Photoinduced Assembly of C-N Bonds

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Nitrogen-containing compounds are a privileged class of molecules, which have applications in medicines, agrochemicals, dyes and materials. This relevance makes the construction of C–N bonds an extremely active area of research.

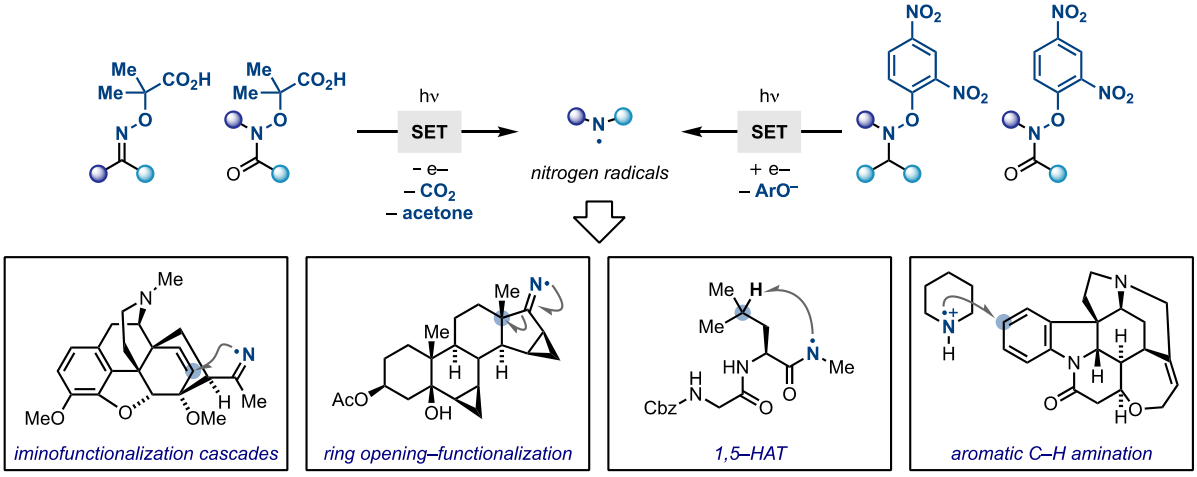
Nitrogen-radicals are versatile synthetic intermediates that can engage in a broad range of chemical reactions.[1] However, the difficulties associated with their generation have somewhat thwarted their use in synthetic chemistry.

Development of Photoinduced Radical-Transposition Reactions

We have developed a class of easy-to-make oximes and hyroxy-amides that upon photoredox oxidation enable access to iminyl and amidyl radicals.[2,3] These species have been used in radical transposition reactions for the site-selective functionalization of unactivated sp^3-carbons. These strategies have been applied to the deconstruction–functionalization of complex steroids (radical ring-opening)[2] and to the preparation of unnatural aminoacids (1,5-HAT).[3]

Development of Photoinduced Aromatic C–H Amination Reactions

Aminated aromatics are a widespread motif in high-value products. In general, these structures are assembled by Pd or Cu-catalysed cross-couplings between aryl halides/organoboron and amines. We have developed an umpolung approach where electrophilic amidyl and aminyl radicals are generated by photoredox reduction of electron poor *N*-aryloxy-amides and -amines.[4,5] These radical species undergo highly selective addition to a broad range of electron rich aromatics thus enabling direct C–H amination.



References

1. Review: S. Z. Zard *Chem. Soc. Rev.* **2008**, *37*, 1603.
2. *Angew. Chem. Int. Ed.* **2018**, *57*, 744.
3. *Angew. Chem. Int. Ed.* **2018**, *57*, 12495.
4. *J. Am. Chem. Soc.* **2016**, *138*, 8092.
5. *Angew. Chem. Int. Ed.* **2017**, *56*, 14948.