

NEW SYNTHETIC PATHWAY FOR PERYLENE SUBSTITUTION

INFIQC-UNC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba, 5000, Argentina, carlos.rivas@unc.edu.ar

Carlos J. Rivas, María T. Baumgartner y Liliana B. Jimenez

INTRODUCTION

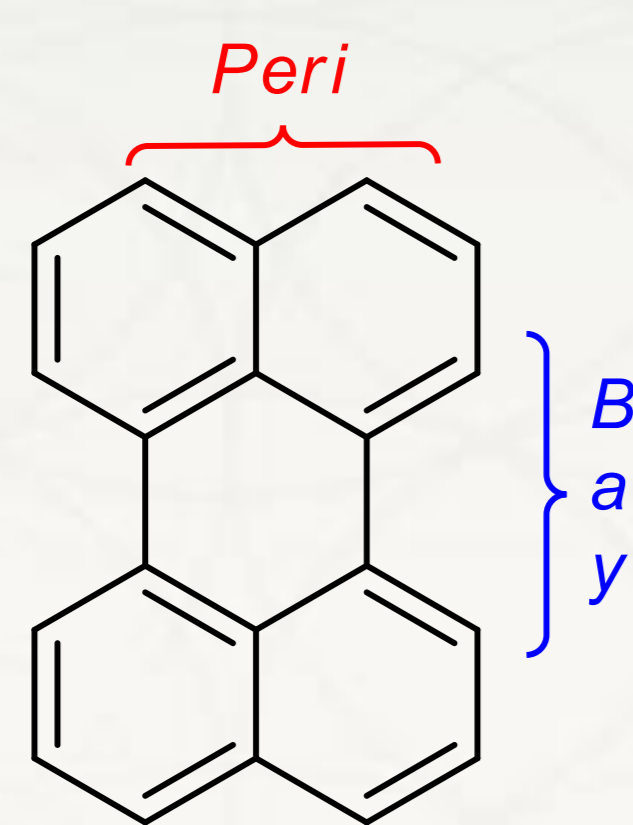
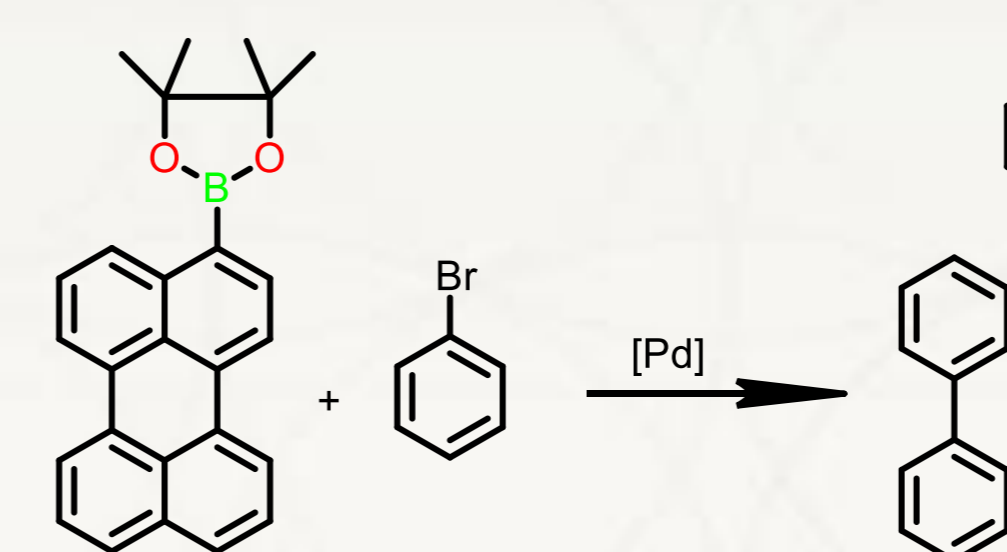


Figure 1

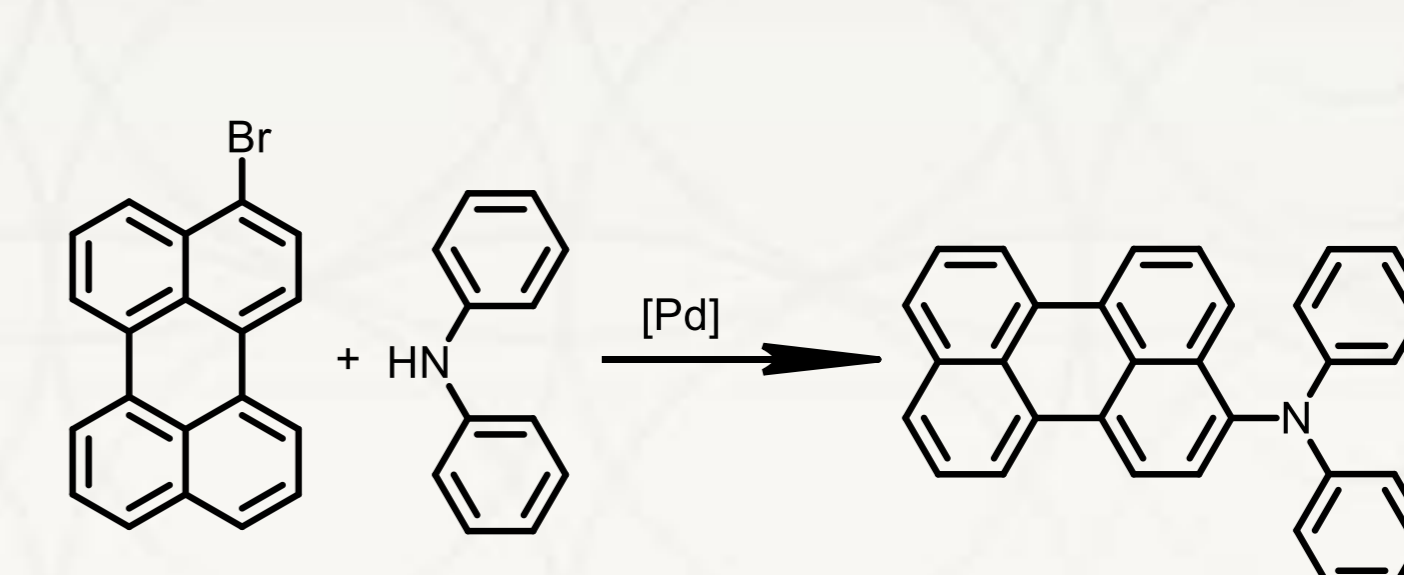
Perylene (Fig. 1) is a polycyclic aromatic hydrocarbon (PAH) that, due to its rigidity, exhibits excellent electronic and optical properties,¹ conferring high fluorescence quantum yields depending on the type of substituent it possesses. Furthermore, if the substituents are located in the *bay* or *peri* region, they also induce modifications to these properties, enabling a wide range of light emission colors in the spectrum to be achieved

SYNTHETIC BACKGROUND

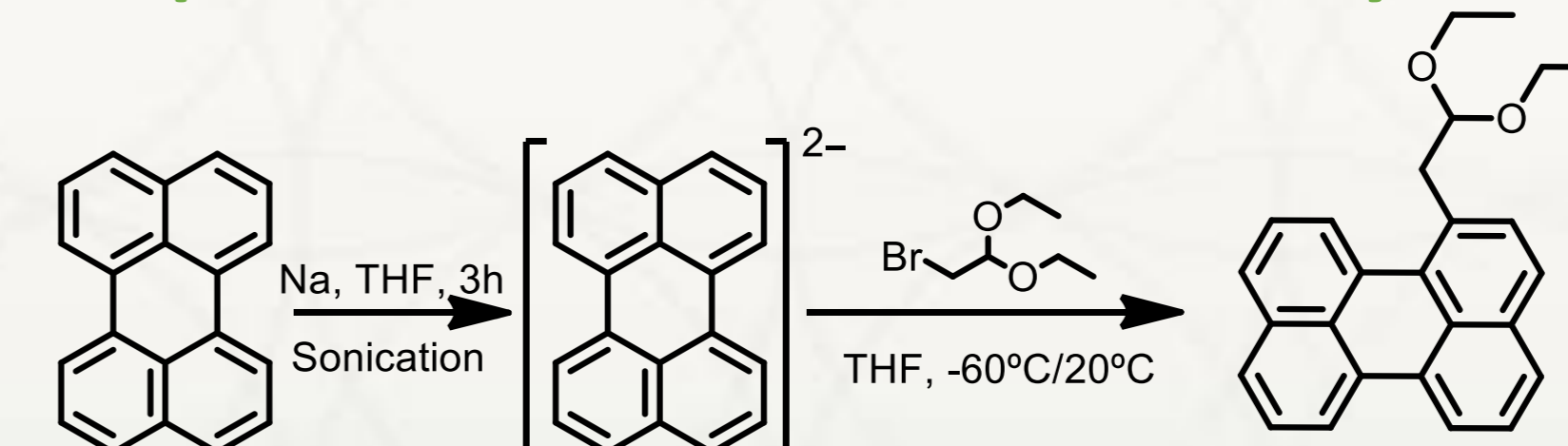
Suzuki-Miyaura Coupling²



Buchwald-Hartwig Coupling³



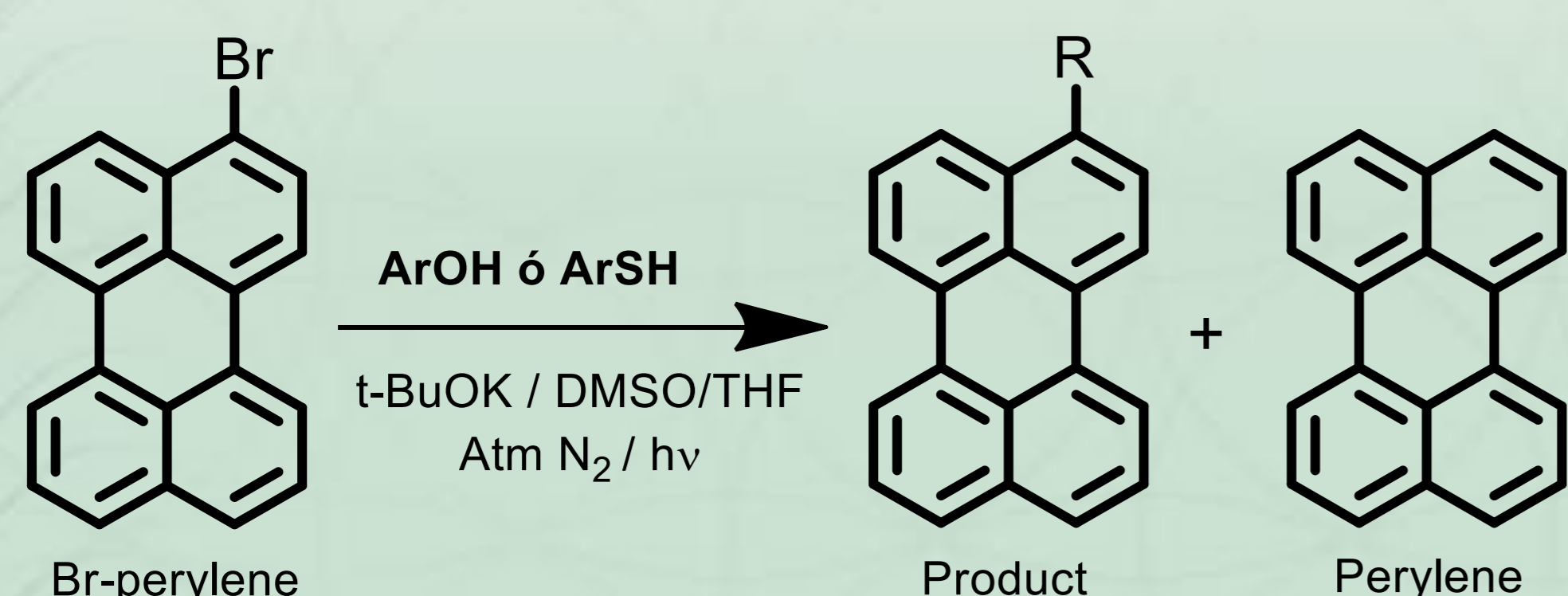
Nucleophilic Substitution from the Perylene Dianion⁴



OBJECTIVES

- ✓ Obtaining new perylene-derived products through substitutions mediated by electron transfer (ET). Specifically, the reaction between Br-perylene and various hydroxyaryls (ArOH) and arylthiols (ArSH) was studied, as shown in Scheme 1.

RESULTS



Scheme 1

R

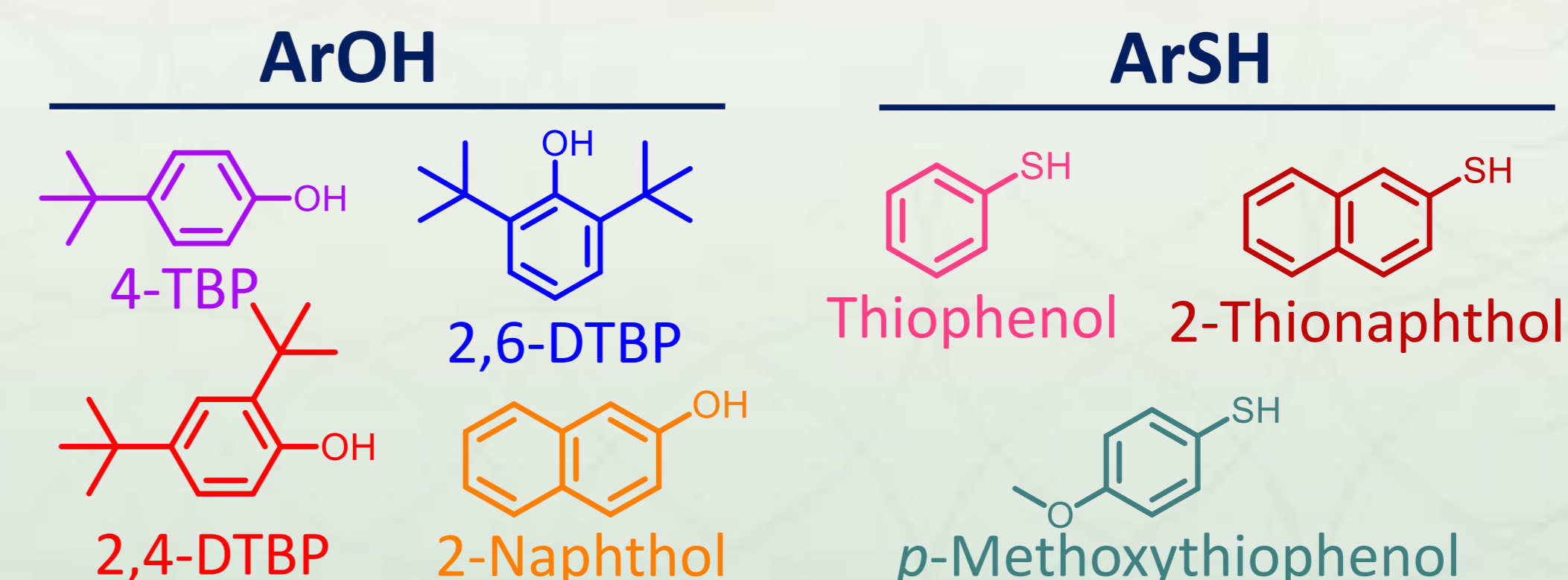
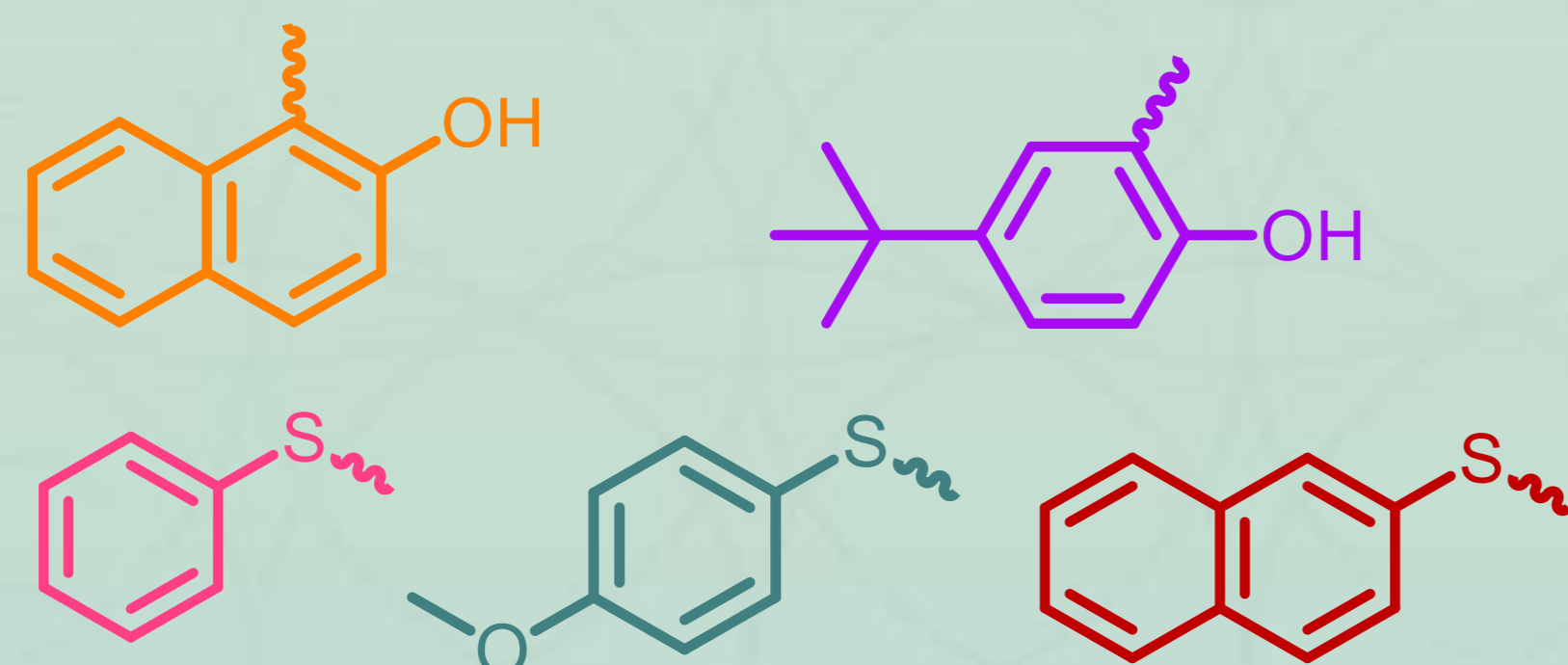


Table 1: Reaction conditions between Br-perylene with ArOH or ArSH.^a

Entry	ArOH /ArSH	Eq. ArOH/ArSH	Eq. Base	t (h)	Product Yield (%)	Perylene Yield (%)
1 ^{b,g}	2-Naphthol	3	3.3	1	-----	-----
2	2-Naphthol	10	10.1	1,5	21	42
3 ^c	2-Naphthol	6	6.1	1,5	19	55
4 ^{d,g}	2-Naphthol	3.3	3.5	2	-----	-----
5	Thiophenol	10	10.4	2	36	12
6 ^{e,g}	Thiophenol	10	10.1	2	-----	-----
7 ^f	p-Methoxythiophenol	9.7	10	2	37	14
8	2-Thionaphthol	9.9	10.2	2	36	11
9 ^g	2,4-DTBP	9.9	10	2	-----	-----
10 ^g	2,6-DTBP	10.2	10.4	5	-----	-----
11	4-TBP	10	11.5	3	8	30

^a [Br-Perylene] = 13,7 mM, Base = t-BuOK, DMSO= 10 mL y THF= 1 mL, T= 40 °C, N₂. Photoreactor equipped with two Hg-Halogen lamp, 100 W. Isolated yields. ^b Only DMSO. ^c [Br-Perylene] = 27,5 mM. ^d T= 100°C, Base= K₂CO₃, Not Irradiation. ^e Solvent= NH₃ liquid, T= -33 °C. ^f (CH₃)₂SO₄ is added at the end of reaction. ^g Starting substrate is recovered.

CONCLUSIONS

- ✓ The synthesis of **new perylene-derived compounds** was achieved, using an **alternative pathway** to the use of metal catalysts, thereby expanding the family of these PAHs.
- ✓ The **selectivity** of the obtained products was demonstrated, with **new C-C bonds formed** in reactions with ArOH and **C-S bonds** in reactions with ArSH, which would allow for better functionalization of this chromophore.

REFERENCE

- Balzani, V. C., A.; Venturi, M. Molecular Devices and Machines. Concepts and Perspectives for the Nanoworld.; 2nd ed.; Wiley-VCH Verlag GmbH & Co., Weinheim, 2008.
- Carrod, A. J. *et al.* J. Mater. Chem. C, 2022,10, 4923-4928
- Ahn, M. *et al.* J. Org. Chem. 2021, 86, 1, 403-413.
- Van Dijk, J. T. M. *et al.* J. Org. Chem. 1996, 61, 1136