JOC The Journal of Organic Chemistry

Note

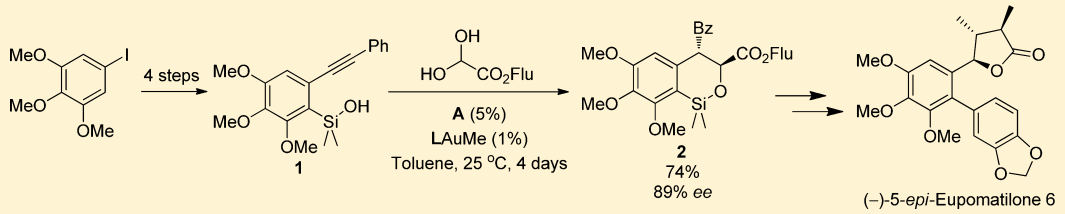
pubs.acs.org/joc

Hybrid Gold/Chiral Brønsted Acid Relay Catalysis Allows an Enantioselective Synthesis of (−)-5-*epi*-Eupomatilone-6

Xiang Wu,* Ming-Li Li, and Pu-sheng Wang

Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

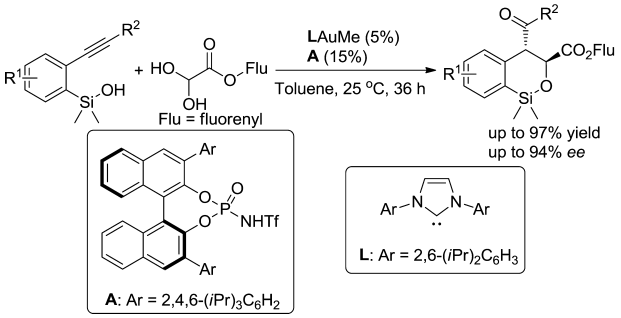
Supporting Information



ABSTRACT: An enantioselective synthesis of (−)-5-*epi*-eupomatilone-6 has been accomplished by using relay catalytic cascade intramolecular hydrosiloxylation and Mukaiyama aldol reaction of 2,3,4-trimethoxy-6-(phenylethynyl)phenyl dimethylsilanol with fluorenylglyoxylate.

Lignans, a large family of phenylpropanoid dimers, have been found in more than 70 families of plants (Figure 1).[1] The biological activities of lignans are diverse, including antitumor, anti-inflammatory, immunosuppression, and so on.[1] In 1991, eupomatilone-6 (Figure 1) and its analogues were isolated from the Australian shrubs *Eupomatia bennettii* by Carroll and Taylor.[2] Later, the stereochemistry of eupomatilone-6 was revised by Coleman and co-workers.[3] Eupomatilone-6 and the epimers have been synthesized by several groups.[3−6] The catalytic enantioselective build-up of stereogenic centers in these syntheses includes asymmetric Sharpless dihydroxylation,[5] enantioselective desymmetrization of mesocyclic anhydrides,[6] dynamic kinetic resolution of unsaturated lactones by using copper-catalyzed reductions,[7] and asymmetric [2,3]-Wittig rearrangement as well.[8] Although the asymmetric catalytic methods provided efficient access to these chiral molecules, the development of new asymmetric synthetic pathways remains highly desired. Herein, we will report that the asymmetric relay catalytic cascade intramolecular hydrosiloxylation and Mukaiyama aldol reaction could be applied to an enantioselective synthesis of eupomatilone-6 or its epimers.

Very recently, we established a practical relay catalytic cascade intramolecular hydrosiloxylation of arylacetylenes and asymmetric Mukaiyama aldol reactions by using a gold complex and chiral Brønsted acid binary system (eq 1).[9] This reaction actually inspired us to investigate a new approach to access eupomatilone-6.



(1)

The retrosynthetic analysis indicates that the eupomatilone-6 and its epimers could be accessed from optically pure lactone **3** presumably by Suzuki−Miyaura coupling. The lactone **3** would be prepared from a conjugate addition to the unsaturated lactone **4**, which might be synthesized from chiral intermediate **5** by dehydration reaction. The chiral intermediate **5** would be reached by a series of classical transformations from **6**, which would be conveniently prepared from the compound **2** by Baeyer−Villiger oxidation and Arndt−Eistert reaction (Scheme 1).

Following up the consideration of the retrosynthetic analysis, the starting material, 2,3,4-trimethoxy-6-(phenylethynyl)phenyl dimethylsilanol **1**, was first prepared from the commercially available 3,4,5-trimethoxyiodobenzene **7** (Scheme 2). The bromination of 3,4,5-trimethoxyiodobenzene **7** in AcOH gave rise to 2-bromo-1-iodo-3,4,5-trimethoxybenzene **8**, which directly underwent Sonogashira coupling[10] with ethynylbenzene in the presence of $Pd(Ph_3P)_2Cl_2$ and CuI to furnish the corresponding alkyne **9** in overall 95% yield in two steps. The lithiation of **9** with *n*-butyllithium at −78 °C afforded the corresponding organolithium intermediate, which reacted with chlorodimethylsilane to deliver a 2,3,4-trimethoxy-6-(phenylethynyl)phenyl dimethylsilane **10** in 92% yield.[11] The oxidation of **10** catalyzed by a ruthenium complex $[RuCl_2(p\text{-Cymene})]_2$ afforded 2,3,4-trimethoxy-6-(phenylethynyl)phenyl dimethylsilanol **1** in 94% yield.[12]

Received: October 30, 2013
Published: December 12, 2013

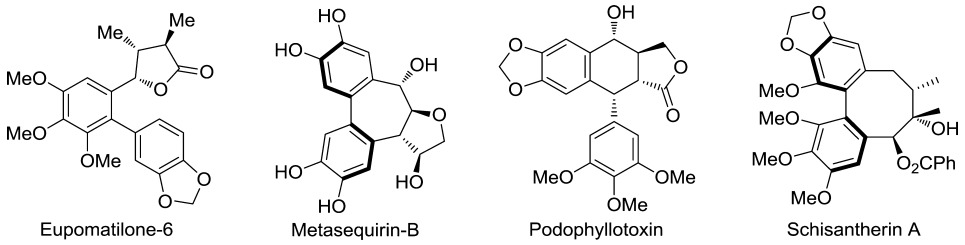
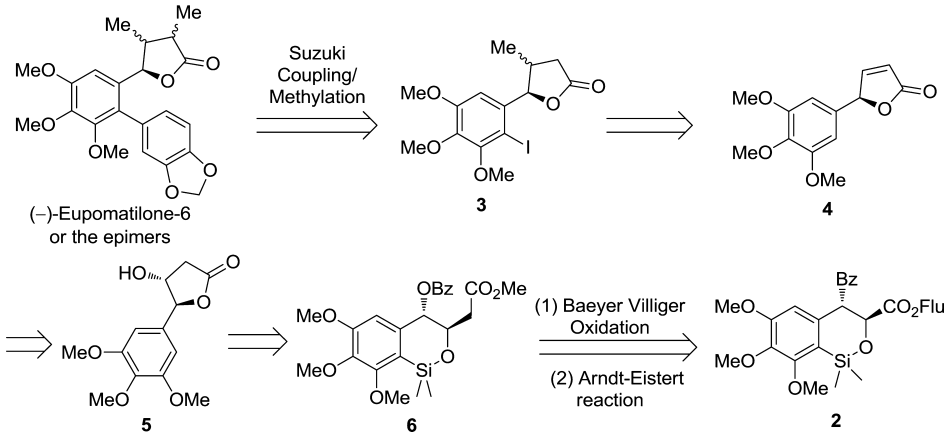
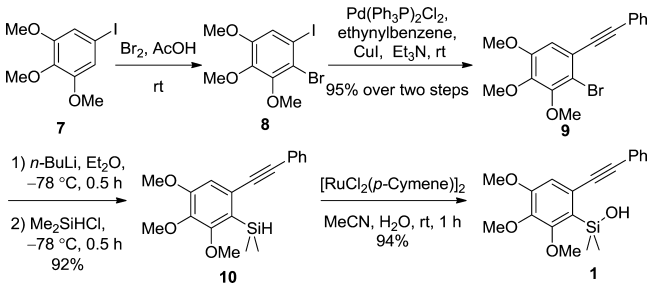


Figure 1. Lignans, structurally diverse family of phenylpropanoid dimers.

Scheme 1. Retrosynthetic Analysis of Eupomatilone-6 and Its Epimers



Scheme 2. Synthesis of Silanol 1



Then, the relay catalytic asymmetric intramolecular hydrosiloxylation and asymmetric aldol reaction with 2,3,4-trimethoxy-6-(phenylethynyl)phenyl dimethylsilanol **1** was carried out in 5 g scale. To our delight, the desired product **2** was obtained in 74% yield with 89% ee and 10:1 dr (Scheme 3). The assignment of the absolute configurations of **2** to be 3*S*,4*S* was determined by X-ray crystallographic analysis of the single crystal.[13] Mechanistically, the intramolecular hydrosiloxylation of alkyne **1** would occur to generate silyl enol ether **I** catalyzed by the gold complex. Subsequently, the ether **I** would participate in the asymmetric Mukaiyama aldol reaction to provide the intermediate **II** in the presence of chiral Brønsted acid **A**. Finally, the oxygen attacks the silyl group to afford intermediate **2** (Scheme 3).

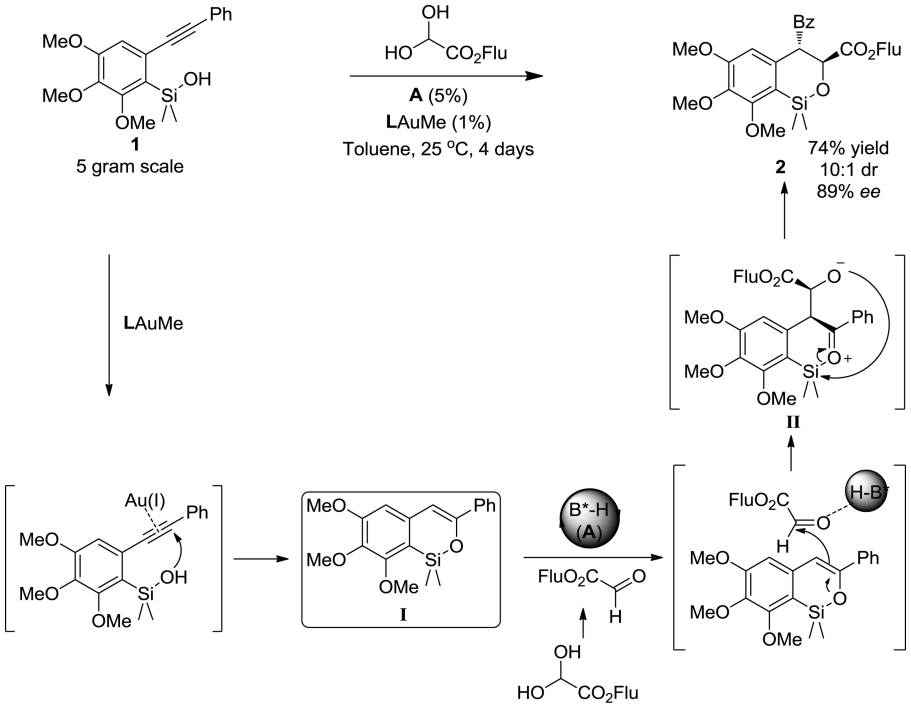
The stereoselectivity of **2** can be explained by proposing a transition-state model as shown in Figure 2. The reactions occur via bidentate binding of glyoxylate with the proton of the chiralphosphoric amide to give intermediate **III**, which places the fluorenyl glyoxylate moiety in a chiral sphere.[14] Since Mukaiyama aldol reaction proceeds through attacking *Si*-face and *Re*-face, four different transition states (TS) originating from intermediate **III** are considered. *Si*-face attack of **III** leading to TS **I** is disfavored because of steric repulsion between the phenyl moiety of substrate and the isopropyl group of **A**. In contrast, formation of TS **II** is favored through *Si*-face attack. However, when the silyl enol ether attacks *Re*-face, the resulting TS **III** and **IV** are disfavored because of steric repulsion between the substrate and the 2,4,6-(*i*Pr)-phenyl group of **A**. As a result, only one (TS **II**) out of the four possible transition states is favored, affording the enantioenriched product.

The treatment of the chiral compound **2** with *meta*-chloroperoxybenzoic acid (*m*-CPBA) and $Na_2HPO_4{\cdot}12H_2O$ in dichloroethane (DCE) led to a smooth Baeyer−Villiger oxidation to furnish **11** in 70% yield without change in its absolute configuration (Scheme 4). The hydrogenolysis of **11** afforded acid **12**, which was directly transformed into a diazoketone **13** without purification by exposure to a mixture of $ClCO_2Et$ and Et_3N at 0 °C and followed by the addition of excess CH_2N_2. The diazoketone **13** was able to undergo Arndt−Eistert reaction[15] to form a homologated ester **6** in 78% yield with 6/1 dr[16] under the catalysis of silver benzoate ($PhCO_2Ag$). Subsequently, we attempted to synthesize **14** via palladium-catalyzed Hiyama cross-coupling reaction[17] of ester **6** with 3,4-methylenedioxyiodobenzene. However, maybe because of the steric hindrance of a methoxyl group ortho to the silanol, the desired cross coupling product **14** could not be obtained, instead leading to complex mixtures.[18]

Therefore, we had to switch to an alternative synthetic route. The mixture of the two diastereoisomers of ester **6** was first treated with sodium methoxide in methanol to provide an unstable alcohol **15**. In the presence of *p*-toluenesulfonic acid, alcohol **15** was transformed into lactone **5** as a single compound after purification, but unfortunately accompanying with the removal of silyl group (Scheme 5). The treatment of alcohol **5** with $MeSO_2Cl/Et_3N$ at 0 °C in anhydrous CH_2Cl_2 led to the generation of butenolide **4** in 92% yield. The

dx.doi.org/10.1021/jo4024232 | J. Org. Chem. 2014, 79, 419−425

Scheme 3. Proposed Mechanism of the Synthesis of Chiral Intermediate 2



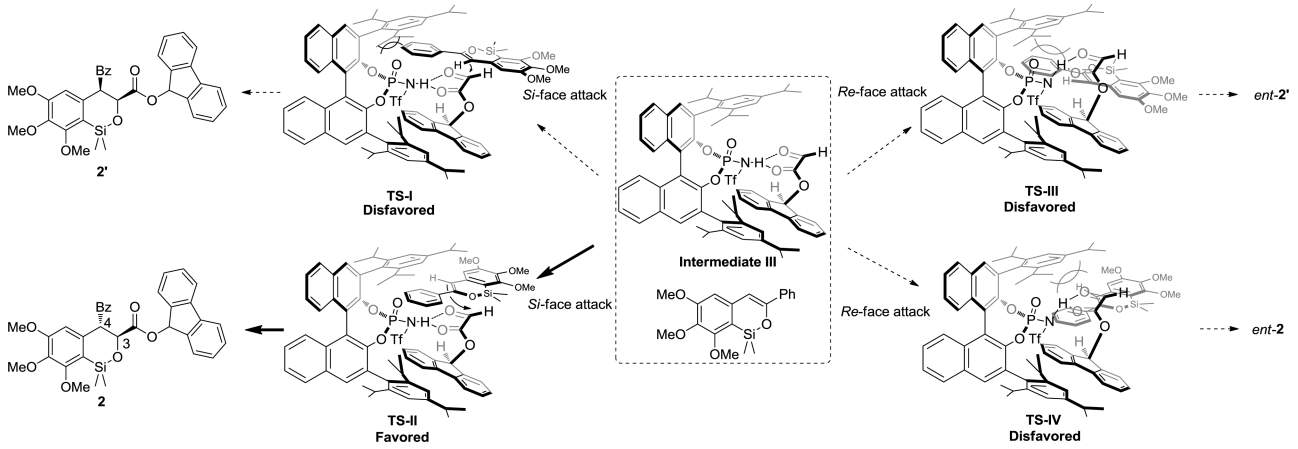
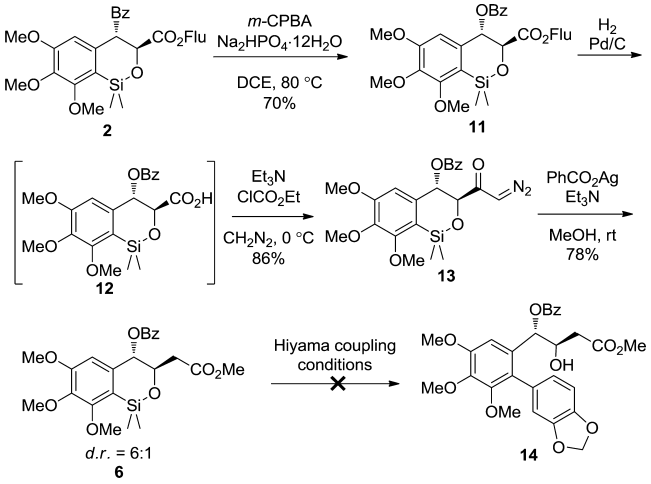


Figure 2. Proposed transition-state model.

Scheme 4. Synthesis of Ester 6

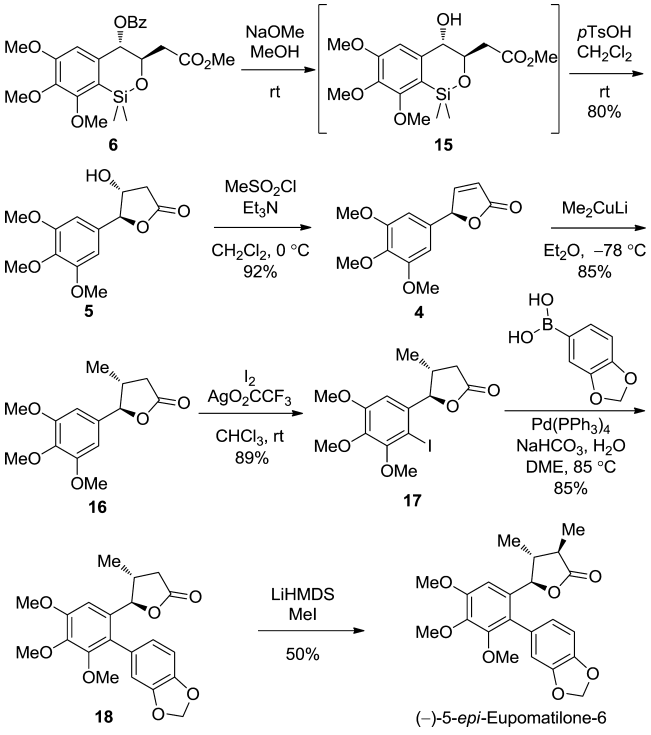


conjugate addition of dimethyl copper lithium (in situ formed from methyllithium and copper iodide in ether at −20 °C) to butenolide **4** provided **16** in 85% yield with perfect diastereoselectivity.[19] Iodination of **16** with I_2 in the presence of silver trifluoroacetate delivered aryl iodide **17** in 89% yield. The Suzuki−Miyaura coupling of compound **17** with 3,4-methylenedioxyphenylboronic acid under the catalysis of $[Pd(PPh_3)_4]$ proceeded cleanly to give biaryl **18** as a 1:1 mixture of atropisomers in 85% yield.[6] The ^1H NMR and ^{13}C NMR spectrum of **18** was in complete agreement with the data provided by Gurjar.[4a] The alkylation of lactone **18** was then executed by using the same reaction (LiHMDS-MeI) as reported by Gurjar[4a] to give synthetic (−)-5-*epi*-eupomatilone-6 in 50% yield with 87% ee. And the spectroscopic data of the final product were in agreement with reported spectra.[4a,b]

In summary, we have established an enantioselective synthesis of (−)-5-*epi*-eupomatilone-6 in 16 linear steps and in close to 9% overall yield via intramolecular hydrosiloxylation of arylacetylenes and asymmetric Mukaiyama aldol reactions,

dx.doi.org/10.1021/jo4024232 | J. Org. Chem. 2014, 79, 419−425

Scheme 5. Synthesis of (−)-5-*epi*-Eupomatilone-6



Arndt−Eistert homologation, and Suzuki coupling. The relay catalytic cascade intramolecular hydrosiloxylation of arylacetylenes and asymmetric Mukaiyama aldol reactions turned out to be the key reaction to provide a chiral building block for the synthesis. This example shows that the asymmetric relay catalytic protocols holds great potential in the enantioselective total synthesis of natural products.

EXPERIMENTAL SECTION

General Methods. NMR spectra were recorded on a 400 MHz spectrometer. Mass spectra were recorded on an Orbitrap ESI-MS spectrometer. Infrared spectra were recorded on a FT-IR spectrometer. The enantiomeric excess of the compounds was determined by chiral HPLC using racemic compounds as references. X-ray crystallography analysis was performed on a CCD diffractionmeter equipped with micro-Cu Kα (λ = 1.54184 Å) radiation at room temperature. Melting points were determined on a melting point apparatus with microscope and were uncorrected. All starting materials, reagents and solvents were purchased from commercial suppliers and used as supplied unless otherwise stated. THF and Et_2O were dried over Na and distilled prior to use.

2-Bromo-1-iodo-3,4,5-trimethoxybenzene (8). To a solution of 3,4,5-trimethoxyiodobenzene **7** (4.04 g, 11.9 mmol, 1.0 equiv) in 35 mL of AcOH, bromine (2.10 g, 13.1 mmol, 1.1 equiv) was added dropwise at 0 °C. The mixture was stirred at room temperature for 1 h and then was quenched with 25 mL of H_2O and 2 mL saturated solution of $Na_2S_2O_3$. The mixture was diluted with 150 mL of CH_2Cl_2. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (150 mL × 2). The combined organic layers were washed with saturated aqueous NaCl (100 mL), dried with anhydrous Na_2SO_4, concentrated in vacuo to give a brown oil, which was used directly without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.19 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.5, 151.4, 143.6, 118.9, 117.0, 93.6, 61.1, 61.0, 56.4; IR (KBr) ν 1006, 1106, 1160, 1232, 1298, 1369, 1421, 1475, 1564 cm^{-1}; HRMS (ESI) exact mass calcd for $C_9H_{10}BrIO_3$ [(M + H)$^+$] requires m/z 372.8931, found m/z 372.8935.

2-Bromo-3,4,5-trimethoxy-1-(phenylethynyl)benzene (9). To a mixture of $Pd(PPh_3)_2Cl_2$ (167 mg, 0.24 mmol, 0.02 equiv), CuI (91 mg, 0.48 mmol, 0.04 equiv), and 2-bromo-1-iodo-3,4,5-trimethoxybenzene (**8**) (4.44 g, 11.9 mmol, 1.0 equiv) in Et_3N (50 mL), ethynylbenzene (2.45 g, 15.5 mmol, 1.3 equiv) was added slowly. The mixture was vigorously stirred at room temperature for 3.5 h and then filtered, and the filtrate was concentrated. The residue was purified by flash chromatography on silica gel (eluent, petroleum ether) to give **9** as a brown oil (3.9 g, 95% yield over two steps): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.61−7.53 (m, 2H), 7.39−7.32 (m, 3H), 6.93 (s, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.6, 151.4, 144.0, 131.7, 128.6, 128.4, 123.0, 120.5, 112.7, 111.8, 93.1, 88.0, 61.3, 61.0, 56.3; IR (KBr) ν 689, 758, 828, 927, 967, 1007, 1047, 1111, 1161, 1196, 1251, 1360, 1380, 1425, 1480, 1494, 1554, 2156, 2828, 2847, 2937, 3002 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{17}H_{15}BrO_3$ [(M + H)$^+$] requires m/z 347.0277, found m/z 347.0279.

Dimethyl(2,3,4-trimethoxy-6-(phenylethynyl)phenyl)silane (10). The brown oil **9** (3.9 g, 11.2 mmol, 1.0 equiv) was dissolved in 55 mL of Et_2O and then cooled down to −78 °C before slow addition of *n*-BuLi (5.6 mL, 2.4 M in *n*-hexane, 1.2 equiv). After stirring at −78 °C for 30 min under argon, chlorodimethylsilane (1.59 g, 16.8 mmol, 1.5 equiv) was slowly added. Then the mixture was stirred at −78 °C for 30 min before quenching with saturated aqueous NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with Et_2O (100 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 50:1) to afford the product **10** as a white solid (3.3 g, 92% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.56−7.49 (m, 2H), 7.39−7.29 (m, 3H), 6.92 (s, 1H), 4.82−4.75 (m, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.88 (s, 3H).0.45 (s, 3H), 0.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 158.5, 154.5, 142.3, 131.3, 128.4, 128.2, 125.2, 124.3, 123.5, 112.6, 91.2, 90.4, 61.1, 60.8, 56.1, −2.7; IR (KBr) ν 686, 751, 847,890, 1019, 1105, 1255, 1340, 1480, 1576, 2156 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{19}H_{22}O_3Si$ [(M + H)$^+$] requires m/z 327.1411, found m/z 327.1416; mp (°C) 67−69.

Dimethyl(2,3,4-trimethoxy-6-(phenylethynyl)phenyl)silanol (1). 10 (5.35 g, 16.4 mmol, 1.0 equiv) was dissolved in 80 mL of MeCN and stirred at room temperature overnight after the addition of $[RuCl_2(p\text{-Cymene})_2]_2$ (200 mg, 0.32 mmol, 0.02 equiv) and H_2O (1.5 mL, 82 mmol, 5.0 equiv). The mixture was concentrated in vacuo when the reaction was complete, and the residue was purified by flash column chromatography (eluent, petroleum ether/ethyl acetate = 40:1) to afford the product as a white solid (5.3 g, 94% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.55−7.46 (m, 2H), 7.40−7.32 (m, 3H), 6.93 (s, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 3.75 (s, 1H), 0.52 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 155.9, 152.4, 140.1, 129.1, 126.4, 126.3, 123.8, 120.6, 120.5, 111.1, 89.5, 88.3, 59.2, 58.6, 53.9, 0.0; IR (KBr) ν 649, 754, 850, 887, 1012, 1049, 1249, 1338, 1375, 1478, 1574, 3522 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{19}H_{22}O_4Si$ [(M + H)$^+$] requires m/z 343.1360, found m/z 343.1366; mp (°C) 47−48.

(3*S*,4*S*)-9*H*-Fluoren-9-yl-4-benzoyl-6,7,8-trimethoxy-1,1-dimethyl-3,4-dihydro-1*H*-benzo[*c*][1,2]oxasiline-3-carboxylate (2). A mixture of IPrAuMe (138 mg, 0.16 mmol, 0.01 equiv), *N*-trifyl phosphoamide **A** (685 mg, 0.78 mmol, 0.05 equiv), silanol **1** (5.3 g, 15.5 mmol, 1.0 equiv), and fluorenyl glyoxylate (5.96 g, 23 mmol, 1.5 equiv) were added in toluene (100 mL) in one portion under argon. The resulting mixture was allowed to stir at 25 °C for 4 days, and then the mixture was concentrated, and the residue was subjected to flash column chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 10:1) directly to afford **2** as a white solid (6.66 g, 74% yield) and **2′** (0.63 g, 7% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02−7.93 (m, 2H), 7.65 (d, J = 7.5 Hz, 2H), 7.60−7.53 (m, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.39 (dt, J = 6.7, 2.8 Hz, 2H), 7.21 (d, J = 4.1 Hz, 2H), 7.15 (dt, J = 7.5, 0.9 Hz, 1H), 7.04 (d, J = 7.5 Hz, 1H), 6.80 (s, 1H), 6.25 (s, 1H), 5.27 (d, J = 2.3 Hz, 1H), 5.09 (d, J = 2.3 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.70 (s, 3H), 0.39 (s, 6H); ^{13}C NMR (100

dx.doi.org/10.1021/jo4024232 | J. Org. Chem. 2014, 79, 419−425

MHz, $CDCl_3$) δ (ppm) 195.3, 171.0, 155.3, 153.2, 139.6, 139.4, 139.2, 139.1, 138.7, 133.8, 133.3, 131.4, 127.7, 127.1, 126.7, 126.0, 125.8, 123.8, 119.0, 118.1, 118.0, 107.4, 73.8, 73.1, 58.7, 58.5, 54.0, 52.3, 25.1, 0.0, −0.7; IR (KBr) ν 742, 788, 835, 854, 1101, 1143, 1190, 1208, 1395, 1456, 1484, 1587, 1685, 1755, 2842, 2903, 2936, 2968 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{34}H_{32}O_7Si$ [(M + H)$^+$] requires m/z 581.1990, found m/z 581.1995; mp (°C) 159−161; $[\alpha]^{20}_D$ +144.0 (c 0.1, $CHCl_3$). HPLC analysis (Chiralpak IC, 95:5 hex/*i*PrOH, 1.0 mL/min, 254 nm; t_R (major) = 13.8 min, t_R (minor) = 15.5 min) gave the isomeric composition of the product, 89% ee.

***cis*-9*H*-Fluoren-9-yl4-benzoyl-6,7,8-trimethoxy-1,1-dimethyl-3,4-dihydro-1*H*-benzo[*c*][1,2]oxasiline-3-carboxylate (2′).** ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81 (dd, J = 8.4, 1.2 Hz, 2H), 7.63 (d, J = 7.5 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.48−7.42 (m, 1H), 7.39 (m, 2H), 7.33−7.27 (m, 3H), 7.21 (m, 2H), 7.00 (dt, J = 7.5, 1.0 Hz, 1H), 6.63 (s, 1H), 6.33 (s, 1H), 5.08 (d, J = 2.6 Hz, 1H), 5.01 (d, J = 2.6 Hz, 1H), 3.92 (s, 3H), 3.80 (s, 3H), 3.65 (s, 3H), 0.58 (s, 3H), 0.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.8, 171.2, 157.2, 154.9, 141.1, 140.9, 140.8, 140.6, 140.0, 137.5, 137.1, 132.6, 129.3, 129.1, 128.4, 128.1, 127.6, 127.5, 126.2, 125.9, 119.6, 119.4, 119.3, 108.3, 75.9, 73.2, 60.3, 60.1, 55.6, 50.5, 0.0, −0.7; IR (KBr) ν 746, 792, 838, 856, 1103, 1145, 1195, 1392, 1456, 1488, 1557, 1594, 1685, 1754, 2839, 2908, 2940, 2963 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{34}H_{32}O_7Si$ [(M + H)$^+$] requires m/z 581.1990, found m/z 581.1995; mp (°C) 138−140. HPLC analysis (Chiralpak IC, 95:5 hex/*i*PrOH, 1.0 mL/min, 254 nm; t_R (major) = 7.4 min, t_R (minor) = 6.6 min) gave the isomeric composition of the product, 40% ee.

(3*S*,4*S*)-9*H*-Fluoren-9-yl 4-(benzoyloxy)-6,7,8-trimethoxy-1,1-dimethyl-3,4-dihydro-1*H*-benzo[*c*][1,2]oxasiline-3-carboxylate (11). To a solution of **2** (6.66 g, 11.5 mmol, 1.0 equiv) in DCE (80 mL) was added *m*-CPBA (7.94 g, 46.0 mmol, 4.0 equiv) and $Na_2HPO_4{\cdot}12H_2O$ (8.9 g, 92.0 mmol, 8.0 equiv) at room temperature. The reaction was allowed to stir at reflux for 15 min. Cooled to room temperature, the reaction was quenched with a saturated aqueous solution of Na_2SO_3 (120 mL) and extracted with Et_2O (150 mL × 3). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ (150 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on basic aluminum oxide (eluent, petroleum ether/ethyl acetate = 10:1) to give compound **11** as a white solid (4.80 g, 70% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.00 (dd, J = 8.4, 1.2 Hz, 2H), 7.63 (dd, J = 7.6, 3.0 Hz, 2H), 7.56−7.49 (m, 1H), 7.43−7.33 (m, 4H), 7.22 (ddd, J = 8.4, 6.8, 0.8 Hz, 2H), 7.10 (dt, J = 7.5, 1.0 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 6.77 (s, 1H), 6.64 (s, 1H), 6.21 (d, J = 2.9 Hz, 1H), 5.21 (d, J = 2.9 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.72 (s, 3H), 0.54 (s, 3H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.2, 164.1, 155.7, 153.7, 140.5, 134.0, 139.7, 139.6, 139.5, 133.3, 131.7, 128.5, 128.3, 128.1, 128.0, 126.9, 126.4, 126.1, 124.3, 124.2, 118.8, 118.5, 118.4, 109.3, 74.1, 73.7, 72.2, 59.1, 59.0, 54.5, 25.5, 0.4, 0.0; IR (KBr) ν 665, 712, 764, 791, 843, 970, 1031, 1101, 1148, 1251, 1321, 1435, 1481, 1584, 1720, 1748, 1831, 2906, 2939 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{34}H_{32}O_8Si$ [(M + H)$^+$] requires m/z 597.1939, found m/z 597.1940; mp (°C) 118−120; $[\alpha]^{20}_D$ +59.0 (c 0.1, $CHCl_3$). HPLC analysis (Chiralpak IC, 95:5 hex/*i*PrOH, 1.0 mL/min, 254 nm; t_R (major) = 9.1 min, t_R (minor) = 7.9 min) gave the isomeric composition of the product, 91% ee.

(3*S*,4*S*)-3-(2-Diazoacetyl)-6,7,8-trimethoxy-1,1-dimethyl-3,4-dihydro-1*H*-benzo[*c*][1,2]oxasilin-4-yl benzoate (13). To a solution of **11** (4.2 g, 7 mmol) in EtOAc (120 mL) was added 10% palladium on carbon (800 mg). The mixture was stirred at room temperature overnight under 1 atm of H_2. The resulting mixture was filtered through Celite, washed with EtOAc, and the combined filtrates were concentrated under reduced pressure. To the solution of the residue **12** in dry THF (30 mL) was added Et_3N (0.97 mL, 8.4 mmol, 1.2 equiv) and $ClCO_2Et$ (0.73 mL, 7.7 mmol, 1.1 equiv) at 0 °C and under an atmosphere of argon. The resulting mixture was stirred at the same temperature for 15 min and then was added dropwise to a stirred solution of diazomethane (ca. 3.0 equiv) in diethyl ether. The resulting mixture was allowed to warm to room temperature and stirred for 2 h. Excess diazomethane was destroyed by 0.5 M solution of AcOH in H_2O. The organic layer was separated, and the aqueous layer was extracted with Et_2O (100 mL × 2). The combined organic phase was washed with saturated $NaHCO_3$ solution (50 mL) and saturated NaCl solution (50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 10:1) to afford **13** as a pale solid (2.75 g, 86% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09−7.96 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 6.84 (s, 1H), 6.43 (d, J = 3.4 Hz, 1H), 5.80 (s, 1H), 4.89 (d, J = 2.8 Hz, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H), 0.55 (s, 3H), 0.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.1, 164.0, 155.3, 154.0, 139.8, 134.4, 131.6, 128.4, 128.2, 126.9, 117.5, 108.7, 78.2, 71.5, 59.0, 58.9, 54.5, 52.4, 0.0; IR (KBr) ν 717, 793, 843, 1019, 1113, 1195, 1262, 1321, 1357, 1627, 1713, 2110 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{22}H_{24}N_2O_7Si$ [(M + H)$^+$] requires m/z 457.1426, found m/z 457.1433; mp (°C) 114−115; $[\alpha]^{20}_D$ +5.1 (c 0.1, $CHCl_3$). HPLC analysis (Chiralpak IC, 95:5 hex/*i*PrOH, 1.0 mL/min, 254 nm; t_R (major) = 28.3 min, t_R (minor) = 24.3 min) gave the isomeric composition of the product, 92% ee.

(3*R*,4*S*)-6,7,8-Trimethoxy-3-(2-methoxy-2-oxoethyl)-1,1-dimethyl-3,4-dihydro-1*H*-benzo[*c*][1,2]oxasilin-4-yl benzoate (6). To a solution of **13** (2.26 g, 5.0 mmol, 1.0 equiv) in methanol (70 mL) was added a solution of $PhCO_2Ag$ (0.34 g, 1.5 mmol, 0.3 equiv) in Et_3N (3.5 mL, 25 mmol, 5.0 equiv). The mixture was stirred in dark overnight. The mixture was concentrated and was purified by flash column chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 12:1) to afford **6** as an oil with 6/1 dr (1.80 g, 78% yield). The two diastereoisomers could not be separated at the step (1.80 g, 78% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.07−8.04 (m, 2.30H), 7.58−7.53 (m, 1.15H), 7.45−7.40 (m, 2.30H), 6.88 (s, 0.15H), 6.71 (s, 1H), 6.01−5.97 (m, 1.15H), 4.79 (dt, J = 6.8, 4.8 Hz, 1H), 4.75−4.69 (m, 0.15H), 3.92 (s, 3H), 3.91 (s, 0.45H), 3.85 (s, 3H), 3.84 (s, 0.45H), 3.81 (s, 3H), 3.69 (s, 0.45H), 3.65 (s, 3H), 2.68 (ddd, J = 21.3, 15.8, 6.7 Hz, 0.30H), 2.56 (d, J = 6.9 Hz, 2H), 0.46 (s, 0.45H), 0.44 (s, 3H), 0.40 (s, 3H), 0.39 (s, 0.45H); ^{13}C NMR (100 MHz, $CDCl_3$) δ169.9, 164.8, 156.0, 154.6, 140.1, 136.1, 132.2, 128.8, 127.4, 118.2, 108.1, 73.1, 70.9, 59.5, 59.4, 55.1, 50.7, 39.0, 0.00, −0.6; 170.3, 165.0, 156.0, 154.4, 140.3, 137.3, 132.1, 128.9, 127.4, 118.2, 109.3, 71.8, 69.3, 59.5 55.0, 38.4, 28.7, −0.8, −1.6; IR (KBr) ν 710, 795, 840, 1019, 1119, 1199, 1263, 1318, 1592, 1712, 1742 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{23}H_{28}O_8Si$ [(M + H)$^+$] requires m/z 461.1632, found m/z 461.1630; $[\alpha]^{20}_D$ +20.0 (c 0.1, $CHCl_3$). HPLC analysis (Chiralpak AD-H, 75:25 hex/*i*PrOH, 1.0 mL/min, 254 nm; t_R (major) = 19.4 min, t_R (minor) = 25.0 min) gave the isomeric composition of the product, 89% ee.

(4*R*,5*S*)-4-Hydroxy-5-(3,4,5-trimethoxyphenyl)dihydrofuran-2(3*H*)-one (5). To a solution of **6** (1.48 g, 3.2 mmol, 1.0 equiv) in methanol (15 mL), NaOMe (0.35g, 6.4 mmol, 2.0 equiv) was added. The reaction mixture was stirred for 3 h. 25 mL saturated aqueous of NaCl and 100 mL of EtOAc were added. The organic layer was separated, and the aqueous layer was extracted with EtOAc (100 mL × 2). The combined organic phase was washed with saturated NaCl solution (50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (15 mL), and *p*-TsOH (61 mg, 0.32 mmol, 0.1 equiv) was added to the mixture. The reaction mixture was stirred for 2 h and then was concentrated. The residue was purified by flash column chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 1:1) to afford **5** as a white solid (0.69 g, 80% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.52 (s, 2H), 5.23 (d, J = 4.3 Hz, 1H), 4.47 (m, 1H), 3.84 (s, 6H), 3.82 (s, 3H), 2.96 (brs, 1H), 2.89 (dd, J = 17.7, 6.8 Hz, 1H), 2.62 (dd, J = 17.7, 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 174.6, 153.6, 137.9, 132.5, 102.0, 87.5, 74.5, 60.9, 56.2, 37.2, 29.7; IR (KBr) ν 941, 1001, 1046, 1128, 1173, 1242, 1337, 1469, 1510, 1601, 1783, 1848, 2925, 3012, 3467 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{13}H_{16}O_6$ [(M + H)$^+$] requires m/z 269.1020, found m/z 269.1021; mp (°C) 99−101; $[\alpha]^{20}_D$ +4.2 (c 0.1, $CHCl_3$). HPLC analysis (Chiralpak IC, 80:20 hex/*i*PrOH, 1.0 mL/min, 254 nm; t_R (major) = 25.8 min, t_R (minor) = 30.0 min) gave the isomeric composition of the product, 90% ee.

dx.doi.org/10.1021/jo4024232 | *J. Org. Chem.* 2014, 79, 419−425

(*R*)-5-(3,4,5-Trimethoxyphenyl)furan-2(5*H*)-one (4). To a stirred solution of **5** (500 mg, 1.86 mmol, 1.0 equiv) in dry DCM (10 mL), Et_3N (0.53 mL, 3.72 mmol, 2.0 equiv) and $MeSO_2Cl$ (0.16 mL, 2.05 mmol, 1.1 equiv) were added dropwise at 0 °C. The reaction mixture was stirred for 3 h and then was diluted with H_2O (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to obtain the residue. The residue was purified by flash column chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 2:1) to afford **4** as a white solid (0.43 g, 92% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.52 (dd, J = 5.6, 1.7 Hz, 1H), 6.45 (s, 2H), 6.22 (dd, J = 5.6, 2.1 Hz, 1H), 5.94 (t, J = 1.9 Hz, 1H), 3.84 (s, 6H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.0, 155.7, 153.8, 138.8, 129.7, 121.0, 103.6, 84.4, 60.9, 56.3; IR (KBr) ν 823, 913, 997, 1033, 1093, 1123, 1159, 1237, 1328, 1424, 1460, 1502, 1586, 1754, 1790, 2836 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{13}H_{14}O_5$ [(M + H)$^+$] requires m/z 251.0914, found m/z 251.0916; mp (°C) 68−70; $[\alpha]^{20}_D$ +178.1 (c 0.1, $CHCl_3$). HPLC analysis (Chiralpak IC, 90:10 hex/*i*PrOH, 1.0 mL/min, 254 nm; t_R (major) = 48.2 min, t_R (minor) = 66.8 min) gave the isomeric composition of the product, 93% ee.

(4*R*,5*R*)-4-Methyl-5-(3,4,5-trimethoxyphenyl)dihydrofuran-2(3*H*)-one (16). To a suspension of CuI (247 mg, 1.30 mmol, 2.0 equiv) in ether (10 mL) cooled at −20 °C was added dropwise a solution of methyllithium 1.5 M in ether (1.73 mL, 2.60 mmol, 4.0 equiv). The reaction mixture was warmed to 0 °C and stirred at this temperature until a colorless clear solution was obtained. To this solution cooled at −78 °C was added a solution of butenolide **4** (162 mg, 0.65 mmol, 1.0 equiv) in ether (5 mL). The mixture was stirred for an additional 4 h at −78 °C and was quenched by saturated NH_4Cl aqueous solution (20 mL). The reaction mixture was warmed to room temperature. The organic layer was separated, and the aqueous layer was extracted with Et_2O (20 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to obtain the residue. The residue was purified by flash chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 1:1) to afford **16** as a white solid (147 mg, 85% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.52 (s, 2H), 4.85 (d, J = 8.4 Hz, 1H), 3.86 (s, 6H), 3.84 (s, 3H), 2.78 (dd, J = 16.9, 7.6 Hz, 1H), 2.56−2.40 (m, 1H), 2.33 (dd, J = 16.9, 10.6 Hz, 1H), 1.20 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.0, 153.5, 138.3, 133.5, 103.0, 88.3, 60.9, 56.3, 39.8, 37.3, 16.6; IR (KBr) ν 689, 831, 944, 983, 1006, 1136, 1159, 1210, 1249, 1328, 1425, 1464, 1509, 1594, 1269, 2827, 2884, 2946, 2974, 3008 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{14}H_{18}O_5$ [(M + H)$^+$] requires m/z 267.1227, found m/z 267.1229; mp (°C) 74−77; $[\alpha]^{20}_D$ +8.8 (c 0.1, $CHCl_3$). HPLC analysis (Chiralpak OD-H, 70:30 hex/*i*PrOH, 1.0 mL/min, 254 nm; t_R (major) = 8.8 min, t_R (minor) = 9.9 min) gave the isomeric composition of the product, 92% ee.

(4*R*,5*R*)-5-(2-Iodo-3,4,5-trimethoxyphenyl)-4-methyldihydrofuran-2(3*H*)-one (17). To a solution of **16** (73 mg, 0.28 mmol, 1.0 equiv) in $CHCl_3$ (4 mL) and $AgOCOCF_3$ (124 mg, 0.56 mmol, 2.0 equiv) was added a solution of I_2 (142 mg, 0.56 mmol, 2.0 equiv) in $CHCl_3$ (3 mL) dropwise via syringe over 0.5 h. The reaction was stirred for an additional 10 min before being filtered through a pad of Celite that was washed thoroughly with $CHCl_3$ (20 mL). The filtrate was concentrated to yield a crude oil that was purified by flash column chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 1:1) to afford **17** as a white solid (98 mg, 89% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.64 (s, 1H), 5.37 (d, J = 5.1 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 2.73 (dd, J = 17.3, 7.9 Hz, 1H), 2.60−2.41 (m, 1H), 2.28 (dd, J = 17.3, 6.3 Hz, 1H), 1.36 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.9, 154.3, 153.2, 142.2, 136.5, 105.7, 89.8, 84.9, 60.9 (d, J = 11.4 Hz), 56.3, 39.2, 35.8, 18.6; IR (KBr) ν 690, 804, 837, 940, 1001, 1100, 1165, 1202, 1366, 1391, 1428, 1477, 1567, 1780, 2850, 2871, 2932, 2965 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{14}H_{17}IO_5$ [(M + H)$^+$] requires m/z 393.0193, found m/z 393.0199; $[\alpha]^{20}_D$ +23.0 (c 0.08, $CHCl_3$). HPLC analysis (Chiralpak IC, 70:30 hex/*i*PrOH, 1.0 mL/min, 254 nm; t_R (major) = 11.9 min, t_R (minor) = 10.8 min) gave the isomeric composition of the product, 92% ee.

Compound 18.[4a] A round-bottom flask equipped with a reflux condenser was charged with **4** (60 mg, 0.15 mmol, 1.0 equiv), 3,4-methylenedioxyphenylboronic acid (41 mg, 0.24 mmol, 1.6 equiv), and $NaHCO_3$ (48 mg, 0.57 mmol, 3.7 equiv) in 1 mL of DME and 0.2 mL of H_2O. $Pd(PPh_3)_4$ (11 mg, 0.0092 mmol, 0.06 equiv) in 1 mL of DME was added, and argon was passed through the solution for 10 min before bringing the reaction to reflux for 18 h. The reaction was quenched with 1 M aqueous HCl (10 mL), and the resulting aqueous layer was extracted with EtOAc (10 mL × 3). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to provide a crude yellow oil that was purified by flash column chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 1:1) to afford **18** as a white solid (49 mg, 85% yield): ^{1}H NMR (400 MHz, $CDCl_3$, two atropisomers) δ (ppm) 6.88 (d, J = 1.7 Hz, 1H), 6.86 (d, J = 1.9 Hz, 1H), 6.73 (d, J = 1.5 Hz, 1H), 6.72−6.66 (m, 4H), 6.63 (dd, J = 7.9, 1.6 Hz, 1H), 6.02 (ddd, J = 4.5, 2.9, 1.4 Hz, 4H), 4.97 (d, J = 7.6 Hz, 1H), 4.92 (d, J = 7.5 Hz, 1H), 3.91 (s, 5H), 3.90 (s, 6H), 3.64 (s, 3H), 3.63 (s, 3H), 2.71 (ddd, J = 17.2, 8.0, 4.7 Hz, 2H), 2.46 (dq, J = 15.3, 7.7 Hz, 2H), 2.15 (ddd, J = 17.2, 9.2, 2.5 Hz, 2H), 0.87 (d, J = 5.4 Hz, 3H), 0.85 (d, J = 5.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, two atropisomers) δ (ppm) 176.5, 176.4, 153.3, 153.2, 151.5, 151.4, 147.6, 147.5, 147.0, 146.9, 142.4, 142.3, 131.8, 131.7, 128.9, 128.9, 128.9, 128.8, 124.2, 123.2, 111.3, 110.4, 108.3, 108.0, 104.5, 101.2, 101.1, 84.8, 84.7, 61.2, 61.1, 60.9, 56.2, 39.3, 39.2, 36.9, 36.8, 16.8; IR (KBr) ν 927, 945, 1008, 1040, 1130, 1157, 1225, 1243, 1324, 1454, 1486, 1594, 1779, 2855, 2941, 2959 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{21}H_{22}O_7$ [(M + H)$^+$] requires m/z 387.1438, found m/z 387.1443; mp (°C) 126−128; $[\alpha]^{20}_D$ −64.2 (c 0.1, $CHCl_3$). HPLC analysis (Chiralpak OD-H, 88:12 hex/*i*PrOH, 1.0 mL/min, 254 nm; t_R (major) = 15.3 min, t_R (minor) = 23.4 min) gave the isomeric composition of the product, 90% ee.

(−)-5-*epi*-Eupomatilone-6.[4a,b] To a solution of **18** (8.4 mg, 0.03 mmol, 1.0 equiv) in anhydrous THF (2 mL) at −78 °C was added LiHMDS (1 M solution in THF, 0.11 mL, 5 equiv). After 1 h, MeI (0.007 mL, 0.11 mmol, 5 equiv) was added, and stirring was continued for an additional 1 h at −78 °C. The reaction mixture was quenched with saturated aqueous NH_4Cl. The organic phase was separated, and the aqueous phase was extracted with Et_2O. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to provide a residue that was purified by flash column chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 1:1) to afford (−)-5-*epi*-eupomatilone-6 (4 mg, 50% yield): ^{1}H NMR (400 MHz, $CDCl_3$, two atropisomers) δ (ppm) 6.93−6.82 (m, 2H), 6.73−6.64 (m, 6H), 6.04−5.98 (m, 4H), 4.80 (t, J = 9.9 Hz, 2H), 3.91 (s, 12H), 3.64 (s, 3H), 3.63 (s, 3H), 2.20−2.12 (m, 2H), 2.07−1.99 (m, 2H), 1.23 (6H), 0.88 (d, 3H, J = 6.4 Hz), 0.87 (d, 3H, J = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 178.7, 178.6, 153.3, 153.2, 147.5, 147.4, 147.0, 146.9, 142.6, 130.8, 130.7, 129.9, 129.0, 128.9, 124.3, 123.4, 111.4, 110.6, 108.2, 107.9, 105.2, 105.1, 101.2, 101.1, 82.7, 82.6, 61.1, 61.0, 60.9, 56.2, 47.6, 43.4, 43.3, 14.3, 12.9; IR (KBr) ν 930, 945, 1020, 1138, 1157, 1243, 1324, 1454, 1486, 1594, 1780, 2855, 2941, 2963 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{22}H_{24}O_7$ [(M + H)$^+$] requires m/z 401.1595, found m/z 401.1600; $[\alpha]^{20}_D$ −19.0 (c 0.1, $CHCl_3$). HPLC analysis (Chiralpak OD-H, 85:15 hex/*i*PrOH, 1.0 mL/min, 254 nm; t_R (major) = 13.5 min, t_R (minor) = 19.5 min) gave the isomeric composition of the product, 87% ee.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR and HPLC spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wxnk@ustc.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Prof. Liu-zhu Gong for his support. We are grateful for financial support from NSFC (21302177), FRFCU (WK2340000043).

■ REFERENCES

(1) (a) Whiting, D. A. *Nat. Prod. Rep.* **1985**, *2*, 191. (b) Ward, R. S. *Nat. Prod. Rep.* **1997**, *14*, 43. (c) Pan, J. Y.; Chen, S. L.; Yang, M. H.; Wu, J.; Sinkkonen, J.; Zou, K. *Nat. Prod. Rep.* **2009**, *26*, 1251.
(2) Carroll, A. R.; Taylor, W. C. *Aust. J. Chem.* **1991**, *44*, 1615.
(3) Mitra, S.; Gurrala, S. R.; Coleman, R. S. *J. Org. Chem.* **2007**, *72*, 8724.
(4) (a) Gurjar, M. K.; Karumudi, B.; Ramana, C. V. *J. Org. Chem.* **2005**, *70*, 9658. (b) Yu, S. H.; Ferguson, M. J.; McDonald, R.; Hall, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 12808. (c) Hutchison, J. M.; Hong, S.-P.; McIntosh, M. C. *J. Org. Chem.* **2004**, *69*, 4185. (d) Coleman, R. S.; Gurrala, S. R. *Org. Lett.* **2004**, *6*, 4025. (e) Hong, S.; McIntosh, M. C. *Org. Lett.* **2002**, *4*, 19.
(5) Gurjar, M. K.; Cherian, J.; Ramana, C. V. *Org. Lett.* **2004**, *6*, 317.
(6) Johnson, J. B.; Bercot, E. A.; Williams, C. M.; Rovis, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 4514.
(7) Rainka, M. P.; Milne, J. E.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 6177.
(8) (a) Hirokawa, Y.; Kitamura, M.; Kato, C.; Kurata, Y.; Maezaki, N. *Tetrahedron Lett.* **2011**, *52*, 581. (b) Hirokawa, Y.; Kitamura, M.; Mizubayashi, M.; Nakatsuka, R.; Kobori, Y.; Kato, C.; Kurata, Y.; Maezaki, N. *Eur. J. Org. Chem.* **2013**, 721.
(9) Wang, P.-S.; Li, K.-N.; Zhou, X.-L.; Wu, X.; Han, Z.-Y.; Guo, R.; Gong, L.-Z. *Chem.—Eur. J.* **2013**, *19*, 6234.
(10) Najera, C.; Chinchilla, R. *Chem. Rev.* **2007**, *107*, 874.
(11) Ilies, L.; Tsuji, H.; Nakamura, E. *Org. Lett.* **2009**, *11*, 3966.
(12) Lee, M.; Ko, S.; Chang, S. *J. Am. Chem. Soc.* **2000**, *122*, 12011.
(13) For details, see Supporting Information.
(14) Rueping, M.; Nachtsheim, B. J.; Ieawsuwan, W.; Atodiresei, I. *Angew. Chem., Int. Ed.* **2011**, *50*, 6706.
(15) (a) Arndt, F.; Eistert, B. *Org. React.* **1942**, *1*, 38. (b) *Organic Syntheses*; Wiley & Sons: New York, 2004; Collect. Vol. *X*, p 194.
(16) Determined by ^{1}H NMR spectroscopy.
(17) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918.
(18) For experimental details, see Supporting Information.
(19) Takahata, H.; Uchida, Y.; Momose, T. *J. Org. Chem.* **1995**, *60*, 5628.