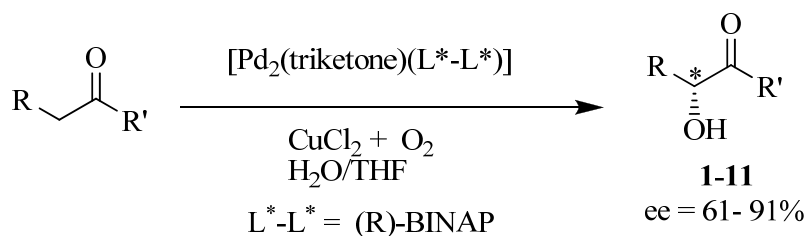


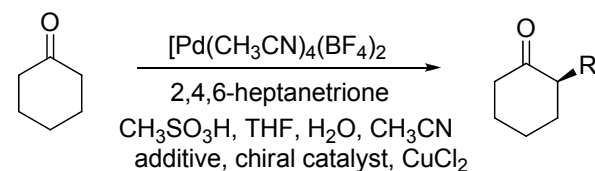
Palladium(II)-Catalyzed Asymmetric Synthesis of α -Substituted Ketones

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The research has as its ultimate goal to explore the enantioselective reaction of enols in palladium(II)-catalyzed systems and the development of a practical and straightforward asymmetric synthesis of α -substituted ketones. We have developed asymmetric α -hydroxylation, α -bromination, and α -azidation reactions in mixed aqueous media using a bimetallic achiral Pd(II) catalyst with triketone and chiral bidentate bridging groups as well as with mono-metallic palladium catalysts with chiral bidentate ligands.

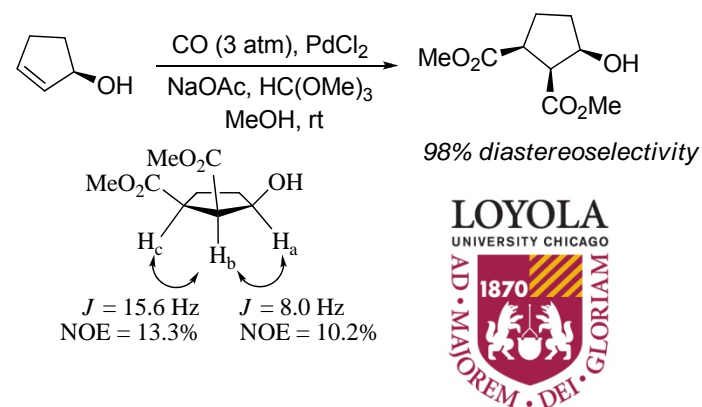


Run/ ID	R	R'	% ee ^e	$[\alpha]^{20}_{\text{D}}$
1	—CH ₂ CH ₂ CH ₂ CH ₂ —		67	14.0
2	CH ₃	Ph	68	62.3
3 ^b	CH ₃	Ph	82	69.8
4 ^c	CH ₃	Ph	51	46.2
5	CH ₃ CH ₂	Ph	71	23.7
6	Ph	Ph	87	141.8
8 ^d	Ph	Ph	85	-139.9
9	CF ₃	Ph	89	-7.8
10	2-furyl	2-furyl	91	59.2
11	3,5-di-flouroPh	3,5-di-flouro	90	46.8



O_2 , (S)-METBOX R = OH 69%, 88% e.e.
 NaBr , (S)-BINAP R = Br 90%, 88% e.e.
 Me_3SiN_3 , (S)-DINDA R = N₃ 90%, 85% e.e.

Independently, we have explored chirality transfer from chiral allylic alcohols utilizing the palladium-catalyzed olefin dicarbonylation reaction for the preparation of molecules with three contiguous chiral centers.



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