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# Stereoselective Intramolecular Carbolithiation of Olefinic $\alpha$ Lithio Amines

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STUDENT HAS RESTRICTED ACCESS TO FULL TEXT OF THE DISSERTATION.

ONLY COVER PAGES AND ABSTRACT ARE AVAILABLE AT THIS TIME

STEREOSELECTIVE INTRAMOLECULAR CARBOLITHIATION OF  
OLEFINIC  $\alpha$  LITHIO AMINES

A Thesis

Submitted to the School of Graduate Studies and Research

in Partial Fulfillment of

the Requirements for the Degree

Master of Science

Donald R. Caldwell

Indiana University of Pennsylvania

August 2011

Indiana University of Pennsylvania  
The School of Graduate Studies and Research  
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We hereby approve the thesis of

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Title: Stereoselective Intramolecular Carbolithiation of Olefinic  $\alpha$  Lithio Amines

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This thesis describes the investigation into asymmetric deprotonation of dipole-stabilized  $\alpha$ -aminoorganolithiums. The lithiation of *N*-Boc-*N*-(3-butenyl)benzylamine provides a configurationally stable organolithium intermediates complexed to an oxygen atom. Preparation of heterocyclic rings is inhibited by this Li-O complex, therefore, restricting cyclization of unsaturated organolithium to form 5-membered rings.

However, the protection group on nitrogen plays a crucial role in the reaction topology, as an unexpected rearrangement occurred to provide for products that contained elimination adducts. An apparent 3-*exo*-trig cyclization occurs, followed by rapid and irreversible fragmentation of the strained 3-membered ring intermediate.

This led to the investigation of a variety of different substituent attached to the nitrogen in place of *N*-Boc. The conditions for the different substituent were probed at various temperature, bases, solvents, and ligands.