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Exploring the Effectiveness of Directing Groups for Rhodium-catalyzed Decarbonylation

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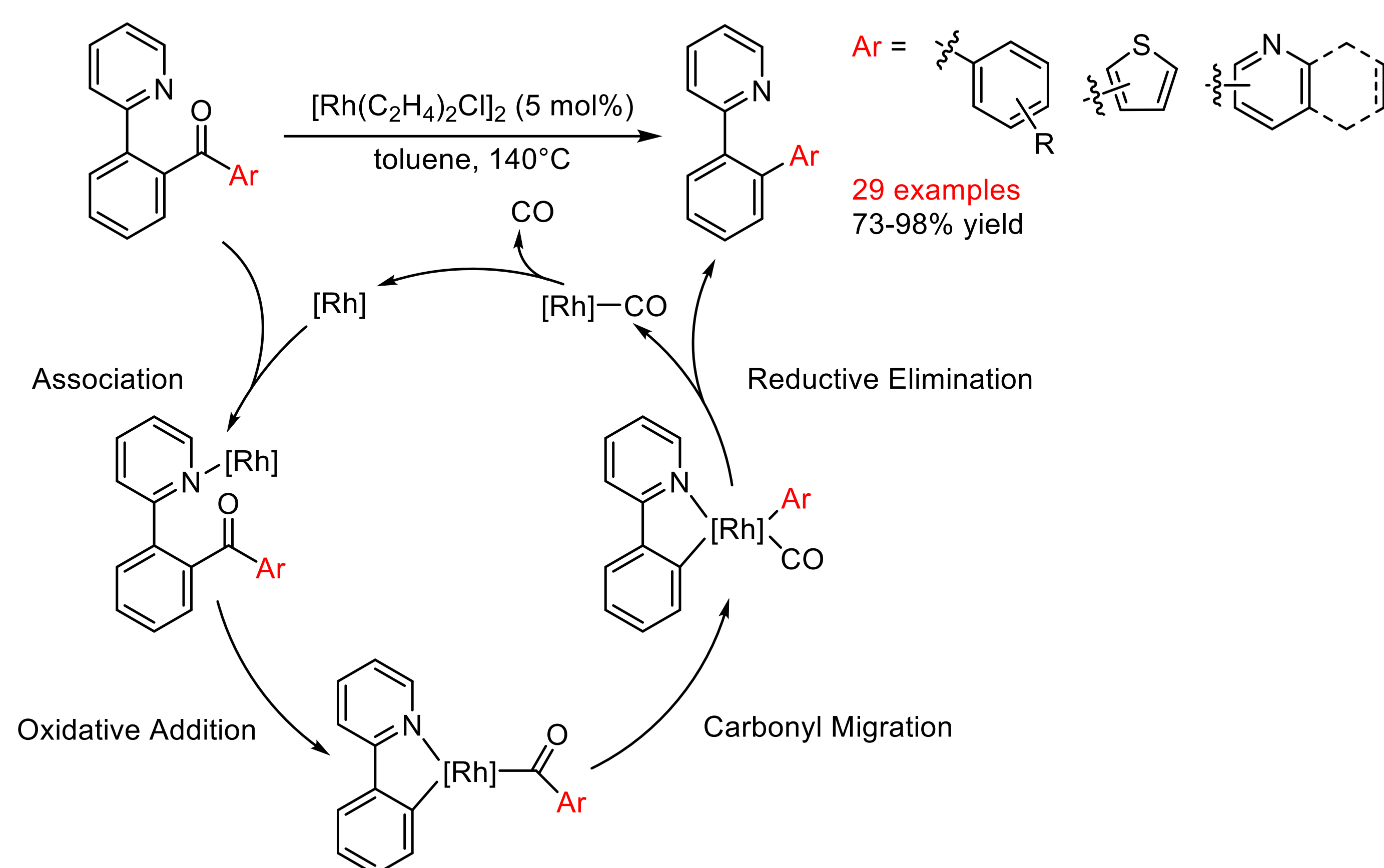
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ABSTRACT

Selective metal-catalyzed C-C bond activation promises to simplify pathways to synthesize complex molecules. Consequently, several methods of C-C bond activation have emerged in the past few decades. Previous work has utilized rhodium-catalyzed decarbonylation to form new C-C bonds from pyridyl ketone starting materials, where the nitrogen on the pyridine ring acts as a directing group. Though this reaction is easily replicated and gives high yields, the need for a pyridine directing group limits the range of molecules that can be synthesized. The goal of this project is to develop new directing groups to increase the scope of this decarbonylation reaction. To this end, various ketones with amine-containing moieties were synthesized, and success was found with several directing groups.

BACKGROUND

Rhodium-Catalyzed Decarbonylation



Lei, Z.; Li, H.; Li, Y.; Zhang, X.; Chen, K.; Wang, X.; Sun, J.; Shi, Z. *Angew. Chem., Int. Ed.* **2012**, *51*, 2690.
Wagner C.; Salisbury E.; Schoonover E.; VanderRoest J.; Johnson J. *Tet. Lett.* **2021**, *73*, 153132.

Goal: Test different directing groups to synthesize a larger range of compounds

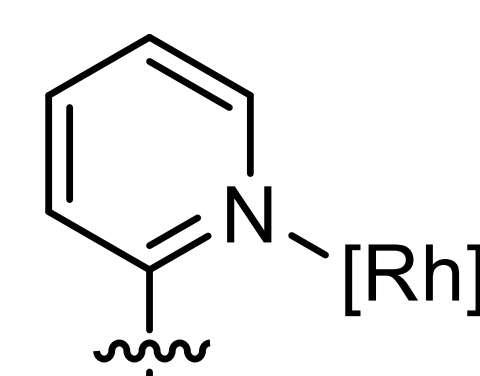
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- Hope College Chemistry Department
- NSF: CHE-1716411



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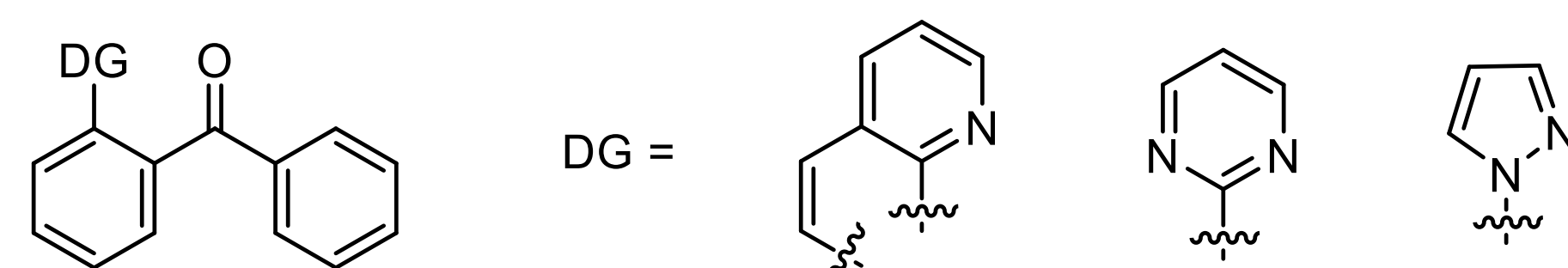
ROLE OF DIRECTING GROUPS



Nitrogen on pyridine directing group coordinates to rhodium, placing catalyst in proximity to C=O and helping to break the C-C bond.

Could other amine-containing functional groups act as directing groups?

Prior Work

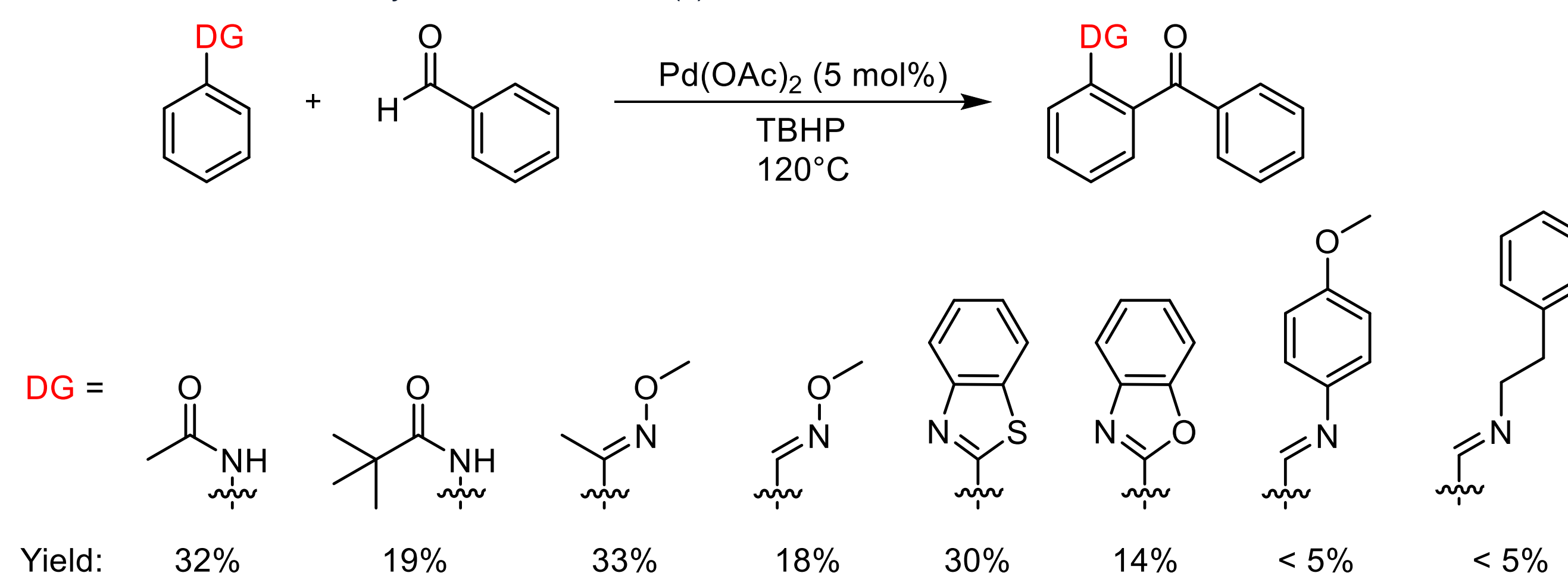


- Previous success was found with aromatic directing groups containing amines
- Other aromatic and non-aromatic directing groups were explored for this project

KETONE SYNTHETIC STRATEGIES

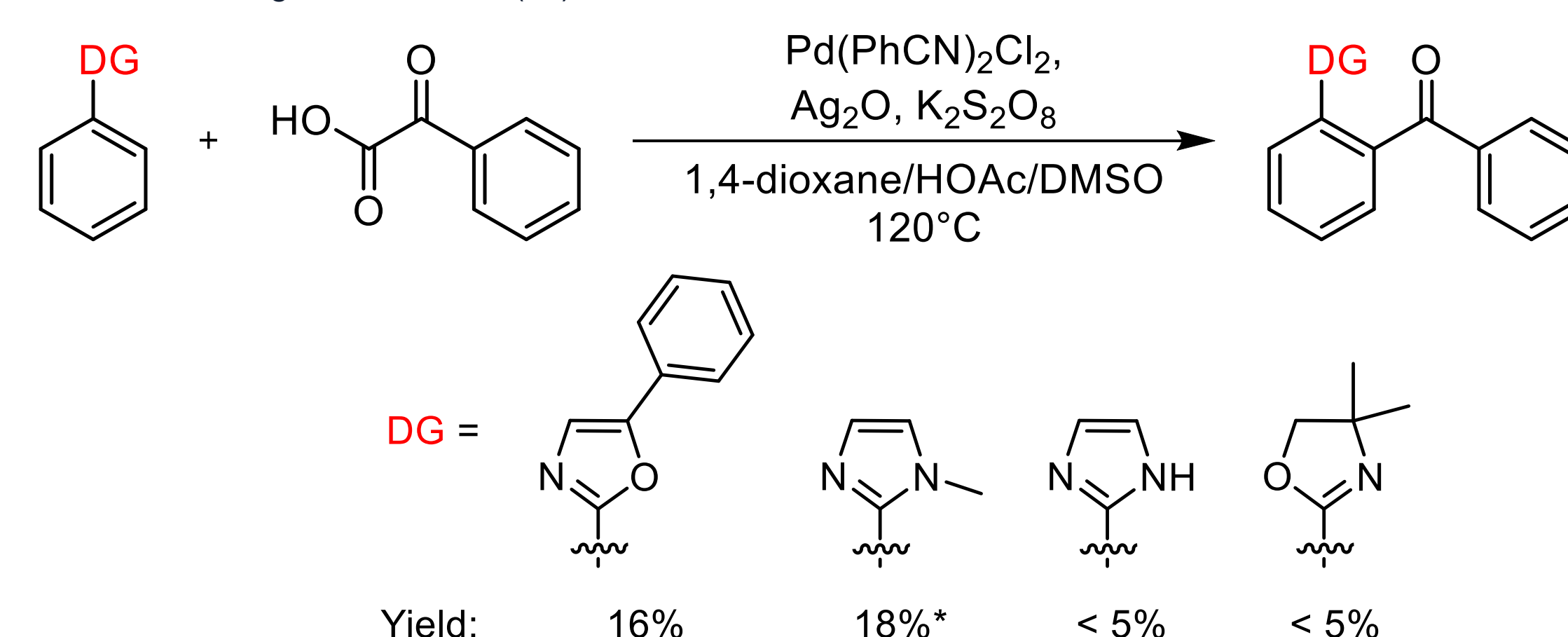
Palladium-Catalyzed Acylation

Baslé, B.; Shuai, L. *Adv. Synth. Catal.* **2010**, *352*(7), 1145-1149.



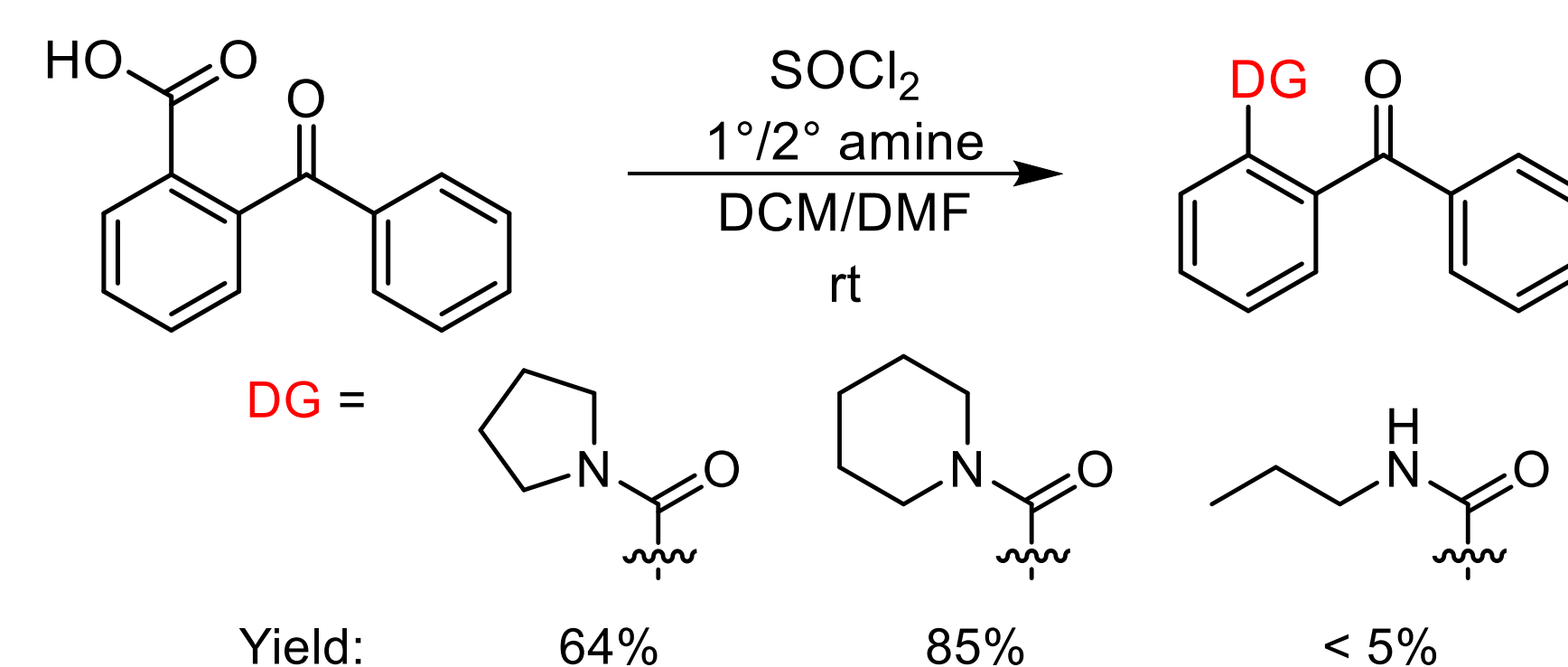
Decarboxylative Acylation

Li, M.; Ge, H. *Org. Lett.* **2010**, *12*(15), 3464-3467.



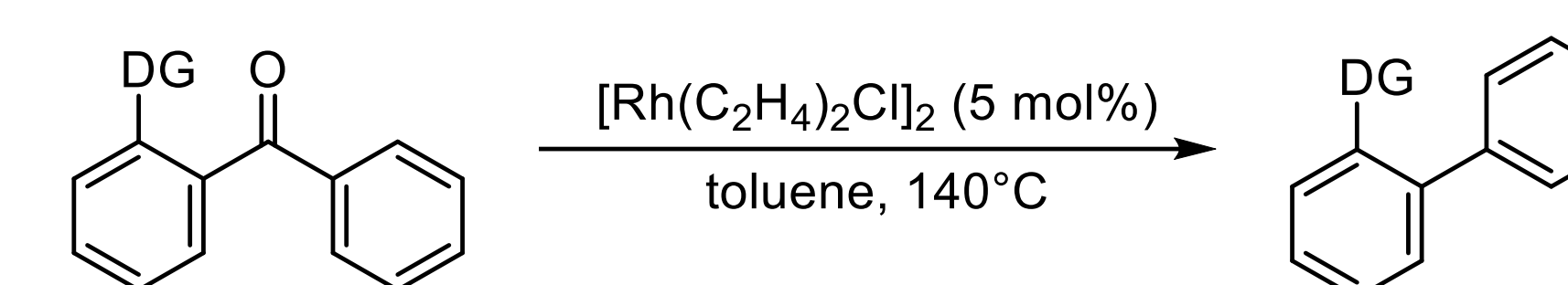
Amide Formation

Maresh, J.; Zhang, J.; et al. *Bioorganic Med. Chem. Lett.* **2007**, *17*(12), 3281-3286.



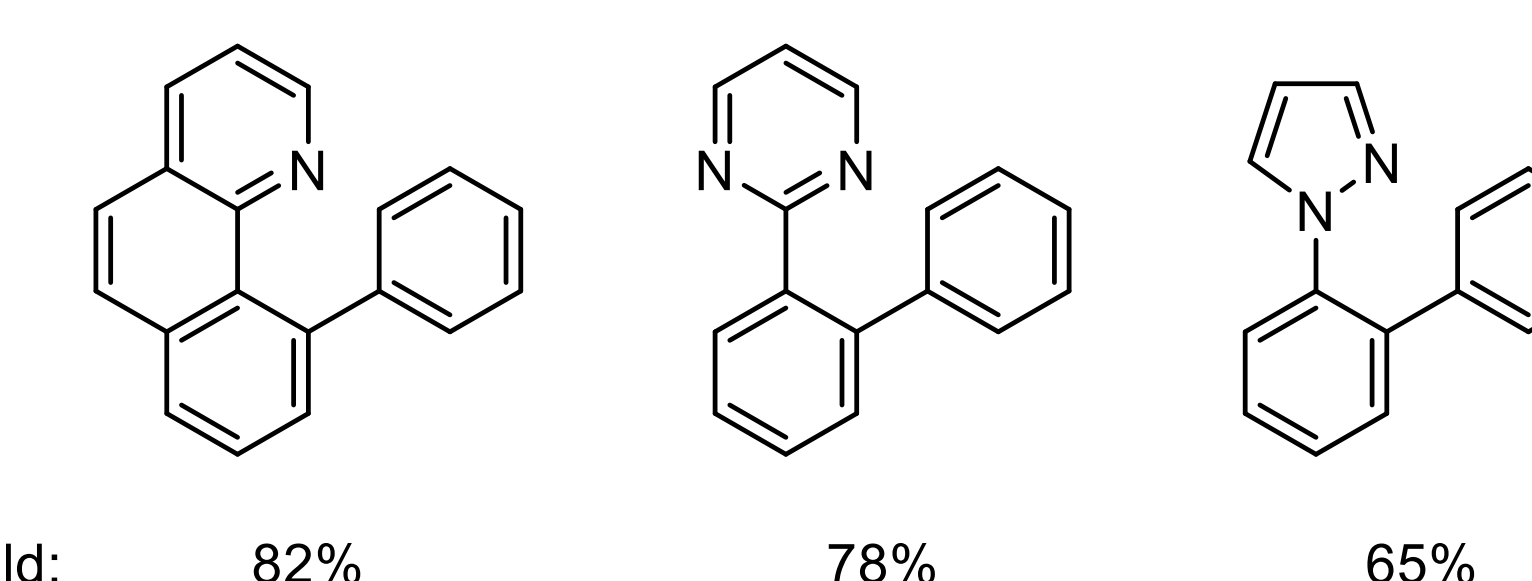
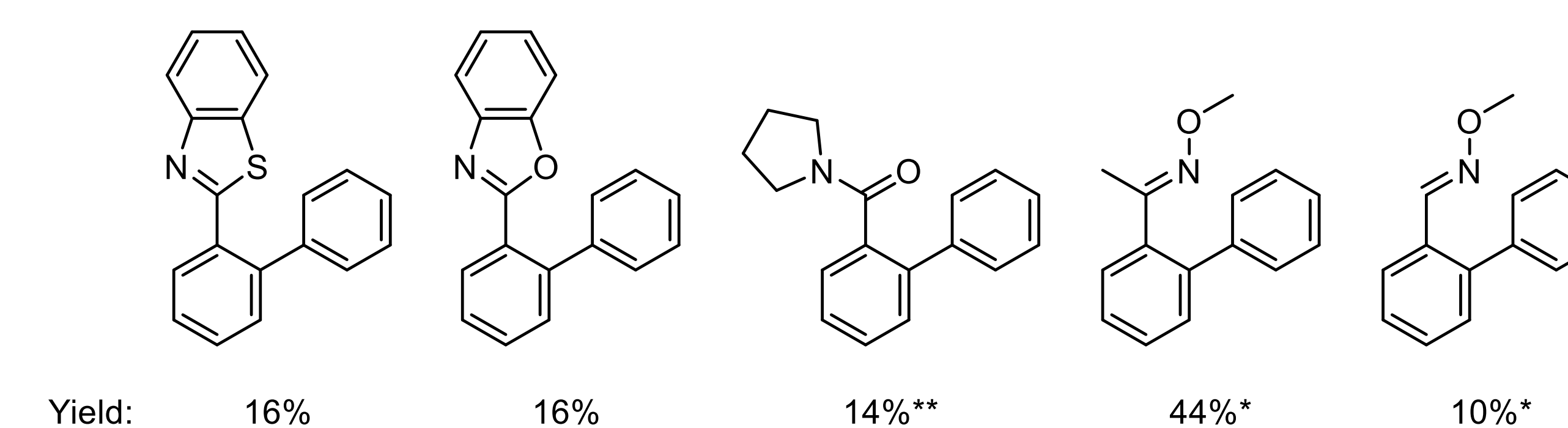
*Product yield as determined by GC/MS

RESULTS

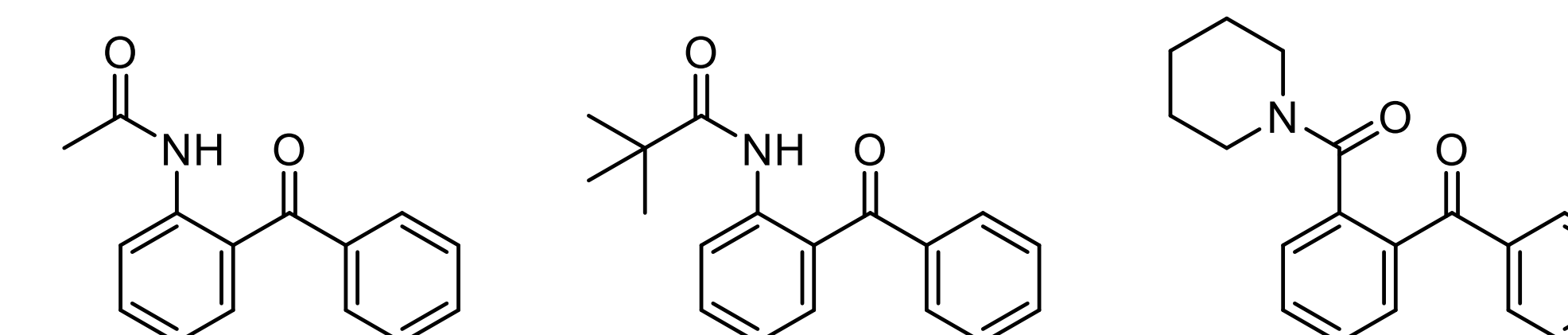


- Reactions are typically stirred for 16-18 hours followed by a work-up consisting of filtering through a silica plug, washing with brine, drying over sodium sulfate, and concentrating *in vacuo*

Decarbonylated Products



Unsuccessful Substrates



- For all reactions, only starting material and product were present

*Product yield as determined by GC/MS

**Decarbonylation proceeded successfully with the catalyst [Rh(CO)2Cl]2

CONCLUSIONS

- Several new directing groups have been successful in the decarbonylation reaction
- Directing groups with competing sites of coordination and extra degrees of freedom exhibit little to no reactivity

Next Steps

- Purify and characterize decarbonylated products
- Conduct decarbonylation reactions on untested ketones
- Explore other functional groups

