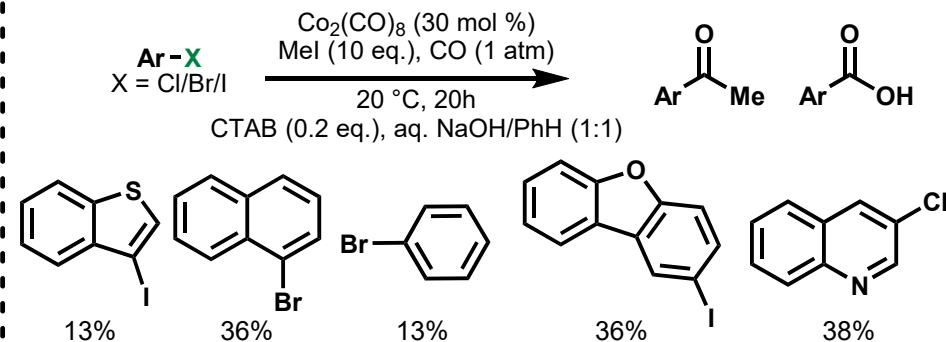
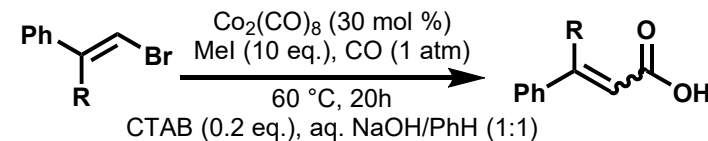
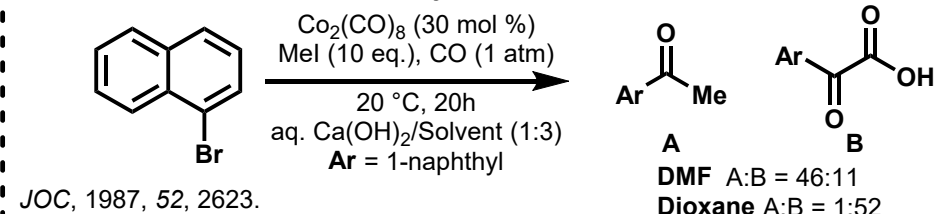
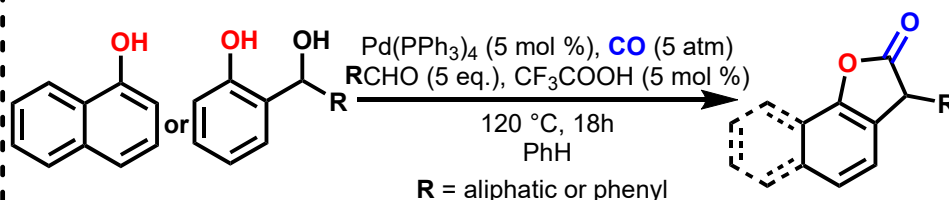
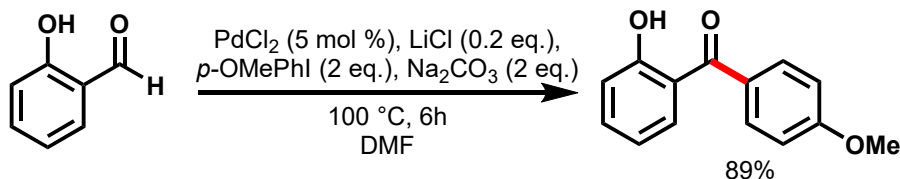


**Professional Positions****1984–2005**Assistant Professor, Graduate School of Engineering,
Osaka University**1998–2005**Associate Professor, Graduate School of Engineering,
Osaka University**2005–present**Professor, Graduate School of Engineering,
Applied Chemistry Division,
Osaka University**Research Interests**Directed C-H Functionalization
Metal-Catalyzed C-C Activation
Oxidative Dehydrogenative Coupling
Synthesis of π -Conjugated Heterocycles
Metal Catalyzed Decarboxylative Coupling**Education and Supervised Research****1978** B.S., Osaka University**1983** Ph.D., Osaka University, (Advs. Prof. S. Kusabayashi & Prof. M. Nojima)Synthesis and characterization of cyclic bisperoxides; Oxidation of alkenes,
organosulfur, and alcohols with polyoxygenated reagents.**1990–1991** Humboldt Fellow with Prof. K. Griesbaum, Karlsruhe University**Awards****2012** Thomson Reuters Research Front Award**494 publications (34 reviews)****9 patents****5 book chapters****Cobalt-catalyzed carbonylation of aryl and vinyl halides****Synthesis of unsymmetrical methyl ketones***J. Chem. Soc. Perkin Trans.*, 1987, 1021.*J. Chem. Soc. Chem. Comm.*, 1986, 241.*E/Z* is dependent on substrate.**Solvent-controlled double carbonylation***JOC*, 1987, 52, 2623.**Pd-catalyzed cross carbonylation of phenols and aldehydes***J. Molecular Cat. A: Chem.*, 1999, 143, 203.

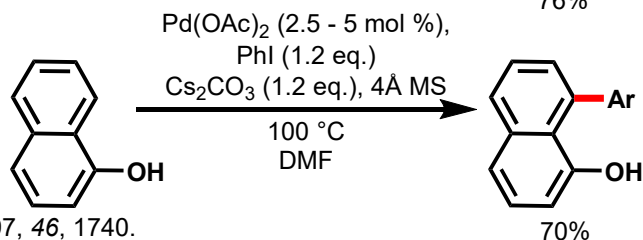
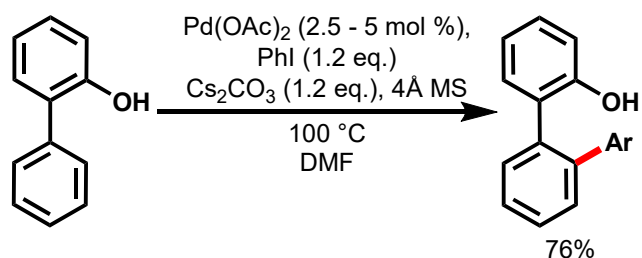
Pd-catalyzed arylation of aldehydic C-H bonds



First direct catalytic arylation of aldehyde C-H bonds using aryl halides.

CL, 1996, 25, 823.

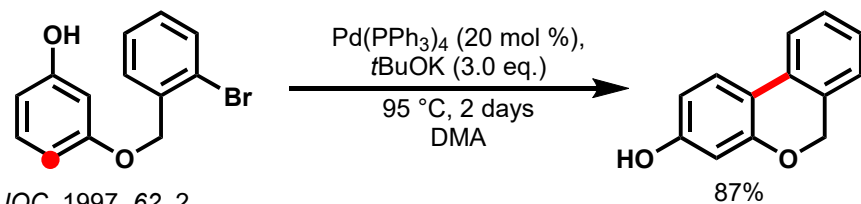
Pd-catalyzed regioselective C-H arylation of 2-phenylphenols and naphthols



ACIE, 1997, 46, 1740.

BCSJ, 1998, 71, 2239.

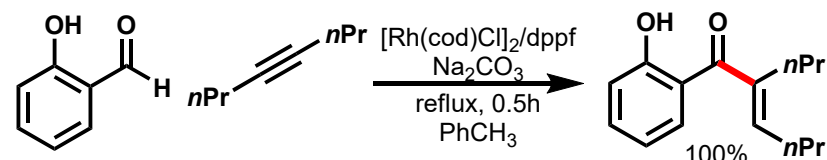
A similar phenoxide chelate-controlled intramolecular variant was developed concurrently by Rawal *et al.*



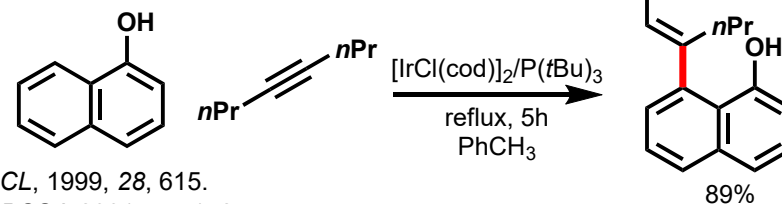
JOC, 1997, 62, 2.

For examples of $\text{C}(\text{sp}_3)\text{-OH}$ directed Pd-catalyzed C-H functionalization, see:
 JACS, 2010, 132, 5916; JACS, 2010, 132, 12203.

Additional methodology using phenolic directing group



JOC, 1997, 62, 4564.

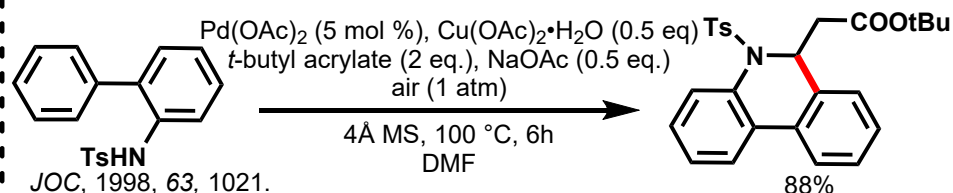


CL, 1999, 28, 615.

BCSJ, 2001, 74, 1727.

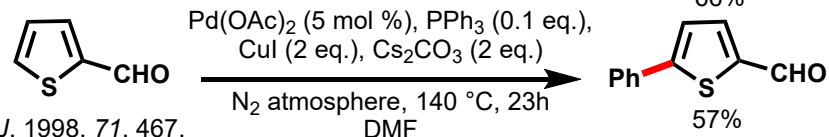
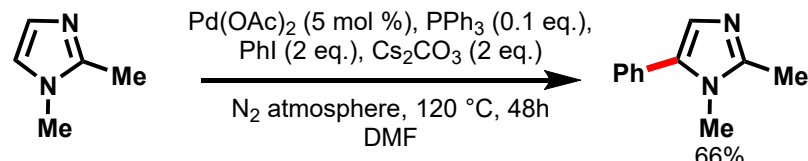
Utilization of other *ortho*-directing functional groups for Pd C-H activation

Benzenesulfonamides



JOC, 1998, 63, 1021.

Nitrogen, sulfur, and oxygen-containing heterocycles



BCSJ, 1998, 71, 467.

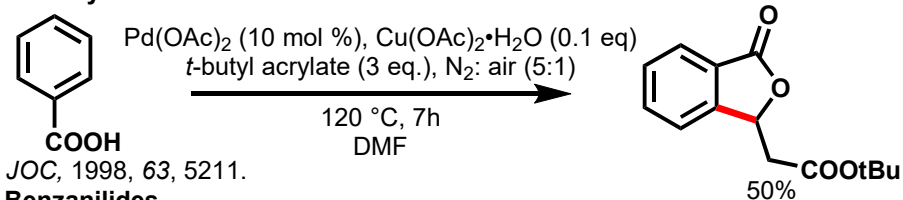
Stoichiometric Cu can be used in lieu of Pd for thiophene arylation (15%)

Other *o*-arylated heterocycles:

1-methyl-1*H*-benzimidazoles, benzofurans, benzothiazoles, and thiazoles, see:

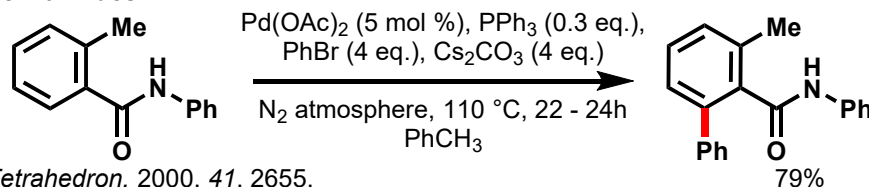
BCSJ, 1998, 71, 467.

Carboxylic Acids

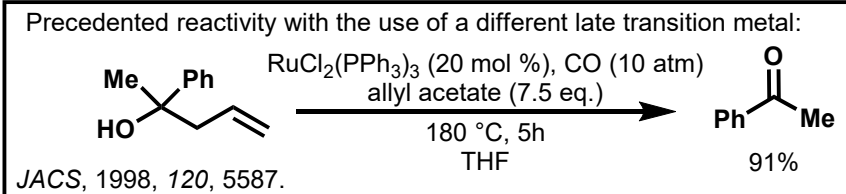


JOC, 1998, 63, 5211.

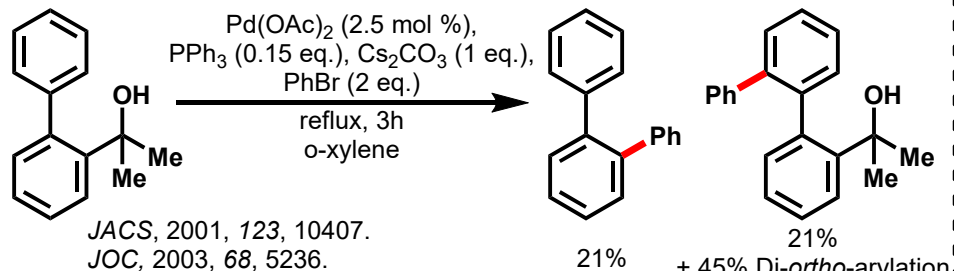
Benzanilides



Tetrahedron, 2000, 41, 2655.

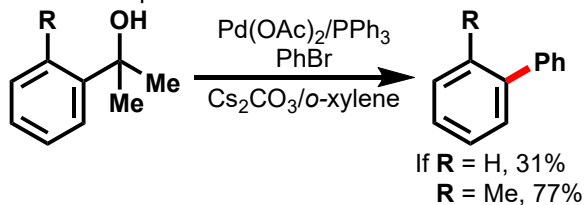
Pd-catalyzed C-C bond activation of tertiary alcohols via β -C elimination

JACS, 1998, 120, 5587.

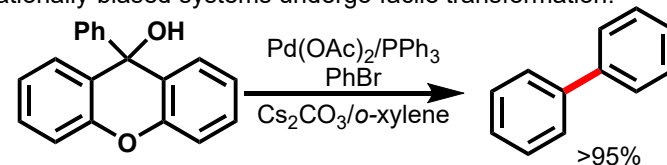


JACS, 2001, 123, 10407.

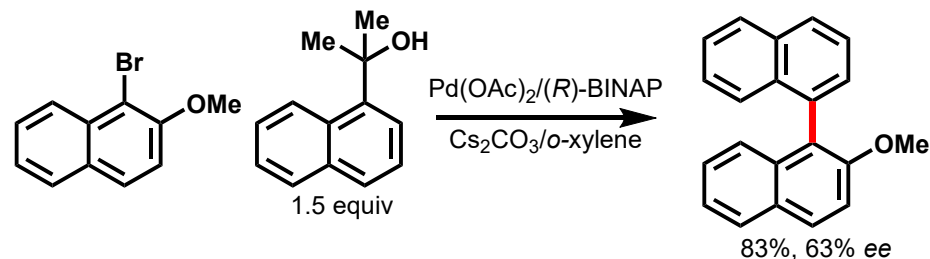
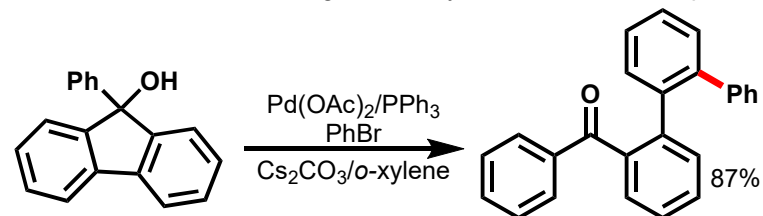
JOC, 2003, 68, 5236.

The *ortho*-substituent has a profound effect on the reaction outcome:

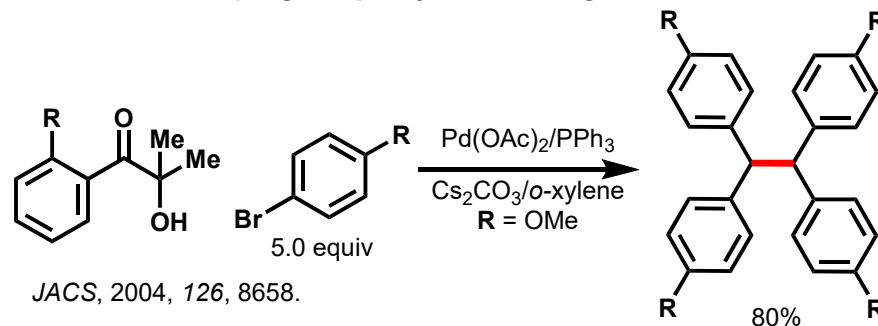
Configurally-biased systems undergo facile transformation:



Release of strained dibenzofuran ring selectively forms the observed product:

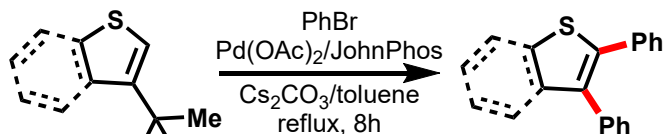


Pd-cat. homocoupling of diphenylmethane fragments



JACS, 2004, 126, 8658.

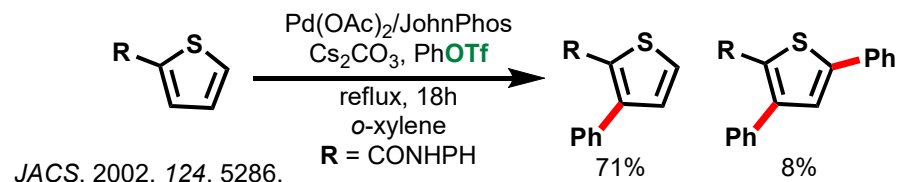
2,3-Diarylation of 3-Thiophenemethanols invoking C-H and C-C activation



JOC, 2006, 71, 8309.

Thiophene: 62%
Benzothiophene: 64%

For related work exploiting this reactivity for stereoselective allylation of aryl halides, see: JACS, 2007, 128, 2210.

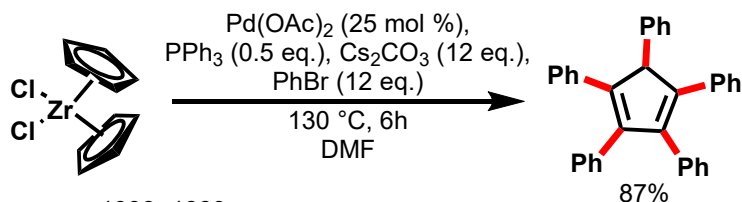


JACS, 2002, 124, 5286.

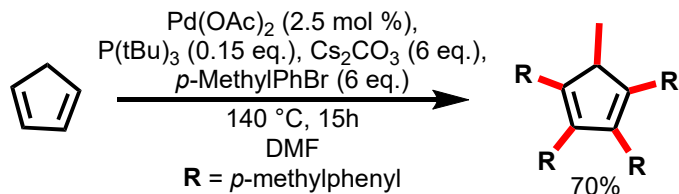
R = CONHPh

Peralkylation and perarylation of aromatics - round and round we go!

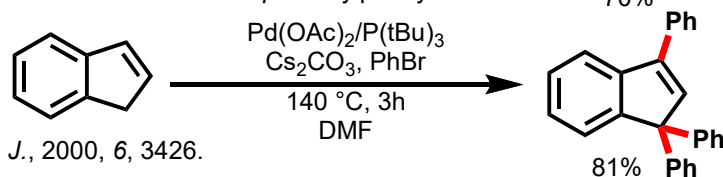
Perarylation of metallocenes and cyclopentadiene



Chem. Commun., 1998, 1889.



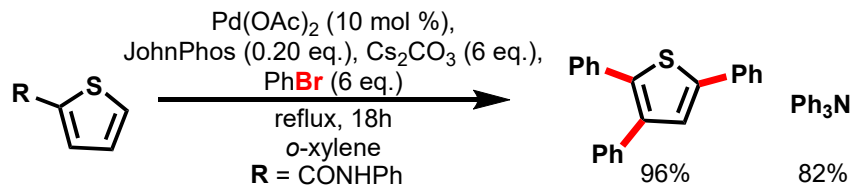
R = p-methylphenyl



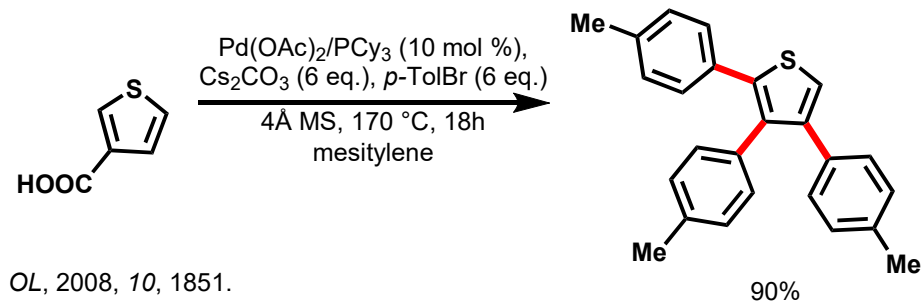
Chem. Eur. J., 2000, 6, 3426.

Electron-rich tri-alkyl phosphine enables successive coupling

Decarboxylative perarylation of thiophenes and Furans

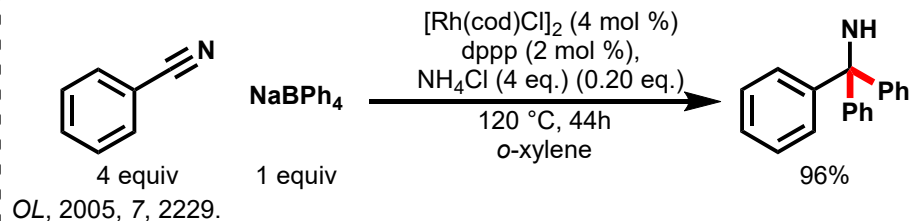
Ph₃N

82%



OL, 2008, 10, 1851.

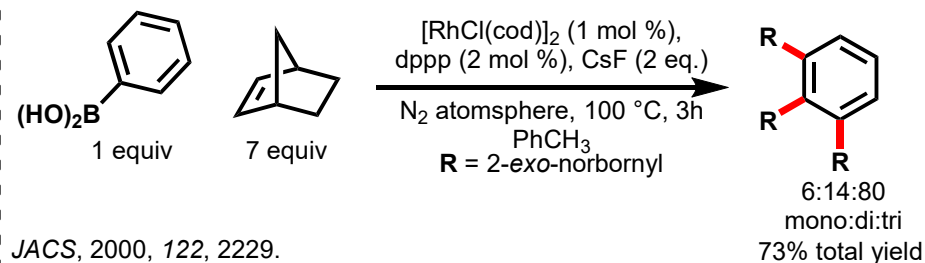
Sequential double o-Arylation and nucleophilic arylation of Benzonitrile



OL, 2005, 7, 2229.

Diphenylimine is intermediate prior to nucleophilic arylation.

Multiple alkylations of arenyl boronic acids with norbornene

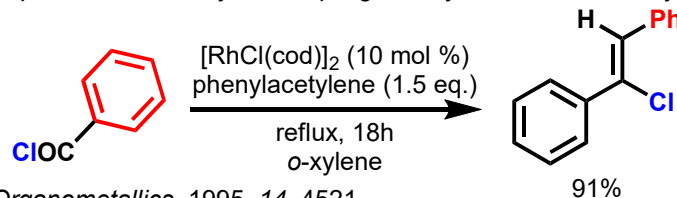


JACS, 2000, 122, 2229.

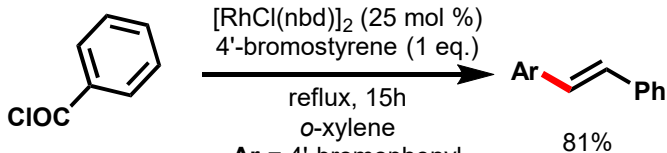
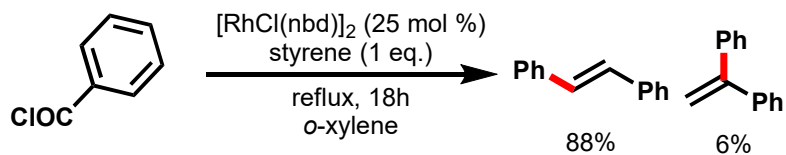
6:14:80
mono:di:tri
73% total yield

Heck-type coupling of aroyl chlorides and olefins

Miura's previous Rh-catalyzed coupling of aroyl chlorides with alkynes:



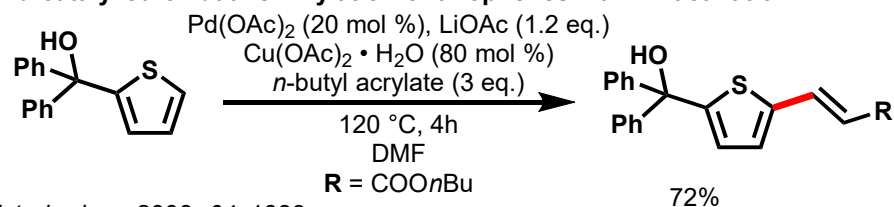
Organometallics, 1995, 14, 4521.
JOC, 1996, 20, 6941.



ACIE, 2003, 42, 4672. Ar = 4'-bromophenyl

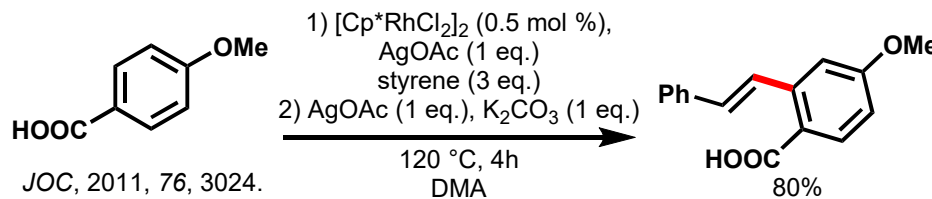
Directed C(sp²)-H *ortho*-alkenylation

Pd-catalyzed oxidative vinylation of thiophenes via C-C activation in DMF



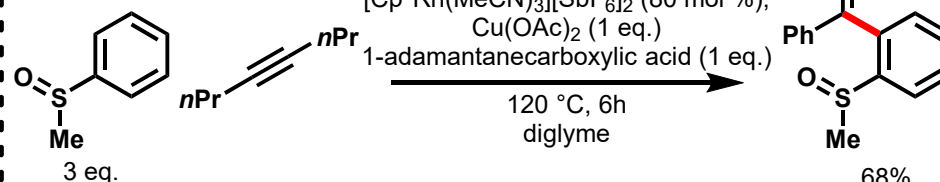
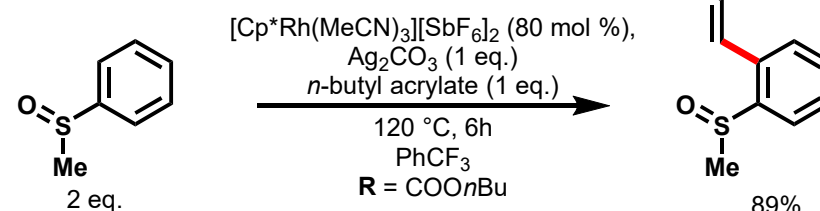
Tetrahedron, 2008, 64, 1889.

Carboxylic acid-directed



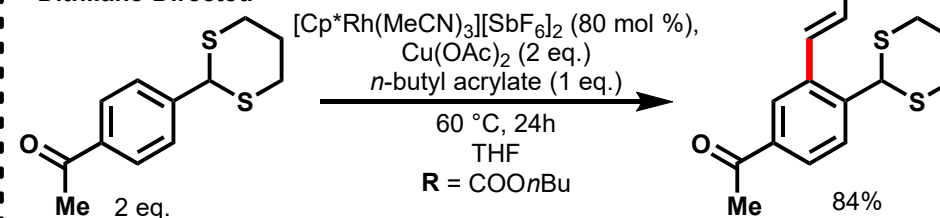
JOC, 2011, 76, 3024.

Sulfoxide-directed



OL, 2014, 16, 1188.

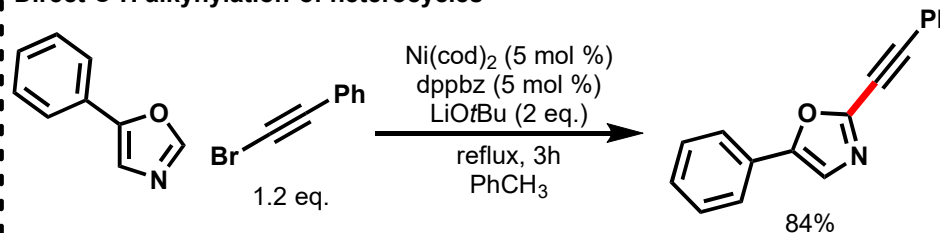
Dithiane-Directed



OL, 2015, 17, 704.

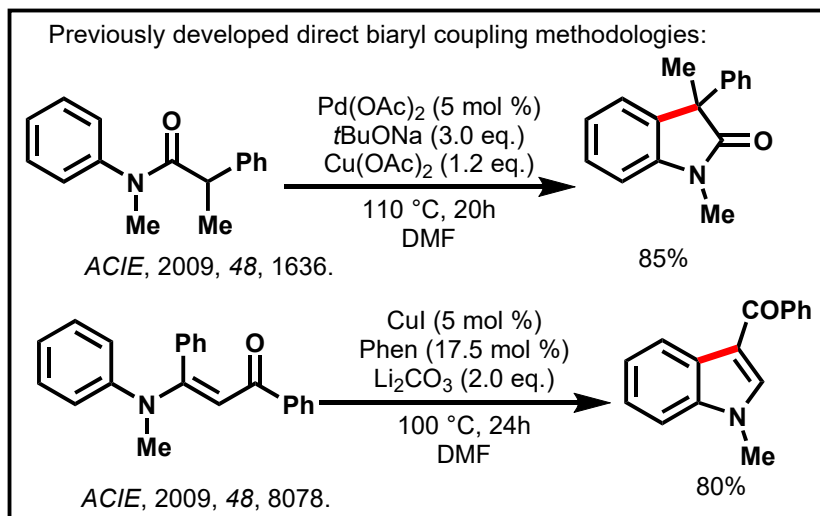
For additional directed C(sp²)-H *ortho*-alkenylation examples, see:
JOC, 2013, 78, 7216; *OL*, 2017, 19, 1800.; *JOC*, 2009, 74, 7094.

Direct C-H alkylation of heterocycles

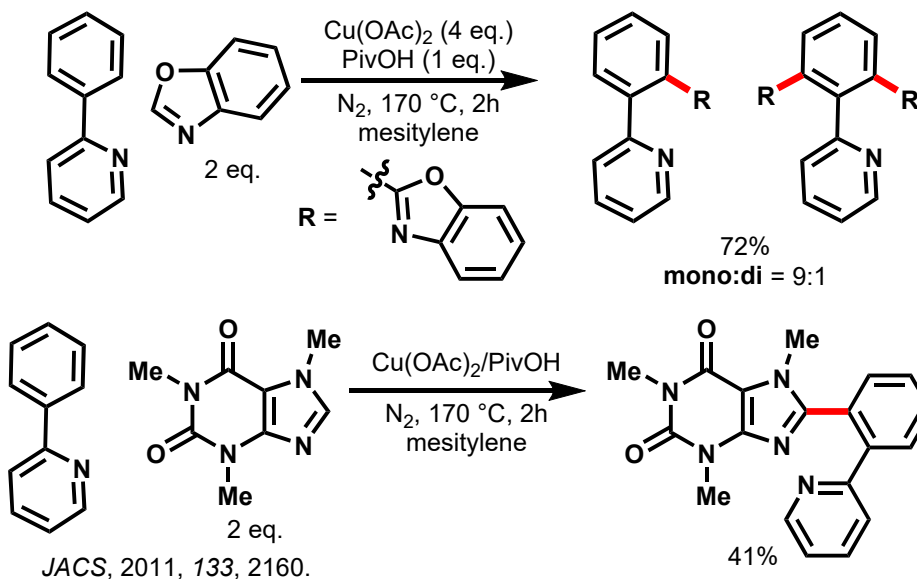


OL, 2009, 11, 4156.

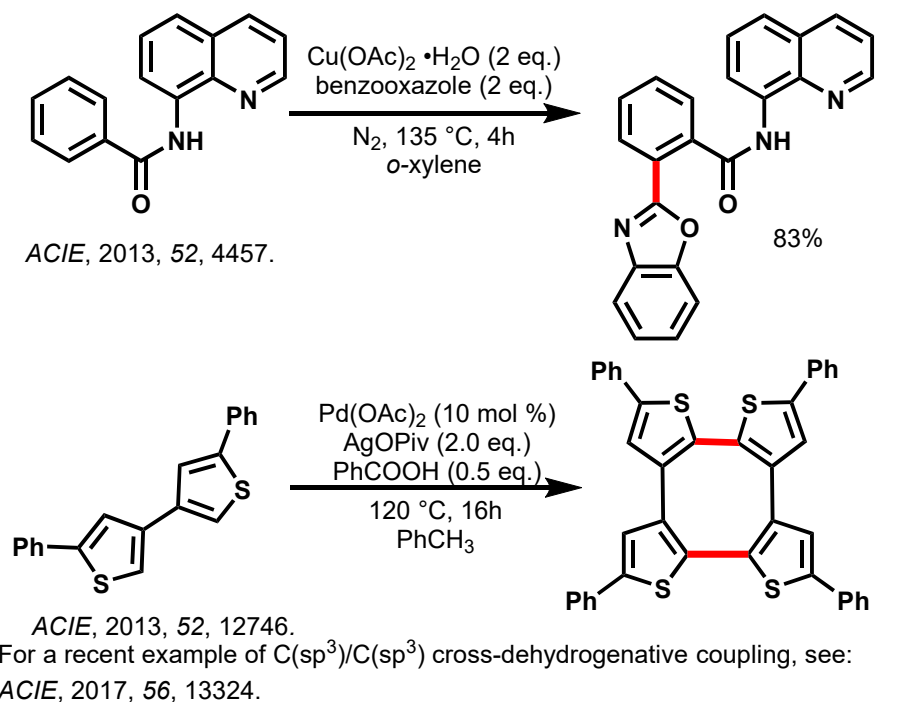
Directed oxidative dehydrogenative cross-coupling of arenes



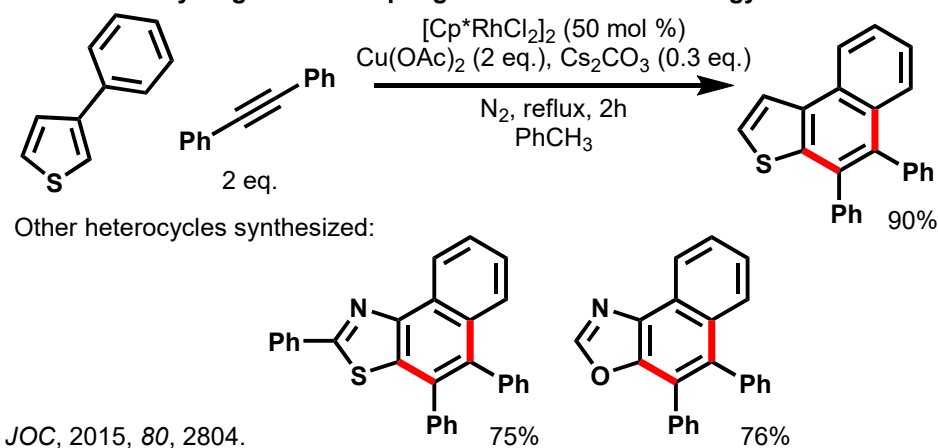
2-Phenylpyridine coupling with heteroarenes

See *ACIE*, 2009, 48, 3296 for previous direct arylation of caffeine with Ar-Br.

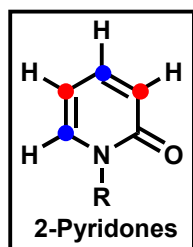
8-aminoquinoline as directing group for heteroarene coupling



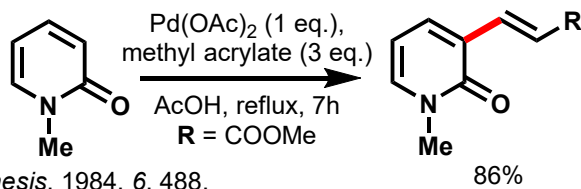
Oxidative dehydrogenative coupling as an annulative strategy



Site-selective C-H functionalization of 2-Pyridones

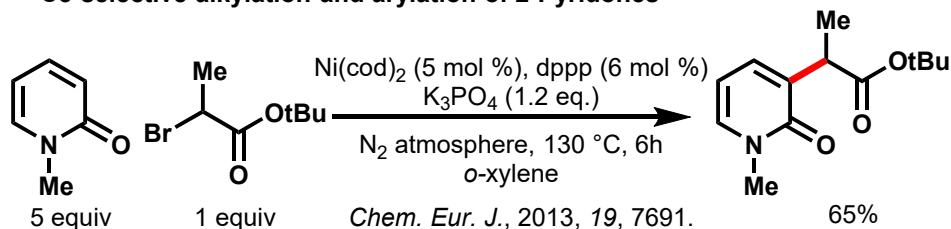


- Electronically biased to react at **C3/C5 with electrophiles**
and **C4/C6 with nucleophiles**

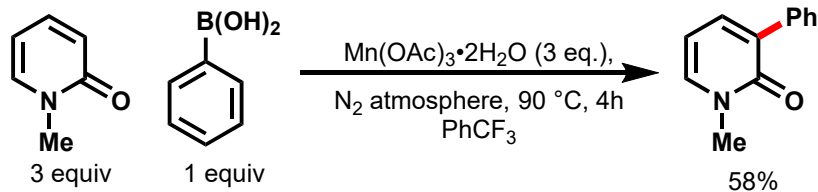
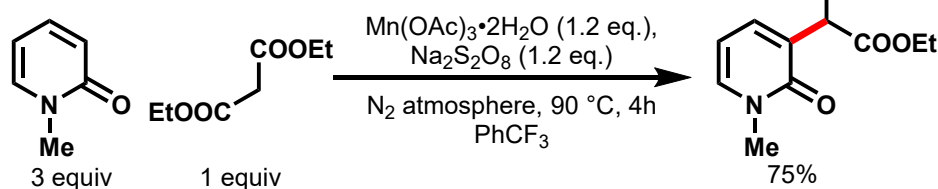


Synthesis, 1984, 6, 488.

C3-selective alkylation and arylation of 2-Pyridones



Chem. Eur. J., 2013, 19, 7691.

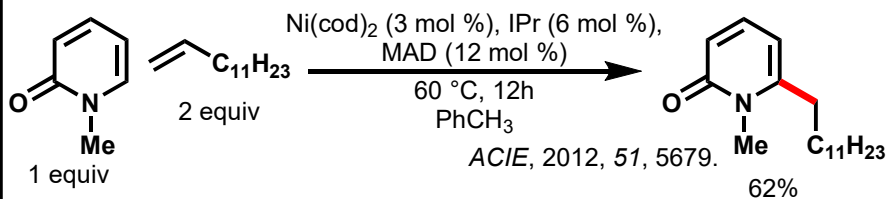


Proposed radical addition reaction: Addition of 2 equiv TEMPO inhibits malonate coupling and decreases yield of arylation to 17%

JOC, 2014, 79, 1377.

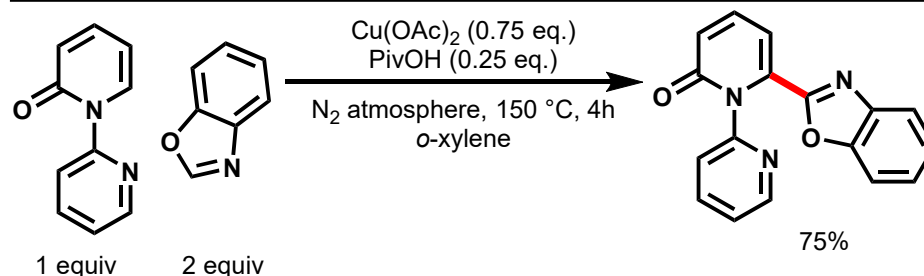
C6-Selective heteroarylation of 2-Pyridones and 4-Pyridones

Previous C6-selective intermolecular alkylation of 2-Pyridones

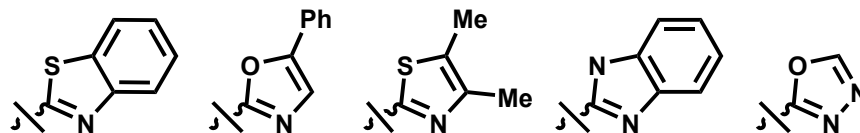


ACIE, 2012, 51, 5679.

For intramolecular alkylation and alkenylation, see: *JACS*, 2009, 131, 15996.



Other coupling partners include:

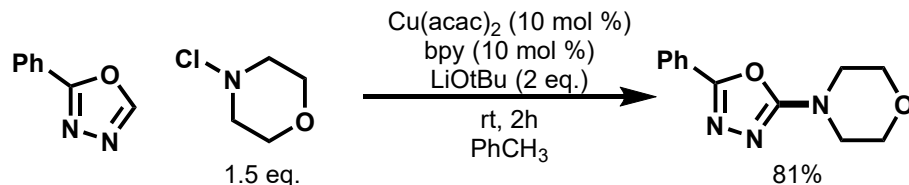


Catalytic conditions:

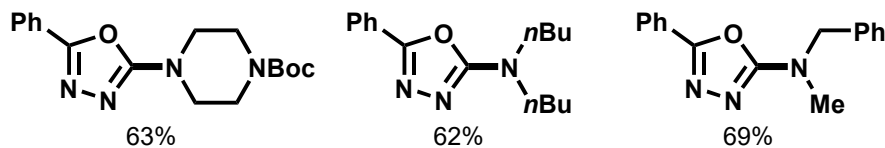


1 equiv 2 equiv
ACIE, 2014, 53, 10784.

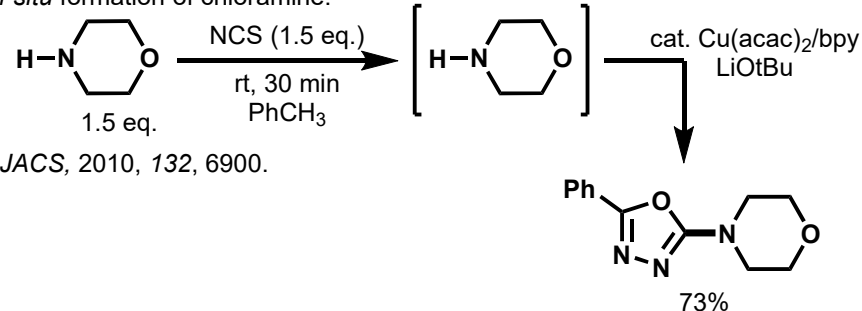
Installation of heteroatoms via directed C-H functionalization Chloramine as a new reagent for C-H amination



Other chloramine partners can be used:

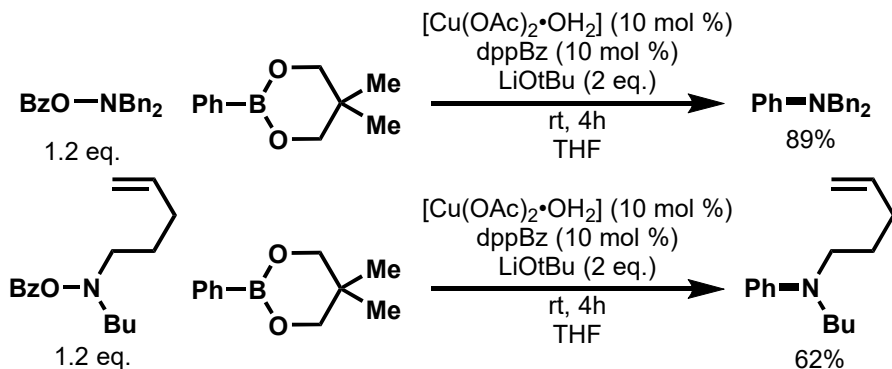


In-situ formation of chloramine:



JACS, 2010, 132, 6900.

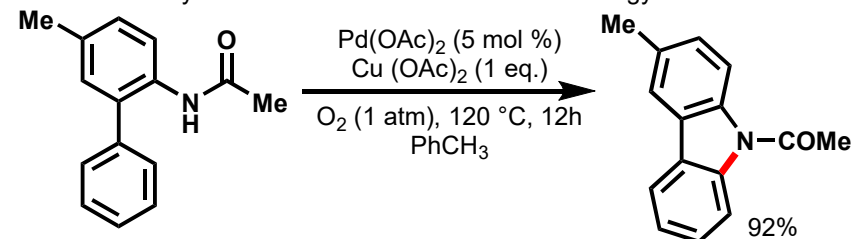
Cu-catalyzed Chan-Lam-type amination of arylboronates



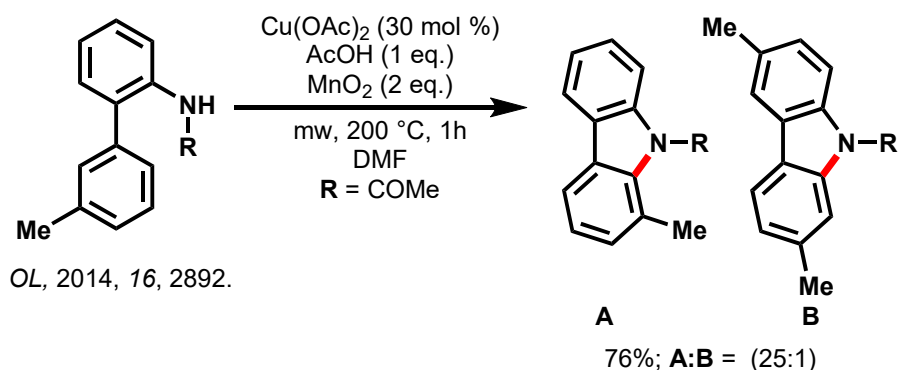
AICE, 2012, 51, 3642.

Piconalimide-directed C-H amination for the synthesis of carbazoles

Related Cu-catalyzed directed C-H amination methodology:

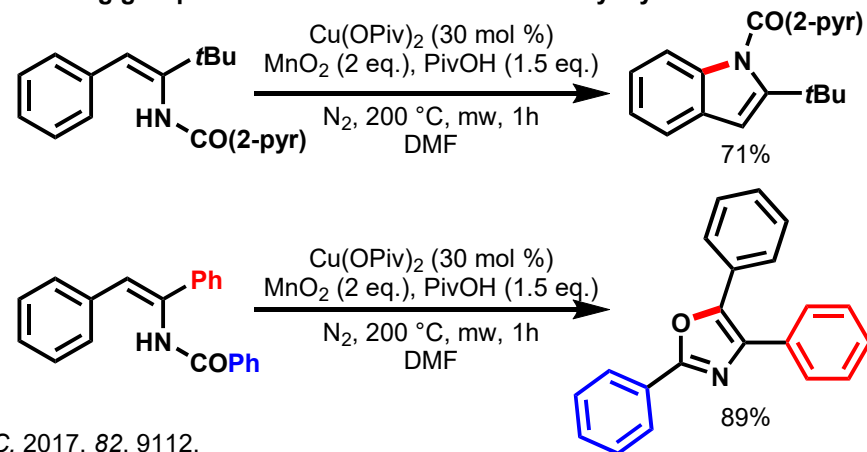


JACS, 2005, 127, 14560.



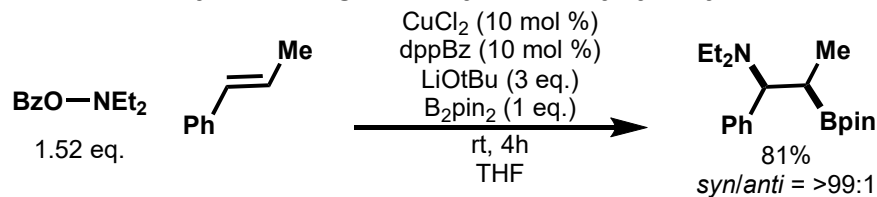
OL, 2014, 16, 2892.

Directing group-controlled C-H amination and alkyoxylation



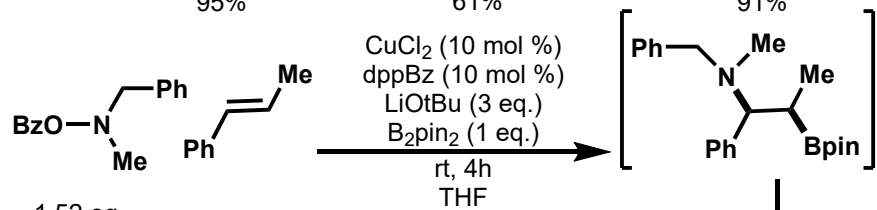
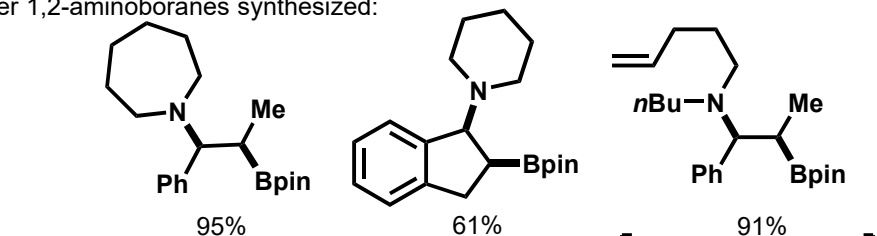
JOC, 2017, 82, 9112.

Aminoboration of styrenes using O-Benzoyl-N,N-dialkylhydroxylamines

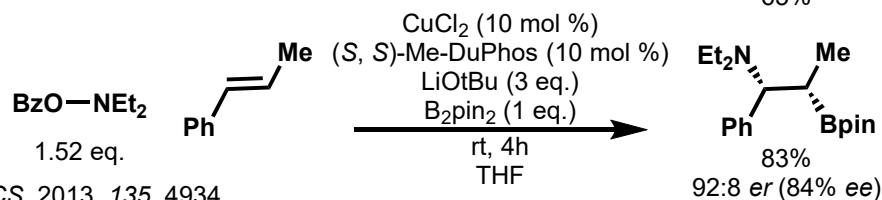
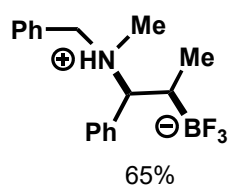


First catalytic aminoboration of C-C unsaturated pi-system.

Other 1,2-aminoboranes synthesized:



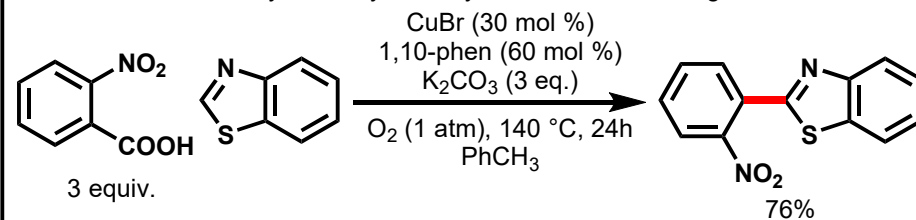
1) KHF₂, THF/H₂O, rt, 2h
2) filtration



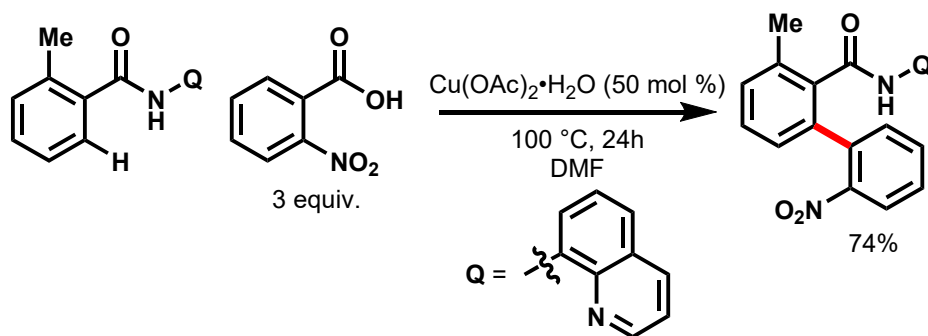
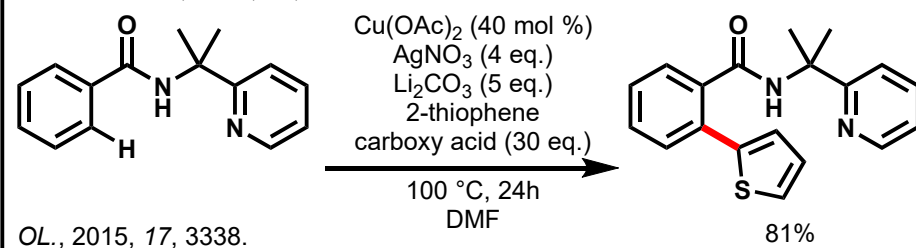
JACS, 2013, 135, 4934.

Decarboxylative coupling and C-H functionalization for biaryl synthesis

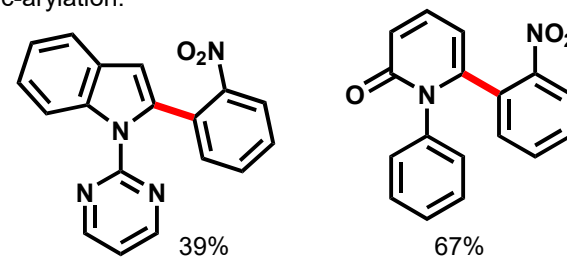
Precedented decarboxylative arylation by directed C-H cleavage:



Chem. Comm., 2016, 52, 1432.



Suitable for heteroaromatic-arylation:



ACIE, 2017, 56, 5353.