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Remote radical alkylation of silyl dienol ether by palladium-photoredox catalysis: a direct access to γ -alkylated α,β -unsaturated ketones

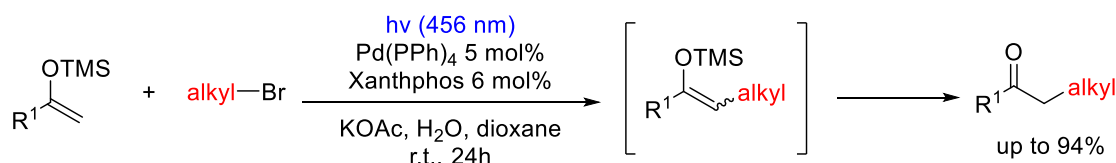
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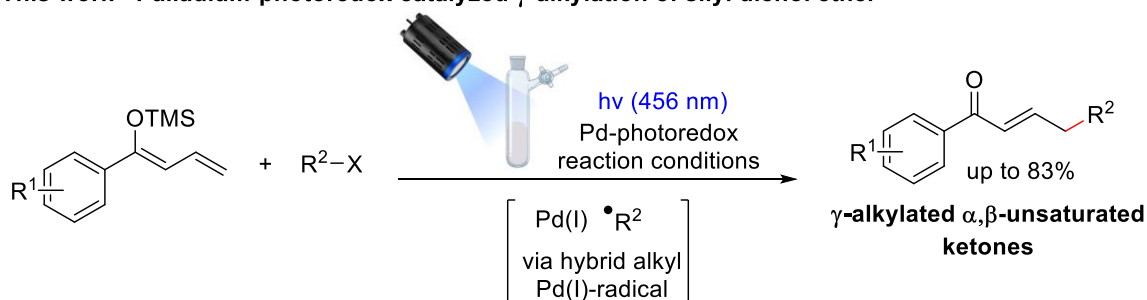
ABSTRACT

Transition metal-photoredox catalysis have become a growing research area in the past few years. The dual function of the catalyst plays an important role for the success of this type of synthetic approach: the metal complex acts as photoredox catalyst and maintains its classical activity in subsequent transformations to provide the desired product, without the need for an exogenous photosensitizer. In particular, for reactions catalyzed by palladium, this strategy makes it possible for transformations inaccessible to classical palladium ground state chemistry to be carried out from the excited state of the catalyst.² A representative example is the Heck reaction involving alkyl substrates, which is very challenging for classical Pd-catalyzed cross-coupling reactions, but is feasible by Pd-photoredox strategy.³ Therefore, in this work, we present an initial study for vinylogous alkyl radical addition to silyl dienol ethers providing direct access to γ -alkylated α,β -unsaturated ketones in up to 83% yield under visible light Pd-photoredox reaction conditions.

Fu (2020)- Palladium-catalyzed α -alkylation of silyl enol ether



This work - Palladium-photoredox catalyzed γ -alkylation of silyl dienol ether



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REFERENCES

- ¹ Cheung, K. P. S.; Sarkar, S.; Gevorgyan, V. *Chem. Rev.* **2022**, *122*, 1543.
- ² Jardim, G. A. M.; Dantas, J. A.; Barboza, A. A.; Paixão, M. W.; Ferreira, M. A. B. *Synthesis* **2022**, *54*, 4629.
- ³ (a) Koy, M.; Sandfort, F.; Tlahuext-Aca, A.; Quach, L.; Daniliuc, C. G.; Glorius, F. *Chem. - Eur. J.* **2018**, *24*, 4552. (b) Wang, G. Z.; Shang, R.; Cheng, W. M.; Fu, Y. *J. Am. Chem. Soc.* **2017**, *139*, 18307. (c) Kancharla, R.; Muralirajan, K.; Maity, B.; Zhu, C.; Krach, P. E.; Cavallo, L.; Rueping, M. *Angew. Chem., Int. Ed.* **2019**, *58*, 3412. (d) Zhao, B.; Shang, R.; Wang, G.-Z.; Wang, S.; Chen, H.; Fu, Y. *ACS Catal.* **2020**, *10*, 1334.