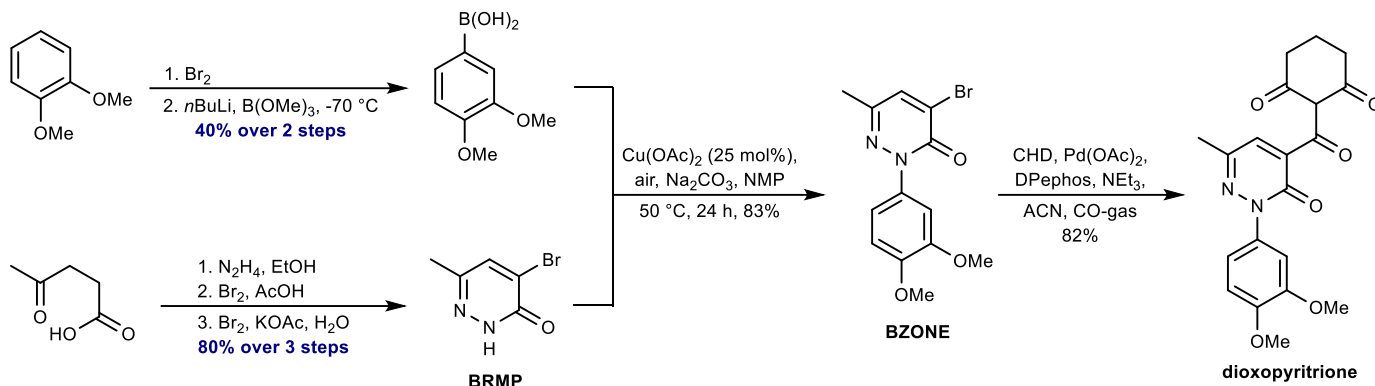
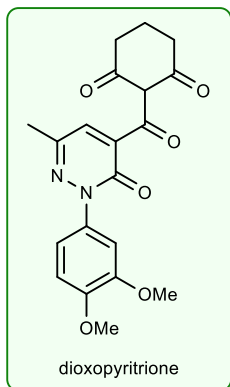
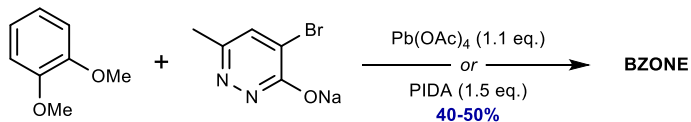


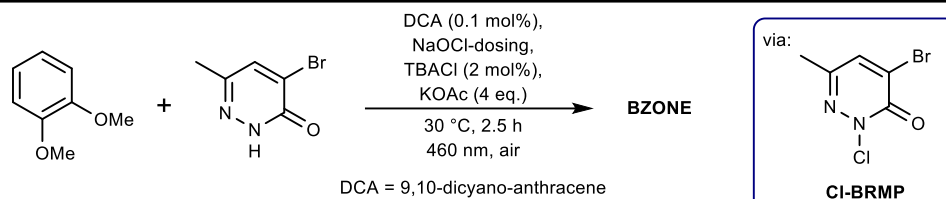
syngenta



- Herbicide candidate original route utilizes a Chan-Lam coupling of pyridazinone BRMP and boronic acid for formation of aryl-pyridazinone BZONE
 - High cost of boronic acid with only 40% yield due to intermediate stability issues
 - High levels of Cu-waste (11.5 kg/kg BZONE)
 - NMP used as solvent

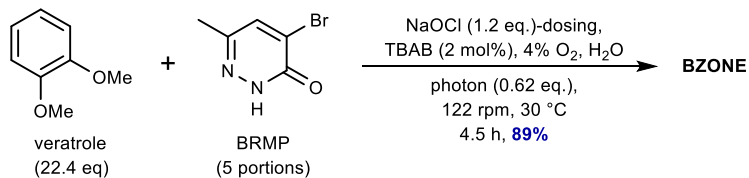


- Proof of concept oxidative coupling

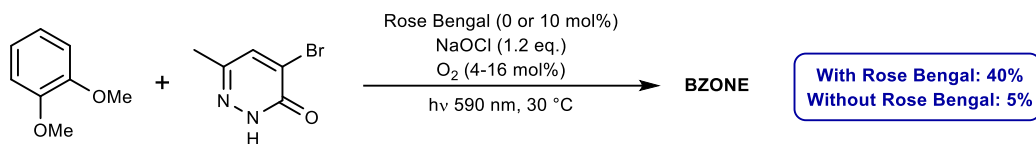


- No difference in conversion or yield when removing photocatalyst DCA

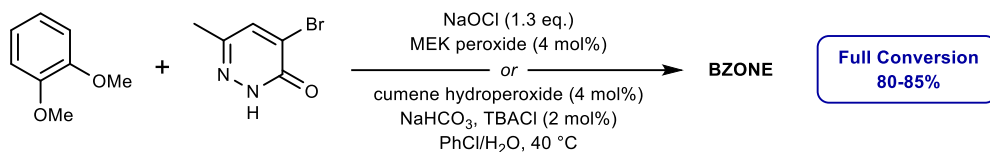
- **Process development and improvements of reaction conditions reveals the following:**



- Increased dosing time of NaOCl (12-15% aq., constant parallel dosing) to minimize accumulation of Cl-BRMP since has limited stability
- KOAc no longer necessary due to the liberation of stoichiometric amounts of hydroxide from reaction of BRMP with NaOCl
- Replace chlorobenzene with veratrole as solvent for 2- rather than 3-phase system
- Positive effect of oxygen in process with a lower limit of 4 mol%
- 2 mol% level of phase transfer catalyst TBAB used based on sourcing availability but shows identical reaction kinetics to TBACl
- Maintain a concentration of 12.3 wt% BZONE (theor. 100% yield)

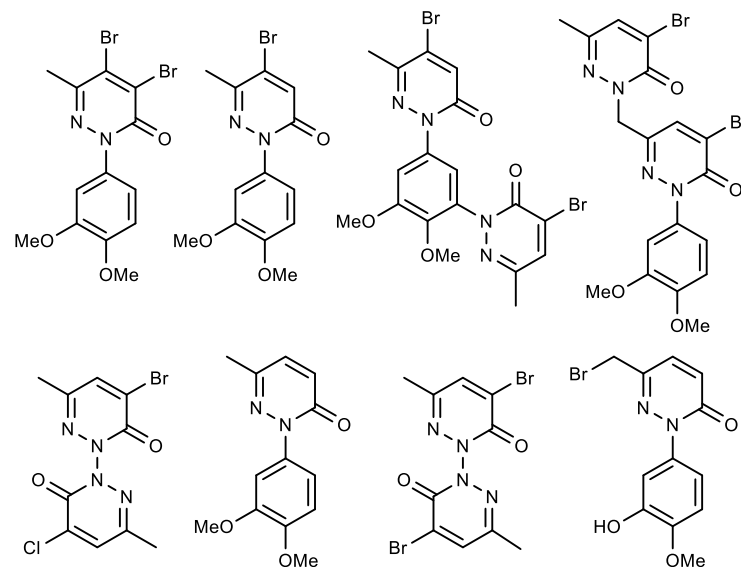


- Oxygen and light required to achieve high levels of conversion and yield suggests singlet oxygen inserts into C-H bonds with low BDE as confirmed by use of singlet oxygen photosensitizer Rose Bengal

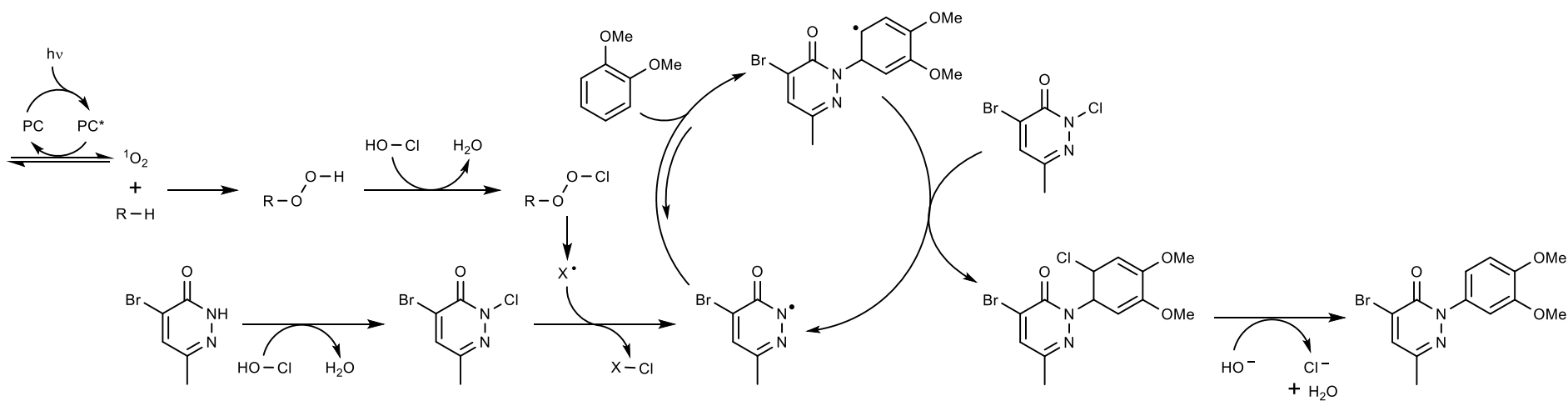


- Catalytic peroxides being involved in mechanism tested by use of MEK peroxide and cumene hydroperoxide in the absence of light which confirmed by having a very similar selectivity profile

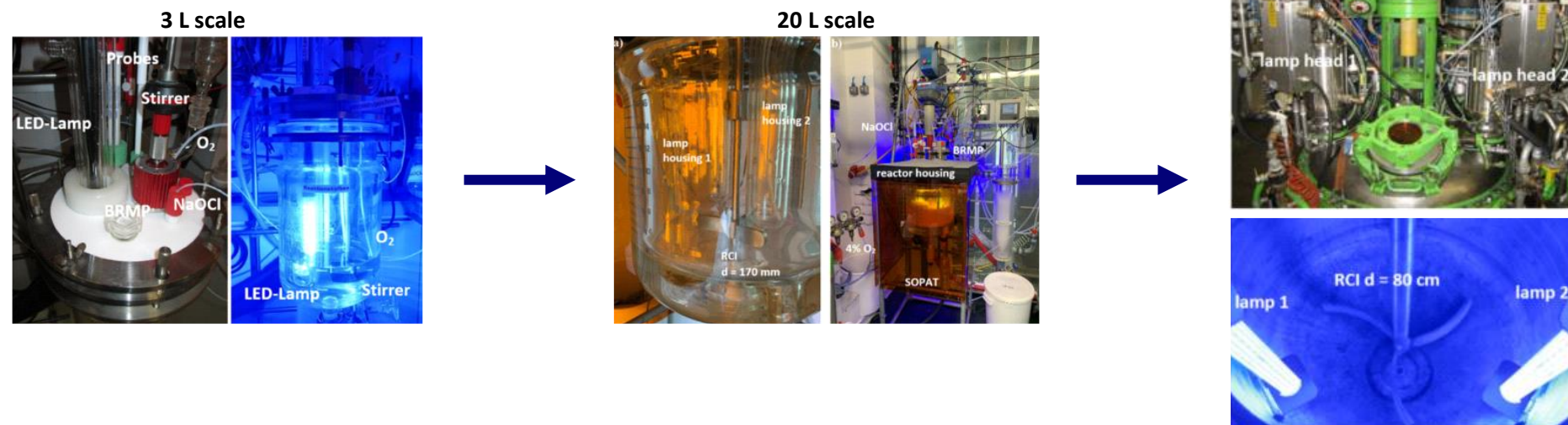
- Byproducts confirm undergoes radical mechanism



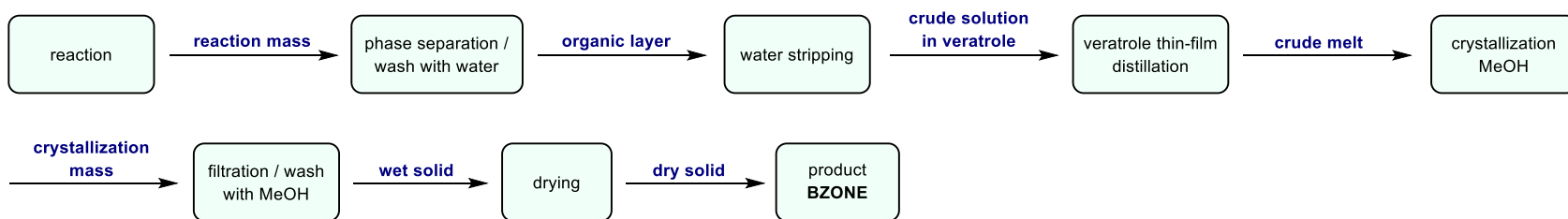
- Mechanism** (photocatalyst (PC) formed *in situ*, undefined species)



- Reactor Scale Development took into account more than 10 reaction parameters



- Workup Process



- First heterogeneous solid-liquid-liquid gas photochemical reaction implemented at process scale
- First Production campaign produced 853 kg of BZONE
- Process judged feasible for future long-term production