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# The First Asymmetric Total Syntheses and Determination of Absolute Configurations of Xestodecalactones B and C

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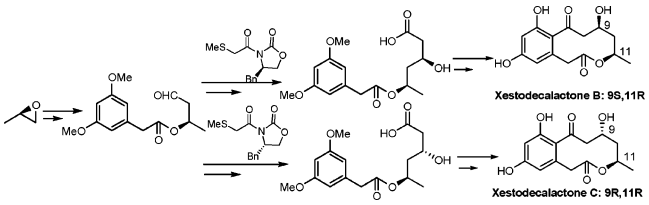


The first efficient asymmetric total syntheses of xestodecalactones **B** and **C** have been accomplished in 10 steps with an overall yield of 22 and 20.2%, respectively. The key steps involve the utility of Evans oxazolidinone-mediated *syn*-aldol condensations to establish the C-9 configuration and the macrolide ring formation by intramolecular acylation. The absolute configurations of xestodecalactones **B** and **C** have been determined via these syntheses.

The xestodecalactones **A**, **B**, and **C** are secondary metabolites of an isolate of the fungus *Penicillium cf. montanense* obtained from the marine sponge *Xestospongia exigua*.[1] As shown in Figure 1, these compounds constitute 10-membered macrolides with a fused 1,3-dihydroxybenzene ring that are structurally related to a number of compounds isolated from terrestrial fungi. such as sporostatin (**3**)[2] and curvularins (**4**, **5a**, and **5b**).[3] A number of these known compounds possess pronounced toxic effects that may be related to fungal pathogenic effects in plants.[3c,4] Xestodecalactone **B** has been shown to exhibit antifungal activity against *Candida albicans*.[1,5] The absolute

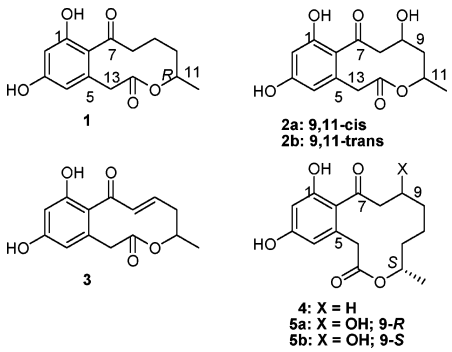


**FIGURE 1.** Xestodecalactones **A**, **B**, and **C** (**1**, **2a**, and **2b**), sporostatin (**3**), and curvularins (**4**, **5a**, and **5b**).

configurations of the natural products xestodecalactones **A**, **B**, and **C** were initially reported as *S* at C-11;[1] however, xestodecalactone **A** was later revised by a stereoselective asymmetric synthesis reported by Bringmann.[6] Xestodecalactones **B** and **C** have been tentatively assumed to have the same absolute configuration at C-11 as xestodecalactone **A** by comparing their CD spectra.[6] Recently, an asymmetric total synthesis of xestodecalactone **A** was also accomplished by Danishefsky.[7] These two strategies are very concise and efficient to synthesize the xestodecalactone **A**; however, the natural products xestodecalactones **B** and **C** have not been synthesized, and their absolute configurations have not been determined yet. Herein we report concise asymmetric total syntheses of xestodecalactones **B** and **C** with high stereoselectivity and assignment of their absolute configurations.

Our envisioned retrosynthetic analysis for the preparation of xestodecalactones **B** and **C** is depicted in Scheme 1. The target molecule xestodecalactone **B** is anticipated to be derived by the intramolecular acylation of the acid **16a**. The chiral center at C-9 of **16a** was to be introduced by the Evans aldol reaction of aldehyde **11** with (*R*)-oxazolidinone **12a**. The aldehyde **11** is easily available in two steps from (*R*)-1-(1,3-dithian-2-yl)-propan-2-ol (DHP) **8**, which in turn could be obtained by regioselective addition of dithiane **7** to (*R*)-(+)-methyloxirane **6**. The xestodecalactone **C** could be achieved in the same strategy as xestodecalactone **B** through the (*S*)-oxazolidinone **18b**.

Our syntheses of xestodecalactones **B** and **C** commenced from (*R*)-(+)-methyloxirane **6** and dithiane **7**. As shown in Scheme 2, the regioselective opening of the epoxy ring on chiral compound (*R*)-(+)-methyloxirane **6** with lithiated dithiane **7** in THF at −78 °C in the presence of HMPA afforded the alcohol (*R*)-DHP **8** in 96% yield.[8] Compared with the method of obtaining (*R*)-DHP by microbial reduction of the (1,3-dithian-2-yl) acetone,[9] this method features high yield, optical purity, available materials, and more convenient operation. Treatment

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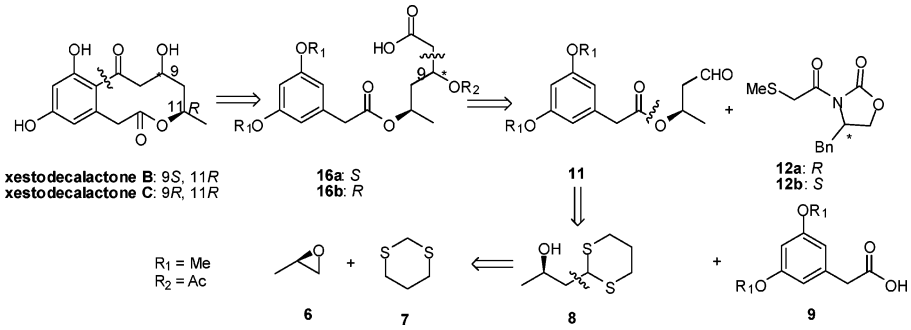
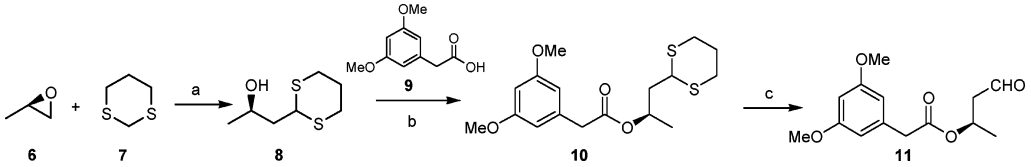
**SCHEME 1. Retrosynthetic Analysis of Xestodecalactones B and C**

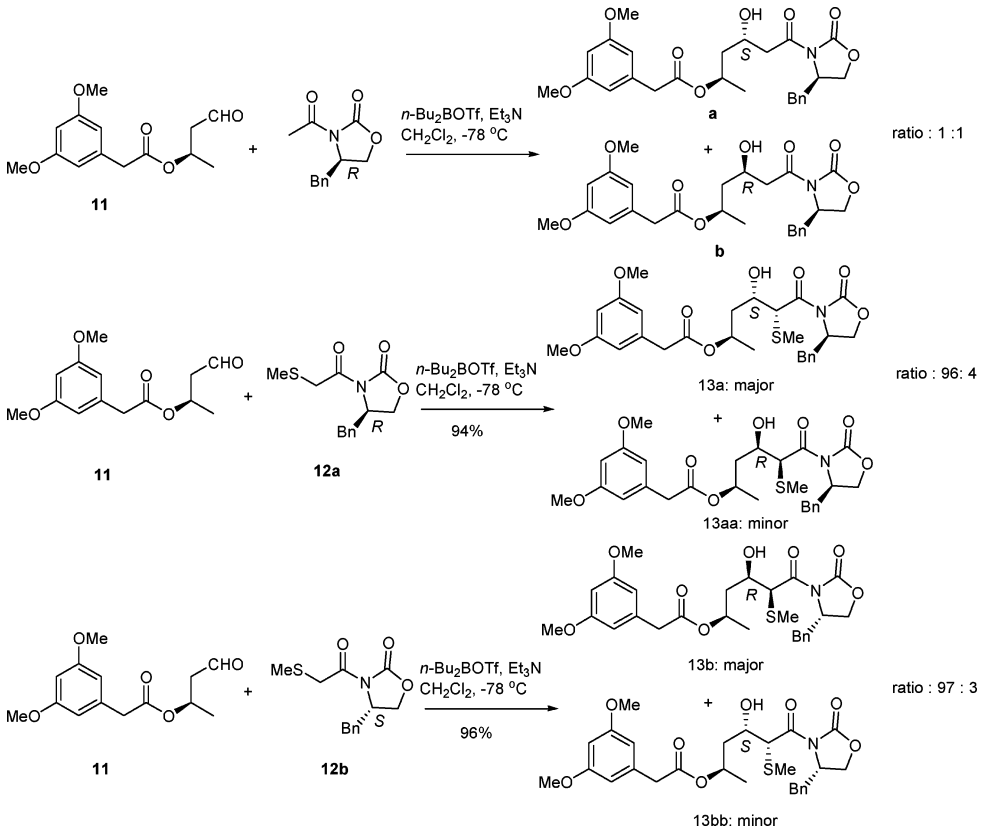



**SCHEME 2** [a]




[a] Reagents and conditions: (a) *n*-BuLi, HMPA, THF, 0 to −78 °C, 96%; (b) DCC, DMAP, $Et_2O$, rt, 97%; (c) $PbO_2$, $BF_3.Et_2O$, THF/$H_2O$, rt, 86%.

**SCHEME 3**




of the compound **8** with 3,5-dimethoxyphenyl acetic acid **9**[10] using DCC and DMAP gave the ester **10**. This ester **10** was converted to the aldehyde **11** with $PbO_2$ and $BF_3{\cdot}Et_2O$.[11]

Having aldehyde **11** in hand, Evans asymmetric aldol reaction was used to establish the C-9 stereochemical center. As shown in Scheme 3, different boryl enolates were tried. However the *N*-acetyloxazolidinone boryl enolate gave low diastereoselectivity (nearly 1:1 ratios of the aldol adducts **a** and **b** which were separated by silica gel column chromatography when the hydroxy group was protected as acetate ester). After many trials, we found that the boryl enolates of oxazolidinone **12a** and **12b** could give high diastereoselectivity (the ratios were 96:4 and 97:3, respectively, which were separated by silica gel column chromatography when the hydroxy group was protected as acetate ester) as the method described by Evans.[12,13]

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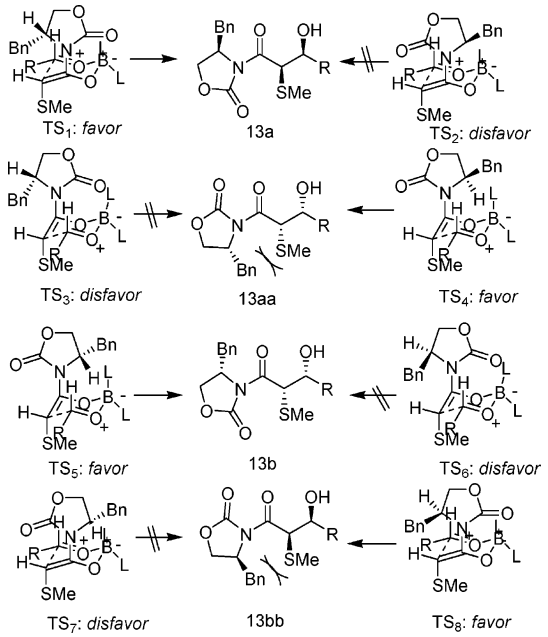
**SCHEME 4**




The absolute configurations of the aldol products were illustrated by the Evans model (Scheme 4).[14] The transition states $TS_1$ and $TS_5$ were believed to be favorable, leading to the major products **13a** and **13b** as shown in Scheme 4.

As shown in Scheme 5, the asymmetric aldol addition adduct **13a** from **12a** and aldehyde **11** was protected as acetate ester **14a** in 96% yield. Desulfurization of **14a** proceeded in 95% yield with *n*-$Bu_3SnH$ and AIBN (benzene, reflux, 45 min).[15] Treatment of **15a** with lithium hydroxide and a 8-fold excess of 30% hydrogen peroxide in aqueous THF for 15 min at 0 °C afforded a 91% yield of the corresponding carboxylic acid **16a**.[13]

The macrolide **17a** was obtained by intramolecular Friedel−Crafts reaction of the carboxylic acid **16a** in a mixture of trifluoroacetic acid and trifluoroacetic acid anhydride in 41% yield (60 °C, reflux, 30 min). The yield of this reaction was higher than the 15% yield reported for the corresponding cyclization reaction in the synthesis of curvularin (**4**).[16] Deprotection of the methoxy groups of **17a** using the fresh prepared $AlI_3$ produced **18a**,[17] which converted into the desired xestodecalactone **B** under acidic conditions (AcCl/MeOH).[18]

Xestodecalactone **C** was synthesized by the same strategy as xestodecalactone **B** using the (*S*)-oxazolidinone **12b** to establish the C-9 reversed hydroxy stereocenter. The diastereoselectivity ratio was 97:3. The analytical and spectral data of the synthetic compound were in agreement with those previously reported in the literature.[1] By comparing their identical CD spectra and polarimeter values with the natural products, the absolute configurations of xestodecalactones **B** and **C** were determined as (9*S*,11*R*) and (9*R*,11*R*), respectively.

In summary, the first concise and efficient asymmetric total syntheses of xestodecalactones **B** and **C** have been achieved using the asymmetric aldol addition and the intramolecular acylation as key steps. Both the stereocenters were established in a facile manner with high selectivity. The syntheses consisted of 10 steps starting from commercially available (*R*)-(+)-methyloxirane **6** and dithiane **7** in 22 and 20.2% overall yield, respectively. The absolute configurations of xestodecalactones **B** and **C** were determined as *R* at C-11 by total syntheses.

## Experimental Section

**(*R*)-1-(1, 3-Dithian-2-yl)propan-2-ol (DHP) (8).** To a solution of dithiane **7** (12.22 g, 102 mmol) in 50 mL of anhydrous THF at −78 °C under argon were added 25.6 mL (204 mmol, 2 equiv) of HMPA and 42.5 mL (102 mmol, 1 equiv) of *n*-BuLi (2.4 M in hexanes). The mixture was warmed to 0 °C slowly and stirred for 2 h. After the solution was recooled to −78 °C, (*R*)-(+)-methyloxirane **6** (6.212 g, 107 mmol) was added. After stirring for 1 h at −78 °C, the reaction mixture was quenched with saturated $NH_4Cl$ solution, and the reaction mixture was warmed to rt. The mixture was extracted with EtOAc (3 × 80 mL) and concentrated in vacuo. The residue was dissolved in 150 mL of ethyl acetate, washed with water (3 × 20 mL), dried ($Na_2SO_4$), and concentrated in vacuo. The residue was purified by column chromatography (hexanes/EtOAc, 4:1) to give compound **8** (17.43 g, 96%) as a colorless oil: $[\alpha]_D^{25}$ −23 (*c* 1.0, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 4.20 (dd, $J$ = 8.1, 6.0 Hz, 1H), 4.05−4.11 (m, 1H), 2.75−2.92 (m, 4H), 2.24 (s, 1H), 2.05−2.14 (m, 1H), 1.78−1.90 (m, 3H), 1.19 (d, $J$ = 2.1 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 64.7, 44.1, 30.2, 30.0, 25.8, 23.5; IR (KBr) 3394, 2900, 1420 1129, 1029 $cm^{-1}$; HRMS *m*/*z* calcd for $C_7H_{14}OS_2$ $[M + H]^+$ 179.0564, found 179.0560.

**Compounds 13a and 13b.** To a solution of 3.03 g (11.4 mmol) of **12a** in 30 mL of $CH_2Cl_2$ at −5 °C were added dropwise 13.7 mL of dibutylboryl triflate (1.0 M in $CH_2Cl_2$) and 2.05 mL (14.82 mmol, 1.2 equiv) of $Et_3N$ at a rate such that the internal temperature stayed below 0 °C. The resulting clear colorless solution was stirred at 0 °C for 1 h, cooled to −78 °C, and 3.2 g (12 mmol) of aldehyde **11** was added over 5 min. After 30 min, the solution was allowed to warm to 0 °C and quenched by addition of 15 mL of 1.5 M aqueous pH 7 phosphate buffer and 60 mL of methanol. The solvent was removed in vacuo, and 40 mL of water was added. The mixture was extracted with three 80 mL portions of ether. The combined organic extracts were washed with 30 mL of 5% aqueous $NaHCO_3$ and 30 mL of brine, dried over $Na_2SO_4$, filtered, and concentrated in vacuo. Flash chromatography on silica gel (hexanes/EtOAc, 4:1) afforded aldol adduct **13a** (5.72 g, 94%) as a colorless oil: $[\alpha]_D^{25}$ +36 (*c* 2.0, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.25−7.38 (m, 5H), 6.46 (d, $J$ = 1.8 Hz, 2H), 6.33 (d, $J$ = 2.4 Hz, 1H), 5.23 (td, $J$ = 9.6, 3.3 Hz, 1H), 4.75 (ddd, $J$ = 13.6, 8.1, 3.0 Hz, 1H), 4.61 (d, $J$ = 6.6 Hz, 1H), 4.16−4.28 (m, 2H), 3.90 (s, 1H), 3.76 (d, $J$ = 9.6 Hz, 6H), 3.56 (s, 2H), 3.27 (dd, $J$ = 13.2, 3.6 Hz, 1H), 3.17 (s, 1H), 2.79 (dd, $J$ = 13.2, 9.6 Hz, 1H), 2.14 (s, 3H), 1.77 (dd, $J$ = 9.6, 4.2 Hz, 2H), 1.28 (d, $J$ = 6.3 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 171.2, 170.2, 160.7, 152.8, 136.3, 134.8, 129.4, 129.0, 127.4, 107.1, 99.2, 68.7, 66.0, 65.7, 55.3, 54.9, 49.6, 42.0, 40.9, 37.5, 20.7, 13.4; IR (KBr) 3395, 2925, 1776, 1684, 1598, 1459, 1361, 1205, 1154, 1061 $cm^{-1}$; HRMS *m*/*z* calcd for $C_{27}H_{33}NO_8S$ $[M + Na]^+$ 554.1825, found 554.1831. **13b** (5.84 g, 96%) was obtained from **12b** (3.03 g, 11.4 mmol) and aldehyde **11** (3.2 g, 12 mmol) by the same operation as the synthesis of **13a**: $[\alpha]_D^{25}$ −31 (*c* 2.04, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.24−7.37 (m, 5H), 6.46 (d, $J$ = 2.4 Hz, 2H), 6.33 (t, $J$ = 2.4 Hz, 1H), 5.21

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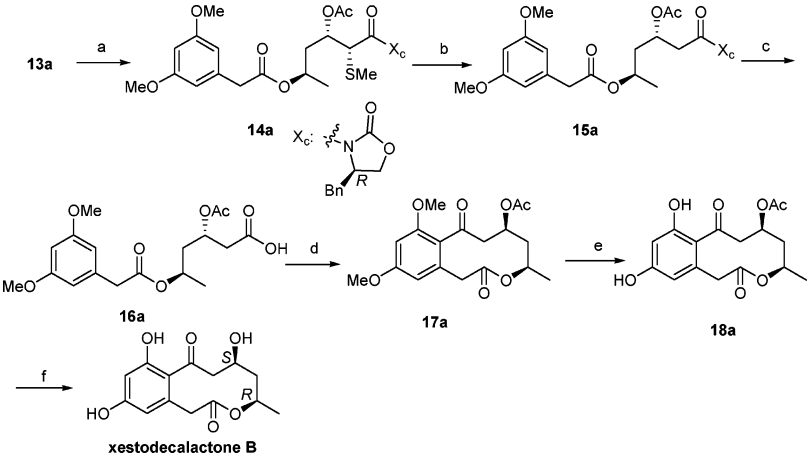
**SCHEME 5** [a]




[a] Reagents and conditions: (a) $Ac_2O$, pyridine, rt, 96%; (b) AIBN, *n*-$Bu_3SnH$, benzene, reflux, 95%; (c) $H_2O_2$, LiOH, THF/$H_2O$, 0 °C, 91%; (d) TFA, TFAA, reflux, 41%; (e) $AlI_3$, $Bu_4N^+I^-$, benzene, rt, 94%; (f) AcCl/MeOH, 0 °C, 90%.

(td, $J$ = 4.8, 1.5 Hz, 1H), 4.75 (ddd, $J$ = 12.9, 7.8, 3.6 Hz, 1H), 4.61 (d, $J$ = 6.3 Hz, 1H), 4.15−4.26 (m, 2H), 3.91 (t, $J$ = 9.6 Hz, 1H), 3.79 (d, $J$ = 1.5 Hz, 6H), 3.55 (s, 2H), 3.26 (dd, $J$ = 13.2, 3.3 Hz, 1H), 3.17 (s, 1H), 2.79 (dd, $J$ = 13.2, 9.6 Hz, 1H), 2.14 (s, 3H), 1.74−1.79 (m, 2H), 1.27 (d, $J$ = 6.3 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 171.2, 170.1, 160.7, 152.8, 136.3, 134.8, 129.4, 129.0, 127.4, 107.1, 99.2, 68.7, 65.9, 65.8, 55.2, 54.9, 49.6, 42.0, 40.9, 37.5, 20.6, 13.4; IR (KBr) 3506, 2926, 1777, 1687, 1599, 1459, 1361, 1294, 1205, 1155, 1064 cm$^{-1}$; HRMS *m*/*z* calcd for $C_{27}H_{33}NO_8S$ [M + Na]$^+$ 554.1825, found 554.1820.

**Macrolides 17a and 17b.** The acid **16a** (368 mg, 1 mmol) was dissolved in a mixture of trifluoroacetic acid (20 mL) and trifluoroacetic acid anhydride (4 mL), and the solution was refluxed for 30 min at 60 °C, cooled to rt, poured into an excess of sodium hydrogen carbonate, and the product was isolated with ether. The combined extracts were washed with water, dried ($Na_2SO_4$), and the solvent removed. The residue was purified by column chromatography (hexanes/EtOAc, 4:1) to give the metabolite **17a** (144 mg, 41%) as a pale yellow foam: $[\alpha]_D^{25}$ +45 (*c* 0.4, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.40 (d, $J$ = 6.3 Hz, 1H), 6.27 (d, $J$ = 9.9 Hz, 1H), 5.31 (t, $J$ = 9.9 Hz, 1H), 5.02 (br s, 1H), 4.26 (d, $J$ = 18.6 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.42 (d, $J$ = 18.6 Hz, 1H), 3.29 (dd, $J$ = 15.3, 10.5 Hz, 1H), 3.01 (d, $J$ = 15.3 Hz, 1H), 2.05 (s, 3H), 1.83−1.98 (m, 2H), 1.19 (d, $J$ = 6.3 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 202.9, 169.8, 168.6, 161.5, 159.0, 134.6, 123.9, 107.8, 97.1, 71.6, 71.2, 55.6, 55.4, 51.6, 42.8, 40.3, 21.3, 20.7; IR (KBr) 2939, 1735, 1603, 1459, 1425, 1334, 1237, 1157, 1093 cm$^{-1}$; HRMS *m*/*z* calcd for $C_{18}H_{22}O_7$ [M + H]$^+$ 351.1444, found 351.1438. **16b** (368 mg,1 mmol) was treated with 20 mL of trifluoroacetic acid and 4 mL of trifluoroacetic acid anhydride as described for the synthesis of **17a** to give **17b** (138 mg, 39%) as a pale yellow foam: $[\alpha]_D^{25}$ +49 (*c* 1.15, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.40 (d, $J$ = 2.0 Hz, 1H), 6.25 (s, 1H), 5.31 (t, $J$ = 10.4 Hz, 1H), 4.99−5.03 (m, 1H), 4.26 (d, $J$ = 18.8 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.42 (d, $J$ = 19.2 Hz, 1H), 3.28 (dd, $J$ = 15.2, 11.2 Hz, 1H), 3.01 (d, $J$ = 15.2 Hz, 1H), 2.04 (s, 3H), 1.95 (d, $J$ = 13.2 Hz, 1H), 1.19 (d, $J$ = 6.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 202.9, 169.7, 168.6, 161.6, 159.1, 134.6, 124.0, 107.8, 97.1, 71.6, 71.1, 55.6, 55.4, 51.6, 42.8, 40.3, 21.3, 20.7; IR (KBr) 2938, 1734, 1680, 1603, 1459, 1337, 1236, 1158, 1093, 1058 cm$^{-1}$; HRMS *m*/*z* calcd for $C_{18}H_{22}O_7$ [M + H]$^+$ 351.1444, found 351.1447.

**Xestodecalactones B and C.** A quantity of 0.2 mL of acety1 chloride was added to anhydrous methanol (5 mL) at 0 °C, and after being stirred for 15 min at 0 °C, a solution of the compound **18a** (30 mg, 0.09 mmol) in chloroform/methanol (1 mL/1 mL) was added and the mixture was stirred at 0 °C for 12 h. The reaction was quenched by water. The methanol and chloroform were distilled out in vacuo, and the mixture was then extracted with ethyl acetate (3 × 20 mL), washed with water, dried over $Na_2SO_4$, concentrated in vacuo, and the residue was purified by column chromatography on silica gel ($CHCl_3$/EtOAc, 1:1) to give xestodecalactone **B** (23 mg, 90%) as a white solid: mp 171−173 °C dec; $[\alpha]_D^{25}$ +19 (*c* 0.3, $CH_3OH$); $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.96 (s, 1H), 9.74 (s, 1H), 6.27 (s, 1H), 6.11 (s, 1H), 4.81 (d, $J$ = 6.4 Hz, 1H), 4.77 (d, $J$ = 4.8 Hz, 1H), 4.02 (s, 1H), 3.63 (d, $J$ = 17.6 Hz, 1H), 3.54 (d, $J$ = 17.6 Hz, 1H), 3.48 (t, $J$ = 14.8 Hz, 1H), 2.59 (dd, $J$ = 14.8, 8.8 Hz, 1H), 1.86 (d, $J$ = 4.4 Hz, 1H), 1.74 (d, $J$ = 4.4 Hz, 1H), 1.15 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 205.0, 169.0, 159.0, 156.8, 135.4, 119.7, 109.8, 101.2, 68.1, 64.1, 52.5, 42.0, 30.6, 19.5; IR (KBr) 3208, 1726, 1608, 1464, 1338, 1263, 1162, 1024, 849 cm$^{-1}$; HRMS *m*/*z* calcd for $C_{14}H_{16}O_6$ [M + H]$^+$ 281.1020, found 281.1024. Xestodecalactone **C** (25 mg, 88%) was obtained as a white solid from **18b** (32 mg, 0.1 mmol) by the same operation for the synthesis of xestodecalactone **B**: mp 167−169 °C dec; $[\alpha]_D^{25}$ +24 (*c* 0.3, $CH_3OH$); $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.91 (s, 1H), 9.72 (s, 1H), 6.27 (d, $J$ = 1.6 Hz, 1H), 6.09 (s, 1H), 4.76 (d, $J$ = 4.0 Hz, 1H), 4.72 (dd, $J$ = 11.2, 5.6 Hz, 1H), 3.95 (br s, 1H), 3.82 (d, $J$ = 18.8 Hz, 1H), 3.48 (d, $J$ = 18.8 Hz, 1H), 3.08 (dd, $J$ = 14.8, 10.4 Hz, 1H), 2.81 (d, $J$ = 14.8 Hz, 1H), 1.83 (d, $J$ = 13.6 Hz, 1H), 1.64 (dd, $J$ = 14.8, 11.2 Hz, 1H), 1.08 (d, $J$ = 6.0 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 204.5, 168.8, 159.1, 157.0, 134.4, 121.2, 109.2, 101.3, 70.6, 67.8, 55.3, 46.0, 20.7; IR (KBr) 3343, 2923, 1721, 1657, 1608, 1463, 1339, 1261, 1162, 1023, 832 cm$^{-1}$; HRMS *m*/*z* calcd for $C_{14}H_{16}O_6$ [M + Na]$^+$ 303.0839, found 303.0843.

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**Supporting Information Available:** Experimental procedures and characterization data for compounds **8**−**11**, **12a/12b**− **18a/18b**, and xestodecalactones **B** and **C**. This material is available free of charge via the Internet at http://pubs.acs.org.

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