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Note

Fast oxidation of thioglycosides to glycosyl sulfones using $KMnO_4/CuSO_4{\cdot}5H_2O$ under neutral reaction conditions☆

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Abstract—A rapid oxidation of thioglycosides to glycosyl sulfones has been achieved using a combination of $KMnO_4$ and $CuSO_4{\cdot}5H_2O$ in acetonitrile and water. This reaction protocol has many advantages compared to other methods available for this transformation, including compatibility with acid and base labile functional groups used for the protection of carbohydrates, high yields, fast reaction times, and moderate reaction temperatures. The yields obtained were excellent in all cases.

Keywords: Carbohydrates; Sulfones; Oxidation; $KMnO_4$; $CuSO_4{\cdot}5H_2O$; Thioglycosides

Sulfones are an important class of synthetic intermediates, which are, for example, used for C–C bond formation and stereocontrolled functional group transformations.[1–4] In carbohydrate chemistry, glycosyl sulfones have been used for the preparation of functionalized glycals as well as *O*- and *C*-glycosides.[5–11] A number of biologically important oligosaccharides having *C*-glycosyl linkages have been synthesized using glycosyl sulfones under samarium mediated reductive reaction conditions with excellent anomeric stereocontrol.[12–15] Apart from being used as glycosyl donors, glycosyl sulfones have also been used as potential glycosyltransferase inhibitors.[16]

In view of the importance of sulfones, several oxidizing agents have been reported for the oxidation of sulfides into sulfones,[17] including *m*-chloroperoxybenzoic acid (*m*-CPBA),[18] aqueous $KMnO_4$,[19] potassium hydrogen sulfate ($KHSO_5$),[20] hydrogen peroxide–acetic acid,[21] peroxytrifluoroacetic acid,[22] tetra-*n*-butylammonium oxone,[23] osmium tetroxide (OsO_4),[24] $PhIO/RuCl_2(PPh_3)_3$,[25] and $RuCl_3/NaIO_4$, or HIO_4.[26] Although a number of methods are available for the oxidation of sulfides to sulfones, fewer methods for the preparation of glycosyl sulfones have been investigated. These include the use of *m*-chloroperoxybenzoic acid (*m*-CPBA), magnesium bis(monoperoxyphthalate) (MMPP),[27] dimethyldioxirane (DMDO),[16] $KMnO_4$/acetic acid,[28] and $RuCl_3/NaIO_4$.[6] In general, the oxidation of thioglycosides to sulfones has been achieved most successfully using *m*-CPBA. However, this method suffers from number of shortcomings including partial solubility of *m*-CPBA in dichloromethane and difficulty in removing the byproduct (*m*-chlorobenzoic acid) from the sulfone. Other methods for the oxidation of thioglycosides into glycosyl sulfones also have notable drawbacks such as strongly acidic reaction conditions or the requirement of high temperatures. Therefore, there is a need to develop mild oxidation protocols for the transformation of thioglycosides to glycosyl sulfones that circumvent the aforementioned drawbacks. Our efforts to prepare several glycosyl sulfones using of *m*-CPBA and aqueous $KMnO_4$/AcOH or H_2O_2/AcOH reaction conditions always resulted in the removal of acid labile functional groups and in some cases deacetylated products.

Prompted by a recent paper[29] in which solid $KMnO_4$ in combination with $CuSO_4{\cdot}5H_2O$ has been successfully

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employed for the preparation of disulfides and sulfones under solvent-free reaction conditions, we envisaged that this combination could oxidize thioglycosides to sulfones under neutral reaction conditions thus avoiding the chance for the removal of acid labile protecting groups. Earlier, the $KMnO_4/CuSO_4{\cdot}5H_2O$ combination has been successfully employed for oxidation of alcohols and preparation of lactones.[30] We describe here, a convenient reaction protocol for the preparation of glycosyl sulfones under neutral reaction conditions using a combination of $KMnO_4/CuSO_4{\cdot}5H_2O$.

For our initial studies, a solution of phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside in dichloromethane was treated with solid $KMnO_4$ (2.0 equiv) at room temperature. The formation of the corresponding glycosyl sulfone was very slow and the reaction did not furnish an acceptable yield of the product. While performing the reaction in acetone the reaction proceeded well but did not reach completion. Gratifyingly, the reaction was complete in a few minutes when the same reaction was carried out at room temperature using a 1:1 mixture of $KMnO_4$ and $CuSO_4{\cdot}5H_2O$ in CH_3CN–H_2O (5:1) and the yield was almost quantitative. After some experimentation, it was observed that the use of a finely powdered premixed combination of $KMnO_4$ and $CuSO_4{\cdot}5H_2O$ (1.5:1 molar ratio) in CH_3CN–H_2O (5:1) at room temperature successfully oxidized several thioglycosides to the corresponding glycosyl sulfones in excellent yield (Scheme 1). It is worth noting that the addition of $CuSO_4{\cdot}5H_2O$ separately after the addition of $KMnO_4$ led to incomplete oxidation. Acid labile functional groups (e.g., benzylidene acetal, isopropylidene acetal, and TBDMS) used for the temporary protection of hydroxyl groups of sugar derivatives were stable to the reaction conditions. It is important to mention that use of $CuSO_4{\cdot}5H_2O$ premixed with $KMnO_4$ is essential for the completion of the reaction. Although earlier $KMnO_4$ in acetic acid at higher temperatures has been used for the preparation of glycosyl sulfones, the reaction condition was very harsh and cannot be applied for the oxidation of thioglycosides containing acid labile functional groups. Among the solvents explored (e.g., dichloromethane, 1,2-dichloroethane, nitromethane, THF, CH_3CN, and acetone), the acetonitrile–water combination was found to be the most effective in producing high yields of the product.

In summary, a series of glycosyl sulfones having a variety of functional groups have been successfully prepared by the oxidation of differentially functionalized thioglycosides using a combination of solid $KMnO_4$ and $CuSO_4{\cdot}5H_2O$ under neutral conditions. The method is compatible with acid and base labile functional groups used for the protection of carbohydrates, and is high yielding and fast. In addition, the ease of product isolation makes this reaction protocol as an attractive alternative to those existing in the literature. Samarium iodide mediated preparation of *C*-glycosides using glycosyl sulfones is underway in our laboratory.

1. Experimental

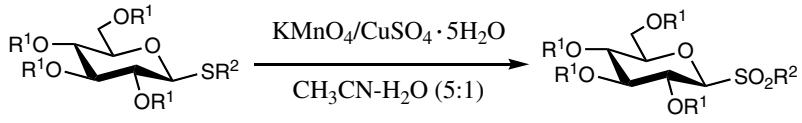
1.1. General methods

The general methods are the same as previously reported.[34]

1.2. Typical experimental protocol for the preparation of glycosyl sulfones

To a solution of thioglycoside (1.0 mmol) in CH_3CN–H_2O (5:1 v/v; 10 mL) was added a finely ground mixture of solid $KMnO_4$ and $CuSO_4{\cdot}5H_2O$ (1.5:1 molar ratio; 500 mg) and the reaction mixture was stirred at room temperature for appropriate time period(Table 1). After completion of the reaction (TLC; hexane–EtOAc 1:1), the reaction mixture concentrated under reduced pressure and the crude mass was extracted with CH_2Cl_2. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure to furnish an almost pure product (Table 1). Analytical samples were prepared by purification over SiO_2 using hexane–EtOAc as eluant. All known compounds gave acceptable ^1H NMR and ^{13}C NMR spectra that matched data reported in the cited references.

1.2.1. Phenyl 2,3,4,6-tetra-*O*-acetyl-1-sulfonyl-β-D-galactopyranoside (2b). Oil; $[\alpha]_D^{25}$ −15 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.98–7.56 (m, 5H, aromatic), 5.45 (t, $J = 9.8$ Hz, 1H), 5.31 (d, $J = 3.5$ Hz, 1H), 5.04 (dd, $J = 9.8$, 3.1 Hz, 1H), 4.50 (d, $J = 9.7$ Hz, 1H), 4.14–4.03 (m, 1H), 3.98–3.88 (m, 2H), 2.14, 1.98, 1.97, 1.89 (4s, 12H, 4COCH_3); IR (Neat): 2363, 1751, 1222, 1080, 758 cm^{-1}; ESI-MS: $m/z = 495$ [M+Na]. Anal. Calcd for $C_{20}H_{24}O_{11}S$: C, 50.84; H, 5.12. Found: C, 51.02; H, 5.35.



Scheme 1.

Table 1. Oxidation of thioglycosides to glycosyl sulfones using $KMnO_4$ and $CuSO_4{\cdot}5H_2O$ in CH_3CN–H_2O at room temperature

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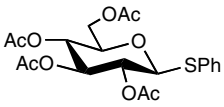
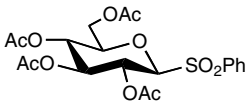
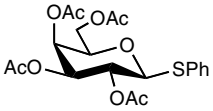
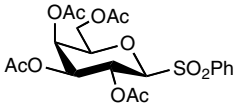
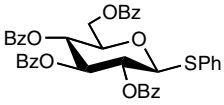
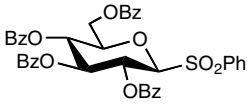
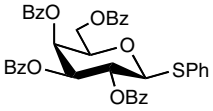
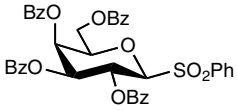
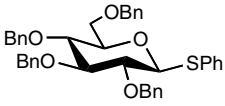
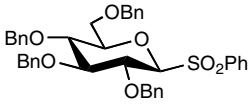
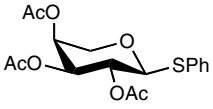
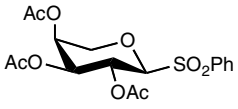
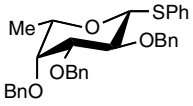
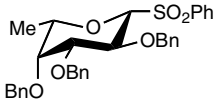
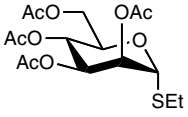
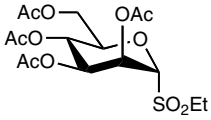
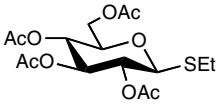
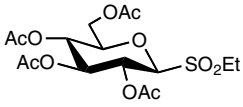
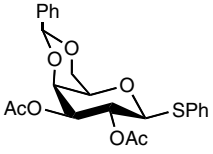
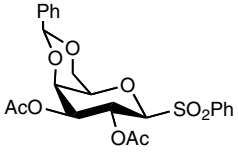
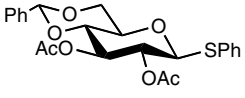
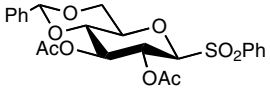
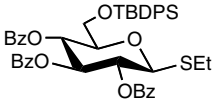
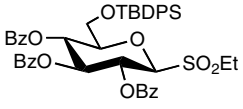
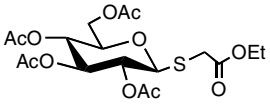
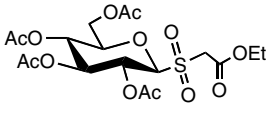
a			30	95	28
b			30	95	—
c			45	92	—
d			45	96	—
e			25	92	31
f			30	90	28
g			25	88	—
h			30	90	—
i			30	92	—
j			30	85	5
k			30	90	—
l			25	90	—
m			60	85	—

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Table 1 (*continued*)

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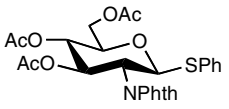
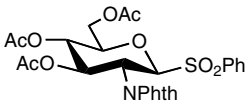
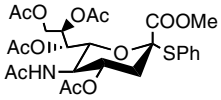
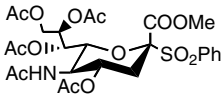
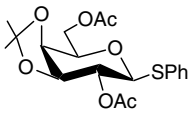
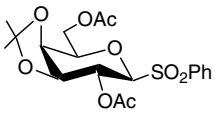
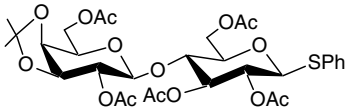
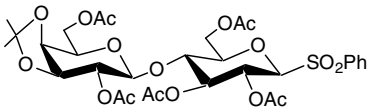
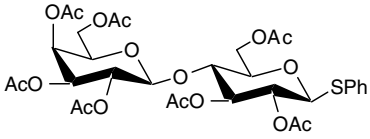
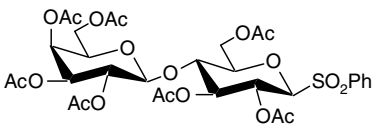
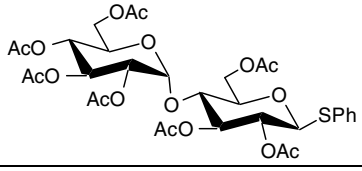
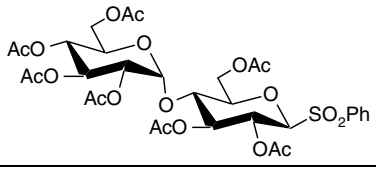
n			45	92	—
o			45	85	32
p			30	95	6
q			45	92	5
r			45	95	33
s			45	95	—

1.2.2. Phenyl 2,3,4,6-tetra-*O*-benzoyl-1-sulfonyl-β-D-glucopyranoside (2c). White solid; mp 175–177 °C; $[\alpha]_D^{25}$ +2.4 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.99–7.26 (m, 25H, aromatic), 5.91 (t, $J = 9.3$ Hz, 1H), 5.87 (t, $J = 9.6$ Hz, 1H), 5.50 (t, $J = 9.6$ Hz, 1H), 4.87 (d, $J = 9.6$ Hz, 1H), 4.60 (d, $J = 11.7$ Hz, 1H), 4.38 (dd, $J = 12.3$, 4.8 Hz, 1H), 4.20–4.17 (m, 1H); IR (KBr): 2366, 1732, 1590, 1263, 1106, 718 cm^{-1}; ESI-MS: $m/z = 743$ [M+Na]. Anal. Calcd for $C_{40}H_{32}O_{11}S$: C, 66.66; H, 4.48. Found: C, 66.48; H, 4.70.

1.2.3. Phenyl 2,3,4,6-tetra-*O*-benzoyl-1-sulfonyl-β-D-galactopyranoside (2d). White solid; mp 168 °C; $[\alpha]_D^{25}$ +36 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz): δ 8.08–7.26 (m, 25H, aromatic), 6.01 (t, $J = 9.8$ Hz, 1H), 5.94 (d, $J = 3.9$ Hz, 1H), 5.58 (dd, $J = 9.8$, 3.1 Hz, 1H), 4.93 (d, $J = 9.9$ Hz, 1H), 4.60 (dd, $J = 10.8$, 6.2 Hz, 1H), 4.50 (t, $J = 6.0$ Hz, 1H), 4/28 (dd, $J = 10.8$, 5.6 Hz, 1H); IR (KBr): 2363, 1727, 1593, 1256, 1099, 711 cm^{-1}; ESI-MS: $m/z = 743$ [M+Na]. Anal. Calcd for $C_{40}H_{32}O_{11}S$: C, 66.66; H, 4.48. Found: C, 66.40; H, 4.70.

1.2.4. Phenyl 2,3,4-tri-*O*-benzyl-6-deoxy-1-sulfonyl-β-L-galactopyranoside (2g). Oil; $[\alpha]_D^{25}$ −63 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.97–7.04 (m, 20H, aromatic), 5.46 (d, $J = 2.1$ Hz, 1H), 5.37 (dd, $J = 9.6$, 3.0 Hz, 1H), 4.94 (d, $J = 9.9$ Hz, 1H), 4.59–4.53 (m, 5H), 4.52–4.39 (m, 2H), 3.75–3.73 (m, 1H), 1.02 (d, $J = 6.0$ Hz, 3H); IR (Neat): 2922, 2364, 1726, 1275, 1100, 757 cm^{-1}; ESI-MS: $m/z = 581$ [M+Na]. Anal. Calcd for $C_{33}H_{34}O_6S$: C, 70.94; H, 6.13. Found: C, 70.70; H, 6.40.

1.2.5. Ethyl 2,3,4,6-tetra-*O*-acetyl-1-sulfonyl-α-D-mannopyranoside (2h). White solid; mp 101–103 °C; $[\alpha]_D^{25}$ +39.6 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz): δ 5.90 (br s, 1H), 5.54 (dd, $J = 9.0$, 3.5 Hz, 1H), 5.24 (t, $J = 9.4$ Hz, 1H), 4.81 (br s, 1H), 4.66–4.59 (m, 1H), 4.27 (dd, $J = 12.4$, 5.4 Hz, 1H), 4.12 (dd, $J = 12.4$, 1.7 Hz, 1H), 3.14 (q, $J = 7.4$ Hz, 2H), 2.17, 2.09, 2.06, 2.02 (4s, 12H, $4COCH_3$), 1.44 (t, $J = 7.4$ Hz, 3H); IR (KBr): 2922, 2363, 1748, 1219, 768 cm^{-1}; ESI-MS: $m/z = 447$ [M+Na]. Anal. Calcd for $C_{16}H_{24}O_{11}S$: C, 45.28; H, 5.70. Found: C, 45.04; H, 6.0.

1.2.6. Ethyl 2,3,4,6-tetra-*O*-acetyl-1-sulfonyl-β-D-glucopyranoside (2i). White solid; mp 153–154 °C; $[\alpha]_D^{25}$ −16.2 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz): δ 5.48 (t, $J = 9.6$ Hz, 1H), 5.31 (t, $J = 9.3$ Hz, 1H), 5.12 (t, $J = 9.6$ Hz, 1H), 4.45 (d, $J = 9.9$ Hz, 1H), 4.30–4.18 (m, 2H), 3.85–3.81 (m, 1H), 3.19–3.09 (m, 2H,

SCH_2CH_3), 2.09, 2.07, 2.05, 2.03 (4s, 12H, $4COCH_3$), 1.40 (t, $J = 7.5$ Hz, 3H, SCH_2CH_3); IR (KBr): 2947, 1748, 1228, 1111, 1037, 722, 595 cm^{-1}; ESI-MS: $m/z =$ 447 [M+Na]. Anal. Calcd for $C_{16}H_{24}O_{11}S$: C, 45.28; H, 5.70. Found: C, 45.05; H, 5.97.

1.2.7. Phenyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-sulfonyl-β-D-glucopyranoside (2k). White solid; mp 189–190 °C, $[\alpha]_D^{25}$ −73.2 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.94–7.26 (m, 10H, aromatic), 5.42 (s, 1H), 5.36–5.28 (m, 2H), 4.60 (d, $J = 9.5$ Hz, 1H), 4.30 (dd, $J = 7.9$, 3.3 Hz, 1H), 3.70–3.51 (m, 3H), 2.10, 2.03 (2s, 6H, $2COCH_3$); IR (KBr): 2926, 1757, 1372, 1234, 1083, 760 cm^{-1}; ESI-MS: $m/z = 499$ [M+Na]. Anal. Calcd for $C_{23}H_{24}O_9S$: C, 57.97; H, 5.08. Found: C, 57.75; H, 5.30.

1.2.8. Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-1-sulfonyl-β-D-glucopyranoside (2l). White solid; mp 156–158 °C, $[\alpha]_D^{25}$ +9 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.96–7.21 (m, 25H, aromatic), 6.02 (t, $J = 9.1$ Hz, 1H), 5.91 (t, $J = 9.0$ Hz, 1H), 5.72 (t, $J = 9.5$ Hz, 1H), 4.78 (d, $J = 9.0$ Hz, 1H), 4.01–3.94 (m, 1H), 3.91–3.86 (m, 2H), 3.20 (q, $J = 15.0$, 6.0 Hz, 2H), 1.40 (t, $J = 7.5$ Hz, 3H), 1.04 (s, 9H); IR (KBr): 2929, 1736, 1262, 1105, 707 cm^{-1}; ESI-MS: $m/z = 829$ [M+Na]. Anal. Calcd for $C_{45}H_{46}O_{10}SSi$: C, 66.97; H, 5.75. Found: C, 66.70; H, 6.0.

1.2.9. Ethoxycarbonylmethyl 2,3,4,6-tetra-*O*-acetyl-1-sulfonyl-β-D-glucopyranoside (2m). White powder; $[\alpha]_D^{25}$ −22.2 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz): δ 5.53 (t, $J = 9.8$ Hz, 1H), 5.30 (t, $J = 9.2$ Hz, 1H), 5.10 (t, $J = 9.8$ Hz, 1H), 4.88 (d, $J = 9.9$ Hz, 1H), 4.33 (d, $J = 15$ Hz, 1H), 4.30–4.22 (m, 4H), 3.87–3.80 (m, 2H), 2.08, 2.05, 2.04, 2.03 (4s, 12H, $4COCH_3$), 1.39–1.32 (t, $J = 7.1$ Hz, 3H); IR (KBr): 2960, 2363, 1750, 1594, 1350, 1224 cm^{-1}; ESI-MS: $m/z = 505$ [M+Na]. Anal. Calcd for $C_{18}H_{26}O_{13}S$: C, 44.81; H, 5.43. Found: C, 44.57; H, 5.55.

1.2.10. Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-sulfonyl-β-D-glucopyranoside (2n). Oil; $[\alpha]_D^{25}$ +13 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.91–7.56 (m, 9H, aromatic), 5.76 (t, $J = 9.6$ Hz, 1H), 5.45 (d, $J = 10.5$ Hz, 1H), 4.99 (t, $J = 9.6$ Hz, 1H), 4.55 (t, $J = 10.2$ Hz, 1H), 4.26–4.09 (m, 2H), 2.01, 1.87 (2s, 9H, $3COCH_3$); IR (Neat): 2924, 2363, 1750, 1722, 1383, 1224, 768 cm^{-1}; ESI-MS: $m/z = 582$ [M+Na]. Anal. Calcd for $C_{26}H_{25}NO_{11}S$: C, 55.81; H, 4.50. Found: C, 55.60; H, 4.79.

1.2.11. Phenyl 2,6-di-*O*-acetyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-1-sulfonyl-β-D-glucopyranoside (2q). White solid; mp 95–97 °C; $[\alpha]_D^{25}$ +5.4 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.91–7.53 (m, 5H, aromatic), 5.32–5.30 (m, 1H), 5.28–5.23 (m, 1H), 4.85–4.78 (m, 1H), 4.46 (d, $J = 9.6$ Hz, 1H), 4.41 (br s, 1H), 4.32–4.25 (m, 3H), 4.13–4.04 (m, 3H), 3.92–3.86 (m, 1H), 3.65–3.60 (m, 2H), 2.11, 2.09, 2.04, 2.03, 1.97 (5s, 15H, $5COCH_3$), 1.50, 1.30 (2s, 6H); IR (KBr): 2992, 2363, 1753, 1592, 1378, 1230, 1051, 590 cm^{-1}; ESI-MS: $m/z = 739$ [M+Na]. Anal. Calcd for $C_{31}H_{40}O_{17}S$: C, 51.95; H, 5.63. Found: C, 51.75; H, 5.90.

1.2.12. Phenyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-1-sulfonyl-β-D-glucopyranoside (2s). Oil; $[\alpha]_D^{25}$ +51 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz): δ 7.90–7.55 (m, 5H, aromatic), 5.35–5.28 (m, 2H), 5.12 (t, $J = 9.3$ Hz, 1H), 5.02 (t, $J = 9.9$ Hz, 1H), 4.82 (dd, $J = 10.5$, 3.9 Hz, 1H), 4.54 (d, $J = 10.2$ Hz, 2H), 4.20 (dd, $J = 12.0$, 3.6 Hz, 1H), 4.14–4.08 (m, 1H), 4.02 (d, $J = 12.6$ Hz, 1H), 3.82 (t, $J = 9.3$ Hz, 2H), 3.70–3.67 (m, 2H), 2.10, 2.08, 2.03, 2.01, 2.00 (5s, 21H, $7COCH_3$); IR (Neat): 2928, 1753, 1235, 1038, 760 cm^{-1}; ESI-MS: $m/z = 783$ [M+Na]. Anal. Calcd for $C_{32}H_{40}O_{19}S$: C, 50.52; H, 5.30. Found: C, 50.30; H, 5.50.

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