Brønsted Acid Catalyzed [4+2] cycloaddition towards 1,4-Naphtho- and 9,10-Anthraquinones

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The 1,4-naphthoquinone (1,4-NQ) and 9,10-anthraquinone (9,10-AQ) scaffold appear in various natural products.[1] They exhibit biological activity but have also recently been used in redox flow batteries.[2] While the functionalization of the quinoidal B-ring in 1,4-NQ is straightforward, the functionalization of the benzenoid A-ring is more difficult. Besides, many various *de novo* strategies like oxidative reactions,[3] Hauser-Kraus annulation[4] or [2+2+2] cycloadditions,[5] *ortho*-C-H functionalization were applied to substitute the C5 position with iodine,[6] hydroxyl,[7] or an alkenyl group.[8] For 9,10-AQ, the tetra aryl substitution can be readily accomplished.[9] Another approach with a long history for the synthesis of substituted 1,4-NQs and 9,10-AQs is the Diels-Alder-Reaction of benzoquinone and 1,4-NQ.[10] Here, we demonstrate that strong Brønsted acids catalyze simple Diels-Alder reactions of various *p*-benzoquinones with 1- or 1,4-substituted 1,3-butadienes. The products are functionalized further, thereby providing easy access to substituted 9,10-AQs and substituted acenes, like hexaphenylanthracene, which can be used as new materials.

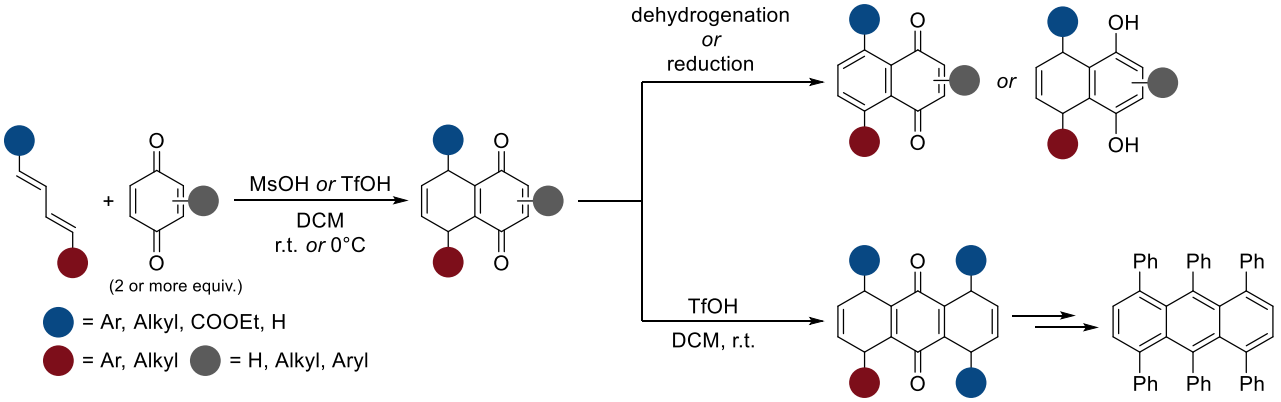

Figure 1. Brønsted acid catalyzed [4+2] cycloadditions of 1,3-butadienes and *p*-benzoquinones.

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