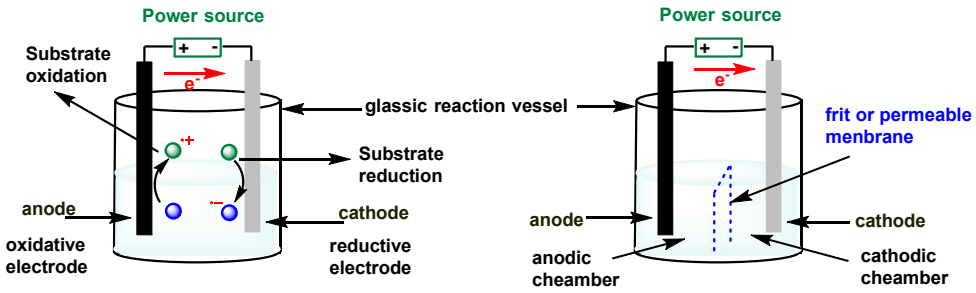
Concept of Organic Electrochemistry

Basic components of an eletrochemical cell



Electrodes: Pt, graphite, Ni, RVC, Zn, Mg.....
Electrolyte: Li^+, $^nBu_4N^+$/ I^-, Br^-, BF_4^-, PF_6^-, ClO_4^-
Solvent: THF, DCM, acetone, MeOH, ACN, DMF, H_2O
Reaction time: t (s) =Q ×96485 (c/mol) ×n (mol)/ I (A).

Advantages

-electron as a traceless reagent in place of the generally used reactive oxidants/reductants
-mild condition, high atom/step efficiency
-lower both the risk and the cost of synthetic protocols
-unique chemo- and regioselectivity

Disdvantages

-poor repeatability of electrochemical reaction
-diverse electrochemical set-up, lack of standard set-up, expensive

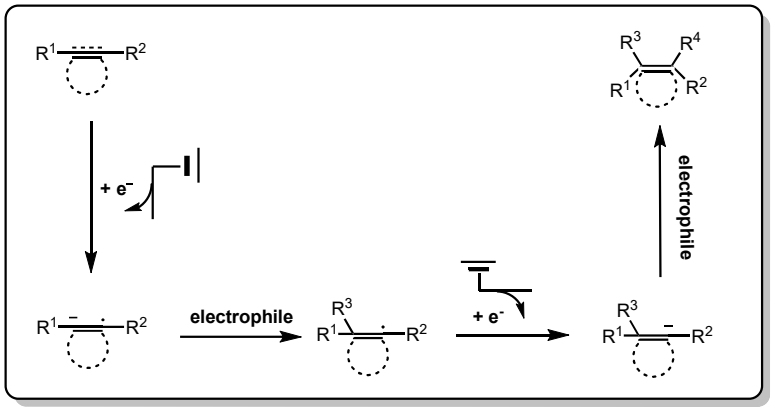
Must-Read Reviews:

-Acc. Chem. Res. 2020, 53, 72 - 83
-Chem. Rev. 2017, 117, 13230.
-Chem. Soc. Rev. 2021, 50, 7941-8002
-eScience 2 (2022) 243-277

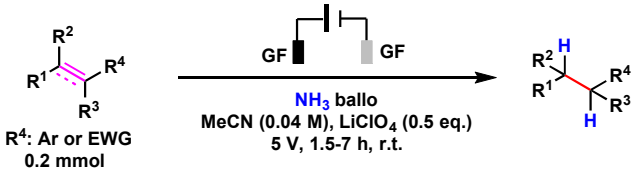
There is a large and increasing body of literature on oxidative electrosynthesis, reductive electro-chemical reactions are substantially less reported

Table of Contents

1. Reaction involving anionic radical from unsaturated hydrocarbons

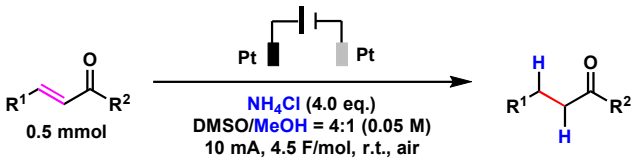


1.1 Electroreductive hydrogenation (deuteration)



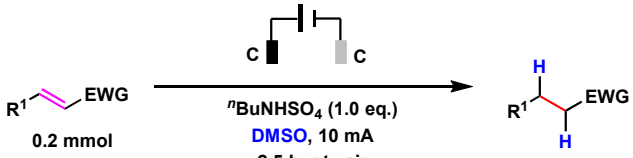
R⁴: Ar or EWG
0.2 mmol

Cheng ACIE 2019, 58,1759



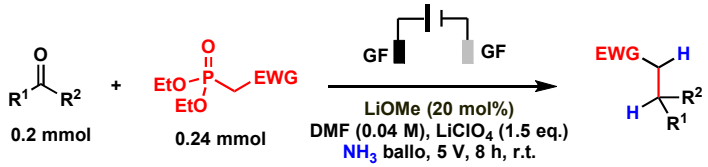
0.5 mmol

Xia CC 2019, 55, 6731



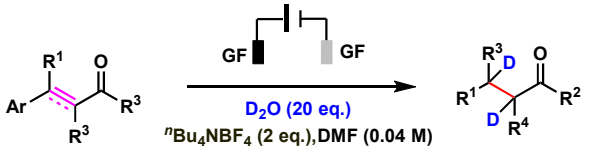
0.2 mmol

Huang OCF 2020, 7, 1817



0.2 mmol 0.24 mmol

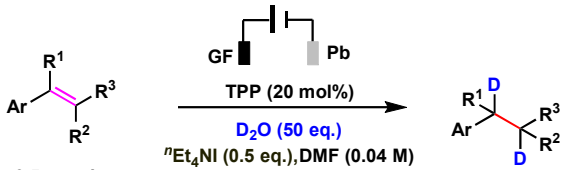
Cheng JOC 2021, 86, 16016



0.3 mmol

substitutes were limited to aryl, ester,carboxy,amide

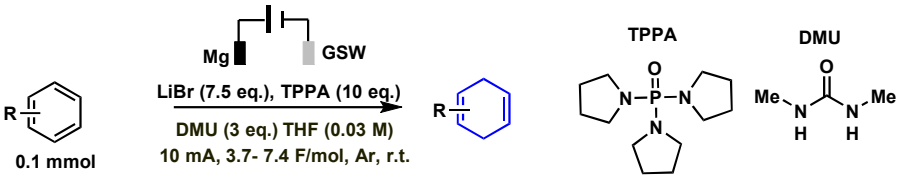
Cheng ACIE 2020, 59, 13962



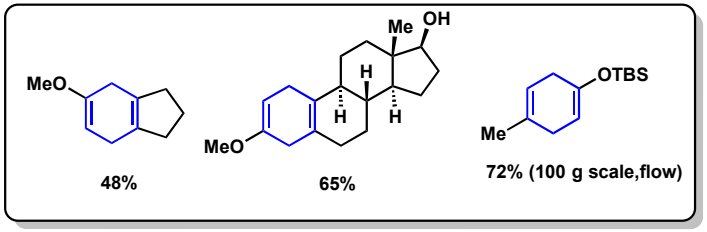
0.5 mmol

high yield
broad FG tolerance
excellent D-inc
TPPO as reductive mediater

Qiu ACIE 2023,e202312803



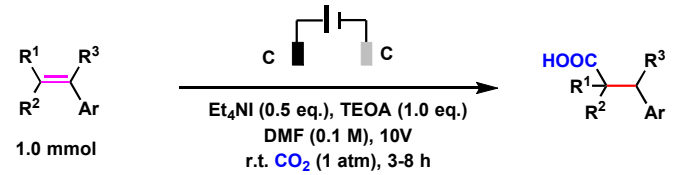
0.1 mmol



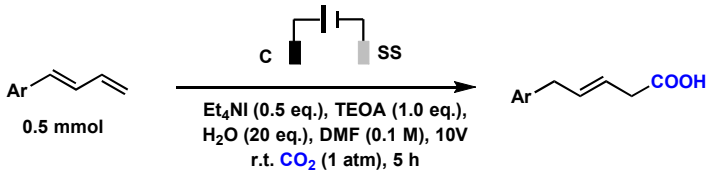
Baran Science 2019, 363, 838

1.2 Electroreductive Carboxylation

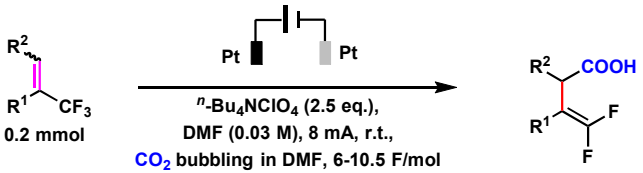
traditional method: strong base, expensive transition metal, toxic reagent, Friedel-Crafts carboxylation



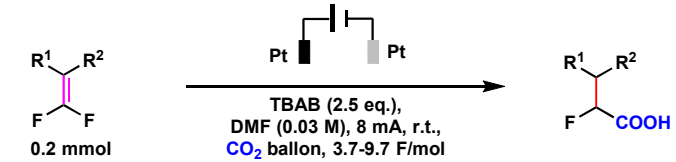
Buckley JACS 2020, 142, 4, 1780



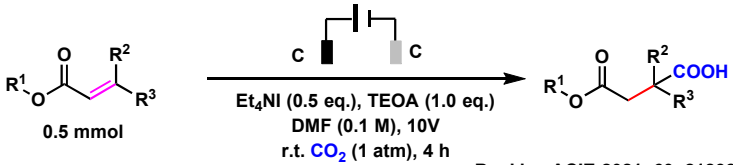
Buckley CS 2020, 11, 9109



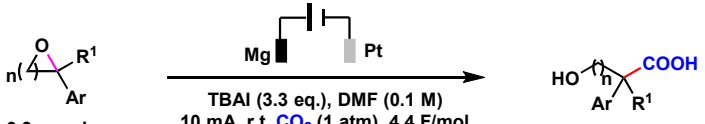
Zhou CS 2020, 11, 10414



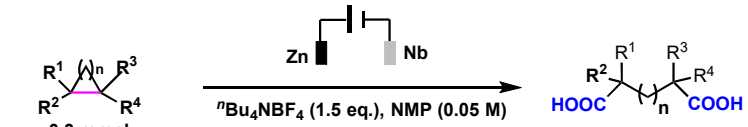
Zhou OL 2020, 22, 8424



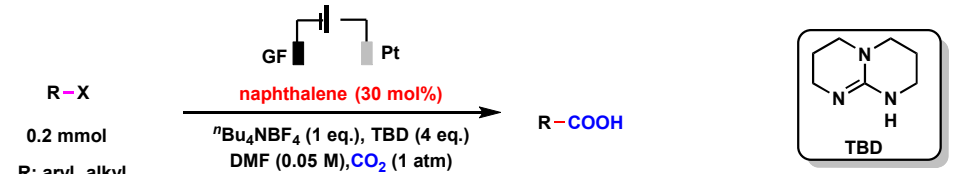
Buckley ACIE 2021, 60, 21832



Qiu ACIE 2022,61,e2022077

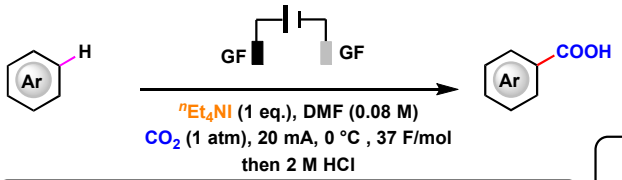


Yu JACS 2022, 144, 2062

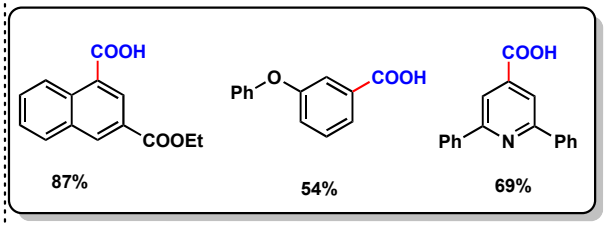


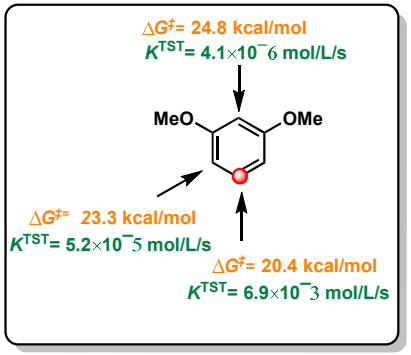
broad FG tolerance
lack of aza-heteroaromatic

Qiu ACIE 2022,61, e2022102

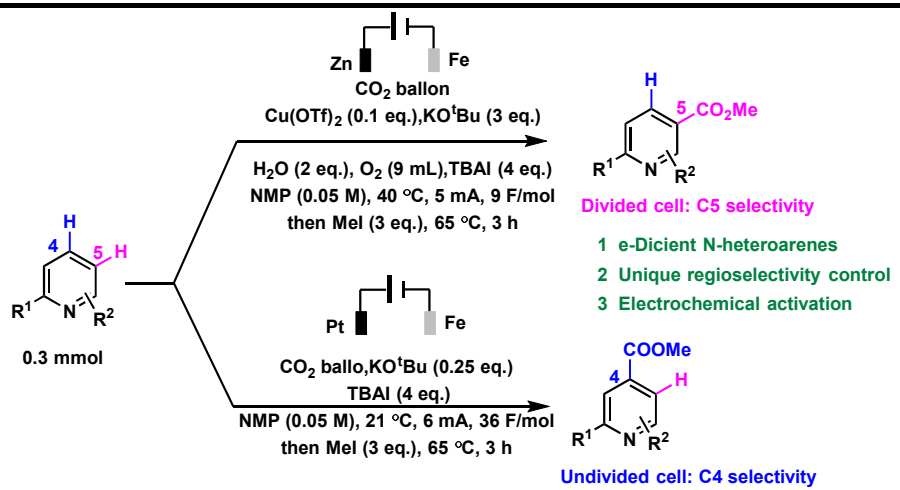


1 direct C-H electrocarboxylation of diverse arenes
2 unique chemo- and regioselectivity
3 good FG tolerance



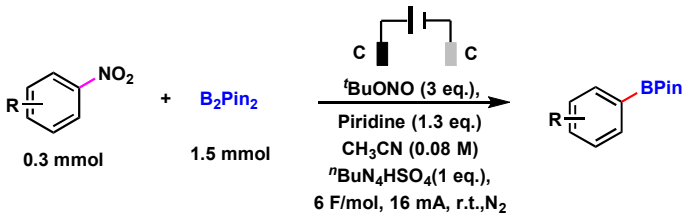


Qiu ACIE 2023,62, e2022147



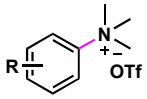
Lin Nature 2023, 615, 67.

1.3 Electrochemical borylation of arenes

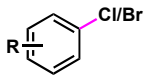


Cai SCC 2023, 66, 534

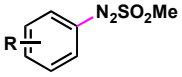
Aryl radical precursors



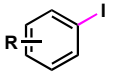
Xu OCF 2021, 8, 702



Lin JACS 2020, 142, 2087

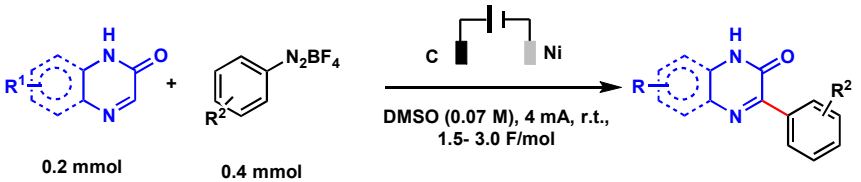


Yi ADSC 2021, 363, 1904



Mo CJC 2019, 37, 347

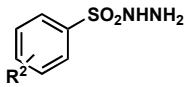
1.4 Electrochemical Minisci-type arylation



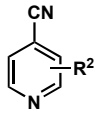
Lei ACIE 2019, 58, 15747

Zeng ADSC 2019, 361, 5170

Aryl radical precursors

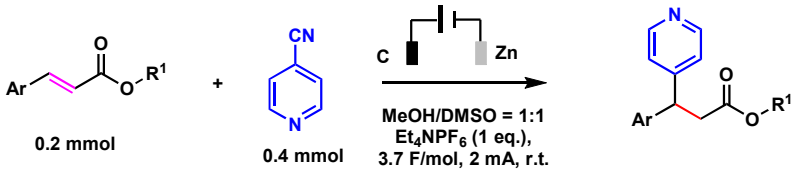


Lei CC 2019, 55, 11091

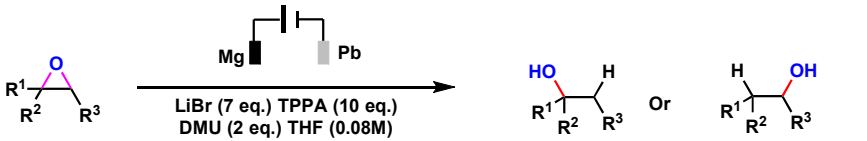


Yang OL 2021, 23, 1081

1.5 Miscellaneou eletroreduction involving anion radical

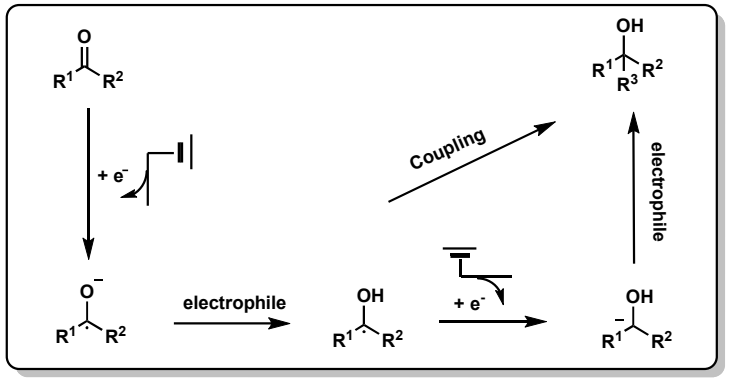


Jiang JOC 2021, 86, 16204

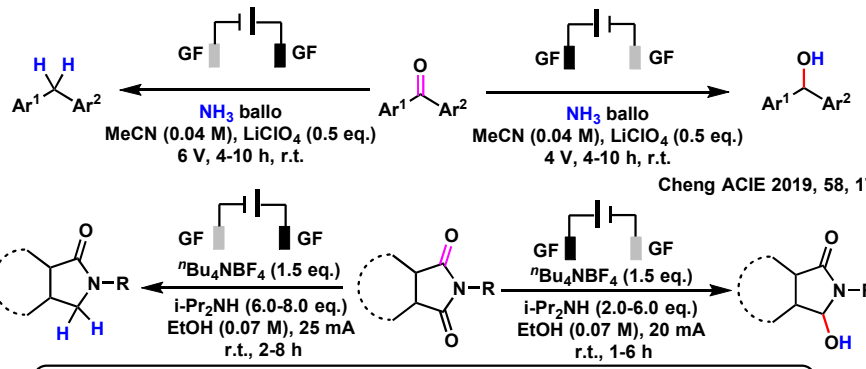


Lu JACS 2022, 144, 1389

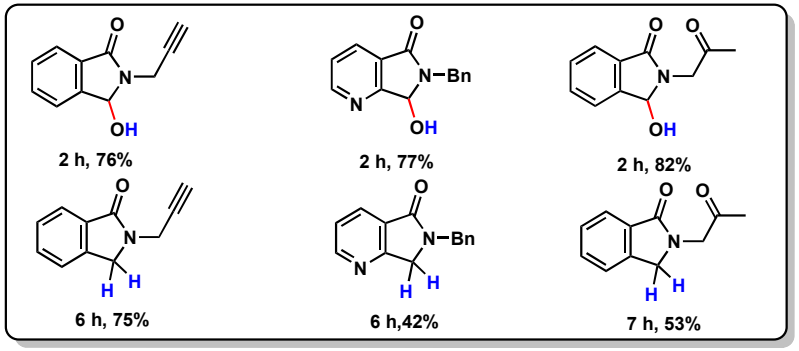
2. Reaction involving ketyl radical



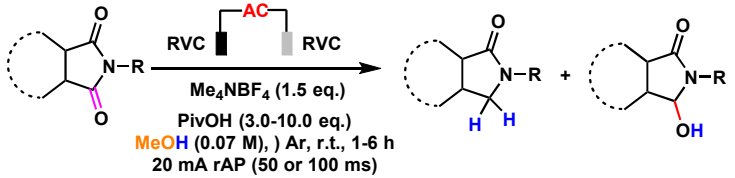
2.1 Reductive hydrogenation

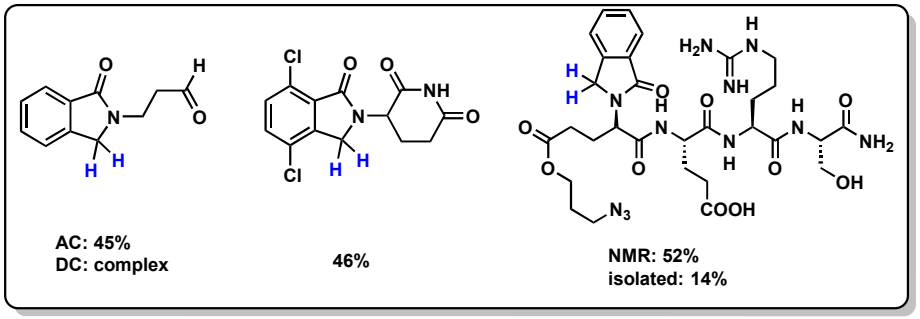


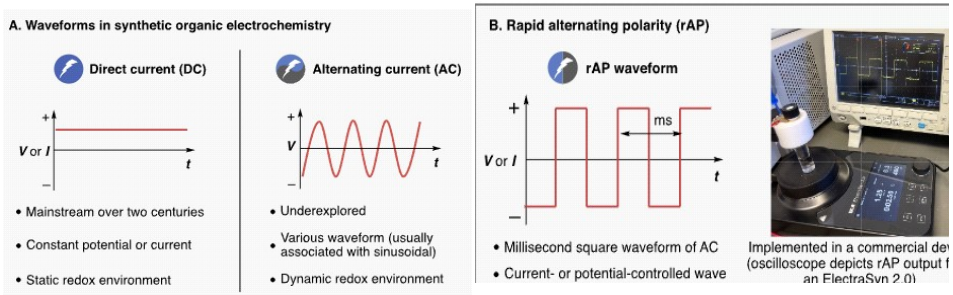
Cheng ACIE 2019, 58, 1759

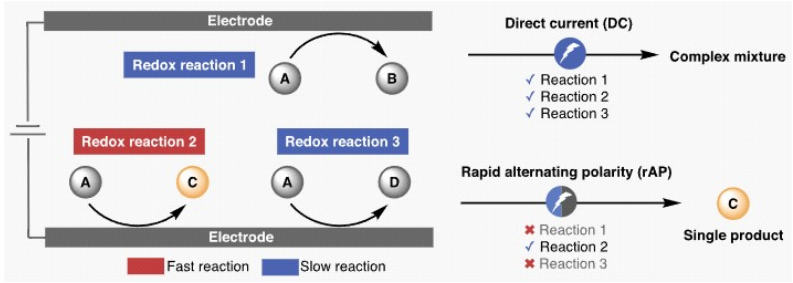


Org. Lett. 2021, 23, 2298-2302





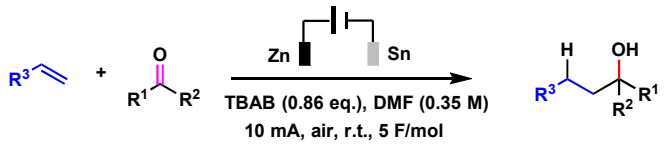




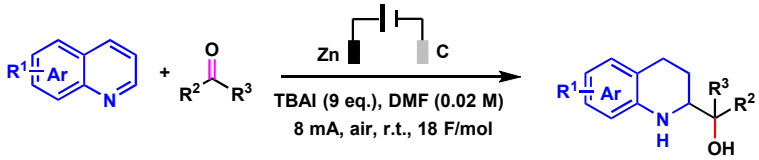
Baran JACS 2021, 143, 16580

2.2 Electroreductive cross-coupling

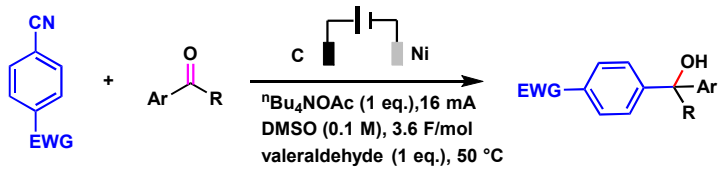
traditional method: strong base, organometallic reagent



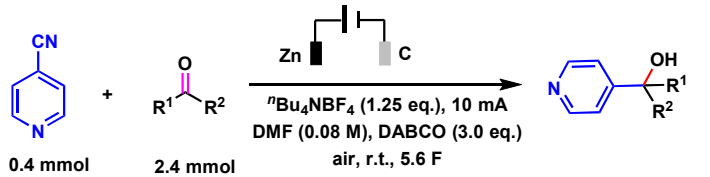
Baran JACS 2020, 142, 50, 20979



Zhang JACS 2023, 145, 20, 10967



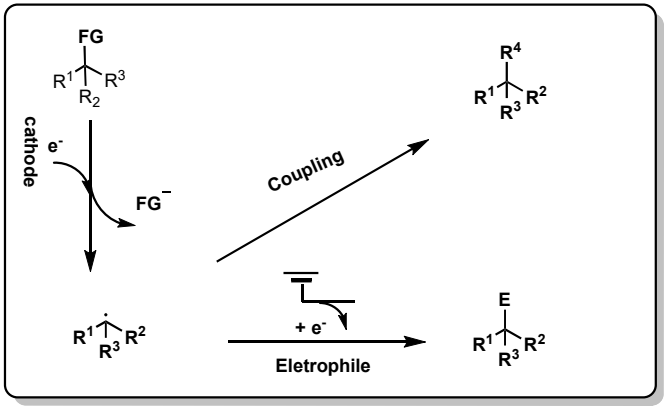
Zhang ACIE 2021, 60, 7275



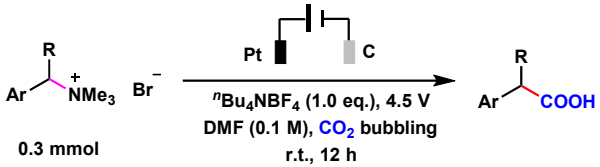
R^1= Aryl, Alkyl
R^2= H, Me

Xia OL 2021,23,3472

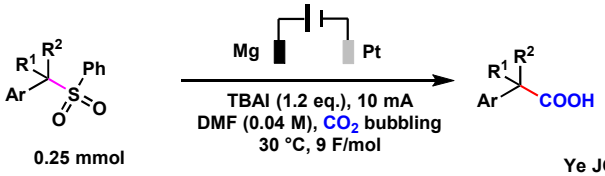
3. Reaction involving alkyl radical



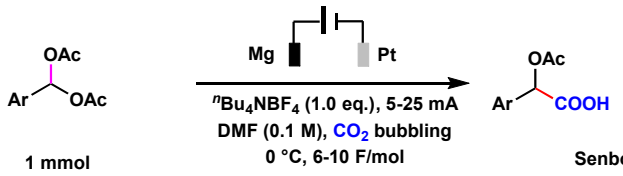
3.1 Electroreductive Carboxylation



ACS Catal. 2019, 9, 5, 4699-4705

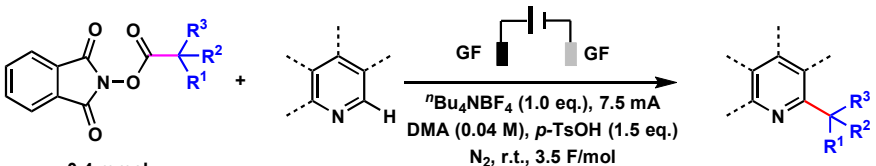


Ye JOC 2021, 86, 16162



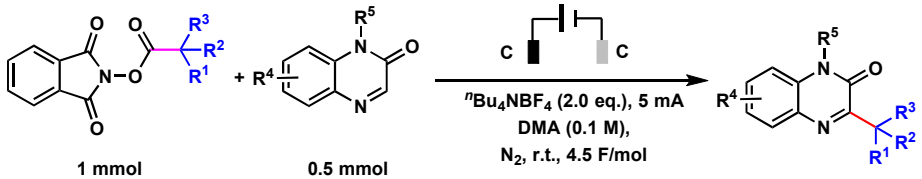
Senboku CEC 2019, 6, 4158

3.2 Electrochemical Minisci-type alkylation



0.4 mmol 0.2 mmol

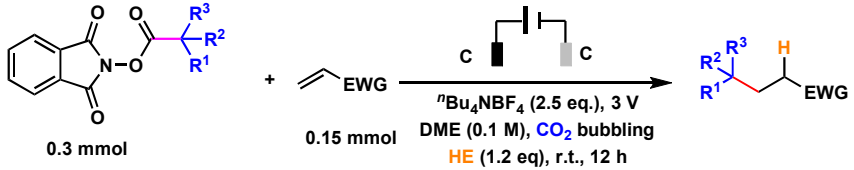
Lei CC 2019, 55, 14922



1 mmol 0.5 mmol

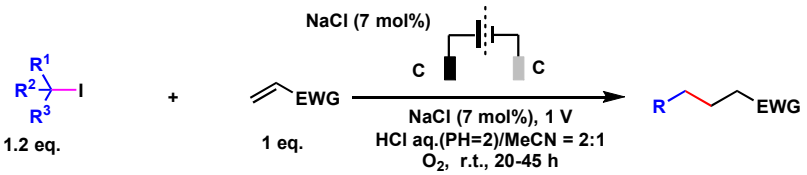
Wang CC 2020, 56, 11673

3.3 Electrochemical Giese-type reaction



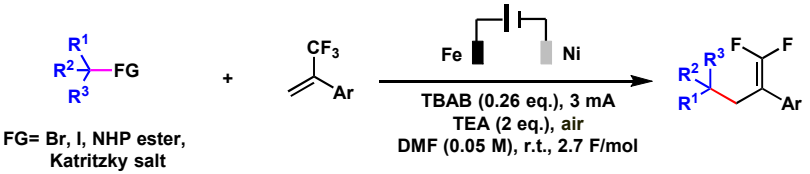
0.3 mmol 0.15 mmol

Wang CEJ 2020, 26, 3226



1.2 eq. 1 eq.

Wilden CS 2020, 11, 5333

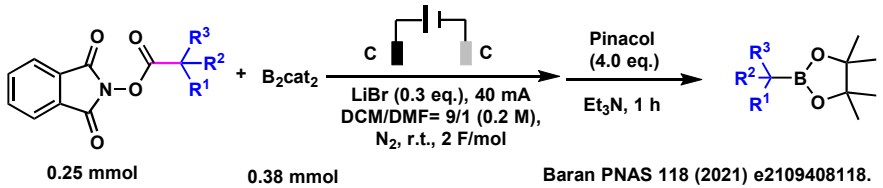


FG= Br, I, NHP ester, Katritzky salt

0.9 mmol 0.5 mmol

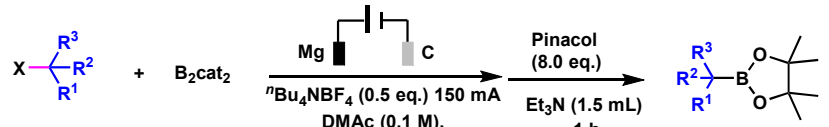
Xia OCF 2022, 9, 95

3.4 Electrochemical alkyl borylation



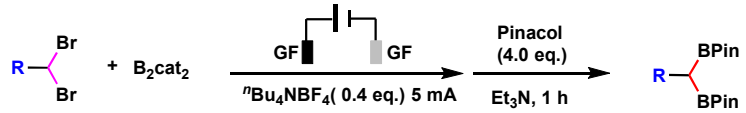
0.25 mmol 0.38 mmol

Baran PNAS 118 (2021) e2109408118.



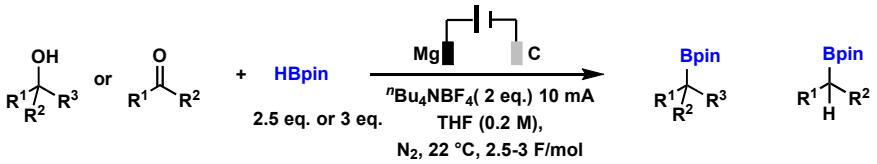
0.6 mmol 2.4 mmol

Lu JACS 2021, 143, 12985



1.5 mmol 4.5 mmol

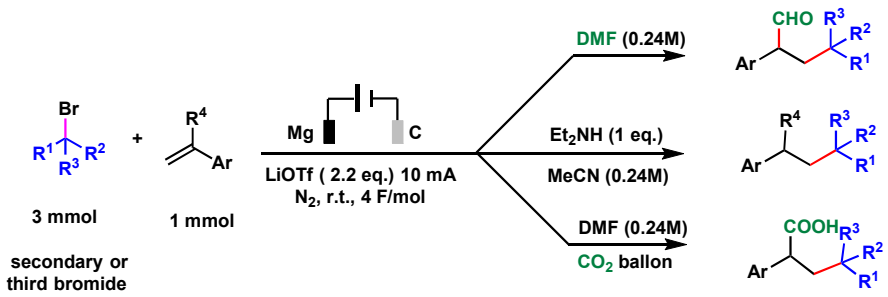
Lu ACIE 2023, 62, e2022181



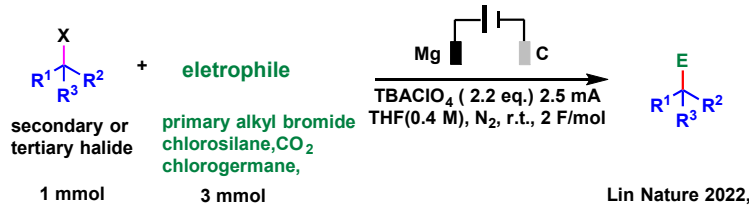
2.5 eq. or 3 eq.

Lin JACS 2023, 145, 16966

3.5 Electroreductive Cross-Electrophile Coupling involving alkyl halides



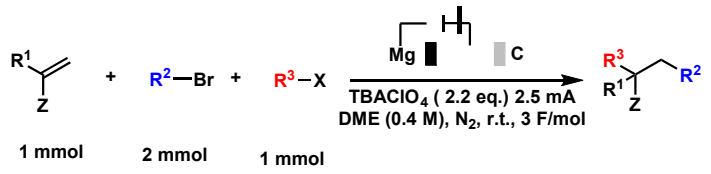
Lin JACS 2020, 142, 20661



Lin Nature 2022, 604, 292

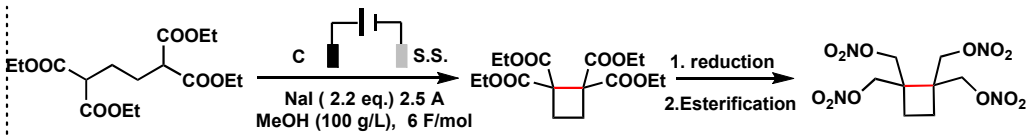
1. Introducing an anion-stabilizing substituents(boryl, aryl, vinyl, alkynyl and silyl) to lower the potential for the second reduction.

2. This stabilization effect also further augments the reduction potential difference between the two alkyl halide couplingpartners and, thus, ensures highchemoselectivity.



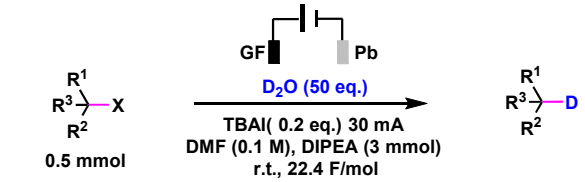
Lin JACS 2023, 145, 41, 22298

Z: radical/anion-stablizing group
R^2: secondary/tertiary alkyl
R^3: primary alkyl, methyl; X: Br, OTs



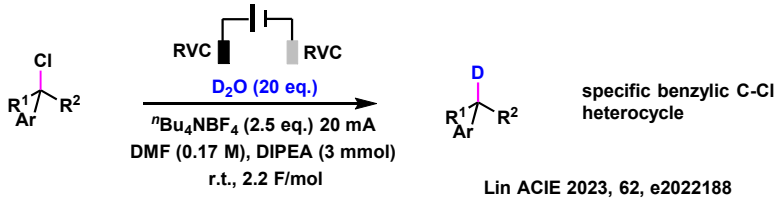
Baran OPRD 2021, 25, 2639

3.6 Electrochemical deuteration of alkyl halides



X = Cl, Br, I, OMs
Alkyl = 1°, 2°, 3°

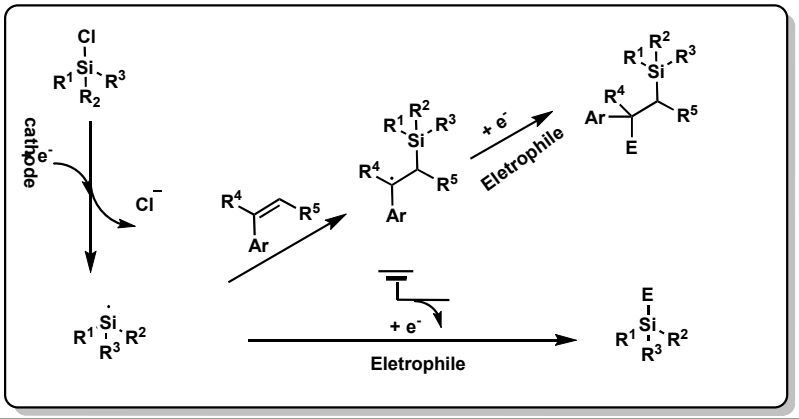
Qiu NC 2022, 13, 3774

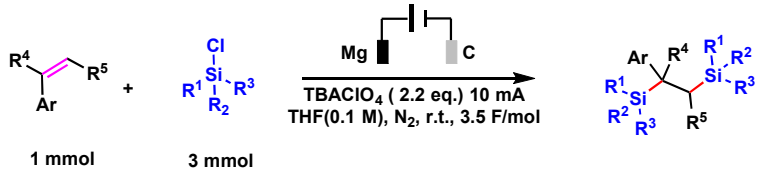


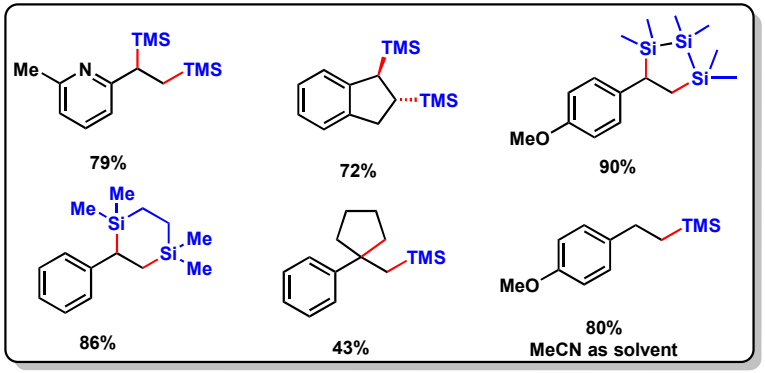
specific benzylic C-Cl heterocycle

Lin ACIE 2023, 62, e2022188

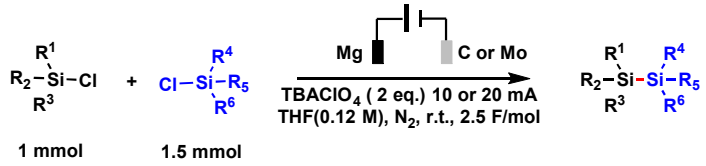
4 Reaction involving silyl radicals via electroreduction

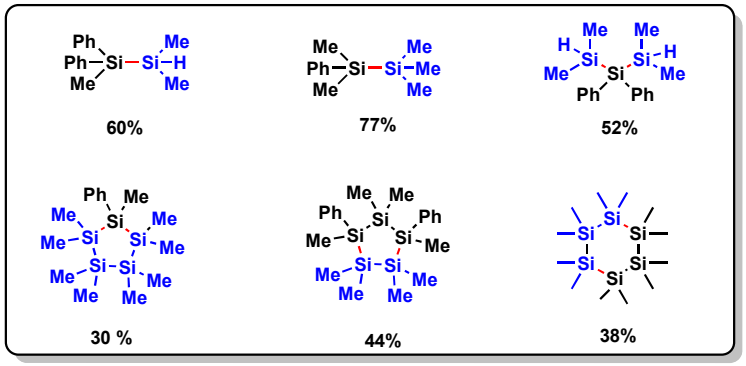






Lin JACS 2020, 142, 21272

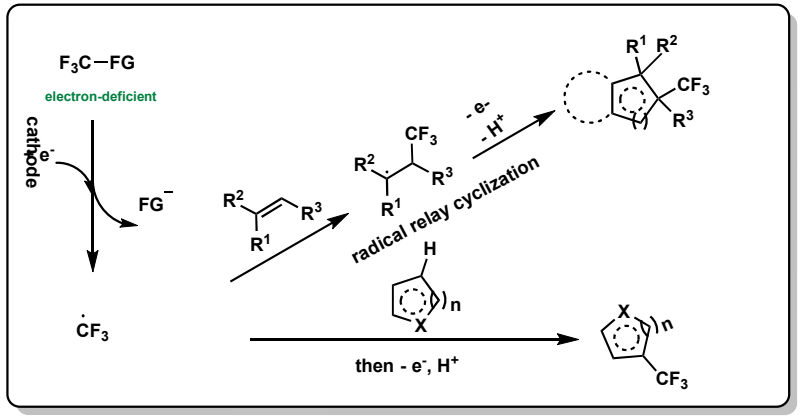


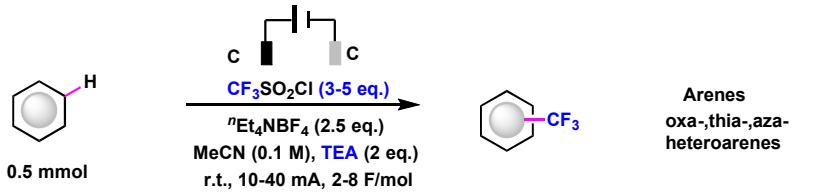


distinct electronic and steric properties of chlorosilanes with different structures

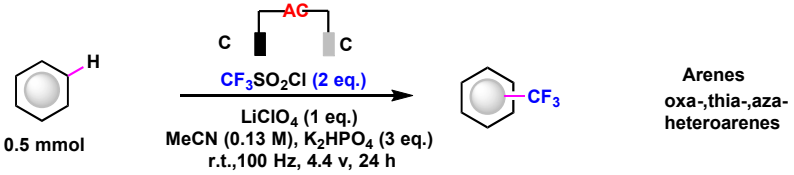
Lin ACIE 2023,62, e2023035

5 Reaction involving trifluoromethyl radicals via electroreduction



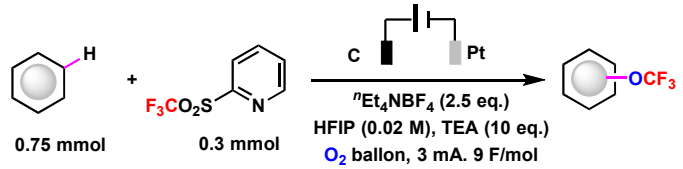


Cantillo OL 2019 21, 7970



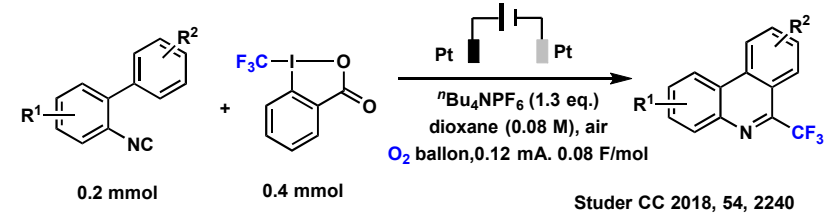
DC: 13%
AC: 84%

Luo OL 2020, 22, 6719



eletron-dificient arenes
heteroarenes

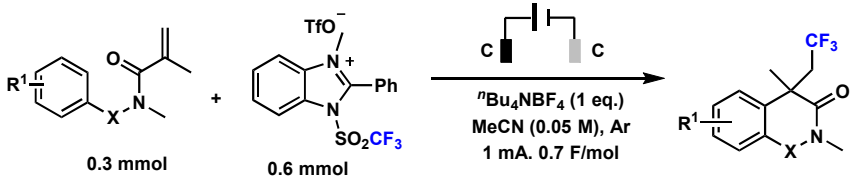
Qing ACIE 2022,61,e202114048



0.2 mmol

0.4 mmol

Studer CC 2018, 54, 2240



0.3 mmol

0.6 mmol

X: none
CO

Wang CC 2021, 57, 8284