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A Strategy for the Synthesis of Anthraquinone-Based Aryl-*C*-glycosides

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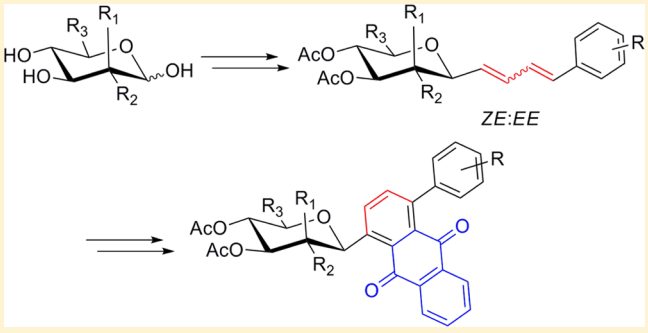
Supporting Information

ABSTRACT: An efficient and simple strategy for the synthesis of a diverse range of anthraquinone-based aryl-*C*-glycosides has been developed. It involves the sequential Diels–Alder reaction and oxidative aromatization with the preformed glycosyl diene and dienophiles. The glycosyl dienes were obtained from simple sugars by tandem one-pot substitution and elimination reaction.



INTRODUCTION

Secondary metabolites, frequently available as glycosides, produced by plants and microorganisms have been the most important chemical entities to date as biologically active compounds. The aryl-*C*-glycosides, both of synthetic and natural origins, are of great significance[1] in medicinal chemistry owing to their stability toward the enzymatic and chemical hydrolysis as compared to the *O*-glycosides.[2] They are well-known antibiotics, potent enzyme inhibitors and possess a wide range of biological activities.[3] Currently several aryl-*C*-glycosides as sodium-glucose linked transporter 2 (SGLT2) inhibitors are undergoing clinical trials for the treatment of diabetes and related complications.[4] The angucycline group of glycosides with anthraquinone as aglycon part are endowed with anticancer, antibacterial, antiviral, enzyme inhibitory, and platelet aggregation inhibition activities.[3]

Synthesis of anthraquinone-based aryl-*C*-glycosides has been the focus of several leading research groups for quite some time.[5] In view of the structural complexity of aglycones, the control of regiochemistry in glycosylation of a polysubstituted aromatic precursor to get the desired aryl-*C*-glycosides is a crucial issue. To overcome this, the benzannulation or cycloaddition strategies for glycosylated aromatics have played key roles.[6] Suzuki's group has developed elegant methods for the total synthesis of gilvocarcin and ravidomycin using cycloaddition reaction of sugar bearing benzyne and substituted furans.[7] Later on furan-benzyne cycloaddition to get aryl-*C*-glycosides was extended by Martin's group with benzyne precursors as quinone equivalents to get the aryl-*C*-glycosides.[8] A sequential intermolecular enyne metathesis of *C*-alkynyl glycosides with ethylene and subsequent Diels–Alder reaction followed by aromatization reaction,[9] and Diels–Alder reactions of preformed *C*-pentadienyl glycosides with quinones[10] were also used for the synthesis of aryl-*C*-glycosides. Thus, the direct Diels–Alder reaction of dienyl glycosides with quinones has rarely been used to get aryl-*C*-glycosides, possibly because of (i) difficulties to access dienyl glycosides, (ii) the drastic conditions required for the cycloaddition between dienyl glycosides and quinones, (iii) cost of Grubbs' second generation catalyst used in metathesis reactions, and (iv) difficulty in deprotection of the protecting groups to get the glycosides with free hydroxyl groups. Therefore, an economical, environmently benign and high yield synthesis of aryl-*C*-glycosides is still a priority area of research. In continuation of our ongoing research on aryl-*C*-glycosides[11] and glycoconjugates[12] as chemotherapeutics, we reported herein a robust, eco-friendly, and economical viable stereoselective synthesis of anthraquinone *C*-glycosides involving a simple synthesis of glycosyl dienes via Et_3N catalyzed sequential *O*-methanesulfonylation and elimination reactions of glycosyl butenols followed by sequential Diels–Alder reaction of these dienes with dienophiles and oxidative aromatization.

RESULTS AND DISCUSSION

The required butadienyl glycoside (**3a–3o**) substrates for Diels–Alder reaction were prepared (Scheme 1) in good yields (82–93%) with *EE*-stereoselectivity from preformed butenoyl glycosides (**1a–1o**).[13]

Luche reduction[14] of butenoyl-*C*-glycosides (**1a–1o**) with $NaBH_4/CeCl_3{\cdot}6H_2O$ in methanol yielded the glycosides (**2a–2o**) as (1:1) diastereoisomeric mixtures in excellent yields (89–

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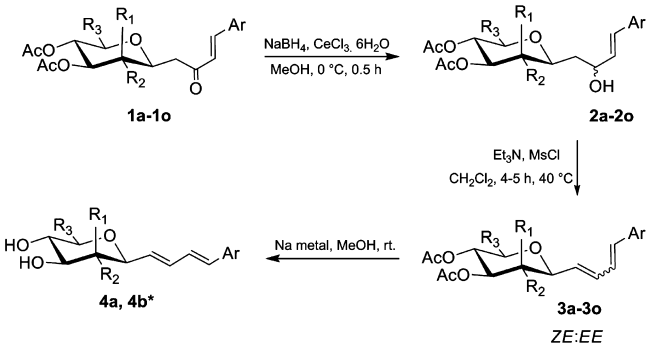
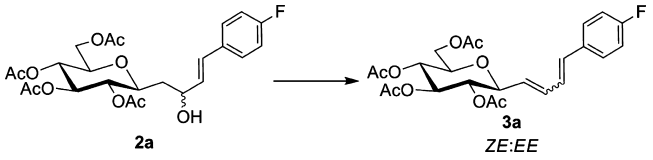
Scheme 1. Synthesis of Glycosylated Dienes



*Purely isolated (*EE*)-diene was used for deacetylation, and this deacetylated diene was directly used in cycloaddition reaction.

97%). The latter on Et_3N catalyzed tandem one-pot in situ methanesulfonylation and elimination reaction provided respective dienyl glycosides (**3a**–**3o**) (Scheme 1). Optimization of this step was made using two different sulfonylating agents tosyl chloride (TsCl) or mesyl chloride (MsCl) and organic bases (DBU, DABCO or Et_3N) with a model glycosyl butenol substrate **2a**, where MsCl (2 equiv)–Et_3N (1.2 equiv) combination proved to be the optimum for the synthesis of dienyl glycoside **3a** (entry 5, Table 1).

Table 1. Optimization of Reaction Conditions for Glycosyl Diene[a]



entry	alkylating agent	base	time (h)	temp[b] (°C)	yield (%)
1	TsCl	TEA	4	40	nr[c]
2	TsCl	DBU	10	40	nr
3	TsCl	TEA	10	70	nr
4	TsCl	DABCO	10	70	nr
5	MsCl	TEA	4	40	90[d]
6	MsCl	DBU	4	40	50
7	MsCl	DABCO	10	40	nr
8	MsCl	DABCO	8	70	20

[a]All reactions were carried out in CH_2Cl_2 (0.4 M). [b]High temperature reactions were performed in sealed tube. [c]No reaction. [d]Isolated yield.

Following the optimized reaction conditions, **3a**–**3o** were obtained as a mixture of *EE* (major, 85–90%) and *ZE* (minor, 10–15%) isomers in excellent yields (Table 2). The structures of the two isomers were well established by detailed NMR studies (see Supporting Information).

Zemplen deacetylation of dienyl glycosides **3k** (*EE*) and **3m** (*EE*) resulted in predominantly (*EE*)-isomer of deacetylated glycosyl dienes **4a** and **4b**, respectively, in good yields (Scheme 1, Table 2).

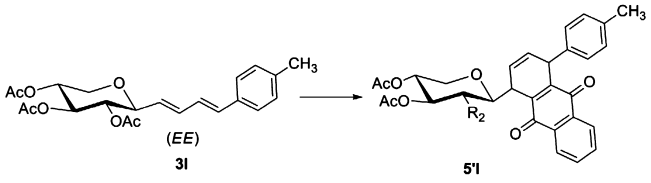
The optimization of cycloaddition reaction of (*EE*)-dienyl-1-*β*-D-xylopyranoside **3l** was carried out with naphthoquinone under different conditions (Table 3). The reaction was unsuccessful up to 40 °C in the presence or absence of any catalyst. Heating the reaction mixture in the presence of different Lewis acid catalysts at 80 °C in different solvents led

Table 2. Synthesized Glycosylated Dienes[a] (3b–3o, 4a, and 4b)

entry	product	Ar	R_1	R_2	R_3	yield[b] (%)
1	**3b**	phenyl	H	OAc	CH_2OAc	91
2	**3c**	4-Br-phenyl	H	OAc	CH_2OAc	89
3	**3d**	4-Cl-phenyl	H	OAc	CH_2OAc	84
4	**3e**	2-Cl-phenyl	H	OAc	CH_2OAc	87
5	**3f**	4-*i*Pr-phenyl	H	OAc	CH_2OAc	92
6	**3g**	4-OMe-phenyl	H	OAc	CH_2OAc	92
7	**3h**	2-naphthyl	H	OAc	CH_2OAc	82
8	**3i**	phenyl	H	OAc	H	90
9	**3j**	4-Cl-phenyl	H	OAc	H	86
10	**3k**	4-F-phenyl	H	OAc	H	85
11	**3l**	4-Me-phenyl	H	OAc	H	92
12	**3m**	4-OMe-phenyl	H	OAc	H	91
13	**3n**	4-Me-phenyl	OAc	H	CH_2OAc	92
14	**3o**	4-OMe-phenyl	OAc	H	CH_2OAc	93
15	**4a**	4-F-phenyl	H	OH	H	97[c]
16	**4b**	4-OMe-phenyl	H	OH	H	96[c]

[a]The dienes were synthesized from respective glycosyl butenols using MsCl (2 equiv)–Et_3N (1.2 equiv) in CH_2Cl_2 at 40 °C. [b]Yields were calculated for the mixture of isomers. [c]Yields for purely isolated acetylated (*EE*)-dienes.

Table 3. Optimization of Reaction Conditions for Diels–Alder Reaction



entry	catalyst (mol %)	time (h)	solvent[a]	temperature (°C)	yield (%)
1	no catalyst	10	toluene	110	nr[b]
2	$AlCl_3$ (5)	5	toluene	100	nr
3	$ZnCl_2$ (5)	5	toluene	80	40
4	$SnCl_2$ (5)	6	toluene	80	50
5	$CuCl_2$ (5)	6	toluene	100	nr
6	$CoCl_2$ (5)	6	toluene	100	nr
7	$FeCl_3{\cdot}6H_2O$ (5)	3	toluene	80	95
8	$InCl_3{\cdot}4H_2O$ (5)	3	toluene	80	99
9	anhyd $InCl_3$ (5)	3	dry toluene	80	96
10	$InCl_3{\cdot}4H_2O$ (5)	8	ethanol	80	nr
11	$InCl_3{\cdot}4H_2O$ (5)	8	DMF	80	30
12	$InCl_3{\cdot}4H_2O$ (5)	5	acetonitrile	80	85
13	$InCl_3{\cdot}4H_2O$ (5)	8	dioxane	80	30
14	$InCl_3{\cdot}4H_2O$ (5)	8	water	80	nr
15	$InCl_3{\cdot}4H_2O$ (2)	5	toluene	80	67
16	$InCl_3{\cdot}4H_2O$ (10)	3	toluene	80	63[c]

[a]0.25 M solvents used. [b]No reaction. [c]Complex mixture therefore low yield.

to the formation of desired *C*-(1,4-dihydroanthraquinon-1-yl)-xylopyranoside (**5′l**) in varying yields.

Among the different catalysts screened, $AlCl_3$, $CuCl_2$, and $CoCl_2$ were found to be ineffective, while $ZnCl_2$ and $SnCl_2$ were moderately effective with 40–50% yields of desired product. However, $FeCl_3{\cdot}6H_2O$ and $InCl_3{\cdot}4H_2O$ were the most effective to give the maximum yields of **5′l** (entries 7 and 8,

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Scheme 2. Synthesis of Aryl-*C*-glycoside

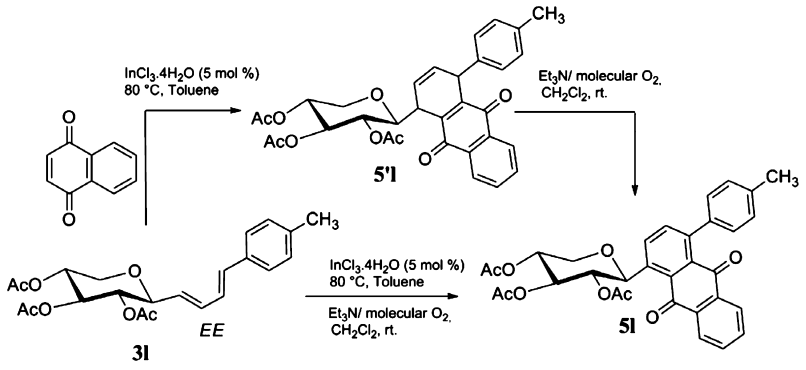

Table 3). The reaction proceeded equally well with anhydrous $InCl_3$ in dry toluene, indicating no significant role of water during reaction (entry 9, Table 3). The effect of solvents were also examined (Table 3); while the polar protic solvents were almost ineffective (entries 10 and 14, Table 3), the aprotic polar solvents were somewhat effective (entries 11−13, Table 3), and aprotic nonpolar solvent (toluene) was found to be the most effective (entries 7 and 8, Table 3) with >95% conversion of **3l** into product **5′l** (Scheme 2). Therefore, for Diels−Alder reaction, 0.25 M toluene as solvent and $InCl_3{\cdot}4H_2O$ as catalyst at 80 °C heating was chosen as the optimum reaction condition for subsequent reactions. Compound **5′l** was isolated, characterized, and found to be an inseparable diastereoisomeric mixture (NMR). Finally, oxidation of **5′l** with molecular O_2/Et_3N allows us to get the aryl-*C*-xylopyranoside **5l** in 98% yield.

The above two steps transformation of dienyl glycoside **3l** to aryl *C*-glycoside **5l** was also carried out without the purification of the intermediate dihydro product **5′l** in 95% yield (Scheme 2). Since the diastereomeric centers were lost during oxidative aromatization, the presence of the isomeric mixture of dienes did not affect the sequential reactions, and therefore these mixtures were used as such for subsequent cycloaddition and oxidative aromatization reactions (Table 4). On the basis of the above observations, we have extended the scope of this cycloaddition-aromatization sequence to other dienyl glycosides derived from D-glucose, D-xylose and D-mannose with naphthoquinone as a dienophiles to get structurally diverse aryl-*C*-*β*-D-glycosides (Table 4).

We were also successful in synthesizing unprotected aryl-*C*-glycosides **6a** and **6b** by reacting the polar unprotected dienyl glycosides **4a** and **4b**, respectively, with naphthoquinone in water:toluene (9:1) at 80 °C followed by oxidative aromatization in very good yields (entries 16 and 17, Table 4).

The scope of the Diels−Alder reaction of dienyl glycosides was extended by reacting dienyl glycoside **3m** with *N*-phenyl maleimide as dienophile to give the cycloaddition *endo* product 4-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-xylopyranosyl)-7-(4-methoxyphenyl)-2-phenyl tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (**7**) exclusively in good yield (81%) (Scheme 3). The structure of the latter was established on the basis of detailed NMR experiments (Supporting Information). However, the product **7** could not be aromatized under the oxidative aromatization reaction conditions.

■ CONCLUSIONS

We have reported a simple but efficient strategy to get aryl-*C*-*β*-D-glycosides with increasing opportunities for diversity generation. This strategy holds potential to access a library of anthraquinone-based *C*-glycosides and related analogues of great medicinal values. The method involved is economical and eco-friendly with no sophistication. The extended scope of this strategy may lead to cycloaddition products with different functional groups on the glycosides.

■ EXPERIMENTAL SECTION

General Chemistry. Commercially available reagent-grade chemicals were used as received. Reactions were monitored by TLC, with detection by UV light, spraying a 5% H_2SO_4 ethanolic solution and applying heat. Column chromatography was performed on silica gel (60−120 mesh). IR spectra were recorded as thin films or in KBr solution. ^1H and ^{13}C NMR spectra were recorded on 200, 300, and 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6. Chemical shift values were reported in ppm relative to TMS (tetramethylsilane) as internal reference, unless otherwise stated; s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet); *J* in hertz. The chemical shift assignments of prototypes were carried out with the help of 2D NMR experiments as COSY, HSQC, HMBC and NOESY. HRMS spectra were performed using a mass spectrometer Q-TOF.

General Procedure for the Synthesis of 1-Glycosyl-4-phenyl Butene-2-ols (2a−2o). *(E)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-2(R/S)-hydroxy-4-(4-fluorophenyl)but-3-ene (**2a**).* To a magnetically stirred solution of *E*-butenoyl-*C*-glycoside **1a** (2.00 g, 4.04 mmol) in methanol (5 mL, 0.81 M) at 0 °C, $CeCl_3{\cdot}6H_2O$ (1.32 g, 4.04 mmol) and $NaBH_4$ (0.15 g, 4.04 mmol) were sequentially added. The solution was allowed to stir for 0.5 h at 0 °C, until the completion of reaction (TLC). Excess of $NaBH_4$ was quenched by saturated aqueous solution of NH_4Cl (10 mL); reaction mixture was filtered and washed with methanol. The filtrate was evaporated under reduced pressure to get a crude mass, which was extracted with ethyl acetate and water. Ethyl acetate layer was dried (anhyd. Na_2SO_4) and concentrated under reduced pressure to afford a crude residue, which was purified by column chromatography (SiO_2, 60−120 mesh) using a gradient of hexane:ethyl acetate (15:7) as eluent to give (1:1) diastereoisomeric mixture of the above compound **2a** in 95% yield (1.88 g) as white solid: mp 135−137 °C; IR (KBr) ν_{max} cm^{-1} 3420, 3302, 1749, 1640, 776; $[\alpha]^{25}_D$ −28.16° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.37−7.31 (m, 2H, ArH), 7.04−6.98 (m, 2H, ArH), 6.63 (d, $J_{3,4}$ = 15.9 Hz, 1H, H-4), 6.16−6.05 (m, 1H, H-3), 5.21−5.15 (m, 1H, H-3′), 5.11−5.03 (m, 1H, H-2′), 5.00−4.92 (m, 1H, H-4′), 4.56−4.52 (m, 1H, H-2), 4.26−4.13 (m, 2H, H-6′a, H-6′b), 3.74−3.66 (m, 2H, H-1′, H-5′), 3.09 (s, 1H, OH), 2.11 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.82−1.76 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.2, 169.4 (2C), 164.0 (d, $^1J_{CF}$ = 248.8 Hz), 132.8, 130.7, 129.5, 128.8 (2C, d, $^3J_{CF}$ = 8.0 Hz), 115.7 (2C, d, $^2J_{CF}$ = 21.6 Hz), 75.9, 74.9, 74.0, 71.9, 71.4, 68.6, 62.5, 38.6, 20.7 (4C); ESI-HRMS calcd for $C_{24}H_{29}FO_{10}Na$ ($[M + Na]^+$) 519.1637, found 519.1637.

*(E)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-2(R/S)-hydroxy-4-phenyl but-3-ene (**2b**).* It was obtained by the reaction of *E*-

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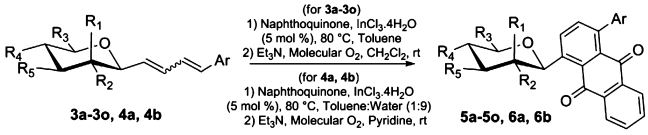
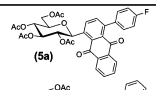
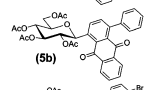
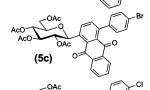
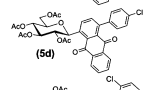
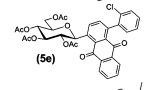
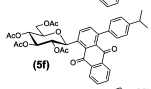
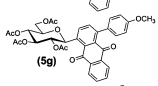
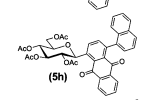
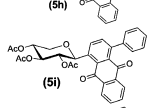
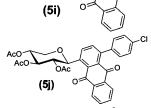
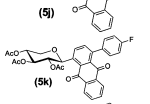
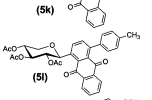
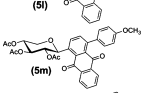
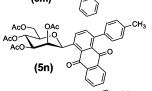
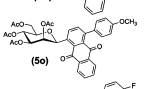
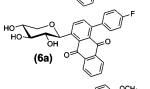
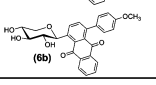
Table 4. Synthesized Aryl-*C*-β-D-glycosides[a]



entry	dienes	aryl-*C*-glycosides	yield[b] (%)
1	**3a**	 (**5a**)	92
2	**3b**	 (**5b**)	91
3	**3c**	 (**5c**)	90
4	**3d**	 (**5d**)	91
5	**3e**	 (**5e**)	90
6	**3f**	 (**5f**)	93
7	**3g**	 (**5g**)	95
8	**3h**	 (**5h**)	88
9	**3i**	 (**5i**)	93
10	**3j**	 (**5j**)	92
11	**3k**	 (**5k**)	93
12	**3l**	 (**5l**)	95
13	**3m**	 (**5m**)	94
14	**3n**	 (**5n**)	93
15	**3o**	 (**5o**)	96
16	**4a**	 (**6a**)	83
17	**4b**	 (**6b**)	80

[a]For reaction molarity see the Experimental Section. [b]Isolated yield.

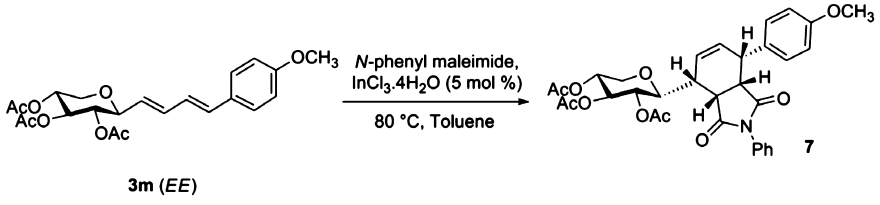
butenoyl-*C*-glycoside **1b** (2.0 g, 4.20 mmol) in methanol (5 mL, 0.84 M) with $CeCl_3·6H_2O$ (1.37 g, 4.20 mmol) and $NaBH_4$ (0.16 g, 4.20 mmol) at 0 °C in 94% yield (1.88 g) as white solid: mp 108−110 °C; IR (KBr) ν_{max} cm^{-1} 3356, 1748, 1640, 1219, 771; $[\alpha]^{25}_D$ −80.53° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.37−7.21 (m, 5H, ArH), 6.65−6.57 (m, 1H, H-4), 6.24−6.12 (m, 1H, H-3), 5.20−5.08 (m, 1H, H-3′), 5.04 (t, *J* = 9.8 Hz, 1H, H-2′), 4.96 (t, *J* = 9.5 Hz, 1H, H-4′), 4.55−4.53 (m, 1H, H-2), 4.24- 4.10 (m, 2H, H-6′a, H-6′b), 3.68−3.65 (m, 2H, H-1′, H-5′), 2.90 (s, 1H, OH), 2.10 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.88−1.76 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 170.3, 170.0, 169.2, 169.1, 136.5, 131.0, 130.5, 128.5, 127.7 (2C), 126.4, 126.4, 76.3, 75.9, 73.9, 71.8, 71.2, 68.5, 62.3, 38.4, 20.7 (2C), 20.5 (2C); ESI-HRMS calcd for $C_{24}H_{30}O_{10}Na$ ([M + Na]$^+$) 501.1731, found 501.1730.

(E)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-2(R/S)-hydroxy-4-(4-bromophenyl)but-3-ene (**2c**). It was obtained by the reaction of *E*-butenoyl-*C*-glycoside **1c** (2.0 g, 3.61 mmol) in methanol (5 mL, 0.72 M) with $CeCl_3·6H_2O$ (1.18 g, 3.61 mmol) and $NaBH_4$ (0.135 g, 3.61 mmol) at 0 °C in 96% yield (1.92 g) as white solid: mp 155−157 °C; IR (KBr) ν_{max} cm^{-1} 3412, 1748, 1640, 1278, 776; $[\alpha]^{25}_D$ −69.13° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.2 Hz, 2H, ArH), 7.26 (d, *J* = 8.3 Hz, 2H, ArH), 6.60 (d, *J* = 15.8 Hz, 1H, H-4), 6.18 (dd, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 15.8 Hz, 1H, H-3), 5.19 (t, *J* = 9.3 Hz, 1H, H-3′), 5.04 (t, *J* = 9.7 Hz, 1H, H-2′), 4.94 (t, *J* = 9.5 Hz, 1H, H-4′), 4.54−4.52 (m, 1H, H-2), 4.26 (dd, $J_{6'a,6'b}$ = 12.2 Hz, $J_{5',6'b}$ = 2.0 Hz, 1H, H-6′a), 4.16−4.10 (m, 1H, H-6′b), 3.72−3.69 (m, 2H, H-1′, H-5′), 3.01 (s, 1H, OH), 2.11 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.85−1.80 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.6, 170.3, 169.4 (2C), 135.5, 131.7 (2C), 129.2 (2C), 128.0 (2C), 121.5, 75.9(2C), 73.9, 71.8, 71.4, 68.6, 62.4, 38.4, 20.7 (2C), 20.6 (2C); ESI-HRMS calcd for $C_{24}H_{29}BrO_{10}Na$ ([M + Na]$^+$) 579.0836, found 579.0835.

(E)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-2(R/S)-hydroxy-4-(4-chlorophenyl)but-3-ene (**2d**). It was obtained by the reaction of *E*-butenoyl-*C*-glycoside **1d** (2.0 g, 3.92 mmol) in methanol (5 mL, 0.78 M) with $CeCl_3·6H_2O$ (1.28 g, 3.92 mmol) and $NaBH_4$ (0.14 g, 3.92 mmol) at 0 °C in 93% yield (1.86 g) as white solid: mp 145−147 °C; IR (KBr) ν_{max} cm^{-1} 3421, 1748, 1637, 1234, 778; $[\alpha]^{25}_D$ −65.13° (*c* 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$ + CCl_4) δ 7.28 (bs, 4H, ArH), 6.61 (d, *J* = 15.8 Hz, 1H, H-4), 6.21−6.12 (m, 1H, H-3), 5.22−5.15 (m, 1H, H-3′), 5.09−5.00 (m, 1H, H-2′), 4.97−4.91 (m, 1H, H-4′), 4.58−4.52 (m, 1H, H-2), 4.11 (dd, $J_{6'a,6'b}$ = 12.2 Hz, $J_{5',6'a}$ = 2.0 Hz, 1H, H-6′a) 4.24 (m, 1H, H-6′b), 3.73−3.65 (m, 2H, H-1′, H-5′), 3.00 (s, 1H, OH), 2.09 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.83−1.77 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.5, 169.8, 169.6, 135.3, 133.5, 132.5, 131.9, 129.4, 128.9, 127.9, 127.8, 76.14, 75.2, 74.1, 72.1, 71.5, 68.8, 62.6, 38.6, 20.9, 20.8, 20.8, 20.7; ESI-HRMS calcd for $C_{24}H_{29}ClO_{10}Na$ ([M + Na]$^+$) 535.1341, found 535.1341.

(E)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-2(R/S)-hydroxy-4-(2-chlorophenyl)but-3-ene (**2e**). It was obtained by the reaction of *E*-butenoyl-*C*-glycosides **1e** (2.0 g, 3.92 mmol) in methanol (5 mL, 0.78 M) with $CeCl_3·6H_2O$ (1.28 g, 3.92 mmol) and $NaBH_4$ (0.14 g, 3.92 mmol) at 0 °C in 91% yield (1.82 g) as white solid: mp 152−155 °C; IR (KBr) ν_{max} cm^{-1} 3425, 1752, 1648, 1234, 776; $[\alpha]^{25}_D$ −57.99° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H, ArH), 7.33−7.31 (m, 2H, ArH), 6.65 (d, *J* = 15.6 Hz, 1H, H-4), 6.30−6.19 (m, 1H, H-3), 5.29−5.21 (m, 1H, H-3′), 5.12−4.96

Scheme 3. Synthesis of Maleimide Adduct 7



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(m, 2H, H-2′, H-4′), 4.61−4.57 (m, 1H, H-2), 4.31−4.09 (m, 2H, H-6′a, H-6′b), 3.79−3.72 (m, 2H, H-1′, H-5′), 3.08 (s, 1H, OH), 2.16 (s, 3H, OAc), 2.11 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.90−1.85 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 170.3, 169.6, 169.5, 135.6, 131.8 (2C), 131.7, 129.3, 128.0 (2C), 121.6, 75.9, 73.9, 71.9, 71.4, 68.6 (2C), 62.4, 38.4, 20.7 (2C), 20.6 (2C); ESI-HRMS calcd for $C_{24}H_{29}ClO_{10}Na$ ([M + Na]$^+$) 535.1341, found 535.1342.

(E)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-2(R/S)-hydroxy-4-(4-isopropylphenyl)but-3-ene (**2f**). It was obtained by the reaction of *E*-butenoyl-*C*-glycoside **1f** (2.0 g, 3.84 mmol) in methanol (5 mL, 0.77 M) with $CeCl_3{\cdot}6H_2O$ (1.26 g, 3.84 mmol) and $NaBH_4$ (0.14 g, 3.84 mmol) at 0 °C in 94% yield (1.88 g) as white solid: mp 103−105 °C; IR (KBr) ν_{max} cm^{-1} 3331, 1746, 1613, 1228, 689; $[\alpha]^{25}_D$ −85.70° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.30 (d, *J* = 2.5 Hz, 2H, ArH), 7.17 (d, *J* = 7.0 Hz, 2H, ArH), 6.68−6.54 (m, 1H, H-4), 6.19−6.07 (m, 1H, H-3), 5.13 (t, *J* = 9.4 Hz, 1H, H-3′), 5.04 (t, *J* = 9.8 Hz, 1H, H-2′), 4.94 (t, *J* = 9.5 Hz, 1H, H-4′), 4.54−4.50 (m, 1H, H-2), 4.22−4.10 (m, 2H, H-6′a, H-6′b), 3.68−3.60 (m, 2H, H-1′, H-5′), 2.94−2.85 (m, 1H, CH), 2.82 (s, 1H, OH), 2.11 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.79−1.74 (m, 2H, CH_2), 1.26 (s, 3H, CH_3), 1.24 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 170.3, 170.0, 169.2 (2C), 148.5, 134.1, 130.5, 130.0, 126.6 (2C), 126.4 (2C), 75.9, 74.9, 74.0, 71.8, 71.3, 68.5, 62.3, 38.4, 33.8, 23.9 (2C), 20.5 (4C); ESI-HRMS calcd for $C_{27}H_{36}O_{10}Na$ ([M + Na]$^+$) 543.2201, found 543.2201.

(E)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-2(R/S)-hydroxy-4-(4-methoxyphenyl)but-3-ene (**2g**). It was obtained by the reaction of *E*-butenoyl-*C*-glycoside **1g** (2.0 g, 3.93 mmol) in methanol (5 mL, 0.79 M) with $CeCl_3{\cdot}6H_2O$ (1.28 g, 3.93 mmol) and $NaBH_4$ (0.15 g, 3.93 mmol) at 0 °C in 94% yield (1.88 g) as white solid: mp 95−97 °C; IR (KBr) ν_{max} cm^{-1} 3556, 1745, 1640, 1278, 791; $[\alpha]^{25}_D$ −89.70° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.29−7.26 (m, 2H, ArH), 6.84 (d, *J* = 8.6 Hz, 2H, ArH), 6.57 (d, *J* = 15.5 Hz, 1H, H-4), 6.08−5.97 (m, 1H, H-3), 5.10 (t, *J* = 9.4 Hz, 1H, H-3′), 5.07−4.97 (m, 1H, H-2′), 4.91 (t, *J* = 9.6 Hz, 1H, H-4′), 4.51−4.46 (m, 1H, H-2), 4.23−4.09 (m, 2H, H-6′a, H-6′b), 3.80 (s, 3H, OCH_3), 3.66−3.60 (m, 2H, H-1′, H-5′), 2.80 (s, 1H, OH), 2.09 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.87−1.73 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 170.3, 170.0, 169.1 (2C), 159.3, 131.9, 130.2, 129.2, 128.7, 127.6, 113.4 (2C), 75.8, 74.0, 71.8, 71.4, 68.5 (2C), 62.3, 55.1, 38.4, 20.5 (4C); ESI-HRMS calcd for $C_{25}H_{32}O_{11}Na$ ([M + Na]$^+$) 531.1837, found 531.1836.

(E)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-2(R/S)-hydroxy-4-(2-naphathalenyl)but-3-ene (**2h**). It was obtained by the reaction of *E*-butenoyl-*C*-glycoside **1h** (2.0 g, 3.80 mmol) in methanol (5 mL, 0.76 M) with $CeCl_3{\cdot}6H_2O$ (1.24 g, 3.80 mmol) and $NaBH_4$ (0.14 g, 3.80 mmol) at 0 °C in 89% yield (1.78 g) as white solid: mp 112−115 °C; IR (KBr) ν_{max} cm^{-1} 3436, 1749, 1640, 1237, 774; $[\alpha]^{25}_D$ −54.64° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.87−7.78 (m, 1H, ArH), 7.61−7.57 (m, 2H, ArH), 7.52−7.38 (m, 5H, ArH, H-4), 6.30−6.19 (m, 1H, H-3), 5.22−5.17 (m, 1H, H-3′), 5.12−4.95 (m, 2H, H-2′, H-4′), 4.70−4.66 (m, 1H, H-2), 4.26−4.12 (m, 2H, H-6′a, H-6′b), 3.73 (m, 2H, H-1′, H-5′), 2.97 (s, 1H, OH), 2.09 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.97−1.89 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 169.5 (2C), 168.7 (2C), 135.3, 134.43, 133.7, 131.3, 128.5, 127.9, 127.4, 125.9, 125.6, 125.4, 123.7 (2C), 76.0, 74.9, 74.0, 71.9, 70.8, 68.5, 62.3, 38.6, 20.5 (2C), 20.4 (2C); ESI-HRMS calcd for $C_{28}H_{32}O_{10}Na$ ([M + Na]$^+$) 551.1888, found 551.1886.

(E)-1-(2′,3′,4′-Tri-O-acetyl-β-D-xylopyranosyl)-2(R/S)-hydroxy-4-phenyl but-3-ene (**2i**). It was obtained by the reaction of *E*-butenoyl-*C*-glycoside **1i** (2.0 g, 4.95 mmol) in methanol (5 mL, 1 M) with $CeCl_3{\cdot}6H_2O$ (1.61 g, 4.95 mmol) and $NaBH_4$ (0.18 g, 4.95 mmol) at 0 °C in 95% yield (1.90 g) as white solid: mp 122−125 °C; IR (KBr) ν_{max} cm^{-1} 3438, 1748, 1642, 1220, 773; $[\alpha]^{25}_D$ −75.82° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.35−7.23 (m, 5H, ArH), 6.63 (d, *J* = 15.8 Hz, 1H, H-4), 6.23−6.13 (m, 1H, H-3), 5.20−5.10 (m, 1H, H-3′), 5.02−4.94 (m, 1H, H-4′), 4.92−4.84 (m, 1H, H-2′), 4.57−4.49 (m, 1H, H-2), 4.18−4.10 (m, 1H, H-5′a), 3.72−3.33 (m, 1H, H-1′), 3.31−3.24 (m, 1H, H-5′b), 2.75 (s, 1H, OH), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.83−1.71 (m, 2H CH_2); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 169.9, 169.4, 169.3, 136.6, 131.9, 130.6, 127.7, 126.4 (2C), 128.5 (2C), 75.2, 73.9, 71.9, 69.4, 68.6, 66.9, 38.7, 20.7 (3C); ESI-HRMS calcd for $C_{21}H_{26}O_8Na$ ([M + Na]$^+$) 429.1520, found 429.1520.

(E)-1-(2′,3′,4′-Tri-O-acetyl-β-D-xylopyranosyl)-2(R/S)-hydroxy-4-(4-chlorophenyl)but-3-ene (**2j**). It was obtained by the reaction of *E*-butenoyl-*C*-glycoside **1j** (2.0 g, 4.73 mmol) in methanol (5 mL, 0.91 M) with $CeCl_3{\cdot}6H_2O$ (1.55 g, 4.73 mmol) and $NaBH_4$ (0.18 g, 4.73 mmol) at 0 °C in 96% yield (1.92 g) as white solid: mp 122−125 °C; IR (KBr) ν_{max} cm^{-1} 3330, 1746, 1627, 1226, 698; $[\alpha]^{25}_D$ −69.78° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.16 (bs, 4H, ArH), 6.58 (d, *J* = 15.0 Hz, 1H, H-4), 6.19−6.08 (m, 1H, H-3), 5.19−5.09 (m, 1H, H-3′), 5.01−4.84 (m, 2H, H-4′, H-2′), 4.55−4.51 (m, 1H, H-2), 4.18−4.11 (m, 1H, H-5′a), 3.70−3.57 (m, 1H, H-1′), 3.31−3.24 (m, 1H, H-5′b), 2.82 (s, 1H, OH), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.78−1.71 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 170.5, 169.6 (2C), 135.2, 133.5, 131.6, 129.4, 128.7 (2C), 127.8 (2C), 76.6, 73.7, 72.0, 71.0, 69.2, 66.9, 38.7, 21.1 (3C); ESI-HRMS calcd for $C_{21}H_{25}ClO_8Na$ ([M + Na]$^+$) 463.1130, found 463.1130.

(E)-1-(2′,3′,4′-Tri-O-acetyl-β-D-xylopyranosyl)-2(R/S)-hydroxy-4-(4-flourophenyl)but-3-ene (**2k**). It was obtained by the reaction of *E*-butenoyl-*C*-glycoside **1k** (2.0 g, 4.56 mmol) in methanol (5 mL, 0.95 M) with $CeCl_3{\cdot}6H_2O$ (1.49 g, 4.56 mmol) and $NaBH_4$ (0.17 g, 4.56 mmol) at 0 °C in 92% yield (1.84 g) as white solid: mp 122−125 °C; IR (KBr) ν_{max} cm^{-1} 3438, 1748, 1632, 1220, 769; $[\alpha]^{25}_D$ −93.6° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.35−7.29 (m, 2H, ArH), 7.02−7.96 (m, 2H, ArH), 6.58 (d, *J* = 15.0 Hz, 1H, H-4), 6.13−6.02 (m, 1H, H-3), 5.19−5.09 (m, 1H, H-3′), 5.01−4.83 (m, 2H, H-4′, H-2′), 4.53−4.47 (m, 1H, H-2), 4.18−4.09 (m, 1H, H-5′a), 3.71−3.52 (m, 1H, H-1′), 3.31−3.24 (t, *J* = 10.6 Hz, 1H, H-5′b), 2.81 (s, 1H, OH), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.81−1.69 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 170.3, 169.4 (2C), 132.8, 131.0, 129.4, 128.8, 128.0 (2C, d, $^3J_{CF}$ = 8.2 Hz), 115.0 (2C, d, $^2J_{CF}$ = 22.1 Hz), 75.3, 72.1, 71.0, 68.9, 66.8, 38.4, 20.6 (3C); ESI-HRMS calcd for $C_{21}H_{25}FO_8$ ([M + H]$^+$) 425.1790, found 425.1795.

(E)-1-(2′,3′,4′-Tri-O-acetyl-β-D-xylopyranosyl)-2(R/S)-hydroxy-4-(4-methylphenyl)but-3-ene (**2l**). It was obtained by the reaction of *E*-butenoyl-*C*-glycoside **1l** (2.0 g, 4.60 mmol) in methanol (5 mL, 0.96 M) with $CeCl_3{\cdot}6H_2O$ (1.50 g, 4.60 mmol) and $NaBH_4$ (0.17 g, 4.60 mmol) at 0 °C in 95% yield (1.90 g) as white solid: mp 152−155 °C; IR (KBr) ν_{max} cm^{-1} 3556, 1748, 1641, 1221, 668, 738; $[\alpha]^{25}_D$ −77.01° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.27−7.23 (m, 2H, ArH), 7.12−7.09 (m, 2H, ArH), 6.58 (d, J_2 = 15.0 Hz, 1H, H-4), 6.17−6.10 (m, 1H, H-3), 5.16−5.09 (m, 1H, H-3′), 5.02−4.93 (m, 1H, H-4′), 4.91−4.83 (m, 1H, H-2′), 4.54−4.47 (m, 1H, H-2), 4.16−4.10 (m, 1H, H-5′a), 3.55−3.48 (m, 1H, H-1′), 3.33−3.26 (m,1H, H-5′b), 2.68 (s, 1H, OH), 2.35 (s, 3H, CH_3), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.79−1.70 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.2, 169.7, 138.1, 133.7, 130.2, 129.0 (2C), 126.6 (3C), 74.1, 72.3, 70.8, 69.3, 66.3, 63.1, 37.8, 21.4, 20.9 (3C); ESI-HRMS calcd for $C_{22}H_{28}O_8Na$ ([M + Na]$^+$) 443.1673, found 443.1679.

(E)-1-(2′,3′,4′-Tri-O-acetyl-β-D-xylopyranosyl)-2(R/S)-hydroxy-4-(4-methoxyphenyl)but-3-ene (**2m**). It was obtained by the reaction of *E*-butenoyl-*C*-glycoside **1m** (2.0 g, 4.78 mmol) in methanol (5 mL, 0.92 M) with $CeCl_3{\cdot}6H_2O$ (1.56 g, 4.78 mmol) and $NaBH_4$ (0.18 g, 4.78 mmol) at 0 °C in 97% yield (1.94 g) as white solid: mp 105−110 °C; IR (KBr) ν_{max} cm^{-1} 3556, 3420, 1745, 1640, 1224, 778; $[\alpha]^{25}_D$ −88.21° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.31−7.27 (m, 2H, ArH), 6.84−6.56 (m, 2H, ArH), 6.56 (dd, J_1 = 2.4 Hz, J_2 = 15.8 Hz, 1H, H-4), 6.08−6.01 (m, 1H, H-3), 5.17−5.10 (m, 1H, H-3′), 5.02−4.91 (m, 1H, H-4′), 4.90−4.83 (m, 1H, H-2′), 4.53−4.46 (m, 1H, H-2), 4.18−4.10 (m, 1H, H-5′a), 3.81 (s, 3H, OCH_3), 3.72−3.48 (m, 1H, H-1′), 3.33−3.24 (m, 1H, H-5′b), 2.64 (s, 1H, OH), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.80−1.70 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 170.4, 169.6 (2C),

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159.5, 130.1, 129.3 (2C),127.3 (2C), 114.1(2C), 73.6, 71.9, 71.2, 69.4 (2C), 66.6, 55.1, 38.9, 20.9 (3C); ESI-HRMS calcd for $C_{22}H_{28}O_9Na$ ([M + Na]$^+$) 459.1626, found 459.1629.

*(E)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-mannopyranosyl)-2(R/S)-hydroxy-4-(4-methylphenyl)but-3-ene (**2n**).* It was obtained by the reaction of *E*-butenoyl-*C*-glycoside **1n** (2.0 g, 4.08 mmol) in methanol (5 mL, 0.82 M) with $CeCl_3{\cdot}6H_2O$ (1.33 g, 4.08 mmol) and $NaBH_4$ (0.15 g, 4.08 mmol) at 0 °C in 95% yield (1.90 g) as white solid: mp 170−173 °C; IR (KBr) ν_{max} cm^{-1} 3496, 1744, 1652, 1220, 779; $[\alpha]^{25}_D$ −73.42° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.27−7.23 (m, 2H, ArH), 7.09−7.06 (d, *J* = 7.7 Hz, 2H, ArH), 6.57−6.48 (m, 1H, H-4), 6.16−6.04 (m, 1H, H-3), 5.34−5.28 (m, 1H, H-2′), 5.21−5.11 (m, 1H, H-4′), 4.06−5.00 (m, 1H, H-3′), 4.42−4.40 (m, 1H, H-2), 4.25−4.06 (m, 2H, H-6′a, H-6′b), 3.97−3.83 (m, 1H, H-1′), 3.64−3.61 (m, 1H, H-5′), 2.92 (s, 1H, OH), 2.32 (s, 3H, CH_3), 2.16 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.96 (s, 3H, OAc), 1.64−1.52 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 170.4 (2C), 169.8, 169.4, 137.4, 133.7, 130.7, 130.4, 129.6 (2C), 126.4 (2C), 75.7, 73.9, 72.1, 70.6, 69.8, 66.6, 62.8, 37.8, 21.1, 20.6 (4C); ESI-HRMS calcd for $C_{25}H_{32}O_{10}Na$ ([M + Na]$^+$) 515.1888, found 515.1888.

*(E)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-mannopyranosyl)-2(R/S)-hydroxy-4-(4-methoxyphenyl) but-3-ene (**2o**).* It was obtained by the reaction of *E*-butenoyl-*C*-glycoside **1o** (2.0 g, 3.93 mmol) in methanol (5 mL, 0.79 M) with $CeCl_3{\cdot}6H_2O$ (1.28 g, 3.93 mmol) and $NaBH_4$ (0.14 g, 3.93 mmol) at 0 °C in 96% yield (1.92 g) as white solid: IR (Neat) ν_{max} cm^{-1} 3445, 1763, 1640, 1228, 779; $[\alpha]^{25}_D$ −91.74° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 2H, ArH), 6.88 (d, *J* = 7.3 Hz, 2H, ArH), 6.85−6.51 (m, 1H, H-4), 6.12−6.02 (m, 1H, H-3), 5.39−5.34 (m, 1H, H-2′), 5.28−5.19 (m, 1H, H-4′), 5.10−5.05 (m, 1H, H-3′), 4.48−4.46 (m, 1H, H-2), 4.28−4.13 (m, 2H, H-6′a, H-6′b), 4.02−3.82 (m, 1H, H-1′), 3.72 (s, 3H, OCH_3), 3.71−3.66 (m, 1H, H-5′), 2.90 (s, 1H, OH), 2.19 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.96−1.92 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.4 (2C), 169.8, 169.4, 159.3, 137.4, 133.7, 130.1, 127.6 (2C), 113.9 (2C), 75.7, 73.9, 72.1, 70.6, 69.8, 66.6, 62.8, 37.8, 21.1, 20.6 (4C); ESI-HRMS calcd for $C_{25}H_{32}O_{11}Na$ ([M + Na]$^+$) 531.1837, found 531.1827.

General Experimental Procedure for the Synthesis of 1-Glycosyl 1,3-Dienes (3a−3o). *(EE)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(4-fluorophenyl)but-1,3-diene (**3a**).* To a stirring solution of 1-glycosyl-4-phenyl butene-2-ol **2a** (1.0 g, 2.01 mmol) in anhydrous CH_2Cl_2 (5 mL, 0.40 M) and Et_3N (2.21 mmol) at 0 °C, methanesulfonyl chloride (0.31 mL, 4.02 mmol) was slowly added. After 15 min the stirring reaction mixture was brought to 40 °C and stirred for 4 h until the reaction is completed (TLC). The reaction mixture was evaporated under reduced pressure and extracted by ethyl acetate/water. The ethyl acetate layer was dried (anhyd. Na_2SO_4) and evaporated under reduced pressure to give a crude mass. The latter was purified by column chromatography (SiO_2, 60−120 mesh) using hexane:ethyl acetate (17:3) as eluent to give compound **3a** in 68% yield (0.66 g) as a white solid: mp 120−122 °C; IR (KBr) ν_{max} cm^{-1} 3526, 2901, 1749, 1510, 1228, 774; $[\alpha]^{25}_D$ −82.83° (*c* 0.1, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.36−7.33 (m, 2H, ArH), 7.04−6.99 (m, 2H, ArH), 6.65 (dd, $J_{3,4}$ = 15.5 Hz, $J_{2,3}$ = 10.1 Hz, 1H, H-3), 6.58 (d, *J* = 15.5 Hz, 1H, H-4), 6.43 (dd, $J_{1,2}$ = 15.2 Hz, $J_{2,3}$ = 10.1 Hz, 1H, H-2), 5.67 (dd, $J_{1,2}$ = 15.2 Hz, $J_{1,1'}$ = 7.5 Hz, 1H, H-1), 5.26 (t, *J* = 9.4 Hz, 1H, H-3′), 5.11 (t, *J* = 9.7 Hz, 1H, H-4′), 4.98 (t, *J* = 9.6 Hz, 1H, H-2′), 4.27 (dd, $J_{6'a,6'b}$ = 12.2 Hz, $J_{5',6'a}$ = 4.7 Hz, 1H, H-6′a), 4.15 (dd, $J_{6'a,6'b}$ = 12.2 Hz, $J_{5',6'b}$ = 2.0 Hz, 1H, H-6′b), 3.97 (t, *J* = 7.7 Hz, 1H, H-1′), 3.74 (ddd, $J_{4',5'}$ = 9.8 Hz, $J_{5',6'a}$ = 4.6 Hz, $J_{5',6'b}$ = 2.2 Hz, 1H, H-5′), 2.10 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.99 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4) δ 170.6, 170.2, 169.4, 169.3, 164.60 (d, $^1J_{CF}$ = 248.6 Hz), 135.1, 133.1, 132.8, 128.08 (2C, d, $^3J_{CF}$ = 7.91 Hz), 127.4, 127.2, 115.8 (2C, d, $^2J_{CF}$ = 22.3 Hz), 79.1, 75.6, 73.9, 71.4, 68.4, 62.2, 20.8, 20.7, 20.6, 20.5; ESI-HRMS calcd for $C_{24}H_{27}FO_9Na$ ([M + Na]$^+$) 501.1531, found 501.1531.

*(ZE)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(4-fluorophenyl)but-1,3-diene (**3a′**).* White solid, 10% yield (0.08 g): mp 118−120 °C; IR (KBr) ν_{max} cm^{-1} 3481, 2896, 1753, 1620, 1228, 779; $[\alpha]^{25}_D$ −82.83° (*c* 0.1, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.40 (m, 2H, ArH), 7.11−7.01 (m, 2H, ArH), 6.90 (dd, $J_{3,4}$ = 15.4 Hz, $J_{2,3}$ = 10.9 Hz, 1H, H-3), 6.60 (d, *J* = 15.3 Hz, 1H, H-4), 6.33 (t, *J* = 11.03 Hz, 1H, H-2), 5.39 (dd, $J_{1,2}$ = 10.5 Hz, $J_{1,1'}$ = 9.0 Hz, 1H, H-1), 5.32 (t, *J* = 9.5 Hz, 1H, H-3′), 5.11 (t, *J* = 9.8 Hz, 1H, H-4′), 4.98 (t, *J* = 9.5 Hz, 1H, H-2′), 4.48 (t, *J* = 9.1 Hz, 1H, H-1′), 4.28 (dd, $J_{6'a,6'b}$ = 12.5 Hz, $J_{5',6'a}$ = 5.0 Hz, 1H, H-6′a), 4.15 (dd, $J_{6'a,6'b}$ = 12.3 Hz, $J_{5',6'b}$ = 2.0 Hz, 1H, H-6′b), 3.79 (ddd, $J_{4',5'}$ = 9.8 Hz, $J_{5',6'a}$ = 4.6 Hz, $J_{5',6'b}$ = 2.0 Hz, 1H, H-5′), 2.07 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.98 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 170.7, 169.8 (2C), 164.6 (d, $^1J_{CF}$ = 251.0 Hz), 134.7, 133.7, 133.2, 128.5 (2C, d, $^3J_{CF}$ = 7.9 Hz), 126.0, 123.3, 116.0 (2C d, $^2J_{CF}$ = 21.9 Hz), 76.1, 74.9, 74.1, 71.9, 68.7, 62.6, 20.9 (4C); ESI-HRMS calcd for $C_{24}H_{27}FO_9$ ([M + H]$^+$) 479.1712, found 479.1709.

*(EE)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-phenyl but-1,3-diene (**3b**).* It was obtained by the reaction of 1-glycosyl-4-phenyl butene-2-ol **2b** (1.00 g, 2.09 mmol) in anhydrous CH_2Cl_2 (5 mL, 0.42 M) at 0−40 °C with Et_3N (2.03 mmol) and methanesulfonyl chloride (0.32 mL, 4.18 mmol) in 70% yield (0.67 g) as white solid: mp 135−137 °C; IR (KBr) ν_{max} cm^{-1} 3452, 1748, 1640, 1219, 783; $[\alpha]^{25}_D$ −7.76° (*c* 0.1, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.40−7.37 (m, 2H, ArH), 7.34−7.24 (m, 3H, ArH), 6.74 (dd, $J_{3,4}$ = 15.1 Hz, $J_{2,3}$ = 10.3 Hz, 1H, H-3), 6.58 (d, *J* = 15.4 Hz, 1H, H-4), 6.45 (dd, $J_{1,2}$ = 15.0 Hz, $J_{2,3}$ = 10.3 Hz, 1H, H-2), 5.67 (dd, $J_{1,1'}$ = 7.2 Hz, $J_{1,2}$ = 15.1 Hz, 1H, H-1), 5.23 (t, *J* = 9.3 Hz, 1H, H-3′), 5.10 (t, *J* = 9.8 Hz, 1H, H-4′), 4.97 (t, *J* = 9.5 Hz, 1H, H-2′), 4.30 (dd, $J_{6'a,6'b}$ = 12.4 Hz, $J_{5',6'a}$ = 4.8 Hz, 1H, H-6′a), 4.15 (dd, $J_{6'a,6'b}$ = 12.5 Hz, $J_{5',6'b}$ = 2.0 Hz, 1H, H-6′b), 3.96 (t, *J* = 8.2 Hz, 1H, H-1′), 3.73−3.71 (m, 1H, H-5′), 2.12 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.00 (s, 3H, OAc); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 170.3, 170.0, 169.1 (2C), 135.2, 134.4 (2C), 128.6 (2C), 128.0, 127.4 (2C), 126.5 (2C), 79.2, 75.7, 73.9, 71.4, 68.4, 62.1, 20.7, 20.6, 20.5 (2C); ESI-HRMS calcd for $C_{24}H_{28}O_9Na$ ([M + Na]$^+$) 483.1626, found 483.1624.

*(EE)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(4-bromophenyl)but-1,3-diene (**3c**).* It was obtained by the reaction of 1-glycosyl-4-phenyl butene-2-ol **2c** (1.00 g, 1.79 mmol) in anhydrous CH_2Cl_2 (5 mL, 0.36 M) at 0−40 °C with Et_3N (2.15 mmol), methanesulfonyl chloride (0.3 mL, 3.58 mmol) in 69% yield (0.66 g) as white solid: mp 142−145 °C; IR (KBr) ν_{max} cm^{-1} 3543, 2892, 1748, 1640, 1246, 1047, 773; $[\alpha]^{25}_D$ −69.70° (*c* 0.1, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.29 (m, 2H, ArH), 7.26 (d, *J* = 7.7 Hz, 2H, ArH), 6.70 (dd, $J_{3,4}$ = 15.4 Hz, $J_{2,3}$ = 10.4 Hz, 1H, H-3), 6.57 (d, 1H, $J_{3,4}$ = 15.5 Hz, 1H, H-4), 6.43 (dd, $J_{1,2}$ = 15.1 Hz, $J_{2,3}$ = 10.4 Hz, 1H, H-2), 5.63 (dd, $J_{1,2}$ = 15.0 Hz, $J_{1,1'}$ = 7.4 Hz, 1H), 5.23 (t, *J* = 9.4 Hz, 1H, H-3′), 5.09 (t, *J* = 9.7 Hz, 1H, H-4′), 4.97 (t, *J* = 9.6 Hz, 1H, H-2′), 4.27 (dd, $J_{6'a,6'b}$ = 12.3 Hz, $J_{5',6'a}$ = 4.9 Hz, 1H, H-6′a), 4.12 (d, *J* = 12.1 Hz, 1H, H-6′b), 3.95 (t, *J* = 7.9 Hz, 1H, H-1′), 3.73 (m, 1H, H-5′), 2.10 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.99 (s, 3H, OAc); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 170.4, 170.1, 169.2 (2C), 137.8, 135.5, 134.4, 133.8, 129.3 (3C), 126.7, 126.5 (2C), 79.2, 75.6, 73.9, 71.5, 68.4, 62.1, 20.6 (4C); ESI-HRMS calcd for $C_{24}H_{27}BrO_9Na$ ([M + Na]$^+$) 561.0836, found 561.0835.

*(EE)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(4-chlorophenyl)but-1,3-diene (**3d**).* It was obtained by the reaction of 1-glycosyl-4-phenyl butene-2-ol **2d** (1.00 g, 1.95 mmol) in anhydrous CH_2Cl_2 (5 mL, 0.39 M) at 0−40 °C with Et_3N (2.15 mmol) and methanesulfonyl chloride (0.3 mL, 3.90 mmol) in 69% yield (0.67 g) as white solid: mp 138−140 °C; IR (KBr) ν_{max} cm^{-1} 3410, 2889, 1743, 1680, 1238, 791; $[\alpha]^{25}_D$ −129.16° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.30 (bs, 4H, ArH), 6.71 (dd, $J_{3,4}$ = 15.4 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H-3), 6.53 (d, *J* = 15.6 Hz, 1H, H-4), 6.44 (dd, $J_{1,2}$ = 15.1 Hz, $J_{2,3}$ = 10.7 Hz, 1H, H-2), 5.69 (dd, $J_{1,2}$ = 15.0 Hz, $J_{1,1'}$ = 7.4 Hz, 1H, H-1), 5.25 (t, *J* = 9.3 Hz, 1H, H-3′), 5.15 (t, *J* = 9.7 Hz, 1H, H-4′), 4.98 (t, *J* = 9.5 Hz, 1H, H-2′), 4.27 (dd, $J_{6'a,6'b}$ = 12.2 Hz, $J_{5',6'a}$ = 4.5 Hz, 1H, H-6′a), 4.14 (d, *J* = 12.2 Hz, 1H, H-6′b), 3.97 (t, *J* = 8.0 Hz, 1H, H-1′), 3.74 (ddd, $J_{4',5'}$ = 9.6 Hz, $J_{5',6'a}$ = 4.2 Hz, $J_{5',6'b}$ = 2.3 Hz, 1H, H-5′), 2.10 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.99 (s, 3H, OAc); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 170.3, 170.0, 169.1 (2C), 135.1, 134.7, 133.7, 133.0, 128.8 (2C), 128.0,

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128.01, 127.6 (2C), 78.9, 75.7, 73.9, 71.4, 68.4, 62.1, 20.7, 20.6, 20.6, 20.5; ESI-HRMS calcd for $C_{24}H_{27}ClO_9Na$ ([M + Na]$^+$) 517.1236, found 517.1236.

*(EE)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(2-chlorophenyl)but-1,3-diene (**3e**).* It was obtained by the reaction of 1-glycosyl-4-phenyl butene-2-ol **2e** (1.00 g, 1.95 mmol) in anhydrous CH_2Cl_2 (5 mL, 0.39 M) at 0−40 °C with Et_3N (2.01 mmol) and methanesulfonyl chloride (0.3 mL, 3.80 mmol) 66% yield (0.63 g) as white solid: mp 130−132 °C; IR (KBr) ν_{max} cm^{-1} 3424, 2910, 1753, 1689, 1232, 669; $[\alpha]^{25}_D$ −57.9° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (s, 1H, ArH), 7.27−7.21 (m, 3H, ArH), 6.76 (m, 1H, H-3), 6.53 (d, *J* = 15.9 Hz, 1H, H-4), 6.44−6.39 (m, 1H, H-2), 5.72 (dd, $J_{1,2}$ = 15.1 Hz, $J_{1,1'}$ = 7.4 Hz, 1H, H-1), 5.25 (t, *J* = 9.4 Hz, 1H, H-3′), 5.11 (t, *J* = 9.8 Hz, 1H, H-4′), 4.97 (t, *J* = 9.6 Hz, 1H, H-2′), 4.28 (dd, $J_{6'a,6'b}$ = 12.4 Hz, $J_{5',6'a}$ = 4.7 Hz, 1H, H-6′a), 4.16 (d, *J* = 12.2 Hz, 1H, H-6′b), 3.97 (m, 1H, H-1′), 3.74 (ddd, $J_{4',5'}$ = 9.9 Hz, $J_{5',6'a}$ = 4.6 Hz, $J_{5',6'b}$ = 2.1 Hz, 1H, H-5′), 2.10 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.99 (s, 3H, OAc); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.7, 170.3, 169.5, 169.4, 138.6, 134.7, 134.6, 132.8, 129.8, 128.8, 128.5, 127.8, 126.5, 124.7, 78.9, 75.7, 73.9, 71.5, 68.5, 62.3, 20.7, 20.6, 20.6, 20.5; ESI-HRMS calcd for $C_{24}H_{27}ClO_9Na$ ([M + Na]$^+$) 517.1236, found 517.1237.

*(EE)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(4-isopropylphenyl)but-1,3-diene (**3f**).* It was obtained by the reaction of 1-glycosyl-4-phenyl butene-2-ol **2f** (1.00 g, 1.92 mmol) in anhydrous CH_2Cl_2 (5 mL, 0.38 M) at 0−40 °C with Et_3N (2.11 mmol) and methanesulfonyl chloride (0.3 mL, 3.84 mmol) in 67% yield (0.64 g) as white solid: mp 92−95 °C; IR (KBr) ν_{max} cm^{-1} 3407, 2849, 2496, 1689, 1460, 1220, 694; $[\alpha]^{25}_D$ −7.15° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.30 (d, *J* = 8.1 Hz, 2H, ArH), 7.18 (d, *J* = 8.0 Hz, 2H, ArH), 6.71 (dd, $J_{3,4}$ = 15.5 Hz, $J_{2,3}$ = 10.3 Hz, 1H, H-3), 6.58 (d, *J* = 15.6 Hz, 1H, H-4), 6.44 (dd, $J_{1,2}$ = 15.0 Hz, $J_{2,3}$ = 10.3 Hz, 1H, H-2), 5.65 (dd, $J_{1,2}$ = 15.0 Hz, $J_{1,1'}$ = 7.6 Hz, 1H, H-1), 5.23 (t, *J* = 9.4 Hz, 1H, H-3′), 5.10 (t, *J* = 9.7 Hz, 1H, H-4′), 4.97 (t, *J* = 9.6 Hz, 1H, H-2′), 4.29 (dd, $J_{6'a,6'b}$ = 12.5 Hz, $J_{5',6'a}$ = 4.9 Hz, 1H, H-6′a), 4.14 (dd, $J_{6'a,6'b}$ = 12.3 Hz, $J_{5',6'b}$ = 1.6 Hz, 1H, H-6′b), 3.95 (t, *J* = 8.0 Hz, 1H, H-1′), 3.74−3.70 (m, 1H, H-5′), 2.95−2.86 (m, 1H, CH), 2.11 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.27 (m, 6H, 2 × CH_3); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 170.2 (2C), 169.4 (2C), 149.0, 136.4 (2C), 135.4 (2C), 134.5, 134.3, 126.4 (3C), 79.2, 75.7, 73.9, 71.5, 69.5, 62.3, 33.9, 23.9 (2C), 20.6 (4C); ESI-HRMS calcd for $C_{27}H_{34}O_9Na$ ([M + Na]$^+$) 525.2095, found 525.2095.

*(EE)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(4-methoxyphenyl)but-1,3-diene (**3g**).* It was obtained by the reaction of 1-glycosyl-4-phenyl butene-2-ol **2g** (1.00 g, 1.96 mmol) in anhydrous CH_2Cl_2 (5 mL, 0.39 M) at 0−40 °C with Et_3N (2.16 mmol) and methanesulfonyl chloride (0.3 mL, 3.92 mmol) as described above in 76% yield (0.78 g) as a white solid: mp 110−112 °C; IR (KBr) ν_{max} cm^{-1} 3368, 2890, 1745, 1652, 1234, 698; $[\alpha]^{25}_D$ −51.02° (*c* 0.1, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.35−7.30 (m, 2H, ArH), 6.85−6.82 (m, 2H, ArH), 6.56−6.53 (m, 1H, H-3), 6.45 (d, *J* = 15.3 Hz, 1H, H-4), 6.41 (dd, $J_{1,2}$ = 15.0 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H-2), 5.63 (dd, $J_{1,2}$ = 15.0 Hz, $J_{1,1'}$ = 7.6 Hz, 1H, H-1), 5.22 (t, *J* = 9.4 Hz, 1H, H-3′), 5.09 (t, *J* = 9.7 Hz, 1H, H-4′), 4.96 (t, *J* = 9.5 Hz, 1H, H-2′), 4.27 (dd, $J_{6'a,6'b}$ = 12.3 Hz, $J_{5',6'a}$ = 4.7 Hz, 1H, H-6′a), 4.11 (d, *J* = 12.2 Hz, 1H, H-6′b), 3.93 (t, *J* = 8.8 Hz, 1H, H-1′), 3.81 (s, 3H, OCH_3), 3.73−3.69 (m, 1H, H-5′), 2.10 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.99 (s, 3H, OAc); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 170.4, 169.9, 169.2 (2C), 159.5, 135.7, 134.0, 129.4, 127.8 (2C), 126.2, 125.3, 114.2 (2C), 79.3, 75.8, 74.1, 71.6, 68.4, 62.3, 55.2, 20.7, 20.6 (3C); ESI-HRMS calcd for $C_{25}H_{30}O_{10}Na$ ([M + Na]$^+$) 513.1731, found 513.1732.

*(EE)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(2-naphathalenyl)but-1,3-diene (**3h**).* It was obtained by the reaction of 1-glycosyl-4-phenyl butene-2-ol **2h** (1.00 g, 1.92 mmol) in anhydrous CH_2Cl_2 (5 mL, 0.38 M) at 0−40 °C with Et_3N (2.11 mmol) and methanesulfonyl chloride (0.3 mL, 3.94 mmol) in 74% yield (0.71 g) as white solid: mp 112−115 °C; IR (KBr) ν_{max} cm^{-1} 3435, 1759, 1641, 1220, 772; $[\alpha]^{25}_D$ −25.81° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 8.12 (d, *J* = 7.3 Hz, 1H, ArH), 7.86−7.83 (m, 1H, ArH), 7.79 (d, *J* = 8.1 Hz, 1H, ArH), 7.65 (d, *J* = 7.0 Hz, 1H, ArH), 7.54−7.42 (m, 3H, ArH), 6.39 (d, *J* = 15.3 Hz, 1H, H-4), 6.82 (dd, $J_{3,4}$ = 15.1 Hz, $J_{2,3}$ = 10.6 Hz, 1H, H-3), 6.65 (dd, $J_{1,2}$ = 15.0 Hz, $J_{2,3}$ = 10.7 Hz, 1H, H-2), 5.74 (dd, $J_{1,2}$ = 15.0 Hz, $J_{1,1'}$ = 7.3 Hz, 1H, H-1), 5.26 (t, *J* = 9.4 Hz, 1H, H-3′), 5.12 (t, *J* = 9.7 Hz, 1H, H-4′), 5.01 (t, *J* = 9.6 Hz, 1H, H-2′), 4.30 (dd, $J_{6'a,6'b}$ = 12.4 Hz, $J_{5',6'a}$ = 4.7 Hz, 1H, H-6′a), 4.15 (dd, $J_{6'a,6'b}$ = 12.3 Hz, $J_{5',6'b}$ = 2.0 Hz, 1H, H-6′b), 4.01 (t, *J* = 7.8 Hz, 1H, H-1′), 3.75 (ddd, $J_{4',5'}$ = 9.8 Hz, $J_{5',6'a}$ = 4.5 Hz, $J_{5',6'b}$ = 2.5 Hz, 1H, H-5′), 2.13 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 170.4, 170.1, 169.2 (2C), 135.4, 133.9, 133.7, 131.2, 131.1, 130.2, 128.6, 128.4, 127.7 (2C), 126.1, 125.5, 123.6, 123.4, 79.0, 75.7, 73.9, 71.5, 68.4, 62.2, 20.7, 20.6, 20.6, 20.5; ESI-HRMS calcd for $C_{28}H_{30}O_9$ ([M + H]$^+$) 511.1962, found 511.1962.

*(EE)-1-(2′,3′,4′-Tri-O-acetyl-β-D-xylopyranosyl)-4-phenyl but-1,3-diene (**3i**).* It was obtained by the reaction of 1-glycosyl-4-phenyl butene-2-ol **2i** (1.00 g, 2.57 mmol) in anhydrous CH_2Cl_2 (5 mL, 0.49 M) at 0−40 °C with Et_3N (2.83 mmol), methanesulfonyl chloride (0.4 mL, 5.14 mmol) in 76% yield (0.78 g) as white solid: mp 122−125 °C; IR (KBr) ν_{max} cm^{-1} 3298, 1743, 1650, 1220, 679; $[\alpha]^{25}_D$ −26.18° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.39−7.20 (m, 5H, ArH), 6.74 (dd, $J_{3,4}$ = 15.6 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H-3), 6.56 (d, *J* = 15.6 Hz, 1H, H-4), 6.45 (dd, $J_{1,2}$ = 15.1 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H-2), 5.66 (dd, $J_{1,2}$ = 15.1 Hz, $J_{1,1'}$ = 7.2 Hz, 1H, H-1), 5.22 (t, *J* = 9.4 Hz, 1H, H-3′), 5.07−4.98 (m, 1H, H-4′), 4.17 (t, *J* = 9.5 Hz, 1H, H-2′), 4.16 (dd, $J_{4',5'a}$ = 5.6 Hz, $J_{5'a,5'b}$ = 11.1 Hz, 1H, H-5′a), 3.87 (t, *J* = 7.6 Hz, 1H, H-1′), 3.34 (t, *J* = 11.1 Hz, 1H, H-5′b), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.99 (s, 3H, OAc); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 170.0, 169.5, 169.3, 136.7, 134.9, 134.3, 128.6 (2C), 127.9, 127.7, 127.5, 126.6 (2C), 79.6, 73.6, 71.8, 69.3, 66.7, 20.7 (3C); ESI-HRMS calcd for $C_{21}H_{24}O_7Na$ ([M + Na]$^+$) 411.1414, found 411.1413.

*(EE)-1-(2′,3′,4′-Tri-O-acetyl-β-D-xylopyranosyl)-4-(4-chlorophenyl)but-1,3-diene (**3j**).* It was obtained by the reaction of 1-glycosyl-4-phenyl butene-2-ol **2j** (1.00 g, 2.27 mmol) in anhydrous CH_2Cl_2 (5 mL, 0.45 M) at 0−40 °C with Et_3N (2.16 mmol) and methanesulfonyl chloride (0.35 mL, 4.54 mmol) in 76% yield (0.78 g) as white solid: mp 142−145 °C; IR (KBr) ν_{max} cm^{-1} 3248, 1748, 1649, 1217, 771; $[\alpha]^{25}_D$ −43.18° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.33−7.30 (m, 4H, ArH), 6.72 (dd, $J_{3,4}$ = 15.5 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H-3), 6.51 (d, *J* = 15.7 Hz, 1H, H-4), 6.44 (dd, $J_{2,3}$ = 10.7 Hz, $J_{1,2}$ = 15.4 Hz, 1H, H-2), 5.67 (dd, $J_{1,2}$ = 15.2 Hz, $J_{1,1'}$ = 7.3 Hz, 1H, H-1), 5.25 (t, *J* = 9.5 Hz, 1H, H-3′), 5.06−5.01 (m, 1H, H-4′), 4.92 (t, *J* = 9.6 Hz, 1H, H-2′), 4.18 (dd, $J_{4',5'a}$ = 5.6 Hz, $J_{5'a,5'b}$ = 11.2 Hz, 1H, H-5′a), 3.89 (t, *J* = 7.8 Hz, 1H, H-1′), 3.36 (t, *J* = 11.0 Hz, 1H, H-5′b), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.00 (s, 3H, OAc); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 170.3, 169.7, 169.5, 135.2, 134.6, 133.6, 132.9, 128.8 (2C), 128.4, 128.1, 127.7 (2C), 79.5, 73.5, 71.8, 69.3, 66.7, 20.7 (3C); ESI-HRMS calcd for $C_{21}H_{23}ClO_7Na$ ([M + Na]$^+$) 445.1025, found 445.1025.

*(EE)-1-(2′,3′,4′-Tri-O-acetyl-β-D-xylopyranosyl)-4-(4-fluorophenyl)but-1,3-diene (**3k**).* It was obtained by the reaction of 1-glycosyl-4-phenyl butene-2-ol **2k** (1.00 g, 2.45 mmol) in anhydrous CH_2Cl_2 (5 mL, 0.47 M) at 0−40 °C with Et_3N (2.70 mmol) and methanesulfonyl chloride (0.38 mL, 4.90 mmol) in 76% yield (0.78 g) as white solid: mp 105−107 °C; IR (KBr) ν_{max} cm^{-1} 3543, 1748, 1640, 1246, 1047, 798; $[\alpha]^{25}_D$ −93.64° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37−7.33 (m, 2H, ArH), 7.03−6.97 (m, 2H, ArH), 6.65 (dd, $J_{3,4}$ = 15.5 Hz $J_{2,3}$ = 10.3 Hz, 1H, H-3), 6.54 (d, *J* = 15.6 Hz, 1H, H-4), 6.42 (dd, $J_{1,2}$ = 15.2 Hz, $J_{2,3}$ = 10.4 Hz, 1H, H-2), 5.65 (dd, $J_{1,2}$ = 15.0 Hz, $J_{1,1'}$ = 7.2 Hz, 1H, H-1), 5.22 (t, *J* = 9.5 Hz, 1H, H-3′), 5.06−4.98 (m, 1H, H-4′), 4.93 (t, *J* = 9.6 Hz, 1H, H-2′), 4.16 (dd, $J_{4',5'a}$ = 5.6 Hz, $J_{5a',5'b}$ = 11.1 Hz, 1H, H-5′a), 3.86 (t, *J* = 7.7 Hz, 1H, H-1′), 3.34 (t, *J* = 11.0 Hz, 1H, H-5′b), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.99 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 169.8, 169.6, 164.2 (d, $^1J_{CF}$ = 251.6 Hz), 134.9, 133.0, 132.9, 128.4 (2C, d, $^3J_{CF}$ = 7.9 Hz), 127.7, 127.3, 116.0 (2C, d, $^2J_{CF}$ = 21.9 Hz), 79.5, 73.5, 71.8, 69.3, 66.7, 20.7 (3C); ESI-HRMS calcd for $C_{21}H_{23}FO_7Na$ ([M + Na]$^+$) 429.1350, found 429.1352.

*(EE)-1-(2′,3′,4′-Tri-O-acetyl-β-D-xylopyranosyl)-4-(4-methylphenyl)but-1,3-diene (**3l**).* It was obtained by the reaction of 1-

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glycosyl-4-phenyl butene-2-ol **2l** (1.00 g, 2.48 mmol) in anhydrous CH_2Cl_2 (5 mL, 0.48 M) at 0−40 °C with Et_3N (2.73 mmol) and methanesulfonyl chloride (0.38 mL, 4.96 mmol) in 76% yield (0.78 g) as white solid: mp 152−155 °C; IR (KBr) ν_{max} cm^{-1} 3483, 1754, 1643, 1223, 1045, 771; $[\alpha]^{25}_D$ −76.82° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.29−7.27 (m, 2H, ArH), 7.13 (d, *J* = 7.8 Hz, 2H, ArH), 6.70 (dd, $J_{3,4}$ = 15.5 Hz, $J_{2,3}$ = 10.3 Hz, 1H, H-3), 6.56 (d, *J* = 15.5 Hz, 1H, H-4), 6.44 (dd, $J_{1,2}$ = 15.1 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H-2), 5.62 (dd, $J_{1,1'}$ = 7.3 Hz, $J_{1,2}$ = 15.1 Hz, 1H, H-1), 5.25 (t, *J* = 9.4 Hz, 1H, H-3′), 5.07−5.00 (m, 1H, H-4′), 4.90 (t, *J* = 9.6 Hz, 1H, H-2′), 4.15 (dd, $J_{4',5'a}$ = 5.6 Hz, $J_{5a',5'b}$ = 11.1 Hz, 1H, H-5′a), 3.87 (t, *J* = 7.8 Hz, 1H, H-1′), 3.35 (t, *J* = 11.0 Hz, 1H, H-5′b), 2.35 (s, 3H, CH_3), 2.06 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.01 (s, 3H, OAc); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 170.1, 169.5, 169.3, 137.7, 135.2, 134.3, 133.9, 129.3 (2C), 127.0 (2C), 126.5 (2C), 79.6, 73.5, 71.8, 69.3, 66.6, 21.2, 20.7 (3C); ESI-HRMS calcd for $C_{22}H_{26}O_7Na$ ($[M + Na]^+$) 425.1571, found 425.1569.

(EE)-1-(2′,3′,4′-Tri-O-acetyl-β-D-xylopyranosyl)-4-(4-methoxyphenyl)but-1,3-diene (**3m**). It was obtained by the reaction of 1-glycosyl-4-phenyl butene-2-ol **2m** (1.00 g, 2.39 mmol) in anhydrous CH_2Cl_2 (5 mL, 0.46 M) at 0−40 °C with Et_3N (2.63 mmol) and methanesulfonyl chloride (0.44 mL, 5.78 mmol) in 76% yield (0.78 g) as white solid: mp 115−117 °C; IR (KBr) ν_{max} cm^{-1} 3520, 1748, 1629, 1213, 773; $[\alpha]^{25}_D$ −40.99° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.38−7.30 (m, 2H, ArH), 6.89−6.82 (m, 2H, ArH), 6.62 (dd, $J_{2,3}$ = 10.3 Hz, $J_{3,4}$ = 15.4 Hz, 1H, H-3), 6.53 (d, *J* = 15.5 Hz, 1H, H-4), 6.41 (dd, $J_{2,3}$ = 10.3 Hz, $J_{1,2}$ = 15.0 Hz, 1H, H-2), 5.61 (dd, $J_{1,1'}$ = 7.4 Hz, $J_{1,2}$ = 15.0 Hz, 1H, H-1), 5.22 (t, *J* = 9.5 Hz, 1H, H-3′), 5.06−4.98 (m, 1H, H-4′), 4.90 (t, *J* = 9.5 Hz, 1H, H-2′), 4.16 (dd, $J_{4',5'a}$ = 5.6 Hz, $J_{5'a,5'b}$ = 11.1 Hz, 1H, H-5′a), 3.83 (m, 4H, H-1′, OCH_3), 3.34 (t, *J* = 10.8 Hz, 1H, H-5′b), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.99 (s, 3H, OAc); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.4, 169.8, 169.7, 159.6, 135.5, 133.9, 134.3, 129.6, 128.0, 127.8, 126.5, 125.5, 114.2, 79.8, 73.5, 71.8, 69.4, 66.6, 55.3, 20.7 (3C); ESI-HRMS calcd for $C_{22}H_{26}O_8$ ($[M + H]^+$) 419.1685, found 419.1689.

(EE)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-mannopyranosyl)-4-(4-methylphenyl)but-1,3-diene (**3n**). It was obtained by the reaction of 1-glycosyl-4-phenyl butene-2-ol **2n** (1.00 g, 2.03 mmol) in anhydrous CH_2Cl_2 (5 mL, 0.41 M) at 0−40 °C with Et_3N (2.23 mmol) and methanesulfonyl chloride (0.3 mL, 4.06 mmol) in 74% yield (0.71 g) as white solid: mp 118−120 °C; IR (KBr) ν_{max} cm^{-1} 3410, 1754, 1631, 1210, 774; $[\alpha]^{25}_D$ −105° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 7.54−7.43 (m, 2H, ArH), 7.36−7.31 (m, 2H, ArH), 6.69 (dd, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 15.4 Hz, 1H, H-3), 6.58 (d, *J* = 15.5 Hz, 1H, H-4), 6.48 (dd, $J_{2,3}$ = 10.3 Hz, $J_{1,2}$ = 15.2 Hz, 1H, H-2), 5.65 (dd, $J_{1,2}$ = 15.2 Hz, $J_{1,1'}$ = 5.7 Hz, 1H, H-1), 5.45 (d, *J* = 2.3 Hz, 1H, H-2′), 5.30 (t, *J* = 10.0 Hz, 1H, H-4′), 5.13 (t, *J* = 9.9 Hz, 1H, H-3′), 4.31 (m, 2H, H-1′ + H-6′a), 4.20 (d, *J* = 12.1 Hz, 1H, H-6′b), 3.79−3.71 (m, 1H, H-5′), 2.34 (s, 3H, CH_3), 2.12 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.01 (s, 3H, OAc); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 170.7, 170.4, 170.1, 169.6, 137.8, 134.0, 133.9, 129.4 (2C), 126.7, 126.4 (2C), 126.0 (2C), 77.6, 76.2, 72.3, 70.1, 66.0, 62.9, 21.3, 20.8, 20.7, 20.6 (2C); ESI-HRMS calcd for $C_{25}H_{30}O_9Na$ ($[M + Na]^+$) 497.1782, found 497.1783.

(EE)-1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-mannopyranosyl)-4-(4-methoxylphenyl)but-1,3-diene (**3o**). It was obtained by the reaction of 1-glycosyl-4-phenyl butene-2-ol **2o** (1.00 g, 1.96 mmol) in anhydrous CH_2Cl_2 (5 mL, 0.39 M) at 0−40 °C with Et_3N (2.34 mmol) and methanesulfonyl chloride (0.3 mL, 3.92 mmol) in 75% yield (0.76 g) as white solid: mp 118−120 °C; IR (KBr) ν_{max} cm^{-1} 3410, 1754, 1631, 1210, 774; $[\alpha]^{25}_D$ −56.2° (*c* 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.39−7.33 (m, 2H, ArH), 6.89−6.86 (m, 2H, ArH), 6.66−6.55 (m, 2H, H-3, H-4), 6.52 (dd, $J_{2,3}$ = 10.2 Hz, $J_{1,2}$ = 15.5 Hz, 1H, H-2), 5.66 (dd, $J_{1,2}$ = 14.9 Hz, $J_{1,1'}$ = 5.7 Hz, 1H, H-1), 5.46 (d, *J* = 3.2 Hz, 1H, H-2′), 5.34- 5.27 (m, 1H, H-4′), 5.15 (dd, $J_{2',3'}$ = 3.3 Hz, $J_{3',4'}$ = 10.1 Hz, 1H, H-3′), 4.35−4.29 (m, 2H, H-6′a, H-1′), 4.23 (dd, $J_{5',6'b}$ = 2.2 Hz, $J_{6'a,6'b}$ = 12.2 Hz, 1H, H-6′b), 3.83 (s, 3H, OCH_3), 3.77−3.72 (m, 1H, H-5′), 2.18 (s, 3H, OAc), 2.14 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.02 (s, 3H, OAc); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.9, 170.6, 170.2, 169.8, 159.6, 134.0, 129.7(2C), 127.9 (2C), 125.7, 125.4, 114.4 (2C), 77.3, 76.2, 72.3, 70.3, 66.2, 63.0, 55.3, 20.8, 20.7, 20.6 (2C); ESI-HRMS calcd for $C_{25}H_{30}O_{10}$ ($[M + H]^+$) 491.1917, found 491.1904.

General Procedure for the Synthesis of Unprotected 1-Glycosyl 1,3-Dienes (4a, 4b). *(EE)-1-(β-D-Xylopyranosyl)-4-(4-fluorophenyl)but-1,3-diene* (**4a**). The above glycosyl diene **3k** (0.50 g, 1.23 mmol) was dissolved in NaOMe solution in MeOH (3 mL, 0.35 M) and was stirred at room temperature for 30 min. The reaction mixture was neutralized with aq. 3 N HCl, and the solvent was evaporated under reduced pressure. The residue, thus obtained, was dissolved in MeOH and filtered off. The filtrate was concentrated to give compound **4a** in 97% yield (0.34 g) as white solid: mp 148−150 °C; IR (KBr) ν_{max} cm^{-1} 3540, 3480, 3359, 2925, 1768, 1672, 779; $[\alpha]^{25}_D$ −70.6° (*c* 0.1, MeOH); ^1H NMR (300 MHz, DMSO-d_6) δ 7.58 (m, 2H, ArH), 7.23−7.17 (m, 2H, ArH), 6.95 (dd, $J_{3,4}$ = 15.6 Hz $J_{2,3}$ = 10.6 Hz, 1H, H-3), 6.65 (d, *J* = 15.7 Hz, 1H, H-4), 6.47 (dd, $J_{2,3}$ = 10.6 Hz $J_{1,2}$ = 15.2 Hz, 1H, H-2), 6.00 (dd, $J_{1,1'}$ = 5.4 Hz $J_{1,2}$ = 15.3 Hz, 1H, H-1), 5.08 (d, *J* = 4.7 Hz, 1H, OH), 5.0 (s, 2H, 2 × OH), 3.84 (dd, J_1 = 5.1 Hz J_2 = 10.7 Hz, 1H, H-5′a), 3.65−3.61 (m, 1H, H-1′), 3.41 (m, 1H, H-4′), 3.25 (m, 2H, H-3′, H-5′b), 3.01 (m, 1H, H-2′);^{13}C NMR (75 MHz, DMSO-d_6) δ 163.8 (d, $^1J_{CF}$ = 256.5 Hz), 134.1, 133.4, 131.3, 131.0, 129.4, 128.7 (2C, d, $^3J_{CF}$ = 9.0 Hz), 115.3 (2C, d, $^2J_{CF}$ = 20.9 Hz), 80.4, 78.9, 74.7, 70.4, 70.1; ESI-HRMS calcd for $C_{15}H_{17}FO_4Na$ ($[M + Na]^+$) 303.1003, found 303.0998.

(EE)-1-(β-D-Xylopyranosyl)-4-(4-methoxyphenyl)but-1,3-diene (**4b**). It was obtained by the reaction of acetylated glycosyl diene **3b** (0.2 g, 0.47 mmol) with NaOMe solution in MeOH (3 mL, 0.14 M), in 98% yield (0.137 g) as white solid: mp 142 °C; IR (KBr) ν_{max} cm^{-1} 3580, 3466, 2928, 1769, 1653, 776; $[\alpha]^{25}_D$ −81.6° (*c* 0.1, MeOH); ^1H NMR (300 MHz, DMSO-d_6) δ 7.44 (d, *J* = 8.7 Hz, 2H, ArH), 6.99 (d, *J* = 8.7 Hz, 2H, ArH), 6.82 (dd, $J_{3,4}$ = 15.5 Hz $J_{2,3}$ = 10.5 Hz, 1H, H-3), 6.57 (d, *J* = 15.7 Hz, 1H, H-4), 6.43 (dd, $J_{2,3}$ = 10.5 Hz $J_{3,4}$ = 15.3 Hz, 1H, H-4), 5.91 (dd, $J_{1,1'}$ = 5.6 Hz $J_{1,2}$ = 15.3 Hz, 1H, H-1), 5.04 (d, *J* = 5.9 Hz, 1H, OH), 4.99−4.97 (m, 2H, 2 × OH), 3.82−3.77 (m, 4H, H-5′a, OCH_3), 3.62−3.57 (m, 1H, H-1′), 3.37−3.29 (m, 1H, H-4′), 3.20−3.07 (m, 2H, H-3′, H-5′b), 2.98−2.92 (m, 1H, H-2′); ^{13}C NMR (75 MHz, DMSO-d_6) δ 159.7, 131.9, 131.4 (2C), 128.2 (3C), 127.1, 114.8 (2C), 80.6, 78.9, 74.7, 70.3, 70.1, 55.7; ESI-HRMS calcd for $C_{16}H_{20}O_5Na$ ($[M + Na]^+$) 315.1203, found 315.1204.

General Procedure for the Synthesis of Anthraquinonyl-*C*-glycosides (5a−5o). *1-(2′,3′,4′-Tri-O-acetyl-β-D-xylopyranosyl)-4-(4-methylphenyl)anthracene-9,10-dione* (**5l**). To a stirring mixture of 1-glycosyl-1,3-diene **3l** (0.5 g, 1.24 mmol), naphthoquinone (0.196 g, 1.24 mmol) in toluene (5 mL, 0.25 M) was added $InCl_3{\cdot}4H_2O$ (0.017 g, 0.06 mmol). The reaction mixture was stirred at 80 °C for 3 h. After completion of reaction (TLC), toluene was evaporated under reduced pressure to give a residual mass, which was partitioned between CH_2Cl_2 and water. Organic layer was dried (anhyd. Na_2SO_4) and concentrated under reduced pressure to afford a crude residue, which was purified by column chromatography (SiO_2, 60−120 mesh) using a gradient of hexane:ethyl acetate (13:7) as eluent to give 1-(2′,3′,4′-tri-*O*-acetyl-β-D-xylopyranosyl)-4-(4-methylphenyl)anthracene-9,10-(1*H*,4*H*)dione (**5′l**) in 99% yield (0.682 g) as yellow solid: mp 222−225 °C; IR (KBr) ν_{max} cm^{-1} 3216, 2922, 1768, 1636, 1594, 759, 671; $[\alpha]^{25}_D$ −0.94° (*c* 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.13* (d, *J* = 7.60 Hz, 1H), 8.08−8.06 (m, 1H), 7.95−7.92 (m*, 2H), 7.70−7.63 (m*, 4H), 7.40−7.38 (m, 2H), 7.21−7.19* (m, 2H), 7.08−7.05 (m*, 4H), 6.04−5.99 (m*, 2H), 5.93−5.90 (m, 1H), 5.80−5.76* (m, 1H), 5.41* (t, *J* = 9.4 Hz, 1H), 5.29 (t, *J* = 9.2 Hz, 1H), 5.22 (t, *J* = 9.6 Hz, 1H), 5.13* (t, *J* = 9.4 Hz, 1H), 4.98−4.90 (m*, 2H), 4.82−4.75 (m*, 2H), 4.06−3.99 (m*, 4H), 3.80 (bs, 1H), 3.60* (dd, J_1 = 9.4 Hz, J_2 = 9.4 Hz, 1H), 2.28−2.27 (m*, 5H), 2.18 (s, 3H), 2.04−2.00 (m*, 12H); (100 MHz, $CDCl_3$ + CCl_4) δ 184.6, 184.5*, 183.7, 183.6*, 170.6, 170.2*, 170.1, 169.9*, 169.8, 169.6*, 146.8, 144.8*, 142.9, 141.6*, 138.7, 138.5*, 136.4, 136.3*, 133.7 (2C*), 133.5, 133.5 (2C*), 132.2, 132.1*, 129.6 (2C*), 129.4 (2C*), 129.1 (2C*), 128.8, 128.1*, 126.7, 126.6*, 126.4, 126.2*, 124.5, 119.5, 81.6, 78.5*, 74.4, 74.1*, 72.7 (2C*), 69.6, 69.3*, 68.9, 66.8*, 66.4 (2C*), 41.34, 40.8*, 36.1, 35.6*, 21.0 (2C*), 20.8 (2C*), 20.7(2C*), 20.7(2C*); ESI-HRMS calcd for $C_{32}H_{30}O_9Na$ ($[M + Na]^+$) 581.1788, found 581.1776.

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Note: Chemical shift value minor isomer, multiplicity* (in ^{1}H NMR data) and carbon* (in ^{13}C NMR data) denotes the mixture of both the isomers

The above *C*-(1,4-dihydroanthraquinon-1-yl-)-xylopyranoside **5l′** was dissolved in CH_2Cl_2 (5 mL, 0.25 M) and reacted with triethyl amine (0.1 M) in presence of molecular oxygen at rt for 6 h. After completion of reaction (TLC), reaction mixture was diluted with water and extracted with CH_2Cl_2 and water. Organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure to afford a crude residue, which was purified by column chromatography (SiO_2, 60−120 mesh) using a gradient of hexane:ethyl acetate (3:1) as eluent to give the above **5l** in 98% yield (0.66 g) as light yellow solid: mp 174−175 °C; IR (KBr) ν_{max} cm^{-1} 3022, 2920, 1750, 1674, 1594, 1221, 1035, 759; $[\alpha]^{25}_D$ 34.4° (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.2 Hz, 1H, ArH), 8.02−8.00 (m, 2H, ArH), 7.77−7.68 (m, 2H, ArH), 7.57 (d, *J* = 8.4 Hz, 1H, ArH), 7.25−7.22 (m, 2H, ArH), 7.14 (d, *J* = 8.0 Hz, 2H, ArH), 6.24 (d, *J* = 10.0 Hz, 1H, H-1′), 5.48 (t, *J* = 9.6 Hz, 1H, H-3′), 5.21−5.14 (m, 2H, H-2′, H-4′), 4.28 (dd, $J_{4',5'a}$ = 5.6 Hz, $J_{5'a,5'b}$ = 11.2 Hz,1H, H-5′a), 3.65 (t, *J* = 11.2 Hz, 1H), 3.66 (t, *J* = 10.8 Hz,1H, H-5′b), 2.43 (s, 3H, CH_3), 2.11 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.63 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4) δ 185.8, 183.9, 170.2, 170.0, 169.3, 145.4, 139.3, 138.6, 137.8, 137.0, 134.4, 134.1, 133.9, 133.3, 132.8, 132.6, 129.1 (2C), 128.0 (2C), 127.0 (2C), 126.9, 74.9, 74.4, 73.4, 70.0, 67.5, 21.6, 20.9,20.6 (2C); ESI-HRMS calcd for $C_{32}H_{28}O_9$ ([M + H]$^+$) 557.1806, found 557.1816.

It was also obtained by the reaction of 1-glycosyl-1,3-diene (**3l**) (0.5 g, 1.24 mmol) in toluene (5 mL, 0.25 M) at 80 °C with naphthoquinone (0.196 g, 1.24 mmol) and $InCl_3{\cdot}4H_2O$ (0.017 g, 0.06 mmol) to afford a crude mass (without purifying) and was again dissolved in CH_2Cl_2 (5 mL, 0.20 M). Triethylamine (0.1M) was added, and this reaction mixture was stirred at room temperature in presence of molecular oxygen for 6 h. Reaction mixture was diluted with water and extracted with CH_2Cl_2 and water. Organic layer was separated, dried over anhyd. Na_2SO_4, and evaporated under reduced pressure. Obtained crude product was purified by column chromatography (SiO_2, 60−120 mesh) using hexane:ethyl acetate (3:1) in 95% yield (0.66 g) as light yellow solid.

1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(4-flouro-phenyl) anthracene-9,10-dione (**5a**). It was obtained by the reaction of 1-glycosyl-1,3-diene **3a** (0.5 g, 1.04 mmol), in toluene (5 mL, 0.21 M) at 80 °C with naphthoquinone (0.165 g, 1.04 mmol) and $InCl_3{\cdot}4H_2O$ (0.015 g, 0.05 mmol) followed by oxidative aromatization. in 92% yield (0.60 g) as yellow solid: mp 198−200 °C; IR (KBr) ν_{max} cm^{-1} 3410, 2930, 1763, 1680, 1243, 776; $[\alpha]^{25}_D$ 69.2° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, *J* = 1.3 Hz, 1H, ArH), 8.22−8.03 (m, 2H, ArH), 7.85−7.77 (m, 2H, ArH), 7.63 (d, *J* = 8.3 Hz, 1H, ArH), 7.31−7.17 (m, 4H, ArH), 6.39 (d, *J* = 9.8 Hz, 1H, H-1′), 5.56 (t, *J* = 9.2 Hz, 1H, H-3′), 5.37−5.29 (m, 2H, H-2′, H-4′), 4.38 (dd, $J_{5',6'a}$ = 4.8 Hz, $J_{6'a,6'b}$ = 12.5 Hz, 1H, H-6′a), 0.4.26 (dd, $J_{5',6'b}$ = 1.8 Hz, $J_{6'a,6'b}$ = 12.3 Hz,1H, H-6′b), 4.14−4.09 (m, 1H, H-5′), 2.13 (s, 6H, 2 × OAc), 2.06 (s, 3H, OAc), 1.41 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.6, 183.7, 170.7, 170.2, 169.7, 169.3, 160.4 (d, $^1J_{CF}$ = 250.5 Hz), 144.3, 138.3, 137.9, 137.8, 134.1 (2C), 134.0, 133.7, 133.1, 132.7, 132.5, 129.6 (2C, d, $^3J_{CF}$ = 8.8 Hz), 126.8, 126.7, 115.3 (2C, d, $^2J_{CF}$ = 21.5 Hz), 76.4, 74.7, 74.2, 72.8, 68.9, 62.4, 20.8 (2C), 20.7, 20.4; ESI-HRMS calcd for $C_{34}H_{29}FO_{11}$ ([M + H]$^+$) 633.1767, found 633.1775.

1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-phenyl anthracene-9,10-dione (**5b**). It was obtained by the reaction of 1-glycosyl-1,3-diene **3b** (0.5 g, 1.08 mmol) in toluene (5 mL, 0.21 M) at 80 °C with naphthoquinone (0.17 g, 1.08 mmol) and $InCl_3{\cdot}4H_2O$ (0.016 g 0.054 mmol) followed by oxidative aromatization in 91% yield (0.60 g) as yellow solid: mp 165−168 °C; IR (KBr) ν_{max} cm^{-1} 3460, 3022, 1750, 1674, 1594,1371, 916; $[\alpha]^{25}_D$ 96.0° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, *J* = 6.7 Hz, 1H, ArH), 8.04−8.00 (m, 2H, ArH), 7.80−7.70 (m, 2H, ArH), 7.63 (d, *J* = 8.1 Hz, 1H, ArH), 7.43−7.42 (d, *J* = 1.1 Hz, 3H, ArH), 7.27−7.25 (m, 1H, ArH), 6.35 (d, *J* = 9.8 Hz,1H, H-1′), 5.51 (t, *J* = 9.2 Hz,1H, H-3′), 5.35−5.24 (m, 2H, H-2′, H-4′), 4.34 (dd, $J_{5',6'a}$ = 4.8 Hz, $J_{6'a,6'b}$ = 12.2 Hz, 1H, H-6′a), 4.21−4.17 (d, *J* = 11.0 Hz, 1H, H-6′b), 4.10−4.00 (m, 1H, H-5′), 2.19 (s, 3H, OAc), 2.18 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.69 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 185.4, 183.5, 170.4, 170.0, 169.4, 169.0, 145.2, 141.9, 138.0, 137.4, 134.1, 133.9, 133.8, 133.7, 133.0, 132.7, 132.3, 128.1 (2C), 127.8 (2C), 127.2, 126.7 (2C), 76.3, 74.7, 74.1, 72.7, 68.8, 62.3, 20.7 (2C), 20.6, 20.3; ESI-HRMS calcd for $C_{34}H_{30}O_{11}$ ([M + H]$^+$) 615.1861, found 615.1863.

1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(4-bromophenyl)anthracene-9,10-dione (**5c**). It was obtained by the reaction of 1-glycosyl-1,3-diene **3c** (0.5 g, 0.93 mmol) in toluene (5 mL, 0.18 M) at 80 °C with naphthoquinone (0.146 g, 0.93 mmol) and $InCl_3{\cdot}4H_2O$ (0.013 g, 0.046 mmol) followed by oxidative aromatization in 90% yield (0.58 g) as light yellow solid: mp 218−220 °C; IR (KBr) ν_{max} cm^{-1} 3410, 2930, 1758, 1680, 1231, 771; $[\alpha]^{25}_D$ −22.0° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 8.22 (d, *J* = 6.5 Hz, 1H, ArH), 8.04−7.99 (m, 2H, ArH), 7.78−7.76 (m, 2H, ArH), 7.62−7.57 (m, 2H, ArH), 7.27−7.13 (m, 4H, ArH), 6.37 (d, *J* = 9.8 Hz,1H, H-1′), 5.51 (t, *J* = 9.0 Hz, 1H, H-3′), 5.32−5.29 (m, 2H, H-2′, H-4′), 4.35−4.32 (m, 1H, H-6′a), 4.23−4.19 (m, 1H, H-6′b), 4.10 (m, 1H, H-5′), 2.10 (s, 6H, 2 × OAc), 2.03 (s, 3H, OAc), 1.69 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 185.5, 183.4, 170.4, 170.0, 169.4, 169.0, 145.4, 138.6, 137.6,134.0, 133.9, 133.7, 133.6, 133.0, 132.5, 132.3, 131.2, 129.5 (2C), 128.9, 127.8, 126.7 (2C), 121.5, 76.4, 74.7, 74.1, 72.7, 68.9, 62.3, 20.7 (2C), 20.6, 20.3; ESI-HRMS calcd for $C_{34}H_{29}O_{11}Br$ ([M + H]$^+$) 693.0966, found 693.0955.

1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(4-chlorophenyl)anthracene-9,10-dione (**5d**). It was obtained by the reaction of 1-glycosyl-1,3-diene **3d** (0.5 g, 1.01 mmol) in toluene (5 mL, 0.20 M) at 80 °C with naphthoquinone (0.159 g, 1.01 mmol) and $InCl_3{\cdot}4H_2O$ (0.014 g, 0.05 mmol) followed by oxidative aromatization in 91% yield (0.60 g) as yellow solid: mp 210−212 °C; IR (KBr) ν_{max} cm^{-1} 3482, 3023, 1750, 1674, 1493, 982; $[\alpha]^{25}_D$ 136.0° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 8.22 (d, *J* = 6.6 Hz, 1H, ArH), 8.03 (d, *J* = 6.9 Hz, 2H, ArH), 7.81−7.74 (m, 2H, ArH), 7.59 (d, *J* = 8.1 Hz, 1H, ArH), 7.42 (d, *J* = 8.0 Hz, 2H, ArH), 7.20−7.25 (d, *J* = 8.1 Hz, 1H, ArH), 6.33 (d, *J* = 9.5 Hz,1H, H-1′), 5.48 (t, *J* = 9.2 Hz,1H, H-3′), 5.31−5.22 (m, 2H, H-2′, H-4′), 4.34 (dd, $J_{5',6'a}$ = 5.0 Hz, $J_{6'a,6'b}$ = 12.6 Hz, 1H, H-6′a), 4.16 (d, $J_{6'a,6'b}$ = 12.5 Hz, 1H, H-6′b), 4.07−4.05 (m, 1H, H-5′), 2.10 (s, 6H, 2 × OAc), 2.03 (s, 3H, OAc), 1.69 (s, 3H, OAc); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 185.1, 183.1, 170.1, 169.7, 169.2, 168.7, 143.8, 140.3, 138.5, 137.2, 134.1, 133.9, 133.8, 133.6, 133.4, 133.0, 132.5, 129.2 (2C), 128.4 (3C), 126.8, 126.7, 76.3, 74.7, 74.1, 72.6, 68.7, 62.1, 20.5 (3C), 20.3; ESI-HRMS calcd for $C_{34}H_{29}O_{11}Cl$ ([M + H]$^+$) 649.1471, found 649.1473.

1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(2-chlorophenyl)anthracene-9,10-dione (**5e**). It was obtained by the reaction of 1-glycosyl-1,3-diene **3e** (0.5 g, 0.95 mmol) in toluene (5 mL, 0.20 M) at 80 °C with naphthoquinone (0.150 g, 0.95 mmol) and $InCl_3{\cdot}4H_2O$ (0.01 g, 0.05 mmol) by oxidative aromatization in 90% yield (0.58 g) as yellow solid: mp 188−190 °C; IR (KBr) ν_{max} cm^{-1} 3482, 3023, 1750, 1674, 1493, 982; $[\alpha]^{25}_D$ 44.2° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 8.29 (d, *J* = 7.0 Hz, 1H, ArH), 8.11 (d, *J* = 5.0 Hz, 2H, ArH), 7.86−7.84 (m, 2H, ArH), 7.66 (d, *J* = 8.1 Hz, 1H, ArH), 7.50 (d, *J* = 7.8 Hz, 2H, ArH), 7.34−7.25 (m, 2H), 6.43 (d, *J* = 9.7 Hz,1H, H-1′), 5.60 (t, *J* = 9.2 Hz, 1H, H-3′), 5.37−5.33 (m, 2H, H-2′, H-4′), 4.41−4.37 (dd, $J_{5',6'a}$ = 4.8 Hz, $J_{6'a,6'b}$ = 12.0 Hz, 1H, H-6′a), 4.30 (d, $J_{6'a,6'b}$ = 12.1 Hz, 1H, H-6′b), 4.16−4.14 (m, 1H, H-5′), 2.17 (s, 6H, 2 × OAc), 2.09 (s, 3H, OAc), 1.74 (s, 3H, OAc); ^{13}C NMR (50 MHz, $CDCl_3$) δ 185.5, 183.7, 170.7, 170.3, 169.7, 169.3, 143.9, 140.5, 138.5, 137.4, 134.2, 134.1, 133.7, 133.4, 133.2, 132.6 (2C), 129.3 (2C), 128.5 (3C), 126.9, 126.8, 76.4, 74.7, 74.1, 72.8, 68.9, 62.4, 20.8 (2C), 20.7, 20.4; ESI-HRMS calcd for $C_{34}H_{29}O_{11}Cl$ ([M + H]$^+$) 649.1471, found 649.1473.

1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(4-isopropylphenyl)anthracene-9,10-dione (**5f**). It was obtained by the reaction of 1-glycosyl-1,3-diene **3f** (0.5 g, 0.99 mmol) in toluene (5 mL, 0.20 M) at 80 °C with naphthoquinone (0.157 g, 0.99 mmol) and $InCl_3{\cdot}4H_2O$ (0.014 g, 0.05 mmol) followed by oxidative aromatization in 93% yield (0.61 g) as light yellow solid: mp 172−175 °C; IR (KBr) ν_{max} cm^{-1} 3435, 1750, 1639, 1366, 1219, 771, 668; $[\alpha]^{25}_D$ 136.7° (*c*

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0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.22−8.20 (m, 1H, ArH, ArH), 8.06 (d, J = 7.2 Hz, 1H, ArH), 8.00 (d, J = 8.2 Hz, 1H, ArH), 7.80−7.71 (m, 2H, ArH), 7.62 (d, J = 8.1 Hz, 1H, ArH), 7.31 (m, 1H, ArH), 7.19 (d, J = 7.8 Hz, 2H, ArH), 6.31 (d, J = 9.7 Hz,1H, H-1′), 5.50 (t, J = 9.1 Hz,1H, H-3′), 5.36−5.24 (m, 2H, H-2′, H-4′), 4.34 (dd, $J_{5',6'a}$ = 4.6 Hz, $J_{6'a,6'b}$ = 12.3 Hz, 1H, H-6′a), 4.19−4.16 (m, 1H, H-6′b), 4.10−4.07 (m, 1H, H-5′), 3.06−2.97 (m, 1H, CH), 2.10 (s, 6H, 2 × CH_3), 2.03 (s, 3H, OAc), 1.70 (s, 3H, OAc), 1.37 (s, 3H, OAc), 1.35 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 185.4, 183.4, 170.1, 169.8, 169.2, 168.8, 147.5, 145.4, 139.3, 137.7, 137.6, 134.2, 133.9, 133.7, 133.5, 133.0, 132.8, 132.2, 128.1, 127.9, 126.7 (2C), 126.1 (2C), 76.4, 74.8, 74.2, 72.6, 68.8, 62.3, 33.8, 24.0 (2C), 20.7 (2C), 20.5, 20.3; ESI-HRMS calcd for $C_{37}H_{36}O_{11}$ ([M + H]$^+$) 657.2330, found 657.2330.

1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(4-methoxyphenyl)anthracene-9,10-dione (**5g**). It was obtained by the reaction of 1-glycosyl-1,3-diene **3g** (0.5 g, 1.02 mmol) in toluene (5 mL, 0.21 M) at 80 °C with naphthoquinone (0.159 g, 1.02 mmol) and $InCl_3{\cdot}4H_2O$ (0.014 g, 0.05 mmol) followed by oxidative aromatization in 95% yield (0.62 g) as light yellow solid: mp 175−178 °C; IR (KBr) ν_{max} cm^{-1} 3021, 2921, 1750, 1673, 1598, 1493, 917, 598; $[\alpha]^{25}_D$ 168.2° (c 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, J = 7.3 Hz, 1H, ArH), 8.05 (d, J = 6.9 Hz, 2H, ArH), 7.99 (d, J = 8.1 Hz, 1H, ArH), 7.79−7.70 (m, 2H, ArH), 7.62 (d, J = 8.1 Hz, 1H, ArH), 7.20 (d, J = 10.3 Hz, 1H, ArH), 6.97 (d, J = 8.5 Hz, 2H, ArH), 6.32 (d, J = 9.6 Hz, 1H, H-1′), 5.49 (t, J = 9.2 Hz,1H, H-3′), 5.34−5.23 (m, 2H, H-2′, H-4′), 4.34 (dd, $J_{5',6'a}$ = 4.7 Hz, $J_{6'a,6'b}$ = 12.3 Hz,1H, H-6′a), 4.16 (d, J = 12.0 Hz, 1H, H-6′b), 4.09−4.05 (m, 1H, H-5′), 3.89 (s, 3H, OCH_3), 2.10 (s, 6H, 2 × OAc), 2.03 (s, 3H, OAc), 1.69 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4) δ 185.4, 183.6, 170.3, 169.8, 169.3, 169.8, 158.9, 145.0, 137.7, 137.6, 134.1, 134.0, 139.0, 133.8, 133.6, 133.1, 132.7, 132.2, 129.1 (2C), 126.7 (2C), 113.6 (2C), 76.2, 74.7, 74.1, 72.6, 68.8, 62.2, 55.0, 21.7 (2C), 20.6, 20.3; ESI-HRMS calcd for $C_{35}H_{32}O_{12}$([M + H]$^+$) 645.1967, found 645.1974.

1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(2-naphathalenyl)anthracene-9,10-dione (**5h**). It was obtained by the reaction of 1-glycosyl-1,3-diene **3h** (0.5 g, 0.98 mmol) in toluene (5 mL, 0.19 M) at 80 °C with naphthoquinone (0.155 g, 0.98 mmol) and $InCl_3{\cdot}4H_2O$ (0.015 g, 0.05 mmol) followed by oxidative aromatization in 88% yield (0.57 g) as light yellow solid: mp 180−182 °C; IR (KBr) ν_{max} cm^{-1} 3482, 2925, 1750, 1673, 1371, 1229, 758, 667; $[\alpha]^{25}_D$ −52.6° (c 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, J = 7.6 Hz 1H, ArH), 8.12 (d, J = 8.1 Hz, 1H, ArH), 7.93−7.85 (m, 2H, ArH), 7.78−7.64 (m, 4H, ArH), 7.55−7.46 (m, 2H, ArH), 7.31−7.23 (m, 3H, ArH), 6.42 (d, J = 9.7 Hz,1H, H-1′), 5.57−5.49 (m, 1H, H-3′), 5.37−5.30 (m, 2H, H-2′, H-4′), 4.41−4.29 (m, 1H, H-6′a), 4.23−4.18 (m, 1H, H-6′b), 4.13−4.11 (m, 1H, H-5′), 2.12 (s, 6H, 2 × OAc), 2.05 (s, 3H, OAc), 1.74 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 185.9, 182.6, 170.5, 170.1, 169.5, 168.9, 143.2, 138.1, 134.3, 133.8 (2C), 133.5, 132.7 (3C), 131.6, 128.5 (2C), 127.7, 126.8 (2C), 126.1 (2C), 125.7 (2C), 125.4, 124.9, 124.6, 74.8, 74.6, 74.3, 73.0, 68.9, 62.4, 20.7 (3C), 20.4; ESI-HRMS calcd for $C_{38}H_{32}O_{11}$([M + H]$^+$) 665.2017, found 665.2013.

1-(2′,3′,4′-Tri-O-acetyl-β-D-xylopyranosyl)-4-phenyl anthracene-9,10-dione (**5i**). It was obtained by the reaction of 1-glycosyl-1,3-diene **3i** (0.5 g, 1.28 mmol) in toluene (5 mL, 0.26 M) at 80 °C with naphthoquinone (0.203 g, 1.28 mmol) and $InCl_3{\cdot}4H_2O$ (0.017 g, 0.06 mmol) followed by oxidative aromatization in 93% yield (0.65 g) as yellow solid: mp 200−202 °C; IR (KBr) ν_{max} cm^{-1} 3480, 2899, 1762, 1680, 1234, 776; $[\alpha]^{25}_D$ 70.7° (c 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, J = 7.2 Hz, 1H, ArH), 8.05 (d, J = 8.0 Hz, 1H, ArH), 7.82−7.75 (m, 2H, ArH), 7.61 (d, J = 8.1 Hz, 2H, ArH), 7.29−7.12 (m, 5H, ArH), 6.30 (d, J = 9.7 Hz, 1H, H-1′), 5.54 (t, J = 9.3 Hz, 1H, H-3′), 5.25−5.19 (m, 2H, H-2′, H-4′), 4.29 (m,1H, H-5′a), 3.68 (t, J = 10.7 Hz, 1H, H-5′b), 2.12 (s, 3H, OAc), 2.06 (s, 3H, OAc), 1.66 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.8, 183.7, 170.1(2C), 169.3, 145.0, 139.8, 137.8, 134.2, 134.0, 133.9 (2C), 133.8, 132.6, 132.5, 132.4, 128.1, 127.8 (2C), 127.2, 127.0, 126.7, 126.3, 74.8, 74.2, 73.3, 69.8, 67.3, 20.8 (2C), 20.3; ESI-HRMS calcd for $C_{31}H_{26}O_9$([M + H]$^+$) 543.1650, found 543.1656.

1-(2′,3′,4′-Tri-O-acetyl-β-D-xylopyranosyl)-4-(4-chlorophenyl)-anthracene-9,10-dione (**5j**). It was obtained by the reaction of 1-glycosyl-1,3-diene **3j** (0.5 g, 1.18 mmol) in toluene (5 mL, 0.24 M) at 80 °C with naphthoquinone (0.187 g, 1.18 mmol) and $InCl_3{\cdot}4H_2O$ (0.017 g, 0.06 mmol) followed by oxidative aromatization in 92% yield (0.63 g) as light yellow solid: mp 147−150 °C; IR (KBr) ν_{max} cm^{-1} 3420, 2921, 1760, 1659, 1242, 771; $[\alpha]^{25}_D$ 63.7° (c 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, J = 7.0 Hz, 1H, ArH), 8.02 (d, J = 8.0 Hz, 1H, ArH), 7.81−7.72 (m, 2H, ArH), 7.58 (d, J = 8.1 Hz, 1H, ArH), 7.42 (d, J = 8.1 Hz, 2H, ArH), 7.21 (d, J = 8.0 Hz, 3H, ArH), 6.27 (d, J = 9.7 Hz,1H, H-1′), 5.49 (t, J = 9.3 Hz,1H, H-3′), 5.19−5.14 (m, 2H, H-2′, H-4′), 4.29 (dd, $J_{4',5'a}$ = 5.8 Hz, $J_{5'a,5'b}$ = 10.8 Hz,1H, H-5′a), 3.66 (t, J = 10.8 Hz,1H, H-5′b), 2.11 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.65 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4) δ 185.5, 183.6, 170.1, 169.9, 169.2, 144.0, 140.7, 139.3, 137.5, 134.2, 134.1, 133.9, 133.7, 133.3, 132.9, 132.6, 129.5 (2C), 128.6 (3C), 127.1, 127.0, 74.9, 74.4, 73.5, 70.0, 67.5, 20.9(2C), 20.6; ESI-HRMS calcd for $C_{31}H_{25}O_9Cl$ ([M + H]$^+$) 577.1260, found 577.1266.

1-(2′,3′,4′-Tri-O-acetyl-β-D-xylopyranosyl)-4-(4-fluorophenyl)-anthracene-9,10-dione (**5k**). It was obtained by the reaction of 1-glycosyl-1,3-diene **3k** (0.5 g, 1.23 mmol) in toluene (5 mL, 0.25 M) at 80 °C with naphthoquinone (0.194 g, 1.23 mmol) and $InCl_3{\cdot}4H_2O$ (0.017g, 0.06 mmol) followed by oxidative aromatization in 93% yield (0.66 g) as light yellow solid: mp 186−187 °C; IR (KBr) ν_{max} cm^{-1} 3021, 1752, 1674, 1220, 771; $[\alpha]^{25}_D$ 21.7° (c 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, J = 7.4 Hz, 1H, ArH), 8.03 (d, J = 7.7 Hz, 2H, ArH), 7.79−7.50 (m, 2H, ArH), 7.58 (d, J = 8.1 Hz, 1H, ArH), 7.24−7.20 (m, 2H, ArH), 7.14−7.08 (m, 2H, ArH), 6.27 (d, J = 9.6 Hz,1H, H-1′), 5.48 (t, J = 9.3 Hz,1H, H-3′), 5.22−5.14 (m, 2H, H-2′, H-4′), 4.29 (dd, $J_{4,5'a}$ = 5.8 Hz, $J_{5'a,5'b}$ = 11.0 Hz, 1H, H-5′a), 3.66 (t, J = 11.0 Hz, 1H, H-5′b), 2.10 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.64 (s, 3H, OAc); ^{13}C NMR (50 MHz, $CDCl_3$ + CCl_4) δ 185.2, 183.3, 169.8, 169.5, 168.8, 143.9, 138.8, 137.3, 134.1 (2C), 133.8, 133.7, 132.5, 132.4, 129.6, 129.4 (2C, d, $^3J_{CF}$ = 8.1 Hz), 126.8, 126.7 (2C), 115.3 (2C, d, $^2J_{CF}$ = 22.0 Hz), 73.2, 72.9, 72.0, 69.7, 67.2, 20.6 (2C), 20.2; ESI-HRMS calcd for $C_{31}H_{25}FO_9$ ([M + H]$^+$) 561.1555, found 561.1563.

1-(2′,3′,4′-Tri-O-acetyl-β-D-xylopyranosyl)-4-(4-methoxyphenyl)-anthracene-9,10-dione (**5m**). It was obtained by the reaction of 1-glycosyl-1,3-diene **3m** (0.5 g, 1.19 mmol) in toluene (5 mL, 0.24 M) at 80 °C with naphthoquinone (0.189 g, 1.19 mmol) and $InCl_3{\cdot}4H_2O$ (0.017g, 0.06 mmol) followed by oxidative aromatization in 94% yield (0.64 g) as yellow solid: mp 192−195 °C; IR (KBr) ν_{max} cm^{-1} 2925, 1751, 1672, 1596, 1221, 771; $[\alpha]^{25}_D$ 161.6° (c 0.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 7.5 Hz, 1H, ArH), 8.05−7.98 (m, 2H, ArH), 7.80−7.71 (m, 2H, ArH), 7.61 (d, J = 7.1 Hz, 1H, ArH), 7.21 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 9.4 Hz, 2H, ArH), 6.28 (d, J = 9.6 Hz,1H, H-1′), 5.52 (t, J = 9.3 Hz,1H, H-3′), 5.25−5.20 (m, 2H, H-2′, H-4′), 4.29 (dd, $J_{4',5'a}$ = 5.7 Hz, $J_{5'a,5'b}$ = 10.9 Hz, 1H, H-5′a), 3.89 (s, 3H, OCH_3), 3.66 (t, $J_{5'a,5'b}$ = 10.8 Hz,1H, H-5′b), 2.11 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.65 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 185.6 183.8, 170.0, 169.8, 169.1, 159.0, 144.9, 138.2, 137.7, 134.2, 134.1, 133.9, 133.7, 133.2, 132.5, 132.4, 129.2 (2C), 126.8, 126.7, 126.6, 113.6 (2C), 74.7, 74.1, 73.2, 69.7, 67.2, 55.16, 20.6 (2C), 20.3; ESI-HRMS calcd for $C_{32}H_{28}O_{10}$ ([M + H]$^+$) 573.1755, found 573.1757.

1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-mannopyranosyl)-4-(4-methylphenyl)anthracene-9,10-dione (**5n**). It was obtained by the reaction of 1-glycosyl-1,3-diene **3n** (0.5 g, 1.05 mmol) in toluene (5 mL, 0.21 M) at 80 °C with naphthoquinone (0.167 g, 1.05 mmol) and $InCl_3{\cdot}4H_2O$ (0.015g, 0.05 mmol) followed by oxidative aromatization in 93% yield (0.62 g) as yellow solid: mp 198−200 °C; IR (KBr) ν_{max} cm^{-1} 3020, 2925, 1746, 1671, 1217, 1053, 770; $[\alpha]^{25}_D$ −31.5° (c 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$ + CCl_4) δ 8.22 (d, J = 7.3 Hz, 1H, ArH), 8.07−8.00 (m, 2H, ArH), 7.75−7.67 (m, 2H, ArH), 7.55 (d, J = 8.2 Hz, 1H, ArH), 7.25−7.21 (m, 2H, ArH), 7.14 (d, J = 7.9 Hz, 2H, ArH), 5.94 (s, 1H, H-1′), 5.88 (d, J = 3.1 Hz,1H, H-2′), 5.59 (dd, $J_{2,3'}$ = 3.1 Hz, $J_{3',4'}$ = 9.9 Hz, 1H, H-3′), 5.34 (t, J = 9.9 Hz, 1H, H-4′), 4.38 (dd, $J_{5',6'a}$ = 6.0 Hz, $J_{6'a,6'b}$ = 12.2 Hz, 1H, 6′a), 4.21 (dd, $J_{5',6'b}$ = 1.7 Hz, $J_{6'a,6'b}$ = 12.2 Hz, 1H, H-6′b), 3.90 (ddd, $J_{5',6'b}$ = 1.7 Hz, $J_{5',6'a}$

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= 6.0 Hz, $J_{4',5'}$ = 4.4 Hz, 1H, H-5′), 2.43 (s, 3H, CH_3), 2.10 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4) δ 185.5, 183.5, 170.3, 169.7, 169.6, 169.5, 144.7, 139.2, 138.8, 136.7 (2C), 133.9, 133.8, 133.6 (2C), 132.8, 132.4 (2C), 131.2, 128.9 (2C), 127.8 (2C), 127.0, 126.7, 76.02, 72.0, 69.9, 66.8 (2C), 63.0, 21.3, 20.7, 20.6, 20.4; ESI-HRMS calcd for $C_{35}H_{32}O_{11}Na$ ([M + Na]$^+$) 651.1842, found 651.1834.

*1-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-mannopyranosyl)-4-(4-methoxyphenyl)anthracene-9,10-dione (**5o**).* It was obtained by the reaction of 1-glycosyl-1,3-diene **3o** (0.5 g, 1.02 mmol) in toluene (5 mL, 0.20 M) at 80 °C with naphthoquinone (0.161 g, 1.02 mmol) and $InCl_3$·$4H_2O$ (0.014 g, 0.05 mmol) followed by oxidative aromatization in 94% yield (0.63 g) as light yellow solid: mp 210−215 °C; IR (KBr) ν_{max} cm^{-1} 3021, 2925, 1765, 1675, 1221, 779; $[\alpha]^{25}_D$ −209.1° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, *J* = 6.7 Hz, 1H, ArH), 8.09−8.03 (m, 2H, ArH), 7.75−7.72 (m, 2H, ArH), 7.58 (d, *J* = 8.1 Hz, 1H, ArH), 7.20 (d, *J* = 8.4 Hz, 2H, ArH), 6.96 (d, *J* = 8.3 Hz, 2H, ArH), 5.95 (s, 1H, H-1′), 5.91 (d, *J* = 2.4 Hz, 1H, H-2′), 5.61 (dd, $J_{2',3'}$ = 3.0 Hz, $J_{3',4'}$ = 9.8 Hz, 1H, H-3′), 5.34 (m, 1H, H-4′), 4.40 (dd, $J_{5',6'a}$ = 6.3 Hz, $J_{6'a,6'b}$ = 12.3 Hz,1H, H-6′a), 4.25 (d, $J_{6'a,6'b}$ = 11.9 Hz, 1H, H-6′b), 3.89 (bs, 4H, OCH_3, H-5′), 2.12 (s, 3H, OAc), 2.11 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.94 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 185.5, 183.5, 170.1, 169.5, 169.4, 169.3, 158.9, 144.4, 138.7, 136.8, 134.2, 134.0, 133.9, 133.6, 133.5, 132.7, 132.4, 131.3, 129.2 (2C), 127.0, 126.7, 113.6 (2C), 76.03, 72.0, 70.01, 66.8 (2C), 63.0, 55.0, 20.7 (2C), 20.6, 20.4; ESI-HRMS calcd for $C_{35}H_{32}O_{12}$ ([M + H]$^+$) 645.1967, found 645.1968.

General Procedure for the Synthesis Uprotected Aryl-*C*-glycosides of Compound (6a, 6b). *1-(β-D-Xylopyranosyl)-4-(4-fluorophenyl)anthracene-9,10-dione (**6a**).* To a solution of 1-glycosyl-1,3-diene **4a** (0.10 g, 0.35 mmol) in water:toluene (9:1), (3 mL, 0.11 M) was added naphthoquinone (0.06 g, 0.35 mmol) and $InCl_3$·$4H_2O$ (0.05 mmol) at 80 °C. The resulting reaction mixture was stirred for 4 h until the glycosyl diene substrate was completely consumed. After completion (TLC), toluene was evaporated under reduced pressure, and the afforded residue was partitioned between ethyl acetate and water. Obtained organic layer was dried over Na_2SO_4, evaporated under reduced pressure, and then dissolved in pyridine (1 mL, 0.36 M). Triethylamine (0.1 M) was added, and this mixture was allowed to stir at room temperature in presence of oxygen for 6 h. After completion (TLC), crude reaction mixture was concentrated under reduced pressure and extracted with ethyl acetate and water. Organic layer was separated, dried over anhydrous sodium sulfate (Na_2SO_4), and evaporated under reduced pressure. The obtained crude product was purified by column chromatography using 60−120 mesh silica gel with $CHCl_3$:MeOH (99:1) as eluent to give **6a** in 76% yield (0.11 g) as yellow solid: mp 60−62 °C; IR (KBr) ν_{max} cm^{-1} 3620, 3471, 2922, 1760, 1678, 961; $[\alpha]^{25}_D$ 35.6° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (m, 3H, ArH), 7.79 (bs, 2H, ArH), 7.76 (d, *J* = 7.7 Hz 1H, ArH), 7.45−7.16 (m, 4H, ArH), 5.56 (d, *J* = 9.3 Hz, 1H, H-1′), 4.78 (s, 1H, OH), 4.22−4.20 (m, 2H, OH, H-5′a), 4.00−3.92 (m, 3H, OH, H-3′, H-4′), 3.60−3.55 (m, 2H, H-5′b, H-2′); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.0, 183.6, 164.2 (d, $^1J_{CF}$ = 241.1 Hz), 143.7, 142.1, 138.2, 137.7, 134.7, 134.1, 132.5, 131.9, 129.6, 128.7, 128.6, 127.7, 127.0, 126.9 (2C, d, $^3J_{CF}$ = 7.5 Hz) 115.5 (2C, d, $^2J_{CF}$ = 21.0 Hz), 80.3, 76.8, 70.5, 70.1, 65.4; ESI-HRMS calcd for $C_{25}H_{19}FO_6$ ([M + H]$^+$) 435.1244, found 435.1234.

*1-(β-D-Xylopyranosyl)-4-(4-methoxyphenyl)anthracene-9,10-dione (**6b**).* It was obtained by the reaction of 1-glycosyl-1,3-diene **4b** (0.10 g, 0.34 mmol) in water:toluene (9:1) (3 mL, 0.11 M) at 80 °C with naphthoquinone (0.053 g, 0.34 mmol) and $InCl_3$·$4H_2O$ (0.05 mmol) followed by oxidative aromatization in 79% yield (0.12 g) as light yellow solid: IR (Neat) ν_{max} cm^{-1} 3642, 3460, 2921, 1768, 1672, 978; $[\alpha]^{25}_D$ −94.1° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 8.19−8.16 (m, 1H, ArH), 8.16−8.06 (m, 2H, ArH), 7.82−7.77 (m, 2H, ArH), 7.68 (d, *J* = 8.1 Hz, 1H, ArH), 7.25 (d, *J* = 8.6 Hz, 2H, ArH), 7.04 (d, *J* = 7.7 Hz, 2H, ArH), 5.84 (d, *J* = 9.5 Hz, 1H, H-1′), 5.34 (s, 1H, OH), 4.24−4.18 (m, 1H, H-5′a), 4.02−3.97 (m, 1H, H-4′), 3.96 (s, 3H, OCH_3), 3.94−3.82 (m, 1H, H-3′), 3.57 (s, 1H, OH), 3.53−3.49 (m, 3H, OH, H-5′b, H-2′); ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4) δ 188.9, 183.4, 159.3, 144.7, 141.9, 138.6, 134.6, 134.4, 134.3, 134.3, 133.9, 133.8, 132.6, 123.1, 129.3 (2C), 128.5, 126.7, 125.6, 113.9 (2C), 80.4, 77.9, 76.9, 70.7, 70.3, 55.4; ESI-HRMS calcd for $C_{26}H_{22}O_7$ ([M + Na]$^+$) 469.1263, found 469.1245.

General Procedure for the Preparation of Compound (7). *4-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-xylopyranosyl)-7-(4-methoxyphenyl)-2-phenyl tetrahydro-1H-isoindole-1,3-(2H)-dione (**7**).* To a solution of (*EE*)-1-glycosyl-1,3-diene **3m** (0.2 g, 0.5 mmol) in toluene (4 mL, 0.12 M) at 80 °C were added *N*-phenyl maleimide (0.086 g, 0.5 mmol) and $InCl_3$·$4H_2O$ (0.02 mmol). The resulting reaction mixture was stirred for 4−5 h until the substrate was completely consumed. After completion (TLC), toluene was evaporated under reduced pressure, and the afforded residue was partitioned between ethyl acetate and water. Obtained organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. Obtained crude product was purified by column chromatography using 60−120 mesh silica gel with hexane:ethyl acetate (3:1) as eluent to give white solid of compound 7 in 81% yield (0.23 g) as white solid: mp 74 °C; IR (KBr) ν_{max} cm^{-1} 3216, 2922, 1768, 1636, 1594, 759, 671; $[\alpha]^{25}_D$ 83° (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.25 (m, 3H, ArH), 7.13 (d, *J* = 7.9 Hz, 2H, ArH), 7.14 (d, *J* = 7.9 Hz, 2H, ArH), 6.87 (d, *J* = 8.37 Hz, 2H, ArH), 6.29−6.26 (m, 1H, H-3), 6.07−6.02 (m, 1H, H-2), 5.27 (t, *J* = 9.4 Hz, 1H, H-3′), 5.09 (t, *J* = 9.3 Hz, 1H, H-2′), 5.06 (t, *J* = 10.6 Hz, 1H, H-4′), 4.23 (t, *J* = 10.0 Hz, 1H, H-1′), 4.17 (dd, $J_{4',5'a}$ = 5.9 Hz, $J_{5'a,5'b}$ = 11.2 Hz, 1H, H-5′a), 3.86 (dd, $J_{1,6}$ = 5.0 Hz, $J_{5,6}$ = 8.3 Hz, 1H, H-6), 3.78 (s, 3H, OCH_3), 3.63 (dd, $J_{4,5}$ =7.8 Hz, $J_{3,4}$ =3.9 Hz, 1H, H-4), 3.45 (t, *J* = 11.1 Hz, 1H, H-5′b), 3.37 (t, *J* = 8.2 Hz, 1H, H-5), 2.64 (d, *J* = 6.6 Hz, 1H, H-1), 2.04(s, 3H, OAc), 2.03 (s, 3H, OAc), 2.01 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 174.9, 170.3, 170.1, 169.8, 158.9, 132.1, 130.6, 129.9 (2C), 129.2 (2C), 128.6, 126.6 (2C), 114.0 (2C), 76.8, 74.0, 69.9, 67.1 (2C), 55.3, 46.3, 41.8, 41.7, 40.6, 20.9 (3C); ESI-HRMS calcd for $C_{32}H_{33}NO_{10}$ ([M + H]$^+$) 592.2177, found 592.2171.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H, ^{13}C, 2D-NOESY, and ^{1}H−^{13}C HMBC spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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