CONSECUTIVE INTRAMOLECULAR DEHYDRO-DIELS-ALDER REACTIONS OF HETEROATOM-TETHERED TETRAYNES FOR THE SYNTHESIS OF HETEROLE-CONTAINING POLYCYCLIC COMPOUNDS

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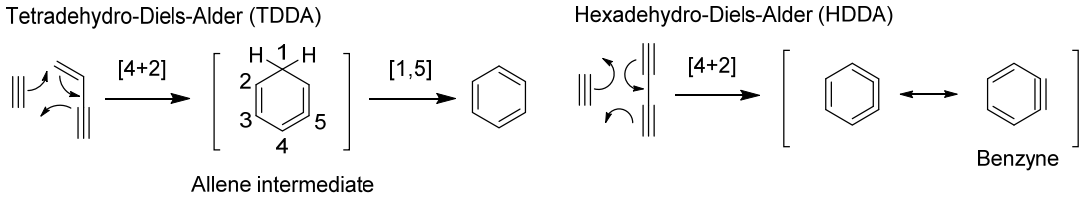
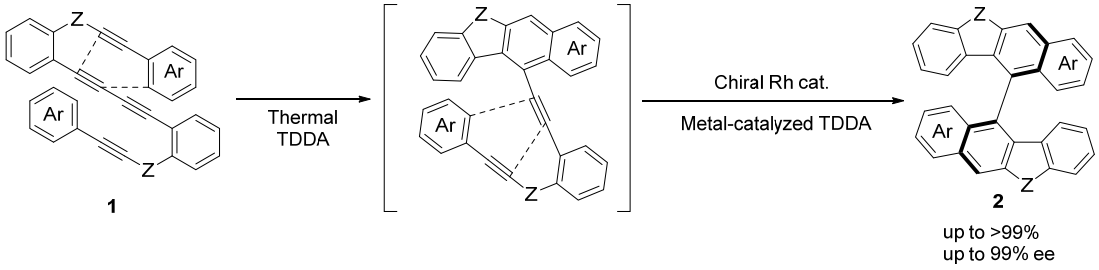
While Diels-Alder reaction is [4+2] cycloaddition of 1,3-dienes with alkenes, cycloaddition involving alkyne moieties is called dehydro-Diels-Alder reaction [1]. For example, tetradehydro-Diels-Alder (TDDA) reaction gives benzene rings via strained cyclic allene intermediates from 1,3-enynes with alkynes and hexadehydro-Diels-Alder (HDDA) reaction provides benzynes from 1,3-diynes with alkynes.



We examined the reaction of tetraynes 1 (Z =S) containing two phenylthio groups tethered by 1,3-diynemoiety as substrates and achieved the first example of enantioselective TDDA reaction to give axially chiral biaryl compounds. The consecutive thermal and Rh-catalyzed tetradehydro-Diels-Alder reactions gave cycloadducts 2 in high yields with excellent enantiomeric excesses [2].



We will also mention the reaction of silicon-tethered tetraynes 1 (Z =SiR_2), which underwent consecutive HDDA and TDDA reactions under thermal condition.

[1] W. Li, L. Zhou, J. Zhang, *Chem. Eur. J.* **2016**, 22, 1558.

[2] T. Shibata, A. Sekine, A. Mitake, K. S. Kanyiva, *Angew. Chem. Int. Ed.*, **2018**, *57*, 15862.