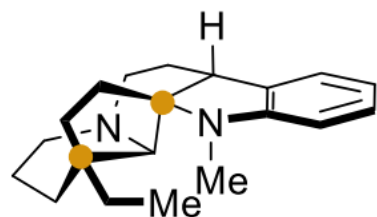
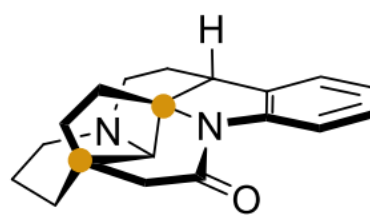


Asymmetric Total Syntheses of Schizozygane Alkaloids

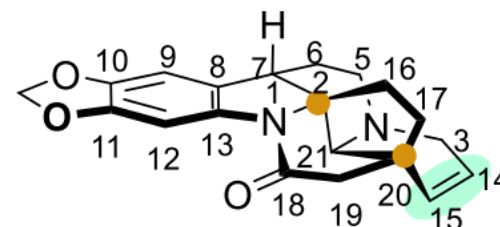
Wenqiang Zhou, Tao Zhou, Mengxing Tian, Yan Jiang, Jiaojiao Yang, Shuai Lei, Qi Wang, Chongzhou Zhang, Hanyue Qiu, Ling He, Zhen Wang, Jun Deng, and Min Zhang*



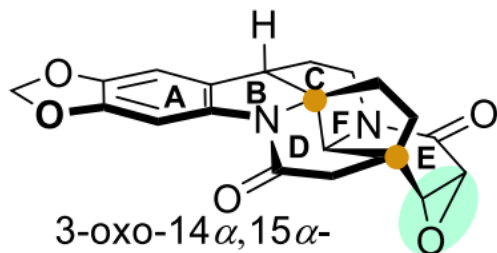
(-)-vallesamidine (1)



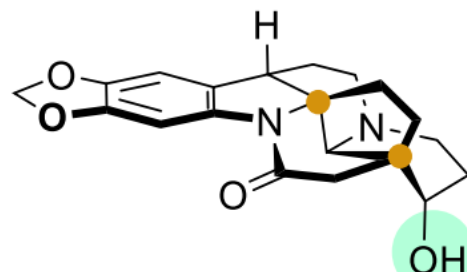
(-)-strempelepine (2)



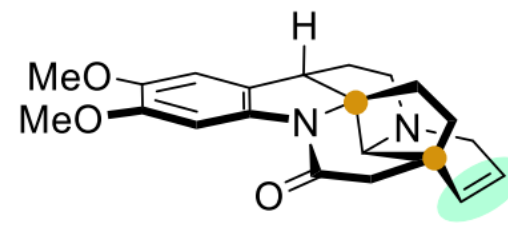
(+)-schizozygine (3)



3-oxo-14 α ,15 α -epoxyschizozygine (4)

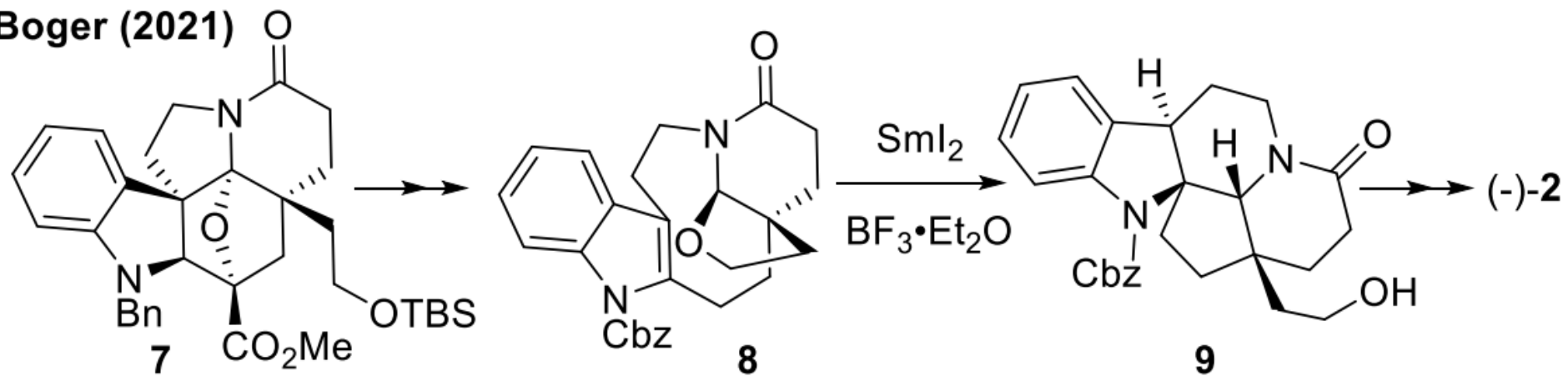


(+)- α -schizozygol (5)

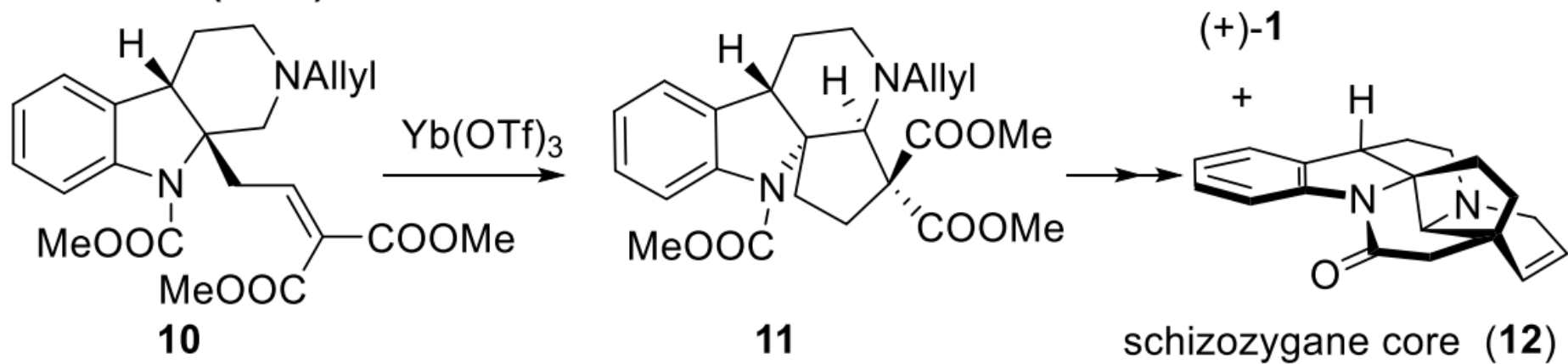


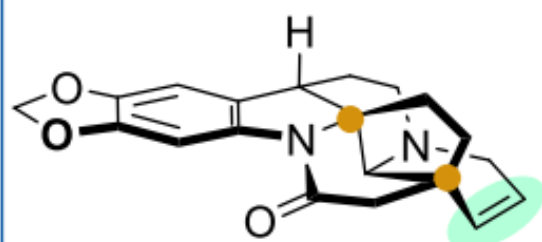
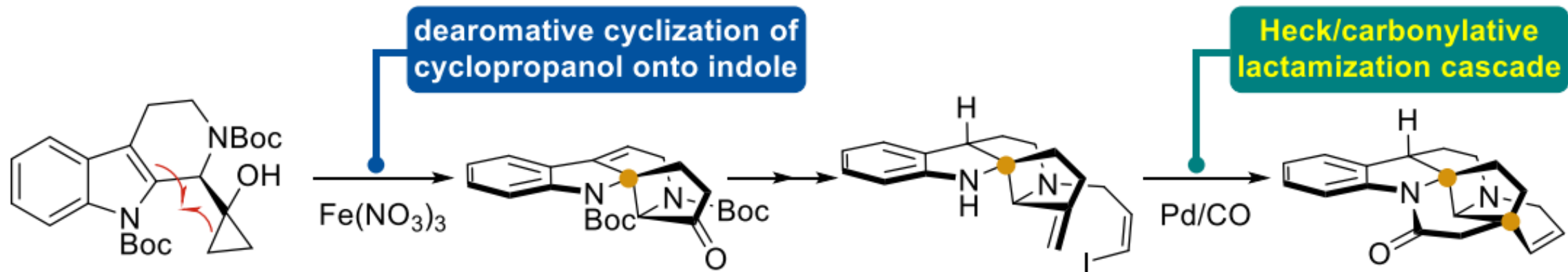
(+)-schizogamine (6)

Boger (2021)

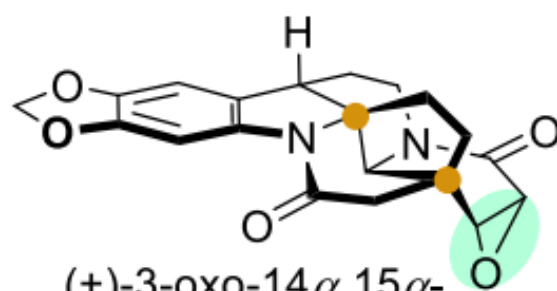


Anderson (2019)

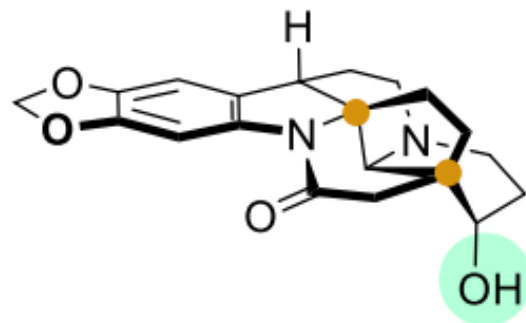




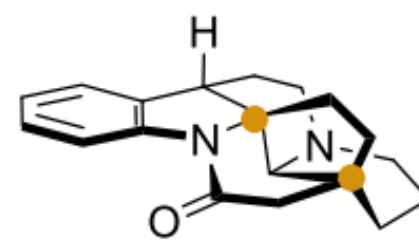
(+)-schizozygine



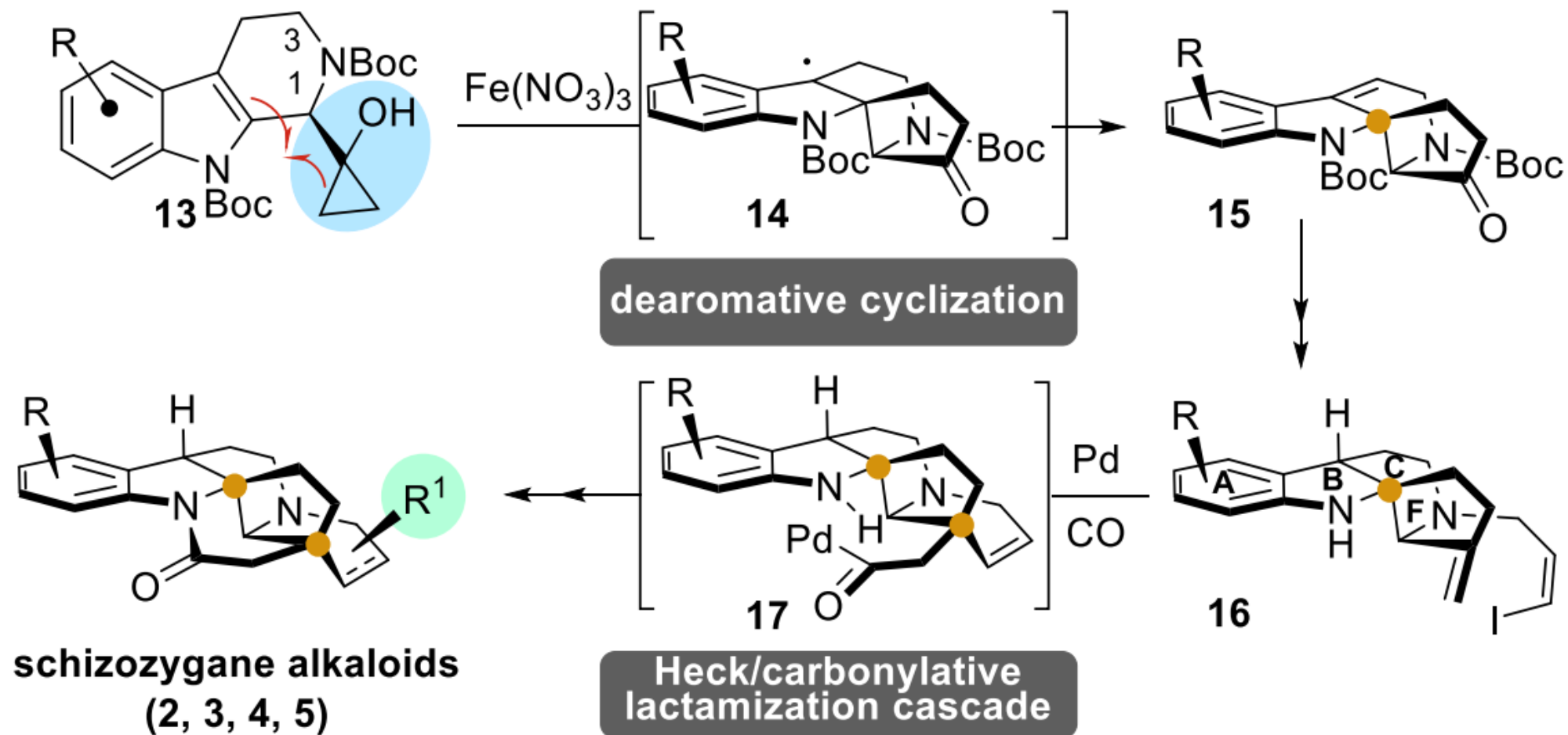
(+)-3-oxo-14 α ,15 α -epoxyschizozygine

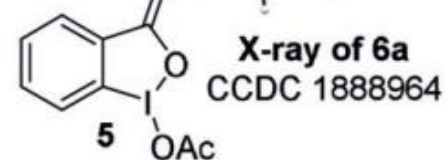
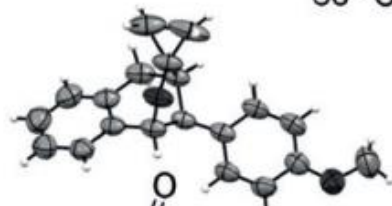
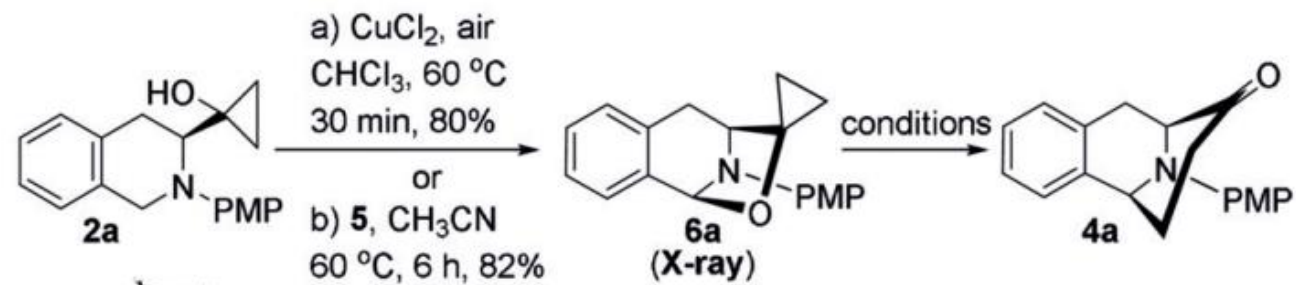


(+)- α -schizozygol



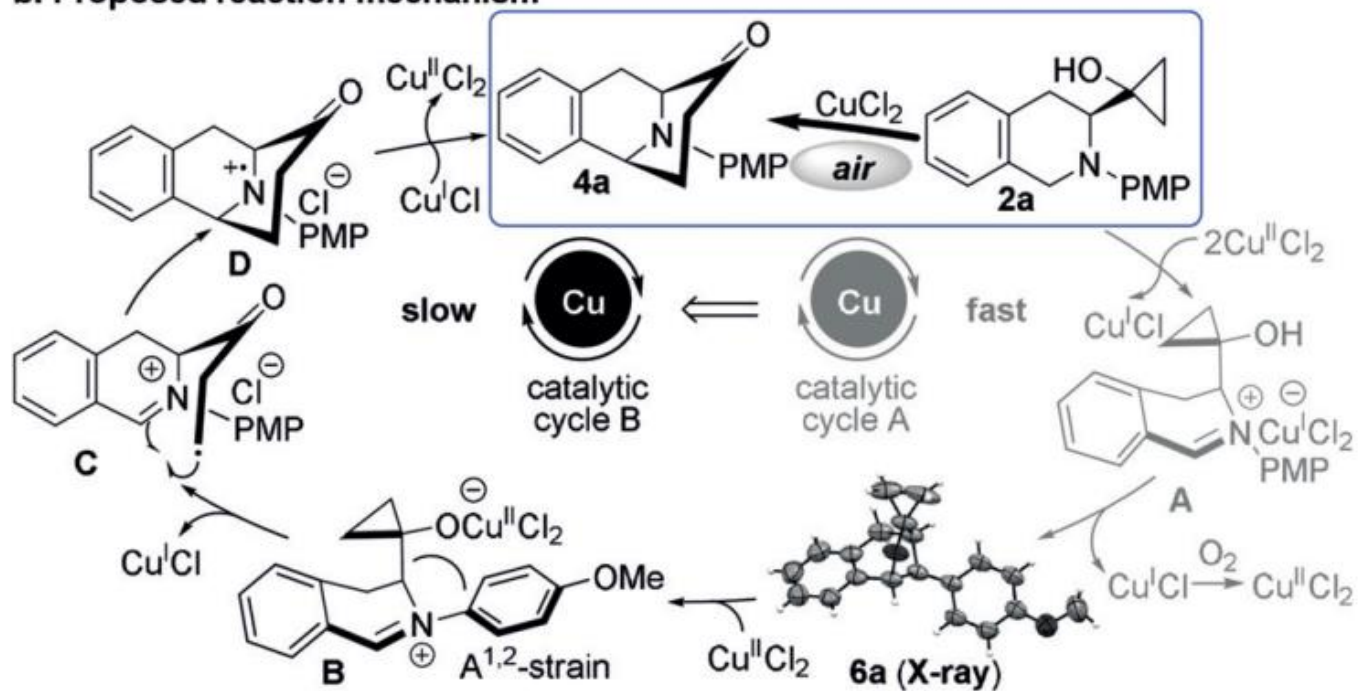
(+)-strempeliopine

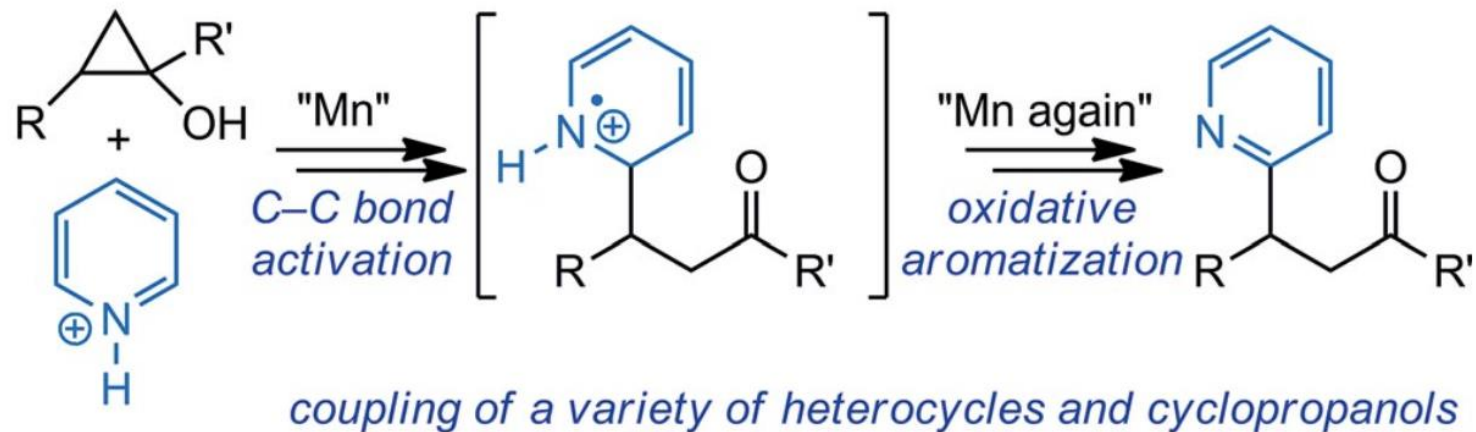




Conditions	yield (4a)
I) CuCl_2 (0.2 eq)/ CHCl_3 /60 °C/18 h/air	65%
II) CuCl_2 (0.2 eq)/ CHCl_3 /60 °C/18 h/Ar	64%
III) CuCl (0.2 eq)/ CH_2Cl_2 /18 h/Ar	0%
IV) $\text{BF}_3 \cdot \text{OEt}_2$ or TiCl_4 (2 eq)/ CH_2Cl_2 /rt/Ar	0%
V) CuCl_2 (0.2 eq)/TEMPO/ CHCl_3 /60 °C/Ar	0%

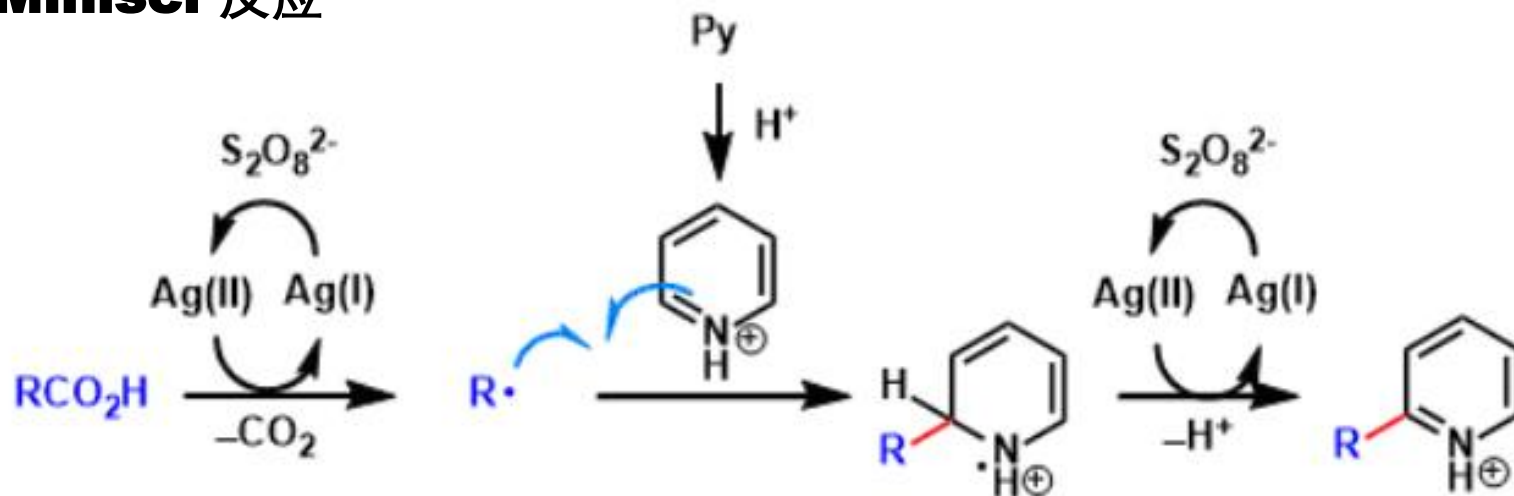
b. Proposed reaction mechanism





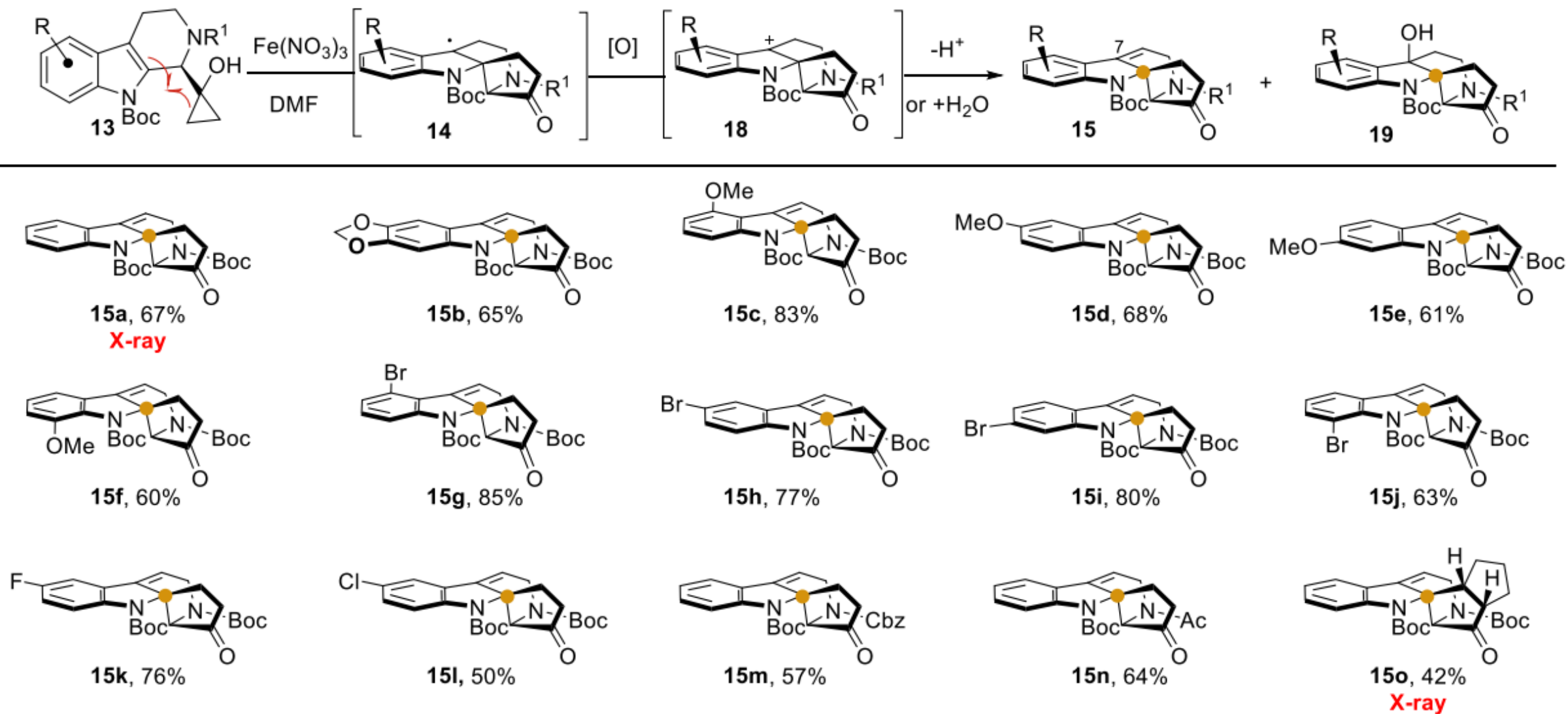
Eur. J. Org. Chem. **2016**, 26.

Minisci 反应

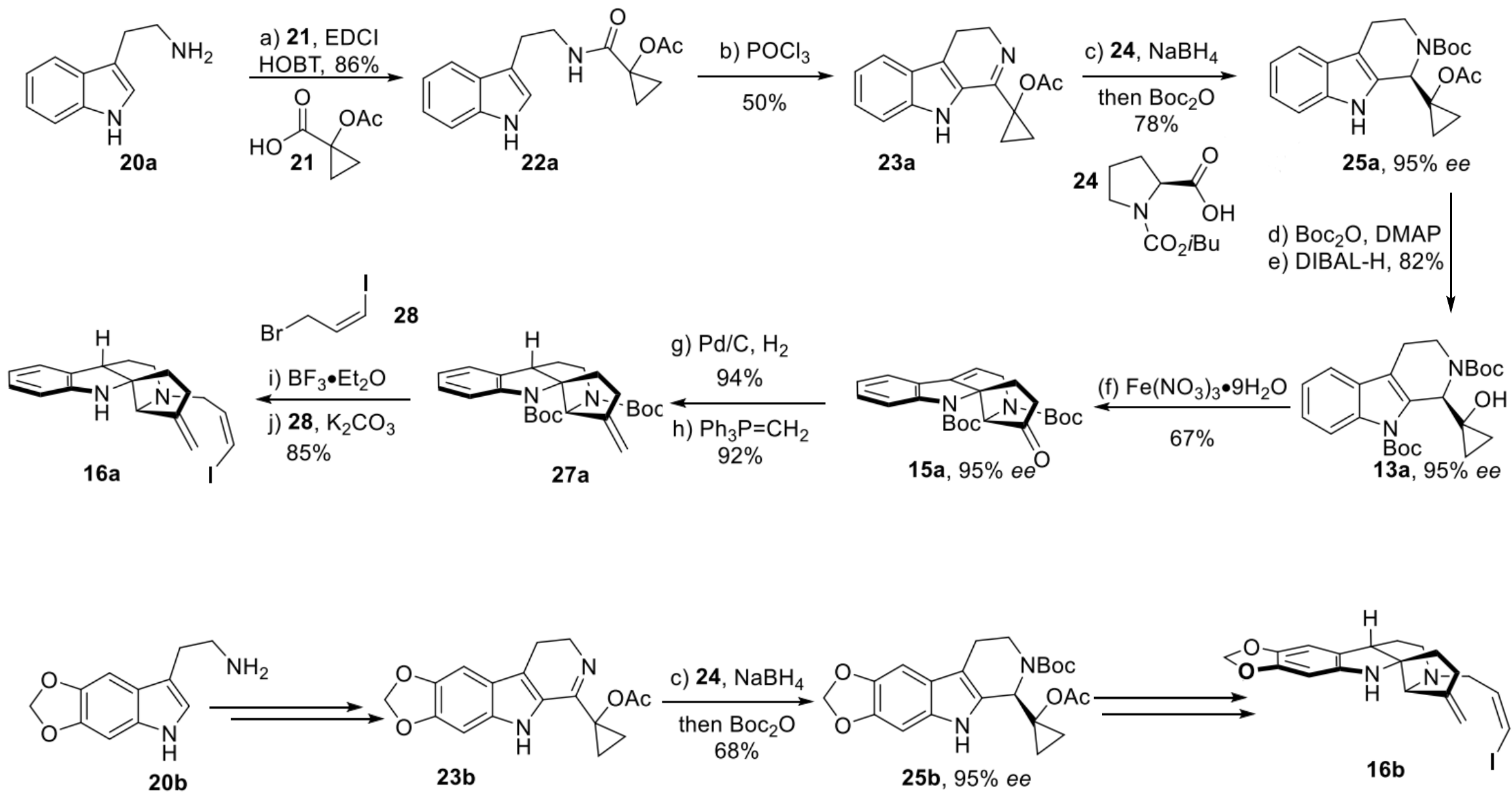


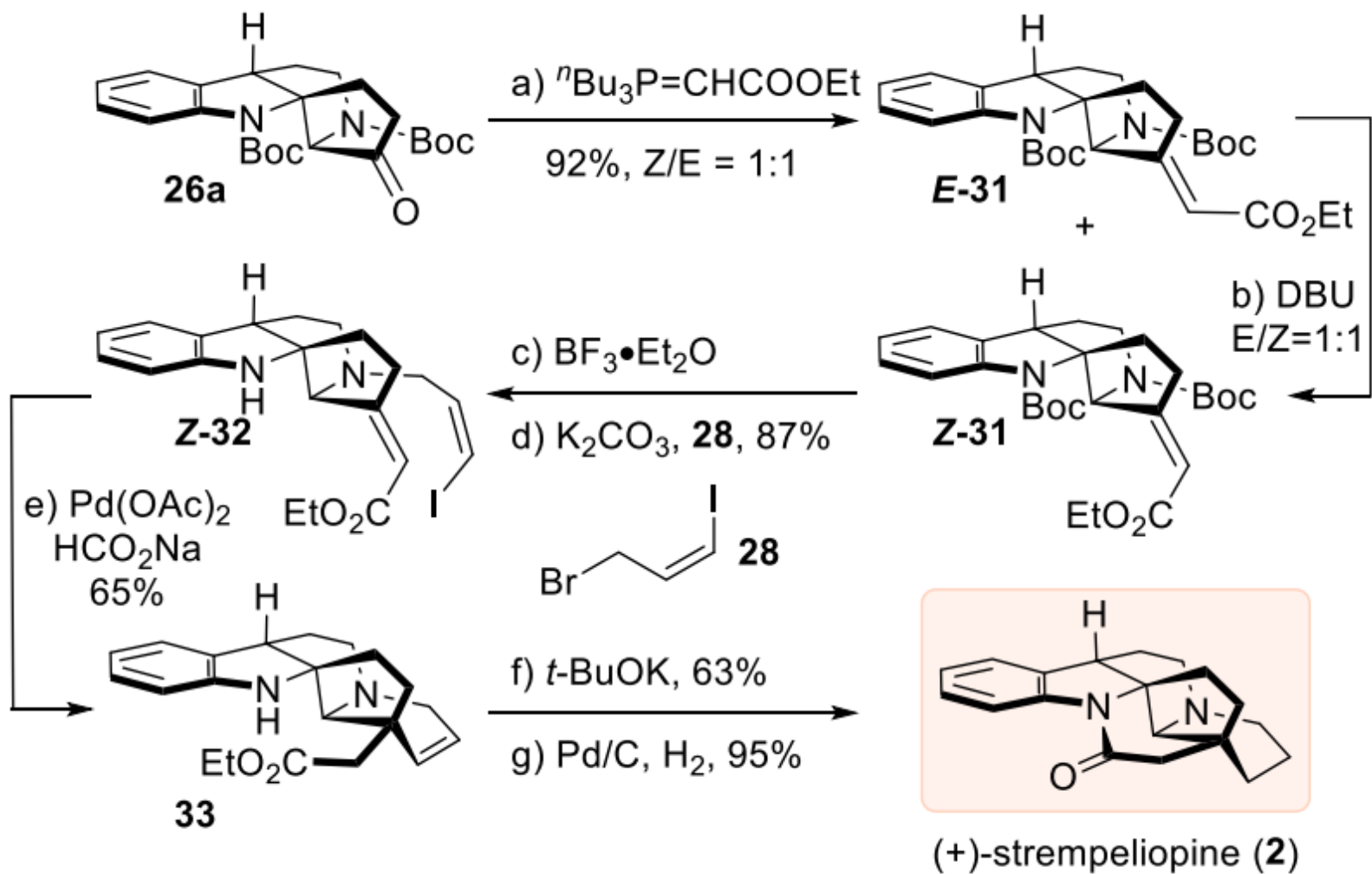
亲核碳自由基对缺电子芳香杂环进行自由基加成生成取代芳香环化合物的反应。该反应与Friedel-Crafts反应的反应活性相反，两反应互为补充。

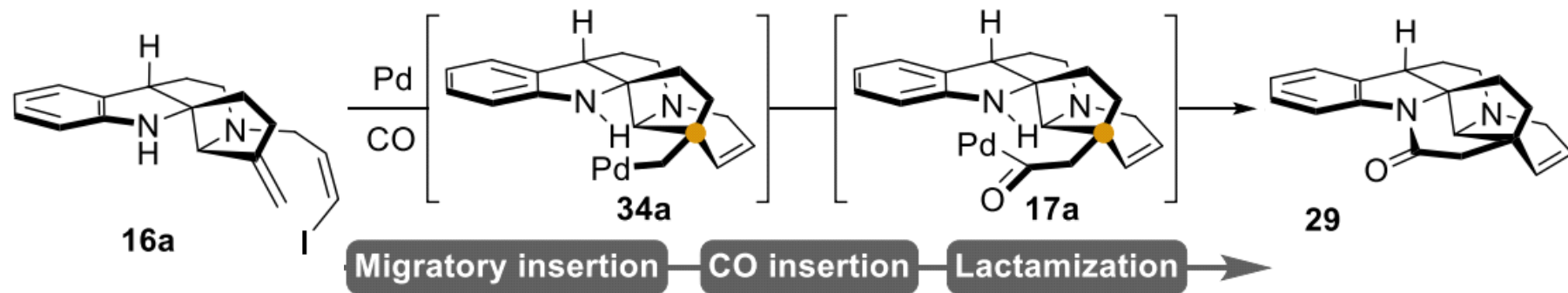
Table 1. Substrate Scope of the Dearomative Cyclization^a



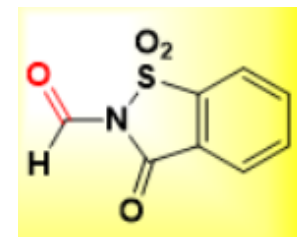
^aReaction conditions: **13** (0.3 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.9 mmol), 4 Å MS (0.6 g), DMF (8 mL), 0 °C or rt, 10 min to 3 h; for **15n**, dioxane was used as the solvent; for **15o**, 2.4 mmol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was used.







entry	conditions	yield (%)
1	Pd(OAc) ₂ /PPh ₃ /CO/NaOAc/DMSO	~5
2	Pd(OAc) ₂ /PPh ₃ /CO/NaOAc/DMSO/EtOH	12
3	Pd(PPh ₃) ₄ / <i>N</i> -formylsaccharin/Et ₃ N/KF/dioxane	0
4	Pd(PPh ₃) ₄ /Mo(CO) ₆ /Et ₃ N/DBU/dioxane	0
5 ^b	Pd(OAc) ₂ /PPh ₃ /CO/NaOAc/toluene	20
6 ^b	Pd(OAc) ₂ /PPh ₃ /CO/Et ₄ NCl/toluene	40
7 ^b	Pd(OAc) ₂ /PPh ₃ /CO/ ⁿ Bu ₄ NCl/toluene	45
8 ^b	Pd(OAc) ₂ /PPh ₃ /CO/ ⁿ Bu ₄ NBr/toluene	53
9 ^{b,c}	Pd(OAc) ₂ /PPh ₃ /CO/ ⁿ Bu ₄ NBr/toluene	61
10 ^{b,c,d}	Pd(OAc) ₂ /PPh ₃ /CO/ ⁿ Bu ₄ NBr/toluene	56



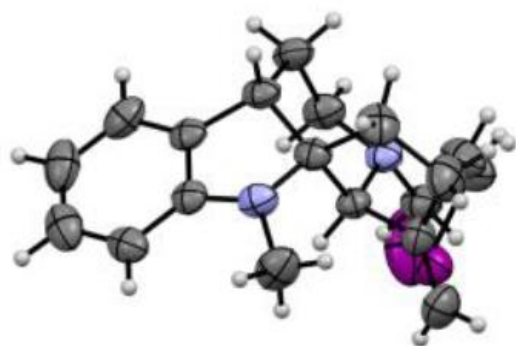
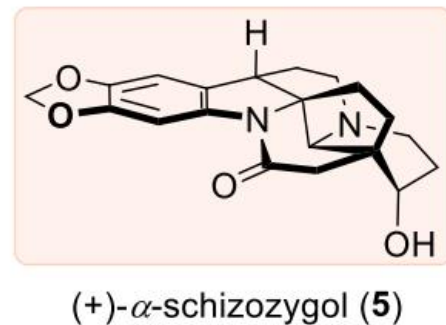
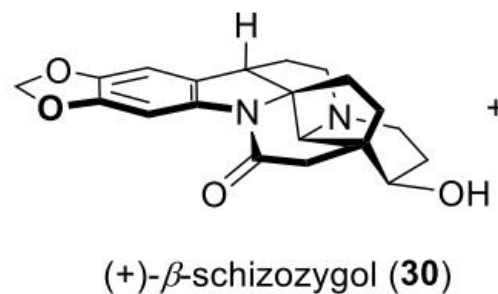
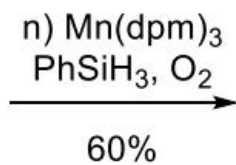
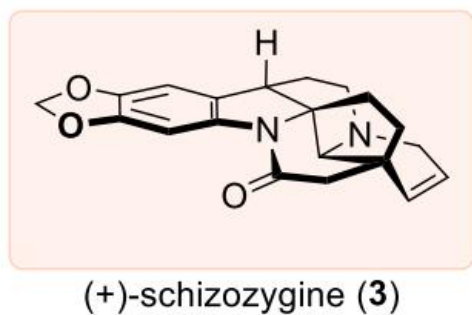
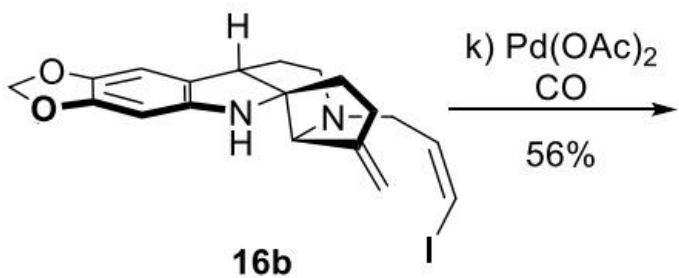
N-formylsaccharin

^aReaction conditions: **16a** (5 mg), [Pd] (0.5 equiv), PPh₃ (1 equiv), base (2 equiv) and/or additive (1 equiv), CO balloon or its substitute (2 equiv), and solvent (2 mL), 100 °C, with full consumption of **16a**.

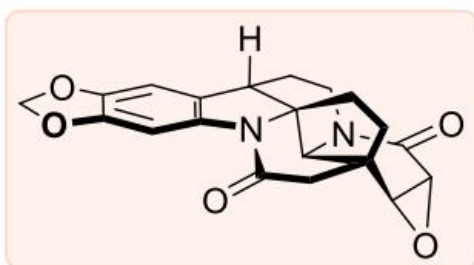
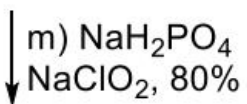
^bHeat at 100 °C for 20 min before exposure to CO (balloon).

^cPd(OAc)₂ (1 equiv), PPh₃ (2 equiv), and ⁿBu₄NBr (1 equiv).

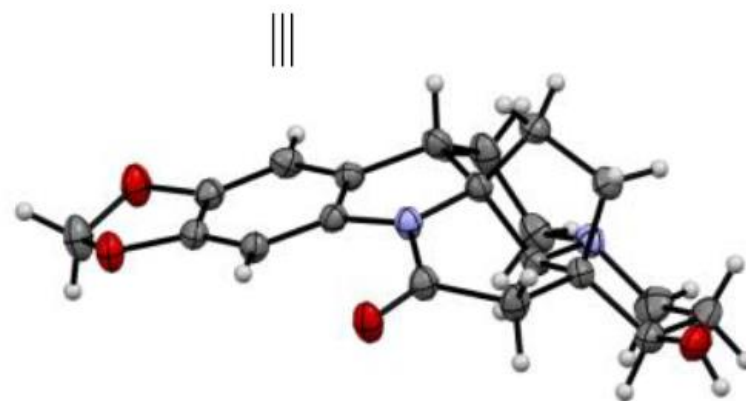
^dReaction was conducted on a 100 mg (0.25 mmol) scale.



X-ray of N-Me-16a



(+)-3-oxo-14α,15α-epoxyschizozigine (4)



X-ray of 30