Topic：梅天胜教授对于电化学催化的研究进展

李蔚鹏

2023.6.21

Part 1. 梅天胜

1997/9 – 2001/7
兰州大学，化学，学士
2001/9 – 2005/7
兰州大学，化学系，助理研究员, 导师：李裕林
2005/9 – 2007/7
Brandeis University，有机化学，硕士，导师：余金权
2007/8 – 2012/2
The Scripps Research Institute，有机化学，博士，导师：余金权
2012/2 – 2014/10
University of Utah，化学系，博士后, 导师：Matt Sigman
2014/11 – 至今
中国科学院上海有机化学研究所，金属有机化学国家重点实验室，研究员

主要工作：金属有机电化学研究；二氧化碳电化学还原转化；电氧化、还原促进的不对称催化反应。

Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
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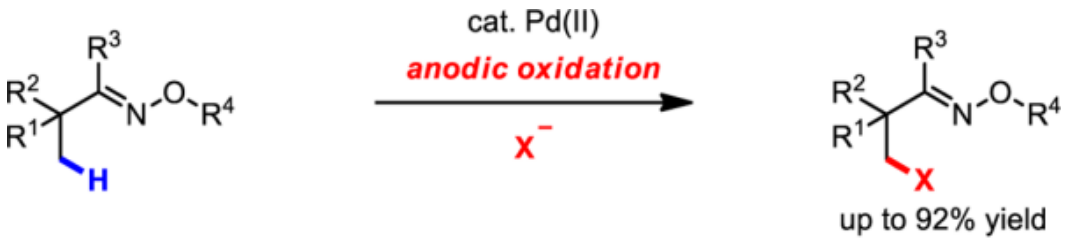
Palladium-Catalyzed C(sp^3)—H Oxygenation via Electrochemical Oxidation

Qi-Liang Yang,[†,‡] Yi-Qian Li,[†] Cong Ma,[†] Ping Fang,[†] Xiu-Jie Zhang,[†] and Tian-Sheng Mei*[,†]



J. Am. Chem. Soc. 2017, 139, 8, 3293–3298

Pd(II)在电化学条件下催化C(sp3)-H与各种氧离子氧化的第一个例子

Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化

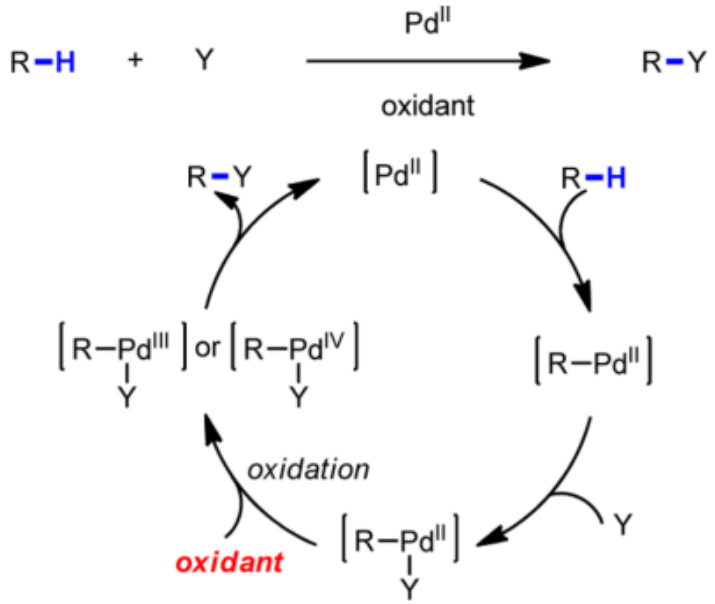
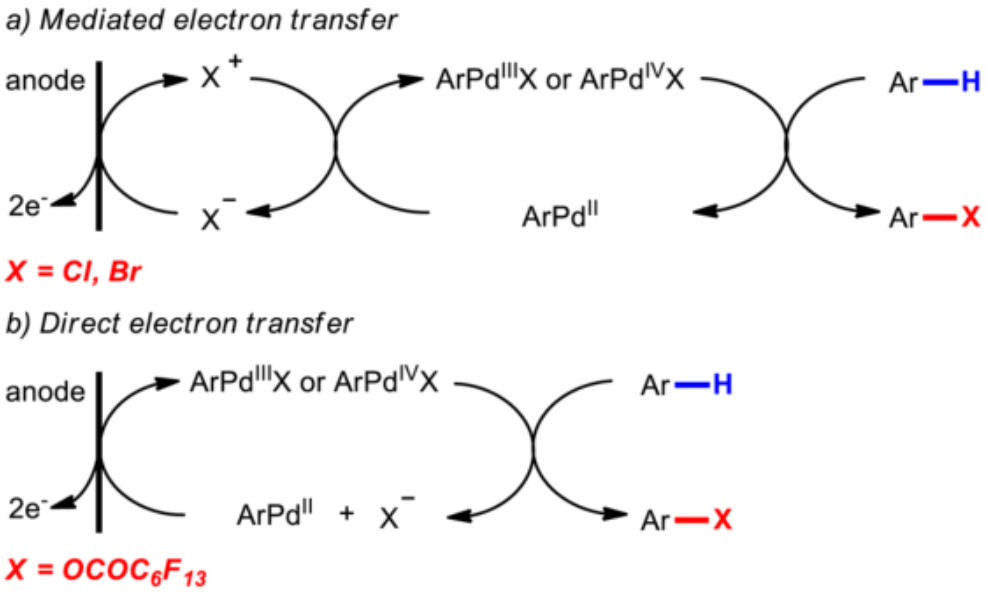


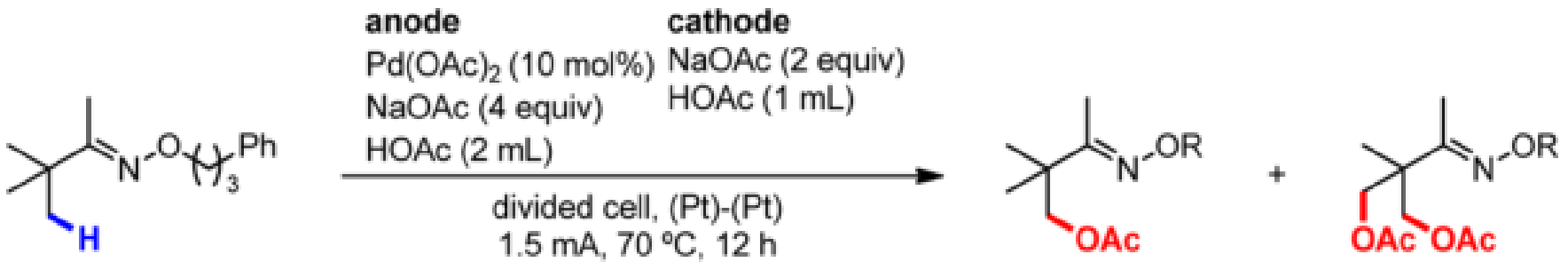
Figure 1. Pd^{II}/Pd^{IV} or Pd^{II}/Pd^{III} catalytic cycles.

氧化循环



电化学氧化法

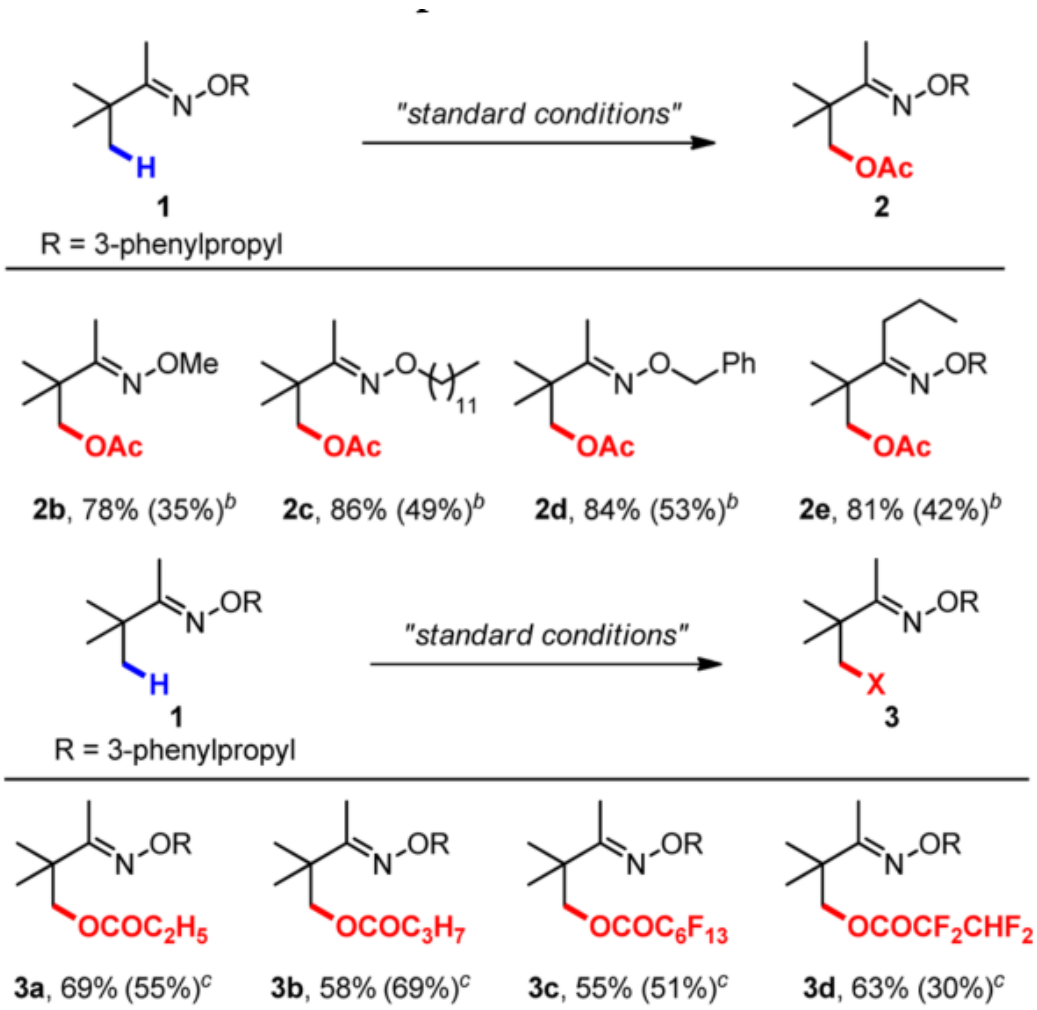
Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化

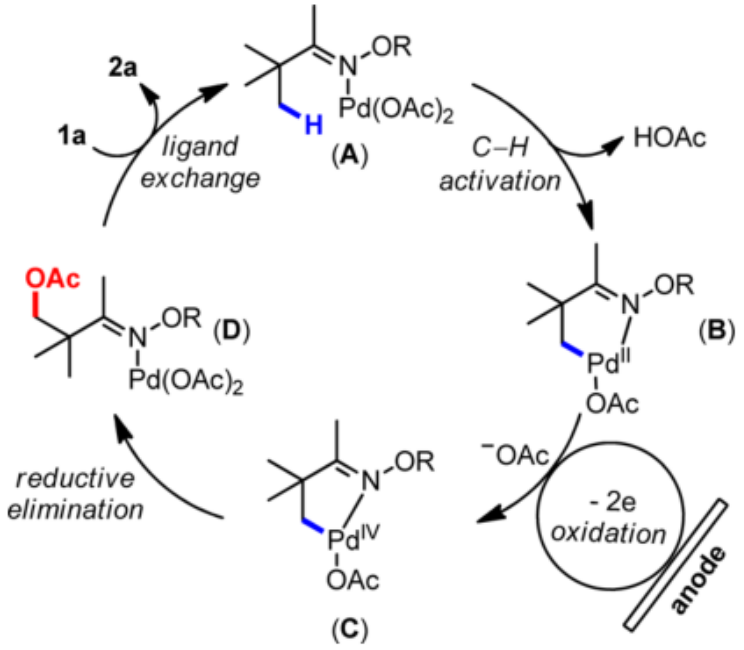


1a **2a** **2aa**

entry	deviation from above conditions	F/mol	yield (%)[b] 2a	2aa
1	none	2.2	84 (82)[c]	5
2	5 mol % $Pd(OAc)_2$ in lieu of 10 mol % $Pd(OAc)_2$	2.2	66	<5
3	10 mol % $PdCl_2$ in lieu of 10 mol % $Pd(OAc)_2$	2.2	66[d]	5
4	KOAc in lieu of NaOAc	2.2	68	8
5	LiOAc in lieu of NaOAc	2.2	74	10
6	CsOAc in lieu of NaOAc	2.2	75	12
7	5 mA in lieu of 1.5 mA (4 h)	2.5	35	<5
8	3 mA in lieu of 1.5 mA (6 h)	2.2	64	<5
9	no electric current		<5	<5
10	no $Pd(OAc)_2$	2.2	<5	<5
11	no electric current, $PhI(OAc)_2$ (2 equiv)		28	56
12	no electric current, *t*-BuOOAc (2 equiv)		46	26
13	no electric current, $NaNO_3/O_2$		62 (53)[c]	30

Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化





Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化

Organic LETTERS

Letter

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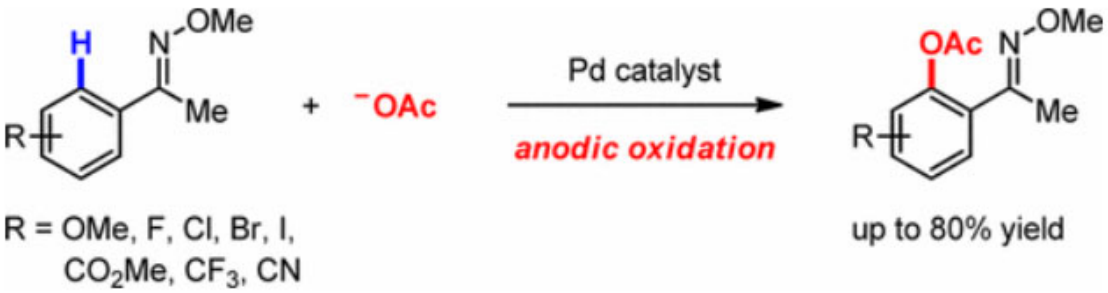
Palladium-Catalyzed C(sp^2)–H Acetoxylation via Electrochemical Oxidation

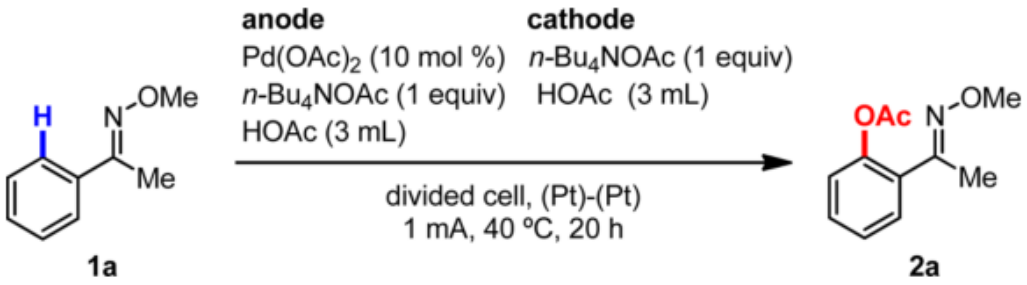
Yi-Qian Li,[†,‡] Qi-Liang Yang,[‡] Ping Fang,[‡] Tian-Sheng Mei,*[,‡] and Dayong Zhang*[,†]



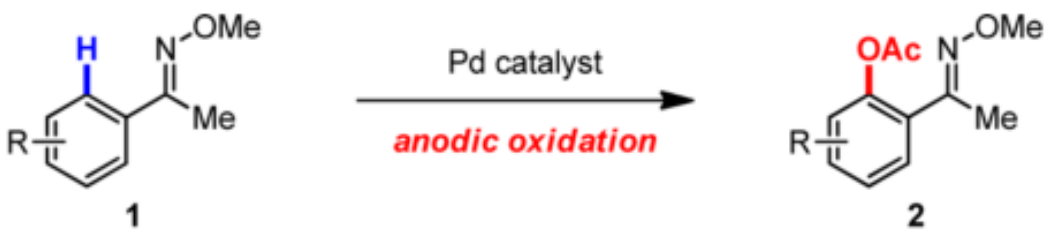
Org. Lett. 2017, 19, 11, 2905–2908

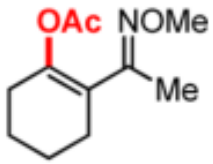
第一个通过阳极氧化的pd催化的氧导向C(sp2)–H乙酰氧基化

Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化



entry	variation from standard conditions above	yield (%)[b]
1	none	78 (75)[c]
2	10 mol % $Pd(TFA)_2$ instead of 10 mol % $Pd(OAc)_2$	74
3	10 mol % $Pd(dba)_2$ instead of 10 mol % $Pd(OAc)_2$	66
4	10 mol % $PdCl_2$ instead of 10 mol % $Pd(OAc)_2$	30
5	5 mol % $Pd(OAc)_2$ instead of 10 mol % $Pd(OAc)_2$	23
6	60 °C instead of 40 °C	69
7	25 °C instead of 40 °C	54
8	LiOAc instead of n-Bu_4NOAc	51
9	NaOAc instead of n-Bu_4NOAc	76
10	KOAc instead of n-Bu_4NOAc	59
11	n-Bu_4NBF_4 instead of n-Bu_4NOAc	14
12	n-Bu_4NCl instead of n-Bu_4NOAc	9
13	0.8 mA instead of 1 mA (25 h)	55
14	1.5 mA instead of 1 mA (19 h)	58
15	no electric current	NR
16	no $Pd(OAc)_2$	NR





2t, 53%[b]

钯催化肟基底物烯基C(sp2)–H键乙酰化的第一个例子。

Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化

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rsc.li/chemcomm

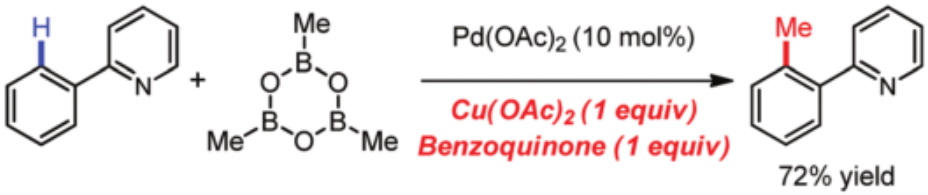
Palladium-catalyzed C–H activation/C–C cross-coupling reactions *via* electrochemistry†

Cong Ma,‡[a] Chuan-Qi Zhao,‡[a] Yi-Qian Li,[bc] Li-Pu Zhang,[bc] Xue-Tao Xu,[bc] Kun Zhang[bc] and Tian-Sheng Mei*[a]

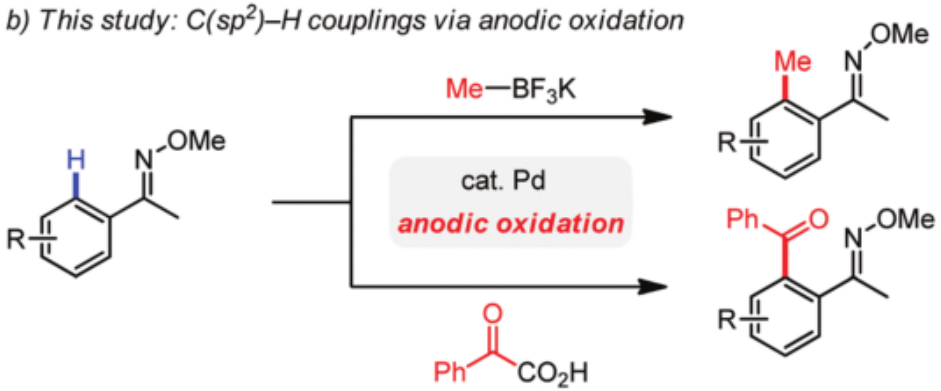
Pd(II)通过阳极氧化催化C(sp2) -H甲基化和酰化的第一个例子

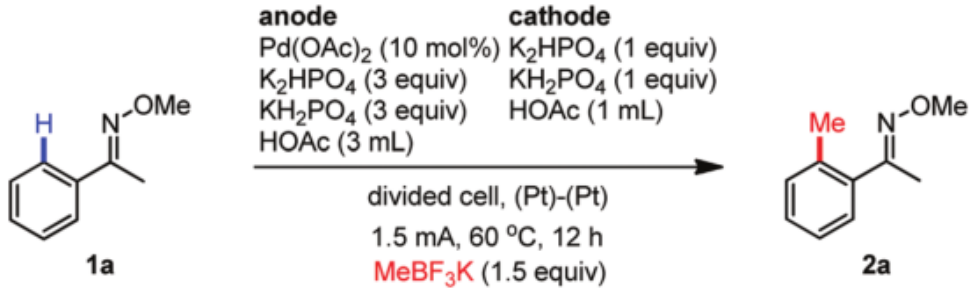
Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化

a) Pioneering work on Pd-catalyzed C(sp^2)–H cross-couplings (ref. 4)



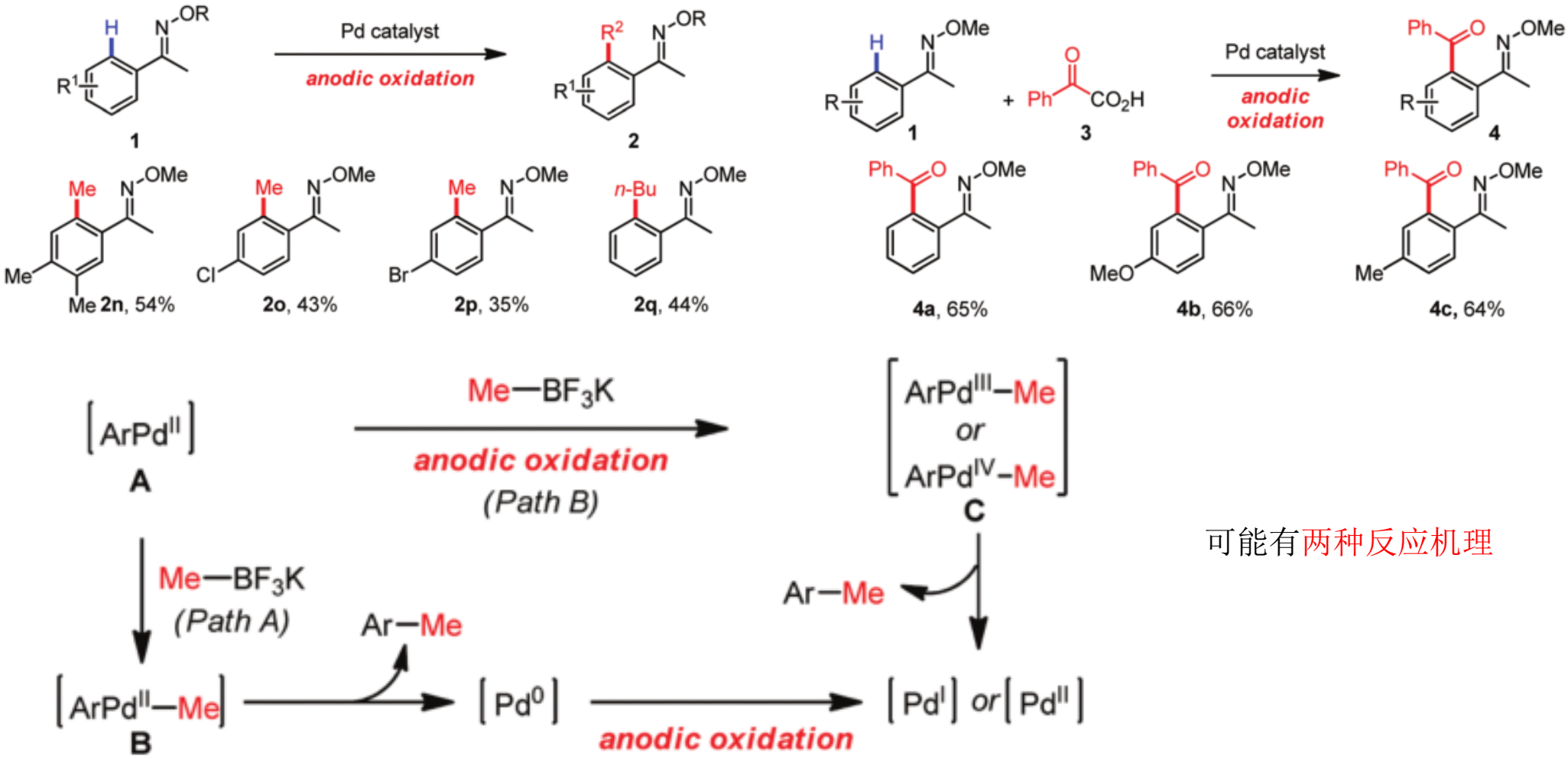
b) This study: C(sp^2)–H couplings via anodic oxidation





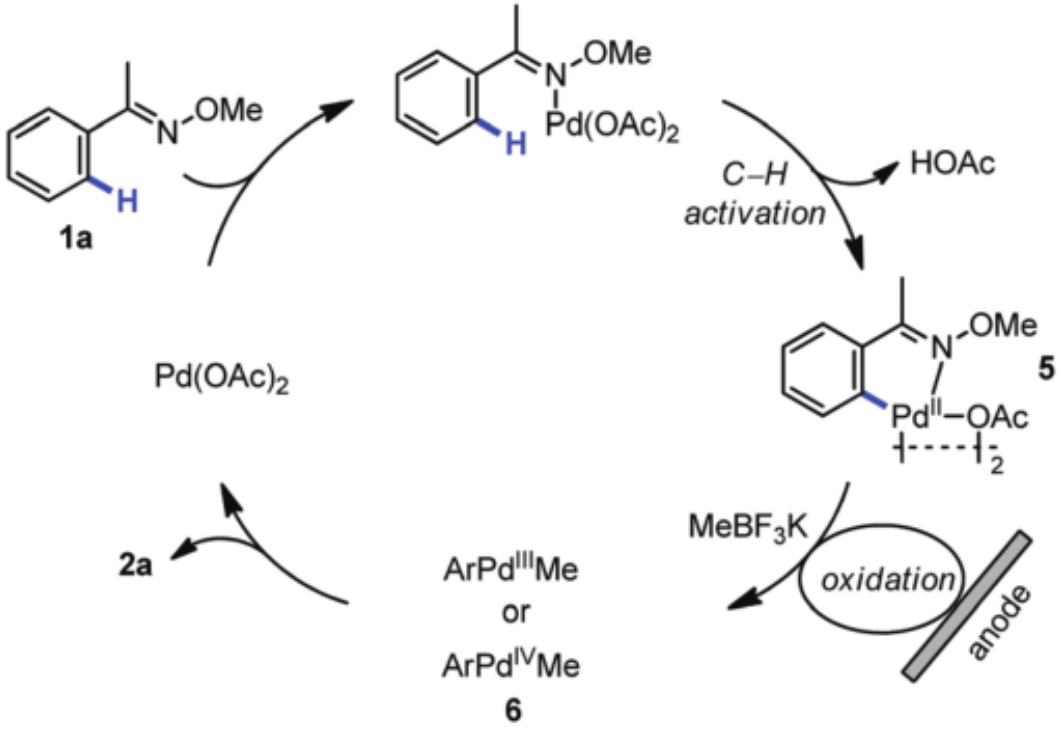
Entry	Variation from the above standard conditions	Yield[b] (%)
1	None	89[c] (79)
2	5 mol% $Pd(OAc)_2$ instead of 10 mol% $Pd(OAc)_2$ (36 h)	75
3	10 mol% $Pd(OTf)_2$ instead of 10 mol% $Pd(OAc)_2$	Trace
4	KH_2PO_4 instead of KH_2PO_4 and KH_2PO_4	45
5	KH_2PO_4 instead of K_2HPO_4 and KH_2PO_4	77
6	2 mA instead of 1.5 mA (9 h)	69
7	1.0 mA instead of 1.5 mA (16 h)	54
8	$MeB(OH)_2$ instead of $MeBF_3K$	NR
9	$(MeBO)_3$ instead of $MeBF_3K$	NR
10	DMF instead of AcOH	NR
11	TFE instead of AcOH	NR
12	No electric current	NR
13	No $Pd(OAc)_2$	NR
14	MnF_3 (4 equiv.), TFE/AcOH/H_2O	Hydrolysis
15	MnF_3 (4 equiv.), TFE/AcOH	NR

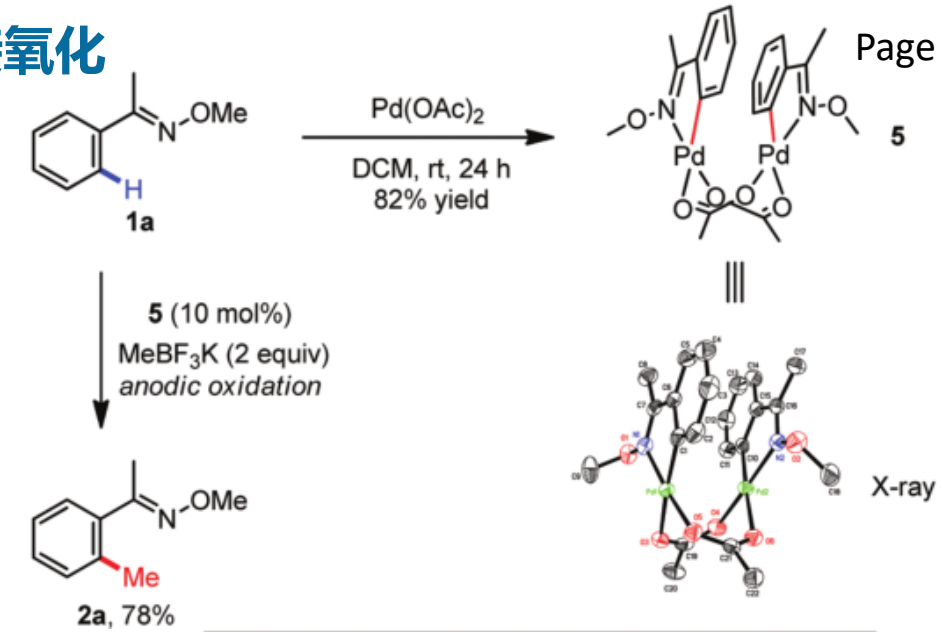
Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化

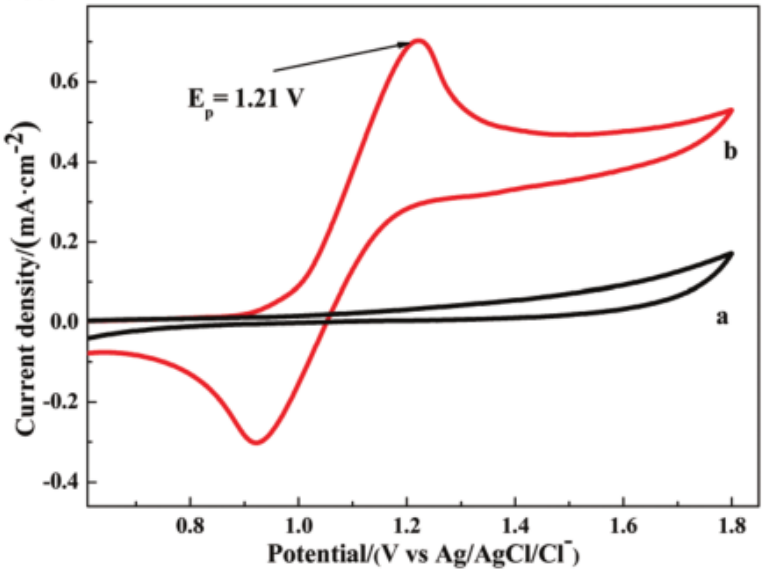


可能有两种反应机理

Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化







Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化

ORGANOMETALLICS

Communication

Cite This: *Organometallics* 2019, 38, 1208–1212

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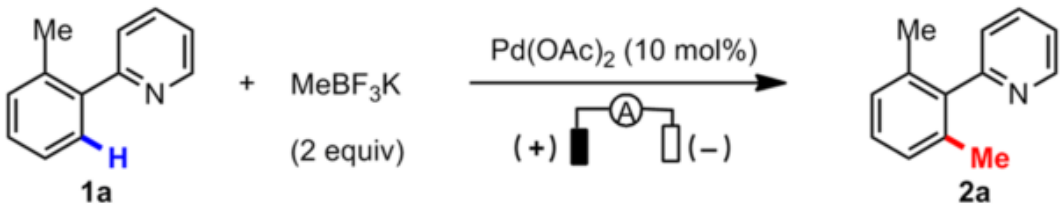
Palladium-Catalyzed Electrochemical C–H Alkylation of Arenes

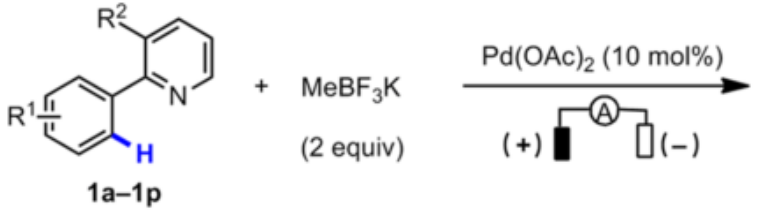
Qi-Liang Yang,[†,‡] Chuan-Zeng Li,[‡,§] Liang-Wei Zhang,[‡] Yu-Yan Li,[*,§] Xiaofeng Tong,[†] Xin-Yan Wu,[*,†] and Tian-Sheng Mei[*,‡]

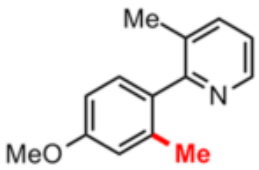
使用未拆分的电化学池在水中钯催化的芳烃电化学C(sp2)–H烷基化的第一个例子

Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化

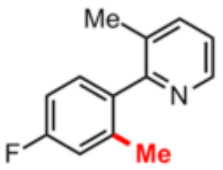


entry	variation from standard conditions	yield (%)[b]
1	none	75 (70)[c]
2	0.5 mA instead of 1 mA	67
3	1.5 mA instead of 1 mA	63
4	40 °C instead of 60 °C	34
5	80 °C instead of 60 °C	32
6	TFE/AcOH = 2.25 mL/2.25 mL instead of TFE/AcOH/H_2O = 2 mL/2 mL/0.5 mL	65
7	TFE/H_2O = 2.25 mL/2.25 mL instead of TFE/AcOH/H_2O = 2 mL/2 mL/0.5 mL	52
8	AcOH/H_2O = 2.25 mL/2.25 mL instead of TFE/AcOH/H_2O = 2 mL/2 mL/0.5 mL	64
9	no $Pd(OAc)_2$	nr
10	no electric current	nr

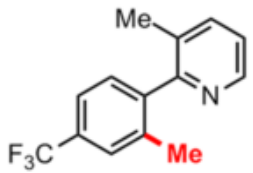




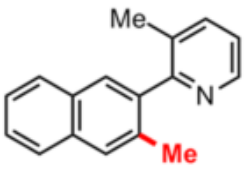
2m, 68%



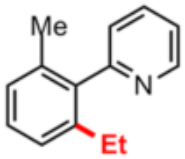
2n, 55%



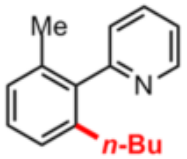
2o, 50%



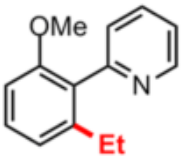
2p, 61%



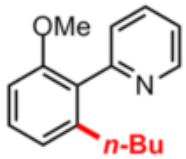
3a, 69%



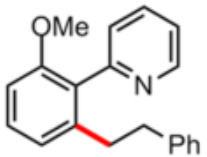
3b, 56%



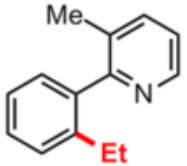
3c, 52%



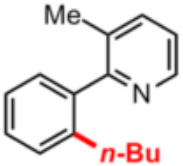
3d, 38%



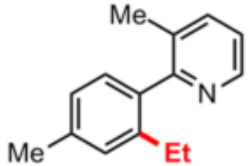
3e, 20%



3f, 50%



3g, 52%



3h, 62%

Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化

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SPECIAL ISSUE: In Honor of Professor Lixin Dai on the Occasion of His 100th Birthday

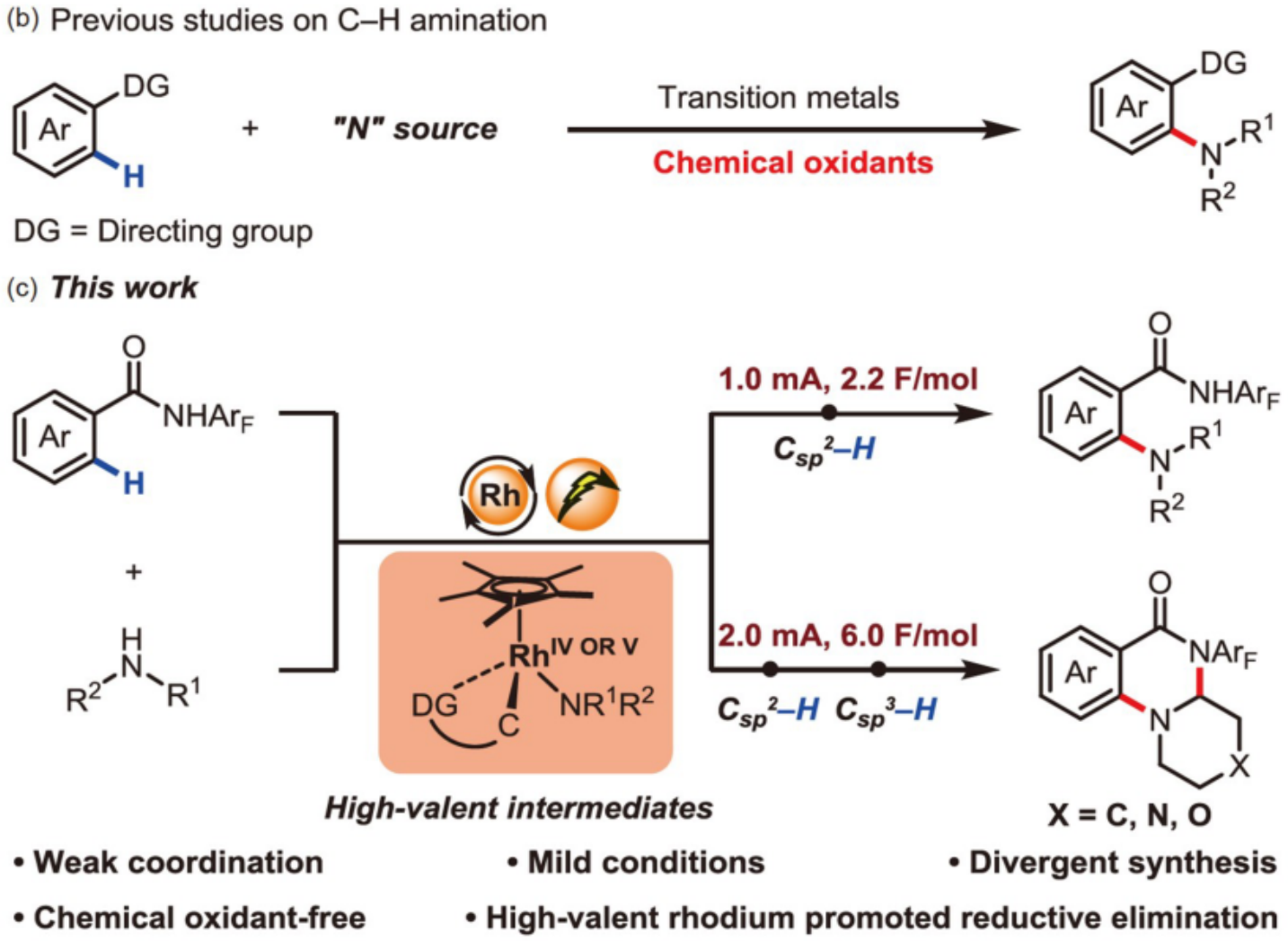
October 2023 Vol.66 No.10: 2863–2870
https://doi.org/10.1007/s11426-023-1603-9

Divergent synthesis of aryl amines and dihydroquinazolinones *via* electrochemistry-enabled rhodium-catalyzed C–H functionalization

Yi-Kang Xing, Zhen-Hua Wang, Ping Fang, Cong Ma & Tian-Sheng Mei*

第一个通过电化学弱配位催化的Rh催化的C - H胺化的例子

Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化



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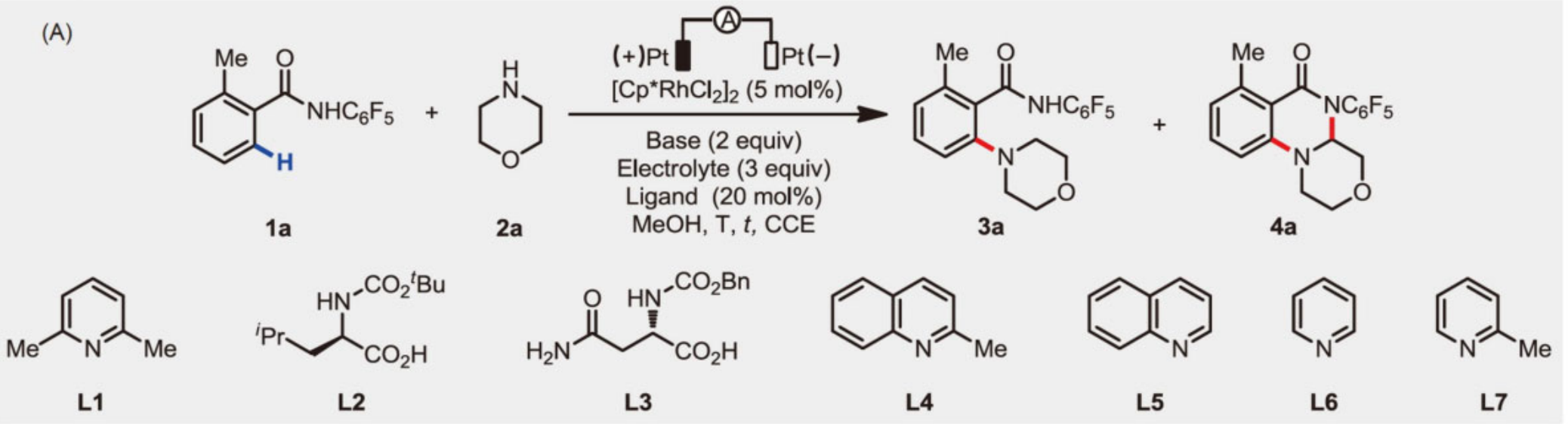
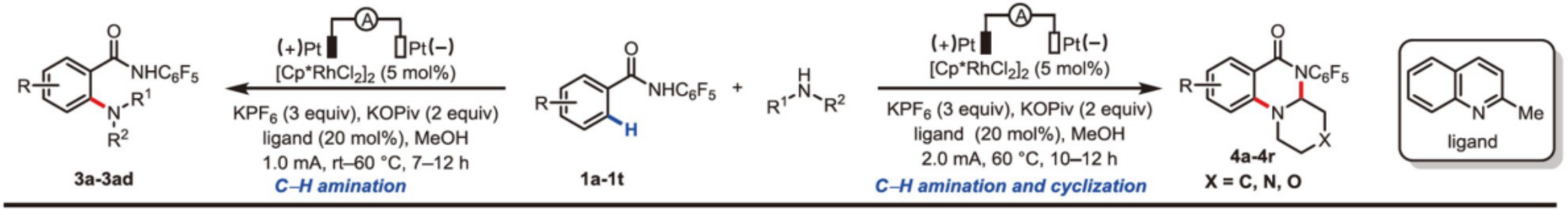
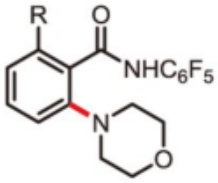


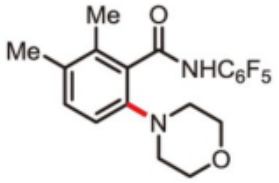
Entry	Ligand	Base	Electrolyte	*I* (mA)	*T* (°C)	*t* (h)	Yield (%)[b]	
							3a	**4a**
1	**L1**	$PhCO_2Na$	*n*-Bu_4NBF_4	2	80	10	35	52
7[c]	**L4**	KOPiv	KPF_6	1	60	7	84 (80)[d]	12
12[c]	**L4**	KOPiv	KPF_6	1	rt	7	64	12
13[c]	**L4**	KOPiv	KPF_6	2	60	10	-	81 (76)[d]

Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化

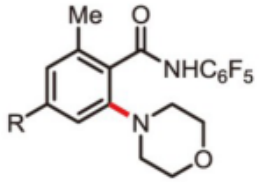




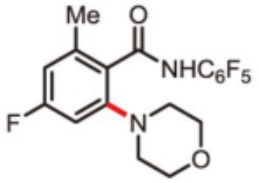
R = Me, **3a**, 80% (7:1); 62% (5:1)[c)]
R = F, **3b**, 57% (5:1); 44% (4:1)[c)]
R = Cl, **3c**, 60% (8:1)
R = Br, **3d**, 50%
R = Ph, **3e**, 67% (5:1)



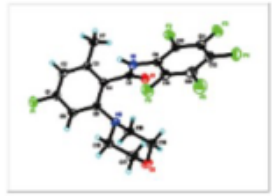
3f, 66% (4:1)



3g, R = Me, 70% (2:1); 64% (5:1)[c)]
3h, R = OMe, 82%
3i, R = NHBoc, 59% (3:1)



3j, 62%



CCDC 2162523

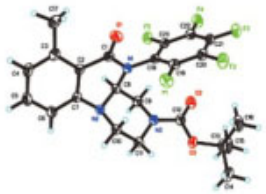
4n, 69%[b)]

4o, 30%[b)]

4p, 52%[b)]

4q, 52%[b)]

4r, 62%[b)]



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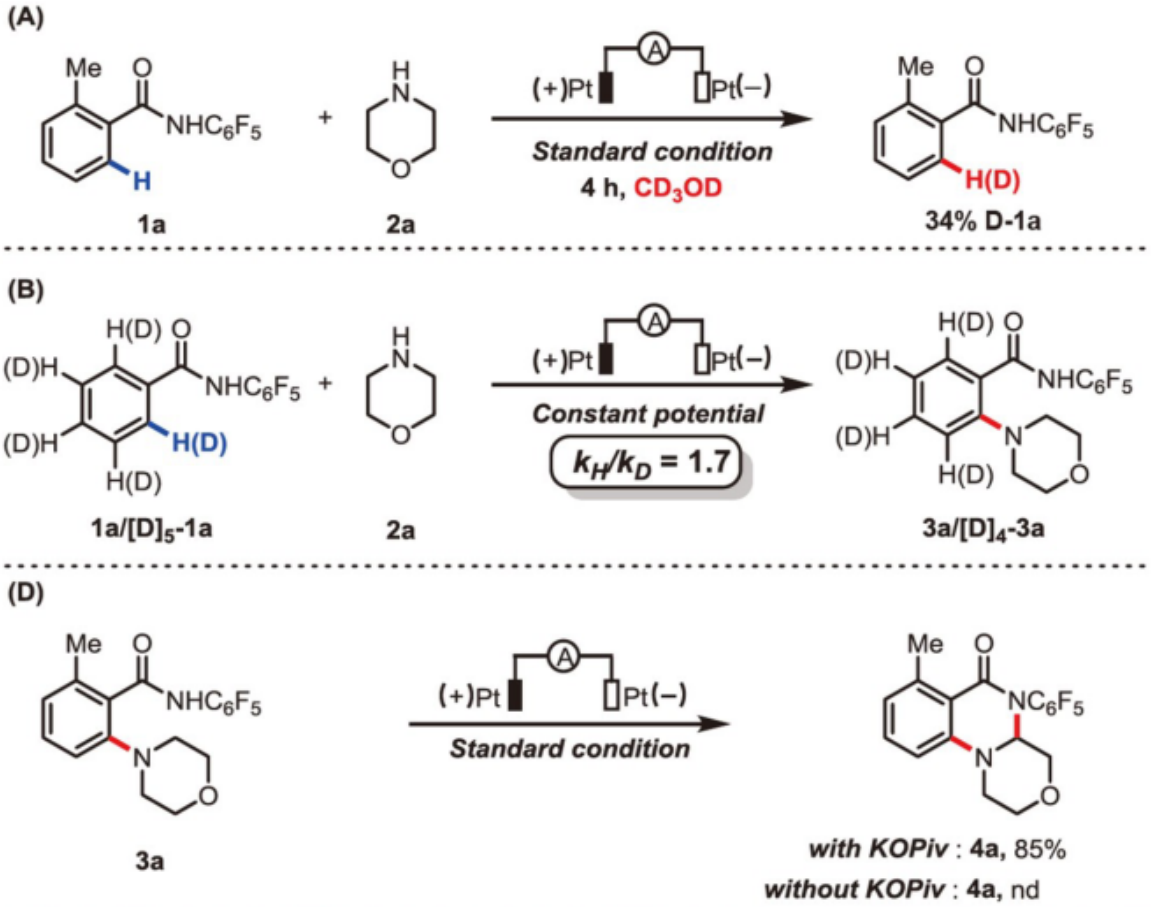
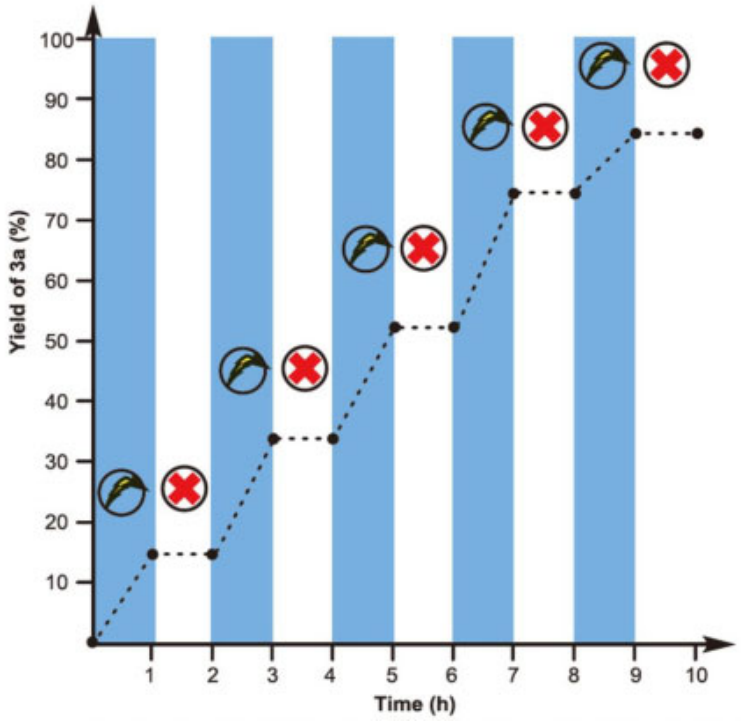
未取代苯胺不反应

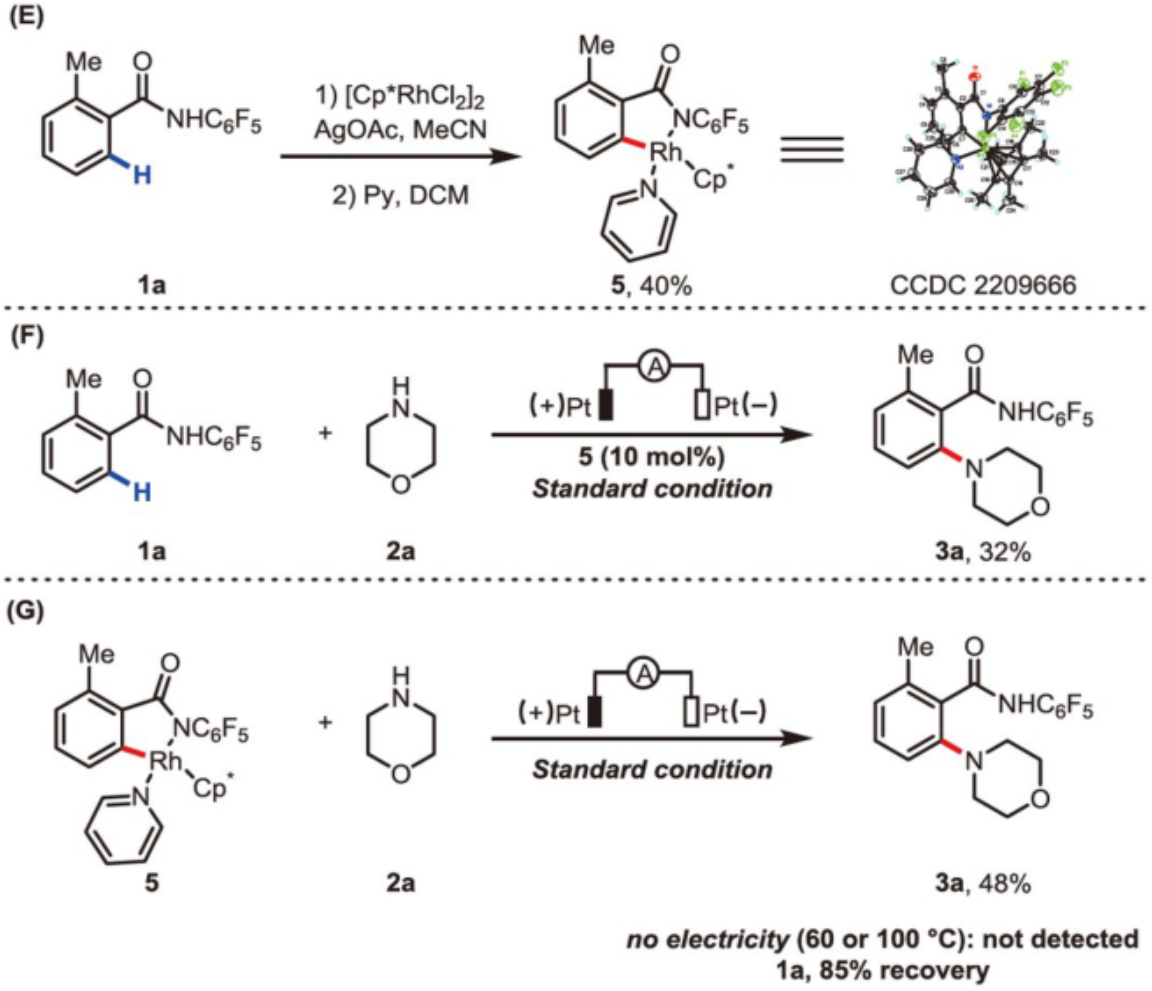
Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化

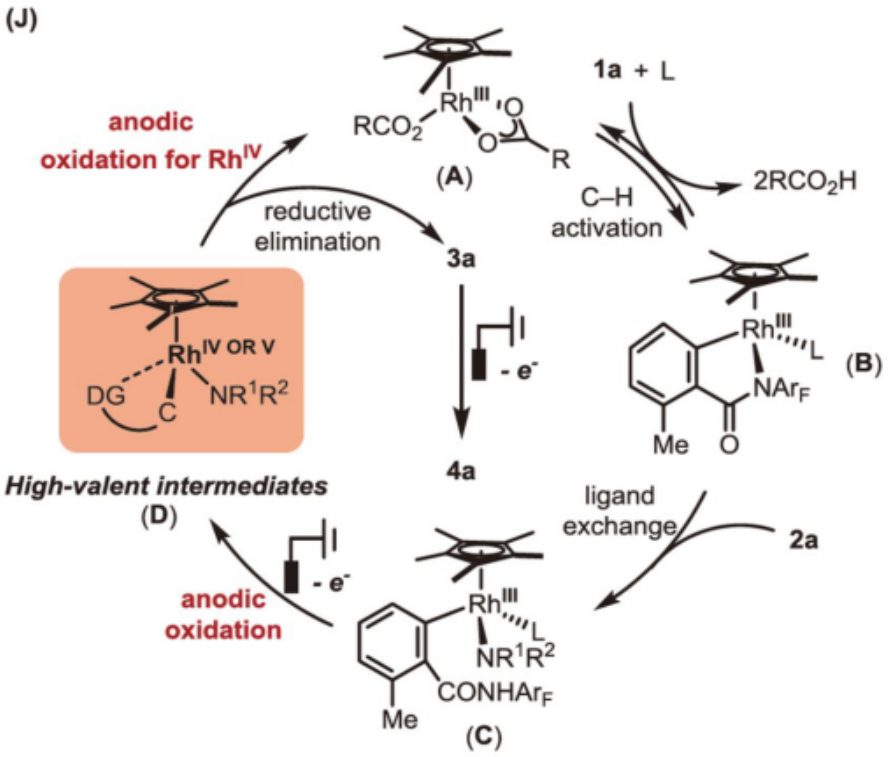


(C)



Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化





Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化

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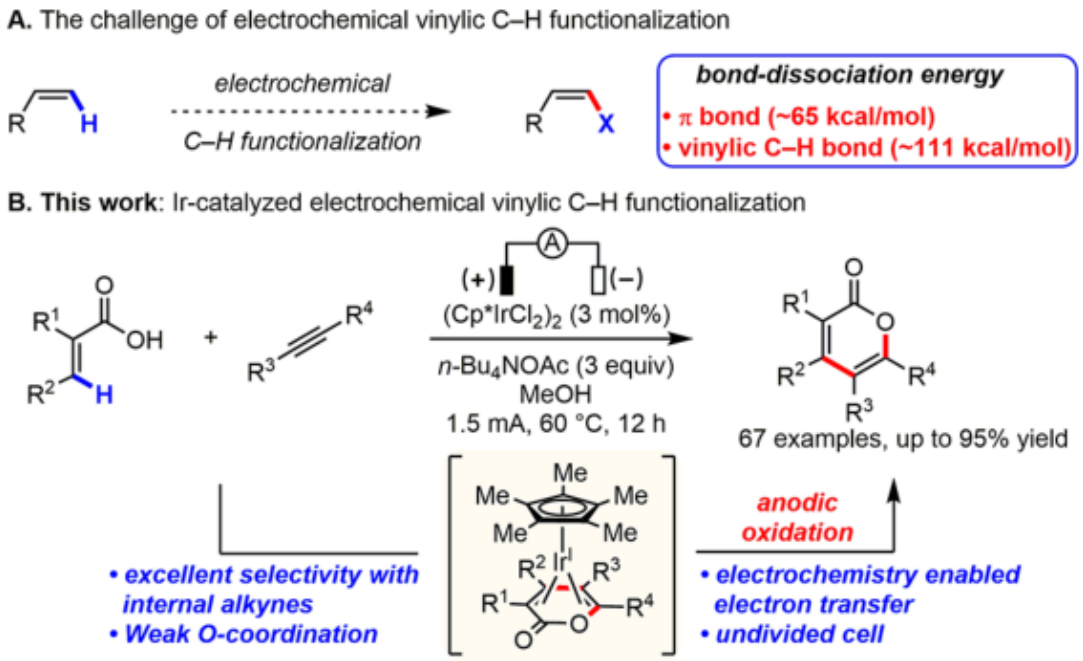
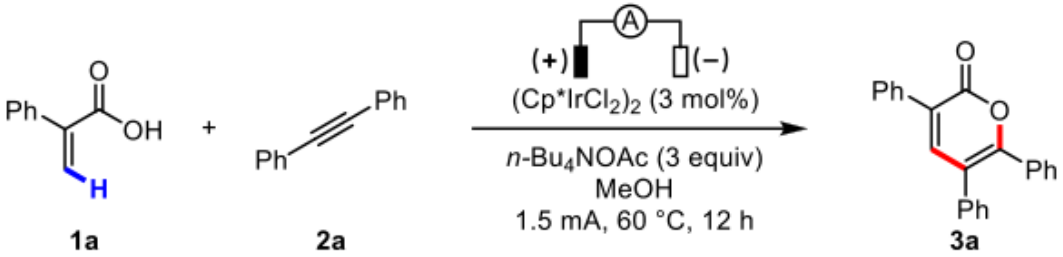
Electrochemistry-Enabled Ir-Catalyzed Vinylic C−H Functionalization

Qi-Liang Yang,[†,‡,§] Yi-Kang Xing,[†,§] Xiang-Yang Wang,[†] Hong-Xing Ma,[†] Xin-Jun Weng,[†] Xiang Yang,[†] Hai-Ming Guo,[‡] and Tian-Sheng Mei*[,†]

在未拆分的电化学池中丙烯酸与炔的Ir催化乙烯基C - H环化的第一个例子

Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化



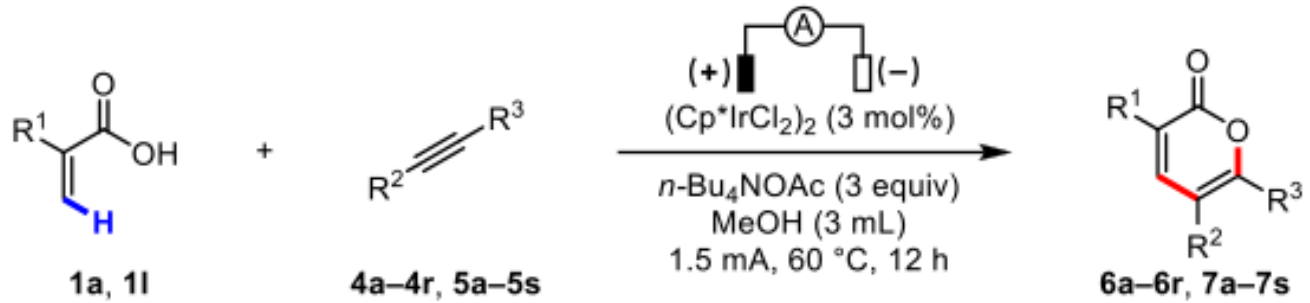


1a 2a 3a

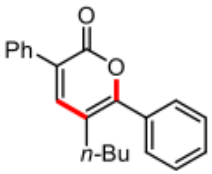
entry	variation from standard conditions[a]	yield[b] (%)
11	KOAc instead of n-Bu_4NOAc	92
12	n-Bu_4NBF_4 instead of n-Bu_4NOAc	<5
13	K_2CO_3 instead of n-Bu_4NOAc	<5
14	O_2 instead of electric current	<5
15	2 equiv of Ag_2CO_3 instead of electric current	<5
16	2 equiv of $Cu(OAc)_2$ instead of electric current	<5
17	2 equiv of $PhI(OAc)_2$ instead of electric current	18

Co、Ru、Rh和Pd催化下可以实现丙烯酸与炔的乙烯基C–H环形成α-吡啶酮，但迄今为止还没有实现Ir催化的相同转化

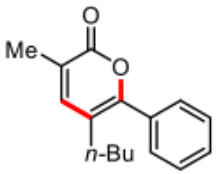
Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化



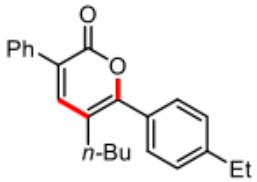
1a, 1l **4a–4r, 5a–5s** **6a–6r, 7a–7s**



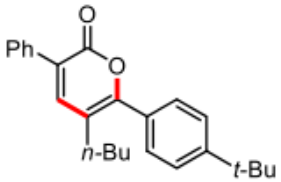
7c, [Ir]: 91% (20:1)
[Ru]: 58% (2.4:1)
[Co]: 66% (1:1.2)



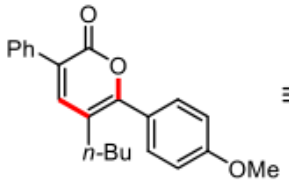
7d, [Ir]: 95% (20:1)
[Ru]: 42% (4:1)
[Co]: 32% (1:1)



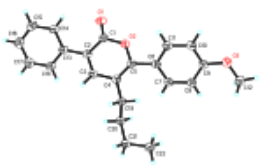
7e, [Ir]: 91% (15:1)
[Ru]: 46% (2.2:1)
[Co]: 36% (1:1.3)



7f, [Ir]: 83% (14:1)
[Ru]: 27% (2.5:1)
[Co]: 39% (1:1.3)



7g, [Ir]: 94% (18:1)
[Ru]: 57% (3:1)
[Co]: 88% (1:1.2)



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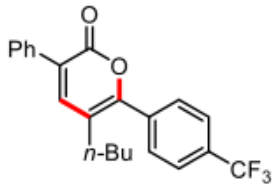
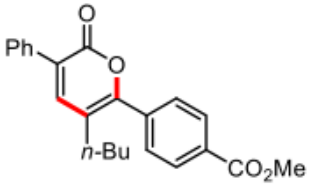
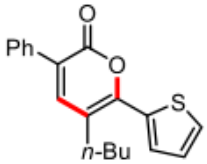


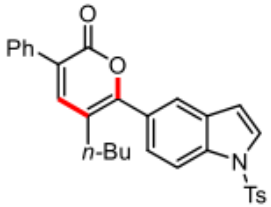
7h, [Ir]: 90% (20:1)
[Ru]: 21% (2:1)
[Co]: 52% (1:1.1)



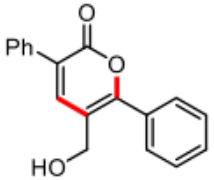
7i, [Ir]: 88% (25:1)
[Ru]: 77% (3:1)
[Co]: 70% (1:1.1)



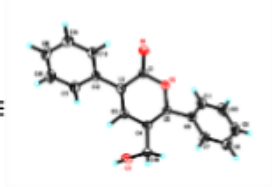
7j, [Ir]: 90% (20:1)
[Ru]: 83% (1.5:1)
[Co]: 75% (1:1)



7k, [Ir]: 94% (15:1)
[Ru]: 55% (3:1)
[Co]: 76% (1:1.3)



7l, [Ir]: 88% (10:1)
[Ru]: <5%
[Co]: 37% (1:4.7)



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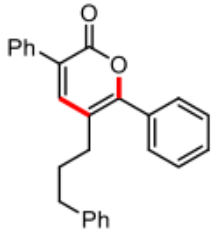
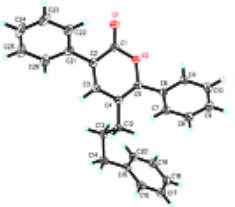
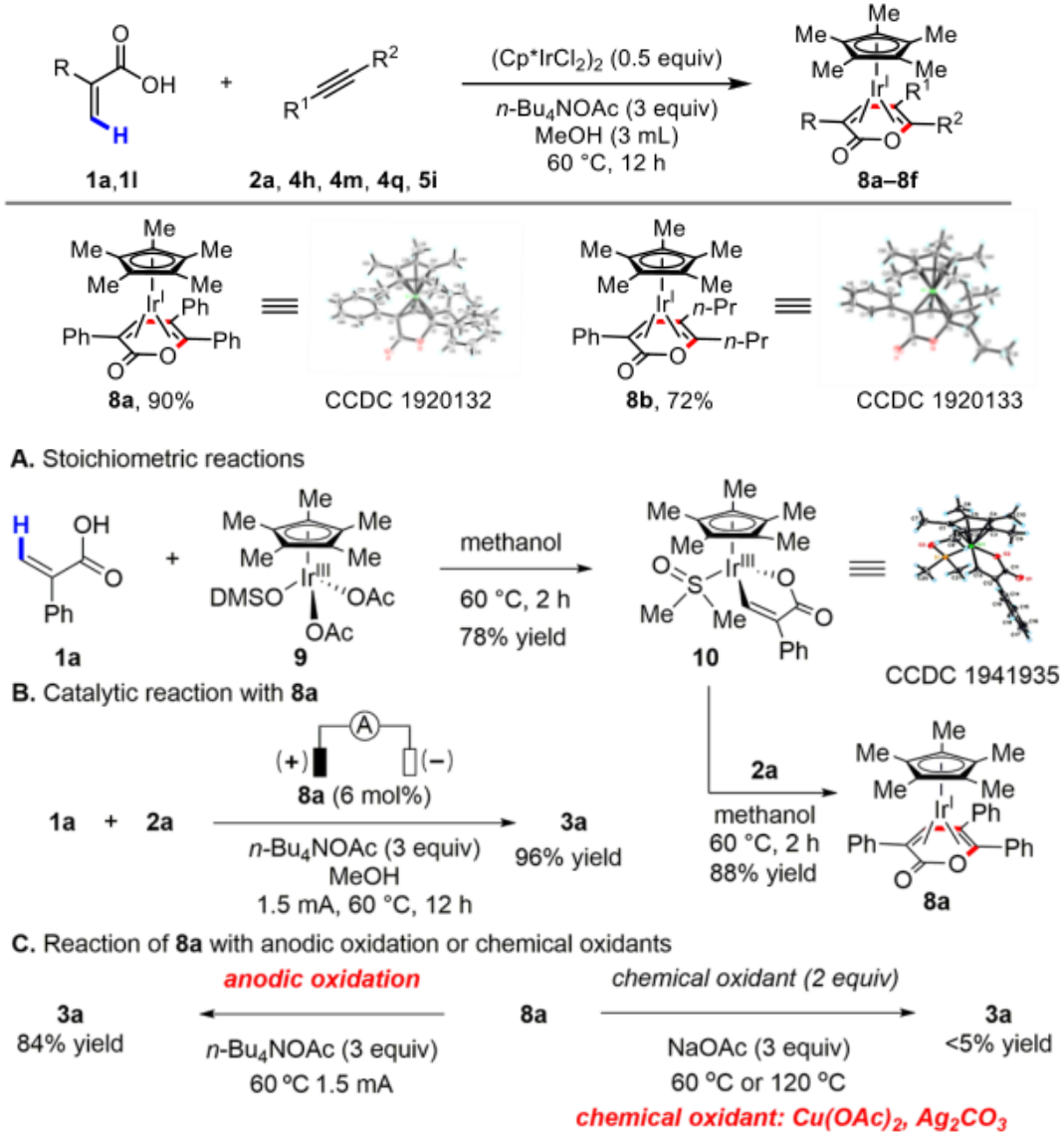


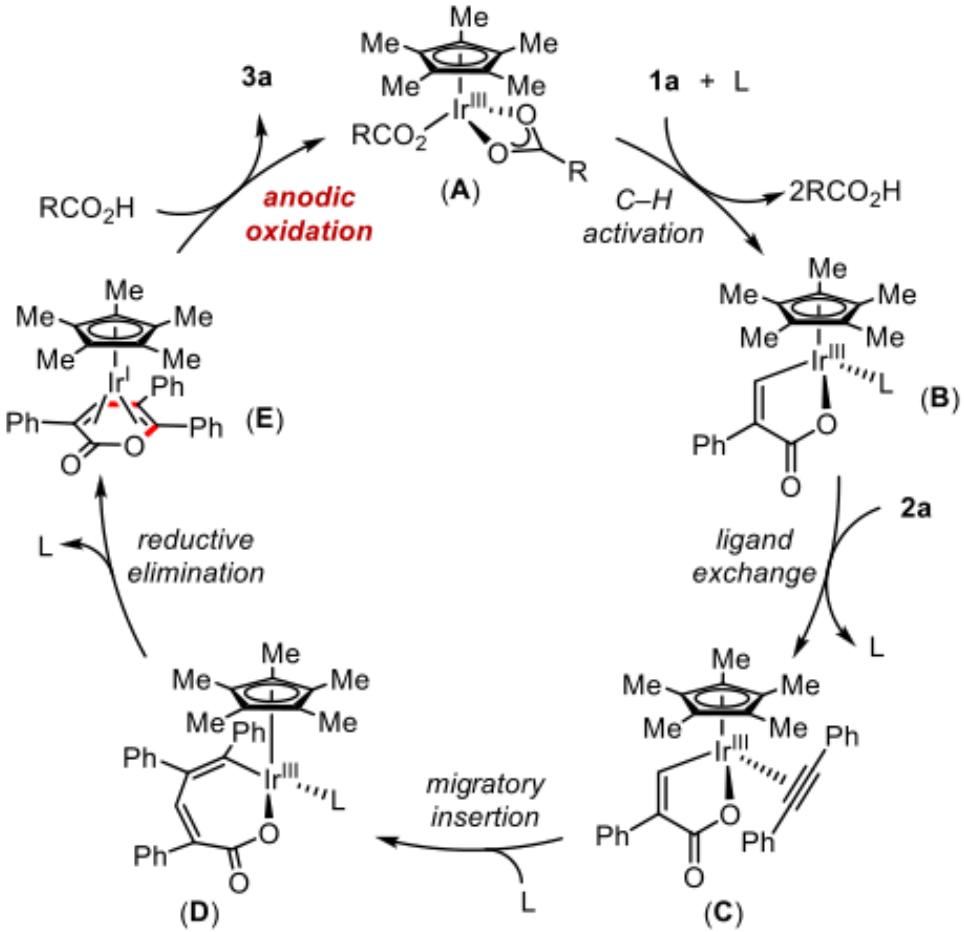
7m, [Ir]: 96% (25:1)
[Ru]: 34% (1.8:1)
[Co]: 68% (1.1:1)



CCDC 1941955

Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化





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Letter

Electrooxidative Iridium-Catalyzed Regioselective Annulation of Benzoic Acids with Internal Alkynes

Qi-Liang Yang,[#] Hong-Wei Jia,[#] Ying Liu, Yi-Kang Xing, Rui-Cong Ma, Man-Man Wang, Gui-Rong Qu, Tian-Sheng Mei,* and Hai-Ming Guo*

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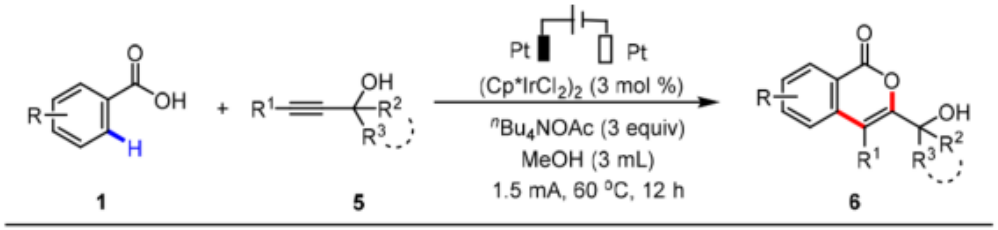
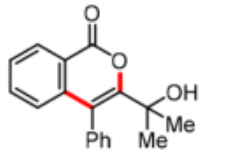
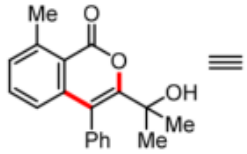
Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化



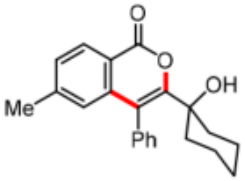


6a, 71%

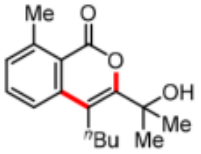


6b, 75%

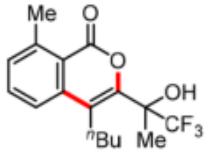
CCDC 2014259



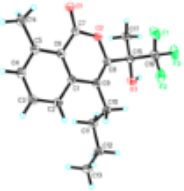
6c, 70%



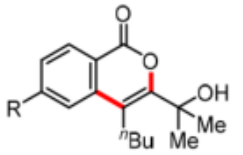
6j, 72%



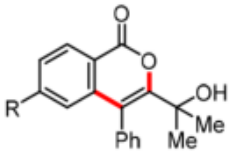
6k, 81%



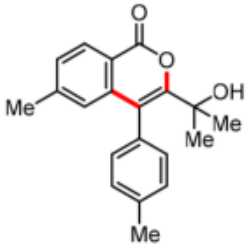
CCDC 2052477



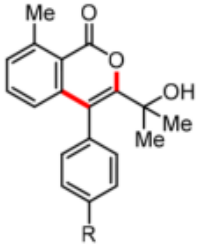
6l, R = Me, 86% (70%)[c]
6m, R = Cl, 59%



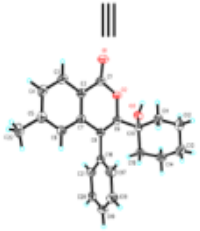
6d, R = OMe, 74%
6e, R = Br, 60%
6f, R = CF_3, 41%



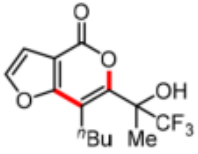
6g, 74%



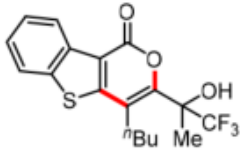
6h, R = OMe, 86%
6i, R = Cl, 69%



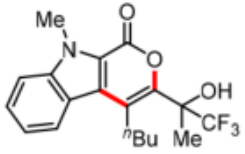
CCDC 2014257



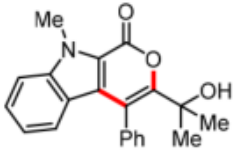
6n, 55%



6o, 31%



6p, 73%



6q, 52%

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https://doi.org/10.1038/s41467-021-21190-8 OPEN

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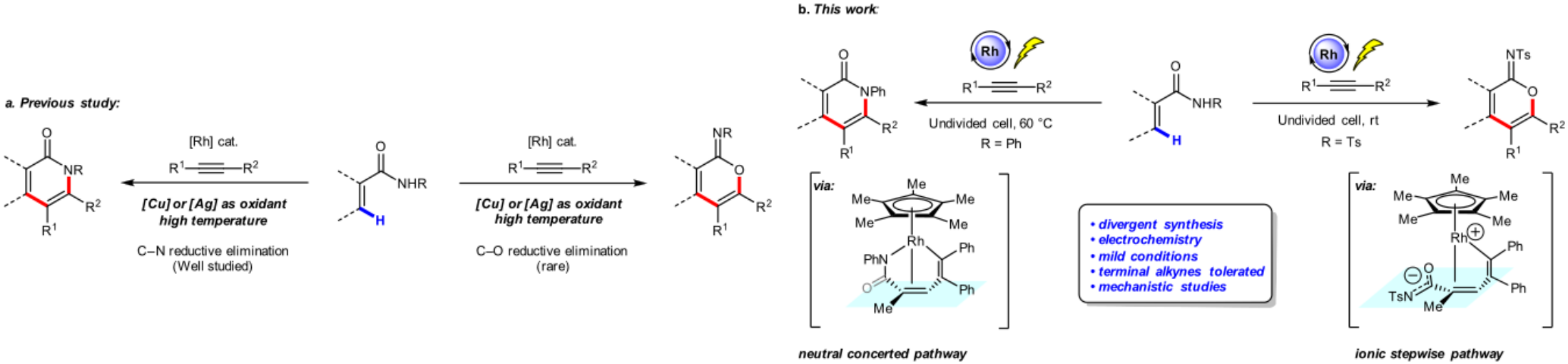
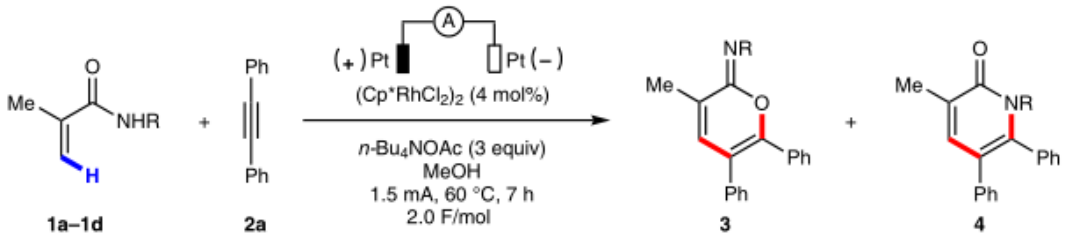
Divergent rhodium-catalyzed electrochemical vinylic C–H annulation of acrylamides with alkynes

Yi-Kang Xing[1,4], Xin-Ran Chen[2,4], Qi-Liang Yang[3,4], Shuo-Qing Zhang[2], Hai-Ming Guo[3], Xin Hong[2✉] & Tian-Sheng Mei[1✉]

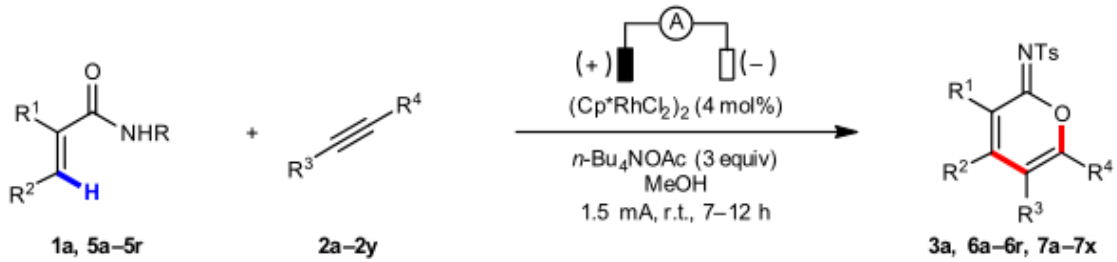
Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化





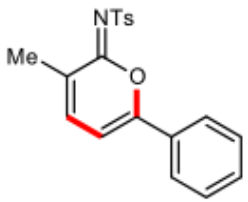
Entry	1(R)	Variation from standard conditions	Yield[b](%) of 3	Yield[b](%) of 4
1	**1a** (Ts)	None	99(91)[c]	n.d.
13	**1b** (Ph)	None	<5	**4b** (95)[c]
14	**1c** (*p*-NO_2-C_6H_4)	None	<5	**4c** (86)[c]
15	**1d** (*p*-OMe-C_6H_4)	None	<5	**4d** (42)[c]

Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化

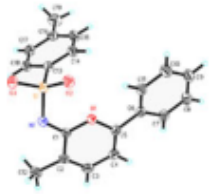


1a, 5a–5r + **2a–2y** → **3a, 6a–6r, 7a–7x**

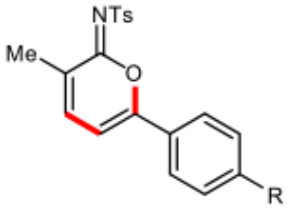
with terminal alkynes



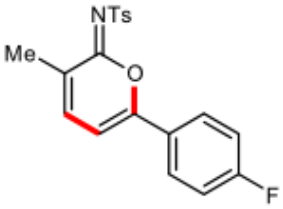
7s, 81%[b]



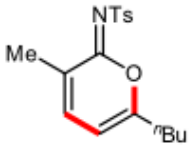
CCDC 1967783



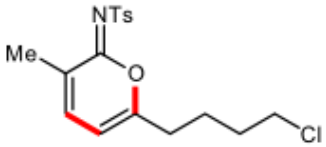
R = OMe, **7t**, 93%[b][c]
R = ^{n}Pr, **7u**, 93%[b][c]



7v, 86%[b]

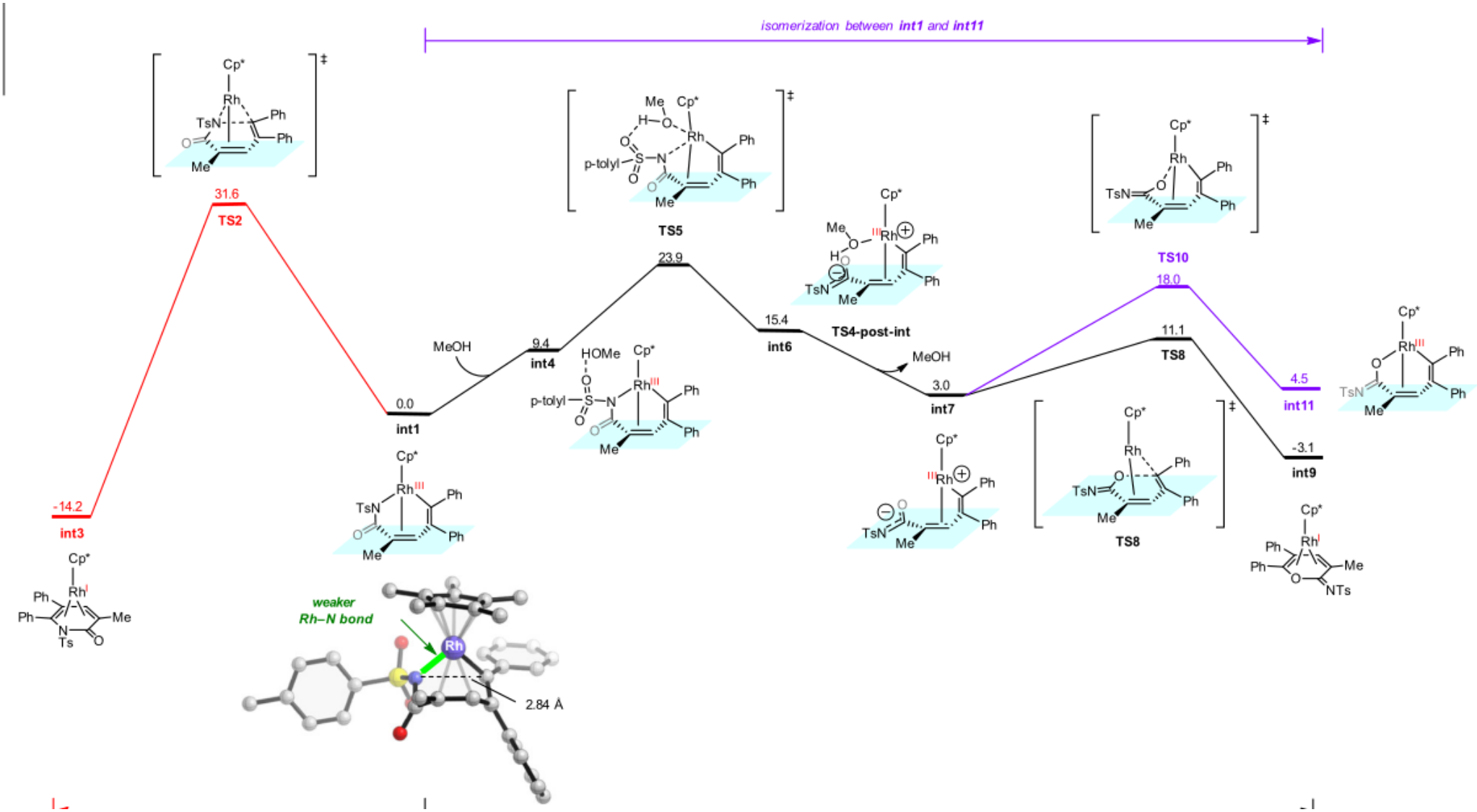


7w, 67%[b]



7x, 79%[b]

Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化



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RESEARCH ARTICLE

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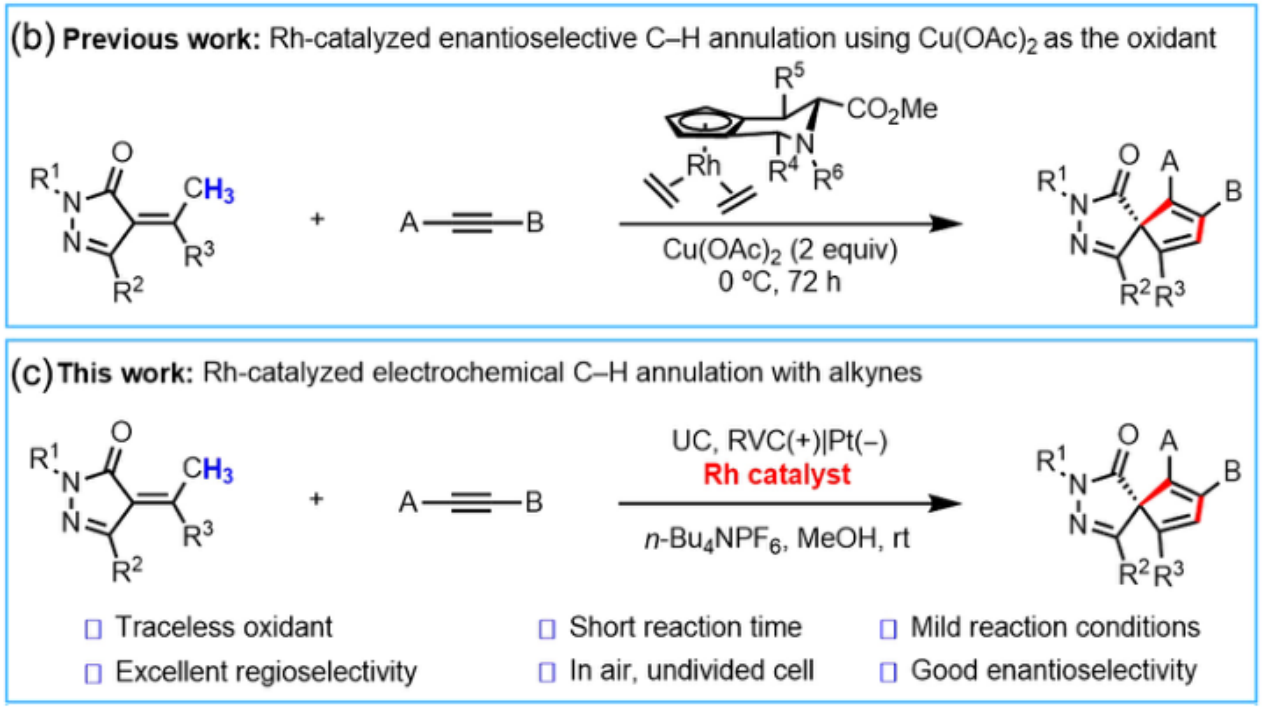
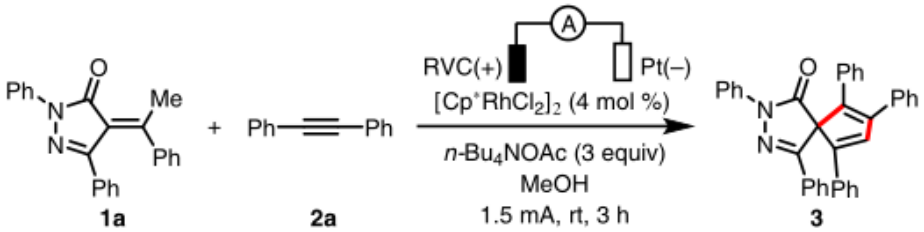
Electrochemical Rhodium-Catalyzed Enantioselective C–H Annulation with Alkynes

Yuan-Qiong Huang[1,2], Zhi-Jie Wu[1], Li Zhu[1], Qing Gu[1], Xiaojie Lu[2*], Shu-Li You[1*] & Tian-Sheng Mei[1*]

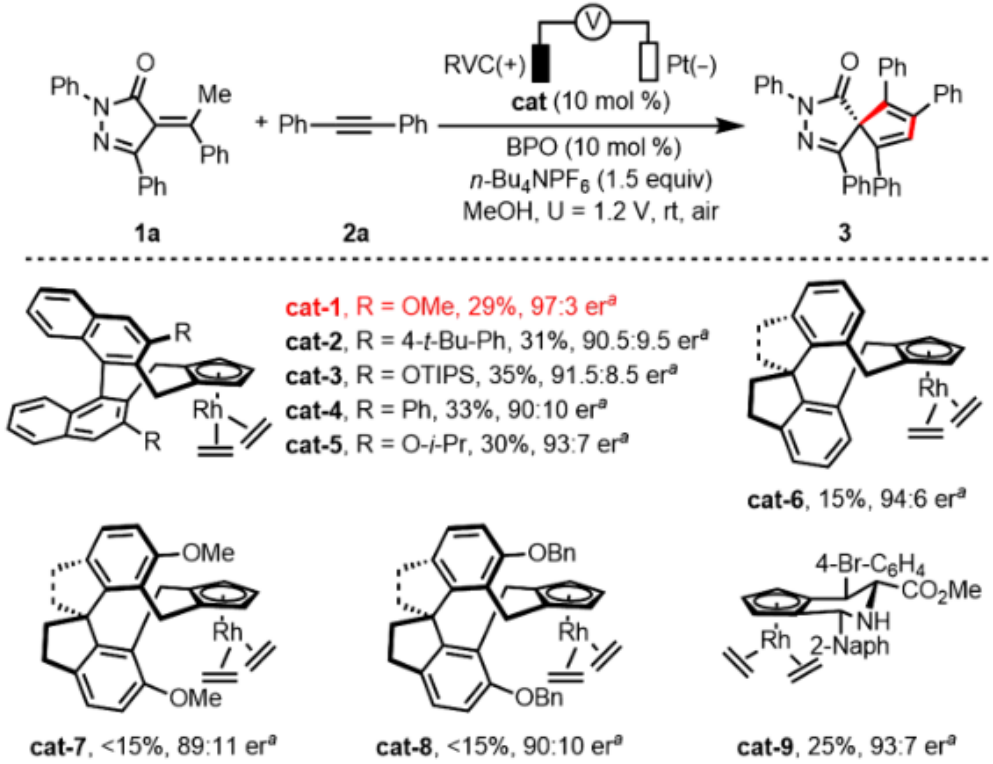
Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化





46, 81%

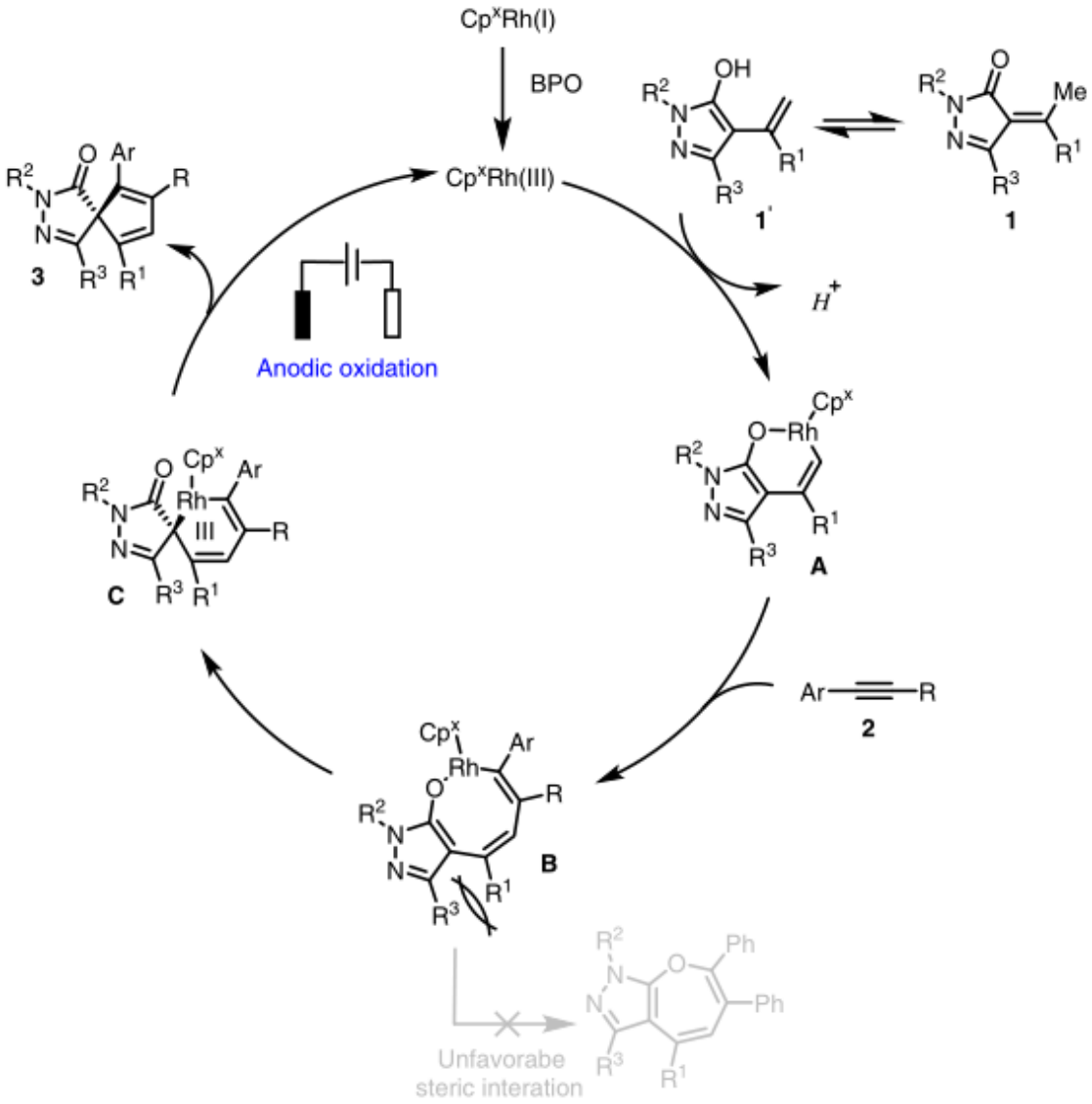
Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化



Entry	Variation from Standard Conditions[b]	Yield (%)[d]	er
1	None	71	94:6

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (1.5 equiv), Cp^{x}Rh (10 mol %), BPO (10 mol %), *n*-Bu_4NOAc (3.0 equiv), MeOH (3.0 mL), in an undivided cell with RVC as anode and Pt as cathode (each 1.0 cm × 1.0 cm), 1.5 mA.

Part 1.1 阳极氧化法，催化剂和底物结合之后被直接氧化



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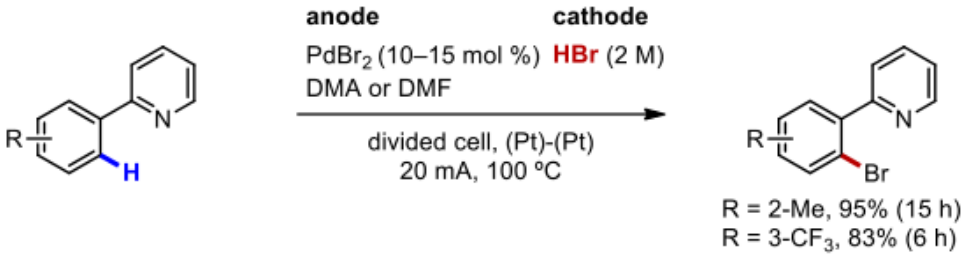
Palladium-Catalyzed Electrochemical C–H Bromination Using NH_4Br as the Brominating Reagent

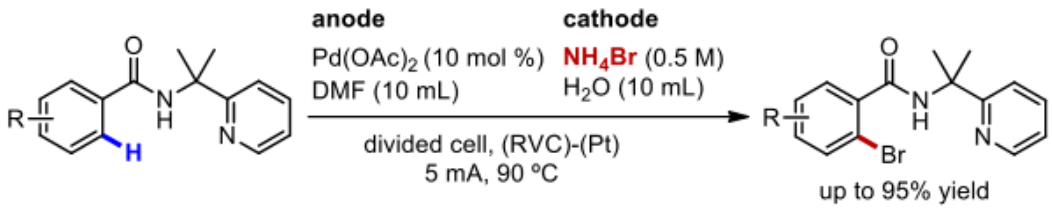
Qi-Liang Yang,[†,‡] Xiang-Yang Wang,[‡] Tong-Lin Wang,[‡] Xiang Yang,[‡] Dong Liu,[‡] Xiaofeng Tong,[†] Xin-Yan Wu,[*,†] and Tian-Sheng Mei[*,‡]

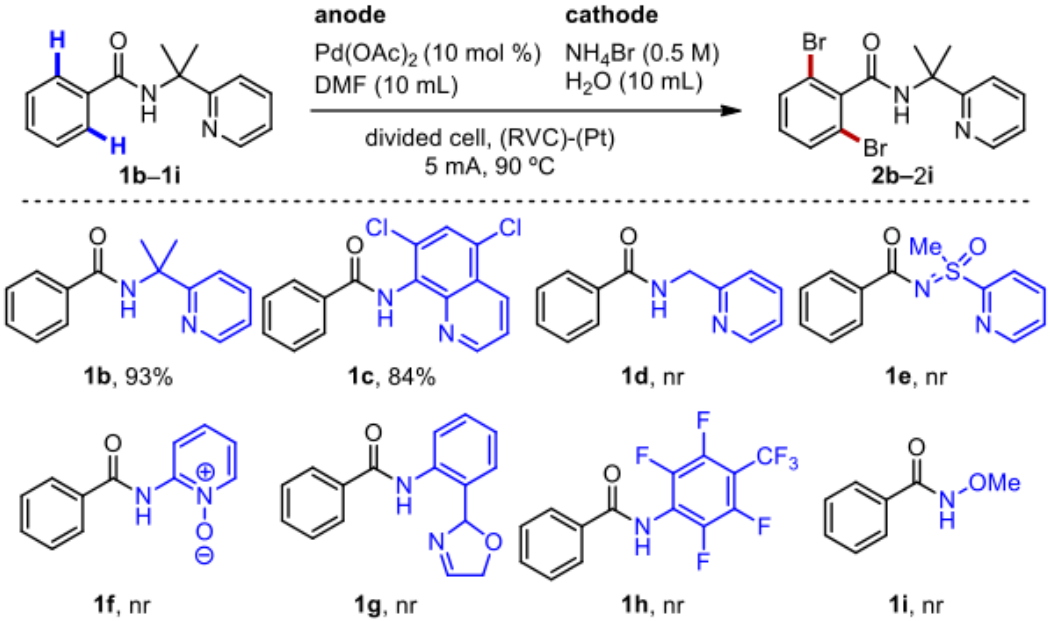
Part 1.2 阳极氧化法，底物直接氧化

a) Sole report on catalytic electrochemical C–H bromination by Kakiuchi (ref. 21c)

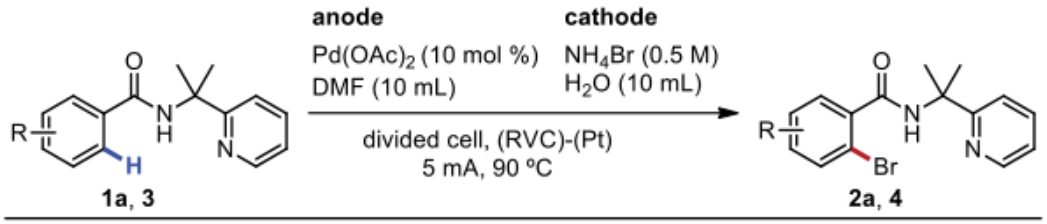


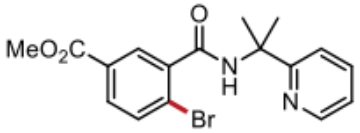
b) ***This work****: removable directing group-assisted electrochemical C–H bromination*

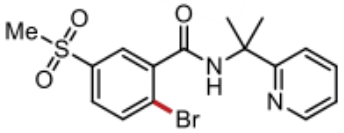


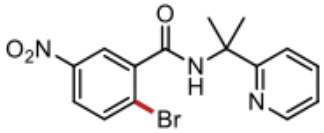


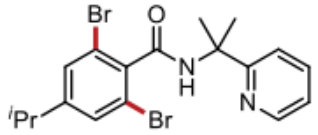
Part 1.2 阳极氧化法，底物直接氧化

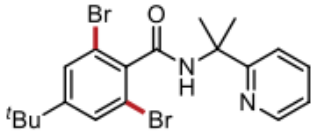


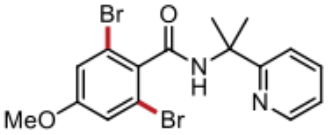

4k, 90%

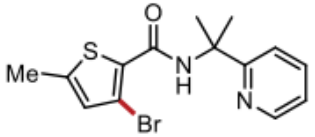

4l, 87%

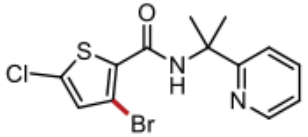

4m, 80%

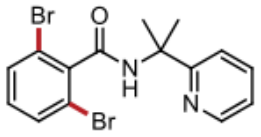

4r, 89%

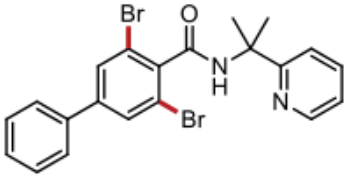

4s, 91%

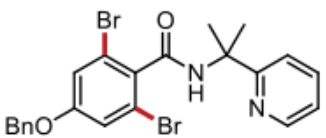

4t, 85%

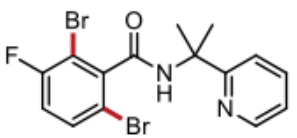

4n, 93%


4o, 91%

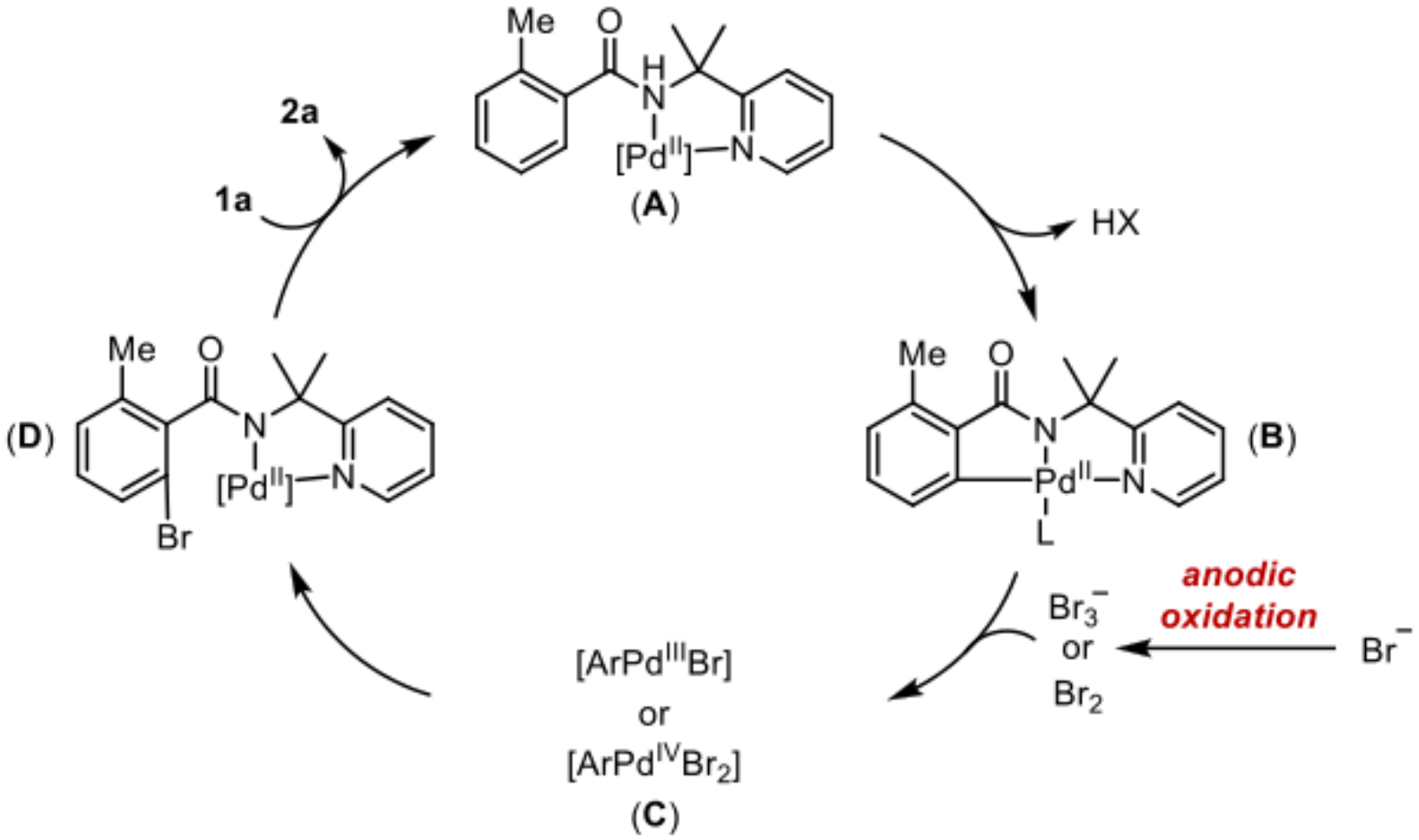

2b, 93%


4u, 90%


4v, 88%


4w, 87%

Part 1.2 阳极氧化法，底物直接氧化



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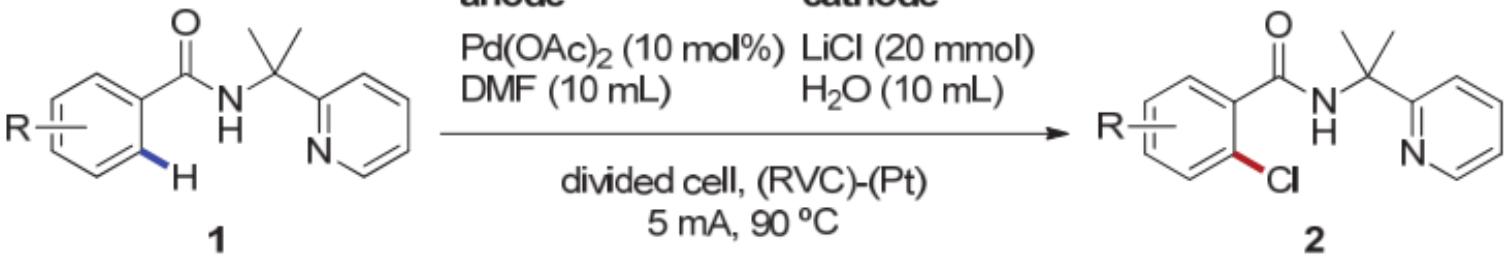
Communication

DOI: 10.6023/A19040135

电氧化促进的钯催化的芳烃 C(sp^2)—H 键氯代反应

杨启亮[†,a,b]　王向阳[†,c]　翁信军[b]　杨祥[b]　徐学涛[c]
童晓峰[a]　方萍[b]　伍新燕[*,a]　梅天胜[*,b]



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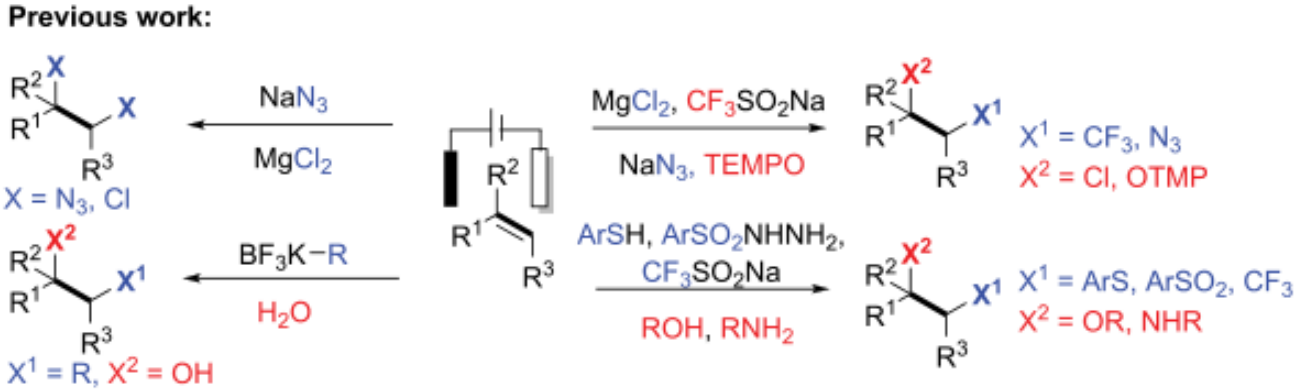
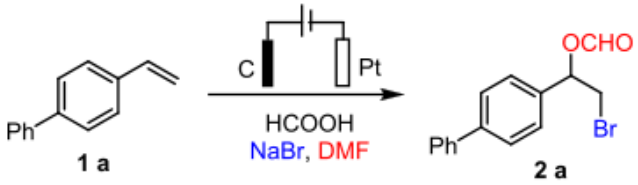
Electrochemical Radical Formyloxylation−Bromination, −Chlorination, and −Trifluoromethylation of Alkenes

Xiang Sun,[†,‡] Hong-Xing Ma,[‡] Tian-Sheng Mei,[‡] Ping Fang,*[,‡] and Yulai Hu*[,†]

Part 1.2 阳极氧化法，底物直接氧化

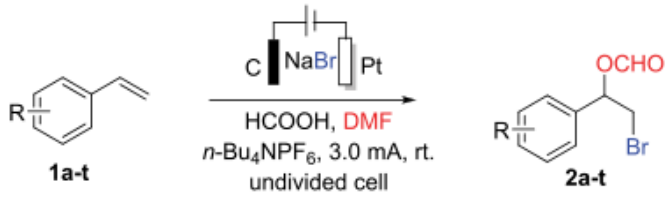


化学计量强氧化剂，降低官能团相容性，又产生废物

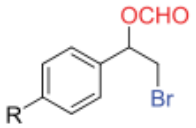


entry	variation from standard conditions	2a yield[b] (%)
1	none	95[c]
2	HOAc (0.4 mL)	67
3	HOAc (1.0 mL)	97
4	HCOOH (0.8 mL)	93
5	TFA (1.0 mL)	79

Part 1.2 阳极氧化法，底物直接氧化

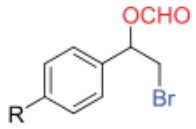


1a-t → **2a-t**



2aa, R = Ph, 95%
2ab, R = H, 87%
2ac, R = *t*-Bu, 96%
2ad, R = OPh, 93%

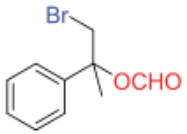
富电子



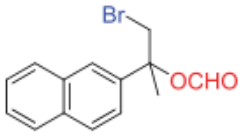
2ca, **2cb**, **2cc**,

2ka, R = F, 84%, 48h
2kb, R = Cl, 85%, 48h
2kc, R = CF_3, 86%, 48h
2kd, R = COOMe, 72%, 48h
2ke, R = COOH, 52%, 48h
2kf, R = CN, 39%, 48h

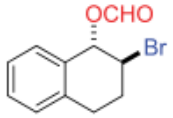
缺电子



2m, 94%

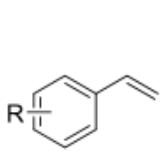


2n, 92%

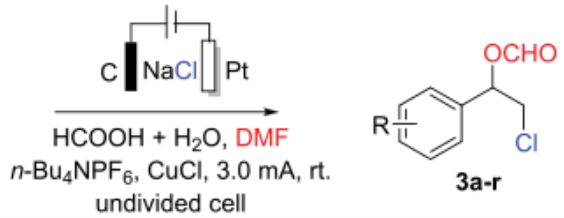


2o, 89%, (dr = 2:1)[b]

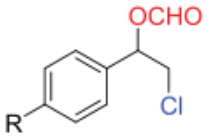
有取代基



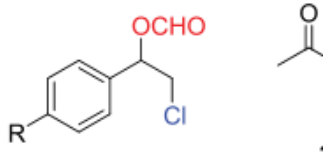
1a-r



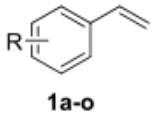
3a-r



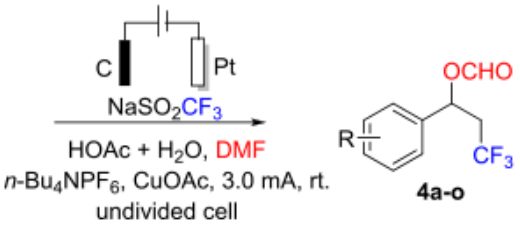
3a, R = Ph, 83%
3b, R = H, 93%
3c, R = *t*-Bu, 87%



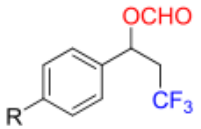
3g, R = Cl, 91%, 48h
3h, R = Br,77%, 48h
3i, R = F, 87%, 48h
3j, R = CF_3, 93%, 48h
3k, R = COOMe, 90%, 48h



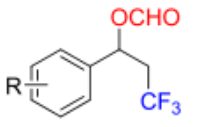
1a-o



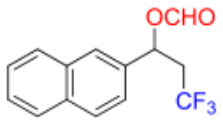
4a-o



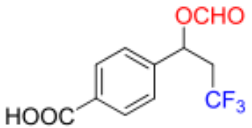
4a, R = Ph, 85%
4b, R = H, 78%
4c, R = *t*-Bu, 69%
4d, R = OPh, 83%



4e, R = *o*-OMe, 75%
4f, R = *m*-OMe, 73%
4g, R = *p*-OMe, 56%

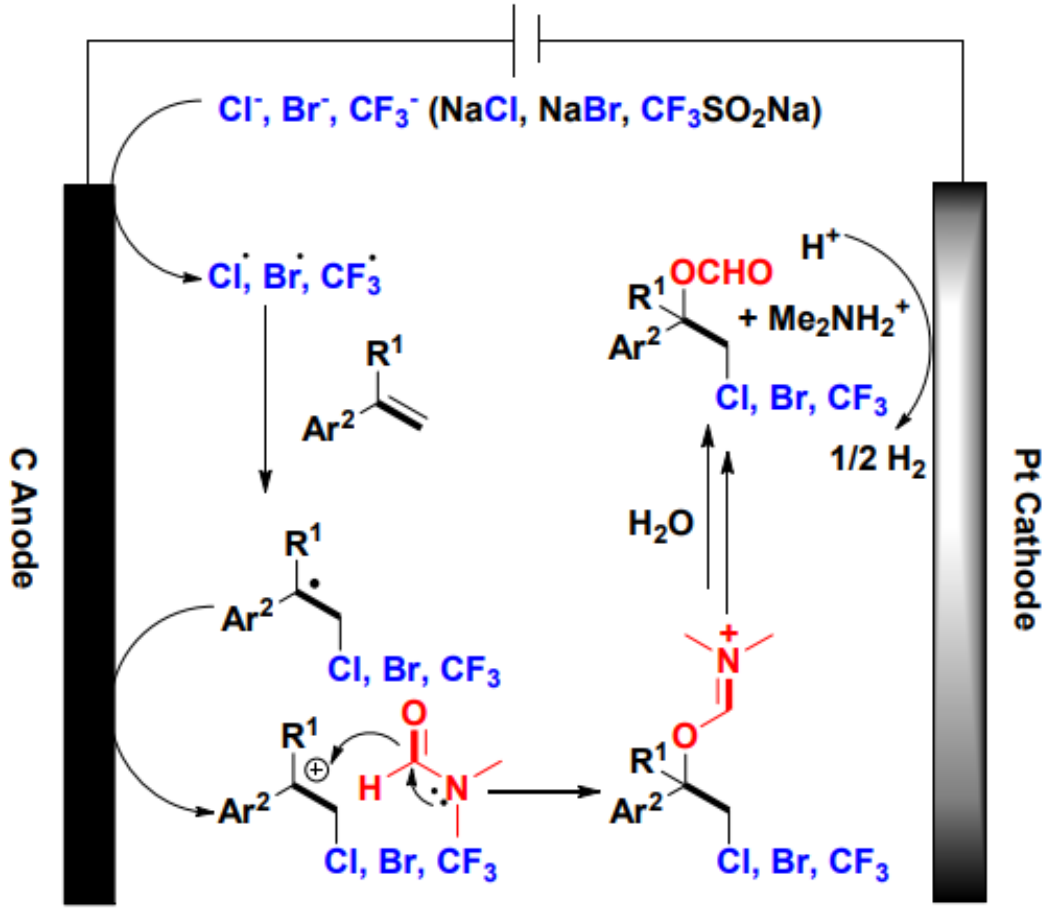


4h, 47%



4l, 63%, 48h

Part 1.2 阳极氧化法，底物直接氧化



JOC The Journal of Organic Chemistry

pubs.acs.org/joc Article

Copper-Catalyzed Electrochemical Selective Bromination of 8-Aminoquinoline Amide Using NH_4Br as the Brominating Reagent

Xiang Yang, Qi-Liang Yang, Xiang-Yang Wang, Hao-Han Xu, Tian-Sheng Mei,* Yan Huang,* and Ping Fang*

Cite This: *J. Org. Chem.* 2020, 85, 3497–3507

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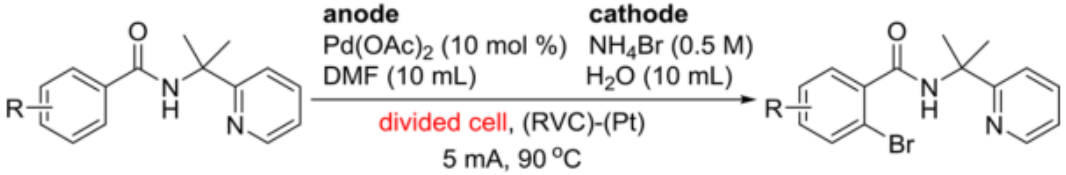
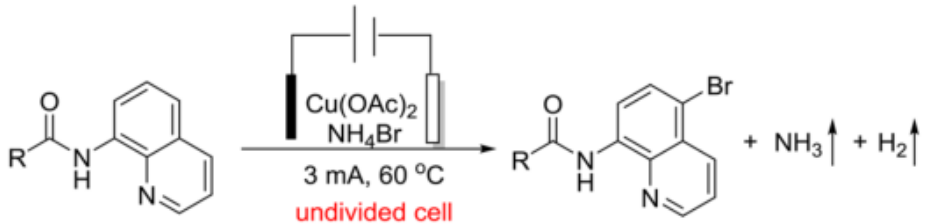
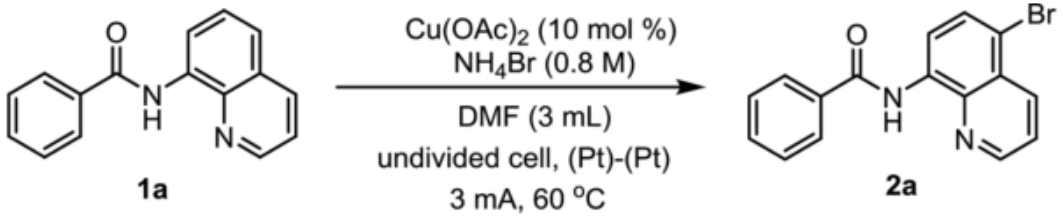
Part 1.2 阳极氧化法，底物直接氧化

a) Previous work: removable directing group-assister electrochemical C-H bromination



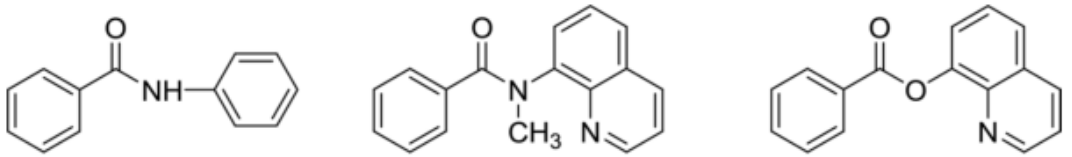
b) This work: copper-catalyzed electrochemical bromination of 8-amidoquinoline amide





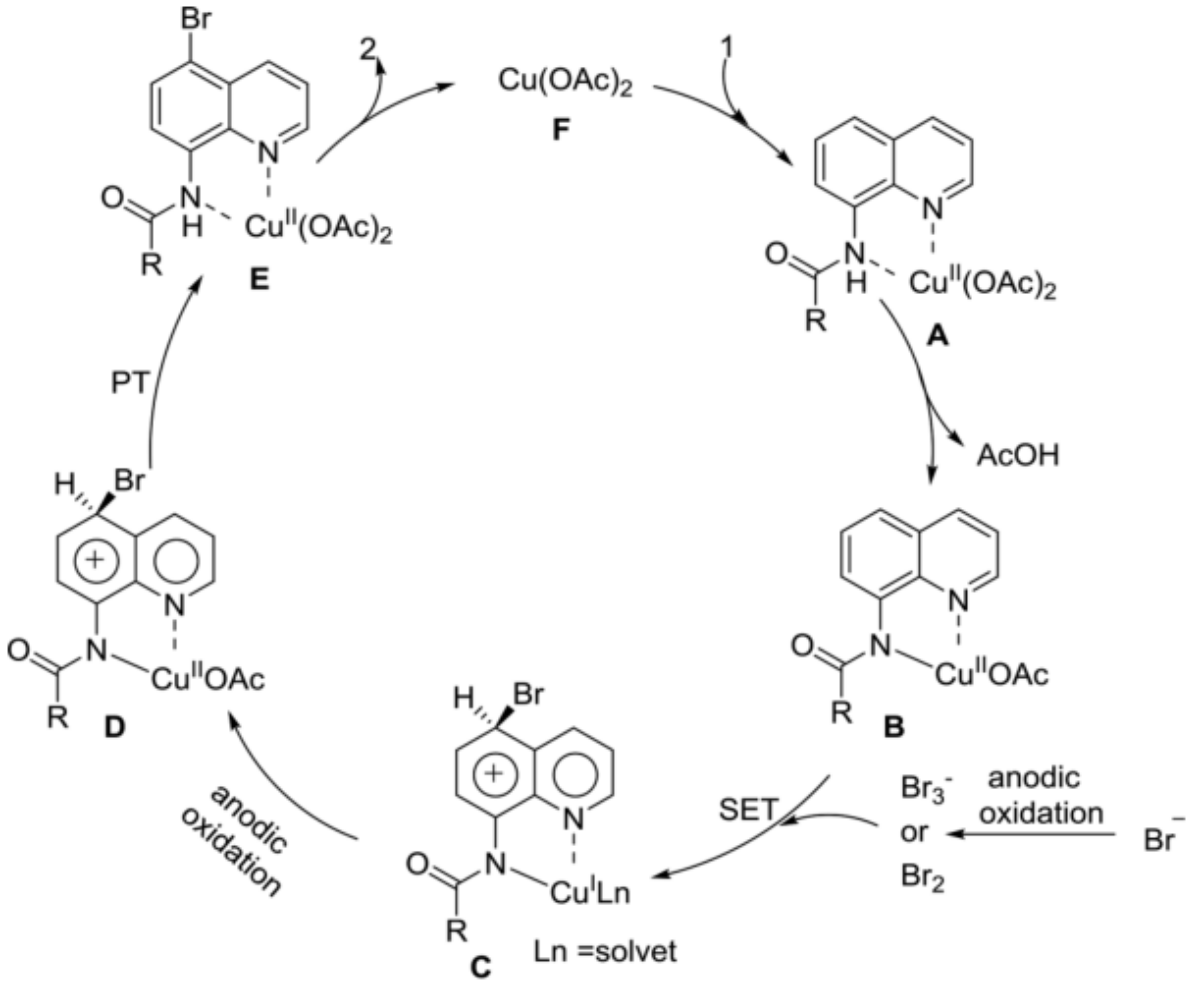
entry	variation from standard conditions above	yield (%)[b]
1	none	99 (94)[c]

Scheme 3. Evaluation of Analogous Substrates



1ab, nr　　**1ac**, nr　　**1ad**, nr

Part 1.2 阳极氧化法，底物直接氧化



JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

Cite This: J. Am. Chem. Soc. 2018, 140, 11487−11494

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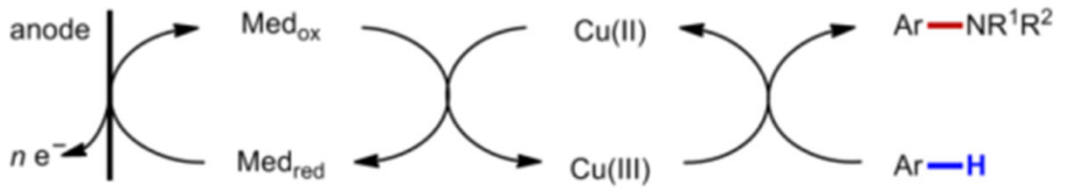
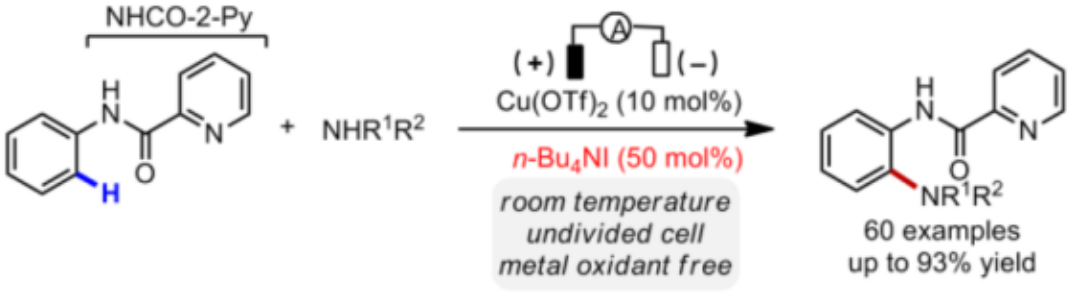
Copper-Catalyzed Electrochemical C−H Amination of Arenes with Secondary Amines

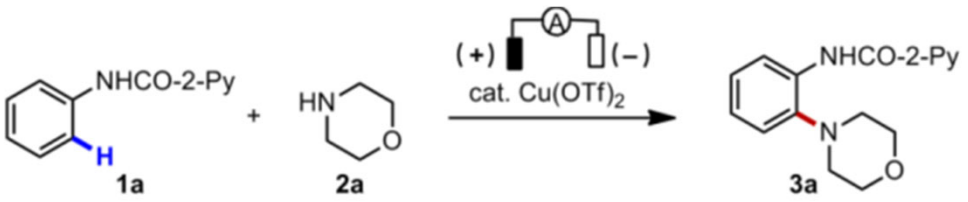
Qi-Liang Yang,[†,‡] Xiang-Yang Wang,[†] Jia-Yan Lu,[†] Li-Pu Zhang,[†] Ping Fang,[†] and Tian-Sheng Mei*[,†]

第一个铜催化芳烃的电化学C−H胺化反应。

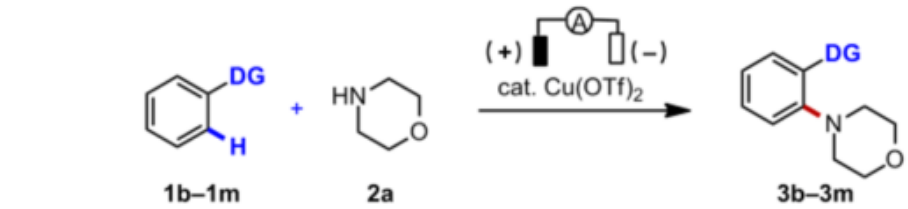
Part 1.3 阳极氧化法，间接氧化

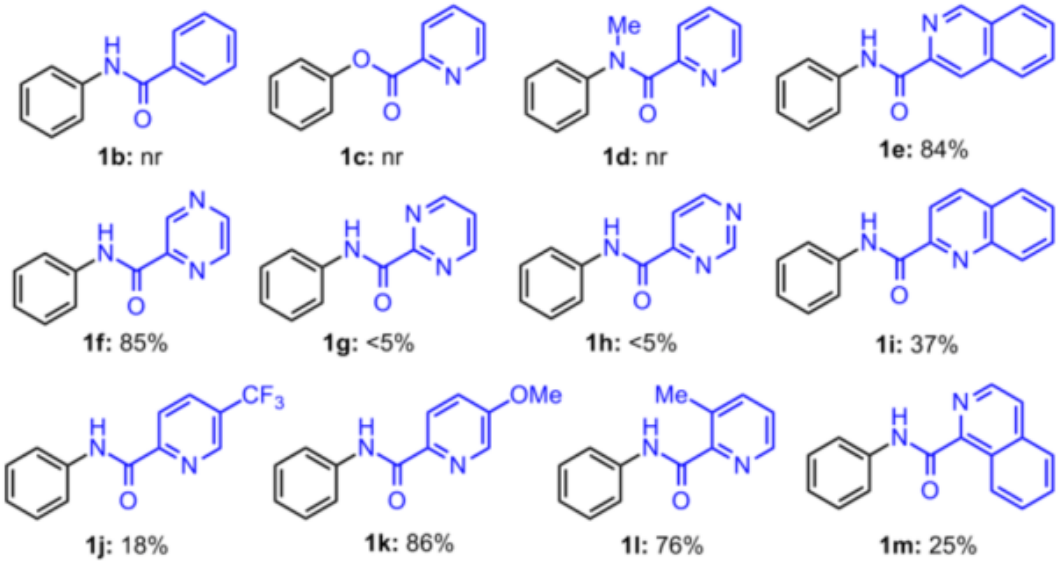




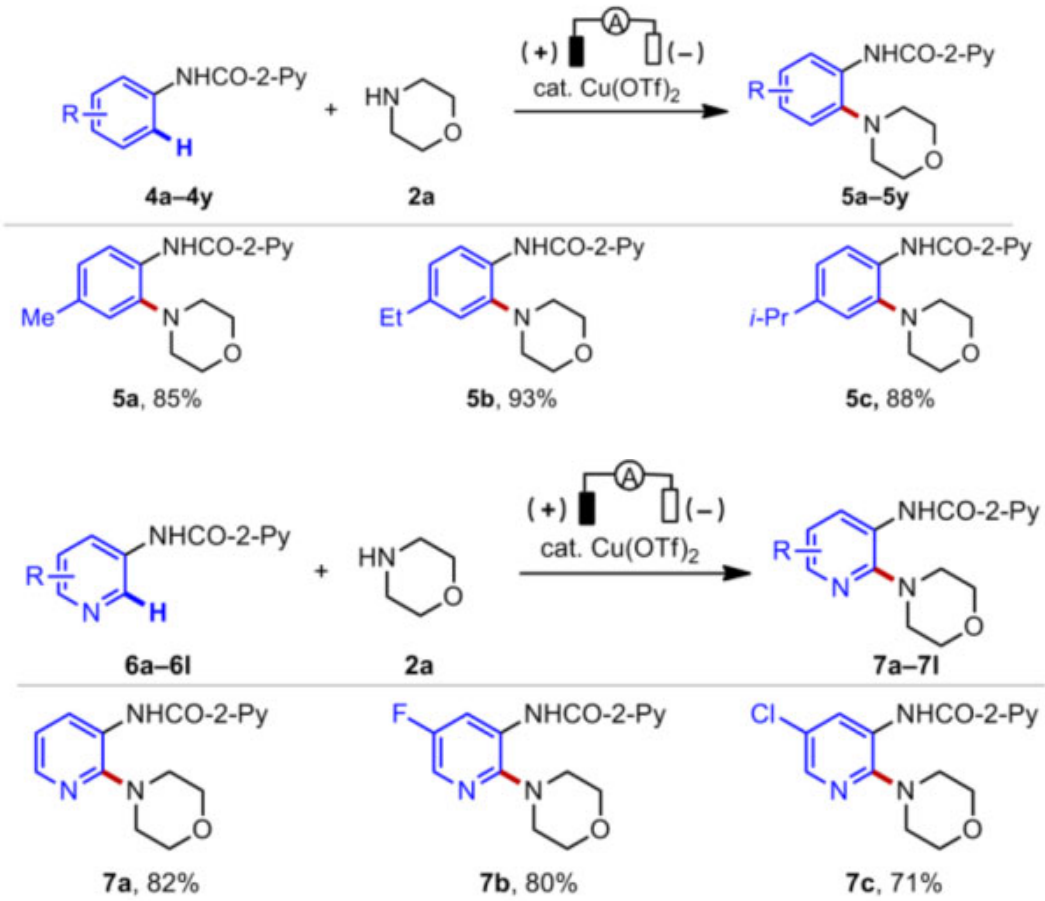


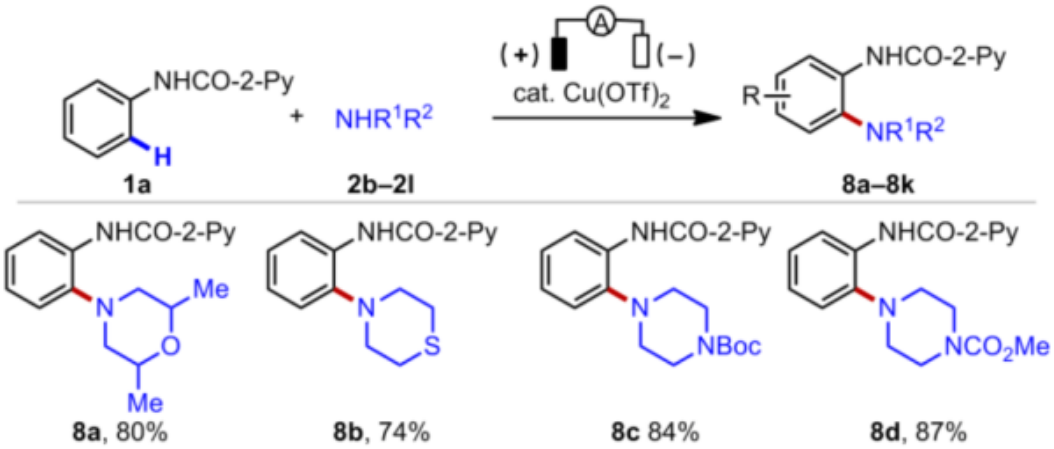
entry	variation from standard conditions[a]	yield (%)[b]
1	none	92 (86)[c]
9	KI instead of n-Bu$_4$NI	44
10	n-Bu$_4$NBr instead of n-Bu$_4$NI	nr
15	1 equiv of Cu(OTf)$_2$, no electric current	nr



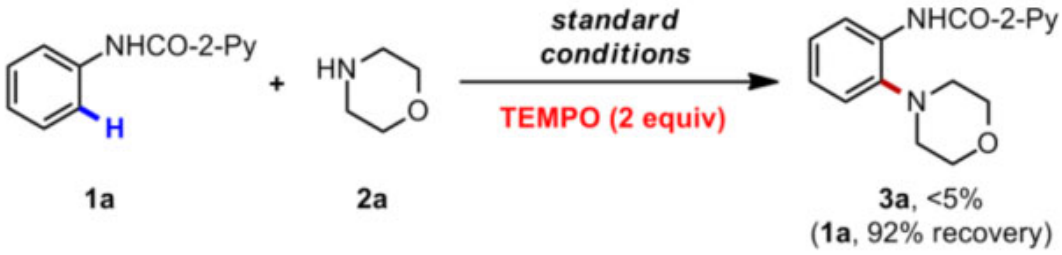


Part 1.3 阳极氧化法，间接氧化



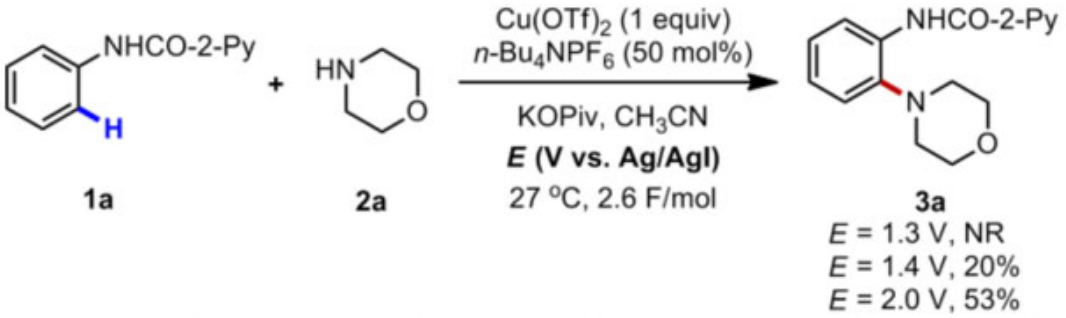


Part 1.3 阳极氧化法，间接氧化

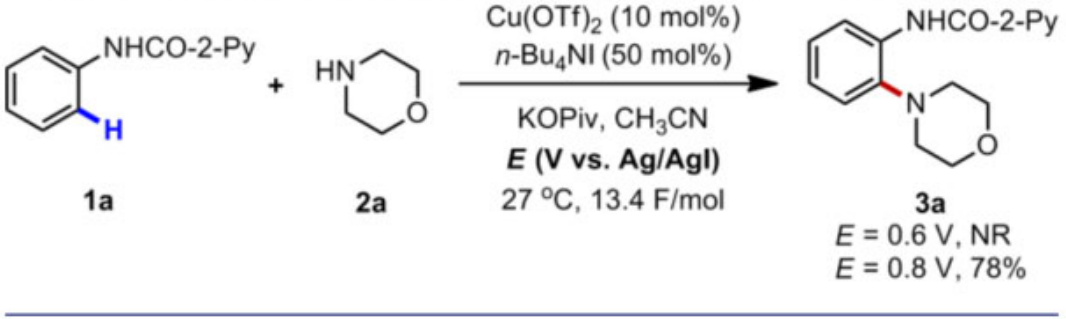


1a　　2a　　**3a**, <5% (**1a**, 92% recovery)

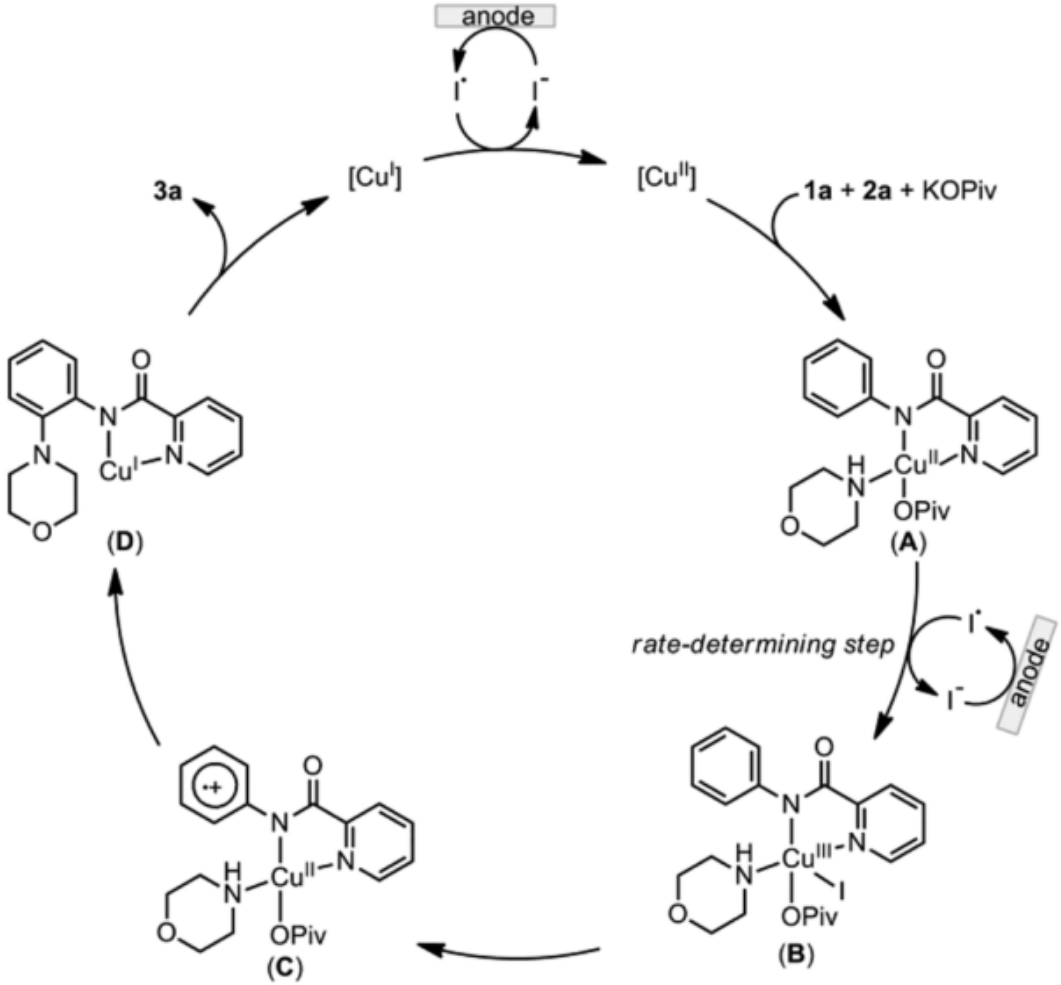
TEMPO的加入抑制反应



1a　　2a　　**3a**
E = 1.3 V, NR
E = 1.4 V, 20%
E = 2.0 V, 53%



1a　　2a　　**3a**
E = 0.6 V, NR
E = 0.8 V, 78%



Part 1.3 阳极氧化法，间接氧化

GDCh Communications Angewandte International Edition Chemie

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How to cite: *Angew. Chem. Int. Ed.* **2020**, *59*, 15254–15259
International Edition: doi.org/10.1002/anie.202005099
German Edition: doi.org/10.1002/ange.202005099

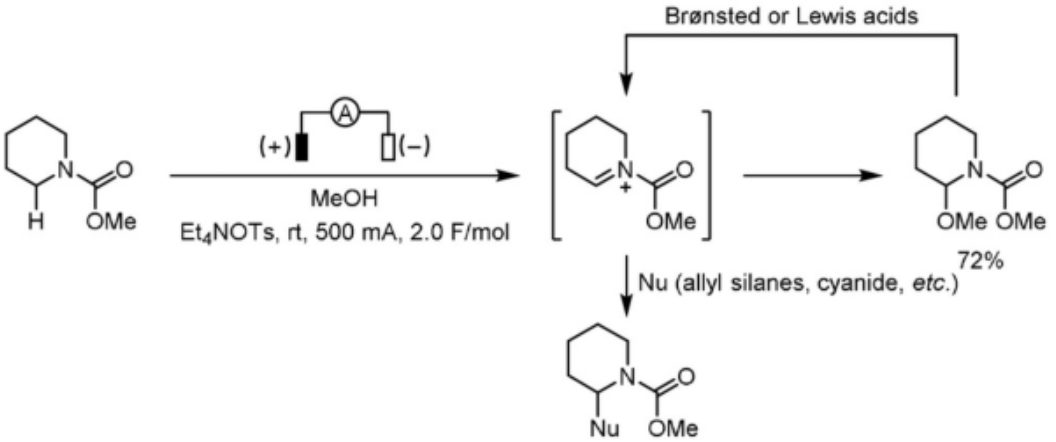
Cu^{II}/TEMPO-Catalyzed Enantioselective C(sp^3)–H Alkynylation of Tertiary Cyclic Amines through Shono-Type Oxidation

*Pei-Sen Gao[+], Xin-Jun Weng[+], Zhen-Hua Wang, Chao Zheng, Bing Sun, Zhi-Hao Chen, Shu-Li You, and Tian-Sheng Mei**

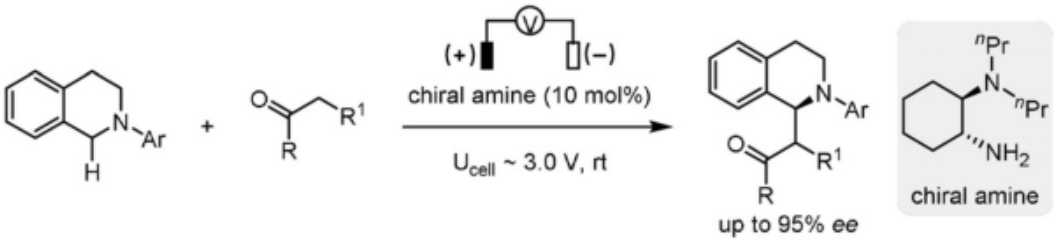
Cu/TEMPO共催化环叔胺和末端炔之间电化学对映选择性氧化偶联的第一个例子

Part 1.3 阳极氧化法，间接氧化

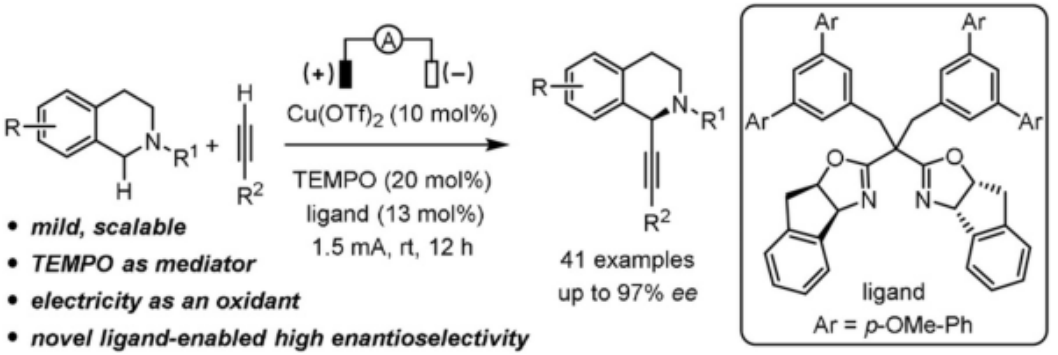
a) Shono oxidation of carbamates (ref. 4 & 5)



b) Chiral amine-catalyzed enantioselective electrochemical C–H alkylation by Luo (ref. 12)

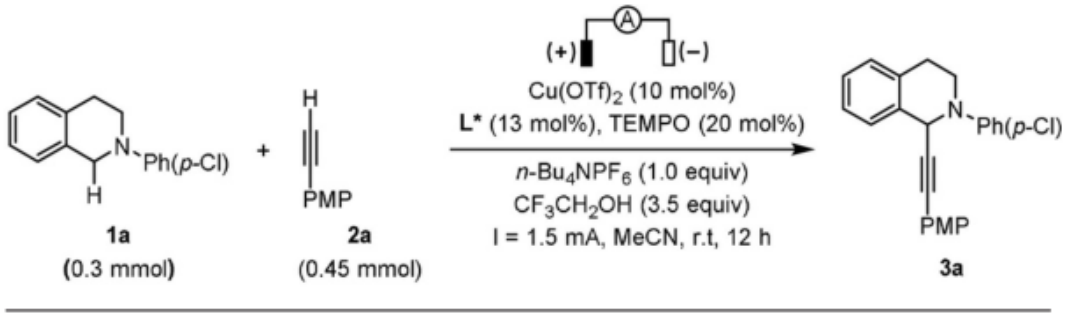


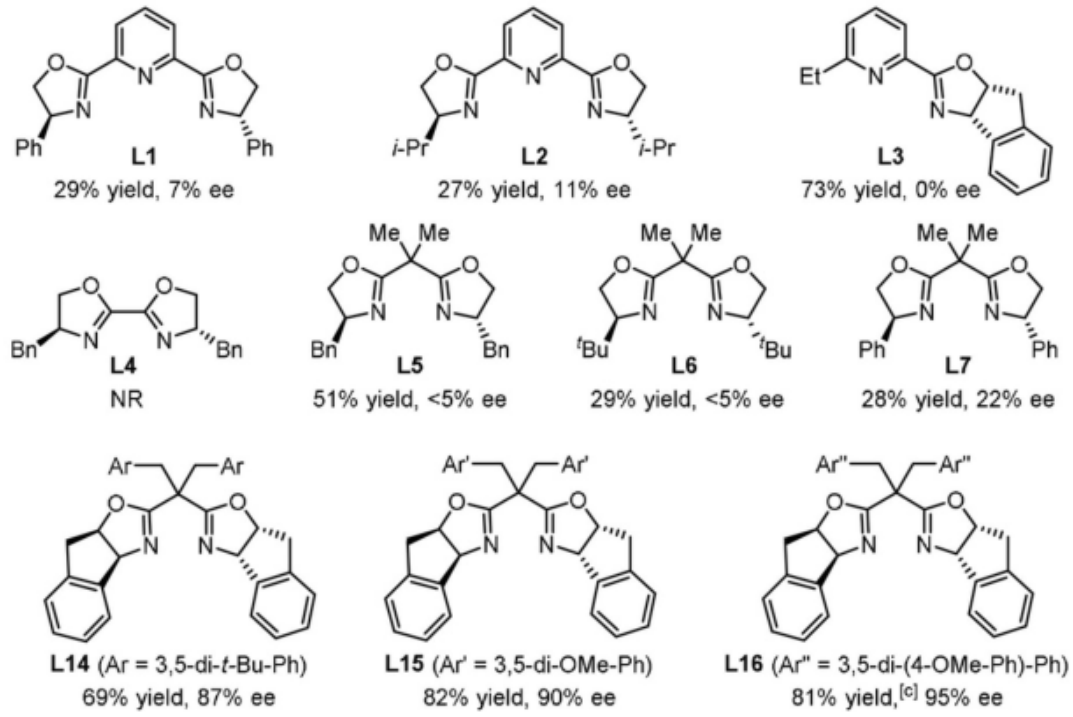
*c) **This work**: Cu(II)/TEMPO-catalyzed enantioselective electrochemical C–H alkynylation*

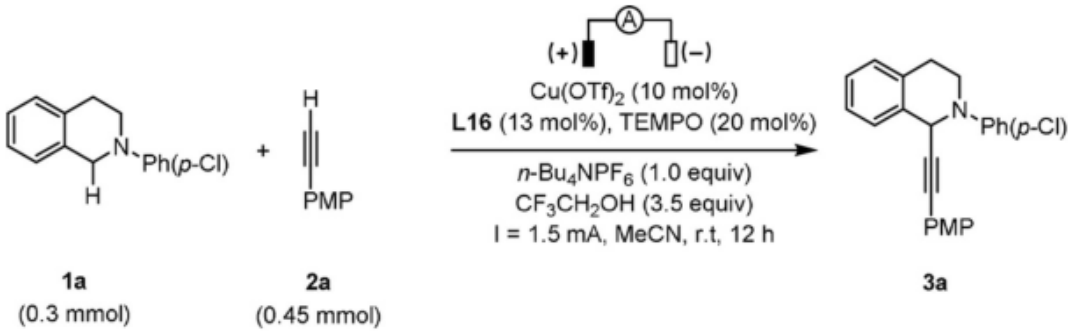


- ***mild, scalable***
- ***TEMPO as mediator***
- ***electricity as an oxidant***
- ***novel ligand-enabled high enantioselectivity***

Part 1.3 阳极氧化法，间接氧化

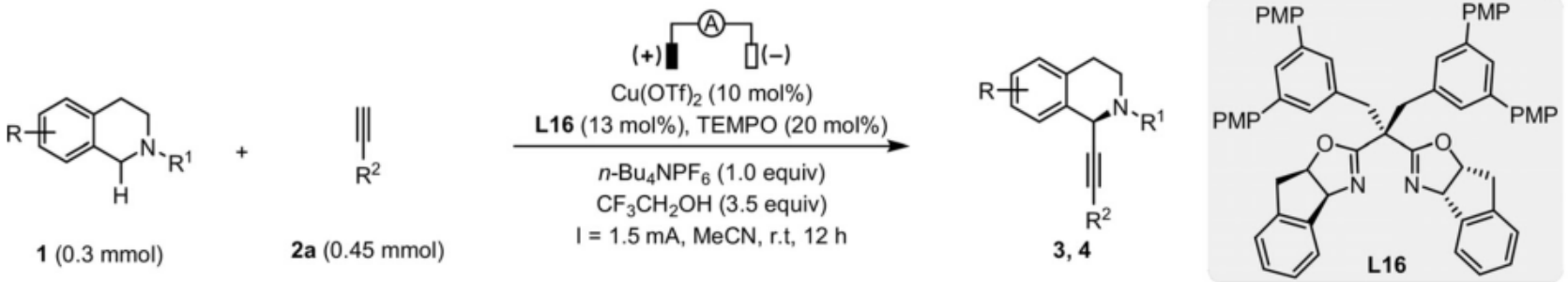


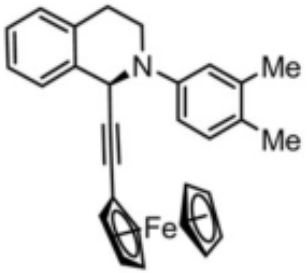




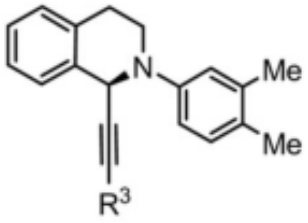
Entry	Variation from standard conditions	Yield[a]	*ee* [%][b]
1	none	81[c]	95
2	no $Cu(OTf)_2$	–	–
3	no ligand	–	–
4	no electric current	–	–
5	no TEMPO	12	89
6	no CF_3CH_2OH	20	87

Part 1.3 阳极氧化法，间接氧化



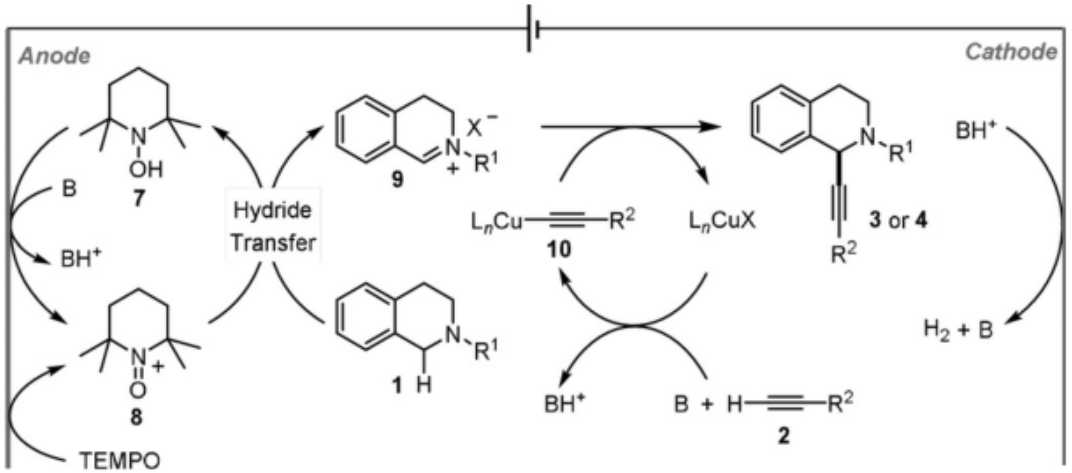


4r, 41%, 90% ee



R^3 = COPh, **4s**, <5%

R^3 = ^{t}Bu, **4t**, <5%



JOC The Journal of Organic Chemistry

pubs.acs.org/joc Note

C(sp^3)–H Aerobic Alkenylation of Tetrahydroisoquinolines via Organic Electrosynthesis

Zeng He,[§] Hui-Lin Liu,[§] Zhen-Hua Wang, Ke-Jing Jiao, Zi-Meng Li, Zhang-Jian Li, Ping Fang,* and Tian-Sheng Mei*

Cite This: *J. Org. Chem.* 2023, 88, 6203–6208

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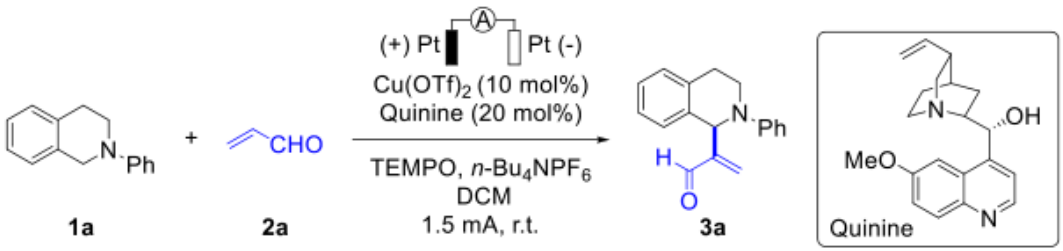
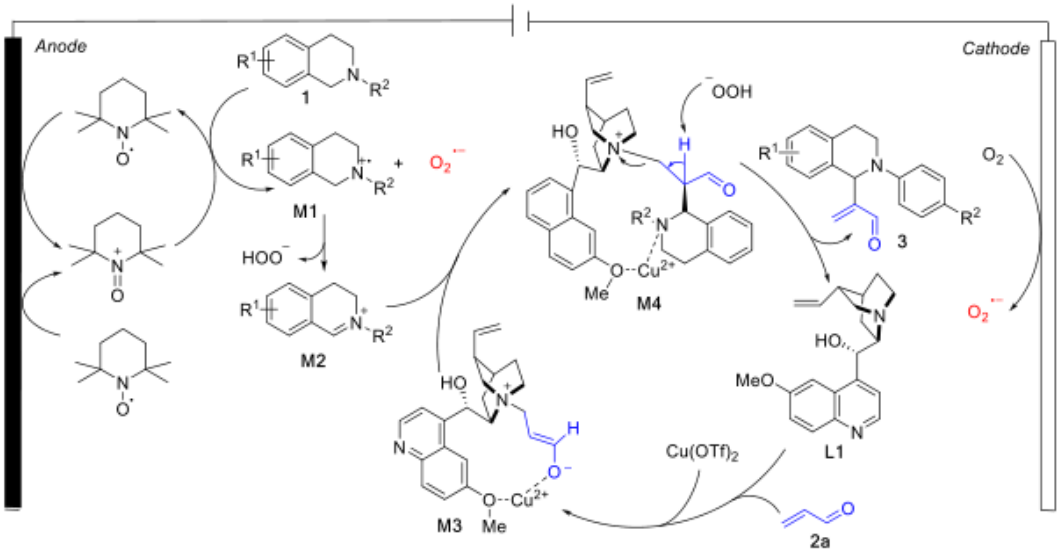
Part 1.3 阳极氧化法，间接氧化



1a　　2a　　3a

entry	deviation from the standard conditions	yield[b] (%)
1	none	98 (90[c])
2	no TEMPO	48
3	no $Cu(OTf)_2$	71
4	under N_2	6
5	no quinine	12
6	no current	
7	0.1 mmol of **1a** was used	20
8	$Cu(acac)_2$ instead of $Cu(OTf)_2$	19
9	$Fe(OTf)_3$ instead of $Cu(OTf)_2$	34
10	5 mol % of $Cu(OTf)_2$ was used	11
11	20 mol % of $NaBArF_4$	62
12	1 mA instead of 1.5 mA	95
13	Ni foam instead of Pt (cathode)	32
14	carbon instead of Pt (cathode)	28
15	without TFE	40



OL | Organic Letters

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Letter

C(sp^3)–H Alkenylation of Tetrahydroisoquinolines via Merging Electrochemistry and Organocatalysis

Hui-Lin Liu,[+] Zeng He,[+] Na-Na Wang, Hao Xu,* Ping Fang,* and Tian-Sheng Mei*

Cite This: *Org. Lett.* 2023, 25, 608–613

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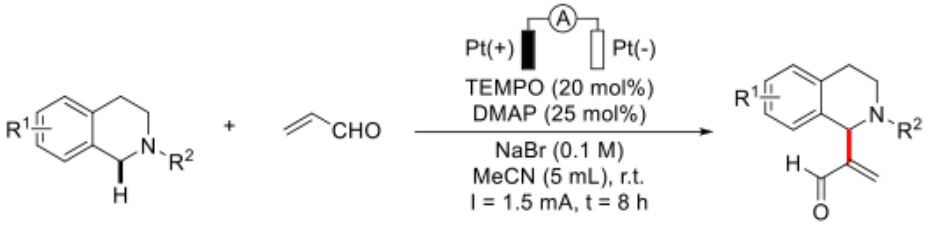
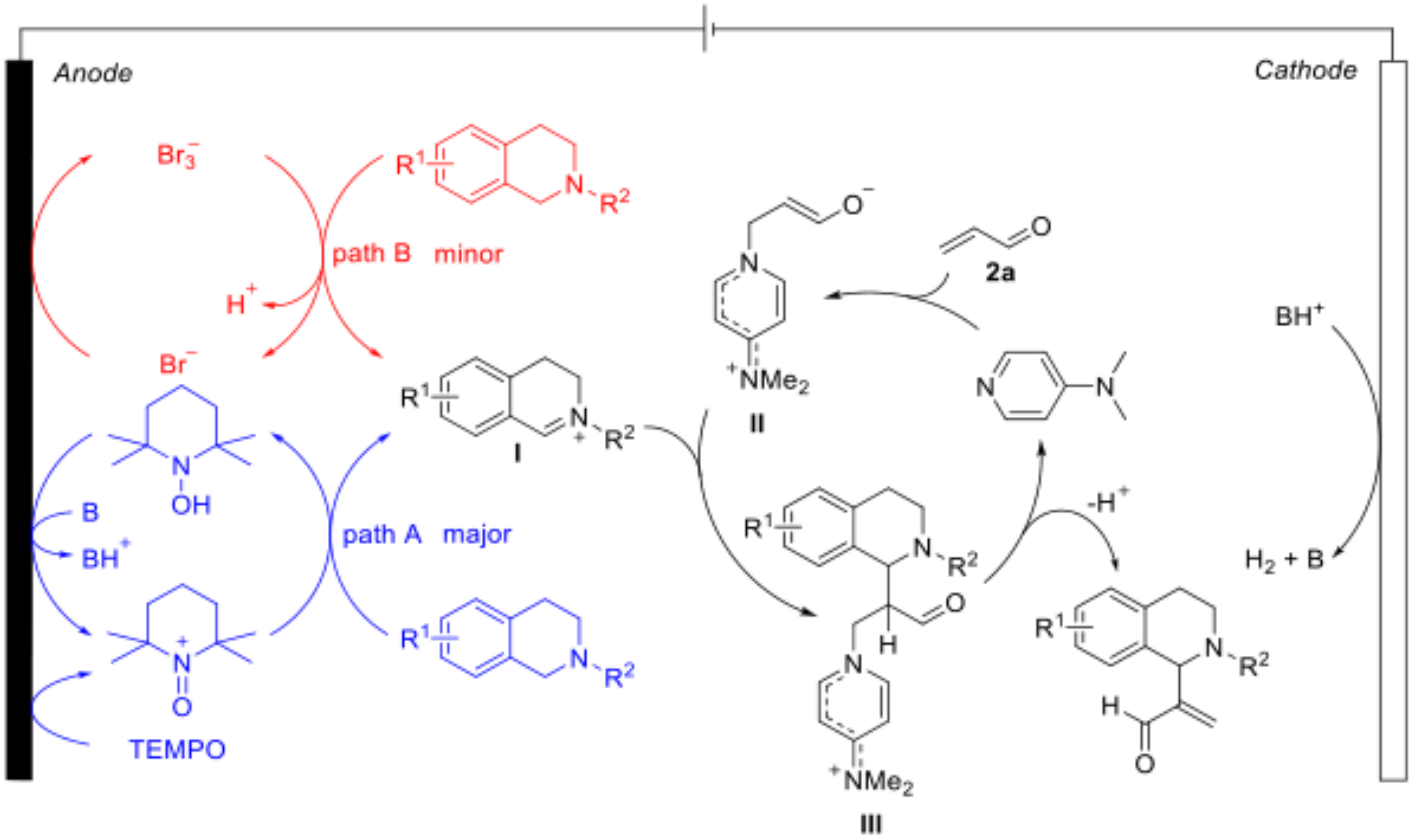


Part 1.3 阳极氧化法，间接氧化



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Communication

TEMPO-Enabled Electrochemical Enantioselective Oxidative Coupling of Secondary Acyclic Amines with Ketones

Zhen-Hua Wang, Pei-Sen Gao, Xiu Wang, Jun-Qing Gao, Xue-Tao Xu, Zeng He, Cong Ma, and Tian-Sheng Mei*

Cite This: J. Am. Chem. Soc. 2021, 143, 15599–15605

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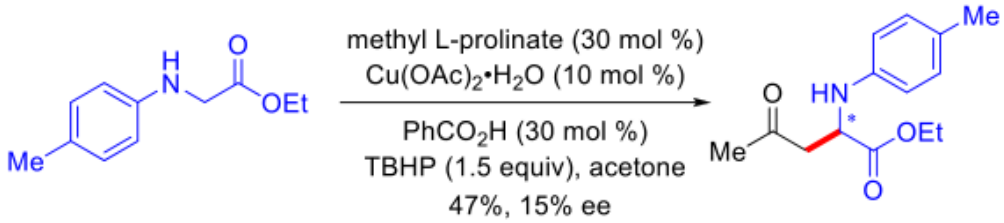
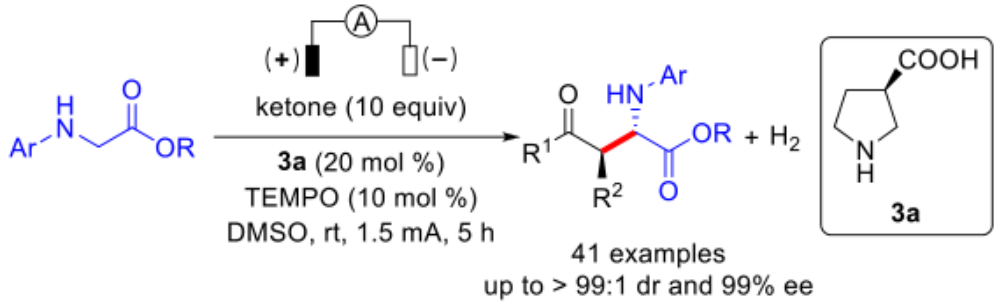
Part 1.3 阳极氧化法，间接氧化

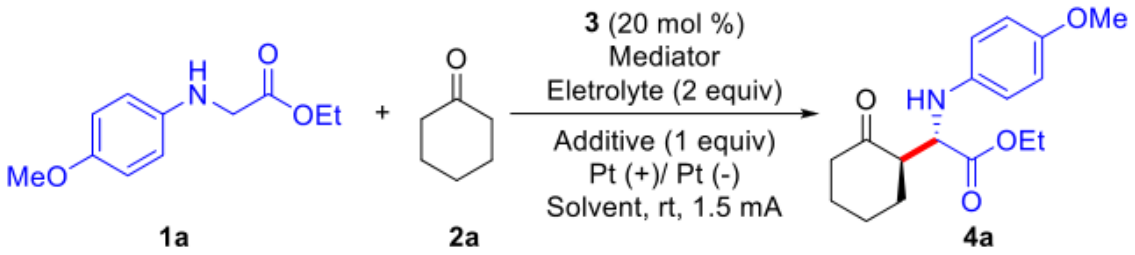
仲无环胺的shono反应很少

b) Cu/aminocatalyst co-catalyzed oxidative coupling mediated by TBHP



c) This work: asymmetric Shono-type oxidative coupling with acyclic amines

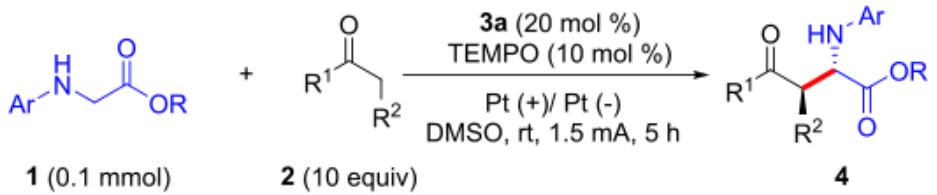


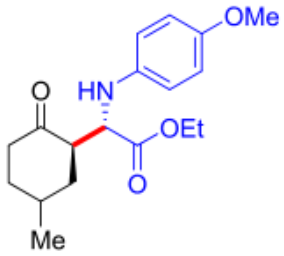


Entry	3	Mediator (mol %)	Electrolyte	Additive	Solvent	Yield (%)	dr (anti/syn)	ee (%)
2[a]	**3a**	TEMPO (20)	*n*-Bu_4NPF_6	CF_3CH_2OH	MeCN	18	> 99/1	97
5[c]	**3a**	TEMPO (10)	-	-	DMSO	75 (70)[d]	> 99/1	97

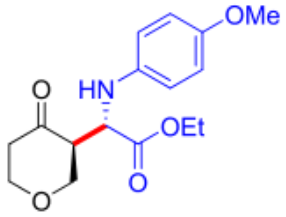
不需要电解质，改善了电导率。不需要添加剂，改善了阴极析氢

Part 1.3 阳极氧化法，间接氧化

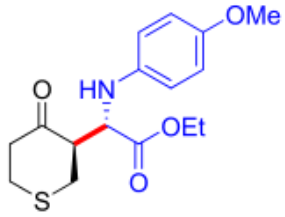




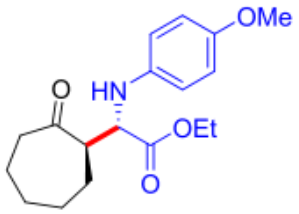
4aj
33%, 83:17 dr, 85% ee



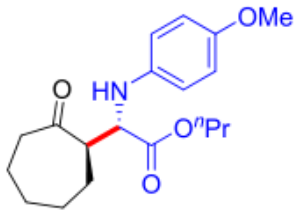
4ak
50%, 51:49 dr, 13% ee



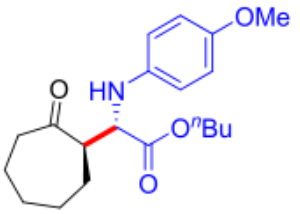
4al[c]
45%, 99:1 dr, 74% ee



4am[c]
42%, 97:3 dr, 89% ee



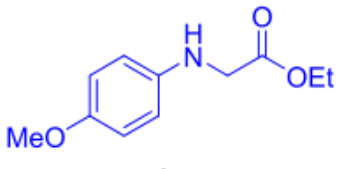
4an[c]
44%, 99:1 dr, 90% ee



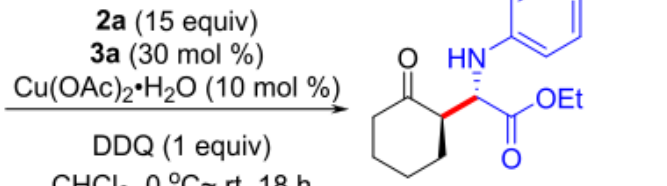
4ao[c]
40%, 99:1 dr, 90% ee

五元环酮，三元环酮，苯乙酮，乙酮等链酮都不反应

(b)



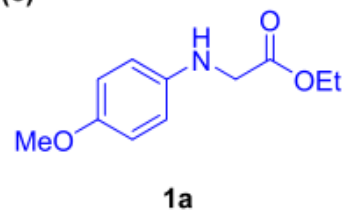
1a



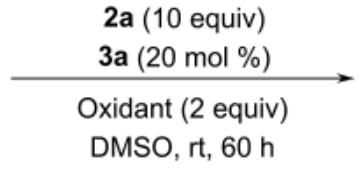
4a
35%, 63:37 dr, *rac*

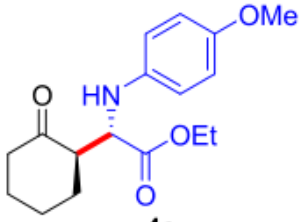
不是有机催化剂3a

(c)



1a



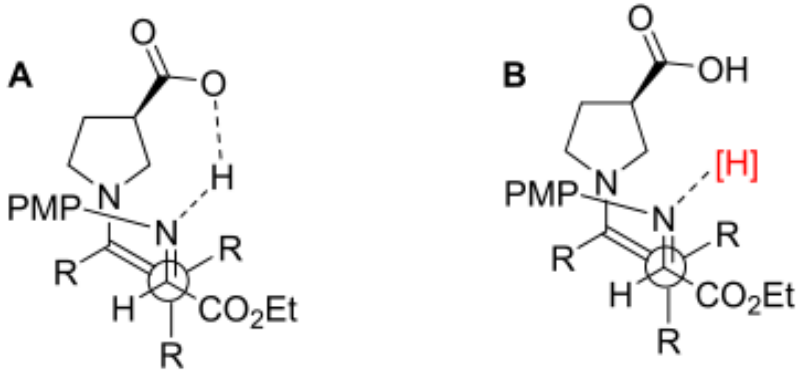


4a

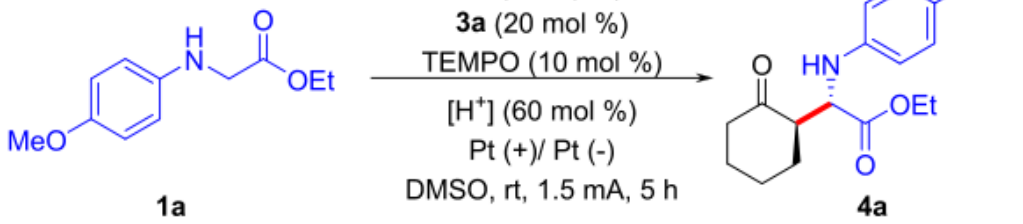
Oxidant	Yield (%)	dr	ee (%)
DDQ	32	61:39	6
$TEMPO^+BF_4^-$	26	63:37	13

也不是化学氧化剂

Part 1.3 阳极氧化法，间接氧化

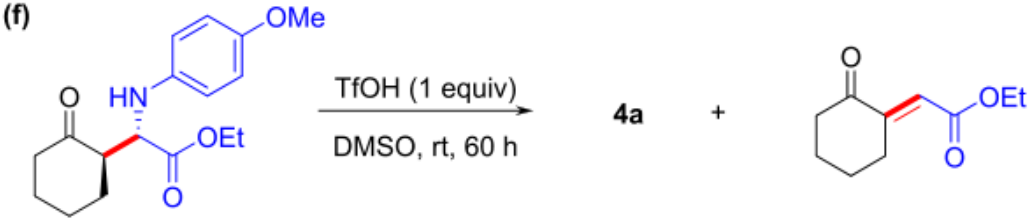


(e)



[H⁺]	Yield (%)	dr	ee (%)
TsOH	83	61:39	rac
TfOH (0.5 h)	10	74:26	14

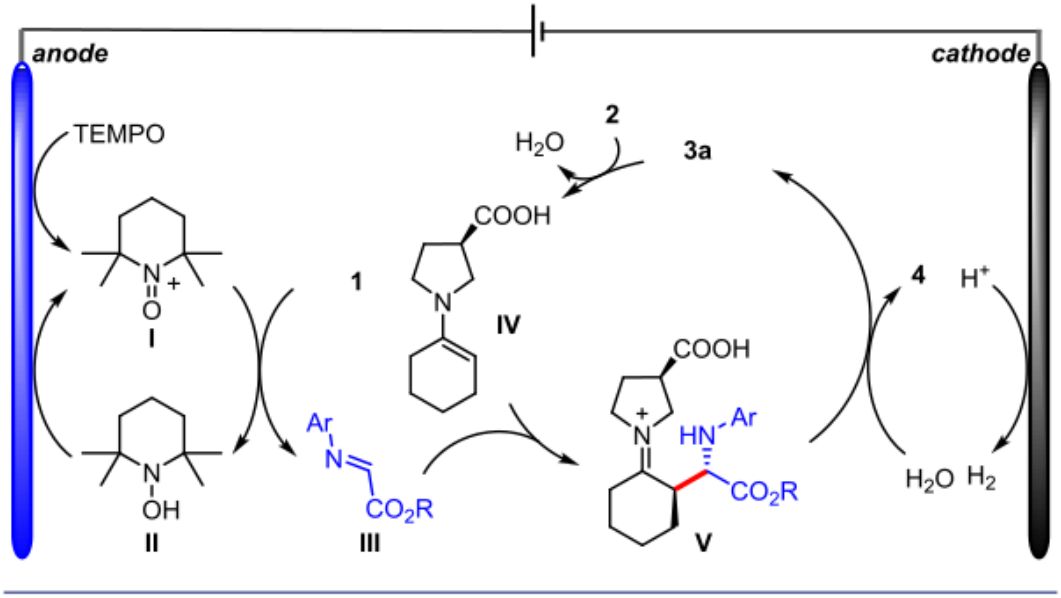
(f)



4a
96:4 dr, 97% ee

61%, 87:13 dr, 92% ee

5a, 39%



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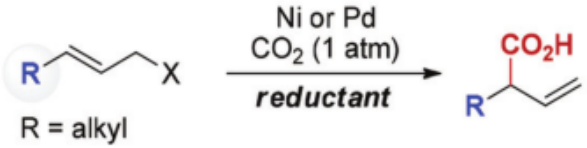
Palladium-catalyzed reductive electrocarboxylation of allyl esters with carbon dioxide†

Ke-Jin Jiao,[a] Zhao-Ming Li,[a] Xue-Tao Xu,[b] Li-Pu Zhang,[b] Yi-Qian Li,[b] Kun Zhang[b] and Tian-Sheng Mei *[a]

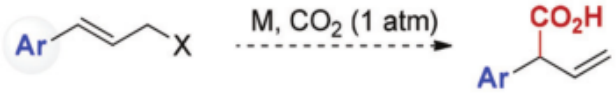
Part 2 阴极还原法

a) Prior art: metal-catalyzed selective carboxylation of allyl electrophiles (refs 5–8)

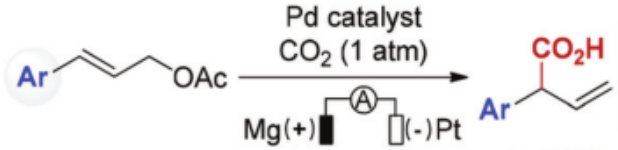


- *chemical reductants*
- *non-conjugated substrates only*
- *not enantioselective*

b) The challenge: avoid metal reductants and enable the use of styrenyl substrates

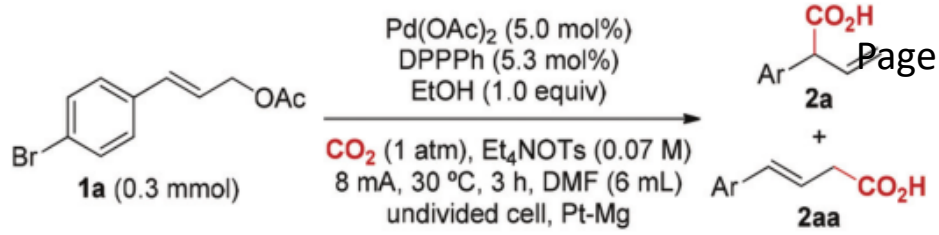


d) This study: an electrocarboxylation of homostyrenyl acetates

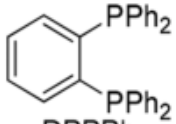


- *electric current as reductant*
- *conjugated allyl electrophiles*
- *first enantioselective example*

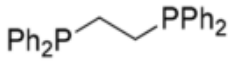
up to 95% yield; 30:1 B/L regioselectivity
up to 67% ee



Entry	Deviation from above conditions	F mol^{-1}	Conv.[b] (%)	Yield[b] (%)	2a/2aa[c]
1	None	3	100	85 (81)[d]	20 : 1
2	PPh_3 (12 mol%) in lieu of DPPPh	3	79	36	2 : 1
3	DPPE in lieu of DPPPh	3	85	70	15 : 1
4	DPPE in lieu of DPPPh	3	81	65	18 : 1
5	DPPE in lieu of DPPPh	3	68	51	6 : 1
6	No EtOH	3	38	21	2 : 1
7	EtOH (0.5 equiv.)	3	94	64	20 : 1
8	EtOH (5.0 equiv.)	3	81	59	11 : 1
9	no $Pd(OAc)_2$	3	32	19	2 : 1
10	no DPPPh	3	72	38	3 : 1
11	no electric current	—	0	NP	—
12	Mn or Zn in lieu of electric current	—	0	NP	—

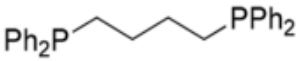


DPPPh



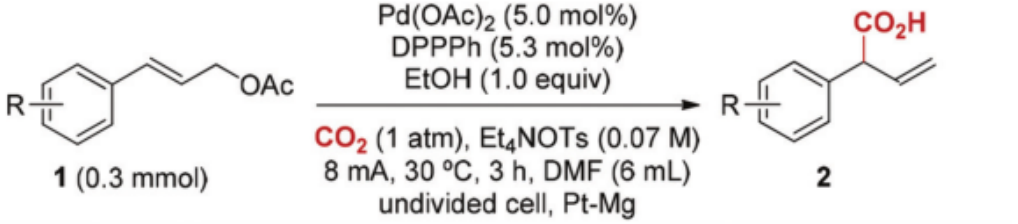
DPPE

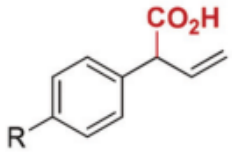
DPPP



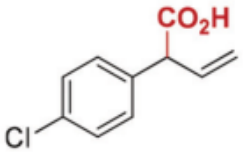
DPPB

Part 2 阴极还原法

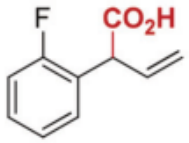




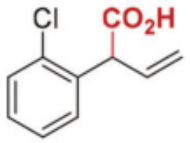
R = Br (**2a**), 20:1, 81%
H (**2b**), 7:1, 58%
Me (**2c**), 4.5:1, 65%
OMe (**2d**), 4:1, 62%
^{t}Bu (**2e**), 4:1, 80%
F (**2f**), 9:1, 78%
CF_3 (**2g**), 12:1, 62%



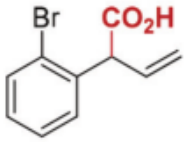
2h, 17:1, 87%



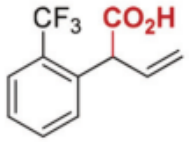
2i, 16:1, 91%



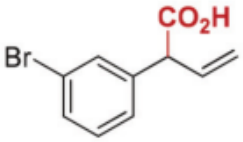
2j, 22:1, 87%



2k, 14:1, 85%[b]

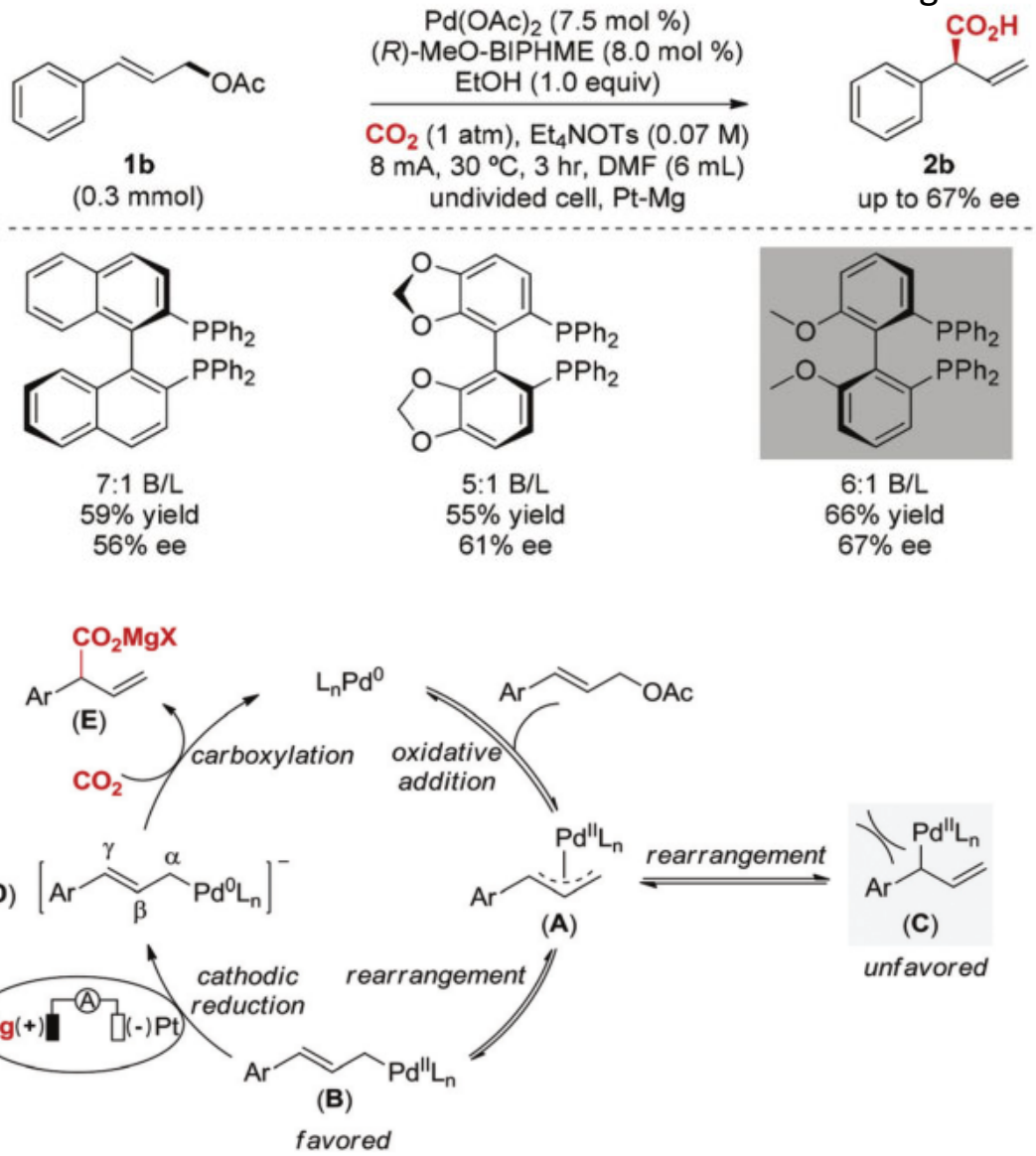


2l, 7:1, 72%



2m, 25:1, 78%

烷基取代和3,3-二取代底物无法反应



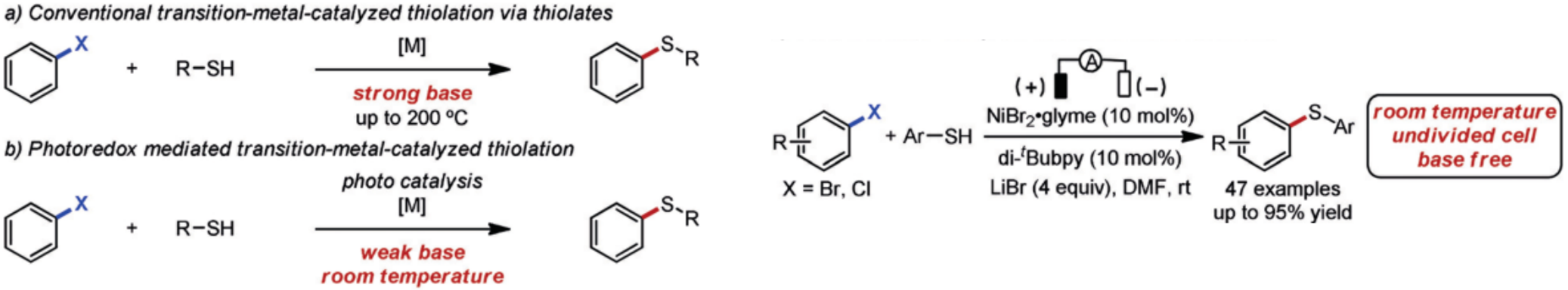
GDCh Communications Angewandte International Edition Chemie

Electrocatalysis

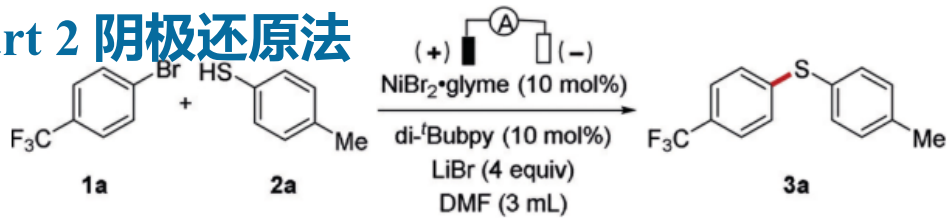
International Edition: DOI: 10.1002/anie.201900956
German Edition: DOI: 10.1002/ange.201900956

Nickel-Catalyzed Thiolation of Aryl Halides and Heteroaryl Halides through Electrochemistry

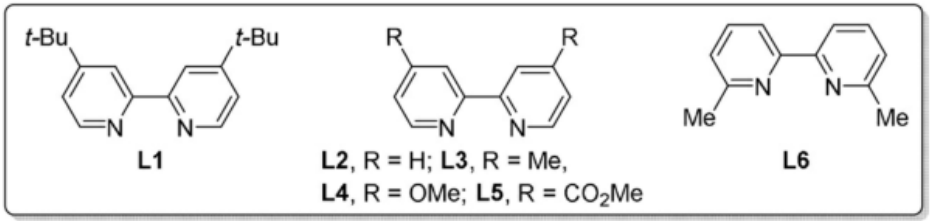
*Dong Liu, Hong-Xing Ma, Ping Fang, and Tian-Sheng Mei**

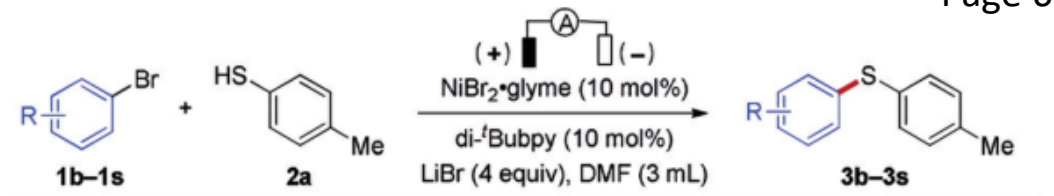


Part 2 阴极还原法

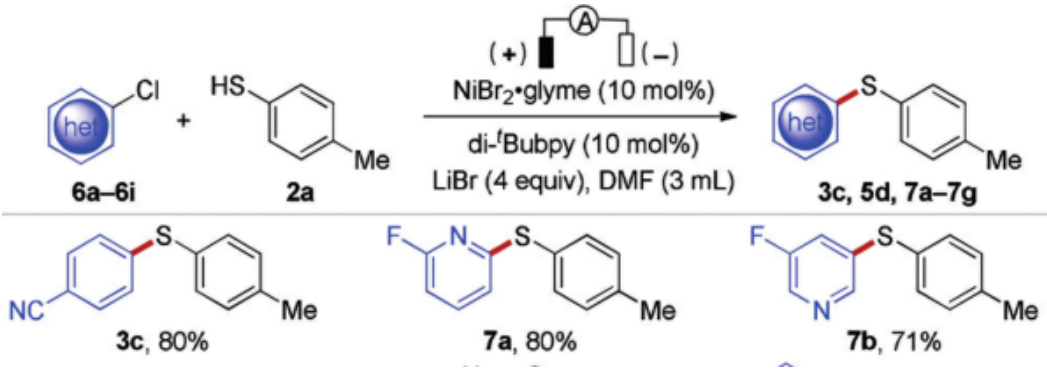


Entry	Variation from standard conditions	Conv. (%)[b]	Yield (%)[b]
1	none	100	95 (85)[c]
2	$NiBr_2$ instead of $NiBr_2$·glyme	86	86
3	$NiCl_2$·glyme instead of $NiBr_2$·glyme	40	40
4	$Ni(OAc)_2$·4 H_2O instead of $NiBr_2$·glyme	61	61
5	$Ni(acac)_2$ instead of $NiBr_2$·glyme	0	0
6	**L2** instead of **L1**	44	40
7	**L3** instead of **L1**	70	65
8	**L4** instead of **L1**	80	75
9	**L5** instead of **L1**	25	20
10	**L6** instead of **L1**	50	45
11	Al instead of Mg	70	70
12	Pt instead of Mg	< 5	< 5
13	RVC instead of Mg	< 5	< 5
14	RVC instead of Ni foam	100	83[c]
15	Graphite instead of Ni foam	100	82[c]
16	Pt instead of Ni foam	100	80[c]
17	no $NiBr_2$·glyme	0	0
18	no electric current	0	0



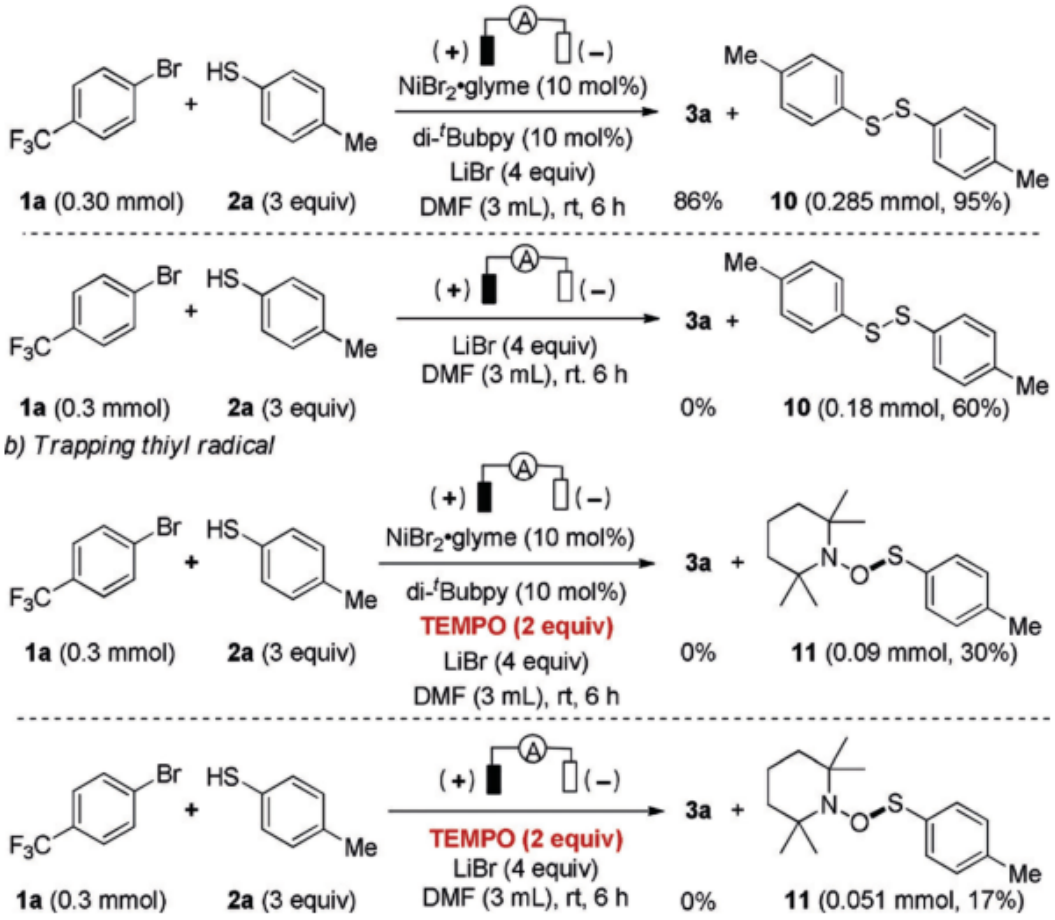


由于相应的芳基卤化物与Ni物种氧化加成的问题，
富电子芳烃在当前条件下不起作用。

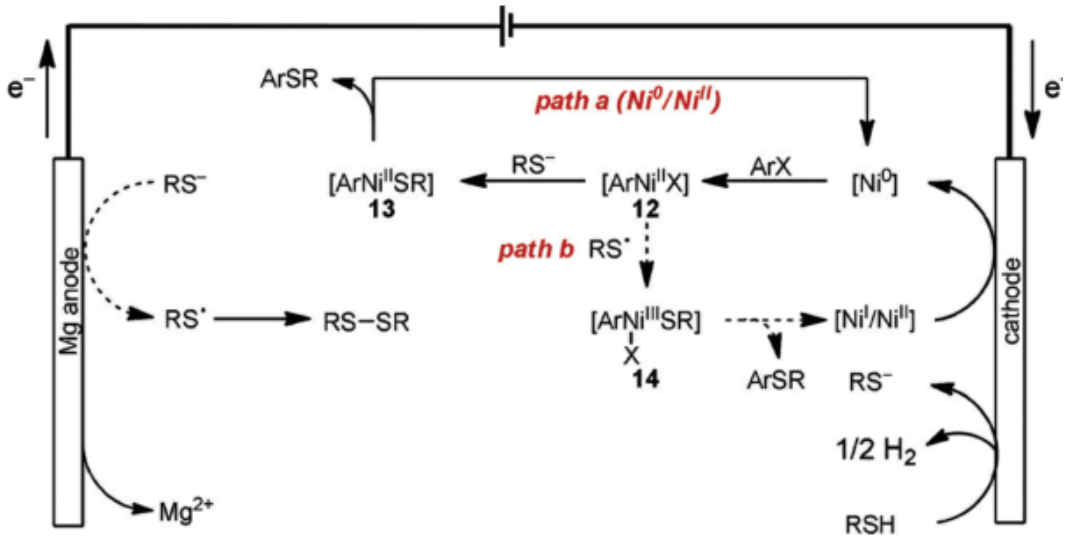


Part 2 阴极还原法

a) Formation of disulfide



b) Trapping thiyl radical



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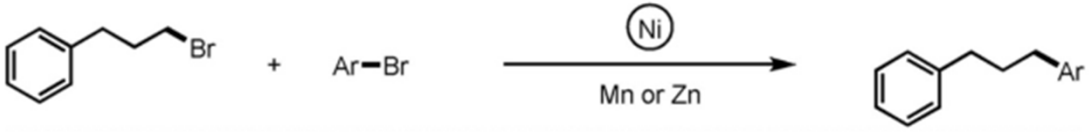
Electrochemistry

International Edition: DOI: 10.1002/anie.201912753
German Edition: DOI: 10.1002/ange.201912753

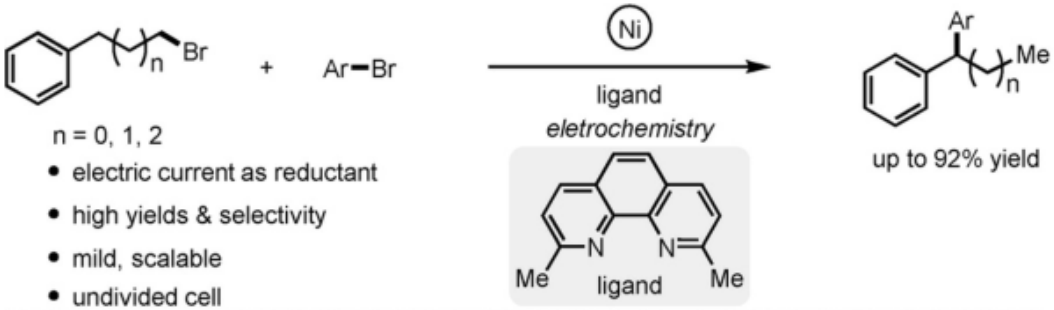
Nickel-Catalyzed Electrochemical Reductive Relay Cross-Coupling of Alkyl Halides to Aryl Halides

*Ke-Jin Jiao, Dong Liu, Hong-Xing Ma, Hui Qiu, Ping Fang, and Tian-Sheng Mei**

a) Ni-catalyzed reductive cross-elecrophile couplings by Weix (Ref. [4])



b) This work: electrochemical reductive relay cross-couplings

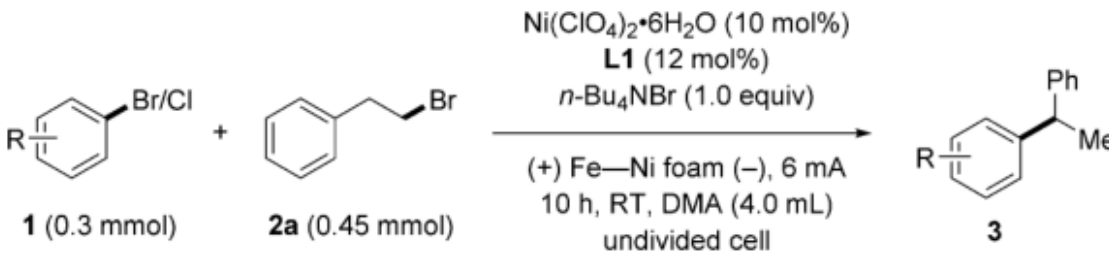


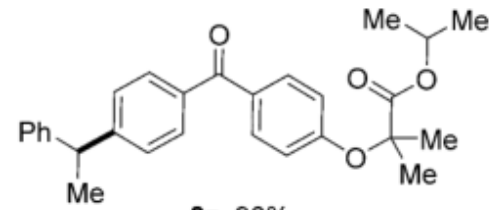
n = 0, 1, 2

- electric current as reductant
- high yields & selectivity
- mild, scalable
- undivided cell

up to 92% yield

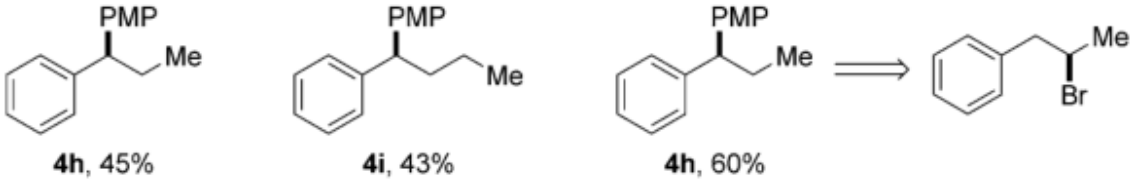
Part 2 阴极还原法

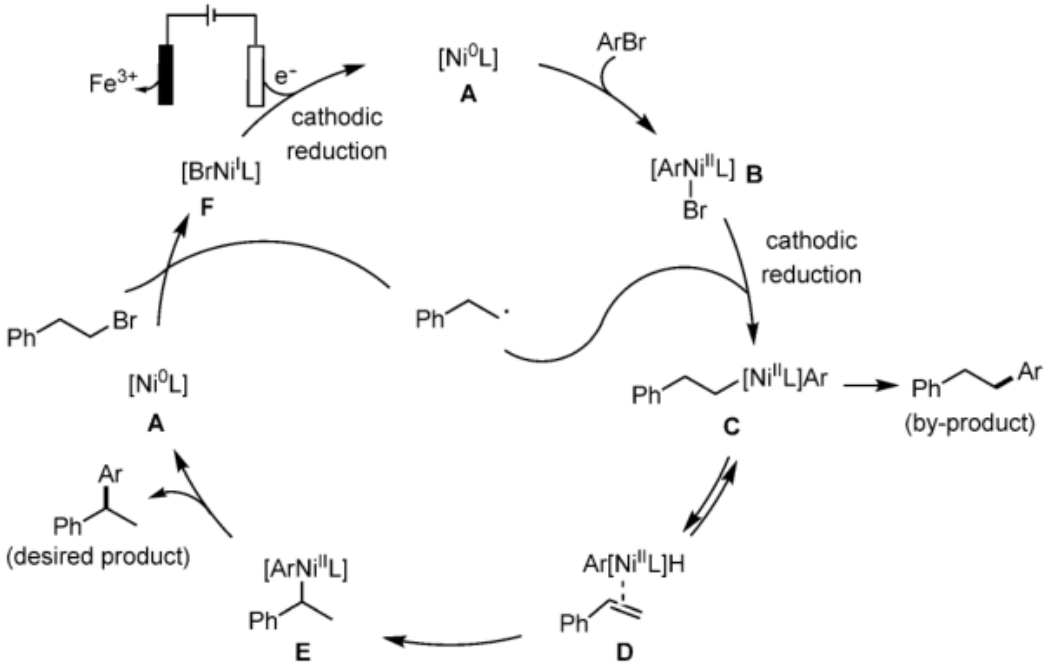




3z, 90%
(84%, 1.08g)

富电子的芳基氯化物是无法反应的





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Communication

Enantioselective Ni-Catalyzed Electrochemical Synthesis of Biaryl Atropisomers

Hui Qiu,[§] Bin Shuai,[§] Yun-Zhao Wang, Dong Liu, Yue-Gang Chen, Pei-Sen Gao, Hong-Xing Ma, Song Chen, and Tian-Sheng Mei*

Cite This: *J. Am. Chem. Soc.* 2020, 142, 9872–9878

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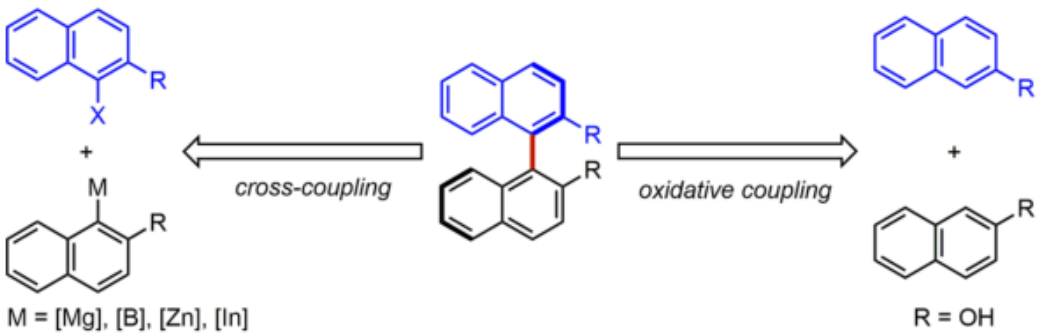
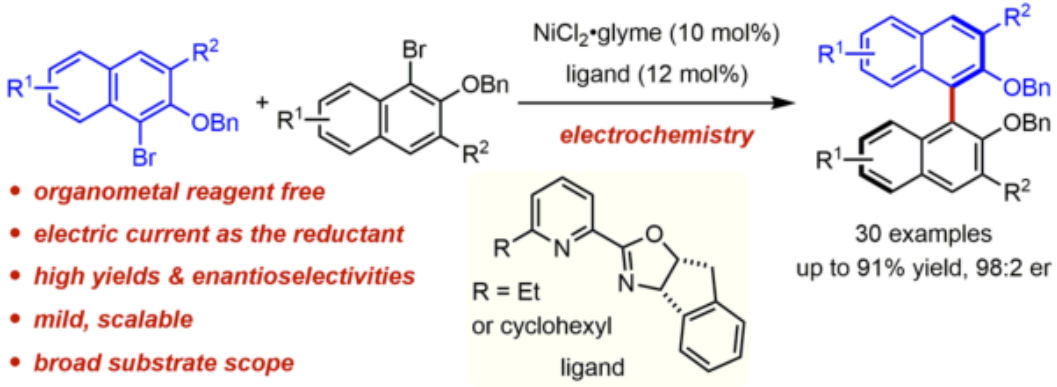
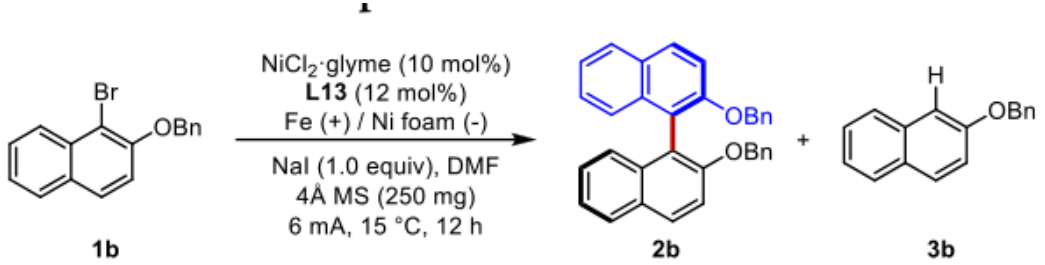
Part 2 阴极还原法

a) Strategies for construction of axially chiral Ar–Ar bonds

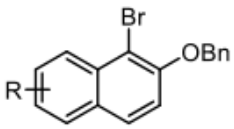






entry	variation from standard conditions	**2b** (%)[b]	ee (%)[c]	**3b** (%)[b]
1[d]	no 4Å MS	10	93	85
2	**-**	**72 (65)[e]**	**93**	**25**
3	Na_2SO_4 in lieu of 4Å MS	13	93	84
4	$MgSO_4$ in lieu of 4Å MS	0	-	95
12[f]	5 mmol scale of 1b (15 °C, 12 mA, 36 h)	81[e]	88	15
13[f]	**5 mmol scale of 1b (0 °C, 12 mA, 36 h)**	**88[e]**	**90**	**10**
16	Mn in lieu of electric current	24	89	22
17	Zn in lieu of electric current	5	86	41

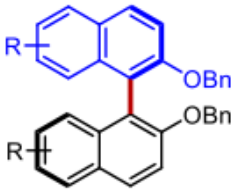
Part 2 阴极还原法



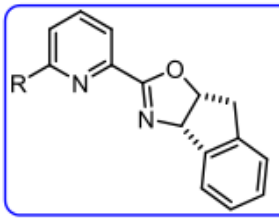
1b–1ae

$NiCl_2$•glyme (10 mol%)
Ligand (12 mol%)

Fe (+) / Ni foam (-)
NaI (0.24 equiv), DMF
12 mA, 0 °C, 36 h



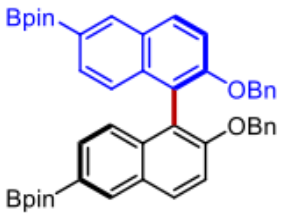
2b–2ae



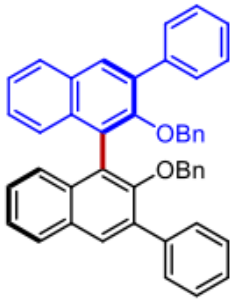
R = ethyl, **L9**
R = cyclohexyl, **L13**

- ***Gram scale synthesis***
- ***High yield and enantioselectivity***
- ***Comparison with Mn powder***

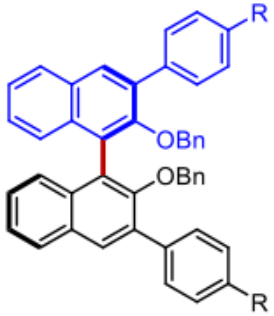
[A][a] **electrochemistry,** 10% [Ni]
[B][b] Mn as the reductant, 10% [Ni]



2n, ***1.44 g***
[A] 81% yield, 95:5 er
[B] 4% yield, 94:6 er



2o, ***1.16 g***
[A] 75% yield, 97:3 er
[B] 22% yield, 95:5 er

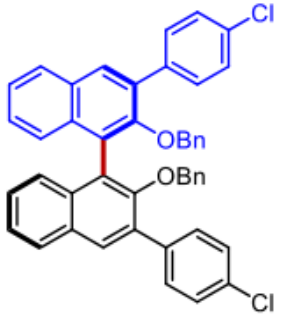


R = Me, **2p**, ***1.32 g***
[A] 82% yield, 96:4 er
[B] 14% yield, 93:7 er

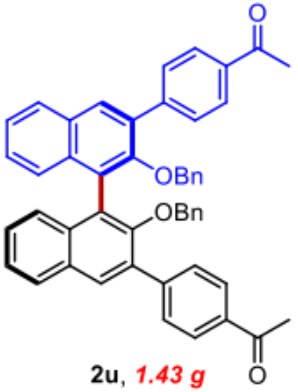
R = Et, **2q**, ***1.35 g***
[A] 80% yield, 97:3 er
[B] 15% yield, 96:4 er

R = Ph, **2r**, ***1.52 g***
[A] 78% yield, 95:5 er
[B] 10% yield, 95:5 er

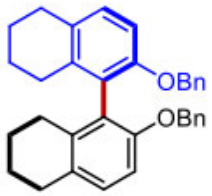
R = F, **2s**, ***1.09 g***
[A] 67% yield, 96:4 er
[B] 16% yield, 96:4 er



2t, ***1.23 g***
[A] 72% yield, 96:4 er
[B] 14% yield, 92:8 er

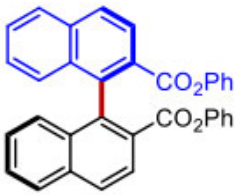


2u, ***1.43 g***
[A] 82% yield, 96:4 er
[B] NR

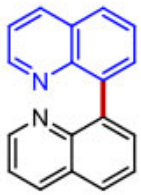


2ad, ***0.79 g***
[A] 66% yield, 84:16 er
[B] 14% yield, 80:20 er

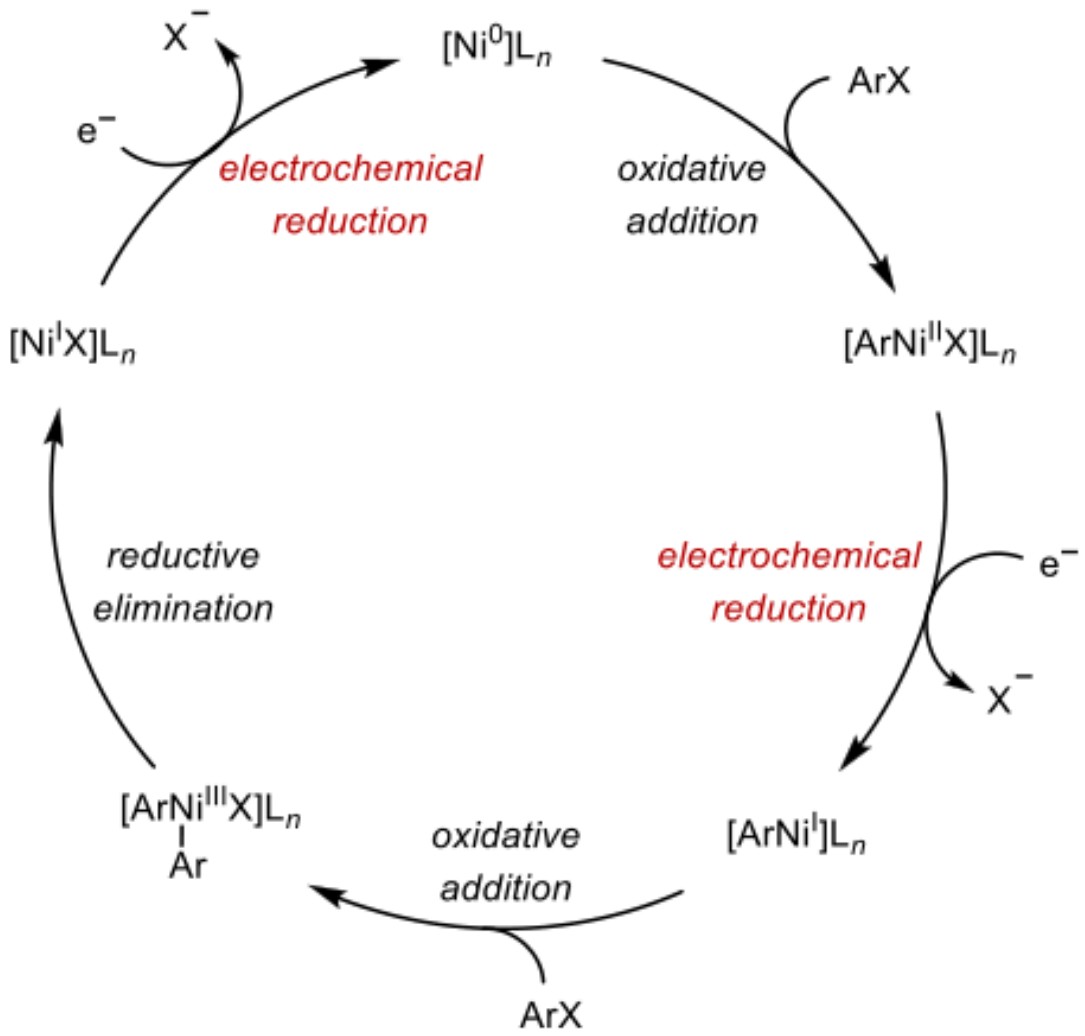
2ae, ***0.86 g***
[A] 75% yield, 89:11 er
[B] 17% yield, 60:40 er



2af[e]
[A] 78% yield, 64:36 er[c]



2ag
[A] 68% yield[c]


[Ni0]Ln
ArX
oxidative addition
[ArNiIIX]Ln
electrochemical reduction
e−
X−
[ArNiI]Ln
oxidative addition
ArX
[ArNiIIIX]Ln
Ar
reductive elimination
[NiIX]Ln
electrochemical reduction
e−
X−

CJC Chinese Journal of Chemistry 中国化学 · An International Journal

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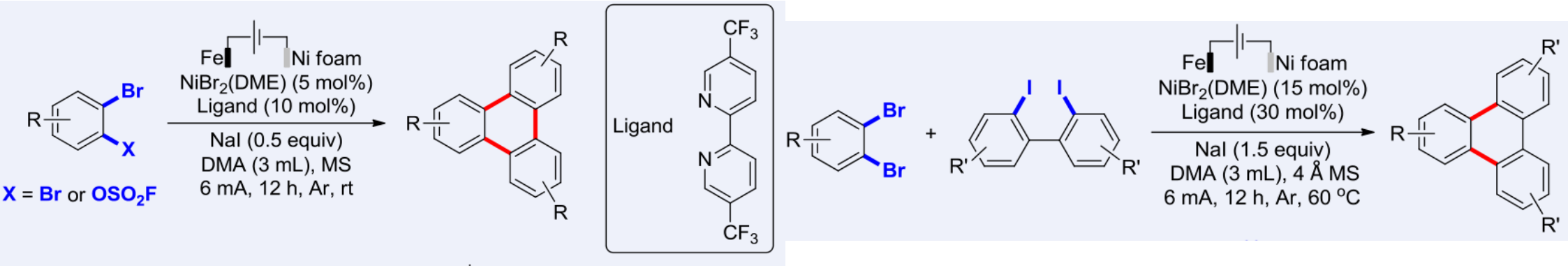
Comprehensive Report

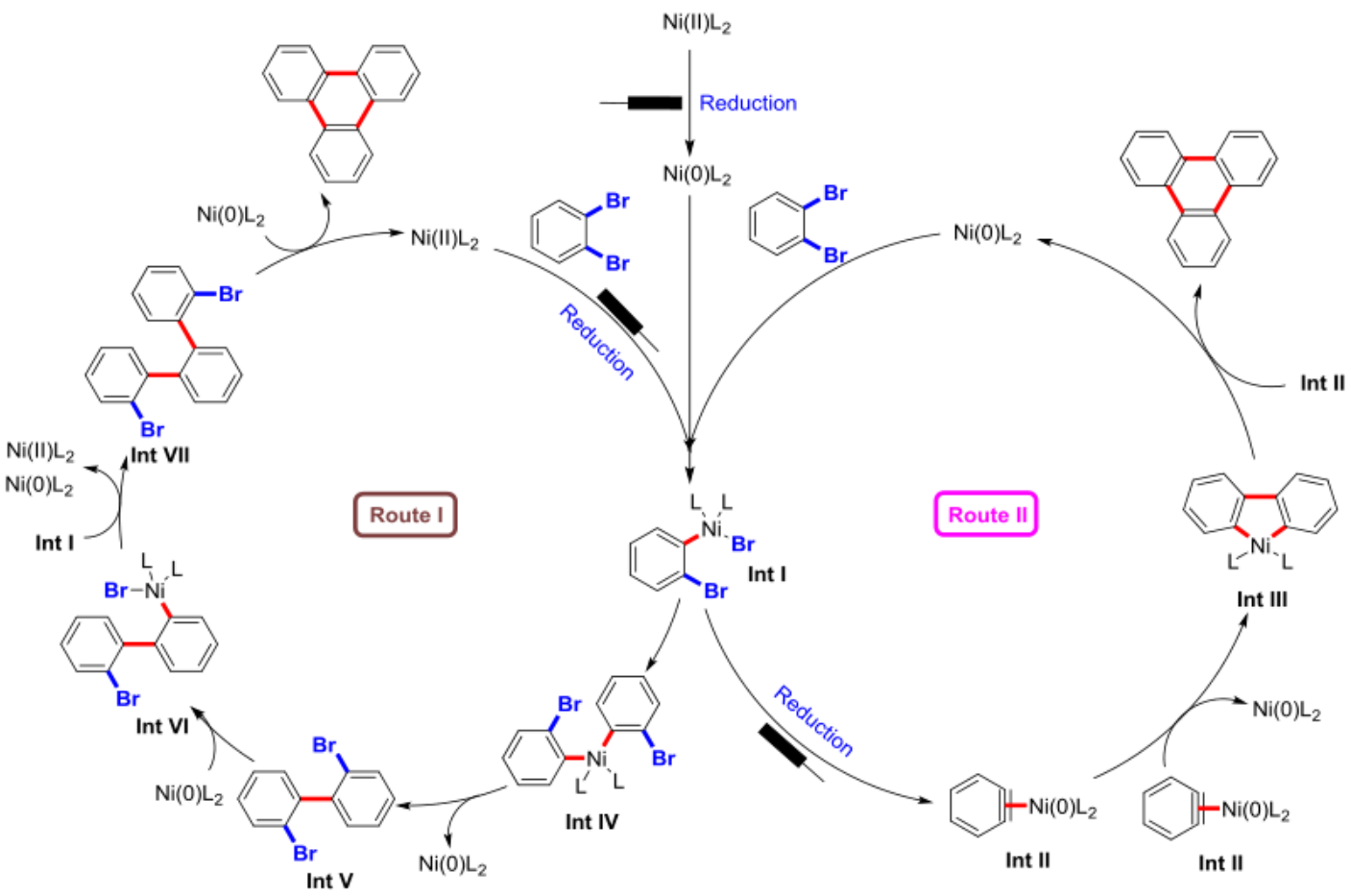
Cite this paper: *Chin. J. Chem.* **2022**, *40*, 2335—2344. **DOI: 10.1002/cjoc.202200245**

Nickel-Catalyzed Electroreductive Syntheses of Triphenylenes Using *ortho*-Dihalobenzene-Derived Benzynes

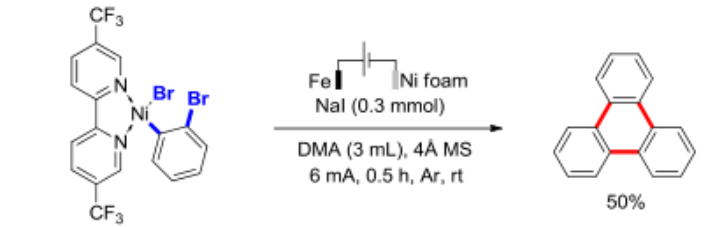
Zhao-Ming Li, Bin Shuai, Cong Ma, Ping Fang, and Tian-Sheng Mei*



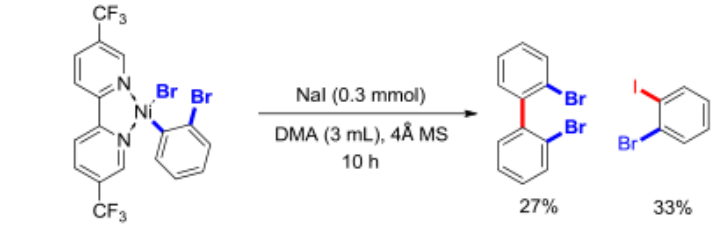
Part 2 阴极还原法



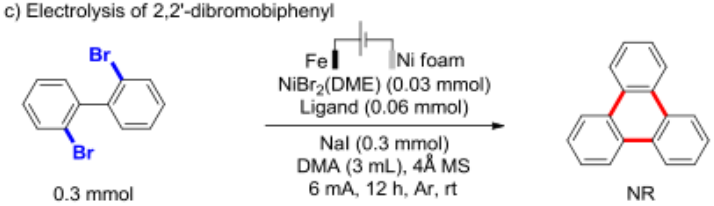
a) Electrolysis of complex **Int I**



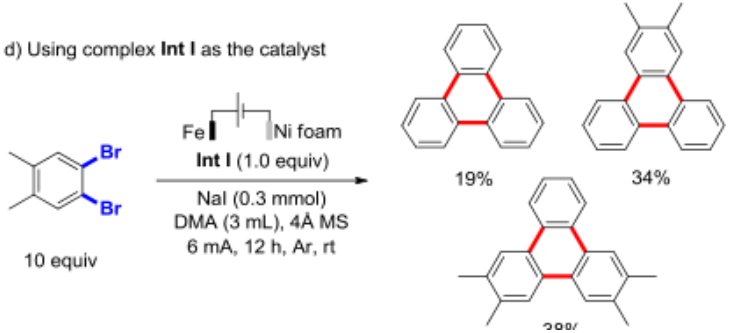
b) Decomposition of complex **Int I**



c) Electrolysis of 2,2'-dibromobiphenyl



d) Using complex **Int I** as the catalyst



CCS Chemistry

RESEARCH ARTICLE

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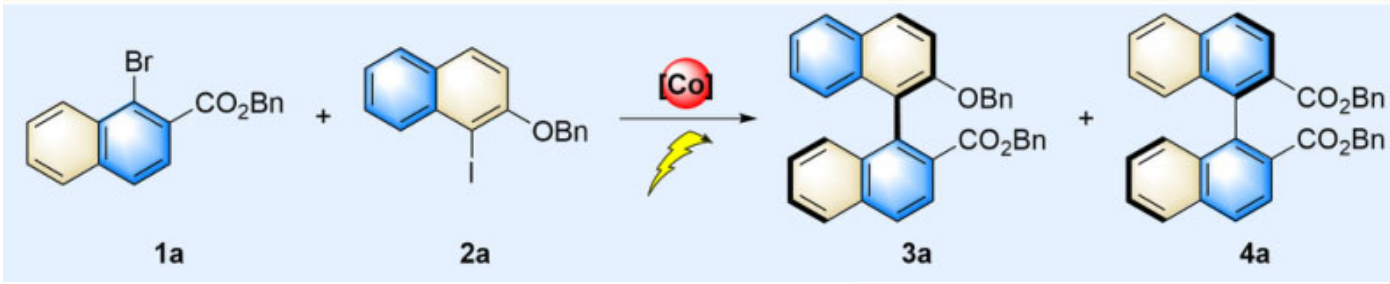
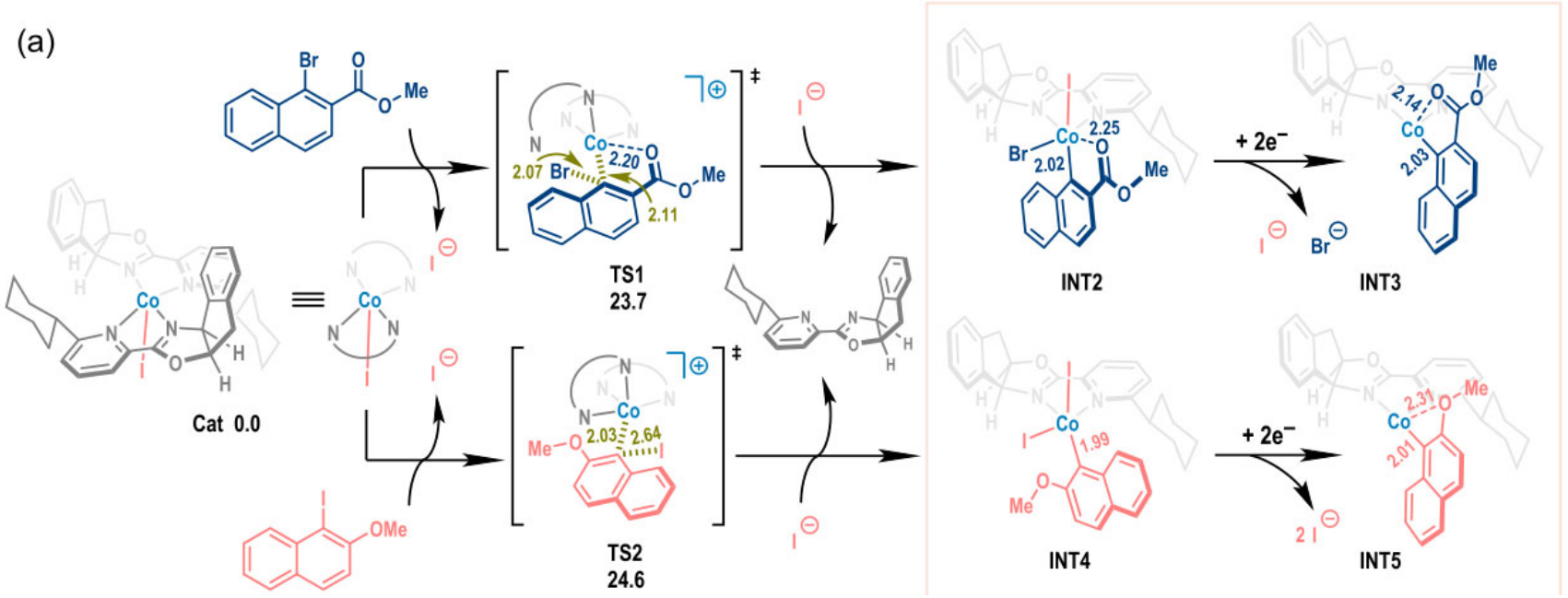
Cobalt-Catalyzed Electrochemical Enantioselective Reductive Cross-Coupling of Organohalides

Shi-Shuo Xu[†], Hui Qiu[†], Pei-Pei Xie[†], Zhen-Hua Wang[†], Xiu Wang, Chao Zheng*, Shu-Li You* & Tian-Sheng Mei*





Thermodynamics of electroreduction processes

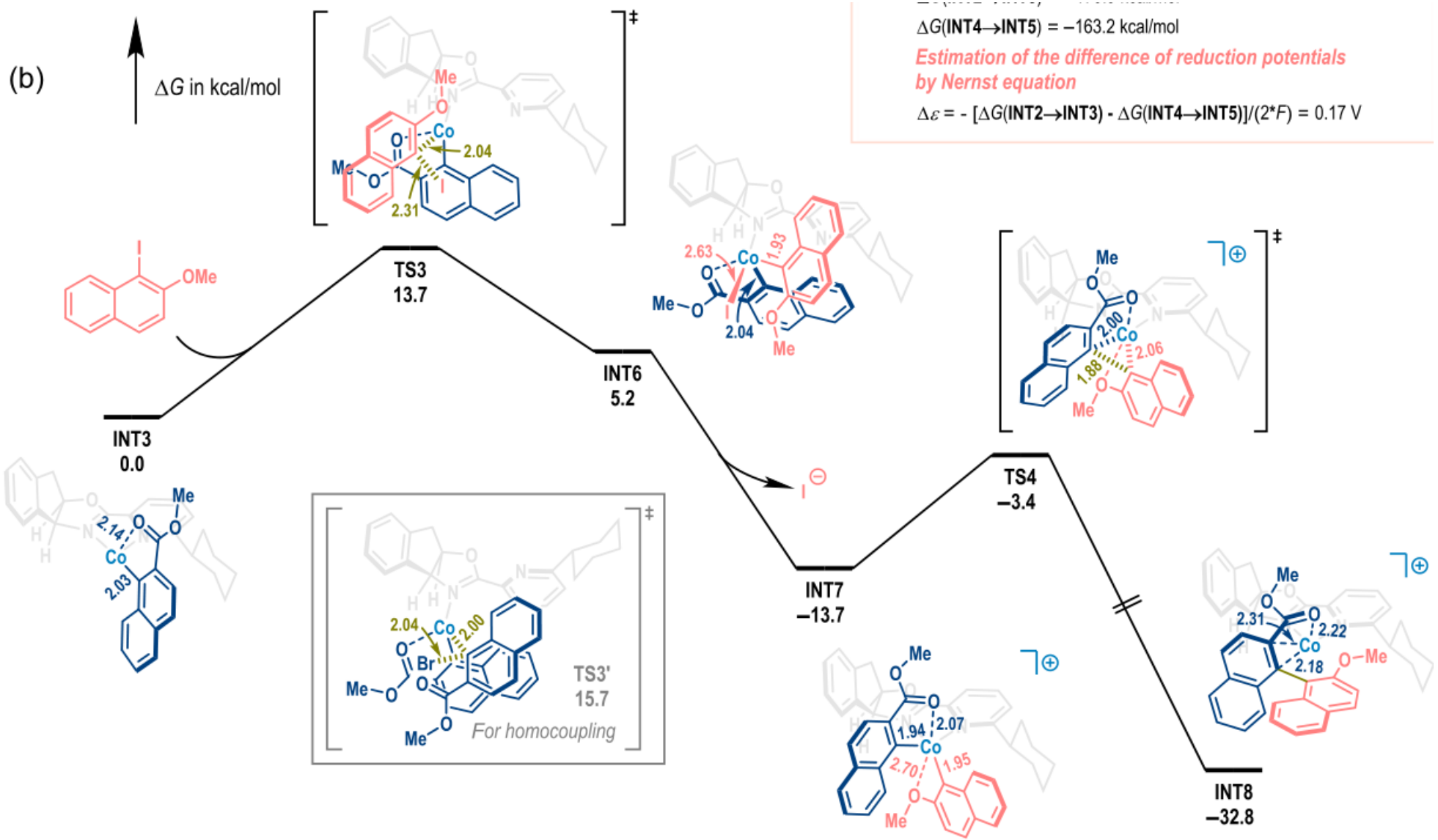
ΔG(**INT2**→**INT3**) = –170.9 kcal/mol

ΔG(**INT4**→**INT5**) = –163.2 kcal/mol

Estimation of the difference of reduction potentials by Nernst equation

$\Delta\varepsilon = -[\Delta G(\textbf{INT2}\rightarrow\textbf{INT3}) - \Delta G(\textbf{INT4}\rightarrow\textbf{INT5})]/(2*F) = 0.17$ V

Part 2 阴极还原法


(b)
ΔG in kcal/mol
ΔG(INT4→INT5) = −163.2 kcal/mol
Estimation of the difference of reduction potentials by Nernst equation
Δε = - [ΔG(INT2→INT3) - ΔG(INT4→INT5)]/(2*F) = 0.17 V
INT3
0.0
TS3
13.7
INT6
5.2
INT7
−13.7
TS4
−3.4
INT8
−32.8
TS3'
15.7
For homocoupling

ORGANIC CHEMISTRY FRONTIERS

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RESEARCH ARTICLE

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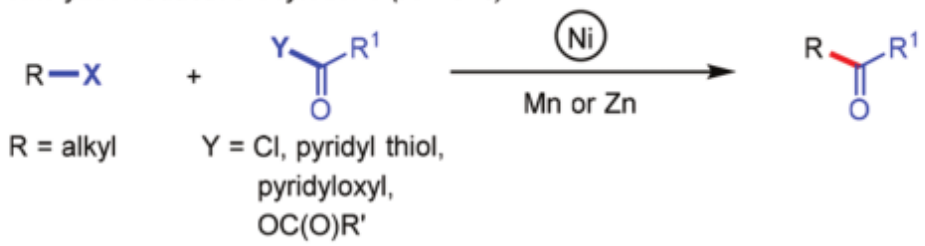
Cite this: *Org. Chem. Front.*, 2021, **8**, 6603

Nickel-catalyzed electrochemical reductive relay cross-coupling of alkyl halides with alkyl carboxylic acids†

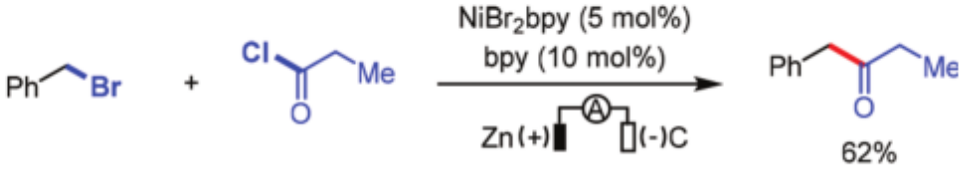
Ke-Jin Jiao,[a,b] Cong Ma,[b] Dong Liu,[b] Hui Qiu,[b] Bin Cheng*[a] and Tian-Sheng Mei *[b]

Part 2 阴极还原法

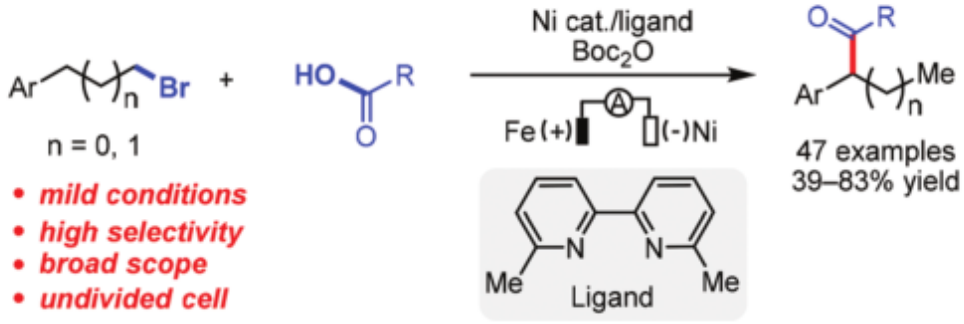
a) Ni-catalyzed reductive acylations (ref. 3–6)



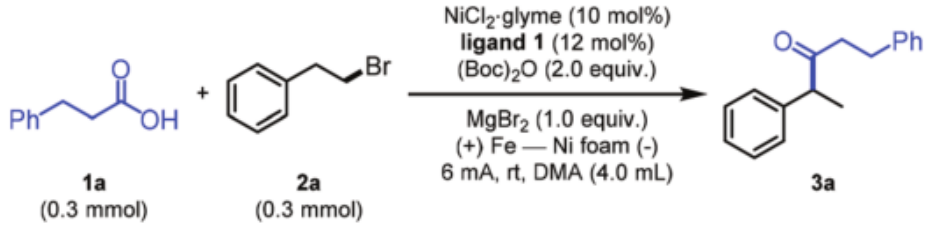
b) Ni-catalyzed electrochemical acylation of benzyl bromides (ref. 10)



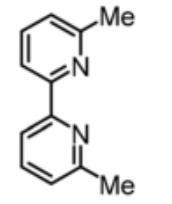
c) This work: electrochemical reductive relay cross-couplings



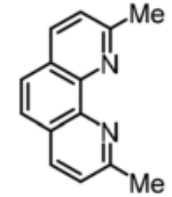
- ***mild conditions***
- ***high selectivity***
- ***broad scope***
- ***undivided cell***



Entry	Variation from the above conditions[a]	*F*/mol	Yield of **3a**[b] (%)
1	None	4.5	77 (72)[c]
2	$NiBr_2$·glyme as the catalyst	4.5	64
3	$NiCl_2$ as the catalyst	4.5	47
4	Mg as the anode	4.5	37
5	Al as the anode	4.5	55
6[d]	RVC as the anode	4.5	31
7	MgI_2 in lieu of $MgBr_2$	4.5	31
8	*n*-Bu_4NBr in lieu of $MgBr_2$	4.5	NP
9	$(Boc)_2O$ (1.0 equiv.)	4.5	40
10	$(Boc)_2O$ (3.0 equiv.)	4.5	40
11	**Ligand 2** as the ligand	4.5	42
12	Without Ni or ligand	4.5	0

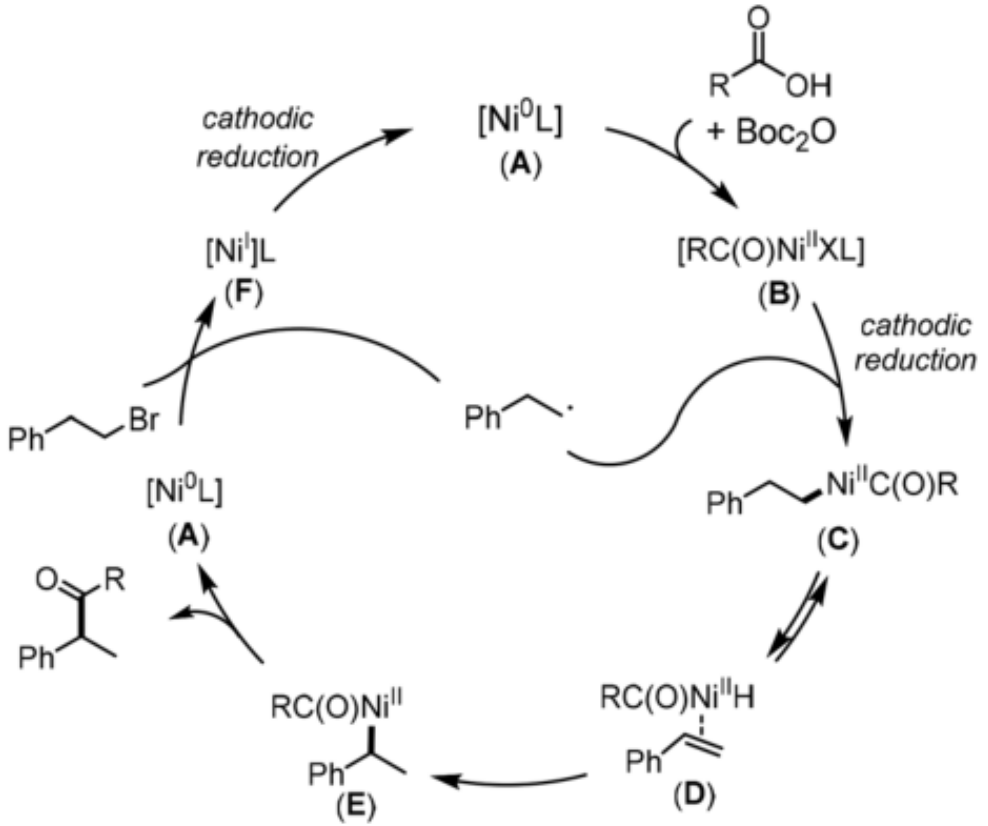


ligand 1



ligand 2


Ph
OH
O
Br
Ni(cod)2 (1.0 equiv)
Ligand 1 (1.2 equiv)
(Boc)2O (2.0 equiv.)
MgBr2 (1.0 equiv.)
rt, DMA (4.0 mL)
Ph
O
1a
(0.3 mmol)
2a
(0.3 mmol)
3a, 65%


cathodic
reduction
[Ni0L]
(A)
R
OH
O
+ Boc2O
[Ni^I]L
(F)
[RC(O)Ni^IIXL]
(B)
cathodic
reduction
Ph
Br
Ph
[Ni0L]
(A)
Ni^IIC(O)R
Ph
(C)
O
R
Ph
RC(O)Ni^II
Ph
(E)
RC(O)Ni^IIH
Ph
(D)

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Communication

Enantioselective Reductive Cross-Couplings of Olefins by Merging Electrochemistry with Nickel Catalysis

Yun-Zhao Wang, Bing Sun, Xiao-Yu Zhu, Yu-Cheng Gu, Cong Ma, and Tian-Sheng Mei*

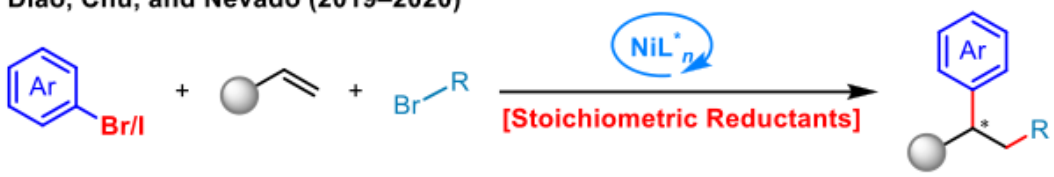
Cite This: *J. Am. Chem. Soc.* 2023, 145, 23910–23917

https://doi.org/10.1021/jacs.3c10109

Part 2 阴极还原法

a) Enantioselective reductive cross-couplings of olefins

Diao, Chu, and Nevado (2019–2020)



Chemical approaches: Reductive cross-coupling with aryl chlorides is unknown

b) Enantioselective electroreductive cross-couplings

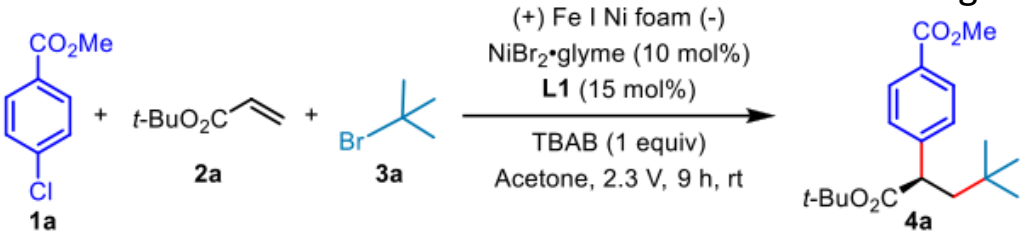
Reisman (2019) | **Mei (2020)** | **Mei (2022)** | **Nevado (2023)** | **Mei (2023)**

Enantioselective electroreductive cross-coupling of alkenes is unknown

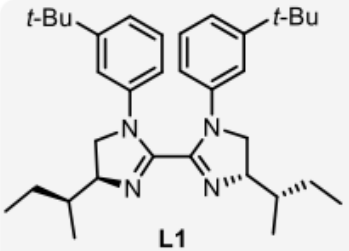
c) This work: Enantioselective electroreductive cross-couplings of olefins

X = Cl, Br, OTf

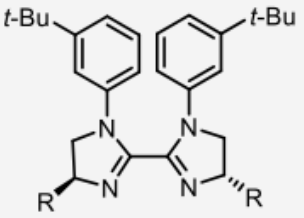
R = alkyl



entry	variations from standard conditions	yield (%)[b]	ee (%)
1	none	71(70)	94
2	**L2** instead of **L1**	40	94
3	**L3** instead of **L1**	43	94
4	**L4** instead of **L1**	<5	70
5	**L5** instead of **L1**	<5	53
6	**L6** instead of **L1**	trace	
7	DMAc instead of Acetone	23	85
8	anode Al instead of Fe	13	75
9	anode Zn instead of Fe	6	87
10	anode Pt instead of Fe[c]	42	93
11	cathode RVC instead of Ni foam	54	94
12	without [Ni], **L1**, or electric current		

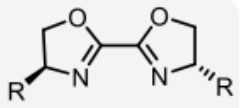


L1



L2 R = *i*-Pr

L3 R = *c*-pentyl

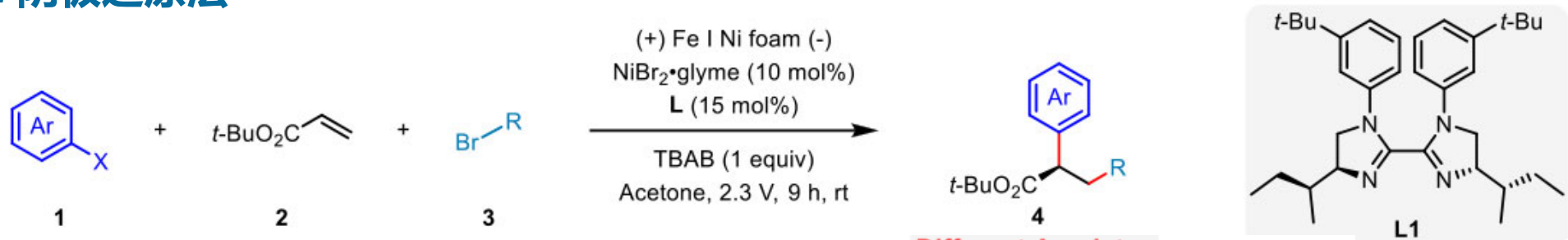


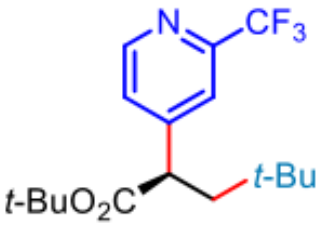
L4 R = *s*-Bu

L5 R = *i*-Pr

L6 R = *c*-pentyl

Part 2 阴极还原法

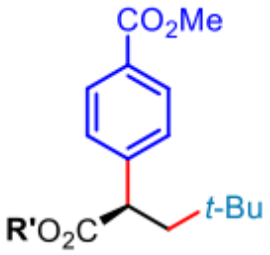




4h, 35%, 90% ee

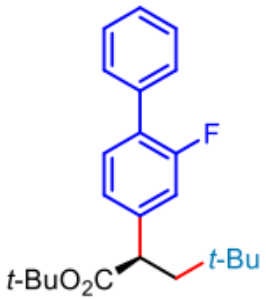
可能是卤代芳烃脱卤导致产率低

Different Acrylates

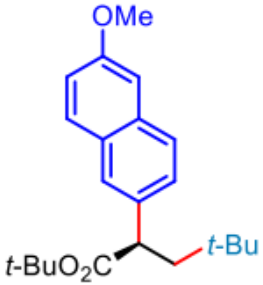


R' = Me	**5q**, 46%, 79% ee
R = *n*-Bu	**5r**, 45%, 72% ee
R = *i*-Pr	**5s**, 72%,75% ee
R = Cy	**5t**, 63%, 71% ee
R = Bn	**5u**, 73%, 70% ee
R = Ph	**5v**, 58%, 57% ee

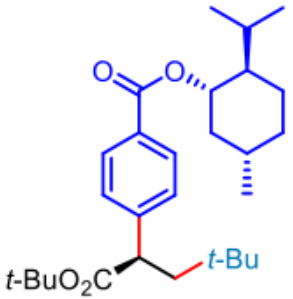
更换基团ee值全部都下降



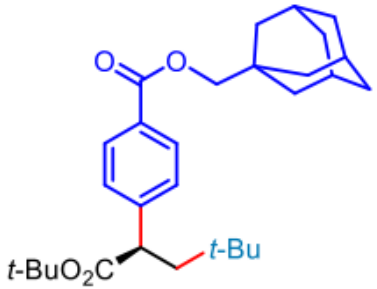
5w, 64%, 93% ee
(from flurbiprofen)



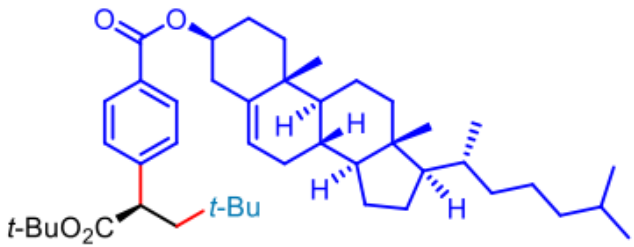
5x, 68%, 92% ee
(from naproxen analog)



5y, 58%, 91% ee
(from menthol analog)



5z, 57%, 95% ee
(from adamantanemethanol)

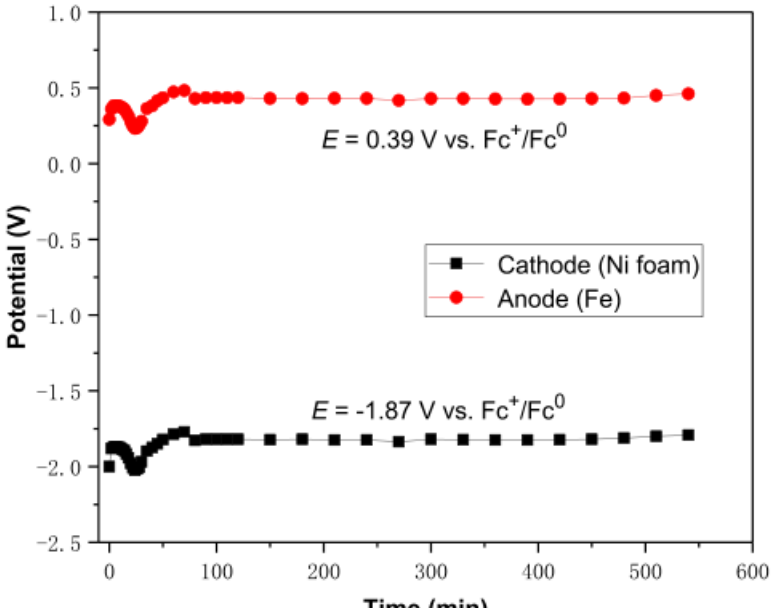


5aa, 61%, 95% ee
(from cholesterol)

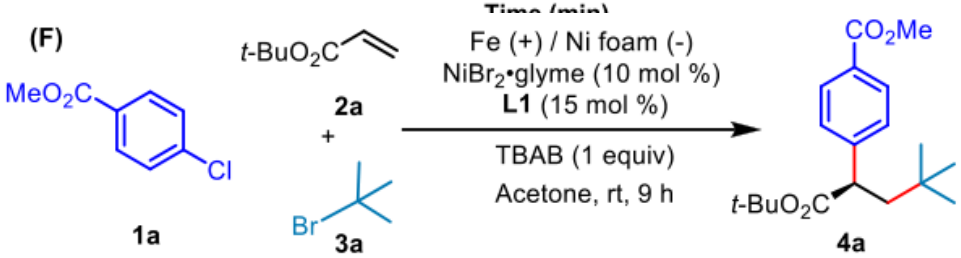
[a]All yields refer to isolated products. [b]Current of 4 mA, 9 h. [c]Addition of 6 mmol of **2a**, 60 h.

Part 2 阴极还原法

(C)



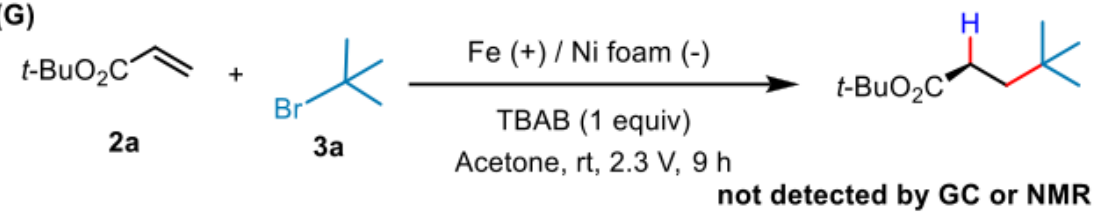
(F)



constant potential (V)	yield (%)	ee (%)
−1.0	0	-
−1.8	68	94
−2.2	27	93

证明是Ni(Ⅱ)/Ni(Ⅰ)循环

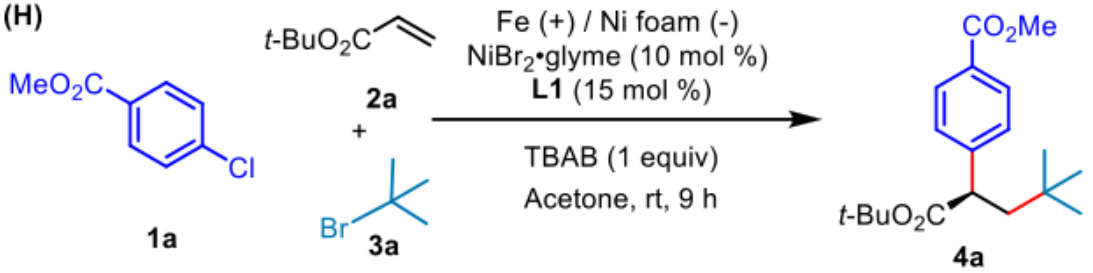
(G)



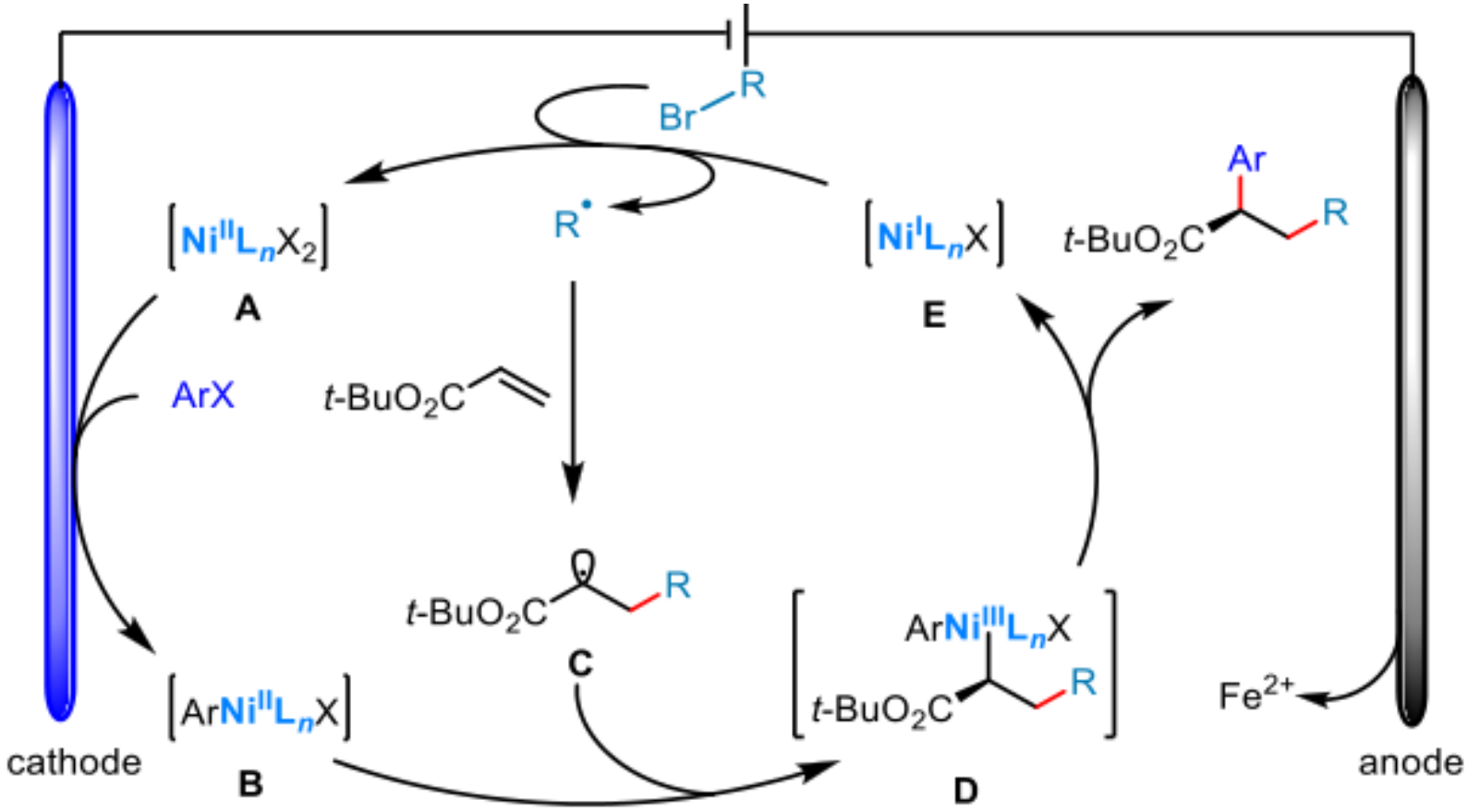
not detected by GC or NMR

证明自由基不是由电极还原产生

(H)



entry	additive	yield (%)	ee (%)
1	TEMPO (2 equiv)	0	-
2	BHT (2 equiv)	0	-
3	Mn (3 equiv)	0	-
4	Zn (3 equiv)	0	-
5	TDAE (3 equiv)	0	-


Br
R
R•
[Ni^II L_n X_2]
A
ArX
t-BuO2C
t-BuO2C
R
C
[ArNi^II L_n X]
B
cathode
[Ni^I L_n X]
E
t-BuO2C
Ar
R
[ArNi^III L_n X
t-BuO2C
R
]
D
Fe2+
anode

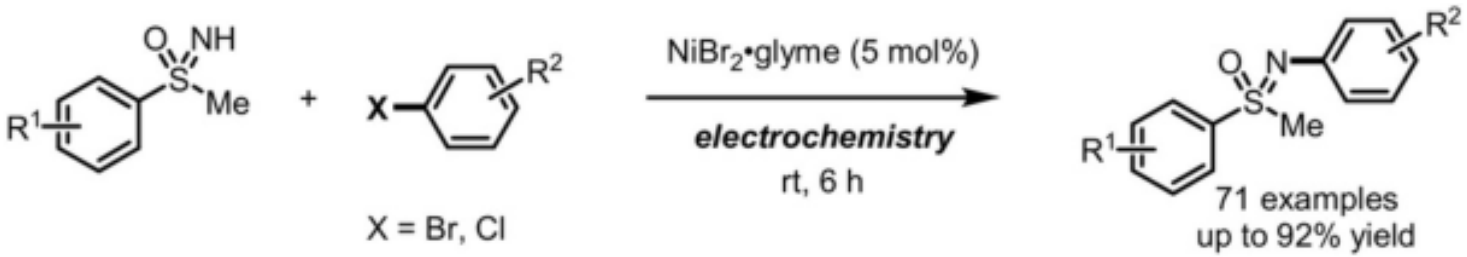
GDCh Communications Angewandte International Edition Chemie

How to cite: *Angew. Chem. Int. Ed.* **2021**, *60*, 9444–9449
International Edition: doi.org/10.1002/anie.202016310
German Edition: doi.org/10.1002/ange.202016310

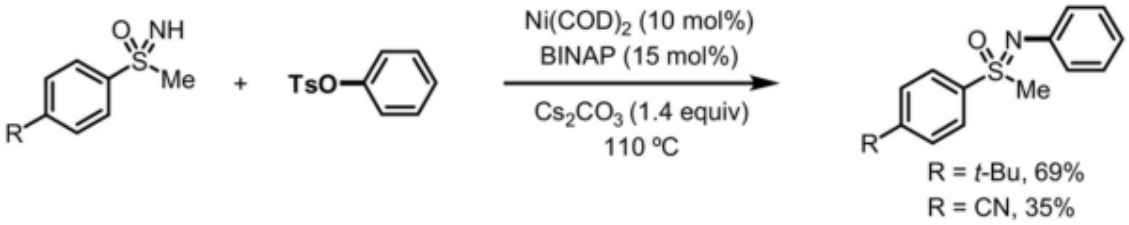
Paired Electrolysis

Nickel-Catalyzed *N*-Arylation of *NH*-Sulfoximines with Aryl Halides via Paired Electrolysis

Dong Liu[+], *Zhao-Ran Liu*[+], *Cong Ma, Ke-Jin Jiao, Bing Sun, Lei Wei, Julien Lefranc, Simon Herbert, and Tian-Sheng Mei**



b) Ni-catalyed N-arylation of NH-sulfoximines via Ni(0)/Ni(II) catalysis by Bolm (ref. 11)



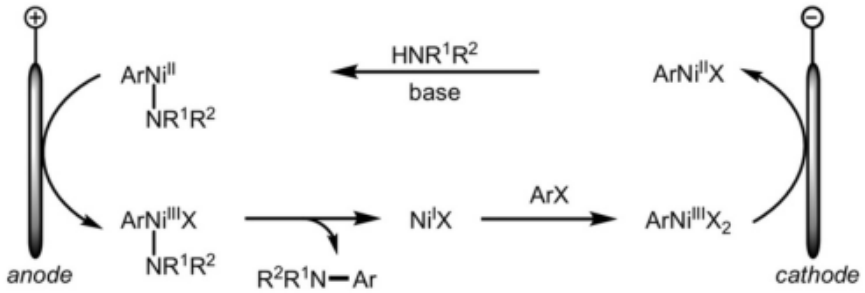
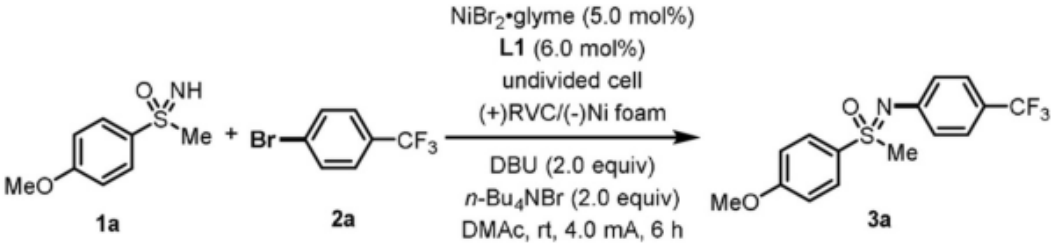


Table 1: Reaction optimization and control studies.[a]

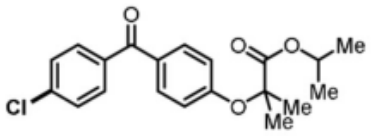


Entry	Deviation from standard conditions	Conv. [%][b]	Yield [%][b]
1	none	100	91 (90)[c]
2	C in lieu of RVC	35	20
3	Pt in lieu of RVC	28	15
4	C in lieu of Ni foam	10	NR
5	Pt in lieu of Ni foam	5	NR

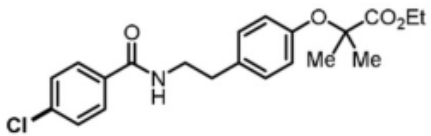
Part 3 成队电解

a) Diversification of pharmaceutical agents

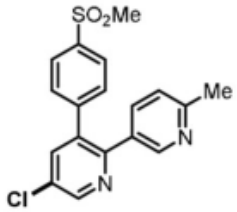
Analogues of pharmaceutical agents



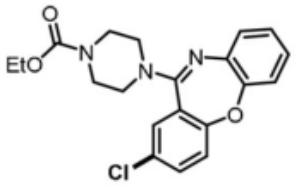
4a, Fenofibrate



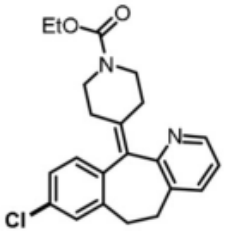
4b, Bezafibrate analogue



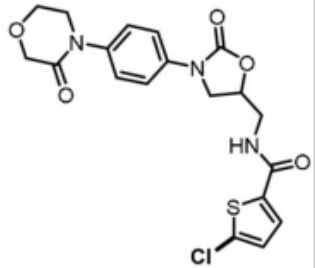
4c, Etoricoxib



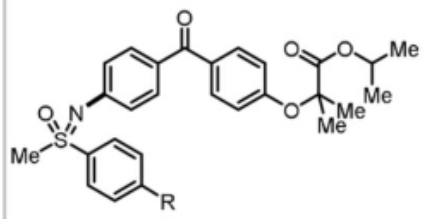
4d, Amoxapine analogue



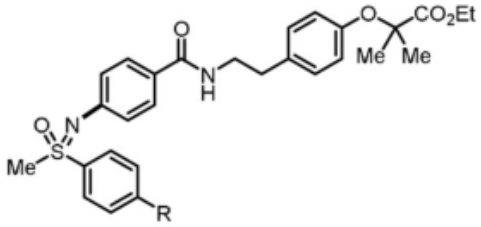
4e, Loratadine



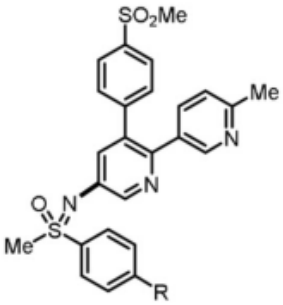
4f, Rivaroxaban



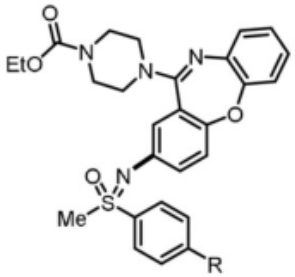
R = OMe, **5a**, 65%[a] (9%)[c]
R = H, **5g**, 70%[a] (8%)[c]



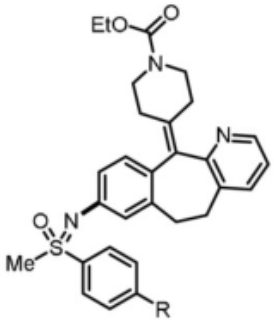
R = OMe, **5b**, 71%[b] (10%)[c]
R = H, **5h**, 64%[b] (10%)[c]



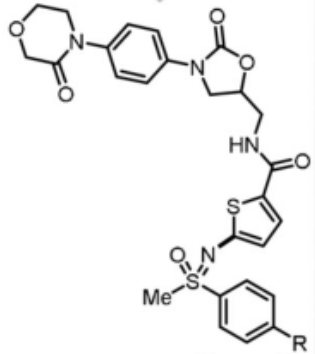
R = OMe, **5c**, 75%[b] (<5%)[c]
R = H, **5i**, 70%[b] (14%)[c]



R = OMe, **5d**, 60%[b]
R = H, **5j**, 55%[b]

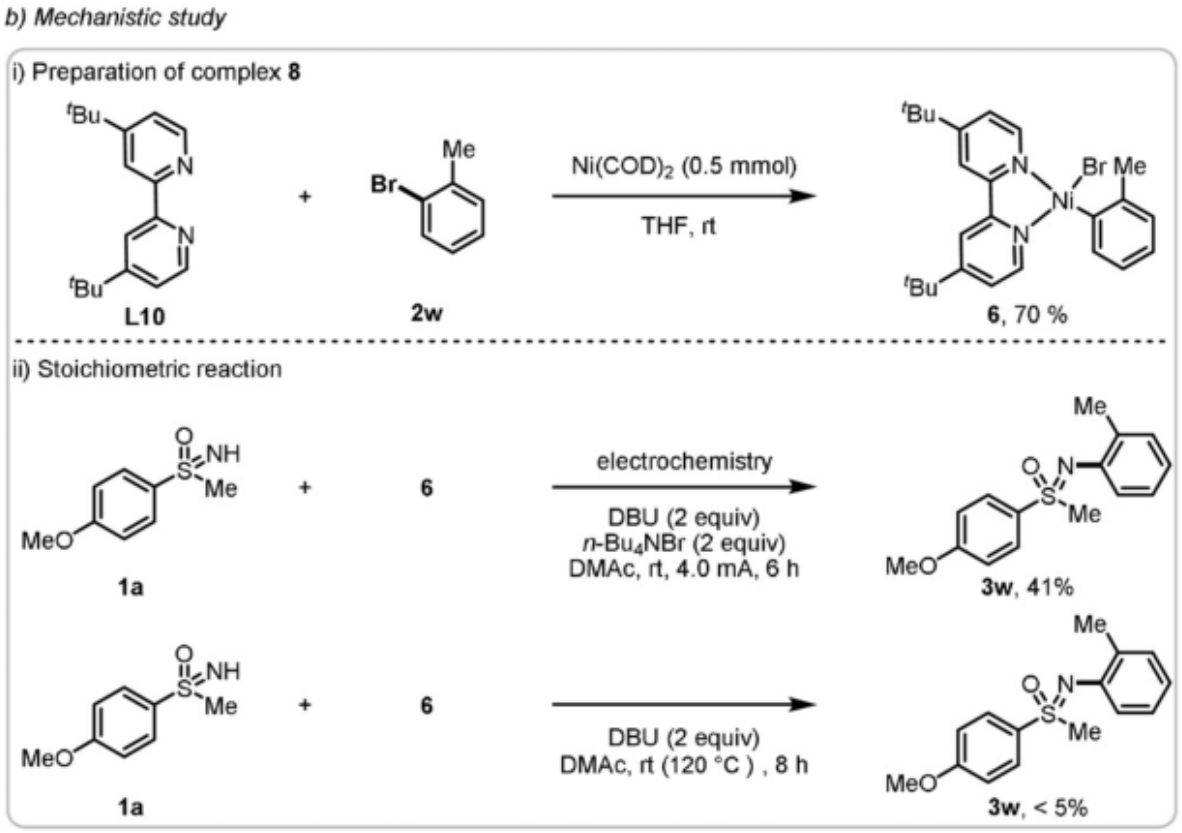


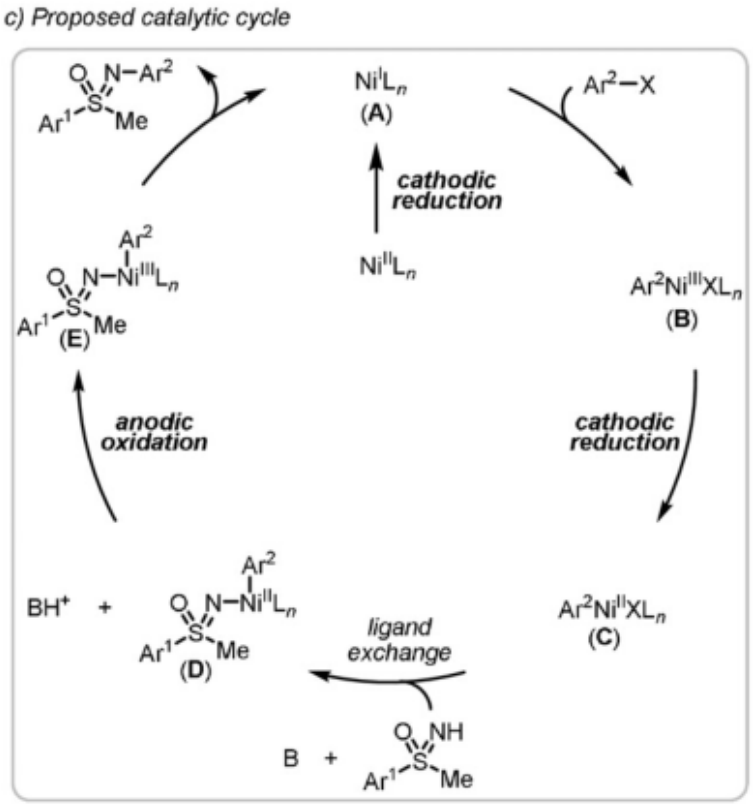
R = OMe, **5e**, 57%[b] (<5%)[c]
R = H, **5k**, 60%[b] (<5%)[c]



R = OMe, **5f**, 51%[b] (<5%)[c]
R = H, **5l**, 57%[b] (<5%)[c]

Part 3 成队电解





阳极氧化步骤至关重要

JOC The Journal of Organic Chemistry

pubs.acs.org/joc Article

Esterification of Carboxylic Acids with Aryl Halides via the Merger of Paired Electrolysis and Nickel Catalysis

Lei Wei, Zhen-Hua Wang, Ke-Jin Jiao, Dong Liu, Cong Ma, Ping Fang, and Tian-Sheng Mei*

Cite This: J. Org. Chem. 2021, 86, 15906−15913

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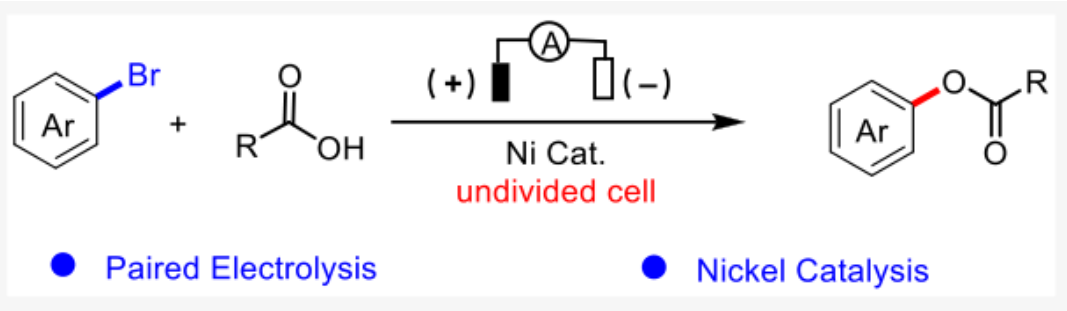

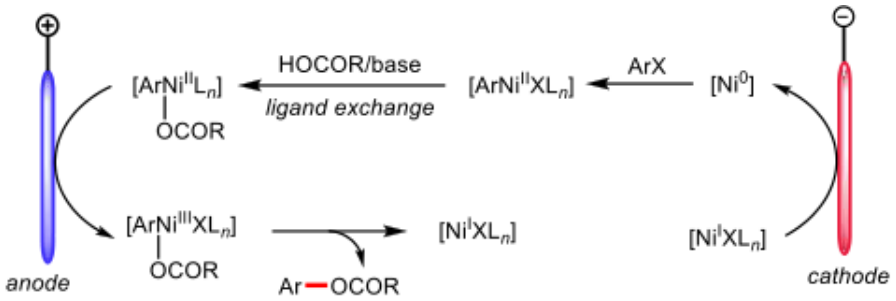

Journal of Electrochemistry

Volume 30
Issue 5 *Special Issue on Organic Electrosynthesis (II)*

2024-05-28

Nickel-Catalyzed α-Arylation of α-Cyanoacetates Enabled by Electrochemistry

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Anat Milo

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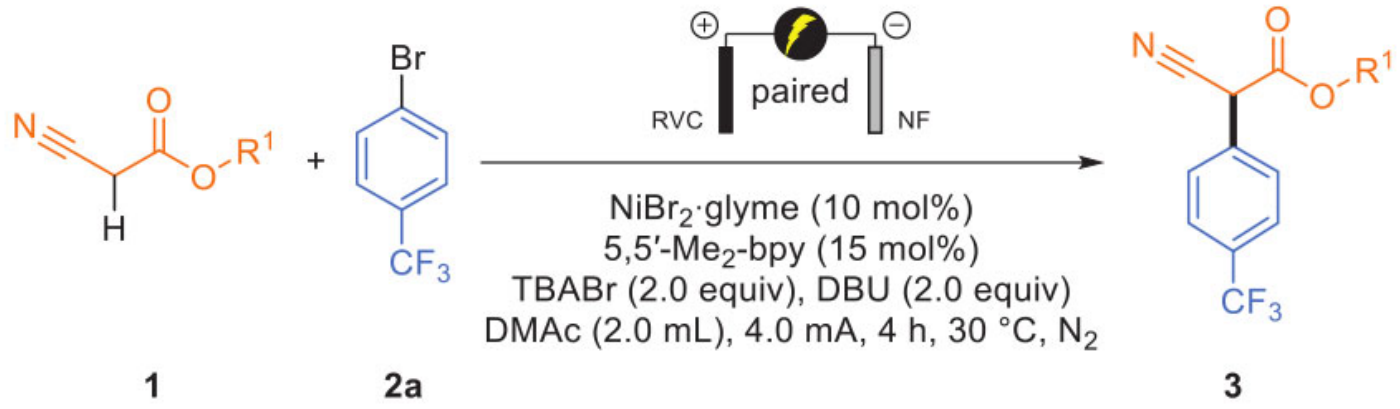
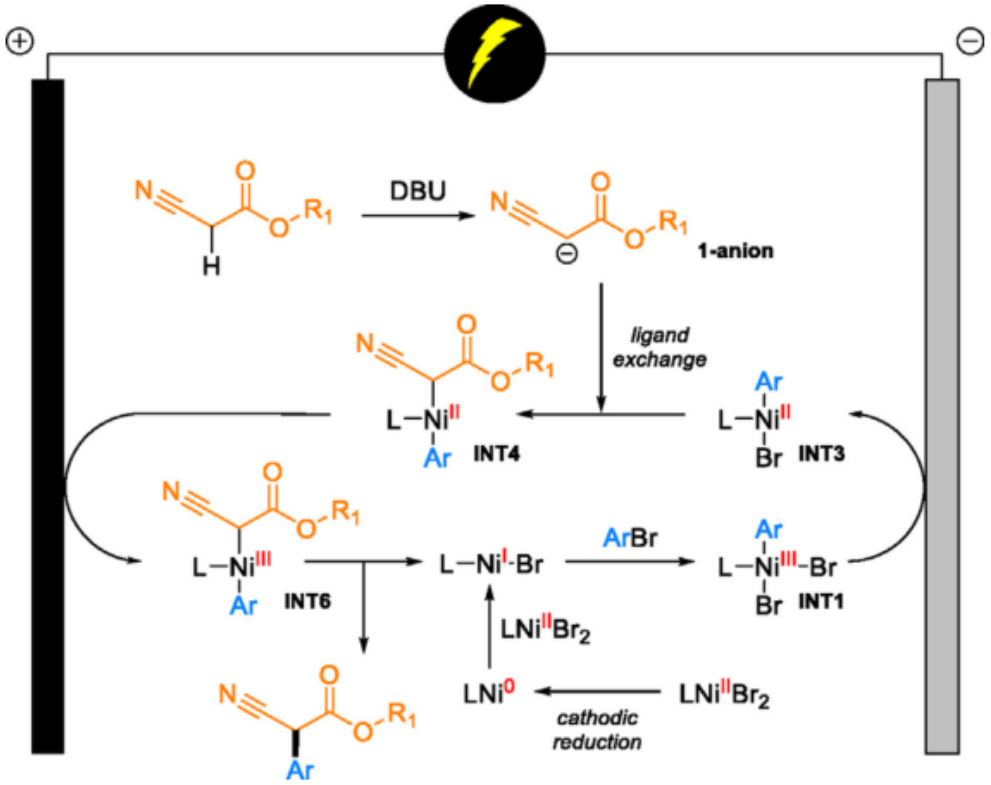
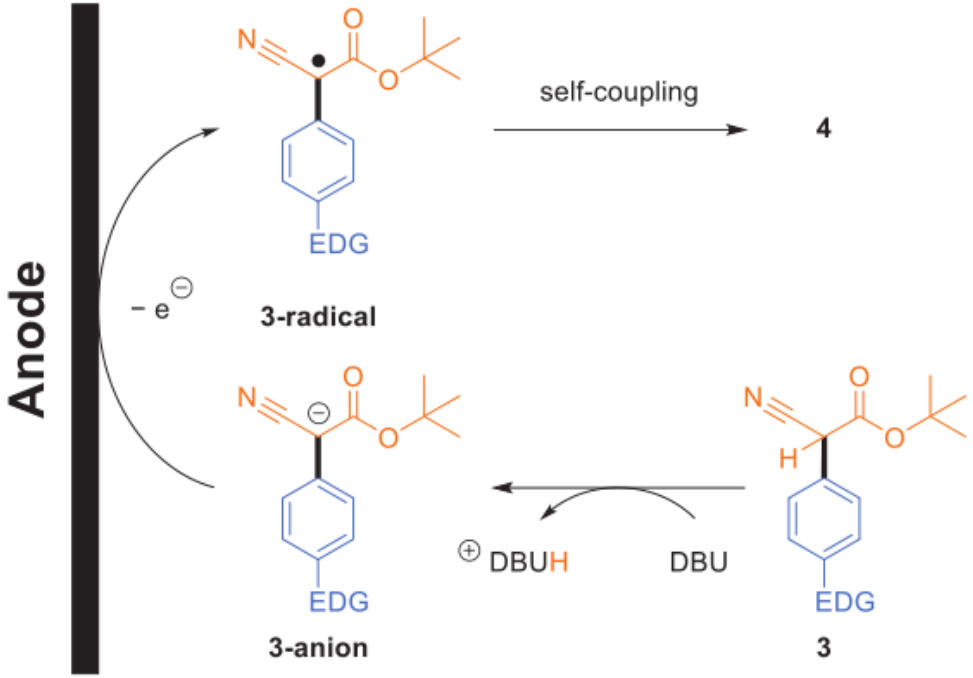


1 2a 3





带有给电子官能团会在阳极被氧化为自由基

nature communications

Article

https://doi.org/10.1038/s41467-022-35073-z

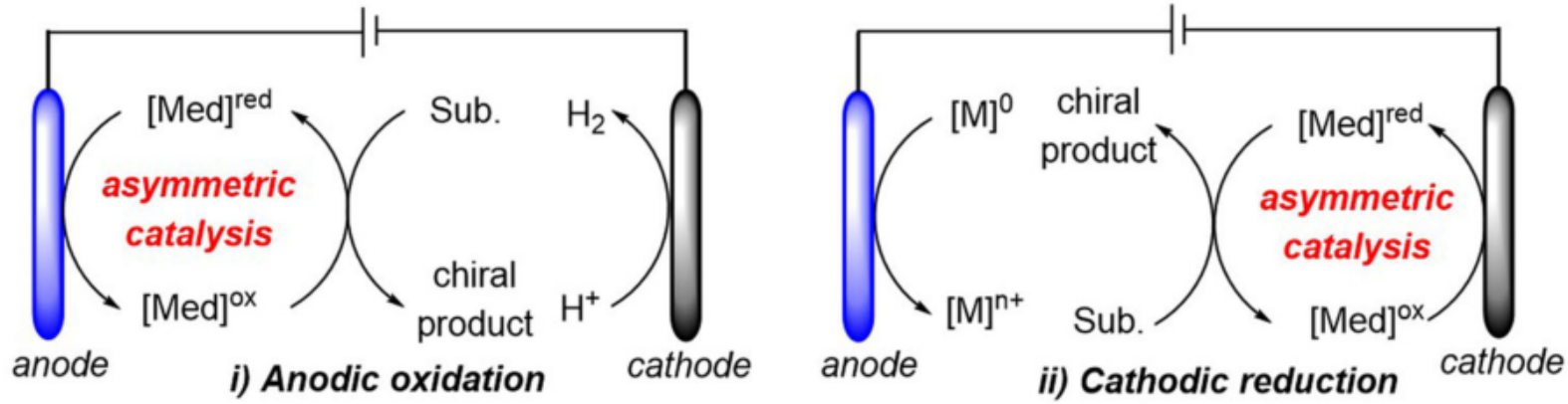
Paired electrolysis-enabled nickel-catalyzed enantioselective reductive cross-coupling between α-chloroesters and aryl bromides

Received: 28 July 2022

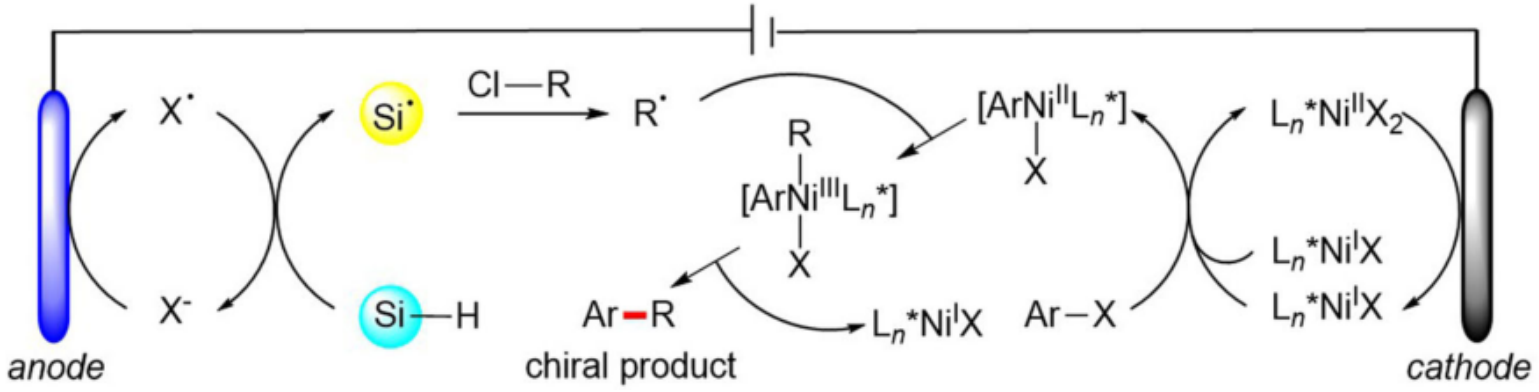
Accepted: 17 November 2022

Dong Liu[1,3], Zhao-Ran Liu[1,3], Zhen-Hua Wang[1,3], Cong Ma[1], Simon Herbert[2], Hartmut Schirok[2] & Tian-Sheng Mei[1]

a) *Traditional strategies for electrochemical asymmetric catalysis*

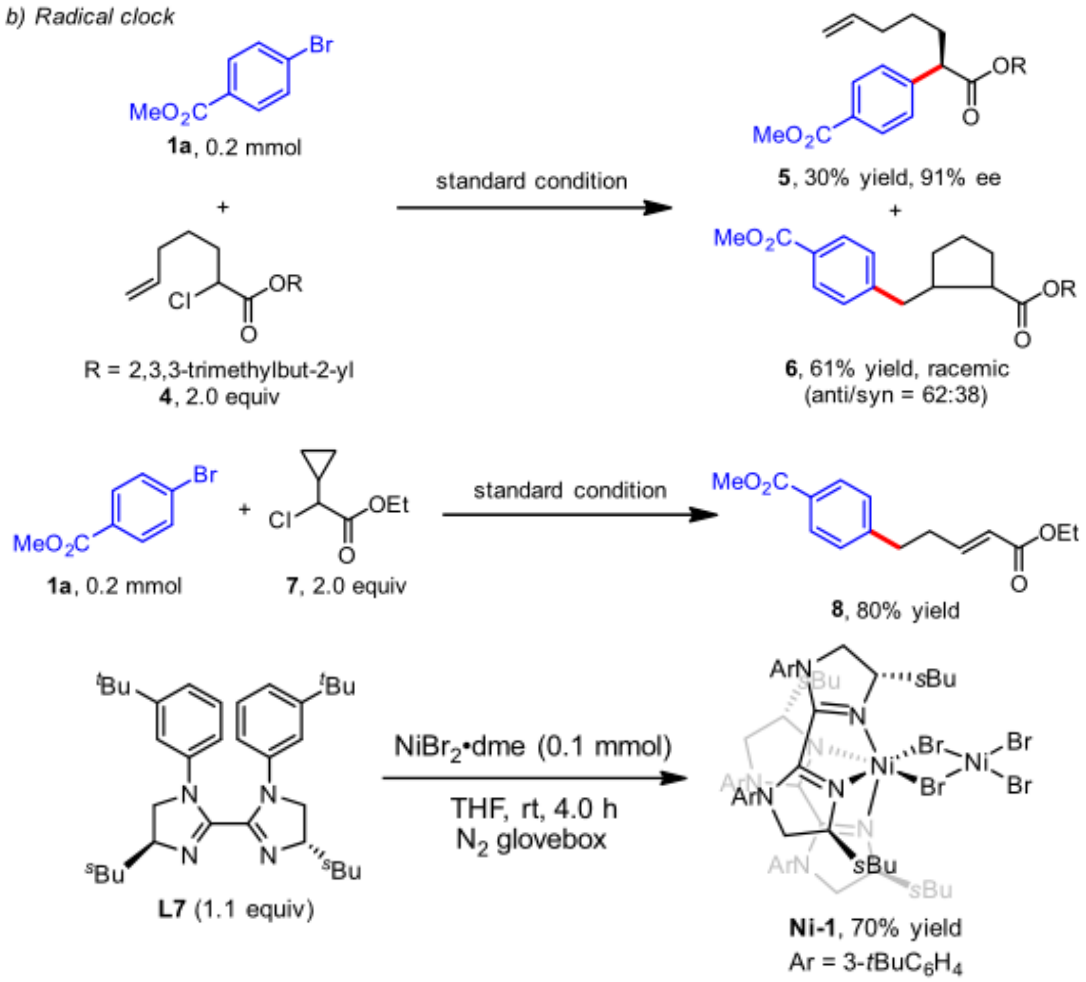


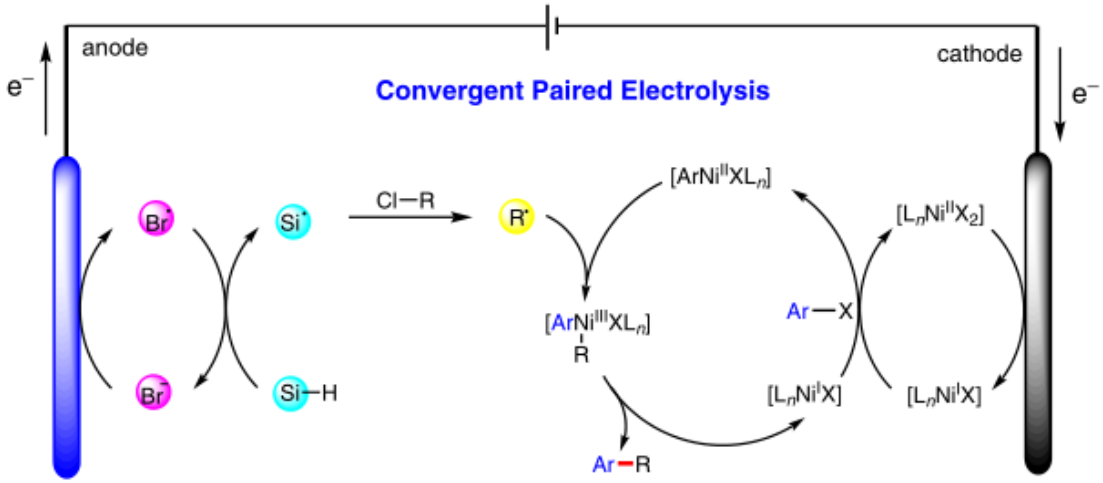
b) ***Our hypothesis***: *paired electrolysis for electrochemical asymmetric catalysis*



Part 3 成队电解

b) Radical clock





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COMMUNICATION

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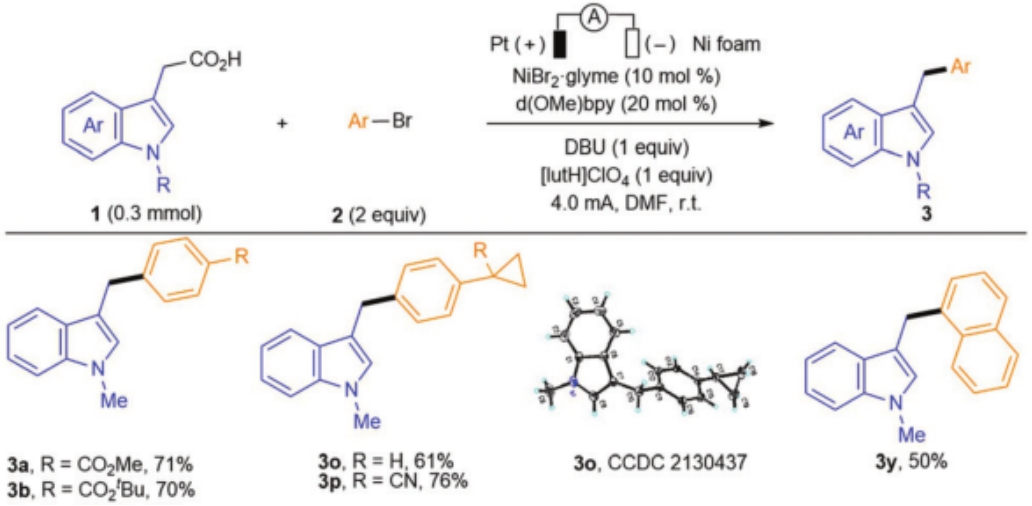
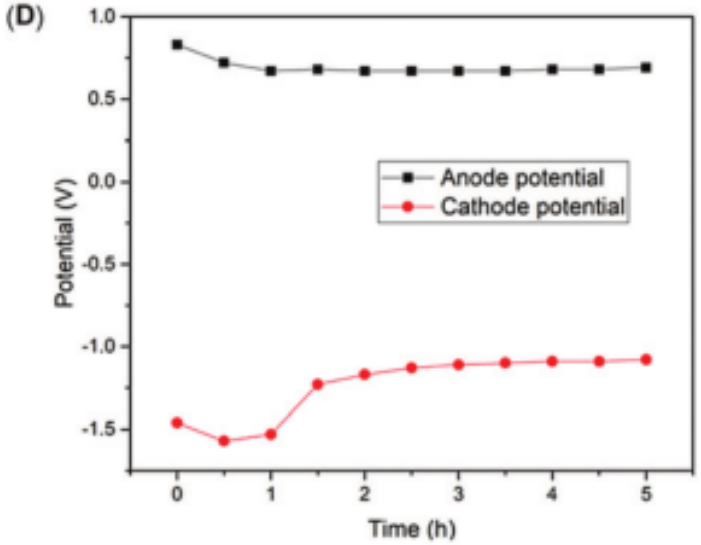
Received 10th May 2022,
Accepted 23rd June 2022

Nickel-catalyzed decarboxylative cross-coupling of indole-3-acetic acids with aryl bromides by convergent paired electrolysis†

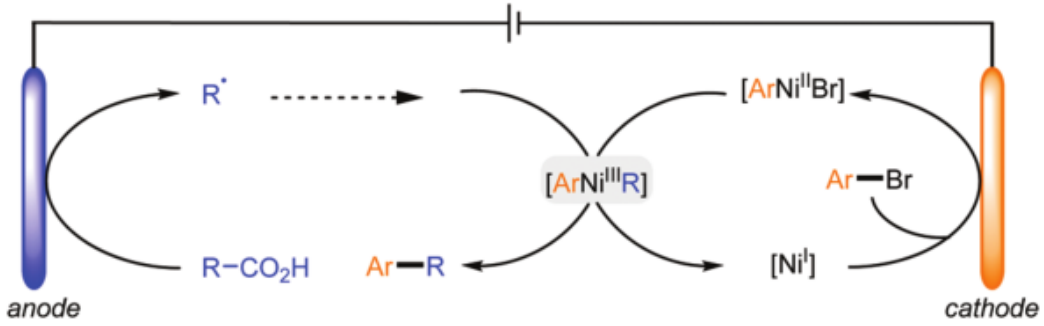
Zhen-Hua Wang,‡ Lei Wei,‡ Ke-Jin Jiao, Cong Ma and Tian-Sheng Mei *

Part 3 成队电解





Ni(I)到Ni(0)需要-1.9V



nature communications

Article

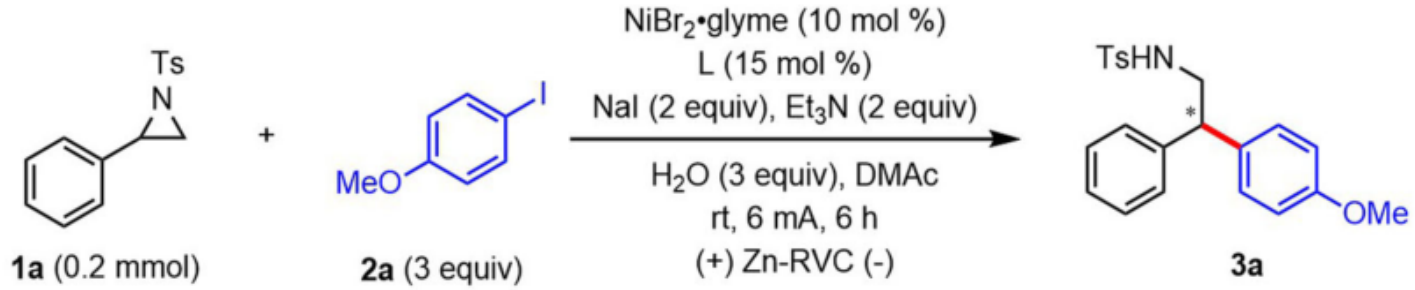
https://doi.org/10.1038/s41467-023-37965-0

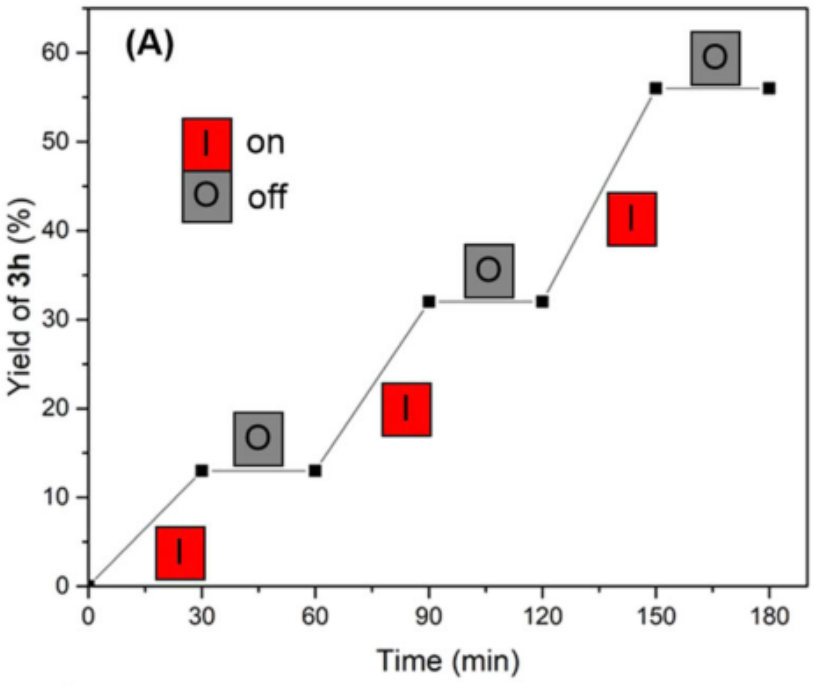
Nickel/biimidazole-catalyzed electrochemical enantioselective reductive cross-coupling of aryl aziridines with aryl iodides

Received: 5 December 2022

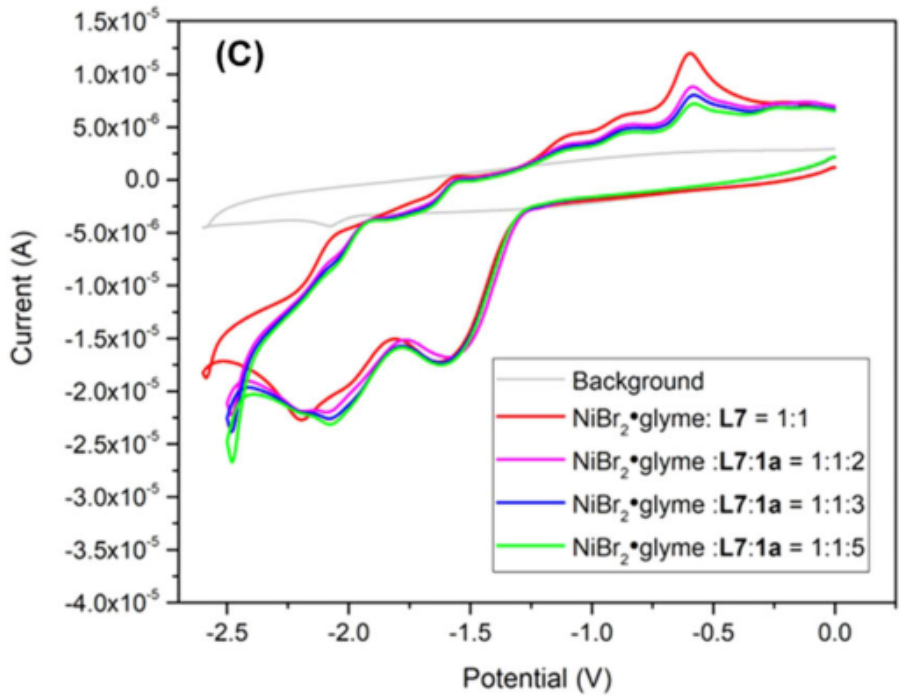
Accepted: 29 March 2023

Yun-Zhao Wang[1,4], Zhen-Hua Wang[1,4], Inbal L. Eshel[2,4], Bing Sun[1], Dong Liu[1], Yu-Cheng Gu[3], Anat Milo[2] ✉ & Tian-Sheng Mei[1] ✉





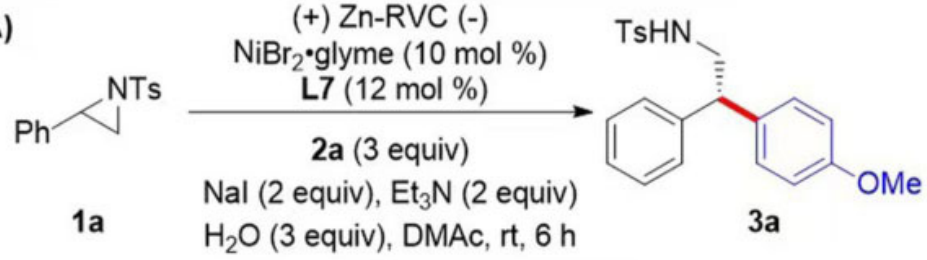
Zn阳极没有参与还原



-1.6V和-2.2V对应Ni(II)/Ni(I)和Ni(I)/Ni0

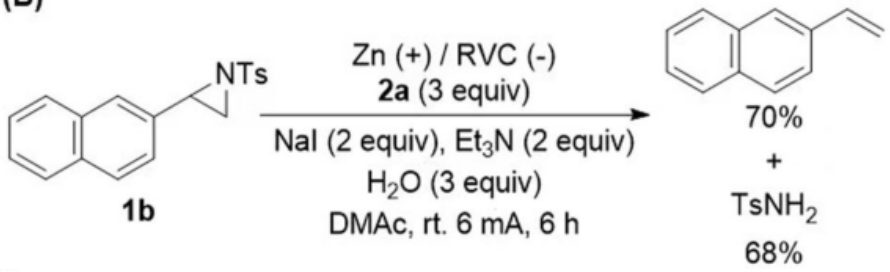
Part 3 成队电解

(A)

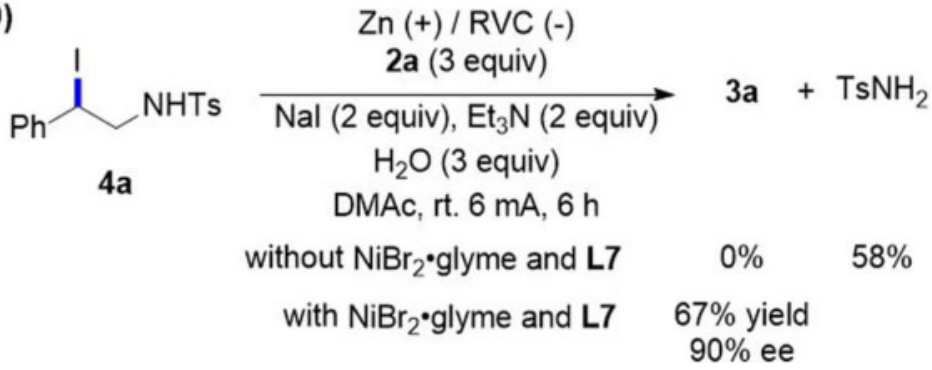


constant potential (V)	yield (%)	ee (%)
-1.0	0	-
-1.8	10	89
-2.2	68	89

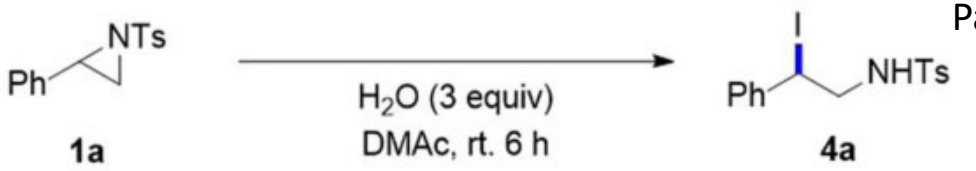
(B)



(D)

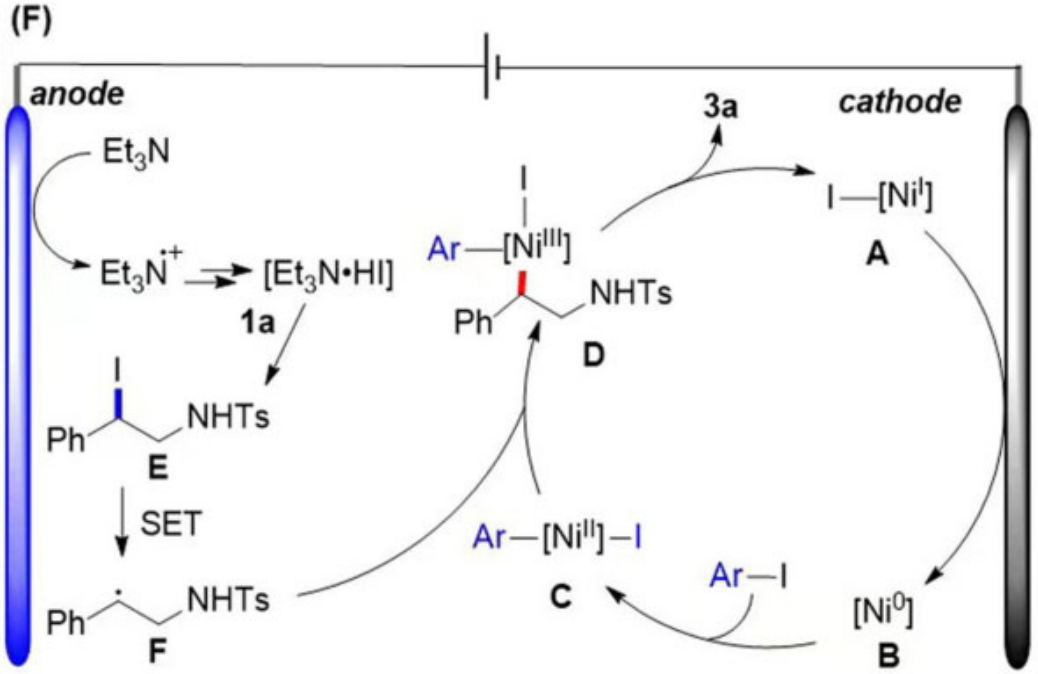


(C)



additive	yield (%)
Et_3N (2 equiv) + I_2 (2 equiv)	0%
Et_3N•HI (2 equiv)	81%
HI	87%

(F)



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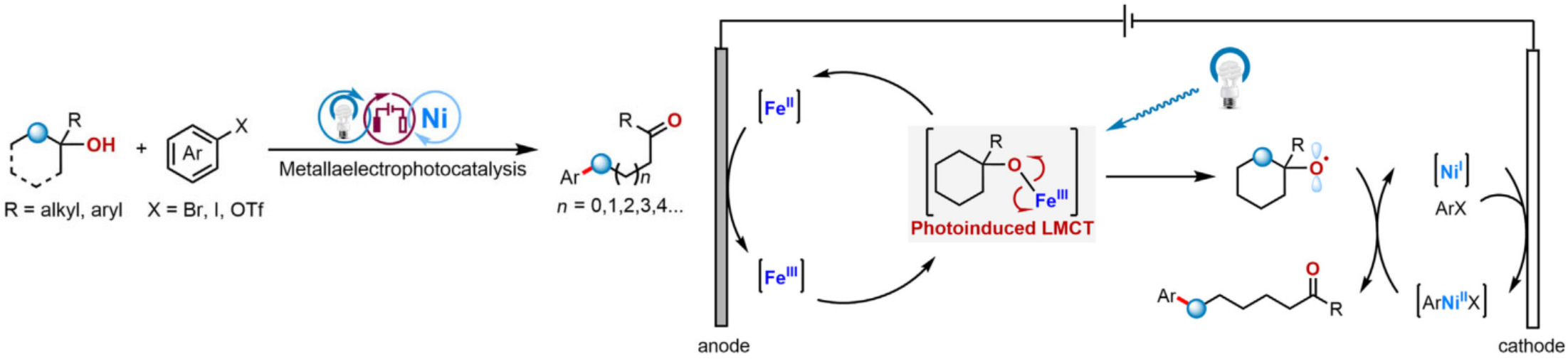
Science Bulletin
www.scibull.com

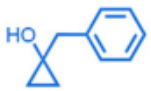
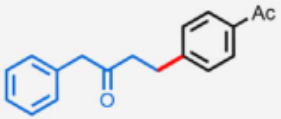
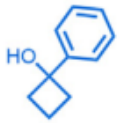
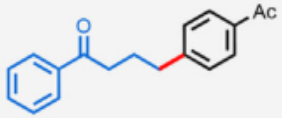
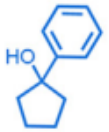
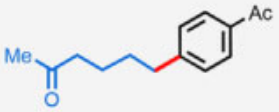
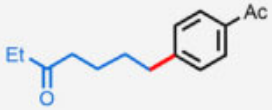
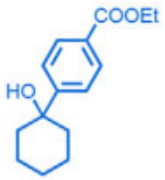
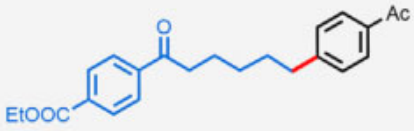
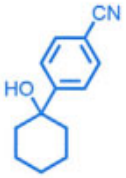
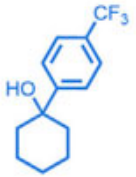
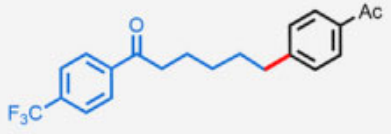
Article

Synergistic use of photocatalysis and convergent paired electrolysis for nickel-catalyzed arylation of cyclic alcohols

Zhao-Ran Liu, Xiao-Yu Zhu, Jian-Feng Guo, Cong Ma *, Zhiwei Zuo *, Tian-Sheng Mei *



Part 3 成队电解

Substrate	Product	Substrate	Product	Substrate	Product
	 4, 72% [PCET], N.D.[d]		 5, 88% [PCET], 6%[d]		 6, 72% [PCET], N.D.[d]
	 25, 72% [PCET], N.D.[d]		 26, 40%[b] [PCET], N.D.[d]		 27, 56% [PCET], N.D.[d]
	 17, 60% [PCET], N.D.[d]		 18, 64%[b] [PCET], N.D.[d]		 19, 59% [PCET], N.D.[d]

对于中性和缺电子芳烃已经烷烃底物能做到PCET过程无法氧化还原的过程

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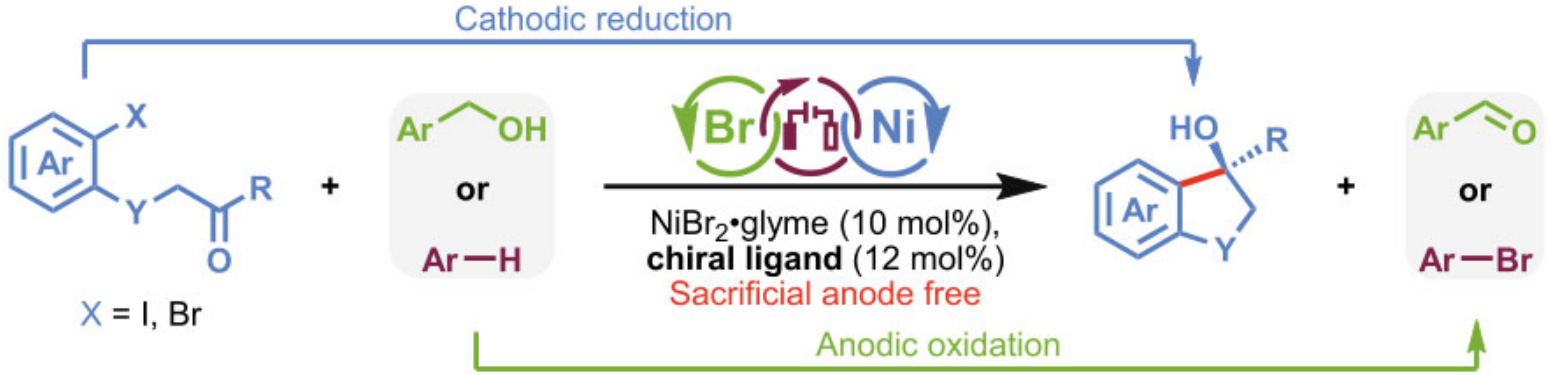
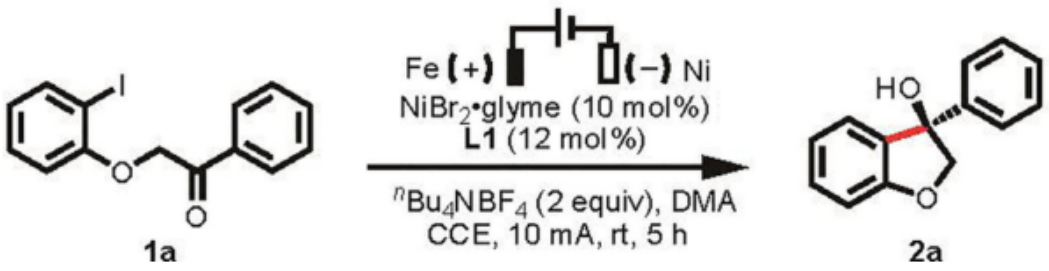
Article

Parallel paired electrolysis-enabled asymmetric catalysis: simultaneous synthesis of aldehydes/aryl bromides and chiral alcohols

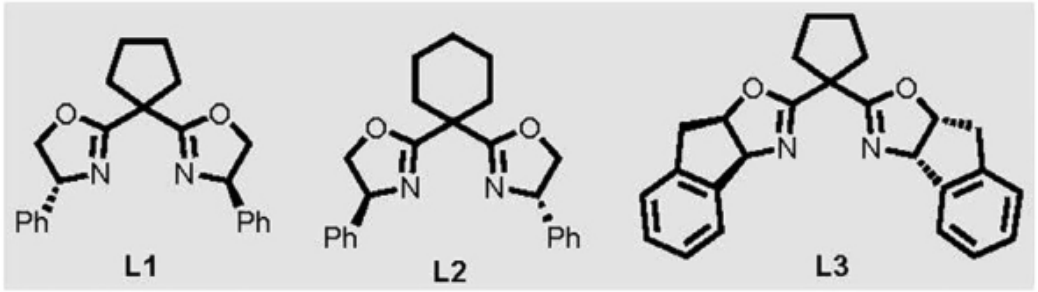
Bing Sun [a,1], Zhen-Hua Wang [a,1], Yun-Zhao Wang [a], Yu-Cheng Gu [b], Cong Ma [a], Tian-Sheng Mei [a,*]

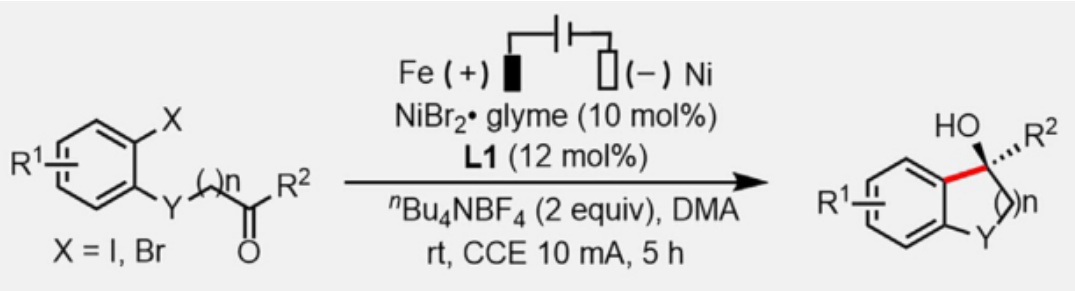


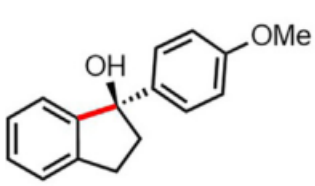
Part 3 成队电解



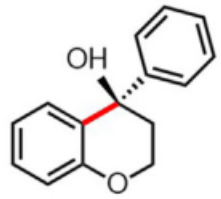
Entry[a]	Deviation from above conditions	Yield (%)[b]	ee (%)
1	None	92 (83)[c]	98
2	**L2** instead of **L1**	32	−85
3	**L3** instead of **L1**	64	−97
4	$^{n}Bu_4NOAc$ instead of $^{n}Bu_4NBF_4$	ND	/
5	$^{n}Bu_4NI$ instead of $^{n}Bu_4NBF_4$	54	92
6	$^{n}Bu_4NPF_6$ instead of $^{n}Bu_4NBF_4$	66	97
7	Al instead of Fe	86	89
8	Zn instead of Fe	44	79
9	No catalyst and ligand	ND	/
10	No electric current	NR	/



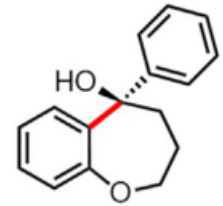




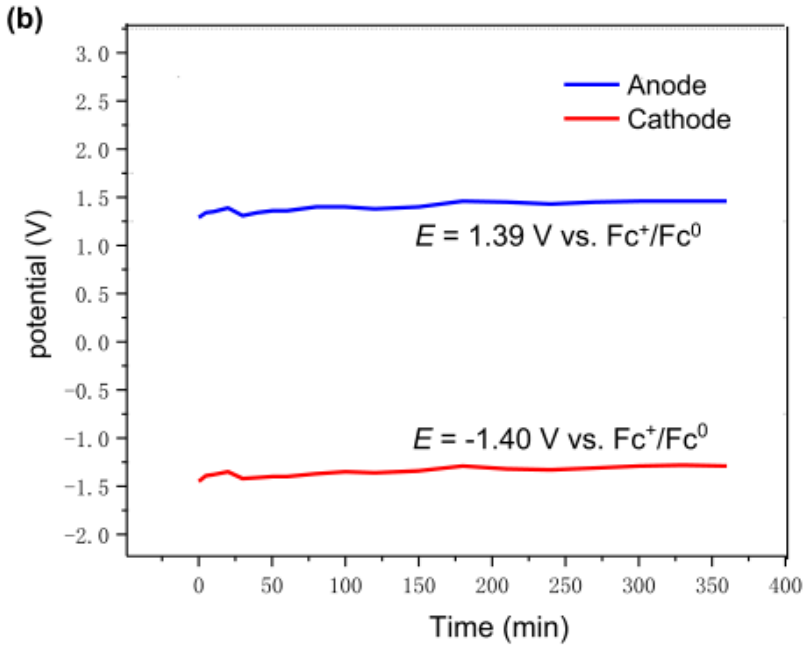
2ae
51% yield, 91% ee[b]

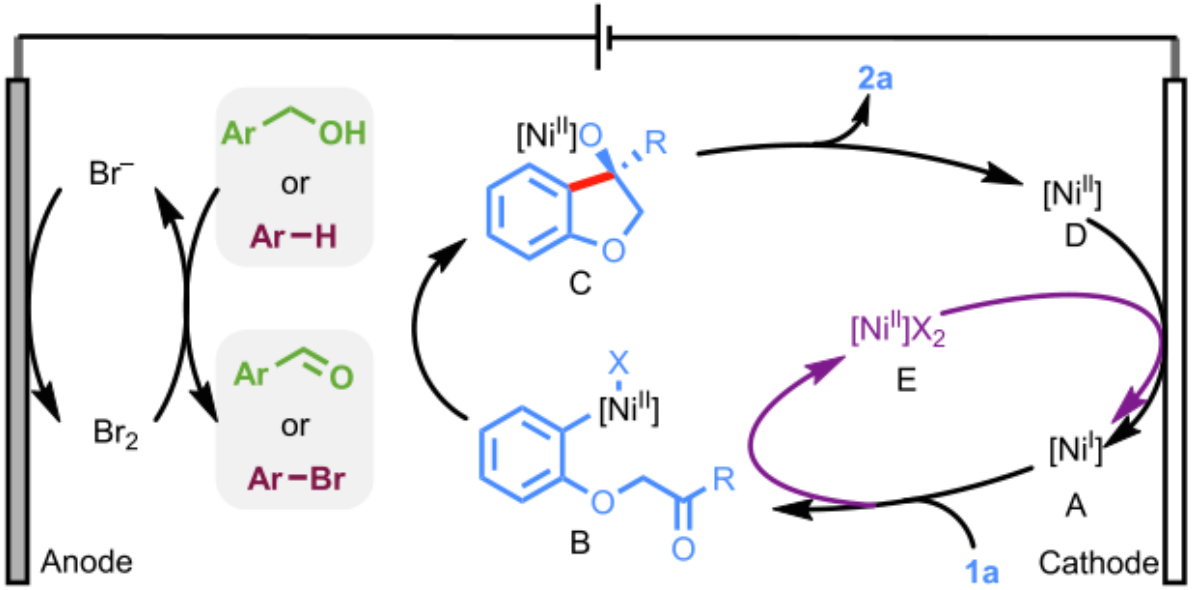


2af
80% yield, 19% ee

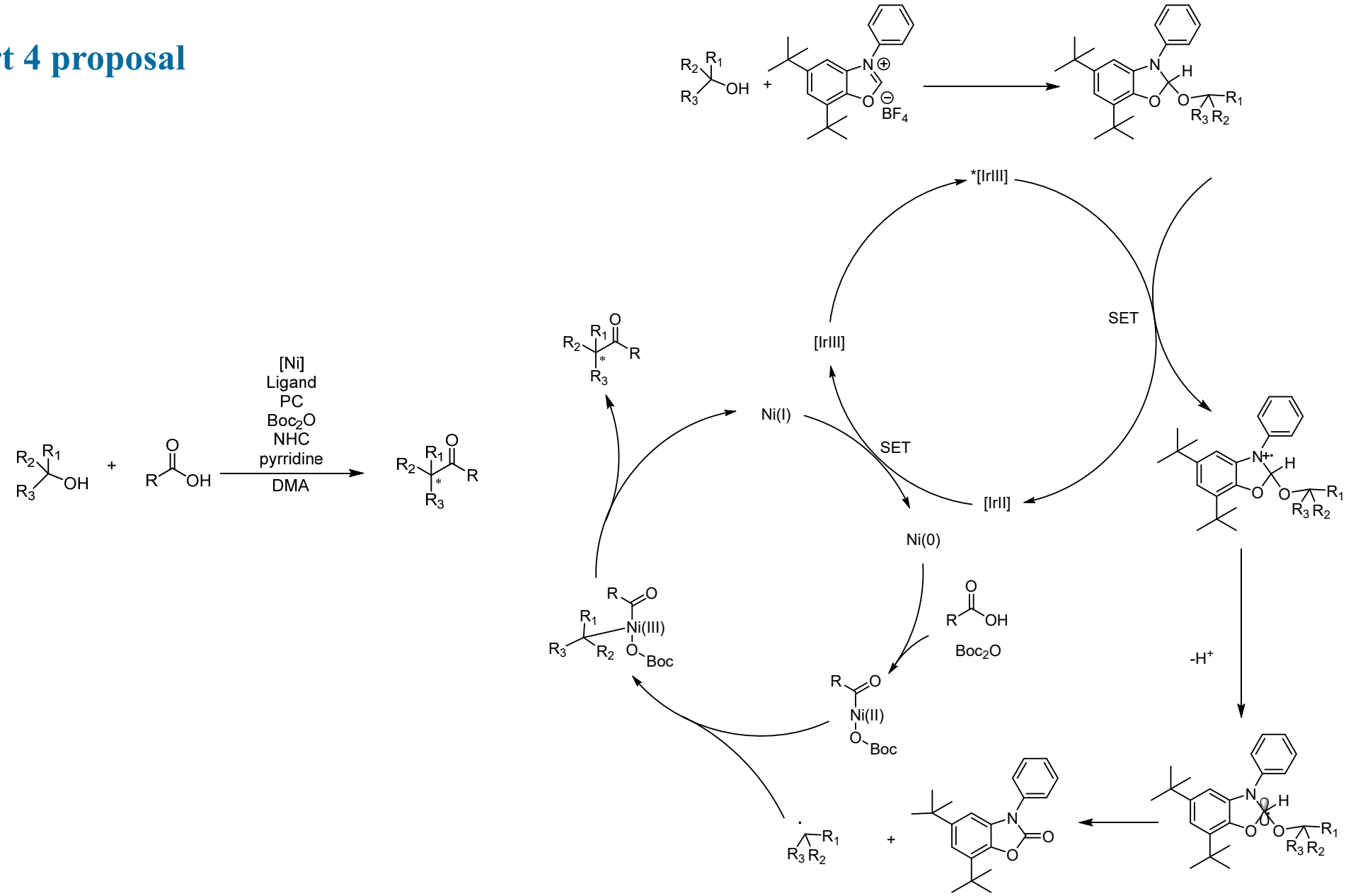


2ag
21% yield, 57% ee


(b)
potential (V)
Time (min)
Anode
Cathode
E = 1.39 V vs. Fc+/Fc0
E = -1.40 V vs. Fc+/Fc0


Br−
Br2
Ar OH
or
Ar−H
Ar O
or
Ar−Br
Anode
[NiII]O R
C
2a
[NiII]
D
[NiII]X2
E
X
[NiII]
B
R
O
O
[NiI]
A
1a
Cathode

Part 4 proposal



请老师批评指正