

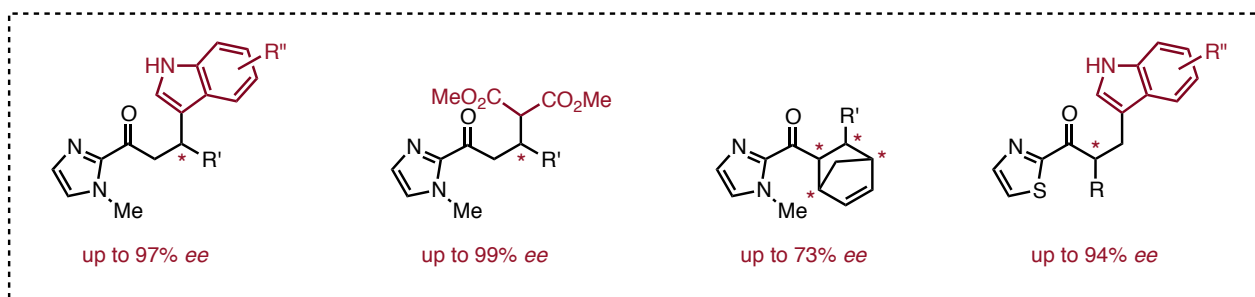
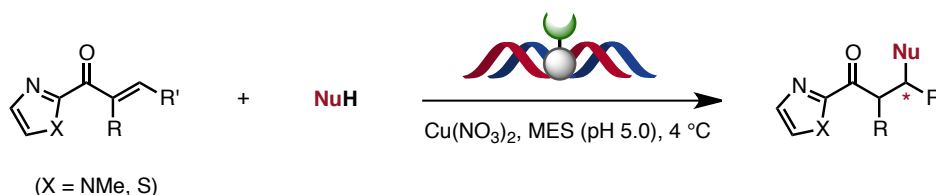
A new benchmark in DNA-based asymmetric catalysis

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The widespread demand for chiral compounds has risen drastically in recent years resulting in the development of new enantioselective catalytic tools. Since the pioneering work of Roelfes and Feringa,^[1] DNA-based hybrid catalysis has emerged as a valuable alternative to standard asymmetric catalysis as it offers high levels of selectivity along with environmentally friendly conditions by simply taking advantage of the chirality inherent to the helical structure of DNA.^[2] By analogy with hybrid metalloenzymes, DNA-based asymmetric catalysts incorporate a metal complex anchored in a covalent, dative, or non-covalent yet kinetically stable fashion to DNA. In this context, we recently developed a highly selective DNA/RNA-hybrid catalyst based on a covalent anchorage strategy, which offers unprecedented levels of selectivity on a broad range of reactions including a particularly challenging protonation following a Friedel-Crafts alkylation (up to 94% ee).^[3] This face selectivity observed during the protonation step is all the more remarkable that the transient highly reactive enolate is generated in water. Moreover, by simply tuning the ligand bound to the DNA, we were able to reliably reverse the selectivity and thus access both enantiomers.



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[3] A. García-Fernández, R. P. Megens, L. Villarino, G. Roelfes, *J. Am. Chem. Soc.* **2016**, *138*, 16308-16314.