

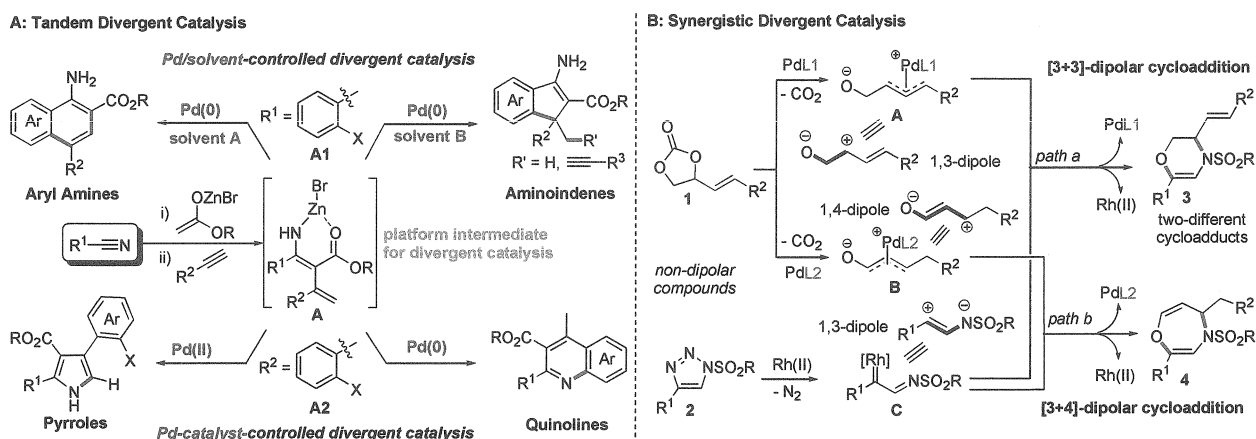
# Divergent Catalysis: Tandem and Synergistic Divergent Catalysis

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Divergent catalytic reactions provide quick access to structurally different compounds from a common precursor through controlled reaction pathways, and are highly attractive tools in the discovery of drugs and functional materials. A more promising, yet challenging strategy that remains largely unexplored is tandem divergent catalysis, which combines the key advantages inherent to both tandem reactions and divergent catalysis to provide a rapid access to different structures from the same simple reagents while minimizing the generation of waste. In the course of our studies on the tandem use of the Blaise reaction in catalysis,<sup>1</sup> we envisioned that the zinc bromide complex **A**, formed by the sequential reaction of nitriles with a Reformatsky reagent and 1-alkynes, may serve as a viable intermediate for divergent catalysis involving selective C-C and C-N bond-forming reactions. The reaction pathway of the intermediate is precisely controlled by the choice of the reaction solvent or the palladium catalyst to quickly form four distinct compound classes—arylamines, aminoindenes, pyrroles, and quinolines—from simple nitriles (Scheme 1A).<sup>2</sup> Quite recently, we also developed a synergistic Pd/Rh dual divergent catalysis that allow divergent [3+3]- and [3+4]-dipolar cycloaddition between common non-dipolar vinyl carbonates and 1-sulfonyl-1,2,3-triazoles to yield oxazines and oxazepins selectively (Scheme 1B).<sup>3</sup>



Scheme 1. (A) Tandem divergent catalysis and (B) Synergistic Divergent Catalysis

## References

1. Kim, J. H.; Ko, Y. O.; Bouffard, J.; Lee, S.-g. *Chem. Soc. Rev.* **2015**, ASAP (DOI:10.1039/c4cs00430b)
2. (a) Kim, J. H.; Bouffard, J.; Lee, S.-g. *Angew. Chem. Int. Ed.* **2014**, *53*, 6435. (b) Kim, J. H.; Choi, S. Y.; Bouffard, J. Lee, S.-g. *J. Org. Chem.* **2014**, *79*, 7253.
3. Manuscript in preparation.