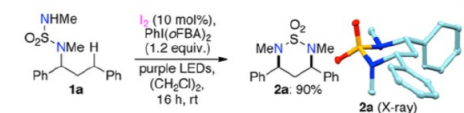


1,3-Diamine Formation from an Interrupted Hofmann–Löffler Reaction: Iodine Catalyst Turnover through Ritter-Type Amination

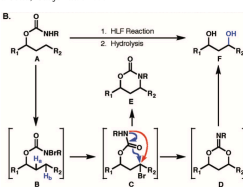
Thomas Duhamel,^{1,2} Mario D. Martínez,¹ Ioanna K. Sideri,¹ and Kilian Muñiz^{1,2}



1,3-Diol Synthesis via Controlled, Radical-Mediated C–H Functionalization

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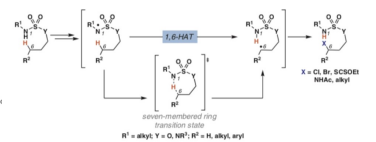


Modifying Positional Selectivity in C–H Functionalization Reactions with Nitrogen-Centered Radicals: Generalizable Approaches to 1,6-Hydrogen-Atom Transfer Processes

Melanie A. Short
J. Miles Blackburn
Jennifer L. Roizen*

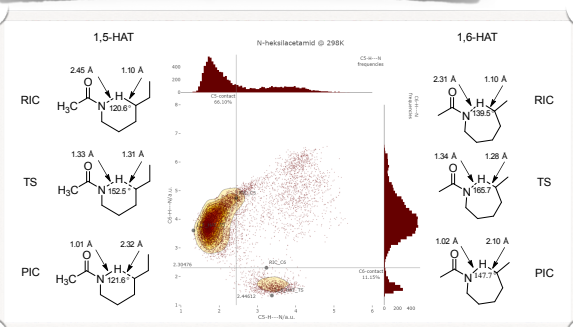
Department of Chemistry, Duke University, Box 90346, Durham, NC 27708-0346, USA
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Dedicated to Prof. Brian M. Stoltz as an early celebration of 50th birthday

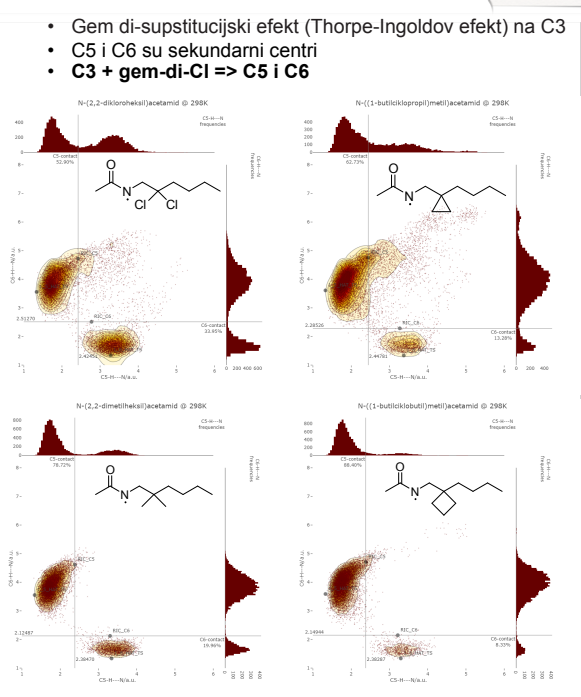


- Kad C5 radikal = C6 radikal
- Regioselektivnost HLF => 1,5-HAT
- QC i MD istraživanja kako do 1,6-HAT bez C6-substitucije?
- Cilj: kontrola regioselektivnosti

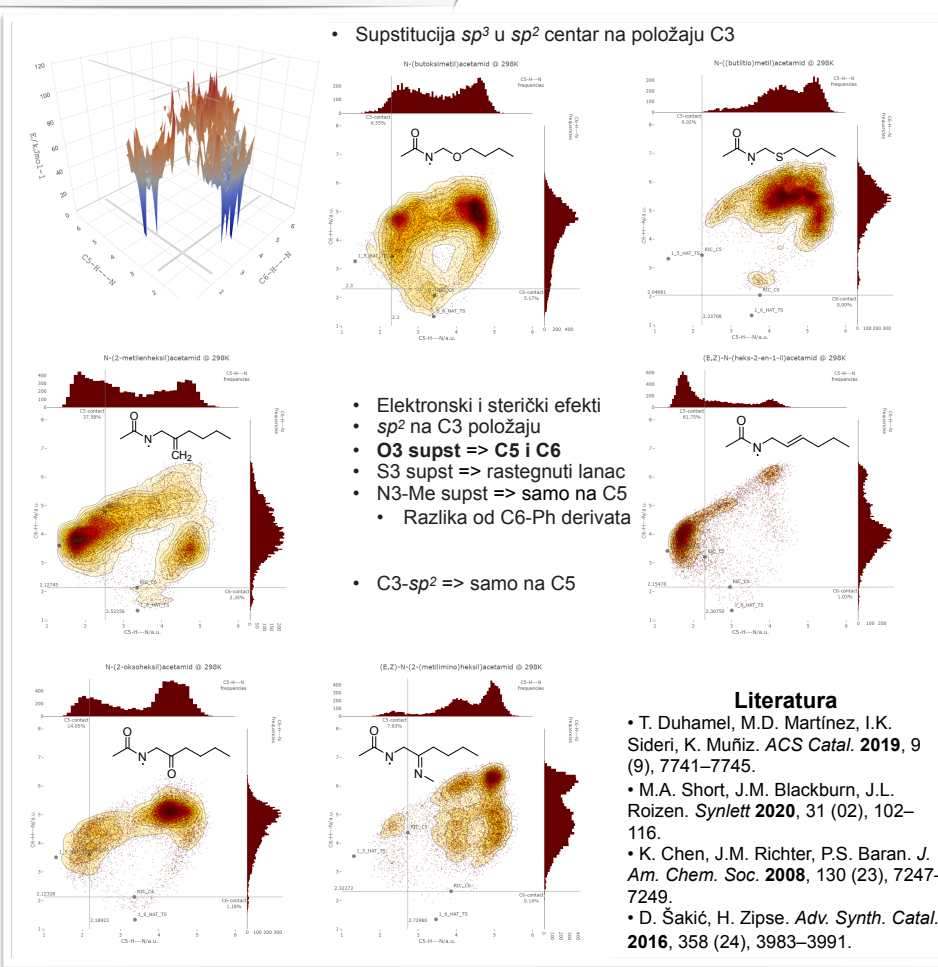
- GaussView, IQmol
- Gaussian 16 opt+freq+IRC @B3LYP/6-31G(d)
- XTB 6.41. CREST+MD @GFN-2-xtb
- Klaster Isabella @SRCE
- Klaster sw.pharma.hr @FarmInova @FBF



- Kako je postignuta regioselektivnost? Postoje tri mogućnosti:
- Supstitucija C6-položaja (npr. Ar-)
 - Nastaje stabilniji C-radikal
 - Supstitucija C3 položaja
 - Thorpe-Ingoldov efekt
 - Promjena iz sp^3 u sp^2
 - Promjena kuta u lancu



- ### Zaključak
- Termodinamički i kinetički parametri HLF reakcije nisu jedini parametri koji upravljaju regioselektivnošću HLF reakcije
 - Thorpe-Ingold efekt utječe na regioselektivnost HLF reakcije
 - Supstitucija kisikom na C3 položaju
 - Promijenjen omjer C6-H---N/C5-H---N



- Supstitucija sp^3 u sp^2 centar na položaju C3
- Elektronski i sterički efekti
- sp^2 na C3 položaju
- C3 supst => C5 i C6
- S3 supst => rastegnuti lanac
- N3-Me supst => samo na C5
- Razlika od C6-Ph derivata
- C3- sp^2 => samo na C5

Literatura

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