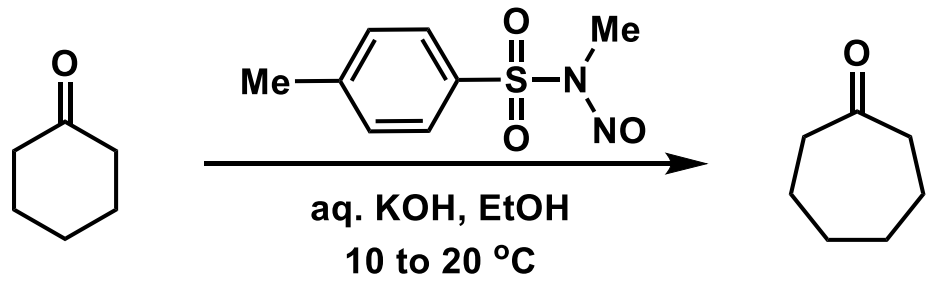
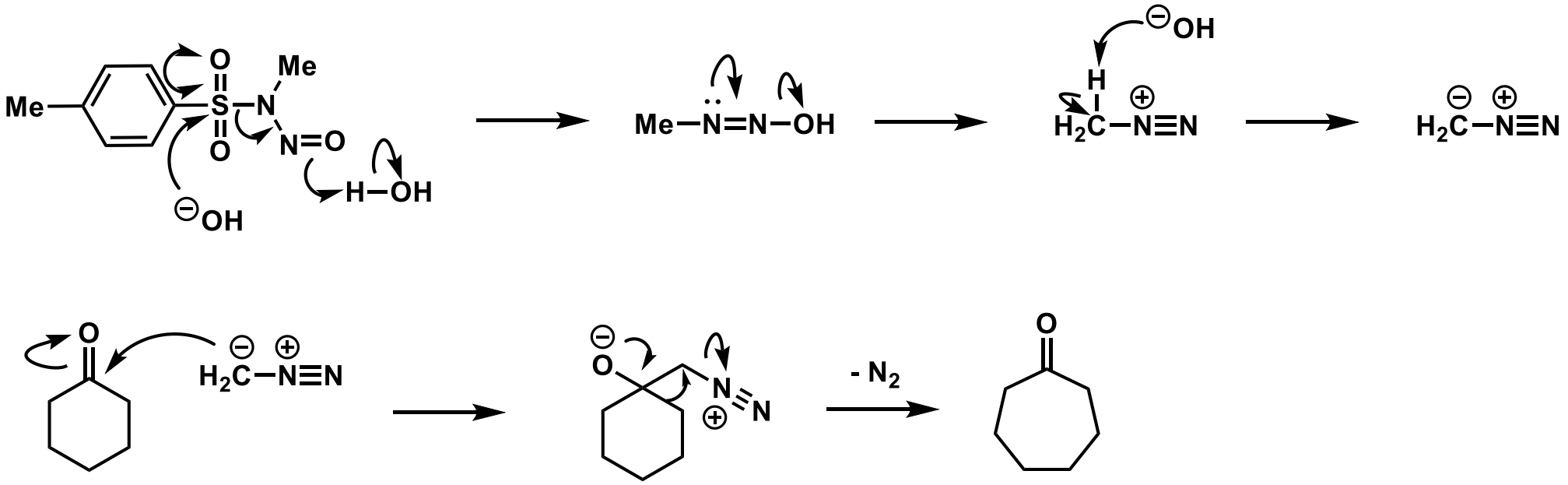
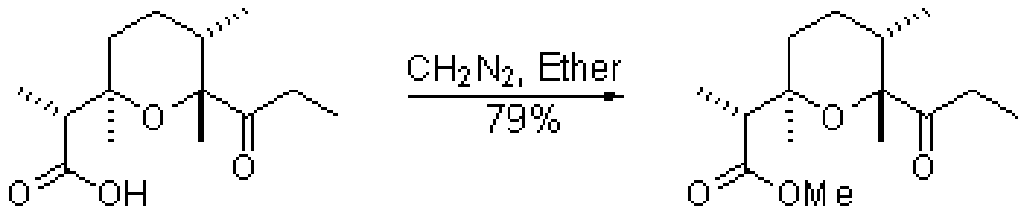
1.




Me
O
S
N
Me
N=O
O
H–OH
OH
Me–N=N–OH
OH
H
H2C–N≡N
H2C–N≡N
O
H2C–N≡N
O
N≡N
- N2
O

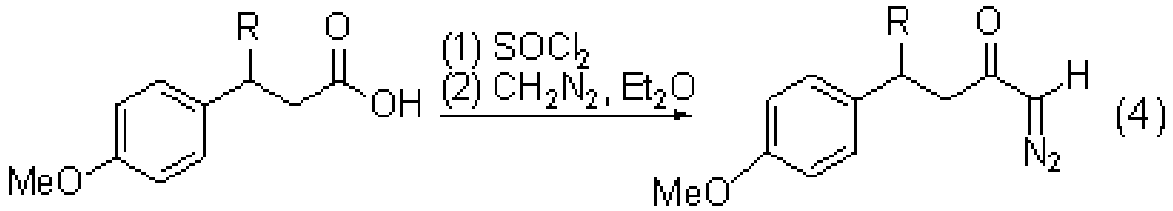
重氮甲烷:常用于羧酸、醇、酚以及酰胺等的甲基化;也可用于合成重氮酮或环丙烷类衍生物。

杂原子的甲基化 羧酸提供质子使重氮甲烷的亚甲基质子化，然后发生类似S_N2的反应而生成羧酸酯 。

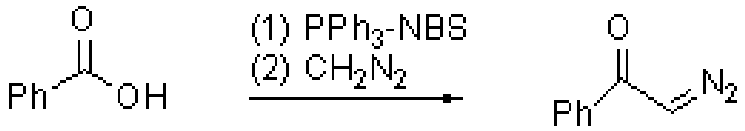


(1)

α-重氮酮的合成 与酰卤试剂作用可生成α-重氮酮。



(4)

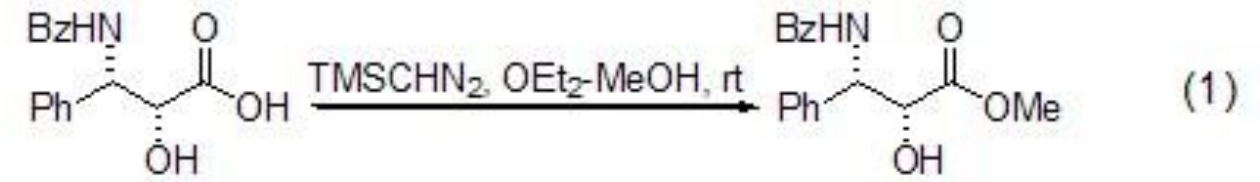


(5)

加成反应 与酮发生加成反应，生成扩环产物。

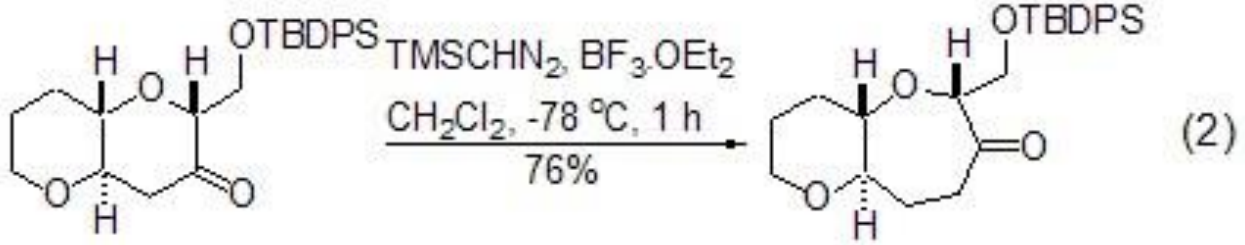
三甲基硅烷化重氮甲烷($TMSCHN_2$)，制备和储存相对比较安全，许多时候可以代替重氮甲烷。

$TMSCHN_2$使用频率最高的功能是与羧酸反应生成羧酸酯。



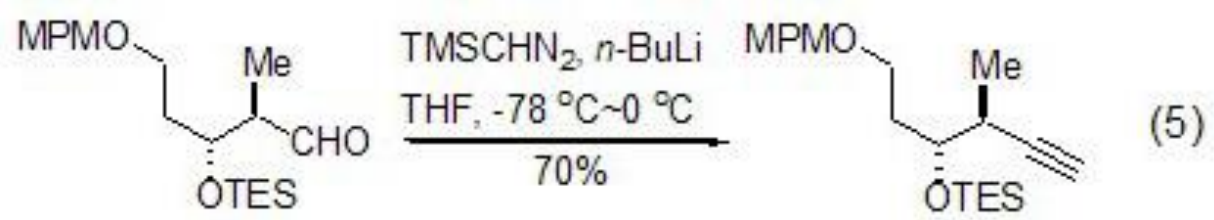
(1)

$TMSCHN_2$也可以发生像重氮甲烷一样的重排反应，与酰氯反应得到多一节碳原子的羧酸衍生物，或者与酮反应得到多一节碳原子的同系物。



(2)

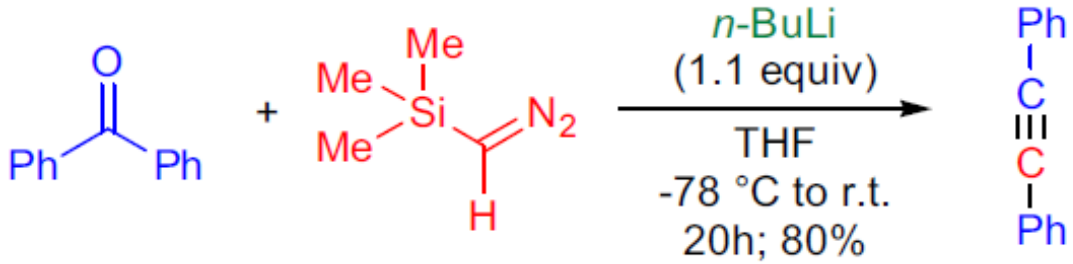
与醛发生Colvin重排反应生成炔烃。Seyferth-Gilbert增碳反应（P402）



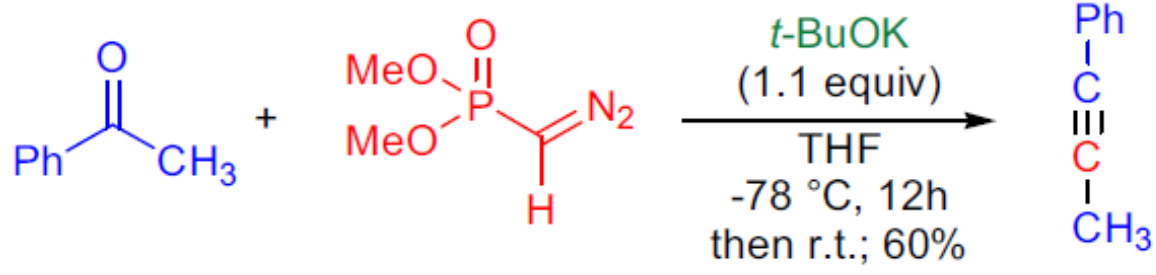
(5)

Seyferth-Gilbert homologation

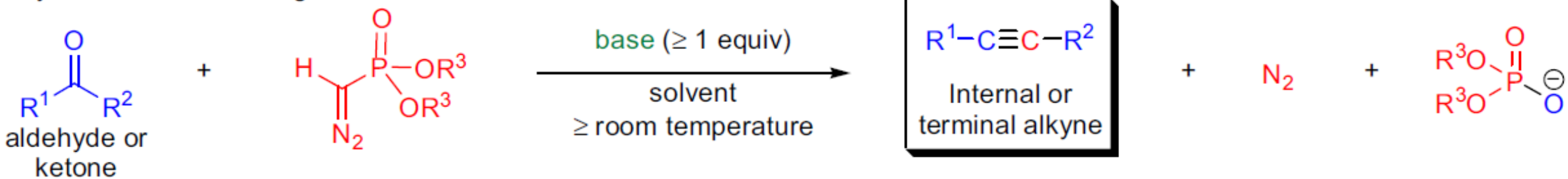
Colvin & Hamill (1973):



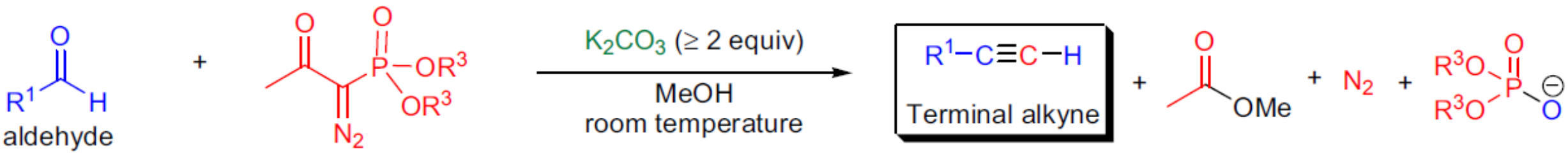
Gilbert & Weerasooriya (1979):



Seyferth-Gilbert homologation:

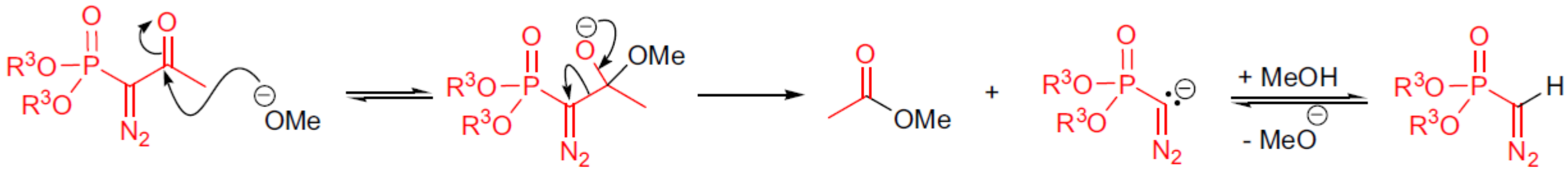


Modification for the synthesis of terminal alkynes (Ohira & Bestmann):

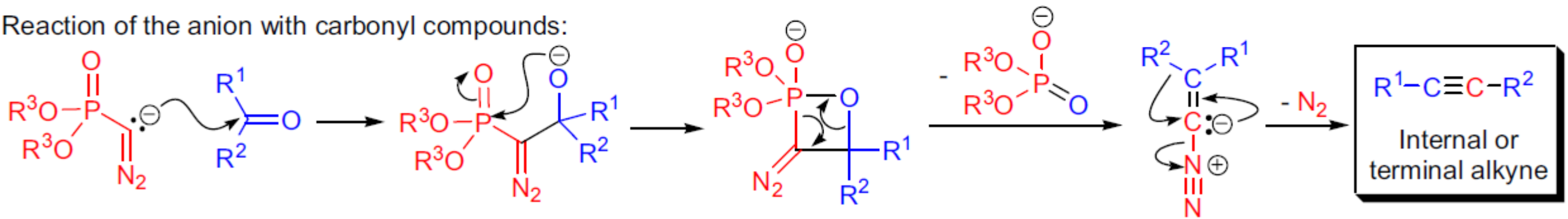


R^1 = alkyl, aryl, heteroaryl; R^2 = H, aryl, heteroaryl; R^3 = Me, Et; base: *n*-BuLi, KO-*t*Bu

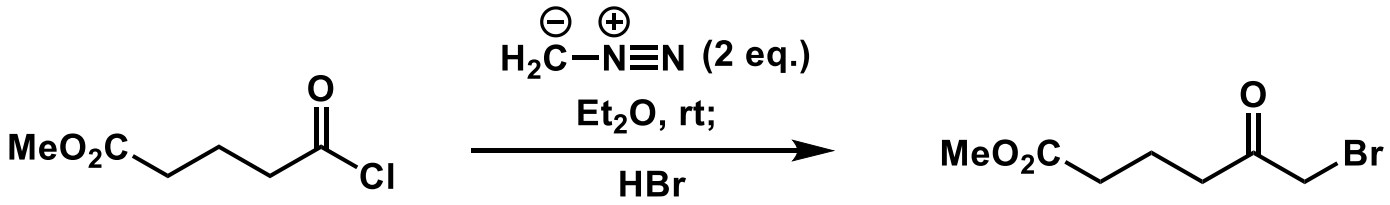
Formation of the dialkylphosphonodiazomethane from dialkyl-1-diazo-2-oxopropylphosphonate:

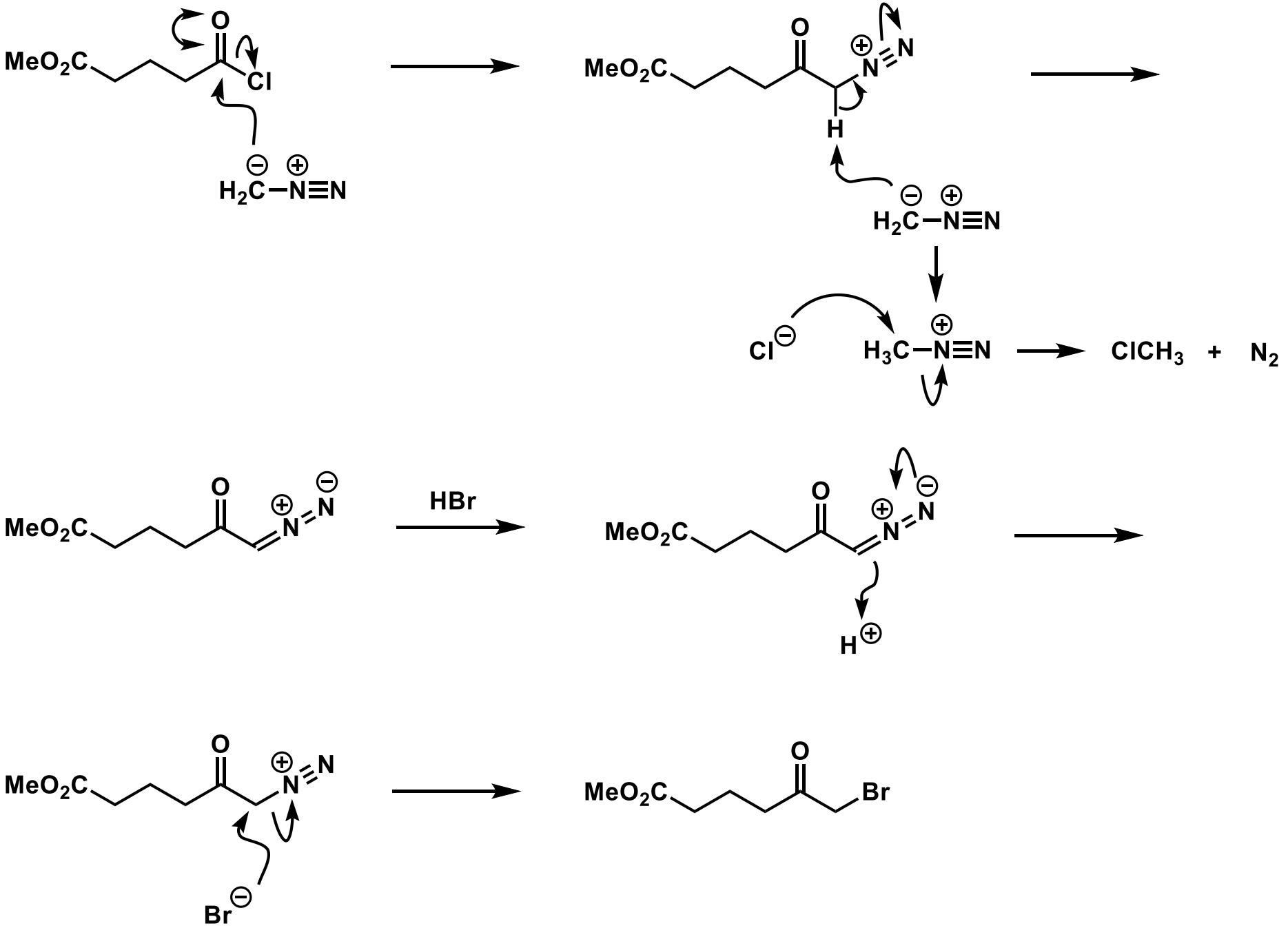


Reaction of the anion with carbonyl compounds:

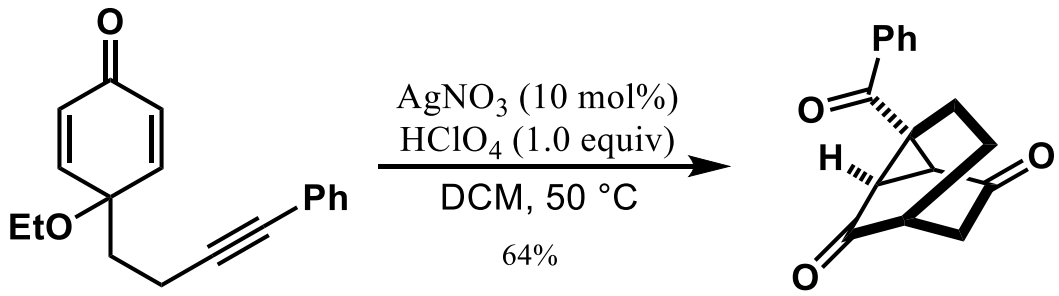


2.

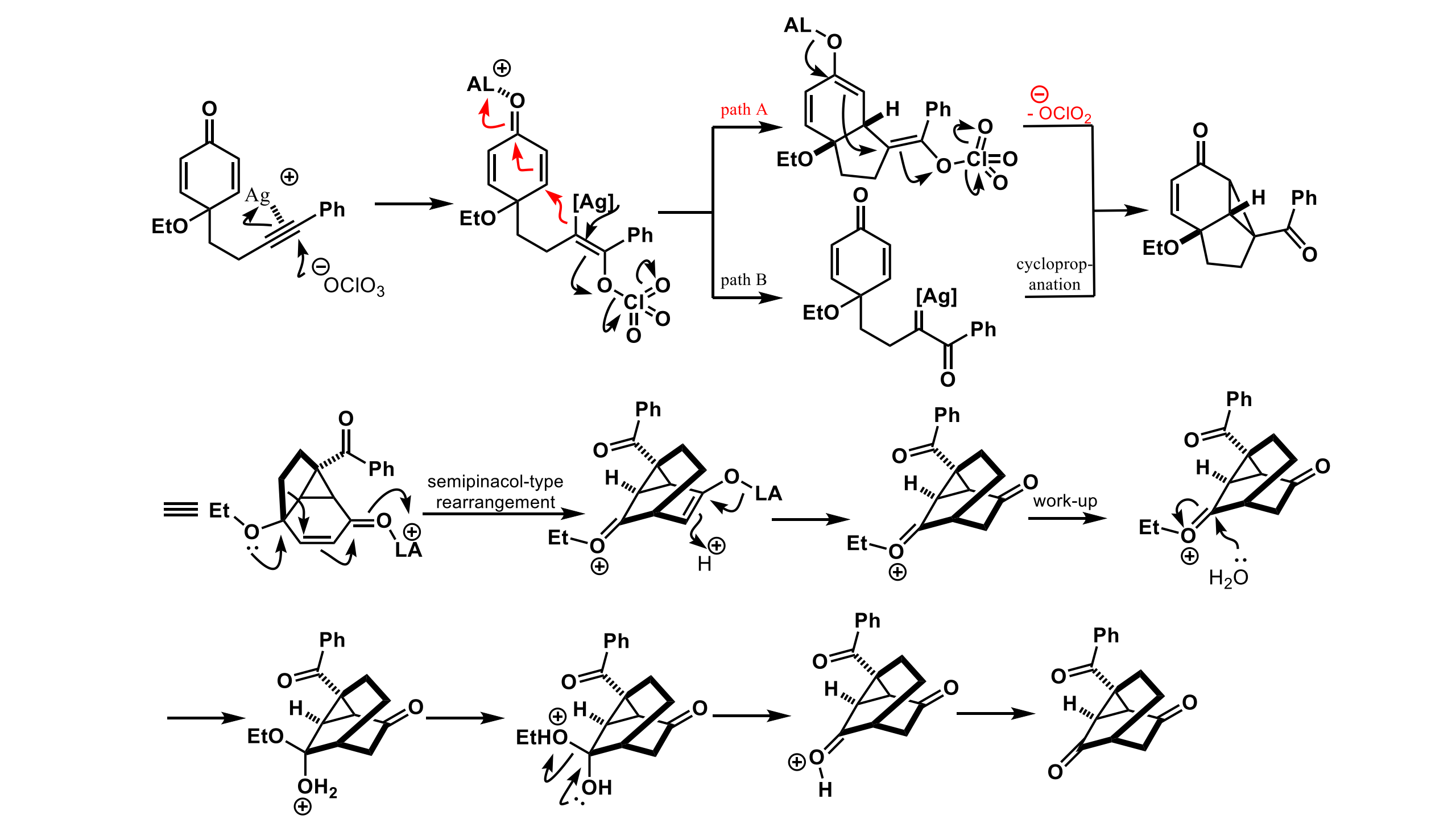



MeO2C
O
Cl
H2C–N≡N
MeO2C
O
N
H
H2C–N≡N
Cl
H3C–N≡N
ClCH3 + N2
MeO2C
O
N
HBr
MeO2C
O
N
H
MeO2C
O
N
Br
MeO2C
O
Br

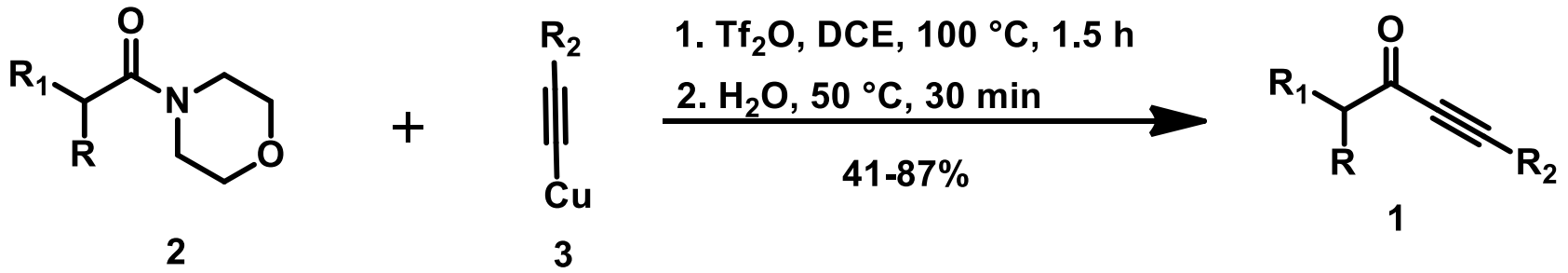
3.

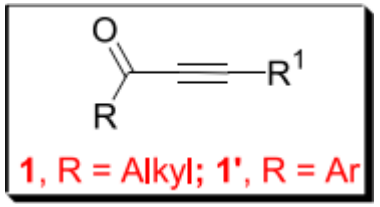


Org. Lett. 2020, **22**, 7019−7024


path A
path B
- OClO2
cyclopropanation
semipinacol-type rearrangement
work-up
H2O

4.

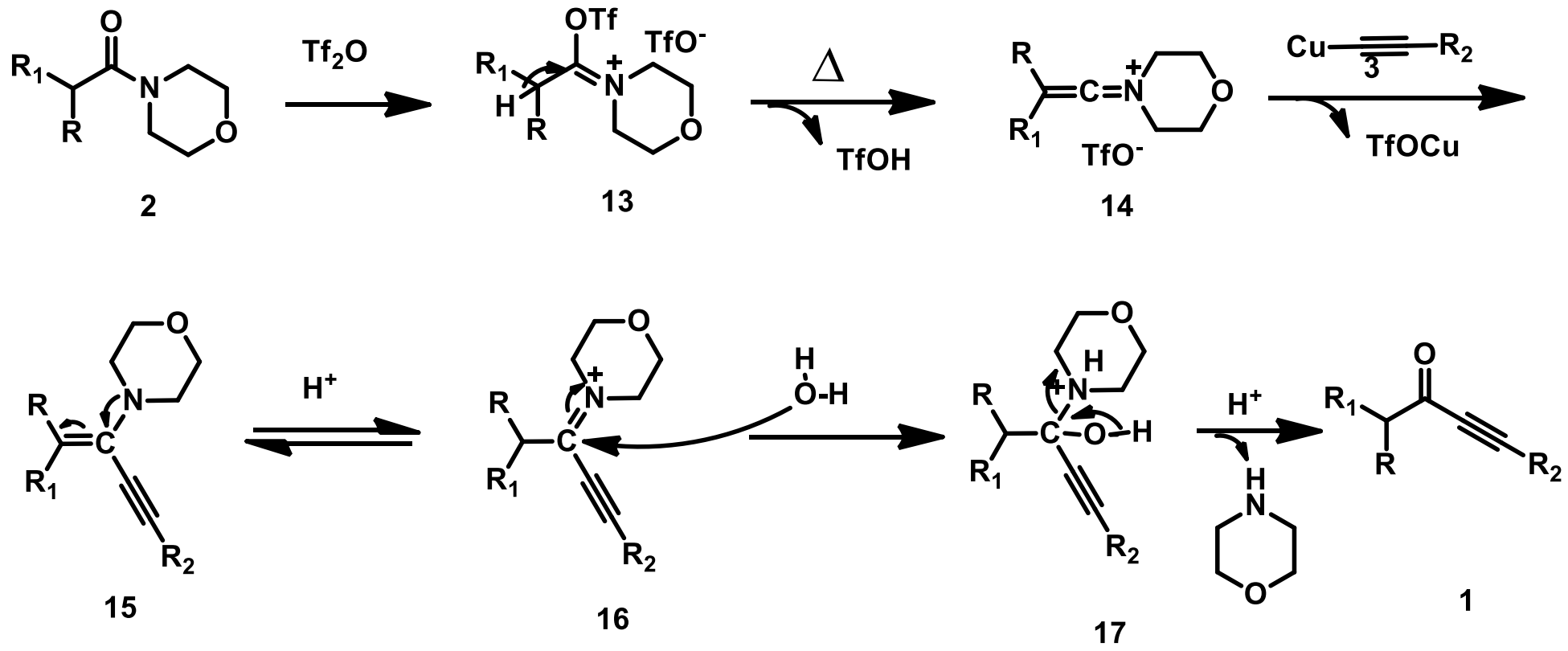




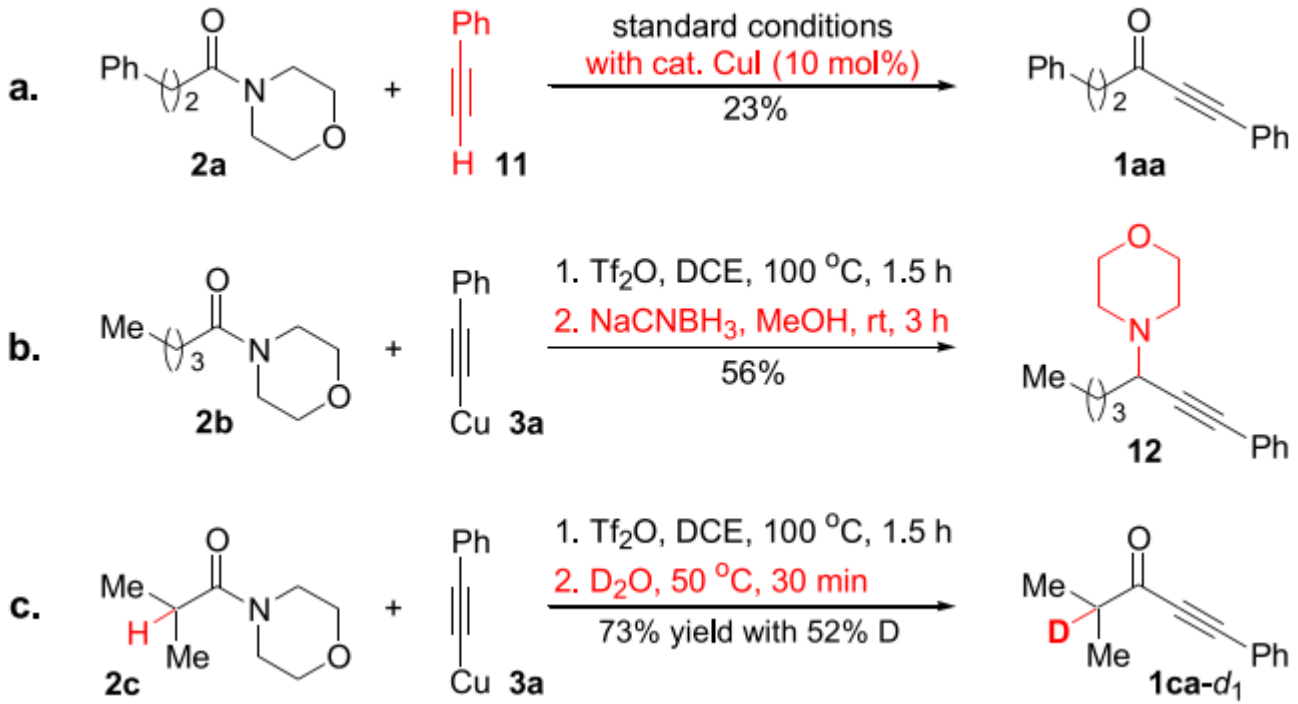
Since 1-copper(I) alkynes (3) are **air-stable solids** with **mild nucleophilicity**, this method can be conveniently operated to give functionalized α-alkyl ynones (1) **without any overaddition product.**

Tf2O has been recognized as the most practical activating agent to convert amides into highly reactive iminium or keteniminium salts.

doi.org/10.1021/acs.orglett.0c02944


R1
O
N
R
O
2
Tf2O
OTf
TfO-
R1
H
R
N
O
13
Δ
TfOH
R
C=N
O
R1
TfO-
14
Cu
R2
3
TfOCu
R
N
C
R1
R2
15
H+
O
R
N
C
R1
R2
16
H
O-H
H
O
R
N
C
O
H
R1
R2
17
H+
H
N
O
H+
O
R1
R
R2
1

Scheme 6. Group of Further Conditional Tests

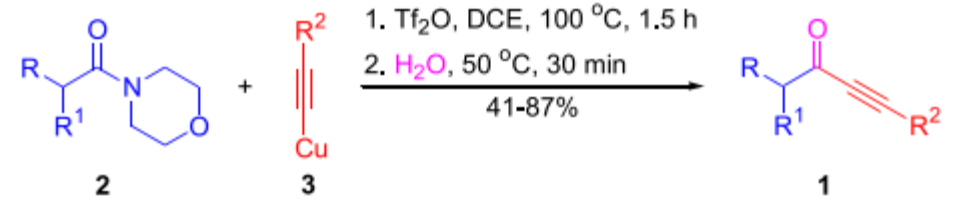


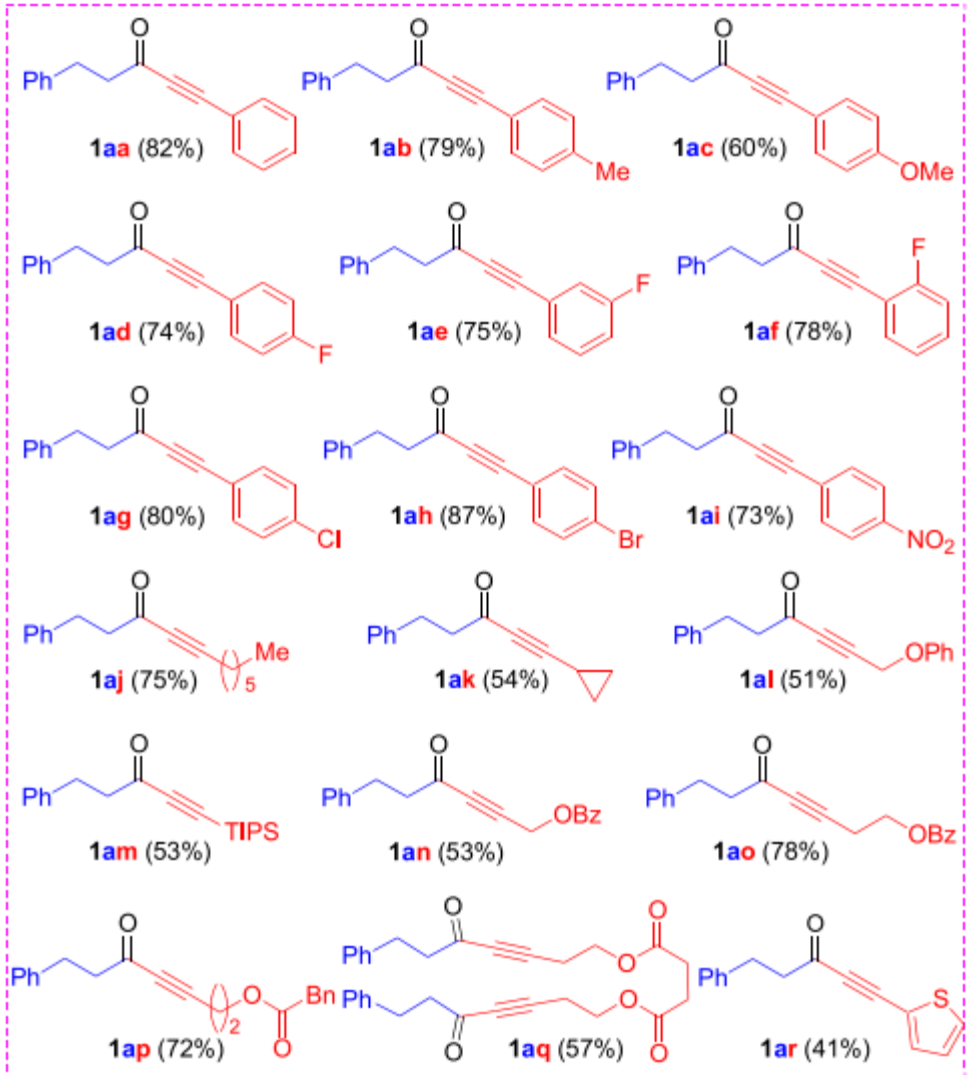
This result indicates that there is no efficient catalytic cycle of Cu(I) species in this method.

there is a corresponding imine intermediate in this method

This result suggests that the α-hydrogen in 2c participates in this method.

Scheme 5. Products Prepared by This Method





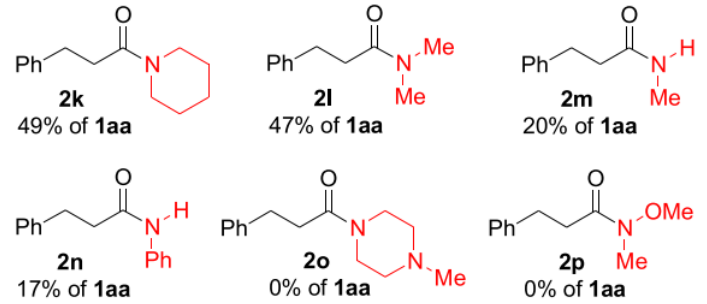
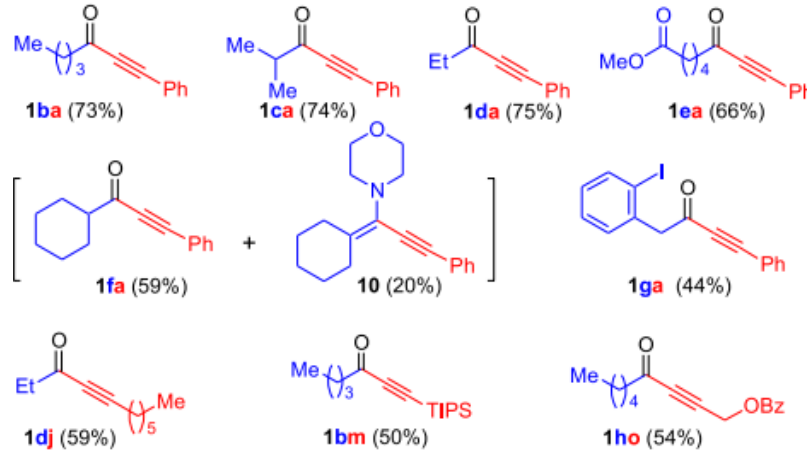


Figure 3. Unsuitable substrates for this method.



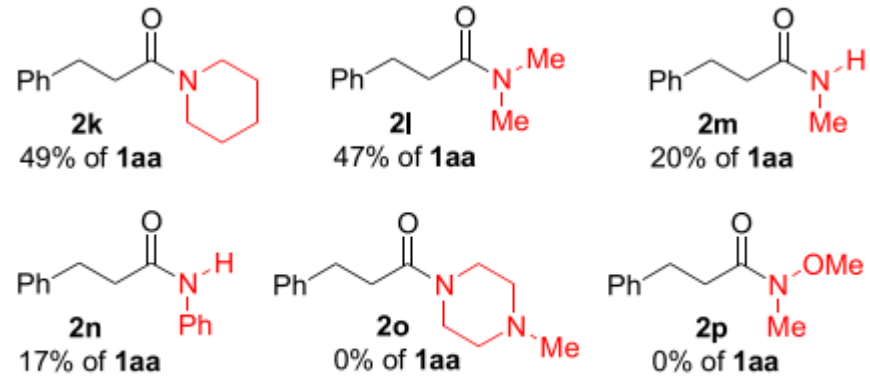


Figure 3. Unsuitable substrates for this method.