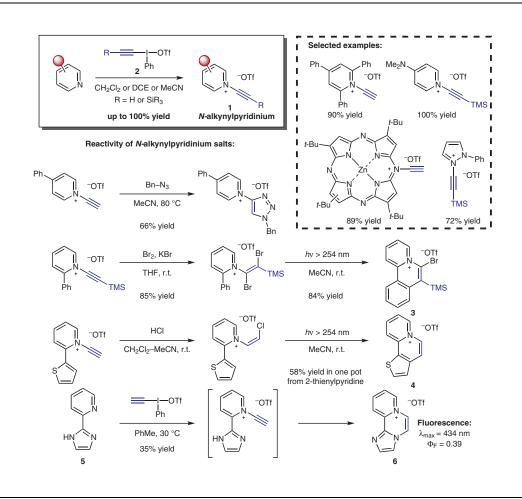
N. TORIUMI*, N. ASANO, K. MIYAMOTO, A. MURANAKA, M. UCHIYAMA* (THE UNIVERSITY OF TOKYO AND RIKEN, SAITAMA, JAPAN) *N*-Alkynylpyridinium Salts: Highly Electrophilic Alkyne–Pyridine Conjugates as Precursors of Cationic Nitrogen-Embedded Polycyclic Aromatic Hydrocarbons

J. Am. Chem. Soc. 2018, 140, 3858–3862.

All Kinds of Alkynylpyridiniums: Elusive Salts Now Plentiful



Category

Synthesis of Materials and Unnatural Products

Key words

pyridinium

hypervalent iodine

photocyclization



Significance: *N*-Alkynylpyridinium salts (e.g., **1**) have eluded isolation in previous attempts to synthesize these electrophilic molecules. Herein, the researchers disclose that alkynyl iodanes **2** are highly effective reagents for the preparation of a wide range of *N*-alkynylpyridinium triflates directly from pyridines. This method enabled the first full characterization of an *N*-alkynylpyridinium salt and the exploration of further transformations, including the synthesis of 'nitrogen-doped' polycyclic aromatic compounds with promising electronic properties for materials applications.

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Comment: Excellent yields are reported for the alkynylation of variously substituted pyridines as well as other aza-heterocycles. The *N*-alkylpyridinium triflates are stable under ambient conditions for at least six months, but the alkyne unit can be transformed in dipolar cycloaddition, halogenation, and hydrofunctionalization reactions. Halogenated products bearing a 2-aryl substituent were further subjected to photocyclization–dehydrohalogenation to generate quinolizinium salts (e.g., **3** and **4**), and fluorescent compounds such as **6** were formed directly in the alkynylation of 2-imidazolylpyridines **5**.