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Photochemical Derivatization of Helicenes

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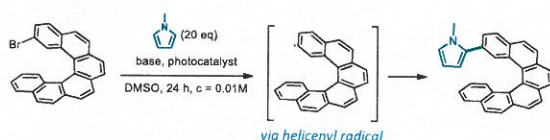
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Introduction. Helicenes are chiral polyaromatic compounds of great potential in many fields, such as asymmetric catalysis, optoelectronics, or material sciences¹. The most commonly used methods of preparation of helicenes – photocyclization and [2+2+2] cycloaddition – can be both successfully used for incorporation of different functional groups into the helicene structure, however the scope of functional groups can be limited and/or requires time consuming multistep procedures². This obstacle can be overcome by functionalization of simple helicene derivatives.

This work is focused on the use of simple helicene derivatives as substrates for modern photochemical methods. Halogen containing substrates are transformed in the reductive pathway to helicenyl radicals, before reacting with various radical traps. In the oxidative pathway, activated alkoxyhelicenes undergo photoredox catalyzed reactions, yielding different carbon-carbon, as well as carbon-heteroatom containing compounds.

Reductive pathway



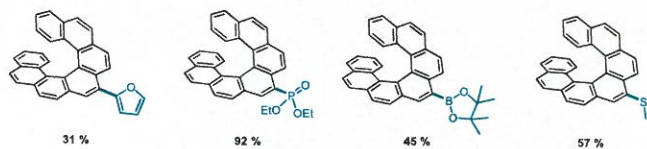
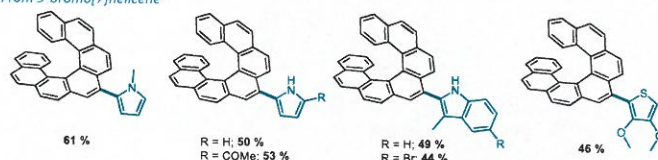
Optimization of the reaction conditions

Run	Photocatalyst	Base	Wavelength	Yield
1	Rhodamine - 6G	DIPEA	450	43%
2	-	DIPEA	450	39%
3	Eosin Y	DIPEA	530	42%
4	-	DIPEA	530	35%
5	Eosin Y	DIPEA/K ₂ CO ₃	530	46%
6	-	DIPEA/K ₂ CO ₃	450	53%
7	-	K ₂ CO ₃	450	55%
8	-	K ₂ CO ₃	450	64%*
9	-	-	450	0%

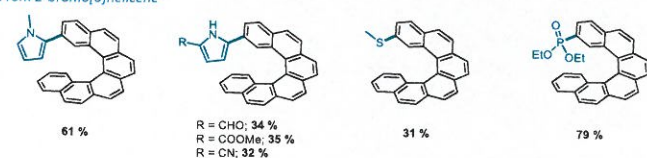
*reaction conducted at c = 0.1M

Activation of brominated helicene was first investigated in the presence of Rhodamine 6G, with N-methylpyrrole as a radical trap. The reaction however proceeds even in the absence of a photocatalyst, and under both blue and green light irradiation. [6]helicene was isolated in all cases as a main byproduct. The highest yield was achieved, when the reaction was conducted at the concentration of 0.1M, despite the starting material not fully dissolved.

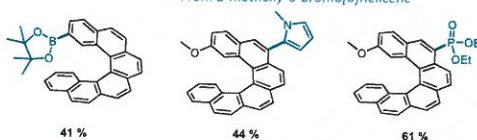
From 9-bromo[7]helicene



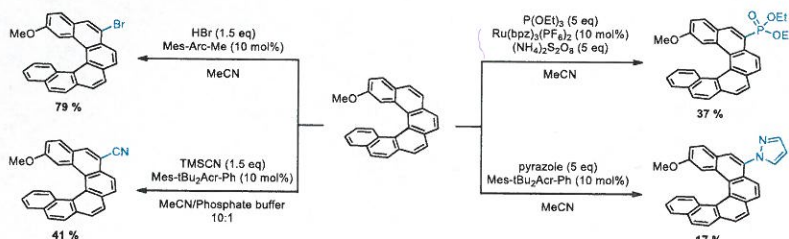
From 2-bromo[6]helicene



From 2-methoxy-6-bromo[6]helicene



Oxidative pathway



2-Methoxy[6]helicene was chosen as a starting material for oxidative photoredox derivatization of helicene moiety. The presence of methoxy group serves both as activating and directing feature. The first studied example was the bromination reaction, conducted under conditions published by Fukuzumi³ with 9-Mesityl-10-methylacridinium perchlorate as a photocatalyst. The reaction proceeds very selectively to the position 6 of the helicene, despite the presence of 2 different *ortho* positions next to the MeO- group.

Another studied reaction was the cyanation reaction. We adopted the conditions described by Nicewicz⁴, to yet again obtain the 6-substituted product in 41 % yield.

Phosphonylation of the starting material was achieved under conditions described by König⁵. The phosphate was formed from triethylphosphite in 36 % yield with excellent regioselectivity in position 6. The *N*-arylated helicene was isolated in low yield when irradiated with blue light in presence of an acridinium photocatalyst⁶. This result, despite the low yield, is very promising, since it provides greater variability for different nitrogen containing aryls.

Further optimization of the reaction conditions as well as introduction of different functionalities is currently underway.

Conclusion. Late stage functionalization of simple helicene derivatives via photochemical transformation was attempted. In the reductive pathway, the reaction conditions were optimized to give moderate to good yields with known radical traps. Formation of both carbon-carbon, as well as carbon-heteroatom bonds was achieved. Oxidative photoreactions provided four new products substituted in the position 6 of the helicene. This methodology provides a useful platform for the synthesis of helicenes with multiple functionalities.