

## Total Synthesis of (+)-Virgatusin via $\text{AlCl}_3$ -Catalyzed [3 + 2] Cycloaddition

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### *Supporting Information*

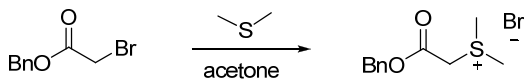
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### **Experimental Section**

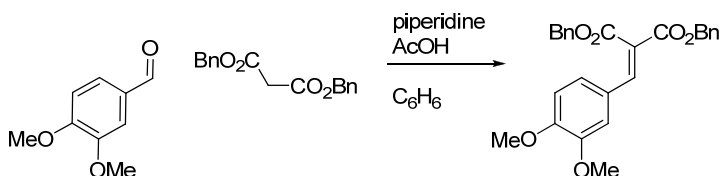
**Materials and Methods: General Information.** Infrared (IR) spectra were obtained using a JACSO FT/IR 460-plus infrared spectrometer. Proton and carbon nuclear magnetic resonance spectra ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) were recorded on the following instruments: Bruker model Avance 400 ( $^1\text{H}$  NMR at 400 MHz and  $^{13}\text{C}$  NMR at 100 MHz) and Varian Gemini 300 ( $^1\text{H}$  NMR at 300 MHz and  $^{13}\text{C}$  at 75 MHz) spectrometers with solvent resonance as the internal standard ( $^1\text{H}$  NMR:  $\text{CDCl}_3$  at 7.27 ppm or TMS at 0.00 ppm and  $^{13}\text{C}$  NMR:  $\text{CDCl}_3$  at 77.0 ppm).  $^1\text{H}$  NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, t = triplet, q = quartet, quint = quintuplet, sep = septet, m = multiplet), coupling constants (Hz), and integration. Combustion analyses were performed by Atlantic Microlab Inc., Norcross, GA. Analytical thin layer chromatography (TLC) was performed on Whatman 0.25 mm silica gel 60 plates. Mass spectra were obtained on a Micromass Quattro II Triple Quadrupole Spectrometer using ESI ionization. Structural assignments were made using NOESY experiments. Enantiomeric ratios were obtained using a Berger Supercritical fluid Chromatograph mode FCM 1100/1200 equipped with an Agilent 1100 series UV-Vis detector using one of the following chiral HPLC columns: Chiralcel Chiralpak AD, WO, or OD column. Samples were eluted with SFC grade  $\text{CO}_2$  and the indicated percentage of MeOH. Visualization was accomplished with UV light and aqueous ceric ammonium nitrate molybdate solution followed by heating. Purification of the reaction products was carried out by flash chromatography using Sorbent Technologies silica gel 60 (32-63  $\mu\text{m}$ ). Yield refers to isolated yield of analytically pure material. Yields are reported for a specific experiment and as a result may differ slightly from those found in the tables and equations, which are averages of at least two experiments. Methylene chloride, THF, and toluene were dried by passage through a

column of neutral alumina under nitrogen prior to use. Unless otherwise noted, reagents were obtained from commercial sources and used without further purification.



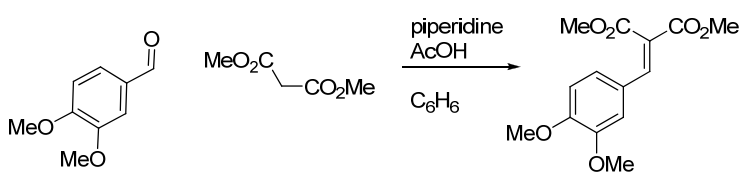
**(2-benzyloxy)-2-oxoethyl dimethylsulfonium bromide:** Benzylbromoacetate (30.00 g, 131 mmol) was stirred with dimethyl sulfide (9.76 g, 157.2 mmol) in 10 mL of acetone. The reaction was allowed to stir overnight. During the course of the reaction small portions of acetone were added to aid in stirring the white precipitate that is formed. An ice bath can be used if the product does not fully precipitate. The mixture was filtered and the white solid was washed with cold hexanes to obtain 29.7 g (78%) of the dimethylsulfonium bromide. The filtrate can be concentrated to obtain more material if desired.

Analytical data: **mp** 94-95 °C; **IR** (thin film,  $\text{cm}^{-1}$ ) 2970, 2723, 1719, 1459, 1377, 1156;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (s, 5H), 5.26 (s, 2H), 5.19 (s, 2H), 3.37 (s, 6H);  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 134.0, 129.0, 128.8, 128.7, 128.6, 68.9, 44.3, 25.3; **Anal.** Calcd. for  $\text{C}_{11}\text{H}_{15}\text{BrO}_2\text{S}$ : C, 45.37; H, 5.19. Found: C, 45.23; H, 5.13; **HRMS** (ESI) calcd. for  $\text{C}_{11}\text{H}_{15}\text{O}_2\text{S} [\text{M}]^+$ : 211.0787. Found  $[\text{M}]^+ = 211.0777$ .



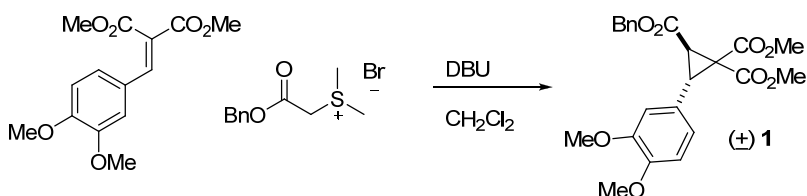
**Dibenzyl 2-(3,4-dimethoxybenzylidene)malonate:** A 250 mL round-bottomed flask equipped with a Dean-stark trap, condenser, and stirbar was charged with benzene (45 mL), dibenzyl malonate (14 g, 49.2 mmol), 3,4-dimethoxybenzaldehyde (9.82 g, 59.1 mmol), and 5 mol % piperidinium acetate. The mixture was brought to reflux and allowed to stir for 16 hours upon which TLC analysis showed disappearance of starting material. The reaction was allowed to cool to room temperature. The clear orange liquid was diluted with 20 mL of  $\text{C}_6\text{H}_6$  and washed twice with 1 M HCl (25 mL). The organic layer was washed once with saturated  $\text{NaHCO}_3$  (20 mL) and once with brine (30 mL). The organic portion was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to an orange oil. The material formed a solid upon standing and was recrystallized with EtOAc/hexanes to yield 16.6 g (78%) of the benzylidene malonate.

Analytical data: **mp** 74-75 °C; **IR** (thin film,  $\text{cm}^{-1}$ ) 2957, 2838, 1729, 1517, 1255, 1226, 1191, 1144;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (s, 1H), 7.36-7.27 (m, 10H), 7.02-6.99 (m, 2H), 6.75 (d,  $J = 8.4$  Hz, 1H), 5.29 (d,  $J = 10.8$  Hz), 3.90 (s, 3H), 3.75 (s, 3H);  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 164.2, 151.5, 149.0, 143.1, 135.7, 135.1, 128.6, 128.5, 128.4, 128.2, 128.0, 125.5, 124.3, 123.3, 112.0, 111.1, 67.4, 55.9, 55.8; **TLC** (30% EtOAc/hexanes)  $R_f$  0.31; **Anal.** Calcd. for  $\text{C}_{26}\text{H}_{24}\text{O}_6$ : C, 72.21; H, 5.59. Found: C, 71.97; H, 5.61; **HRMS** (ESI) calculated for  $\text{C}_{26}\text{H}_{24}\text{O}_6\text{Cs} [\text{M}+\text{Cs}]^+$ : 565.0627. Found:  $[\text{M}+\text{Cs}]^+ = 565.0651$ .



**Dimethyl 2-(3,4-dimethoxybenzylidene)malonate:** A 250 mL round bottomed flask equipped with a Dean-stark trap, condenser, and stirbar was charged with benzene (45 mL), dimethyl malonate (10 g, 75.7 mmol), 3,4-dimethoxybenzaldehyde (15.1 g, 90.8 mmol), and 10 mol % piperidinium acetate. The mixture was brought to reflux and allowed to stir for 24 hours upon which TLC analysis showed disappearance of starting material. The reaction was allowed to cool to room temperature. The clear orange liquid was diluted with C<sub>6</sub>H<sub>6</sub> (20 mL) and washed with 1M HCl (25 mL). The organics were then washed once with saturated NaHCO<sub>3</sub> (20 mL) and once with brine (30 mL). The organic portion was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to an orange oil. The material formed a solid upon standing and was recrystallized with EtOAc/hexanes to yield 17.6 g (83%) of the benzylidene malonate.

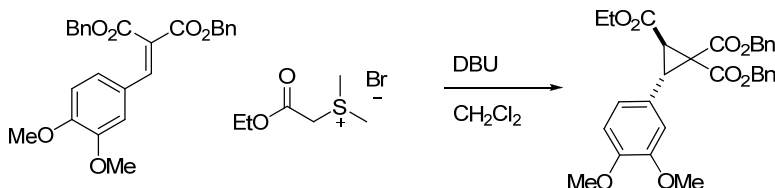
Analytical Data: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.71 (s, 1H), 7.09-7.07 (m, 1H), 7.00-6.99 (m, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H), 3.88 (s, 6H), 3.85 (s, 3H). Complete analytical data for this compound has been published previously.<sup>1</sup>



**(2*R*,3*S*)-2-benzyl 1,1-dimethyl 3-(3,4-dimethoxyphenyl)cyclopropane-1,1,2-tricarboxylate (±)-1:** The sulfonium salt (8.3 g, 28.4 mmol) was placed in a round-bottomed flask under N<sub>2</sub> and partially dissolved in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> at 0 °C. DBU (4.2 mL, 28.4 mmol) was added and the mixture was allowed to stir for 30 minutes, at which time all solids had gone into solution. The benzylidene malonate (5.3 g, 18.9 mmol) was added and the reaction was allowed to stir at 0 °C for 12 hours. The reaction was then washed with 1 M HCl (20 mL) and brine (20 mL). The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated. The material was subjected to flash chromatography with 30% EtOAc/hexanes to give 6.6 g (82%) of the product as a viscous liquid. Upon standing, this material formed a white solid. This material can also be purified by adding MeOH to precipitate the solid and recrystallizing with EtOAc/hexanes.

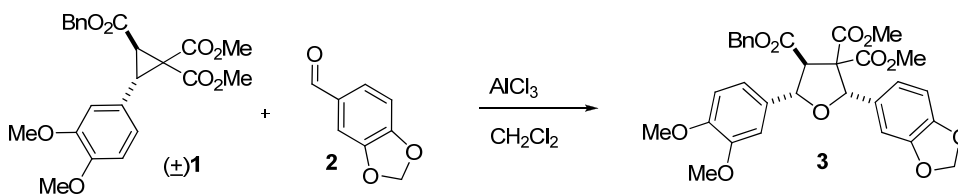
Analytical data: mp 70-72 °C; IR (thin film, cm<sup>-1</sup>) 2954, 2838, 1739, 1590, 1520, 1252, 1162, 1027; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39-7.36 (m, 5H), 6.78-6.76 (m, 3H), 5.21 (d, *J* = 12 Hz, 1H), 5.15 (d, *J* = 12 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.68 (s, 3H), 3.62 (d, *J* = 7.6 Hz, 1H), 3.51 (s, 3H), 3.26 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR δ 168.9, 166.4, 165.6, 148.7, 148.6, 135.2, 128.6, 128.6, 128.5, 125.1, 120.8, 111.6, 110.8, 67.4, 55.9, 55.8, 53.0, 53.0, 44.3, 35.8, 31.3; TLC (30% EtOAc/hexanes) R<sub>f</sub> 0.18; Anal. Calcd. for

$C_{23}H_{24}O_8$ : C, 64.48; H, 5.65. Found: C, 64.59; H, 5.61; **HRMS (ESI)** calculated for  $C_{23}H_{24}O_8Cs$   $[M+Cs]^+$ : 565.0525. Found:  $[M+Cs]^+$  = 565.0651.



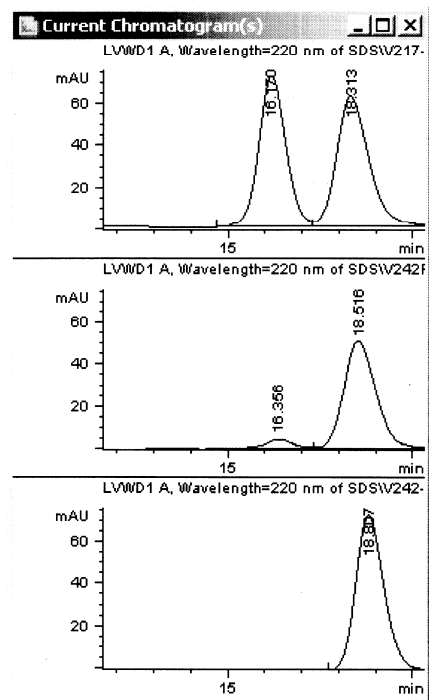
**(2*R*,3*S*)-1,1-dibenzyl 2-ethyl 3-(3,4-dimethoxyphenyl)cyclopropane-1,1,2-tricarboxylate**: The sulfonium salt (6 g, 13.9 mmol) was placed in a round-bottomed flask under  $N_2$  and partially dissolved in 20 mL of toluene/ $CH_2Cl_2$  (3:2) at 0 °C. DBU (3.1 mL, 20.8 mmol) was added and the mixture was allowed to stir for 30 minutes. At this time, all solids had gone into solution. The benzylidene malonate (4.8 g, 20.8 mmol) was added and the reaction was allowed to stir at 45 °C for 6 hours. The reaction was then washed with 1 M HCl (20 mL) and brine (20 mL). The organic layer was dried with  $Na_2SO_4$  and concentrated. Upon standing, a solid was formed which was recrystallized with EtOH to give 6.7 g (80%) of the product as a white solid.

Analytical data: **mp** 98-100 °C; **IR** (thin film,  $cm^{-1}$ ) 2959, 2837, 1734, 1520, 1456, 1252, 1028;  **$^1H$  NMR** (400MHz,  $CDCl_3$ )  $\delta$  7.35-7.22 (m, 7H), 6.99 (d,  $J$  = 6.8 Hz, 1H), 6.79-6.71 (m, 3H), 5.25 (d,  $J$  = 12.4 Hz, 1H) 5.21 (d,  $J$  = 12.4 Hz, 1H), 4.96 (d,  $J$  = 12 Hz, 1H), 4.87 (d,  $J$  = 12 Hz, 1H) 4.17-4.11 (m, 2H), 3.87 (s, 3H), 3.75 (s, 3H), 3.67 (d,  $J$  = 7.6 Hz, 1H), 3.26 (d,  $J$  = 7.6 Hz, 1H) 1.26 (t,  $J$  = 7.2 Hz, 3H);  **$^{13}C$  NMR**  $\delta$  168.8, 165.8, 165.1, 148.8, 148.6, 135.4, 134.9, 128.5, 128.4, 128.3, 128.2, 128.1, 125.1, 121.1, 111.9, 110.8, 67.8, 67.5, 61.6, 55.8, 44.3, 35.8, 31.5, 14.1; **TLC** (30% EtOAc/hexane)  $R_f$  0.32; **Anal.** Calcd. for  $C_{30}H_{30}O_8$ : C, 69.49; H, 5.83. Found: C, 69.30; H, 5.81; **HRMS (ESI)** calculated for  $C_{30}H_{30}O_8Cs$   $[M+Cs]^+$ : 651.0995. Found:  $[M+Cs]^+$  = 651.1064.

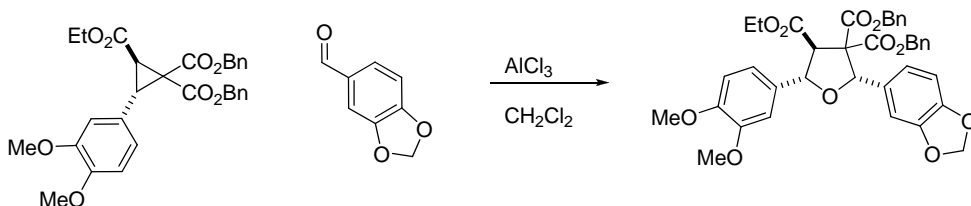


**(2*S*,4*S*,5*S*)-4-benzyl 3,3-dimethyl 2-(benzo[*d*][1,3]dioxol-5-yl)-5-(3,4-dimethoxyphenyl)dihydrofuran-3,3,4(2*H*)-tricarboxylate (3)**: A 125 mL round bottom flask with a stirbar was charged with 9.8 g of the cyclopropane (23 mmol), aldehyde (6.9 g, 46 mmol), and  $AlCl_3$  (0.46 g, 3.5 mmol). Outside the glove box,  $CH_2Cl_2$  was added under  $N_2$  and the reaction was allowed to stir at room temperature. The reaction was allowed to become homogenous and then diluted with diethyl ether after 5 minutes. The solution was run through a silica plug with  $CH_2Cl_2$  and concentrated. The reaction was flashed with 60% ether/petroleum ether to give the product in 80 % yield (10.7 g). Upon concentration the cycloadduct was obtained as an oil; MeOH can be used to precipitate the product, which can be recrystallized with EtOAc/hexanes to give a white solid. This material was also synthesized asymmetrically from (2*R*,3*S*)-1 on a 0.55 mmol (0.24 g) scale. The crude material measured 90:10 er by chiral SFC analysis. After a single

recrystallization the er was 99:1 (Chiralpak AD, 6.0% MeOH, 2.0 mL/min, 200 psi, 27 °C, 220 nm,  $t_{r-major}$ , 18.5 min,  $t_{r-minor}$  16.3 min).



Analytical data:  $[\alpha]_D^{24.7}$  -15.5 ( $c = 0.40$ ,  $\text{CH}_2\text{Cl}_2$ ) at 80 % ee;  $[\alpha]_D^{24.5}$  -20.32 ( $c = 0.50$ ,  $\text{CH}_2\text{Cl}_2$ ) at 98 % ee; **mp** 117-118; **IR** (thin film,  $\text{cm}^{-1}$ ) 2953, 1735, 1519, 1446, 1265, 1165, 1036;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.025 (m, 8H), 6.99 (d,  $J = 8$  Hz, 1H), 6.83 (d,  $J = 8.4$  Hz, 1H), 6.78 (d,  $J = 8.4$  Hz, 1H), 5.94 (s, 2H), 5.75 (s, 1H), 5.11 (m, 2H), 5.02 (d,  $J = 8.8$  Hz, 1H), 4.13, (d,  $J = 8.8$  Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.51 (s, 3H) 3.26 (s, 3H);  **$^{13}\text{C}$  NMR**  $\delta$  171.1, 168.5, 168.5, 149.4, 149.2, 147.6, 147.3, 135.4, 130.7, 130.3, 128.5, 128.3, 128.3, 120.8, 119.4, 111.1, 110.1, 107.8, 107.8, 101.0, 84.85, 83.8, 69.1, 67.0, 58.9, 55.9, 55.9, 52.7, 52.5; **Anal.** Calcd. for  $\text{C}_{31}\text{H}_{30}\text{O}_{11}$ : C, 64.35; H, 5.23. Found: C, 64.33; H, 5.12; **HRMS (ESI)** calculated for  $\text{C}_{31}\text{H}_{30}\text{O}_{11}\text{Cs}$   $[\text{M}+\text{Cs}]^+$  : 711.0842. Found:  $[\text{M}+\text{Cs}]^+ = 711.0831$ .



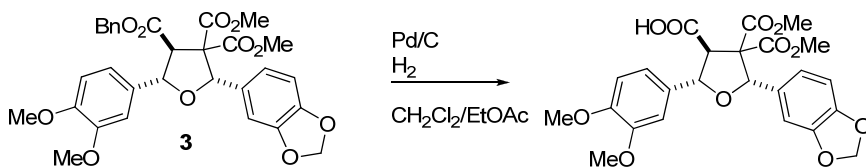
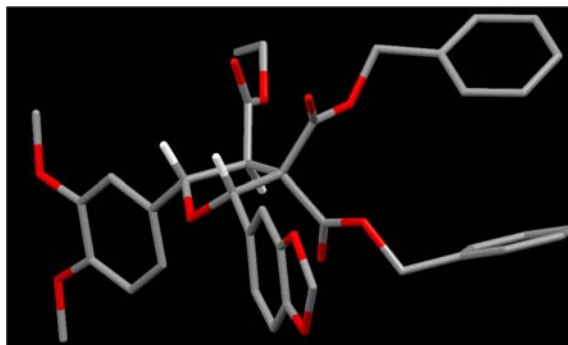
**(2*S*,4*S*,5*S*)-3,3-dibenzyl 4-ethyl 2-(benzo[*d*][1,3]dioxol-5-yl)-5-(3,4-dimethoxyphenyl) dihydrofuran-3,3,4(2*H*)-tricarboxylate:** A 125 mL round bottom flask with a stirbar was charged with 1.29 g of the cyclopropane (2.5 mmol), piperonal (0.75 g, 5 mmol), and  $\text{AlCl}_3$  (0.07 g, 0.5 mmol). Outside the glove box,  $\text{CH}_2\text{Cl}_2$  was added under  $\text{N}_2$  and the reaction was allowed to stir. The reaction was allowed to become homogenous and then diluted with diethyl ether after 5 minutes. The solution was run through a silica plug and

concentrated. The reaction was flashed with 60% ether/petroleum ether to give the product in 81 % yield (1.35 g). Upon concentration the cycloadduct was obtained as an oil; MeOH can be used to precipitate the product as a white solid, which can be recrystallized with EtOAc/hexanes.

Analytical data: **mp** 129-130 °C; **IR** (thin film,  $\text{cm}^{-1}$ ) 2937, 2834, 1733, 1519, 1447, 1264, 1037;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23-7.04 (m, 12 H), 6.92 (s, 1H), 6.90 (s, 1H), 6.86 (d,  $J = 8.4$  Hz, 1H), 6.71 (d,  $J = 8.4$  Hz, 1H), 5.88 (d,  $J = 13.6$  Hz, 2H), 5.80 (s, 1H), 5.14 (d,  $J = 12$  Hz, 1H), 5.06 (d,  $J = 8.8$  Hz, 1H), 5.00 (d,  $J = 12$ , 1H), 4.84 (d,  $J = 12.4$  Hz, 1H), 4.41 (d,  $J = 12.4$  Hz, 1H), 4.11 (d,  $J = 8.8$  Hz, 1H), 3.97-3.95 (m, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.85-3.83 (m, 1H), 1.07 (t,  $J = 6.8$  Hz, 3H);  **$^{13}\text{C NMR}$**   $\delta$  149.3, 149.1, 147.6, 147.3, 134.6, 134.5, 130.8, 130.1, 128.5, 128.4, 128.3, 128.2, 127.9, 120.8, 119.4, 110.9, 109.9, 107.9, 101.0, 84.9, 83.9, 69.2, 67.8, 61.3, 59.0, 55.9, 14.0; TLC (30% EtOAc/hexane)  $R_f$  0.21; **Anal.** Calcd. for  $\text{C}_{38}\text{H}_{36}\text{O}_{11}$ : C, 68.25; H, 5.43. Found: C, 68.03; H, 5.53; **HRMS (ESI)** calculated for  $\text{C}_{38}\text{H}_{36}\text{O}_{11}\text{Cs}$   $[\text{M}+\text{Cs}]^+$  : 801.1312. Found:  $[\text{M}+\text{Cs}]^+ = 801.1338$ .

The relative stereochemistry was confirmed via an X-ray diffraction study. CCDC 734858 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via

[www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

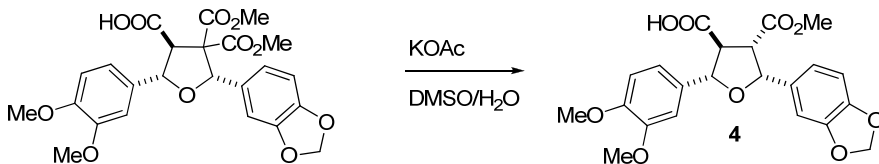


**(2*S*,3*S*,5*S*)-5-(benzo[*d*][1,4]dioxol-5-yl)-2-(3,4-dimethoxyphenyl)-4,4-**

**bis(methoxycarbonyl)tetrahydrofuran-3-carboxylic acid:** 10 % Pd/C (975 mg, 0.92 mmol) was added to a round bottom flask. The benzyl ester cycloadduct (5.3 g, 9.2 mmol) was then added in a 9:1  $\text{CH}_2\text{Cl}_2/\text{EtOAc}$  mixture. A hydrogen balloon was added and the reaction was allowed to stir for 18 hours. After removal of the hydrogen balloon, the reaction contents were run through a celite plug and washed with EtOAc and  $\text{CH}_2\text{Cl}_2$ . To ensure product removal from the celite, a final wash was done with 5% MeOH/ $\text{CH}_2\text{Cl}_2$ . This material was also synthesized asymmetrically on a 0.4 mmol (0.22 g) scale.

Analytical data:  $[\alpha]_D^{24.5} -24.1$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ); **mp** 129 °C; **IR** (thin film,  $\text{cm}^{-1}$ ) 2954, 2841, 1734, 1610, 1519, 1446, 1265, 1037;  **$^1\text{H NMR}$**  (400MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-6.99 (m, 4H), 6.86 (d,  $J = 8$  Hz, 1H), 6.77 (d,  $J = 8.8$  Hz, 1H), 5.94 (s, 2H), 5.72 (s, 1H), 5.04 (d,  $J = 8.8$  Hz, 1H), 4.12 (d,  $J = 9.2$  Hz, 1H), 3.93 (s, 3H), 3.88 (s, 3H), 3.67 (s, 3H), 3.28 (s,

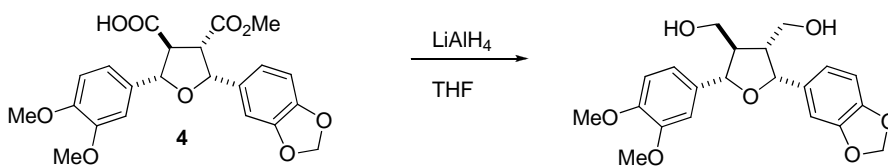
3H);  $^{13}\text{C}$  NMR  $\delta$  176.4, 168.4, 168.4, 149.6, 149.3, 147.7, 147.3, 130.3, 130.0, 120.8, 119.6, 111.1, 110.2, 107.9, 107.7, 101.1, 84.8, 83.5, 69.4, 58.6, 56.0, 55.9, 52.8, 52.7; TLC (5% MeOH/CH<sub>2</sub>Cl<sub>2</sub>) R<sub>f</sub> 0.31; **HRMS (ESI)** calculated for C<sub>24</sub>H<sub>24</sub>O<sub>11</sub>Cs [M+Cs]<sup>+</sup>: 621.0373. Found: [M+Cs]<sup>+</sup> = 621.0340.



**(2*S*,3*S*,4*S*,5*R*)-5-(benzo[*d*][1,3]dioxol-5-yl)-2-(3,4-dimethoxyphenyl)-4-**

**(methoxycarbonyl)tetrahydrofuran-3-carboxylic acid (4):** The tetrahydrofuran acid (3.0 g, 6.1 mmol) was added to a reaction tube with KOAc (1.2 g, 12.3 mmol). DMSO (10 mL) was added to dissolve the reagents followed by 0.5 mL of H<sub>2</sub>O. The reaction tube was heated to 100 °C with stirring. After 16 hours the reaction was allowed to cool to room temperature and partitioned between Et<sub>2</sub>O (20 mL) and H<sub>2</sub>O (20 mL). After separation, the aqueous layer was extracted with three portions of Et<sub>2</sub>O (20 mL). The combined organic extracts were washed with three portions of H<sub>2</sub>O (20 mL), brine (20 mL), dried over MgSO<sub>4</sub>, filtered and concentrated under rotary evaporation. This material was also synthesized asymmetrically on a 0.3 mmol (0.16 g) scale.

Analytical data:  $[\alpha]_{\text{D}}^{24.9}$  33.3 (*c* = 1.00, CH<sub>2</sub>Cl<sub>2</sub>); **IR** (thin film, cm<sup>-1</sup>) 2951, 2834, 1735, 1519, 1445, 1242, 1035;  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 (s, 1H), 7.16-7.13 (m, 1H), 6.91-6.78 (m, 4H), 5.97 (s, 2H), 5.26 (d, *J* = 7.6 Hz, 1H), 5.02 (d, *J* = 6.8 Hz, 1H), 3.96 (s, 3H), 3.91 (s, 3H), 3.80-3.77 (m, 2 H), 3.33 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  177.3, 171.5, 149.3, 149.2, 147.4, 147.4, 131.1, 130.8, 120.1, 119.7, 110.9, 110.2, 108.1, 107.1, 101.1, 83.3, 82.4, 56.0, 55.9, 54.4, 54.3, 52.0; TLC (5% MeOH/CH<sub>2</sub>Cl<sub>2</sub>) R<sub>f</sub> 0.34; **Anal.** Calcd. for C<sub>22</sub>H<sub>22</sub>O<sub>9</sub>: C, 61.39; H, 5.15. Found: C, 61.10; H, 5.26; **HRMS (ESI)** calculated for C<sub>22</sub>H<sub>22</sub>O<sub>9</sub>Cs [M+Cs]<sup>+</sup>: 563.0318. Found: [M+Cs]<sup>+</sup> = 563.0321.



**((2*R*,3*R*,4*R*,5*S*)-2-(benzo[*d*][1,3]dioxol-5-yl)-5-(3,4-**

**dimethoxyphenyl)tetrahydrofuran-3,4-diyl)dimethanol:** A solution of 1 M LiAlH<sub>4</sub> (7.5 mL) in THF (10 mL) at 0 °C was treated with a solution of the cycloadduct (1.15 g, 2.5 mmol) in THF (5 mL) via syringe. After the addition the reaction was allowed to warm to room temperature with stirring. After two hours the reaction was quenched with 0.5 mL H<sub>2</sub>O, 0.5 mL of a 15% NaOH solution, and 1.5 mL of H<sub>2</sub>O. The solution was filtered through a Buchner funnel and the filter cake was washed with several portions of Et<sub>2</sub>O (5 mL). The filtrate was dried over MgSO<sub>4</sub>, filtered, and concentrated by rotary evaporation affording a white solid in 99% yield (0.97 g). This material was also synthesized asymmetrically on a 0.3 mmol (0.15 g) scale.













































