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Synthetic Methods

A Visible-Light-Driven *O*-Glycosylation with Selenoglycosides Mediated by Chalcogen Bonding to Umemoto's Reagent

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Abstract: The activation of chalcogenoglycosides for *O*-glycosylation typically involves strong electrophiles requiring low temperature. Herein, we demonstrate that visible-light irradiation of selenoglycosides in the presence of Umemoto's reagent results in often high-yielding *O*-glycosylation. We provide evidence that this process is mediated by a novel mode of reactivity, specifically photoinduced electron transfer within a chalcogen-bonded complex.

O-Glycosylation remains the most critical transformation in the assembly of oligosaccharides and glycoconjugates, and the diversity of approaches to this transformation reported through the past 110+ years serves as a testament to the unsolved nature of this problem. Of the glycosylation donors utilized by chemists, chalcogenoglycosides, especially thioglycosides, are a workhorse for *O*-glycosylation protocols. Chalcogenoglycosides are prized for their stability, ease of manipulation in multistep synthesis, and also the tunability of their reactivity.[1,2] However, the very stability of chalcogenoglycosides often means that they require activation with highly reactive electrophiles. In situ generation of strongly reactive electrophiles from relatively moribund precursors serves as one solution to this problem[3,4]; however, photochemistry is also proving an effective alternative to reactive electrophiles wherein photons supply much of the free energy needed to activate chalcogenoglycosides.[5–10]

In the realm of photochemical *O*-glycosylation with chalcogenoglycosides, those methods which employ commercially available reagents, avoid the use of catalysts, employ irradiation with visible-light sources, homogeneous solutions (enabling automated and "flow" approaches to synthesis),[11,12] and relatively simple chalcogenoglycoside donors are the most desirable. In our opinion, no single method in the chemical literature up to this point meets all of these criteria. An early method from our lab employed visible-light sources but utilized an unusual thioaglycone and heterogeneous conditions.[13] Likewise, contributions from Niu and co-workers employed an unusual allylsulfone aglycone and heterogeneous conditions but were nevertheless characterized by versatility, high yields, and high 1,2-*cis*-selectivity.[14] Further, the elegant work of Ye and Xiong has employed thioglycoside donors along with Umemoto's reagent, a copper catalyst, and irradiation with an ultraviolet source or employment of a visible-light source and a precious metal photocatalyst.[11,15,16] Nevertheless, their approach has proven amenable to both automated synthesis and the preparation of complex glycans.

An underexplored but promising approach to *O*-glycosylation involves the employment of halogen bonding and chalcogen bonding for the activation of donors. Halogen bonding and chalcogen bonding involve the interaction of electron-pair donors (the chalcogen/halogen-bond acceptor) with low-lying σ^* orbitals (sometimes termed the "sigma hole") of C─X bonds (chalcogen/halogen-bond donor) wherein X is a group VIA or VIIA atom other than oxygen and fluorine and only rarely chlorine. Such interactions have proven useful in synthesis, materials science, and supramolecular chemistry.[17–22] Further, Loh and co-workers have published reports on ground-state, strain-release-driven *O*-glycosylation with cyclopropane-bearing donors utilizing both halogen and chalcogen bonding[23–26] while Codée and Huber have published limited results on a halogen-bond-activated glycosylation with glycosyl halides.[27]

Particularly intriguing to us was a recent report indicating a chalcogen-bonding interaction between diselenide chalcogen-bond acceptors and *S*-alkynyl dibenzothiophenium salt donors.[28] Visible-light irradiation of these complexes resulted in generation of *Se*-alkynylated products. Inspired by these observations, we envisioned (Scheme 1) a photochemical *O*-glycosylation in which chalcogen bond formation between the Se of a phenylselenoglycoside (e.g., **1**) and the positively charged sulfur of a commercially available *S*-trifluoromethyldibenzothiophenium salt (Umemoto's reagent, **2**) will result in a chalcogen-bonded EDA complex **3** capable of absorbing visible light.[14,28] Formation of **3** would be a prerequisite to a photoinduced electron transfer (which is characteristic of EDA complexes upon visible-light

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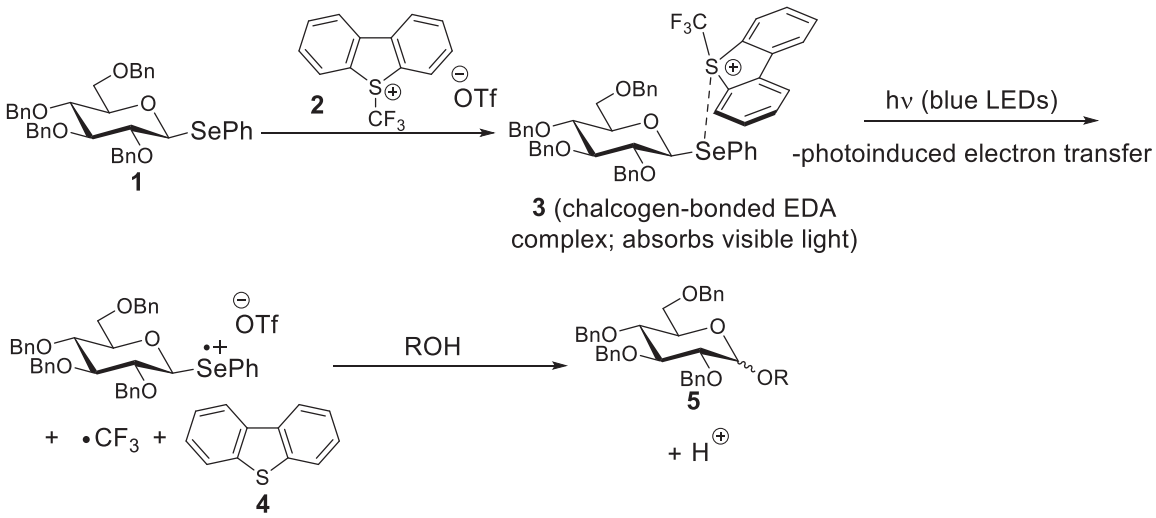
Additional supporting information can be found online in the Supporting Information section

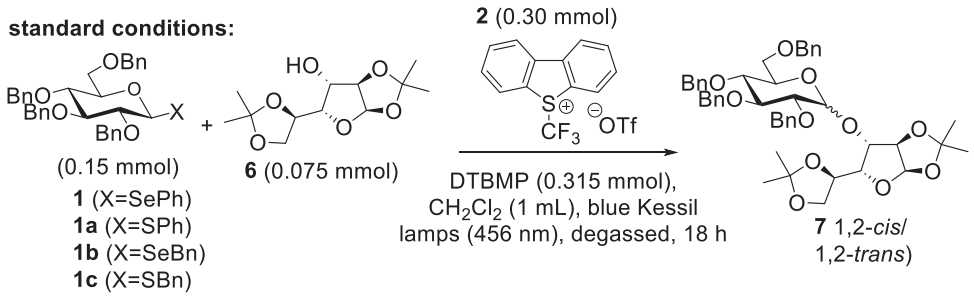


Scheme 1. Mechanistic hypothesis.

irradiation[29–31]) and eventual *O*-glycosylation (**1→5**). The commercial availability of Umemoto's reagent, judicious choice of solvents, and irradiation with blue light-emitting diodes (LEDs) imply steps taken toward the development of a photochemical *O*-glycosylation meeting all of the previously mentioned criteria. Worthy of emphasis is the relatively *low* toxicity of organoselenides and unfair stigma against these species[32,33] in addition to their relatively scant use in photochemical *O*-glycosylation[34–36] despite their stability and predicted ease of ionization relative to thioglycosides per Scheme 1. Herein, we report our results on the investigation of the mechanistic hypothesis in Scheme 1. We have developed a novel chalcogen-bond-mediated *O*-glycosylation characterized by high yields, ease of setup, relatively simple substrates, homogeneous reaction mixtures (under certain conditions), irradiation with visible light, amenability toward flow chemistry, and high 1,2-*cis*-selectivity under certain circumstances.

After a series of trials, we noted (Scheme 2, entry 1) a near-quantitative yield of *O*-glycoside **7** after 18 h irradiation (two blue Kessil lamps 50 W, $\lambda_{max} = 456$ nm, see Supporting Information section) of a degassed CH_2Cl_2 solution of selenoglycoside **1** (2 equiv.) and acceptor **6** (1 equiv.) in the presence of Umemoto's reagent (**2**, 4 equiv.) and the base 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, 4.2 equiv.). Conditions such as this would serve us well in subsequent substrate scope studies. In addition, similar arylthio-, alkylseleno-, and alkylthioglycoside donors (entries 2, 3, and 4, respectively) provided inferior results, and this may reflect an increased barrier to photoinduced electron transfer and/or inefficient formation of EDA complexes. Further, heating to 30 °C in the dark also failed to produce **7**, suggesting that visible-light irradiation is necessary while any adventitious heating is not likely the cause of reaction (entry 5). A 20 mol.% quantity of Umemoto's reagent failed to produce any product **7** (entry 6) while reduction to 3 equiv. had a minimal effect on the yield (entry 7). Use of only 1 equiv. of DTBMP likewise resulted in decomposition, suggesting that acid by-products may be damaging (entry 8). In addition, degassing proved essential (entry 9) while irradiation for only 5 h was not notably deleterious to yield (entry 10). The generally poor selectivity that we observe in the D-glucose series here and throughout this study, *especially with the most reactive acceptors*, may reflect reaction of alcohols of varying nucleophilicity with rapidly equilibrating α- and β-glycosyl triflates.[37] Further, with addition of 0.2 mL of DMF using conditions that were otherwise identical to entry 1, we saw homogeneous reaction and an improvement in 1,2-*cis*-selectivity from 2.3:1 (1,2-*cis*/1,2-*trans*) to 16:1 with comparable yields to entry 1 (entry 11). This is a well-documented phenomenon,[38] and it is significant that Lewis-basic DMF did not interfere with the reaction measurably. It is worthy of mention that homogeneity in the presence of DMF suggests the potential adaptability of methods like this to a flow apparatus or to automated systems.[11,12] Finally, conducting the reaction under conditions otherwise identical to entry 1 but with violet (390 nm) Kessil lamps resulted in comparable yield (95%, entry 12).

With successes in Scheme 2 noted, we conducted a substrate scope study which also incorporated some investigation on 1,2-*cis*-selectivity using the aforementioned DMF approach (Scheme 3). In the D-glucose series (donor **1**), we obtained good yields and moderate 1,2-*cis* selectivity using DMF in preparing 1→6-linked product **11** (entry 1). Good yields are obtained in most cases in the D-glucose series (entries 1–9). Noteworthy is the orthogonal activation of selenoglycoside in entry 1 as well as synthetically challenging linkages in entries 4 and 5 in addition to the glycosylation of "linker" alcohols (entries 6, 7). We also employed benzylidene-bearing acceptors in the synthesis of products **18** and **19** with modest yield and varying 1,2-*cis*-selectivity with DMF additive (entries 8, 9). In a parallel D-galactose series (donor **8**), we observed high yields in the *O*-glycosylation of alcohols with varying steric demand (entries 10–13). The 1,2-*cis*-selectivity afforded in this series *without* DMF ranges from modest to high, possibly due to the axial 4-position benzyloxy. By contrast, three examples from the D-mannose series (donor **9**) provided high yields



Entry	Deviation from Std. Cond.	Isolated Yield (%)	1,2-*cis*/1,2-*trans*
1	none	99	2.3:1
2	donor **1a**	0	-----
3	donor **1b**	16%	1.1:1
4	donor **1c**	trace	-----
5	in the dark/30 ^{0}C	0	-----
6	20 mol. % **2**	0	-----
7	3.0 equiv. **2**	93	2.4:1
8	1.0 equiv. DTBMP	0	-----
9	without degassing	0	-----
10	5 h irradiation	86	2.4:1
11	0.2 mL DMF additive	95	16:1
12	violet Kessil (390 nm)	95	4:1

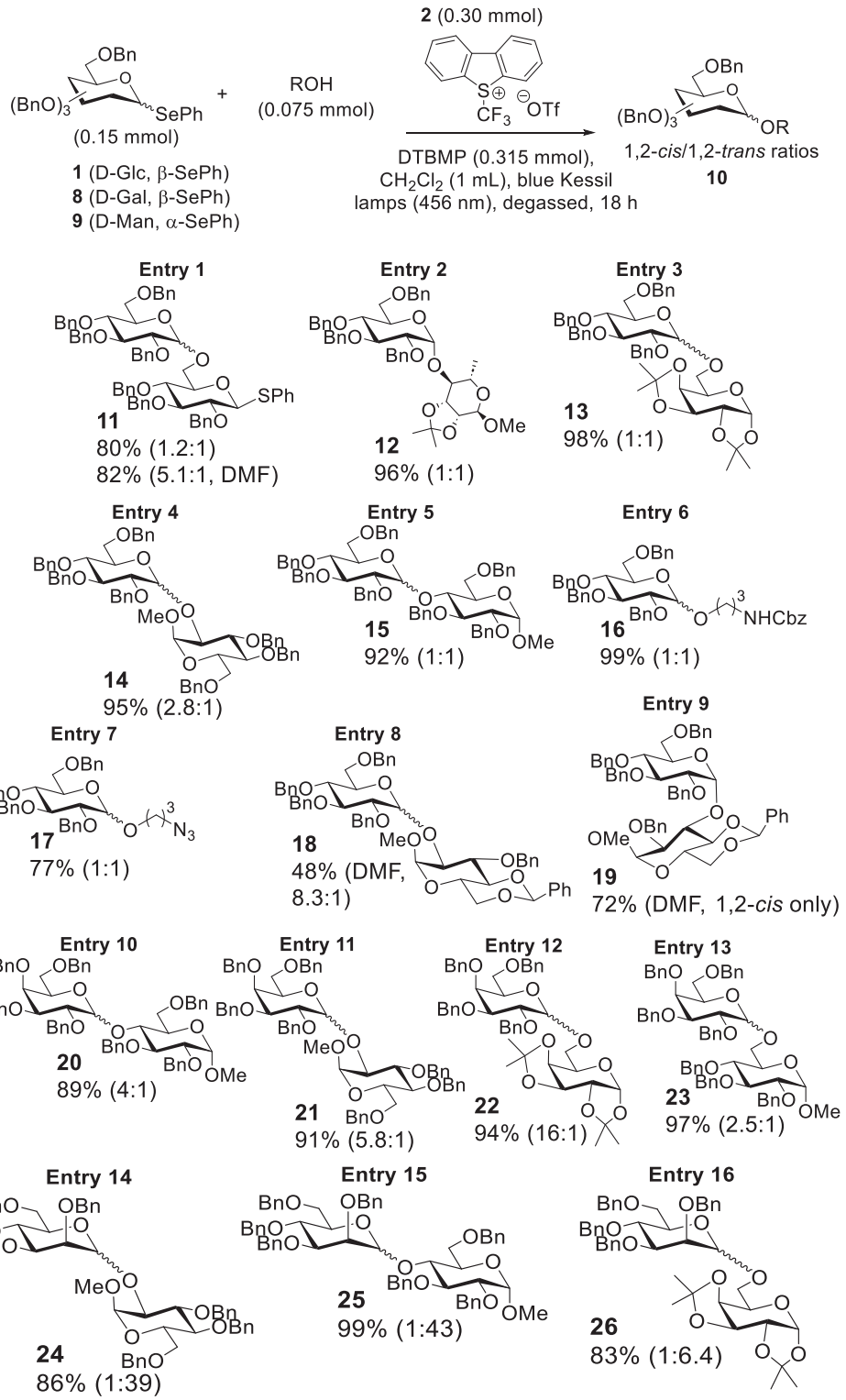
Scheme 2. Optimization.

and 1,2-*trans* selectivity likely due to the 2-position benzyloxy (entries 14–16).

We were interested in the applicability of this chemistry to donors with non-permanent protecting groups (e.g., acyl and benzylidene) as a test of its compatibility with intermediates amenable to multistep synthesis (Scheme 4). In this regard, we were especially interested in the utility of DMF for 1,2-*cis*-selective protocols. Benzylidene-bearing products **30–32** were afforded with varying yields and varying 1,2-*cis* selectivity (entries 1–3). Benzoyl-protected products **33** and **34** were also afforded in moderate yields and with varying 1,2-*cis*-selectivity (entries 4, 5). Further, it is important to note that a series of strongly disarmed donors were unreactive under our conditions. These appear in the Supporting Information and include a perbenzoylated analog of **1** and a peracetylated 2-azido-2-deoxy-D-galactose. To date, this process has not worked with a donor bearing acyl protecting groups at the 2-position. This may be due to high barriers to photoinduced electron transfer or impeded formation of EDA complexes, and these observations are fully consistent with the mechanistic hypothesis in Scheme 1 as well as our previous observations of poor reactivity with disarmed systems.[13]

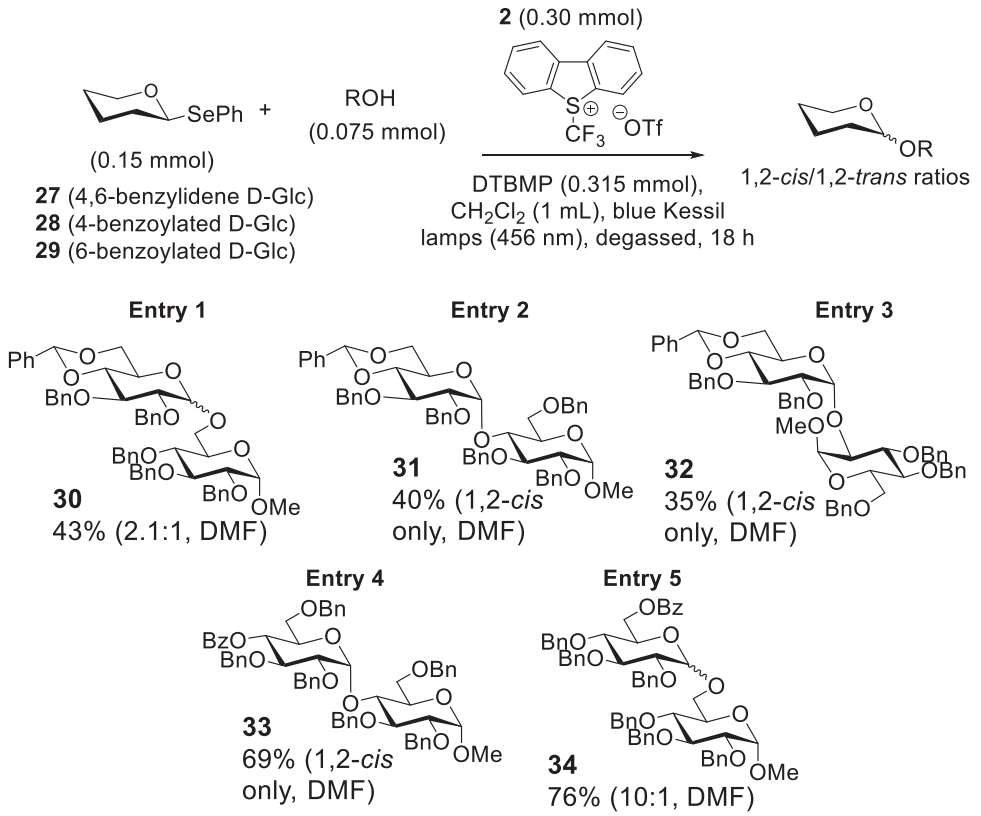
We were interested in further investigating our mechanistic hypothesis, and a series of experiments and theoretical work provide further evidence for it. With regard to the plausibility of formation of chalcogen-bonded complexes such as **3**, dilute solutions of Umemoto's reagent (**2**) alone and phenylselenoglucoside **1** alone in CH_2Cl_2 were colorless and pale-yellow to the naked eye, respectively. However, a solution of both species had a noticeably darker yellow color than just **1** (see photos in the Supporting Information section). More compelling was a series of UV–vis experiments conducted with CH_3CN as solvent (Figure 1) to ensure homogeneity. The spectrum of **2** alone (0.03 mM, x's) indicates that absorbance is negligible past ~ 435 nm whereas the highest concentration of **1** (circles, 0.09 mM) demonstrated measurable extinction well into the visible range in keeping with our prior ("pale-yellow") observations. However, substantial increases in absorbance over that seen with **2** alone were observed upon its admixture with increasing concentrations of **1**, and the resulting absorbances tailed well into the visible range (diamonds, triangles). Finally, admixture of **1** and **2** at the maximum concentration of **1** (squares) showed an absorbance also tailing well into the visible range and being dramatically larger than the sum of **1** and **2** at the same concentrations (0.09 and 0.03 mM, respectively). These results are consistent with the formation of an EDA complex as we and others have observed previously.[13,29–31]

To quantify binding of **1** and **2**, we conducted a series of ^{1}H and ^{77}Se NMR titrations in D_6-acetone and determined a K_A of 0.6 ± 0.1 M $^{-1}$ based on global fitting (see Supporting Information section). While this measurement suggests low affinity, complicating factors such as ion pairing in **2** are worthy of consideration. Also noteworthy is that D_6-acetone, while necessary for homogeneity, is a Lewis-basic solvent that may partially disrupt EDA formation. It is possible that the affinity in CH_2Cl_2, our reaction solvent of choice, is even higher, though the low solubility of **3** in this solvent precluded the analysis. Particularly compelling was the observation that increasing equivalents of **2** led to a steady downfield shift in the anomeric, 1-position proton of **1** which is consistent with



Scheme 3. Substrate scope.

the expected Lewis acidity of **2** in the proposed EDA complex **3** or which may be due to polarization of Se (vide infra). On the other hand, there was a steady upfield shift of *ortho* protons associated with the phenylselenyl moiety of **1**, and this may be due to anisotropic shielding by Umemoto's reagent (**3**, Scheme 1). Finally, we observed an *upfield* shift of ^{77}Se with increasing equivalents of **2**. This somewhat counterintuitive result was predicted by density functional theory (DFT) (see Supporting Information section) and may be explained by buildup of negative charge on polarizable Se when in proximity to positively charged **2**. Similar phenomena have been observed in the area of halogen bonding.[39]



Scheme 4. Benzylidene-/benzoate-protected donors.

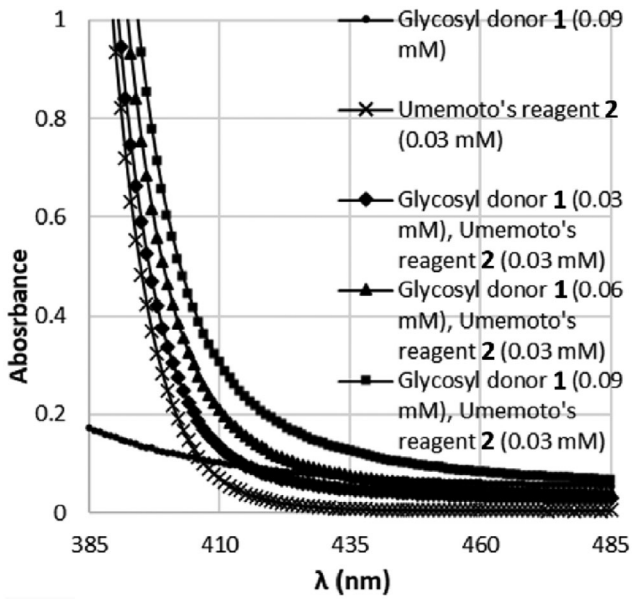


Figure 1. UV–vis analysis of mixtures of **1** and **2** in MeCN.

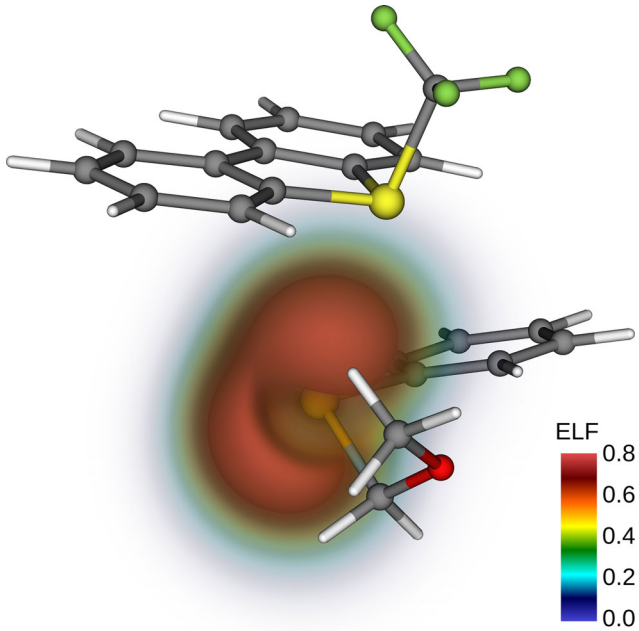
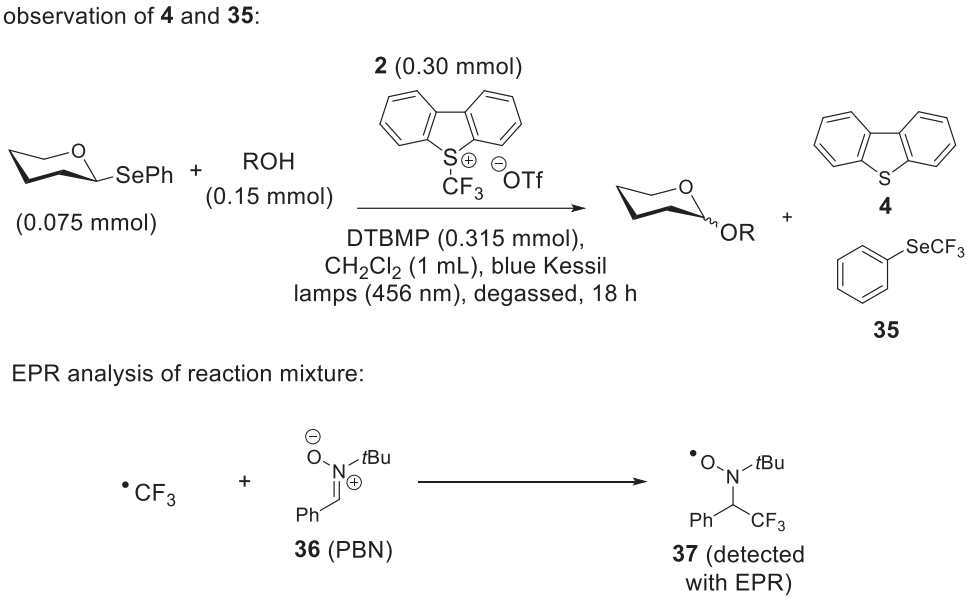


Figure 2. Computational evidence for chalcogen bonding.

To further probe the hypothesis that a complex such as **3** had been generated, we conducted a series of calculations with the *S*-trifluoromethyl dibenzothiophenium ion of Umemoto's reagent and a simplified analog of **1** (methoxymethyl phenyl selenide, Figure 2). To assess the nature of bonding, we utilized the DFT module. The calculated bond length between the selenium and sulfur was observed to be 3.39 Å, and the bond angle associated with Se, S, and carbon of CF_3 was 175°. These observations are consistent with the chalcogen-bonding hypothesis wherein one would expect a



Scheme 5. Evidence for photoinduced, single-electron transfer.

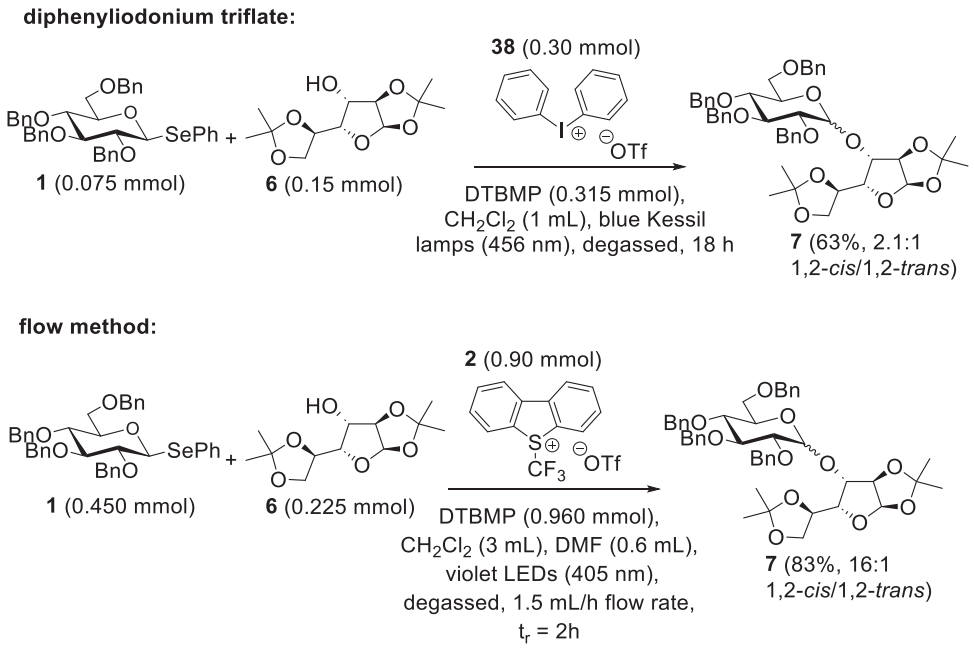
bonding angle close to 180°.[20,21] Further, we computed the electron localization function (ELF) using Se-centered atomic orbitals. The Se lone-pair electrons align with the σ^* associated with S─CF_3 (the location of which was confirmed using electrostatic potential mapping, see Supporting Information) as would be expected with a chalcogen-bonded complex.

The selenium-centered ELF for methoxymethyl phenyl selenide/Umemoto's reagent complex in CH_2Cl_2 simulated using def2-TZVP/B3LYP. The ELF shows that the Se lone pairs are aligned with, and donate to, the S atom. Along with the observed C─S─Se 175° bond angle, this demonstrates that this complex associates via chalcogen bonding.

Satisfied with the series of experiments bolstering the notion of EDA complex **3** as a plausible intermediate, we were interested in probing the feasibility of photoinduced electron transfer as a conduit to chemical reactivity per Scheme 1.[13,29–31] Evidence in support of the mechanistic hypothesis in Scheme 1 (Scheme 5) includes our isolation of dibenzothiophene (**4**) as well as our observation (using ^{19}F NMR of crude reaction mixtures and GC-MS of non-polar reaction by-products)[40] of phenyl trifluoromethyl selenide (**35**) which would result from the combination of, e.g., trifluoromethyl radical and phenylselenyl radical resulting from photoinduced single-electron transfer from **1** to **3**. Direct evidence for the formation of trifluoromethyl radical came through EPR analysis of reaction mixtures irradiated in the presence of *N-tert*-butyl phenylnitrone (PBN, **36**). EPR was able to positively identify formation of the spin-trapped product **37** resulting from reaction of trifluoromethyl radical with **36**,[13] further bolstering the mechanistic hypothesis in Scheme 1.

Having provided evidence in support of our mechanistic hypothesis, we became interested in other factors such as the scalability of this process and its applicability with less expensive reagents than **2**. In particular, diphenyliodonium triflate (**38**, Scheme 6) is a known halogen-bond donor and an excellent single-electron acceptor,[41] and we hypothesized that it could serve as a stand-in for **2**. Further, at 15$ per 5 g, this species is less expensive than Umemoto's reagent ($128 per g). In the event (Scheme 6), performing reaction under our standard conditions but substituting diphenyliodonium triflate for Umemoto's reagent, we obtained a 63% unoptimized yield of **7** demonstrating the promise that halogen bonding may hold. Conversely, performing the same experiment in the dark at 30 °C resulted in no detected conversion of **1**. This result is the topic of further investigation in our lab. Further, we constructed a flow apparatus using PTFE tubing, a syringe pump, and irradiation with violet LEDs (which proved superior to blue Kessil lamp irradiation). Implementation of a 5:1 mixture of CH_2Cl_2 and DMF ensured both homogeneity and 1,2-*cis*-selectivity. We were able to obtain an 83% yield of product **7** on a "3x" scale relative to our standard conditions, also demonstrating the promise that flow chemistry holds for scale-up. Worthy of note is that the flow protocol was also effective on larger scale (employing 1.00 mmol of acceptor **6**) but at a diminished yield (53%, see Supporting Information).

In conclusion, we have demonstrated that visible-light irradiation of mixtures of selenoglycosides and either Umemoto's reagent or diphenyliodonium triflate in the presence of alcohol acceptors results in (often high-yielding) *O*-glycosylation. In the case of Umemoto's reagent, extensive experimentation and computational work support a mechanistic hypothesis involving EDA complex formation with chalcogen bonding. Photoinduced electron transfer provides a probable route to chemical reactivity, and similar processes may be at play, albeit with halogen bonding, in the presence of diphenyliodonium triflate. Our future work will address ongoing issues of stereoselectivity as well as the low reactivity of electron-poor donors. Because of the tunability of the



Scheme 6. Alternative reagent and flow method.

redox potential associated with selenoglycosides and because of the remarkable diversity of redox-active chalcogen- and halogen-bond donors, we are confident that continued investigation will result in solutions to problems incurred with electron-poor donors.

Supporting Information

The authors have cited additional references within the Supporting Information.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Carbohydrates · Chalcogen bonding · Glycosylation · Photochemistry

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Synthetic Methods

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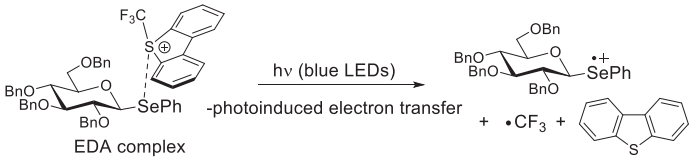
A Visible-Light-Driven *O*-Glycosylation with Selenoglycosides Mediated by Chalcogen Bonding to Umemoto's Reagent



Visible-light irradiation of solutions of phenylselenoglycosides and Umemoto's reagent in the presence of alcohols results in often high-yielding formation of *O*-glycosidic products. Experimental and computational work suggests that chalcogen-bonded electron–donor–acceptor (EDA) complexes are critical intermediates in this process which may proceed through photoinduced electron transfer.