THE YANG RESEARCH GROUP

NICKEL-CATALYZED REDUCTIVE COUPLING REACTIONS

Peiyi Huang

2022.3.18

Author Introduction

Hegui Gong

1991年9月-1995年7月： 郑州轻工业学院化学工程系， 精细化工本科 (指导老师：候守君教授)。

1995年9月-1998年7月： 清华大学化学系，有机化学硕士 (指导老师：李兆陇副教授，赵玉芬院士)。

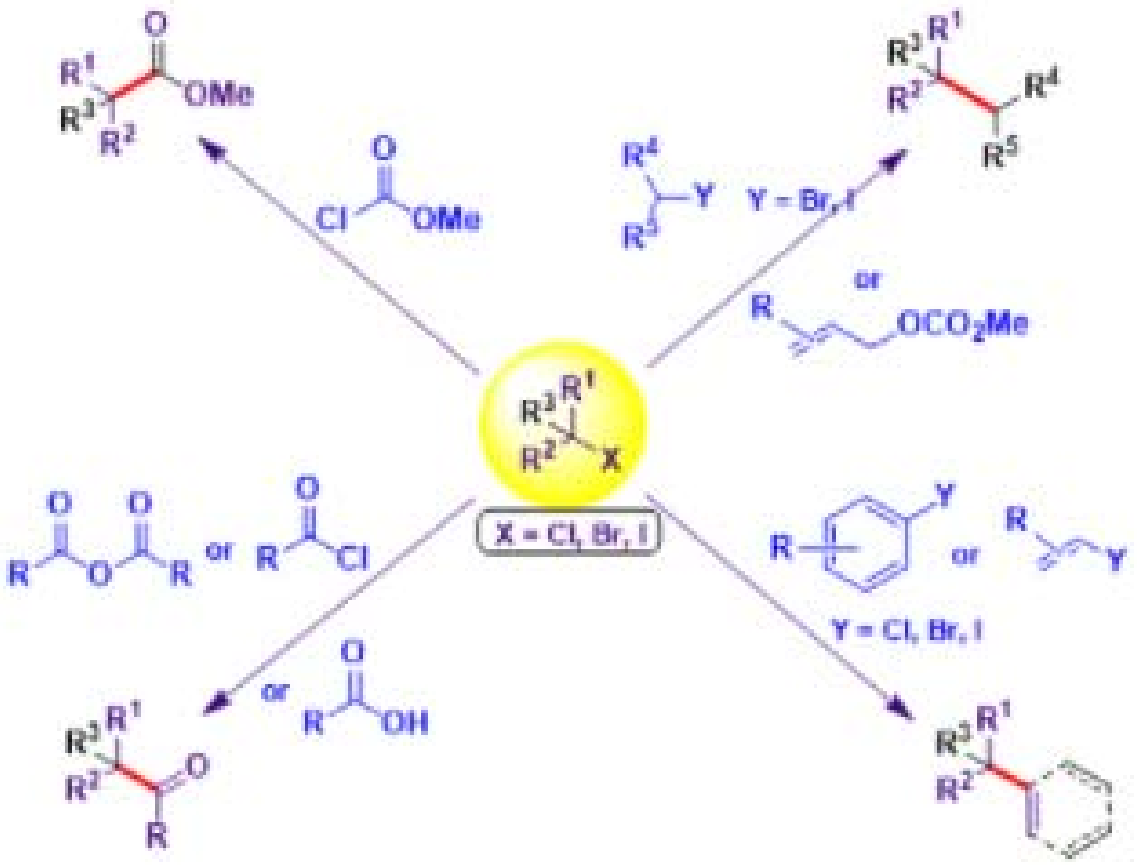
1999年8月-2005年7月： 美国 University of Texas at Austin，化学博士 (指导老师：Professor Michael J. Krische)。

2005年7月到2008年11月在美国 University of North Carolina at Chapel Hill做博后。

2008年12月，上海大学特聘教授。

research interests：
①H-bond mediated supramolecular chemistry
②organic synthetic methodology

Group Research



Nickel-catalyzed formation of quaternary carboncenters

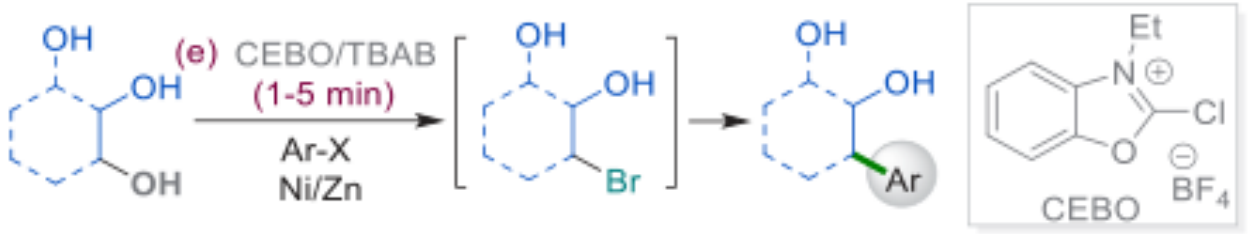
91 912696511, 2022/3/24

ACS Catalysis

pubs.acs.org/acscatalysis Research Article

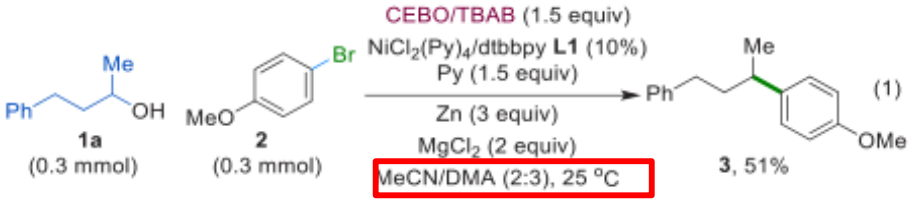
Ni-Catalyzed Formal Cross-Electrophile Coupling of Alcohols with Aryl Halides

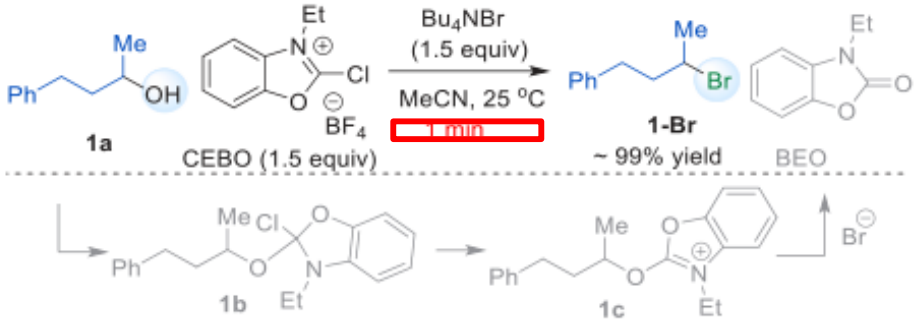
Quan Lin, Guobin Ma,* and Hegui Gong*



https://doi.org/10.1021/acscatal.1c04239
ACS Catal. 2021, 11, 14102−14109

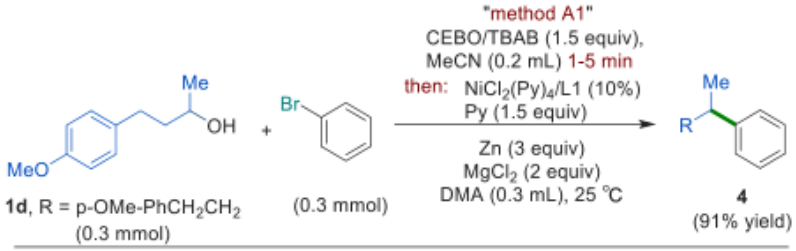
Reaction condition optimization

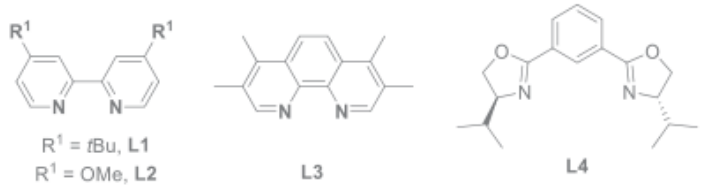




entry	variation	1-Br (%)	1a (%)	1-Cl (%)
1	none	~99[a]	ND[b]	trace
2	CEBO/TBAB (1 equiv)	92	4	4
3	without Bu_4NBr	NA[b]	~100	trace
4	DMA instead of MeCN	trace	~100	ND[a]
5	DCM instead of MeCN	trace	~100	ND[a]
6	with Zn (3 equiv)	27	68	5
7	with Zn (3 equiv) after 30 min	23	67	10

[a]The yield referred to GC yield. [b]ND = not detected, NA = not available.

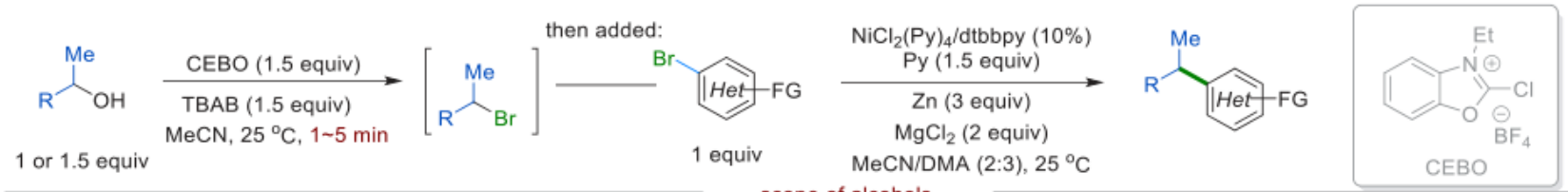




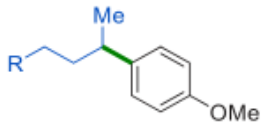
entry	variation from the standard conditions	yield[a] (%)
1	none	91 (89)[b]
2	w/o Ni	not detected
3	w/o Zn	not detected
4	w/o CEBO/TBAB	not detected
5	w/o L1	14
6	w/o $MgCl_2$	38
7	w/o Py	78
8	Mn instead	69
9	L2 instead of L1	55
10	L3 instead of L1	91
11	L4 instead of L1	not detected
12	NiI_2 instead of $NiCl_2(Py)_4$	79
13	$Ni(COD)_2$ instead of $NiCl_2(Py)_4$	90
14	MeCN instead of MeCN/DMA	12
15	DMA instead of MeCN/DMA	9
16	6 mmol of **1d** (gram-scale)	83[b]

[a]NMR yield using 2,5-dimethyl furan as the internal standard. [b]Isolated yield. Py = Pyridine, DMA = *N,N*-dimethylacetamide.

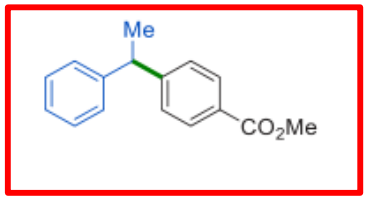
scope of substrates



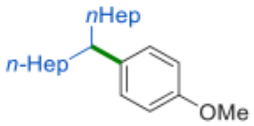
scope of alcohols



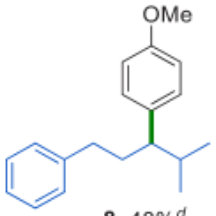
3, R = Ph, 91%
5, R = OBz, 84%



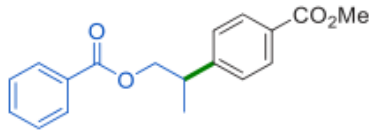
6, 77%[a,b]



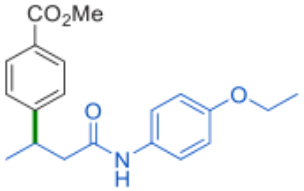
7, 69%[c]



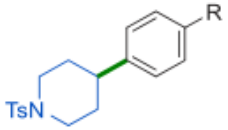
8, 48%[d]



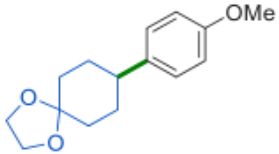
9, 52%[a] (7:1)



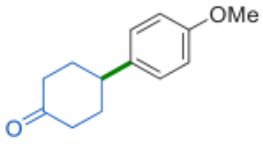
10, 88%[a]
from bucetin



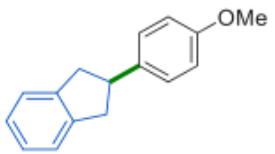
11, R = OMe, 88%
12, R = CO_2Me, 86%[a]



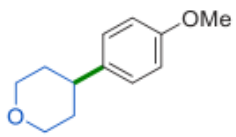
13, 69%[c]



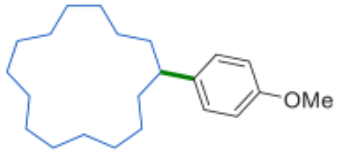
14, 65%[c]



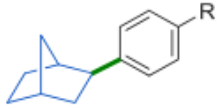
15, 65%



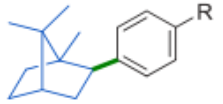
16, 53%[c]



17, 75%[c]

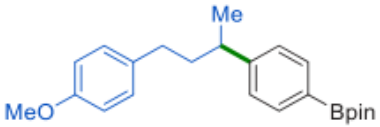


18, R = OMe, 70%[c]
19, R = CO_2Me, 80%[a]
from exo-norborneol

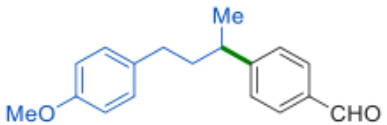


20, R = OMe, 65%
21, R = CO_2Me, 64%[a]
from *(-)-borneol*

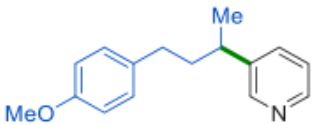
scope of aryl halides



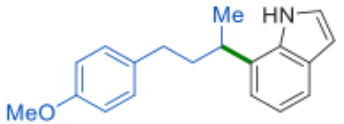
35, 91%



36, 68%[a]

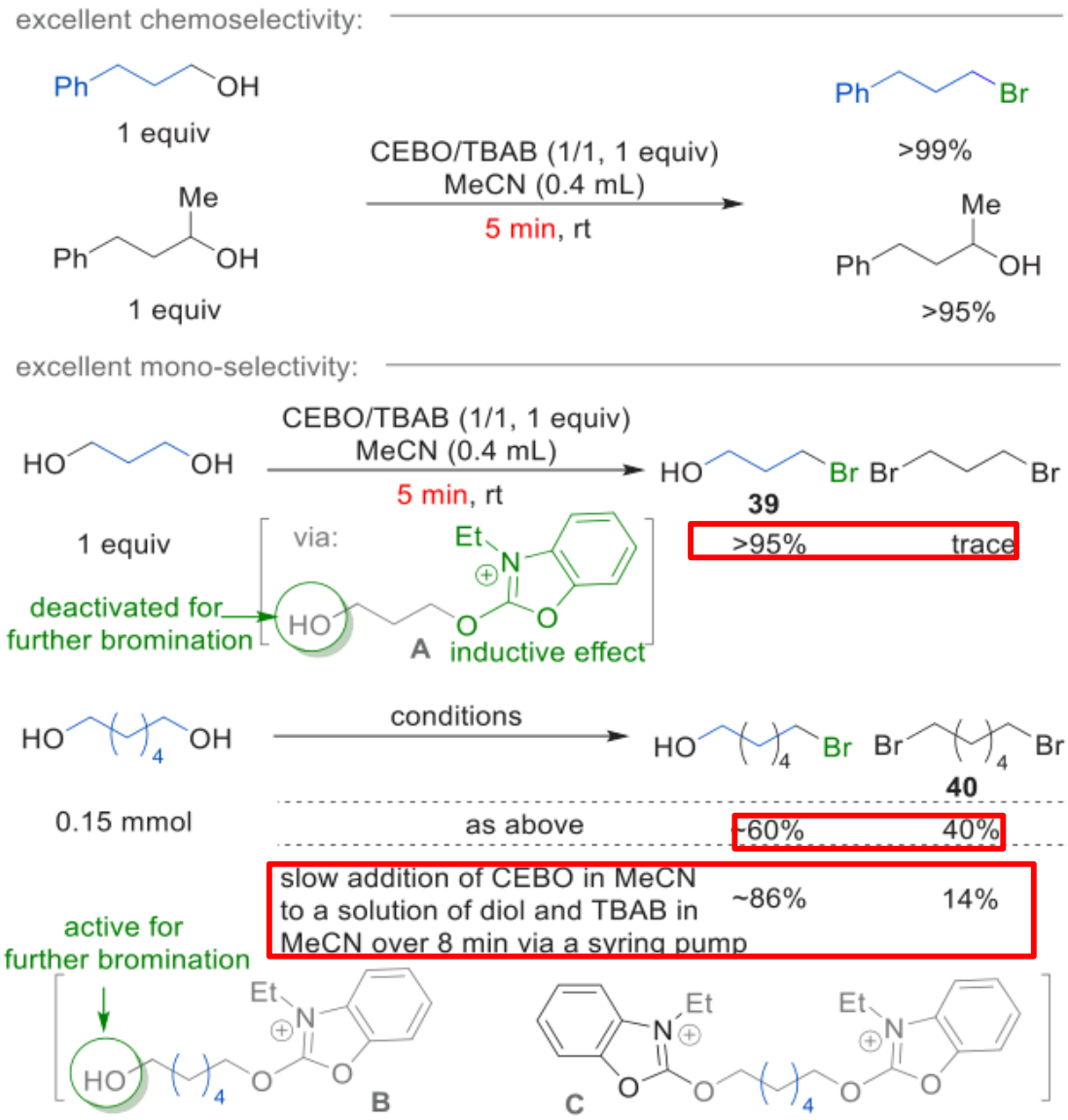


37, 81%[a] (5:1)

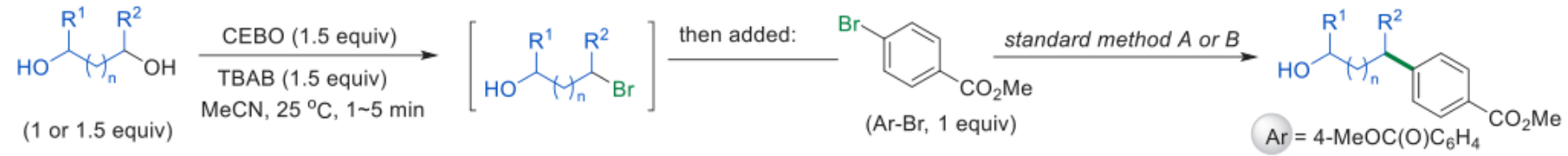


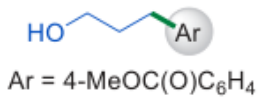
38, 87%

Reaction condition optimization



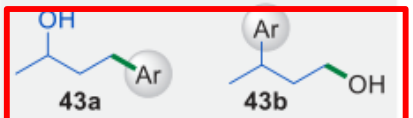
scope of substrates



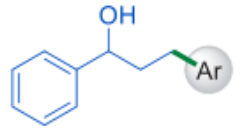


41, 69%[a]

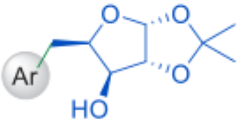
42, 72%[a,c]



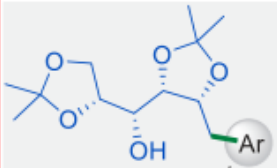
75% (6:1)[a]



44, 69%[a]

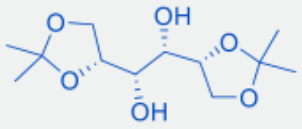


45, 65%[a]

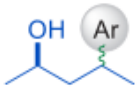


46, 82%[b]

from

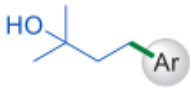


1,2:5,6-Di-O-isopropylidene-D-mannitol

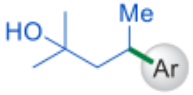


47, 82% (dr =1:1)[b]

48, 67%[a]

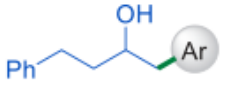


49, 71%[a]

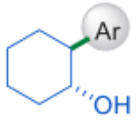


50, 73%[b]

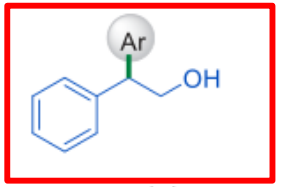
51, 77%[a]



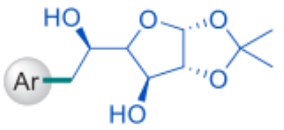
52, 67%[a]



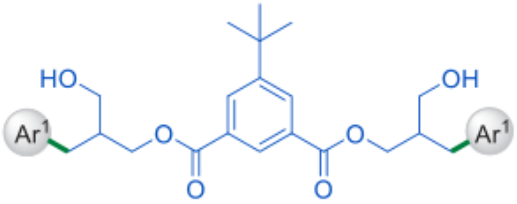
53, 42%[b]



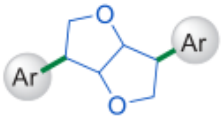
54, 35%[b,d,e]



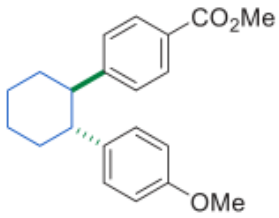
55, 47%[a]



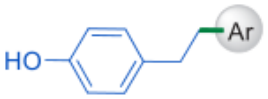
56, 10% (36%)[a,f] (Ar[1] = *p*-*t*BuOC(O)C$_6$H$_4$)



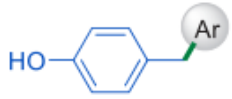
57, 58%[b,g]



58,32% over 2 steps[b]

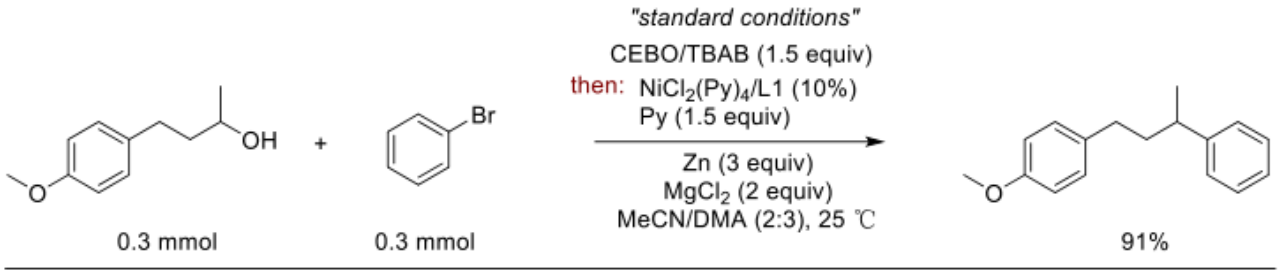


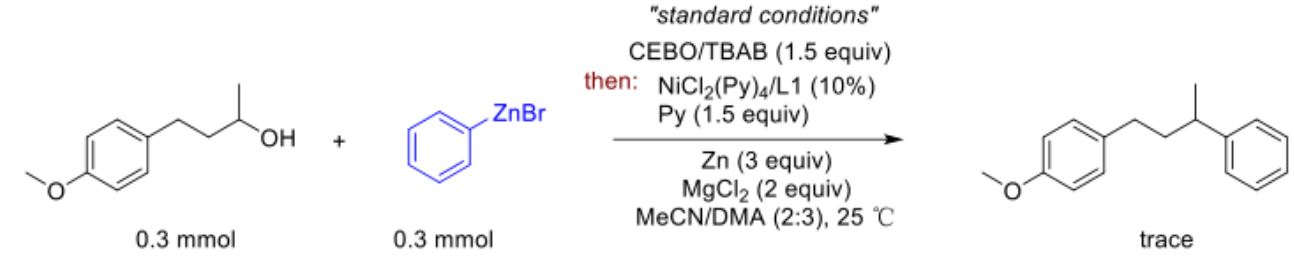
59, 75%[a]

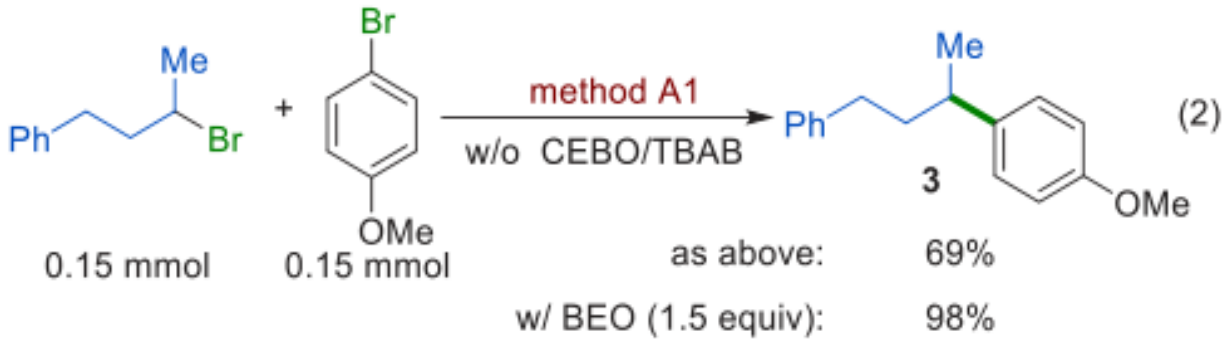


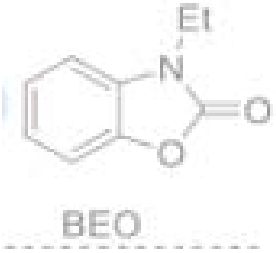
60, 70%[a,e]

Mechanism research









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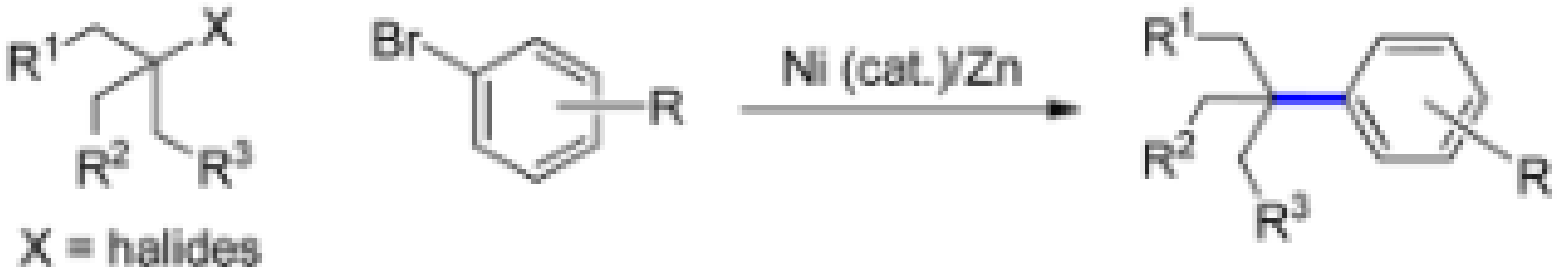
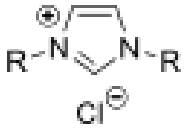
Nickel-Catalyzed Reductive Coupling of Aryl Bromides with Tertiary Alkyl Halides

Xuan Wang,[†,‡] Shulin Wang,[‡] Weichao Xue,[‡] and Hegui Gong*[,†,‡]

[†]School of Materials Science and Engineering and [‡]Department of Chemistry, Shanghai University, 99 Shang-Da Road, Shanghai 200444, China



4a: R = *i*Pr
4b: R = cyclohexyl
4c: R = *t*Bu

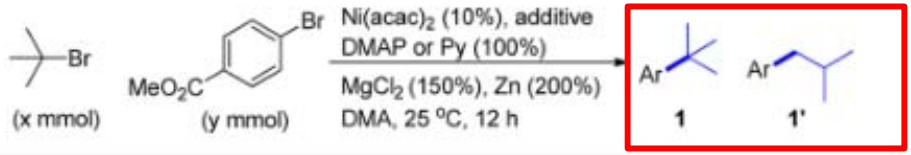


4d: R = $EtOC(O)CH_2$

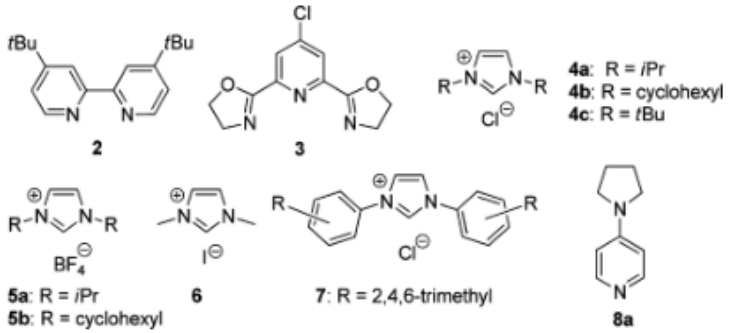
4e

DOI: 10.1021/jacs.5b06255
J. Am. Chem. Soc. 2015, 137, 11562−11565

Reaction condition optimization

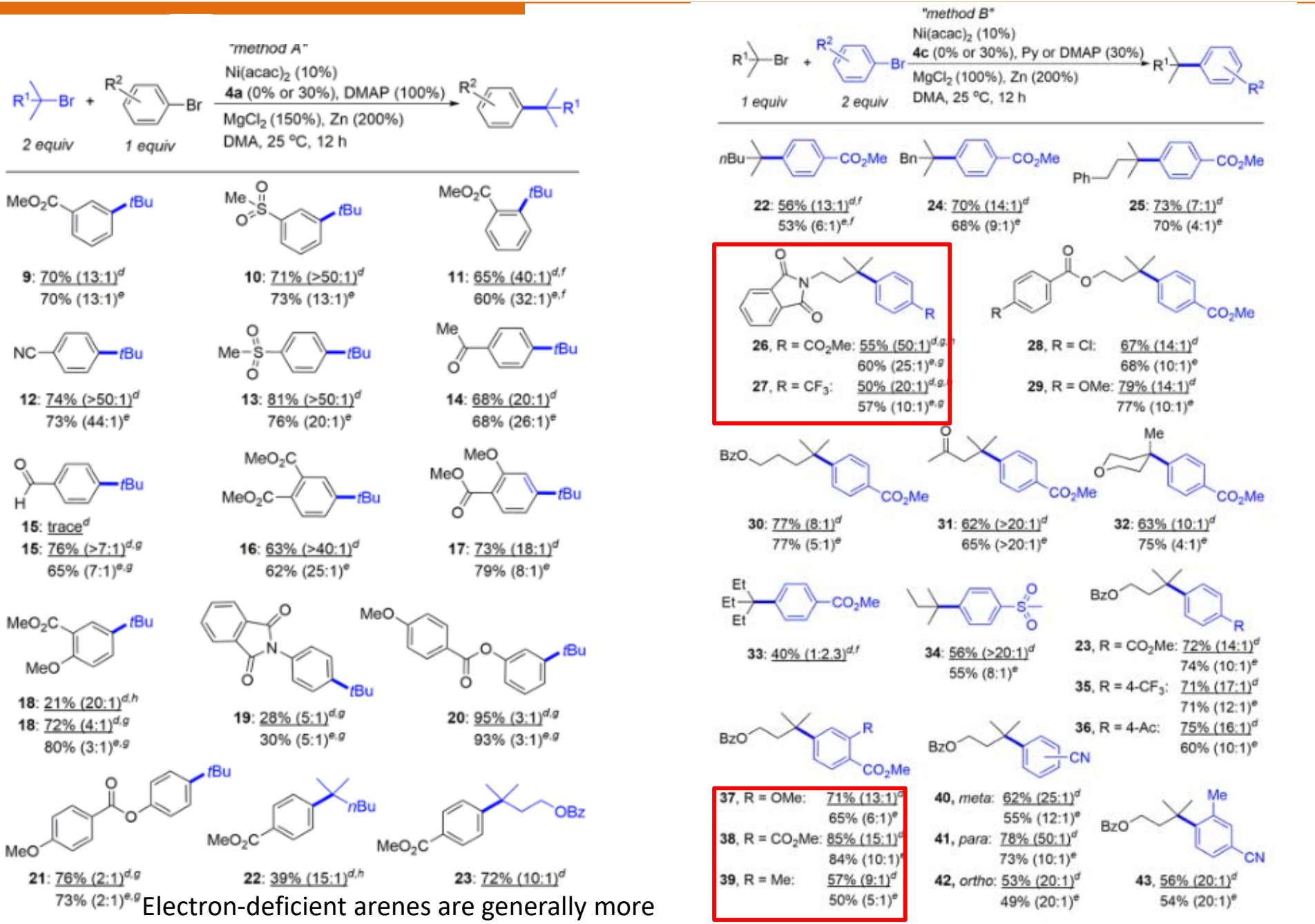


entry	x:y	ligand or additive	DMAP or Py	% yield (1:1′)
1	1:2	**2**	Py	12[c]
2	1:2	**3**	Py	trace
3	1:2	**4a**	Py	61 (8:1)
4	1:2	**4a**	DMAP	60 (20:1)
5	**2:1**	**4a**	**DMAP**	**81 (40:1)**[d]
6	2:1	**4a**	Py	45 (5:1)
7	2:1	**4b**	DMAP	68 (45:1)
8	2:1	**4c**	DMAP	82 (15:1)
9	2:1	**5a**	DMAP	78 (25:1)
10	2:1	**5b**	DMAP	63 (13:1)
11	2:1	**6a**	DMAP	79 (32:1)
12	2:1	**7a**	DMAP	78 (25:1)
13	2:1	**7b**	DMAP	61 (6:1)[c]
14	2:1	none	DMAP	75 (20:1)
15	2:1	none	**8a**	62 (18:1)
16	2:1	**4a**, w/o $MgCl_2$	DMAP	trace
17	2:1	**4a**	none	6%



- the carbene precursors may serve as additives rather than ligands.
- DMAP may function as a labile ligand
- $MgCl_2$ may accelerate the reduction of Ni species

Scope of substrates



Electron-deficient arenes are generally more effective in inhibiting alkyl isomerization.

Organic LETTERS

Letter

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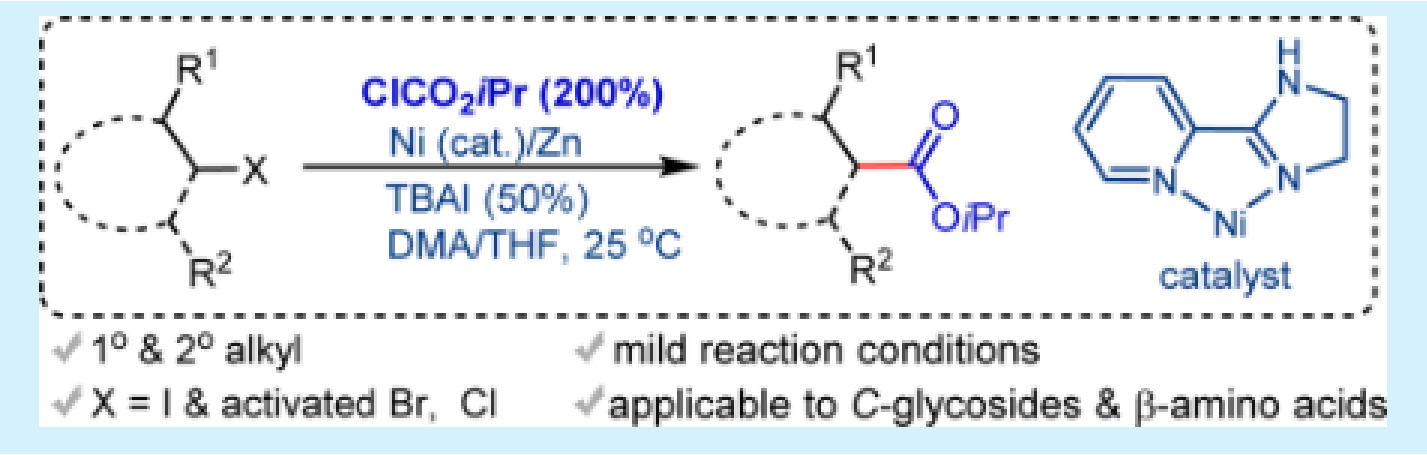
Ester Formation via Nickel-Catalyzed Reductive Coupling of Alkyl Halides with Chloroformates

Min Zheng,[†] Weichao Xue,[†] Teng Xue,[†] and Hegui Gong*[,†,‡]

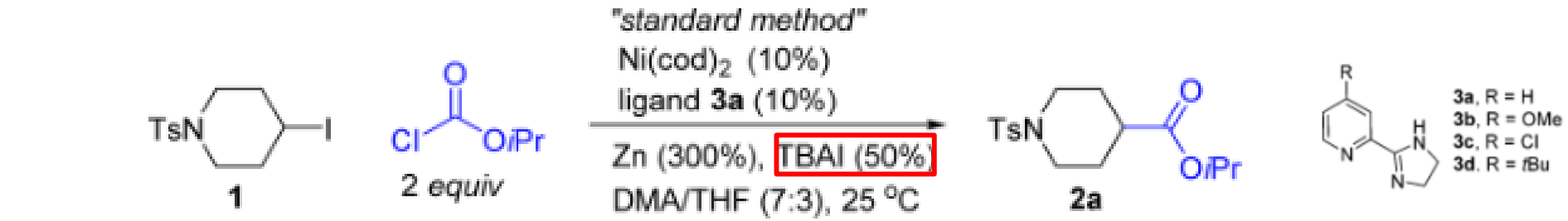
[†]Center for Supramolecular Chemistry and Catalysis and Department of Chemistry, Shanghai University, 99 Shang-Da Road, Shanghai 200444, China

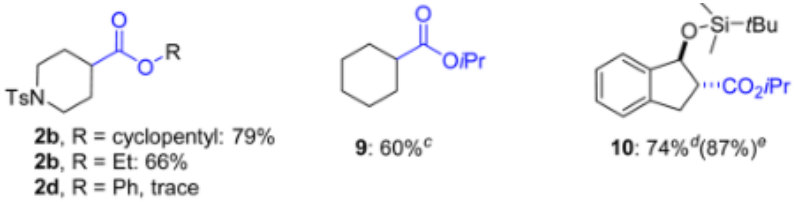
[‡]Shanghai Key Lab of Chemical Assessment and Sustainability, Tongji University, 1239 Siping Road, Shanghai 200092, China



DOI: 10.1021/acs.orglett.6b03158
Org. Lett. 2016, 18, 6152−6155

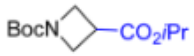
Scope of substrates



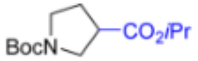


9: 60%[c]

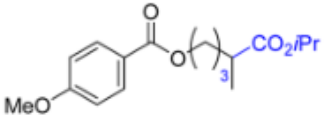
10: 74%[d](87%)[e]



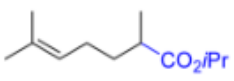
11: 75%



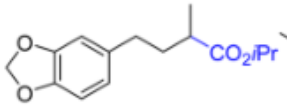
12: 60%[e,f]



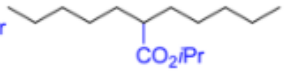
13: 79%



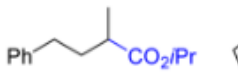
14: 80%



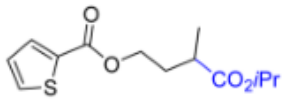
15: 80%



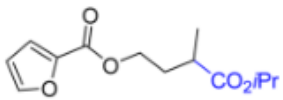
16: 70%



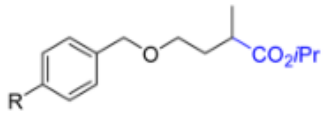
17: 88%



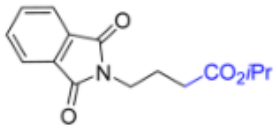
18: 59%



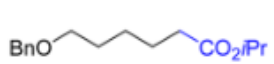
19:77%



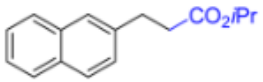
20: R = H: 68%
21: R = F: 75%
22: R = OMe: 70%



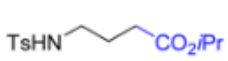
23: 74%



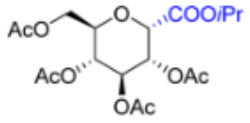
24: 58%



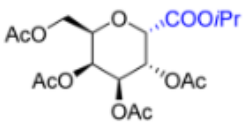
25: 81%



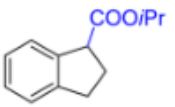
26: 67%



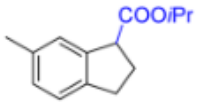
27: 70% (α:β = 2.6:1)[c,d]



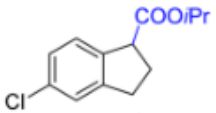
28: 65% (α:β = 5.8:1)[c,d]



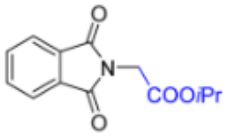
29: 75%[e]



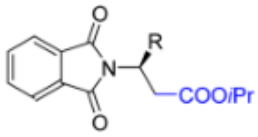
30: 60%[e]



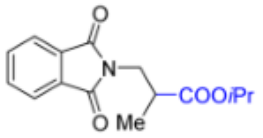
31: 61%[e]



32: 30%[d,e]

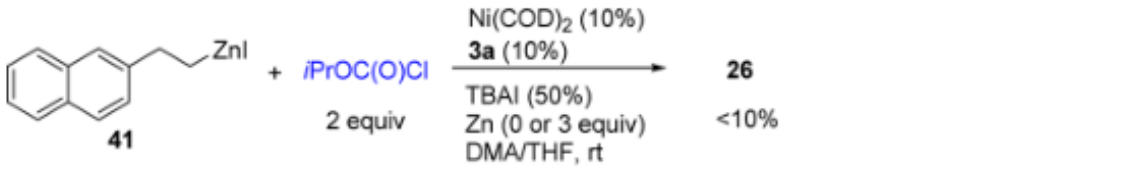


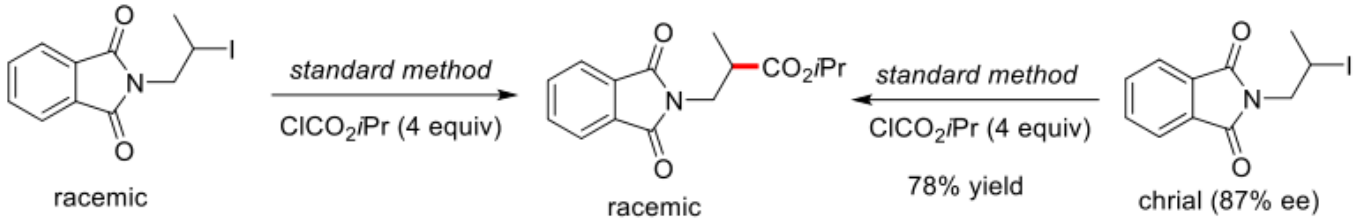
33, R = Ph: 68%
34, R = iPr: 87%
35, R = Me: 82%
36, R = Et: 85%
37, R = Bn: 80%

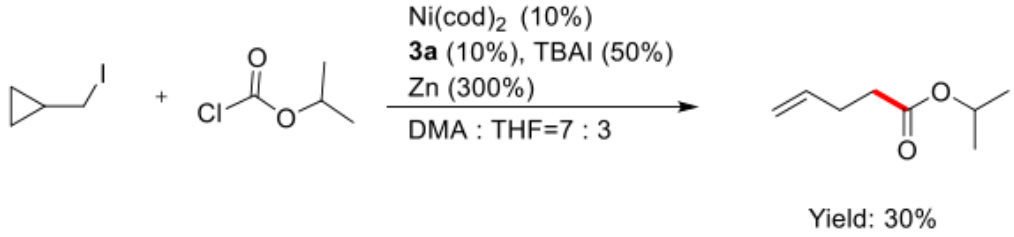


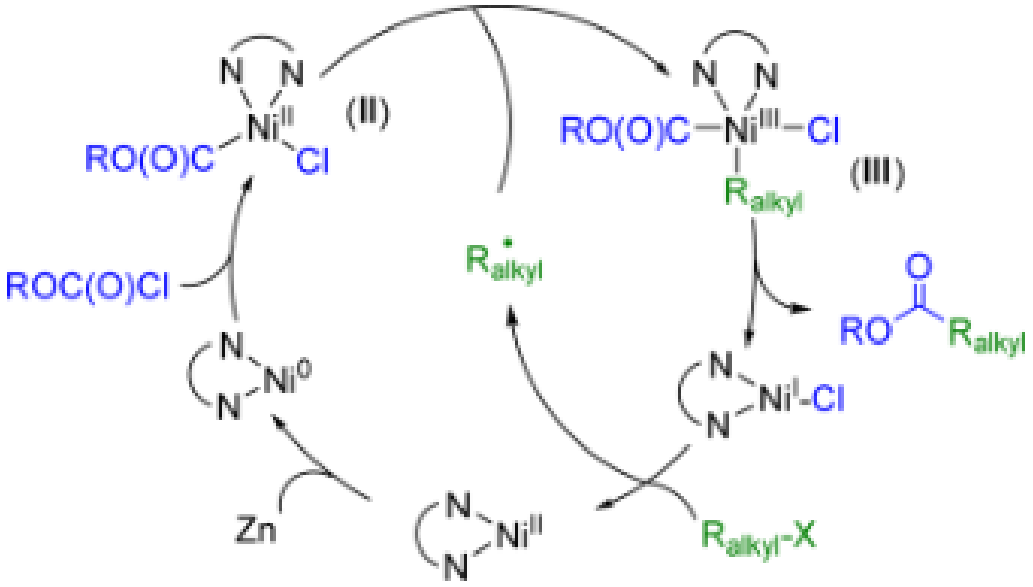
38: 78%

Mechanism research









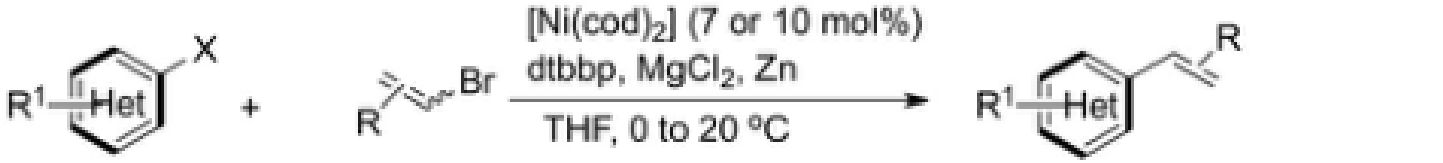
GDCh Communications Angewandte International Edition Chemie

Cross-Coupling

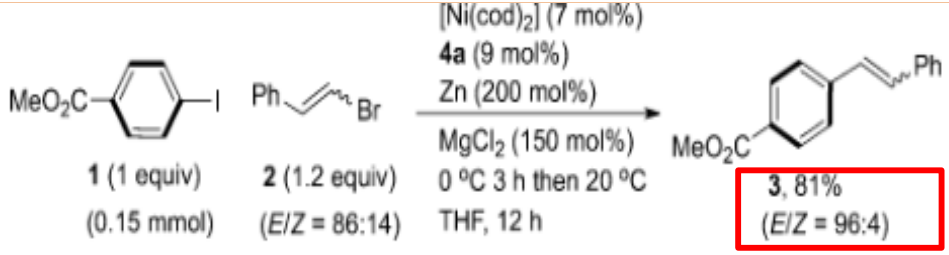
International Edition: DOI: 10.1002/anie.201607959
German Edition: DOI: 10.1002/ange.201607959

Preparation of Vinyl Arenes by Nickel-Catalyzed Reductive Coupling of Aryl Halides with Vinyl Bromides

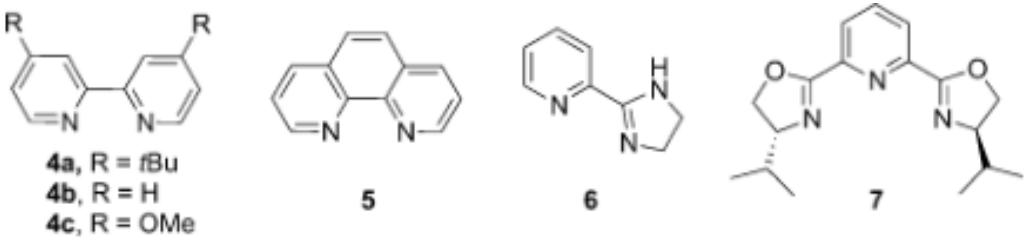
Jiandong Liu, Qinghua Ren, Xinghua Zhang,* and Hegui Gong**



Reaction condition optimization and scope of substrates



Entry[a]	Variation from the standard conditions	Yield [%][b]
1	none	81[c]
2	30 °C	60
3	1 equiv of *E*-vinyl bromide	75
4	1.2 equiv of *E*-vinyl bromide	82
5	1.2 equiv of *Z*-vinyl bromide	trace
6	$Ni(ClO_4)_2 \cdot 6H_2O$	79
7	$NiBr_2$·diglyme	80
8	$Ni(cod)_2$ (5%), **4a** (7%)	73
9	**4b** instead of **4a**	21
10	**4c** instead of **4a**	10
11	**5** instead of **4a**	13
12	**6** instead of **4a**	trace
13	**7** instead of **4a**	trace
14	without $MgCl_2$	63
15	$Ni(ClO_4)_2 \cdot 6H_2O$ (5%), **4a** (7%), **1** (10 mmol)	68[c]



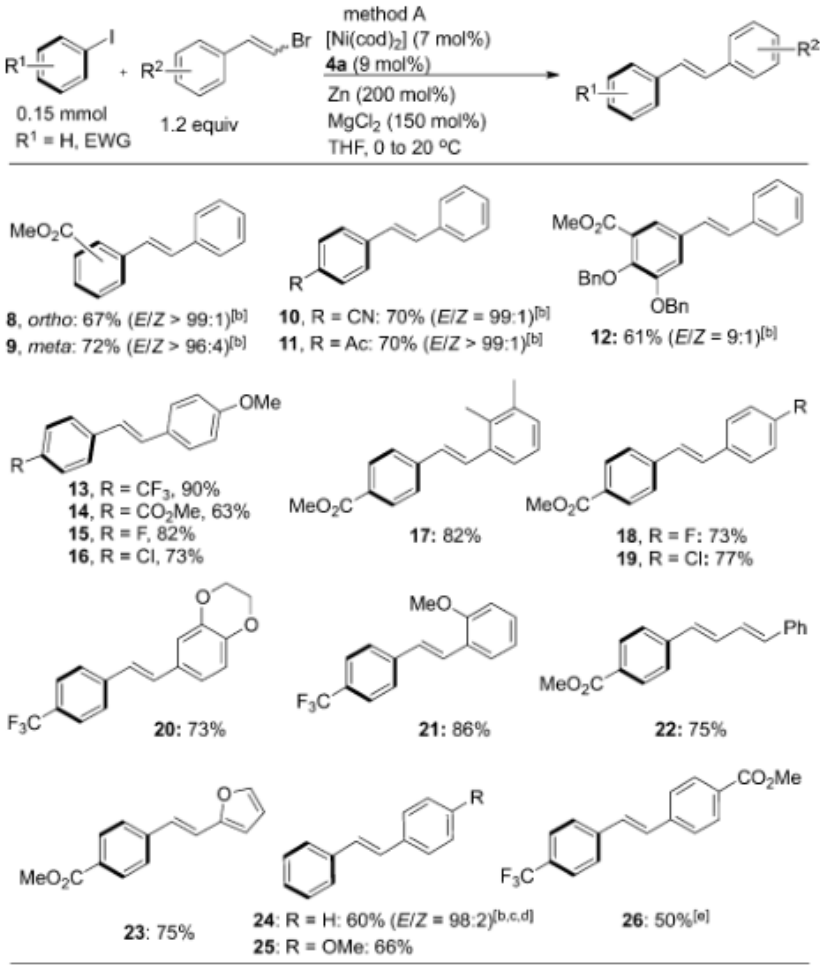


Figure 1. [a] See Table 1, entry 1 for the reaction conditions. [b] (2-Bromovinyl)benzene (*E*/*Z* = 86:14) was used. Unless otherwise noted *E*-vinyl bromides were used throughout Figure 1. [c] Yield determined by ^{1}H NMR spectroscopy using 2,5-dimethylfuran as the internal reference. [d] 1.5 equiv of vinyl–Br and LiCl (1 equiv) were added. [e] Use of 2 equiv of ArI and 1 equiv of vinyl–Br. EWG = electron-withdrawing group, THF = tetrahydrofuran.

Scope of substrates

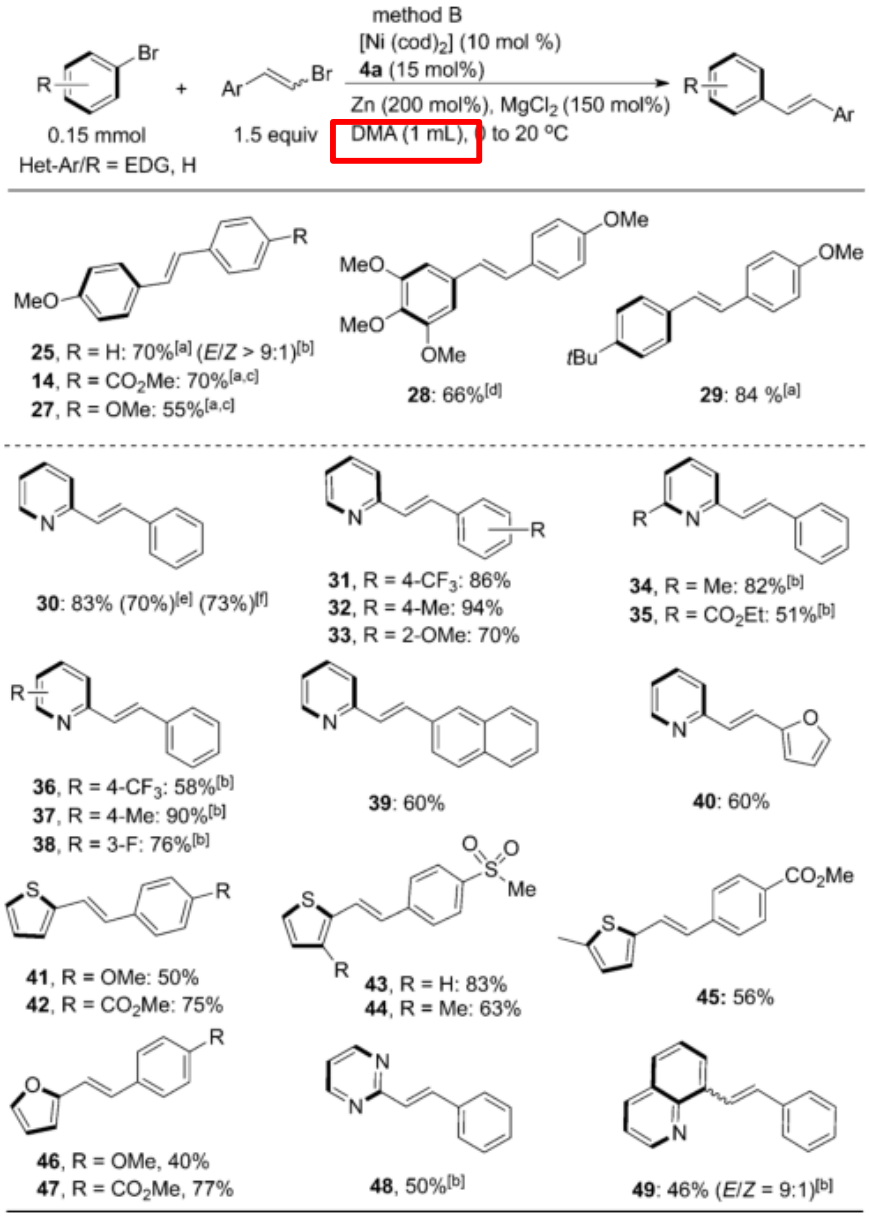


Figure 2. [a] KF (1 equiv) was added. [b] (2-Bromovinyl)benzene ($E/Z = 86:14$) was used. Unless otherwise noted *E*-vinyl bromides were used. [c] ArI was used. [d] KF was replaced by AgF (1 equiv). [e] Use of 1.2 equiv of vinyl–Br. [f] Use of 1.5 equiv of (*Z*)-vinyl-Br (1.5 equiv). DMA = *N*,*N*-dimethylacetamide, EDG = electron-donating group.

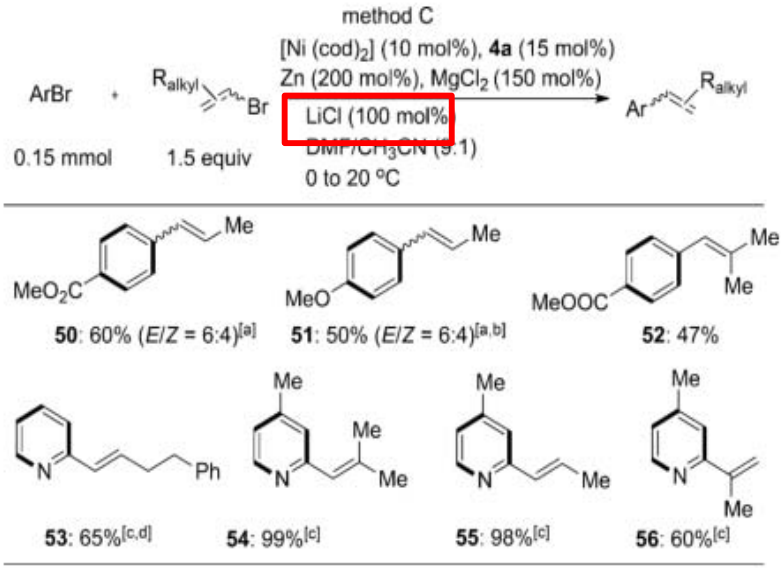
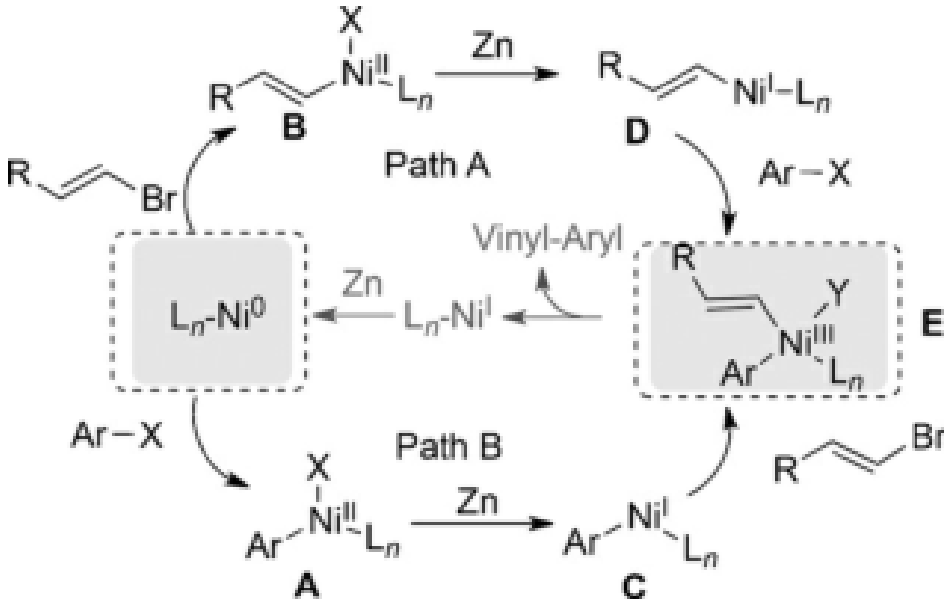
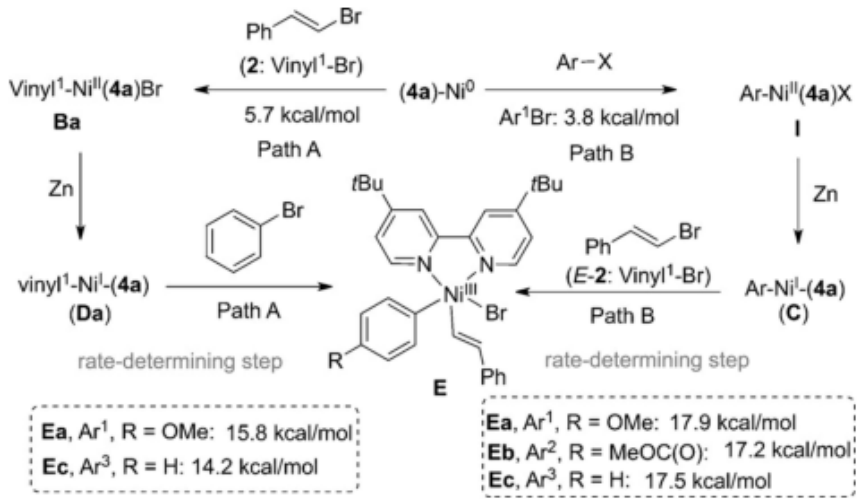
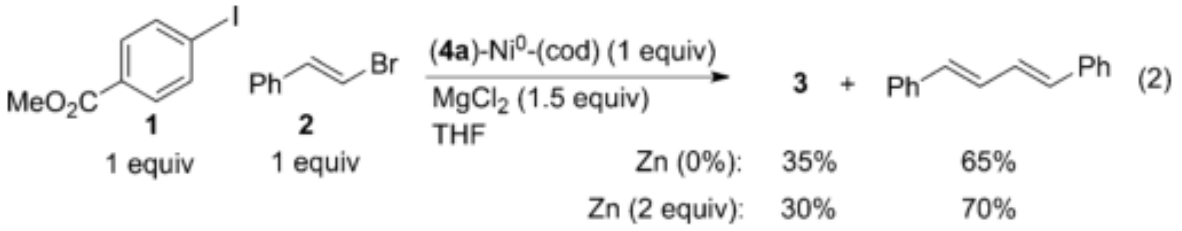


Figure 3. [a] 1-Bromoprop-1-ene ($E/Z = 6:4$) was used. [b] ArI was used. [c] Method B was used. [d] Use of 1.5 equiv of (*Z*)-vinyl-Br. DMF = *N*,*N*-dimethylformamide.

Mechanism research





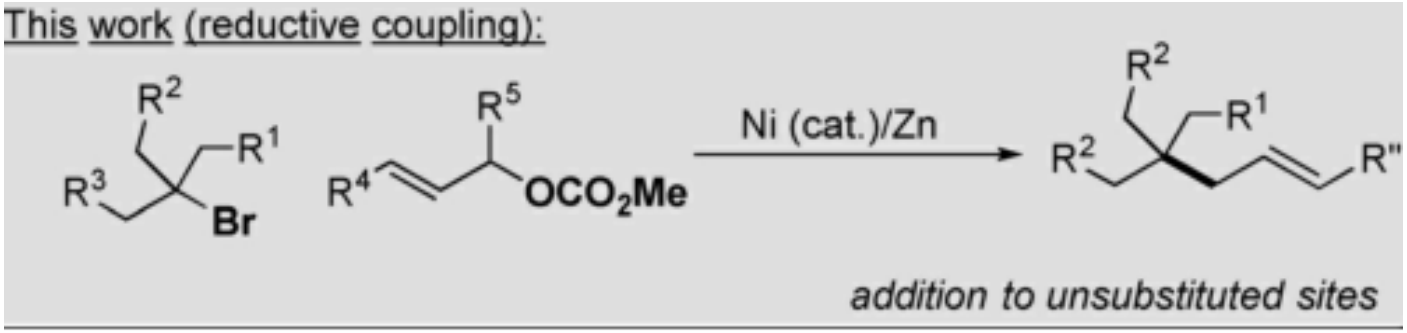


Cross-Coupling

International Edition: DOI: 10.1002/anie.201705521
German Edition: DOI: 10.1002/ange.201705521

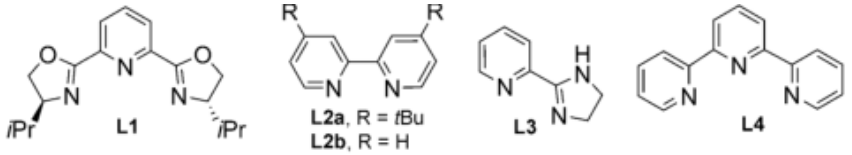
Nickel-Catalyzed Reductive Allylation of Tertiary Alkyl Halides with Allylic Carbonates

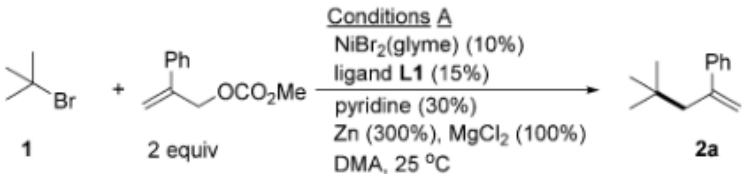
*Haifeng Chen[+], Xiao Jia[+], Yingying Yu[+], Qun Qian, and Hegui Gong**

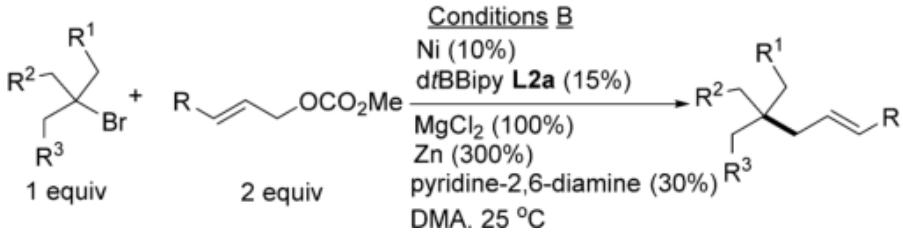


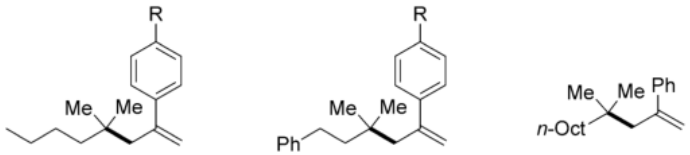
Angew. Chem. Int. Ed. **2017**, *56*, 13103 –13106

Scope of substrates





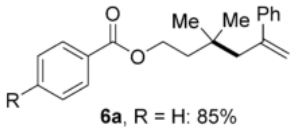




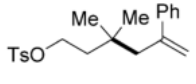
3a, R = H: 85%
3b, R = CF_3: 74%

4a, R = H: 83%
4b, R = OMe: 87%

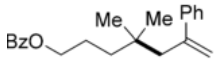
5: 76%



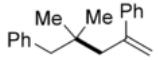
6a, R = H: 85%
6b, R =Cl: 81%
6c, R = OMe: 86%



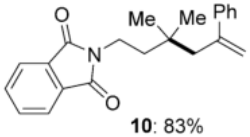
7: 71%



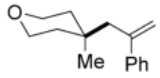
8: 80%



9: 74%

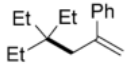


10: 83%

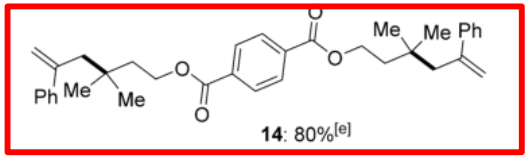


11: 85%

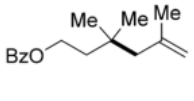
12: 73%[c,d]



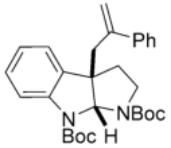
13: 49%



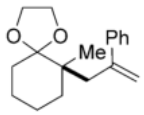
14: 80%[e]



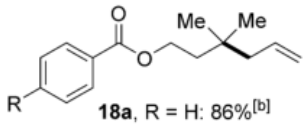
15: 46%



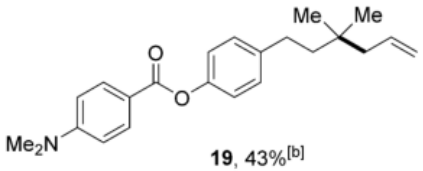
16: 66%[f]



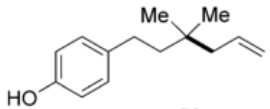
17: 65%[g]



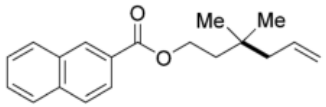
18a, R = H: 86%[b]
18b, R= OMe: 87%[b]
18c, R = CF_3: 83%[b]
18d, R = Ac: 63%[b]



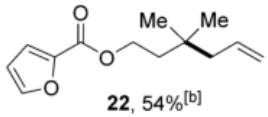
19, 43%[b]



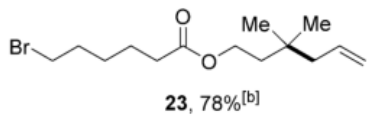
20, 56%[b]



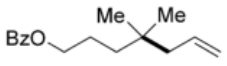
21, 96%[b]



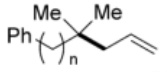
22, 54%[b]



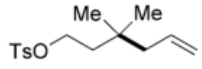
23, 78%[b]



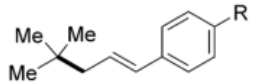
24, 83%[b]



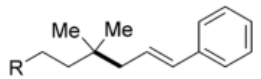
25, n =1, 43%[b]
26, n =2, 51%[b]



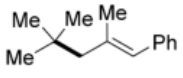
27, 82%[b]



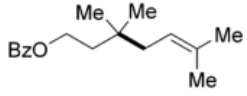
28a, R = H: 62%[c,d]
28b, R = OMe: 53%[c,d]



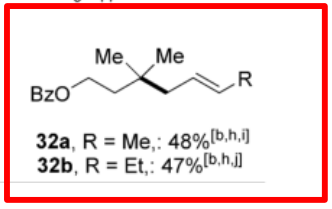
29a, R = BzO: 73%[b,d] (55%)[b,e]
29b, R = nC_5H_{11}: 53%[b,d]



30: 15%[b,f]

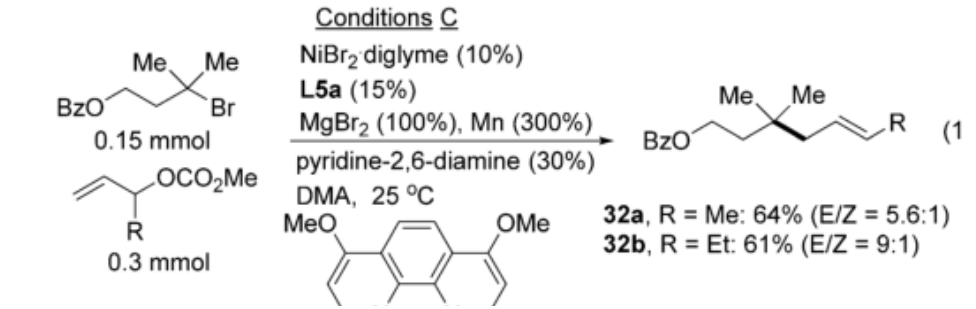


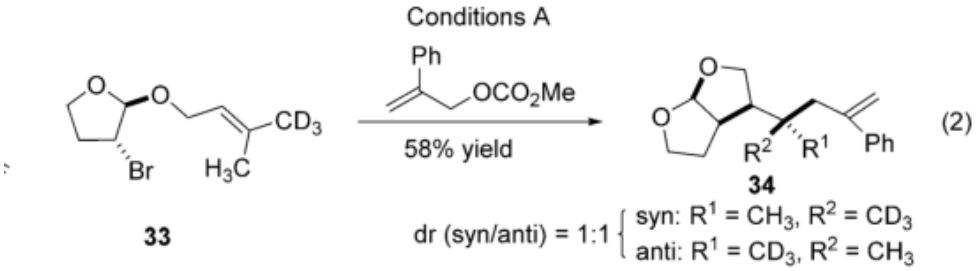
31: 33%[b,g]

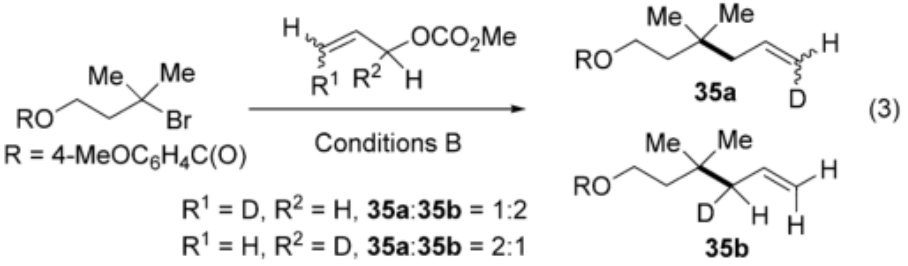


32a, R = Me,: 48%[b,h,i]
32b, R = Et,: 47%[b,h,j]

Mechanism research







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Article
Cite This: J. Am. Chem. Soc. 2018, 140, 14490−14497
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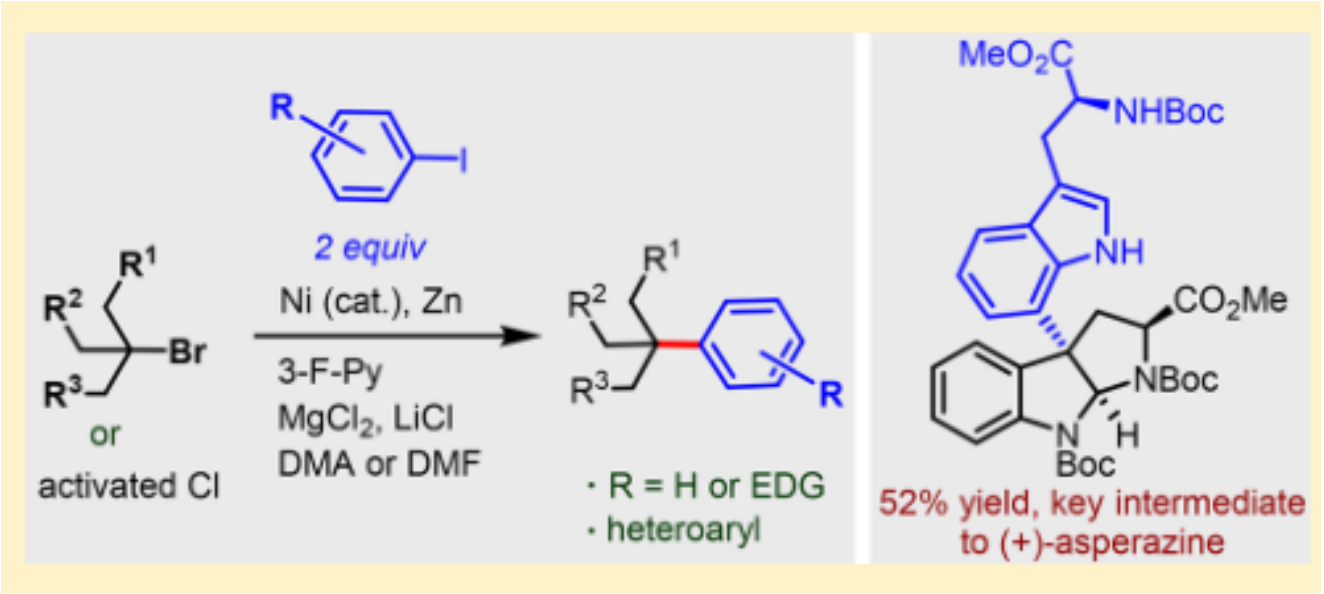
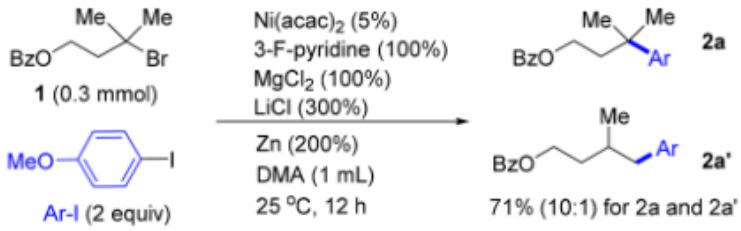
Ni-Catalyzed Reductive Coupling of Electron-Rich Aryl Iodides with Tertiary Alkyl Halides

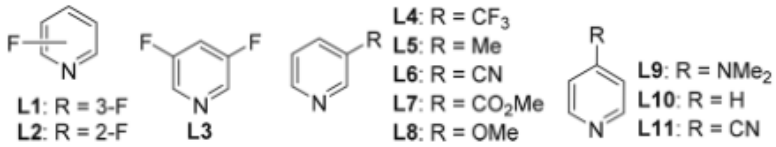
Xuan Wang,[†,∥] Guobin Ma,[†,∥] Yu Peng,[⊥] Chloe E. Pitsch,[‡] Brenda J. Moll,[‡] Thu D. Ly,[‡] Xiaotai Wang,*[,‡] and Hegui Gong*[,†]



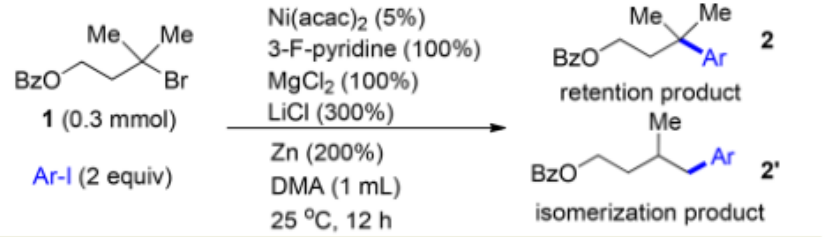
DOI: 10.1021/jacs.8b09473
J. Am. Chem. Soc. 2018, 140, 14490−14497

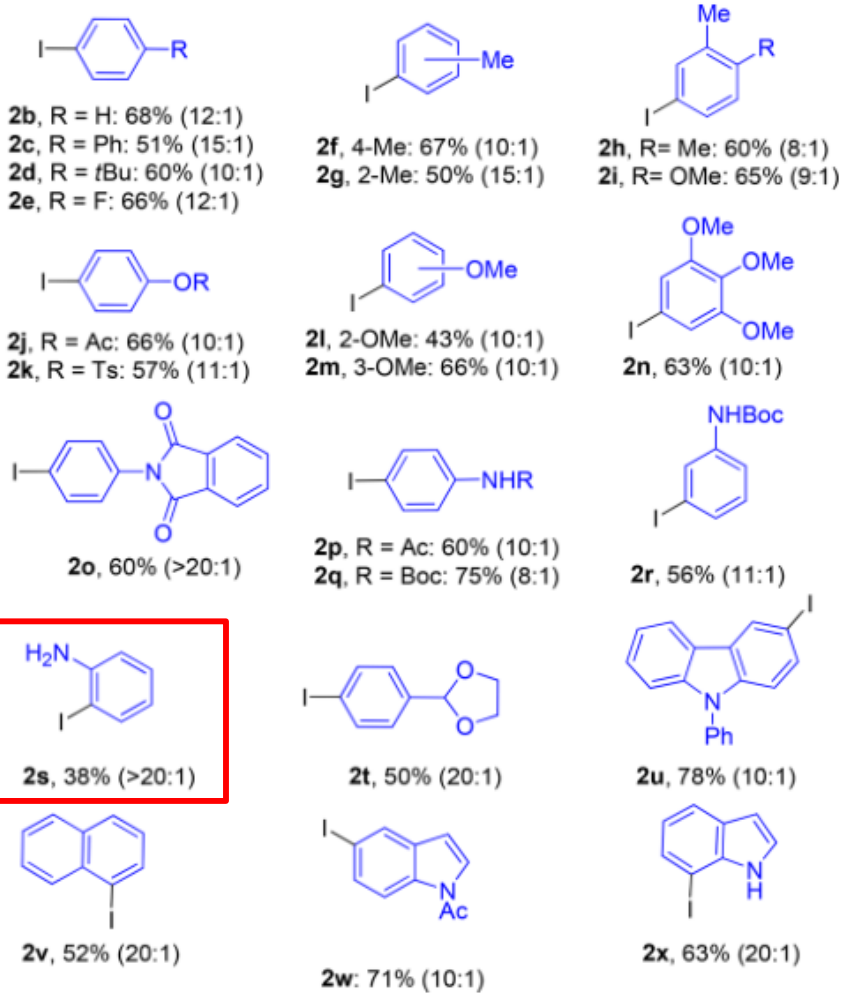
Reaction condition optimization and scope of substrates



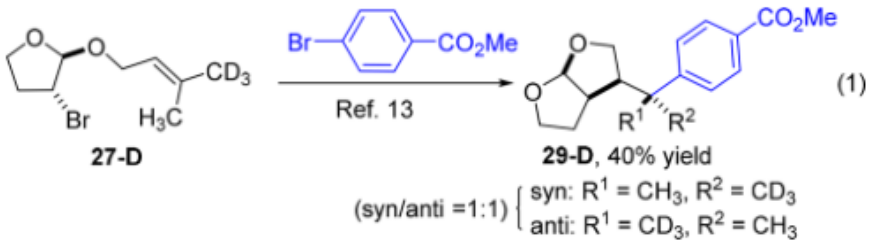


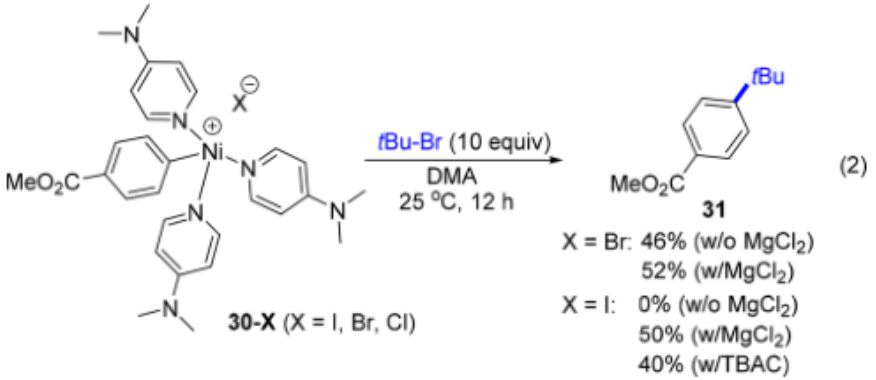
entry[a]	variation from the standard conditions	yield[b] (%)	R:I[c]
1	no changes	65 (71)[d]	10:1
2	without Ni	trace	NA
3	without Zn	trace	NA
4	without 3-F pyridine	trace	NA
5	without $MgCl_2$	18	50:1
6	without LiCl	30	12:1
7	50% 3-F pyridine	54	11:1
8	Mn instead	52	10:1
9	**L2** instead of **L1**	trace	NA
10	**L3** instead of **L1**	44	10:1
11	**L4** instead of **L1**	58	10:1
12	**L5** instead of **L1**	46	10:1
13	**L6** instead of **L1**	50	>10:1
14	**L7** instead of **L1**	60	10:1
15	**L8** instead of **L1**	52	9:1
16	**L9** instead of **L1**	22	>20:1
17	**L10** instead of **L1**	50	6:1
18	**L11** instead of **L1**	50	20:1

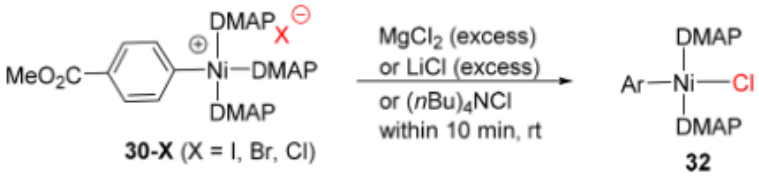


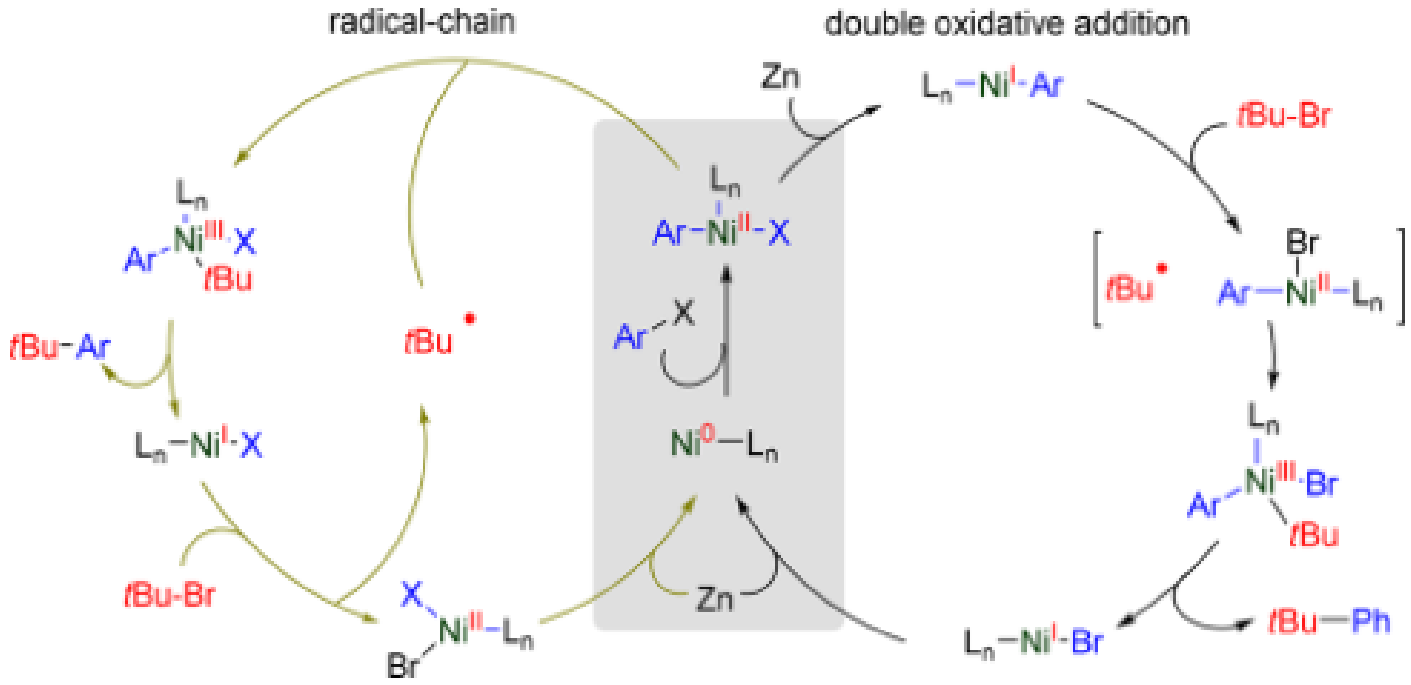


Mechanism research









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Cite this: *Org. Biomol. Chem.*, 2019, **17**, 4230

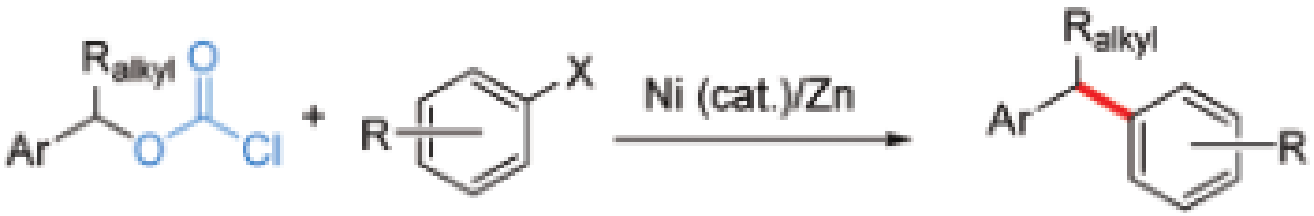
Received 18th March 2019,
Accepted 28th March 2019

DOI: 10.1039/c9ob00628a

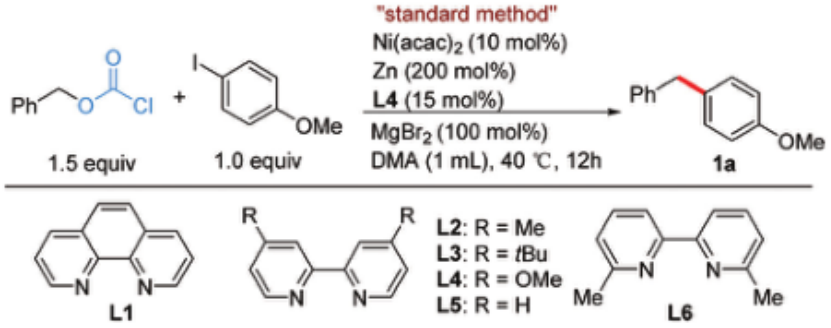
rsc.li/obc

Deoxygenative cross-electrophile coupling of benzyl chloroformates with aryl iodides†

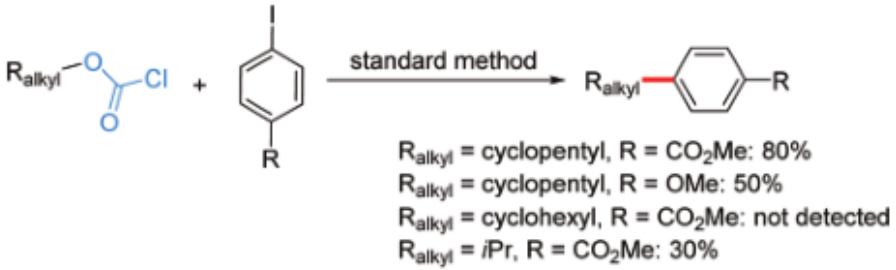
Yingying Pan,‡ Yuxin Gong,‡ Yanhong Song, Weiqi Tong and Hegui Gong *

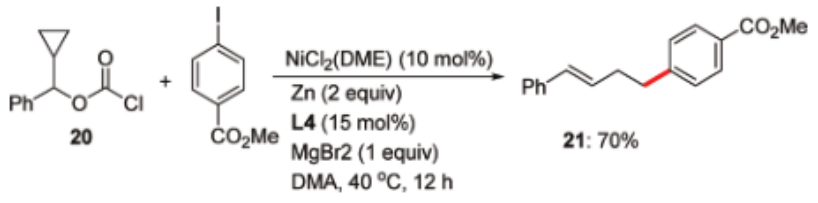


Reaction condition optimization and Mechanism research

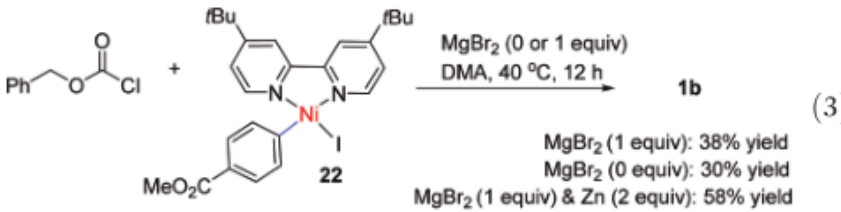


Entry[a]	Variation from the "standard conditions"	Yield[b] %
1	None	96 (95)[c]
2	50 °C	89
3	25 °C	86
4	1.2 equiv. of benzyl chloroformate	92
5	1.0 equiv. of benzyl chloroformate	74
6	**L5** instead of **L4**	75
7	**L2** instead of **L4**	72
8	Pyridine instead of **L4**	70
9	**L1** instead of **L4**	42
10	**L3** instead of **L4**	94
11	**L6** instead of **L4**	23
12	$MgCl_2$ instead of $MgBr_2$, 50 °C	60
13	LiBr instead of $MgBr_2$, 50 °C	Trace
14	CH_3CN instead of DMA	60
15	THF instead of DMA	43
16	w/o $Ni(acac)_2$	nd[d]
17	w/o **L4**	18
18	w/o $MgBr_2$	53
19	4-Chloroanisole instead of 4-iodoanisole	nd
20	4-Bromoanisole instead of 4-iodoanisole	<10





(2)



(3)

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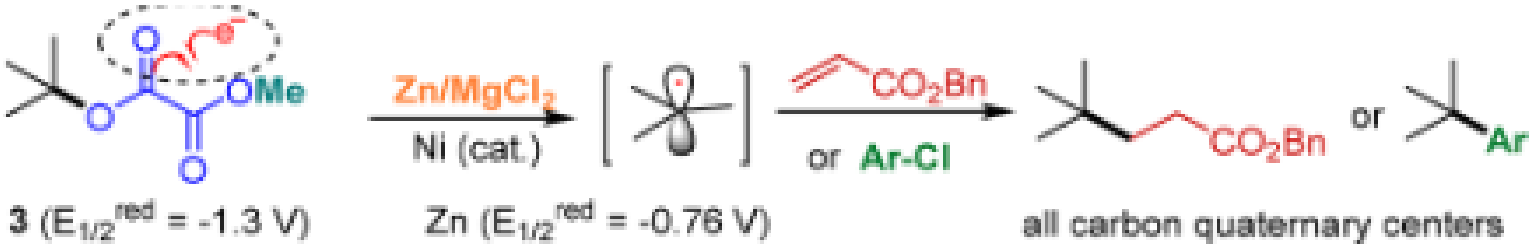
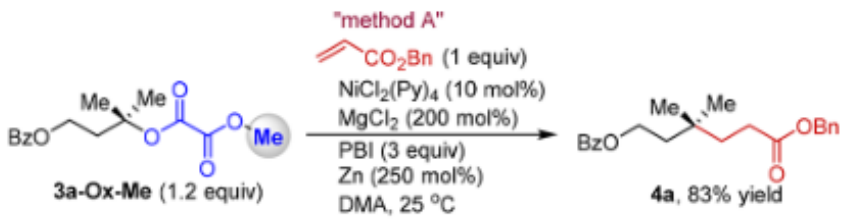
Zn-Mediated Fragmentation of Tertiary Alkyl Oxalates Enabling Formation of Alkylated and Arylated Quaternary Carbon Centers

Yang Ye,[†] Haifeng Chen,[†] Jonathan L. Sessler, and Hegui Gong*

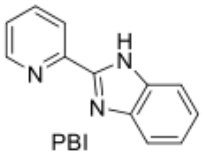


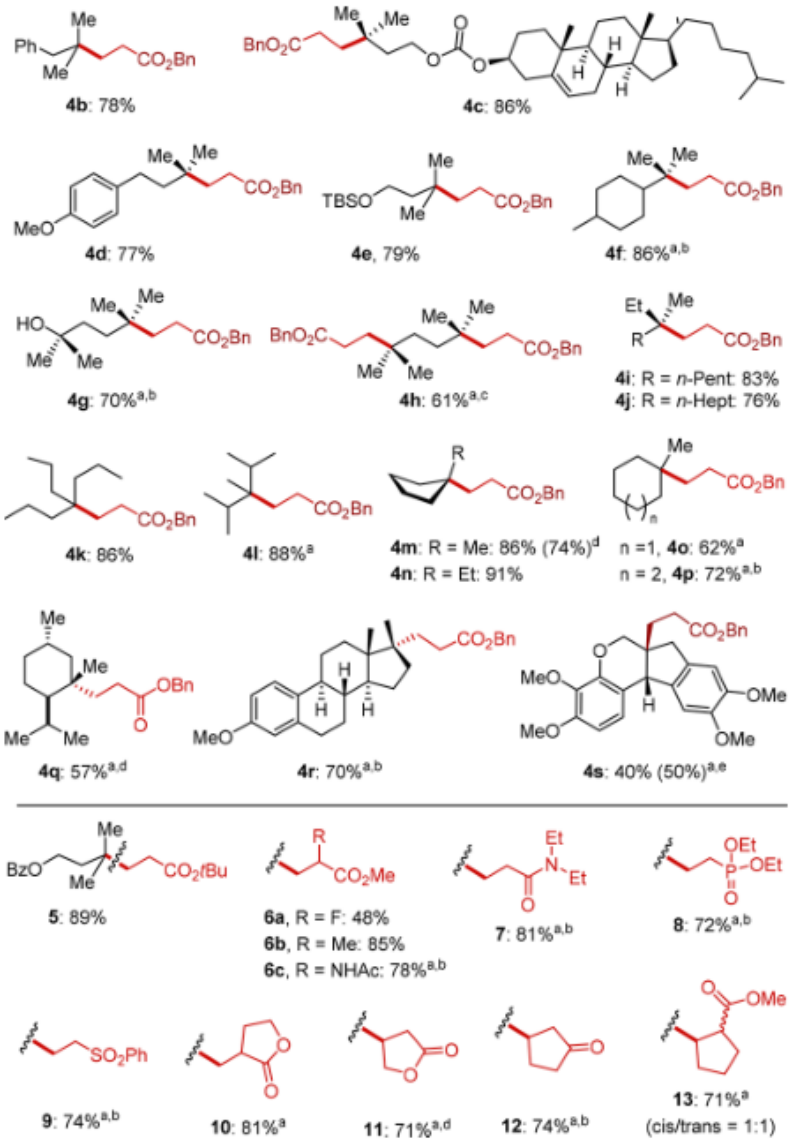
DOI: 10.1021/jacs.8b12801
J. Am. Chem. Soc. 2019, 141, 820−824

Reaction condition optimization and Mechanism research

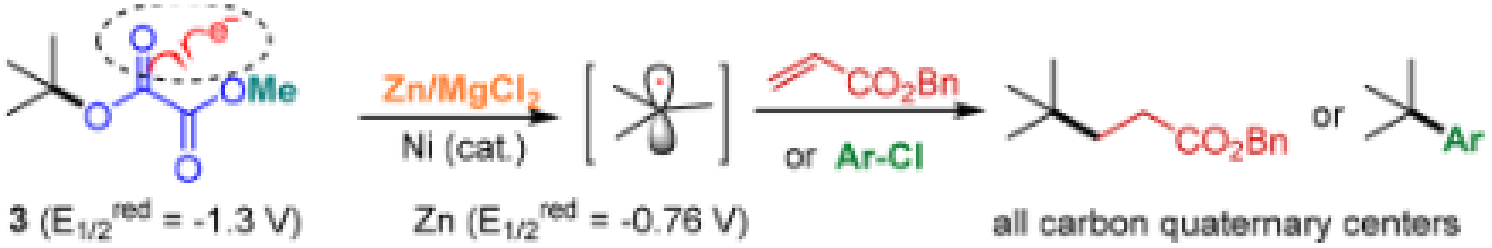


entry	variation from the standard conditions	yield %[a]
1	none	83[b]
2	w/o $MgCl_2$	no reaction
3	w/o PBI	trace
4	w/o Zn	no reaction
5	w/o Ni	32
6	Mn in place of Zn	47
7	Mg in place of Zn	no reaction
8	DMAP in place of PBI	21
9	dtbbp in place of PBI	45
10	*i*Pr-Pybox in place of PBI	24
11	$NiCl_2$	68
12	$NiBr_2$	46
13	NiI_2	69
14	$ZnCl_2$ instead of $MgCl_2$	no reaction



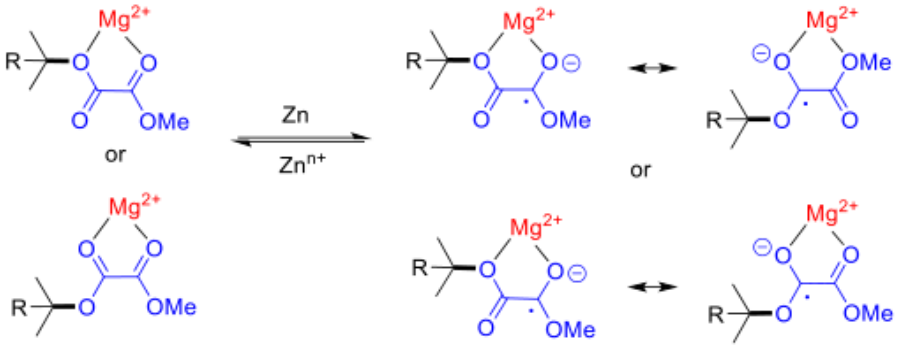


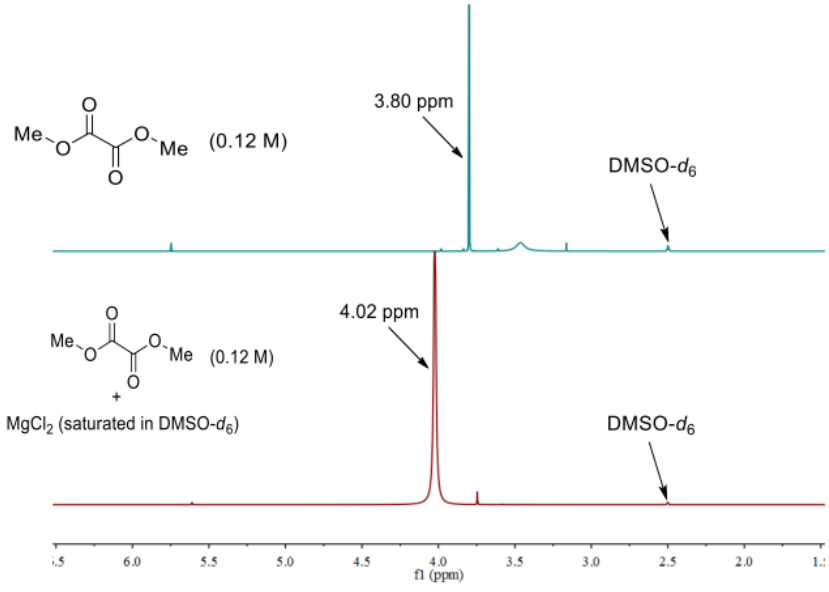
Mechanism research



1	Unk: 样品-1 2018-10-16 13:51:18 CONC Custom ID1: Custom ID2: Custom ID3:	
	Mg2795	
单位	ppm	$Mg(DMAP)_xCl_2$: 19mg/L
平均值 average	1.339	
标准偏差	.005	
% RSD	.3736	ICP report
Rep #1	1.333	
Rep #2	1.342	
Rep #3	1.341	
2	Unk: 样品-2 2018-10-16 13:52:51 CONC Custom ID1: Custom ID2: Custom ID3:	
	Mg2795	
单位	ppm	$Mg(PBI)_yCl_2$: 3mg/L
平均值 average	2.566	
标准偏差	.008	
% RSD	.3243	ICP report
Rep #1	2.564	
Rep #2	2.559	
Rep #3	2.575	

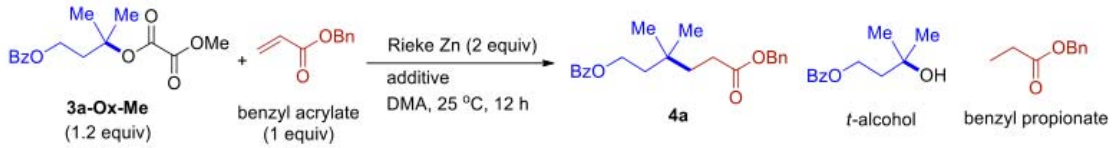
ICP-AES： $Mg(PBI)Cl_2$ and $Mg(DMAP)_2Cl^2$



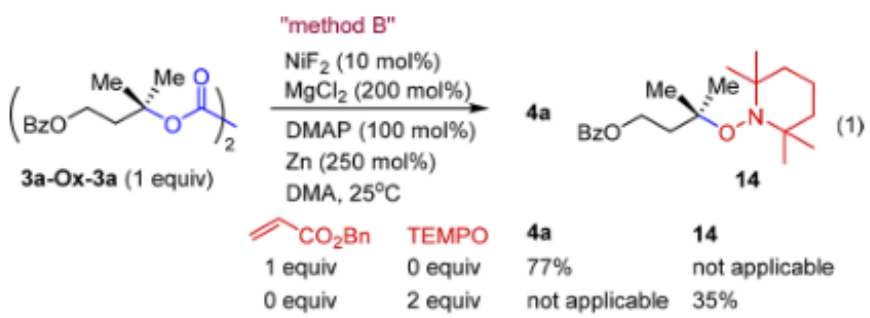


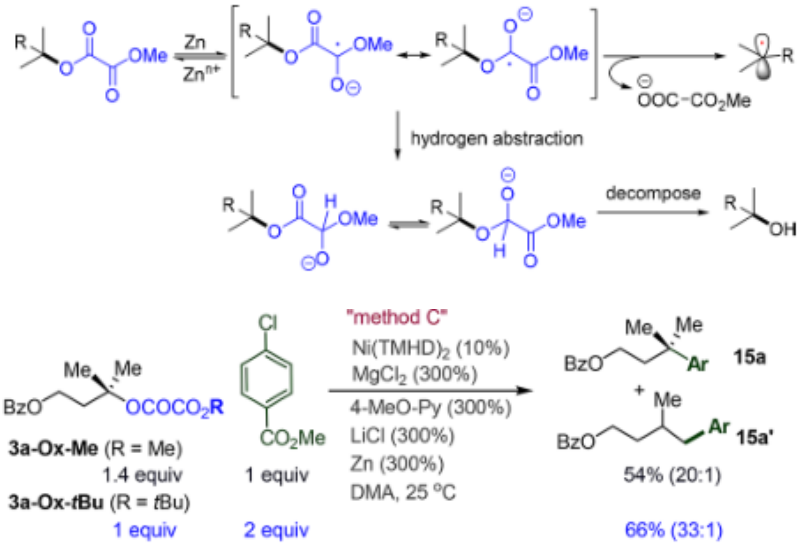
Mechanism research

Table S3. Rieke Zn-mediated coupling of **3a-Ox-Me** with benzyl acrylate.[a]



entry	variation from the standard conditions	**4a**	**3a-Ox-Me**	benzyl acrylate	*t*-alcohol	benzyl propionate
1	Rieke Zn (only)	4%	7%	50%	108%	40%
2	Rieke Zn/ $MgCl_2$	48%	13%	28%	51%	18%
3	Rieke Zn/ PBI	10%	20%	38%	90%	48%
4	Rieke Zn/ $NiCl_2(Py)_4$	4%	7%	26%	110%	65%
5	Rieke Zn (only)/ 50 °C	5%	30%	6%	74%	86%
6	Rieke Zn/ $MgCl_2$/ PBI	33%	35%	16%	40%	50%
7	Rieke Zn/ $MgCl_2$/ $NiCl_2(Py)_4$	54%	20%	24%	45%	20%
8	Rieke Zn/ PBI/ $NiCl_2(Py)_4$	11%	55%	36%	54%	48%
9	$NiCl_2(py)_4$/ Rieke Zn/ $MgCl_2$/ PBI	68%	25%	12%	20%	18%





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Letter

Cite This: *Org. Lett.* 2019, 21, 1645−1648

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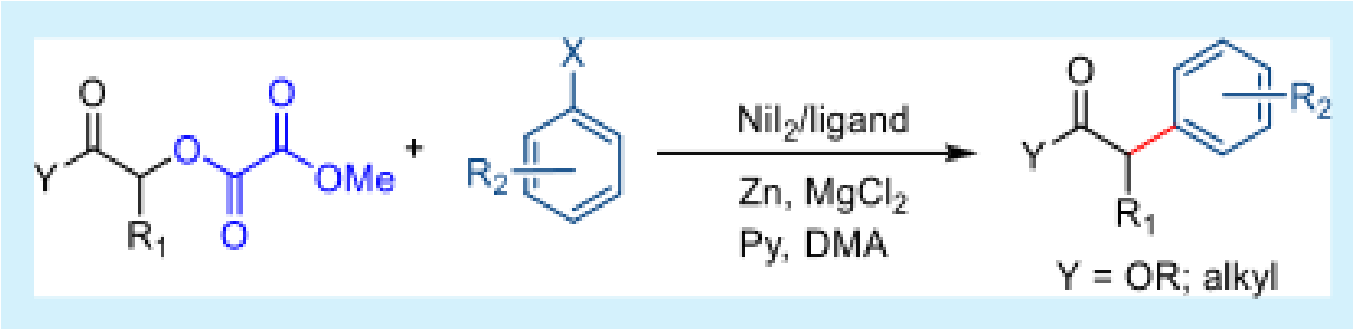
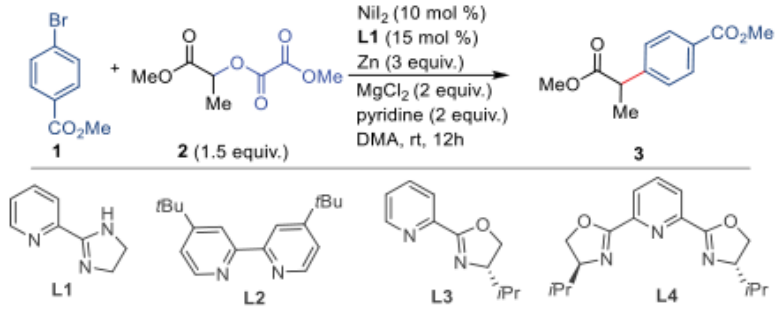
Ni-Catalyzed Reductive C−O Bond Arylation of Oxalates Derived from α-Hydroxy Esters with Aryl Halides

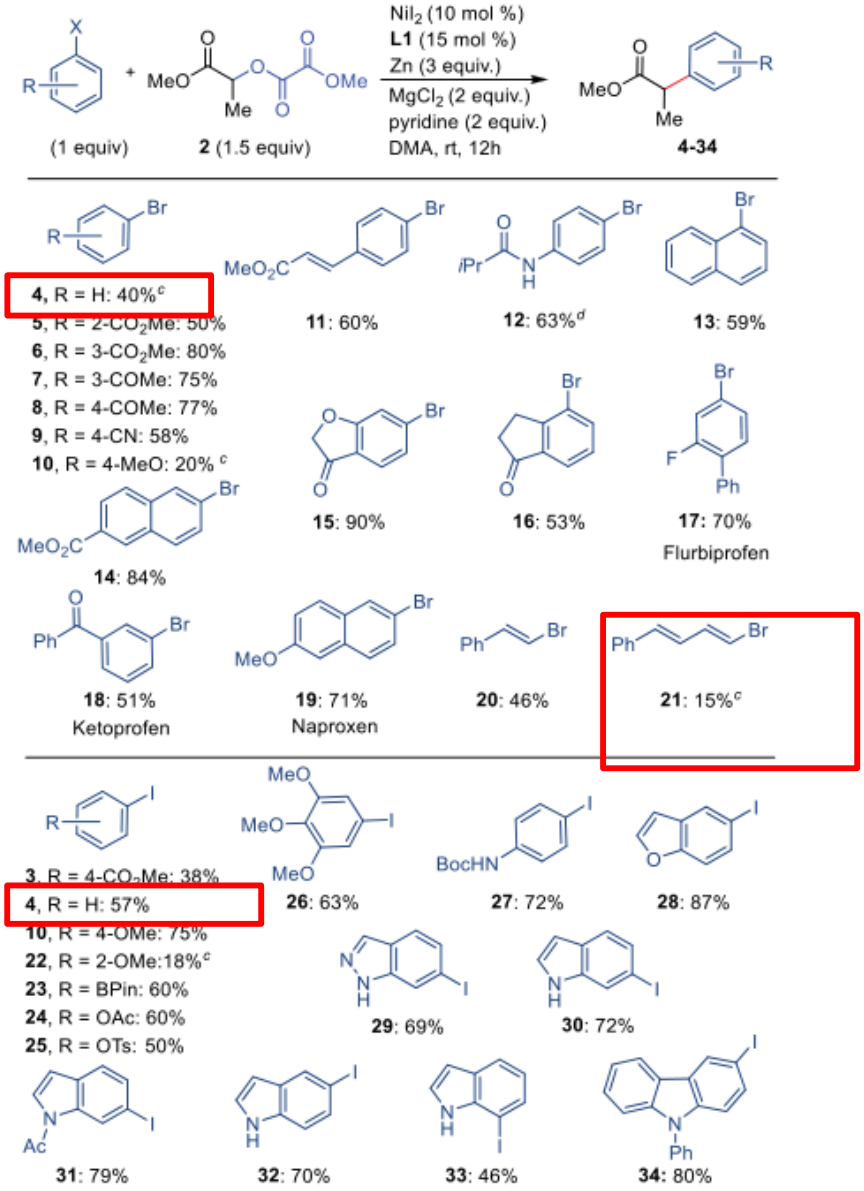


DOI: 10.1021/acs.orglett.9b00174
Org. Lett. 2019, 21, 1645−1648

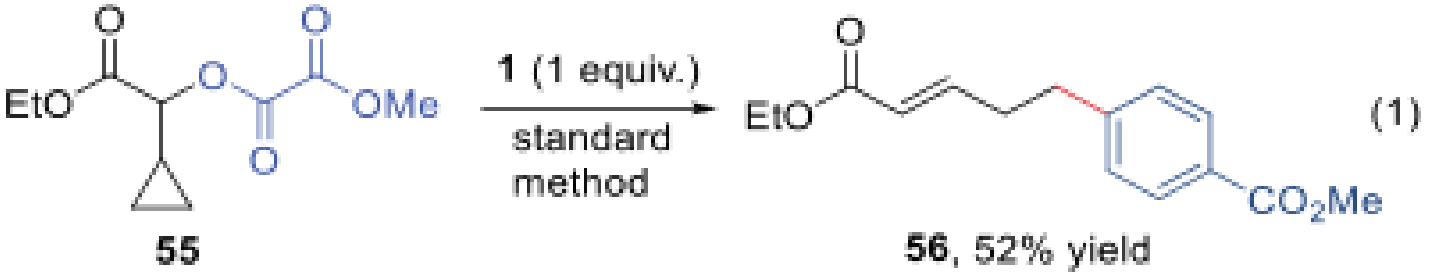
Reaction condition optimization and scope of substrates

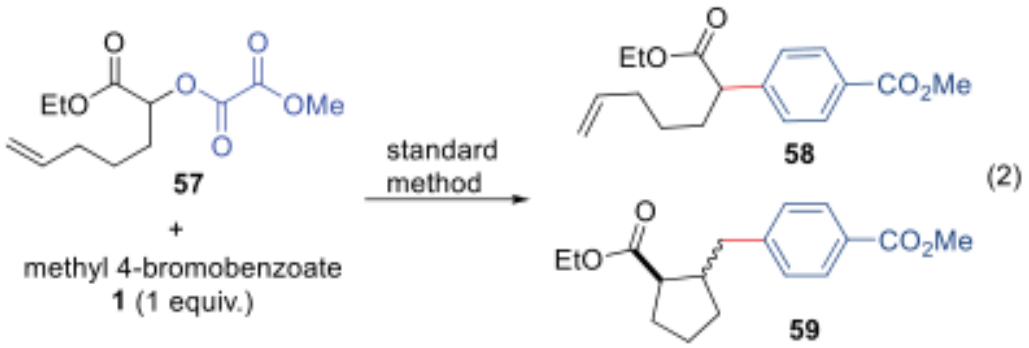


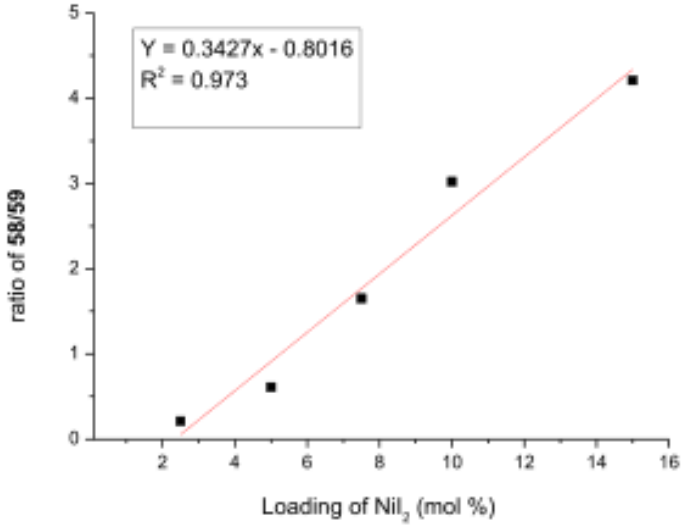
entry	variation	yield (%)[b]
1	none	86[c]
2	$NiCl_2$ instead of NiI_2	80
3	$NiBr_2$ instead of NiI_2	70
4	**L2** instead of **L1**	71
5	**L3** instead of **L1**	70[d]
6	**L4** instead of **L1**	trace
7	Mn instead of Zn	45
8	$MgBr_2$ instead of $MgCl_2$	9
9	NiI_2 (5%)/**L1** (10%)	69
10	1.2 equiv of **2**	57
11	without NiI_2	ND[e]
12	without $MgCl_2$	ND
13	without Py	55
14	without **L1**	17
15	**1** (3 mmol)	75[c]



Mechanism research





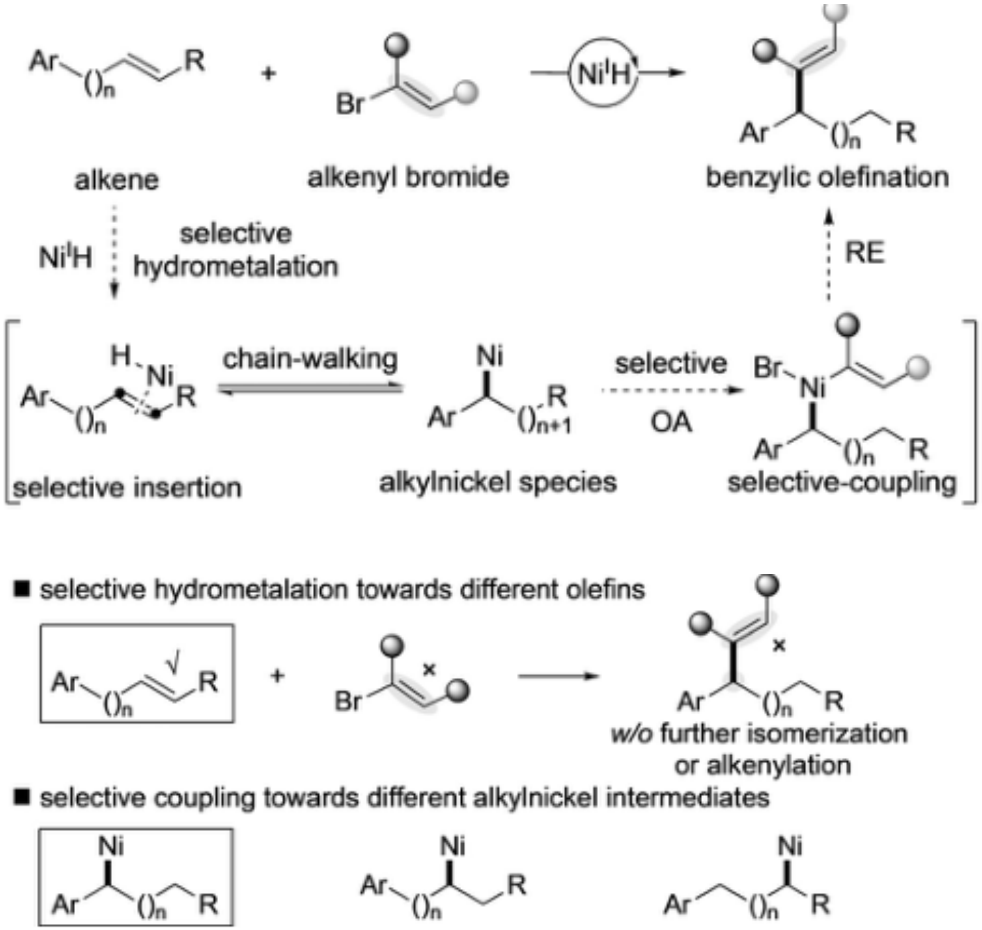


Asymmetric Catalysis

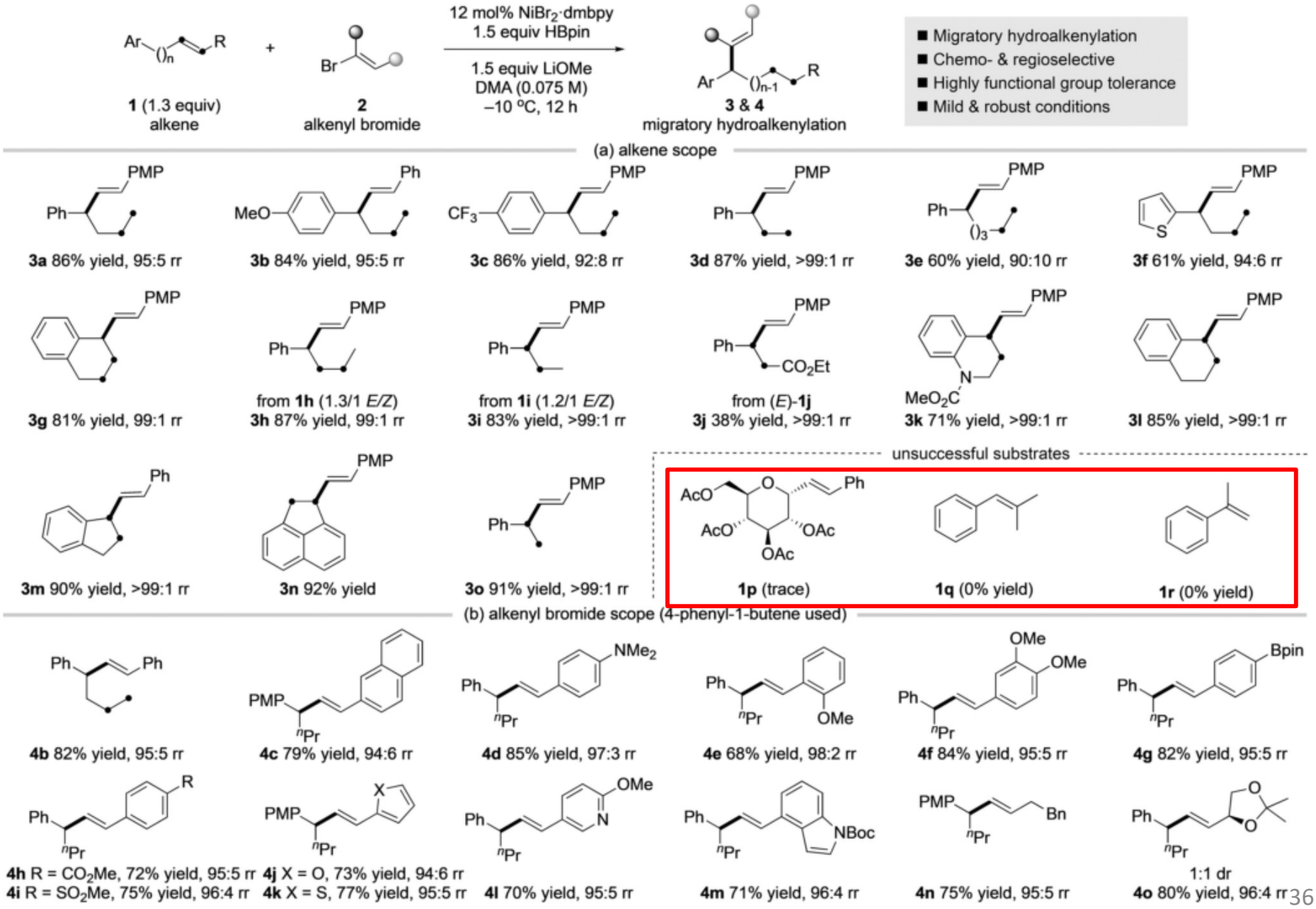
How to cite: *Angew. Chem. Int. Ed.* **2021**, *60*, 4060–4064
International Edition: doi.org/10.1002/anie.202012614
German Edition: doi.org/10.1002/ange.202012614

Nickel-Catalyzed, Regio- and Enantioselective Benzylic Alkenylation of Olefins with Alkenyl Bromide

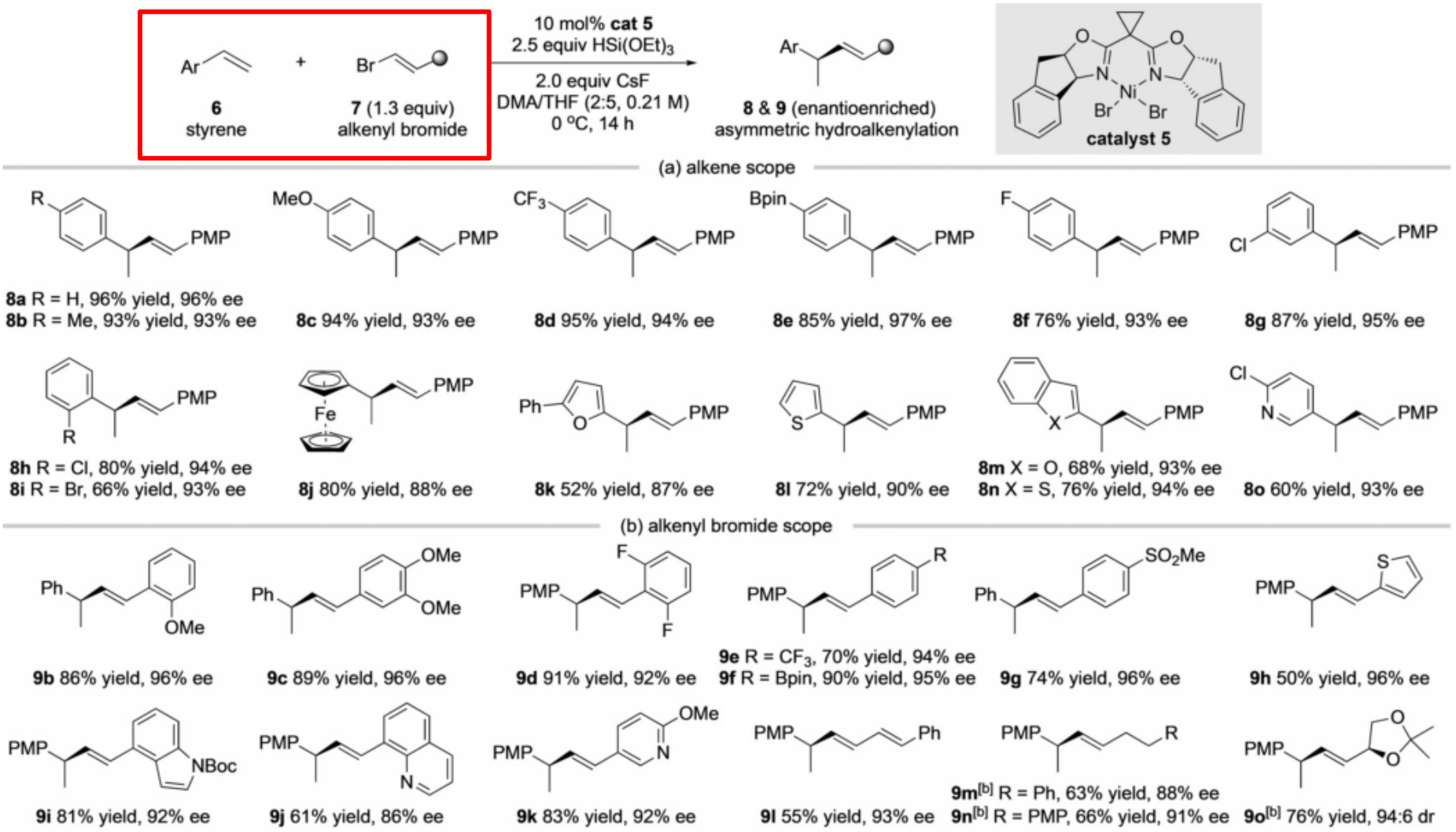
Jiandong Liu, Hegui Gong, and Shaolin Zhu**



scope of substrates

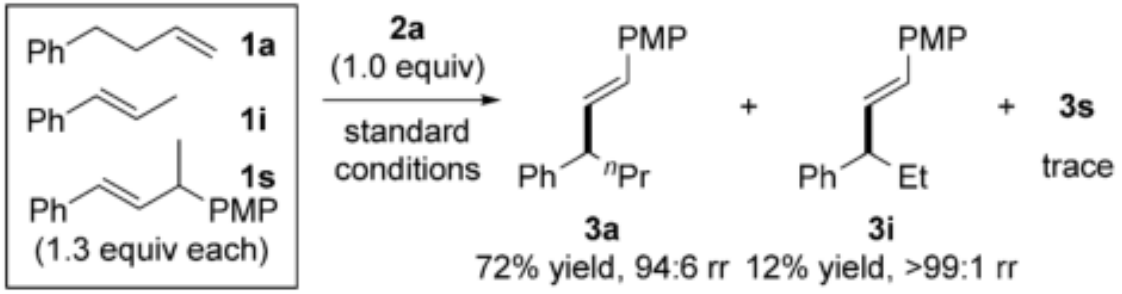


scope of substrates



Mechanism research

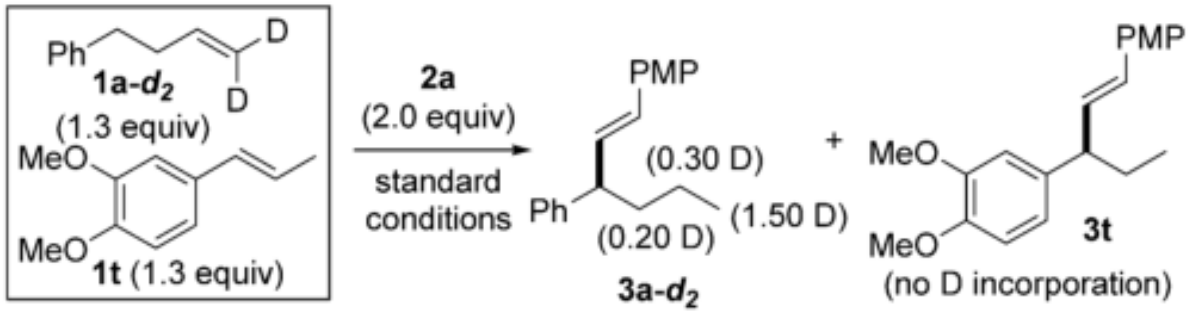
a Competition experiment: terminal alkene vs internal alkene



the reactivities of various olefins:

terminal olefin (**1a**) > internal olefin (**1i**) > sterically hindered internal olefin (**1s**)

b Crossover experiment: no intermolecular H/D scrambled crossover products



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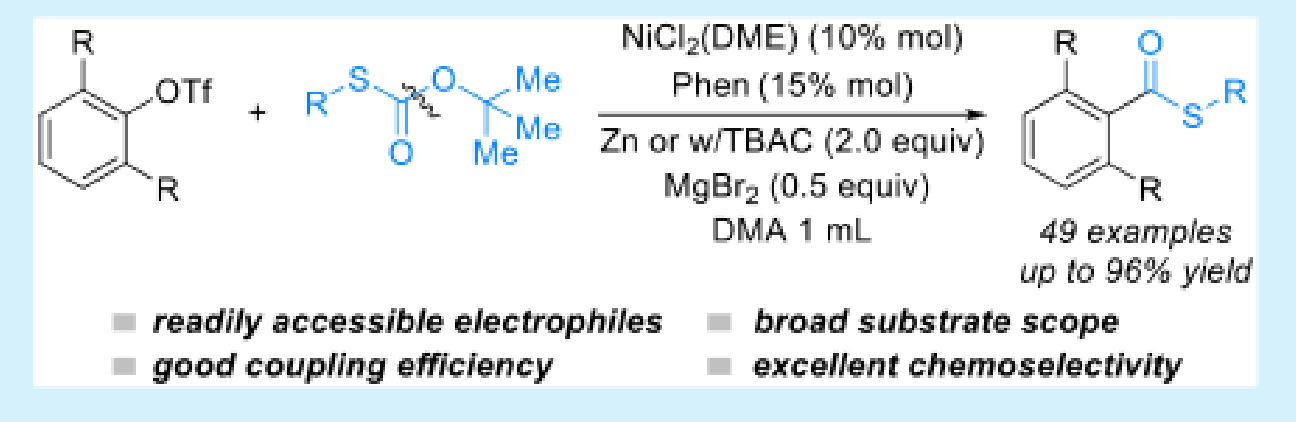
Ni-Catalyzed Cross-Electrophile Coupling of Aryl Triflates with Thiocarbonates via C–O/C–O Bond Cleavage

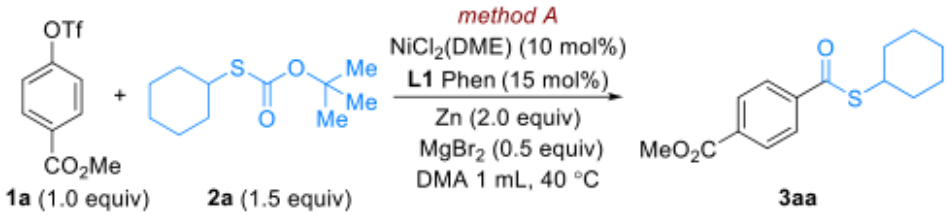
Zhaodong Zhu,† Yuxin Gong,† Weiqi Tong, Weichao Xue,* and Hegui Gong*

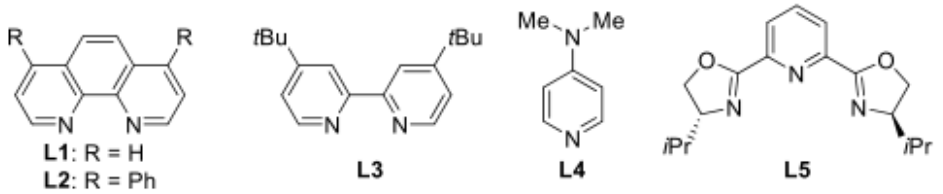


https://dx.doi.org/10.1021/acs.orglett.1c00313
Org. Lett. 2021, 23, 2158–2163

Reaction condition optimization

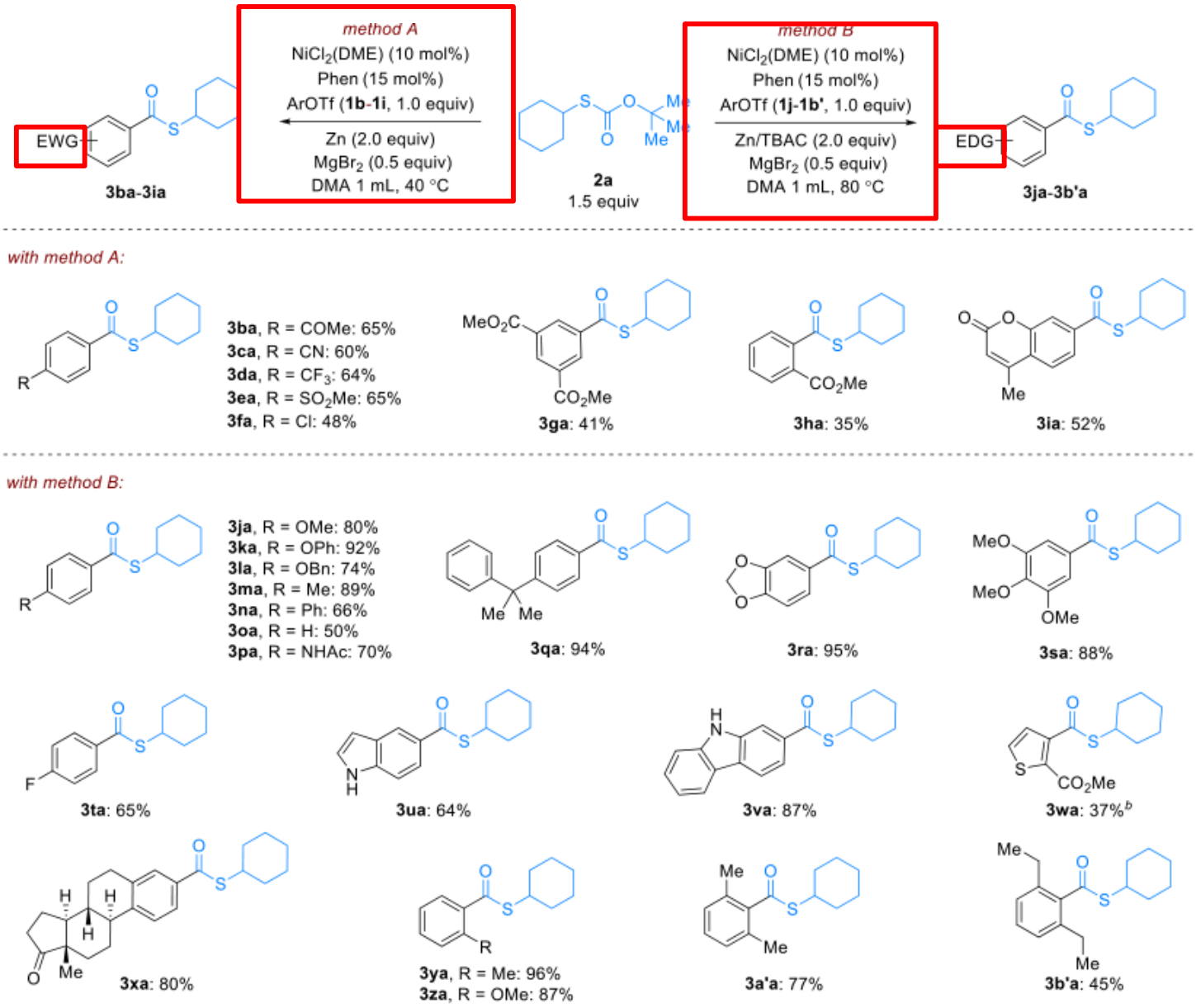
Table 1. Selected Examples of Optimization Reactions[a]





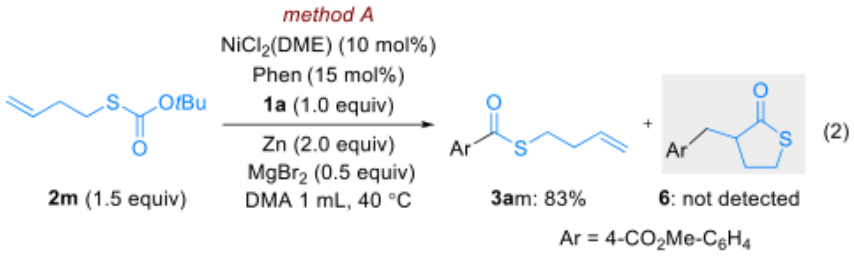
entry	variation of standard conditions	yield[b]
1	None	95% (91%)[c]
2	w/o $NiCl_2(DME)$	trace
3	w/o Phen	trace
4	w/o Zn	trace
5	w/o $MgBr_2$	42%
6	**L2** instead of Phen	72%
7	**L3** instead of Phen	43%
8	**L4** instead of Phen	trace
9	**L5** instead of Phen	trace
10	I instead of OTf	34%
11	Br instead of OTf	49%
12	Cl instead of OTf	trace
13	OTs instead of OTf	trace
14	3.0 mmol of **1a**	89%[c]

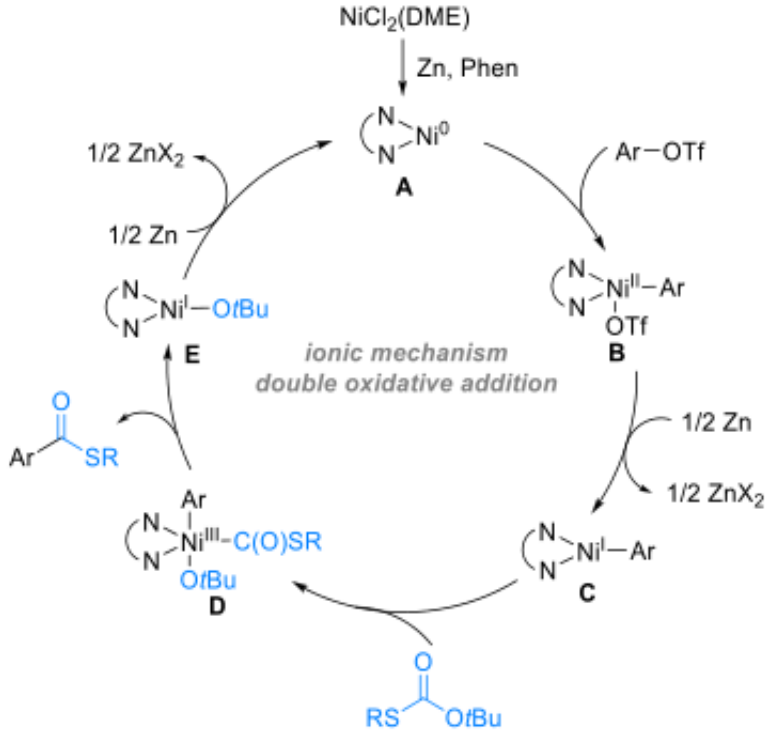
scope of substrates



C–O bonds (≈100 kcal/mol)

Mechanism research





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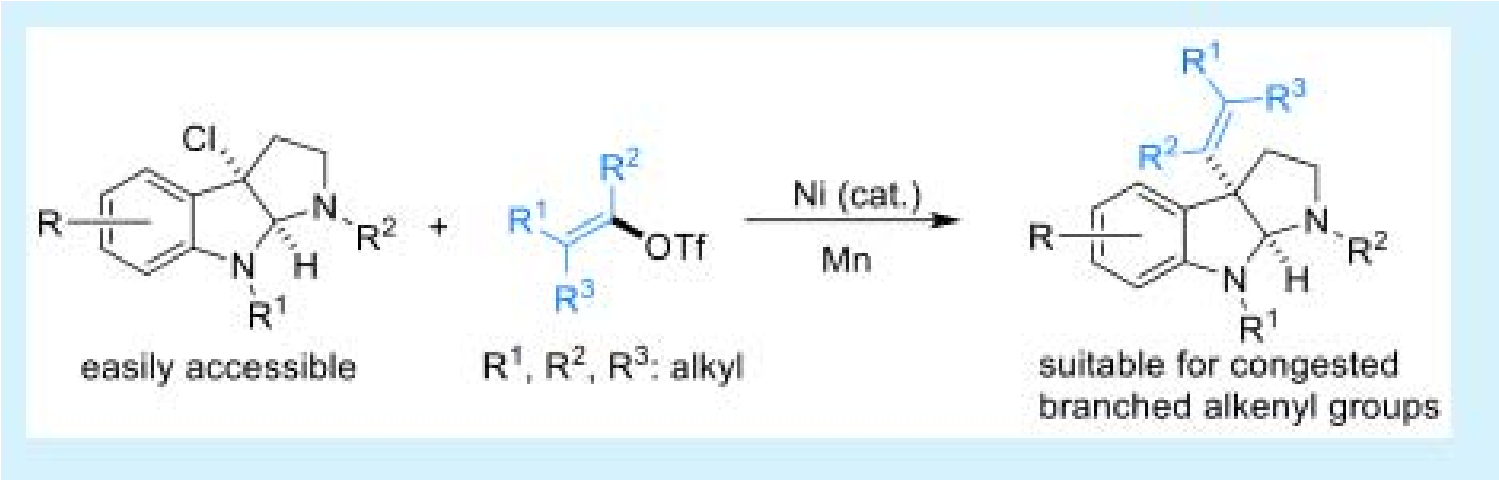
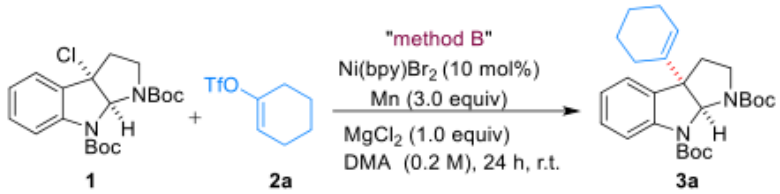
Nickel-Catalyzed Reductive Vinylation of Chloro-hexahydropyrroloindoline Derivatives with Vinyl Triflates

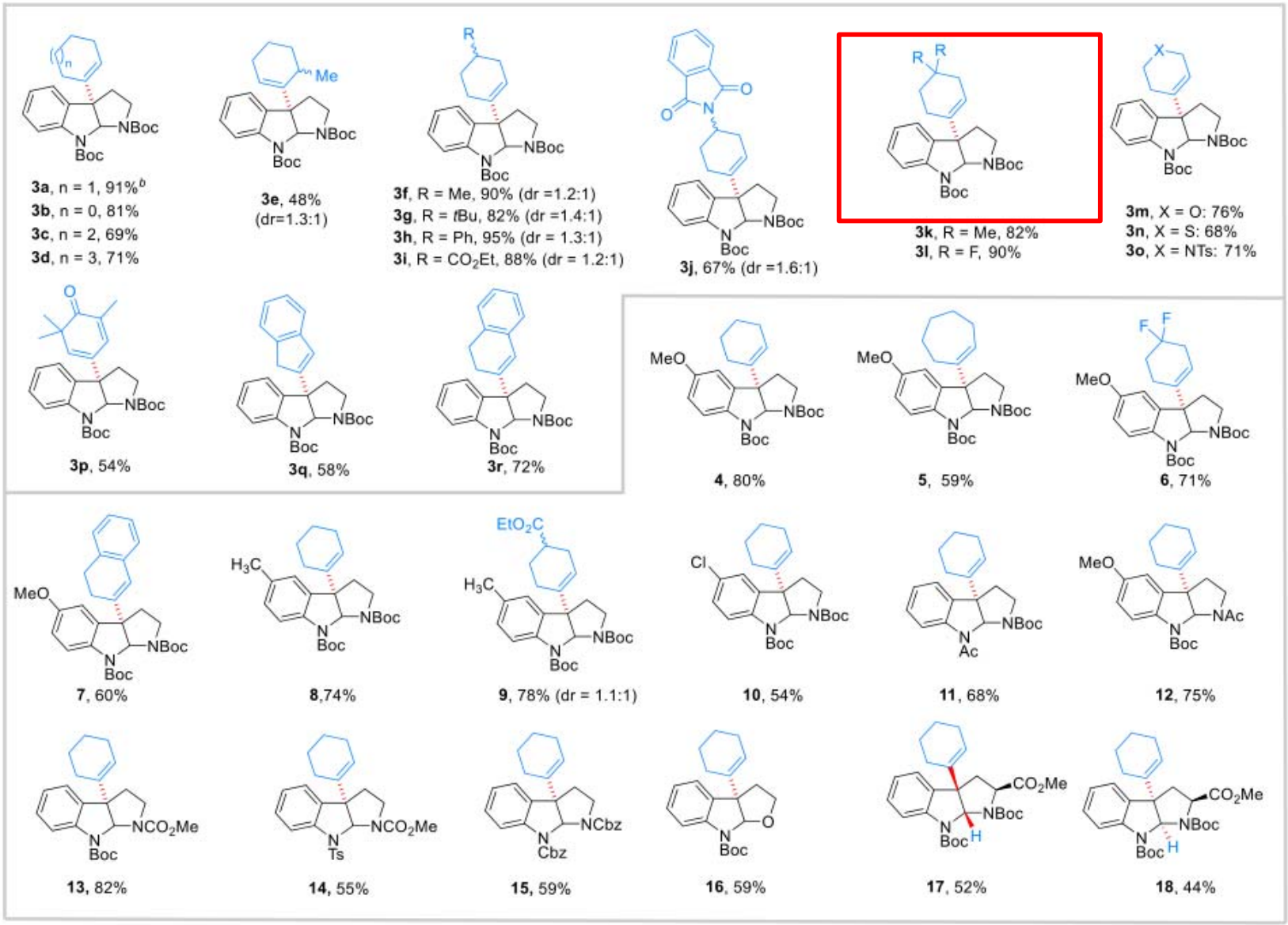
Lei Su,[†] Guobin Ma,*[,†] Yanhong Song, and Hegui Gong*



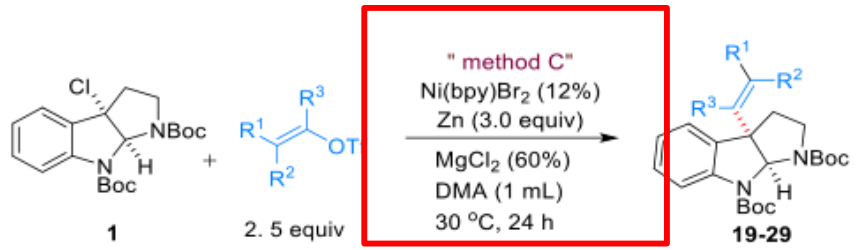
https://doi.org/10.1021/acs.orglett.1c00431
Org. Lett. 2021, 23, 2493−2497

scope of substrates

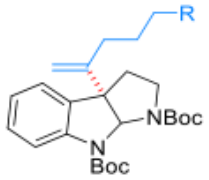




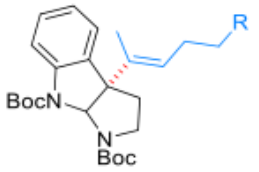
scope of substrates



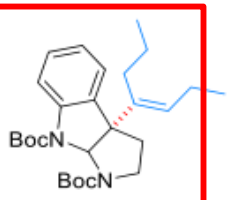
linear vinyl triflate scope



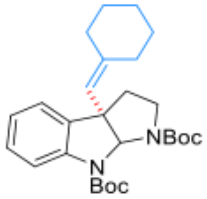
19a, R = Me: 82%
19b, R = Et: 65%



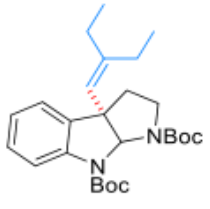
19c, R = Me: 50%[a,b]
19d, R = Et: 58%[a,b,c]



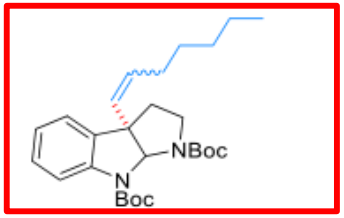
19e, 68%[a,b,c]



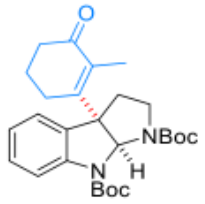
19f, 73%[d]



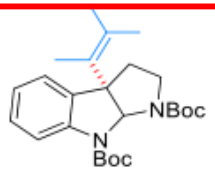
19g, 44%[d]



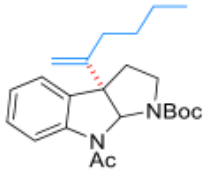
19h, 78% (*Z*/*E*=1:1)[e]



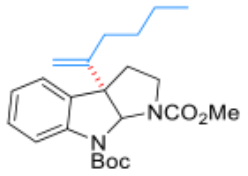
19i, 33%



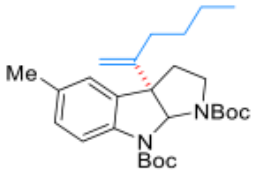
19j, trace
(2-bromo-3-methylbut-2-ene was used)



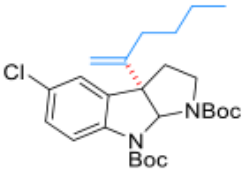
20, 58%



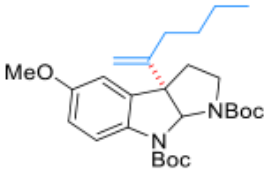
21, 70%



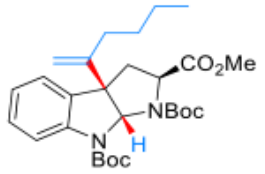
22, 62%



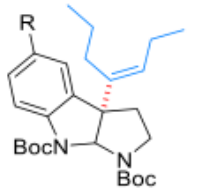
23, 65%



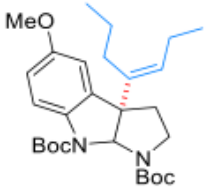
24, 71%



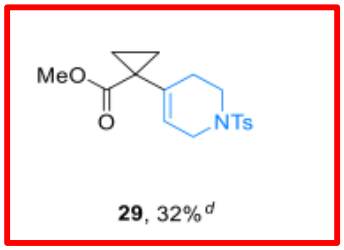
25, 53%



R = Me: **26**, 54%[a,b,c]
R = Cl: **27**, 52%[a,b,c]

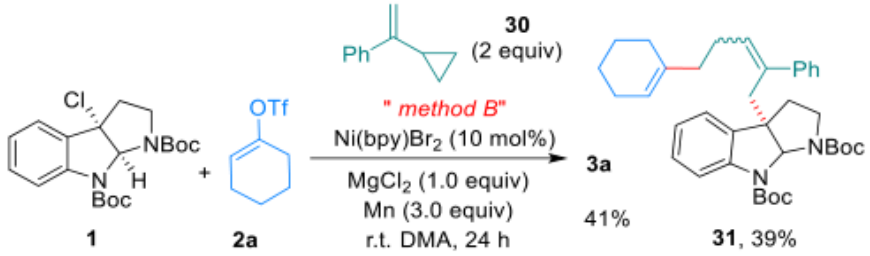


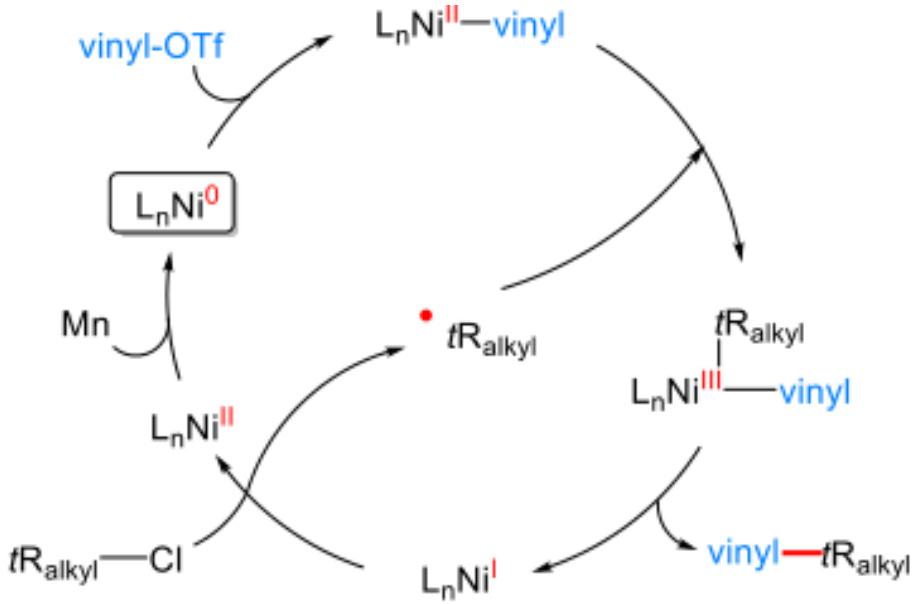
28, 65%[a,b,c]

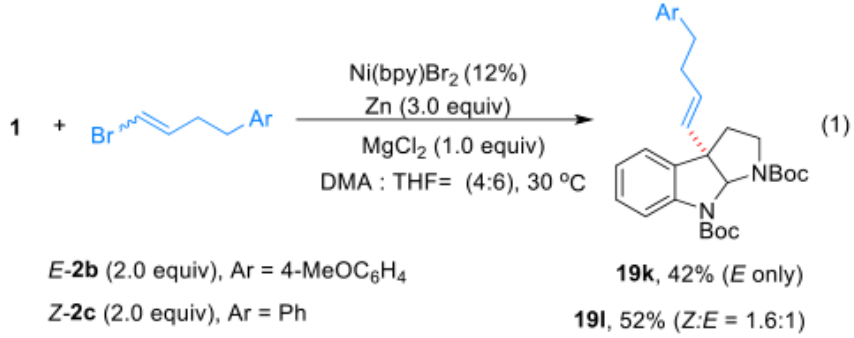


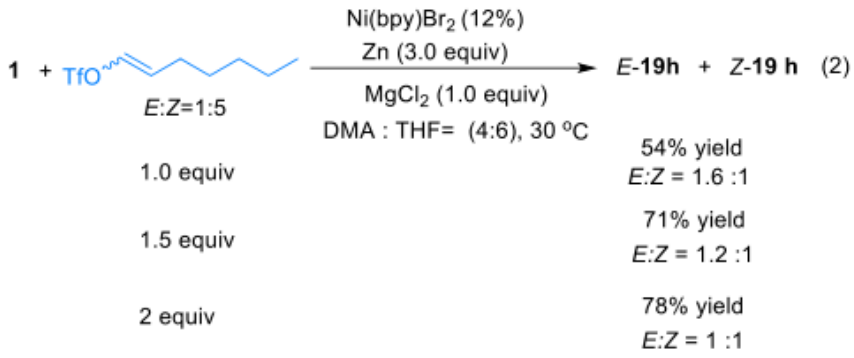
29, 32%[d]

Mechanism research







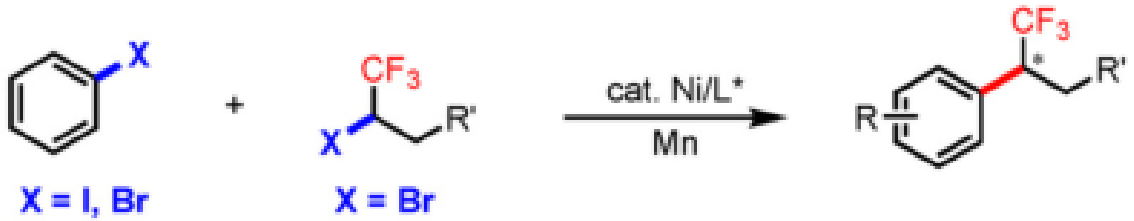


Asymmetric Catalysis

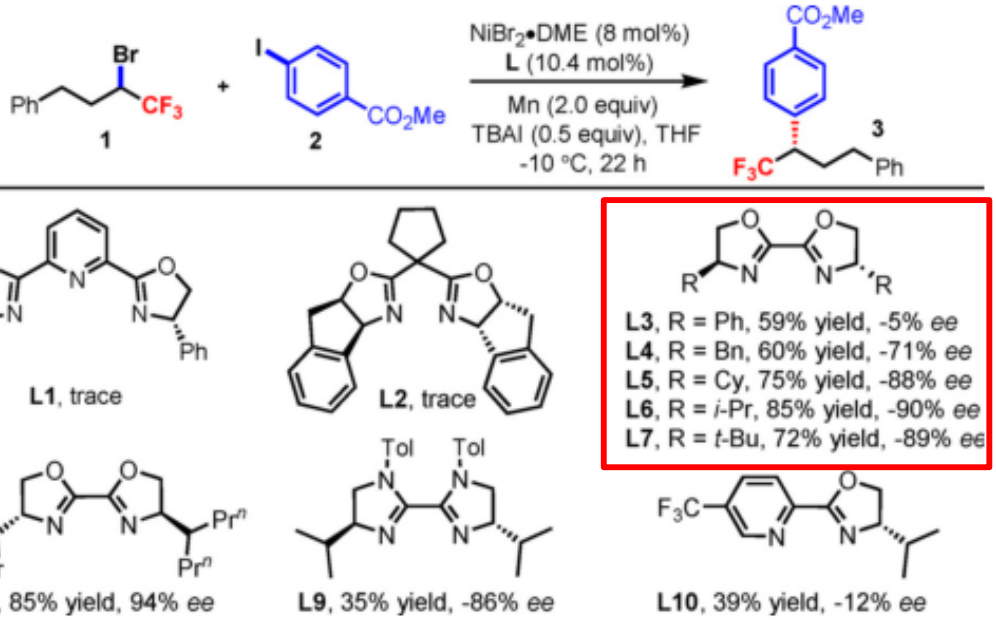
How to cite: *Angew. Chem. Int. Ed.* **2021**, *60*, 9947–9952
International Edition: doi.org/10.1002/anie.202101076
German Edition: doi.org/10.1002/ange.202101076

Diverse Synthesis of Chiral Trifluoromethylated Alkanes via Nickel-Catalyzed Asymmetric Reductive Cross-Coupling Fluoroalkylation

*Yue Min[+], Jie Sheng[+], Jian-Liang Yu, Shan-Xiu Ni, Guobin Ma, Hegui Gong, and Xi-Sheng Wang**



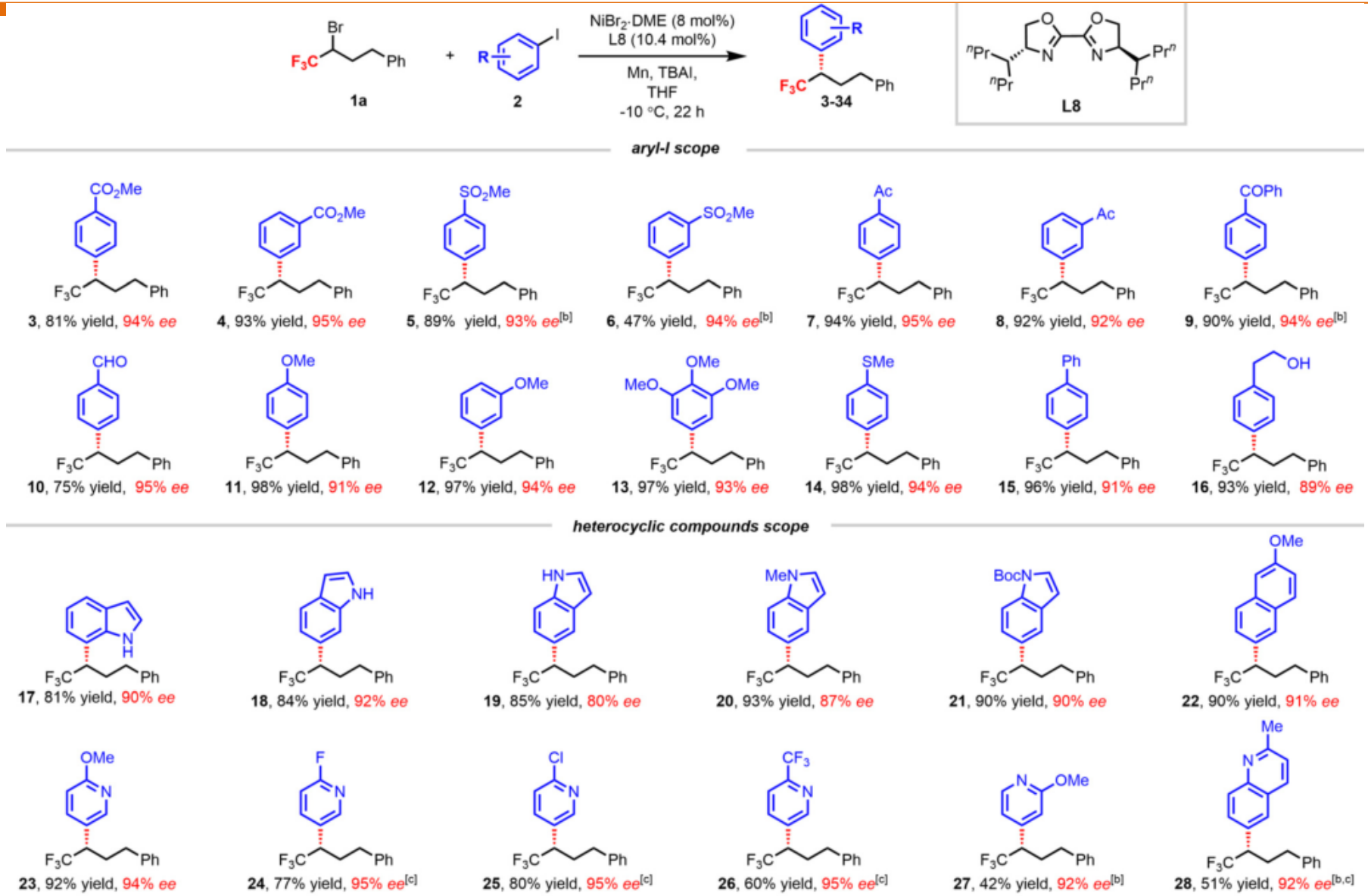
Reaction condition optimization



Entry	Variation from standard conditions[a]	Yield [%][b]	*ee* [%][c]
1	none	83 (85)	94
2	17 °C instead of −10 °C	52	72
3	DME, DMF, DMAc instead of THF	49–54	75–89
4	$FeCl_3$, TMSCl, NaI instead of TBAI	27–33	61–72
5	$NiCl_2$·DME, $NiBr_2$ instead of $NiBr_2$·DME	44–71	92–94
6	w/o $NiBr_2$·DME, L8 or Mn	0	–
7	w/o TBAI	12	–

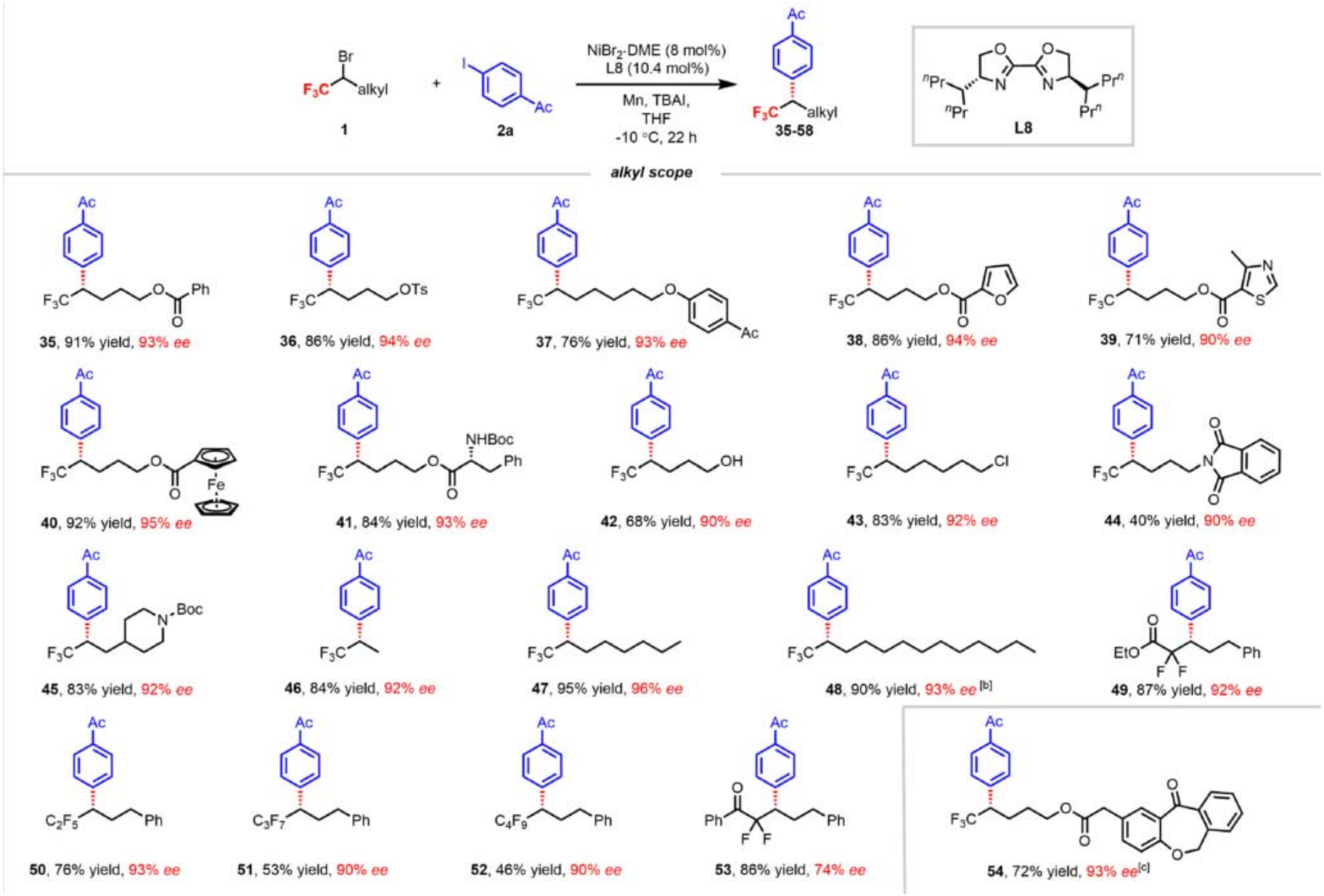
[a] Standard conditions: **1** (0.255 mmol, 1.7 equiv), **2** (0.15 mmol, 1 equiv), $NiBr_2$·DME (8 mol%), **L8** (10.4 mol%), Mn (0.3 mmol, 2 equiv), TBAI (0.075 mmol, 0.5 equiv), THF (0.8 mL), −10 °C, 22 h. [b] Yields determined by crude ^{1}H NMR using 2,5-dimethylfuran as the internal standard. The yield in parentheses is the isolated yield. [c] The *ee* values were determined by HPLC on a chiral stationary phase.

scope of substrates



use of aryl bromides in place of the corresponding iodides could afford slightly higher yields with similar enantioselectivities in some cases (5,6,9,27,28)

scope of substrates



Thanks!