

hyperbeanol A: $R^1 = OH, R^2 = CH_3$
 revised hyperpatulol A: $R^1 = CH_3, R^2 = OH$

hyperbeanol C: $R^3 = OH, R^4 = CH_3$
 revised hyperbeanol B: $R^3 = CH_3, R^4 = OH$

hypercophane G

11, 2 steps
 from (R)-linalool

1. IBX, DMSO
 2. MEMCl, TBAI
 DIPEA, 60 °C
 66% (2 steps)

12

10

3. 9
 piperidine
 CH₂Cl₂, rt
 46%

13

4. Hantzsch Ester
 DMF, 50 °C
 80%

8

5. Mn(OAc)₃·2H₂O
 O₂, MeCN
 then Me₂S
 88%

6 (50%)

7 (38%)

hybrid of Mn mediated cyclization and Mukaiyama hydration

Reaction scheme showing the synthesis of 13 from 9 and 10, and the subsequent synthesis of 14a and 14b from 13. The reaction involves amines in CH_2Cl_2 at room temperature (rt).

Chemical structures shown:

- 9: A bicyclic compound with a fused ring system and a hydroxyl group.
- 10: A substituted cyclohexene derivative with a methyl group and a MEMO group.
- 13: A complex bicyclic product.
- 14a and 14b: Two isomeric bicyclic products.

Reaction conditions: amines, CH_2Cl_2 , rt.

entry	equiv(9/10)	amines	isolated yields (%)	
			13	14a + 14b
1 ^b	1.0/1.0	L-proline	18	30
2 ^b	1.0/1.0	piperidine	25	20
3 ^b	1.0/1.0	diethylamine	20	28
4 ^c	2.0/1.0	piperidine	30	35
5 ^c	3.0/1.0	piperidine	22	36
6 ^d	1.0/2.0	piperidine	11	30
7 ^d	1.0/3.0	piperidine	trace	26
8 ^c	2.5/1.0	piperidine	46	35

^aSee the [Supporting Information](#) for detailed procedures. ^bBoth **9** and **10** remained. ^cA high conversion for compound **10** was observed. ^dCompound **10** was recovered in substantial quantities, and aldehyde **12** was observed.

[illegible]

7

6. MOMBr, DIPEA
7. LDA, THF
8. TBSCl, imid.
68% (3 steps)

22

9. LHMDS
prenyl bromide
TBAI, THF
-78 °C to rt

23 (44%)

10. LTMP, BzCl, THF

25

11. TBAF, THF
12. (COCl)₂
DMSO, Et₃N
then DBU
then 2 M HCl
26% (3 steps)

nominal (+)-hyperpatulol A
revised (+)-hyperbeanol B (4)

10'. LTMP, BzCl, THF

26

11'. TBAF, THF
12'. (COCl)₂
DMSO, Et₃N
then DBU
then 2 M HCl
23% (3 steps)

nominal (+)-hyperbeanol B
revised (+)-hyperpatulol A (2)