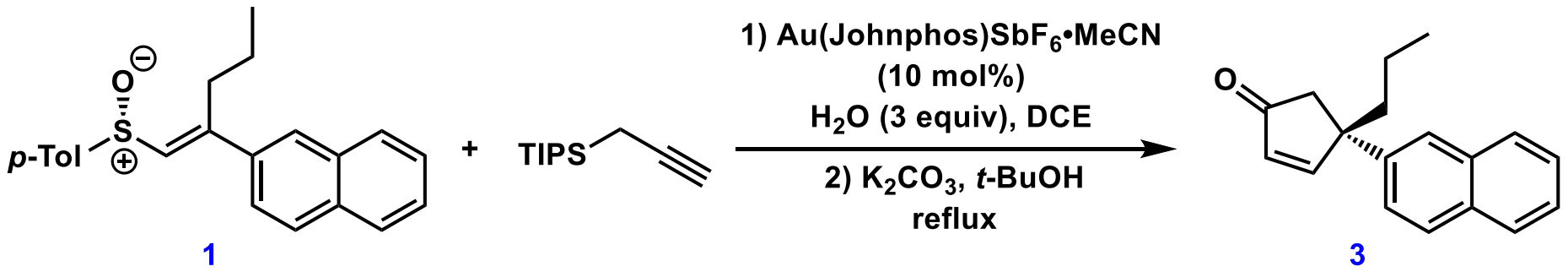
1.



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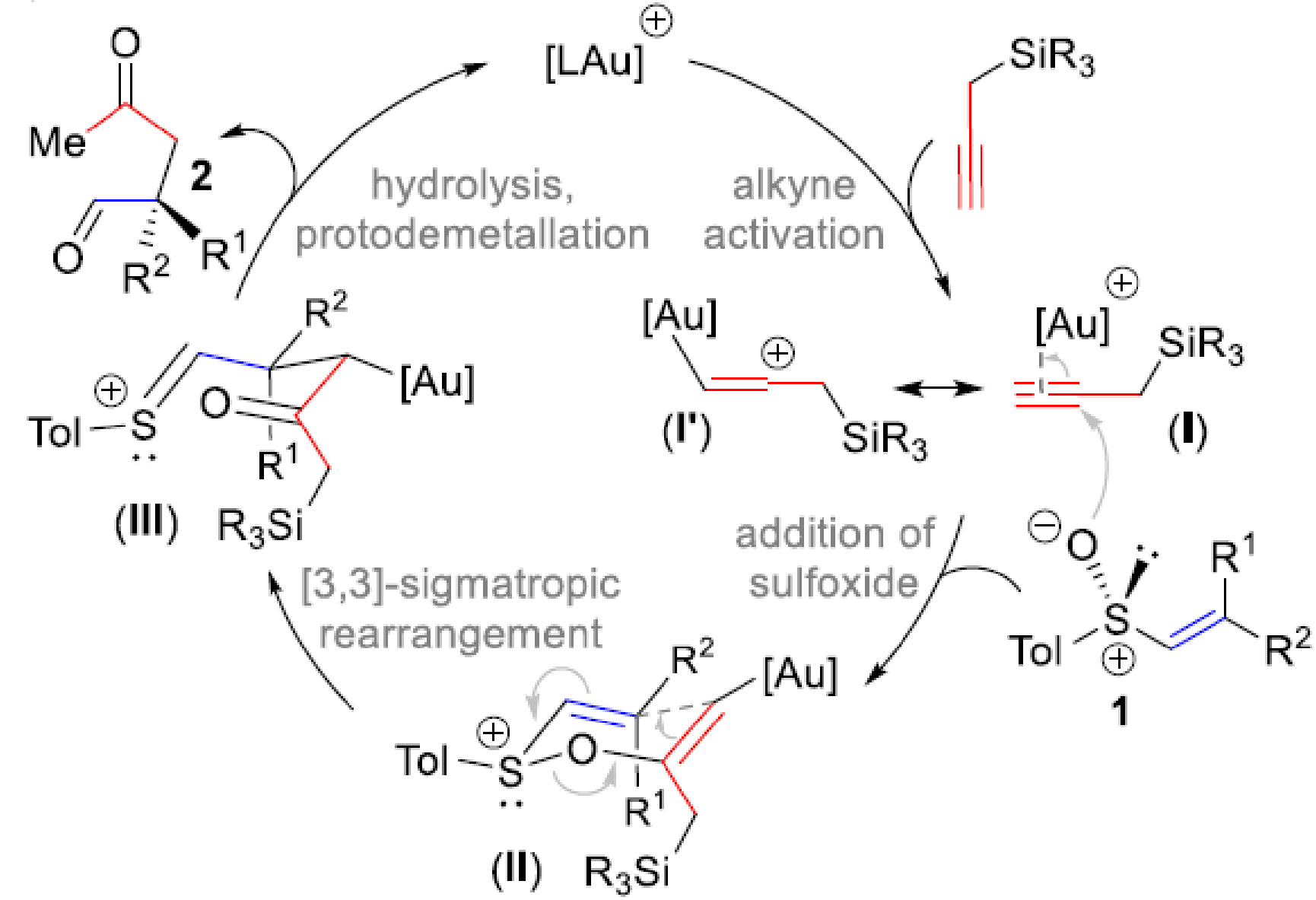
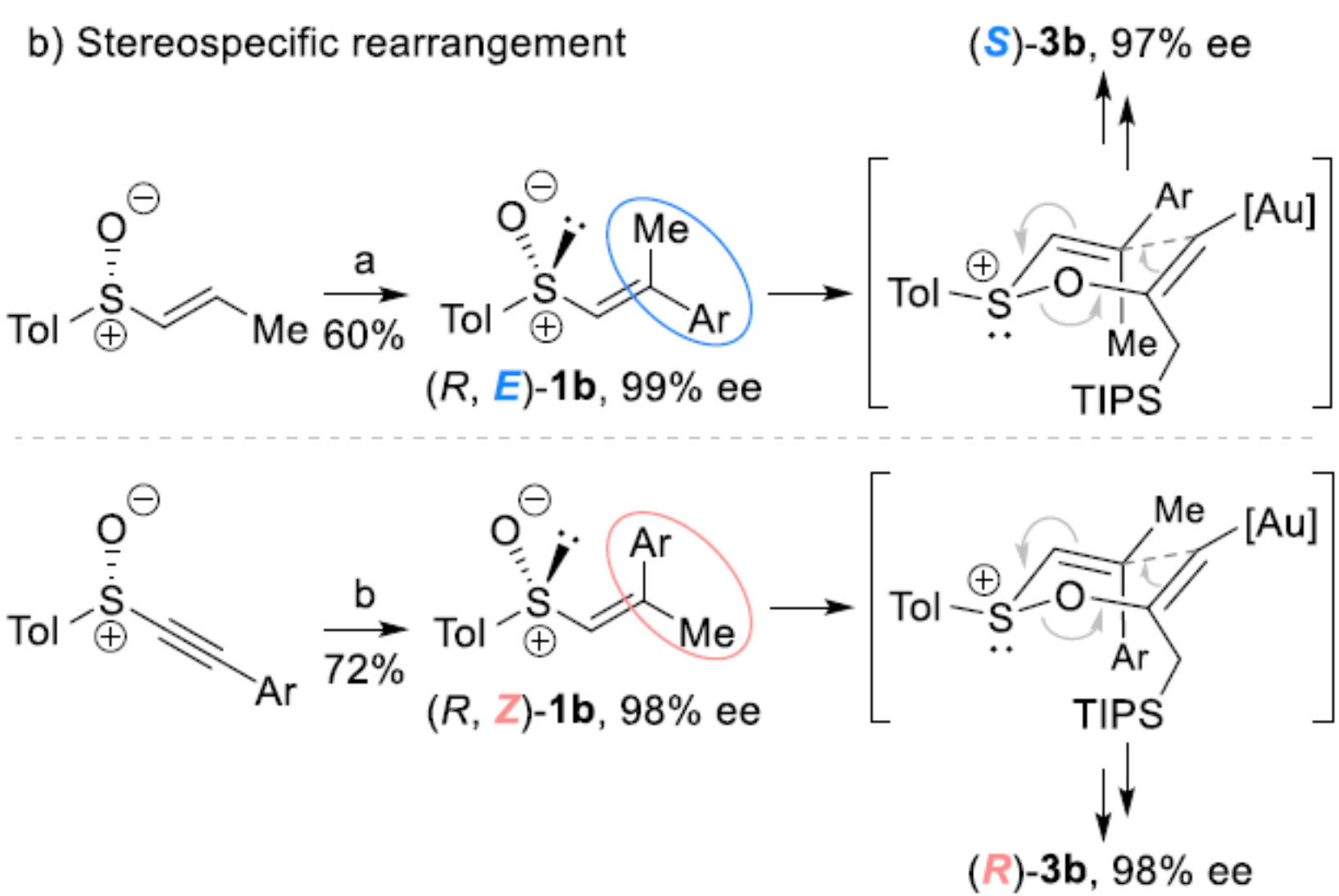
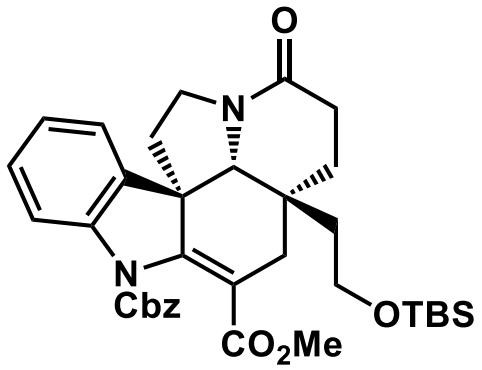
a) Proposed mechanism





[a]Reagents and conditions: (a) ArI, $Pd(OAc)_2$(10 mol %), dppp (10 mol %), Ag_2CO_3, DMF, 100 °C, 36 h; (b) $CuOTf_2$ (2 mol %), $ZnMe_2$, THF, −78 °C to rt, 12 h; dppp = 1,3-bis-(diphenylphosphanyl)propane; Ar = *p*-Me-C_6H_4.

2.



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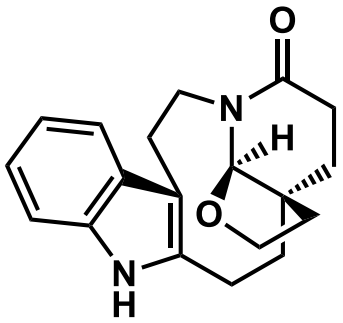
1) KOH
THF/MeOH/H_2O
70 °C
2) toluene, 108 °C



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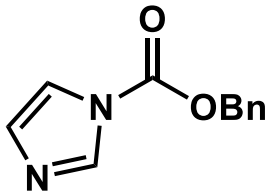
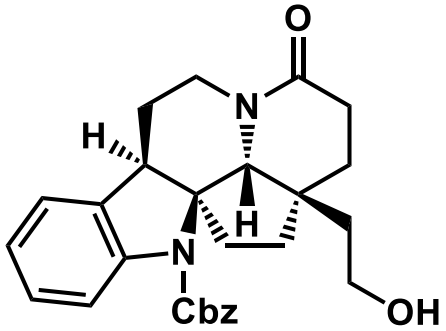
3)



DBU, MeCN, rt
4) SmI_2, BF_3•OEt, rt



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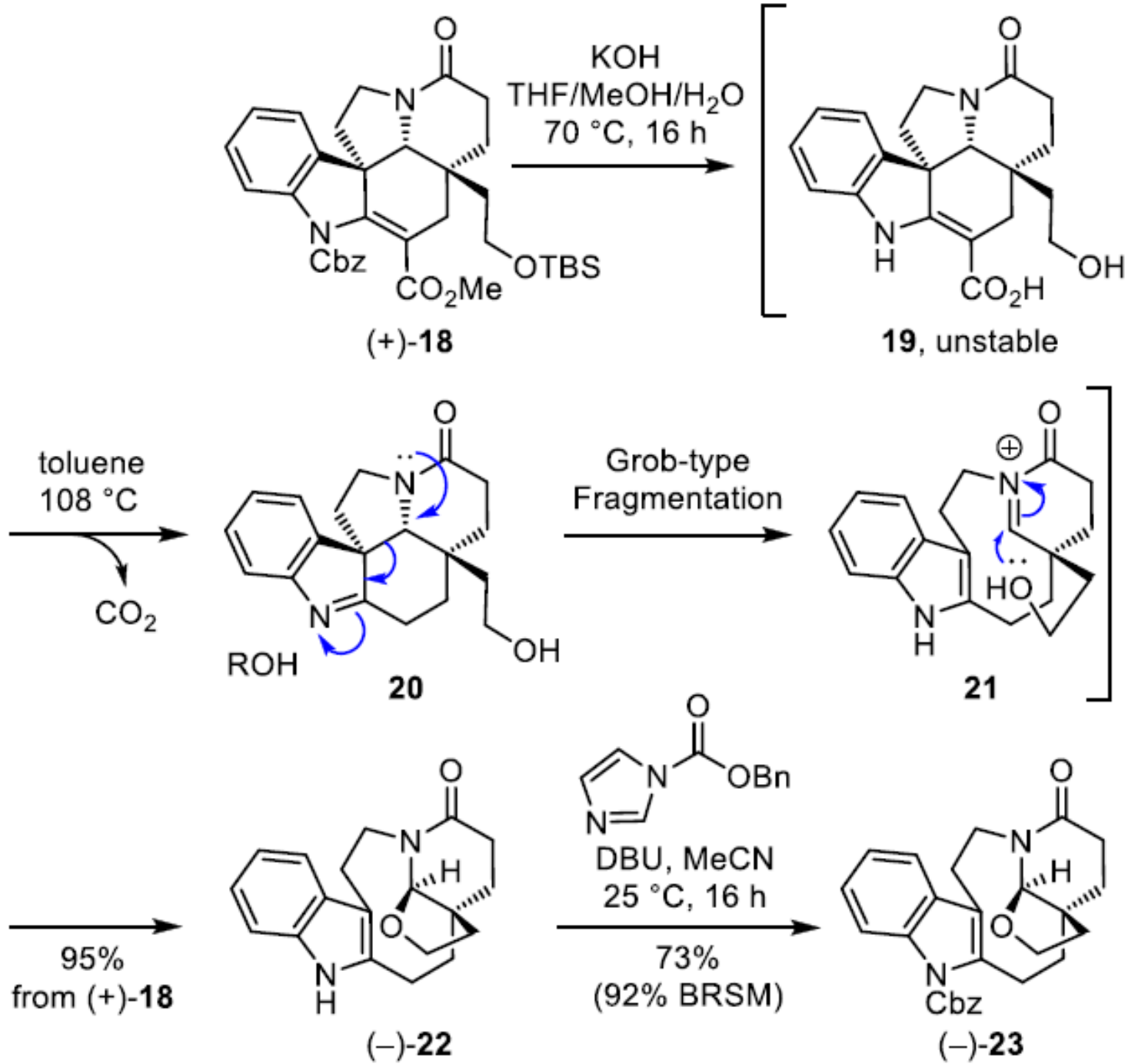
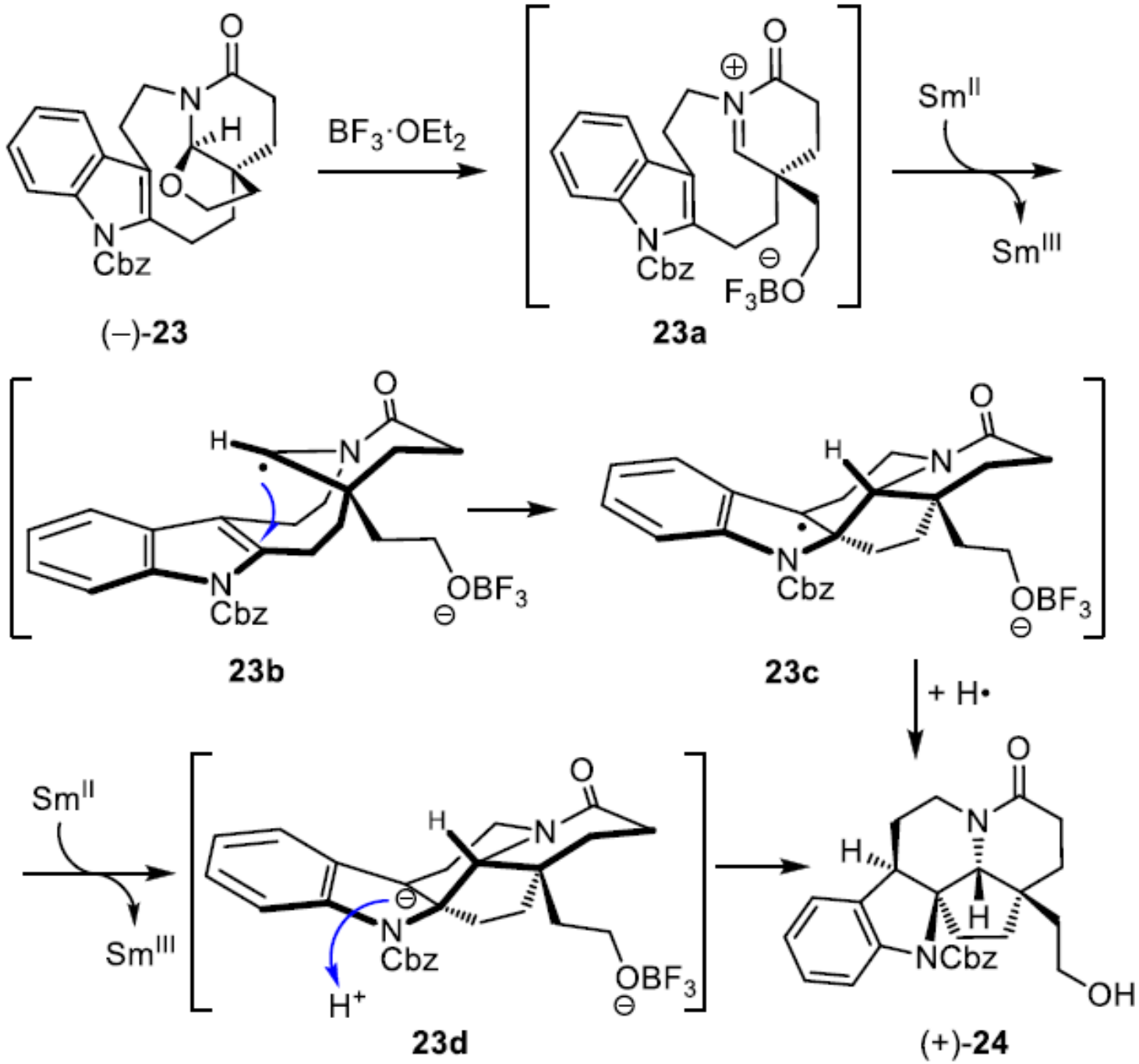
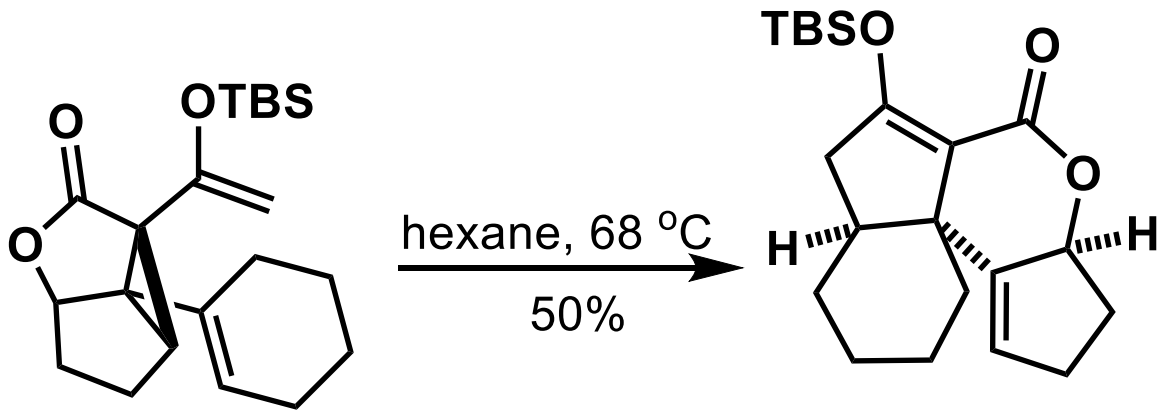

KOH
THF/MeOH/H2O
70 °C, 16 h
Cbz
CO2Me
OTBS
(+)-18
19, unstable
toluene
108 °C
CO2
ROH
20
Grob-type
Fragmentation
HO
21
95%
from (+)-18
(–)-22
DBU, MeCN
25 °C, 16 h
OBn
73%
(92% BRSM)
(–)-23


O
N
H
O
N
Cbz
(–)-23
BF3·OEt2
O
N
N
Cbz
F3BO
23a
SmII
SmIII
H
N
O
N
Cbz
OBF3
23b
H
N
O
N
Cbz
OBF3
23c
+ H•
SmII
SmIII
H
N
O
N
Cbz
H+
OBF3
23d
H
N
O
H
H
NCbz
OH
(+)-24

3.



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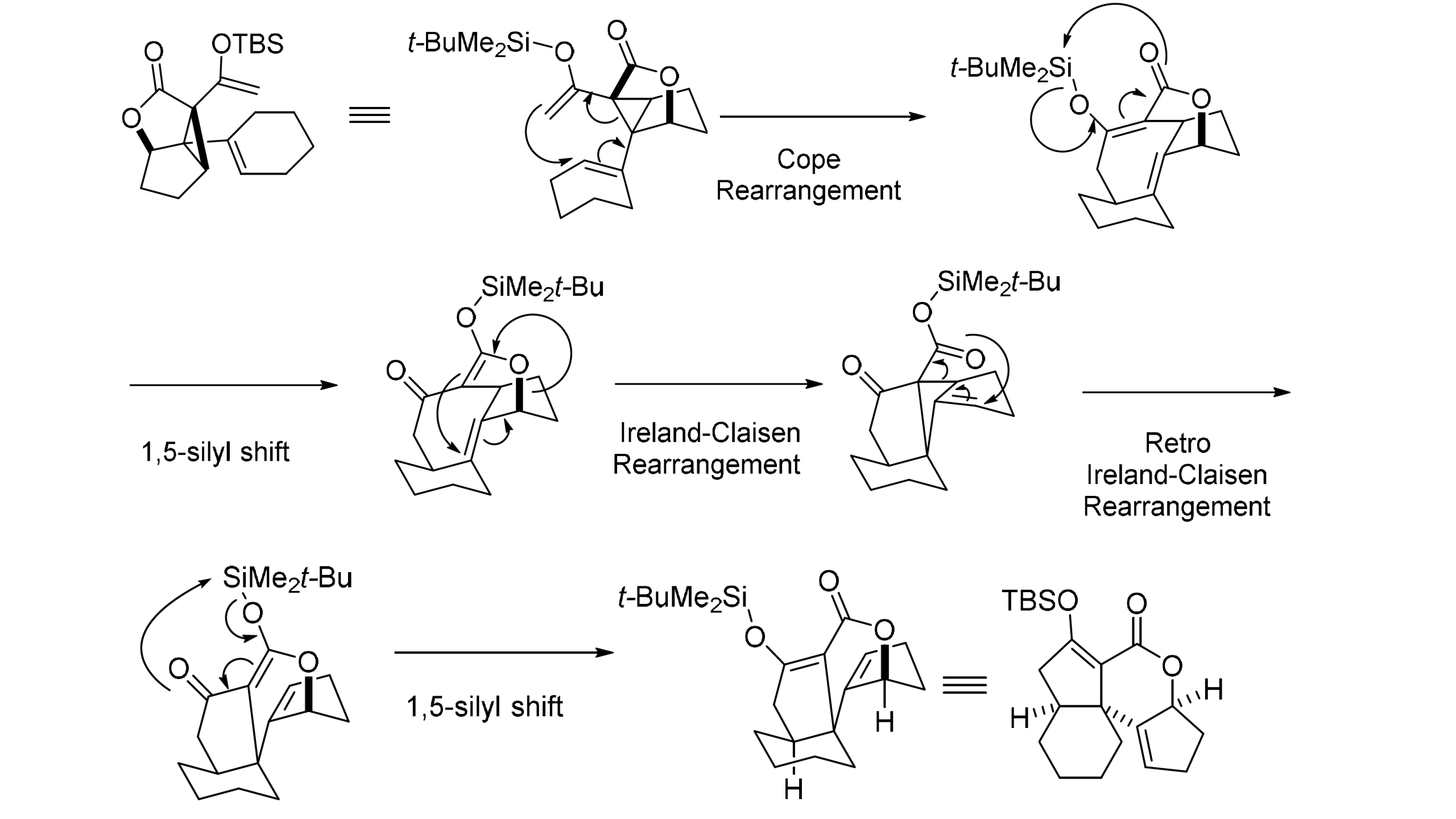
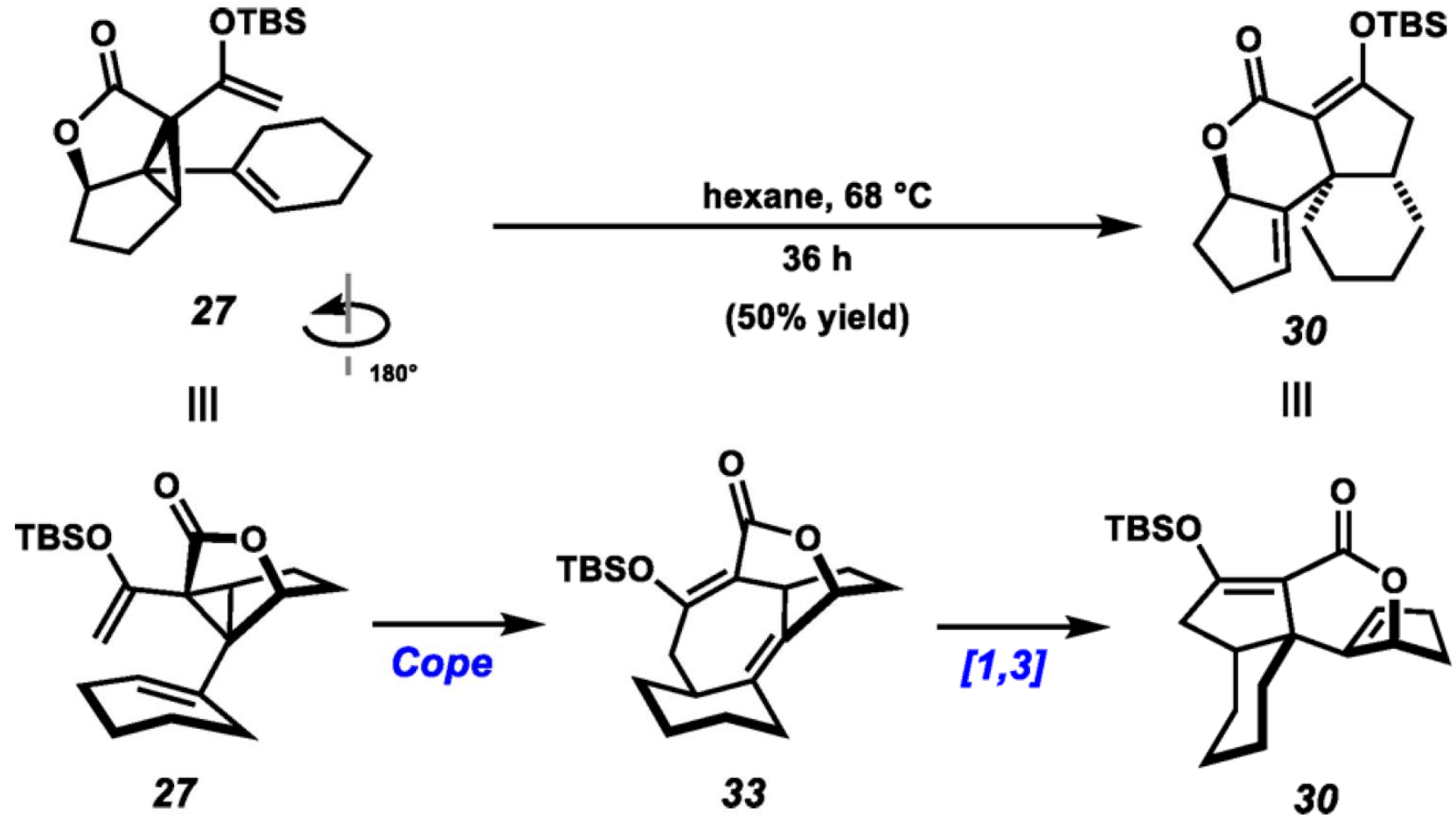
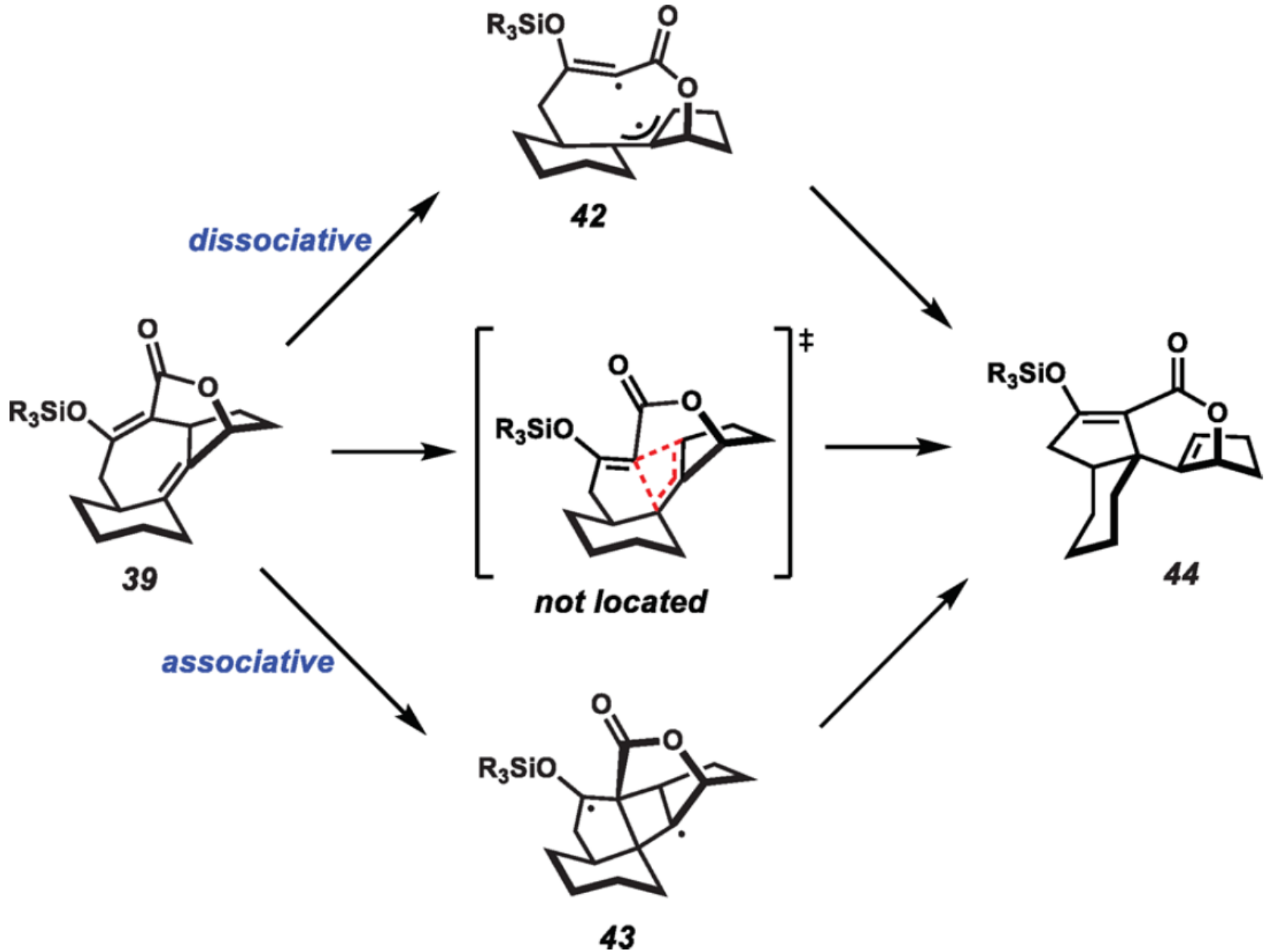

OTBS
t-BuMe2Si
Cope
Rearrangement
1,5-silyl shift
SiMe2t-Bu
Ireland-Claisen
Rearrangement
Retro
Ireland-Claisen
Rearrangement
1,5-silyl shift
TBSO
H

Mechanistic Hypothesis



Scheme 9. Possible Mechanisms for Formal 1,3-Shift



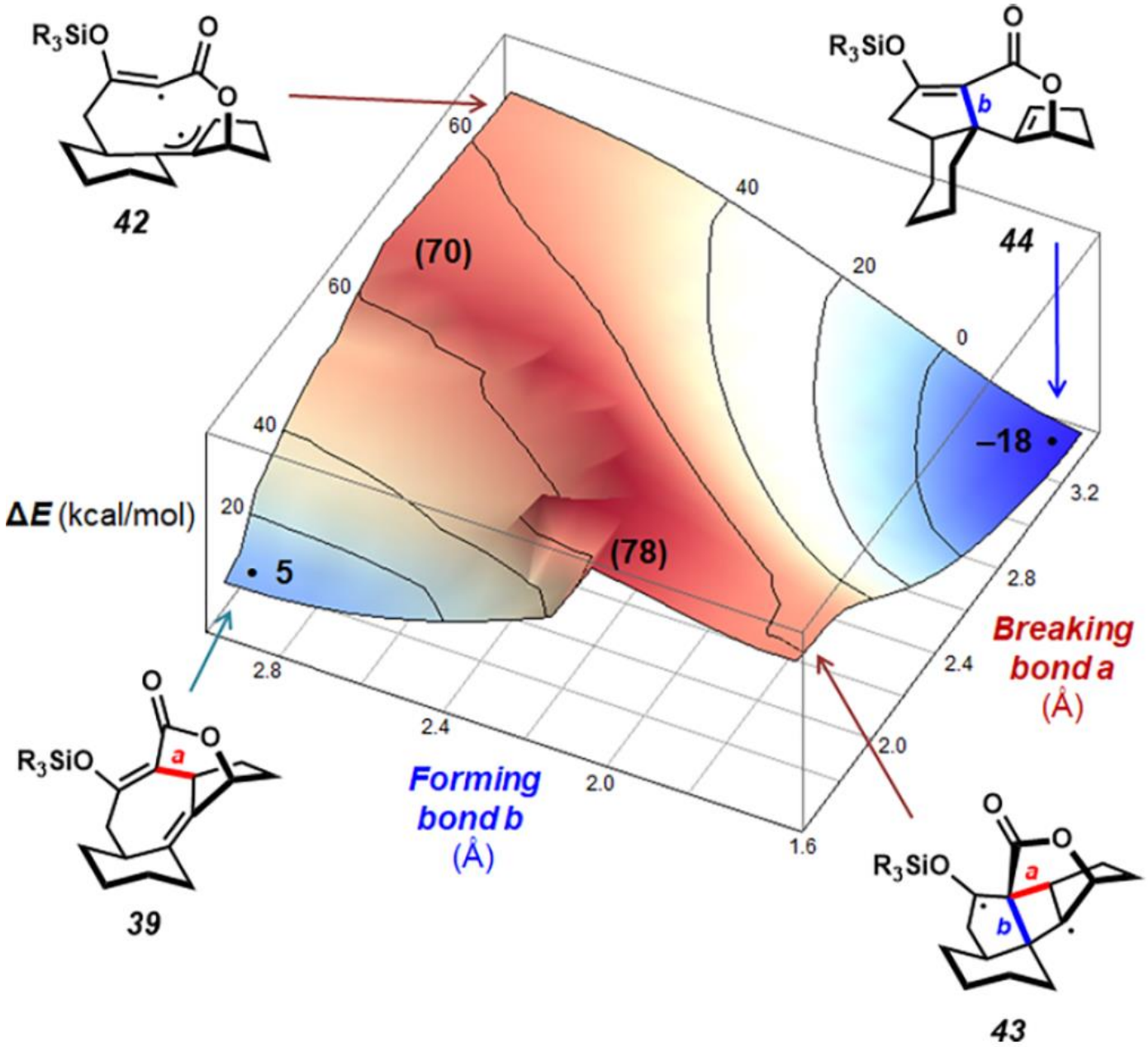
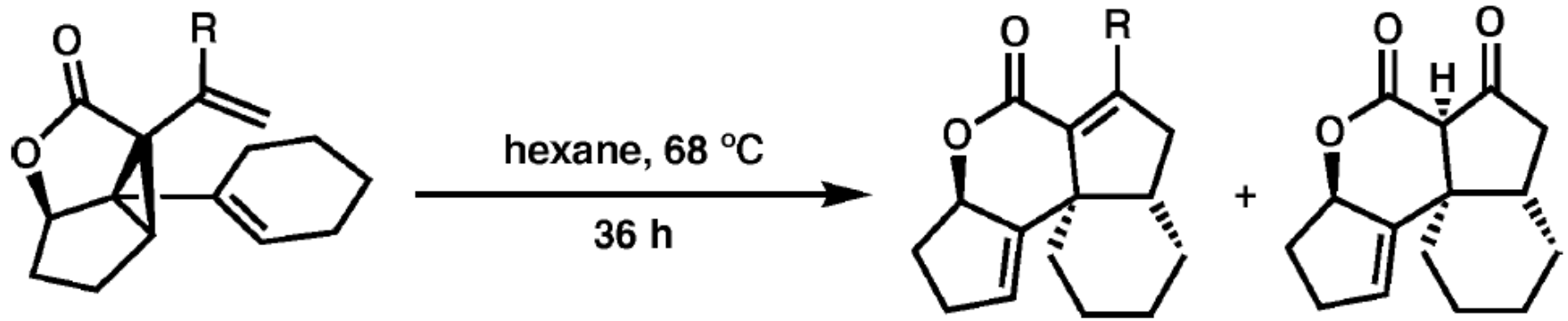


Figure 5. Potential energy surface directly connecting intermediates **39** and **44** calculated using UB3LYP/6-31G(d).

Table 1. Rearrangement of Enol Ethers



entry	R	yield (%)	
1	OTES		57
2	OTBS	50	trace
3	OTIPS	39	
4	Me	not observed	

Figure 7. Formation and ring-opening of alkylidene cyclobutane **48**.

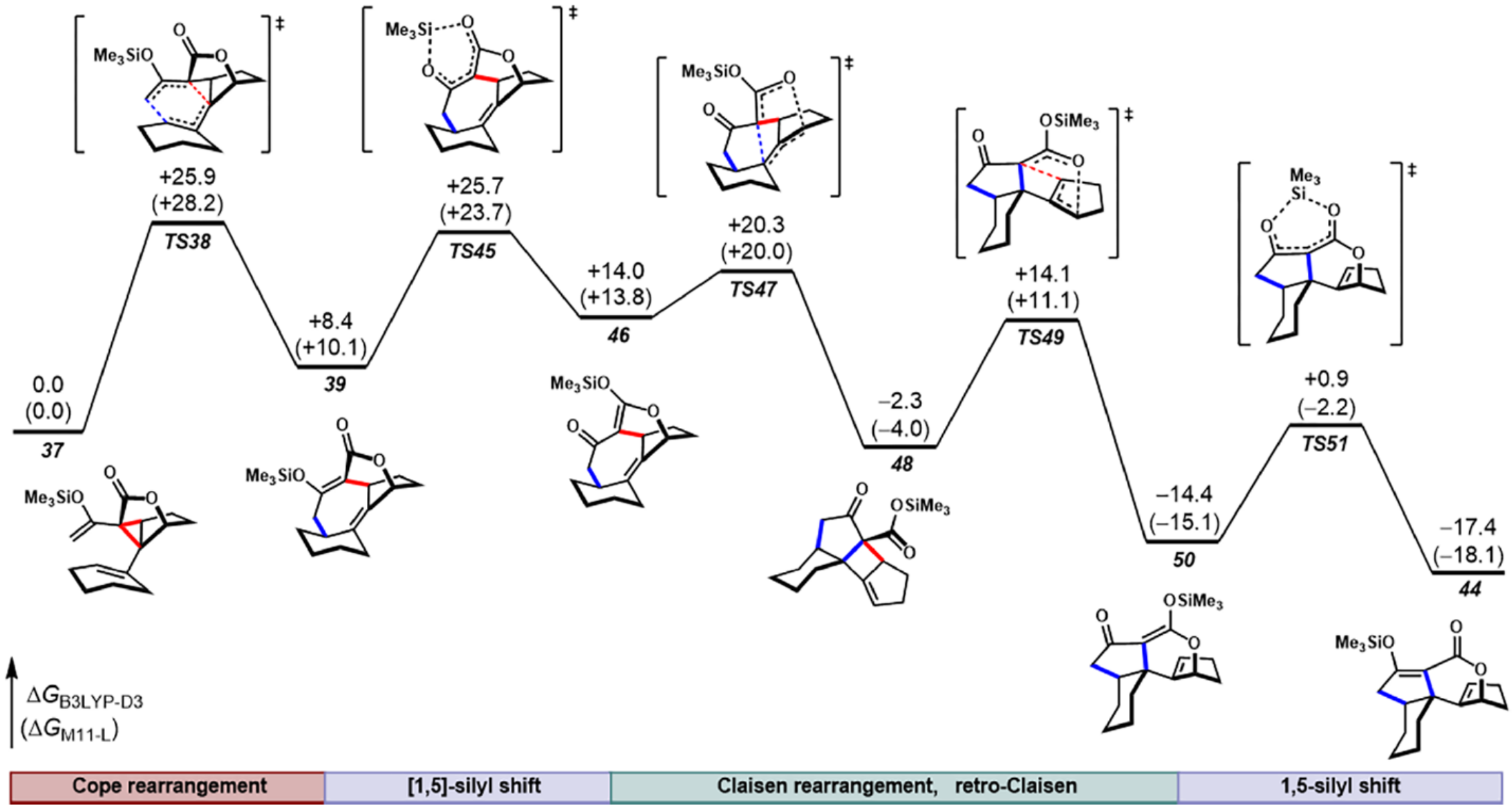
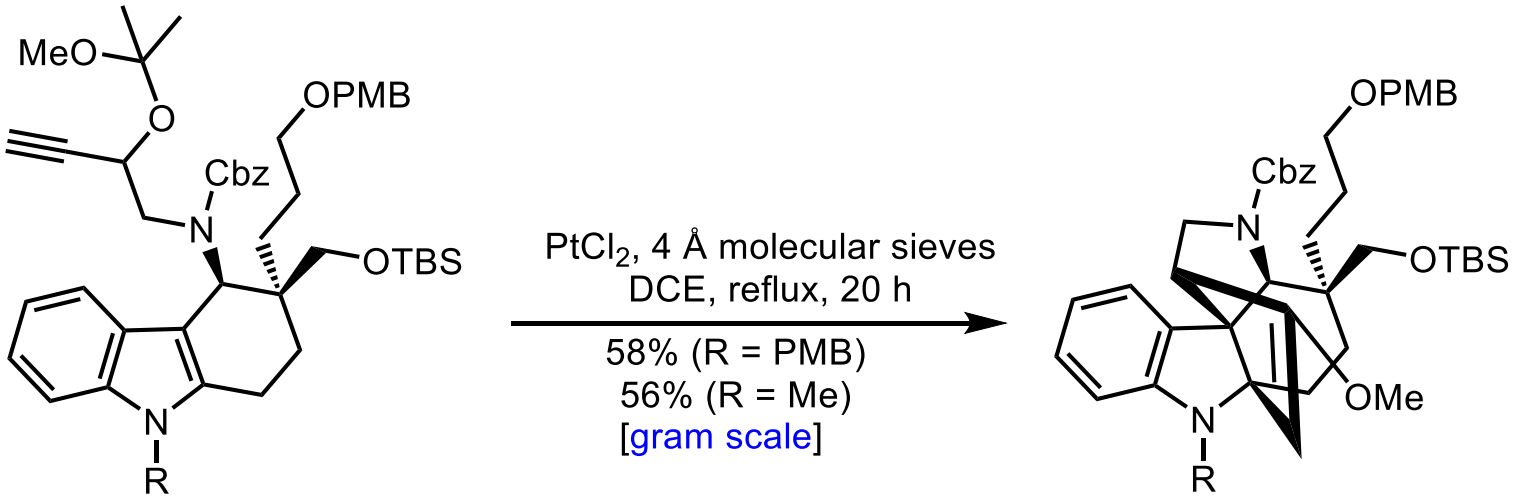


Figure 8. Free-energy profile for formation of **44** by a [1,5]-silyl shift/Claisen/retro-Claisen rearrangement cascade.

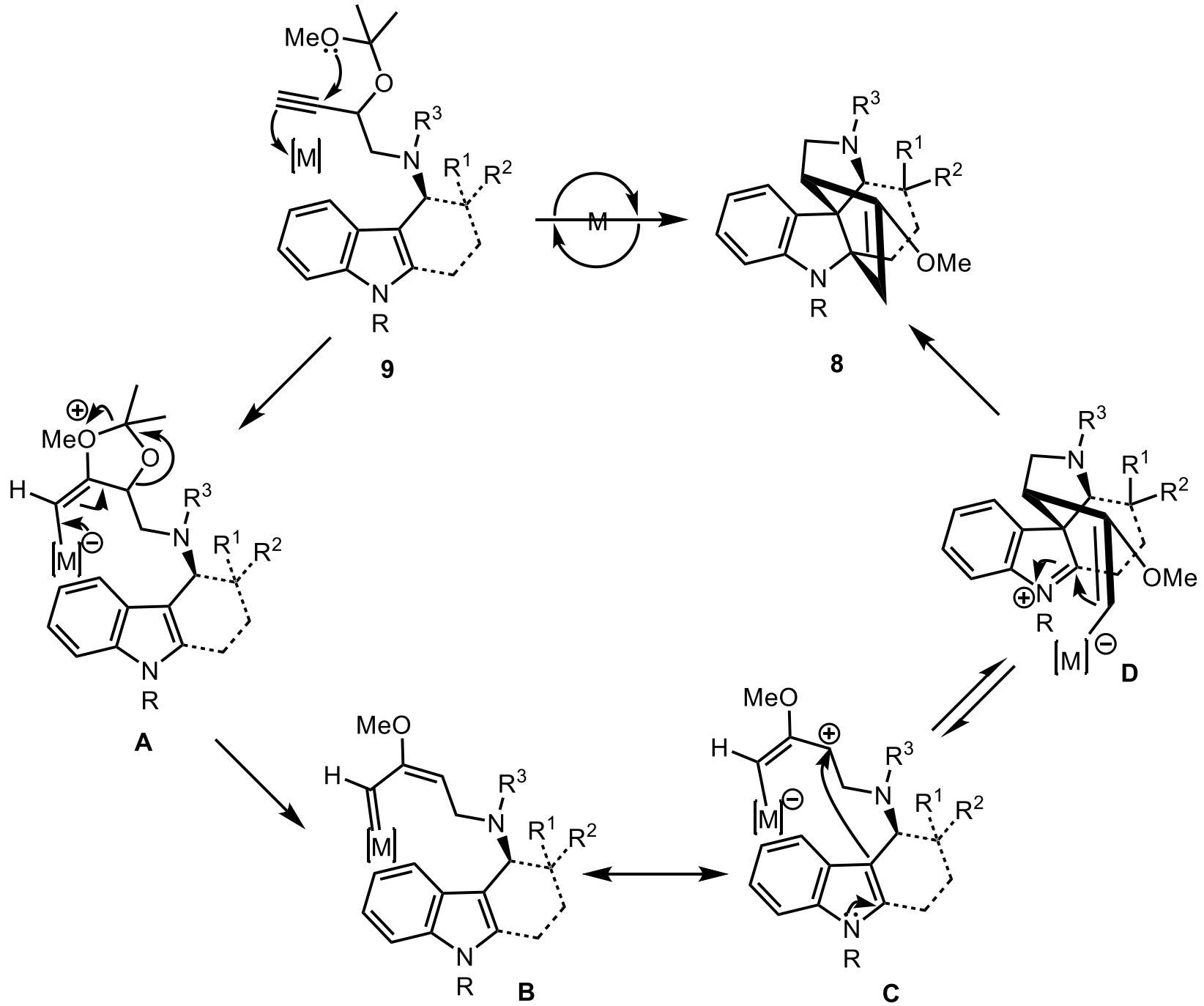
4.



9a: R = PMB
9b: R = Me

8a: R = PMB
8b: R = Me

DOI: 10.1002/anie.202005048.


MeO
O
R3
[M]
N
R1
R2
R
9
M
8
OMe
A
B
C
D