1. Propose and explain a plausible mechanism for the following transformation reported by Glorius and co-workers. (*ACIE* **2010**, *49*, 9761–9764). [★]

The success of this transformation relies on two key steps. On one hand, the use of N-heterocyclic carbene catalyst results in the formation of the corresponding Breslow intermediate, allowing the reactivity umpolung of the electrophilic aldehyde moiety. On the other hand, the commonly employed aryne precursors developed by Kobayashi in 1983 promotes the in situ formation of the desired aryne counterpart.

2. In 2020, Wei and co-coworkers reported the following Pd-catalyzed transformation (*Org. Lett.* **2020**, *22*, 7470-7474). Identifying the product and propose a plausible mechanism. [★★]

In this oxidative annulation reaction, mechanistic studies revealed the formation of a 5-membered palladium intermediate through subsequent activations of the amino and the alpha-carbon of the sulfoximine starting material. Once more, Kobayashi's precursor serves to generate the involved arynes species. This later then inserts in the catalytic cycle to now form a 7-membered ring, which after reductive elimination affords the corresponding tricyclic dibenzothiazines. CuO works as an oxidant of palladium, re-forming the Pd(II) species and continuing with the catalytic cycle.

arvne precursor

3. Identifying the product and propose a plausible mechanism for the following transformation reported by Biju and coworkers (*Chem. Commun.* **2019**, *55*, 3004-3007). [★★]

4. Propose the structure of the product formed in this transformation reported by Sing and co-workers (*J. Org. Chem.* **2022**, 87, 7219-7228). Justify your answer with a plausible mechanism. [★★★]



5. In 2022, Arun and co-workers reported the following transformation (*J. Org. Chem.* **2021**, *23*, 6372-6376). Identifying the missing starting materials and propose a plausible mechanism. [★★]

