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# An efficient and recyclable catalyst for the cleavage of *tert*-butyldiphenylsilyl ethers

Shiqiang Yan [a], Ning Ding [b], Wei Zhang [b], Peng Wang [a], Yingxia Li [b,*], Ming Li [a,*]

[a] Key Lab of Marine Drugs, Ministry of Education, School of Medicine and Pharmacy, Ocean University of China, Qingdao 266003, China
[b] School of Pharmacy, Fudan University, Shanghai 201203, China

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ABSTRACT

An efficient, chemoselective, and environment-friendly method for the deprotection of *tert*-butyldiphenylsilyl ethers mediated by triflic acid supported on silica gel is reported. A wide range of *tert*-butyldiphenylsilyl ethers derived from carbohydrate and saponin residues can be smoothly cleaved in the presence of various types of other protecting groups in good to excellent yields in acetonitrile. This heterogeneous reaction does not require aqueous workup, and the supported catalyst can be readily recycled.



## 1. Introduction

Protection and deprotection strategies are very common tactics in multi-step synthesis of natural or non-natural products. Efficient protection and then deprotection of hydroxyl group have become increasingly crucial due to the abundance of this group in natural products. As far as hydroxyl group protection is concerned, silyl ether is one of the most popular.[1] Since its introduction by Hanessian in 1975, *tert*-butyldiphenylsilyl (TBDPS) group has become a choice of protecting groups for hydroxyl functionality because of its easy introduction and its tolerance to a variety of chemical conditions.[2] This trait is extraordinarily suitable in the synthesis of complex oligosaccharides, because less hindered silyl ethers such as TBDMS, TES, and TMS have restricted stability under typical conditions for deacylation, deacetalization, and glycosylation. Furthermore, the use of TBDPS has been extended to the protection of phenols, amines, carboxylic acids, amides, and other functional groups.[3]

Most typically, silyl ethers are removed by fluoride anion by taking advantage of its hard–hard interaction with silicon,[4] and the most common source of fluoride ions is tetrabutylammonium fluoride (TBAF). Unfortunately, the strong basicity of fluoride, particularly under anhydrous conditions, can affect base-sensitive groups. To circumvent this problem, a vast array of acidic, neutral, basic, reducing, and oxidizing reagents have been developed for the deprotection of TBDMS over the past years.[5] Nevertheless, fewer options have come to serve the removal of TBDPS ethers as a consequence of their great bulkiness and prominent stability.[6] What is worse, most of the known procedures suffer from the drawback of prolonged reaction time,[6b,d] drastic reaction conditions,[6a,f] a large excess of reagents,[6c,e] use of toxic reagent[6g] or expensive ones unsuitable for large-scale preparation. In addition, among these methods, the comprehensive discussion of chemoselective cleavage of TBDPS ethers has so far been described in sporadic publications.[6c,f,h] Therefore, the development of a mild, efficient, and chemoselective method for the cleavage of TBDPS ethers would be of great value for organic synthesis.

Possessing the merits over homogeneous catalysts such as stability, insensitivity toward air and moisture, ease of handling, recovery and regeneration, solid supported acid catalysts,[7] regarded as green catalyst,[8] are playing a more and more important role in modern organic synthesis. Acidic or neutral substances such as silica gel, active carbon, and acidic ion-exchange resin are suitable supports, and the most often used is silica gel.[9]

Triflic acid has been used as a catalyst in a vast array of organic reactions. However, as a fuming and highly corrosive liquid, difficulties in storage, transportation, handling, and waste disposal have greatly limited the application of triflic acid. Following the urgent demand of 'green chemistry', triflic acid supported on functionalized silica has been reported,[10] while the study of triflic acid supported on unmodified chromatographic silica gel is still very rare.[11]

Considering all the situations mentioned above, herein, we described a facile, chemoselective, and environment-benign method

* Corresponding authors. Tel.: +86 21 51980127 (Y.L.); +86 532 82032150 (M.L.).
*E-mail addresses:* liyx417@fudan.edu.cn (Y. Li), lmsnouc@ouc.edu.cn (M. Li).

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for the rapid direct cleavage of TBDPS ethers that involves triflic acid adsorbed on unmodified chromatographic silica gel (TfOH–$SiO_2$) as a catalyst without any additional reagent.

## 2. Results and discussion

To find optimized conditions under which desilylation was realized with TfOH–$SiO_2$, we took TBDPS ether **1** as a model to investigate the effects of solvents, temperature, and amount of catalyst on the reaction. The results were summarized in Table 1. At first, using DCM as solvent in the presence of 10 mol % TfOH–$SiO_2$ at 50 °C, we obtained the alcohol **2** in 24% yield after 2 days (Table 1, entry **1**). Substitution of THF for DCM led to a yield increase up to 46% (Table 1, entry **2**). Treatment of **1** with TfOH–$SiO_2$ in MeOH afforded **2** in 85% yield in a shorter reaction time (24 h) (Table 1, entry **3**). Importantly, desilylation of **1** was further accelerated in MeCN, which resulted in **2** in 93% yield in 30 min (Table 1, entry **4**). Lower temperature (Table 1, entries **5** and **6**) and decreasing amount of TfOH–$SiO_2$ (Table 1, entries **7** and **8**) furnished **2** in prolonged reaction time and in lower yield. Thus, 10 mol % of TfOH–$SiO_2$ at 50 °C in acetonitrile emerged as an optimized protocol for removal of TBDPS group on compound **1**.

To test the scopes and limitations of the reaction, a wide range of TBDPS ethers deriving from various carbohydrates were treated with 10 mol % of TfOH–$SiO_2$ at 50 °C in acetonitrile, and the results were listed in Table 2. Under the optimitical conditions, the respective silyl group of propargoyl, *p*-nitrophenoyl, phenoyl, and *p*-methoxyphenoyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsiyl-β-D-gluco-pyranosides **3**, **5**, **7**, and **9** was removed to furnish the corresponding products **4**, **6**, **8**, and **10** in excellent yields (Table 2, entries **2–5**). This method was further extended to mannopyranosides, galactopyranosides, and 2-amio-2-deoxy-glucopyranosides bearing a TBDPS protecting group at 6 position (Table 2, entries **7–14**). To our delight, under the conditions TBDPS groups were readily removed with Ac, Bz, Piv, Ms, and Bn intact. Lactosides **29** and **31** with two TBDPS groups were exposed to the protocol to furnish the corresponding dialcohols **30** and **32** in 70% and 78% yields, respectively in 3 h (Table 2, entries **15** and **16**).

It should be noted that the migration of levulinoyl or acetyl group was observed under our conditions. For example, **34** and **36** were obtained in 71% and 79% yield, respectively, when **33** and **35** were exposed to our conditions, which indicated that the migration of Lev or Ac from 4-OH to 6-OH occurred (Table 2, entries **17** and **18**). In addition, we found that the regioselective cleavage of the primary TBDPS ether was possible in the presence of the secondary TBDPS ether according to our procedure. Thus, primary alcohol **38** was obtained from **37** in 88% yield (Table 2, entry **19**). However, it should be pointed out that secondary TBDPS ether could also be cleavaged, if the reaction time was prolonged and the amount of the catalyst was increased (Table 2, entry **20**).

In conjunction with saponin derivatives synthesis in our laboratory,[12] we prepared a variety of TBDPS ethers arising from sapogenins (Table 3). With these compounds in hand, their deprotection following our methodology proceeded smoothly, which produced the corresponding parent hydroxyl compounds in 0.5–1.5 h in 78–94% yields. It is worthy to mention that both the carbonyl group (Table 3, entry **1**) and the double bonds (Table 3, entries **2, 3, 5**, and **9**) were compatible to the experimental conditions, which demonstrated that our methodology has advantages over the documented procedures, especially, those based on bromine reagents. The TBDPS ester was also smoothly deprotected under our conditions (Table 3, entry **9**).

The TfOH–$SiO_2$ could be easily separated from the reaction mixture by simple filtration and was reusable up to three times without any decrease in activity. The deprotection of **1** with TfOH–$SiO_2$ after drying under vacuum produced **2** in about 90% yield (Table 4).

## 3. Conclusion

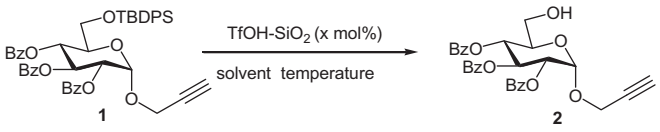
In conclusion, we have developed a new, efficient, and selective protocol for the deprotection of TBDPS ethers mediated by TfOH–$SiO_2$ in acetonitrile. It was found that a wide variety of other protecting groups survived under the present experimental conditions. TfOH–$SiO_2$ catalyst was easily handled and was readily reused without any decrease in activity, which demonstrated that TfOH–$SiO_2$ was a novel green catalyst, should find its own place in the synthesis of oligosaccharides and complex natural products.

## 4. Experimental procedures

### 4.1. General methods

Products were characterized by comparison with authentic samples and by spectroscopic data ($^1$H NMR spectra, $^{13}$C NMR spectra, HRMS spectra). The NMR spectra were recorded on a Bruker Avance DPX 400 MHz instrument. Chemical shifts are reported in parts per million (ppm). For $^1$H NMR spectra ($CDCl_3$), the residual solvent peak was used as the internal reference (7.26 ppm), whereas the central solvent peak as the reference (77.03 ppm) for $^{13}$C NMR spectra ($CDCl_3$). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad singlet), coupling constants (Hz) and integration. Mass spectra were recorded on an Agilent technologies 5973 network mass selective detector (MSD) operating at an ionization potential

**Table 1**
Optimization of the reaction conditions




| Entry | Solvent | Equivalent (mol %) | Temperature (°C) | Time (h) | Yield[a] (%) |
|---|---|---|---|---|---|
| 1 | DCM | 10 | 50 | 48 | 24 |
| 2 | THF | 10 | 50 | 48 | 46 |
| 3 | MeOH | 10 | 50 | 24 | 85 |
| 4 | MeCN | 10 | 50 | 0.5 | 93 |
| 5 | MeCN | 10 | 40 | 5 | 82 |
| 6 | MeCN | 10 | 20 | 24 | 49 |
| 7 | MeCN | 5 | 50 | 8 | 78 |
| 8 | MeCN | 2 | 50 | 24 | 41 |

[a] Yield refers to the isolated product.

**Table 2**
TfOH–$SiO_2$ catalyzed cleavage of TBDPS ethers derived from sugar derivatives[a]

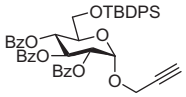
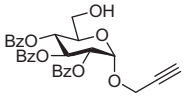
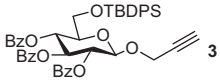
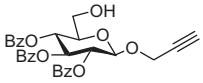
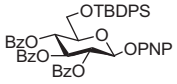
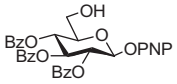
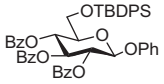
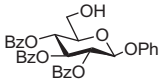
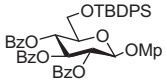
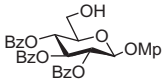
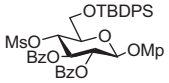
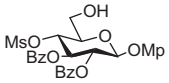
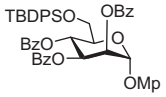
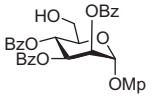
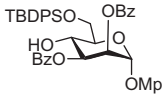
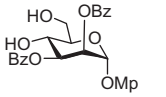
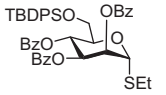
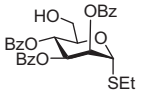
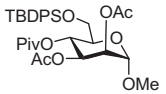
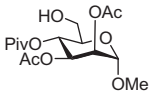
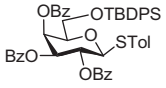
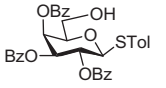
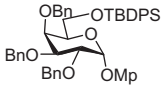
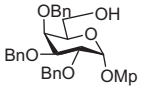
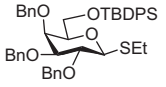
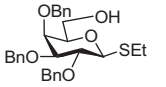
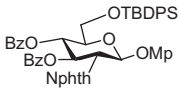
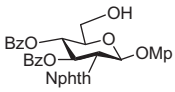
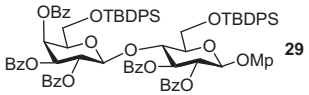
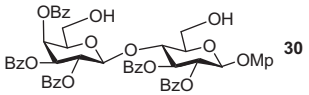
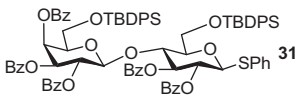
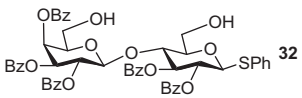
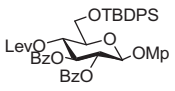
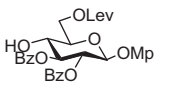
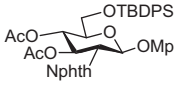
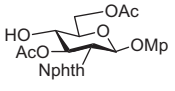
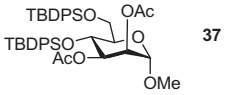
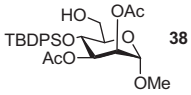
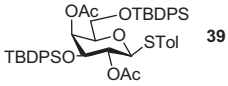
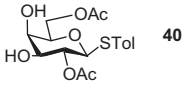
| Entry | Substrate | Product | Time (h) | Yield[b] (%) |
|---|---|---|---|---|
| 1 |  **1** |  **2** | 0.5 | 93 |
| 2 |  **3** |  **4** | 0.5 | 91 |
| 3 |  **5** |  **6** | 0.5 | 90 |
| 4 |  **7** |  **8** | 0.5 | 92 |
| 5 |  **9** |  **10** | 0.5 | 94 |
| 6 |  **11** |  **12** | 0.5 | 83 |
| 7 |  **13** |  **14** | 0.5 | 96 |
| 8 |  **15** |  **16** | 0.5 | 91 |
| 9 |  **17** |  **18** | 0.5 | 93 |
| 10 |  **19** |  **20** | 0.5 | 89 |
| 11 |  **21** |  **22** | 0.5 | 95 |
| 12 |  **23** |  **24** | 0.5 | 89 |
| 13 |  **25** |  **26** | 0.5 | 96 |
| 14 |  **27** |  **28** | 0.5 | 88 |
| 15 |  **29** |  **30** | 3.0 | 70 |
| 16 |  **31** |  **32** | 3.0 | 78 |
| 17 |  **33** |  **34** | 3.0 | 71 |
| 18 |  **35** |  **36** | 2.0 | 79 |

**Table 2** (*continued*)

| Entry | Substrate | Product | Time (h) | Yield[b] (%) |
|---|---|---|---|---|
| 19 |  **37** |  **38** | 0.2 | 88 |
| 20 |  **39** |  **40** | 2.0 | 72[c] |

[a] Reactions were conducted with the starting material of 1.0 mmol.
[b] Yield refers to the pure isolated product.
[c] 30 mol % TfOH–$SiO_2$ was used.

of 70 eV. Thin-layer chromatography (TLC) was performed on silica gel HF with detection by charring with 5% (v/v) $H_2SO_4$ in MeOH or by UV detection. Column chromatography was conducted by elution of a column of silica gel (200–300 mesh) with EtOAc/petroleum ether (bp 60–90 °C) as the eluent. Solns were concd at a temperature <60 °C under diminished pressure.

### 4.2. General procedure for the preparation of triflic acid immobilized on silica gel (TfOH–$SiO_2$)[11]

To a suspension of silica gel (10 g, mesh no. 300–400) in $Et_2O$ (40 mL) was added TfOH (3.06 g, 20 mmol) and the mixture was stirred magnetically for 30 min at room temperature. $Et_2O$ was removed under reduced pressure (rotary evaporator) and the residue heated at 100 °C for 24 h under vacuum to afford TfOH–$SiO_2$ (2 mmol/g) as a free-flowing powder.

### 4.3. Procedure A: Typical experimental protocol for the protection of saponin OH with TBDPS ethers

To a solution of hydroxyl saponin compound (2.0 mmol) in anhydrous DMF (20 mL) was added at 0 °C imidazole (0.34 g, 5.0 mmol), and the mixture was stirred for 15 min. Subsequently was added TBDPSCl (1.02 mL, 4.0 mmol), and the resulting mixture was stirred at 50 °C overnight. The reaction mixture was quenched with saturated aqueous $NH_4Cl$, and the mixture was stirred for an additional 30 min at room temperature. The solvent was evaporated in vacuo, the residue was diluted with ethyl acetate, and the organic layer was washed with water and brine and was dried over $Na_2SO_4$. The solvent was removed in vacuo followed by flash column chromatography.

### 4.4. Procedure B: Typical experimental protocol for the synthesis of 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsiyl anomeric protected sugars

TBDPSCl (0.55 mL, 2.2 mmol) was added to a stirred mixture of anomeric protected sugar (1.5 mmol) and imidazole (306 mg, 4.5 mmol) in dry Py (10 mL) at room temperature under Ar atmosphere, and the mixture was then stirred at the same temperature followed by TLC. After the completion of the reaction, benzoyl chloride (1.05 mL, 9.0 mmol) was added dropwise to the reaction mixture at 0 °C, and then catalytic DMAP added. The reaction was monitored by TLC, after completion, methanol (2 mL) added and the mixture concentrated under vacuum, then the residue diluted with $CH_2Cl_2$ (50 mL). The organic layer was washed sequentially with 1 M HCl (10 mL × 2) and then brine (20 mL × 2) and dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum, and the residue was purified by flash column chromatography.

### 4.5. Procedure C: Typical experimental protocol for the deprotection of TBDPS ethers catalyzed by TfOH–$SiO_2$

To a solution of TBDPS ether (1.0 mmol) in $CH_3CN$ (5.0 mL) was added TfOH–$SiO_2$ (50 mg, 0.1 mmol). The heterogeneous mixture was stirred at 50 °C and the reaction was followed by TLC. After completion, the mixture was filtered and washed with $CH_3CN$. The combined filtrate was concentrated under vacuum and the residue was purified by column chromatography to obtain the pure product.

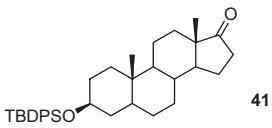
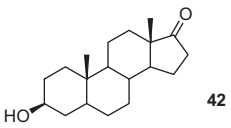
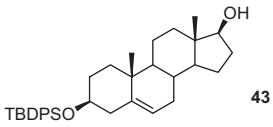
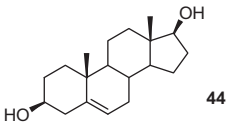
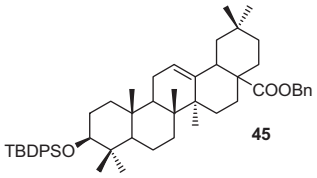
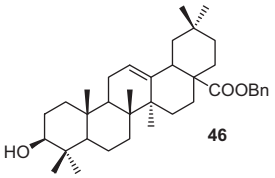
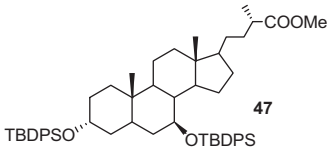
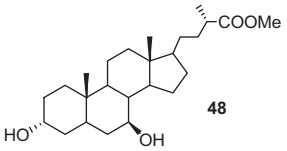
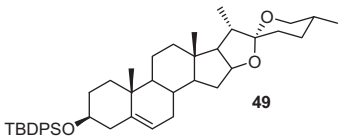
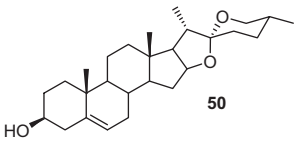
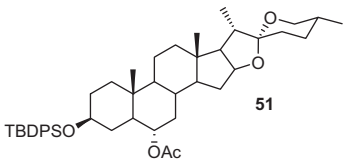
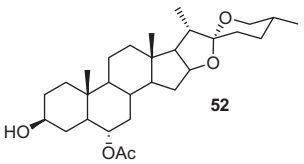
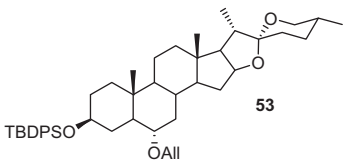
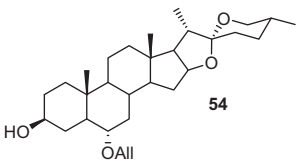
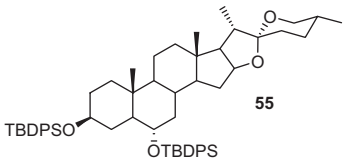
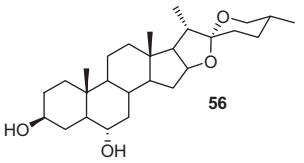
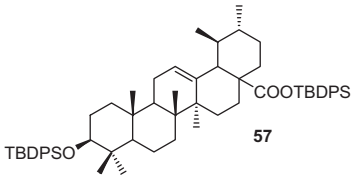
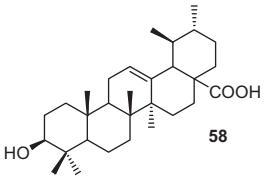
### 4.6. Propargyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsiyl-α-D-glucopyranoside (1)

Product **1** was obtained from propargyl α-D-glucopyranoside (327 mg, 1.5 mmol) following the procedure B. The pure product **1** was obtained by column chromatography on silica gel as a white foam (934 mg, 81%): $[\alpha]_D^{25}$ +75.0 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) *δ:* 8.01 (m, 2H, Ar-*H*), 7.90 (m, 4H, Ar-*H*), 7.74–7.65 (m, 2H, Ar-*H*), 7.61 (m, 2H, Ar-*H*), 7.53 (m, 2H, Ar-*H*), 7.46–7.20 (m, 13H, Ar-*H*), 6.14 (t, *J* = 10.1 Hz, 1H, H-3), 5.67 (t, *J* = 10.0 Hz, 1H, H-4), 5.59 (d, *J* = 3.6 Hz, 1H, H-1), 5.33 (dd, *J* = 10.2, 3.7 Hz, 1H, H-2), 4.35 (m, 2H, –*CH*$_2$C≡CH), 4.24–4.15 (m, 1H, H-5), 3.94–3.77 (m, 2H, H-6), 2.34–2.28 (m, 1H, –CH$_2$C≡C*H*), 1.05 (s, 9H, –C(*CH*$_3$)$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) *δ:* 165.82 (2) (*C*OPh), 165.06 (*C*OPh), 135.59 (2), 135.51 (2), 133.26, 133.16, 132.98, 132.94, 129.91 (2), 129.78 (2), 129.68 (2), 129.60, 129.57, 129.28, 129.19, 129.12, 128.34 (2), 128.30 (2), 128.22 (2), 127.61 (2), 127.57 (2) (Ar-*C*), 94.46 (*C*-1), 78.31, 75.10, 71.80, 71.04, 70.68, 69.10, 62.56, 54.98, 26.64 (3) (–C(*CH*$_3$)$_3$), 19.13; HRMS calcd for $C_{46}H_{44}O_9SiNa$ $(M+Na)^+$: 791.2652, found: 791.2667.

### 4.7. Propargyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (2)[13]

Product **2** was obtained from **1** (769 mg, 1.0 mmol) following the procedure C. The pure product **2** was obtained by column chromatography on silica gel as a white foam (493 mg, 93%): $[\alpha]_D^{25}$ +61.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) *δ*: 8.02–7.95 (m, 4H, Ar-*H*), 7.91–7.86 (m, 2H, Ar-*H*), 7.53 (ddd, *J* = 10.1, 8.8, 4.4 Hz, 2H, Ar-*H*), 7.46–7.36 (m, 5H, Ar-*H*), 7.30 (t, *J* = 7.7 Hz, 2H, Ar-*H*), 6.24 (t, *J* = 10.0 Hz, 1H, H-3), 5.58 (d, *J* = 3.7 Hz, 1H, H-1), 5.52 (t, *J* = 9.9 Hz, 1H, H-4), 5.34 (dd, *J* = 10.3, 3.8 Hz, 1H, H-2), 4.36 (dd, *J* = 2.3, 1.2 Hz, 2H, –*CH*$_2$C≡CH), 4.16–4.10 (m, 1H, H-5), 3.88–3.80 (m, 1H, H-6a), 3.77–3.69 (m, 1H, H-6b), 2.69 (dd, *J* = 8.6, 5.7 Hz, 1H, –O*H*), 2.37 (t, *J* = 2.4 Hz, 1H, –CH$_2$C≡C*H*); $^{13}$C NMR (100 MHz, $CDCl_3$) *δ*: 166.39 (*C*OPh), 165.76 (2) (*C*OPh), 133.74, 133.37, 133.18, 129.99 (2), 129.90 (2), 129.65 (2), 129.10, 128.98, 128.52 (2), 128.40 (2), 128.30 (2) (Ar-*C*), 95.19 (*C*-1), 78.36, 75.30, 71.59, 70.49, 69.94, 69.41, 60.86, 55.71; HRMS calcd for $C_{30}H_{26}O_9Na$ $(M+Na)^+$: 553.1475, found: 553.1467.

**Table 3**
TfOH–$SiO_2$ catalyzed cleavage of TBDPS ethers derived from saponin derivatives[a,b]

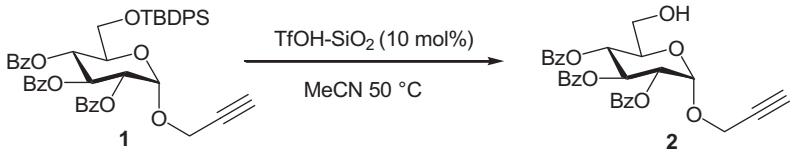
| Entry | Substrate | Product | Time (h) | Yield[c] (%) |
|---|---|---|---|---|
| 1 |  **41** |  **42** | 0.5 | 88 |
| 2 |  **43** |  **44** | 0.5 | 94 |
| 3 |  **45** |  **46** | 0.5 | 93 |
| 4 |  **47** |  **48** | 1.5 | 81 |
| 5 |  **49** |  **50** | 0.5 | 84 |
| 6 |  **51** |  **52** | 0.5 | 87 |
| 7 |  **53** |  **54** | 0.5 | 89 |
| 8 |  **55** |  **56** | 1.5 | 79 |
| 9 |  **57** |  **58** | 0.5 | 73 |

[a] Reactions were conducted with the starting material of 1.0 mmol.
[b] DCM was added when the starting material did not dissolve in MeCN.
[c] Yield refers to the isolated product.

### 4.8. Propargyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsiyl-β-D-glucopyranoside (3)

Product **3** was obtained from propargyl β-D-glucopyranoside (327 mg, 1.5 mmol) following the procedure B. The pure product **3** was obtained by column chromatography on silica gel (969 mg, 84%): $[\alpha]_D^{25}$ +81.5 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.99 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.91–7.82 (m, 4H, Ar-*H*), 7.71 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.61 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.53 (dd, *J* = 13.8, 7.3 Hz, 2H, Ar-*H*), 7.45–7.24 (m, 13H, Ar-*H*), 5.89 (t, *J* = 9.6 Hz, 1H, H-3), 5.67 (t, *J* = 8.6 Hz, 1H), 5.54 (t, *J* = 8.8 Hz, 1H), 5.12 (d, *J* = 7.9 Hz, 1H, H-1), 4.43 (d, *J* = 2.4 Hz, 2H, $-CH_2C{\equiv}CH$), 3.91 (m, 3H, H-5, H-6), 2.43 (d, *J* = 2.3 Hz, 1H, $-CH_2C{\equiv}CH$), 1.06 (s, 9H, $-C(CH_3)_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 165.88 (COPh),

**Table 4**
Reusability of TfOH–$SiO_2$ catalyzed cleavage of TBDPS ether




| Entry | Catalyst use | Yield (%) |
|---|---|---|
| 1 | Fresh | 93 |
| 2 | 1st recycle | 91 |
| 3 | 2nd recycle | 90 |
| 4 | 3rd recycle | 88 |

165.20 (*C*OPh), 164.95 (*C*OPh), 135.63 (2), 135.45 (2), 133.18, 133.08 (2), 132.96, 130.14, 129.85 (2), 129.75 (2), 129.72 (2), 129.64, 129.58, 129.40, 129.14, 128.91, 128.45, 128.31 (2), 128.22 (3), 127.60 (2), 127.58 (2) (Ar-*C*), 98.20 (*C*-1), 78.24, 75.37, 75.25, 73.29, 71.73, 69.17, 62.66, 55.55, 26.60 (3) (–C($CH_3$)$_3$), 19.15; HRMS calcd for $C_{46}H_{44}O_9SiNa$ (M+Na)$^+$: 791.2652, found: 791.2598.

### 4.9. Propargyl 2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (4)[14]

Product **4** was obtained from **3** (769 mg, 1.0 mmol) following the procedure C. The pure product **4** was obtained by column chromatography on silica gel as a white foam (482 mg, 91%): $[\alpha]_D^{25}$ +107.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.97 (t, *J* = 8.3 Hz, 4H, Ar-*H*), 7.85 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 7.53 (dd, *J* = 17.6, 7.5 Hz, 2H, Ar-*H*), 7.41 (dq, *J* = 15.3, 7.5 Hz, 5H, Ar-*H*), 7.29 (t, *J* = 7.8 Hz, 2H, Ar-*H*), 5.98 (t, *J* = 9.7 Hz, 1H, H-3), 5.58–5.47 (m, 2H, H-2, H-4), 5.13 (d, *J* = 7.9 Hz, 1H, H-1), 4.50 (dd, *J* = 16.1, 2.3 Hz, 1H, –C*H*$_2$C≡CHa), 4.40 (dd, *J* = 16.1, 2.3 Hz, 1H, –C*H*$_2$C≡CHb), 3.92–3.72 (m, 3H, H-5, H-6), 2.64 (br, 1H, –O*H*), 2.43 (t, *J* = 2.2 Hz, 1H, –CH$_2$C≡C*H*); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 166.10 (*C*OPh), 165.85 (*C*OPh), 165.14 (*C*OPh), 133.73, 133.29, 133.12, 129.91 (2), 129.85 (2), 129.72 (2), 129.10, 128.98, 128.53 (2), 128.34 (2), 127.85 (2) (Ar-*C*), 98.72 (*C*-1), 78.33, 75.51, 74.78, 72.84, 71.66, 69.57, 61.25, 56.27; HRMS calcd for $C_{30}H_{26}O_9Na$ (M+Na)$^+$: 553.1475, found: 553.1477.

### 4.10. *p*-Nitrophenyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsiyl-β-D-glucopyranoside (5)

Product **5** was obtained from *p*-nitrophenyl β-D-glucopyranoside (451 mg, 1.5 mmol) following the procedure B. The pure product **5** was obtained by column chromatography on silica gel (997 mg, 78%): $[\alpha]_D^{25}$ +63.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.10 (m, 2H, Ar-*H*), 7.95 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 7.86 (dd, *J* = 7.0, 4.7 Hz, 3H, Ar-*H*), 7.62–7.11 (m, 22H, Ar-*H*), 5.96 (t, *J* = 9.5 Hz, 1H, H-3), 5.80 (dd, *J* = 7.7, 9.5 Hz, 1H, H-2), 5.65 (t, *J* = 9.7 Hz, 1H, H-4), 5.49 (d, *J* = 7.7 Hz, 1H, H-1), 4.12 (m, 1H), 3.95–3.83 (m, 2H), 1.04 (s, 9H, –C($CH_3$)$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 165.82 (*C*OPh), 165.03 (*C*OPh), 161.49 (*C*OPh), 143.14, 135.55 (2), 135.42 (2), 133.52, 133.47, 133.37, 132.84, 132.50, 130.20, 129.93, 129.83 (3), 129.80 (3), 128.91, 128.85, 128.70, 128.51, 128.49 (2), 128.45 (2), 128.37 (2), 127.69 (2), 127.68 (2), 125.76 (2), 116.93 (2) (Ar-*C*), 98.76 (*C*-1), 76.16, 72.85, 71.65, 68.83, 62.66, 26.65 (3) (–C($CH_3$)$_3$), 19.20; HRMS calcd for $C_{49}H_{45}O_{11}NSiNa$ (M+Na)$^+$: 874.2654, found: 874.2657.

### 4.11. *p*-Nitrophenyl 2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (6)

Product **6** was obtained from **5** (852 mg, 1.0 mmol) following the procedure C. The pure product **6** was obtained by column chromatography on silica gel as a white foam (551 mg, 90%): $[\alpha]_D^{25}$ +161.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.20 (d, *J* = 9.2 Hz, 2H, PNP-Ar-*H*), 7.96 (t, *J* = 8.7 Hz, 4H, Ar-*H*), 7.87 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.55 (dt, *J* = 14.9, 7.4 Hz, 2H, Ar-*H*), 7.42 (t, *J* = 15.2, 7.7 Hz, 5H, Ar-*H*), 7.32 (t, *J* = 7.7 Hz, 2H, Ar-*H*), 7.10 (d, *J* = 9.2 Hz, 2H, PNP-Ar-*H*), 6.06 (t, *J* = 9.7 Hz, 1H, H-3), 5.83 (t, *J* = 9.1 Hz, 1H, H-2), 5.61 (t, *J* = 9.7 Hz, 1H, H-4), 5.55 (d, *J* = 7.8 Hz, 1H, H-1), 4.02 (d, *J* = 10.0 Hz, 1H), 3.98–3.88 (m, 1H), 3.87–3.78 (m, 1H), 2.59 (br, 1H, –O*H*); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 165.74 (*C*OPh), 164.95 (*C*OPh), 161.22 (*C*OPh), 143.20, 133.94, 133.57, 133.49, 129.98 (2), 129.77 (3), 128.71, 128.60 (2), 128.49 (2), 128.40 (2), 128.23, 126.21, 125.84 (2), 116.66 (2), 115.61 (Ar-*C*), 98.53 (*C*-1), 75.31, 72.28, 71.38, 69.03, 61.11; HRMS calcd for $C_{33}H_{27}O_{11}NNa$ (M+Na)$^+$: 636.1482, found: 636.1487.

### 4.12. Phenyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsiyl-β-D-glucopyranoside (7)

Product **7** was obtained from phenyl β-D-glucopyranoside (384 mg, 1.5 mmol) following the procedure B. The pure product **7** was obtained by column chromatography on silica gel (968 mg, 80%): $[\alpha]_D^{25}$ +41.9 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.12 (d, *J* = 8.1 Hz, 1H, Ar-*H*), 7.97 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 7.86 (d, *J* = 7.6 Hz, 4H, Ar-*H*), 7.68–7.28 (m, 16H, Ar-*H*), 7.22 (dd, *J* = 15.5, 7.8 Hz, 5H, Ar-*H*), 7.07 (dd, *J* = 17.0, 7.7 Hz, 3H, Ar-*H*), 5.93 (t, *J* = 9.6 Hz, 1H, H-3), 5.82–5.75 (m, 1H, H-2), 5.67 (t, *J* = 9.6 Hz, 1H, H-4), 5.38 (d, *J* = 7.8 Hz, 1H, H-1), 4.04 (m, 1H), 3.94–3.84 (m, 2H), 1.05 (s, 11H, –C($CH_3$)$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 165.92 (*C*OPh), 165.18 (*C*OPh), 165.06 (*C*OPh), 157.23, 135.61 (2), 135.50 (2), 133.31, 133.26, 133.23, 132.93, 132.73, 130.19, 129.84 (2), 129.79 (2), 129.66 (2), 129.64 (2), 129.54 (2), 129.28, 129.07, 128.90, 128.50, 128.40 (2), 128.32 (2), 127.66 (2), 127.65 (2), 123.19, 117.38 (2) (Ar-*C*), 99.79 (*C*-1), 75.70, 73.23, 71.96, 69.13, 62.69, 26.62 (3) (–C($CH_3$)$_3$), 19.15; HRMS calcd for $C_{49}H_{46}O_9SiNa$ (M+Na)$^+$: 829.2803, found: 829.2810.

### 4.13. Phenyl 2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (8)

Product **8** was obtained from **7** (830 mg, 1.0 mmol) following the procedure C. The pure product **7** was obtained by column chromatography on silica gel as a white foam (522 mg, 92%): $[\alpha]_D^{25}$ +91.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.01–7.96 (m, 4H, Ar-*H*), 7.91–7.86 (m, 2H, Ar-*H*), 7.59–7.29 (m, 11H, Ar-*H*), 7.10–7.01 (m, 3H, Ar-*H*), 6.04 (t, *J* = 9.7 Hz, 1H, H-3), 5.81 (dd, *J* = 9.8, 7.9 Hz, 1H, H-2), 5.61 (t, *J* = 9.7 Hz, 1H, H-4), 5.45 (d, *J* = 7.9 Hz, 1H, H-1), 3.99 (ddd, *J* = 9.8, 4.8, 2.3 Hz, 1H, H-5), 3.93 (dd, *J* = 12.8, 2.0 Hz, 1H, H-6a), 3.82 (dd, *J* = 12.8, 4.9 Hz, 1H, H-6b); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 165.97 (*C*OPh), 165.83 (*C*OPh), 165.09 (*C*OPh), 156.91, 133.77, 133.36, 133.34, 129.98 (2), 129.82 (2), 129.80 (2), 129.66 (2), 129.10, 128.77, 128.56 (2), 128.52, 128.42 (2), 128.37 (2), 123.36, 117.08 (2) (Ar-*C*), 99.55 (*C*-1), 74.99, 72.70, 71.69,

69.37, 61.44; HRMS calcd for $C_{33}H_{28}O_9Na$ $(M+Na)^+$: 591.1626, found: 591.1632.

### 4.14. *p*-Methoxyphenyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsiyl-β-D-gluco pyranoside (9)

Product **9** was obtained from *p*-methoxyphenyl β-D-glucopyranoside (429 mg, 1.5 mmol) following the procedure B. The pure product **9** was obtained by column chromatography on silica gel (1.07 g, 85%): $[\alpha]_D^{25}$ +68.8 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.98 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.85 (d, *J* = 7.9 Hz, 4H, Ar-*H*), 7.67 (d, *J* = 6.9 Hz, 2H, Ar-*H*), 7.59 (d, *J* = 7.0 Hz, 2H, Ar-*H*), 7.55–7.49 (m, 2H, Ar-*H*), 7.46–7.19 (m, 13H, Ar-*H*), 7.02 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 6.74 (d, *J* = 9.1 Hz, 2H, Ar-*H*), 5.90 (t, *J* = 9.6 Hz, 1H, H-3), 5.77–5.70 (dd, *J* = 7.9, 9.6 Hz, 1H, H-2), 5.65 (t, *J* = 9.6 Hz, 1H, H-4), 5.24 (d, *J* = 7.9 Hz, 1H, H-1), 4.00–3.94 (m, 1H), 3.92–3.82 (m, 2H), 3.74 (s, 3H, $-OCH_3$), 1.04 (s, 9H, $-C(CH_3)_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 165.91 (*C*OPh), 165.17 (*C*OPh), 165.05 (*C*OPh), 155.66, 151.34, 135.63 (2), 135.50 (2), 133.29, 133.25, 133.20, 132.98, 132.79, 129.83 (3), 129.78 (2), 129.68, 129.63, 129.34, 129.09, 128.93, 128.41 (2), 128.38 (2), 128.31 (2), 127.67 (2), 127.65 (2), 119.03 (2), 114.51 (2) (Ar-*C*), 100.97 (*C*-1), 75.61, 73.25, 72.02, 69.14, 62.70, 55.64, 26.64 (3) ($-C(CH_3)_3$), 19.18; HRMS calcd for $C_{50}H_{48}O_{10}SiNa$ $(M+Na)^+$: 859.2909, found: 859.2917.

### 4.15. *p*-Methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (10)

Product **10** was obtained from **9** (837 mg, 1.0 mmol) following the procedure C. The pure product **10** was obtained by column chromatography on silica gel as a white foam (562 mg, 94%): $[\alpha]_D^{25}$ +70.1 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 7.96 (m, 4H, Ar-*H*), 7.86 (m, 2H, Ar-*H*), 7.53 (m, 2H, Ar-*H*), 7.41 (m, 5H, Ar-*H*), 7.30 (m, 2H, Ar-*H*), 6.95 (d, *J* = 7.3 Hz, 2H, Mp-Ar-*H*), 6.79 (d, *J* = 6.9 Hz, 2H, Mp-Ar-*H*), 5.99 (t, *J* = 9.1 Hz, 1H, H-3), 5.74 (t, *J* = 9.4 Hz, 1H, H-2), 5.57 (t, *J* = 9.7 Hz, 1H, H-4), 5.29 (d, *J* = 7.9 Hz, 1H, H-1), 3.90 (m, 2H), 3.77 (m, 4H, $-OCH_3$), 2.54 (br, 1H, $-OH$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 165.93 (*C*OPh), 165.73 (*C*OPh), 165.00 (*C*OPh), 155.68, 150.87, 133.68, 133.26 (2), 129.88 (2), 129.73 (2), 129.71 (2), 129.05, 128.67, 128.46 (2), 128.34 (2), 128.28 (2), 118.77 (2), 114.50 (2) (Ar-*C*), 100.73 (*C*-1), 74.81, 72.58, 71.66, 69.29, 61.31, 55.55; HRMS calcd for $C_{34}H_{30}O_{10}Na$ $(M+Na)^+$: 621.1731, found: 621.1741.

### 4.16. *p*-Methoxyphenyl 2,3-di-*O*-benzoyl-4-*O*-mesyl-6-*O*-*tert*-butyldiphenylsiyl-β-D-glucopyranoside (11)

*p*-Methoxyphenyl 2,3-di-*O*-benzoyl-β-D-glucopyranoside (742 mg, 1.5 mmol) was dissolved in dry Py (10 mL) and cooled to 0 °C. Under Ar atmosphere TBDPSCl (0.55 mL, 2.2 mmol) and imidazole (306 mg, 4.5 mmol) were added to this solution, after which the mixture was stirred at room temperature overnight and concentrated, then diluted with $CH_2Cl_2$. The organic layer was washed with 1 M HCl and brine, then dried over $Na_2SO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography to afford *p*-methoxyphenyl 2,3-di-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsiyl-β-D-glucopyranoside **11a** as a white solid (967 mg, 88%). To the solution of compound **11a** (879 mg, 1.2 mmol) in dry Py (10 mL) was added methyl sulfonylchloride (0.28 mL, 3.6 mmol) dropwise and catalytic DMAP. The reaction was monitored by TLC, after completion, methanol (2 mL) added and the mixture concentrated under vacuum, then the residue diluted with $CH_2Cl_2$. The organic layer was washed with 1 M HCl and brine, then dried over $Na_2SO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography to afford **11** (905 mg, 93%): $[\alpha]_D^{25}$ +87.2 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 8.05–7.93 (m, 4H, Ar-*H*), 7.78–7.71 (m, 4H, Ar-*H*), 7.53 (t, *J* = 7.4 Hz, 2H, Ar-*H*), 7.44–7.34 (m, 8H, Ar-*H*), 7.29 (t, *J* = 7.3 Hz, 2H, Ar-*H*), 6.99–6.92 (m, 2H, Mp-Ar-*H*), 6.75–6.71 (m, 2H, Mp-Ar-*H*), 5.82 (t, *J* = 9.6 Hz, 1H, H-3), 5.65 (dd, *J* = 9.8, 7.9 Hz, 1H, H-2), 5.24–5.14 (m, 2H, H-1, H-4), 4.08–3.97 (m, 2H), 3.86–3.79 (m, 1H), 3.75 (s, 3H, $-OCH_3$), 2.77 (s, 3H, $-CH_3$), 1.13 (s, 9H, $-C(CH_3)_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 165.75 (*C*OPh), 165.05 (*C*OPh), 155.69, 151.13, 135.86 (2), 135.65 (2), 133.53, 133.32, 133.07, 132.65, 129.94 (2), 129.79 (2), 129.73 (2), 129.06, 128.76, 128.50 (2), 128.40 (2), 127.71 (2), 127.67 (2), 118.94 (2), 114.48 (2) (Ar-*C*), 100.66 (*C*-1), 74.89, 74.23, 72.63, 71.81, 61.97, 55.61, 38.75, 26.74 (3) ($-C(CH_3)_3$), 19.27; HRMS calcd for $C_{44}H_{46}O_{11}SSiNa$ $(M+Na)^+$: 833.2428, found: 833.2417.

### 4.17. *p*-Methoxyphenyl 2,3-di-*O*-benzoyl-4-*O*-mesyl-β-D-glucopyranoside (12)

Product **12** was obtained from **11** (811 mg, 1.0 mmol) following the procedure C. The pure product **12** was obtained by column chromatography on silica gel as a white foam (475 mg, 83%): $[\alpha]_D^{25}$ +81.8 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 8.02–7.97 (m, 2H, Ar-*H*), 7.96–7.91 (m, 2H, Ar-*H*), 7.52 (m, 2H, Ar-*H*), 7.38 (m, 4H, Ar-*H*), 6.95–6.88 (m, 2H, Mp-Ar-*H*), 6.80–6.74 (m, 2H, Mp-Ar-*H*), 5.86 (t, *J* = 9.6 Hz, 1H, H-3), 5.67 (dd, *J* = 9.8, 8.0 Hz, 1H, H-2), 5.22 (d, *J* = 7.9 Hz, 1H, H-1), 5.11 (t, *J* = 9.6 Hz, 1H, H-4), 4.05 (m, 1H), 3.96 (m, 1H), 3.83 (ddd, *J* = 9.7, 3.7, 2.4 Hz, 1H), 3.74 (s, 3H, $-OCH_3$), 2.90 (s, 3H, $CH_3SO_2$-), 2.48 (br, 1H, $-OH$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 165.56 (*C*OPh), 164.96 (*C*OPh), 155.76, 150.74, 133.66, 133.39, 129.84 (2), 129.75 (2), 128.81, 128.56 (2), 128.51, 128.40 (2), 118.79 (2), 114.52 (2) (Ar-*C*), 100.59 (*C*-1), 74.45, 74.34, 72.30, 71.56, 60.74, 55.55, 38.55, 29.66; HRMS calcd for $C_{28}H_{28}O_{11}SNa$ $(M+Na)^+$: 595.1250, found: 595.1247.

### 4.18. *p*-Methoxyphenyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsiyl-α-D-mannopyranoside (13)

Product **13** was obtained from compound **15** (879 mg, 1.2 mmol) through benzoylation. The pure product **13** was obtained by column chromatography on silica gel (824 mg, 82%): $[\alpha]_D^{25}$ +30.5 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 8.15 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.91 (dd, *J* = 11.9, 8.0 Hz, 4H, Ar-*H*), 7.68 (d, *J* = 6.8 Hz, 2H, Ar-*H*), 7.63–7.50 (m, 4H, Ar-*H*), 7.46 (t, *J* = 7.7 Hz, 3H, Ar-*H*), 7.41–7.27 (m, 8H, Ar-*H*), 7.15 (dd, *J* = 11.7, 8.3 Hz, 4H, Ar-*H*), 6.83 (d, *J* = 9.0 Hz, 2H, Mp-Ar-*H*), 6.23 (t, *J* = 10.2 Hz, 1H, H-4), 6.04 (dd, *J* = 10.3, 3.2 Hz, 1H, H-3), 5.88 (s, 1H, H-2), 5.70 (s, 1H, H-1), 4.30 (d, *J* = 9.7 Hz, 1H), 3.89 (dd, *J* = 11.6, 4.0 Hz, 1H, H-6a), 3.80 (m, 1H), 3.78 (s, 3H, $-OCH_3$), 1.03 (s, 9H, $-C(CH_3)_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 165.69 (*C*OPh), 165.61 (*C*OPh), 165.27 (*C*OPh), 155.27, 150.23, 135.74 (2), 135.51 (2), 133.52, 133.23, 133.16, 133.03, 132.89, 130.04 (2), 129.83 (2), 129.76 (2), 129.60, 129.55, 129.39, 129.28, 129.20, 128.60 (2), 128.40 (2), 128.33 (2), 127.57 (3), 117.95 (2), 114.68 (2) (Ar-*C*), 96.89 (*C*-1), 71.94, 70.66, 70.47, 66.45, 62.38, 55.67, 26.60 (3) ($-C(CH_3)_3$), 19.21; HRMS calcd for $C_{50}H_{48}O_{10}SiNa$ $(M+Na)^+$: 859.2909, found: 859.2917.

### 4.19. *p*-Methoxyphenyl 2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (14)[15]

Product **14** was obtained from **13** (837 mg, 1.0 mmol) following the procedure C. The pure product **14** was obtained by column chromatography on silica gel as a white foam (574 mg, 96%): $[\alpha]_D^{25}$ +31.6 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 8.13 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 8.00 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.86 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.64 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.57–7.37 (m, 6H, Ar-*H*), 7.32–7.25

(m, 2H, Ar-*H*), 7.15–7.09 (m, 2H, Mp-Ar-*H*), 6.88 (m, 2H, Mp-Ar-*H*), 6.21 (dd, *J* = 10.1, 3.4 Hz, 1H, H-3), 5.94 (t, *J* = 10.1 Hz, 1H, H-4), 5.87 (dd, *J* = 3.1, 1.9 Hz, 1H, H-2), 5.73 (d, *J* = 1.3 Hz, 1H, H-1), 4.21 (d, *J* = 10.0 Hz, 1H), 3.86–3.70 (m, 5H, –O*CH*$_3$), 2.69 (dd, *J* = 8.3, 6.1 Hz, 1H, –O*H*); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 166.58 (*C*OPh), 165.51 (*C*OPh), 165.47 (*C*OPh), 155.38, 149.84, 133.72, 133.63, 133.25, 129.94 (2), 129.91 (2), 129.70 (2), 129.12, 129.03, 128.65 (2), 128.60, 128.51 (2), 128.32 (2), 117.72 (2), 114.74 (2) (Ar-*C*), 96.75 (*C*-1), 71.52, 70.46, 69.43, 67.09, 61.12, 55.64; HRMS calcd for $C_{34}H_{30}O_{11}Na$ $(M+Na)^+$: 621.1737, found: 621.1732.

### 4.20. *p*-Methoxyphenyl 2,3-di-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsiyl-α-D-mannopyranoside (15)

*p*-Methoxyphenyl 2,3-di-*O*-benzoyl-β-D-mannopyranoside (742 mg, 1.5 mmol) was dissolved in dry Py (10 mL) and cooled to 0 °C. Under Ar atmosphere TBDPSCl (0.55 mL, 2.2 mmol) and imidazole (306 mg, 4.5 mmol) were added to this solution, after which the mixture was stirred at room temperature overnight and concentrated, then diluted with $CH_2Cl_2$. The organic layer was washed with 1 M HCl and brine, then dried over $Na_2SO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography to afford **15** as a white solid (967 mg, 88%): $[\alpha]_D^{25}$ +101.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.10 (dd, *J* = 8.2, 1.2 Hz, 2H, Ar-*H*), 7.97 (dd, *J* = 8.2, 1.2 Hz, 2H, Ar-*H*), 7.72 (td, *J* = 8.0, 1.4 Hz, 4H, Ar-*H*), 7.61 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.53 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.48–7.33 (m, 10H, Ar-*H*), 7.08–7.01 (m, 2H, Mp-Ar-*H*), 6.83–6.76 (m, 2H, Mp-Ar-*H*), 5.85–5.74 (m, 2H, H-2, H-3), 5.58 (d, *J* = 1.2 Hz, 1H, H-1), 4.50 (t, *J* = 9.3 Hz, 1H, H-4), 4.07 (dd, *J* = 10.5, 3.5 Hz, 1H, H-6a), 4.03–3.93 (m, 2H, H-5, H-6b), 3.77 (s, 3H, –O*CH*$_3$), 1.08 (s, 9H, –C(*CH*$_3$)$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 166.61 (*C*OPh), 165.47 (*C*OPh), 155.07, 150.02, 135.69 (2), 135.51 (2), 133.41, 133.25, 133.05, 132.87, 129.84 (2), 129.81 (2), 129.71 (2), 129.35, 128.47 (2), 128.30 (2), 127.68 (2), 127.61 (2), 117.85 (2), 114.52 (2) (Ar-*C*), 96.77 (*C*-1), 72.75, 72.73, 70.44, 67.08, 63.53, 55.56, 26.76 (3) (–C(*CH*$_3$)$_3$), 19.23; HRMS calcd for $C_{43}H_{44}O_9SiNa$ $(M+Na)^+$: 755.2652, found: 755.2663.

### 4.21. *p*-Methoxyphenyl 2,3-di-*O*-benzoyl-α-D-mannopyranoside (16)

Product **16** was obtained from **15** (732 mg, 1.0 mmol) following the procedure C. The pure product **16** was obtained by column chromatography on silica gel as a white foam (450 mg, 91%): $[\alpha]_D^{25}$ +66.0 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.08 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.94 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.61 (dd, *J* = 10.8, 4.1 Hz, 1H, Ar-*H*), 7.54–7.45 (m, 3H, Ar-*H*), 7.35 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 7.07–7.01 (m, 2H, Mp-Ar-*H*), 6.85 (m, 2H, Mp-Ar-*H*), 5.83–5.74 (m, 2H), 5.60 (s, 1H, H-1), 4.45 (t, *J* = 9.4 Hz, 1H), 4.04–3.91 (m, 3H, H-5, H-6), 3.77 (s, 3H, –O*CH*$_3$), 3.03 (br, 1H, –O*H*), 2.21 (br, 1H, –O*H*); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 166.77 (*C*OPh), 165.42 (*C*OPh), 155.25, 149.76, 133.61, 133.44, 129.80 (3), 129.19, 129.12, 128.61 (2), 128.39 (2), 117.81 (2), 114.64 (2) (Ar-*C*), 96.75 (*C*-1), 72.92, 72.71, 70.42, 66.43, 61.92, 55.59; HRMS calcd for $C_{27}H_{26}O_9Na$ $(M+Na)^+$: 517.1475, found: 517.1463.

### 4.22. Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsiyl-1-thio-α-D-mannopyranoside (17)

Product **17** was obtained from ethyl 1-thio-α-D-mannopyranoside (336 mg, 1.5 mmol) following the procedure B. The pure product **17** was obtained by column chromatography on silica gel as a white foam (965 mg, 83%): $[\alpha]_D^{25}$ +61.8 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.16 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.95 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.88 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.72 (dd, *J* = 6.7, 1.1 Hz, 2H, Ar-*H*), 7.65–7.53 (m, 4H, Ar-*H*), 7.52–7.34 (m, 7H, Ar-*H*), 7.29 (dd, *J* = 10.6, 5.0 Hz, 4H, Ar-*H*), 7.19 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 6.19 (t, *J* = 9.8 Hz, 1H, H-4), 5.89–5.74 (m, 2H), 5.62 (s, 1H), 4.56 (dd, *J* = 8.0, 1.9 Hz, 1H, H-3), 4.00–3.92 (m, 1H), 3.89–3.79 (m, 1H), 2.85–2.65 (m, 2H, –*CH*$_2$CH$_3$), 1.38 (t, *J* = 7.4 Hz, 3H, –CH$_2$*CH*$_3$), 1.08 (s, 9H, –C(*CH*$_3$)$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 165.59 (*C*OPh), 165.56 (*C*OPh), 165.30 (*C*OPh), 135.72 (2), 135.53 (2), 133.74, 133.44, 133.23, 133.14, 133.05, 132.89, 130.21, 130.01 (2), 129.80 (2), 129.78 (2), 129.60, 129.58, 129.44, 129.41, 129.13, 128.58 (2), 128.51, 128.41 (2), 128.31 (2), 127.59 (3) (Ar-*C*), 82.03 (*C*-1), 72.43, 71.96, 71.10, 66.82, 62.56, 26.61 (3) (–C(*CH*$_3$)$_3$), 25.38, 19.21, 14.78; HRMS calcd for $C_{45}H_{46}O_8SSiNa$ $(M+Na)^+$: 797.2575, found: 797.2583.

### 4.23. Ethyl 2,3,4-tri-*O*-benzoyl-1-thio-α-D-mannopyranoside (18)

Product **18** was obtained from **17** (775 mg, 1.0 mmol) following the procedure C. The pure product **18** was obtained by column chromatography on silica gel as a white foam (498 mg, 93%): $[\alpha]_D^{25}$ +21.9 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.09 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 7.97 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.83–7.76 (m, 2H, Ar-*H*), 7.60 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.55–7.35 (m, 6H, Ar-*H*), 7.24 (m, 2H, Ar-*H*), 5.93–5.81 (m,2H), 5.76 (s, 1H), 5.57 (s, 1H), 4.43 (d, *J* = 8.8 Hz, 1H), 3.80 (m, 2H), 2.79–2.65 (m, 2H, –*CH*$_2$CH$_3$), 1.35 (t, *J* = 7.4 Hz, 3H, –CH$_2$*CH*$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 166.52 (*C*OPh), 165.41 (*C*OPh), 165.32 (*C*OPh), 133.68, 133.52, 133.20, 129.87 (2), 129.84 (2), 129.61 (2), 129.18, 128.86, 128.57 (2), 128.51, 128.47 (2), 128.25 (2) (Ar-*C*), 82.27 (*C*-1), 72.22, 71.31, 69.95, 67.35, 61.23, 25.55, 14.75; HRMS calcd for $C_{29}H_{28}O_8SNa$ $(M+Na)^+$: 559.1403, found: 559.1415.

### 4.24. Methyl 2,3-di-*O*-acetyl-4-*O*-pivaloyl-6-*O*-*tert*-butyldiphenylsiyl-α-D-mannopyranoside (19)

TBDPSCl (0.55 mL, 2.2 mmol) was added to a stirred mixture of Methyl 2,3-di-*O*-acetyl-α-D-mannopyranoside (417 mg, 1.5 mmol) and imidazole (306 mg, 4.5 mmol) in dry Py (20 mL) at room temperature under Ar atmosphere, and the mixture was then stirred at the same temperature followed by TLC. After the completion of the reaction, a solution of pivaloyl chloride (0.56 mL, 4.5 mmol) in $CH_2Cl_2$ (5 mL) was added dropwise at 0 °C, and then catalytic DMAP added. The reaction was stirred at the same temperature for 6 h. The reaction was monitored by TLC, after completion, methanol (2 mL) added and the mixture concentrated under vacuum, then the residue diluted with $CH_2Cl_2$ (50 mL). The organic layer was washed sequentially with 1 M HCl (10 mL × 2) and then brine (20 mL × 2) and dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum, and the residue was purified by flash column chromatography to afford **19** (549 mg, 61%): $[\alpha]_D^{25}$ +59.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.68 (ddd, *J* = 12.5, 7.9, 1.5 Hz, 4H, Ar-*H*), 7.45–7.32 (m, 6H, Ar-*H*), 5.44–5.36 (m, 2H, H-3, H-4), 5.23 (dd, *J* = 2.8, 1.7 Hz, 1H, H-2), 4.75 (d, *J* = 1.5 Hz, 1H, H-1), 3.87 (t, *J* = 6.7 Hz, 1H, H-5), 3.75 (dd, *J* = 11.3, 5.6 Hz, 1H, H-6a), 3.65 (dd, *J* = 11.3, 1.7 Hz, 1H, H-6b), 3.43 (s, 3H, –O*CH*$_3$), 2.13 (s, 3H, –*CH*$_3$), 1.96 (s, 3H, –*CH*$_3$), 1.04 (s, 9H, –C(*CH*$_3$)$_3$), 1.06 (s, 9H, –C(*CH*$_3$)$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 176.92 (*C*OC(CH$_3$)$_3$), 170.22 (*C*OCH$_3$), 169.92 (*C*OCH$_3$), 135.64 (2), 135.54 (2), 133.22, 133.01, 129.62 (2), 129.60 (2), 127.59 (2) (Ar-*C*), 98.26 (*C*-1), 71.34, 69.90, 69.30, 65.50, 62.36, 54.97, 38.66, 26.81 (3) (–C(*CH*$_3$)$_3$), 26.55 (3) (–C(*CH*$_3$)$_3$), 20.87, 20.66, 19.20; HRMS calcd for $C_{32}H_{44}O_9SiNa$ $(M+Na)^+$: 623.2647, found: 623.2649.

### 4.25. Methyl 2,3-di-*O*-acetyl-4-*O*-pivaloyl-α-D-mannopyranoside (20)

Product **20** was obtained from **19** (600 mg, 1.0 mmol) following the procedure C. The pure product **20** was obtained by column

chromatography on silica gel as a white foam (322 mg, 89%): $[\alpha]_D^{25}$ +61.3 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 5.46 (dd, *J* = 10.3, 3.5 Hz, 1H, H-3), 5.24 (dd, *J* = 3.4, 1.7 Hz, 1H, H-2), 5.20 (t, *J* = 10.1 Hz, 1H, H-4), 4.73 (d, *J* = 1.4 Hz, 1H, H-1), 3.76–3.64 (m, 2H), 3.57 (m, 1H), 3.40 (s, 3H, –O*CH*$_3$), 2.59 (dd, *J* = 9.3, 5.1 Hz, 1H, –O*H*), 2.14 (s, 3H, –CO*CH*$_3$), 1.98 (s, 3H, –CO*CH*$_3$), 1.17 (s, 9H, –C(*CH*$_3$)$_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 178.67 (*C*OC(CH$_3$)$_3$), 170.11 (*C*OCH$_3$), 169.68 (*C*OCH$_3$), 98.65 (*C*-1), 70.54, 69.66, 68.56, 66.06, 61.12, 55.26, 38.90, 26.87 (3) (–C(*CH*$_3$)$_3$), 20.88 (COCH$_3$), 20.60 (COCH$_3$); HRMS calcd for $C_{16}H_{26}O_9Na$ (M+Na)$^+$: 385.1469, found: 385.1479.

### 4.26. *p*-Tolyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsiyl-1-thio-β-D-galactopyranoside (21)

Product **21** was obtained from *p*-tolyl 1-thio-β-D-galactopyranoside (429 mg, 1.5 mmol) following the procedure B. The pure product **21** was obtained by column chromatography on silica gel as a white foam (1.02 g, 81%): $[\alpha]_D^{25}$ +60.5 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 8.19–8.12 (m, 1H, Ar-*H*), 8.04–7.97 (m,2H, Ar-*H*), 7.92–7.85 (m, 2H, Ar-*H*), 7.84–7.77 (m,2H, Ar-*H*), 7.74–7.68 (m, 2H, Ar-*H*), 7.65 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.59–7.39 (m, 12H, Ar-*H*), 7.34–7.24 (m, 3H, Ar-*H*), 7.14–7.18 (m, 4H, Ar-*H*), 6.12–6.05 (m, 1H), 5.72–5.59 (m, 2H), 4.95 (dd, *J* = 9.0, 6.4 Hz, 1H), 4.15 (dd, *J* = 12.9, 6.4 Hz, 1H, H-6a), 3.92 (dt, *J* = 11.9, 6.0 Hz, 1H, H-6b), 3.81 (td, *J* = 10.1, 7.3 Hz, 1H, H-5), 2.42 (s, 3H, –*CH*$_3$), 1.04 (s, 9H, –C(*CH*$_3$)$_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 165.61 (*C*OPh), 165.25 (*C*OPh), 165.10 (*C*OPh), 138.57, 135.65 (2), 135.50 (2), 134.50 (2), 133.75, 133.26, 133.12, 132.87, 132.64, 130.22, 129.99 (2), 129.84 (2), 129.82 (2), 129.69, 129.60 (2), 129.51, 129.44, 129.02, 128.51, 128.44 (2), 128.42 (2), 128.24 (2), 127.84 (2), 127.64 (2), 127.31 (Ar-*C*), 85.94 (*C*-1), 77.70, 73.41, 68.15, 68.04, 61.46, 26.69 (3) (–C(*CH*$_3$)$_3$), 21.39, 19.03; HRMS calcd for $C_{50}H_{48}O_8SSiNa$ (M+Na)$^+$: 859.2731, found: 859.2729.

### 4.27. *p*-Tolyl 2,3,4-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside (22)

Product **22** was obtained from **21** (837 mg, 1.0 mmol) following the procedure C. The pure product **22** was obtained by column chromatography on silica gel as a white foam (568 mg, 95%): $[\alpha]_D^{25}$ +19.9 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 8.03–7.97 (m, 2H, Ar-*H*), 7.94–7.86 (m, 2H, Ar-*H*), 7.83–7.74 (m, 2H, Ar-*H*), 7.62 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.54 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.49–7.38 (m, 7H, Ar-*H*), 7.24 (dd, *J* = 12.8, 4.8 Hz, 2H, Ar-*H*), 7.16 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 5.83 (d, *J* = 3.1 Hz, 1H, H-4), 5.78 (t, *J* = 9.9 Hz, 1H, H-2), 5.58 (dd, *J* = 9.9, 3.2 Hz, 1H, H-3), 4.97 (d, *J* = 9.9 Hz, 1H, H-1), 4.09 (m, 1H, H-5), 3.86 (dd, *J* = 11.9, 6.7 Hz, 1H, H-6a), 3.62 (dd, *J* = 11.9, 6.7 Hz, 1H, H-6b), 2.60 (br, 1H, –O*H*), 2.39 (s, 3H, –*CH*$_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 166.52 (*C*OPh), 165.49 (*C*OPh), 165.17 (*C*OPh), 138.77, 134.49 (2), 133.76, 133.36, 133.32, 130.09 (2), 129.81 (2), 129.75 (2), 129.68 (2), 129.30, 128.69, 128.60, 128.55 (2), 128.45 (2), 128.31 (2), 126.98 (Ar-*C*), 85.78 (*C*-1), 76.72, 73.15, 68.97, 68.00, 60.73, 21.37 (*C*H$_3$); HRMS calcd for $C_{34}H_{30}O_8SNa$ (M+Na)$^+$: 621.1554, found: 621.1562.

### 4.28. *p*-Methoxyphenyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldiphenylsiyl-α-D-galactopyranoside (23)

TBDPSCl (0.55 mL, 2.2 mmol) was added to a stirred mixture of *p*-Methoxyphenyl α-D-galactopyranoside (429 mg, 1.5 mmol) and imidazole (306 mg, 4.5 mmol) in dry DMF (20 mL) at room temperature under Ar atmosphere, and the mixture was then stirred at the same temperature followed by TLC. After the completion of the reaction, 60% NaH (0.78 g, 18.0 mmol) and BnBr (1.07 mL, 9.0 mmol) were added at 0 °C. After the complication of the addition, the reaction was stirred at room temperature for 6 h. The reaction mixture was then diluted with EtOAc (50 mL) and sequentially washed with an aqueous solution of 1 N HCl (10 mL × 4), and then brine (5 mL × 2). The organic layer was dried over anhydrous $Na_2SO_4$, the solvent was removed under vacuum, and the residue was subject to flash column chromatography to give the pure compound **23** as a white solid (847 mg, 71%): $[\alpha]_D^{25}$ +29.3 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 7.58 (d, *J* = 7.7 Hz, 4H, Ar-*H*), 7.48–7.23 (m, 21H, Ar-*H*), 6.98 (d, *J* = 9.0 Hz, 2H, Mp-Ar-*H*), 6.76 (d, *J* = 9.0 Hz, 2H, Mp-Ar-*H*), 5.34 (d, *J* = 2.7 Hz, 1H, H-4), 5.03–4.94 (m, 2H), 4.84 (t, *J* = 11.1 Hz, 2H), 4.74 (d, *J* = 11.9 Hz, 1H), 4.64 (d, *J* = 11.3 Hz, 1H), 4.20–4.10 (m, 2H), 4.06 (s, 1H), 4.00 (t, *J* = 6.3 Hz, 1H), 3.76 (s, 3H, –O*CH*$_3$), 3.72 (d, *J* = 6.6 Hz, 2H), 1.03 (s, 9H, –C(*CH*$_3$)$_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 155.00, 151.13, 138.84, 138.53, 138.40, 135.48 (3), 133.17, 129.66 (2), 128.40 (2), 128.35 (2), 128.18 (2), 128.13 (2), 127.92 (2), 127.67 (3), 127.55 (2), 127.50 (2), 119.05 (2), 114.38 (2) (Ar-*C*), 97.81 (*C*-1), 78.97, 76.40, 75.04, 74.89, 73.31 (2), 71.46, 62.60, 55.56, 26.81 (3) (–C(*CH*$_3$)$_3$), 19.12; HRMS calcd for $C_{50}H_{54}O_7SiNa$ (M+Na)$^+$: 817.3531, found: 817.3542.

### 4.29. *p*-Methoxyphenyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranoside (24)

Product **24** was obtained from **23** (795 mg, 1.0 mmol) following the procedure C. The pure product **24** was obtained by column chromatography on silica gel as a white foam (495 mg, 89%): $[\alpha]_D^{25}$ +100.6 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 7.48–7.24 (m, 15H, Ar-*H*), 6.99 (d, *J* = 8.9 Hz, 2H, Mp-Ar-*H*), 6.81 (d, *J* = 8.9 Hz, 2H, Mp-Ar-*H*), 5.42 (s, 1H, H-1), 4.99 (dd, *J* = 20.9, 11.6 Hz, 2H, –*CH*$_2$Ph), 4.85 (dd, *J* = 16.9, 12.0 Hz, 2H, –*CH*$_2$Ph), 4.71 (dd, *J* = 23.0, 11.8 Hz, 2H, –*CH*$_2$Ph), 4.18 (m, 2H), 3.97 (m, 2H), 3.77 (s, 3H, –O*CH*$_3$), 3.69 (d, *J* = 10.9 Hz, 1H), 3.49 (s, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 155.02, 150.83, 138.60, 138.25, 138.01, 128.59 (2), 128.50 (2), 128.45 (2), 128.38 (2), 128.04, 127.95 (2), 127.74, 127.64, 127.53 (2), 118.49 (2), 114.47 (2) (Ar-*C*), 97.38 (*C*-1), 78.94, 76.26, 74.77, 74.51, 73.56, 73.44, 71.02, 62.20, 55.56; HRMS calcd for $C_{34}H_{36}O_7Na$ (M+Na)$^+$: 579.2353, found: 579.2359.

### 4.30. Ethyl 2,3,4-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (26)

Product **26** was obtained from **25** (733 mg, 1.0 mmol) following the procedure C. The pure product **26** was obtained by column chromatography on silica gel as a white foam (475 mg, 96%): $[\alpha]_D^{25}$ +69.0 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 7.46–7.24 (m, 15H, Ar-*H*), 5.52 (d, *J* = 5.5 Hz, 1H, H-1), 4.98 (d, *J* = 11.5 Hz, 1H, –*CH*$_2$Ph), 4.89 (d, *J* = 11.8 Hz, 1H, –*CH*$_2$Ph), 4.79–4.68 (m, 3H, –*CH*$_2$Ph), 4.65 (d, *J* = 11.6 Hz, 1H, –*CH*$_2$Ph), 4.32 (dd, *J* = 9.9, 5.5 Hz, 1H), 4.13 (t, *J* = 5.4 Hz, 1H), 3.89 (s, 1H), 3.81 (dd, *J* = 9.9, 2.7 Hz, 1H), 3.74 (dd, *J* = 13.3, 3.8 Hz, 1H), 3.53 (dd, *J* = 14.8, 9.9 Hz, 1H), 2.54 (ddd, *J* = 30.3, 12.8, 7.3 Hz, 2H, –*CH*$_2$CH$_3$), 1.74 (d, *J* = 5.5 Hz, 1H, –O*H*), 1.27 (t, *J* = 7.4 Hz, 3H, –CH$_2$*CH*$_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 138.56, 138.08, 138.03, 128.53 (2), 128.43 (2), 128.35 (2), 128.26 (2), 127.95, 127.88 (2), 127.63, 127.54, 127.52 (2) (Ar-*C*), 83.28 (*C*-1), 79.42, 76.09, 74.98, 74.45, 73.64, 72.42, 70.52, 62.30, 23.47 (-*CH*$_2$CH$_3$), 14.58 (–CH$_2$*CH*$_3$); HRMS calcd for $C_{29}H_{34}O_5SNa$ (M+Na)$^+$: 517.2025, found: 517.2031.

### 4.31. *p*-Methoxyphenyl 3,4-di-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsiyl-2-deoxy-2-phthalimdo-β-D-glucopyranoside (27)

TBDPSCl (0.55 mL, 2.2 mmol) was added to a stirred mixture of *p*-Methoxyphenyl 2-deoxy-2-phthalimdo-β-D-glucopyranoside (622 mg, 1.5 mmol) and imidazole (306 mg, 4.5 mmol) in dry Py

(20 mL) at room temperature under Ar atmosphere, and the mixture was then stirred at the same temperature followed by TLC. After the completion of the reaction, BzCl (0.70 mL, 6.0 mmol) was added dropwise to the reaction mixture, and then catalytic DMAP added. The reaction was monitored by TLC, after completion, methanol (2 mL) added and the mixture concentrated under vacuum, then the residue diluted with $CH_2Cl_2$ (50 mL). The organic layer was washed sequentially with 1 M HCl (10 mL × 2) and then brine (20 mL × 2) and dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum, and the residue was purified by flash column chromatography to afford **27** (1.06 g, 82%): $[\alpha]_D^{25}$ +18.8 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.91–7.79 (m, 6H, Ar-*H*), 7.70 (dd, *J* = 12.4, 5.7 Hz, 4H, Ar-*H*), 7.63–7.59 (m, 2H, Ar-*H*), 7.54 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.46 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.42–7.19 (m, 10H, Ar-*H*), 7.01–6.96 (m, 2H, Mp-Ar-*H*), 6.78–6.72 (m, 2H, Mp-Ar-*H*), 6.32 (dd, *J* = 10.7, 9.3 Hz, 1H, H-3), 6.05 (d, *J* = 8.4 Hz, 1H, H-1), 5.72 (t, *J* = 9.7 Hz, 1H, H-4), 4.84 (dd, *J* = 10.7, 8.5 Hz, 1H, H-2), 4.10 (ddd, *J* = 10.0, 5.1, 2.1 Hz, 1H, H-5), 3.94–3.85 (m,2H, H-6), 3.74 (s, 3H, –O*CH*$_3$), 1.07 (s, 9H, –C(*CH*$_3$)$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 165.83 (*C*OPh), 165.04 (*C*OPh), 155.59, 150.84, 135.64 (2), 135.50 (2), 134.24 (2), 133.25 (2), 133.01, 132.77, 131.44, 129.86 (2), 129.79 (2), 129.64, 129.60, 129.13, 128.68, 128.37 (2), 128.32 (2), 127.80, 127.66 (2), 127.63 (2), 123.68 (2), 118.95 (2), 114.47 (2) (Ar-*C*), 97.65 (*C*-1), 75.37, 71.47, 69.60, 62.66, 55.63, 55.01, 26.62 (3) (–C(*CH*$_3$)$_3$), 19.17; HRMS calcd for $C_{51}H_{47}O_{10}NSiNa$ (M+Na)$^+$: 884.2861, found: 884.2850.

### 4.32. *p*-Methoxyphenyl 3,4-Di-*O*-benzoyl-2-deoxy-2-phthalimdo-β-D-glucopyranoside (28)

Product **28** was obtained from **27** (862 mg, 1.0 mmol) following the procedure C. The pure product **28** was obtained by column chromatography on silica gel as a white foam (548 mg, 88%): $[\alpha]_D^{25}$ +11.7 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.95 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.79 (m, 4H, Ar-*H*), 7.67 (m, 2H, Ar-*H*), 7.51 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.44–7.33 (m, 3H, Ar-*H*), 7.27 (m, 2H, Ar-*H*), 6.91 (d, *J* = 9.0 Hz, 2H, Mp-Ar-*H*), 6.76 (d, *J* = 9.0 Hz, 2H, Mp-Ar-*H*), 6.40 (t, *J* = 10.0 Hz, 1H, H-3), 6.08 (d, *J* = 8.5 Hz, 1H, H-1), 5.60 (t, *J* = 9.6 Hz, 1H,H-4), 4.81 (dd, *J* = 10.6, 8.6 Hz, 1H, H-2), 4.03–3.95 (m, 1H), 3.92–3.83 (m, 1H), 3.76 (d, *J* = 12.7 Hz, 1H), 3.72 (s, 3H, –O*CH*$_3$), 2.68 (br, 1H, –O*H*); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 165.96 (*C*OPh), 165.65 (*C*OPh), 155.67, 150.45, 134.28 (2), 133.66, 133.34, 131.29, 129.91 (2), 129.74 (2), 128.51, 128.47 (2), 128.33 (2), 123.65 (2), 118.77 (2), 114.53 (2) (Ar-*C*), 97.52 (*C*-1), 74.64, 70.84, 69.88, 61.31, 55.56, 54.76; HRMS calcd for $C_{35}H_{29}O_{10}NNa$ (M+Na)$^+$: 646.1684, found: 646.1690.

### 4.33. *p*-Methoxyphenyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsiyl-β-D-galactopyranosyl (1→4)-2,3-di-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsiyl-β-D-gluco pyranoside (29)

TBDPSCl (0.55 mL, 2.2 mmol) was added to a stirred mixture of *p*-Methoxyphenyl β-D-galactopyranosyl (1→4)-β-D-glucopyranoside (448 mg, 1.0 mmol) and imidazole (306 mg, 4.5 mmol) in dry Py (20 mL) at room temperature under Ar atmosphere, and the mixture was then stirred at the same temperature followed by TLC. After the completion of the reaction, BzCl (1.41 mL, 12.0 mmol) was added dropwise to the reaction mixture, and then catalytic DMAP added. The reaction was monitored by TLC, after completion, methanol (2 mL) added and the mixture concentrated under vacuum, then the residue diluted with $CH_2Cl_2$ (50 mL). The organic layer was washed sequentially with 1 M HCl (10 mL × 2) and then brine (20 mL × 2) and dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum, and the residue was purified by flash column chromatography to afford **29** (910 mg, 63%): $[\alpha]_D^{25}$ +91.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.97–7.70 (m, 12H, Ar-*H*), 7.68–7.28 (m, 24H, Ar-*H*), 7.25–7.13 (m, 5H, Ar-*H*), 6.96 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 6.87–6.79 (m, 3H, Ar-*H*), 6.72–6.65 (m, 4H, Ar-*H*), 6.00 (d, *J* = 2.6 Hz, 1H, H-4'), 5.68 (t, *J* = 9.6 Hz, 1H, H-3), 5.61–5.51 (m, 3H), 5.18 (d, *J* = 7.6 Hz, 1H, H-1), 5.01 (d, *J* = 7.8 Hz, 1H, H-1'), 4.52 (t, *J* = 9.6 Hz, 1H), 3.97–3.90 (m, 3H), 3.73 (s, 3H, –O*CH*$_3$), 3.52 (dd, *J* = 9.7, 5.3 Hz, 1H), 3.41 (d, *J* = 9.5 Hz, 1H), 3.10 (t, *J* = 9.7 Hz, 1H), 1.19 (s, 9H, –C(*CH*$_3$)$_3$), 0.94 (s, 9H, –C(*CH*$_3$)$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 165.50 (*C*OPh), 165.45 (*C*OPh), 165.28 (*C*OPh), 165.18 (*C*OPh), 164.57 (*C*OPh), 155.60, 151.22, 136.00, 135.95, 135.65, 135.55, 135.50, 135.46, 133.52, 133.15, 133.07, 132.75, 132.57, 132.34, 132.05, 130.40, 130.06, 129.99, 129.94, 129.87, 129.84, 129.65, 129.59, 129.51, 129.45, 129.43, 129.10, 128.98, 128.48, 128.43, 128.37, 128.26, 128.22, 128.14, 127.99, 127.83, 127.79, 127.58, 119.17, 114.41 (Ar-*C*), 100.87 (*C*-1), 100.20 (*C*-1'), 75.33, 73.39, 73.16, 72.75, 72.06, 71.94, 70.23, 67.18, 60.96, 59.70, 55.64, 27.02 (3) (–C(*CH*$_3$)$_3$), 26.57 (3) (–C(*CH*$_3$)$_3$), 19.55, 18.87; HRMS calcd for $C_{86}H_{84}O_{17}Si_2Na$ (M+Na)$^+$: 1467.5139, found: 1467.5128.

### 4.34. *p*-Methoxyphenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl (1→4)-2,3-di-*O*-benzoyl-β-D-glucopyranoside (30)

Product **30** was obtained from **29** (722 mg, 0.5 mmol) following the procedure C. The pure product **30** was obtained by column chromatography on silica gel as a white foam (339 mg, 70%): $[\alpha]_D^{25}$ +61.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.04 (t, *J* = 8.0 Hz, 4H, Ar-*H*), 7.96 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 7.85 (d, *J* = 7.0 Hz, 2H, Ar-*H*), 7.79 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 7.69 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.60–7.50 (m, 4H, Ar-*H*), 7.45–7.36 (m, 6H, Ar-*H*), 7.25 (t, *J* = 7.8 Hz, 2H, Ar-*H*), 7.10 (t, *J* = 7.8 Hz, 2H, Ar-*H*), 6.87 (d, *J* = 8.9 Hz, 2H, Mp-Ar-*H*), 6.75 (d, *J* = 9.1 Hz, 2H, Mp-Ar-*H*), 5.83–5.71 (m, 2H), 5.70–5.59 (m, 2H), 5.54–5.43 (m, 1H), 5.16 (d, *J* = 7.7 Hz, 1H, H-1), 5.01 (t, *J* = 8.7 Hz, 1H), 4.35 (t, *J* = 9.4 Hz, 1H), 3.91–3.78 (m, 3H), 3.73 (s, 3H, –O*CH*$_3$), 3.61 (d, *J* = 9.7 Hz, 1H), 2.99–2.88 (m, 1H), 2.74 (dd, *J* = 12.0, 6.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 166.41 (*C*OPh), 165.46 (*C*OPh), 165.28 (*C*OPh), 165.27 (*C*OPh), 164.92 (*C*OPh), 155.68, 150.97, 133.84, 133.48, 133.33, 133.31, 133.04, 130.16, 129.89, 129.80, 129.76, 129.73, 129.49, 129.16, 129.02, 128.69, 128.58, 128.42, 128.33, 128.25, 118.56, 114.57 (Ar-*C*), 100.85 (*C*-1), 100.63 (*C*-1'), 75.27, 74.70, 73.89, 73.21, 71.90, 71.53, 70.35, 68.53, 60.35, 59.83, 55.61; HRMS calcd for $C_{54}H_{48}O_{17}Na$ (M+Na)$^+$: 991.2784, found: 991.2768.

### 4.35. Phenyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl (1→4)-2,3-di-*O*-benzoyl-1-thio-β-D-glucopyranoside (32)

Product **32** was obtained from **31** (715 mg, 0.5 mmol) following the procedure C. The pure product **32** was obtained by column chromatography on silica gel as a white foam (372 mg, 78%): $[\alpha]_D^{25}$ +68.9 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.98 (t, *J* = 8.1 Hz, 4H, Ar-*H*), 7.84 (t, *J* = 8.8 Hz, 4H, Ar-*H*), 7.65 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.55–7.45 (m, 7H, Ar-*H*), 7.42–7.24 (m, 12H, Ar-*H*), 7.15 (t, *J* = 7.8 Hz, 2H, Ar-*H*), 5.74 (t, *J* = 9.5 Hz, 1H, H-3), 5.47 (d, *J* = 3.2 Hz, 1H, H-4'), 5.43 (t, *J* = 9.8 Hz, 1H, H-2), 5.24 (dd, *J* = 10.1, 3.3 Hz, 1H, H-3'), 4.99 (d, *J* = 10.0 Hz, 1H, H-1'), 4.67 (d, *J* = 7.6 Hz, 1H, H-1), 4.27 (t, *J* = 9.6 Hz, 1H, H-2'), 4.10–4.01 (m, 3H), 3.74 (d, *J* = 9.8 Hz, 1H), 3.52 (t, *J* = 6.8 Hz, 1H), 3.30 (br, 1H, –O*H*), 2.89 (s, 1H), 2.84 (s, 1H), 2.50 (br, 1H, –O*H*); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 166.31 (*C*OPh), 166.00 (*C*OPh), 165.53 (*C*OPh), 165.16 (*C*OPh), 133.74, 133.35, 133.31, 133.21, 132.88 (2), 131.88, 129.96 (2), 129.83 (2), 129.73 (2), 129.47 (2), 129.44 (2), 129.10, 129.03 (2), 128.99, 128.79, 128.54 (2), 128.37 (3), 128.31 (3) (Ar-*C*), 103.46 (*C*-1'), 86.28 (*C*-1), 79.29, 75.55, 74.99, 73.83, 73.28,

70.66, 70.36, 68.52, 61.32, 59.84; HRMS calcd for $C_{53}H_{46}O_{15}SNa$ $(M+Na)^+$: 977.2455, found: 977.2468.

### 4.36. *p*-Methoxyphenyl 2,3-di-*O*-benzoyl-4-*O*-levulinoyl-6-*O*-*tert*-butyl diphenylsiyl-β-D-glucopyranoside (33)

To a solution of **11a** (879 mg, 1.2 mmol) in dry DCM (20 mL) under Ar atmosphere was added Levulinic acid (209 mg, 1.8 mmol), EDCI (460 mg, 2.4 mmol) and catalytic DMAP. The mixture was stirred at room temperature followed by TLC, after completion, the organic layer was washed with 1 M HCl and brine, then dried over $Na_2SO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography to afford **33** (907 mg, 91%): $[\alpha]_D^{25}$ +91.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.96 (dd, *J* = 15.1, 7.5 Hz, 4H, Ar-*H*), 7.76–7.67 (m, 4H, Ar-*H*), 7.52 (dd, *J* = 12.0, 7.3 Hz, 2H, Ar-*H*), 7.46–7.30 (m, 10H, Ar-*H*), 7.00 (d, *J* = 9.0 Hz, 2H, Mp-Ar-*H*), 6.73 (d, *J* = 9.0 Hz, 2H, Mp-Ar-*H*), 5.70 (dt, *J* = 17.4, 9.7 Hz, 2H), 5.43 (t, *J* = 9.4 Hz, 1H), 5.19 (d, *J* = 7.6 Hz, 1H, H-1), 3.88 (m, 3H, H-5, H-6), 3.74 (s, 3H, –O$CH_3$), 2.51 (dd, *J* = 12.6, 6.4 Hz, 2H, $CH_3COCH_2CH_2COO$–), 2.44–2.28 (m, 2H, $CH_3COCH_2CH_2COO$–), 2.01 (s, 3H, $CH_3COCH_2CH_2COO$–), 1.10 (s, 9H, C($CH_3$)$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 205.54 ($CH_3COCH_2CH_2$-CO), 171.20 ($CH_3COCH_2CH_2CO$), 165.87 (*C*OPh), 165.12 (*C*OPh), 155.57, 151.28, 135.73 (2), 135.61 (2), 133.30, 133.22, 133.15, 132.95, 129.89 (2), 129.78 (2), 129.67 (2), 129.26, 128.94, 128.37 (3), 127.68 (3), 118.90 (2), 114.45 (2) (Ar-*C*), 100.77 (*C*-1), 75.21, 73.34, 71.82, 68.64, 62.48, 55.60, 37.77, 29.49, 27.77, 26.69 (3) (–C($CH_3$)$_3$), 19.25; HRMS calcd for $C_{48}H_{50}O_{11}SiNa$ $(M+Na)^+$: 853.3020, found: 853.3009.

### 4.37. *p*-Methoxyphenyl 2,3-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-glucopyranoside (34)

Product **34** was obtained from **33** (831 mg, 1.0 mmol) following the procedure C. The pure product **34** was obtained by column chromatography on silica gel as a white foam (420 mg, 71%): $[\alpha]_D^{25}$ +100.7 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.03–7.92 (m, 4H, Ar-*H*), 7.52 (m, 2H, Ar-*H*), 7.38 (m, 4H, Ar-*H*), 6.93 (d, *J* = 9.1 Hz, 2H, Mp-Ar-*H*), 6.77 (d, *J* = 9.1 Hz, 2H, Mp-Ar-*H*), 5.65 (t, *J* = 9.1 Hz, 1H, H-3), 5.50 (t, *J* = 9.4 Hz, 1H, H-2), 5.14 (d, *J* = 7.9 Hz, 1H, H-1), 4.59 (dd, *J* = 12.2, 4.7 Hz, 1H, H-6a), 4.43 (d, *J* = 12.1 Hz, 1H, H-6b), 4.00–3.90 (m, 1H), 3.83–3.78 (m, 1H), 3.75 (s, 3H, –O$CH_3$), 3.50 (d, *J* = 4.3 Hz, 1H, –O*H*), 2.79 (t, *J* = 6.4 Hz, 2H, $CH_3COCH_2CH_2COO$–), 2.65 (t, *J* = 6.6 Hz, 2H, $CH_3COCH_2CH_2COO$–), 2.19 (s, 3H, $CH_3COCH_2CH_2COO$–); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 206.18 ($CH_3COCH_2CH_2CO$), 173.10 ($CH_3COCH_2CH_2COO$), 167.09 (*C*OPh), 165.17 (*C*OPh), 155.60, 151.03, 133.45, 133.21, 129.93 (2), 129.68 (2), 129.12, 128.83, 128.35 (2), 128.32 (2), 118.80 (2), 114.39 (2) (Ar-*C*), 100.71 (*C*-1), 76.16, 74.37, 71.26, 69.09, 62.93, 55.53, 37.93, 29.76, 27.84; HRMS calcd for $C_{32}H_{32}O_{11}Na$ $(M+Na)^+$: 615.1842, found: 615.1849.

### 4.38. *p*-Methoxyphenyl 3,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsiyl-2-deoxy-2-phthalimdo-β-D-glucopyranoside (35)

TBDPSCl (0.55 mL, 2.2 mmol) was added to a stirred mixture of *p*-Methoxyphenyl 2-deoxy-2-phthalimdo-β-D-glucopyranoside (622 mg, 1.5 mmol) and imidazole (306 mg, 4.5 mmol) in dry Py (20 mL) at room temperature under Ar atmosphere, and the mixture was then stirred at the same temperature followed by TLC. After the completion of the reaction, $Ac_2O$ (0.60 mL, 6.0 mmol) was added dropwise to the reaction mixture, and then catalytic DMAP added. The reaction was monitored by TLC, after completion, methanol (2 mL) added and the mixture concentrated under vacuum, then the residue diluted with $CH_2Cl_2$ (50 mL). The organic layer was washed sequentially with 1 M HCl (10 mL × 2) and then brine (20 mL × 2) and dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum, and the residue was purified by flash column chromatography to afford **35** (875 mg, 79%): $[\alpha]_D^{25}$ +51.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.89–7.87 (m, 2H, Ar-*H*), 7.75–7.73 (m, 2H, Ar-*H*), 7.69–7.65 (m, 4H, Ar-*H*), 7.40–7.30 (m, 6H, Ar-*H*), 6.91 (d, *J* = 8.5 Hz, 2H, Mp-Ar-*H*), 6.69 (d, *J* = 8.6 Hz, 2H, Mp-Ar-*H*), 5.87–5.83 (m, 2H, H-3, H-1), 5.23 (t, *J* = 9.6 Hz, 1H, H-4), 4.56 (t, *J* = 9.6 Hz, 1H, H-2), 3.84 (d, *J* = 10.2 Hz, 1H), 3.80–3.69 (m, 2H), 3.71 (s, 3H, –O$CH_3$), 1.90 (s, 3H, –$CH_3$), 1.88 (s, 3H, –$CH_3$), 1.06 (s, 9H, –C($CH_3$)$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 170.35 (*C*O$CH_3$), 169.35 (*C*O$CH_3$), 155.55, 150.77, 135.71 (2), 135.59 (2), 134.35, 133.11, 132.91, 131.43, 129.73 (2), 127.73 (2), 127.71 (2), 123.70 (2), 118.81 (2), 114.45 (2) (Ar-*C*), 97.37 (*C*-1), 75.07, 71.08, 69.11, 62.62, 55.61, 54.75, 26.68 (3) (–C($CH_3$)$_3$), 20.58, 20.54, 19.21; HRMS calcd for $C_{41}H_{43}O_{10}NSiNa$ $(M+Na)^+$: 760.2548, found: 760.2554.

### 4.39. *p*-Methoxyphenyl 3,6-di-*O*-acetyl-2-deoxy-2-phthalimdo-β-D-glucopyrano side (36)[16]

Product **36** was obtained from **35** (737 mg, 1.0 mmol) following the procedure C. The pure product **36** was obtained by column chromatography on silica gel as a white foam (394 mg, 79%): $[\alpha]_D^{25}$ +16.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.86–7.73 (m, 4H, Phth-Ar-*H*), 6.87–6.72 (m, 4H, Ar-*H*), 5.88 (d, *J* = 8.4 Hz, 1H, H-1), 5.74 (dd, *J* = 8.8, 10.6 Hz, 1H, H-3), 4.54 (dd, *J* = 4.1, 11.8 Hz, 1H, H-6a), 4.49 (dd, *J* = 8.5, 10.6 Hz, 1H, H-2), 4.40 (dd, *J* = 1.9, 12.1 Hz, 1H, H-6b), 3.85 (ddd, *J* =2.6, 4.8, 9.9 Hz, 1H, H-5), 3.75 (t, *J* = 9.5 Hz, 4H), 3.72 (s, 3H, –O$CH_3$), 3.28 (br s, 1H, O*H*), 2.14 (s, 3H, –$CH_3$), 1.95 (s, 3H, –$CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 171.67 (*C*O$CH_3$), 171.30 (*C*O$CH_3$), 155.62, 150.58, 134.40 (2), 131.37, 123.68 (3), 118.75 (3), 114.43 (3) (Ar-*C*), 97.42 (*C*-1), 74.15, 73.20, 69.58, 62.99, 55.60, 54.50, 21.07, 20.91, 20.70.

### 4.40. Methyl 2,3-di-*O*-acetyl-4,6-di-*O*-*tert*-butyldiphenylsiyl-α-D-mannopyranoside (37)

TBDPSCl (1.13 mL, 4.5 mmol) and catalytic DMAP were added to a stirred mixture of Methyl 2,3-di-*O*-acetyl-α-D-mannopyranoside (417 mg, 1.5 mmol) and imidazole (612 mg, 9.0 mmol) in dry Py (20 mL) at room temperature, and the mixture was then stirred at the same temperature. The reaction was monitored by TLC, after completion, methanol (2 mL) added and the mixture concentrated under vacuum, then the residue diluted with $CH_2Cl_2$ (50 mL). The organic layer was washed sequentially with 1 M HCl (10 mL × 2) and then brine (20 mL × 2) and dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum, and the residue was purified by flash column chromatography to afford **37** (657 mg, 58%): $[\alpha]_D^{25}$ +69.3 (*c* 0.5 $CHCl_3$);$^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.76–7.68 (m, 6H, Ar-*H*), 7.53–7.49 (m, 2H, Ar-*H*), 7.46–7.29 (m, 12H, Ar-*H*), 5.20 (d, *J* = 1.7 Hz, 1H, H-2), 5.07 (dd, *J* = 9.7, 3.1 Hz, 1H, H-3), 4.56 (s, 1H, H-1), 4.09–4.00 (m, 2H), 3.95 (dd, *J* = 11.0, 5.1 Hz, 1H, H-6a), 3.86 (dd, *J* = 8.6, 4.1 Hz, 1H), 3.37 (s, 3H, –O$CH_3$), 1.77 (s, 3H, –$COCH_3$), 1.07 (s, 3H, –$COCH_3$), 1.04 (s, 9H, –C($CH_3$)$_3$), 0.89 (s, 9H, –C($CH_3$)$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 170.10 (*C*O$CH_3$), 169.87 (*C*O$CH_3$), 136.14 (2), 135.96 (2), 135.66 (2), 135.24 (2), 134.41, 133.84, 133.29, 131.81, 129.70, 129.52, 129.46, 129.25, 128.16, 127.50 (2), 127.47 (2), 127.41 (2), 126.61 (Ar-*C*), 98.08 (*C*-1), 73.68, 72.83, 69.32, 66.73, 63.02, 54.67, 26.77 (3) (–C($CH_3$)$_3$), 26.74 (3) (–C($CH_3$)$_3$), 20.38, 19.89, 19.45, 19.29; HRMS calcd for $C_{43}H_{54}O_8Si_2Na$ $(M+Na)^+$: 777.3249, found: 777.3239.

### 4.41. Methyl 2,3-di-*O*-acetyl-4-*O*-*tert*-butyldiphenylsiyl-α-D-mannopyranoside (38)

Product **38** was obtained from **37** (755 mg, 1.0 mmol) following the procedure C. The pure product **38** was obtained by column

chromatography on silica gel as a white foam (454 mg, 88%): $[\alpha]_D^{25}$ +63.1 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 7.84–7.79 (m, 2H, Ar-*H*), 7.60–7.54 (m, 2H, Ar-*H*), 7.47–7.32 (m, 6H, Ar-*H*), 5.19 (dd, *J* = 2.9, 1.8 Hz, 1H, H-2), 5.08 (dd, *J* = 9.7, 3.1 Hz, 1H, H-3), 4.54 (d, *J* = 1.4 Hz, 1H, H-1), 3.98 (m, 2H), 3.89 (m, 2H), 3.40 (s, 3H, –O$CH_3$), 2.91 (d, *J* = 29.1 Hz, 1H, –O*H*), 1.73 (s, 3H, –CO$CH_3$), 1.06 (s, 3H, –CO$CH_3$), 1.00 (s, 9H, –C($CH_3$)$_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 170.04 (*C*O$CH_3$), 169.63 (*C*O$CH_3$), 136.27 (2), 135.26 (2), 134.15, 131.58, 129.83, 129.30, 127.47 (2) (Ar-*C*), 98.56 (*C*-1), 72.89, 72.37, 69.17, 66.51, 61.85, 55.03, 26.83 (3) (–C($CH_3$)$_3$), 20.24 (-*C*($CH_3$)$_3$), 19.81 (CO$CH_3$), 19.54 (CO$CH_3$); HRMS calcd for $C_{27}H_{36}O_8SiNa$ $(M+Na)^+$: 539.2072, found: 539.2069.

### 4.42. *p*-Tolyl 2,4-di-*O*-acetyl-3,6-di-*O*-*tert*-butyldiphenylsiyl-1-thio-β-D-galacto pyranoside (39)

TBDPSCl (1.13 mL, 4.5 mmol) and catalytic DMAP was added to a stirred mixture of *p*-Tolyl 1-thio-β-D-galactopyranoside (429 mg, 1.5 mmol) and imidazole (612 mg, 9.0 mmol) in dry Py (20 mL) at room temperature, and the mixture was then stirred at the same temperature followed by TLC. After the completion of the reaction, $Ac_2O$ (0.60 mL, 6.0 mmol) was added to the reaction mixture, and then catalytic DMAP added. The reaction was monitored by TLC, after completion, methanol (2 mL) added and the mixture concentrated under vacuum, then the residue diluted with $CH_2Cl_2$ (50 mL). The organic layer was washed sequentially with 1 M HCl (10 mL × 2) and then brine (20 mL × 2) and dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum, and the residue was purified by flash column chromatography to afford **39** (902 mg, 71%): $[\alpha]_D^{25}$ +65.5 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 7.73 (d, *J* = 6.7 Hz, 2H, STol-Ar-*H*), 7.64 (d, *J* = 6.8 Hz, 6H, Ar-*H*), 7.49–7.32 (m, 14H, Ar-*H*), 7.02 (d, *J* = 8.0 Hz, 2H, STol-Ar-*H*), 5.32 (m, 2H, H-2, H-4), 4.43 (d, *J* = 10.0 Hz, 1H, H-1), 3.97 (dd, *J* = 9.4, 3.1 Hz, 1H, H-3), 3.69 (dd, *J* = 10.5, 6.5 Hz, 1H, H-6a), 3.60 (dd, *J* = 10.5, 6.1 Hz, 1H, H-6b), 3.51–3.46 (m, 1H, H-5), 2.31 (s, 3H, –$CH_3$), 2.10 (s, 3H, –CO$CH_3$), 1.60 (s, 3H, –CO$CH_3$), 1.05 (2s, 18H, 2 × –C($CH_3$)$_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 169.94 (*C*O$CH_3$), 169.93 (*C*O$CH_3$), 137.44, 136.23 (2), 135.95 (2), 135.68 (2), 135.62 (2), 133.58, 133.13, 132.97, 132.53, 131.62 (2), 130.64, 130.10, 129.79, 129.76, 129.70, 129.56 (2), 127.77 (2), 127.73 (2), 127.70 (2), 127.61 (2) (Ar-*C*), 87.78 (*C*-1), 77.94, 73.38, 70.46, 70.34, 62.19, 26.80 (3) (–C(*C*$H_3$)$_3$), 26.56 (3) (–C(*C*$H_3$)$_3$), 21.11, 20.87, 20.82, 19.21, 19.11; HRMS calcd for $C_{49}H_{58}O_7SSi_2Na$ $(M+Na)^+$: 869.3334, found: 869.3329.

### 4.43. *p*-Tolyl 2,6-di-*O*-acetyl-1-thio-β-D-galactopyranoside (40)

Product **40** was obtained from **39** (847 mg, 0.5 mmol) following the procedure C. The pure product **40** was obtained by column chromatography on silica gel as a white foam (266 mg, 72%): $[\alpha]_D^{25}$ +81.0 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 7.39–7.35 (d, *J* = 8.0 Hz, 2H, STol-Ar-*H*), 7.09 (d, *J* = 8.0 Hz, 2H, STol-Ar-*H*), 4.94 (t, *J* = 9.7 Hz, 1H, H-2), 4.53 (d, *J* = 10.0 Hz, 1H, H-1), 4.35 (dd, *J* = 11.6, 5.9 Hz, 1H, H-6a), 4.28 (dd, *J* = 11.6, 6.9 Hz, 1H, H-6b), 3.90 (d, *J* = 3.1 Hz, 1H, H-4), 3.70–3.60 (m, 2H, H-3, H-5), 2.31 (s, 3H, –$CH_3$), 2.15 (s, 3H, –CO$CH_3$), 2.06 (s, 3H, –CO$CH_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 171.25 (*C*O$CH_3$), 171.12 (*C*O$CH_3$), 138.30, 133.03 (2), 129.67 (2), 128.78 (Ar-*C*), 86.29 (*C*-1), 75.91, 73.51, 71.21, 68.85, 62.83, 21.16, 21.09, 20.84; HRMS calcd for $C_{17}H_{22}O_7SNa$ $(M+Na)^+$: 393.0978, found: 393.0969.

### 4.44. 3β-(*tert*-Butyldiphenylsilyloxy)-androstan-17-one (41)[17]

Product **41** was obtained from **42** (290 mg, 1.0 mmol) following the procedure A. The pure product **41** was obtained by column chromatography on silica gel as a white foam (501 mg, 95%): $[\alpha]_D^{25}$ +60.0 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 7.67 (d, *J* = 6.4 Hz, 4H, Ar-*H*), 7.39 (dd, *J* = 14.2, 6.1 Hz, 6H, Ar-*H*), 3.57 (s, 1H), 2.41 (dd, *J* = 19.2, 8.5 Hz, 1H), 2.09–1.95 (m, 1H), 1.89 (s, 1H), 1.74 (d, *J* = 9.1 Hz, 2H), 1.65–1.38 (m, 10H), 1.29–1.12 (m, 6H), 1.05 (d, *J* = 11.1 Hz, 2H), 1.04 (s, 9H, –C($CH_3$)$_3$), 0.83 (s, 3H, –$CH_3$), 0.97–0.69 (m, 4H), 0.81 (s, 3H, –$CH_3$), 0.59–0.53 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 221.09 (*C*=O), 135.71, 134.73, 129.36, 127.38 (Ar-*C*), 72.58, 54.31, 51.34, 47.76, 44.68, 38.22, 36.90, 35.81, 35.52, 34.93, 31.59, 31.47, 30.82, 28.32, 26.94 (3) (–C(*C*$H_3$)$_3$), 21.71, 20.38, 19.10, 13.75, 12.28.

### 4.45. Androstan-17-one (42)[18]

Product **42** was obtained from **41** (529 mg, 1.0 mmol) following the procedure C. The pure product **42** was obtained by column chromatography on silica gel as a white foam (255 mg, 88%): $[\alpha]_D^{25}$ +31.9 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 3.59 (m, 1H), 2.43 (dd, *J* = 19.0, 8.6 Hz, 1H), 2.12–1.99 (m, 1H), 1.91 (dd, *J* = 15.5, 10.6 Hz, 1H), 1.78 (d, *J* = 10.8 Hz, 3H), 1.74–1.62 (m, 2H), 1.48 (ddd, *J* = 31.0, 24.9, 14.3 Hz, 5H), 1.26 (dd, *J* = 25.2, 12.8 Hz, 6H), 1.20–1.03 (m, 1H), 0.96 (dd, *J* = 26.9, 15.1 Hz, 2H), 0.85 (s, 3H, –$CH_3$), 0.82 (s, 3H, –$CH_3$), 0.67 (dd, *J* = 15.3, 7.1 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 221.32 (*C*=O), 71.11, 54.42, 51.41, 47.77, 44.82, 38.05, 36.92, 35.82, 35.62, 35.03, 31.54, 31.42, 30.87, 28.37, 21.75, 20.48, 13.79 (–*C*$H_3$), 12.28 (–*C*$H_3$).

### 4.46. 3β-(*tert*-Butyldiphenylsilyloxy)-17β-hydroxy-5-androstene (43)[19]

Product 3β-(*tert*-butyldiphenylsilyloxy)-5-androsten-17-one **41a** was obtained from dehydroepiandrosterone (DHEA) (5.00 g, 17.3 mmol) following the procedure A. The pure product **41a** was obtained by column chromatography on silica gel as a white solid (7.20 g, 79%). To a suspension of $LiAlH_4$ (0.36 g, 9.5 mmol) in anhydrous THF (20 mL) was added dropwise at 0 °C a solution of ketone **41a** (2.50 g, 4.7 mmol) in anhydrous THF (50 mL), and the resulting mixture was stirred at room temperature for 3 h. Subsequently, the reaction was quenched at 0 °C by a mixture of $H_2O$/THF (1:1) (30 mL) followed by addition of ethyl acetate (300 mL). The resulting mixture was dried over $Na_2SO_4$, the solid was filtered, and the filtrate was evaporated in vacuo. The residue was purified by flash column chromatography to afford alcohol **43** as a white solid (2.30 g, 92%): $[\alpha]_D^{25}$ +37.3 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 7.74–7.61 (m, 4H, Ar-*H*), 7.46–7.30 (m, 6H, Ar-*H*), 5.12 (d, *J* = 5.2 Hz, 1H, C=C*H*), 3.61 (t, *J* = 8.1 Hz, 1H), 3.52 (dt, *J* = 15.4, 5.3 Hz, 1H), 2.34 (dd, *J* = 16.3, 8.1 Hz, 1H), 2.14 (ddd, *J* = 13.3, 4.8, 2.0 Hz, 1H), 2.09–1.99 (m, 1H), 1.95–1.87 (m, 1H), 1.79 (dt, *J* = 12.3, 3.4 Hz, 1H), 1.74–1.48 (m, 6H), 1.47–1.38 (m, 5H), 1.29–1.19 (m, 1H), 1.06 (s, 9H, –C($CH_3$)$_3$), 1.00 (s, 3H, –$CH_3$), 0.92–0.78 (m, 4H), 0.73 (s, 3H, –$CH_3$).

### 4.47. 17β-Hydroxy-5-androstene (44)

Product **44** was obtained from **43** (529 mg, 1.0 mmol) following the procedure C. The pure product **44** was obtained by column chromatography on silica gel as a white foam (272 mg, 94%): $[\alpha]_D^{25}$ +50.6 (*c* 0.5 $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 5.35 (d, *J* = 4.5 Hz, 1H, C=C*H*), 3.64 (t, *J* = 8.4 Hz, 1H), 3.56–3.46 (m, 1H), 2.26 (dt, *J* = 25.2, 10.8 Hz, 2H), 2.12–1.93 (m, 2H), 1.84 (m, 3H), 1.65–1.55 (m, 10H), 1.45 (m, 6H), 1.33–1.22 (m, 6H), 1.13–1.03 (m, 2H), 1.02 (s, 3H, –$CH_3$), 0.98–0.85 (m, 2H), 0.75 (s, 3H, –$CH_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 140.65(*C*=CH), 121.35 (C=*C*H), 106.96, 81.84, 71.67, 51.22, 50.13, 42.65, 42.18, 37.19, 36.48, 31.86, 31.55, 31.42, 30.43, 29.66, 23.38, 20.60, 19.40, 10.93; HRMS calcd for $C_{19}H_{30}O_2Na$ $(M+Na)^+$: 313.2143, found: 313.2138.

### 4.48. Benzyl 3β-(*tert*-butyldiphenylsilyloxy) oleanolate (45)

A solution of oleanolic acid (1.07 g, 2.3 mmol), BnBr (0.39 mL, 3.3 mmol), $Et_3N$ (0.45 mL, 3.3 mmol) and $Bu_4NI$ (86.0 mg, 0.24 mmol) in dry THF (20 mL) was stirred at room temperature overnight. The solvent was evaporated in vacuum and the residue was purified through a silica gel column chromatography to give benzyl oleanolate **46** as a white amorphous solid (1.24 g, 97%). Product **45** was obtained from compound **46** (1.09 g, 2.0 mmol) following the procedure A. The pure product **45** was obtained by column chromatography on silica gel as a white solid (1.38 g, 88%): $[\alpha]_D^{25}$ +51.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.73–7.65 (m, 4H, Ar-*H*), 7.44–7.30 (m, 11H, Ar-*H*), 5.22 (s, 1H), 5.05 (q, *J* = 12.6 Hz, 2H), 3.25 (dd, *J* = 11.6, 4.2 Hz, 1H), 2.86 (d, *J* = 9.6 Hz, 1H), 1.94 (dd, *J* = 13.3, 9.6 Hz, 1H), 1.80–1.42 (m, 11H), 1.40–1.23 (m, 6H), 1.20 (d, *J* = 10.8 Hz, 2H), 1.05 (s, 9H, –C($CH_3$)$_3$), 1.04 (s, 3H, –$CH_3$), 0.96 (s, 3H, –$CH_3$), 0.91 (s, 3H, –$CH_3$), 0.89 (s, 3H, –$CH_3$), 0.87 (s, 3H, –$CH_3$), 0.84 (s, 3H, –$CH_3$), 0.56 (s, 3H, –$CH_3$), 0.62–0.52 (m, 2H).

### 4.49. Benzyl oleanolate (46)[20]

Product **46** was obtained from **45** (785 mg, 1.0 mmol) following the procedure C. The pure product **46** was obtained by column chromatography on silica gel as a white foam (508 mg, 93%): $[\alpha]_D^{25}$ +50.7 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.30–7.12 (m, 5H, Ar-*H*), 5.19 (s, 1H), 4.97 (q, *J* = 12.6 Hz, 2H, –$CH_2$Ph), 3.16–3.03 (m, 1H), 2.80 (d, *J* = 9.9 Hz, 1H), 1.88 (m, 1H), 1.75 (dd, *J* = 8.6, 3.2 Hz, 2H), 1.66–1.37 (m, 12H), 1.37–1.18 (m, 4H), 1.17–1.05 (m, 3H), 1.02 (s, 3H, –$CH_3$), 0.94 (d, *J* = 14.7 Hz, 1H), 0.88 (s, 3H, –$CH_3$), 0.82 (s, 3H, –$CH_3$), 0.79 (s, 3H, –$CH_3$), 0.77 (s, 3H, –$CH_3$), 0.67 (s, 3H, –$CH_3$), 0.61 (d, *J* = 11.0 Hz, 1H), 0.50 (s, 3H, –$CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 177.38 (*C*OOBn), 143.59 (*C*=CH), 136.33 (Ar-*C*), 128.33 (2) (Ar-*C*), 127.89 (2) (Ar-*C*), 127.83 (Ar-*C*), 122.41 (C=*C*H), 78.88, 65.85, 55.11, 47.51, 46.65, 45.77, 41.59, 41.28, 39.18, 38.66, 38.35, 36.91, 33.77, 33.05, 32.61, 32.28, 30.63, 28.04, 27.54, 27.10, 25.82, 23.59, 23.31, 22.96, 18.24, 16.79, 15.53, 15.24.

### 4.50. Methyl 3α-(*tert*-butyldiphenylsiyloxy)-7α-(*tert*-butyldiphenylsiyloxy)-cholanoate (47)

Product **47** was obtained from compound **48** (0.81 g, 2.0 mmol) following the procedure A. The pure product **47** was obtained by column chromatography on silica gel as a white solid (1.40 g, 79%): $[\alpha]_D^{25}$ +91.0 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.75 (ddd, *J* = 9.3, 6.0, 1.9 Hz, 4H, Ar-*H*), 7.58 (ddd, *J* = 12.7, 8.0, 1.4 Hz, 4H, Ar-*H*), 7.42–7.31 (m, 12H, Ar-*H*), 3.77 (td, *J* = 11.5, 4.5 Hz, 1H), 3.68 (s, 3H, –O$CH_3$), 3.37–3.27 (m, 1H), 2.38 (ddd, *J* = 15.1, 10.2, 4.9 Hz, 1H), 2.29–2.20 (m, 1H), 2.07 (dd, *J* = 13.0, 6.8 Hz, 1H), 1.98–1.79 (m, 3H), 1.63–1.51 (m, 5H), 1.46–1.07 (m, 14H), 1.02 (s, 9H, –C($CH_3$)$_3$), 0.98 (s, 9H, –C($CH_3$)$_3$), 0.94 (d, *J* = 6.3 Hz, 3H), 0.89 (d, *J* = 13.7 Hz, 2H), 0.72 (s, 3H, –$CH_3$), 0.71 (s, 3H, –$CH_3$), 0.62 (dd, *J* = 14.2, 11.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 174.83 (*C*=O), 136.22, 135.88 (2), 135.72 (2), 135.69 (2), 135.59 (2), 134.87, 134.67, 134.59, 129.41 (2), 129.37, 129.02, 127.43 (2), 127.38 (2), 127.37 (2), 127.11 (2) (Ar-*C*), 77.33, 77.01, 76.70, 74.64, 73.04, 55.67, 54.98, 51.51, 43.86, 43.79, 42.36, 40.03, 39.44, 37.04, 36.39, 35.32, 34.80, 33.67, 31.15, 31.06, 30.53, 28.57, 28.38, 27.11 (3) (–C(*C*H$_3$)$_3$), 27.01 (3) (–C(*C*H$_3$)$_3$), 23.37, 21.41, 19.34, 19.10, 18.49, 12.28; HRMS calcd for $C_{57}H_{78}O_4Si_2Na$ $(M+Na)^+$: 905.5331, found: 905.5327.

### 4.51. Methyl cholanoate (48)

Product **48** was obtained from **47** (883 mg, 1.0 mmol) following the procedure C. The pure product **48** was obtained by column chromatography on silica gel as a white foam (329 mg, 81%): $[\alpha]_D^{25}$ +61.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 3.67 (s, 3H, –O$CH_3$), 3.64–3.54 (m, 2H), 2.36 (m, 1H), 2.27–2.18 (m, 1H), 2.02–1.97 (m, 1H), 1.94–1.86 (m, 1H), 1.84–1.75 (m, 4H), 1.62 (m, 5H), 1.55–1.40 (m, 7H), 1.38–1.21 (m, 5H), 1.18–0.98 (m, 3H), 0.96–0.89 (m, 6H), 0.68 (s, 3H, –$CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 174.76 (*C*OOMe), 71.39, 71.33, 55.70, 54.87, 51.52, 43.73, 43.70, 42.40, 40.10, 39.17, 37.24, 36.81, 35.25, 34.90, 34.04, 31.05, 30.99, 30.26, 28.59, 26.87, 23.38, 21.15, 18.36, 12.11.

### 4.52. 3β-(*tert*-Butyldiphenylsiyloxy) diosgenin (49)[21]

Product **49** was obtained from diosgenin **50** (10.00 g, 24.1 mmol) following the procedure A. The pure product **49** was obtained by column chromatography on silica gel as a white solid (90%, 14.1 g): $[\alpha]_D^{25}$ −86.8 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.71–7.64 (m, 4H, Ar-*H*), 7.39 (ddd, *J* = 15.6, 10.5, 5.5 Hz, 6H, Ar-*H*), 5.12 (d, *J* = 4.5 Hz, 1H, C=C*H*), 4.39 (q, *J* = 7.3 Hz, 1H), 3.57–3.43 (m, 2H), 3.37 (t, *J* = 10.9 Hz, 1H), 2.34 (t, *J* = 11.9 Hz, 1H), 2.14 (dd, *J* = 12.8, 4.0 Hz, 1H), 1.99–1.80 (m, 3H), 1.78–1.54 (m, 11H), 1.43 (t, *J* = 10.6 Hz, 4H), 1.31–1.21 (m, 1H), 1.06 (s, 9H, –C($CH_3$)$_3$), 1.00 (s, 3H, –$CH_3$), 0.96 (d, *J* = 6.9 Hz, 3H, –$CH_3$), 0.79 (d, *J* = 6.3 Hz, 3H, –$CH_3$), 0.77 (s, 3H, –$CH_3$).

### 4.53. Diosgenin (50)[22]

Product **50** was obtained from **49** (653 mg, 1.0 mmol) following the procedure C. The pure product **50** was obtained by column chromatography on silica gel as a white foam (348 mg, 84%): $[\alpha]_D^{25}$ +11.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 5.36 (d, *J* = 5.1 Hz, 1H), 4.42 (dd, *J* = 15.0, 7.5 Hz, 1H), 3.61–3.47 (m, 2H), 3.39 (t, *J* = 10.9 Hz, 1H), 2.37–2.20 (m, 2H), 2.06–1.97 (m, 2H), 1.88 (dt, *J* = 16.7, 8.4 Hz, 3H), 1.75 (dd, *J* = 19.9, 6.9 Hz, 2H), 1.71–1.41 (m, 12H), 1.35–1.26 (m, 1H), 1.22–1.09 (m, 3H), 1.04 (s, 3H, –$CH_3$), 0.98 (d, *J* = 6.9 Hz, 3H), 0.80 (2s, 6H, 2 × –$CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 140.75 (*C*=CH), 121.40 (C=*C*H), 109.26, 80.79, 71.70, 66.82, 62.04, 56.48, 50.01, 42.24, 41.57, 40.23, 39.75, 37.19, 36.61, 32.02, 31.82, 31.59, 31.40, 31.35, 30.27, 28.77, 20.84, 19.40, 17.12, 16.27, 14.51.

### 4.54. 3β-(*tert*-Butyldiphenylsiyloxy)-6α-acetyloxy diosgenin (51)

To a solution of 3-β-TBDPS diosgenin **49** (7.84 g, 12.0 mmol) in dry THF (150 mL) under an argon atmosphere at 0 °C, 1 M $BH_3$ in THF (36 mL, 36.0 mmol) was added slowly. The mixture was allowed to stir overnight at room temperature. NaOH (10 N, 7.50 mL, 75.0 mmol) was added over 30 min at 0 °C. Subsequently, 30% hydrogen peroxide (7.50 mL, 65.0 mmol) was added and vigorous stirring was continued at room temperature for 2 h. Extraction with $CH_2Cl_2$ (100 mL × 3) and the combined extracts were washed successively with 1 N HCl, saturated $NaHCO_3$, and brine, dried (anhydrous $Na_2SO_4$), and concentrated in vacuo. Purification by column chromatography gave 3-β-OTBDPS-6-α-OH diosgenin **51a** as a white solid (7.33 g, 91%). To a stirred solution of compound **51a** (1.34 g, 2.0 mmol) in pyridine (10 mL) was added $Ac_2O$ (0.61 mL, 6.0 mmol). The reaction was stirred at the same temperature for 6 h. The reaction mixture was then diluted with ethyl acetate (25 mL) and sequentially washed with an aqueous solution of 1 N HCl (10 mL × 4), a saturated $NaHCO_3$ solution (5 mL × 3), and then water (5 mL × 2). The organic layer was dried over anhydrous $Na_2SO_4$, the solvent was removed under vacuum, and the residue was subject to flash column chromatography to give the pure compound **51** as a white solid (97%, 1.42 g): $[\alpha]_D^{25}$ +21.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.67–7.65 (m, 4H, Ar-*H*), 7.44–7.33 (m, 6H, Ar-*H*), 4.62 (d, *J* = 10.9 Hz, 1H), 4.34 (d, *J* = 7.4 Hz, 1H), 3.54 (s,

1H), 3.44 (d, $J$ = 10.4 Hz, 1H), 3.35 (t, $J$ = 10.9 Hz, 1H), 1.91 (s, 3H, –CO$CH_3$), 1.95–1.77 (m, 3H), 1.75–1.53 (m, 12H), 1.43 (d, $J$ = 12.0 Hz, 2H), 1.31–1.17 (m, 3H), 1.10–0.98 (m, 3H), 1.03 (s, 9H, –C($CH_3$)$_3$), 0.93 (d, $J$ = 6.9 Hz, 3H, –$CH_3$), 0.86 (s, 3H, –$CH_3$), 0.82 (s, 1H), 0.78 (d, $J$ = 6.2 Hz, 3H, –$CH_3$), 0.72 (s, 3H, –$CH_3$), 0.57 (t, $J$ = 11.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 170.70 ($COCH_3$), 135.71, 134.72, 134.61, 129.39, 127.37 (Ar-*C*), 109.21, 80.58, 77.53, 72.27, 72.09, 66.79, 61.93, 55.89, 53.56, 48.51, 41.50, 40.47, 39.73, 37.66, 37.09, 36.47, 33.58, 32.21, 31.56, 31.25, 30.24, 28.68, 26.89 (3) (–C($CH_3$)$_3$), 21.17, 20.79, 19.05, 17.09, 16.36, 14.44, 13.32; HRMS calcd for $C_{45}H_{64}O_5SiNa$ (M+Na)$^+$: 735.4415, found: 735.4429.

### 4.55. 6α-Acetyloxy diosgenin (52)

Product **52** was obtained from **51** (713 mg, 1.0 mmol) following the procedure C. The pure product **52** was obtained by column chromatography on silica gel as a white foam (412 mg, 87%): $[\alpha]_D^{25}$ +65.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 4.75–4.66 (m, 1H), 4.37 (dd, $J$ = 14.9, 7.3 Hz, 1H), 3.54 (s, 1H), 3.46 (d, $J$ = 8.1 Hz, 1H), 3.36 (t, $J$ = 10.8 Hz, 1H), 2.04 (s, 3H), 1.95 (ddd, $J$ = 24.4, 12.1, 5.2 Hz, 2H), 1.88–1.77 (m, 4H), 1.76–1.56 (m, 9H), 1.45 (dd, $J$ = 29.1, 18.7 Hz, 4H), 1.16 (ddt, $J$ = 54.4, 26.9, 14.9 Hz, 9H), 0.95 (d, $J$ = 6.9 Hz, 4H), 0.88 (s, 3H), 0.78 (d, $J$ = 6.2 Hz, 3H), 0.75 (s, 3H), 0.69 (d, $J$ = 10.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 170.72 ($COCH_3$), 109.22, 80.60, 72.13, 70.90, 66.83, 62.06, 55.94, 53.68, 48.68, 41.57, 40.53, 39.78, 37.76, 37.10, 36.60, 33.70, 32.24, 31.63, 31.30, 31.12, 30.26, 28.72, 21.23, 20.90, 17.08, 16.38, 14.44, 13.36; HRMS calcd for $C_{29}H_{46}O_5Na$ (M+Na)$^+$: 497.3237, found: 497.3246.

### 4.56. 3β-(*tert*-Butyldiphenylsiyloxy)-6α-allyloxy diosgenin (53)

To a stirred solution of compound **51a** (1.34 g, 2.0 mmol) in dry DMF (10 mL) was added 60% NaH (0.26 g, 6.0 mmol) and AllBr (0.26 mL, 3.0 mmol) at 0 °C. After the complication of the addition, the reaction was stirred at room temperature for 6 h. The reaction mixture was then diluted with EtOAc (50 mL) and sequentially washed with an aqueous solution of 1 N HCl (10 mL × 4), and then brine (5 mL × 2). The organic layer was dried over anhydrous $Na_2SO_4$, the solvent was removed under vacuum, and the residue was subject to flash column chromatography to give the pure compound **53** as a white solid (90%, 1.28 g): $[\alpha]_D^{25}$ +41.6 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.67 (d, $J$ = 6.6 Hz, 4H, Ar-*H*), 7.42–7.30 (m, 6H, Ar-*H*), 5.84 (ddt, $J$ = 16.1, 10.7, 5.4 Hz, 1H, –C*H*=$CH_2$), 5.21 (d, $J$ = 17.1 Hz, 1H, –CH=C$H_2$a), 5.12 (d, $J$ = 10.3 Hz, 1H, –CH=C$H_2$b), 4.37 (dd, $J$ = 14.0, 6.1 Hz, 1H), 4.00 (dd, $J$ = 12.7, 5.5 Hz, 1H), 3.80 (dd, $J$ = 11.3, 6.7 Hz, 1H), 3.60–3.49 (m, 1H), 3.45 (d, $J$ = 7.1 Hz, 1H), 3.40–3.30 (m, 1H), 3.01 (td, $J$ = 10.7, 4.3 Hz, 1H), 2.20 (d, $J$ = 12.6 Hz, 1H), 1.98 (td, $J$ = 12.2, 7.5 Hz, 2H), 1.82 (dd, $J$ = 13.6, 6.8 Hz, 1H), 1.75–1.69 (m, 1H), 1.68–1.37 (m, 15H), 1.26 (dt, $J$ = 24.5, 12.3 Hz, 3H), 1.12–1.00 (m, 3H), 1.05 (s, 9H, –C($CH_3$)$_3$), 0.94 (d, $J$ = 6.9 Hz, 3H, –$CH_3$), 0.80 (s, 3H, –$CH_3$), 0.78 (d, $J$ = 6.3 Hz, 3H, –$CH_3$), 0.73 (s, 3H, –$CH_3$), 0.55 (t, $J$ = 9.3 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 135.75, 135.50, 134.70, 129.35, 127.40, 127.37, 116.06 (–$CH_2$*C*H=$CH_2$), 109.18 (–$CH_2$CH=*C*$H_2$), 80.67, 72.71, 70.03, 66.80, 62.06, 56.05, 53.60, 50.00, 41.57, 40.52, 39.79, 37.86, 37.20, 36.25, 33.74, 32.43, 31.69, 31.43, 31.32, 30.27, 28.78, 27.01 (3) (–C($CH_3$)$_3$), 20.86, 19.14, 17.11, 16.39, 14.46, 13.47; HRMS calcd for $C_{46}H_{66}O_4SiNa$ (M+Na)$^+$: 4733.4623, found: 733.4632.

### 4.57. 6α-Allyloxy diosgenin (54)

Product **54** was obtained from **53** (711 mg, 1.0 mmol) following the procedure C. The pure product **54** was obtained by column chromatography on silica gel as a white foam (420 mg, 89%): $[\alpha]_D^{25}$ +61.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 5.89 (qd, $J$ = 11.1, 5.6 Hz, 1H), 5.24 (dd, $J$ = 17.2, 1.4 Hz, 1H), 5.13 (d, $J$ = 10.3 Hz, 1H), 4.38 (dd, $J$ = 14.8, 7.5 Hz, 1H), 4.09–4.02 (m, 1H), 3.86 (m, 1H), 3.59–3.51 (m, 1H), 3.48–3.42 (m, 1H), 3.38–3.31 (m, 1H), 3.06 (td, $J$ = 10.2, 4.2 Hz, 1H), 2.25 (m, 1H), 2.10–1.95 (m, 3H), 1.81 (m, 4H), 1.68 (m, 3H), 1.63–1.34 (m, 8H), 1.24 (dt, $J$ = 15.2, 11.2 Hz, 3H), 1.18–0.98 (m, 6H), 0.94 (d, $J$ = 6.9 Hz, 3H), 0.81 (s, 3H), 0.78 (d, $J$ = 6.2 Hz, 3H), 0.74 (s, 3H), 0.66 (td, $J$ = 11.7, 3.9 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 135.35, 116.53, 109.18, 80.64, 76.68, 76.57, 71.09, 70.16, 66.79, 62.04, 56.00, 53.64, 50.03, 41.57, 40.51, 39.76, 37.75, 37.19, 36.33, 33.71, 32.26, 31.68, 31.30, 30.87, 30.23, 28.74, 20.91, 17.10, 16.39, 14.45, 13.45; HRMS calcd for $C_{30}H_{48}O_4Na$ (M+Na)$^+$: 495.3445, found: 495.3432.

### 4.58. 3β-(*tert*-Butyldiphenylsiyloxy)-6α-(*tert*-butyldiphenylsiyloxy) diosgenin (55)

Product **55** was obtained from **51a** (1.34 g, 2.0 mmol) following the procedure A. The pure product **55** was obtained by column chromatography on silica gel as a white solid (1.62 g, 89%): $[\alpha]_D^{25}$ +88.9 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.74–7.60 (m, 8H, Ar-*H*), 7.46–7.29 (m, 12H, Ar-*H*), 4.33–4.22 (m, 1H), 3.62–3.49 (m, 2H), 3.45 (d, $J$ = 7.5 Hz, 1H), 3.34 (t, $J$ = 10.9 Hz, 1H), 2.43 (d, $J$ = 12.7 Hz, 1H), 1.77 (dd, $J$ = 13.9, 7.0 Hz, 1H), 1.69–1.47 (m, 12H), 1.47–1.08 (m, 11H), 1.06 (s, 9H, –C($CH_3$)$_3$), 1.03 (s, 9H, –C($CH_3$)$_3$), 0.99–0.82 (m, 10H), 0.78 (d, $J$ = 6.4 Hz, 3H, –$CH_3$), 0.65 (s, 3H, –$CH_3$), 0.61 (s, 3H, –$CH_3$), 0.49 (t, $J$ = 9.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 135.97, 135.91, 135.73, 135.24, 135.12, 134.58, 134.18, 129.49, 129.38, 127.46, 127.38, 127.23 (Ar-*C*), 109.13, 80.63, 73.00, 71.43, 66.79, 61.97, 55.82, 53.66, 51.85, 41.89, 41.51, 40.37, 39.80, 37.33, 36.31, 33.73, 33.10, 31.35, 30.26, 28.76, 27.15 (3) (–C(*C*$H_3$)$_3$), 27.00 (3) (–C($CH_3$)$_3$), 20.81, 19.38, 19.18, 17.11, 16.33, 14.42, 13.48; HRMS calcd for $C_{59}H_{80}O_4Si_2Na$ (M+Na)$^+$: 931.5487, found: 931.5472.

### 4.59. Chlorogenin (56)[23]

Product **56** was obtained from **55** (909 mg, 1.0 mmol) following the procedure C. The pure product **56** was obtained by column chromatography on silica gel as a white foam (341 mg, 79%): $[\alpha]_D^{25}$ +106.1 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, pyridine) $\delta$: 6.05 (br, 1H), 5.81 (br, 1H), 4.56 (dd, $J$ = 14.6, 7.6 Hz, 1H), 3.97–3.91 (m, 1H), 3.70–3.64 (m, 1H), 3.59 (d, $J$ = 11.3 Hz, 1H), 3.50 (t, $J$ = 10.5 Hz, 1H), 3.03 (d, $J$ = 12.1 Hz, 1H), 2.26 (d, $J$ = 11.6 Hz, 1H), 2.15–2.04 (m, 2H), 2.00–1.95 (m, 1H), 1.87–1.81 (m, 1H), 1.80–1.63 (m, 7H), 1.62–1.42 (m, 6H), 1.39–0.99 (m, 9H), 1.16 (d, $J$ = 6.9 Hz, 3H, –$CH_3$), 0.90 (s, 3H, –$CH_3$), 0.87 (s, 3H, –$CH_3$), 0.74–0.69 (m, 1H), 0.70 (d, $J$ = 5.5 Hz, 3H, –$CH_3$).

### 4.60. *tert*-butyldiphenylsiyl 3β-(*tert*-butyldiphenylsiyloxy) ursolate (57)

TBDPSCl (1.58 mL, 6.0 mmol) was added to a stirred mixture of ursolic acid (0.91 g, 2.0 mmol) and imidazole (0.81 g, 12.0 mmol) in dried DMF (30 mL) at room temperature, and the mixture was then stirred at the same temperature for 12 h. The reaction was worked up with saturated $NH_4Cl$ solution (10 mL), the mixture was extracted with EtOAc (50 mL × 3), and the combined organic layer was washed sequentially with a saturated $NaHCO_3$ aqueous solution (10 mL × 2) and then saturated NaCl solution (20 mL × 2) and dried over anhydrous $Na_2SO_4$. The solvent was removed under vacuum, and the residue was purified by flash column chromatography to afford compound **57** as a white solid (1.47 g, 79%): $[\alpha]_D^{25}$ +101.3 (*c* 0.5 $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$:

7.76–7.65 (m, 8H, Ar-*H*), 7.46–7.32 (m, 12H, Ar-*H*), 5.18 (s, 1H, –C=C*H*), 3.27 (dd, *J* = 11.5, 4.2 Hz, 1H), 2.23 (d, *J* = 11.3 Hz, 1H), 1.99 (dd, *J* = 14.5, 10.9 Hz, 1H), 1.83–1.66 (m, 6H), 1.56 (q, *J* = 13.4 Hz, 3H), 1.48–1.15 (m, 10H), 1.13 (s, 9H, –C(*CH*$_3$)$_3$), 1.06 (s, 9H, –C(*CH*$_3$)$_3$), 1.01 (s, 3H, –*CH*$_3$), 0.98 (s, 3H, –*CH*$_3$), 0.95 (s, 3H, –*CH*$_3$), 0.94 (s, 3H, –*CH*$_3$), 0.84 (s, 3H, –*CH*$_3$), 0.81 (d, *J* = 6.3 Hz, 3H, –*CH*$_3$), 0.58 (dd, *J* = 28.7, 11.6 Hz, 2H), 0.40 (s, 3H, –*CH*$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 176.20 (*C*=O), 137.71, 135.93, 135.82, 135.77, 135.48, 134.18, 133.49, 131.99, 129.84, 129.57, 129.39, 129.19, 127.65, 127.43, 127.17, 125.65 (Ar-*C*), 81.05, , 55.16, 53.26, 52.18, 49.35, 47.34, 42.24, 39.58, 39.39, 39.34, 38.95, 38.45, 36.64, 33.22, 30.84, 28.59, 27.87, 27.53, 27.10 (3) (–C(*CH*$_3$)$_3$), 26.74 (3) (–C(*CH*$_3$)$_3$), 24.71, 23.18, 21.19, 19.60, 19.32, 19.09, 18.39, 17.28, 16.99, 16.58, 15.48; HRMS calcd for $C_{62}H_{84}O_3Si_2Na$ $(M+Na)^+$: 955.5851, found: 955.5862.

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## Supplementary data

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