

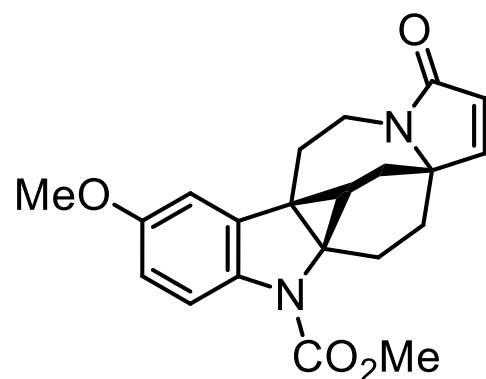
Concise Total Synthesis of Lundurines A–C Enabled by Gold Catalysis and a Homodienyl Retro-Ene/Ene Isomerization

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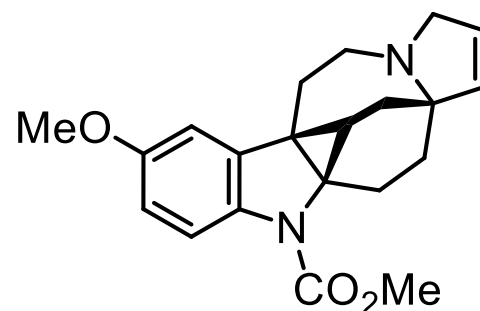


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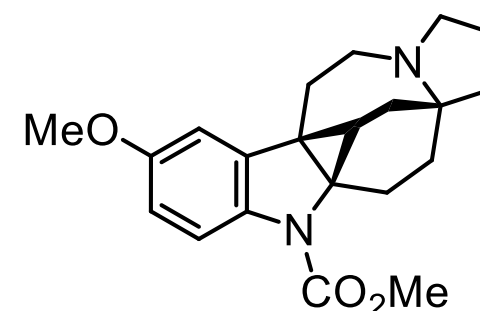
[‡]Departament de Química Orgànica i Analítica, Universitat Rovira i Virgili, C/Marcel·lí Domingo s/n, 43007 Tarragona, Spain



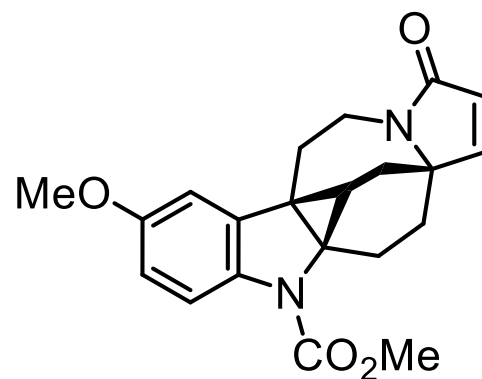
(-)-Lundurine A



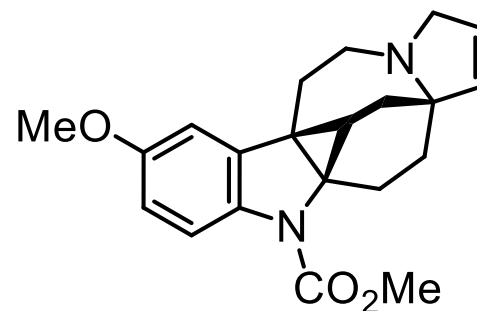
(-)-Lundurine B



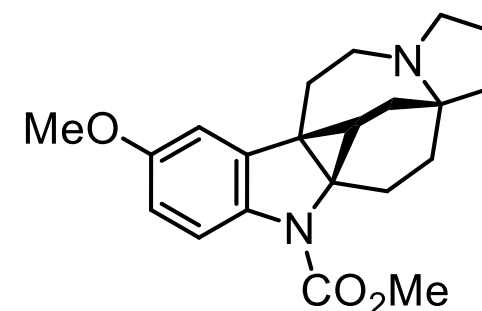
(-)-Lundurine C



(-)-Lundurine A



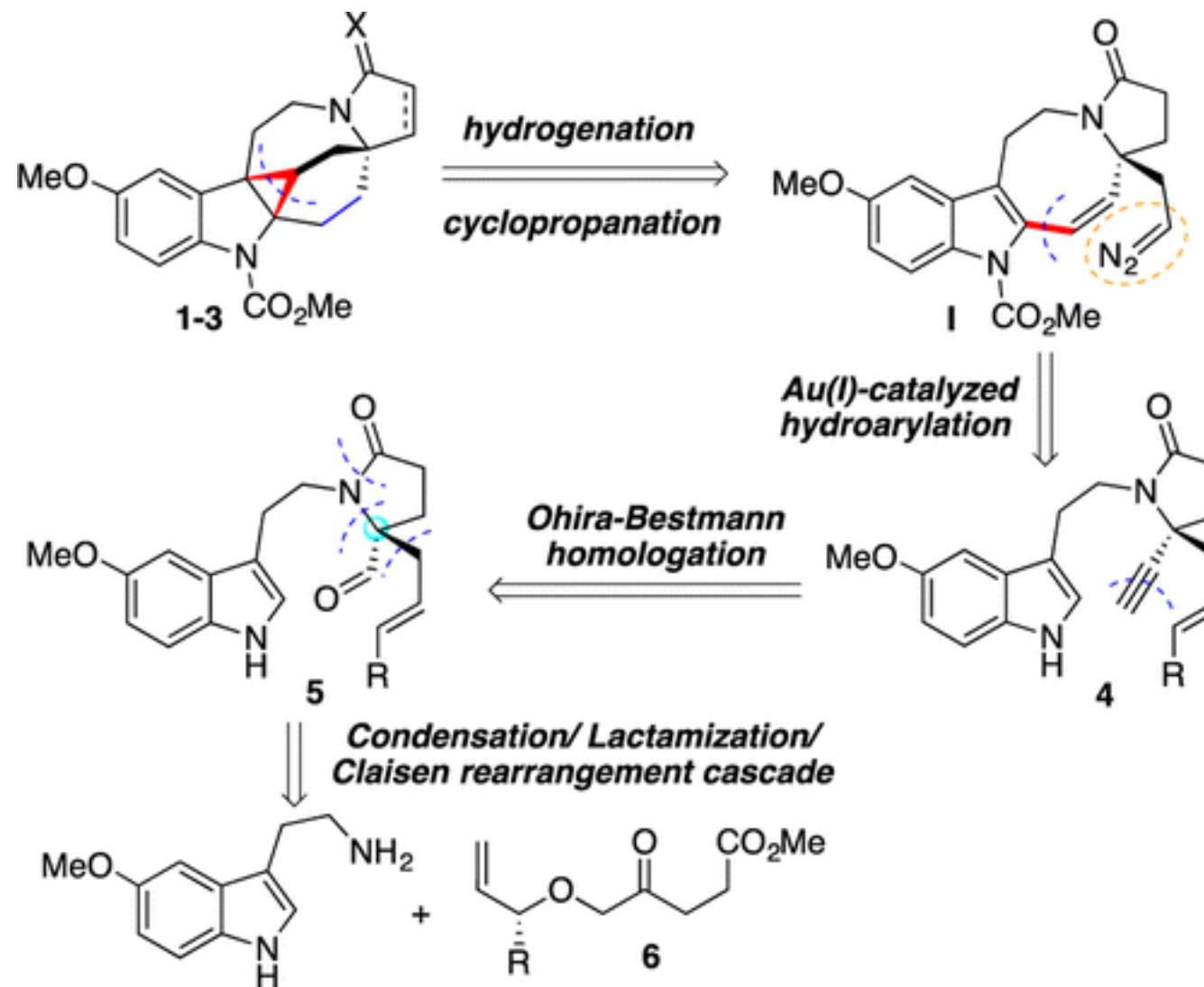
(-)-Lundurine B

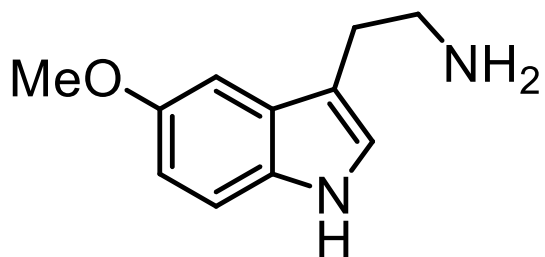


(-)-Lundurine C

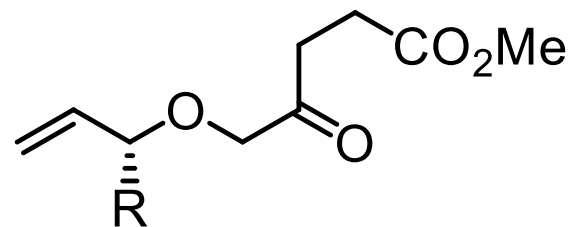
- Isolated from *Kopsia tenuis*, a plant endemic to the north of Borneo
- Show cytotoxicity
- Unique indoline-fused polyhydropyrroloazocine, cyclopropyl moiety fused to indoline
- Current syntheses of lundurines A and B involve over 20 linear steps
- This work reports the total synthesis of the lundurine family, including the first total synthesis of racemic and enatiopure lundurine C.
- Syntheses are done without protection/deprotection

Retrosynthetic Approach



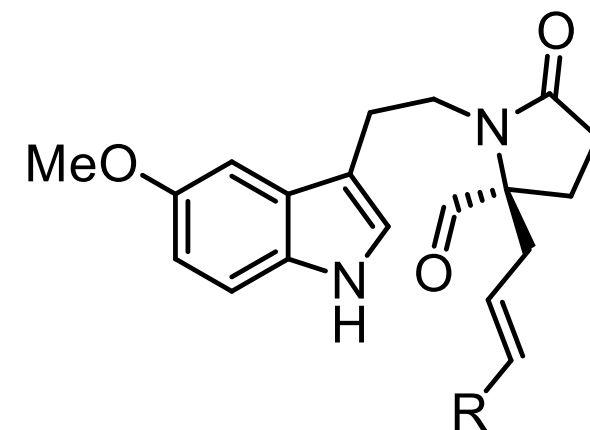


commercially available



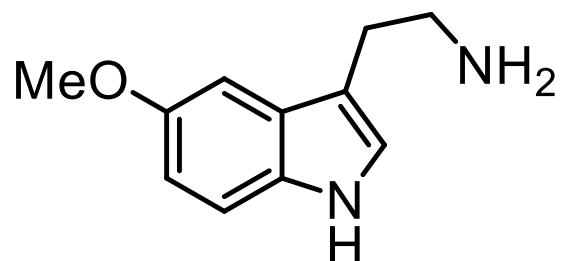
6

From (S)-alcohol

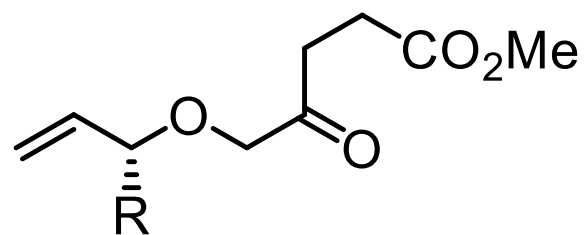


R = H, 74% (**5a**)

R = *c*-C₅H₉, 84% (**5f**)



commercially available

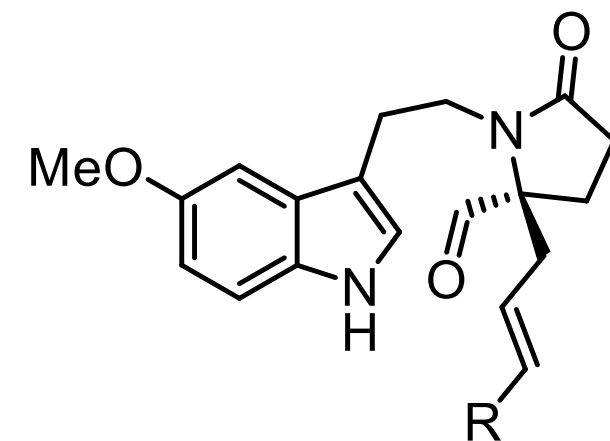


6

From (*S*)-alcohol

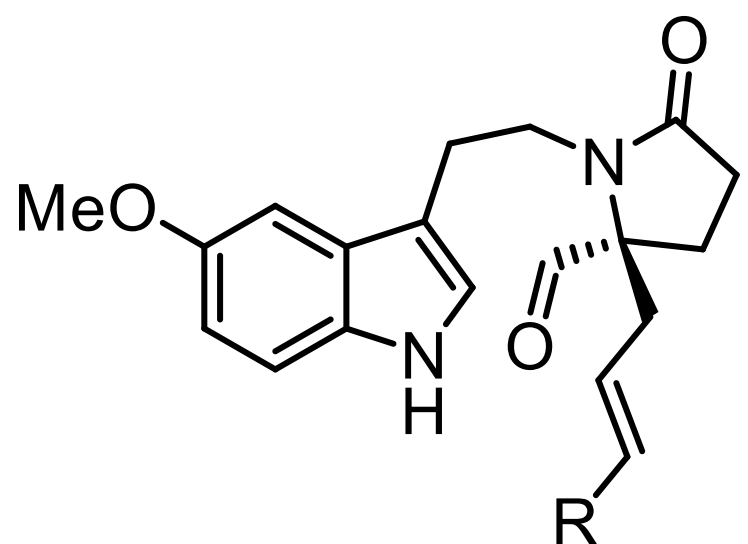
Toluene/py 1:2
reflux, 40 h (for 5a)

Toluene/Et₃N 1:2
reflux, 16h (for 5f)



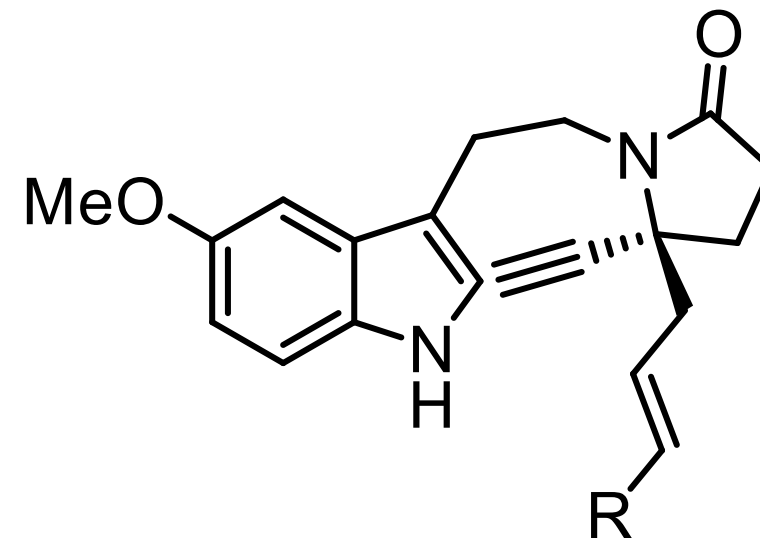
R = H, 74% (**5a**)

R = *c*-C₅H₉, 84% (**5f**)



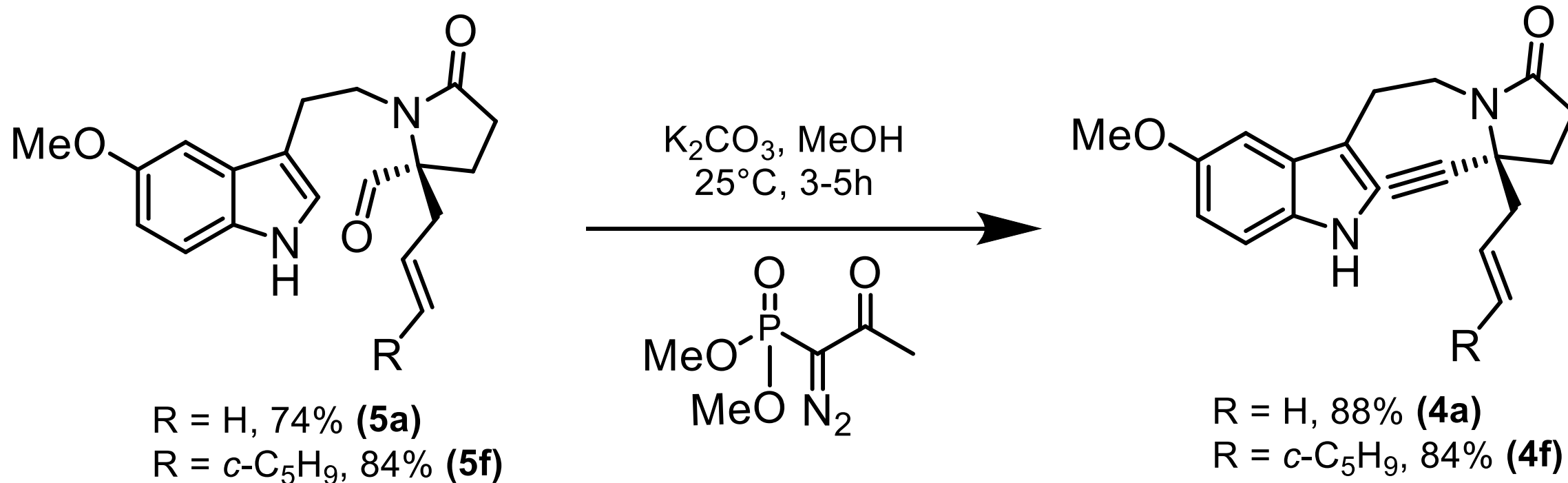
R = H, 74% (**5a**)

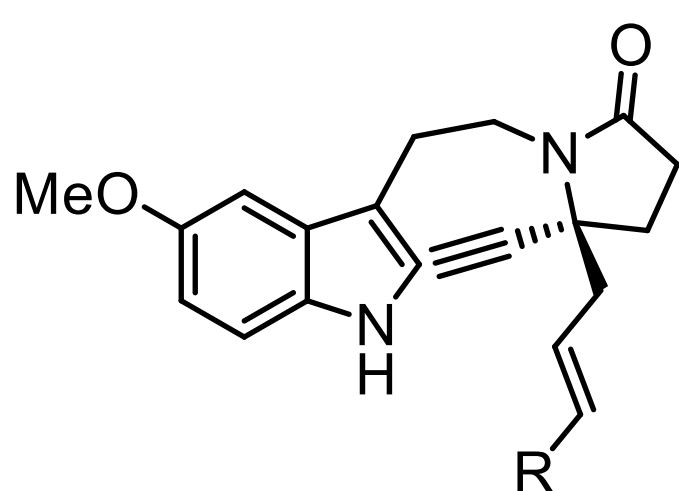
R = *c*-C₅H₉, 84% (**5f**)



R = H, 88% (**4a**)

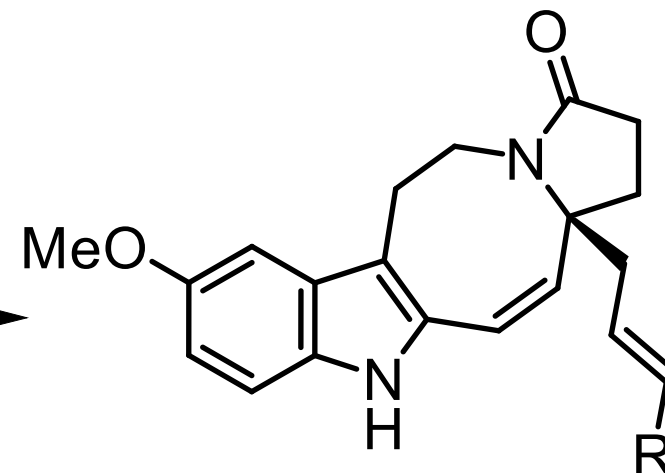
R = *c*-C₅H₉, 84% (**4f**)





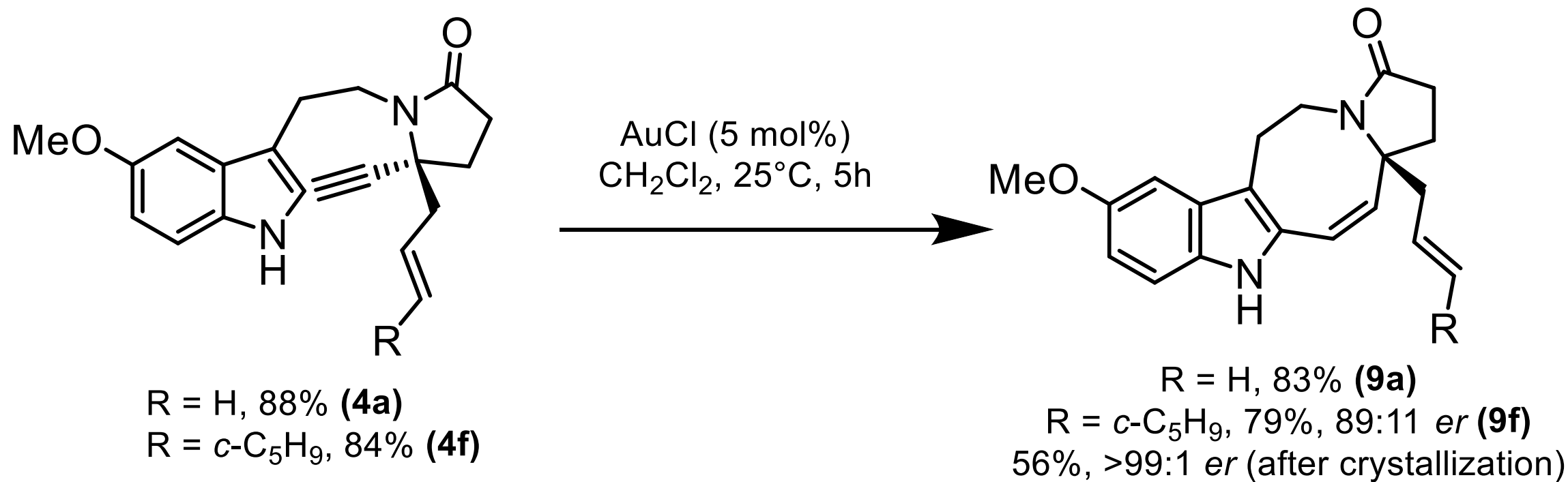
R = H, 88% (**4a**)

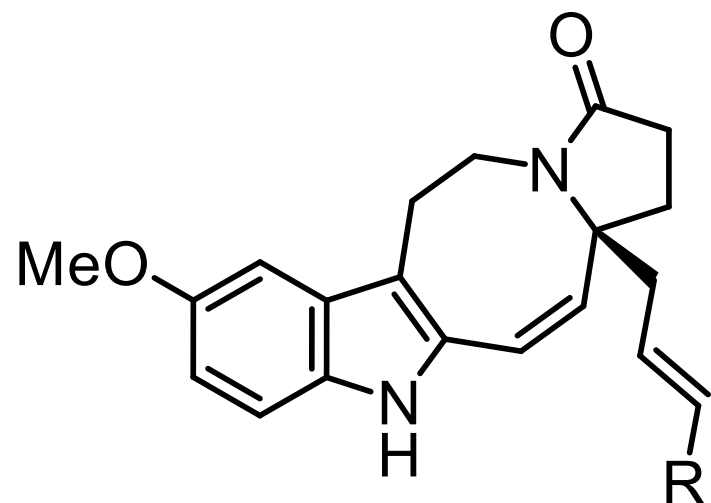
R = *c*-C₅H₉, 84% (**4f**)



R = H, 83% (**9a**)

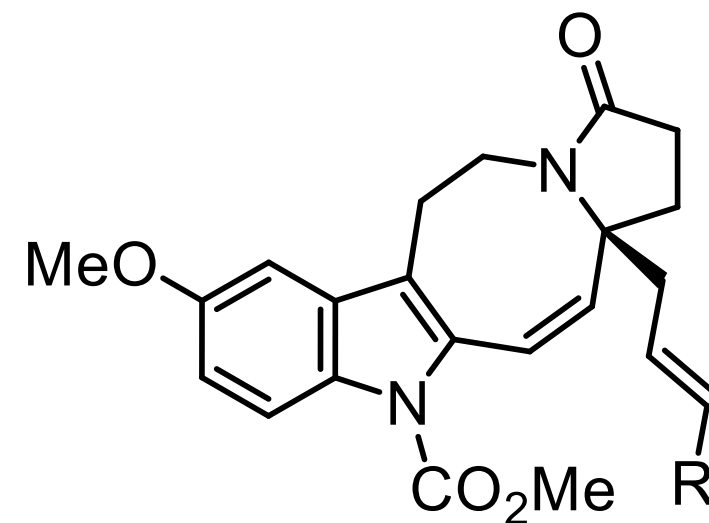
R = *c*-C₅H₉, 79%, 89:11 *er* (**9f**)
56%, >99:1 *er* (after crystallization)





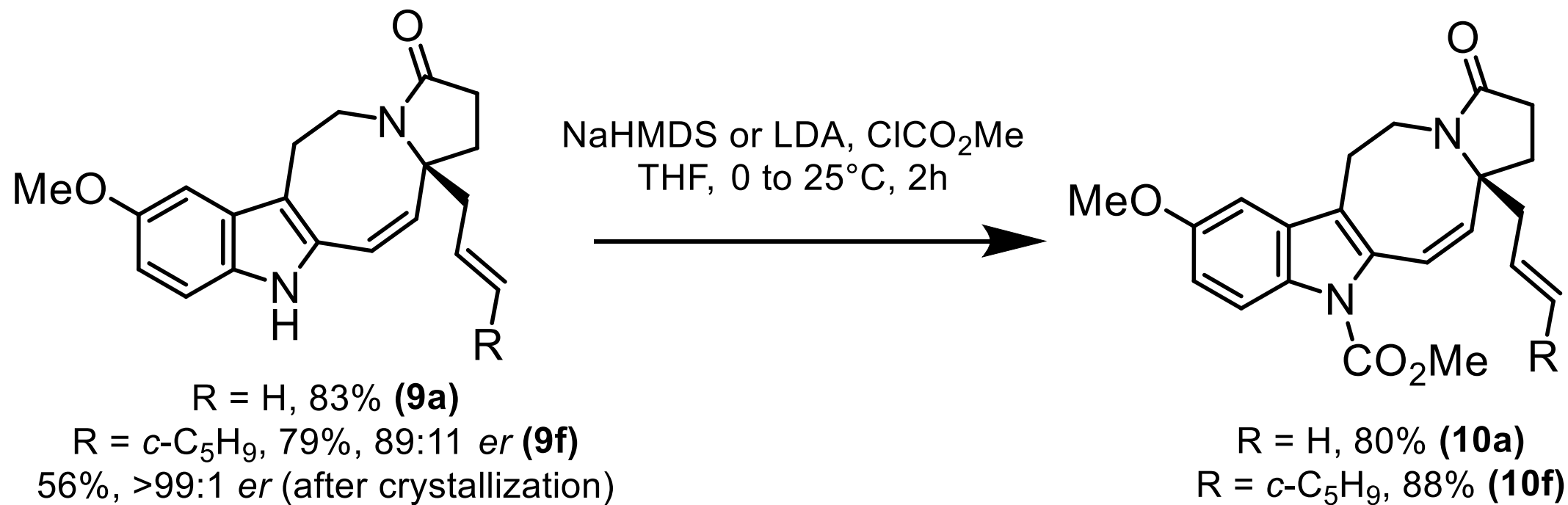
R = H, 83% (**9a**)

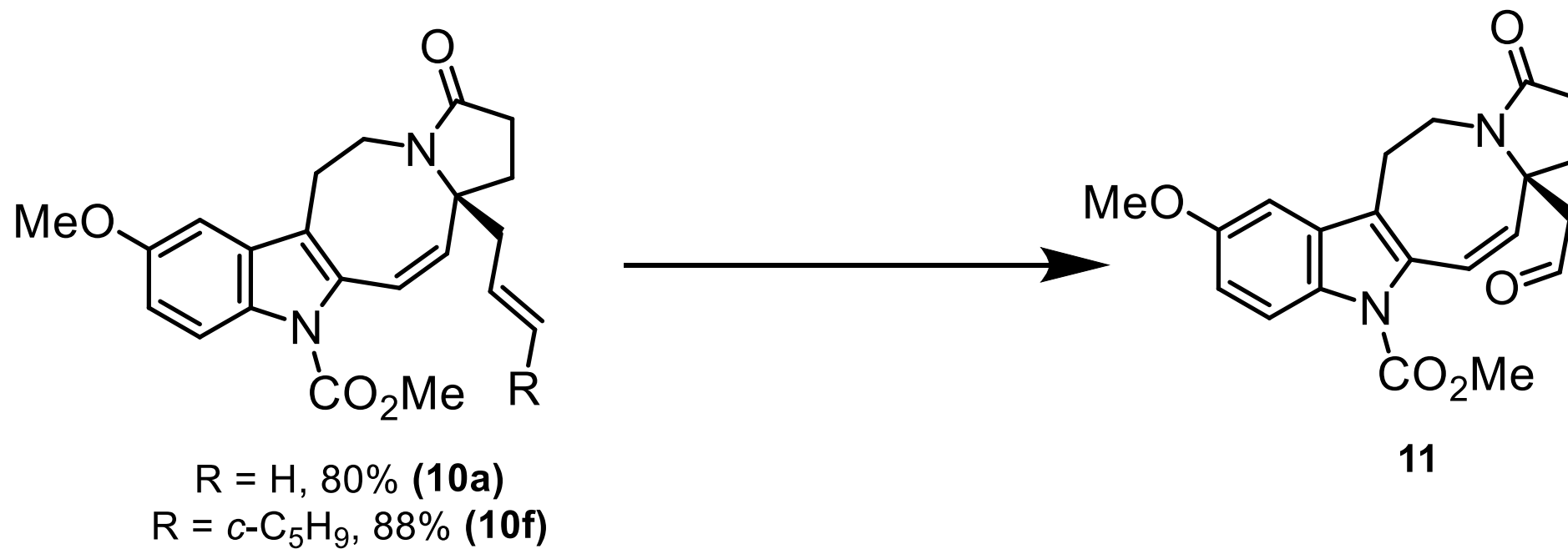
R = *c*-C₅H₉, 79%, 89:11 *er* (**9f**)
56%, >99:1 *er* (after crystallization)

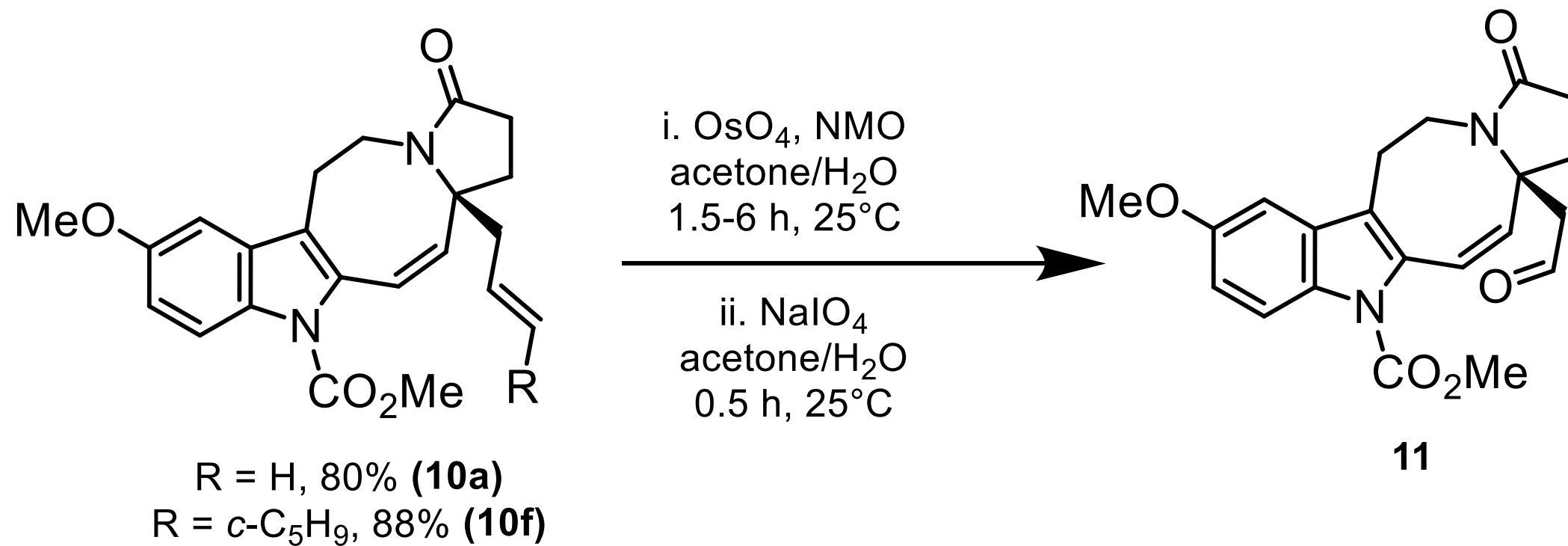


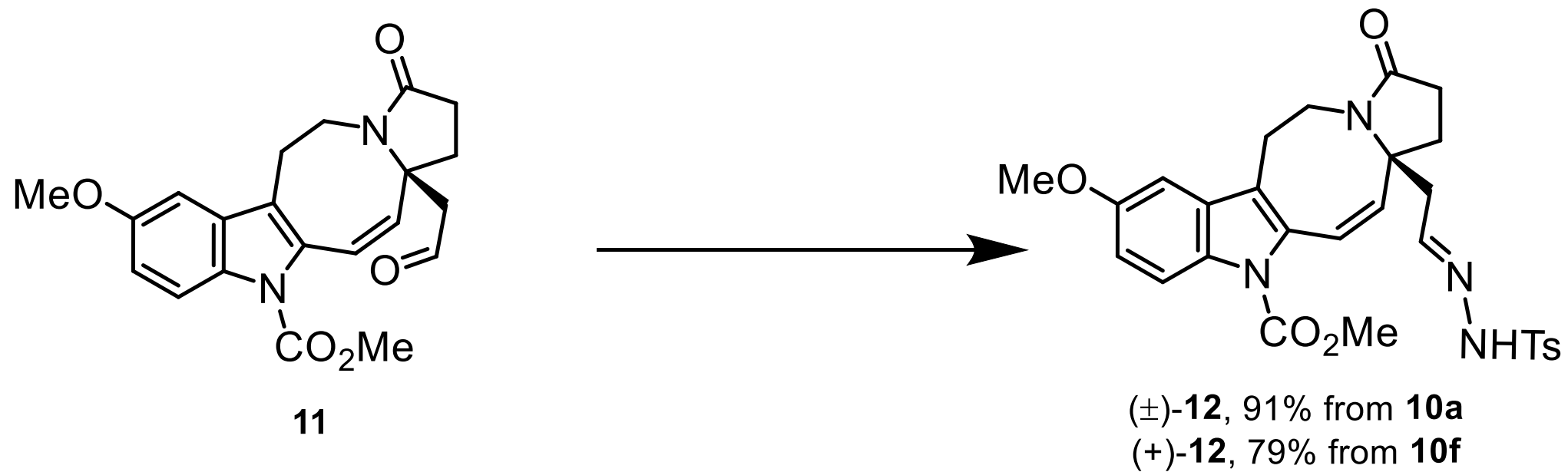
R = H, 80% (**10a**)

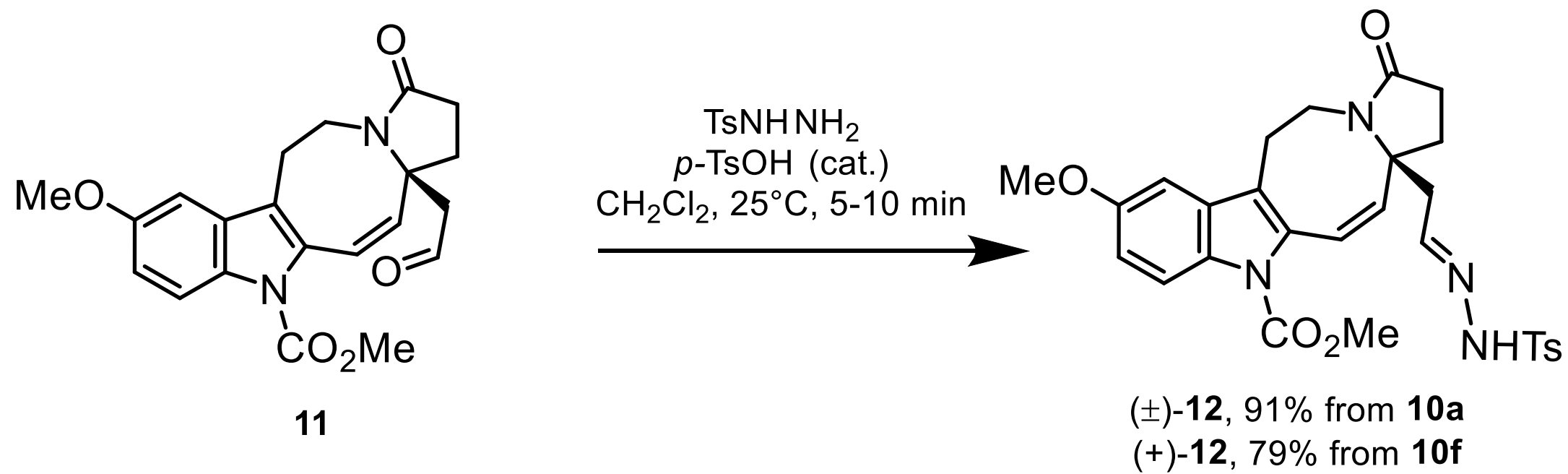
R = *c*-C₅H₉, 88% (**10f**)

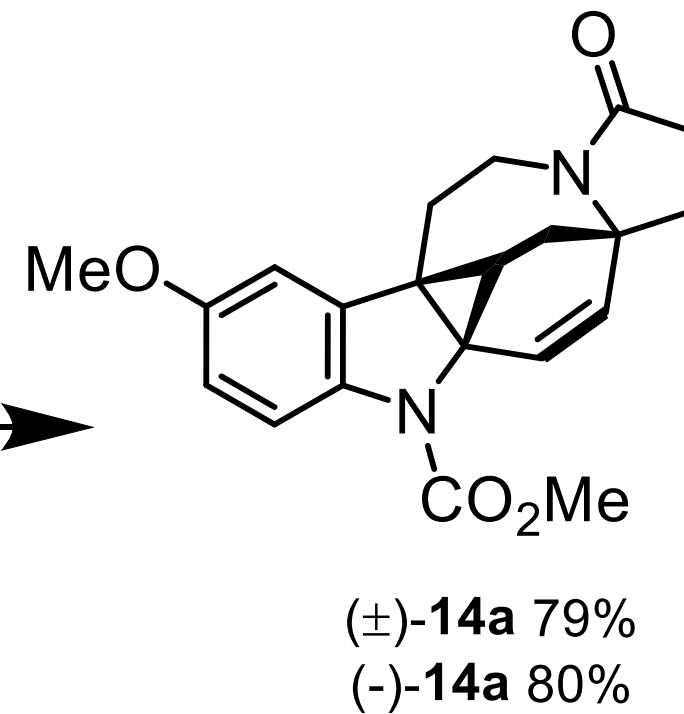
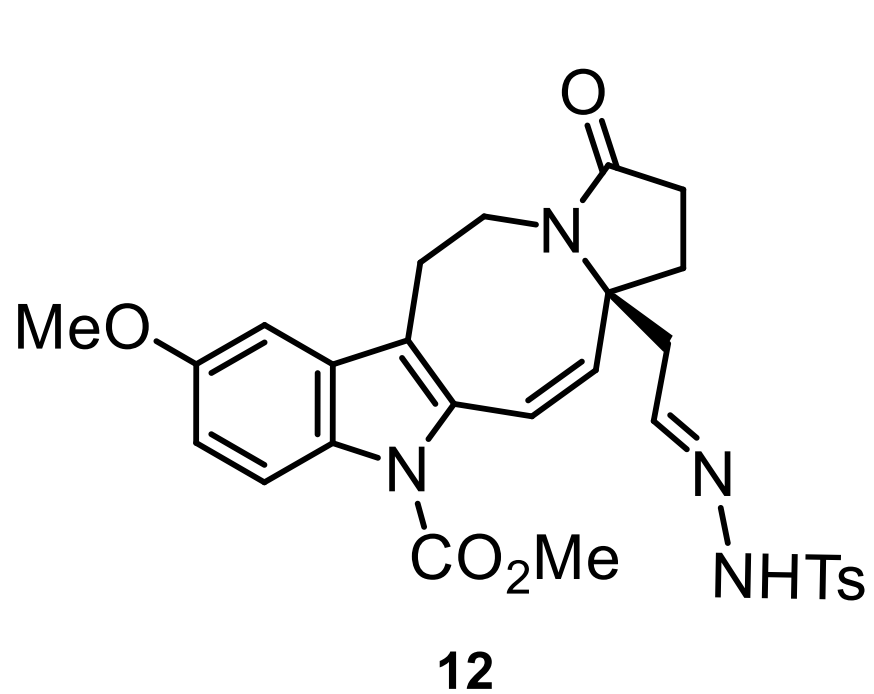


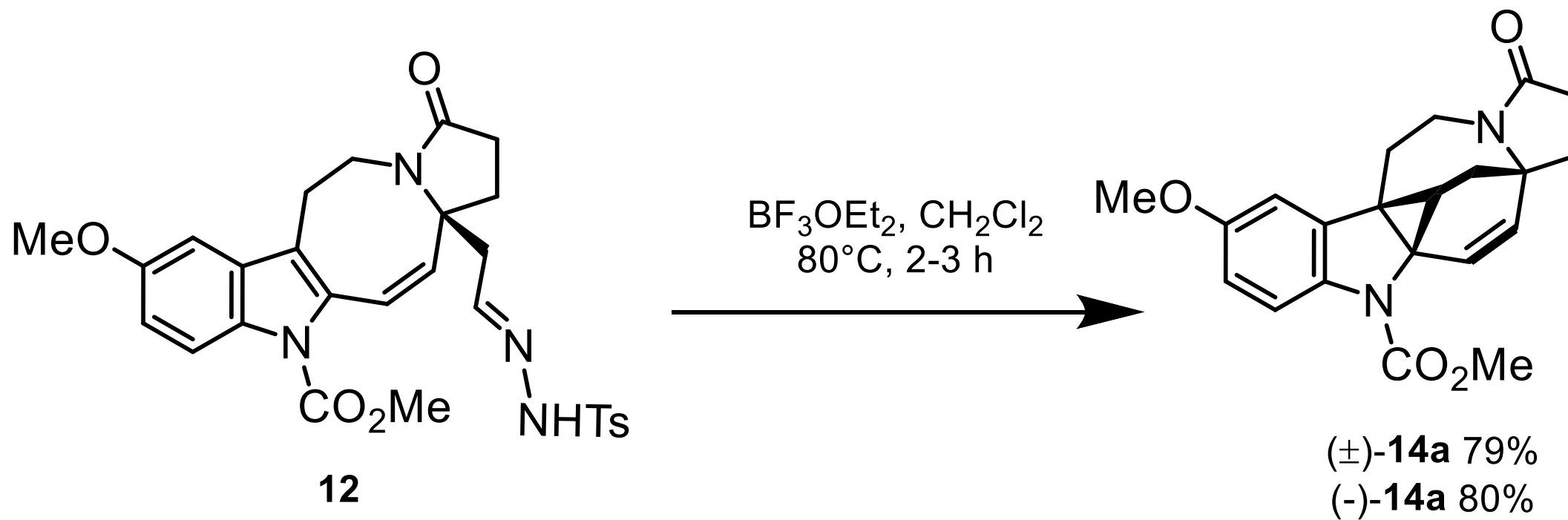


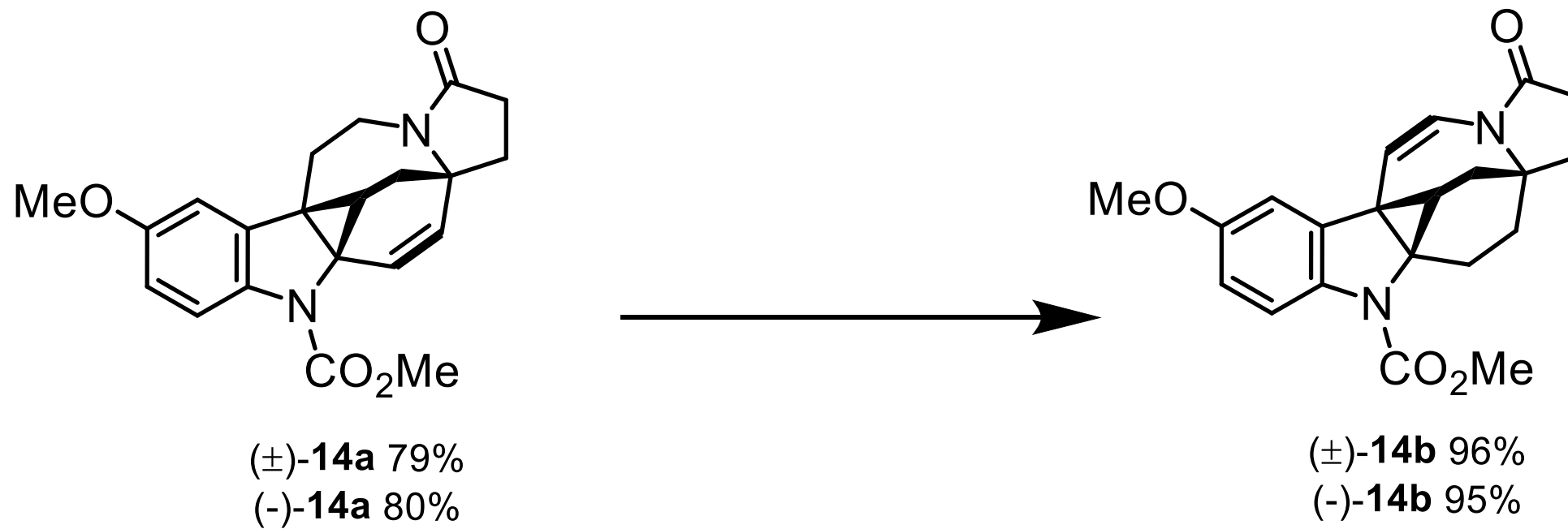


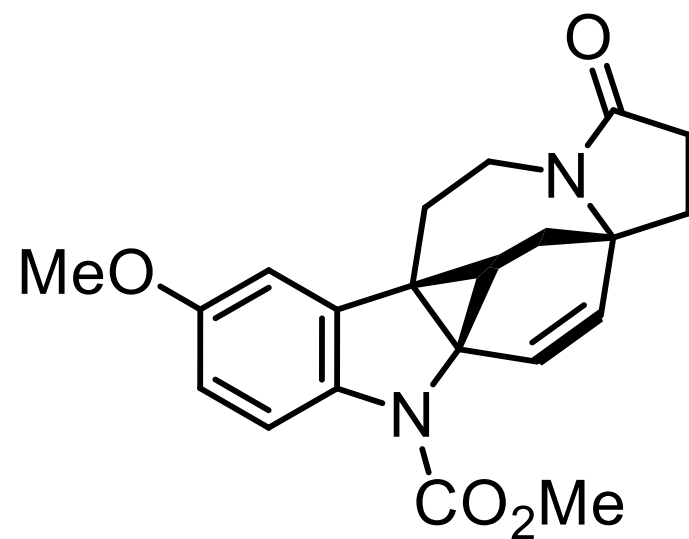






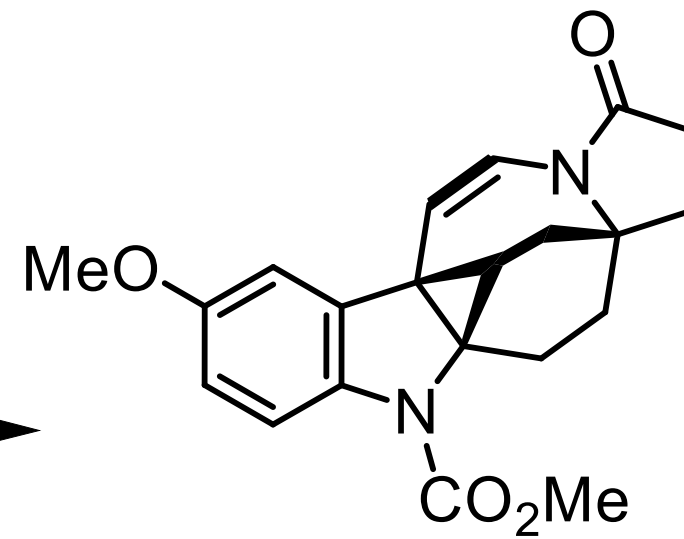




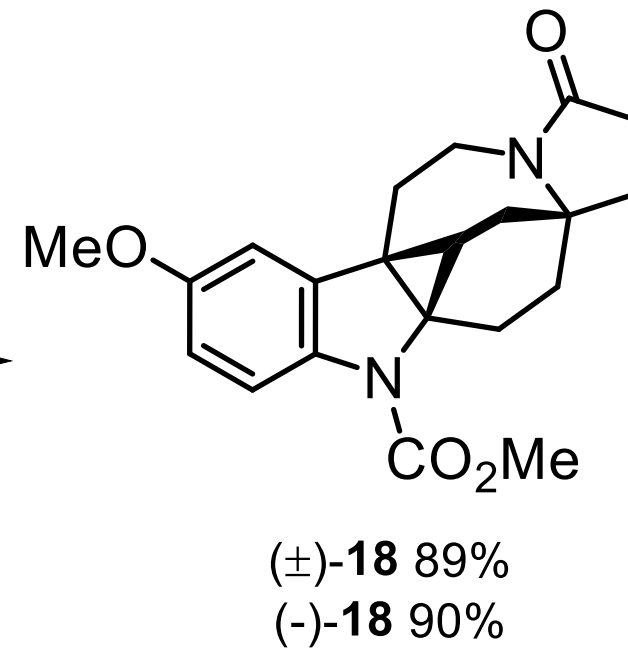
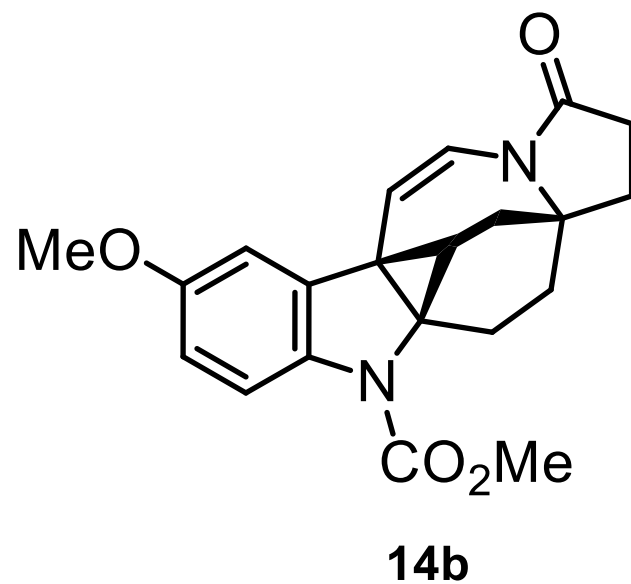


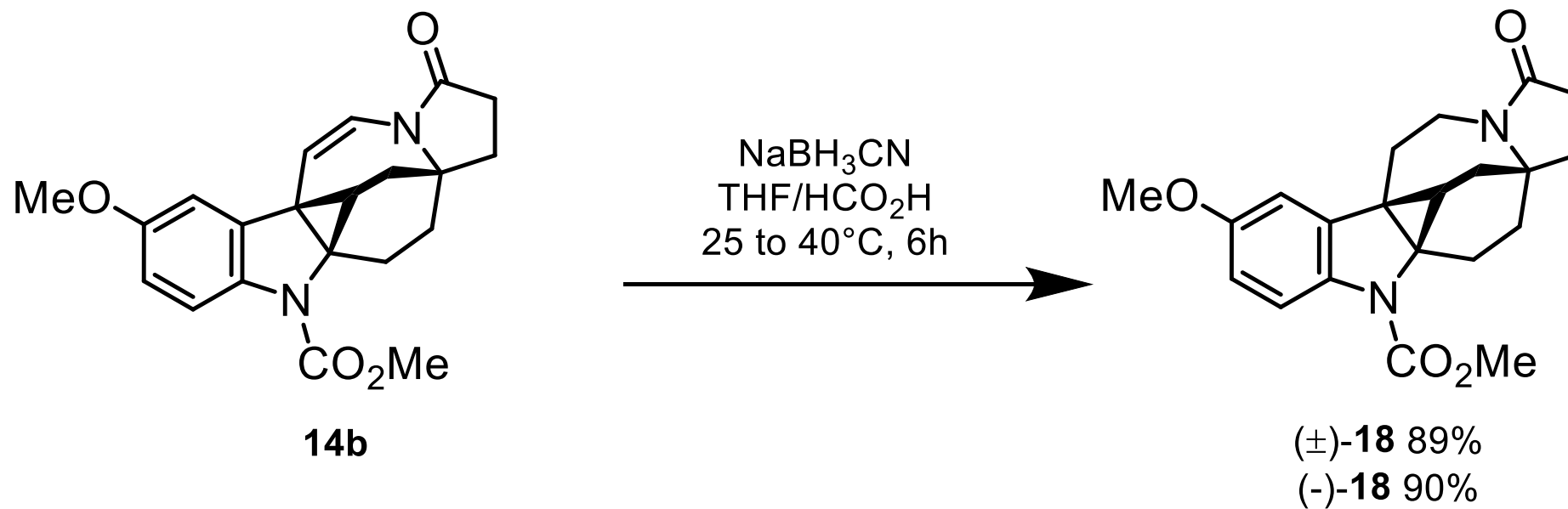
(±)-**14a** 79%
(-)-**14a** 80%

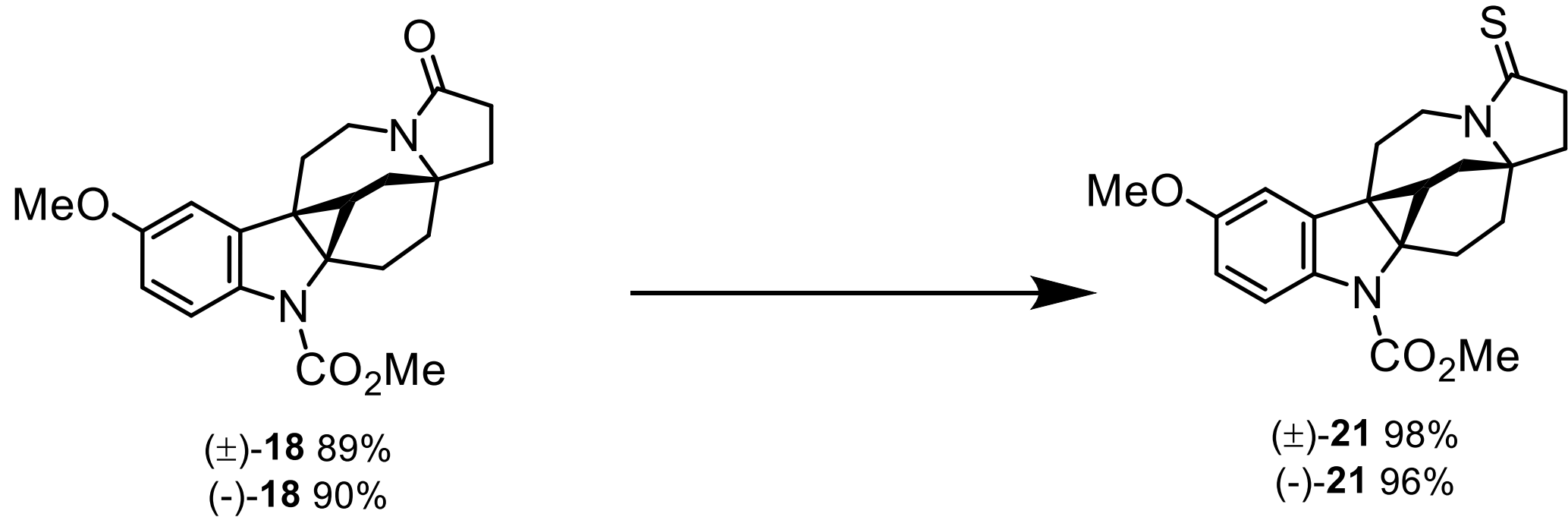
155°C, toluene, 2h

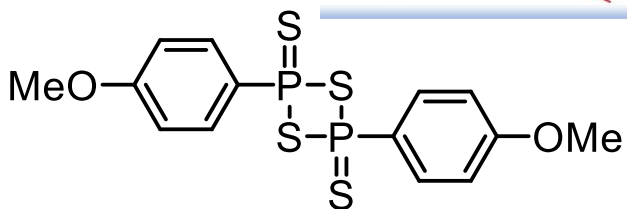


(±)-**14b** 96%
(-)-**14b** 95%

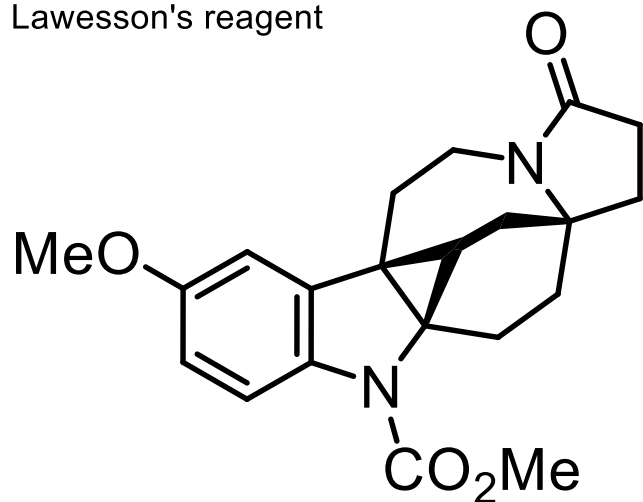






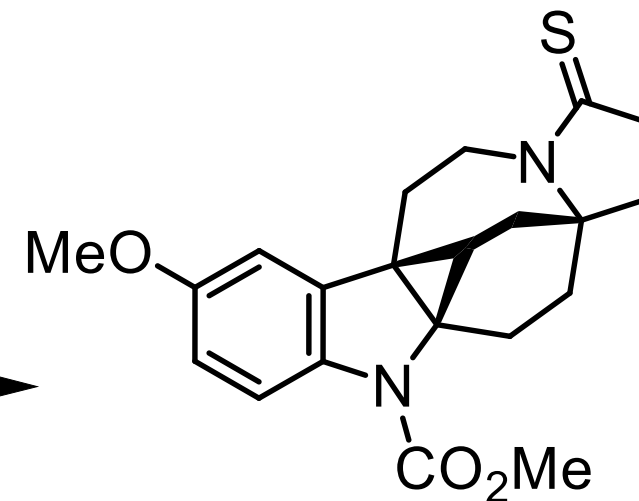


Lawesson's reagent

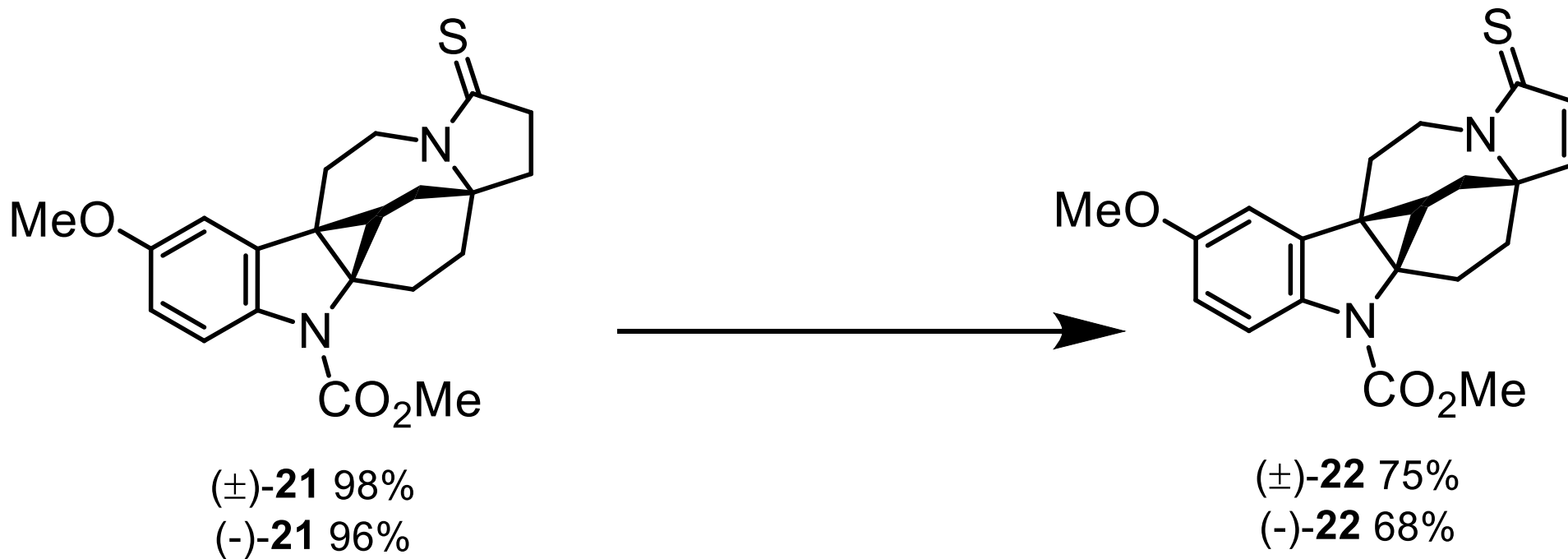


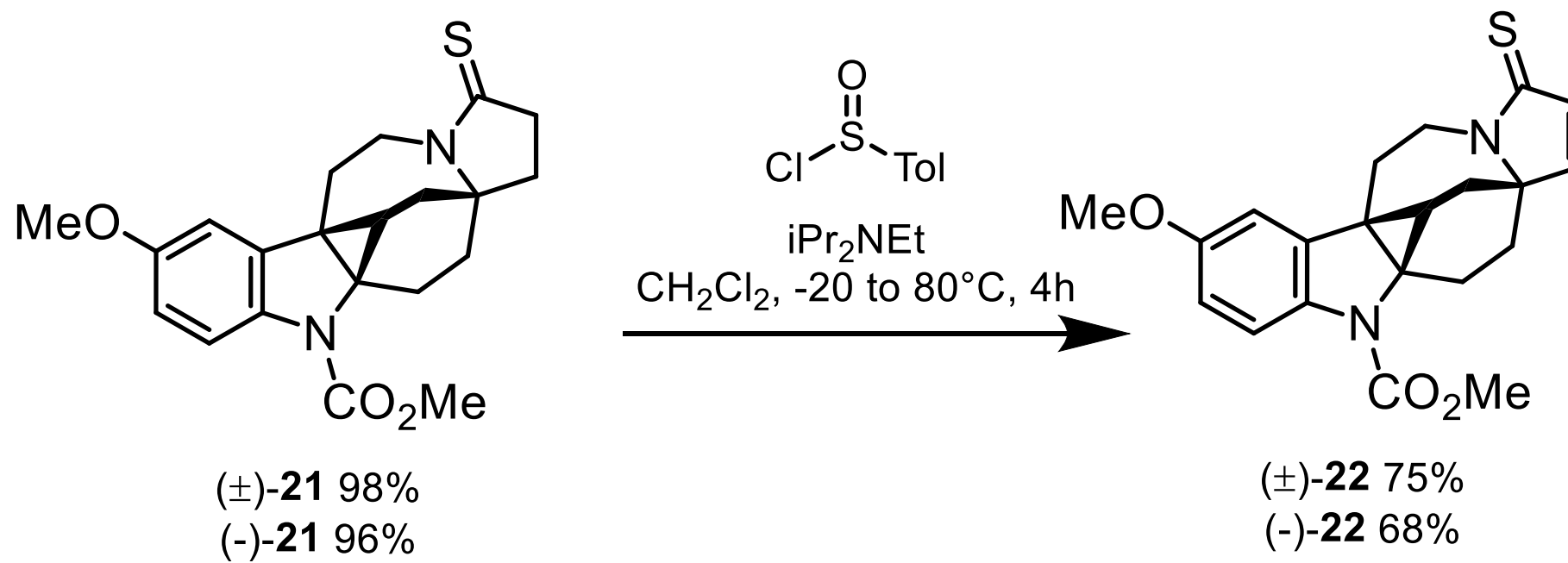
(±)-**18** 89%
(-)-**18** 90%

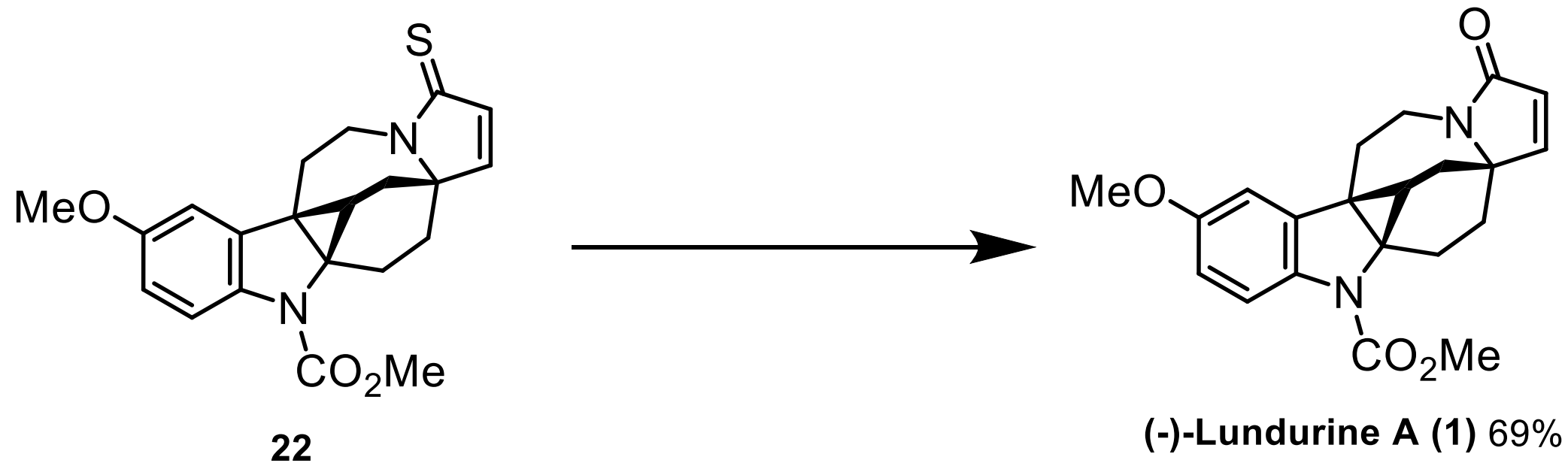
Lawesson's reagent
toluene, 90°C, 1 h

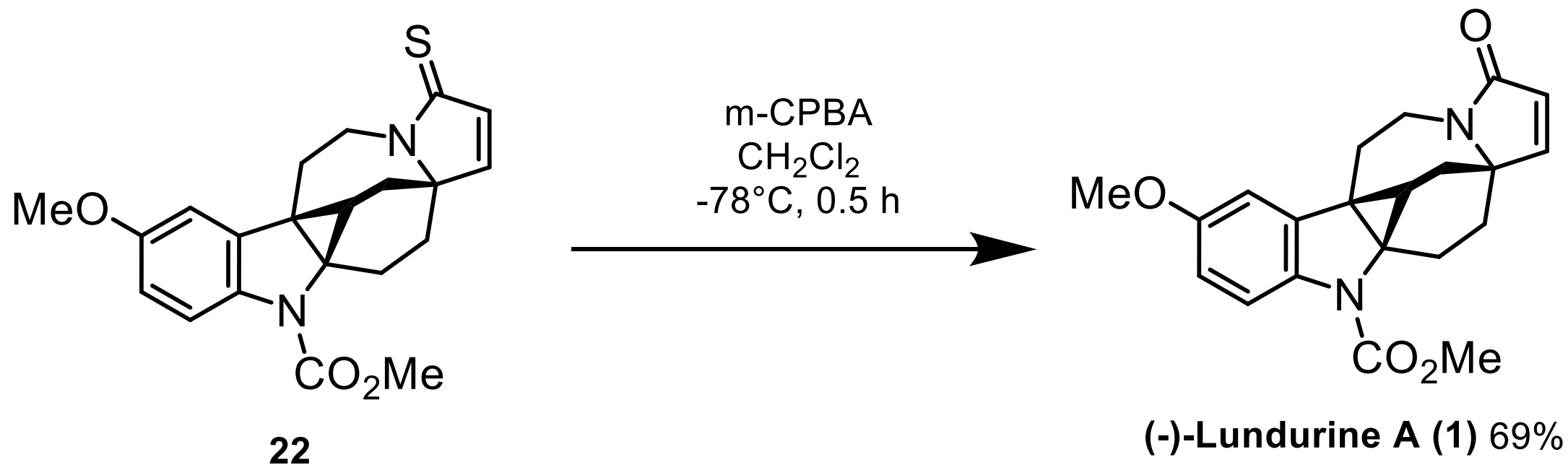


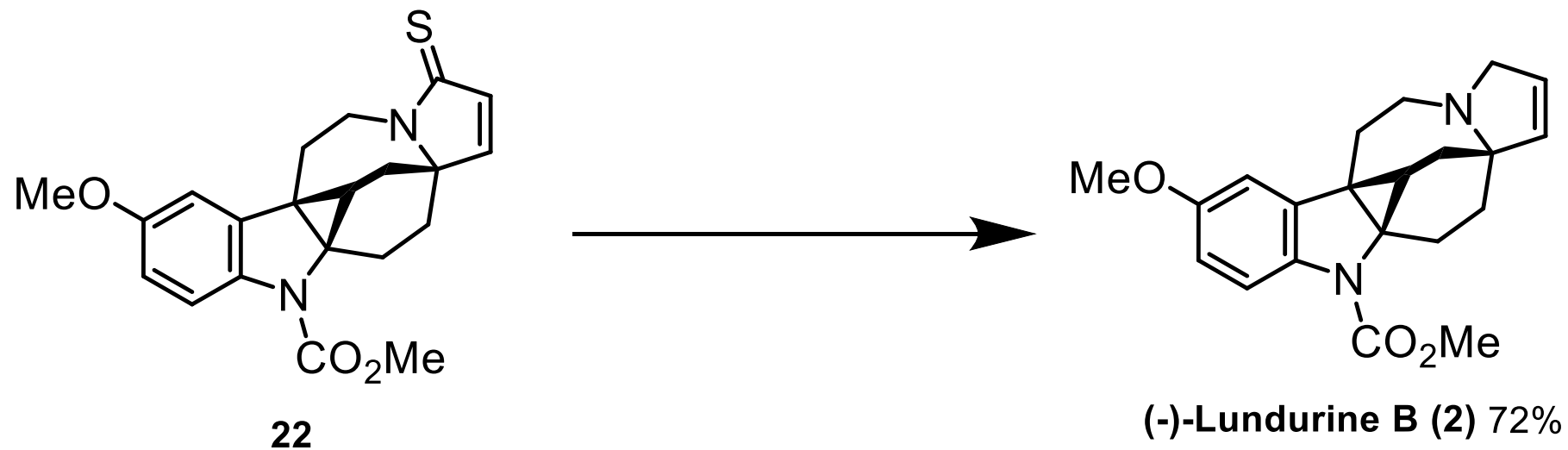
(±)-**21** 98%
(-)-**21** 96%

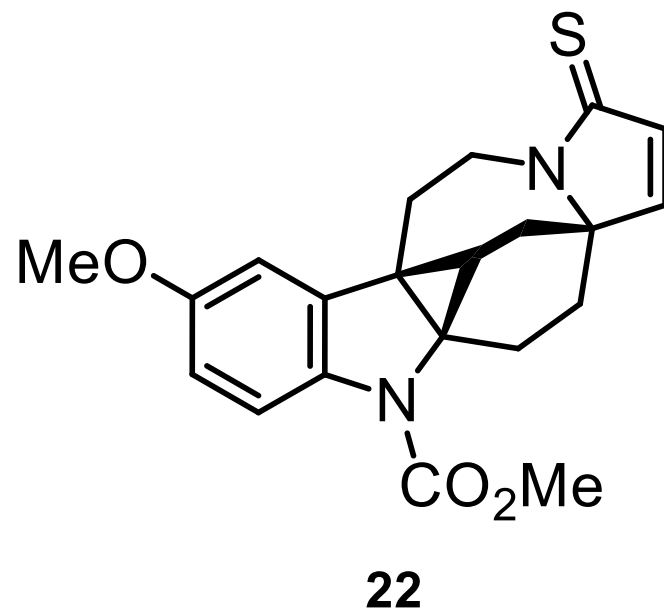




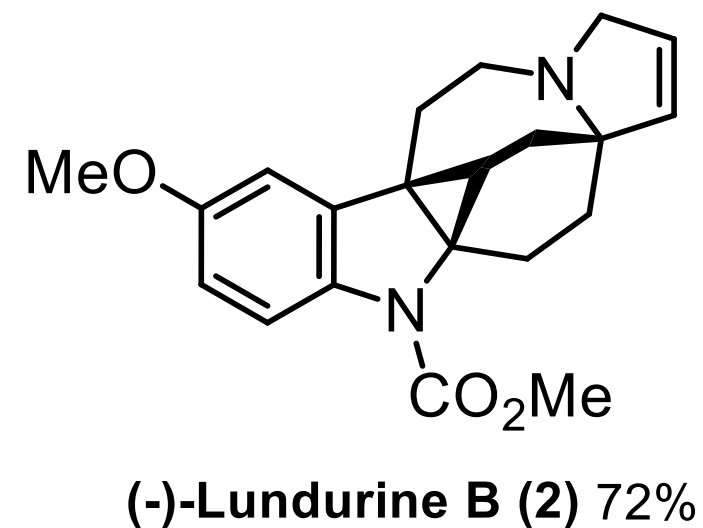


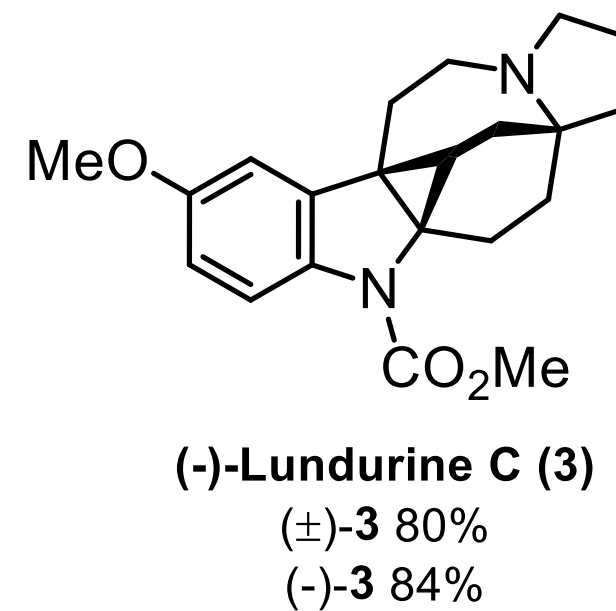
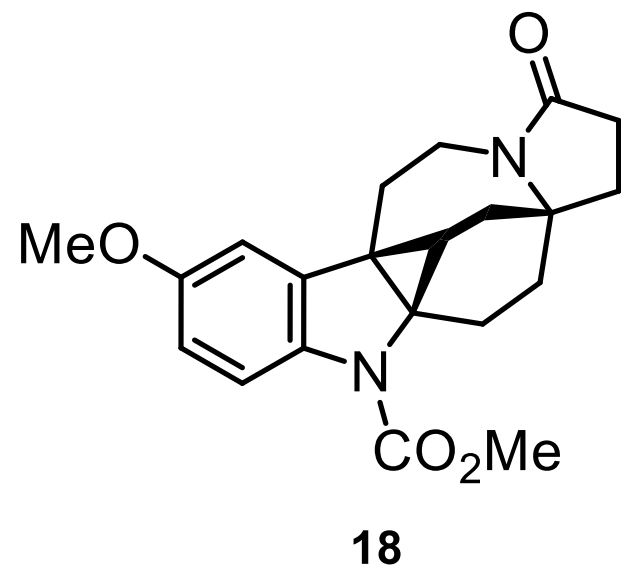


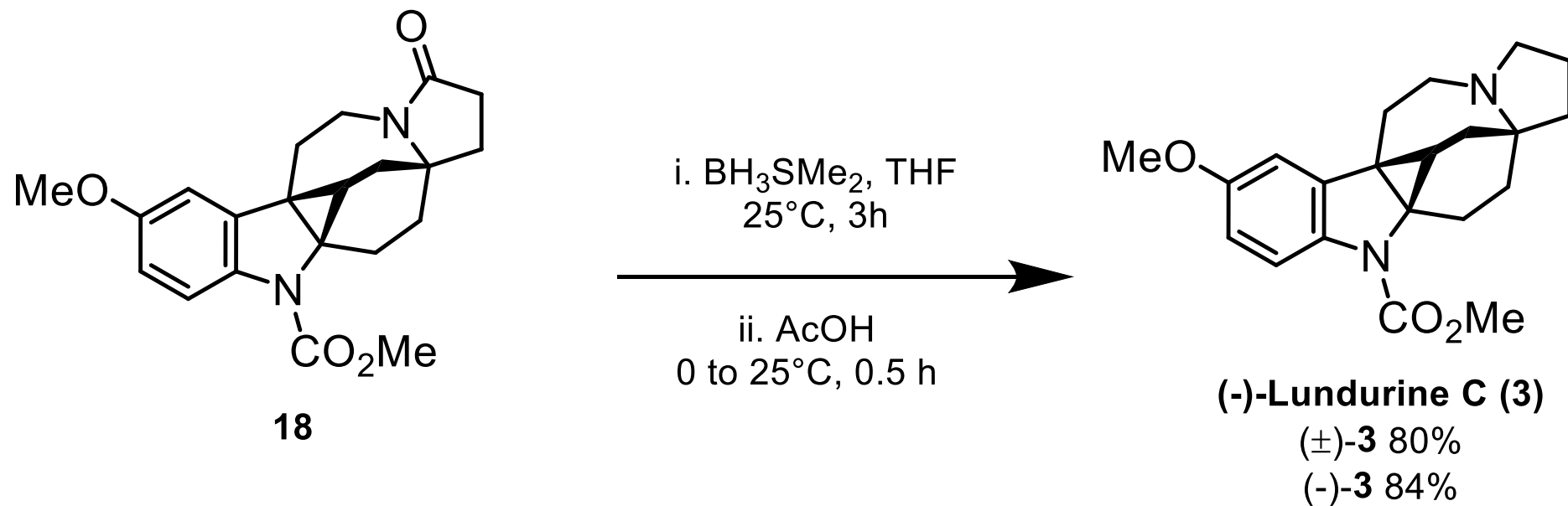


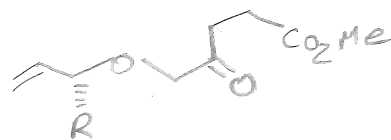
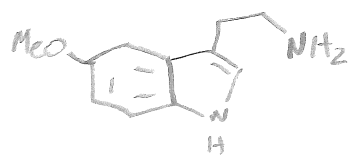


i. MeI, 50°C, 2h
ii. NaBH₄, MeOH
0 to 25°C, 2.5h









Toluene/py

