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Vortrag

von Herrn

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**“Molecular Editing of
Aromatic Heterocycles
with Organometallic
Reagents”**

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um: 09:30 Uhr im

WO: Raum A12.232

Gäste sind herzlich willkommen!



**Prof. Dr. Mark R.
 Crimmin**

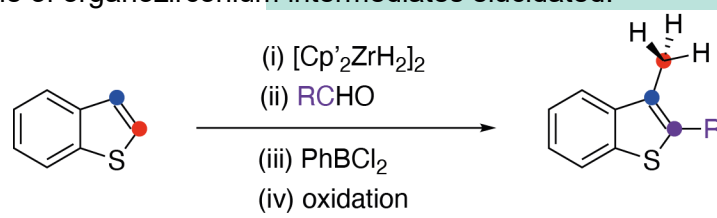
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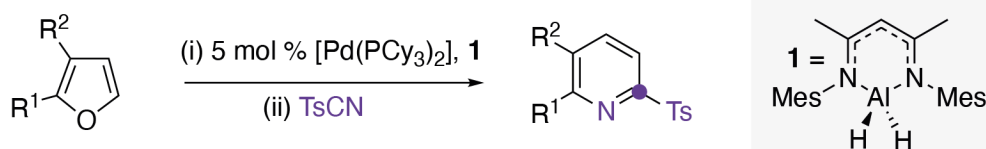
Molecular Editing of Aromatic Heterocycles with Organometallic Reagents

Molecular editing is an emerging aspect of synthetic chemistry that involves the manipulation of structures through reactions that either add, delete, or exchange atoms.^[1] In this lecture, I will describe two approaches to use organometallic reagents in the editing of aromatic heterocycles.

The first, involves the editing of benzothiophenes using the zirconocene dihydride reagent $[\text{Cp}'_2\text{ZrH}_2]_2$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$). We report a new ring-inflection reaction sequence that first breaks down the sulfur-containing ring and then rebuilds it – allowing an introduction of a methyl substituent at the 3-position and a broad range of functionality at the 2-position of benzothiophene. The procedure can be carried out in one-pot reaction with one purification step. Aspects of scope, mechanism and selectivity will be discussed and a key role of organozirconium intermediates elucidated.



The second approach involves the ring-expansion of furans into pyridines. This reaction is initiated through a palladium-catalysed insertion of an aluminium reagent into the carbon–oxygen bond of the furan.^[2] Subsequent addition of TsCN to the organoaluminium intermediate directly leads to deoxygenation and the corresponding 2-tosylated pyridine.



References

- Jurczyk, J. Woo, J. Kim, S. F. Dherange, B. D. Sarpong, R. Levin, M. D. *Nat. Synth.* **2022**, *1*, 352–364.
- Hooper, T. N. Brown, R. K. Rekhroukh, F. Garçon, M. White, A. J. P. Costa, P. J. Crimmin, M. R. *Chem. Sci.* **2020**, *11*, 7850–7857.