P. SPIEß, M. BERGER, D. KAISER, N. MAULIDE* (UNIVERSITY OF VIENNA, AUSTRIA) Direct Synthesis of Enamides via Electrophilic Activation of Amides *J. Am. Chem. Soc.* **2021**, *143*, 10524–10529, DOI: 10.1021/jacs1c04363.

Enamide Synthesis from Amides Using Tf₂O for Electrophilic Activation

LiHMDS (4.8 equiv)

$$Tf_2O$$
 (2.4 equiv)

 R^1
 R^2
 R^3

Et₂O, -94 °C, 30 min

Up to 90% yield >40 examples

 $R^1 = Ar; R^2 = Alk, Bn; R^3 = H, Alk, Ar$

Selected examples:

Significance: The authors report the direct synthesis of enamides from amides. Tf₂O is used for the electrophilic activation of amides as well as an oxidant in the reaction. The products are obtained in moderate to good yields and a range of functional groups are tolerated by the procedure. Gramscale reactions also proved to be successful.

Comment: To show the utility of the procedure, several downstream reactions were conducted including cycloadditions, ring functionalizations and ring deconstructions. A mechanism based on experimental studies is proposed. The proton next to the nitrogen is thereby acidified by the cationic nature of the activated iminium triflate intermediate.

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Metals in Synthesis

Key words

electrophilic activation

enamides

lithium bis(trimethylsilyl)amide

