Palladium-Catalyzed C(sp^3)-H Activation/C(sp^3)-O Bond Formation

Petr Novak, Arkaitz Correa, Joan Gallardo-Donaire, and Ruben Martin*

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Reporter : Rong Ben
Advisor : Prof. Jing Zhao

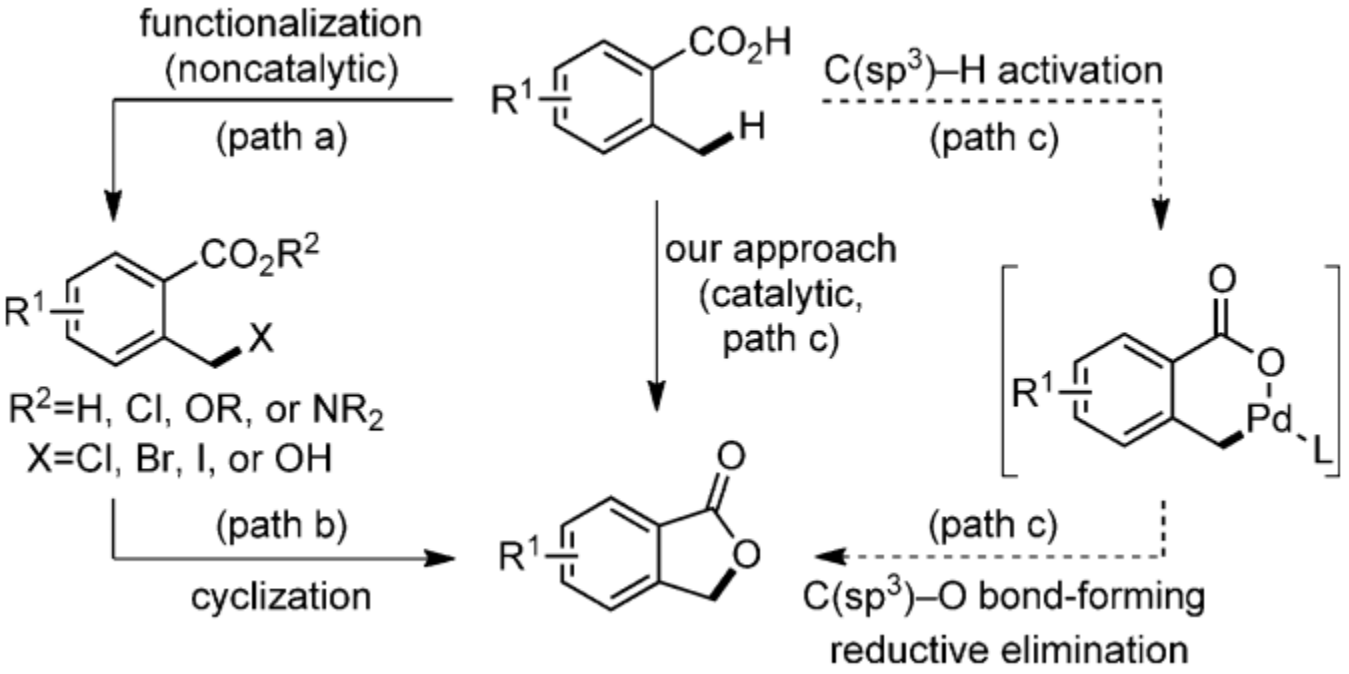
Ruben Martin's Profile

Research interests:

- Metal-catalyzed Activation of CO_2
- Metal-catalyzed Activation of C-H Bonds
- Metal-catalyzed Activation of C-O Bonds

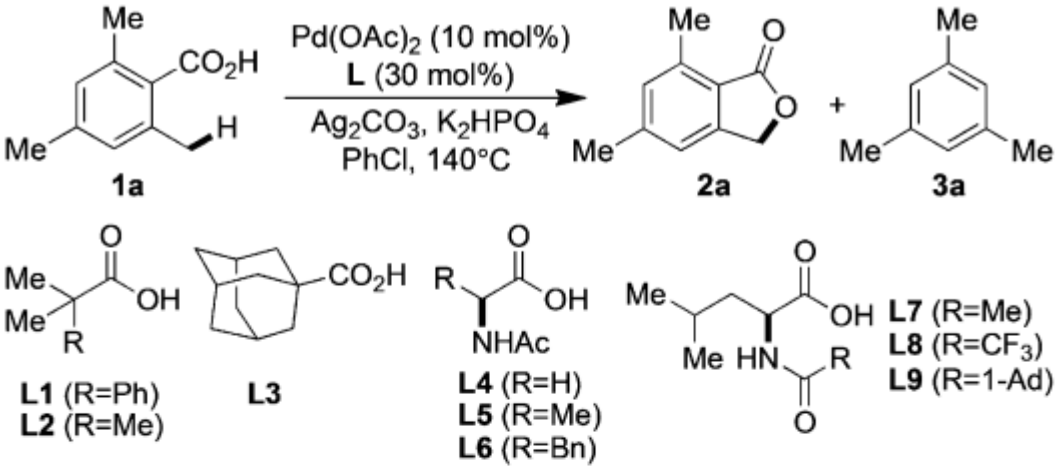
Group leader at ICIQ(the Institute of Chemical Research of Catalonia)

Introduction



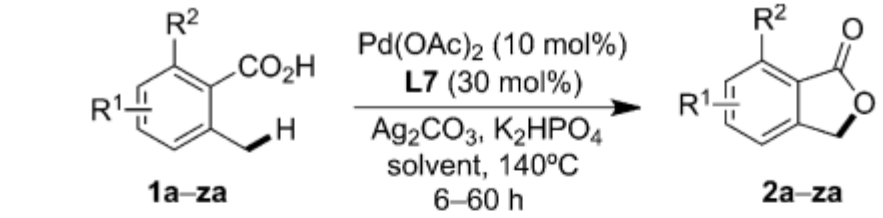
- Step-Economical approach
- Activation of $C(sp^3)$-H bond

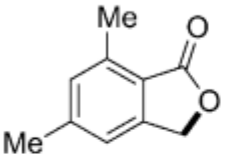
Condition Optimization



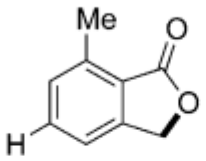
Entry	Ligand	Yield [%][b]	
		2a	**3a**
1	L1	22	17
2	L2	63[c]	1
3	L3	71[c]	13
4	L4	7	3
5	L5	74	12
6	L6	43	11
7	**L7**	**95[c]**	**1**
8	L7	80[c,d]	1
9	L8	36	32
10	L9	42	37
11[e]	–	22	14

Substrate Scope

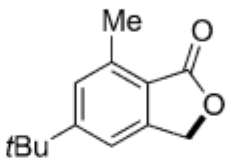




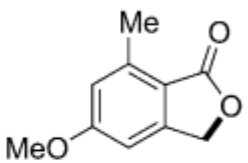
95% (**2a**)



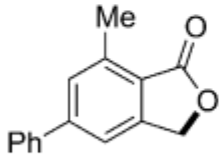
70% (**2b**)



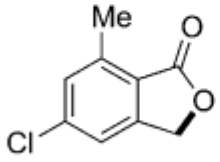
75% (**2c**)



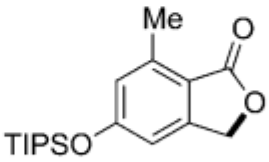
65% (**2d**)



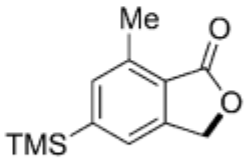
68% (**2e**)



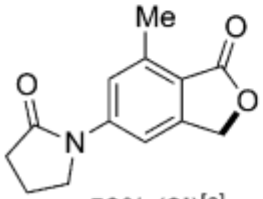
41% (**2f**)[a]



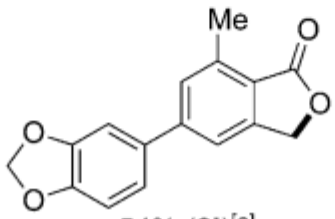
57% (**2g**)



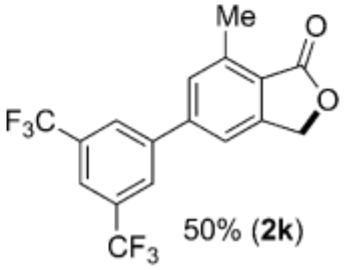
76% (**2h**)



53% (**2i**)[a]

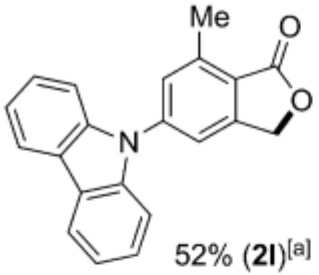


54% (**2j**)[a]

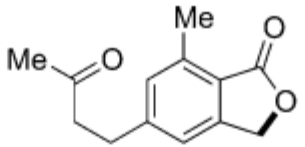


50% (**2k**)

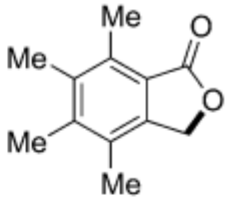
Substrate Scope



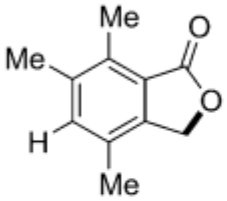
52% (**2l**)[a]



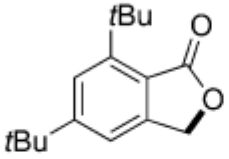
52% (**2m**)[b]



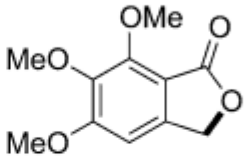
55% (**2n**)



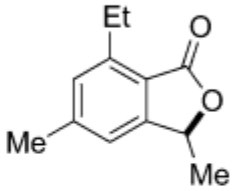
50% (**2o**)



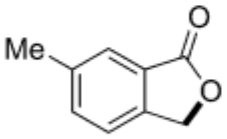
52% (**2p**)



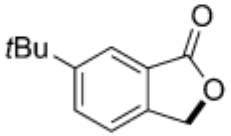
50% (**2q**)



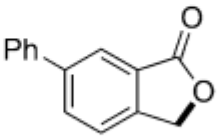
38% (**2r**)



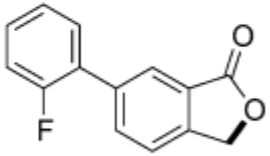
70% (**2s**)
0%[c]



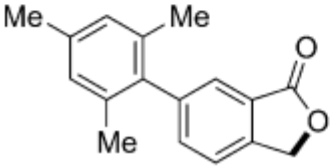
72% (**2t**)
0%[c]



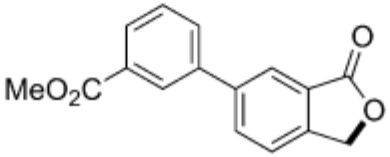
55% (**2u**)
0%[c]



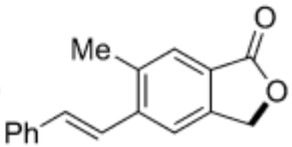
53% (**2v**)
0%[c]



62% (**2w**)

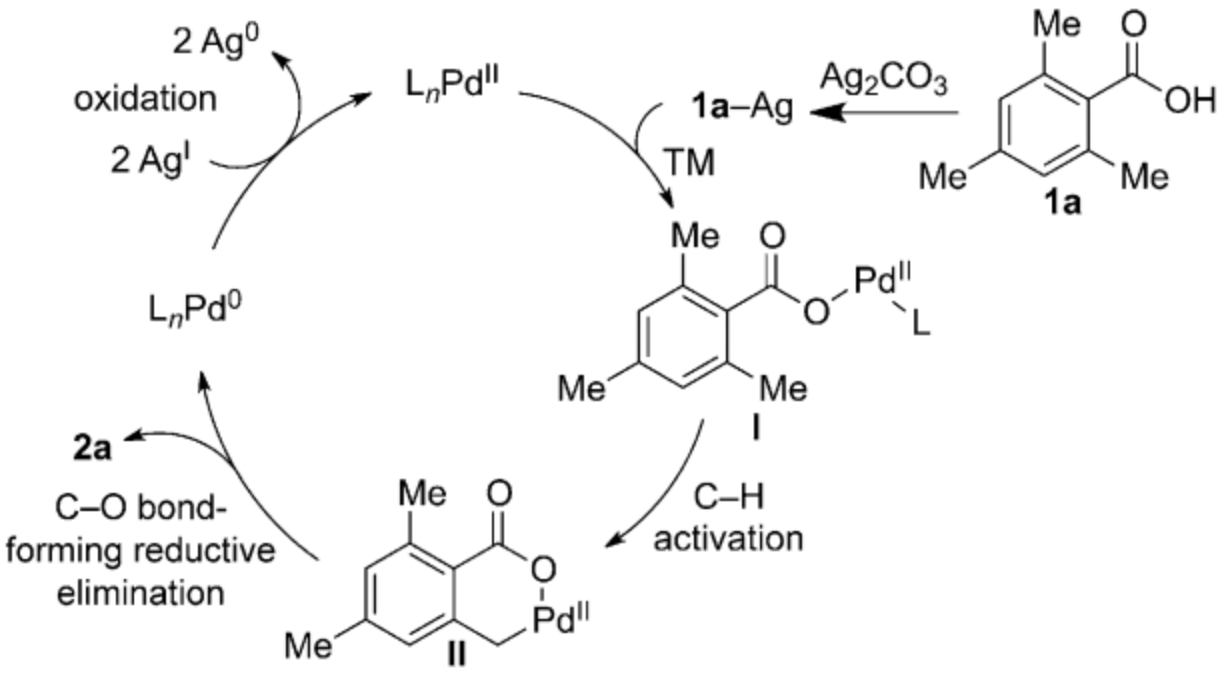


47% (**2x**)[a]



51% (**2y**)[a]

Tentative Mechanism



Cu-Catalyzed Mild C(sp^2)–H Functionalization Assisted by Carboxylic Acids

Joan Gallardo-Donaire and Ruben Martin*

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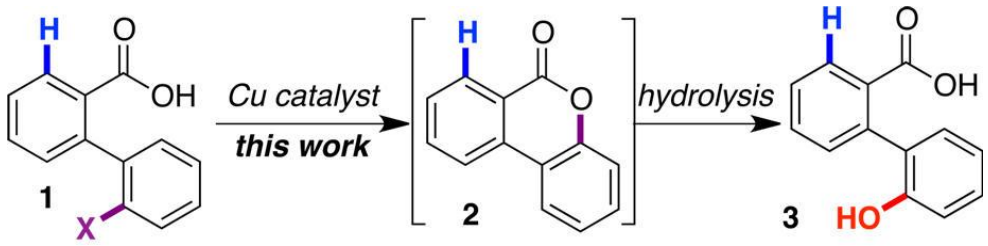
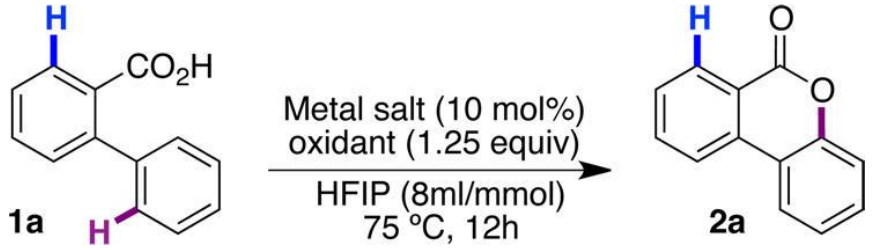
Introduction

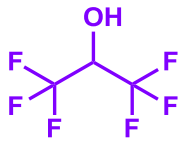


- Cheap Cu catalysts
- Mild reaction conditions
- C-H hydroxylation

Condition Optimization

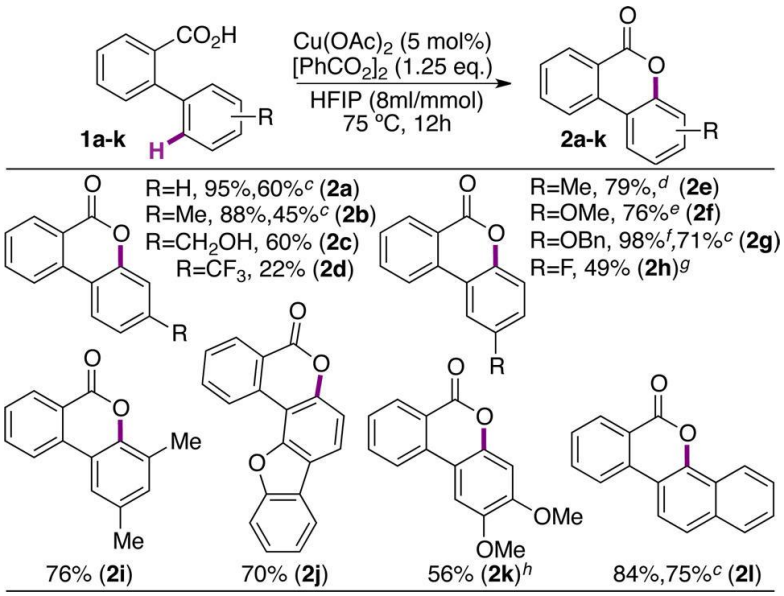


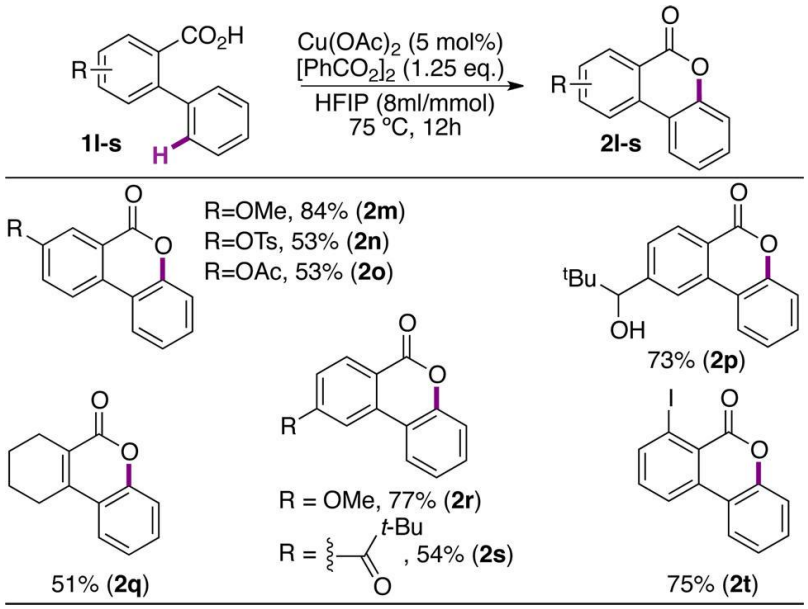
HFIP:



entry	metal source	oxidant	additive (x mol %)	**4a** (%)[b]
1	$Pd(OAc)_2$	$K_2S_2O_8$	2-$FC_6H_4CO_2H$ (30)	70[c]
2	$Pd(OAc)_2$	BQ (1 equiv)	KOAc (200)	0[d]
3	$Cu(OAc)_2$	^tBuOOH	–	15
4	$Cu(OAc)_2$	^tBuOOBz	–	3
5	$Cu(OAc)_2$	$K_2S_2O_8$	–	3
6	$Cu(OAc)_2$	$[PhCO_2]_2$	–	95,88[e]
7	$Cu(OAc)_2$	$[PhCO_2]_2$	–	66,[f] 0[g]
8	$Cu(OTf)_2$	$[PhCO_2]_2$	–	21
9	$CuBr_2$	$[PhCO_2]_2$	–	79
10	CuOAc	$[PhCO_2]_2$	–	88
11	$Cu(OAc)_2$	$[PhCO_2]_2$	phen(10)[h]	58
12	–	$[PhCO_2]_2$	–	15
13	***$Cu(OAc)_2$***	***$[PhCO_2]_2$***	–	***97(95)***[i,j,k]

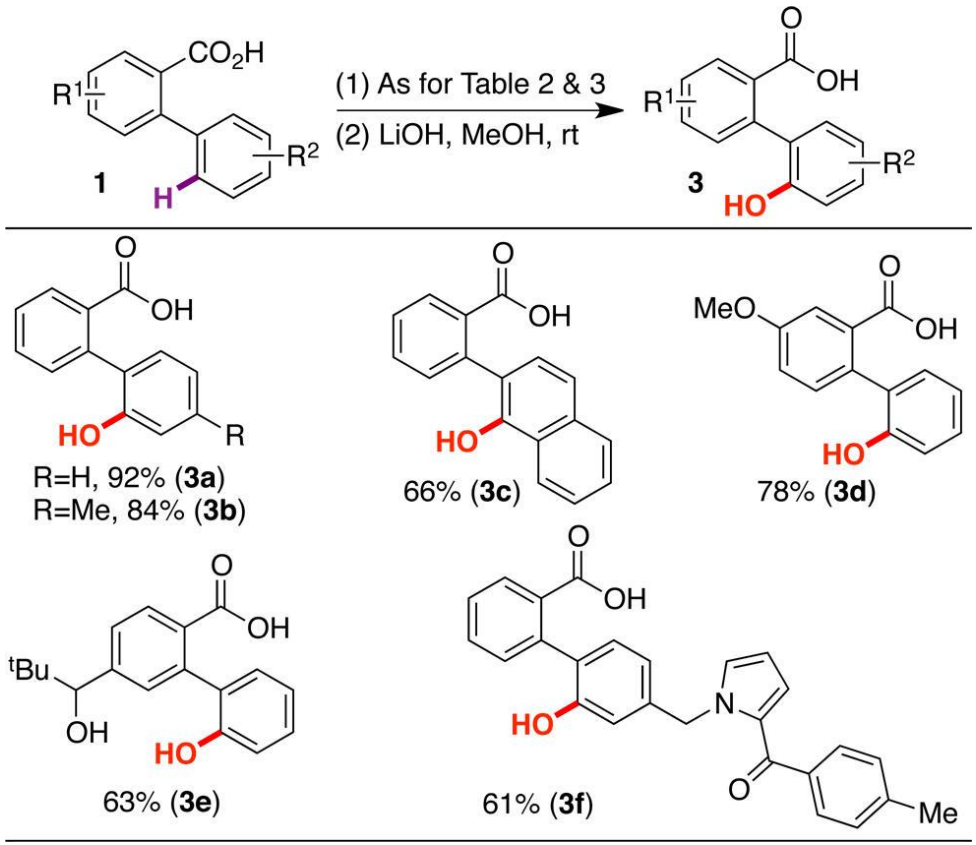
Substrate Scope





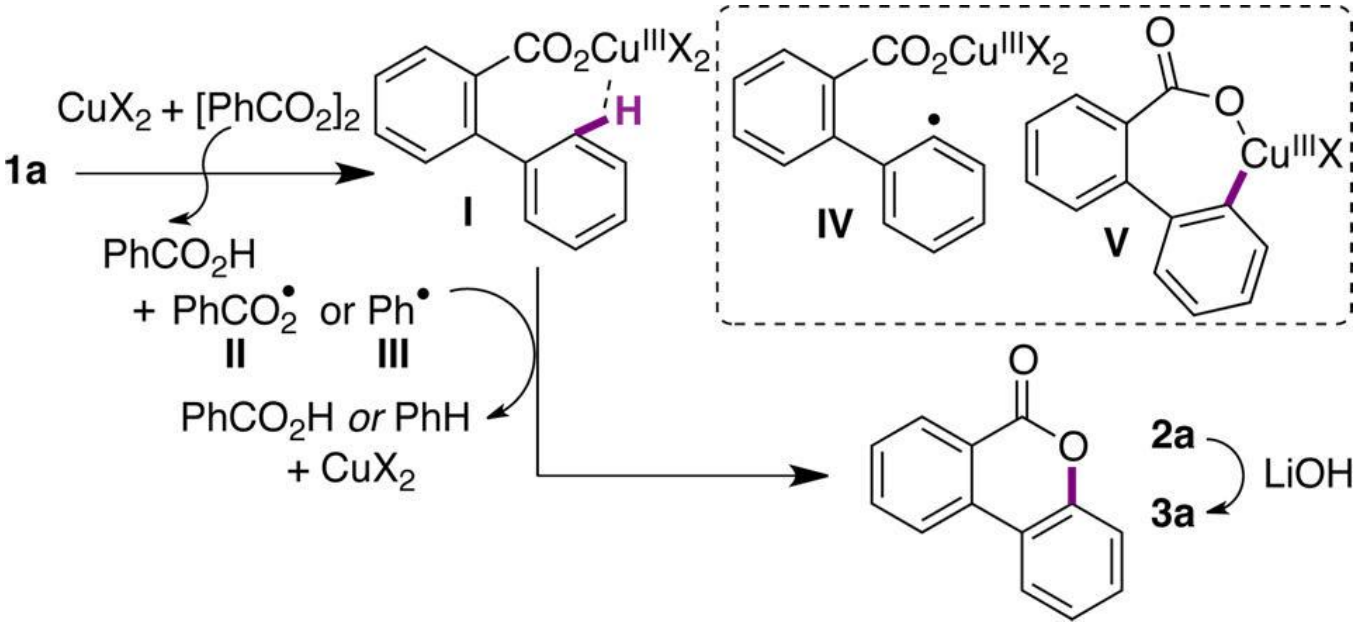
Substrate Scope

Remote C – H Hydroxylation



High overall yields from available starting materials!

Mechanistic Hypothesis



Thank you for your attention!