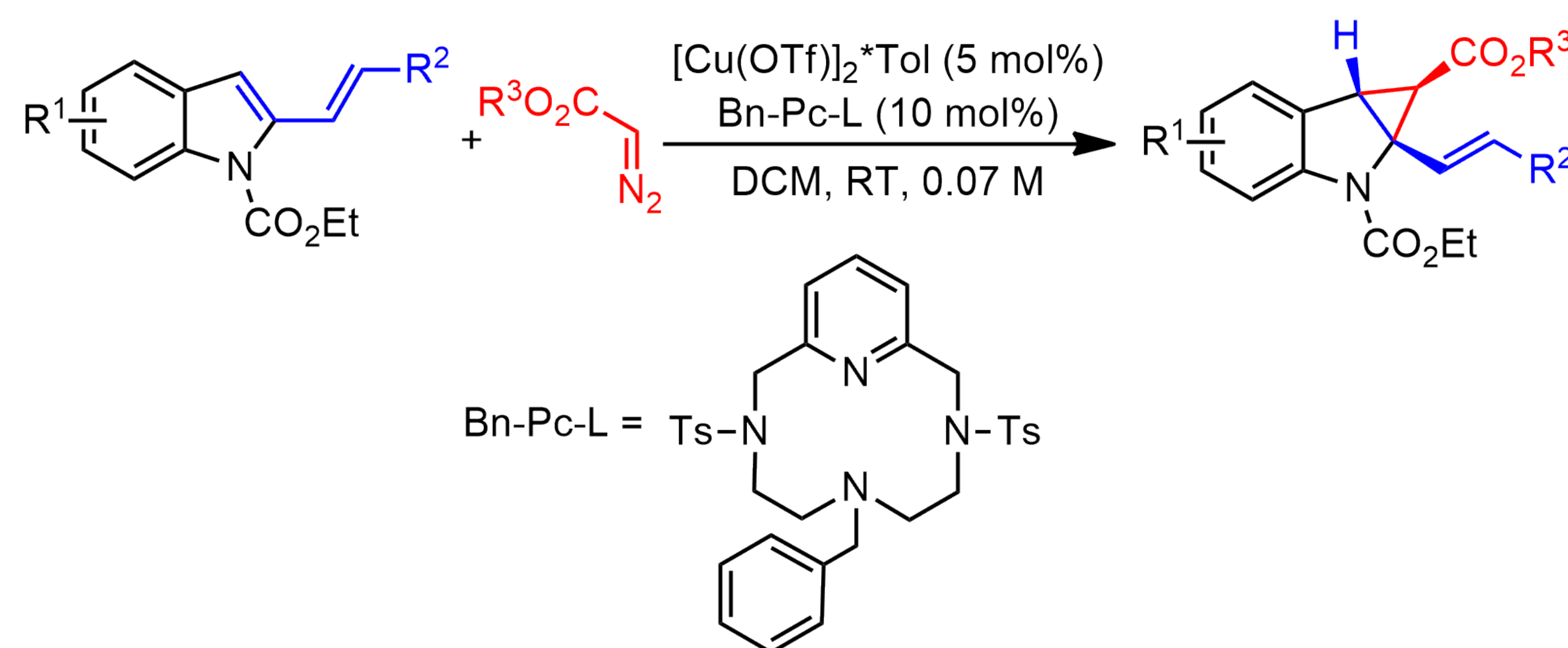
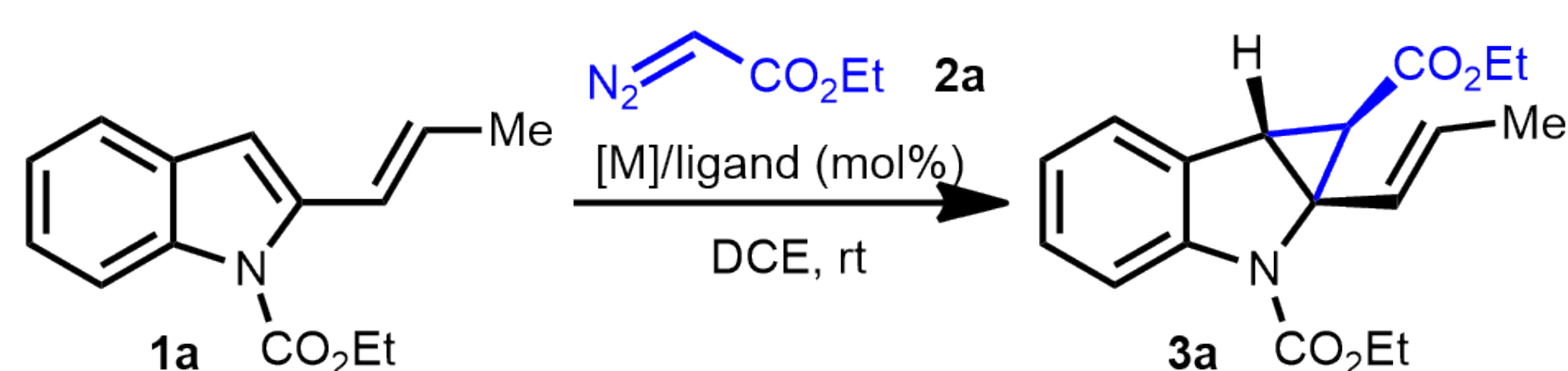


General purpose:

new methodologies for indole synthesis and functionalization^[1-4]

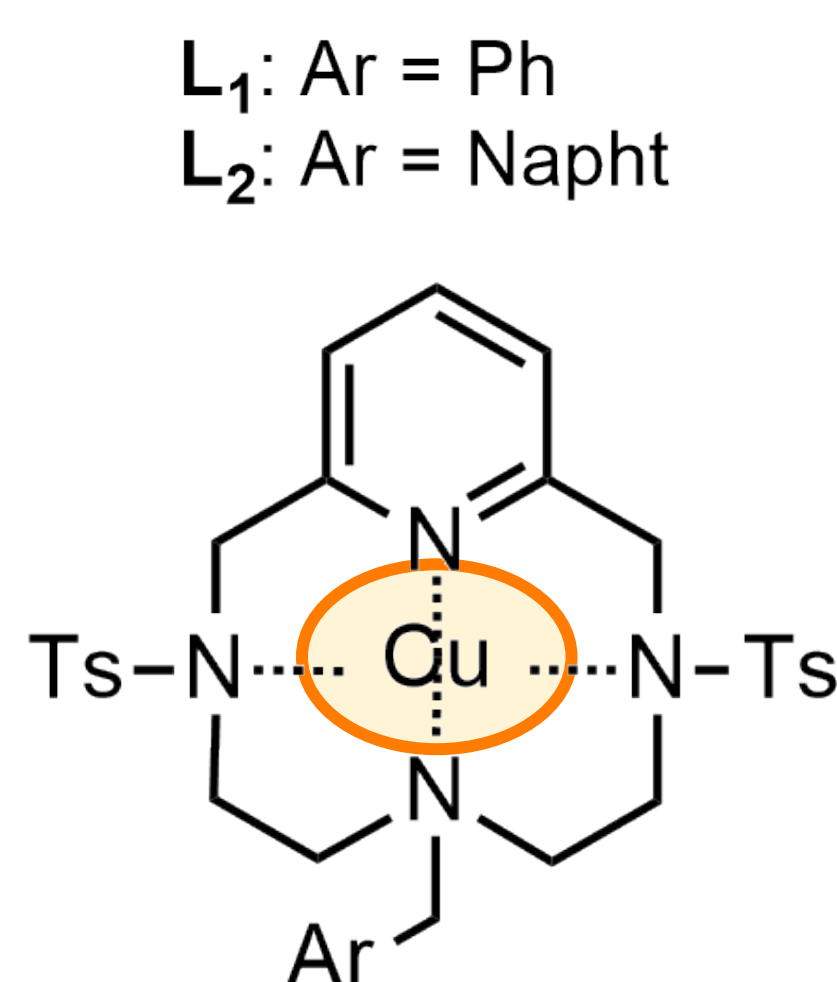


Optimization



Screening:

- Transition metal
- Ligand
- Reaction condition

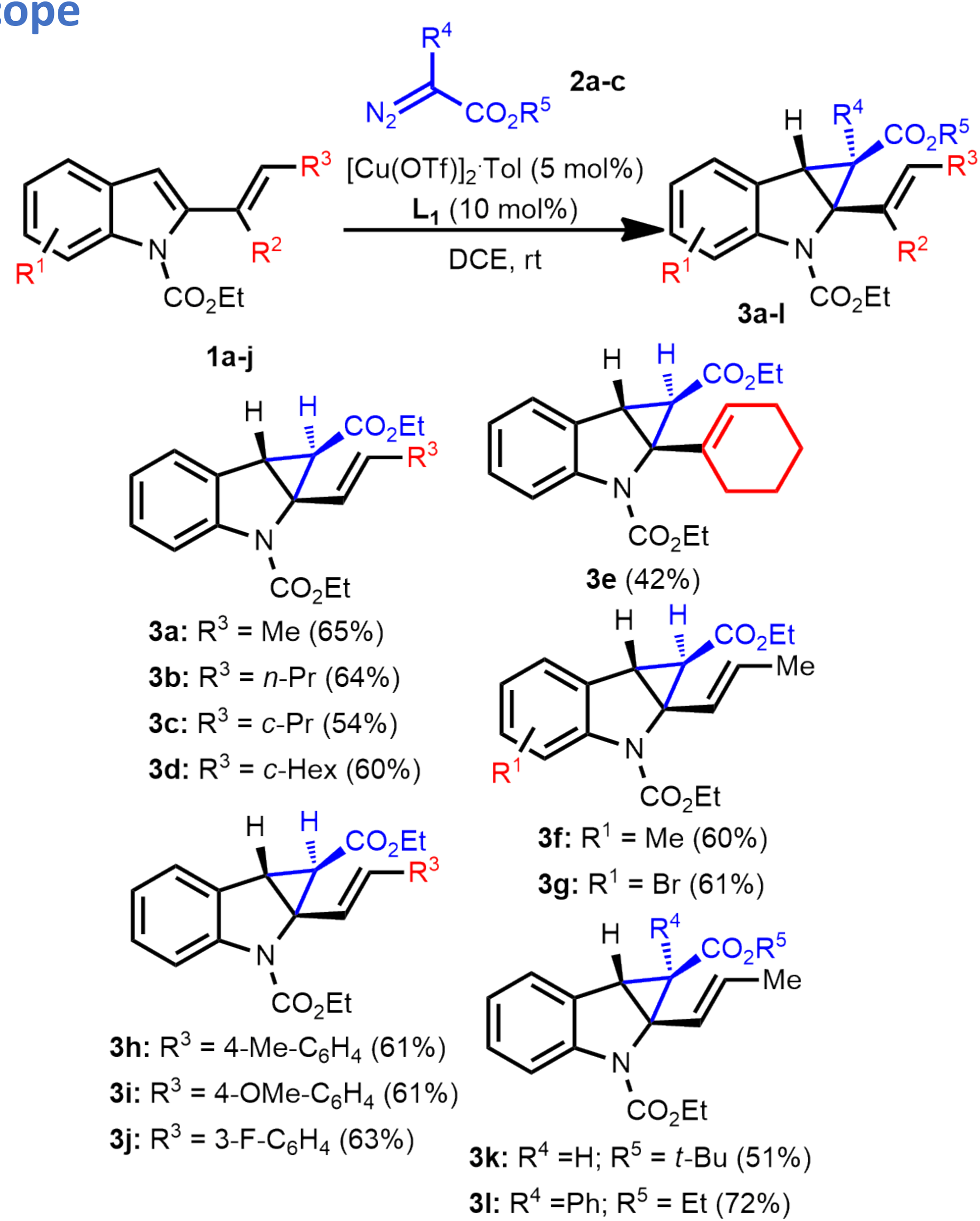


Macrocyclic ligand containing four nitrogen atoms able to coordinate the metal.

Entry	[M]/ligand	Time, h	3a, Yield ^b (%)
1	[Cu(OTf) ₂ ·Tol (2.5 mol%)	3	10
2	[Rh(OAc) ₂] ₄ (2.5 mol%)	3	<10
3	[Cu(OTf) ₂ ·Tol (2.5 mol%) L ₁ (5 mol%)	3	43
4	[Cu(OTf) ₂ ·Tol (2.5 mol%) L ₂ (5 mol%)	3	19
5	IPrCuCl (5 mol%) NaBAR _F (5 mol%)	3	n.r.
6	[Cu(OTf) ₂ ·Tol (5 mol%) L ₁ (10 mol%)	12	68 ^c

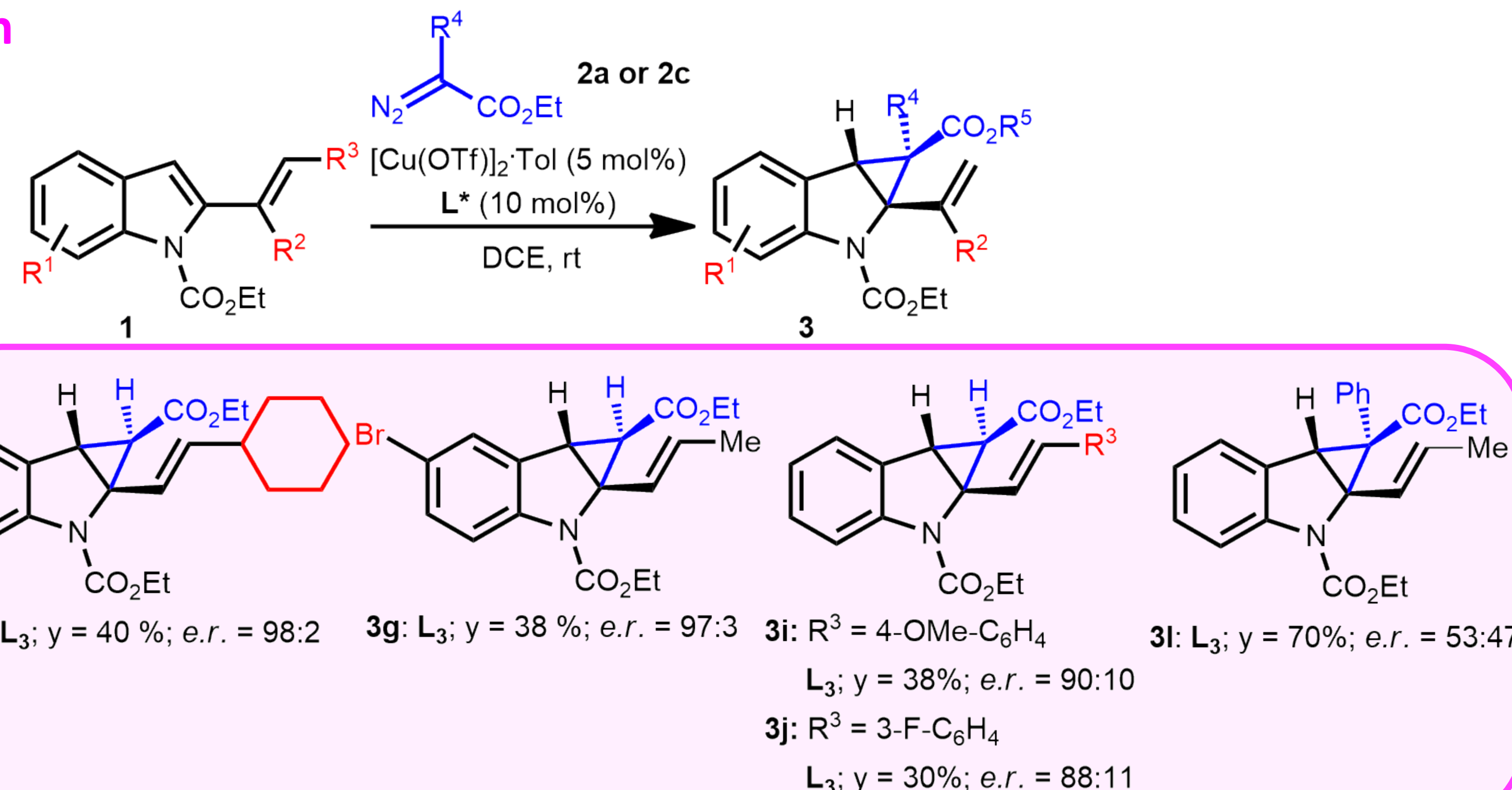
^a Unless otherwise mentioned, all reactions were carried out using 1a (0.2 mmol) and 2a (0.3 mmol) in DCE (0.1 M). EDA was added with a syringe pump at 0.5 or 0.17 mL/h. ^b Isolated yield. ^c 2a (0.5 mmol), DCE (0.07 M) and 200 mg of 4Å molecular sieves were added. IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene.

Scope



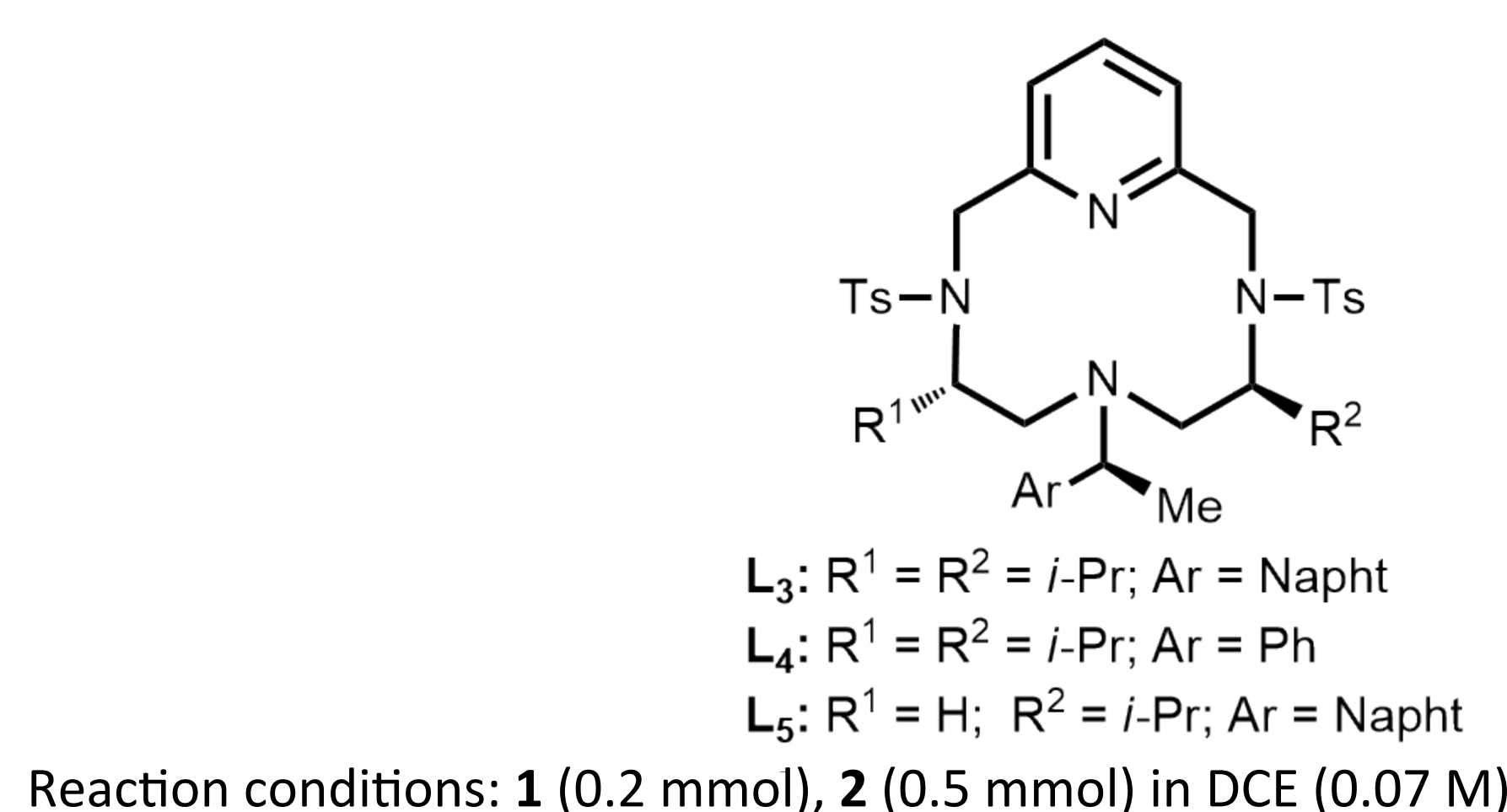
Reaction conditions: 1 (0.2 mmol), 2 (0.5 mmol) in DCE (0.07 M)

Enantioselective version



Screening

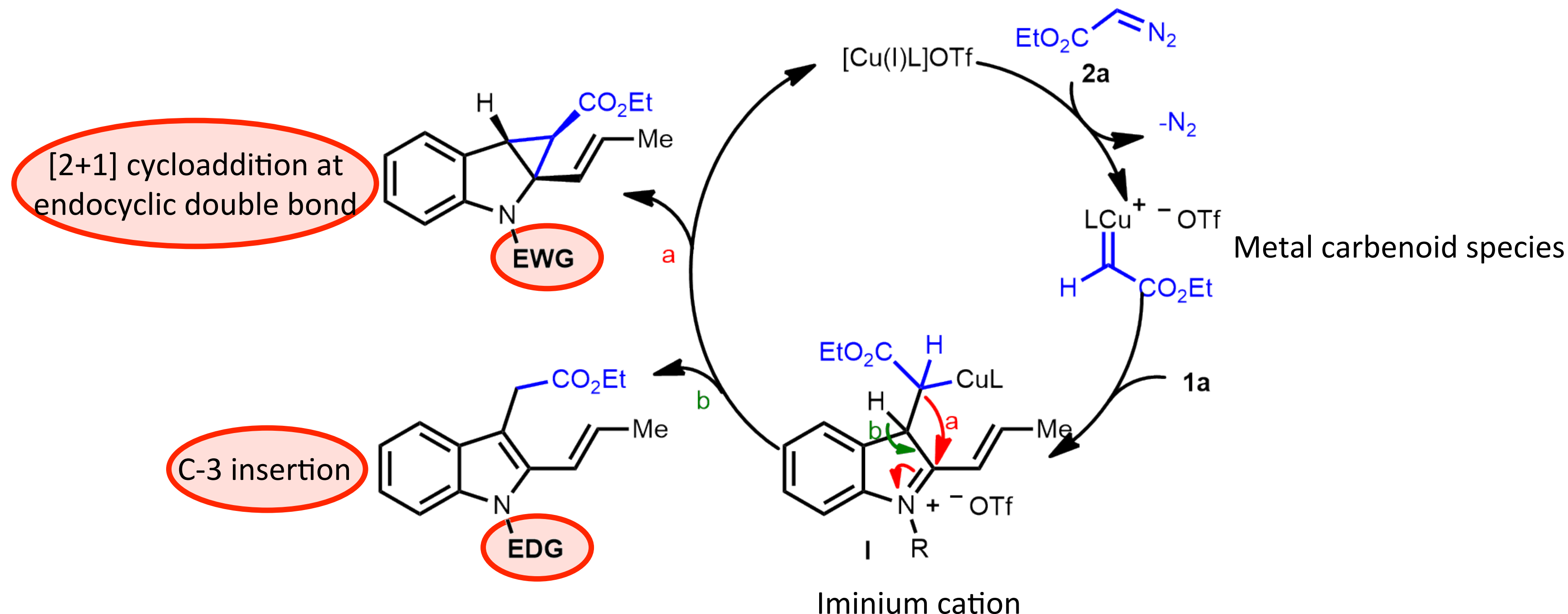
Scope



Proposed mechanism

Mechanistic proposal is based on several experiments with indole derivatives bearing different protecting groups.

Using an EW group we assisted to the [2+1] cycloaddition at the endocyclic double bond product, while using an ED group the main product arose from a C-3 insertion reaction.



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