

Ph.D. Open Seminar

Title of Thesis: "Total Syntheses of 3a,3a'-Bis-Pyrrolo[2,3-b]indoline Alkaloids via the Development of Catalytic Deacylative Alkylations (DaA)"

Speaker: Mr. Nivesh Kumar

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Time: 4:00 PM

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Venue: AB2-401

Abstract

The presence of all-carbon quaternary stereocenters invariably increases the difficulty of a chemical synthesis in the target molecule.¹ Due to the steric congestion imposed by the four attached carbons, a very limited number of reports on C-C bond-forming reactions that reliably assemble quaternary carbons, are known in literature.¹ Therefore, synthesis of molecules with an all-carbon quaternary center puts forward a great synthetic challenge.² The challenge is aggravated even further when two all-carbon quaternary stereocenters are contiguous. Typically, one of the ways to solve this problem is typically by installing the quaternary stereocenters sequentially.³ Towards this architecturally complex biologically relevance C₂-symmetric indole alkaloids possessing contiguous stereogenic quaternary carbons [e.g. folicanthine (1), chimonanthine (2), and calycanthine (3)] drew our interest (Figure 1).²⁻³

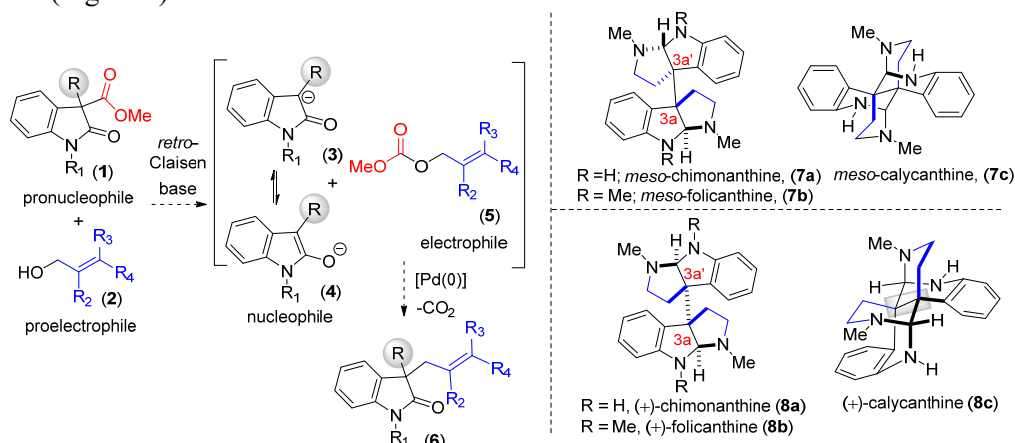


Figure 1. Indole alkaloids sharing vicinal all-carbon quaternary stereocenters.

During my Ph.D. programme, I undertook synthetic approaches to the cyclotryptamine alkaloids having hexacyclic 3a,3a'-bis-pyrrolo[2,3-b]indoline ring from 2-oxindoles (Figure 1). Towards this, I have been engaged in developing Pd(0)-catalyzed highly efficient synthesis of 2-oxindoles with C3-quaternary centers,⁴ which goes through via *retro*-Claisen activation.^{5a} Gratifyingly, this method has been extended for the synthesis of dimeric 2-oxindoles sharing vicinal all-carbon quaternary stereocenters.^{5b} Finally, I have also developed a direct formation of pyrrolo[2,3-b]indoline ring from tryptamine derivative through Pd(0)-catalyzed deacylative alkylations.⁶

References and Notes:

- (a) C. J. Douglas, L. E. Overman, *Proc. Natl. Acad. Sci. U.S.A.* 2004, **101**, 5363. (b) B. N. Kakde, N. Kumar, P. K. Mondal, A. Bisai *Org. Lett.* 2016, **18**, 1752.
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- (a) L. E. Overman, D. V. Paone, B. A. Sterns, *J. Am. Chem. Soc.* 1999, **121**, 7702. (b) S. Ghosh, S. Bhunia, B. N. Kakde, S. De, A. Bisai *Chem. Commun.* 2014, **50**, 2434.
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- N. Kumar, V. R. Gavit, A. Maity, A. Bisai *Manuscript under preparation*.