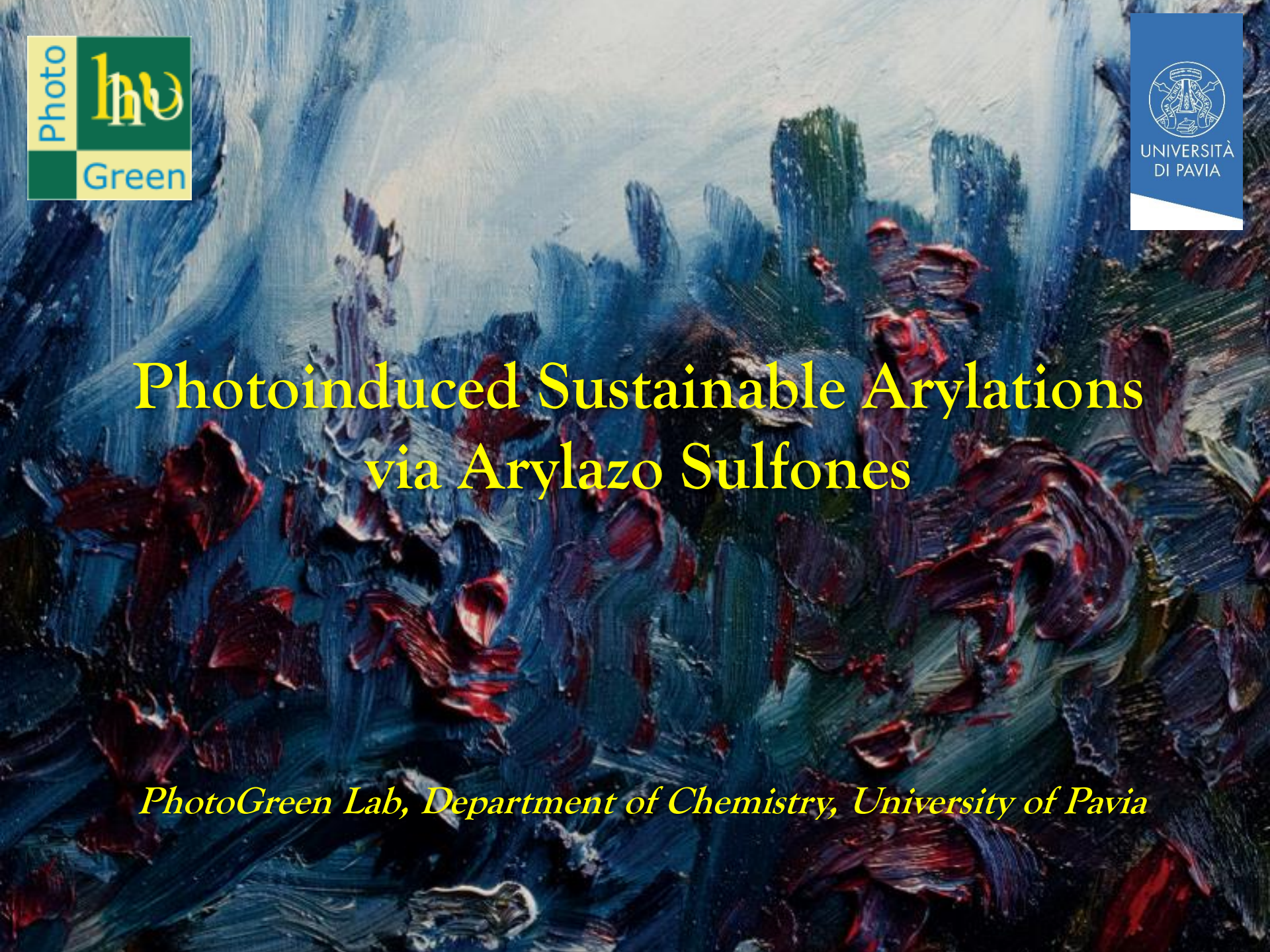
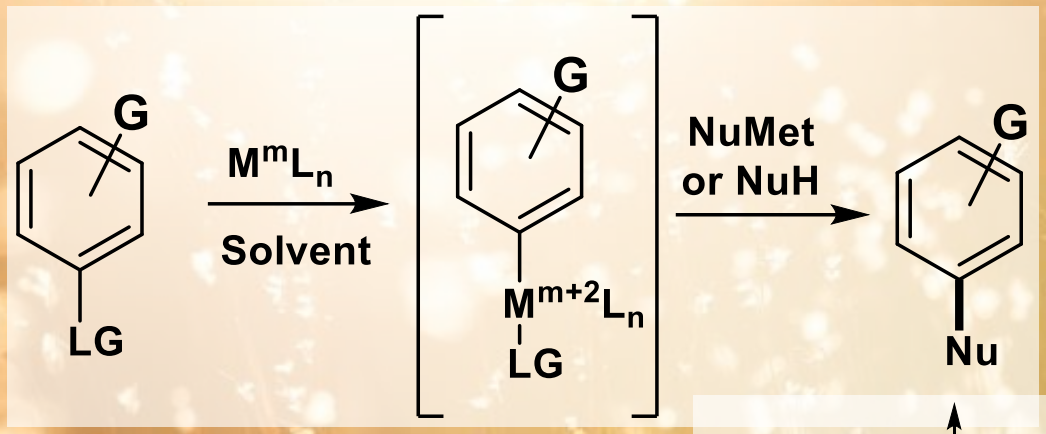


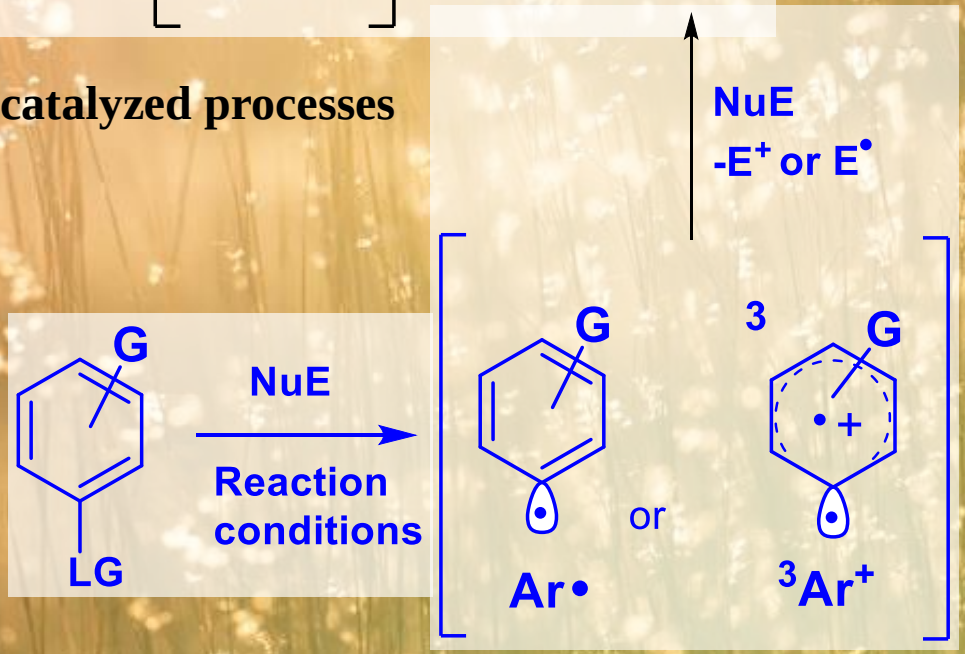
Photoinduced Sustainable Arylations via Arylazo Sulfones

PhotoGreen Lab, Department of Chemistry, University of Pavia

Arylation reactions

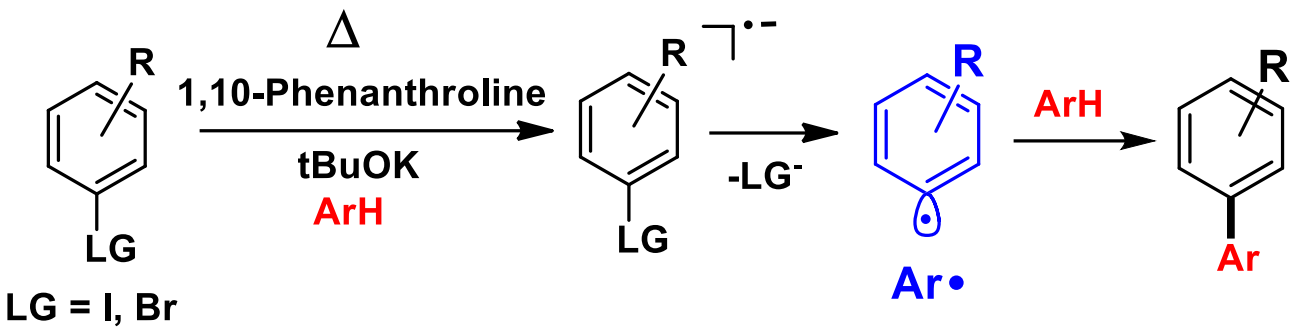


Transition metal catalyzed processes

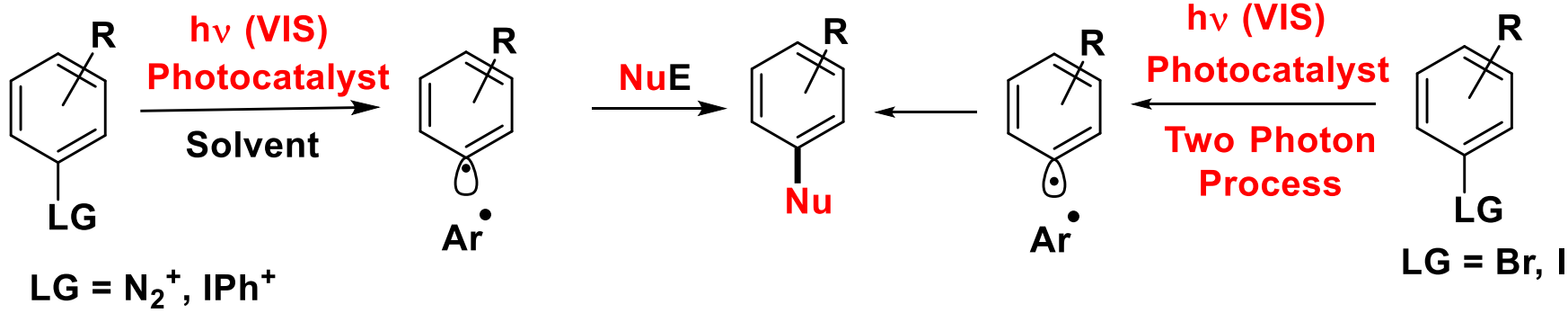


Metal-free arylations

Metal-free arylations

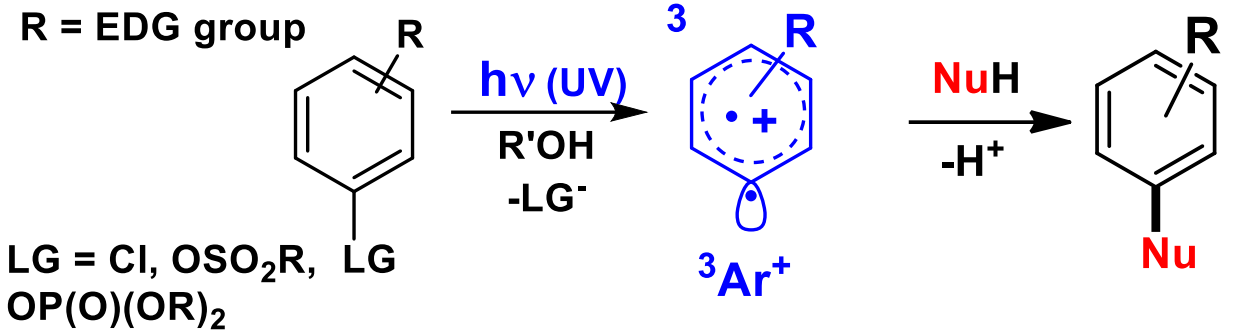


S. Yanagisawa, K. Itami, *ChemCatChem* **2011**, *3*, 827.

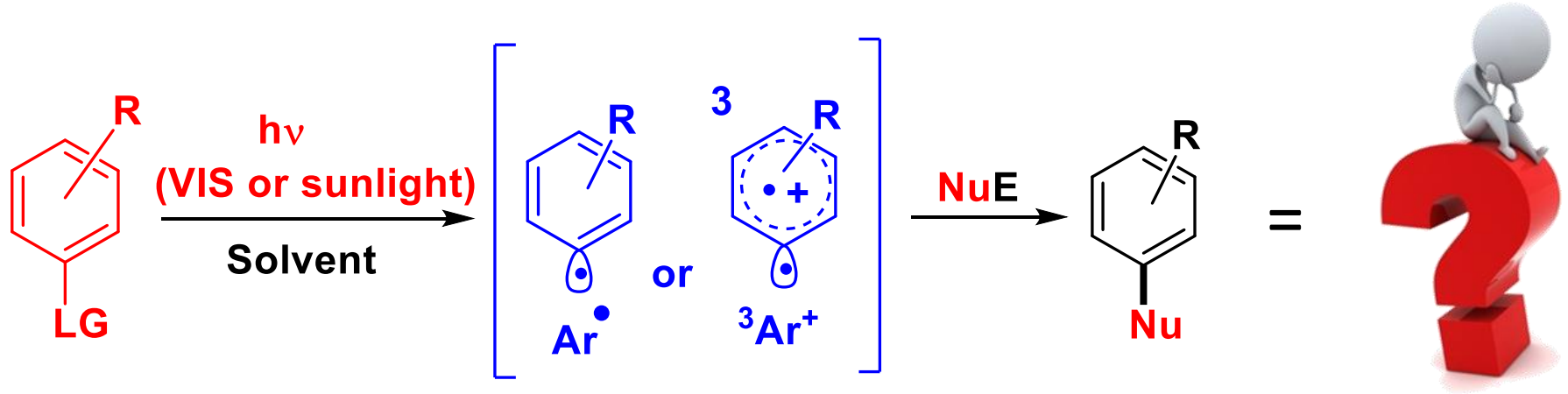


I. Ghosh, L. Marzo, A. Das, R.Shaikh, B. König, *Acc. Chem. Res.* **2016**, *49*, 1566; I. Ghosh, T. Ghosh, J. I. Bardagi, B. König, *Science* **2014**, *346*, 725

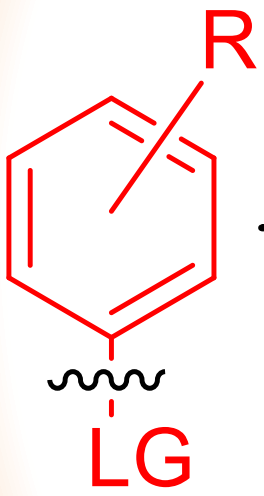
Metal-free arylations



C. Raviola, D: Ravelli, S. Protti, A. Albini, M. Fagnoni, *Synlett* **2015**, 471



(Solar) Metal-free arylations



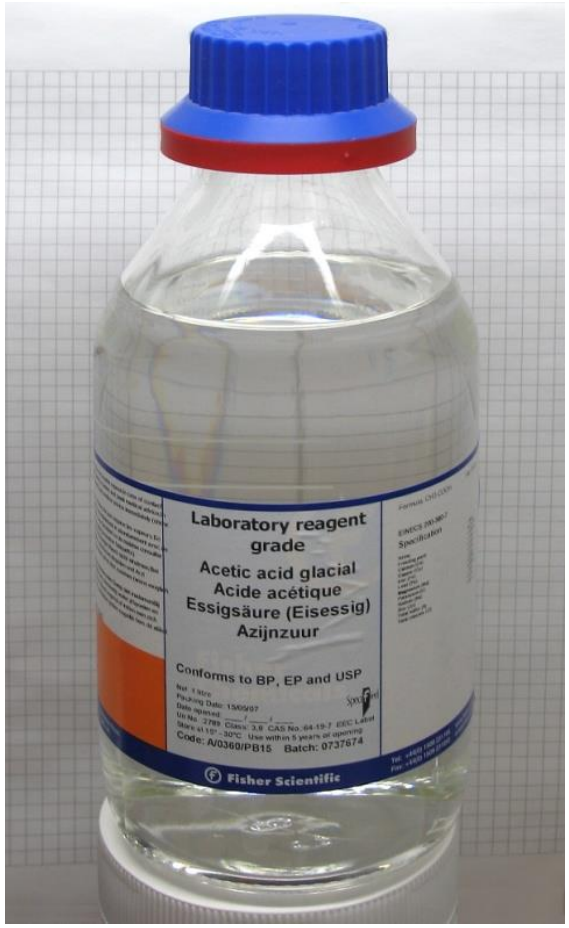
Thermal stability

Photolabile Ar-LG bond

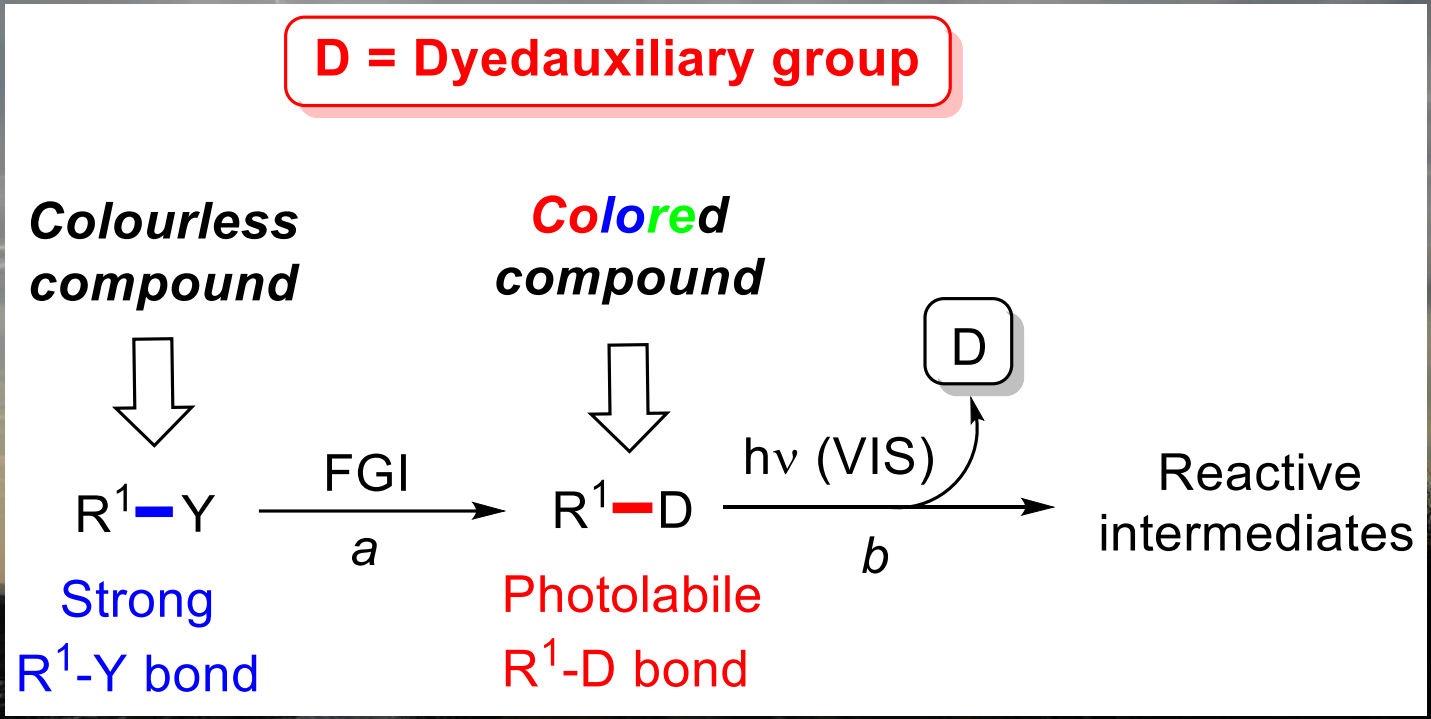
Significant absorption in the sunlight emission spectrum

Reaction mechanism independent from the nature of the aromatic ring.

Organic compounds:
colorless liquids and white solids !



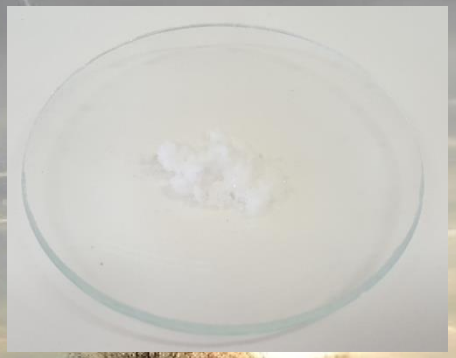
Dyedauxiliary group: the concept

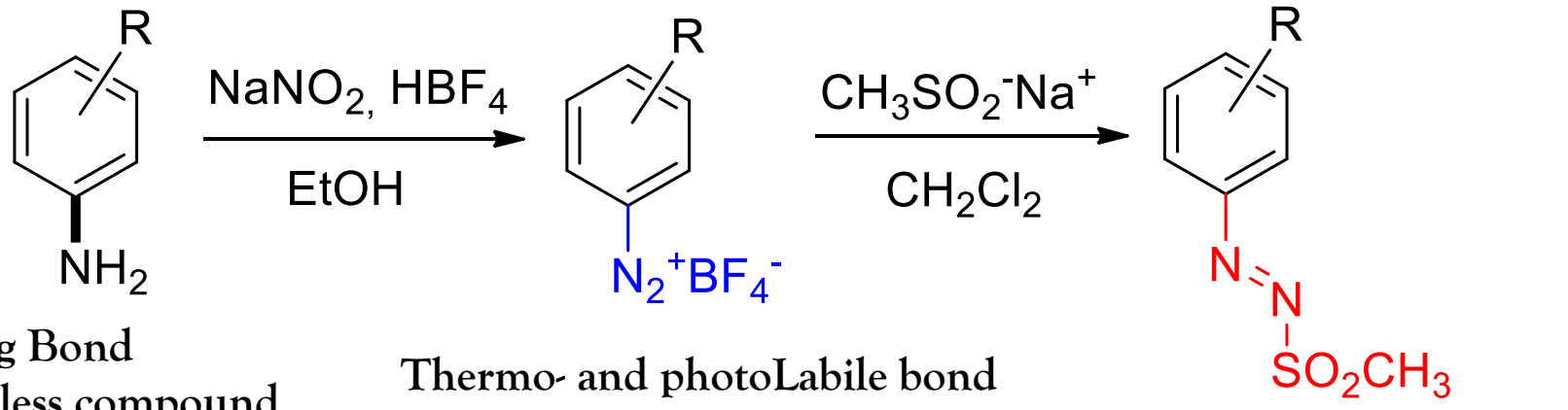


Effects imparted by the dyedauxiliary group:

1- Makes the compound colored
2- Makes the R-D bond labile
3- Makes the compound photoreactive

Azosulfones: a New Dyedauxiliary Group



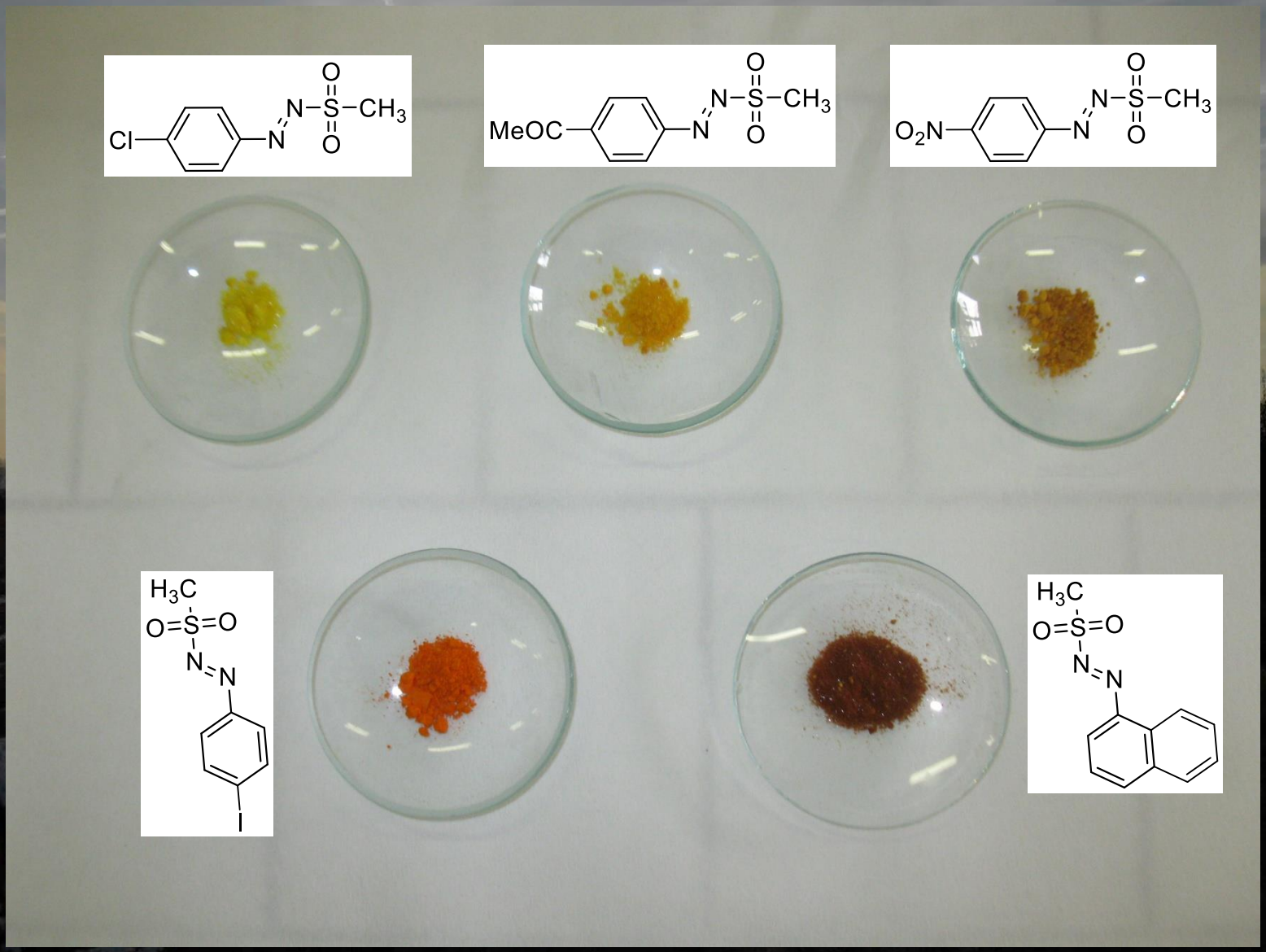


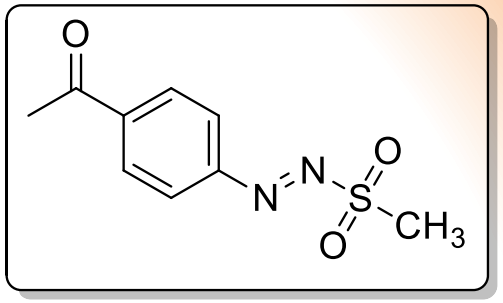
Strong Bond
Colorless compound

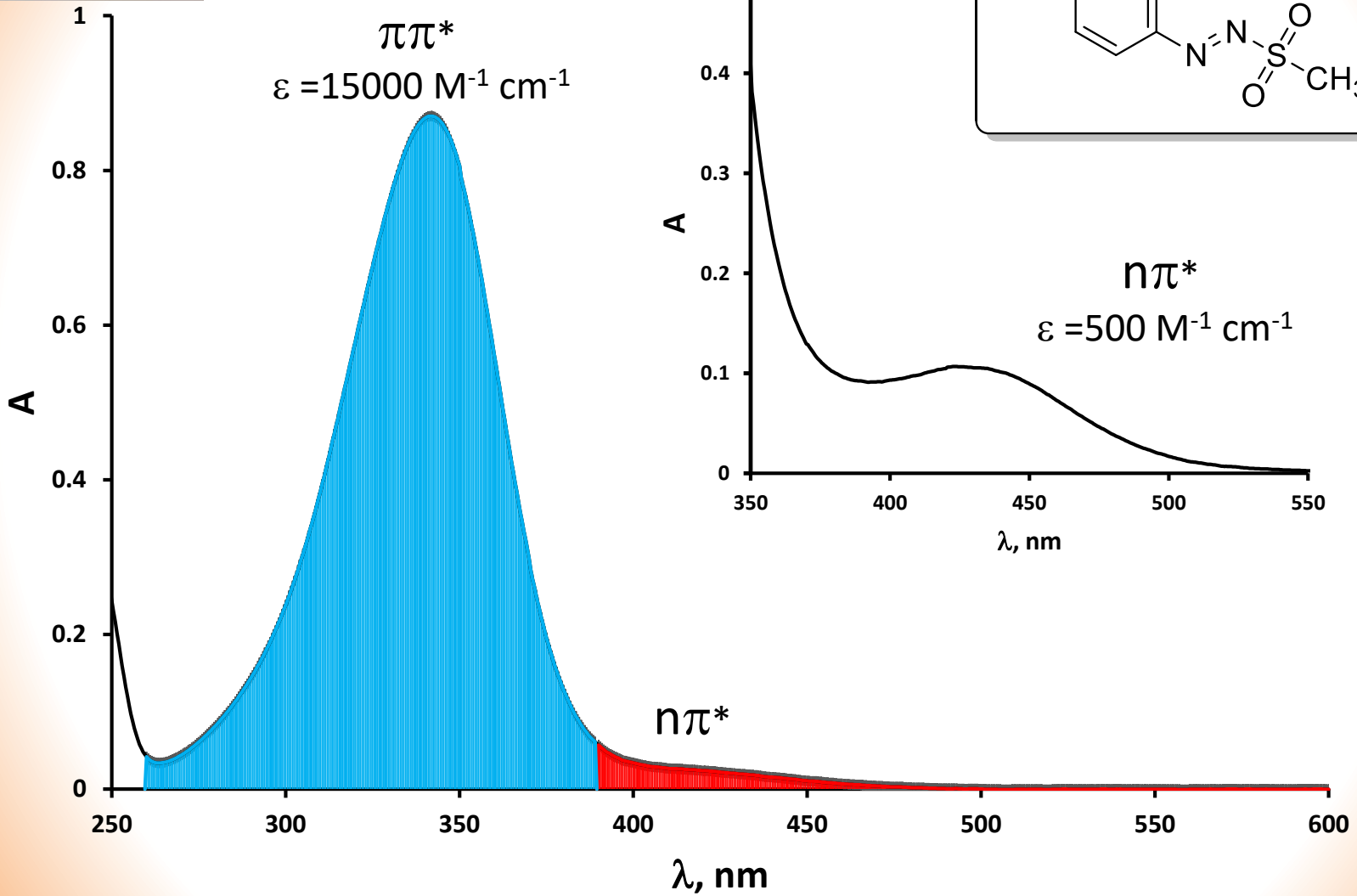
Thermo- and photoLabile bond
Colorless compound

PhotoLabile moiety
Colored compound

Different structure, different color.....

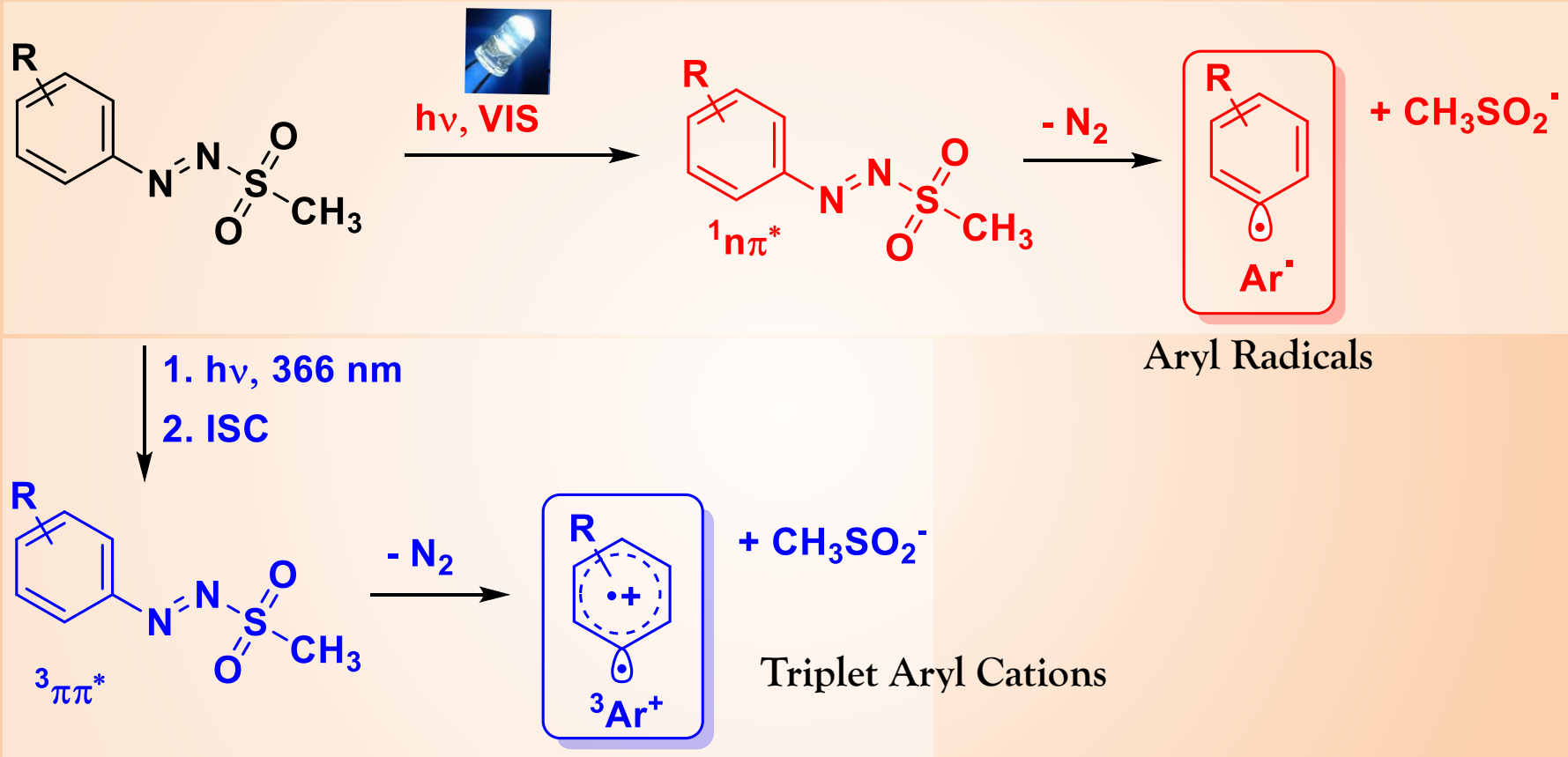






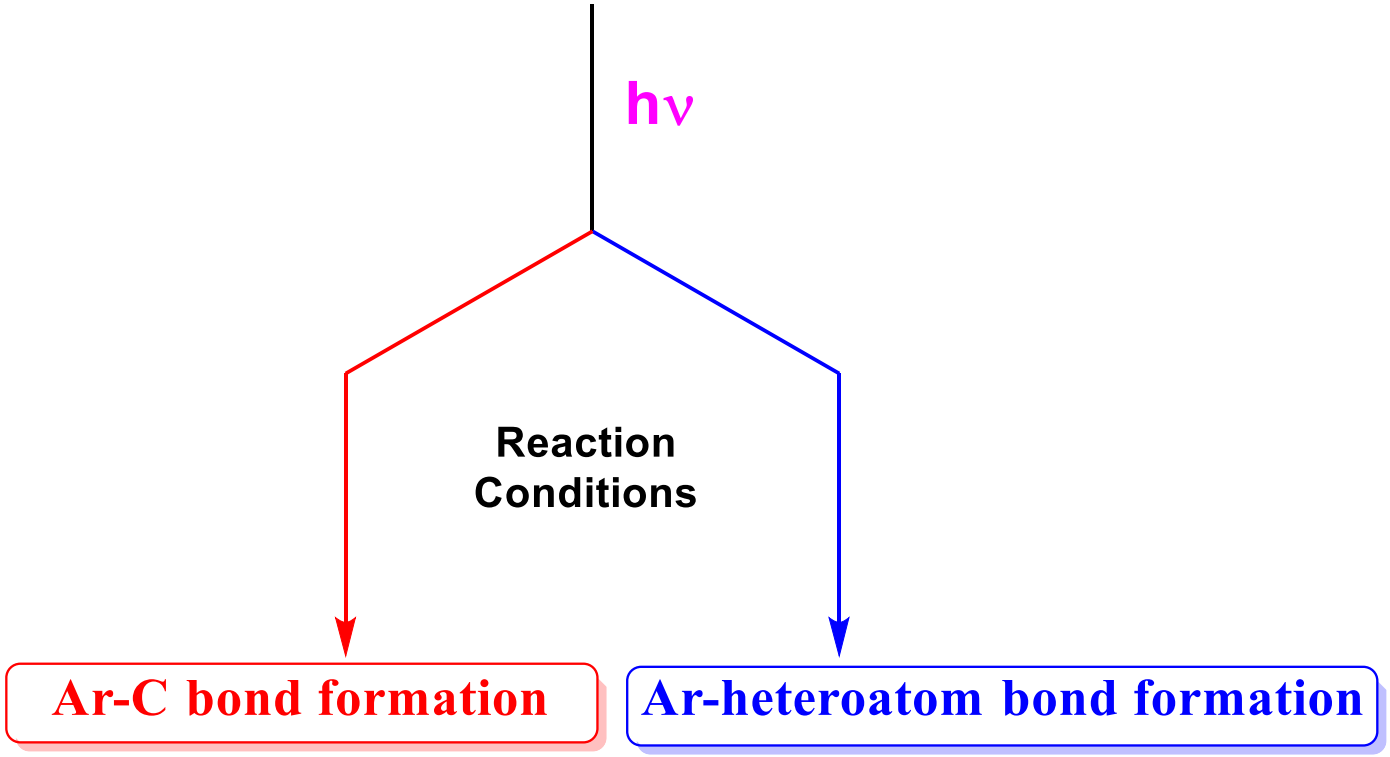
S. Crespi, S. Protti, M. Fagnoni, *J. Org. Chem.* **2016**, *81*, 9612.

A wavelength selective reactivity

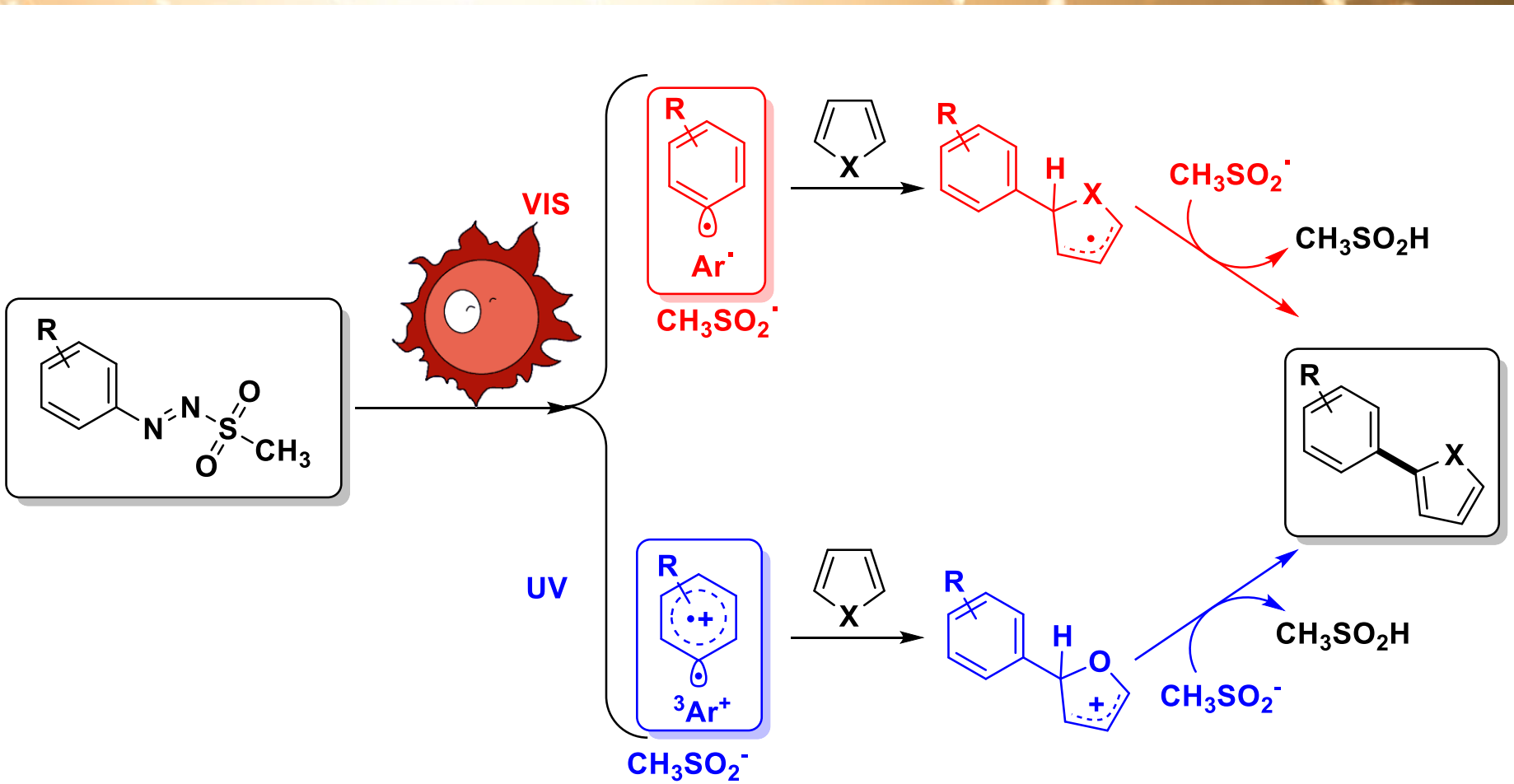


S. Protti, D. Ravelli, M. Fagnoni, *Photochem. Photobiol. Sci*. **2019**, DOI: 10.1039/C8PP00512E

Arylazo Sulfones: Photoactivatable Substrates For Metal-free Arylations

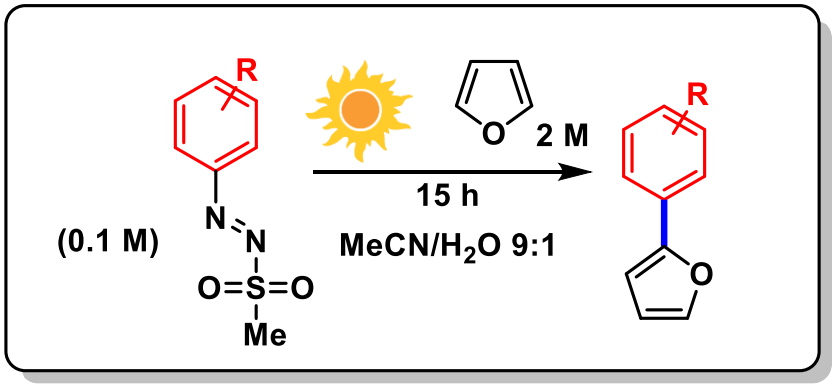


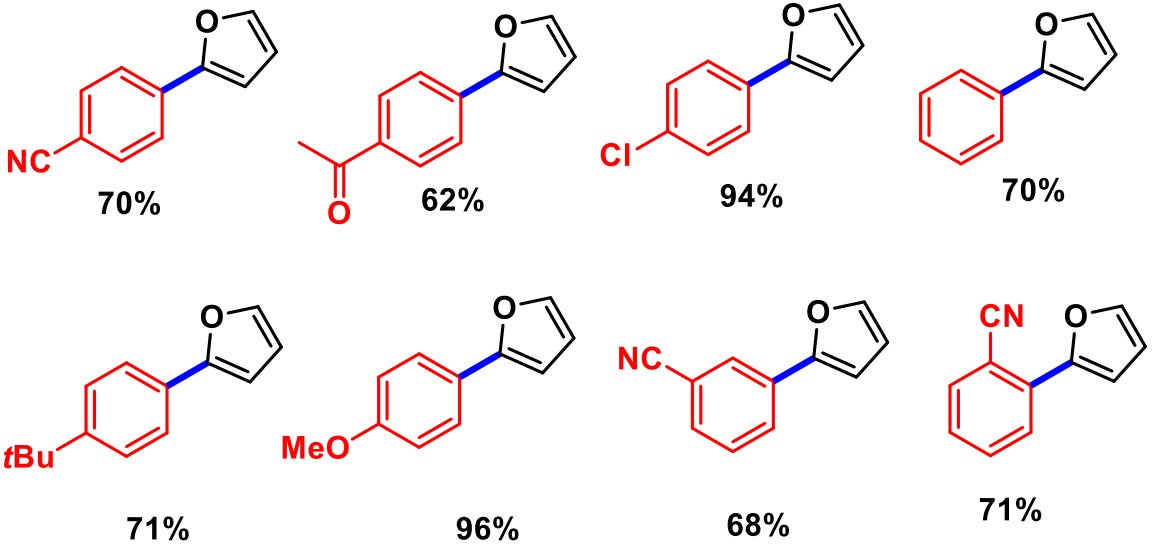
Upon solar exposition, both species are generated



S. Crespi, S. Protti, M. Fagnoni, *J. Org. Chem.* **2016**, *81*, 9612.

Solar driven arylations of azosulfones: arylation of furans

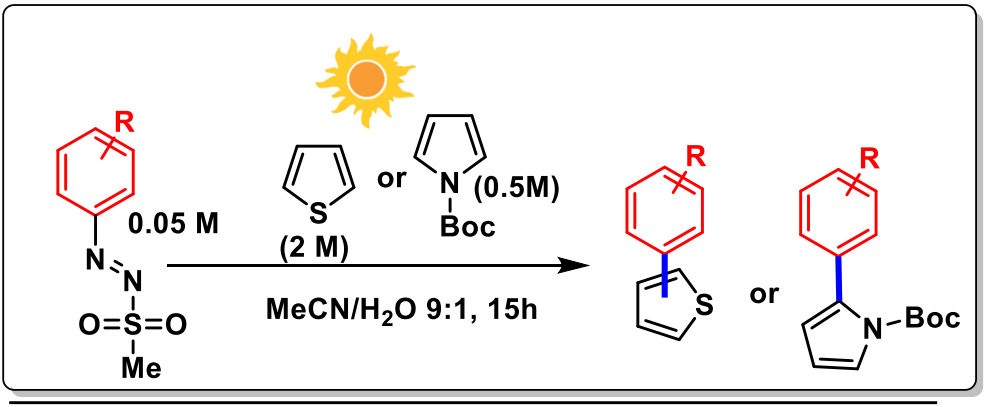


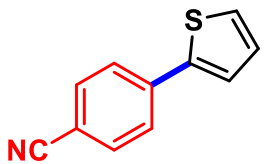


Solar box (500 W)
or Natural Sunlight

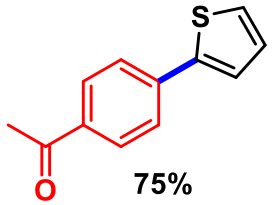
S. Crespi, S. Protti, M. Fagnoni, *J. Org. Chem.* **2016**, *81*, 9612.

Solar driven arylations of heterocycles and arenes

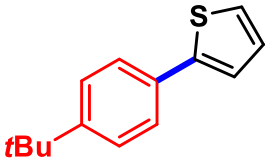




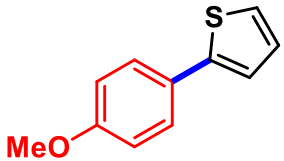
74%



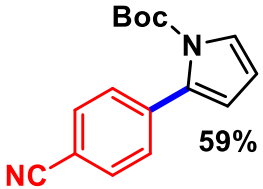
75%



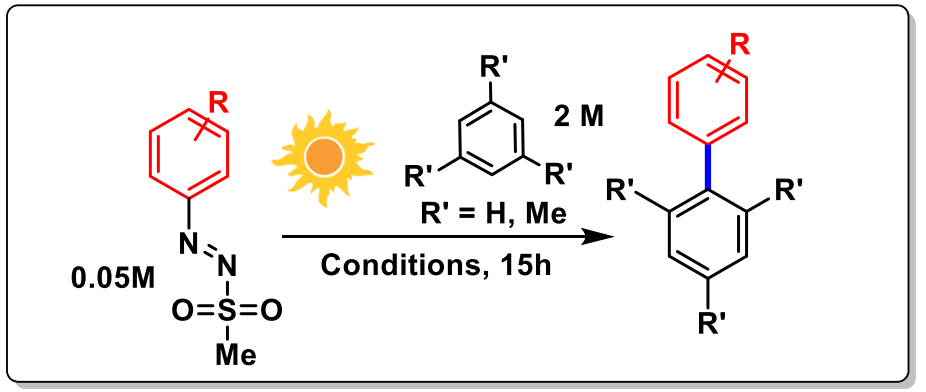
69% (27 % of tBuPh)

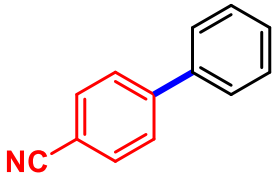


57% (27% of anisole)

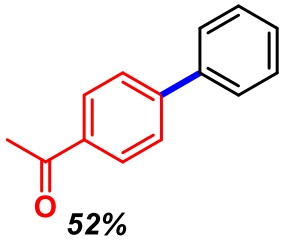


59%

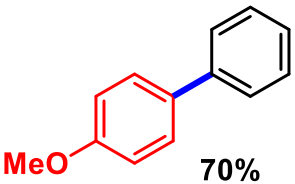




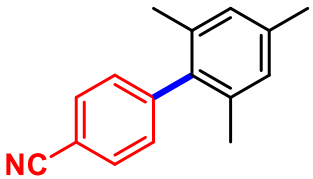
74%



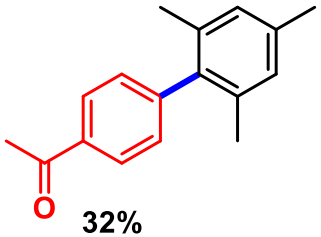
52%



70%



56%
71%

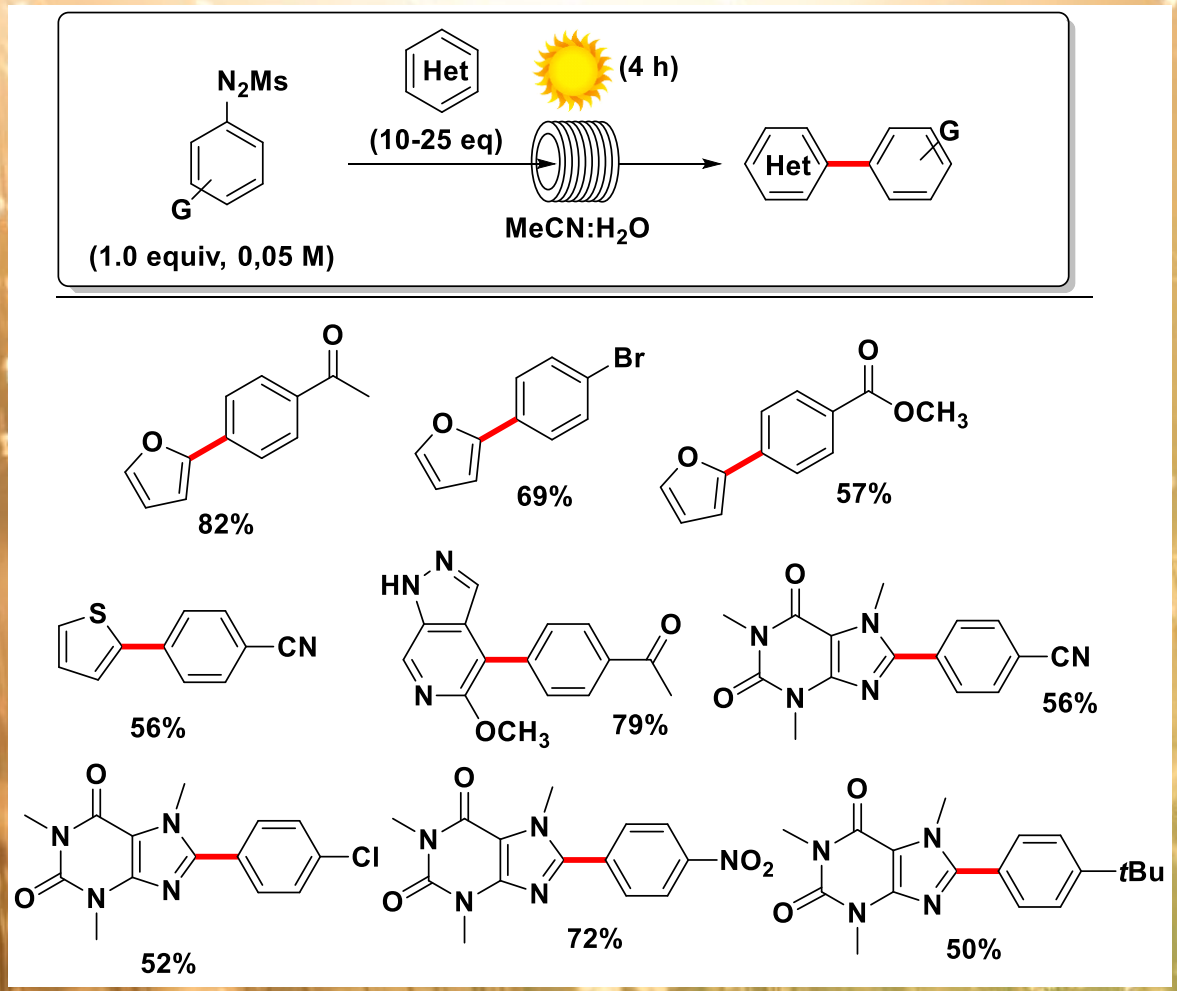


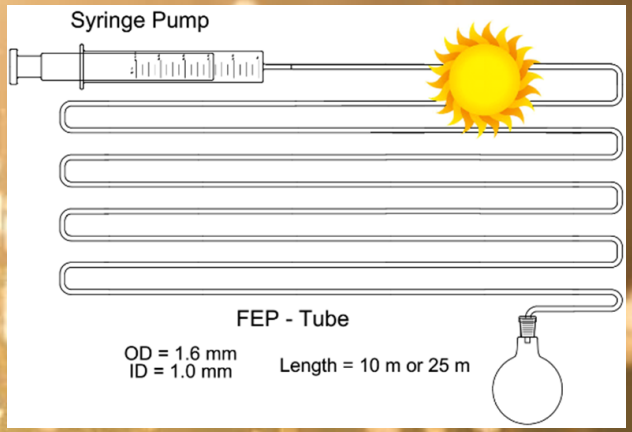
32%
73% *in neat mesytilene*

S. Crespi, S. Protti, M. Fagnoni, *J. Org. Chem.* 2016, *81*, 9612.

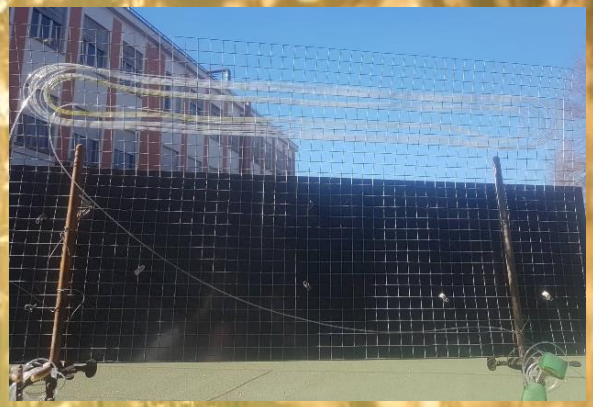
Stopped flow, solar synthesis of heteroarenes

(with prof. Till Opatz, Mainz University)



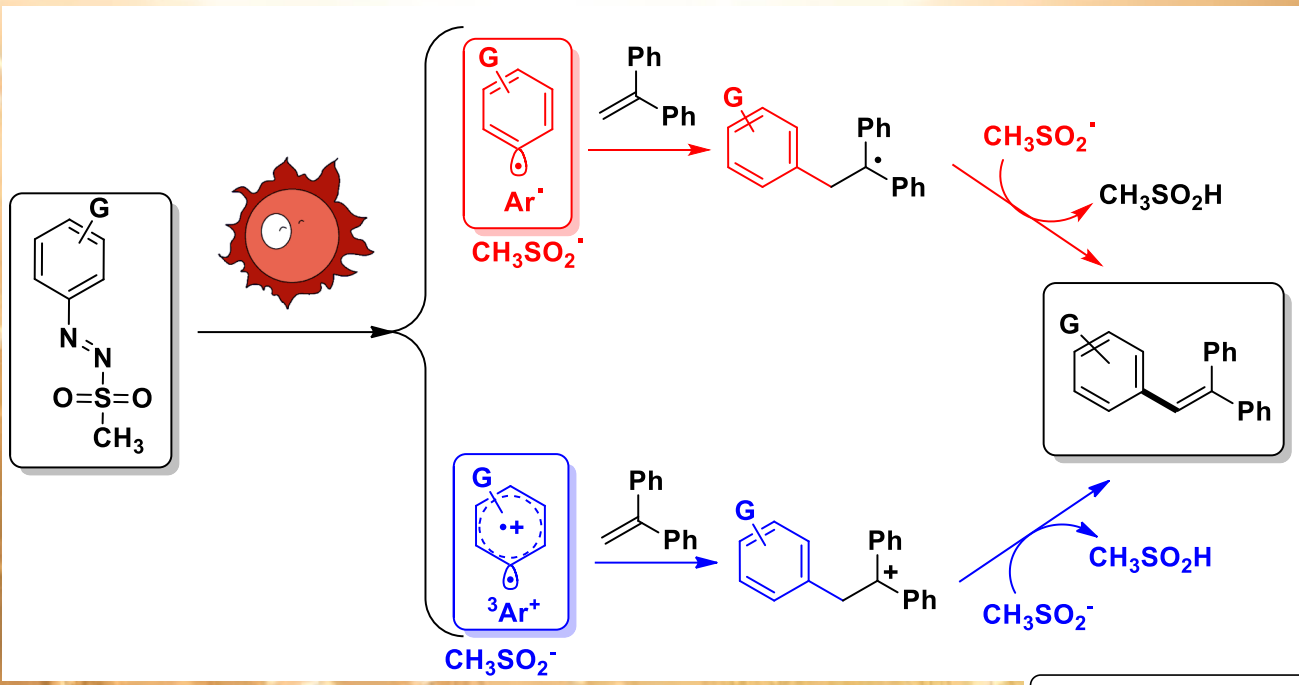


The "Sunflow" Reactor

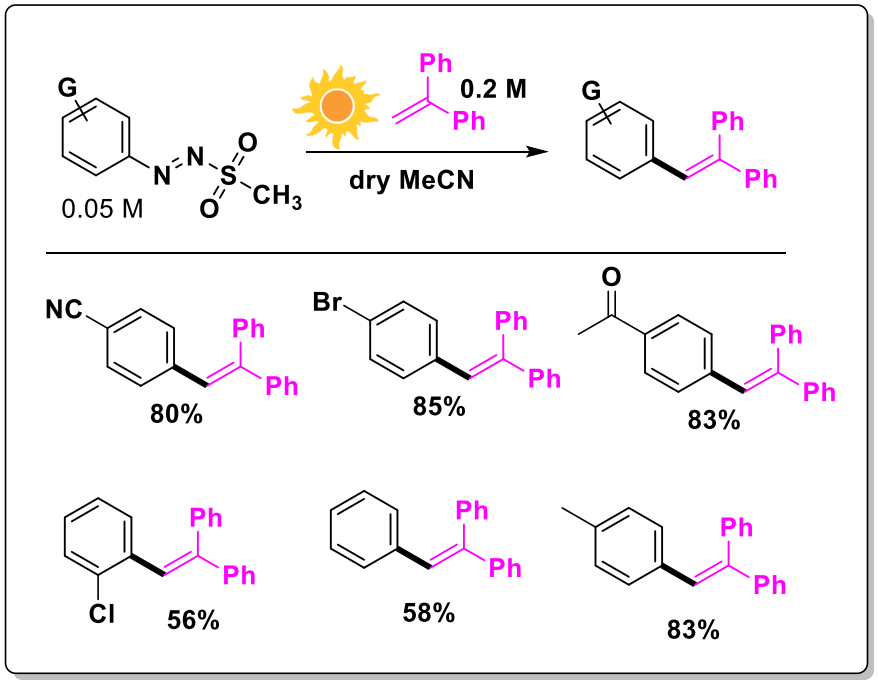


P. E. da Silva Júnior, H. I. M. Amin, A. M. Nauth, F. da Silva Emery, S. Protti, T. Opatz, *ChemPhotoChem*, 2018, *2*, 878; H. O. Abdulla, A. A. Amin, C. Raviola, T. Opatz, S. Protti, M. Fagnoni, *Eur. J. Org. Chem*. 2019, DOI: 10.1002/ejoc.201900638

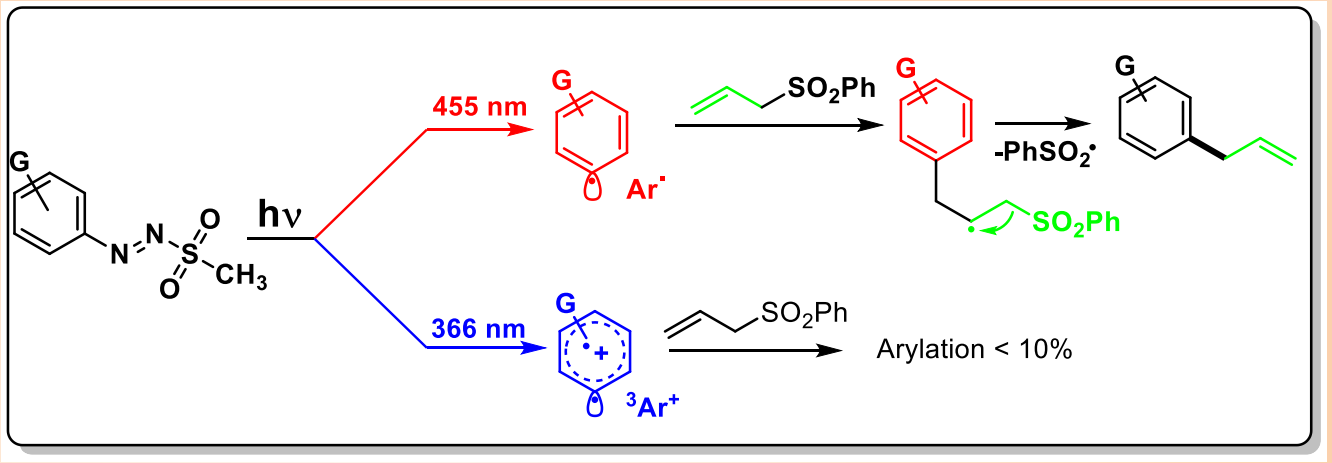
Synthesis of Triarylethylenes (TAEs)

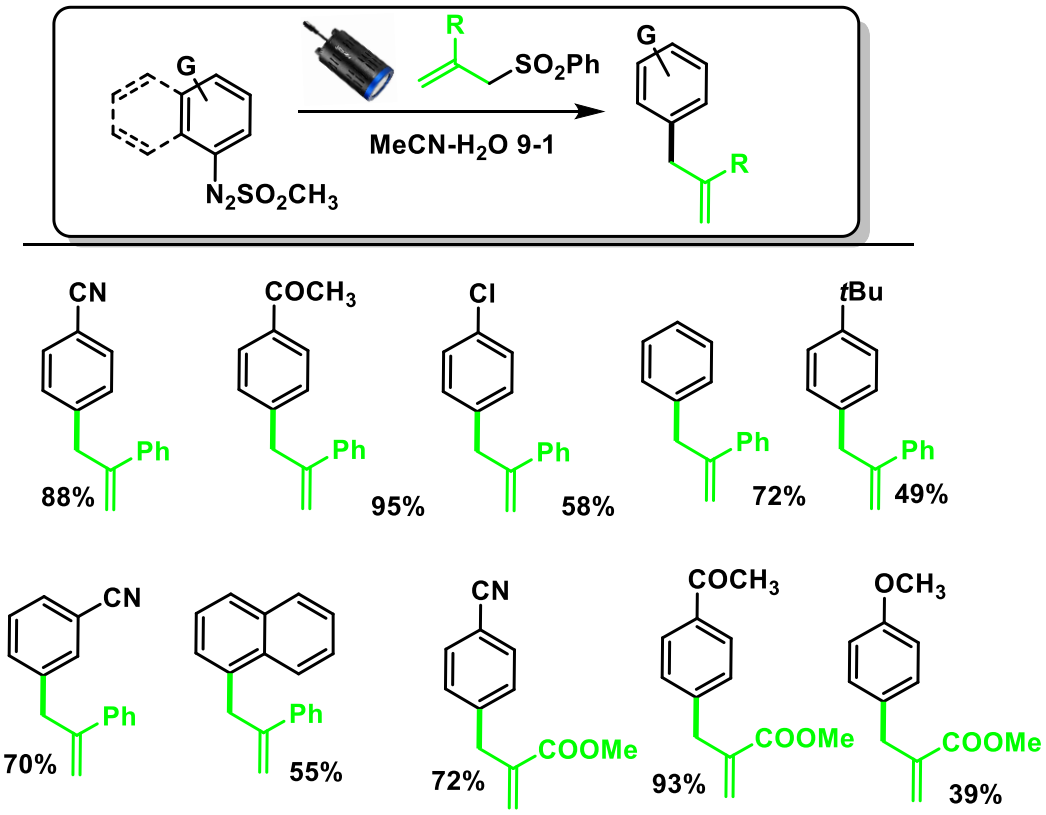


L. Onuigbo, C. Raviola, A. Di Fonzo, S. Protti, M. Fagnoni, *Eur. J. Org. Chem.* **2018**, 5297.



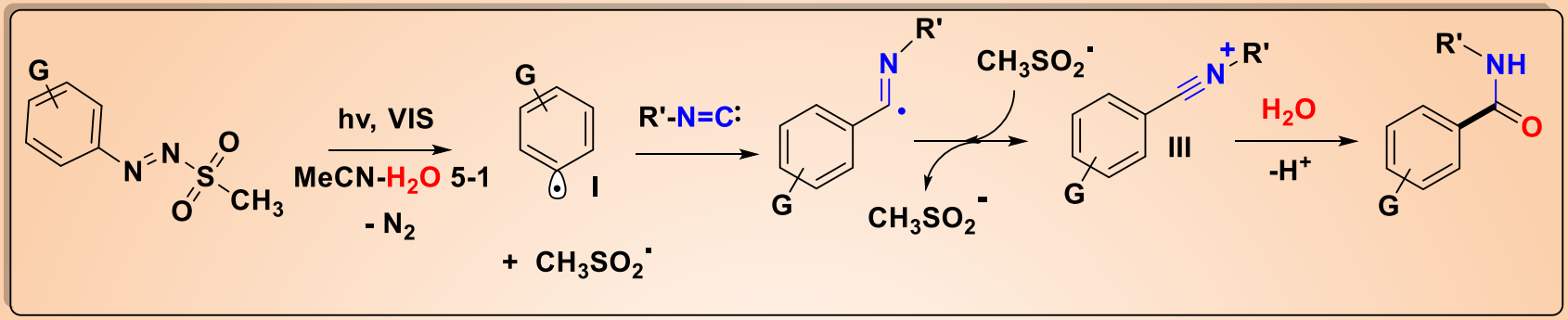
Synthesis of allylarenes upon visible light irradiation

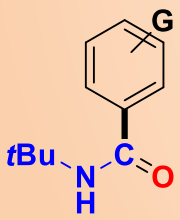




A. Dossena, S. Sampaolesi, A. Palmieri, S. Protti, M. Fagnoni, *J. Org. Chem.* **2017**, *82*, 10687

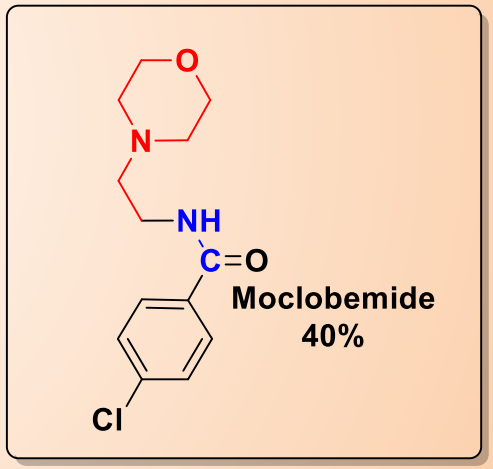
Visible light driven synthesis of aromatic amides.

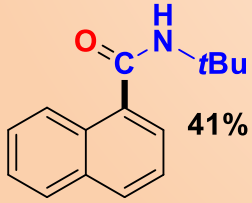




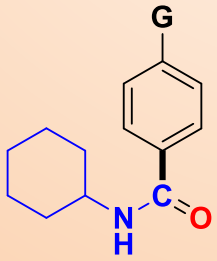
G = 4-NO_2, 98%
G = 4-CN, 70%
G = 4-OMe, 77%
G = 3-CN, 72%
G = 3-NO_2, 95%
G = 3-F, 59%

G = 4-Cl, 70%
G = 4-COOMe, 62%
G = 4- NMe_2, 38%
G = 2-CN, 71%
G = 2-Cl, 64%
G = 2,3-F, 52%





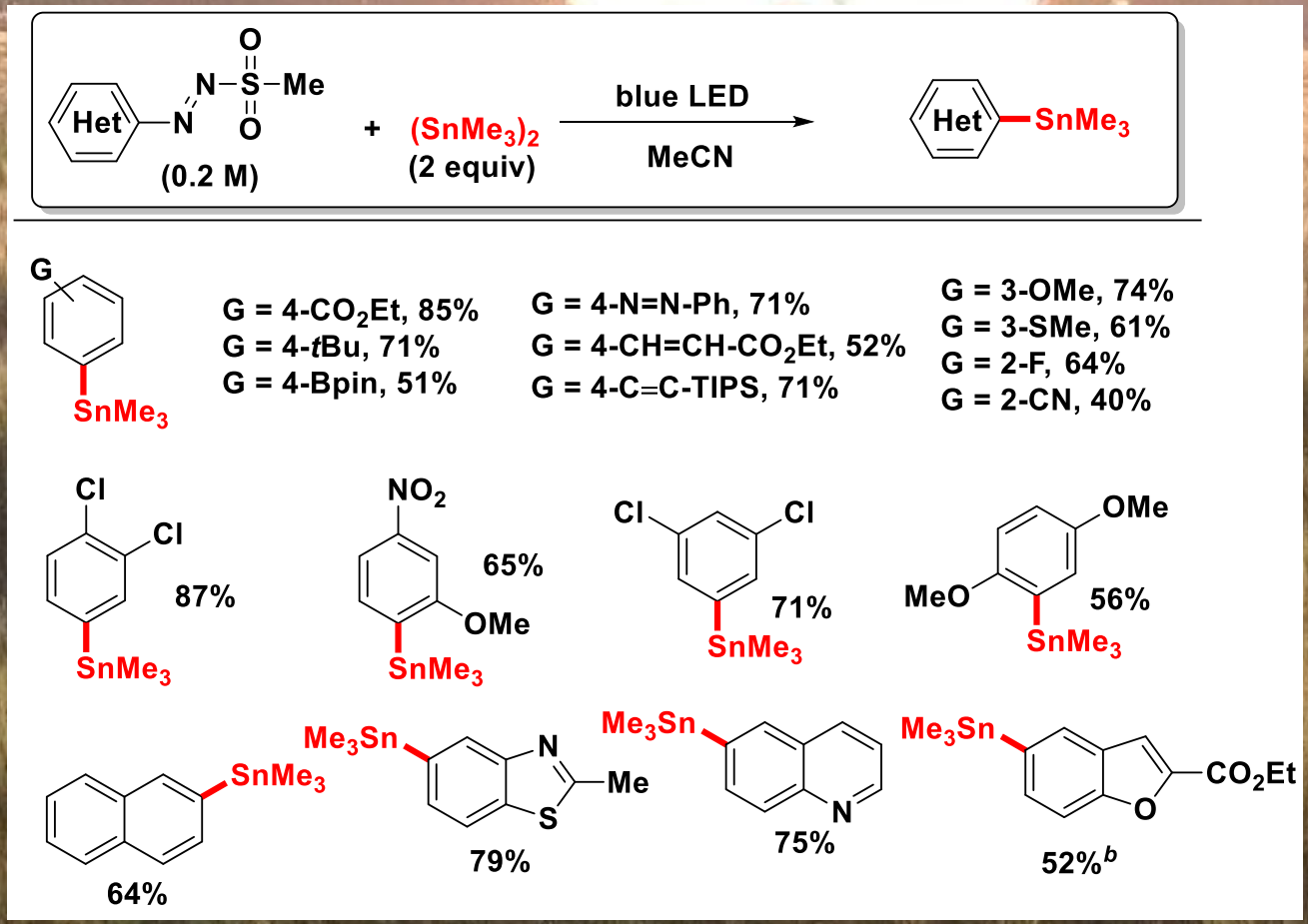
41%



G = $COCH_3$, 71%
G = NO_2, 96%
G = CN, 81%
G = OMe, 29%

M. Malacarne, S. Protti, M. Fagnoni, *Adv. Synth. Catal.* **2017**, *359*, 3826

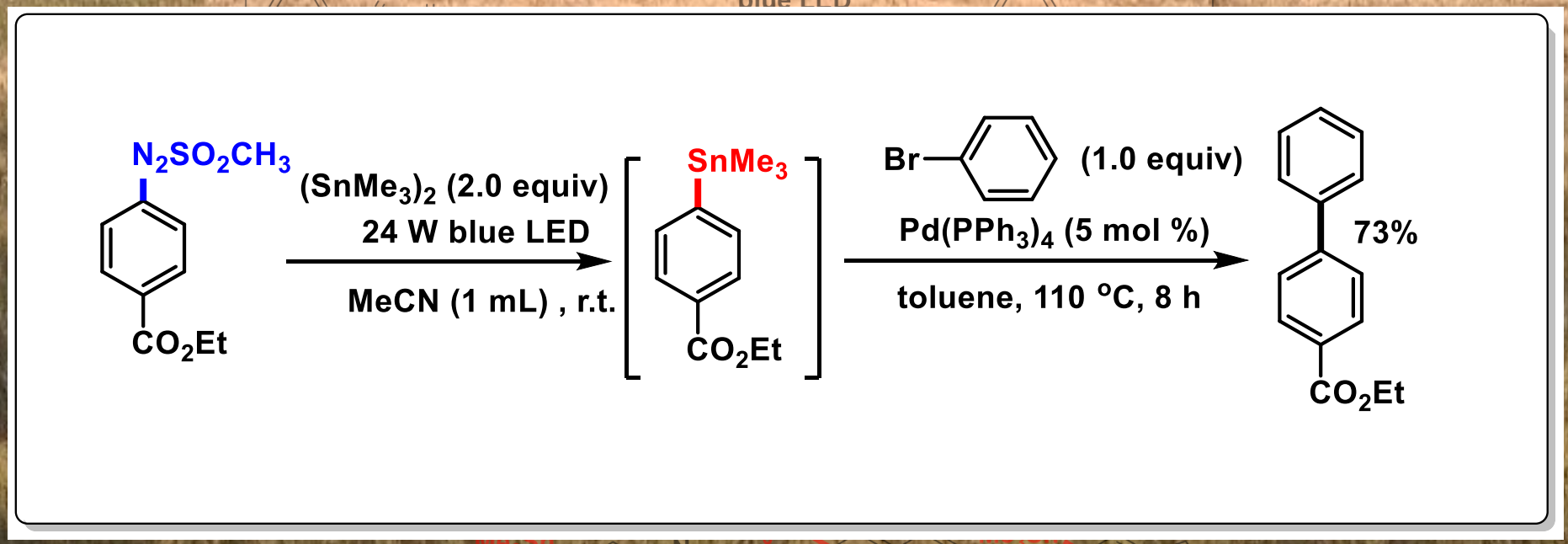
Visible-Light, transition metal-free preparation of aryl stannanes



With Prof. Di Qiu and Xia Zhao (Peking University)

C. Lian, G. Yue, J. Mao, D. Liu, Y. Ding, Z. Liu, D. Qiu, X. Zhao, K. Lu, M. Fagnoni, S. Protti, *Org. Lett.* **2019**, *21*, 5187

Visible-Light, transition metal-free preparation of aryl stannanes



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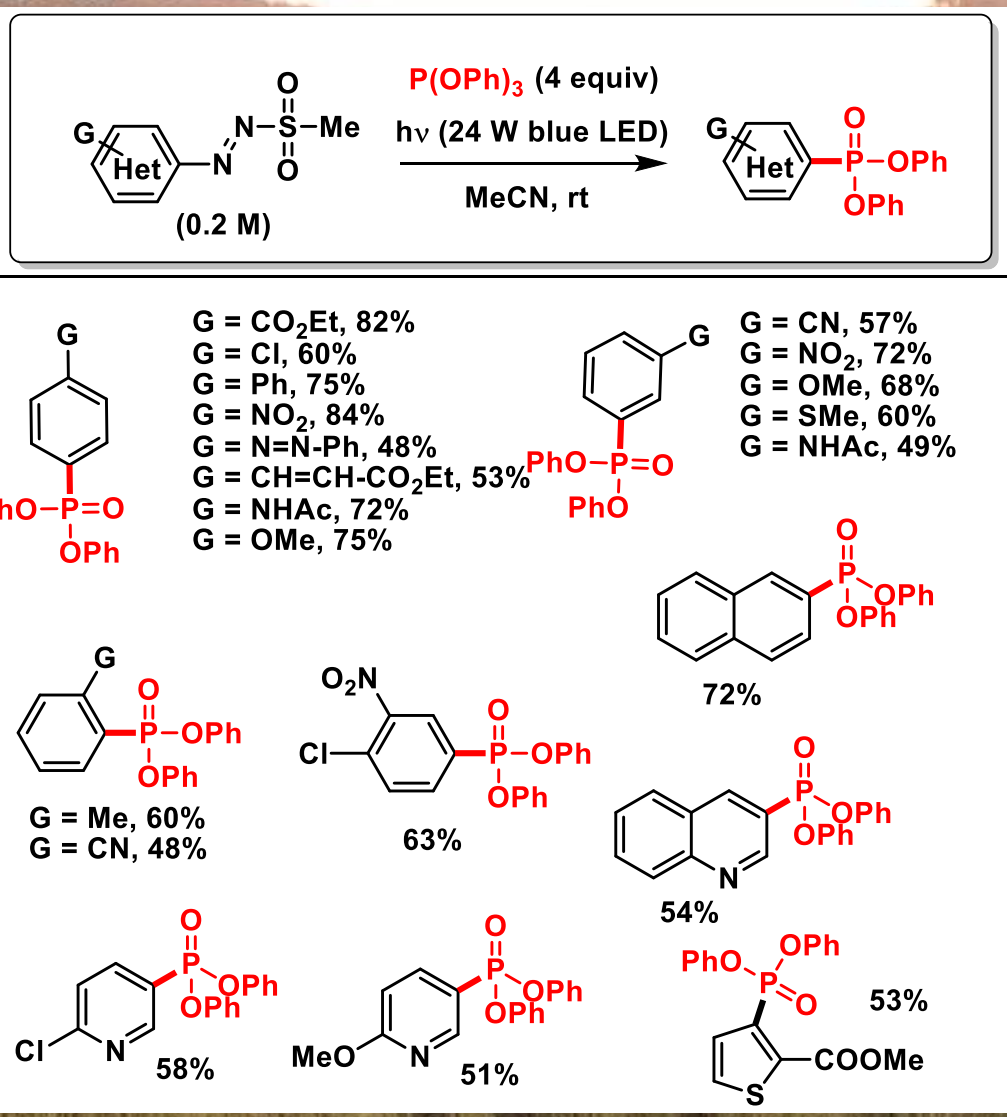
C. Lian, G. Yue, J. Mao, D. Liu, Y. Ding, Z. Liu, D. Qiu, X. Zhao, K. Lu, M. Fagnoni, S. Protti, *Org. Lett.* **2019**, *21*, 5187

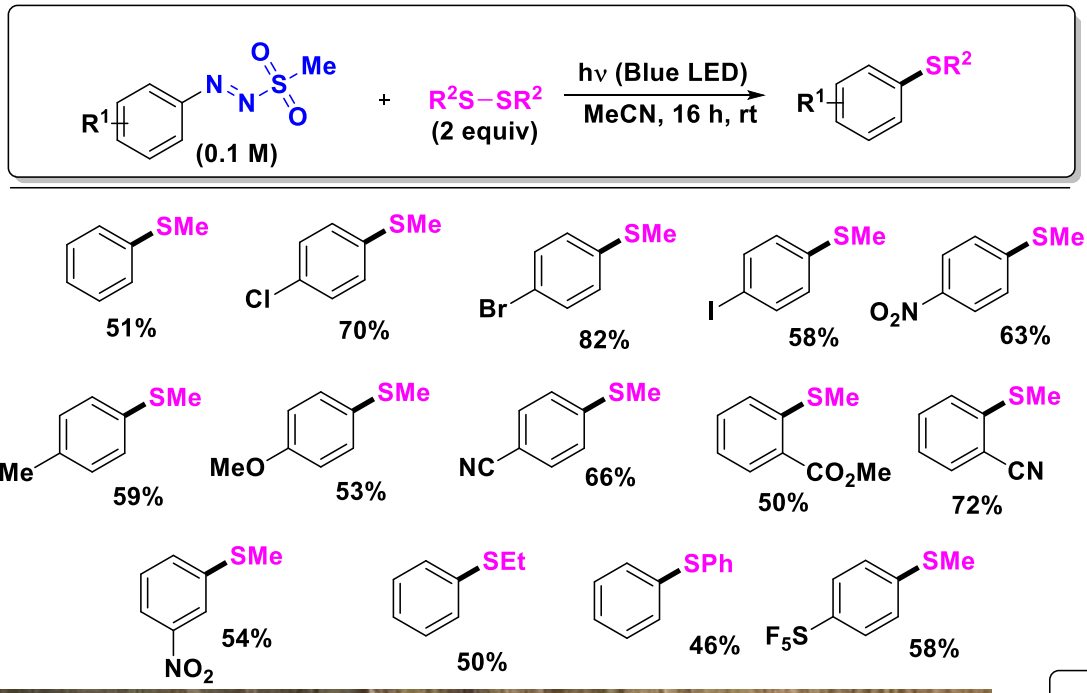
Visible-Light, transition metal-free preparation of aryl phosphonates



With Prof. Di Qiu (Peking University)

D Qiu, C. Lian, J. Mao, Y. Ding, Z. Liu, L. Wei, M. Fagnoni and S. Protti, *submitted*

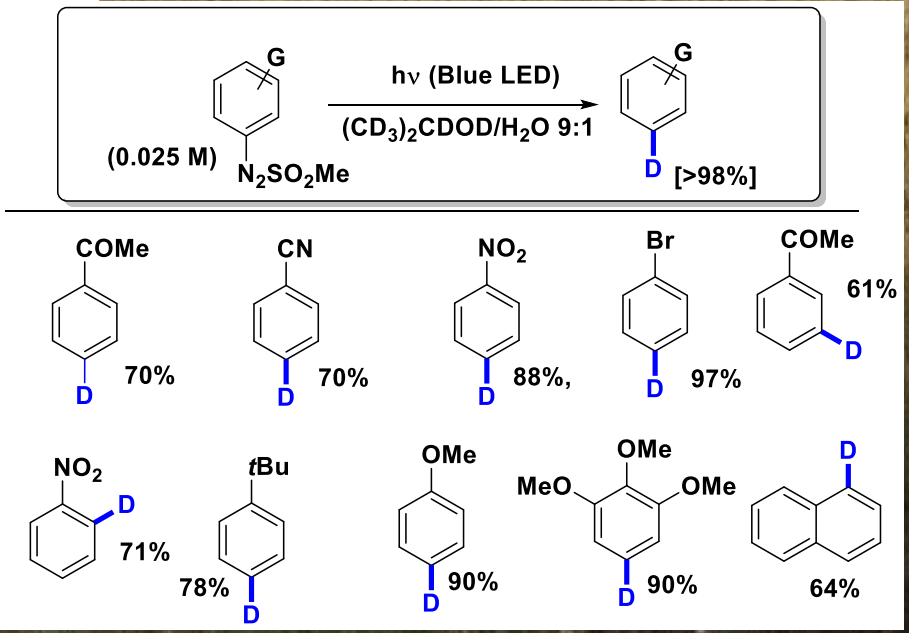
Visible-Light, transition metal-free preparation of aryl sulfides and deuterated arenes



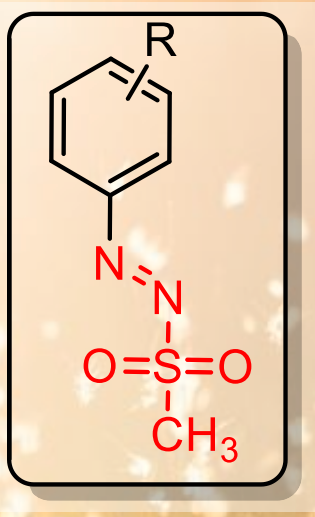
With Prof. Magnus Rueping (Kaust Catalysis Center)

L. Blank, M. Fagnoni, S. Protti, M. Rueping, *Synthesis*, **2019**, *51*, 1243.

H. I. M. Amin, C. Raviola, B. Mannucci, A. A. Amin, S. Protti, M. Fagnoni, *Molecules*, **2019**, *24*, 2164



Conclusions



Aryl azosulfones

1. Versatile substrates for the metal-free functionalization of (hetero)arenes.

2. Sunlight or visible light as the only energy source needed to activate the substrates.

3. Reactions carried out at room temperature and neither (photo)catalysts nor additives (e.g. bases) are required.

4. Wavelength selective generation of high energy intermediates (aryl radicals, aryl cations).