# Synthesis of Deoxyhalogeno Sugars. Reaction of Halide Ions with 1,2,3,4-Tetra-*O*-acetyl-6-*O*-[(trifluoromethyl)sulfonyl]-β-D-glucopyranose

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The reaction of bromide, chloride, and iodide ions with 1,2,3,4-tetra-*O*-acetyl-6-*O*-[(trifluoromethyl)-sulfonyl]-β-D-glucopyranose under the proper conditions gives excellent yields of the corresponding deoxyhalogeno sugars. Deoxyiodo sugars form readily under all conditions studied. Difficulties with displacements by bromide and chloride are encountered but can be overcome by appropriate modification of reaction conditions. Displacement with fluoride ion is difficult and produces only a low yield of the expected fluorinated carbohydrate.

## Introduction

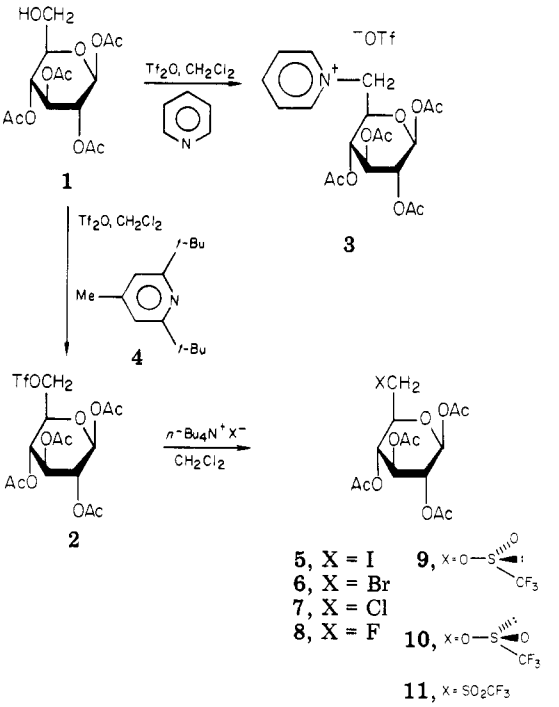
Reaction of sulfonic acid esters with halide ions has been recognized for many years as one of the best methods for synthesizing deoxyhalogeno sugars.[1] The primary limitation upon this method has been that displacements of sulfonyloxy groups often require forcing and, sometimes, destructive reaction conditions. A relatively recent solution to this problem has been to replace common leaving groups such as the tosyloxy group with the much more reactive triflyoxy((trifluoromethyl)sulfonyloxy) group. This change has made it possible to conduct many reactions under mild conditions and, consequently, increased considerably the synthetic possibilities of displacement reactions involving sulfonate esters.

Several years ago we began a systematic investigation of the displacement of the triflyoxy group in carbohydrate systems.[2-6] A part of this research included the synthesis of a number of protected deoxyhalogeno sugars, usually ones containing ketal and acetal protecting groups.[2,3] Continuing study of triflate displacements now has led us to consider the stability during reaction of other protecting groups, particularly esters, and to explore simplifying modifications in experimental procedures. These studies, described below, have shown that triflate formation and reaction under proper conditions lead to excellent yields of deoxyhalogeno sugars but alteration in these conditions can produce other displacement products.

## Results and Discussion

Previous investigation has shown that reaction of 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose (1) with trifluoromethanesulfonic (triflic) anhydride in the presence of pyridine (typical conditions for triflate formation) did not result in formation of the expected triflate **2**; rather, only water-soluble materials were produced.[3] This finding marked the beginning point for the present study. The initial goal was to determine the identity of this water-soluble carbohydrate. One explanation for failure to isolate **2** was that it reacted with pyridine to yield the corresponding pyridinium salt **3** (Scheme I). This suspicion was confirmed by isolation and characterization of the carbohydrate material in the aqueous phase. Compound **3** was the reaction product; thus, triflate isolation required modification in reactants or reaction conditions to avoid displacement by pyridine.

Scheme I[a]




[a] Ac = $CH_3C(O)$, Tf = $CF_3SO_2$.

The first modification considered was replacement of pyridine with one of its less nucleophilic derivatives. Use of the sterically hindered 2,6-di-*tert*-butyl-4-methylpyridine (**4**) was successful. It allowed formation and isolation of the triflate **2**, a compound that was stable in solution at room temperature in the absence of nucleophiles and could be stored indefinitely at −20 °C. The triflate **2** reacted readily with halide ions to produce the corresponding deoxyhalogeno sugars **5**–**8** (Table I). Separation of the triflate **2** from the base **4** required chromatography, a process that caused some triflate decomposition; thus, although **2** is isolable, the optimum yields of **5**–**8** were obtained when it (**2**) was reacted, without isolation, in the flask in which it was generated.

Although the problem of triflate isolation had been solved, the solution required the use of the relatively expensive hindered base **4**. For general synthetic purposes an alternative that did not depend upon this compound (**4**) was desirable. One possibility was suggested by the work of Perlin[7] and Schuerch;[8] it consisted of generating

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Table I

| product | yield, % | nucleophile | procedure[a] | temp, °C | time,[b] min |
|---|---|---|---|---|---|
| 3 | 84 | pyridine | A | 25 | 60 |
| 5 | 97 | $Bu_4NI$ | A | 25 | 60 |
| 5 | 97 | $Bu_4NI$ | B | −78 | 0 |
| 6 | 94 | $Bu_4NBr$ | A | 25 | 60 |
| 6 | 59 | $Bu_4NBr$ | B | −78 | 0 |
| 9 | 20 | | | | |
| 10 | 20 | | | | |
| 7 | 0 | $C_6H_5CH_2(Et)_3NCl$ | B | −78 | 0 |
| 7 | 9 | $C_6H_5CH_2(Et)_3NCl$ | C | −20 | 60 |
| 7 | 67 | $C_6H_5CH_2(Et)_3NCl$ | C | 0 | 20 |
| 7 | 85 | $C_6H_5CH_2(Et)_3NCl$ | A | 25 | 60 |
| 8 | 0 | $Bu_4NF\cdot 3H_2O$ | A | 25 | 60 |
| 8 | 27 | $Bu_4NF\cdot 3H_2O$ | A[c] | 80 | 60 |
| 9 | 31 | $CF_3SO_2K$ | A | 25 | 60 |
| 10 | 31 | $CF_3SO_2K$ | | | |

[a] See Experimental Section for complete procedure. [b] Time allowed for triflate formation prior to introduction of the nucleophile. [c] Procedure slightly modified; see Experimental Section.

Table II. $^1H$ NMR Spectral Data[a]

| compd | H-1 | H-2 | H-3 | H-4 | H-5 | H-6 | H-6′ | $OOCH_3$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 5.75 ($J_{1,2}$ = 7) | 5.50 — | | 4.83 | 3.83 — | | 3.50 | 2.07 (6 H), 2.10, 2.13 |
| 2 | 5.78 ($J_{1,2}$ = 7) | 5.60 — | | 4.87 | 4.20–3.80 | 4.78 — | 4.43 | 2.07 (6 H), 2.10, 2.15 |
| 3[b] | 5.70 ($J_{1,2}$ = 7.5) | 5.50 — | | | | | 4.80 | 1.95, 2.05, 1.98, 2.08 |
| 5 | 5.75 ($J_{1,2}$ = 8) | 5.62 — | | 4.75 | 3.82–3.48 | 3.55 — | 2.95 | 2.02, 2.05, 2.09, 2.15 |
| 6 | 5.73 ($J_{1,2}$ = 7) | 5.60 — | | 4.80 | 4.07–3.67 | 3.67 — | 3.13 | 1.98 (6 H), 2.02, 2.07 |
| 7 | 5.70 ($J_{1,2}$ = 7) | 5.53 — | | 4.80 | 4.07–3.67 | 3.67 — | 3.23 | 1.93, 1.95, 1.98, 2.03 |
| 8 | 5.73 ($J_{1,2}$ = 7) | 5.37 — | | 4.90 | 4.23–3.83 | 4.42 ($^2J_{HF}$ = 47.0) | | 2.07, 2.01, 2.00 (6 H) |
| A[c] | 5.76 ($J_{1,2}$ = 7.0) | 5.13 ($J_{2,3}$ = 9.8) | 5.29 ($J_{3,4}$ = 10.0) | 5.13 ($J_{4,5}$ = 9.7) | 3.91 ($J_{5,6}$ = 5.0, $J_{5,6'}$ = 3.0) | 4.51 ($J_{6,6'}$ = 11.5) | 4.13 | 2.01, 2.03, 2.05, 2.11 |
| B[c] | 5.76 ($J_{1,2}$ = 7.0) | 5.13 ($J_{2,3}$ = 9.8) | 5.29 ($J_{3,4}$ = 10.0) | 5.11 ($J_{4,5}$ = 9.7) | 3.94 ($J_{5,6}$ = 4.0, $J_{5,6}$ = 2.0) | 4.50 ($J_{6,6'}$ = 12.0) | 4.14 | 2.01, 2.03, 2.05, 2.11 |

[a] Chemical shifts are in parts per million from $Me_4Si$. Coupling constants are in hertz. [b] Absorptions also at 9.17–7.97 due to hydrogens attached to the pyridinium ring. [c] Chemical shifts for H-2, H-3, H-4, H-5, H-6, and H-6′ and all coupling constants except $J_{1,2}$ were obtained by spectral simulation. A and B are compounds **9** and **10**.

the triflate **2** at −78 °C in the presence of an appropriate nucleophile. As the reaction mixture warmed to room temperature and displacement began, pyridine would not be expected to compete with a more reactive nucleophile such as a halide ion. This approach already had proved successful in the reaction of **1** with tetrabutylammonium iodide and triflic anhydride in the presence of pyridine to give 1,2,3,4-tetra-*O*-acetyl-6-deoxy-6-iodo-β-D-glucopyranose[3] (**5**, Table I). Surprisingly, however, when bromide ion replaced iodide in this reaction, three products were formed. One was the exected 1,2,3,4-tetra-*O*-acetyl-6-bromo-6-deoxy-β-D-glucopyranose (**6**), but the other two (A and B) contained no bromine. Mass spectrometry indicated these compounds (A and B) to be isomers with a molecular weight of 464, a value 16 mass units less than the triflate **2**. A reasonable assumption was that A and B were two of the three compounds **9**–**11** (Scheme I). These possibilities were narrowed by the $^1H$ and $^{13}C$ NMR spectra (Tables II and III), which showed A and B to be two very similar compounds. Because of this spectral information, the synthesis of **9** and **10** was undertaken.

Several years ago Hendrickson and co-workers[9] reported that the trifluoromethanesulfinate anion ($CF_3SO_2^-$, **12**) was a reactive, ambident nucleophile. When this anion (**12**) displaced a very reactive leaving group, an oxygen–carbon bond was formed, but displacement of a less reactive group resulted in sulfur–carbon bond formation. Based upon this observation, reaction of the triflate **2** with **12** would be expected to produce the sulfinate esters **9** and **10**. When this reaction was conducted, it gave the same two compounds (A and B) that were produced by reaction of **2** with triflic anhydride and tetrabutylammonium bromide. This result confirmed the assignment of structures **9** and **10** to A and B. Unfortunately, it was not possible to determine which stereoisomer (A or B) was **9** and which was **10**.

Since **9** and **10** appeared to be formed by a displacement involving the sulfinate anion **12** even in experiments where **12** was not directly introduced, a question existed concerning how this ion was formed. An answer to this question, summarized in eq 1 and 2, has been offered by

$$(CF_3SO_2)_2O + X^- \rightarrow CF_3SO_2X + CF_3SO_3^- \quad (1)$$

$$CF_3SO_2X + X^- \rightarrow CF_3SO_2^- + X_2 \quad (2)$$

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Table III. $^{13}C$ NMR Spectral Data[a]

| | 1 | 2 | 3[b] | 5 | 6 | 7 | 8 | A[c] | B[c] |
|---|---|---|---|---|---|---|---|---|---|
| C-1 | 91.88 | 91.58 | 92.40 | 91.56 | 91.64 | 91.70 | 91.57 | 91.46 | 91.33 |
| C-2, C-3, | 75.14 | 72.97 | 73.49 | 73.63 | 73.61 | 74.02 | 73.70 | 72.64 | 72.64 |
| C-4, C-5 | 72.85 | 72.52 | 72.91 | 72.57 | 72.75 | 72.83 | 72.77 | 72.38 | 72.38 |
| | 70.59 | 72.03 | 70.73 | 72.11 | 70.53 | 70.38 | 70.16 | 69.91 | 69.91 |
| | 68.39 | 70.11 | 69.98 | 70.49 | 70.39 | 69.46 | 67.52[d] | 67.84 | 67.40 |
| C-6 | 60.94 | 68.02 | 61.87 | 2.35 | 30.20 | 42.75 | 80.64[d] | 65.38 | 63.92 |
| $CH_3CO$ | 170.09 | 169.99 | 170.78 | 169.96 | 170.04 | 170.07 | 170.03 | 169.81 | 169.26 |
| | 169.26 | 169.35 | 170.17 | 169.23 | 169.26 | 169.27 | 169.21 | 169.09 | 168.91 |
| | 169.10 | 169.06 | 169.66 | 169.05 | 169.10 | 169.10 | 169.08 | 168.60 | 168.54 |
| | | 168.71 | 169.27 | 168.74 | 168.84 | 168.86 | 168.85 | | |
| $CH_3CO$ | 20.73 | 20.60 | 20.79 | 20.73 | 20.74 | 20.75 | 20.67 | 20.43 | 20.43 |
| | 20.55 | 20.47 | 20.47 | 20.64 | 20.53 | 20.53 | 20.46 | 20.27 | 20.27 |
| | | | 20.44 | 20.51 | | | | | |
| $CF_3$ | | 118.66 (q, $J_{CF}$ = 319.53 Hz) | | | | | | 122.73 (q, $J_{CF}$ = 339.37 Hz) | 122.73 (q, $J_{CF}$ = 339.37 Hz) |

[a] Chemical shifts are in parts per million from $Me_4Si$. [b] Absorptions also at 147.53, 146.83, and 128.92 ppm due to carbons in the pyridinium ring. [c] A and B are compounds **9** and **10**. [d] $^2J_{CF}$ = 6.5 Hz, $^1J_{CF}$ = 176.61 Hz.

Creary,[10] who showed that magnesium bromide reacted with the triflic anhydride to give **12**. Our results (Table I) suggest that **12** is comparable in nucleophilicity to bromide and, if it (**12**) is formed in reactions involving iodide, it is significantly less nucleophilic than iodide.

Attempted generation of the chloride **7** by formation and reaction of the triflate **2** at low temperature in the presence of benzyltriethylammonium chloride (**13**) resulted only in isolation of unreacted starting material (**1**). The triflate **2** could not have been formed under these conditions since if it had been produced, it would have reacted with chloride by the time the reaction mixture warmed to room temperature (Table I). The lack of formation of **2** under these conditions appeared to be a direct result of the difficulty in removing water from **13**. Even with careful drying and handling of this salt (**13**), sufficient water was present in the reaction mixture to destroy the triflic anhydride added.

It was possible to generate the chlorodeoxy sugar **7** if the starting material (**1**), triflic anhydride, and the base **4** were combined before introducing the chloride salt **13**. Under these conditions **7** was the only product formed (Table I). The temperature of the reaction mixture had a decided effect upon product yield. For example, raising the temperature from −20 to 0 °C during triflate formation dramatically improved the yield of **7**. Triflate formation must be relatively slow even at −20 °C.

One conclusion that can be drawn from the relatively slow triflate (**2**) formation at −20 °C is that in the iodide (**5**) and bromide (**6**) syntheses at −78 °C, an agent other than triflic anhydride must be responsible for esterification. It is reasonable to assume that at the lower temperature the sulfonic acid halides, which are present as a result of reaction between triflic anhydride and halide ion[10] (eq 3) and which are more reactive esterifying agents than triflic anhydride, were responsible for triflate (**2**) formation.

$$CF_3SO_2X + ROH \rightarrow ROSO_2CF_3 + HX \quad (3)$$

The final halogenated carbohydrate to be synthesized was the deoxyfluoro sugar **8**. Attempted synthesis of this compound under the conditions that were most effective for formation of **7** resulted only in isolation of the triflate **2**. When the temperature of the reaction mixture was raised to 80 °C after initial triflate formation, the desired fluoro compound **8** was produced in low (27%) yield along with considerable black, insoluble material.

Our findings and conclusions concerning the synthesis of the deoxyhalogeno sugars **5**–**8** by triflate displacement can be summarized in the following manner. Three compounds (**5**–**7**) can be produced in excellent yield from displacement of the triflyloxy group from **2**. Isolation of **2** is not possible in the presence of pyridine; rather, it requires the use of the nonnucleophilic base **4**. Compound **4** should be useful in the synthesis of other triflates that react readily with pyridine. The deoxyiodo sugar **5** is much more convenient to prepare than its bromo (**6**), chloro (**7**), and fluoro (**8**) analogues since it alone can be synthesized in high yield without the use of this relatively expensive base **4**.

## Experimental Section

**General Procedures.** $^1H$ NMR spectra were run on a Varian T-60 spectrometer, and $^{13}C$ NMR spectra were obtained from a Varian FT-80A spectrometer. Spectral simulation was done by using Varian Associates Simeq spin simulation program. Mass spectra were determined with a Finnigan 1015-D spectrometer with methane as a reagent gas and an ionizing voltage of 150 eV.

Column chromatography was done on a 2.5 × 10 cm column of 230–400-mesh silica gel with a 3:2 ratio of ether–pentane. The column effluent was monitored by an ISCO UA-2 UV analyzer; 50-mL fractions were collected. Compound **4** was found in fractions 1 and 2. Carbohydrate-containing material was in fractions 3–6. Tetraalkylammonium salts remained on the column.

**Preparation of 1,2,3,4-Tetra-*O*-acetyl-6-*O*-[(trifluoromethyl)sulfonyl]-β-D-glucopyranose (2).** Trifluoromethanesulfonic (triflic) anhydride (0.32 mL, 1.90 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine[11] (0.396 g, 1.93 mmol) were dissolved in 20 mL of anhydrous $CH_2Cl_2$ at 25 °C, and to this solution was added 0.475 g (1.36 mmol) of 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose[12] (**1**) in 10 mL of $CH_2Cl_2$. After stirring at 25 °C for 1 h, the reaction mixture was poured into 200 mL of ice water containing 2 g of $NaHCO_3$ and shaken vigorously. The layers were separated, and the aqueous layer was extracted with 20 mL of $CH_2Cl_2$. The combined organic extracts were dried over $Na_2SO_4$, and the solvent was removed by distillation under reduced pressure. Chromatography according to the general procedure described above produced **2** in 84% yield, mp 85 °C dec. Compound **2** was identified by its $^1H$ and $^{13}C$ NMR spectra (Tables II and III) and its conversion into the iodide **5**. Rapid chromatography minimized decomposition of **2** on the column.

**Synthesis of the 1,2,3,4-Tetra-*O*-acetyl-β-D-glucopyranose Derivatives 3 and 5–10. Procedure A.** Triflic anhydride (0.34 mL, 1.9 mmol) and compound **4** (0.41 g, 2.0 mmol) were dissolved in 20 mL of anhydrous $CH_2Cl_2$. To this solution was added 0.49 g (1.4 mmol) of the tetraacetate **1** in 10 mL of $CH_2Cl_2$ and the

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reaction mixture stirred for 60 min. A solution of 4.0 mmol of the appropriate nucleophile (Table I) in 20 mL of $CH_2Cl_2$ then was added and the mixture stirred for 3 h. (When $Bu_4NF \cdot 3H_2O$ was used as the nucleophile, the triflate **2** was isolated. Reaction required the $CH_2Cl_2$ to be distilled at this point, benzene (50 mL) added, and the reaction mixture heated to reflux for 5 min.) The reaction mixture next was poured into 200 mL of cold 1% $NaHCO_3$ solution and shaken vigorously in a separatory funnel. The organic phase was removed and the aqueous phase extracted with 20 mL of $CH_2Cl_2$. The combined organic layers were washed with 50 mL of 5% $NaHSO_3$ and 50 mL of saturated $NaHCO_3$ and dried over anhydrous $Na_2SO_4$. After distillation of the solvent under reduced pressure, the residue was chromatographed as described in the general procedures. Product yields are given in Table I. The structures of the deoxyhalogeno sugars **5**–**8** were determined from their $^1H$ and $^{13}C$ NMR spectra (Tables II and III). These spectra, in addition to exhibiting all the proper absorptions, differed significantly only in absorptions for H-6, H-6′, and C-6. As a further confirmation of these structural assignments (**5**–**8**) the following melting point comparisons were made: **5**, mp 150–153 °C (lit.[13] mp 148 °C); **6**, mp 125–127 °C (lit.[14] 124–125 °C); **7**, mp 113–115 °C (lit.[15] 114–115 °C); **8**, 126.5–127.5 °C (lit.[16] 123–124 °C). Compound **5** was found to be identical with an independently synthesized sample.[13] Also, the $^1H$ NMR spectrum of **8** was compared to the published spectrum.[16]

**Procedure B.** The appropriate nucleophile (4.0 mmol, Table I) and pyridine were dissolved in 40 mL of anhydrous $CH_2Cl_2$ and placed in a three-necked flask. Attached to this flask were two pressure-equalizing addition funnels, one containing 0.49 g (1.4 mmol) of the tetraacetate **1** in 15 mL of $CH_2Cl_2$ and the second 0.32 mL (1.9 mmol) of triflic anhydride in 15 mL of $CH_2Cl_2$. The system was closed and cooled to −78 °C in a dry ice–acetone bath. The carbohydrate was added and then the triflic anhydride. (Color formation was immediate when iodide or bromide ions were present.) The reaction mixture was stirred while it warmed to room temperature over a 2-h period. The reaction mixture was poured into 300 mL of a cold 1% aqueous $NaHCO_3$ solution and shaken. The layers were separated, and the aqueous phase was extracted with three 40-mL portions of $CH_2Cl_2$. The combined organic extracts were washed with 40 mL of 5% $NaHSO_3$, 40 mL of 3% HCl (twice), 50 mL of 5% $Na_2CO_3$, and 50 mL of water, and the organic phase was dried over anhydrous $Na_2SO_4$. The solvent was distilled under reduced pressure and the residue chromatographed as described in the general procedures. Product yields are given in Table I.

**Procedure C.** The tetraacetate **1** (0.49 g, 1.4 mmol) and the pyridine derivative **4** (0.41 g, 2.0 mmol) were dissolved in 20 mL of anhydrous $CH_2Cl_2$ and placed in a three-necked flask. Attached to this flask were two pressure-equalizing addition funnels, one containing 0.32 mL (1.9 mmol) of triflic anhydride in 20 mL of $CH_2Cl_2$ and the second 4.0 mmol of trimethylphenylammonium chloride. The system was closed and cooled to the temperature shown in Table I. Without changing the temperature, the triflic anhydride was added and the reaction stirred for the period of time shown in Table I. The benzyltriethylammonium chloride was added and the reaction mixture allowed to warm to room temperature over a 2-h period. Product isolation was conducted as described in procedure A. Product yields are given in Table I.

**Synthesis of the Sulfinate Esters 9 and 10 (A and B).** The tetraacetate **1** (0.82 g, 2.35 mmol) and the base **4** (0.619 g, 3.02 mmol) were combined in 25 mL of $CH_2Cl_2$ at room temperature, and 0.48 mL (2.9 mmol) of triflic anhydride in 10 mL of $CH_2Cl_2$ was added. After stirring for 90 min, 25 mL of $CH_2Cl_2$ was distilled, and the remaining mixture was added to 2.39 g of $KSO_2CF_3$[9] in 25 mL of $CH_3CN$. The reaction mixture was allowed to stand for 36 h and then poured into 200 mL of 1% $NaHCO_3$ solution. $CH_2Cl_2$ (60 mL) was added, the mixture was shaken, and the layers were separated. The aqueous phase was extracted with a second 60-mL portion of $CH_2Cl_2$. The organic extracts were combined and washed with 60 mL of 5% $NaHSO_3$ and 60 mL of $NaHCO_3$ and dried over anhydrous $Na_2SO_4$. The solvent was distilled under reduced pressure and the residue chromatographed as described in the general procedures. Tables I–III contain product yields and NMR data. In addition, for compound **A**: mp 113–115 °C; mass spectrum, $m/z$ (relative intensity) 405 (100), 399 (5), 345 (14), 331 (22), 243 (21), 169 (20); TLC (ethyl acetate–toluene, 1:4) $R_f$ 0.28. Anal. Calcd for $C_{15}H_{19}SO_{11}F_3$: C, 38.79; H, 4.12; S, 6.91; F, 12.27. Found: C, 39.00; H, 4.23; S, 6.72; F, 11.96. For compound **B**: mp 127–129 °C; mass spectrum, $m/z$ (relative intensity) 405 (100), 345 (2), 331 (22), 289 (17), 243 (10), 169 (17); TLC (ethyl acetate–toluene, 1:4) $R_f$ 0.25. Anal. Calcd for $C_{15}H_{19}SO_{11}F_3$: C, 38.79; H, 4.12; S, 6.91; F, 12.27. Found: C, 38.97; H, 4.21; S, 6.72; F, 11.99.

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