

RICHARD C. BUNT

Burr Professor of Chemistry and the Natural Sciences
Department of Chemistry and Biochemistry
Middlebury College
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Education

Massachusetts Institute of Technology, Cambridge, MA.

Postdoctoral Fellow, Department of Chemistry, April 1996-August 1998.

Advisor: Professor JoAnne Stubbe.

Stanford University, Stanford, CA.

Doctor of Philosophy, Department of Chemistry, April 1996.

Advisor: Professor Barry M. Trost.

Northwestern University, Evanston, IL.

Bachelor of Arts and Master of Science in Chemistry, with distinction, departmental honors, June 1990.

Teaching

Middlebury College

Associate Dean for the Sciences, 2020-present

Chair, Faculty Council, 2018-2021

Burr Professor of Chemistry and the Natural Sciences, 2012-present

Department Chair, Chemistry and Biochemistry, 2010-2015.

Professor of Chemistry and Biochemistry 2014-present

Associate Professor of Chemistry and Biochemistry, 2005-2013.

Assistant Professor of Chemistry and Biochemistry, 1998-2005.

General Chemistry (CHEM 0103)

Organic Chemistry (CHEM 0203, CHEM 0204)

Medicinal Chemistry (CHEM 0301)

Instrumental Analysis (CHEM 0311)

Advanced Inorganic and Physical Chemistry Laboratory (CHEM 0312)

Seminar in Chemical Research (CHEM 0400)

Organic Mechanisms of Enzyme Catalysis (CHEM 0441)

First-Year Seminar: Science and Science Fiction (FYSE 1259)

First-Year Seminar: Science Risk, Reward and Public Policy (FYSE 1008)

First-Year Seminar: Modern Age of Science (FYSE 1007)

Stanford University

Acting Instructor-Graduate. January-March, 1995.

Synthesis Laboratory (CHEM 136)

Research

Middlebury College

- Using electronically modified phosphinooxazoline chiral ligands to study the mechanism of stereochemical induction in palladium-catalyzed allylic-alkylation reactions.

Massachusetts Institute of Technology

Postdoctoral research with Professor JoAnne Stubbe, April 1996-August 1998.

- Synthesized site-specific DNA lesion in short oligonucleotide, determined structure of DNA lesion by 2D NMR, studied binding and cleavage of lesion by metallo-Bleomycins.
- Directed undergraduate in synthesis of isotopically labeled inhibitors of ribonucleotide reductase for EPR spectroscopy and radiolabeling studies.

Stanford University

Graduate research with Professor Barry M. Trost, September 1990-March 1996.

- Developed new methodologies and chiral ligands for enantioselective π -allylpalladium catalysis, established novel features of palladium catalyzed allylic alkylation reaction mechanisms and ion pair structures, discovered new method for determining absolute configuration of primary amines.
- Directed undergraduates in total synthesis and methodology projects resulting in publications.

Kraft General Foods

Research intern with Dr. Rich Fisher, June-September 1989.

- Accomplished synthesis, purification, molecular modeling, and structure-activity relationship analysis of flavor compounds.

Northwestern University

Undergraduate research with Professor Joseph B. Lambert, September 1988-June 1990.

- Performed synthesis and small-molecule NMR binding studies of aza-crown ethers.

Honors and Awards

Perkins Award for Excellence in Teaching, Middlebury College, 2007.

Damon Runyon–Walter Winchell Cancer Research Fellow, MIT, 1996-1999.

The Roche Award for Excellence in Organic Chemistry, Hoffmann-La Roche Inc., 1994.

Franklin Veatch Memorial Fellow, Stanford University, 1993-1994.

National Science Foundation Predoctoral Fellow, Stanford University, 1990-1993.

Linus Pauling Award, Stanford University, 1990.

Marple-Schweitzer Memorial Award, Northwestern University, 1990.

Phi Beta Kappa, Northwestern University, 1989.

National Merit Scholar, Northwestern University, 1986-1990.

External Grants in Support of Undergraduate Research

National Science Foundation (NSF-RUI) “Hammett Studies of P,N-Chiral Ligands” (\$145,857, 2007-2010).

American Chemical Society-Petroleum Research Fund (ACS-PRF), Type B, “Hammett Studies of P,N-Chiral Ligands” (\$55,000, 2007-2010).

Vermont Genetics Network (NIH-BRIN), Equipment Grant for “A Solvent Purification System” Co-PI with Jeff Byers (\$24,700, 2005).

National Institutes of Health (NIH-AREA), “Mechanism of Base-Flipping by DNA Modifying Enzymes” (\$137,971, 2003-2006).

Vermont Genetics Network (NIH-BRIN), Partial Sabbatical Leave Support for “Altering the Rate of Base Flipping in DNA” (\$20,000, 2002-2003).

Pfizer Summer Undergraduate Research Fellowship for Sarah S. Goodwin (\$5,000, 2002).

American Chemical Society-Petroleum Research Fund (ACS-PRF), Type G, “Probing the Electronic Origins of Chiral Ligand Asymmetry in Palladium-Catalyzed Allylic-Alkylation Reactions” (\$25,000, 2001-2004).

Cottrell College Science Award from Research Corporation, “Probing the Electronic Origins of Chiral Ligand Asymmetry in Palladium-Catalyzed Allylic-Alkylation Reactions” (\$41,381, 2001-2004).

Pfizer Summer Undergraduate Research Fellowship for Agnes Makingwe (\$5,000, 2000).

VT EPSCoR Award, “Electronic Control of Chiral Ligand Asymmetry” (\$5,500, 2000).

Camille and Henry Dreyfus Faculty Start-up Grant, “The Mechanism of Base-Flipping in DNA Repair Enzymes,” (\$20,000, 1998-2003).

Publications

Middlebury College undergraduate co-authors underlined.

21. Isabelle N. –M. Leibler, Madison B. Goodstein, Bryan S. Holtzman, Nicholas S. Caminiti, Michael L. Martini, Zitong B. Jia, Staci A. Hill, Gina M. Mendolia, Sarah B. Nodder, Nathaniel C. Nelson, Jacob A. Fox, Eric T. Roberts, Molly S. Costanza-Robinson and Richard C. Bunt, Reversibility and Enantioselectivity of Palladium-Catalyzed Allylic Aminations: Ligand, Base-Additive, and Solvent Effects. *manuscript in preparation*, 2019.
20. Bryan S. Holtzman, Eric T. Roberts, Nicholas S. Caminiti, Jacob A. Fox, Madison B. Goodstein, Staci A. Hill, Zitong B. Jia, Isabelle N. –M. Leibler, Michael L. Martini, Gina M. Mendolia, Sarah B. Nodder, Molly S. Costanza-Robinson and Richard C. Bunt, Ligand and base additive effects on the reversibility of nucleophilic addition in palladium-catalyzed allylic aminations monitored by nucleophile crossover. *Tetrahedron Lett.* **2017**, 58, 432–436.
19. Nicholas S. Caminiti, Madison B. Goodstein, Isabelle N. –M. Leibler, Bryan S. Holtzman, Zitong B. Jia, Michael L. Martini, Nathaniel C. Nelson, and Richard C. Bunt, Reversible nucleophilic addition can lower the observed enantioselectivity in palladium-catalyzed allylic amination reactions with a variety of chiral ligands. *Tetrahedron Lett.* **2015**, 56, 5445–5448.
18. Charlotte Majerczyk, Mitchell Brittnacher, Michael Jacobs, Christopher Armour, Matthew Radey, Richard Bunt, Hillary Hayden, Ryland Bydalek, and E. Peter Greenberg, Cross-Species Comparison of the *Burkholderia pseudomallei*, *Burkholderia thailandensis*, and *Burkholderia mallei* Quorum Sensing Regulons. *J. Bacteriol.* **2014**, 196, 22, 3862–3871.
17. Charlotte Majerczyk, Mitchell Brittnacher, Michael Jacobs, Christopher D. Armour, Mathew Radey, Emily Schneider, Somsak Phattarasokul, Richard Bunt and E. Peter Greenberg, Global Analysis of the *Burkholderia thailandensis* Quorum Sensing-Controlled Regulon. *J. Bacteriol.* **2014**, 196, 7, 1412–1424.
16. Charlotte Majerczyk, Loren Kinman, Tony Han, Richard Bunt, and E. Peter Greenberg, Virulence of *Burkholderia mallei* Quorum-Sensing Mutants. *Infect. Immun.* **2013**, 81, 5, 1471–1478.
15. Paul B. Armstrong, Elizabeth A. Dembicer, Andrew J. DesBois, Jay T. Fitzgerald, Janet K. Gehrman, Nathaniel C. Nelson, Amelia Noble, and Richard C. Bunt, Investigation of the

- Electronic Origin of Asymmetric Induction in Palladium-Catalyzed Allylic- Substitutions with Phosphinooxazoline (PHOX) Ligands by Hammett and Swain–Lupton Analysis of the ^{13}C NMR Chemical Shifts of the π -Allylpalladium Intermediates. *Organometallics* **2012**, *31*, 6933–6946.
14. Paul B. Armstrong, Lisa M. Bennett, Ryan N. Constantine, Jessica L. Fields, Jerry P. Jasinski, Richard J. Staples, Richard C. Bunt, Hammett ^{13}C NMR and X-ray studies of allylpalladium phosphinooxazoline chiral ligand complexes. *Tetrahedron Lett.* **2005**, *46*, 1441–1445.
 13. Sunhee Choi, Richard B. Cooley, Amanda S. Hakemian, Yuna C. Larrabee, Richard C. Bunt, Stéphane D. Maupas, James G. Muller, and Cynthia J. Burrows, Mechanism of Two-Electron Oxidation of Deoxyguanosine 5'-Monophosphate by a Platinum(IV) Complex. *J. Am. Chem. Soc.* **2004**, *126*, 591–598.
 12. Ryan N. Constantine, Naomi Kim, and Richard C. Bunt, “Hammett Studies of Enantiocontrol by PHOX Ligands in Pd-Catalyzed Allylic Substitution Reactions,” *Org. Lett.* **2003**, *5*, 2279–2282.
 11. Hans-Dieter Junker, Silvia T. Hoehn, Richard C. Bunt, Vasilios Marathius, Jingyang Chen, Christopher J. Turner, and Joanne Stubbe “Synthesis, Characterization and Solution Structure of Tethered Oligonucleotides Containing an Internal 3'-Phosphoglycolate, 5'-Phosphate Gapped Lesion,” *Nucleic Acids Res.* **2002**, *30*, 5497.
 10. Silvia T. Hoehn, Hans-Dieter Junker, Richard C. Bunt, Christopher J. Turner, and Joanne Stubbe “Solution Structure of Co(III)-Bleomycin-OOH Bound to a Phosphoglycolate Lesion Containing Oligonucleotide: Implications for Bleomycin-Induced Double-Strand DNA Cleavage,” *Biochemistry* **2001**, *40*, 5894–5905.
 9. Barry M. Trost, Richard C. Bunt, Reme C. Lemoine, and Trevor L. Calkins “Dynamic Asymmetric Transformation of Butadiene Monoepoxide. A Practical Asymmetric Synthesis of Vinylglycinol, Vigabatrin, and Ethambutol,” *J. Am. Chem. Soc.* **2000**, *122*, 5968.
 8. Lisa A. Marzilli, Richard C. Bunt, JoAnne Stubbe, Paul Vouros, and Andreas Harsch “Accurate and Rapid Modeling of Iron-Bleomycin Induced DNA Damage Using Tethered Oligonucleotides and Electrospray Ion Trap Mass Spectrometric Analysis,” *Nucleic Acids Res.* **2000**, *28*, 1978.
 7. Barry M. Trost and Richard C. Bunt “On the Effect of the Nature of Ion Pairs as Nucleophiles in a Metal Catalyzed Substitution Reaction,” *J. Am. Chem. Soc.* **1998**, *120*, 70.
 6. Barry M. Trost, A. Chris Kruger, Richard C. Bunt, and Jorge Zambrano “On the Question of Asymmetric Induction with Acyclic Allylic Substrates. An Asymmetric Synthesis of (+)-Polyoxamic Acid,” *J. Am. Chem. Soc.* **1996**, *118*, 6520.
 5. Barry M. Trost and Richard C. Bunt “On the Question of the Symmetry of Formally Symmetrical π -(Allyl)palladium Cationic Intermediates in Allylic Alkylations,” *J. Am. Chem. Soc.* **1996**, *118*, 235.
 4. Barry M. Trost and Richard C. Bunt “On Ligand Design for Outer Sphere Catalytic Reactions. A Simple Asymmetric Synthesis of Vinylglycinol,” *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 99.
 3. Barry M. Trost, Richard C. Bunt, and Shon R. Pulley "On the Use of *O*-Methylmandelic Acid for the Establishment of Absolute Configuration of α -Chiral Primary Amines," *J. Org. Chem.* **1994**, *59*, 4202.

2. Barry M. Trost and Richard C. Bunt "Asymmetric Induction in Allylic Alkylations of 3-Acyloxycycloalkenes," *J. Am. Chem. Soc.* **1994**, *116*, 4089.
1. Barry M. Trost and Richard C. Bunt "On the Nature of the Ion Pair as a Nucleophile in Pd Catalyzed Alkylations with Dienyl Carboxylates," *Tetrahedron Lett.* **1993**, *34*, 7513.

Patents

Barry M. Trost, David L. van Vranken, and Richard C. Bunt "Asymmetric Ligands Useful for Transition Metal Catalyzed Bond Forming Reactions," **1998** U.S. Patent 5,739,396.

External Presentations and Talks

Middlebury College undergraduate co-authors underlined.

"Reversible Palladium-Catalyzed Allylic-Amination: Ligands and Solvents and Bases, Oh My!" Invited talk at Lafayette College, Easton, PA, April 11, 2019.

"A Palladium Catalyzed Mystery: Reversible Allylic-Amination Ruins the Day?" Invited talk at Haverford College, Haverford, PA, January 24, 2014.

"Hammett NMR Studies of Phosphinooxazoline (PHOX) Chiral Ligands in π -Allyl Palladium Catalysis," Elizabeth A. Dembicer, Nathaniel C. Nelson, and Richard C. Bunt* Poster Presentation at 42nd National Organic Symposium, Princeton University, Princeton, NJ. June 5-9, 2011.

"Hammett Studies of Phosphinooxazoline Chiral Ligands in π -Allyl Palladium Catalysis" Invited Talk at New England Regional Meeting of American Chemical Society for the Arthur C. Cope Scholar Award Symposium, Burlington, VT, July 1, 2008.

"Chiral Ligands for Pd-Catalyzed Allylic Alkylations", Invited talk at NSF Workshop on Organic Synthesis and Natural Products Chemistry, Minary Conference Center, Holderness, NH, June 1-5, 2006.

"Hammett Studies of Phosphinooxazoline Chiral Ligands in Pd-Catalyzed Allylic Substitutions", Invited talk at College of Charleston, Charleston, SC, March 25, 2004.

"Hammett Studies of Phosphinooxazoline Chiral Ligands in Pd-Catalyzed Allylic Substitutions", Invited talk at Smith College, Northampton, MA, March 4, 2004.

"Hammett Studies of Phosphinooxazoline Chiral Ligands in Pd-Catalyzed Allylic Substitutions", Invited talk at Merck Process Research, Rahway, NJ, July 11, 2003.

"Hammett Studies of Enantiocontrol by PHOX Ligands in Pd-Catalyzed Allylic Substitution Reactions", Paul B. Armstrong, Ryan N. Constantine, Naomi Kim and Richard C. Bunt, Poster Presentation at National Organic Symposium, Bloomington, IN, June 11, 2003.

"DNA Base-Flipping and Hammett Studies of Asymmetric Palladium Catalysis", Invited talk at Chiron Corporation, Emeryville, CA, June 14, 2001.

Senior Thesis Projects Supervised

26. Ashley T. Fox, 2018 "The Road to MeO-, CF₃-BIPHEP Chiral Ligands: A Focus Upon Enantioselectivity and Electronics."

25. Katherine R. Johnson, 2018 “A Systematic Investigation of Coupling Reactions for use in the Synthesis of Electronically Differentiated Chiral Ligands.”
24. Isabelle N. –M. Leibler, 2017, “Synthesis and Characterization of Precursors and Preliminary Constructs of “X,Y-BIPHEP” Chiral Ligands.”
23. Cameron Pierce, 2017, “Electronic Effects of Chiral Ligands on Enantioselectivity: Synthesis and Investigation of OMe,CF₃-BIPHEP.”
22. Madison B. Goodstein, 2016, “Synthesis of “X,Y-BIPHEP” Ligands with the Aim of Understanding the Influence of Electronic Effects in Chiral Ligands.”
21. Nicholas S. Caminiti, 2015, “The Impact of Reversibility on the Enantioselectivity of Several Chiral Ligands in Allylic Aminations.”
20. Michael L. Martini, 2014.5, “Investigating the Natural Bite Angle as an Important Ligand Parameter for Reversibility in Palladium-Catalyzed Allylic Aminations with Achiral Ligands.”
19. Eric T. Roberts, 2013, “Reversibility in Palladium Catalyzed Allylic Additions with PHOX Ligands.”
18. Nathaniel C. Nelson, 2011, “Hammett Studies of Enantiocontrol by Electronically-Modified PHOX Ligands in Pd-catalyzed Allylic Substitution Reactions.”
17. Elizabeth A. Dembicer, 2011, “Hammett ¹³C NMR Studies of Modified π -Allylpalladium PHOX Ligand Complexes.”
16. Anna Eisenstein, 2007, “Investigation of the DNA Base-Flipping Mechanism by NMR and Fluorescence Spectroscopy.”
15. Muayad Almahariq, 2007, “Studying the Kinetics of Uracil-flipping in the 2-Aminopurine: Uracil Base-pair using Fluorescence Spectroscopy.”
14. Jay T. Fitzgerald, 2006, “Probing the Mode of Enantioselection of Chiral PHOX Ligands Through a Comparison of Electronically Modified Isomers.”
13. Abdel Sumerin, 2005, “Probing The Mechanism of Enantioselection Using Isomeric PHOX Ligands.”
12. Naomi Kim, 2005, “Enantiocontrol by Phosphinooxazoline Ligands in Pd-Catalyzed Allylic Substitution Reactions.”
11. Sarah S. Goodwin, 2004, “Base Pair Flipping: The Kinetics and Dynamics of a Modified G:U Mismatch in the Dodecamer 5’-d(CGCGAATTUGCG)-3’.”
10. Paul B. Armstrong, 2004, “The Mechanism of Asymmetric Induction by Chiral PHOX Ligands in Pd-Catalyzed Allylic Substitution Reactions.”
9. Agnes Mwakingwe, 2002, “Synthesis of Modified 5’C of Deoxyuridine: Study of Base-Flipping Mechanism in DNA.”
8. Nicole R. LeBoeuf, 2002, “Rates of Imino Proton Exchange in 5’-d(CGCGAATTUGCG)-3’ Containing a G-U Mismatch: Kinetic Studies of Base Flipping Dynamics.”
7. Ryan N. Constantine, 2002, “Palladium-Catalyzed Allylic-Alkylation Reactions: Using Modified Phosphinooxazoline Ligands to Understand Enantiocontrol.”

6. Fritzline L. Montalmant, 2001 “Kinetics and Energetics of Base-Pair Opening in the 5'-d(CGCGAATTUGCG)-3' Dodecamer Containing a GU Mismatch.”
5. Jessica L. Fields, 2001, “Hammett Studies of Pd-Chiral Ligand Complexes by ¹³C NMR.”
4. Michael R. Cooley, 2001, “5'-Modification of Deoxyuridine to Aid in Kinetic Studies of Uracil-DNA Glycosylase.”
3. Charlene M. Weigel, 2000, “The Addition of a Methyl Group to a Deoxyribose Sugar with the Goal of Studying the DNA Repair Enzyme Uracil DNA-Glycosylase.”
2. Rachel T. Davis, 2000, “Addition of a Uracil Base to a Deoxyribose Sugar to Study the Mechanism of DNA Repair by Uracil-DNA Glycosylase.”
1. Suzanne M. Muchene, 1999, “Synthesis of Nucleoside Analogs with Restricted Backbone Conformation.”

Current and Past non-Thesis Research Students Supervised

13. Katherine Merrick ('17)
12. Zitong Bruce Jia ('16)
11. Jacob Fox ('15)
10. Staci Hill ('15)
9. Sarah Nodder ('15)
8. Bryan Holtzman ('14)
7. Gina Mendolia ('14)
6. Andrew DesBois ('13)
5. Janet Gehrman ('12)
4. Amelia Noble ('11)
3. Zach DeVore ('10)
2. Koby Osei-Mensah ('10)
1. Evan Smith ('9.5)