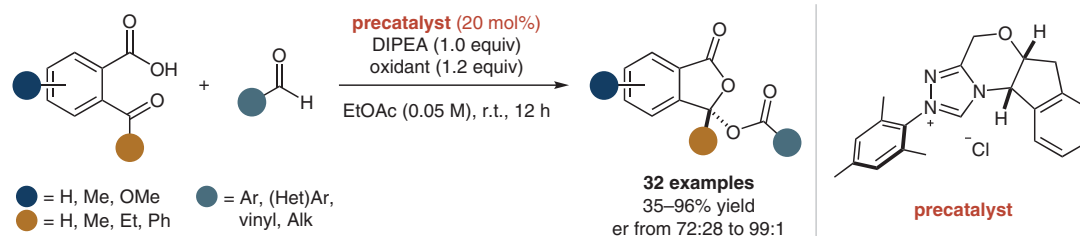
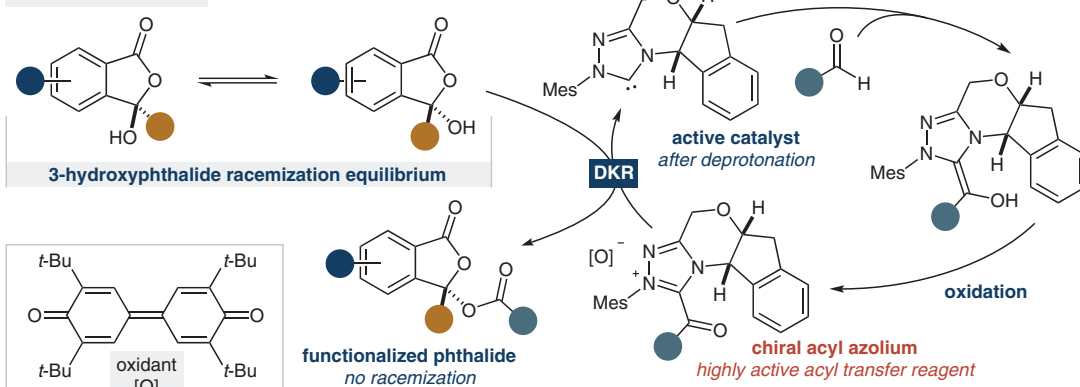
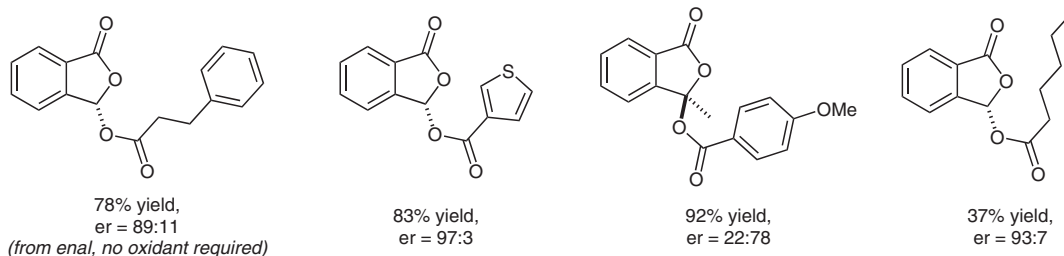


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Carbene-Catalyzed Dynamic Kinetic Resolution and Asymmetric Acylation of Hydroxyphthalides and Related Natural Products
Angew. Chem. Int. Ed. **2019**, DOI: 10.1002/anie.201912926.

Chiral Acyl Azolium Permits Dynamic Kinetic Resolution of Hydroxyphthalides

**Plausible mechanism:**

Selected examples:



Significance: The Chai and Chi groups report a practical method for the dynamic kinetic resolution of hydroxyphthalides by means of N-heterocyclic carbene catalyzed acylation. Acyl transfer from a chiral acyl azolium resulting from oxidation of a Breslow-type intermediate gives rise to functionalized hydroxyphthalides in moderate to excellent yields and with excellent enantioselectivities.

Comment: The authors recently disclosed an asymmetric synthesis of similar target compounds starting from phthalaldehydes and carboxylic acids (*Nature Commun.* **2019**, *10*, 1675). Building upon these results, this work now gives practical access to functionalized ketal-based phthalides and, in addition, permits the use of oxidant-free conditions through redox isomerization of the corresponding α,β -unsaturated aldehydes.

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Synfacts 2020, 16(03), 0338 Published online: 18.02.2020
DOI: 10.1055/s-0039-1690366; **Req-No.:** B00820SF