

Half-Sandwich d^6 -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

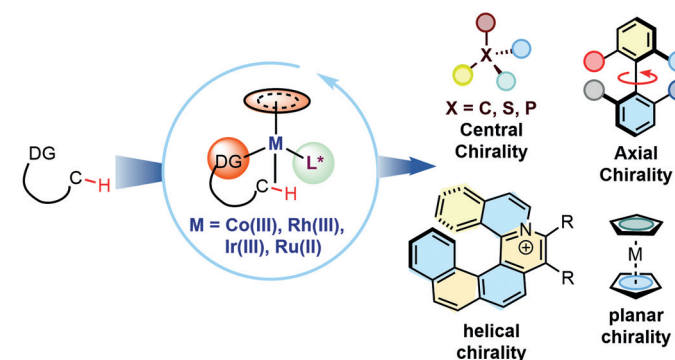
^b College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, Henan, 450001, P. R. of China
taozhou@zju.edu.cn

^c School of Chemistry and Chemical Engineering, Henan Normal University, Xixiang 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



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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 d^6 -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 co-workers 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 en-

antioselective $\text{C}(\text{sp}^2)\text{--H}$ and $\text{C}(\text{sp}^3)\text{--H}$ 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 d^6 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 d^6 -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 broad substrate scope and various functionalization. Besides, several types of well-designed monodentate chiral carboxylic acids (CCAs) have also been developed to realize half-sandwich d^6 -metal-catalyzed enantioselective C–H functionalization reactions. The third strategy takes advantage of a chiral transient directing group (cTDG). 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 have 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 d^6 -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.

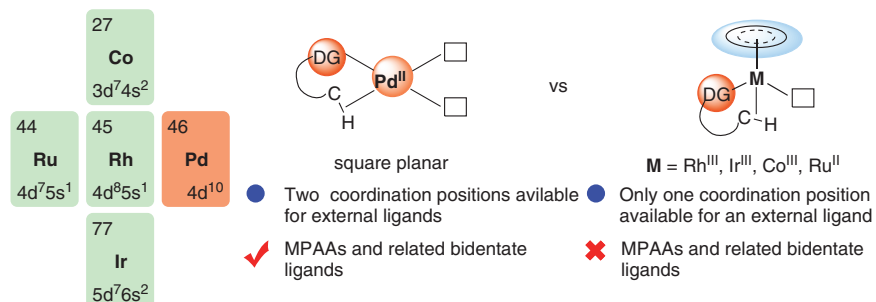
Jun-Yi Li was born in 2000 in Zhejiang Province, China. He received his B.Sc. degree from Zhejiang University in 2022. In the same year, he joined the Department of Chemistry, Zhejiang University for his Ph.D. studies in the laboratories of Prof. Dr. Bing-Feng Shi. His research interests focus on transition-metal-catalyzed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

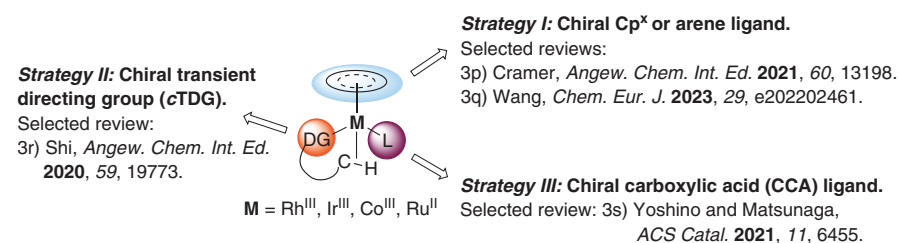


Selected reviews on transition-metal-catalyzed asymmetric C–H activation

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

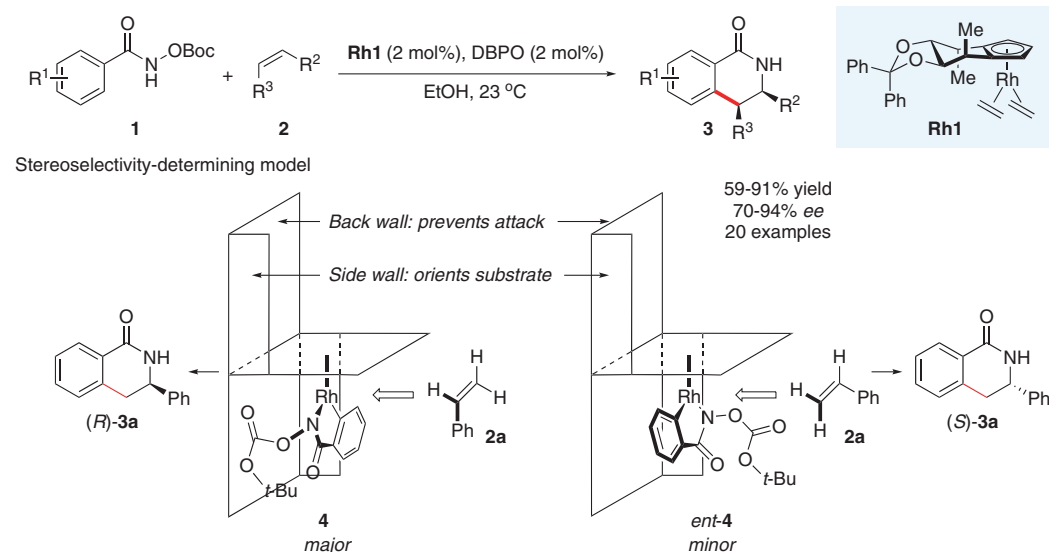
Selected reviews on applications of C–H activation in organic synthesis

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

Three main strategies for half-sandwich d⁶-metal-catalyzed enantioselective C–H activation

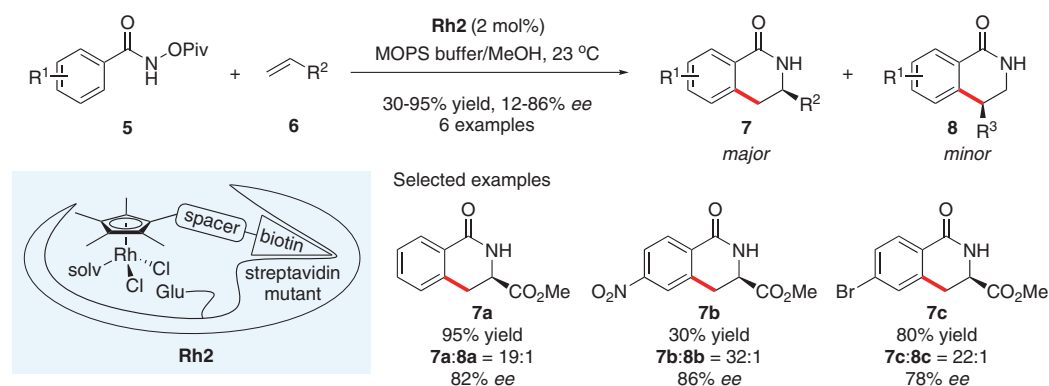
Other selected reviews on half-sandwich metal-catalyzed asymmetric C–H activation

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

Two pioneering reports on half-sandwich metal-catalyzed enantioselective C–H activation with Cp^xRh catalysts Using a chiral Cp^x ligand as the enantiocontrol element

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

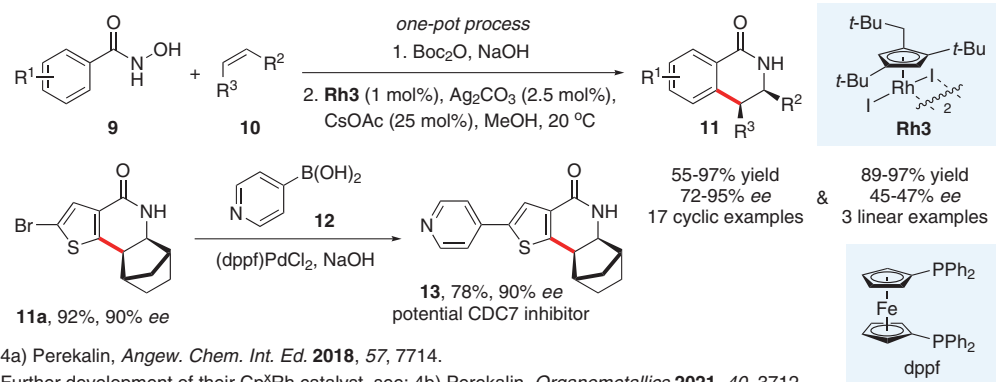
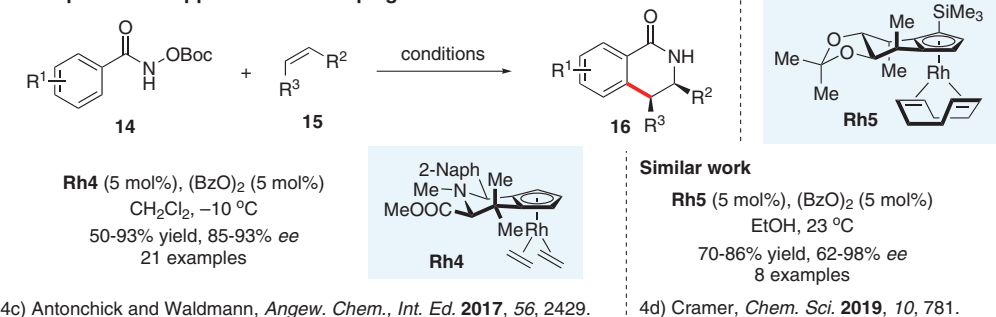
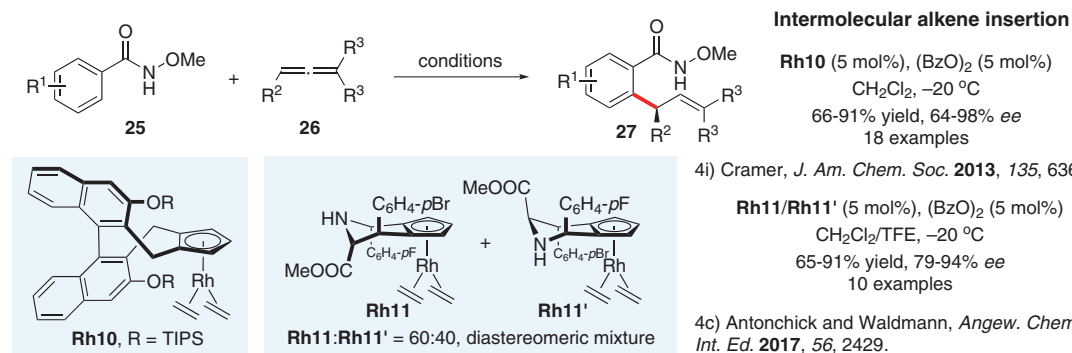
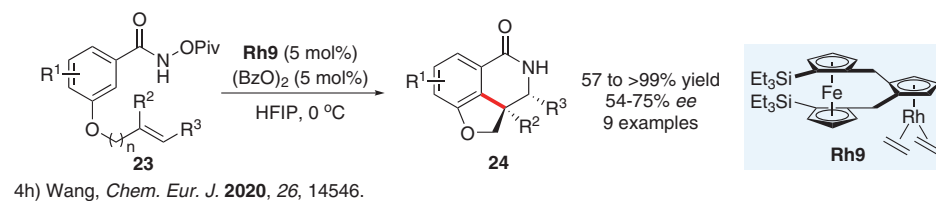
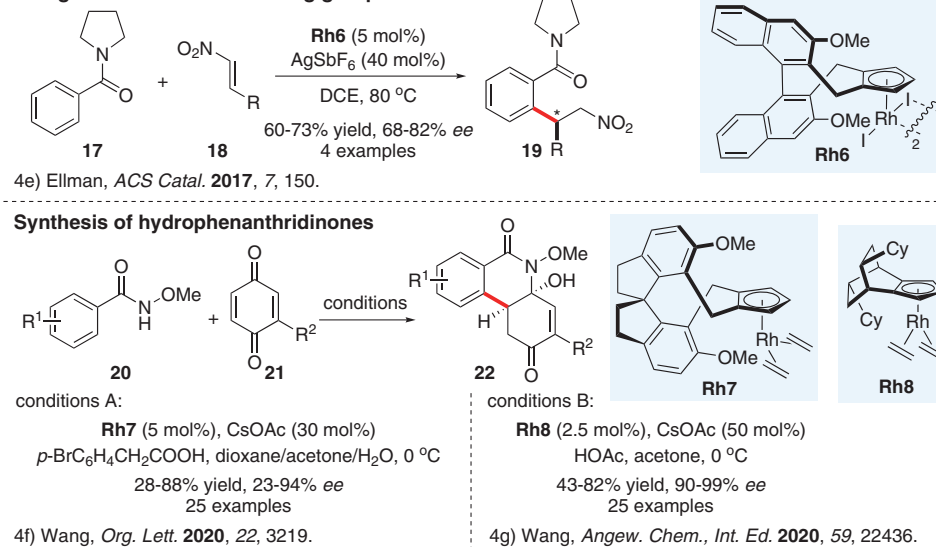
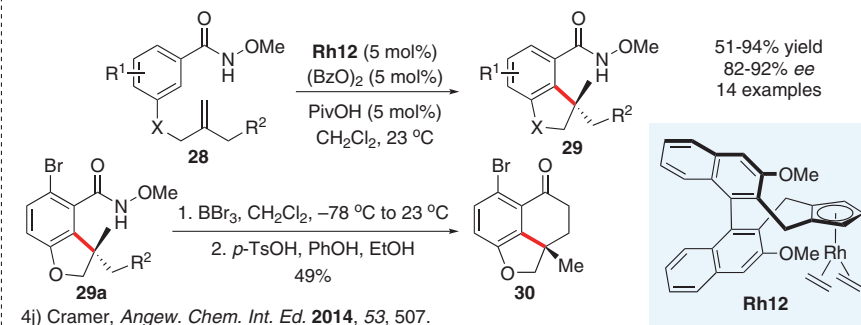
Using biomimetic catalysis to control the enantioselectivity of C–H functionalization

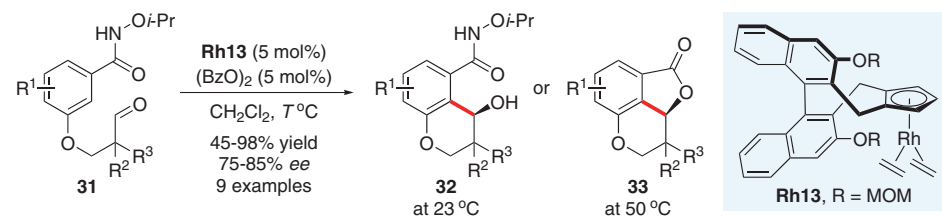


3ac) Ward and Rovis, *Science* **2012**, *338*, 500.

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 d⁶-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}

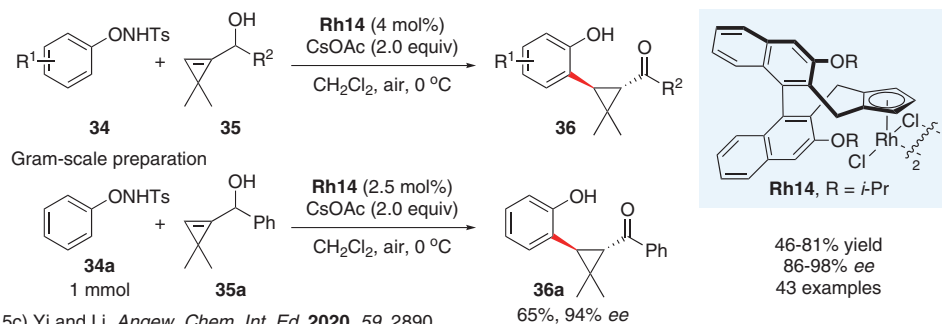
Enantioselective C–H activation catalyzed by planar chiral Cp*Rh^{III}

Development and application of JasCp ligands

Using an amide as the directing group

Intramolecular alkene insertion

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

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

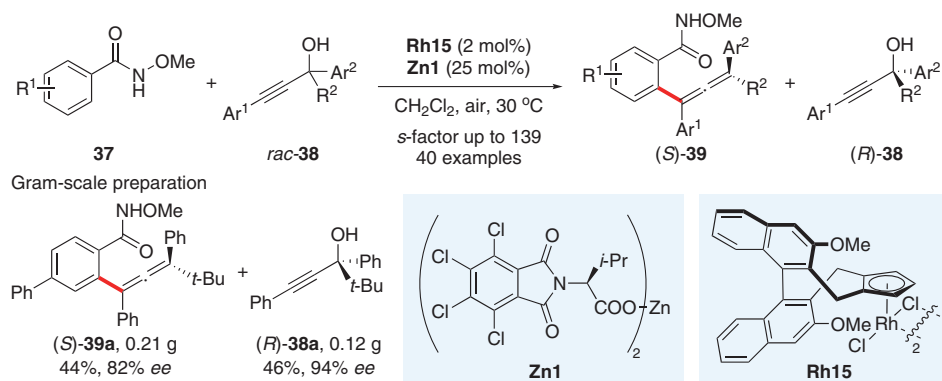
32 could be converted into **33** under the standard conditions at 50 °C.

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

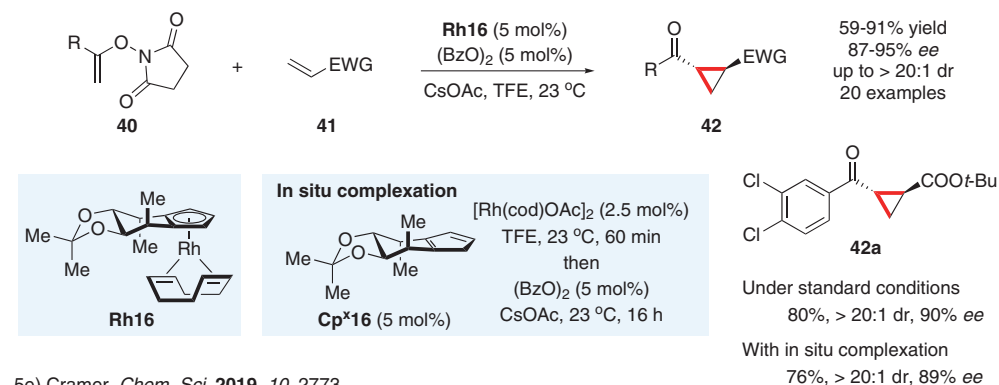
Construction of two C-stereogenic center in a single step



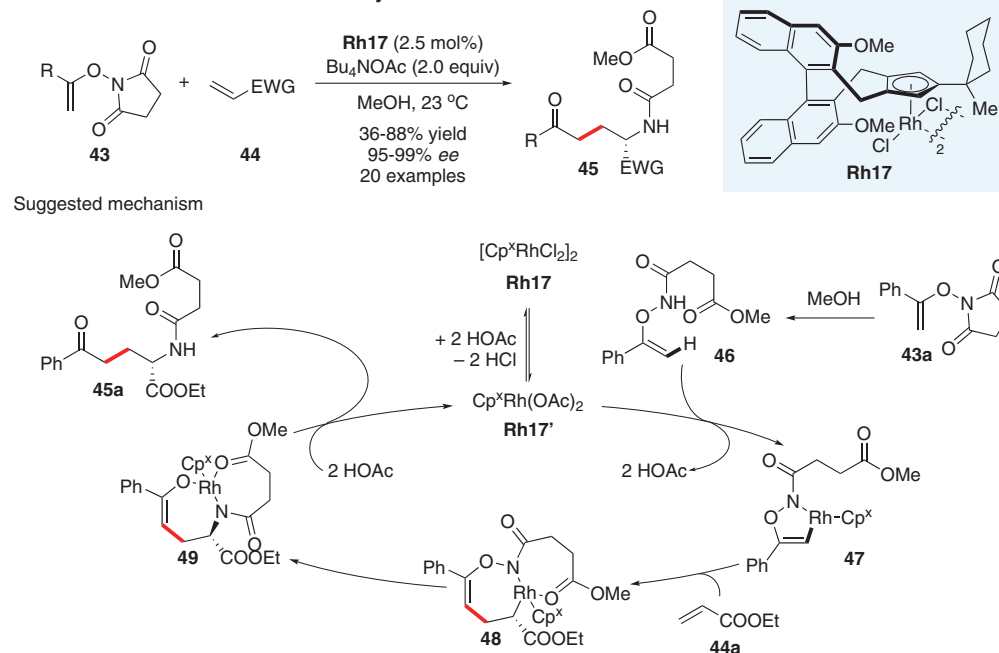
5c) Yi and Li, *Angew. Chem. Int. Ed.* **2020**, 59, 2890.

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

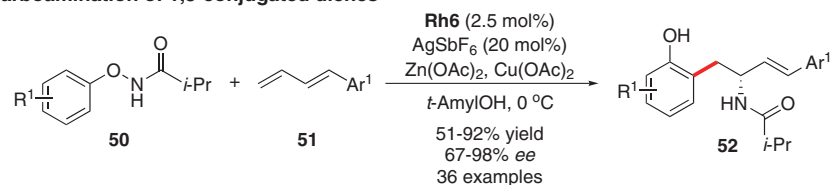
5e) Cramer, *Chem. Sci.* **2019**, 10, 2773.

Intermolecular carboamination *via* vinylic C–H activation

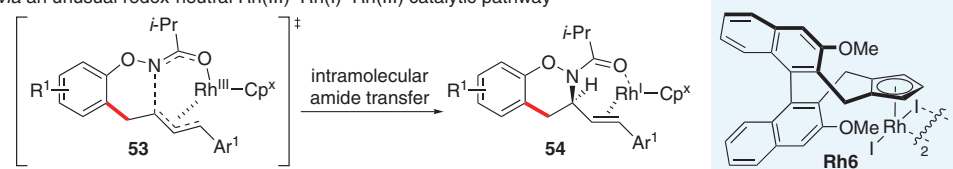
5f) Cramer, *Angew. Chem. Int. Ed.* **2020**, 59, 14129.

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

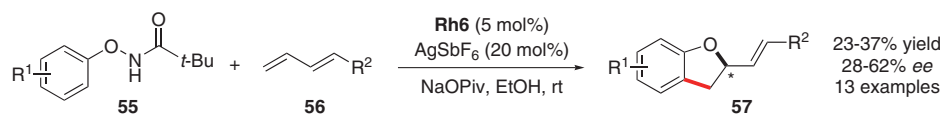
Carboamination of 1,3-conjugated dienes



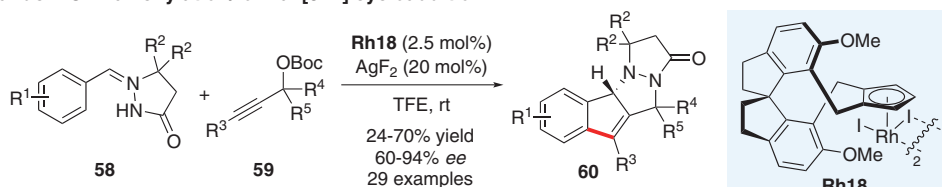
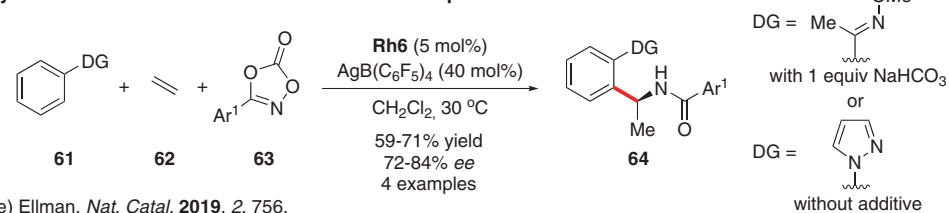
via an unusual redox-neutral Rh(III)–Rh(I)–Rh(III) catalytic pathway

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

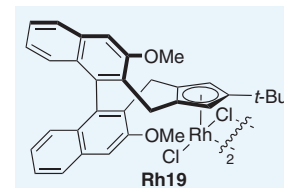
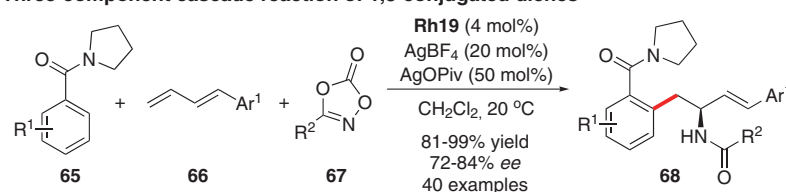
[3+2] annulation of 1,3-conjugated dienes

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

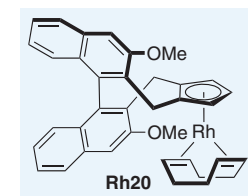
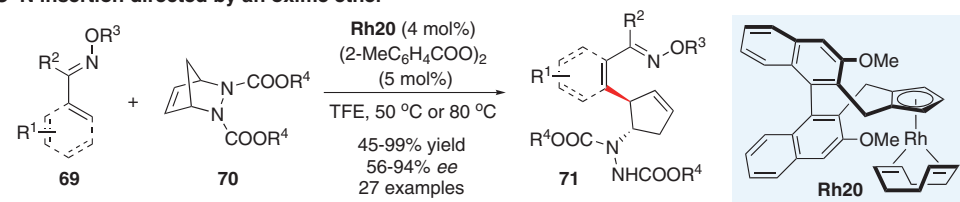
Tandem C–H alkenylation/formal [3+2] cycloaddition

6d) Yi and Zhou, *Chin. Chem. Lett.* **2022**, *33*, 842.Synthesis of α -branched amides via a three-component cascade reaction6e) Ellman, *Nat. Catal.* **2019**, *2*, 756.

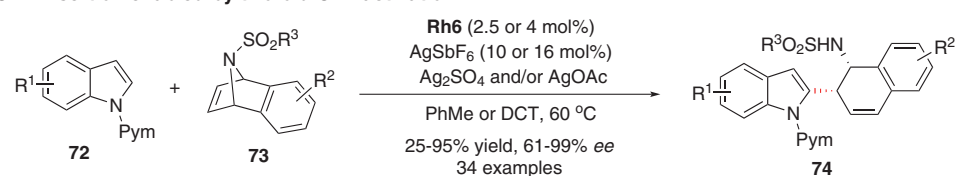
Three-component cascade reaction of 1,3-conjugated dienes

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

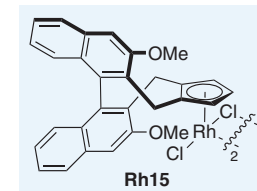
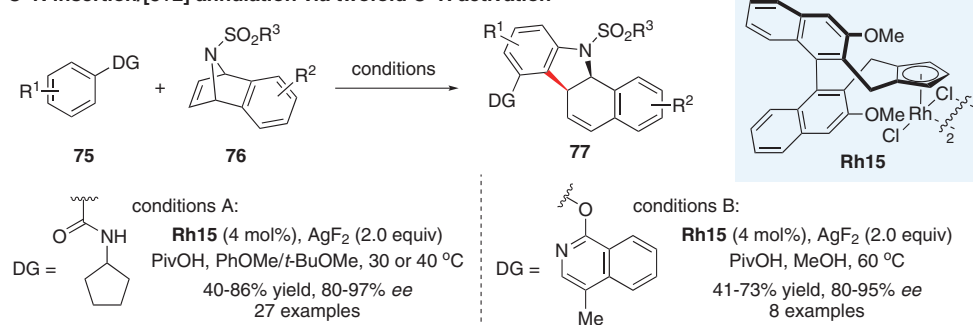
C–N insertion directed by an oxime ether

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

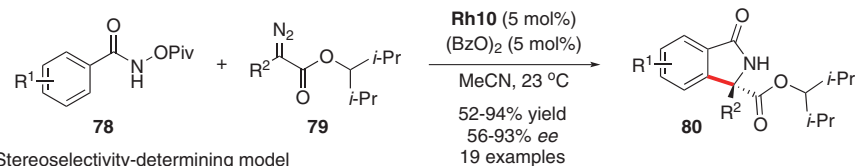
C–N insertion enabled by twofold C–H activation

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

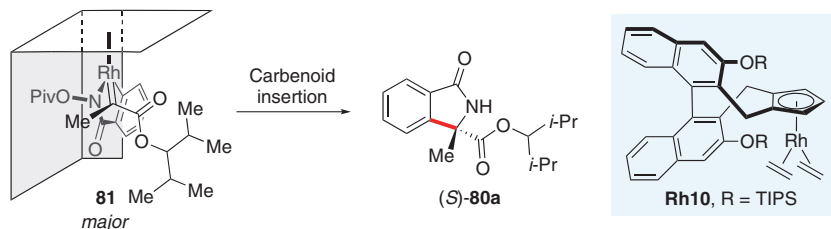
C–N insertion/[3+2] annulation via twofold C–H activation

6j) Li, *Angew. Chem. Int. Ed.* **2019**, *58*, 17666.Figure 4 Chiral Cp*Rh-catalyzed asymmetric synthesis of chiral amides and heterocycles^{6a-j}

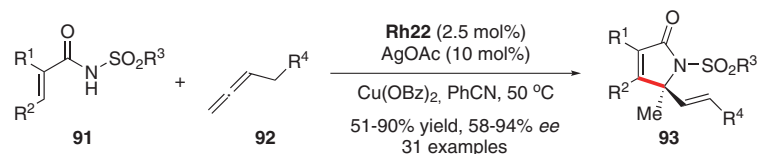
Asymmetric synthesis of isoindolines via carbenoid insertion



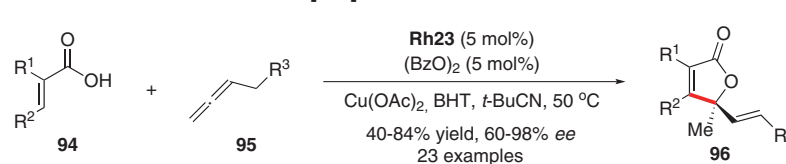
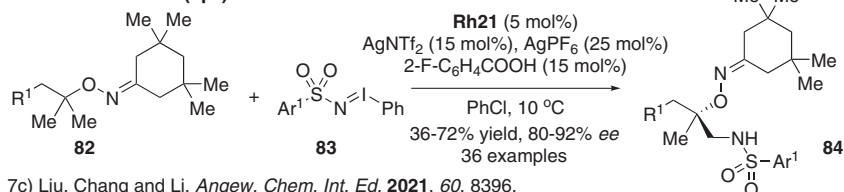
Stereoselectivity-determining model

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

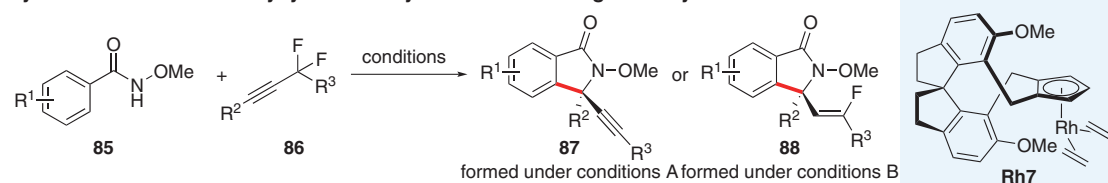
Asymmetric [4+1]-annulation of acrylamides and allenes

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(sp³)-H activation/amidation7c) Liu, Chang and Li, *Angew. Chem. Int. Ed.* **2021**, *60*, 8396.

Asymmetric formation of alkynyl and alkenyl isoindolinones regulated by solvents



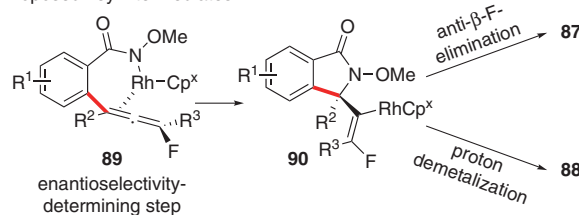
conditions A:

Rh7 (6 mol%)
(BzO)₂ (6 mol%)
3 Å MS, PhCOOK
MeOH, 40 °C
32-86% yield
93-99% ee
26 examples of **87**

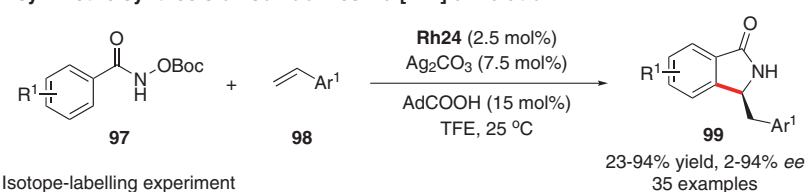
conditions B:

Rh7 (8 mol%)
(BzO)₂ (8 mol%)
5 Å MS, *p*-EtC₆H₄COOK
i-PrCN, 40 °C
26-93% yield
50-86% ee
15 examples of **88**

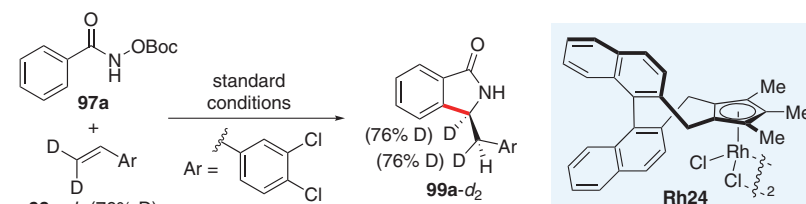
Proposed key intermediates

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

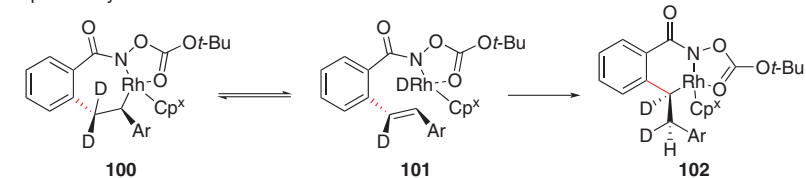
Asymmetric synthesis of isoindolines via [4+1]-annulation



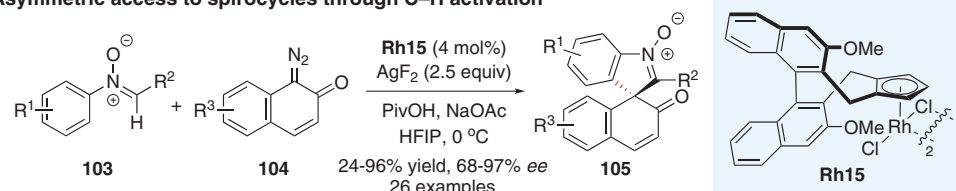
Isotope-labelling experiment



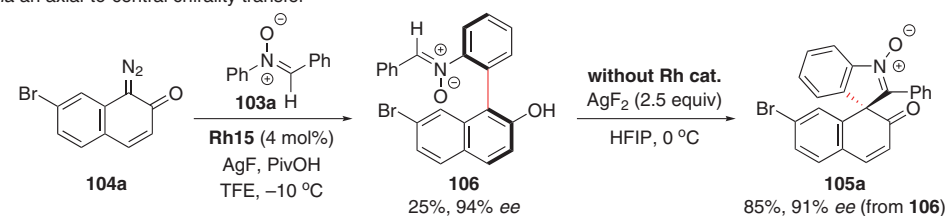
Proposed key intermediates

7g) You, *J. Am. Chem. Soc.* **2020**, *142*, 7379.Figure 5 Enantioselective [4+1]-annulations of acrylamides/acids catalyzed by chiral Cp*Rh catalysts^{7a-g}

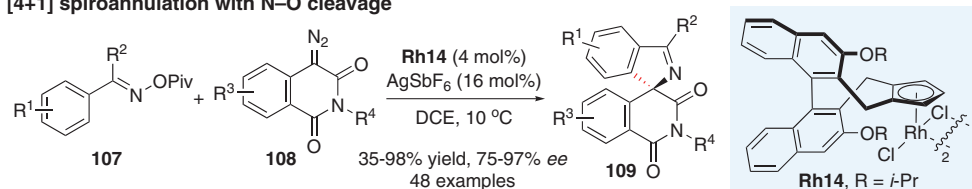
Asymmetric access to spirocycles through C–H activation



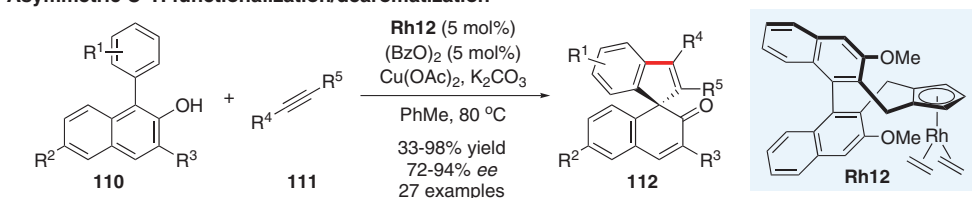
via an axial-to-central chirality transfer

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

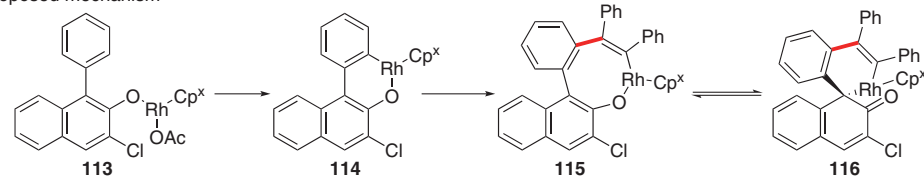
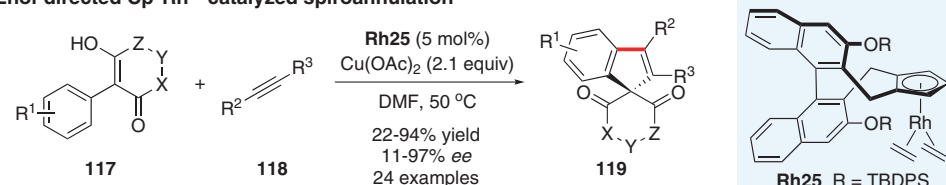
[4+1] spiroannulation with N–O cleavage

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

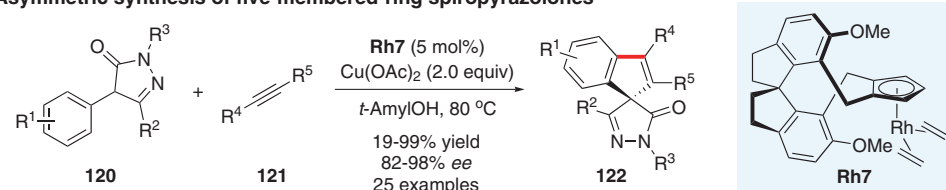
Asymmetric C–H functionalization/dearomatization



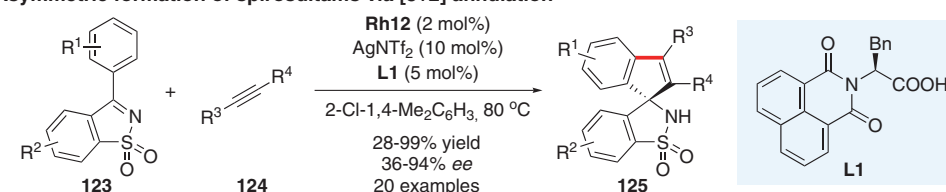
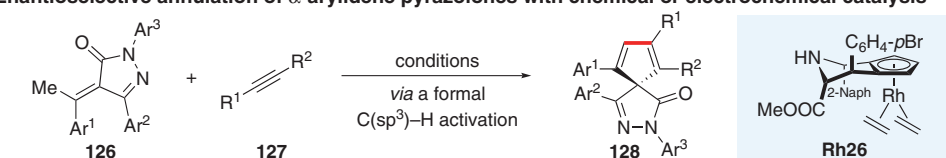
Proposed mechanism

8c) You, *J. Am. Chem. Soc.* **2015**, *137*, 4880. For DFT studies, see: 8d) You, *ACS Catal.* **2016**, *6*, 262.Enol-directed $\text{Cp}^*\text{Rh}^{\text{III}}$ -catalyzed spiroannulation8e) Lam, *Angew. Chem. Int. Ed.* **2015**, *54*, 13975.

Asymmetric synthesis of five-membered-ring spiropyrazolones

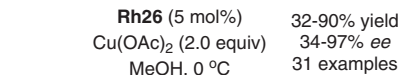
8f) You, *Angew. Chem. Int. Ed.* **2017**, *56*, 4540.

Asymmetric formation of spiro-sultams via [3+2] annulation

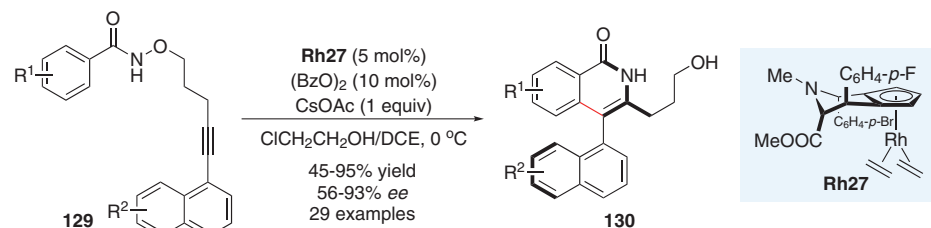
8g) Cramer, *Chem. Eur. J.* **2016**, *22*, 2270.Enantioselective annulation of α -arylidene pyrazolones with chemical or electrochemical catalysis

Antonchick and Waldmann, 2019, chemical catalysis

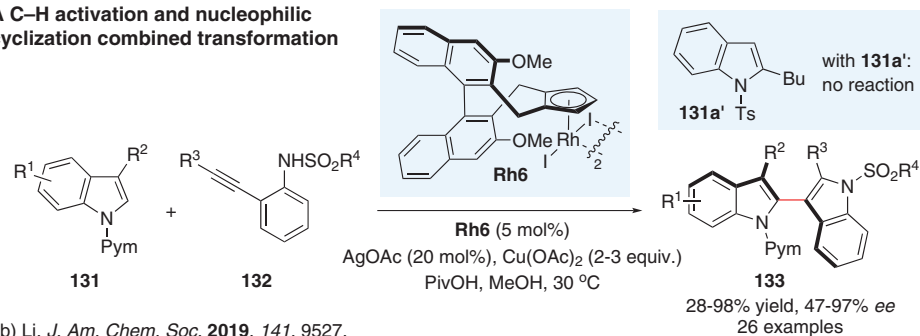
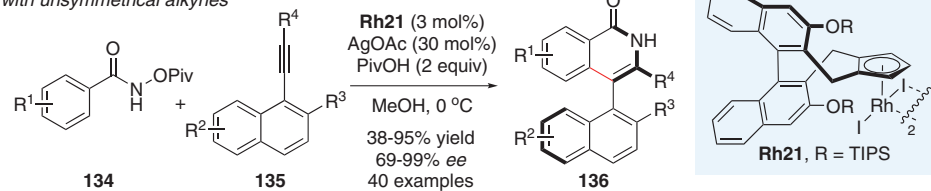
Lu, You and Mei, 2022 electrochemical catalysis

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^*Rh -catalyzed annulations^{8a–j}

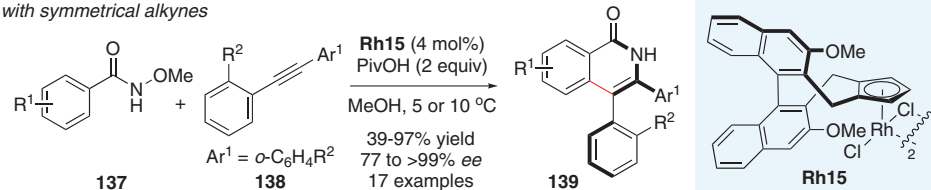
Asymmetric access to heterocyclic atropisomers

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

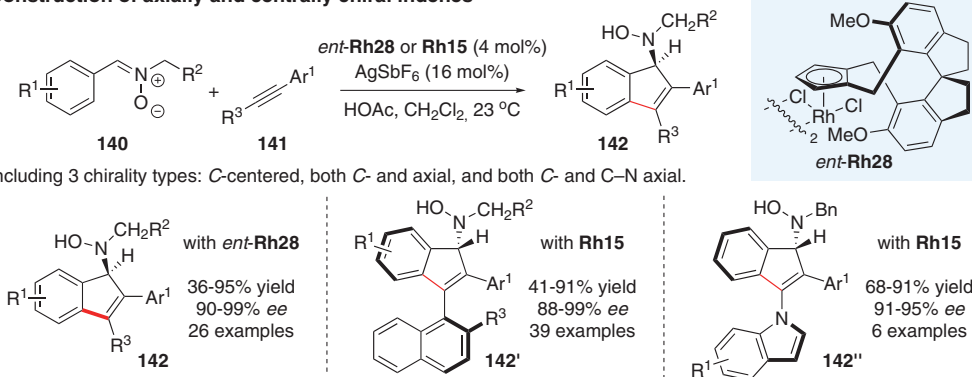
A C–H activation and nucleophilic cyclization combined transformation

9b) Li, *J. Am. Chem. Soc.* **2019**, *141*, 9527.Intermolecular [4+2] annulation with sterically hindered alkynes
with unsymmetrical alkynes

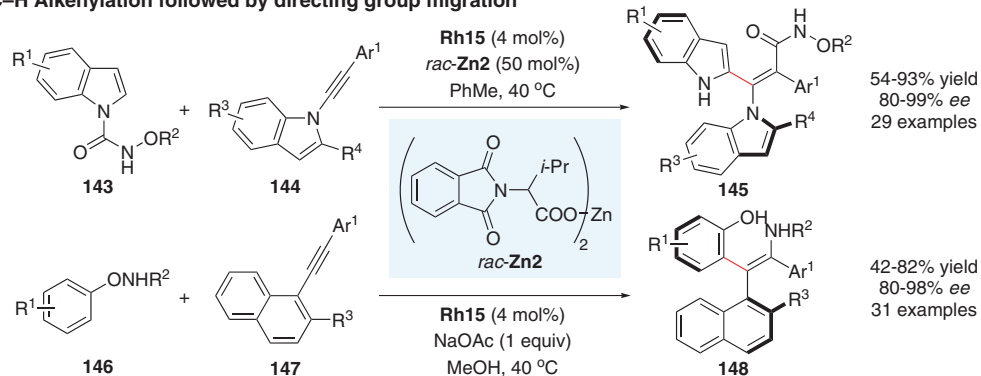
with symmetrical alkynes

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

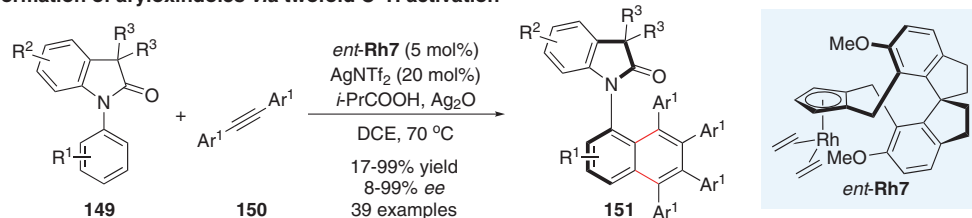
Construction of axially and centrally chiral indenes

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

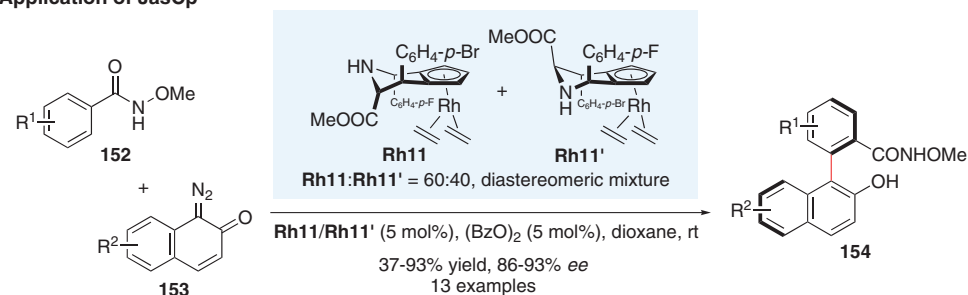
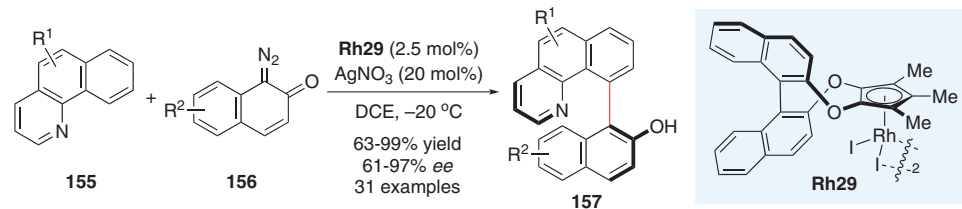
C–H Alkenylation followed by directing group migration

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

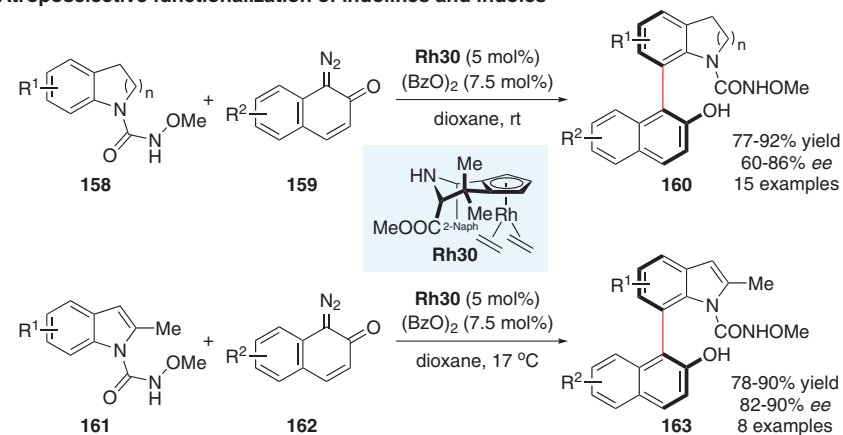
Formation of aryloxindoles via twofold C–H activation

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*Rh-catalyzed annulations with alkynes^{9a–g}

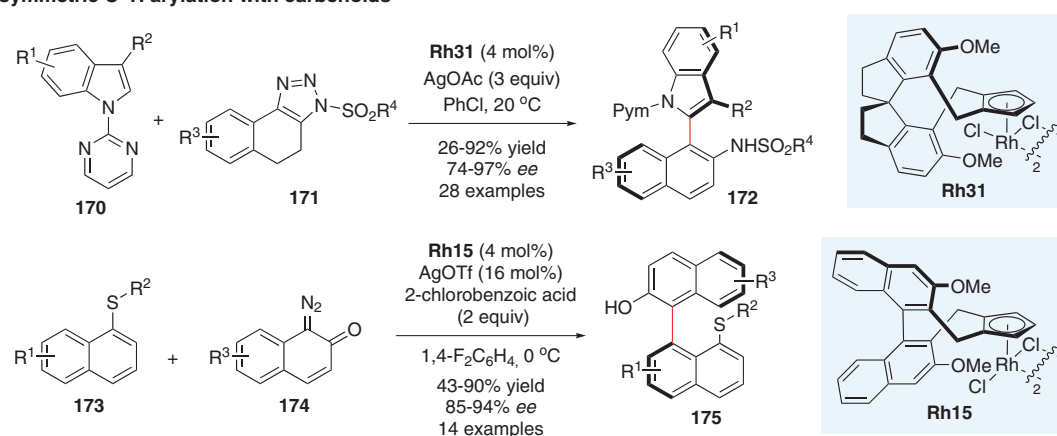
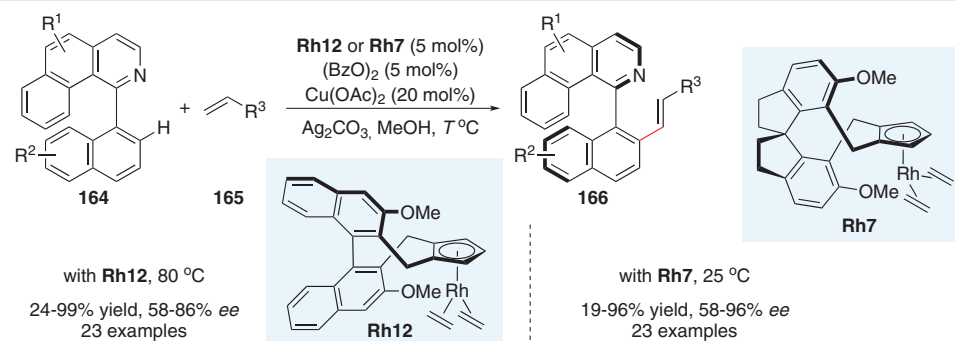
Application of JasCP

4c) Antonchick and Waldmann, *Angew. Chem. Int. Ed.* **2017**, *56*, 2429.Asymmetric C–H arylation catalyzed by O-linked Cp^xRh^{III}10a) You, *Angew. Chem. Int. Ed.* **2021**, *60*, 15510.

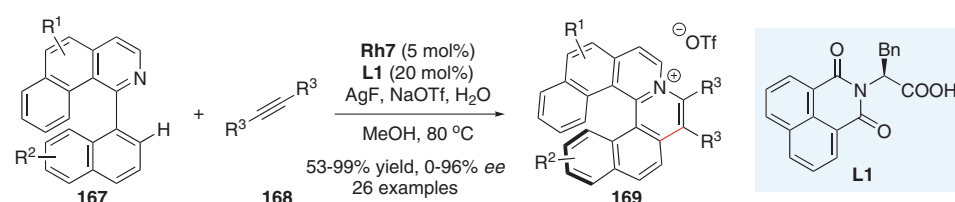
Atroposelective functionalization of indolines and indoles

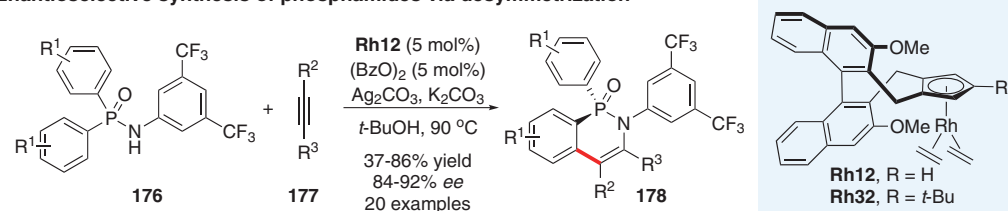
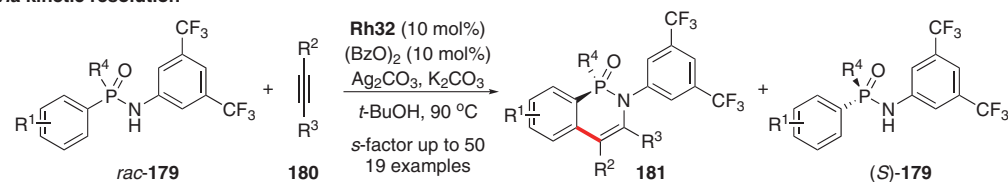
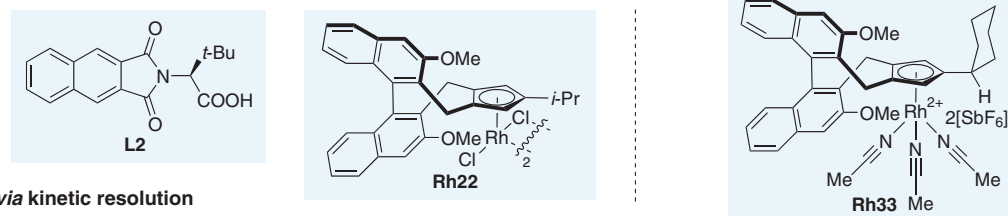
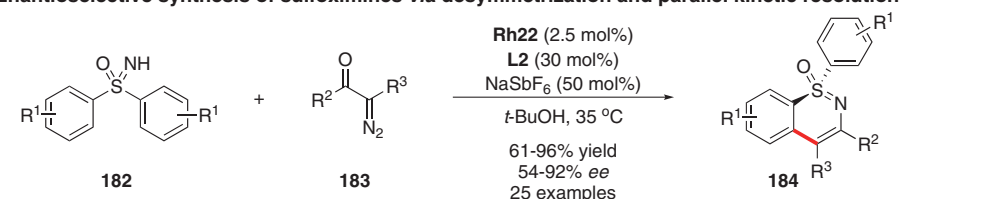
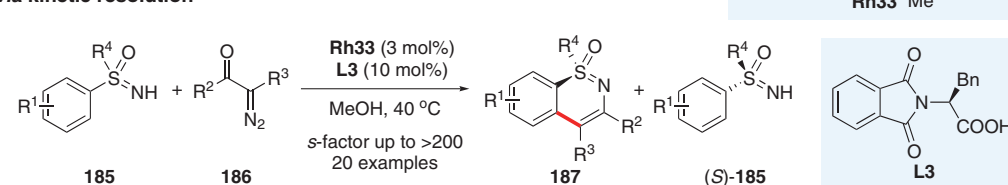
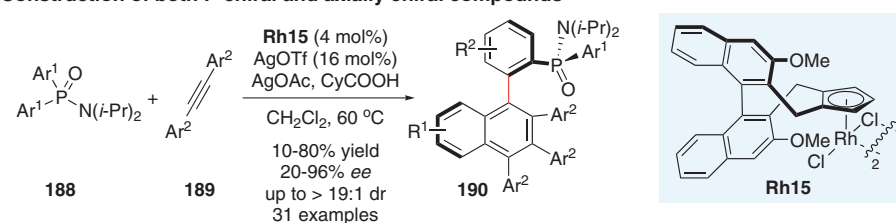
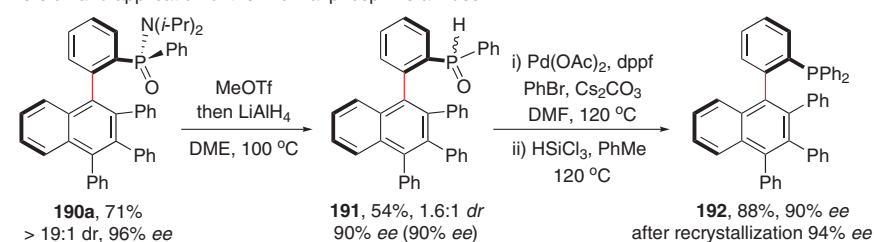
10b) Waldmann, *Chem. Eur. J.* **2022**, *28*, e202103365.

Asymmetric C–H arylation with carbenoids

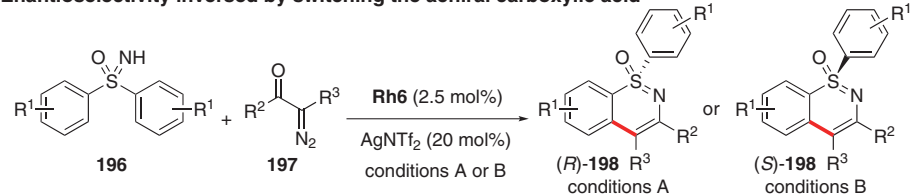
10f) Li, *Org. Lett.* **2022**, *24*, 3189.10c) You, *Angew. Chem. Int. Ed.* **2014**, *53*, 13244.10d) You, *J. Am. Chem. Soc.* **2016**, *138*, 5242.

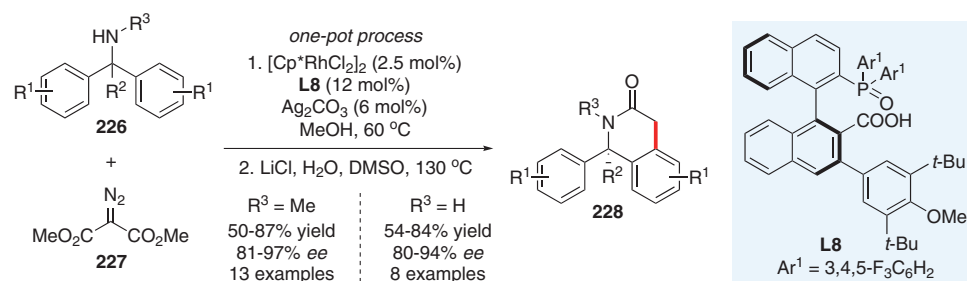
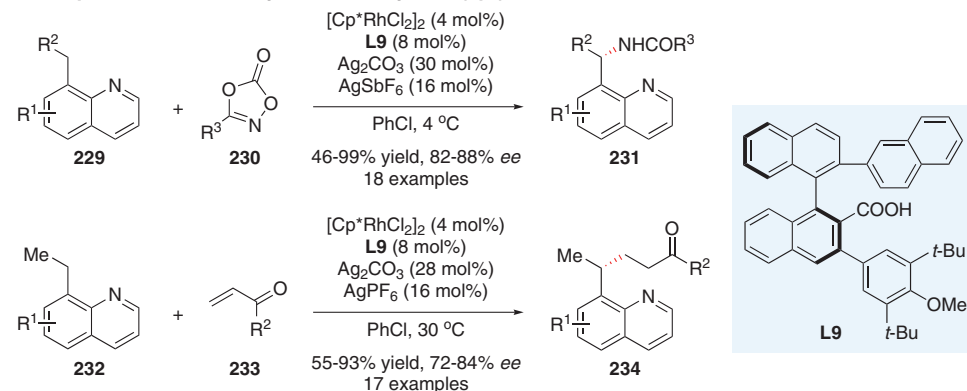
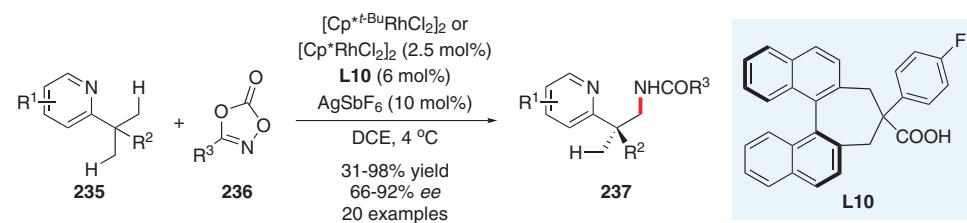
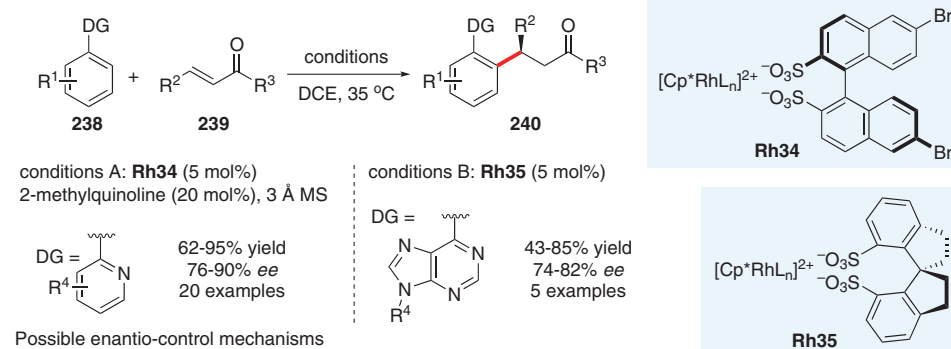
Enantioselective construction of azoniahelicenes

10e) You, *J. Am. Chem. Soc.* **2021**, *143*, 114.Figure 8 Chiral Cp^xRh-catalyzed asymmetric formation of axially chiral compounds and chiral helicenes^{4c,10a-f}

Enantioselective synthesis of phosphamides *via* desymmetrization*via* kinetic resolution11a) 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 resolution11c) 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 compoundsConversion and application of the *P*-chiral phosphine amides11e) Wang and Li, *Angew. Chem. Int. Ed.* **2021**, *60*, 20424.

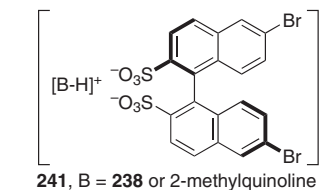
Enantioselectivity inverted by switching the achiral carboxylic acid

11f) Li, *Angew. Chem. Int. Ed.* **2018**, *57*, 15534.Figure 9 Synthesis of *P*- and *S*-stereogenic compounds *via* chiral Cp*Rh-catalyzed enantioselective C–H functionalization^{11a–f}

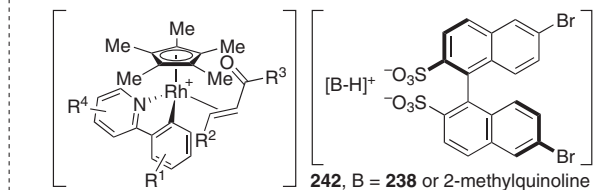
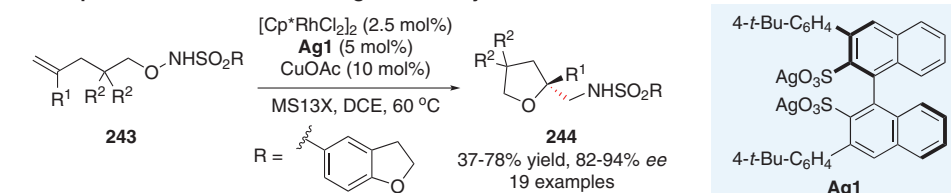
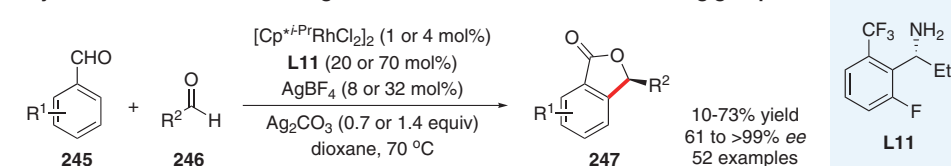
Achiral Cp*Rh^{III}/chiral carboxylic acid catalyzed C(sp²)-H activation
13a) Lin, Yoshino and Matsunaga, *Angew. Chem., Int. Ed.* **2018**, *57*, 12048.
Achiral Cp*Rh^{III}/chiral carboxylic acid catalyzed C(sp³)-H activation
13b) Yoshino and Matsunaga, *Angew. Chem. Int. Ed.* **2019**, *58*, 18154.13c) Yoshino and Matsunaga, *Org. Lett.* **2020**, *22*, 8256.
Development of pseudo-C₂-symmetric acids
13d) Lin, Yoshino and Matsunaga, *ACS Catal.* **2021**, *11*, 4271.
Enantioselective C-H activation controlled by disulfonates


Possible enantio-control mechanisms

(a) Chiral proton source

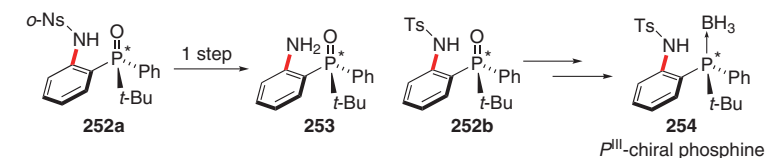
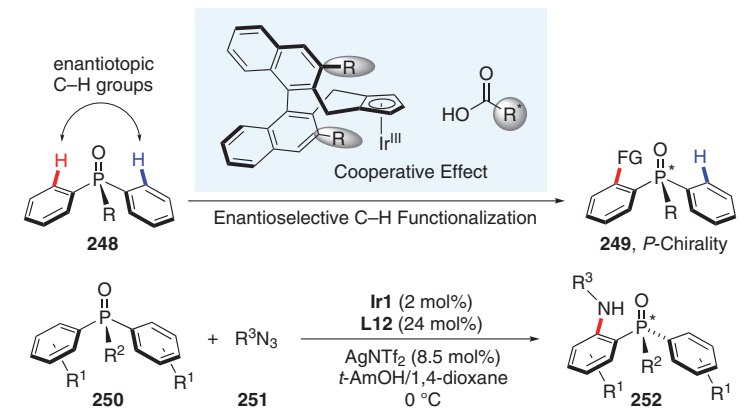


(b) Chiral counteranion

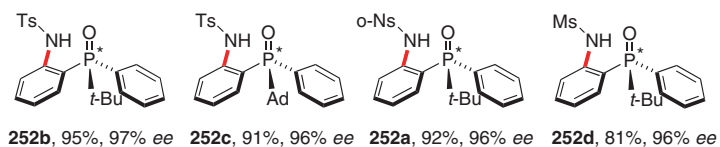

Development of chiral disulfonate ligands for asymmetric addition of olefins
13e) Yoshino and Matsunaga, *Nat. Catal.* **2018**, *1*, 585.13f) Yoshino and Matsunaga, *ACS Catal.* **2021**, *11*, 15187.
Asymmetric C-H activation using an amine as a chiral transient directing group
13g) Wang, *Chem. Eur. 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

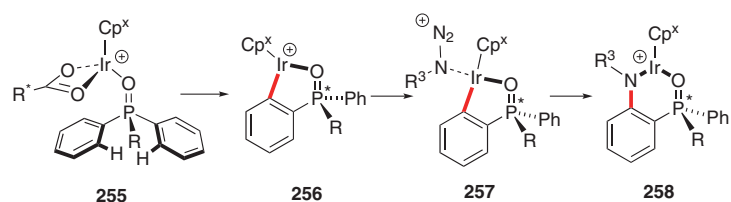
A cooperative effect of a chiral Cp^xIr^{III}/chiral carboxylic acid pair



Selected scope



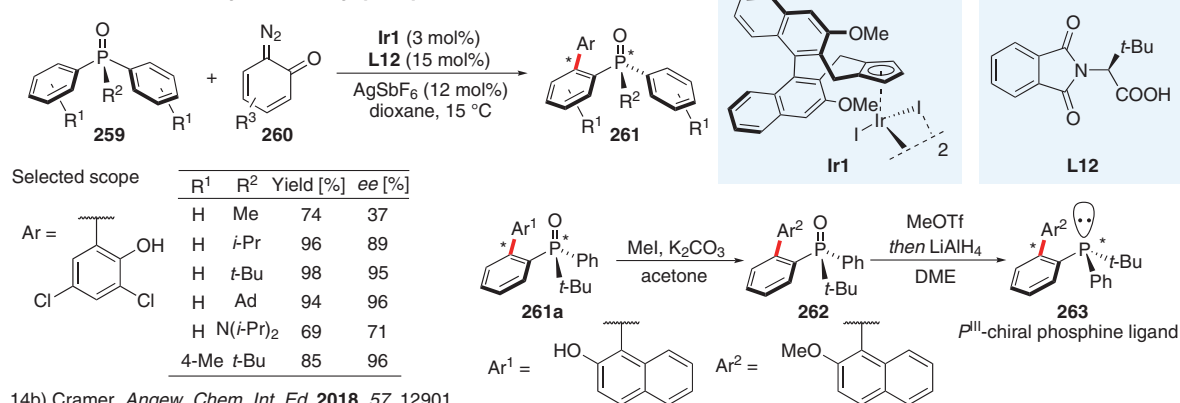
Key intermediates in the proposed catalytic cycle



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

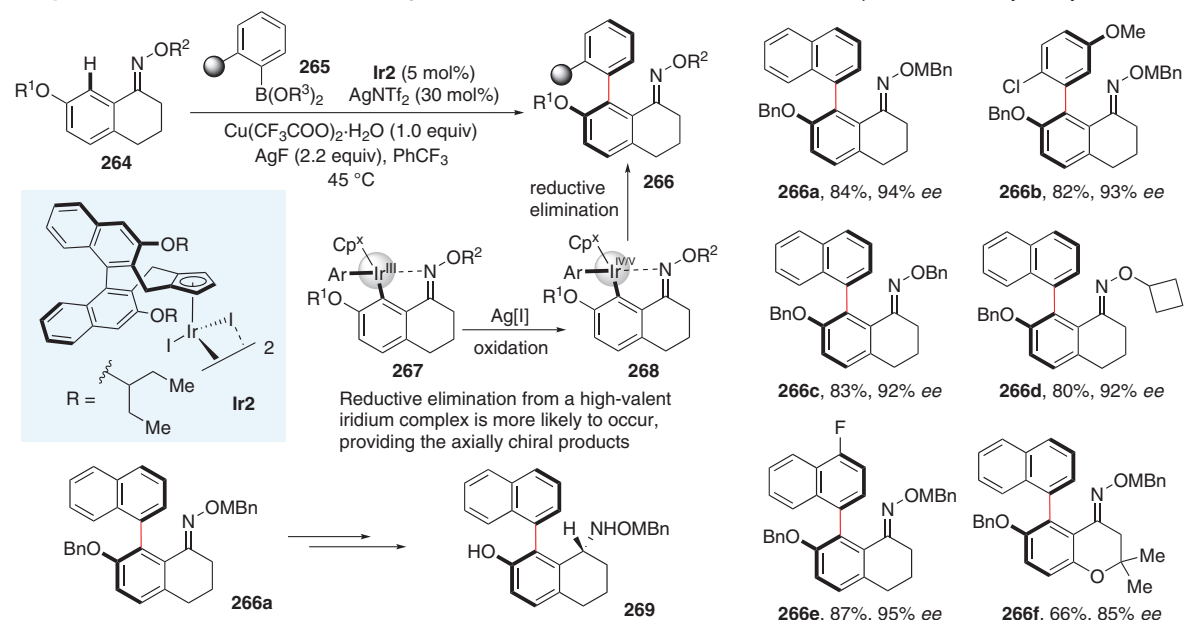


Selected scope

Ar =	R ¹	R ²	Yield [%]	ee [%]
	H	Me	74	37
	H	<i>i</i> -Pr	96	89
	H	<i>t</i> -Bu	98	95
	H	Ad	94	96
	H	N(<i>i</i> -Pr) ₂	69	71
	4-Me	<i>t</i> -Bu	85	96

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

Atroposelective oxidation-enabled C–H arylation

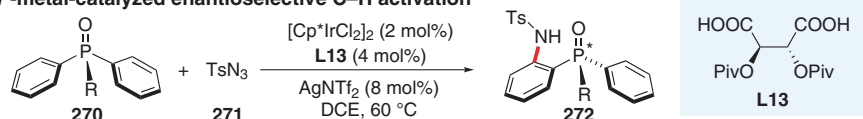


14c) Cramer, *Angew. Chem. Int. Ed.* **2021**, *60*, 18532.

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

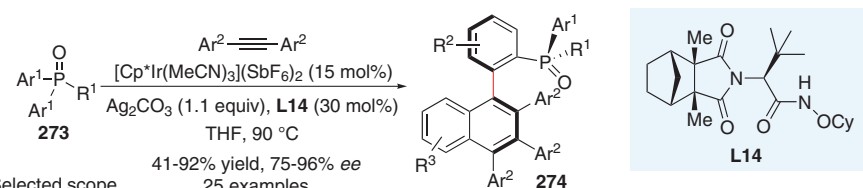
Figure 12 Ir^{III}-catalyzed enantioselective C–H functionalization with chiral Cp^xIr^{III}14a–d

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

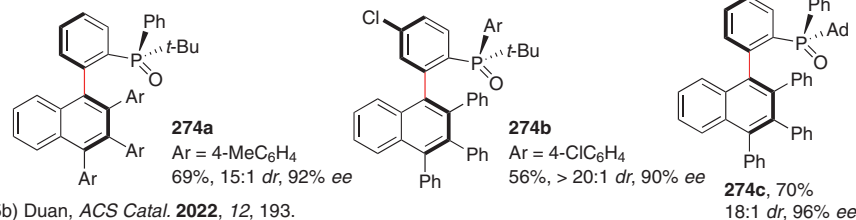


15a) Chang, *Tetrahedron* **2015**, *71*, 4504. 44–91% yield, 11–32% ee, 5 examples

Asymmetric C–H activation of biaryl phosphine oxides

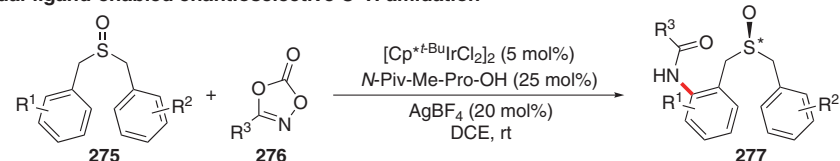


Selected scope 41–92% yield, 75–96% ee 25 examples

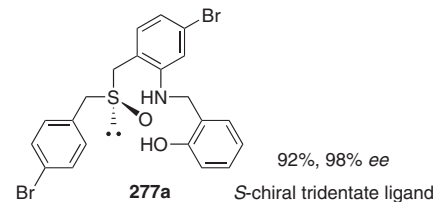


15b) Duan, *ACS Catal.* **2022**, *12*, 193.

Dual-ligand-enabled enantioselective C–H amidation

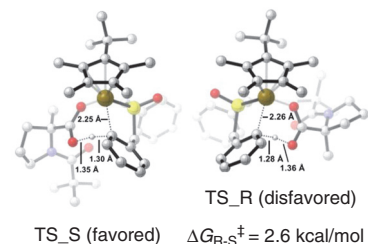


Derivatization of amidated sulfones

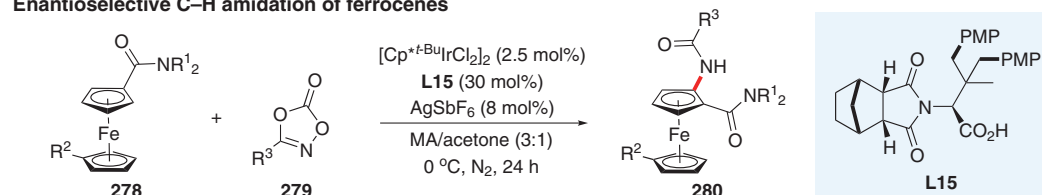


15c) He, *ACS Catal.* **2020**, *10*, 7207.

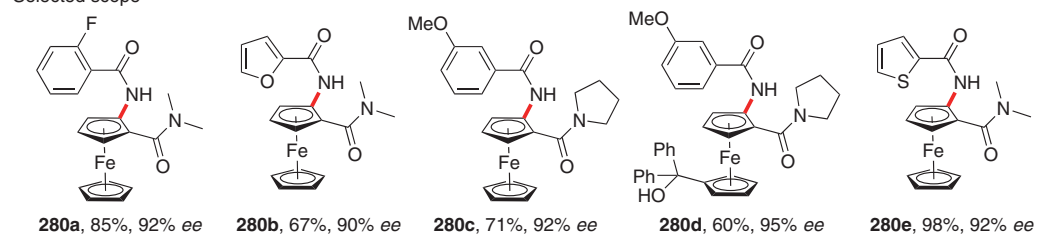
Stereocontrol model



Enantioselective C–H amidation of ferrocenes

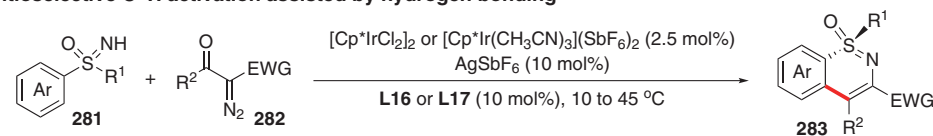


Selected scope

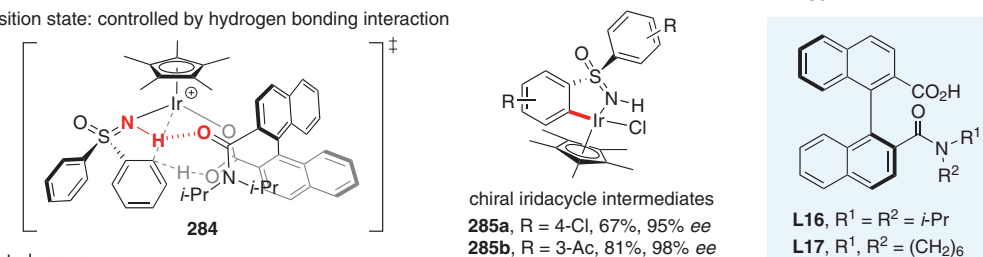


15d) Shi, *ACS Catal.* **2020**, *10*, 7117.

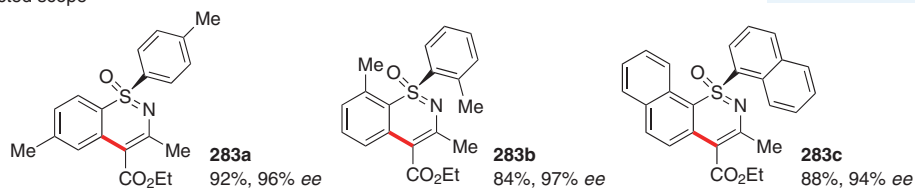
Enantioselective C–H activation assisted by hydrogen bonding



Transition state: controlled by hydrogen bonding interaction

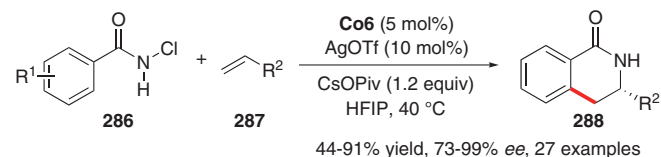


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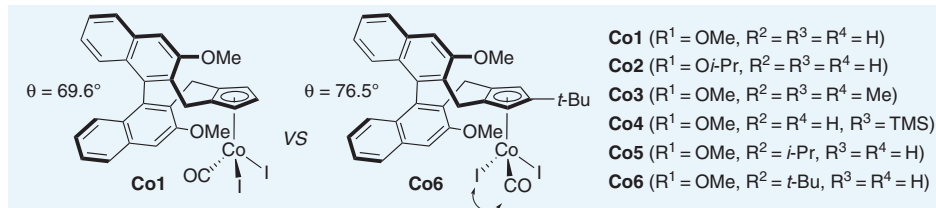


15e) Zhou, Hong and Shi, *ACS Catal.* **2022**, *12*, 9083.

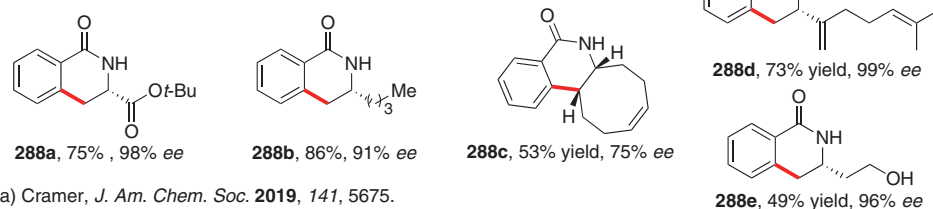
Figure 13 Achiral Cp*Ir^{III}-catalyzed enantioselective C–H functionalization using chiral carboxylic acids as ligands^{15a–e}

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

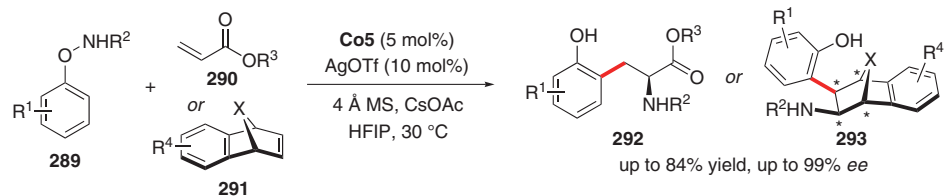
Comparison of Co1 and Co6:

Co6 possesses a greater θ angle and a swapped CO ligand

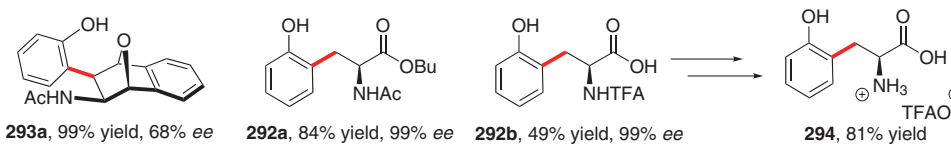
Selected scope:

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

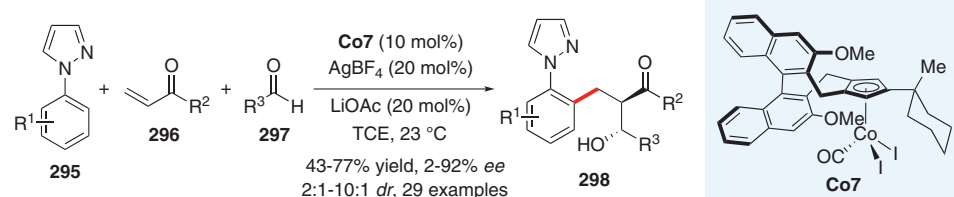
Asymmetric intermolecular amidation with different alkenes



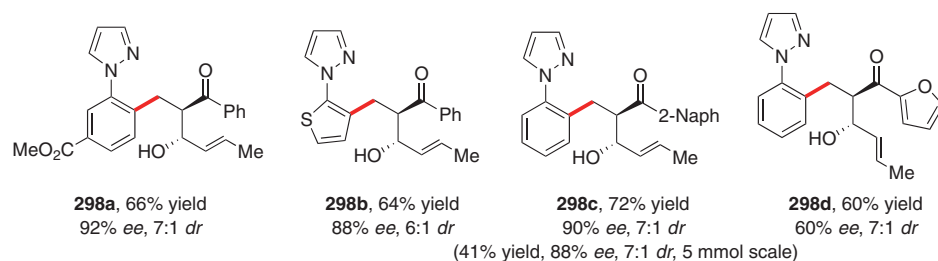
Selected scope:

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

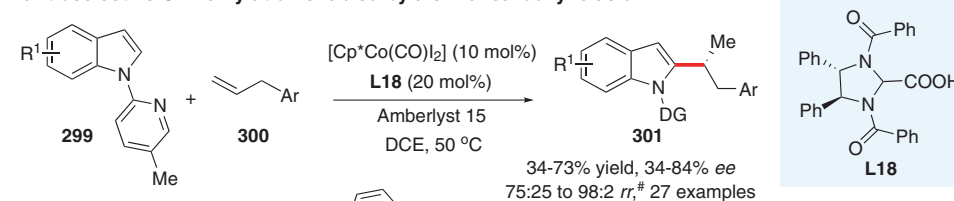
Three-component asymmetric C–H activation/functionalization



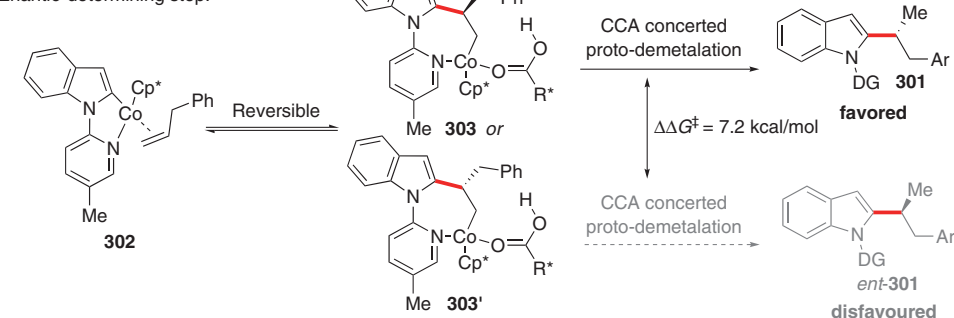
Selected scope:

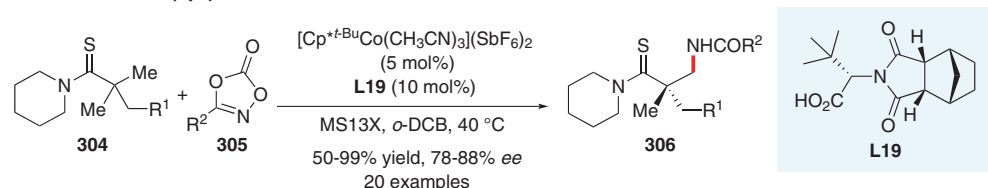
16c) Cramer, *ACS Catal.* **2021**, *11*, 11938.

Enantioselective C–H alkylation enabled by a chiral carboxylic acid

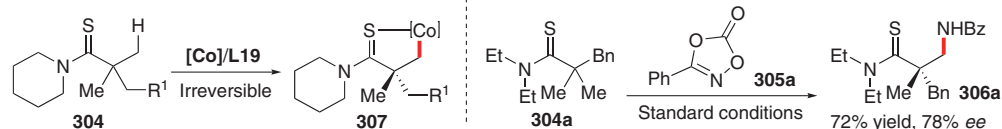


Enantio-determining step:

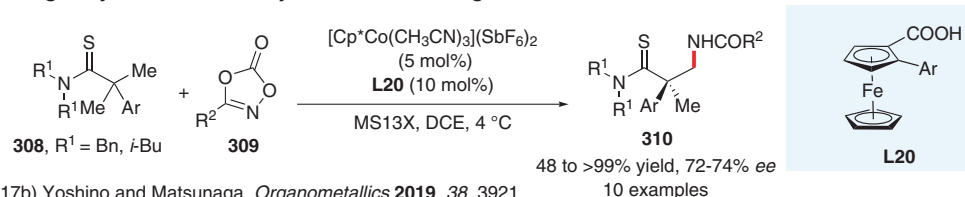
16d) Ackermann, *Angew. Chem. Int. Ed.* **2018**, *57*, 15425. [#]Markovnikov:anti-MarkovnikovFigure 14 Cp^xCo^{III}-catalyzed enantioselective C–H functionalization via asymmetric alkylation^{16a–d}

Enantioselective C(sp³)-H amidation of thioamides

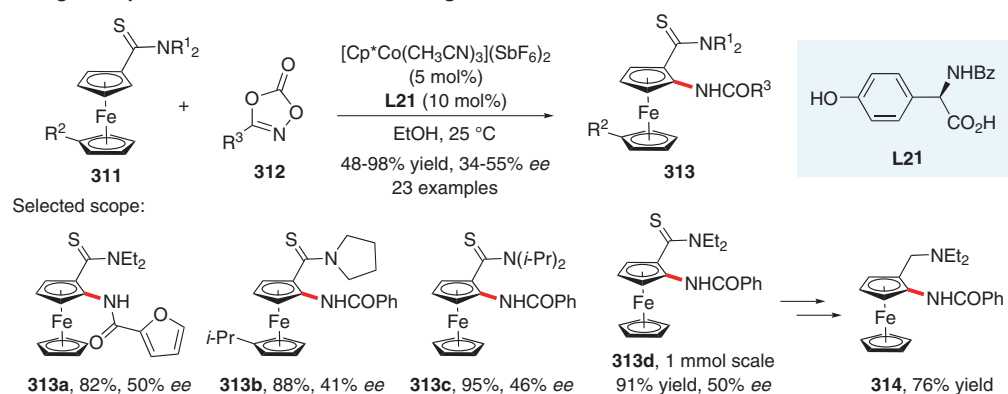
Enantio-determining step:

17a) Yoshino and Matsunaga, *Angew. Chem. Int. Ed.* **2019**, *58*, 1153.

Using 2-arylferrocene carboxylic acids as chiral ligands

17b) Yoshino and Matsunaga, *Organometallics* **2019**, *38*, 3921.

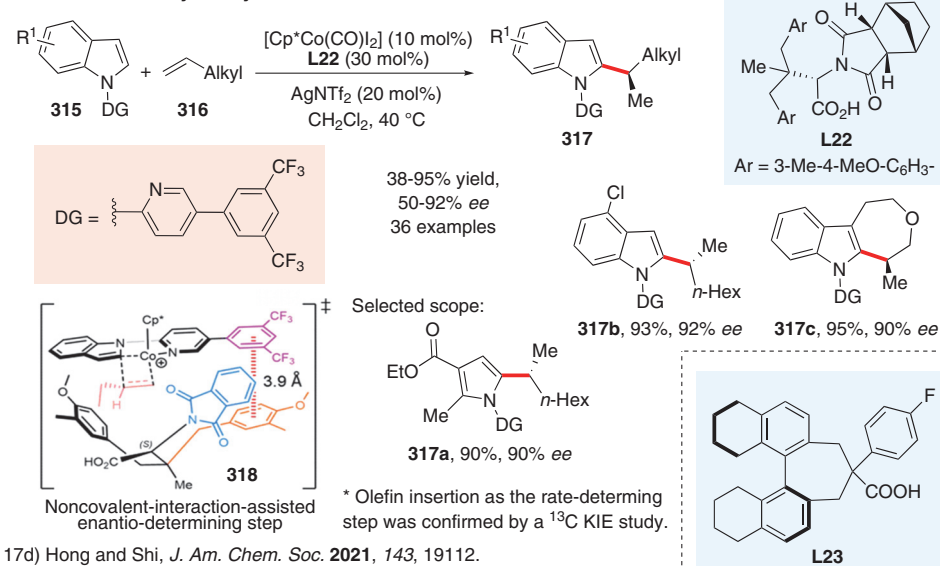
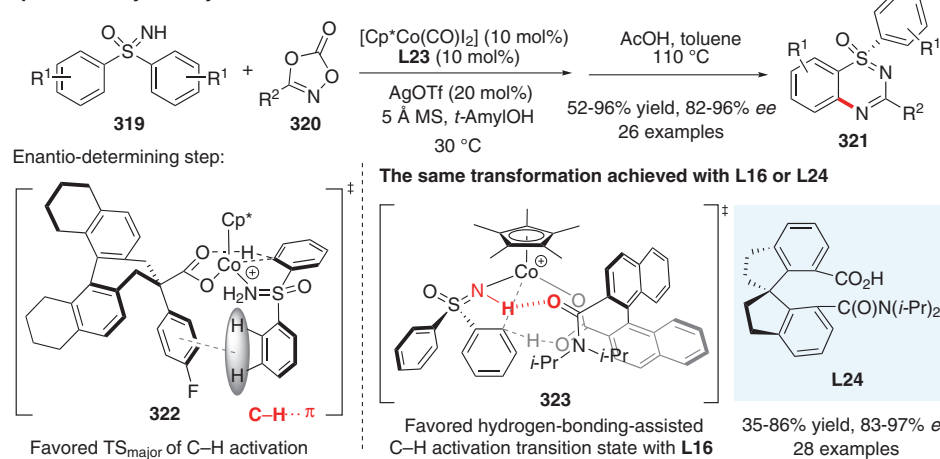
Using monoprotected amino acids as chiral ligands



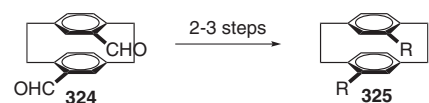
*EtOH was observed to offer a significant ligand-accelerating effect, which is critical for good enantioselectivity.

17c) Shi, *Org. Lett.* **2019**, *21*, 1895.

Enantioselective hydroarylation of unactivated terminal alkenes

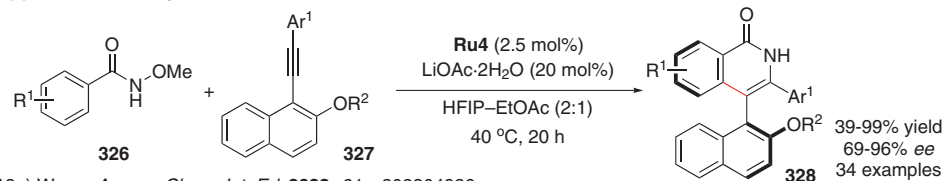
Cp*Co^{III}-catalyzed asymmetric amidationFigure 15 Achiral Cp*Co^{III}-catalyzed enantioselective C-H functionalization using chiral carboxylic acids as ligands^{17a-f}

Synthesis of chiral arene ligands

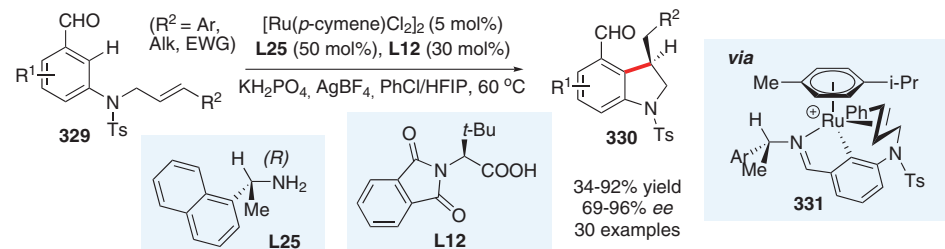


Ru1, R = Et
 Ru2, R = CH₂*i*-Pr
 Ru3, R = CH₂Cy
 Ru4, R = *i*-Pr
 Ru5, R = CHEt₂
 Ru6, R = CH(*n*-Bu)₂

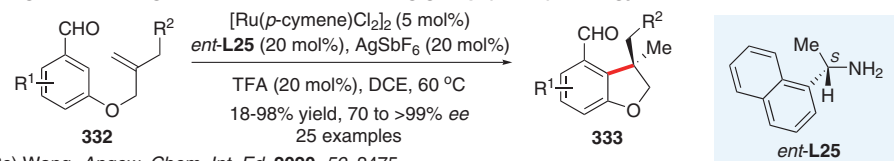
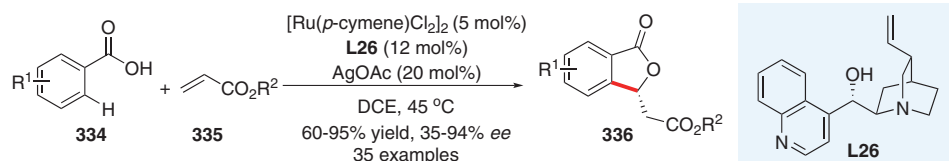
Applications in asymmetric C–H activation

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

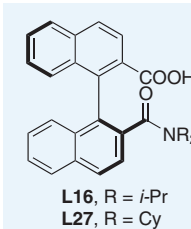
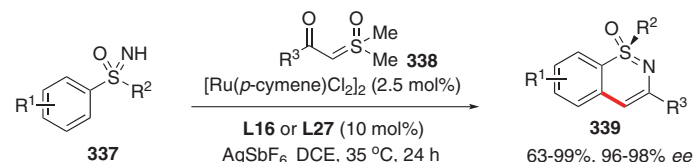
Cui's work using a chiral transient directing group (cTDG) strategy

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

Wang's work using a chiral transient directing group (cTDG) strategy

18c) Wang, *Angew. Chem. Int. Ed.* **2020**, *59*, 3475.One-pot asymmetric synthesis with Ru^{II}/cinchonine dual catalysis18d) Dethe, *J. Org. Chem.* **2022**, *87*, 4617.

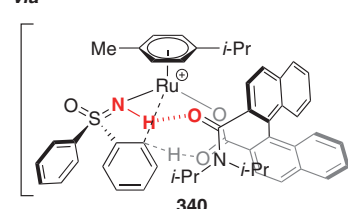
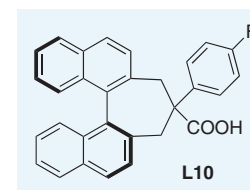
Enantioselective C–H activation enabled by chiral carboxylic acids

Reacted with ketones **341**
 [4+3] annulation

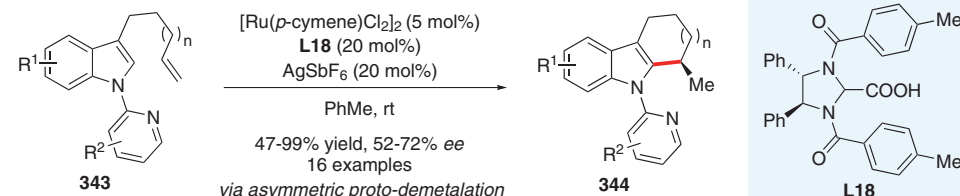
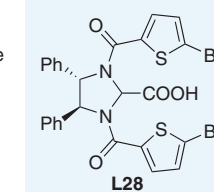
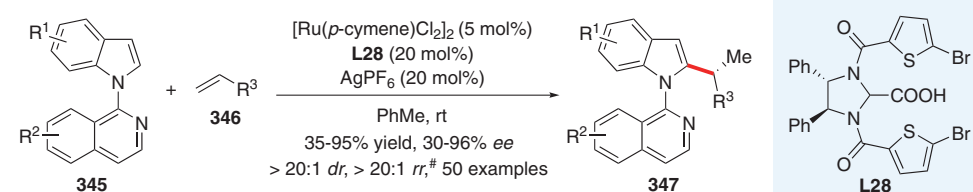
with L16

**342**, 48-90%, 90 to >99% ee
 37 examples

via

The same transformation with L10
339, 68 to >99%, 52-84% ee
 15 examples18e) 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 hydroarylation18i) Ackermann, *Angew. Chem. Int. Ed.* **2022**, *61*, e202212595. #Markovnikov:anti-MarkovnikovFigure 16 Ru^{II}-catalyzed enantioselective C–H functionalization^{18a-i}

Conflict of Interest

The authors declare no conflict of interest.

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