Total Synthesis of *C*-Glycosylangucycline, Urdamycinone B, Using an Unprotected Sugar

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The total synthesis of urdamycinone B (**1**), a prototypical member of the *C*-glycosylangucycline antibiotics, was achieved by a novel and effective strategy without any protecting group in the sugar moiety. The unprotected *C*-glycosyljuglone **6** was effectively synthesized by the aryl *C*-glycosidation of 1,5-naphthalenediol (**16**) with the totally unprotected D-olivose (**8**) and the subsequent regioselective photooxygenation of the resultant *C*-glycosylnaphthalenediol **17**. On the other hand, the diene **7** was prepared from 3-methyl-2-cyclohexen-1-one (**9**) in a short step via the cross-coupling of the vinyl triflate **20** and vinylbutyltin (**21**) and the Wittig reaction of the aldehyde **24** and the phosphine **25**. Finally, the regioselective Diels−Alder reaction of the unprotected *C*-glycosyljuglone **6** and the diene **7**, followed by the regioselecitive introduction of the ketone function at the C1 position, led to the total synthesis of **1**.

Introduction

The angucyclines with a unique benz[*a*]anthraquinone as a common structure are a rapidly growing new class of antibiotics. They show a variety of biological activities including antitumor activity and enzyme inhibition.[2] The *C*-glycoside structure is uniquely involved in some members of this class as shown in Figure 1. Among them, urdamycinone B (**1**), a prototypical member of the *C*-glycosylangucyclines, which is obtained from antibiotic urdamycin B (**2**) by careful cleavage of the two *O*-glycoside moieties, also exhibits antitumor activity.[3] The elegant total syntheses of (−)-urdamycinone B, the enantiomer of the natural urdamycinone B, and urdamycinone B (**1**) have been reported by Yamaguchi[4] and Sulikowski,[5] respectively. On the other hand, another *C*-glycosylangucycline, C104 (**3**), was effectively synthesized by Suzuki and Matsumoto.[6] However, they are the only successful achievements of the total synthesis of the full structure of *C*-glycosylangucycline. Previously, we have disclosed a novel and practical aryl *C*-glycosidation method using an unprotected sugar. In this paper, we now report the full account of the significant application of this method, that is the highly effective total synthesis of urdamycinone B (**1**) by a novel strategy without using any protecting group in the sugar moiety.[7]

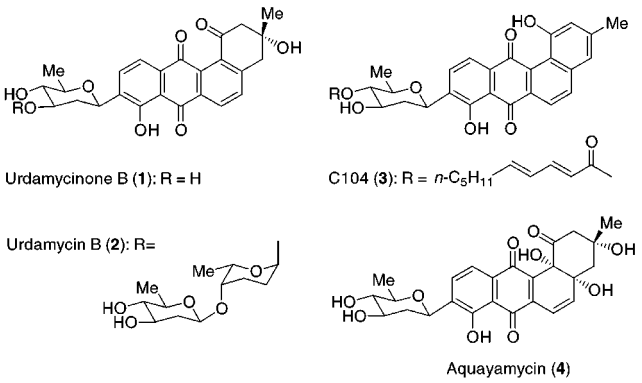

Figure 1. Molecular structures of the representative angucycline antibiotics.

Synthetic Plan

The retrosynthetic analysis of urdamycinone B (**1**) is shown in Figure 2 along with our synthetic plan. The target molecule **1** would be obtained by the conversion of the masked tertiary alcohol into the free alcohol at the C3 position and the introduction of the ketone function using regioselective oxygenation at the C1 position in the key intermediate **5**. The key intermediate **5** was partitioned into two Diels−Alder fragments, the dienophile **6** and the diene **7**. The unprotected *C*-glycosyljuglone **6** would be synthesized by the aryl *C*-glycosidation method, which was recently developed in our laboratories,[8] using the totally unprotected D-olivose (**8**) and an appropriate glycosyl acceptor. On the other hand, the diene **7** would be derived from 3-methylcyclohex-2-enone (**9**) via the introduction of the masked tertiary alcohol by Fleming's method[9] and the appropriate diene function for the Diels−Alder reaction with **6**. The highly effective synthesis of the unprotected *C*-glycosyljuglone **6** and the suitably protected diene **7** and the regioselective Diels−Alder reaction of **6** and **7** leading to the total synthesis of **1** are described in the following discussion.

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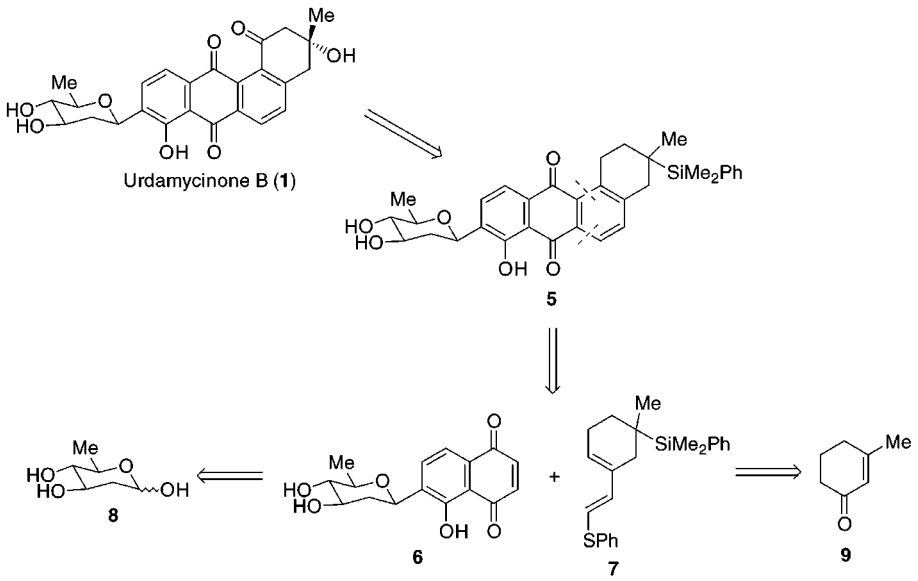


Figure 2. Retrosynthetic analysis of urdamycinone B (**1**).

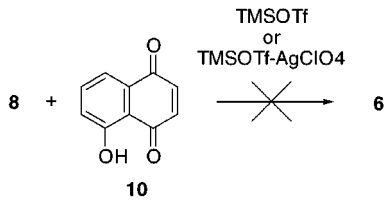
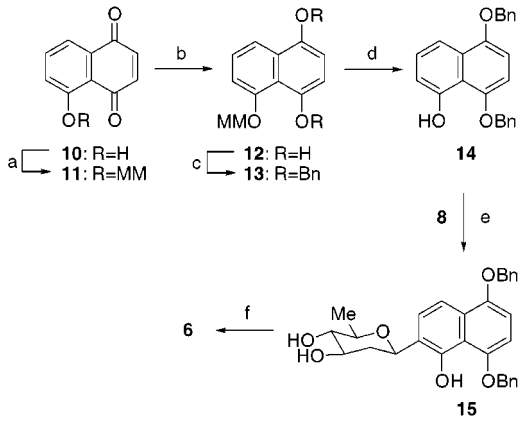


Figure 3. Aryl *C*-Glycosidatins of juglone (**10**) and D-olivose (**8**).

Results and Discussion

Synthesis of the Unprotected *C*-Glycosyljuglone 6. *C*-Glycosyljuglone, a 5-hydroxy-1,4-naphthoquinone bearing a *C*-glycoside at C6, is a common structural feature among the many members of angucycline antibiotics. The *C*-glycosyljuglone is also a promising synthetic intermediate for this class of antibiotics. Therefore, several approaches to the *C*-glycosyljuglone have been developed[5,7b,10,11] and the syntheses of angucycline antibiotics via the *C*-glycosyljuglone have also been reported.[5,7b] Our synthetic approach began with the synthesis of the unprotected *C*-glycosyljuglone **6** using the totally unprotected sugar, D-olivose (**8**). We first tried the direct aryl *C*-glycosidation of juglone (**10**) with the totally unprotected D-olivose (**8**) (Figure 3). However, this reaction did not proceed by the activators, trimethylsilyl trifluoromethanesufonate (TMSOTf) or TMSOTf-$AgClO_4$, which were developed as novel and effective activators for the aryl *C*-glycosidations of unprotected sugars in our laboratories.[8] Furthermore, the corresponding protected *C*-glycosyljuglones possessing benzyl or acetyl groups were not obtained even when other appropriate aryl *C*-glycosidation methods[12] using protected sugars were applied to this reaction. At this stage, it was considered that these unfavorable results came from the extremely low reactivity of the glycosyl acceptor **10** due to the quinone skeleton. Therefore, we next converted the juglone (**10**) into the suitable glycosyl acceptor **14** as shown in Scheme 1. Thus, the juglone (**10**) was first protected using methoxymethyl chloride (MMCl) and *i*-Pr_2NEt in CH_2Cl_2 to give the protected juglone **11** in 92% yield. **11** was then treated with a catalytic amount of 10% Pd−C under a hydrogen atmosphere to afford the labile dihydroxyquinone **12**, which was rapidly protected with benzyl groups by the standard manner to give the protected naphthol **13**. The fully protected naphthol **13** was then converted into the glycosyl acceptor **14** by the selective deprotection of the methoxymethyl group under acidic conditions. The aryl *C*-glycosidation of **14** and the un-

Scheme 1[a]



[a] Key: (a) MMCl, *i*-Pr_2NEt, CH_2Cl_2, 0 °C, 1 h then 25 °C 0.5 h, 92%; (b) H_2, 10% Pd−C, EtOAc, 25 °C, 1 h; (c) BnBr, NaH, DMF, 25 °C, 1 h, 86% from **11**; (d) CF_3CO_2H, CH_2Cl_2, 25 °C, 1 h, 85%; (e) TMSOTf, MeCN, 25 °C, 1 h, 27%; (f) H_2, 10% Pd−C, MeOH, 25 °C, 1 h, 78%.

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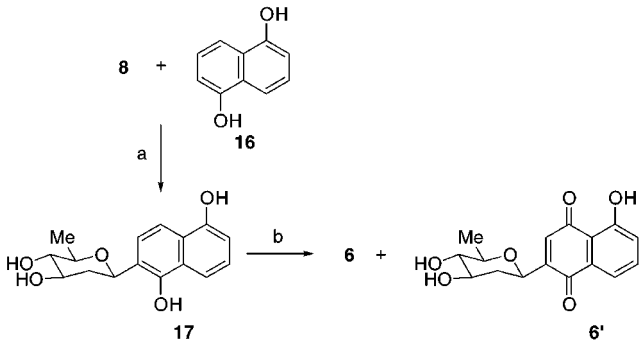
Scheme 2[a]



[a] Key: (a) TMSOTf, MeCN, 25 °C, 1 h, 65%; (b) O_2, sunlight, *t*-BuOH−$CHCl_3$ (1:3), rt, 12 h, 57% of **6** and 13% of **6′**.

protected D-olivose (**8**) was realized by the method that was recently developed in our laboratories.[8] Thus, the reaction of **14** (2.0 equiv) and **8** (1.0 equiv) in the presence of TMSOTf (0.5 equiv) in MeCN at 25 °C for 1 h gave the desired aryl *β*-*C*-glycoside **15** in 27% yield as the only isolated product. The *β*-*C*-glycoside **15** was then debenzylated by hydrogenolysis using 10% Pd−C in MeOH at 25 °C for 1 h to afford the unprotected *C*-glycosyljuglone **6** in 78% yield. Although the desired unprotected *C*-glycosyljuglone **6** was in hand, the yield of the key reaction, that is the aryl *C*-glycosidation of the unprotected sugar **8** was very low and not satisfactory. Therefore, we further investigated a more effective synthesis of the unprotected *C*-glycosyljuglone **6**. After many attempts for searching such a synthesis, we finally developed the novel two-step synthesis of the unprotected *C*-glycosyljuglone **6** from the unprotected D-olivose (**8**) as shown in Scheme 2. The first step was the *C*-glycosidations of 1,5-naphthalenediol (**16**) with the unprotected sugar, D-olivose (**8**). Thus, the *C*-glycosidation of **16** (2.0 equiv) and **8** (1.0 equiv) using TMSOTf (0.2 equiv) in MeCN at 25 °C for 1 h proceeded smoothly to give the unprotected aryl *β*-*C*-glycoside **17** in 65% yield as a single isomer. Furthermore, it was found that the unprotected methyl D-olivoside also coupled with **16** under similar conditions to afford **17** in a similar yield. The second step was the oxygenation of **17** to **6**. At this stage, we first examined the oxygenation of **17** using ammonium cerium(IV) nitrate (CAN),[13] potassium nitrosodisulfonate (Fremy's salt),[14] thallium(III) nitrate trihydrate (TTN),[15] and oxygen in the presence of Triton B[16] as the oxygenating agents that are widely used for the conversion of naphthol to quinone. From the results shown in Table 1, however, the desired *C*-glycosyljuglone **6** was not detected at all or isolated in a very low yield while the regioisomer **6′** was predominantly produced in some cases. Therefore, our attention next turned to the photooxygenation[17] of **17**. These results are summarized in Table 2. Remarkably, the regioselectivity of the oxygenation of **17** dramatically changed, and the desired *C*-glycosyljuglone **6** was predominantly obtained by choice of the appropriate reaction solvent. Thus, the photooxygenation of **17** without any reagent was best effected by the irradiation of sunlight in *t*-BuOH−$CHCl_3$ (1:3, 0.0069 M for **17**) under an oxygen atmosphere at room temperature for 12 h to give the desired unprotected *C*-glycosyljuglone **6** in 57% yield along with a 13% yield of **6′** (entry 8 in Table 2). Thus, the short step and effective synthesis of the *C*-glycosyljuglone **6** without any protecting group both in the aglycon and in the glycon moieties was achieved.

Table 1. Oxygenations of 17

17 $\xrightarrow[25\ °C]{}$ **6** + **6′**

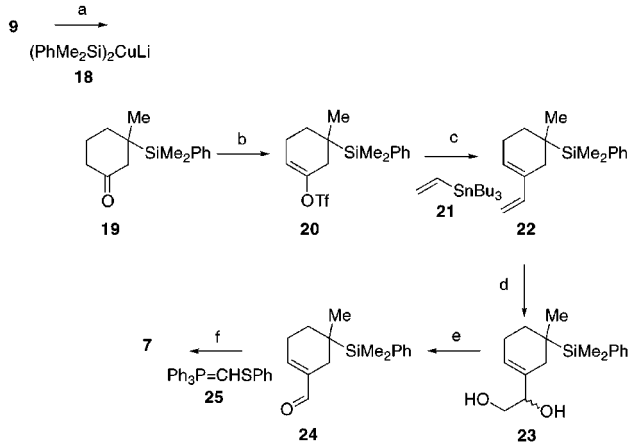
entry	reagent/(equiv)	solvent	time (h)	yield (%) **6**	yield (%) **6′**
1	CAN (2.5)	CH_3CN-H_2O	0.5	0	25
2	Fremy's salt (3.6)	MeOH	1	10	55
3	TTN (1.8)	MeOH	0.5	1	74
4	Triton B (2.0)/O_2	MeOH	1	0	0

Table 2. Photooxygenations of 17

17 $\xrightarrow[12\ h]{O_2,\ \text{sunlight}}$ **6** + **6′**

entry	solvent	yield (%) **6**	yield (%) **6′**
1	MeOH	7	12
2	EtOH	19	17
3	*i*-PrOH	30	17
4	*t*-BuOH	52	22
5	*t*-BuOH−hexane (1:1)	41	13
6	*t*-BuOH−PhH (1:1)	51	15
7	*t*-BuOH−$CHCl_3$ (1:1)	52	14
8	*t*-BuOH−$CHCl_3$ (1:3)	57	13

Scheme 3[a]



[a] Key: (a) ref 18; (b) LDA, Tf_2NPh, THF, −78 → 25 °C, 1 h, 94%; (c) $(Ph_3P)_4Pd$, LiCl, DMF, 70 °C, 1 h, 93%; (d) AD-mix-*β*, *t*-BuOH−H_2O, 0 °C, 12 h, 92%; (e) $NaIO_4$, THF−H_2O, 25 °C, 1.5 h, 87%; (f) THF, 25 °C, 0.5 h, 77%.

Synthesis of the Diene 7. With the unprotected *C*-glycosyljuglone **6** as a dienophile for the Diels−Alder reaction in hand, our attention next turned to the preparation of an appropriate diene (Scheme 3). For this purpose, cyclohexanone **19**,[18] which was obtained using 3-methyl-2-cyclohexen-1-one (**9**) and the silylcuprate **18**, was selected as the starting material. The cyclohexanone **19** had a phenyldimethylsilyl group as the masked form of a hydroxyl group.[9] Regioselective enolate formation of **19** with lithium diisopropylamide (LDA) and trapping of

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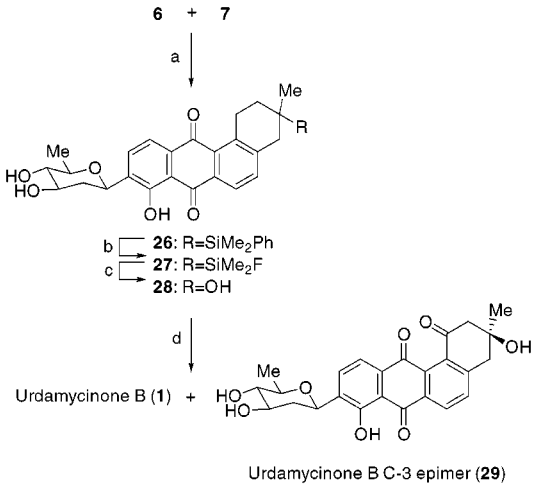
the intermediate enolate with *N*-phenyltrifluoromethanesulfonimide (Tf_2NPh) afforded only the desired regioisomer of the vinyl triflate **20** in 94% yield. The high regioselectivity resulted from a combination of the steric shielding arisen from the methyl and silyl groups and the β-effect of the silicon.[19] The cross-coupling reaction[20] of the vinyl triflate **20** and vinyltributyltin (**21**) using a catalytic amount of $(Ph_3P)_4Pd$ and LiCl in DMF at 70 °C for 1 h yielded the diene **22** in 93% yield. At this stage, we tried the regioselective dihydroxylation of the exo double bond in **22** using several reagents. It was finally found that the dihydroxylation by Sharpless AD reaction[21] using a bulky AD-mix-β gave good selectivity to afford the desired diol **23** in 92% yield, while OsO_4 gave poor selectivity and produced a significant amount of the corresponding tetraol. The oxidative cleavage of **23** using $NaIO_4$ gave the α,β-unsaturated aldehyde **24** in 87% yield. Finally, the Wittig reaction of **24** with 2.0 equiv of triphenyl(phenylthiomethylene)phosphine (**25**)[22] in THF at 25 °C proceeded stereospecifically to give only the desired *E,E*-diene **7** in 77% yield.

Total Synthesis of 1. Following the completion of the syntheses of dienophile **6** and diene **7**, we focused on their cycloaddition by Diels−Alder reaction and total synthesis of **1** (Scheme 4). The Diels−Alder cycloaddition between the unprotected *C*-glycosyljuglone **6** (1.0 equiv) and the diene **7** (1.0 equiv) using $B(OAc)_3$[23] followed by treatment of the resulting Diels−Alder product by 1,8-diazabicyclo-[5.4.0]undec-8-ene (DBU) afforded the cycloadduct **26** in 58% overall yield. The high regioselectivity came from the coordination of $B(OAc)_3$ between the C5 hydroxy group and the C4 carbonyl oxygen in **6** and the electron-donating nature of the thiophenyl group in **7**. The conversion of the silyl group into the tertiary hydroxyl group was achieved using Fleming's method[9,24] in two steps. Thus, **26** was first treated with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 at 25 °C for 2 h to afford the fluoride **27**, which was then treated with KF, $KHCO_3$, and 31% H_2O_2 in THF−MeOH at 25 °C for 14 h to give the tertiary alcohol **28** in 42% overall yield. Finally, the regioselective oxygenation of **28** was successfully carried out by mild photooxygenation,[25] in which a MeOH solution of **28** was exposed to daylight, to furnish urdamycinone B (**1**) (36%) and the C3 epimer **29** (35%) after their separation by reversed-phase preparative thin-layer chromatography.[4] The faster moving isomer was in good agreement with natural urdamycinone B based on the 270 MHz ^1H and ^{13}C NMR, $[\alpha]_D$, and mp.

Conclusions

The present work demonstrates the total synthesis of *C*-glycosylangucycline, urdamycinone B (**1**), by a novel strategy that includes the higly stereoselective aryl *C*-glycosidation of the unprotected sugar **8** and the highly regioselective Diels−Alder reaction of the unprotected *C*-glycosyljuglone **6** and the diene **7** as the key steps. This novel approach would provide a significant new entry for the synthesis of the *C*-glycosylangucycline family of antibiotics, which is a large group of biologically active secondary metabolites of microbial origin.

Scheme 4[a]



[a] Key: (a) $B(OAc)_3$, CH_2Cl_2, 25 °C, 2 h, then DBU, CH_2Cl_2, 25 °C, 0.5 h, 58%; (b) $HBF_4{\cdot}Et_2O$, CH_2Cl_2, 25 °C, 2 h, 78%; (c) KF, $KHCO_3$, 31% H_2O_2, THF−MeOH, 25 °C, 14 h, 53%; (d) O_2, sunlight, MeOH, 25 °C, 24 h, 71%, then separation, 36% for **1**, 35% for **29**.

Experimental Section

General Methods. Melting points are uncorrected. ^1H NMR spectra were measured in $CDCl_3$ using TMS as internal standard unless otherwise noted. High-resolution mass spectra (HRMS) were recorded under electron impact (EI) conditions. Silica gel TLC and column chromatography were performed on Merck TLC 60F-254 (0.25 mm) and Fuji-Davison BW-820MH or BW-300, respectively. Air- and/or moisture-sensitive reactions were carried out under an atomosphere of argon with oven-dried glassware. In general, organic solvents were purified and dried by the appropriate procedure, and evaporation and concentration were carried out under reduced pressure below 30 °C, unless otherwise noted.

Naphthoquinone 11. To a stirred solution of **10** (5.15 g, 29.6 mmol) and methoxymethyl chloride (8.9 mL, 118 mmol) in dry CH_2Cl_2 (155 mL) at 0 °C was added *i*-Pr_2NEt (15.5 mL, 88.7 mmol). After 1 h of stirring at 0 °C and 0.5 h of stirring at 25 °C, saturated aqueous NH_4Cl (150 mL) was added slowly to the reaction mixture under ice-cooling, and the resultant mixture was then extracted with diethyl ether. The extracts were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification of the residue by flash column chromatography (600 g of silica gel, 2:1 *n*-hexane−ethyl acetate) gave **11** (5.95 g, 92%) as an orange solid: R_f 0.32 (2:1 *n*-hexane−ethyl acetate); mp 102.5−103.0 °C (*n*-hexane, needles); ^1H NMR δ 3.55 (3H, s), 5.36 (2H, s), 6.86 (1H, d, J = 10.2 Hz), 6.91 (1H, d, J = 10.2 Hz), 7.54 (1H, dd, J = 8.0, 1.8 Hz), 7.67 (1H, dd, J = 8.0, 8.0 Hz), 7.80 (1H, dd, J = 8.0, 1.8 Hz). Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.09; H, 4.57.

Naphthalene 13. To a stirred solution of **11** (5.95 g, 27.3 mmol) in ethyl acetate (179 mL) was added a catalytic amount of 10% Pd−C. After the reaction mixture was vigorously stirred at 25 °C for 1 h under H_2, the mixture was filtered, and the catalytst was washed with ethyl acetate. The combined filtrate and washings were concentrated in vacuo. To an ice-cold solution of the residue in dry DMF (180 mL) were added benzyl bromide (9.7 mL, 68.2 mmol) and NaH (60% in mineral oil, 3.71 g, 92.8 mmol). After the reaction mixture was stirred at 25 °C for 1 h, ethanol (100 mL) and saturated aqueous NH_4Cl (200 mL) were added slowly to the reaction mixture under ice-

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cooling, and the resultant mixture was then extracted with diethyl ether. The extracts were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification of the residue by flash column chromatography (600 g of silica gel, 8:1 *n*-hexane−ethyl acetate) gave **13** (9.39 g, 86%) as a white solid: R_f 0.65 (3:1 *n*-hexane−ethyl acetate); mp 110.5−111.0 °C (*n*-hexane, cubes); ^{1}H NMR δ 3.47 (3H, s), 5.12 (2H, s), 5.19 (4H, s), 6.78 (1H, d, J = 8.4 Hz), 6.84 (1H, d, J = 8.4 Hz), 7.17 (1H, dd, J = 8.0, 1.2 Hz), 7.3−7.6 (11H, m), 8.07 (1H, dd, J = 8.0, 1.2 Hz). Anal. Calcd for $C_{26}H_{24}O_4$: C, 77.98; H, 6.04. Found: C, 77.86; H, 5.91.

Naphthol 14. To an ice-cold solution of **13** (6.23 g, 15.6 mmol) in dry CH_2Cl_2 (187 mL) was added trifluoroacetic acid (1.44 mL, 18.7 mmol) with stirring. After the reaction mixture was stirred at 25 °C for 1 h, the mixture was concentrated in vacuo. Purification of the residue by flash column chromatography (550 g of silica gel, 10:1 *n*-hexane−ethyl acetate) gave **14** (4.71 g, 85%) as a white solid: R_f 0.42 (5:1 *n*-hexane−ethyl acetate); mp 108.5−109.5 °C (*n*-hexane, needles); ^{1}H NMR δ 5.19 (2H, s), 5.23 (2H, s), 6.70 (1H, d, J = 8.4 Hz), 6.75 (1H, d, J = 8.4 Hz), 6.91 (1H, dd, J = 8.0, 1.2 Hz), 7.3−7.6 (11H, m), 7.82 (1H, dd, J = 8.0, 1.2 Hz), 9.52 (1H, s). Anal. Calcd for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66. Found: C, 80.76; H, 5.39.

***C*-Glycoside 15.** To a stirred mixture of D-olivose (**8**) (50.0 mg, 0.337 mmol) and **14** (241.0 mg, 0.676 mmol) in dry MeCN (13 mL) was added trimethylsilyl trifluoromethanesulfonate (40.0 μL, 0.207 mmol) dropwise at 0 °C under argon. After the reaction mixture was stirred at 25 °C for 1 h, Et_3N was added slowly to the reaction mixture under ice-cooling, and the resultant mixture was then concentrated in vacuo. Purification of the residue by flash column chromatography (30 g of silica gel, 10:1 chloroform−methanol) gave **15** (44.3 mg, 27%) as a yellow foam: R_f 0.33 (1:1 *n*-hexane−acetone); $[\alpha]^{28}_D$ +48.2° (*c* 0.51, MeOH); ^{1}H NMR δ 1.40 (3H, d, J = 6.0 Hz), 1.64 (1H, ddd, J = 13.2, 11.4, 11.4 Hz), 2.36 (1H, ddd, J = 13.2, 5.0, 2.2 Hz), 3.22 (1H, dd, J = 8.8, 8.8 Hz), 3.51 (1H, dq, J = 8.8, 6.0 Hz), 3.81 (1H, ddd, J = 11.4, 9.0, 5.0 Hz), 5.03 (1H, dd, J = 11.4, 2.2 Hz), 5.19 (2H, s), 5.21 (2H, s), 6.68 (1H, d, J = 9.0 Hz), 6.75 (1H, d, J = 9.0 Hz),7.3−7.55 (10H, m), 7.60 (1H, d, J = 8.8 Hz), 7.84 (1H, d, J = 8.8 Hz), 9.78 (1H, s). Anal. Calcd for $C_{30}H_{30}O_6$: C, 74.06; H, 6.21. Found: C, 73.98; H, 6.43.

***C*-Glycoside 17.** To a stirred mixture of D-olivose (**8**) (85.0 mg, 0.574 mmol) and 1,5-naphthalenediol (**16**) (183.8 mg, 1.15 mmol) in dry MeCN (5.7 mL) was added trimethylsilyl trifluoromethanesulfonate (22.0 μL, 0.115 mmol) under ice-cooling. After being stirred for 1 h at 25 °C, the reaction was quenched with Et_3N and the resulting mixture was then concentrated in vacuo. Purification of the residue by flash column chromatography (25 g of silica gel, 10:1 chloroform−methanol) gave **17** (108.8 mg, 65%) as a white solid: R_f 0.34 (4:1 chloroform−methanol); $[\alpha]^{28}_D$ +34.5° (*c* 1.12, MeOH); mp 223.5−224.5 °C (acetone−*n*-hexane, needles); ^{1}H NMR (CD_3-OD) δ 1.41 (3H, d, J = 5.8 Hz), 1.78 (1H, ddd, J = 11.6, 11.6, 11.0 Hz), 2.26 (1H, ddd, J = 13.2, 5.0, 2.2 Hz), 3.10 (1H, dd, J = 9.0, 9.0 Hz), 3.50 (1H, dq, J = 9.2, 5.8 Hz), 3.71 (1H, ddd, J = 11.0, 9.0, 4.4 Hz), 4.98 (1H, dd, J = 11.6, 2.0 Hz), 6.75−7.7 (5H, m). Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.20; H, 6.25. Found: C, 65.96; H, 6.25.

***C*-Glycosyljuglone 6. Method A.** To a solution of **15** (136.0 mg, 0.28 mmol) in MeOH (13.6 mL) was added a catalytic amount of 10% Pd−C. After the reaction mixture was vigorously stirred at 25 °C for 1 h under H_2, the mixture was filtered, and the catalytst was washed with ethyl acetate. The combined filtrate and washings were concentrated in vacuo. Purification of the residue by flash column chromatography (8.5 g of silica gel, 3:2 *n*-hexane−acetone) gave **6** (66.0 mg, 78%) as an orange solid. **Method B.** A solution of **17** (108.8 mg, 0.375 mmol) in *t*-BuOH−$CHCl_3$ (1:3, 54.4 mL) was irradiated with diffuse sunlight (a 75 W xenon lamp, Wacom Sunray Lamp, I-Sunsun) under O_2 for 12 h and then concentrated in vacuo. Purification of the residue by flash column chromatography (23 g of silica gel, 2:1 *n*-hexane−acetone) gave **6** (64.4 mg, 57%) and **6′** (14.8 mg, 13%) as orange solids, respectively. **6**: R_f 0.46 (3:2 *n*-hexane−acetone); $[\alpha]^{30}_D$ +143.5° (*c* 0.023, $CHCl_3$); mp 171.5−172.5 °C (diethyl ether−*n*-hexane, cubes); ^{1}H NMR δ 1.42 (3H, d, J = 6.4 Hz), 1.47 (1H, ddd, J = 12.2, 11.2, 11.2 Hz), 2.50 (1H, ddd, J = 12.2, 5.2 and 2.0 Hz), 3.21 (1H, dd, J = 9.0, 9.0 Hz), 3.52 (1H, dq, J = 9.8, 6.4 Hz), 3.85 (1H, ddd, J = 11.2, 9.8, 5.2 Hz), 4.92 (1H, dd, J = 11.2, 2.0 Hz), 6.94 (2H, s), 7.64 (1H, d, J = 8.0 Hz), 7.83 (1H, d, J = 8.0 Hz), 12.31 (1H, s). Anal. Calcd for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30. Found: C, 63.15; H, 5.49. **6′**: R_f 0.50 (3:2 *n*-hexane-acetone); $[\alpha]^{23}_D$ +140.7 ° (*c* 0.027, $CHCl_3$); ^{1}H NMR δ 1.38 (1H, ddd, J = 12.2, 10.8, 10.8 Hz), 1.39 (3H, d, J = 6.0 Hz), 2.46 (1H, ddd, J = 12.2, 5.2 and 2.0 Hz), 3.16 (1H, dd, J = 9.2, 9.2 Hz), 3.48 (1H, dq, J = 9.2, 6.0 Hz), 3.83 (1H, ddd, J = 10.8, 9.2, 5.2 Hz), 4.66 (1H, ddd, J = 10.8, 2.0, 1.4 Hz), 7.08 (1H, d, J = 1.4 Hz), 7.27 (1H, dd, J = 5.4, 5.4 Hz), 7.62 (2H, d, J = 5.4 Hz), 11.97 (1H, s). Anal. Calcd for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30. Found: C, 63.24; H, 5.56.

Vinyl Triflate 20. To a stirred solution of lithium diisopropylamide (LDA) (18.6 mmol) in dry THF (46 mL) at −78 °C was added dropwise a solution of **19**[18] (4.59 g, 18.6 mmol) in dry THF (23.0 mL). After the reaction mixture was stirred at −78 °C for 0.5 h, *N*-phenyltrifluoromethanesulfonimide (Tf_2-NPh) (7.32 g, 20.5 mmol) was added to the reaction mixture at −78 °C. The resulting solution was then stirred at −78 °C for 0.5 h and allowed to warm to 0 °C for 0.5 h with stirring. The reaction was quenched with saturated aqueous NH_4Cl (46 mL) under ice-cooling, and the resulting mixture was then extracted with diethyl ether. The extracts were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification of the residue by flash column chromatography (210 g of silica gel, 20:1 *n*-hexane−ethyl acetate) gave **20** (6.60 g, 94%) as a colorless oil: R_f 0.53 (20:1 *n*-hexane−ethyl acetate); ^{1}H NMR δ 0.32 (6H, s), 0.96 (3H, s), 1.35−2.55 (6H, m), 5.70 (1H, m), 7.3−7.6 (5H, m); HRMS (EI) *m*/*z* 378.0916 (378.0933 calcd for $C_{16}H_{21}F_3O_3SSi$, M^+).

Diene 22. To a stirred solution of **20** (6.60 g, 17.4 mmol) in dry DMF (198 mL) at 25 °C were added $(Ph_3P)_4Pd$ (403 mg, 0.349 mmol), LiCl (5.17 g, 122 mmol), and vinyltributyltin (**21**) (5.61 mL, 19.2 mmol). After the reaction mixture was stirred at 70 °C for 1 h under argon, the mixture was poured into ice-cold water (200 mL), and the resulting mixture was then extracted with diethyl ether. The extracts were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification of the residue by flash column chromatography (225 g of silica gel, 1000:1 *n*-hexane−ethyl acetate) gave **22** (4.16 g, 93%) as a colorless oil: R_f 0.67 (20:1 *n*-hexane−ethyl acetate); ^{1}H NMR δ 0.32 (6H, s), 0.91 (3H, s), 1.35−2.3 (6H, m), 4.87 (1H, d, J = 10.5 Hz), 5.03 (1H, d, J = 17.2 Hz), 5.72 (1H, s), 6.34 (1H, dd, J = 17.2, 10.5 Hz), 7.3−7.6 (5H, m). Anal. Calcd for $C_{17}H_{24}Si$: C, 79.62; H, 9.43. Found: C, 79.41; H, 9.64.

Diol 23. To a stirred solution of AD-mix-β (11.25 g) in *t*-BuOH−H_2O (1:1, v/v, 60 mL) at 0 °C was added a solution of **22** (2.06 g, 8.03 mmol) in *t*-BuOH−H_2O (1:1, v/v, 20 mL). After the reaction mixture was stirred vigorously at 0 °C for 12 h, the mixture was poured into ice-cold saturated aqueous NH_4Cl (100 mL), and the resulting mixture was then extracted with ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification of the residue by flash column chromatography (200 g of silica gel, 1:1 *n*-hexane−ethyl acetate) gave **23** (2.15 g, 92%) as a colorless oil: R_f 0.46 (1:2 *n*-hexane−ethyl acetate); ^{1}H NMR δ 0.00 (6H, s), 0.58 (3H, s), 1.0−1.95 (8H, m), 3.1−3.4 (1H, m), 5.43 (1H, m), 7.0−7.3 (5H, m). Anal. Calcd for $C_{17}H_{26}O_2Si$: C, 70.29; H, 9.02. Found: C, 70.25; H, 9.29.

Aldehyde 24. To an ice-cold solution of **23** (2.15 g, 7.40 mmol) in THF−H_2O (3:1, v/v, 86 mL) at 0 °C was added $NaIO_4$ (1.58 g, 7.43 mmol) with stirring. The reaction mixture was stirred at 25 °C for 1.5 h and then poured into ice-cooled water (80 mL). The resultant mixture was then extracted with ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification of the residue by flash column chromatography (200 g of silica gel, 20:1 *n*-hexane−ethyl acetate) gave **24** (1.67 g, 87%) as a colorless oil: R_f 0.86 (1:2 *n*-hexane−ethyl acetate); ^{1}H NMR δ 0.30 (6H, s), 0.86 (3H, s), 1.45−2.4 (6H,

m), 6.73 (1H, m), 7.3−7.6 (5H, m), 9.39 (1H, m); HRMS (EI) *m*/*z* 258.1440 (258.1441 calcd for $C_{16}H_{22}OSi$, M^+).

***E,E*-Diene 7.** To a stirred solution of **24** (1.67 g, 6.46 mmol) in dry THF (50 mL) at 0 °C was added 0.19 M triphenyl(phenylthiomethylene)phosphine (**25**)[22]/THF (68 mL, 12.9 mmol). After the reaction mixture was stirred at 25 °C for 1 h, the reaction was quenched with saturated aqueous NH_4Cl (150 mL) under ice-cooling, and the resultant mixture was then extracted with diethyl ether. The extracts were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification of the residue by flash column chromatography (120 g of silica gel, *n*-hexane) gave **7** (1.81 g, 77%) as a colorless oil: R_f 0.64 (10:1 *n*-hexane−ethyl acetate); ^{1}H NMR δ 0.33 (6H, s), 0.92 (3H, s), 1.1−2.4 (6H, m), 5.72 (1H, m), 6.18 (1H, d, J = 15.2 Hz), 6.44 (1H, d, J = 15.2 Hz), 7.1−7.7 (10H, m), 9.39 (1H, m). Anal. Calcd for $C_{23}H_{28}SSi$: C, 75.76; H, 7.74. Found: C, 75.50; H, 7.83.

Cycloadduct 26. To a stirred solution of **6** (74.0 mg, 0.243 mmol) in dry CH_2Cl_2 (24 mL) at 0 °C was added $B(OAc)_3$ (50.0 mg, 0.266 mmol). After the mixture was stirred for 0.5 h at 0 °C, a solution of **7** (98.0 mg, 0.269 mmol) in dry CH_2Cl_2 (2 mL) was added to the reaction mixture at 0 °C. After the resultant mixture was stirred at 25 °C for 1.5 h, ice-cooled saturated aqueous $NaHCO_3$ (12 mL) was added to the reaction mixture, and the resulting mixture was then extracted with diethyl ether. The extracts were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. To a solution of the residue in dry CH_2Cl_2 (2 mL) at 0 °C was added 1,8-diazabicyclo[5.4.0]undec-8-ene (DBU) (80.0 μL, 0.535 mmol). After the reaction mixture was stirred at 0 °C for 0.5 h, ice-cooled saturated aqueous NH_4Cl (8 mL) was added to the reaction mixture, and the resulting mixture was then extracted with ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification of the residue by flash column chromatography (14 g of silica gel, 3:2 *n*-hexane−acetone) gave **26** (78.5 mg, 58%) as a yellow solid: R_f 0.31 (3:2 *n*-hexane−acetone); ^{1}H NMR δ 0.34 (3H, s), 0.35 (3H, s), 0.96 (3H, s), 1.42 (3H, d, J = 6.0 Hz), 1.4−1.6 (1H, m), 1.75 (2H, dd, J = 8.2, 5.2 Hz), 2.45−2.6 (1H, m), 2.53 (1H, d, J = 16.1 Hz), 3.01 (1H, d, J = 16.1 Hz), 3.15−3.5 (1H, m), 3.22 (1H, dd, J = 9.2, 9.2 Hz), 3.53 (1H, dq, J = 9.2, 6.0 Hz), 3.86 (1H, m), 4.94 (1H, dd, J = 11.2, 1.8 Hz), 7.3−7.6 (5H, m), 7.43 (1H, d, J = 8.0 Hz), 7.74 (1H, d, J = 8.0 Hz), 7.87 (1H, d, J = 8.0 Hz), 8.11 (1H, d, J = 8.0 Hz), 12.97 (1H, s). Anal. Calcd for $C_{33}H_{36}O_6Si$: C, 71.19; H, 6.52. Found: C, 70.92; H, 6.54.

Fluoride 27. To an ice-cold solution of **26** (78.5 mg, 0.141 mmol) in dry CH_2Cl_2 (3.1 mL) was added $HBF_4{\cdot}Et_2O$ (488 μL, 2.82 mmol). After the reaction mixture was stirred at 25 °C for 2 h, the reaction was quenched with saturated aqueous $NaHCO_3$ (3 mL) under ice-cooling, and the resultant mixture was then extracted with diethyl ether. The extracts were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification of the residue by flash column chromatography (7 g of silica gel, 2:1 *n*-hexane−acetone) gave **27** (54.8 mg, 78%) as a yellow solid: R_f 0.50 (1:1 *n*-hexane−acetone); ^{1}H NMR δ 0.23 (3H, s), 0.26 (3H, s), 1.03 (3H, s), 1.42 (3H, d, J = 6.4 Hz), 1.4−1.6 (1H, m), 1.65−2.0 (2H, m), 2.53 (1H, ddd, J = 12.4, 5.2, 1.8 Hz), 2.63 (1H, d, J = 17.0 Hz), 3.11 (1H, d, J = 17.0 Hz), 3.22 (1H, ddd, J = 9.0, 9.0, 4.0 Hz), 3.54 (1H, dq, J = 9.0, 6.4 Hz), 3.50 (2H, m), 3.86 (1H, m), 4.95 (1H, dd, J = 11.2, 1.8 Hz), 7.50 (1H, d, J = 8.0 Hz), 7.77 (1H, d, J = 8.0 Hz), 7.89 (1H, d, J = 8.0 Hz), 8.17 (1H, d, J = 8.0 Hz), 12.96 (1H, s); HRMS (EI) *m*/*z* 498.1866 (498.1873 calcd for $C_{27}H_{31}O_6FSi$, M^+).

Alcohol 28. To a solution of **27** (46.0 mg, 0.0922 mmol) in THF−MeOH (1:1, 3.7 mL) were added KF (16.1 mg, 0.277 mmol), $KHCO_3$ (27.7 mg, 0.277 mmol), and 31% H_2O_2 (aq) (91.1 μL, 0.830 mmol) under ice-cooling. After the reaction mixture was stirred at 25 °C for 19 h, the reaction mixture was quenched with 10% aqueous $Na_2S_2O_3$ (4 mL) under ice-cooling, and the resultant mixture was then extracted with ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification of the residue by flash column chromatography (8 g of silica gel, 2:1 *n*-hexane−acetone) gave **28** (25.5 mg, 53%) as a yellow solid: R_f 0.24 (1:1 *n*-hexane−acetone); ^{1}H NMR δ 1.43 (3H, d, J = 6.0 Hz), 1.45−1.55 (1H, m), 1.55 (3H, s), 1.8−2.1 (2H, m), 2.53 (1H, ddd, J = 13.0, 6.0, 3.0 Hz), 2.53 (1H, d, J = 17.0 Hz), 3.00 (1H, s), 3.21 (1H, ddd, J = 10.0, 10.0, 4.0 Hz), 3.5−3.6 (3H, m), 3.8−3.95 (1H, m), 4.95 (1H, dd, J = 11.0, 3.0 Hz), 7.48 (1H, d, J = 6.4 Hz), 7.70 (1H, d, J = 8.0 Hz), 7.80 (1H, d, J = 8.0 Hz), 8.17 (1H, d, J = 6.4 Hz), 12.95 (1H, s); HRMS (EI) *m*/*z* 438.1653 (438.1679 calcd for $C_{25}H_{26}O_7$, M^+).

Urdamycinone B (1). A stirred solution of **28** (9.8 mg, 0.0223 mmol) in MeOH (2.0 mL) was irradiated with diffuse sunlight (a 75 W xenon lamp, Wacom Sunray Lamp, I-Sunsun) under O_2 for 24 h and then concentrated in vacuo. Purification of the residue by flash column chromatography (2 g of silica gel, 1:1 *n*-hexane−acetone) gave a mixture of **1** and **29** (7.2 mg, 71%). Their separation using reversed-phase preparative thin-layer chromatography (Merk 15389-1M, RP-18 F_{2548}, 1:3 H_2O−methanol) gave **1** (3.6 mg, 36%) and **29** (3.5 mg, 35%) as yellow solids, respectively. **1**: R_f 0.32 (1:2 *n*-hexane−acetone); $[\alpha]^{32}_D$ +50.0° (*c* 0.012, MeOH); [lit.[5] $[\alpha]_D$ +50° (*c* 0.012, MeOH)]; $[\alpha]^{32}_D$ +25.00° (*c* 0.016, $CHCl_3$); [lit.[4] $[\alpha]^{32}_D$ +25° (*c* 0.016, $CHCl_3$)]; mp 239.5−240.5 °C dec (lit.[4] mp 240 °C dec); ^{1}H NMR (acetone-d_6) δ 1.36 (3H, d, J = 6.4 Hz), 1.41 (1H, ddd, J = 12.6, 11.2, 11.2 Hz), 1.49 (3H, s), 2.44 (1H, ddd, J = 12.6, 5.0, 2.0 Hz), 2.88 (1H, dd, J = 14.5, 2.0 Hz), 3.08 (1H, d, J = 14.5 Hz), 3.09 (1H, ddd, J = 9.2, 9.2, 2.2 Hz), 3.21 (1H, dd, J = 16.8, 1.4 Hz), 3.32 (1H, d, J = 16.8 Hz), 3.48 (1H, dq, J = 9.2, 6.4 Hz), 3.74 (1H, dddd, J = 11.2, 9.2, 5.0, 2.2 Hz), 4.92 (1H, dd, J = 11.2, 2.0 Hz), 7.61 (1H, d, J = 8.0 Hz), 7.73 (1H, d, J = 8.0 Hz), 7.94 (1H, d, J = 8.0 Hz), 8.31 (1H, d, J = 8.0 Hz), 12.71 (1H, s); ^{13}C NMR (acetone-d_6) δ 18.7, 40.9, 44.7, 54.2, 71.9, 72.6, 73.5, 77.2, 78.7, 115.9, 119.4, 129.5, 134.1 (2), 134.4, 134.8, 135.1, 137.1, 138.1, 150.1, 158.9, 183.4, 189.1, 196.9; HRMS (EI) *m*/*z* 453.1562 (453.1549 calcd for $C_{25}H_{24}O_8$, M + H^+). **29**: R_f 0.31 (1:2 *n*-hexane−acetone); $[\alpha]^{32}_D$ +150.00° (*c* 0.023, $CHCl_3$); [lit.[4] $[\alpha]_D$ +150° (*c* 0.023, $CHCl_3$)]; mp 289.0−289.5 °C dec; (lit.[4] mp 290 °C dec); ^{1}H NMR (acetone-d_6) δ 1.36 (3H, d, J = 6.4 Hz), 1.41 (1H, ddd, J = 12.6, 11.2, 11.2 Hz), 1.49 (3H, s), 2.44 (1H, ddd, J = 12.6, 5.0, 2.0 Hz), 2.88 (1H, dd, J = 14.5, 2.0 Hz), 3.08 (1H, d, J = 14.5 Hz), 3.09 (1H, ddd, J = 9.2, 9.2, 2.2 Hz), 3.21 (1H, dd, J = 16.8, 1.4 Hz), 3.32 (1H, d, J = 16.8 Hz), 3.48 (1H, dq, J = 9.2, 6.4 Hz), 3.74 (1H, dddd, J = 11.2, 9.2, 5.0, 2.2 Hz), 4.92 (1H, dd, J = 11.2, 2.0 Hz), 7.61 (1H, d, J = 8.0 Hz), 7.73 (1H, d, J = 8.0 Hz), 7.94 (1H, d, J = 8.0 Hz), 8.31 (1H, d, J = 8.0 Hz), 12.71 (1H, s); HRMS (EI) *m*/*z* 453.1526 (453.1549 calcd for $C_{25}H_{24}O_8$, M + H^+).

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Supporting Information Available: ^{1}H NMR spectra for compounds **20**, **24**, **27**, **28**, **1**, and **29**. This material is available free of charge via the Internet at http://pubs.acs.org.

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