Regio-divergent [3+2] Cycloaddition of *gem*-Difluorocyclopropane Derivatives Based on the Control of Bidirectional Bond Cleavage

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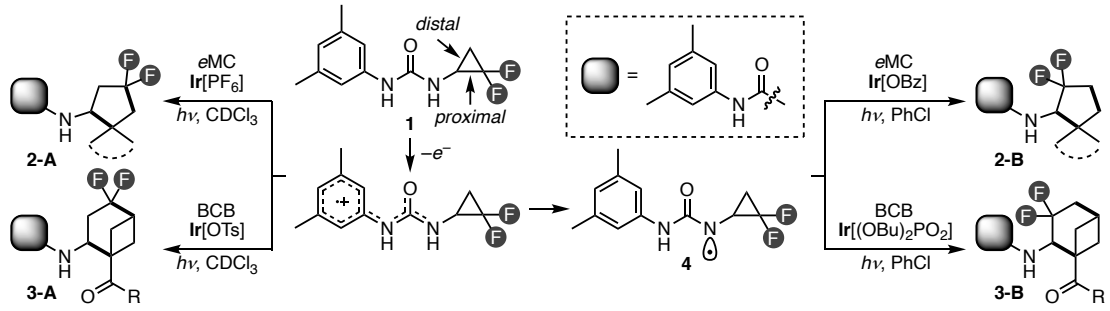
As aliphatic fluorine compounds play an important role in pharmaceutical and biofunctional chemistry, their regio-divergent synthesis provides a powerful method for rapidly expanding the chemical library.[1] Cyclopropane derivatives featuring the activated bonds that can be easily cleaved would serve as C3 units suitable for addressing the regioselectivity issue. Here, we report the regio-divergent synthesis of aliphatic fluorine compounds, which relies on the control of bidirectional bond cleavage of *gem*-difluorocyclopropane. Based on our previous experience of utilizing an urea group as an anion-binding and redox-active amine equivalent,[2] we hypothesized that the difference in the interactions between a difluorocyclopropyl urea and a counter anion of a cationic iridium photoredox catalyst would lead to control the direction of the bond cleavage of difluorocyclopropane, thereby enabling the regio-divergent synthesis.

To substantiate our hypothesis, urea **1** was treated with *exo*-methylene cyclic compounds (*e*MC) in the presence of [Ir(dF(CF$_3$)ppy)(dtbbpy)][PF$_6$] (**Ir**[PF$_6$]) under blue LED irradiation in CDCl$_3$, which afforded **2-A** as a major product, while the use of **Ir**[OBz] as a catalyst in chlorobenzene led to the formation of **2-B** as a major product. This strategy was also applicable to the reactions with bicyclobutanes (BCB), affording **3-A** and **3-B**, respectively. Importantly, the urea group was readily transformed into a free amino group. DFT calculations revealed the origin of the effect exerted by the counter anion of the iridium cation on the selectivity. With less basic counter anions such as PF$_6$ and OTs, the C–C bond cleavage proceeds from a radical cation intermediate, which prefers the proximal C–C bond cleavage to give terminal CF$_2$ radical. Meanwhile, basic OBz or (OBu)$_2$PO$_2$ deprotonates radical cation intermediate to generate neutral radical **4**, which prefers the distal C–C bond cleavage to give terminal CH$_2$ radical.



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