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# Selective synthesis of *C*-arylglycosides *via* Cp*RuCl-catalyzed partially intramolecular cyclotrimerizations of *C*-alkynylglycosides

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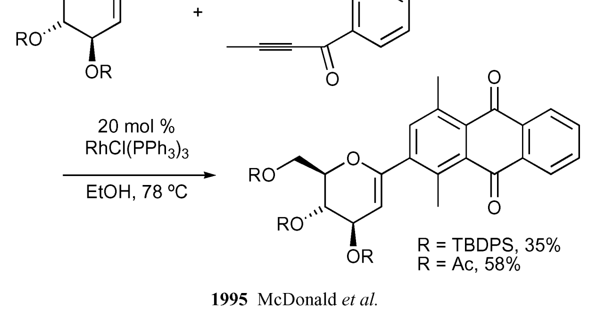
In the presence of catalytic amounts of Cp*RuCl(cod), the partially intramolecular cyclotrimerizations of various *C*-alkynylglycosides and *C*-diynylglycosides proceeded at ambient temperature to afford *C*-arylglycosides.

## Introduction

The synthesis of *C*-glycosides, in which the glycosidic oxygen is replaced by a carbon atom, has been an area of intense study in bioorganic and synthetic chemistry.[1] This is because the stability of *C*-glycosides towards the enzymatic and chemical hydrolysis renders them unique applicability. For example, the enzymatically stable *C*-glycosides are potent enzyme inhibitors and substrates for carbohydrate-binding proteins.[1]

Frequently encountered *C*-glycoside motifs in nature are *C*-arylglycosides. Owing to their significant biological activities, the synthesis of naturally occurring *C*-arylglycosides such as anthracyclinone *C*-glycosides, gilvocarcins, or kidamycins has been an important subject in synthetic organic chemistry.[2–5] *C*-Arylglycosides are generally obtained by the direct arylation of appropriate carbohydrate substrates,[2] but the control of regiochemistry is a crucial problem when a multiply substituted aromatic precursor is employed for this purpose. To address this issue, alternative methods of directly constructing a glycosylated benzene skeleton have recently been developed by exploiting benzannulation or cycloaddition strategy.[6]

In this context, the [2 + 2 + 2] cycloaddition of α,ω-diynes with *C*-alkynylglycosides might be a promising approach to obtain C-arylglycosides in a convergent and atom-economical manner. McDonald and co-workers realized this method for the first time as shown in Scheme 1.[7] In this example, they use Wilkinson catalyst, $RhCl(PPh_3)_3$, in EtOH at 78 °C to achieve the cycloaddition of a diketodiyne with protected alkynylglycals. Although the anthraquinone *C*-glycoside structure relevant to vienomycinone B was elegantly assembled in a single operation, relatively high catalyst loadings (20 mol%) are required and the isolated yields were lower than 60%. In addition, the scope of the [2 + 2 + 2] cycloaddition strategy has remained largely unexplored with respect to both diyne and *C*-alkynylglycoside substrates. With these backgrounds in mind, we recently applied our ruthenium catalysis[8] to the [2 + 2 + 2] cycloaddition of *C*-alkynylglycosides with diynes leading to bicyclic *C*-arylglycosides.[9] Herein, we report the full details of the study on the *C*-arylglycoside synthesis by means of the Ru(II)-catalyzed partially intramolecular cyclotrimerizations.



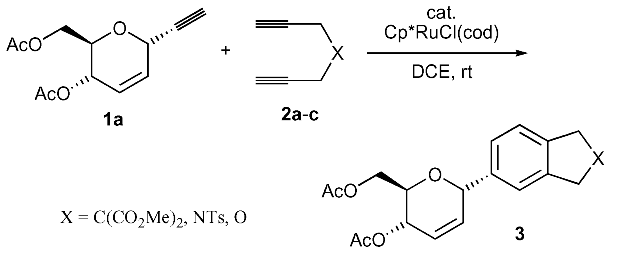
**1995** McDonald *et al.*

**Scheme 1**

## Results and discussion

### Optimization of Cp*RuCl-catalyzed cycloaddition with *C*-alkynylglycoside and scope of α,ω-diyne substrate

At the outset, *C*-alkynylglycoside **1a**, which was readily prepared from commercially available D-glucal and bis(trimethylsilyl)-acetylene according to the procedure of Isobe and co-workers,[10] was subjected to the ruthenium-catalyzed cycloaddition with dimethyl dipropargylmalonate **2a** (Scheme 2). Our previously reported protocol,[8] however, gave rise to considerable amounts of the diyne dimer. In order to suppress the dimerization, a solution of **2a** in dry degassed 1,2-dichloroethane (DCE) was added to a DCE solution containing 5 mol% Cp*RuCl(cod) (Cp* = $\eta^5$-$C_5Me_5$, cod = 1,5-cyclooctadiene) and 2 equiv. of **1a** over 2.5 h *via* syringe pump at ambient temperature, and the solution was further stirred for 24 h (method A). Purification with silica gel chromatography afforded the desired *C*-arylglycoside **3aa** in 50% yield together with the recovered **1a** (16%) and **2a** (40%) (Table 1, run 1). The yield was successfully improved to 85% by adding the solution of **2a** and 2 equiv of **1a** to the catalyst solution (method B, run 2). In this case, most of unreacted **1a** was recovered intact after chromatography. The prolonged syringe pump addition over 5 h realized the highest yield of 93% (method C, run 3). With a reduced amount of **1a** (1.5 equiv), the reaction was not completed even after overnight stirring, and the yield was lowered to 62% (method D, run 4).



**Scheme 2**

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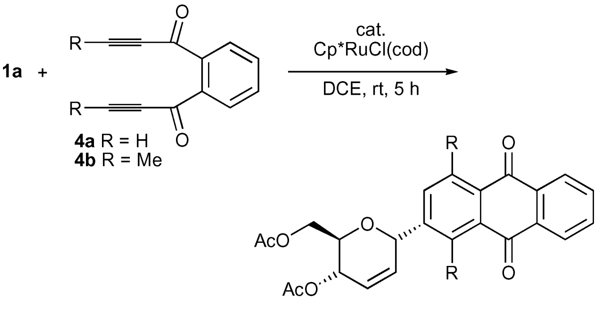
**Table 1** Ru(II)-catalyzed cycloaddition of **1a** with **2a–c**

| Run | Diyne, X | Method[a] | **3**, yield | Recovered **1a** |
|---|---|---|---|---|
| 1 | **2a**, $C(CO_2Me)_2$ | A | **3aa**, 50%[b] | 16% |
| 2 | **2a**, $C(CO_2Me)_2$ | B | **3aa**, 85% | 49% |
| 3 | **2a**, $C(CO_2Me)_2$ | C | **3aa**, 93% | 32% |
| 4 | **2a**, $C(CO_2Me)_2$ | D | **3aa**, 62%[b] | 50% |
| 5 | **2b**, NTs | C | **3ab**, 89% | 34% |
| 6 | **2c**, O | C | **3ac**, 46% | 40% |

[a] A: To a solution of 5 mol% Cp*RuCl(cod) and **1a** (2 equiv) was added a solution of **2** over 2.5 h, and the solution was stirred at rt for 24 h. B: To a solution of 5 mol% Cp*RuCl(cod) was added a solution of **2** and **1a** (2 equiv) over 2.5 h, and the solution was stirred at rt for 1.5 h. C: To a solution of 5 mol% Cp*RuCl(cod) (10 mol% for run 6) was added a solution of **2** and **1a** (2 equiv.) over 5 h (10 h for run 6). D: To a solution of 5 mol% Cp*RuCl(cod) was added a solution of **2** and **1a** (1.5 equiv.) over 5 h at rt, and the solution was stirred overnight. [b] The diyne **2a** was recovered in 40% (run 1) and 30% (run 4).

Under the optimal reaction conditions (method C), the generality of the present protocol was examined with respect to the diyne substrate. The tosylamide derivative **2b** was allowed to react with **1a** in the same manner with **2a** to afford **3ab** in 89% yield (Table 1, run 5). On the other hand, the less reactive propargyl ether **2c** required the increased catalyst loading of 10 mol% as well as the longer dropping time of 10 h (run 6). The desired product **3ac** was obtained in 46% yield.

In addition to the above 1,6-diynes, 1,7-diynes, 1,2-bis-(propiolyl)benzene **4a** and its derivative **4b**, could be used for the Ru(II)-catalyzed cycloaddition. Whereas the transition-metal-catalyzed cycloaddition of 1,2-bis(propiolyl)benzene derivatives with monoynes were reported to give anthraquinones,[7,11] previous Ni-, Co-, or Rh-based catalyses seem less suitable for *C*-alkynylglycosides. They require sub-stoichiometric amounts of a precatalyst and/or a reaction temperature above 60 °C, and the product yields were not higher than 80%. On the other hand, the ruthenium-catalyzed reaction proceeded at room temperature with catalyst loadings of 1–10 mol% to afford the desired products in 33–92% yields.[12] Indeed, in the presence of 5 mol% Cp*RuCl(cod), the reaction of **4a** with **1a** successfully proceeded at ambient temperature to furnish anthraquinone *C*-glycoside **5aa** in 87% yield (Scheme 3). Whereas internal diyne **4b** required an increased catalyst loading of 10 mol%, the desired *C*-glycosylquinone **5ab** was also obtained in a similar high yield.



**4a** R = H
**4b** R = Me

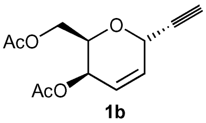
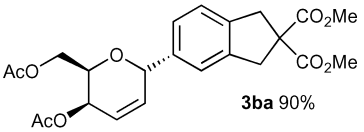
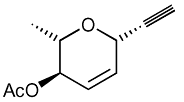
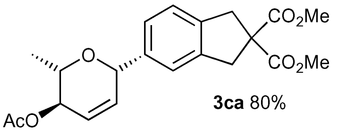
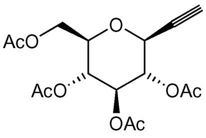
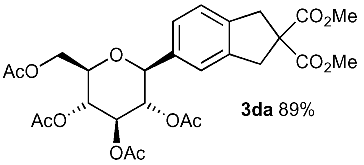
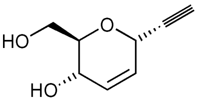
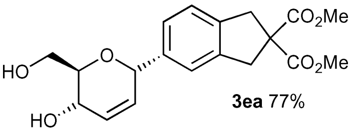
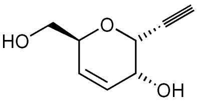
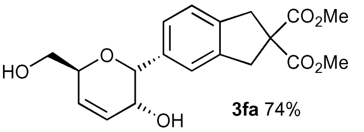
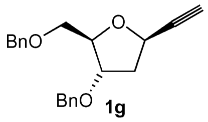
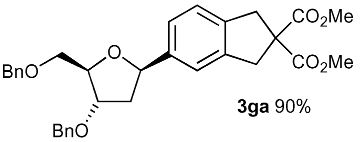
**5aa** R = H, 5 mol %, 87%
**5ab** R = Me, 10 mol %, 83%

**Scheme 3**

### Scope of *C*-alkynylglycoside

Next we examined the generality of the present method with respect to the *C*-alkynylglycoside. The ruthenium catalysis proved to be applicable to various types of *C*-alkynylglycosides as summarized in Table 2. The reaction of diyne **2a** with *C*-alkynylglycoside **1b** and **1c** derived from D-galactal and L-rhamnal gave the corresponding *C*-arylglycosides **3ba** and **3ca** in 90 and 80% yields, respectively. In addition to the unsaturated carbohydrate precursors **1a–c**, D-glucose derivative **1d**[13] underwent cycloaddition with **2a** to uneventfully give **3da** in 89% yield. More significantly, the ruthenium catalysis well tolerates hydroxy groups. Thus, unprotected carbohydrates **1e** and **1f**[14] were allowed to react with **2a** under the same reaction conditions to afford **3ea** and **3fa** in 77 and 74% yields, respectively. We also examined deoxy-D-ribose derivative **1g**[15] as an alkynylated furanose, because *C*-nucleosides have been reported to exhibit antiviral, antitumor, and anticancer activity, and nonpolar *C*-arylnucleosides were used as probes of noncovalent interactions in nucleic acids.[16] As a result, the same procedure with those for the above pyranose derivatives gave rise to the expected arylribose **3ga** in 90% yield.

**Table 2** Synthesis of *C*-arylglycosides from *C*-alkynylglycosides **1b–g** and diynes **2a**.[a]

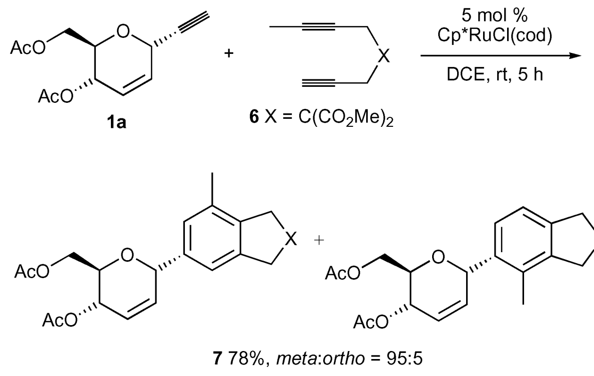
| *C*-Alkynylglycosides | *C*-Arylglycosides |
|---|---|
|  **1b** |  **3ba** 90% |
|  **1c** |  **3ca** 80% |
|  **1d** |  **3da** 89% |
|  **1e** |  **3ea** 77% |
|  **1f** |  **3fa** 74% |
|  **1g** |  **3ga** 90% |

[a] To a solution of 5 mol% Cp*RuCl(cod) was added a solution of **2a** and **1** (2 equiv.) over 5 h *via* syringe pump at room temperature.

### Regioselectivity of the cycloaddition of unsymmetrical diynes and regioselective synthesis of bis(glycosyl)benzenes

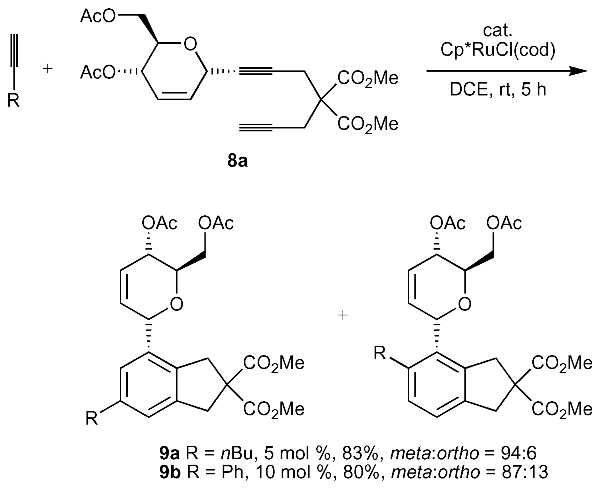
Previously, we found that the Cp*RuCl-catalyzed [2 + 2 + 2] cycloaddition of unsymmetrical diynes bearing a terminal substituent with terminal monoalkynes selectively gave *meta*-substituted benzenes.[8] In accordance with this finding, unsymmetrical 1,6-diyne **6** underwent regioselective cycloaddition with *C*-alkynylglycoside **1a** in the presence of 5 mol% Cp*RuCl(cod) at room temperature for 5 h (Scheme 4). As a consequence, tetra-substituted benzene **7** was obtained in 78% yield with the good regioselectivity of *meta* : *ortho* = 95 : 5.

In the next step, we prepared unsymmetrical *C*-glycosyldiyne **8a** and examined its cycloaddition with terminal alkynes



**Scheme 4**

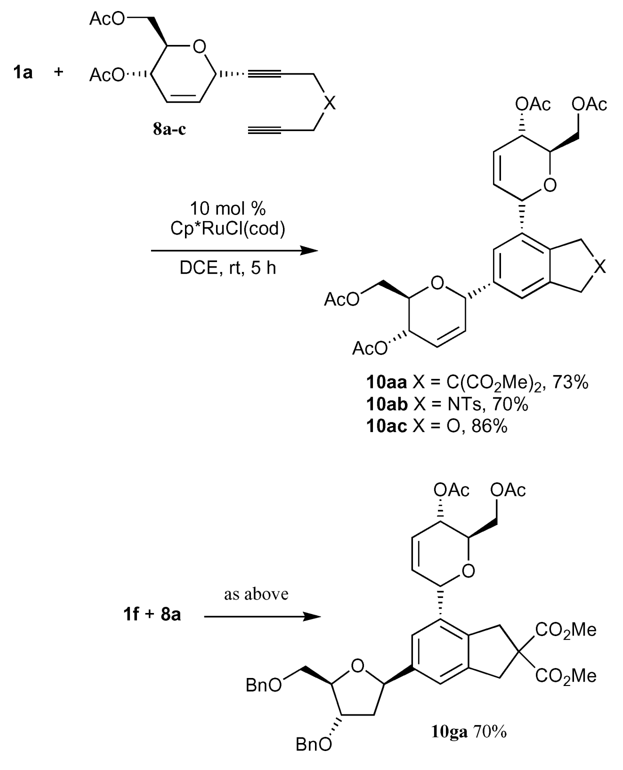
(Scheme 5). In a similar manner as above, **8a** was added to the DCE solution containing 5 mol% Cp*RuCl(cod) and 2 equiv. of 1-hexyne at room temperature over 5 h. The desired cycloadduct **9a** was obtained in 83% yield with the good isomer ratio of *meta* : *ortho* = 94 : 6. On the other hand, the use of ethynylbenzene required an increased catalyst loading of 10 mol%, and led to the formation of **9b** in 80% with the somewhat diminished regioselectivity of *meta* : *ortho* = 87 : 13.



**Scheme 5**

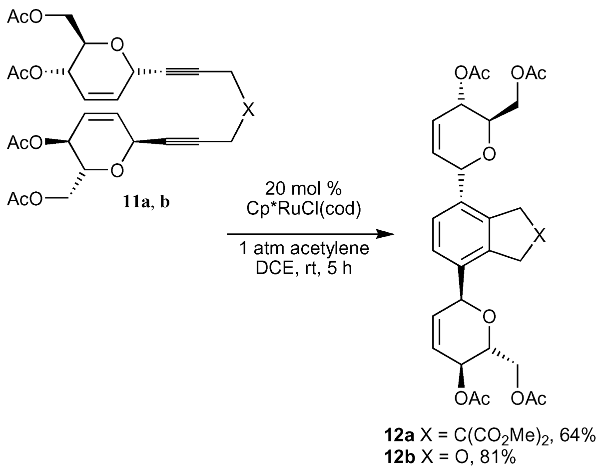
Taking advantage of the useful regioselectivity demonstrated in the above examples, a bicyclic benzene possessing two *C*-glycosyl groups, which are placed in mutually *meta*-positions, might be synthesized by the combination of *C*-glycosyldiynes **8** and *C*-alkynylglycosides **1**. Whereas oligosaccharides have found significant medicinal applications, their instability toward enzymatic hydrolysis is a crucial problem. Thus, the synthesis of stable *O*-saccharide mimics, *C*-disaccharides or pseudo-*C*-disaccharides, in which the two sugar rings are connected by several carbon atoms, has became more and more important in glycobiology.[17] Among those *C*-disaccharides, bis(*C*-glycosyl)benzenes are an attractive target, because such a benzene-bridged *C*-disaccharide motif has been found in the naturally occurring antibiotic kidamycin and its analogues.[5] With these in mind, we attempted the cycloaddition of **8a–c** with **1a** as outlined in Scheme 6. In the presence of 10 mol% Cp*RuCl(cod), *C*-glycosyldiyne **8a** was allowed to react with **1a** under the same reaction conditions. Gratifyingly, only the desired *meta*-substituted indan *C*-disaccharide **10aa** was formed in 73% yield. In the same manner, tosylamide- or ether-tethered *C*-glycosyldiynes **8b** or **8c** afforded the corresponding isoindoline **10ab** and phthalan **10ac** in 70 and 86% yields, respectively.

The present method can be essentially extended to various combinations of *C*-glycosyldiynes and *C*-alkynylglycoside. In fact, the reaction of **1g** and **8a** led to the formation of indan derivative **10ga** possessing both the furanose and the pyranose moieties in 70% yield.



**Scheme 6**

In addition to the *meta*-bis(*C*-glycosyl)benzenes, the corresponding *para*-isomers were also selectively synthesized from bis(*C*-glycosyl)diynes **11** and gaseous acetylene (Scheme 7). The reactions of these sterically demanding diynes requires 20 mol% catalyst loadings. Under an acetylene atmosphere, malonate-derived diyne **11a** was added to the catalyst solution by syringe pump over 5 h at ambient temperature. The desired **12a** was obtained in 64% yield. The reaction of ether-tethered diyne **11b** gave **12b** in a higher yield of 81%. It is noteworthy that the ether-tethered diynes **8c** and **11b** gave better results than the corresponding malonate analogues **8a** or **11a**, although the diynes bearing a quaternary center generally show higher cyclization ability owing to the kinetic Thorpe–Ingold effect.[18]

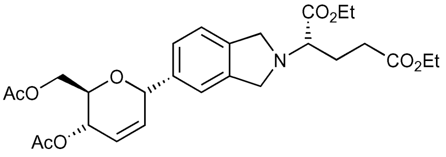
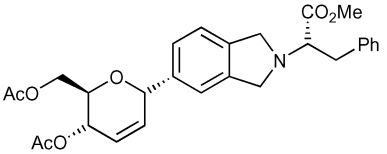
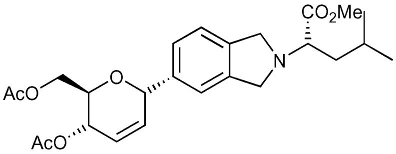


**Scheme 7**

## Synthesis of novel sugar-amino acid conjugate molecules

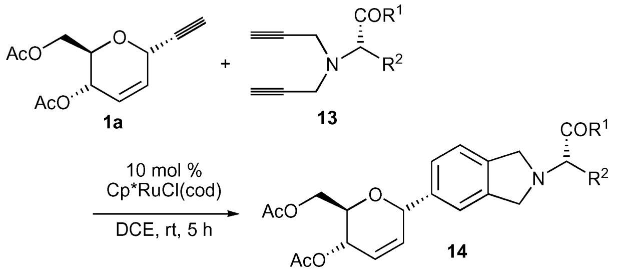
Recently, synthetic sugar amino acids have received increasing attention as mimics of natural ones found in glycopeptides.[19] In particular, sugar amino acids, in which the sugar unit was

**Table 3** Synthesis of *C*-arylglycoside amino acids from *C*-alkynylglycoside **1a** and diynes **13**.[a]

| *C*-Arylglycoside amino acids | Yields |
|---|---|
|  | **14a** 83% |
|  | **14b** 70% |
|  | **14c** 63% |

[a] To a solution of 10 mol% Cp*RuCl(cod) was added a solution of **13** and **1a** (2 equiv.) over 5 h *via* syringe pump at room temperature.

connected with amino acid moiety by an all-carbon tether, are of significance because they are metabolitically resistant analogues of natural sugar amino acids that exhibit inhibitory activity toward glycosidases. In this respect, we finally explored the synthesis of a novel type of sugar-amino acid conjugate molecule *via* our Ru(II)-catalyzed cycloaddition technique. Previously, Kotha and co-workers developed the [2 + 2 + 2] cycloaddition of amino acid-tethered diyne derivatives with monoalkynes by means of rhodium and cobalt catalysis, leading to constrained phenylalanine analogues in various yields.[20] However, the synthesis of sugar amino acids through the [2 + 2 + 2] cycloaddition of diynes containing an amino acid moiety with *C*-alkynylglycosides have remained unexplored (Scheme 8). In our hands, The *N*,*N*-dipropargylated L-glutamic acid diethyl ester **13a** was allowed to react with **1a** in the presence of 10 mol% Cp*RuCl(cod) to give the expected sugar amino acid **14a** in 83% yield (Table 3). Similarly, L-phenylalanine and L-leucine analogues **14b** and **14c** were also obtained in 70 and 63% yields, respectively.



**Scheme 8**

## Conclusions

In conclusion, we successfully developed a general protocol to synthesize *C*-arylglycosides by means of the Cp*RuCl-catalyzed [2 + 2 + 2] cycloaddition of α,ω-diynes with *C*-alkynylglycosides under mild reaction conditions. The functional group compatibility of the ruthenium catalysis towards a wide variety of functional groups allows us to synthesize interesting *C*-arylglycosides including anthraquinone *C*-glycosides, bis(*C*-glycosyl)benzenes as well as *C*-arylglycoside amino acids.

## Experimental

Flash chromatography was performed with a silica gel column (Cica silica gel 60N) eluted with mixed solvents [hexane–AcOEt]. $^1$H and $^{13}$C NMR spectra were obtained for samples in $CDCl_3$ solution at 25 °C on a Varian Mercury 300 spectrometer. $^1$H NMR chemical shifts are reported in $\delta$ units, in ppm relative to the singlet at 7.26 ppm for chloroform. Coupling constants are reported in Hz. Infrared spectra were recorded for $CHCl_3$ sample solutions in 0.2 mm path length sodium chloride cavity cells on a JASCO FT/IR-230 spectrometer. Mass spectra were recorded on a JEOL JMS700 mass spectrometer. Elemental analyses were performed by the Microanalytical Center of Kyoto University and Instrumental Analysis Facility of Nagoya University. Melting points were obtained on a Büchi B-540 apparatus. $CH_2Cl_2$ and 1,2-dichloroethane were dried over $CaH_2$ and distilled. Cp*RuCl(cod) was prepared according to the reported method.[21]

### Representative procedure for Cp*RuCl-catalyzed synthesis of *C*-arylglycosides: synthesis of *C*-arylglycoside 3aa from 1a and 2a

To a solution of Cp*RuCl(cod) (5.7 mg, 0.015 mmol) in dry degassed DCE (1 mL) was added a solution of **2a** (67.4 mg, 0.32 mmol) and **1a** (143.0 mg, 0.6 mmol) in DCE (4 mL) over 5 h *via* syringe pump at room temperature. The reaction mixture was concentrated *in vacuo* and the residue was purified by silica gel column flash chromatography (eluent, hexane : AcOEt = 6 : 1) to afford **3aa** (132.8 mg, 93%) as a colorless solid: mp. 106.2–107.2 °C; $[\alpha]^{25}{}_{D} = -27.8$ ($c = 0.05$, $CHCl_3$); IR ($CHCl_3$) 1734, 1247 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 2.06 (s, 3 H), 2.08 (s, 3 H), 3.58 (s, 4 H), 3.73 (s, 3 H), 3.74 (s, 3 H), 3.84 (ddd, $J$ = 6.6, 6.0, 3.0 Hz, 1 H), 4.08 (dd, $J$ = 12.0, 3.0 Hz, 1 H), 4.26 (dd, $J$ = 12.0, 6.0 Hz, 1 H), 5.25–5.30 (m, 2 H), 5.96 (ddd, $J$ = 10.2, 2.4, 1.8 Hz, 1 H), 6.14 (ddd, $J$ = 10.2, 3.0, 1.5 Hz, 1 H), 7.18–7.19 (m, 2 H), 7.23 (s, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.73, 20.99, 40.23, 40.41, 52.86, 60.24, 62.70, 64.86, 69.22, 73.40, 123.53, 123.97, 124.57, 126.61, 131.43, 137.57, 139.77, 140.06, 170.08, 170.41, 171.60; MS (FAB): $m/z$ (%): 445 (14) [$M^+$ − H], 385 (35) [$M^+$ − H − HOAc], 327 (100) [$M^+$ − H − 2OAc]; EA calcd (%) for $C_{23}H_{26}O_9$ (446.45): C 61.88, H 5.87; found: C 61.96, H 5.86.

**3ab.** Mp. 134.5–135.4 °C; $[\alpha]_D^{25} = -39.2$ ($c = 0.05$, $CHCl_3$); IR ($CHCl_3$) 1737, 1235 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 2.05 (s, 3 H), 2.07 (s, 3 H), 2.40 (s, 3 H), 3.79 (ddd, $J$ = 6.3, 6.0, 3.0 Hz, 1 H), 4.06 (dd, $J$ = 12.0, 3.0 Hz, 1 H), 4.25 (dd, $J$ = 12.0, 6.0 Hz, 2 H), 4.61 (s, 4 H), 5.23–5.39 (m, 2 H), 5.97 (ddd, $J$ = 10.2, 2.4, 1.5 Hz, 1 H), 6.11 (ddd, $J$ = 10.2, 2.7, 1.2 Hz, 1 H), 7.17 (d, $J$ = 7.8 Hz, 1 H), 7.21 (s, 1 H), 7.28 (d, $J$ = 7.8 Hz, 1 H), 7.31 (d, $J$ = 8.4 Hz, 2 H), 7.76 (d, $J$ = 8.4 Hz, 2 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.87, 21.11, 21.57, 53.51, 53.61, 62.69, 64.82, 69.60, 73.15, 121.96, 122.63, 124.95, 127.41, 127.48, 129.70, 131.15, 133.58, 136.09, 136.48, 138.80, 143.58, 170.18, 170.52; MS (FAB): $m/z$ (%): 484 (100) [$M^+$ − H], 366 (25) [$M^+$ − H − 2OAc]; EA calcd (%) for $C_{25}H_{27}NO_7S$ (485.88): C 61.84, H 5.60, N 2.88; found: C 61.71, H 5.60, N 2.82.

**3ac.** Mp. 53.3–54.1 °C; $[\alpha]_D^{25} = -12.7$ ($c = 0.53$, $CHCl_3$); IR ($CHCl_3$) 1737, 1238 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 2.07 (s, 3 H), 2.09 (s, 3 H), 3.85 (ddd, $J$ = 6.9, 6.0, 3.0 Hz, 1 H), 4.09 (dd, $J$ = 12.0, 3.0 Hz, 1 H), 4.28 (dd, $J$ = 12.0, 6.0 Hz, 2 H), 5.11 (s, 4 H), 5.27–5.34 (m, 2 H), 5.99 (ddd, $J$ = 10.5, 3.0, 2.1 Hz, 1 H), 6.17 (ddd, $J$ = 10.5, 3.0, 1.5 Hz, 1 H), 7.23 (d, $J$ = 7.5 Hz, 1 H), 7.29 (s, 1 H), 7.31 (dd, $J$ = 7.5, 1.5 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.87, 21.13, 62.79, 64.94, 69.42, 73.34, 73.40, 73.46, 120.40, 120.91, 124.91, 127.10, 131.37, 138.14, 139.17, 139.53, 170.22, 170.56; MS (FAB): $m/z$ (%): 331 (100) [$M^+$ − H], 273 (51) [$M^+$ − OAc], 213 (79) [$M^+$ − H − 2OAc]; EA calcd (%) for $C_{18}H_{20}O_6$ (332.35): C 65.05, H 6.07; found: C 65.00, H 6.07.

**3ba.** Mp. 97.0–98.0 °C; $[\alpha]_{\mathrm{D}}^{25} = -176.1$ ($c = 1.02$, CHCl$_3$); IR (CHCl$_3$) 1733, 1247 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ 2.01 (s, 3 H), 2.11 (s, 3 H), 3.59 (s, 4 H), 3.74 (s, 3 H), 3.75 (s, 3 H), 3.93 (ddd, $J = 6.9$, 6.0, 2.7 Hz, 1 H), 4.15 (dd, $J = 11.5$, 5.7 Hz, 1 H), 4.21 (dd, $J = 11.5$, 6.0 Hz, 1 H), 5.10 (dd, $J = 5.1$, 2.4 Hz, 1 H), 5.33–5.37 (m, 1 H), 6.17 (ddd, $J = 10.2$, 5.4, 2.4 Hz, 1 H), 6.37 (ddd, $J = 10.2$, 3.6, 0.6 Hz, 1 H), 7.18 (br s, 2 H), 7.21 (br s, 1 H); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta$ 20.81, 21.00, 40.33, 40.52, 53.02, 60.36, 62.70, 63.75, 68.21, 73.63, 123.20, 123.53, 124.07, 126.55, 123.26, 137.10, 139.84, 140.15, 170.31, 170.37, 171.73; MS (FAB): $m/z$ (%): 447 (75) [MH$^+$], 387 (53) [M$^+$ − OAc], 327 (100) [M$^+$ − H − 2OAc]; EA calcd (%) for C$_{23}$H$_{26}$O$_9$ (446.45): C 61.88, H 5.87; found: C 61.84, H 5.90.

**3ca.** Oil; $[\alpha]_{\mathrm{D}}^{27} = -25.2$ ($c = 1.06$, CHCl$_3$); IR (CHCl$_3$) 1732, 1249 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ 1.24 (d, $J = 6.3$ Hz, 3 H), 2.10 (s, 3 H), 3.59 (s, 2 H), 3.60 (s, 2 H), 3.75 (s, 6 H), 3.86 (quint, $J = 6.3$ Hz, 1 H), 5.00–5.04 (m, 1 H), 5.17 (dd, $J = 4.5$, 2.4 Hz, 1 H), 5.93 (ddd, $J = 10.2$, 3.3, 1.8 Hz, 1 H), 6.09 (ddd, $J = 10.2$, 2.7, 1.2 Hz, 1 H), 7.18–7.20 (m, 2 H), 7.22 (br s, 1 H); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta$ 17.27, 21.25, 40.29, 40.48, 52.95, 60.35, 68.04, 69.67, 72.58, 123.60, 123.85, 124.02, 126.71, 132.18, 138.30, 139.66, 140.08, 170.50, 171.73; MS (FAB): $m/z$ (%): 389 (64) [MH$^+$], 329 (100) [M$^+$ − OAc]; EA calcd (%) for C$_{21}$H$_{24}$O$_7$ (388.41): C 64.94, H 6.23; found: C 64.67, H 6.50.

**3da.** Mp. 62.0–63.2 °C; $[\alpha]_{\mathrm{D}}^{25} = -53.1$ ($c = 0.05$, CHCl$_3$); IR (CHCl$_3$) 1750, 1231 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ 1.80 (s, 3 H), 2.00 (s, 3 H), 2.05 (s, 3 H), 2.08 (s, 3 H), 3.57 (s, 4 H), 3.73 (s, 3 H), 3.74 (s, 3 H), 3.81 (ddd, $J = 9.9$, 4.5, 2.1 Hz, 1 H), 4.13 (dd, $J = 12.0$, 2.1 Hz, 1 H), 4.27 (dd, $J = 12.0$, 4.8 Hz, 1 H), 4.36 (d, $J = 9.9$ Hz, 1 H), 5.11 (t, $J = 9.9$ Hz, 1 H), 5.21 (t, $J = 9.3$ Hz, 1 H), 5.31 (t, $J = 9.3$ Hz, 1 H), 7.13–7.19 (m, 3 H), 6.37 (ddd, $J = 10.2$, 3.6, 0.6 Hz, 1 H), 7.18 (br s, 2 H), 7.21 (br s, 1 H); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta$ 20.52, 20.74, 20.77, 20.89, 40.40, 40.46, 60.42, 62.40, 68.58, 72.58, 74.31, 76.15, 80.25, 122.96, 124.12, 126.05, 134.98, 140.15, 140.67, 168.73, 169.33, 170.21, 170.58, 171.69, 171.73; MS (FAB): $m/z$ (%): 565 (55) [MH$^+$], 505 (42) [M$^+$ − OAc], 473 (100) [M$^+$ − HOMe − OAc]; EA calcd (%) for C$_{27}$H$_{32}$O$_{13}$ (564.54): C 57.44, H 5.71; found: C 57.40, H 5.78.

**3ea.** Mp. 106.2–107.2 °C; $[\alpha]_{\mathrm{D}}^{25} = -74.4$ ($c = 1.10$, CHCl$_3$); IR (KBr) 3247, 1734 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ 2.47 (br s, 2 H), 3.40 (dt, $J = 7.8$, 4.8 Hz, 1 H), 3.57 (s, 4 H), 3.71 (s, 1 H), 3.73 (s, 1 H), 3.74 (s, 6 H), 4.23 (dd, $J = 8.4$, 2.1 Hz, 1 H), 5.20 (s, 1 H), 6.01 (s, 2 H), 7.16 (d, $J = 8.1$ Hz, 1 H), 7.16 (d, $J = 8.1$ Hz, 1 H), 7.20 (s, $J = 8.1$ Hz, 1 H), 7.21 (s, 1 H); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta$ 40.33, 40.50, 53.04, 60.36, 62.83, 64.08, 72.39, 73.90, 123.88, 124.07, 127.02, 128.76, 129.86, 137.98, 139.74, 140.04, 171.83; MS (FAB): $m/z$ (%): 361 (100) [M$^+$ − H], 303 (71) [M$^+$ − CO$_2$Me]; EA calcd (%) for C$_{19}$H$_{22}$O$_7$ (362.57): C 62.97, H 6.12; found: C 62.96, H 6.13.

**3fa.** Oil; $[\alpha]_{\mathrm{D}}^{25} = -201.9$ ($c = 1.00$, CHCl$_3$); IR (neat) 3431, 1728 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ 1.90 (br s, 2 H), 3.54–3.60 (m, 1 H), 3.59 (s, 2 H), 3.54–3.60 (m, 1 H), 3.60 (s, 2 H), 3.74 (s, 6 H), 3.75–3.82 (m, 1 H), 3.98–4.01 (m, 1 H), 4.50–4.57 (m, 1 H), 4.87 (s, 1 H), 5.92 (dd, $J = 10.2$, 3.0 Hz, 1 H), 6.20–6.26 (m, 1 H), 7.20 (s, 2 H), 7.29 (s, 1 H); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta$ 40.32, 40.54, 52.97, 60.34, 61.65, 64.52, 73.42, 75.03, 122.28, 123.94, 125.17, 128.15, 128.76, 137.11, 139.20, 139.95, 171.79; MS (FAB): $m/z$ (%): 361 (33) [M$^+$ − H], 345 (71) [M$^+$ − OH]; EA calcd (%) for C$_{19}$H$_{22}$O$_7$ (362.57): C 62.97, H 6.12; found: C 62.97, H 6.11.

**3ga.** Oil; $[\alpha]_{\mathrm{D}}^{25} = +5.2$ ($c = 1.05$, CHCl$_3$); IR (CHCl$_3$) 1706, 1362 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ 1.90 (ddd, $J = 13.2$, 10.8, 6.0 Hz, 1 H), 2.33 (ddd, $J = 13.2$, 5.4, 1.2 Hz, 1 H), 3.56 (s, 4 H), 3.58 (dd, $J = 9.9$, 5.4 Hz, 1 H), 3.74 (s, 6 H), 3.67 (dd, $J = 9.9$, 4.5 Hz, 1 H), 4.14–4.17 (m, 1 H), 4.28 (ddd, $J = 5.3$, 4.8, 2.4 Hz, 1 H), 4.56 (s, 2 H), 4.60 (s, 2 H), 5.09 (dd, $J = 10.8$, 5.1 Hz, 1 H), 7.13–7.14 (m, 3 H), 7.21 (s, 1 H), 7.29–7.38 (m, 10 H); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta$ 40.26, 40.45, 41.19, 52.87, 60.37, 70.90, 71.04, 73.32, 80.32, 81.47, 83.65, 121.74, 123.78, 125.00, 127.38, 127.45, 127.48, 128.16, 128.20, 137.89, 137.99, 139.05, 139.84, 140.34, 171.73, 171.76; MS (EI): $m/z$ (%): 361 (9) [M$^+$], 439 (100) [M$^+$ − CH$_2$Ph], 439 (100) [M$^+$ − H − CH$_2$Ph − CO$_2$Me]; EA calcd (%) for C$_{32}$H$_{34}$O$_7$ (530.61): C 72.43, H 6.46; found: C 72.44, H 6.45.

**5aa.** Mp. 121.6–122.0 °C; $[\alpha]_{\mathrm{D}}^{25} = -94.9$ ($c = 0.05$, CHCl$_3$); IR (CHCl$_3$) 1739, 1676, 1234 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ 2.11 (s, 3 H), 2.15 (s, 3 H), 3.88 (ddd, $J = 6.9$, 6.0, 3.0 Hz, 1 H), 4.17 (dd, $J = 12.0$, 3.0 Hz, 1 H), 4.31 (dd, $J = 12.0$, 6.9 Hz, 2 H), 5.28–5.33 (m, 1 H), 5.46–5.49 (m, 1 H), 6.07 (ddd, $J = 10.5$, 3.0, 2.1 Hz, 1 H), 6.29 (ddd, $J = 10.5$, 3.0, 1.8 Hz, 1 H), 7.81 (d, $J = 3.3$ Hz, 1 H), 7.83 (d, $J = 3.3$ Hz, 1 H), 7.87 (ddd, $J = 7.8$, 2.0, 0.5 Hz, 1 H), 8.31–8.37 (m, 4 H); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta$ 20.84, 21.06, 62.82, 64.71, 70.19, 72.73, 125.71, 125.77, 127.08, 127.09, 127.57, 130.17, 132.73, 132.87, 133.25, 133.29, 133.48, 134.02, 134.05, 145.78, 170.15, 170.60, 182.46, 182.59; MS (FAB): $m/z$ (%): 421 (66) [MH$^+$], 361 (66) [M$^+$ − OAc], 301 (100) [M$^+$ − H − 2OAc]; EA calcd (%) for C$_{24}$H$_{20}$O$_7$ (420.41): C 68.57, H 4.80; found: C 68.33, H 5.04.

**5ab.** Mp. 153.7–154.7 °C; $[\alpha]_{\mathrm{D}}^{25} = +25.1$ ($c = 1.01$, CHCl$_3$); IR (CHCl$_3$) 1739, 1668, 1251 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ 2.04 (s, 3 H), 2.12 (s, 3 H), 2.80 (s, 6 H), 3.86 (dt, $J = 6.6$, 3.3 Hz, 1 H), 4.51 (dd, $J = 12.3$, 3.3 Hz, 1 H), 4.31 (dd, $J = 12.0$, 6.9 Hz, 1 H), 5.27 (ddd, $J = 6.6$, 2.0 Hz, 1 H), 5.66 (s, 1 H), 6.13–6.14 (m, 2 H), 7.53 (s, 1 H), 7.70–7.76 (m, 2 H), 8.12–8.17 (m, 2 H); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta$ 17.52, 20.81, 21.10, 23.91, 62.45, 64.77, 70.03, 70.14, 125.71, 126.12, 126.30, 131.04, 132.35, 133.17, 133.33, 133.68, 134.41, 134.54, 136.94, 138.87, 139.59, 142.82, 170.14, 170.46, 185.27, 186.26; MS (FAB): $m/z$ (%): 449 (100) [MH$^+$], 389 (50) [M$^+$ − OAc], 329 (70) [M$^+$ − H − 2OAc]; EA calcd (%) for C$_{26}$H$_{24}$O$_7$ (448.46): C 69.63, H 5.39; found: C 69.97, H 5.36.

***meta*-7.** Oil; $[\alpha]_{\mathrm{D}}^{28} = -11.6$ ($c = 1.08$, CHCl$_3$); IR (CHCl$_3$) 1734, 1246 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ 2.08 (s, 3 H), 2.09 (s, 3 H), 2.26 (s, 3 H), 3.51 (s, 2 H), 3.75 (s, 6 H), 3.74 (s, 3 H), 3.84 (ddd, $J = 7.1$, 6.0, 3.0 Hz, 1 H), 4.08 (dd, $J = 12.0$, 3.0 Hz, 1 H), 4.27 (dd, $J = 12.0$, 6.0 Hz, 1 H), 5.23–5.30 (m, 2 H), 5.96 (ddd, $J = 10.5$, 2.7, 2.1 Hz, 1 H), 6.14 (ddd, $J = 10.5$, 3.0, 1.8 Hz, 1 H), 7.02 (s, 1 H), 7.05 (s, 1 H); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta$ 19.11, 20.87, 21.13, 39.28, 40.74, 53.00, 59.84, 62.85, 65.00, 69.35, 73.55, 120.92, 124.52, 127.52, 131.66, 133.69, 137.91, 138.76, 139.84, 170.24, 170.59, 171.89; MS (FAB): $m/z$ (%): 459 (29) [M$^+$ − H], 399 (34) [M$^+$ − H − HOAc], 341 (100) [M$^+$ − H − 2OAc]; EA calcd (%) for C$_{24}$H$_{28}$O$_9$ (460.47): C 62.60, H 6.13; found: C 62.67, H 6.12.

***meta*-9a.** Oil; $[\alpha]_{\mathrm{D}}^{24} = +36.9$ ($c = 1.15$, CHCl$_3$); IR (CHCl$_3$) 1733, 1248 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ 0.92 (t, $J = 7.5$ Hz, 3 H), 1.34 (sext, $J = 7.5$ Hz, 2 H), 1.51–1.61 (m, 2 H), 2.07 (s, 3 H), 2.09 (s, 3 H), 2.56 (t, $J = 7.8$ Hz, 2 H), 3.57 (s, 2 H), 3.66 (d, $J = 1.5$ Hz, 2 H), 3.73 (s, 3 H), 3.74 (s, 3 H), 3.85 (dt, $J = 6.6$, 3.6 Hz, 1 H), 4.07 (dd, $J = 12.0$, 3.6 Hz, 1 H), 4.27 (dd, $J = 12.0$, 6.3 Hz, 1 H), 5.23–5.27 (m, 1 H), 5.30 (dd, $J = 4.5$, 2.1 Hz, 1 H), 6.02 (ddd, $J = 10.5$, 3.0, 2.1 Hz, 1 H), 6.15 (ddd, $J = 10.5$, 2.7, 1.5 Hz, 1 H), 6.92 (s, 1 H), 7.00 (s, 1 H); $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta$ 13.98, 20.81, 21.03, 22.44, 33.79, 35.48, 39.06, 40.39, 52.86, 52.89, 60.13, 62.54, 64.86, 69.76, 71.80, 124.12, 124.51, 126.59, 131.47, 133.69, 136.74, 140.71, 141.72, 170.23, 170.56, 171.77, 171.91; MS (FAB): $m/z$ (%): 503 (13) [MH$^+$], 443 (100) [M$^+$ − OAc], 382 (94) [M$^+$ − 2HOAc]; EA calcd (%) for C$_{27}$H$_{34}$O$_9$ (502.55): C 64.53, H 6.82; found: C 64.52, H 6.83.

***meta*-9b.** Oil; $[\alpha]_{\mathrm{D}}^{24} = -18.0$ ($c = 1.35$, CHCl$_3$); IR (CHCl$_3$) 1734, 1244 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ 2.07 (s, 3 H), 2.08 (s, 3 H), 3.67 (s, 2 H), 3.74 (s, 2 H), 3.76 (s, 3 H), 3.77 (s, 3 H), 3.88 (dt, $J = 6.3$, 3.3 Hz, 1 H), 4.06–4.12 (m, 1 H), 4.28 (dd, $J = 12.0$, 6.6 Hz, 1 H), 5.25–5.30 (m, 1 H), 5.40 (dd, $J = 4.8$, 2.1 Hz, 1 H), 6.06 (ddd, $J = 10.5$, 3.0, 2.1 Hz, 1 H), 6.22 (ddd, $J =$ 10.5, 3.0, 1.5 Hz, 1 H), 7.31–7.46 (m, 5 H), 7.53–7.56 (m, 2 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.79, 21.00, 39.15, 40.44, 52.94, 52.96, 60.15, 62.57, 64.81, 69.74, 71.79, 122.95, 125.01, 125.49, 126.98, 127.09, 128.54, 131.03, 134.48, 138.72, 140.23, 140.75, 141.37, 170.19, 170.54, 171.61, 171.78; MS (FAB): $m/z$ (%): 523 (19) [MH$^+$], 463 (88) [M$^+$ − OAc], 402 (100) [M$^+$ − 2HOAc]; EA calcd (%) for $C_{29}H_{30}O_9$ (522.54): C 66.66, H 5.79; found: C 66.57, H 5.88.

**10aa.** Mp. 52.3–53.0 °C; $[\alpha]_D^{25} = +35.6$ ($c = 1.07$, $CHCl_3$); IR ($CHCl_3$) 1735, 1240 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 2.06 (s, 3 H), 2.07 (s, 3 H), 2.08 (s, 3 H), 2.09 (s, 3 H), 3.60 (s, 2 H), 3.70 (d, $J = 2.7$ Hz, 2 H), 3.73 (s, 3 H), 3.75 (s, 3 H), 3.81–3.89 (m, 2 H), 4.08 (dt, $J = 12.3$, 2.7 Hz, 2 H), 4.27 (dd, $J =$ 12.0, 6.6 Hz, 1 H), 4.30 (dd, $J = 12.0$, 5.7 Hz, 1 H), 5.22–5.33 (m, 4 H), 5.98 (ddd, $J = 10.2$, 2.4, 1.8 Hz, 1 H), 6.04 (ddd, $J =$ 10.5, 3.3, 1.8 Hz, 1 H), 6.15 (ddd, $J = 10.5$, 2.6, 1.5 Hz, 1 H), 7.14 (s, 1 H), 7.24 (s, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.80, 20.84, 20.99, 21.09, 39.20, 40.40, 52.97, 52.99, 60.12, 62.45, 62.63, 64.76, 64.80, 69.56, 70.02, 71.64, 73.30, 123.50, 124.59, 124.79, 126.15, 131.06, 131.44, 134.43, 137.92, 139.79, 141.23, 170.19, 170.25, 170.57, 171.58, 171.75; MS (EI): $m/z$ (%): 657 (35) [M$^+$ − H], 599 (45) [M$^+$ − H − OAc], 539 (100) [M$^+$ − H − 2OAc], 479 (92) [M$^+$ − 2H − 3OAc]; EA calcd (%) for $C_{33}H_{38}O_{14}$ (658.65): C 60.18, H 5.82; found: C 60.10, H 5.90.

**10ab.** Mp. 57.7–58.3 °C; $[\alpha]_D^{28} = -6.3$ ($c = 1.00$, $CHCl_3$); IR ($CHCl_3$) 1737, 1241 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 2.06 (s, 3 H), 2.07 (s, 3 H), 2.08 (s, 3 H), 2.17 (s, 3 H), 2.40 (s, 3 H), 3.81 (dt, $J = 6$, 3.6 Hz, 1 H), 3.93 (dt, $J = 7.5$, 4.2 Hz, 1 H), 4.27 (dd, $J = 12.0$, 6.0 Hz, 1 H), 4.28 (dd, $J = 12.0$, 8.1 Hz, 1 H), 4.56 (d, $J = 14.1$ Hz, 1 H), 4.62 (d, $J = 14.1$ Hz, 1 H), 4.70 (d, $J = 14.7$ Hz, 1 H), 4.82 (d, $J = 14.7$ Hz, 1 H), 5.16–5.28 (m, 4 H), 5.96–6.12 (m, 4 H), 7.15 (s, 1 H), 7.20 (s, 1 H), 7.31 (d, $J =$ 7.8 Hz, 2 H), 7.75 (d, $J = 7.81$ Hz, 2 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.84, 21.03, 21.08, 21.53, 52.83, 53.27, 61.87, 62.54, 64.22, 64.66, 69.74, 71.10, 71.56, 72.89, 121.76, 124.23, 124.92, 126.71, 127.41, 129.68, 130.87, 131.03, 135.81, 137.76, 139.14, 143.56, 170.11, 170.43, 170.48, 170.53; MS (EI): $m/z$ (%): 696 (100) [M$^+$ − H], 638 (50) [M$^+$ − OAc]; EA calcd (%) for $C_{35}H_{39}NO_{12}S$ (697.75): C 60.25, H 5.63, N 2.01; found: C 60.43, H 5.66, N 1.80.

**10ac.** Mp. 46.2–47.2 °C; $[\alpha]_D^{25} = +10.2$ ($c = 1.05$, $CHCl_3$); IR ($CHCl_3$) 1738, 1228 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 2.07 (s, 3 H), 2.08 (s, 3 H), 2.09 (s, 3 H), 2.10 (s, 3 H), 3.87 (dt, $J$ = 6.6, 3.3 Hz, 1 H), 3.89 (dt, $J = 6.9$, 3.3 Hz, 1 H), 4.09 (dd, $J =$ 12.0, 3.3 Hz, 2 H), 4.29 (dd, $J = 12.0$, 5.7 Hz, 1 H), 4.31 (dd, $J$ = 12.0, 4.5 Hz, 1 H), 5.10 (br s, 2 H), 5.16–5.34 (m, 6 H), 6.01 (ddd, $J = 7.2$, 2.7, 1.8 Hz, 1 H), 6.03 (ddd, $J = 7.8$, 3.3, 2.1 Hz, 1 H), 6.14 (ddd, $J = 7.8$, 2.7, 1.2 Hz, 1 H), 6.17 (ddd, $J = 8.1$, 2.7, 1.2 Hz, 1 H), 7.20 (s, 1 H), 7.28 (s, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.84, 20.87, 21.07, 21.12, 62.27, 62.65, 64.59, 64.78, 69.61, 70.58, 71.92, 72.79, 73.08, 73.21, 120.20, 124.62, 124.89, 126.44, 130.93, 131.25, 132.88, 138.60, 138.71, 140.72, 170.16, 170.20, 170.46, 170.52; MS (EI): $m/z$ (%): 543 (100) [M$^+$ − H], 485 (16) [M$^+$ − OAc], 425 (15) [M$^+$ − H − 2OAc]; EA calcd (%) for $C_{28}H_{32}O_{11}$ (544.55): C 61.76, H 5.92; found: C 61.78, H 5.90.

**10ga.** Oil; $[\alpha]_D^{24} = +18.0$ ($c = 1.35$, $CHCl_3$); IR ($CHCl_3$) 1734, 1246 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 1.92 (ddd, $J =$ 13.2, 10.8, 6.0 Hz, 1 H), 2.06 (s, 3 H), 2.07 (s, 3 H), 3.57 (d, $J =$ 2.1 Hz, 2 H), 3.58 (dd, $J = 10.2$, 5.4 Hz, 1 H), 3.67 (s. 2 H), 3.68 (dd, $J = 13.8$, 4.5 Hz, 1 H), 3.73 (s, 3 H), 3.75 (s, 3 H), 3.83 (dt, $J = 6.3$, 3.6 Hz, 1 H), 4.06 (dd, $J = 12.0$, 3.0 Hz, 1 H), 4.16–4.19 (m. 1 H), 4.26 (dd, $J = 12.0$, 6.3 Hz, 1 H), 4.28–4.31 (m, 1 H), 4.56 (s, 2 H), 4.60 (s, 2 H), 5.10 (dd, $J = 10.8$, 5.1 Hz, 1 H), 5.22–5.26 (m, 1 H), 5.29–5.31 (m, 1 H), 5.98 (ddd, $J = 10.5$, 2.8, 2.1 Hz, 1 H), 6.10 (ddd, $J = 10.5$, 2.7, 1.2 Hz, 1 H), 7.10 (s, 1 H), 7.23 (s, 1 H), 7.29–7.36 (m, 10 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.73, 20.94, 39.09, 40.32, 41.15, 52.82, 52.85, 60.11, 62.43, 64.71, 69.70, 70.88, 70.97, 71.64, 73.30, 80.23, 81.41, 83.69, 121.79, 124.60, 124.71, 127.24, 127.40, 127.45, 128.13, 128.19, 131.09, 133.87, 137.78, 137.92, 139.05, 140.35, 140.92, 170.12, 170.45, 171.59, 171.66; MS (EI): $m/z$ (%): 741 (100) [M$^+$ − H], 683 (28) [M$^+$ − OAc], 651 (12) [M$^+$ − $CH_2Ph$], 623 (15) [M$^+$ − H − 2OAc]; EA calcd (%) for $C_{42}H_{46}O_{12}$ (742.81): C 67.91, H 6.24; found: C 67.89, H 6.26.

**12a.** Mp. 83.1–84.1 °C; $[\alpha]_D^{24} = +59.9$ ($c = 0.98$, $CHCl_3$); IR ($CHCl_3$) 1735, 1244 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 2.06 (s, 6 H), 2.08 (s, 6 H), 3.71 (s, 2 H), 3.74 (s, 6 H), 3.75 (s, 2 H), 3.81 (dt, $J = 6.3$, 3.3 Hz, 2 H), 4.04 (dd, $J = 12.0$, 3.6 Hz, 2 H), 4.26 (dd, $J = 12.0$, 6.0 Hz, 2 H), 5.24–5.28 (m, 2 H), 5.33 (dd, $J = 4.5$, 2.1 Hz, 2 H), 6.03 (ddd, $J = 10.2$, 2.7, 1.8 Hz, 2 H), 6.13 (ddd, $J = 10.2$, 2.7, 0.9 Hz, 2 H), 7.14 (s, 2 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.86, 21.06, 39.26, 52.97, 62.51, 64.76, 64.80, 69.72, 71.61, 124.95, 126.44, 131.01, 134.36, 140.77, 170.22, 170.60, 171.73; MS (EI): $m/z$ (%): 658 (56) [M$^+$], 599 (100) [M$^+$ − OAc], 539 (33) [M$^+$ − H − 2OAc]; EA calcd (%) for $C_{33}H_{38}O_{14}$ (658.65): C 60.18, H 5.82; found: C 60.22, H 5.77.

**12b.** Oil; $[\alpha]_D^{20} = +38.4$ ($c = 1.05$, $CHCl_3$); IR ($CHCl_3$) 1737, 1236 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 2.07 (s, 6 H), 2.09 (s, 6 H), 3.84 (dt, $J = 6.6$, 2.7 Hz, 2 H), 4.06 (dd, $J = 12.0$, 3.6 Hz, 2 H), 4.27 (dd, $J = 12.0$, 6.9 Hz, 2 H), 5.15–5.31 (m, 8 H), 6.03 (ddd, $J = 10.5$, 3.0, 1.2 Hz, 2 H), 6.13 (ddd, $J = 10.5$, 2.4, 1.2 Hz, 2 H), 7.18 (s, 2 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.90, 21.12, 62.37, 64.68, 70.23, 71.83, 72.67, 124.88, 126.84, 130.04, 132.66, 139.81, 170.16, 170.23, 170.55; MS (EI): $m/z$ (%): 544 (40) [M$^+$], 484 (37) [M$^+$ − H − OAc], 425 (100) [M$^+$ − H − 2OAc]; EA calcd (%) for $C_{28}H_{32}O_{11}$ (544.55): C 61.76, H 5.92; found: C 61.73, H 5.92.

**14a.** Oil; $[\alpha]_D^{25} = -30.4$ ($c = 1.00$, $CHCl_3$); IR ($CHCl_3$) 1733, 1259 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 1.19 (t, $J =$ 6.9 Hz, 3 H), 1.22 (t, $J = 7.5$ Hz, 3 H), 2.03 (s, 3 H), 2.05 (s, 3 H), 2.05–2.15 (m, 2 H), 2.43 (t, $J = 7.5$ Hz, 2 H), 3.53 (t, $J = 7.5$ Hz, 1 H), 3.75–3.81 (m, 1 H), 4.03 (dd, $J = 12.0$, 3.0 Hz, 1 H), 4.03 (dd, $J = 12.0$, 6.0 Hz, 1 H), 4.06 (q, $J = 7.2$ Hz, 2 H), 4.12 (s, 4 H), 4.14 (q, $J = 7.2$ Hz, 2 H), 4.22 (dd, $J = 12.0$, 6.0 Hz, 1 H), 5.24–5.30 (m, 2 H), 5.94 (d, $J = 10.5$ Hz, 1 H), 6.12 (dd, $J = 10.5$ 1.2 Hz, 1 H), 7.15 (d, $J = 8.4$ Hz, 1 H), 7.20 (s, 1 H), 7.21 (d, $J = 8.4$ Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 14.21, 14.38, 20.83, 21.08, 25.90, 30.73, 54.91, 55.05, 60.39, 60.53, 62.80, 63.11, 64.92, 68.96, 73.63, 121.84, 122.21, 124.83, 126.62, 131.32, 137.32, 139.21, 139.41, 170.18, 170.55, 171.85, 172.78; MS (FAB): $m/z$ (%): 518 (100) [MH$^+$], 444 (25) [M$^+$ − $CO_2Et$]; EA calcd (%) for $C_{27}H_{35}NO_9$ (517.57): C 62.66, H 6.82, N 2.71; found: C 62.76, H 7.00, N 2.43.

**14b.** Oil; $[\alpha]_D^{27} = -128.3$ ($c = 1.22$, $CHCl_3$); IR ($CHCl_3$) 1736, 1239 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 2.06 (s, 3 H), 2.08 (s, 3 H), 3.12 (dd, $J = 13.5$, 7.0 Hz, 1 H), 3.18 (dd, $J = 13.5$, 8.0 Hz, 1 H), 3.60 (s, 3 H), 3.77–3.86 (m, 2 H), 4.06 (dd, $J = 12.0$, 3.0 Hz, 1 H), 4.15 (d, $J = 11.7$ Hz, 2 H), 4.26 (dd, $J = 11.7$, 5.7 Hz, 1 H), 4.27 (d, $J = 11.7$ Hz, 2 H), 5.28–5.32 (m, 2 H), 5.97 (dt, $J = 10.5$, 1.8 Hz, 1 H), 6.15 (ddd, $J = 10.5$, 2.7, 1.2 Hz, 1 H), 7.18–7.31 (m, 8 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.82, 21.06, 37.27, 51.29, 55.14, 55.24, 62.79, 64.93, 66.22, 68.95, 73.63, 121.86, 122.21, 124.84, 126.40, 126.59, 128.23, 128.75, 131.31, 137.29, 137.51, 139.30, 139.52, 170.17, 170.53, 172.23; MS (FAB): $m/z$ (%): 494 (100) [MH$^+$], 434 (17) [M$^+$ − OAc], 402 (27) [M$^+$ − $CH_2Ph$]; EA calcd (%) for $C_{28}H_{31}NO_7$ (493.55): C 68.14, H 6.33, N 2.84; found: C 68.17, H 6.22, N 2.92.

**14c.** Oil; $[\alpha]_D^{27} = -24.7$ ($c = 1.13$, $CHCl_3$); IR ($CHCl_3$) 1736, 1239 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 0.94 (d, $J$ = 6.0 Hz, 3 H), 0.97 (d, $J$ = 6.3 Hz, 3 H), 1.64–1.77 (m, 3 H), 2.07 (s, 3 H), 2.08 (s, 3 H), 3.62 (t, $J$ = 7.8 Hz, 1 H), 3.70 (s, 3 H), 3.80 (ddd, $J$ = 7.0, 5.7, 3.0 Hz, 1 H), 4.05 (dd, $J$ = 12.0, 3.0 Hz, 1 H), 4.07 (d, $J$ = 11.4 Hz, 2 H), 4.19–4.24 (m, 2 H), 4.25 (dd, $J$ = 12.0, 5.7 Hz, 1 H), 5.28–5.33 (m, 2 H), 5.97 (dt, $J$ = 10.2, 1.8 Hz, 1 H), 6.15 (ddd, $J$ = 10.5, 3.0, 1.5 Hz, 1 H), 7.19 (d, $J$ = 8.1 Hz, 1 H), 7.23–7.25 (m, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.88, 21.13, 22.48, 22.78, 25.07, 39.99, 51.27, 54.81, 54.95, 62.05, 62.87, 64.99, 68.91, 73.76, 121.94, 122.26, 124.91, 122.26, 124.91, 126.58, 131.37, 137.19, 139.60, 139.80, 170.23, 170.61, 173.60; MS (FAB): $m/z$ (%): 460 (100) [MH$^+$], 400 (32) [M$^+$ − OAc]; EA calcd (%) for $C_{25}H_{33}NO_7$ (459.53): C 65.34, H 7.24, N 3.05; found: C 65.42, H 6.97, N 3.23.

### Representative procedure for preparation of *C*-arylglycosyldiynes: synthesis of diyne 8a

To a solution of 4,4-dimethoxycarbonyl-1-trimethylsilylhept-1,6-diyne (1.95 g, 7.0 mmol) and $SnCl_4$ (912 mg, 3.5 mmol) in dry $CH_2Cl_2$ (10 mL) was added dropwise a solution of tri-*O*-acetyl-D-glucal (955 mg, 3.5 mmol) in $CH_2Cl_2$ (40 mL) and the reaction mixture was stirred for overnight at room temperature. the reaction mixture was poured into 10% potassium sodium tartrate (70 mL), and stirred for 3 h. The aqueous layer was extracted with $CH_2Cl_2$ (20 mL × 3). The combined organic layers were washed with sat. $NaHCO_3$ and brine (each 20 mL), dried over $Mg_2SO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column flush chromatography (eluent, hexane : AcOEt = 6 : 1 ∼ 3 : 1) to afford the recovered diyne (548.5 mg, 28%) and then **8a** (961.7 mg, 65% based on the glucal) as pale yellow oil; $[\alpha]_D^{30} = -28.5$ ($c = 1.05$, $CHCl_3$); IR ($CHCl_3$) 3307, 2260, 1739, 1234 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 2.03 (t, $J$ = 2.7 Hz, 1 H), 2.09 (s, 3 H), 2.12 (s, 3 H), 2.97 (d, $J$ = 2.7 Hz, 2 H), 3.04 (d, $J$ = 2.1 Hz, 2 H), 3.76 (s, 6 H), 4.03 (dt, $J$ = 9.0, 3.9 Hz, 1 H), 4.22 (d, $J$ = 4.2 Hz, 2 H), 4.90–4.93 (m, 1 H), 5.27 (ddd, $J$ = 9.0, 3.9, 1.8 Hz, 1 H), 5.74 (dt, $J$ = 10.2, 1.8 Hz, 1 H), 5.84 (ddd, $J$ = 10.2, 3.6, 1.8 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.79, 21.01, 22.76, 23.02, 53.08, 56.49, 63.00, 63.84, 64.68, 69.73, 71.79, 78.15, 79.36, 81.36, 125.14, 129.11, 168.70, 169.99, 170.63; MS (FAB): $m/z$ (%): 421 (53) [MH$^+$], 376 (29) [M$^+$ − H − Ac], 361 (100) [M$^+$ − OAc], 301 (71) [M$^+$ − H − 2OAc]; EA calcd (%) for $C_{21}H_{24}O_9$ (420.41): C 59.99, H 5.75; found: C 59.95, H 5.79.

**8b.** Oil; $[\alpha]_D^{28} = -22.1$ ($c = 1.05$, $CHCl_3$); IR ($CHCl_3$) 3306, 2253, 1740, 1240 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 2.09 (s, 3 H), 2.10 (s, 3 H), 2.13 (t, $J$ = 2.4 Hz, 1 H), 2.43 (s, 3 H), 3.95 (dt, $J$ = 9.0, 3.9 Hz, 1 H), 4.14 (d, $J$ = 2.4 Hz, 2 H), 4.19 (d, $J$ = 4.2 Hz, 2 H), 4.21 (d, $J$ = 1.8 Hz, 2 H), 4.80–4.83 (m, 1 H), 5.25 (ddd, $J$ = 9.0, 3.6, 1.8 Hz, 1 H), 5.69 (ddd, $J$ = 10.2, 3.0, 1.5 Hz, 1 H), 5.75 (dt, $J$ = 9.9, 1.5 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.72, 20.93, 21.50, 36.24, 36.45, 62.79, 63.55, 64.43, 69.84, 74.06, 75.98, 79.16, 81.52, 125.46, 127.61, 128.24, 129.34, 134.87, 143.70, 169.86, 170.45; MS (FAB): $m/z$ (%): 460 (24) [MH$^+$], 400 (100) [M$^+$ − OAc], 340 (20) [M$^+$ − H − 2OAc]; EA calcd (%) for $C_{23}H_{25}NO_7S$ (459.51): C 60.12, H 5.48, N 3.05; found: C 60.42, H 5.39, N 2.84.

**8c.** Oil; $[\alpha]_D^{23} = -31.6$ ($c = 1.15$, $CHCl_3$); IR ($CHCl_3$) 3306, 2120, 1740, 1236 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 2.07 (s, 3 H), 2.08 (s, 3 H), 2.46 (t, $J$ = 2.4 Hz, 1 H), 4.07 (dt, $J$ = 9.0, 3.9 Hz, 1 H), 4.21 (d, $J$ = 3.9 Hz, 2 H), 4.23 (d, $J$ = 2.4 Hz, 2 H), 4.30 (d, $J$ = 1.8 Hz, 2 H), 4.98–5.02 (m, 1 H), 5.27 (ddd, $J$ = 9.0, 3.6, 1.8 Hz, 1 H), 5.77 (dt, $J$ = 10.2, 1.8 Hz, 1 H), 5.87 (ddd, $J$ = 10.2, 3.6, 1.8 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.87, 21.05, 56.49, 56.67, 62.91, 63.83, 64.55, 69.91, 75.14, 78.62, 81.82, 82.63, 125.52, 128.63, 170.02, 170.62; MS (FAB): $m/z$ (%): 307 (100) [MH$^+$]; EA calcd (%) for $C_{16}H_{18}O_6$ (306.31): C 62.74, H 5.92; found: C 60.72, H 5.94.

**11a.** Oil; $[\alpha]_D^{25} = -30.3$ ($c = 1.05$, $CHCl_3$); IR ($CHCl_3$) 1740, 1235 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 2.08 (s, 6 H), 2.10 (s, 6 H), 2.98 (s, 2 H), 2.99 (s, 2 H), 3.74 (s, 6 H), 4.00 (dt, $J$ = 9.0, 4.2 Hz, 2 H), 4.20 (d, $J$ = 3.6 Hz, 4 H), 4.89–4.92 (m, 2 H), 5.26 (ddd, $J$ = 9.0, 3.6, 1.8 Hz, 2 H), 5.73 (dt, $J$ = 10.2, 1.8 Hz, 2 H), 5.82 (ddd, $J$ = 10.2, 3.3, 1.8 Hz, 2 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.87, 21.08, 23.20, 53.13, 56.70, 63.01, 63.88, 64.70, 69.78, 79.50, 81.36, 125.27, 129.09, 168.70, 170.02, 170.66; MS (FAB): $m/z$ (%): 633 (100) [MH$^+$], 573 (99) [M$^+$ − OAc]; EA calcd (%) for $C_{31}H_{36}O_{14}$ (632.61): C 58.86, H 5.74; found: C 59.85, H 5.75.

**11b.** Mp. 103.8–104.5 °C; $[\alpha]_D^{20} = -109.6$ ($c = 1.05$, $CHCl_3$); IR ($CHCl_3$) 1739, 1238 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 2.09 (s, 6 H), 2.10 (s, 6 H), 4.07 (dd, $J$ = 9.0, 4.8 Hz, 2 H), 4.23 (s, 2 H), 4.24 (d, $J$ = 1.5 Hz, 2 H), 4.29 (d, $J$ = 1.5 Hz, 2 H), 5.00–5.04 (m, 2 H), 5.30 (ddd, $J$ = 9.0, 3.6, 1.8 Hz, 2 H), 5.79 (dt, $J$ = 10.2, 1.5 Hz, 2 H), 5.88 (ddd, $J$ = 10.2, 3.3, 2.1 Hz, 2 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 20.55, 20.73, 56.46, 62.57, 63.49, 64.24, 69.64, 76.38, 81.48, 82.43, 125.27, 128.31, 169.66, 170.22; MS (FAB): $m/z$ (%): 519 (49) [MH$^+$], 459 (100) [M$^+$ − OAc], 399 (6) [M$^+$ − H − 2OAc]; EA calcd (%) for $C_{26}H_{30}O_{11}$ (518.51): C 60.23, H 5.83; found: C 60.22, H 5.83.

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