# Rapid Approach to Cationic Organic Triflates Based on Flash

# **Electrolysis in Flow**

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#### 1. General Remarks

# 1.1. Abbreviations

aqueous (aq.), aryl (Ar), broad (br), degrees Celsius (°C), calculated (calcd), deuterated chloroform (CDCl<sub>3</sub>), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), centimeter(s) (cm), doublet (d), electron ionization (EI), equivalent (equiv or eq), electrospray ionization (ESI), gram(s) (g), gas chromatography (GC), hour(s) (h), high resolution mass-spectrometry (HRMS), hertz (Hz), coupling constant (*J*), length of tubes (L), liter(s) (L), mol L<sup>-1</sup> of molar concentration (M), multiplet (m), methyl (Me), milligram(s) (mg), megahertz (MHz), minute(s) (min), milliliter(s) (mL), millimole(s) (mmol), mole(s) (mol), nuclear magnetic resonance (NMR), para (*p*), parts per million (ppm), polytetrafluoroethylene (PTFE), quartet (q), retention factor for TLC (Rf), room temperature (25 ± 3 °C, rt), second(s) (s), singlet (s), saturated (sat.), triplet (t), tertiary (tert), 1,1,2,2-tetrachloroethane (TCE), thin layer chromatography (TLC), tetramethylsilane (TMS), residence time of microtube reactor Rn ( $t^{Rn}$ ), chemical shift in ppm downfield from TMS ( $\delta$ ), inner diameter of microtubes and micromixers ( $\phi$ ).

#### 1.2. General

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Varian MERCURY plus-400 (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 100 MHz, <sup>19</sup>F: 377 MHz) and JEOL JNM-ECZ500R (<sup>1</sup>H: 500 MHz, <sup>13</sup>C: 125 MHz, HMQC). Chemical shifts are recorded using TMS (0.0 ppm) or CDCl<sub>3</sub> (7.26 ppm) signals as an internal standard for <sup>1</sup>H NMR, methin signal of CHCl<sub>3</sub> for <sup>13</sup>C NMR (77.0 ppm), and CF<sub>3</sub> signal of benzotrifluoride for <sup>19</sup>F NMR (-63.2 ppm) unless otherwise noted. NMR yields were calculated by <sup>1</sup>H NMR analyses with 10 seconds relaxation delay using TCE as an internal standard. GC analysis was performed on a Shimadzu GC-2014 gas chromatograph equipped with a flame ionization detector using a fused silica capillary column (Rtx-200; 30 m x 0.25 mm x 0.25 µm). GC yields were calculated by GC analysis using calibration lines derived from commercial or isolated compounds with the internal standards. Mass spectra were recorded on Thermo Fisher Scientific EXACTIVE plus (ESI) or JEOL JMS-700 (EI). Flash chromatograph was carried out on a silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40–100 µm). Gel permeation chromatography (GPC) was carried out on a Japan Analytical Industry LC-9201 equipped with JAIGEL-1H and 2H using CHCl<sub>3</sub> as eluent. Merck pre-coated silica gel F<sub>254</sub> plates (thickness 0.25 mm) were used for TLC analyses. Infrared absorption (IR) spectra were recorded on Mettler Toledo ReactIR 15 or SHIMADZU IRSpirit and selected absorption maxima ( $v_{max}$ ) were reported in wavenumbers (cm<sup>-1</sup>). Melting points were recorded on a Yanaco micro melting point apparatus and reported in degrees Celsius. All solution preparations and reactions were carried out in a flame-dried glassware under argon atmosphere using dehydrated solvent unless otherwise noted.

#### 1.3. Flow Equipment

Stainless steel (SUS304) T-shaped micromixer ( $\phi = 500 \ \mu m$ ) was manufactured by Sanko Seiki Co., Inc. Stainless steel (SUS316) microtube reactors ( $\phi = 500 \ \text{and} \ 1000 \ \mu m$ ) were purchased from GL Sciences. PTFE tube ( $\phi = 1000 \ \mu m$ ) was purchased from ISIS Co., Ltd. The syringe pumps (Harvard Model PHD ULTRA) equipped with gastight syringes (purchased from SGE) were used for introduction of the solutions into the microreactor systems *via* stainless steel fittings (GL Sciences, 1/16 OUW).

#### **<u>2. Experimental Procedures</u>**

#### 2.1. Reagents

Reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Tetrabutylammonium tetrafluoroborate ( $Bu_4NBF_4$ ) and tetrabutylammonium trifluoromethanesulfonate ( $Bu_4NOTf$ ) were purchased from Sigma-Aldrich and dried at 80 °C/1 mmHg over 12 hours before use. Tetrabutylammonium tetrakis(pentafluorophenyl)borate  $Bu_4NB(C_6F_5)_4$  was synthesized according to the literature procedure<sup>[1]</sup> and dried at 80 °C/1 mmHg over 12 hours. The supporting

electrolyte solution was prepared by dissolving supporting electrolyte (39.5 g for  $Bu_4NBF_4$ , 15.7 g for  $Bu_4NOTf$  and 36.8 g for  $Bu_4NB(C_6F_5)_4$  to 400 mL of dehydrated  $CH_2Cl_2$  (0.3 M for  $Bu_4NBF_4$ , 0.1 M for  $Bu_4NOTf$  and 0.1 M for  $Bu_4NB(C_6F_5)_4$ ) and was stored over molecular sieves 4A (MS4A).

#### **2.2. Preparation of Reagents**

Bis(4-fluorophenyl) disulfide<sup>[2]</sup>, bis(4-methoxyphenyl) disulfide<sup>[2]</sup>, bis(4-bromophenyl) disulfide<sup>[2]</sup>, 1-ethoxy-2-octyne<sup>[3]</sup>, 2-((4-fluorophenyl)thio)tetrahydrofuran<sup>[4]</sup>, 4-fluorophenyl 2,3,4,6-tetra-*O*-acetyl-1-thio- $\beta$ -D-glucopyranoside<sup>[5]</sup> and methyl 2,3,4-tri-*O*-benzyl- $\alpha$ -D-glucopyranoside<sup>[6]</sup> were synthesized according to the reported procedures.

#### 4-Fluorophenyl 2,3,4-tri-O-benzyl-6-O-((1,1-dimethylethyl)diphenylsilyl)-1-thio-β-D-glucopyranoside S1



4-Fluorophenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (2.30 g, 5.02 mmol) was dissolved in MeOH (10 mL), and sodium methoxide (28 wt% in MeOH, 0.2 mL) was added to the solution. The solution was stirred at room temperature for 24 h and the solution was evaporated under reduced pressure. The residue was passed through silica plug using ethyl acetate as an eluent and the solvent was removed under reduced pressure to give white solid. The white solid was dissolved in DMF (50 mL) and imidazole (0.68 g, 10.0 mmol) was added. To the solution was added *tert*-butyldiphenylchlorosilane TBDPSCI (2.07g, 7.5 mmol) at 0 °C. The reaction solution was warmed to room temperature and stirred for 1 h. The reaction was quenched by H<sub>2</sub>O. After separating and extracting with ethyl acetate, the organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pression in paraffin liquid, 0.90 g, 22.5 mmol) at the same temperature. After stirring for 1 h, benzyl bromide (3.89 g, 22.7 mmol) was slowly added at 0 °C. Then, the reaction solution was slowly warmed to room temperature and stirred for 12 h. The reaction was quenched by adding sat. NH<sub>4</sub>Cl aq. After separating and extracting with ethyl acetate, the organic layer was washed with brine, and extracting with ethyl acetate and the solvent was quenched by adding sat. NH<sub>4</sub>Cl aq. After separating and extracting with ethyl acetate, the organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was partice for 12 h. The reaction was quenched by adding sat. NH<sub>4</sub>Cl aq. After separating and extracting with ethyl acetate, the organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was partice layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure to room temperature and stirred for 12 h. The reaction was quenched by adding sat. NH<sub>4</sub>Cl aq. After separating and extracting with ethyl acetate, the organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub></sub>

TLC: Rf = 0.54 (hexane/ethyl acetate = 10/1)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.10 (s, 9H), 3.36-3.40 (m, 1H), 3.51 (t, *J* = 8.0 Hz, 1H), 3.69-3.81 (m, 2H), 3.91-4.01 (m, 2H), 4.61 (d, *J* = 9.7 Hz, 1H), 4.70 (d, *J* = 10.6 Hz, 1H), 4.77 (d, *J* = 10.1 Hz, 1H), 4.85-4.92 (m, 4H), 6.84-6.91 (m, 2H), 7.11-7.17 (m, 2H), 7.23-7.44 (m, 19H), 7.55-7.60 (m, 2H), 7.69-7.73 (m, 2H), 7.75-7.79 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 19.3, 26.8, 62.6, 75.1, 75.4, 75.9, 77.3 (The peak overlapped with chloroform), 79.9, 80.7, 86.8, 87.7, 115.9 (d, *J* = 22.0 Hz), 127.6, 127.7, 127.8, 127.9, 128.1, 128.4, 128.5, 128.7, 128.8, 129.6, 129.7, 132.9, 133.3, 134.4 (d, *J* = 8.0 Hz), 135.6, 135.8, 137.9, 138.0, 138.2, 162.4 (d, *J* = 247.7 Hz).

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>); δ–114.4- –114.6 (m, 1F).

IR (CHCl<sub>3</sub> solution) v<sub>max</sub>:701, 835, 906, 1081, 1238, 1491, 2032, 2174 cm<sup>-1</sup>.

HRMS (ESI) calcd for C<sub>49</sub>H<sub>51</sub>FO<sub>5</sub>SSiNa [M+Na<sup>+</sup>]: 821.3103, found 821.3098.

#### 4-Fluorophenyl 6-O-((4-methoxyphenyl)methyl)-2,3,4-tri-O-methyl)-1-thio-β-D-glucopyranoside S2



4-Fluorophenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (4.59 g, 10.0 mmol) was dissolved in MeOH (30 mL), and sodium methoxide (28 wt% in MeOH, 0.5 mL) was added to the solution. The solution was stirred at room temperature for 24 h and the solution was neutralized by 1.0 M HCl in Et<sub>2</sub>O (3.0 mL). The solution was evaporated under reduced pressure to give a white solid. The white solid was dissolved in DMF (100 mL) and cooled to 0 °C. To the solution was added NaH (60 wt.% dispersion in paraffin liquid, 1.59 g, 39.8 mmol) at the same temperature. After stirring for 30 min, *p*-methoxybenzyl chloride (2.0 g, 13.0 mmol) was slowly added at 0 °C. Then, the reaction solution was slowly warmed to room temperature and stirred for 12 h. The reaction was quenched by adding sat. NH<sub>4</sub>Cl aq. After separating and extracting with ethyl acetate, the organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was dissolved in DMF (100 mL) and cooled to 0 °C. To the solution was added NaH (60 wt.% dispersion in paraffin liquid, 1.80 g, 45.0 mmol) at the same temperature. After stirring for 30 min, methyl iodide (6.38 g, 45.0 mmol) was slowly added at 0 °C. Then, the reaction solution was slowly added at 0 °C. The solution was added NaH (60 wt.% dispersion in paraffin liquid, 1.80 g, 45.0 mmol) at the same temperature. After stirring for 30 min, methyl iodide (6.38 g, 45.0 mmol) was slowly added at 0 °C. Then, the reaction solution was slowly warmed to room temperature and stirred for 12 h. The reaction was quenched by adding sat. NH<sub>4</sub>Cl aq. After separating with ethyl acetate, the organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (hexane/ethyl acetate = 2/1) to give the title compound as a white solid **S2** (3.1 g, 6.85 mmol, 69% yield).

TLC: Rf = 0.37 (hexane/ethyl acetate = 2/1)

Melting point: 51-53 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.98-3.03 (m, 1H), 3.12-3.23 (m, 2H), 3.29-3.33 (m, 1H), 3.49 (s, 1H), 3.60 (s, 3H), 3.61-3.66 (m, 1H), 3.64 (s, 3H), 3.70-3.74 (m, 1H), 3.82 (s, 3H), 4.40 (d, *J* = 9.7 Hz, 1H), 4.50 (pseudo q, *J* = 11.4 Hz), 6.87-6.93 (m, 4H), 7.24-7.27 (m, 2H), 7.52-7.57 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 55.3, 60.5, 60.8, 60.9, 68.8, 73.0, 78.8, 79.5, 82.4, 87.2, 88.6, 113.7, 115.8 (d, *J* = 22.0 Hz), 128.4, 129.2, 130.3, 134.6 (d, *J* = 8.0 Hz), 159.1, 162.5 (d, *J* = 247.7 Hz).

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>); δ–114.4- –114.6 (m, 1F).

IR (CHCl<sub>3</sub> solution) v<sub>max</sub>: 835, 1096, 1252, 1491, 1514, 2200 cm<sup>-1</sup>.

HRMS (ESI) calcd for C<sub>23</sub>H<sub>29</sub>FO<sub>6</sub>SNa [M+Na<sup>+</sup>]: 475.1561, found 475.1570.

## 2.3. Electrochemical Generation and Accumulation of [ArS(ArSSAr)]+ [OTf]- in a Batch Electrochemical Reactor

The anodic oxidation was carried out using an H-type divided electrochemical reactor equipped with a carbon felt anode (Nippon Carbon GF-20-P7, ca 350 mg, dried at 300 °C/1 mm Hg for 3 hours before use) and a platinum plate cathode (Nilaco, 20 mm x 30 mm) (Figure S1). Although the reactor was custom designed, similar reactors are commercially available at EC Frontier., Inc. (https://ec-frontier.co.jp/VB9.html). A Kikusui PMC350-0.2A was used as a direct current power supply for the electrolysis.



Figure S1. H-type divided electrochemical reactor.



In the anodic chamber were placed disulfide **1** (127 mg, 0.50 mmol) and 0.10 M Bu<sub>4</sub>NOTf in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (TfOH) (44  $\mu$ L, 0.50 mmol) and 0.10 M Bu<sub>4</sub>NOTf in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The constant current electrolysis (8 mA) was carried out at T °C with magnetic stirring until 0.67 F of electricity was consumed (ca. 70 min). After the electrolysis, a CH<sub>2</sub>Cl<sub>2</sub> solution of 1,3,5-trimethoxybenzene **2** (2.5 M, 1 mL, 2.5 mmol) was added to the anodic chamber at T °C, and the resulting mixture was stirred at T °C for 10 min. After addition of triethylamine (1 mL) to both chambers, the solution was warmed to room temperature. The solution in the anodic chamber was collected and the solvent was removed under reduced pressure. Et<sub>2</sub>O was added to the residue and the mixture was analyzed by GC using pentadecane as an internal standard. The results are summarized in Table S1, and the presumable reaction mechanism is shown in Scheme S1.

entry	Supporting electrolyte	Temperature T [°C]	Yield of <b>3</b> [%]	Yield of <b>4</b> [%]	Reacted [ArS(ArSSA)] <sup>+</sup> [a] [%]	Recovered 1 [%]
1	Bu <sub>4</sub> NOTf	-78	61	0	61	58
2		-50	58	2	62	59
3		0	44	3	50	62
4 <sup>[b]</sup>	Bu <sub>4</sub> NBF <sub>4</sub>	-78	80	trace	80	58
5 <sup>[b]</sup>		0	76	1	78	53
6 <sup>[b]</sup>	$Bu_4NB(C_6F_5)_4$	-78	77	2	81	52
7 <sup>[b]</sup>		0	69	3	75	52

Table S1. Electrochemical generation and accumulation of [ArS(ArSSAr)]+ in a batch electrochemical reactor.

# [a] (Reacted $[ArS(ArSSAr)]^+$ ) = (Yield of 3) + (Yield of 4) x 2

[b] Conditions: 1 (0.05M, 0.25 mmol) in Bu<sub>4</sub>NX (X = BF<sub>4</sub> or B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>)/CH<sub>2</sub>Cl<sub>2</sub>, TfOH (0.05 M, 0.25 mmol) in Bu<sub>4</sub>NX (X = BF<sub>4</sub> or B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>)/CH<sub>2</sub>Cl<sub>2</sub>, 2 (1.7 M, 0.5 mL, 0.84 mmol) in CH<sub>2</sub>Cl<sub>2</sub>, current = 8 mA, electrolysis time = ca. 35 min.

# (4-Fluorophenyl)(2,4,6-trimethoxyphenyl)sulfane 3



Electrochemical oxidation (0.67 F/mol) of bis(4-fluorophenyl) disulfide 1 and subsequent reaction with 1,3,5-trimethoxybenzene 2 gave the title compound 3. The crude was analyzed by GC using pentadecane as an internal standard. GC retention time = 26.5 min; initial oven temperature, 50 °C for 5 min; rate of temperature increase, 10 °C /min; final oven temperature, 300 °C for 10 min; white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.81 (s, 6H), 3.86 (s, 3H), 6.20 (s, 2H), 6.83–6.89 (m, 2H), 7.00–7.05 (m, 2H).

The NMR spectrum was in a good agreement with the reported one<sup>[7]</sup>.

(2,4,6-Trimethoxy-1,3-phenylene)bis((4-fluorophenyl)sulfane) 4



Electrochemical oxidation (0.67 F/mol) of bis(4-fluorophenyl) disulfide 1 and subsequent reaction with 1,3,5-trimethoxybenzene 2 gave the title compound 4. The crude was analyzed by GC using pentadecane as an internal standard. GC retention time = 32.4 min; initial oven temperature, 50 °C for 5 min; rate of temperature increase, 10 °C /min; final oven temperature, 300 °C for 10 min; white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.79 (s, 3H), 3.87 (s, 6H), 6.41 (s, 1H), 6.86–6.93 (m, 4H), 7.05–7.11 (m, 4H).

The NMR spectrum was in a good agreement with the reported one<sup>[7]</sup>.

Scheme S1. Presumable mechanism for the electrochemical generation of [ArS(ArSSAr)]<sup>+</sup> and recovering of disulfide.



## 2.4. Divided Flow Electrochemical Reactor

#### **Equipment**

The divided flow electrochemical reactor is composed of stainless-steel chambers and PTFE plates, formed by a mechanical manufacturing technique at DFC Co., Ltd. (Figure S2). Carbon felt for anode (GF-20-P7) was purchased from Nippon Carbon Co., Ltd. and dried at 300 °C/1 mm Hg for 3 hours before use. Pt plate for cathode was purchased from Nilaco Co., Ltd. Glass filter (Whatman, GF/A) and PTFE membrane (Millipore, pore size is 0.2 µm) for filtration were purchased from commercial suppliers and cut before use. Peltier cooling system was purchased from DFC Co., Ltd. A Kikusui PMC350-0.2A was used as a direct current power supply for the electrolysis.



Figure S2. Components of divided flow electrochemical reactor

# <u>Set Up</u>

A carbon felt anode (length: 40 mm, width: 10 mm, thickness: 1 mm) and two Pt plates (length: 40 mm, width: 10 mm, thickness: ca. 0.1 mm) were used as anode and cathode respectively. The electrodes were set in the flow channel, and the PTFE layer equipped with diaphragm composed of two glass filters (length: 55 mm, width: 15 mm) and three PTFE membranes (length: 55 mm, width: 15 mm) was inserted between flow channel layers. All components were assembled by four PTFE screws (Figure S3). Microtube reactors were connected to the assembled reactor. The reactor was fixed to the Peltier cooling system by PTFE screws and covered by PTFE plate. The overall system was shown in Figure S4.



Figure S3. Schematic diagram of assembled divided flow electrochemical reactor.



Figure S4. Reaction in flow electrochemical reactor system.

# 2.5. Generation of Arylbis(arylthiol)sulfonium Ions Using Flow Electrochemical Reactor



An electrochemical flow reactor system consisting of a divided flow electrochemical reactor, a T-shaped micromixer (**M1**), two microtube reactors (**R1** and **R2**), and three pre-cooling units (**P1** (L = 200 cm), **P2** (200 cm) and **P3** (100 cm)) was used. The reactor was cooled at 0 °C by a Peltier cooling system, and the flow microreactor system was cooled in acetone baths at 0 °C. During the operation, the volume of solution was monitored by sampling the solution and adjusted by changing diameter and length of tube reactor connected to the cathodic chamber. A solution of TfOH (0.05 M in Bu<sub>4</sub>NX/CH<sub>2</sub>Cl<sub>2</sub>, flow rate: F mL/min) was introduced to the cathodic chamber through **P1**. A solution of bis(4-fluorophenyl) disulfide **1** (0.05 M in Bu<sub>4</sub>NX/CH<sub>2</sub>Cl<sub>2</sub>, flow rate: F mL/min) was introduced to the anodic chamber through **P2**. The constant current electrolysis was carried out at 0 °C. Current value was set to consume 0.67 F/mol of electricity. The resulting solution from anodic chamber was passed through **R1** (L<sub>1</sub> cm, residence time  $t^{R1}$  = 11.8 s) and introduced to **M1** ( $\phi$  = 1000 µm), where a solution of 1,3,5-trimethoxybenzene **2** (0.335 M in CH<sub>2</sub>Cl<sub>2</sub>, flow rate: 1/2F mL/min) was reached, the product solution was collected to a vessel containing triethylamine (1 mL). Reactions were performed on a 0.10 mmol scale based on **1**. After removing the solvent under reduced pressure, Et<sub>2</sub>O and pentadecane were added, and the mixture was analyzed by GC. The results are summarized in Table S2.

Table S2. Generation of arylbis(arylthiol)sulfonium ion using divided flow electrochemical reactor.

		5	/		C						
entry	supporting electrolyte	Flow rate F [mL/min]	Electrolysis time <sup>[a]</sup> [sec]	Current [mA]	Current density [mA/cm <sup>2</sup> ]	L <sub>1</sub> [cm]	L <sub>2</sub> [cm]	Yield of <b>3</b> [%] <sup>[b]</sup>	Yield of <b>4</b> [%] <sup>[b]</sup>	Reacted [ArS(ArSSA)] <sup>+</sup> [%] <sup>[c]</sup>	Recovered 1 [%] <sup>[b]</sup>
1	Bu <sub>4</sub> NOTf	0.6	42.0	32	8.4	15	15	59	5	69	66
2	(0.1 M)	1.0	25.2	54	14.2	25	25	84	4	92	66
3		2.0	12.6	108	28.4	50	50	91	3	97	67
4		3.0	8.4	162	42.6	75	75	96	1	98	67
5	$Bu_4NBF_4$	0.6	42.0	32	8.4	15	15	65	10	85	68
6	(0.3 M)	1.0	25.2	54	14.2	25	25	85	5	95	66
7		2.0	12.6	108	28.4	50	50	91	2	95	69
8		3.0	8.4	162	42.6	75	75	96	0	96	67
9	$Bu_4NB(C_6F_5)_4$	0.6	42.0	32	8.4	15	15	63	6	75	65
10	(0.1 M)	1.0	25.2	54	14.2	25	25	70	4	78	62
11		2.0	12.6	108	28.4	50	50	72	4	80	63
12		3.0	8.4	162	42.6	75	75	74	2	78	65

[a] Calculated from the volume of the anodic flow channel and the flow rate.

[b] Determined by GC.

[c] (Reacted [ArS(ArSSAr)]<sup>+</sup>) = (Yield of  $\mathbf{3}$ ) + (Yield of  $\mathbf{4}$ ) x 2

#### 2.6. Vinyl Triflates Synthesis Using Flow Electrochemical Reactor System (Preliminary Experiment)



An electrochemical flow reactor system consisting of a divided flow electrochemical reactor, a T-shaped micromixer (M1), two

microtube reactors (**R1** and **R2**), and three pre-cooling units (**P1** (L = 200 cm), **P2** (200 cm) and **P3** (100 cm)) was used. The reactor was cooled at 0 °C by a Peltier cooling system, and the flow microreactor system was cooled in acetone baths at 0 °C. During the operation, the volume of solution was monitored by sampling the solution and adjusted by changing diameter and length of tube reactor connected to the cathodic chamber. A solution of TfOH (0.05 M in 0.1M Bu<sub>4</sub>NOTf/CH<sub>2</sub>Cl<sub>2</sub>, flow rate: 3.0 mL/min) was introduced to the cathodic chamber through **P1**. A solution of bis(4-fluorophenyl) disulfide **1** (0.05 M in 0.1M Bu<sub>4</sub>NOTf/CH<sub>2</sub>Cl<sub>2</sub>, flow rate: 3.0 mL/min) was introduced to the anodic chamber through **P2**. The constant current electrolysis was carried out at 0 °C. Current value was set to consume 0.67 F/mol of electricity (162 mA). The resulting solution from anodic chamber was passed through **R1** (50 cm, residence time  $t^{R1} = 7.9$  s) and introduced to **M1** ( $\phi \ \mu m$ ), where a solution of 1-chloro-2-octyne (0.045 M in CH<sub>2</sub>Cl<sub>2</sub>, flow rate: F mL/min) was also introduced. The mixed solution was passed through **R2** (500 cm, residence time  $t^{R2}$  s). After a steady state was reached, the product solution was collected to a flask at 0 °C. The reaction mixture was stirred at 0 °C for *t* min under Ar. Then triethylamine (1 mL) was added, and the solvent was removed under reduced pressure. The residue was dissolved in Et<sub>2</sub>O and filtered, and the crude mixture was analyzed by <sup>1</sup>H NMR using TCE as an internal standard. The crude was purified by GPC. Note that GPC purification and freezing of the compound are recommended as the product decomposes on a silica gel column chromatography and is slightly unstable at room temperature. The results are summarized in Table S3.

entry	Inner diameter of <b>M1</b> [µm]	Flow rate F [mL/min]	Equiv. of [ArS(ArSSAr)]+ [OTf] <sup>_</sup>	Residence time in <b>R2</b> t <sup>R2</sup> [sec]	Additional stirring <i>t</i> [min]	Yield of <b>5</b> [%] <sup>[a]</sup>
1	1000	1.5	1.5	52	0	57
2	500	1.5	1.5	52	0	63
3	500	1.3	1.7	55	0	69
4	500	1.3	1.7	55	1	74
5	500	1.3	1.7	55	30	80 (64) <sup>[b]</sup>

Table S3. Preliminary experiment for vinyl triflate synthesis in a flow electrochemical reactor system

[a] Determined by <sup>1</sup>H NMR analysis using TCE as an internal standard.

[b] Yield of the Isolated compound.

## (E)-1-chloro-2-((4-fluorophenyl)thio)oct-2-en-3-yl trifluoromethanesulfonate 5



Electrochemical oxidation (0.67 F/mol) of bis(4-fluorophenyl) disulfide 1 (0.30 mmol) in  $Bu_4NOTf/CH_2Cl_2$  and subsequent reaction with 1-chloro-2-octyne (0.12 mmol) gave the title compound 5. The yields were determined by <sup>1</sup>H NMR using TCE as an internal standard and purified by GPC; 31.3 mg, 64% isolated yield, pale yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.91 (t, *J* = 6.8 Hz, 3H), 1.32-1.38 (m, 4H), 1.62 (quint, *J* = 7.3 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 4.09 (s, 2H), 7.04-7.10 (m, 2H), 7.37-7.42 (m, 2 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>); δ 13.8, 22.2, 26.3, 30.9, 31.9, 39.8, 116.8 (d, J = 21.9 Hz), 118.3 (q, J = 317.8 Hz) 126.4 (d, J = 3.2 Hz), 127.3, 133.8 (d, J = 8.3 Hz), 152.6, 162.9 (d, J = 248.0 Hz).

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>); δ –74.7 (s, 3F), –112.6-–112.7 (m, 1F).

IR (neat)  $v_{\text{max}}$ : 1135, 1216, 1418, 1491, 1591, 1636, 2936, 2969 cm<sup>-1</sup>.

HRMS (EI) calcd for  $C_{15}H_{17}O_3ClF_4S_2$  420.0244, found 420.0241.

#### 2.7. Reactions of Anodically Generated [ArS(ArSSAr)]+ [OTf]- with Alkynes



An electrochemical flow reactor system consisting of a divided flow electrochemical reactor, a T-shaped micromixer (**M1**), two microtube reactors (**R1** and **R2**), and three pre-cooling units (**P1** (L = 200 cm), **P2** (200 cm) and **P3** (100 cm)) was used. The reactor was cooled at 0 °C by a Peltier cooling system, and the flow microreactor system was cooled in acetone baths at 0 °C. During the operation, the volume of solution was monitored by sampling the solution and adjusted by changing diameter and length of tube reactor connected to the cathodic chamber. A solution of TfOH (0.05 M in Bu<sub>4</sub>NOTf/CH<sub>2</sub>Cl<sub>2</sub>, flow rate: 3.0 mL/min) was introduced to the cathodic chamber through **P1**. A solution of disulfide (0.05 M in Bu<sub>4</sub>NOTf/CH<sub>2</sub>Cl<sub>2</sub>, flow rate: 3.0 mL/min) was introduced to the anodic chamber through **P2**. The constant current electrolysis was carried out at 0 °C. Current value was set to consume 0.67 F/mol of electricity (162 mA). The resulting solution from anodic chamber was passed through **R1** (50 cm, residence time  $t^{R1} = 7.9$  s) and introduced to **M1** ( $\phi = 500 \mu$ m), where a solution of alkyne (C<sub>1</sub> M in CH<sub>2</sub>Cl<sub>2</sub>, flow rate: F mL/min) was also introduced. The mixed solution was passed through **R2** (500 cm, residence time  $t^{R2}$  s). After a steady state was reached, the product solution was collected to a flask at 0 °C. The reaction mixture was stirred at 0 °C for 30 min under Ar. Then triethylamine (1 mL) was added, and the solvent was removed under reduced pressure. The residue was dissolved in Et<sub>2</sub>O and filtered, and the crude mixture was analyzed by <sup>1</sup>H NMR using TCE as an internal standard. The crude was purified by GPC. Note that GPC purification and freezing of the compound are recommended as the product decomposes on a silica gel column chromatography and is slightly unstable at room temperature. The results are summarized in Table S4.

Table S4. Reactions of anodically generated [ArS(ArSSAr)]<sup>+</sup> [OTf]<sup>-</sup> with alkynes in flow electrochemical reactor system



<sup>a</sup> Determined by <sup>1</sup>H NMR using TCE as an internal standard. The numbers in parentheses are the yield of the isolated compound.

#### (E)-1-ethoxy-2-((4-fluorophenyl)thio)oct-2-en-3-yl trifluoromethanesulfonate 6



Electrochemical oxidation (0.67 F/mol) of bis(4-fluorophenyl) disulfide **1** (0.45 mmol) in  $Bu_4NOTf/CH_2Cl_2$  and subsequent reaction with 1-ethoxy-2-octyne ( $C_1 = 0.045$  M, F = 1.3 mL/min, 0.18 mmol) gave the title compound **6**. The yield was determined by <sup>1</sup>H NMR using TCE as an internal standard and purified by GPC; 52.0 mg, 69 % isolated yield, pale yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.90 (t, *J* = 7.0 Hz, 3H), 1.14 (t, *J* = 7.0 Hz, 3H), 1.31-1.37 (m, 4H), 1.59 (quint, *J* = 7.5 Hz, 2H), 2.77 (t, *J* = 7.4 Hz, 2H), 3.35 (q, *J* = 6.9 Hz, 2H), 4.03(s, 2H), 7.01-7.06 (m, 2H), 7.35-7.40 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>); δ 13.9, 14.9, 22.2, 26.4, 31.0, 31.9, 65.9, 66.0, 116.4 (q, *J* = 317.8 Hz), 127.5 (d, *J* = 3.1 Hz), 127.6, 133.2 (d, *J* = 8.3 Hz), 152.3, 162.5 (d, *J* = 246.8 Hz).

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>); δ –75.0 (s, 3F), –113.9- –114.1 (m, 1F).

IR (neat)  $v_{\text{max}}$ : 1138, 1209, 1417, 1490, 1591, 1643, 2962 cm<sup>-1</sup>.

HRMS (EI) calcd for  $C_{16}H_{20}O_4ClF_3S_2$  430.0896, found 430.0893.

#### (E)-2-((4-fluorophenyl)thio)-1-phenylvinyl trifluoromethanesulfonate 7



Electrochemical oxidation (0.67 F/mol) of bis(4-fluorophenyl) disulfide **1** (0.45 mmol) in Bu<sub>4</sub>NOTf/CH<sub>2</sub>Cl<sub>2</sub> and subsequent reaction with phenylacetylene (C<sub>1</sub> = 0.030 M, F = 1.5 mL/min, 0.135 mmol) gave the title compound 7. The yield was determined by <sup>1</sup>H NMR using TCE as an internal standard and purified by GPC; 46.5 mg, 91 % isolated yield, pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.60 (s, 1H), 7.05-7.12 (m, 2H), 7.40-7.52 (m, 6H), 7.58-7.62 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>);  $\delta$  116.4 (d, *J* = 22.4 Hz), 118.4 (q, *J* = 320.8 Hz), 121.7, 127.5, 128.6, 128.9 (d, *J* = 3.2 Hz), 130.1, 131.1, 132.9 (d, *J* = 8.4 Hz), 142.7, 162.8 (d, *J* = 249.7 Hz). <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>);  $\delta$  -74.1 (s, 3F), -112.8- -113.0 (m, 1F). IR (neat)  $v_{max}$ : 978, 1138, 1209, 1418, 1491, 1591 cm<sup>-1</sup>.

HRMS (EI) calcd for  $C_{15}H_{10}F_4O_3S_2$  378.0007, found 378.0006.

(*E*)-1-((4-fluorophenyl)thio)dec-1-en-2-yl trifluoromethanesulfonate 8 and (*E*)-2-((4-fluorophenyl)thio)dec-1-en-1-yl trifluoromethanesulfonate 8'



Electrochemical oxidation (0.67 F/mol) of bis(4-fluorophenyl) disulfide 1 (0.54 mmol) in  $Bu_4NOTf/CH_2Cl_2$  and subsequent reaction with 1-decyne ( $C_1 = 0.045$  M, F = 1.0 mL/min, 0.16 mmol) gave the title compound 8 and 8' as an inseparable mixture. The yield was determined by <sup>1</sup>H NMR using TCE as an internal standard and purified by GPC; 46.5 mg (8/8' = 93/7), 71 % isolated yield, pale yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.88 (8 and 8', t, *J* = 6.8 Hz, 3H), 1.21-1.41 (8 and 8', m, 10H), 1.54-1.65 (8 and 8', m, 2H), 2.23 (8', t, *J* = 7.0 Hz, 2H), 2.56 (t, *J* = 7.5 Hz, 2H), 6.27 (8, s, 1H), 6.76 (8', s, 3H), 7.01-7.09 (8 and 8', m, 2H), 7.29-7.35 (8, m, 2H), 7.35-7.40 (8', m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, selected); δ 14.1, 22.6, 25.9, 28.6, 29.1, 31.0, 31.8, 116.5 (d, *J* = 22.4 Hz), 117.8, 118.4 (q, *J* = 320.4 Hz), 128.9 (d, 3.2 Hz), 131.7 (d, *J* = 8.4 Hz), 150.7, 162.3 (d, *J* = 248.1 Hz).

13.8, 22.2, 26.3, 30.9, 31.9, 39.8, 116.6 (d, *J* = 22.2 Hz), 117.9, 118.5 (q, *J* = 318.2 Hz), 128.9 (d, *J* = 3.2 Hz), 131.7 (d, *J* = 7.9 Hz), 134.0-134,1 (m), 150.7, 162.4 (d, *J* = 246.4 Hz).

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>); δ -74.2 (**8**', s, 3F), -74.4 (**8**, s, 3F), -74.2 (**8**', s, 3F), -112.59- -113.1 (**8**', m, 1F), -114.1- -114.4 (**8**, m, 1F).

IR (neat)  $v_{\text{max}}$ : 1142, 1215, 1418, 1491, 1592, 2931 cm<sup>-1</sup>.

HRMS (EI) calcd for  $C_{17}H_{22}O_3F_4S_2$  414.0947, found 414.0945.

# (E)-2-((4-bromophenyl)thio)-1-chlorooct-2-en-3-yl trifluoromethanesulfonate 9



Electrochemical oxidation (0.67 F/mol) of bis(4-bromophenyl) disulfide (0.45 mmol) in  $Bu_4NOTf/CH_2Cl_2$  and subsequent reaction with 1-chloro-2-octyne **5** ( $C_1 = 0.045$  M, F = 1.3 mL/min, 0.15 mmol) gave the title compound **9**. The yield was determined by <sup>1</sup>H NMR using TCE as an internal standard and purified by GPC; 49.1 mg, 70 % isolated yield, colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.90 (t, *J* = 7.0 Hz, 3H), 1.31-1.37 (m, 4 H), 1.61 (quint, *J* = 7.4 Hz, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 4.14 (s, 2H), 7.21-7.24 (m, 2H), 7.46-7.50 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>); δ 13.8, 22.2, 26.3, 30.9, 31.9, 40.2, 118.3 (q, J = 317.8 Hz), 122.2, 126.2, 131.1, 132.0, 132.7, 154.1. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>); δ -74.6 (s, 3F). IR (neat)  $v_{max}$ : 1135, 1216, 1417, 1472, 1640, 2938 cm<sup>-1</sup>. HRMS (EI) calcd for C<sub>15</sub>H<sub>17</sub>O<sub>3</sub>ClBrF<sub>3</sub>S<sub>2</sub> 479.9443, found 479.9445.

# (E)-1-chloro-2-((4-methoxyphenyl)thio)oct-2-en-3-yl trifluoromethanesulfonate 10



Electrochemical oxidation (0.67 F/mol) of bis(4-mehoxyphenyl) disulfide (0.45 mmol) in  $Bu_4NOTf/CH_2Cl_2$  and subsequent reaction with 1-chloro-2-octyne **5** ( $C_1 = 0.045$  M, F = 1.0 mL/min, 0.14 mmol) gave the title compound **10**. The yield was determined by <sup>1</sup>H NMR using TCE as an internal standard and purified by GPC; 40.2 mg, 69 % isolated yield, pale yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.92 (t, *J* = 6.8 Hz, 3H), 1.33-1.39 (m, 4H), 1.62 (quint, *J* = 7.3 Hz, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 3.82 (s, 3H), 4.04 (s, 2H), 6.87-6.91 (m, 2H), 7.37-7.40 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>); δ 13.9, 22.3, 26.3, 30.9, 31.7, 39.4, 55.4, 115.1, 118.3 (q, *J* = 320.0 Hz), 121.0, 128.4, 134.7, 150.7, 160.3.

 $^{19}$ F NMR (377 MHz, CDCl<sub>3</sub>);  $\delta$  –74.8 (s, 3F).

IR (neat)  $v_{\text{max}}$ : 1135, 1215, 1247, 1418, 1494, 1592, 1636, 2958 cm<sup>-1</sup>.

HRMS (EI) calcd for C<sub>16</sub>H<sub>20</sub>O<sub>4</sub>ClF<sub>3</sub>S<sub>2</sub> 432.0444, found 432.0437.

#### (E)-1-chloro-2-(phenylthio)oct-2-en-3-yl trifluoromethanesulfonate 11



Electrochemical oxidation (0.67 F/mol) of diphenyl disulfide (0.45 mmol) in  $Bu_4NOTf/CH_2Cl_2$  and subsequent reaction with 1chloro-2-octyne ( $C_1 = 0.020$  M, F = 1.5 mL/min, 0.066 mmol) gave the title compound **11**. The yield was determined by <sup>1</sup>H NMR using TCE as an internal standard and purified by GPC; 10.3 mg, 39% isolated yield, colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.91 (t, *J* = 6.8 Hz, 3H), 1.32-1.37 (m, 4H), 1.62 (quint, *J* = 7.4 Hz, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 4.14 (s, 2H), 7.29-7.38 (m, 5H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>); δ 13.8, 22.2, 26.3, 30.9, 31.9, 40.2, 118.3 (q, *J* = 318.2 Hz), 126.8, 128.0, 130.0, 130.7, 131.8, 153.5. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>); δ -74.7 (s, 3F).

IR (neat) v<sub>max</sub>: 1135, 1213, 1249, 1418, 1457, 1477, 1636, 2932, 2963 cm<sup>-1</sup>.

HRMS (EI) calcd for C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>ClF<sub>3</sub>O<sub>3</sub>S<sub>2</sub> 402.0338, found 402.0334.

# (E)-5-((4-fluorophenyl)thio)oct-4-en-4-yl trifluoromethanesulfonate 12



Electrochemical oxidation (0.67 F/mol) of bis(4-fluorophenyl) disulfide 1 (0.45 mmol) in Bu<sub>4</sub>NOTf/CH<sub>2</sub>Cl<sub>2</sub> and subsequent reaction

with 4-octyne ( $C_1 = 0.045$  M, F = 1.5 mL/min, 0.20 mmol) gave the title compound **12**. The yield was determined by <sup>1</sup>H NMR using TCE as an internal standard and purified by GPC; 41.8 mg, 53% isolated yield, pale yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.85 (t, *J* = 7.6 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H), 1.52 (sext, *J* = 7.4 Hz, 2H), 1.62 (sext, *J* = 7.4 Hz, 2H), 2.22 (t, *J* = 7.8 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 7.01-7.05 (m, 2H), 7.27-7.30 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>); δ 13.2, 13.6, 21.0, 21.3, 35.6, 38.9, 116.1 (d, *J* = 21.8 Hz), 130.07, 130.14 (d, *J* = 3.2 Hz), 131.4 (d, *J* = 8.0 Hz), 139.1, 161.8 (d, *J* = 244.7 Hz).

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>); δ –75.3 (s, 3F), –114.5- –114.7 (m, 1F).

IR (neat)  $v_{\text{max}}$ : 917, 1138, 1209, 1414, 1491, 1592, 1643, 2879, 2971 cm<sup>-1</sup>.

HRMS (EI) calcd for  $C_{15}H_{18}O_3F_4S_2$  386.0634, found 386.0633.

## (E)-(5-fluorooct-4-en-4-yl)(4-fluorophenyl)sulfane 13



Electrochemical oxidation (0.67 F/mol) of bis(4-fluorophenyl) disulfide **1** (0.67 mmol) in Bu<sub>4</sub>NBF<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> and subsequent reaction with 4-octyne (C<sub>1</sub> = 0.045 M, F = 1.5 mL/min, 0.34 mmol) gave the title compound **13**. The yield was determined by <sup>1</sup>H NMR using TCE as an internal standard and purified by GPC; 56.3 mg, 65% isolated yield, colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.85 (t, *J* = 7.2 Hz, 3H) and 0.95 (t, *J* = 7.6 Hz, 3H), 1.48 (sext, *J* = 7.4 Hz, 2H), 1.59 (sext, *J* = 7.1 Hz, 2H), 2.18 (td, *J* = 7.4, 3.2 Hz, 2H), 2.62 (dt, *J* = 23.2, 7.4 Hz, 2H), 6.94-7.01 (m, 2H), 7.17-7.23 (m, 2H).

The NMR spectrum was in a good agreement with the reported one<sup>[3]</sup>.

#### 2.8. Generation of Oxocarbenium Ions Using Integrated Flow Electrochemical Reactor System



An integrated flow electrochemical reactor system consisting of a divided flow electrochemical reactor, a T-shaped micromixers (**M1** and **M2**), three microtube reactors (**R1**, **R2** and **R3**), and four pre-cooling units (**P1** (L = 200 cm), **P2** (200 cm), **P3** (100 cm) and **P4** (100 cm)) was used. The reactor was cooled at T<sub>1</sub> °C by a Peltier cooling system, and the flow microreactor system was cooled in acetone baths. During the operation, the volume of solution was monitored by sampling the solution and adjusted by changing diameter and length of tube reactor connected to the cathodic chamber. A solution of TfOH (0.05 M in Bu<sub>4</sub>NX/CH<sub>2</sub>Cl<sub>2</sub>, flow rate: 3.0 mL/min) was introduced to the cathodic chamber through **P1**. A solution of bis(4-fluorophenyl) disulfide **1** (0.05 M in Bu<sub>4</sub>NX/CH<sub>2</sub>Cl<sub>2</sub>, flow rate: 3.0 mL/min) was introduced to the anodic chamber through **P2**. The constant current electrolysis was

carried out at T<sub>1</sub> °C. Current value was set to consume 0.67 F/mol of electricity (162 mA). The resulting solution from anodic chamber was passed through **R1** (L<sub>1</sub> cm) and introduced to **M1** ( $\phi = 500 \mu$ m), where a solution of thioacetal **14** (C<sub>1</sub> M in CH<sub>2</sub>Cl<sub>2</sub>, flow rate: 1.5 mL/min) was also introduced. The mixed solution was passed through **R2** (L<sub>2</sub> cm, residence time *t*<sup>R2</sup> s). The resulting solution was introduced to **M2** ( $\phi = 500 \mu$ m), where a solution of silyl enol ether (C<sub>2</sub> M in CH<sub>2</sub>Cl<sub>2</sub>, flow rate: 1.5 mL/min) was also introduced. The mixed solution of silyl enol ether (C<sub>2</sub> M in CH<sub>2</sub>Cl<sub>2</sub>, flow rate: 1.5 mL/min) was also introduced. The mixed solution was passed through **R3** (L<sub>3</sub> = 100 cm, residence time *t*<sup>R3</sup> = 7.9 s). After a steady state was reached, the product solution was collected and stirred at room temperature for 30 min. Reactions were performed on a 0.068 mmol scale based on **14**. After addition of triethylamine (1 mL) to the mixture, the solvent was removed under reduced pressure. To the crude, Et<sub>2</sub>O and pentadecane were added, and the mixture was analyzed by GC. The results are summarized in Table S5 and S6.

entry	supporting electrolyte	$C_1$	$C_2$	$T_1$	$T_2$	$L_1$	$L_2$	$t^{R2}$	Conversion of	Yield of
entry	supporting electrolyte	[M]	[M]	[°C]	[°C]	[cm]	[cm]	[sec]	14 [%] <sup>[a]</sup>	15 [%] <sup>[a]</sup>
1	Bu <sub>4</sub> NOTf	0.045	0.225	0	0	15	3.5	0.37	99	7
2	(0.1 M)						12.5	1.3	98	5
3							25	2.6	100	5
4							50	5.2	100	2
5							100	10.5	99	2
6		0.045	0.225	-25	-25	15	3.5	0.37	83	20
7							12.5	1.3	100	9
8							25	2.6	100	9
9							50	5.2	100	6
10							100	10.5	99	9
11		0.045	0.225	-50	-50	15	3.5	0.37	75	72
12							12.5	1.3	88	88
13							25	2.6	>99	85
14							50	5.2	>99	71
15							100	10.5	>99	43
16		0.045	0.225	-75	-75	15	3.5	0.37	74	41
17							12.5	1.3	88	51
18							25	2.6	95	68
19							50	5.2	95	93
20							100	10.5	>99	83

Table S5. Generation of oxocarbenium triflate using flow	v electrochemical	reactor system
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[a] Determined by GC using pentadecane as an internal standard.

Table S6. Generation of oxocarbenium ions using flow electrochemical reactor system

ontru	supporting algotrolyta	C1	C <sub>2</sub>	$T_1$	T <sub>2</sub>	L <sub>1</sub>	L <sub>2</sub>	t <sup>R2</sup>	Conversion of	Yield of
entry	supporting electrolyte	[M]	[M]	[°C]	[°C]	[cm]	[cm]	[sec]	14 [%] <sup>[a]</sup>	15 [%] <sup>[a]</sup>
1	$Bu_4NBF_4$	0.045	0.225	-50	-50	15	3.5	0.37	57	42
2	(0.3 M)						12.5	1.3	71	60
3							25	2.6	81	61
4							50	5.2	90	70
5							100	10.5	>99	82
6 <sup>[b]</sup>	$Bu_4NB(C_6F_5)_4$	0.031	0.155	0	-50	65	3.5	0.37	97	23
7 <sup>[b]</sup>	(0.1 M)						12.5	1.3	97	24
8 <sup>[b]</sup>							25	2.6	98	23
9 <sup>[b]</sup>							50	5.2	98	20
10 <sup>[b]</sup>							100	10.5	99	17

[a] Determined by GC using pentadecane as an internal standard.

[b] Reactions were performed on a 0.047 mmol scale based on 14.



Electrochemical oxidation (0.67 F/mol) of bis(4-fluorophenyl) disulfide 1, subsequent treatment with 2-((4-fluorophenyl)thio)tetrahydrofuran 14, followed by the reaction with 1-phenyl-1-(trimethylsilyloxy)ethylene gave the title compound 15. The crude was analyzed by GC using pentadecane as an internal standard. GC retention time = 20.9 min; initial oven temperature, 50 °C for 5 min; rate of temperature increase, 10 °C /min.; pale yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 1.54 (m, 1H), 1.93 (m, 2H), 2.20 (m, 1H), 3.06 (dd,  $J_1 = 6.8$  Hz,  $J_2 = 9.6$  Hz, 1H), 3.40 (dd,  $J_1 = 6.4$  Hz,  $J_2 = 10.0$  Hz, 1H), 3.76 (q, J = 7.2 Hz, 1H), 3.90 (q, J = 7.2 Hz, 1H), 4.41 (m, 1H), 7.47 (t, J = 7.2 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.94 (d, J = 6.4 Hz, 2H). The NMR spectrum was in a good agreement with the reported one.<sup>[8]</sup>



Figure S5. ESI-MS analysis of crude product in the condition of Table S5, entry 15.

# 2.9. Direct Generation of Glycosyl Triflates Using Flow Electrochemical Reactor System



A flow electrochemical reactor system consisting of a divided flow electrochemical reactor, a T-shaped micromixer (**M1**), two microtube reactors (**R1** and **R2**), and three pre-cooling units (**P1** (L = 200 cm), **P2** (200 cm) and **P3** (100 cm)) was used. The reactor was cooled at -75 °C by a Peltier cooling system, and the flow microreactor system was cooled in acetone baths at -75 °C. During the operation, the volume of solution was monitored by sampling the solution and adjusted by changing diameter and length of tube reactor connected to the cathodic chamber. A solution of TfOH (0.05 M in 0.1M Bu<sub>4</sub>NOTf/CH<sub>2</sub>Cl<sub>2</sub>, flow rate: 3.0 mL/min) was introduced to the cathodic chamber through **P1**. A solution of thioglycoside (0.02 M in 0.1 M Bu<sub>4</sub>NOTf/CH<sub>2</sub>Cl<sub>2</sub>, flow rate: 3.0 mL/min) was introduced to the anodic chamber through **P2**. The constant current electrolysis was carried out at -75 °C. Current value was set to consume 1.25 F/mol of electricity (121 mA). The resulting solution from anodic chamber was passed through **R1** (15 cm, residence time  $t^{R1} = 2.4$  s) and introduced to **M1** ( $\phi = 500 \mu$ m), where a solution of MeOH (0.2 M in CH<sub>2</sub>Cl<sub>2</sub>, flow rate: 1.5 mL/min) was also introduced. The mixed solution was passed through **R2** (L<sub>2</sub> cm, residence time  $t^{R2}$  s). After a steady state was reached, the product solution was collected to a flask at rt. The reaction mixture was stirred at rt for 1 min under Ar. Then triethylamine (2 mL) was added, and the solvent was removed under reduced pressure. The crude was purified by flash chromatography.

#### Methyl 6-O-[(1,1-dimethylethyl)diphenylsilyl]-2,3,4-tris-O-(phenylmethyl)-β-D-glucopyranoside 16

Electrochemical oxidation (1.25 F/mol) of 4-fluorophenyl 2,3,4-tri-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-1-thio- $\beta$ -D-glucopyranoside (0.09 mmol) in Bu<sub>4</sub>NOTf/CH<sub>2</sub>Cl<sub>2</sub> and subsequent reaction with MeOH (0.2 M in CH<sub>2</sub>Cl<sub>2</sub>, 0.45 mmol) gave the title compound **16**. L<sub>2</sub> = 175 cm, *t*<sup>R2</sup> = 18.3 s. The crude was purified by flash chromatography (hexane/ethyl acetate = 20/1); 42.3 mg, 67% ( $\beta$  only) isolated yield, pale yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.06 (s, 9H), 3.34 (dt,  $J_1$  = 3.0 Hz,  $J_2$  = 9.7 Hz, 1H), 3.44-3.48 (m,1H), 3.60 (s, 3H), 3.67 (t, J = 9.2 Hz, 1H), 3.78 (t, J = 9.2 Hz, 1H), 3.90-3.99 (m, 2H), 4.33 (d, J = 7.5 Hz, 1H), 4.70 (d, J = 10.6 Hz, 1H), 4.74 (d, J = 11.0 Hz, 1H), 4.82 (d, J = 11.0 Hz, 1H), 4.88-4.98(m, 3H), 7.17-7.46 (m, 21H), 7.69-7.79 (m, 5H).

The NMR spectrum was in a good agreement with the reported one<sup>[9]</sup>.

#### Methyl 2,3,4-tri-O-methyl-6-O-((4-methoxyphenyl)methyl)-β-D-glucopyranoside 17

MeO MeO OMe MeO ÒМе 17

Electrochemical oxidation (1.25 F/mol) of 4-fluorophenyl 6-*O*-((4-methoxyphenyl)methyl)-2,3,4-tri-*O*-methyl)-1-thio- $\beta$ -D-glucopyranoside (0.15 mmol) in Bu<sub>4</sub>NOTf/CH<sub>2</sub>Cl<sub>2</sub> and subsequent reaction with MeOH (0.2 M in CH<sub>2</sub>Cl<sub>2</sub>, 0.75 mmol) gave the title compound **17**. L<sub>2</sub> = 75 cm,  $t^{R2}$  = 7.9 s. The crude was purified by flash chromatography (hexane/ethyl acetate = 10/1 to 2/1); 11.2 mg, 21% ( $\beta$  only) isolated yield.

TLC: Rf = 0.19 (hexane/ethyl acetate = 2/1)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.96-3.02 (m, 1H), 3.14-3.18 (m, 2H), 3.28-3.34 (m,1H), 3.48 (s, 3H), 3.53 (s, 3H), 3.57 (s, 3H), 3.60-3.65 (m, 1H), 3.62 (s, 3H), 3.68-3.72 (m, 1H), 3.80 (s, 3H), 4.14 (d, *J* = 7.9 Hz, 1H), 4.54 (pseudo q, *J* = 11.9 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 55.2, 56.9, 60.3, 60.4, 60.8, 68.6, 73.1, 74.7, 79.5, 83.6, 86.5, 104.1, 113.6, 129.3, 130.3, 159.1. HRMS (ESI) calcd for C<sub>18</sub>H<sub>28</sub>O<sub>7</sub>Na [M+Na<sup>+</sup>]: 379.1727, found 379.1728.



2.10. Indirect Generation of Glycosyl Triflates Using Integrated Flow Electrochemical Reactor System

An integrated flow electrochemical reactor system consisting of a divided flow electrochemical reactor, a T-shaped micromixers (M1, M2 and M3), four microtube reactors (R1, R2, R3 and R4), and five pre-cooling units (P1 (L = 200 cm), P2 (200 cm), P3 (100 cm), P4 (100 cm) and P5 (100 cm)) was used. The reactor was cooled at -75 °C by a Peltier cooling system, the pre-cooling units P1 and P2 were cooled in an acetone bath at -75 °C, and the flow microreactor system composed with P3-P5, R1-R4, M1-M3 was cooled in acetone baths at -75 °C. During the operation, the amount of solution was monitored by sampling the solution and adjusted by changing diameter and length of tube reactor connected to the cathodic chamber. A solution of TfOH (0.05 M in 0.1 M Bu<sub>4</sub>NOTf/CH<sub>2</sub>Cl<sub>2</sub>, flow rate: 5.0 mL/min) was introduced to the cathodic chamber through P1. A solution of bis(4fluorophenyl) disulfide (0.05 M in 0.1 M Bu<sub>4</sub>NOTf/CH<sub>2</sub>Cl<sub>2</sub>, flow rate: 5.0 mL/min) was introduced to the anodic chamber through P2. The constant current electrolysis was carried out at -75 °C. Current value was set to consume 0.67 F/mol of electricity (270 mA). The resulting solution from anodic chamber was passed through R1 (15 cm,  $t^{R1} = 1$  s) and introduced to M1 ( $\phi = 500 \mu m$ ), where a solution of thioglycoside (0.022 M in CH<sub>2</sub>Cl<sub>2</sub>) was also introduced (flow rate: 1.5 mL/min). The mixed solution was passed through R2 (L<sub>2</sub> cm,  $t^{R2}$  s). The resulting solution was passed through R3 (L<sub>3</sub> cm,  $t^{R3}$  s) and mas mixed with a CH<sub>2</sub>Cl<sub>2</sub> solution of nucleophile (flow rate: 1.5 mL/min). After quenching the reaction by mixing Et<sub>3</sub>N (neat, flow rate: 1.5 mL/min) at M3, the product solution was passed through R4 ( $L_4 = 25$  cm) and collected to a vessel. The solvent was removed under reduced pressure. Then, the solution was passed through silica plug using diethyl ether as an eluent. After concentration under reduced pressure, the crude was purified by flash chromatography.

Methyl 6-O-[(1,1-dimethylethyl)diphenylsilyl]-2,3,4-tris-O-(phenylmethyl)-β-D-glucopyranoside 16



Electrochemical oxidation (0.67 F/mol) of bis(4-fluorophenyl) disulfide **1** (0.38 mmol), subsequent treatment with 4-fluorophenyl 2,3,4-tri-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-1-thio- $\beta$ -D-glucopyranoside (0.0495 mmol), followed by the reaction with MeOH (1.10 M in CH<sub>2</sub>Cl<sub>2</sub>, 2.48 mmol) gave the title compound **16**. L<sub>2</sub> = 150 cm, *t*<sup>R2</sup> = 10.9 s, L<sub>3</sub> = 100 cm, *t*<sup>R3</sup> = 5.9 s. The crude was purified by flash chromatography (hexane/ethyl acetate = 5/1); 32.8 mg, 94% ( $\beta$  only) isolated yield.

#### Methyl 2,3,4-tri-O-methyl-6-O-((4-methoxyphenyl)methyl)-β-D-glucopyranoside 17



Electrochemical oxidation (0.67 F/mol) of bis(4-fluorophenyl) disulfide **1** (0.75 mmol), subsequent treatment with 4-fluorophenyl 6-O-((4-methoxyphenyl)methyl)-2,3,4-tri-O-methyl)-1-thio- $\beta$ -D-glucopyranoside (0.099 mmol), followed by the reaction with MeOH (1.10 M in CH<sub>2</sub>Cl<sub>2</sub>, 4.95 mmol) gave the title compound **17**. L<sub>2</sub> = 100 cm,  $t^{R2}$  = 7.3 s, L<sub>3</sub> = 100 cm,  $t^{R3}$  =5.9 s. The crude was purified by flash chromatography (hexane/ethyl acetate = 20/1 to 2/1); 29.0 mg, 82% ( $\beta$  only) isolated yield.

# Methyl 2,3,4-tris-*O*-benzyl-6-*O*-(2,3,4-tris-*O*-methyl-6-*O*-((4-methoxyphenyl)methyl)-β-D-glucopyranosyl)- α-D glucopyranoside 18

MeO OMe BnO

Electrochemical oxidation (0.67 F/mol) of bis(4-fluorophenyl) disulfide **1** (0.75 mmol), subsequent treatment with 4-fluorophenyl 6-*O*-((4-methoxyphenyl)methyl)-2,3,4-tri-*O*-methyl)-1-thio- $\beta$ -D-glucopyranoside (0.099 mmol), followed by the reaction with methyl 2,3,4-tri-*O*-benzyl- $\alpha$  -D-glucopyranoside (0.22 M in CH<sub>2</sub>Cl<sub>2</sub>, 0.99 mmol) gave the title compound **18**. L<sub>2</sub> = 25 cm,  $t^{R2}$  = 1.8 s, L<sub>3</sub> = 500 cm,  $t^{R3}$  = 29.5 s. The crude was purified by flash chromatography (hexane/ethyl acetate = 5/1) and GPC; 63.5 mg, 81% ( $\beta$  only) isolated yield, white solid.

TLC: Rf = 0.07 (hexane/ethyl acetate = 5/1)

Melting point: 66-68 °C

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.02-3.16 (m, 3H), 3.26-3.30 (m, 1H), 3.37 (s, 3H), 3.47 (s, 3H), 3.51-3.55 (m, 2H), 3.56-3.62 (m, 1H), 3.58 (s, 3H), 3.60 (s, 3H), 3.66-3.70 (m, 2H), 3.78 (s, 3H), 3.79-3.82 (m, 1H), 3.99 (t, *J* = 9.2 Hz, 1H), 4.14 (dd, *J*<sub>1</sub> = 1.8 Hz, *J*<sub>2</sub> = 10.8 Hz, 1H), 4.21 (d, *J* = 7.6 Hz, 1H), 4.46-4.55 (m, 2H), 4.61 (d, *J* = 3.4 Hz, 1H), 4.63-4.67 (m, 2H), 4.78-4.83 (m, 2H), 4.89 (d, *J* = 10.8 Hz, 1H), 4.97 (d, *J* = 10.8 Hz, 1H), 6.82-6.86 (m, 2H), 7.22-7.37 (m, 17H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ55.1, 55.2, 60.4, 60.7, 60.8, 68.3, 68.9, 69.8, 73.0, 73.4, 74.9, 75.0, 75.9, 77.9, 79.7, 79.8, 82.1, 83.5, 86.7, 98.1, 103.5, 113.7, 127.6, 127.7, 127.8, 127.9, 128.07, 128.11, 128.38, 128.40, 128.43, 129.2, 130.4, 138.1, 138.4, 138.7, 159.1.

IR (CHCl<sub>3</sub> solution) v<sub>max</sub>: 1088, 1245, 1364, 1458, 1514, 2166 cm<sup>-1</sup>.

HRMS (ESI) calcd for C45H56O12Na [M+Na+]: 811.3664, found 811.3669.

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# 4. 1H and 13C NMR Spectra of Compounds



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (*E*)-1-chloro-2-((4-fluorophenyl)thio)oct-2-en-3-yl trifluoromethanesulfonate 5



<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) of (*E*)-1-chloro-2-((4-fluorophenyl)thio)oct-2-en-3-yl trifluoromethanesulfonate 5



 $^{1}\mathrm{H}\ \mathrm{NMR}\ (400\ \mathrm{MHz}, \mathrm{CDCl}_{3})\ \mathrm{of}\ (\emph{E})\ -1\ -e\ thoxy\ -2\ -((4\ -f\ luorophenyl)\ thio)\ oct\ -2\ -e\ n-3\ -y\ l\ trifluorom\ e\ than e\ sulfonate\ 6\ -2\ -e\ n-3\ -y\ l\ trifluorom\ e\ than e\ sulfonate\ 6\ -2\ -e\ n-3\ -y\ l\ trifluorom\ e\ than e\ sulfonate\ 6\ -2\ -e\ n-3\ -y\ l\ trifluorom\ e\ than e\ sulfonate\ 6\ -2\ -e\ n-3\ -y\ l\ trifluorom\ e\ than e\ sulfonate\ 6\ -2\ -e\ n-3\ -y\ l\ trifluorom\ e\ than e\ sulfonate\ 6\ -2\ -e\ n-3\ -y\ l\ trifluorom\ e\ than e\ sulfonate\ 6\ -2\ -e\ n-3\ -y\ l\ trifluorom\ e\ than e\ sulfonate\ 6\ -2\ -e\ n-3\ -y\ l\ trifluorom\ e\ than e\ sulfonate\ 6\ -2\ -e\ n-3\ -y\ l\ trifluorom\ e\ than e\ sulfonate\ 6\ -2\ -e\ n-3\ -y\ l\ trifluorom\ e\ sulfonate\ b\ sulfonate\ 6\ -2\ -e\ n-3\ -y\ sulfonate\ b\ sulfonate\ sul$ 



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of (*E*)-1-ethoxy-2-((4-fluorophenyl)thio)oct-2-en-3-yl trifluoromethanesulfonate 6



<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) of (*E*)-1-ethoxy-2-((4-fluorophenyl)thio)oct-2-en-3-yl trifluoromethanesulfonate 6



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (*E*)-2-((4-fluorophenyl)thio)-1-phenylvinyl trifluoromethanesulfonate 7



<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) of (*E*)-2-((4-fluorophenyl)thio)-1-phenylvinyl trifluoromethanesulfonate 7



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (*E*)-1-((4-fluorophenyl)thio)dec-1-en-2-yl trifluoromethanesulfonate 8 and (*E*)-2-((4-fluorophenyl)thio)dec-1-en-1-yl trifluoromethanesulfonate 8'



fluorophenyl)thio)dec-1-en-1-yl trifluoromethanesulfonate 8'



<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) of (*E*)-1-((4-fluorophenyl)thio)dec-1-en-2-yl trifluoromethanesulfonate 8 and (*E*)-2-((4-fluorophenyl)thio)dec-1-en-1-yl trifluoromethanesulfonate 8'



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (*E*)-2-((4-bromophenyl)thio)-1-chlorooct-2-en-3-yl trifluoromethanesulfonate 9



<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) of (*E*)-2-((4-bromophenyl)thio)-1-chlorooct-2-en-3-yl trifluoromethanesulfonate 9

-90.0

-100.0

-110.0

-120.0

-130.0

-140.0

-150.0

-160.0

-170.0

-180.0

-200.0

-190.0

-70.0

8.00-0

-80.0

0

-10.0

-20.0

-30.0

-40.0

-50.0

-60.0



 $^{1}\mathrm{H}\ \mathrm{NMR}\ (400\ \mathrm{MHz},\ \mathrm{CDCl}_{3})\ \mathrm{of}\ (\textit{E})\ -1\ -\ chloro\ -2\ -\ ((4\ -\ methoxyphenyl)\ thio)\ oct\ -2\ -\ en\ -3\ -\ yl\ trifluoromethanesulfonate\ 10\ -\$ 



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of (*E*)-1-chloro-2-((4-methoxyphenyl)thio)oct-2-en-3-yl trifluoromethanesulfonate 10



<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) of (*E*)-1-chloro-2-((4-methoxyphenyl)thio)oct-2-en-3-yl trifluoromethanesulfonate 10



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (*E*)-1-chloro-2-(phenylthio)oct-2-en-3-yl trifluoromethanesulfonate 11



<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) of (*E*)-1-chloro-2-(phenylthio)oct-2-en-3-yl trifluoromethanesulfonate 11



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (*E*)-5-((4-fluorophenyl)thio)oct-4-en-4-yl trifluoromethanesulfonate 12



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of (*E*)-5-((4-fluorophenyl)thio)oct-4-en-4-yl trifluoromethanesulfonate 12



<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) of (*E*)-5-((4-fluorophenyl)thio)oct-4-en-4-yl trifluoromethanesulfonate 12



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of Methyl 2,3,4-tri-*O*-methyl-6-*O*-((4-methoxyphenyl)methyl)-β-D-glucopyranoside 17



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of Methyl 2,3,4-tri-O-methyl-6-O-((4-methoxyphenyl)methyl)-β-D-glucopyranoside 17



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of Methyl-6-O-(2,3,4-tri-*O*-methyl-6-*O*-((4-methoxyphenyl)methyl)-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D glucopyranoside 18



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of Methyl-6-O-(2,3,4-tri-O-methyl-6-O-((4-methoxyphenyl)methyl)-β-D-glucopyranosyl)-2,3,4-



tri-O-benzyl-α-D glucopyranoside 18

HMQC of Methyl-6-O-(2,3,4-tri-*O*-methyl-6-*O*-((4-methoxyphenyl)methyl)-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D glucopyranoside 18



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **4-Fluorophenyl 2,3,4-tri-***O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-1-thio- β-D-glucopyranoside S1



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 4-Fluorophenyl 2,3,4-tri-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-1-thio- β-D-glucopyranoside



<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) of **4-Fluorophenyl 2,3,4-tri-***O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-1-thio- β-D-glucopyranoside S1



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **4-Fluorophenyl 6-***O***-((4-methoxyphenyl)methyl)-2,3,4-tri-***O***-methyl)-1-thio-β-D-glucopyranoside S2** 



<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) of **4-Fluorophenyl 6-***O***-((4-methoxyphenyl)methyl)-2,3,4-tri-***O***-methyl)-1-thio-β-D**glucopyranoside S2