Outline

1. **Asymmetric Copper Catalysis**
   1. **Dehydrogenative Coupling**
   2. **Cyanation**
2. **Asymmetric Nickel Catalysis**
   1. **Arylation**
   2. **Acylation**
3. **Asymmetric Palladium Catalysis**
   1. **Allylation**
   2. **Alkylation**
4. **Asymmetric Chromium Catalysis**
   1. **Allylic C(sp^3)–H Functionalization**
5. **Asymmetric Iridium Catalysis**
   1. **Allylic Alkylation**

Not covered: asymmetric pericyclic reactions, SOMO catalysis, metals as chiral Lewis acids

Useful reviews:

Lu, F.-D.; Chen, J.; Jiang, X.; Chen, J.-R.; Lu, L.-Q.; Xiao, W.-J. *Chem. Soc. Rev.* **2021,** *50*, 12808. https://doi.org/10.1039/D1CS00210D

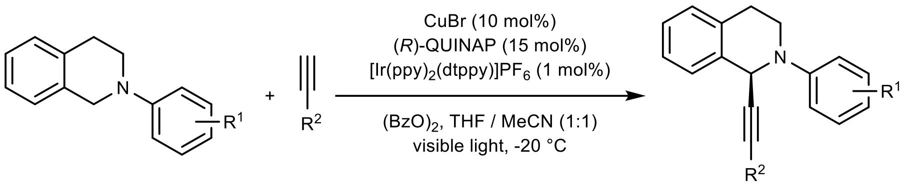
Chan, A. Y.; Perry, I. B.; Bissonnette, N. B.; Buksh, B. F.; Edwards, G. A.; Frye, L. I.; Garry, O. L.; Lavagnino, M. N.; Li, B. X.; Liang, Y.; Mao, E.; Millet, A.; Oakley, J. V.; Reed, N. L.; Sakai, H. A.; Seath, C. P.; MacMillan, D. W. C. *Chem. Rev.* **2022,** *122*, 1485. https://doi.org/10.1021/acs.chemrev.1c00383

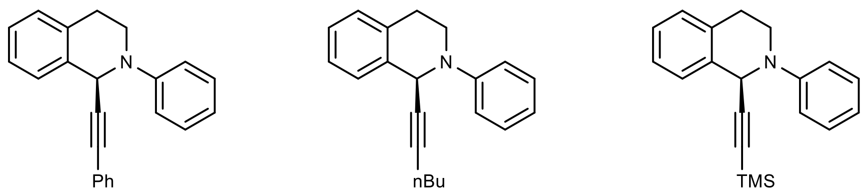
Cheung, K. P. S.; Sarkar, S.; Gevorgyan, V. *Chem. Rev.* **2022,** *122*, 1543. https://doi.org/10.1021/acs.chemrev.1c00403

Electrochemical Series of Photocatalysts and Common Organic Compounds https://macmillan.princeton.edu/wp-content/uploads/Merck-Photocatalysis-Chart.pdf

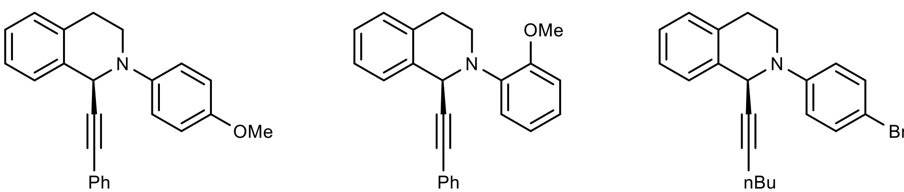
Asymmetric Copper Catalysis

Dehydrogenative Alkynylation (Li, 2015)

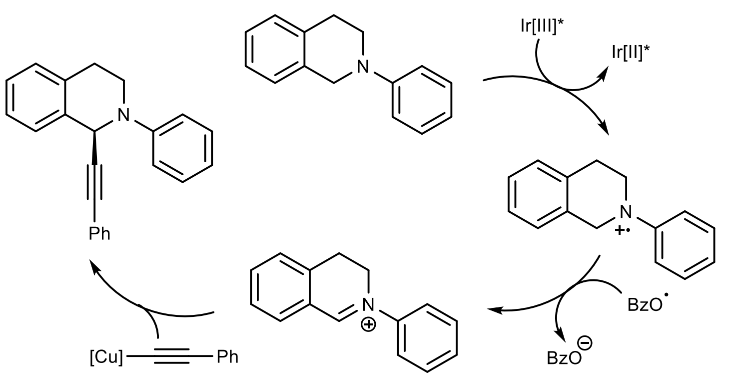




64%, 94% ee | 48%, 87% ee | 40%, 60% ee

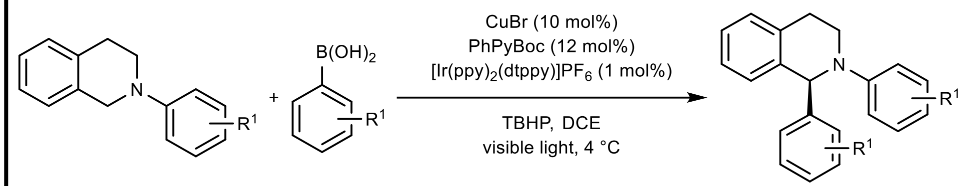


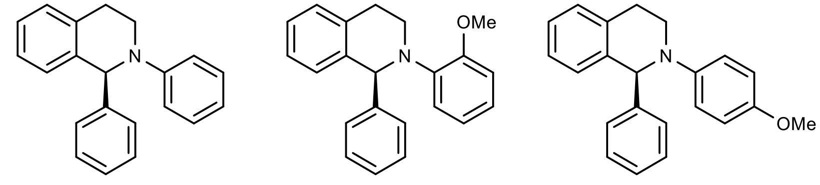
55%, 94% ee | 80%, 80% ee | 20%, 87% ee



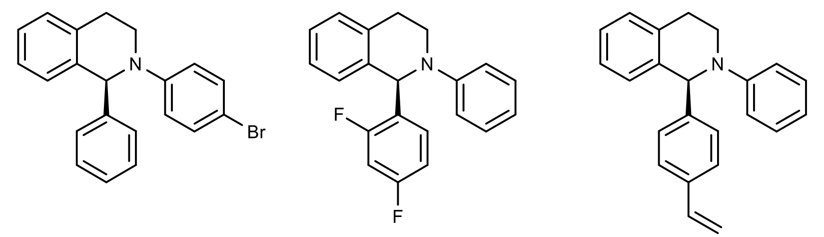
Perepichka, I.; Kundu, S.; Hearne, Z.; Li, C.-J. *Org. Biomol. Chem.* **2015,** *13*, 447.
https://doi.org/10.1039/C4OB02138J

Dehydrogenative Arylation (Li, 2016)

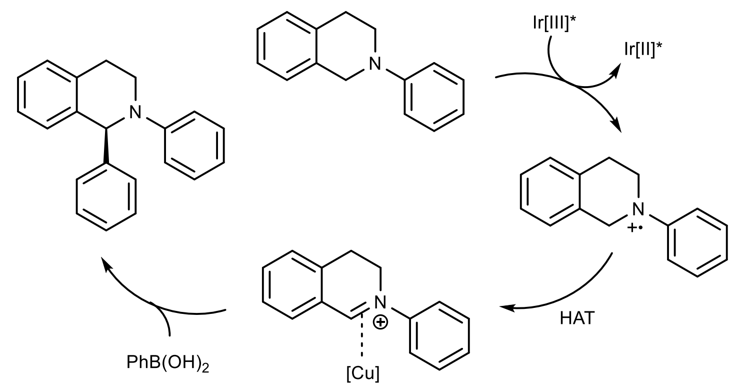




19:81 er | 84:16 er | 15:85 er



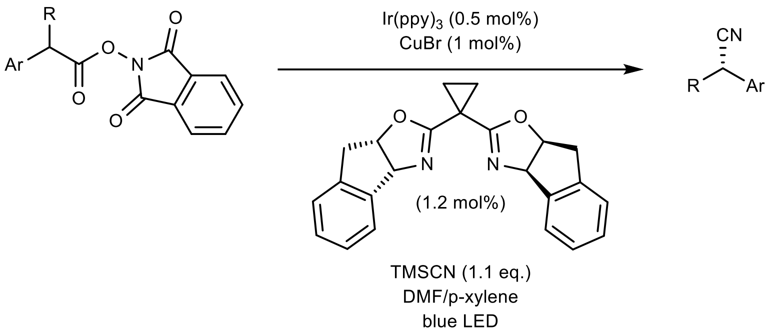
19:81 er | 37:63 er | 19:81 er

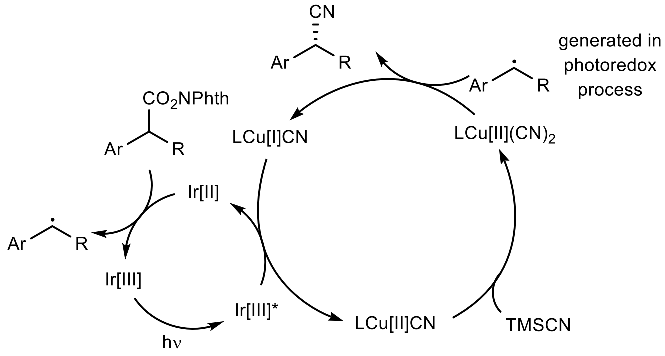


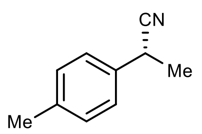
Querard, P.; Perepichka, I.; Zysman-Colman, E.; Li, C.-J.
Beilstein J. Org. Chem. **2016,** *12*, 2636. https://doi.org/10.3762/bjoc.12.260

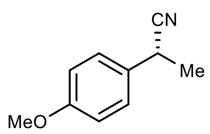
Asymmetric Copper Catalysis

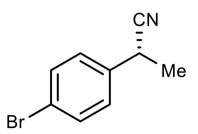
NHPI ester-based Decarboxylative Cyanation (Liu, 2017)

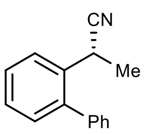


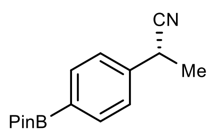


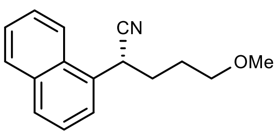

98%, 87% ee

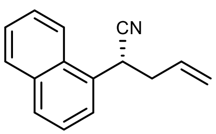

71%, 82% ee

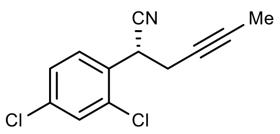

77%, 90% ee

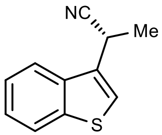

90%, 91% ee

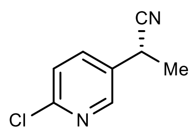

38%, 94% ee

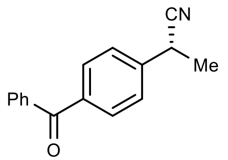

84%, 91% ee

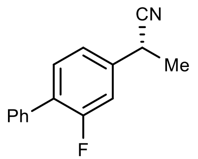

66%, 92% ee

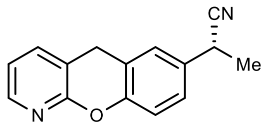

92%, 93% ee

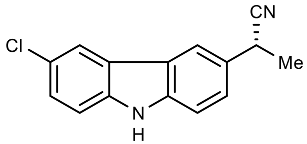

67%, 88% ee

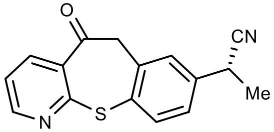

71%, 90% ee


98%, 85% ee
from (±)-ketoprofen


92%, 92% ee
from (±)-flurbiprofen


92%, 92% ee
from (±)-pranoprofen

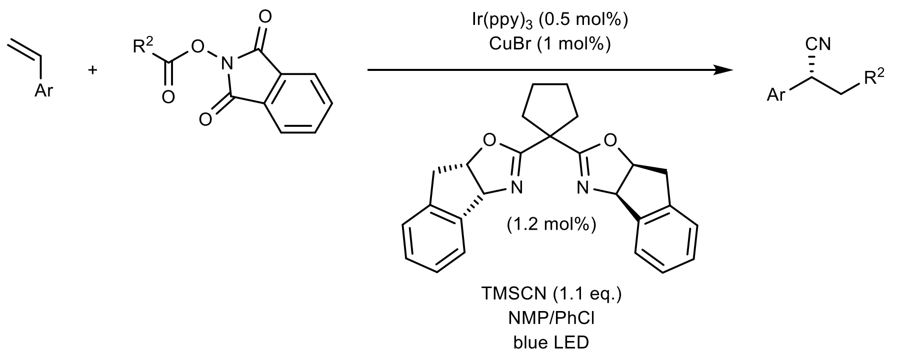

59%, 85% ee
from (±)-carprofen

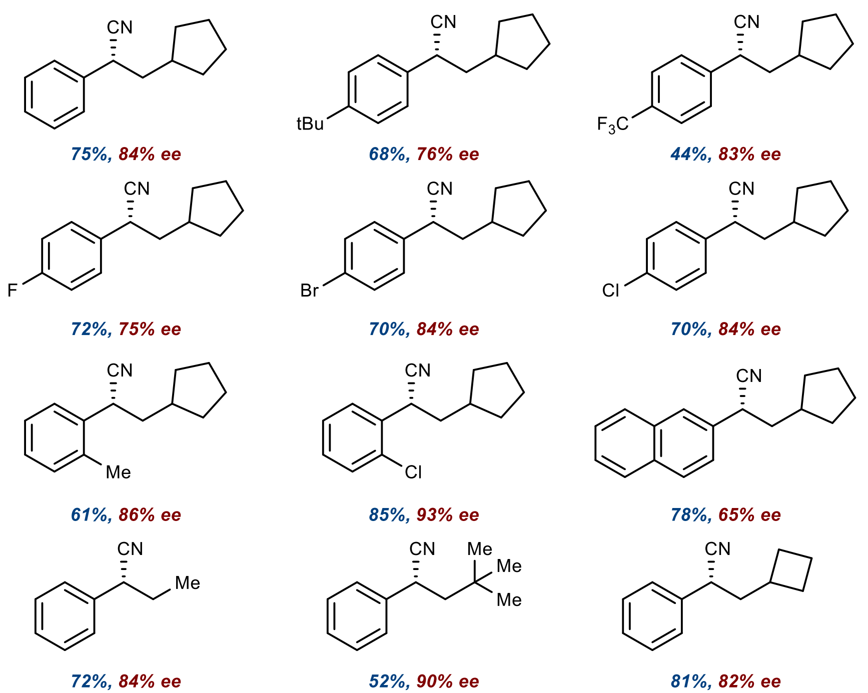

79%, 88% ee
from (±)-zaltoprofen

Wang, D.; Zhu, N.; Chen, P.; Lin, Z.; Liu, G. *J. Am. Chem. Soc.* **2017,** *139*, 15632. https://doi.org/10.1021/jacs.7b09802

Asymmetric Copper Catalysis

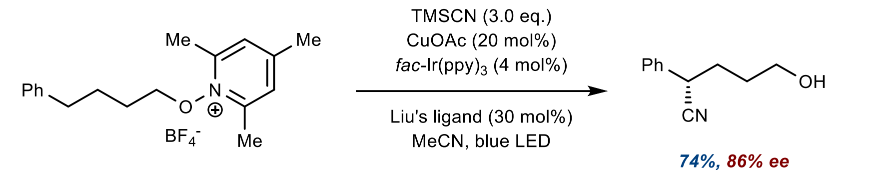
Cyanoalkylation of Styrenes (Mei & Han, 2018)

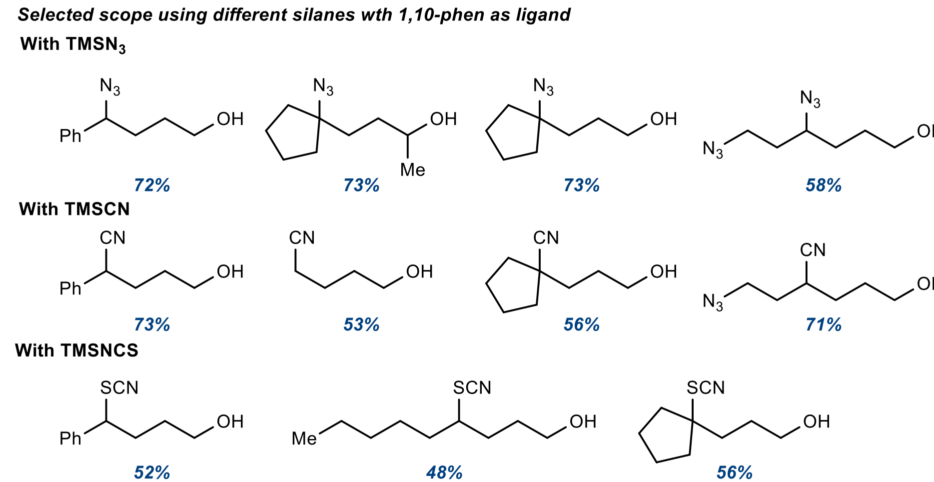


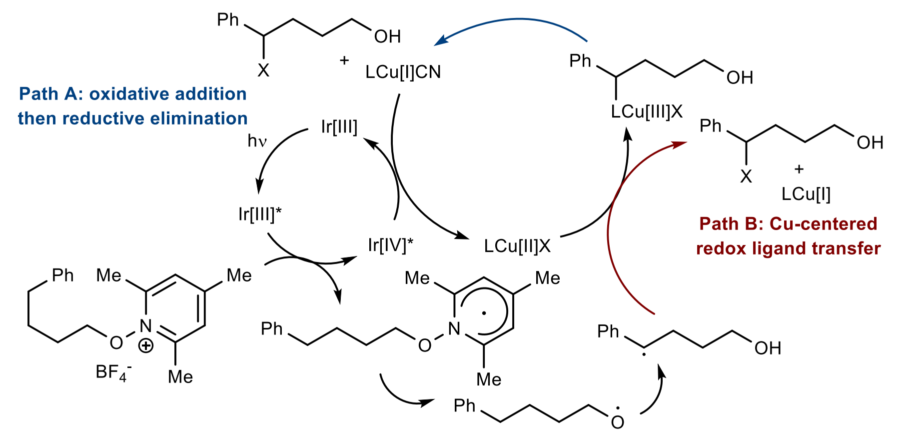


Sha, W.; Deng, L.; Ni, S.; Mei, H.; Han, J.; Pan, Y. *ACS Catal.* **2018,** *8*, 7489.
https://doi.org/10.1021/acscatal.8b01863

C(sp³)-H Cyanation (Zhu, 2019)

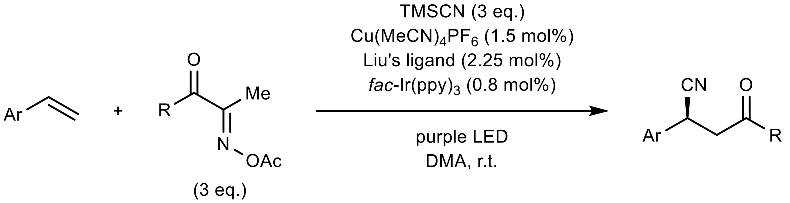


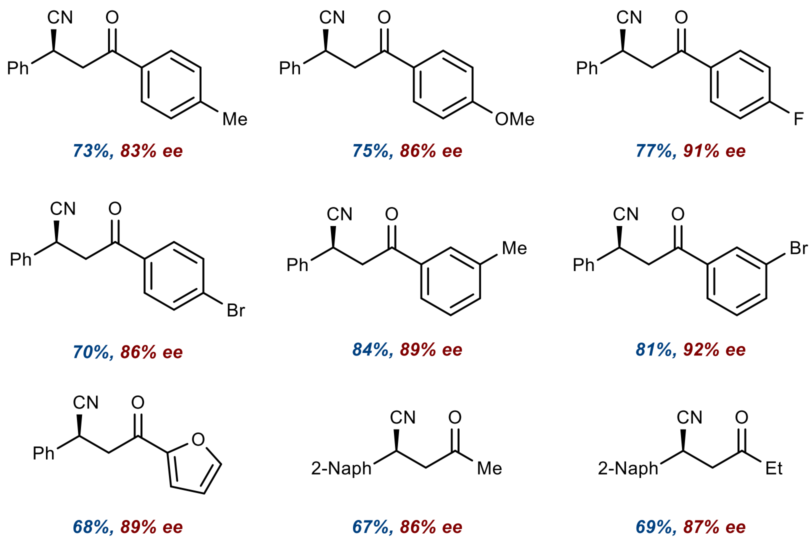


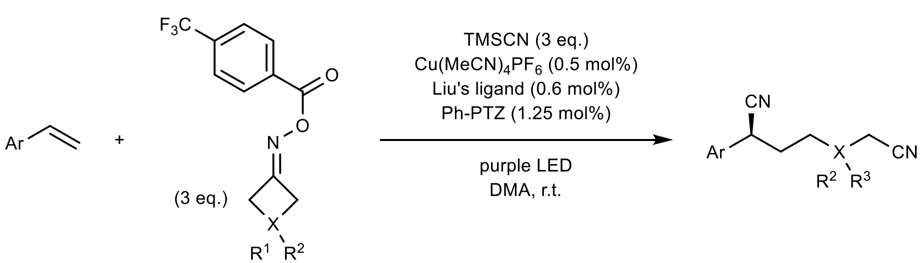


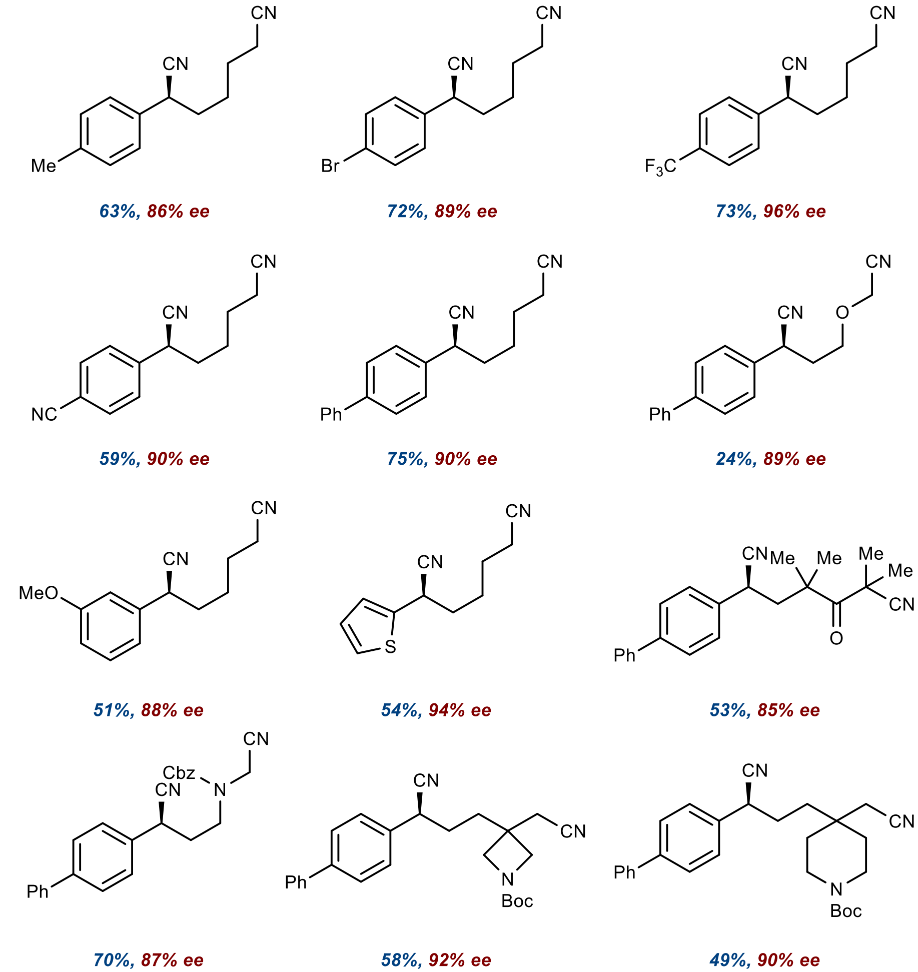
Bao, X.; Wang, Q.; Zhu, J. *Angew. Chem. Int. Ed.* **2019,** *58*, 2139.
https://doi.org/10.1002/anie.201813356

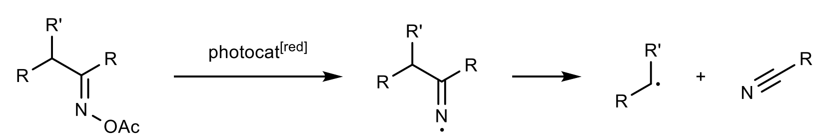
Cyanoalkylation of Styrenes (Xiao & Chen, 2021)









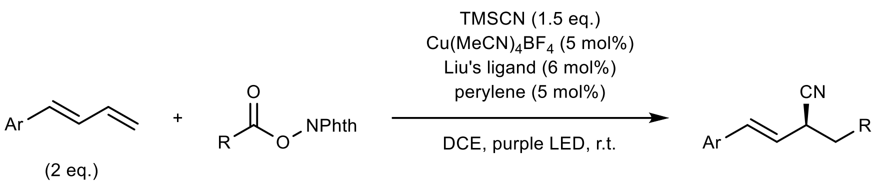


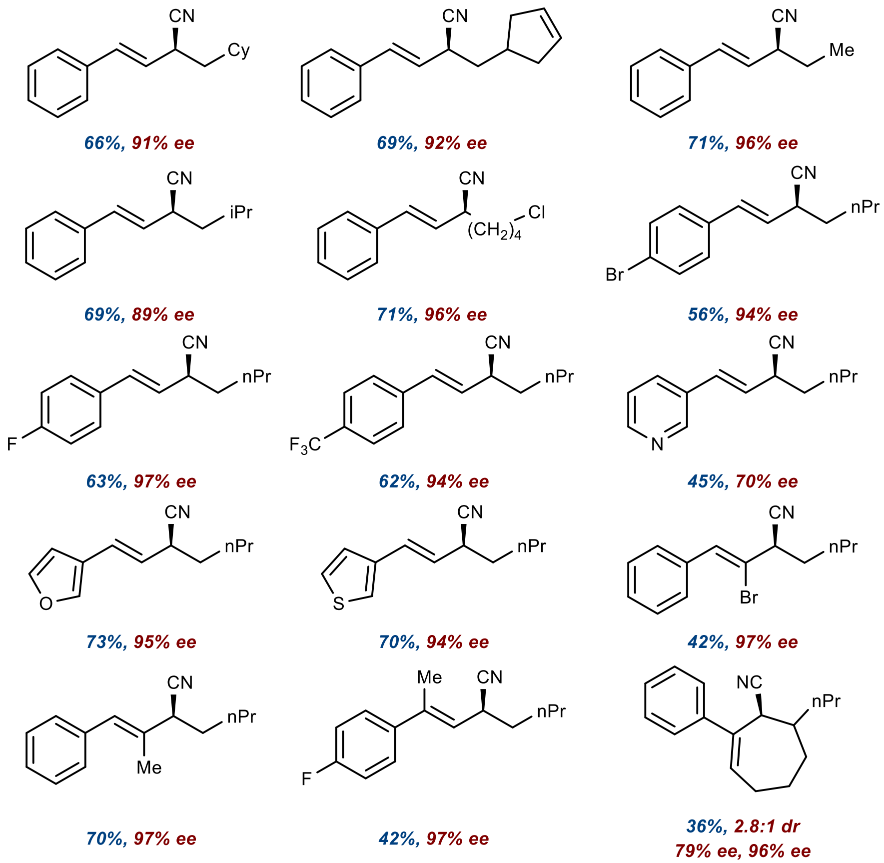
radical addition
then oxidative addition to Cu[II]

Wang, P.-Z.; Gao, Y.; Chen, J.; Huan, X.-D.; Xiao, W.-J.; Chen, J.-R. *Nat. Commun.* **2021,** *12*, 1815. https://doi.org/10.1038/s41467-021-22127-x

Asymmetric Copper Catalysis

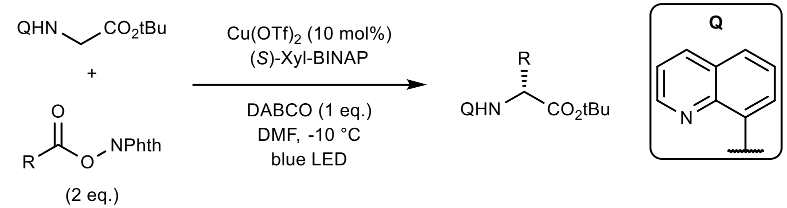
Cyanoalkylation of Aromatic 1,3-Diene (Xiao, 2021)

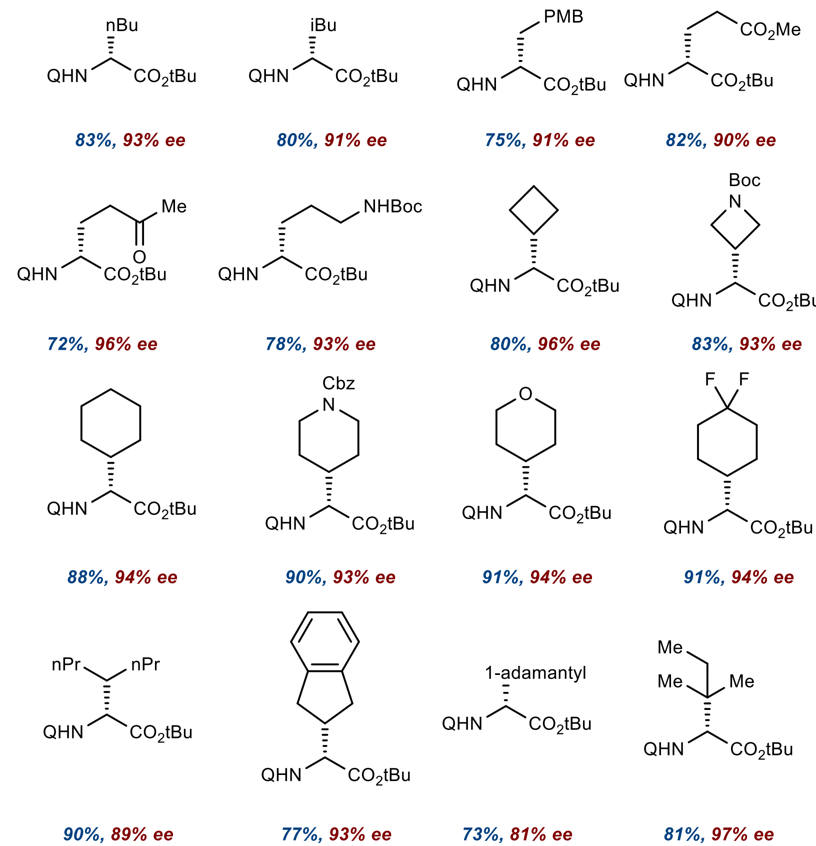




Lu, F.-D.; Lu, L.-Q.; He, G.-F.; Bai, J.-C.; Xiao, W.-J. *J. Am. Chem. Soc.* **2021,** *143*, 4168.
https://doi.org/10.1021/jacs.1c01260

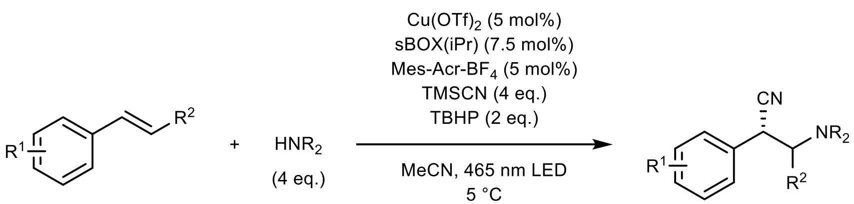
C(sp³)-H Cyanation of Amino Esters (Wang & Xu, 2021)

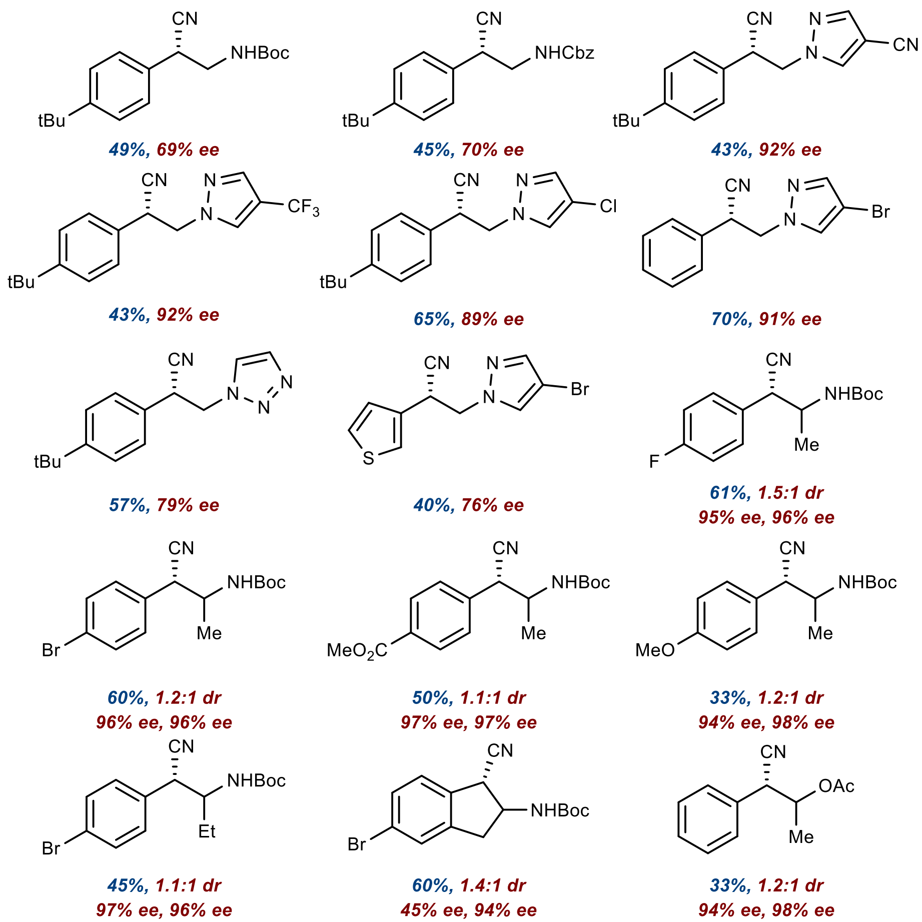


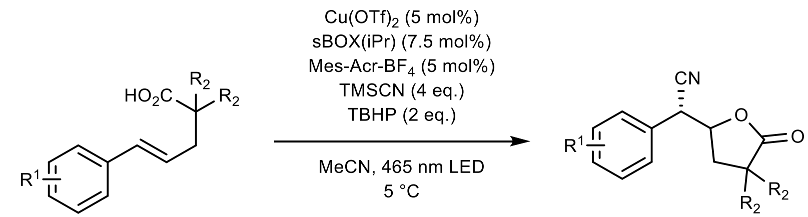


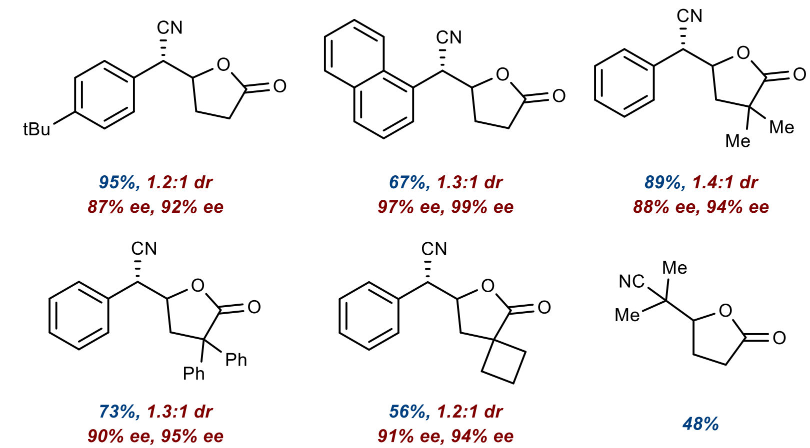
Qi, R.; Wang, C.; Huo, Y.; Chai, H.; Wang, H.; Ma, Z.; Liu, L.; Wang, R.; Xu, Z. *J. Am. Chem. Soc.* **2021,** *143*, 12777. https://doi.org/10.1021/jacs.1c05890

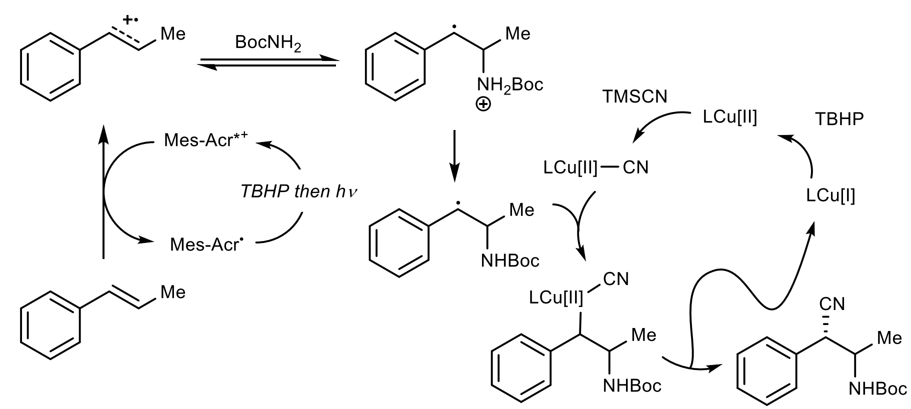
Amino-and Oxycyanation of Alkenes (Nicewicz, 2023)







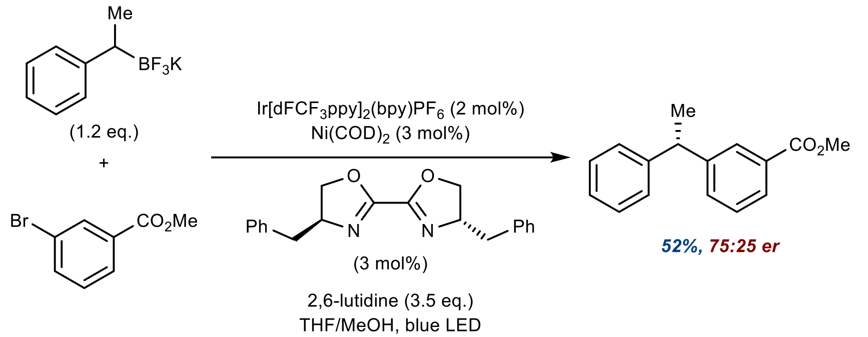


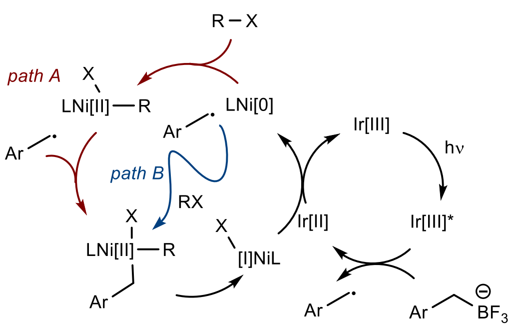


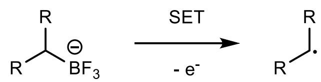
Qian, S.; Lazarus, T. M.; Nicewicz, D. A. *J. Am. Chem. Soc.* **2023,** *145*, 18247. https://doi.org/10.1021/jacs.3c06936

Asymmetric Nickel Catalysis

Deborylative Arylation (Molander, 2014, 2015)

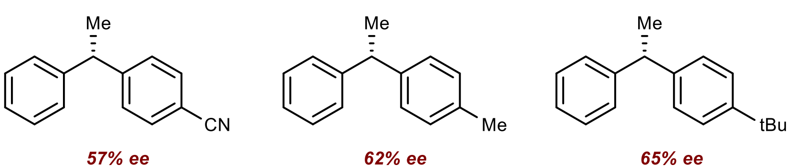






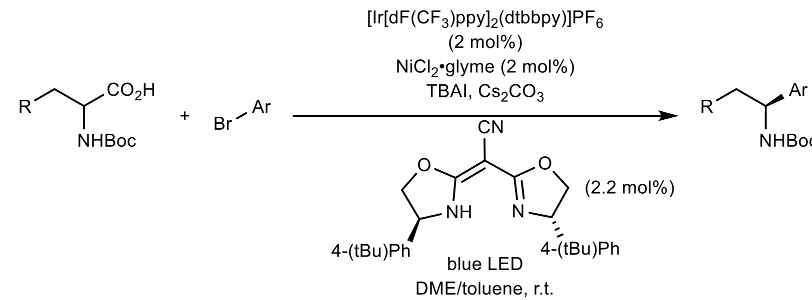
1. Low activation energy
2. no base or heat needed
3. rate determined by the stability of the product.

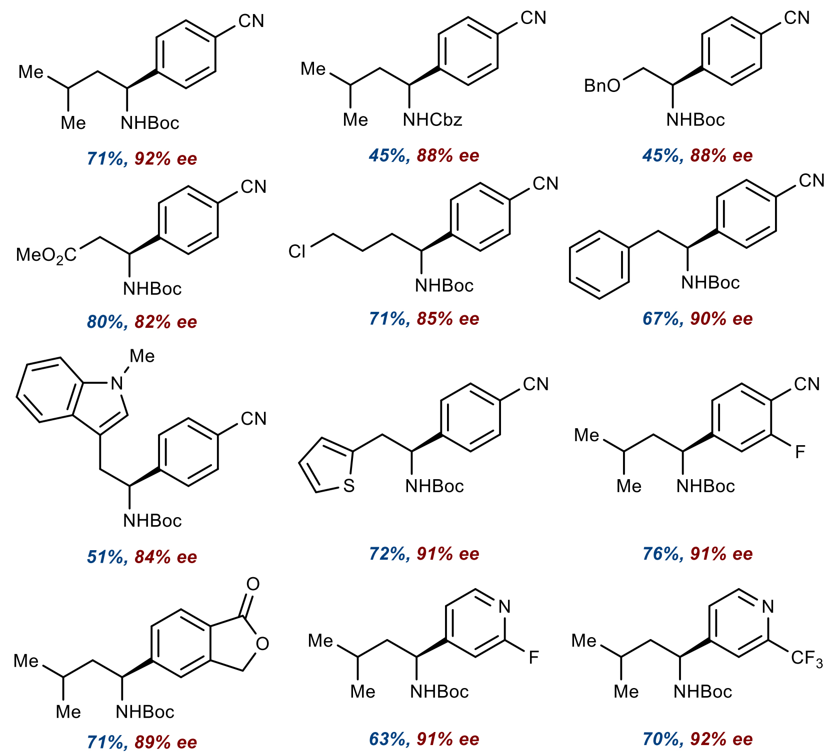
Tellis, J. C.; Primer, D. N.; Molander, G. A. *Science* **2014,** *345*, 433.
https://doi.org/doi:10.1126/science.1253647



Gutierrez, O.; Tellis, J. C.; Primer, D. N.; Molander, G. A.; Kozlowski, M. C.
J. Am. Chem. Soc. **2015,** *137*, 4896. https://doi.org/10.1021/ja513079r

Decarboxylative Arylation (Fu & MacMillan, 2016)

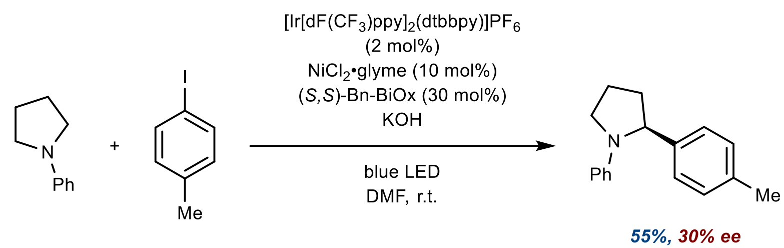


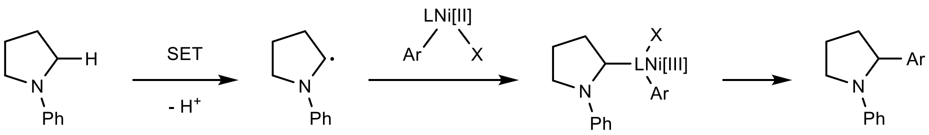


Zuo, Z.; Cong, H.; Li, W.; Choi, J.; Fu, G. C.; MacMillan, D. W. C.
J. Am. Chem. Soc. **2016,** *138*, 1832. https://doi.org/10.1021/jacs.5b13211

Asymmetric Nickel Catalysis

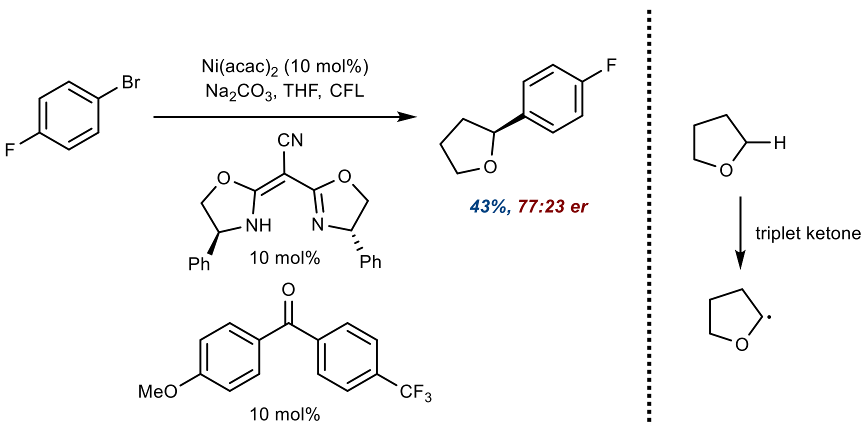
C(sp³)-H Arylation (Doyle, 2016)





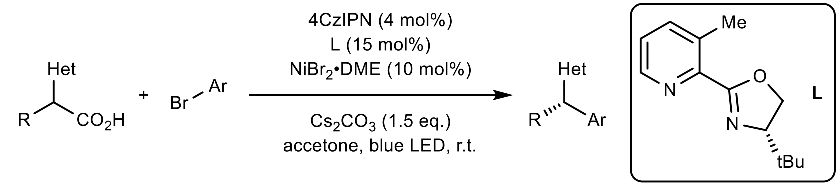
Ahneman, D. T.; Doyle, A. G. *Chem. Sci.* **2016**, *7*, 7002. https://doi.org/10.1039/C6SC02815B

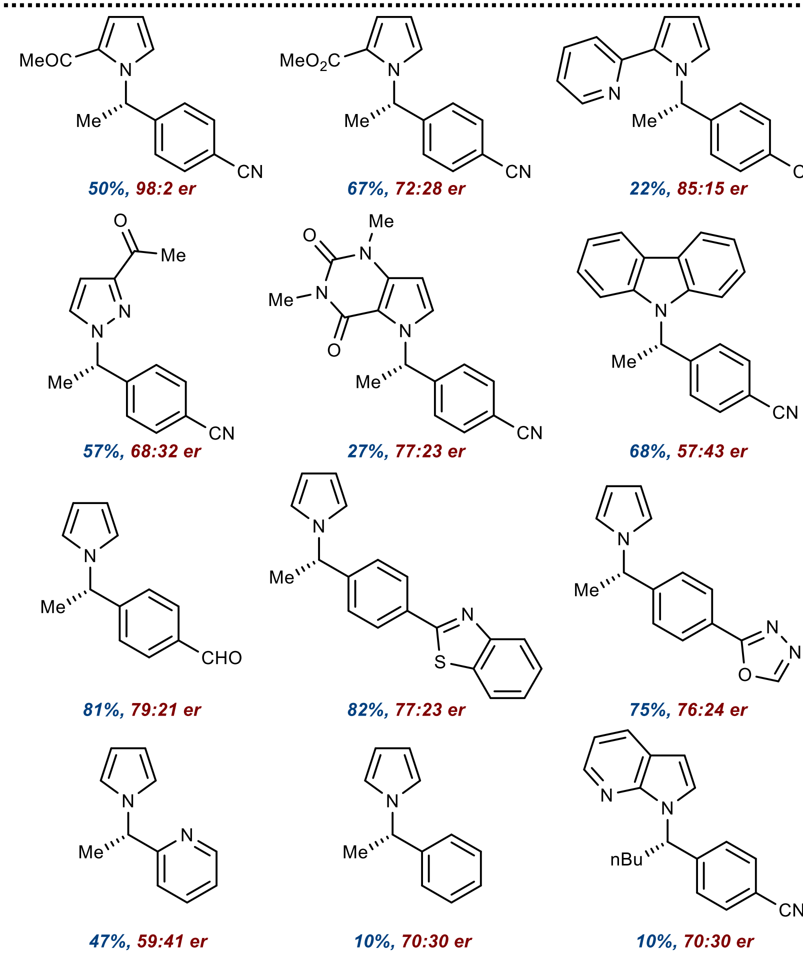
C(sp³)-H Arylation (Matin, 2018)



Shen, Y.; Gu, Y.; Martin, R. *J. Am. Chem. Soc.* **2018**, *140*, 12200.
https://doi.org/10.1021/jacs.8b07405

Decarboxylative Arylation (Bonifazi & Davidson, 2019)

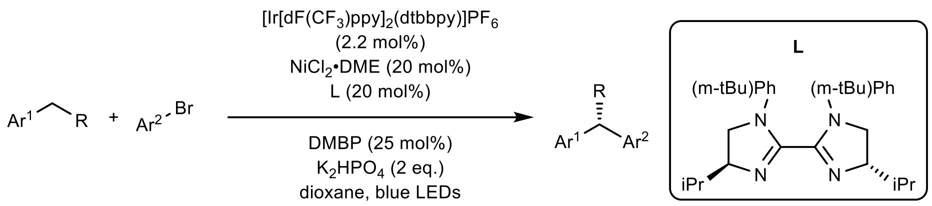


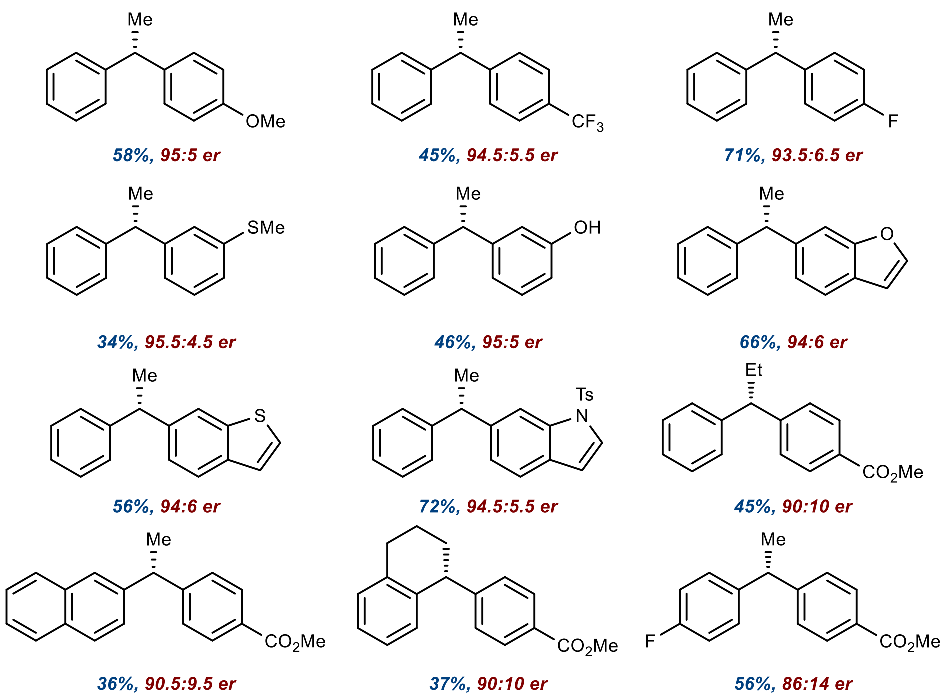


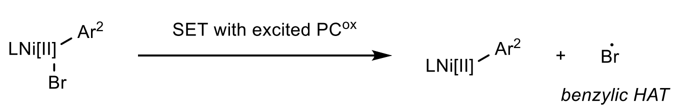
Pezzetta, C.; Bonifazi, D.; Davidson, R. W. M. *Org. Lett.* **2019**, *21*, 8957.
https://doi.org/10.1021/acs.orglett.9b03338

Asymmetric Nickel Catalysis

C(sp³)-H Arylation (Lu, 2019)

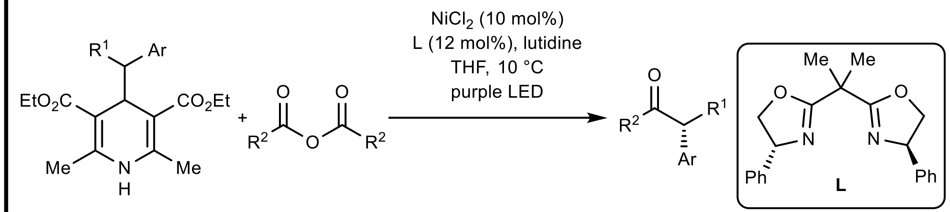


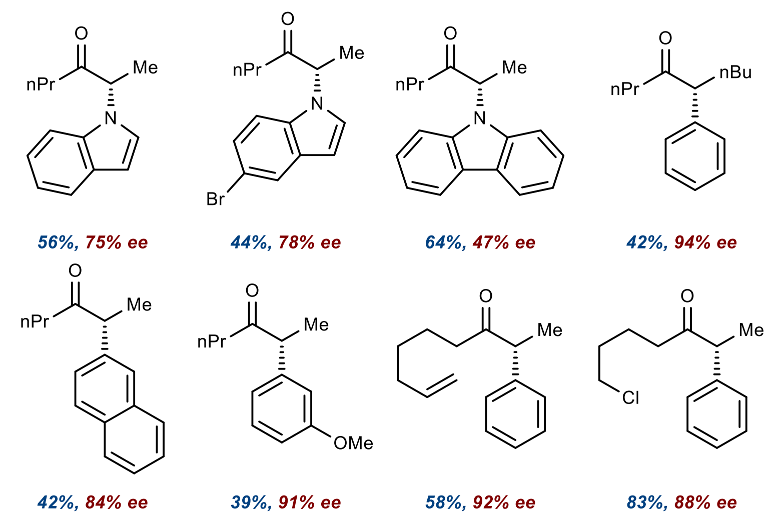


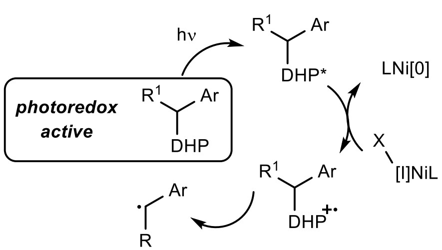


Cheng, X.; Lu, H.; Lu, Z. *Nat. Commun.* **2019**, *10*, 3549.
https://doi.org/10.1038/s41467-019-11392-6

Acyl Cross-Coupling (Melchiorre, 2019)



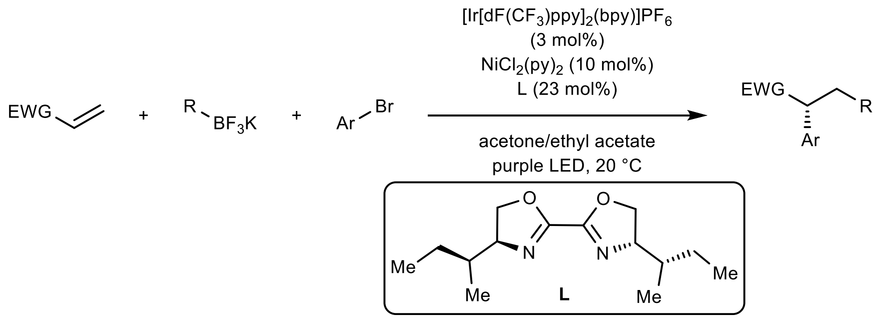


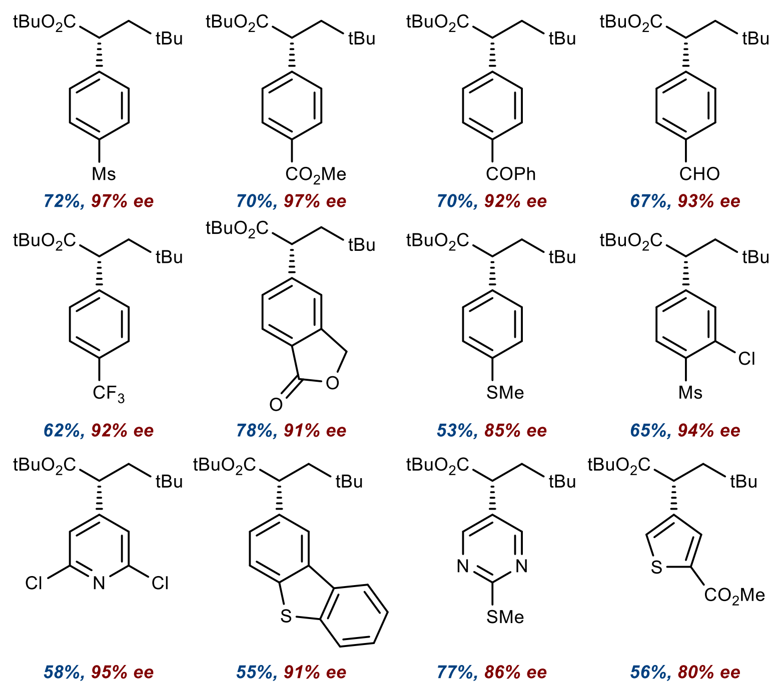


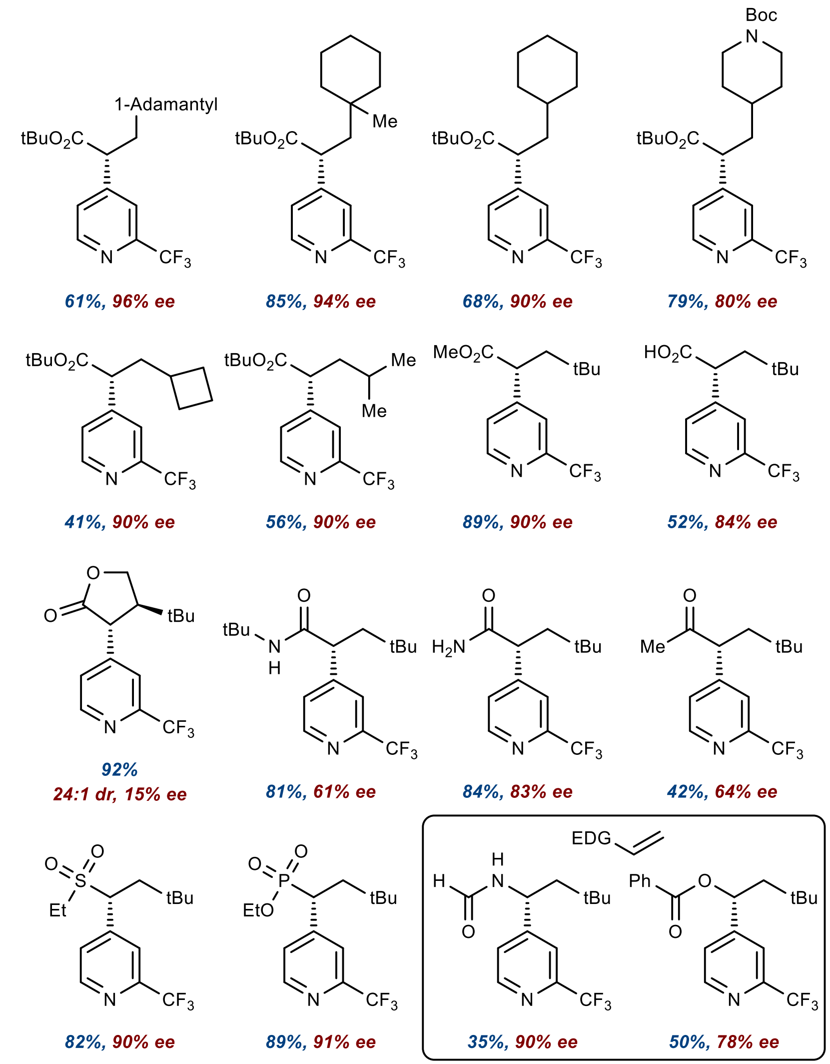
Gandolfo, E.; Tang, X.; Raha Roy, S.; Melchiorre, P. *Angew. Chem. Int. Ed.* **2019**, *58*, 16854.
https://doi.org/10.1002/anie.201910168

Asymmetric Nickel Catalysis

Carboarylation of Alkenes (Gutierrez & Chu, 2020)



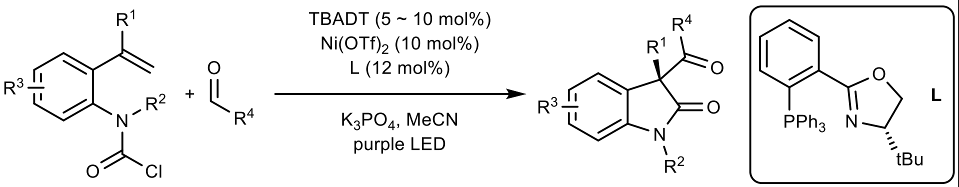


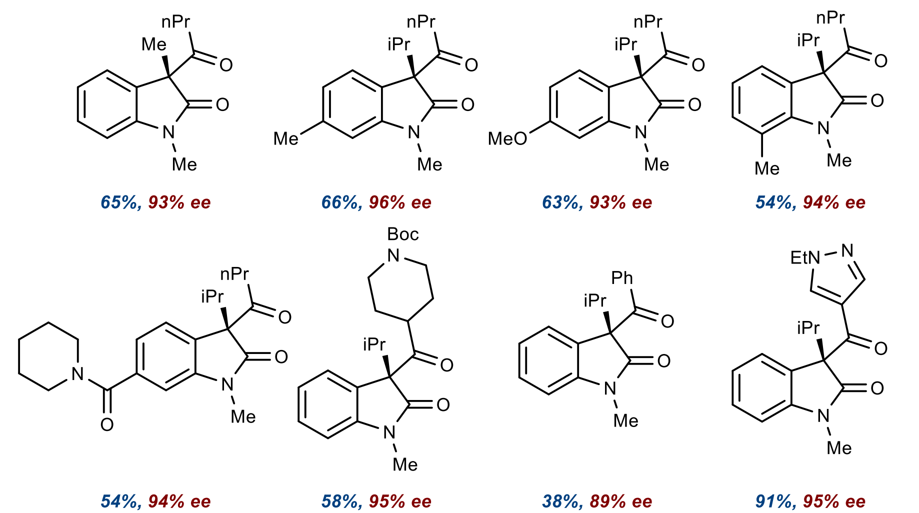


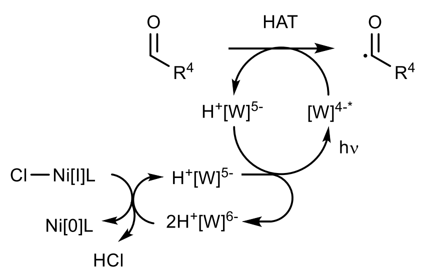
Guo, L.; Yuan, M.; Zhang, Y.; Wang, F.; Zhu, S.; Gutierrez, O.; Chu, L. *J. Am. Chem. Soc.* **2020,** *142*, 20390. https://doi.org/10.1021/jacs.0c08823

Asymmetric Nickel Catalysis

Acyl-Carbamoylation of Alkenes (Wang, 2020)

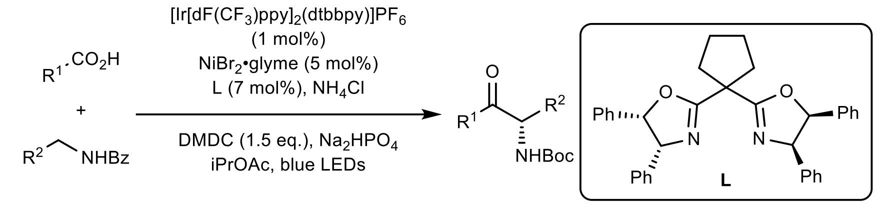


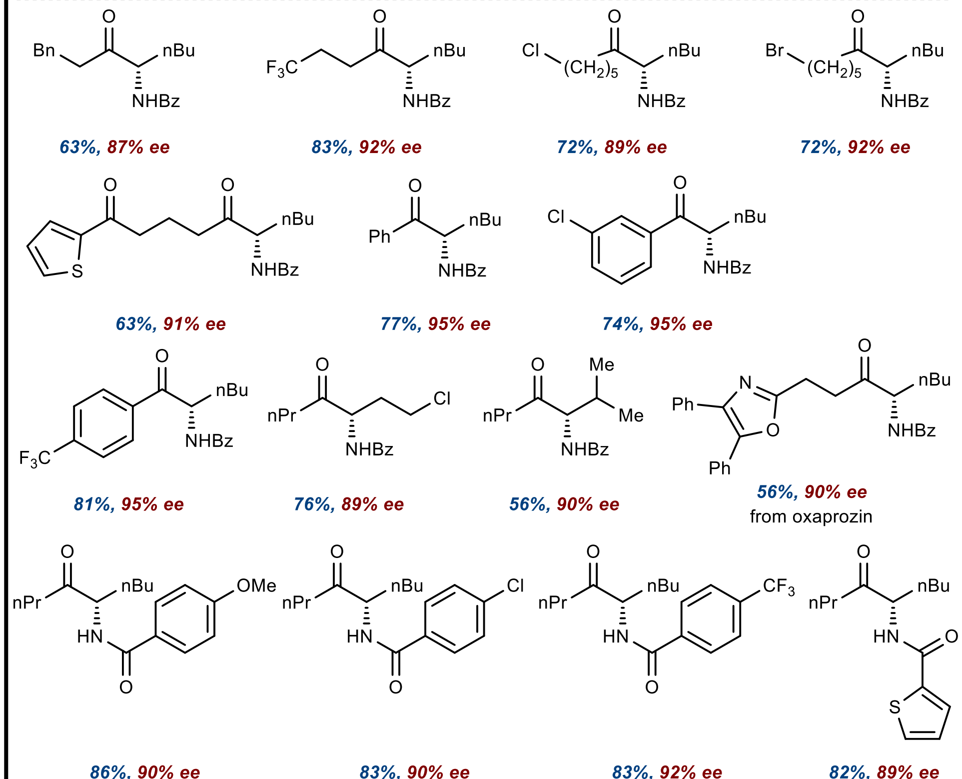


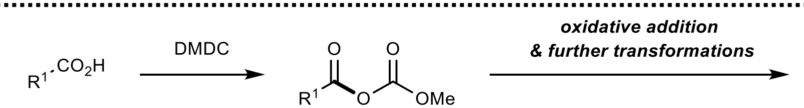


Fan, P.; Lan, Y.; Zhang, C.; Wang, C. *J. Am. Chem. Soc.* **2020,** *142*, 2180.
https://doi.org/10.1021/jacs.9b12554

C(sp³)–H Acylation (Hou, 2020)



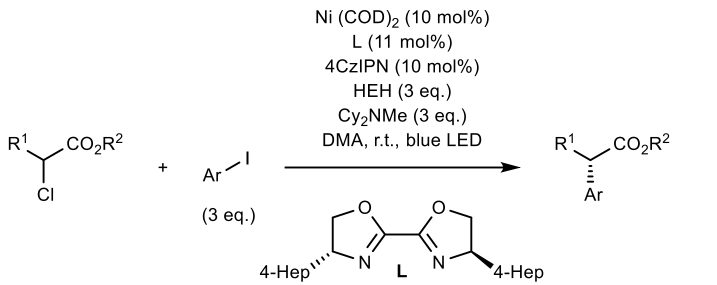


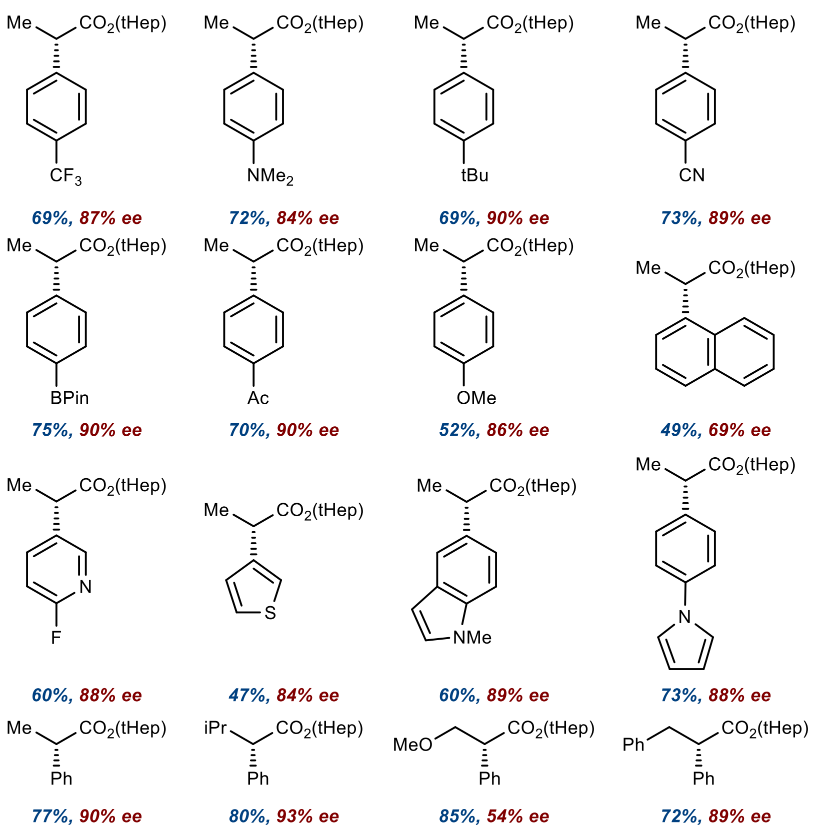


Shu, X.; Huan, L.; Huang, Q.; Huo, H. *J. Am. Chem. Soc.* **2020,** *142*, 19058.
https://doi.org/10.1021/jacs.0c10471

Asymmetric Nickel Catalysis

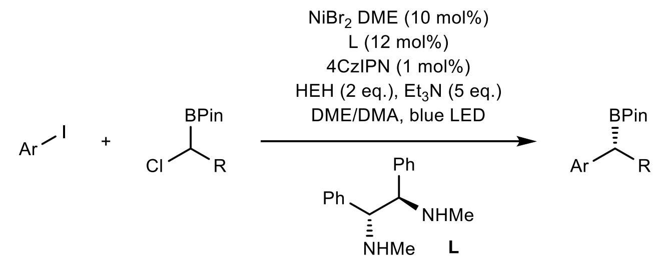
Cross-electrophile Coupling (Walsh & Mao, 2020)

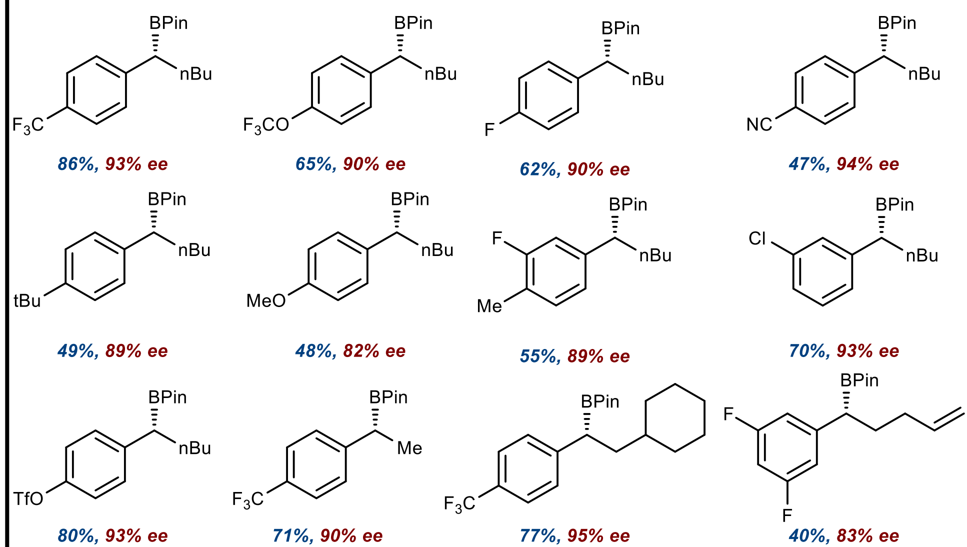


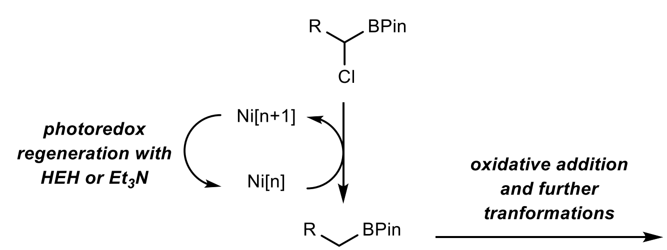


Guan, H.; Zhang, Q.; Walsh, P. J.; Mao, J. *Angew. Chem. Int. Ed.* **2020,** *59*, 5172.
https://doi.org/10.1002/anie.201914175

Cross-electrophile Coupling (Xu, 2021)





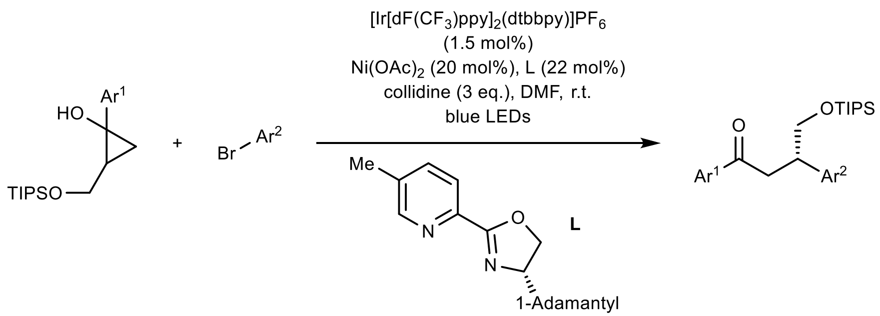


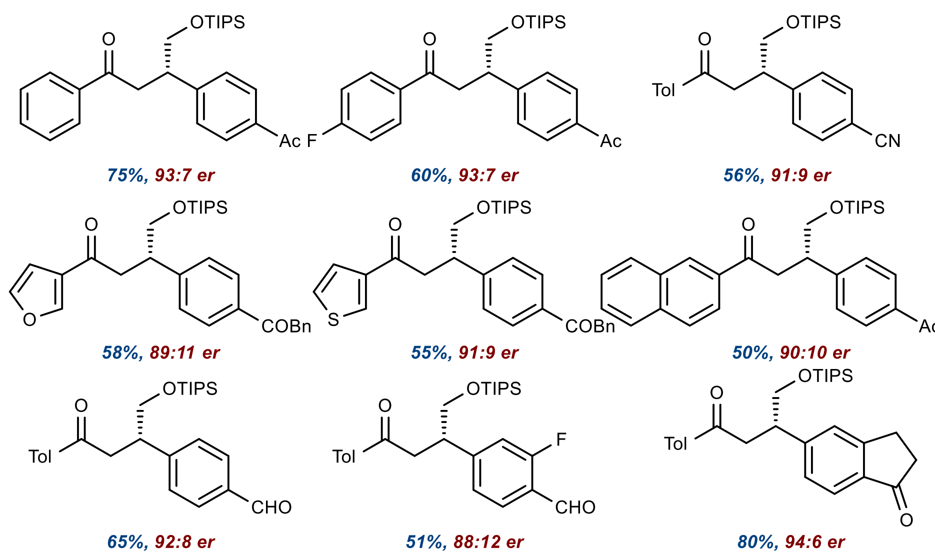
Zheng, P.; Zhou, P.; Wang, D.; Xu, W.; Wang, H.; Xu, T. *Nat. Commun.* **2021,** *12*, 1646.
https://doi.org/10.1038/s41467-021-21947-1

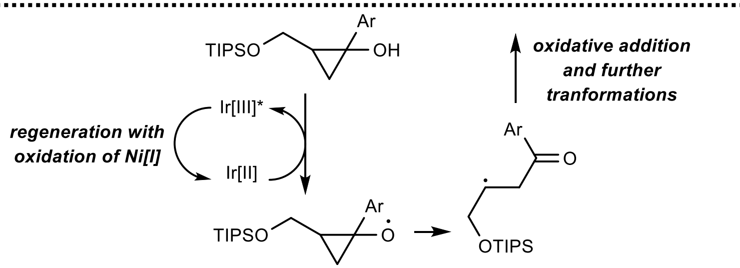
Asymmetric Nickel Catalysis

The SARLAH Group

β-Arylation of Cyclopropanols (Li, 2022)

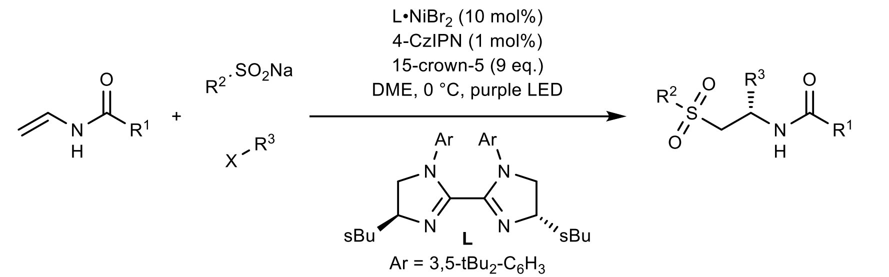


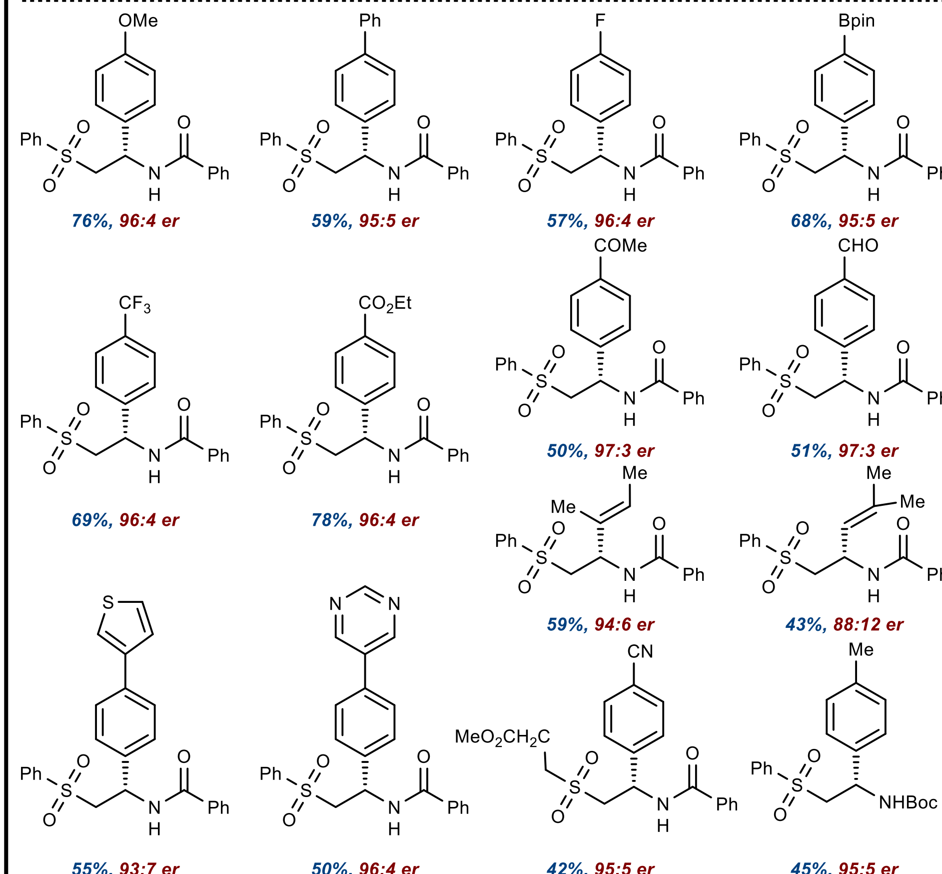




Wang, J.; Li, X. *Chem. Sci.* **2022,** *13*, 3020. https://doi.org/10.1039/D1SC07237D

Carbosulfonylation of Alkenes (Nevado, 2023)



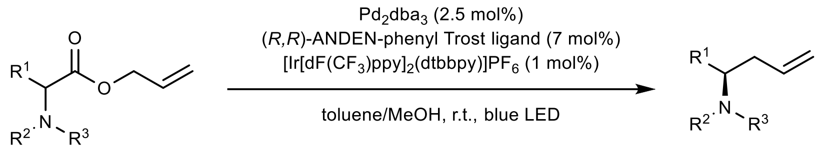


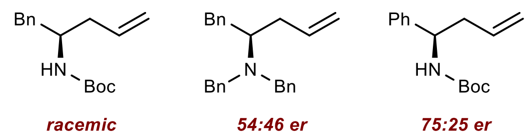
Du, X.; Cheng-Sánchez, I.; Nevado, C. *J. Am. Chem. Soc.* **2023,** *145*, 12532.
https://doi.org/10.1021/jacs.3c00744

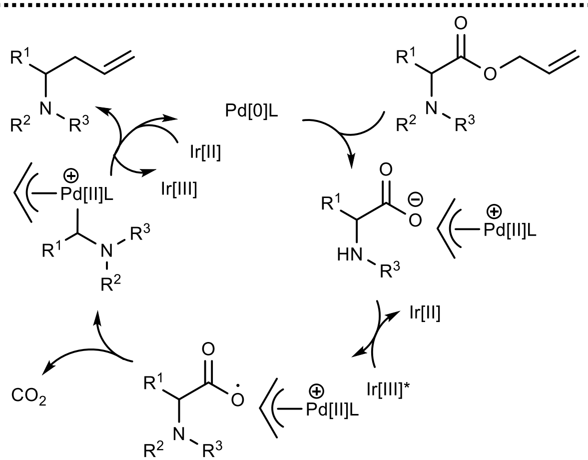
Asymmetric Palladium Catalysis

The SARLAH Group

Decarboxylative Allylation of AAs (Tunge, 2015)

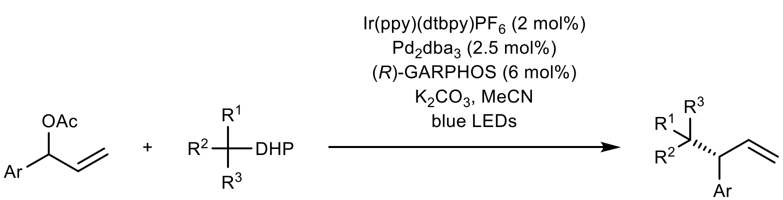




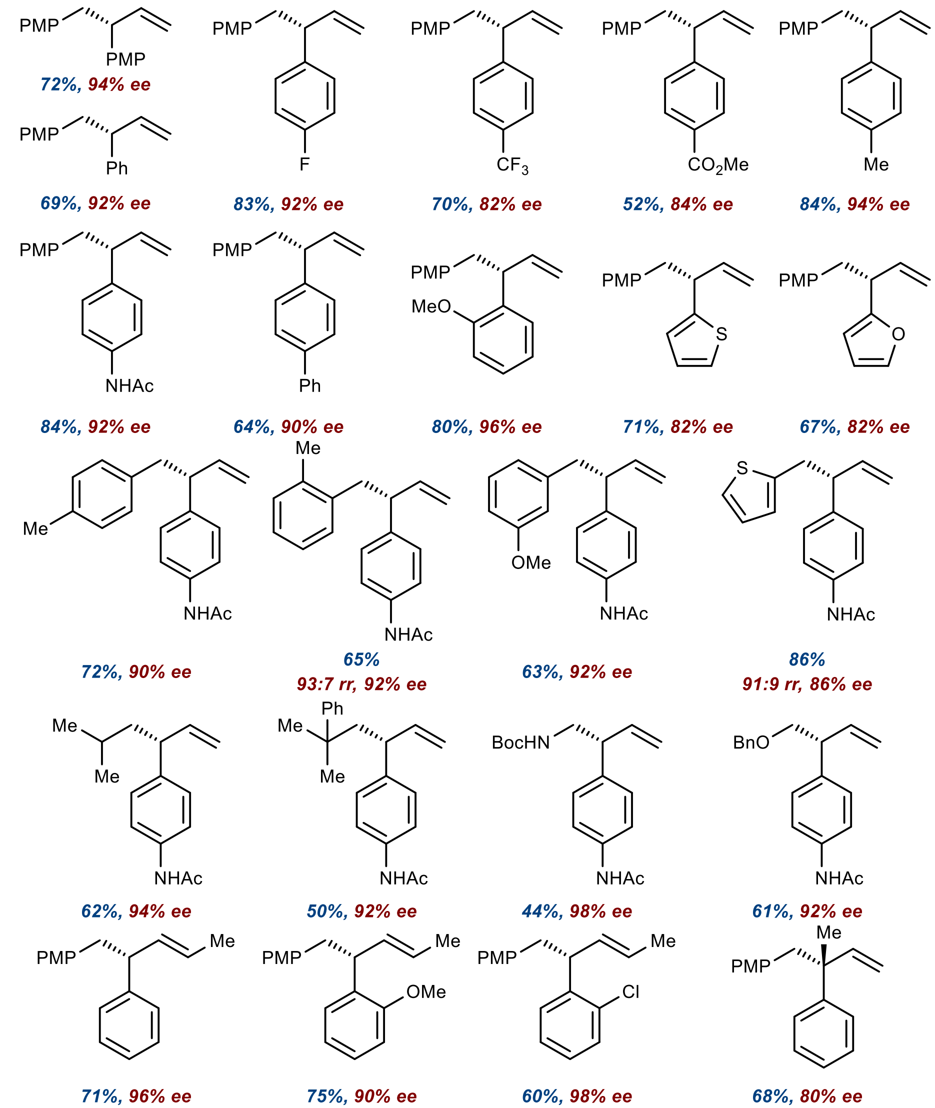


Lang, S. B.; O'Nele, K. M.; Douglas, J. T.; Tunge, J. A. *Chem. Eur. J.* **2015,** *21*, 18589.
https://doi.org/https://doi.org/10.1002/chem.201503644

Allylic & Benzylic Alkylation (Yu, 2018, 2020)



Zhang, H.-H.; Zhao, J.-J.; Yu, S. *J. Am. Chem. Soc.* **2018,** *140*, 16914.
https://doi.org/10.1021/jacs.8b10766

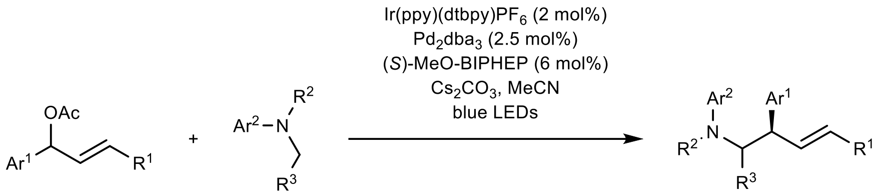


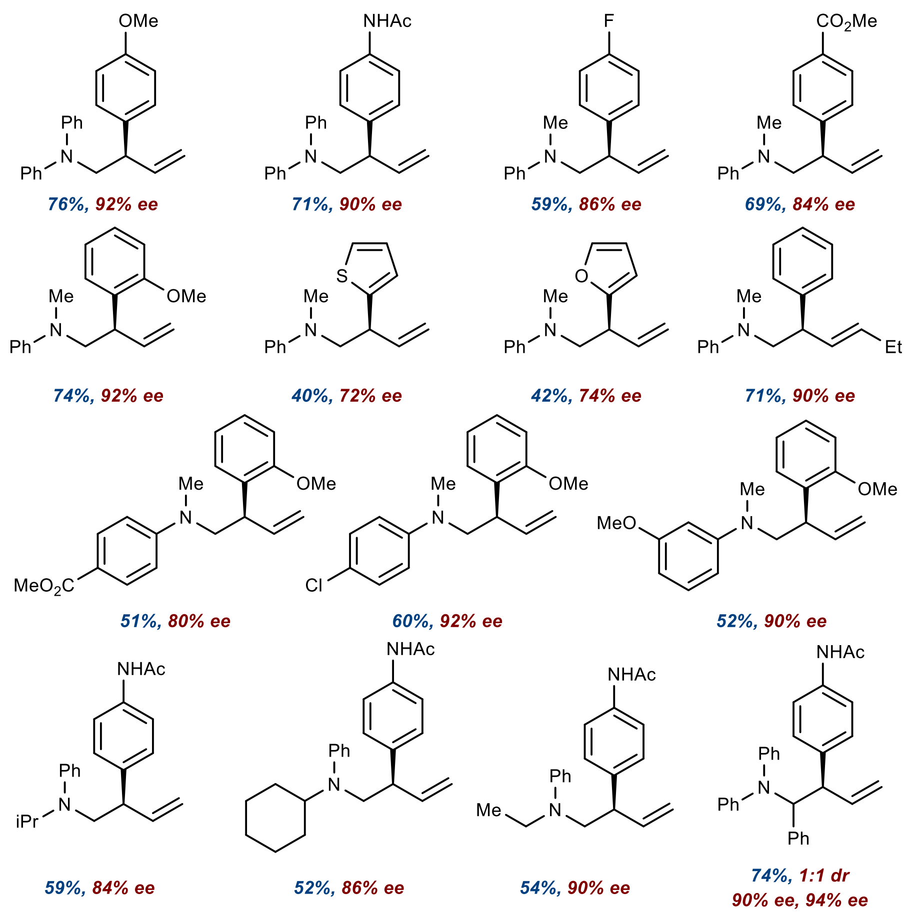
Similar works:
Shen, X.; Qian, L.; Yu, S. *Sci. China Chem.* **2020,** *63*, 687.
https://doi.org/10.1007/s11426-019-9732-5

Xue, S.; Limburg, B.; Ghorai, D.; Benet-Buchholz, J.; Kleij, A. W. *Org. Lett.* **2021,** *23*, 4447.
https://doi.org/10.1021/acs.orglett.1c01380

Asymmetric Palladium Catalysis

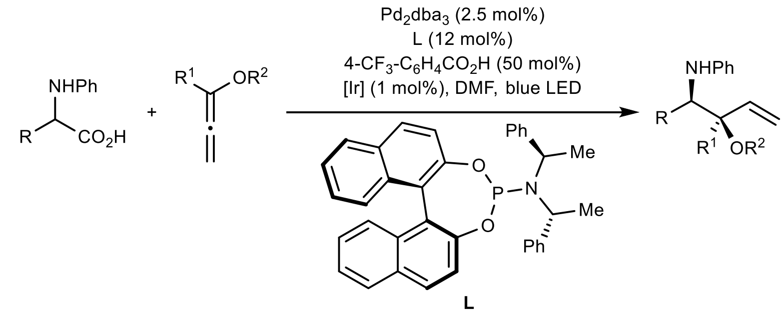
α-Allylation of Anilines (Yu, 2020)

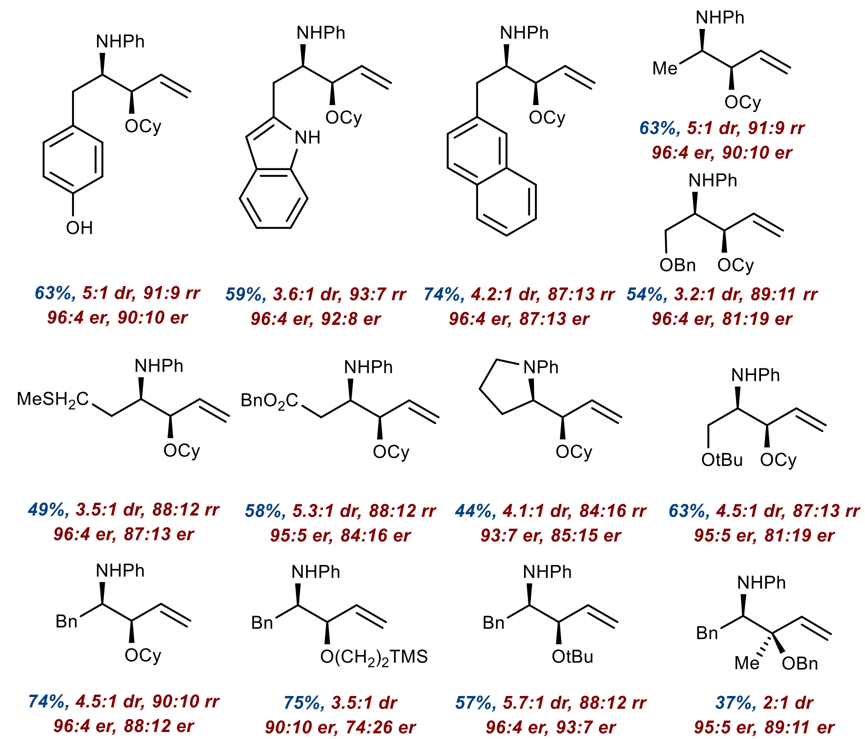




Zhang, H.-H.; Zhao, J.-J.; Yu, S. *ACS Catal.* **2020**, *10*, 4710.
https://doi.org/10.1021/acscatal.0c00871

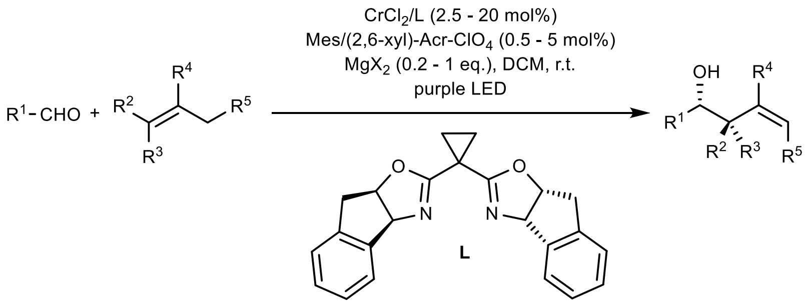
Hydroaminoalkylation of Allenes (Breit, 2021)

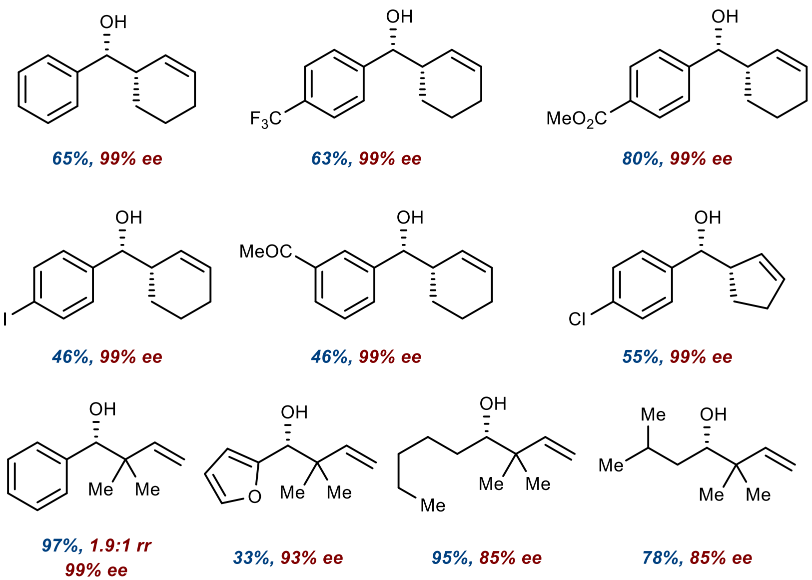


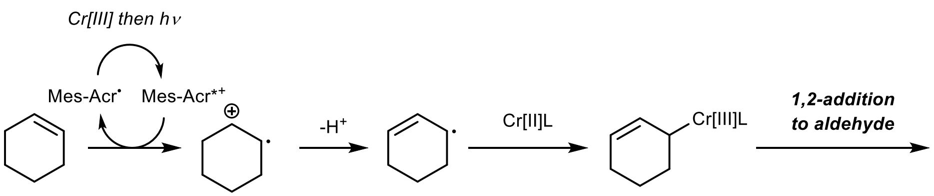


Zheng, J.; Nikbakht, A.; Breit, B. *ACS Catal.* **2021**, *11*, 3343.
https://doi.org/10.1021/acscatal.1c00153

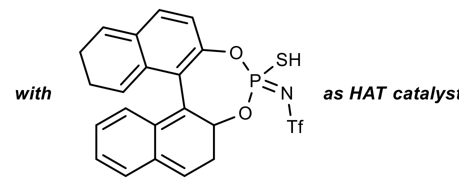
Allylic C(sp³)–H Functionalization (Kanai, 2019, 2020)

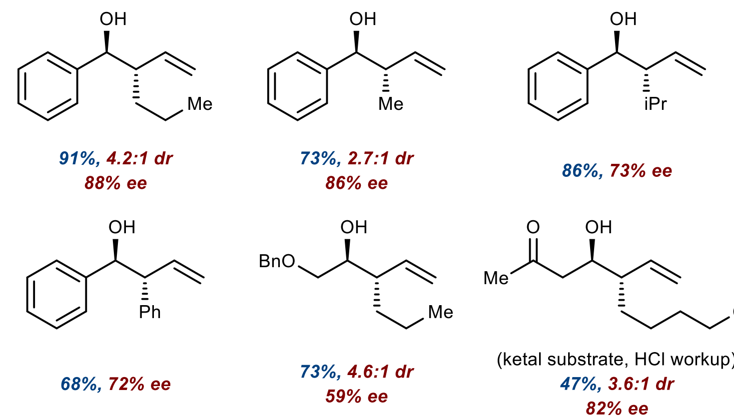






Mitsunuma, H.; Tanabe, S.; Fuse, H.; Ohkubo, K.; Kanai, M. *Chem. Sci.* **2019,** *10*, 3459. https://doi.org/10.1039/C8SC05677C





Tanabe, S.; Mitsunuma, H.; Kanai, M. *J. Am. Chem. Soc.* **2020,** *142*, 12374. https://doi.org/10.1021/jacs.0c04735

Similar works by Glorius group:

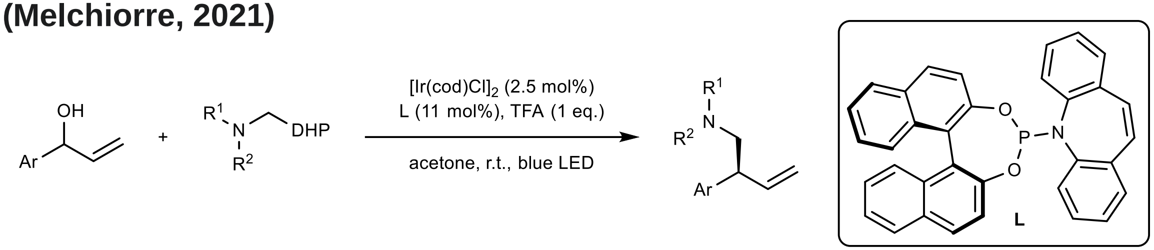
Allylbenzyl C(sp³)-H functionalization:

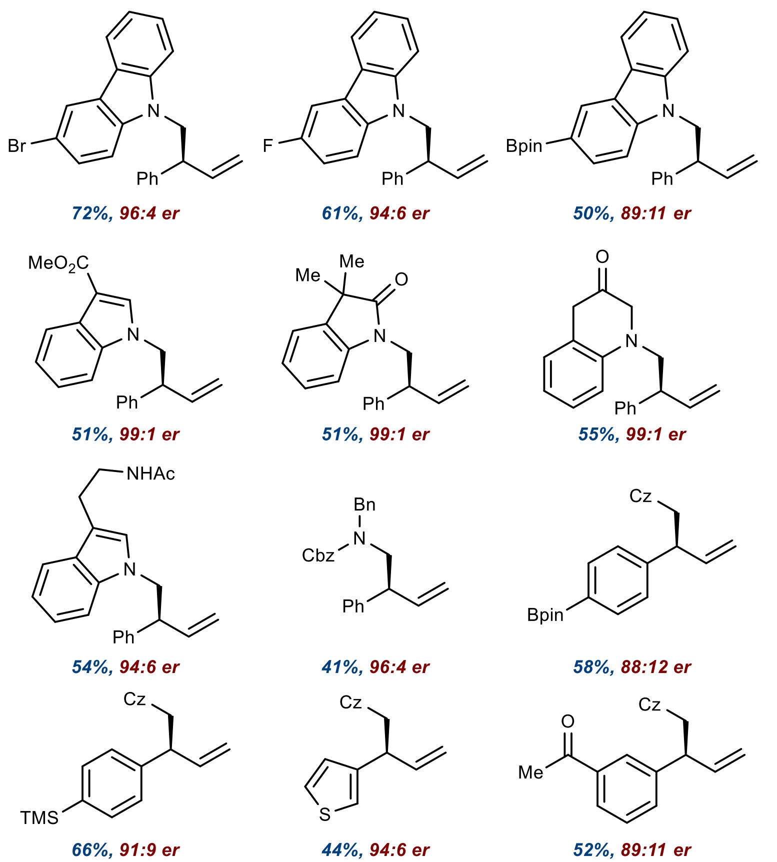
Schwarz, J. L.; Schäfers, F.; Tlahuext-Aca, A.; Lückemeier, L.; Glorius, F. *J. Am. Chem. Soc.* **2018,** *140*, 12705. https://doi.org/10.1021/jacs.8b08052

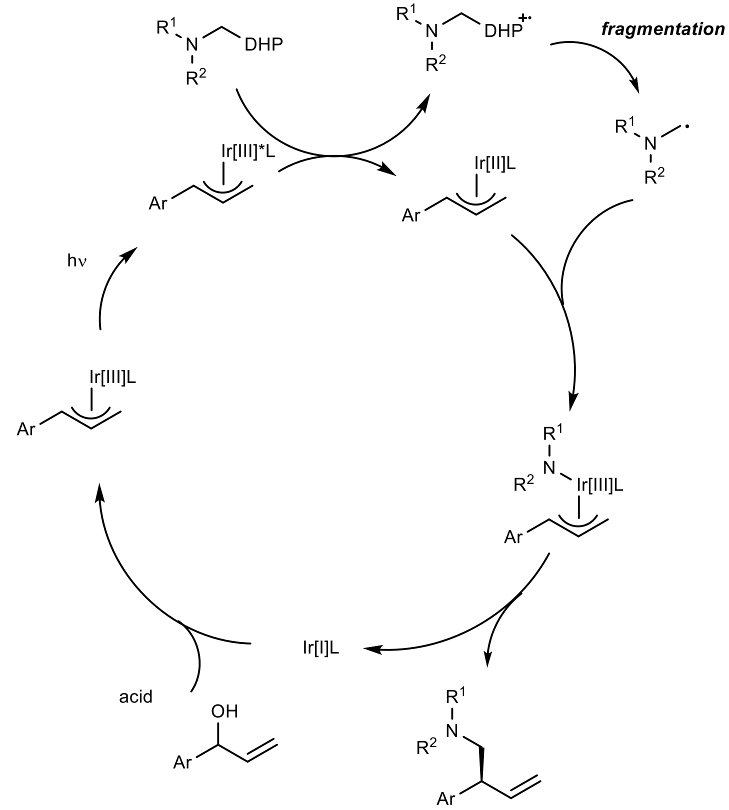
β-Silyl allylic C(sp³)-H functionalization:

Schäfers, F.; Dutta, S.; Kleinmans, R.; Mück-Lichtenfeld, C.; Glorius, F. *ACS Catal.* **2022,** *12*, 12281. https://doi.org/10.1021/acscatal.2c03960

Allylic Aminoalkylation (Melchiorre, 2021)







Crisenza, G. E. M.; Faraone, A.; Gandolfo, E.; Mazzarella, D.; Melchiorre, P. *Nat. Chem.* **2021,** *13*, 575. https://doi.org/10.1038/s41557-021-00683-5