



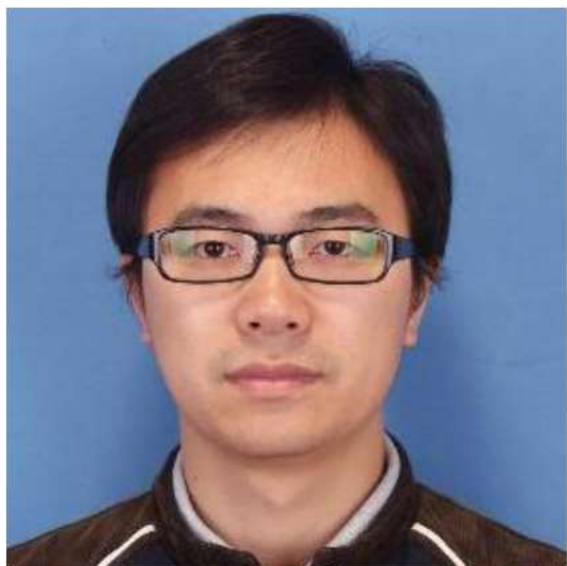
Research Article |  Full Access

# Electrochemical NiH-Catalyzed C(sp<sup>3</sup>)–C(sp<sup>3</sup>) Coupling of Alkyl Halides and Alkyl Alkenes

Pengfei Li, Guangsheng Kou, Tian Feng, Prof. Dr. Minyan Wang , Prof. Dr. Youai Qiu 

First published: 14 September 2023 | <https://doi.org/10.1002/anie.202311941>

Wenqian Miao



仇友爱

## 工作经历

2003-2007年 中国矿业大学化工学院, 本科, 导师: 魏贤勇教授

2010-2015年 浙江大学化学系, 博士, 导师: 麻生明教授

2015-2017年 瑞典斯德哥尔摩大学, 博士后, 导师: Jan-Erling Bäckvall教授

2017-2019年 德国哥廷根大学, 博士后, 导师: Lutz Ackermann教授

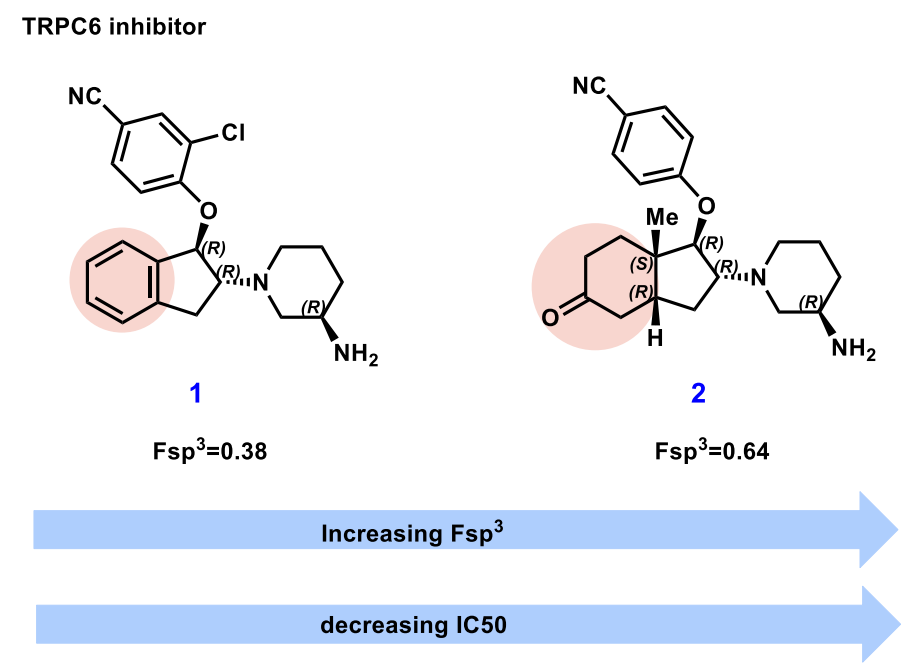
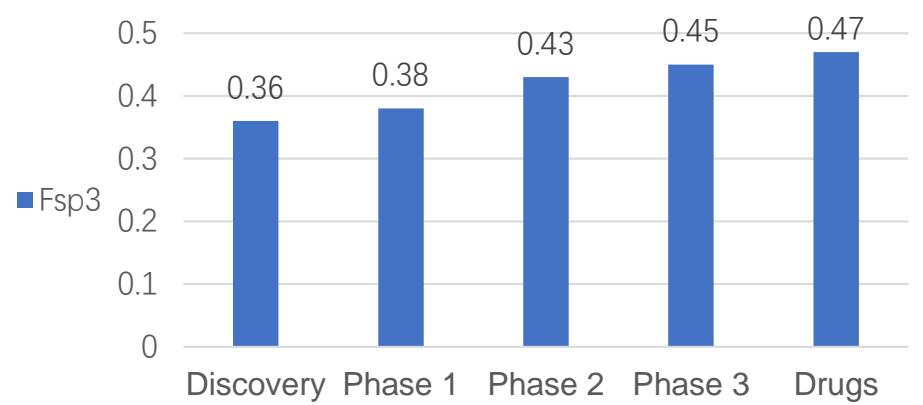
2019-2020年 日本理化学研究所, 访问研究员, 导师: 侯召民主任研究员

2020.09至今 南开大学化学学院, 元素有机化学国家重点实验室, 特聘研究员,  
博士生导师

研究方向  
有机电化学

过渡金属催化

自由基化学



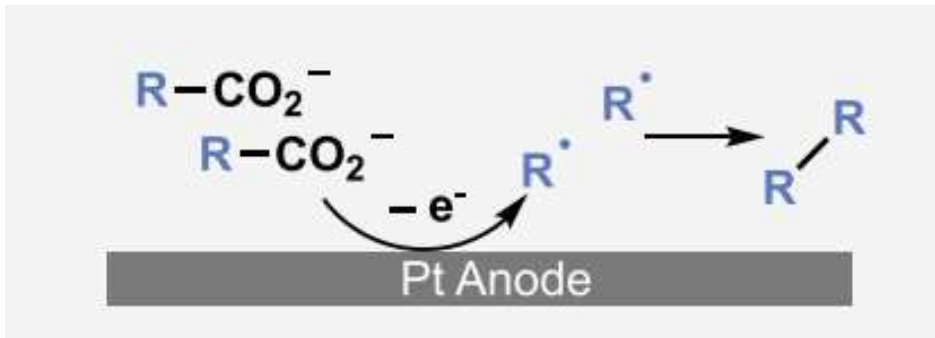
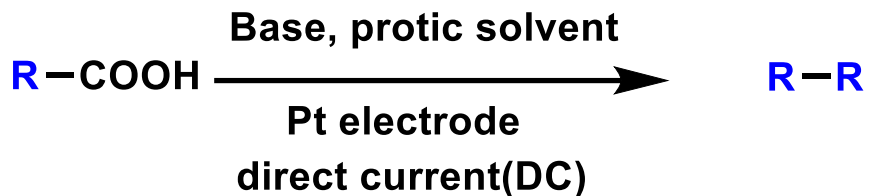
One of alternative methods--

Kolbe electrolysis



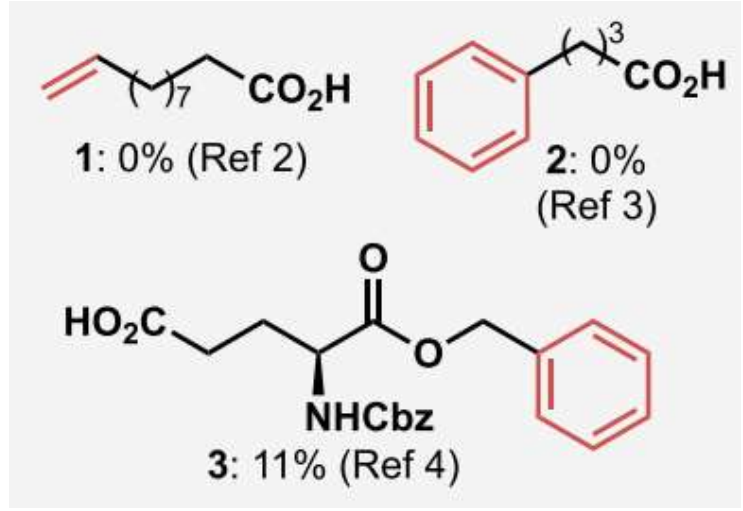
~1834

### Typical condition and mechanism

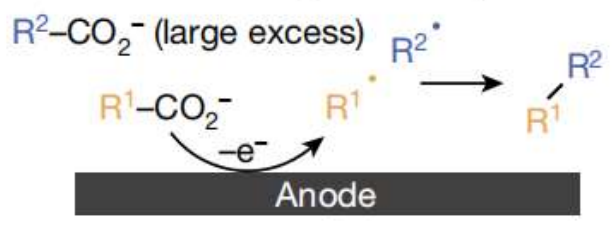


### Poor functional group tolerance

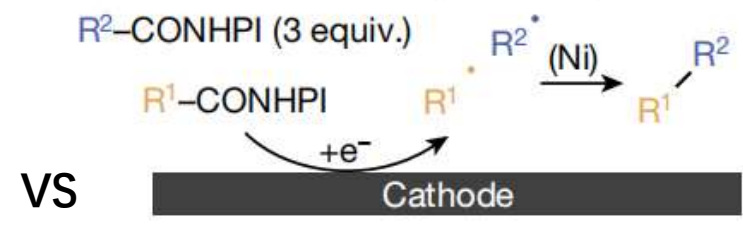
harsh oxidative conditions



High current density ( $>250 \text{ mA cm}^{-2}$ ) is required to ensure high anodic potential

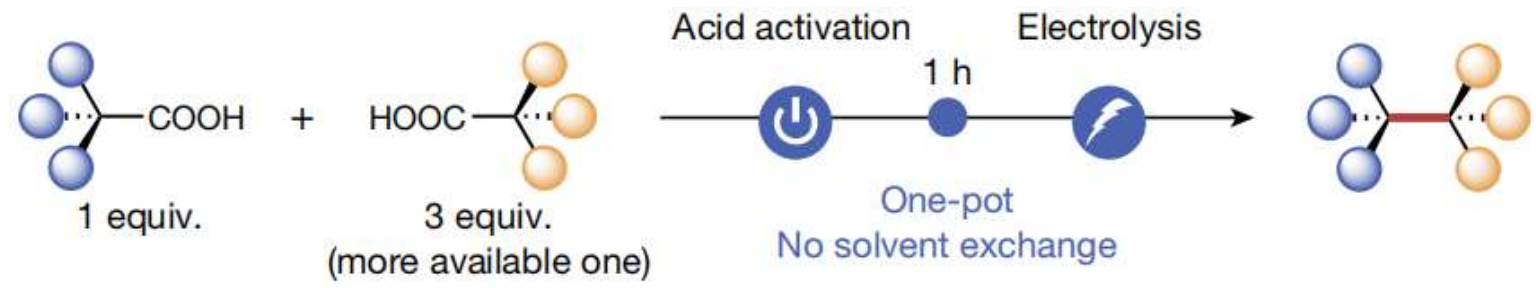


oxidative

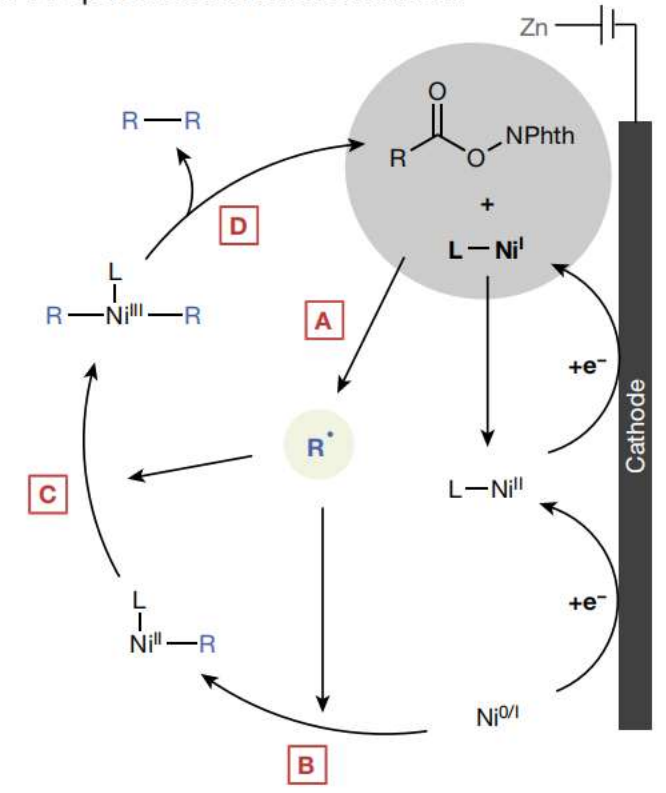


reductive

VS

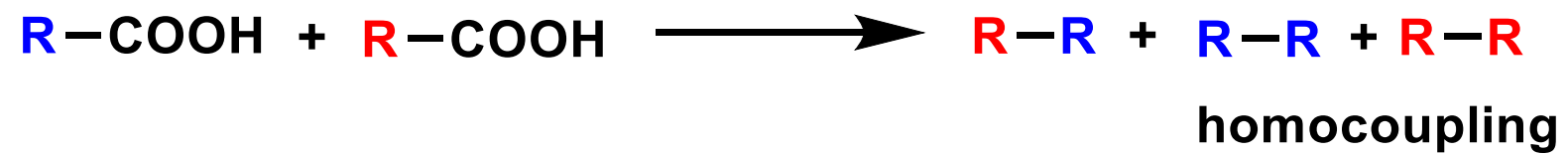


e Proposed reaction mechanism



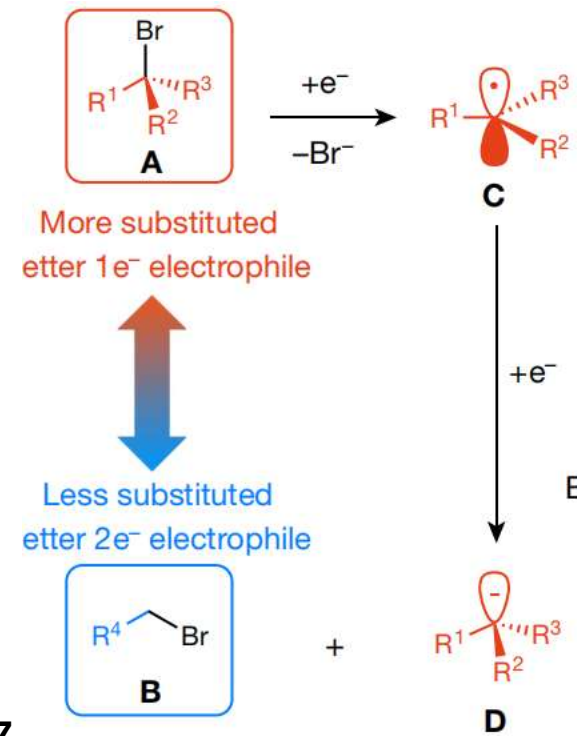
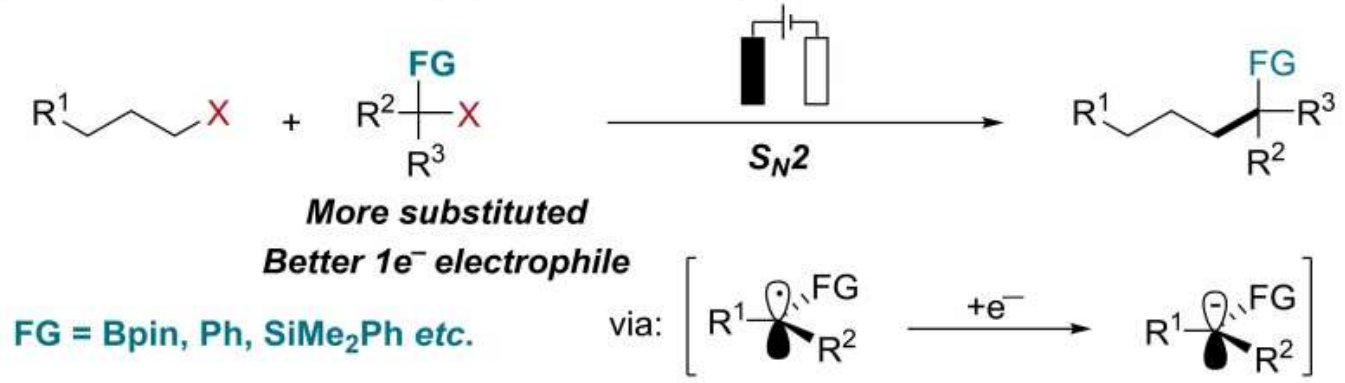
- A** Carbon radical formation via SET from Ni(I) to RAE
- B C** Ni-C bond formation (bimetallic oxidative addition)
- D** Reductive elimination

Low selectivity



# Lin's work: cross-electrophile coupling of alkyl halides

(b) Lin's work: eXEC via an S<sub>N</sub>2 process from alkyl halides

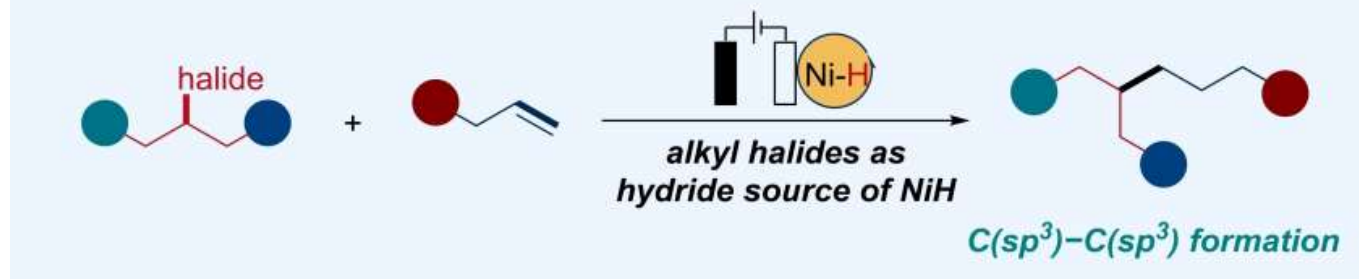


Reduction potential	
R-X	E <sub>red</sub> (versus Ag wire)
<sup>n</sup> BuBr	-2.69 V
<sup>s</sup> BuBr	-2.42 V
<sup>t</sup> BuBr	-2.13 V

**Highlight:**  
high selectivity

**Key:**  
anion-stabilizing substituent

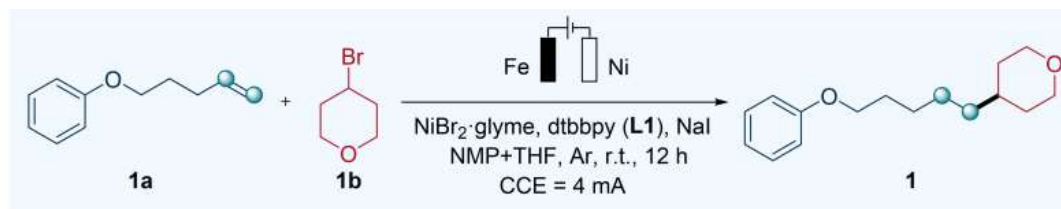
(c) This work: NiH-catalyzed  $C(sp^3)-C(sp^3)$  coupling of alkyl halides and alkyl alkenes



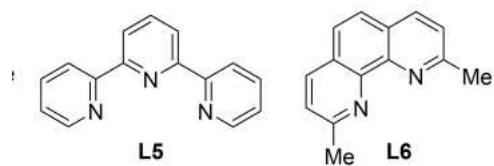
- The dual function of halides as both coupling substrates and hydrogen sources
- Avoiding the use of silanes as hydrogen sources and the addition of reductive metal reagents
- Mild electroreductive conditions with good functional group compatibility
- Good chemoselectivity and regioselectivity
- Late-stage modification of biorelevant molecules
- Tunable synthesis of linear and branched coupling products.



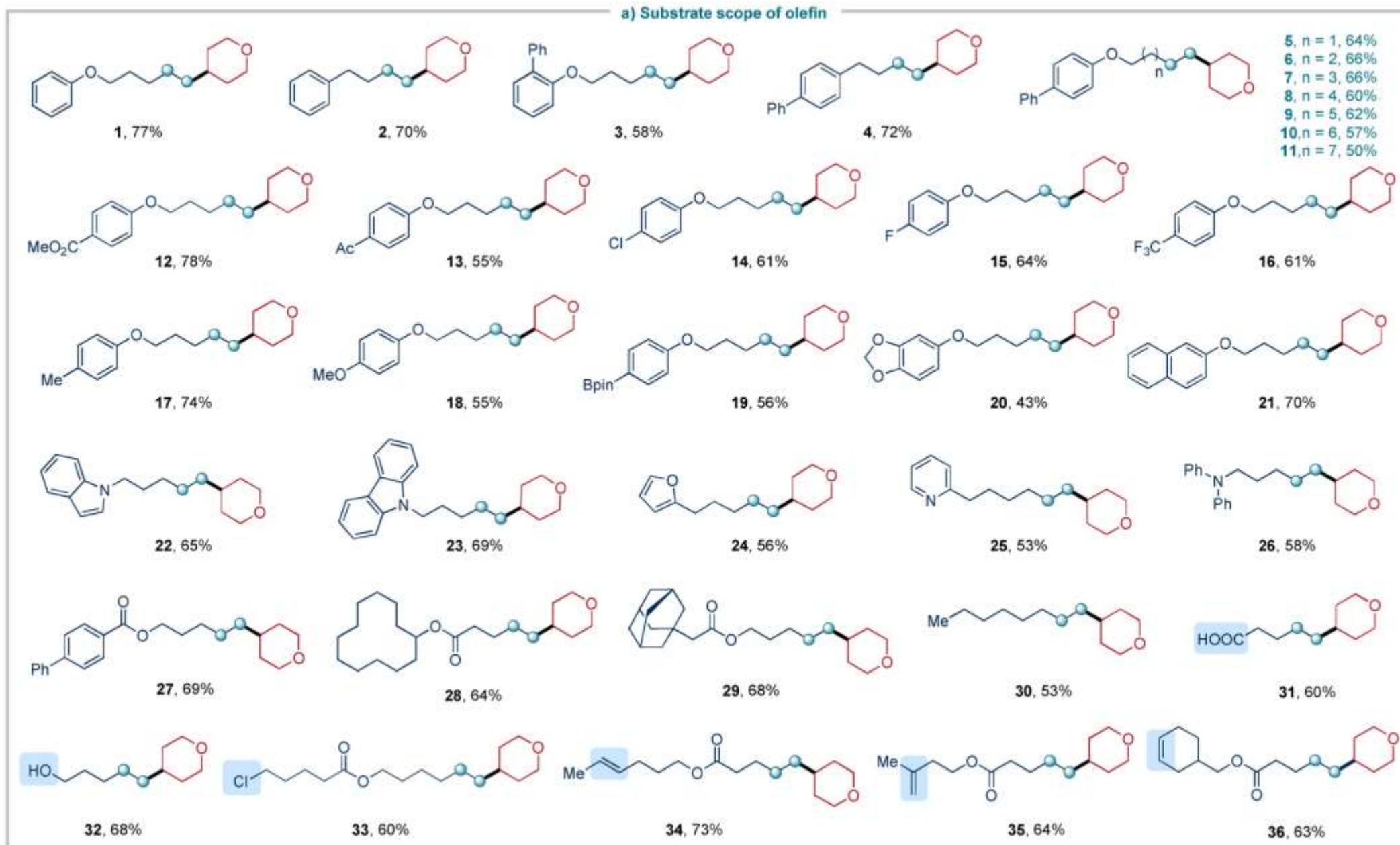
# Optimization of reaction conditions



Entry	Variation	Yield (%) <sup>a</sup>
1	none	77
2	w/o electricity	n.r.
3	w/o nickel catalyst	n.r.
4	TBAI instead of NaI	52
5	TBABF <sub>4</sub> instead of NaI	28
6	Et <sub>4</sub> NBr instead of NaI	23
7	THF as solvent	18
8	NMP as solvent	70
9	DMSO as solvent	35
10	DMF as solvent	32
11	Zn (+) instead of Fe (+)	28
12	Mg (+) instead of Fe (+)	trace
13	Pt (-) instead of Ni foam (-)	37
14	NiCl <sub>2</sub> instead of NiBr <sub>2</sub> ·glyme	17
15	NiBr <sub>2</sub> instead of NiBr <sub>2</sub> ·glyme	52
16	L2 instead of L1	28
17	L3 instead of L1	48
18	L4 instead of L1	28
19	L5 instead of L1	trace
20	L6 instead of L1	trace



# Substrate scope of olefin



b) Substrate scope of halide



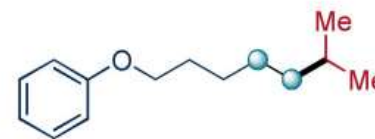
37, 71%



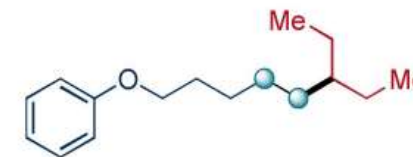
38, 64%



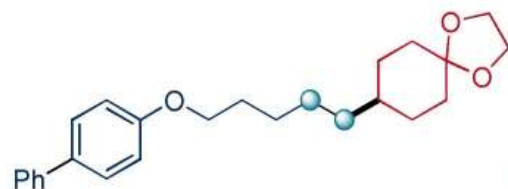
39, 52%



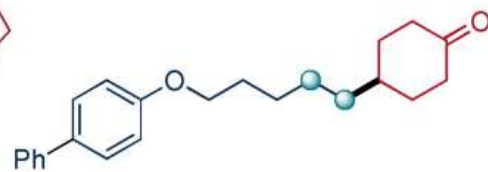
40, 47%



41, 53%



42, 51%



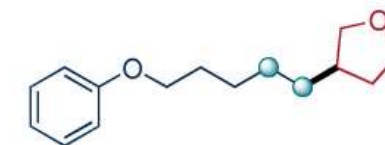
43, 49%



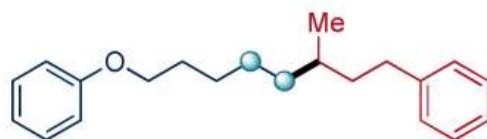
44, 61%



45, 66%



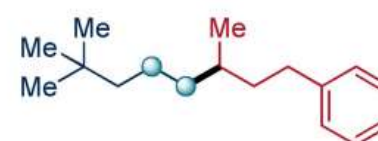
46, 69%



47, 57%



48, 63%



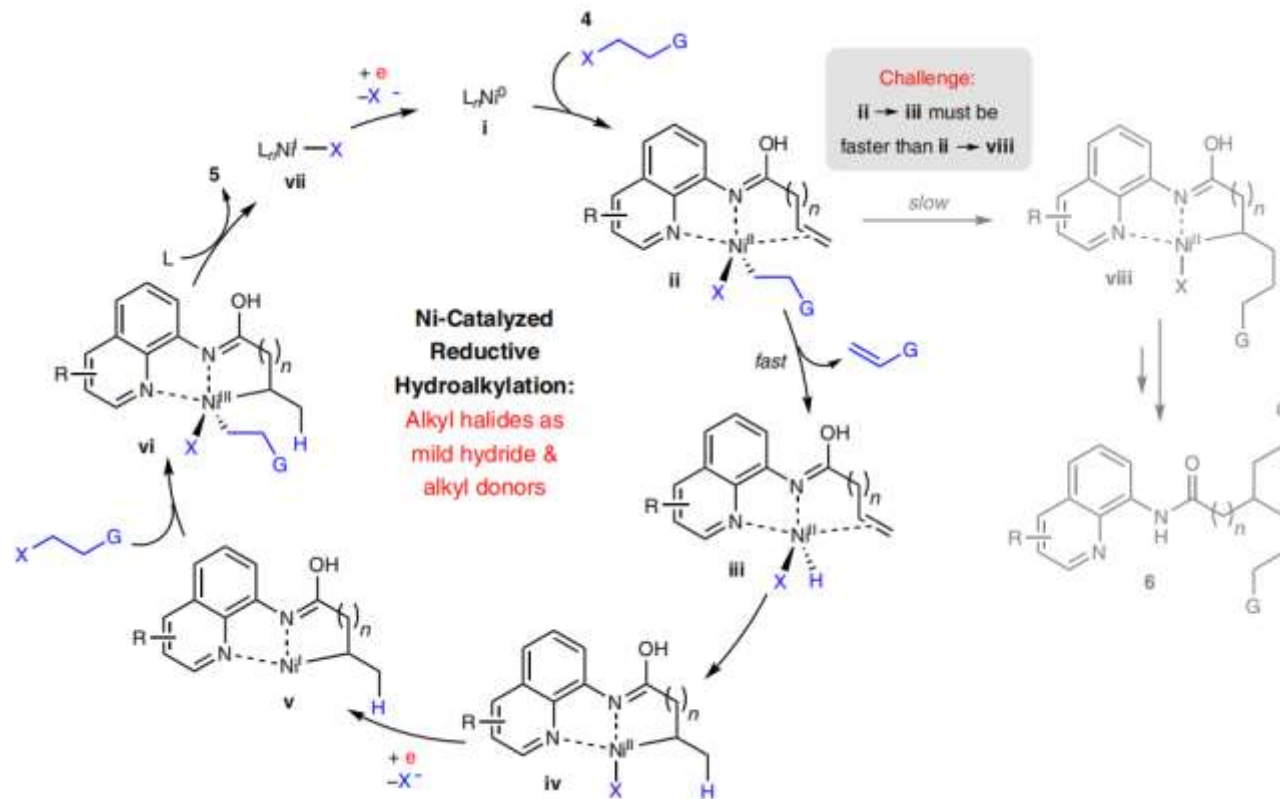
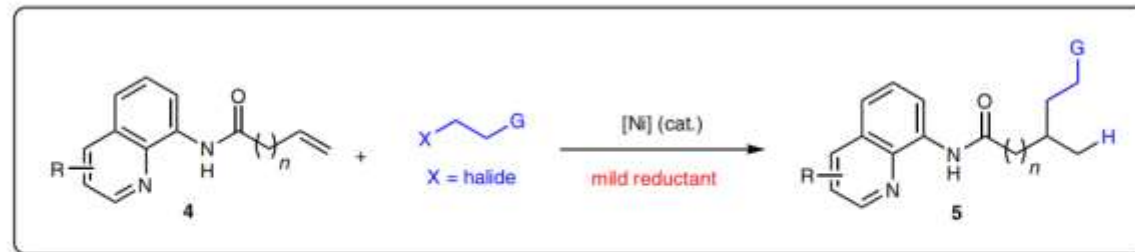
49, 59%



50, 47%

**If the reaction could go further by the installation of nitrogen-based ligands directly within the framework of the alkene substrate?**

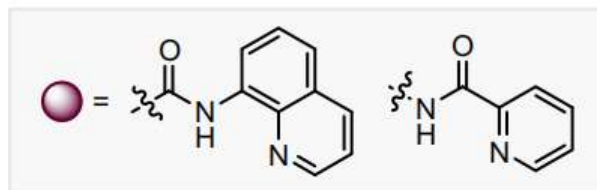
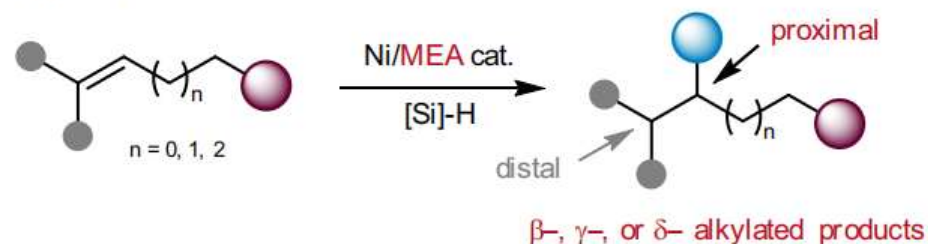
Inspired by Ming Joo Koh



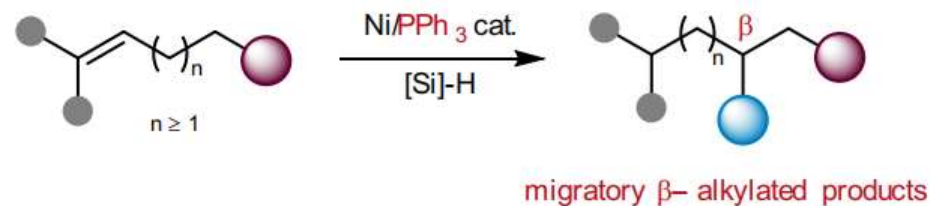
## Inspired by Yao Fu

**b** this work: directed NiH-catalysed alkene hydroalkylation

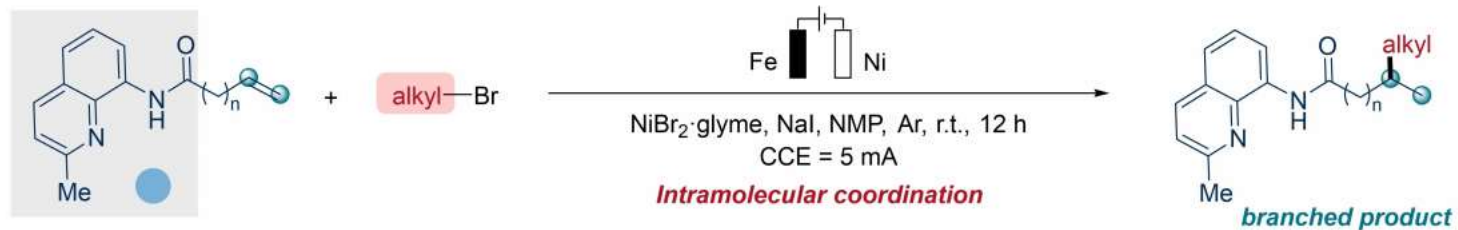
(4) *ipso*-proximal-selective hydroalkylation



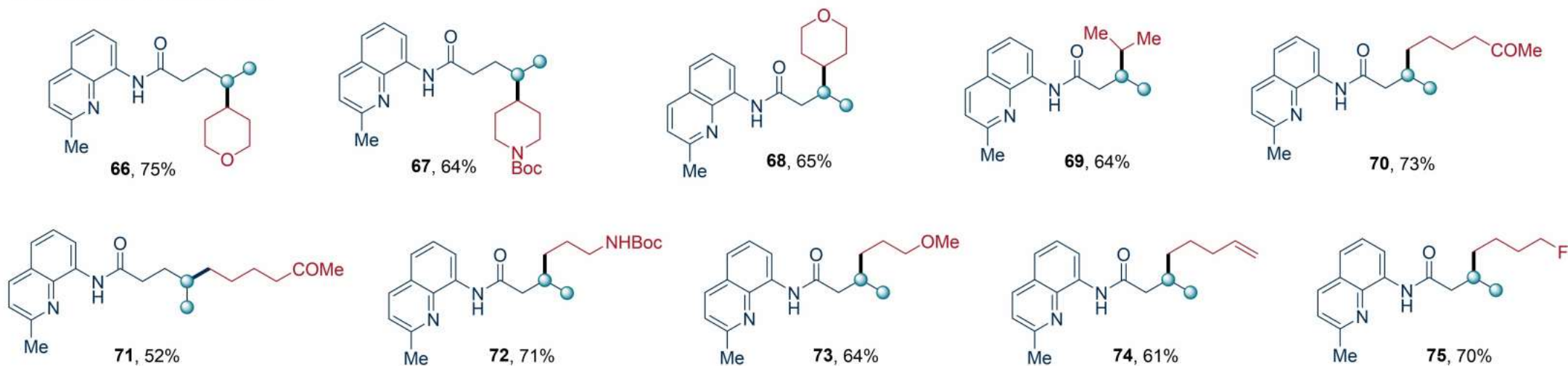
(5) migratory  $\beta$ -selective hydroalkylation



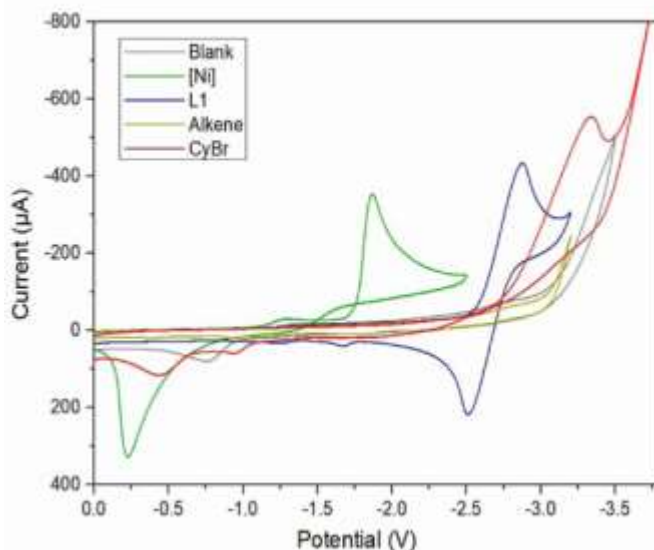
- terminal and internal alkenes
- wide scope of alkyl halides
- late-stage modification
- high proximal-selectivity
- ligand-regulatable migratory  $\beta$ -selective hydroalkylation



b) Examples for branch products<sup>b</sup>



a) Cyclic voltammetry (CV)



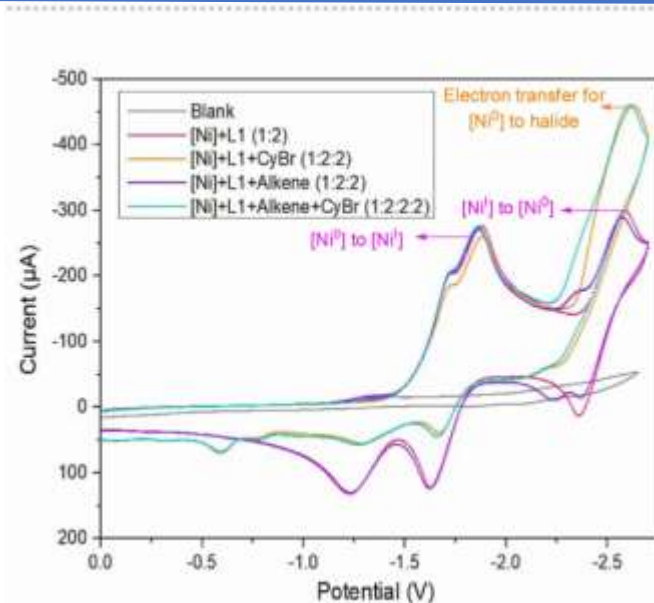
Reduction peak

[Ni]: -1.71V

L1: -2.76V

CyBr: -3.92V

**Alkene**: no reduction peaks of alkyl alkene could be observed



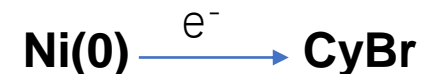
[Ni]+L1; [Ni]+L1+Alkene

-1.82V reduction of Ni(II)/Ni(I)

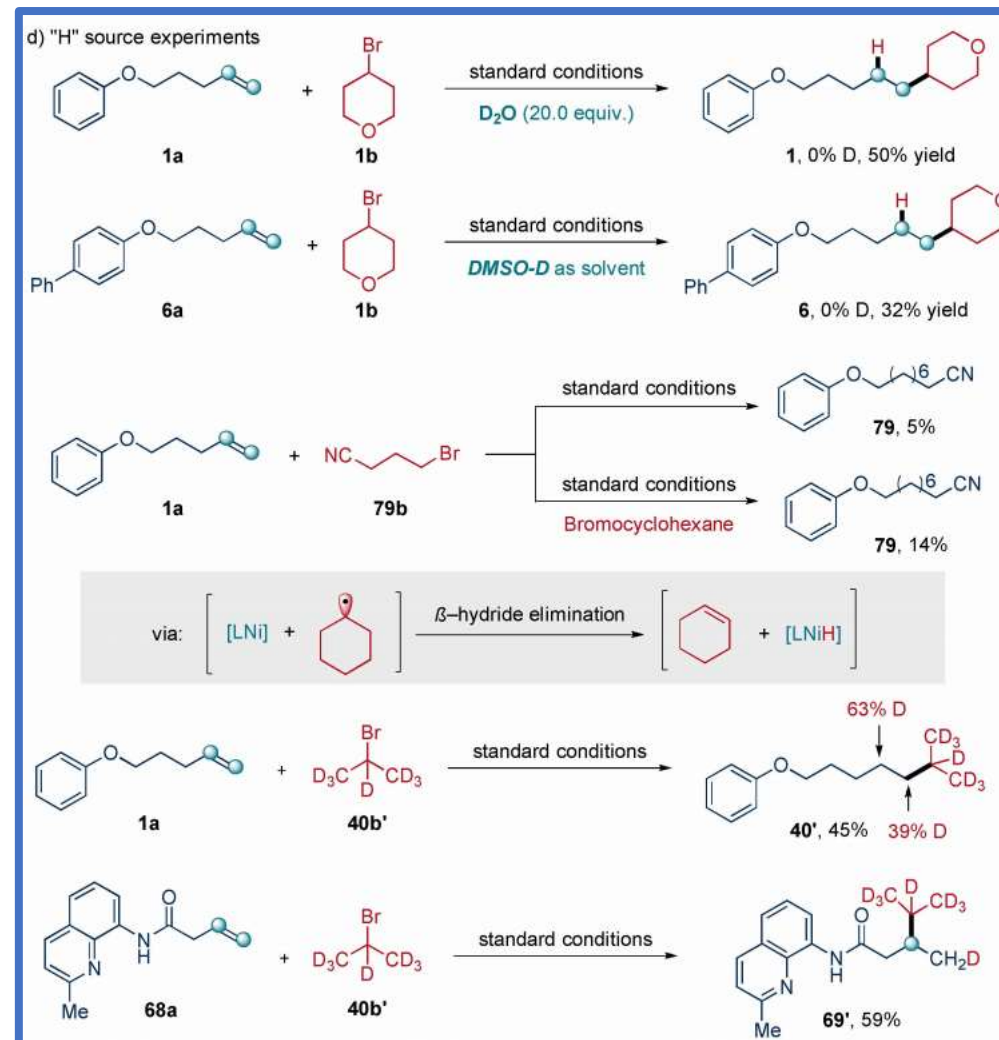
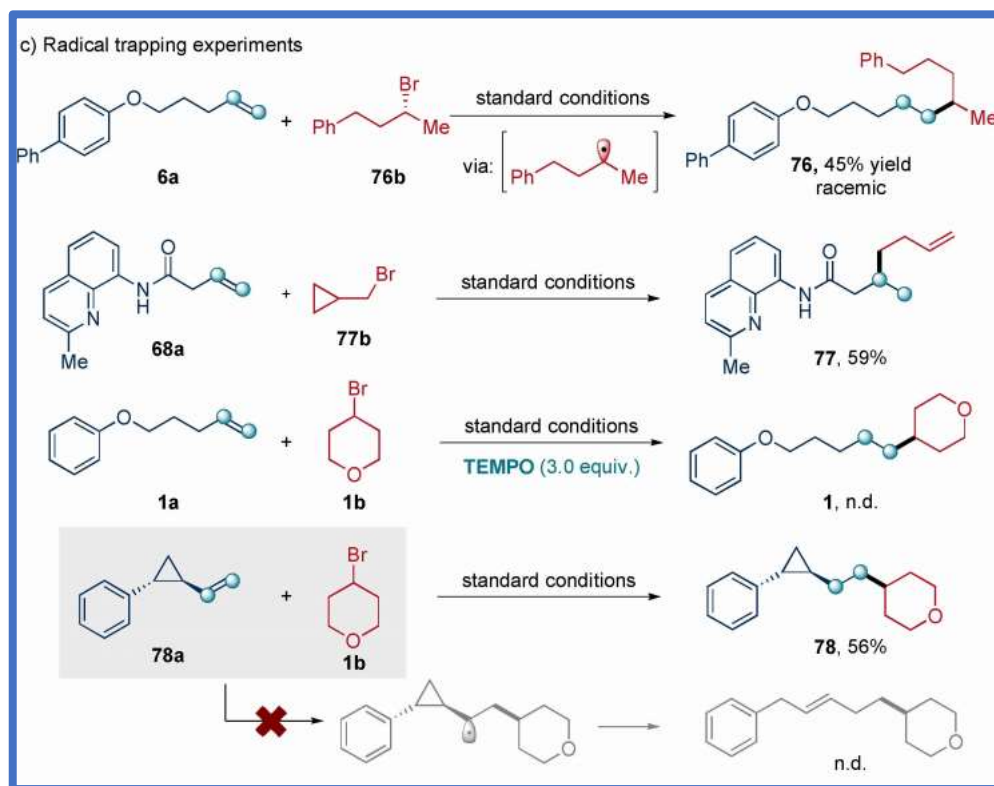
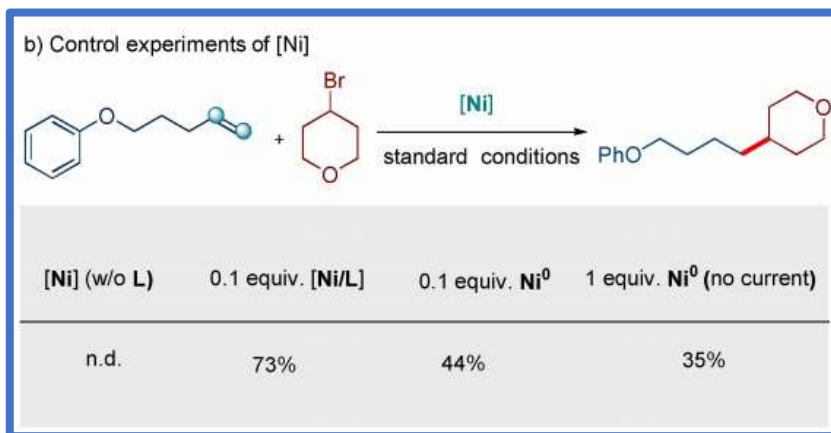
-2.59V reduction of Ni(I)/Ni(0)

[Ni]+L1+**CyBr**; [Ni]+L1+Alkene+**CyBr**

second reduction peak showed a distinct peak shift

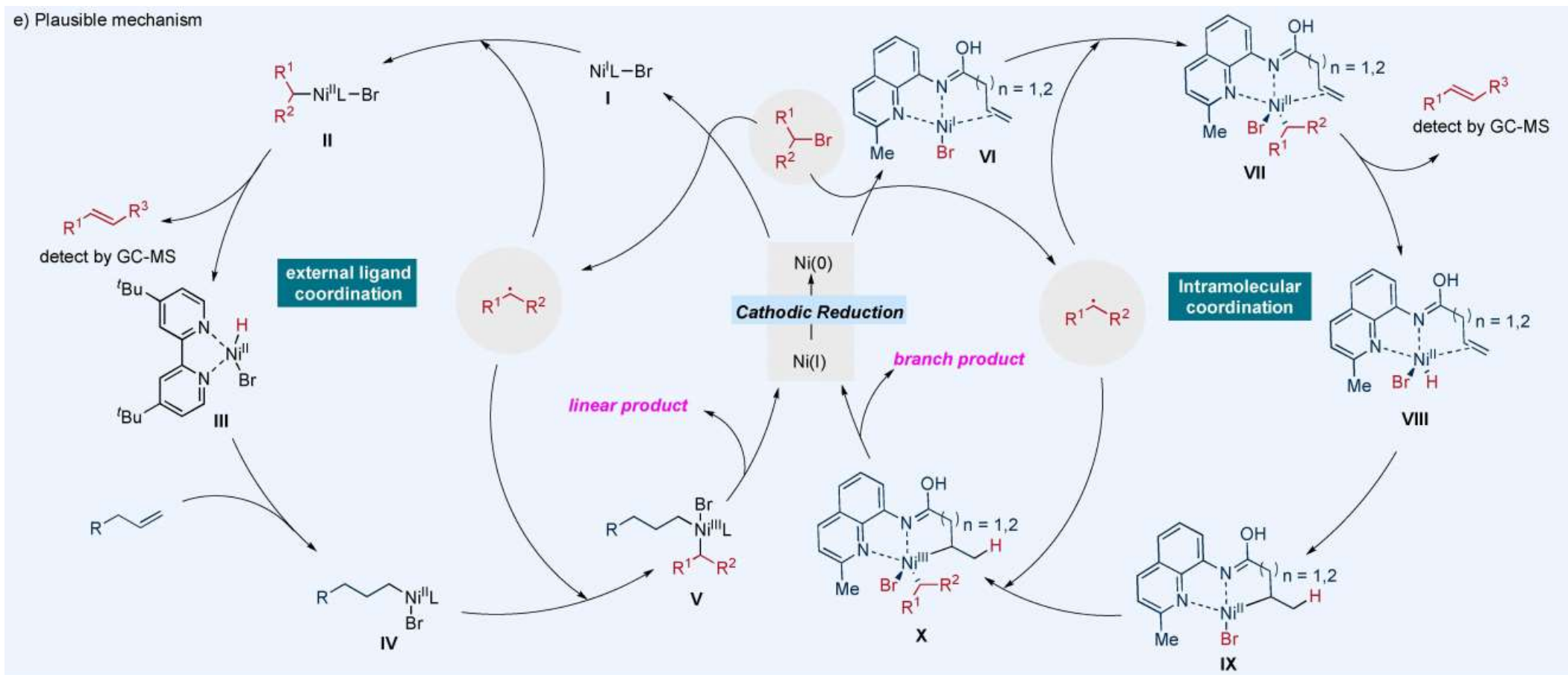






control experiments

e) Plausible mechanism



**Thank you for your attention**