

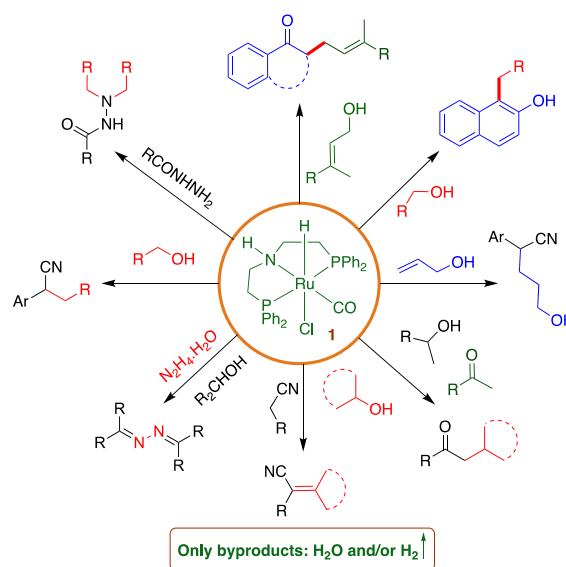
# Sustainable Catalysis Enabled by Metal-Ligand Cooperation

Chidambaram Gunanathan\*

School of Chemical Sciences, National Institute of Science Education and Research, An OCC of Homi Bhabha National Institute, Bhubaneswar-752 050, India

e-mail: [gunanathan@niser.ac.in](mailto:gunanathan@niser.ac.in)

Construction of C-C and C-N bonds are important reactions in organic synthesis. Catalytic alkylation using alcohol as an alkylation reagent is a green alternative to the conventional alkylation reactions involving alkyl halides and stoichiometric reagents. Employing Ru-macho pincer catalyst which operates via amine-amide metal-ligand cooperation, simple and atom-economical direct alkylation of nitriles was attained. We have also discovered the catalytic cross-coupling of secondary alcohols.  $\alpha$ -Alkylation and  $\alpha$ -prenylation of ketones using secondary alcohols and prenyl, respectively, were reported.  $\alpha$ -Alkylation of  $\beta$ -naphthols using primary alcohols was reported recently. Catalytic formal conjugate addition of nitriles with allylic alcohols was developed. Using secondary alcohols,  $\alpha$ -alkenylation of nitriles and synthesis of ketazine were also reported. Remarkably, water and liberated molecular hydrogen are the only byproducts in these reactions making these catalytic transformations environmentally benign.



Scheme 1. Green catalysis by Ru-MACHO catalyst.

## References

1. Thiyagarajan, S.; Gunanathan, C. *ACS Catal.* **2017**, *7*, 5483-5490.
2. Thiyagarajan, S.; Gunanathan, C. *ACS Catal.* **2018**, *8*, 2473-2478.
3. Kishore, J.; Thiyagarajan, S.; Gunanathan, C. *Chem. Commun.* **2019**, *55*, 4542-4545.
4. Thiyagarajan, S.; Gunanathan, C. *J. Am. Chem. Soc.* **2019**, *141*, 3822-3827.
5. Thiyagarajan, S.; Gunanathan, C. *Org. Lett.* **2020**, *22*, 6617-6622.
6. Thiyagarajan, S.; Vijaya Sankar, R.; Gunanathan, C. *Org. Lett.* **2020**, *22*, 7879-7884.
7. Thiyagarajan, S.; Gunanathan, C. *Org. Lett.* **2019**, *21*, 9774-9778.
8. Thiyagarajan, S.; Vijaya Sankar, R.; Anjalikrishna, P. K.; Suresh, C. H.; Gunanathan, C. *ACS Catal.* **2022**, *12*, 2191-2204.
09. Vijaya Sankar, R.; Manikpuri, D.; Gunanathan, C. *Org. Biomol. Chem.* **2023**, *21*, 273-278
10. Kumar, N.; Sankar, R. V.; Gunanathan, C. *J. Org. Chem.* **2023**, *88*, 17155-17163.
11. Manikpuri, D.; Vijaya Sankar, R.; Gunanathan, C. *Chem. Asian J.* **2023**, e202300678.
12. Vijaya Sankar, R.; Mathew, A.; Pradhan, S; Kuniyil, R.; Gunanathan, C. *Chem. Eur. J.* **2023**, e202302102.