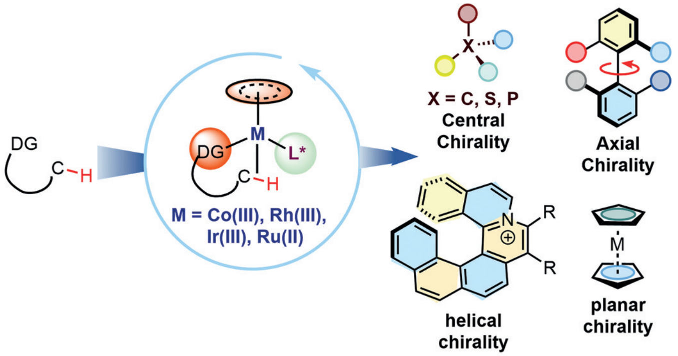
Half-Sandwich d⁶-Metal (Co^{III}, Rh^{III}, Ir^{III}, Ru^{II})-Catalyzed Enantioselective C–H Activation

Pu-Fan Qian[◊a]
Jun-Yi Li[◊a]
Yi-Bo Zhou[◊a]
Tao Zhou[*a]
Bing-Feng Shi[*a,b,c,d,e]

[a] Center of Chemistry for Frontier Technologies, Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. of China
bfshi@zju.edu.cn
taozhou@zju.edu.cn
[b] College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, Henan, 450001, P. R. of China
[c] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, P. R. of China
[d] College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 311121, P. R. of China
[e] School of Biotechnology and Health Sciences, Wuyi University, Jiangmen, Guangdong 529020, P. R. of China
[◊] These authors contributed equally



Received: 25.07.2023
Accepted after revision: 04.09.2023
Published online: 06.09.2023 (Accepted Manuscript), 05.10.2023 (Version of Record)
DOI: 10.1055/a-2167-8298; Art ID: SO-2023-07-0052-GR

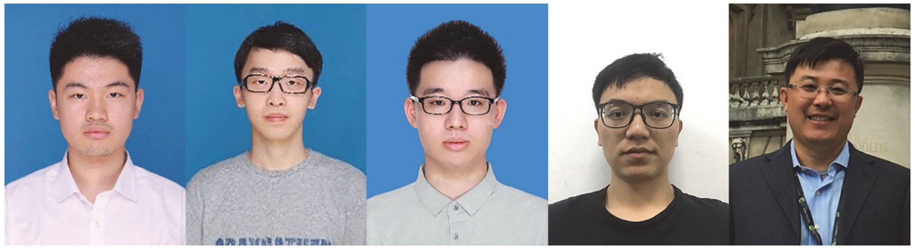
Abstract Transition-metal-catalyzed enantioselective C–H activation provides a straightforward strategy to synthesize chiral molecules from readily available sources. In this graphical review, we summarize the progress on half-sandwich d⁶-metal (Co^{III}, Rh^{III}, Ir^{III}, Ru^{II})-catalyzed enantioselective C–H functionalization reactions. The review is categorized according to the type of metal catalyst and chiral ligand employed. Representative enantio-determining models and catalytic cycles are presented.

Keywords enantioselectivity, C–H activation, half-sandwich, cobalt, rhodium, iridium, ruthenium, chiral carboxylic acid

Direct asymmetric C–H activation, which is a process capable of transforming C–H bonds into C–C or C–X bonds and generating new stereocenters in a single step, is a particularly attractive strategy for the concise synthesis of chiral molecules from readily available sources. To date, one of the most successful methods is directing-group-assisted enantioselective C–H activation using high-valent metal catalysts. In 2008, pioneering work was reported by Yu and coworkers on Pd(II)-catalyzed enantioselective C–H activation using monoprotected amino acids (MPAAs) as chiral ligands.[1] The use of MPAAs or related bidentate ligands realized various enantioselective C(sp^2)–H and C(sp^3)–H functionalization reactions. Furthermore, mechanistic studies indicated that chelation of the MPAAs or related bidentate ligands at the square planar Pd center with four coordination sites is key to the high enantiocontrol. However, the bidentate monoprotected amino acids and related ligands could not be applied to piano-stool Co^{III}, Rh^{III}, Ir^{III}, and Ru^{II} catalysts as there is only one coordination site available for an external chiral ligand.

On the other hand, half-sandwich d⁶ metals (e.g., Co^{III}, Rh^{III}, Ir^{III}, Ru^{II}) have attracted significant attentions due to their versatile reactivity and selectivity, good functional group tolerance, and stability. Through the continuous efforts of chemists, three main strategies have been developed to enable half-sandwich d⁶-metal-catalyzed asymmetric C–H activation. The first strategy involves the use of tailor-made chiral Cp^x ligands to bind with Co^{III}, Rh^{III}, or Ir^{III}, or chiral arene ligands to bind with Ru^{II}. The chiral Cp^x or chiral arene pre-coordinating strategy is powerful for its board substrate scope and various functionalization. Besides, several types of well-designed monodentate chiral carboxylic acids (CCAs) have also been developed to realize half-sandwich d⁶-metal-catalyzed enantioselective C–H functionalization reactions. The third strategy takes advantage of a chiral transient directing group (*c*TDG). Some other specialized strategies have also been disclosed, including enantioselective alkylation of olefins enabled by disulfonates, transition-metal/organocatalyst synergetic catalysis and so on. These works has greatly promote the development of enantioselective C–H activation and provide efficient and convenient methods to access diverse chiral skeletons. In this graphical review, we have summarized the rapid progress made on half-sandwich d⁶-metal-catalyzed enantioselective C–H activation in the past years, which was categorized according to different metal catalysts. We hope that this graphical review will stimulate further researches on the development of novel chiral ligands and strategies in this emerging research topic.[2]

Biographical Sketches



from left to right

Pu-Fan Qian was born in Zhejiang, China. He joined the research group of Prof. Dr. Bing-Feng Shi in 2019 and received his B.Sc. degree from Zhejiang University in 2022. He is currently a Ph.D. student at Zhejiang University under the guidance of Prof. Dr. Bing-Feng Shi. His research interests focus on transition-metal-catalyzed asymmetric C–H functionalization.

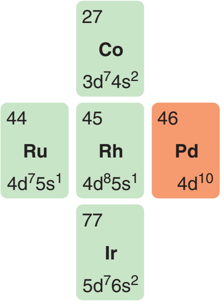
Jun-Yi Li was born in 2000 in Zhejiang Province, China. He received his B.Sc. degree from Zhejiang University in 2022. In the same year, he joined the Department of Chemistry, Zhejiang University for his Ph.D. studies in the laboratories of Prof. Dr. Bing-Feng Shi. His research interests focus on transition-metal-catalyzed asymmetric C–H functionalization.

Yi-Bo Zhou was born in Henan, China. He joined the Bing-Feng Shi group in 2020 and received his B.Sc. degree from Zhejiang University in 2022. He is currently a Ph.D. student at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. His research interests focus on asymmetric C–H functionalization.

Tao Zhou was born in Hubei, China. He received his B.Sc. degree in 2012 at Shandong University and his Ph.D. in 2017 from Nankai University under the supervision of Professor Bai-Quan Wang. He subsequently worked as a postdoctoral fellow in the group of Prof. Bing-Feng Shi at Zhejiang University, and was promoted to associate professor in 2021. His current research interests are focused on transition-metal-catalyzed asymmetric C–H activation.

Bing-Feng Shi was born in Shandong, China. He received his B.S. degree from Nankai University in 2001 and his Ph.D. in 2006 from the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences under the guidance of Professor Biao Yu. Following a period as a postdoctoral fellow at the University of California, San Diego (2006–2007), he moved to The Scripps Research Institute working with Professor Jin-Quan Yu as a research associate. In 2010, he joined the Department of Chemistry at Zhejiang University as a professor. His research focus is directed towards transition metal-catalyzed C–H functionalization and its application in the synthesis of biologically important small molecules.

Development of high-valent-metal-catalyzed enantioselective C–H functionalization



- ● Two coordination positions avilable for external ligands
- ✓ MPAAs and related bidentate ligands
- ● Only one coordination position available for an external ligand
- ✗ MPAAs and related bidentate ligands

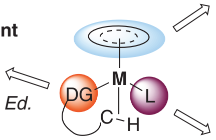
Selected reviews on transition-metal-catalyzed asymmetric C–H activation

3a) Yu, *Chem. Soc. Rev.* **2009**, *38*, 3242.
3b) Colobert, *Chem. Eur. J.* **2013**, *19*, 14010.
3c) You, *RSC Adv.* **2014**, *4*, 6173.
3d) Cramer, *Chem. Rev.* **2017**, *117*, 8908.
3e) Yu, *Science* **2018**, *359*, eaao4798.
3f) Ackermann, *Chem. Rev.* **2019**, *119*, 2192.
3g) Cramer, *Trends Chem.* **2019**, *1*, 471.
3h) Yoshino and Matsunaga, *Chem. Eur. J.* **2020**, *26*, 7346.
3i) Shi, *Acc. Chem. Res.* **2021**, *54*, 2750.
3j) Shi, *Trends Chem.* **2022**, *4*, 220.

Selected reviews on applications of C–H activation in organic synthesis

3k) Gaunt, *Chem. Soc. Rev.* **2011**, *40*, 1885.
3l) Baran, *Chem. Soc. Rev.* **2011**, *40*, 1976.
3m) Yamaguchi and Itami, *Angew. Chem. Int. Ed.* **2012**, *51*, 8960.
3n) Sorensen, *Chem. Soc. Rev.* **2018**, *47*, 8925.
3o) Yu, *Angew. Chem. Int. Ed.* **2021**, *60*, 15767.

Three main strategies for half-sandwich d^6-metal-catalyzed enantioselective C–H activation



M = Rh^{III}, Ir^{III}, Co^{III}, Ru^{II}

Strategy I: **Chiral Cp^x or arene ligand.**
Selected reviews:
3p) Cramer, *Angew. Chem. Int. Ed.* **2021**, *60*, 13198.
3q) Wang, *Chem. Eur. J.* **2023**, *29*, e202202461.

Strategy II: **Chiral transient directing group (*c*TDG).**
Selected review:
3r) Shi, *Angew. Chem. Int. Ed.* **2020**, *59*, 19773.

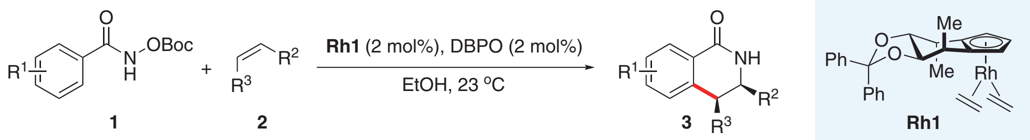
Strategy III: **Chiral carboxylic acid (CCA) ligand.**
Selected review: 3s) Yoshino and Matsunaga, *ACS Catal.* **2021**, *11*, 6455.

Other selected reviews on half-sandwich metal-catalyzed asymmetric C–H activation

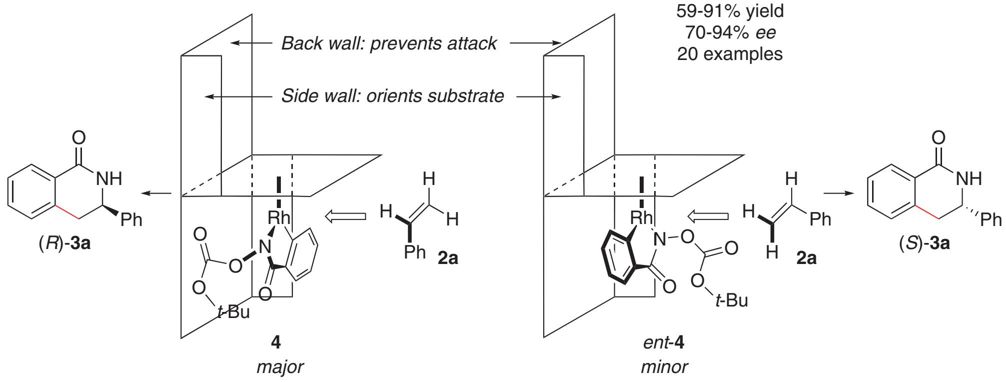
3t) Cramer, *Acc. Chem. Res.* **2015**, *48*, 1308.
3u) Waldmann, *Eur. J. Org. Chem.* **2020**, 6512.
3v) Maiti, *ACS Catal.* **2020**, *10*, 13748.
3w) You, *Sci. Bull.* **2021**, *66*, 210.
3x) You, *Org. Biomol. Chem.* **2021**, *19*, 7264.
3y) Liao and Shi, *ACS Catal.* **2022**, *12*, 9359
3z) Yoshino, *Bull. Chem. Soc. Jpn.* **2022**, *95*, 1280.
3aa) Zhou and Shi, *Synthesis* **2022**, *54*, 4784.

Two pioneering reports on half-sandwich metal-catalyzed enantioselective C–H activation with Cp^{x}Rh catalysts

Using a chiral Cp^x ligand as the enantiocontrol element

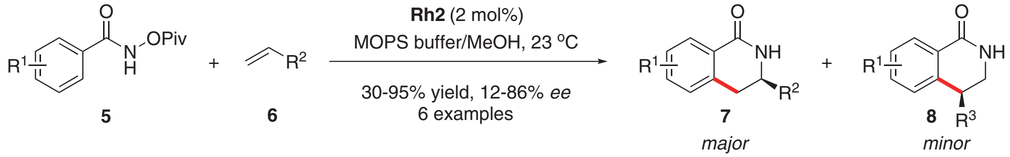


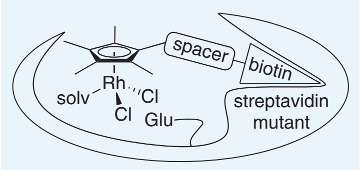
Stereoselectivity-determining model



3ab) Cramer, *Science* **2012**, *338*, 504.

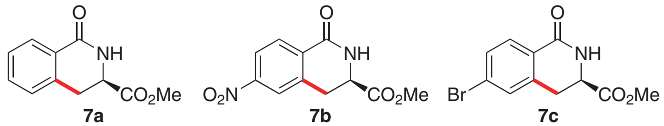
Using biomimetic catalysis to control the enantioselectivity of C–H functionalization





Rh2

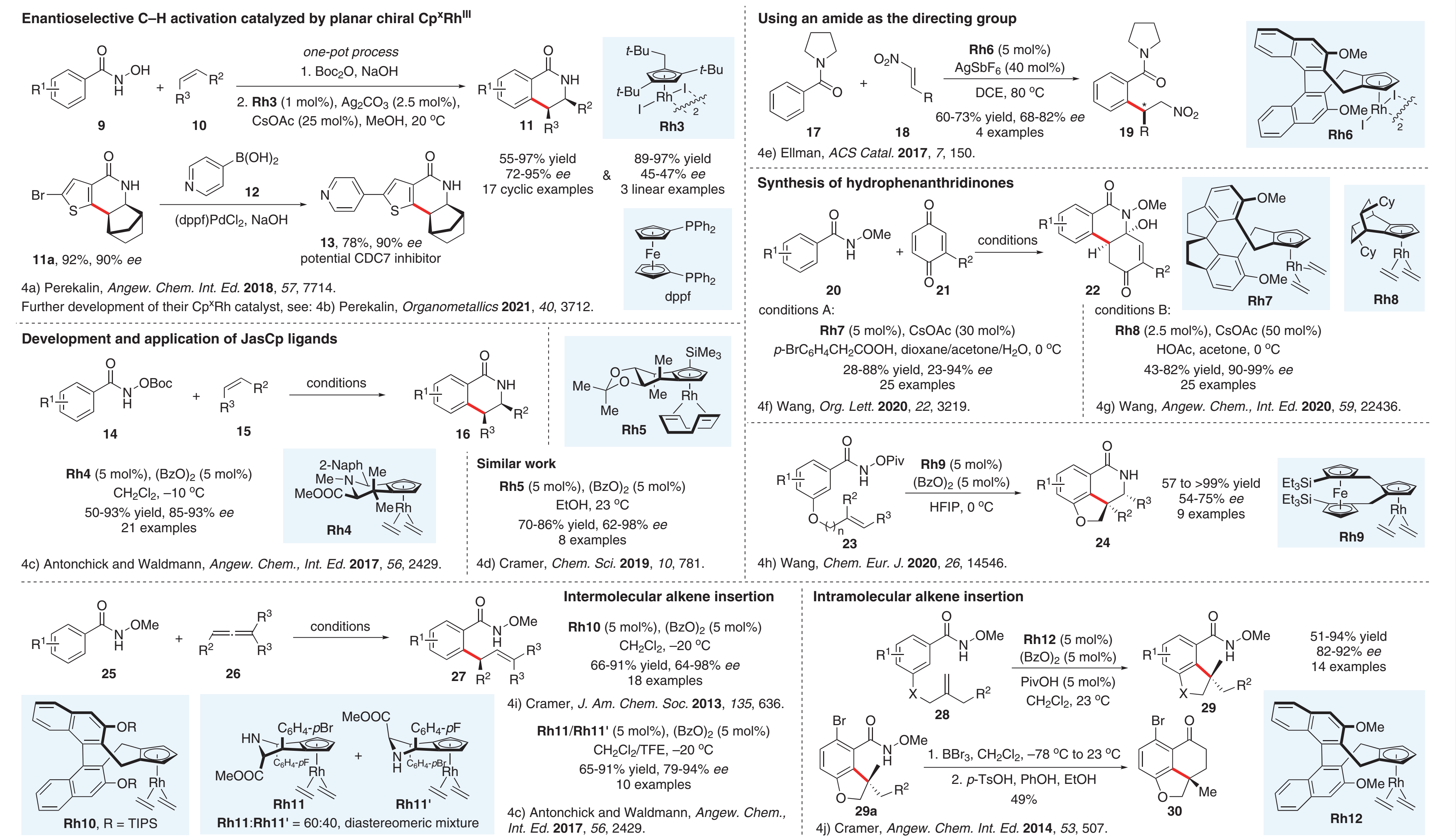
Selected examples



7a	**7b**	**7c**
95% yield	30% yield	80% yield
7a:**8a** = 19:1	**7b**:**8b** = 32:1	**7c**:**8c** = 22:1
82% *ee*	86% *ee*	78% *ee*

3ac) Ward and Rovis, *Science* **2012**, *338*, 500.
For a further development of biomimetic catalysis, see: 3ad) McNaughton and Rovis, *J. Am. Soc. Chem.* **2019**, *141*, 4815.

Figure 1 The development and challenges of half-sandwich d^6-metal (Co^{III}, Rh^{III}, Ir^{III}, Ru^{II})-catalyzed enantioselective C–H activation and two pioneering reports on Rh-catalyzed asymmetric C–H activation in 2012[3a–ad]



Enantioselective C–H activation catalyzed by planar chiral Cp^{x}Rh^{III}

4a) Perekalin, *Angew. Chem. Int. Ed.* **2018**, *57*, 7714.
Further development of their Cp^{x}Rh catalyst, see: 4b) Perekalin, *Organometallics* **2021**, *40*, 3712.

Development and application of JasCp ligands

4c) Antonchick and Waldmann, *Angew. Chem., Int. Ed.* **2017**, *56*, 2429.

Similar work

4d) Cramer, *Chem. Sci.* **2019**, *10*, 781.

Using an amide as the directing group

4e) Ellman, *ACS Catal.* **2017**, *7*, 150.

Synthesis of hydrophenanthridinones

4f) Wang, *Org. Lett.* **2020**, *22*, 3219.
4g) Wang, *Angew. Chem., Int. Ed.* **2020**, *59*, 22436.

4h) Wang, *Chem. Eur. J.* **2020**, *26*, 14546.

Intermolecular alkene insertion

4i) Cramer, *J. Am. Chem. Soc.* **2013**, *135*, 636.

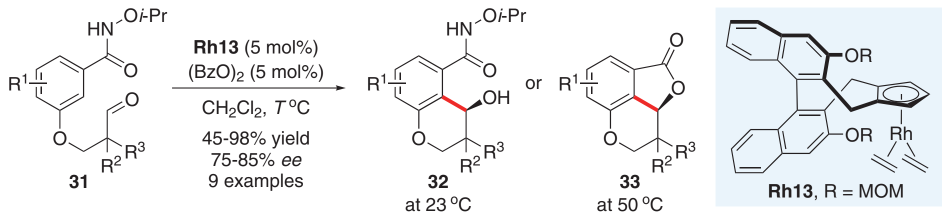
4c) Antonchick and Waldmann, *Angew. Chem., Int. Ed.* **2017**, *56*, 2429.

Intramolecular alkene insertion

4j) Cramer, *Angew. Chem. Int. Ed.* **2014**, *53*, 507.

Figure 2 Chiral Cp^{x}Rh-catalyzed enantioselective C–H activation with olefins[4a–j]

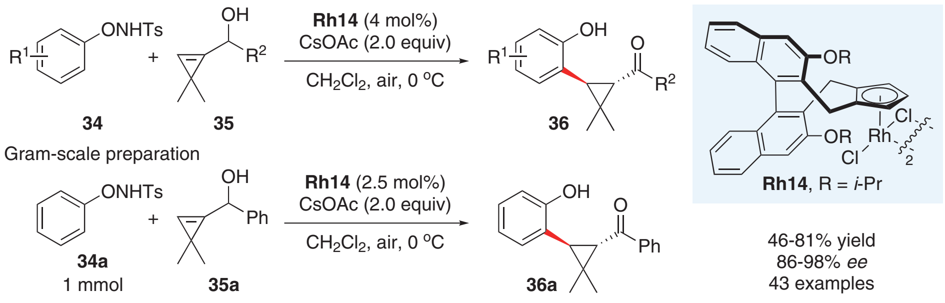
Intramolecular C–C coulping *via* enantioselective C–H activation



32 could be converted into **33** under the standard conditions at 50 °C.

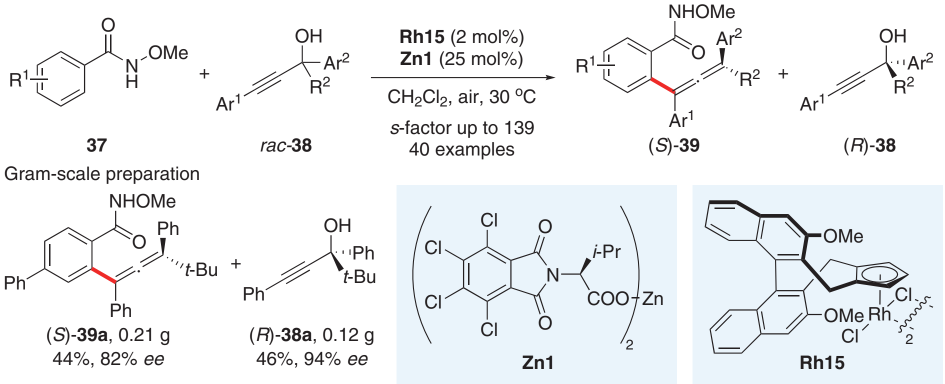
5a) Cramer, *Synlett* **2015**, *26*, 1490. Also see: 5b) Wang, *Org. Lett.* **2020**, *22*, 3586.

Construction of two *C*-stereogenic center in a single step



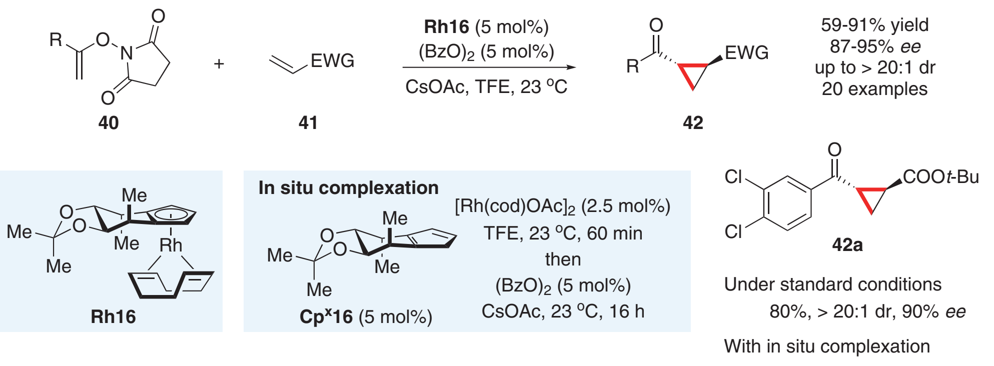
5c) Yi and Li, *Angew. Chem. Int. Ed.* **2020**, *59*, 2890.

Construction of compounds with different classes of chirality *via* kinetic resolution



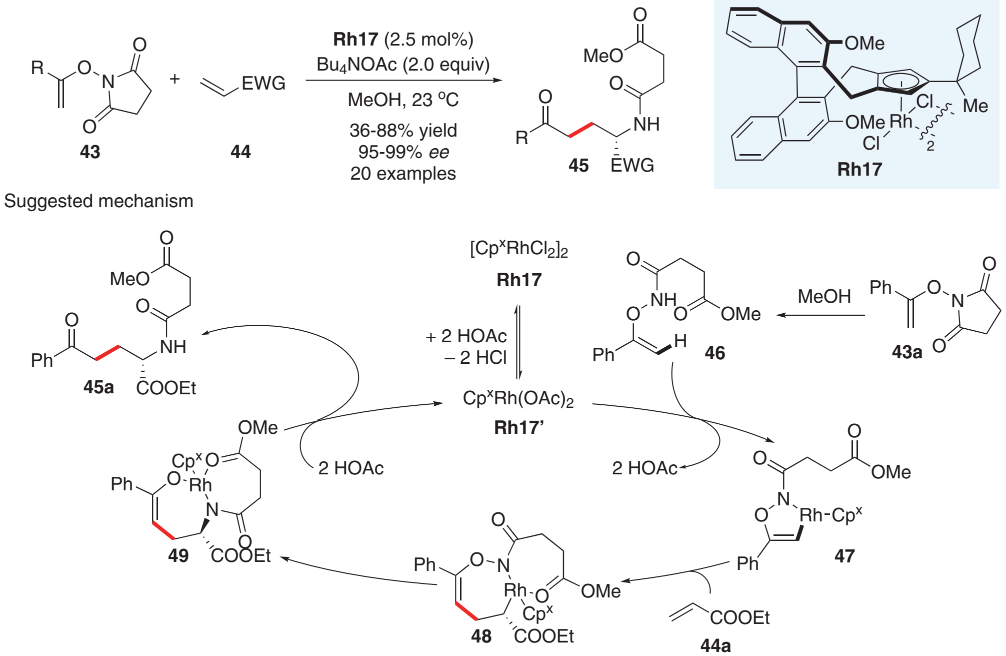
5d) Deng and Li, *Org. Lett.* **2021**, *23*, 7038.

Construction of two *C*-stereogenic centers *via* [2+1] annulation



5e) Cramer, *Chem. Sci.* **2019**, *10*, 2773.

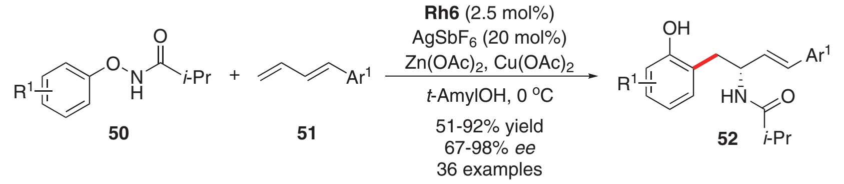
Intermolecular carboamination *via* vinylic C–H activation



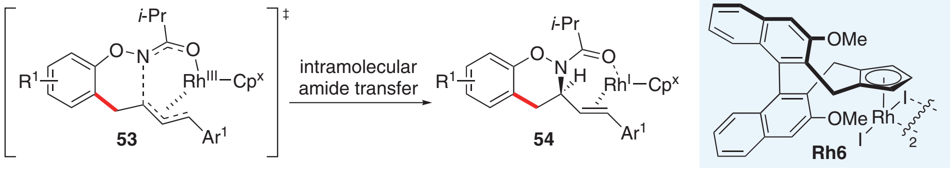
5f) Cramer, *Angew. Chem. Int. Ed.* **2020**, *59*, 14129.

Figure 3 Chiral Cp^{x}Rh-catalyzed enantioselective C–H activation/nucleophilic addition with alkenes, alkynes and aldehydes[5a–f]

Carboamination of 1,3-conjugated dienes

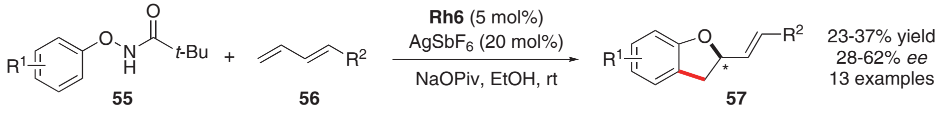


via an unusual redox-neutral Rh(III)–Rh(I)–Rh(III) catalytic pathway



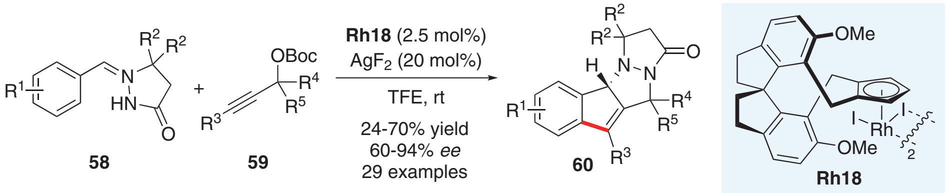
6a) Zhou and Yi, *ACS Catal.* **2021**, *11*, 2279.

[3+2] annulation of 1,3-conjugated dienes



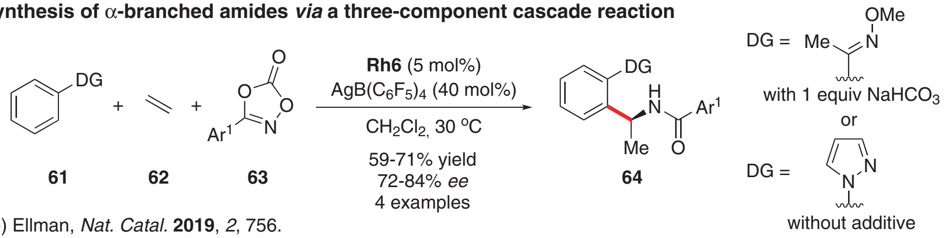
6b) Zhou and Yi, *Org. Lett.* **2021**, *23*, 3844. Also see: 6c) Yi and Zhou, *New J. Chem.* **2022**, *46*, 5705.

Tandem C–H alkenylation/formal [3+2] cycloaddition



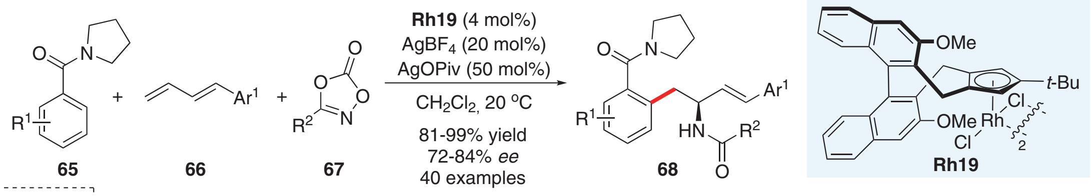
6d) Yi and Zhou, *Chin. Chem. Lett.* **2022**, *33*, 842.

Synthesis of α-branched amides *via* a three-component cascade reaction



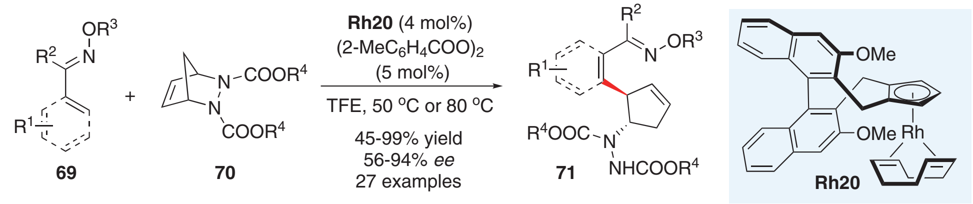
6e) Ellman, *Nat. Catal.* **2019**, *2*, 756.

Three-component cascade reaction of 1,3-conjugated dienes



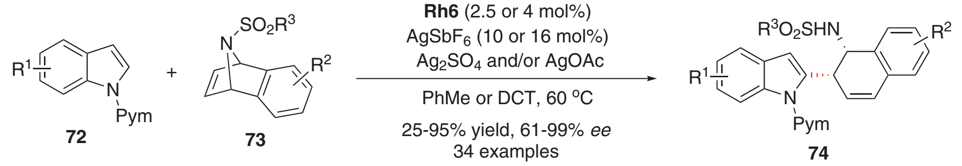
6f) Wang and Li, *ACS Catal.* **2021**, *11*, 6692. Also see a similar work: 6g) Ellman, *Org. Lett.* **2021**, *23*, 2836.

C–N insertion directed by an oxime ether



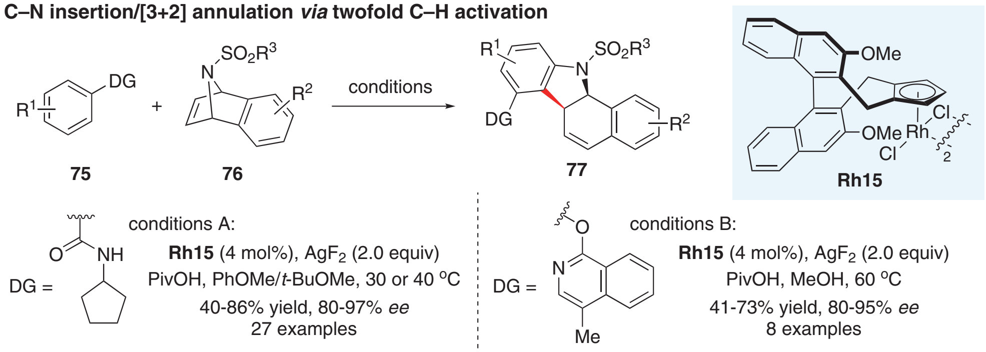
6h) Cramer, *Angew. Chem., Int. Ed.* **2019**, *58*, 2514.

C–N insertion enabled by twofold C–H activation



6i) Zheng and Li, *Angew. Chem. Int. Ed.* **2019**, *58*, 322.

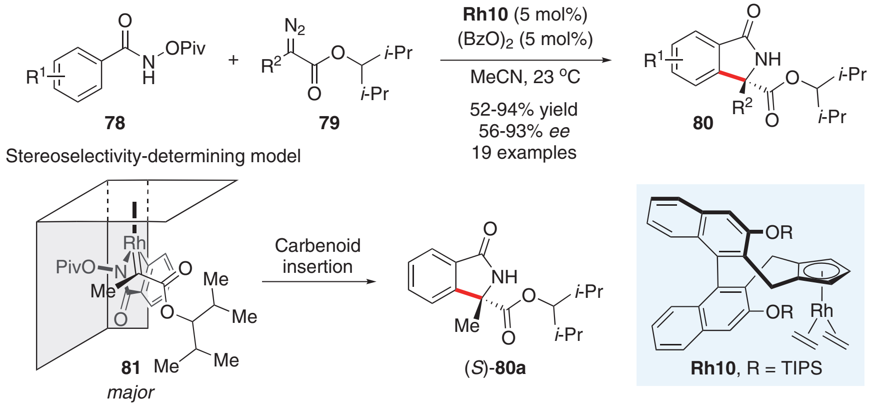
C–N insertion/[3+2] annulation *via* twofold C–H activation



6j) Li, *Angew. Chem. Int. Ed.* **2019**, *58*, 17666.

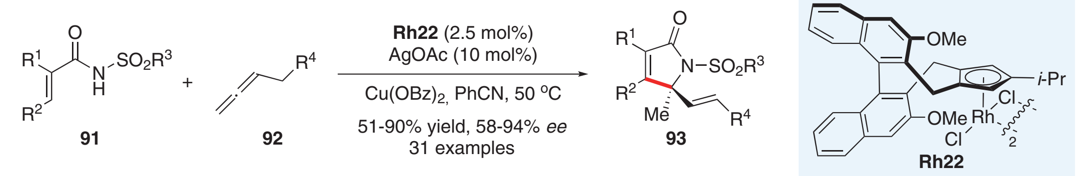
Figure 4 Chiral Cp^{x}Rh-catalyzed asymmetric synthesis of chiral amides and heterocycles[6a–j]

Asymmetric synthesis of isoindolines *via* carbenoid insertion



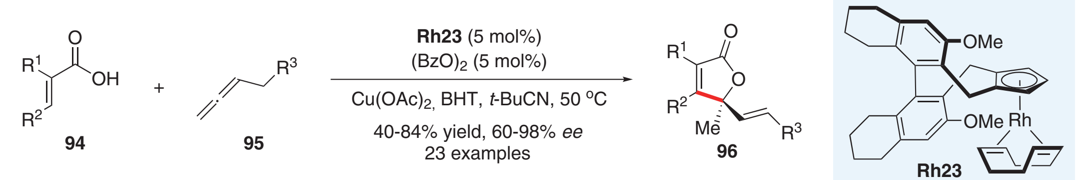
7a) Cramer, *Angew. Chem. Int. Ed.* **2014**, *53*, 7896. Also see: 7b) Song, *ACS Catal.* **2017**, *7*, 2392.

Asymmetric [4+1]-annulation of acrylamides and allenes



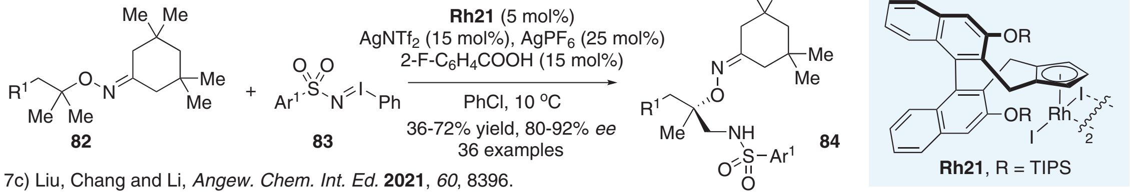
7e) Cramer, *Angew. Chem. Int. Ed.* **2019**, *58*, 18136.

Formation of chiral L-lactones *via* [4+1]-annulation



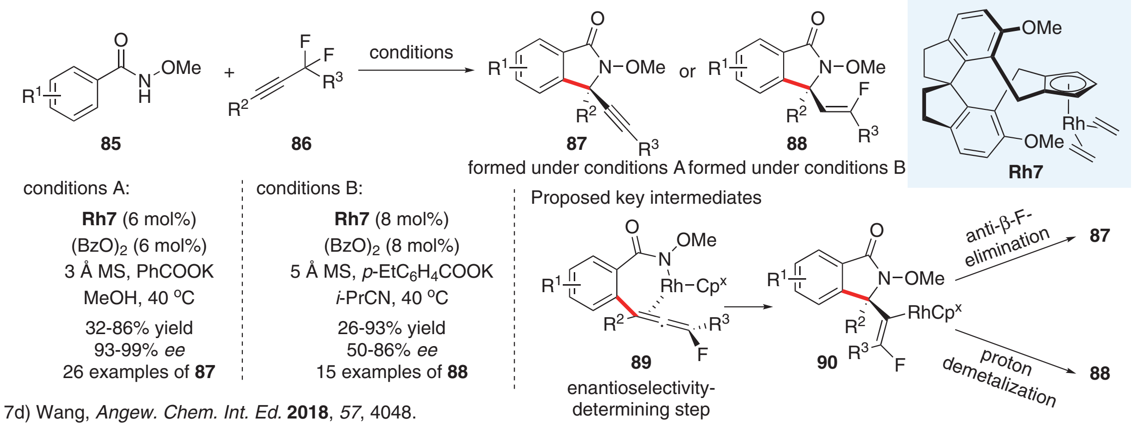
7f) Cramer, *ACS Catal.* **2020**, *10*, 8231.

Enantioselective C(sp^3)–H activation/amidation



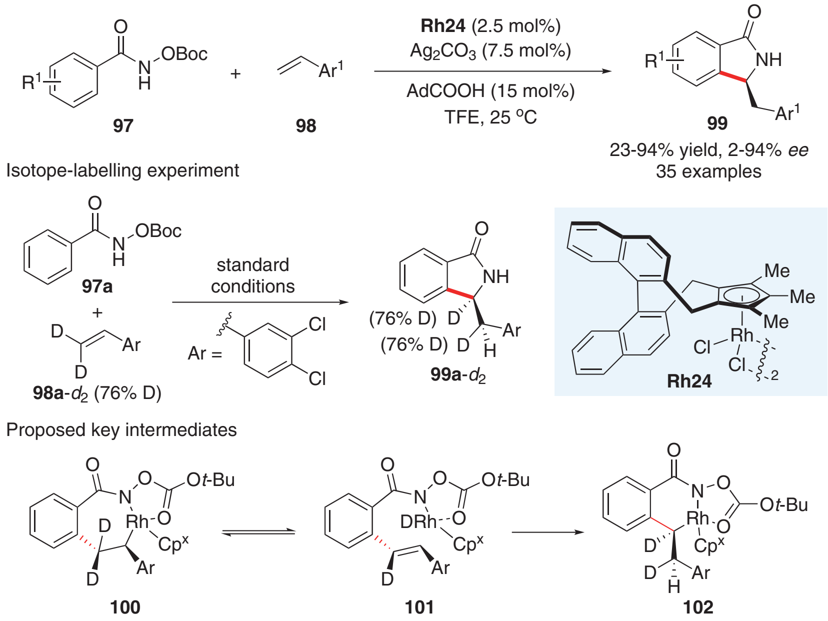
7c) Liu, Chang and Li, *Angew. Chem. Int. Ed.* **2021**, *60*, 8396.

Asymmetric formation of alkynyl and alkenyl isoindolinones regulated by solvents



7d) Wang, *Angew. Chem. Int. Ed.* **2018**, *57*, 4048.

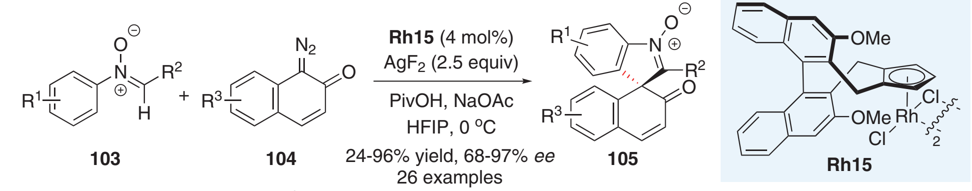
Asymmetric synthesis of isoindolines *via* [4+1]-annulation



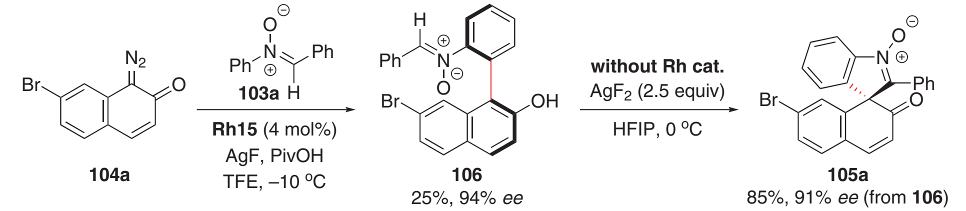
7g) You, *J. Am. Chem. Soc.* **2020**, *142*, 7379.

Figure 5 Enantioselective [4+1]-annulations of acrylamides/acids catalyzed by chiral Cp^{x}Rh catalysts[7a–g]

Asymmetric access to spirocycles through C–H activation

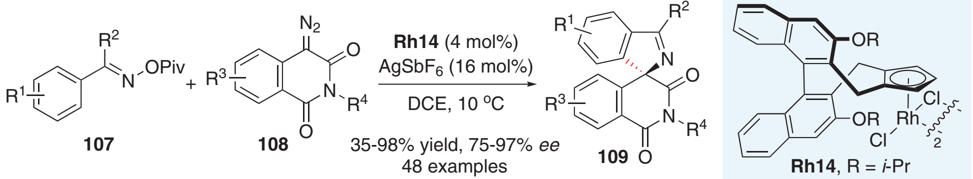


via an axial-to-central chirality transfer



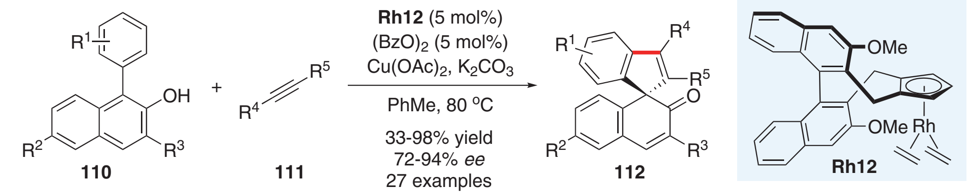
8a) Li, *Angew. Chem. Int. Ed.* **2020**, *59*, 7188.

[4+1] spiroannulation with N–O cleavage

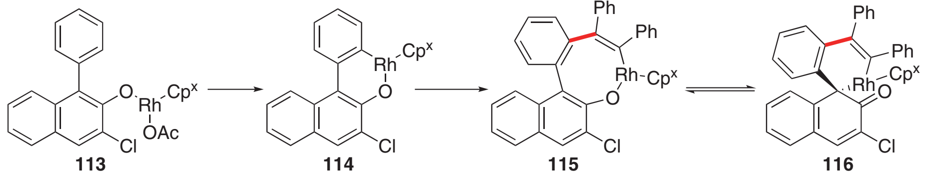


8b) Li, *Chem. Commun.* **2021**, *57*, 8268.

Asymmetric C–H functionalization/dearomatization

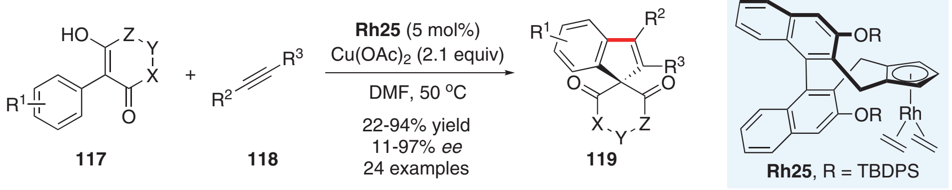


Proposed mechanism



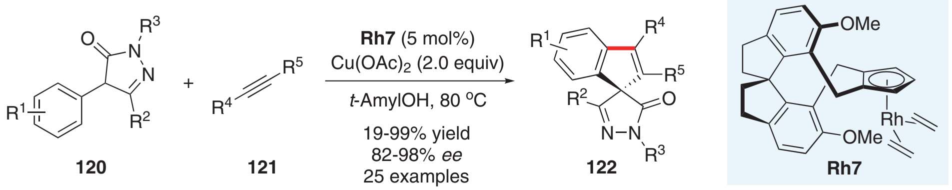
8c) You, *J. Am. Chem. Soc.* **2015**, *137*, 4880. For DFT studies, see: 8d) You, *ACS Catal.* **2016**, *6*, 262.

Enol-directed Cp^{x}Rh^{III}-catalyzed spiroannulation



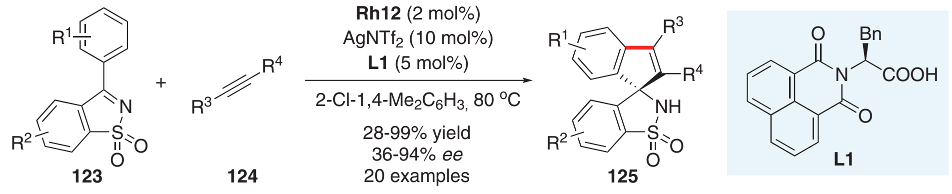
8e) Lam, *Angew. Chem. Int. Ed.* **2015**, *54*, 13975.

Asymmetric synthesis of five-membered-ring spiropyrazolones



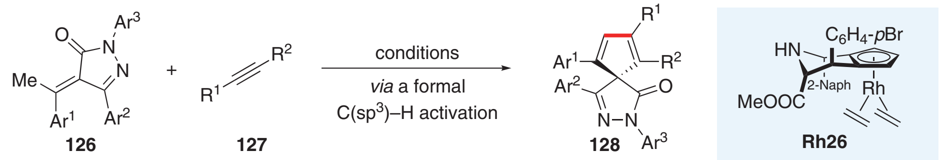
8f) You, *Angew. Chem. Int. Ed.* **2017**, *56*, 4540.

Asymmetric formation of spirosultams *via* [3+2] annulation



8g) Cramer, *Chem. Eur. J.* **2016**, *22*, 2270.

Enantioselective annulation of α-arylidene pyrazolones with chemical or electrochemical catalysis

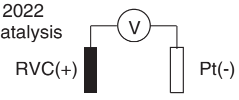


Antonchick and Waldmann, 2019, chemical catalysis

Rh26 (5 mol%)
$Cu(OAc)_2$ (2.0 equiv)
MeOH, 0 °C

32-90% yield
34-97% *ee*
31 examples

Lu, You and Mei, 2022
electrochemical catalysis



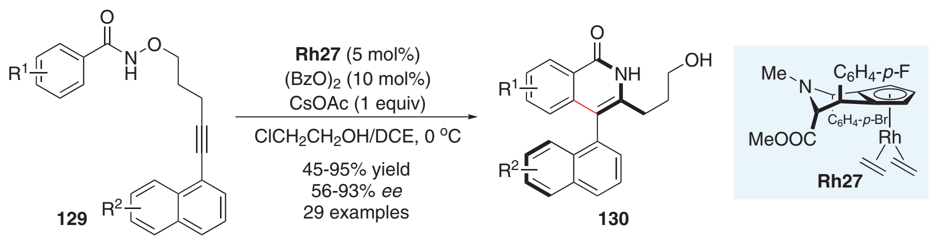
Rh12 (10 mol%)
BPO (10 mol%)
n-Bu_4NPF_6 (1.5 equiv.)
MeOH, U = 1.2 V, rt

45-82% yield
76-88% *ee*
43 examples

8h) Antonchick and Waldmann, *Angew. Chem. Int. Ed.* **2019**, *58*, 307.
8i) Lu, You and Mei, *CCS Chem.* **2022**, *4*, 3181.
Also see a related work: 8j) Ackermann, *Chem. Sci.* **2022**, *13*, 2783.

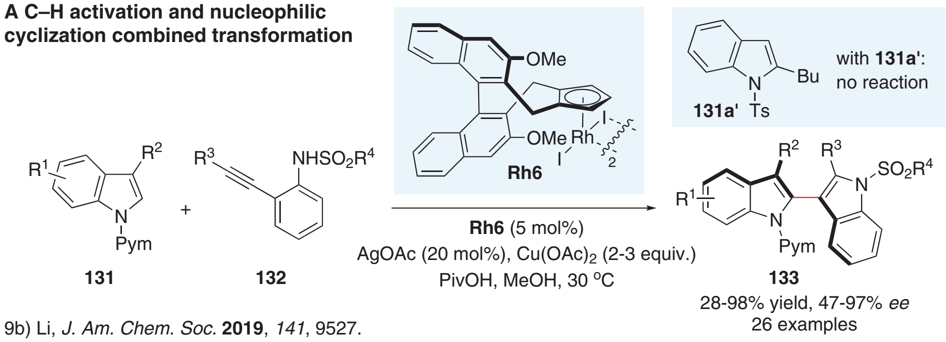
Figure 6 Asymmetric construction of quaternary carbon centers in spirocyclic compounds *via* chiral Cp^{x}Rh-catalyzed annulations[8a–j]

Asymmetric access to heterocyclic atropisomers



9a) Antonchick and Waldmann, *Angew. Chem. Int. Ed.* **2018**, *57*, 14250.

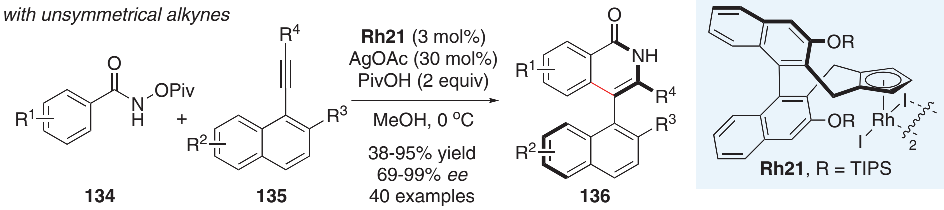
A C–H activation and nucleophilic cyclization combined transformation



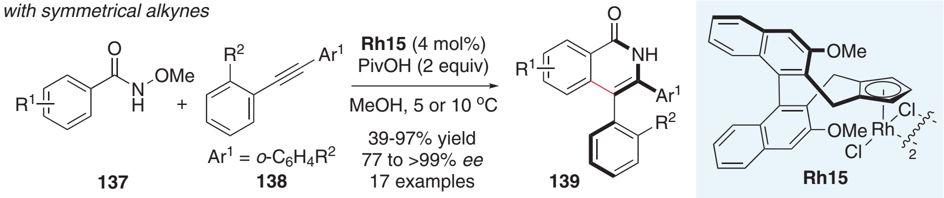
9b) Li, *J. Am. Chem. Soc.* **2019**, *141*, 9527.

Intermolecular [4+2] annulation with sterically hindered alkynes

with unsymmetrical alkynes

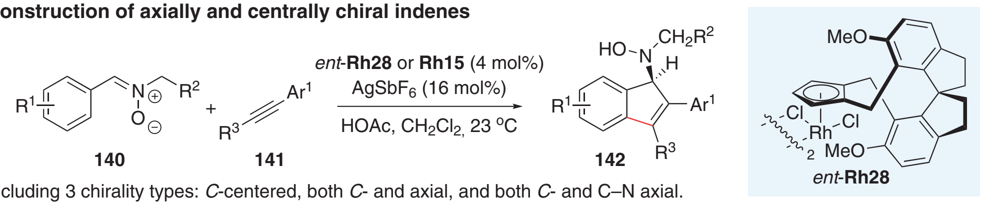


with symmetrical alkynes

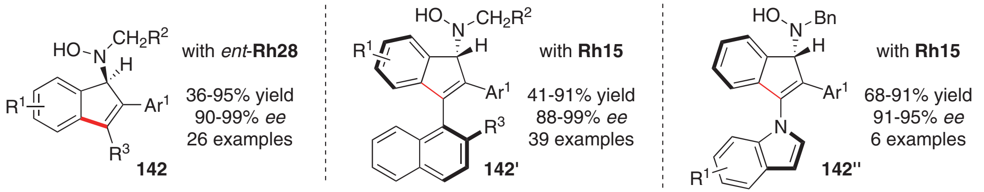


9c) Li, *Angew. Chem. Int. Ed.* **2020**, *59*, 13288.

Construction of axially and centrally chiral indenes

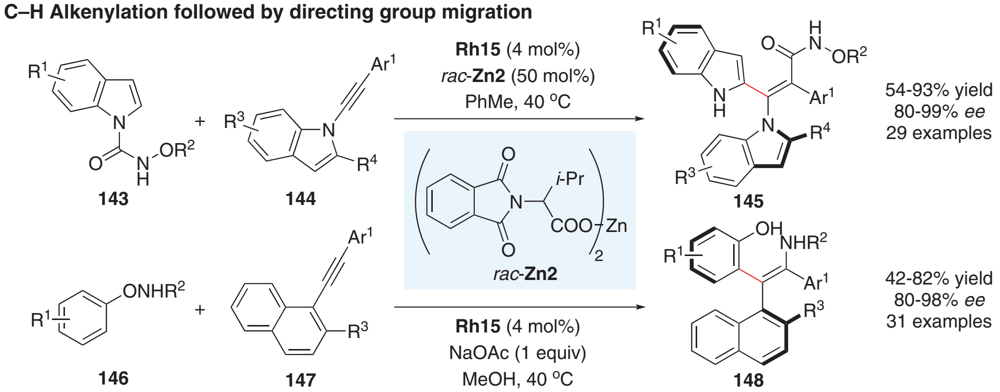


Including 3 chirality types: *C*-centered, both *C*- and axial, and both *C*- and C–N axial.



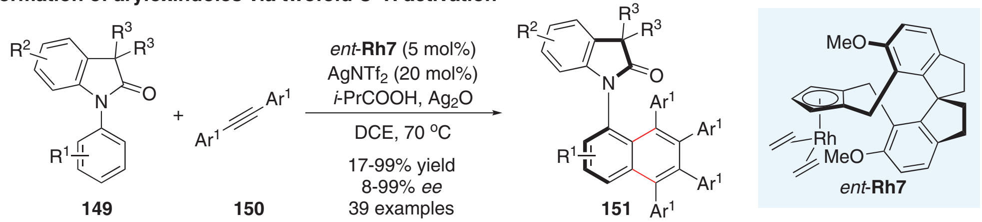
9d) Li, *Angew. Chem. Int. Ed.* **2021**, *60*, 16628.

C–H Alkenylation followed by directing group migration



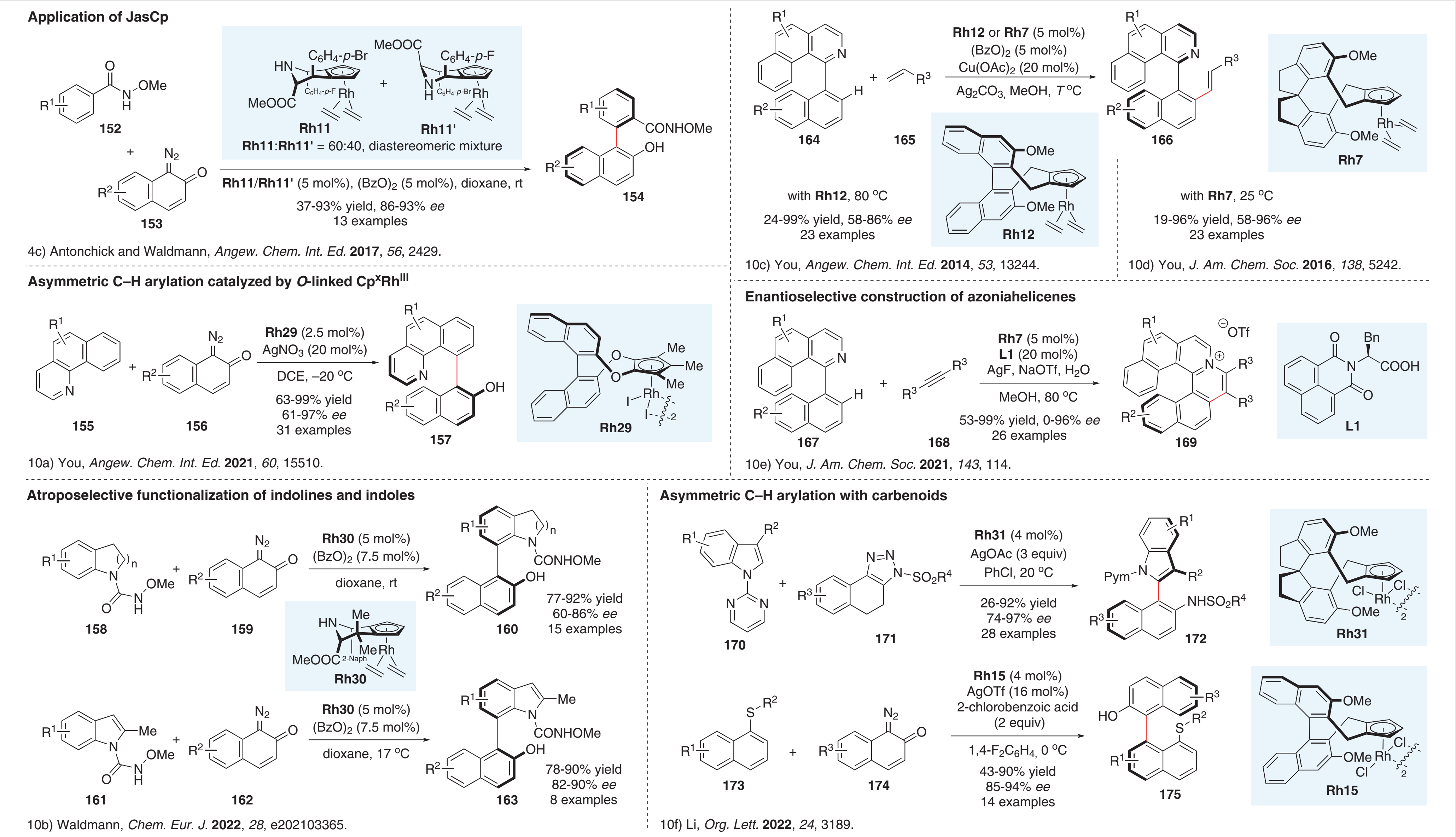
9e) Wang and Li, *Angew. Chem. Int. Ed.* **2022**, *61*, e202111860.

Formation of aryloxindoles *via* twofold C–H activation



9f) Wang, *Angew. Chem. Int. Ed.* **2019**, *58*, 6732. Also see: 9g) Wang, *Angew. Chem. Int. Ed.* **2022**, *61*, e202201522.

Figure 7 Asymmetric construction of axially chiral compounds *via* chiral Cp^{x}Rh-catalyzed annulations with alkynes[9a–g]


Application of JasCp

4c) Antonchick and Waldmann, *Angew. Chem. Int. Ed.* **2017**, *56*, 2429.

Asymmetric C–H arylation catalyzed by *O*-linked Cp^{x}Rh^{III}

10a) You, *Angew. Chem. Int. Ed.* **2021**, *60*, 15510.

10c) You, *Angew. Chem. Int. Ed.* **2014**, *53*, 13244.

10d) You, *J. Am. Chem. Soc.* **2016**, *138*, 5242.

Enantioselective construction of azoniahelicenes

10e) You, *J. Am. Chem. Soc.* **2021**, *143*, 114.

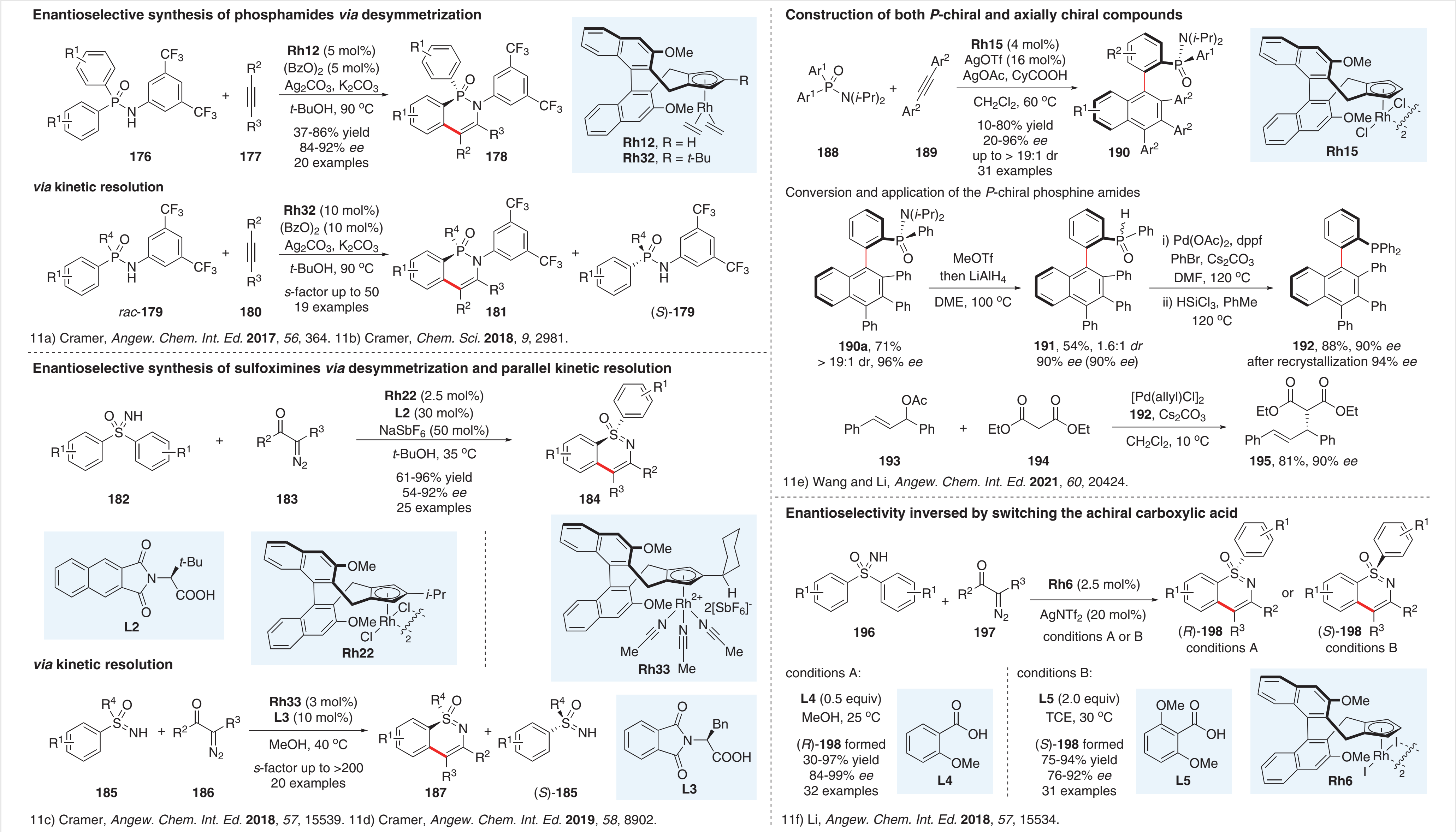
Atroposelective functionalization of indolines and indoles

10b) Waldmann, *Chem. Eur. J.* **2022**, *28*, e202103365.

Asymmetric C–H arylation with carbenoids

10f) Li, *Org. Lett.* **2022**, *24*, 3189.

Figure 8 Chiral Cp^{x}Rh-catalyzed asymmetric formation of axially chiral compounds and chiral helicenes[4c,10a–f]



Enantioselective synthesis of phosphamides *via* desymmetrization

***via* kinetic resolution**

11a) Cramer, *Angew. Chem. Int. Ed.* **2017**, *56*, 364. 11b) Cramer, *Chem. Sci.* **2018**, *9*, 2981.

Enantioselective synthesis of sulfoximines *via* desymmetrization and parallel kinetic resolution

***via* kinetic resolution**

11c) Cramer, *Angew. Chem. Int. Ed.* **2018**, *57*, 15539. 11d) Cramer, *Angew. Chem. Int. Ed.* **2019**, *58*, 8902.

Construction of both *P*-chiral and axially chiral compounds

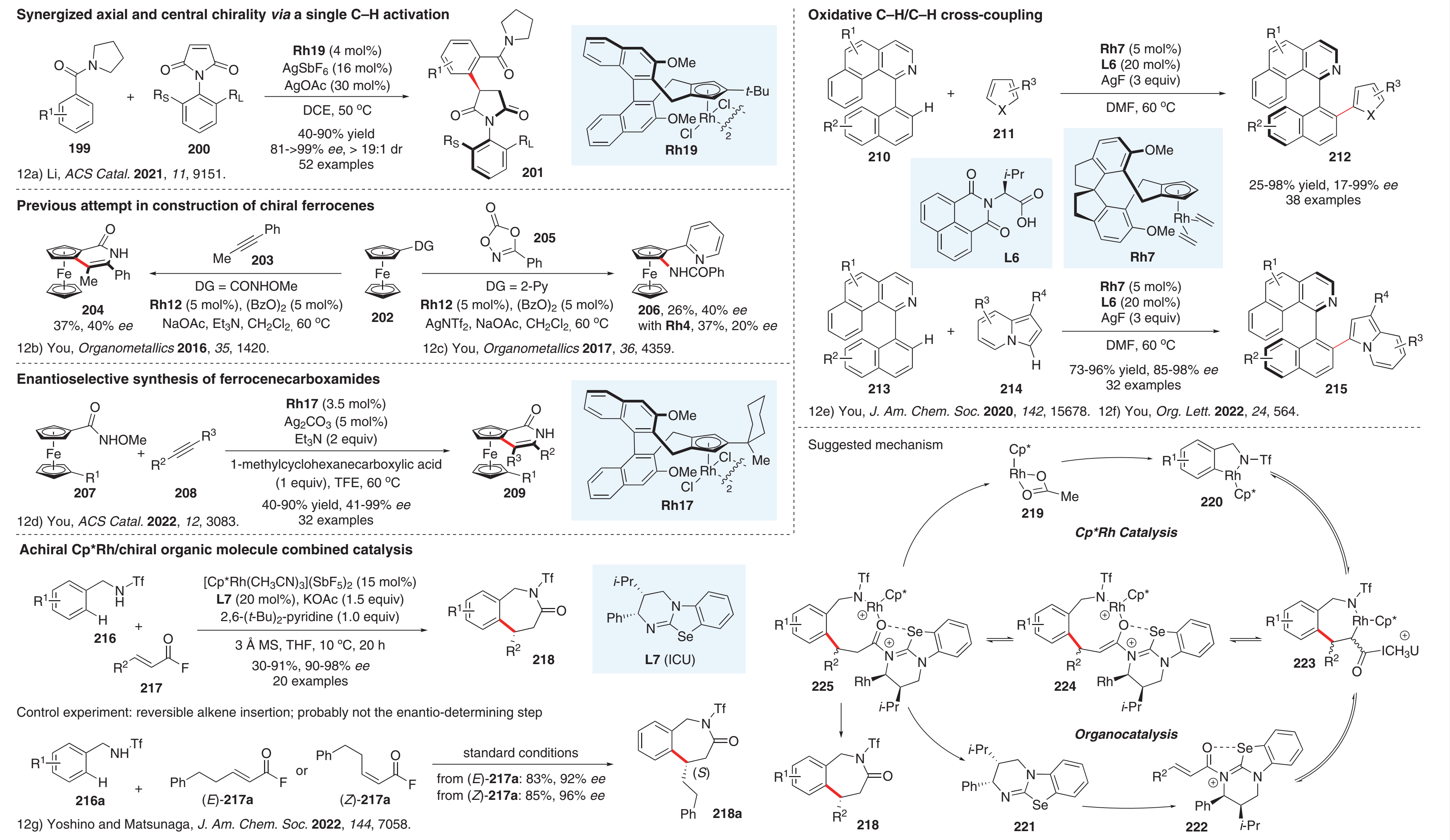
Conversion and application of the *P*-chiral phosphine amides

11e) Wang and Li, *Angew. Chem. Int. Ed.* **2021**, *60*, 20424.

Enantioselectivity inversed by switching the achiral carboxylic acid

11f) Li, *Angew. Chem. Int. Ed.* **2018**, *57*, 15534.

Figure 9 Synthesis of *P*- and *S*-stereogenic compounds *via* chiral Cp^{x}Rh-catalyzed enantioselective C–H functionalization[11a–f]


Synergized axial and central chirality *via* a single C–H activation

12a) Li, *ACS Catal.* **2021**, *11*, 9151.

Previous attempt in construction of chiral ferrocenes

12b) You, *Organometallics* **2016**, *35*, 1420. 12c) You, *Organometallics* **2017**, *36*, 4359.

Enantioselective synthesis of ferrocenecarboxamides

12d) You, *ACS Catal.* **2022**, *12*, 3083.

Achiral Cp*Rh/chiral organic molecule combined catalysis

Control experiment: reversible alkene insertion; probably not the enantio-determining step

12g) Yoshino and Matsunaga, *J. Am. Chem. Soc.* **2022**, *144*, 7058.

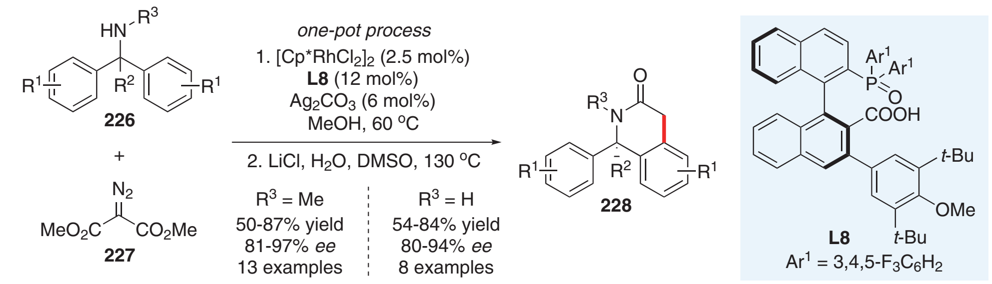
Oxidative C–H/C–H cross-coupling

12e) You, *J. Am. Chem. Soc.* **2020**, *142*, 15678. 12f) You, *Org. Lett.* **2022**, *24*, 564.

Suggested mechanism

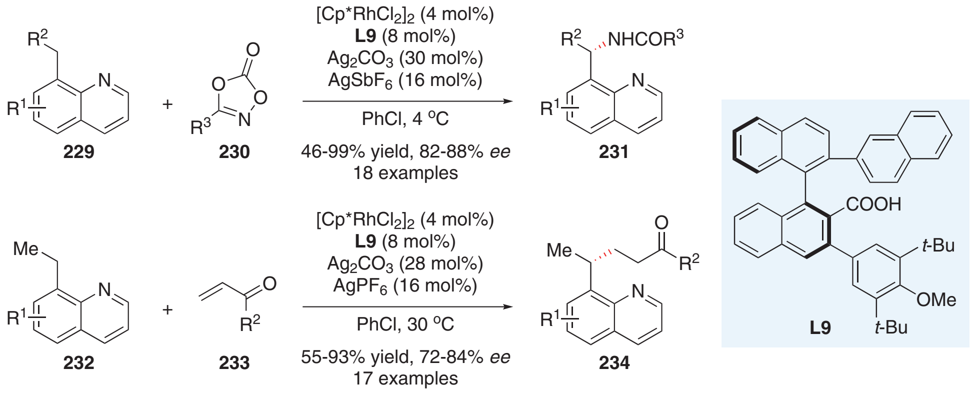
Figure 10 Construction of compounds with multiple chirality using a chiral Cp^{x}Rh complex or an achiral Cp*Rh species combined with asymmetric organocatalysis[12a–g]

Achiral Cp*Rh^{III}/chiral carboxylic acid catalyzed C(sp^2)–H activation



13a) Lin, Yoshino and Matsunaga, *Angew. Chem., Int. Ed.* **2018**, *57*, 12048.

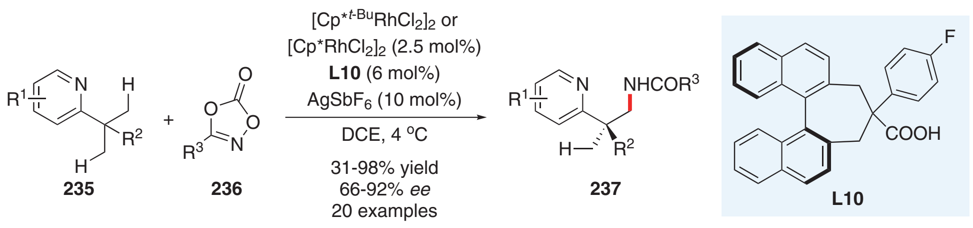
Achiral Cp*Rh^{III}/chiral carboxylic acid catalyzed C(sp^3)–H activation



13b) Yoshino and Matsunaga, *Angew. Chem. Int. Ed.* **2019**, *58*, 18154.

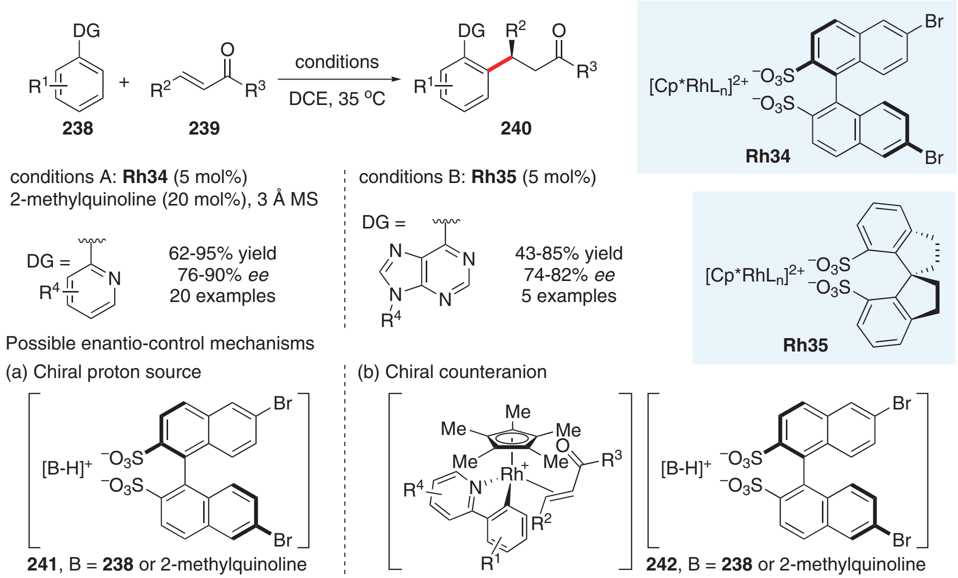
13c) Yoshino and Matsunaga, *Org. Lett.* **2020**, *22*, 8256.

Development of pseudo-C_2-symmetric acids

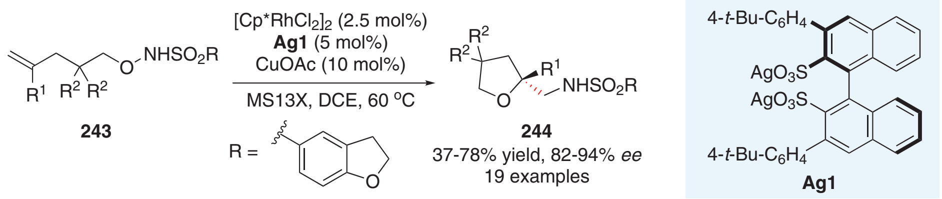


13d) Lin, Yoshino and Matsunaga, *ACS Catal.* **2021**, *11*, 4271.

Enantioselective C–H activation controlled by disulfonates



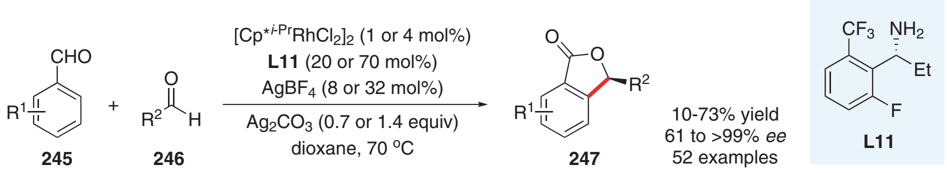
Development of chiral disulfonate ligands for asymmetric addition of olefins



13e) Yoshino and Matsunaga, *Nat. Catal.* **2018**, *1*, 585.

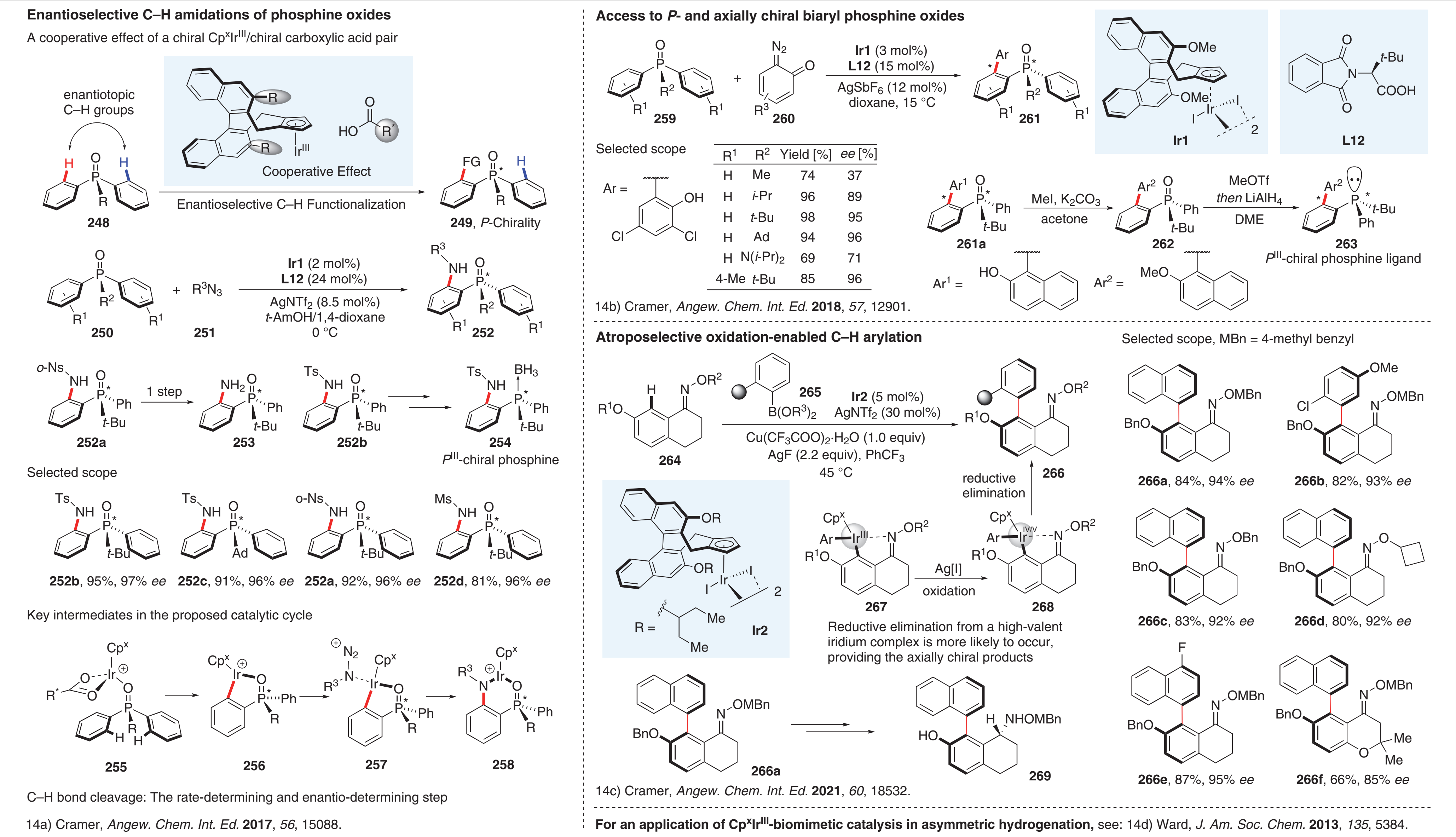
13f) Yoshino and Matsunaga, *ACS Catal.* **2021**, *11*, 15187.

Asymmetric C–H activation using an amine as a chiral transient directing group



13g) Wang, *Chem. Eur. J.* **2019**, *25*, 4688.

Figure 11 Cp*Rh^{III}-catalyzed enantioselective C–H functionalization enabled by chiral carboxylic acids/disulfonates as ligands or by a chiral amide as a chiral transient directing group[13a–g]



Enantioselective C–H amidations of phosphine oxides

A cooperative effect of a chiral Cp^{x}Ir^{III}/chiral carboxylic acid pair

Selected scope

Key intermediates in the proposed catalytic cycle

C–H bond cleavage: The rate-determining and enantio-determining step

14a) Cramer, *Angew. Chem. Int. Ed.* **2017**, *56*, 15088.

Access to *P*- and axially chiral biaryl phosphine oxides

Selected scope

R^1	R^2	Yield [%]	*ee* [%]
H	Me	74	37
H	*i*-Pr	96	89
H	*t*-Bu	98	95
H	Ad	94	96
H	N(*i*-Pr)$_2$	69	71
4-Me	*t*-Bu	85	96

14b) Cramer, *Angew. Chem. Int. Ed.* **2018**, *57*, 12901.

Atroposelective oxidation-enabled C–H arylation

Reductive elimination from a high-valent iridium complex is more likely to occur, providing the axially chiral products

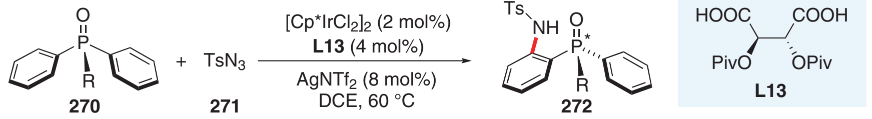
Selected scope, MBn = 4-methyl benzyl

14c) Cramer, *Angew. Chem. Int. Ed.* **2021**, *60*, 18532.

For an application of Cp^{x}Ir^{III}-biomimetic catalysis in asymmetric hydrogenation, see: 14d) Ward, *J. Am. Soc. Chem.* **2013**, *135*, 5384.

Figure 12 Ir^{III}-catalyzed enantioselective C–H functionalization with chiral Cp$^{x14a–d}$

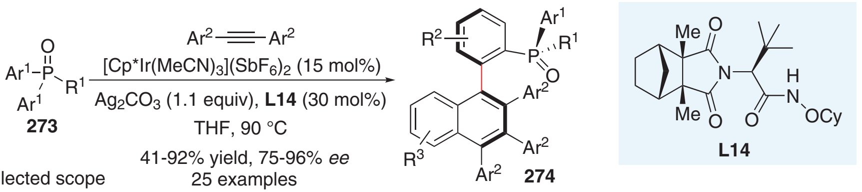
An initial attempt using chiral carboxylic acids (CCAs) as ligands in high-valent d^6-metal-catalyzed enantioselective C–H activation



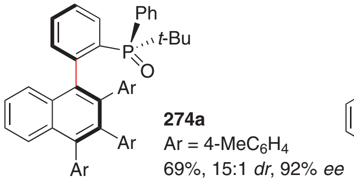
15a) Chang, *Tetrahedron* **2015**, *71*, 4504.

44-91% yield, 11-32% *ee*, 5 examples

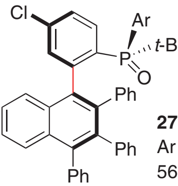
Asymmetric C–H activation of biaryl phosphine oxides



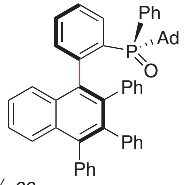
Selected scope



274a
Ar = 4-MeC$_6$H$_4$
69%, 15:1 *dr*, 92% *ee*



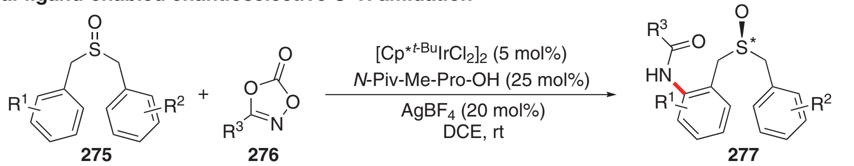
274b
Ar = 4-ClC$_6$H$_4$
56%, > 20:1 *dr*, 90% *ee*



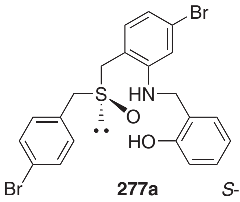
274c, 70%
18:1 *dr*, 96% *ee*

15b) Duan, *ACS Catal.* **2022**, *12*, 193.

Dual-ligand-enabled enantioselective C–H amidation



Derivatization of amidated sulfoxides

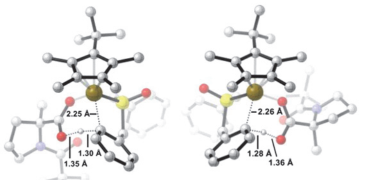


277a

92%, 98% *ee*

S-chiral tridentate ligand

Stereocontrol model

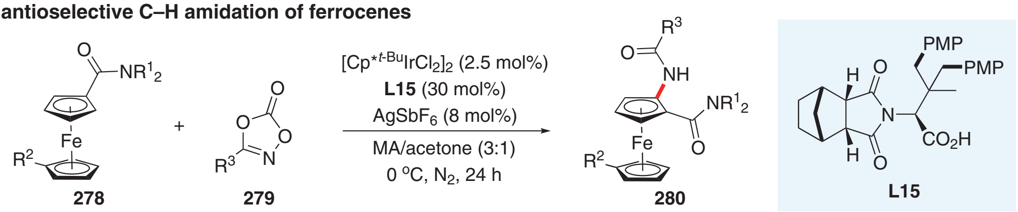


TS_S (favored) TS_R (disfavored)

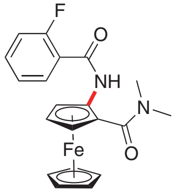
$\Delta G_{R\text{-}S}^{\ddagger}$ = 2.6 kcal/mol

15c) He, *ACS Catal.* **2020**, *10*, 7207.

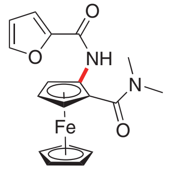
Enantioselective C–H amidation of ferrocenes



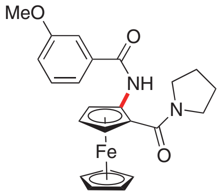
Selected scope



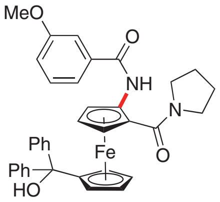
280a, 85%, 92% *ee*



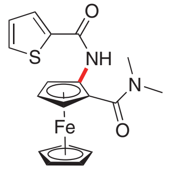
280b, 67%, 90% *ee*



280c, 71%, 92% *ee*



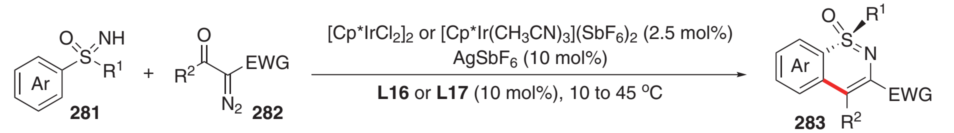
280d, 60%, 95% *ee*



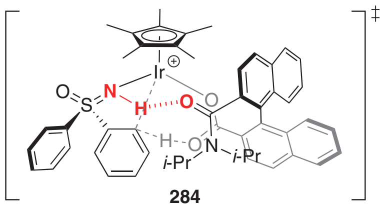
280e, 98%, 92% *ee*

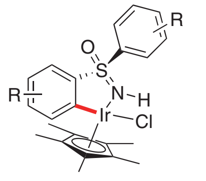
15d) Shi, *ACS Catal.* **2020**, *10*, 7117.

Enantioselective C–H activation assisted by hydrogen bonding

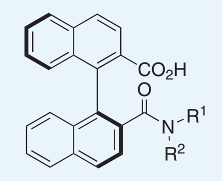


Transition state: controlled by hydrogen bonding interaction



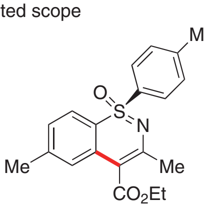


chiral iridacycle intermediates
285a, R = 4-Cl, 67%, 95% *ee*
285b, R = 3-Ac, 81%, 98% *ee*

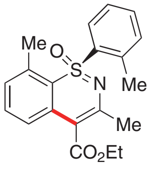


L16, R^1 = R^2 = *i*-Pr
L17, R^1, R^2 = (CH$_2$)$_6$

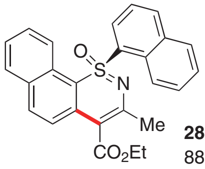
Selected scope



283a
92%, 96% *ee*



283b
84%, 97% *ee*

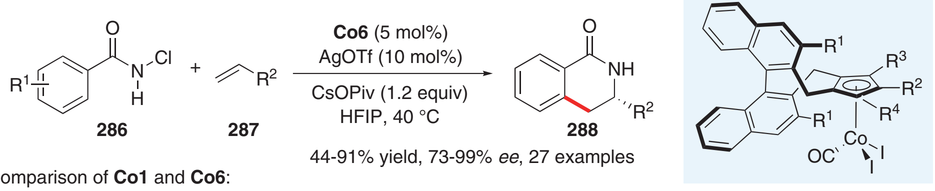


283c
88%, 94% *ee*

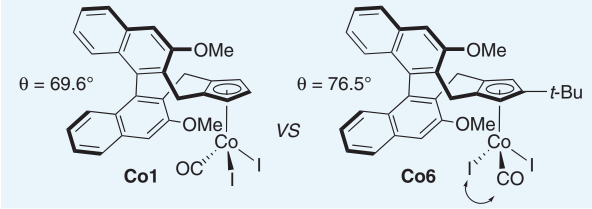
15e) Zhou, Hong and Shi, *ACS Catal.* **2022**, *12*, 9083.

Figure 13 Achiral Cp*Ir^{III}-catalyzed enantioselective C–H functionalization using chiral carboxylic acids as ligands[15a–e]

Chiral Cp^{x}Co^{III}-catalyzed enantioselective C–H alkylation



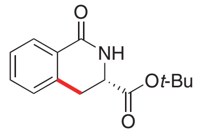
Comparison of **Co1** and **Co6**:



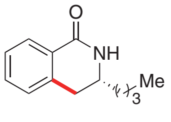
Co1 (R^1 = OMe, R^2 = R^3 = R^4 = H)
Co2 (R^1 = O*i*-Pr, R^2 = R^3 = R^4 = H)
Co3 (R^1 = OMe, R^2 = R^3 = R^4 = Me)
Co4 (R^1 = OMe, R^2 = R^4 = H, R^3 = TMS)
Co5 (R^1 = OMe, R^2 = *i*-Pr, R^3 = R^4 = H)
Co6 (R^1 = OMe, R^2 = *t*-Bu, R^3 = R^4 = H)

Co6 possesses a greater θ angle and a swapped CO ligand

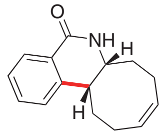
Selected scope:



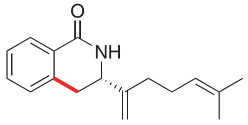
288a, 75% , 98% *ee*



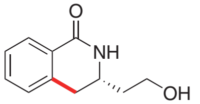
288b, 86%, 91% *ee*



288c, 53% yield, 75% *ee*



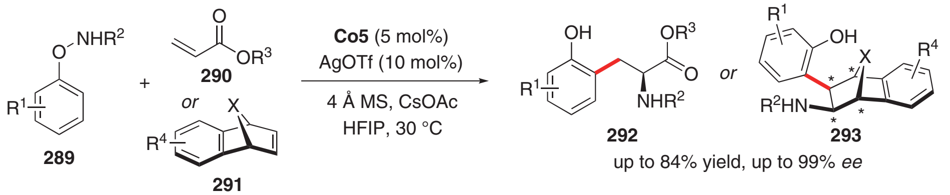
288d, 73% yield, 99% *ee*



288e, 49% yield, 96% *ee*

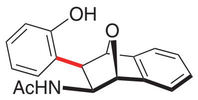
16a) Cramer, *J. Am. Chem. Soc.* **2019**, *141*, 5675.

Asymmetric intermolecular amidation with different alkenes

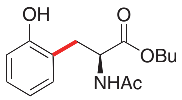


up to 84% yield, up to 99% *ee*

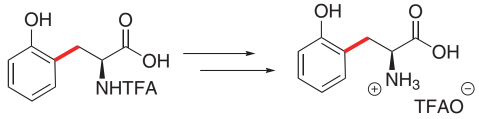
Selected scope:



293a, 99% yield, 68% *ee*



292a, 84% yield, 99% *ee*

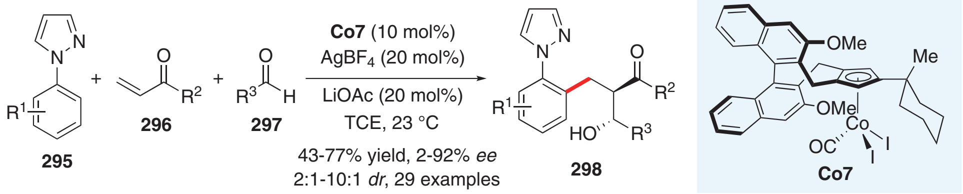


292b, 49% yield, 99% *ee*

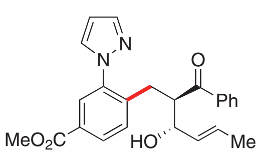
294, 81% yield

16b) Cramer, *Angew. Chem. Int. Ed.* **2021**, *60*, 655.

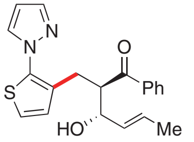
Three-component asymmetric C–H activation/functionalization



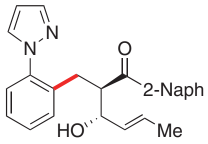
Selected scope:



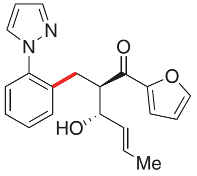
298a, 66% yield
92% *ee*, 7:1 *dr*



298b, 64% yield
88% *ee*, 6:1 *dr*



298c, 72% yield
90% *ee*, 7:1 *dr*

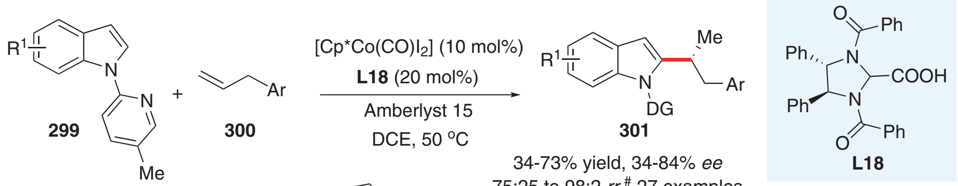


298d, 60% yield
60% *ee*, 7:1 *dr*

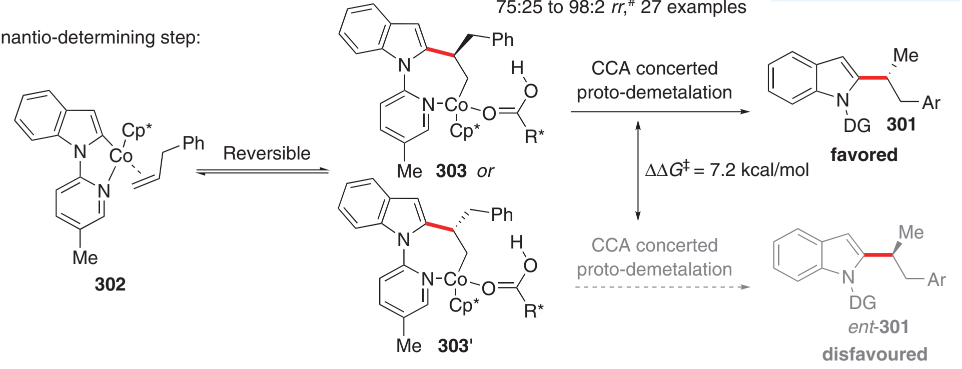
(41% yield, 88% *ee*, 7:1 *dr*, 5 mmol scale)

16c) Cramer, *ACS Catal.* **2021**, *11*, 11938.

Enantioselective C–H alkylation enabled by a chiral carboxylic acid



Enantio-determining step:



16d) Ackermann, *Angew. Chem. Int. Ed.* **2018**, *57*, 15425. #Markovnikov:*anti*-Markovnikov

Figure 14 Cp^{x}Co^{III}-catalyzed enantioselective C–H functionalization *via* asymmetric alkylation[16a–d]

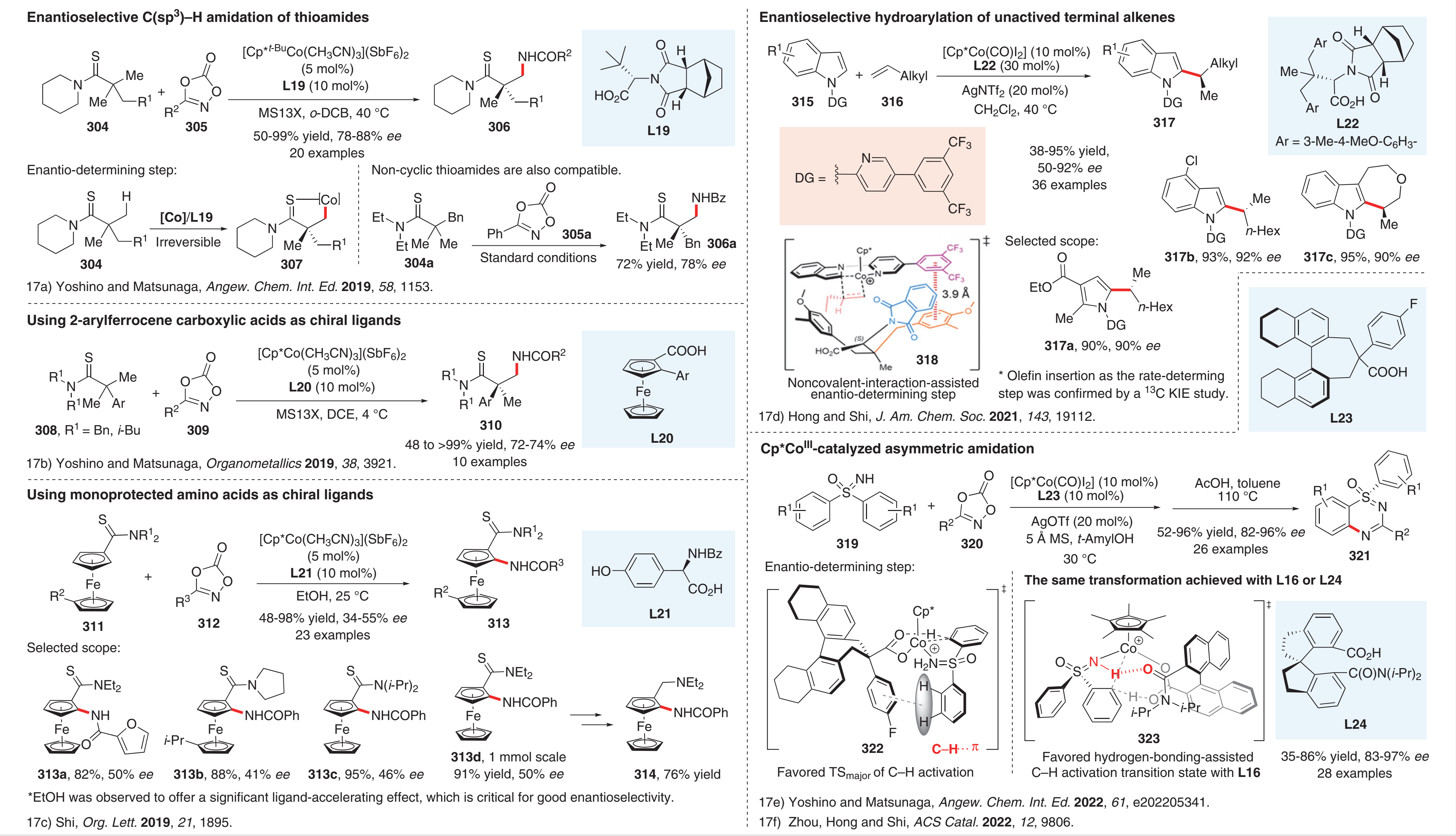
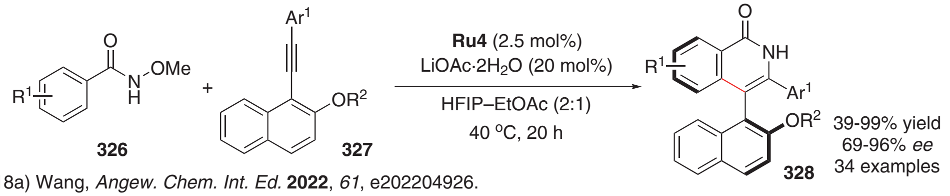


Figure 15 Achiral Cp*Co^{III}-catalyzed enantioselective C–H functionalization using chiral carboxylic acids as ligands[17a–f]

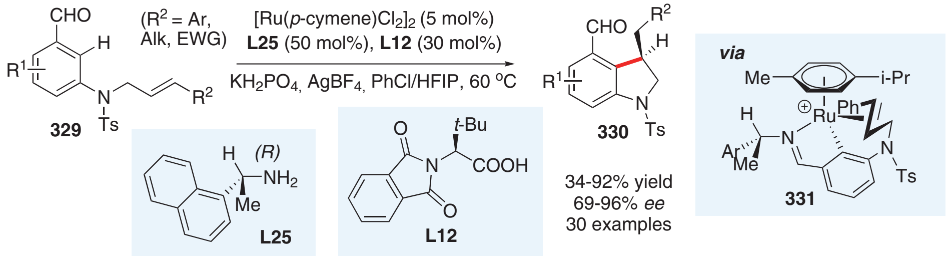
Synthesis of chiral arene ligands

Applications in asymmetric C–H activation



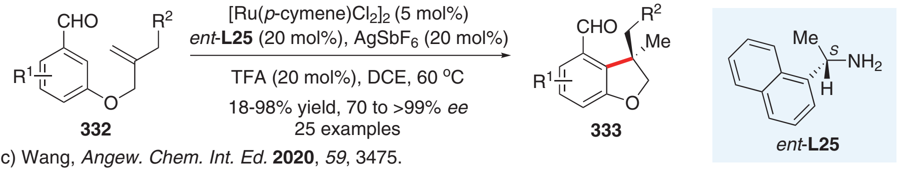
18a) Wang, *Angew. Chem. Int. Ed.* **2022**, *61*, e202204926.

Cui's work using a chiral transient directing group (*c*TDG) strategy



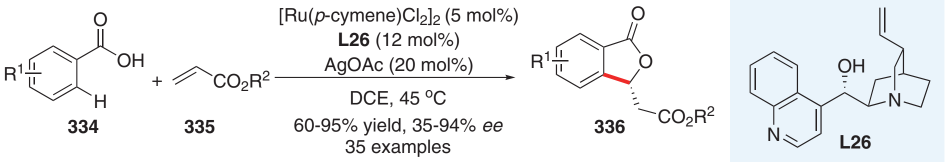
18b) Cui, *J. Am. Chem. Soc.* **2019**, *141*, 15730.

Wang's work using a chiral transient directing group (*c*TDG) strategy



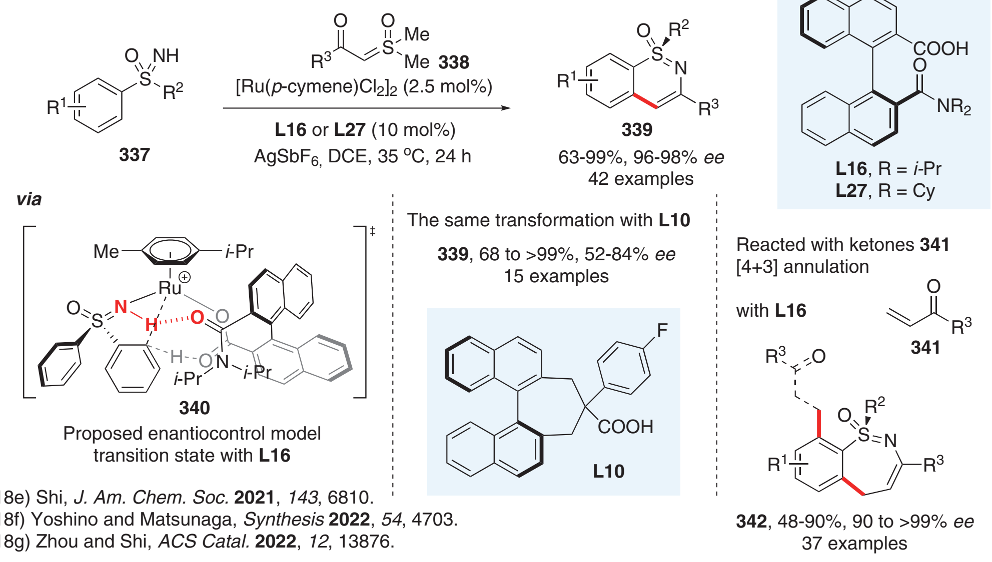
18c) Wang, *Angew. Chem. Int. Ed.* **2020**, *59*, 3475.

One-pot asymmetric synthesis with Ru^{II}/cinchonine dual catalysis



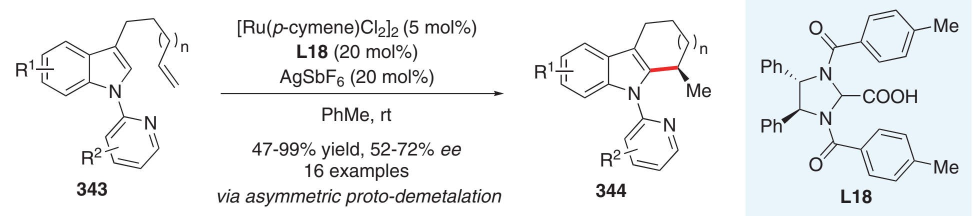
18d) Dethe, *J. Org. Chem.* **2022**, *87*, 4617.

Enantioselective C–H activation enabled by chiral carboxylic acids



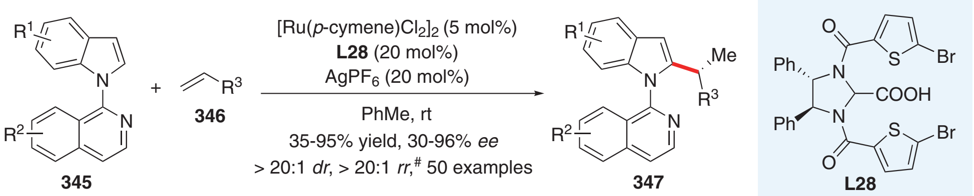
18e) Shi, *J. Am. Chem. Soc.* **2021**, *143*, 6810.
18f) Yoshino and Matsunaga, *Synthesis* **2022**, *54*, 4703.
18g) Zhou and Shi, *ACS Catal.* **2022**, *12*, 13876.

Enantioselective alkylation controlled by a chiral carboxylic acid



18h) Ackermann, *Org. Lett.* **2021**, *23*, 2760.

Construction of both *C*- and axially chiral compounds *via* Ru^{II}-catalyzed intermolecular hydroarylation



18i) Ackermann, *Angew. Chem. Int. Ed.* **2022**, *61*, e202212595. #Markovnikov:*anti*-Markovnikov

Figure 16 Ru^{II}-catalyzed enantioselective C–H functionalization[18a–i]

Conflict of Interest

The authors declare no conflict of interest.

Funding Information

Financial support from the National Natural Science Foundation of China [22271250 (T.Z.), 21925109 (B.-F.S.)], Zhejiang Provincial Natural Science Foundation [LD22B030003 (B.-F.S.)], the National Key Research and Development Program of China [2021YFF0701600 (B.-F.S.)], the Fundamental Research Funds for the Central Universities [226-2022-00224 (B.-F. S.), 226-2022-00175 (T.Z.)], the Open Research Fund of School Chemistry and Chemical Engineering, Henan Normal University and the Center of Chemistry for Frontier Technologies of Zhejiang University is gratefully acknowledged.

Acknowledgment

We are grateful to current and former members of the Shi group who have contributed to the development of this field.

References

(1) Shi, B.-F.; Maugel, N.; Zhang, Y.-H.; Yu, J.-Q. *Angew. Chem. Int. Ed.* **2008**, *47*, 4882.

(2) During the preparation of this graphical review, several reports on this topic appeared highlighting the importance of these chiral catalysts, see: (a) Huang, L.-T.; Kitakawa, Y.; Yamada, K.; Kamiyama, F.; Kojima, M.; Yoshino, T.; Matsunaga, S. *Angew. Chem. Int. Ed.* **2023**, *62*, e202305480. (b) Yang, H.; Zhang, R.; Zhang, S.-Z.; Gu, Q.; You, S.-L. *ACS. Catal.* **2023**, *13*, 8838. (c) Yang, H.; Yang, Z.-Q.; Zhang, S.-Z.; Zhang, W.-W.; Gu, Q.; You, S.-L. *Sci. China Chem.* **2023**, *66*, in press; DOI: 10.1007/s11426–023-1637-8. (d) Zhang, S.-Z.; Zhang, W.-W.; Yang, H.; Gu, Q.; You, S.-L. *Chin. J. Org. Chem.* **2023**, *43*, 2926. (e) Zheng, Y.; Zhang, W.-Y.; Gu, Q.; Zheng, C.; You, S.-L. *Nat. Commun.* **2023**, *14*, 1094. (f) Zhang, W.-W.; Wang, Q.; Zhang, S.-Z.; Zheng, C.; You, S.-L. *Angew. Chem. Int. Ed.* **2023**, *62*, e202214460. (g) Guo, W.; Pang, X.; Jiang, J.; Wang, J. *Org. Lett.* **2023**, *25*, 3823. (h) Zhu, X.; Wu, H.; Wang, Y.; Huang, G.; Wang, F.; Li, X. *Chem. Sci.* **2023**, *14*, 8564. (i) Zhu, X.; Mi, R.; Yin, J.; Wang, F.; Li, X. *Chem. Sci.* **2023**, *14*, 7999. (j) Mi, R.; Ding, Z.; Yu, S.; Crabtree, R. H.; Li, X. *J. Am. Chem. Soc.* **2023**, *145*, 8150. (k) Zhu, M.; Zhao, Y.; Li, X.; Liu, B. *Org. Lett.* **2023**, *25*, 1839. (l) Wang, P.; Wu, H.; Zhang, X.-P.; Huang, G.; Crabtree, R. H.; Li, X. *J. Am. Chem. Soc.* **2023**, *145*, 8417. (m) Zheng, D.-S.; Zhang, W.-W.; Gu, Q.; You, S.-L. *ACS Catal.* **2023**, *13*, 5127.

(3) (a) Giri, R.; Shi, B.-F.; Engle, K. M.; Maugel, N.; Yu, J.-Q. *Chem. Soc. Rev.* **2009**, *38*, 3242. (b) Wencel-Delord, J.; Colobert, F. *Chem. Eur. J.* **2013**, *19*, 14010. (c) Zheng, C.; You, S.-L. *RSC Adv.* **2014**, *4*, 6173. (d) Newton, C. G.; Wang, S.-G.; Oliveira, C. C.; Cramer, N. *Chem. Rev.* **2017**, *117*, 8908. (e) Saint-Denis, T. G.; Zhu, R.-Y.; Chen, G.; Wu, Q.-F.; Yu, J.-Q. *Science* **2018**, *359*, eaao4798. (f) Gandeepan, P.; Müller, T.; Zell, D.; Cera, G.; Warratz, S.; Ackermann, L. *Chem. Rev.* **2019**, *119*, 2192. (g) Wozniak, Ł.; Cramer, N. *Trends Chem.* **2019**, *1*, 471. (h) Yoshino, T.; Satake, S.; Matsunaga, S. *Chem. Eur. J.* **2020**, *26*, 7346. (i) Zhang, Q.; Shi, B.-F. *Acc. Chem. Res.* **2021**, *54*, 2750. (j) Zhan, B.-B.; Jin, L.; Shi, B.-F. *Trends Chem.* **2022**, *4*, 220. (k) McMurray, L.; O'Hara, F.; Gaunt, M. J. *Chem. Soc. Rev.* **2011**, *40*, 1885. (l) Gutekunsta, W. R.; Baran, P. S. *Chem. Soc. Rev.* **2011**, *40*, 1976. (m) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 8960. (n) Abrams, D. J.; Provencher, P. A.; Sorensen, E. J. *Chem. Soc. Rev.* **2018**, *47*, 8925. (o) Lam, N. Y. S.; Wu, K.; Yu, J.-Q. *Angew. Chem. Int. Ed.* **2021**, *60*, 15767. (p) Mas-Roselló, J.; Herraiz, A. G.; Audic, B.; Laverny, A.; Cramer, N. *Angew. Chem. Int. Ed.* **2021**, *60*, 13198. (q) Liang, H.; Wang, J. *Chem. Eur. J.* **2023**, *29*, e202202461. (r) Liao, G.; Zhang, T.; Lin, Z.-K.; Shi, B.-F. *Angew. Chem. Int. Ed.* **2020**, *59*, 19773. (s) Yoshino, T.; Matsunaga, S. *ACS Catal.* **2021**, *11*, 6455. (t) Ye, B.; Cramer, N. *Acc. Chem. Res.* **2015**, *48*, 1308. (u) Shaaban, S.; Davies, C.; Waldmann, H. *Eur. J. Org. Chem.* **2020**, 6512. (v) Achar, T.; Maiti, K. S.; Jana, S.; Maiti, D. *ACS Catal.* **2020**, *10*, 13748. (w) Wang, Q.; Liu, C.-X.; Gu, Q.; You, S.-L. *Sci. Bull.* **2021**, *66*, 210. (x) Pan, C.; Yin, S.-Y.; Gua, Q.; You, S.-L. *Org. Biomol. Chem.* **2021**, *19*, 7264. (y) Yue, Q.; Liu, B.; Liao, G.; Shi, B.-F. *ACS Catal.* **2022**, *12*, 9359. (z) Yoshino, T. *Bull. Chem. Soc. Jpn.* **2022**, *95*, 1280. (aa) Qian, P.-F.; Li, J.-Y.; Zhou, T.; Shi, B.-F. *Synthesis* **2022**, *54*, 4784. (ab) Ye, B.; Cramer, N. *Science* **2012**, *338*, 504. (ac) Hyster, T. K.; Knörr, L.; Ward, T. R.; Rovis, T. *Science* **2012**, *338*, 500. (ad) Hassan, I. S.; Ta, A. N.; Danneman, M. W.; Semakul, N.; Burns, M.; Basch, C. H.; Dippon, V. N.; McNaughton, B. R.; Rovis, T. *J. Am. Chem. Soc.* **2019**, *141*, 4815.

(4) (a) Trifonova, E. A.; Ankudinov, N. M.; Mikhaylov, A. A.; Chusov, D. A.; Nelyubina, Y. V.; Perekalin, D. S. *Angew. Chem. Int. Ed.* **2018**, *57*, 7714. (b) Kolos, A. V.; Nelyubina, Y. V.; Sundararaju, B.; Perekalin, D. S. *Organometallics* **2021**, *40*, 3712. (c) Jia, Z.-J.; Merten, C.; Gontla, R.; Daniliuc, C. G.; Antonchick, A. P.; Waldmann, H. *Angew. Chem. Int. Ed.* **2017**, *56*, 2429. (d) Audic, B.; Wodrich, M. D.; Cramer, N. *Chem. Sci.* **2019**, *10*, 781. (e) Potter, T. J.; Kamber, D. N.; Mercado, D. N.; Ellman, J. A. *ACS Catal.* **2017**, *7*, 150. (f) Yan, X.; Zhao, P.; Liang, H.; Xie, H.; Jiang, J.; Gou, S.; Wang, J. *Org. Lett.* **2020**, *22*, 3219. (g) Li, G.; Yan, X.; Jiang, J.; Liang, H.; Zhou, C.; Wang, J. *Angew. Chem. Int. Ed.* **2020**, *59*, 22436. (h) Liang, H.; Vasamsetty, L.; Li, T.; Jiang, J.; Pang, X.; Wang, J. *Chem. Eur. J.* **2020**, *26*, 14546. (i) Ye, B.; Cramer, N. *J. Am. Chem. Soc.* **2013**, *135*, 636. (j) Ye, B.; Donets, P. A.; Cramer, N. *Angew. Chem. Int. Ed.* **2014**, *53*, 507.

(5) (a) Ye, B.; Cramer, N. *Synlett* **2015**, *26*, 1490. (b) Chen, W.; Li, J.; Xie, H.; Wang, J. *Org. Lett.* **2020**, *22*, 3586. (c) Zheng, G.; Zhou, Z.; Zhu, G.; Zhai, S.; Xu, H.; Duan, X.; Yi, W.; Li, X. *Angew. Chem. Int. Ed.* **2020**, *59*, 2890. (d) Mao, R.; Zhao, Y.; Zhu, X.; Wang, F.; Deng, W.-Q.; Li, X. *Org. Lett.* **2021**, *23*, 7038. (e) Duchemin, C.; Cramer, N. *Chem. Sci.* **2019**, *10*, 2773. (f) Duchemin, C.; Cramer, N. *Angew. Chem. Int. Ed.* **2020**, *59*, 14129.

(6) (a) Wu, L.; Xu, H.; Gao, H.; Li, L.; Chen, W.; Zhou, Z.; Yi, W. *ACS Catal.* **2021**, *11*, 2279. (b) Wu, L.; Li, L.; Zhang, H.; Gao, H.; Zhou, Z.; Yi, W. *Org. Lett.* **2021**, *23*, 3844. (c) Wei, Y.; Xu, H.; Chen, F.; Gao, H.; Huang, Y.; Yi, W.; Zhou, Z. *New J. Chem.* **2022**, *46*, 5705. (d) Wu, M.; Gao, H.; Xu, H.; Yi, W.; Zhou, Z. *Chin. Chem. Lett.* **2022**, *33*, 842. (e) Maity, S.; Potter, T. J.; Ellman, J. A. *Nat. Catal.* **2019**, *2*, 756. (f) Mi, R.; Zhang, X.; Wang, J.; Chen, H.; Lan, Y.; Wang, F.; Li, X. *ACS Catal.* **2021**, *11*, 6692. (g) Brandes, D. S.; Sirvent, A.; Mercado, B. Q.; Ellman, J. A. *Org. Lett.* **2021**, *23*, 2836. (h) Wang, S.-G.; Cramer, N. *Angew. Chem. Int. Ed.* **2019**, *58*, 2514. (i) Yang, X.; Zheng, G.; Li, X. *Angew. Chem. Int. Ed.* **2019**, *58*, 322. (j) Mi, R.; Zheng, G.; Qi, Z.; Li, X. *Angew. Chem. Int. Ed.* **2019**, *58*, 17666.

(7) (a) Ye, B.; Cramer, N. *Angew. Chem. Int. Ed.* **2014**, *53*, 7896. (b) Chen, X.; Yang, S.; Li, H.; Wang, B.; Song, G. *ACS Catal.* **2017**, *7*, 2392. (c) Liu, B.; Xie, P.; Zhao, J.; Wang, J.; Wang, M.; Jiang, Y.; Chang, J.; Li, X. *Angew. Chem. Int. Ed.* **2021**, *60*, 8396. (d) Li, T.; Zhou, C.; Yan, X.; Wang, J. *Angew. Chem. Int. Ed.* **2018**, *57*, 4048. (e) Wang, S.-G.; Liu, Y.; Cramer, N. *Angew. Chem. Int. Ed.* **2019**, *58*, 18136. (f) Wang, S.-G.; Cramer, N. *ACS Catal.* **2020**, *10*, 8231. (g) Cui, W.-J.; Wu, Z.-J.; Gu, Q.; You, S.-L. *J. Am. Chem. Soc.* **2020**, *142*, 7379.

(8) (a) Kong, L.; Han, X.; Liu, S.; Zou, Y.; Lan, Y.; Li, X. *Angew. Chem. Int. Ed.* **2020**, *59*, 7188. (b) Sun, L.; Liu, B.; Wang, F.; Deng, W.-Q.; Zhao, Y.; Chang, J.; Kong, L.; Li, X. *Chem. Commun.* **2021**, *57*, 8268. (c) Zheng, J.; Wang, S.-B.; Zheng, C.; You, S.-L. *J. Am. Chem. Soc.* **2015**, *137*, 4880. (d) Zheng, C.; Zheng, J.; You, S.-L. *ACS Catal.* **2016**, *6*, 262. (e) Chidipudi, S. R.; Burns, D. J.; Khan, I.; Lam, H. W. *Angew. Chem. Int. Ed.* **2015**, *54*, 13975. (f) Zheng, J.; Wang, S.-B.; Zheng, C.; You, S.-L. *Angew. Chem. Int. Ed.* **2017**, *56*, 4540. (g) Pham, M. V.; Cramer, N. *Chem. Eur. J.* **2016**, *22*, 2270. (h) Li, H.; Gontla, R.; Flegel, J.; Merten, C.; Ziegler, S.; Antonchick, A. P.; Waldmann, H. *Angew. Chem. Int. Ed.* **2019**, *58*, 307. (i) Huang, Y.-Q.; Wu, Z.-J.; Zhu, L.; Gu, Q.; Lu, X.; You, S.-L.; Mei, T.-S. *CCS Chem.* **2022**, *4*, 3181. (j) Wei, W.; Scheremetjew, A.; Ackermann, L. *Chem. Sci.* **2022**, *13*, 2783.

(9) (a) Shan, G.; Flegel, J.; Li, H.; Merten, C.; Ziegler, S.; Antonchick, A. P.; Waldmann, H. *Angew. Chem. Int. Ed.* **2018**, *57*, 14250. (b) Tian, M.; Bai, D.; Zheng, G.; Chang, J.; Li, X. *J. Am. Chem. Soc.* **2019**, *141*, 9527. (c) Wang, F.; Qi, Z.; Zhao, Y.; Zhai, S.; Zheng, G.; Mi, R.; Huang, Z.; Zhu, X.; He, X.; Li, X. *Angew. Chem. Int. Ed.* **2020**, *59*, 13288. (d) Wang, F.; Jing, J.; Zhao, Y.; Zhu, X.; Zhang, X.-P.; Zhao, L.; Hu, P.; Deng, W.-Q.; Li, X. *Angew. Chem. Int. Ed.* **2021**, *60*, 16628. (e) Mi, R.; Chen, H.; Zhou, X.; Li, N.; Ji, D.; Wang, F.; Lan, Y.; Li, X. *Angew. Chem. Int. Ed.* **2022**, *61*, e202111860. (f) Li, H.; Yan, X.; Zhang, J.; Guo, W.; Jiang, J.; Wang, J. *Angew. Chem. Int. Ed.* **2019**, *58*, 6732. (g) Yan, Y.; Jiang, J.; Wang, J. *Angew. Chem. Int. Ed.* **2022**, *61*, e202201522.

(10) (a) Pan, C.; Yin, S.-Y.; Wang, S.-B.; Gu, Q.; You, S.-L. *Angew. Chem. Int. Ed.* **2021**, *60*, 15510. (b) Shaaban, S.; Merten, C.; Waldmann, H. *Chem. Eur. J.* **2022**, *28*, e202103365. (c) Zheng, J.; You, S.-L. *Angew. Chem. Int. Ed.* **2014**, *53*, 13244. (d) Zheng, J.; Cui, W.-J.; Zheng, C.; You, S.-L. *J. Am. Chem. Soc.* **2016**, *138*, 5242. (e) Wang, Q.; Zhang, W.-W.; Zheng, C.; Gu, Q.; You, S.-L. *J. Am. Chem. Soc.* **2021**, *143*, 114. (f) Zou, Y.; Wang, P.; Kong, L.; Li, X. *Org. Lett.* **2022**, *24*, 3189.

(11) (a) Sun, Y.; Cramer, N. *Angew. Chem. Int. Ed.* **2017**, *56*, 364. (b) Sun, Y.; Cramer, N. *Chem. Sci.* **2018**, *9*, 2981. (c) Sun, Y.; Cramer, N. *Angew. Chem. Int. Ed.* **2018**, *57*, 15539. (d) Brauns, M.; Cramer, N. *Angew. Chem. Int. Ed.* **2019**, *58*, 8902. (e) Hu, P.; Kong, L.; Wang, F.; Zhu, X.; Li, X. *Angew. Chem. Int. Ed.* **2021**, *60*, 20424. (f) Shen, B.; Wan, B.; Li, X. *Angew. Chem. Int. Ed.* **2018**, *57*, 15534.

(12) (a) Wang, J.; Chen, H.; Kong, L.; Wang, F.; Lan, Y.; Li, X. *ACS Catal.* **2021**, *11*, 9151. (b) Wang, S.-B.; Zheng, J.; You, S.-L. *Organometallics* **2016**, *35*, 1420. (c) Wang, S.-B.; Gu, Q.; You, S.-L. *Organometallics* **2017**, *36*, 4359. (d) Wang, Q.; Nie, Y.-H.; Liu, C.-X.; Zhang, W.-W.; Wu, Z.-J.; Gu, Q.; Zheng, C.; You, S.-L. *ACS Catal.* **2022**, *12*, 3083. (e) Wang, Q.; Zhang, W.-W.; Song, H.; Wang, J.; Zheng, C.; Gu, Q.; You, S.-L. *J. Am. Chem. Soc.* **2020**, *142*, 15678. (f) Zhang, W.-W.; Liu, C.-X.; Yang, P.; Zhang, S.-Z.; Gu, Q.; You, S.-L. *Org. Lett.* **2022**, *24*, 564. (g) Kurihara, T.; Kojima, M.; Yoshino, T.; Matsunaga, S. *J. Am. Chem. Soc.* **2022**, *144*, 7058.

(13) (a) Lin, L.; Fukagawa, S.; Sekine, D.; Tomita, E.; Yoshino, T.; Matsunaga, S. *Angew. Chem. Int. Ed.* **2018**, *57*, 12048. (b) Fukagawa, S.; Kojima, M.; Yoshino, T.; Matsunaga, S. *Angew. Chem. Int. Ed.* **2019**, *58*, 18154. (c) Huang, L.-T.; Fukagawa, S.; Kojima, M.; Yoshino, T.; Matsunaga, S. *Org. Lett.* **2020**, *22*, 8256. (d) Kato, Y.; Lin, L.; Kojima, M.; Yoshino, T.; Matsunaga, S. *ACS Catal.* **2021**, *11*, 4271. (e) Satake, S.; Kurihara, T.; Nishikawa, K.; Mochizuki, T.; Hatano, M.; Ishihara, K.; Yoshino, T.; Matsunaga, S. *Nat. Catal.* **2018**, *1*, 585. (f) Hirose, J.; Wakikawa, T.; Satake, S.; Kojima, M.; Hatano, M.; Ishihara, K.; Yoshino, T.; Matsunaga, S. *ACS Catal.* **2021**, *11*, 15187. (g) Li, G.; Jiang, J.; Xie, H.; Wang, J. *Chem. Eur. J.* **2019**, *25*, 4688.

(14) (a) Jang, Y.-S.; Dieckmann, M.; Cramer, N. *Angew. Chem. Int. Ed.* **2017**, *56*, 15088. (b) Jang, Y.-S.; Wozniak, Ł.; Pedroni, J.; Cramer, N. *Angew. Chem. Int. Ed.* **2018**, *57*, 12901. (c) Wozniak, Ł.; Cramer, N. *Angew. Chem. Int. Ed.* **2021**, *60*, 18532. (d) Zimbron, J. M.; Heinisch, T.; Schmid, M.; Hamels, D.; Nogueira, E. S.; Schirmer, T.; Ward, T. R. *J. Am. Chem. Soc.* **2013**, *135*, 5384.

(15) (a) Gwon, D.; Park, S.; Chang, S. *Tetrahedron* **2015**, *71*, 4504. (b) Zhang, C.-W.; Hu, X.-Q.; Dai, Y.-H.; Yin, P.; Wang, C.; Duan, W.-L. *ACS Catal.* **2022**, *12*, 193. (c) Liu, W.; Yang, W.; Zhu, J.; Guo, Y.; Wang, N.; Ke, J.; Yu, P.; He, C. *ACS Catal.* **2020**, *10*, 7207. (d) Liu, L.; Song, H.; Liu, Y.-H.; Wu, L.-S.; Shi, B.-F. *ACS Catal.* **2020**, *10*, 7117. (e) Li, J.-Y.; Xie, P.-P.; Zhou, T.; Qian, P.-F.; Zhou, Y.-B.; Li, H.-C.; Hong, X.; Shi, B.-F. *ACS Catal.* **2022**, *12*, 9083.

(16) (a) Ozols, K.; Jang, Y.-S.; Cramer, N. *J. Am. Chem. Soc.* **2019**, *141*, 5675. (b) Ozols, K.; Onodera, S.; Woźniak, Ł.; Cramer, N. *Angew. Chem. Int. Ed.* **2021**, *60*, 655. (c) Herraiz, A. G.; Cramer, N. *ACS Catal.* **2021**, *11*, 11938. (d) Pesciaioli, F.; Dhawa, U.; Oliveira, J. C. A.; Yin, R.; John, M.; Ackermann, L. *Angew. Chem. Int. Ed.* **2018**, *57*, 15425.

(17) (a) Fukagawa, S.; Kato, Y.; Tanaka, R.; Kojima, M.; Yoshino, T.; Matsunaga, S. *Angew. Chem. Int. Ed.* **2019**, *58*, 1153. (b) Sekine, D.; Ikeda, K.; Fukagawa, S.; Kojima, M.; Yoshino, T.; Matsunaga, S. *Organometallics* **2019**, *38*, 3921. (c) Liu, Y.-H.; Li, P.-X.; Yao, Q.-J.; Zhang, Z.-Z.; Huang, D.-Y.; Le, M. D.; Song, H.; Liu, L.; Shi, B.-F. *Org. Lett.* **2019**, *21*, 1895. (d) Liu, Y.-H.; Xie, P.-P.; Liu, L.; Fan, J.; Zhang, Z.-Z.; Hong, X.; Shi, B.-F. *J. Am. Chem. Soc.* **2021**, *143*, 19112. (e) Hirata, Y.; Sekine, D.; Kato, Y.; Lin, L.; Kojima, M.; Yoshino, T.; Matsunaga, S. *Angew. Chem. Int. Ed.* **2022**, *61*, e202205341. (f) Zhou, Y.-B.; Zhou, T.; Qian, P.-F.; Li, J.-Y.; Shi, B.-F. *ACS Catal.* **2022**, *12*, 9806.

(18) (a) Liang, H.; Guo, W.; Li, J.; Jiang, J.; Wang, J. *Angew. Chem. Int. Ed.* **2022**, *61*, e202204926. (b) Li, Z.-Y.; Lakmal, H. H. C.; Qian, X.; Zhu, Z.; Donnadieu, B.; McClain, S. J.; Xu, X.; Cui, X. *J. Am. Chem. Soc.* **2019**, *141*, 15730. (c) Li, G.; Liu, Q.; Vasamsetty, L.; Guo, W.; Wang, J. *Angew. Chem. Int. Ed.* **2020**, *59*, 3475. (d) Dethe, D. H.; Beeralingappa, N. C.; Siddiqui, S. A.; Chavan, P. N. *J. Org. Chem.* **2022**, *87*, 4617. (e) Zhou, T.; Qian, P-F.; Li, J.-Y.; Zhou, Y.-B.; Li, H.-C.; Chen, H.-Y.; Shi, B.-F. *J. Am. Chem. Soc.* **2021**, *143*, 6810. (f) Huang, L.-T.; Hirata, Y.; Kato, Y.; Lin, L.; Kojima, M.; Yoshino, T.; Matsunaga, S. *Synthesis* **2022**, *54*, 4703. (g) Qian, P.-F.; Zhou, T.; Li, J.-Y.; Zhou, Y.-B.; Shi, B.-F. *ACS Catal.* **2022**, *12*, 13876. (h) Dhawa, U.; Connon, R.; Oliveira, J. C. A.; Steinbock, R.; Ackermann, L. *Org. Lett.* **2021**, *23*, 2760. (i) Li, Y.; Liou, Y.-C.; Oliveira, J. C. A.; Ackermann, L. *Angew. Chem. Int. Ed.* **2022**, *61*, e202212595.