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Letter

Synthesis of Glycosyl Fluorides by Photochemical Fluorination with Sulfur(VI) Hexafluoride

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lycosyl fluorides have been of great importance to the ${f J}$ synthesis of oligosaccharides and glycoconjugates, as well as studies of the enzymatic reactions.¹⁻³ Its small molecular weight (MW), low toxicity, and simple methods for scavenging make the fluoride anion an ideal leaving group for the glycosylation reactions.² The use of glycosyl fluorides is often advantageous, because of their high thermal and chemical stability, in particular, to water and chromatography. For example, Miller group has taken advantage of glycosyl fluoride stability in aqueous media to achieve selective and mild glycosylations in water.⁴ At the same time, the activation of glycosyl fluorides with Lewis acids that have high affinity to the anion may result in powerful glycosylative agents, which F^{-} was recently highlighted by Montgomery and co-workers, who observed rapid glycosylations of various sterically hindered acceptors with tris(pentafluorophenyl)borane (BCF) catalysts.

continuous flow to accomplish fluorination on an 7.7 g scale and

Many studies have focused on improving the synthesis of glycosyl fluorides; however, only few practical methods are available. The primary way to generate these species is based on deoxyfluorination of the anomeric position of sugars using (diethylamino)sulfur(IV) trifluoride (DAST).⁶ DAST exhibits a great reactivity profile; however, its high toxicity, corrosiveness and potential explosiveness pose limitations for its use, in particular, on a large scale.⁷ Other methods such as fluorination with corrosive and toxic HF•pyridine as the solvent or cosolvent (>50%)^{1,8} require a plastic or a metal vessel, special work-up conditions, and substrates that can survive an acidic environment.

While SF_6 has been sporadically used to achieve fluorination,⁹ SF_6 activation only recently was achieved under mild and catalytic reaction conditions. Thus, the recent study by Jamison and co-workers disclosed a photoredox activation of SF_6 with Ir(III)-based catalysts resulting in deoxyfluorination of allylic alcohols (Scheme 1A).¹⁰ This study suggested





that the reduction of SF₆ leads to unidentified sulfur fluoride species (SF_n) that fluorinates the substrate. Subsequently, Rueping and co-workers (Scheme 1B)¹¹ and Braun and Kemnitz¹² described reductive activations of SF₆ that resulted in the stoichiometric reagents that could be used for deoxyfluorination, and Wagenknecht described photoactivations of SF₆ that resulted in SF₅ group transfer.¹³

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Unlike many other fluorinating agents, SF₆ is an inexpensive and safe-to-handle gas produced on a large scale. The utilization of SF₆ represents an important challenge,¹⁴ because of its chemical inertness, and has great significance, because of its potency as a greenhouse gas.¹⁵

Building on the aforementioned studies, this manuscript describes a mild, safe, and efficient fluorination of 16 protected carbohydrates with SF₆ using commercially available UV-A LED source ($\lambda_{max} = 365$ nm) and inexpensive 4,4'-dimethoxybenzophenone as the photocatalyst. Importantly, all of the substrates and products were found to be stable under the reaction conditions, which permitted to carry gramscale fluorination reactions both in batch and continuous flow. Based on preliminary mechanistic studies, we propose that this reaction proceeds through the formation of SF₄ that is formed in trace quantities and either fluorinates the substrate or gets further reduced to S_nF_m or elementary sulfur under the photochemical conditions.

Our studies commenced by subjecting the disarmed 2,3,4,6-tetra-O-acetyl- α -D-mannose **1a** to the fluorination reaction condition previously developed by Jamison and co-workers (Table 1, entry 1).¹⁰ Excitingly, **1a** showed no signs of

Table 1. Photocatalyst Screening^a

م	AcO OAc Photocatalysi AcO I O OAc DipEA, AcO I O OAC DipEA, 1a OH 20	,, <i>hv</i> A t (40 mol%) AcC DCE Ac h	2a CO OAC OAC
entry	photocatalyst	light source	yield ^b (%)
1 ^c	Ir(ppy) ₂ (dtbbpy)PF ₆ (5 mol %)	blue LED	38
2	Eosin Y	blue LED	7
3	Rose Bengal	UV-A LED	_
4	Methylene Blue	UV-A LED	33
5	N-phenylphenothiazine	UV-A LED	43
6	benzophenone	UV-A LED	33
7	Michler's ketone	UV-A LED	47
8	xanthone	UV-A LED	25
9	9-fluorenone	UV-A LED	7
10	4-fluoro-4'- methoxybenzophenone	UV-A LED	56
11	4-chloro-3'- methoxybenzophenone	UV-A LED	29
12	4,4'-dimethoxybenzophenone	UV-A LED	60
13 ^d	4,4′- dimethoxybenzophenone	UV-A Flood Lamp	72 (95% BRSM) ^e

^{*a*}Reactions in entries 1–13 were performed on 0.1 mmol scale, with 40 mol % catalyst, 20 equiv of DIPEA in 0.033 M DCE for 20 h with UV-A LED ($\lambda_{max} = 365$ nm) or blue LED ($\lambda_{max} = 452$ nm). ^{*b*19}F NMR yield of the major α -anomer with α,α,α -trifluorotoluene as an internal standard. ^{*c*}5 mol % of Ir(ppy)₂(dtbbpy)PF₆ and 3 eq. of DIPEA were used. ^{*d*}Performed with 30 mol % of the catalyst, 10 equiv of DIPEA in a plastic syringe as the reaction vessel. ^{*e*}Isolated yield, $\alpha:\beta = 13:1$.

decomposition under these conditions, and the reaction proceeded to 38% conversion of **2a** after 20 h. However, the significant deceleration of the reaction progression after 12 h, and the high price and low availability of $Ir(ppy)_2(dtbpy)PF_6$, prompted us to investigate more cost-effective organic photocatalysts,¹⁶ using commercially available LED light sources (Table 1, entries 2–13). Fluorescein derivative Eosin Y^{17} was able to activate SF₆ to form **2a** in low conversions (Table 1, entry 2). A related dye, Rose Bengal, was also tested, but it did not show any catalytic activity (Table 1, entry 3). Next, we proceeded with testing the derivatives of thiazine because some of them have been used for the photoactivation of SF₆ with UV-A LED by Wagenknecht and co-workers¹³ (Table 1, entries 4 and 5). Both N-phenylphenothiazine and Methylene Blue demonstrated fair catalytic activity that was comparable with $Ir(ppy)_2(dtbpy)PF_6$. Subsequently, we evaluated benzophenone (Table 1, entry 6), since this compound is often an indispensable catalyst for various photochemical transformations.¹⁶ Benzophenone was also found to promote the fluorination with both Blue and UV-A $(\lambda_{\text{max}} = 365 \text{ nm})$ LEDs, although the yield was found to be higher with the UV-A LED. This is not surprising, because the $n \rightarrow \pi^*$ band of benzophenone has a λ_{max} value of ~340 nm.¹⁶ It is known that additional substitution on benzophenones may increase the λ_{max} (cf. Figures SI 9–SI 11 in the Supporting Information), affect the lifetime of the triplet state, and increase the reduction potential of the benzophenone-derived ketyl radicals.¹⁸ Therefore, six other benzophenone derivatives (Table 1, entries 7-13) were tested. Among these six photocatalysts, Michler's ketone, 4,4'-dimethoxybenzophenone, and 4-fluoro-4'-methoxybenzophenone showed enhanced catalytic activity with 4.4'-dimethoxybenzophenone providing the highest yield (60%; see Table 1, entry 12). Considering its low cost and high catalytic activity, we subsequently employed 4,4'-dimethoxybenzophenone (DMBP) as our default photocatalyst and proceeded to further optimize the reaction parameters, such as reaction stoichiometry, base, solvent, light intensity, irradiation surface, and reaction vessel (cf. Tables SI 2-SI 4). These optimizations permitted us to reduce the catalyst loading to 30 mol % and resulted in the enhanced formation of 2a (72% isolated yield, 95% BRSM, $\alpha:\beta = 13:1$; see Table 1, entry 13).

With the optimized conditions in hand, the evaluation of the substrate scope was performed next (cf. Scheme 2, as well as Table SI5 in the Supporting Information). First, we investigated the formation of other disarmed peracetylated



"Reactions were performed in plastic syringes on 0.1 mmol scale, with 30 mol % of the DMBP catalyst for substrates 1a-1d and 20 mol % of the DMBP catalyst for substrates 1e-1p, DIPEA (10 equiv), DCE (0.03 M), rt, for 20 h. The yields are the average of duplicate experiments, and in all cases the actual isolated yields were within $\pm 2\%$ from the average yield.

fluorides such as D-glucose derivative **2b**, D-galactose derivative **2c**, and L-rhamnose derivative **2d**. Similar to the D-mannose derivative **2a**, the transformations leading to **2b** and **2c** were relatively slow, because of the disarmed nature of the substrates, and provided the products in yields of only 43%–53% after 20 h, albeit with good BRSM yields. At the same time, more reactive 6-deoxy sugar **1d** provided significantly higher yield for product **2d** (70% yield, 77% BRSM).

Subsequently, we performed the evaluation of armed donors 1e-1p. These armed donors are significantly more reactive, and their interconversion to products 2e-2p was efficiently performed with only 20 mol % of the DMBP catalyst (cf. Scheme 2). The fluorination of the benzylated hexoses 1e, 1f, and 1g proceeded in good yields (85%, 69%, and 81%, respectively) to provide the resultant glycosyl fluorides as mixtures of the $\alpha:\beta$ anomers. Interestingly, the reactions of 1e and 1g favored the formation of the more valuable β -anomer with \sim 3:1 to 4:1 selectivities. The preference for the β -anomer was the general trend that was observed for other substrates lacking axial C2 substitution such as 2i, 2j, 2n, and 2p. Similar to 1d, the benzylated derivatives of deoxysugars such as 1h, 1i, and 1j were also viable substrates for the fluorination reaction providing the glycosyl fluorides in yields of 68% (83% BRSM), 80% (87% BRSM), and 80% (99% BRSM), respectively.

In addition, the benzylated ribose derivative 1k was fluorinated to provide primarily β -anomer of glycosyl fluoride in 13:1 dr and 78% yield (90% BRSM). Finally, the application of this chemistry to substrate with acid-labile linkages (1i–1p) was investigated. This included the successful formation of Dmannose benzylidene acetal-containing derivative 2l (66% yield, $\alpha:\beta = 7.8:1$), disaccharide 2o (70%, $\alpha:\beta = 1:3.4$) as well as sugar derivatives 2m (73%, $\alpha:\beta = 36:1$), 2n (72%, $\alpha:\beta =$ 1:2.4), and 2p (70%, $\alpha:\beta = 1:3.7$) carrying the multiple pmethoxybenzyl (PMB) group protections. These results demonstrate that fluorination with SF₆ is mild and does not affect the majority of the protecting groups used in carbohydrate chemistry.

The scaleup of the photochemical experiments in the batch is notoriously challenging and requires further optimization of various experimental parameters. While the setup depicted in Scheme 3A was not optimized, it was successfully used for the 1.0 g scale fluorination of 1g to produce product 2g in 93% yield (0.93 g), using a standard glass tube and an extended irradiation time (166 h). Arguing that larger-scale reactions

Scheme 3. Gram-Scale Fluorination in Batch and Continuous Flow



would be more feasible in continuous flow, we have performed 7.7 g scale fluorination of **1e** in continuous flow using the setup depicted in Scheme 3B. Thus, the solution of **1e**, photocatalyst (DMBP), and DIPEA in DCE was cycled with pressurized $SF_6(100 \text{ psi})$ through the loop containing Teflon tubing that had been irradiated by the UV-A lamp and a back-pressure regulator (BPR) using a standard prep HPLC pump. The irradiated solution was returned back to the container with **1e**, and the resulting mixture was reintroduced back to the photochemical reactor for the total duration of 120 h. These conditions led to the formation of 7.2 g of **2e** (93% yield), and

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Several control experiments were performed using substrate **1g** to elucidate the mechanism of this transformation, and the tentative mechanism is depicted in Figure 1A.

0.5 g of 1e was recovered (99.8% BRSM).



Figure 1. (A) Tentative reaction mechanism. (B) Catalyst decomposition products and side-products resulting from SF_{6-} (C) Direct fluorination with sodium ketylate. (D) Light on/off control experiment.

The reaction did not proceed without a light source, which reinforces that light irradiation is required to initiate the first SET step between the excited DMBP and DIPEA.¹⁹ This also suggests that DIPEA cannot reduce SF₆ by itself. Similarly, the reduction of SF₆ did not happen in the absence of DIPEA, which indicates that the presence of this reagent is essential. Surprisingly, the omission of DMBP did not completely shut down the fluorination of 1g, and we observed some formation of 2g without a presence of a photocatalyst. Presumably, the open aldehyde form of 1g may participate in the SET process to activate SF_{6i} but further mechanistic investigations are required for a better understanding of this phenomenon. To eliminate the possibility of the chain processes initiated by light, we performed the light on/off experiment depicted in Figure 1C. After the reaction was irradiated with UV-A light for 4 h, the light was turned off and the reaction vessel was covered with aluminum foil for 2 h, and no reaction progression happened in the absence of light. However, the

formation of 2g was resumed when the reaction was exposed to the light again. These results suggest that the photoexcitation of DMBP leads to the formation of its triplet state (DMBP*), and the observed catalyst decomposition products such as benzylic alcohol and pinacol adduct provide further evidence for this step (cf. Figure 1B).¹⁹ The resultant DMBP* species undergoes a known oxidation of DIPEA ($E_{1/2(SCE)}$ ~ species undergoes a known oxidation of DTEA ($E_{1/2(\text{SCE})}$ 0.8 V)^{15,18} to generate a ketyl radical ($E_{1/2(\text{SCE})} = -2.2$ V) that reduces SF₆ to [SF₆]^{•-} ($E_{1/2(\text{SCE})} = -1.9$ V).¹⁰ The subsequent reduction of the [SF₆]^{•-} radical anion results in the in situ formation of a strong fluorinating agent, SF₄,^{7a,20} that is likely to exist in dynamic equilibrium with its fluoride-complexed form $[SF_5]^{-1}$. Our attempts to directly detect SF_4 or $[SF_5]^{-1}$ via low-temperature ¹⁹F NMR under the optimized reaction conditions were not successful, which implies that these species are transient under the photochemical conditions. Similarly, the attempts to detect the SF₆ reduction products arising from the reaction of the ketyl radical pregenerated from DMBP and lithium metal and SF₆ were not successful, although $\sim 1\%$ of the fluorinated product 2e was observed when the ketyl reduction of SF₆ was immediately followed by the addition of 1e (cf. Figure 1C, as well as Section VI-f in the Supporting Information).

This might suggest that unreacted SF_4 is further reduced,²¹ and the ¹⁹F NMR analysis of the crude reaction mixture indeed contains a singlet at -124 ppm that could be contributed to S_2F_2 or a related S_nF_2 species.²² This is in agreement with the observation that the addition of the PPh₃ to the crude reaction mixture leads to the formation of $S=PPh_3$ and F_2PPh_3 . In addition, the significant quantities of $FSO_3^{-}(NHi-Pr_2Et)^+$ were accumulated as the reaction side-product (cf. Figure 1B and the Supporting Information for additional details). This could be attributed to the mechanism involving energy transfer to SF_{6i} followed by further reactions with trace water.

In conclusion, we have developed a new convenient method for the photocatalytic generation of glycosyl fluorides using SF₆ as an inexpensive and safe fluorinating agent and 4,4'dimethoxybenzophenone as a readily available organic photocatalyst. This mild method was employed to generate 16 different glycosyl fluorides, including the substrates with acid and base labile functionalities, in yields of 43%–97%, and was applied in continuous flow to accomplish fluorination on a 7.7 g scale. The subsequent studies suggest that this reaction might proceed through the transient formation of SF₄ that serves as a fluorinating agent, but does not accumulate throughout the reaction progression. We believe that, because of its safety and mildness, this method holds great potential for the large-scale synthesis of glycosyl fluorides.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03915.

¹H, ¹³C, and ¹⁹F NMR spectra of products; experimental information; description of the continuous flow experiments; and studies of the reaction mechanism (PDF)

Accession Codes

CCDC 2017701 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data request@ccdc.cam.ac.uk, or by contacting The Cam-

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) (a) Yokoyama, M. Methods of Synthesis of Glycosyl Fluorides. *Carbohydr. Res.* 2000, 327, 5. (b) Uhrig, M. L.; Lantano, B.; Postigo, A. Synthetic Strategies for Fluorination of Carbohydrates. *Org. Biomol. Chem.* 2019, 17, 5173. (c) Card, P. J. Synthesis of Fluorinated Carbohydrates. J. Carbohydr. Chem. 1985, 4, 451.

(2) (a) Shimizu, M. Chemistry of Glycosyl Fluorides. Synthesis 1998, 1998, 799. (b) Toshima, K. Glycosyl Fluorides in Glycosidations. Carbohydr. Res. 2000, 327, 15. (c) Mukaiyama, T.; Jona. Glycosyl Fluoride: A Superb Glycosyl Donor in Glycosylation. H. Proc. Jpn. Acad., Ser. B 2002, 78, 73. (d) Randall, J. L.; Nicolaou, K. C. Preparation and Reactions of Glycosyl Fluorides. In Fluorinated Carbohydrates; Taylor, N. F., Ed.; ACS Symposium Series, Vol. 374; American Chemical Society: Washington, DC, 1988; Chapter 2, p 13.

(3) (a) Williams, S. J.; Withers, S. G. Glycosyl fluorides in enzymatic reactions. *Carbohydr. Res.* **2000**, 327, 27. (b) Rempel, B. P.; Withers, S. G. Covalent inhibitors of glycosidases and applications in biochemistry and biology. *Glycobiology* **2008**, *18*, 570.

(4) (a) Pelletier, G.; Zwicker, A.; Allen, C. L.; Schepartz, A.; Miller, S. J. Aqueous Glycosylation of Unprotected Sucrose Employing Glycosyl Fluorides in the Presence of Calcium Ion and Trimethylamine. *J. Am. Chem. Soc.* **2016**, *138*, 3175. (b) Wadzinski, T. J.; Steinaur, A.; Hie, L.; Pelletier, G.; Schepartz, A.; Miller, S. J. Rapid phenolic O-glycosylation of small molecules and complex unprotected peptides in aqueous solvent. *Nat. Chem.* **2018**, *10*, 644.

(5) Sati, G. C.; Martin, J. L.; Xu, Y.; Malakar, T.; Zimmerman, P. M.; Montgomery, J. Fluoride Migration Catalysis Enables Simple, Stereoselective, and Iterative Glycosylation. J. Am. Chem. Soc. **2020**, 142, 7235.

(6) (a) Johnson, A. L. New Reaction of (Diethylamino)sulfur Trifluoride: bis(Diphenylmethyl) Ethers as Dehydration Products of (Diethylamino)sulfur Trifluoride and Diarylcarbinols. J. Org. Chem. **1982**, 47, 5220. (b) Rosenbrook, Wm., Jr.; Riley, D. A.; Lartey, P. A. A New Method for the Synthesis of Glycosyl Fluorides. Tetrahedron Lett. **1985**, 26, 3. (c) Posner, G. H.; Haines, S. R. A Convenient, Onestep, High-yield Replacement of an Anomeric Hydroxyl Group by a Fluorine Atom Using DAST. Preparation of glycosyl fluorides. Tetrahedron Lett. **1985**, 26, 5.

(7) (a) Hudlicky, M. Fluorination with Diethylaminosulfur Trifluoride and Related Aminofluorosulfuranes. In *Organic Reactions*, Vol. 35; Kende, A. S., Ed.; John Wiley & Sons, Inc., 1988; Chapter 3, p 513. (b) Ni, C.; Hu, M.; Hu, J. Good Partnership between Sulfur and Fluorine: Sulfur-Based Fluorination and Fluoroalkylation Reagents for Organic Synthesis. *Chem. Rev.* **2015**, *115*, 765.

(8) Hayashi, M.; Hashimoto, S.; Noyori, R. Simple Synthesis of Glycosyl Fluorides. Chem. Lett. 1984, 13, 1747.

(9) For selected examples, see: (a) Das, P. S.; Adhikari, B.; Maiti, S. Fluorination of Polymers by Sulfur Hexafluoride Gas under Electric Discharge. J. Polym. Sci., Part A: Polym. Chem. **1994**, 32, 39. (b) Basta, R.; Harvey, B. G.; Arif, A. M.; Ernst, R. D. Reactions of SF₆ with Organotitanium and Organozirconium Complexes: The 'Inert' SF₆ as a Reactive Fluorinating Agent. J. Am. Chem. Soc. **2005**, 127, 11924. (c) Buss, F.; Muck-Lichtenfeld, C.; Mehlmann, P.; Dielmann, F. Nucleophilic Activation of Sulfur Hexafluoride: Metal-Free, Selective Degradation by Phosphines. Angew. Chem., Int. Ed. **2018**, 57, 4951. (d) Iakobson, G.; Posta, M.; Beier, P. Reductive Activation of Sulfur Hexafluoride with TEMPOLi: Addition of the Pentafluorosulfanyl Group and TEMPO to Terminal Alkenes. J. Fluorine Chem. **2018**, 213, 51.

(10) McTeague, T. A.; Jamison, T. F. Photoredox Activation of SF_6 for Fluorination. Angew. Chem., Int. Ed. **2016**, 55, 15072.

(11) Rueping, M.; Nikolaienko, P.; Lebedev, Y.; Adams, A. Metal-Free Reduction of the Greenhouse Gas Sulfur Hexafluoride, Formation of SF₅ Containing Ion Pairs and the Application in Fluorinations. *Green Chem.* **2017**, *19*, 2571.

(12) Tomar, P.; Braun, T.; Kemnitz, E. Photochemical Activation of SF_6 by N-heterocyclic Carbenes to Provide a Deoxyfluorinating Reagent. *Chem. Commun.* **2018**, *54*, 9753.

(13) (a) Rombach, D.; Wagenknecht, H.-A. Photoredox Catalytic Activation of Sulfur Hexafluoride for Pentafluorosulfanylation of α -Methyl- and α -PhenylStyrene. ChemCatChem 2018, 10, 2955. (b) Rombach, D.; Wagenknecht, H.-A. Photoredox Catalytic α -Alkoxypentafluorosulfanylation of α -Methyl- and α -Phenylstyrene Using SF₆. Angew. Chem., Int. Ed. 2020, 59, 300.

(14) (a) Maiss, M.; Brenninkmeijer, C. A. M. Atmospheric SF₆: Trends, Sources, and Prospects. *Environ. Sci. Technol.* **1998**, *32*, 3077. (b) Dervos, C. T.; Vassiliou, P. Sulfur Hexafluoride (SF₆): Global Environmental Effects and Toxic Byproduct Formation. *J. Air Waste Manage. Assoc.* **2000**, *50*, 137.

(15) For selected studies on chemical degradation of SF₆, see: (a) Huang, L.; Gu, D.; Yang, L.; Xia, L.; Zhang, R.; Hou, H. Photoreductive Degradation of Sulfur Hexafluoride in the Presence of Styrene. J. Environ. Sci. **2008**, 20, 183. (b) Berg, C.; Braun, T.; Ahrens, M.; Wittwer, P.; Herrmann, R. Activation of SF₆ at Platinum Complexes: Formation of SF₃ Derivatives and Their Application in Deoxyfluorination Reactions. Angew. Chem., Int. Ed. **2017**, 56, 4300. (c) Zhang, J.; Zhou, J. Z.; Liu, Q.; Qian, G.; Xu, Z. P. Efficient Removal of Sulfur Hexafluoride (SF₆) Through Reacting with Recycled Electroplating Sludge. Environ. Sci. Technol. **2013**, 47, 6493. (16) Romero, N. A.; Nicewicz, D. A. Organic Photoredox Catalysis. Chem. Rev. **2016**, 116, 10075.

(17) (a) Zhao, G.; Wang, T. Stereoselective Synthesis of 2-Deoxyglycosidesfrom Glycals by Visible-Light-Induced Photoacid Catalysis. *Angew. Chem., Int. Ed.* **2018**, *57*, 6120. (b) Liu, J.; Yin, S.; Wang, H.; Li, H.; Ni, G. A Visible Light Promoted O-Glycosylation with Glycosyl Trichloroacetimidates using Eosin Y as an Organo Photoacid. *Carbohydr. Res.* **2020**, *490*, 107963.

(18) Leigh, W. J.; Arnold, D. R.; Humphreys, R. W. R.; Wong, P. C. Merostabilization in Radical Ions, Triplets, and Biradicals. 4. Substituent Effects on the Half-wave Reduction Potentials and n,π^* Triplet Energies of Aromatic Ketones. *Can. J. Chem.* **1980**, *58*, 2537. (19) (a) Wayner, D. D. M.; Dannenberg, J. J.; Griller, D. Oxidation Potentials of α -Aminoalkyl Radicals: Bond Dissociation Energies for Related Radical Cations. *Chem. Phys. Lett.* **1986**, *131*, 189. (b) Cohen, S. G.; Litt, A. D. Rate Constants of Interaction of Benzophenone Triplet with Amines. *Tetrahedron Lett.* **1970**, *11*, 837. (c) Inbar, S.; Linschitz, H.; Cohen, S. G. Nanosecond Flash Studies of Reduction of Benzophenone by Aliphatic Amines. Quantum Yields and Kinetic Isotope Effects. J. Am. Chem. Soc. 1981, 103, 1048.

(20) Pitts, J. N., Jr.; Letsinger, R. L.; Taylor, R. P.; Patterson, J. M.; Recktenwald, G.; Martin, R. B. Photochemical Reactions of Benzophenone in Alcohols. J. Am. Chem. Soc. **1959**, 81, 1068.

(21) Wang, C.-L. J. Fluorination by Sulfur Tetrafluoride. In *Organic Reactions*, Vol. 34; Kende, A. S., Ed.; John Wiley & Sons, Inc., 1985; Chapter 2, p 319.

(22) Gombler, W.; Schaebs, J.; Willner, H. Fluorine-19 NMR Chemical Shift of Sulfur Difluoride in the Gas Phase. *Inorg. Chem.* **1990**, *29*, 2697.