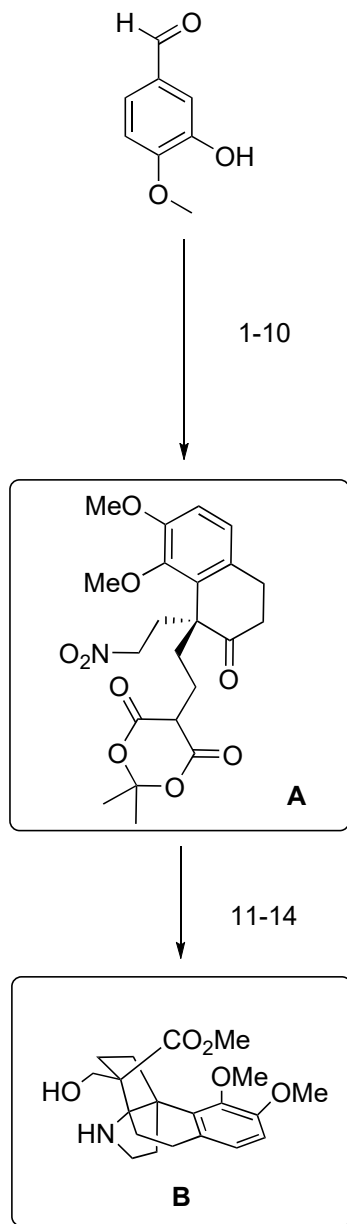
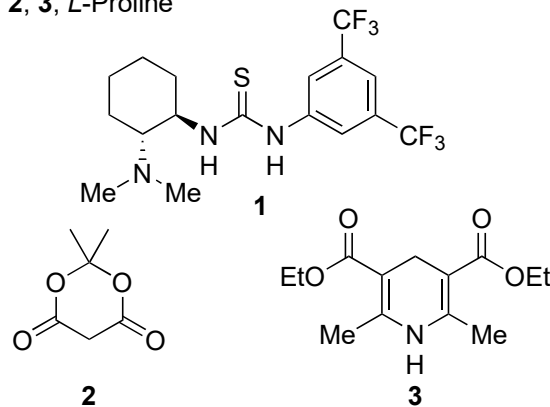


## Enantioselective Total Synthesis of (+)-Stephadiamine

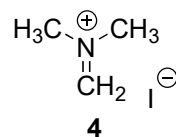
B. Yang, G. Li, Q. Wang, J. Zhu, *J. Am. Chem. Soc.* **2023**, *145*, 5001–5006.



- 1) Allyl bromide,  $K_2CO_3$
- 2) 180 °C
- 3) MeI,  $K_2CO_3$
- 4)  $PdCl_2$ ,  $CuCl_2$ ,  $O_2$ ,  $H_2O$
- 5) NaOH
- 6) Allyl bromide,  $K_2CO_3$
- 7) 180 °C
- 8) **1**, nitroethylene
- 9)  $OsO_4$ ,  $NaIO_4$ , 2,6-lutidine
- 10) **2**, **3**, *L*-Proline



- 11) *L*-Selectride
- 12) **4**, MeOH, 65 °C
- 13)  $Na_2S_2O_4$
- 14) Zn, AcOH



- 1) Name of starting material?

**Isovanillin**

- 8) Name of **1**

**Takemoto catalyst**

- 9) Name of the reaction?

**Lemieux-Johnson**

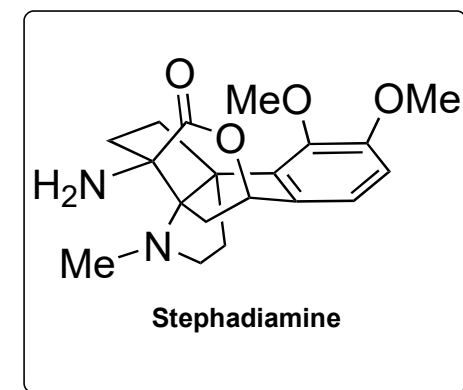
- 10) Name of **2** and **3**?

**Meldrum's acid**

**Hantzsch ester**

- 13) Hint: 3 transformations:

**Reduction to hydroxylamine/  
condensation with ketone/  
1,3-dipolar cycloaddition**



15-22

Stephadiamine

- 15) HCO<sub>2</sub>Et, *then* DMP
- 16) NaClO<sub>2</sub>, NaH<sub>2</sub>PO<sub>4</sub>, 2-methyl-2-butene
- 17) DIPEA, diphenyl chlorophosphate, *then* NaN<sub>3</sub>
- 18) Allyl alcohol, 80 °C
- 19) [Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(5,5'-dCF<sub>3</sub>bpy)]PF<sub>6</sub>,  
Cu(TFA)<sub>2</sub>(MeCN), K<sub>2</sub>HPO<sub>4</sub>, blue LED, air
- 20) NaBH<sub>4</sub>, CeCl<sub>3</sub>·7H<sub>2</sub>O
- 21) NaH
- 22) Pd(PPh<sub>3</sub>)<sub>4</sub>, dimedone

16) Name of the reaction?

**Pinnick oxidation**

18) Name of the reaction?

**Curtius-rearrangement**

