

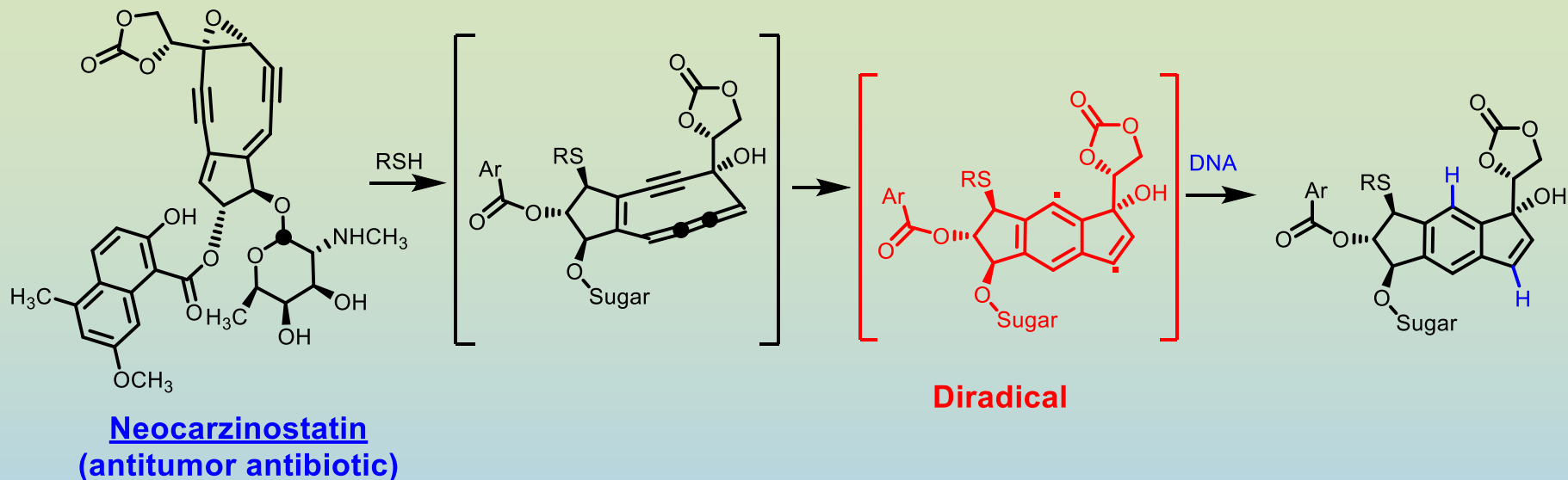


Photogeneration of diradicals as potential chemotherapeutics

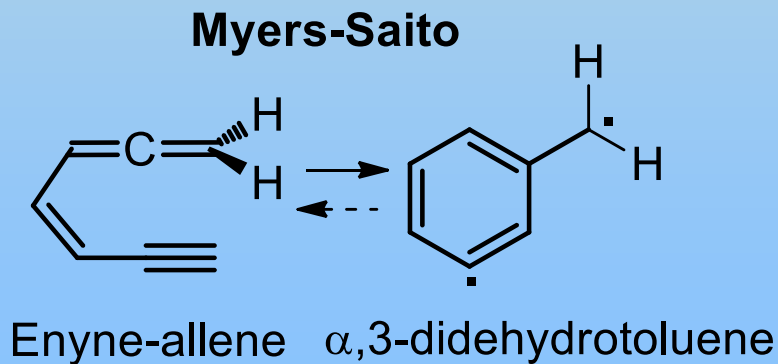
PhotoGreen Lab, Department of Chemistry,
University of Pavia, viale Taramelli 12, 27100 Pavia

website: www.unipv.it/photogreenlab

Biological importance of diradicals against tumors

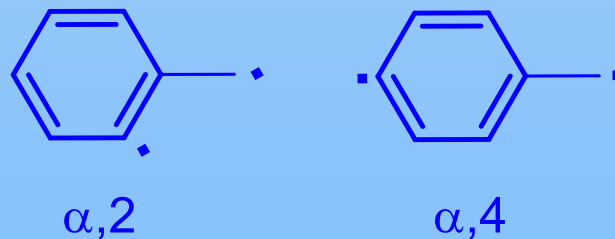


Generation of didehydrotoluenes. Via enyne-allene cyclization.

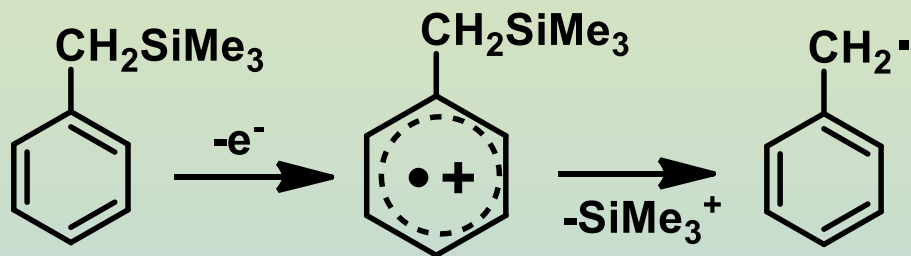


J. Am. Chem. Soc. **1992**, *114*, 9369.

Generation limited so far to
ONLY $\alpha,3$ isomers

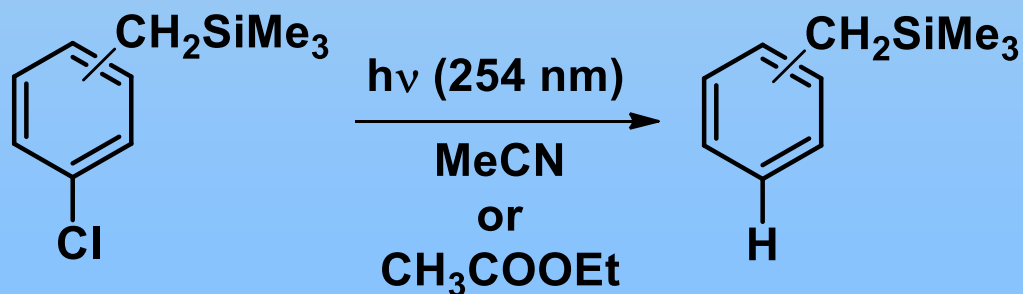
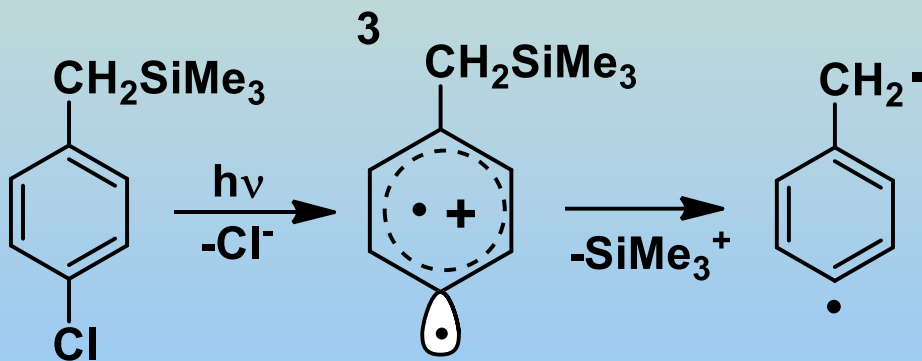


Generation of α,n -didehydrotoluenes (α,n -DHTs) via phenyl cations



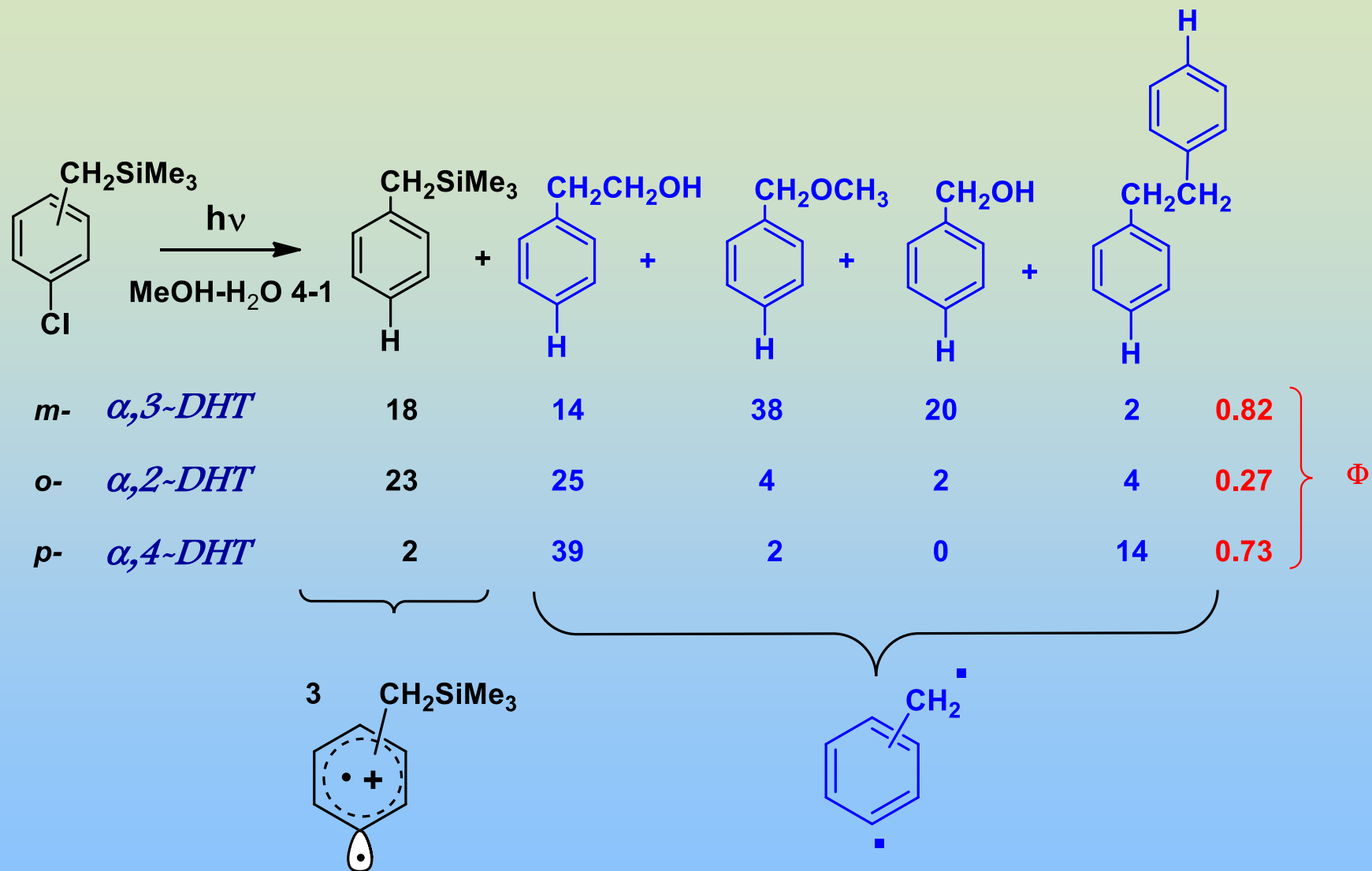
Known behaviour of benzyl silanes

Our proposal

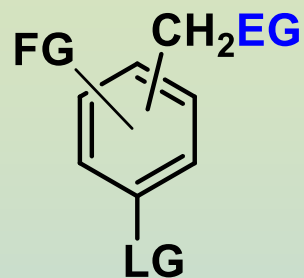


Photodechlorination in non protic solvents

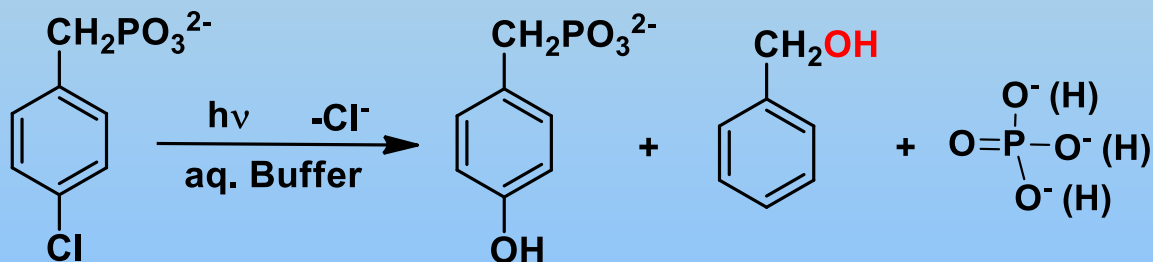
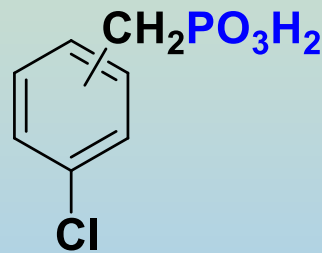
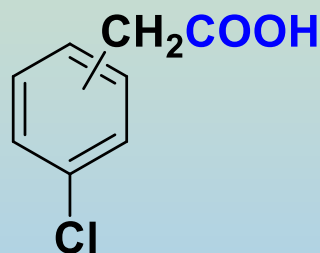
Generation of α,n -didehydrotoluenes (α,n -DHTs) via phenyl cations



In search for an ideal water soluble DHT precursor



- Good electrofugal group (EG)
- High solubility in neat water at physiological pH.
- Electron donating substituent (-CH₂EG)



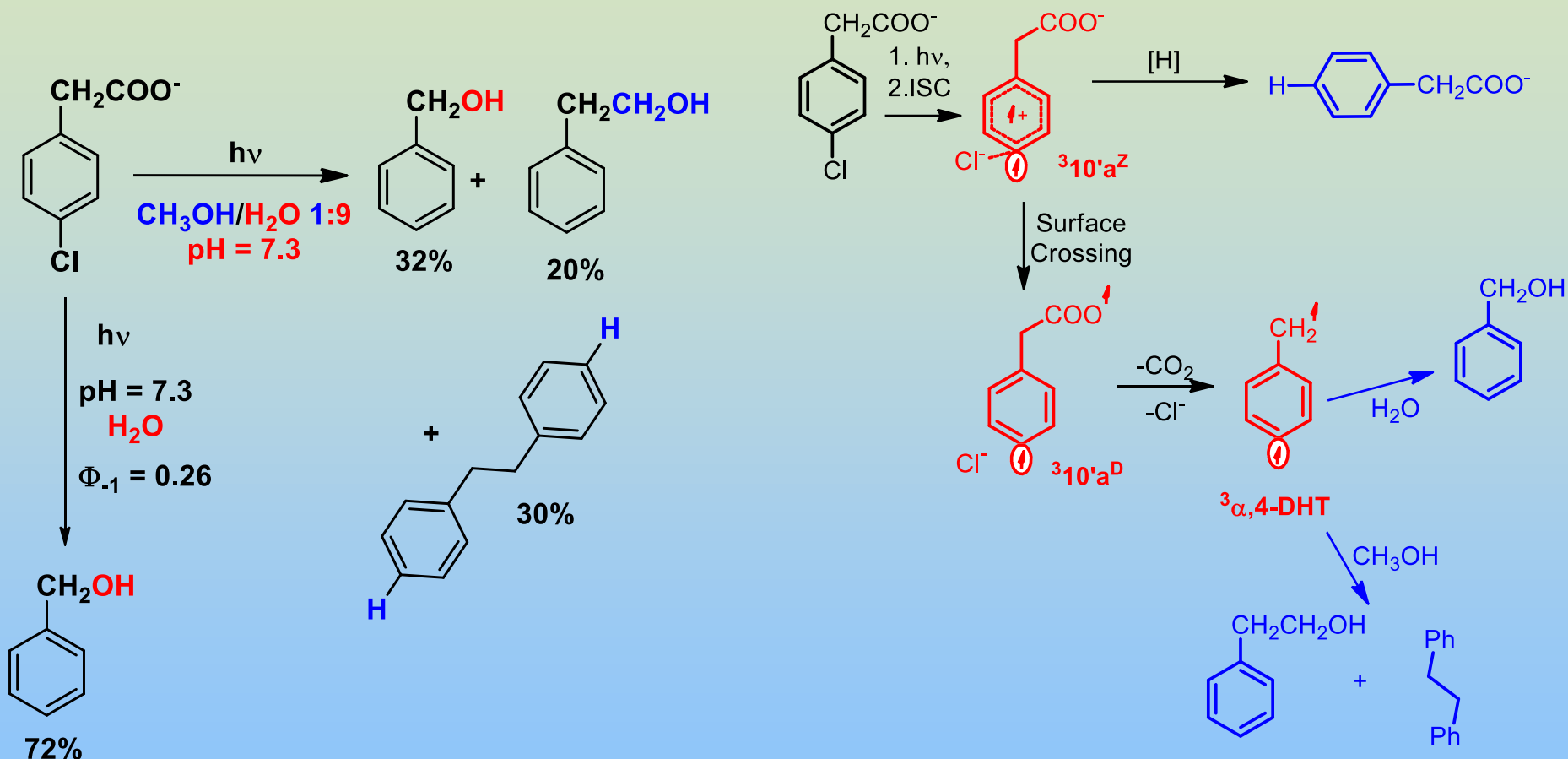
Quantitative release
of phosphate anion
at pH = 11

$\Phi_{-1} = 0.13$ pH = 2.5 (PO₃H₂)
 $\Phi_{-1} = 0.16$ pH = 7.2 (PO₃H⁻)
 $\Phi_{-1} = 0.26$ pH = 11 (PO₃²⁻)

73% 26%
 47% 35%
 0% 57%

pH dependent
distribution products

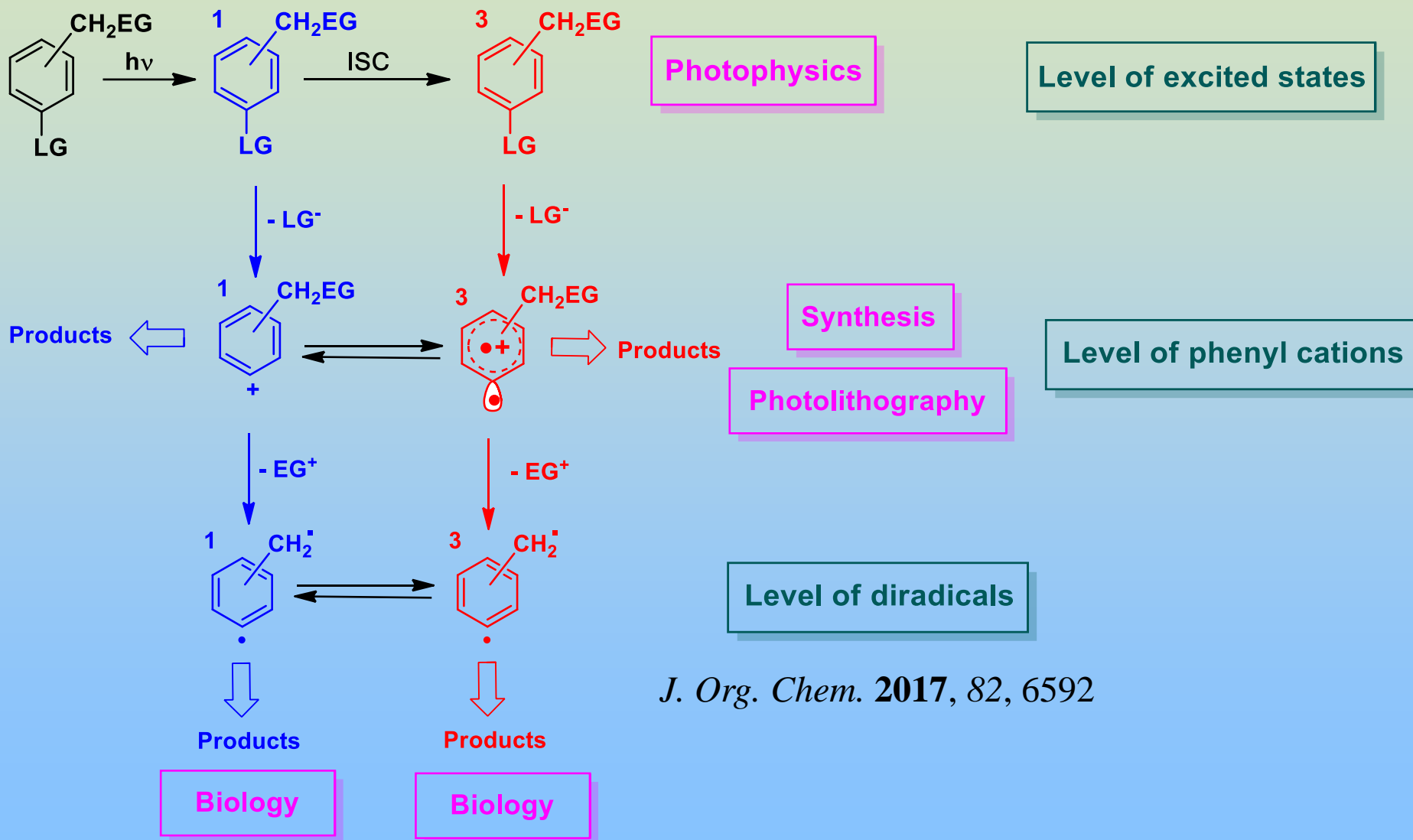
Photogeneration of α,n -DHTs under physiological conditions



J. Org. Chem. **2015**, *80*, 852–858.

Multi-configurational method
 CASSCF/6-31G(d) level of theory in bulk water

The multifaceted life of Aryl cations



J. Org. Chem. **2017**, *82*, 6592