio of 86:14) (entry 3 in Table 1).** Yield

40%; colorless oil; IR (neat) 2968, 2880, 1504 cm^{-1} ; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 0.74 (2.58H, t, $J = 7.2$ Hz), 0.97 (3H, t, $J = 7.5$ Hz), 1.04 (0.42H, t, $J = 7.5$ Hz), 1.35–1.75 (7H, m), 3.14 (0.86H, s), 3.49 (0.14H, s), 3.77 (3H, s), 4.91 (0.14H, q, $J = 7.5$ Hz), 5.22 (0.86H, q, $J = 6.9$ Hz), 6.82 (2H, dt, $J = 9.0$ and 3.5 Hz), 6.91 (2H, dt, $J = 9.0$ and 3.5 Hz); MS m/z 262 (M^+); HRMS m/z calcd for $\text{C}_{16}\text{H}_{22}\text{O}_3$ 262.1569 (M^+), found 262.1600.

1,2-Carbonyldioxy-1,1-diethyl-2-[1-(4-methoxyphenoxy)-(2*Z*)-pentylvinyl]ethane [(*Z*)-3ba] (entry 6 in Table 1). Yield 64%; colorless oil; IR (neat) 2930, 2858, 1805, 1504 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.85 (3H, t, $J = 5.1$ Hz), 0.86 (3H, t, $J = 7.5$ Hz), 1.02 (3H, t, $J = 7.5$ Hz), 1.23–1.38 (6H, m), 1.71–2.07 (6H, m), 3.77 (3H, s), 4.70 (1H, s), 5.53 (1H, t, $J = 7.5$ Hz), 6.82 (2H, dt, $J = 9.0$ and 3.0 Hz), 6.87 (2H, dt, $J = 9.0$ and 3.0 Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 7.0, 7.5, 13.8, 22.2, 24.8, 25.6, 28.3, 28.7, 31.3, 55.6, 80.3, 89.0, 114.9, 114.9, 116.0, 116.0, 121.1, 143.5, 150.3, 153.9, 155.0; MS m/z 362 (M^+); HRMS m/z calcd for $\text{C}_{21}\text{H}_{30}\text{O}_5$ 362.2093 (M^+), found 362.2097.

1,2-Carbonyldioxy-1,1-diethyl-2-[1-(4-methoxyphenoxy)-(2*E*)-pentylvinyl]ethane [(*E*)-3ba] (entry 6 in Table 1). Yield 17%; colorless oil; IR (neat) 2932, 2858, 1780, 1504 cm^{-1} ; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 0.87 (3H, t, $J = 7.2$ Hz), 1.02 (3H, t, $J = 7.2$ Hz), 1.03 (3H, t, $J = 7.8$ Hz), 1.21–1.33 (6H, m), 1.82–1.96 (3H, m), 1.99–2.01 (2H, m), 2.03–2.20 (1H, m), 3.79 (3H, s), 4.82 (1H, t, $J = 7.8$ Hz), 5.16 (1H, s), 6.85 (2H, dt, $J = 9.0$ and 2.9 Hz), 6.95 (2H, dt, $J = 9.0$ and 2.9 Hz); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 7.2, 7.8, 13.8, 22.2, 24.6, 25.8, 29.0, 29.6, 31.2, 55.5, 78.0, 88.3, 112.4, 114.8, 114.8, 121.6, 121.6, 148.4, 149.0, 154.7, 156.3; MS m/z 362 (M^+); HRMS m/z calcd for $\text{C}_{21}\text{H}_{30}\text{O}_5$ 362.2093 (M^+), found 362.2090.

1,2-Carbonyldioxy-1,1-diethyl-2-[1-(4-methoxyphenoxy)-(2*Z*)-phenylvinyl]ethane [(*Z*)-3ca] (entry 6 in Table 1). Yield 32%; colorless oil; IR (neat) 2926, 1806, 1504 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.86 (3H, t, $J = 7.6$ Hz), 1.03 (3H, t, $J = 7.6$ Hz), 1.75–2.03 (4H, m), 3.75 (3H, s), 4.82 (1H, s), 6.42 (1H, s), 6.81 (2H, dt, $J = 9.0$ and 3.7 Hz), 6.91 (2H, dt, $J = 9.0$ and 3.7 Hz), 7.19–7.29 (3H, m), 7.51 (2H, d, 7.8 Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 7.0, 7.5, 26.0, 28.6, 55.6, 79.6, 89.6, 115.2, 115.2, 116.6, 116.6, 118.9, 122.3, 128.3, 128.7, 128.7, 129.2, 129.2, 132.8, 144.0, 148.6, 155.6; MS m/z 368 (M^+); HRMS m/z calcd for $\text{C}_{22}\text{H}_{24}\text{O}_5$ 368.1624 (M^+), found 368.1634.

Characterization Data of the Cyclic Carbonates for Table 2

(2*S*)-1,2-Carbonyldioxy-1,1-diethyl-2-[1-(4-methoxyphenoxy)-(2*Z*)-methylvinyl]ethane [(*Z,S*)-3aa] (entry 1 in Table 2). Yield 60%; 95% ee; colorless oil; $[\alpha]_D^{24} -120.2$ (c 1.3 in CHCl₃); Enantiomeric excess was determined by HPLC analysis [CHIRALPAK OD-H column, 10% isopropanol-hexane, 0.5 mL/min, $\lambda = 254$ nm, 23°C, retention times 14.4 min (*R*) and 20.7 min (*S*)]. Other spectral data coincides with those of the racemic (*Z*)-3aa.

(2*R*)-1,2-Carbonyldioxy-1,1-diethyl-2-[1-(4-methoxyphenoxy)-(2*E*)-methylvinyl]ethane [(*E,R*)-3aa] (entry 1 in Table 2). Yield 6%; 95% ee; colorless oil; $[\alpha]_D^{24} +88.6$ (c 0.7 in CHCl₃); Enantiomeric excess was determined by HPLC analysis [CHIRALPAK OD-H column, 10% isopropanol-hexane, 0.5 mL/min, $\lambda = 254$ nm, 23°C, retention times 17.6 min (*R*) and 21.9 min (*S*)]. Other spectral data coincides with those of the racemic (*E*)-3aa.

(2*S*)-1,2-Carbonyldioxy-1,1-diethyl-2-[1-(2-methoxyphenyl)-(2*Z*)-methylvinyl]ethane [(*Z,S*)-3ab] (entry 3 in Table 2). Yield 57%; 94% ee; colorless oil; $[\alpha]_D^{28} -116.2$ (c 2.1 in CHCl₃); IR (neat) 2974, 1807, 1504 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 0.83 (3H, t, $J = 7.8$ Hz), 1.03 (3H, t, $J = 7.2$ Hz), 1.64 (3H, d, $J = 6.9$ Hz), 1.73–2.06 (4H, m), 3.86 (3H, s), 4.69 (1H, s), 5.64 (1H, q, $J = 6.9$ Hz), 6.85–7.04 (4H, m); ¹³C-NMR (75 MHz, CDCl₃) δ 6.8, 7.4, 10.3, 25.6, 28.5, 55.9, 79.8, 89.2, 112.7, 114.6, 115.2, 121.0, 123.1, 144.2, 145.3, 149.3, 153.9; MS m/z 306 (M^+); HRMS m/z calcd for C₁₇H₂₂O₅ 306.1467 (M^+), found 306.1450.; Enantiomeric excess was determined by HPLC analysis [CHIRALPAK OD-H column, 5% isopropanol-hexane, 0.5 mL/min, $\lambda = 254$ nm, 23°C, retention times 17.5 min (*R*) and 19.8 min (*S*)].

(2*R*)-1,2-Carbonyldioxy-1,1-diethyl-2-[1-(2-methoxyphenoxy)-(2*E*)-methylvinyl]ethane [(*E,R*)-3ab] (entry 3 in Table 2). Yield 8%; 94% ee; colorless oil; $[\alpha]_D^{27} +59.3$ (c 0.8 in CHCl₃); IR (neat) 2974, 1798, 1501 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 1.02 (3H, t, $J = 7.8$ Hz), 1.03 (3H, t, $J = 7.2$ Hz), 1.62 (3H, d, $J = 7.5$ Hz), 1.86–2.06 (3H, m), 2.20–2.32 (1H, m), 3.81 (3H, s), 4.68 (1H, q, $J = 7.5$ Hz), 5.19 (1H, s), 6.90–7.15 (4H, m); ¹³C-NMR (75 MHz, CDCl₃) δ 7.2, 7.88, 10.8, 24.4, 29.1, 56.0, 78.1, 88.1, 103.9, 113.3, 121.3, 122.8, 125.7, 143.0, 148.5, 152.1, 155.0; MS m/z 306 (M^+); HRMS m/z calcd for C₁₇H₂₂O₅ 306.1467 (M^+), found 306.1449.; Enantiomeric excess was determined by HPLC analysis [CHIRALPAK OD-H column, 5% isopropanol-hexane, 0.5 mL/min, $\lambda = 254$ nm, 23°C, retention times 32.5 min (*S*) and 45.5 min (*R*)].

(2*S*)-1,2-Carbonyldioxy-1,1-diethyl-2-[1-(4-methylphenoxy)-(2*Z*)-methylvinyl]ethane [(*Z,S*)-3ac] (entry 5 in Table 2). Yield 61%; 95% ee; colorless oil; $[\alpha]_D^{28} -85.5$ (c 1.5 in CHCl₃); IR (neat) 2976,

1807, 1504 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 0.87 (3H, t, $J = 7.2$ Hz), 1.02 (3H, t, $J = 7.5$ Hz), 1.59 (3H, d, $J = 6.8$ Hz), 1.69–1.99 (4H, m), 2.30 (3H, s), 4.71 (1H, s), 5.62 (1H, q, $J = 6.8$ Hz), 6.83 (2H, d, $J = 8.5$ Hz), 7.09 (2H, d, $J = 8.5$ Hz); ^{13}C -NMR (75 MHz, CDCl_3) δ 7.0, 7.5, 10.4, 20.4, 25.6, 28.7, 80.4, 89.0, 99.2, 114.9, 114.9, 115.6, 130.4, 130.4, 131.8, 144.1, 154.0; MS m/z 290 (M^+); HRMS m/z calcd for $\text{C}_{17}\text{H}_{22}\text{O}_4$ 290.1518 (M^+), found 290.1511.; Enantiomeric excess was determined by HPLC analysis [CHIRALPAK OJ-H column, 5% isopropanol-hexane, 0.5 mL/min, $\lambda = 254$ nm, 23°C , retention times 18.9 min (*R*) and 25.9 min (*S*)].

(2*R*)-1,2-Carbonyldioxy-1,1-diethyl-2-[1-(4-methylphenoxy)-(2*E*)-methylvinyl]ethane [(*E,R*)-3ac] (entry 5 in Table 2). Yield 11%; 95% ee; colorless oil; $[\alpha]_{\text{D}}^{28} +64.9$ (c 0.8 in CHCl_3); IR (neat) 2976, 1800, 1506 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 1.02 (6H, t, $J = 7.3$ Hz), 1.64 (3H, t, $J = 7.3$ Hz), 1.83–1.92 (3H, m), 2.09–2.19 (1H, m), 2.34 (3H, s), 4.94 (1H, q, $J = 7.3$ Hz), 5.17 (1H, s), 6.89 (2H, d, $J = 8.4$ Hz), 7.11 (2H, d, $J = 8.4$ Hz); ^{13}C -NMR (75 MHz, CDCl_3) δ 7.4, 8.0, 11.2, 20.8, 24.8, 29.2, 77.9, 88.4, 107.2, 120.0, 120.0, 130.1, 130.1, 133.5, 148.8, 152.7, 154.4; MS m/z 290 (M^+); HRMS m/z calcd for $\text{C}_{17}\text{H}_{22}\text{O}_4$ 290.1518 (M^+), found 290.1513.; Enantiomeric excess was determined by HPLC analysis [CHIRALPAK OD-H column, 5% isopropanol-hexane, 0.5 mL/min, $\lambda = 254$ nm, 23°C , retention times 19.3 min (*R*) and 21.5 min (*S*)].

(2*S*)-1,2-Carbonyldioxy-1,1-diethyl-2-[1-(4-fluorophenoxy)-(2*Z*)-methylvinyl]ethane [(*Z,S*)-3ad] (entry 7 in Table 2). Yield 54%; 94% ee; colorless oil; $[\alpha]_{\text{D}}^{26} -88.8$ (c 3.0 in CHCl_3); IR (neat) 2978, 1800, 1501 cm^{-1} ; ^1H -NMR (500 MHz, CDCl_3) δ 0.87 (3H, t, $J = 7.0$ Hz), 0.99 (3H, t, $J = 7.0$ Hz), 1.55 (3H, d, $J = 7.0$ Hz), 1.72–1.83 (3H, m), 1.90–1.96 (1H, m), 4.68 (1H, s), 5.59 (1H, q, $J = 7.0$ Hz), 6.86–6.89 (2H, m), 6.94–6.97 (2H, m); ^{13}C -NMR (125 MHz, CDCl_3) δ 7.0, 7.5, 10.5, 25.5, 28.7, 80.9, 88.9, 116.1, 116.2, 116.3, 116.5, 124.5, 152.3, 153.8, 156.6, 159.8; MS m/z 294 (M^+); HRMS m/z calcd for $\text{C}_{16}\text{H}_{19}\text{O}_4\text{F}$ 294.1267 (M^+), found 294.1271. Enantiomeric excess was determined by HPLC analysis [CHIRALPAK OD-H column, 5% isopropanol-hexane, 0.5 mL/min, $\lambda = 254$ nm, 23°C , retention times 19.8 min (*R*) and 21.8 min (*S*)].

(2*S*)-1,2-Carbonyldioxy-1,1-diethyl-2-[1-(1-naphthoxy)-(2*Z*)-methylvinyl]ethane [(*Z,S*)-3ae] (entry 8 in Table 2). Yield 38%; 93% ee; colorless oil; $[\alpha]_{\text{D}}^{27} -118.9$ (c 0.8 in CHCl_3); IR (neat) 2976, 1805 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 0.79 (3H, t, $J = 7.3$ Hz), 1.03 (3H, t, $J = 7.3$ Hz), 1.58 (3H, d, $J = 6.9$ Hz), 1.70–1.83 (2H, m), 1.96–2.12 (2H, m), 4.81 (1H, s), 5.76 (1H, q, $J = 6.9$ Hz), 6.91 (1H, d, $J = 7.3$ Hz), 7.25–7.54 (4H, m), 7.78–7.85 (1H, m), 8.14–8.17 (1H, m); ^{13}C -NMR (100 MHz, CDCl_3) δ 7.2, 7.8, 10.6, 26.0, 29.0, 80.2, 89.1, 106.5, 116.0, 121.2, 122.0, 124.7, 125.7, 125.7, 126.6, 127.7, 134.8, 143.7, 151.4, 153.6; MS m/z 326 (M^+); HRMS m/z calcd for $\text{C}_{20}\text{H}_{22}\text{O}_4$ 326.1518 (M^+),

found 326.1538.; Enantiomeric excess was determined by HPLC analysis [CHIRALPAK OD-H column, 5% isopropanol-hexane, 0.5 mL/min, λ = 254 nm, 23°C, retention times 20.5 min (*R*) and 22.5 min (*S*)].

(2*R*)-1,2-Carbonyldioxy-1,1-diethyl-2-[1-(1-naphthoxy)-(2*E*)-methylvinyl]ethane [(*E,R*)-3ae]
(entry 8 in Table 2). Yield 13%; 93% ee; colorless oil; $[\alpha]_D^{27} +114.0$ (c 0.7 in CHCl₃); IR (neat) 2976, 1798 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 1.05 (3H, t, *J* = 7.6 Hz), 1.09 (3H, t, *J* = 7.6 Hz), 1.64 (3H, d, *J* = 7.3 Hz), 1.93 (2H, q, *J* = 7.6 Hz), 2.00–2.09 (1H, m), 2.25–2.34 (1H, m), 4.95 (1H, q, *J* = 7.3 Hz), 5.29 (1H, s), 7.10 (1H, d, *J* = 7.6 Hz), 7.36–7.51 (3H, m), 7.62 (1H, d, *J* = 8.3 Hz), 7.81–7.84 (1H, m), 8.04–8.07 (1H, m); ¹³C-NMR (100 MHz, CDCl₃) δ 7.4, 8.1, 11.2, 25.1, 29.3, 78.1, 88.5, 107.8, 115.1, 121.9, 124.2, 125.5, 126.1, 126.5, 126.9, 127.7, 134.8, 148.5, 150.8, 154.3; MS *m/z* 326 (*M*⁺); HRMS *m/z* calcd for C₂₀H₂₂O₄ 326.1518 (*M*⁺), found 326.1526.; Enantiomeric excess was determined by HPLC analysis [CHIRALPAK OD-H column, 5% isopropanol-hexane, 0.5 mL/min, λ = 254 nm, 23°C, retention times 30.9 min (*S*) and 38.7 min (*R*)].

(2*S*)-1,2-Carbonyldioxy-1,1-diethyl-2-[1-(4-methoxyphenoxy)-(2*Z*)-pentylvinyl]ethane [(*Z,S*)-3ba]
(entry 9 in Table 2). Yield 64%; 98% ee; colorless oil; $[\alpha]_D^{26} -88.1$ (c 1.6 in CHCl₃); Enantiomeric excess was determined by HPLC analysis [CHIRALPAK OD-H column, 5% isopropanol-hexane, 0.5 mL/min, λ = 254 nm, 23°C, retention times 15.4 min (*R*) and 24.4 min (*S*)]. Other spectral data coincides with those of the racemic (*Z*)-3ba.

(2*R*)-1,2-Carbonyldioxy-1,1-diethyl-2-[1-(4-methoxyphenoxy)-(2*E*)-pentylvinyl]ethane [(*E,R*)-3ba]
(entry 9 in Table 2). Yield 17%; 98% ee; colorless oil; $[\alpha]_D^{27} +82.5$ (c 0.6 in CHCl₃); Enantiomeric excess was determined by HPLC analysis [CHIRALPAK OD-H column, 5% isopropanol-hexane, 0.5 mL/min, λ = 254 nm, 23°C, retention times 20.8 min (*R*) and 27.0 min (*S*)]. Other spectral data coincides with those of the racemic (*E*)-3ba.

Determination of Stereochemistry

The stereochemistry of (*Z*)- and (*E*)-**3aa**, **4aa** and (*Z*)-**3da** were determined by NOESY as shown in Figure S-1.

Figure S-1. NOESY correlations of (*Z*)- and (*E*)-**3aa**, **4aa** and (*Z*)-**3da**.

Scheme S-1. Determination of Absolute Configurations of (*S*)-**1a**-derived (*Z*)- and (*E*)-**3aa**.

Figure S-2

Determination of Absolute Configuration

Absolute configurations of (*Z*)- and (*E*)-**3aa** which were produced from the reaction of (*S*)-**1a** with *p*-methoxyphenol **2a** were determined as follows (Scheme S-1). The products (*Z*)- and (*E*)-**3aa** are subjected to hydrolysis in the presence of 1N NaOH to give diol (*Z*)- and (*E*)-**S1**, respectively. The products are each transformed to (*R*)- and (*S*)-MTPA ester (*Z*)- and (*E*)-**S2** by the reaction with (*S*)- and (*R*)-MTPA chloride. On the basis of the $\Delta\delta$ values ($\Delta\delta = \delta_{(S)\text{-ester}} - \delta_{(R)\text{-ester}}$) (Figure S-2), the absolute configuration of (*Z*)- and (*E*)-**3aa** are determined as *S* and *R*, respectively.

Experimental Details of Scheme S-1.

1,1-Diethyl-1,2-dihydroxy-2-[1-(4-methoxyphenoxy)-(2*Z*)-methylvinyl]ethane [(*Z*)-S1**].** To a stirred solution of the cyclic carbonate (*Z*)-**3aa** (30.0 mg, 0.098 mmol), which was obtained from (*S*)-**1a**, in dioxane (2.0 mL) was added 1N NaOH (2.0 mL) at rt. After stirring had been continued for 1 h at the same temperature, the reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with aqueous NH₄Cl and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane-AcOEt (85:15 v/v) as eluent to give the diol (*Z*)-**S1** (27.5 mg, quantitative yield) as a colorless oil; $[\alpha]_D^{27} -45.6$ (c 0.6 in CHCl₃); IR (neat) 3449, 2970, 1504 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.84 (3H, t, *J* = 7.6 Hz), 0.91 (3H, t, *J* = 7.3 Hz), 1.48 (3H, d, *J* = 6.8 Hz), 1.52–1.67 (4H, m), 2.09 (1H, brs), 2.69 (1H, brs), 3.76 (3H, s), 3.92 (1H, s), 5.34 (1H, q, *J* = 6.8 Hz), 6.80 (2H, dt, *J* = 9.0 and 2.4 Hz), 6.95 (2H, dt, *J* = 9.0 and 2.4 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 7.8, 7.9, 10.8, 26.3, 27.8, 55.7, 74.8, 77.1, 113.5, 114.6, 114.6, 116.1, 116.1, 151.1, 151.2, 154.3; MS *m/z* 280 (M⁺); HRMS *m/z* calcd for C₁₆H₂₄O₄ 280.1675 (M⁺), found 280.1694.

(*R*)-MTPA ester [(*Z,R*)-S2**].** To a stirred solution of the diol (*Z*)-**S1** (13.0 mg, 0.020 mmol) in CH₂Cl₂ (2 mL) was added (*S*)-MTPA chloride (10 μ L, 0.051 mmol), NEt₃ (30.0 μ L, 0.23 mmol) and a catalytic amount of DMAP at 0 °C. After stirring had been continued for 2 h at the same temperature, the reaction mixture was diluted with water and extracted with Et₂O. The combined extracts were washed with 1N HCl, aqueous NaHCO₃ and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane-AcOEt (90:10 v/v) as eluent to give the (*R*)-MTPA ester (*Z,R*)-**S2** (20.6 mg, 89%) as a colorless oil.; $[\alpha]_D^{27} -9.6$ (c 1.5 in CHCl₃); IR (neat) 3503, 2947, 1747, 1504 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.77 (3H, t, *J* = 7.6 Hz), 0.83 (3H, t, *J* = 7.3 Hz), 1.36–1.58 (4H, m), 1.50 (3H, d, *J* = 7.0 Hz), 1.99 (1H, brs), 3.42 (3H, s), 3.76 (3H, s), 5.32 (1H, s), 5.39 (1H, q, *J* = 7.0 Hz), 6.79 (2H, dt, *J* = 9.0 and 2.4 Hz), 6.86 (2H, dt, *J* = 9.0 and 2.4 Hz), 7.35–7.42 (3H, m), 7.52 (2H, d, *J* = 8.1 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 7.3, 7.7, 11.1, 27.2, 27.4, 55.4, 55.5, 55.7, 76.1, 78.1, 114.7, 114.7, 116.0, 116.2, 116.2, 121.8, 127.4, 127.4, 128.3, 128.3, 129.6, 131.5, 146.3, 149.9, 154.6, 165.6; MS *m/z* 496 (M⁺); HRMS *m/z* calcd for C₂₆H₃₁O₆F₃ 496.2073 (M⁺), found 496.2041.

(S)-MTPA ester [(Z,S)-S2]. By following the same procedure described for (Z,R)-S2, (S)-MTPA ester (Z,S)-S2 was prepared from (Z)-S1 and (R)-MTPA chloride: 47% yield; colorless oil; $[\alpha]_D^{28} -42.8$ (c 0.6 in CHCl₃); IR (neat) 3557, 2945, 1747, 1504 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.83 (3H, t, $J = 7.6$ Hz), 0.85 (3H, t, $J = 7.3$ Hz), 1.46 (3H, d, $J = 7.0$ Hz), 1.47–1.63 (4H, m), 2.01 (1H, brs), 3.44 (3H, s), 3.72 (3H, s), 5.25 (1H, q, $J = 7.0$ Hz), 5.33 (1H, s), 6.70 (2H, dt, $J = 9.3$ and 3.4 Hz), 6.80 (2H, dt, $J = 9.3$ and 3.4 Hz), 7.39–7.43 (3H, m), 7.54–7.56 (2H, m); ¹³C-NMR (100 MHz, CDCl₃) δ 7.2, 7.4, 10.7, 27.2, 27.5, 55.5, 55.5, 76.0, 84.5, 114.7, 114.7, 115.8, 116.2, 116.2, 121.4, 125.3, 127.7, 127.7, 128.5, 128.5, 129.8, 131.5, 146.3, 150.1, 154.8, 165.9; MS m/z 496 (M⁺); HRMS m/z calcd for C₂₆H₃₁O₆F₃ 496.2073 (M⁺), found 496.2112.

1,1-Diethyl-1,2-dihydroxy-2-[1-(4-methoxyphenoxy)-(2E)-methylvinyl]ethane [(E)-S1]. By following the same procedure described for (Z)-S1, the diol (E)-S1 was prepared from (E)-3aa: quantitative yield; colorless oil; $[\alpha]_D^{27} +3.1$ (c 0.7 in CHCl₃); IR (neat) 3543, 2966, 1504 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 0.74–0.97 (6H, m), 1.53–1.80 (4H, m), 1.60 (3H, d, $J = 7.2$ Hz), 2.50 (1H, brs), 3.10 (1H, brs), 3.79 (3H, s), 4.38–4.41 (1H, m), 4.63 (1H, q, $J = 7.2$ Hz), 6.86 (2H, dt, $J = 9.0$ and 4.3 Hz), 6.95 (2H, dt, $J = 9.0$ and 4.3 Hz); ¹³C-NMR (75 MHz, CDCl₃) δ 7.0, 7.5, 10.8, 25.5, 27.3, 55.1, 68.4, 77.4, 102.9, 114.4, 114.4, 121.6, 121.6, 147.9, 155.6, 156.0; MS m/z 280 (M⁺); HRMS m/z calcd for C₁₆H₂₄O₄ 280.1675 (M⁺), found 280.1655.

(R)-MTPA ester [(E,R)-S2]. By following the same procedure described for (Z,R)-S2, (R)-MTPA ester (E,R)-S2 was prepared from (E)-S1 and (S)-MTPA chloride: 48% yield; colorless oil; $[\alpha]_D^{28} +41.2$ (c 0.3 in CHCl₃); IR (neat) 3564, 2932, 1746, 1504 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.90 (3H, t, $J = 7.6$ Hz), 0.95 (3H, t, $J = 7.6$ Hz), 1.56–1.69 (4H, m), 1.72 (3H, d, $J = 7.3$ Hz), 2.88 (1H, brs), 3.59 (3H, s), 3.76 (3H, s), 4.69 (1H, q, $J = 7.3$ Hz), 5.86 (1H, s), 6.63 (2H, dt, $J = 9.0$ and 3.4 Hz), 6.75 (2H, dt, $J = 9.0$ and 3.4 Hz), 7.38–7.45 (3H, m), 7.58–7.60 (2H, m); ¹³C-NMR (75 MHz, CDCl₃) δ 7.4, 7.8, 11.5, 27.0, 27.8, 55.5, 55.6, 73.1, 76.2, 105.6, 114.5, 114.5, 121.7, 122.0, 122.0, 124.6, 127.5, 128.3, 128.3, 129.4, 129.4, 131.6, 147.0, 151.5, 156.1, 166.0; MS m/z 496 (M⁺); HRMS m/z calcd for C₂₆H₃₁O₆F₃ 496.2073 (M⁺), found 496.2061.

(S)-MTPA ester [(E,S)-S2]. By following the same procedure described for (Z,R)-S2, (S)-MTPA ester (E,S)-S2 was prepared from (E)-S1 and (R)-MTPA chloride; quantitative yield; colorless oil; $[\alpha]_D^{28} -5.2$ (c 0.8 in CHCl₃); IR (neat) 3578, 2953, 1747, 1506 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.83 (3H, t, $J = 7.8$ Hz), 0.92 (3H, t, $J = 7.6$ Hz), 1.48–1.69 (4H, m), 1.72 (3H, d, $J = 7.1$ Hz), 2.69 (1H, brs), 3.62 (3H, s), 3.79 (3H, s), 4.77 (1H, q, $J = 7.1$ Hz), 5.75 (1H, s), 6.85 (4H, s), 7.34–7.41 (3H, m), 7.63–7.64

(2H, m); ^{13}C -NMR (75 MHz, CDCl_3) δ 7.1, 7.7, 11.4, 26.9, 27.4, 55.6, 55.6, 73.6, 76.4, 76.6, 105.7, 114.9, 114.9, 122.3, 122.3, 127.5, 127.5, 128.5, 128.5, 129.7, 129.7, 132.3, 147.4, 151.4, 156.6, 166.2; MS m/z 496 (M^+); HRMS m/z calcd for $\text{C}_{26}\text{H}_{31}\text{O}_6\text{F}_3$ 496.2073 (M^+), found 496.2082.

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^{**}For reviews about the determination of absolute configuration by use of MTPA, see: (a) Seco, J. M.; Quiñoá, E.; Riguera, R. *Tetrahedron: Asymmetry* **2001**, *12*, 2915. (b) Kusumi, T. *J. Synth. Org. Chem., Jpn.* **1993**, *51*, 462.