Literature Report

Reporter: Yu Bole

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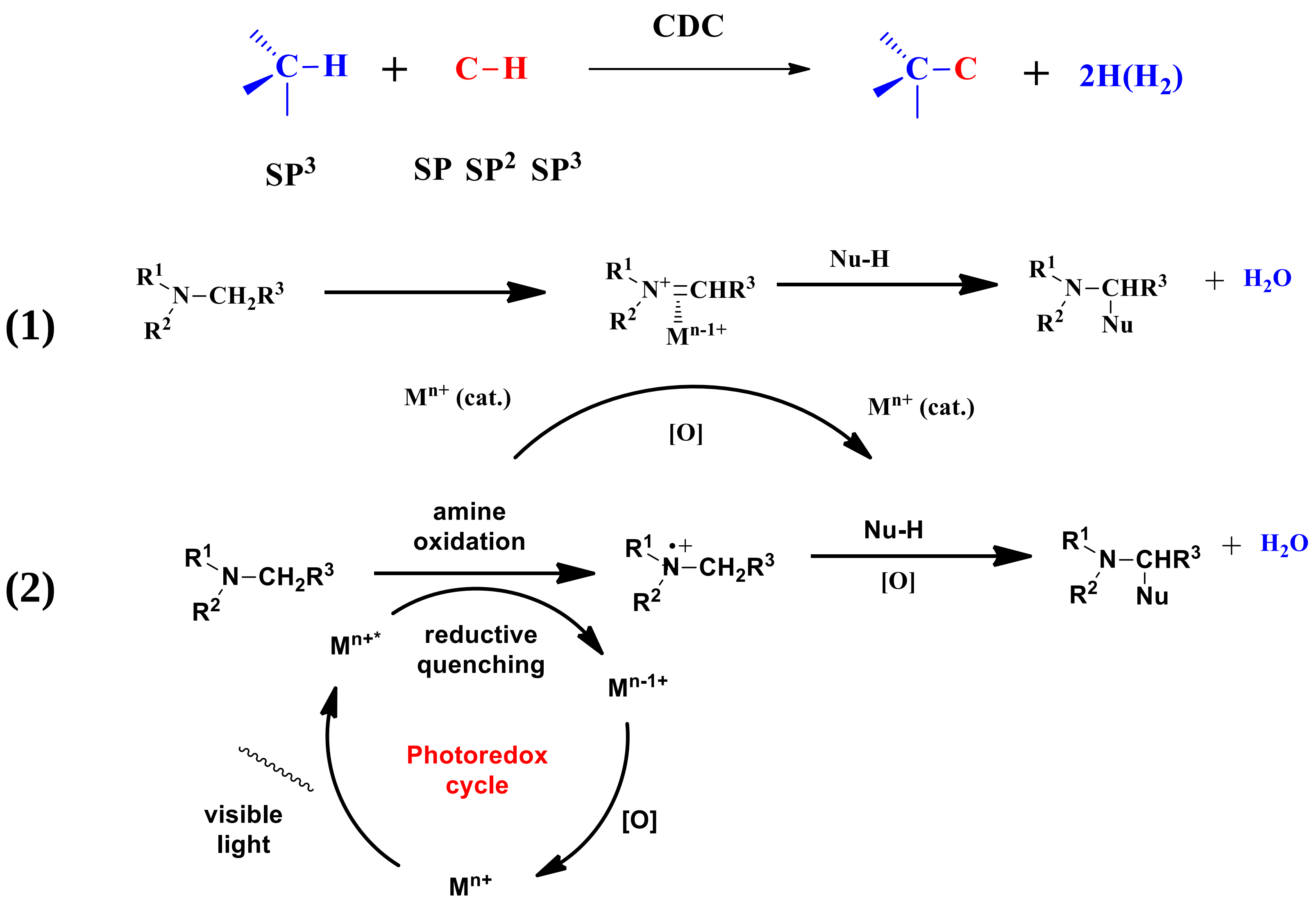
2014-03-03

Cross-Dehydrogenative Coupling



Graphene-Supported RuO_2 Nanoparticles for Efficient Aerobic Cross-Dehydrogenative Coupling Reaction in Water

ORGANIC LETTERS

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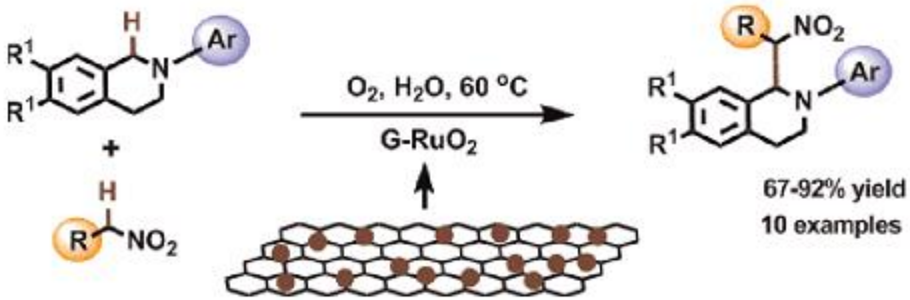
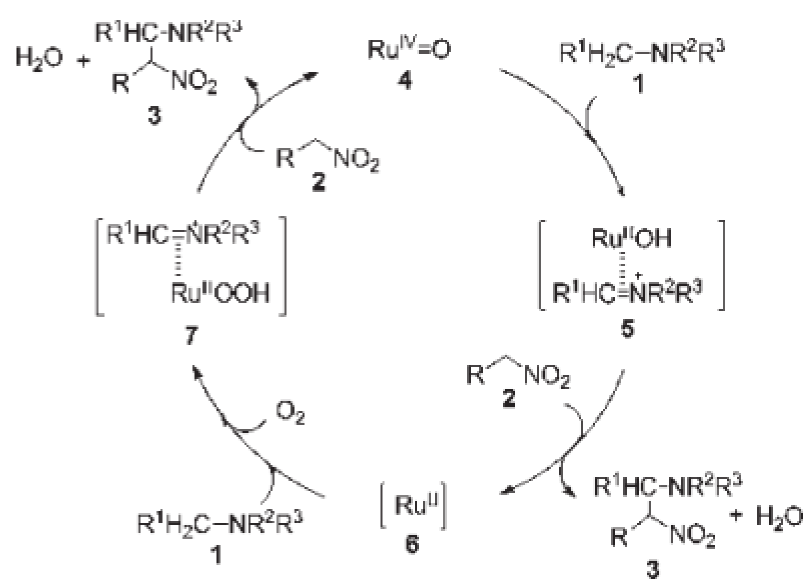
Qing-Yuan Meng,[†] Qiang Liu,[†,‡] Jian-Ji Zhong,[†] Hui-Hui Zhang,[†] Zhi-Jun Li,[†] Bin Chen,[†] Chen-Ho Tung,[†] and Li-Zhu Wu*,[†]



entry	catalyst	solvent	gas (1 atm)	yield (%)[b]
1	G-RuO_2[c]	H_2O	O_2	78
2	$RuCl_3 \cdot nH_2O$	H_2O	O_2	43
3	$RuO_2 \cdot nH_2O$	H_2O	O_2	54
4	G-RuO_2[c]	H_2O	air	36
5	no	H_2O	O_2	0
6	G-RuO_2[c]	H_2O	N_2	0



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Communication

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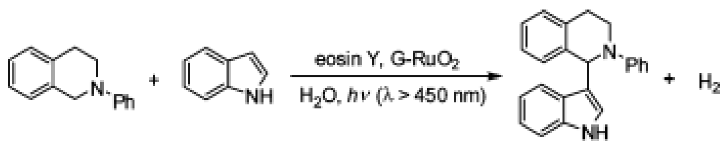
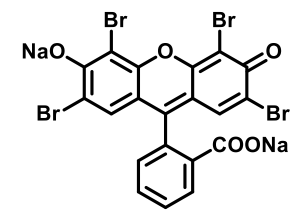
A Cascade Cross-Coupling Hydrogen Evolution Reaction by Visible Light Catalysis

Qing-Yuan Meng,† Jian-Ji Zhong,† Qiang Liu,†,‡ Xue-Wang Gao,† Hui-Hui Zhang,† Tao Lei,† Zhi-Jun Li,† Ke Feng,† Bin Chen,† Chen-Ho Tung,† and Li-Zhu Wu*,†



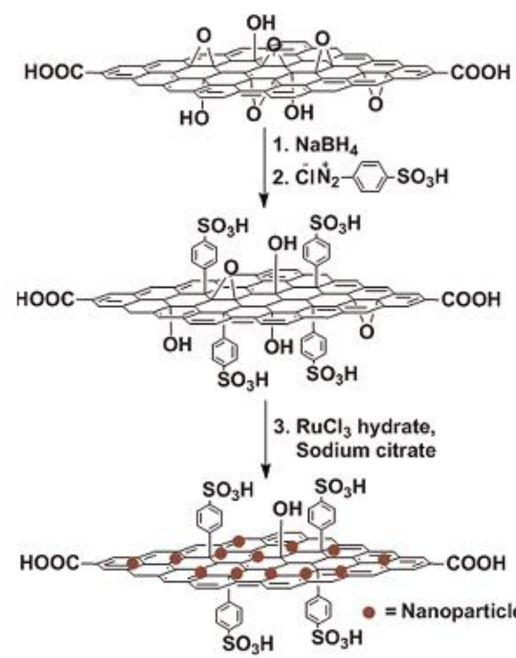
1a 2a 3a

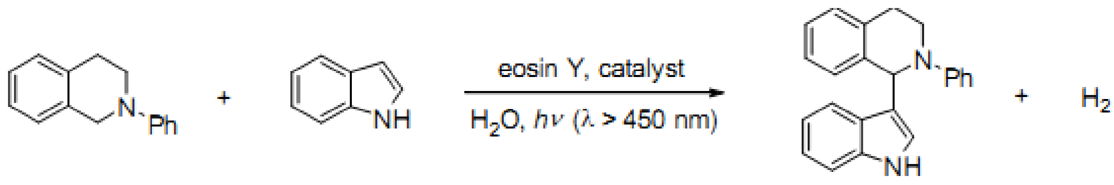
Eosin Y



entry	eosin Y (equiv %)	time (h)	conv (%)[b]	yield 3a (%)[c]	yield H_2 (%)[d]
1	5	10	30	50	25
2	20	10	70	62	78
3	20	20	90	89	76
4	15	20	68	77	58
5	25	20	84	81	75
6	50	20	85	77	52
7[e]	20	20	90	92	83
8[f]	20	20	94	94	88
9[g]	20	20	98	95	90

[a]Conditions: 0.1 mmol **1a**, 0.2 mmol **2a**, 0.0003 mmol G-RuO_2, and corresponding amount of eosin Y in 5 mL of H_2O under N_2, irradiation of $\lambda > 450$ nm at room temperature. [b]Corresponding to **1a**. [c]Based on **1a** and determined by NMR using 4-nitroacetophenone as an internal standard. [d]Based on **1a**. [e]2.5 equiv of **2a**. [f]3.0 equiv of **2a**. [g]4.0 equiv of **2a**.

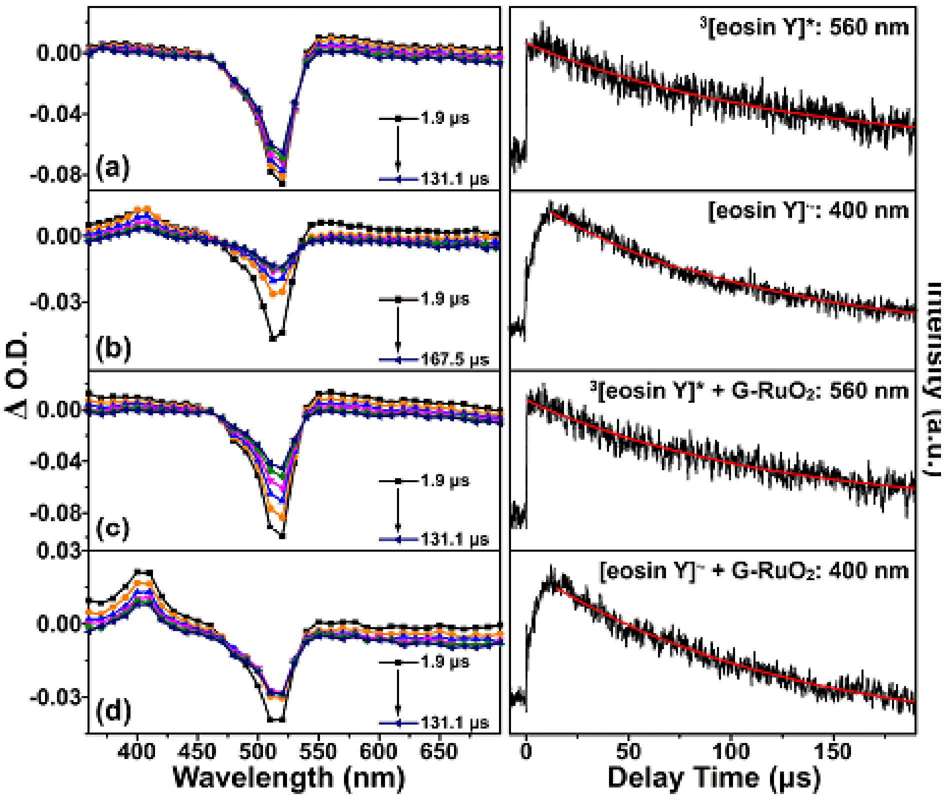




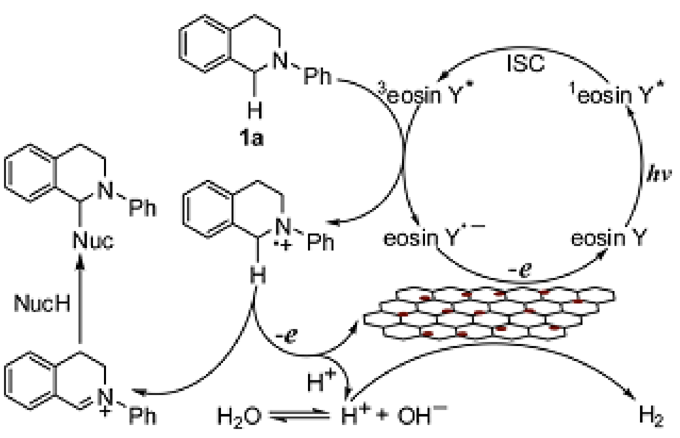
Entry	Solvent	Catalyst	Conversion (%)[b]	Yield (%)[c]	H_2 (%)[d]
1	H_2O:CH_3OH (1:1)	G-RuO_2	83	67	56
2	H_2O:CH_3CN (1:1)	G-RuO_2	89	40	trace
3	H_2O:DMF (1:1)	G-RuO_2	68	63	trace
4[e]	H_2O	--	9	10	0
5[f]	H_2O	G-RuO_2	trace	trace	0
6[g]	H_2O	G-RuO_2	trace	trace	0
7	H_2O	$RuO_2 \cdot nH_2O$	90	65	23
8	H_2O	Al_2O_3-RuO_2[h]	50	53	27

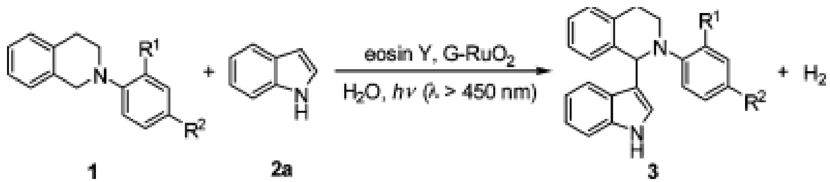
[a] Conditions: 0.1 mmol **1a**, 0.3 mmol **2a**, 0.0003 mmol G-RuO_2, and 0.02 mmol eosin Y in 5 mL of H_2O under N_2, irradiation of $\lambda > 450$ nm at room temperature, and 600 μL CH_4 as an internal standard. [b] Corresponding to **1a**. [c] Based on **1a** and determined by NMR using 4-nitroacetophenone as an internal standard. [d] Based on **1a**. [e] In the absence of G-RuO_2. [f] In the absence of eosin Y. [g] The reaction was carried out in the dark. [h] RuO_2 supported on Al_2O_3.

Transient absorption spectra

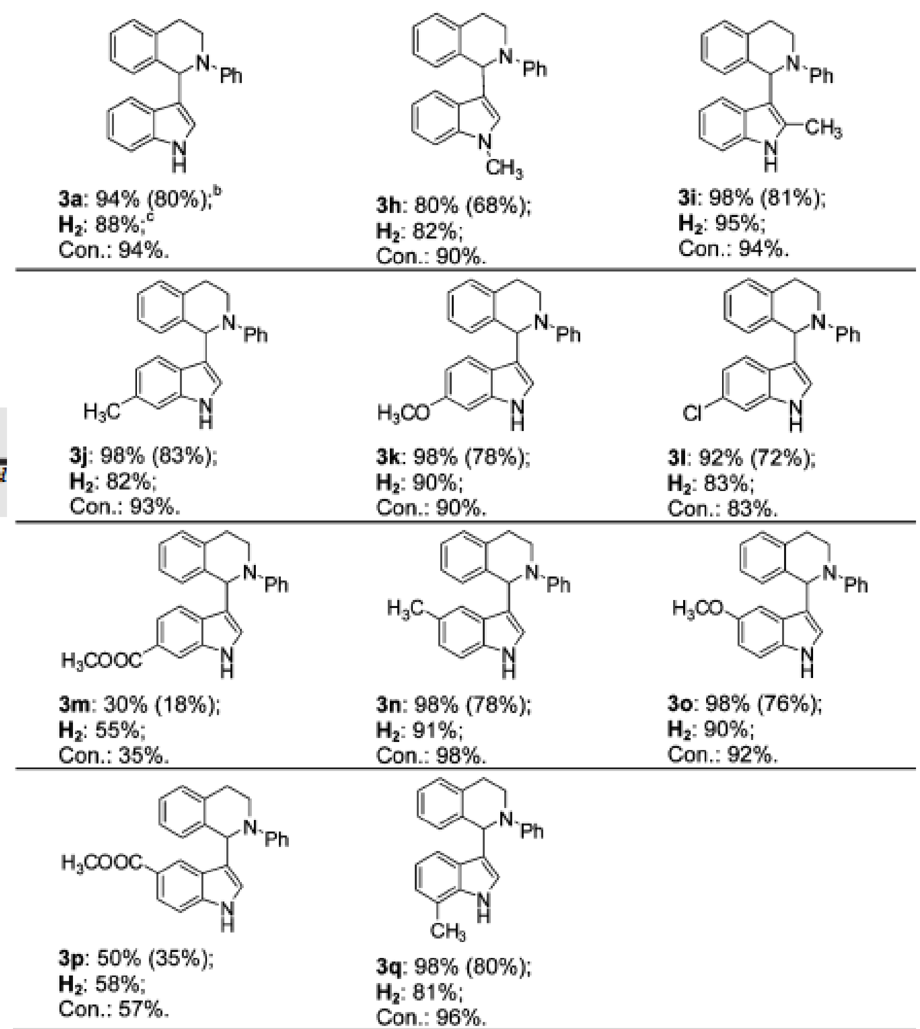


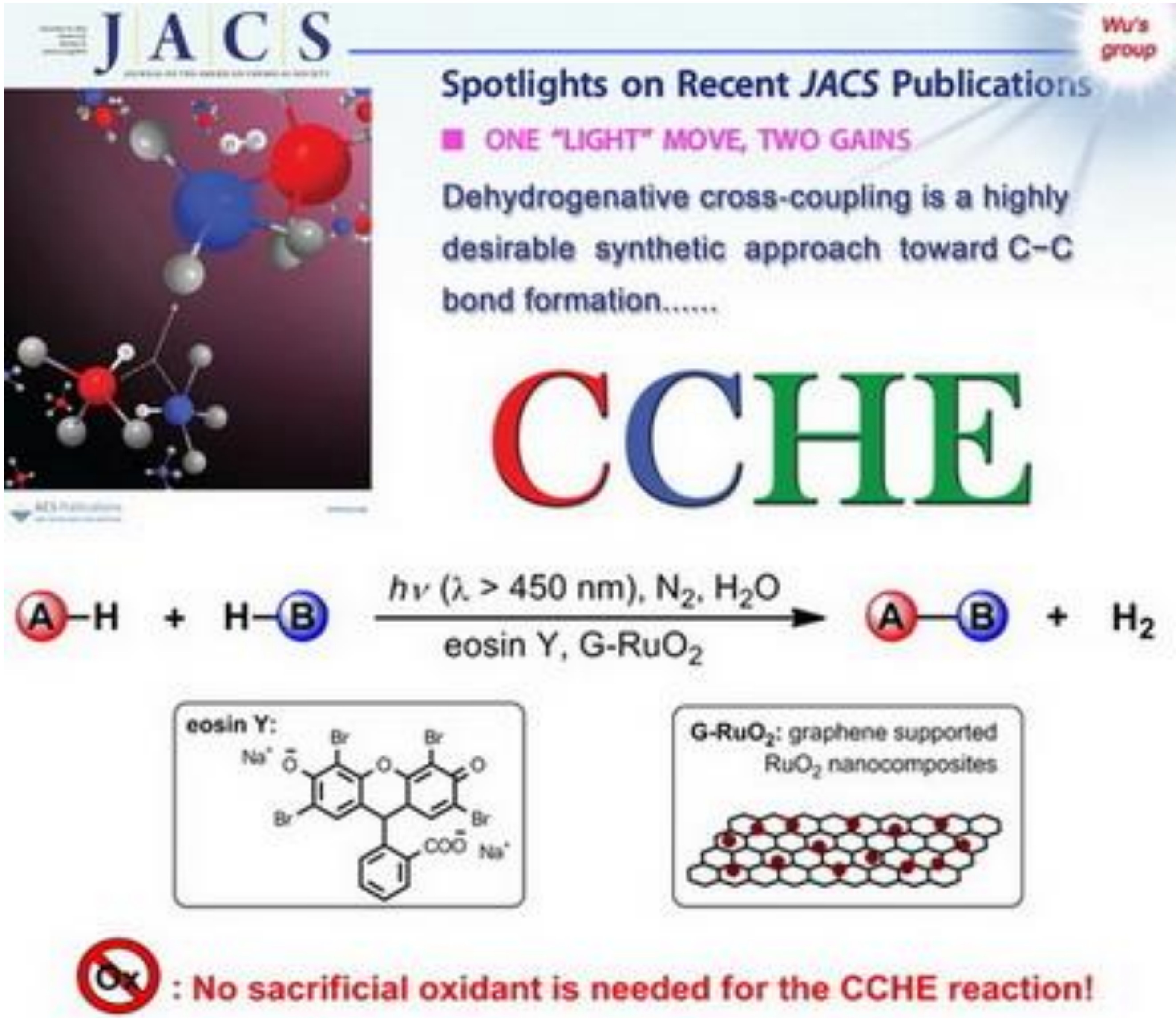
Scheme 3. Proposed Mechanism



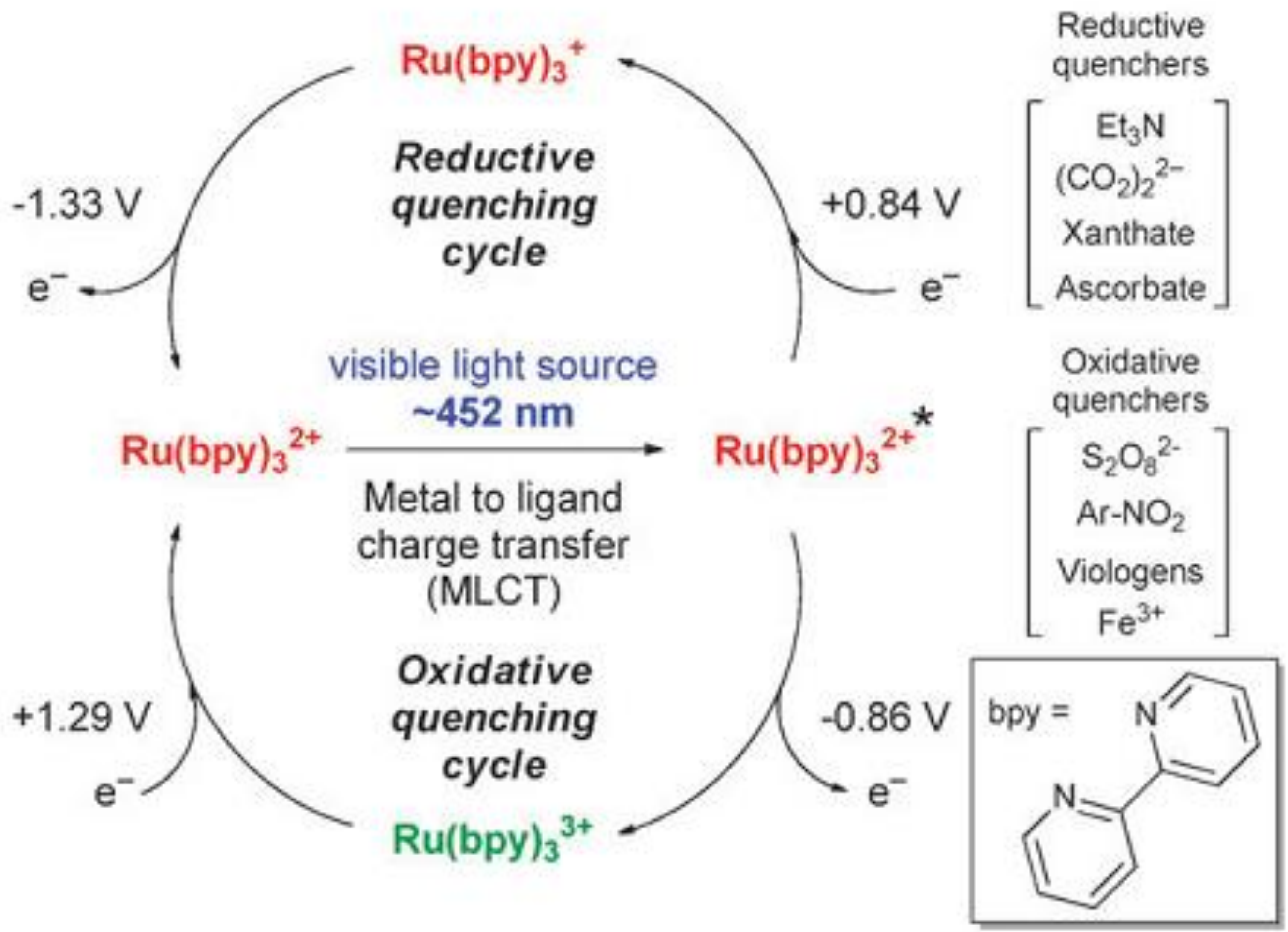


entry	R^1	R^2	conv (%)[b]	yield	
				3 (%)[c]	H_2 (%)[d]
1	H	H	94	**3a**, 94(80)	88
2	H	CH_3	85	**3b**, 96(78)	96
3	H	OCH_3	35	**3c**, 83(58)	43
4	OCH_3	H	21	**3d**, 89(56)	80
5	H	F	91	**3e**, 96(82)	96
6	H	Cl	83	**3f**, 91(74)	76
7	H	Br	80	**3g**, 89(70)	73
8	H	CN	trace	0	trace




JACS
Wu's group
Spotlights on Recent JACS Publications
ONE "LIGHT" MOVE, TWO GAINS
Dehydrogenative cross-coupling is a highly desirable synthetic approach toward C−C bond formation......
CCHE
A−H + H−B
hν (λ > 450 nm), N2, H2O
eosin Y, G-RuO2
A−B + H2
eosin Y:
Br
Br
Na+
O
O
Br
Br
COO−
Na+
G-RuO2: graphene supported RuO2 nanocomposites
Ox
: No sacrificial oxidant is needed for the CCHE reaction!

Photoredox (one-electron redox)



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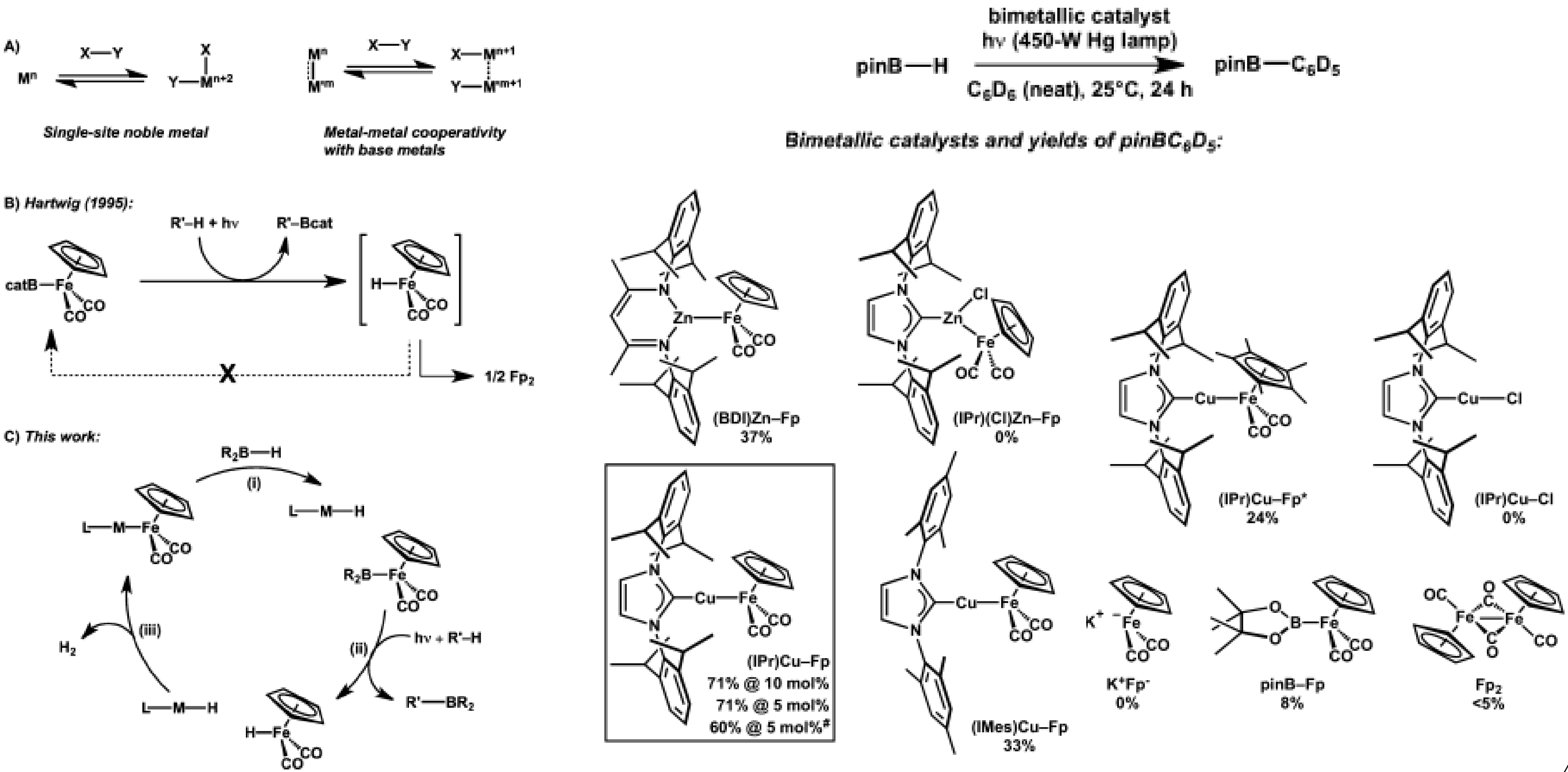
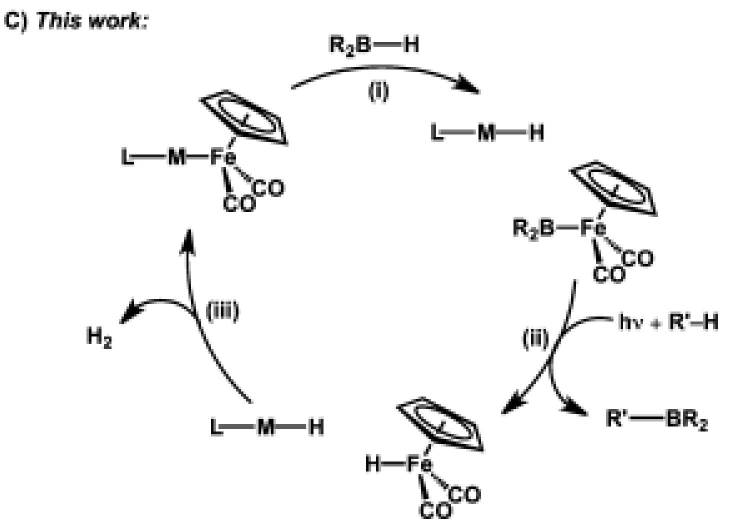
Base Metal Catalysts for Photochemical C–H Borylation That Utilize Metal–Metal Cooperativity

Thomas J. Mazzacano and Neal P. Mankad*



Mechanistic studies



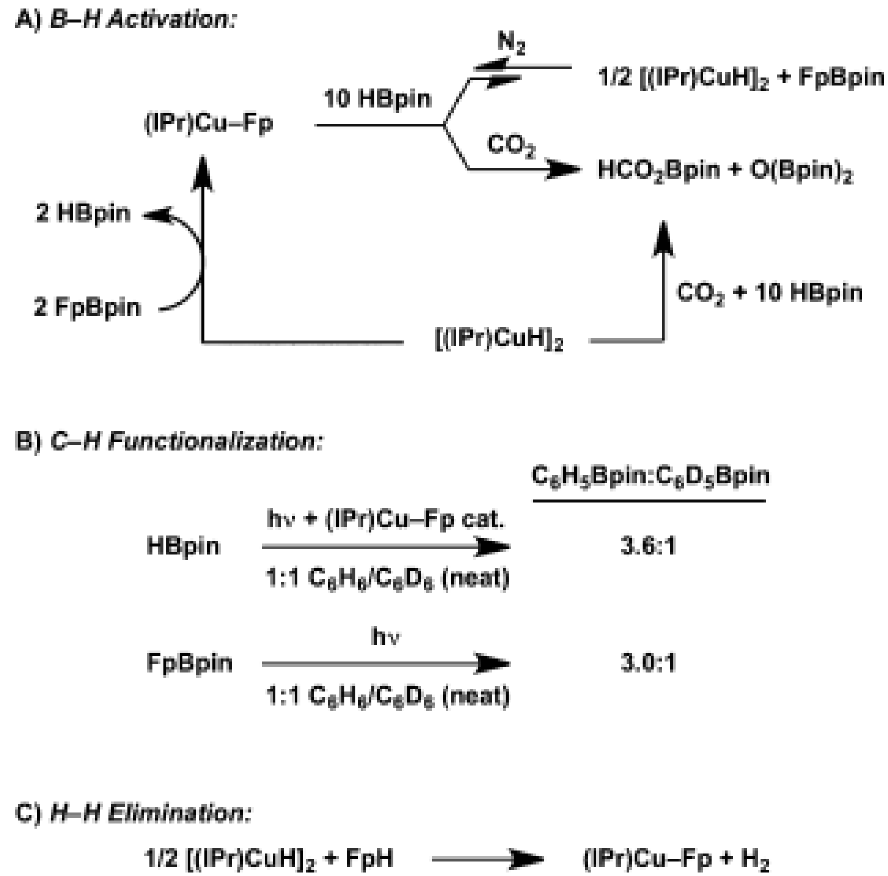


Figure 4. Mechanistic studies for the proposed elementary steps: (A) reversible B−H activation, (B) C−H functionalization, and (C) H_2 elimination.

THANK YOU !