Literature Report

Reporter: Ben Rong
Advisor: Prof. Zhao Jing
13/07/20

Prof. Sukbok Chang's Profile

Education:

B.S. : Korea University

Ph.D. : Harvard University
(Advisor: Prof. Eric. N. Jacobsen)

Postdoc. : California Institute of Technology
(Advisor: Prof. Robert H. Grubbs)

Prof. Sukbok Chang, Korea Advanced Institute Science and Technology (KAIST)

Research Interests:

Catalytic C-H bond Activation for Direct C-C, C-O and C-N bond Formation

Rhodium-Catalyzed Intermolecular Amidation of Arenes with Sulfonyl Azides

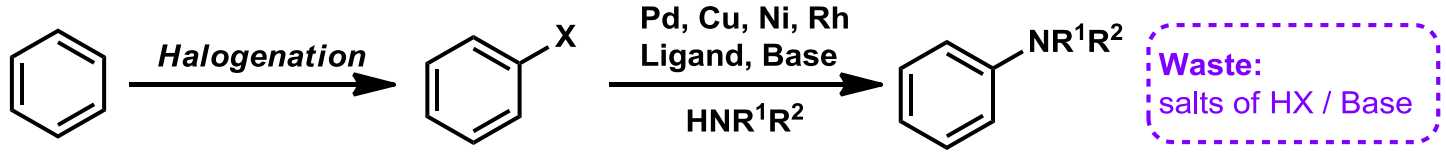
Ji Young Kim,† Sae Hume Park,† Jaeyune Ryu, Seung Hwan Cho, Seok Hwan Kim, and Sukbok Chang*

J. Am. Chem. Soc. **2012**, *134*, 9110 – 9113

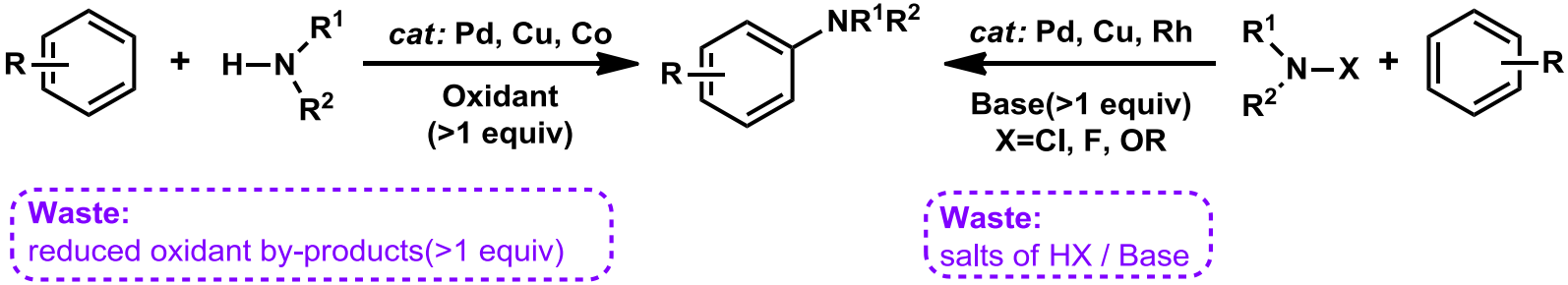
Introduction

C–N Bond Formation Routes to Aryl Amine

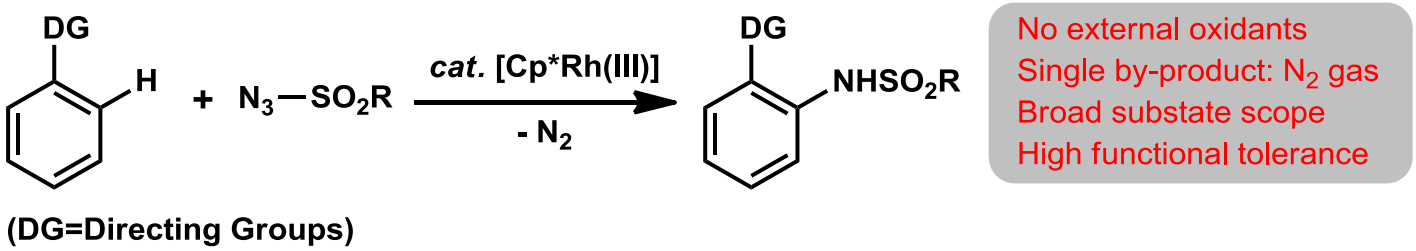
a) *Metal-mediated N-arylation coupling*



b) *Direct C-N bond formation*

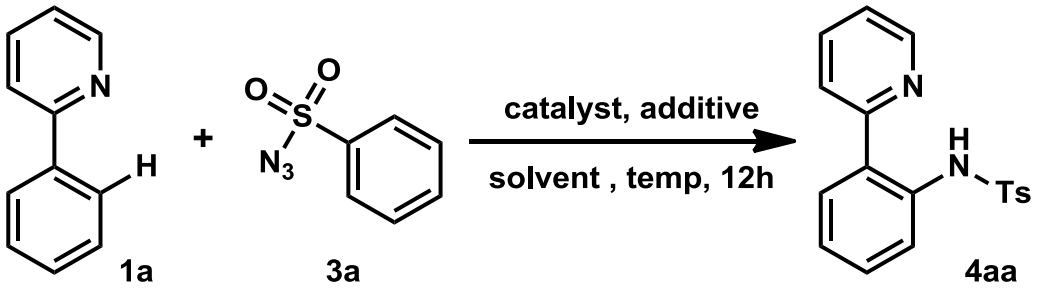


c) This work: *Direct C-H amidation with sulfonyl azides*



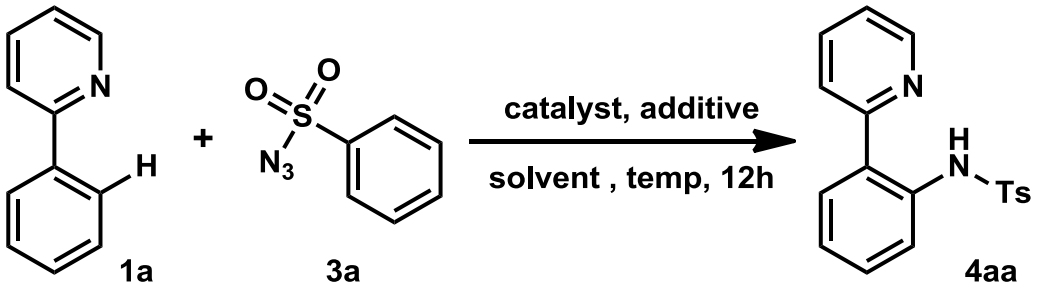
No external oxidants
Single by-product: N_2 gas
Broad substate scope
High functional tolerance

Condition Optimization



entry	catalyst system (mol %)	solvent	temp (°C)	yield (%)[b]
1	$Rh_2(O_2CCF_3)_4$ (4)	toluene	110	11
2	$[Rh(cod)Cl]_2$ (4)	toluene	110	10
3	$[Rh(cod)Cl]_2$ (4)/$AgSbF_6$ (8)	toluene	110	20
4	$[RhCp^*Cl_2]_2$ (4)	toluene	110	10
5	$[RhCp^*Cl_2]_2$ (4)/$AgSbF_6$ (16)	toluene	110	77
6	$[RhCp^*Cl_2]_2$ (4)/$AgSbF_6$ (16)	toluene	80	59
7	$[RhCp^*Cl_2]_2$ (4)/$AgSbF_6$ (16)	1,2-DCE	80	96
8	$[RhCp^*Cl_2]_2$ (4)/$AgSbF_6$ (16)	*t*-amylOH	80	45
9	$[RhCp^*Cl_2]_2$ (4)/$AgBF_4$ (16)	1,2-DCE	80	54
10	$[RhCp^*Cl_2]_2$ (4)/KPF_6 (16)	1,2-DCE	80	<1

Condition Optimization

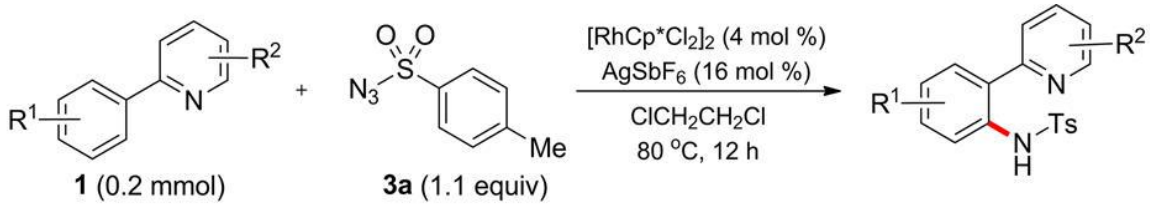


11	$[RhCp^*Cl_2]_2$ (2.5)/$AgSbF_6$ (10)	1,2-DCE	80	84
12	$[RhCp^*Cl_2]_2$ (4)/$AgSbF_6$ (16)	1,2-DCE	50	27
13	$[RhCp^*(MeCN)_3][SbF_6]_2$ (8)	1,2-DCE	80	64
14	$[Ru(p\text{-cymene})Cl_2]_2$ (4)/ KPF_6 (16)	1,2-DCE	80	n.r.
15	$Pd(OAc)_2$ (8)/$PhI(OAc)_2$ (110)	1,2-DCE	80	n.r.

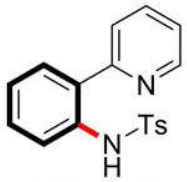
[a] **1a** (0.2 mmol), **3a** (1.1 equiv), catalyst, additive, and solvent (0.5 mL) at the indicated temperature for 12 h. [b] NMR yield.

Substrate Scope

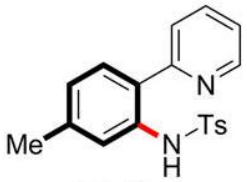
2-Phenylpyridine Derivatives



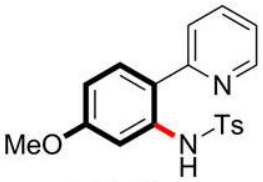
1 (0.2 mmol) **3a** (1.1 equiv)



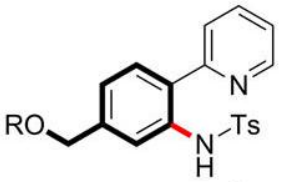
94% (**4aa**)



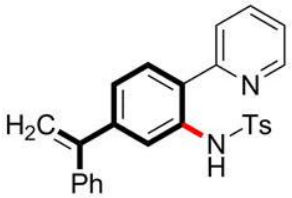
86% (**4ba**)



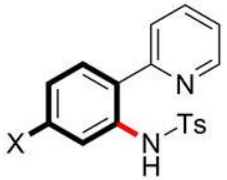
84% (**4ca**)



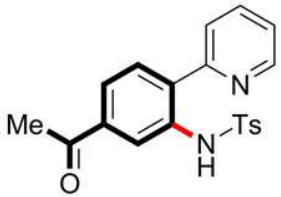
R: H, 73% (**4da**)[b]
Ac, 67% (**4ea**)
Bn, 70% (**4fa**)



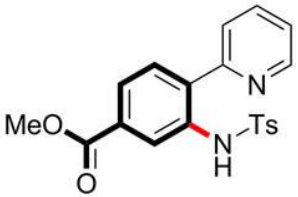
82% (**4ga**)



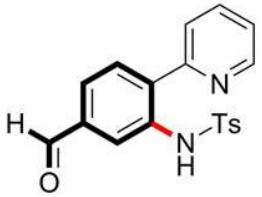
X: F, 77% (**4ha**)
Cl, 78% (**4ia**)



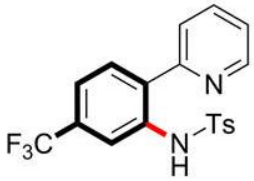
84% (**4ja**)



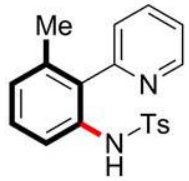
93% (**4ka**)



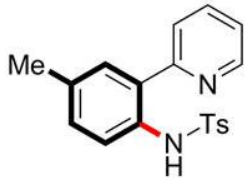
91% (**4la**)



80% (**4ma**)



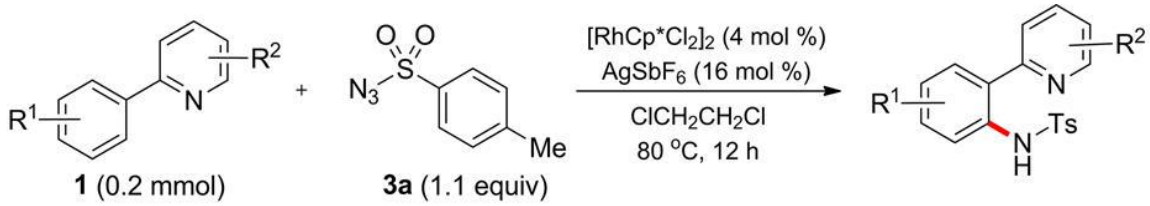
45% (**4na**)[b]



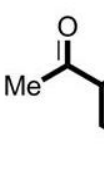
75% (**4oa**)

Substrate Scope

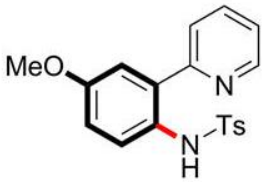
2-Phenylpyridine Derivatives



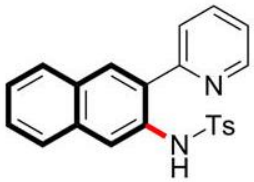
1 (0.2 mmol) **3a** (1.1 equiv)



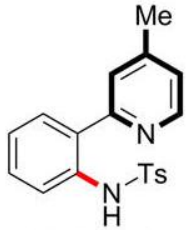
62% (**4pa**)



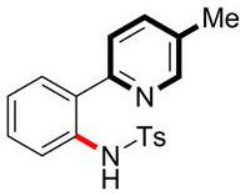
50% (**4qa**:**4qa'** = 7.3:1)[c]



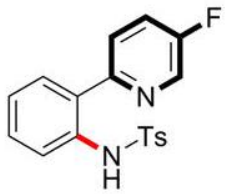
75% (**4ra**)



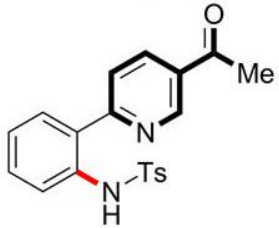
70% (**4sa**)



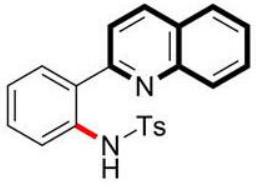
71% (**4ta**)



85% (**4ua**)



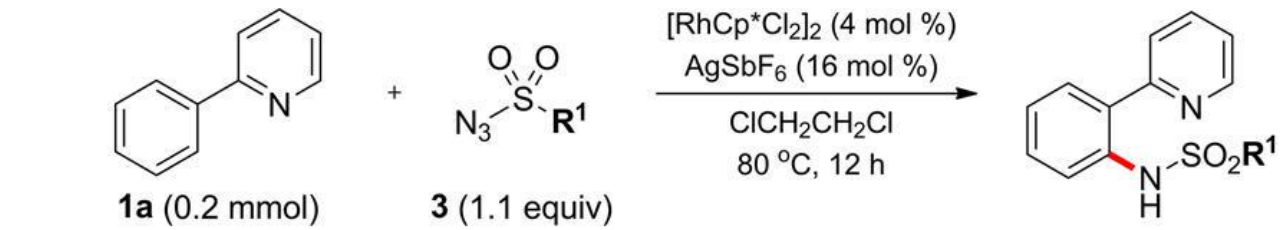
74% (**4va**)

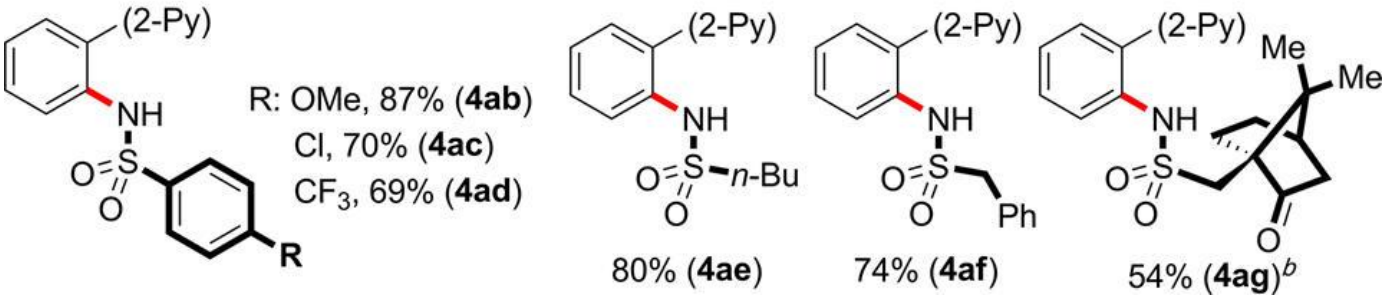


63% (**4wa**)[b]

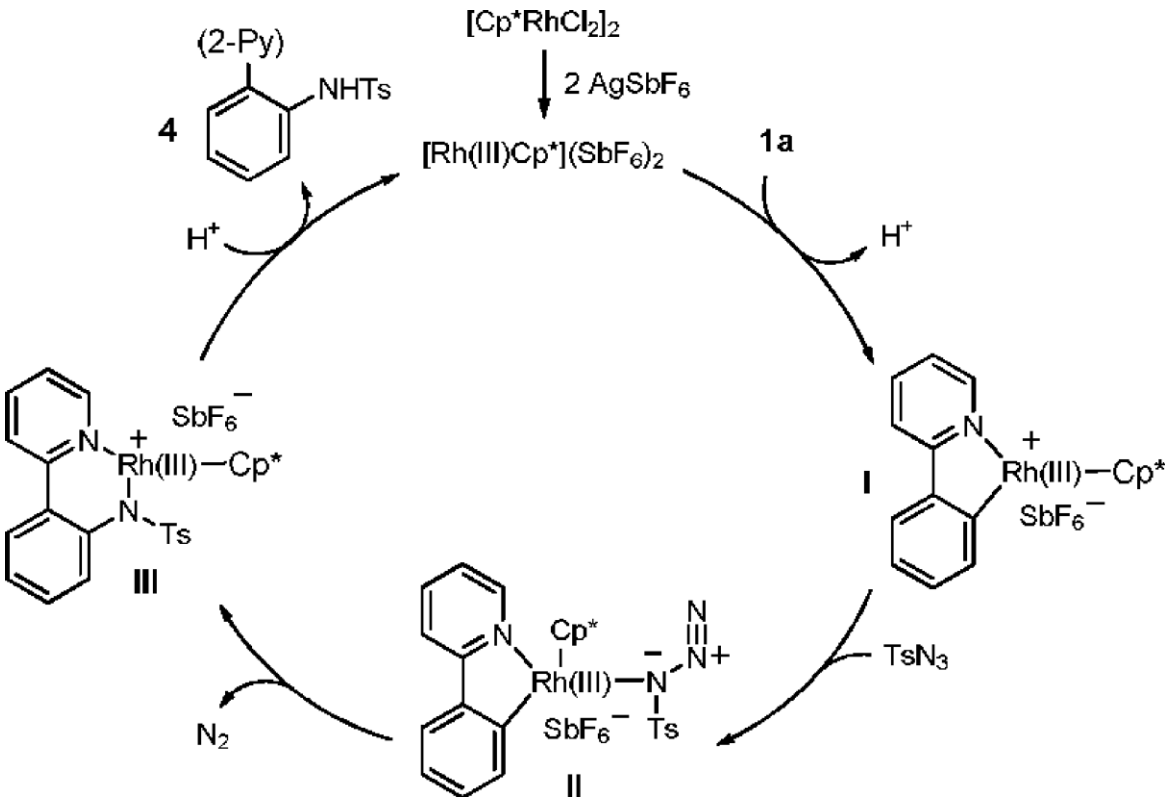
Substrate Scope

Sulfonyl Azides





Proposed Reaction Pathway



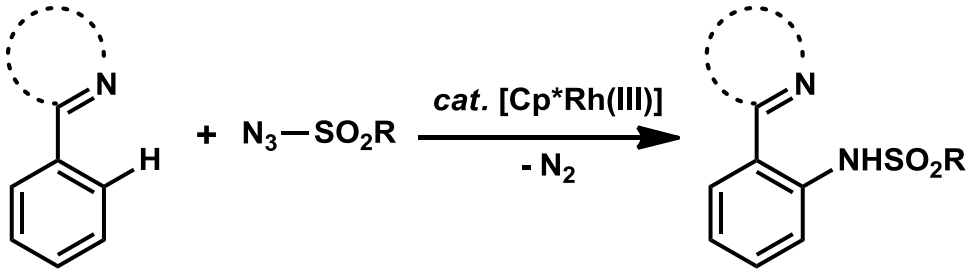
Rhodium-Catalyzed Direct C-H Amination of Benzamides with Aryl Azides

Jaeyune Ryu, Kwangmin Shin, Sae Hume Park, Ji Young Kim, and Sukbok Chang*

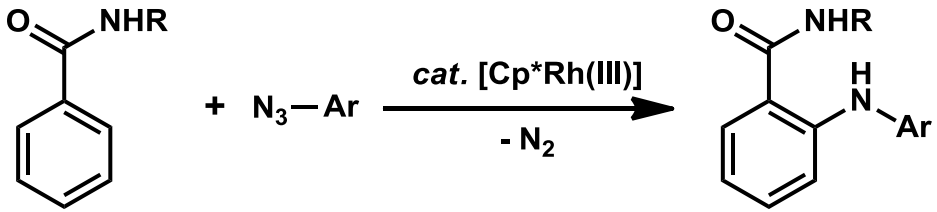
Angew. Chem. Int. Ed. **2012** , *51* , 9904 –9908

Introduction

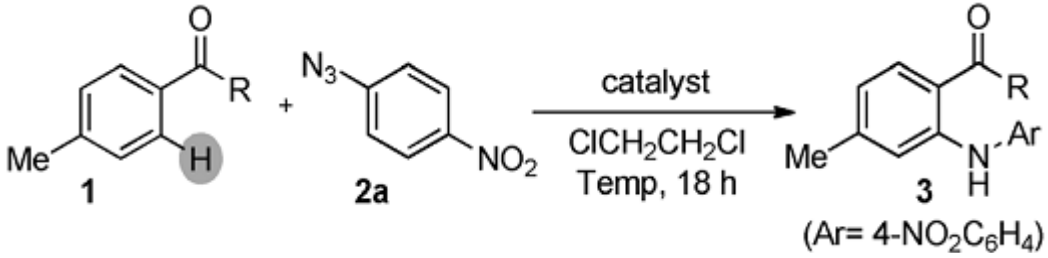
Previous work: *Direct C-H amidation with sulfonyl azides*



This work: *Direct C-H amidation with aryl azides*



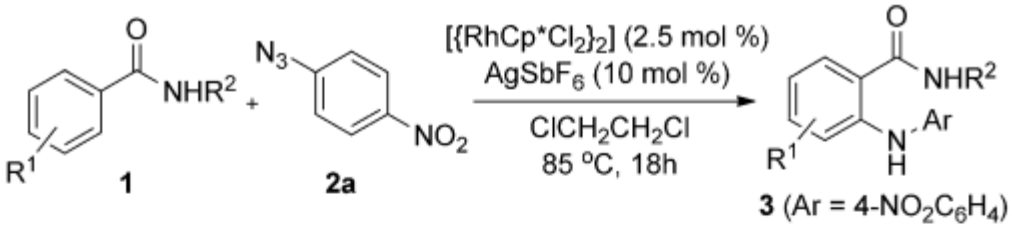
Optimization of Directing Group

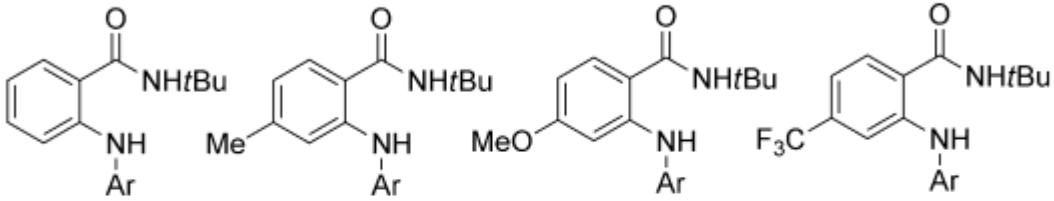


Entry	R	Catalyst (mol%)	*T* [°C]	Yield [%][b]
1	NH_2	[{RhCp*Cl_2}$_2$] (4)/$AgSbF_6$ (16)	85	< 5
2	NMe_2	[{RhCp*Cl_2}$_2$] (4)/$AgSbF_6$ (16)	85	< 5
3	NHOPiv	[{RhCp*Cl_2}$_2$] (4)/$AgSbF_6$ (16)	85	< 5
4	NHMe	[{RhCp*Cl_2}$_2$] (4)/$AgSbF_6$ (16)	85	40
5	NH*t*Bu	[{RhCp*Cl_2}$_2$] (2.5)/$AgSbF_6$ (10)	85	85(80)
6	NH*t*Bu	[{RhCp*Cl_2}$_2$] (2.5)/$AgSbF_6$ (10)	70	73
7	NH*t*Bu	[{RhCp*Cl_2}$_2$] (2.5)/$AgSbF_6$ (10)	50	49
8	NH*t*Bu	[$Rh_2(O_2CCF_3)_4$] (4)	85	< 5
9[c]	NH*t*Bu	[{Ru(*p*-cymene)Cl_2}$_2$] (4)	85	< 5
10	Me	[{RhCp*Cl_2}$_2$] (4)/$AgSbF_6$ (16)	85	< 1
11	OMe	[{RhCp*Cl_2}$_2$] (4)/$AgSbF_6$ (16)	85	< 1
12	OH	[{RhCp*Cl_2}$_2$] (4)/$AgSbF_6$ (16)	85	< 1

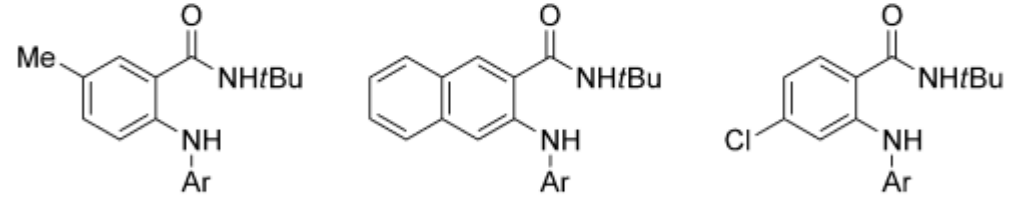
Substrate Scope

Aromatic amides

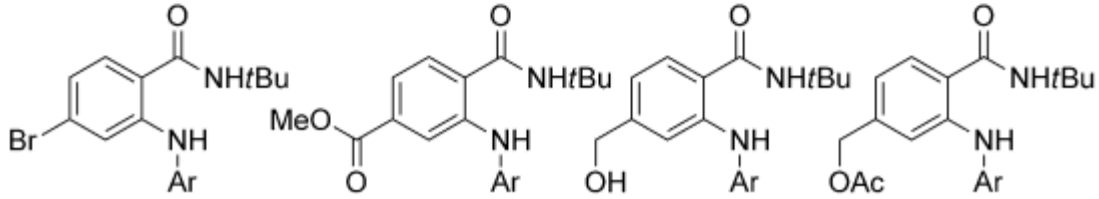




83% (70%) **3a** 80% (67%) **3b** 97% (75%) **3c** 90% (80%) **3d**



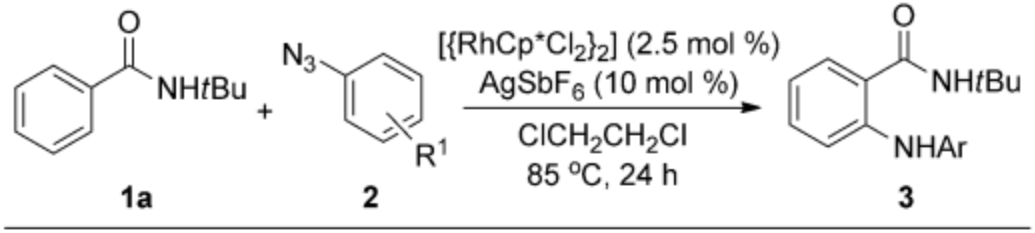
70% (60%) **3e** 72% (55%) **3f** 93% (81%) **3g**



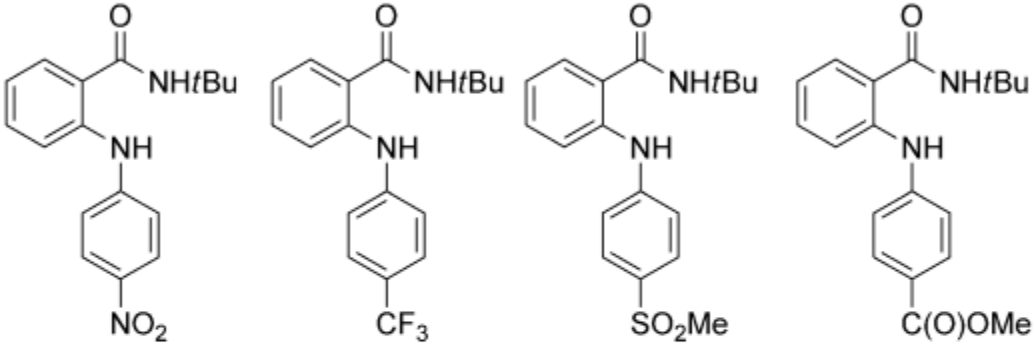
86% (85%) **3h** 85% (70%) **3i** 65%[a] (61%) **3j** 90% (78%) **3k**

Substrate Scope

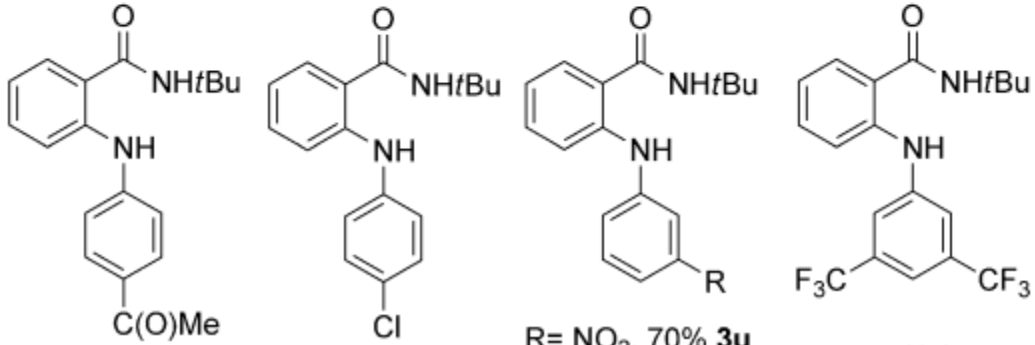
Aryl azides



1a **2** **3**



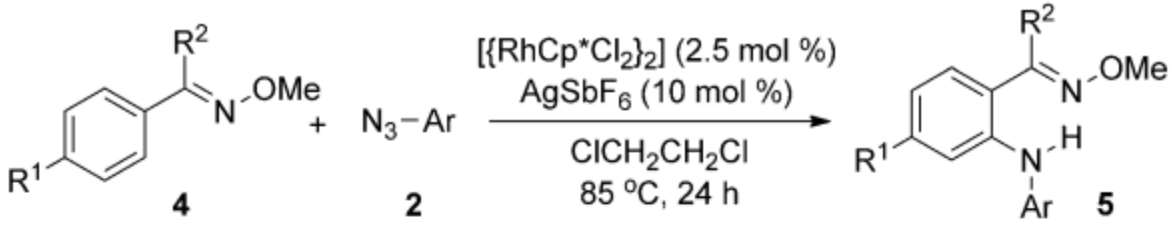
83% **3a** 68% **3p** 77% **3q** 71% **3r**

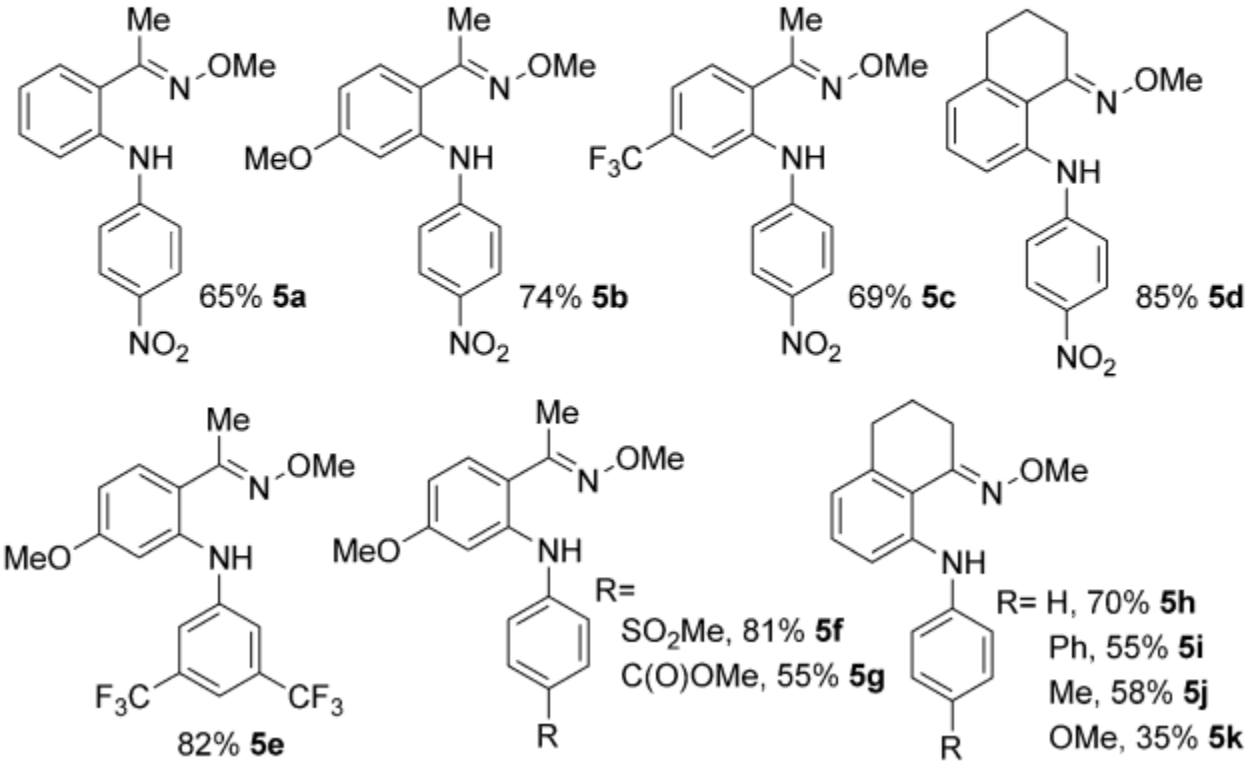


56% **3s** 45%[a] **3t** R= NO_2, 70% **3u**; CF_3, 63% **3v** 94% **3w**

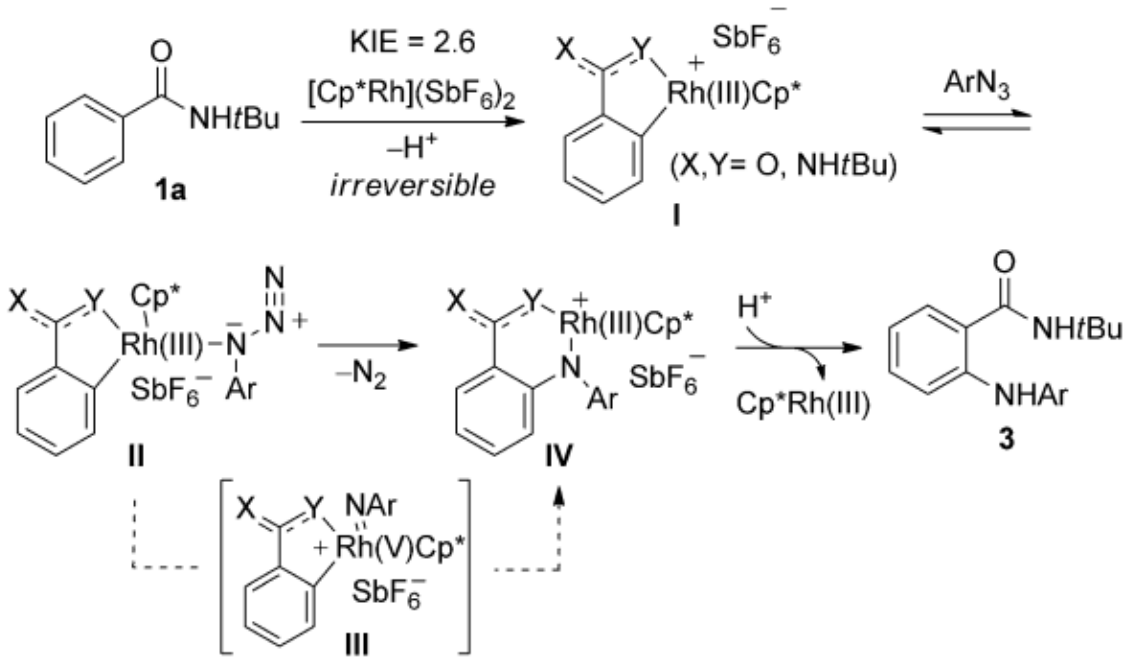
Substrate Scope

Aromatic Ketoximes





Proposed Reaction Pathway



Thank you for your attention!