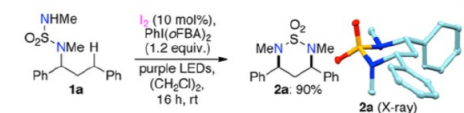


## 1,3-Diamine Formation from an Interrupted Hofmann–Löffler Reaction: Iodine Catalyst Turnover through Ritter-Type Amination

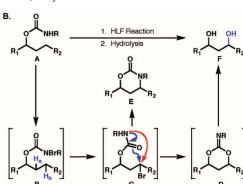
Thomas Duhamel,<sup>1,2</sup> Mario D. Martínez,<sup>1</sup> Ioanna K. Sideri,<sup>1</sup> and Kilian Muñiz<sup>1,2</sup>



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

Ke Chen, Jeremy M. Richter, and Phil S. Baran\*

Department of Chemistry, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, California 92037

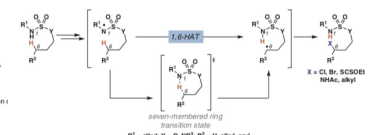


## Modifying Positional Selectivity in C–H Functionalization Reactions with Nitrogen-Centered Radicals: Generalizable Approaches to 1,6-Hydrogen-Atom Transfer Processes

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

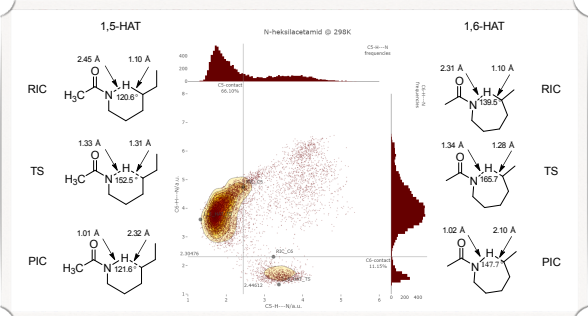
Department of Chemistry, Duke University, Box 90346, Durham, NC 27708-0346, USA  
j.roizen@duke.edu

Dedicated to Prof. Brian M. Stoltz as an early celebration of 50<sup>th</sup> birthday



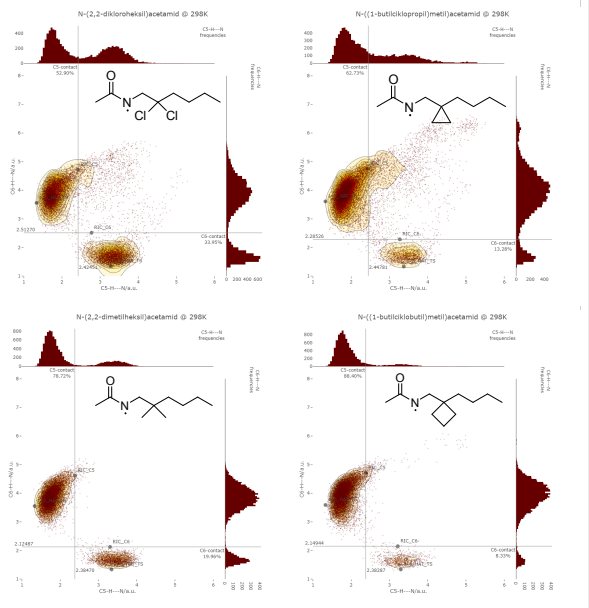
- Kad C5 radikal = C6 radikal
- Regioselektivnost HLF => 1,5-HAT
- QC i MD istraživanja kako do 1,6-HAT bez C6-substitucije?
- Cilj: kontrola regioselektivnosti

- 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](http://sw.pharma.hr) @FarmInova @FBF

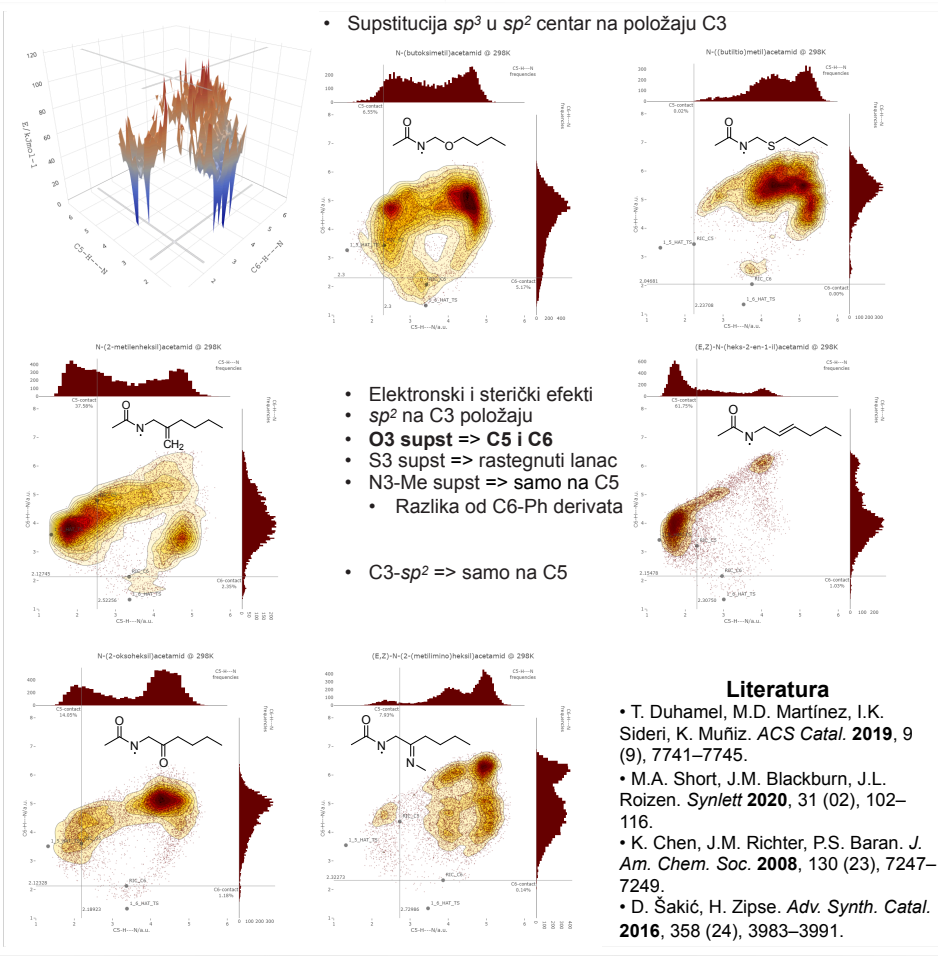


- Kako je postignuta regioselektivnost? Postoje tri mogućnosti:
- Supstitucija C6-položaja (npr. Ar-)
  - Nastaje stabilniji C-radikal
  - Supstitucija C3 položaja
  - Thorpe-Ingoldov efekt
  - Promjena iz  $sp^3$  u  $sp^2$
  - Promjena kuta u lancu

- Gem di-supstitucijski efekt (Thorpe-Ingoldov efekt) na C3
- C5 i C6 su sekundarni centri
- C3 + gem-di-Cl => C5 i C6



- ### 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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