

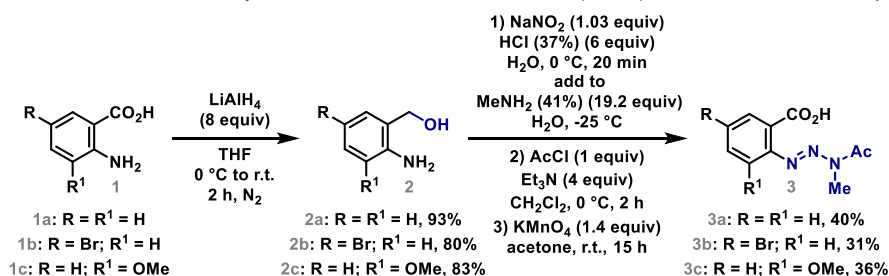
## Photoprecursors of arynes in visible-light promoted cycloaddition and nucleophilic coupling reactions

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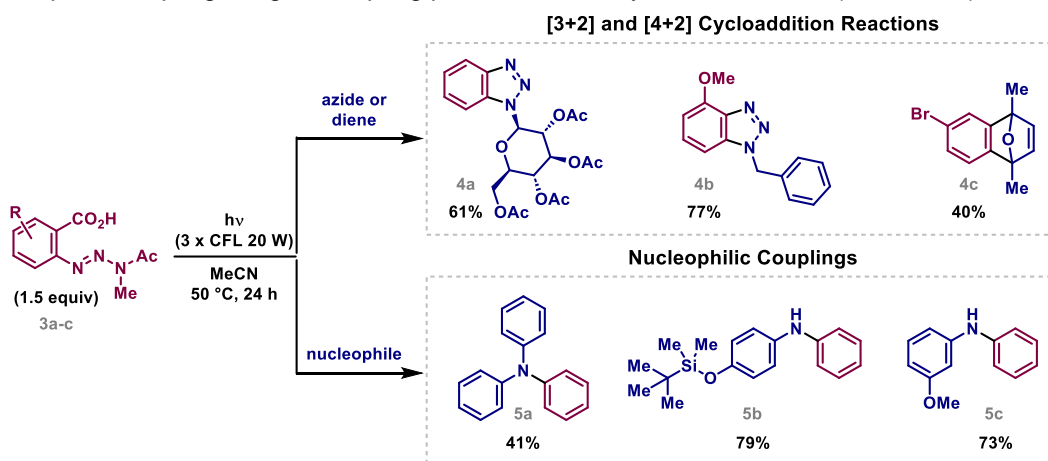
### ABSTRACT

2-(3-Acetyl-3-methyl-1-triazen-1-yl)benzoic acids (**3a-c**) are understudied benzyne and aryne precursors, which are prepared from commercially available anthranilic acids (**1a-c**) in four reaction steps (**Scheme 1**).<sup>1,2</sup>



**Scheme 1.** Synthesis of compounds **3a-c**.

After extensive optimization of the reaction conditions, compounds **3a-c** promoted the formation of arynes with white light, which were used in cycloaddition reactions to provide cycloadducts **4a-c** in yields of 40-77% and in nucleophilic couplings to give coupling products **5a-c** in yields of 41-79% (**Scheme 2**).



**Scheme 2.** Preparations of compounds **4a-c** and **5a-c**.

Twenty-two compounds were isolated in yields from 13% to 85% using aryne photoprecursors **3a-c**. It is noteworthy that this chemistry is compatible with functionalized groups containing sulfur, boron, and silicon. These groups are not tolerated under the conditions required to generate arynes via Kobayashi precursors.<sup>3</sup> A mechanistic investigation using TEMPO and mass spectrometry suggests a radical mechanism for the photogeneration of arynes.

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### REFERENCES

- Yuan, W. K.; Sun, S. Z.; Zhang, L. B.; Wen, L. R.; Li, M. *Org. Chem. Front.* **2019**, *6*, 2892.
- Khan, H.; Barman, D.; Sen, S. *J. Org. Chem.* **2024**, *89*, 6257.
- Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, *12*, 1211.