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# Photoinduced C−S Bond Cleavage of Thioglycosides and Glycosylation

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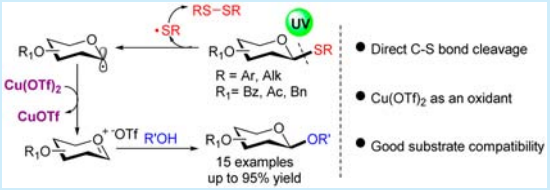
Supporting Information

**ABSTRACT:** A glycosyl coupling reaction via photoinduced direct activation of thioglycosides and subsequent *O*-glycosylation in the absence of photosensitizer was developed for the first time. This reaction underwent a selectively homolytic cleavage of a C−S bond to generate a glycosyl radical, which was oxidized to an oxacarbenium ion by $Cu(OTf)_2$, and a sequential *O*-glycosylation. A wide range of glycosides were synthesized in moderate to excellent yield using sugars, amino acids, or cholesterol as the acceptors.

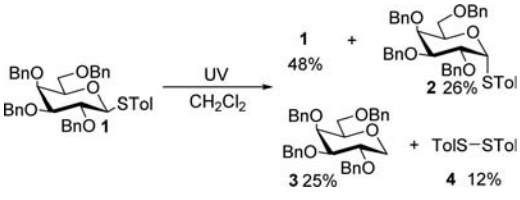



The vital role of carbohydrates in biology has made them very popular synthetic targets in modern synthetic chemistry. The construction of oligosaccharides mainly depends on the development of glycosylation methods.[1] Chemical glycosylation refers to the cleavage of the glycosidic bond of a donor using chemical or physical means to generate a glycosyl oxacarbenium species, which undergoes the following coupling reaction with an acceptor.[2] Although many methods for glycosylation have been reported,[3] the development of universal and efficient approaches for oligosaccharide synthesis is still highly desirable. In the process of glycosylation, fragmentation of the glycosidic bond of a donor with high selectivity and efficiency is of great importance.[4] Therefore, the activation of a donor by chemical or physical means is a subject of continuous research. Thioglycosides are one of the most enduring and widely used donors, owing to their stability, accessibility, and compatibility.[5] The sulfur atom in a thioglycoside is able to selectively react with a soft electrophile. A series of promoters for the activation of thioglycosides have been developed, including metal salts,[6] halonium reagents,[7] organosulfur reagents,[8] and single electron transfer (SET) reagents.[9] Thioglycosides could also be electrochemically activated via the SET mechanism.[10]

Photoinduced electron transfer is undoubtedly one of the emerging strategies to meet the increasing demand for more sustainable chemical processes.[11] The activation of thioglycosides by light usually required a photosensitizer or a photocatalyst. Some methods involving the photoinduced activation of thioglycosides have been reported. Armed (*p*-methoxy)phenyl thioglycosides could undergo a visible light mediated photoredox *O*-glycosylation reaction,[12] while disarmed (*p*-methoxy)phenyl thioglycosides were unreactive. Unprotected deoxythioglycosyl donors were able to perform a reaction with alcohols using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in the presence of a boronic acid. Nevertheless, sugar substrates could not be used as acceptors.[13] Irradiation of a permethylated thioglycoside with a high-pressure mercury lamp in the presence of 1,4-dicyanonaphthalene and methanol resulted in the methyl glycoside and other byproducts in low yields.[14] This method was not compatible with benzyl ether protected substrates and incapable of activating the disarmed thioglycosides. In addition, the photoinduced activation of other donors such as phenyl glycosides,[15] selenoglycosides,[16] and glycosyl trichloroacetimidates[17] also provided good proof-of-concepts for chemical glycosylation. However, all these photomediated glycosylation methods lack generality to some extent, either for the donor or for the acceptor. Improvement of the activation of a donor by light is still an important issue.

It was found that UV light had the energy capable of breaking the C−S bond.[18] As part of our continuous studies on the activation of thioglycosides and glycosylation,[19] we imagined that UV light could directly make the C−S bond rupture in thioglycosides without a photosensitizer. To verify this, *β*-thiogalactopyranoside **1** was irradiated for 22 h (Scheme 1). Indeed, the C−S bond cleavage took place; thus, *β*-thiogalactopyranoside **1** (48% yield), *α*-thiogalactopyranoside **2** (26% yield), 1,5-anhydro-galactitol **3** (25% yield), and TolSSTol (**4**,

**Scheme 1. Irradiation of Thioglycoside 1 with UV Light**

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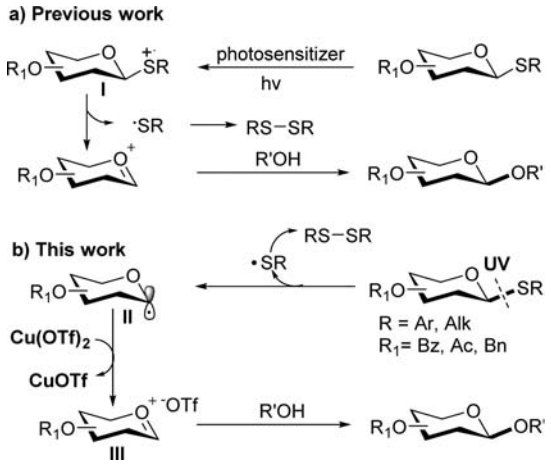
12% yield) were isolated. This suggested a possible homolytic cleavage of **1** to produce galactosyl radical and *p*-tolylthiyl radical, which underwent recombination, dimerization, or hydrogen atom abstraction to generate the above-mentioned products. Therefore, we envisaged that the glycosylation of a thioglycoside with an acceptor would proceed upon ultraviolet illumination in the presence of a proper oxidant, which oxidizes a glycosyl radical (II) to a glycosyl oxacarbenium ion (III), as shown in Scheme 2. This glycosylation protocol would differ

**Scheme 2. Strategy for Light-Induced Activation of Thioglycosides and Glycosylation**

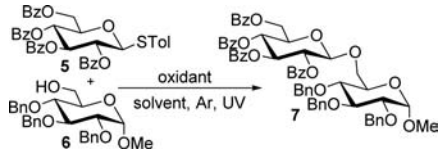



from the traditional light-mediated glycosylation involving a *S*-radical cation (I). Herein, we report a new *O*-glycosylation protocol via photoinduced direct C−S bond cleavage of thioglycosides and a subsequent oxidation by $Cu(OTf)_2$.

To test the feasibility of our idea, examination and optimization of the reaction parameters were explored using the model reaction between perbenzoylated thioglucopyranoside **5** and the glucosyl acceptor **6** with the C-6 hydroxyl exposed by varing different oxidants and conditions. The results are shown in Table 1. Either photoirradiation in the absence of oxidants, or oxidants in the absence of photoirradiation, resulted in no glycosylation, and the glycosyl donor **5** was recovered quantitatively (entries 1, 13−14). As expected, the desired disaccharide **7** was obtained by the addition of metal salts as oxidants (entries 2−7, 0−28% yields). These results clearly indicated that the combination of an oxidant and photoirradiation together triggered the glycosylation. Among the metal salts, $Cu(OTf)_2$ afforded the most remarkable result (entry 8, 75% yield). The yield of **7** was improved gradually as the equivalent of $Cu(OTf)_2$ was increased (entries 8−10, 75−90%). The glycosylation yield decreased when increasing the amount of glycosyl acceptor **6** (entries 10−12). Dichloromethane was the most appropriate solvent (entries 15−16). So the optimized conditions included a donor (1.0 equiv), an acceptor (0.5 equiv), $Cu(OTf)_2$ (1.7 equiv), and activated 4 Å molecular sieves (200 mg), in $CH_2Cl_2$ (0.01 M) under the irradiation of UV light at room temperature for 22 h. The symmetric bis(*p*-methylphenyl)disulfide (**4**) was isolated as another major product.

The scope of glycosylation of the disarmed donor **5** with various acceptors was next investigated under the optimal conditions (Table 2, entries 1−7). The reactions of **5** with primary alcohol **8** (entry 1, 70%), secondary alcohol **10** (entry

**Table 1. Optimization of the Glycosylation Reaction Conditions**[a]




| entry[a] | **5** (equiv)/**6** (equiv) | oxidant (equiv) | solvent | yield (%)[b] |
|---|---|---|---|---|
| 1 | 1/0.5 | – | $CH_2Cl_2$ | 0 |
| 2 | 1/0.5 | $InBr_3$ (1.0) | $CH_2Cl_2$ | 13 |
| 3 | 1/0.5 | $CuCl_2$ (1.0) | $CH_2Cl_2$ | trace |
| 4 | 1/0.5 | $CuSO_4$ (1.0) | $CH_2Cl_2$ | 28 |
| 5 | 1/0.5 | $Cu(OAc)_2$ (1.0) | $CH_2Cl_2$ | trace |
| 6 | 1/0.5 | $RuCl_3$ (1.0) | $CH_2Cl_2$ | trace |
| 7 | 1/0.5 | $InCl_3$ (1.0) | $CH_2Cl_2$ | 20 |
| 8 | 1/0.5 | $Cu(OTf)_2$ (1.0) | $CH_2Cl_2$ | 75 |
| 9 | 1/0.5 | $Cu(OTf)_2$ (1.5) | $CH_2Cl_2$ | 79 |
| 10 | 1/0.5 | $Cu(OTf)_2$ (1.7) | $CH_2Cl_2$ | 90 |
| 11 | 1/0.75 | $Cu(OTf)_2$ (1.7) | $CH_2Cl_2$ | 80 |
| 12 | 1/1 | $Cu(OTf)_2$ (1.7) | $CH_2Cl_2$ | 67 |
| 13[c] | 1/0.5 | $Cu(OTf)_2$ (1.0) | $CH_2Cl_2$ | 0 |
| 14[d] | 1/0.5 | $Cu(OTf)_2$ (1.0) | $CH_2Cl_2$ | 0 |
| 15 | 1/0.5 | $Cu(OTf)_2$ (1.7) | $CH_3CN$ | 86 |
| 16 | 1/0.5 | $Cu(OTf)_2$ (1.7) | $Et_2O$ | 62 |

[a]The reactions were carried out with **5** (0.04 mmol), **6**, oxidant, activated 4 Å molecular sieves (200 mg), solvent (2.0 mL) in a quartz flask at room temperature for 22 h under argon atmosphere. [b]Isolated yield. [c]No UV irradiation. [d]Reflux in the absence of UV.

2, 88%), or tertiary alcohol **12** (entry 3, 81%) gave the corresponding glycosides in moderate to excellent yields. However, in the case of acceptor **14**, the desired glycosyl coupling product **15** was obtained in moderate yield (entry 4, 52%), and a large amount of complicated byproducts was detected. It was also found that cholesterol **16** (entry 5, 75%) or the appropriately protected amino acid **18** (entry 6, 86%) could be employed as glycosyl acceptors. This glycosylation protocol was compatible with isopropylidene, benzyl, and other conventional protective groups. Furthermore, the reaction of the disarmed donor **5** with low-reactive acceptor **20** proceeded smoothly (entry 7, 55% yield). This is attractive because it is unable to be achieved by the existing photomediated glycosylation protocols.

Encouraged by these results, we further evaluated the reaction between a wide range of thioglycoside donors and glycosyl acceptors. The glycosylations of the acylated galactosyl (**22** and **24**, entries 8−9, 76% and 69%, respectively) or rhamnosyl donor (**27**, entry 10, 80%) with the glucosyl acceptor **6** or **25**, having a free hydroxyl group at the C-6 or C-3 position, proceeded in good yield. The reactions of the benzylated glucosyl donor **29** with acceptors **6** or **20** afforded the desired disaccharides in moderate (entry 11, 65%, $\alpha/\beta$ = 1.2/1) to excellent (entry 12, 95%, $\alpha/\beta$ = 1.7/1) yields, but with poor stereoselectivity. The stereoselectivity was shifted toward the $\alpha$ isomer by the use of ether or toward the $\beta$ isomer by the use of acetonitrile as solvent, which might be explained by the participation of the solvent (entry 12).[20] Interestingly, the $\alpha$-linked disaccharide **32** was obtained with exceptionally high $\alpha$-anomeric selectivity by using the benzylated galactosyl donor **1** (entry 13, 87%). The activation and *O*-glycosylation of ethyl thioglycoside **33** under the same conditions also worked well (entry 14, 85%).



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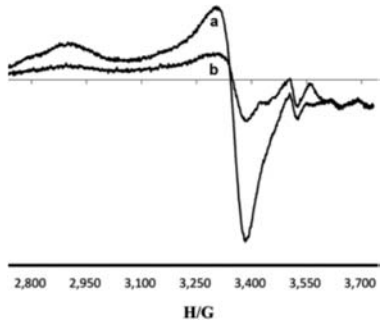
**Table 2. Reactions of Glycosyl Donors and Acceptors**[a]

| entry | donor | acceptor | product (yield)[b] |
|---|---|---|---|
| 1 | 5 | 8 | 9 (70%) |
| 2 | 5 | 10 | 11 (88%) |
| 3 | 5 | 12 | 13 (81%) |
| 4 | 5 | 14 | 15 (52%) |
| 5 | 5 | 16 | 17 (75%) |
| 6 | 5 | 18 | 19 (86%) |
| 7 | 5 | 20 | 21 (55%) |
| 8 | 22 | 6 | 23 (76%) |
| 9 | 24 | 25 | 26 (69%) |
| 10 | 27 | 25 | 28 (80%) |
| 11 | 29 | 20 | 30 (65%, α/β = 1.2/1) |
| 12 | 29 | 6 | 31 (95%, α/β = 1.7/1; 90%;[c] 59%;[d]) |
| 13 | 1 | 6 | 32 (87%) |
| 14 | 33 | 6 | 23 (85%) |

[a]Reaction conditions: donor (0.04 mmol), acceptor (0.5 equiv), $Cu(OTf)_2$ (1.7 equiv), activated 4 Å molecular sieves (200 mg), $CH_2Cl_2$ (2.0 mL) in a quartz flask at room temperature under argon atmosphere. [b]Isolated yield. [c]Acetonitrile as solvent, $\alpha/\beta$ = 1/2.7. [d]Diethyl ether as solvent, $\alpha/\beta$ = 2.8/1.

Finally, we probed the mechanism of this new type of glycosylation protocol using the reaction of **1** with **6**. The dark control experiments showed no conversion of the thioglycoside either at room temperature or with heating to 40 °C (entries 13−14, Table 1). Compounds **2**, **3**, and **4** could be detected under the irradiation of UV light, whether in the presence of $Cu(OTf)_2$ or not. The reaction was almost inhibited by the addition of 2,2,6,6-tetramethylpiperidinooxy (TEMPO, 3.0 equiv), a radical trapper. These observations indicated the presence of a glycosyl radical and *p*-tolylthiyl radical, resulting from a direct homolytic cleavage of the C−S bond upon UV irradiation. In the reaction process, the remarkable decrease of $Cu(OTf)_2$, which was determined by EPR spectroscopy,[21] confirmed that the $Cu(OTf)_2$ served as the oxidant (Scheme 3). The overall mechanism differs substantially from other

**Scheme 3. EPR Experiments**[a]




[a]The reaction was carried out with **1**, **6**, $Cu(OTf)_2$ (1.7 equiv), and $CH_2Cl_2$ (1.0 M solution) in a quartz capillary tube with UV irradiation at room temperature. (a) Before and (b) after UV irradiation for 30 min.

photomediated glycosylation reactions that involve a *S*-radical cation intermediate, and it is what we imagined (Scheme 2). Even so, we could not rule out the possibility that part of the thioglycosides were activated by a newly generated thioradical, or copper(II) was involved in the photolytic cleavage of the thioglycoside bond.

In conclusion, we have shown that the activation of thioglycosides upon the UV irradiation followed by the oxidation of $Cu(OTf)_2$ leads to the *in situ* formation of species that can undergo glycosylation to afford glycosides in moderate to excellent yields without the need for a photosensitizer. A wide range of substrates were tolerated, including sugars, amino acids, and cholesterol. Acyl, benzyl, benzyloxycarbonyl, and isopropylidene protective groups and double bond functionality were compatible with these conditions. Specially, the thorny reactions of the "disarmed" donors with the low-reactive acceptors proceeded smoothly. The reaction mechanism via a homolytic cleavage of a C−S bond and a subsequent oxidation was supported by analysis of the products and byproducts, TEMPO-inhibition experiments, and EPR experiments. In contrast with the existing light-induced glycosylation methods, this protocol features a broad substrate scope, excellent functional group compatibility, and a unique mechanism involving the direct C−S bond cleavage of thioglycosides to generate a glycosyl radical and a subsequent oxidation by $Cu(OTf)_2$. The disclosed protocol not only provides a novel glycosylation method with high generality and applicability but also paves a new avenue for the reaction via a glycosyl radical.[22] Further studies toward this direction are underway in our laboratory and will be reported in due course.



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## ■ ASSOCIATED CONTENT

### Supporting Information

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Experimental details, characterization data for compounds (PDF)

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### Notes

The authors declare no competing financial interest.

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