Zinc-Mediated Anionic Spiro Annulation for Expedient Synthesis of Spiro Conjugated Molecules

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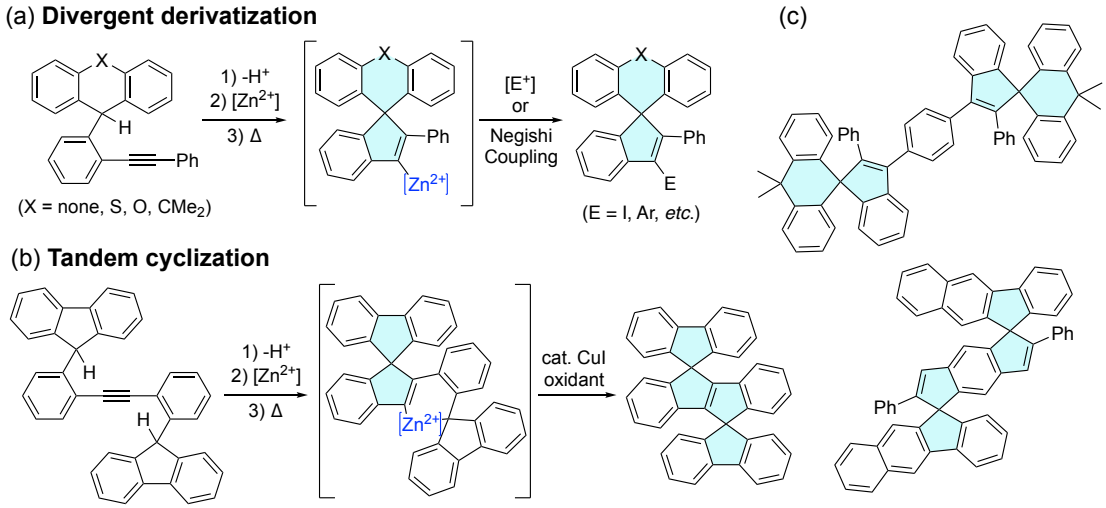
π -Conjugated molecules with spiro structures have attracted attention as organic optoelectronic materials due to their excellent processability and charge-optical properties.[1] However, conventional synthesis methods based on cationic cyclization encounter limitations in design flexibility and ease of derivatization.[2,3] We herein report the efficient synthesis of novel spiro-π molecules and one-pot derivatization initiated by a Zn-mediated anionic *5-endo-dig* spiro cyclization, that simultaneously generates spiro-π centers and organozinc species. This reaction is applicable to a variety of spiro units and allows one-pot derivatization using electrophile trapping or Negishi coupling. The combination of this cyclization with Cu(I)-catalyzed oxidative C-C bond formation afforded a double-cyclized compound. These reactions enable expedient access to a variety of functional materials, including the candidates of circularly polarized luminescence.



Figures. Zn-mediated anionic spiro cyclization for functional materials. (a) One-pot divergent derivatization. (b) Tandem cyclization with Zn-Cu system. (c) Example of compounds synthesized through the new methodology.

1) Saragi, T. P. I.; Spehr, T.; Siebert, A.; Fuhrmann-Lieker, T.; Salbeck, J. *Chem. Rev.* **2007**, *107*, 1011– 1055. 2) Li, Wang, *et.al., Chem. Mater.* **2015**, *27,* 1100−1109. 3) Chan, Wang, *et.al., ACS Appl. Mater. Interfaces* **2016**, *8, 24782−24792.*