



CATALYTIC APPROACH TOWARD HIGHLY FUNCTIONALIZED QUATERNARY STEREOCENTERS

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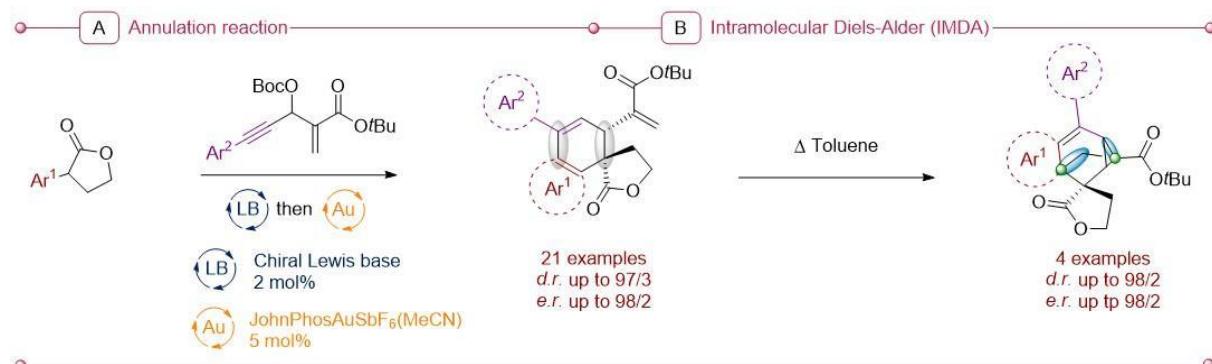
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Merging organo- and gold-catalysis by sequential catalysis is a highly valuable approach for the synthesis of chiral complex molecules.¹ We will disclose a route to functionalized chiral heteroatomic polycyclic compounds leveraging these two unfriendly catalytic cycles in a one-pot sequential process. α -Heteroaromatic- γ -butyrolactones have been engaged in a highly stereoselective Lewis base asymmetric allylic alkylation with alkyne functionalized Morita-Baylis-Hillman (MBH) carbonates. Gratefully to the low Lewis base catalyst loading, subsequent gold catalyzed Friedel-Crafts alkylation, entailing the formation of fused polycyclic compounds, can proceed efficiently leading to structurally complex products in high enantiomeric ratio (Scheme 1.A).

These chiral polycyclic skeleton enable the Intramolecular Diels-Alder (IMDA), which provides a straightforward approach towards interesting tricyclo[3.2.1.0^{2,7}]octene² scaffolds containing five stereocenters, including two quaternary³ (Scheme 1 B).



Scheme 1.

References

- ¹a) H. Pellissier, *Tetrahedron*. **2013**, *69*, 7171-7210. b) A. Patwa, C. Pegu, B. Paroi, N.T. Patil, *Tetrahedron Letters*. **2025**, *154*, 155382. c) N.T. Patil, V. S. Shinde, B. Gajula, *Org. Biomol. Chem.*, **2012**, *10*, 211-224. d) C. Pegu, B. Paroi, N.T. Patil, *Chem. Eur. J.* **2024**, *60*, 3607-3623. e) C.C. J. Loh, J. Badorre, G. Raabe, D. Enders, *Chem. – Eur. J.*, **2011**, *17*, 13409-13414.
- ²a) A. G. Fallis, *Can. J. Chem.* **1983**, *62*, 183-234. b) S. N. Ng, C. M. Beaudry, D. Trauner, *Org. Lett.* **2003**, *5*, 1701-1704.
- ³Y. Liu, S.-J. Han, W.-B. Liu, B. M. Stoltz, *Acc. Chem. Res.* **2015**, *48*(3), 740-751.