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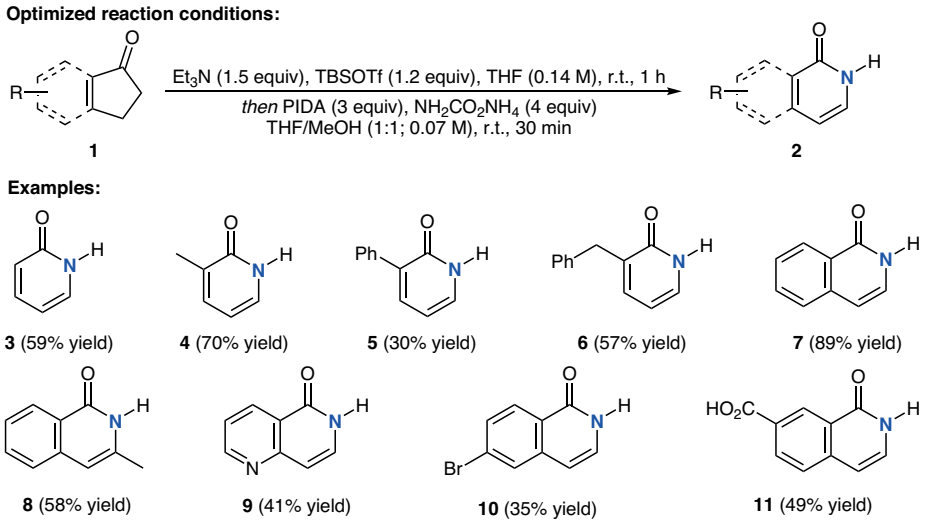
Streamlining the Synthesis of Pyridones through Oxidative Amination of Cyclopentenones
Angew. Chem. Int. Ed. **2024**, *63*, e202408230, DOI: 10.1002/anie.202408230

Facile Synthesis of Pyridones from Cyclopentenones



Significance: 2-Pyridones are found in a range of biologically active molecules and serve as both ligands for C–H activation reactions and as intermediates in the synthesis of functionalized pyridines. Several routes exist for the synthesis of 2-pyridones, including Knoevenagel-type condensations, rearrangements of pyridine *N*-oxides, and the Guareschi synthesis, though these are often lengthy, limited in scope and/or require harsh reaction conditions. The current report describes an operationally simple synthesis of 2-pyridones through the ring expansion of cyclopentenones that proceeds through the intermediacy of the corresponding silyl enol ether.

Comment: Proof-of-concept studies initially utilized the pre-formed silyl enol ether with increased steric bulk of the silyl moiety shown to be important for optimal yields to be obtained. The use of protic solvents was critical for the ring-expansion, with a mixed solvent system being utilized to enable direct transformation of the cyclopentenone to the 2-pyridone in a one-pot process. Model studies allowed identification of the most efficient oxidants and nitrogen sources with the reaction proceeding rapidly at ambient temperature. A range of cyclopentenones were successful substrates with 1-indanones interestingly displaying different regioselectivity in the process when compared to the traditional Beckmann rearrangement. The reaction was also effective for the synthesis of ^{15}N-labelled pyridones, with mechanistic studies suggesting the intermediacy of *N*-iodonium aziridine derivatives.

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Synfacts 2025; 21(01), 9 Published online: 20.12.2024
DOI: 10.1055/a-2467-5080; **Reg-No.:** V01125SF

Category
Synthesis of Heterocycles
Key words
pyridones
^{15}N-labelling
Beckmann rearrangement
silyl enol ethers
oxidative amination