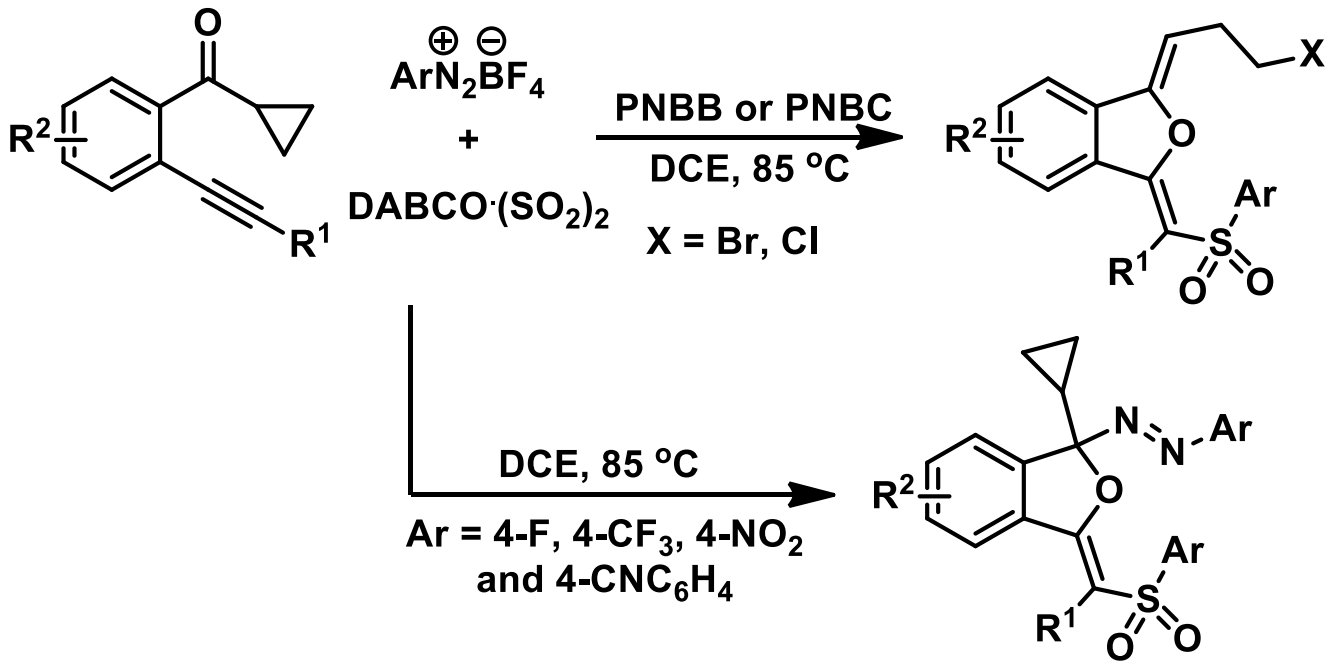
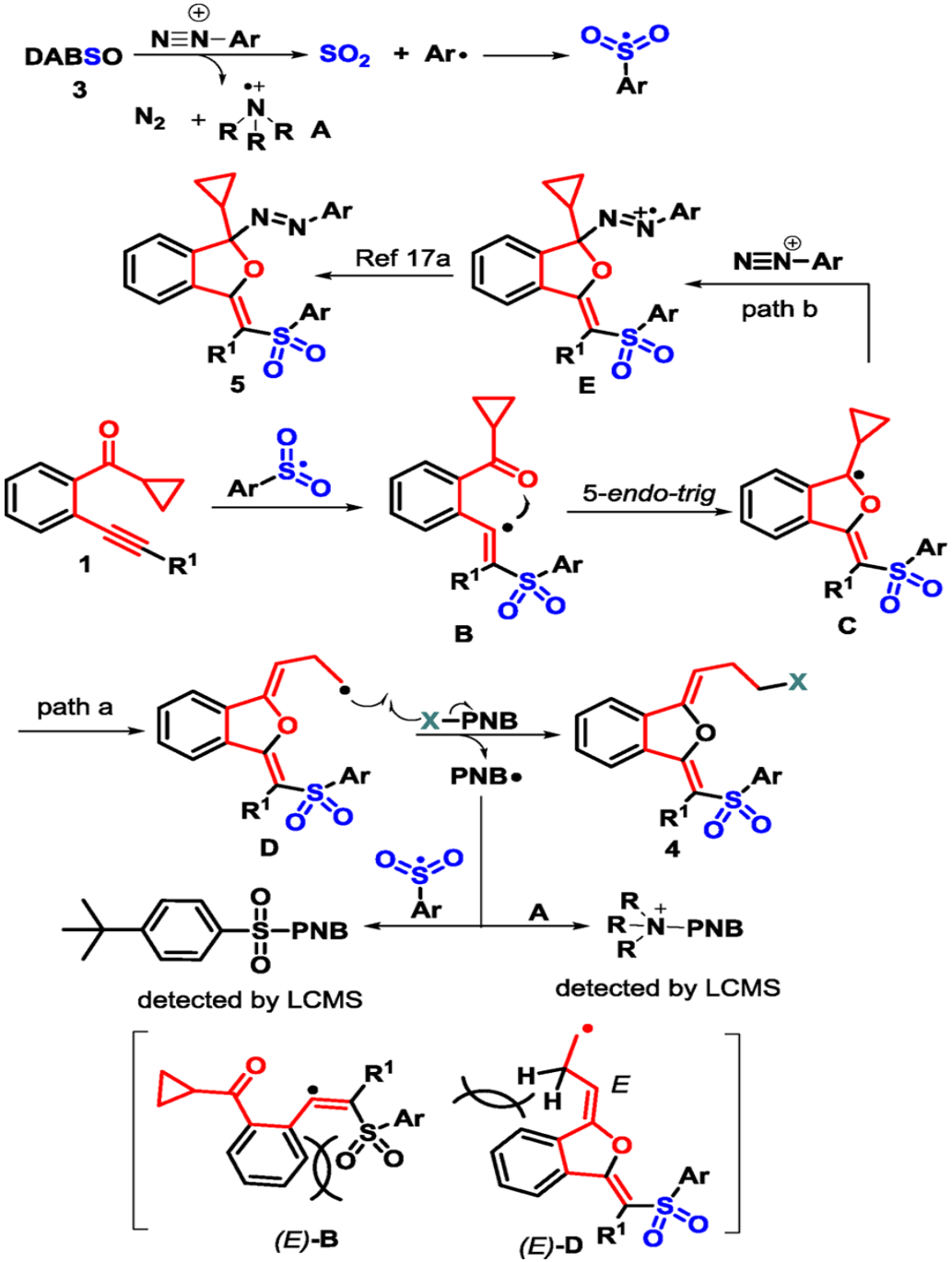
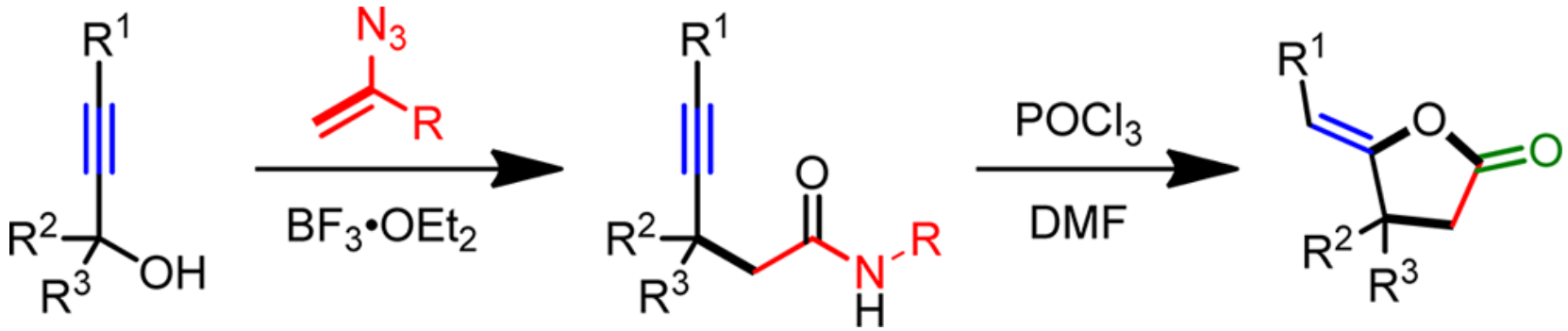
1.



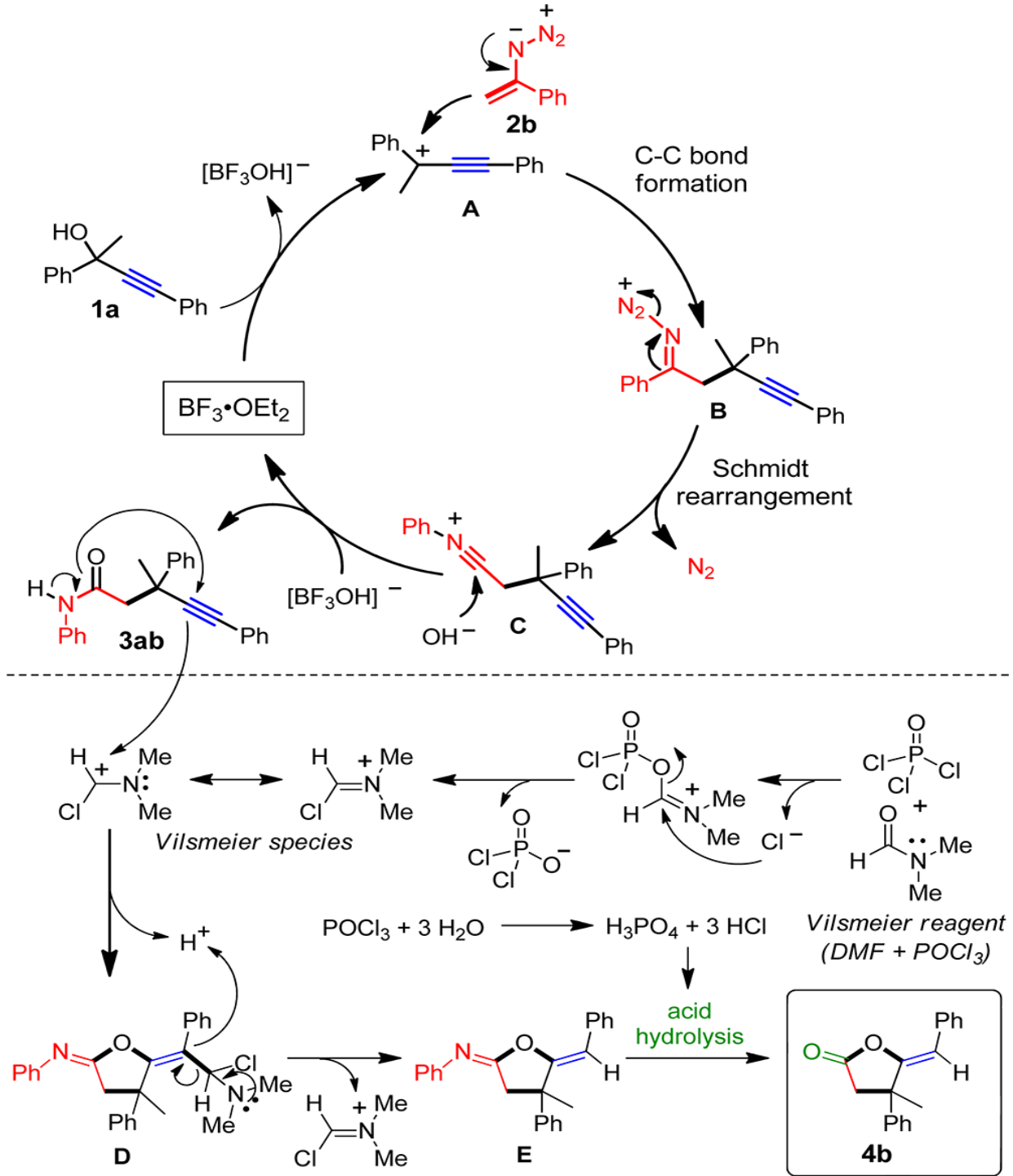
DOI: 10.1021/acs.joc.9b01918.


DABSO
3
N≡N–Ar
SO2
+ Ar•
N2
+
R
R
R
A
Ar
Ref 17a
5
E
path b
1
R1
5-endo-trig
B
C
path a
X–PNB
PNB•
D
4
X
PNB
A
detected by LCMS
detected by LCMS
(E)-B
(E)-D
H
H
E

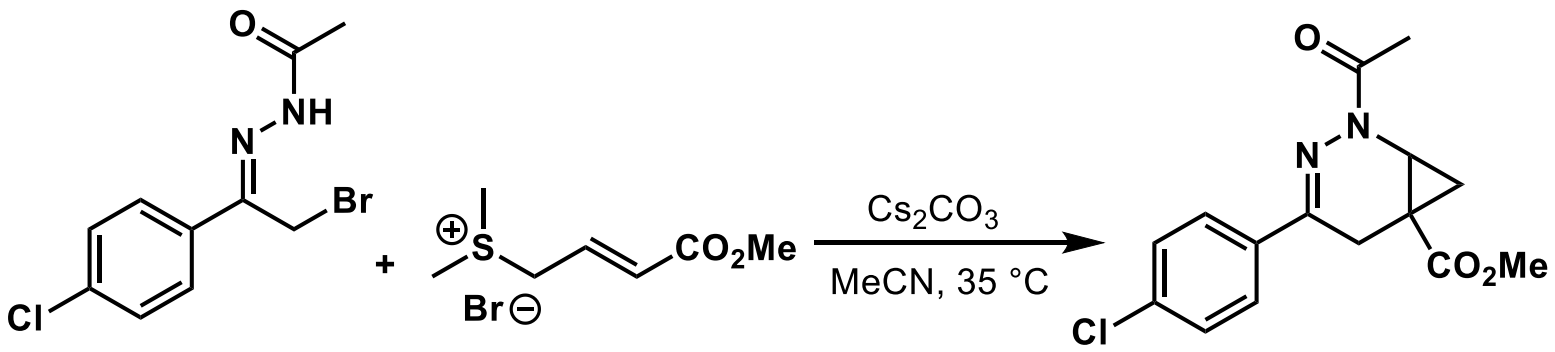
2.



Org. Lett. **2015,** *17*, 6190-6193.


2b
A
C-C bond formation
B
Schmidt rearrangement
N2
C
OH−
[BF3OH]−
3ab
BF3•OEt2
[BF3OH]−
1a
Vilsmeier species
Vilsmeier reagent
(DMF + POCl3)
POCl3 + 3 H2O
H3PO4 + 3 HCl
acid hydrolysis
D
E
4b

3.



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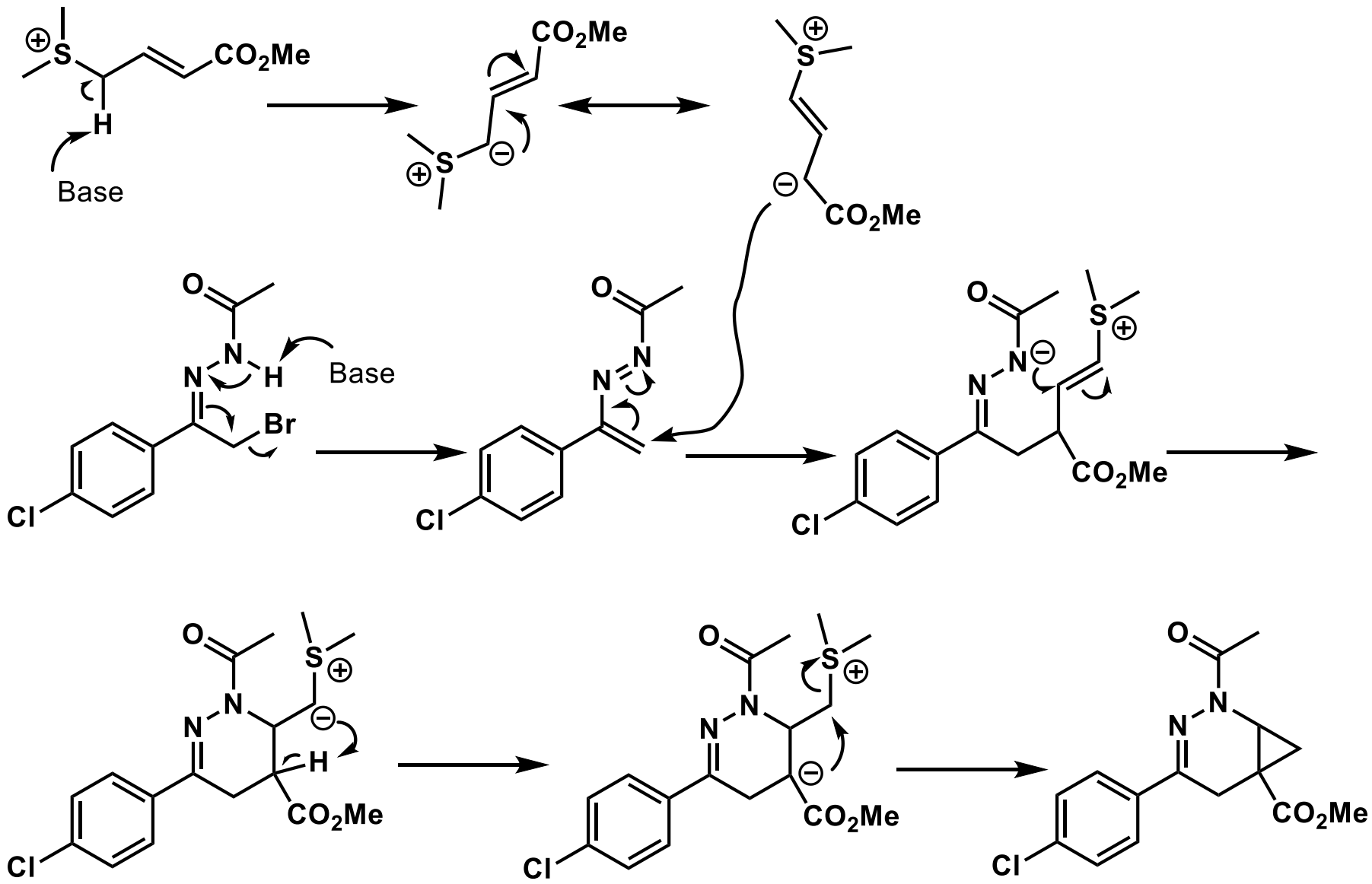
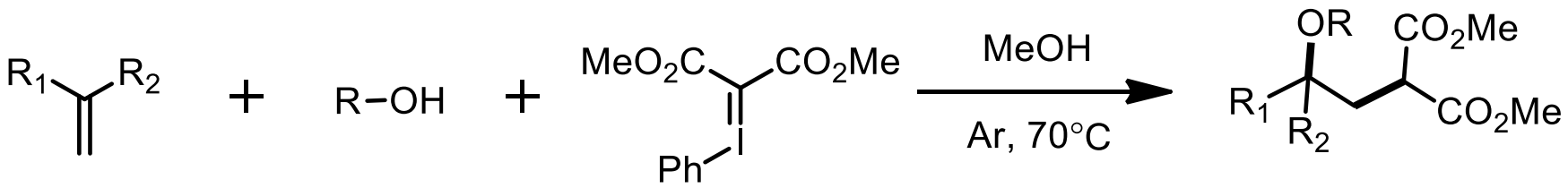
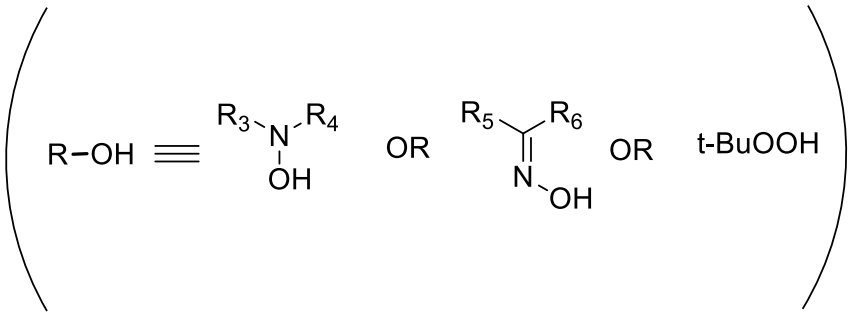

Base
Base

4.





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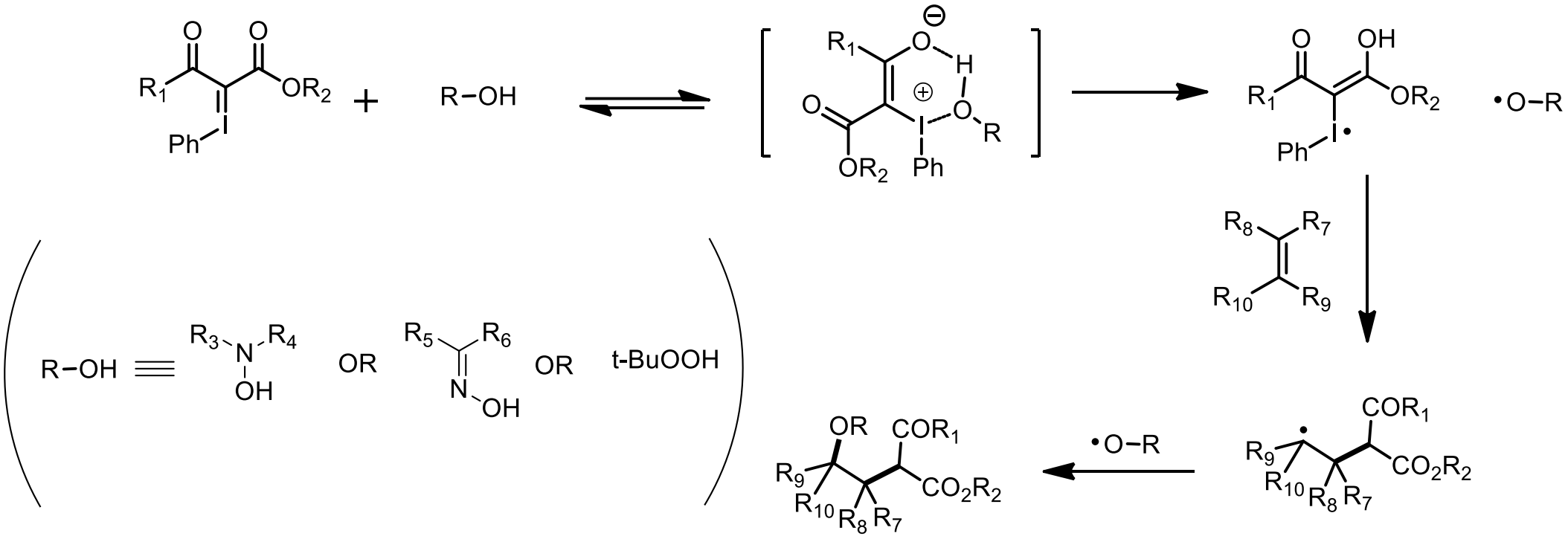
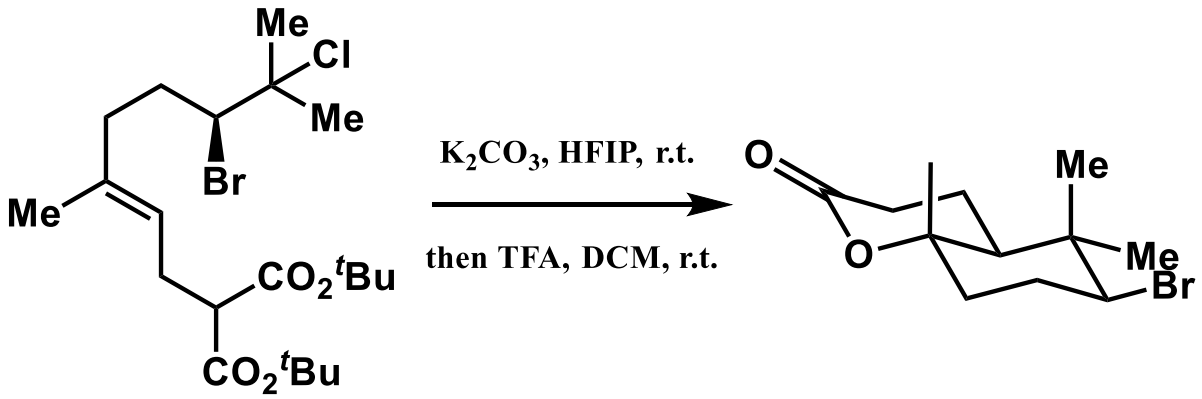
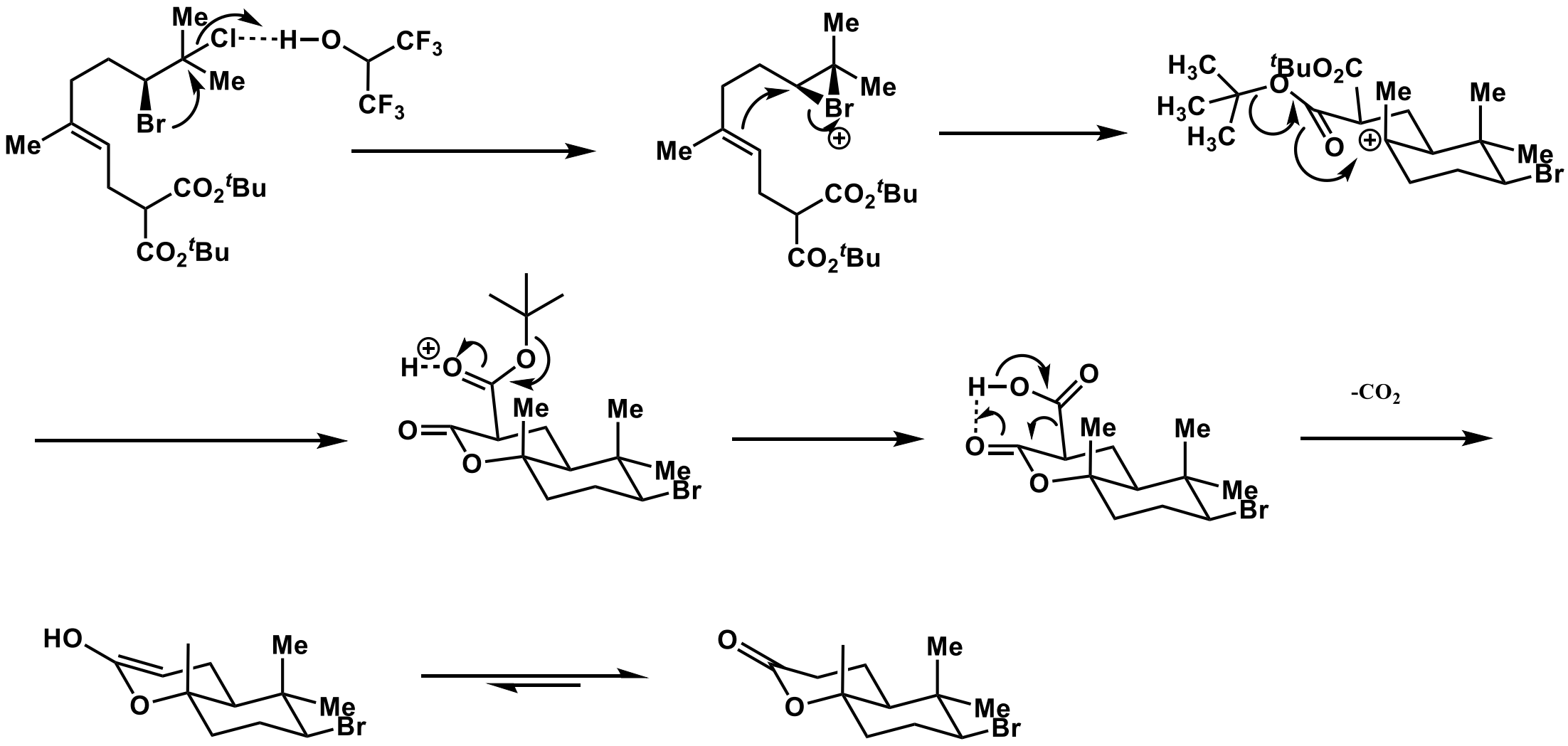

R1
O
O
OR2
Ph
I
+
R–OH
R1
O
H
O
R
I
Ph
OR2
R1
O
OH
OR2
Ph
I
•O–R
R8
R7
R10
R9
COR1
R9
CO2R2
R10
R8
R7
•O–R
OR
COR1
R9
CO2R2
R10
R8
R7
R–OH
R3
N
R4
OH
OR
R5
R6
N
OH
OR
t-BuOOH

5.



J. Am. Chem. Soc. **2017,** *139,* 13562-13569.


Me
Cl
H
O
CF3
CF3
Me
Br
Me
CO2tBu
CO2tBu
Me
Br
Me
Me
CO2tBu
CO2tBu
H3C
H3C
H3C
tBuO2C
O
O
Me
Me
Me
Br
H
O
O
O
Me
Me
Me
Br
H
O
O
O
Me
Me
Me
Br
-CO2
HO
O
Me
Me
Br
O
O
Me
Me
Br

Electronic Structure of Persistent Radicals: Nitroxides

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CHART 1

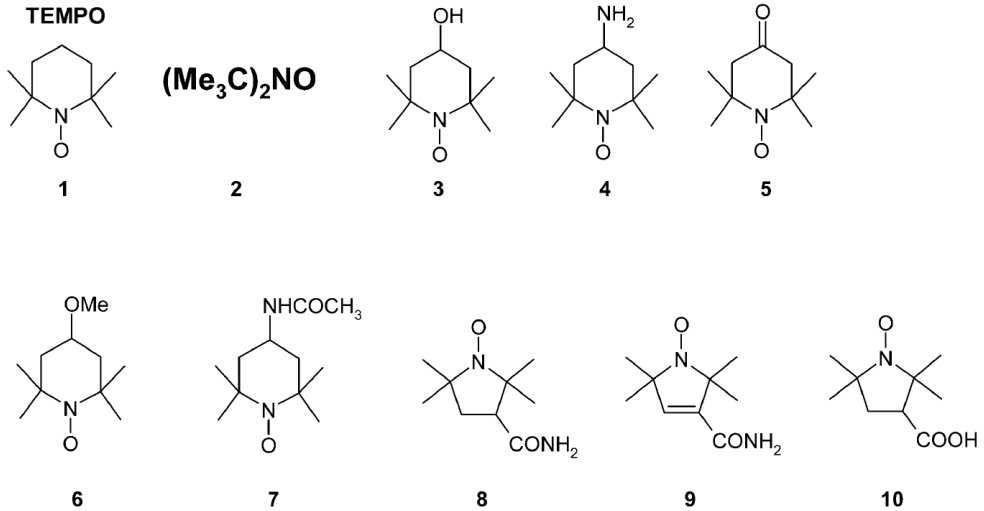

TABLE 2. Molecular Structure Parameters for Nitroxide Radicals, Calculated at the UB3PW91/6-31+G(d) Level and Compared to X-ray Diffraction Data (*) Where Available[a]

radical	N−O bond/Å	C−NO bond/Å	∠CNO/deg	∠C(NO)C/deg
1[18]	1.279, 1.283*	1.496, 1.488*	115.9, 116.7*	124.5, 123.6*
2	1.281	1.510	112.8	134.5
3	1.278	1.495	116	124.5
4	1.279	1.495	116	124.4
5[19]	1.278, 1.276*	1.497, 1.488*	115.7, 118*	124.5, 123.5*
6	1.278	1.495	115.9	124.4
7				
8[20]	1.269, 1.268*	1.482, 1.490*	122.2, 122.5*	115.8, 115.0*
9	1.268	1.481	122.2	114.8
10[21]	1.272, 1.280*	1.482, 1.481*	121.8, 122.0*	116, 116*

[a] Superscripts indicate references to X-ray diffraction studies.

普通的N-O键键长为1.46Å

Structure and Reactivity. Nitroxide radicals have delocalization energy for the unpaired electron of approximately 120 kJ/mol[2] which can be related to the resonance structures shown below.

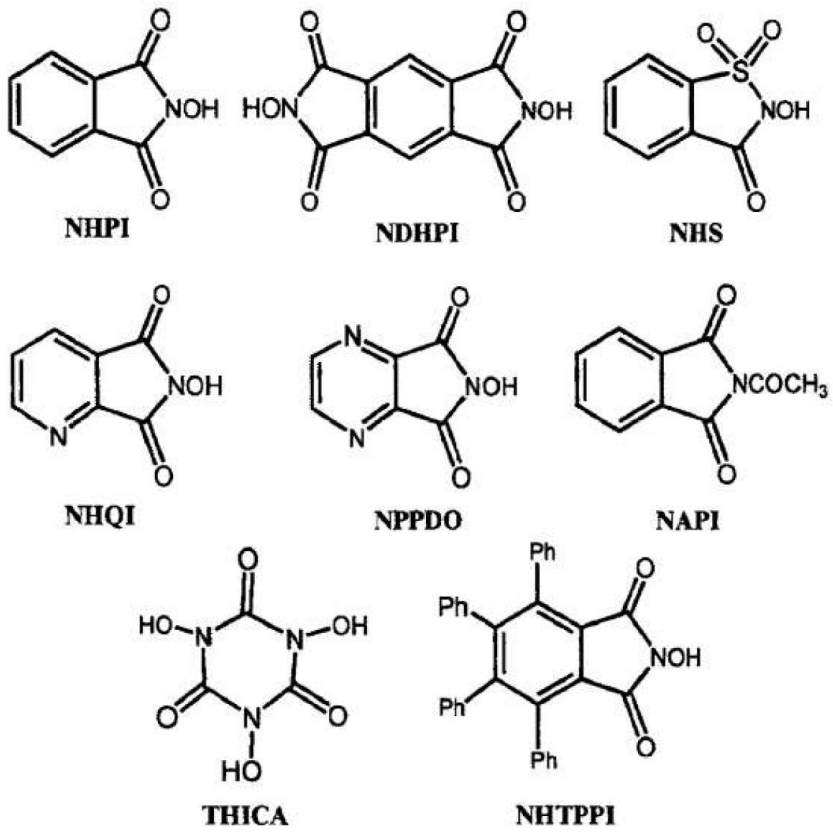

Figure **2.2** Common nitroxides used as catalysts in the oxidation of hydrocarbons

图 **2.2** 碳氢化合物氧化中常用的氮氧化物催化剂

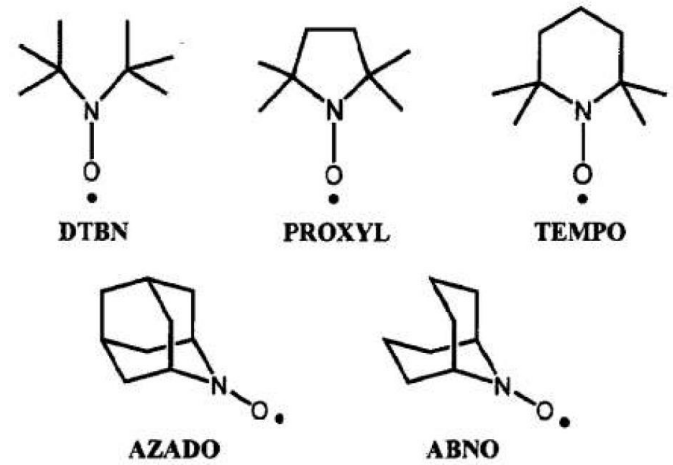

Figure **2.3** Series of persistent *N*-oxyl radicals used in the oxidation

图 **2.3** 氧化反应中常用的持久性氮氧自由基