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Nicolas Joly, Alessandro Colella, Monique-Edwige Mendy, Diagne Mbaye, Marie-Samira Abdallah, et al.. Blue Light Induced Iron-Catalysed α -Alkylation of Ketones with alcohols. 5th International Symposium on Synthesis and Catalysis 2023 (ISySyCat 2023), Sep 2023, Evora, Portugal. . hal-04599662

HAL Id: hal-04599662

<https://hal.science/hal-04599662v1>

Submitted on 3 Jun 2024

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Blue Light Induced Iron-Catalysed α -Alkylation of Ketones with alcohols

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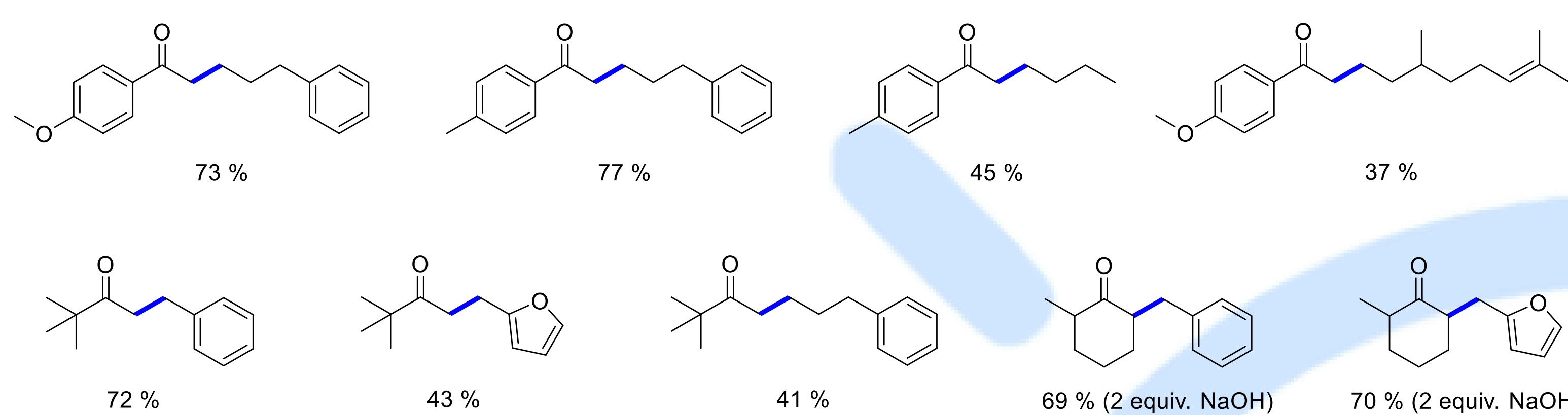
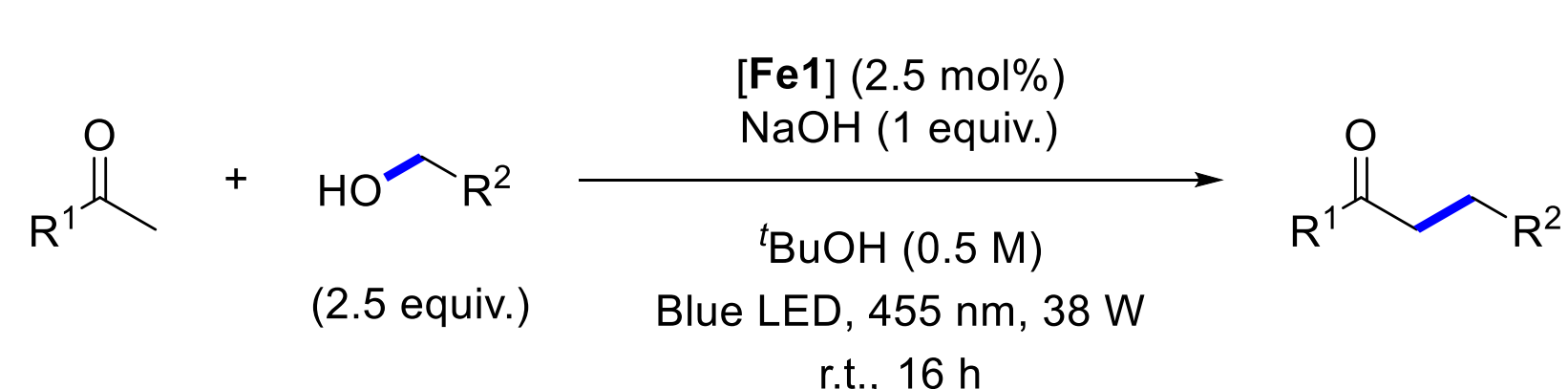
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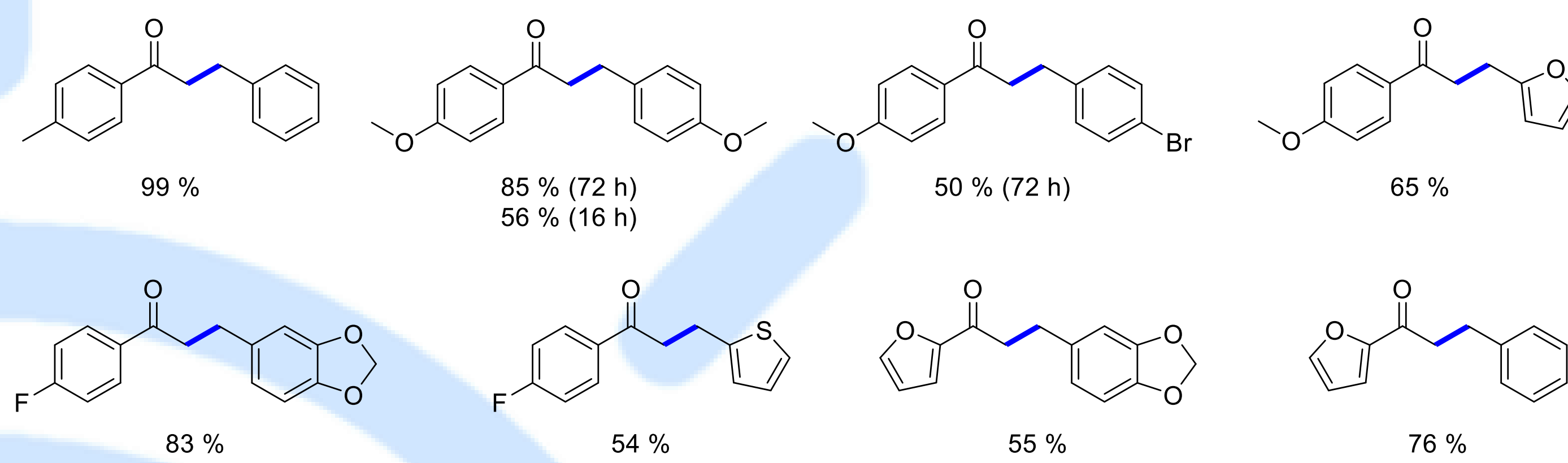
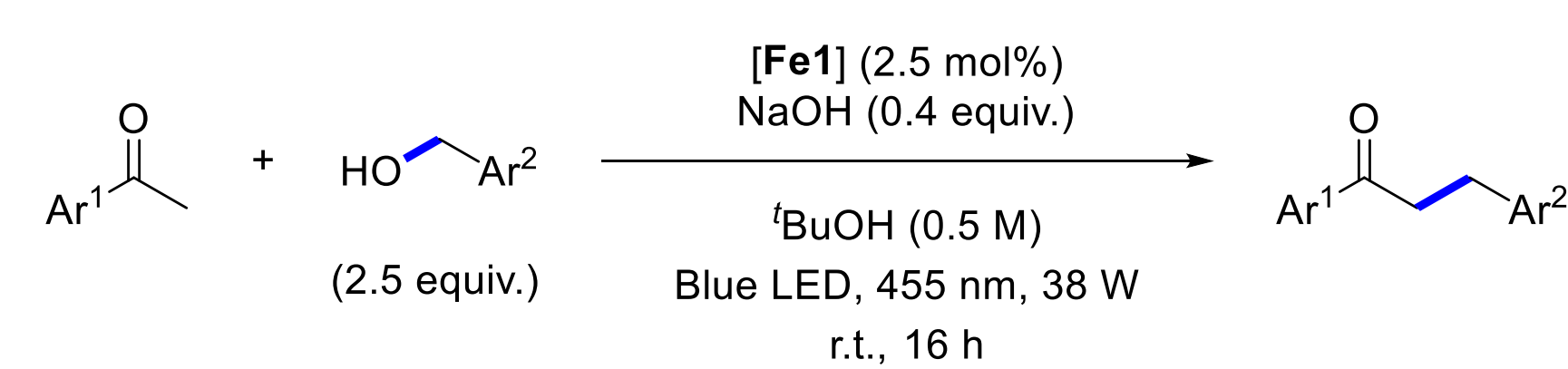
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Hydrogen auto-transfer reaction consists in the alkylation of a pro-nucleophile (amines, ketones, esters, amides, indoles, ...) by an alcohol as pro-electrophile, catalyzed by an organometallic complex. This methodology represents a greener and safer procedure than the well-established enolate alkylation for the C-C bond formation or the nucleophilic substitution for the C-N bond formation. Despite the success of these approaches and catalysts, there is still room to develop C-C or C-N bond formation methodologies under milder conditions. The borrowing hydrogen strategy has been applied in the α -alkylation of ketones with alcohols at room temperature under visible light photoirradiation. The reaction was catalyzed by a chromophoric phosphine-free diaminocyclopentadienone iron tricarbonyl complex. Different aromatic and aliphatic ketones gave the alkylated products using aliphatic, benzylic, allylic and propargylic primary alcohols. Mechanistic investigations highlighted the role of light in both the dehydrogenation and the reduction steps.

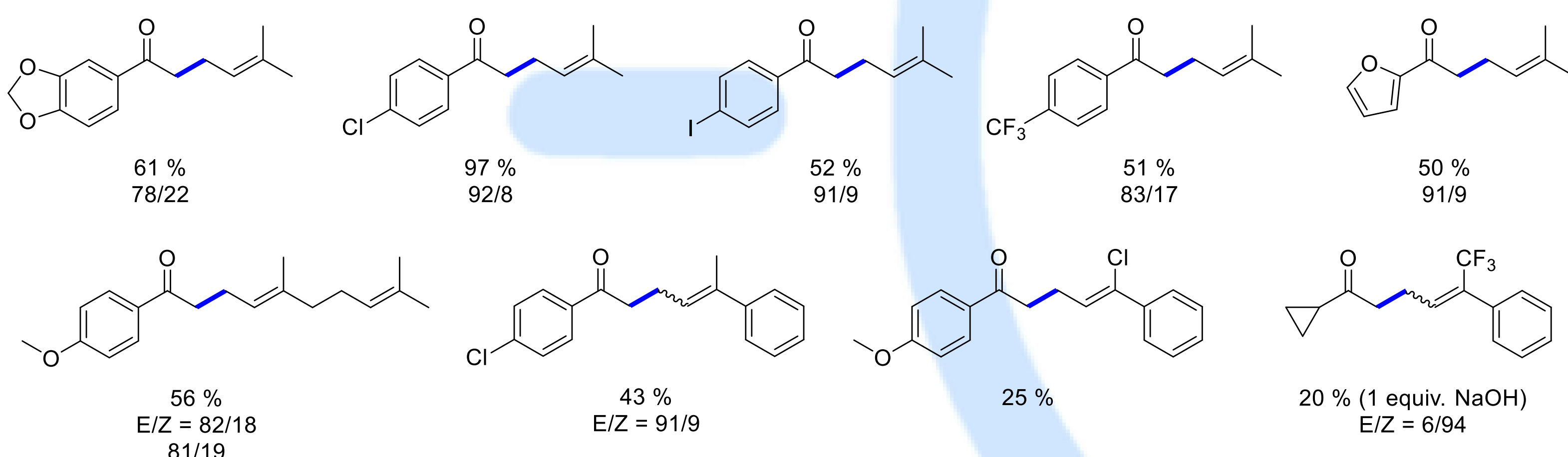
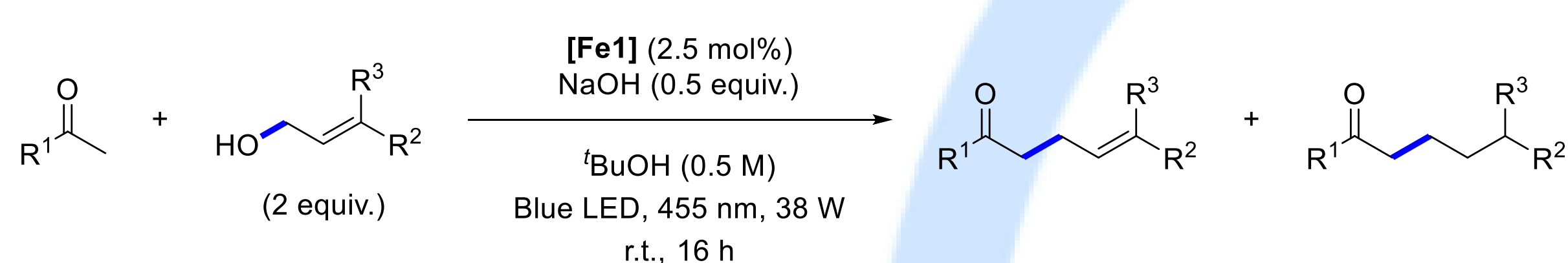
Alkylation of ketones with aliphatic compounds



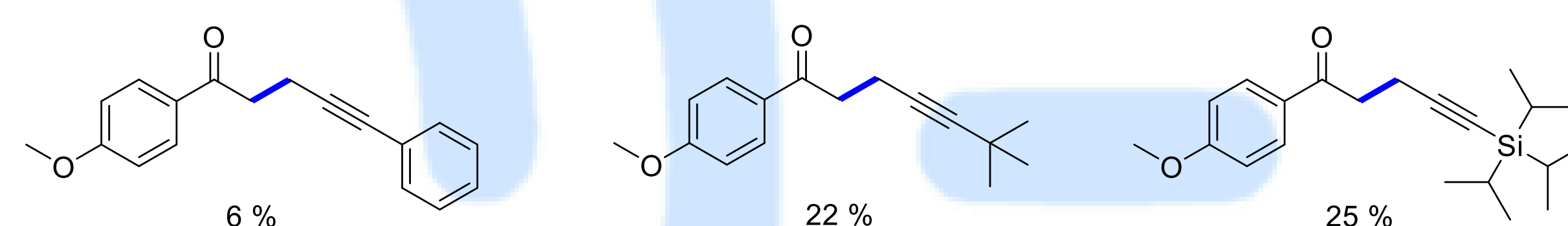
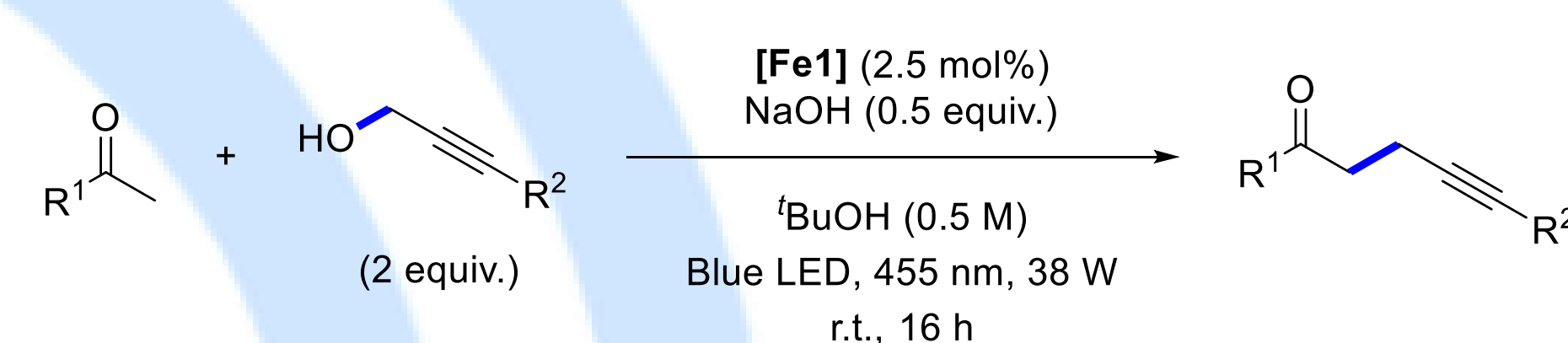
Alkylation of aryl ketones with benzylic alcohols



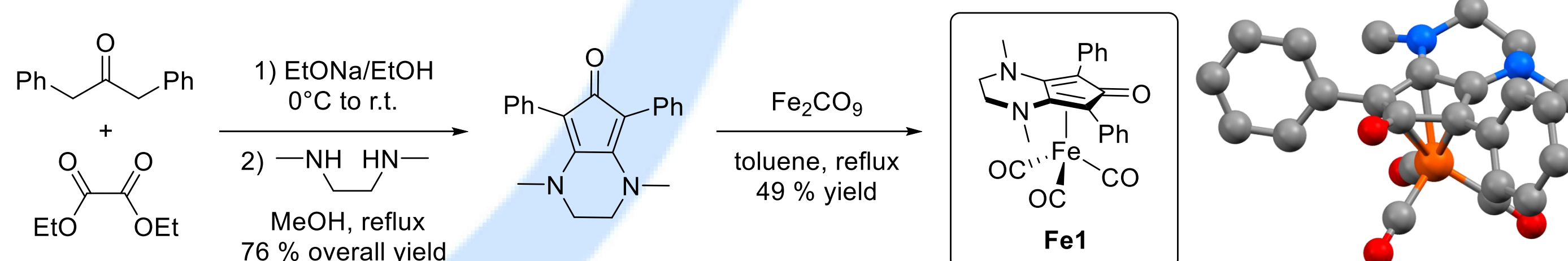
Alkylation of ketones with allylic alcohols



Alkylation of ketones with propargylic alcohols

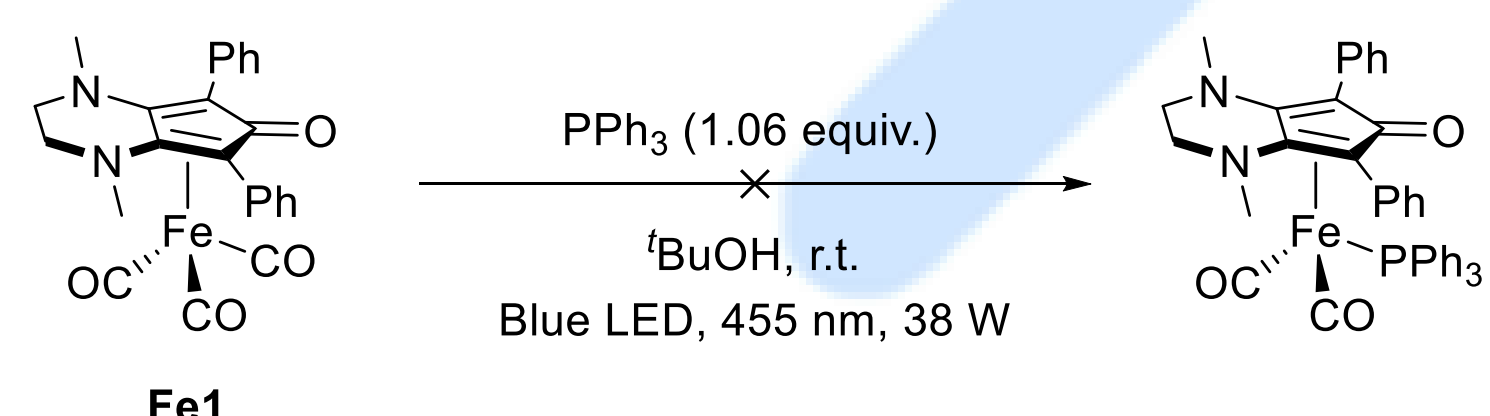


Synthesis of iron complex

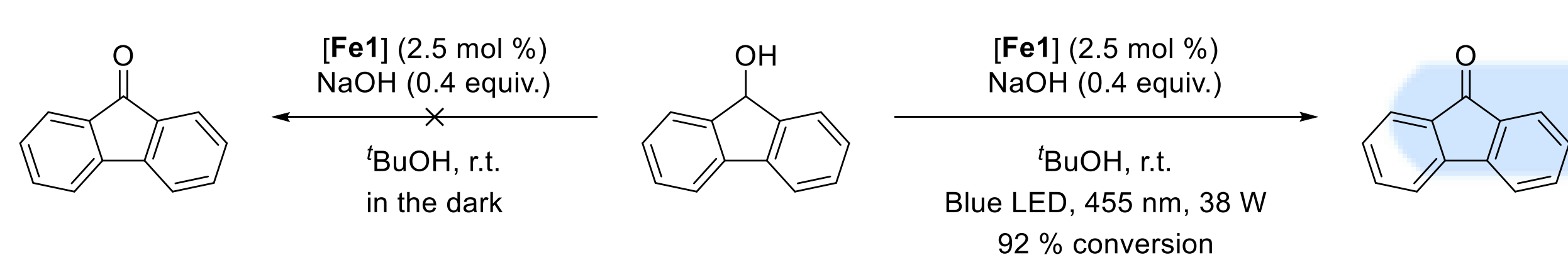


Mechanistic investigations

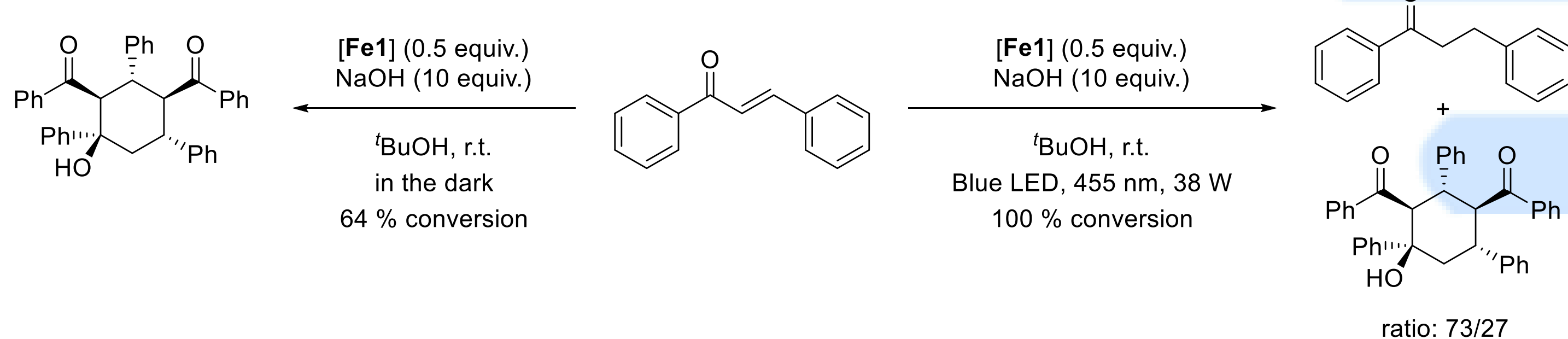
Role of light regarding the activation of the catalyst: X



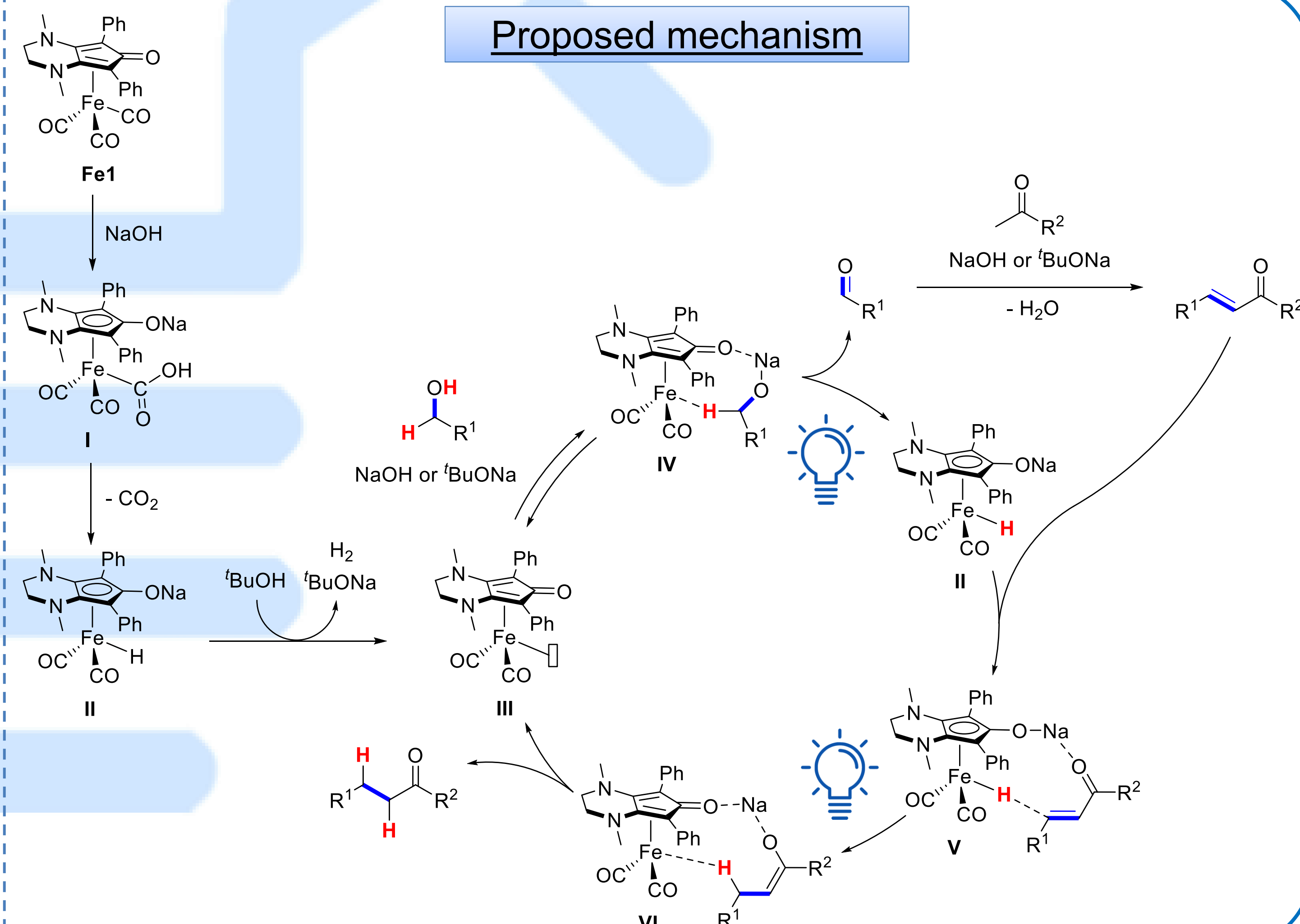
Role of light regarding the dehydrogenation step: ✓



Role of light regarding the reduction step: ✓



Proposed mechanism



¹ Abdallah, M.-S.; Joly, N.; Gaillard, S.; Poater, A.; Renaud, J.-L. *Org. Lett.* **2022**, *24*, 5584-5589.

² Joly, N.; Colella, A.; Mendy, M.-E.; Mbaye M. D.; Gaillard, S.; Poater, A.; Renaud, J.-L. *ChemSusChem* **2024**, *17*, e202301472.