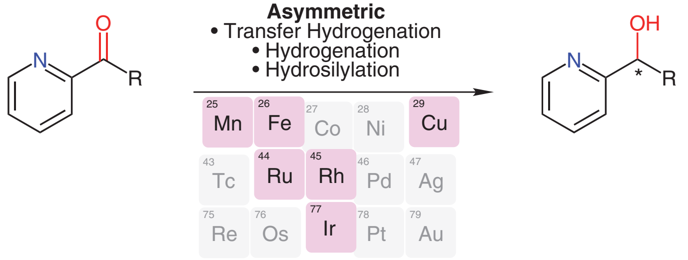
Transition-Metal-Catalyzed Asymmetric Reduction of 2-Pyridine Ketones

Vidhul Vasudevan
Harishankar M. S.
Thierry Ollevier*

Département de chimie, Université Laval, 1045 avenue de la Médecine, Québec, QC, G1V 0A6, Canada
thierry.ollevier@chm.ulaval.ca



Received: 08.11.2024
Accepted after revision: 11.12.2024
Published online: 13.12.2024 (Accepted Manuscript), 19.12.2024 (Version of Record)
DOI: 10.1055/a-2501-4247; Art ID: SO-2024-11-0043-GR

License terms: cc by

© **2024**. The Author(s). This is an open access article published by Thieme under the terms of the Creative Commons Attribution License, permitting unrestricted use, distribution and reproduction, so long as the original work is properly cited.
(https://creativecommons.org/licenses/by/4.0/)

Abstract This graphical review provides a concise overview of transition-metal-catalyzed asymmetric reduction of 2-pyridine ketones to produce enantiopure chiral 2-pyridine aryl/alkyl alcohols, which are present in many chiral ligands and pharmaceuticals. Key methods include metal-catalyzed hydrogenation, transfer hydrogenation, and hydrosilylation, with a focus on sustainable catalysts like iron and manganese. This review serves as a foundation for future advancements in sustainable and enantioselective keto group reductions.

Key words asymmetric reduction, ketones, transfer hydrogenation, hydrogenation, hydrosilylation, iron catalysis

The development of catalytic methods for the asymmetric reduction of keto groups, particularly in 2-pyridine ketones, has garnered considerable interest due to the transformative potential of these reactions in the synthesis of enantiomerically pure compounds. Enantiopure chiral 2-pyridine aryl/alkyl alcohols are not only essential intermediates in creating chiral ligands, such as Bolm's ligand, but are also foundational in the synthesis of complex, stereochemically defined molecules in fields like pharmaceuticals and materials science. As a result, there has been substantial effort to design catalysts that facilitate these reductions with high enantioselectivity, efficiency, and versatility.

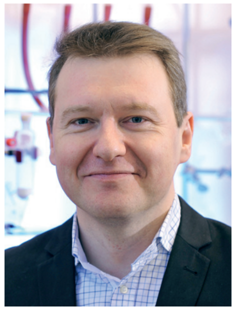
A wide array of catalytic approaches has emerged for the asymmetric reduction of 2-pyridine ketones, utilizing transition metals such as iron, manganese, ruthenium, copper, rhodium, and iridium. These systems often differ significantly in their mechanistic pathways, with some involving direct hydrogenation, others employing transfer hydrogenation, and others relying on hydrosilylation. Each method offers unique advantages, yet also presents challenges related to reaction scope, operational simplicity, cost, scalability, and environmental impact, with green chemistry principles driving much of the recent innovation in this field.

Despite these advancements, there remain open questions and unsolved challenges, particularly in the quest for more sustainable, non-precious metal catalysts and methods that maximize atom economy. Furthermore, the sheer pace of development in this area can sometimes obscure which transformations have reached maturity and which require further optimization or exploration. This graphical review seeks to clarify these developments, providing a structured overview of current catalytic systems for asymmetric reduction of 2-pyridine ketones. By highlighting well-established techniques alongside emerging approaches, it aims to illuminate future directions for research, particularly in the context of eco-friendly synthetic methodologies and the expanding role of iron-based catalysis in asymmetric synthesis.

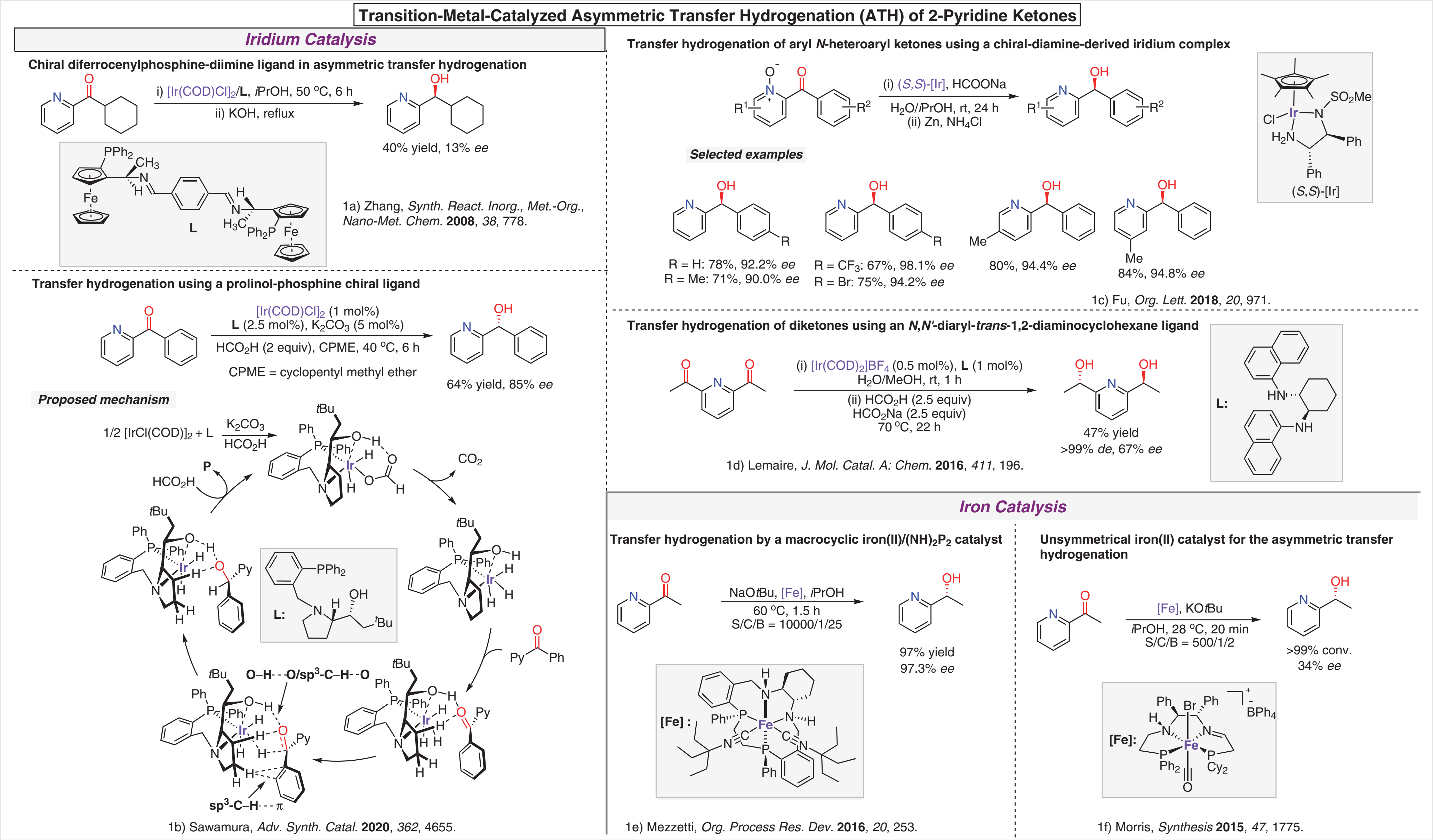
Biosketches

Vidhul Vasudevan was born in Kerala, India, and obtained his BS-MS dual degree in chemistry from the Indian Institute of Science Education and Research, Kolkata, India. He was a MITACS Globalink Intern at Université Laval (Québec, Canada) under the supervision of Prof. Thierry Ollevier during the summer of 2023. His research was focused on the development of new bipyridine-based chiral ligands. Currently, he is a Ph.D. student at McGill University (Montréal), Canada.

Harishankar M. S was born in Kerala, India, and obtained his BS-MS dual degree in chemistry from the Indian Institute of Science Education and Research, Bhopal, India. He was a MITACS Globalink Intern at Université Laval (Québec, Canada) under the supervision of Prof. Thierry Ollevier during the summer of 2023, where he worked on the development of new bipyridine-based chiral ligands.



Thierry Ollevier was born in Brussels and obtained his B.Sc. (1991) and Ph.D. (1997) at the Université of Namur (Belgium) under A. Krief, and was a research associate at the Université catholique de Louvain (Belgium) under I. E. Markó (1997), a NATO postdoctoral fellow at Stanford University under B. M. Trost (1998–2000), then a postdoctoral fellow at the Université de Montréal under A. B. Charette (2000–2001). After an assistant professor appointment (2001) at Université Laval (Québec, Canada), he became associate professor (2006) and is currently a full professor. Current research in his group aims at designing novel catalysts, developing catalytic reactions, and applying these methods to chemical synthesis. He is active in the areas of iron catalysis, ligand design, asymmetric catalysis, fluorine chemistry, diazo and diazirine chemistry, flow chemistry, and bismuth chemistry. He has published more than 85 papers and 35 encyclopedia articles and book chapters. He served as an Associate Editor of *RSC Advances* from 2015 to 2022 and was admitted as a Fellow of the Royal Society of Chemistry (2016). After 5 years served as an Advisory Board member of *SynOpen*, he was appointed as Editor-in-Chief of *SynOpen* in 2023.



Transition-Metal-Catalyzed Asymmetric Transfer Hydrogenation (ATH) of 2-Pyridine Ketones

Iridium Catalysis

Chiral diferrocenylphosphine-diimine ligand in asymmetric transfer hydrogenation

1a) Zhang, *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.* **2008**, *38*, 778.

Transfer hydrogenation using a prolinol-phosphine chiral ligand

1b) Sawamura, *Adv. Synth. Catal.* **2020**, *362*, 4655.

Transfer hydrogenation of aryl *N*-heteroaryl ketones using a chiral-diamine-derived iridium complex

1c) Fu, *Org. Lett.* **2018**, *20*, 971.

Transfer hydrogenation of diketones using an *N,N'*-diaryl-*trans*-1,2-diaminocyclohexane ligand

1d) Lemaire, *J. Mol. Catal. A: Chem.* **2016**, *411*, 196.

Iron Catalysis

Transfer hydrogenation by a macrocyclic iron(II)/$(NH)_2P_2$ catalyst

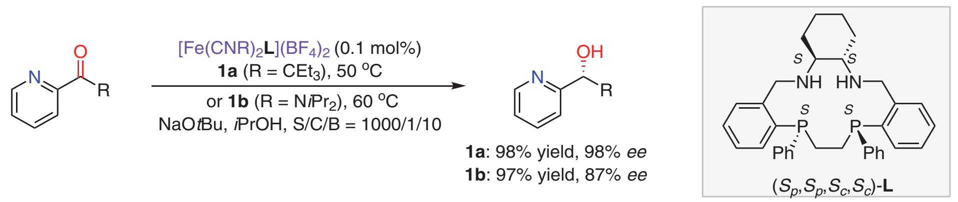
1e) Mezzetti, *Org. Process Res. Dev.* **2016**, *20*, 253.

Unsymmetrical iron(II) catalyst for the asymmetric transfer hydrogenation

1f) Morris, *Synthesis* **2015**, *47*, 1775.

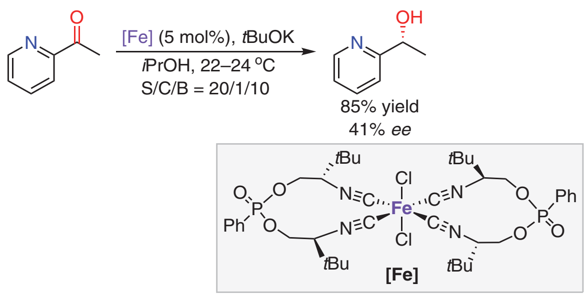
Figure 1 Catalytic asymmetric transfer hydrogenation using iridium and iron[1]

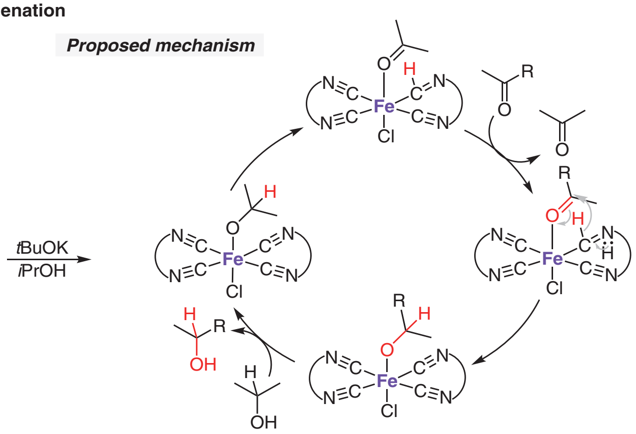
Transfer hydrogenation using bis(isonitrile) iron(II) complexes with a C_2-symmetric diamino $(NH)_2P_2$ macrocyclic ligand



2a) Mezzetti, *Angew. Chem. Int. Ed.* **2015**, *54*, 5171. Similar report: 2b) Mezzetti, *ACS Catal.* **2016**, *6*, 6455.

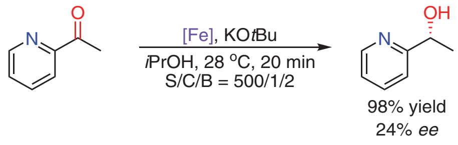
Chiral iron(II)-bis(isonitrile) complexes in asymmetric transfer hydrogenation

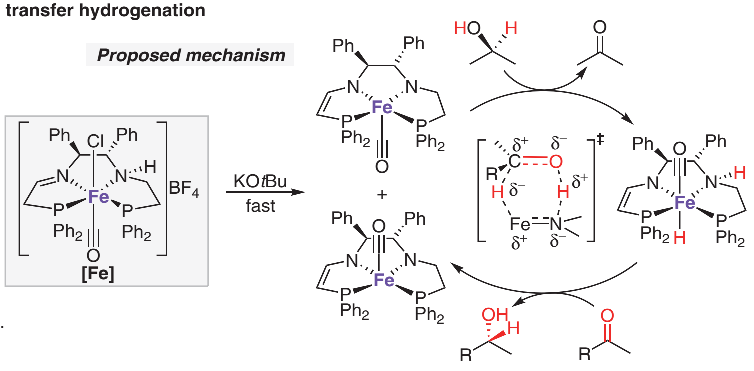




2c) Reiser, *Chem. Commun.* **2010**, *46*, 4475.

Amine(imine)diphosphine iron catalysts for asymmetric transfer hydrogenation

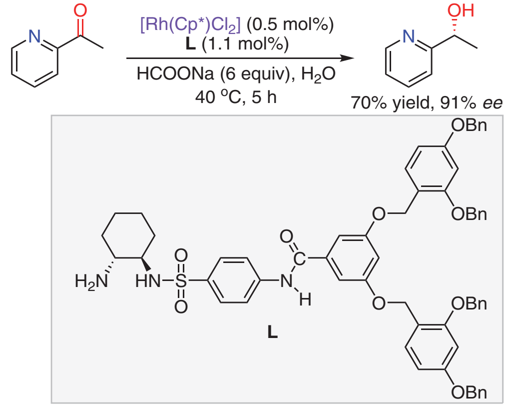




2d) Morris, *Science* **2013**, *342*, 1080.

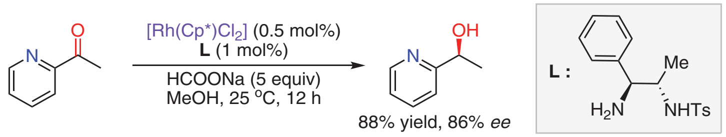
Rhodium Catalysis

ATH by a hydrophobic dendritic DACH–rhodium complex in water



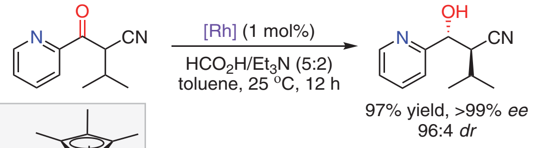
2e) Deng, *Org. Biomol. Chem.* **2006**, *4*, 3319.

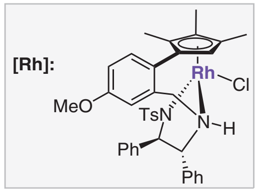
Rhodium complex with an unsymmetrical vicinal diamine ligand in ATH



2f) Kelkar, *RSC Adv.* **2015**, *5*, 51722.

ATH of a-substituted-ß-keto carbonitriles via dynamic kinetic resolution



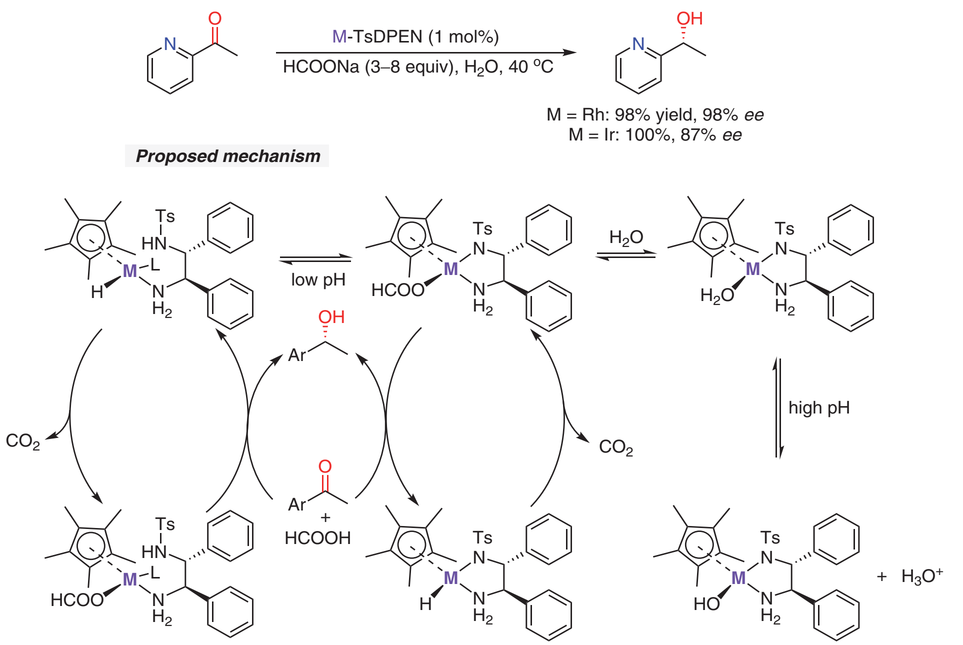


2g) Chen and Zhang, *J. Am. Chem. Soc.* **2021**, *143*, 2477.

Similar reports: 2h) Ratovelomanana-Vidal, *Chem. Commun.* **2018**, *54*, 283.
2i) Ratovelomanana-Vidal, *Catal. Commun.* **2015**, *62*, 95.

Figure 2 Catalytic asymmetric transfer hydrogenation using iron and rhodium[2]

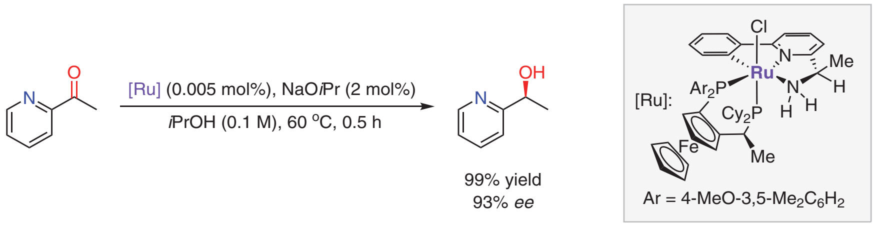
Rh- and Ir-catalyzed asymmetric transfer hydrogenation of ketones by using formate in water



3a) Xiao, *Chem. Eur. J.* **2008**, *14*, 2209.

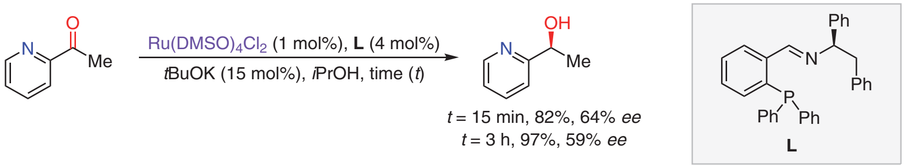
Ruthenium Catalysis

CNN pincer ruthenium catalysts for the asymmetric reduction of alkyl aryl ketones



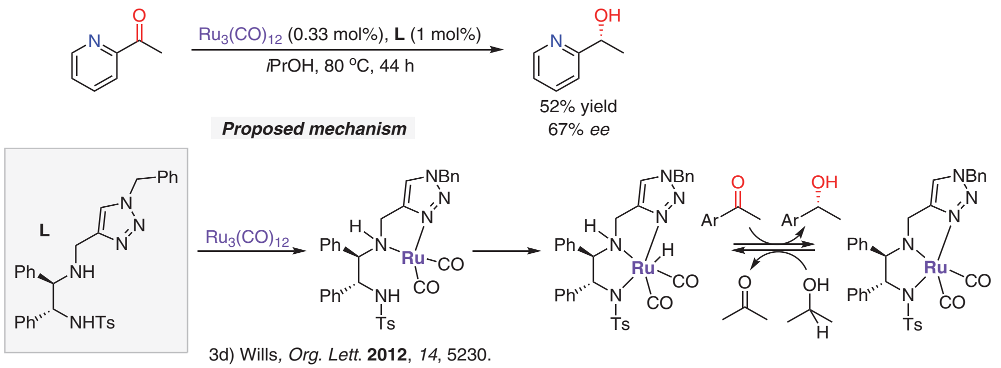
3b) Baratta, *Chem. Eur. J.* **2009**, *15*, 726.

Ruthenium-catalyzed asymmetric transfer hydrogenation using chiral P,N,O Schiff base ligands



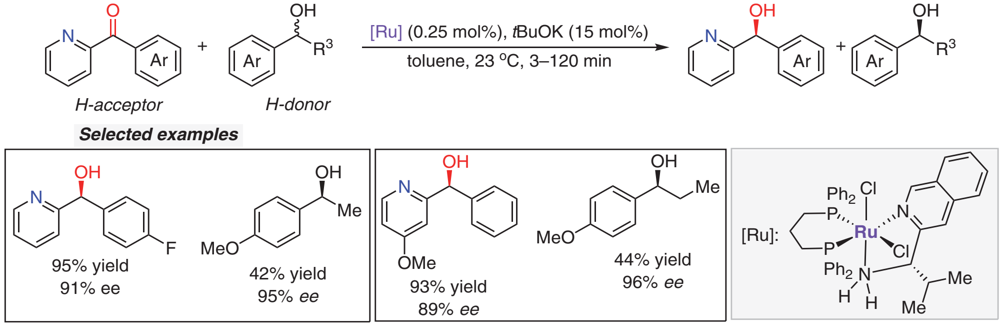
3c) Kwong, *Inorg. Chem. Commun.* **1999**, *2*, 66.

Ruthenium complexes of triazole-containing tridentate ligands in asymmetric transfer hydrogenation



3d) Wills, *Org. Lett.* **2012**, *14*, 5230.

Ruthenium-catalyzed cross-asymmetric hydrogen transfer between H-donor racemic alcohols and H-acceptor prochiral ketones

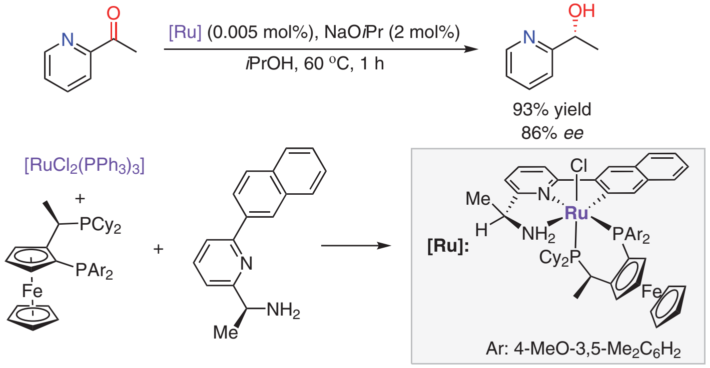


3e) Xu, Wang and Xing, *ACS Catal.* **2022**, *12*, 14429.

Figure 3 Catalytic asymmetric transfer hydrogenation using rhodium and ruthenium[3]

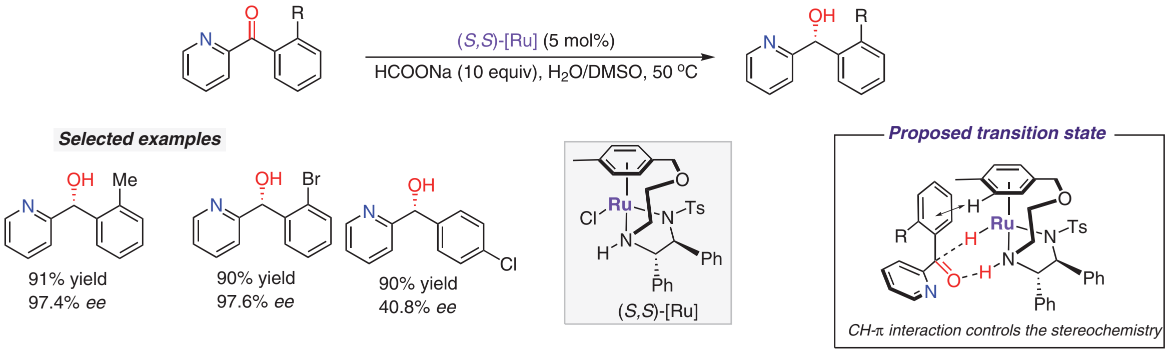
© 2024. Thieme. All rights reserved. *SynOpen* **2024**, *8*, 387–400
Georg Thieme Verlag KG, Oswald-Hesse-Straße 50, 70469 Stuttgart, Germany

Chiral pincer HCNN ligands containing a Ru-complex in ATH



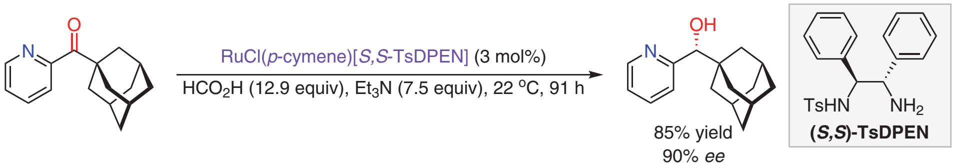
4a) Baratta, *Organometallics* **2010**, *29*, 3563.

Bifunctional oxo-tethered ruthenium complex catalyzed ATH



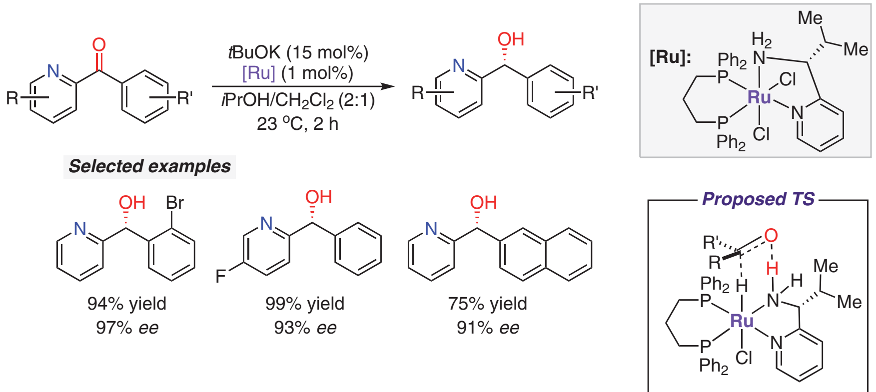
4f) Zhou, *Org. Lett.* **2017**, *19*, 2094.

Asymmetric reduction of adamantan-1-yl(pyridin-2-yl)methanone



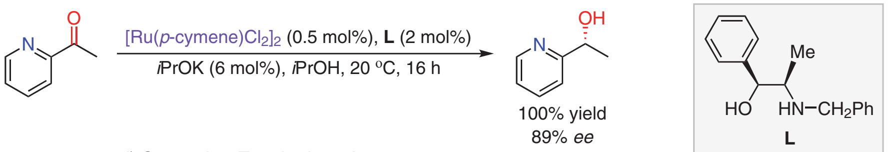
4b) Ollevier, *Org. Lett.* **2022**, *24*, 1116.
Similar report: 4c) Kobayashi, *Synthesis* **2005**, 2176.

ATH of ketones by Ru catalysts of minimal stereogenicity



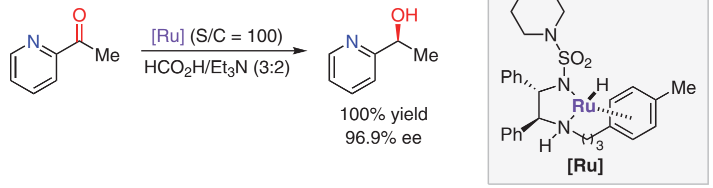
4g) Xing, *ACS Catal.* **2019**, *9*, 5562.
Similar report: 4h) Xing, *Org. Lett.* **2020**, *22*, 8458.

***N*-Benzyl-norephedrine derivatives as ligands in Ru-catalyzed ATH**



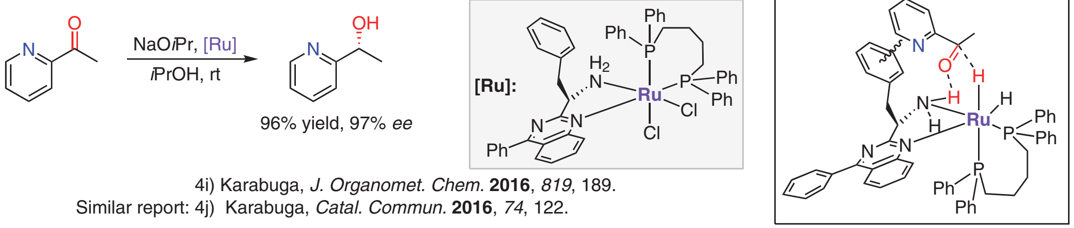
4d) Carpentier, *Tetrahedron: Asymmetry* **1999**, *10*, 4083.

***ansa*-Ruthenium(II) complexes with *N,C*-alkylene-tethered *N,N*-dialkylsulfamoyl-DPEN/η⁶-arene ligands in ATH**



4e) Stephen and Mohar, *Adv. Synth. Catal.* **2015**, *357*, 2540.

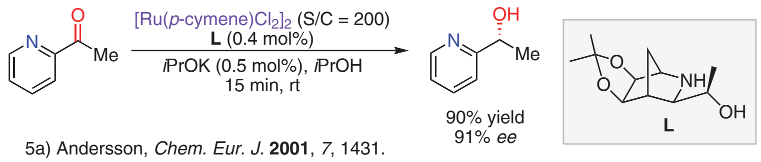
An aminomethyl quinazoline based ruthenium(II) complex in ATH



4i) Karabuga, *J. Organomet. Chem.* **2016**, *819*, 189.
Similar report: 4j) Karabuga, *Catal. Commun.* **2016**, *74*, 122.

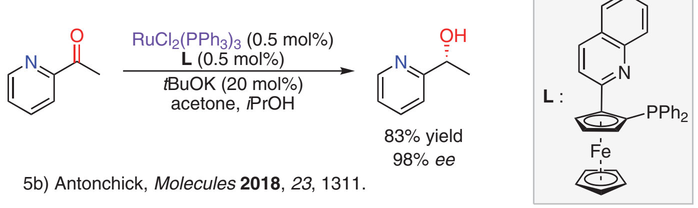
Figure 4 Ruthenium-catalyzed asymmetric transfer hydrogenation[4]

[Ru(amino alcohol)]-catalyzed transfer hydrogenation



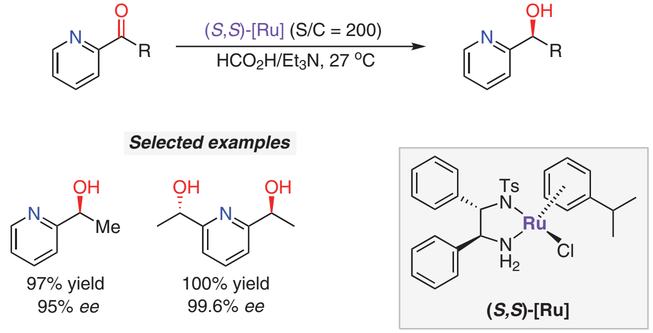
5a) Andersson, *Chem. Eur. J.* **2001**, *7*, 1431.

A 1,2-P,N-bidentate ferrocenyl ligand for Ru-catalyzed ATH



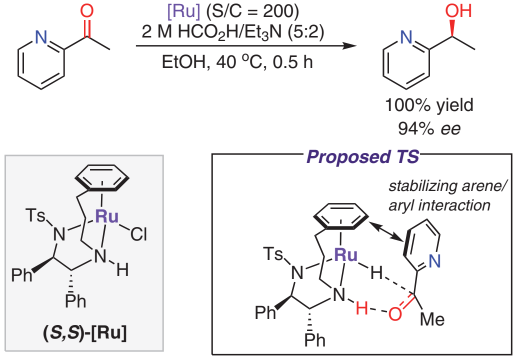
5b) Antonchick, *Molecules* **2018**, *23*, 1311.

Chiral Ru(II)-complex-catalyzed reduction of 2-pyridine ketones



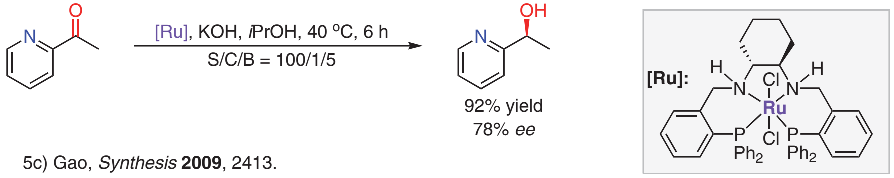
5e) Ikariya, *Tetrahedron Lett.* **2000**, *41*, 9277.

A reverse-tethered ruthenium(II) catalyst for ATH



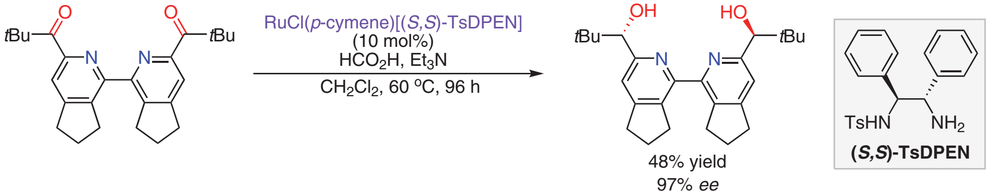
5f) Wills, *J. Org. Chem.* **2006**, *71*, 7035.
5g) Wills, *Org. Lett.* **2007**, *9*, 4659.

A chiral diaminodiphosphine–ruthenium(II) complex in ATH



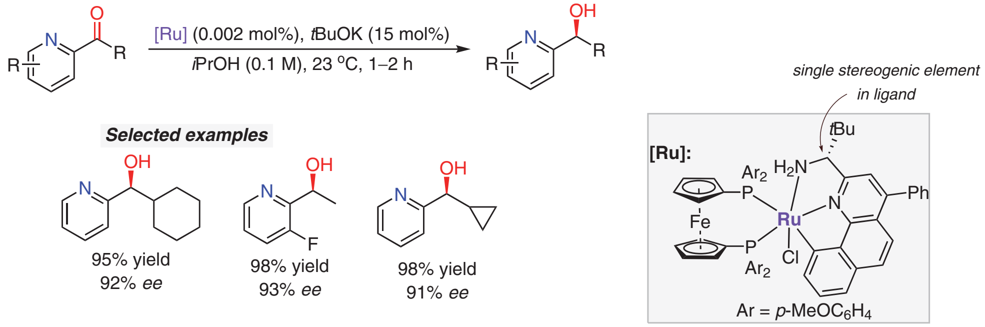
5c) Gao, *Synthesis* **2009**, 2413.

Asymmetric reduction of a 2,2'-bipyridine-diketone analogue by double hydrogen transfer



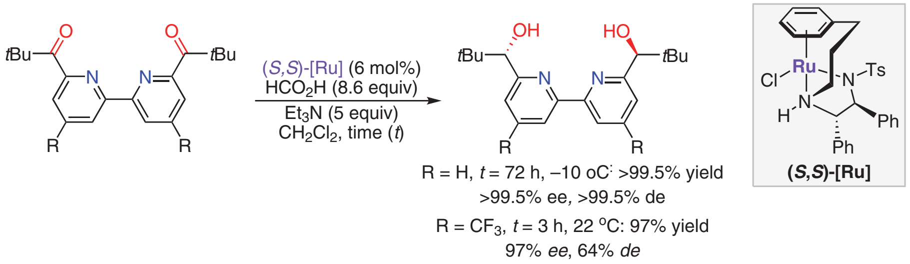
5h) Kotora, *Adv. Synth. Catal.* **2018**, *360*, 2869.

A pincer–Ru with a single stereogenic identity for ATH



5d) Xu and Xing, *Sci. China Chem.* **2023**, *66*, 1443.

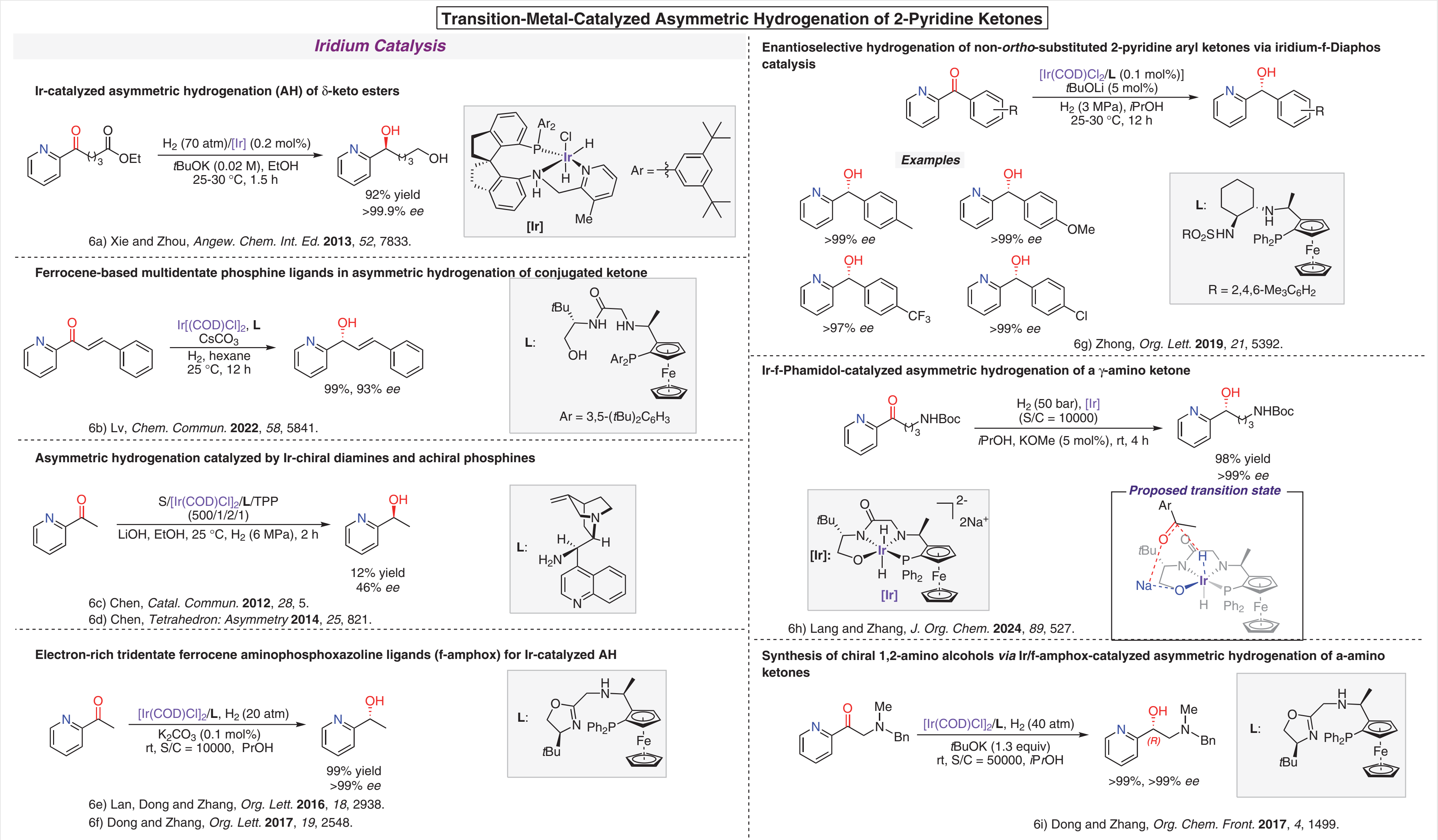
Ru-catalyzed stereoselective double hydrogen transfer to 2,2'-bipyridine-diketones



5i) Ollevier, *Chem. Eur. J.* **2024**, *30*, e202402449.

Figure 5 Ruthenium-catalyzed asymmetric transfer hydrogenation (cont.)[5]

© 2024. Thieme. All rights reserved.



Transition-Metal-Catalyzed Asymmetric Hydrogenation of 2-Pyridine Ketones

Iridium Catalysis

Ir-catalyzed asymmetric hydrogenation (AH) of δ-keto esters

6a) Xie and Zhou, *Angew. Chem. Int. Ed.* **2013**, *52*, 7833.

Ferrocene-based multidentate phosphine ligands in asymmetric hydrogenation of conjugated ketone

6b) Lv, *Chem. Commun.* **2022**, *58*, 5841.

Asymmetric hydrogenation catalyzed by Ir-chiral diamines and achiral phosphines

6c) Chen, *Catal. Commun.* **2012**, *28*, 5.
6d) Chen, *Tetrahedron: Asymmetry* **2014**, *25*, 821.

Electron-rich tridentate ferrocene aminophosphoxazoline ligands (f-amphox) for Ir-catalyzed AH

6e) Lan, Dong and Zhang, *Org. Lett.* **2016**, *18*, 2938.
6f) Dong and Zhang, *Org. Lett.* **2017**, *19*, 2548.

Enantioselective hydrogenation of non-*ortho*-substituted 2-pyridine aryl ketones via iridium-f-Diaphos catalysis

6g) Zhong, *Org. Lett.* **2019**, *21*, 5392.

Ir-f-Phamidol-catalyzed asymmetric hydrogenation of a γ-amino ketone

6h) Lang and Zhang, *J. Org. Chem.* **2024**, *89*, 527.

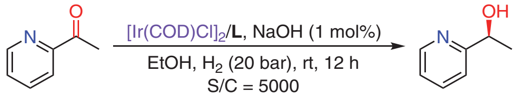
Synthesis of chiral 1,2-amino alcohols *via* Ir/f-amphox-catalyzed asymmetric hydrogenation of a-amino ketones

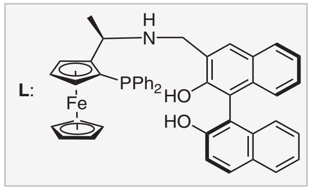
6i) Dong and Zhang, *Org. Chem. Front.* **2017**, *4*, 1499.

Figure 6 Iridium-catalyzed asymmetric hydrogenation[6]

© 2024. Thieme. All rights reserved.
Georg Thieme Verlag KG, Oswald-Hesse-Straße 50, 70469 Stuttgart, Germany

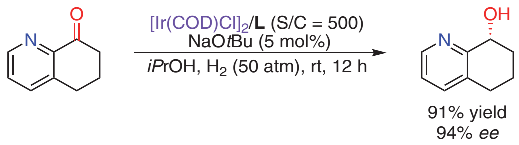
Iridium-catalyzed asymmetric hydrogenation with f-Amphbinol ligand

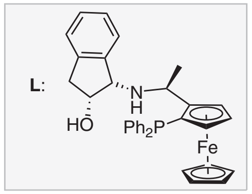




7a) Zhou and Ji, *Org. Lett.* **2023**, *25*, 8845.

Iridium/f-Amphol-catalyzed asymmetric hydrogenation of benzo-fused cyclic ketones

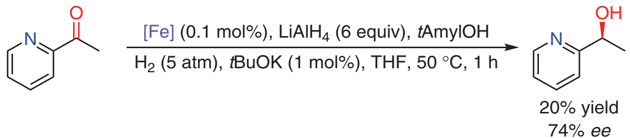


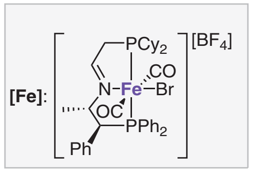


7b) Dong and Zhang, *Adv. Synth. Catal.* **2018**, *360*, 4319.

Iron Catalysis

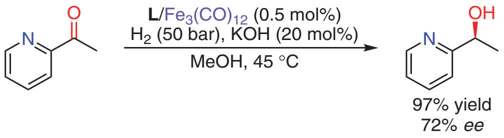
Iron(II) complexes containing unsymmetrical P–N–P' pincer ligands for asymmetric hydrogenation

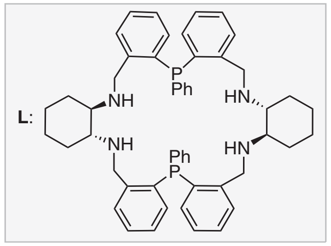




7c) Morris, *J. Am. Chem. Soc.* **2014**, *136*, 1367.

Fe-catalyzed AH using a 22-membered macrocyclic ligand

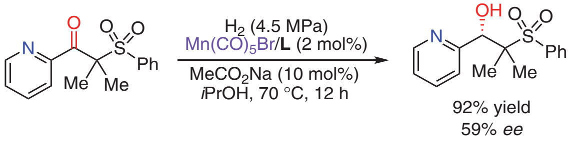


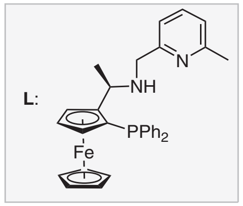


7d) Xiao and Gao, *J. Am. Chem. Soc.* **2014**, *136*, 4031.

Manganese Catalysis

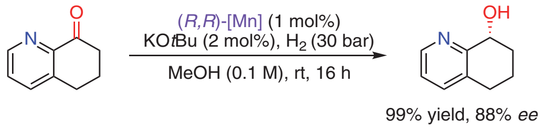
Enantioselective synthesis of chiral ß-hydroxy sulfones *via* manganese-catalyzed asymmetric hydrogenation

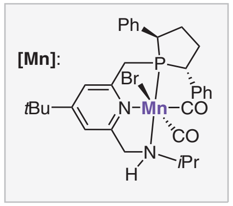




7e) Ling, *Org. Chem. Front.* **2023**, *10*, 3321.

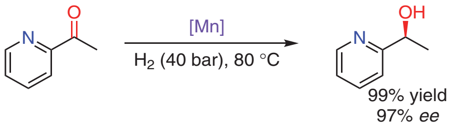
A lutidine-based chiral pincer manganese catalyst for enantioselective hydrogenation

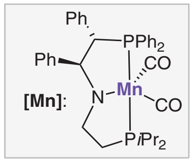




7f) Han and Ding, *Angew. Chem. Int. Ed.* **2019**, *58*, 4973.

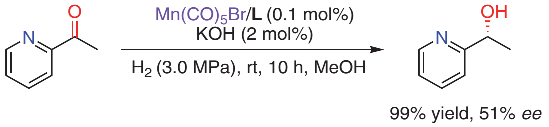
Base-free AH of ketones by a Mn-amido complex of a homochiral, unsymmetrical P–N–P' ligand

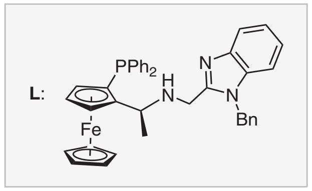




7g) Morris, *Catal. Sci. Technol.* **2021**, *11*, 3153.

An imidazole-based chiral PNN tridentate ligand in Mn-catalyzed AH

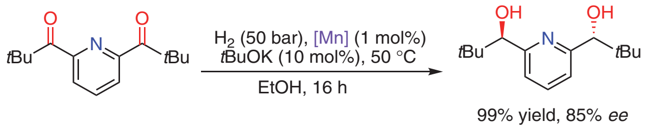


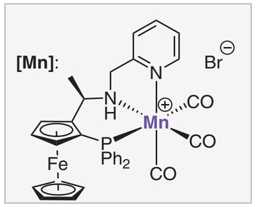


7h) Zhong, *Synlett* **2020**, *31*, 285.

Figure 7 Catalytic asymmetric hydrogenation using iridium, iron and manganese[7]

A Mn complex of a chiral P,N,N ligand in the AH of a 2,5-diketo pyridine

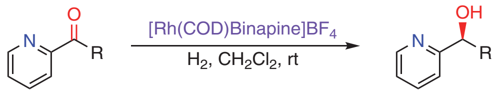




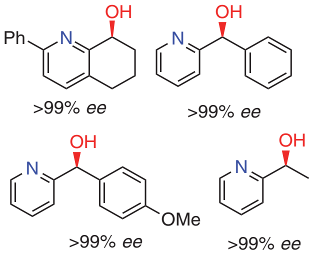
8a) Clarke, *Angew. Chem. Int. Ed.* **2017**, *56*, 5825.

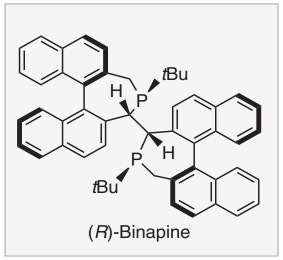
Rhodium Catalysis

Rhodium-catalyzed asymmetric hydrogenation of 2-pyridine ketones



Examples

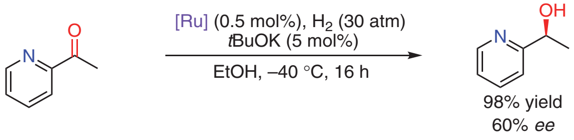


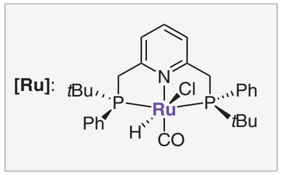


8b) Zhang, *Org. Lett.* **2015**, *17*, 4144.

Ruthenium Catalysis

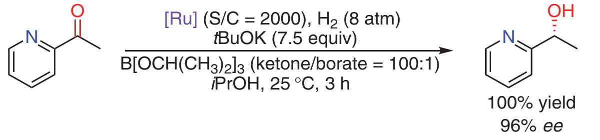
A *P*-stereogenic PNP^{tBu,Ph} Ru-complex in the AH of 2-pyridine ketones

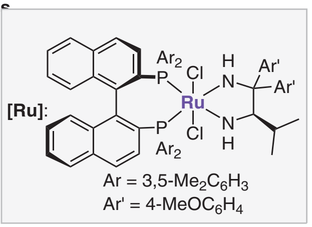




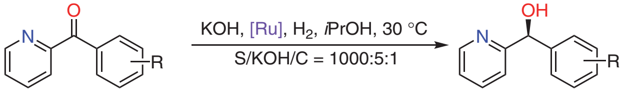
8c) Diaz and Castillón, *Eur. J. Org. Chem.* **2015**, 3666.

A ruthenium–diamine–diphosphine complex in the AH of pyridinyl aryl ketones

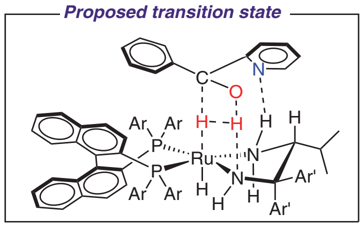


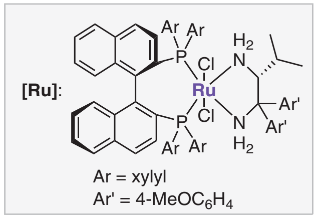


8d) Noyori, *Org. Lett.* **2000**, *2*, 1749.



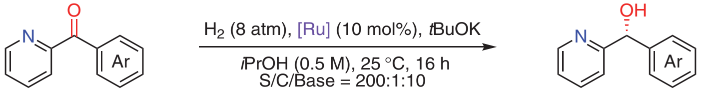
R = H, >99% yield, 70% *ee*
R = 2-Me, >99% yield, 99% *ee*



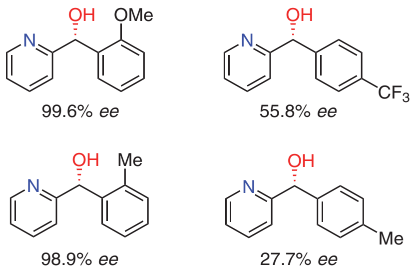


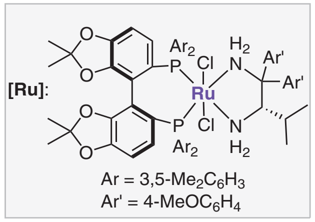
8e) Niedercorn and Castanet, *Tetrahedron* **2008**, *64*, 8700.

Enantioselective hydrogenation of aryl-pyridyl ketones with a Ru-XylSunPhos-Daipen bifunctional catalytic system



Examples

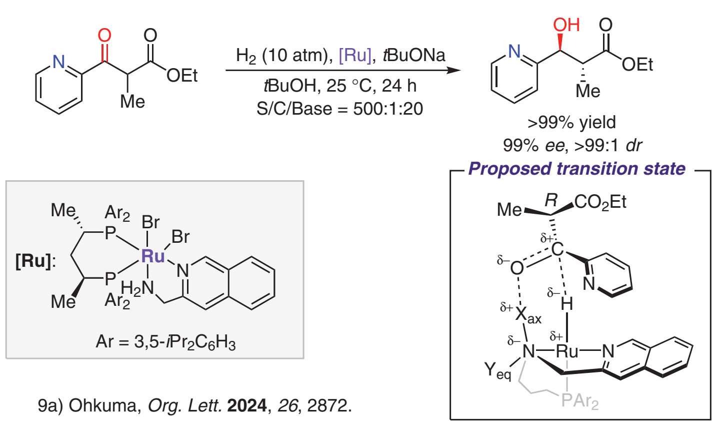




8f) Ratovelomanana-Vidal and Zhang, *J. Org. Chem.* **2012**, *77*, 612.

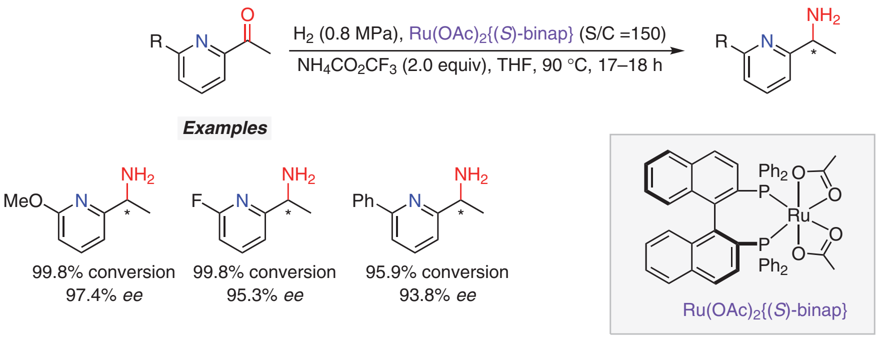
Figure 8 Catalytic asymmetric hydrogenation using manganese, rhodium and ruthenium[8]

Asymmetric hydrogenation of a-alkyl-substituted ß-keto esters through dynamic kinetic resolution



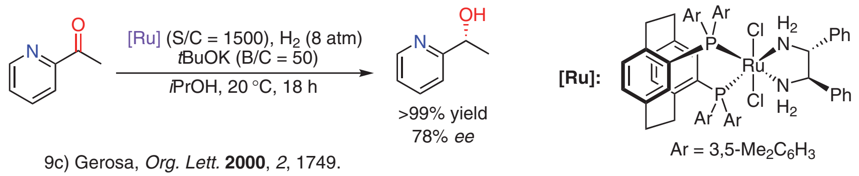
9a) Ohkuma, *Org. Lett.* **2024**, *26*, 2872.

Enantioselective direct asymmetric reductive amination of 2-acetyl-6-substituted pyridines



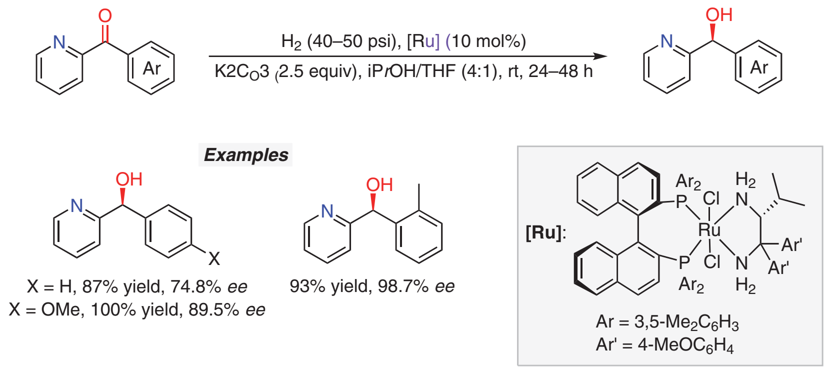
9b) Yamada, *Org. Lett.* **2021**, *23*, 3364.

PhanePhos-Ru-diamine complexes catalyzed asymmetric hydrogenation



9c) Gerosa, *Org. Lett.* **2000**, *2*, 1749.

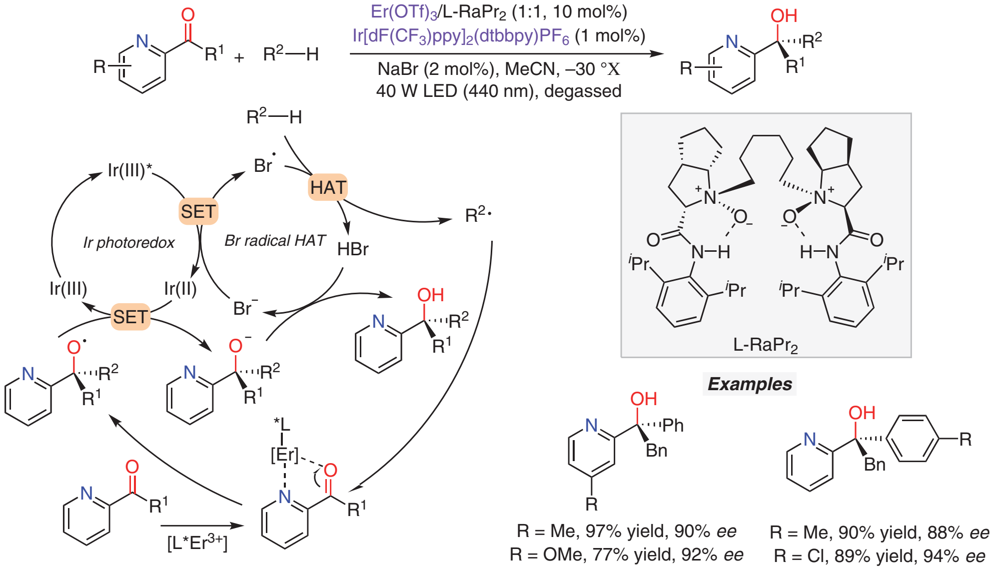
Enantioselective hydrogenation of aromatic-heteroaromatic ketones



9d) Chen, *Org. Lett.* **2003**, *5*, 5039.

Other Reactions

Visible-light-activated asymmetric addition of hydrocarbons to pyridine-based ketones



9e) Feng, *ACS Catal.* **2022**, *12*, 5136.

Figure 9 Catalytic asymmetric hydrogenation using ruthenium and other reactions[9]

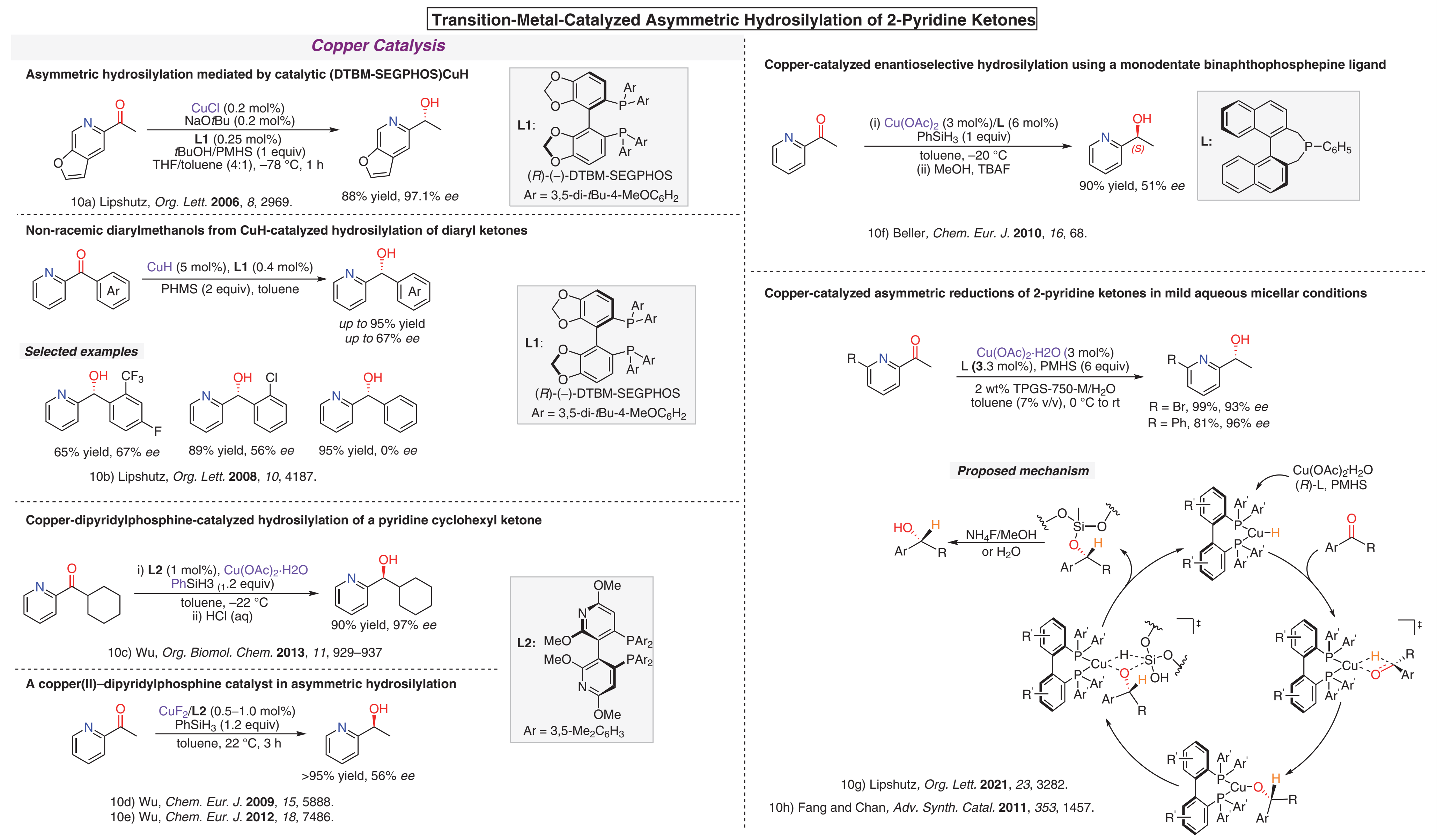
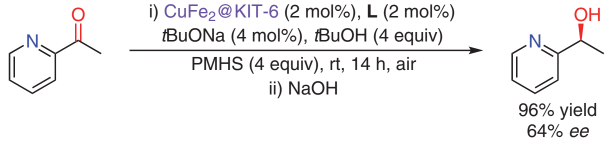
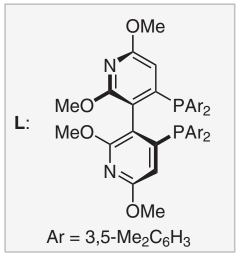


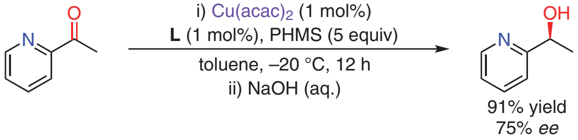
Figure 10 Copper-catalyzed asymmetric hydrosilylation[10]

Mesoporous silica KIT-6-supported superparamagnetic $CuFe_2O_4$ nanoparticles for asymmetric hydrosilylation in air



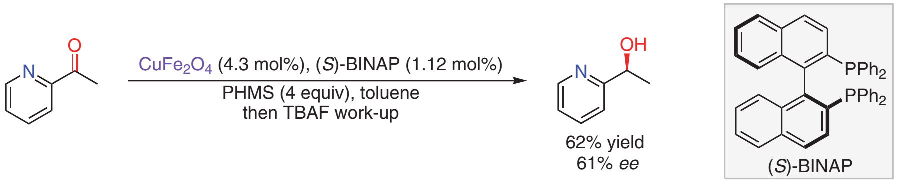
11a) Wu and Shi, *Green Chem.* **2014**, *16*, 2680.





10h) Fang and Chan, *Adv. Synth. Catal.* **2011**, *353*, 1457.

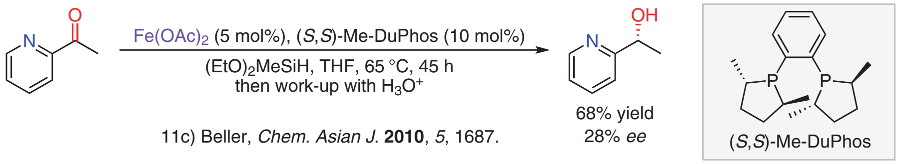
Copper-dipyridylphosphine-polymethylhydrosiloxane system for asymmetric catalytic hydrosilylation



11b) Figueras, *J. Org. Chem.* **2009**, *74*, 4608.

Iron Catalysis

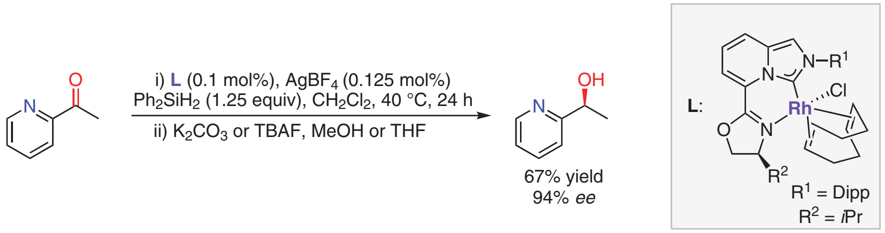
Stereoselective iron-catalyzed hydrosilylation of 2-pyridine ketones



11c) Beller, *Chem. Asian J.* **2010**, *5*, 1687.

Rhodium Catalysis

Chiral imidazo[1,5-*a*]pyridine–oxazolines as versatile NHC ligands for enantioselective hydrosilylation



11d) de Ruiter, *Organometallics* *2020*, *39*, 247.

Figure 11 Catalytic asymmetric hydrosilylation using copper, iron and rhodium[10h,11]

© 2024. Thieme. All rights reserved.

Conflict of Interest

The authors declare no conflict of interest.

Funding Information

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) (Discovery Grant RGPIN-2023-03591), the FRQNT Centre in Green Chemistry and Catalysis (CGCC) Strategic Cluster FRQNT-2020-RS4-265155-CCVC, and Université Laval. V.V and H.M.S. thank MITACS for Globalink Research Innovation award scholarships.

References

(1) (a) Zhang, Y. M.; Liu, P.; Zhang, H. L. *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.* **2008**, *38*, 778. (b) Murayama, H.; Heike, Y.; Higashida, K.; Shimizu, Y.; Yodsin, N.; Wongnongwa, Y.; Jungsuttiwong, S.; Mori, S.; Sawamura, M. *Adv. Synth. Catal.* **2020**, *362*, 4655. (c) Liu, Q.; Wang, C.; Zhou, H.; Wang, B.; Lv, J.; Cao, L.; Fu, Y. *Org. Lett.* **2018**, *20*, 971. (d) El-Asaad, B.; Guicheret, B.; Métay, E.; Karamé, I.; Lemaire, M. *J. Mol. Catal. A: Chem.* **2016**, *411*, 196. (e) Bigler, R.; Mezzetti, A. *Org. Process Res. Dev.* **2016**, *20*, 253. (f) Smith, S. A.; Morris, R. H. *Synthesis* **2015**, *47*, 1775.

(2) (a) Bigler, R.; Huber, R.; Mezzetti, A. *Angew. Chem. Int. Ed.* **2015**, *54*, 5171. (b) Bigler, R.; Huber, R.; Stöckli, M.; Mezzetti, A. *ACS Catal.* **2016**, *6*, 6455. (c) Naik, A.; Maji, T.; Reiser, O. *Chem. Commun.* **2010**, *46*, 4475. (d) Zuo, W.; Lough, A. J.; Li, Y. F.; Morris, R. H. *Science* **2013**, *342*, 1080. (e) Jiang, L.; Wu, T. F.; Chen, Y. C.; Zhu, J.; Deng, J. G. *Org. Biomol. Chem.* **2006**, *4*, 3319. (f) Deshpande, S. H.; Shende, V. S.; Shingote, S. K.; Chakravarty, D.; Puranik, V. G.; Chaudhari, R. V.; Kelkar, A. A. *RSC Adv.* **2015**, *5*, 51722. (g) Wang, F.; Yang, T.; Wu, T.; Zheng, L. S.; Yin, C.; Shi, Y.; Ye, X. Y.; Chen, G. Q.; Zhang, X. *J. Am. Chem. Soc.* **2021**, *143*, 2477. (h) Zheng, L. S.; Férard, C.; Phansavath, P.; Ratovelomanana-Vidal, V. *Chem. Commun.* **2018**, *54*, 283. (i) Echeverria, P. G.; Férard, C.; Phansavath, P.; Ratovelomanana-Vidal, V. *Catal. Commun.* **2015**, *62*, 95.

(3) (a) Wu, X.; Li, X.; Zanotti-Gerosa, A.; Pettman, A.; Liu, J.; Mills, A. J.; Xiao, J. *Chem. Eur. J.* **2008**, *14*, 2209. (b) Baratta, W.; Chelucci, G.; Magnolia, S.; Siega, K.; Rigo, P. *Chem. Eur. J.* **2009**, *15*, 726. (c) Kwong, H. L.; Lee, W. S.; Lai, T. S.; Wong, W. T. *Inorg. Chem. Commun.* **1999**, *2*, 66. (d) Johnson, T. C.; Totty, W. G.; Wills, M. *Org. Lett.* **2012**, *14*, 5230. (e) Chen, F.; Jin, M. Y.; Wang, D. Z.; Xu, C.; Wang, J.; Xing, X. *ACS Catal.* **2022**, *12*, 14429.

(4) (a) Baratta, W.; Benedetti, F.; Del Zotto, A.; Fanfoni, L.; Felluga, F.; Magnolia, S.; Putignano, E.; Rigo, P. *Organometallics* **2010**, *29*, 3563. (b) Lauzon, S.; Schouwey, L.; Ollevier, T. *Org. Lett.* **2022**, *24*, 1116. (c) Ishikawa, S.; Hamada, T.; Manabe, K.; Kobayashi, S. *Synthesis* **2005**, 2176. (d) Everaere, K.; Carpentier, J. F.; Mortreux, A.; Bulliard, M. *Tetrahedron: Asymmetry* **1999**, *10*, 4083. (e) Kišić, A.; Stephan, M.; Mohar, B. *Adv. Synth. Catal.* **2015**, *357*, 2540. (f) Wang, B.; Zhou, H.; Lu, G.; Liu, Q.; Jiang, X. *Org. Lett.* **2017**, *19*, 2094. (g) Chen, F.; He, D.; Chen, L.; Chang, X.; Wang, D. Z.; Xu, C.; Xing, X. *ACS Catal.* **2019**, *9*, 5562. (h) He, D.; Xu, X.; Lu, Y.; Zhou, M. J.; Xing, X. *Org. Lett.* **2020**, *22*, 8458. (i) Agac, A.; Karakaya, I.; Sahin, I.; Emir, S.; Karabuga, S.; Ulukanli, S. *J. Organomet. Chem.* **2016**, *819*, 189. (j) Kucukturkmen, C.; Agac, A.; Eren, A.; Karakaya, I.; Aslantas, M.; Celik, O.; Ulukanli, S.; Karabuga, S. *Catal. Commun.* **2016**, *74*, 122.

(5) (a) Nordin, S. J.; Roth, P.; Tarnai, T.; Alonso, D. A.; Brandt, P.; Andersson, P. G. *Chem. Eur. J.* **2001**, *7*, 1431. (b) Utepova, I. A.; Serebrennikova, P. O.; Streltsova, M. S.; Musikhina, A. A.; Fedorchenko, T. G.; Chupakhin, O. N.; Antonchick, A. P. *Molecules* **2018**, *23*, 1311. (c) Shen, W. Y.; Li, Y. Y.; Dong, Z. R.; Gao, J. X. *Synthesis* **2009**, 2413. (d) Xu, X.; You, Y.; Jin, M. Y.; Meng, F. J.; Xu, C.; Xing, X. *Sci. China Chem.* **2023**, *66*, 1443. (e) Okano, K.; Murata, K.; Ikariya, T. *Tetrahedron Lett.* **2000**, *41*, 9277. (f) Morris, D. J.; Hayes, A. M.; Wills, M. *J. Org. Chem.* **2006**, *71*, 7035. (g) Cheung, F. K.; Lin, C.; Minissi, F.; Crivillé, A. L.; Graham, M. A.; Fox, D. J.; Wills, M. *Org. Lett.* **2007**, *9*, 4659. (h) Bednářová, E.; Dračínský, M.; Malatinec, Š.; Císařová, I.; Lamaty, F.; Kotora, M. *Adv. Synth. Catal.* **2018**, *360*, 2869. (i) Bouzid, S.; Marcoux, A.; Ollevier, T. *Chem. Eur. J.* **2024**, *30*, e202402449.

(6) (a) Yang, X. H.; Xie, J. H.; Liu, W. P.; Zhou, Q. L. *Angew. Chem. Int. Ed.* **2013**, *52*, 7833. (b) Ma, J.; Li, W.; He, L.; Lv, H. *Chem. Commun.* **2022**, *58*, 5841. (c) Li, C.; Zhang, L.; Du, Y.; Zheng, X. L.; Fu, H. Y.; Chen, H.; Li, R. X. *Catal. Commun.* **2012**, *28*, 5. (d) Li, C.; Zhang, L.; Zheng, C.; Zheng, X.; Fu, H.; Chen, H.; Li, R. *Tetrahedron: Asymmetry* **2014**, *25*, 821. (e) Wu, W.; Liu, S.; Duan, M.; Tan, X.; Chen, C.; Xie, Y.; Lan, Y.; Dong, X. Q.; Zhang, X. *Org. Lett.* **2016**, *18*, 2938. (f) Wu, W.; You, C.; Yin, C.; Liu, Y.; Dong, X. Q.; Zhang, X. *Org. Lett.* **2017**, *19*, 2548. (g) Nian, S.; Ling, F.; Chen, J.; Wang, Z.; Shen, H.; Yi, X.; Yang, Y. F.; She, Y.; Zhong, W. *Org. Lett.* **2019**, *21*, 5392. (h) Yin, C.; Zhang, R.; Pan, Y.; Gao, S.; Ding, X.; Bai, S. T.; Lang, Q.; Zhang, X. *J. Org. Chem.* **2024**, *89*, 527. (i) Hu, Y.; Wu, W.; Dong, X. Q.; Zhang, X. *Org. Chem. Front.* **2017**, *4*, 1499.

(7) (a) Wu, W.; Zhao, N.; Liu, Y.; Du, S.; Wang, X.; Mo, W.; Yan, X.; Xu, C.; Zhou, Y.; Ji, B. *Org. Lett.* **2023**, *25*, 8845. (b) Yin, C.; Dong, X. Q.; Zhang, X. *Adv. Synth. Catal.* **2018**, *360*, 4319. (c) Lagaditis, P. O.; Sues, P. E.; Sonnenberg, J. F.; Wan, K. Y.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2014**, *136*, 1367. (d) Li, Y.; Yu, S.; Wu, X.; Xiao, J.; Shen, W.; Dong, Z.; Gao, J. *J. Am. Chem. Soc.* **2014**, *136*, 4031. (e) He, J.; Mao, W.; Lin, J.; Wu, Y.; Chen, L.; Yang, P.; Song, D.; Zhu, P.; Zhong, W.; Ling, F. *Org. Chem. Front.* **2023**, *10*, 3321. (f) Zhang, L.; Tang, Y.; Han, Z.; Ding, K. *Angew. Chem. Int. Ed.* **2019**, *58*, 4973. (g) Seo, C. S.; Tsui, B. T.; Gradiski, M. V.; Smith, S. A.; Morris, R. H. *Catal. Sci. Technol.* **2021**, *11*, 3153. (h) Ling, F.; Chen, J.; Nian, S.; Hou, H.; Yi, X.; Wu, F.; Xu, M.; Zhong, W. *Synlett* **2020**, *31*, 285.

(8) (a) Widegren, M. B.; Harkness, G. J.; Slawin, A. M.; Cordes, D. B.; Clarke, M. L. *Angew. Chem. Int. Ed.* **2017**, *56*, 5825. (b) Yang, H.; Huo, N.; Yang, P.; Pei, H.; Lv, H.; Zhang, X. *Org. Lett.* **2015**, *17*, 4144. (c) Arenas, I.; Boutureira, O.; Matheu, M. I.; Díaz, Y.; Castillón, S. *Eur. J. Org. Chem.* **2015**, 3666. (d) Ohkuma, T.; Koizumi, M.; Yoshida, M.; Noyori, R. *Org. Lett.* **2000**, *2*, 1749. (e) Maerten, E.; Agbossou-Niedercorn, F.; Castanet, Y.; Mortreux, A. *Tetrahedron* **2008**, *64*, 8700. (f) Tao, X.; Li, W.; Ma, X.; Li, X.; Fan, W.; Xie, X.; Ayad, T.; Ratovelomanana-Vidal, V.; Zhang, Z. *J. Org. Chem.* **2012**, *77*, 612.

(9) (a) Yurino, T.; Nishihara, R.; Yasuda, T.; Yang, S.; Utsumi, N.; Katayama, T.; Arai, N.; Ohkuma, T. *Org. Lett.* **2024**, *26*, 2872. (b) Yamada, M.; Azuma, K.; Yamano, M. *Org. Lett.* **2021**, *23*, 3364. (c) Burk, M. J.; Hems, W.; Herzberg, D.; Malan, C.; Zanotti-Gerosa, A. *Org. Lett.* **2000**, *2*, 1749. (d) Chen, C. Y.; Reamer, R. A.; Chilenski, J. R.; McWilliams, C. J. *Org. Lett.* **2003**, *5*, 5039. (e) Yu, H.; Zhan, T.; Zhou, Y.; Chen, L.; Liu, X.; Feng, X. *ACS Catal.* **2022**, *12*, 5136.

(10) (a) Lipshutz, B. H.; Lower, A.; Kucejko, R. J.; Noson, K. *Org. Lett.* **2006**, *8*, 2969. (b) Lee, C. T.; Lipshutz, B. H. *Org. Lett.* **2008**, *10*, 4187. (c) Qi, S. B.; Li, M.; Li, S.; Zhou, J. N.; Wu, J. W.; Yu, F.; Zhang, X. C.; Chan, A. S.; Wu, J. *Org. Biomol. Chem.* **2013**, *11*, 929. (d) Zhang, X.-C.; Wu, Y.; Yu, F.; Wu, F.-F.; Wu, J.; Chan, A. S. C. *Chem. Eur. J.* **2009**, *15*, 5888. (e) Sui, Y. Z.; Zhang, X. C.; Wu, J. W.; Li, S.; Zhou, J. N.; Li, M.; Fang, W.; Chan, A. S. C.; Wu, J. *Chem. Eur. J.* **2012**, *18*, 7486. (f) Junge, K.; Wendt, B.; Addis, D.; Zhou, S.; Das, S.; Beller, M. *Chem. Eur. J.* **2010**, *16*, 68. (g) Fialho, D. M.; Etemadi-Davan, E.; Langner, O. C.; Takale, B. S.; Gadakh, A.; Sambasivam, G.; Lipshutz, B. H. *Org. Lett.* **2021**, *23*, 3282. (h) Zhang, X. C.; Wu, F. F.; Li, S.; Zhou, J. N.; Wu, J.; Li, N.; Fang, W.; Lam, K. H.; Chan, A. S. C. *Adv. Synth. Catal.* **2011**, *353*, 1457.

(11) (a) Li, M.; Li, B.; Xia, H. F.; Ye, D.; Wu, J.; Shi, Y. *Green Chem.* **2014**, *16*, 2680. (b) Kantam, M. L.; Yadav, J.; Laha, S.; Srinivas, P.; Sreedhar, B.; Figueras, F. *J. Org. Chem.* **2009**, *74*, 4608. (c) Addis, D.; Shaikh, N.; Zhou, S.; Das, S.; Junge, K.; Beller, M. *Chem. Asian J.* **2010**, *5*, 1687. (d) Swamy, C. A.; Varenikov, A.; de Ruiter, G. *Organometallics* **2020**, *39*, 247.