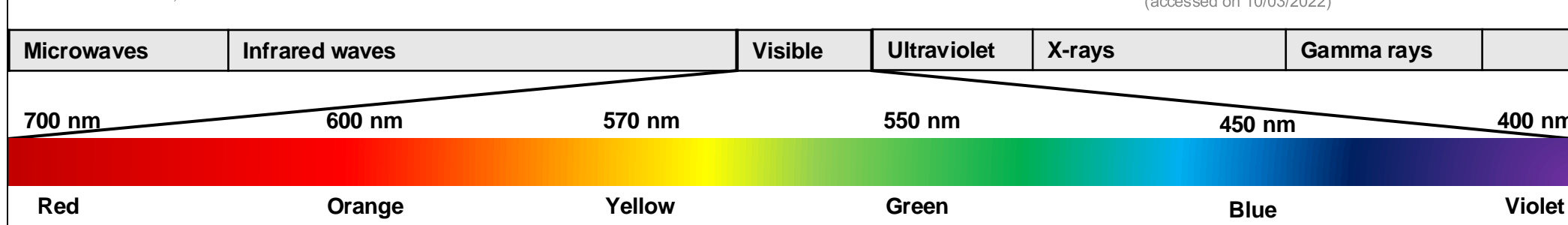
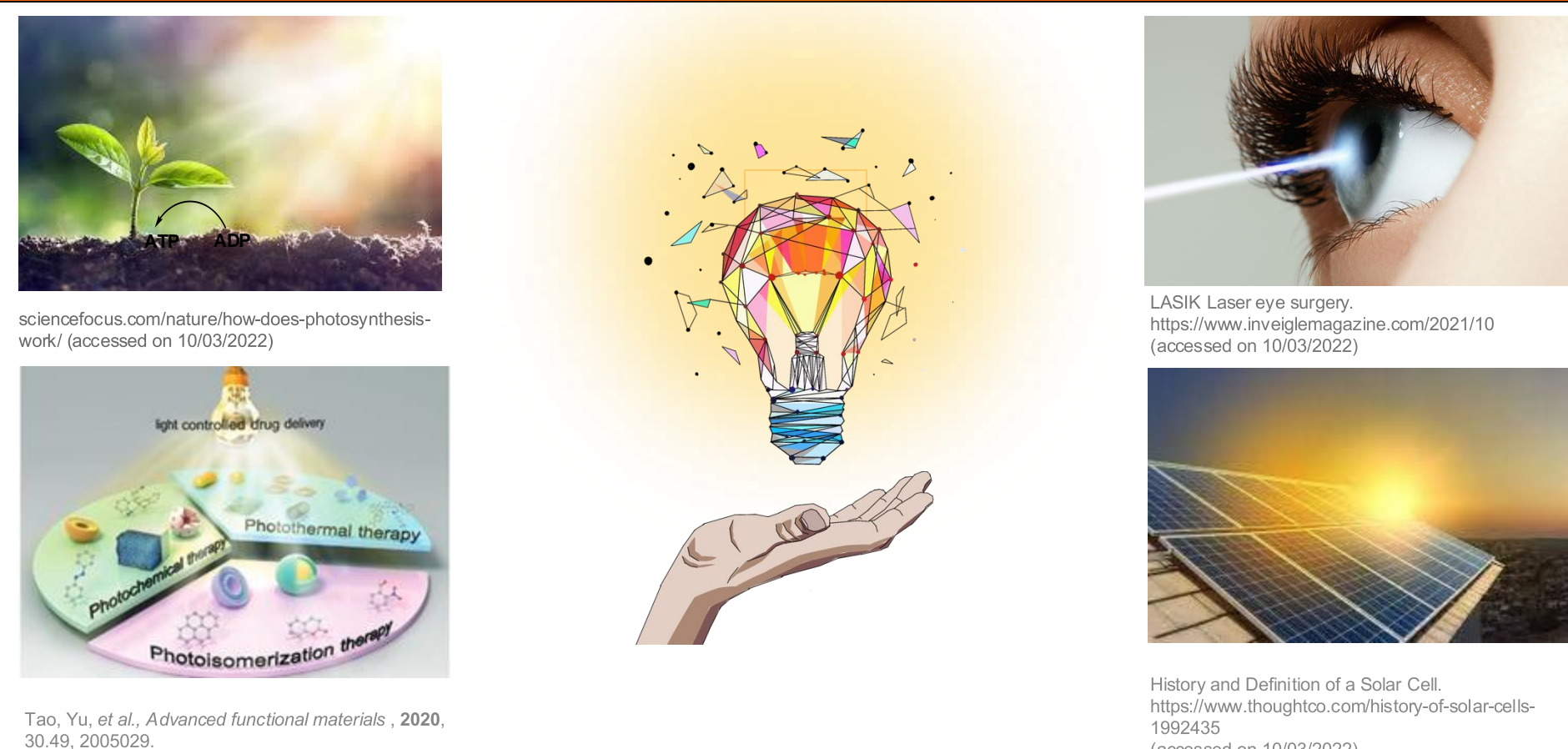
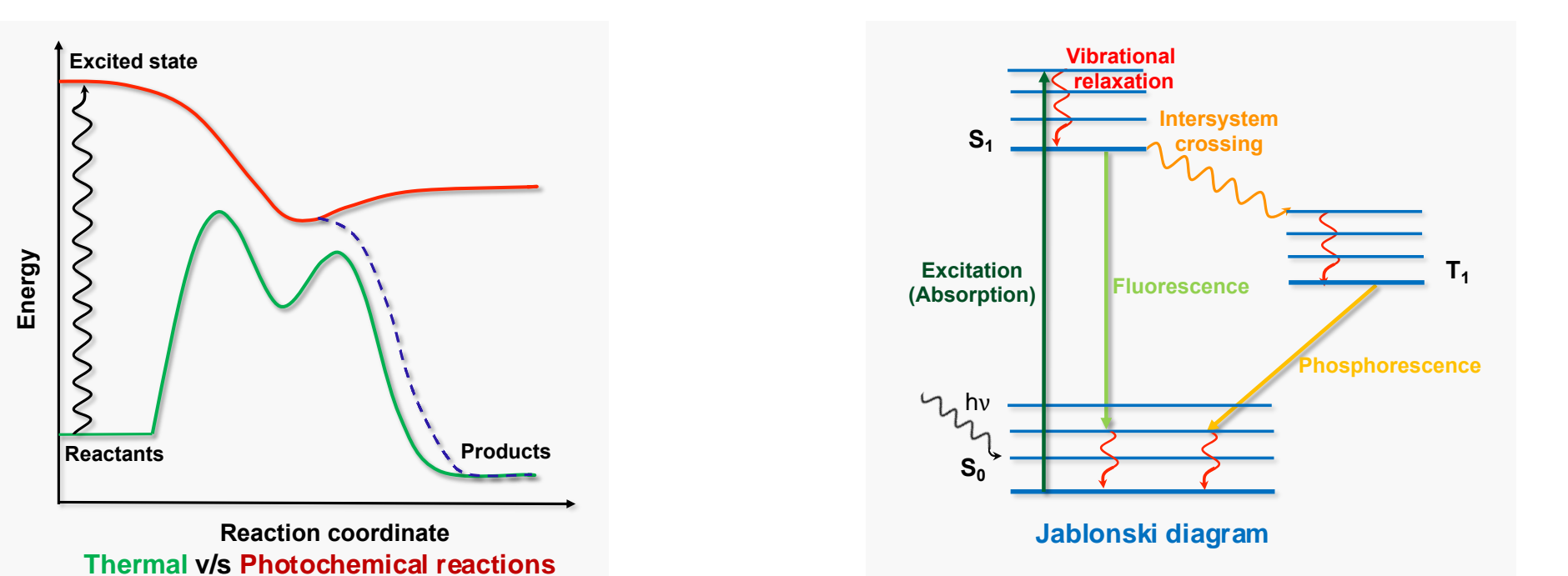


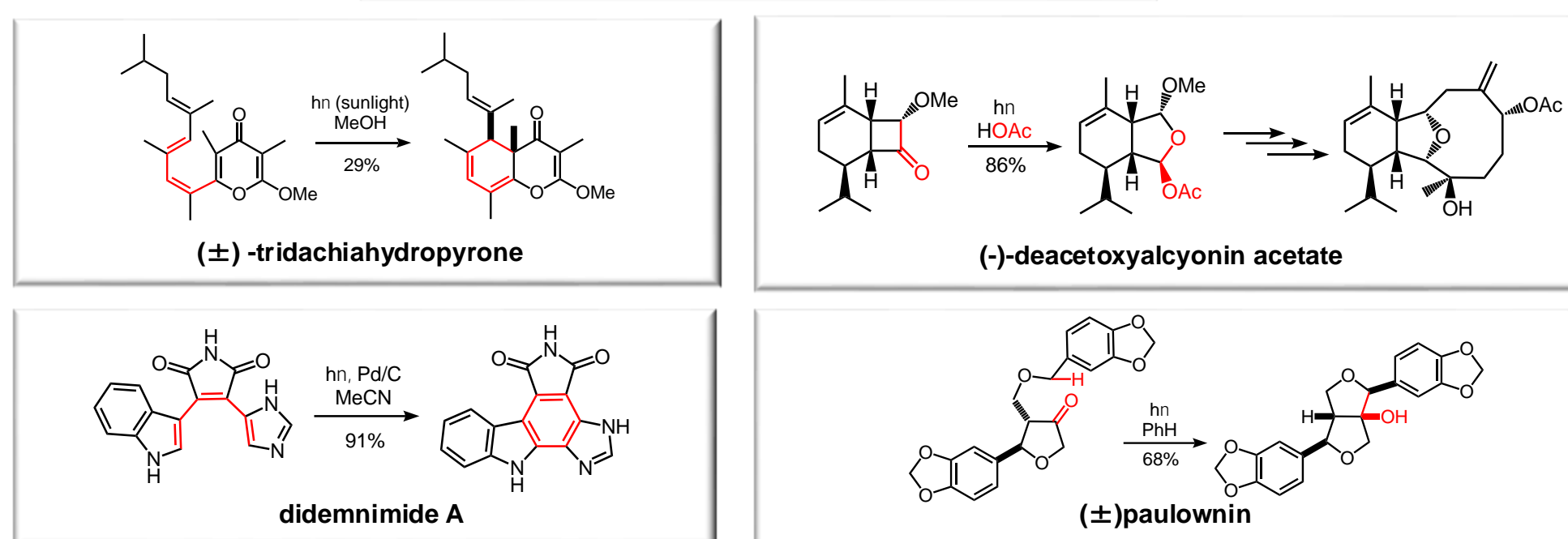
## Introduction



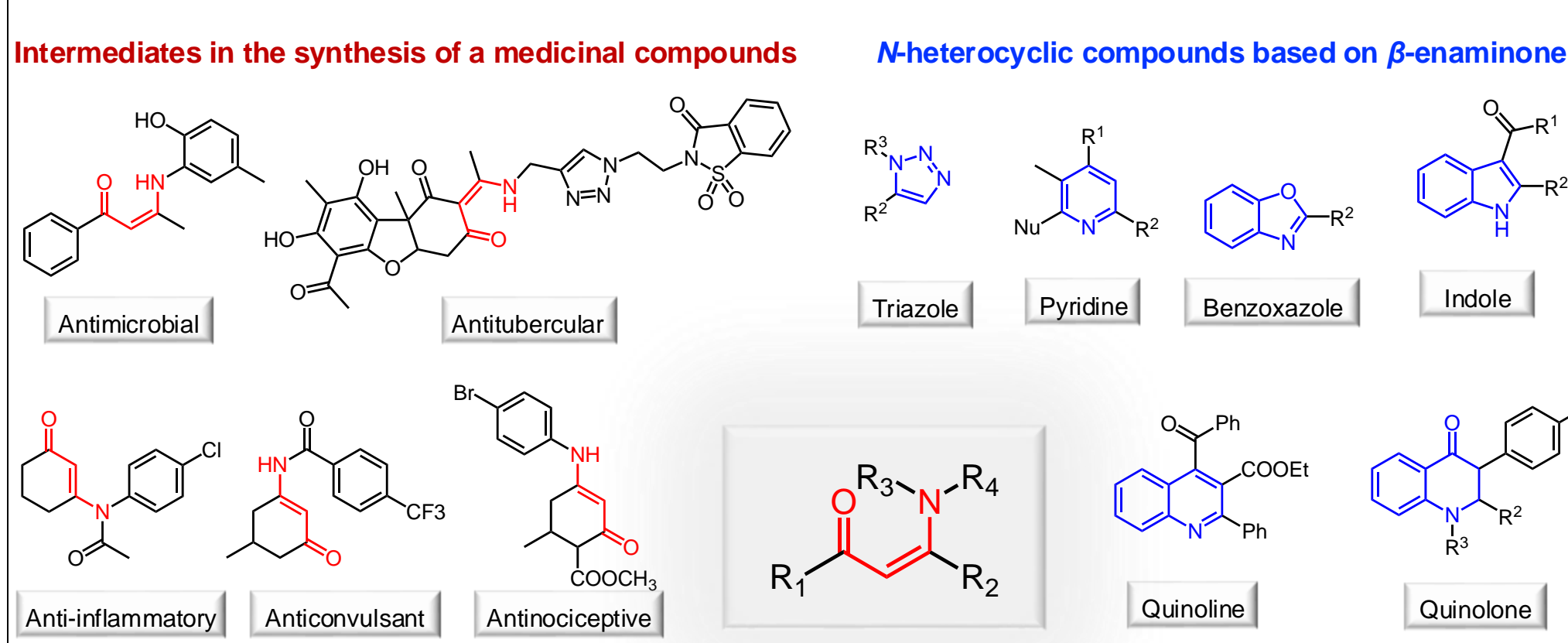
## Photochemistry



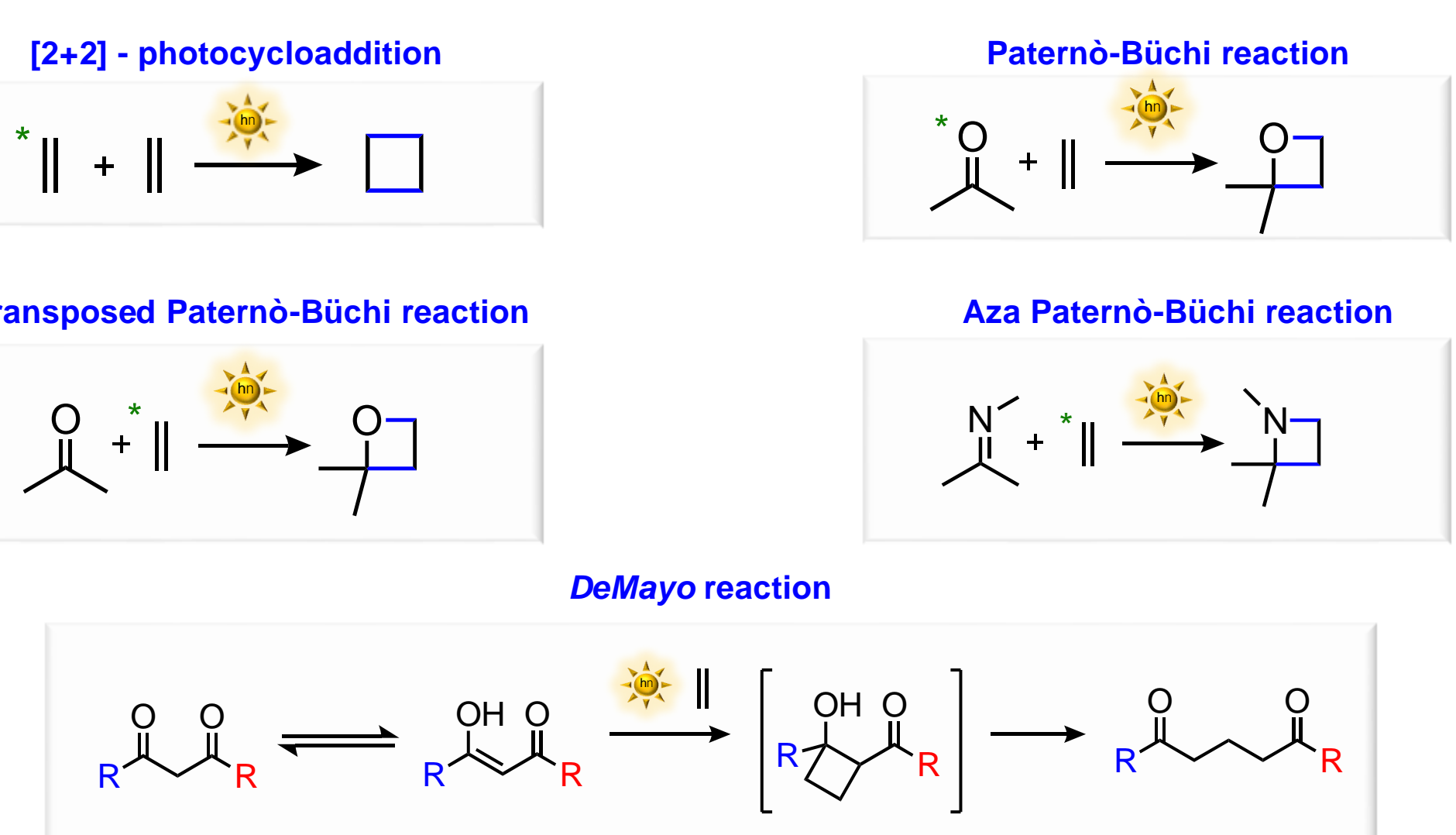
### Photochemistry in natural product synthesis



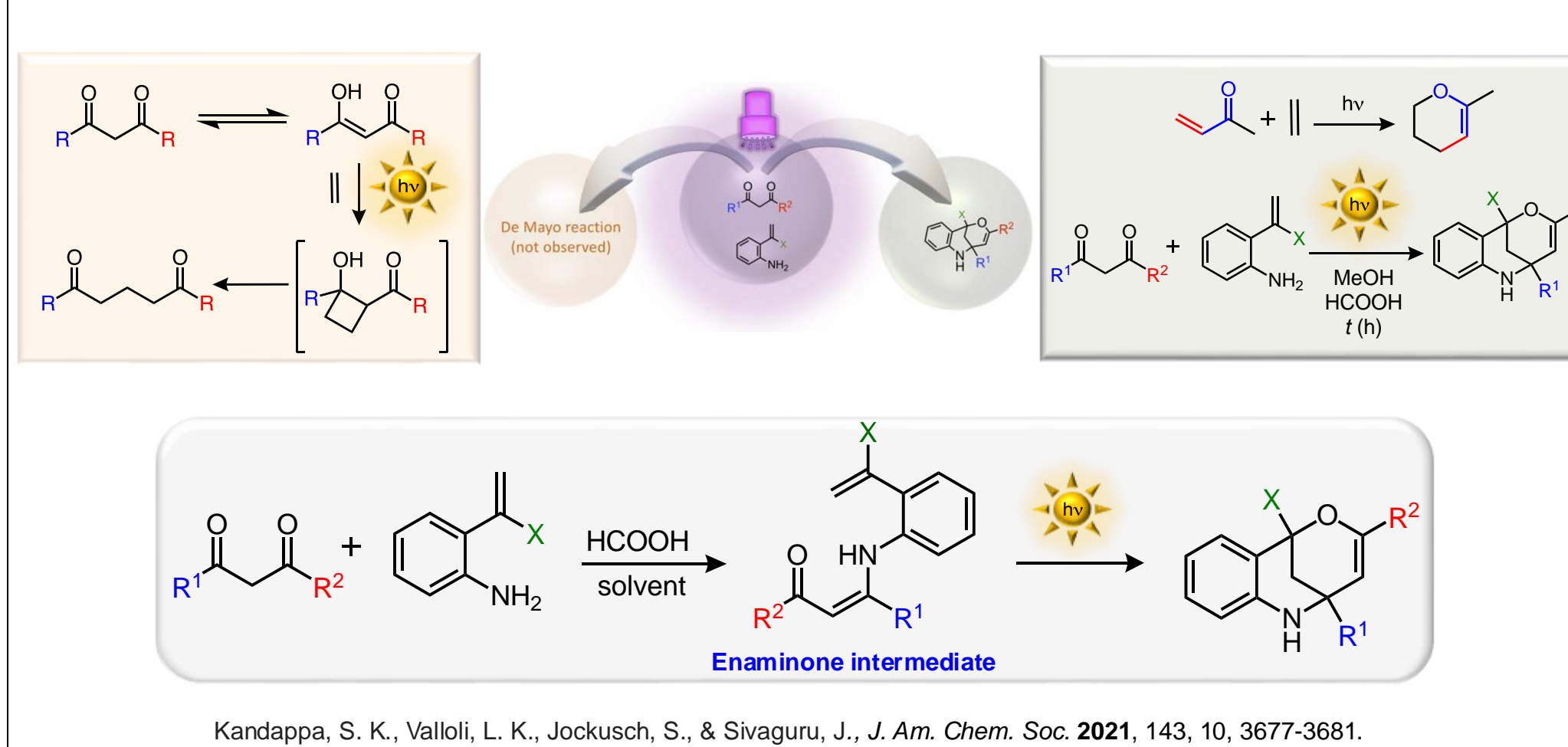
## Enaminones as important scaffold



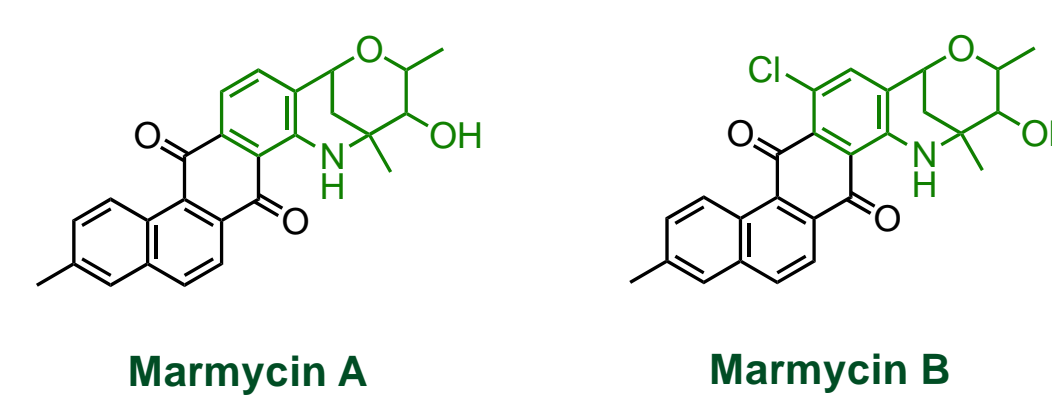
## Photocycloaddition reactions



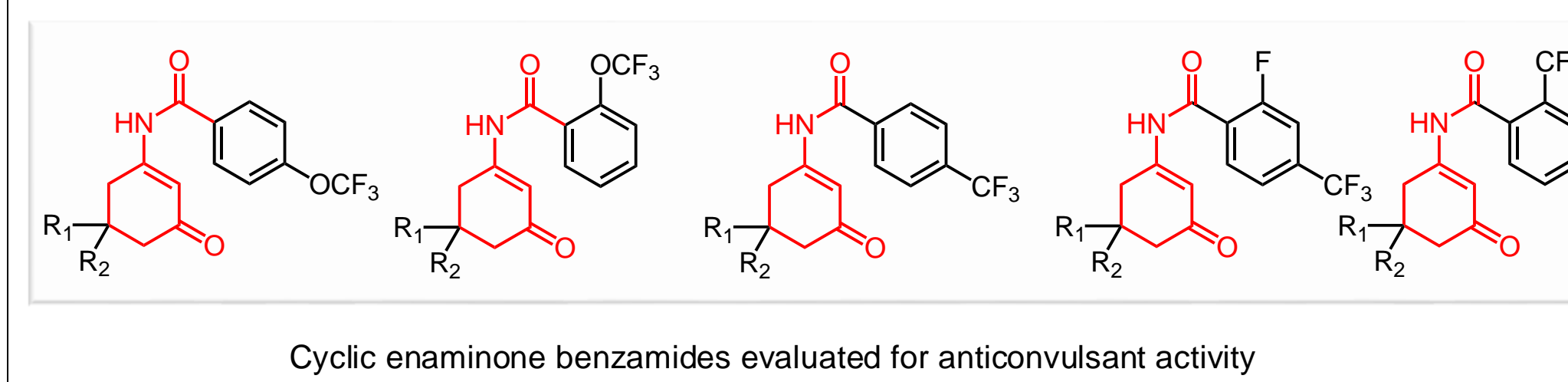
## Previous work



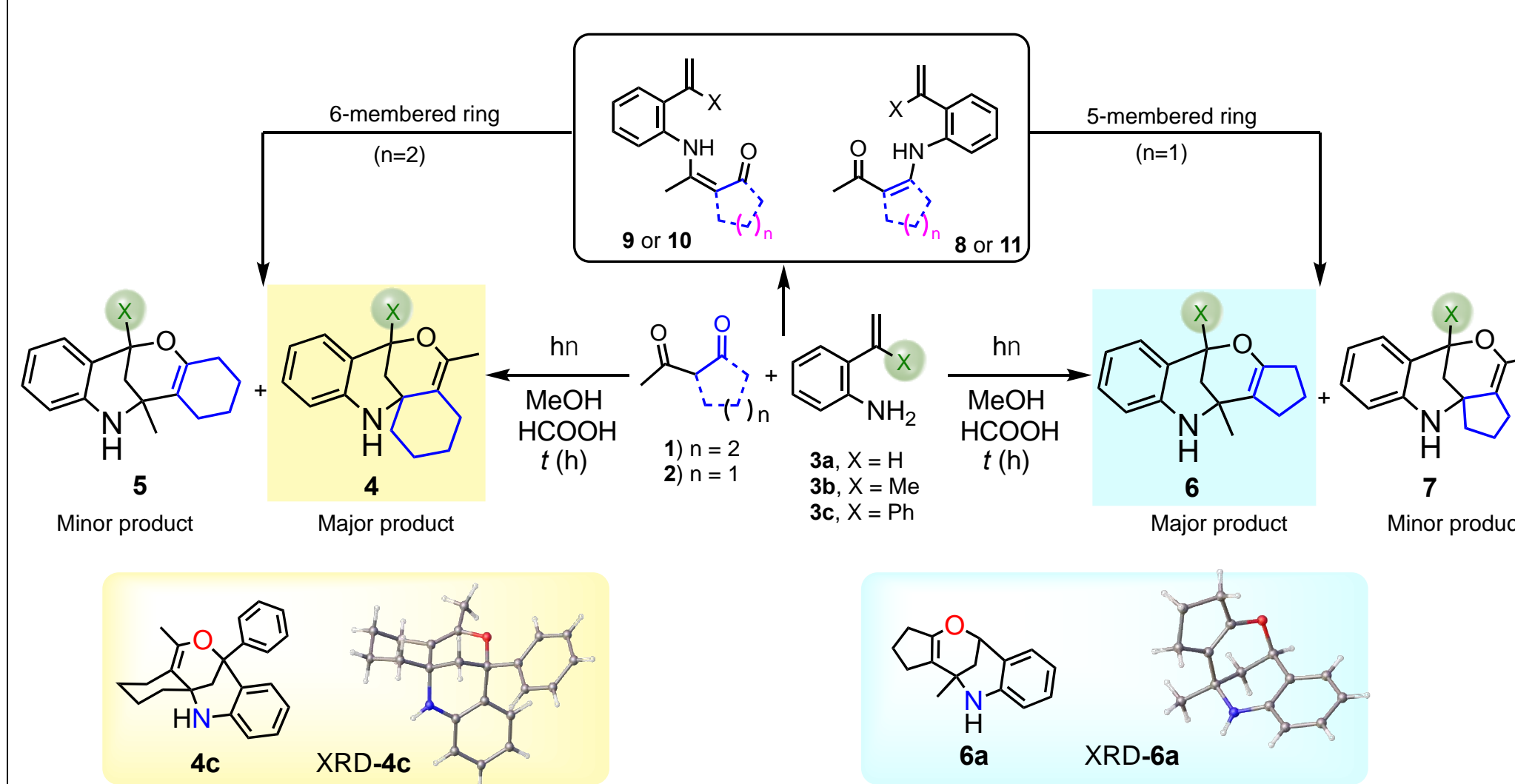
- Marmycin is a marine sediment isolated from a bacterium related to the *Streptomyces* that shows cytotoxicity against several cancer cell lines



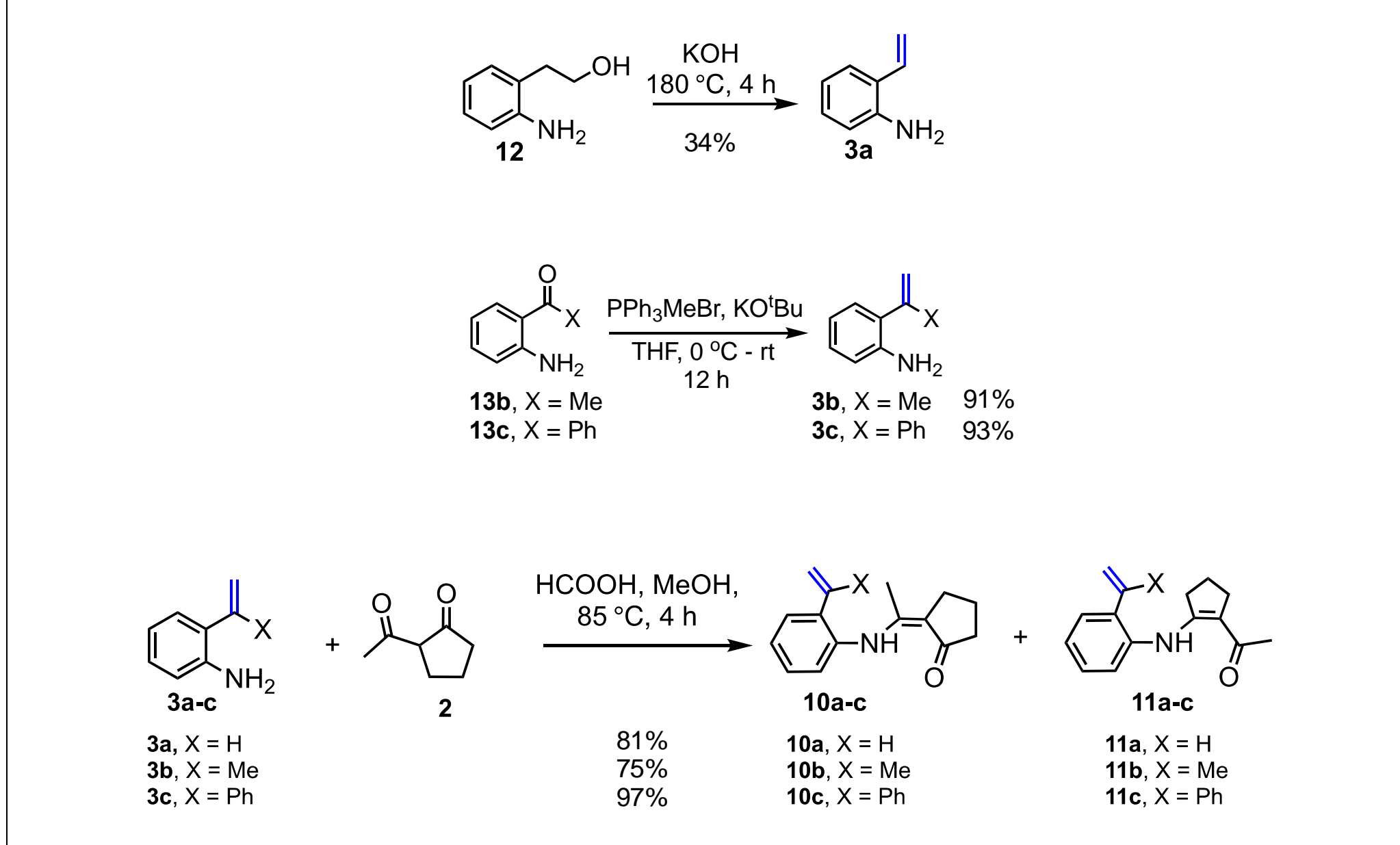
## Altering ring size of reactants



Dickmann Kon rule - Exo double bond stabilizes a 5-membered ring and destabilize a 6-membered ring

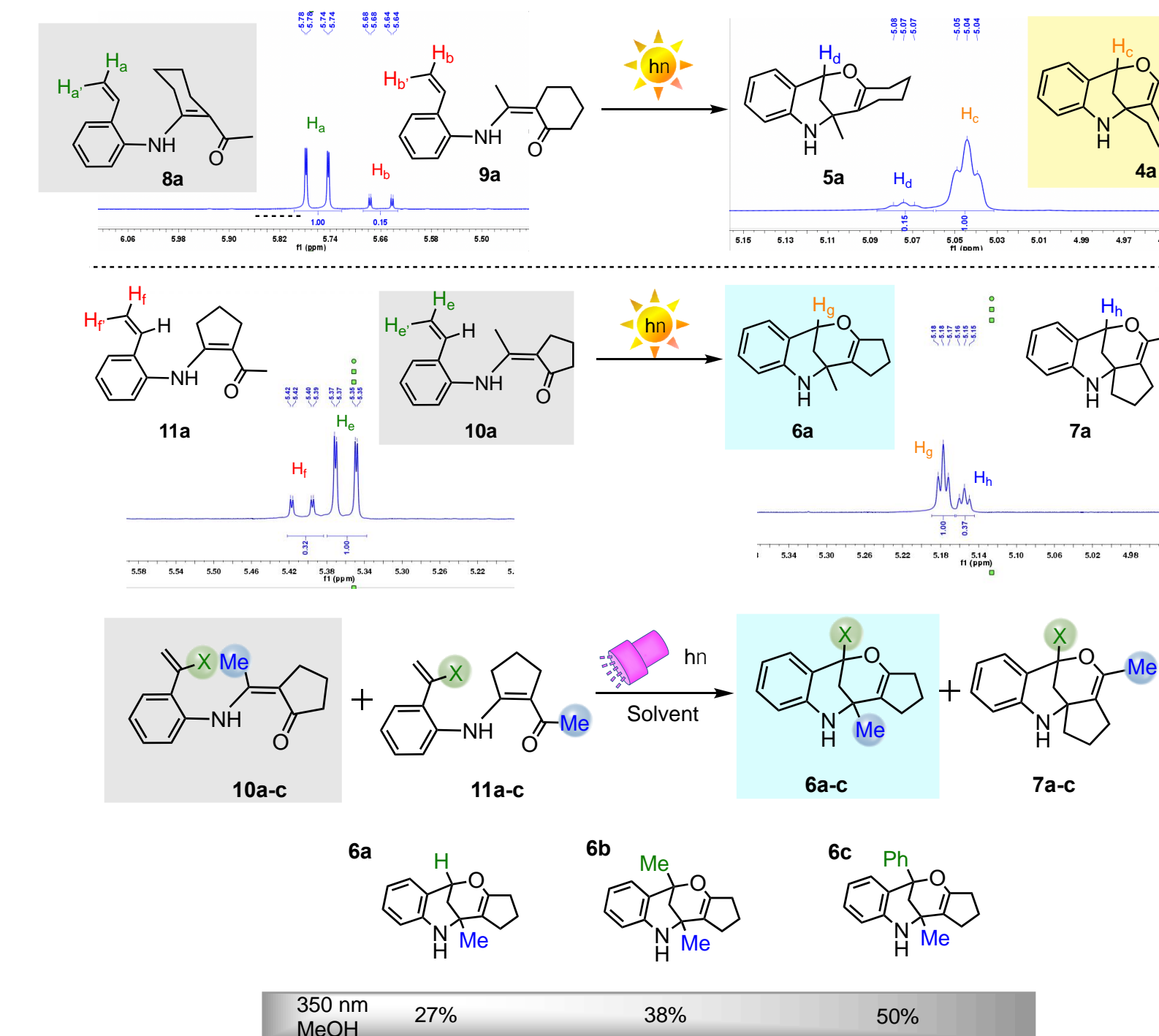


## Synthesis of photoreaction precursors

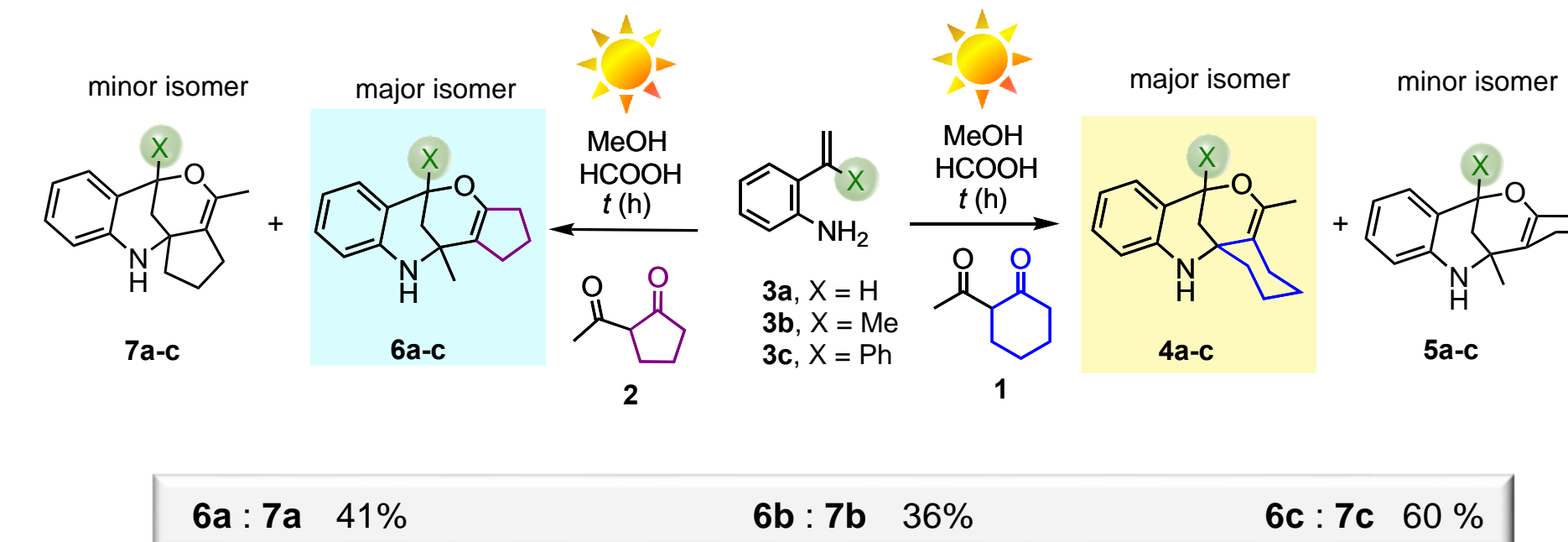


## Photoreaction of enaminone

- The vinylic hydrogens were used as an NMR handle to gauge the *endo/exo* cyclic enaminones ratios (left) and the bridge head hydrogen was used as an NMR handle to determine the ratio of the isomeric photoproducts (right).



## One pot reaction



## Temperature and solvent effects on photoreaction

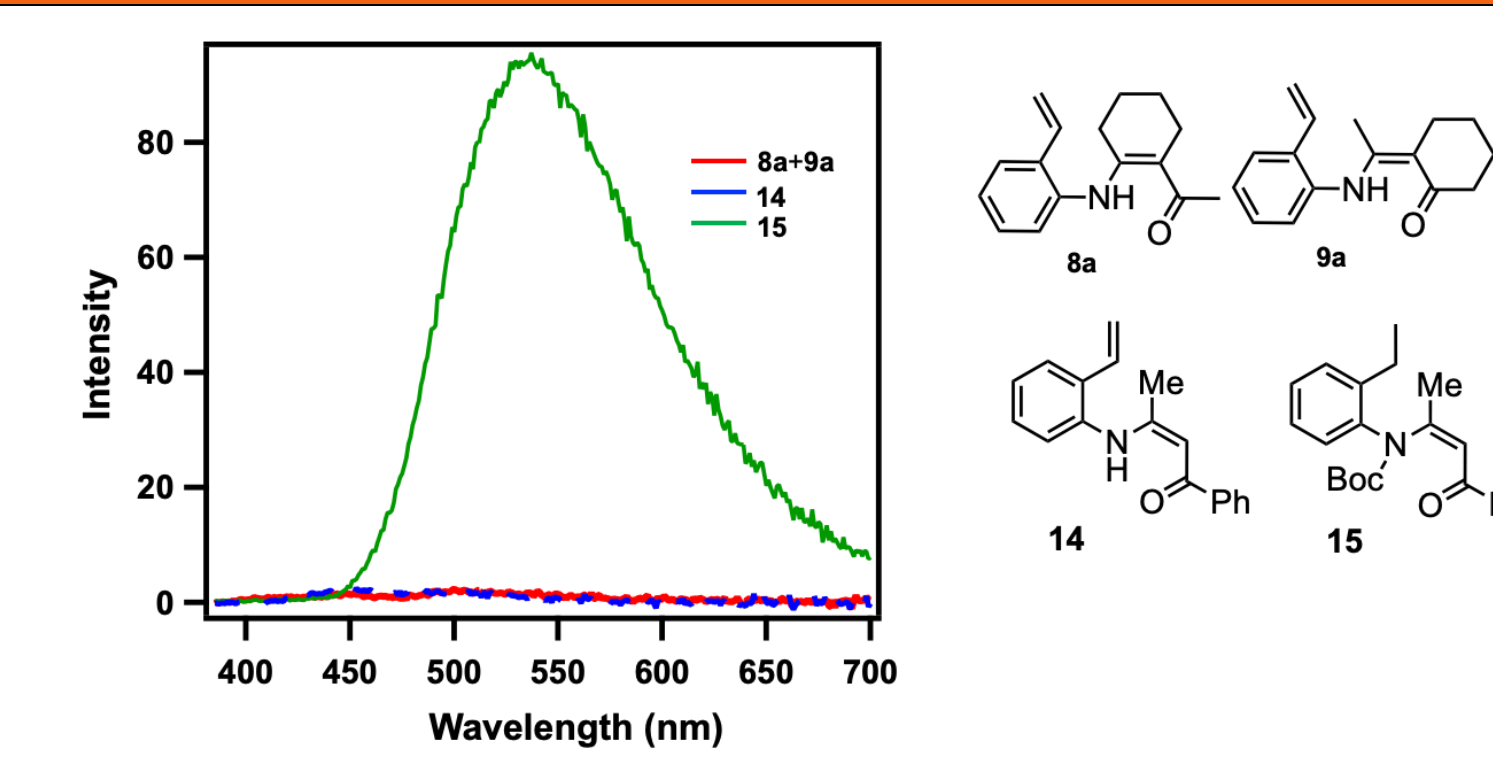
- In the case of photoreaction of 2-acetylcyclohexanone 1 with 3a, the ratio of the minor photoproduct 5a increased upon lowering the temperature in all the investigated solvents

Entry	Reactants	Solvents	T °C	Ratio of isomers (4a:5a) <sup>a</sup>
1	1 + 3a	MeOH	rt	1:0.15
2			-20	1:0.55
3		MeCN	60	1:0.33
4			rt	1:0.31
5			-20	1:0.50
6		Toluene	60	1:0.33
7			rt	1:0.43
8			-20	1:0.63

- The photoreactivity of 2-acetyl-cyclopentanone 2 with *o*-vinylaniline 3a did not show significant temperature dependence in all the investigated solvents

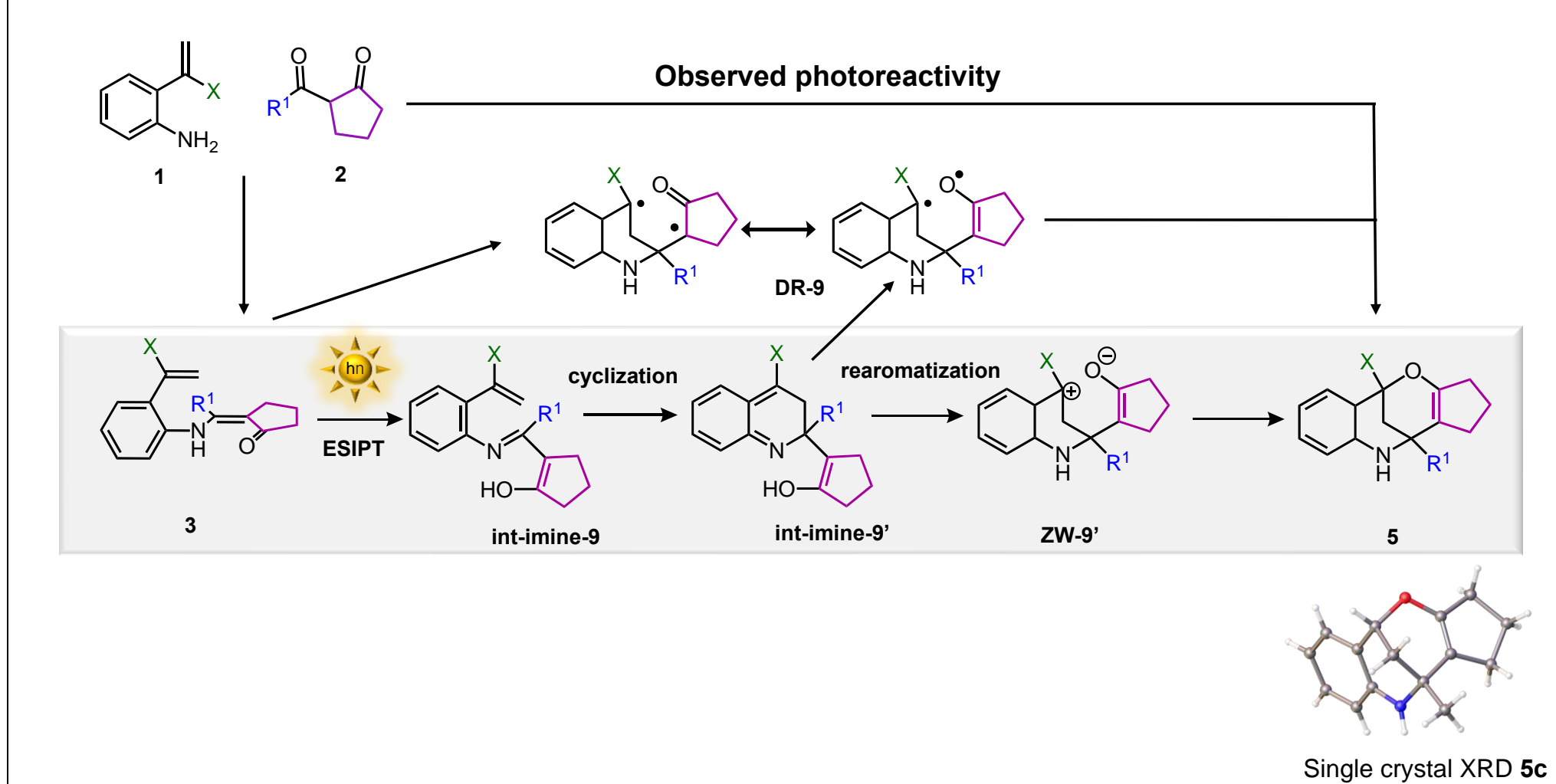
Entry	Reactants	Solvents	T °C	Ratio of isomers (6a:7a) <sup>a</sup>
1	2 + 3a	MeOH	60	1:0.13
2			rt	1:0.20
3			-20	1:0.08
4		MeCN	60	1:0.16
5			rt	1:0.17
6			-20	1:0.20
7		Toluene	60	1:0.16
8			rt	1:0.40
9			-20	1:0.15

## Photophysical studies



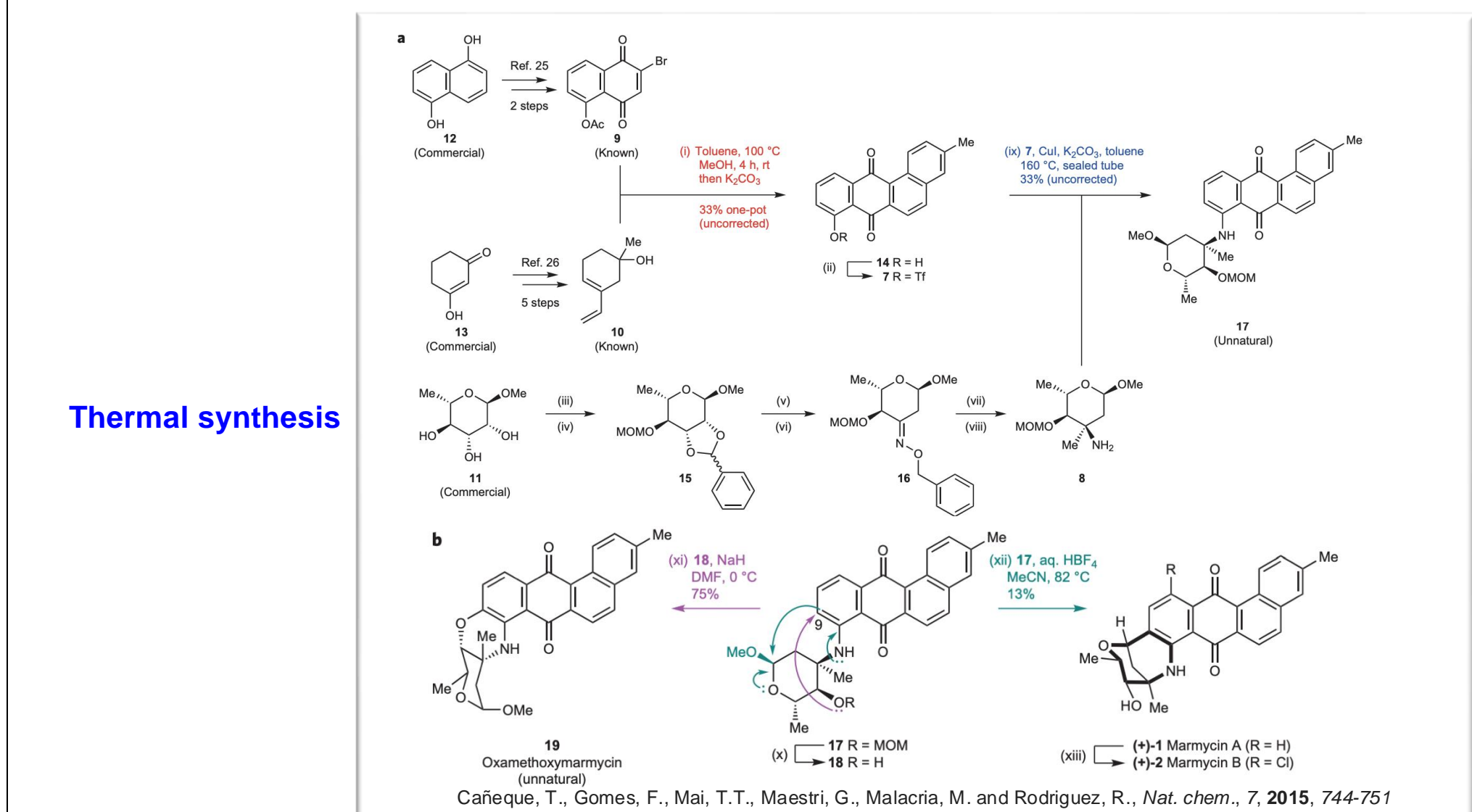
- Phosphorescence of cyclic  $\beta$ -enaminones 8a/9a in EtOH at 77 K. For comparison of the luminescence, the emission of acyclic  $\beta$ -enaminones 14 and 15 is provided.
- Even at 77K in frozen ethanol matrix only weak phosphorescence was observed for enaminone 8a/9a indicating a fast deactivation of its excited state.

## Proposed mechanism for this reaction



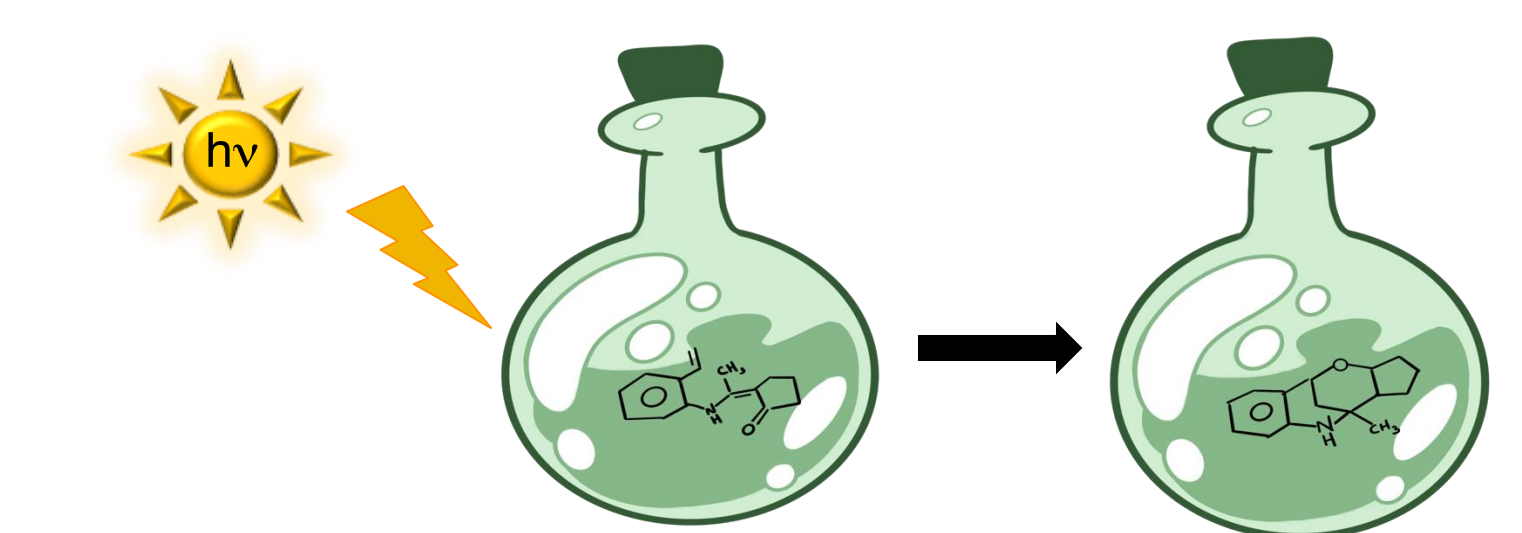
## Photochemical vs Thermal synthesis of Marmycin

- Marmycins are synthesized by multistep thermal reactions.



## Conclusion

- $\beta$ -enaminones can be utilized for accessing photoproducts in which the ring system in the enaminone size (hexa- vs. penta-cyclic system) dictates the mode of photochemical reactivity.
- Further efforts are underway in our lab to exploit this phenomenon to tailor excited-state reactivity.



## Acknowledgments



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