The Yang Research Group
Precise Synthesis Lab at Tongji University

同济大学
TONGJI UNIVERSITY

Group Topic

Han Wei Group’s Research on Iron

reporter: Zhang Jun-Chun

CONTENT

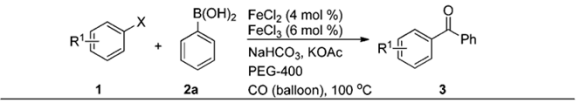
01 Professor Introduction

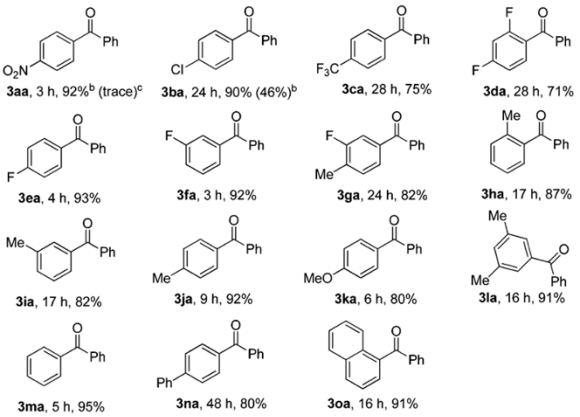
Prof. Han Wei

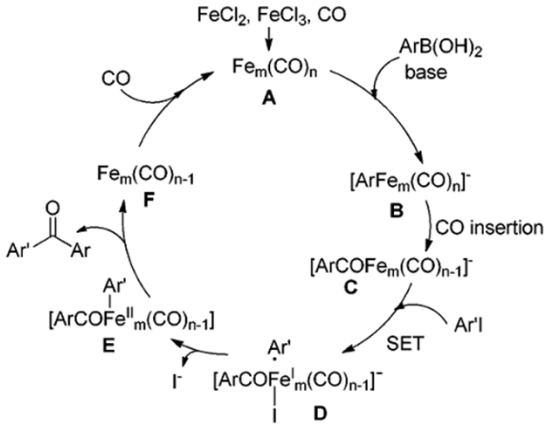
2001-09-01 to 2005-06-30	School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology	Bachelor	
2005-09-01 to 2008-06-30	Dalian University of Technology	Master	Prof. Jin Zi-Lin
2008-10-01 to 2011-06-22	Ludwig-Maximilians-Universität München: Munich, Bavaria, DE	Ph.D.	Prof. Herbert Mayr
2011-10-28 to present	School of Chemistry and Materials Science, Nanjing Normal University	professor	

research interests: Biomimetic Catalysis, Earth-Abundant Metal Catalysis, Activation and Transformation of Inert Bonds, Activation and Functionalization of Small Molecules, Organic Reactions via In Situ Nanocatalysis.

02 Ligand-Free Suzuki Coupling

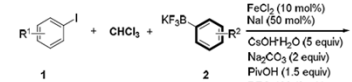


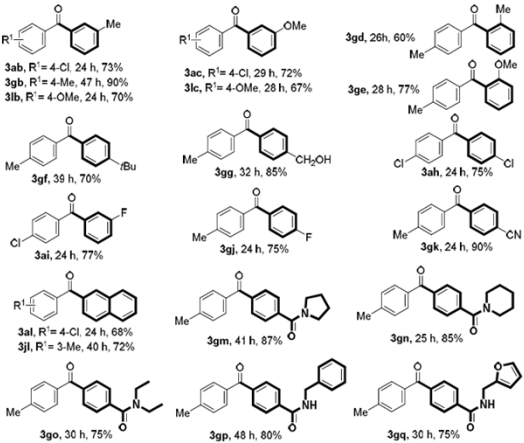


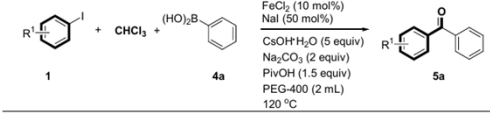


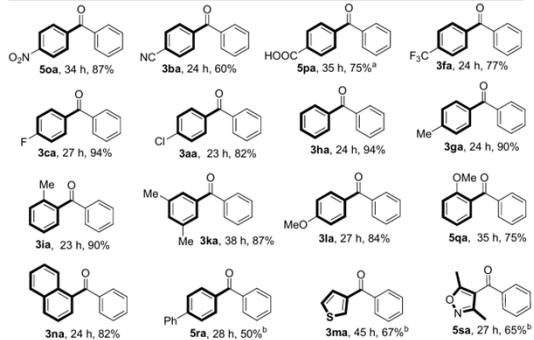
Chem. Commun. **2014**, *50*, 3874.

02 Ligand-Free Suzuki Coupling



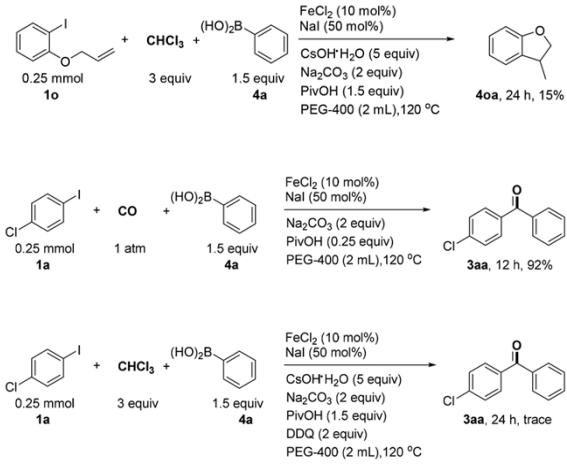


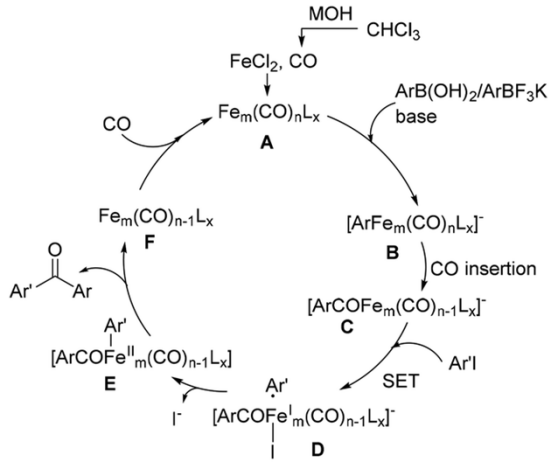




Green Chem. **2016**, *18*, 5782.

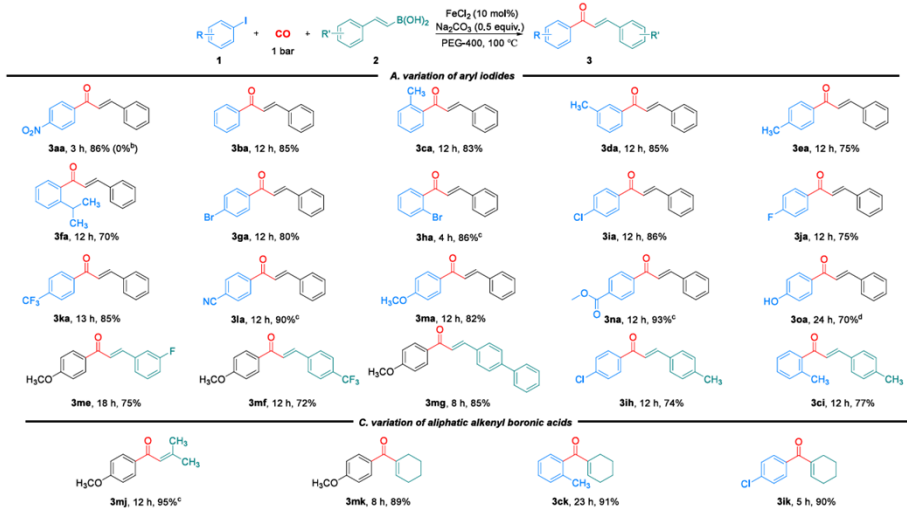
02 Ligand-Free Suzuki Coupling





Green Chem. **2016**, *18*, 5782.

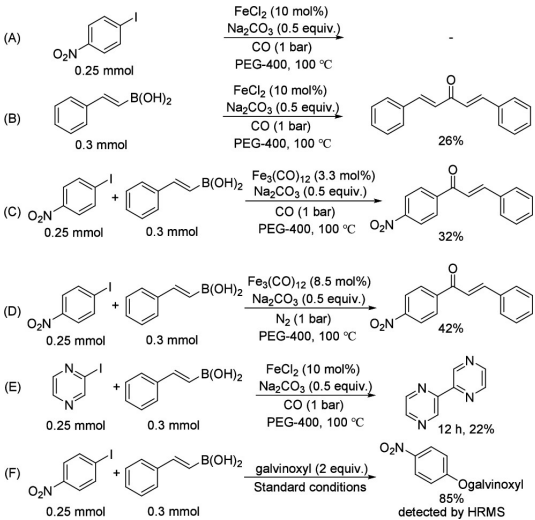
02 Ligand-Free Suzuki Coupling

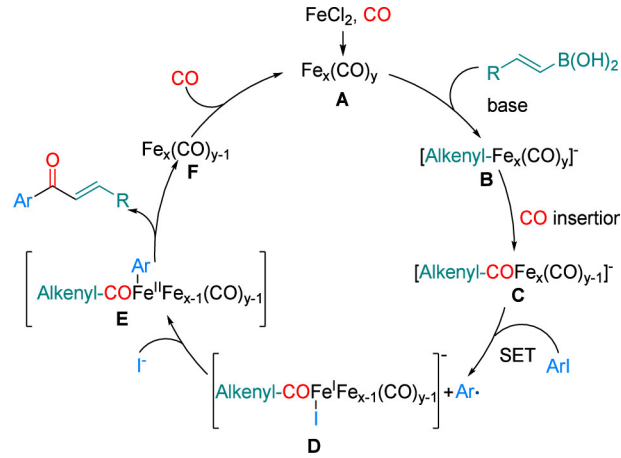


[a]Reaction conditions: **1** (0.25 mmol), **2** (0.3 mmol), CO (1 bar), $FeCl_2$ (10 mol%), Na_2CO_3 (0.5 equiv.), PEG-400 (2.0 mL), yields of isolated products. [b]1-Bromo-4-nitrobenzene was used as a substrate. [c]Na_2CO_3 (0.75 equiv.). [d]Na_2CO_3 (1.75 equiv.), 120 °C.

Org. Lett. **2024**, *26*, 9460.

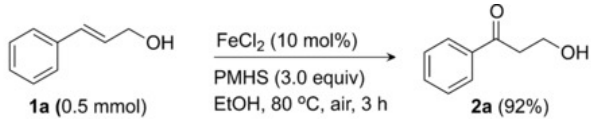
02 Ligand-Free Suzuki Coupling





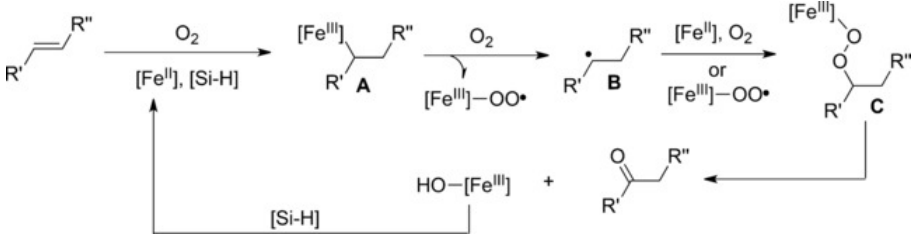
Org. Lett. **2024**, *26*, 9460.

Ligand-Free Oxidation



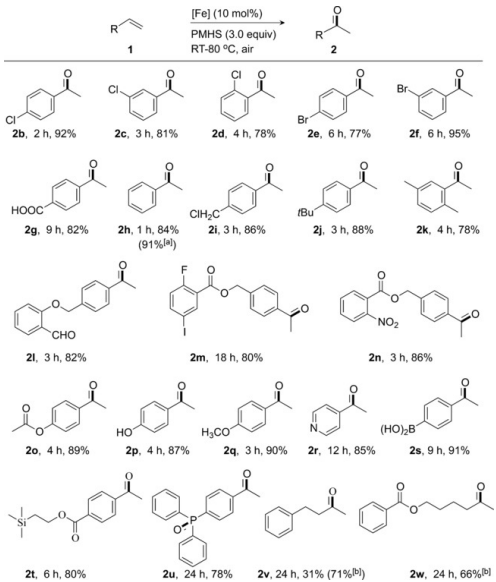
1a (0.5 mmol) **2a** (92%)

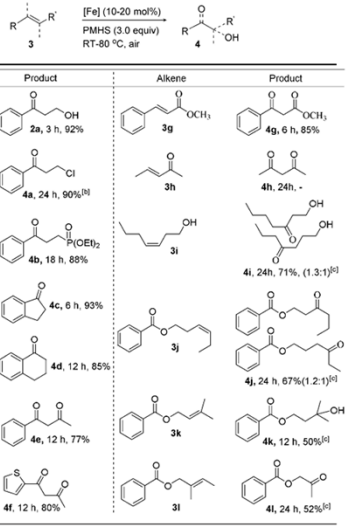
Entry	Deviation from above	Yield [%]	Entry	Deviation from above	Yield [%]
1	$[Fe(acac)_2]$	39	5	Et_3SiH or $PhSiH_3$	trace
2	$[Fe(acac)_3]$	30	6	$(EtO)_3SiH$	58
3	no [Fe]	0	7	$NaBH_4$ instead of PMHS	0
4	no [Si-H]	0	8	$FeCl_2$	94[a]



Angew. Chem., Int. Ed. **2017**, *56*, 12712.

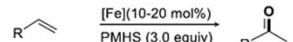
Ligand-Free Oxidation

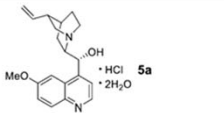
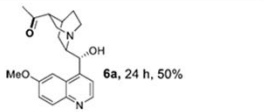
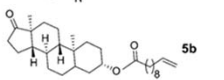
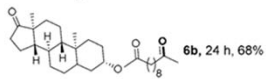
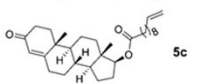
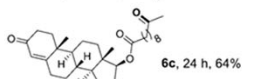
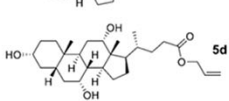
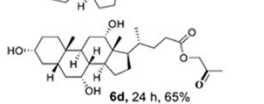
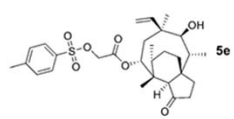
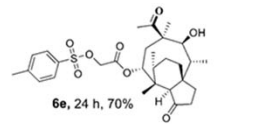
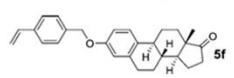
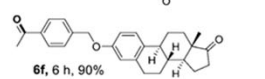
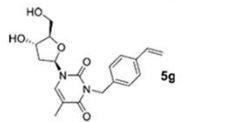
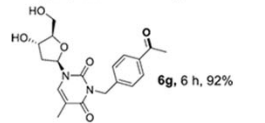
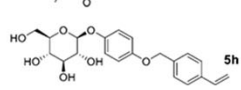
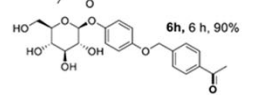




Angew. Chem., Int. Ed. **2017**, *56*, 12712.

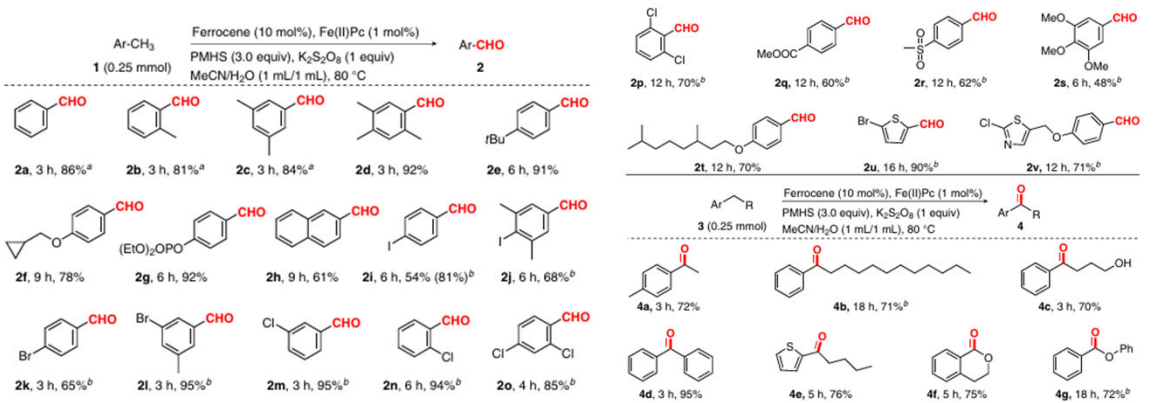
Ligand-Free Oxidation



Entry	Olefin	Product
1	 5a	 6a, 24 h, 50%
2	 5b	 6b, 24 h, 68%
3	 5c	 6c, 24 h, 64%
4[b]	 5d	 6d, 24 h, 65%
5	 5e	 6e, 24 h, 70%
6[c]	 5f	 6f, 6 h, 90%
7[c]	 5g	 6g, 6 h, 92%
8[c]	 5h	 6h, 6 h, 90%

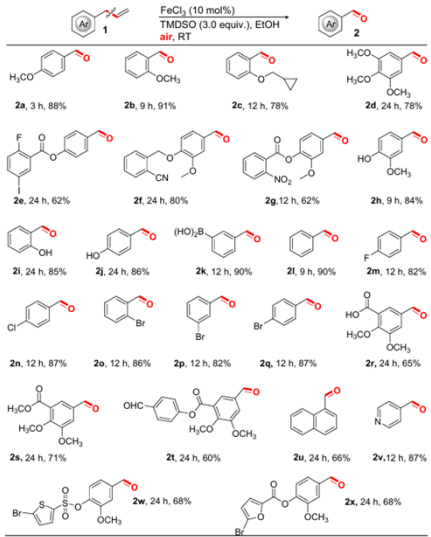
Angew. Chem., Int. Ed. **2017**, *56*, 12712.

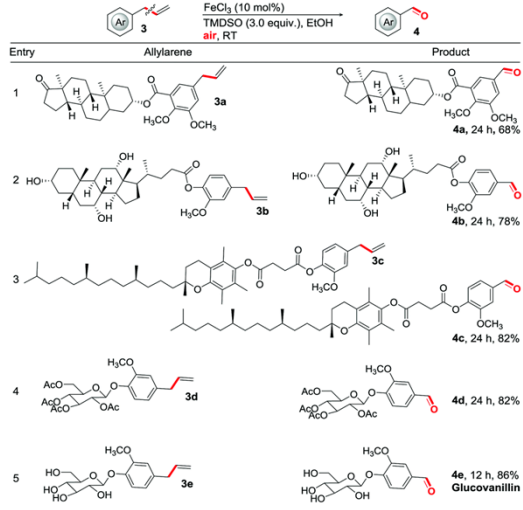
Ligand-Free Oxidation



Nat. Commun. **2019**, *10*, 2425.

Ligand-Free Oxidation





Chem. Commun. **2019**, *55*, 4817.

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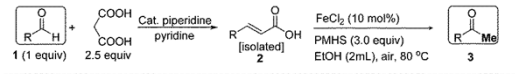

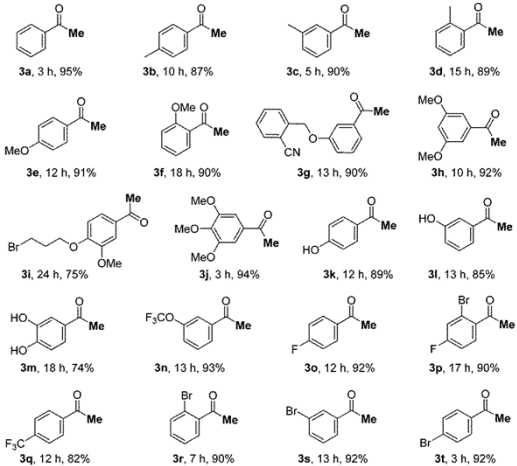

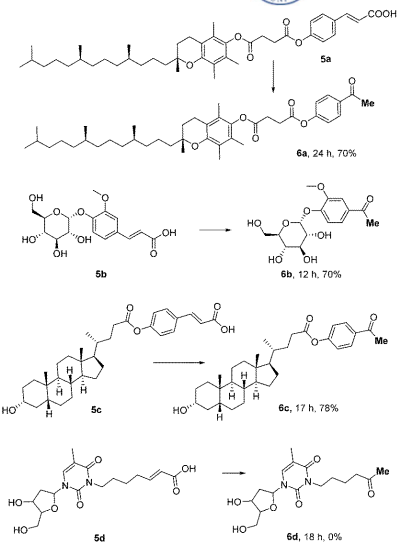

Chem. Commun. **2021**, *57*, 5905.

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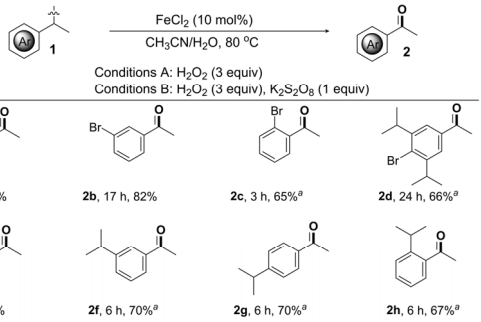

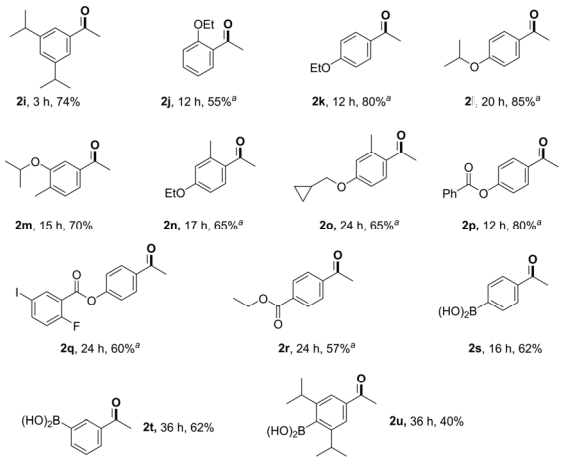

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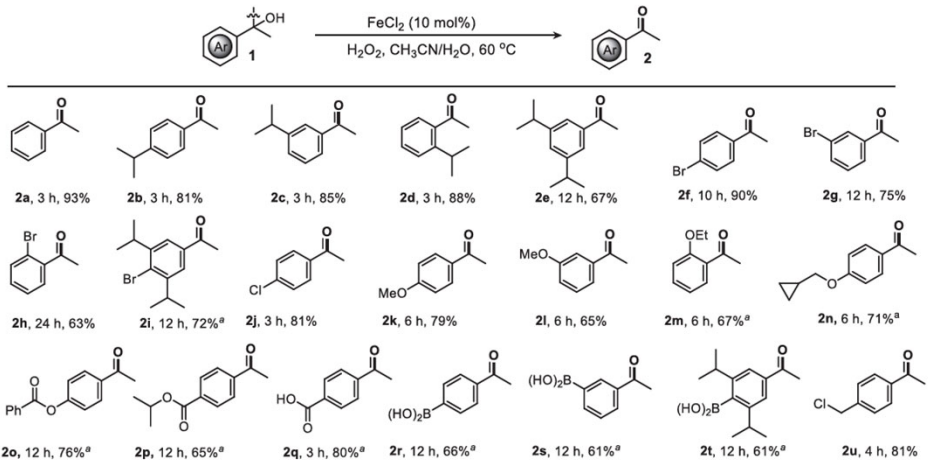
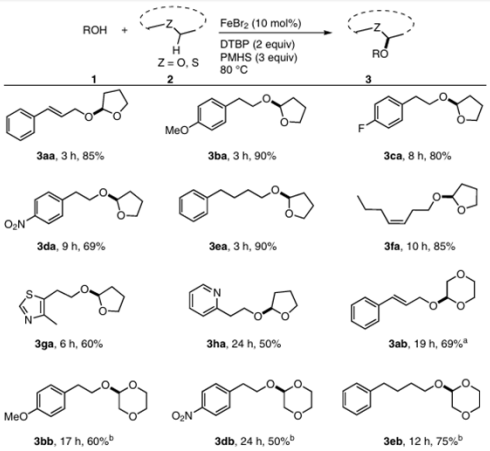
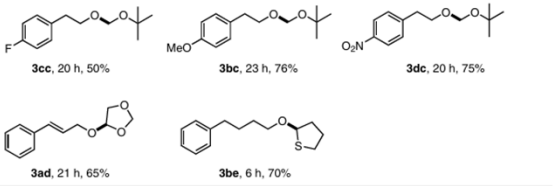
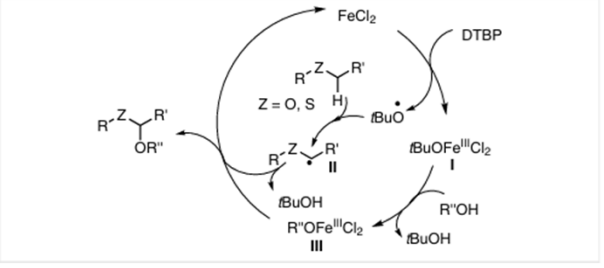


Chin. Chem. Lett. **2024**, *35*, 108835.

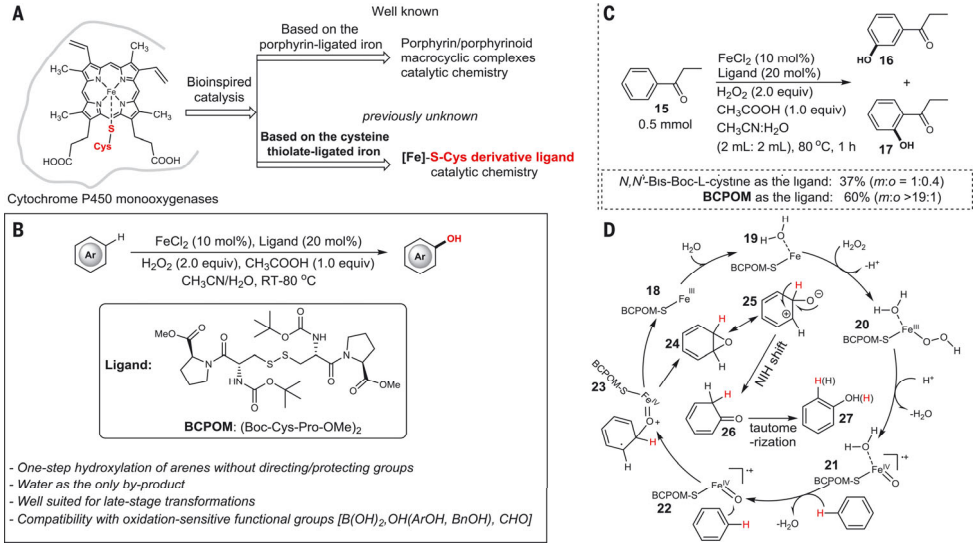
04 Ligand-Free Oxidation Coupling



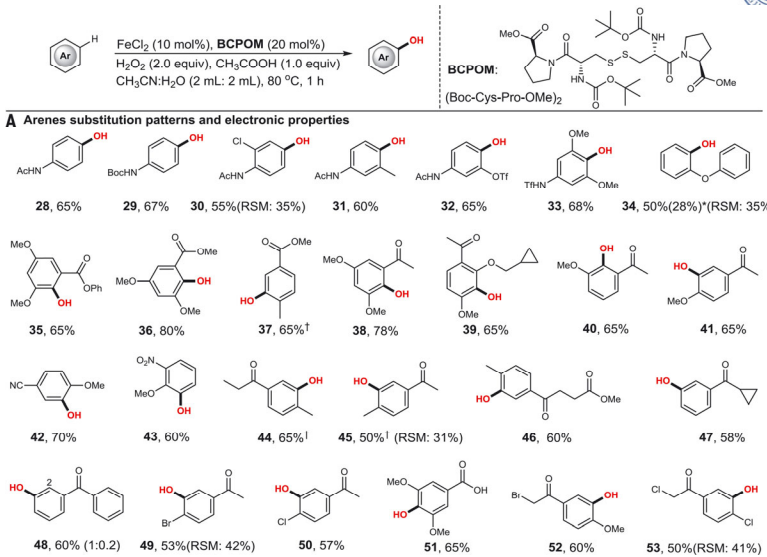




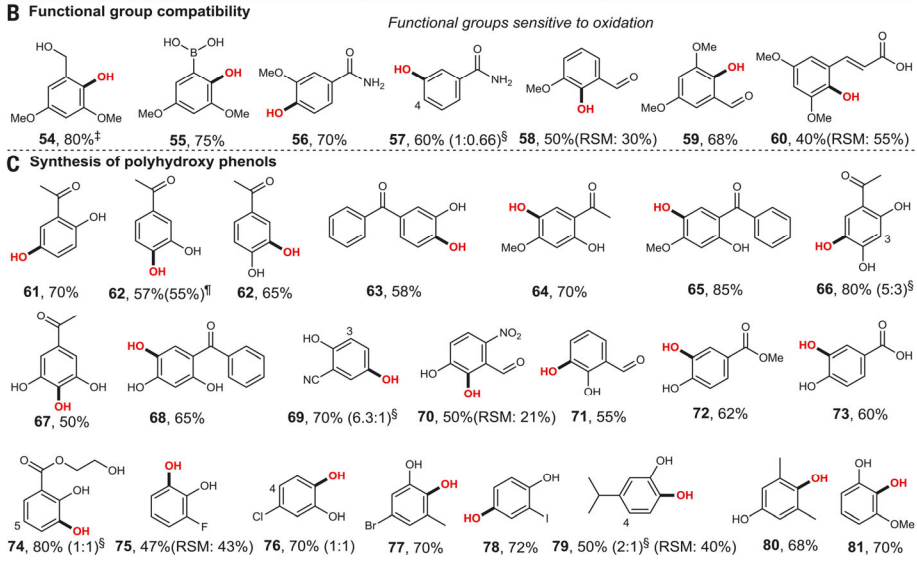
05 Amino Acid Ligand



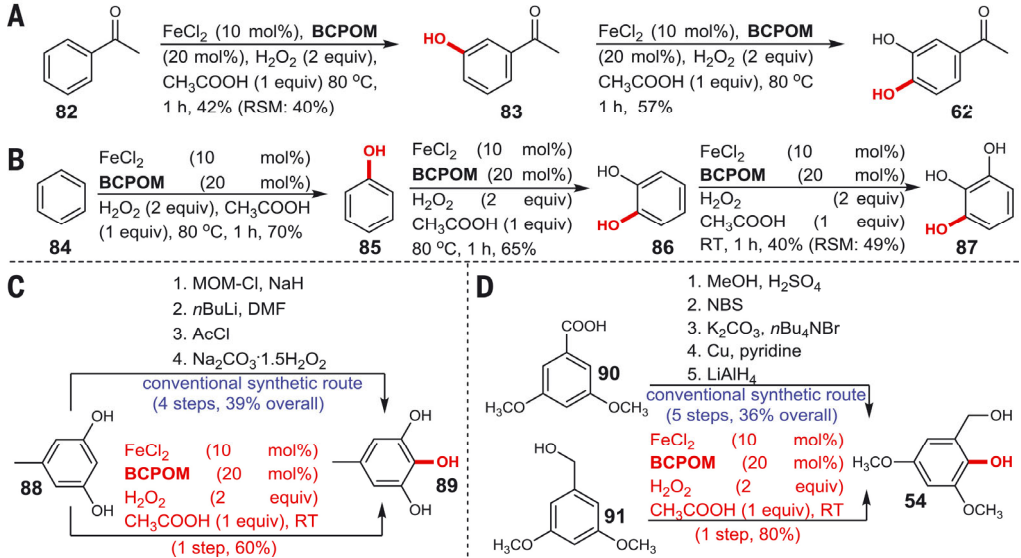
Science **2021**, *374*, 77.



Science **2021**, *374*, 77.

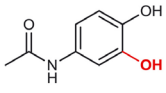


Science **2021**, *374*, 77.

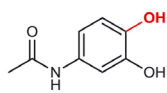


Science **2021**, *374*, 77.

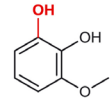
Amino Acid Ligand



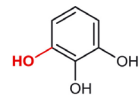
Antipyretic analgesics
HO-Paracetamol
92, 35%(RSM: 60%)



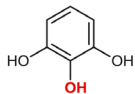
Analgesic
HO-Metacetamol
92, 60%(RSM: 25%)



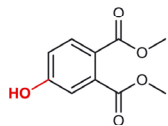
Expectorant
HO-Guaiacol
81, 67%*(RSM: 30%)



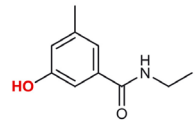
Topical antiseptic
HO-Catechol
87, 40%*(RSM: 49%)



Anthelmintic
HO-Resorcinol
87, 65%(RSM: 35%)



Broad-spectrum insect repellent
HO-Dimethyl phthalate
93, 60%(RSM: 35%)



Broad-spectrum insect repellent
HO-Detamide precursor
94, 75%

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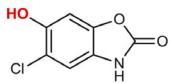
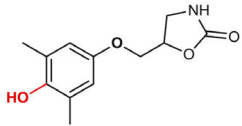
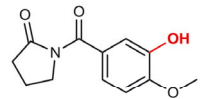


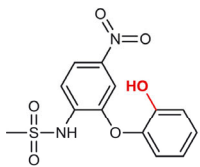
Central skeletal muscle relaxant
HO-Chlorzoxazone
a drug metabolite
95, 70%(RSM: 22%)



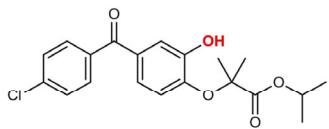
Muscle relaxant and pain reliever
HO-Metaxalone
96, 70%(RSM: 17%)



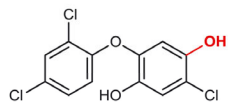
Treatment of cognitive impairment
HO-Aniracetam
97, 40%(RSM: 36%)



Antiinflammatory
HO-Nimesulide
98, 45%(RSM: 49%)



Antihyperlipidemic
HO-Fenofibrate
99, 46%† (RSM: 51%)



Broad-spectrum topical antimicrobial disinfectant
HO-Triclosan
100, 50%(RSM: 30%)

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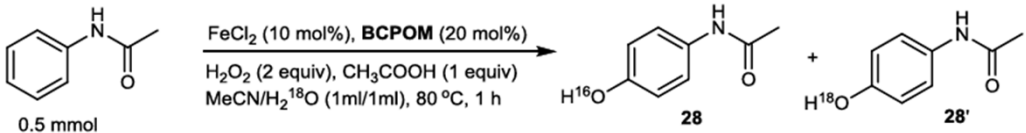
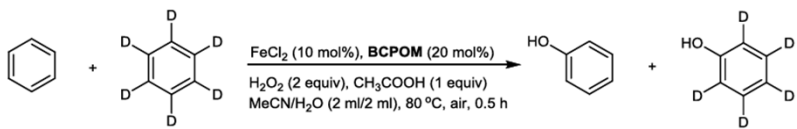


HRMS both found

(2) Intermolecular kinetic isotope effect



58% (**85**:**85'** = 1:1)

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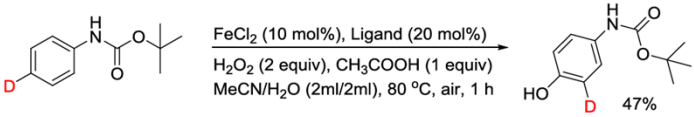
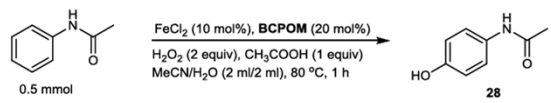
(3) NIH shift experiment



(4) Effect of radical scavengers



No scavenger	65%
TEMPO (3.0 equiv)	0

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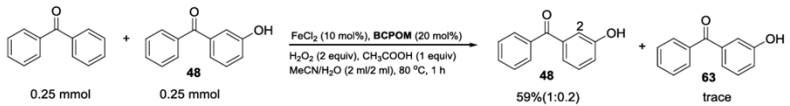
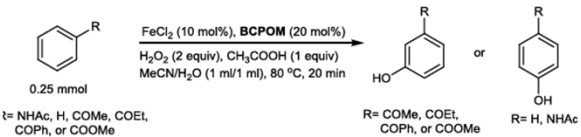
(6) Competitive reaction of benzophenone and **48**





R	σ[a]	Conv. R/Conv. H	log(Conv. R/Conv. H)
p-NHAc	0	1.01	0.007
H	0	1.0	0
m-COPh	0.34	0.71	-0.146
m-COOMe	0.37	0.73	-0.137
m-COMe	0.38	0.67	-0.176
m-COEt	0.38	0.68	-0.167

[a]From C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **91**, 165–195(1991).

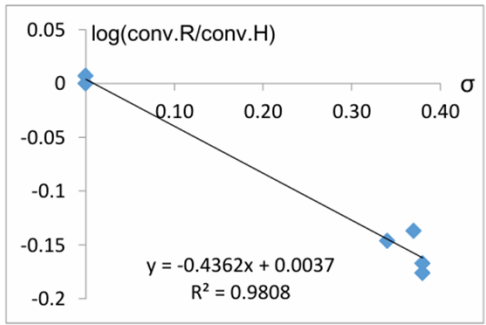


Fig. S2. The Hammett plot of the arene C-H hydroxylation

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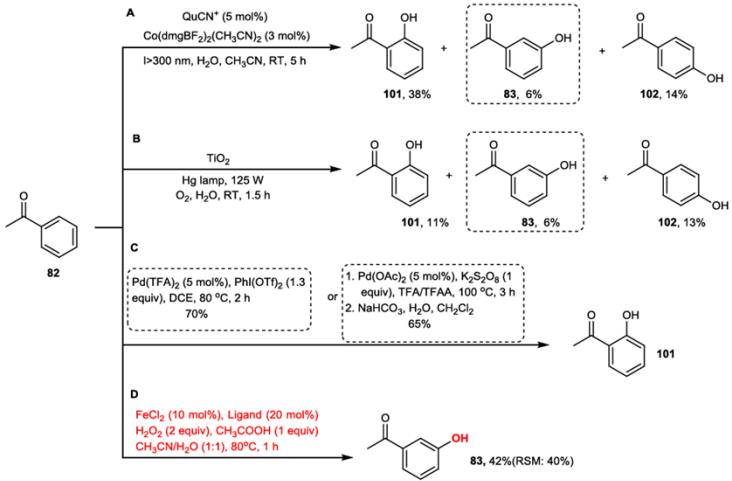
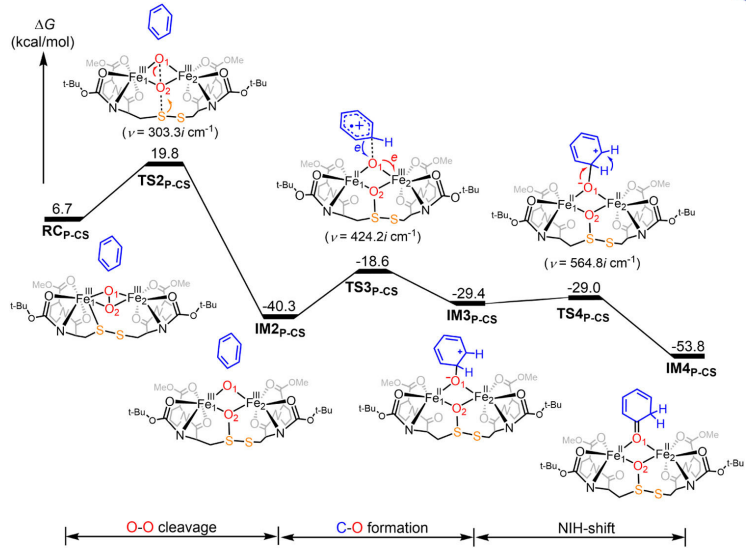
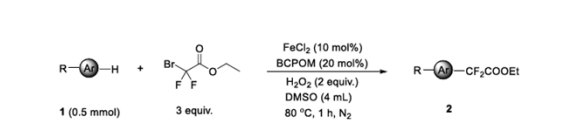
Comparison with methods from literatures

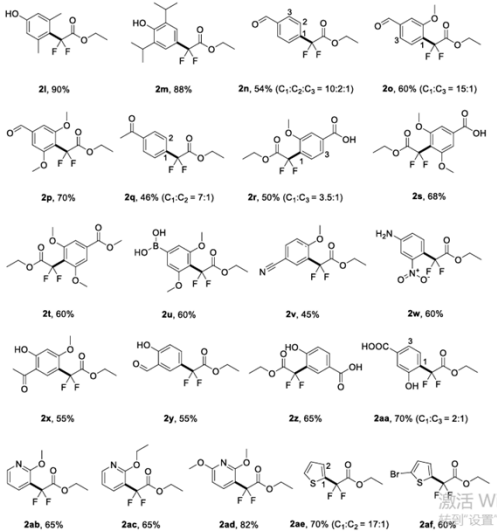


Science **2021**, *374*, 77.

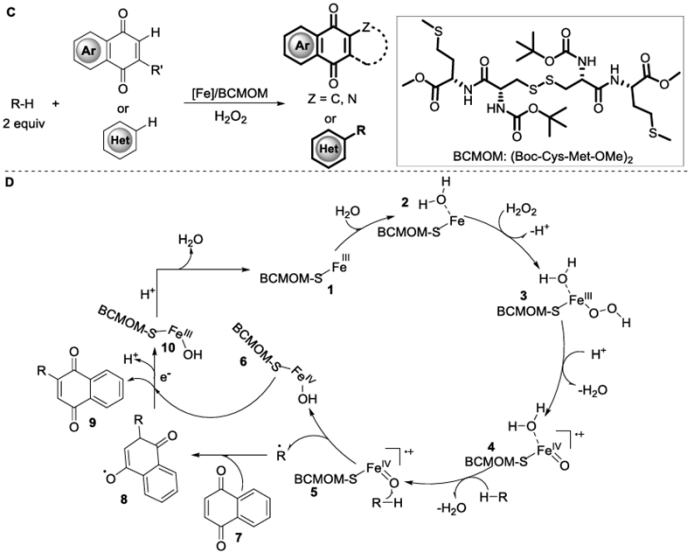


ACS Catal. **2024**, *14*, 17901.

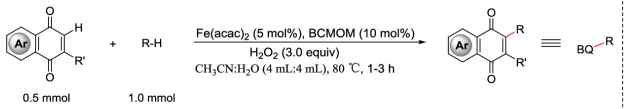




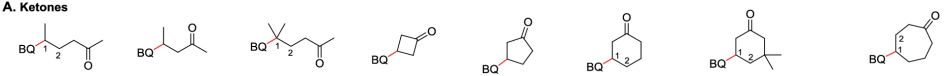
Green Synth. Catal. **2026**, *7*, 114.



Nat. Commun **2025**, *16*, 4673.

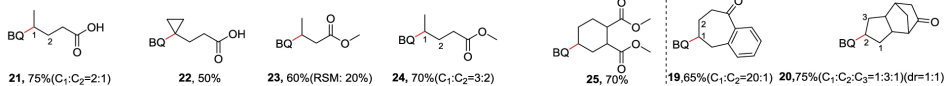


A. Ketones

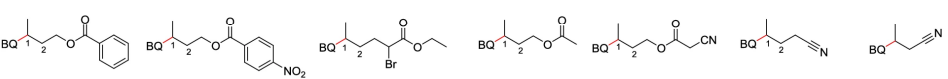


11, 83%(C_1:C_2= 2.3:1) **12,** 60%(RSM: 21%) **13,** 70%(C_1:C_2=1:1) **14,** 32% **15,** 70%(RSM: 11%) **16,** 70%(C_1:C_2=3:1) **17,** 70%(C_1:C_2= 4:1) **18,** 74%(C_1:C_2=1.3:1)

B. Carboxylic acid and carboxylic acid derivatives

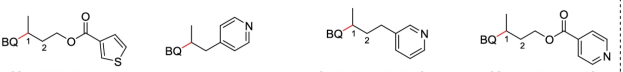


21, 75%(C_1:C_2=2:1) **22,** 50% **23,** 60%(RSM: 20%) **24,** 70%(C_1:C_2=3:2) **25,** 70% **19**,65%(C_1:C_2=20:1) **20**,75%(C_1:C_2:C_3=1:3:1)(dr=1:1)



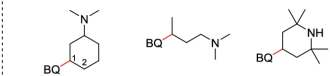
26, 75%(C_1:C_2=3:1) **27,** 72%(C_1:C_2=4:1) **28,** 73%(C_1:C_2=20:1) **29,** 73%(C_1:C_2=4:1) **30,** 75% (C_1:C_2=5:1) **31,** 70%(C_1:C_2=2:1) **32,** 50%(RSM:10%)

C. Heterocycles



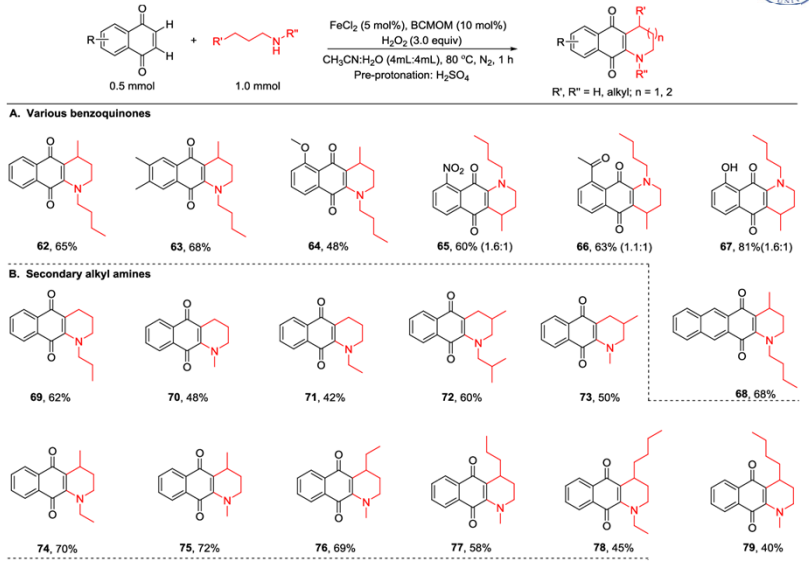
33, 68%(C_1:C_2=3:1) **34,** 60%* **35,** 65%(C_1:C_2=2:1)* **36,** 81%(C_1:C_2=4:1)*

D. Amines and amides

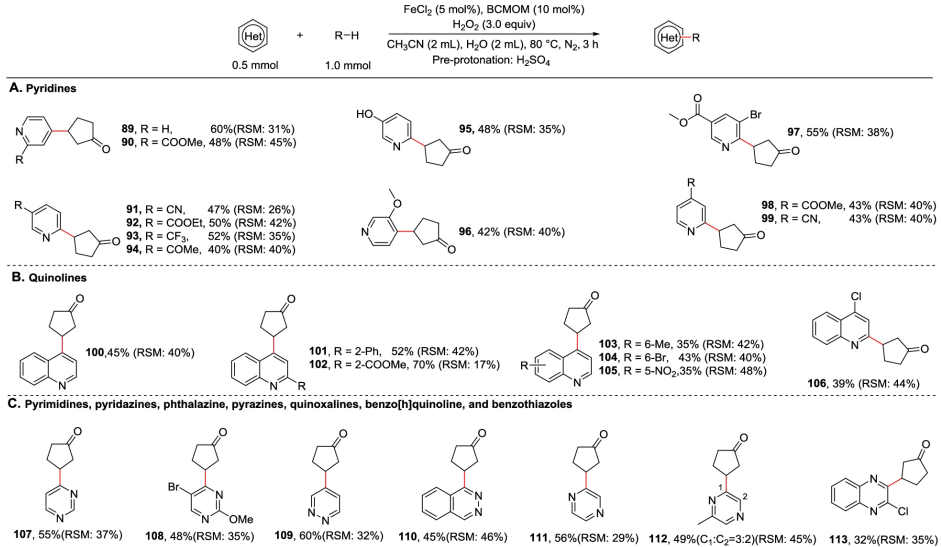


37, 65%(C_1:C_2=3:1)* **38,** 60%* **39,** 75%*†

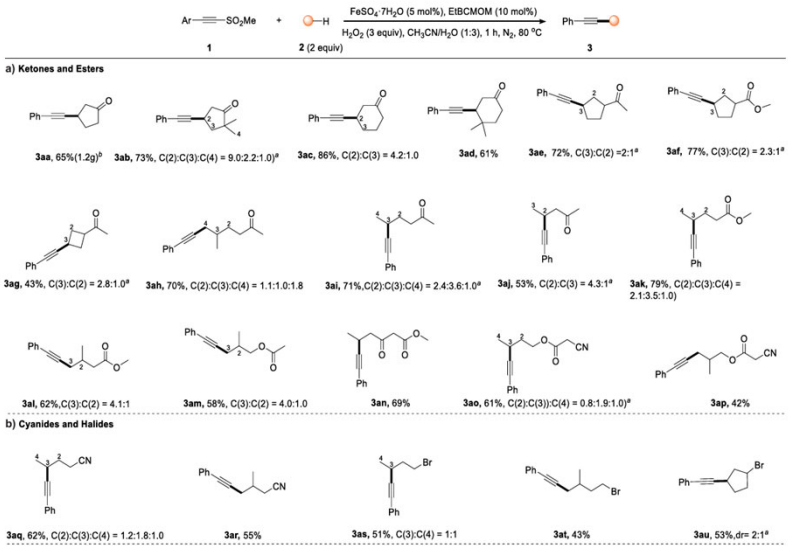
Nat. Commun **2025**, *16*, 4673.



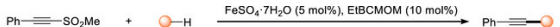
Nat. Commun **2025**, *16*, 4673.

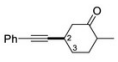


Nat. Commun **2025**, *16*, 4673.



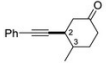
Angew. Chem. Int. Ed. **2026**, *65*, e18736.





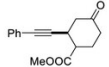
From 2-methylcyclohexanone (Dihydrocarvone derivative)

5aa, 75%, C(2):C(3) = 5.2:1.0[a]



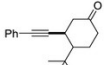
From 4-Methylcyclohexanone (Antitumor drug semustine intermediate)

5ab, 71%, C(2):C(3) = 2.4:1.0



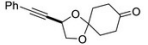
From Methyl 4-ketocyclohexanecarboxylate (Additive in resins and coatings)

5ac, 45%



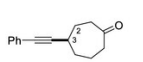
From 4-tert-Butylcyclohexanone (Fragrance)

5ad, 45%



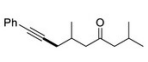
From 1,4-Dioxaspiro[4.5]decan-8-one (Antitumor drug bortezomib intermediate)

5ae, 35%



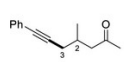
From Cycloheptanone (Antispasmodic tropinone intermediate)

5af, 70%, C(3:C(2) = 1.3:1.0[a]



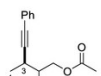
From 2,6-Dimethyl-4-heptanone (Food flavoring)

5ag, 41%



From 4-Methyl-2-pentanone (Dewaxing agent)

5ah, 62%, C(3):C(2) = 4:1

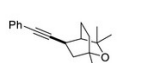


From 2-Ethylbutyl acetate (Flavor and Fragrance)

5ai, 75%, C(3):C(4) = 1.3:1

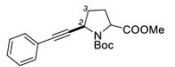
From Norcamphor (Natural product)

5aj, 75%, C(2):C(3) = 1.8:1.0[a]



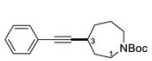
From Eucalyptol (Flavor and Fragrance)

5ak, 79%



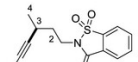
From L-proline

5al, 72%, C(2):C(3) = 2:1, dr=1.4:1



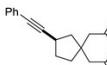
From Azepane (>20 azepane-containing FDA approved drugs)

5am, 53%,C(1):C(3) = 20:1[a]



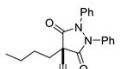
From N-butylsaccharin (Skin penetration enhancer)

5an, 32%, C(3):C(4):C(2) = 7.1:3.7:1



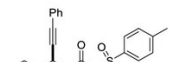
From 3,3-Tetramethyleneglutarimide (Anti-anxiety drug buspirone Intermediate)

5ao, 48%



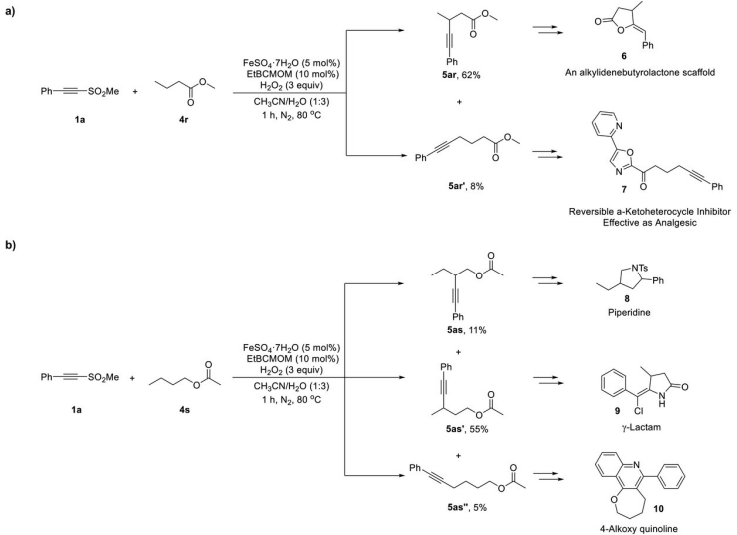
From Butazolidin (Nonsteroidal antiinflammatory drug)

5ap, 56%



From tolbutamide (Oral blood-glucose-lowering drug)

5aq, 32%



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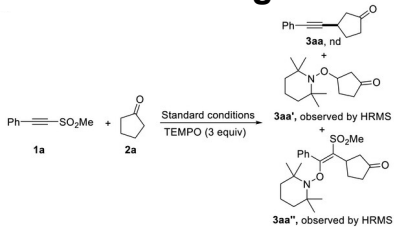
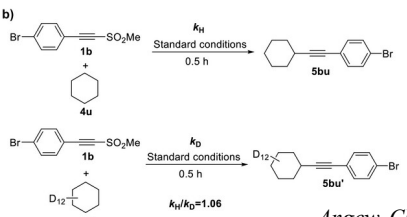
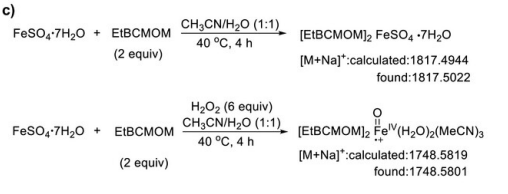
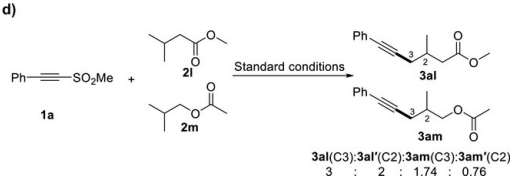
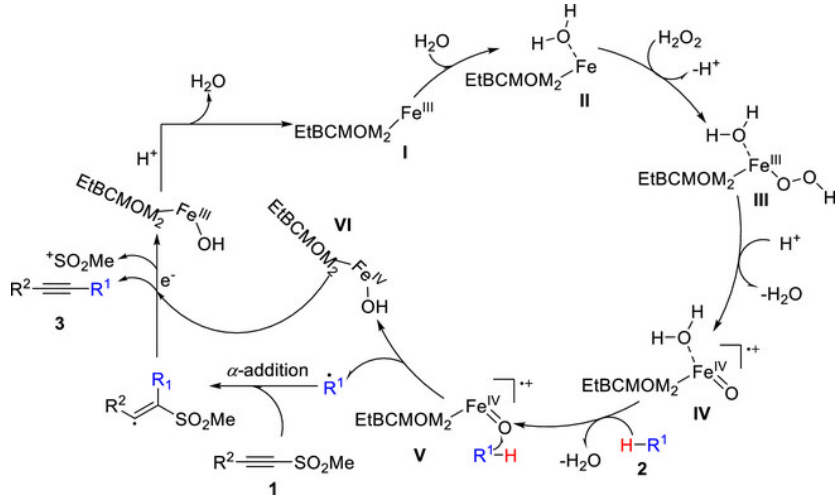

Ph—≡—SO2Me
1a
2a
Standard conditions
TEMPO (3 equiv)
3aa, nd
3aa', observed by HRMS
3aa'', observed by HRMS
Standard conditions
BrCCl3 (3 equiv)
3aa, nd
3aa''', observed by GC-MS


b)
1b
4u
kH
Standard conditions
0.5 h
5bu
4u'
kD
Standard conditions
0.5 h
5bu'
kH/kD=1.06


c)
FeSO4·7H2O + EtBCMOM (2 equiv)
CH3CN/H2O (1:1)
40 °C, 4 h
[EtBCMOM]2 FeSO4 ·7H2O
[M+Na]+:calculated:1817.4944
found:1817.5022
H2O2 (6 equiv)
CH3CN/H2O (1:1)
40 °C, 4 h
[EtBCMOM]2 Fe(IV)(H2O)2(MeCN)3
[M+Na]+:calculated:1748.5819
found:1748.5801
1a + 2a
80°C, 1 h
3aa, 65%


d)
1a
2l
2m
Standard conditions
3al
3am
3al(C3):3al'(C2):3am(C3):3am'(C2)
3 : 2 : 1.74 : 0.76



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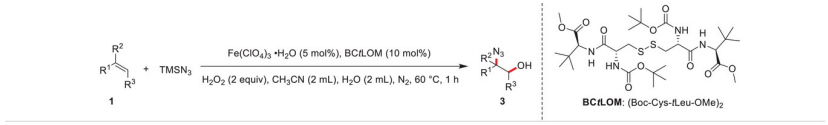

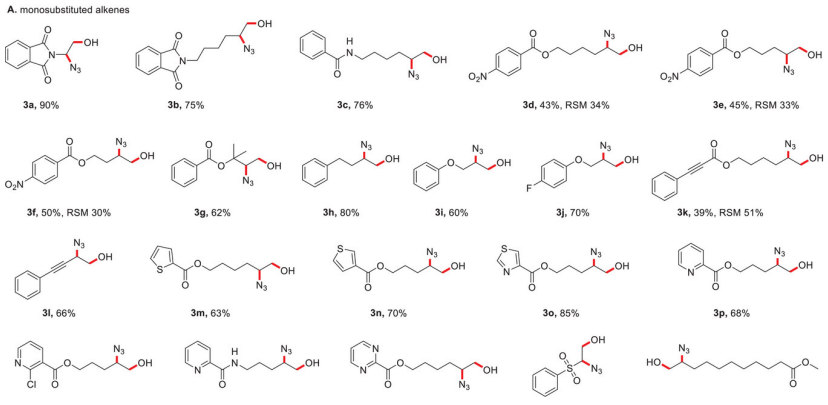

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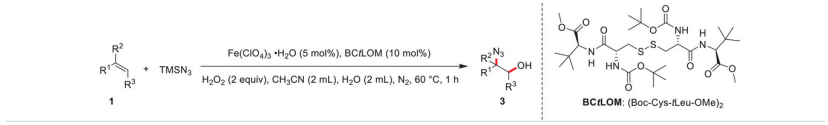

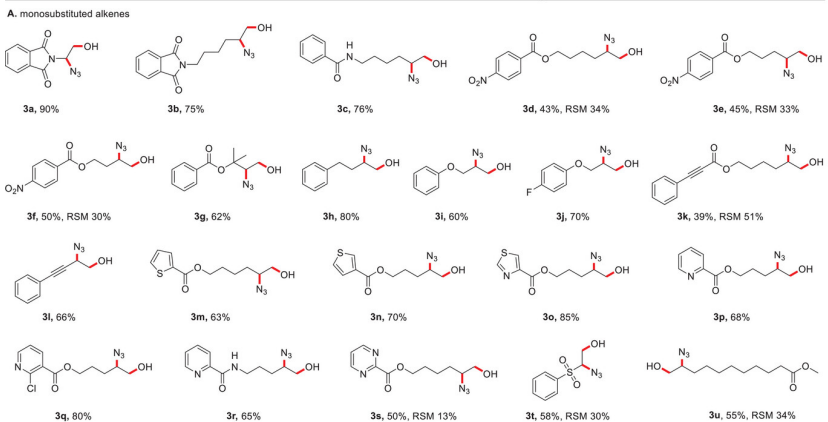

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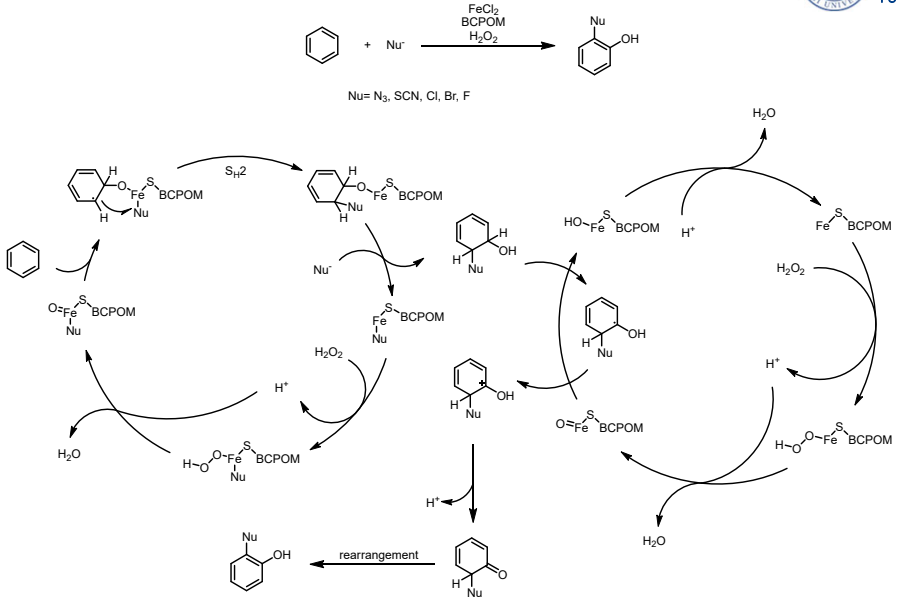
proposal


FeCl2
BCPOM
H2O2
Nu
OH
Nu= N3, SCN, Cl, Br, F
SH2
BCPOM
Nu-
H+
H2O
rearrangement

敬请各位同门批评指正！