



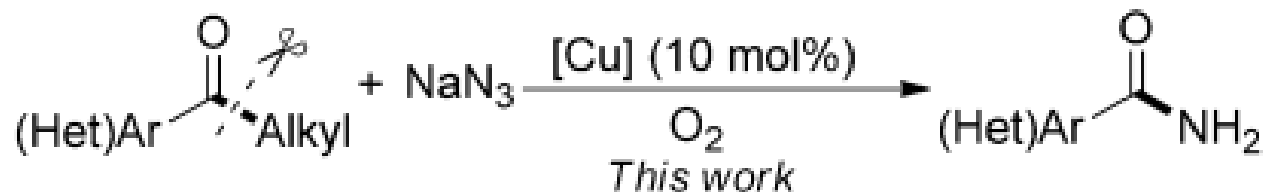
Literature Report

Reporter: Pingping Duan
Supervisor: Prof. Zhao
2014.05.25

 **C–C Bond Cleavage** *Hot Paper*

Copper-Catalyzed Aerobic Oxidative C–C Bond Cleavage for C–N Bond Formation: From Ketones to Amides**

Conghui Tang and Ning Jiao*

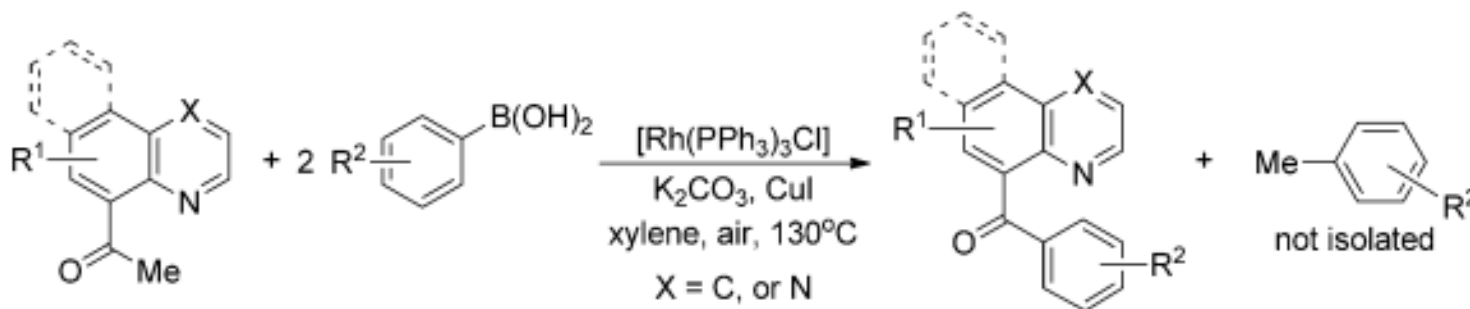


Two Strategies for C-C Cleavage

1. strained skeletons (three- and four-membered rings)

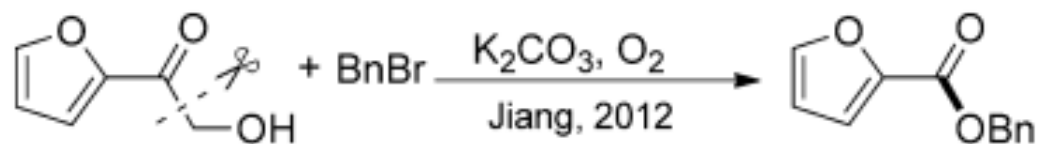


2. chelation assistance

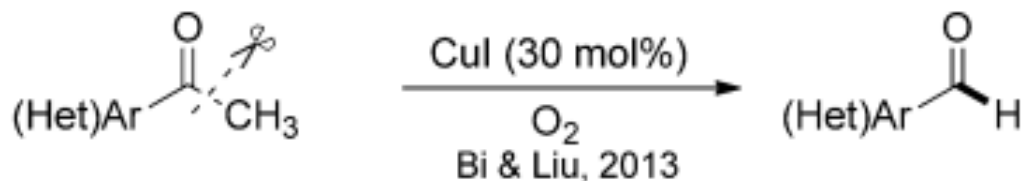


Aerobic Oxidative C-C Single-Bond Cleavage

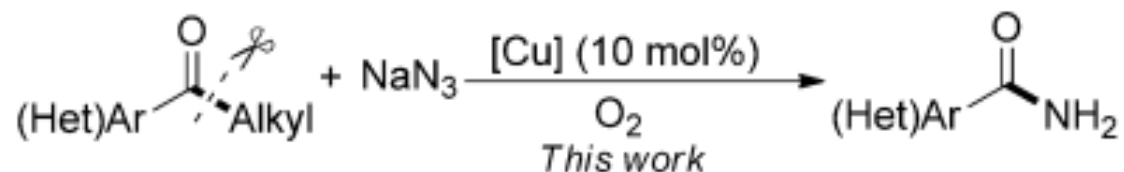
a) C-O bond formation



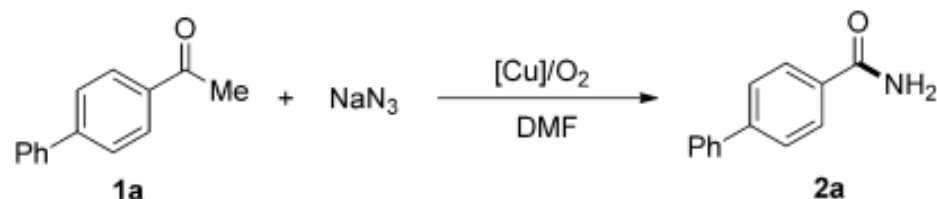
b) C-H bond formation



c) C-N bond formation



Screening of the Reaction Conditions^[a]

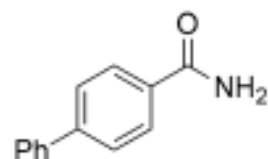
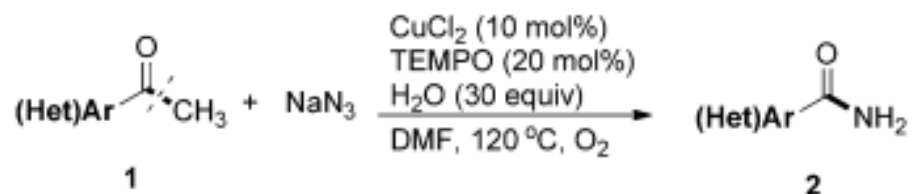


Entry	[Cu] (mol%)	Additive (mol%)	H ₂ O (equiv)	T [°C]	Yield ^[b] [%]
1	CuI (10)	TEMPO (20)	H ₂ O (20)	90	56
2	CuI (10)	4-MeO-TEMPO (20)	H ₂ O (20)	90	42
3	CuI (10)	4-oxo-TEMPO (20)	H ₂ O (20)	90	37
4	CuI (10)	TEMPO (20)	H ₂ O (30)	90	59
5	CuI (10)	TEMPO (20)	H ₂ O (30)	110	70
6	CuCl (10)	TEMPO (20)	H ₂ O (30)	110	79
7	CuBr (10)	TEMPO (20)	H ₂ O (30)	110	79
8	CuBr ₂ (10)	TEMPO (20)	H ₂ O (30)	110	78
9	CuCl ₂ (10)	TEMPO (20)	H ₂ O (30)	110	82
10	CuCl₂ (10)	TEMPO (20)	H₂O (30)	120	84
11 ^[c]	CuCl ₂ (10)	TEMPO (20)	H ₂ O (30)	120	0
12	–	TEMPO (20)	H ₂ O (30)	120	0
13	CuCl ₂ (10)	–	H ₂ O (30)	120	70
14	CuCl ₂ (10)	TEMPO (20)	–	120	47

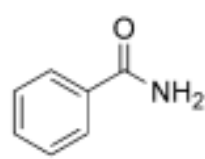
[a] Reaction conditions: **1a** (0.4 mmol), NaN₃ (1.2 mmol), copper precursor (0.04 mmol), DMF (2 mL), under O₂ (1 atm) for 16 h. [b] Yields of isolated products.

[c] The reaction was carried out under argon atmosphere. DMF = *N,N*-dimethylformamide, TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxy.

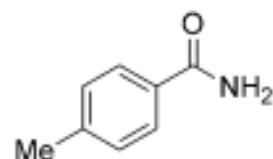
Scope of Substrates



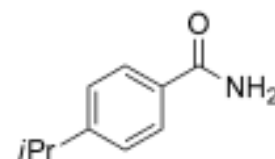
2a 84%



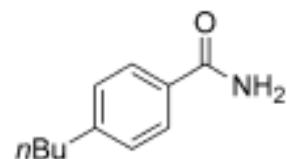
2b 66%



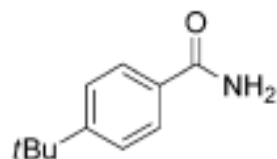
2c 63%



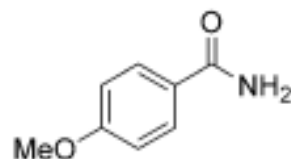
2d 76%



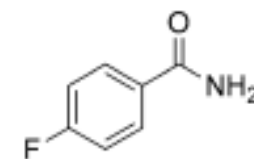
2e 79%



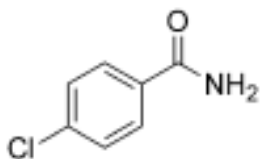
2f 80%



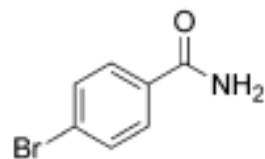
2g 67%



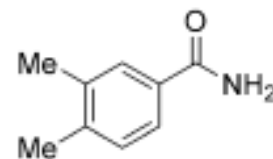
2h 58%



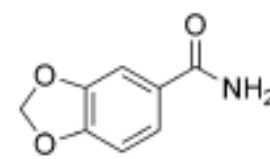
2i 62%



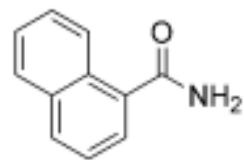
2j 68%



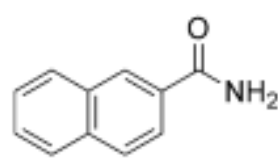
2k 76%



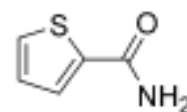
2l 65%



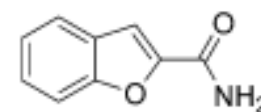
2m 64%



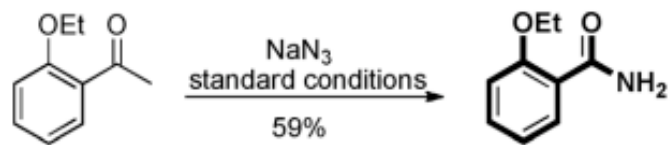
2n 73%



2o 50%



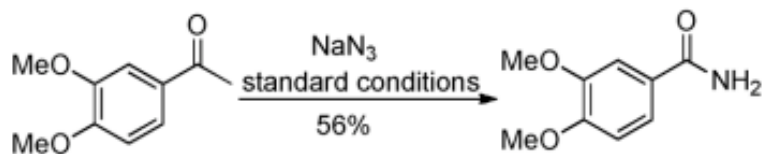
2p 43%



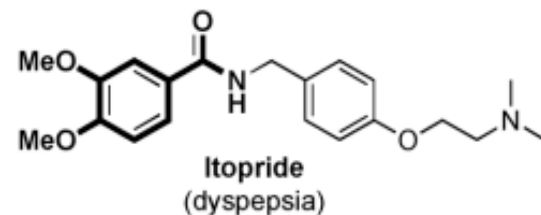
Ethenzamide
(analgesic, anti-inflammatory)

(1)

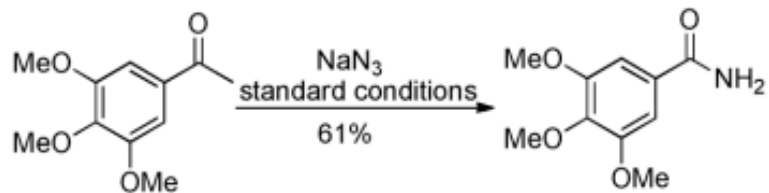
2q



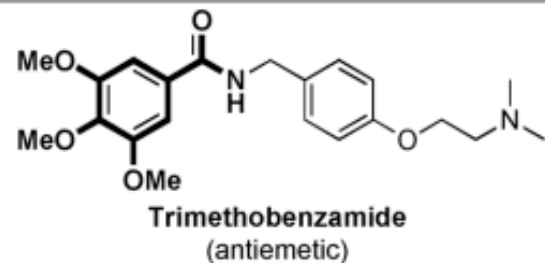
2r



(2)



2s

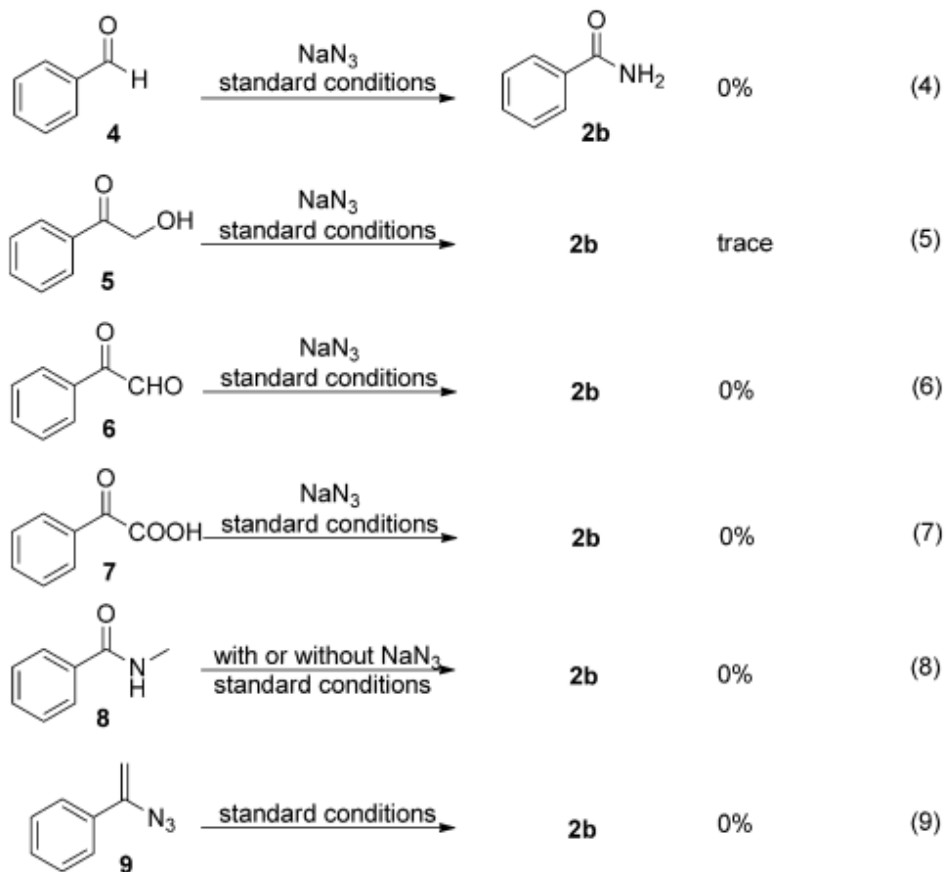


(3)

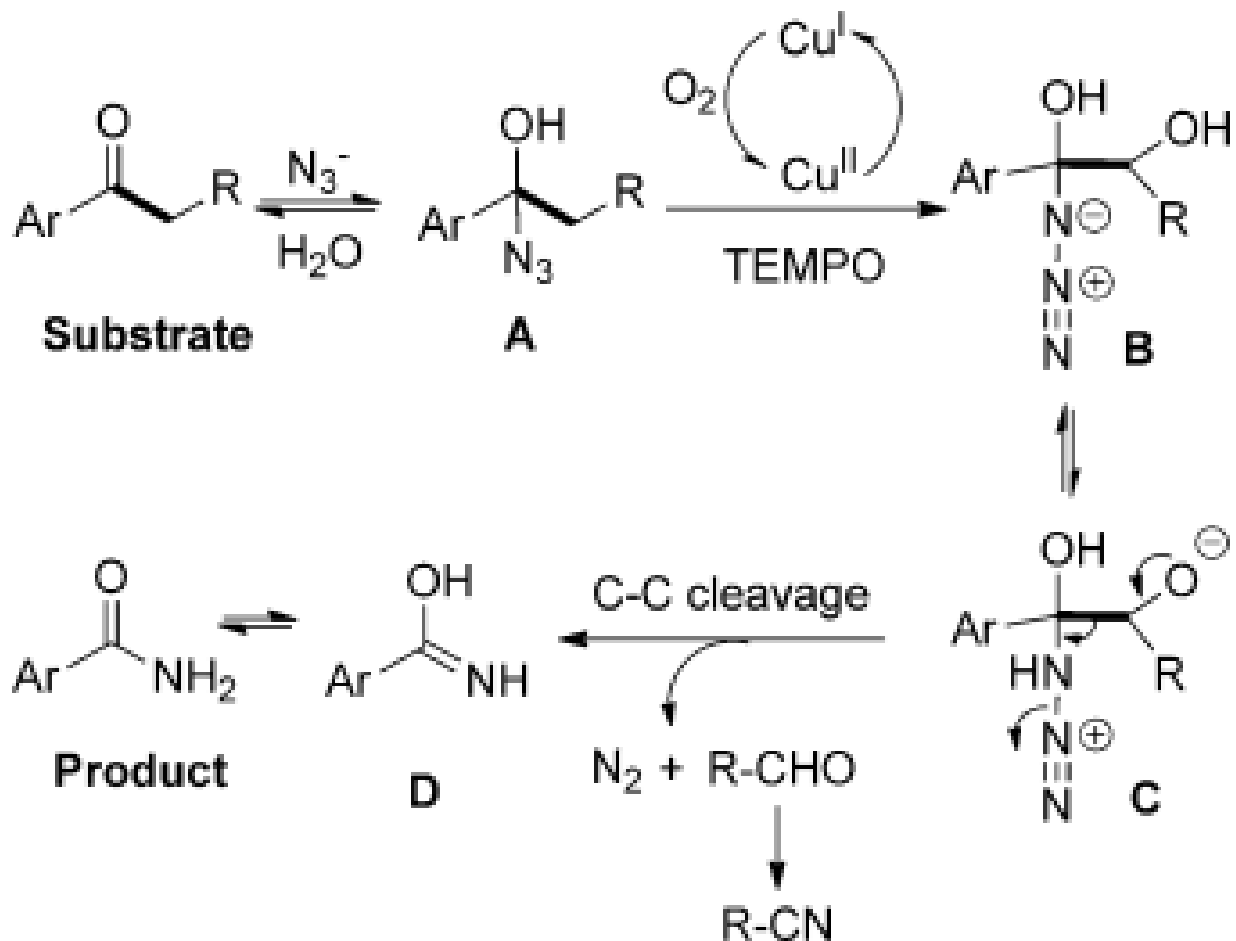


substrate	product	substrate	product
<p>3a</p>	2c, 60%	<p>3b</p>	2g, 40%
<p>3c</p>	2i, 62%	<p>3d</p>	2b, 43%
<p>3e</p>	2b, 59%	<p>3f</p>	2b, 58%

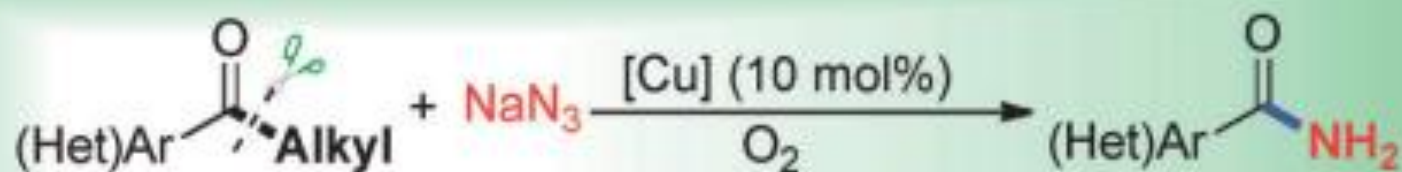
Potential Intermeidates



Proposed Mechanism



Summary



- 1) Cleavage of challenging aryl alkyl ketones
- 2) C-N bond formation through C-C bond cleavage
- 3) Aerobic oxidation



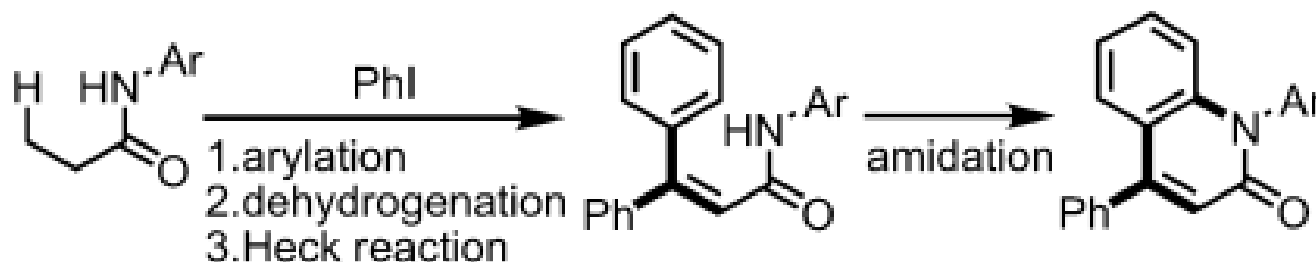
Cascade C-H Activation **Hot Paper**

DOI: 10.1002/anie.201403878

Ligand-Enabled Triple C–H Activation Reactions: One-Pot Synthesis of Diverse 4-Aryl-2-quinolinones from Propionamides**

Youqian Deng, Wei Gong, Jian He, and Jin-Quan Yu*

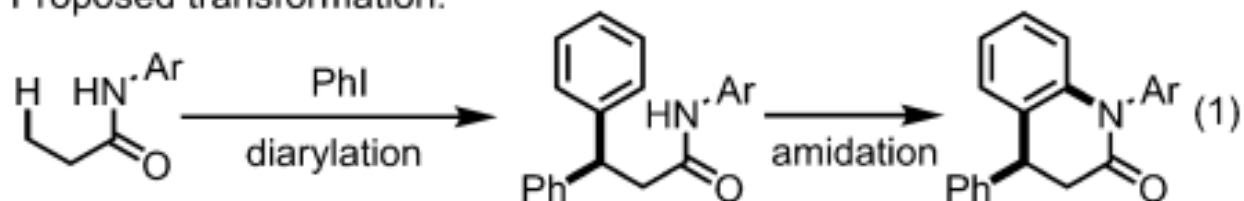
Dedicated to Professor Björn Åkermark on the occasion of his 80th birthday



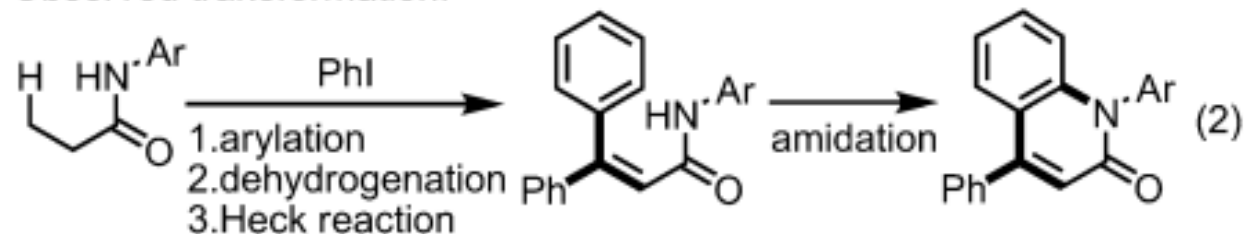
Origin of the Idea



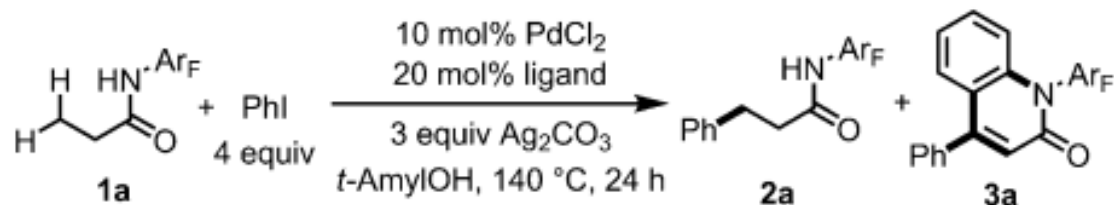
Proposed transformation:



Observed transformation:



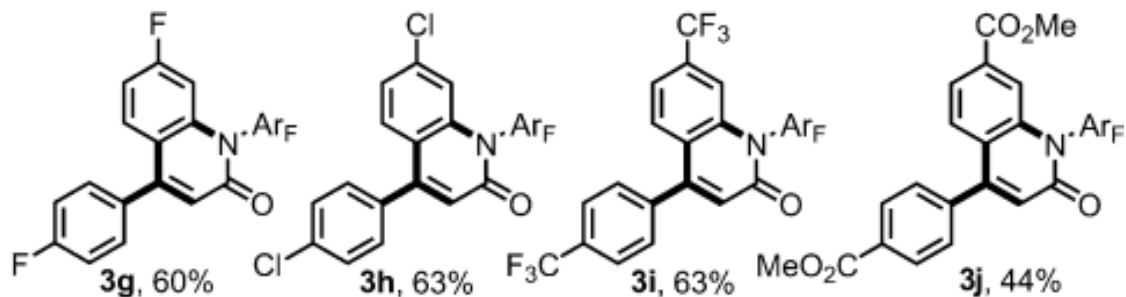
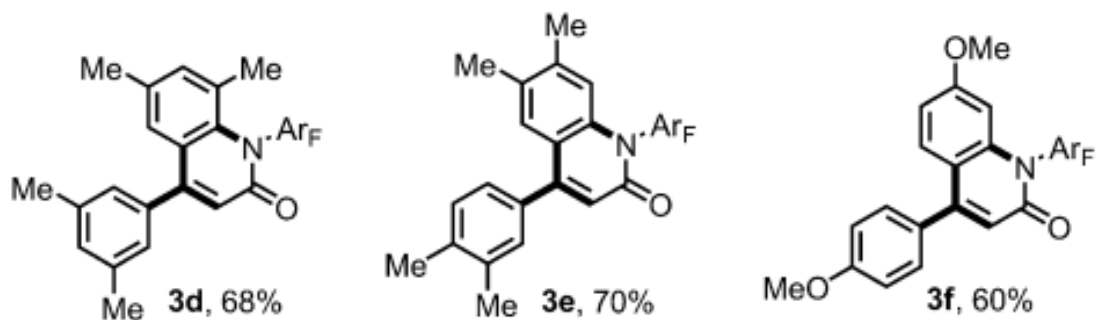
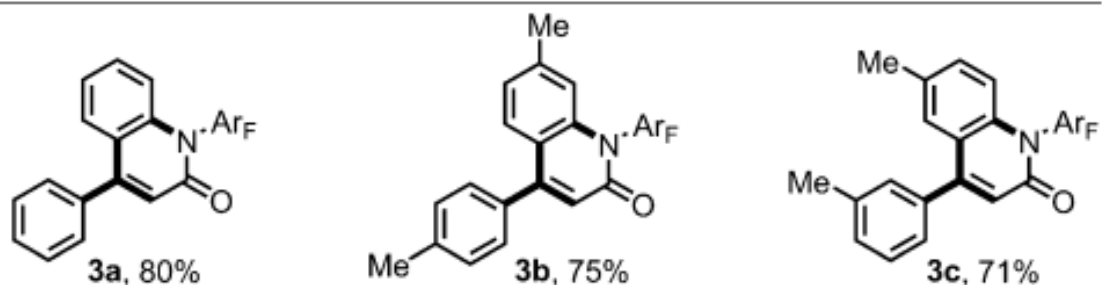
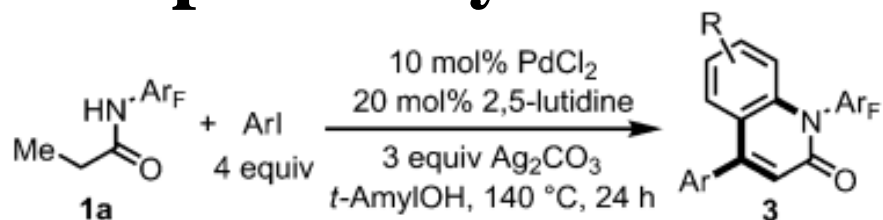
Reaction Discovery and Ligand Screening^[a,b,c]



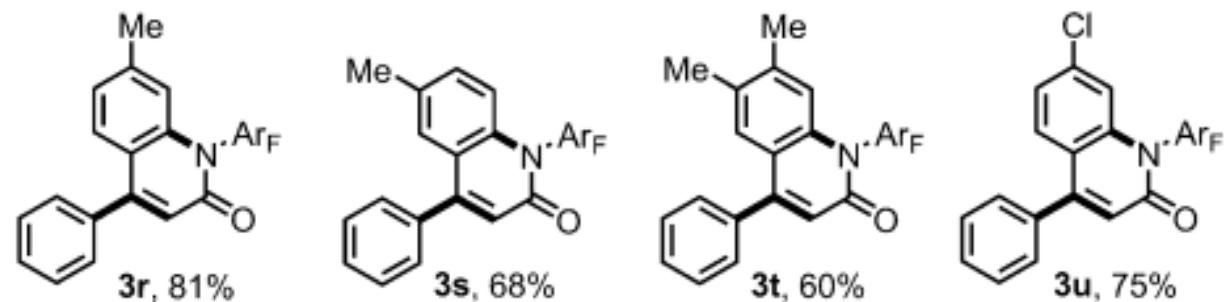
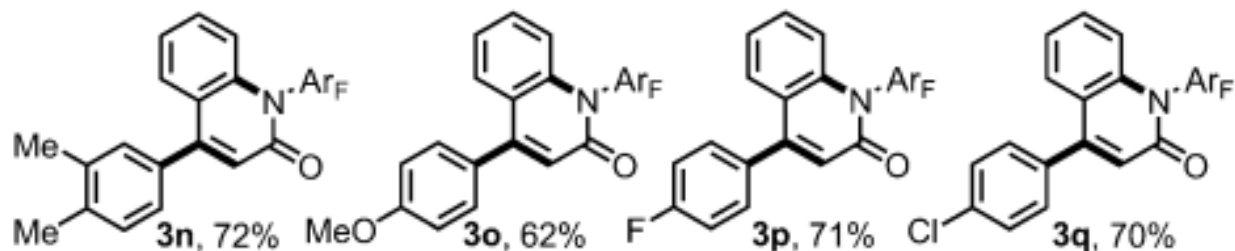
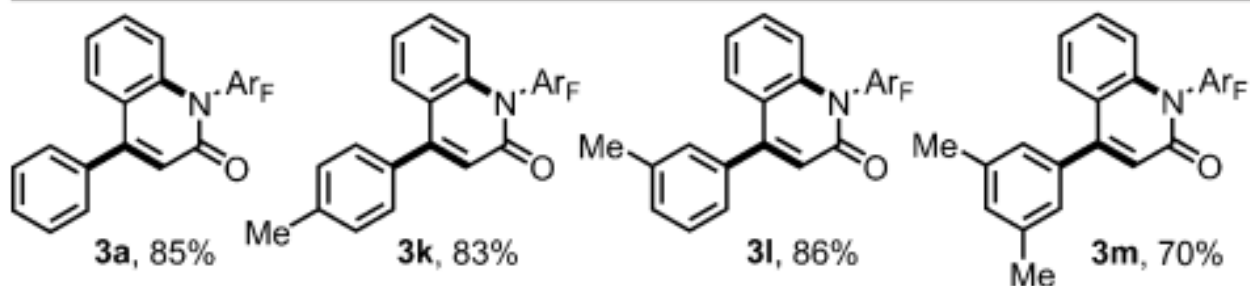
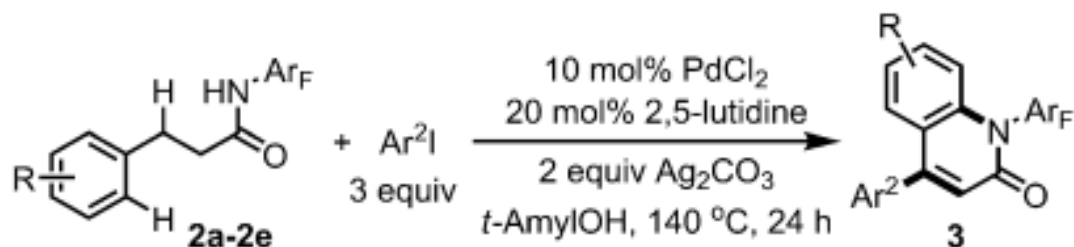
Ligand	2a (%)	3a (%)
without ligand	11%	0%
L1	17%	58%
L2	26%	16%
L3	23%	68%
L4	33%	40%
L5	42%	7%
L6	10%	66%
L7	20%	64%
L8	13%	0%
L9	42%	0%
L10	8%	80%
L11	9%	84%
L12	11%	80%
L13	37%	47%
L14	24%	60%
L15	37%	42%
L16	30%	22%
L17	50%	35%

[a] ArF = (4-CF₃)C₆F₄. [b] 1a (0.2 mmol), PdCl₂ (0.02 mmol), Ag₂CO₃ (0.6 mmol), PhI (0.8 mmol), ligand (0.04 mmol), *t*-AmylOH (0.5 mL), 140°C, 24 h. [c] Yield determined by NMR spectroscopy with CH₂Br₂ as the internal standard.

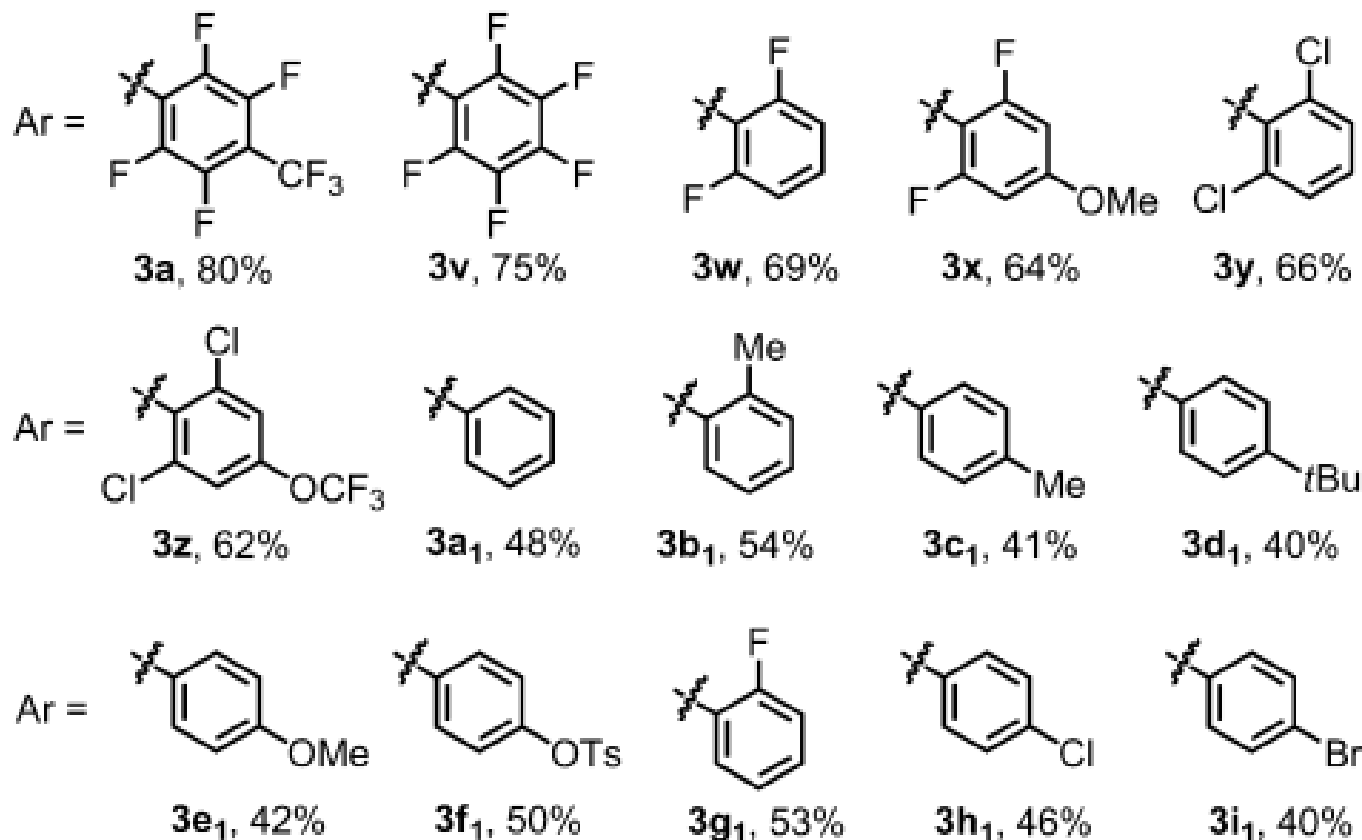
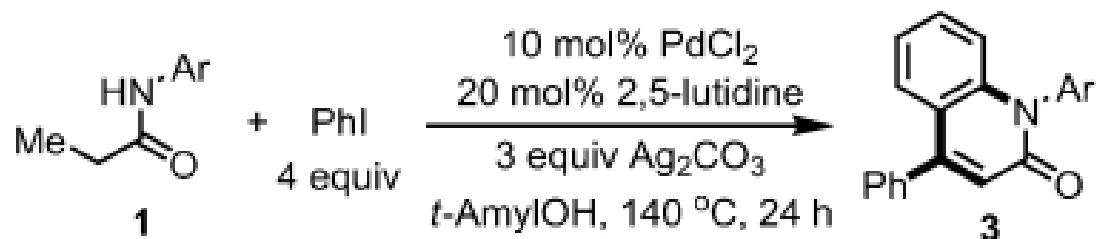
Scope of Aryl Iodides



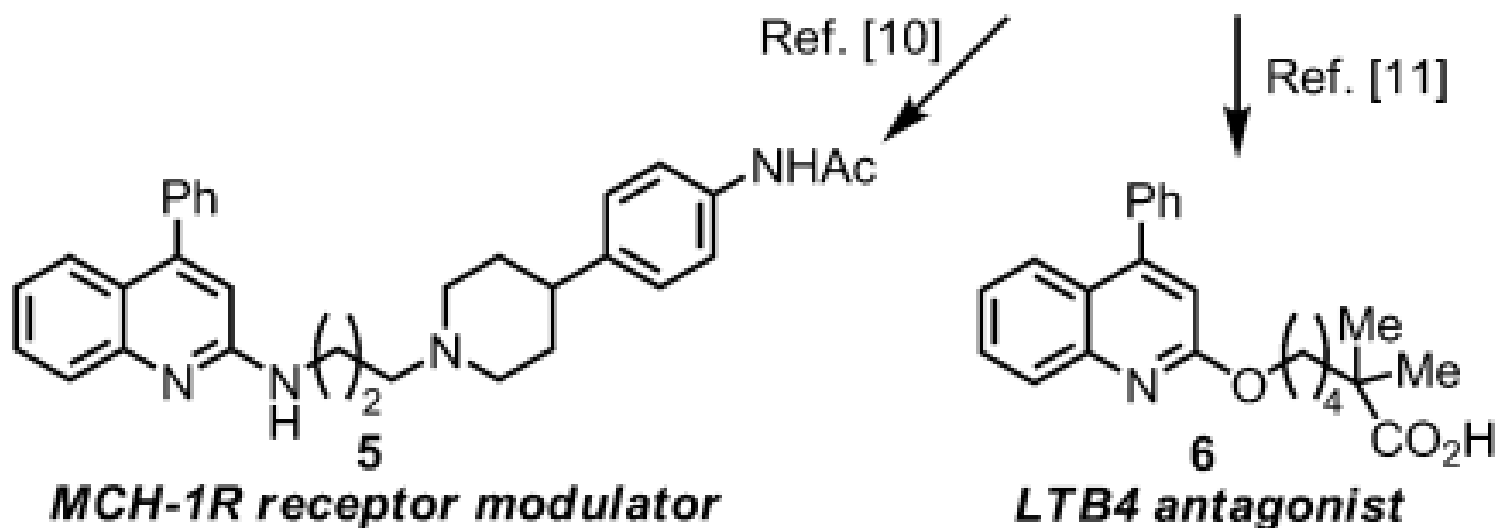
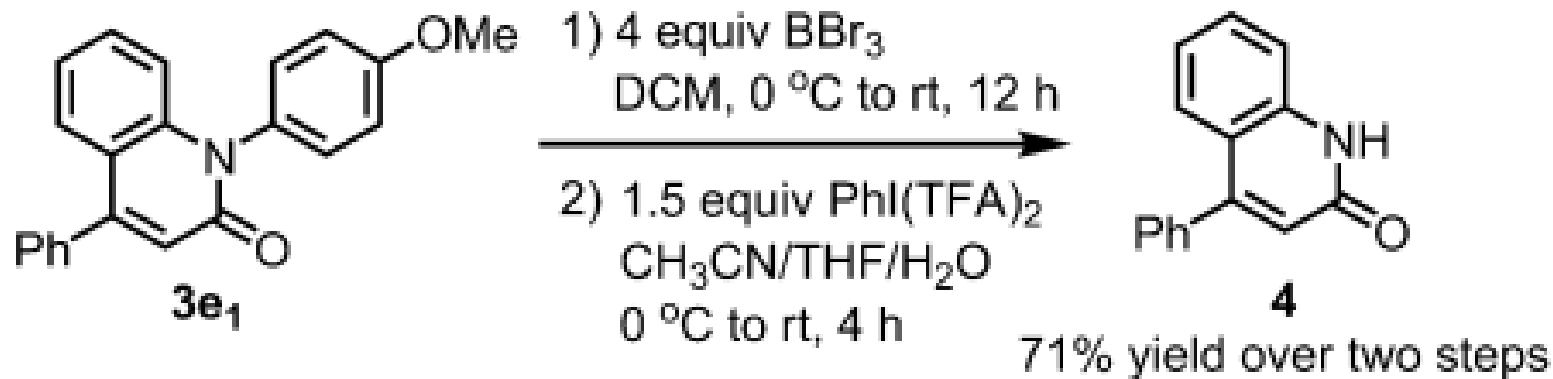
Incorporation of Two Different Aryl Groups



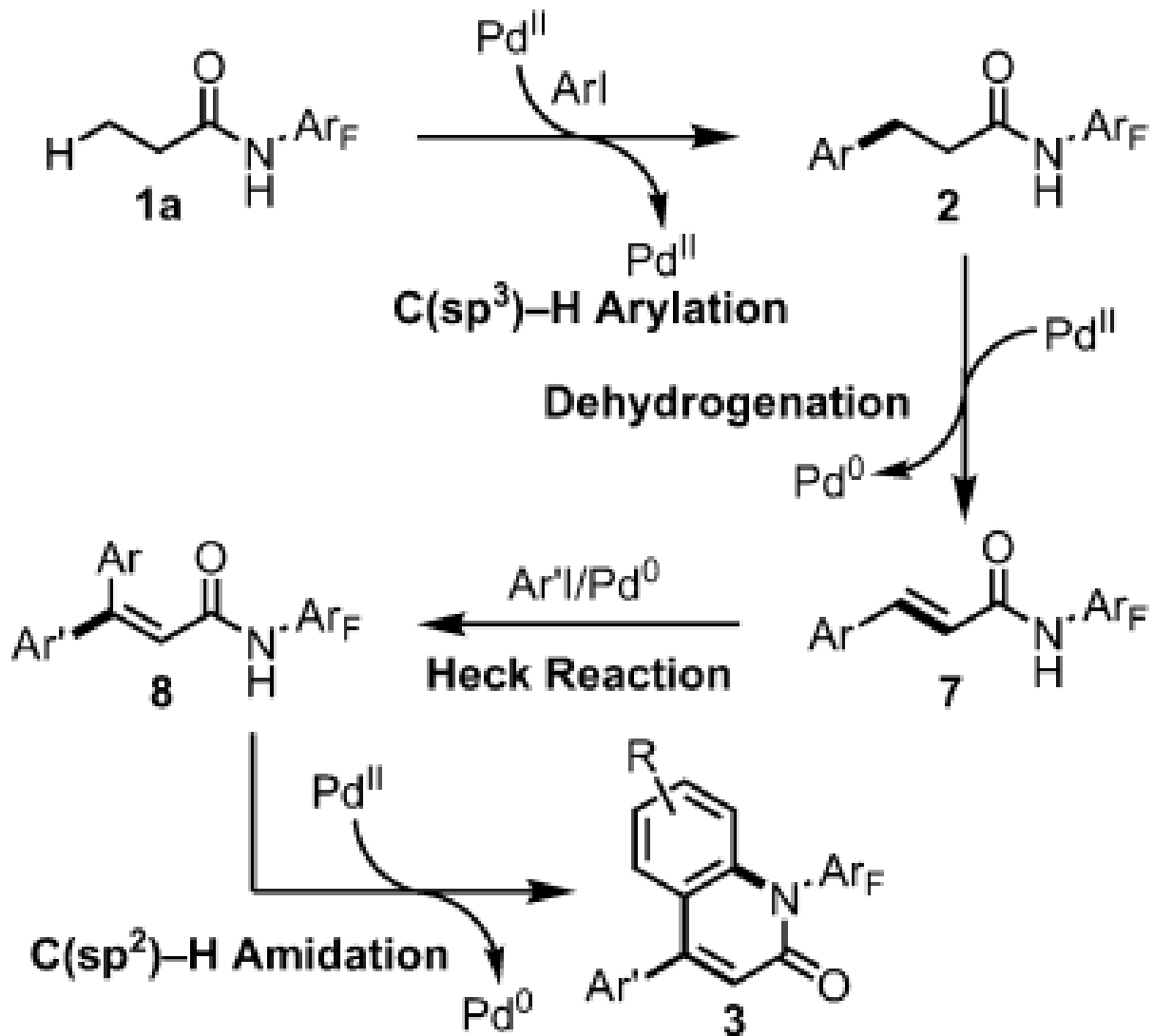
Scope of the N-aryl Group



Synthetic Applications

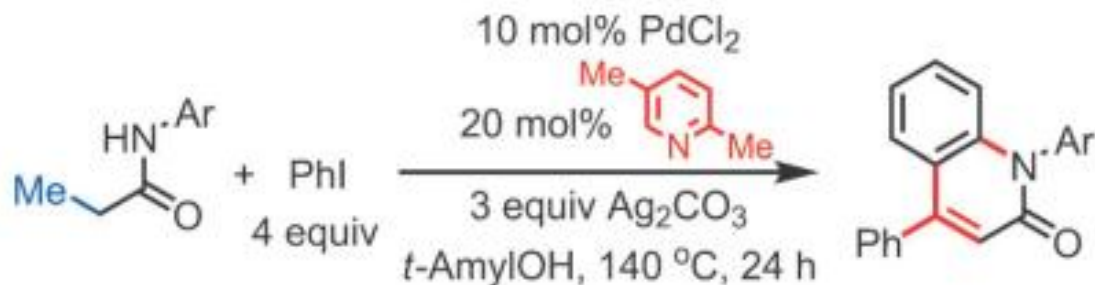


Proposed Catalytic Pathway



Summary

- pyridine ligand-promoted triple sequential C-H activation reactions and a stereospecific Heck reaction
- cleavage of five C-H bonds, two C-I bonds, and one N-H bond
- formation of three C-C bonds and one C-N bond via four different types of palladium catalytic cycles



Thanks for your attention!