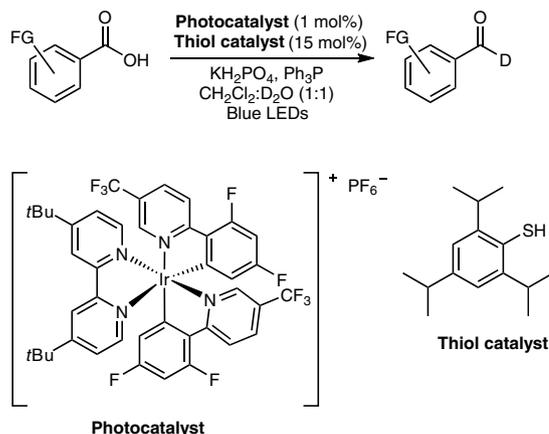


## PHOTOREDOX CATALYSIS

### Deoxygenative deuteration

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Reducing carboxylic acids to aldehydes is not easy. The main difficulty encountered is over-reduction: anything strong enough to reduce a carboxylic acid is likely also able to reduce the aldehyde product. As such, the corresponding alcohol is easier to produce, and access to the aldehyde is typically achieved by selective reoxidation of the fully reduced product. Perhaps the most promising direct routes from carboxylic acids to aldehydes come from the recently developed photoredox methods, in which an acyl radical is formed through deoxygenation of the acid, followed by hydrogen atom transfer to form the aldehyde.

Now Jin Xie and colleagues at Nanjing University, Qufu Normal University and the Shanghai Institute of Organic Chemistry have taken this one step further by using it as a route to form deuterated aldehydes. Interestingly they can employ  $\text{D}_2\text{O}$  as the deuterating reagent, making it more attractive with respect to handling and cost compared to  $\text{D}_2$  gas or metal deuterides. Due to the high bond dissociation energy of  $\text{D}_2\text{O}$  a hydrogen atom transfer catalyst is needed, and previously reported thiols prove capable in this regard.

The overall reaction scheme is similar to earlier photoredox strategies. The photoexcited iridium catalyst extracts an electron from triphenylphosphine, and the

resulting radical cation deoxygenates the carboxylic acid, leaving an acyl radical. This radical then abstracts deuterium from the thiol catalyst (which has reoxidized the photocatalyst and subsequently undergone deuterium–hydrogen exchange with the  $\text{D}_2\text{O}$ ). Regarding substrate scope, aromatic and heteroaromatic acids were converted with good yields, and reactive functional groups — including hydroxyl, amino and alkynyl — were tolerated. Aliphatic carboxylic acids were also converted, albeit in lower yields (presumably due to competing decarboxylation). For these cases  $\text{Ph}_2\text{POEt}$  proved superior to  $\text{Ph}_3\text{P}$ , and a slightly different catalyst system was employed. Overall the mild conditions, good functional group tolerance, high selectivity and high levels of deuterium incorporation make this a synthetically attractive method for both deoxygenation and deuteration in complex molecules. Based on the current work in this area, the synthetic versatility of the intermediates produced during photoredox catalysis seems certain to continue to expand well into the future.

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