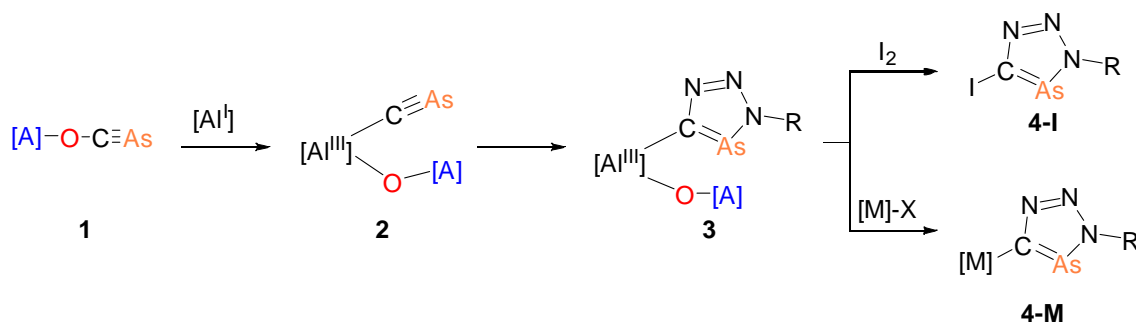


# SYNTHESIS OF CYARSIDE (-C≡AS) BY SELECTIVE OXIDATIVE ADDITION AND ITS REACTIVITY TO FORM HETEROCYCLES

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The synthesis of arsaalkynes ( $R-C\equiv As$ ) remains challenging due to the inherent reactivity of the  $C\equiv As$  triple bond [1]. Consequently, only a limited number of isolable compounds have been reported to date, typically synthesized through laborious and low-yielding processes. [2–4] Here we demonstrate that the selective oxidative addition of the C–O bond of an activated arsaethynolate anion ( $AsCO^-$ ) **1** is a viable approach for accessing the cyarside functional group **2** (which is valence isoelectronic with nitriles). This strategy generates reactive  $C\equiv As$  triple bonds that undergo intermolecular cyclization reactions to afford novel arsenic-containing heterocycles **3** [5]. These products can be further functionalized **4**, highlighting the synthetic potential of this approach for accessing previously inaccessible arsenic-containing molecules.



- [1] J.-C. Guillemin, L. Lassalle, P. Drean, G. Wlodarczak, J. Demaison, Synthesis and Spectroscopic Characterization of Ethylidynearsine. *Journal of the American Chemical Society* **116**, 8930–8936 (1994).
- [2] G. Märkl, H. Sejpka, 2-(2,4,6-Tri-*tert*-butylphenyl)-1-arsaethyne—the First Compound Containing an Arsenic–Carbon Triple Bond. *Angewandte Chemie International Edition in English* **25**, 264–264 (1986).
- [3] M. Finze, E. Bernhardt, H. Willner, C. W. Lehmann,  $[(CF_3)_3BCP]^-$  and  $[(CF_3)_3BCAs]^-$ : Thermally Stable Phosphaethynyl and Arsaethynyl Complexes. *Angewandte Chemie International Edition* **43**, 4160–4163 (2004).
- [4] C. J. Hoerger *et al.*, Cyarside ( $CAs^-$ ) and 1,3-Diarsaallendiide ( $AsCAs_2^-$ ) Ligands Coordinated to Uranium and Generated via Activation of the Arsaethynolate Ligand ( $O-CAs^-$ ). *Angewandte Chemie International Edition* **58**, 1679–1683 (2019).
- [5] G. Pfeifer *et al.*, Clicking the Arsenic–Carbon Triple Bond: An Entry into a New Class of Arsenic Heterocycles. *Angewandte Chemie International Edition* **55**, 11760–11764 (2016).