

Enantioselective Synthesis of (-)-Cajanusine

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1) PhMgBr, Ni(PPh₃)₂Cl₂
PhMe, 110°C, 12 h
2) CuI, bipy, TEMPO
N-methylimidazole
MeCN, 9h, open air

A

3) CH₂Br₂, **A**
then ^tBuLi
THF, -78°C to rt, 16 h

B

4) OTBDPS
^tBuLi, 30 min, then BF₃·OEt₂, 15 min
then **B**
THF, -78°C, 2 h

C

5) DMP, CH₂Cl₂
DCM, 0°C to rt, 3 h
6) cat. **TU**
DCM, 0°C, 1 h
then cat. Bi(OTf)₃
MeNO₂, 0°C to rt, 10 min
>20:1 dr

D

7) (*E*)-styrenyl boronic acid, LiOH·H₂O,
cat. [Rh(cod)Cl]₂
dioxane/H₂O, 60°C, 12 h
>20:1 dr
8) TBAF
THF, 0°C to rt, 24 h

E

9) DMP
DCM, 0°C to rt, 1.5 h
10) NaClO₂, NaH₂PO₄·H₂O
2-methyl-2-butene
^tBuOH/H₂O, 0°C to rt, 1 h
11) TCNHPI, DCC
cat. DMAP
DCM, 0°C to rt, 12 h

F

12) **ArZnBr**, NiCl₂·DME
BPhen
DMF/THF, rt, 16 h
14) *N*-MePMP, TMSOTf
DCM, -78°C, 3 h
15) IBX·MPO
DMSO, rt, 12 h

G

16) B₂Pin₂, MeOH
CuCl, DPEPhos, ^tBuONa
THF, rt, 3 h
then NaBO₃·4 H₂O
H₂O, rt, 3 h
17) CrO₃, H₂SO₄
acetone, -20°C, 30 min
18) 3 eq. allyl acetate, 5 eq. K₂CO₃
[Pd(allyl)Cl]₂, dppe
THF, 50°C, 1 h

H

19) AlEt₃, Ni(PPh₃)₂Br₂
PhMe, 2 h
then TMSCHN₂
MeOH, 30 min
73% **I**, 19% **J**

I
major

J
minor

20) xs isobutene
HG-II
DCM, 50°C, 48 h
then TBAF
THF, 0°C, 30 min

Hints:

Step 1) Ring opening
After 6) no more triple bond

