The Yang Research Group
Precise Synthesis Lab at Tongji University

Paper Report

王兆彬课题组相关研究介绍

Reporter: Canxiang Liu
Date: 2025.7.4

Zhaobin Wang, Ph. D.

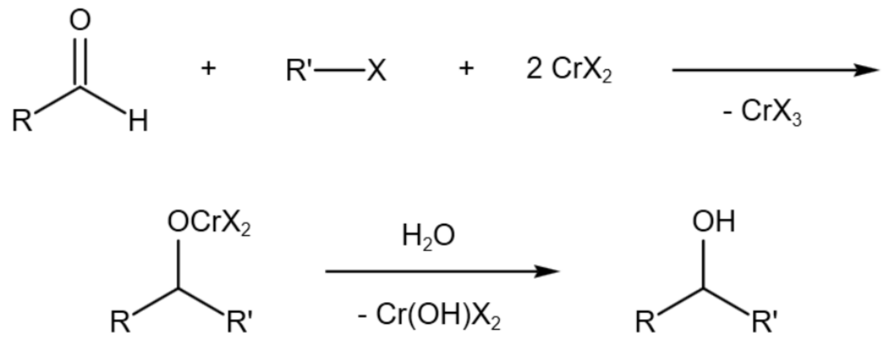
- **Education and research experience**

2011	**B.S.** Nanjing University. Advisor: Prof. Leyong Wang
2015	**Ph.D.** Hong Kong University of Science and Technology Advisor: Prof. Jianwei Sun
2016 – 2019	**Postdoctoral Fellow.** California Institute of Technology. Advisor: Prof. Gregory C. Fu
2019 – Present	**Assistant Professor.** Westlake University

Asymmetric catalytic synthesis

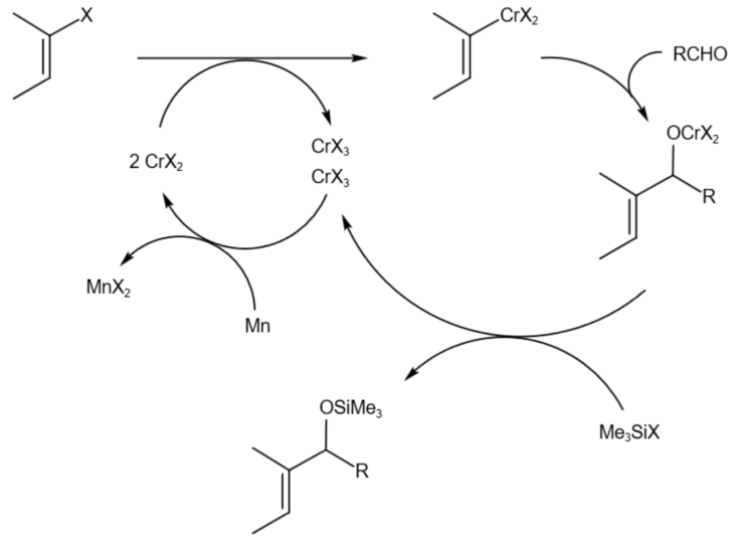
contents

Nozaki-Hiyama-Kishi反应

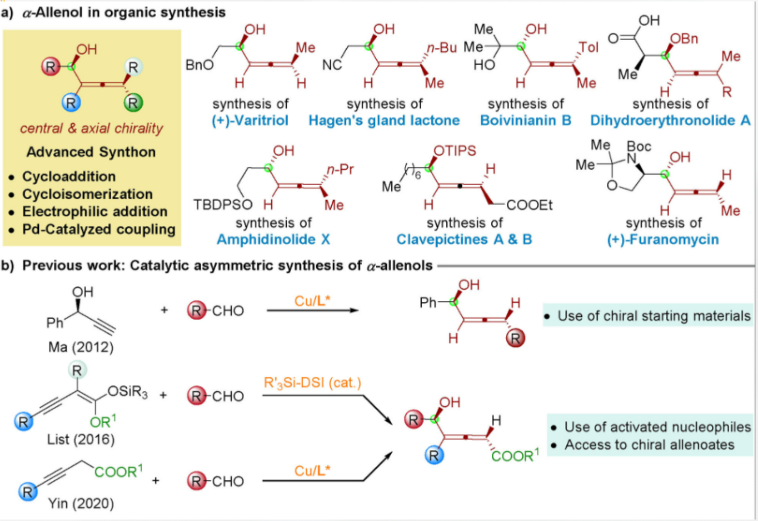


铬诱导下卤代烷和醛进行偶联的氧化还原反应

Nozaki-Hiyama-Kishi反应



Cr Catalysis.铬催化醛与炔丙基卤化物的不对称联烯基化反应

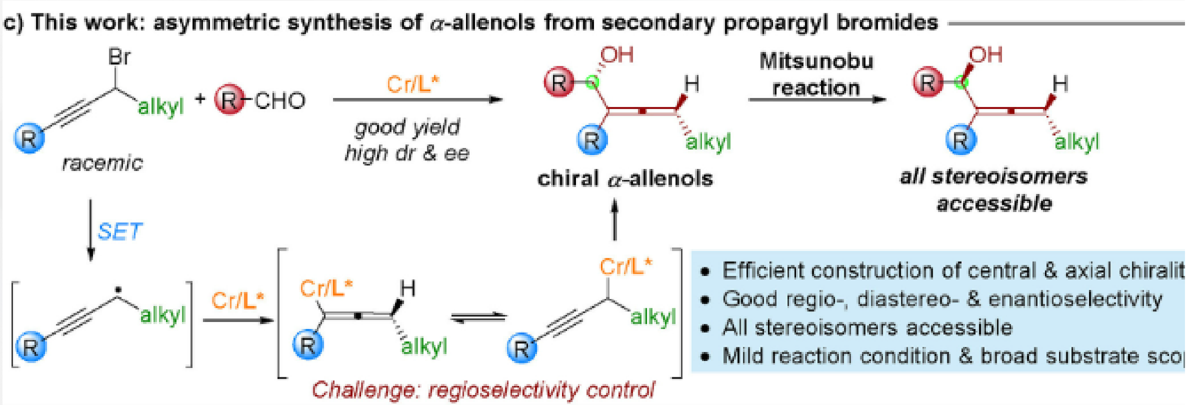


挑战：α-联烯醇分子在特定取代下可以同时具有中心手性和轴向手性。同时高效、立体选择性地控制这两个手性元素（非对映选择性 dr 和对映选择性 ee）是合成化学中的重大难题。

现有方法的局限：传统方法通常依赖手性原料通过手性转移，或者只能控制其中一种手性（中心或轴向），或者需要预先活化的底物（如联烯酸酯）。

Angew. Chem. Int. Ed. **2022**, *61*, e202117114.

Cr Catalysis:铬催化醛与炔丙基卤化物的不对称联烯基化反应



- Efficient construction of central & axial chiralit
- Good regio-, diastereo- & enantioselectivity
- All stereoisomers accessible
- Mild reaction condition & broad substrate sco

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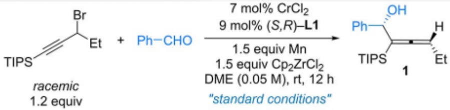
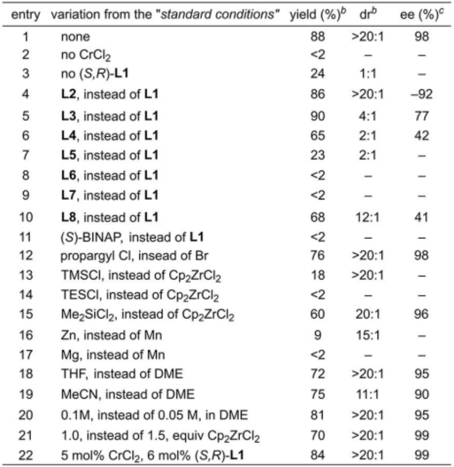
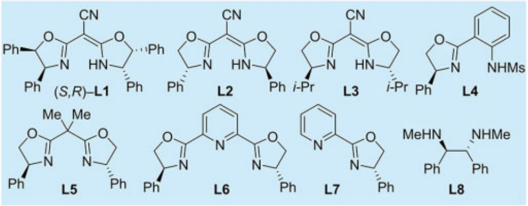
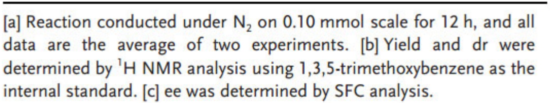




entry	variation from the "*standard conditions*"	yield (%)[b]	dr[b]	ee (%)[c]
1	none	88	>20:1	98
2	no $CrCl_2$	<2	–	–
3	no (*S*,*R*)-**L1**	24	1:1	–
4	**L2**, instead of **L1**	86	>20:1	–92
5	**L3**, instead of **L1**	90	4:1	77
6	**L4**, instead of **L1**	65	2:1	42
7	**L5**, instead of **L1**	23	2:1	–
8	**L6**, instead of **L1**	<2	–	–
9	**L7**, instead of **L1**	<2	–	–
10	**L8**, instead of **L1**	68	12:1	41
11	(*S*)-BINAP, instead of **L1**	<2	–	–
12	propargyl Cl, insead of Br	76	>20:1	98
13	TMSCl, instead of Cp_2ZrCl_2	18	>20:1	–
14	TESCl, instead of Cp_2ZrCl_2	<2	–	–
15	Me_2SiCl_2, instead of Cp_2ZrCl_2	60	20:1	96
16	Zn, instead of Mn	9	15:1	–
17	Mg, instead of Mn	<2	–	–
18	THF, instead of DME	72	>20:1	95
19	MeCN, instead of DME	75	11:1	90
20	0.1M, instead of 0.05 M, in DME	81	>20:1	95
21	1.0, instead of 1.5, equiv Cp_2ZrCl_2	70	>20:1	99
22	5 mol% $CrCl_2$, 6 mol% (*S*,*R*)-**L1**	84	>20:1	99





[a] Reaction conducted under N_2 on 0.10 mmol scale for 12 h, and all data are the average of two experiments. [b] Yield and dr were determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. [c] ee was determined by SFC analysis.

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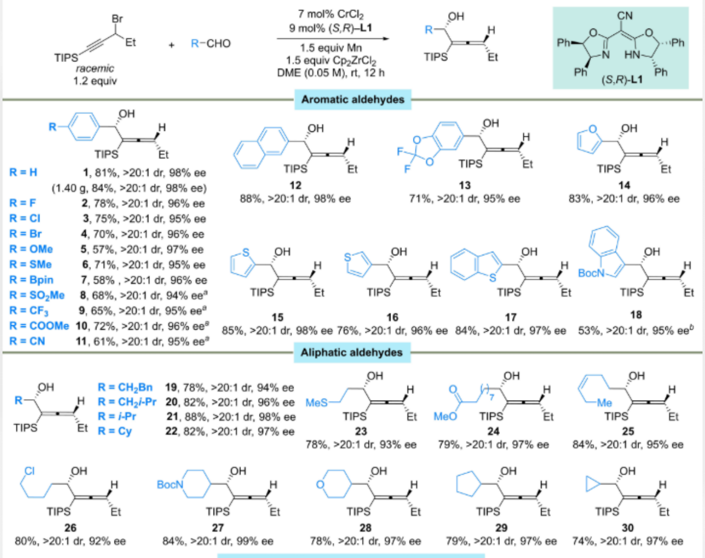
Cr Catalysis:铬催化醛与炔丙基卤化物的不对称联烯基化反应



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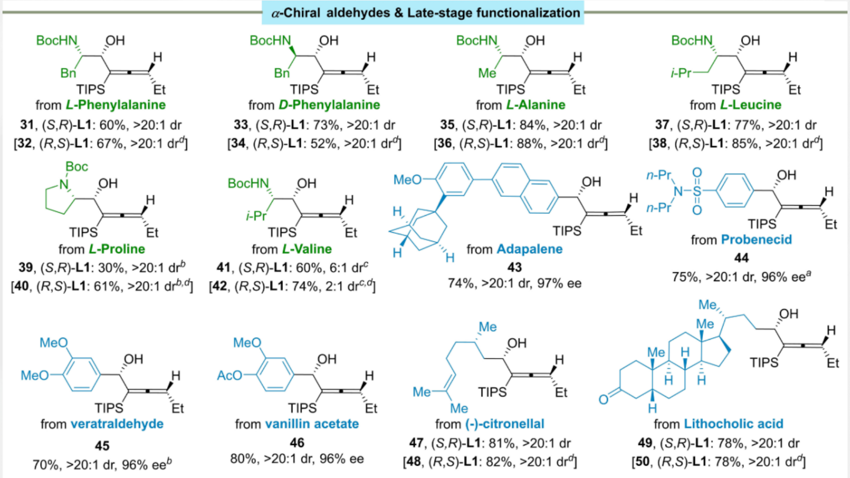

Figure 2. Substrate scope for aldehydes. Reactions were conducted on a 0.4 mmol scale; yields were determined after column chromatography. The dr values were determined by ^{1}H NMR analysis of the crude product. [a] 10 mol% $CrCl_2$, 12 mol% **L1**, 40°C. [b] TMSCl (1.5 equiv) instead of Cp_2ZrCl_2, THF (8.0 mL) instead of DME. [c] 2.2 equiv. propargyl bromide was used. [d] The major stereoisomer is not the one depicted.

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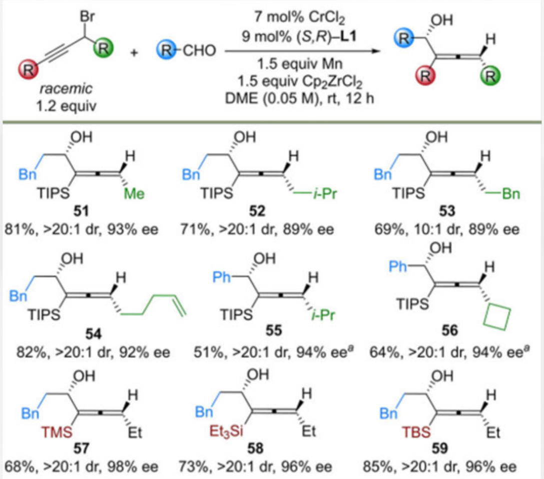

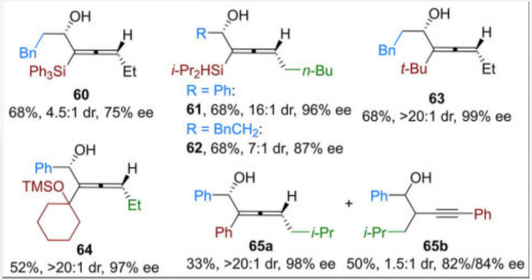

Figure 3. Substrate scope for propargyl bromides. Reactions were conducted on a 0.4 mmol scale; yields were determined after column chromatography. The dr values were determined by ^1H NMR analysis of the crude product. [a] TMSCl (1.5 equiv) instead of Cp_2ZrCl_2, THF (8.0 mL) instead of DME.

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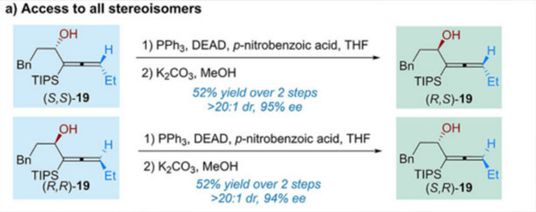

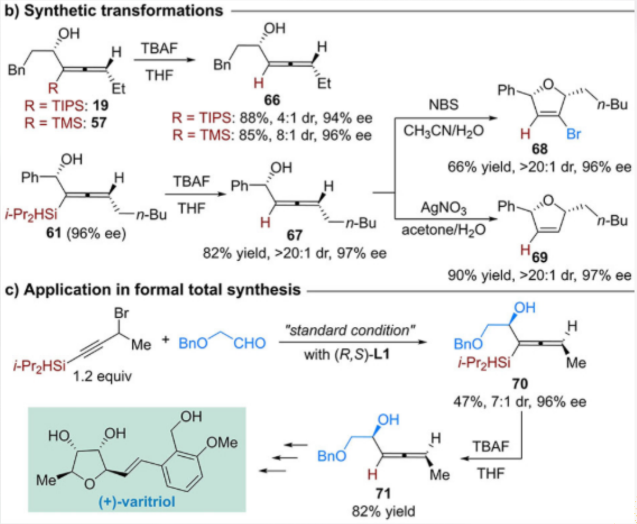

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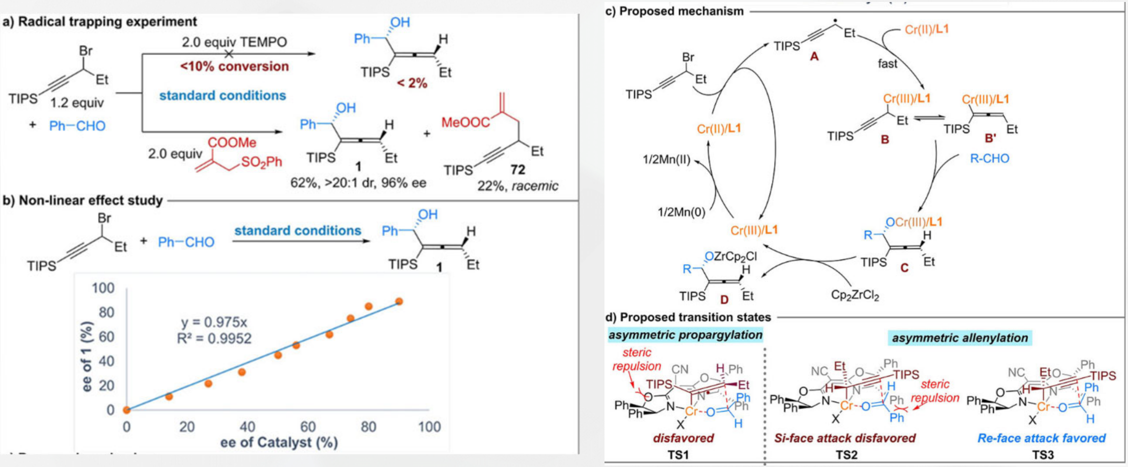
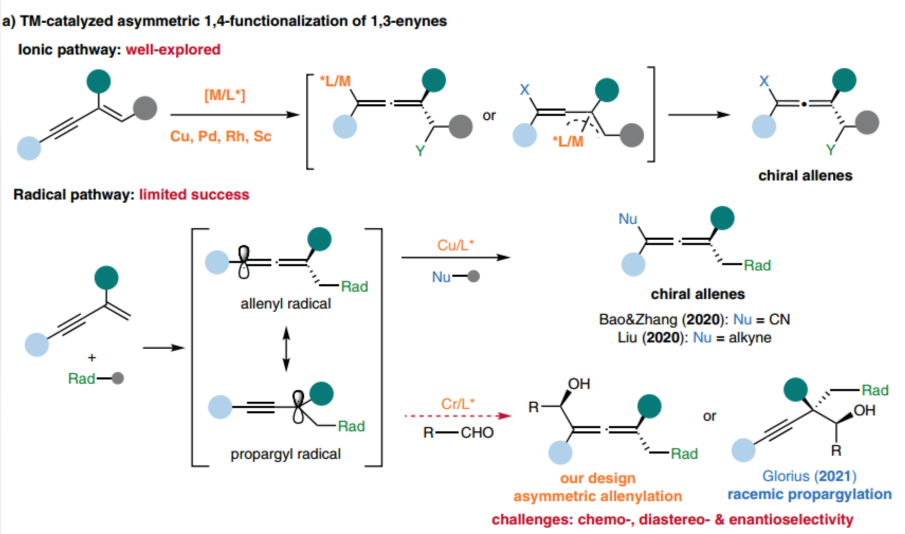


Angew. Chem. Int. Ed. **2022**, *61*, e202117114.

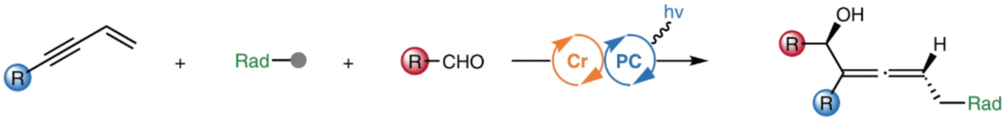
Cr Catalysis.光氧化还原/铬催化实现1,3-烯炔的不对称1,4-官能团化



Nat. Commun. **2022**, *13*, 3804.

Cr Catalysis:光氧化还原/铬催化实现1,3-烯炔的不对称1,4-官能团化

b) This work: Radical 1,4-functionalization of 1,3-enynes by dual photoredox and Cr catalysis



chiral α-allenols

- **Merging photoredox and Cr catalysis**
- **Control both central and axial chirality**
- **Radical 1,4-dialkylation of 1,3-enynes**
- **Good regio-, diastereo- & enantioselectivity**
- **Mild reaction condition & broad substrate scope**
- **Efficient access to valuable chiral a-allenols**

◆ 控制1,4-官能团化相对于1,2-官能团化的区域选择性;

◆ 选择合适的自由基前体和光催化剂以维持催化循环;

◆ 抑制由活性自由基中间体或有机铬配合物快速发生的副反应。

◆ 传统的铬催化NHK反应需要化学计量的还原剂和强路易斯酸,

且氧化还原中性、光催化的不对称NHK变体非常有限(仅限于烯丙基化)。

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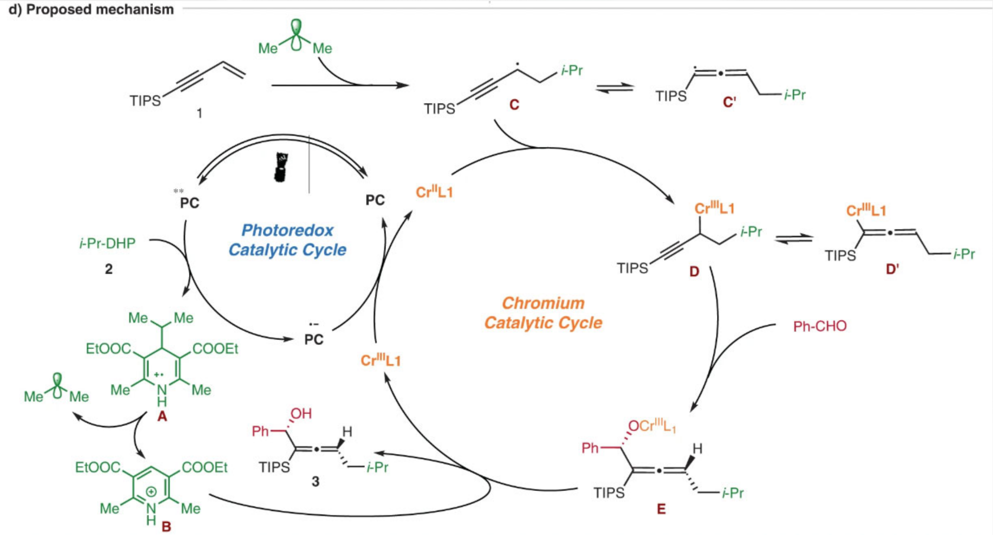

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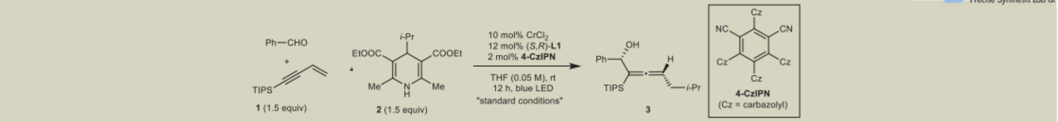
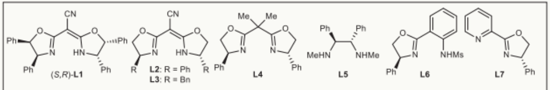


Entry	Variation from "standard conditions"	Yield[a] [%]	dr[b]	ee[c] [%]
1	None	>95	20:1	94
2	Without $CrCl_2$	<2	-	-
3	Without **4-CzIPN**	<2	-	-
4	Without blue LED	<2	-	-
5	**L2**, instead of (*S*,*R*)-**L1**	>95	20:1	92
6	**L3**, instead of (*S*,*R*)-**L1**	84	3.1:1	47
7	**L4**, instead of (*S*,*R*)-**L1**	68	1.6:1	19
8	**L5**, instead of (*S*,*R*)-**L1**	52	5.5:1	34
9[d]	**L6**, instead of (*S*,*R*)-**L1**	71	1.8:1	46
10	**L7**, instead of (*S*,*R*)-**L1**	79	2.8:1	93
11	DME, instead of THF	72	10:1	94
12	MeCN, instead of THF	85	20:1	95
13	EtOAc, instead of THF	>95	20:1	94
14	$[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$ instead of 4-CzIPN	>95	11:1	88
15	5 mol% $CrCl_2$, 6 mol% (*S*,*R*)-**L1**	74	20:1	94
16	0.1 M, instead of 0.05 M, in THF	>95	12:1	93
17	1.2, instead of 1.5, equiv **1** and **2**	80	20:1	94
18	1.2, instead of 1.5, equiv **1**	90	18:1	93
19	1.0 equiv H_2O was added	<2	-	-
20	1 mL air (added via syringe)	55	14:1	87



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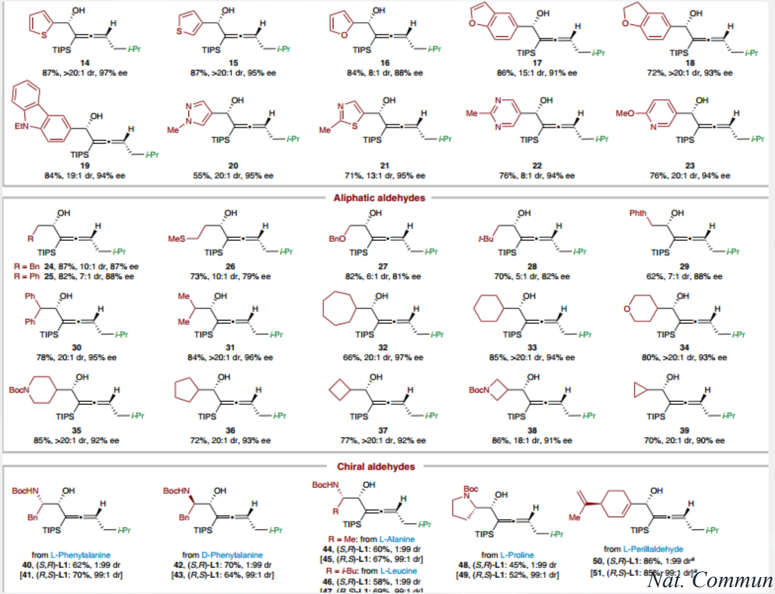

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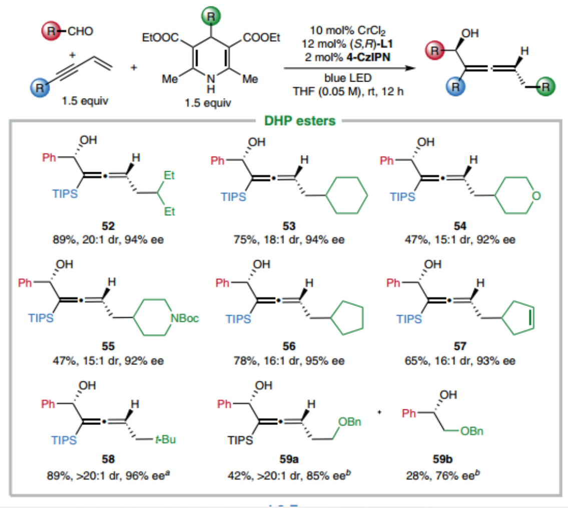

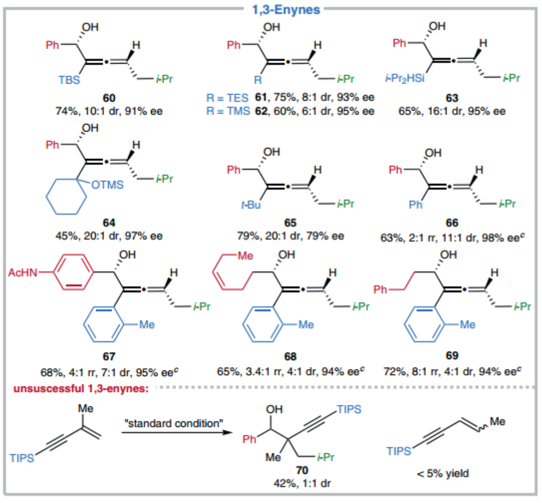

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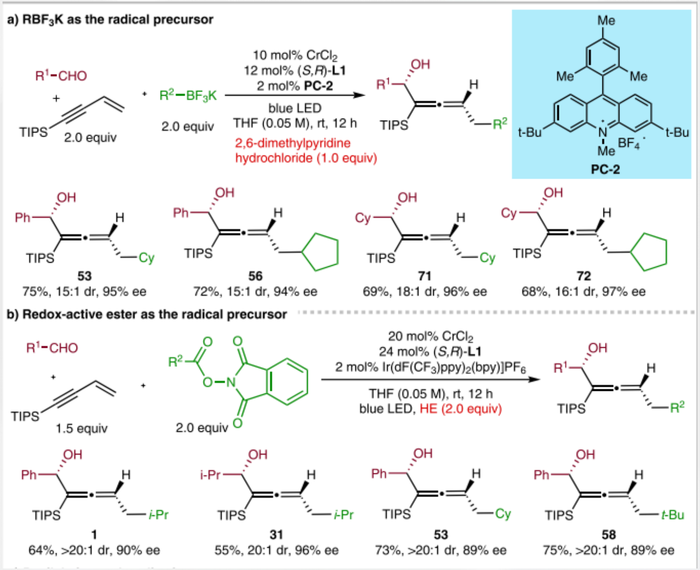
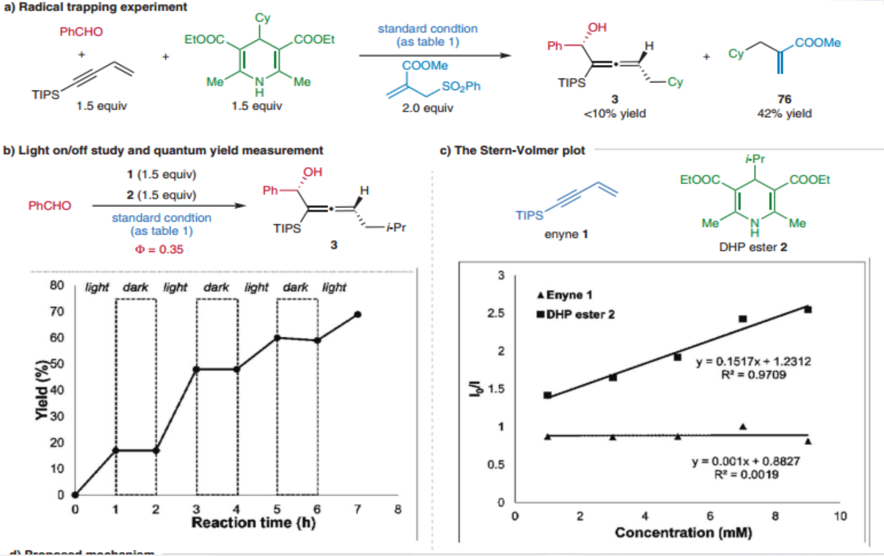


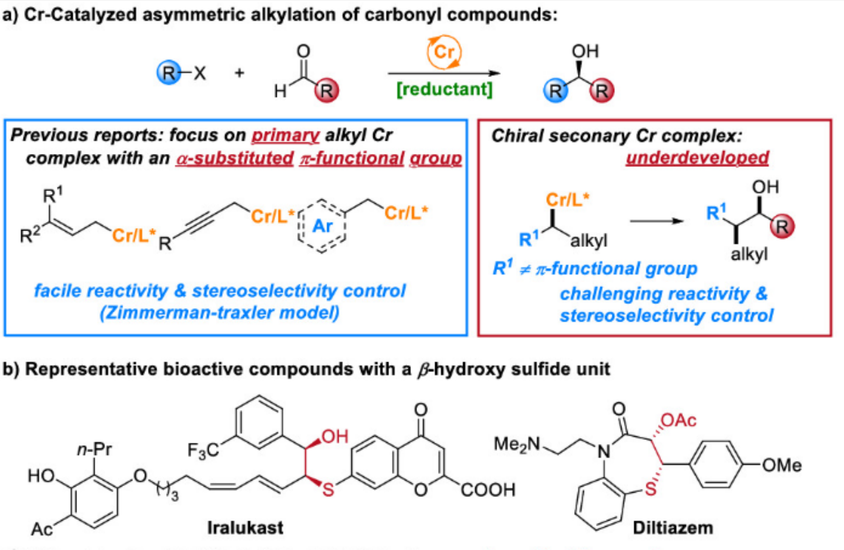
Nat. Commun. **2022**, *13*, 3804.

Cr Catalysis: 光氧化还原/铬催化实现1, 3-烯炔的不对称1, 4-官能团化



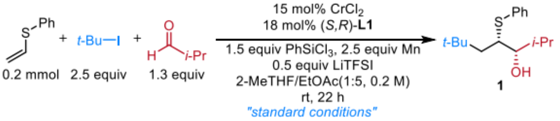
Nat. Commun. **2022**, *13*, 3804.

Cr Catalysis:铬催化的β-羟基硫醚和硒醚的非对映选择性合成

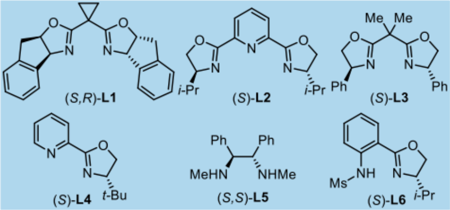


ACS Catal. **2022**, *12*, 11152.

*Cr Catalysis:*铬催化的β-羟基硫醚和硒醚的非对映选择性合成



entry	variation from the *"standard conditions"*	yield [%][a]	ee [%][b]	dr[a]
1	none	85	98	>20:1
2	no $CrCl_2$	<2	–	–
3	no **L1**	55	–	5:1
4	no LiTFSI	45	98	8:1
5	**L2**, instead of **L1**	<5	–	–
6	**L3**, instead of **L1**	26	89	1.5:1
7	**L4**, instead of **L1**	19	10	1:1
8	**L5**, instead of **L1**	35	0	2.5:1
9	**L6**, instead of **L1**	<5	–	–
10	Zn, instead of Mn	28	76	3:1
11	TMSCl, instead of $PhSiCl_3$	50	50	6:1
12	2-MeTHF as solvent	66	98	15:1
13	EtOAc as solvent	81	97	>20:1
14	0.1 M, instead of 0.2 M	76	97	>20:1
15	1.0, instead of 1.3, equiv of aldehyde	82	98	11:1
16	10 mol% $CrCl_2$, 12 mol% **L1**	84	95	>20:1
17	12 h, instead of 20 h	82	97	>20:1
18	1.0 ml air, added *via* syringe to the 4 mL vial	80	98	13:1
19	1.0 equiv of H_2O was added	10	89	2:1



[a] Yield and dr were determined via ^1H NMR analysis with CH_2Br_2 as the internal standard, and all data are the average of two experiments. [b] Ee was determined by SFC analysis.

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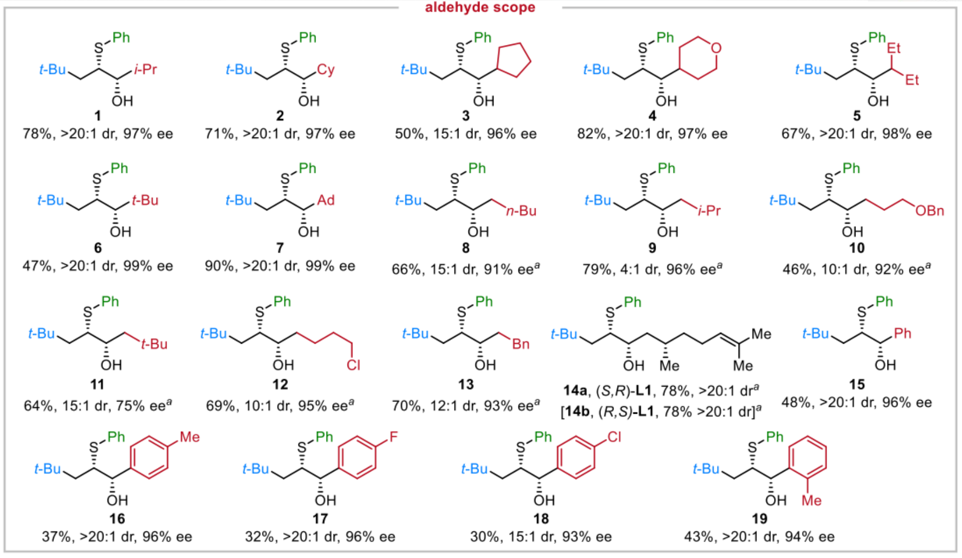

aldehyde scope

1 78%, >20:1 dr, 97% ee

2 71%, >20:1 dr, 97% ee

3 50%, 15:1 dr, 96% ee

4 82%, >20:1 dr, 97% ee

5 67%, >20:1 dr, 98% ee

6 47%, >20:1 dr, 99% ee

7 90%, >20:1 dr, 99% ee

8 66%, 15:1 dr, 91% ee^a

9 79%, 4:1 dr, 96% ee^a

10 46%, 10:1 dr, 92% ee^a

11 64%, 15:1 dr, 75% ee^a

12 69%, 10:1 dr, 95% ee^a

13 70%, 12:1 dr, 93% ee^a

14a, (*S*,*R*)-**L1**, 78%, >20:1 dr^a
[**14b**, (*R*,*S*)-**L1**, 78% >20:1 dr]^a

15 48%, >20:1 dr, 96% ee

16 37%, >20:1 dr, 96% ee

17 32%, >20:1 dr, 96% ee

18 30%, 15:1 dr, 93% ee

19 43%, >20:1 dr, 94% ee

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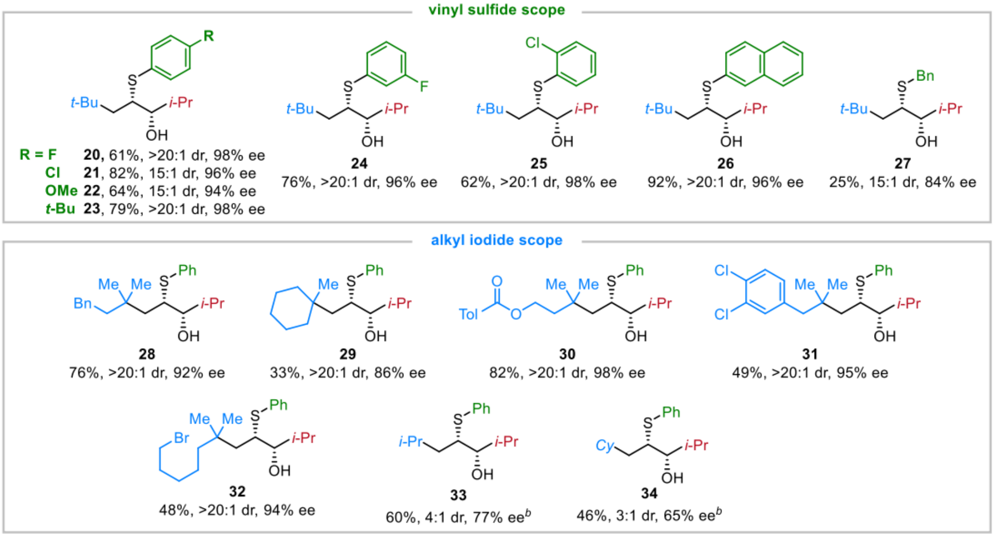

vinyl sulfide scope

R = F **20**, 61%, >20:1 dr, 98% ee
Cl **21**, 82%, 15:1 dr, 96% ee
OMe **22**, 64%, 15:1 dr, 94% ee
t-Bu **23**, 79%, >20:1 dr, 98% ee

24
76%, >20:1 dr, 96% ee

25
62%, >20:1 dr, 98% ee

26
92%, >20:1 dr, 96% ee

27
25%, 15:1 dr, 84% ee

alkyl iodide scope

28
76%, >20:1 dr, 92% ee

29
33%, >20:1 dr, 86% ee

30
82%, >20:1 dr, 98% ee

31
49%, >20:1 dr, 95% ee

32
48%, >20:1 dr, 94% ee

33
60%, 4:1 dr, 77% ee^{b}

34
46%, 3:1 dr, 65% ee^{b}

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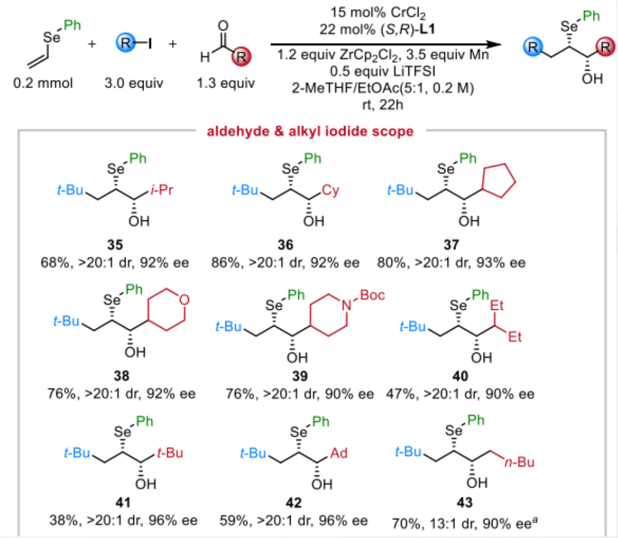


35
68%, >20:1 dr, 92% ee

36
86%, >20:1 dr, 92% ee

37
80%, >20:1 dr, 93% ee

38
76%, >20:1 dr, 92% ee

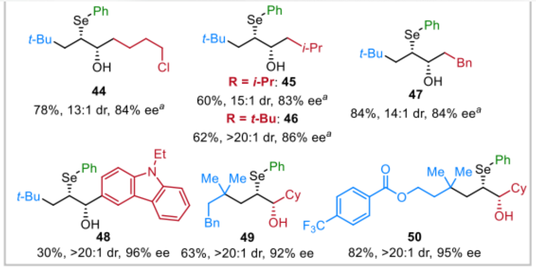
39
76%, >20:1 dr, 90% ee

40
47%, >20:1 dr, 90% ee

41
38%, >20:1 dr, 96% ee

42
59%, >20:1 dr, 96% ee

43
70%, 13:1 dr, 90% ee[a]



44
78%, 13:1 dr, 84% ee[a]

R = *i*-Pr: **45**
60%, 15:1 dr, 83% ee[a]
R = *t*-Bu: **46**
62%, >20:1 dr, 86% ee[a]

47
84%, 14:1 dr, 84% ee[a]

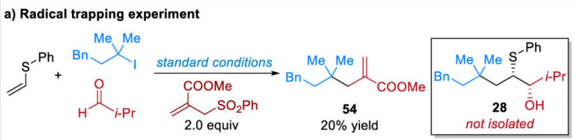
48
30%, >20:1 dr, 96% ee

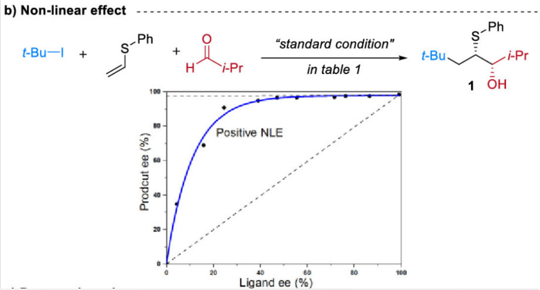
49
63%, >20:1 dr, 92% ee

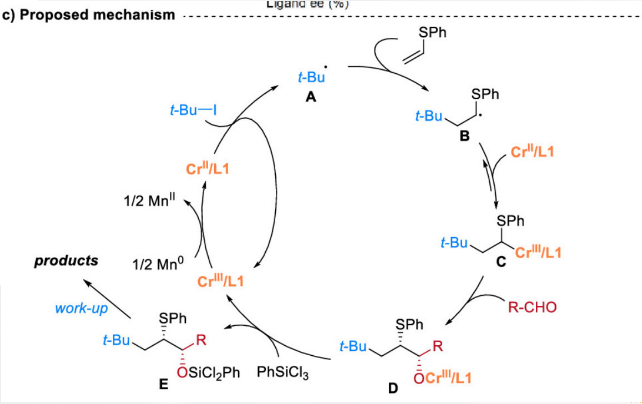
50
82%, >20:1 dr, 95% ee

ACS Catal. **2022**, *12*, 11152.

Cr Catalysis:铬催化的β-羟基硫醚和硒醚的非对映选择性合成

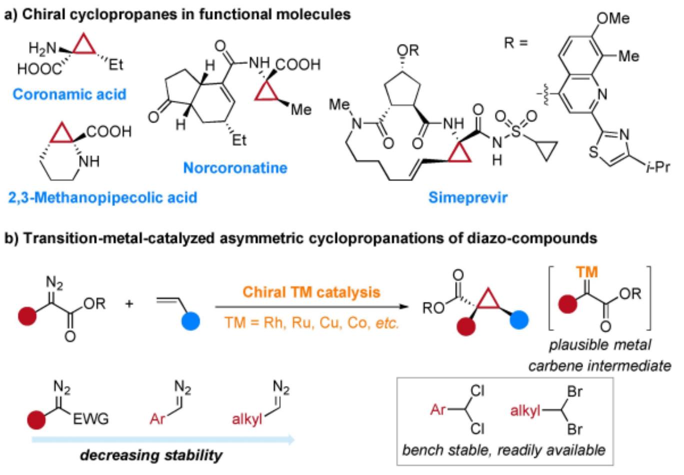

a) Radical trapping experiment


b) Non-linear effect


c) Proposed mechanism

ACS Catal. **2022**, *12*, 11152.

Cr Catalysis:催化偕二卤代烷烃和端烯的不对称环丙烷化

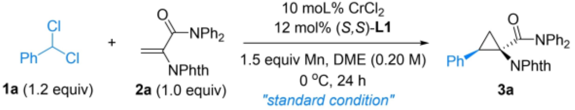


手性环丙烷衍生物在合成化学和药物发现中扮演了非常重要的角色。其中，过渡金属催化的不对称环丙烷化反应是构建这类结构的主要方法之一，在近年来取得重要进展。但是，该方法通常依赖重氮化物作为卡宾前体。重氮化合物活性较高，一般需要官能团取代基进行稳定，例如吸电子或给电子取代基。目前，非稳定的烷基重氮化物作为卡宾前体的不对称环丙烷化反应仍然是一个巨大挑战。

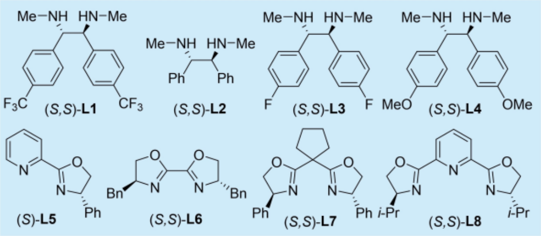
偕二卤代烷烃相对稳定且容易获得，因此在卡宾转移反应中与不稳定的重氮烷烃具有很好的互补性。相关研究已具备一定基础，例如在Simmons-Smith反应中，二碘甲烷被广泛地用于合成环丙烷。此外，还有一些方法使用偕二卤代烷烃制备外消旋环丙烷，包括使用化学计量的金属试剂、过渡金属催化以及光氧化还原等。这些报道证明了偕二卤代烷烃作为卡宾前体的可行性。然而，关于偕二氯代烷烃或偕二溴代烷烃与烯烃的催化不对称环丙烷化问题仍未得到很好解决。

Angew. Chem. Int. Ed. 2023, 62, e202305987.

*Cr Catalysis:*催化偕二卤代烷烃和端烯的不对称环丙烷化



Entry [a]	variation from the "*standard condition*"	yield (%)[b]	dr [b]	ee (%)[c]
1	none	92	>20:1	94
2	no $CrCl_2$	<2	–	–
3	no (*S*,*S*)-**L1**	4	>20:1	0
4	(*S*,*S*)-**L2**, instead of **L1**	63	>20:1	84
5	(*S*,*S*)-**L3**, instead of **L1**	68	>20:1	88
6	(*S*,*S*)-**L4**, instead of **L1**	27	>20:1	75
7	(*S*)-**L5**, instead of **L1**	14	>20:1	14
8	(*S*,*S*)-**L6**, instead of **L1**	25	>20:1	0
9	(*S*,*S*)-**L7**, instead of **L1**	23	>20:1	18
10	(*S*,*S*)-**L8**, instead of **L1**	11	>20:1	4
11	THF, instead of DME	20	>20:1	42
12	MeCN, instead of DME	83	>20:1	87
13	DMF, instead of DME	16	>20:1	42
14	5.0 mol% $CrCl_2$, 6.0 mol% **L1**	43	>20:1	78
15	rt, instead of 0 °C	95	>20:1	71
16	-10 °C, instead of 0 °C	89	>20:1	91
17	Zn, instead of Mn	36	>20:1	67
18	Fe, instead of Mn	4	>20:1	–
19	$CrCl_3{\cdot}(THF)_3$, instead of $CrCl_2$	88	>20:1	91
20	with 1.0 mL air, added via syringe	11	>20:1	90
21	with 1.0 equiv H_2O	20	>20:1	70



[a] All data are the average of two experiments. [b] Yields were determined via ^1H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard, and dr values were determined via ^1H NMR analysis of crude products. [c] ee values were determined via SFC analysis. NPhth = phthalimide. DME = 1,2-dimethoxyethane. THF = Tetrahydrofuran. DMF = *N*,*N*-dimethylformamide.

Angew. Chem. Int. Ed. 2023, 62, e202305987.

Cr Catalysis:催化偕二卤代烷烃和端烯的不对称环丙烷化

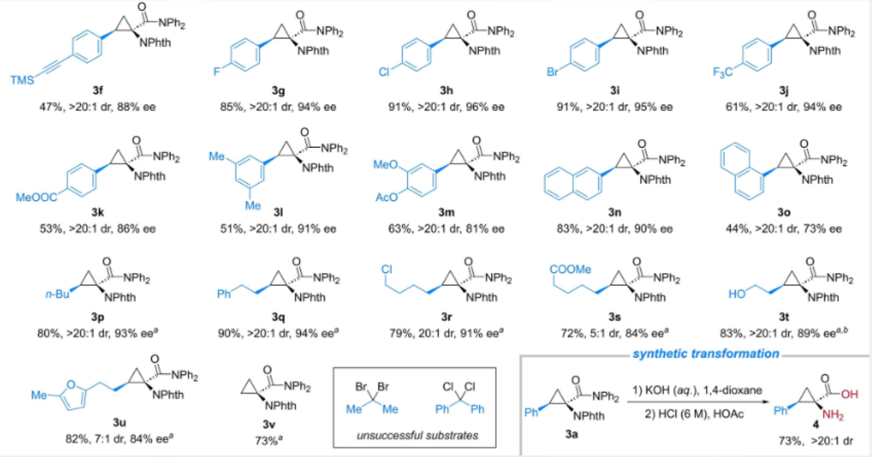
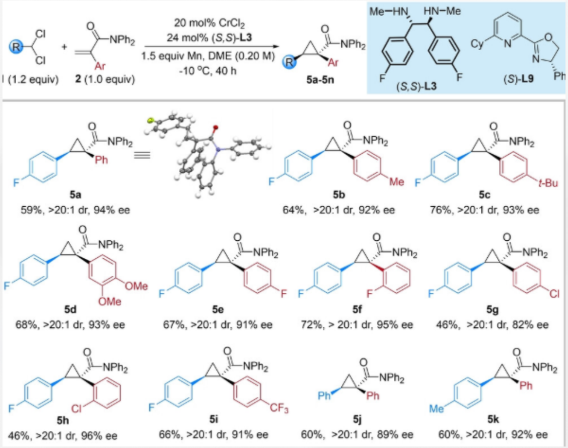


Figure 2. Substrate scope for *gem*-dihaloalkanes. Reactions were conducted on 0.40 mmol scale, and all data are the average of two experiments. The dr values were determined by ^{1}H NMR analysis of the crude product. [a] Use a modified reaction condition: *gem*-dibromoalkanes were used, 20 mol% $CrCl_2$, 24 mol% (*S*,*S*)-**L2**, Mn (1.5 equiv), DME (0.20 M), −10 °C, 24 h. [b] (*tert*-Butyl(3,3-dibromopropoxy)dimethylsilane) was used, while *tert*-butyldimethylsilyl was deprotected during the reaction and work-up. TMS = trimethylsilyl. Ac = acetyl. Bu = butyl.

Angew. Chem. Int. Ed. 2023, 62, e202305987.

Cr Catalysis:催化偕二卤代烷烃和端烯的不对称环丙烷化



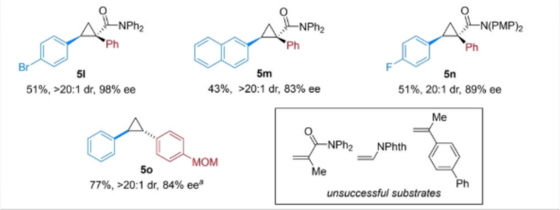
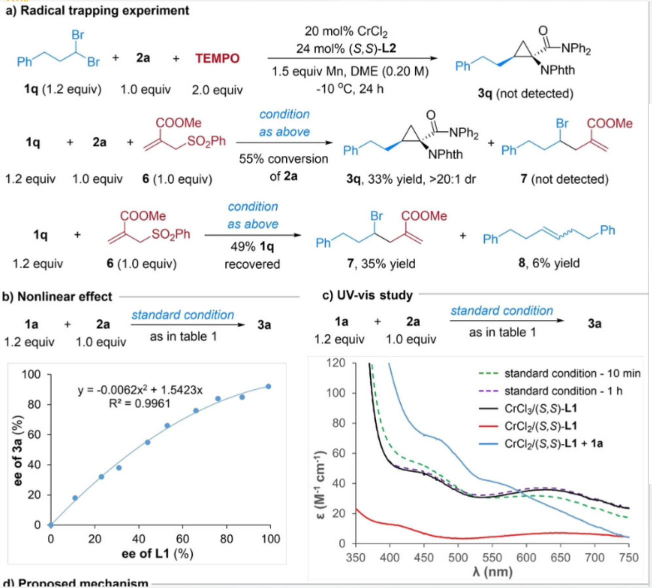
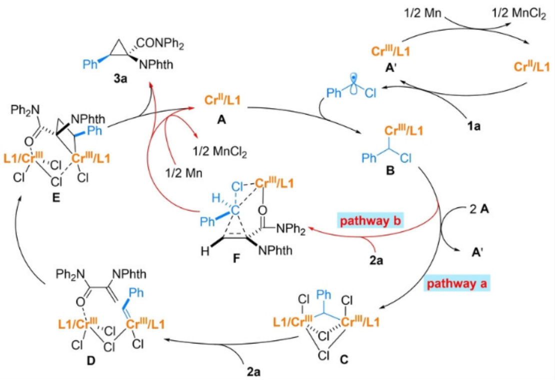


Figure 3. Asymmetric cyclopropanation of 2-arylacrylic amides. Reactions were conducted on 0.40 mmol scale; all data are the average of two experiments. The dr values were determined by ^{1}H NMR analysis of the crude product. [a] The reaction was conducted on 0.20 mmol scale with 15 mol% $CrCl_2$, 18 mol% (*S*)-**L9**, 24 h. Cy = cyclohexyl. MOM = methoxymethyl. PMP = *p*-methoxyphenyl.

Angew. Chem. Int. Ed. 2023, 62, e202305987.

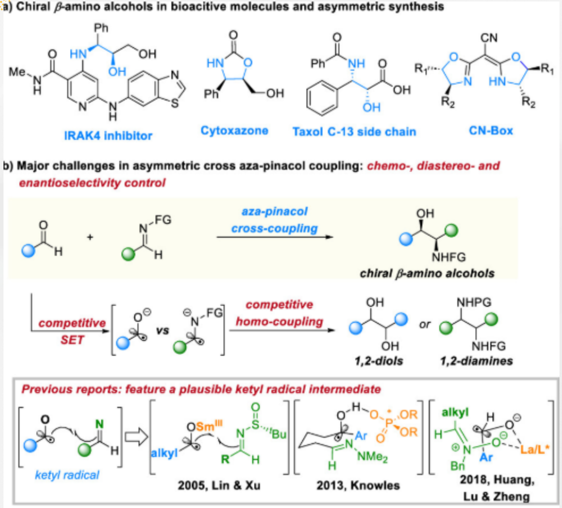
*Cr Catalysis:*催化偕二卤代烷烃和端烯的不对称环丙烷化



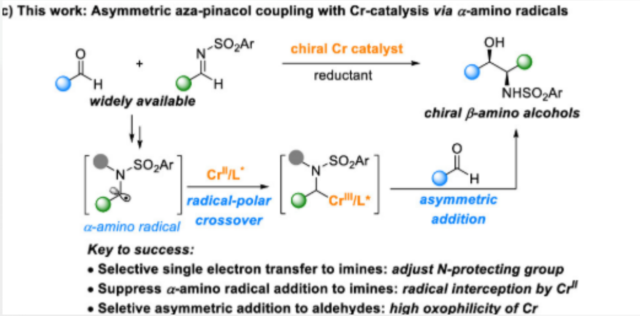


Angew. Chem. Int. Ed. 2023, *62*, e202305987.

*Cr Catalysis:*铬催化的不对称交叉偶联合成β-氨基醇


a) Chiral β-amino alcohols in bioacitive molecules and asymmetric synthesis

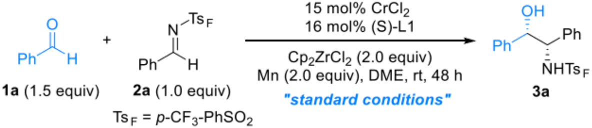
b) Major challenges in asymmetric cross aza-pinacol coupling: *chemo-, diastereo- and enantioselectivity control*


c) This work: Asymmetric aza-pinacol coupling with Cr-catalysis *via* α-amino radicals

Key to success:
- Selective single electron transfer to imines: *adjust N-protecting group*
- Suppress α-amino radical addition to imines: *radical interception by* Cr^{II}
- Seletive asymmetric addition to aldehydes: *high oxophilicity of Cr*

J. Am. Chem. Soc. **2023**, *145*, 20775.

Cr Catalysis:铬催化的不对称交叉偶联合成β-氨基醇

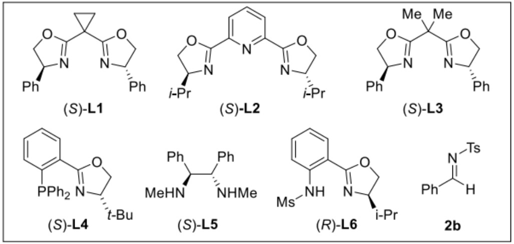


1a (1.5 equiv) **2a** (1.0 equiv) **3a**

Ts_F = *p*-CF_3-$PhSO_2$

15 mol% $CrCl_2$
16 mol% (S)-L1
Cp_2ZrCl_2 (2.0 equiv)
Mn (2.0 equiv), DME, rt, 48 h
"standard conditions"

Entry	Variation from the ***"standard conditions"***	yield [%][a]	ee [%][b]	dr[a]
1	none	82	91	> 20:1
2	no $CrCl_2$	< 2	–	–
3	no (*S*)-**L1**	10	0	> 20:1
4	(*S*)-**L2**, instead of (*S*)-**L1**	< 2	–	–
5	(*S*)-**L3**, instead of (*S*)-**L1**	78	75	> 20:1
6	(*S*)-**L4**, instead of (*S*)-**L1**	20	3	> 20:1
7	(*S*)-**L5**, instead of (*S*)-**L1**	35	-7	> 20:1
8	(*R*)-**L6**, instead of (*S*)-**L1**	43	40	> 20:1
9	THF, instead of DME	78	90	> 20:1
10	EtOAc, instead of DME	73	78	> 20:1
11	MeCN, instead of DME	66	43	> 20:1
12	10 mol% $CrCl_2$, 12 mol% (*S*)-**L1**	74	91	> 20:1
13	TMSCl, instead of Cp_2ZrCl_2	43	87	> 20:1
14	Zn, instead of Mn	23	17	> 20:1
15	24 h, instead of 48 h	58	91	> 20:1
16[c]	**2b**, instead of **2a**	52	70	> 20:1
17	1.0 equiv of **1a** and 1.5 equiv of **2a**	78	90	> 20:1
18	1.2, instead of 1.5, equiv of **1a**	73	90	> 20:1
19	1.0 mL air, added to the 4mL vial	71	90	> 20:1
20	1.0 equiv H_2O was added	< 2	–	–



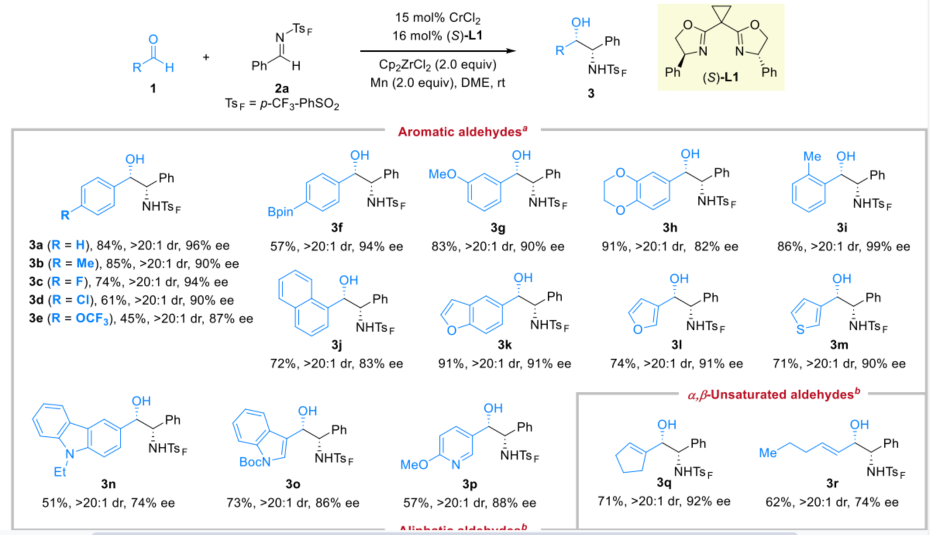
(*S*)-**L1** (*S*)-**L2** (*S*)-**L3**

(*S*)-**L4** (*S*)-**L5** (*R*)-**L6** **2b**

[a] Yield and dr were determined *via* ^{19}F NMR analysis with CF_3Ph as the internal standard. [b] The ee was determined *via* SFC analysis. [c] Yield and dr were determined *via* ^1H NMR analysis with mesitylene as the internal standard.

J. Am. Chem. Soc. **2023**, *145*, 20775.

*Cr Catalysis:*铬催化的不对称交叉偶联合成β-氨基醇



15 mol% $CrCl_2$
16 mol% (*S*)-**L1**
Cp_2ZrCl_2 (2.0 equiv)
Mn (2.0 equiv), DME, rt

Aromatic aldehydes[a]

3a (R = H), 84%, >20:1 dr, 96% ee
3b (R = Me), 85%, >20:1 dr, 90% ee
3c (R = F), 74%, >20:1 dr, 94% ee
3d (R = Cl), 61%, >20:1 dr, 90% ee
3e (R = OCF_3), 45%, >20:1 dr, 87% ee

3f
57%, >20:1 dr, 94% ee

3g
83%, >20:1 dr, 90% ee

3h
91%, >20:1 dr, 82% ee

3i
86%, >20:1 dr, 99% ee

3j
72%, >20:1 dr, 83% ee

3k
91%, >20:1 dr, 91% ee

3l
74%, >20:1 dr, 91% ee

3m
71%, >20:1 dr, 90% ee

3n
51%, >20:1 dr, 74% ee

3o
73%, >20:1 dr, 86% ee

3p
57%, >20:1 dr, 88% ee

***α,β*-Unsaturated aldehydes**[b]

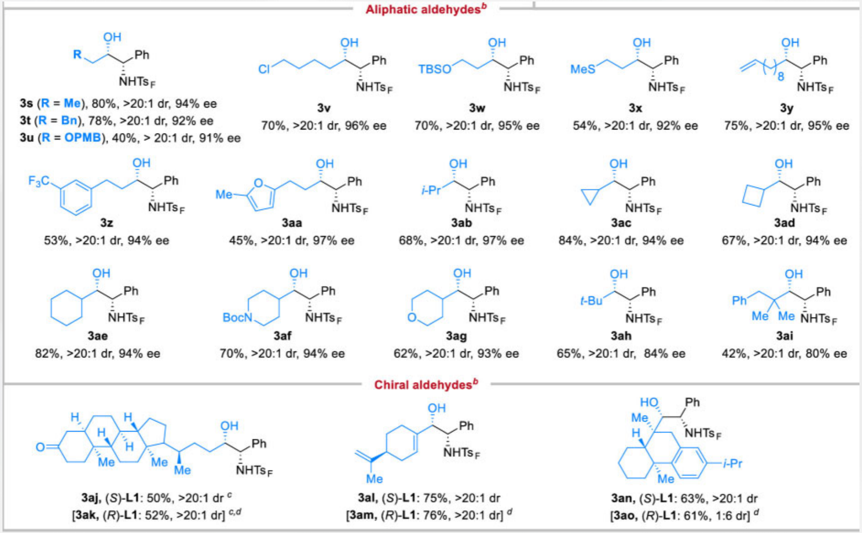
3q
71%, >20:1 dr, 92% ee

3r
62%, >20:1 dr, 74% ee

Aliphatic aldehydes[b]

J. Am. Chem. Soc. **2023**, *145*, 20775.

*Cr Catalysis.*铬催化的不对称交叉偶联合成β-氨基醇



3s (R = Me), 80%, >20:1 dr, 94% ee
3t (R = Bn), 78%, >20:1 dr, 92% ee
3u (R = OPMB), 40%, > 20:1 dr, 91% ee

3v 70%, >20:1 dr, 96% ee

3w 70%, >20:1 dr, 95% ee

3x 54%, >20:1 dr, 92% ee

3y 75%, >20:1 dr, 95% ee

3z 53%, >20:1 dr, 94% ee

3aa 45%, >20:1 dr, 97% ee

3ab 68%, >20:1 dr, 97% ee

3ac 84%, >20:1 dr, 94% ee

3ad 67%, >20:1 dr, 94% ee

3ae 82%, >20:1 dr, 94% ee

3af 70%, >20:1 dr, 94% ee

3ag 62%, >20:1 dr, 93% ee

3ah 65%, >20:1 dr, 84% ee

3ai 42%, >20:1 dr, 80% ee

3aj, (*S*)-**L1**: 50%, >20:1 dr [c]
[**3ak**, (*R*)-**L1**: 52%, >20:1 dr] [c,d]

3al, (*S*)-**L1**: 75%, >20:1 dr
[**3am**, (*R*)-**L1**: 76%, >20:1 dr] [d]

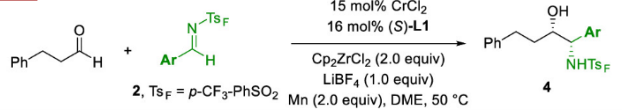
3an, (*S*)-**L1**: 63%, >20:1 dr
[**3ao**, (*R*)-**L1**: 61%, 1:6 dr] [d]

LiBF4可能作为路易斯酸促进亚胺的单电子还原

[a] Condition A: 15 mol % $CrCl_2$, 16 mol % (*S*)-**L1**, 2.0 equiv Mn, 2.0 equiv Cp_2ZrCl_2, 1 mL DME (0.2 M), 1.5 equiv **1**, 1.0 equiv **2**. [b] Condition B: 15 mol % $CrCl_2$, 16 mol % (*S*)-**L1**, 2.0 equiv Mn, 2.0 equiv Cp_2ZrCl_2, 1.0 equiv $LiBF_4$, 1 mL DME (0.2 M), 2.0 equiv **1**, 1.0 equiv **2**, 50 °C, 24 h. [c] 1.0 equiv aldehyde and 1.5 equiv **2a** were used. [d] The major stereoisomer is not the one depicted.

J. Am. Chem. Soc. **2023**, *145*, 20775.

Cr Catalysis:铬催化的不对称交叉偶联合成β-氨基醇



2, Ts_F = p-CF_3-$PhSO_2$

4

4a

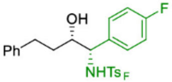
76%, >20:1 dr, 94% ee[b]

4b

63%, >20:1 dr, 93% ee[b]

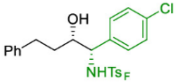
4c

79%, >20:1 dr, 99% ee



4d

66%, >20:1 dr, 95% ee

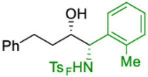


4e

73%, >20:1 dr, 94% ee

4f

47%, >20:1 dr, 94% ee



4g

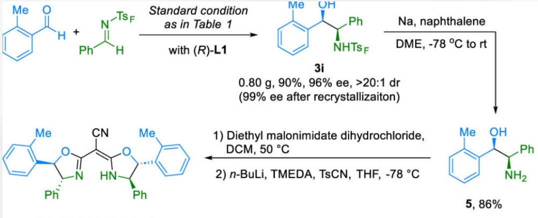
44%, >20:1 dr, 90% ee

4h

55%, >20:1 dr, 94% ee[b]

4i

47%, >20:1 dr, 93% ee[b]

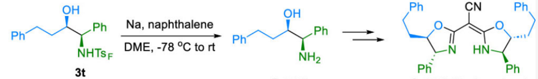


3i

0.80 g, 90%, 96% ee, >20:1 dr
(99% ee after recrystallizaiton)

5, 86%

6, 58% (*for two steps*)



3t

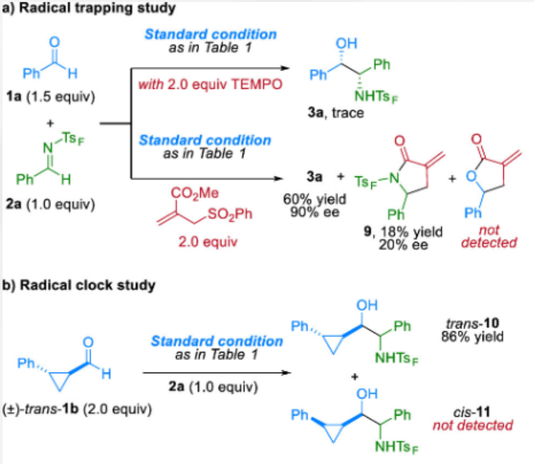
65%, 96% ee, >20:1 dr
(99% ee after recrystallizaiton)

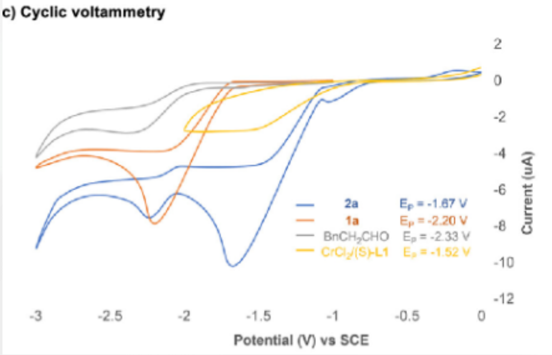
7, 50%

8, 40% (*for two steps*)

J. Am. Chem. Soc. **2023**, *145*, 20775.

Cr Catalysis:铬催化的不对称交叉偶联合成β-氨基醇

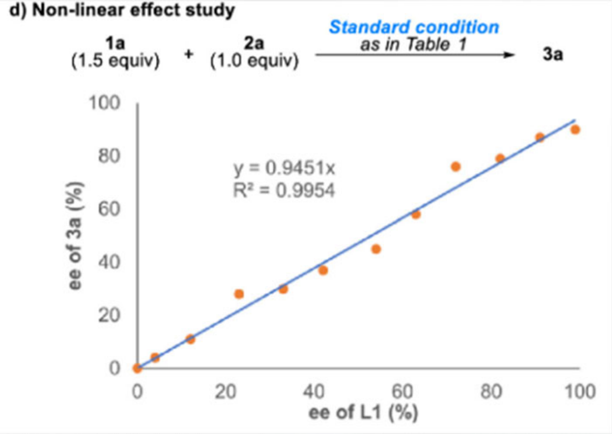


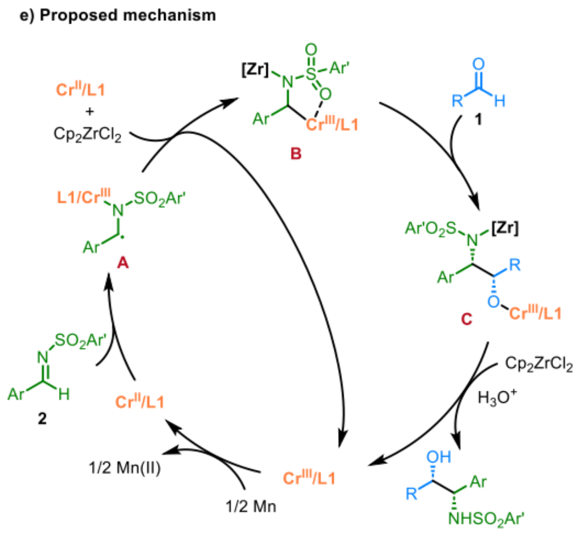


推测铬(II)和 N-磺酰亚胺的预配位促进了还原过程。值得注意的是，尽管醛与 CrCl$_2$/(S)-L1 络合物之间存在相当大的还原电位差，但在优化条件下，由于铬离子的高亲氧性，一小部分芳香醛也可能被还原成醇。

J. Am. Chem. Soc. **2023**, *145*, 20775.

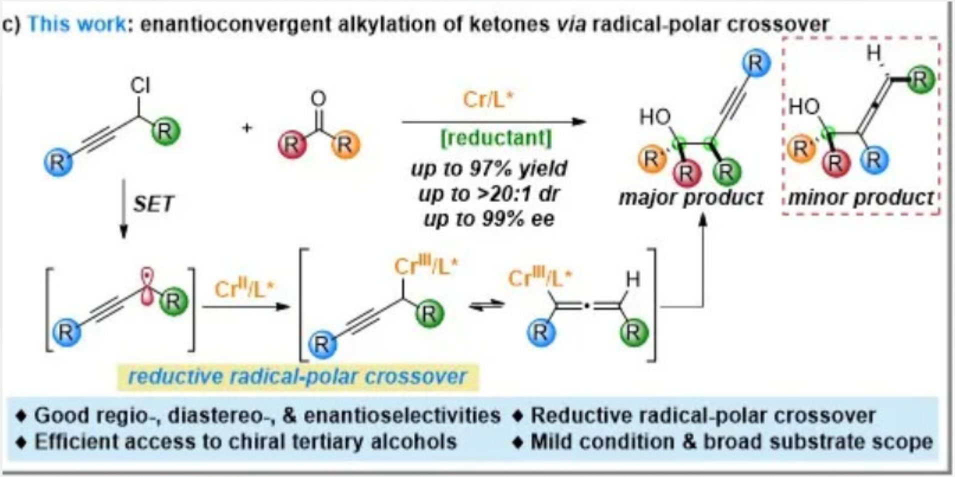
*Cr Catalysis:*铬催化的不对称交叉偶联合成β-氨基醇


d) Non-linear effect study


e) Proposed mechanism

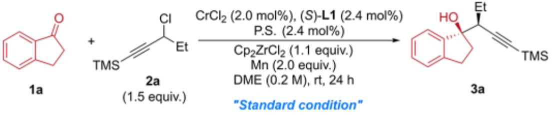
J. Am. Chem. Soc. **2023**, *145*, 20775.

Cr Catalysis:铬催化炔丙基氯代物对酮的区域、对映和非对映选择性加成反应

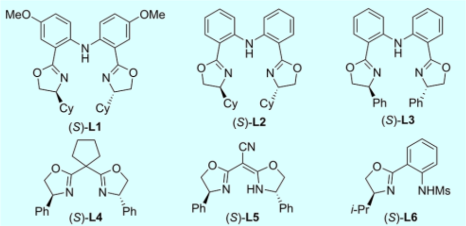


ACS Catal. **2023**, *13*, 3170.

Cr Catalysis:铬催化炔丙基氯代物对酮的区域、对映和非对映选择性加成反应



Entry	Variation from *"Standard condition"*	Yield (%)^b	dr^b	ee (%)^c
1	none	98	>20:1	99
2	no CrCl$_2$	<3	-	-
3	no ligand	39	>10:1	rac.
4	no P.S.	88	>20:1	93
5	2.4 mol% NEt$_3$, instead of P.S.	92	>20:1	99
6	1.0 mol% CrCl$_2$, 1.2 mol% (*S*)-**L1**, 2.4 mol% P.S.	94	>20:1	99
7	(*S*)-**L2**, instead of (*S*)-**L1**	77	>20:1	91
8	(*S*)-**L3**, instead of (*S*)-**L1**	40	>20:1	71
9	(*S*)-**L4**, instead of (*S*)-**L1**	95	7:1	50
10	(*S*)-**L5**, instead of (*S*)-**L1**	<3	-	-
11	(*S*)-**L6**, instead of (*S*)-**L1**	87	4:1	12
12	1.1 equiv. TMSCl, instead of Cp$_2$ZrCl$_2$	48	>20:1	98
13	Zn, instead of Mn	93	>20:1	6
14	THF, instead of DME	88	>20:1	98
15	MeCN, instead of DME	45	2:1	83
16	0.1 M, instead of 0.2 M, in DME	96	>20:1	99
17	1.0, instead of 1.1 equiv. Cp$_2$ZrCl$_2$	96	>20:1	99
18	1.2, instead of 1.5 equiv. **2a**	96	>20:1	95
19	1.0 mL air, added through syringe	73	>20:1	99
20	with 1.0 equiv. H$_2$O	<3	-	-



^{a}Reactions were performed under a N$_2$ atmosphere, and conditions are as follows: **1a** (0.2 mmol), **2a** (0.3 mmol), 1.0 mL of DME, CrCl$_2$ (2.0 mol%), ligand (2.4 mol%), proton sponge (P.S.) (2.4 mol%), Cp$_2$ZrCl$_2$ (0.22 mmol), and Mn (0.4 mmol). ^{b}Yield and dr were determined *via* ^{1}H NMR analysis of the reaction mixture with CH$_2$Br$_2$ as the internal standard. ^{c}ee was determined *via* HPLC analysis.

ACS Catal. **2023**, *13*, 3170.

Cr Catalysis:铬催化炔丙基氯代物对酮的区域、对映和非对映选择性加成反应

158496 ▶ Sigma-Aldrich.

Proton-sponge®

99%

别名: 1,8-双二甲氨基萘, *N,N,N′,N′*-四甲基-1,8-萘二胺

P.S. 的化学特性

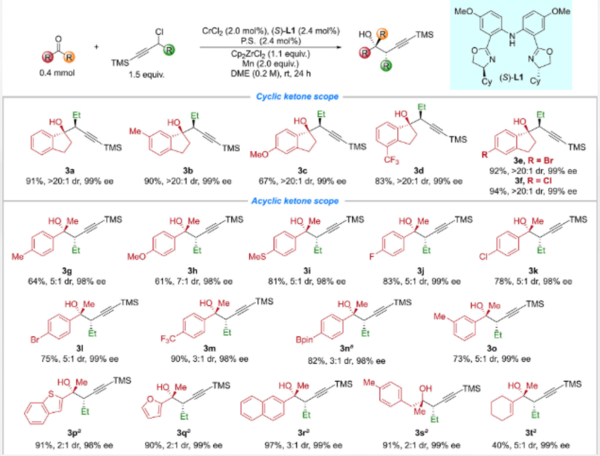
□ 强有机碱（pKa = 12.1），能高效捕获质子而不易被空间位阻影响。

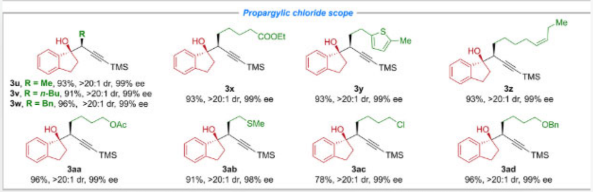
□ 在过渡金属催化中常用于稳定活性催化剂，防止酸性副产物导致的失活。

质子海绵（P. S.）在本文中是**关键添加剂**，通过促进配体–金属配位和维持反应体系稳定性，确保了铬催化酮与炔丙基氯的还原偶联反应的高效性和立体选择性。其作用虽可被三乙胺部分替代，但 P. S. 仍是实现最佳结果的首选碱。

ACS Catal. **2023**, *13*, 3170.

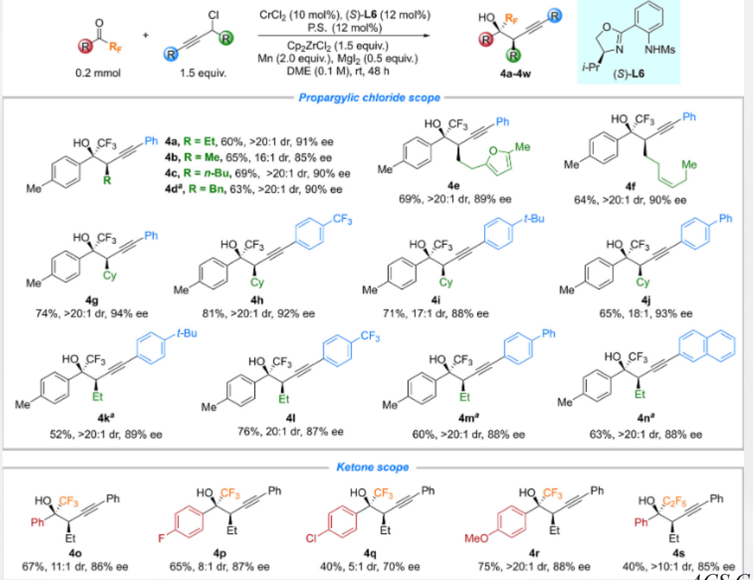
*Cr Catalysis:*铬催化炔丙基氯代物对酮的区域、对映和非对映选择性加成反应





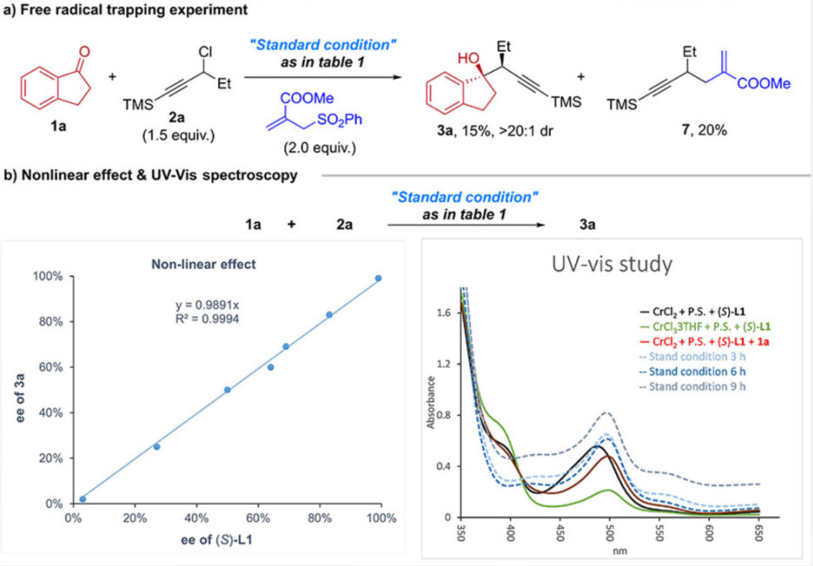
ACS Catal. **2023**, *13*, 3170.

*Cr Catalysis:*铬催化炔丙基氯代物对酮的区域、对映和非对映选择性加成反应



ACS Catal. **2023**, *13*, 3170.

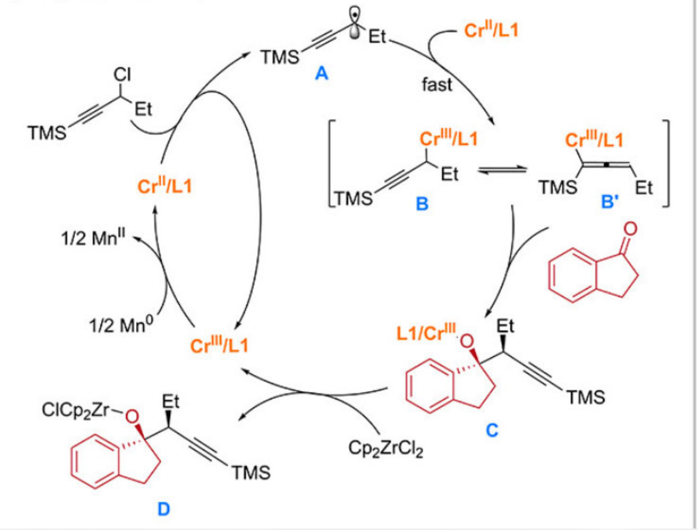
Cr Catalysis.铬催化炔丙基氯代物对酮的区域、对映和非对映选择性加成反应

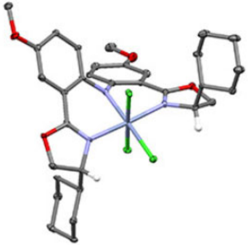


ACS Catal. **2023**, *13*, 3170.

Cr Catalysis: 铬催化炔丙基氯代物对酮的区域、对映和非对映选择性加成反应

c) Proposed mechanism

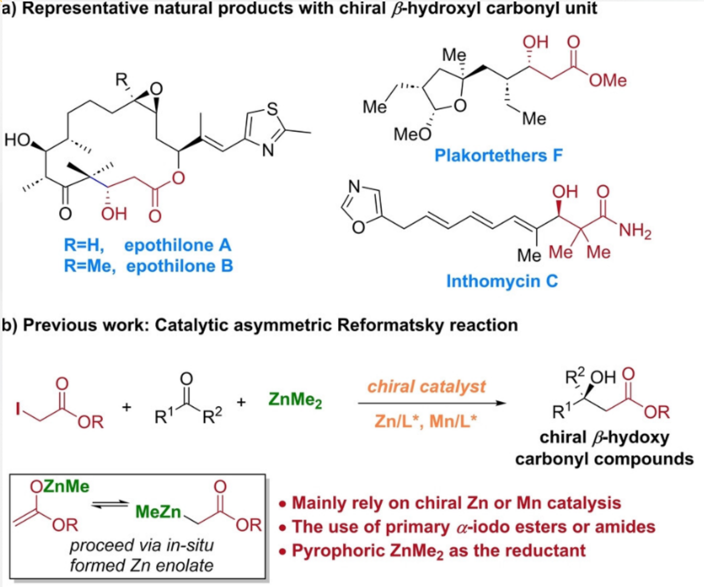




Cr^{III}/(*R*)-L1

ACS Catal. **2023**, *13*, 3170.

*Cr Catalysis.*铬催化的不对称Reformatsky反应



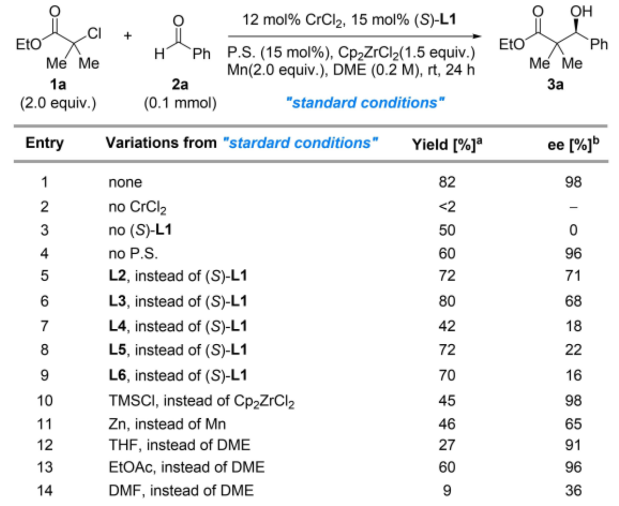
- Mainly rely on chiral Zn or Mn catalysis
- The use of primary α-iodo esters or amides
- Pyrophoric $ZnMe_2$ as the reductant

手性β-羟基羰基类结构单元存在于许多天然产物和活性药物分子中。经典的Reformatsky反应于1887年首次发现，通常涉及锌介导的α-卤代羰基化合物与醛或酮的还原偶联。与传统的羰基加成反应中涉及预先形成的有机金属试剂不同，该反应通常在中性和温和条件下形成烯醇盐。因此，它被公认为一种构建C-C键的高效方法，广泛应用于复杂有机分子的合成中。特别是，不对称Reformatsky反应在合成手性β-羟基羰基化合物方面具有显著的实用性。

已知的催化不对称Reformatsky反应策略主要使用易燃二甲基锌试剂作为还原剂，以及使用α-碘代羰基化合物作为烯醇盐前体。因此亟需进一步拓展不对称Reformatsky反应，发展一种高效、普适的策略来制备手性β-羟基羰基类化合物。

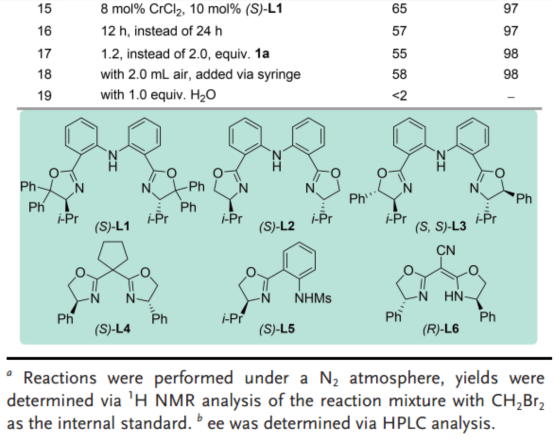
Angew. Chem. Int. Ed. **2024**, *63*, e202406109

*Cr Catalysis:*铬催化的不对称Reformatsky反应



1a (2.0 equiv.) + **2a** (0.1 mmol) $\xrightarrow[\text{P.S. (15 mol\%), Cp}_2\text{ZrCl}_2\text{(1.5 equiv.) Mn(2.0 equiv.), DME (0.2 M), rt, 24 h}]{\text{12 mol\% CrCl}_2\text{, 15 mol\% (}S\text{)-}\mathbf{L1}}$ **3a**

"standard conditions"



Entry	Variations from *"stardard conditions"*	Yield [%][a]	ee [%][b]
1	none	82	98
2	no $CrCl_2$	<2	–
3	no (*S*)-**L1**	50	0
4	no P.S.	60	96
5	**L2**, instead of (*S*)-**L1**	72	71
6	**L3**, instead of (*S*)-**L1**	80	68
7	**L4**, instead of (*S*)-**L1**	42	18
8	**L5**, instead of (*S*)-**L1**	72	22
9	**L6**, instead of (*S*)-**L1**	70	16
10	TMSCl, instead of Cp_2ZrCl_2	45	98
11	Zn, instead of Mn	46	65
12	THF, instead of DME	27	91
13	EtOAc, instead of DME	60	96
14	DMF, instead of DME	9	36
15	8 mol% $CrCl_2$, 10 mol% (*S*)-**L1**	65	97
16	12 h, instead of 24 h	57	97
17	1.2, instead of 2.0, equiv. **1a**	55	98
18	with 2.0 mL air, added via syringe	58	98
19	with 1.0 equiv. H_2O	<2	–

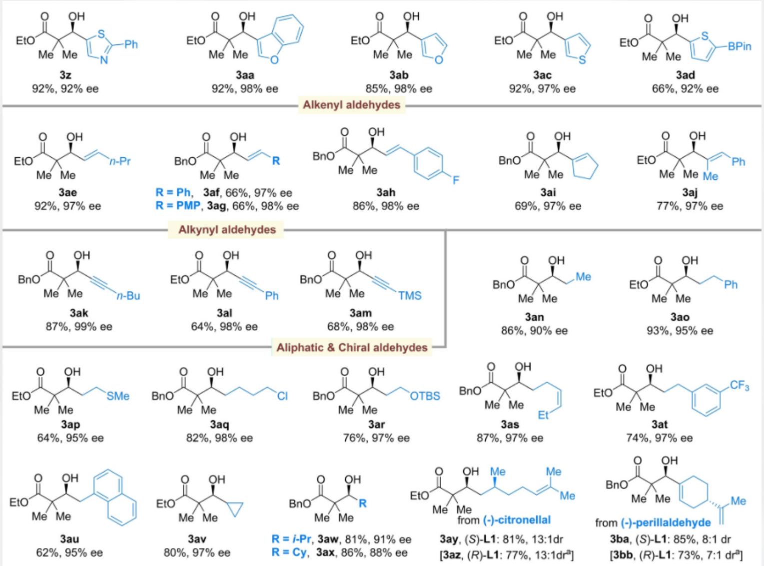
---

[a] Reactions were performed under a N_2 atmosphere, yields were determined via ^{1}H NMR analysis of the reaction mixture with CH_2Br_2 as the internal standard. [b] ee was determined via HPLC analysis.

Angew. Chem. Int. Ed. **2024**, *63, e202406109*

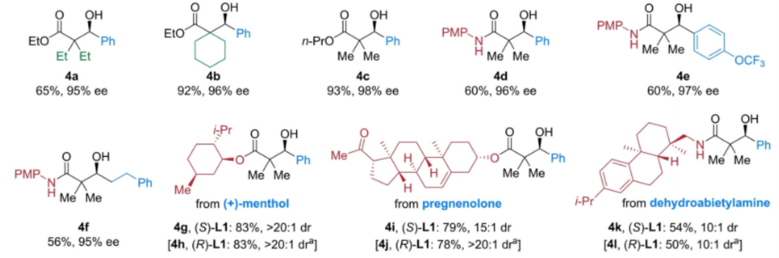
Cr Catalysis:铬催化的不对称Reformatsky反应

The Yang Research Group
Precise Synthesis Lab at Tongji University



Angew. Chem. Int. Ed. **2024**, *63*, *e202406109*

*Cr Catalysis:*铬催化的不对称Reformatsky反应



4a
65%, 95% ee

4b
92%, 96% ee

4c
93%, 98% ee

4d
60%, 96% ee

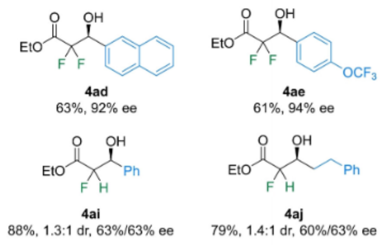
4e
60%, 97% ee

4f
56%, 95% ee

from (+)-menthol
4g, (*S*)-**L1**: 83%, >20:1 dr
[**4h**, (*R*)-**L1**: 83%, >20:1 dr[a]]

from pregnenolone
4i, (*S*)-**L1**: 79%, 15:1 dr
[**4j**, (*R*)-**L1**: 78%, >20:1 dr[a]]

from dehydroabietylamine
4k, (*S*)-**L1**: 54%, 10:1 dr
[**4l**, (*R*)-**L1**: 50%, 10:1 dr[a]]

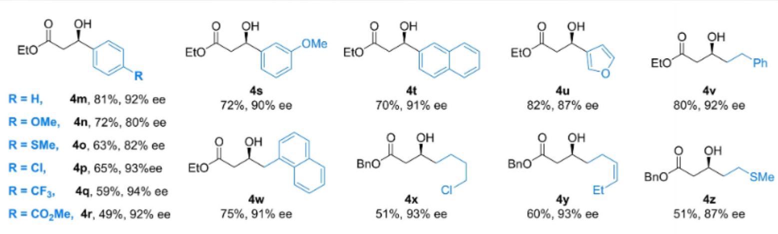


4ad
63%, 92% ee

4ae
61%, 94% ee

4ai
88%, 1.3:1 dr, 63%/63% ee

4aj
79%, 1.4:1 dr, 60%/63% ee



R = H, **4m**, 81%, 92% ee
R = OMe, **4n**, 72%, 80% ee
R = SMe, **4o**, 63%, 82% ee
R = Cl, **4p**, 65%, 93%ee
R = CF_3, **4q**, 59%, 94% ee
R = CO_2Me, **4r**, 49%, 92% ee

4s
72%, 90% ee

4t
70%, 91% ee

4u
82%, 87% ee

4v
80%, 92% ee

4w
75%, 91% ee

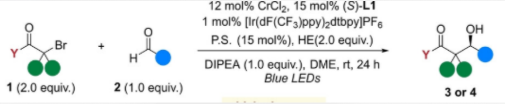
4x
51%, 93% ee

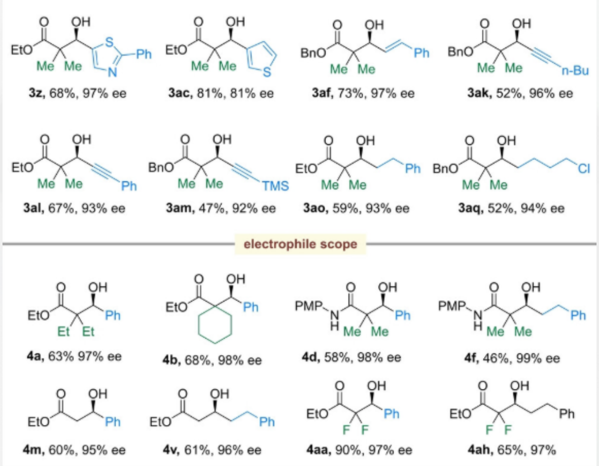
4y
60%, 93% ee

4z
51%, 87% ee

Angew. Chem. Int. Ed. **2024**, *63*, *e202406109*

Cr Catalysis:铬催化的不对称Reformatsky反应

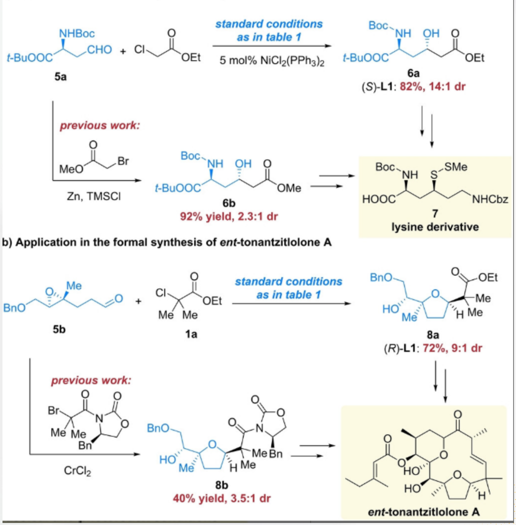




3z, 68%, 97% ee
3ac, 81%, 81% ee
3af, 73%, 97% ee
3ak, 52%, 96% ee
3al, 67%, 93% ee
3am, 47%, 92% ee
3ao, 59%, 93% ee
3aq, 52%, 94% ee
4a, 63% 97% ee
4b, 68%, 98% ee
4d, 58%, 98% ee
4f, 46%, 99% ee
4m, 60%, 95% ee
4v, 61%, 96% ee
4aa, 90%, 97% ee
4ah, 65%, 97%

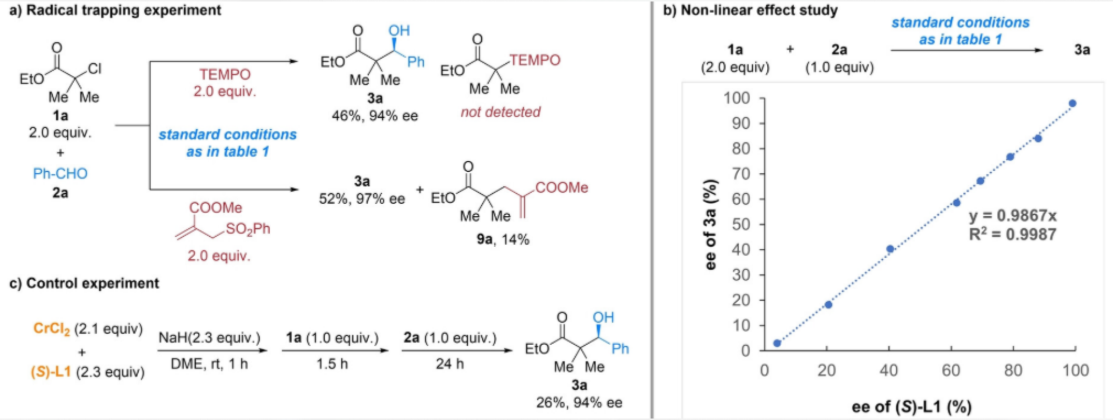
a) Application in the formal synthesis of lysine derivatives

b) Application in the formal synthesis of *ent*-tonantzitlolone A



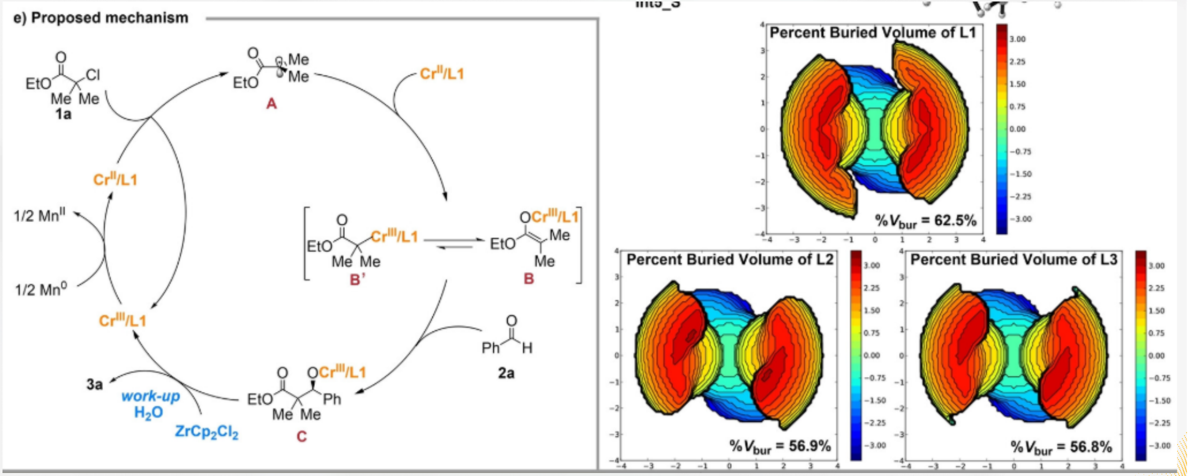
Angew. Chem. Int. Ed. **2024**, *63*, e202406109

*Cr Catalysis:*铬催化的不对称Reformatsky反应



Angew. Chem. Int. Ed. ***2024****, 63, e202406109*

Cr Catalysis:铬催化的不对称Reformatsky反应



Angew. Chem. Int. Ed. **2024**, *63*, *e202406109*

Cr Catalysis:铬催化的不对称Reformatsky反应

SambVca 2 是一款专业的**计算化学工具**，主要用于**量化配体的空间位阻效应**，尤其在过渡金属催化领域（如不对称催化）中用于分析配体（如膦配体、氮杂环卡宾等）的三维空间参数。

核心功能与原理

◆ **空间位阻量化**

通过计算配体围绕金属中心的**立体占位体积**，生成以下关键参数：

- ➢ **%V_{bur}**：配体在金属周围占据的空间体积百分比（核心指标，值越大表示位阻越大）。
- ➢ **立体角（Solid Angle）**：描述配体对金属中心的遮蔽程度。
- ➢ **到金属中心的距离分布**。

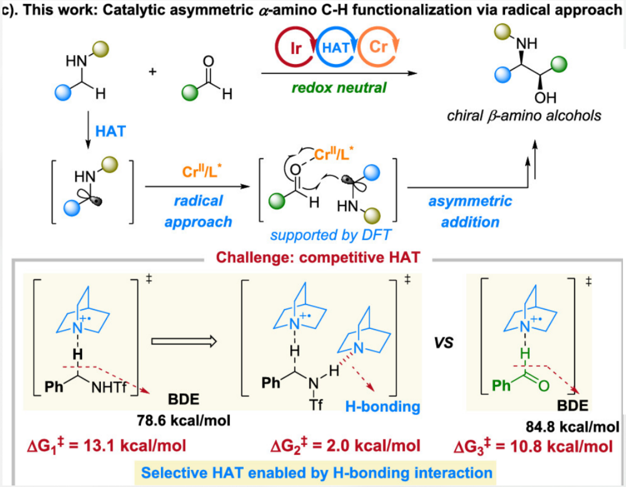
基于**范德华半径和几何构型**，精确模拟配体的空间拥挤度。

◆ **可视化分析**

生成配体-金属复合物的**3D空间填充模型**，直观展示位阻区域（如图中不同颜色的占位区域）。

Angew. Chem. Int. Ed. **2024**, *63*, *e202406109*

Cr Catalysis: N -磺酰基苄胺与醛不对称α - C–H加成


c). This work: Catalytic asymmetric α-amino C-H functionalization via radical approach

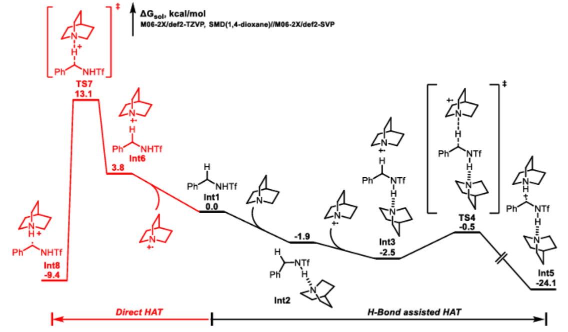
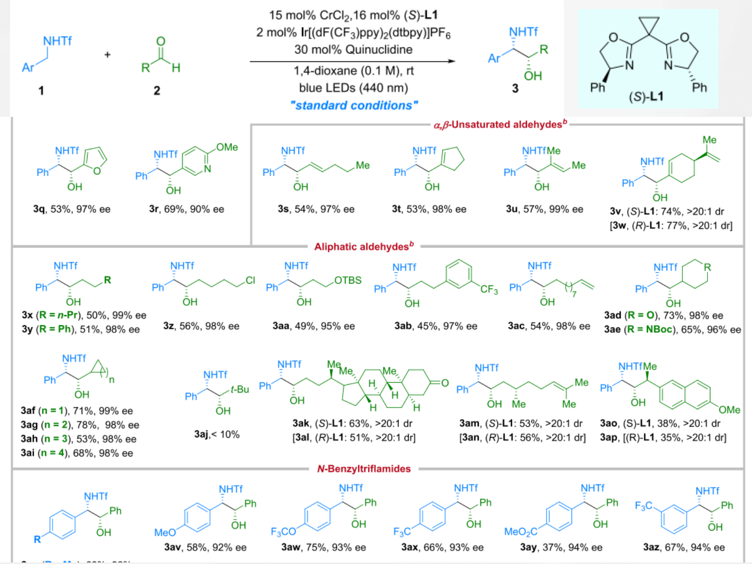


Figure S19. HAT process of substrate

J. Am. Chem. Soc. **2024**, *146*, 5316

Cr Catalysis:N -磺酰基苄胺与醛不对称α - C–H加成



15 mol% $CrCl_2$, 16 mol% (*S*)-**L1**
2 mol% $Ir[(dF(CF_3)ppy)_2(dtbpy)]PF_6$
30 mol% Quinuclidine
1,4-dioxane (0.1 M), rt
blue LEDs (440 nm)
"standard conditions"

α,β-Unsaturated aldehydes[b]

Aliphatic aldehydes[b]

N-Benzyltriflamides

3q, 53%, 97% ee

3r, 69%, 90% ee

3s, 54%, 97% ee

3t, 53%, 98% ee

3u, 57%, 99% ee

3v, (*S*)-**L1**: 74%, >20:1 dr
[**3w**, (*R*)-**L1**: 77%, >20:1 dr]

3x (**R = *n*-Pr**), 50%, 99% ee
3y (**R = Ph**), 51%, 98% ee

3z, 56%, 98% ee

3aa, 49%, 95% ee

3ab, 45%, 97% ee

3ac, 54%, 98% ee

3ad (**R = O**), 73%, 98% ee
3ae (**R = NBoc**), 65%, 96% ee

3af (**n = 1**), 71%, 99% ee
3ag (**n = 2**), 78%, 98% ee
3ah (**n = 3**), 53%, 98% ee
3ai (**n = 4**), 68%, 98% ee

3aj,< 10%

3ak, (*S*)-**L1**: 63%, >20:1 dr
[**3al**, (*R*)-**L1**: 51%, >20:1 dr]

3am, (*S*)-**L1**: 53%, >20:1 dr
[**3an**, (*R*)-**L1**: 56%, >20:1 dr]

3ao, (*S*)-**L1**, 38%, >20:1 dr
3ap, [(*R*)-**L1**, 35%, >20:1 dr]

3av, 58%, 92% ee

3aw, 75%, 93% ee

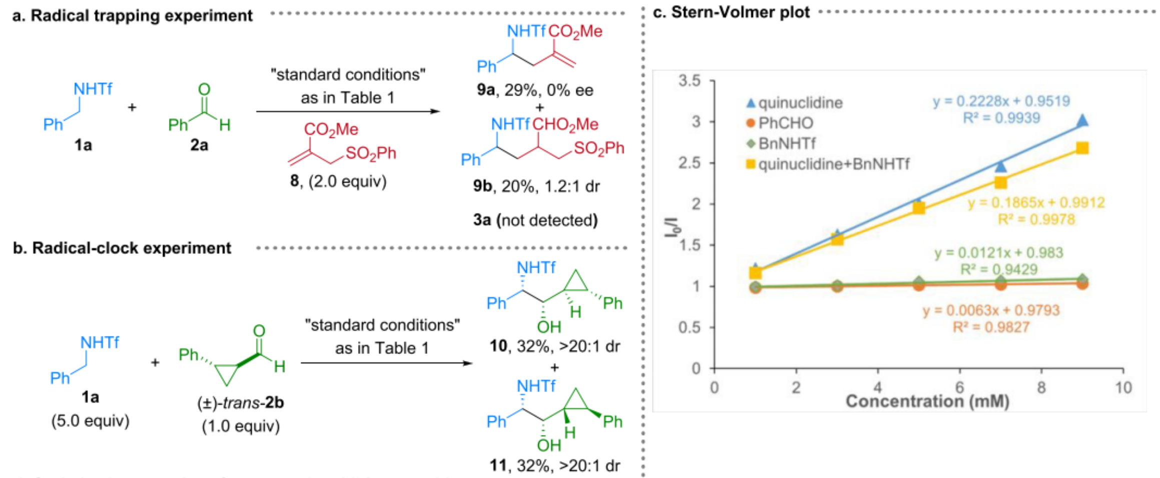
3ax, 66%, 93% ee

3ay, 37%, 94% ee

3az, 67%, 94% ee

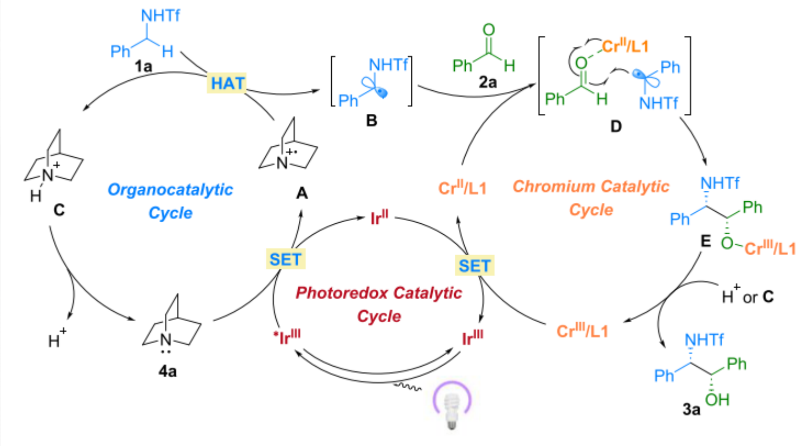
J. Am. Chem. Soc. **2024**, *146*, 5316

Cr Catalysis:N -磺酰基苄胺与醛不对称α - C–H加成



J. Am. Chem. Soc. **2024**, *146*, 5316

Cr Catalysis：N-磺酰基苄胺与醛不对称α-C–H加成

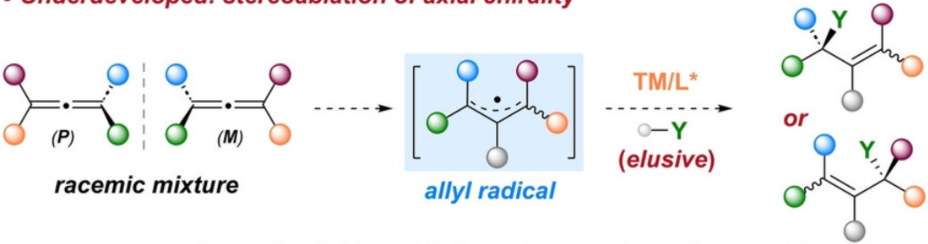


- 通过高选择性氢原子转移（HAT）生成α-氨基自由基；
- 促进Cr–O键解离

J. Am. Chem. Soc. **2024**, *146*, 5316

*Cr Catalysis:*基于三催化循环的消旋联烯与醛的对映汇聚式还原偶联反应

- ***Underdeveloped: stereoablation of axial chirality***

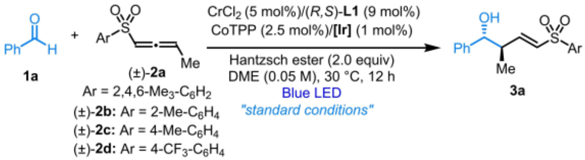


- **Lack of suitable catalytic systems and reaction models**
- **Challenging *E/Z*-, regio- and enantioselectivity control**

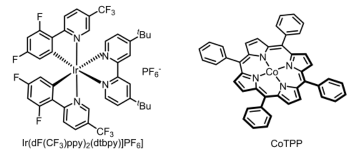
联烯是一类含有两个相互垂直的累积双键的特殊化合物。由于其独特的结构，联烯类化合物表现出丰富的反应活性，在药物分子和天然产物等功能性分子合成中具有十分重要的研究价值。其中，联烯与醛的催化不对称还原偶联反应为合成手性烯丙醇提供了一条有效的途径。目前已报道的策略旨在实现单取代或者1,1-二取代联烯与醛的不对称还原偶联反应，然而消旋联烯与醛的催化不对称还原偶联反应则尚未实现。相对于单取代或者1,1-二取代联烯，使用消旋联烯为前体面临着如下问题：1. 联烯位阻的增大可能会降低反应性；2. 区域选择性控制；3. 立体选择性控制，特别是同时控制中心手性的立体化学以及烯烃的构型。

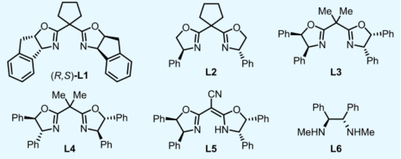
Angew. Chem. Int. Ed. **2025**, *64, e202413198*

Cr Catalysis:基于三催化循环的消旋联烯与醛的对映汇聚式还原偶联反应



Entry	Variations from *"standard conditions"*	***yield*** [%]^a	***E/Z*** ^{b}	***dr*** ^{b}	***ee*** [%]^c
1	none	81 (80)^d	14:1	15:1	91
2	w/o CrCl$_2$, CoTPP, **[Ir]**, light	<2	–	–	–
3	NiCl$_2$, instead of CrCl$_2$	< 2	–	–	–
4	TiCl$_4$, instead of CrCl$_2$	36	> 20:1	2:1	30
5	**L2**, instead of (*R*,*S*)-**L1**	77	6:1	9:1	70
6	**L3**, instead of (*R*,*S*)-**L1**	63	6:1	5:1	62
7	**L4**, instead of (*R*,*S*)-**L1**	63	1:2	> 20:1	6
8	**L5**, instead of (*R*,*S*)-**L1**	64	1:20	> 20:1	10
9	**L6**, instead of (*R*,*S*)-**L1**	< 2	–	–	–
10	**2b**, instead of **2a**	64	4:1	5:1	82
11	**2c**, instead of **2a**	61	1.3:1	5:1	68
12	**2d**, instead of **2a**	57	1.6:1	5:1	70
13	EtOAc, instead of DME	71	12:1	13:1	88
14	THF, instead of DME	70	12:1	11:1	87
15	CH$_3$CN, instead of DME	16	5:1	11:1	86



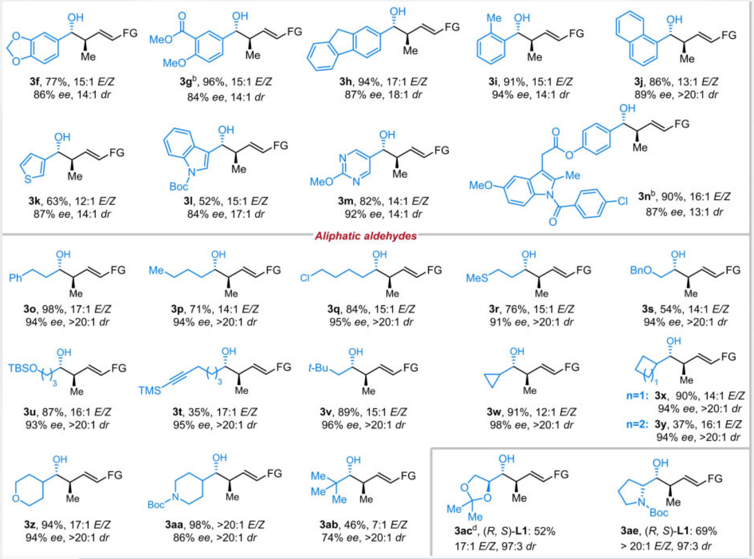


Standard reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (1.1 equiv.), CrCl$_2$ (5 mol%), (*R*,*S*)-**L1** (9 mol%), **[Ir]** (1 mol%), CoTPP (2.5 mol%), Hantzsch ester (2.0 equiv.), DME (0.05 M), upon Blue LEDs (440 nm, 20 W) irradiation for 12 h under N$_2$ at 30°C. **[Ir]**=Ir(dF(CF$_3$)ppy)$_2$(dtbpy)]PF$_6$. [a]The yield of product as mixture stereoisomers were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. [b]The *Z/E* and *dr* value were determined by ^{1}H NMR analysis of crude reaction mixture. [c]The ee value was determined by SFC analysis. [d]Isolated yields as mixture stereoisomers based on aldehyde **1a**.

Angew. Chem. Int. Ed. **2025**, *64*, *e202413198*

Cr Catalysis:基于三催化循环的消旋联烯与醛的对映汇聚式还原偶联反应

The Yang Research Group
Precise Synthesis Lab at Tongji University



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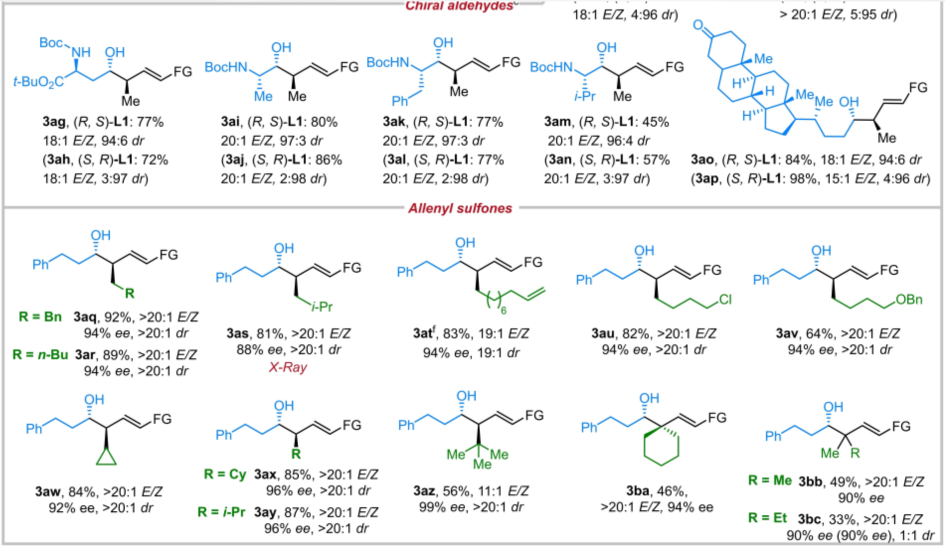

18:1 *E/Z*, 4:96 *dr*)

> 20:1 *E/Z*, 5:95 *dr*)

3ag, (*R*, *S*)-**L1**: 77%
18:1 *E/Z*, 94:6 *dr*
(**3ah**, (*S*, *R*)-**L1**: 72%
18:1 *E/Z*, 3:97 *dr*)

3ai, (*R*, *S*)-**L1**: 80%
20:1 *E/Z*, 97:3 *dr*
(**3aj**, (*S*, *R*)-**L1**: 86%
20:1 *E/Z*, 2:98 *dr*)

3ak, (*R*, *S*)-**L1**: 77%
20:1 *E/Z*, 97:3 *dr*
(**3al**, (*S*, *R*)-**L1**: 77%
20:1 *E/Z*, 2:98 *dr*)

3am, (*R*, *S*)-**L1**: 45%
20:1 *E/Z*, 96:4 *dr*
(**3an**, (*S*, *R*)-**L1**: 57%
20:1 *E/Z*, 3:97 *dr*)

3ao, (*R*, *S*)-**L1**: 84%, 18:1 *E/Z*, 94:6 *dr*
(**3ap**, (*S*, *R*)-**L1**: 98%, 15:1 *E/Z*, 4:96 *dr*)

R = Bn **3aq**, 92%, >20:1 *E/Z*
94% *ee*, >20:1 *dr*
R = *n*-Bu **3ar**, 89%, >20:1 *E/Z*
94% *ee*, >20:1 *dr*

3as, 81%, >20:1 *E/Z*
88% *ee*, >20:1 *dr*
X-Ray

3at[f], 83%, 19:1 *E/Z*
94% *ee*, 19:1 *dr*

3au, 82%, >20:1 *E/Z*
94% *ee*, >20:1 *dr*

3av, 64%, >20:1 *E/Z*
94% *ee*, >20:1 *dr*

3aw, 84%, >20:1 *E/Z*
92% ee, >20:1 *dr*

R = Cy **3ax**, 85%, >20:1 *E/Z*
96% *ee*, >20:1 *dr*
R = *i*-Pr **3ay**, 87%, >20:1 *E/Z*
96% *ee*, >20:1 *dr*

3az, 56%, 11:1 *E/Z*
99% *ee*, >20:1 *dr*

3ba, 46%,
>20:1 *E/Z*, 94% ee

R = Me **3bb**, 49%, >20:1 *E/Z*
90% *ee*
R = Et **3bc**, 33%, >20:1 *E/Z*
90% *ee* (90% *ee*), 1:1 *dr*

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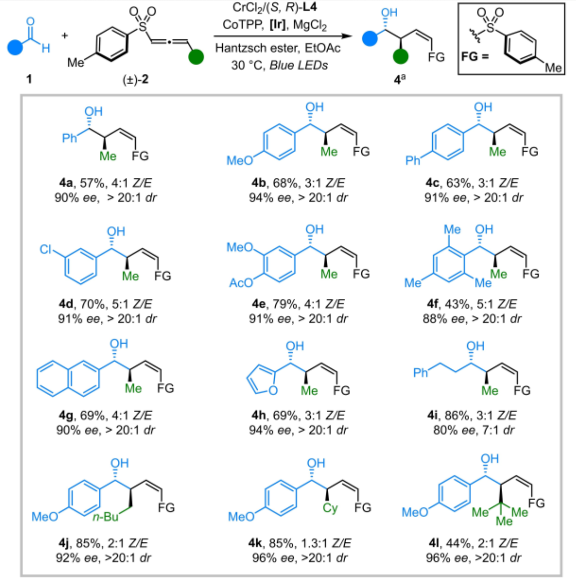
Cr Catalysis.基于三催化循环的消旋联烯与醛的对映汇聚式还原偶联反应



4a, 57%, 4:1 *Z/E*
90% *ee*, > 20:1 *dr*

4b, 68%, 3:1 *Z/E*
94% *ee*, > 20:1 *dr*

4c, 63%, 3:1 *Z/E*
91% *ee*, > 20:1 *dr*

4d, 70%, 5:1 *Z/E*
91% *ee*, > 20:1 *dr*

4e, 79%, 4:1 *Z/E*
91% *ee*, > 20:1 *dr*

4f, 43%, 5:1 *Z/E*
88% *ee*, > 20:1 *dr*

4g, 69%, 4:1 *Z/E*
90% *ee*, > 20:1 *dr*

4h, 69%, 3:1 *Z/E*
94% *ee*, > 20:1 *dr*

4i, 86%, 3:1 *Z/E*
80% *ee*, 7:1 *dr*

4j, 85%, 2:1 *Z/E*
92% *ee*, >20:1 *dr*

4k, 85%, 1.3:1 *Z/E*
96% *ee*, >20:1 *dr*

4l, 44%, 2:1 *Z/E*
96% *ee*, >20:1 *dr*

Scheme 2. The substrate scope for *Z*-selectivity. Standard reaction conditions: **1** (0.2 mmol, 1.0 equiv.), **2** (2.0 equiv.), $CrCl_2$ (15 mol%), (*S*,*R*)-**L4** (25 mol%), **[Ir]** (1 mol%), CoTPP (2.5 mol%), $MgCl_2$ (10 mol%), Hantzsch ester (2.0 equiv.), EtOAc (0.05 M), upon Blue LEDs (440 nm, 20 W) irradiation for 12 h under N_2 at 30°C. [a]Yields indicate the yield of the isolated product as mixture stereoisomers based on aldehyde **1**.

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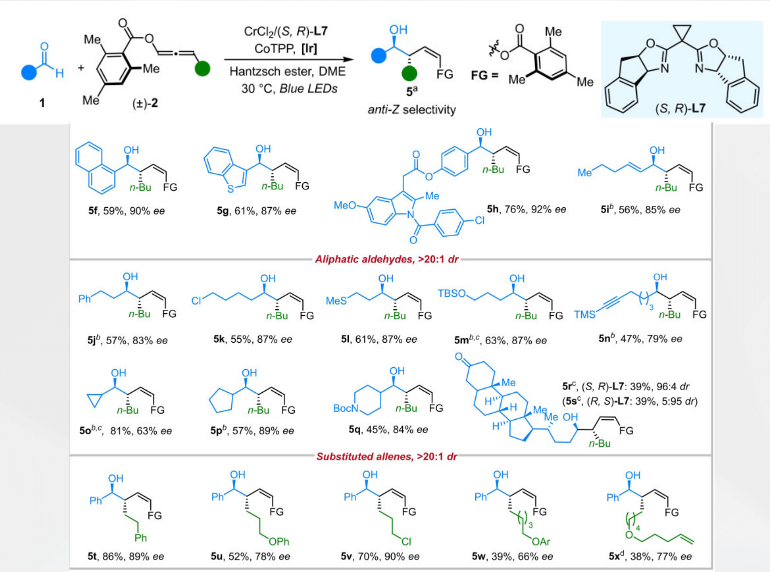

5f, 59%, 90% *ee*

5g, 61%, 87% *ee*

5h, 76%, 92% *ee*

5i[b], 56%, 85% *ee*

5j[b], 57%, 83% *ee*

5k, 55%, 87% *ee*

5l, 61%, 87% *ee*

5m[b,c], 63%, 87% *ee*

5n[b], 47%, 79% *ee*

5o[b,c], 81%, 63% *ee*

5p[b], 57%, 89% *ee*

5q, 45%, 84% *ee*

5r[c], (*S*, *R*)-**L7**: 39%, 96:4 *dr*
(**5s**[c], (*R*, *S*)-**L7**: 39%, 5:95 *dr*)

5t, 86%, 89% *ee*

5u, 52%, 78% *ee*

5v, 70%, 90% *ee*

5w, 39%, 66% *ee*

5x[d], 38%, 77% *ee*

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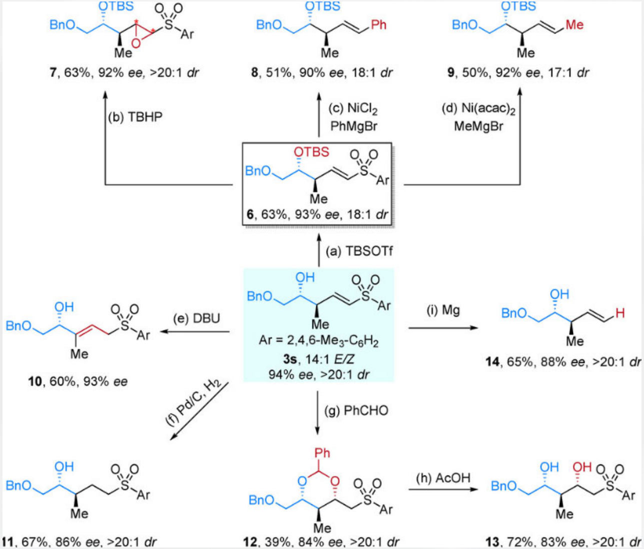

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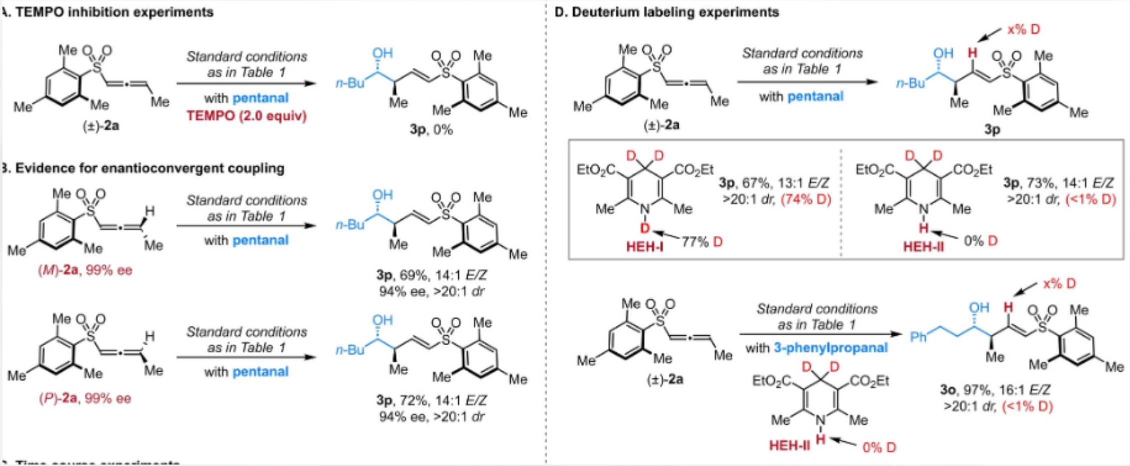

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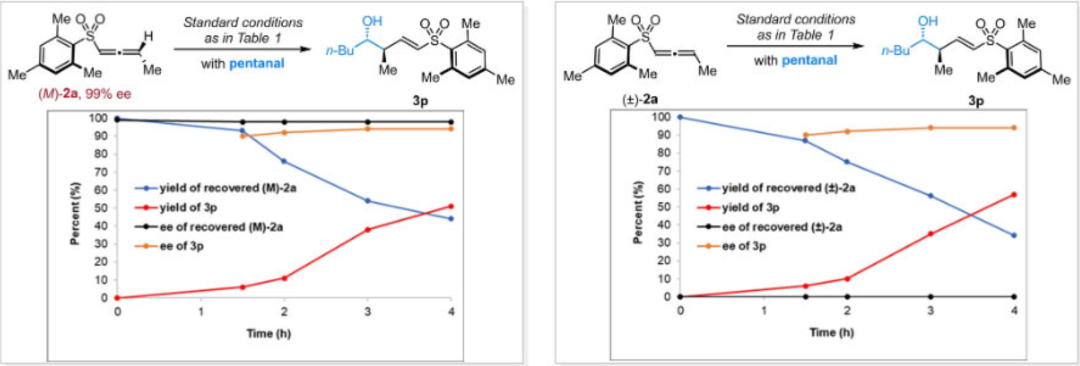
C. Time course experiments



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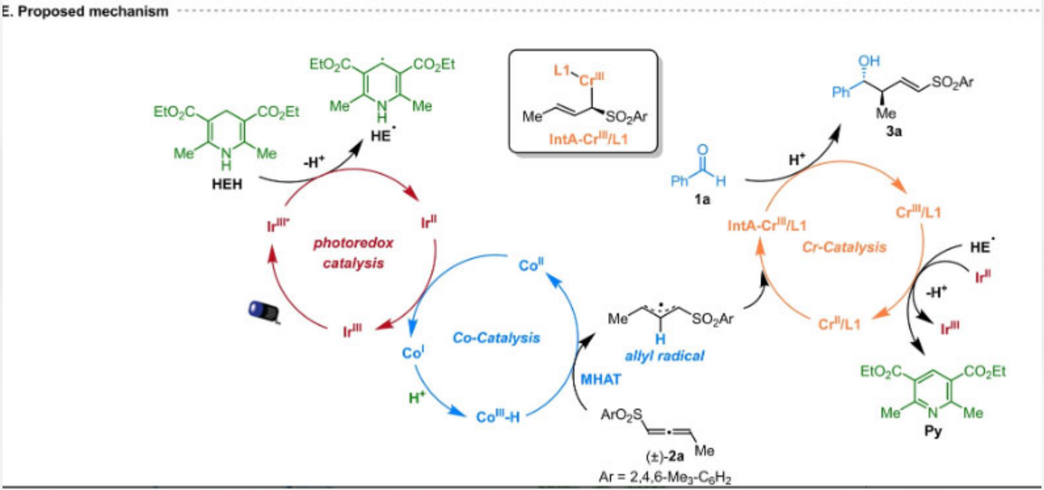

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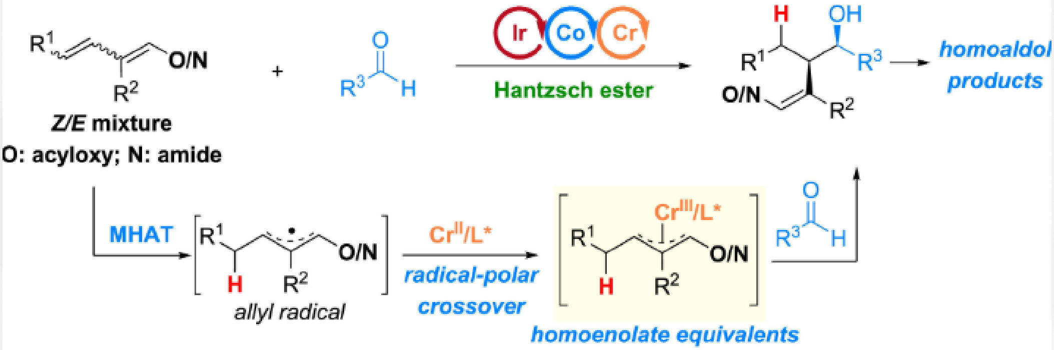
*Cr Catalysis.*基于三催化循环的消旋联烯与醛的对映汇聚式还原偶联反应

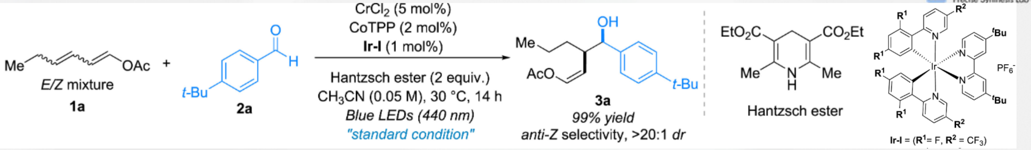
C This work: A radical approach to catalytic asymmetric homoaldol addition

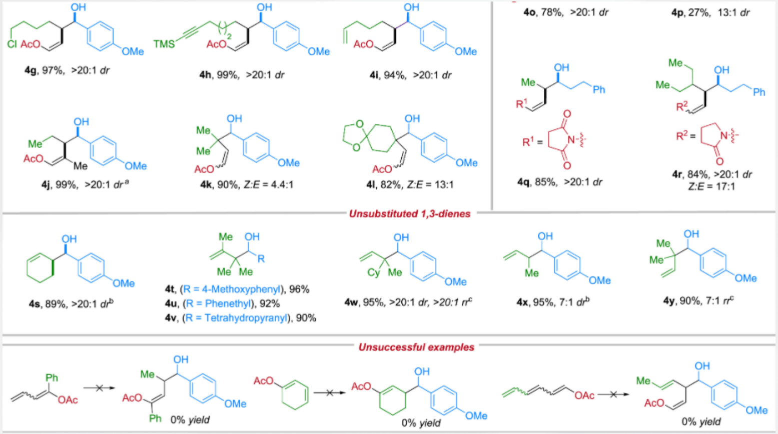


- Catalytic asymmetric homoaldol addition in a radical approach
- Quadruple selectivity control via photoredox/Cr/Co triple catalysis
- Using easily accessible internal 1,3-dienes as homoenolate equivalent
- Regioselective MHAT of internal 1,3-dienes

Chem **2024** *10*, 998

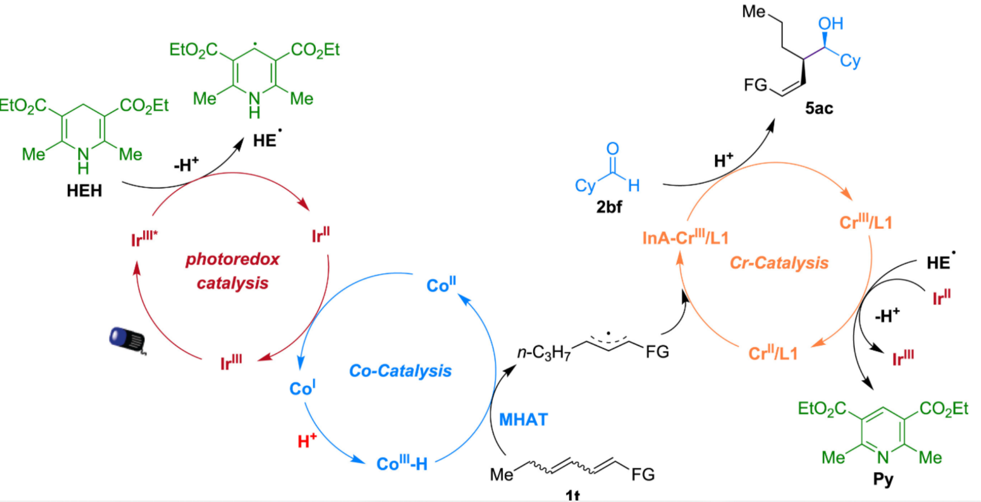
Cr Catalysis:基于三催化循环的消旋联烯与醛的对映汇聚式还原偶联反应

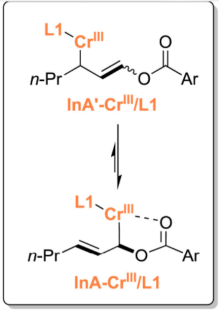


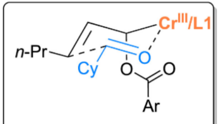


Chem **2024** *10*, 998

*Cr Catalysis.*基于三催化循环的消旋联烯与醛的对映汇聚式还原偶联反应



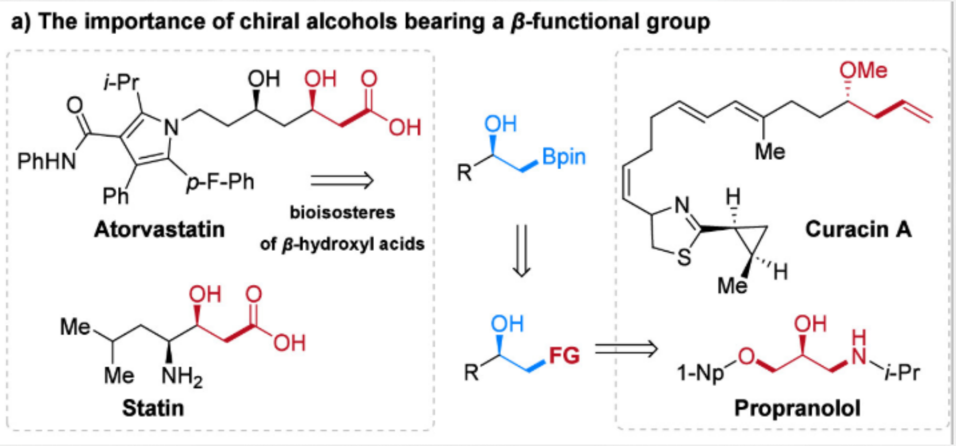




plausible Zimmerman-Traxler TS

Chem **2024** *10*, 998

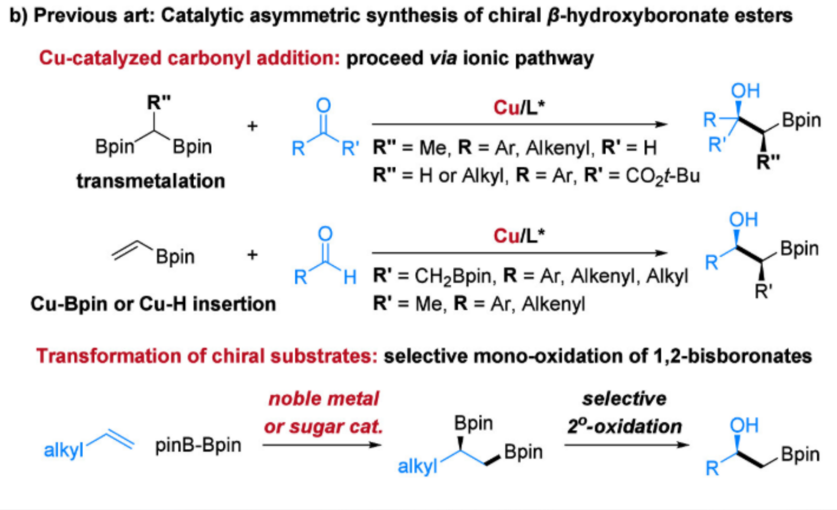
Cr Catalysis:钴/铬协同催化自由基反应合成手性β-羟基硼酸酯化合物



手性β-羟基硼酸酯是一类具有重要应用价值的合成砌块，可作为手性β-羟基羧酸的生物电子等排体。得益于有机硼化合物的多样化转化特性，该类化合物可高效转化为手性氨基醇、1,2−二醇及高烯丙醇等β-官能团化手性醇。

ACS Catal. **2025**, *15*, 8454

Cr Catalysis:基于三催化循环的消旋联烯与醛的对映汇聚式还原偶联反应



b) Previous art: Catalytic asymmetric synthesis of chiral *β*-hydroxyboronate esters

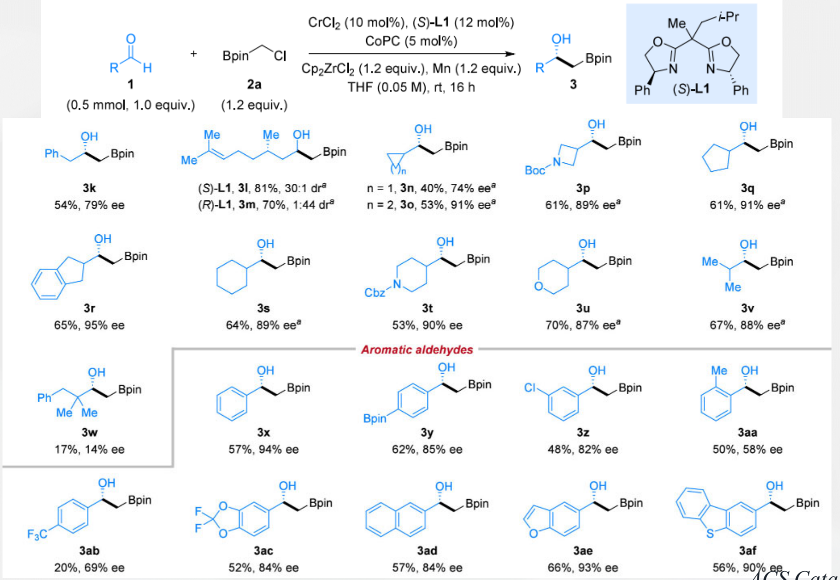
Cu-catalyzed carbonyl addition: proceed *via* ionic pathway

Transformation of chiral substrates: selective mono-oxidation of 1,2-bisboronates

- 铜催化α-硼烷基铜中间体对羰基化合物的不对称加成；
- 手性1, 2-二硼酸酯的选择性氧化。

ACS Catal. **2025**, *15*, 8454

*Cr Catalysis.*基于三催化循环的消旋联烯与醛的对映汇聚式还原偶联反应



1 (0.5 mmol, 1.0 equiv.) + **2a** (1.2 equiv.)

$CrCl_2$ (10 mol%), (*S*)-**L1** (12 mol%)
CoPC (5 mol%)
Cp_2ZrCl_2 (1.2 equiv.), Mn (1.2 equiv.)
THF (0.05 M), rt, 16 h

→ **3**

3k 54%, 79% ee

(*S*)-**L1**, **3l**, 81%, 30:1 dr[a]
(*R*)-**L1**, **3m**, 70%, 1:44 dr[a]

n = 1, **3n**, 40%, 74% ee[a]
n = 2, **3o**, 53%, 91% ee[a]

3p 61%, 89% ee[a]

3q 61%, 91% ee[a]

3r 65%, 95% ee

3s 64%, 89% ee[a]

3t 53%, 90% ee

3u 70%, 87% ee[a]

3v 67%, 88% ee[a]

3w 17%, 14% ee

3x 57%, 94% ee

3y 62%, 85% ee

3z 48%, 82% ee

3aa 50%, 58% ee

3ab 20%, 69% ee

3ac 52%, 84% ee

3ad 57%, 84% ee

3ae 66%, 93% ee

3af 56%, 90% ee

- 对空间位阻敏感
- 富电子芳香醛虽然能形成所需产物，但在硅胶纯化过程中容易分解

ACS Catal. **2025**, *15*, 8454

Cr Catalysis: 基于三催化循环的消旋联烯与醛的对映汇聚式还原偶联反应

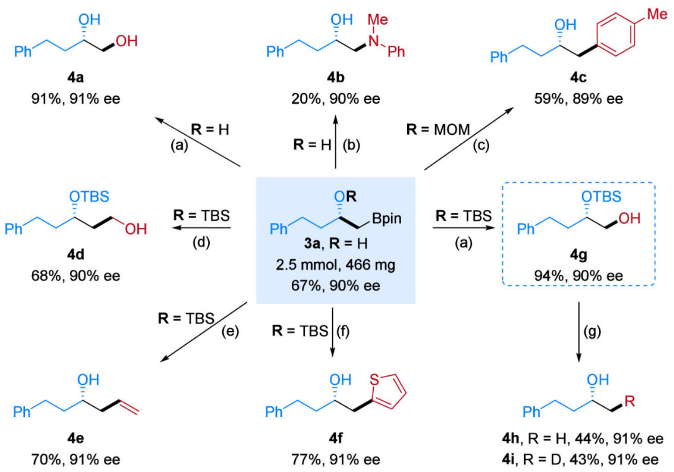
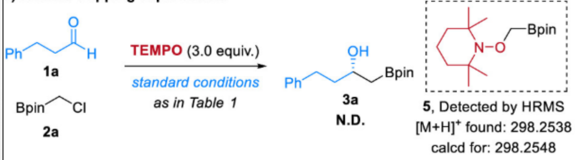


Figure 3. Product derivatization. Legend: (a) $NaBO_3 \cdot 4H_2O$, THF/H_2O, rt, 1 h; (b) $Cu(OAc)_2$, *N*-methylaniline, $(t\text{-}BuO)_2$, *m*-xylene, 100 °C, 24 h; (c) $Pd_2(dba)_3$, RuPhos, 4-bromotoluene, *t*-BuOK, $THF/PhCH_3/H_2O$, 70 °C, 24 h, then HCl, MeOH, 65 °C, 30 min; (d) CH_2Br_2, *n*-BuLi, THF, −78 °C to rt, 14 h, then $NaBO_3 \cdot 4H_2O$, THF/H_2O, rt, 1 h; (e) vinylmagnesium bromide, I_2, NaOMe, THF/DMSO, 0 °C, 1 h, then TBAF, 50 °C, 4 h; (f) thiophene, *n*-BuLi, NBS, THF, −78 °C, 2.5 h, then TBAF, 50 °C, 4 h; (g) TsCl, Et_3N, DMAP, DCM, rt, 16 h, then $LiAlH_4$ or $LiAlD_4$, THF, 0 °C to rt, 12 h, and then TBAF, 50 °C, 4 h.

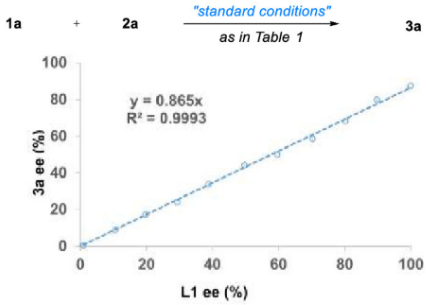
ACS Catal. **2025**, *15*, 8454

Cr Catalysis:基于三催化循环的消旋联烯与醛的对映汇聚式还原偶联反应

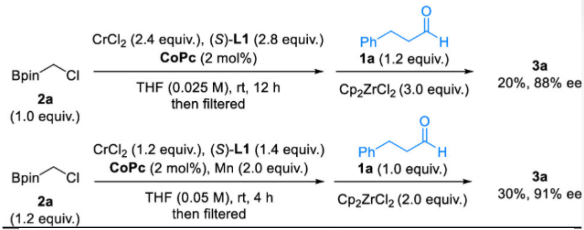
a) Radical trapping experiments

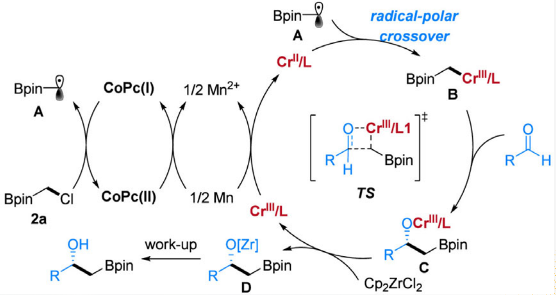


b) Non-linear effect



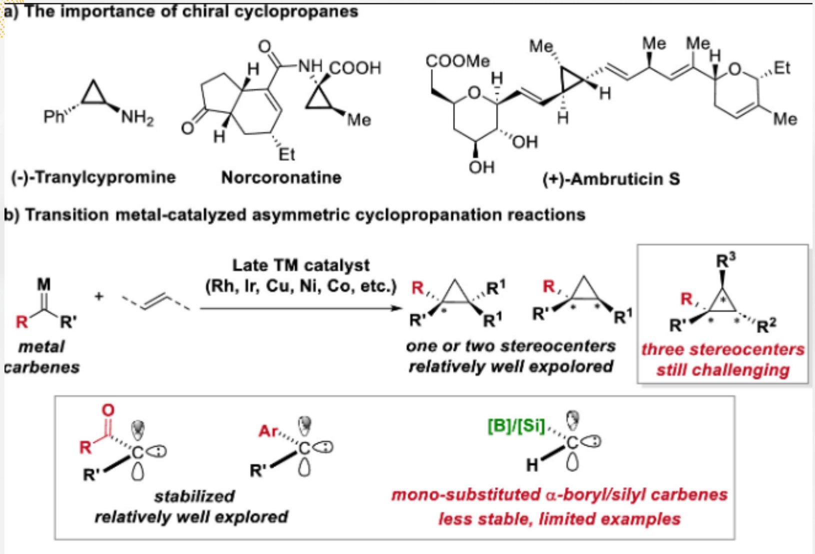
c) Control experiment with stoichiometric amounts of Cr/L1





ACS Catal. **2025**, *15*, 8454

Cr Catalysis:α,β-不饱和酰胺的不对称自由基环丙烷化反应



环丙烷是一类具有刚性三维结构的三元环化合物，因其独特的结构和化学性质，在药物化学中具有重要的应用价值。环丙烷的存在可以显著增强生物活性分子的结合亲和力和特异性，这使得它们在药物发现和开发中备受关注。

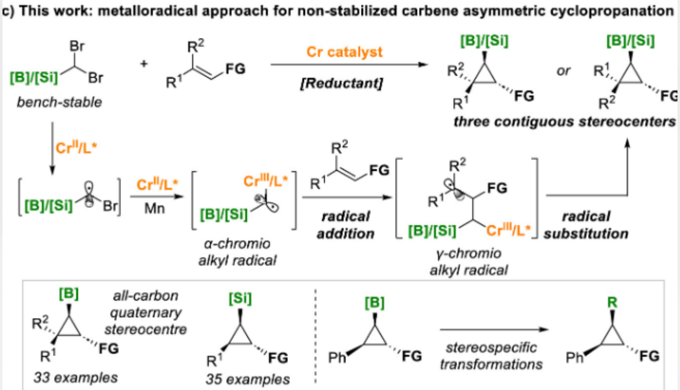
卡宾转移反应是合成环丙烷的经典方法之一。过渡金属催化的不对称卡宾转移反应因其高效性和立体选择性而成为合成手性环丙烷的重要策略。这类反应通常依赖于过渡金属催化剂（如铜、铑、铱等）和稳定的卡宾中间体（如α－π－共轭的卡宾前体）。

J. Am. Chem. Soc. **2025**, *147*, 7282

*Cr Catalysis.*α,β-不饱和酰胺的不对称自由基环丙烷化反应

局限性：

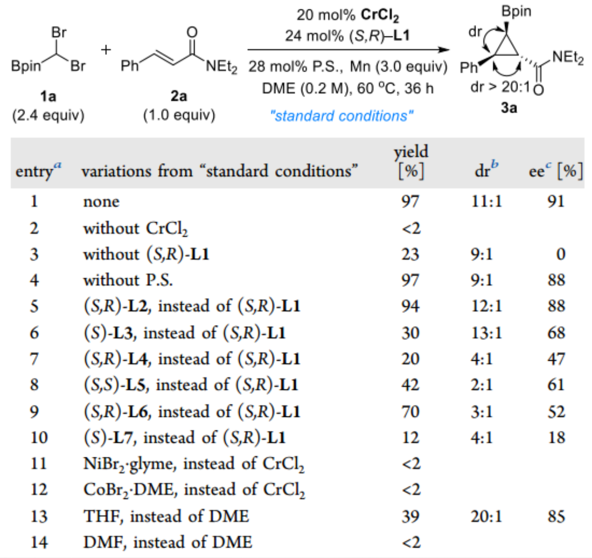
- 依赖于稳定的卡宾前体：大多数方法需要使用α-π-共轭的卡宾前体（如α-取代的重氮化合物），这限制了对非共轭的α-硅基和α-硼基卡宾的合成能力。
- 合成手性环丙烷的挑战：尽管已有许多方法可以合成具有一个或两个立体中心的环丙烷，但合成具有三个连续立体中心的环丙烷仍然是一个未被充分探索的领域。
- 反应条件的限制：许多现有方法需要高温或强碱等苛刻条件，限制了其在复杂底物中的应用。

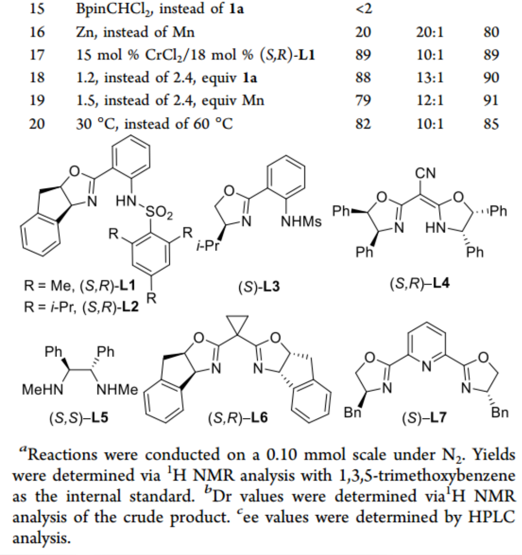


c) This work: metalloradical approach for non-stabilized carbene asymmetric cyclopropanation

J. Am. Chem. Soc. **2025**, *147*, 7282

Cr Catalysis:α,β-不饱和酰胺的不对称自由基环丙烷化反应



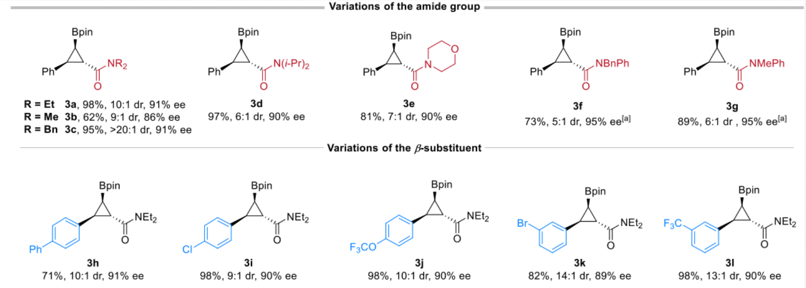


entry[a]	variations from "standard conditions"	yield [%]	dr[b]	ee[c] [%]
1	none	97	11:1	91
2	without $CrCl_2$	<2		
3	without (*S,R*)-**L1**	23	9:1	0
4	without P.S.	97	9:1	88
5	(*S,R*)-**L2**, instead of (*S,R*)-**L1**	94	12:1	88
6	(*S*)-**L3**, instead of (*S,R*)-**L1**	30	13:1	68
7	(*S,R*)-**L4**, instead of (*S,R*)-**L1**	20	4:1	47
8	(*S,S*)-**L5**, instead of (*S,R*)-**L1**	42	2:1	61
9	(*S,R*)-**L6**, instead of (*S,R*)-**L1**	70	3:1	52
10	(*S*)-**L7**, instead of (*S,R*)-**L1**	12	4:1	18
11	$NiBr_2$·glyme, instead of $CrCl_2$	<2		
12	$CoBr_2$·DME, instead of $CrCl_2$	<2		
13	THF, instead of DME	39	20:1	85
14	DMF, instead of DME	<2		
15	$BpinCHCl_2$, instead of **1a**	<2		
16	Zn, instead of Mn	20	20:1	80
17	15 mol % $CrCl_2$/18 mol % (*S,R*)-**L1**	89	10:1	89
18	1.2, instead of 2.4, equiv **1a**	88	13:1	90
19	1.5, instead of 2.4, equiv Mn	79	12:1	91
20	30 °C, instead of 60 °C	82	10:1	85

[a]Reactions were conducted on a 0.10 mmol scale under N_2. Yields were determined via ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard. [b]Dr values were determined via ^{1}H NMR analysis of the crude product. [c]ee values were determined by HPLC analysis.

J. Am. Chem. Soc. **2025**, *147*, 7282

Cr Catalysis.α,β-不饱和酰胺的不对称自由基环丙烷化反应



R = Et **3a**, 98%, 10:1 dr, 91% ee
R = Me **3b**, 62%, 9:1 dr, 86% ee
R = Bn **3c**, 95%, >20:1 dr, 91% ee

3d 97%, 6:1 dr, 90% ee

3e 81%, 7:1 dr, 90% ee

3f 73%, 5:1 dr, 95% ee[a]

3g 89%, 6:1 dr , 95% ee[a]

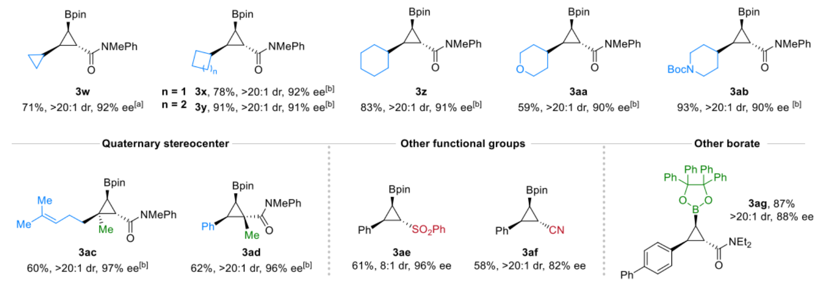
3h 71%, 10:1 dr, 91% ee

3i 98%, 9:1 dr, 90% ee

3j 98%, 10:1 dr, 90% ee

3k 82%, 14:1 dr, 89% ee

3l 98%, 13:1 dr, 90% ee



3w 71%, >20:1 dr, 92% ee[a]

n = 1 **3x**, 78%, >20:1 dr, 92% ee[b]
n = 2 **3y**, 91%, >20:1 dr, 91% ee[b]

3z 83%, >20:1 dr, 91% ee[b]

3aa 59%, >20:1 dr, 90% ee[b]

3ab 93%, >20:1 dr, 90% ee [b]

3ac 60%, >20:1 dr, 97% ee[b]

3ad 62%, >20:1 dr, 96% ee[b]

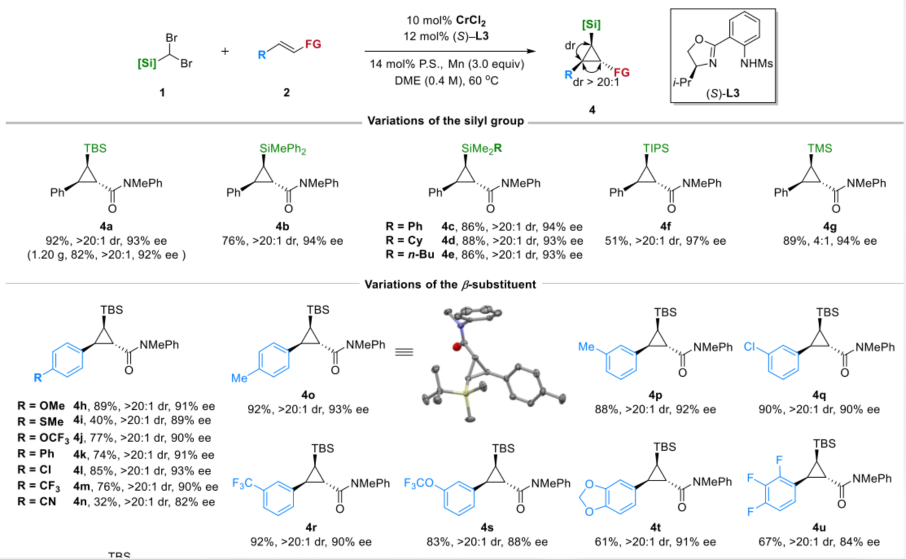
3ae 61%, 8:1 dr, 96% ee

3af 58%, >20:1 dr, 82% ee

3ag, 87%
>20:1 dr, 88% ee

J. Am. Chem. Soc. **2025**, *147*, 7282

Cr Catalysis:α,β-不饱和酰胺的不对称自由基环丙烷化反应



J. Am. Chem. Soc. **2025**, *147*, 7282

Cr Catalysis:α,β-不饱和酰胺的不对称自由基环丙烷化反应

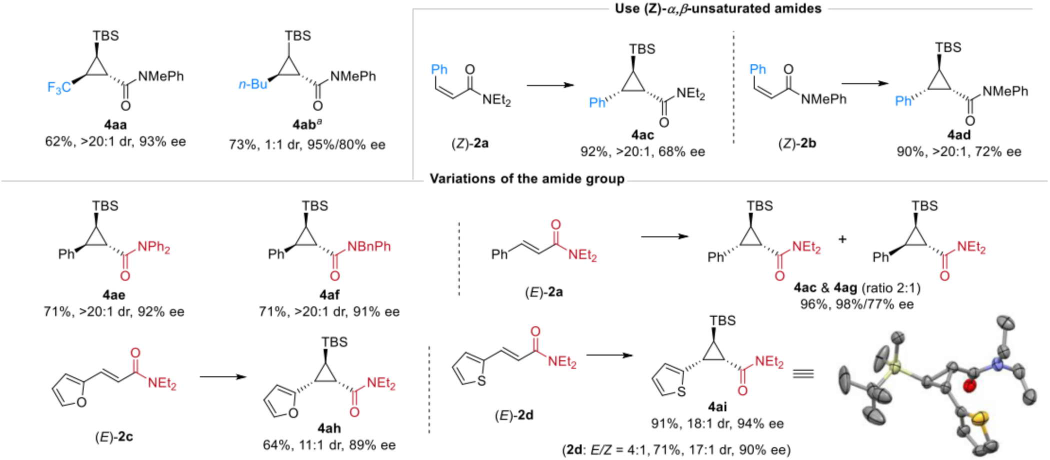
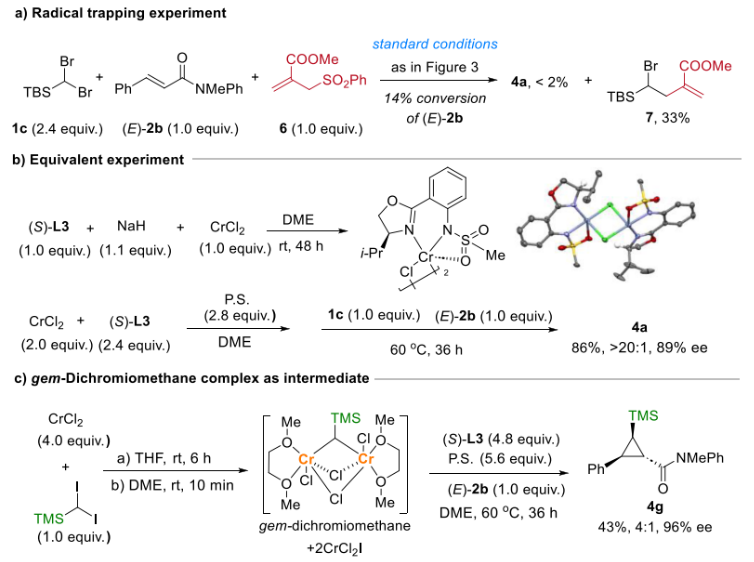


Figure 3. Substrate scope for the cyclopropanation of silyl dibromomethanes. Reactions were conducted on a 0.20 mmol scale, and all data were the average of two experiments. Dr values were determined by ^{1}H NMR analysis of crude products. ee values were determined by HPLC or SFC analysis. [a]20 mol % $CrCl_2$, 24 mol % (*S*)-**L3**, 28 mol % P.S.

J. Am. Chem. Soc. **2025**, *147*, 7282

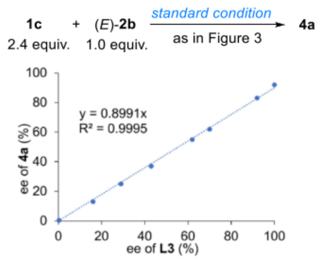
Cr Catalysis:α,β-不饱和酰胺的不对称自由基环丙烷化反应



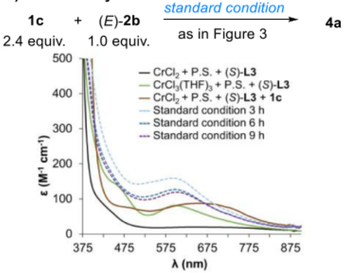
J. Am. Chem. Soc. **2025**, *147*, 7282

Cr Catalysis: α,β-不饱和酰胺的不对称自由基环丙烷化反应

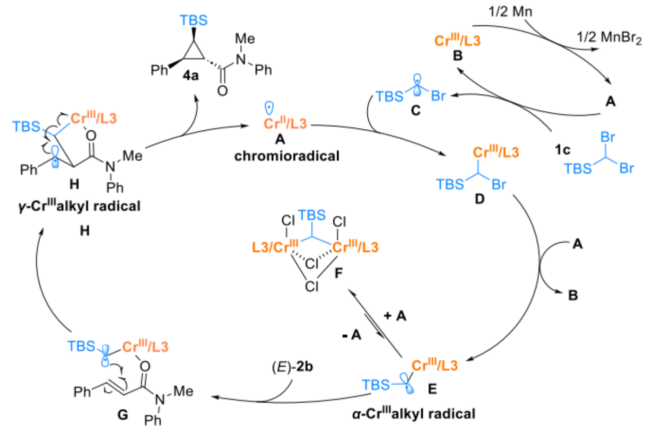
d) Nonlinear effect



e) UV-vis study

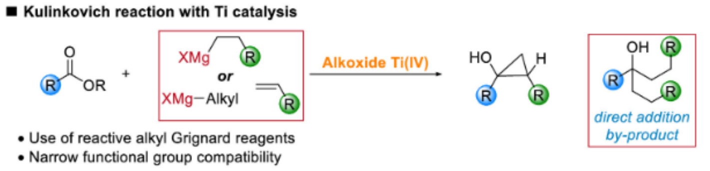


f) Proposed mechanism

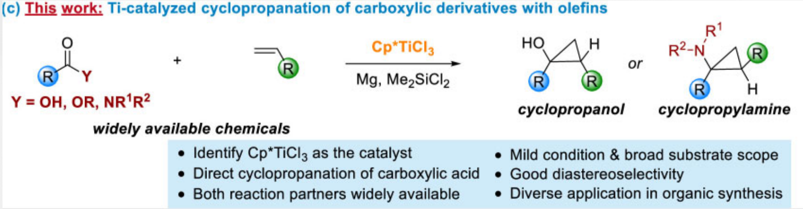


J. Am. Chem. Soc. **2025**, *147*, 7282

Ti Catalysis.钛催化实现羧酸衍生物和末端烯烃的非对映选择性环丙烷化反应

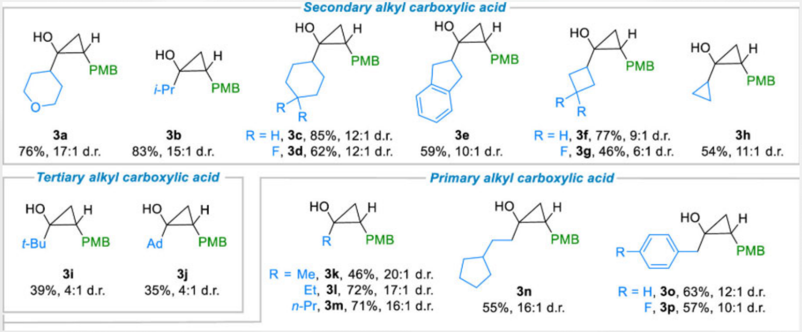


Kulinkovich反应 (库林科维奇反应) 是一种简洁高效合成环丙醇的方法。该反应是由Kulinkovich 等人在1989年报道，在烷氧基钛介导下以羧酸酯和烷基格式试剂为底物合成相应的环丙醇。虽然后续有一定的研究改进，但是该反应体系中需要使用当量的高活性烷基格式试剂，这导致反应的官能团兼容性较差。此外，该反应操作较为繁琐，需要使用注射泵缓慢滴加烷基格式试剂减少副产物生成和提高反应收率。鉴于此，开发原料简单易得，条件温和、官能团兼容性良好且操作便捷的高效环丙烷化反应具有非常重要的意义。



J. Am. Chem. Soc. **2022**, *144*, 7889

*Ti Catalysis:*钛催化实现羧酸衍生物和末端烯烃的非对映选择性环丙烷化反应



Secondary alkyl carboxylic acid

3a 76%, 17:1 d.r.

3b 83%, 15:1 d.r.

R = H, **3c**, 85%, 12:1 d.r.
F, **3d**, 62%, 12:1 d.r.

3e 59%, 10:1 d.r.

R = H, **3f**, 77%, 9:1 d.r.
F, **3g**, 46%, 6:1 d.r.

3h 54%, 11:1 d.r.

Tertiary alkyl carboxylic acid

3i 39%, 4:1 d.r.

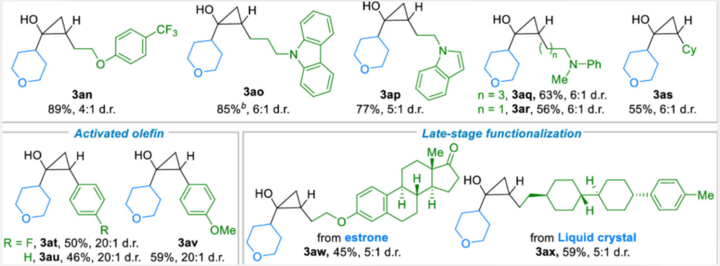
3j 35%, 4:1 d.r.

Primary alkyl carboxylic acid

R = Me, **3k**, 46%, 20:1 d.r.
Et, **3l**, 72%, 17:1 d.r.
n-Pr, **3m**, 71%, 16:1 d.r.

3n 55%, 16:1 d.r.

R = H, **3o**, 63%, 12:1 d.r.
F, **3p**, 57%, 10:1 d.r.



3an 89%, 4:1 d.r.

3ao 85%[b], 6:1 d.r.

3ap 77%, 5:1 d.r.

n = 3, **3aq**, 63%, 6:1 d.r.
n = 1, **3ar**, 56%, 6:1 d.r.

3as 55%, 6:1 d.r.

Activated olefin

R = F, **3at**, 50%, 20:1 d.r.
H, **3au**, 46%, 20:1 d.r.

3av 59%, 20:1 d.r.

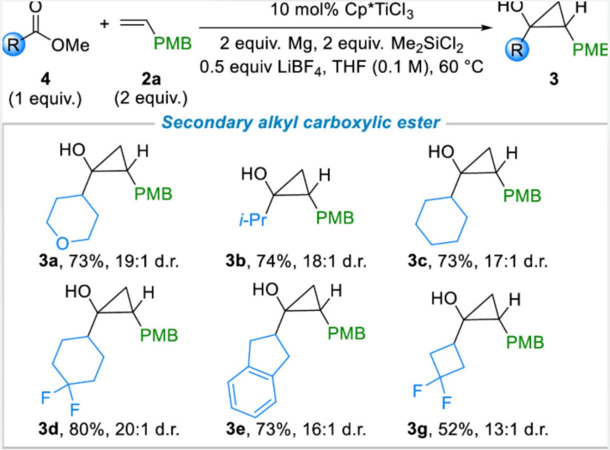
Late-stage functionalization

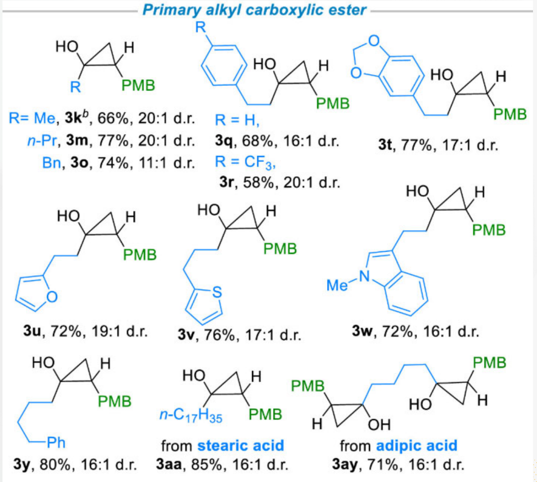
from estrone
3aw, 45%, 5:1 d.r.

from Liquid crystal
3ax, 59%, 5:1 d.r.

J. Am. Chem. Soc. **2022**, *144*, 7889

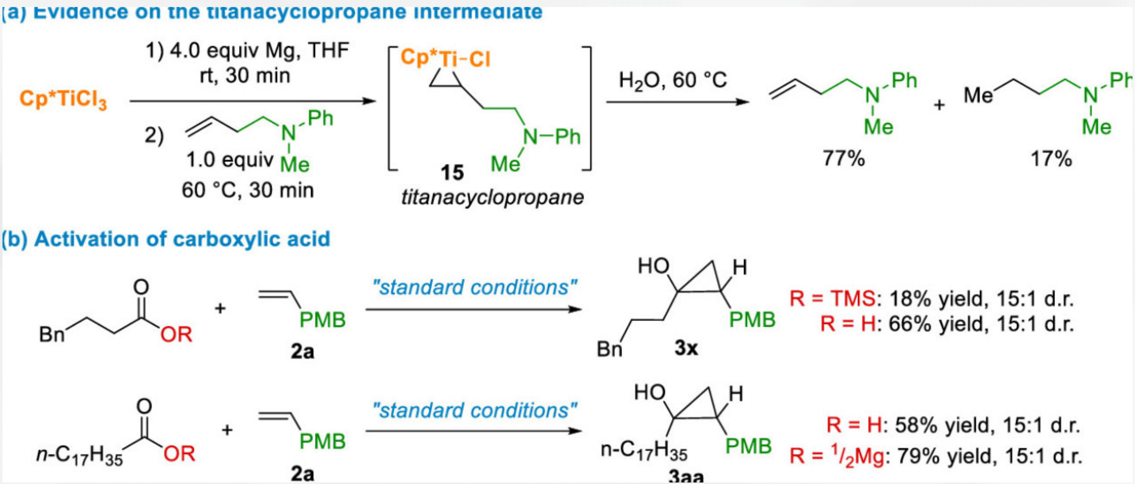
Ti Catalysis:钛催化实现羧酸衍生物和末端烯烃的非对映选择性环丙烷化反应





J. Am. Chem. Soc. **2022**, *144*, 7889

Ti Catalysis:钛催化实现羧酸衍生物和末端烯烃的非对映选择性环丙烷化反应

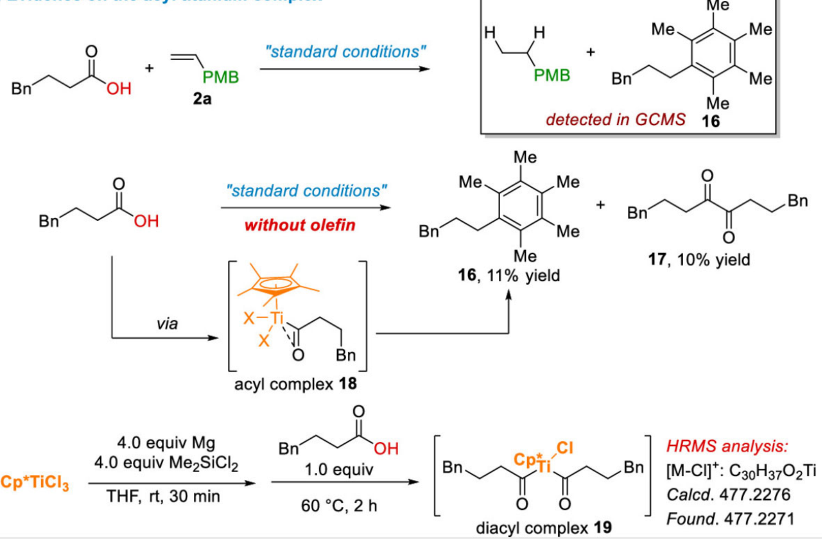


J. Am. Chem. Soc. **2022**, *144*, 7889

Ti Catalysis:钛催化实现羧酸衍生物和末端烯烃的非对映选择性环丙烷化反应

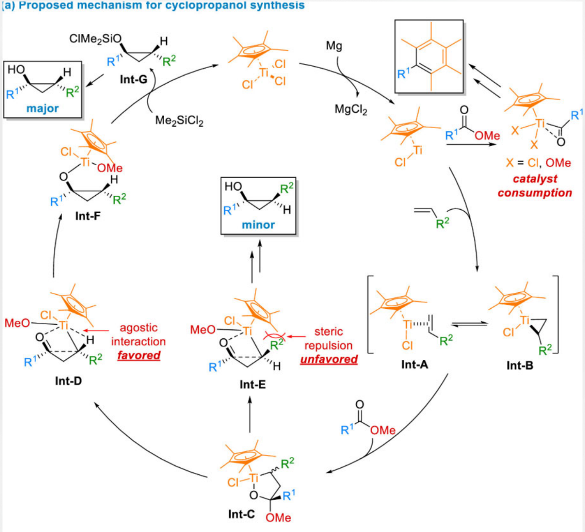
The Yang Research Group
Precise Synthesis Lab at Tongji University

(c) Evidence on the acyl titanium complex



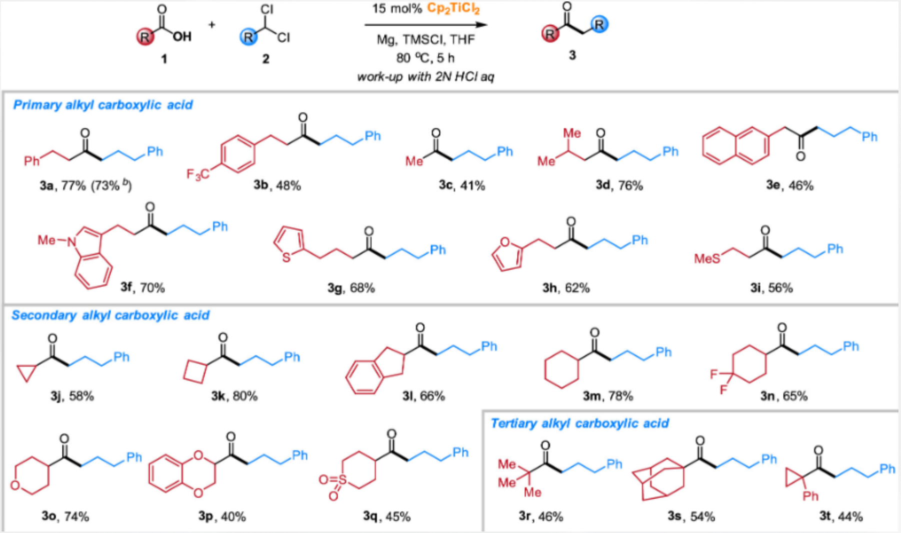
J. Am. Chem. Soc. **2022**, *144*, 7889

Ti Catalysis:钛催化实现羧酸衍生物和末端烯烃的非对映选择性环丙烷化反应


(a) Proposed mechanism for cyclopropanol synthesis

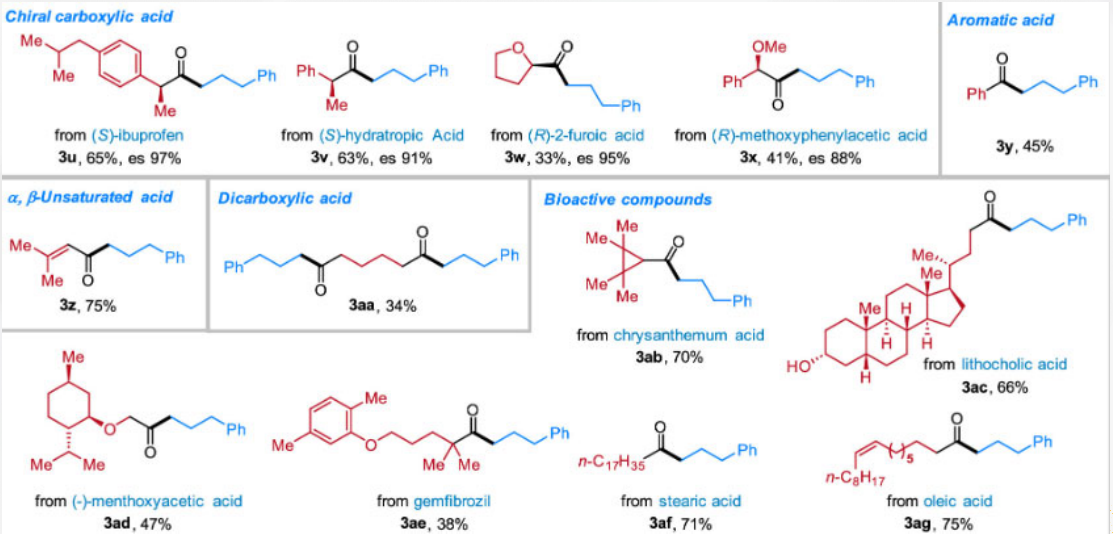
J. Am. Chem. Soc. **2022**, *144*, 7889

Ti Catalysis:钛催化实现从羧酸及其衍生物和偕二卤代烷烃到酮类产物的模块化合成



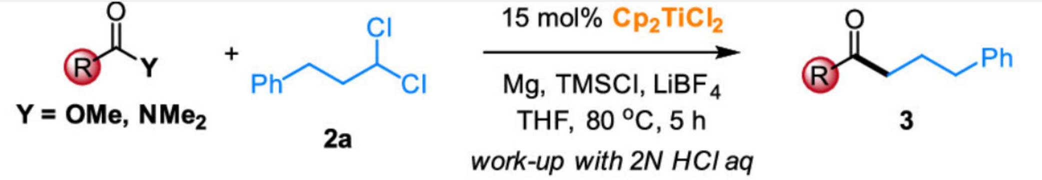
J. Am. Chem. Soc. **2023**, *145*, 14884

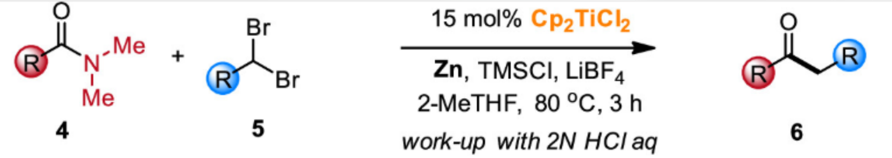
Ti Catalysis:钛催化实现从羧酸及其衍生物和偕二卤代烷烃到酮类产物的模块化合成

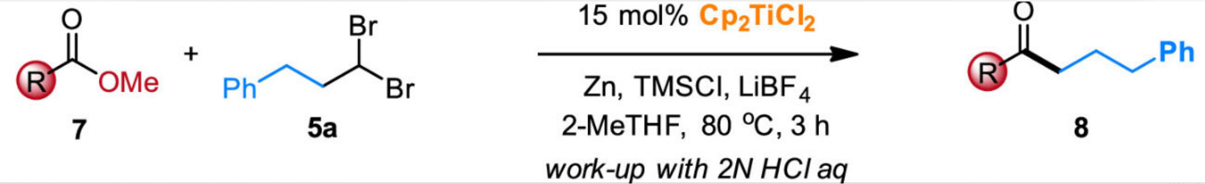


J. Am. Chem. Soc. **2023**, *145*, 14884

Ti Catalysis:钛催化实现从羧酸及其衍生物和偕二卤代烷烃到酮类产物的模块化合成

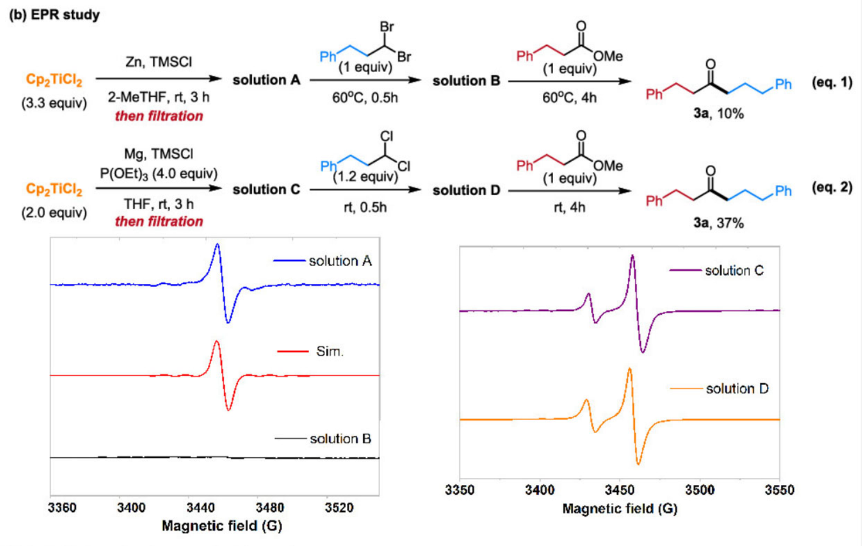






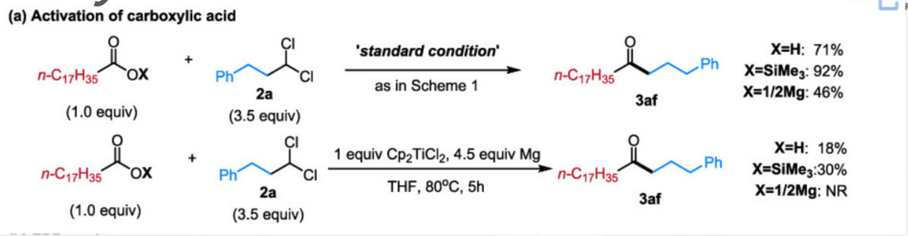
J. Am. Chem. Soc. **2023**, *145*, 14884

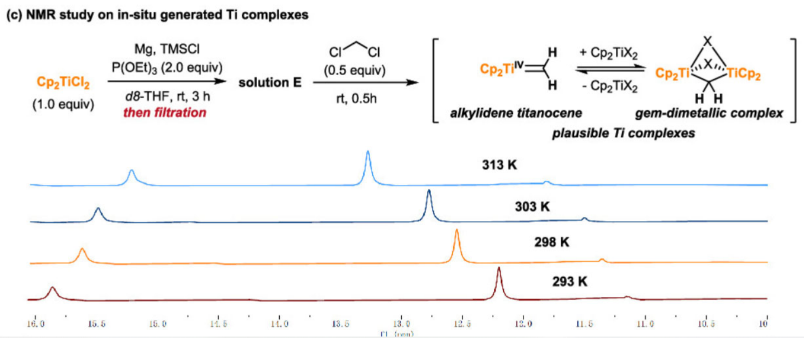
Ti Catalysis:钛催化实现从羧酸及其衍生物和偕二卤代烷烃到酮类产物的模块化合成



J. Am. Chem. Soc. **2023**, *145*, 14884

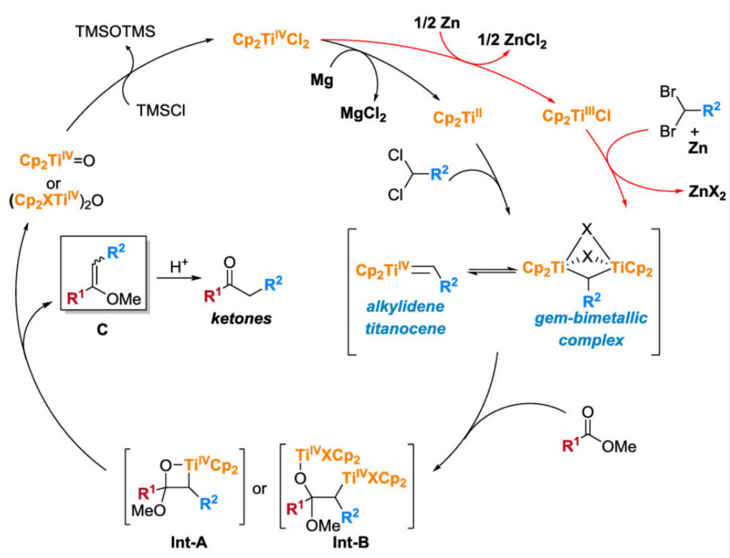
Ti Catalysis:钛催化实现从羧酸及其衍生物和偕二卤代烷烃到酮类产物的模块化合成


(a) Activation of carboxylic acid


(c) NMR study on in-situ generated Ti complexes

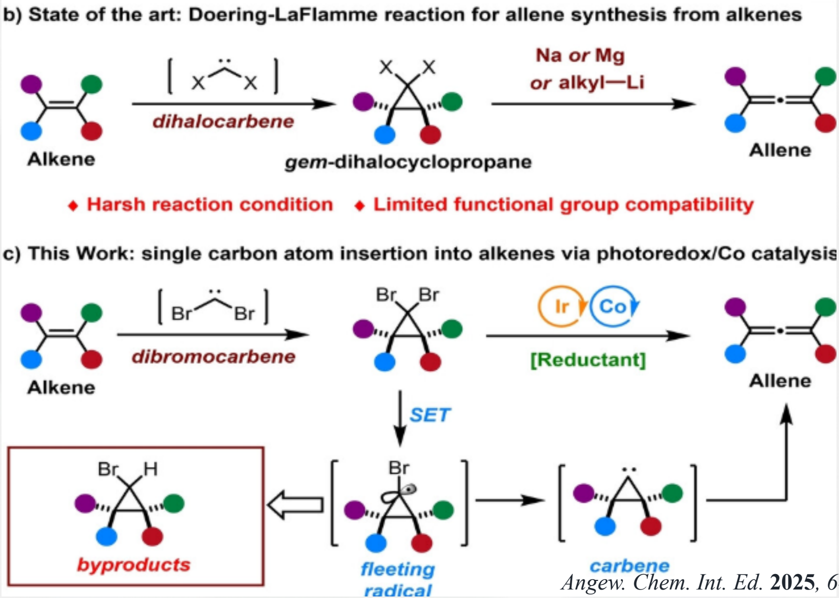
J. Am. Chem. Soc. **2023**, *145*, 14884

Ti Catalysis:钛催化实现从羧酸及其衍生物和偕二卤代烷烃到酮类产物的模块化合成



J. Am. Chem. Soc. **2023**, *145*, 14884

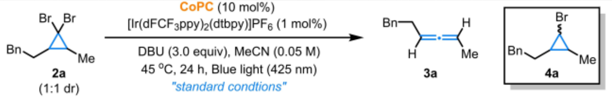
Co Catalysis:金属光氧化还原催化碳原子插入烯烃合成联烯


b) State of the art: Doering-LaFlamme reaction for allene synthesis from alkenes

c) This Work: single carbon atom insertion into alkenes via photoredox/Co catalysis

Angew. Chem. Int. Ed. **2025**, *64*, e202418746

Co Catalysis:金属光氧化还原催化碳原子插入烯烃合成联烯

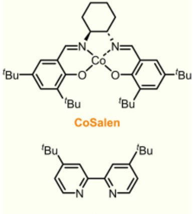


2a
(1:1 dr)
3a
4a

Entry	*Variations of "standard condtions"*	Conv. (%)^a	3a (%)^a	4a (%)^a
1	none	>95	90	<1
2	w/o CoPC, **[Ir]**, light	--	<2	70, <1, <1
3	Vitamin B_{12}, instead of CoPC	29	9	15
4	CoTPP, instead of CoPC	>95	34	44
5	Co(salen), instead of CoPC	>95	86	8
6	$CoBr_2$/dtbbpy, instead of CoPC	>95	<2	76
7	FePC, instead of CoPC	>95	69	12
8	NiPC, instead of CoPC	92	<2	67
9	CuPC, instead of CoPC	89	22	30
10	$Ir(ppy)_3$, instead of **[Ir]**	65	6	44
11	4-CzIPN, instead of **[Ir]**	92	81	7
12	HE, instead of DBU	>95	<2	91
13	DIPEA, instead of DBU	92	64	23
14	THF, instead of MeCN	46	24	15
15	DCE, instead of MeCN	<5	<2	<1
16	DMF, instead of MeCN	85	61	11
17	strictly degassed MeCN	>95	87	<1
18	rt, instead of 45°C	84	75	<1
19	60 °C, instead of 45°C	>95	76	<1
20	0.10 M, instead of 0.05M, in MeCN	90	78	<1
21	0.03 M, instead of 0.05M, in MeCN	>95	86	<1
22	with 2.0 equiv H_2O	10	<2	<1
23	with 2.0 mL air, added *via* syringe	71	53	9
24	36 h, instead of 24 h	>95	77	<1

M = Co, CoPC
M = Fe, FePC
M = Cu, CuPC
M = Ni, NiPC

CoTPP



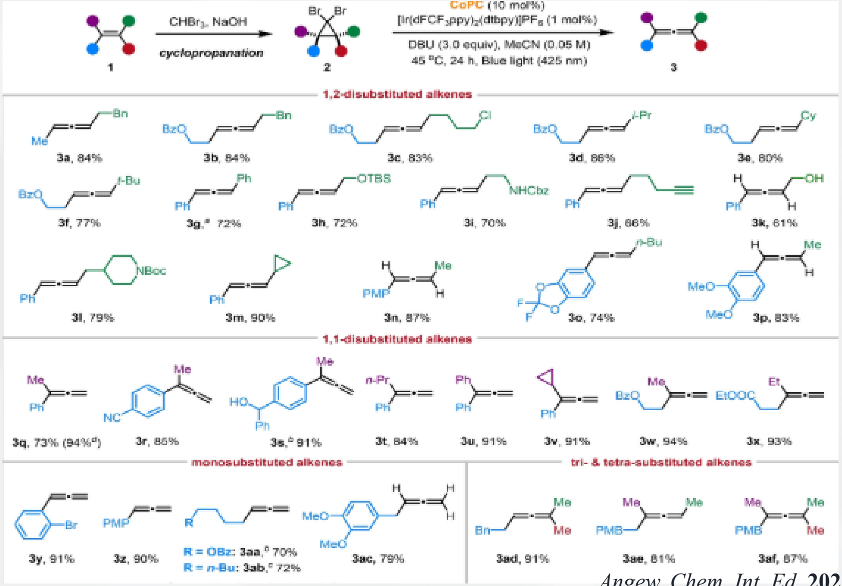
CoSalen

Dtbbpy

Standard reaction conditions: **2a** (0.1 mmol, 1 equiv.), CoPC (10 mol%), $[Ir(dFCF_3ppy)_2(dtbpy)]$ (1 mol%), DBU (3.0 equiv.) in MeCN (2 mL, 0.05 M) upon Blue LEDs (425 nm, 15 W) irradiation for 24 h under N_2 at 45 °C. ^{a} Yields were determined by GC analysis with *n*-dodecane as the internal standard.

Angew. Chem. Int. Ed. **2025**, *64*, e202418746

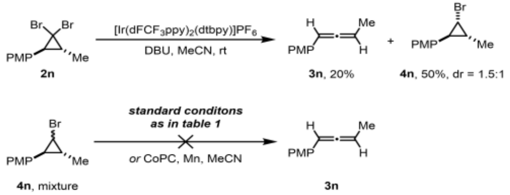
Co Catalysis:金属光氧化还原催化碳原子插入烯烃合成联烯



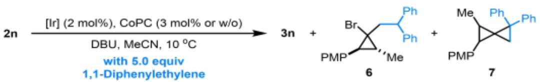
Angew. Chem. Int. Ed. **2025**, *64*, e202418746

Co Catalysis:金属光氧化还原催化碳原子插入烯烃合成联烯

a) Control experiments

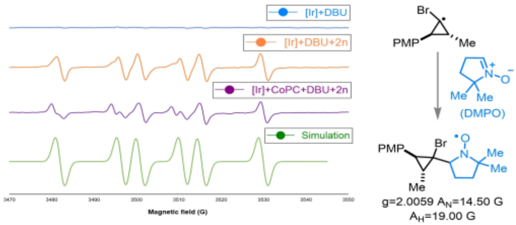


b) Radical trapping experiments



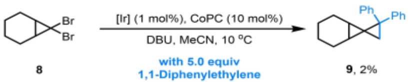
Entry	CoPC	3n	6	7
1	w/o	8%	12%	-
2	3 mol%	41%	2%	-

c) EPR study



g=2.0059 A_N=14.50 G
A_H=19.00 G

d) Carbene or carbenoid trapping experiments

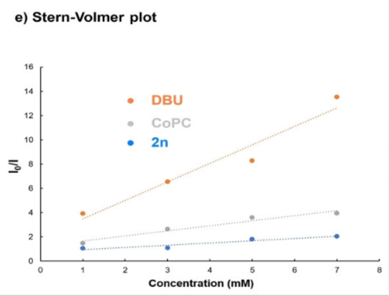


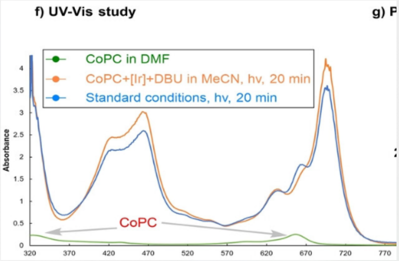
Possible intermediate

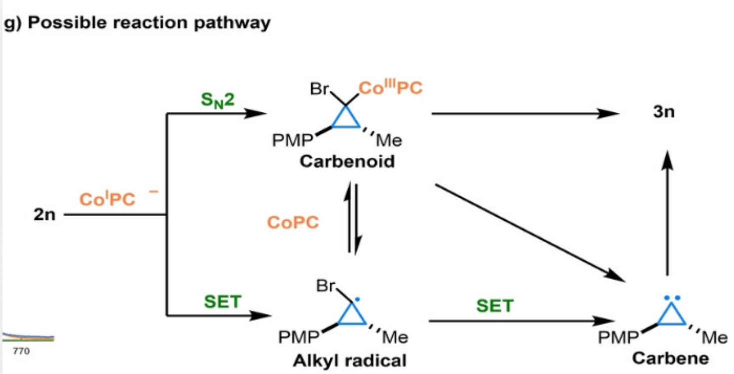
Carbene
Carbenoid
Metalloradical

Angew. Chem. Int. Ed. **2025**, *64*, e202418746

Co Catalysis:金属光氧化还原催化碳原子插入烯烃合成联烯


e) Stern-Volmer plot

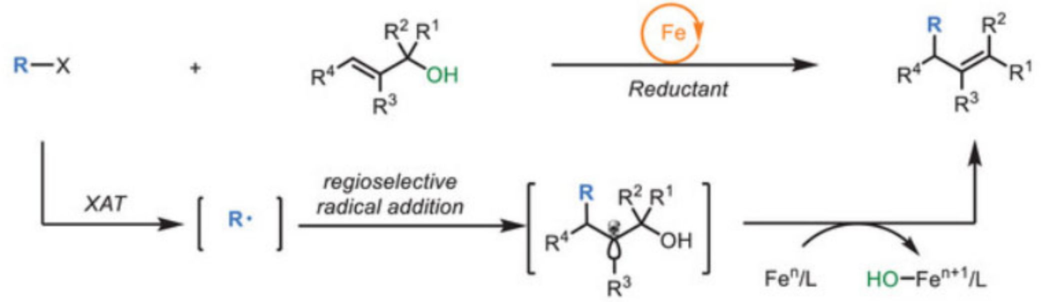

f) UV-Vis study


g) Possible reaction pathway

Angew. Chem. Int. Ed. **2025**, *64*, e202418746

*Fe Catalysis:*铁催化未保护烯丙醇的自由基烯丙基取代反应

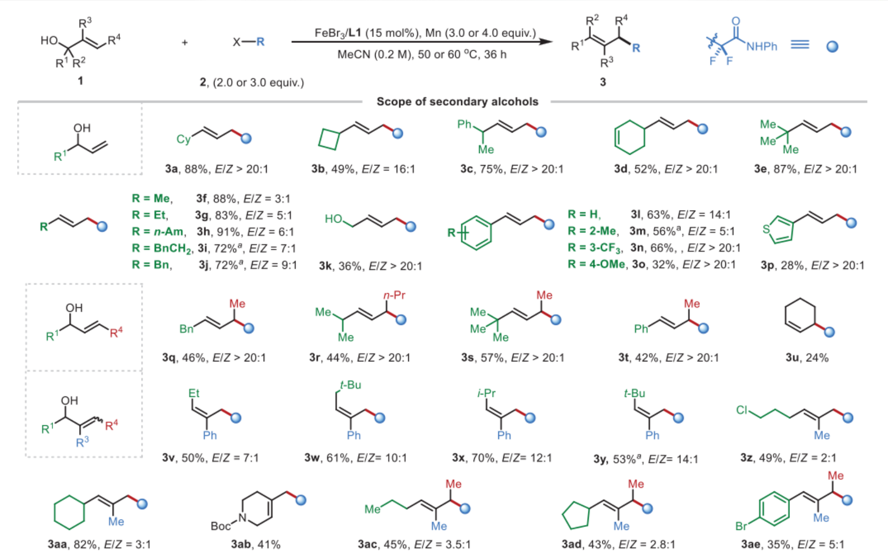
d) **This work: Fe-catalyzed homolytic substitution of unactivated allylic alcohols**



□ Good regioselectivity control □ Iron promoted hydroxyl transfer □ Moderate to excellent *E/Z* selectivity contro

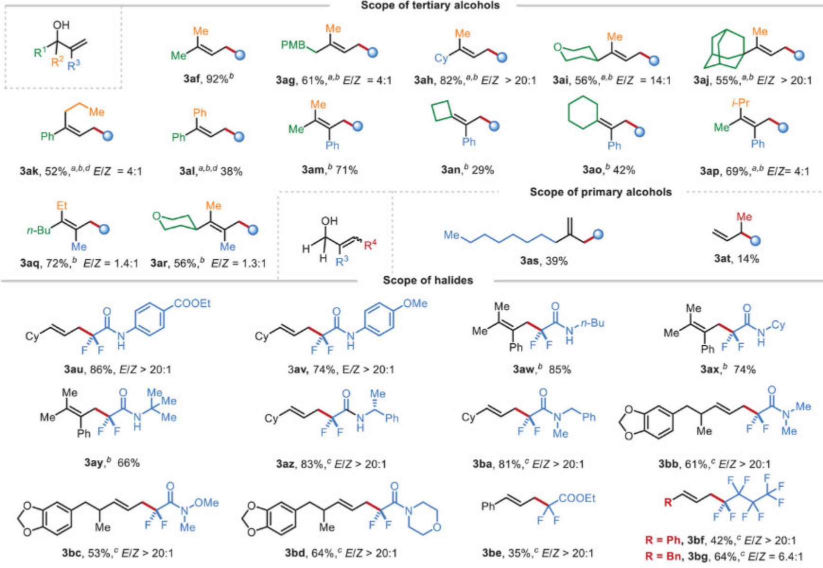
Angew. Chem. Int. Ed. **2025**, e202500781

*Fe Catalysis:*铁催化未保护烯丙醇的自由基烯丙基取代反应



Angew. Chem. Int. Ed. **2025**, e202500781

Fe Catalysis:铁催化未保护烯丙醇的自由基烯丙基取代反应



Scope of tertiary alcohols

3af, 92%[b]
3ag, 61%,[a,b] *E/Z* = 4:1
3ah, 82%,[a,b] *E/Z* > 20:1
3ai, 56%,[a,b] *E/Z* = 14:1
3aj, 55%,[a,b] *E/Z* > 20:1
3ak, 52%,[a,b,d] *E/Z* = 4:1
3al,[a,b,d] 38%
3am,[b] 71%
3an,[b] 29%
3ao,[b] 42%
3ap, 69%,[a,b] *E/Z*= 4:1
3aq, 72%,[b] *E/Z* = 1.4:1
3ar, 56%,[b] *E/Z* = 1.3:1

Scope of primary alcohols

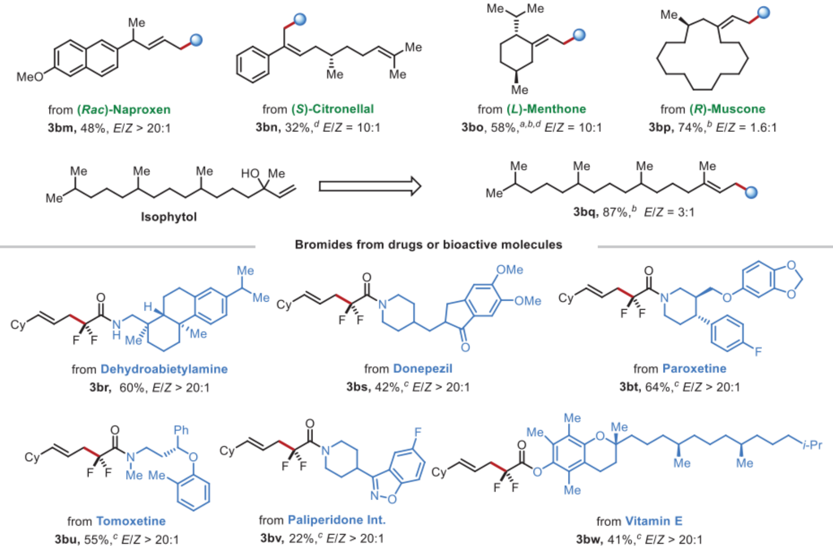
3as, 39%
3at, 14%

Scope of halides

3au, 86%, *E/Z* > 20:1
3av, 74%, *E/Z* > 20:1
3aw,[b] 85%
3ax,[b] 74%
3ay,[b] 66%
3az, 83%,[c] *E/Z* > 20:1
3ba, 81%,[c] *E/Z* > 20:1
3bb, 61%,[c] *E/Z* > 20:1
3bc, 53%,[c] *E/Z* > 20:1
3bd, 64%,[c] *E/Z* > 20:1
3be, 35%,[c] *E/Z* > 20:1
R = Ph, **3bf**, 42%,[c] *E/Z* > 20:1
R = Bn, **3bg**, 64%,[c] *E/Z* = 6.4:1

Angew. Chem. Int. Ed. **2025**, e202500781

*Fe Catalysis:*铁催化未保护烯丙醇的自由基烯丙基取代反应



from (*Rac*)-Naproxen
3bm, 48%, *E*/*Z* > 20:1

from (*S*)-Citronellal
3bn, 32%,[d] *E*/*Z* = 10:1

from (*L*)-Menthone
3bo, 58%,[a,b,d] *E*/*Z* = 10:1

from (*R*)-Muscone
3bp, 74%,[b] *E*/*Z* = 1.6:1

3bq, 87%,[b] *E*/*Z* = 3:1

Bromides from drugs or bioactive molecules

from **Dehydroabietylamine**
3br, 60%, *E*/*Z* > 20:1

from **Donepezil**
3bs, 42%,[c] *E*/*Z* > 20:1

from **Paroxetine**
3bt, 64%,[c] *E*/*Z* > 20:1

from **Tomoxetine**
3bu, 55%,[c] *E*/*Z* > 20:1

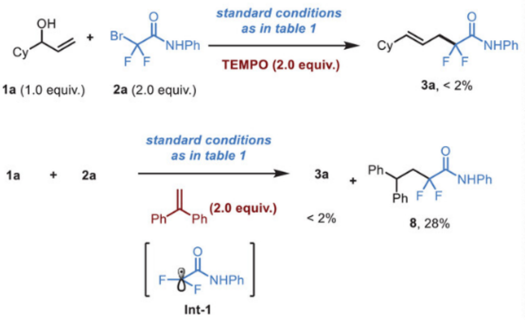
from **Paliperidone Int.**
3bv, 22%,[c] *E*/*Z* > 20:1

from **Vitamin E**
3bw, 41%,[c] *E*/*Z* > 20:1

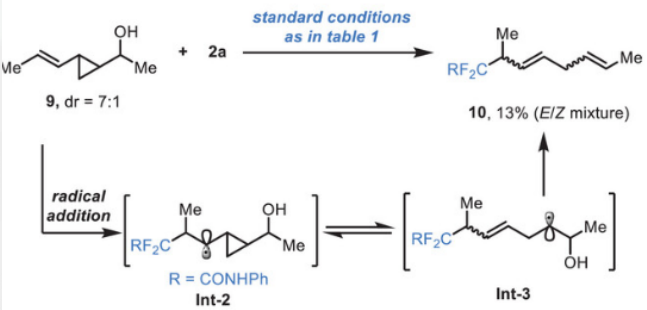
Angew. Chem. Int. Ed. **2025**, e202500781

*Fe Catalysis:*铁催化未保护烯丙醇的自由基烯丙基取代反应

a) Radical trapping experiments

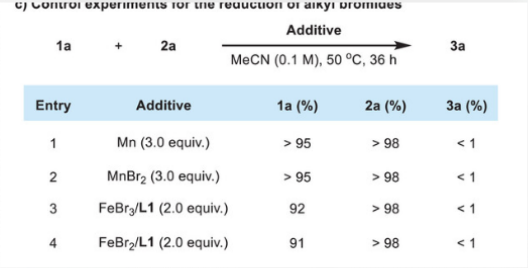


b) Radical clock experiment



Angew. Chem. Int. Ed. **2025**, e202500781

Fe Catalysis:铁催化未保护烯丙醇的自由基烯丙基取代反应

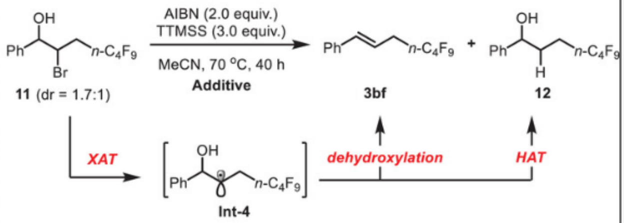


c) Control experiments for the reduction of alkyl bromides

$$\mathbf{1a} + \mathbf{2a} \xrightarrow[\text{MeCN (0.1 M), 50 °C, 36 h}]{\textbf{Additive}} \mathbf{3a}$$

Entry	Additive	1a (%)	2a (%)	3a (%)
1	Mn (3.0 equiv.)	> 95	> 98	< 1
2	$MnBr_2$ (3.0 equiv.)	> 95	> 98	< 1
3	$FeBr_3$/**L1** (2.0 equiv.)	92	> 98	< 1
4	$FeBr_2$/**L1** (2.0 equiv.)	91	> 98	< 1

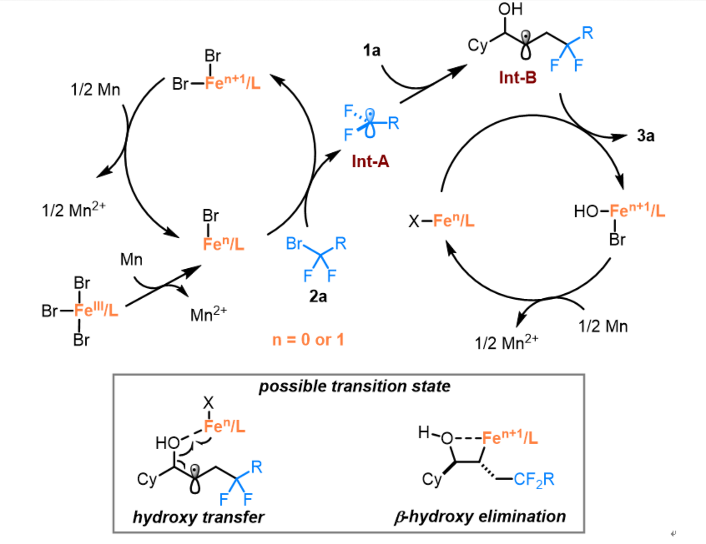
d) Control experiments for involved radical intermediate



Entry	Additive	Conv. (%)	3bf (%)	12 (%)
1	$FeBr_3$/**L3** (1.0 equiv.)	94	< 1	16
2	$FeBr_2$/**L3** (1.0 equiv.)	90	< 1	44
3	$FeBr_2$/**L3** (1.0 equiv.) Mn (3.0 equiv.)	94	15, *E*/*Z* = 6:1	71
4	$FeBr_2$/**L3** (15 mol%) Mn (3.0 equiv.)	91	20, *E*/*Z* = 6:1	64

Angew. Chem. Int. Ed. **2025**, e202500781

Fe Catalysis:铁催化未保护烯丙醇的自由基烯丙基取代反应



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THANK YOU

Thanks for your kind attention