Decarboxylative Arylation of α-Amino Acids via Photoredox Catalysis

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Supervisor: Prof. Zhao Jing

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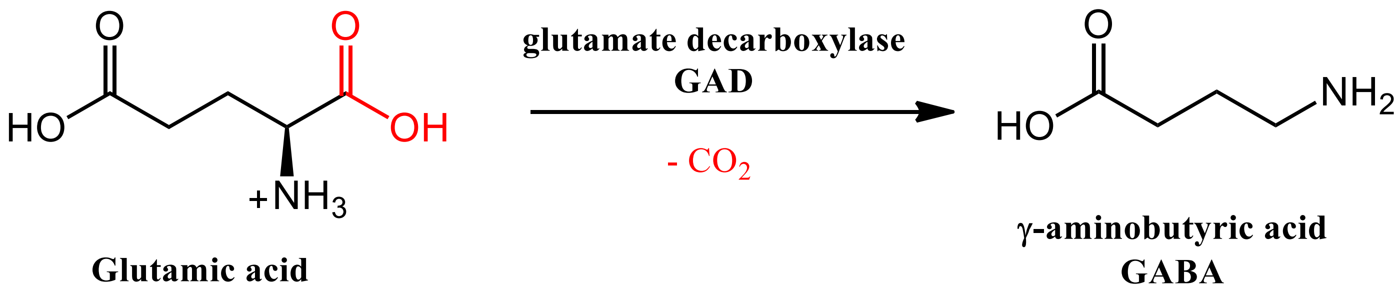
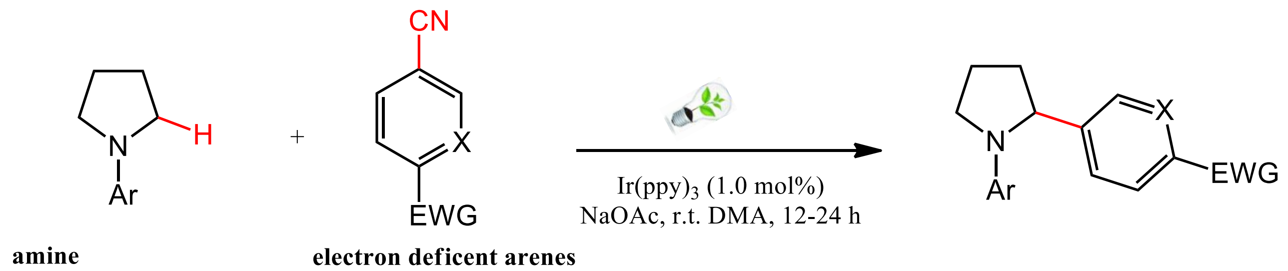
Decarboxylation

- Biochemical Precedent

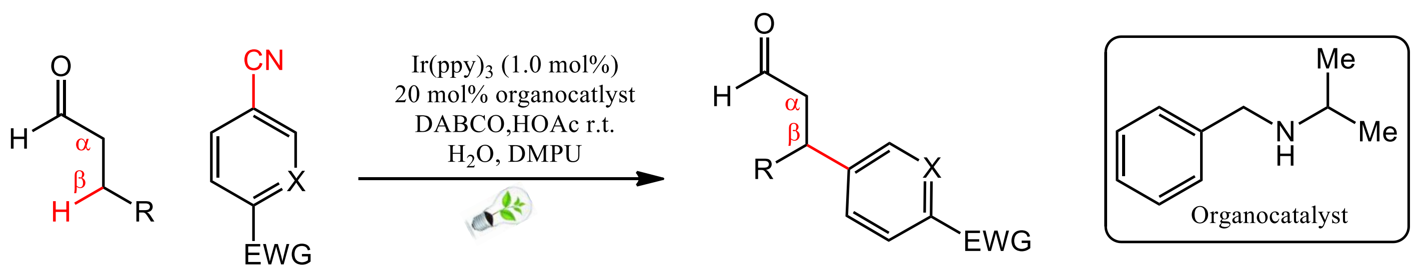


- Chemical Precedents
  - Hunsdiecker, Kolbe, Barton decarboxylation
  - Coupling reaction (Myers and Gooβen)

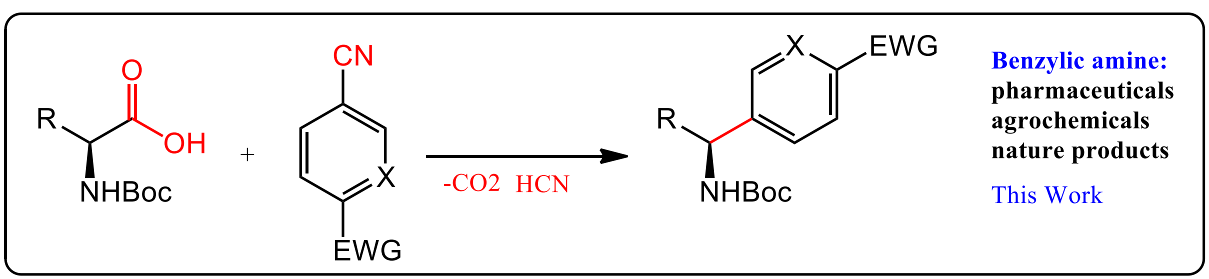
Previous Work



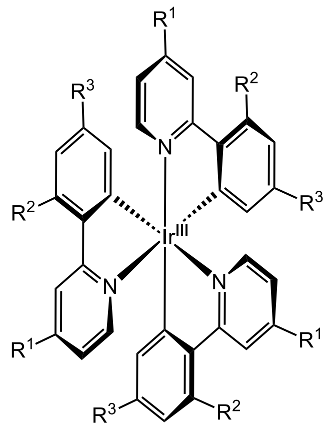
McNally, A.; Prier, C. K.; MacMillan, D. W. C. *Science* **2011**, *334*, 1114.



Pirnot, M. T.; Rankic, D. A.; Martin, D. B.; MacMillan, D. W. *Science* **2013**, *339*, 1593.



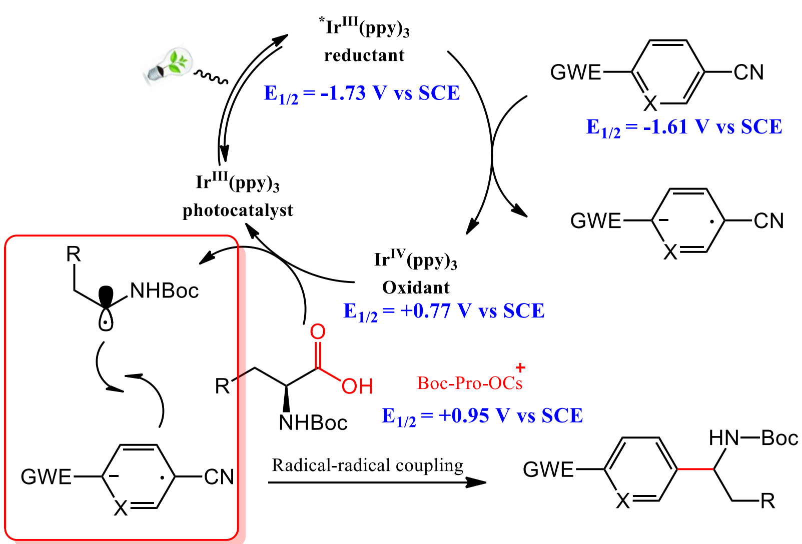
Ligand effects on ground-state redox properties of catalysts



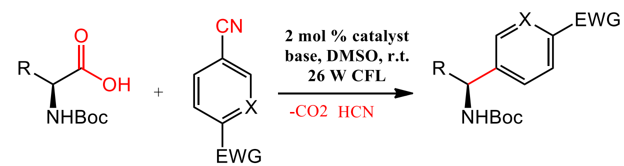
Group	Photocatalyst	$E_{1/2}^{red}[Ir^{IV}/Ir^{III}]$ vs SCE (Oxidant)	$E_{1/2}^{red}[Ir^{IV}/{}^{*}Ir^{III}]$ vs SCE (Reductant)	Entry
$R^1 = R^2 = R^3 = H$	$Ir(ppy)_3$	+ 0.77 V	- 1.73 V	A
$R^1 = R^2 = H,\ R^3 = F$	$Ir(p\text{-}F\text{-}ppy)_3$	+ 0.97 V	- 1.60 V	B
$R^1 = H,\ R^2 = R^3 = F$	$Ir(dFppy)_3$	+ 1.13 V	- 1.44 V	C
$R^1 = t\text{-}Bu,\ R^2 = H,\ R^3 = F$	$Ir[p\text{-}F(t\text{-}Bu)\text{-}ppy]_3$	---	---	D
$R^1 = t\text{-}Bu,\ R^2 = R^3 = F$	$Ir[dF(t\text{-}Bu)\text{-}ppy]_3$	---	- 1.67 V	E
	$Ir[dF(CF_3)ppy)_3(dtbpy)^+$	+ 1.69 V	- 0.89 V	F

Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem.* **2012**, *77*, 1617.

Design

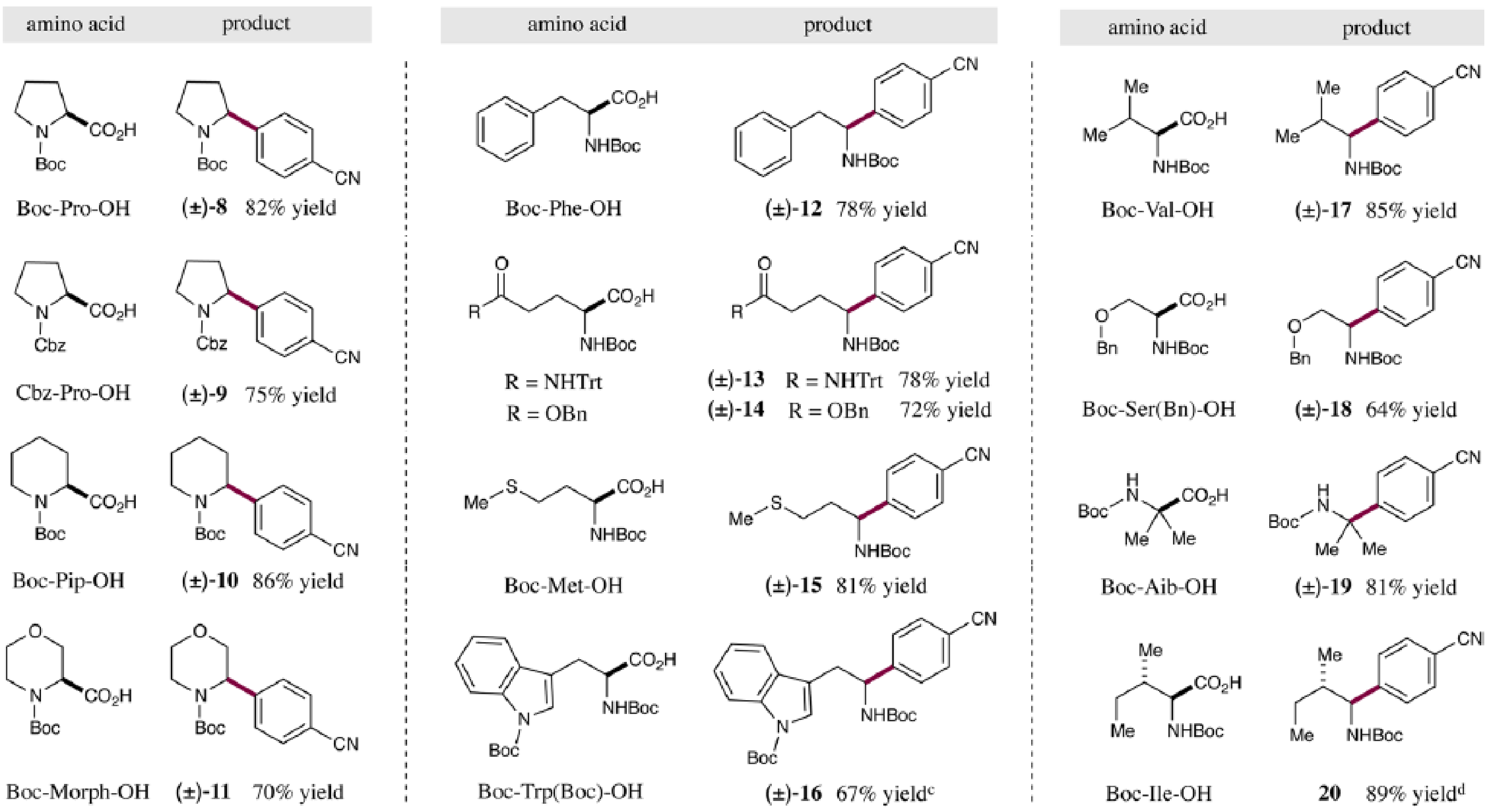


Conditions Screening

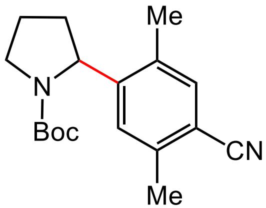


entry	photocatalyst	base	% yield[a]
1	$Ir(ppy)_3$	K_2HPO_4	12
2	$Ir(p\text{-}F\text{-}ppy)_3$	K_2HPO_4	58
3	$Ir(dFppy)_3$	K_2HPO_4	54
4	$Ir[dF(CF_3)ppy]_2(dtbbpy)$	K_2HPO_4	trace
5	$Ir[p\text{-}F(t\text{-}Bu)\text{-}ppy]_3$	K_2HPO_4	73
6	$Ir[dF(t\text{-}Bu)\text{-}ppy]_3$	K_2HPO_4	68
7	$Ir[p\text{-}F(t\text{-}Bu)\text{-}ppy]_3$	CsF	83
8[b]	$Ir[p\text{-}F(t\text{-}Bu)\text{-}ppy]_3$	CsF	0
9	none	CsF	0
10	$Ir[p\text{-}F(t\text{-}Bu)\text{-}ppy]_3$	none	trace

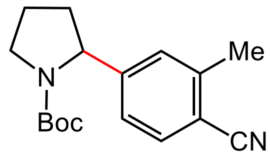
α-Amino Acid Scope



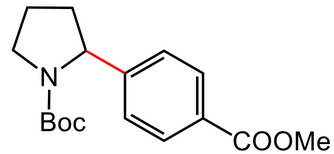
Aromatic Scope



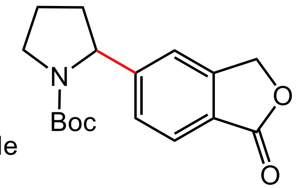
2a 85% yield



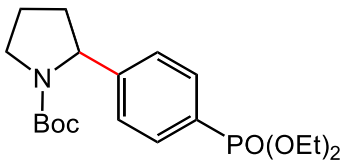
2b 77% yield



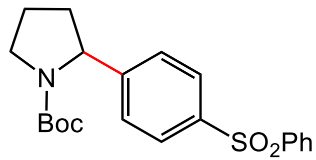
2c 52% yield



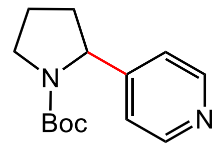
2d 70% yield



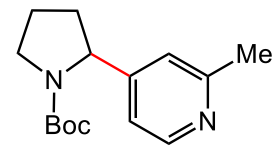
2e 65% yield



2f 64% yield

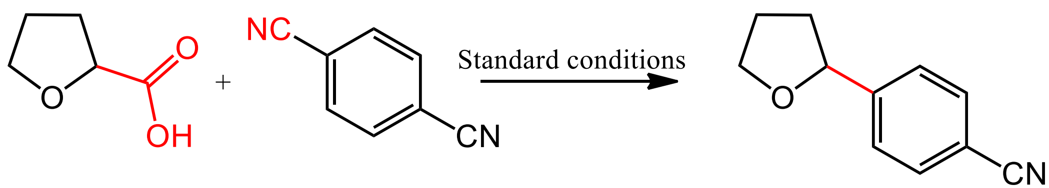


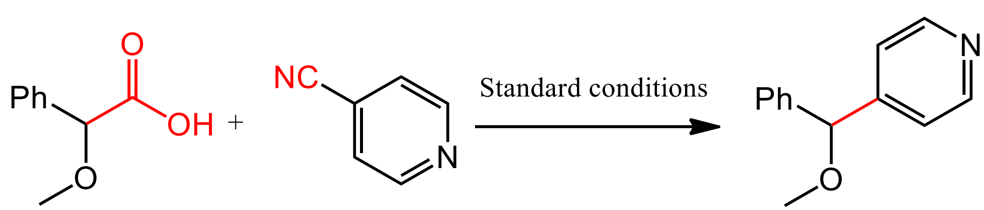
2g 73% yield



2h 83% yield

Another Two Examples





Summary

- Ligand effects are important for Photo-catalyzed reactions.
- The substrates are limited in electron-deficient aromatic compounds.