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Note

An efficient and selective method for preparing glycosyl sulfoxides by oxidizing glycosyl sulfides with OXONE☆ or *t*-BuOOH on SiO_2

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Abstract

Silica gel adsorbed with OXONE or *t*-BuOOH was used as a mild oxidant to selectively oxidize glycosyl sulfides to corresponding sulfoxides in good yields and without sulfones formation. This method was also found compatible with various other functional groups in the glycosides.

Keywords: OXONE; *t*-BuOOH; Glycosyl sulfoxide; Oxidation; Silica gel support

Sulfoxide function is important for stereocontrol in synthesizing various chemically and biologically important molecules.[2–5] Notably, glycosyl donors[6,7] and, more recently, glycosyl carbanions,[7] based on glycosyl sulfoxides are especially interesting to carbohydrate chemistry. The sulfoxide glycosylation method, has emerged as an effective method for the synthesis of oligosaccharides[8–11] and other glycoconjugates[12–15] because of its mild reaction conditions,[6,7,16–19] highly reactive intermediate, generally good to excellent anomeric stereocontrol,[6,7,20,21] and compatibility with both solution-[22,23] and solid-phase[24–26] glycosylations. Furthermore, it was observed that the stereochemical outcome of the glycosylation is not influenced by the configuration of sulfur atom of sulfoxide donor.[6,7] Consequently, considerable importance is attached to the efficient and selective synthesis of glycosyl sulfoxides.

The selectively oxidation of sulfides to sulfoxides has been extensively studied using various oxidation protocols.[20,27–33] Among the various reagents available for oxidizing sulfides to sulfoxides, *m*-chloro peroxybenzoic acid (*m*-CPBA)[34] is the most commonly used reagent. However, this method suffers several drawbacks, i.e., the need for strict control of temperature (to below −30 °C) and over-oxidation, the partial solubility of *m*-CPBA in dichloromethane (CH_2Cl_2), and the difficulty in separating of the byproduct, *m*-chlorobenzoic acid, from the sulfoxide. Therefore, the development of a simple method for the oxidation of sulfides to sulfoxides, which overcomes the drawbacks aforementioned, remains highly desirable.

The surfaces of silica gel, alumina and K10 have been reported to modify the chemical reactivities of organic molecules on them.[35–38] More simple and efficient methods, such as $H_2O_2/SiO_2/Ac_2O$,[28] *t*-BuOOH/SiO_2,[29,30] or OXONE/SiO_2,[30,39] have been reported to oxidize sulfides to corresponding sulfoxides, and the use of OXONE/K10[40] directly affords sulfones. Moreover, using silica gel as solid support has been demonstrated to mediate oxidation of sulfides to sulfoxides, not only increasing the rate of reaction but also suppressing the over-oxidation of the sulfoxides to sulfone, thus enabling the selective formation of sulfoxides.[40] Although a number of sulfoxides have been prepared by this method, the application of this protocol to the oxidation of glycosyl sulfides remains to be discovered. This study reports an alternative method based on the use of OXONE/SiO_2 as an oxidant for preparing glycosyl

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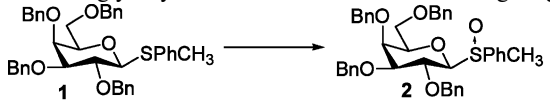
sulfoxides from corresponding sulfides, where it achieved selective oxidation with excellent yields.

Initially, this investigation attempted to oxidize **1** using OXONE or *tert*-butyl hydroperoxide [$(CH_3)_3COOH$] in CH_2Cl_2 to obtain low yields of sulfoxide **2** as shown in Table 1. Alumina and silica gel were then screened as supports to compare their efficiency, while *t*-BuOOH and OXONE were screened as oxidants (Table 1). The screening revealed that the silica gel/OXONE or *t*-BuOOH combinations obtained better yields within shorter reaction times than using alumina or no support.

This study then applied the silica gel/OXONE or *t*-BuOOH combinations as a reagent for oxidizing other glycosyl sulfides, as shown in Table 2. The combination of silica gel/oxidant was found to be compatible with various protecting groups on glycosides. Especially, the levulinyl protecting group (Entry 4, Table 2), which has potential to undergo Baeyer–Villiger oxidation with *m*-CPBA as oxidant, survived under these mild oxidation conditions. Both oxidants achieved similar reaction yields, but the reaction time required by *t*-BuOOH/SiO_2 was longer than with OXONE/SiO_2, and no sulfone products were found on the basis of thin-layer chromatography (TLC) analysis. In general, the oxidation rates of glycosides with electron-donating protecting groups were faster than those with electron-withdrawing protecting groups. The reaction rate differences indicate that the protecting group (ether vs. ester) at C-2 of the thioglycosides greatly affected the rate of the sulfide oxidation. Clearly, the more electron rich of the sulfur atom is, the easier oxidation is.[28] Interestingly, in the presence of TBDPS protecting group enhanced the oxidation rate (entries 3 and 5, and 6 and 7) while levulinyl protecting group decreased the reaction rate (entries 4 and 5). It should be noted that oxidation of selenide **12** using OXONE/SiO_2 yielded hydrolysis product **22** (Entry 12 of Table 2). The diastereomeric ratios of the sulfoxides were determined by ^{1}H NMR based on H-1 chemical shifts. In general, the H-1 chemical shifts of major isomers show more downfield shift.

Table 1
Oxidation of glycosyl sulfides **1** with various oxidizing reagents



Adsorbent	Oxidant	Time (h)[a]	Yield (%)[b]
None	OXONE	52	31
	$(CH_3)_3COOH$	52	27
SiO_2	OXONE	35	71
	$(CH_3)_3COOH$	35	74
Al_2O_3	OXONE	52	48
	$(CH_3)_3COOH$	47	30

[a] Oxidation proceeded at room temperature.
[b] Mixture of diastereomers.

In conclusion, the silica gel/OXONE or *t*-BuOOH combinations provide inexpensive and selective methods of oxidizing glycosyl sulfides to corresponding sulfoxides in good yields without over-oxidation, and are compatible with various other functional groups in the glycosides. Our methods show a more convenient and efficient alternative to oxidation of glycosyl sulfides through *m*-CPBA or H_2O_2. In addition, to the greater safety in handling of OXONE/SiO_2, the products can be isolated by simple filtration through Celite and removal of the solvent, avoiding the tedious extraction with aqueous based required to separate the carboxylic acid byproducts in oxidations involving peroxy acids.

1. Experimental

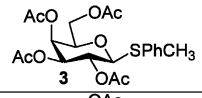
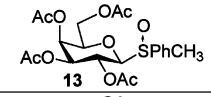
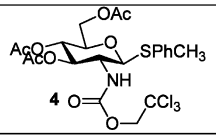
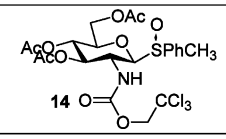
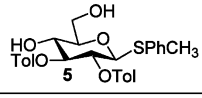
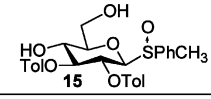
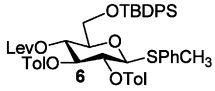
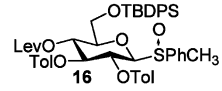
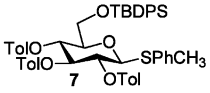
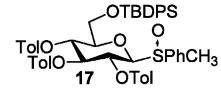
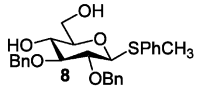
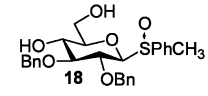
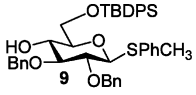
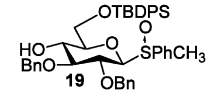
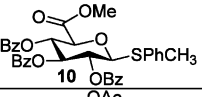
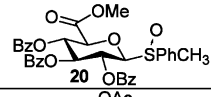
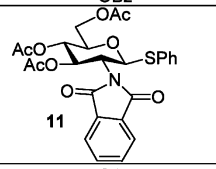
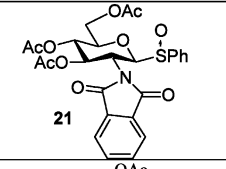
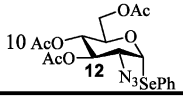
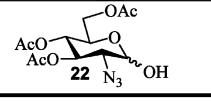
1.1. General methods

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-300 MHz. Chemical shifts are expressed in ppm using residual $CDCl_3$ as reference. High-resolution mass spectra were obtained by means of a Micromass (Autospec) mass spectrometer. Analytical TLC was performed on precoated plates (silica gel 60 F-254). Silica gel 60 (E. Merck Co.) was employed for all flash chromatography. All reactions were carried out in oven-dried glassware (120 °C) under an atmosphere of nitrogen unless indicated otherwise. All solvents were dried and distilled by standard techniques.

1.2. General procedure for oxidation of glycosyl sulfides to glycosyl sulfoxide

Into a 25 mL round-bottomed flask was weighted 2.5 g of Merk 10181 silica gel or Fisher A540 alumina that had been equilibrated with the atmosphere at 120 °C for at least 48 h. The flask was stoppered and the contents allowed to cool to room temperature (−25 °C). For oxidation with OXONE, 0.5 mL of water was added and the adsorbent was tumbled on rotary evaporator at atmospheric pressure until uniformly free-flowing. A solution of glycosyl sulfides (1.0 mmol) in 5 mL CH_2Cl_2 was added with stirring followed by adding 462 mg of OXONE (1.5 mmol of $KOSO_2OOH$) or 137 μL (1.0 mmol) of 70% aq $(CH_3)_3COOH$. The slurry was stirred at 25 °C for the specified period of time. The adsorbent was then removed by vacuum filtration and washed with

Table 2
Oxidation of glycosyl sulfides using OXONE/SiO_2 and *t*-BuOOH/SiO_2

Entry	Substrate[a]	Product	Oxidant[b]	Time (h)	Yield (%)[c]
1	 **3**	 **13**	A	15	82 (2:1)
			B	21	75 (3:1)
2	 **4**	 **14**	A	32	75 (1:1)
			B	36	76 (3:2)
3	 **5**	 **15**	A	33	82 (10:1)
			B	42	85 (9:1)
4	 **6**	 **16**	A	37	92 (5:1)
			B	45	89 (4:1)
5	 **7**	 **17**	A	22	88 (3:2)
6	 **8**	 **18**	A	36	58 (1:1)
7	 **9**	 **19**	A	28	80 (4:1)
8	 **10**	 **20**	A	39	75 (1:4)
9	 **11**	 **21**	A	20	81 (4:1)
10	 **12**	 **22**	A	2	68 (1:1)

[a] Tol = *p*-Methylbenzoyl, Lev = Levulinyl ($CH_3COCH_2CH_2COO$).
[b] A = OXONE/SiO_2; B = *t*-ButOOH/SiO_2.
[c] The isolated yield after chromatographic purification. The number in parenthesis indicates the ratio of diastereomers on the basis of H-1 chemical shifts (downfield:upfield).

50 mL of EtOAc. The combined organic fractions were washed with 30 mL of a saturated, aq soln of $FeSO_4$, dried over anhyd Na_2SO_4, and concentrated under reduced pressure. Further purification was achieved on a flash chromatograph with silica gel and EtOAc–hexane.

1.2.1. *p*-Methylphenylsulfenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (2) (mixture). R_f 0.17 (1:2 EtOAc–hexane); ^{1}H NMR ($CDCl_3$): δ 2.34 (s, 3 H), 3.47–3.55 (m, 3 H), 3.47–3.70 (m, 4 H), 3.85–3.95 (m, 1 H), 4.02 (d, 0.5 H, *J* 9.8 Hz), 4.15 (d, 0.5 H, *J* 9.8 Hz), 4.26–4.67 (m, 4 H), 4.72–5.05 (m, 5 H), 7.16–7.44 (m, 22 H), 7.82 (d, 2 H, *J* 8.1 Hz); ^{13}C NMR ($CDCl_3$): δ 21.6 (21.5), 68.7 (67.5), 69.0, 69.5 (69.2), 72.9 (71.6), 73.1, 73.5 (73.2), 74.3 (74.0), 78.1 (77.8), 83.8 (85.5), 91.8 (90.9), 127.5, 127.6 (2C), 127.7, 128.2, 128.3 (2C), 128.4, 128.5, 128.7, 129.0 (2C), 129.2 (2C), 129.7, 134.1, 135.2, 137.9, 138.4, 144.6; HRMS (FAB) Calcd for $C_{41}H_{43}O_6S$ $[M+H]^+$: 663.2132. Found: 663.2153.

1.2.2. *p*-Methylphenylsulfenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (13). R_f 0.25 (1:1 EtOAc–hexane); ^{1}H NMR ($CDCl_3$): δ 1.87 (s, 3 H), 1.93 (s, 3 H), 1.94 (s,

3 H), 2.09 (s, 3 H), 2.42 (s, 3 H), 3.88–3.94 (m, 2 H), 4.05 (m, 1 H), 4.47 (d, 1 H, *J* 9.8 Hz), 5.01 (dd, 1 H, *J* 9.9, 3.2 Hz), 5.28 (m, 1 H), 5.39 (d, 1 H, *J* 9.9, 9.8 Hz), 7.34 (d, 2 H, *J* 8.0 Hz), 7.79 (d, 2 H, *J* 8.0 Hz); ^{13}C NMR ($CDCl_3$): δ 20.1, 20.3, 20.4, 20.7, 21.6, 60.8, 64.0, 66.5, 71.4, 74.5, 89.0, 129.2, 130.5, 131.8, 145.4, 169.3, 169.6, 169.8, 170.1; HRMS (FAB) Calcd for $C_{21}H_{27}O_{10}S$ $[M+H]^+$: 470.1324. Found: 471.1316. For another isomer: R_f 0.20 (1:1 EtOAc–hexane); ^{1}H NMR ($CDCl_3$): δ 1.96 (br s, 6 H), 1.99 (s, 3 H), 2.00 (s, 3 H), 2.40 (s, 3 H), 3.87 (m, 1 H), 3.94 (dd, 1 H, *J* 11.1, 6.1 Hz), 4.03 (dd, 1 H, *J* 11.1, 6.6 Hz), 4.30 (d, 1 H, *J* 9.9 Hz), 5.05 (dd, 1 H, *J* 9.8, 3.5 Hz), 5.28 (m, 1 H), 5.47 (d, 1 H, *J* 9.9, 9.8 Hz), 7.32 (d, 2 H, *J* 7.9 Hz), 7.60 (d, 2 H, *J* 7.9 Hz); ^{13}C NMR ($CDCl_3$): δ 20.3, 20.4 (2C), 20.5, 20.6, 60.9, 65.2, 66.7, 71.5, 74.9, 92.2, 125.9, 129.3, 132.4, 142.1, 169.5, 169.8, 169.9, 170.1; HRMS (FAB) Calcd for $C_{21}H_{27}O_{10}S$ $[M+H]^+$: 471.1324. Found: 471.1337.

1.2.3. *p*-Methylphenylsulfenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (14) (mixture). R_f 0.3 (1:1 EtOAc–hexane); ^{1}H NMR ($CDCl_3$): δ 1.91–2.17 (s, 9 H), 2.45 (s, 3 H), 3.79 (m, 1 H), 4.07–4.18 (m, 3 H), 4.25–4.38 (m, 2 H), 4.91 (d, 0.5 H, *J* 9.9 Hz), 4.93 (dd, 1 H, *J* 9.9, 9.7 Hz), 5.22 (dd, 1 H, *J* 9.9, 9.7 Hz), 5.31 (d, 0.5 H, *J* 9.9 Hz), 6.30 (br s, 0.5 H, NH), 6.89 (br s, 0.5 H, NH), 7.35 (d, 1 H, *J* 8.3 Hz), 7.61 (d, 1 H, *J* 8.7 Hz, NH), 7.77 (d, 2 H, *J* 8.3 Hz); ^{13}C NMR ($CDCl_3$): δ 20.4, 20.6, 20.7, 21.7, 37.6 (40.3), 61.4, 67.1 (67.8), 69.9 (70.1), 72.0 (76.2), 87.8, 89.6, 92.0 (91.8), 129.6, 130.4, 131.4, 146.0, 162.0, 169.1 (168.3), 169.3 (170.3), 170.6 (171.7); HRMS (FAB) Calcd for $C_{22}H_{27}Cl_3NO_{10}S$ $[M+H]^+$: 603.1045. Found: 603.1059.

1.2.4. *p*-Methylphenylsulfenyl 2,3-di-*O*-*p*-methylbenzoyl-β-D-glucopyranoside (15). R_f 0.27 (3:1 EtOAc–hexane); ^{1}H NMR ($CDCl_3$): δ 2.25–2.30 (s, 9 H), 2.67 (br s, 2 H, OH), 3.62 (m, 1 H), 3.72–3.80 (m, 2 H), 3.87 (m, 1 H), 4.70 (d, 1 H, *J* 9.7 Hz), 5.34 (dd, 1 H, *J* 9.3, 9.3 Hz), 5.60 (dd, 1 H, *J* 9.7, 9.7 Hz), 7.02–7.10 (m, 4 H), 7.18–7.23 (m, 2 H), 7.68–7.78 (m, 6 H); ^{13}C NMR ($CDCl_3$): δ 21.6 (2C), 21.9, 60.4, 61.8, 67.3, 68.8, 80.8, 89.2, 125.9, 126.3, 129.0, 129.1, 129.7, 129.9, 130.0 (2C), 132.4, 144.0, 144.4, 145.8, 165.0, 167.3; HRMS (FAB) Calcd for $C_{29}H_{31}O_8S$ $[M+H]^+$: 539.1569. Found: 539.1580. For another isomer: R_f 0.20 (3:1 EtOAc–hexane); ^{1}H NMR ($CDCl_3$): δ 2.29–2.42 (s, 9 H), 2.36 (s, 3 H), 2.42 (s, 3 H), 2.97 (br s, 2 H, OH), 3.47 (m, 1 H), 3.82–3.92 (m, 2 H), 4.14 (m, 1 H), 4.27 (d, 1 H, *J* 9.8 Hz), 5.57 (dd, 1 H, *J* 9.5, 9.4 Hz), 5.78 (dd, 1 H, *J* 9.7, 9.6 Hz), 7.07–7.21 (m, 4 H), 7.43 (d, 2 H, *J* 8.1 Hz), 7.47 (d, 2 H, *J* 8.1 Hz), 7.78–7.87 (m, 4 H); ^{13}C NMR ($CDCl_3$): δ 21.4 (2C), 21.7, 60.0, 61.8, 65.1, 67.8, 80.5, 91.6, 126.0, 126.2, 129.0, 129.1, 129.6, 129.8, 130.0, 130.1, 132.6, 144.2, 144.4, 146.0, 165.0, 166.8; HRMS (FAB) Calcd for $C_{29}H_{31}O_8S$ $[M+H]^+$: 539.1569. Found: 539.1557.

1.2.5. *p*-Methylphenylsulfenyl 2,3-di-*O*-*p*-methylbenzoyl-4-levulinyl-6-*tert*-butyldiphenylsilyl-β-D-glucopyranoside (16). R_f 0.26 (1:1 EtOAc–hexane); ^{1}H NMR ($CDCl_3$):δ 1.08 (s, 9 H), 2.00 (s, 3 H), 2.25 (s, 3 H), 2.27 (s, 3 H), 2.39–2.42 (m, 2 H), 2.40 (s, 3 H), 2.43–2.49 (m, 2 H), 3.73–3.80 (m, 3 H), 4.87 (d, 1 H, *J* 10.0 Hz), 5.29–5.38 (m, 2 H), 5.59 (dd, 1 H *J* 9.6, 9.4 Hz), 6.82 (d, 2 H, *J* 8.8 Hz), 6.86 (d, 2 H, *J* 8.8 Hz), 7.01 (d, 2 H, *J* 8.0 Hz), 7.38–7.43 (m, 8 H), 7.70–7.77 (m, 4 H), 7.84 (d, 2 H, *J* 9.0 Hz), 7.92 (d, 2 H, *J* 9.0 Hz); HRMS (FAB) Calcd for $C_{50}H_{55}O_{10}SSi$ $[M+H]^+$: 875.4036. Found: 875.4051. For another isomer: R_f 0.20 (1:1 EtOAc–hexane); ^{1}H NMR ($CDCl_3$): δ 1.01 (s, 9 H), 1.98 (s, 3 H), 2.06–2.09 (s, 6 H), 2.26–2.29 (m, 2 H), 2.36 (s, 3 H), 2.39–2.42 (m, 2 H), 3.73–3.85 (m, 3 H), 4.74 (d, 1 H, *J* 9.4 Hz), 5.27 (m, 1 H), 5.57–5.61 (m, 2 H), 6.82 (d, 2 H, *J* 8.8 Hz), 6.85 (d, 2 H, *J* 8.8 Hz), 7.22 (d, 1 H, *J* 8.2 Hz), 7.24 (d, 1 H, *J* 7.1 Hz), 7.38–7.46 (m, 6 H), 7.62–7.68 (m, 4 H), 7.83 (d, 2 H, *J* 8.9 Hz), 7.84 (d, 2 H, *J* 8.2 Hz), 7.91 (d, 2 H, *J* 8.9 Hz); ^{13}C NMR ($CDCl_3$) (mixture): δ 14.1, 19.1 (21.0), 21.7 (22.6), 25.8, 26.7, 27.7, 29.1, 29.4, 60.4 (60.2), 61.9, 67.6 (66.5), 74.2 (75.6), 79.5, 89.8 (90.1), 127.8, 128.2, 129.0, 129.6 (2C), 129.8 (2C), 130.2, 132.1, 132.2 (2C), 132.8, 133.0, 135.6 (2C), 145.5, 163.6 (163.7), 164.5 (165.4), 170.9, 205.4 (202.0); MS (FAB) 875 (24, $[M+H]^+$) 860 (100).

1.2.6. *p*-Methylphenylsulfenyl 2,3,4-tri-*O*-*p*-methylbenzoyl-6-*tert*-butyldiphenylsilyl-β-D-glucopyranoside (17) (mixture). R_f 0.3 (1:2 EtOAc–hexane); ^{1}H NMR ($CDCl_3$): δ 0.95 (s, 9 H), 2.24–2.38 (s, 9 H), 3.72 (m, 1 H), 3.81–3.87 (m, 2 H), 4.57 (d, 0.4 H, *J* 9.4), 4.80 (d, 0.6 H, *J* 9.4), 5.49 (m, 1 H), 5.61–5.85 (m, 2 H), 7.03–7.68 (m, 26 H); ^{13}C NMR ($CDCl_3$): δ 19.0, 21.5, 21.6, 21.8 (2C), 26.6 (25.1), 62.0, 67.6, 67.8, 74.2, 79.9, 89.9 (89.2), 125.6, 126.0 (2C), 127.3 (2C), 128.2, 129.0 (3C), 129.6, 130.5, 131.2 (2C), 132.2, 133.9, 134.3, 135.7, 136.2, 144.5, 145.1, 162.5, 164.7 (165.0), 165.7; HRMS (FAB) Calcd for $C_{53}H_{55}O_9SSi$ $[M+H]^+$: 895.4330. Found: 895.4325.

1.2.7. *p*-Methylphenylsulfenyl 2,3-di-*O*-benzyl-β-D-glucopyranoside (18) (mixture). R_f 0.31 (4:1 EtOAc–hexane); ^{1}H NMR ($CDCl_3$): δ 2.44 (s, 3 H), 3.23 (m, 1 H), 3.50–3.61 (m, 3 H), 3.69 (m, 1 H), 4.08 (m, 1 H), 4.38 (d, 0.5 H, *J* 9.8 Hz), 4.60–4.71 (m, 2 H), 4.83 (d, 0.5 H, *J* 9.8 Hz), 4.99–5.13 (m, 2 H), 7.26–7.38 (m, 10 H), 7.43–7.46 (m, 2 H), 7.81 (d, 2 H, *J* 8.2 Hz); ^{13}C NMR ($CDCl_3$): δ 21.5 (21.3), 68.5 (67.3), 69.0 (69.2), 69.5, 72.9 (72.6), 73.2, 73.6, 82.1 (80.7), 91.8 (89.9), 126.4 (126.6), 127.6 (127.3), 128.2, 128.3, 128.4 (128.5), 128.7, 129.2, 129.7, 132.2 (134.1), 137.9 (136.6), 142.2, 144.6; HRMS

(FAB) Calcd for $C_{27}H_{31}O_6S$ $[M+H]^+$: 483.1131. Found: 483.1126.

1.2.8. *p*-Methylphenylsulfenyl 2,3-di-*O*-benzyl-6-*tert*-butyldiphenylsilyl-β-D-glucopyranoside (19) (mixture). R_f 0.22 (2:1 EtOAc–hexane); ^{1}H NMR ($CDCl_3$): δ 1.04 (s, 9 H), 2.20 (s, 3 H), 3.04 (br s, 1 H, OH), 3.65 (m, 1 H), 3.94–4.00 (m, 3 H), 4.21–4.60 (m, 4 H), 4.63 (d, 0.2 H, *J* 9.7 Hz), 4.70 (d, 0.8 H, *J* 9.7 Hz), 5.44–5.56 (m, 1 H), 5.60–5.75 (m, 1 H), 7.10 (d, 2 H, *J* 8.1 Hz), 7.26–7.54 (m, 14 H), 7.66–7.75 (m, 6 H), 7.95 (dd, 2 H, *J* 8.5, 1.4 Hz); ^{13}C NMR ($CDCl_3$): δ 19.2, 21.3, 26.8 (26.9), 63.3, 67.1, 69.5, 71.5, 73.8, 77.9, 80.3, 93.3, 125.4, 127.8, 128.2, 128.4, 129.0, 129.6, 129.8, 129.9, 130.0, 132.7, 133.2, 133.4, 133.6, 135.6, 144.2, 145.5; MS (FAB): 721 (45, $[M+H]^+$), 706 (100).

1.2.9. Methyl [(4-methylphenyl)sulfenyl 2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside] uronate (20). R_f 0.33 (1:1 EtOAc–hexane); ^{1}H NMR ($CDCl_3$): δ 2.36 (s, 3 H), 3.70 (s, 3 H), 4.78 (d, 1 H, *J* 10.0 Hz), 5.28 (d, 1 H, *J* 9.9), 5.71 (dd, 1 H, *J* 10.2, 3.6 Hz), 5.79 (dd, 1 H, *J* 10.0, 9.8 Hz), 6.33 (dd, 1 H, *J* 10.2, 9.8 Hz), 6.93 (d, 1 H, *J* 3.6 Hz), 7.27–7.55 (m, 10 H), 7.67 (m, 1 H), 7.87–7.95 (m, 4 H), 7.99 (dd, 2 H, *J* 8.2, 1.2 Hz), 8.16 (dd, 2 H, *J* 7.8, 1.5 Hz); ^{13}C NMR ($CDCl_3$): δ 21.9, 52.0, 61.3, 66.8, 69.1, 76.1, 89.2, 128.3 (2C), 128.4, 128.5, 128.9, 129.0, 129.7 (2C), 129.8, 129.9 (2C), 130.9, 132.2, 133.5, 133.8, 145.0, 164.8, 165.2, 166.4, 171.0; HRMS (FAB) Calcd for $C_{35}H_{31}O_{10}S$ $[M+H]^+$: 643.1073. Found: 643.1058. For another isomer: R_f 0.27 (1:1 EtOAc–hexane); ^{1}H NMR ($CDCl_3$): δ 2.47 (s, 3 H), 3.64 (s, 3 H), 4.41 (d, 1 H, *J* 9.2 Hz), 4.89 (d, 1 H, *J* 9.7 Hz), 5.45 (dd, 1 H, *J* 9.2, 9.0 Hz), 5.67 (dd, 1 H, *J* 9.7, 8.8 Hz), 5.89 (dd, 1 H, *J* 9.0, 8.8 Hz), 7.26–7.45 (m, 9 H), 7.46–7.52 (m, 2 H), 7.78 (dd, 2 H, *J* 7.5, 1.5 Hz), 7.89–7.98 (m, 6 H); ^{13}C NMR ($CDCl_3$): δ 22.6, 52.8, 60.3, 67.5, 69.3, 72.6, 88.9, 128.3 (2C), 128.4, 128.5, 128.9, 129.0, 129.7 (2C), 129.8, 129.9 (2C), 130.9, 131.2, 133.4, 133.6, 146.1, 164.9, 165.0, 166.1, 171.1; MS (FAB): 643 (25, $[M+H]^+$), 428(100).

1.2.10. Phenylsulfenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (21) (mixture). R_f 0.24 (1:1 EtOAc–hexane); ^{1}H NMR ($CDCl_3$): δ 1.80 (s, 2.4 H), 1.81 (s, 0.6 H), 1.97 (s, 2.4 H), 1.98 (s, 0.6 H), 2.00 (s, 2.4 H), 2.02 (s, 0.6 H), 3.80 (m, 0.8 H), 3.88 (m, 0.2 H), 4.06 (m, 1 H), 4.17 (m, 1 H), 4.52 (dd, 0.2 H, *J* 10.3, 10.2 Hz), 4.61 (dd, 0.8 H, *J* 8.0, 7.9 Hz), 5.05 (m, 1 H), 5.40 (d, 0.8 H, *J* 10.0 Hz), 5.46 (d, 0.2 H, *J* 10.3 Hz), 5.72 (dd, 0.8 H, *J* 10.0, 9.2 Hz), 5.77 (dd, 0.2 H, *J* 10.0, 9.9 Hz), 7.21–7.43 (m, 2 H), 7.44–7.47 (m, 2 H), 7.70–7.74 (m, 3 H), 7.80–7.84 (m, 2 H); ^{13}C NMR ($CDCl_3$): δ 20.3, 20.5, 21.4 (20.3, 21.1, 21.7), 49.7 (49.5), 61.7 (61.4), 68.2 (68.0), 71.6 (71.0), 85.5 (77.5), 86.4 (89.3), 123.3 (123.7), 126.0 (125.5), 129.2 (129.5), 129.6, 133.4 (134.1), 135.1, 142.3, 166.8 (166.6), 169.2 (168.1), 169.9 (169.9), 170.1 (170.4); HRMS (FAB) Calcd for $C_{26}H_{26}NO_{10}S$ $[M+H]^+$: 544.1220. Found: 544.1216.

1.2.11. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-azido-D-glucopyranoside (22) (mixture). R_f 0.21 (1:2 EtOAc–hexane); ^{1}H NMR ($CDCl_3$): δ 2.04–2.15 (m, 9 H), 3.65 (dd, 0.5 H, *J* 10.8, 8.0 Hz), 3.73 (dd, 0.5 H, *J* 11.0, 3.4 Hz), 3.91 (dd, 0.5 H, *J* 6.6, 6.4 Hz), 4.06–4.13 (m, 2 H), 4.46 (dd, 0.5 H, *J* 6.6, 6.5 Hz), 4.69 (d, 0.5 H, *J* 8.0 Hz), 4.81 (dd, 0.5 H, *J* 10.8, 3.3 Hz), 5.32–5.45 (m, 2 H); ^{13}C NMR ($CDCl_3$): δ 20.3 (20.4), 20.5, 20.6, 58.0, 61.8 (61.6), 66.5, 67.7 (68.3), 71.2 (70.9), 92.3 (96.4), 170.0, 170.1, 170.6; HRMS (FAB) Calcd for $C_{12}H_{18}N_3O_8$ $[M+H]^+$: 332.1094. Found: 332.1090.

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