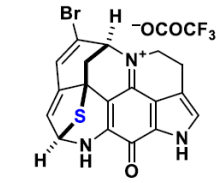

(–)-Aleutianamine (**7**)

pyrroloiminoquinone alkaloid recently isolated from a North Pacific sponge

Tokuyama, *JACS* **2023**, *145*, *47*, 18233.

HSCH2COOMe, K2CO3
DMF, rt to 60 ºC

19

1) Mg, AcOH
MeOH, 84%
2) 2 M NaOH aq.
3) DPPA, Et_3N;
t-BuOH, reflux

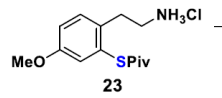
92% (2 steps)

21

Na
liq. NH_3
THF
70%

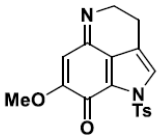
22

1) PivCl, Et_3N
CH_2Cl_2
quant.
2) 4 M HCl
1,4-dixoane
quant.



23

MeOH
83%



24

PIFA
TFE
87%

25

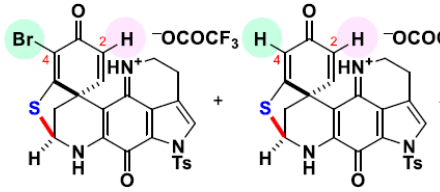
Mechanism?

Table

entry	X	solvent	time (h)	**28** (%)	**29** (%)
1	1	MeCN	14	15	-
2	1	THF	3	-	56
3	0.3 (air)	THF	2	-	52

$CuBr_2$ (X eq)
solvent, 80 °C

Table



28 + **29**

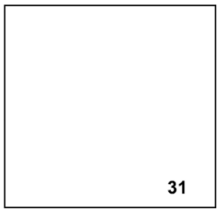
26

Mechanism?

26

$PyHBr_3$
$CHCl_3$/MeCN
69%

$CuBr_2$
(0.3 eq)
$CHCl_3$
80 ºC, air
51%

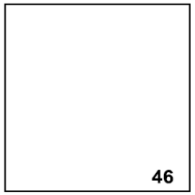


31

diastereomers
separation

(+)-**31**

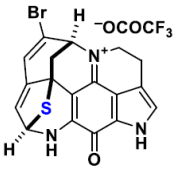
$NaBH_4$
$CeCl_3 \cdot 7H_2O$
MeOH
0 ºC, 1 h;
HPLC (H^+)
39%



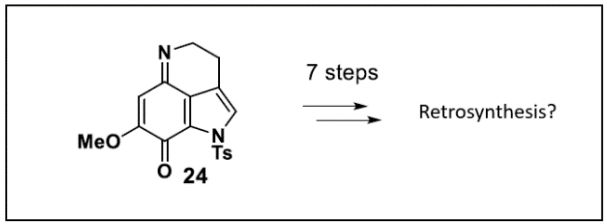
46

Mechanism?

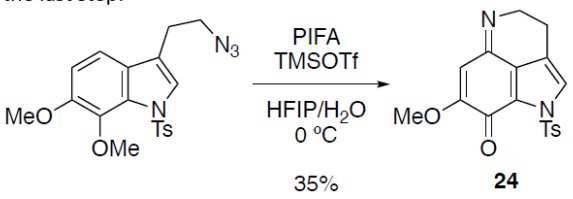
NaOMe
THF/MeOH
0 ºC, 15 min



(–)-Aleutianamine (**7**)



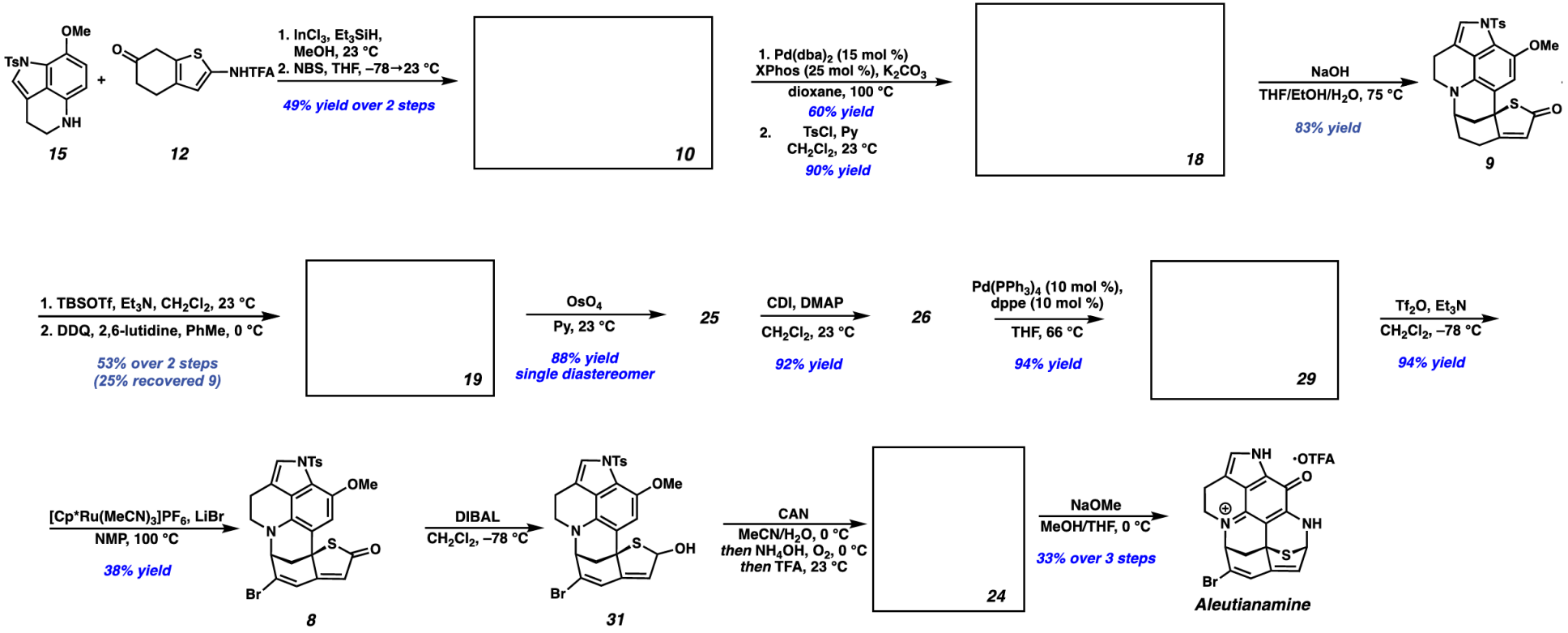
Hint on the last step:



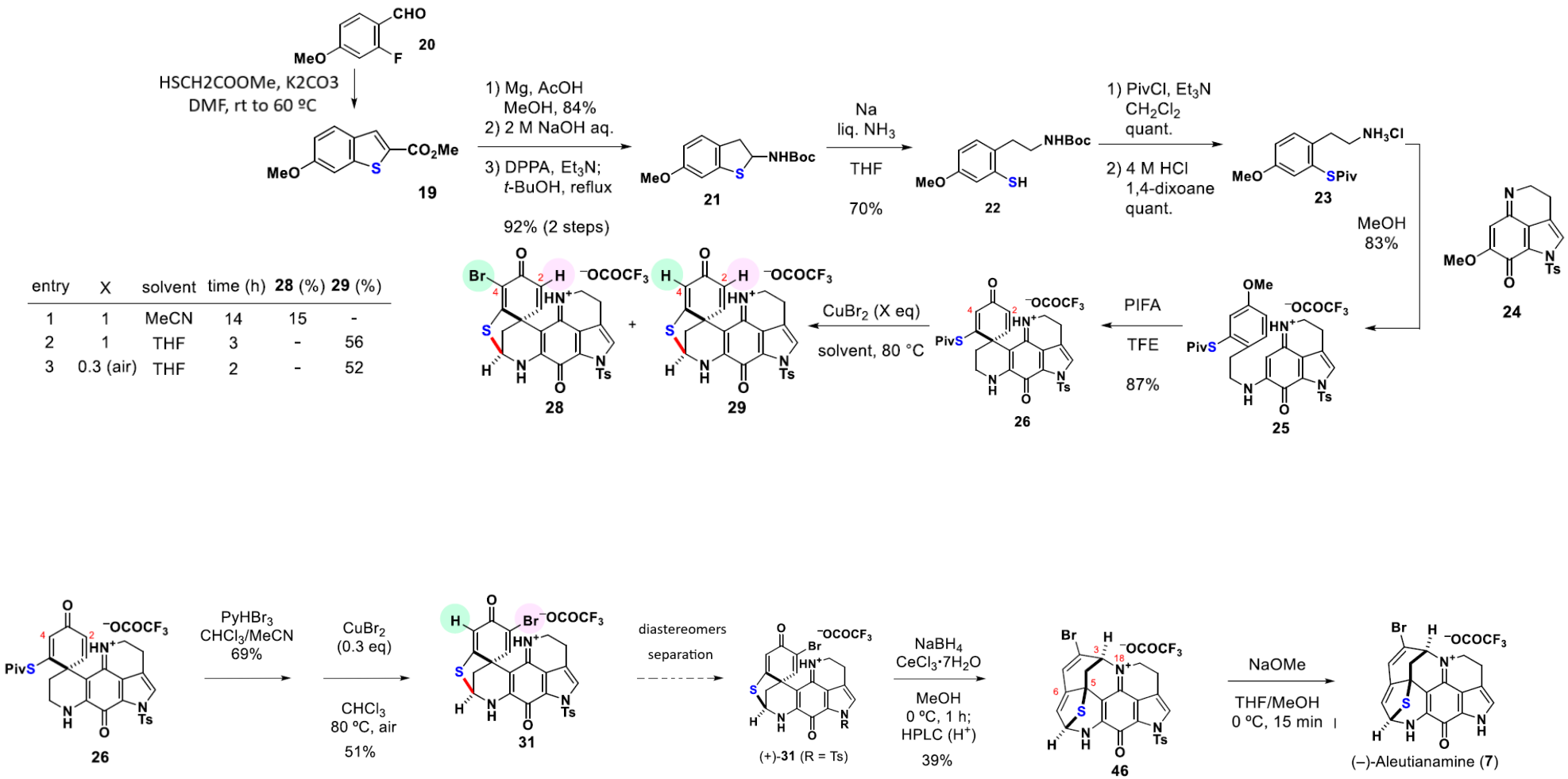
Mechanism?

Alternative synthesis:

Stoltz, *JACS* **2023**, *145*, *47*, 25533.

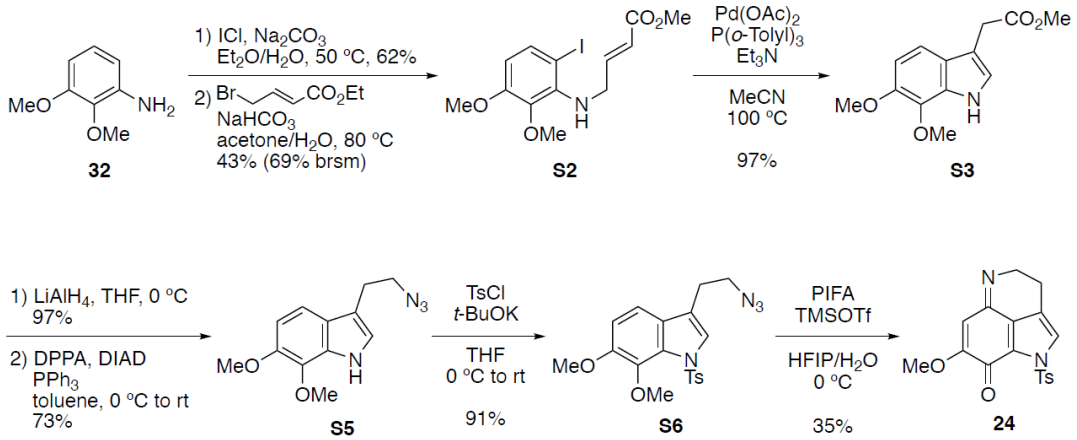


Solution:



entry	X	solvent	time (h)	**28** (%)	**29** (%)
1	1	MeCN	14	15	-
2	1	THF	3	-	56
3	0.3 (air)	THF	2	-	52

Synthesis **24**:



Alternative synthesis: