Supporting Information

Novel Catalytic CO₂ Incorporation Reaction: Nickel-Catalyzed Regio- and Stereoselective Ring-Closing Carboxylation of Bis-1,3-Dienes

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General Information. All ¹H NMR and ¹³C NMR were recorded on a JEOL EX-270 (270 MHz for ¹H, 67.5 MHz for ¹³C), or JEOL AL-400 (400 MHz for ¹H, 100 MHz for ¹³C) instrument in CDCl₃ with tetramethylsilane as an internal standard otherwise mentioned. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), integration. Infrared spectra (IR) were obtained on a Perkin Elmer 1605 FTIR spectrometer and absorptions are reported in reciprocal centimeters. Mass spectra were obtained on a JEOL JMS-700TZ (EI), a JEOL JMS-FABmate (EI), or a JEOL JMS-HX110 (FAB). Elemental Analyses were performed at the Center for Instrumental Analysis of Hokkaido University. Melting points were recorded on a Yanagimoto Micro Melting Point Apparatus and those were uncorrected. Silica gel column chromatography was performed with Merck Silica Gel 60 (230-400 mesh ASTM).

Materials or Methods. All reactions were performed under an argon atmosphere using standard Schlenk techniques unless otherwise mentioned. THF (dehydrated, stabilizer-free) was obtained from Kanato Kagaku Co. and used without further purification. Carbon dioxide (CO₂) gas was dried by passing through a column filled with Sicapent® and used without further purification. Ni(acac)₂ was dried under high vacuum (<10⁻³ mmHg) at 90 °C overnight and stored under argon atmosphere. All other solvents and reagents were purified when necessary using standard procedures. Bis-1,3-dienes **1b**, **1c**, **1d**, and **1e** were prepared according to the procedures described in the literature.¹

Preparation of 4-Methyl-N,N-di-[(2E)-penta-2,4-dienyl]benzenesulfonamide (1a). To a cooled (0 °C) suspension of NaH (60% dispersion in mineral oil, 711 mg, 17.8 mmol) in DMF (10 mL) was added a solution of *p*-toluenesulfonamide (1.27 g, 7.41 mmol) in DMF (10 mL). The mixture was stirred at 0 °C for 30 min, after which a solution of (2E)-bromopenta-2,4-diene² (2.5 g, 17.1 mmol) in DMF (5 mL) was added. The resulting mixture was stirred at room temperature for 1.5 h, then quenched by the addition of saturated aqueous solution of NH₄Cl at 0 °C, and extracted with ether. The combined organics were dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc = 10/1) to afford bis-diene **1a** (1.57 g, 69%) as a pale yellow oil: IR (neat) 3085, 3039, 2974, 2921, 1924, 2826, 1654, 1601, 1494 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.69 (d, *J* = 8.3 Hz, 2 H), 7.30 (d, *J* = 8.3 Hz, 2 H), 6.25 (ddd, *J* = 16.7, 10.3, 10.3 Hz, 2 H), 6.08 (dd, *J* = 15.0, 10.3 Hz, 2 H), 5.45 (dt, *J* = 15.1, 6.7 Hz, 2 H), 5.16 (d, *J* = 16.7 Hz, 2 H), 5.08 (d, *J* = 10.3 Hz, 2 H), 3.82 (d, *J* = 6.4 Hz, 4 H), 2.43 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.53, 48.45, 117.88, 127.10, 127.59, 129.52, 134.66, 135.68, 137.18, 143.10; LR MS (EI, *m/z*) 303 (M⁺), 262, 236, 148; Anal. Calcd for C₁₇H₂₁NO₂S: C, 67.29; H, 6.98; N, 4.62. Found: C, 67.21; H, 7.00; N, 4.40.

Ring-Closing Carboxylation of **1a using Ni(cod)₂ and Et₂Zn.** In a Schlenk-type flask were placed Ni(cod)₂ (10.9 mg, 0.0395 mmol) and PPh₃ (20.7 mg, 0.0790 mmol), and dissolved in degassed THF (2 mL) at 0 °C. The solution was frozen in a liquid nitrogen bath and the flask was evacuated in vacuo (<0.01 mmHg). A balloon filled with CO₂ was attached to the reaction flask to introduce CO₂, and then the frozen mixture was allowed to stand ambient temperature until it thawed. To the resulting solution were added a solution of **1a** (60 mg, 0.20 mmol) in degassed THF (2 mL) and a solution of Et₂Zn in hexane (1.0 M, 0.80 mL, 0.80 mmol) at 0 °C. After 3.5 hr at 0 °C, the reaction mixture was hydrolyzed with 10 % aqueous solution of HCl at 0 °C, and aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was treated with diazomethane in Et₂O at 0 °C according to standard procedures. The obtained crude material was purified by silica gel column chromatography (hexane/EtOAc=5/1) to afford ester **2a** (colorless oil, 55 mg, 75%).

Ring-Closing Carboxylation of **1a using Ni(acac)₂ and Et₂Zn.** To a solution of Ni(acac)₂ (2.5 mg, 0.0097 mmol) and PPh₃ (5.2 mg, 0.020 mmol) in THF (2 mL) in a Schlenk-type flask was added a solution of **1a** (60 mg, 0.20 mmol) in THF (2 mL). The mixture was frozen in a liquid nitrogen bath and the flask was evacuated in vacuo (<0.01 mmHg). A balloon filled with CO₂ was attached to the reaction flask to introduce CO₂, and then the frozen mixture was allowed to stand ambient temperature until it thawed. To the resulting solution was added a solution of Et₂Zn in hexane (1.0 M, 0.90 mL, 0.90 mmol) at 0 °C. After 24 hr at 0 °C, the reaction mixture was hydrolyzed with 10 % aqueous solution of HCl at 0 °C, and aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was treated with diazomethane in Et₂O at 0 °C according to standard procedures. The obtained crude material was purified by silica gel column chromatography (hexane/EtOAc=5/1) to afford ester **2a** (53 mg, 72%).

Typical Procedure for Methylative Ring-Closing Carboxylation. To a solution of Ni(acac)₂ (5.1 mg, 0.019 mmol) and PPh₃ (10.4 mg, 0.039 mmol) in THF (0.5 mL) in a Schlenk-type flask was added a solution of **1a** (60 mg, 0.20 mmol) in THF (3.5 mL). The mixture was frozen in a liquid nitrogen bath and the flask was evacuated in vacuo (<0.01 mmHg). A balloon filled with CO₂ was attached to the reaction flask to introduce CO₂, and then the frozen mixture was allowed to stand ambient temperature until it thawed. To the resulting solution was added a solution of Me₂Zn in hexane (1.0 M, 0.90 mL, 0.90 mmol) at 0 °C. After 19 hr at room temperature, the reaction mixture was hydrolyzed with 10 % aqueous solution of HCl at 0 °C, and aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was treated with diazomethane in Et₂O at 0 °C according to standard procedures. The obtained crude material was purified by silica gel column chromatography (hexane/EtOAc=5/1) to afford ester **9a** (colorless oil, 70 mg, 94%).

Typical Procedure for Phenylative Ring-Closing Carboxylation. To a solution of Ni(acac)₂ (7.6 mg, 0.029 mmol) and PPh₃ (15.6 mg, 0.059 mmol) in THF (0.5 mL) in a Schlenk-type flask was added a solution of **1a** (60 mg, 0.20 mmol) in THF (3.5 mL). The mixture was frozen in a liquid nitrogen bath and the flask was evacuated in vacuo (<0.01 mmHg). A balloon filled with CO₂ was attached to the reaction flask to introduce CO₂, and then the frozen mixture was allowed to stand ambient temperature until it thawed. To the resulting solution was added a solution of Ph₂Zn in xylene (0.45 M, 2.2

mL, 0.98 mmol) at 0 °C. After 20 hr at room temperature, the reaction mixture was hydrolyzed with 10 % aqueous solution of HCl at 0 °C, and aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was treated with diazomethane in Et₂O at 0 °C according to standard procedures. The obtained crude material was purified by silica gel column chromatography (hexane/EtOAc=5/1) to afford ester **10a** (colorless oil, 78 mg, 90%).

- Spectral Data of Ring-Closing Carboxylation Product -

Methyl (2*S)-2-[(3*S**,4*R**)-4-(prop-2-enyl)-1-(4-methylbenzenesulfonyl)pyrrolidin-3-yl]but-3-enoate (2a).** IR (neat) 3078, 2989, 2951, 1732, 1639, 1597, 1345, 1163 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.2 Hz, 2 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 5.68 (ddd, *J* = 17.0, 10.3, 10.3 Hz, 1 H), 5.58 (dddd, *J* = 17.0, 10.2, 6.7, 6.7 Hz, 1 H), 5.17 (d, *J* = 10.3 Hz, 1 H), 5.13 (d, *J* = 17.0 Hz, 1 H), 4.98 (d, *J* = 10.2 Hz, 1 H), 4.92 (d, *J* = 17.0 Hz, 1 H), 3.65 (s, 3 H), 3.34 (dd, *J* = 10.3, 7.6 Hz, 1 H), 3.29 (dd, *J* = 10.3, 7.0 Hz, 1 H), 3.01 (dd, *J* = 10.2, 5.6 Hz, 1 H), 2.84-2.91 (m, 2 H), 2.44 (s, 3 H), 2.17-2.35 (m, 2 H), 2.06-2.15 (m, 1 H), 1.95-2.04 (m, 1 H), 1.78-1.99 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.42, 37.46, 40.22, 44.46, 50.89, 51.82, 51.93, 53.03, 116.94, 119.32, 127.50, 129.43, 132.72, 133.48, 135.02, 143.36, 172.49; LR MS (EI, *m/z*) 363 (M⁺), 332, 304, 264, 208; Anal. Calcd for C₁₉H₂₅NO₄S: C, 62.78; H, 6.93; N, 3.85. Found: C, 62.62; H, 6.84; N, 3.85.

Methyl (2*S)-2-[(3*S**,4*R**)-4-[(1*E*)-But-1-enyl]-1-(4-methylbenzenesulfonyl)pyrrolidin-3-yl]but-3-enoate (9a).** IR (neat) 2955, 2872, 1735, 1638, 1595 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 7.9 Hz, 2 H), 7.33 (d, *J* = 7.9 Hz, 2 H), 5.71 (ddd, *J* = 17.3, 10.2, 10.0 Hz, 1 H), 5.42 (dt, *J* = 15.3, 6.5 Hz, 1 H), 5.14 (d, *J* = 10.2 Hz, 1 H), 5.09 (d, *J* = 17.3 Hz, 1 H), 5.02 (dd, *J* = 15.3, 8.5 Hz, 1 H), 3.63 (s, 3 H), 3.42 (dd, *J* = 10.7, 7.6 Hz, 1 H), 3.38 (dd, *J* = 10.0, 7.9 Hz, 1 H), 3.10 (dd, *J* = 10.0, 7.6 Hz, 1 H), 2.96 (dd, *J* = 8.2, 8.2 Hz, 1 H), 2.88 (dd, *J* = 10.0, 8.2 Hz, 2 H), 2.47 (dddd, *J* = 8.5, 8.2, 7.9, 7.6 Hz, 1 H), 2.44 (s, 3 H), 2.20 (dddd, *J* = 8.2, 8.2, 7.6, 7.6 Hz, 1 H), 1.92 (qd, *J* = 7.3, 6.5 Hz, 2 H), 0.90 (t, *J* = 7.3 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 13.41, 21.57, 25.43, 44.51, 45.72, 50.71, 51.79, 51.93, 52.96, 119.00, 127.34, 127.52, 129.53, 133.19, 133.41, 135.12, 143.37, 172.37; LR MS (EI, *m/z*) 377 (M⁺), 362, 350, 346, 222. Anal. Calcd for C₂₀H₂₇NO₄S: C, 63.63; H, 7.21; N, 3.71. Found: C, 63.66; H, 7.15; N, 3.70.

Dimethyl (3*R,4*S**)-3-[(1*E*)-But-1-enyl]-4-[(1*S**)-1-methoxycarbonylprop-2-enyl]cyclopentane-1,1-dicarboxylate (9b).** IR (neat) 2960, 2872, 2837, 1734, 1637, 1597 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.83 (ddd, *J* = 17.0, 10.0, 9.4 Hz, 1 H), 5.45 (dt, *J* = 15.2, 6.4 Hz, 1 H), 5.17 (dd, *J* = 15.2, 8.2 Hz, 1 H), 5.12 (d, *J* = 10.0 Hz, 1 H), 5.08 (d, *J* = 17.0 Hz, 1 H), 3.71 (s, 3 H), 3.70 (s, 3 H), 3.64 (s, 3 H), 3.08 (dd, *J* = 9.4, 5.4 Hz, 1 H), 2.42-2.51 (m, 2 H), 2.29-2.41 (m, 1 H), 2.02-2.19 (m, 2 H), 1.88-2.01 (m, 3 H), 0.93 (t, *J* = 7.6 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 13.62, 25.52, 37.15, 40.93, 45.84, 46.84, 51.57, 52.28, 52.68, 52.67, 57.90, 117.89, 129.97, 133.75, 134.32, 172.48, 172.49, 172.88; LR MS (EI, *m/z*) 339 (M⁺+1), 307, 275, 239, 129; Anal. Calcd for C₁₈H₂₆O₆: C, 63.89; H, 7.74. Found: C, 63.77; H, 7.44.

Methyl (2*S)-2-[(3*S**,4*R**)-4-[(1*E*)-3-phenylpropenyl]-1-(4-methylbenzenesulfonyl)pyrrolidin-3-yl]-but-3-enoate (10a).** IR (neat) 3083, 3025, 2952, 1734, 1637, 1602 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 8.2 Hz, 2 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 7.27 (dd, *J* = 7.4, 7.0 Hz, 2 H), 7.18 (t, *J* = 7.4 Hz, 1 H), 7.09 (d, *J* = 7.0 Hz, 2 H), 5.68 (ddd, *J* = 17.0, 10.3, 9.4 Hz, 1 H), 5.53 (dt, *J* = 15.2, 6.7 Hz, 1 H), 5.15 (dd, *J* = 15.2, 8.5 Hz, 1 H), 5.09 (d, *J* = 10.3 Hz, 1 H), 5.07 (d, *J* = 17.0

Hz, 1 H), 3.61 (s, 3 H), 3.36-3.46 (m, 2 H), 3.25 (d, $J = 6.7$ Hz, 2 H), 3.09 (dd, $J = 10.3, 7.6$ Hz, 1 H), 2.88-2.99 (m, 2 H), 2.46-2.58 (m, 1 H), 2.42 (s, 3 H), 2.19-2.29 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.49, 38.71, 44.49, 45.60, 50.73, 51.89, 51.92, 52.81, 118.96, 125.94, 127.44, 128.21, 128.23, 129.50, 129.84, 131.96, 133.01, 133.50, 139.63, 143.37, 172.23; LR MS (EI, m/z) 439 (M^+), 408, 380, 284; Anal. Calcd for $\text{C}_{25}\text{H}_{29}\text{NO}_4\text{S}$: C, 68.31; H, 6.65; N, 3.19. Found: C, 68.11; H, 6.81; N, 3.06.

Dimethyl

(3*S,4*R**)-3-[(1*S**)-1-Methoxycarbonylprop-2-enyl]-4-[(1*E*)-3-phenylpropenyl]cyclopentane-1,1-dicarboxylate (10b).**

IR (neat) 3026, 2950, 1733, 1653, 1638, 1598 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.25-7.30 (m, 2 H), 7.12-7.21 (m, 3 H), 5.82 (ddd, $J = 16.4, 11.2, 9.1$ Hz, 1 H), 5.59 (dt, $J = 15.2, 6.7$ Hz, 1 H), 5.31 (dd, $J = 15.2, 8.2$ Hz, 1 H), 5.09 (d, $J = 16.4$ Hz, 1 H), 5.08 (d, $J = 11.2$ Hz, 1 H), 3.71 (s, 3 H), 3.70 (s, 3 H), 3.63 (s, 3 H), 3.31 (d, $J = 6.7$ Hz, 2 H), 3.09 (dd, $J = 9.1, 6.4$ Hz, 1 H), 2.35-2.53 (m, 3 H), 2.11-2.22 (m, 1 H), 2.09 (ddd, $J = 12.9, 9.9$ Hz, 1 H), 1.98 (dd, $J = 12.9, 9.7$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 37.24, 38.88, 40.89, 45.88, 46.83, 51.64, 52.65, 52.72, 52.74, 57.93, 117.91, 125.82, 126.19, 128.31, 130.55, 132.70, 134.41, 140.22, 172.39, 172.42, 172.86; LR MS (EI, m/z) 400 (M^+), 368, 337, 301, 241; Anal. Calcd for $\text{C}_{23}\text{H}_{28}\text{O}_6$: C, 68.98; H, 7.05. Found: C, 68.81; H, 7.07.

Methyl (2*S)-2-[(3*S**,4*R**)-4-[(1*E*)-3-Methylbut-1-enyl]-1-(4-methylbenzenesulfonyl)pyrrolidin-3-yl]but-3-enoate (9c).**

IR (neat) 2956, 2870, 1732, 1638, 1597 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.2$ Hz, 2 H), 7.32 (d, $J = 8.2$ Hz, 2 H), 5.68 (ddd, $J = 17.0, 10.5, 9.7$ Hz, 1 H), 5.32 (dd, $J = 15.2, 6.4$ Hz, 1 H), 5.11 (d, $J = 10.5$ Hz, 1 H), 5.08 (d, $J = 17.0$ Hz, 1 H), 4.96 (dd, $J = 15.2, 8.4$ Hz, 1 H), 3.62 (s, 3 H), 3.41 (dd, $J = 10.2, 7.6$ Hz, 1 H), 3.38 (dd, $J = 10.2, 7.9$ Hz, 1 H), 3.08 (dd, $J = 9.7, 7.4$ Hz, 1 H), 2.94 (dd, $J = 10.0, 7.6$ Hz, 1 H), 2.87 (dd, $J = 10.0, 7.9$ Hz, 1 H), 2.46-2.41 (m, 1 H), 2.43 (s, 3 H), 2.08-2.24 (m, 2 H), 0.99 (d, $J = 6.7$ Hz, 3 H), 0.98 (d, $J = 6.7$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.57, 22.13, 22.19, 30.89, 44.60, 45.70, 50.79, 51.93, 51.95, 52.98, 118.97, 126.37, 127.50, 129.53, 133.17, 133.48, 140.56, 143.37, 172.37; LR MS (EI, m/z) 391 (M^+), 376, 360, 332, 292, 236; Anal. Calcd for $\text{C}_{21}\text{H}_{29}\text{NO}_4\text{S}$: C, 64.42; H, 7.47; N, 3.58. Found: C, 64.28; H, 7.39; N, 3.43.

Dimethyl

(3*S,4*R**)-3-[(1*S**)-1-Methoxycarbonylprop-2-enyl]-4-[(1*E*)-3-methylbut-1-enyl]cyclopentane-1,1-dicarboxylate (9d).**

IR (neat) 2955, 2872, 1732, 1638, 1595 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.81 (ddd, $J = 16.7, 10.3, 9.4$ Hz, 1 H), 5.36 (dd, $J = 15.2, 6.6$ Hz, 1 H), 5.03-5.16 (m, 3 H), 3.70 (s, 3 H), 3.69 (s, 3 H), 3.64 (s, 3 H), 3.06 (dd, $J = 6.6, 9.1$ Hz, 1 H), 2.40-2.48 (m, 2 H), 2.32 (dd, $J = 10.2, 7.9$ Hz, 1 H), 2.00-2.23 (m, 3 H), 1.91 (dd, $J = 13.2, 10.2$ Hz, 1 H), 0.93 (d, $J = 6.7$ Hz, 3 H), 0.92 (d, $J = 6.7$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.38, 22.41, 30.98, 37.34, 41.09, 46.03, 46.84, 51.66, 52.60, 52.71, 52.73, 57.87, 117.91, 127.97, 134.48, 139.30, 172.53, 172.55, 172.96; LR MS (EI, m/z) 352 (M^+), 321, 292, 253, 221, 193; Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{O}_6$: C, 64.75; H, 8.01. Found: C, 64.55; H, 7.93.

Methyl (2*S)-2-[(3*R**,4*S**)-3-[(1*E*)-3-Methylbut-1-enyl]-1-(4-methylbenzenesulfonyl)piperidin-4-yl]but-3-enoate (9e).**

Colorless crystal; mp 89-91 $^{\circ}\text{C}$ (recryst. from hexane); IR (CHCl_3) 3019, 2958, 2927, 2867, 1729, 1637, 1598 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 8.2$ Hz, 2 H), 7.32 (d, $J = 8.2$ Hz, 2 H), 5.90 (ddd, $J = 17.0, 10.3, 10.3$ Hz, 1 H), 5.55 (dd, J

= 15.3, 6.5 Hz, 1 H), 5.15 (d, J = 10.3 Hz, 1 H), 5.01 (d, J = 17.0 Hz, 1 H), 4.96 (dd, J = 15.3, 9.4 Hz, 1 H), 3.73-3.79 (m, 1 H), 3.63 (s, 3 H), 3.56-3.63 (m, 1 H), 3.09 (dd, J = 8.8, 2.6 Hz, 1 H), 2.43 (s, 3 H), 2.18-2.30 (m, 3 H), 2.00 (dd, J = 11.1, 11.1 Hz, 1 H), 1.50-1.78 (m, 3 H), 0.97 (d, J = 6.8 Hz, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.54, 22.21, 22.23, 27.38, 31.12, 42.43, 43.61, 46.22, 51.35, 51.55, 51.62, 118.10, 125.31, 127.55, 129.49, 132.91, 133.80, 141.91, 143.31, 172.74; LR MS (EI, m/z) 455 (M^+), 390, 374, 346, 250; Anal. Calcd for $\text{C}_{22}\text{H}_{31}\text{NO}_4\text{S}$: C, 65.15; H, 7.70; N, 3.459. Found: C, 65.16; H, 7.72; N, 3.27.

Methyl

(2*S)-2-((3*S**,4*R**)-4-(((3*R**,1*E*)-3-Phenylbut-1-enyl)-1-(4-methylbenzenesulfonyl)pyrrolidin-3-yl)but-3-enoate (10c).**

IR (neat) 3026, 2961, 2872, 1732, 1676, 1638, 1598 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, J = 8.2 Hz, 2 H), 7.26-7.38 (m, 4 H), 7.18 (dd, J = 7.3, 7.0 Hz, 1 H), 7.11 (d, J = 7.0 Hz, 2 H), 5.62 (ddd, J = 16.8, 9.7, 9.4 Hz, 1 H), 5.55 (dd, J = 16.4, 7.6 Hz, 1 H), 5.09 (dd, J = 16.4, 8.5 Hz, 1 H), 5.03 (d, J = 16.8 Hz, 1 H), 5.02 (d, J = 9.7 Hz, 1 H), 3.59 (s, 3 H), 3.45 (dd, J = 9.9, 7.6 Hz, 1 H), 3.39 (dd, J = 9.7, 7.9 Hz, 1 H), 3.33 (dd, J = 9.4, 8.2 Hz, 1 H), 3.07 (dd, J = 9.9, 7.3 Hz, 1 H), 2.88-2.96 (m, 2 H), 2.45-2.55 (m, 1 H), 2.43 (s, 3 H), 2.18-2.27 (m, 1 H) 1.26 (d, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.09, 21.34, 42.06, 44.66, 45.67, 50.85, 51.92, 52.09, 52.92, 118.96, 126.02, 126.92, 127.31, 127.48, 128.25, 29.55, 133.10, 133.42, 138.00, 143.40, 145.12, 172.30 (see also Chart S1); LR MS (EI, m/z) 453 (M^+), 422, 394, 354, 298; Anal. Calcd for $\text{C}_{26}\text{H}_{31}\text{NO}_4\text{S}$: C, 68.85; H, 6.89; N, 3.09. Found: C, 68.72; H, 6.93; N, 2.97.

Chemical structure of compound 10c is shown above the spectrum. The structure is a bicyclic system with a TsN group, a CO₂Me group, and a phenyl group. The spectrum displays chemical shifts (δ) in ppm on the x-axis, ranging from 0 to 190 ppm. The spectrum shows several peaks, with the following chemical shifts (δ) in ppm labeled on the left side of the spectrum:

172.3048, 145.1255, 143.4098, 138.0070, 133.4207, 133.1073, 129.5521, 128.5518, 128.2571, 127.4817, 127.3167, 126.8126, 126.0299, 118.9609, 76.6866, 77.3217, 77.0000, 52.9222, 52.0973, 51.9241, 50.8518, 45.6717, 44.6653, 42.0670, 21.5444, 21.0989.

- Procedure for Determination of Stereochemistry of RingClosing Carboxylation Product -

Procedure For Determination of Stereochemistry of 2a. The stereochemistry of **2a** was determined by the results of an NOE experiment for **2a** and by the analysis of the coupling constants of Ha in ^1H NMR spectrum of **3**, which was obtained from **2a** according to the procedures shown in Scheme S1. The detailed experimental procedures for conversion of **2a** to **3** were described below.

Scheme S1. Determination of Stereochemistry of **2a**

Preparation of Compound II. To a solution of ruthenium catalyst **I** (5.6 mg, 6.8 mmol) in degassed CH_2Cl_2 (1 mL) was added a solution of **2a** (50.0 mg, 0.138 mmol) in degassed CH_2Cl_2 (1.5 mL). The mixture was stirred at room temperature for 6 hr and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc = 3.5/1) to afford bicyclic compound **II** (colorless crystal, 37 mg, 80%): mp 128-130 $^\circ\text{C}$ (recyst. from methanol/AcOEt); IR (CHCl_3) 3019, 2953, 2924, 2844, 1733, 1642, 1598 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) 7.87 (d, $J = 8.2$ Hz, 2 H), 7.36 (d, $J = 8.2$ Hz, 2 H), 5.79-5.85 (m, 1 H), 5.75 (br d, $J = 10.2$ Hz, 1 H), 3.85 (dd, $J = 9.7, 7.0$ Hz, 1 H), 3.74 (s, 3 H), 3.71 (dd, $J = 9.7, 6.4$ Hz, 1 H), 3.03 (dd, $J = 10.0, 9.7$ Hz, 1 H), 2.96-3.03 (m, 1 H), 2.90 (dd, $J = 10.0, 9.7$ Hz, 1 H), 2.47 (s, 3 H), 2.22-2.33 (m, 1 H), 1.77-1.97 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.56, 28.15, 39.57, 42.04, 46.33, 52.14, 52.61, 52.77, 124.19, 127.22, 127.92, 129.61, 134.33, 143.26, 172.85; LR MS (EI, m/z) 335 (M^+), 303, 276, 222, 180; Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_4\text{S}$: C, 60.87; H, 6.31; N, 4.18. Found: C, 60.85; H, 6.39; N, 4.07.

Methyl (3aS*,4S*,7aS*)-2-(4-Methylbenzenesulfonyl)octahydroisindole-4-carboxylate (3). To a solution of **II** (15.0 mg, 0.0447 mmol) in AcOEt (2.0 mL) was added Pd on activated carbon (10wt%, 2.5 mg). The mixture was stirred at room temperature for 6 hr under an atmosphere of hydrogen, and then catalyst was filtered off. The filtered solution was concentrated in vacuo and the residue was purified by silica gel column chromatography (hexane/EtOAc = 3/1) to afford **3** (colorless crystal, 14.2 mg, 94%): mp 141-143 $^\circ\text{C}$ (recryst. from AcOEt/hexane); IR (CHCl_3) 3011, 2942, 2887, 2861, 1730, 1598 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 8.2$ Hz, 2 H), 7.32 (d, $J = 8.2$ Hz, 2 H), 3.65 (dd, $J = 10.0, 7.0$ Hz, 1 H), 3.66 (s, 3 H), 3.56 (dd, $J = 9.7, 7.0$ Hz, 1 H), 2.89 (dd, $J = 10.3, 10.0$ Hz, 1 H), 2.79 (dd, $J = 10.8, 9.7$ Hz, 1 H), 2.44 (s, 3 H), 2.13 (ddd, $J = 11.2, 10.8, 3.5$ Hz, 1 H), 1.96-2.03 (m, 1 H), 1.78-1.88 (m, 2 H), 1.52 (dddd, $J = 11.2, 11.0, 11.0, 7.0$ Hz, 1 H), 1.23-1.47 (m, 3 H), 1.00 (dddd, $J = 13.0, 12.8, 4.4$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.60, 24.89, 27.52, 28.76, 43.65, 45.56, 45.82, 51.80, 51.87, 52.55, 127.18, 129.60, 134.56, 143.14, 174.31.; LR MS (EI, m/z) 337 (M^+), 278, 182; Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_4\text{S}$: C, 60.51; H, 6.87; N, 4.15. Found: C, 60.56; H, 6.88; N, 4.14.

Procedure for Determination of Stereochemistry of 9a. The stereochemistry of **9a** was determined by the results of NOE experiments for compound **III** (summarized in Figure S1), which was prepared from carboxylic acid **9a'** according to

the procedure shown in Scheme S2 and the following text. Carboxylic acid **9a'** was obtained by methylative carboxylation of **2a** according to the typical procedure mentioned above except that the product was isolated without diazomethane treatment.

Scheme S2. Determination of Stereochemistry of **9a**

Preparation of Compound III. To a cooled (0 °C) solution of carboxylic acid **9a'** (25 mg, 0.069 mmol) in THF (1.5 mL) was added *N*-bromosuccinimide (24 mg, 0.14 mmol). After 1 hr at 0 °C in dark, an aqueous solution of Na₂S₂O₃ was added to the mixture. The aqueous layer was extracted with Et₂O and the combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc=3/2) to afford bromolactone **III** (colorless crystal, 12 mg, 38%): mp 161-163 °C (recyst. from AcOEt/hexane); IR (CHCl₃) 2977, 2934, 2874, 1740, 1710, 1637, 1598 cm⁻¹; ¹H NMR (400 MHz, C₆D₆) δ 7.79 (d, *J* = 8.2 Hz, 2 H), 6.89 (d, *J* = 8.2 Hz, 2 H), 5.19 (ddd, *J* = 16.0, 10.0, 7.6 Hz, 1 H), 5.10 (d, *J* = 16.0 Hz, 1 H), 4.97 (d, *J* = 10.0 Hz, 1 H), 3.73 (dd, *J* = 10.0, 7.3 Hz, 1 H), 3.45-3.51 (m, 1 H), 3.39 (dd, *J* = 10.4, 5.1 Hz, 1 H), 3.14 (dd, *J* = 9.9, 7.9 Hz, 1 H), 2.94 (dd, *J* = 7.6, 5.2 Hz, 1 H), 2.81 (dd, *J* = 10.0, 9.9 Hz, 1 H), 2.68 (dd, *J* = 10.0, 10.0 Hz, 1 H), 1.94 (s, 3 H), 1.72-1.85 (m, 1 H), 1.24-1.44 (m, 3 H), 0.78 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 12.33, 21.65, 27.49, 36.91, 41.97, 46.65, 47.66, 50.49, 59.35, 84.67, 122.78, 127.22, 128.37, 129.89, 133.89, 143.94, 168.23; LR MS (EI, *m/z*) 443, 441 (M⁺), 362, 320, 286, 288; Anal. Calcd for C₁₉H₂₄BrNO₄S: C, 51.59; H, 5.47; N, 3.17. Found: C, 51.75; H, 5.53; N, 2.91.

Figure S1. Summary of NOE Experiments for **III**

Procedure for Determination of Stereochemistry of 9b. The stereochemistry of **9b** was determined by the results of NOE experiments for compound **IV** (summarized in Figure S2), which was prepared from carboxylic acid **9b'** according to the procedure shown in Scheme S3 and the following text. Carboxylic acid **9b'** was obtained by methylative carboxylation of **2b** according to the typical procedure mentioned above except that the product was isolated without diazomethane treatment.

Scheme S3. Determination of Stereochemistry of **9b**

Preparation of Compound IV. To a cooled (0 °C) solution of carboxylic acid **9b'** (50 mg, 0.15 mmol) in THF (1.5 mL) was added *N*-bromosuccinimide (55 mg, 0.31 mmol). After 30 min at 0 °C in dark, an aqueous solution of Na₂S₂O₃ was added to quench. The aqueous layer was extracted with Et₂O and the combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc=3/2) to afford bromolactone **II** (colorless crystal, 38 mg, 61%); mp 89-90 °C (recyst. from AcOEt/hexane); IR (CHCl₃) 2953, 1727 (broad), 1636 cm⁻¹; ¹H NMR (400 MHz, C₆D₆) δ 5.62 (ddd, *J* = 17.4, 10.2, 7.9 Hz, 1 H), 5.24 (d, *J* = 17.4 Hz, 1 H), 5.08 (d, *J* = 10.2 Hz, 1 H), 3.73 (ddd, *J* = 10.2, 3.5, 3.5 Hz, 1 H), 3.65 (dd, *J* = 10.0, 3.5 Hz, 1 H), 3.40 (s, 3 H), 3.30 (s, 3 H), 3.26 (dd, *J* = 7.8, 5.3 Hz, 1 H), 2.76 (dd, *J* = 13.4, 7.3 Hz, 1 H), 2.35 (dd, *J* = 13.2, 6.7 Hz, 1 H), 2.11-2.25 (m, 1 H), 1.91 (dd, *J* = 13.2, 12.3 Hz, 1 H), 1.76 (dd, *J* = 13.4, 10.9 Hz, 1 H), 1.67-1.77 (m, 1 H), 1.50-1.61 (m, 1 H), 1.33-1.46 (m, 1 H), 0.80 (dd, *J* = 7.0, 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 12.73, 27.40, 35.12, 37.00, 37.33, 42.98, 48.22, 53.11, 53.14, 59.09, 59.99, 76.68, 77.00, 77.32, 86.99, 122.05, 129.32, 169.57, 171.83, 172.11; LR MS (EI, *m/z*) 404, 402 (M⁺), 373, 371; Anal. Calcd for C₁₇H₂₃BrO₆: C, 50.63; H, 5.75. Found: C, 50.56; H, 5.77.

Figure S2. Summary of NOE Experiments for **IV**

Procedure for Determination of Stereochemistry of 10a and 9c. According to the procedures shown in Scheme S4, compound **10a** were converted to compound **V**, whose ^1H NMR spectrum was completely identical with that of the material independently derived from **9a**. The stereochemistry of **9c** was also confirmed based on independent conversion of **9c** to **VI** according to the similar procedures.

Scheme S4. Determination of Stereochemistry of **10a** and **9c**

Preparation of Compound V. To a cooled solution (0°C) of **10a** (55 mg, 0.13 mmol) in Et_2O (3 mL) was added LiAlH_4 (47 mg, 1.25 mmol). After the mixture was stirred at 0°C for 30 min, finely powdered $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was slowly added to this. The resulting mixture was stirred at ambient temperature until excess LiAlH_4 was decomposed, and then solids were removed by filtration. The filtrate was concentrated in vacuo to afford a crude alcohol.

To a solution of the crude alcohol in THF/DMF (4/1, 2.5 mL) was added NaH (60% dispersion in oil, 25 mg, 0.63 mmol) and MeI (77 μL , 1.25 mmol) at 0°C . After the resulting mixture was stirred at room temperature for 20 hr, saturated aqueous solution of NH_4Cl was added at 0°C . The aqueous layer was extracted with Et_2O . The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/ EtOAc =4/1) to afford compound **V** (37 mg, 70% from **10a**) as a colorless oil: IR (neat) 3026, 2823, 2890, 1638, 1598 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, J = 8.2 Hz, 2 H), 7.32 (d, J = 8.2 Hz, 2 H), 7.23-7.31 (m, 2 H), 7.16-7.22 (m, 1 H), 7.10 (d, J = 7.0 Hz, 2 H), 5.50-5.63 (m, 2 H), 5.19 (dd, J = 15.2, 8.5 Hz, 1 H), 5.02 (d, J = 11.4 Hz, 1 H), 4.99 (d, J = 17.0 Hz, 1 H), 3.36-3.42 (m, 2 H), 3.21-3.28 (m, 7 H), 3.06 (dd, J = 8.5, 8.5 Hz, 1 H), 2.89 (dd, J = 8.5, 8.5 Hz, 1 H), 2.49-2.59 (m, 1 H), 2.43 (s, 3 H), 2.19-2.28 (m, 1 H), 1.95-2.05 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.57, 38.89, 44.40, 44.95, 45.55, 51.04, 53.26, 58.82, 74.29, 117.27, 126.02, 127.51, 127.71, 128.34, 129.53, 130.99, 131.43, 133.49; LR MS (EI, m/z) 425 (M^+), 393, 380, 270; Anal. Calcd for $\text{C}_{25}\text{H}_{31}\text{NO}_3\text{S}$: C, 70.55; H, 7.34; N, 3.29. Found: C, 70.57; H, 7.32; N, 3.32.

Conversion of Compound V to VI. A solution of **V** (20 mg, 0.046 mmol) in pentane/ Et_2O (1/1, 4 mL) was cooled to -78°C and treated with a stream of O_3 at -78°C until the color of the solution had changed to blue. The mixture was treated with a stream of dry O_2 at -78°C to purge an excess amount of O_3 . To the reaction mixture was added LiAlH_4 (34 mg, 0.92 mmol) at -78°C and the resulting mixture was allowed to stir at ambient temperature for 7 hr. To this was added $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ at 0°C and the mixture was stirred at room temperature for 2 hr. The solids were removed by filtration, and then the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography ($\text{CHCl}_3/\text{MeOH}$ =10/1) to afford compound **VI** (7.2 mg, 45%) as colorless viscous oil: IR (neat) 3412, 2925, 2884, 1654,

1597 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, J = 8.2 Hz, 2 H), 7.34 (d, J = 8.2 Hz, 2 H), 3.79 (dd, J = 11.7, 2.9 Hz, 1 H), 3.74 (dd, J = 11.7, 4.4 Hz, 1 H), 3.58 (dd, J = 11.0, 5.8 Hz, 1 H), 3.54 (dd, J = 11.0, 6.7 Hz, 1 H), 3.39-3.51 (m, 3 H), 3.32 (s, 3 H), 3.21 (dd, J = 10.0, 8.2 Hz, 1 H), 2.99 (dd, J = 10.5, 5.9 Hz, 1 H), 2.88 (dd, J = 9.7, 7.6 Hz, 1 H), 2.79 (br s, 2 H), 2.44 (s, 3 H), 2.18-2.35 (m, 2 H), 1.55-1.63 (m, 1 H); ^{13}C NMR (100MHz, CDCl_3) δ 21.63, 38.42, 43.30, 43.49, 50.63, 52.10, 59.29, 63.63, 64.49, 74.37, 127.81, 129.57, 132.04, 143.63; LR MS (EI, m/z) 344 (M^+), 326, 310, 188; Anal. Calcd for $\text{C}_{16}\text{H}_{25}\text{NO}_5\text{S}$: C, 55.95; H, 7.34; N, 4.08. Found: C, 55.87; H, 7.52; N, 3.99.

Preparation of Compound VII. To a cooled solution (0 $^\circ\text{C}$) of **9a** (28 mg, 0.074 mmol) in THF (5 mL) was added LiAlH_4 (6 mg, 0.16 mmol). After the mixture was stirred at 0 $^\circ\text{C}$ for 15 min, finely powdered $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was slowly added to this. The resulting mixture was stirred at ambient temperature until excess LiAlH_4 was decomposed, and then solids were removed by filtration. The filtrate was concentrated in vacuo to afford a crude alcohol.

To a solution of the crude alcohol in THF/DMF (3/1, 4 mL) was added NaH (60% dispersion in oil, 15 mg, 0.37 mmol) and MeI (50 μL , 0.08 mmol) at 0 $^\circ\text{C}$. After the resulting mixture was stirred at room temperature for 3 hr, saturated aqueous solution of NH_4Cl was added at 0 $^\circ\text{C}$. The aqueous layer was extracted with Et_2O . The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/ EtOAc =4/1) to afford compound **VII** (19.4 mg, 72% from **9a**): IR (neat) 2962, 2926, 2874, 1637, 1597 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, J = 8.2 Hz, 2 H), 7.33 (d, J = 8.2 Hz, 2 H), 5.58 (ddd, J = 17.0, 10.2, 8.8 Hz, 1 H), 5.42 (dt, J = 15.3, 6.2 Hz, 1 H), 5.02-5.10 (m, 2 H), 5.01 (d, J = 17.0 Hz, 1 H), 3.34-3.41 (m, 2 H), 3.28 (d, J = 6.4 Hz, 2 H), 3.25 (s, 3 H), 3.07 (dd, J = 9.9, 8.5 Hz, 1 H), 2.87 (dd, J = 10.0, 8.5 Hz, 1 H), 2.45-2.55 (m, 1 H), 2.44 (s, 3 H), 2.21-2.29 (m, 1 H), 1.90-2.01 (m, 3 H), 0.91 (t, J = 7.6 Hz, 3 H). ^{13}C NMR (100MHz, CDCl_3) δ 13.51, 21.59, 25.50, 44.34, 44.81, 45.31, 50.94, 53.35, 58.81, 74.18, 117.29, 127.53, 128.44, 129.50, 133.46, 134.50, 137.05; LR MS (EI, m/z) 363 (M^+), 348, 318, 208; Anal. Calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_5\text{S}$: C, 66.08; H, 8.04; N, 3.85. Found: C, 66.06; H, 8.45; N, 3.83.

Conversion of Compound VII to VI. A solution of **VII** (8.5 mg, 0.023 mmol) in pentane (2.5 mL) was cooled to -78 $^\circ\text{C}$ and treated with a stream of O_3 at -78 until the color of the solution had changed to blue. The mixture was treated with a stream of dry O_2 at -78 $^\circ\text{C}$ to purge an excess amount of O_3 , and then diluted with Et_2O (2.5 mL). To the diluted mixture was added LiAlH_4 (10 mg, 0.26 mmol) at -78 $^\circ\text{C}$ and the mixture was allowed to stir at ambient temperature for 4 hr. To this was added $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ at 0 $^\circ\text{C}$ and the resulting mixture was stirred at room temperature for 1 hr. The solid were removed by filtration, and then the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography ($\text{CHCl}_3/\text{MeOH}$ =10/1) to afford compound **VI** (3.5 mg, 43%).

Preparation of Compound VIII. To a cooled solution (0 $^\circ\text{C}$) of **9c** (50 mg, 0.13 mmol) in Et_2O (3 mL) was added LiAlH_4 (24 mg, 0.63 mmol). After the mixture was stirred at 0 $^\circ\text{C}$ for 30 min, finely powdered $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was slowly added to this. The resulting mixture was stirred at ambient temperature until excess LiAlH_4 was decomposed, and then solids were removed by filtration. The solvents were evaporated in vacuo to afford a crude alcohol.

To a solution of the crude alcohol in THF/DMF (4/1, 2.5 mL) was added NaH (60% dispersion in oil, 25 mg, 0.64 mmol) and MeI (80 μL , 1.3 mmol) at 0 $^\circ\text{C}$. After the resulting mixture was stirred at room temperature for 15 hr, saturated aqueous solution of NH_4Cl was added at 0 $^\circ\text{C}$. The aqueous layer was extracted with Et_2O . The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/ EtOAc =4/1) to afford compound **VIII** (34 mg, 71% from **9c**) as a colorless oil: IR (neat) 2958, 2925, 2871, 1638, 1597 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, J = 8.2 Hz, 2 H), 7.33 (d, J = 8.2 Hz, 2 H), 5.59 (ddd, J

= 17.0, 10.3, 9.0 Hz, 1 H), 5.35 (dd, J = 15.6, 6.8 Hz, 1 H), 4.97-5.10 (m, 3 H), 3.36-3.41 (m, 2 H), 3.23-3.30 (m, 5 H), 3.06 (dd, J = 8.8, 8.8 Hz, 1 H), 2.85 (dd, J = 8.8, 8.8 Hz, 1 H), 2.40-2.52 (m, 1 H), 2.44 (s, 3 H), 2.12-2.29 (m, 2 H), 1.91-2.02 (m, 1 H), 0.91 (d, J = 6.8 Hz, 3 H), 0.90 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.61, 22.20, 22.32, 30.96, 44.42, 44.85, 45.45, 51.03, 53.40, 58.80, 117.28, 126.48, 127.50, 127.55, 129.51, 133.57, 137.10, 139.97, 143.23; LR MS (EI, m/z) 377 (M^+), 362, 332, 222; Anal. Calcd for $\text{C}_{21}\text{H}_{31}\text{NO}_3\text{S}$: C, 66.81; H, 8.28; N, 3.71. Found: C, 66.88; H, 8.31; N, 3.65.

Conversion of VIII to VI. A solution of **VIII** (10.8 mg, 0.029 mmol) in pentane (2.5 mL) was cooled to -78°C and treated with a stream of O_3 at -78°C until the color of the solution had changed to blue. The mixture was treated with a stream of dry O_2 at -78°C to purge an excess amount of O_3 , and then diluted with Et_2O (2.5 mL). To the diluted mixture was added LiAlH_4 (21mg, 0.56 mmol) at -78°C and the mixture was allowed to stir at ambient temperature for 5 hr. To this was added $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ at 0°C and the resulting mixture was stirred at room temperature for 2 hr. The solid were removed by filtration, and then the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography ($\text{CHCl}_3/\text{MeOH}=10/1$) to afford compound **VI** (4.4 mg, 45%).

Procedure for Determination of Stereochemistry of 10b and 9d. According to the procedures shown in Scheme S5, compound **10b** were converted to compound **X**, whose ^1H NMR spectrum was completely identical with that of the material independently derived from **9b**. The stereochemistry of **9d** was also confirmed based on independent conversion of **9d** to **X** according to the similar procedure.

Scheme S5. Determination of Stereochemistry of **10b** and **9d**

Preparation of Compound IX. To a cooled solution (0°C) of **10b** (64 mg, 0.16 mmol) in THF (3 mL) was added LiAlH_4 (30 mg, 0.80 mmol). After the mixture was refluxed for 1 hr, finely powdered $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was slowly added at 0°C . The resulting mixture was stirred at ambient temperature until excess LiAlH_4 was decomposed, and then solids were removed by filtration. The solvents were evaporated in vacuo to afford a crude alcohol.

To a solution of the crude alcohol in THF/DMF (3/1, 2 mL) was added NaH (60% dispersion in oil, 50 mg, 1.23 mmol) and MeI (0.15 mL, 0.08 mmol) at 0°C . After the resulting mixture was stirred at room temperature for 40 hr, saturated aqueous solution of NH_4Cl was added at 0°C . The aqueous layer was extracted with Et_2O . The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/ $\text{EtOAc}=12/1$) to afford compound **IX** (33 mg, 57% from **10b**): IR (neat) 3025, 2976, 2922, 2873, 2823, 2636, 2603 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.12-7.30 (m, 5 H), 5.70 (ddd, J = 17.0, 10.2, 10.2 Hz, 1 H), 5.54 (dt,

$J = 15.3, 6.7$ Hz, 1 H), 5.33 (dd, $J = 15.3, 8.5$ Hz, 1 H), 5.05 (d, $J = 10.2$ Hz, 1 H), 5.03 (d, $J = 17.0$ Hz, 1 H), 3.25-3.38 (m, 13 H), 3.13-3.24 (m, 4 H), 2.30-2.41 (m, 2 H), 1.75-1.88 (m, 1 H), 1.60-1.72 (m, 2 H), 1.19-1.39 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 36.38, 39.04, 40.40, 45.03, 45.08, 46.11, 46.40, 58.72, 59.24 (two ^{13}C signals were overlapped), 74.53, 77.36, 77.51, 116.21, 128.22, 128.39, 128.62, 135.51, 138.81, 140.72; LR MS (EI, m/z) 358 (M^+), 326, 313, 294; Anal. Calcd for $\text{C}_{23}\text{H}_{34}\text{O}_3$: C, 77.05; H, 9.56. Found: C, 77.06; H, 9.53.

Conversion of IX to X. A solution of **IX** (16.6 mg, 0.046 mmol) in pentane (3.5 mL) was cooled to -78°C and treated with a stream of O_3 at -78°C until the color of the solution had changed to blue. The mixture was treated with a stream of dry O_2 at -78°C to purge an excess amount of O_3 , and then diluted with Et_2O (2.5 mL). To the diluted mixture was added LiAlH_4 (35mg, 0.92 mmol) at -78°C and the mixture was allowed to stir at ambient temperature for 6 hr. To this was added $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ at 0°C and the resulting mixture was stirred at room temperature for 2 hr. The solid were removed by filtration, and then the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography ($\text{CHCl}_3/\text{MeOH} = 10/1$) to afford compound **X** (8.0 mg, 62%): IR (neat) 3404, 2924, 2875, 2813 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.72-3.81 (m, 2 H), 3.49-3.67 (m, 4 H), 3.34 (s, 3 H), 3.33 (s, 3 H), 3.32 (s, 3 H), 3.23 (dd, $J = 8.8, 3.3$ Hz, 2 H), 3.19 (d, $J = 8.8$ Hz, 2 H), 2.91 (br s, 2 H), 1.96-2.06 (m, 2 H), 1.67-1.79 (m, 3 H), 1.23-1.36 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 36.32, 37.18, 39.23, 44.32, 44.54, 45.50, 59.15, 59.23, 59.25, 77.14, 77.54; LR MS (EI, m/z) 277 ($\text{M}^+ + 1$), 259, 246, 226, 212; Anal. Calcd for $\text{C}_{14}\text{H}_{28}\text{O}_5$: C, 60.84; H, 10.21. Found: C, 60.82; H, 10.33.

Preparation of XI. To a cooled solution (0°C) of **9b** (70 mg, 0.21 mmol) in Et_2O (5 mL) was added LiAlH_4 (40 mg, 1.0 mmol). After the mixture was refluxed for 1 hr, finely powdered $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was slowly added at 0°C . The resulting mixture was stirred at ambient temperature until excess LiAlH_4 was decomposed, and then solids were removed by filtration. The solvents were evaporated in vacuo to afford a crude alcohol.

To a solution of the crude alcohol in THF/DMF (3/1, 2 mL) was added NaH (60% dispersion in oil, 82 mg, 2.1 mmol) and MeI (0.25 mL, 4.12 mmol) at 0°C . After the resulting mixture was stirred at room temperature for 14 hr, saturated aqueous solution of NH_4Cl was added at 0°C . The aqueous layer was extracted with Et_2O . The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/ $\text{EtOAc} = 15/1$) to afford compound **XI** (45 mg, 73% from **9b**): IR (neat) 2960, 2922, 2873, 2823, 1638 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 5.72 (ddd, $J = 17.0, 10.5, 8.9$ Hz, 1 H), 5.42 (dt, $J = 15.4, 6.2$ Hz, 1 H), 5.21 (dd, $J = 15.4, 8.5$ Hz, 1 H), 5.09 (d, $J = 10.5$ Hz, 1 H), 5.03 (d, $J = 17.0$ Hz, 1 H), 3.38 (d, $J = 6.9$ Hz, 2 H), 3.32 (s+s, 6 H), 3.30 (s, 3 H), 3.14-3.24 (m, 4 H), 2.22-2.48 (m, 2 H), 1.98 (qd, $J = 7.5, 6.2$ Hz, 2 H), 1.71-1.89 (m, 1 H), 1.66 (dd, $J = 7.5, 7.5$ Hz, 1 H), 1.62 (dd, $J = 7.5, 7.5$ Hz, 1 H), 1.14-1.30 (m, 2 H), 0.95 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.89, 25.64, 36.28, 40.45, 45.00, 45.02, 46.10, 46.14, 58.68, 59.23 (two ^{13}C signals were overlapped), 74.47, 77.43, 77.58, 116.11, 131.78, 132.89, 138.87; LR MS (EI, m/z) 296 (M^+), 281, 264, 251, 219, 187; Anal. Calcd for $\text{C}_{18}\text{H}_{32}\text{O}_3$: C, 72.93; H, 10.88. Found: C, 72.95; H, 10.76.

Conversion of XI to X. A solution of **XI** (21.4 mg, 0.072mmol) in pentane (2.5 mL) was cooled to -78°C and treated with a stream of O_3 at -78°C until the color of the solution had changed to blue. The mixture was treated with a stream of dry O_2 at -78°C to purge an excess amount of O_3 , and then diluted with Et_2O (2.5 mL). To the diluted mixture was added LiAlH_4 (53 mg, 1.4 mmol) at -78°C and the mixture was allowed to stir at ambient temperature for 5 hr. To this was added $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ at 0°C and the resulting mixture was stirred at room temperature for 2 hr. The solid were removed by filtration, and then the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography ($\text{CHCl}_3/\text{MeOH} = 10/1$) to afford compound **X** (12 mg, 60%).

Preparation of Compound XII. To a cooled solution (0 °C) of **9d** (48 mg, 0.14 mmol) in Et₂O (3.5 mL) was added LiAlH₄ (51 mg, 1.4 mmol). After the mixture was refluxed for 1 hr, finely powdered Na₂SO₄·10H₂O was slowly added at 0 °C. The resulting mixture was stirred at ambient temperature until excess LiAlH₄ was decomposed, and then solids were removed by filtration. The filtrate was concentrated in vacuo to afford a crude alcohol.

To a solution of the crude alcohol in THF/DMF (3/1, 2 mL) was added NaH (60% dispersion in oil, 34 mg, 0.85 mmol) and MeI (0.10 mL, 1.70 mmol) at 0 °C. After the resulting mixture was stirred at room temperature for 24 hr, saturated aqueous solution of NH₄Cl was added at 0 °C. The aqueous layer was extracted with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc=10/1) to afford compound **XII** (30 mg, 69%): IR (neat) 2957, 2923, 2871, 2823, 1636 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.71 (ddd, *J* = 17.0, 10.0, 10.0 Hz, 1 H), 5.34 (dd, *J* = 15.6, 6.8 Hz, 1 H), 5.17 (dd, *J* = 15.6, 8.5 Hz, 1 H), 5.08 (d, *J* = 10.0 Hz, 1 H), 5.03 (d, *J* = 17.0 Hz, 1 H), 3.38 (d, *J* = 6.4 Hz, 2 H), 3.33 (s, 6 H), 3.30 (s, 3 H), 3.14-3.23 (m, 4 H), 2.33-2.41 (m, 1 H), 2.17-2.32 (m, 2 H), 1.74-1.83 (m, 1 H), 1.59-1.69 (m, 2 H), 1.14-1.29 (m, 2 H), 0.96 (d, *J* = 6.8 Hz, 3 H), 0.94 (d, *J* = 7.3 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 22.52, 22.64, 31.03, 36.46, 40.57, 44.92, 45.02, 46.03, 46.31, 58.70, 59.24 (two ¹³C signals were overlapped), 74.62, 77.39, 77.56, 116.26, 130.79, 137.31, 138.77; LR MS (EI, *m/z*) 310 (M⁺), 295, 278, 265, 246, 233; Anal. Calcd for C₁₉H₃₄O₃: C, 73.50; H, 11.04. Found: C, 73.53; H, 11.06.

Conversion of Compound XII to X. A solution of **XII** (20.3 mg, 0.065 mmol) in pentane (2.5 mL) was cooled to -78 °C and treated with a stream of O₃ at -78 °C until the color of the solution had changed to blue. The mixture was treated with a stream of dry O₂ at -78 °C to purge an excess amount of O₃, and then diluted with Et₂O (2.5 mL). To the diluted mixture was added LiAlH₄ (50 mg, 1.3 mmol) at -78 °C and the mixture was allowed to stir at ambient temperature for 6 hr. To this was added Na₂SO₄·10H₂O at 0 °C and the resulting mixture was stirred at room temperature for 2 hr. The solid were removed by filtration, and then filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (CHCl₃/MeOH=10/1) to afford compound **X** (11 mg, 63%).

Procedure for Determination of Stereochemistry of 9e. The stereochemistry of **9e** was determined by the results of NOE experiments for **XII** (Figure S3), which was derived from **9a** according to the procedures shown in Scheme S6.

Scheme S6. Determination of Stereochemistry of **9e**

Preparation of XIII. To a solution of ruthenium catalyst **I'** (1.4 mg, 1.7 μmol) in degassed toluene (1.0 mL) was added a solution of **9e** (6.8 mg, 0.017 mmol) in degassed toluene (1.0 mL). The mixture was stirred at 50 °C for 14 hr and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc=4/1) to afford bicyclic compound **XIII** (4.7 mg, 83%): IR (CHCl₃) 2982, 2933, 2872, 1731, 1629, 1598 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 8.2 Hz, 2 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 5.84-5.90 (m, 2 H), 4.16 (dd, *J* = 10.8, 3.5 Hz, 1 H), 3.96 (ddd, *J* =

12.0, 4.4, 2.6 Hz, 1 H), 3.68 (s, 3 H), 3.15 (dd, $J = 10.5, 1.8$ Hz, 1 H), 2.43 (s, 3 H), 2.37-2.42 (m, 1 H), 2.31 (ddd, $J = 12.0, 12.0, 3.2$ Hz, 1 H), 219 (dd, $J = 10.8, 10.8$ Hz, 1 H), 1.98-2.04 (m, 1 H), 1.73 (dddd, $J = 12.0, 12.0, 12.0, 4.4$ Hz, 1 H), 1.55 (dddd, $J = 12.0, 12.0, 12.0, 2.8$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.59, 28.00, 46.81, 48.76, 50.44, 50.49, 51.93, 53.21, 127.41, 129.55, 131.74, 133.20, 133.48, 143.37, 173.34; LR MS (EI, m/z) 335 (M^+), 303, 276, 198, 180; HR MS (EI, m/z) calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_4\text{S}$ 335.1192, found 335.1188.

Figure S3. Summary of NOE Experiments for **XIII**

Procedure for Determination of Stereochemistry of 10c. Relative configuration of three stereogenic centers, which were indicated as C1, C2, and C3 in Scheme S7, was determined first. According to the procedures shown in Scheme S7, compound **10c** were converted to compound **VI**. The ^1H NMR spectrum of this material was completely identical with that of the material independently derived from **9a** (see Scheme S5). This result indicated that the relative configuration of C1, C2, and C3 in compound **10c**, was same as that of corresponding stereogenic centers in compound **9a**.

Scheme S7. Determination of Relative Configuration of C1, C2, and C3 on **10c**

Subsequently, stereochemistry of C4 was determined (Schemes S8 and S9). Carboxylic acid **10c'**, which was obtained by phenylative carboxylation of **1c** according to the typical procedure, was condensed with (*S*)-phenylglycine methylester [(*S*)-PGME] to afford amide **XV** and **XVI**. These diastereomers could be separated by AgNO_3 -impregnated silica gel column chromatography to afford analytically pure **XV** and **XVI**. Absolute configurations of C1-position of these diastereomers were established according to the Kusumi's method using an anisotropic effect of the chiral auxiliary on ^1H NMR chemical shift.³ The ^1H NMR spectrum of **XV** and **XVI** were compared in detail and the differences of the chemical shifts were calculated. The calculated $\Delta\delta$ values ($\Delta\delta = \delta_{\text{XV}} - \delta_{\text{XVI}}$, see Figure S4) for compound **XV** indicated that the configuration of C1 in compound **XV** is (*S*) and that in **XVI** is (*R*).

Scheme S8. Optical Resolution of **10c'**

^a Isolated yield calculated from the amount of **1c**.

Figure S4. $\Delta\delta$ values for **XV**

The diastereomer **XVI** was then ozonolyzed to afford 2-phenylpropanol **XVII**, whose ¹H NMR spectrum was fully identical with that of commercially available one. The absolute configuration of this material was established to be (*R*) by comparing ¹H NMR spectra of its (*R*)-MTPA ester **XVIII** with those of (*R*)-MTPA esters derived independently from commercially available (*R*)- and (*S*)-2-phenylpropanol.⁴ This result indicated that the absolute configuration of C4-position in **XVI** was (*S*) as shown in Scheme S8. In the consequence of these experiments, the relative configuration of all stereogenic centers in compound **10c** was determined as shown in our manuscripts.

Scheme S8. Determination of Configuration of C4 on **XVI**

Preparation of Compound XIV. To a cooled solution (0 °C) of **10c** (26.4 mg, 0.058 mmol) in Et₂O (2 mL) was added LiAlH₄ (5.5 mg, 0.145 mmol). After the mixture was stirred at 0 °C for 30 min, finely powdered Na₂SO₄·10H₂O was slowly added to this. The resulting mixture was stirred at ambient temperature until excess LiAlH₄ was decomposed, and then solids were removed by filtration. The filtrate was concentrated in vacuo to afford a crude alcohol.

To a solution of the crude alcohol in THF/DMF (3/1, 2 mL) was added NaH (60% dispersion in oil, 9.5 mg, 0.23 mmol) and MeI (30 µL, 0.47 mmol) at 0 °C. After the resulting mixture was stirred at room temperature for 15 hr, saturated aqueous solution of NH₄Cl was added at 0 °C. The aqueous layer was extracted with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc=4/1) to afford compound **XII** (20 mg, 76%): IR (neat) 3025, 2964, 2925, 2873, 1654, 1598 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.2 Hz, 2 H), 7.24-7.34 (m, 5 H), 7.10-7.20 (m, 2 H), 5.47-5.59 (m, 2 H), 5.12 (dd, *J* = 15.5, 8.8 Hz, 1 H), 4.97 (d, *J* = 10.2 Hz, 1 H), 4.95 (d, *J* = 17.4 Hz, 1 H), 3.31-3.42 (m, 3 H), 3.15-3.23 (m, 2 H), 3.18 (s, 3 H), 3.05 (dd, *J* = 8.8, 8.8 Hz, 1 H), 2.89 (dd, *J* = 8.5, 8.5 Hz, 1 H), 2.46-2.58 (m, 1 H), 2.43 (s, 3 H), 2.16-2.24 (m, 1 H), 1.93-2.02 (m, 1 H), 1.28 (d, *J* = 7.0 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 21.20, 21.60, 41.19, 44.45, 44.87, 45.60, 51.09, 53.31, 58.78, 74.31, 117.31, 126.05, 126.97, 127.51, 128.31, 129.53, 136.98, 137.46, 143.29, 145.29; LR MS (EI, *m/z*) 439 (M⁺), 407, 394, 284; Anal. Calcd for C₂₆H₃₃NO₃S: C, 71.04; H, 7.57; N, 3.19. Found: C, 71.21; H, 7.45; N, 3.21.

Conversion of Compound XIV to VI. A solution of **XIV** (14 mg, 0.033 mmol) in pentane/Et₂O (1/1, 5 mL) was cooled to -78 °C and treated with a stream of O₃ at -78 °C until the color of the solution had changed to blue. The mixture was treated with a stream of dry O₂ at -78 °C to purge an excess amount of O₃. To the reaction mixture was added LiAlH₄ (12 mg, 0.31 mmol) at -78 °C and the mixture was allowed to stir at ambient temperature for 7 hr. To this was added Na₂SO₄·10H₂O at 0 °C and the resulting mixture was stirred at room temperature for 2 hr. The solids were removed by filtration, and then filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (CHCl₃/MeOH=10/1) to afford compound **VI** (5.2 mg, 45%).

Preparation of Compound XV and XVI. According to the typical procedure described above, a phenylative carboxylation of **1c** (180 mg, 0.567 mmol) was carried out at 30 °C for 24 hr by using Ni(acac)₂ (29 mg, 0.113 mmol), PPh₃ (59 mg, 0.226 mmol), and Ph₂Zn (0.5 M in xylene, 4.5 mL, 2.25 mmol). After the usual workup procedure (without diazomethane treatment), the obtained material was passed through a short column of silica gel (eluent; hexane/EtOAc=2/1~1/1) to afford crude carboxylic acid **10c'** (156 mg, major impurities were triphenylphosphine oxide and benzoic acid). This material was used for the next reaction without further purification.

To a cooled solution (0 °C) of the crude **10c'** (156 mg) in DMF (3 mL), was added (*S*)-phenylglycine methyl ester hydrochloride (106 mg, 0.53 mmol), diethyl cyanophosphonate (0.11 mL, 0.70 mmol), and Et₃N (0.30 mL, 2.11 mmol). The mixture was stirred at 0 °C for 1 hr, and then diluted with AcOEt. The organic layer was washed with saturated aqueous solution of NaHCO₃ and brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/AcOEt=3/1) to afford compound **XV** and **XVI** as a mixture. Chromatography on AgNO₃-impregnated silica gel (10 wt.% AgNO₃ on silica gel, 230-400 mesh) afforded analytically pure **XV** (51 mg, 15%, colorless crystal) and **XVI** (51 mg, 15%, colorless crystal) along with unseparated mixture (23 mg, 7%). The absolute configuration of these diastereomers were determined according to the Kusumi's method by comparing those high-resolution ¹H NMR spectrum.

Compound XV. mp 146-147 °C (recyst. from AcOEt/hexane); Rf = 0.29 (AcOEt/hexane = 1/1, AgNO₃-impregnated silica gel TLC); IR (neat) 3414, 3022, 2928, 2848, 1742, 1676, 1637, 1599 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.2 Hz, 2 H), 7.13-7.40 (m, 10 H), 7.08 (d, *J* = 7.0 Hz, 2 H), 6.48 (d, *J* = 7.0 Hz, 1 H), 5.62 (ddd, *J* = 17.0, 10.0, 9.7 Hz, 1 H), 5.53 (dd, *J* = 15.2, 6.8 Hz, 1 H), 5.42 (d, *J* = 7.0 Hz, 1 H), 5.08 (dd, *J* = 15.2, 8.2 Hz, 1 H), 5.06 (d, *J* = 17.0 Hz, 1 H), 5.04 (d, *J* = 10.0 Hz, 1 H), 3.72 (s, 3 H), 3.46 (dd, *J* = 10.0, 7.6 Hz, 1 H), 3.36 (dd, *J* = 10.3, 7.6 Hz, 1 H), 3.26 (dd, *J* = 10.3, 6.8 Hz, 1 H), 3.21-3.31 (m, 1 H), 2.86 (dd, *J* = 10.0, 7.6 Hz, 1 H), 2.74 (dd, *J* = 9.7, 8.8 Hz, 1 H), 2.55-2.64 (m, 1 H), 2.42 (s, 3 H), 2.20-2.31 (m, 1 H), 1.22 (d, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.00, 21.57, 42.06, 44.45, 45.36, 50.96, 52.68, 52.82, 53.86, 56.56, 119.15, 126.02, 126.89, 127.05, 127.58, 127.78, 128.27, 128.52, 128.90, 129.56, 133.25, 134.65, 135.79, 137.70, 143.36, 145.22, 170.66, 170.77; LR MS (FAB, *m/z*) 587 (M⁺+1), 431 (M⁺-Ts). Anal. Calcd for C₃₄H₃₈N₂O₅S: C, 69.60; H, 6.53; N, 4.77. Found: C, 69.61; H, 6.49; N, 4.65.

Compound XVI. mp 133-135 °C (recyst. from AcOEt/hexane); Rf = 0.23 (AcOEt/hexane = 1/1, AgNO₃-impregnated silica gel TLC); IR (neat) 3418, 3064, 2977, 2933, 2873, 1741, 1676, 1635, 1598 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.63 (dd, *J* = 8.2 Hz, 1 H), 7.14-7.40 (m, 10 H), 7.07 (d, *J* = 6.8 Hz, 2 H), 6.53 (d, *J* = 7.0 Hz, 1 H), 5.68 (dd, *J* = 17.0, 10.0, 9.0 Hz, 1 H), 5.44 (d, *J* = 7.0 Hz, 1 H), 5.41 (dd, *J* = 15.6, 6.8 Hz, 1 H), 5.11 (d, *J* = 17.0 Hz, 1 H), 5.09 (d, *J* = 10.0 Hz, 1 H), 5.06 (dd, *J* = 15.6, 7.3 Hz, 1 H), 3.70 (s, 3 H), 3.42 (dd, *J* = 9.7, 7.3 Hz, 1 H), 3.28 (qd, *J* = 7.0, 6.8 Hz, 1 H), 3.23 (dd, *J* = 10.3, 7.3 Hz, 1 H), 3.08 (dd, *J* = 10.3, 6.4 Hz, 1 H), 2.83 (dd, *J* = 9.7, 7.6 Hz, 1 H), 2.71 (dd, *J* = 9.0, 9.0 Hz, 1 H), 2.48-2.57 (m, 1 H), 2.40 (s, 3 H), 2.18-2.28 (m, 1 H), 1.21 (d, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 20.95, 21.53, 42.03, 44.36, 45.28, 50.95, 52.63, 52.81, 53.89, 56.38, 119.43, 126.02, 126.87, 127.11, 127.51, 127.78, 128.26, 128.53, 128.94, 129.51, 133.05, 134.46, 136.11, 137.59, 143.36, 145.15, 170.60, 170.80; LR MS (FAB, *m/z*). Anal. Calcd for C₃₄H₃₈N₂O₅S: C, 69.60; H, 6.53; N, 4.77. Found: C, 69.67; H, 6.53; N, 4.77.

Ozonolysis of Compound XVI. A solution of **XVI** (17 mg, 0.029 mmol) in MeOH (3 mL) was cooled to -78 °C and treated with a stream of O₃ at -78 °C until the color of the solution had changed to blue (ca. 5 min). The solution was then treated with a stream of dry O₂ at -78 °C to purge an excess amount of O₃ (ca. 10 min) and NaBH₄ (22 mg, 0.58 mmol) was added. The mixture was stirred for 1 hr at low temperature and for additional 1 hr at 0 °C, then H₂O was added. The solvent was evaporated in vacuo and 10% HCl was added. The mixture was extracted with Et₂O and the organic layer was washed with sat. NaHCO₃, brine and dried over Na₂SO₄. Removal of the solvent in vacuo and silica gel column chromatography (hexane/AcOEt=4/1) afforded 2-phenylpropanol **XVII** (3.1 mg, 45%, colorless oil). ¹H and ¹³C NMR spectra of **XVII** were completely identical with those of commercially available authentic sample. ¹H NMR (400 MHz, CDCl₃) δ 7.31-7.37 (m, 2 H), 7.21-7.27 (m, 3 H), 3.71 (br d, *J* = 6.7 Hz, 2 H), 2.96 (qd, *J* = 7.0, 6.7 Hz, 1 H), 1.29 (d, *J* = 7.0 Hz, 3 H), 1.25 (br s, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 17.59, 42.37, 68.56, 126.47, 127.33, 128.43, 143.56

Preparation of (R)-MTPA Ester of Compound XVII. To establish the absolute configuration of compound **XVII**, this material was converted to (R)-MTPA ester. To a solution of **XVII** (3.1 mg, 0.023 mmol) in CH₂Cl₂ (0.2 mL), were successively added DMAP (6mg, 0.049 mmol), DCC (15 mg, 0.73 mmol), and a solution of (R)-MTPA (11 mg, 0.047 mmol) in CH₂Cl₂ (0.3 mL). The mixture was stirred at room temperature for 13 hr. Chromatography of this mixture on silica gel (hexane/EtOAc=25/1) afforded (R)-MTPA ester of **XVII** (8.0 mg, 100%, colorless oil). ¹H NMR spectrum of this material was completely identical with that of (R)-MTPA ester prepared from (R)-phenylpropanol. ¹H NMR (400 MHz,

CDCl₃) δ 7.18-7.42 (m, 10 H), 4.51 (dd, J = 10.8, 6.7 Hz, 1 H), 4.31 (dd, J = 10.8, 7.0 Hz, 1 H), 3.41 (s, 3 H), 3.19 (qdd, J = 7.0, 7.0, 6.7 Hz, 1 H), 1.29 (d, J = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 17.93, 38.71, 55.34, 121.73, 124.59, 126.80, 127.22, 128.23, 128.27, 128.47, 129.40, 132.03, 142.16, 166.36.

Preparation of (*R*)-MTPA Ester of (*R*)-2-Phenylpropanol. To a solution of (*R*)-2-phenylpropanol (10 mg, 0.073 mmol) in CH₂Cl₂ (0.5 mL), were successively added DMAP (18 mg, 0.14 mmol), DCC (45 mg, 0.22 mmol), and a solution of (*R*)-MTPA (30 mg, 0.13 mmol) in CH₂Cl₂ (0.5 mL). The mixture was stirred at room temperature for 24 hr. Chromatography of this mixture on silica gel (hexane/EtOAc=25/1) afforded (*R*)-MTPA ester (17 mg, 66%, colorless oil). ¹H NMR spectrum of this material was fully identical with that of (*R*)-MTPA ester derived from compound **XVII**.

Preparation of (*R*)-MTPA ester of (*S*)-Phenylpropanol. To a solution of (*S*)-2-phenylpropanol (10 mg, 0.073 mmol) in CH₂Cl₂ (0.5 mL), were successively added DMAP (18 mg, 0.14 mmol), DCC (45 mg, 0.22 mmol), and a solution of (*R*)-MTPA (30 mg, 0.13 mmol) in CH₂Cl₂ (0.5 mL). The mixture was stirred at room temperature for 48 hr. Chromatography of this mixture on silica gel (hexane/EtOAc=25/1) afforded (*R*)-MTPA ester (23 mg, 90%, colorless oil). ¹H NMR spectrum of this material was not identical with that of (*R*)-MTPA ester derived from **XVII**. Most significant difference was seen in a chemical shift of methoxy group of MTPA moiety. The signal of methoxy group appeared at 3.39 ppm in the case of (*R*)-MTPA ester derived from (*S*)-2-phenylpropanol derivative but at 3.41 ppm in the case of (*R*)-2-phenylpropanol derivative. ¹H NMR (400 MHz, CDCl₃) δ 7.17-7.39 (m, 10 H), 4.48 (dd, J = 10.8, 7.6 Hz, 1 H), 4.32 (dd, J = 10.8, 6.7 Hz, 1 H), 3.39 (s, 3 H), 3.17 (dq, J = 7.6, 7.0, 6.7 Hz, 1 H), 1.29 (d, J = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 18.03, 38.82, 55.31, 71.23, 121.72, 124.58, 126.83, 127.16, 127.21, 128.25, 128.51, 129.38, 132.10, 142.38, 166.31.

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