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Amide activation: an emerging tool for chemoselective synthesis

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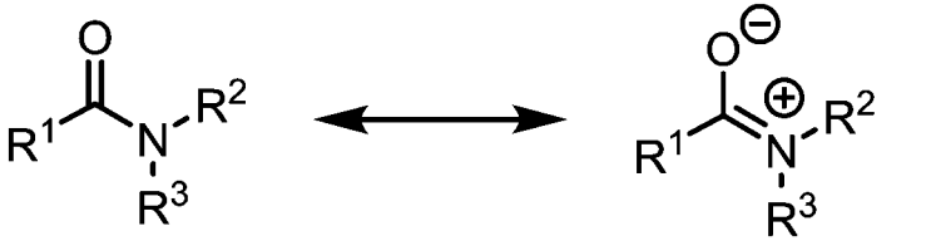
Table of Content



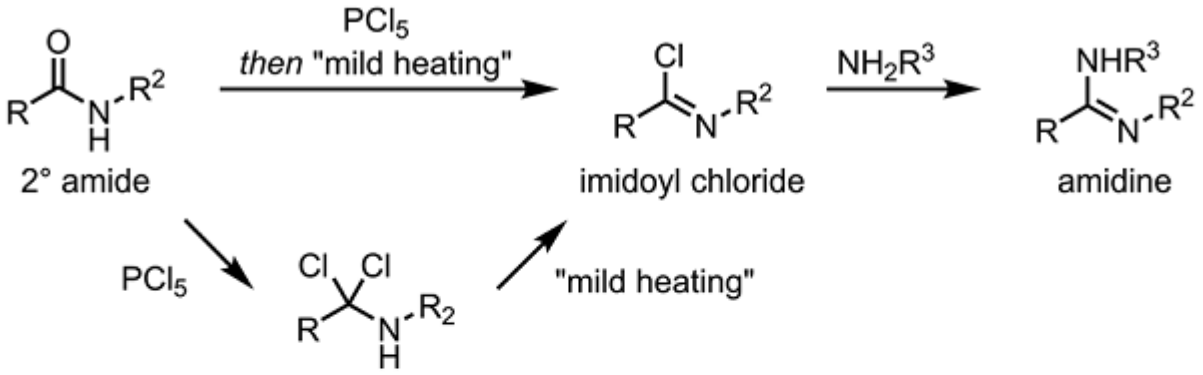
classical representation of an amide

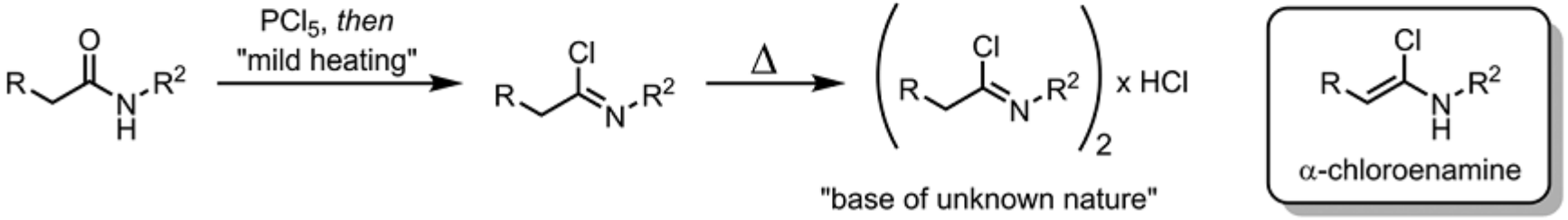
zwitterionic amide mesomer

1. Electrophilic activation of amides (2º, 3º)

1) Discovery of electrophilic activation of amides (2º, 3º)

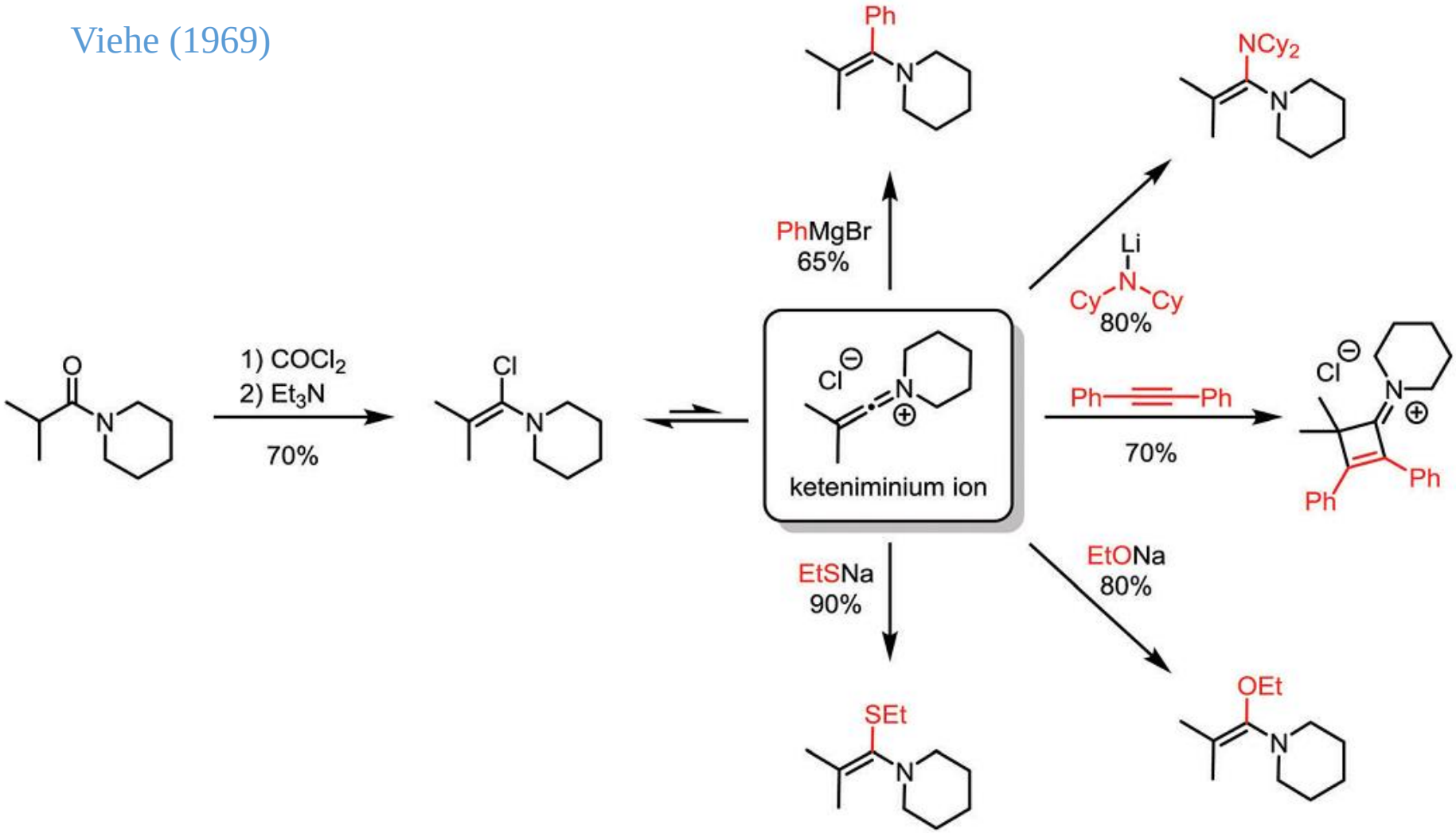
Wallach (1877)





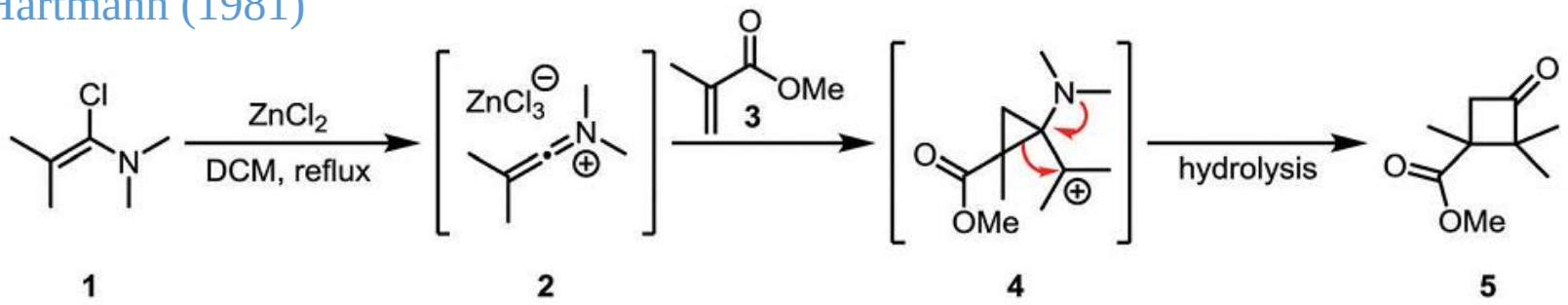
1) Discovery of electrophilic activation of amides (2º, 3º)

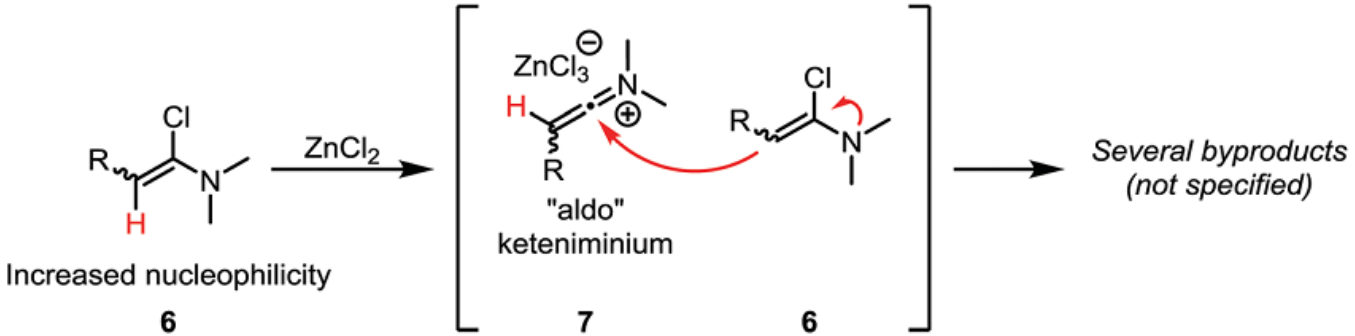
Viehe (1969)



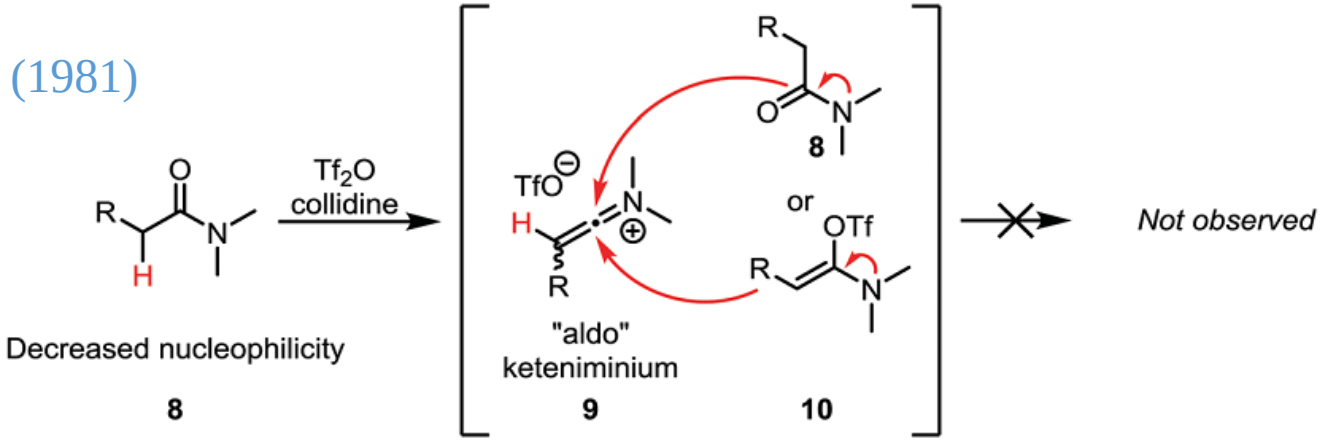
1) Discovery of electrophilic activation of amides (2º, 3º)

Hartmann (1981)



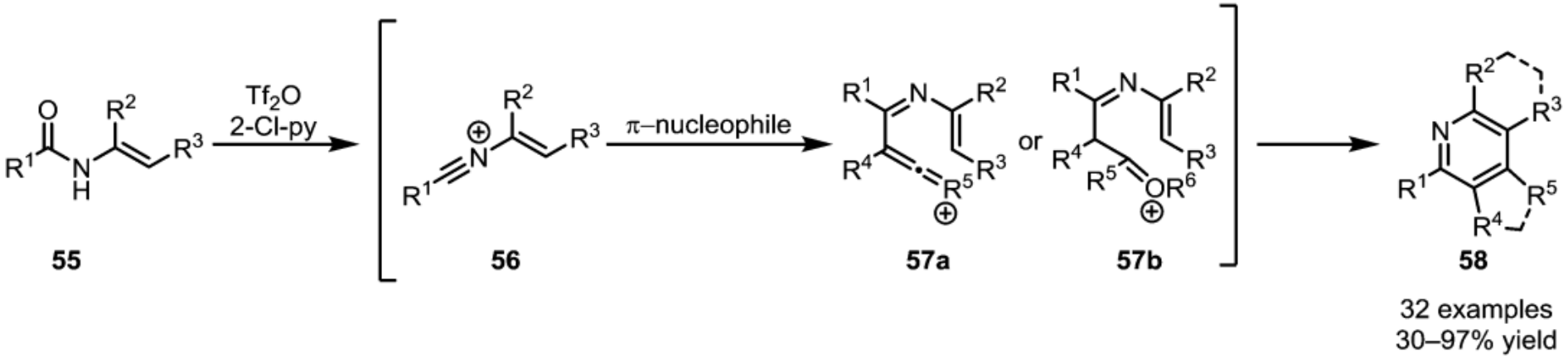


Ghosez (1981)

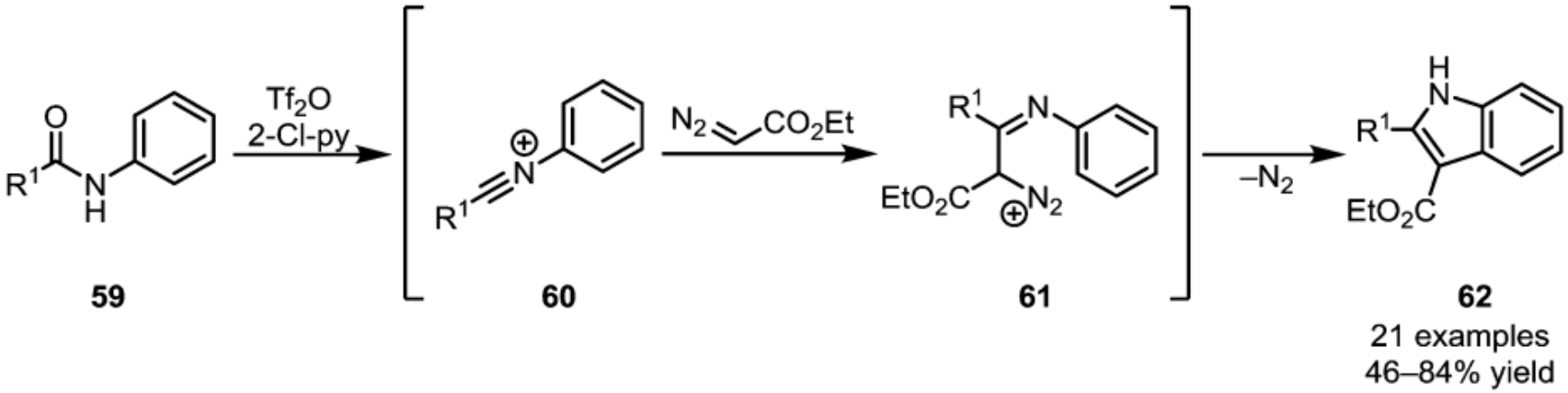


2) Applications of electrophilic activation of amides (2º)

Movassaghi (2007)

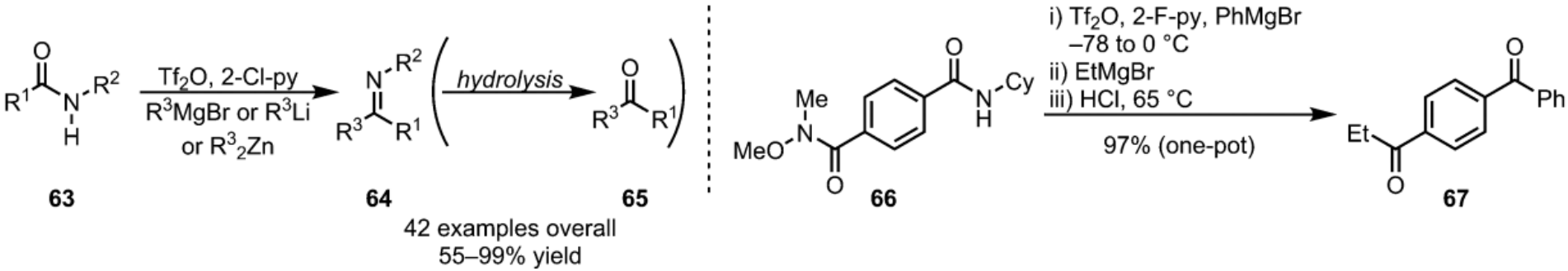


Wang (2008)

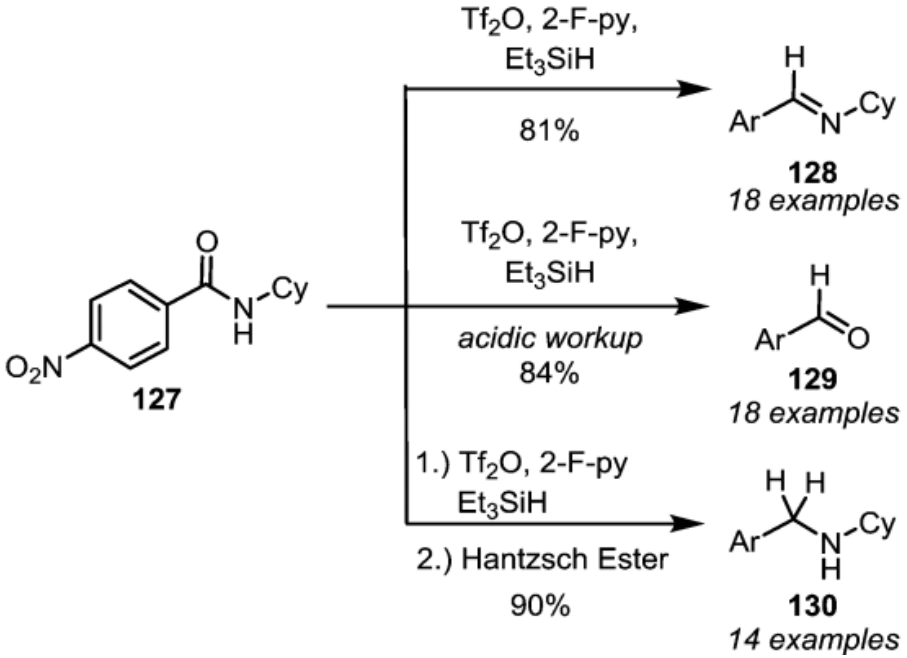


2) Applications of electrophilic activation of amides (2º)

Charette and Huang (2012)

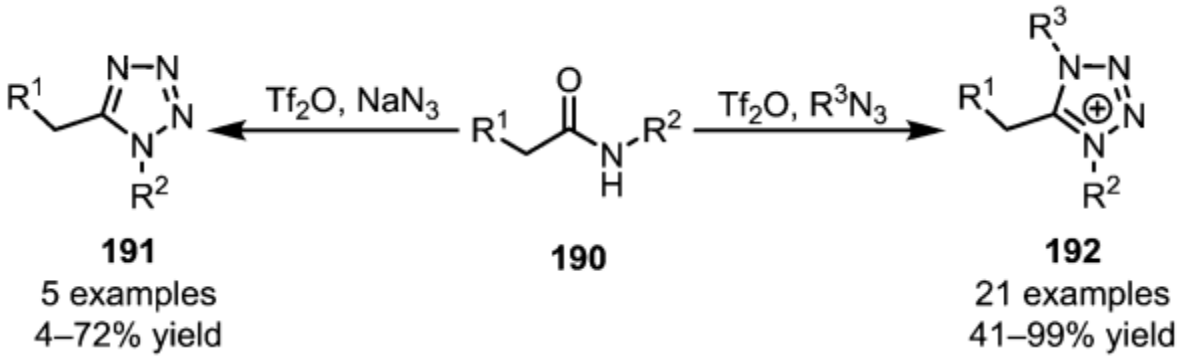


Charette (2010)



2) Applications of electrophilic activation of amides (2º)

Thomas (1993) Maulide (2017)



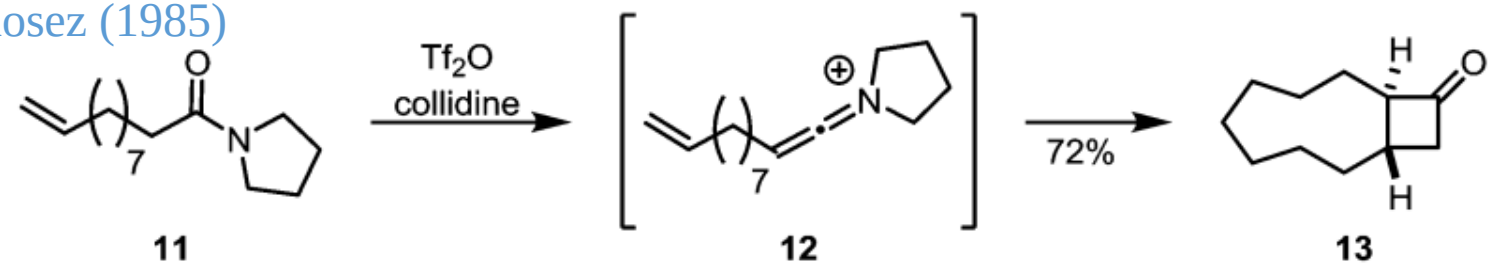
191
5 examples
4–72% yield

190

192
21 examples
41–99% yield

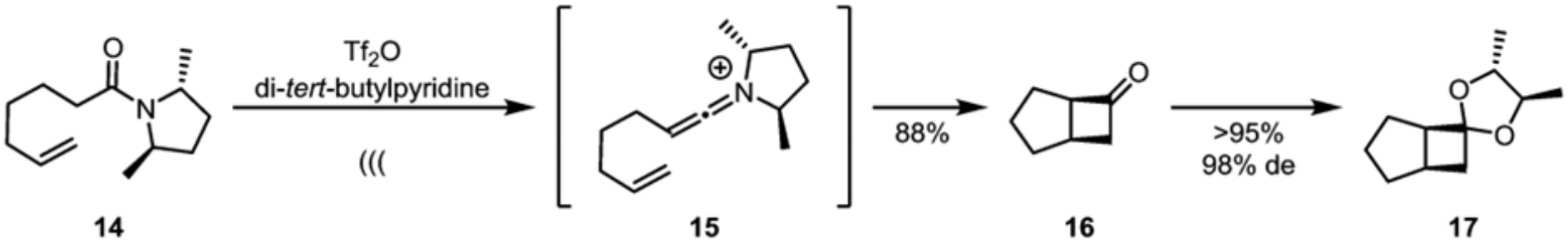
3) Applications of electrophilic activation of amides (3º)

Ghosez (1985)



Not accessible through ketene [2+2]
15 examples

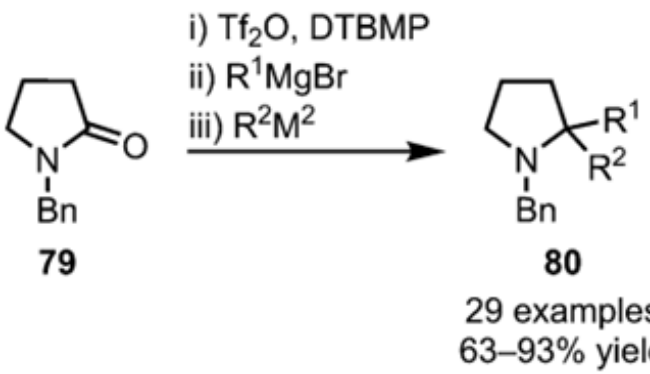
Ghosez (1990)



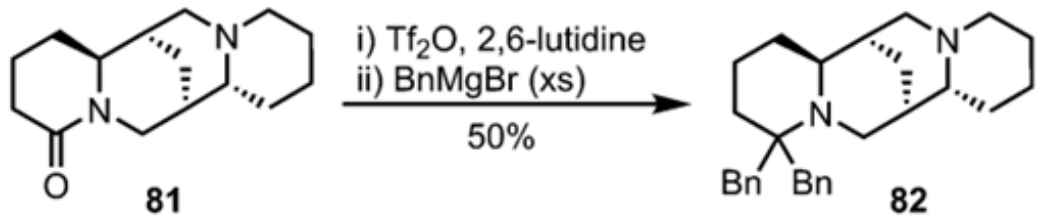
Ghosez (1999)

3) Applications of electrophilic activation of amides (3º)

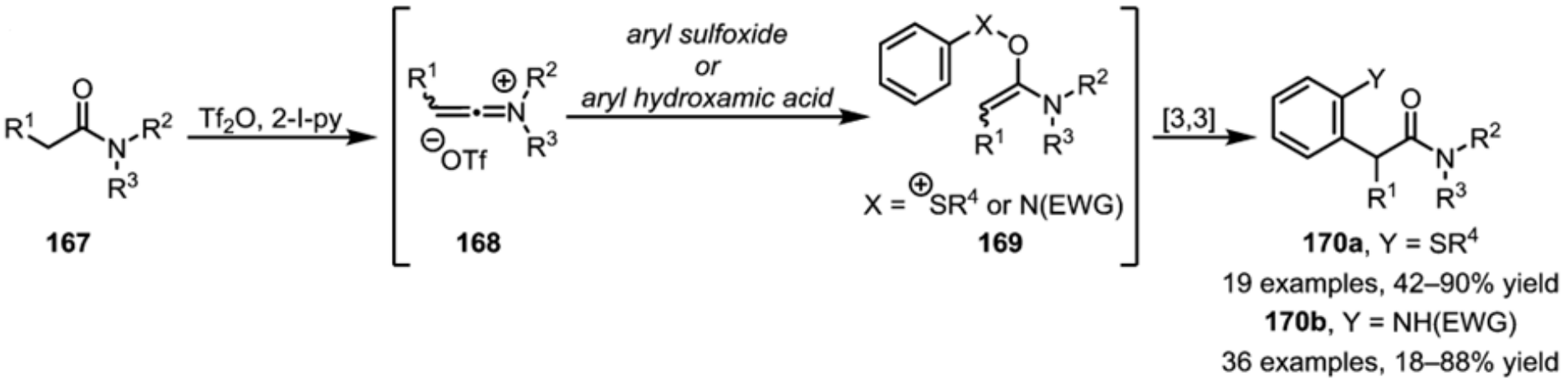
Huang (2010)



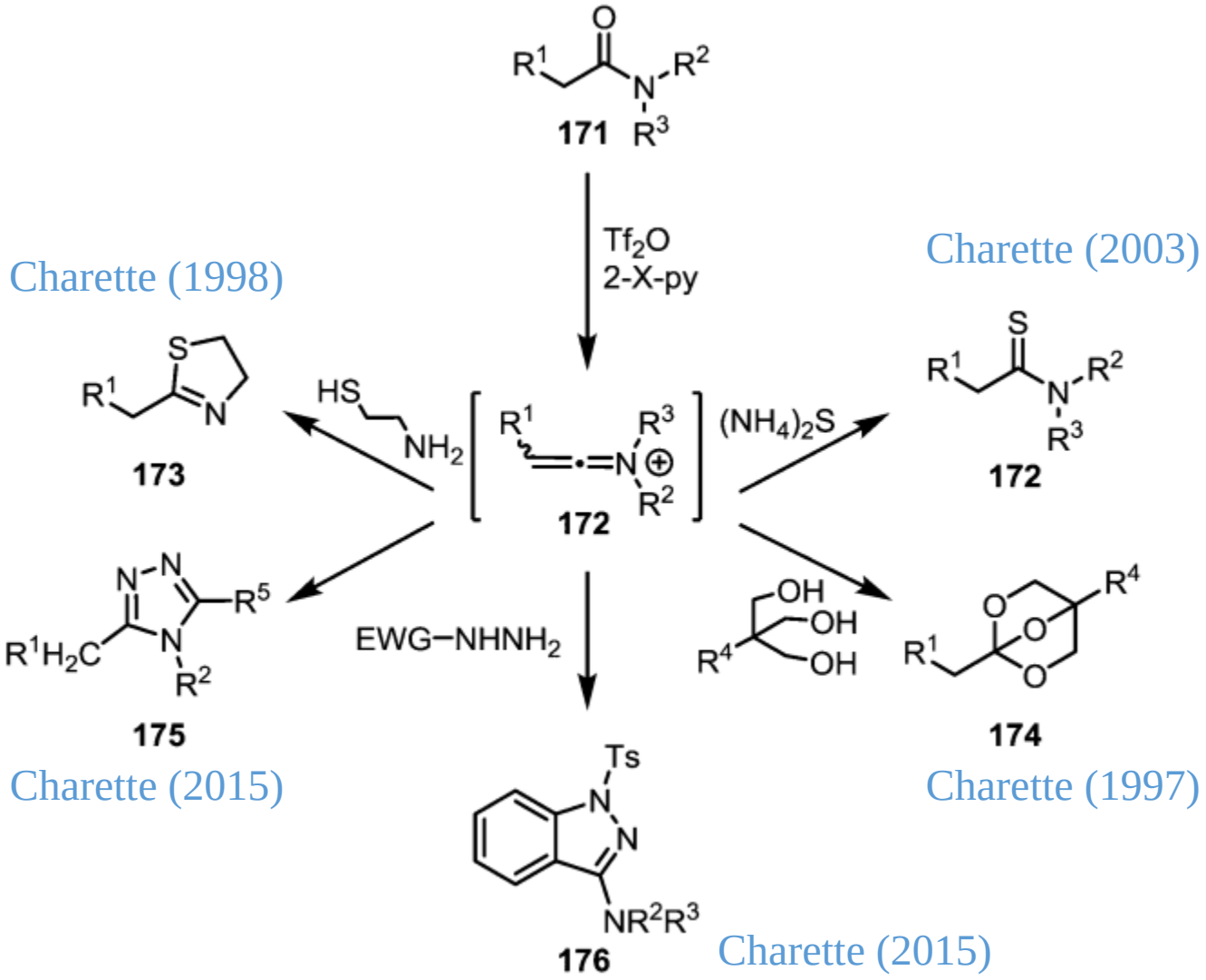
Todt & Maulide (2017)



Maulide (2014, 2017)

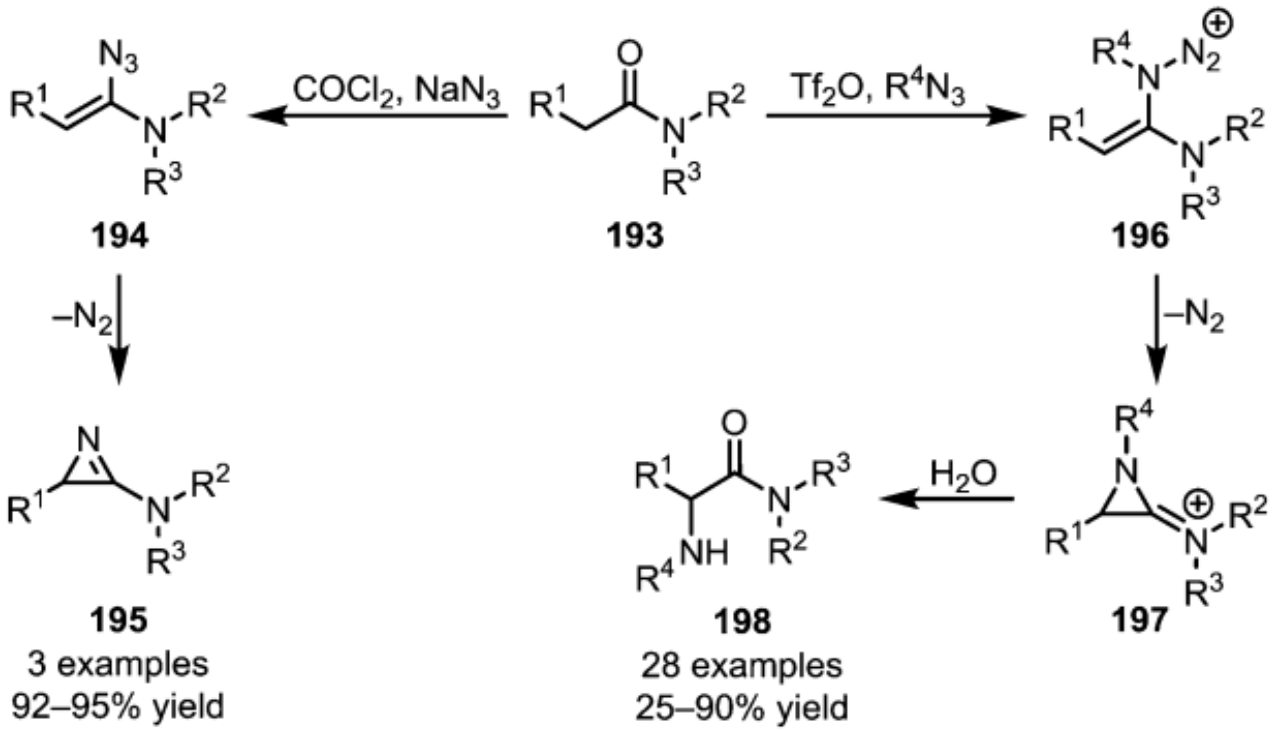


3) Applications of electrophilic activation of amides (3º)



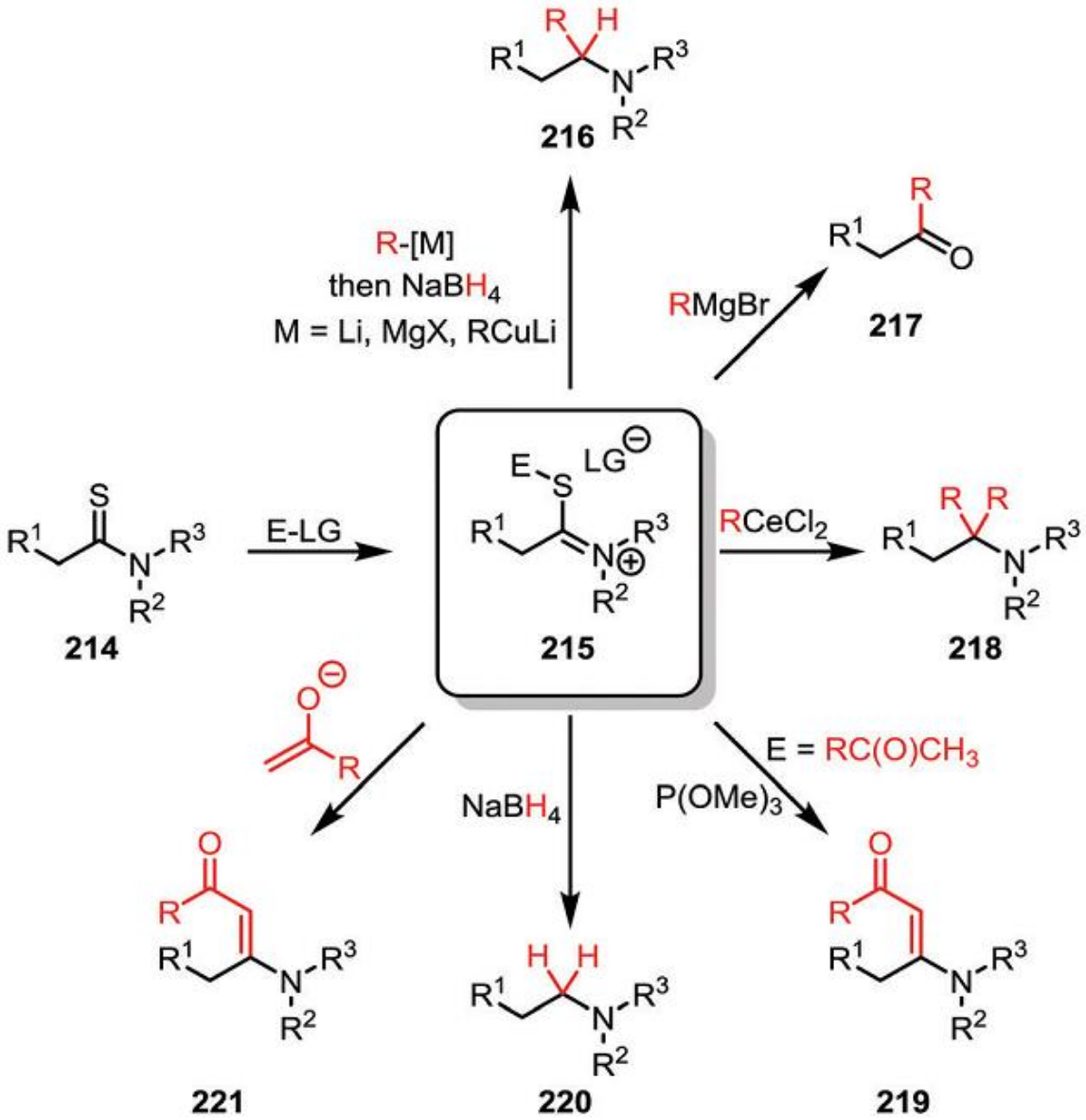
3) Applications of electrophilic activation of amides (3º)

Ghosez (1970) Maulide (2016)



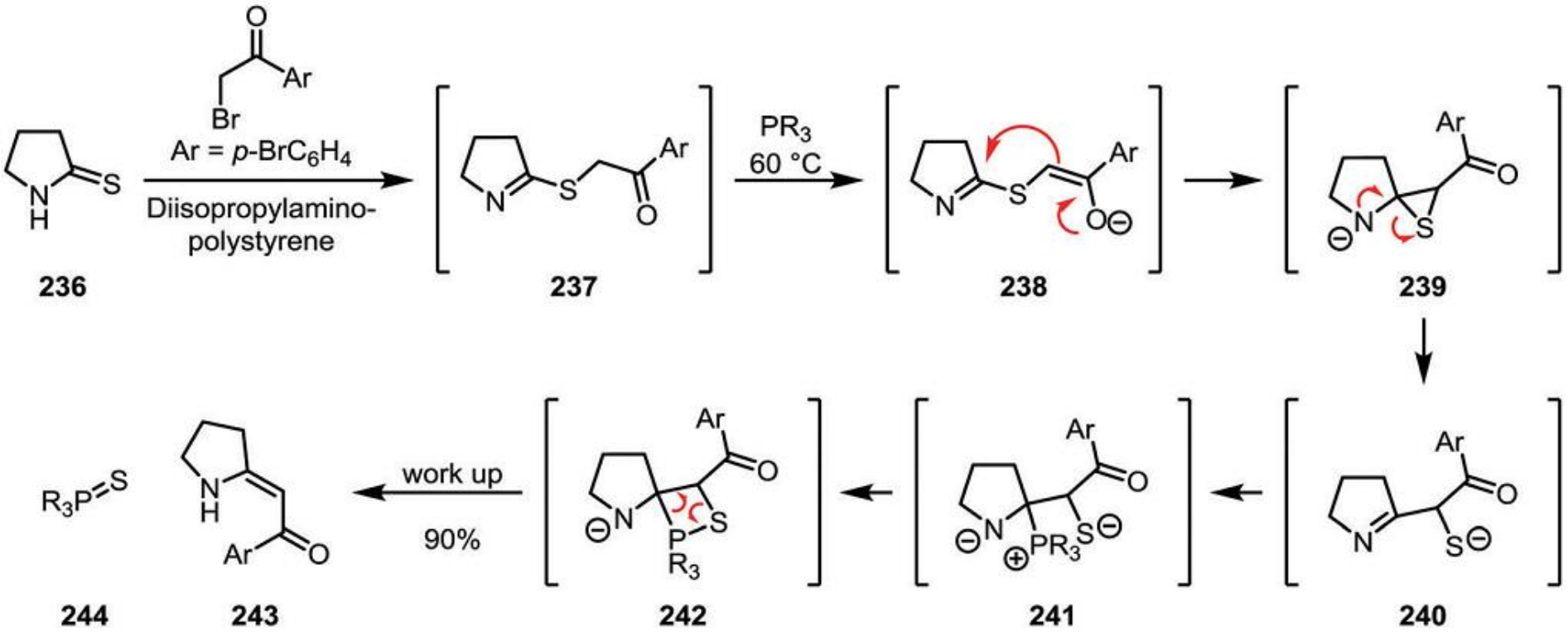
2. Thioamide activation

Application of thioamide activation



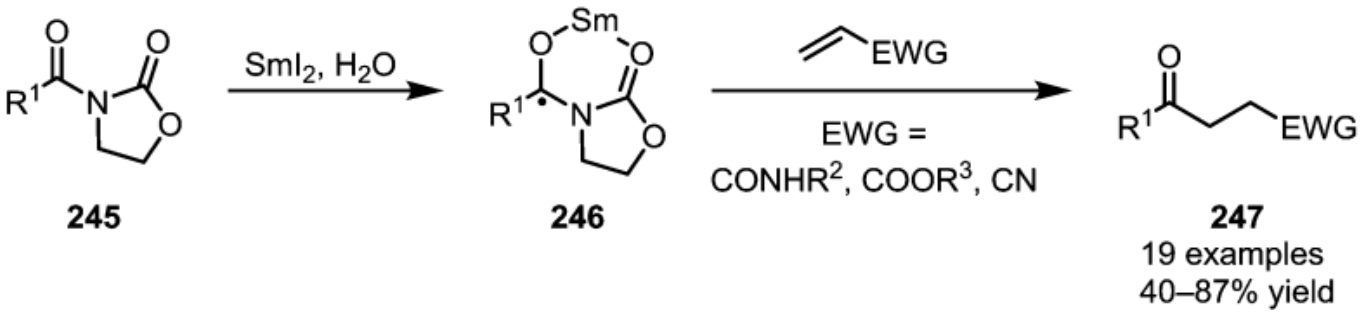
Application of thioamide activation (sulfide contraction)

Eschenmoser (1971)



3. SmI_2-mediated functionalization

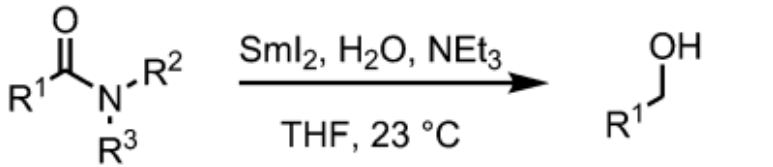
Skrydstrup (2005)



245 **246** **247**

19 examples
40–87% yield

Procter (2014)

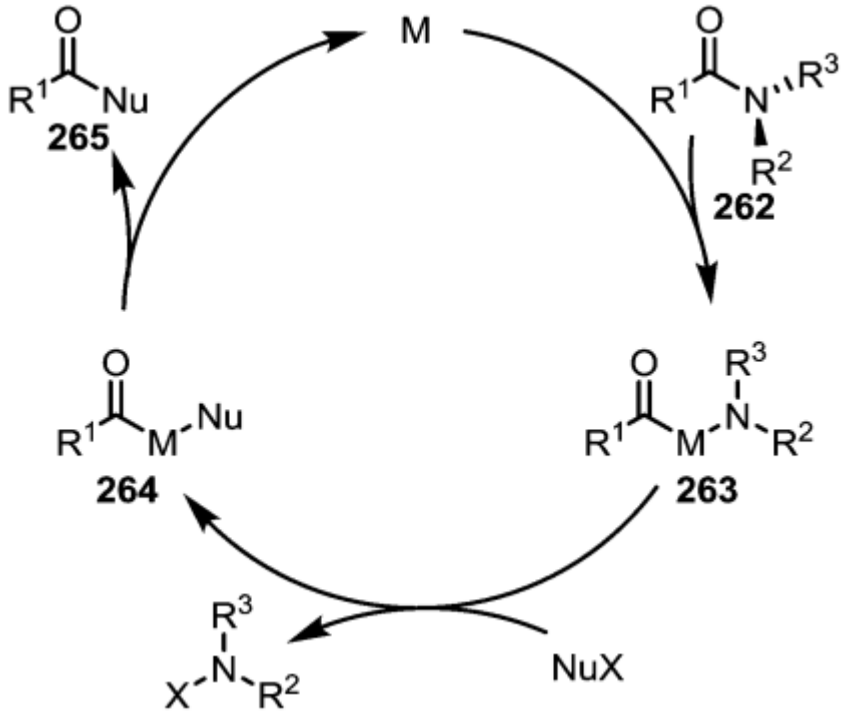


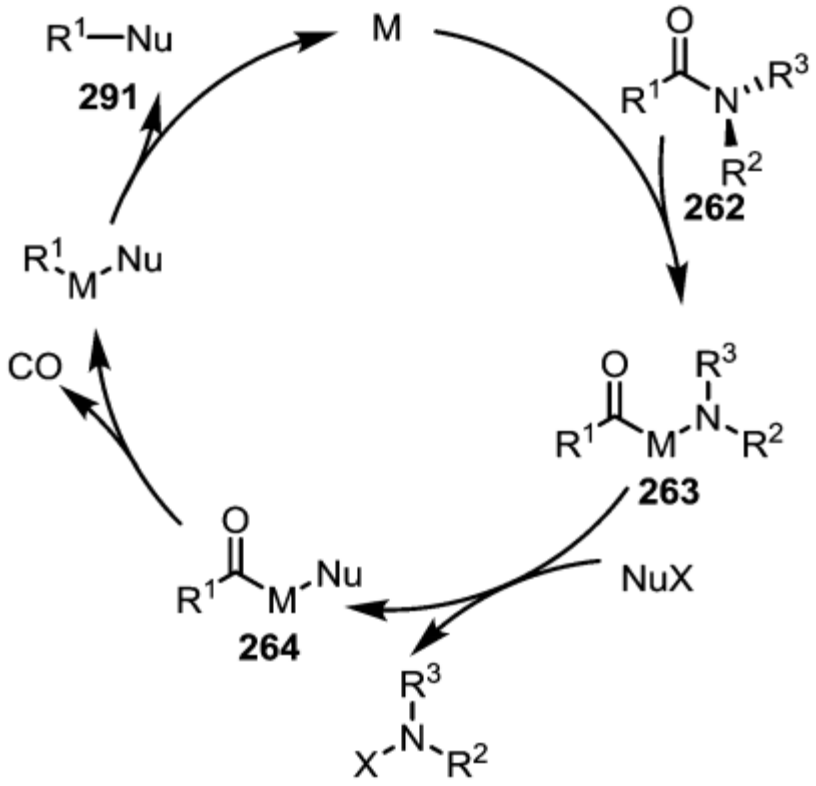
260 **261**

37 examples
61–99% yield

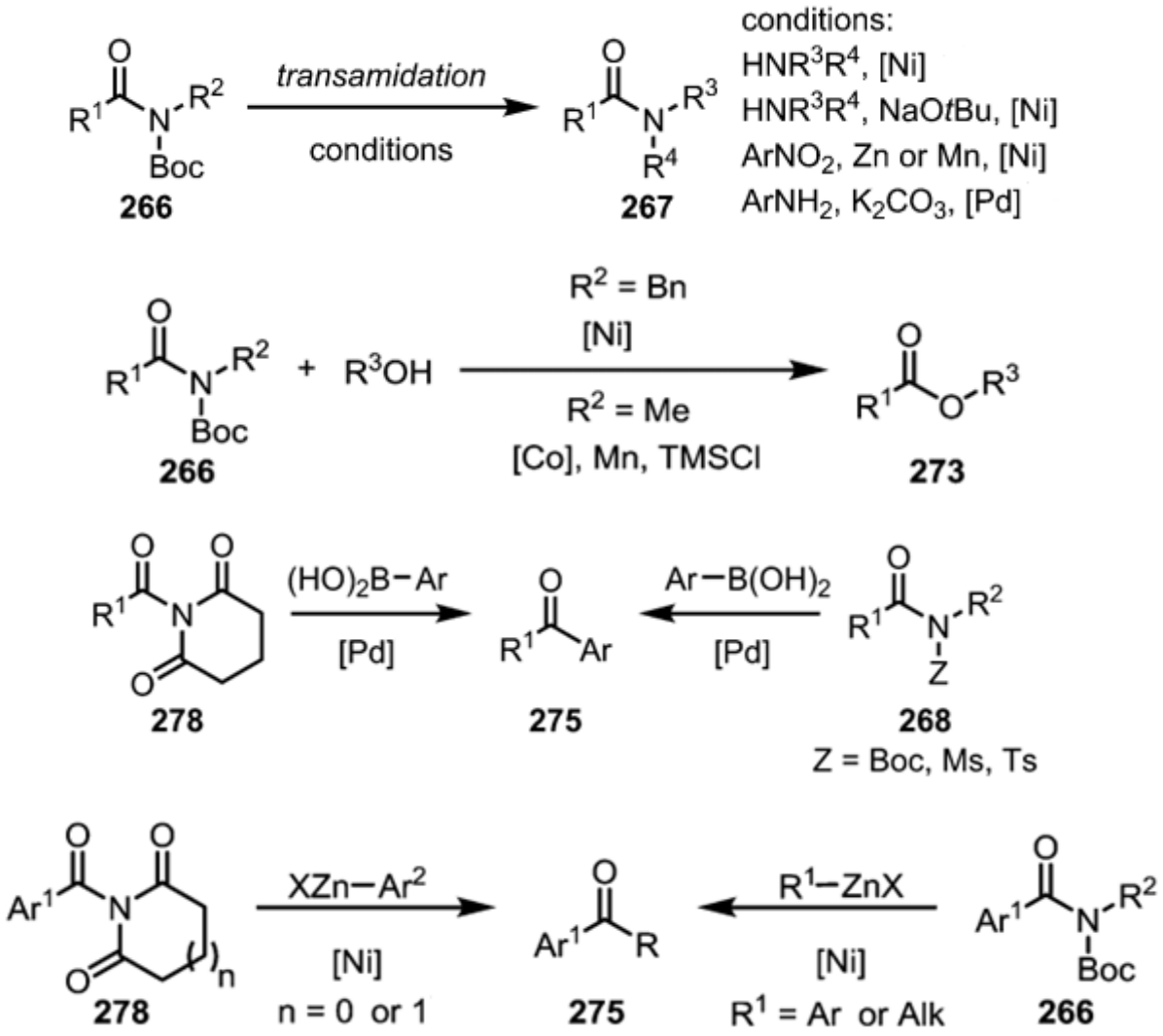
4. Transition metal catalyzed transformations

1) Transition metal catalyzed transformations

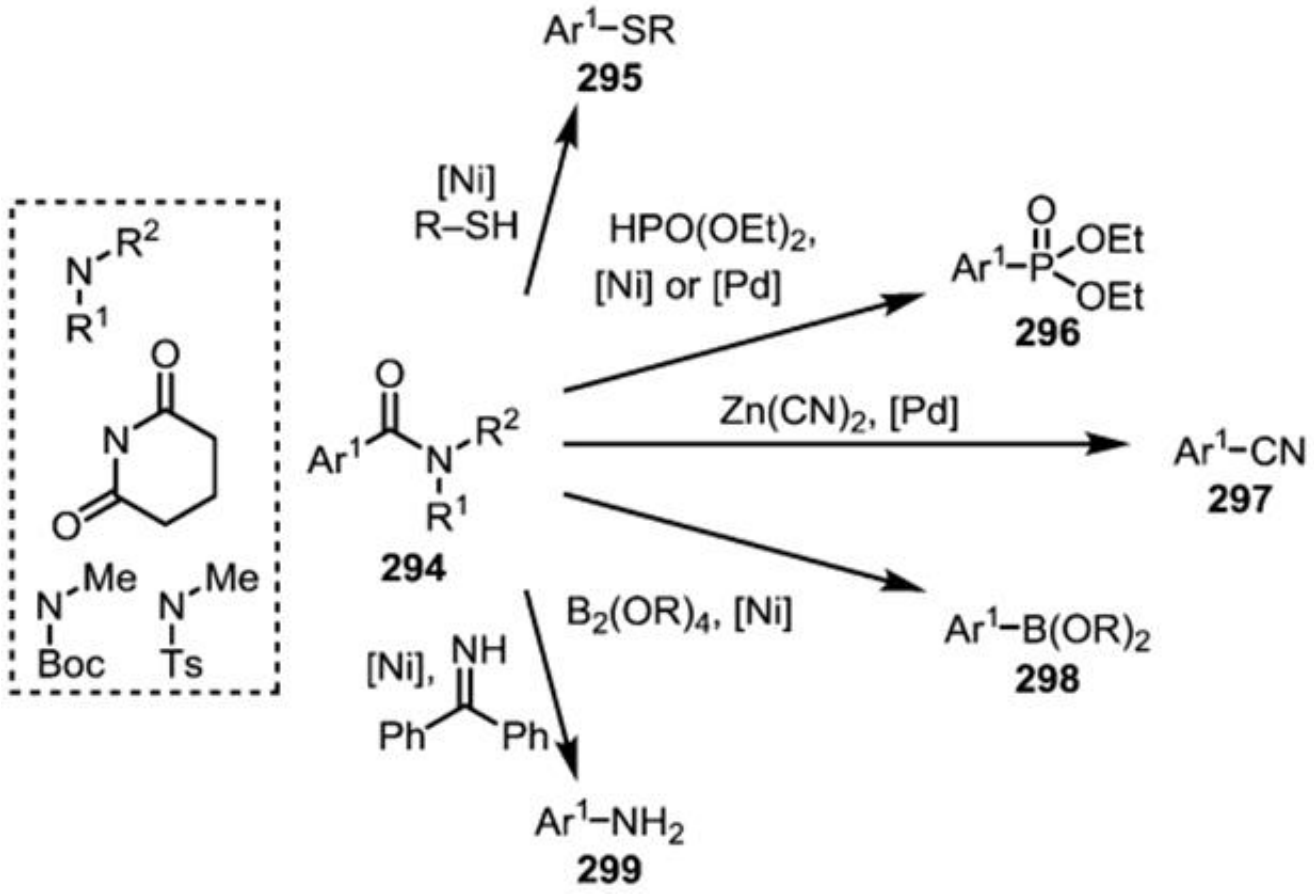




2) Transition metal catalyzed C–N bond activation

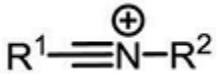


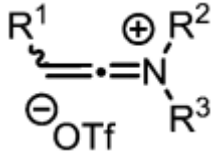
3) Transition metal catalyzed decarbonylative couplings



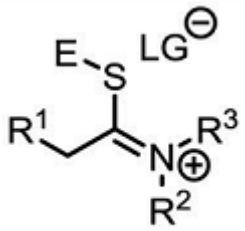
Summary

Electrophilic activation of amides (2º, 3º)



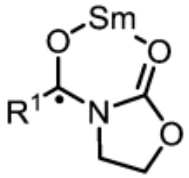


Thioamide activation



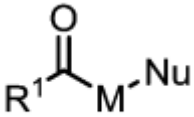
215

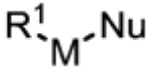
SmI_2-mediated functionalization



246

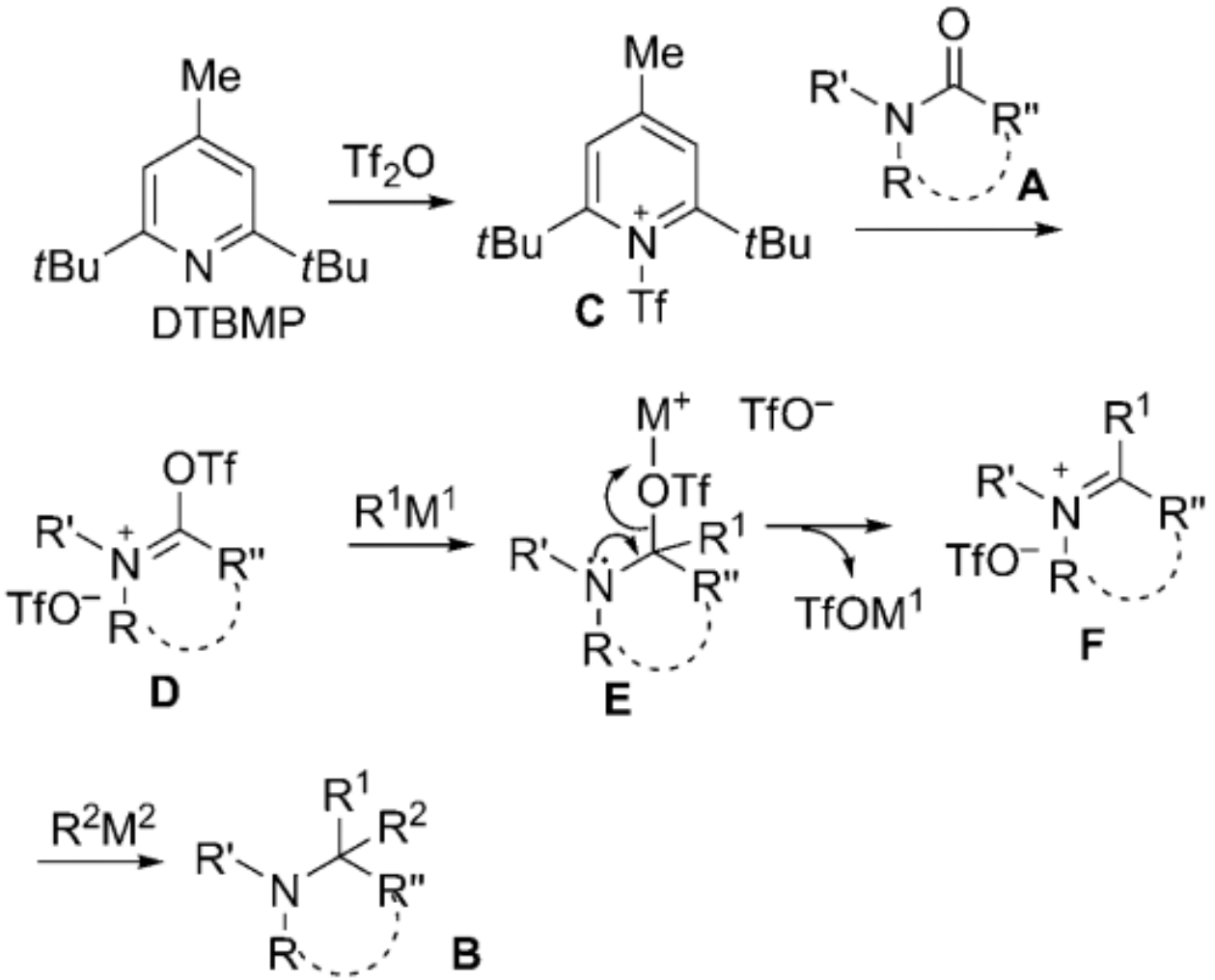
Transition metal catalyzed transformations

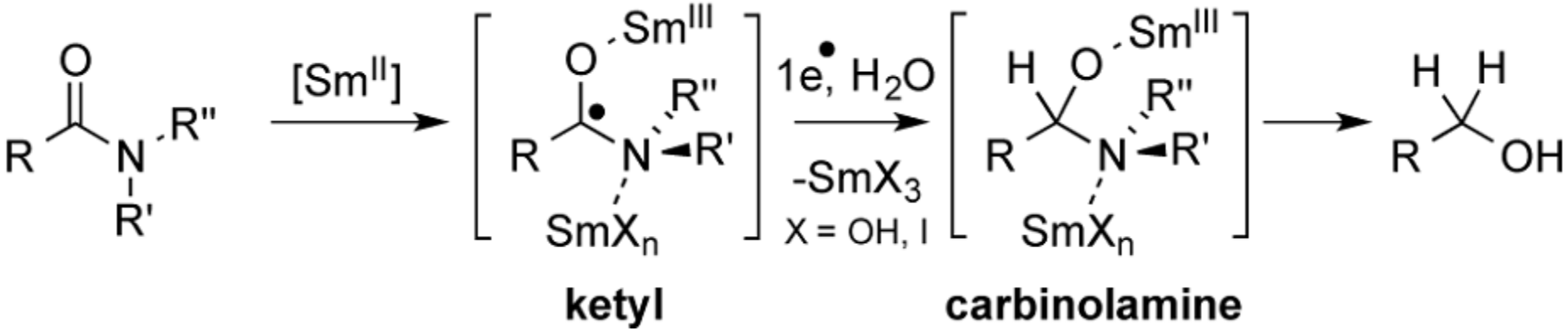




264

End
Thank You


Me
tBu
N
tBu
DTBMP
Tf2O
Me
tBu
N
tBu
Tf
C
O
R'
N
R"
R
A
OTf
R'
N
R"
TfO−
R
D
R1M1
M+
TfO−
OTf
R1
R'
N
R"
R
E
TfOM1
R1
R'
N
R"
TfO−
R
F
R2M2
R1
R2
R'
N
R"
R
B


[Sm^II]
Sm^III
1e, H2O
-SmX3
X = OH, I
SmXn
ketyl
carbinolamine