Dearomatising amination protocols triggered by electrophilic nitrogen sources enable the conversion of easily prepared planar molecules to synthetically desirable 3D-scaffolds. Despite the usefulness of these transformations there are few examples in the literature of these kind of processes.

We have developed a simple protocol for intramolecular C-N bond forming dearomatisation which affords unprotected nitrogen ring systems [1]. The approach builds upon the work of Falck and co-workers who developed intramolecular aryl C-H amination processes triggered by Rh-nitrenoids, generated from activated hydroxylamines [2]. Whilst adopting this approach to C-N bond forming dearomatisations, we found that hydroxylammonium intermediates of this kind are sufficiently reactive for C-N bond formation to occur effectively in the absence of a rhodium catalyst. Upon treatment with acid, Boc-deprotection occurs to generate a potent electrophilic aminating agent which reacts with pendant arenes in a $S_{E2}$-Ar-like process to generate the dearomatized or aryl C-H amination product. The application of hydroxylamine derived intermediates can be further expanded to reactions with alkenes. Here, the key electrophilic intermediate promotes stereospecific aziridination of pendant alkenes to generate bicyclic aziridine structures in a process resembling an aza-variant of the $m$-CPBA promoted Prilezhayev reaction. [3] Recently we have extended this methodology to intermolecular aziridinations.

---

