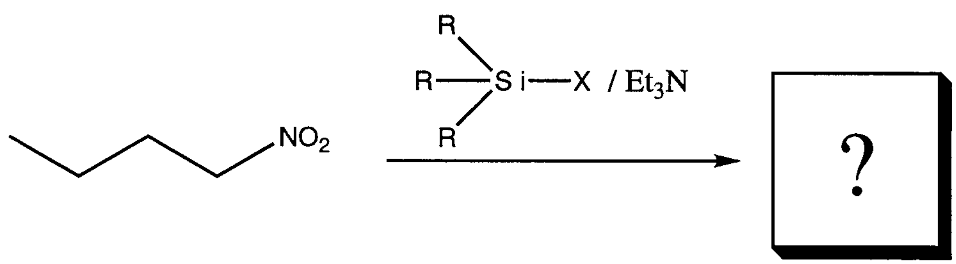
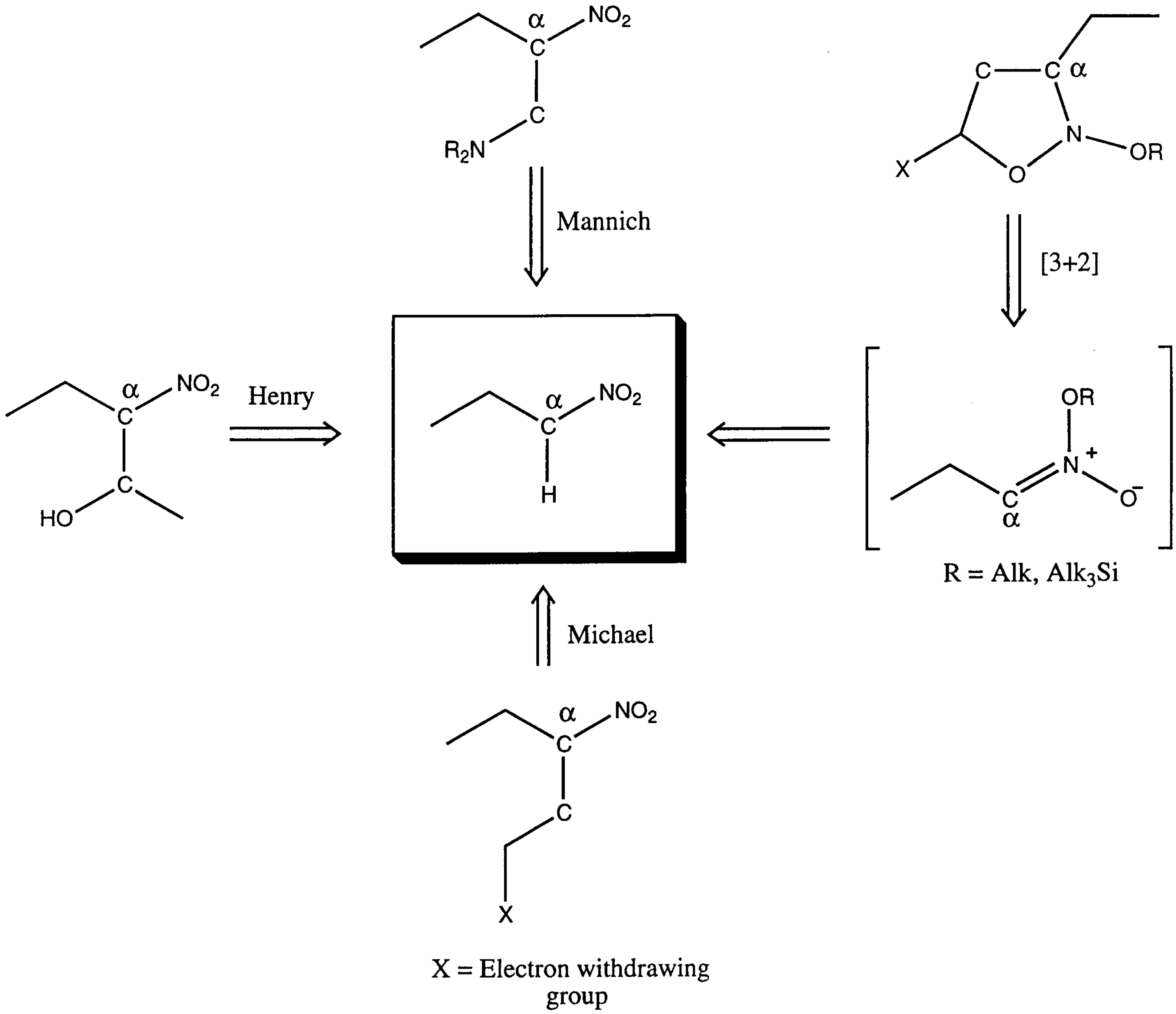
# THE SILYLATION OF NITRO COMPOUNDS:

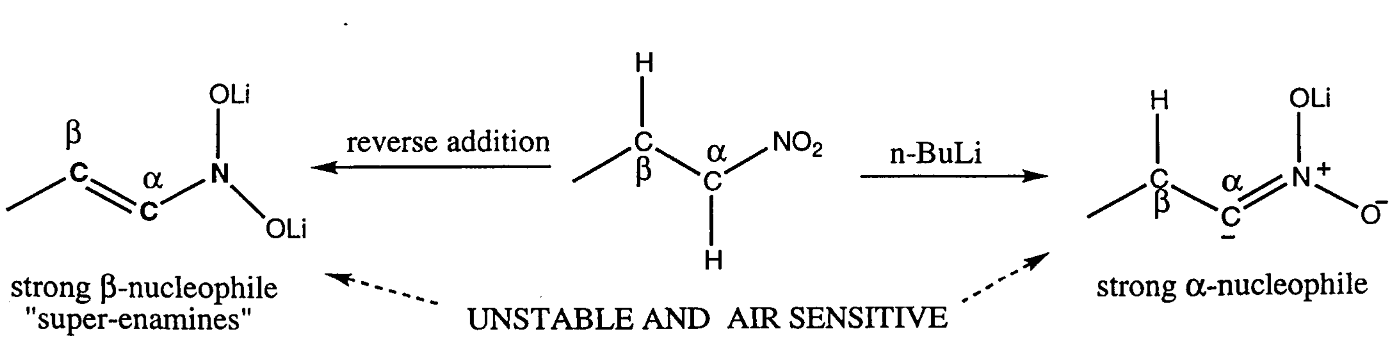
# ONLY A SET OF REACTIONS OR SYNTHETIC METHODOLOGY TO COME?



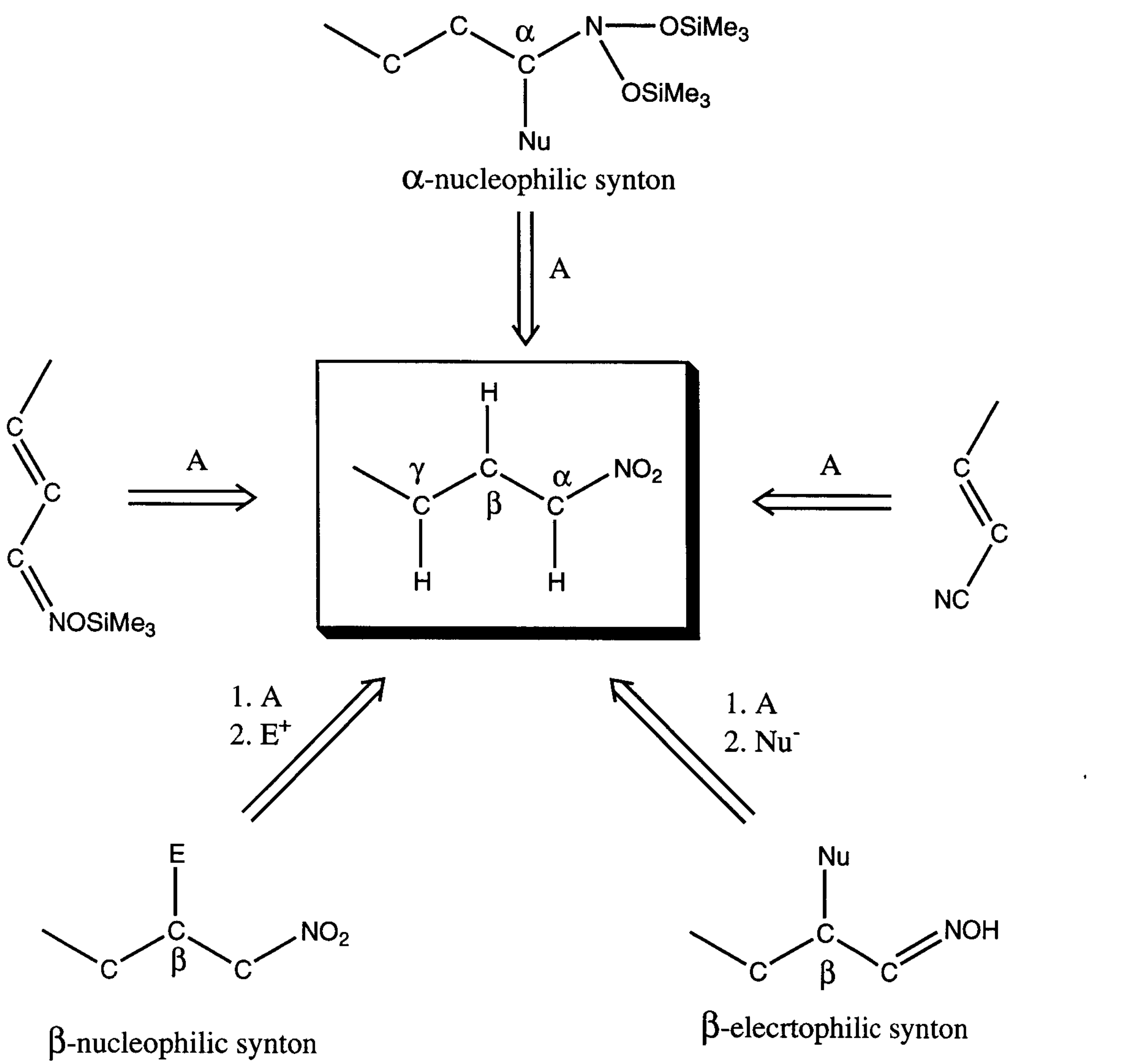

Alexander A. Tishkov
A brief report about the ongoing research conducting in Scientific Educational Center
(Moscow, N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences)

# THE CLASSIC METHODOLOGY OF UTILIZATION OF NITRO ALIPHATICS IN ORGANIC SYNTHESIS:
## NITRO COMPOUNDS AS α– NUCLEOPHILES

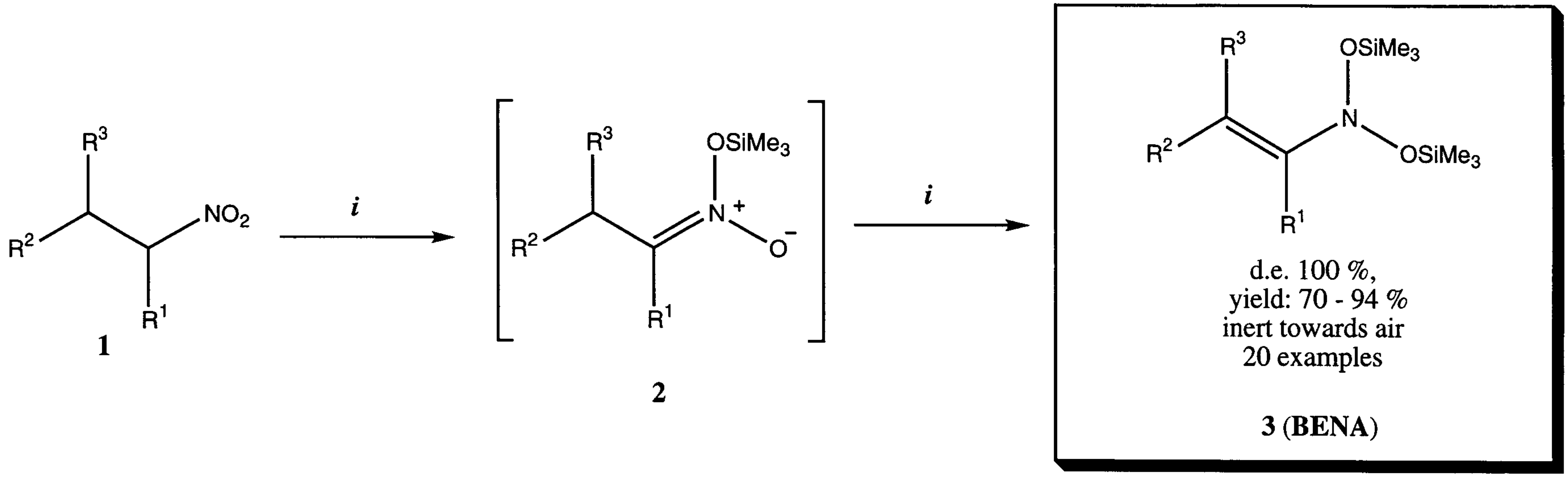


# THE NOVEL STRATEGY OF UTILIZATION OF NITRO ALIPHATICS IN ORGANIC SYNTHESIS VIA THEIR SILYLATION: NITRO COMPOUNDS AS α– AND β-ELECTROPHILES, AS WELL AS β-NUCLEOPHILES




A: SILYLATION ($Me_3SiX$ / Base, X = Cl, Br, $OSO_2CF_3$)




*i*: 1. $R^4Me_2SiX$ / $Et_3N$; $R^4$ = Me, t-Bu; X = Cl, Br, $OSO_2CF_3$.
2. aq. $NaHSO_4$ (to remove $Et_3N$)

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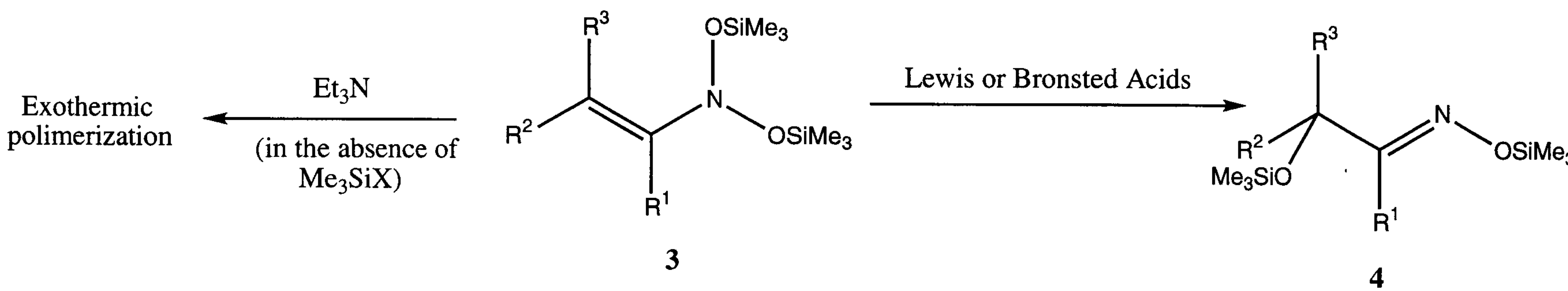
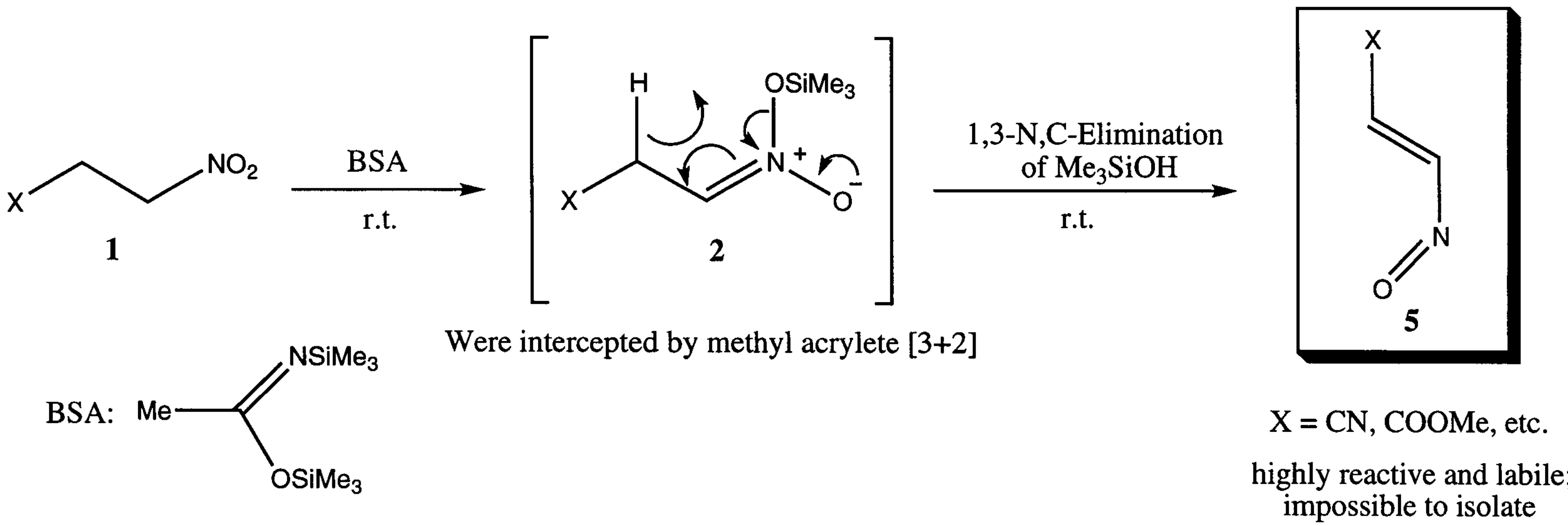
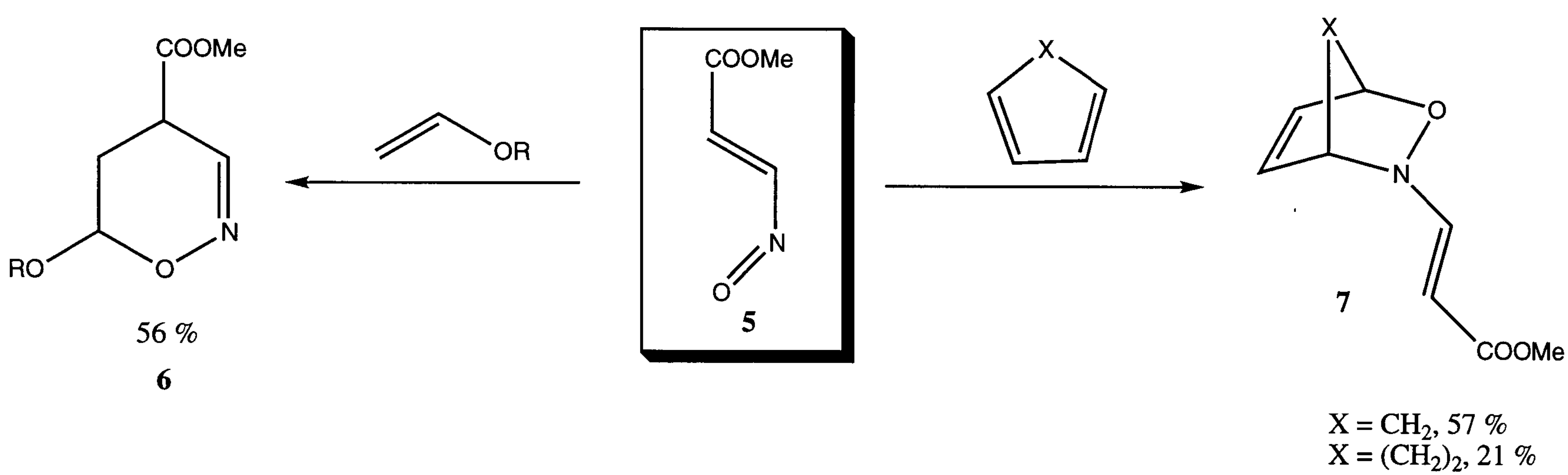
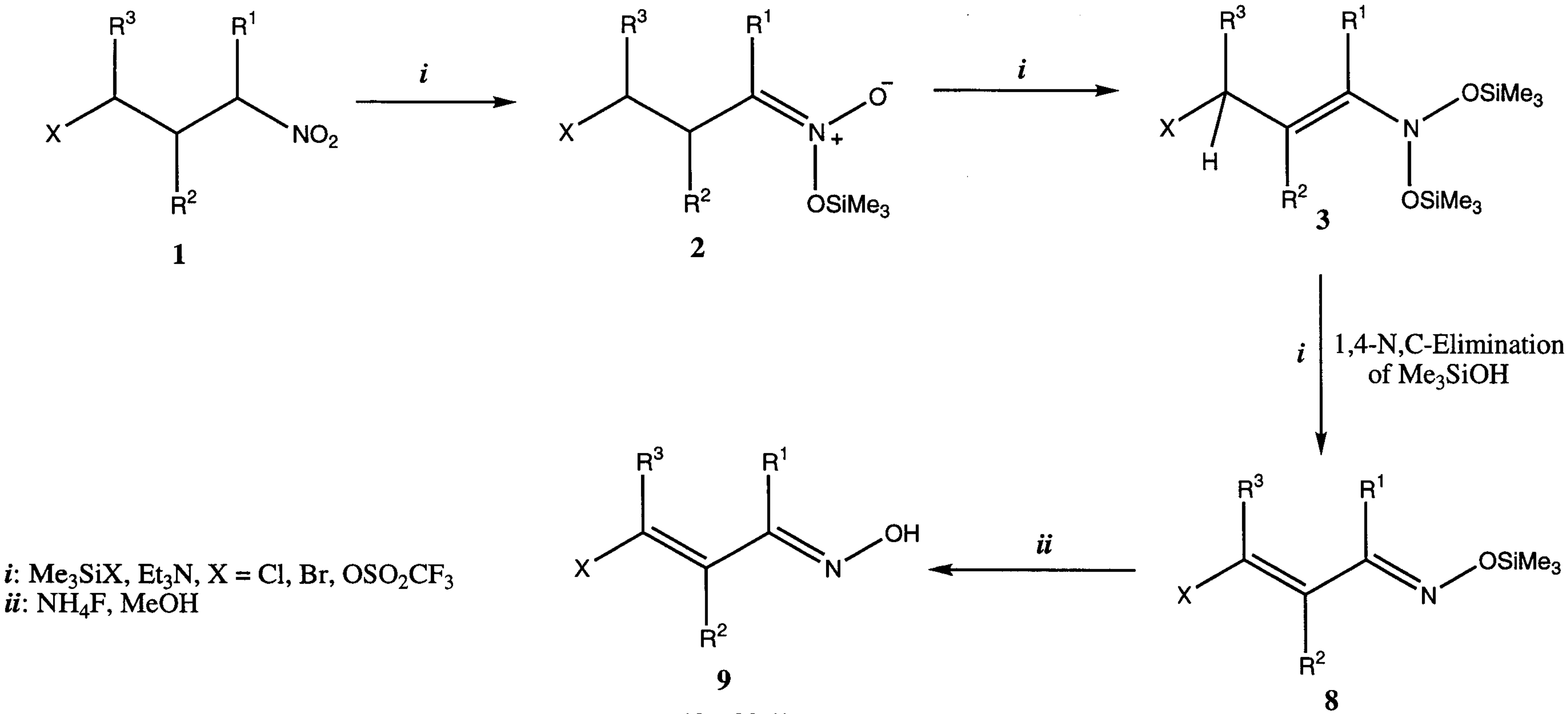


## ELIMINATION OF $Me_3SiOH$ UPON SILYLATION OF NITRO ALIPHATICS
## THE NOVEL METHOD OF GENERATION OF β-FUNCTIONALIZED NITROSO ALKENES

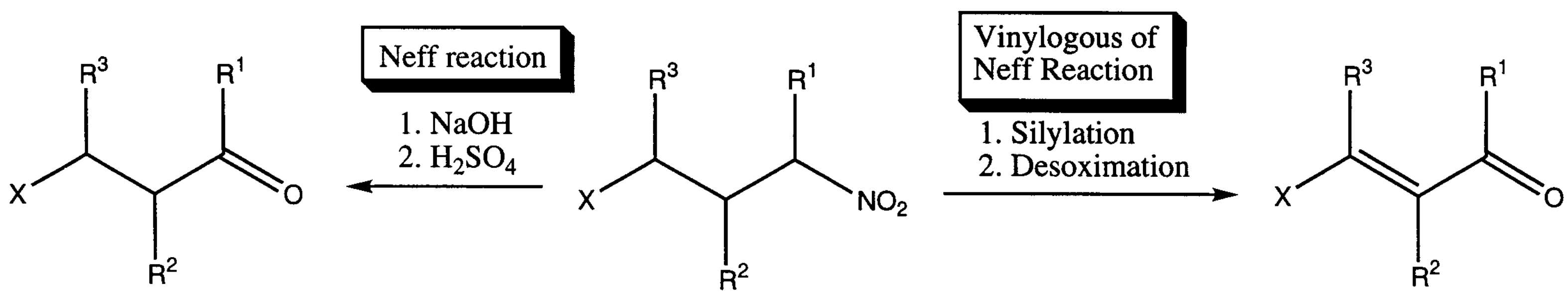


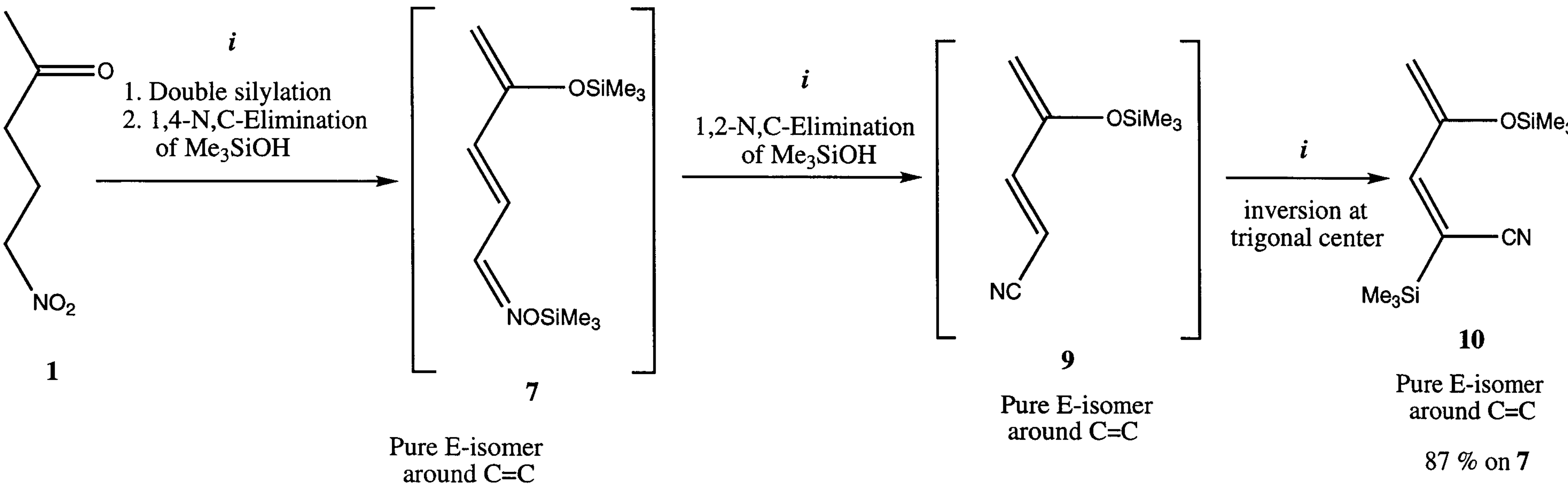






40 - 80 %
18 examples

X = CN, $NO_2$, COOMe, C(O)Me, C(O)Ph
$R^1$, $R^2$, $R^3$ = H, Ar, COOMe, Alk






*i*: $Me_3SiOSO_2CF_3$ / $Et_3N$

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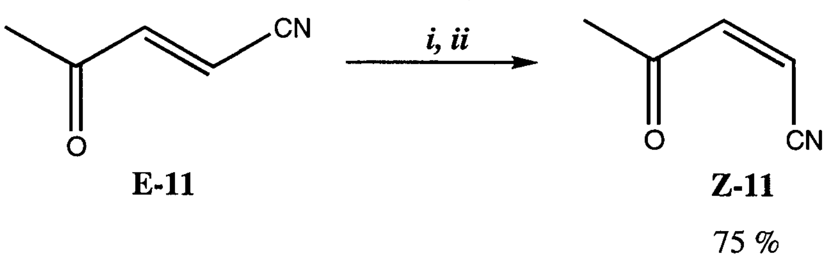
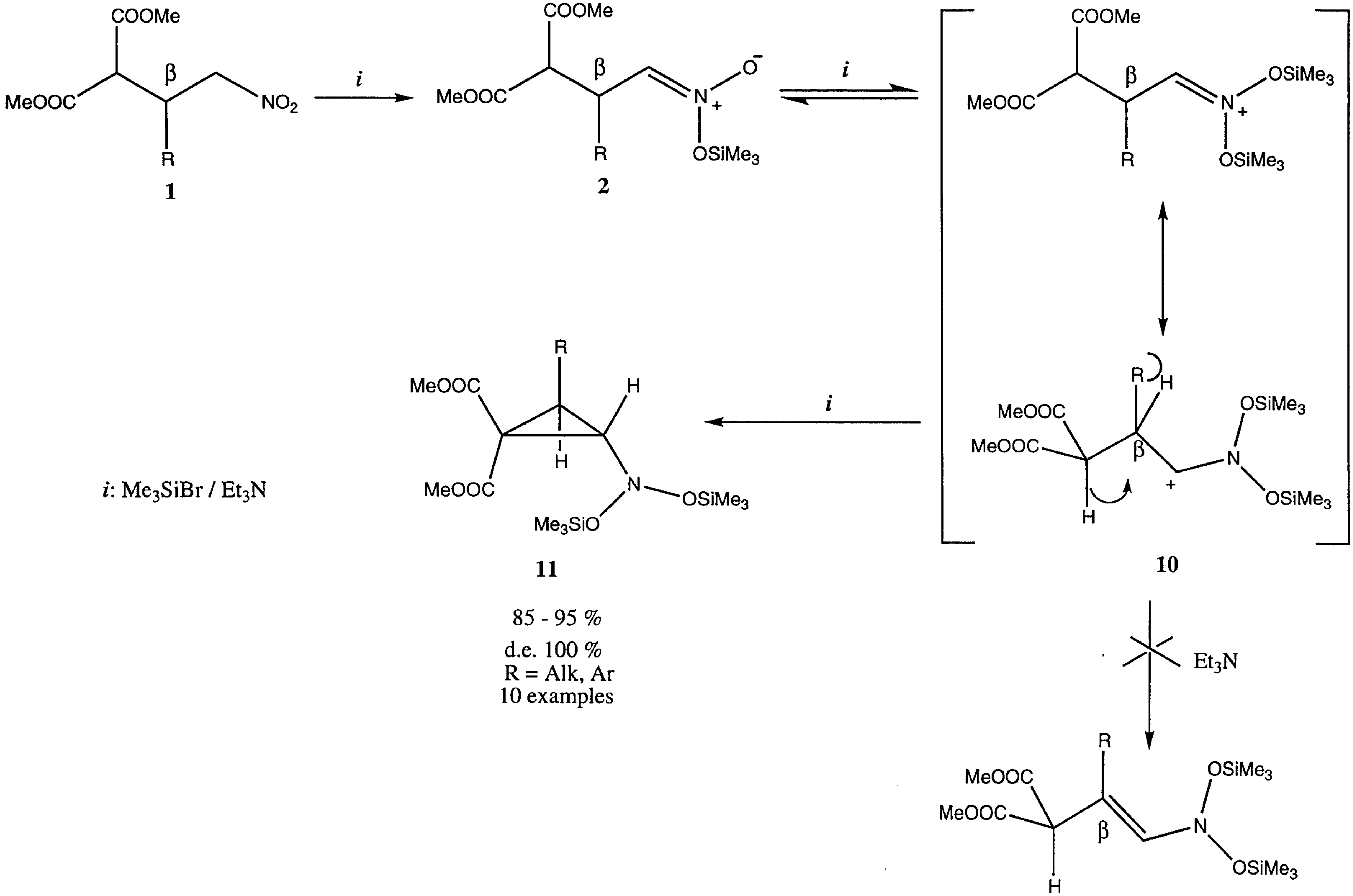


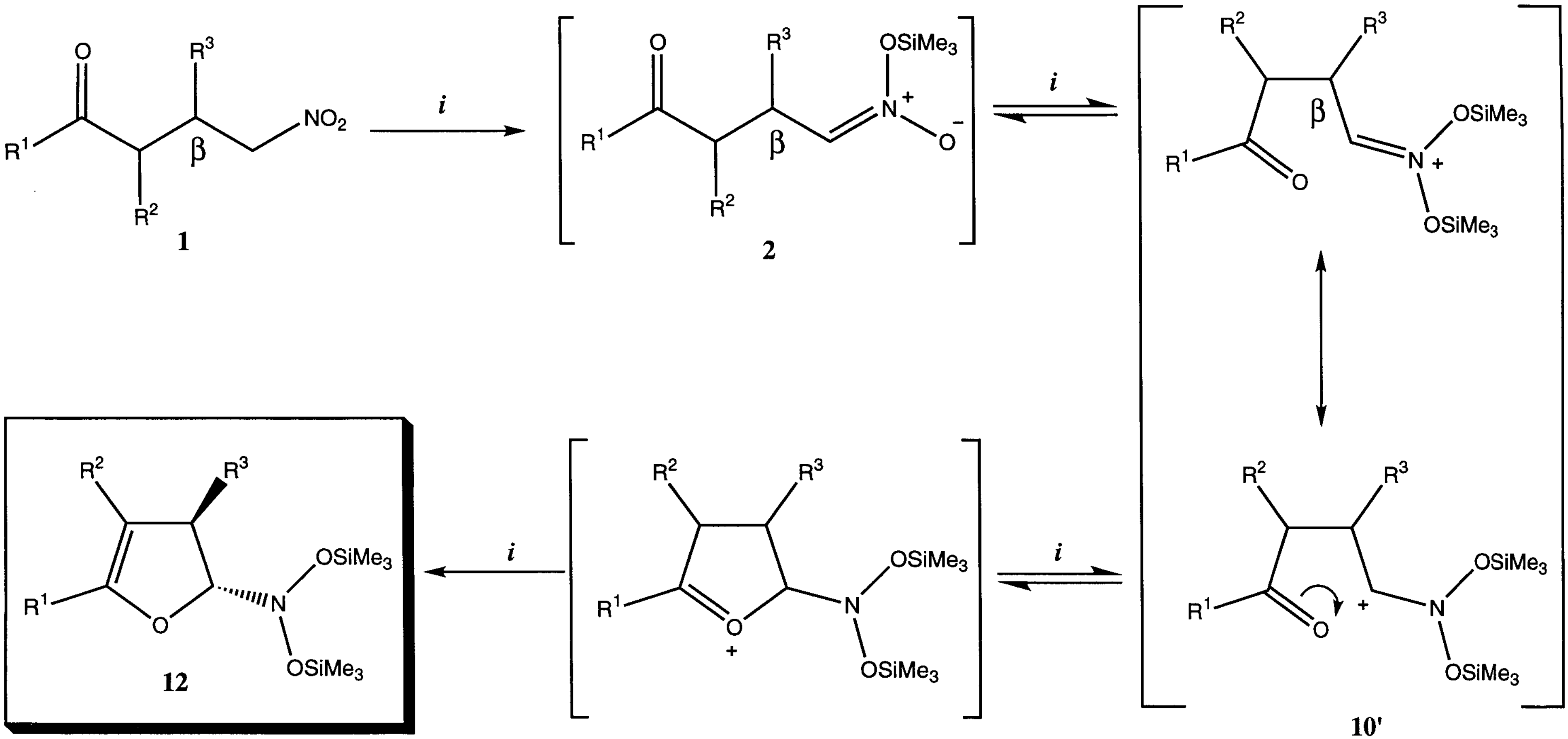

*i*: $Me_3SiOSO_2CF_3$ / $Et_3N$, r.t.
*ii*: $NH_4F$, MeOH, 1 hour, r.t.,
then evaporation followed by extraction of crude product with pentane to give analytically pure crystalline product after cooling of the resulting solution.

# THE INTRAMOLECULAR TRAPPING OF N,N-BIS(SILYLOXY)IMMONIUM CATION




*i*: $Me_3SiBr$ / $Et_3N$

85 - 95 %
d.e. 100 %
R = Alk, Ar
10 examples

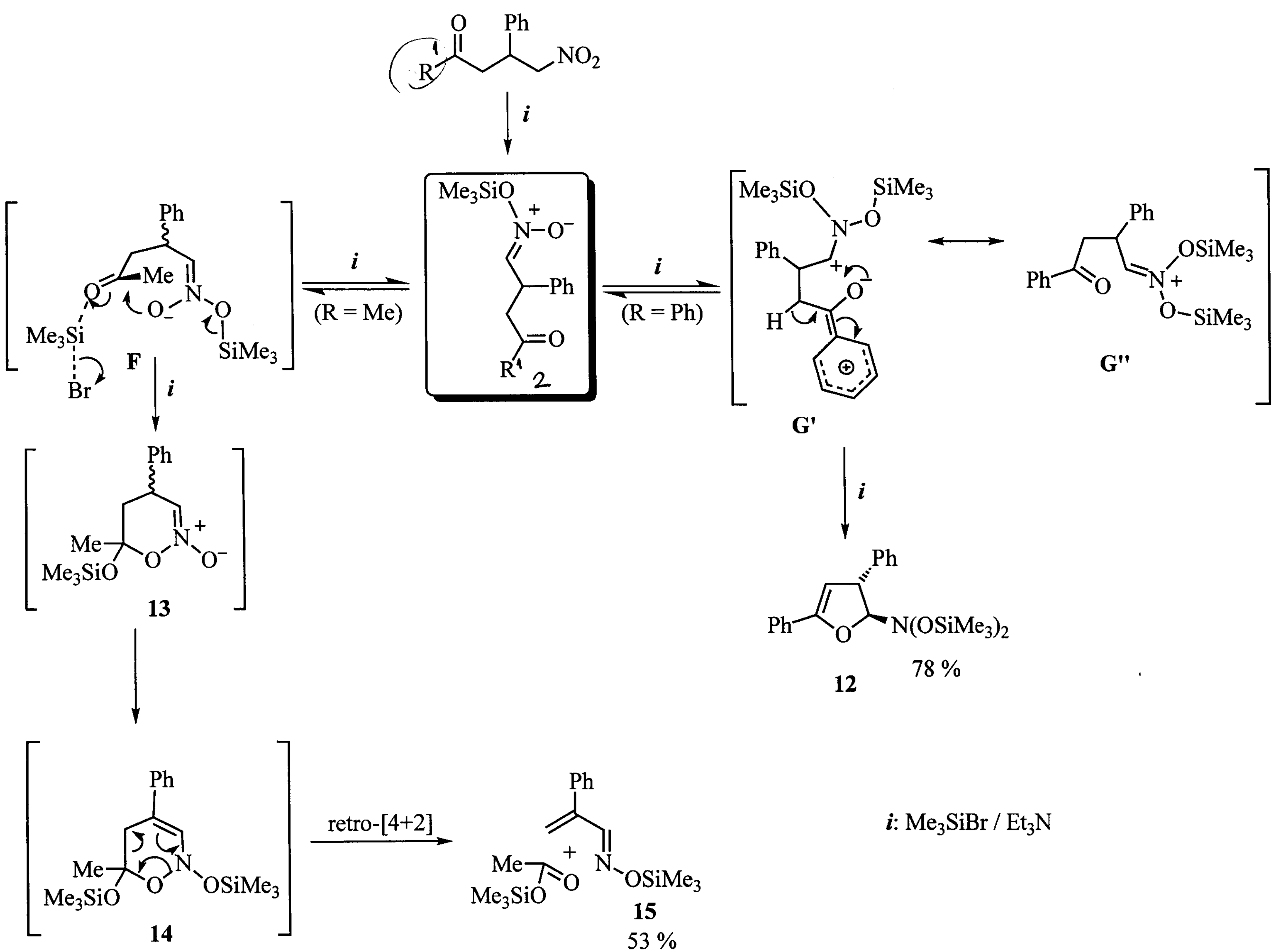



d.e. 100 %

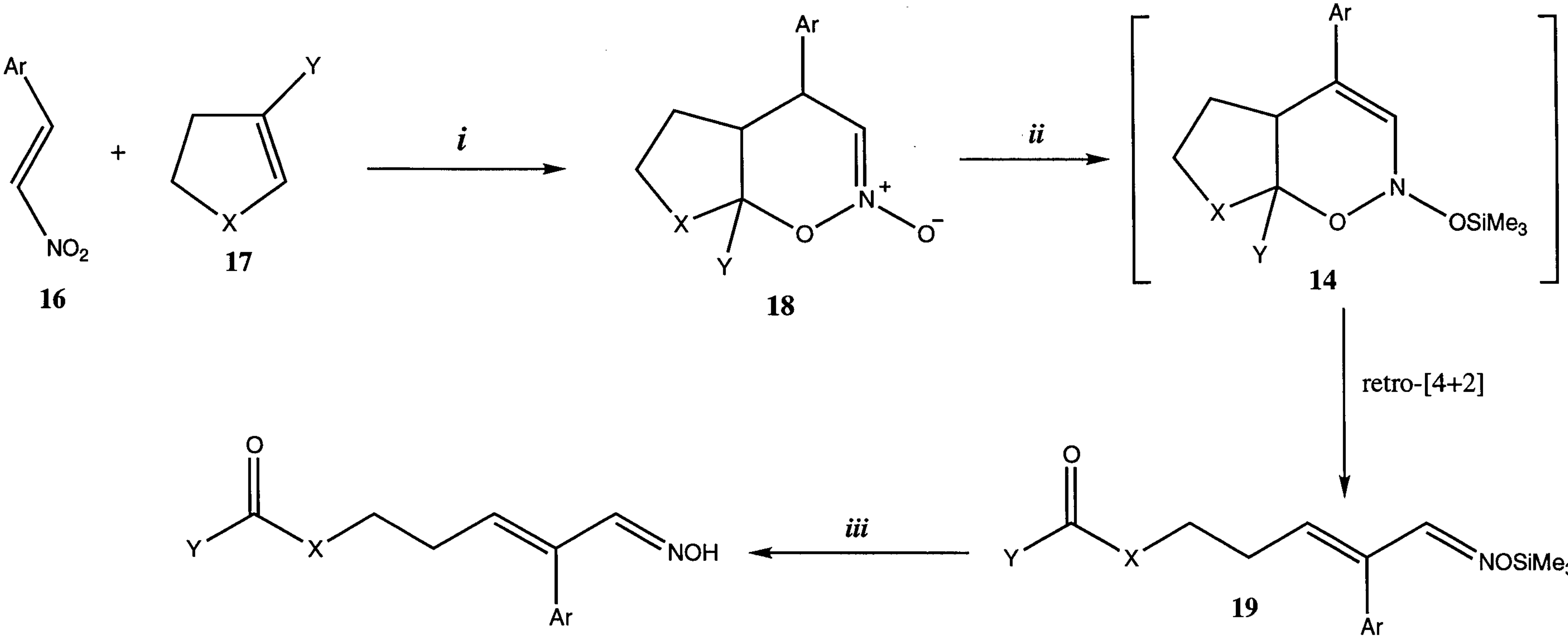
70 - 95 %

$R^1, R^2, R^3$ = H, Alk, Ar, cyclo-Pr

12 examples



O
Ph
R
$NO_2$
i
$Me_3SiO$
N–O⁻
Ph
O
R
2
i
(R = Me)
(R = Ph)
Ph
Me
N
O
$Me_3Si$
Br
$SiMe_3$
F
$SiMe_3$
Ph
H
G'
OSiMe₃
G''
13
Me
$Me_3SiO$
14
OSiMe₃
retro-[4+2]
15
53 %
12
$N(OSiMe_3)_2$
78 %
*i*: $Me_3SiBr$ / $Et_3N$




*i*: $SnCl_4$ or $(i\text{-}PrO)_2TiCl_2$;
*ii*: $Me_3SiBr$ or $Me_3SiOTf$ / $Et_3N$;
*iii*: $NH_4F$ / MeOH

Ar = Ph, 4-$MeOC_6H_4$;
Y = H, $OSiMe_3$, OMe;
X = $(CH_2)_n$; n = 1 - 4;
50 - 86 %
7 examples

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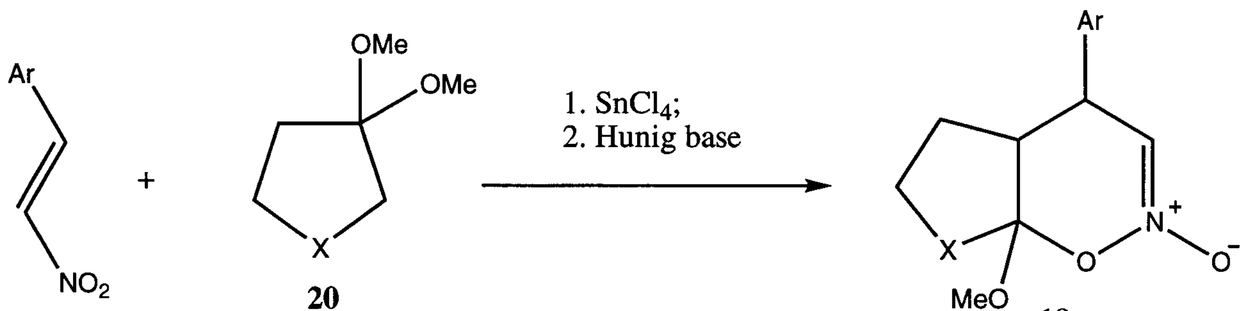
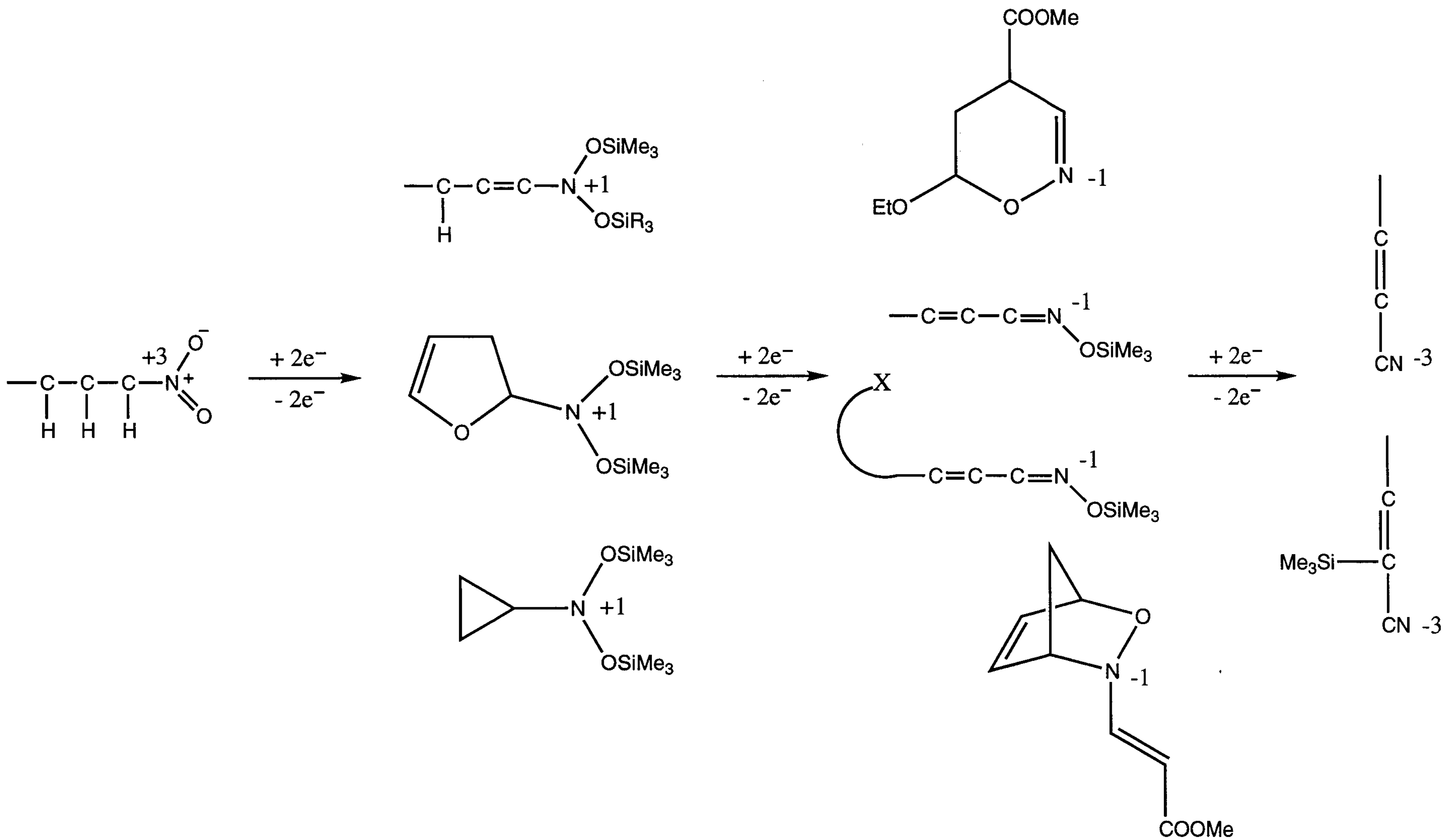
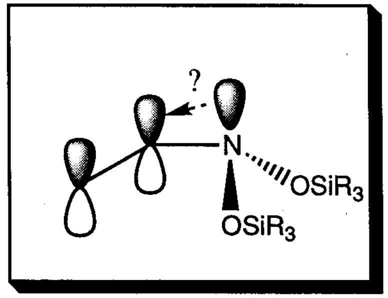


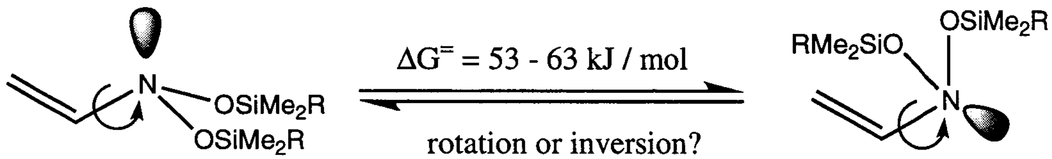

X = $(CH_2)_n$, n = 1 - 3; 4 examples

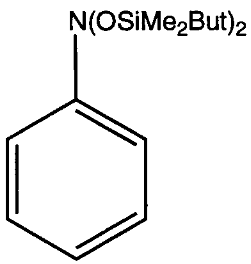
60 - 85 %
d.e. > 90 : 10



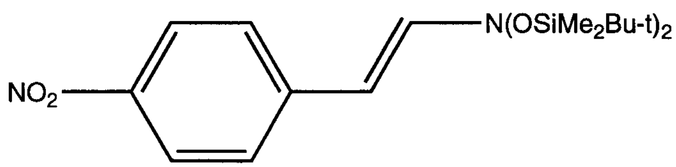

The nitrogen's oxidation state decreases
The carbon chain oxidation level increases



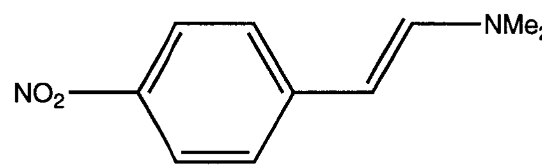




ΔG= = 48 kJ / mol
only inversion can be
observed by NMR



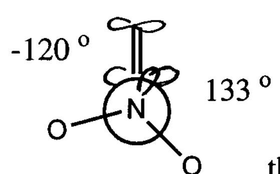

ΔG= = 37 kJ / mol
both inversion or rotation
can be observed by NMR




ΔG= = 47 kJ / mol
only rotation can be
observed by NMR

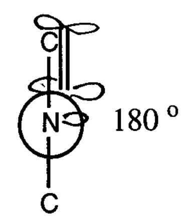
C,N-bonds as Numan's
projections with torsion angles

X-ray



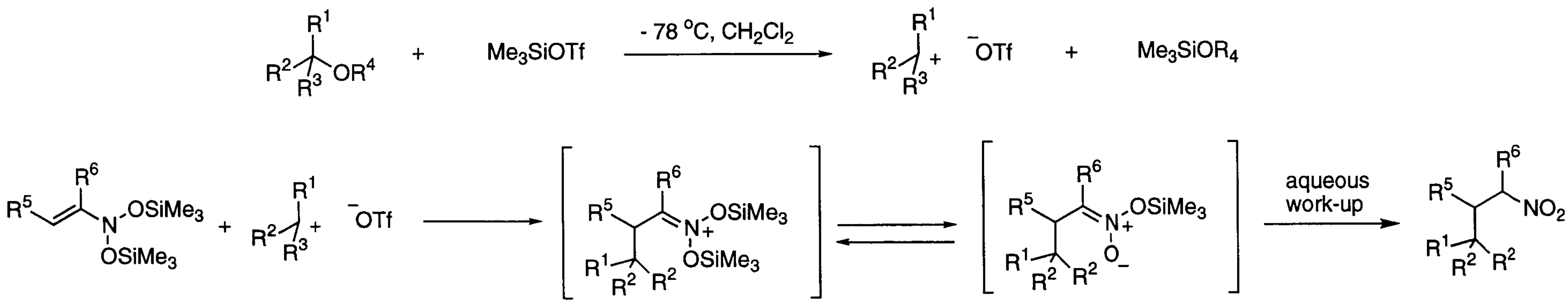

the hight of pyramid: 0.6 A

by X-Ray
N lone pair is out of conjugation
with C,C-double bond



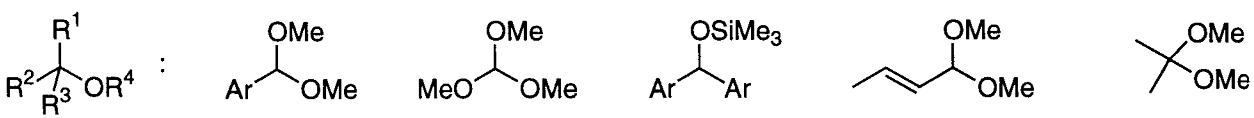

by X-Ray
N lone pair is in conjugation
with C,C-double bond

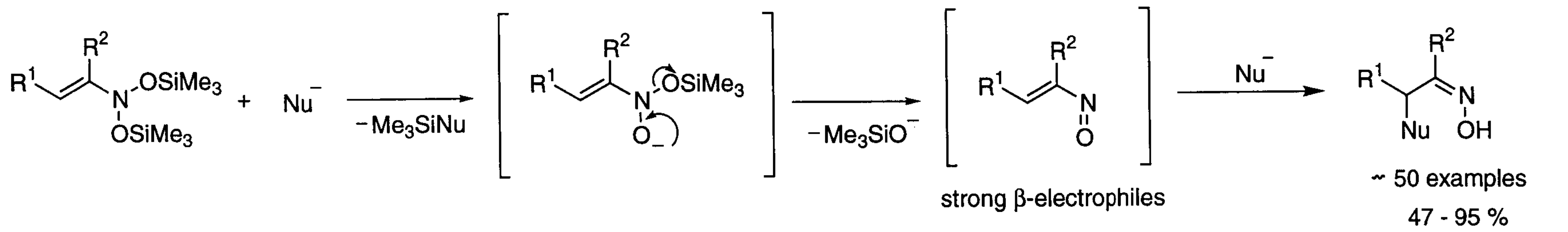
## N,N-BIS(SILYLOXY)ENAMINES AS β-NUCLEOPHILES



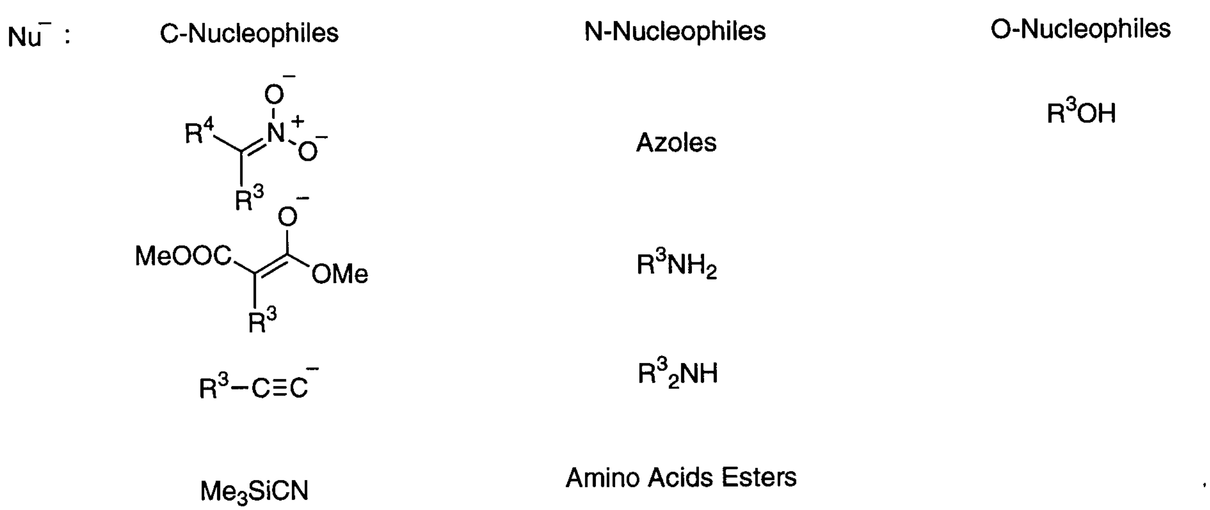

10 examples,
35 - 85 %

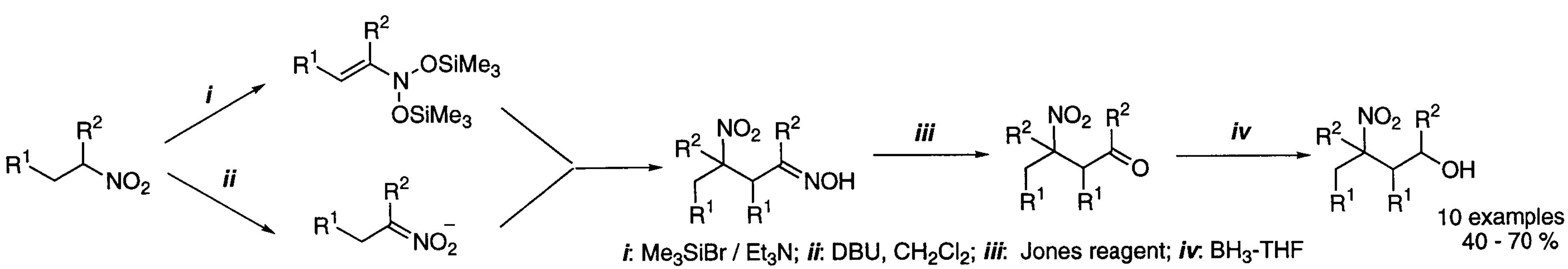
The nucleophilicity of N,N-bissiloxy)enamines is closed to allylsilanes (by kinetic studies).






$$Me_3SiNu + Me_3SiO^- \longrightarrow Me_3SiOSiMe_3 + Nu^-$$



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