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BSc (Honours – Organic Chemistry), Saint Mary's University, 2014

DEPARTMENT OF CHEMISTRY

TITLE OF THESIS:	ADVANCES IN NICKEL-CATALYZED C-N CROSS-COUPLING ENABLED BY TAILORED ANCILLARY LIGAND DESIGN
TIME/DATE:	9:30 am, Friday, November 9, 2018
PLACE:	Room 430, The Goldberg Computer Science Building, 6050 University Avenue

EXAMINING COMMITTEE:

Dr. Samuel Johnson, Chemistry and Biochemistry Department, University of Windsor (External Examiner)

Dr. Alex Speed, Department of Chemistry, Dalhousie University (Reader)

Dr. Laura Turculet, Department of Chemistry, Dalhousie University (Reader)

Dr. Heather Andreas, Department of Chemistry, Dalhousie University (Reader)

Dr. Mark Stradiotto, Department of Chemistry, Dalhousie University (Supervisor)

DEPARTMENTAL REPRESENTATIVE:	Dr. Josef Zwanziger, Department of Chemistry, Dalhousie University
CHAIR:	Dr. Bernard Boudreau, PhD Defence Panel, Faculty of Graduate Studies

ABSTRACT

The nickel-catalyzed C(sp^2)-N cross-coupling of NH substrates and (hetero)aryl (pseudo)halides for the synthesis of (hetero)anilines is in the midst of a resurgence. Reactivity breakthroughs that have been achieved in this field within the past five years have served to establish Ni catalysis as being competitive with, and in some cases superior to, more well-established Pd- or Cu-based protocols. Whereas the repurposing of useful ancillary ligands from the Pd domain has been the most frequently employed approach in the quest to develop effective Ni-based catalysts for such transformations, considerable progress has been made as of late in the design of ancillary ligands tailored specifically for use with Ni. Bisphosphine ancillary ligands have proven to be well-suited for such an approach, given their modular and facile syntheses. As part of this thesis research, several new bidentate phosphine ancillary ligands were developed that are particularly effective in enabling a range of otherwise challenging Ni-catalyzed C(sp^2)-N cross-couplings. Presented herein is a comprehensive summary of my contributions to the field of Ni-catalyzed C(sp^2)-N cross-coupling, achieved by the application of the newly developed PAd-DalPhos ancillary ligand class. It is anticipated that the advancements made within my research, along with the discussion of key ancillary ligand design concepts and mechanistic considerations presented herein, will provide a useful platform for researchers to initiate ancillary ligand design efforts for the continued development of high performing Ni cross-coupling catalysts.