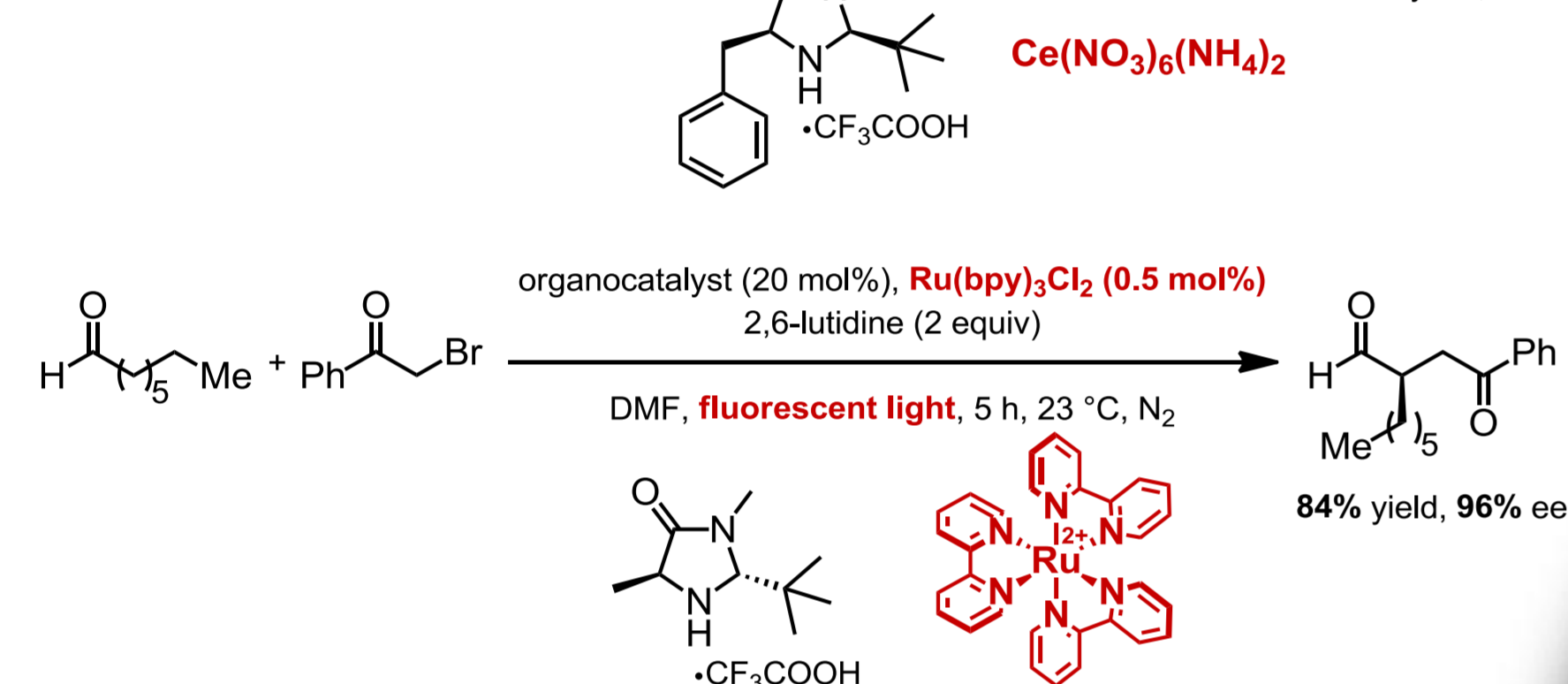
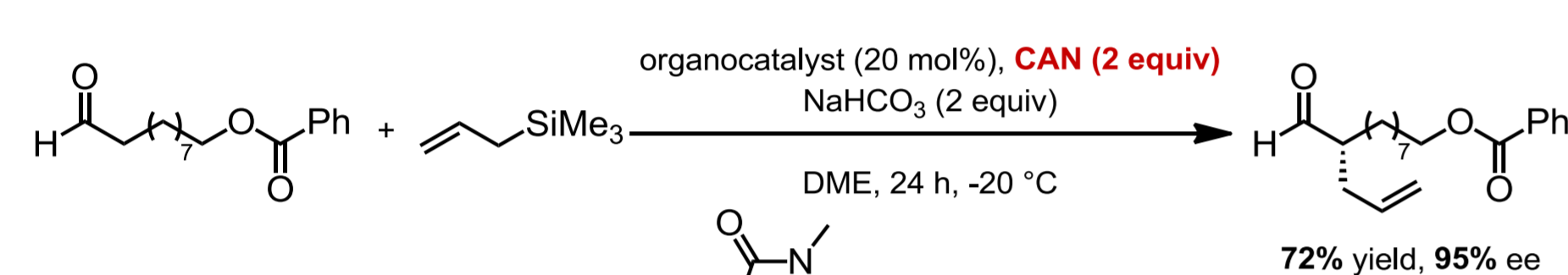
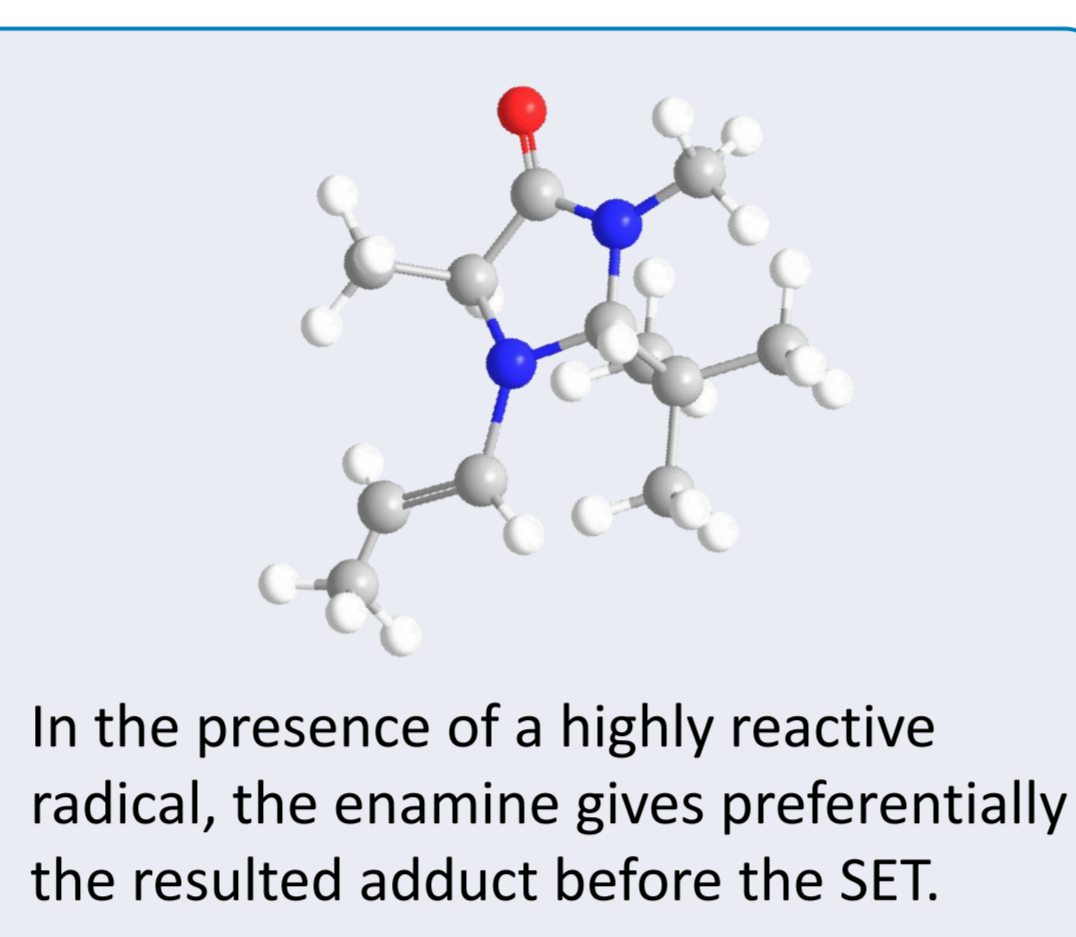
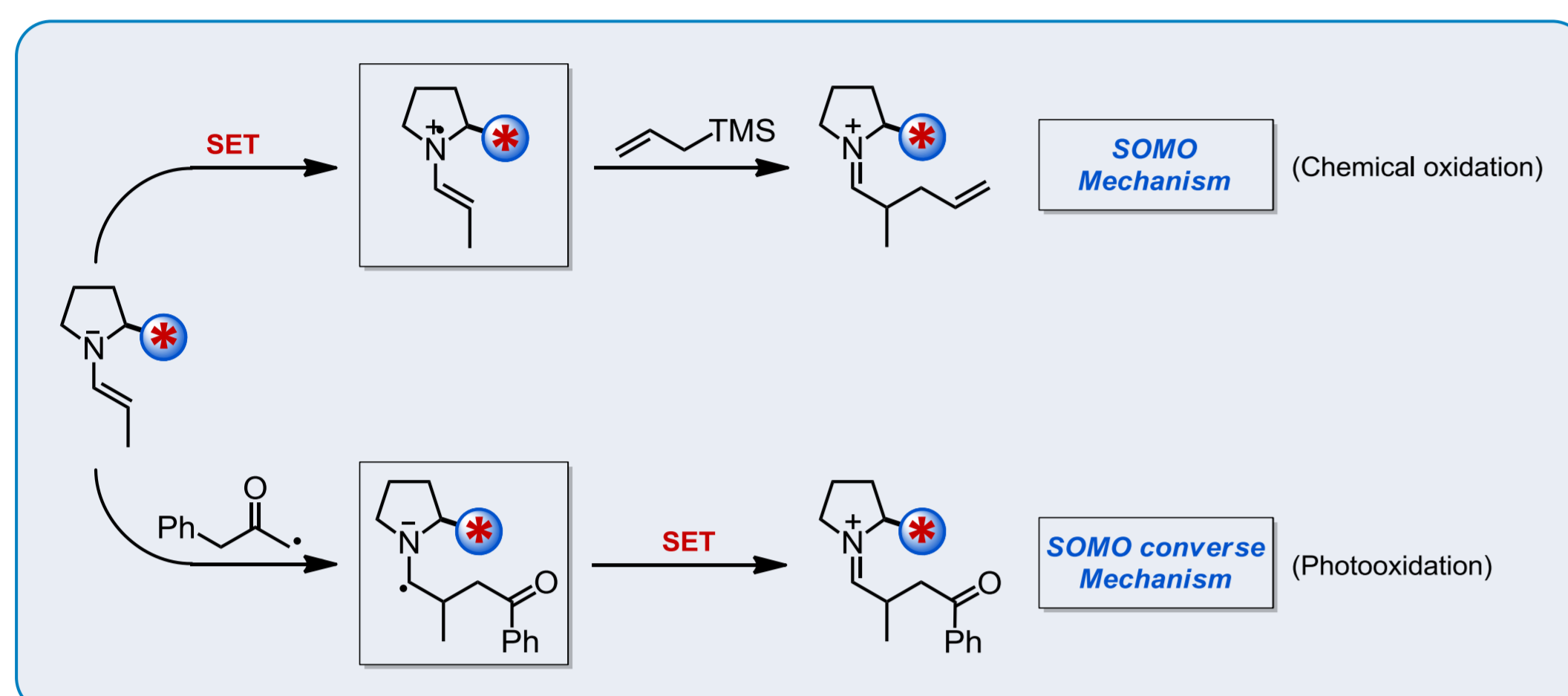


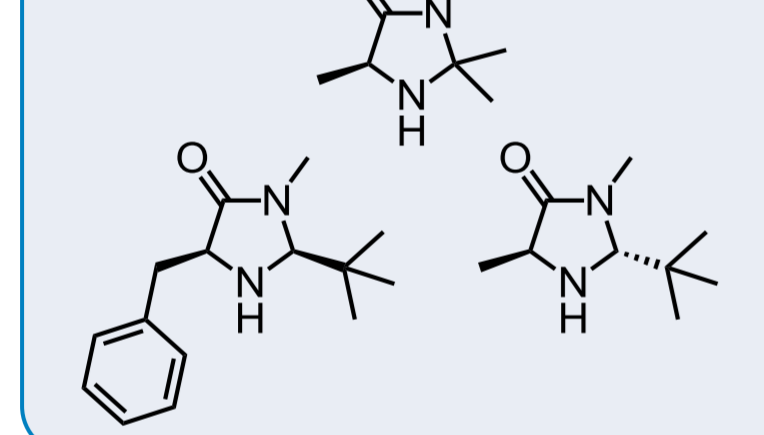
Since these last ten years, the number of publications in the field of organocatalysis has dramatically increased in the literature.

The SOMO activation is based on highly reactive radical species. A photocatalytic system in the visible domain could avoid the use of noxious chemical oxidants taken full advantage of a "metal-free" process.

## ORGANO-SOMO CATALYSIS



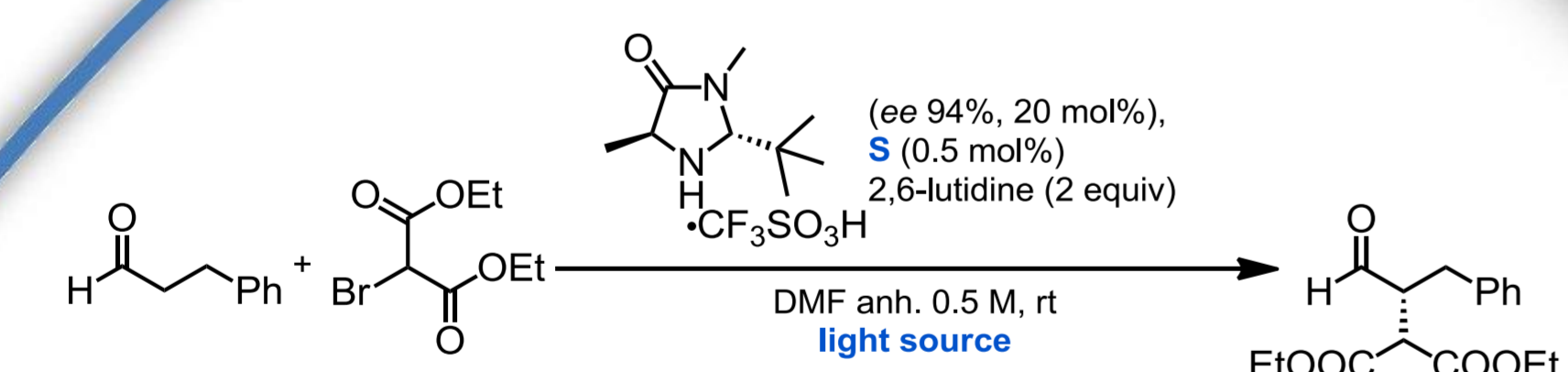
## Reactions involving SOMO activation



α-enolation  
α-allylation  
α-arylation  
α-alkylation  
α-nitroalkylation  
α-chlorination  
α-trifluoromethylation

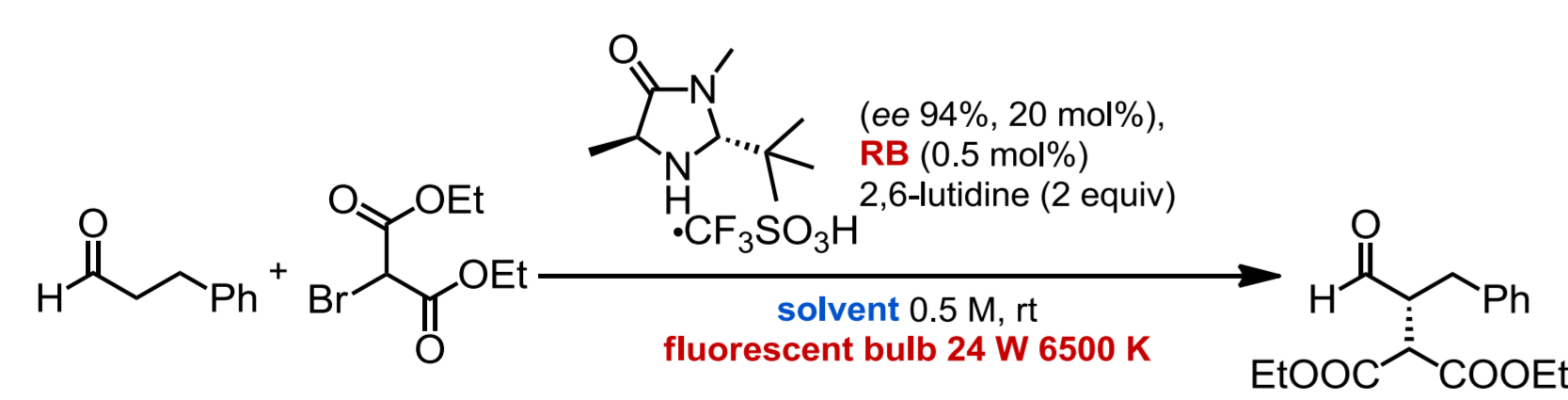
Beeson, T. D.; Mastracchio, A.; Hong, J.-B.; Ashton, K.; MacMillan, D. W. C. *Science* **2007**, 316, 582.  
MacMillan, D. W. C. *Nature* **2008**, 455, 304.  
Nicewicz, D. A.; MacMillan, D. W. C. *Science* **2008**, 322, 77.

## Mariage of organocatalysis with organic photoredox catalysis for the enantioselective α-alkylation of aldehydes



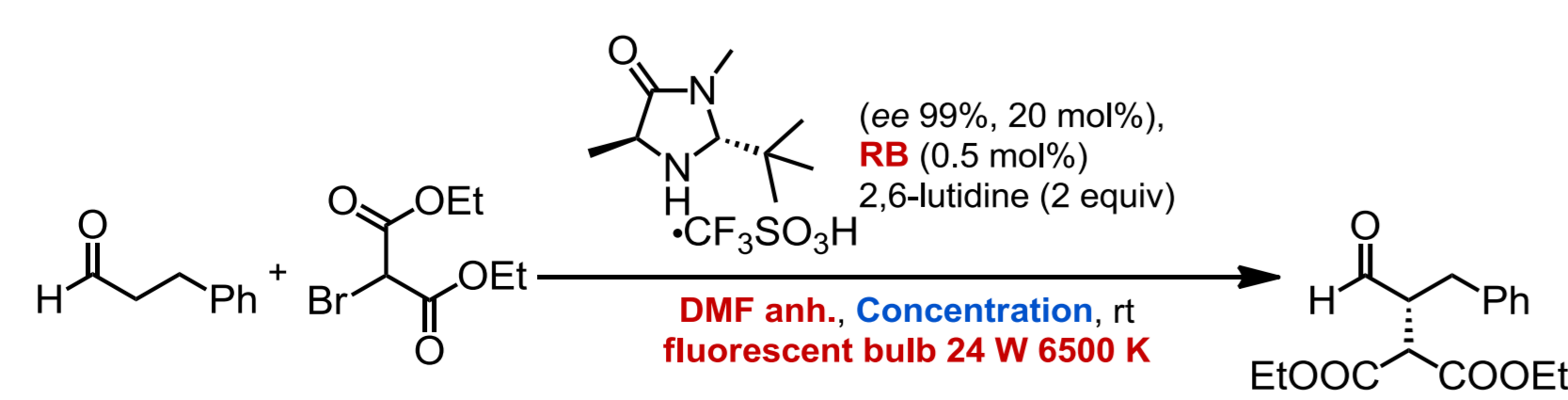
Entry	Light source	S	Time	Conv. (%)	Yield (%)	ee (%)
1	Hg 150 W	EB	4 h	100	87	82
2	Hg 150 W	EY	4 h	100	80	83
3	Hg 150 W	RB	2 h	100	quant.	83
4	fluores. bulb 24 W 6500 K	RB	2 h	100	quant.	82

Among the different xanthene dyes, Rose Bengal with a simple economic fluorescent bulb involves short reaction times.



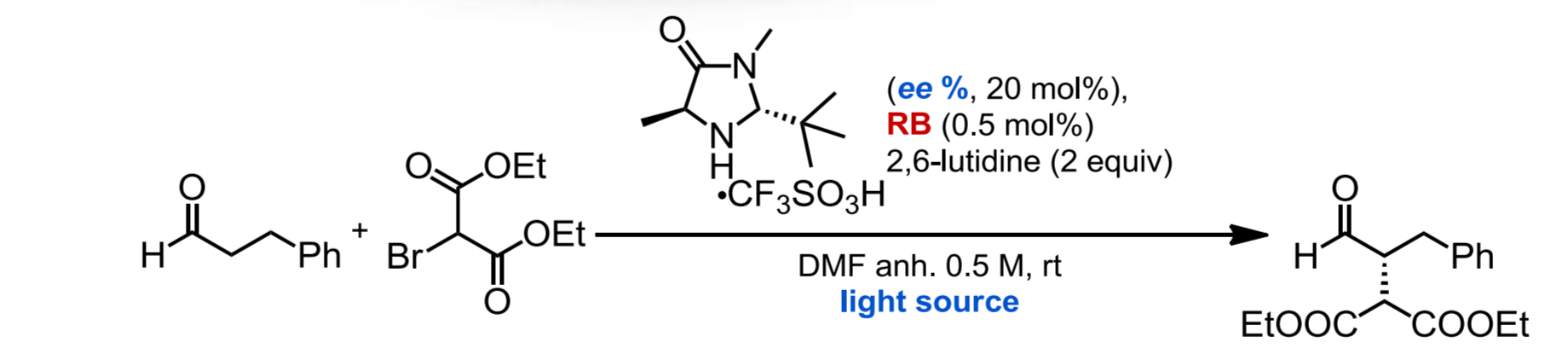
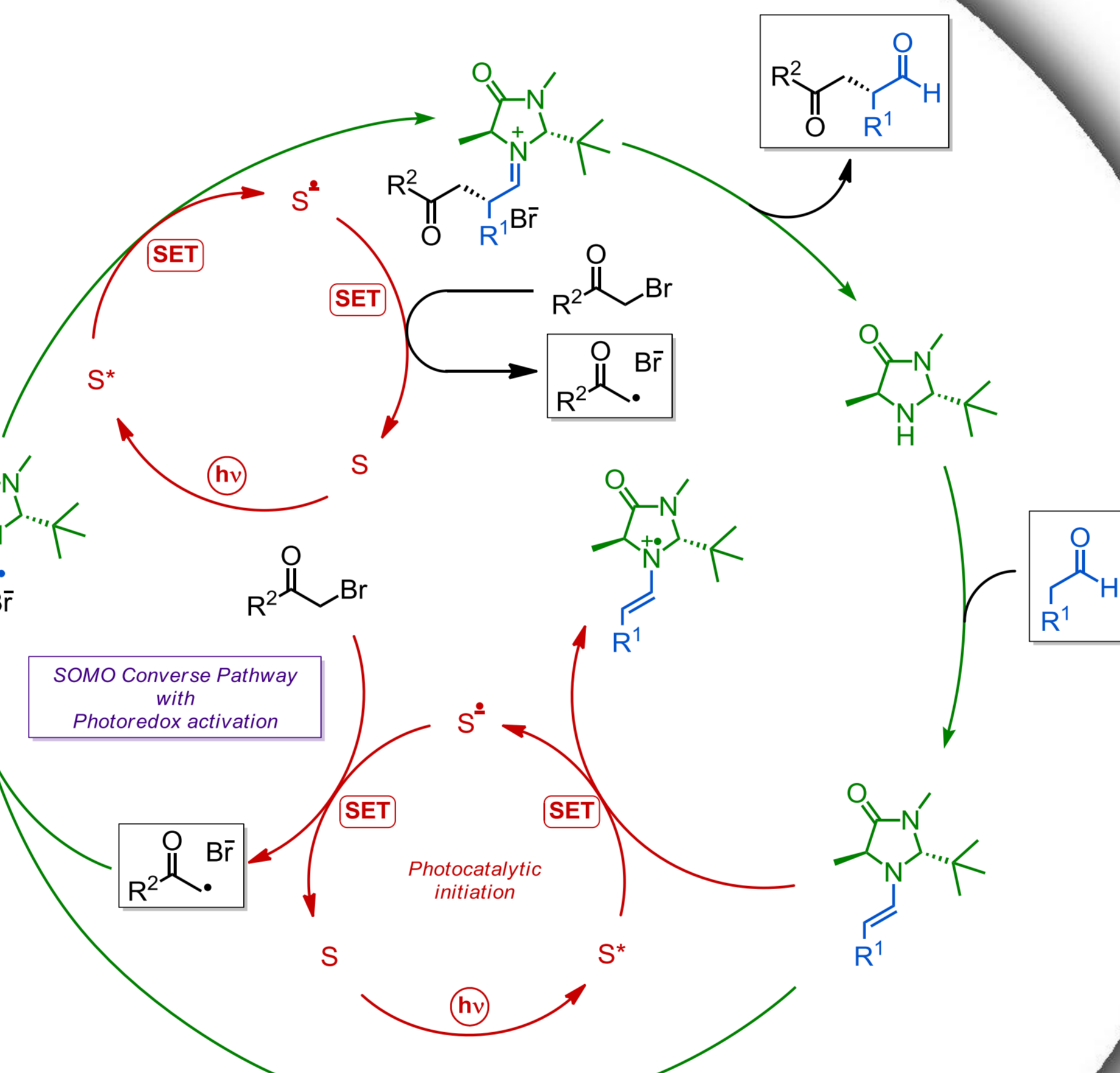
Entry	Solvent	Time	Conv. (%)	Yield (%)	ee (%)
1	DME anh.	6 h	92	34	70
2	THF anh.	6 h	100	45	63
3	ACN anh.	6 h	100	48	74
4	DMF anh.	3 h	100	86	76
5	DMSO anh.	3 h	100	quant.	75

Further investigations show that an increase in solvent polarity provides the best yields together with a decrease in reaction time.



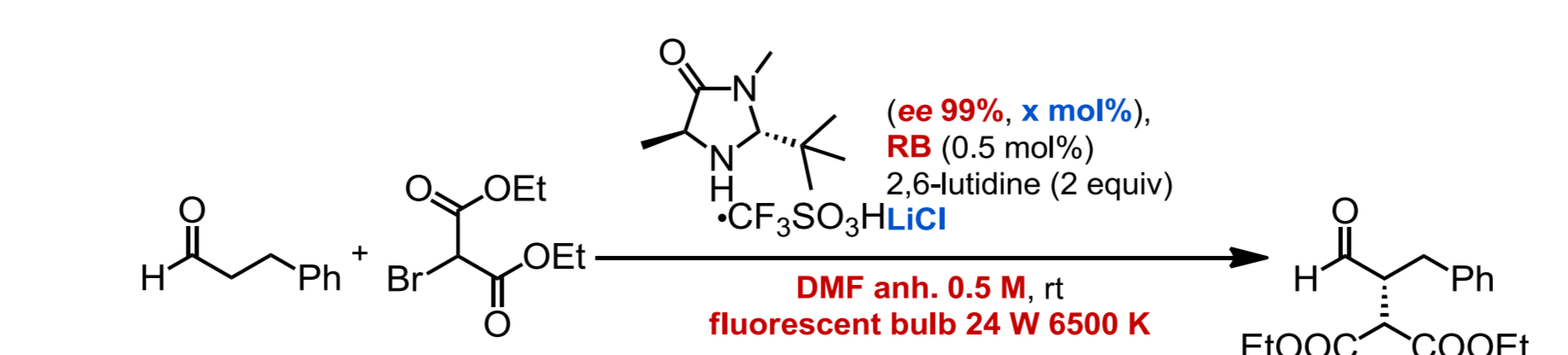
Entry	Conc. C	Time	Conv. (%)	Yield (%)	ee (%)
1	0.1 M	3 h	100	66	77
2	0.25 M	3 h	100	75	80
3	0.5 M	3 h	100	quant.	82
4	0.75 M	45 min	100	97	78
5	1 M	30 min	100	85	79

In addition, a screening of concentrations reveals that 0.5 M gives the best yields and ees.



Entry	Cat. ee (%)	Light source	Time	Conv. (%)	Yield (%)	ee (%)
1	89	fluores. bulb 23W 4000 K	3 h	100	75	60
2	89	fluores. bulb 24 W 6500 K	3 h	100	86	76
3	99	fluores. bulb 24 W 6500 K	2 h	100	quant.	82
4	99	LED 530 nm / EY	3 h	100	86	75
5	99	LED 530 nm / RB	3 h	100	66	76
6	99	LED 558 nm / RB	16 h	100	66	84

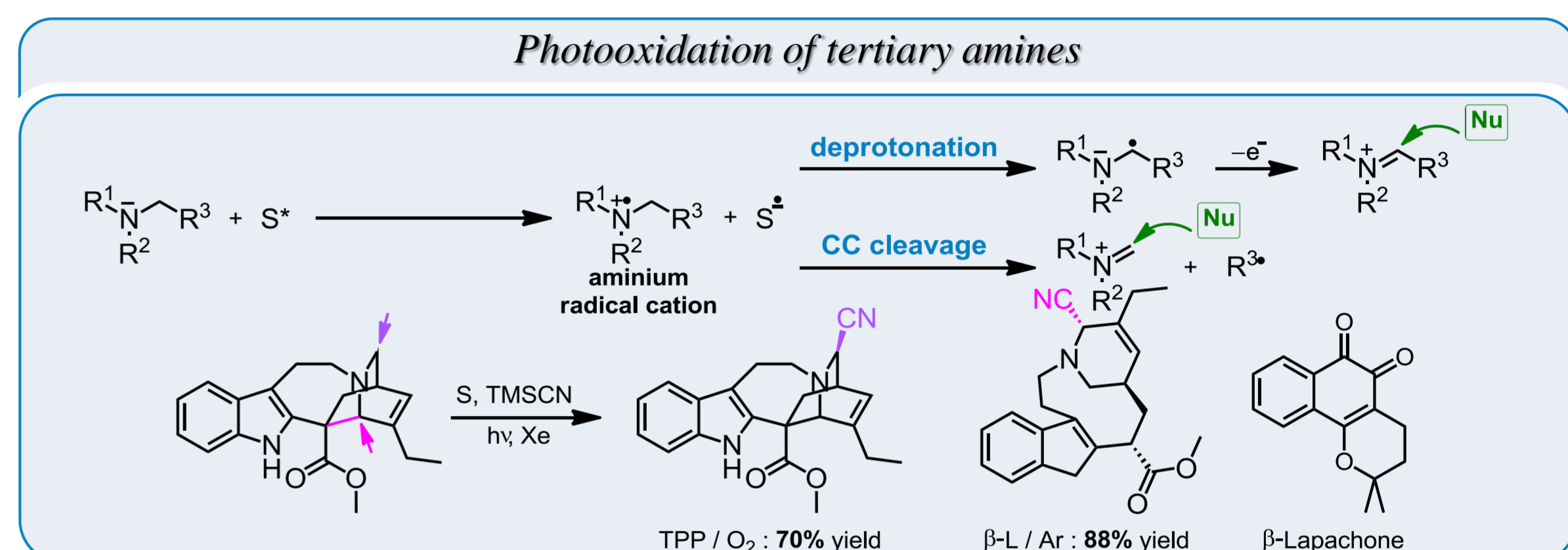
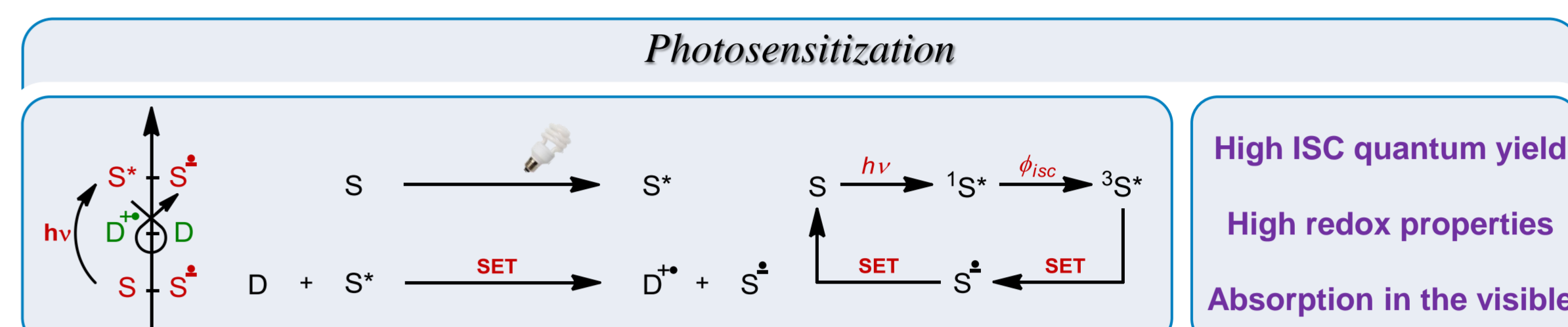
The use of a daylight 4000 K is unfavourable to both yield and ee. Replacement of the fluorescent bulb by an appropriate LED source leads to the same yields and ees even so with higher reaction time.



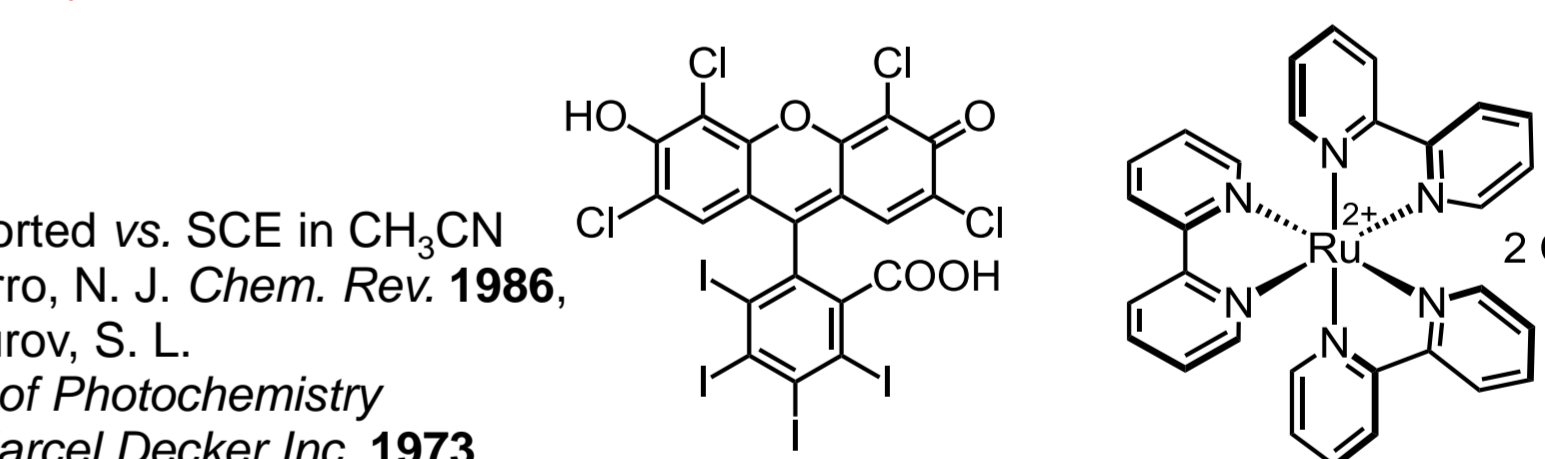
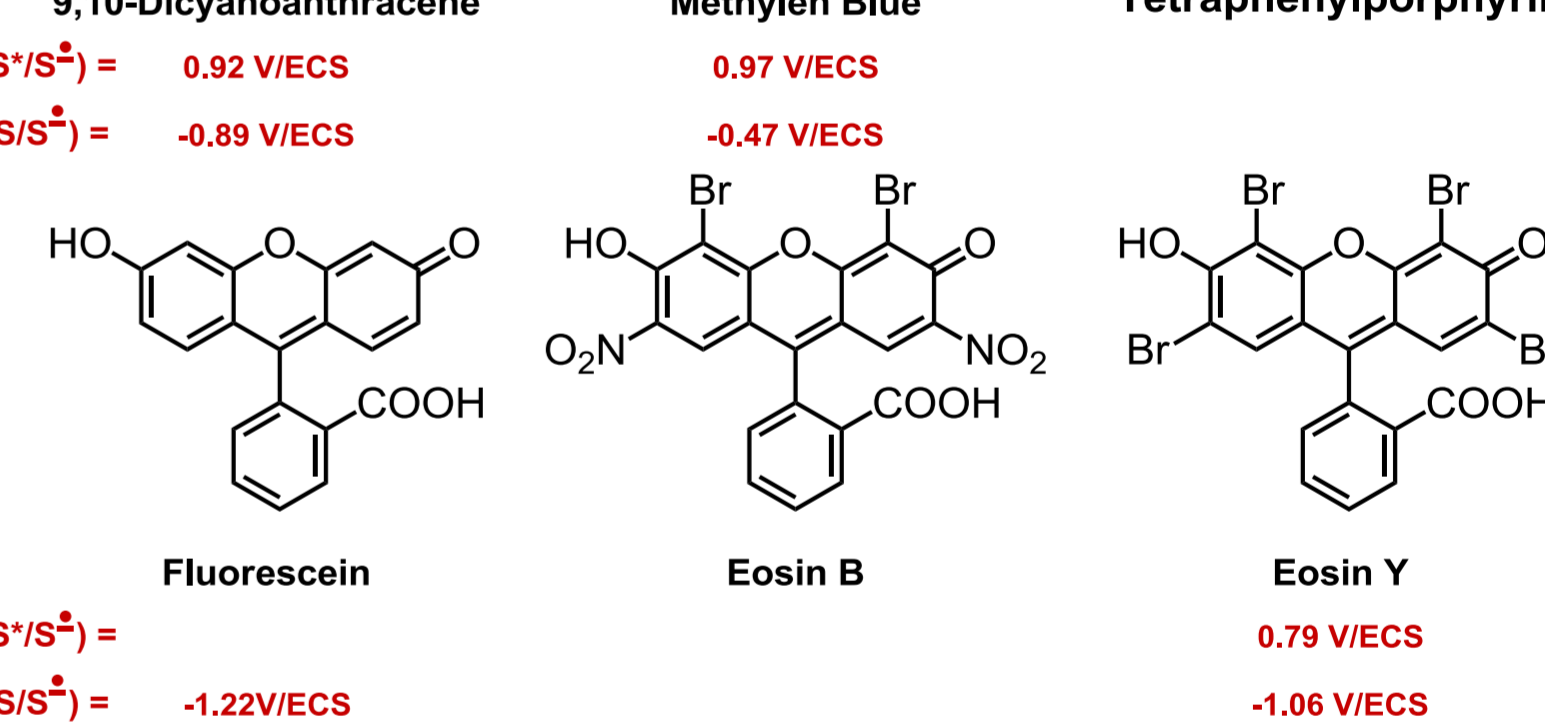
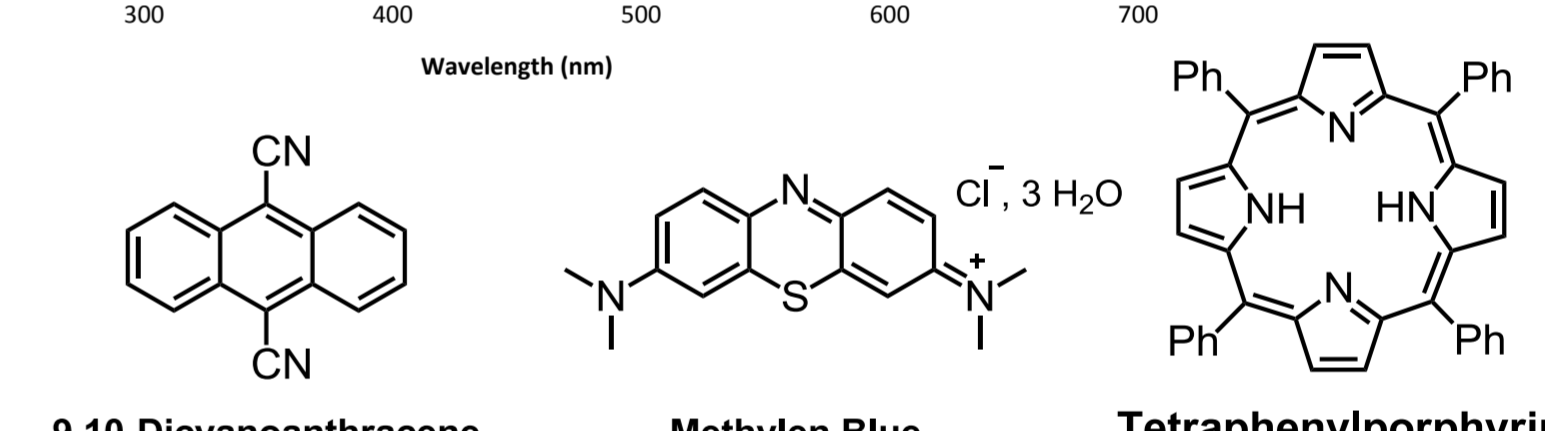
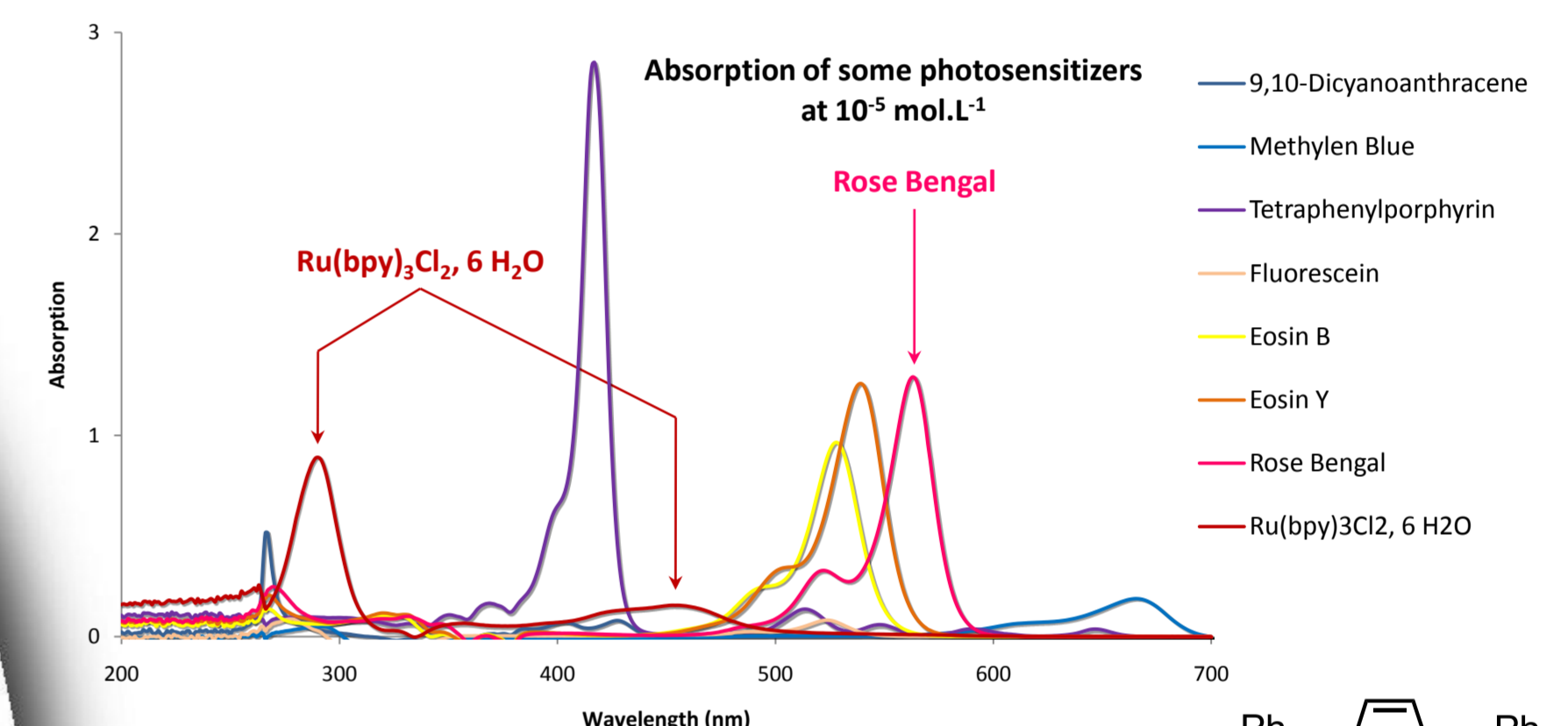
Entry	Catalyst	LiCl	Time	Conv. (%)	Yield (%)	ee (%)
1	20 mol%	0	2 h	100	quant.	82
2	10 mol%	0	6 h	87	47	81
3	10 mol%	5 mol%	6 h	89	46	73
4	10 mol%	10 mol%	4 h	100	55	77
5	15 mol%	10 mol%	2 h	100	82	81

The use of LiCl as an additive allowed us to reduce slightly the catalyst amount probably owing to the carbonyl activation in the enamine formation step.

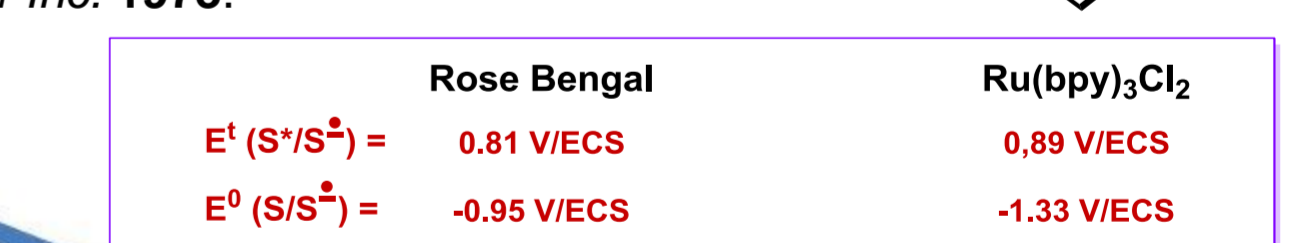
## PHOTOREDOX CATALYSIS



Santamaria, J.; Kaddachi, M. T.; Ferroud, C. *Tetrahedron Lett.* **1992**, 33, 781.  
Ferroud, C.; Rool, P.; Santamaria, J. *Tetrahedron Lett.* **1998**, 39, 9423.  
Cocquet, G.; Rool, P.; Ferroud, C. *J. Chem. Soc. Perkin Trans. 1* **2000**, 2277.



Potential values are reported vs. SCE in CH<sub>3</sub>CN  
Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, 86, 401 and Murov, S. L. *Handbook of Photochemistry*. Ed. Marcel Decker Inc. **1973**.



## Results after optimization

