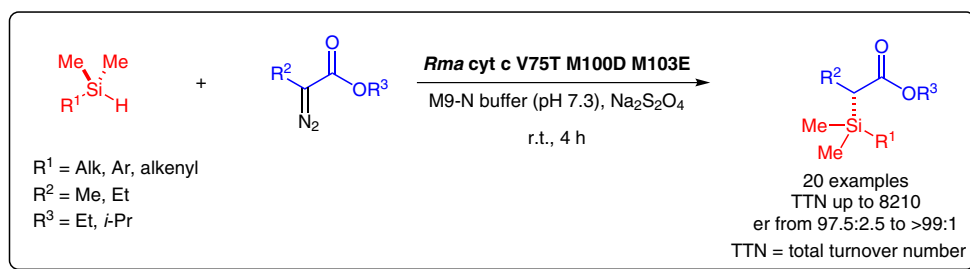
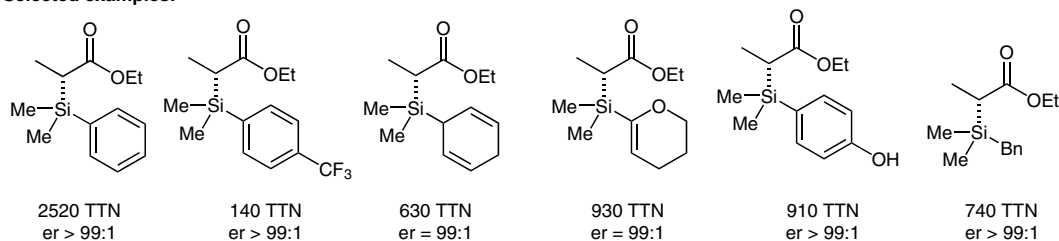


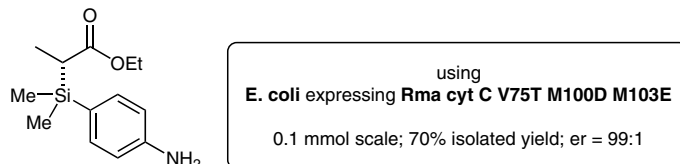
Asymmetric Enzymatic Carbon–Silicon Bond Formation



Selected examples:



Application to *in vivo* synthesis:



Significance: The insertion of carbenes into silicon–hydrogen bonds under physiological conditions is reported by the Arnold group. Three selective modifications of the active site of cytochrome c from *Rhodothermus marinus* resulted in a highly active catalyst (*Rma cyt c*, V75T M100D M103E) that gave the desired products with remarkable total turnover numbers (≤ 8210) and enantioselectivities (er > 97.5:2.5). The transformation was performed *in vivo* on a preparative scale by using *Escherichia coli* expressing the mutant enzyme.

Comment: Despite the high abundance of carbon and silicon, no known lifeform can form a bond between these two elements. The authors impressively showed that just three modifications of the wild-type enzyme can force nature to create this unusual bond with extraordinary efficiency. Interestingly, no cyclopropanation, cyclopropanation or insertion into O–H or N–H bonds occurs when the required functional groups are present. The system achieved a 15-fold higher activity and chemoselectivity than the best synthetic catalysts.