## Supporting Information

# Electrophilic Triflyl-arylation and Triflyl-pyridylation by Unsymmetrical Aryl/Pyridyl-$\lambda^{3}$-iodonium Salts: Synthesis of Aryl and Pyridyl Triflones 

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General Procedure A:


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:


Yield for reagent $\mathbf{1 b}$ and $\mathbf{1 e}$ is with respect to $\mathbf{9 b}$ and for $\mathbf{1 c}$ and $\mathbf{1 f}$ is with respect to $\mathbf{9 c}$.

General Procedure D (Method 1):


Genereal Procedure D (Method 2):


General Procedure E:


General Procedure F (Method 1):


General Procedure F (Method 2):



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



9b






























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| 20 | 10 | 0 | -10 | -20 | -30 | $-40$ | -50 | -60 | -70 |  |  | -100 | -110 | -120 | -130 | $-140$ | $-150$ | -160 | $-170$ | -180 | -190 | -200 |

















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