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Electrochemical Trifluoromethylation of Glycals

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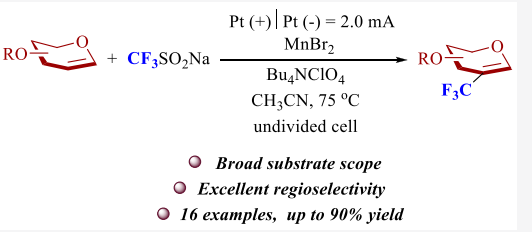
ABSTRACT: Carbohydrates play essential roles in various physiological and pathological processes. Trifluoromethylated compounds have wide applications in the field of medicinal chemistry. Herein, we report a practical and efficient trifluoromethylation of glycals by an electrochemical approach using CF_3SO_2Na as the trifluoromethyl source and $MnBr_2$ as the redox mediator. A variety of trifluoromethylated glycals bearing different protective groups are obtained in 60−90% yields with high regioselectivity. The successful capture of a CF_3 radical indicates that a radical mechanism is involved in this reaction.

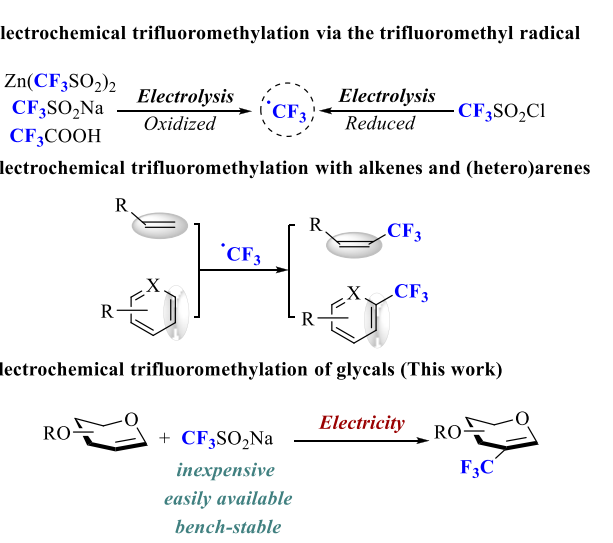


Carbohydrates mainly exist in the form of glycoconjugates and polysaccharides. They participate in many critical biological processes such as immune response, inflammation, virus infection, and sperm−egg recognition.[1] Thus, carbohydrate-based drug discovery is becoming one of the frontiers in medicinal chemistry. However, the druggability of most natural carbohydrates is not good due to their structural complexity, weak metabolic stability, and low biological activity.[2] Therefore, the structural modification of carbohydrates is crucial for the identification of new carbohydrate-related drugs.[3]

Trifluoromethylation of bioactive natural compounds has emerged as one of the promising modification strategies for drug discovery.[4] The introduction of the trifluoromethyl (CF_3) group could usually improve the lipophilicity, metabolic stability, and bioavailability of compounds.[5] As a result, the development of efficient methods for the preparation of CF_3-containing compounds is in great demand. In the past few years, organic electrochemistry has represented an environmentally friendly and powerful alternative to traditional redox methods, wherein the use of extra oxidants or reductants could be reduced or even avoided.[6] In this context, electro-trifluoromethylation via a free radical mechanism has been widely studied and turned out to be highly practical. Various trifluoromethylating reagents such as CF_3SO_2Cl,[7] CF_3COOH,[8] CF_3SO_2Na (Langlois' reagent),[9] and $Zn(CF_3SO_2)_2$ (Baran's reagent)[10] could be easily electrolyzed to generate a reactive trifluoromethyl radical involving a diversity of trifluoromethylations of alkenes,[11] (hetero)arenes,[12] vinyl carboxylic acids,[13] and thiophenols[14] (Scheme 1a,b). Although the trifluoromethylated endo- and exoglycals via copper and photoredox catalysis have been successfully synthesized through a radical mechanism,[15] the electrochemical trifluoromethylation of carbohydrates has not been reported so far.

CF_3SO_2Na, as an inexpensive, readily available, and bench-stable trifluoromethyl source, has attracted great attention and has been widely used to prepare diverse trifluormethylated compounds in the electrochemical trifluoromethylation.[16] In continuation of our research interests[17] in the synthesis of carbohydrates and carbohydrate-related drugs, we herein report

Scheme 1. Electrochemical Trifluoromethylation



an electrochemical trifluoromethylation of glycals using the readily available CF_3SO_2Na as the trifluoromethyl source and $MnBr_2$ as the redox mediator (Scheme 1c).

Initially, benzylated glucal **1a** was chosen as the model substrate to evaluate the feasibility of the electrochemical trifluoromethylation process using CF_3SO_2Na (**2a**) as the trifluoromethyl (CF_3) source, Pt as the anode and cathode, and dry CH_3CN as the solvent under a constant electric current of 2 mA at room temperature in an undivided cell (Table 1 and Table

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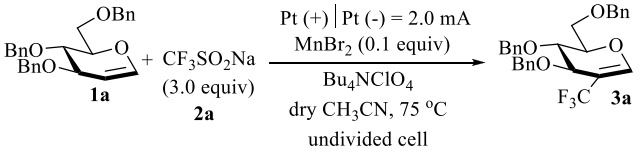
Table 1. Optimization of Reaction Conditions[a]



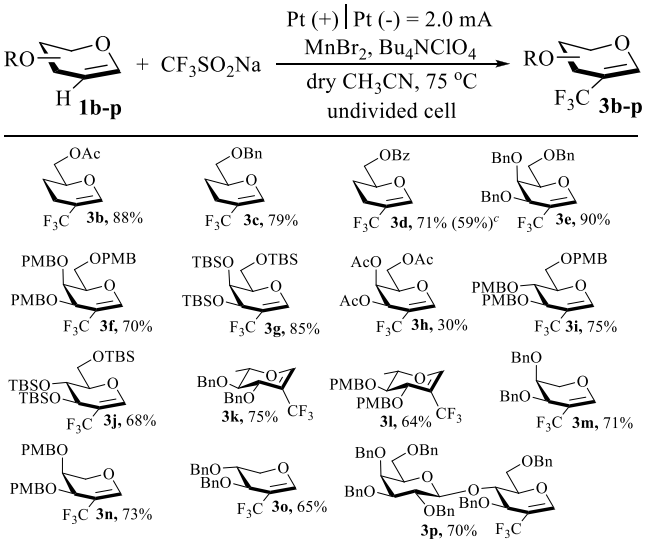
entry	variation from standard conditions	yield (%)[b]
1	standard conditions	80 (61)[c]
2	CF_3SO_2Na (2.0 equiv)	62
3	$MnBr_2$ (0.20 equiv)	60
4	$MnBr_2$ (0.05 equiv)	30
5	1.0 mA	23
6	3.0 mA	78
7	50 °C	72
8	r.t.	33
9	C(+)/C(−)	10
10	C(+)/Pt(−)	42
11	Pt(+)/C(−)	6
12	$ClCH_2CH_2Cl$ instead of CH_3CN	0
13	1,2-dimethoxyethane instead of CH_3CN	trace
14	CH_3CN/H_2O (3:1) instead of CH_3CN	0
15	Bu_4NOTf instead of Bu_4NClO_4	20
16	Bu_4NPF_6 instead of Bu_4NClO_4	50
17	Me_4NClO_4 instead of Bu_4NClO_4	40
18	without $MnBr_2$	14%
19	air	trace
20	without current	no reaction

[a]Reaction conditions: **1a** (0.05 mmol), CF_3SO_2Na (0.15 mmol, 3.0 equiv), $MnBr_2$ (0.005 mmol, 0.1 equiv), Bu_4NClO_4(0.10 mmol, 2.0 equiv), and dry CH_3CN (4.0 mL) in an undivided cell with Pt as the anode and cathode, constant current = 2.0 mA, 75 °C, under an argon atmosphere, 4 h. [b]Yield of the isolated product. [c]Reaction conditions: **1a** (0.25 mmol), CF_3SO_2Na (0.75 mmol, 3.0 equiv), $MnBr_2$ (0.025 mmol, 0.1 equiv), Bu_4NClO_4 (0.50 mmol, 2.0 equiv), and dry CH_3CN (20.0 mL) in an undivided cell with Pt as the anode and cathode, constant current = 2.0 mA, 75 °C, under an argon atmosphere, 4 h.

S1). Unfortunately, no desired 2-trifluoromethyl-substituted glucal **3a** was obtained (Table S1, entry 1). With Bu_4NBr[18] as the additive, the reaction could proceed, albeit in a very low yield (Table S1, entry 2). When the temperature was raised to 75 °C, the yield increased slightly (Table S1, entry 3). To our delight, using $MnCl_2$[19] instead of Bu_4NBr, a 40% isolated yield of the desired product **3a** was observed (Table S1, entry 4). Replacing $MnCl_2$ with $MnBr_2$,[20] an increased yield was obtained (Table 1, entry 2; Table S1, entry 5). The yield could be elevated to 80% when the amount of CF_3SO_2Na was increased to 3.0 equiv (Table 1, entry 1). However, the yield could not be improved whether the equivalent of $MnBr_2$ was increased or decreased (Table 1, entries 3 and 4). Moreover, the similar reaction efficiency was achieved by increasing the electric current to 3.0 mA or reducing the reaction temperature to 50 °C (Table 1, entries 6 and 7), whereas either the reduced electric current or room temperature led to low conversion (Table 1, entries 5 and 8). Besides, changing the electrode materials resulted in a noticeable loss in yield (Table 1, entries 9−11). Further experiments showed that the reaction outcome was significantly influenced by the solvent. Only a trace amount of product **3a** was isolated when CH_3CN was replaced with 1,2-dimethoxyethane, whereas when $ClCH_2CH_2Cl$ or CH_3CN/H_2O (3:1) was employed, no desired product **3a** was detected (Table 1, entries 12−14). Meanwhile, when water was used as the cosolvent, the corresponding lactols were also detected in the reaction mixtures. Bu_4NOTf, Bu_4NPF_6, or Me_4NClO_4 instead of Bu_4NClO_4 as the supporting electrolyte also showed a decreased conversion (Table 1, entries 15−17). Only 14% yield of the desired product was detected in the absence of $MnBr_2$ (Table 1, entry 18). The yield of the electrochemical reaction declined sharply in an atmosphere of air, indicating an inert atmosphere was essential (Table 1, entry 19). As expected, the reaction could not be carried out without an electric current (Table 1, entry 20).

With the optimized reaction conditions in hand, we then explored the substrate scope of this electrochemical trifluoromethylation of diverse types of glycals with CF_3SO_2Na (Table 2). The 3,4-dideoxy-glycals **1b−d** with different functional

Table 2. Substrate Scope of Glycals[a,b]



[a]Reaction conditions: glycals **1b−p** (0.05 mmol), CF_3SO_2Na (0.15 mmol, 3.0 equiv), $MnBr_2$ (0.005 mmol, 0.1 equiv), Bu_4NClO_4 (0.10 mmol, 2.0 equiv), and dry CH_3CN (4.0 mL) in an undivided cell with Pt as the anode and cathode, constant current = 2.0 mA, 75 °C, under an argon atmosphere, 4−6 h. [b]Yield of the isolated product. [c]Reaction conditions: **1d** (0.50 mmol), CF_3SO_2Na (1.50 mmol, 3.0 equiv), $MnBr_2$ (0.025 mmol, 0.05 equiv), Bu_4NClO_4 (1.00 mmol, 2.0 equiv), and dry CH_3CN (10.0 mL) in an undivided cell with Pt as the anode and cathode, constant current = 2.0 mA, 75 °C, under an argon atmosphere, 6 h.

groups were investigated. Both 3,4-dideoxyglycals with electron-withdrawing (acetyl, benzoyl) and electron-donating (benzyl) groups could be successfully converted to the desired trifluoromethylated products **3b−d** in good yields in this electrochemical oxidative process. Similarly, the treatment of benzylated galactal **1e** led to 2-trifluoromethyl galactal **3e** in an excellent yield (90%). Notably, galactals **1f−g** with acid-sensitive protecting groups such as *p*-methoxybenzyl (PMB) and *tert*-butyldimethylsilyl (TBS) also furnished the corresponding products **3f−g** in moderate to good yields under the standard conditions. However, product **3h** was obtained in only 30% yield when peracetylated galactal **1h** was used as the substrate, which might be attributed to the effect of the three electron-withdrawing acetyl groups. In addition, *p*-methoxybenzylated and *tert*-butyldimethylsilylated D-glucals delivered the desired products **3i−j** in 68−75% yields. Furthermore, the

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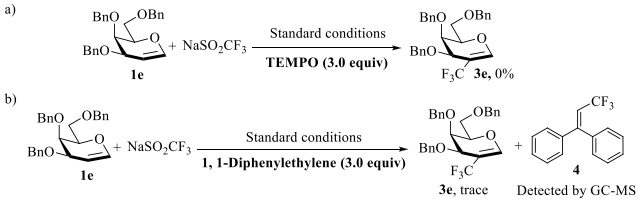
benzylated L-rhamnal/L-arabinal/D-xylal and *p*-methoxybenzylated L-rhamnal/L-arabinal were suitable substrates in this electrochemical transformation, affording the corresponding products **3k−o** in 64−75% yields. To our delight, the conversion of benzylated lactal **1p** was also realized in good yield (70%).

To explore the reaction mechanism of the electro-oxidative trifluoromethylation, radical trapping experiments were carried out. After the addition of 3.0 equiv of radical scavengers such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 1,1-diphenylethylene, the conversion was almost completely suppressed, and no desired product **3e** was obtained. Meanwhile, the trapping product **4** was detected by GC−MS (Scheme 2, Figure S2), implying that the reaction might involve a radical mechanism.

Scheme 2. Radical Trapping Experiments



Finally, cyclic voltammetry (CV) experiments were conducted to investigate the reaction mechanism. As shown in Figure 1, the obvious oxidation peaks of the redox mediator,

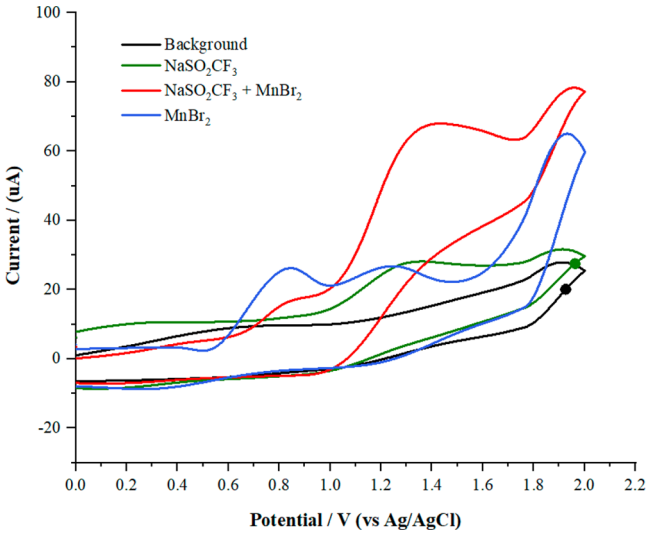
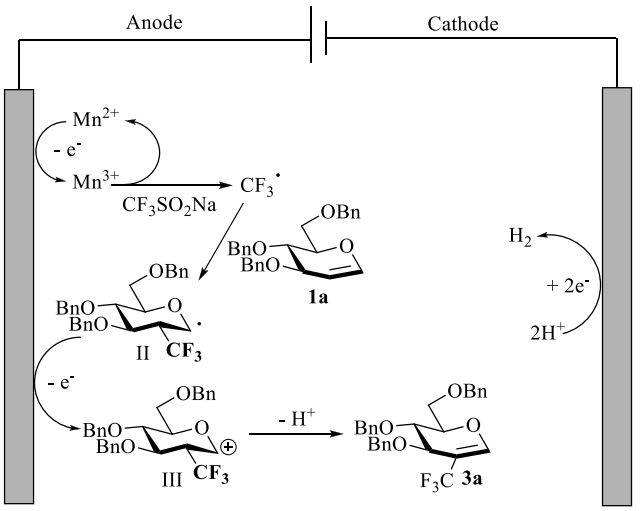


Figure 1. Cyclic voltammetry of CF_3SO_2Na, $MnBr_2$, and the mixture of $MnBr_2$ and CF_3SO_2Na. Conditions: A glassy carbon disk electrode (diameter is 3.0 mm, PTFE shroud) used as a working electrode, a platinum wire used as a counter electrode, Ag/AgCl electrode (3.5 M KCl solution) used as a reference electrode, Bu_4NClO_4 (0.10 M in MeCN), under an argon atmosphere, cyclic voltammogram at 0.05 V/s with $MnBr_2$ (2 mM), CF_3SO_2Na (8 mM) or $MnBr_2$ (2 mM), and CF_3SO_2Na (8 mM).

$MnBr_2$, were recorded at 0.84 and 1.22 V (vs Ag/AgCl) (Figure 1, blue curve), which could be attributed to the direct oxidation of Mn^{II} and the bromide ion (Br^-).[20] CF_3SO_2Na showed a higher oxidation potential than that of $MnBr_2$ (1.31 V vs 0.84 and 1.22 V, Figure 1, green curve), indicating $MnBr_2$ is more easily to be oxidized at the anode. Furthermore, the CV of the mixture of $MnBr_2$ and CF_3SO_2Na exhibited a new oxidation peak at 1.41 V (vs Ag/AgCl), along with an obvious catalytic current, which could be attributed to the $MnBr_2$ redox couple of the CF_3SO_2Na-bound complex (Figure 1, red curve).

Based on the results of control experiments and cyclic voltammetry experiments, a plausible reaction mechanism for the electrochemical trifluoromethylation was illustrated in Scheme 3. Mn^{II} was first oxidized to Mn^{III} at the anode. The

Scheme 3. Plausible Reaction Mechanism for the Electrochemical Trifluoromethylation



CF_3 radical was produced from CF_3SO_2Na by the Mn^{III}-mediated oxidation via a single -electron transfer (SET) process.[21] The attack of the CF_3 radical onto the double bond of glucal **1a** provided radical intermediate **II**, which could be further oxidized and transformed to glycosyl oxocarbenium ion **III** on the surface of an anode. Subsequently, the deprotonation of intermediate **III** afforded the desired trifluoromethylated product **3a**. H^+ could be correspondingly reduced to release H_2 on the surface of the cathode.

In summary, an efficient protocol has been developed for the electrochemical trifluoromethylation of a wide range of glycals with different protective groups in a regioselective manner by using inexpensive, easily available, and bench-stable CF_3SO_2Na as the trifluoromethyl source and a catalytic amount of $MnBr_2$ as the redox mediator. Mechanistic studies have revealed that the CF_3 radical might come from CF_3SO_2Na via the Mn^{II}-mediated oxidation process. We anticipate that this novel approach will not only enrich the methods for trifluoromethylation modification of carbohydrates but also promote the discovery of carbohydrate-related drugs.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all reagents were purchased from commercial suppliers and were used directly without further purification. CH_2Cl_2 and CH_3CN were distilled over calcium hydride prior to use. Reactions were monitored by thin-layer chromatography (TLC). Spots were visualized with a solution of concentrated sulfuric acid (5 mL) in CH_3CH_2OH (95 mL) or a solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (12.00 g, 9.7 mmol) and $Ce(NH_4)_2(NO_3)_6$ (0.25 g, 0.45 mmol) in sulfuric acid (5%, 250 mL). Flash column chromatography was carried out on silica gel (300−400 mesh). ^1H, ^{19}F, and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AV 400 (400 MHz) or Bruker AV 600 (600 MHz) at room temperature. The following abbreviations are used to indicate multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m =

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multiplet, dd = doublet of doublets, and br = broad. High-resolution mass spectra data were recorded on a Waters Xevo G2 Q-TOF mass spectrometer. Pt electrodes were purchased from Xuzhou Xinke Instrument Corp. The potentiostats were purchased from Taobao.com, HYELEC 3005B. Cyclic voltammetry was conducted in Metronm Autolab. Compounds **1a** and **1h** are commercially available. Compounds **1e**, **1f**, **1l**, and **1m** were synthesized according to the reported literature.[22]

Preparation of Glycals. *2-Acetoxymethyl-3,4-dihydro-2H-pyran (**1b**).* To a solution of the commercially available 2-hydroxymethyl-3,4-dihydro-2*H*-pyran (1.0 g, 8.77 mmol) in dry pyridine (8.0 mL) was added acetic anhydride (1.23 mL, 13.16 mmol) at 0 °C slowly. The reaction mixture was stirred at room temperature for 3 h. The mixture was diluted with ethyl acetate, washed with water, saturated aqueous NH_4Cl, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was purified by flash column chromatography to give compound **1b** as a yellow oil (eluent: petroleum ether/ethyl acetate = 10:1 (v/v); 1.2 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.39 (d, J = 6.1 Hz, 1H), 4.74−4.70 (m, 1H), 4.24−4.12 (m, 2H), 4.08−4.01 (m, 1H), 2.18−2.07 (m, 4H), 2.05−1.95 (m, 1H), 1.89−1.81 (m, 1H), 1.75−1.63 (m, 1H). The ^{1}H NMR data for **1b** coincide with the reported data.[23]

*2-Benzyloxymethyl-3,4-dihydro-2H-pyran (**1c**).* To a solution of the commercially available 2-hydroxymethyl-3,4-dihydro-2*H*-pyran (1.0 g, 8.77 mmol) in dry DMF (10.0 mL) were added NaH (701.6 mg, 17.54 mmol, 60%) and BnBr (1.5 mL, 13.15 mmol) at 0 °C slowly. The reaction mixture was stirred at room temperature for 5 h. After completion, the mixture was quenched with CH_3OH at 0 °C, diluted with ethyl acetate, washed with saturated aqueous NH_4Cl, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was purified by flash column chromatography to give compound **1c** as a yellow oil (eluent: petroleum ether/ethyl acetate = 10:1 (v/v); 1.6 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.27 (m, 5H), 6.40 (d, J = 6.2 Hz, 1H), 4.71−4.65 (m, 1H), 4.64−4.55 (m, 2H), 4.06−3.99 (m, 1H), 3.59 (dd, J = 10.2, 6.3 Hz, 1H), 3.52 (dd, J = 10.2, 4.3 Hz, 1H), 2.15−2.04 (m, 1H), 2.01−1.91 (m, 1H), 1.89−1.81 (m, 1H), 1.74−1.64 (m, 1H). The ^{1}H NMR data for **1c** coincide with the reported data.[24]

*2-Benzoylmethyl-3,4-dihydro-2H-pyran (**1d**).* To a solution of the commercially available 2-hydroxymethyl-3,4-dihydro-2*H*-pyran (1.0 g, 8.77 mmol) in dry pyridine (8.0 mL) was added BzCl (1.53 mL, 13.15 mmol) at 0 °C slowly. The reaction mixture was stirred at room temperature for 3 h. After completion, the mixture was quenched with CH_3OH at 0 °C, diluted with ethyl acetate, washed with 1 M HCl solution, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was purified by flash column chromatography to give compound **1d** as a yellow oil (eluent: petroleum ether/ethyl acetate = 8:1 (v/v); 1.6 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11−8.03 (m, 2H), 7.60−7.54 (m, 1H), 7.47−7.42 (m, 2H), 6.40 (d, J = 6.2 Hz, 1H), 4.75−4.71 (m, 1H), 4.43 (d, J = 5.2 Hz, 2H), 4.22−4.13 (m, 1H), 2.20−2.10 (m, 1H), 2.10−2.00 (m, 1H), 1.98−1.90 (m, 1H), 1.86−1.74 (m, 1H). The ^{1}H NMR data for **1d** coincide with the reported data.[24]

*3,4,6-Tri-O-tert-butyldimethylsilyl-D-galactal (**1g**).* To a solution of the commercially available 3,4,6-tri-*O*-acetyl-D-galactal (2.0 g, 7.34 mmol) in CH_3OH (40.0 mL) was added CH_3ONa (40.0 mg, 0.74 mmol) slowly at 0 °C. The reaction mixture was stirred at room temperature for 1 h and evaporated in vacuo. Then the residue was dissolved in dry DMF (15.0 mL), imidazole (3.0 g, 43.92 mmol), and TBSCl (5.0 g, 33.03 mmol) were successively added at 0 °C. The reaction mixture was stirred at room temperature for 5 h. After completion, the mixture was quenched with H_2O, diluted with ethyl acetate, washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was purified by flash column chromatography to give compound **1g** as a yellow oil (eluent: petroleum ether/ethyl acetate = 30:1 (v/v); 2.5 g, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.24 (d, J = 6.1 Hz, 1H), 4.72−4.63 (m, 1H), 4.12−4.04 (m, 4H), 3.88 (d, J = 8.1 Hz, 1H), 0.93 (s, 9H), 0.92 (s, 18H), 0.122 (s, 3H), 0.118 (s, 3H), 0.09 (s, 6H), 0.08 (s, 6H). The ^{1}H NMR data for **1g** coincide with the reported data.[25]

*3,4,6-Tri-O-(p-methoxybenzyl)-D-glucal (**1i**).* To a solution of the commercially available 3,4,6-tri-*O*-acetyl-D-glucal (1.0 g, 3.67 mmol) in CH_3OH (20.0 mL) was added CH_3ONa (20.0 mg, 0.37 mmol) slowly at 0 °C. The reaction mixture was stirred at room temperature for 1 h and evaporated in vacuo. Then the residue was dissolved in dry DMF (20.0 mL), and NaH (880.8 mg, 22.02 mmol, 60%) and PMBCl (2.2 mL, 16.51 mmol) were successively added at 0 °C. The reaction mixture was stirred at room temperature for 5 h. After completion, the mixture was quenched with CH_3OH at 0 °C, diluted with ethyl acetate, washed with saturated aqueous NH_4Cl, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was purified by flash column chromatography to give compound **1i** as a yellow oil (eluent: petroleum ether/ethyl acetate = 8:1 (v/v); 1.3 g, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29−7.26 (m, 4H), 7.18−7.15 (m, 2H), 6.90−6.83 (m, 6H), 6.43 (dd, J = 6.1, 1.1 Hz, 1H), 4.86 (dd, J = 6.1, 2.6 Hz, 1H), 4.76 (d, J = 10.9 Hz, 1H), 4.63−4.49 (m, 5H), 4.19 (dd, J = 4.3, 1.9 Hz, 1H), 4.06−4.01 (m, 1H), 3.83 (s, 3H), 3.82 (s, 6H), 3.82−3.73 (m, 3H). The ^{1}H NMR data for **1i** coincide with the reported data.[24]

*3,4,6-Tri-O-tert-butyldimethylsilyl-D-glucal (**1j**).* Following the procedure for the synthesis of compound **1g**, compound **1j** was obtained starting from commercially available 3,4,6-tri-*O*-acetyl-D-glucal (2.0 g, 7.34 mmol) as a yellow oil (eluent: petroleum ether/ethyl acetate = 30:1 (v/v); 2.3 g, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.32 (d, J = 6.3 Hz, 1H), 4.72−4.67 (m, 1H), 4.02−3.97 (m, 1H), 3.96−3.86 (m, 2H), 3.81−3.72 (m, 2H), 0.90 (s, 9H), 0.888 (s, 9H), 0.887 (s, 9H), 0.10 (s, 6H), 0.079 (s, 3H), 0.076 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H). The ^{1}H NMR data for **1j** coincide with the reported data.[25]

*3,4-Di-O-benzyl-L-rhamnal (**1k**).* Following the procedure for the synthesis of compound **1c**, compound **1k** was obtained starting from L-rhamnal (477.1 mg, 3.67 mmol) as a yellow oil (eluent: petroleum ether/ethyl acetate = 8:1 (v/v); 967.0 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.27 (m, 10H), 6.36 (dd, J = 6.2, 1.4 Hz, 1H), 4.90−4.81 (m, 2H), 4.73−4.64 (m, 2H), 4.57 (d, J = 11.7 Hz, 1H), 4.23−4.18 (m, 1H), 4.02−3.90 (m, 1H), 3.49 (dd, J = 9.0, 6.5 Hz, 1H), 1.38 (d, J = 6.4 Hz, 3H). The ^{1}H NMR data for **1k** coincide with the reported data.[26]

*3,4-Di-O-(p-methoxybenzyl)-L-arabinal (**1n**).* Following the procedure for the synthesis of compound **1i**, compound **1n** was obtained starting from 3,4-di-*O*-acetyl-L-arabinal (928.6 mg, 4.64 mmol) as a yellow oil (eluent: petroleum ether/ethyl acetate = 9:1 (v/v); 1.1 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.26 (m, 4H), 6.95−6.86 (m, 4H), 6.41 (d, J = 6.0 Hz, 1H), 4.89−4.83 (m, 1H), 4.66 (s, 2H), 4.63 (d, J = 11.8 Hz, 1H), 4.54 (d, J = 11.8 Hz, 1H), 4.07−3.93 (m, 3H), 3.833 (s, 3H), 3.829 (s, 3H), 3.76−3.71 (m, 1H). The ^{1}H NMR data for **1n** coincide with the reported data.[15b]

*3,4-Di-O-benzyl-D-xylal (**1o**).* Following the procedure for the synthesis of compound **1c**, compound **1o** was obtained starting from D-xylal (425.5 mg, 3.67 mmol) as a yellow oil (eluent: petroleum ether/ethyl acetate = 8:1 (v/v); 956.0 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40−7.27 (m, 10H), 6.55 (d, J = 6.2 Hz, 1H), 4.95−4.91 (m, 1H), 4.70−4.50 (m, 4H), 4.14−4.08 (m, 1H), 3.96 (dd, J = 11.7, 1.9 Hz, 1H), 3.84 (t, J = 3.4 Hz, 1H), 3.67 (t, J = 3.3 Hz, 1H). The ^{1}H NMR data for **1o** coincide with the reported data.[15b]

*2,3,3′,4,6,6′-Hexa-O-benzyl-D-lactal (**1p**).* To a solution of the commercially available D-lactose (10.0 g, 29.24 mmol) in dry pyridine (60 mL) was added acetic anhydride (43.9 mL, 0.47 mol) at 0 °C slowly. The reaction mixture was stirred at room temperature for 5 h. After completion, the mixture was diluted with ethyl acetate, washed with water, 1 M HCl solution, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was dissolved in dry CH_2Cl_2 (50.0 mL), and 33% HBr/HOAc (30 mL) was added at 0 °C slowly. The reaction mixture was stirred at room temperature for 2 h, diluted with CH_2Cl_2, washed with water, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was dissolved in acetone (20.0 mL), and then NaH_2PO_4 (41.3 g, 0.28 mol) and Zn dust (13.1 g, 0.20 mol) were added. The reaction mixture was stirred at room temperature for 10 min, and H_2O (8.0 mL) was

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added. The reaction mixture was stirred at room temperature for 6 h. After completion, the mixture was quenched with H_2O and extracted with ethyl acetate. The organic layers were combined, washed with water, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was purified by flash column chromatography to give 2,3,3′,4,6,6′-hexa-*O*-acetyl-D-lactal as a yellow oil (eluent: petroleum ether/ethyl acetate = 4:1 (v/v); 11.1 g, 68% yield). 2,3,3′,4,6,6′-Hexa-*O*-acetyl-D-lactal (5.0 g, 8.9 mmol) was dissolved in CH_3OH (40.0 mL), and CH_3ONa (48.06 mg, 0.89 mmol) was added slowly at 0 °C. The reaction mixture was stirred at room temperature for 1 h and evaporated in vacuo. Then the residue was dissolved in dry DMF (50.0 mL), and NaH (5.7 g, 0.14 mol, 60%) and BnBr (12.7 mL, 0.10 mol) were successively added at 0 °C. The reaction mixture was stirred at room temperature for 5 h. After completion, the mixture was quenched with CH_3OH at 0 °C, diluted with ethyl acetate, washed with saturated aqueous NH_4Cl, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was purified by flash column chromatography to give compound **1p** as a yellow oil (eluent: petroleum ether/ethyl acetate = 8:1 (v/v); 6.7 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.19 (m, 30H), 6.43 (d, J = 6.3 Hz, 1H), 4.93 (d, J = 11.6 Hz, 1H), 4.87 (dd, J = 6.1, 3.6 Hz, 1H), 4.83 (d, J = 10.8 Hz, 1H), 4.75−4.66 (m, 3H), 4.62−4.53 (m, 4H), 4.47 (s, 2H), 4.37 (d, J = 11.8 Hz, 1H), 4.32 (d, J = 11.7 Hz, 1H), 4.26 (dd, J = 9.2, 5.5 Hz, 1H), 4.17−4.10 (m, 2H), 3.89−3.74 (m, 3H), 3.67 (dd, J = 10.7, 3.5 Hz, 1H), 3.58−3.41 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 144.5, 138.80, 138.75, 138.7, 138.5, 138.1, 137.9, 128.41, 128.36, 128.31, 128.25, 128.22, 128.18, 127.9, 127.8, 127.7, 127.6, 127.5, 127.3, 102.9, 99.8, 82.3, 79.5, 75.9, 75.2, 74.6, 73.6, 73.53, 73.49, 73.3, 73.2, 73.0, 72.3, 70.4, 68.6, 68.0. HRMS (ESI): m/z $[M + NH_4]^+$ calcd for $C_{54}H_{60}NO_9$, 866.4263; found, 866.4282.

Electrochemical Trifluoromethylation. *General Procedure A.* An oven-dried three-neck flask fitted with a stir bar was charged with glycal (0.05 mmol), $NaSO_2CF_3$ (23.4 mg, 0.15 mmol), Bu_4NClO_4 (34.2 mg, 0.10 mmol), $MnBr_2$ (1.0 mg, 0.005 mmol), and dry CH_3CN (4.0 mL). The flask was equipped with two platinum electrodes (2.0 × 1.5 × 0.01 cm^3). Then the reaction flask was sealed, degassed, and filled with argon. The electrolysis was conducted at 75 °C under an argon atmosphere with a constant current of 2.0 mA for 4−6 h. After completion, the reaction mixture was concentrated in vacuo and eluted by flash column chromatography with petroleum ether/ethyl acetate to give the desired product.

General Procedure B. An oven-dried three-neck flask fitted with a stir bar was charged with glycal (0.25 mmol), $NaSO_2CF_3$ (117.0 mg, 0.75 mmol), Bu_4NClO_4 (171.0 mg, 0.50 mmol), $MnBr_2$ (5.0 mg, 0.025 mmol), and dry CH_3CN (20.0 mL). The flask was equipped with two platinum electrodes (2.0 × 1.5 × 0.01 cm^3). Then the reaction flask was sealed, degassed, and filled with argon. The electrolysis was conducted at 75 °C under an argon atmosphere with a constant current of 2.0 mA for 4 h. After completion, the reaction mixture was concentrated in vacuo and eluted by flash column chromatography with petroleum ether/ethyl acetate to give the desired product.

General Procedure C. An oven-dried three-neck flask fitted with a stir bar was charged with glycal (0.50 mmol), $NaSO_2CF_3$ (234.0 mg, 1.50 mmol), Bu_4NClO_4 (342.0 mg, 1.00 mmol), $MnBr_2$ (5.0 mg, 0.025 mmol), and dry CH_3CN (10.0 mL). The flask was equipped with two platinum electrodes (2.0 × 1.5 × 0.01 cm^3). Then the reaction flask was sealed, degassed, and filled with argon. The electrolysis was conducted at 75 °C under an argon atmosphere with a constant current of 2.0 mA for 6 h. After completion, the reaction mixture was concentrated in vacuo and eluted by flash column chromatography with petroleum ether/ethyl acetate to give the desired product.

*2-Trifluoromethyl-3,4,6-tri-O-benzyl-D-glucal (**3a**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3a** was obtained as a yellow oil (19.4 mg, 80%) after flash column chromatography (petroleum ether/ethyl acetate = 15:1, v/v). According to the general procedure B of the electrochemical trifluoromethylation, compound **3a** was obtained as a yellow oil (73.8 mg, 61%) after flash column chromatography (petroleum ether/ethyl acetate = 15:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.14 (m, 15H), 7.06 (s, 1H), 4.57−4.43 (m, 7H), 4.09 (s, 1H), 3.89 (t, J = 3.2 Hz, 1H), 3.77 (dd, J = 10.4, 6.9 Hz, 1H), 3.66 (dd, J = 10.5, 5.1 Hz, 1H). The ^{1}H NMR data for **3a** coincide with the reported data.[27]

*2-Acetoxymethyl-5-trifluoromethyl-3,4-dihydro-2H-pyran (**3b**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3b** was obtained as a yellow oil (9.9 mg, 88%) after flash column chromatography (petroleum ether/ethyl acetate = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (d, J = 1.3 Hz, 1H), 4.25 (dd, J = 11.8, 3.7 Hz, 1H), 4.18 (dd, J = 11.8, 6.3 Hz, 1H), 4.13−4.07 (m, 1H), 2.26−2.19 (m, 2H), 2.11 (s, 3H), 2.02−1.93 (m, 1H), 1.79−1.67 (m, 1H). The ^{1}H NMR data for **3b** coincide with the reported data.[15b]

*2-Benzyloxymethyl-5-trifluoromethyl-3,4-dihydro-2H-pyran (**3c**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3c** was obtained as a yellow oil (10.7 mg, 79%) after flash column chromatography (petroleum ether/ethyl acetate = 15:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.27 (m, 5H), 6.99 (d, J = 1.2 Hz, 1H), 4.64−4.53 (m, 2H), 4.09−4.04 (m, 1H), 3.64−3.55 (m, 2H), 2.23−2.13 (m, 2H), 2.02−1.92 (m, 1H), 1.82−1.68 (m, 1H). The ^{1}H NMR data for **3c** coincide with the reported data.[15b]

*2-Benzoylmethyl-5-trifluoromethyl-3,4-dihydro-2H-pyran (**3d**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3d** was obtained as a yellow oil (10.2 mg, 71%) after flash column chromatography (petroleum ether/ethyl acetate = 8:1, v/v). According to the general procedure C of the electrochemical trifluoromethylation, compound **3d** was obtained as a yellow oil (84.4 mg, 59%) after flash column chromatography (petroleum ether/ethyl acetate = 8:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11−8.01 (m, 2H), 7.59 (t, J = 8.0 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.02 (d, J = 0.5 Hz, 1H), 4.53−4.41 (m, 2H), 4.33−4.16 (m, 1H), 2.29−2.25 (m, 2H), 2.06−2.05 (m, 1H), 1.91−1.76 (m, 1H). The ^{1}H NMR data for **3d** coincide with the reported data.[15b]

*2-Trifluoromethyl-3,4,6-tri-O-benzyl-D-galactal (**3e**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3e** was obtained as a yellow oil (21.8 mg, 90%) after flash column chromatography (petroleum ether/ethyl acetate = 15:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.26 (m, 15H), 6.93 (s, 1H), 4.78−4.73 (m, 2H), 4.68−4.52 (m, 3H), 4.49−4.42 (m, 2H), 4.30 (d, J = 3.0 Hz, 1H), 3.96−3.90 (m, 2H), 3.83 (dd, J = 11.3, 2.9 Hz, 1H). The ^{1}H NMR data for **3e** coincide with the reported data.[27]

*2-Trifluoromethyl-3,4,6-tri-O-(p-methoxybenzyl)-D-galactal (**3f**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3f** was obtained as a yellow oil (20.1 mg, 70%) after flash column chromatography (petroleum ether/ethyl acetate = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24−7.18 (m, 6H), 6.90 (d, J = 1.0 Hz, 1H), 6.89−6.83 (m, 6H), 4.68 (dd, J = 11.1, 6.0 Hz, 2H), 4.59−4.45 (m, 3H), 4.42−4.37 (m, 1H), 4.35 (d, J = 11.5 Hz, 1H), 4.25 (d, J = 3.2 Hz, 1H), 3.89 (t, J = 3.9 Hz, 1H), 3.85 (dd, J = 10.9, 8.6 Hz, 1H), 3.81 (s, 9H), 3.76 (dd, J = 11.2, 3.1 Hz, 1H). The ^{1}H NMR data for **3f** coincide with the reported data.[15b]

*2-Trifluoromethyl-3,4,6-tri-O-tert-butyldimethylsilyl-D-galactal (**3g**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3g** was obtained as a yellow oil (23.6 mg, 85%) after flash column chromatography (petroleum ether/ethyl acetate = 60:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 (d, J = 1.4 Hz, 1H), 4.26−4.19 (m, 2H), 4.16−4.10 (m, 1H), 4.04−4.01 (m, 1H), 3.92 (d, J = 12.1 Hz, 1H), 0.94 (s, 9H), 0.89 (s, 9H), 0.88 (s, 9H), 0.153 (s, 3H), 0.151 (s, 3H), 0.11 (s, 6H), 0.054 (s, 3H), 0.052 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −61.28. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 147.1 (q, J = 7.0 Hz), 124.7 (q, J = 270.0 Hz), 106.1 (q, J = 30.4 Hz), 80.8, 69.6, 63.1, 60.9, 26.2, 26.0, 25.8, 18.5, 18.4, 18.2, −3.7, −4.2, −5.0, −5.2, −5.3, −5.6. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{25}H_{52}F_3O_4Si_3$, 557.3120; found, 557.3126.

*2-Trifluoromethyl-3,4,6-tri-O-acetyl-D-galactal (**3h**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3h** was obtained as a yellow oil (5.1 mg, 30%) after flash column chromatography (petroleum ether/ethyl acetate = 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (s, 1H), 5.84 (d, J = 5.0 Hz, 1H), 5.45 (dd, J = 4.3, 3.1 Hz, 1H), 4.47−4.43 (m, 1H), 4.42−4.35 (m, 1H),

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4.27 (dd, J = 11.8, 4.1 Hz, 1H), 2.12 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H). The ^{1}H NMR data for **3h** coincide with the reported data.[15b]

*2-Trifluoromethyl-3,4,6-tri-O-(p-methoxybenzyl)-D-glucal (**3i**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3i** was obtained as a yellow oil (21.5 mg, 75%) after flash column chromatography (petroleum ether/ethyl acetate = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21−7.13 (m, 6H), 7.03 (d, J = 1.5 Hz, 1H), 6.89−6.80 (m, 6H), 4.54−4.36 (m, 7H), 4.04 (d, J = 1.8 Hz, 1H), 3.83 (t, J = 3.4 Hz, 1H), 3.81 (s, 6H), 3.80 (s, 3H), 3.72 (dd, J = 10.5, 6.9 Hz, 1H), 3.61 (dd, J = 10.5, 5.0 Hz, 1H). The ^{1}H NMR data for **3i** coincide with the reported data.[15b]

*2-Trifluoromethyl-3,4,6-tri-O-tert-butyldimethylsilyl-D-glucal (**3j**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3j** was obtained as a yellow oil (18.9 mg, 68%) after flash column chromatography (petroleum ether/ethyl acetate = 60:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (d, J = 1.7 Hz, 1H), 4.22−4.18 (m, 1H), 4.01 (s, 1H), 3.96 (dd, J = 11.6, 8.2 Hz, 1H), 3.91−3.88 (m, 1H), 3.75 (dd, J = 11.6, 4.5 Hz, 1H), 0.90 (s, 9H), 0.87 (s, 9H), 0.86 (s, 9H), 0.11 (s, 3H), 0.09 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.79. ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 146.6 (q, J = 6.9 Hz), 125.3 (q, J = 264.2 Hz), 103.9 (q, J = 30.4 Hz), 81.4, 67.9, 63.3, 61.4, 25.9, 25.6, 25.5, 18.4, 17.83, 17.80, −4.2, −4.7, −5.2, −5.3, −5.6. HRMS (ESI): m/z [M + HCOO]$^-$ calcd for $C_{26}H_{52}F_3O_6Si_3$, 601.3029; found, 601.3030.

*2-Trifluoromethyl-3,4-di-O-benzyl-L-rhamnal (**3k**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3k** was obtained as a yellow oil (14.2 mg, 75%) after flash column chromatography (petroleum ether/ethyl acetate = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.27 (m, 10H), 7.02 (d, J = 1.2 Hz, 1H), 4.65−4.59 (m, 2H), 4.57−4.52 (m, 2H), 4.43−4.35 (m, 1H), 4.14 (d, J = 3.1 Hz, 1H), 3.60 (t, J = 3.7 Hz, 1H), 1.38 (d, J = 7.0 Hz, 3H). The ^{1}H NMR data for **3k** coincide with the reported data.[15b]

*2-Trifluoromethyl-3,4-di-O-(p-methoxybenzyl)-L-rhamnal (**3l**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3l** was obtained as a yellow oil (14.0 mg, 64%) after flash column chromatography (petroleum ether/ethyl acetate = 9:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.18 (m, 4H), 7.00 (d, J = 1.1 Hz, 1H), 6.91−6.84 (m, 4H), 4.58−4.53 (m, 2H), 4.50−4.46 (m, 2H), 4.38−4.29 (m, 1H), 4.11 (d, J = 3.2 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.56 (t, J = 3.8 Hz, 1H), 1.36 (d, J = 6.9 Hz, 3H). The ^{1}H NMR data for **3l** coincide with the reported data.[15b]

*2-Trifluoromethyl-3,4-di-O-benzyl-L-arabinal (**3m**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3m** was obtained as a yellow oil (12.9 mg, 71%) after flash column chromatography (petroleum ether/ethyl acetate = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.27 (m, 10H), 6.97 (d, J = 1.5 Hz, 1H), 4.90 (d, J = 10.9 Hz, 1H), 4.75−4.61 (m, 3H), 4.30 (d, J = 2.3 Hz, 1H), 4.17−4.07 (m, 2H), 3.80−3.75 (m, 1H). The ^{1}H NMR data for **3m** coincide with the reported data.[15b]

*2-Trifluoromethyl-3,4-di-O-(p-methoxybenzyl)-L-arabinal (**3n**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3n** was obtained as a yellow oil (15.5 mg, 73%) after flash column chromatography (petroleum ether/ethyl acetate = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.26 (m, 4H), 6.95 (d, J = 1.4 Hz, 1H), 6.92−6.84 (m, 4H), 4.82 (d, J = 10.5 Hz, 1H), 4.66−4.61 (m, 2H), 4.56 (d, J = 11.5 Hz, 1H), 4.25 (d, J = 2.2 Hz, 1H), 4.13−4.02 (m, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 3.77−3.71 (m, 1H). The ^{1}H NMR data for **3n** coincide with the reported data.[15b]

*2-Trifluoromethyl-3,4-di-O-benzyl-D-xylal (**3o**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3o** was obtained as a yellow oil (11.8 mg, 65%) after flash column chromatography (petroleum ether/ethyl acetate = 15:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.27 (m, 10H), 7.16 (d, J = 1.4 Hz, 1H), 4.62−4.48 (m, 4H), 4.29−4.24 (m, 1H), 4.03−3.96 (m, 2H), 3.65−3.63 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.77. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 149.9 (q, J = 6.9 Hz), 137.5, 137.4, 128.6, 128.5, 128.11, 128.05, 127.8, 125.0 (q, J = 270.7 Hz), 103.5 (q, J = 31.1 Hz), 72.0, 71.1, 69.9, 66.4, 64.2. HRMS (ESI): m/z [M + NH_4]$^+$ calcd for $C_{20}H_{23}F_3NO_3$, 382.1625; found, 382.1624.

*2′-Trifluoromethyl-2,3,3′,4,6,6′-hexa-O-benzyl-D-lactal (**3p**).* According to the general procedure A of the electrochemical trifluoromethylation, compound **3p** was obtained as a yellow oil (32.1 mg, 70%) after flash column chromatography (petroleum ether/ethyl acetate = 6:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.22 (m, 30H), 7.05 (d, J = 1.5 Hz, 1H), 4.93 (d, J = 11.7 Hz, 1H), 4.79 (d, J = 10.8 Hz, 1H), 4.77−4.54 (m, 7H), 4.49−4.33 (m, 5H), 4.26 (s, 1H), 4.23 (t, J = 2.5 Hz, 1H), 3.86 (d, J = 2.9 Hz, 1H), 3.81−3.74 (m, 2H), 3.61 (dd, J = 10.5, 5.1 Hz, 1H), 3.54−3.42 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.60. ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 147.7 (q, J = 6.7 Hz), 138.5, 138.4, 137.78, 137.75, 128.5, 128.4, 128.32, 128.25, 127.9, 127.8, 127.73, 127.67, 127.64, 127.62, 127.5, 124.9 (q, J = 270.3 Hz), 103.6 (q, J = 30.9 Hz), 102.8, 82.0, 79.0, 75.8, 75.2, 74.6, 73.7, 73.6, 73.5, 73.3, 73.2, 72.1, 70.9, 68.9, 68.8, 67.4. HRMS (ESI): m/z [M + HCOO]$^-$ calcd for $C_{56}H_{56}F_3O_{11}$, 961.3780; found, 961.3771.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01318.

Copies of ^{1}H, ^{19}F and ^{13}C{^{1}H} NMR spectra of compounds (PDF)

FAIR data, including the primary NMR FID files, for compounds **1b−1d**, **1g**, **1i−1k**, **1n−1p**, and **3a−3p** (ZIP)

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Notes

The authors declare no competing financial interest.

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