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*J. Org. Chem.*, **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.0c00442 • Publication Date (Web): 12 Apr 2020

# Total Synthesis and Structural Revision of Rebaudioside S, A Steviol Glycoside

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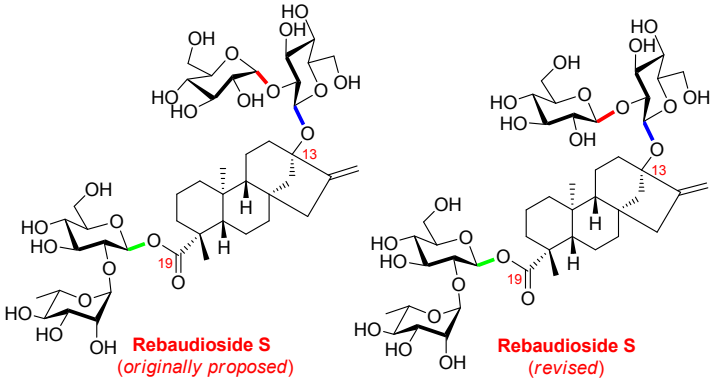



## Abstract

The total synthesis of rebaudioside S, a minor steviol glycoside from the leaves of *Stevia rebaudiana* was investigated via a modular strategy, culminating not only in the first and highly efficient synthesis of Reb-S and analogues thereof but also in the revision of the originally proposed structure. The modular strategy dictated the application of C2-branched disaccharide Yu donors to forge C-13 steviol glycosidic linkages, posing considerable challenging in stereoselectivity control. Through systematic investigations the effect of the internal glycosidic linkage configuration on the glycosylation stereoselectivity of 1,2-linked disaccharide donors was disclosed and the intensified solvent effect by the 4,6-*O*-benzylidene protecting group was also observed with glucosyl donors. Orchestrated application these favorable effects, the stereoselectivity problems were tackled exquisitely.

## Introduction

The acceptance of the statement that steviol glycosides (rebaudiosides, Figure 1)

are 'Generally Recognized As Safe' (GRAS) by the FDA in 2010 boosts the development of steviol glycoside industry rapidly in the past decade.[1] The natural origin, high sweetness, as well as reliably safety[2] renders steviol glycosides as the most popular sweeteners all over the world.[3] Furthermore, the beneficial effects of steviol glycosides on human health were also disclosed recently,[4] thus the pharmaceutical use of rebaudiosides with high added-value is also looming. Along with these factors beneficial to the development of stevioside industry, impediments retarding the advance also exist, among which the unpleasant after-taste bitter of available rebaudioside sweeteners as well as the difficulties associated with precise quality-control of feedstock for stevioside sweeteners are prominent. The tackling of these bottle-necks and the searching for ideal lead compounds for stevioside-drug development are highly dependent on the easy access of steviosides and analogues thereof with definite chemical structures, which heavily relies on conventional phytochemical isolation from the crude extracts of *S. rebaudiana* at present.[5] However, the microheterogeneities of naturally occurring steviosides make the separation of individual steviosides from natural sources a formidable task, especially for members with extremely low natural content.[6] With easily accessible steviosides as starting materials, the enzymatic synthesis has also been tried, but the tedious purification process could not be avoided because of the complex product mixtures.[7] Chemical synthesis provides a reliable means for steviosides supply; nevertheless, this approach has been being seriously under-developed due to the lack of efficient strategies for steviosides synthesis.[8]

Our recent studies on chemical synthesis of steviosides have led to the establishment of efficient strategies for syntheses of different type of steviol glycosides,[9] which encourages us to investigate the chemical synthesis of rebaudioside S (Figure 1), a minor steviol glycoside isolated from the leaves of *S. rebaudiana* in 2016.[10] The studies finally culminate in not only the first total synthesis of Reb-S via a modular strategy but also the revision of the originally proposed chemical structure.

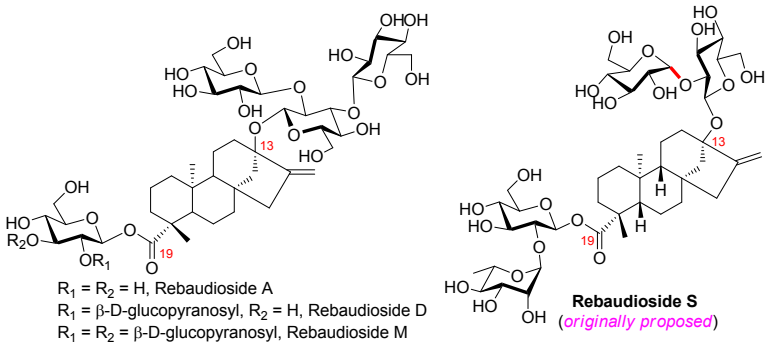



**Figure 1**. The chemical structures of rebaudiosides.

## Results and discussion

The structural characters of the proposed Reb-S, especially the 1,2-*cis*-glucosidic linkage in C-13 sugar chain, promoted us to adopt a modular synthetic strategy, and the target molecule could be assembled by building blocks disaccharide Yu donor **2** (or **2'**), steviol aglycon **3**,[9] and disaccharide bromide **4** (Figure 2). In the forward sense, the C-13 sugar chain could be installed to the acid-sensitive steviol core[11] with glycosyl *o*-alkynylbenzoate **2** or **2'** via Yu glycosylation,[12] wherein the challenging 1,2-*cis*-glycosidic linkage would be selectively forged through the long-distance participation (LDP) effect[13] of C-6 located acyl group of the distal glucosyl donor while the pivotal C-13 glycosidic linkage was conceived to be constructed β-selectively either by the nitrile solvent effect[14] or by the C2-branched donor.[15] Analogous to the syntheses of Reb-A, D, M, and S congeners,[9] the introduction of C-19 sugar residues was envisioned to be achieved via phase-transfer catalysis (PTC) protocol with disaccharide bromide **4** as donor, which could not only ensure the 1,2-*trans*-selectivity of the C-19 ester-type glycosidic linkage but also guarantee the modularity of the synthesis.

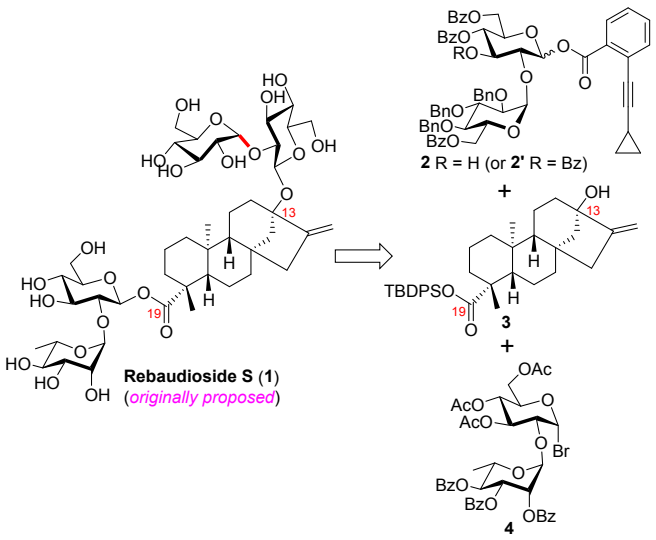
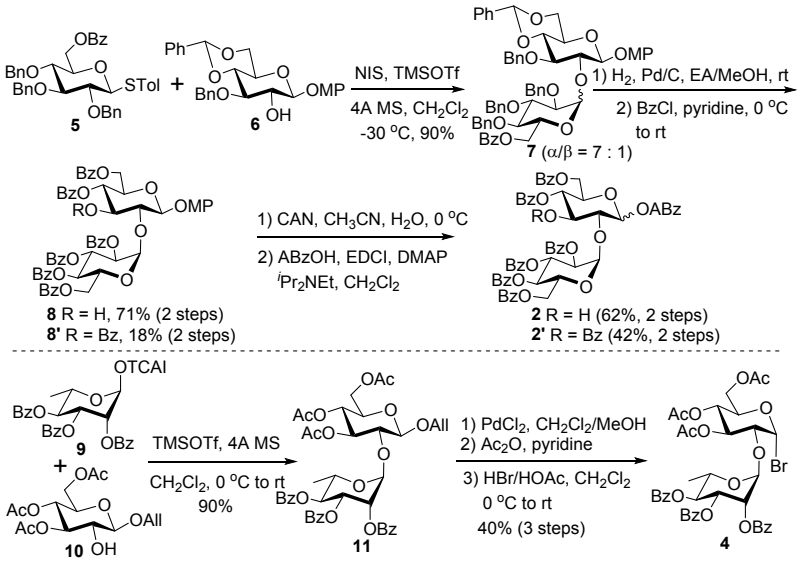



**Figure 2**. Retrosynthetic analysis of the proposed structure of rebaudioside S.

The synthetic investigation commenced with the syntheses of donors **2**, **2'**, and **4** (Scheme 1). Under the combined effect of NIS/TMSOTf, the coupling between **5**[16] and **6**[17] proceeded smoothly affording disaccharide **7** as a mixture of α/β stereoisomers with the desired α-isomer predominating remarkably due to the favorable LDP effect of the C-6 benzoyl (Bz) group in **5** (90%, α/β = 7 : 1, $J$ = 3.6 Hz for the α-isomer). Unifying the protecting groups (PGs) of **5** to benzoyl group was conducted via a sequence of benzyl and benzylidene groups removal under hydrogenolysis conditions and benzoylation under conventional conditions (BzCl, pyridine, 0 °C to rt). Surprisingly, the desired fully benzoylated **8'** was isolated only as a minor product with the partially blocked disaccharide **8** bearing a free C3-OH as the major product. The reluctance of C3-OH of **8** to further benzoylation reveals that the reactivity of C3-OH is rather low, presumably due to the bulky and electron-withdrawing property of the α-linked vicinal perbenzoylated glucosyl substituent.[18] Considering that the inert C3-OH may not interfere with the following reactions, both **8** and **8'** were advanced to *o*-alkynylbenzoate donors **2** and **2'** separately (62% and 42% yields, respectively) without the overacylation byproduct being observed for donor **2**.

The synthesis of **4** entailed the glycosylation of **10**[19] with rhamnosyl trichloroacetimidate donor **9**[20] under Schmidt glycosylation conditions[21] to provide

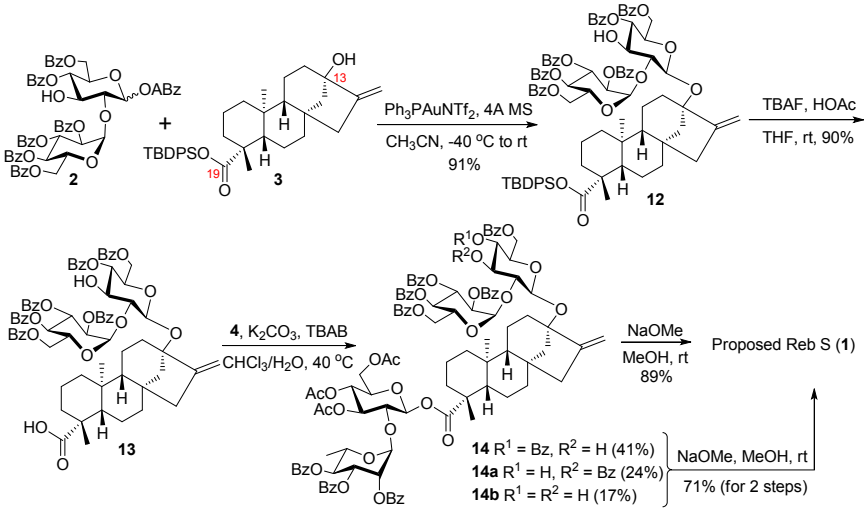
disaccharide **11** (90%), which was then successively subjected to deallylation, acetylation, and bromination conditions to deliver **4** fluently (40%, for 3 steps).




**Scheme 1**. Synthesis of donors **2**, **2'**, and **4**.

With all donors in hand, now the stage was set for the assembly of the proposed structure of Reb-S (Scheme 2). The major **2** was chosen as donor to condense with **3** under the effect of Au(I) complex. In order to take advantage of the solvent effect to enhance the β-stereoselectivity of the Yu glycosylation reaction, acetonitrile was selected as solvent. Although the reaction proceeded sluggishly under the effect of catalytic amount of $Ph_3PAuNTf_2$ (0.2 eq), stoichiometric amount of Au(I) complex promoted the reaction to reach completion with reasonable rate as well as excellent yield and stereoselectivity (91%, only β-isomer was isolated),[22] and no detrimental effect of the free C3-OH was detected. The subsequent cleavage of silyl ester was effected under buffered conditions, delivering the carboxylic acid acceptor **13** efficiently (90%), which is ready for C-19 sugar chain incorporation under PTC conditions. Under the previously optimized conditions ($K_2CO_3$, TBAB, $CHCl_3/H_2O$, 40 °C),[23] all **13** was consumed leading to three new compounds, among which the desired **14** was isolated in 41% yield, accompanied by C4-*O*-benzoyl group migrated and cleaved byproducts (**14a** and **14b**) elicited by the free OH in C-13 sugar residue. Global saponification of all ester-type PGs of **14** gave the proposed Reb-S (**1**), yet

with compromised overall efficiency because of the undesired intervention of the free OH of **13** (36%, 2 steps). Nevertheless, the low overall yield was remedied by putting the PTC glycosylation products mixture to the final deprotection step all together, providing the proposed Reb-S (**1**) with 71% yield (2 steps). The comparison of the spectroscopic data of the synthetic sample with those reported in literature was subsequently made, and evident discrepancy was observed especially for the $^{13}C$ NMR signals corresponding to the four anomeric sugar carbons, which were reported to have the chemical shifts of 94.1, 98.5, 102.0, and 107.0 ppm while being proved to be 93.9, 99.2, 101.8, and 99.9 ppm for the corresponding carbons of the synthetic sample.

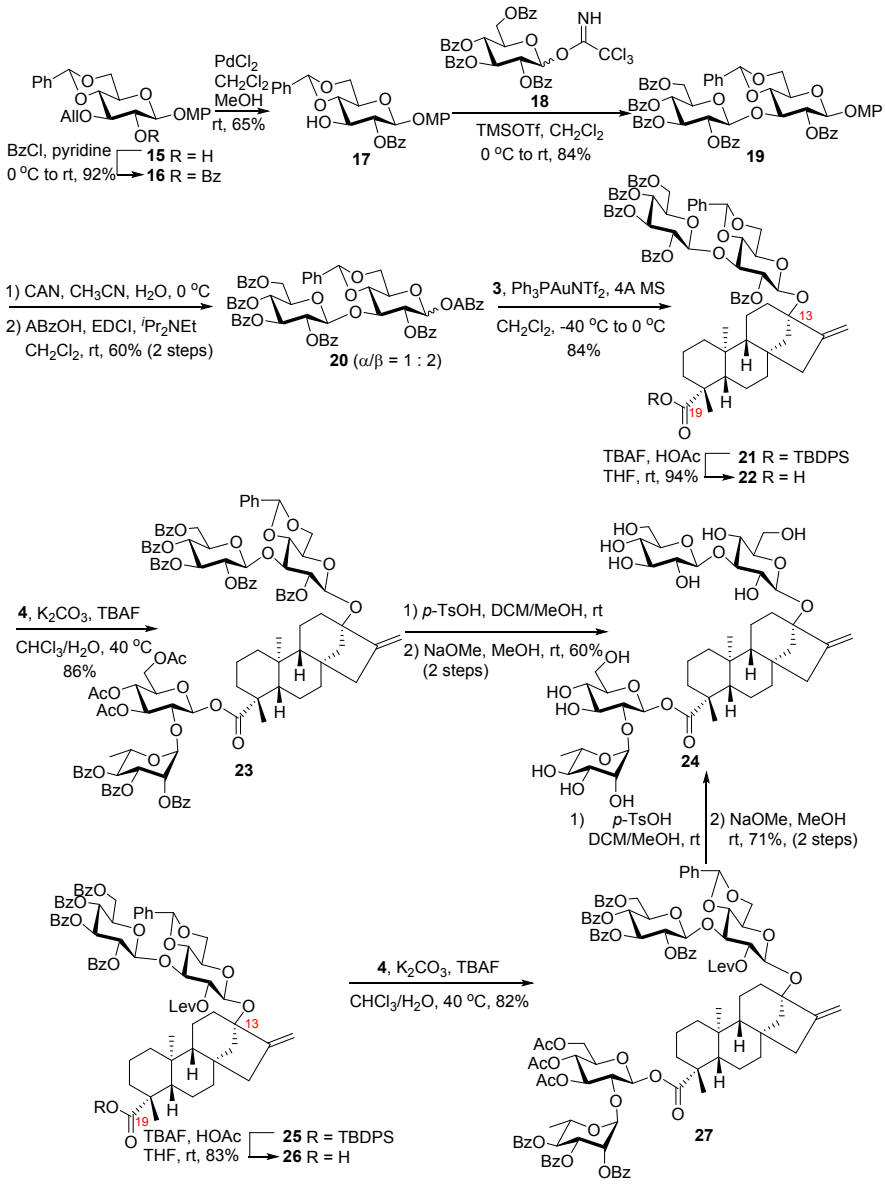



**Scheme 2**. Synthesis of the proposed structure of Reb S (**1**).

The evident downfield shift of the anomeric carbons of the C-13 branch glucosyl moiety (107.0 ppm) in authentic Reb-S promote us to conjecture that the 1,2-*cis*-glucosidic linkage was incorrectly assigned. In addition, careful scrutiny of the original spectra provided in the supporting information of the isolation literature also laid suspicion on the linkage position between the two glucosyl moieties because of the severe coalescence of proton signals between 4.50-3.50 ppm.[10] In combination with the prevailing C-13 glycoform of 2,3-dibranched triglucoside such as in Reb-A, D, and M, the authentic structure of Reb-S was tentatively proposed to **24** with a 1,3-β-linked C-13 disaccharide moiety (Scheme 3).

Similar to the synthesis of **1**, a modular strategy was also applied to assemble **24** (Scheme 3). Thus, the synthesis commenced with the preparation of 1,3-linked disaccharide Yu donor **20**. Benzoylation of **15**[24] was followed by palladium-mediated deallylation to afford **17** via **16** (60%, for 2 steps). Acceptor **17** was then glycosylated with Schmidt donor **18**[25] to furnish disaccharide **19**, which was then subjected to anomeric MP group removal and *o*-alkynylbenzoate installation conditions sequentially to provide disaccharide alkynylbenzoate donor **20** (60%, for 2 steps). With the assistance of the anchimeric effect of C2-OBz of the reducing-end sugar in **20**, the condensation between **3** and **20** proceeded stereoselectively in dichloromethane to afford **21** exclusively under the promotion of Au(I) complex (84% yield, for the anomeric proton of sugar residue directly appended to C13-OH of steviol: 5.05 ppm, $J$ = 7.8 Hz). Desilylation of **21** provided **22**, which was then exposed to the PTC glycosylation conditions in the presence of disaccharide bromide **4**. The obtained fully protected tetrasaccharide glycoside **23** (86%) was then put to deprotection process to give **24** (60%, 2 steps). Although the comparison of the $^{13}$C NMR data of **24** with the reported ones revealed a narrowed chemical shift discrepancy for the anomeric carbons (93.9, 99.3, 101.7, and 106.1 ppm, respectively), especially for the anomeric carbon of C-13 branched glucosyl residue (106.1 ppm vs 107.0 ppm), the desired good accordance was still not observed.

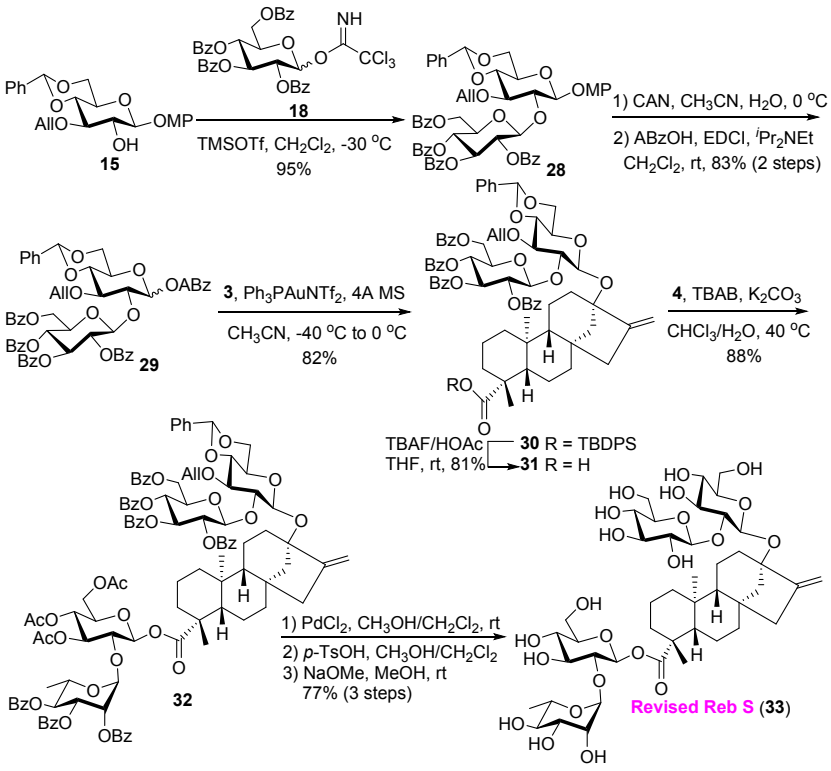
To further corroborate the structure of **24**, an alternative route to produce it from known compound **25**[9] was also conducted (Scheme 3). Similar procedures as those applied for the synthesis of **24** from **21** were adopted to convert **25** to **24** via a sequence of desilylation, PTC glycosylation, and deprotection (48%, for 4 steps). The $^{1}$H NMR of thus obtained **24** was proved to essentially identical to that of the compound derived from **21** via a modular strategy, further testifying the correctness of the structure of **24**.




**Scheme 3**. Synthesis of the proposed Reb-S (**24**) via two different routes.

The diminished spectroscopic divergence between **24** and the authentic Reb-S verifies our previous assumption that 1,2-*trans* glucosidic linkage is contained in C-13 sugar chain. Along this direction, we then turned to **33** with a 1,2-connected interglucosyl linkage (Scheme 4). To secure **33**, the required disaccharide alkynylbenzoate **29** was prepared from Schmidt donor **18** and acceptor **15** via switching the anomeric substituent of **28** from MP to ABz (**29**, 79% for 3 steps). The coupling between **29** and **3** proceeded stereoselectively in acetonitrile to deliver **30** efficiently (82%), albeit with stoichiometric amount of Au(I) complex as promoter. The releasing of the C-19 carboxylic group (**31**, 81%) was followed by PTC-mediated

glycosylation to install the C-19 disaccharide moiety to furnish **32** (88%). Deprotection of **32** was eventually realized by successive deallylation, debenzylidenation, and saponification to give **33** (77%, 3 steps). Fortunately, the spectroscopic data of **33** were shown to be in good accordance with those of the authentic sample,[26] demonstrating that the true structure of Reb-S should be **33**.




**Scheme 4**. Synthesis of the revised Reb-S (**33**).

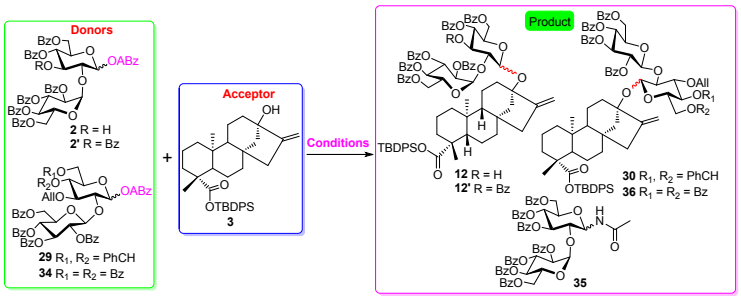
To secure satisfactory efficiency in the synthesis of Reb-S and its analogues via the modular strategy, the installation of C-13 disaccharide moiety with C2-branched disaccharide alnylbenzoate donors were optimized systematically in order to achieve high stereoselectivity (Table 1). In fact, dichloromethane was first chosen as media for the coupling between **2** and **3** under the promotion of Au(I) catalyst. However, although excellent yield was recorded (93%), almost no stereoselectivity was secured (**12**, α/β = 1.5 : 1, entry 1). Similarly, the glycosylation of **3** with **2'**, the fully benzoylated variant of **2**, in dichloromethane afforded **12'** also nonstereoselectively (95%, α/β = 1.2 : 1, entry 2). Surprisingly, when the same reaction was conducted in acetonitrile, the only detected products was *N*-acetyl-glucosylamine **35**, derived from

the hydrolysis of glycosyl acetonitrilium intermediate responsible for the β-eliciting effect of the nitrile solvent (80%, α/β = 6.5 : 1, entry 3). Donor **29** with a β internal glycosidic linkage provided **30α** exclusively when dichloromethane was selected as solvent, while affording **30β** selectively with acetonitrile as reaction media (88% and 82% yields, respectively, entries 4 and 5). The α/β ratio of **35** (6.5 : 1) reflects the capability of the nitrile effect in stereoselective control of the forged disaccharide glycosidic linkages, at most biasing the β isomers with a β to α ratio of 6.5 : 1. Thus, the sole production of **12β** as well as **30β** with donors **2** and **29** in acetonitrile cannot be attributed to the solvent effect exclusively. Presumably, the excellent β-stereoselectivities are results of the cooperative influences of solvent effect and favorable C2-OH appended bulkiness resulted from the 1,2-linked perbenzoylated glucosyl residues, as it is well known that donors with steric demanding PGs at C2-OH tend to give 1,2-*trans* glycosylation products preferentially.[27] However, the strikingly different stereoselectivity of **2** (α/β = 1.5 : 1) and **29** (α only) in $CH_2Cl_2$ implies that the anomeric configuration of the C2-*O*-linked glucosyl moiety may affect the stereoselectivity of the C2-branched donors, and the α-linked perbenzoylated glucosyl residue favors the formation of β glycosylation product more robustly than its β-linked counterpart. To exclude the possible stereo-steering effect of the 4,6-*O*-benzylidene PG in **29**, donor **34** with two benzoyl groups replacing the original 4,6-*O*-benzylidene PG was prepared[26] and was subjected to react with acceptor **3**. The condensation between **29** and **3** in dichloromethane afforded **36α** predominately but not exclusively (90%, α/β = 15 : 1, entry 6); while only a 1 : 6 ratio of α to β isomers was recorded when the same reaction was conducted in acetonitrile (83%, entry 7).

The results listed in Table 1 firmly corroborate the assumption that the anomeric configuration of C2-*O*-linked glucosyl residue has a profound effect on the stereoselectivity of the C2-branched disaccharide donor, and the α-oriented internal glycosidic linkage favors the formation of 1,2-*trans*-glycoside products while the same effect of the β-counterpart can be negligible (entries 1 vs 6). The desired β-inducing influence of the internal C2-*O*-α-glycosidic linkage could be ascribed to

the close proximity of the two glucosyl residues imposed by the α anomeric configuration. The stereoselectivity obtained in entry 7 (α/β = 1 : 6) coincides quite well with that of entry 3 (α/β = 6.5 : 1),[14] further unveiling the β-stereoselective contribution made by the favorable solvent effect. The excellent α- and β-selectivity for **29** in dichloromethane and acetonitrile, respectively, can be attributed to the α-biased effect of 4,6-*O*-benzylidene group,[28] which also guaranteed the generation of **30β** in acetonitrile by promoting the formation of α-glucosyl acetonitrium species (entries 4 and 5).

**Table 1**. Optimization of conditions for the glycosylation of **3** with C2-branched disaccharide o-alkynylbenzoates as donors.




| Entry | Donors | Acceptor | Conditions | Results[a] |
|---|---|---|---|---|
| 1 | **2** | **3** | $Ph_3PAuNTf_2$ (**0.4 eq**), $CH_2Cl_2$, **-40 to 0 °C** | **12** 93% (α/β = 1.5 : 1)[b] |
| 2 | **2'** | **3** | $Ph_3PAuNTf_2$ (**0.6 eq**), $CH_2Cl_2$, **-40 °C to 0 °C** | **12'** 95% (α/β = 1.2 : 1)[c] |
| 3 | **2'** | **3** | $Ph_3PAuNTf_2$ (**1.0 eq**), $CH_3CN$, **0 °C to rt** | **35** 80% (α/β = 6.5 : 1)[b] |
| 4 | **29** | **3** | $Ph_3PAuNTf_2$ (**0.4 eq**), $CH_2Cl_2$, **-40 °C to 0 °C** | **30** 88% (only α isomer) |
| 5 | **29** | **3** | $Ph_3PAuNTf_2$ (**1.0 eq**), $CH_3CN$, **-40 °C to rt** | **30** 82% (only β) |
| 6 | **34** | **3** | $Ph_3PAuNTf_2$ (**0.5 eq**), $CH_2Cl_2$, **-40 to 0 °C** | **36** 90% (α/β = 15 : 1)[b] |
| 7 | **34** | **3** | $Ph_3PAuNTf_2$ (**1.0 eq**), $CH_3CN$, **-40 °C to rt** | **36** 83% (α/β = 1 : 6)[b] |

[a]Isolated yield, [b]α/β ratio were determined by $^1$H NMR, [c]α/β ratio was determined by separation of both isomers.

In summary, a modular and highly efficient route to synthesize Reb-S and analogues thereof were established, through which the first total synthesis as well as structural revision of Reb-S was achieved. With C2-branched disaccharide *o*-alkynylbenzoates as donors, the effect of internal glycosidic linkage configuration on the glycosylation stereoselectivity of the 1,2-linked disaccharide donors were disclosed, and the potential of nitrile solvent effect, which was also proved intensified by the 4,6-*O*-benzylidene PG of the glucosyl donor, in β-stereoselective control of glycosylations was also evaluated. The established modular synthetic strategy is applicable to the preparation of Reb-S analogues, thus holding the promise to speed

up the process of searching for ideal sweeteners and promising lead compounds.

## Experimental Section

All reagents were of commercial grade and used as received. All moisture sensitive reactions were performed under an argon atmosphere. DCM and acetonitrile used in the glycosylation was distilled over $CaH_2$ and stored on activated 4Å molecular sieves before being used. Analytical thin-layer chromatography (TLC) was conducted with silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by exposure to UV light (254 nm) or by staining with sulfuric acid. Column chromatography was performed using silica gel (Qingdao Marine Chemical Inc., China), and Sephadex LH-20 (GE Healthcare Bio-Sciences AB, Sweden). NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz). Chemical shifts (δ) are given in ppm relative to tetramethylsilane as internal standard ($^1$H NMR in $CDCl_3$) or the residual signals of the deuterated solvents. Coupling constants (*J*) are given in Hz. All $^{13}$C spectra are proton decoupled. Optical rotations were measured at 20 °C with a Rudolph Autopol IV automatic polarimeter using a quartz cell with 2 mL capacity and a 1 dm path length. Concentrations (c) are given in g/100 mL. High resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II spectrometer using electrospray ionization (ESI).

***p*-Methoxyphenyl 2-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-benzoyl-α-D-glucopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (7)**

A solution of **5** (1066 mg, 1.6 mmol) and **6** (500 mg, 1.11 mmol) in dry dichloromethane (20 mL) was stirred at room temperature in the presence of powdered 4A molecular sieves for 30 min under $N_2$ atmosphere. After being chilled to -30 °C, NIS (453 mg, 2.01 mmol) and TMSOTf (56 μL, 0.31 mmol) were added to the suspension successively under $N_2$ atmosphere. The resultant mixture was stirred at the same temperature for another 1 h, then $Et_3N$ was added to quench the reaction. Filtration through a pad of Celite and filtrate was concentrated under reduced pressure to give the crude product, which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1) to provide **7** (990 mg, 1.0 mmol, 90%) as a mixture of α/β isomers, and the α/β isomers can be completely separated by silica gel column chromatography with toluene/ethyl acetate as eluent (toluene/ethyl acetate = 40 : 1). For **7α**: $[\alpha]_D^{25}$ = +30.5 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, DMSO-$d_6$, 50 °C) δ 7.98 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.68 – 7.64 (m, 1H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.48 – 7.38 (m, 5H), 7.34 – 7.26 (m, 12H), 7.18 – 7.05 (m, 8H), 6.87 – 6.83 (m, 4H), 5.70 (d, *J* = 3.6 Hz, 2H), 5.47 (d, *J* = 7.6 Hz, 1H), 4.89 – 4.82 (m, 3H), 4.77 (d, *J* = 11.2 Hz, 1H), 4.72 (d, *J* = 10.8 Hz, 1H), 4.59 (d, *J* = 11.2 Hz, 1H), 4.55 – 4.51 (m, 1H), 4.44 (d, *J* = 11.6 Hz, 1H), 4.38 (d, *J* = 11.6 Hz, 1H), 4.32 – 4.25 (m, 2H), 4.10 (dd, *J* = 12.0, 4.8 Hz, 1H), 3.95 – 3.88 (m, 2H), 3.86 – 3.80 (m, 2H), 3.78 – 3.71 (m, 2H), 3.69 (s, 3H), 3.63 – 3.56 (m, 2H); $^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$, 50 °C) δ 165.2, 154.6, 149.9, 138.5, 138.1, 137.8,

137.4, 137.3, 133.0, 129.6, 129.1, 128.6, 128.5, 128.4, 128.0, 127.9 (2 C), 127.8, 127.7, 127.4 (2 C), 127.3, 127.2, 127.1, 127.0, 125.7, 116.6, 114.6, 100.1, 100.0, 94.3, 81.4, 81.0, 79.4, 77.8, 77.4, 74.6, 74.4, 74.1, 73.9, 71.3, 68.2, 67.7, 64.8, 62.8, 55.3; HRMS (ESI) calcd for $C_{61}H_{61}O_{13}$ $[M+H]^+$ 1001.4107, found 1001.4108. For **7β**: $[\alpha]_D^{25}$ = +17.8 (*c* 0.5, $CHCl_3$); $^1H$ NMR (400 MHz, DMSO-$d_6$) δ 7.98 (d, *J* = 7.2 Hz, 2 H), 7.67 (t, *J* = 7.6 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 2 H), 7.40-7.37 (m, 5 H), 7.30-7.22 (m, 20 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 6.64 (d, *J* = 9.2 Hz, 2 H), 5.71 (s, 1 H), 5.27 (d, *J* = 7.2 Hz, 1 H), 5.00 (d, *J* = 4.8 Hz, 1 H), 4.99 (d, *J* = 7.2 Hz, 1 H), 4.87 (d, *J* = 11.2 Hz, 1 H), 4.77 (dd, *J* = 11.2, 3.2 Hz, 2 H) , 4.74-4.64 (m, 3 H), 4.57 (d, *J* = 11.2 Hz, 1 H), 4.31-4.23 (m, 3 H), 3.97 (t, *J* = 8.4 Hz, 1 H), 3.88 (t, *J* = 7.6 Hz, 1 H), 3.84-3.73 (m, 3 H), 3.72-3.66 (m, 2 H), 3.63 (s, 3 H), 3.61 (d, *J* = 8.4 Hz, 1 H), 3.38 (d, *J* = 7.6 Hz, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$) δ 165.4, 154.4, 150.8, 138.5, 138.4, 138.3, 138.0, 137.5, 133.4, 129.5, 129.3, 128.8, 128.2 (2 C), 128.1, 128.0 (2 C), 127.8 (2 C), 127.7 (2 C), 127.5, 127.4, 127.3, 125.9, 117.2, 114.3, 102.2, 100.1, 99.4, 83.9, 82.1, 81.1, 80.4, 78.9, 77.1, 74.6, 74.0, 73.9, 73.8, 71.9, 67.8, 64.8, 62.9, 55.3; HRMS (ESI) calcd for $C_{61}H_{60}O_{13}K$ $[M+K]^+$ 1039.3665, found 1039.3664.

***p*-Methoxyphenyl**

**2-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-4,6-di-*O*-benzoyl-β-D-glucopyranoside (8) and *p*-methoxyphenyl**

**2-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-3,4,6-tri-*O*-benzoyl-β-D-glucopyranoside (8')**

To a solution of **7** (1.15 g, 1.15 mmol) in a mixed solvent of ethyl acetate and MeOH (60 mL, v/v = 1 : 1) was added 10% Pd/C (124 mg). The flask containing the resultant black suspension was evacuated under reduced pressure and refilled with $H_2$. After this process was repeated for 3 times, the mixture was stirred at room temperature for another 17 h. Filtration through a pad of Celite and silica gel was followed by filtrate concentration under reduced pressure to afford the crude product, which was briefly purified by flash chromatography ($CH_3OH/CH_2Cl_2$ = 1 : 5). The crude product was used for the next step without further characterization. To a solution of above obtained intermediate (600 mg, 1.08 mmol) in dry pyridine was added BzCl (1.2 mL, 10.3 mmol) dropwise at 0 °C under $N_2$ atmosphere. After the addition was completed, the reaction mixture was warmed up to room temperature gradually and the stirring was continued for another 10 h. Ethyl acetate was added to dilute the reaction mixture and the resulting solution was washed with water, 1N HCl, saturated aqueous $NaHCO_3$, and brine successively. After being dried over anhydrous $Na_2SO_4$ and filtrating to remove the desiccant, the

filtrate was concentrated in *vacuo* to provide the crude product, which was further purified by silica gel chromatography (petroleum ether/ethyl acetate = 2 : 1) to afford **8** (886 mg, 0.82 mmol, 71%) as a white foam and **8'** (250 mg, 0.21 mmol, 18%) as a white foam. For **8**: $[\alpha]_D^{25}$ = +40.3 (*c* 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.08 (t, *J* = 8.3 Hz, 4H), 7.92 (dd, *J* = 13.9 Hz, 8.2 Hz, 4H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.24 (m, 16H), 7.14 (t, *J* = 7.7 Hz, 2H), 6.66 (d, *J* = 9.1 Hz, 2H), 6.33 (d, *J* = 9.1 Hz, 2H), 6.21 (t, *J* = 10.0 Hz, 1H), 5.91 (d, *J* = 3.8 Hz, 1H), 5.72 (t, *J* = 10.0 Hz, 1H), 5.46 (dd, *J* = 10.4, 3.8 Hz, 1H), 5.25 (t, *J* = 9.6 Hz, 1H), 5.11 – 5.06 (m, 1H), 4.98 (d, *J* = 7.8 Hz, 1H), 4.62 (t, *J* = 12.2 Hz, 2H), 4.47 (dd, *J* = 12.3, 4.8 Hz, 1H), 4.37 (dd, *J* = 12.0, 7.1 Hz, 1H), 4.21 (t, *J* = 9.2 Hz, 1H), 4.10 – 4.03 (m, 2H), 3.59 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.6, 166.5, 166.1, 166.0, 165.5, 165.4, 155.0, 150.2, 133.9, 133.4, 133.3, 133.2 (2 C), 133.0, 130.1, 129.9 (2 C), 129.8 (2 C), 129.7, 129.6, 129.2, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4 (2 C), 128.1, 117.5, 114.2, 101.0, 96.3, 78.9, 74.2, 72.8, 71.9, 71.4, 70.4, 69.6, 68.2, 63.5, 63.1, 55.5. HRMS (ESI) calcd for $C_{61}H_{53}O_{18}$ $[M+H]^+$ 1073.3226, found 1073.3220. For **8'**: $[\alpha]_D^{25}$ = +83.4 (*c* 2.2, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 2H), 8.05 (m, *J* = 7.8 Hz, 2H), 7.99 – 7.93 (m, 4H), 7.86 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.72 – 7.69 (m, 4H), 7.59 – 7.47 (m, 6H), 7.40 – 7.32 (m, 9H), 7.25 – 7.16 (m, 6H), 6.72 (d, *J* = 9.2 Hz, 2H), 6.40 (d, *J* = 9.2 Hz, 2H), 6.12 – 6.03 (m, 3H), 6.68 – 5.59 (m, 2H), 5.42 (dd, *J* = 10.4, 3.8 Hz, 1H), 5.16 (d, *J* = 7.8 Hz, 1H), 4.60 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.47 (dd, *J* = 12.4, 7.2 Hz, 1H), 4.41 (dd, *J* = 9.6, 7.6 Hz, 1H), 4.25 – 4.11 (m, 3H), 3.71 (dd, *J* = 12.4, 4.0 Hz, 1H), 3.62 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.0 ( 2 C), 165.7, 165.6, 165.5, 165.4, 164.9, 155.2, 149.9, 133.7, 133.6, 133.4, 133.2, 133.2, 133.1, 133.0, 129.9, 129.8 (4 C), 129.7 (2 C), 129.6, 129.2, 128.9, 128.8, 128.7 (2 C), 128.6 (2 C), 128.4, 128.3 (2 C), 128.1, 117.6, 114.2, 101.4, 95.8, 77.4, 75.7, 73.2, 72.2, 70.9, 70.1, 70.0, 68.8, 68.2, 63.2, 61.9, 55.4; HRMS (ESI) calcd for $C_{68}H_{57}O_{19}$ $[M+H]^+$ 1177.3488, found 1177.3486.

**2-*O*-(2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyronosyl)-4,6-di-*O*-benzoyl-D-glucopyranosyl *ortho*-cyclopropylethynylbenzoate (2)**

To a solution of **8** (886 mg, 0.826 mmol) in a mixed solvent of $CH_3CN$ (23.7 mL) and $H_2O$ (5.5 ml) was added CAN (1.36 g, 2.48 mmol) at 0 °C under $N_2$ atmosphere. The resulting mixture was stirred at same temperature for 10 min, then ethyl acetate was added to dilute the reaction. The resultant mixture was washed with water, saturated aqueous $Na_2S_2O_3$ and $NaHCO_3$, and brine successively, and dried over anhydrous $Na_2SO_4$. Filtration was followed by concentration to provide a residue, which was

further subjected to silica gel column chromatography to give the hemiacetal intermediate, which was used for the next step without further characterization. The above obtained hemiacetal intermediate (740 mg, 0.765 mmol) was dissolved in dry $CH_2Cl_2$ (5 mL), to which ABzOH (220 mg, 1.18 mmol), DMAP (188 mg, 1.54 mmol), $^{i}Pr_2NEt$ (0.19 mL, 1.15 mmol), and EDCI (439.6 mg, 2.29 mmol) were added successively at room temperature under $N_2$ atmosphere. The resulting mixture was stirred at the same temperature for 8 h, then ethyl acetate was added to dilute the reaction mixture. The resultant solution was washed with water, 1N HCl, saturated aqueous $NaHCO_3$, and brine successively, and dried over anhydrous $Na_2SO_4$. Filtration and concentration gave a residue, which was further subjected to silica gel column chromatography (petroleum ether/ethyl acetate = 3 : 1) to yield **2** (580 mg, 0.51 mmol, 62% for 2 steps) as a mixture of α/β isomers (α/β = 1 : 3). An aliquot of pure **2β** was obtained for detailed characterization: $[\alpha]_D^{25}$ = +65.2 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 4H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.64 – 7.12 (m, 24H), 6.17 (t, *J* = 10.0 Hz, 1H), 5.94 (d, *J* = 8.0 Hz, 1H), 5.86 (d, *J* = 3.8 Hz, 1H), 5.68 (t, *J* = 10.0 Hz, 1H), 5.38 – 5.30 (m, 2H), 5.11 – 5.06 (m, 1H), 4.63 (dd, *J* = 12.4, 2.8 Hz, 1H), 4.56 (dd, *J* = 12.0, 2.4 Hz, 1H), 4.48 – 4.39 (m, 2H), 4.25 (t, *J* = 9.1 Hz, 1H), 4.20 – 4.06 (m, 2H), 1.48-1.40 (m, 1H), 0.86-0.74 (m, 4H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 166.6 (2 C), 166.2, 165.9, 165.4, 165.2, 163.3, 134.6, 133.9, 133.4, 133.3, 133.2 (2 C), 133.1, 132.5, 131.4, 130.1, 130.0, 129.9, 129.8, 129.7 (3 C), 129.2, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4 (2 C), 128.3 (2 C), 126.9, 125.7, 100.2, 96.6, 94.0, 78.4, 75.2, 74.4, 72.6, 72.5, 71.3, 70.4, 69.6, 68.2, 63.1, 63.0, 8.9, 0.8; HRMS (ESI) calcd for $C_{66}H_{54}O_{18}K$ $[M+K]^+$ 1173.2942, found 1173.2952.

**2-*O*-(2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyronosyl)-3,4,6-tri-*O*-benzoyl-D-glucopyranosyl *ortho*-cyclopropylethynylbenzoate (2')**

Similar procedure as that used for the synthesis of **2** was adopted to convert **8'** (340 mg, 0.289 mmol) to **2'** (150 mg, 0.121 mmol, 42% for 2 steps) as a mixture of α/β epimers (α/β = 1 : 2). An aliquot of pure **2' β** was obtained for detailed characterization: $[\alpha]_D^{25}$ = +113.7 (*c* 2.3, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.07 (m, 2H), 8.03 – 7.98 (m, 4H), 7.93 – 7.90 (m, 2H), 7.80 – 7.78 (m, 2H), 7.72 – 7.67 (m, 5H), 7.54 – 7.12 (m, 24H), 6.11 – 5.98 (m, 4H), 5.80 (t, *J* = 9.6 Hz, 1H), 5.55 (t, *J* = 10.0 Hz, 1H), 5.23 (dd, *J* = 10.4, 4.0 Hz, 1H), 4.55 (dd, *J* = 12.4, 3.2 Hz, 1H), 4.50 – 4.43 (m, 2H), 4.34 – 4.30 (m, 1H), 4.23 – 4.19 (m, 1H), 4.10 (dd, *J* = 12.4, 2.8 Hz, 1H), 3.70 (dd, *J* = 12.4, 4.4 Hz, 1H), 1.49 – 1.42 (m, 1H), 0.87 – 0.75 (m, 4H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 166.1, 166.0, 165.8,

165.5, 165.3 (2 C), 164.9, 163.2, 134.6, 133.7, 133.6, 133.4 (2 C), 133.3, 133.1 (2 C), 132.6, 131.4, 129.9 (3 C), 129.8 (2 C), 129.7 (2 C), 129.2, 129.0, 128.9, 128.8 (2 C), 128.7, 128.6 (2 C), 128.5, 128.4 (2 C), 128.3 (2 C), 127.0, 125.6, 100.4, 95.8, 94.4, 75.1, 74.8, 73.6, 72.8, 71.1, 70.1, 69.4, 68.8, 68.2, 62.7, 62.0, 29.8, 8.9, 0.8; HRMS (ESI) calcd for $C_{73}H_{58}O_{19}Na$ $[M+Na]^+$ 1261.3464, found 1261.3468.

**Allyl 2-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-3,4,6-tri-*O*-acetyl-β-D-glucopyranoside (11)**

A solution of **9** (2.68 g, 4.32 mmol) and **10** (1.0 g, 2.89 mmol) in dry $CH_2Cl_2$ (10 mL) was stirred in the presence of powdered 4A MS for 30 min at room temperature under $N_2$ atmosphere. After being chilled to 0 °C, TMSOTf (160 μL, 0.884 mmol) was added. The reaction mixture was then allowed to warm up to room temperature gradually, and the stirring was continued for 1 h before $Et_3N$ was added to quench the reaction. Filtration and the filtrate was concentrated under reduced pressure to provide a residue, which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3 : 1) to yield **11** (2.1 g, 2.61 mmol, 90%) as a white foam: $[\alpha]_D^{25}$ = +192.8 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.61 – 7.58 (m, 1H), 7.52 – 7.45 (m, 3H), 7.40 – 7.35 (m, 3H), 7.24 (t, *J* = 7.8 Hz, 1H), 6.05 – 5.95 (m, 1H), 5.79 (dd, *J* = 10.2, 3.4 Hz, 1H), 5.68 (t, *J* = 10.0 Hz, 1H), 5.43 – 5.34 (m, 3H), 5.25 (dd, *J* = 7.1, 1.7 Hz, 2H), 5.03 (t, *J* = 9.7 Hz, 1H), 4.64 (d, *J* = 7.8 Hz, 1H), 4.55 (dd, *J* = 9.9, 6.1 Hz, 1H), 4.49 – 4.44 (m, 1H), 4.31 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.23 – 4.13 (m, 2H), 3.86 (dd, *J* = 9.5, 7.8 Hz, 1H), 3.76 (m, 1H), 2.17 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 1.29 (d, *J* = 6.0 Hz, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 170.7, 170.5, 169.7, 165.8, 165.5 (2 C), 133.6, 133.3, 133.2, 129.9, 129.7 (2 C), 129.4, 129.3, 129.2, 128.6, 128.4, 128.3, 118.8, 100.6, 97.8, 77.4, 76.3, 74.8, 71.9, 71.8, 71.3, 71.1, 70.8, 69.5, 68.8, 67.0, 62.1, 20.8 (2 C), 20.7, 17.5; HRMS (ESI) calcd for $C_{42}H_{44}O_{16}K$ $[M+K]^+$ 843.2261, found 843.2261.

**2-*O*-(2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl)-3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl bromide (4)**

To a solution of **11** (1.0 g, 1.24 mmol) in a mixed solvent of $CH_2Cl_2$ and methanol (40 mL, v/v = 1 : 1) was added $PdCl_2$ (65.06 mg, 0.37 mmol) at room temperature. The black suspension was stirred at the same temperature for 1 h before filtration through a pad of Celite and silica gel was adopted to remove the catalyst. The filtrate was condensed in *vacuo* and the obtained residue was co-evaporated with toluene for three times before being used for next step. The above obtained residue was dissolved in dry pyridine (4 mL), to which $Ac_2O$ (0.1 mL, 1.06 mmol) was added dropwise at 0 °C under $N_2$ atmosphere. After the addition was completed, the reaction mixture was gradually warmed up to room

temperature and the stirring was continued for 10 h, at which time TLC showed that all starting materials were consumed completely. Ethyl acetate was added to dilute the reaction mixture and the resulting solution was washed successively with water, 1N HCl, saturated aqueous $NaHCO_3$, and brine, and was then dried over anhydrous $Na_2SO_4$. Filtration was followed by concentration to provide a residue, which was further co-evaporated with toluene for 3 times. The thus obtained residue was put to next step without further purification. To a solution of the above obtained residue in dry $CH_2Cl_2$ (5 mL) was added HBr/HOAc (2 mL) at 0 °C. The resulting solution was gradually warmed up to room temperature and the stirring was continued at the same temperature for another 3 h. Ethyl acetate was added to dilute the reaction mixture and the resulting solution was thoroughly washed with water, saturated aqueous $NaHCO_3$, and brine, and was then dried over anhydrous $Na_2SO_4$. Filtration, concentration in *vacuo*, and purification by silica gel chromatography (petroleum ether/ethyl acetate = 3 : 1) delivered **4** (408 mg, 0.493 mmol, 40% for 3 steps) as a white foam: $[\alpha]_D^{25}$ = +156.3 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.0, 1.2 Hz, 2H), 8.00 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.83 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.64 – 7.60 (m, 1H), 7.53 – 7.48 (m, 3H), 7.44 – 7.38 (m, 3H), 7.28 – 7.24 (m, 2H), 6.51 (d, *J* = 4.0 Hz, 1H), 5.76 – 5.67 (m, 3H), 5.61 (t, *J* = 9.6 Hz, 1H), 5.51 (dd, *J* = 3.1, 1.7 Hz, 1H), 5.19 – 5.14 (m, 2H), 4.38 – 4.35 (m, 2H), 4.16 – 4.11 (m, 1H), 3.88 (dd, *J* = 9.8, 3.9 Hz, 1H), 2.21 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 1.35 (d, *J* = 6.0 Hz, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 170.6, 170.3, 169.8, 166.0, 165.7, 165.3, 133.8, 133.6, 133.3, 130.0 (2 C), 129.8, 129.3, 128.8, 128.6, 128.4, 100.2, 88.9, 78.8, 72.5, 71.7, 71.4, 70.9, 69.6, 68.6, 67.3, 61.2, 20.8 (2 C), 17.7; HRMS (ESI) calcd for $C_{39}H_{39}BrO_{15}K$ $[M+K]^+$ 865.1104, found 865.1096.

**13-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl)-4,6-di-*O*-benzoyl-β-D-glucopyranosyl]-steviol *tert*-butyldiphenylsilyl ester (12β)**

A solution of **2** (68.1 mg, 0.06 mmol) and **3** (28 mg, 0.05 mmol) in dry $CH_3CN$ (3 mL) was stirred in the presence of powdered 4A MS at room temperature for 30 min under $N_2$ atmosphere. After being chilled to -40 °C, $Ph_3PAuNTf_2$ (44.3 mg, 0.06 mmol) was added. The resultant reaction mixture was then gradually warmed up to room temperature and the stirring was continued for another 4 h at the same temperature. After the 4A MS was removed by filtration, the filtrate was condensed in *vacuo*. The obtained residue was further subjected to purification by silica gel column chromatography (petroleum ether/ethyl acetate = 4 : 1) to provide **12** (69 mg, 0.458 mmol, 91%) as a white foam: $[\alpha]_D^{25}$ = +28.2 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 4H), 7.93 – 7.87 (m, 6H), 7.76 (d, 7.6 Hz,

2H), 7.67 (t, 6.8 Hz, 4H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.19 (m, 22H), 6.20 (t, *J* = 9.9 Hz, 1H), 5.81 (d, *J* = 3.7 Hz, 1H), 5.65 – 5.56 (m, 2H), 5.25 – 5.20 (m, 1H), 5.13 (t, *J* = 9.5 Hz, 1H), 4.88 (s, 1H), 4.69 – 4.67 (m, 2H), 4.55 (dd, *J* = 12.2, 2.6 Hz, 1H), 4.47 (dd, *J* = 12.3, 5.2 Hz, 1H), 4.41 – 4.36 (m, 2H), 4.18 (t, *J* = 9.2 Hz, 1H), 3.95 – 3.89 (m, 2H), 3.29 (s, 1H), 2.20 (d, *J* = 13.3 Hz, 1H), 1.99 (d, *J* = 16.2 Hz, 1H), 1.84 – 1.73 (m, 4H), 1.62 (p, *J* = 8.4, 6.6 Hz, 3H), 1.46 – 1.34 (m, 2H), 1.25 (m, 3H), 1.18 (s, 3H), 1.11 (s, 9H), 1.06 – 0.75 (m, 5H), 0.64 (d, *J* = 8.0 Hz, 1H), 0.57 – 0.49 (m, 1H), 0.30 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 176.6, 166.6, 166.2, 166.1, 165.6, 165.4, 152.4, 135.8 (2 C), 133.2, 132.3, 130.1 (2 C), 130.0 (2 C), 129.9, 129.8 (2 C), 129.7, 129.2 (3 C), 129.1, 128.7, 128.6 (2 C), 128.4 (2 C), 128.3, 127.7 (2 C), 104.8, 98.8, 95.4, 86.4, 76.7, 74.7, 73.4, 71.4, 71.0, 70.7, 70.0, 67.9, 64.0, 63.4, 56.9, 53.5, 47.2, 45.3, 42.6, 41.2, 40.2, 39.2, 38.7, 37.6, 29.8, 29.3, 27.2, 22.0, 19.9, 19.4, 19.3, 16.2; HRMS (ESI) calcd for $C_{90}H_{96}NO_{19}Si$ $[M+NH_4]^+$ 1522.6340, found 1522.6386.

**13-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl)-4,6-di-*O*-benzoyl-β-D-glucopyranosyl]-steviol (13)**

To a solution of **12** (132 mg, 0.088 mmol) in dry THF (5 mL) were added HOAc (10.03 μL, 0.175 mmol) and TBAF (1 N solution in THF, 98 μL, 0.098 mmol) at room temperature. After the mixture was stirred at the same temperature for 30 min, ethyl acetate was added to dilute the reaction mixture. The resulting solution was successively washed with water and brine and dried over anhydrous $Na_2SO_4$. Filtration was followed by concentration under reduced pressure to deliver a residue, which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2 : 1) to provide **13** (100 mg, 0.079 mmol, 90%) as a white solid: $[\alpha]_D^{25}$ = +66.7 (*c* 0.5, $CHCl_3$); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 2H), 8.04 (d, *J* = 8.0 Hz, 2H), 7.95 (dd, *J* = 11.2, 7.6 Hz, 4H), 7.77 (t, *J* = 7.1 Hz, 4H), 7.55 – 7.43 (m, 7H), 7.40 – 7.26 (m, 8H), 7.18 – 7.12 (m, 4H), 6.26 (t, *J* = 9.9 Hz, 1H), 5.89 (d, *J* = 3.7 Hz, 1H), 5.68 – 5.63 (m, 2H), 5.30 – 5.25 (m, 1H), 5.09 (t, *J* = 9.6 Hz, 1H), 4.94 (s, 1H), 4.76 (d, *J* = 8.2 Hz, 2H), 4.56 (dd, *J* = 12.4, 2.5 Hz, 1H), 4.50 – 4.45 (m, 2H), 4.32 (dd, *J* = 12.1, 7.2 Hz, 1H), 4.13 (t, *J* = 9.2 Hz, 1H), 3.99 – 3.93 (m, 2H), 2.14 (d, *J* = 13.2 Hz, 1H), 2.02 (d, *J* = 16.8 Hz, 1H), 1.89 – 1.81 (m, 2H), 1.71 (s, 1H), 1.52 – 1.35 (m, 5H), 1.27 (s, 2H), 1.19 (s, 4H), 0.97 – 0.86 (m, 5H), 0.68 (d, *J* = 8.0 Hz, 1H), 0.60 – 0.54 (m, 1H), 0.45 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 183.2, 166.6, 166.5, 166.4, 166.2, 165.5, 165.4, 152.3, 133.6, 133.5, 133.3, 133.2, 133.1 (2 C), 130.1, 129.9 (2 C), 129.8, 129.7 (2 C), 129.3, 129.1, 129.0, 128.9, 128.7, 128.5 (2 C), 128.3, 104.9, 98.6, 95.2, 86.3, 76.7, 74.2, 73.2, 71.4, 71.0, 70.9, 69.9, 67.9, 64.2, 63.4, 56.6, 53.5, 47.2, 43.7, 42.5,

42.4, 41.0, 40.2, 39.2, 37.8, 29.8, 29.1, 21.6, 19.9, 18.9, 15.4; HRMS (ESI) calcd for $C_{74}H_{74}O_{19}Na$ $[M+Na]^+$ 1289.4716, found 1289.4744.

**13-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl)-4,6-di-*O*-benzoyl-β-D-glucopyranosyl]-steviol 2-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnosyl)-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl ester (14), (14a) and (14b)**

To a solution of **13** (80 mg, 0.063 mmol) in a mixed solvent of $CHCl_3$ and $H_2O$ (3 mL, v/v = 1.5 : 1.5) was added $K_2CO_3$ (26 mg, 0.188 mmol) and TBAB (40.6 mg, 0.126 mmol) at room temperature. After the mixture was stirred at the same temperature for 20 min, disaccharide bromide donor **4** (104 mg, 0.126 mmol) was added. After being stirred at 40 °C in oil bath for another 16 h, the reaction mixture was cooled to room temperature. Ethyl acetate was added to dilute the reaction mixture, and the resulting solution was washed successively with water, 1N HCl, saturated aqueous $NaHCO_3$, and brine, and dried over anhydrous $Na_2SO_4$. Filtration, filtrate concentration in *vacuo*, and purification by silica gel column chromatography (petroleum ether/ethyl acetate = 2 : 1) provided **14** (52 mg, 0.0258 mmol, 41%) as a white solid, **14a** (30 mg, 0.0149 mmol, 24%) as a white solid, and **14b** (20 mg, 0.0105 mmol, 17%) as a white solid. For **14**: $[\alpha]_D^{25}$ = +61.8 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 6H), 8.01 – 7.88 (m, 9H), 7.83 – 7.78 (m, 4H), 7.63 – 7.16 (m, 26H), 6.20 (t, *J* = 10.0 Hz, 1H), 5.84 (d, *J* = 3.7 Hz, 1H), 5.80 (d, *J* = 7.8 Hz, 1H), 5.69 – 5.59 (m, 5H), 5.52 (s, 1H), 5.44 (t, *J* = 9.0 Hz, 1H), 5.32 (s, 1H), 5.26 – 5.19 (m, 2H), 5.14 (t, *J* = 9.5 Hz, 1H), 4.91 (s, 1H), 4.79 (d, *J* = 7.8 Hz, 1H), 4.73 (s, 1H), 4.57 (dd, *J* = 12.4, 2.8 Hz, 1H), 4.52 – 4.48 (m, 2H), 4.42 – 4.29 (m, 4H), 4.19 (t, *J* = 9.1 Hz, 1H), 4.08 (t, *J* = 8.2 Hz, 2H), 3.94 (t, *J* = 8.0 Hz, 1H), 2.20 (s, 3H), 2.17 (s, 3H), 2.17 – 2.12 (m, 1H), 2.09 (s, 3H), 2.03 (d, *J* = 17.5 Hz, 1H), 1.95 (d, *J* = 11.0 Hz, 1H), 1.86 – 1.65 (m, 5H), 1.54 – 1.46 (m, 13H), 0.94 – 0.84 (m, 3H), 0.78 – 0.73 (m, 1H), 0.67 (d, *J* = 8.0 Hz, 1H), 0.52 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 174.5, 170.5 (2 C), 169.9, 166.6 (2 C), 166.4, 166.0, 165.8, 165.7, 165.6, 165.4, 152.2, 133.8 (2 C), 133.6, 133.4, 133.3, 133.2 (2 C), 130.2, 130.1, 130.0, 129.9, 129.8 (3 C), 129.7, 129.3 (2 C), 129.2 (2 C), 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 105.0, 98.5, 97.9, 95.4, 92.4, 86.4, 76.2, 74.5, 73.4, 72.2, 71.5, 71,0, 70.6, 69.9, 69.6, 68.5, 67.9, 67.8, 64.3, 63.4, 61.8, 57.8, 53.5, 47.3, 44.0, 42.6, 41.1, 40.0, 39.3, 37.6, 37.4, 29.8, 29.3, 21.5, 21.1, 21.0, 20.9, 19.8, 19.2, 17.9, 16.2; HRMS (ESI) calcd for $C_{113}H_{116}NO_{34}$ $[M+NH_4]^+$ 2030.7373, found 2030.7418. For **14a**: $[\alpha]_D^{25}$ = +78.1 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.6 Hz, 2H), 8.11 – 8.08 (m, 6H), 7.97 (t, *J* = 8.4 Hz, 4H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.4 – 7.58 (m, 2H),

7.55 – 7.18 (m, 27H), 5.95 (d, *J* = 3.6 Hz, 1H), 5.90 (t, *J* = 9.9 Hz, 1H), 5.79 – 5.68 (m, 4H), 5.58 – 5.42 (m, 4H), 5.32 (s, 1H), 5.25 (t, *J* = 9.7 Hz, 1H), 4.92 (s, 1H), 4.86 (d, *J* = 7.7 Hz, 1H), 4.77 (s, 1H), 4.63 (d, *J* = 4.1 Hz, 2H), 4.49 – 4.25 (m, 5H), 4.17 – 4.07 (m, 3H), 3.93 – 3.87 (m, 2H), 3.68 (t, *J* = 9.5 Hz, 1H), 2.26 (s, 3H), 2.21 (s, 3H), 2.14 (d, *J* = 14.6 Hz, 1H), 2.10 (s, 3H), 2.05 (d, *J* = 17.2 Hz, 1H), 1.99 (d, *J* = 11.2 Hz, 1H), 1.84 (d, *J* = 17.2 Hz, 1H), 1.77 – 0.57 (m, 31H), 0.55 (s, 3H), 0.51 (d, *J* = 11.6 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 174.5, 171.1, 170.5, 169.9, 167.1, 166.6, 166.2, 165.9, 165.7, 165.6, 165.5, 165.4, 165.1, 152.2, 133.8, 133.6, 133.5, 133.4, 133.3, 133.0, 130.2, 130.1, 130.0, 129.9, 129.8 (3 C), 129.7 (2 C), 129.4, 129.2 (3 C), 128.8, 128.6 (3 C), 128.4, 128.3, 104.9, 99.0, 97.9, 94.8, 92.8, 86.7, 77.4, 76.5, 76.4, 74.5, 73.9, 73.1, 72.0, 71.5, 71.0 (2 C), 70.5, 70.3, 69.6, 69.1, 68.6, 67.9, 67.8, 64.7, 62.9, 61.9, 57.8, 53.3, 47.2, 43.9, 42.6, 41.0, 39.9, 39.2, 37.2, 37.1, 30.0, 29.8, 29.6, 22.8, 21.5, 21.1, 21.0, 20.8, 19.7, 19.2, 18.0, 16.0, 14.2; HRMS (ESI) calcd for $C_{113}H_{112}O_{34}K$ $[M+K]^+$ 2051.6666, found 2051.6623. For **14b**: $[\alpha]_D^{25}$ = +58.0 (*c* 1.0, $CHCl_3$); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 6H), 7.96 – 7.92 (m, 6H), 7.83 – 7.80 (m, 4H), 7.64 – 7.23 (m, 24H), 6.22 (t, *J* = 10.0 Hz, 1H), 5.79 (t, *J* = 5.6 Hz, 2H), 5.68 (d, *J* = 6.8 Hz, 2H), 5.64 – 5.55 (m, 2H), 5.51 (s, 1H), 5.42 (t, *J* = 8.8 Hz, 1H), 5.31 (s, *J* = 2.0 Hz, 1H), 5.21 – 5.16 (m, 2H), 4.85 (s, 1H), 4.70 (d, *J* = 7.2 Hz, 2H), 4.65 – 4.61 (m, 2H), 4.50 (dd, *J* = 12.4, 2.0 Hz, 1H), 4.42 (dd, *J* = 12.0, 5.6 Hz, 1H), 4.32 – 4.26 (m, 3H), 4.12 – 4.05 (m, 2H), 3.92 – 3.90 (m, 1H), 3.82 – 3.70 (m, 2H), 3.65 – 3.61 (m, 1H), 3.27 (t, *J* = 9.2 Hz, 1H), 2.19 (s, 3H), 2.17 – 2.11 (m, 4H), 2.08 (s, 3H), 2.03 (brs, 1H), 1.97 (d, *J* = 11.2 Hz, 1H), 1.87 – 0.75 (m, 31H), 0.69 (d, *J* = 8.0 Hz, 1H), 0.58 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 174.7, 170.6, 170.5, 169.9, 167.5, 166.5, 166.1, 165.9, 165.7 (2 C), 165.5, 165.4, 152.3, 133.8, 133.6 133.4, 133.3, 133.2, 133.1, 130.2, 130.1, 130.0, 129.9 (2 C), 129.8, 129.7, 129.3, 129.2 (3 C), 129.1, 128.8, 128.6 (2 C), 128.5 (2 C), 128.4 (3 C), 104.9, 98.5, 97.9, 95.5, 92.5, 86.2, 77.4, 76.7, 76.3, 75.6, 74.4, 73.4, 72.1, 71.5, 71.1, 70.9, 70.6, 70.0, 69.6, 68.6, 68.0, 67.8, 64.6, 63.4, 62.0, 57.8, 53.5, 50.7, 47.3, 44.0, 43.0, 42.6, 41.1, 40.1, 39.3, 37.3, 37.2, 30.0, 29.8, 29.4, 22.8, 22.7, 21.5, 21.1, 21.0, 20.8, 19.8, 19.2, 18.0, 16.2, 14.2; HRMS (ESI) calcd for $C_{106}H_{108}O_{33}K$ $[M+K]^+$ 1947.6404, found 1947.6358.

**Proposed Reb-S (1)**

To a solution of **14** (52 mg, 0.0258 mmol) in absolute MeOH (4 mL) was added freshly prepared NaOMe (in absolute MeOH, 1 mL) at room temperature. The resulting solution was stirred at the same temperature for another 1 h before resins ($H^+$ form) was added to adjust the pH value of the reaction

mixture to around 7.0. Filtration, washing the resins thoroughly with methanol, and filtrate concentration in *vacuo* provided a residue, which was further purified by RP-18 silica gel column chromatography ($H_2O$/MeOH = 1 : 2) to furnish the proposed Reb-S (**1**) (22 mg, 0.023 mmol, 89%) as a white solid: $[\alpha]_D^{25} = -13.6$ (*c* 1.0, $CH_3OH$); $^1H$ NMR (400 MHz, pyridine-$d_5$) δ 6.45 (s, 1H), 6.28 (d, *J* = 7.7 Hz, 1H), 6.16 (d, *J* = 3.8 Hz, 1H), 5.69 (s, 1H), 5.23 – 5.19 (m, 1H), 5.13 (d, *J* = 7.5 Hz, 1H), 5.05 (s, 1H), 4.75 (d, *J* = 3.2 Hz, 1H), 4.66 (t, *J* = 9.1 Hz, 1H), 4.55 – 4.14 (m, 17H), 3.88 (s, 1H), 3.67 (s, 1H), 2.68 (d, *J* = 13.2 Hz, 1H), 2.57 – 2.51(m, 2H), 2.30 – 2.23 (m, 1H), 2.15 – 2.04 (m, 4H), 1.93 – 1.85 (m, 2H), 1.77 – 1.62 (m, 6H), 1.49 (s, 3H), 1.44 – 1.24 (m, 2H), 1.16 (s, 3H), 1.01 – 0.97 (m, 3H), 0.89 (d, *J* = 5.2 Hz, 1H), 0.74 – 0.68 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, pyridine-$d_5$) δ 176.0, 155.0, 104.8, 101.8, 99.9, 99.2, 93.9, 86.4, 79.8, 79.7, 79.0, 77.7, 77.4, 76.7, 75.8, 74.5, 74.1, 73.8, 72.7, 72.5, 72.1, 71.3, 70.1, 62.8, 62.7, 62.4, 58.2, 54.1, 48.0, 46.5, 44.6, 44.4, 42.7, 41.8, 40.8, 39.8, 37.8, 37.1, 29.5, 22.2, 20.7, 20.0, 19.1, 16.9, 11.6, 7.6; HRMS (ESI) calcd for $C_{44}H_{74}NO_{22}$ $[M+NH_4]^+$ 968.4697, found 968.4708.

**_p_-Methoxyphenyl 2-_O_-benzoyl-3-_O_-allyl-4,6-_O_-benzylidene-β-D-glucopyranoside (16)**

To a solution of **15** (1.3 g, 3.14 mmol) in dry pyridine was added BzCl (0.6 mL, 5.17 mmol) dropwise at 0 °C under $N_2$ atmosphere. After the addition was completed, the reaction mixture was warmed up to room temperature gradually and the stirring was continued for another 4 h. Ethyl acetate was added to dilute the reaction mixture and the resulting solution was washed with water, 1N HCl, saturated aqueous $NaHCO_3$, and brine successively. After being dried over anhydrous $Na_2SO_4$ and filtrating to remove the desiccant, the filtrate was concentrated in *vacuo* to provide the crude product, which was further purified by silica gel chromatography (petroleum ether/ethyl acetate = 5 : 1) to afford **16** (1.5 g, 2.89 mmol, 92%) as a white solid: $[\alpha]_D^{25} = -0.9$ (*c* 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, acetone-$d_6$) δ 8.11 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.68 – 7.64 (m, 1H), 7.55 – 7.53 (m, 4H), 7.42 – 7.37 (m, 3H), 6.94 (d, *J* = 9.2 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 5.76 – 5.72 (m, 2H), 5.45 – 5.38 (m, 2H), 5.15 (dd, *J* = 17.2, 2.0 Hz, 1H), 4.96 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.40 – 4.32 (m, 2H), 4.18 – 4.12 (m, 1H), 4.06 (t, *J* = 9.2 Hz, 1H), 3.94 – 3.88 (m, 2H), 3.85 – 3.79 (m, 1H), 3.71 (s, 3H); $^{13}C$ NMR (100 MHz, acetone-$d_6$) δ 165.7, 156.6, 152.2, 139.0, 136.2, 134.3, 131.1, 130.5, 129.7, 129.6, 129.0, 127.2, 119.2, 116.5, 115.4, 102.0, 101.7, 82.1, 79.6, 74.4, 73.8, 69.2, 67.3, 55.9; HRMS (ESI) calcd for $C_{30}H_{30}O_8K$ $[M+K]^+$ 557.1572, found 557.1582.

**_p_-Methoxyphenyl 2-_O_-benzoyl-4,6-_O_-benzylidene-β-D-glucopyranoside (17)**

To a solution of **16** (1.5 g, 2.89 mmol) in a mixed solvent of $CH_2Cl_2$ and MeOH (40 mL, v/v = 1 : 1) was added $PdCl_2$ (154 mg, 0.87 mmol) at room temperature. The black suspension was stirred at the same temperature for 1 h before filtration through a pad of Celite and silica gel was adopted to remove the catalyst. The filtrate was condensed in *vacuo* to yield a residue, which was further purified by silica gel chromatography (petroleum ether/ethyl acetate = 3 : 1) to afford **17** (900 mg, 1.88 mmol, 65%) as a white solid: $[\alpha]_D^{25}$ = − 12.3 (*c* 0.5, $CHCl_3$); $^1$H NMR (400 MHz, acetone-$d_6$) δ 8.09 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.50 (m, 4H), 7.42 – 7.35 (m, 3H), 6.94 (d, *J* = 9.2 Hz, 2H), 6.80 (d, *J* = 9.2Hz, 2H), 5.71 (s, 1H), 5.41 – 5.35 (m, 2H), 5.05 (d, *J* = 4.8 Hz, 1H), 4.36 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.22 – 4.16 (m, 1H), 3.92 – 3.85 (m, 1H), 3.82 – 3.75 (m, 2H), 3.71 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, acetone-$d_6$) δ 165.9, 156.6, 152.3, 139.1, 134.1, 131.3, 130.5, 129.7, 129.5, 128.9, 127.4, 119.2, 115.4, 102.4, 101.8, 81.9, 75.9, 72.6, 69.2, 67.5, 55.9; HRMS (ESI) calcd for $C_{27}H_{30}NO_8[M+NH_4]^+$ 496.1966, found 496.1962.

***p*-Methoxyphenyl 2-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (19)**

Similar procedure as that used for the synthesis of **11** was adopted to conduct the coupling between **17** (380 mg, 0.794 mmol) and **18** (882.5 mg, 1.191 mmol) to provide **19** (707 mg, 0.669 mmol, 84%) as a white foam: $[\alpha]_D^{25}$ = +26.0 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, acetone-$d_6$) δ 8.00 (dd, *J* =8.4, 1.2 Hz, 2H), 7.84 (dd, *J* =7.2, 1.2 Hz, 4H), 7.72 (dd, *J* =8.0, 1.2 Hz, 2H), 7.63 – 7.37 (m, 15H), 7.32 – 7.23 (m, 7H), 6.84 (d, *J* =9.2 Hz, 2H), 6.74 (d, *J* =9.2 Hz, 2H), 5.87 (t, *J* =9.6 Hz, 1H), 5.80 (s, 1H), 5.70 (t, *J* =9.6 Hz, 1H), 5.53 – 5.46 (m, 3H), 5.33 (d, *J* = 7.6 Hz, 1H), 4.59 (t, *J* =9.2 Hz, 1H), 4.54 (dd, *J* =12.0, 3.2 Hz, 1H), 4.44 (dd, *J* =12.0, 4.4 Hz, 1H), 4.38 (dd, *J* =10.0, 4.8 Hz, 1H), 4.34 – 4.30 (m, 1H), 4.06 (t, *J* =9.2 Hz, 1H), 3.94 (t, *J* =9.6 Hz, 1H), 3.89 – 3.79 (m, 1H), 3.68 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, acetone-$d_6$) δ 166.4, 166.1, 165.8 165.5, 165.3, 156.5, 152.1, 138.8, 134.4, 134.2, 134.0 (2 C), 133.8, 130.8, 130.6, 130.5 (2 C), 130.4, 130.3, 130.2 (2 C), 130.1, 130.0, 129.6, 129.4, 129.3 (3 C), 129.1, 128.8, 127.2, 119.1, 115.3, 108.4, 102.0, 101.7, 101.4, 80.0, 79.6, 74.3, 74.2, 73.1, 72.5, 70.8, 69.1, 67.6, 67.4, 64.0, 55.8, 24.6; HRMS (ESI) calcd for $C_{61}H_{52}O_{17}K$ $[M+K]^+$ 1095.2836, found 1095.2859.

**2-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-D-glucopyranosyl *o*-cyclopropylethynylbenzoate (20)**

Similar procedure as that used for the synthesis of **2** was adopted to convert **19** (707 mg, 0.669 mmol)

to **20** (450 mg, 0.402 mmol, 60% for 2 steps) as a mixture of α/β epimers (α/β = 1 : 2). An aliquot of pure **20β** was obtained for detailed characterization as a white foam: $[\alpha]_D^{25}$ = +21.6 (*c* 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, acetone-$d_6$) δ 8.02 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.86 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.81 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.72 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.64 – 7.54 (m, 7H), 7.50 – 7.35 (m, 10H), 7.32 – 7.21 (m, 8H), 6.21 (d, *J* = 7.6 Hz, 1H), 5.92 – 5.87 (m, 1H), 5.83 (s, 1H), 5.72 (t, *J* = 9.6 Hz, 1H), 5.58 – 5.50 (m, 3H), 4.74 (t, *J* = 8.8 Hz, 1H), 4.58 (dd, *J* = 12.0, 3.2 Hz, 1H), 4.47 (dd, *J* = 12.0, 5.2 Hz, 1H), 4.42 – 4.36 (m, 2H), 4.12 (t, *J* = 9.2 Hz, 1H), 3.99 – 3.90 (m, 2H), 1.51 – 1.44 (m, 1H), 0.91 – 0.85 (m, 2H), 0.79 – 0.72 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone-$d_6$) δ 166.5, 166.1, 165.8, 165.6, 165.5, 163.8, 138.7, 135.0, 134.4, 134.2, 134.0, 133.8, 133.5, 131.3, 130.8, 130.6, 130.5, 130.4, 130.3, 130.2, 130.1 (2 C), 130.0, 129.6, 129.4 (3 C), 129.3, 129.1, 128.8, 128.2, 127.2, 126.2, 102.0, 101.4, 101.0, 93.7, 79.7, 79.4, 74.8, 74.4, 73.6, 73.1, 72.6, 70.8, 69.0, 68.1, 64.0, 9.3, 9.2, 1.2; HRMS (ESI) calcd for $C_{66}H_{54}O_{17}K$ $[M+K]^+$ 1157.2993, found 1157.3006.

**13-*O*-[2-*O*-Benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl]-steviol *tert*-butyldiphenylsilyl ester (21)**

A solution of **20** (36.3 mg, 0.0324 mmol) and **3** (15 mg, 0.027 mmol) in dry $CH_2Cl_2$ (1.5 mL) was stirred in the presence of powered 4A MS at room temperature for 30 min under $N_2$ atmosphere. After being chilled to -40 °C, $Ph_3PAuNTf_2$ (9.6 mg, 0.013 mmol) was added. The resultant reaction mixture was then gradually warmed up to room temperature and the stirring was continued for another 5 h at the same temperature. After the MS was removed by filtration, the filtrate was condensed in *vacuo*. The obtained residue was further subjected to purification by silica gel column chromatography (petroleum ether/ethyl acetate = 4 : 1) to provide **21** (34 mg, 0.0228 mmol, 84%) as a white solid: $[\alpha]_D^{25}$ = +17.2 (*c* 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, acetone-$d_6$) δ 7.98 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.84 – 7.69 (m, 10H), 7.63 – 7.22 (m, 28H), 5.84 (t, *J* = 9.6 Hz, 1H), 5.77 (s, 1H), 5.68 (t, *J* = 9.6 Hz, 1H), 5.49 – 5.42 (m, 2H), 5.25 (dd, *J* = 9.2, 7.6 Hz, 1H), 5.04 (d, *J* = 8.0 Hz, 1H), 4.74 (s, 1H), 4.61 (s, 1H), 4.53 (dd, *J* = 12.0, 3.6 Hz, 1H), 4.50 – 4.42 (m, 2H), 4.32 – 4.28 (m, 1H), 4.17 (dd, *J* = 10.4, 4.8 Hz, 1H), 3.91 (t, *J* = 9.2 Hz, 1H), 3.85 (t, *J* = 10.0 Hz, 1H), 3.64 – 3.58 (m, 1H), 2.22 (d, *J* = 13.2 Hz, 1H), 2.01 (s, 1H), 1.97 – 1.90 (m, 2H), 1.86 – 1.59 (m, 6H), 1.47 – 1.28 (m, 5H), 1.27 (s, 3H), 1.15 (s, 9H), 1.08 – 1.04 (m, 2H), 0.89 (dd, *J* = 13.6, 6.8 Hz, 2H), 0.78 (dd, *J* = 13.2, 3.6 Hz, 1H), 0.72 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone-$d_6$) δ 177.0, 166.5, 166.2, 165.8, 165.6, 165.3, 153.5, 139.0, 136.6, 136.5, 134.4, 134.3, 134.0 (2 C), 133.8, 133.2, 133.1, 131.1 (2 C), 131.0, 130.9, 130.6, 130.4 (2 C), 130.3, 130.2 ( 2

C), 130.1, 129.6, 129.5, 129.4 (2 C), 129.1, 128.9, 128.6, 127.3, 105.0, 102.0, 101.4, 97.5, 86.7, 80.4, 79.9, 74.8, 74.4, 73.2, 72.6, 71.0, 69.5, 67.4, 64.1, 57.6, 54.5, 48.0, 46.0, 45.1, 43.2, 42.1, 41.3, 40.2, 39.4, 37.4, 27.6, 22.9, 20.9, 20.2, 19.9, 17.0; HRMS (ESI) calcd for $C_{90}H_{92}O_{18}SiNa$ $[M+Na]^+$ 1511.5945, found 1511.5981.

**13-*O*-[2-*O*-Benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl]-steviol (22)**

Similar procedure as that used for the synthesis of **13** was adopted to convert **21** (190 mg, 0.128 mmol) to **22** (150 mg, 0.12 mmol, 94%) as a white foam: $[\alpha]_D^{25}$ = +16.1 (*c* 3.5, $CHCl_3$); $^1$H NMR (400 MHz, acetone-$d_6$) δ 7.99 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.85 – 7.82 (m, 4H), 7.70 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.65 – 7.47 (m, 8H), 7.45 – 7.36 (m, 7H), 7.31 – 7.22 (m, 7H), 5.84 (t, *J* = 9.6 Hz, 1H), 5.76 (s, 1H), 5.68 (t, *J* = 9.6 Hz, 1H), 5.50 – 5.41 (m, 2H), 5.26 (dd, *J* = 9.2, 7.6 Hz, 1H), 5.05 (d, *J* = 8.0 Hz, 1H), 4.90 (s, 1H), 4.71 (s, 1H), 4.53 (dd, *J* = 13.4, 3.6 Hz, 1H), 4.48 (t, *J* = 9.6 Hz, 1H), 4.44 (dd, *J* = 12.0, 4.4 Hz, 1H), 4.32 – 4.28 (m, 1H), 4.24 (dd, *J* = 10.4, 4.8 Hz, 1H), 3.90 (q, *J* = 9.2 Hz, 2H), 3.65 – 3.59 (m, 1H), 2.09 – 1.29 (m, 15H), 1.16 – 1.12 (m, 4H), 1.01 – 0.92 (m, 2H), 0.88 (d, *J* = 8.0 Hz, 1H), 0.79 – 0.71 (m, 1H), 0.67 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, acetone-$d_6$) δ 179.0, 166.4, 166.1, 165.7, 165.4, 165.1, 152.9, 138.9, 134.3, 134.2, 134.0, 133.9, 133.7, 130.8 (2 C), 130.5, 130.4, 130.3 (2 C), 130.2, 130.1 (2 C), 129.9, 129.5, 129.4, 129.3, 129.2, 129.0, 128.8, 127.2, 105.3, 101.9, 101.3, 97.3, 87.3, 80.3, 79.7, 74.7, 74.3, 73.1, 72.4, 70.8, 69.3, 67.3, 64.0, 57.4, 54.5, 48.3, 44.6, 43.9, 42.7, 42.1, 41.3, 40.0, 38.8, 38.4, 22.5, 20.7, 19.9, 15.7; HRMS (ESI) calcd for $C_{74}H_{74}O_{18}K$ $[M+K]^+$ 1289.4507, found 1289.4531.

**13-*O*-[2-*O*-Benzoyl-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl]-steviol**

**2-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl ester (23)**

Similar procedure as that used for the synthesis of **14** was applied to mediate the coupling between **22** (80 mg, 0.064 mmol) and **4** (107.6 mg, 0.13 mmol) to provide **23** (110 mg, 0.055 mmol, 86%) as a white solid: $[\alpha]_D^{25}$ = +59.4 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, acetone-$d_6$) δ 8.09 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.98 (td, *J* = 8.0, 1.2 Hz, 4H), 7.86 – 7.80 (m, 6H), 7.73 – 7.68 (m, 4H), 7.62 – 7.23 (m, 29H), 6.14 (d, *J* = 8.0 Hz, 1H), 5.84 (t, *J* = 9.2 Hz, 1H), 5.76 (s, 1H), 5.71 – 5.59 (m, 5H), 5.49 – 5.42 (m, 3H), 5.27 (dd, *J* = 9.2, 7.6 Hz, 1H), 5.12 (t, *J* = 9.2 Hz, 1H), 5.04 (d, *J* = 8.0 Hz, 1H), 4.92 (s, 1H), 4.72 (s, 1H), 4.53 (dd, *J* = 12.4, 3.6 Hz, 1H), 4.48 – 4.40 (m, 3H), 4.32 – 4.23 (m, 4H), 4.19 – 4.13 (m, 2H), 3.94 – 3.86 (m, 2H), 3.62 (td, *J* = 9.6, 4.8 Hz, 1H), 2.25 (d, *J* = 13.2 Hz, 1H), 2.14 (s, 3H), 2.06 – 1.00

(m, 26H), 0.89 (d, $J$ = 8.4 Hz, 1H), 0.77 – 0.71 (m, 1H), 0.68 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO) δ 173.8, 169.9, 169.7, 169.5, 165.4, 165.0 (2 C), 164.8, 164.6 (2 C), 164.5, 164.2, 151.7, 137.5, 134.1, 133.9, 133.8, 133.6, 133.3, 133.1, 129.3, 129.2 (3 C), 129.1, 129.0, 128.9 (2 C), 128.8, 128.7, 128.6 (2 C), 128.5 (2 C), 128.4, 128.3, 128.2, 127.8, 126.0, 104.5, 100.1, 99.8, 96.9, 95.8, 91.1, 86.0, 78.5, 78.4, 75.2, 73.6, 73.5, 73.2, 72.0, 71.1, 71.0, 70.5, 70.0, 69.4, 68.5, 67.9, 66.7, 65.8, 62.8, 61.9, 56.8, 52.8, 47.1, 43.3, 41.5, 40.8, 38.7, 37.3, 36.7, 29.0, 28.5, 20.9, 20.6, 20.5, 19.6, 18.8, 17.5, 15.5; HRMS (ESI) calcd for $C_{113}H_{112}O_{33}Na$ $[M+Na]^+$ 2019.6978, found 2019.7010.

**Reb-S analogue (24)**---derived from **23**

To a solution of **23** (56 mg, 0.028 mmol) in a mixed solvent of $CH_2Cl_2$ and MeOH (2 mL, v/v = 1 : 1) was added *p*-TsOH (26.7 mg, 0.155 mmol) at room temperature. The resultant solution was stirred at the same temperature overnight before $Et_3N$ was added to quench the reaction. The solvent was removed under reduced pressure, and the obtained residue was briefly purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 1 : 1) to provide diol intermediate, which was not characterized in detail and was applied directly to the next step.

The above obtained diol intermediate was then dissolved in absolute methanol (4 mL), to which the freshly prepared NaOMe (in absolute methanol, 1 mL) was added at room temperature. The reaction mixture was stirred at the same temperature for 1 h, which was followed by addition of resins ($H^+$ form) to adjust the pH value of the reaction mixture to around 7. Filtration was followed by a through washing of the resins with methanol. The filtrate was then condensed in *vacuo*, and the resulting residue was purified by RP-C18 silica gel column chromatography ($H_2O$/MeOH = 1 : 2) to yield **24** (16 mg, 0.0168 mmol, 60% for 2 steps) as a white solid: $[\alpha]_D^{25}$ = − 36 (*c* 0.5, $CH_3OH$); $^1H$ NMR (400 MHz, pyridine-$d_5$) δ 6.47 (s, 1H), 6.31 (d, $J$ = 7.9 Hz, 1H), 5.66 (s, 1H), 5.35 (d, $J$ = 7.8 Hz, 1H), 5.07 (s, 1H), 5.04 (s, 1H), 4.76 (s, 1H), 4.63 – 4.49 (m, 3H), 4.45 (t, $J$ = 7.9 Hz, 1H), 4.40 – 4.02 (m, 15H), 3.94 (d, $J$ = 8.7 Hz, 1H), 3.75 (s, 1H), 2.69 (d, $J$ = 13.2 Hz, 1H), 2.48 (d, $J$ = 11.0 Hz, 1H), 2.24 – 2.01 (m, 6H), 1.90 (m, 2H), 1.78 (d, $J$ = 6.1 Hz, 3H), 1.65 – 1.56 (m, 3H), 1.51 (s, 3H), 1.48 – 1.23 (m, 3H), 1.12 (brs, 4H), 1.01 (d, $J$ = 11.8 Hz, 1H), 0.91 (brs, 1H), 0.80 – 0.66 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, pyridine-$d_5$) δ 175.9, 153.7, 106.1, 105.2, 101.7, 99.3, 93.9, 88.9, 87.0, 79.7, 78.9, 78.8, 78.4, 77.8, 76.6, 75.8, 74.3, 74.1, 72.7, 72.5, 71.78, 71.3, 70.1, 70.0, 62.7, 62.5, 62.3, 58.2, 54.1, 48.4, 44.7, 44.4, 42.2, 41.8, 40.8, 39.9, 38.7, 37.9, 29.4, 22.2, 20.7, 20.0, 19.1, 16.8; HRMS (ESI) calcd for $C_{44}H_{74}NO_{22}$ $[M+NH_4]^+$ 968.4697, found 968.4696.

**13-*O*-[2-*O*-Levulinyl-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl]-steviol (26)**

Similar procedure as that used for the synthesis of **13** was applied to transform **25** (200 mg, 0.135 mmol) to **26** (140 mg, 0.112 mmol, 83%) as a white solid: $[\alpha]_D^{25}$ = +17.6 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 7.7 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.69 – 7.21 (m, 17H), 6.06 (t, *J* = 9.2 Hz, 1H), 5.75 – 5.70 (m, 2H), 5.48 – 5.43 (m, 2H), 4.99 (t, *J* = 8.3 Hz, 1H), 4.89 (d, *J* = 8.0 Hz, 2H), 4.76 (s, 1H), 4.56 – 4.44 (m, 2H), 4.36 – 4.32 (m, 1H), 4.28 (t, *J* = 9.1 Hz, 1H), 4.19 (dd, *J* = 10.3, 4.8 Hz, 1H), 3.80 (m, 2H), 3.58– 3.52 (m, 1H), 2.68 – 2.40 (m, 4H), 2.14 (brs, 4H), 2.08 (d, *J* = 2.8 Hz, 1H), 2.05 – 2.02 (m, 1H), 2.01 – 1.74 (m, 7H), 1.67 – 1.25 (m, 6H), 1.19 (s, 3H), 1.12 – 0.96 (m, 2H), 0.97 (s, 3H), 0.93 – 0.80 (m, 2H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 206.5, 179.1, 171.4, 166.3, 166.1, 165.7, 153.3, 138.8, 134.3, 134.1 (2 C), 133.9, 130.7, 130.5 (2 C), 130.4, 130.3, 130.1, 130.0 (2 C), 129.4, 129.3, 129.2, 128.7, 127.1, 105.1, 101.8, 100.7, 97.1, 86.6, 80.2, 79.0, 74.4, 74.3, 73.5, 72.4, 70.9, 69.2, 66.9, 63.9, 57.3, 54.5, 48.1, 44.4, 44.0, 43.0, 42.0, 41.4, 40.1, 38.7, 38.2, 37.8, 28.5, 22.6, 20.9, 19.9, 16.1; HRMS (ESI) calcd for $C_{72}H_{80}NO_{19}$ $[M+NH_4]^+$ 1262.5319, found 1262.5317.

**13-*O*-[2-*O*-Levulinyl-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl]-steviol**

**2-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnosyl)-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl ester (27)**

Similar procedure as that used for the synthesis of **14** was applied to mediate the coupling between **26** (76 mg, 0.061 mmol) and **4** (101 mg, 0.122 mmol) to provide **27** (100 mg, 0.05 mmol, 82%) as a white solid: $[\alpha]_D^{25}$ = +70.3 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.7 Hz, 2H), 8.01 – 7.94 (m, 6H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.81 – 7.78 (m, 4H), 7.71 – 7.24 (m, 26H), 6.10 – 6.05 (m, 2H), 5.75 – 5.68 (m, 4H), 5.64 (s, 1H), 5.58 (t, *J* = 9.1 Hz, 1H), 5.51 – 5.44 (m, 3H), 5.13 (t, *J* = 9.5 Hz, 1H), 5.00 (t, *J* = 8.3 Hz, 1H), 4.92 – 4.89 (m, 2H), 4.76 (s, 1H), 4.57 – 4.42 (m, 3H), 4.36 – 4.17 (m, 7H), 3.81 (t, *J* = 9.0 Hz, 2H), 3.60 – 3.54 (m, 1H), 2.68 – 2.44 (m, 4H), 2.32 – 2.28 (m, 1H), 2.16 (s, 3H), 2.15 (s, 3H), 2.11 (d, *J* = 6.4 Hz, 1H), 2.04 – 0.76 (m, 30H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 206.6, 175.3, 171.6, 170.7, 170.6, 170.3, 166.5, 166.2, 166.1, 165.9, 165.8, 153.5, 138.9, 134.7, 134.5, 134.4, 134.3, 134.2 (2 C), 134.0, 130.8, 130.6 (2 C), 130.5 (2 C), 130.4 (2 C), 130.3, 130.2 (4 C), 130.1, 129.8, 129.6, 129.5, 129.4 (3 C), 129.3, 128.8, 127.3, 105.1, 101.9, 100.9, 98.5, 97.4, 93.0, 86.8, 80.3, 79.2, 77.0, 75.0, 74.5, 74.4, 73.6, 72.8, 72.6, 72.4, 71.5, 71.0, 70.8, 69.6, 69.4, 68.3, 67.0, 64.0,

62.9, 58.5, 54.5, 48.3, 44.7, 44.2, 43.2, 42.1, 41.2, 40.3, 38.4, 38.3, 38.1, 29.6 28.7, 22.3, 21.1, 21.0, 20.8, 20.1, 18.4, 17.2; HRMS (ESI) calcd for $C_{111}H_{115}O_{34}$ $[M+H]^+$ 1991.7264, found 1991.7267.

**Reb-S analogue (24)**---derived from **27**

Similar procedures as those applied for the synthesis of **24** from **23** were applied to convert **27** (53 mg, 0.0266 mmol) to **24** (18 mg, 0.0189 mmol, 71% for 2 steps), whose $^1$H NMR data were shown to be identical to those of **24** derived from **23**.

***p*-Methoxyphenyl**

**2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-3-*O*-allyl-4,6-*O*-benzylidene-β-D-glucopyranoside (28)**

Except for the reaction temperature (-30 °C), similar procedure as that used for the synthesis of **11** was applied to mediate the coupling between **15** (50 mg, 0.121 mmol) and **18** (134.8 mg, 0.182 mmol) to provide disaccharide **28** (114 mg, 0.115 mmol, 95%) as a white foam: $[\alpha]_D^{25} = -2.4$ (*c* 2.0, $CHCl_3$); $^1$H NMR (400 MHz, acetone-$d_6$) δ 8.12 (dd, *J* = 8.4, 1.6 Hz, 2H), 8.01 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.93 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.83 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.58 – 7.31 (m, 16H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 6.09 (t, *J* = 9.6 Hz, 1H), 5.93 – 5.80 (m, 2H), 5.66 – 5.59 (m, 3H), 5.22 (d, *J* = 7.6 Hz, 1H), 5.13 (dd, *J* = 17.2, 2.0 Hz, 1H), 4.99 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.53– 4.42 (m, 3H), 4.33 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.20 – 4.15 (m, 1H), 4.07 – 3.99 (m, 2H), 3.78 (t, *J* = 9.2 Hz, 1H), 3.71 (dd, *J* = 5.6, 4.0 Hz, 3H), 3.68 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, acetone-$d_6$) δ 166.3, 166.1, 165.7, 155.9, 152.3, 138.8, 136.4, 134.2, 134.1, 133.9, 130.8, 130.4 (2 C), 130.3 (2 C), 130.1, 130.0, 129.9, 129.5, 129.3 (2 C), 129.2, 128.8, 126.9, 118.3, 116.3, 115.2, 101.8, 101.6, 101.2, 81.9, 81.4, 81.05, 74.4, 74.0, 73.4, 72.4, 70.2, 69.1, 66.2, 63.2, 55.8; HRMS (ESI) calcd for $C_{57}H_{53}O_{16}$ $[M+H]^+$ 993.3328, found 993.3365.

**2-*O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-3-*O*-allyl-4,6-*O*-benzylidene-D-glucopyranosyl *o*-cyclopropylethynylbenzoate (29)**

Similar procedure as that applied for the synthesis of **2** was applied to convert **28** (400 mg, 0.403 mmol) to **29** (352 mg, 0.334 mmol, 83% for two steps) as a mixture of α/β isomers (α/β = 1 : 1.3). An aliquot of pure **29α** was obtained for detailed characterization: $[\alpha]_D^{25} = -32.8$ (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, acetone-$d_6$) δ 8.07 (dd, *J* = 8.4, 1.6 Hz, 2H), 8.01 – 7.91 (m, 5H), 7.81 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.65 – 7.53 (m, 3H), 7.49 – 7.27 (m, 18H), 6.82 (d, *J* = 3.6 Hz, 1H), 6.07 (t, *J* = 9.2 Hz, 1H), 5.77 (t, *J* = 9.6 Hz, 1H), 5.66 (s, 1H), 5.64 – 5.52 (m, 3H), 5.00 (dd, *J* = 17.6, 2.0 Hz, 1H), 4.82 (dd, *J* = 10.4,

2.0 Hz, 1H), 4.69 (t, *J* = 4.0 Hz, 2H), 4.59 (dt, *J* = 10.0, 3.6 Hz, 1H), 4.27 (dd, *J* = 10.0, 4.8 Hz, 1H), 4.19– 3.96 (m, 5H), 3.78 (t, *J* = 10.0 Hz, 1H), 3.74 (t, *J* = 9.6 Hz, 1H), 1.68 – 1.61 (m, 1H), 0.79 – 0.72 (m, 4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, acetone-$d_6$) δ 166.5, 166.2, 165.8, 165.6, 165.2, 138.8, 136.3, 135.2, 134.4, 134.3, 133.9, 132.8, 132.2, 131.9, 131.0, 130.5 (2 C), 130.4 (2 C), 130.2, 130.1, 129.9, 129.6, 129.4 (2 C), 129.3, 128.9, 128.2, 126.9, 125.3, 116.1, 102.8, 101.8, 100.3, 93.2, 82.1, 80.4, 77.8, 75.7, 74.2, 74.1, 73.0, 72.7, 70.3, 69.2, 65.7, 63.5, 9.5, 9.4, 1.4; HRMS (ESI) calcd for $C_{62}H_{54}O_{16}K$ $[M+K]^+$ 1093.3044, found 1093.3055.

**13-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-3-*O*-allyl-4,6-*O*-benzylidene-β-D-glucopyranosyl]-steviol *tert*-butyldiphenylsilyl ester (30β)**

Similar procedure as that used for the synthesis of **12β** was applied to mediate the coupling between **29** (22.7 mg, 0.0215 mmol) and **3** (10 mg, 0.0179 mmol) to provide **30β** (21 mg, 0.0147 mmol, 82%) as a white solid. The data was in good accordance with reported data.[9a]

**13-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-3-*O*-allyl-4,6-*O*-benzylidene-β-D-glucopyranosyl]-steviol (31)**

Similar procedure as that used for the synthesis of **13** was applied to convert **30** (208 mg, 0.146 mmol) to **31** (140 mg, 0.118 mmol, 81%) as a white solid: $[\alpha]_D^{25} = -33.1$ (*c* 0.5, $CHCl_3$); $^{1}H$ NMR (400 MHz, acetone-$d_6$) δ 8.06(dd, *J* = 8.2, 1.6 Hz, 2H), 7.98 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.93 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.88 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.65 – 7.31 (m, 17H), 6.06 – 5.96 (m, 2H), 5.75 (t, *J* = 9.6 Hz, 1H), 5.60 – 5.54 (m, 3H), 5.22 – 5.16 (m, 2H), 5.06 – 5.02 (m, 1H), 4.82 (d, *J* = 7.6 Hz, 1H), 4.69 (dd, *J* = 12.0, 2.8 Hz, 2H), 4.58 (dd, *J* = 12.0, 4.4 Hz, 1H), 4.52 – 4.48 (m, 1H), 4.28 – 4.23 (m, 1H), 4.16 (dd, *J* = 10.4, 4.8 Hz, 1H), 4.04 – 3.98 (m, 1H), 3.85 – 3.76 (m, 1H), 3.72 (t, *J* = 10.2 Hz, 1H), 3.62 – 3.53 (m, 2H), 3.46 – 3.40 (m, 1H), 2.28 (dd, *J* = 11.6, 2.8 Hz, 1H), 2.17 (d, *J* = 13.2 Hz, 1H), 2.03 – 1.68 (m, 7H), 1.64 – 1.37 (m, 6H), 1.29 (s, 1H), 1.22 (s, 3H), 1.11 (dd, *J* = 12.0, 2.8 Hz, 1H), 1.04 (s, 3H), 0.98 (d, *J* = 8.0 Hz, 1H), 0.91 – 0.82 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Acetone) δ 178.9, 166.4, 166.1, 166.0, 165.5, 163.8, 153.6, 138.9, 136.6, 134.4, 134.2 ( 2 C), 133.8, 130.8, 130.4 ( 3 C), 130.3 ( 2 C), 130.0, 129.9, 129.4, 129.3 ( 2 C), 129.2, 128.7, 126.9, 116.1, 108.2, 105.0, 101.6, 101.5, 97.4, 86.7, 82.4, 79.8, 74.3, 73.9, 73.5, 72.4, 70.9, 69.4, 67.5, 66.1, 64.0, 57.4, 54.7, 48.2, 44.6, 44.0, 42.9, 42.2, 41.4, 40.2, 38.8, 38.1, 24.5, 22.7, 21.0, 19.9, 16.3; HRMS (ESI) calcd for $C_{70}H_{78}NO_{17}$ $[M+NH_4]^+$ 1204.5254, found 1204.5260.

**13-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-3-*O*-allyl-4,6-*O*-benzylidene-β-D-glucop**

**yranosyl]-steviol 2-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnosyl)-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl ester (32)**

Similar procedure as that used for the synthesis of **14** was adopted to mediate the condensation between **31** (80 mg, 0.067 mmol) and **4** (110.9 mg, 0.134 mmol) to provide **32** (115 mg, 0.059 mmol, 88%) as a white solid: $[\alpha]_D^{25}$ = +31.0 (*c* 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, acetone-$d_6$) δ 8.11 – 8.05 (m, 4H), 8.02 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.99 – 7.91 (m, 4H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.80 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.72 – 7.29 (m, 26H), 6.15 (d, *J* = 7.8 Hz, 1H), 6.08– 5.95 (m, 2H), 5.79 (t, *J* = 9.6 Hz, 1H), 5.72 – 5.70 (m, 2H), 5.65 – 5.53 (m, 5H), 5.50 (brs, 1H), 5.22 – 5.21 (m, 2H), 5.12 (t, *J* = 9.6 Hz, 1H), 5.06 – 5.02 (m, 1H), 4.81 (d, *J* = 7.4 Hz, 1H), 4.70 – 4.66 (m, 2H), 4.60 (dd, *J* = 12.1, 4.4 Hz, 1H), 4.53 – 4.45 (m, 2H), 4.29 – 4.16 (m, 6H), 4.04 – 3.98 (m, 1H), 3.80 (t, *J* = 7.9 Hz, 1H), 3.72 (t, *J* = 10.2 Hz, 1H), 3.64 – 3.52 (m, 2H), 3.48 – 3.42 (m, 1H), 2.35 – 2.27 (m, 2H), 2.14 (s, 3H), 2.03 – 0.80 (m, 33H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone-$d_6$) δ 175.3, 170.7, 170.6, 170.2, 166.6, 166.2 (2 C), 166.1, 166.0, 165.8, 165.6, 153.8, 139.0, 136.8, 134.7, 134.4 (2 C), 134.3 (3 C), 133.9, 131.0, 130.6, 130.5 (2 C), 130.4 (3 C), 130.3, 130.2 (3 C), 130.0, 129.8, 129.5, 129.4 (3 C), 128.9, 127.0, 116.2, 105.1, 101.8, 98.6, 97.7, 92.9, 86.8, 82.6 (2 C), 80.0, 76.7, 75.2, 74.5, 74.0, 73.5, 72.8, 72.5, 72.4, 71.5, 71.0, 70.8, 69.5, 68.2, 66.2, 64.1, 62.6, 58.7, 54.7, 48.4, 44.8, 44.3, 43.2, 42.3, 41.3, 40.3, 38.3, 38.2, 22.4, 21.1, 21.0, 20.8, 20.2, 18.3, 17.3; HRMS (ESI) calcd for $C_{109}H_{112}O_{32}Na$ $[M+Na]^+$ 1955.7029, found 1955.7048.

**Revised Reb-S (33)**

To a solution of **32** (65 mg, 0.0336 mmol) in a mixed solvent of $CH_2Cl_2$ and MeOH (4 mL, v/v = 2 : 2) was added $PdCl_2$ (1.8 mg, 0.010 mmol) at room temperature. The resultant black suspension was stirred at the same temperature for 35 min before filtrating through a pad of Celite and silica gel. The filtrate was concentrated under reduced pressure and the resulting residue was then subjected to flash silica gel column chromatography (petroleum ether/ethyl acetate = 2 : 1) to give the alcohol intermediate. The above obtained alcohol intermediate was dissolved in a mixed solvent of $CH_2Cl_2$/MeOH (2 mL, v/v = 1 : 1), to which *p*-TsOH (25 mg, 0.145 mmol) was added at room temperature. The resultant mixture was stirred at the same temperature for overnight before $Et_3N$ was added to quench the reaction. The solvent was removed under reduced pressure, and the obtained residue was briefly purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 1 : 1) to provide triol intermediate, which was not characterized in detail and was applied directly to the next step. The above obtained triol intermediate was then dissolved in absolute methanol (4 mL), to

which freshly prepared NaOMe (in absolute methanol, 1 mL) was added at room temperature. The reaction mixture was stirred at the same temperature for 1 h, which was followed by addition of resins ($H^+$ form) to adjust the pH value of the reaction mixture to around 7. Filtration was followed by a through washing of the resins with methanol. The filtrate was then condensed in *vacuo*, and the resulting residue was purified by RP-C18 silica gel column chromatography ($H_2O$/MeOH = 1 : 2) to yield **33** (25 mg, 0.026 mmol, 77% for 3 steps) as a white solid: $[\alpha]_D^{25}$ = − 19.6 (*c* 1.0, $CH_3OH$); $^1H$ NMR (400 MHz, Pyridine-$d_5$) δ 6.48 (d, *J* = 1.6 Hz, 1H), 6.29 (d, *J* = 8.0 Hz, 1H), 5.74 (s, 1H), 5.29 (d, *J* = 7.6 Hz, 1H), 5.13 (d, *J* = 7.6 Hz, 2H), 4.74 (s, 1H), 4.58 – 4.42 (m, 7H), 4.39 – 4.12 (m, 11H), 3.98 – 3.94 (m, 1H), 3.90 – 3.86 (m, 1H), 3.69 – 3.65 (m, 1H), 2.67 (d, *J* = 13.2 Hz, 1H), 2.53 (d, *J* = 11.6 Hz, 1H), 2.11 – 1.98 (m, 2H), 1.82 (d, *J* = 12.8 Hz, 1H), 1.76 (d, *J* = 6.0 Hz, 4H), 1.69 (d, *J* = 11.2 Hz, 1H), 1.60 (d, *J* = 16.0 Hz, 2H), 1.49 (s, 4H), 1.38 (d, *J* = 13.6 Hz, 2H), 1.28 – 1.20 (m, 4H), 1.13 (s, 4H), 0.95 (d, *J* = 12.0 Hz, 1H), 0.83 (dd, *J* = 7.2, 2.4 Hz, 2H), 0.68 (dd, *J* = 15.2, 11.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, Pyridine-$d_5$) δ 176.3 155.0, 107.1, 105.4, 102.1, 98.4, 94.2, 86.6, 85.0, 80.1, 79.3, 79.1, 78.6, 78.5, 78.2, 77.8, 76.8, 74.5, 73.0, 72.9, 72.1, 71.8, 71.6, 70.5, 63.2, 62.8, 62.7, 58.6, 54.4, 48.5, 48.4, 45.2, 44.7, 43.1, 42.2, 41.2, 40.2, 38.2, 37.7, 29.8, 22.6, 21.1, 20.4, 19.4, 17.3; HRMS (ESI) calcd for $C_{44}H_{70}O_{22}K$ $[M+K]^+$ 989.3990, found 989.3994.

**13-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl)-4,6-di-*O*-benzoyl-D-glucopyranosyl]-steviol *tert*-butyldiphenylsilyl ester (12α/β)**

Similar procedure as that used for the synthesis of **21** was adopted to mediate the coupling between **2** (24.4 mg, 0.0215 mmol) and **3** (10 mg, 0.0179 mmol) to provide **12** (25 mg, 0.0166 mmol, 93%) as a mixture of α/β isomers (α/β = 1.5 : 1).

**13-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl)-3,4,6-tri-*O*-benzoyl-D-glucopyranosyl]-steviol *tert*-butyldiphenylsilyl ester (12'α and 12'β)**

Similar procedure as that used for the synthesis of **21** was applied to mediate the coupling between **2'** (53.4 mg, 0.043 mmol) and **3** (20 mg, 0.0359 mmol) to give **12'** (55 mg, 0.0342 mmol, 95%) as a mixture of α/β isomers (α/β = 1.2 : 1). For **12'α**: $[\alpha]_D^{25}$ = +66.1 (*c* 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 11H), 7.76 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.70 – 7.65 (m, 4H), 7.60 – 7.20 (m, 28H), 6.20 (t, *J* = 9.6 Hz, 1H), 5.94 (t, *J* = 10.0 Hz, 1H), 5.54 (t, *J* = 9.6 Hz, 1H), 5.50 (t, *J* = 9.6 Hz, 1H), 5.40 (d, *J* = 3.6 Hz, 1H), 5.42 (d, *J* = 3.6 Hz, 1H), 5.33 (dd, *J* = 10.0, 3.6 Hz, 1H), 5.20 (s, 1H), 4.80 (s, 1H), 4.57– 4.53 (m, 1H), 4.50 – 4.35 (m, 5H), 4.15 (dd, *J* = 9.6, 3.6 Hz, 1H), 2.25 (d, *J* = 13.2

Hz, 1H), 2.07 – 2.02 (m, 2H), 1.90 – 1.25 (s, 15H), 1.14 (s, 9H), 1.02 – 0.84 (m, 4H), 0.76 – 0.69 (m, 1H), 0.59 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 176.6, 166.2 (2 C), 165.8 (2 C), 165.6, 165.4, 165.1, 151.0, 135.8, 135.7, 133.7, 133.4, 133.3, 133.2, 133.0, 132.2, 132.1, 130.2, 130.1, 130.0 (2 C), 129.9, 129.8 (2 C), 129.7, 129.6, 129.2, 129.1, 128.8 (2 C), 128.6, 128.5 (2 C), 128.4, 128.3 (2 C), 127.7, 127.6, 105.5, 95.1, 92.1, 87.0, 77.4, 75.6, 71.9, 71.5, 70.4, 70.3, 68.9, 68.4, 67.5, 63.3, 62.4, 57.1, 53.8, 47.4, 45.2, 42.5, 42.1, 41.2, 40.6, 39.4 (2 C), 38.7, 29.8, 29.3, 27.2, 22.1, 20.3, 19.4, 16.2; HRMS (ESI) calcd for $C_{97}H_{96}O_{20}SiK$ $[M+K]^+$ 1647.5896, found 1647.5915.

For **12'β**: $[\alpha]_D^{25}$ = +57.0 (*c* 1.0, $CHCl_3$); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 6.8, 1.6 Hz, 2H), 8.05 – 8.00 (m, 4H), 7.90 (t, *J* = 9.2 Hz, 4H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.69 (t, *J* = 7.2 Hz, 4H), 7.60 – 7.40 (m, 15H), 7.36 – 7.21 (m, 12H), 7.10 (t, *J* = 7.6 Hz, 2H), 6.04 (t, *J* = 9.6 Hz, 1H), 5.95 (t, *J* = 9.6 Hz, 1H), 5.94 (d, *J* = 5.0 Hz, 1H), 5.60– 5.55 (m, 2H), 5.46 (t, *J* = 10.0 Hz, 1H), 4.92 (s, 1H), 4.88 (d, *J* = 7.6 Hz, 1H), 4.75 (s, 1H), 4.47 – 4.33 (m, 3H), 4.28 (dd, *J* = 9.6, 7.6 Hz, 1H), 4.17 (dd, *J* = 12.4, 2.4 Hz, 1H), 4.07 – 4.03 (m, 2H), 2.30 – 2.20 (m, 2H), 2.07 – 2.03 (m, 2H), 1.87 (t, *J* = 11.6 Hz, 1H), 1.70 – 1.26 (m, 12H), 1.20 (s, 3H), 1.13 (s, 9H), 1.06 – 0.77 (m, 4H), 0.68 (d, *J* = 8.0 Hz, 1H), 0.56 (dd, *J* = 13.2, 9.2 Hz, 1H), 0.34 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 176.6, 166.3, 166.1, 165.7, 165.6, 165.5, 165.4, 165.1, 152.3, 135.8, 135.7, 133.5 (2 C), 133.4 (2 C), 133.3, 133.1, 133.0, 132.2, 130.2 (2 C), 129.9 (2 C), 129.8, 129.7 (2 C), 129.6, 129.1, 129.0, 128.9 (2 C), 128.8, 128.7, 128.5, 128.4, 128.3 (2 C), 127.7, 104.9, 99.2, 94.9, 86.9, 77.4, 73.6, 73.5, 71.6, 70.5, 70.3, 70.2, 69.1, 68.0, 63.9 62.7, 56.8, 53.4, 47.2, 45.2, 42.6, 42.5, 41.1, 40.2, 39.2, 38.7, 37.5, 29.8, 29.3, 27.2, 22.0, 19.9, 19.4, 19.2, 16.1; HRMS (ESI) calcd for $C_{97}H_{96}O_{20}SiNa$ $[M+Na]^+$ 1631.6157, found 1631.6170.

**1-*N*-Acetyl-2-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-3,4,6-tri-*O*-benzoyl-D-glucopyranosamine (35)**

Similar procedure as that used for the synthesis of **12β** was applied to conduct the coupling between **2'** (70 mg, 0.056 mmol) and **3** (26 mg, 0.047 mmol) to provide **35** (50 mg, 0.045 mmol, 80%) as a mixture of α/β-isomers (α/β = 6.5 : 1). An aliquot of pure **35α** was obtained for detailed characterization: $[\alpha]_D^{25}$ = +146.0 (*c* 1.0, $CHCl_3$); $^{1}H$ NMR (400 MHz, acetone-$d_6$) δ 8.63 (d, *J* = 8.8 Hz, 1H), 8.14 – 8.12 (m, 4H), 7.98 – 7.96 (m, 4H), 7.91 (d, *J* = 6.9 Hz, 2H), 7.84 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.61 – 7.31 (m, 23H), 6.21 (dd, *J* = 9.2, 5.2 Hz, 1H), 6.10 (t, *J* = 10.0 Hz, 1H), 5.95 (t, *J* = 10.0 Hz, 1H), 5.72 – 5.64 (m, 3H), 5.38 (dd, *J* = 8.0, 3.6 Hz, 1H), 4.73 (dd, *J* = 10.4, 5.6 Hz, 1H), 4.53 – 4.49 (m, 2H, $H_6$ or $H_{6'}$), 4.46 – 4.40 (m, 2H), 4.34 – 4.21 (m, 2H), 1.37 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz,

acetone-$d_6$) δ 170.7, 166.4 (3 C), 166.2, 166.0, 165.6, 134.5, 134.4, 134.3, 134.2, 134.0, 130.9, 130.8 (2 C), 130.6, 130.4 (2 C), 130.3 (2 C), 130.2 (3 C), 130.0, 129.6, 129.5 (2 C), 129.4 (2 C), 94.2, 74.2, 72.6, 72.3 (2 C), 71.1, 71.0, 69.8, 69.0 (2 C), 63.9, 63.5; HRMS (ESI) calcd for $C_{63}H_{54}NO_{18}$ $[M+H]^+$ 1112.3335, found 1112.3331.

**13-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-3-*O*-allyl-4,6-*O*-benzylidene-α-D-glucopyranosyl]-steviol *tert*-butyldiphenylsilyl ester (30α)**

Similar procedure as that used for the synthesis of **21** was applied to mediate the coupling between **29** (45.4 mg, 0.043 mmol) and **3** (20 mg, 0.0359 mmol) to give **30α** (45 mg, 0.0316 mmol, 88%) as a white solid: $[\alpha]_D^{25} = -1.3$ (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.98 – 7.95 (m, 4H), 7.82 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.76 – 7.66 (m, 5H), 7.63 – 7.35 (m, 22H), 6.05 (t, *J* = 9.6 Hz, 1H), 5.73 (t, *J* = 9.6 Hz, 1H), 5.69 – 5.58 (m, 3H), 5.42 (d, *J* = 7.6 Hz, 1H), 5.41 (s, 1H), 5.30 (d, *J* = 2.4 Hz, 1H), 5.01 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.94 (s, 1H), 4.85 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.80 – 4.75 (m, 1H), 4.56 – 4.49 (m, 2H), 4.10 – 4.00 (m, 2H), 3.97 – 3.88 (m, 2H), 3.82 – 3.76 (m, 2H), 3.71 (t, *J* = 10.0 Hz, 1H), 3.60 – 3.53 (m, 1H), 2.16 (d, *J* = 14.0Hz, 1H), 1.94 – 0.77 (m, 31H), 0.73 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 177.4, 166.4, 166.3, 166.0, 165.6, 150.5, 139.2, 136.7, 136.6 (2 C), 134.6, 134.4, 134.2, 132.8 (2 C), 131.0, 130.7, 130.6 (2 C), 130.5 (2 C), 130.3, 130.1 (2 C), 129.6 (2 C), 129.5, 129.4, 129.0, 128.6, 128.5, 127.1, 115.7, 106.9, 102.7, 102.0, 95.4, 86.5, 83.5, 80.3, 78.0, 74.4, 74.0, 73.1, 72.6, 70.8, 69.7, 63.6, 63.3, 57.6, 54.2, 48.2, 45.8, 44.7, 42.4, 42.0, 41.2, 40.2, 39.2, 27.6, 23.2, 20.8, 20.0, 19.8, 16.7; HRMS (ESI) calcd for $C_{86}H_{93}O_{17}Si$ $[M+H]^+$ 1425.6176, found 1425.6175.

***p*-Methoxyphenyl**
**2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-3-*O*-allyl-4,6-di-*O*-benzoyl-β-D-glucopyranoside (S1)**

To a solution of **28** (480 mg, 0.483 mmol) in a mixed solvent of dichloromethane and methanol (10 mL, v/v = 1 : 1) was added TsOH (249.7 mg, 1.45 mmol) at room temperature. The reaction mixture was then stirred at the same temperature for 15 h, at which time TLC showed that all starting materials were disappeared. $Et_3N$ was added to quench the reaction and the volatile solvent were removed in *vacuo* to obtained the diol intermediate, which was used directly to the next step after being coevaporated with toluene for three times.

To a solution of the above obtained intermediate in dry pyridine (5 mL) was added BzCl (0.171 mL, 1.47 mmol) dropwise at 0 °C under $N_2$ atmosphere. After the addition was completed, the reaction mixture was gradually warmed up to room temperature, and the stirring was continued at the same temperature for another 9 h. After ethyl acetate being added to dilute the reaction mixture, the resulting solution was washed with water, 1N HCl, saturated aqueous $NaHCO_3$, and brine, and was then dried over anhydrous $Na_2SO_4$. Filtration was followed by concentration to provide the crude product, which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3 : 1) to give **S1** (380 mg, 0.341 mmol, 71% for 2 steps) as a white solid: $[\alpha]_D^{25} = -4.5$ (*c* 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.98 – 7.93 (m, 6H), 7.87 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.80 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.56 – 7.24 (m, 18H), 6.98 (d, *J* = 9.2 Hz, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 5.90 (t, *J* = 9.6 Hz, 1H), 5.78 (t, *J* = 9.6 Hz, 1H), 5.61 (dd, *J* = 9.6, 8.0 Hz, 1H), 5.53 – 5.43 (m, 1H), 5.36 (d, *J* = 8.0 Hz, 1H), 5.31 (t, *J* = 9.6 Hz, 1H), 5.10 (d, *J* = 7.6 Hz, 1H), 4.86 – 4.80 (m, 2H), 4.52 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.37 – 4.24 (m, 3H), 4.13– 3.93 (m, 4H), 3.84 (dd, *J* = 12.4, 6.4 Hz, 1H), 3.76 (t, *J* = 8.8 Hz, 1H), 3.67 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.1 (2 C), 165.9, 165.3 (2 C), 165.2, 155.3, 151.0, 134.3, 133.6, 133.5, 133.4, 133.3, 133.2, 133.1, 129.9 (2 C), 129.8 (2 C), 129.3, 129.2, 128.9 (2 C), 128.6, 128.5(3 C), 128.4 (2 C), 117.7, 117.4, 114.6, 100.9, 100.4, 81.2, 80.8, 74.3, 73.4, 72.5, 72.3, 72.0, 71.2, 69.4, 63.6, 62.6, 55.7; HRMS (ESI) calcd for $C_{64}H_{56}O_{18}K$ $[M+K]^+$ 1151.3098, found 1151.3096.

**2-*O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-3-*O*-allyl-4,6-di-*O*-benzoyl-D-glucopyranosyl *o*-cyclopropylethynylbenzoate (34)**

Similar procedure as that used for the synthesis of **2** was applied to convert **S1** (320 mg, 0.287 mmol) to **34** (260 mg, 0.22 mmol, 77% for 2 steps) as a mixture of α/β isomers (α/β = 1 : 2). An aliquot of pure **34β** was obtained for detailed characterization: $[\alpha]_D^{25} = -77.5$ (*c* 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.01 – 7.92 (m, 8H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.55 – 7.14 (m, 21H), 6.08 (d, *J* = 8.0 Hz, 1H), 5.87 (t, *J* = 9.6 Hz, 1H), 5.60 – 5.48 (m, 4H), 5.33 (d, *J* = 8.0 Hz, 1H), 4.87 – 4.79 (m, 2H), 4.57 (dd, *J* = 12.4, 2.8 Hz, 1H), 4.45 (dd, *J* = 12.0, 3.6 Hz, 1H), 4.34 (dd, *J* = 12.4, 4.8Hz, 1H), 4.21 – 4.13 (m, 2H), 4.08 – 4.02 (m, 3H), 3.85 – 3.78 (m, 2H), 1.63 – 1.56 (m, 1H), 0.98 – 0.86 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2, 166.0, 165.8, 165.2, 165.0 (2 C), 163.5, 134.4, 134.0, 133.5 (2 C), 133.4, 133.3, 133.1, 133.0, 132.4, 130.9, 130.1, 129.9, 129.8, 129.7 (3 C), 129.5, 129.2, 129.1, 128.7 (2 C), 128.5, 128.4 (2 C), 128.3, 127.0, 125.5,

117.7, 101.0, 100.4, 92.8, 81.8, 78.9, 74.8, 74.5, 73.2, 72.7, 72.3, 72.1, 70.6, 69.9, 63.4, 63.0, 9.1 (2 C), 0.9; HRMS (ESI) calcd for $C_{69}H_{58}O_{18}K$ $[M+K]^+$ 1213.3255, found 1213.3249.

**13-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-3-*O*-allyl-4,6-di-*O*-benzoyl-D-glucopyranosyl]-steviol *tert*-butyldiphenylsilyl ester (36α and 36β)**---Conducted in dichloromethane

Similar procedure as that used for the synthesis of **21** was applied to mediate the coupling between **34** (50.5 mg, 0.043 mmol) and **3** (20 mg, 0.036 mmol) to give **36** (50 mg, 0.0323 mmol, 90%) as a mixture of α/β isomers (α/β = 15 : 1). For **36α**: $[\alpha]_D^{25}$ = +14.6 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.02– 7.98 (m, 6H), 7.94 – 7.91 (m, 4H), 7.82 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.68 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.64 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.53 – 7.24 (m, 24H), 5.89 (t, *J* = 9.6 Hz, 1H), 5.64 (t, *J* = 9.6 Hz, 1H), 5.59 (dd, *J* = 10.0, 8.0 Hz, 1H), 5.42– 5.29 (m, 4H), 5.16 (d, *J* = 8.0 Hz, 1H), 5.02 (s, 1H), 4.72 – 4.60 (m, 3H), 4.45 (dd, *J* = 12.0, 5.6 Hz, 1H), 4.36– 4.26 (m, 3H), 4.14 (ddd, *J* = 9.2, 5.6, 3.2 Hz, 1H), 3.98 – 3.88 (m, 2H), 3.84 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.70 (dd, *J* = 12.4, 6.4 Hz, 1H), 2.24 (d, *J* = 13.2 Hz, 1H), 2.00 – 1.23 (m, 18H), 1.12 (s, 9H), 1.07 – 0.99 (m, 2H), 0.93 (d, *J* = 6.4 Hz, 1H), 0.80 (t, *J* = 3.6 Hz, 1H), 0.74 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 176.7, 166.2, 166.1, 165.9, 165.3, 165.2, 164.9, 149.6, 135.8, 135.7, 134.4, 133.6, 133.3 (2 C), 133.2 (2 C), 132.9, 132.2, 132.1, 130.0, 129.9 (3 C), 129.8, 129.6, 129.3, 128.8 (2 C), 128.5 (2 C), 128.4 (2 C), 127.6, 127.5, 116.6, 106.4, 101.8, 93.9, 86.5, 79.4, 78.4, 77.4, 74.2, 73.2, 72.2, 71.9, 71.4, 69.9, 67.2, 63.4, 63.1, 57.1, 53.8, 48.0, 45.2, 43.5, 41.6, 41.5, 40.7, 39.5, 38.7, 29.3, 27.2, 22.2, 20.2, 19.4, 19.3, 16.1; HRMS (ESI) calcd for $C_{93}H_{96}O_{19}SiK$ $[M+K]^+$ 1583.5947, found 1583.5939. For **36β**: $[\alpha]_D^{25}$ = −9.6 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.96 – 7.87 (m, 8H), 7.79 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.69 – 7.65 (m, 6H), 7.56 – 7.22 (m, 24H), 5.87 (t, *J* = 9.6 Hz, 1H), 5.73 (t, *J* = 9.6 Hz, 1H), 5.68 – 5.58 (m, 1H), 5.55 (dd, *J* = 9.6, 7.6 Hz, 1H), 5.33 (d, *J* = 8.0 Hz, 1H), 5.25 (t, *J* = 9.6 Hz, 1H), 5.15 (s, 1H), 4.90 – 4.84 (m, 2H), 4.68 (d, *J* = 7.6 Hz, 2H), 4.60 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.50 (dd, *J* = 12.4, 4.8Hz, 1H), 4.37 – 4.28 (m, 2H), 4.16 – 4.11 (m, 1H), 4.08 – 4.03 (m, 1H), 3.95 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.87 – 3.78 (m, 2H), 3.66 (t, *J* = 9.2 Hz, 1H), 2.28 (dd, *J* = 12.0, 3.6 Hz, 1H), 2.08 (dt, *J* = 17.2, 2.8 Hz, 1H), 2.01 (dd, *J* = 11.6, 2.8 Hz, 1H), 1.94 – 1.26 (m, 12H), 1.24 (s, 3H), 1.10 (s, 9H), 1.06 – 0.98 (m, 1H), 0.94 – 0.83 (m, 2H), 0.78 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ 176.6, 166.3, 166.2, 166.0, 165.2, 165.1, 152.6, 135.8, 135.7, 134.4 (2 C), 134.2, 133.5, 133.4 (2 C), 133.3, 133.1, 132.9, 132.3 (2 C), 132.1 (2 C), 130.0, 129.9, 129.8 (3 C), 129.5, 129.4 (2 C), 129.3, 129.0, 128.9, 128.5 (2 C), 128.4 (3 C), 127.7, 127.6, 117.4, 105.0, 100.9, 97.0, 86.1, 82.4, 78.7, 77.4, 74.2, 73.4, 72.7, 72.4, 71.8, 71.5,

69.6, 64.0, 63.3, 57.1, 54.1, 47.6, 45.4, 43.3, 42.8, 41.4, 40.7, 39.5, 38.9, 37.1, 29.8, 29.4, 27.2, 22.1, 20.5, 19.6, 19.4, 16.5; HRMS (ESI) calcd for $C_{93}H_{96}O_{19}SiK$ $[M+K]^+$ 1583.5948, found 1583.5943.

**13-*O*-[2-*O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-3-*O*-allyl-4,6-di-*O*-benzoyl-D-glucopyranosyl]-steviol *tert*-butyldiphenylsilyl ester (36α and 36β)**---Conducted in acetonitrile

Similar procedure as that used for the synthesis of **12β** was adopted to mediate the coupling between **34** (25.38 mg, 0.0216 mmol) and **3** (10 mg, 0.018 mmol) to provide **36** (23 mg, 0.0149 mmol, 83%) as a mixture of α/β isomers (α/β = 1 : 6).

## Associated content:

Supporting Information

The comparisons of the key $^1$H NMR and $^{13}$C NMR signals between synthetic molecules (**1**, **24**, **33**) and authentic rebaudioside S and $^1$H, $^{13}$C NMR spectra for all new compounds prepared (PDF).

## Acknowledgements:

This work was financially supported by the National Natural Science Foundation of China (21762024, 21867012, and 21877055) and the project of Building of Leading and innovative Team of Science and Technology of Jiangxi Province (20181BCB24004).

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