Supporting Information

Electrophilic Triflyl-arylation and Triflyl-pyridylation by Unsymmetrical Aryl/Pyridyl- λ^3 -iodonium Salts: Synthesis of Aryl and Pyridyl Triflones

Prajwalita Das and Norio Shibata*

Department of Nanopharmaceutical Sciences, Nagoya Institute of Technology, Gokiso-cho, Showaku, Nagoya 466-8555, Japan

nozshiba@nitech.ac.jp

Table of Contents

General Procedure A–F	S1–S2
Ortep diagram of 1b	S3
NMR Spectra	S4

General Procedure A:

$$F_3CS + X$$
Br
$$\frac{\text{RuCl}_3 \text{ (5 mol\%)}}{\text{NaIO}_4 \text{ (3.0 eq.)}}$$

$$H_2O/CCl_4/\text{MeCN}$$

$$\text{rt, 1 h}$$

$$F_3CO_2S + X$$

$$S$$

$$X = C, N$$

General Procedure B:

1-iodo-4-((trifluoromethyl)sulfonyl)benzene **5a**, 1-iodo-3-((trifluoromethyl)sulfonyl)benzene **5b**, 1-iodo-2-((trifluoromethyl)sulfonyl)benzene **5c**, 5-iodo-2-((trifluoromethyl)sulfonyl)pyridine **5d** were prepared from corresponding aryl bromide **9** by aromatic Finkelstein reaction. The resulting aryl iodides **5a** and **5d** were obtained after full conversion of the starting material aryl bromide. However, the reactions to obtain **5b** and **5c** didn't undergo complete conversion of the aryl bromide starting material **9**, because of which the end products contained parts of the starting material due to separation difficulties. **5b–c** were characterised by only HRMS and used in the next step without further purification.

General Procedure C:

F₃CO₂S
$$+$$
 X $+$ X $+$

Yield for reagent 1b and 1e is with respect to 9b and for 1c and 1f is with respect to 9c.

General Procedure D (Method 1):

Genereal Procedure D (Method 2):

$$\begin{array}{c} \overline{O} \\ R1 \end{array} \begin{array}{c} \overline{O} \\ CO_2R \\ + F_3CO_2S \end{array} \begin{array}{c} \overline{O} \\ X \end{array} \begin{array}{c} \overline{O} \\ \overline{O} \\ \overline{I} \\ \overline{I} \\ \overline{I} \\ \overline{I} \end{array} \begin{array}{c} \overline{I} \\ \overline{I} \\ \overline{I} \\ \overline{I} \\ \overline{I} \end{array} \begin{array}{c} \overline{I} \\ \overline{I} \\ \overline{I} \\ \overline{I} \\ \overline{I} \\ \overline{I} \\ \overline{I} \end{array} \begin{array}{c} \overline{O} \\ \overline{CO}_2R \\ \overline{I} \\ \overline$$

General Procedure E:

$$R + F_3CO_2S + F_3CO_2S + F_3CO_2S + F_3CO_2S + F_3CO_2CF_3$$

$$(1.1 \text{ eq})$$

$$1$$

$$Cu (10 \text{ mol}\%)$$

$$NMP, 80 °C$$

$$R + R$$

$$3$$

$$X = C, N$$

General Procedure F (Method 1):

R-OH +
$$F_3CO_2S$$
 NaOH (2 eq)

General Procedure F (Method 2):

R-OH +
$$F_3CO_2S$$
 N $\frac{tBuOK (1.2 eq)}{OMe}$ R $\frac{tBuOK (1.2 eq)}{THF, 40 °C}$ R $\frac{tBuOK (1.2 eq)}{N}$ SO₂CF₃

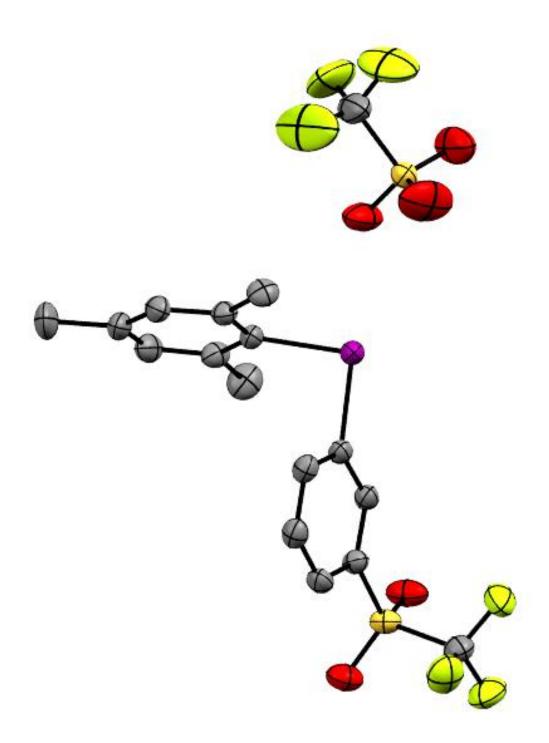


Figure 1: Ortep diagram of ${\bf 1b}$ drawn at 50% probability. The hydrogen atoms have been omitted for clarity.

