Late-Stage Functionalization of Azahelicenes *via* Multiple C(sp^2)–H Insertions of Metal Carbenes

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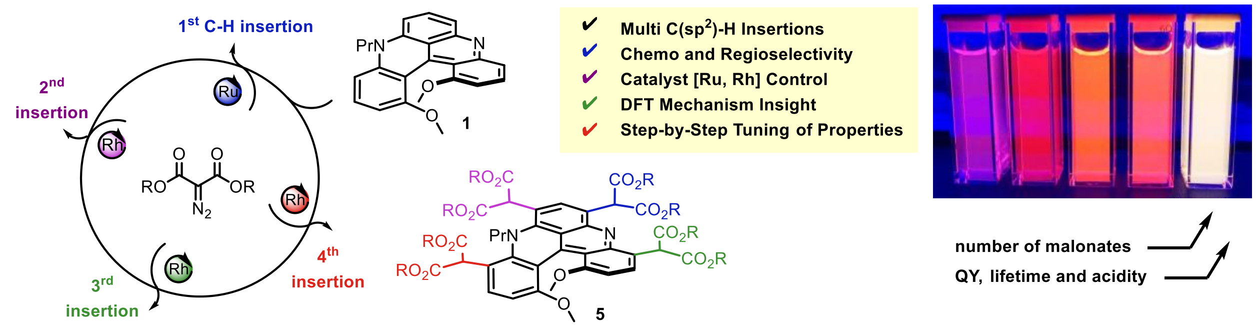
Late-stage functionalization (LSF) strategies are particularly attractive for providing large scope of products or promoting specific reactivities at single site only.[1-4] Herein, in the context of heterohelicene chemistry, metal-catalyzed decompositions of α-diazomalonates are shown to afford multi-functionalized chiral diaza [4]helicenes – in a controlled stepwise manner. By selecting the catalyst, [CpRu(CH$_3$CN)$_3$][PF$_6$] or Rh$_2$(oct)$_4$, chemo and regioselective insertions of derived metal carbenes are achieved in favour of mono- or bis-functionalized malonate derivatives, respectively (r.r. > 49:1, up to 77% yield, 12 examples). Mechanism of formation and origin of selectivity are elucidated based on DFT calculations. Controlled formation of products of tris- and tetra-malonate insertions can be further achieved thanks to the higher reactivity of rhodium carbenes. This step-by-step multi-introduction of malonate groups is particularly useful to tune / increase important properties of the [4]helicene core such as absorption (Δλ −44 nm), emission (quantum yield 5-22%, lifetime 3.0-8.4 ns) and Brønsted acidity (pKa **1•H**$^+$ to **5•H**$^+$, from 6.63 to −0.42 and lower).



- ✔ Multi C(sp^2)-H Insertions
- ✔ Chemo and Regioselectivity
- ✔ Catalyst [Ru, Rh] Control
- ✔ DFT Mechanism Insight
- ✔ Step-by-Step Tuning of Properties

number of malonates ↗
QY, lifetime and acidity ↗

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