

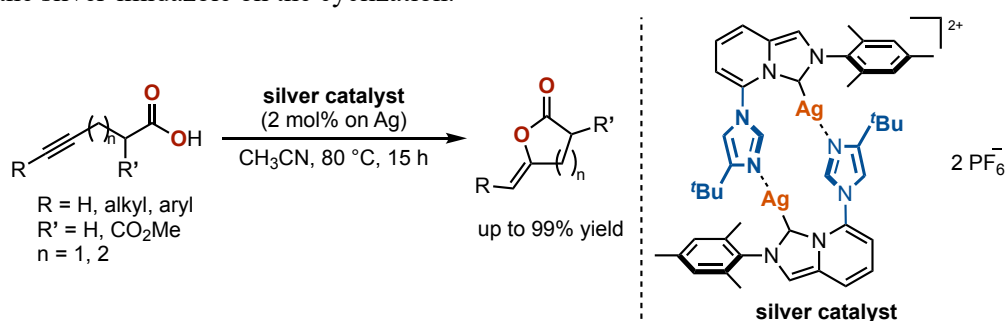
Cyclization of Alkyne-Tethered Carboxylic Acid with Silver Complexes Bearing Imidazo[1,5-*a*]pyridine-3-ylidene Ligand as an Acid-Base Cooperative Catalyst

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Imidazo[1,5-*a*]pyridine-3-ylidene¹ is an attractive *N*-heterocyclic carbene (NHC) ligand in terms of their rigidity and tunability, since a substituent at the C5 position of the ligand impacts on the environment around the NHC-bound metal center. A various kind of transition metal catalysts has been developed by utilizing imidazo[1,5-*a*]pyridine-3-ylidene bearing sterically bulky aromatic rings, coordinative substituents, and chiral auxiliaries at the C5 position.² Thus, we envisioned that imidazo[1,5-*a*]pyridine-3-ylidene could be applicable to acid-base cooperative catalysis by locating a Lewis acidic transition metal center and a basic functional group at the C3 carbene carbon and the C5 position, respectively.

We prepared dinuclear cationic silver(I) complexes with novel imidazo[1,5-*a*]pyridine-3-ylidene ligand including 4-(*tert*-butyl)-1*H*-imidazol-1-yl group at the C5 position. Single crystal XRD analysis revealed the detail structure of silver(I) complex, in which imidazole ring was located in the vicinity of the silver metal. These silver complexes served as the efficient catalysts for the cyclization of alkyne-tethered carboxylic acids to afford (*Z*)-alkylidene lactones. NMR experiments indicated that dinuclear silver(I) complexes dissociated to mononuclear complexes in acetonitrile in the presence of carboxylic acid, and DFT calculation supported the acid-base cooperative action of the silver-imidazole on the cyclization.



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