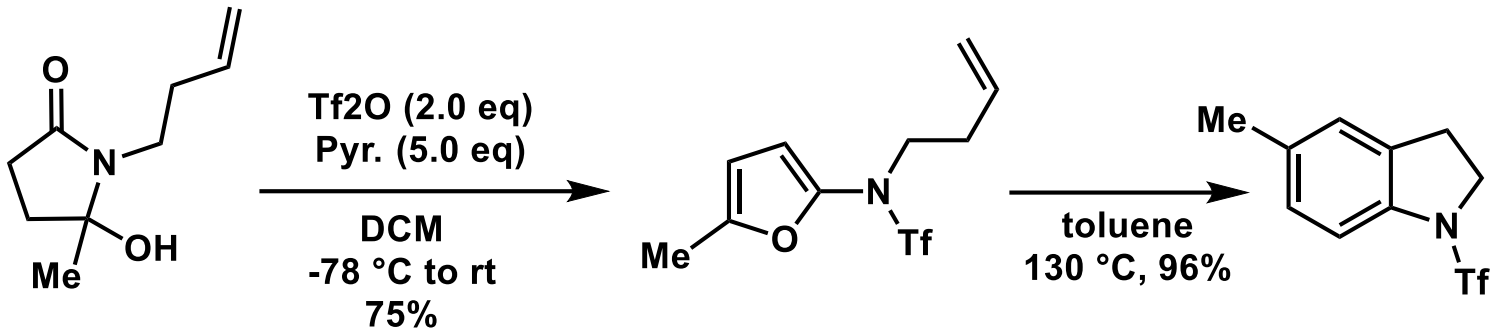
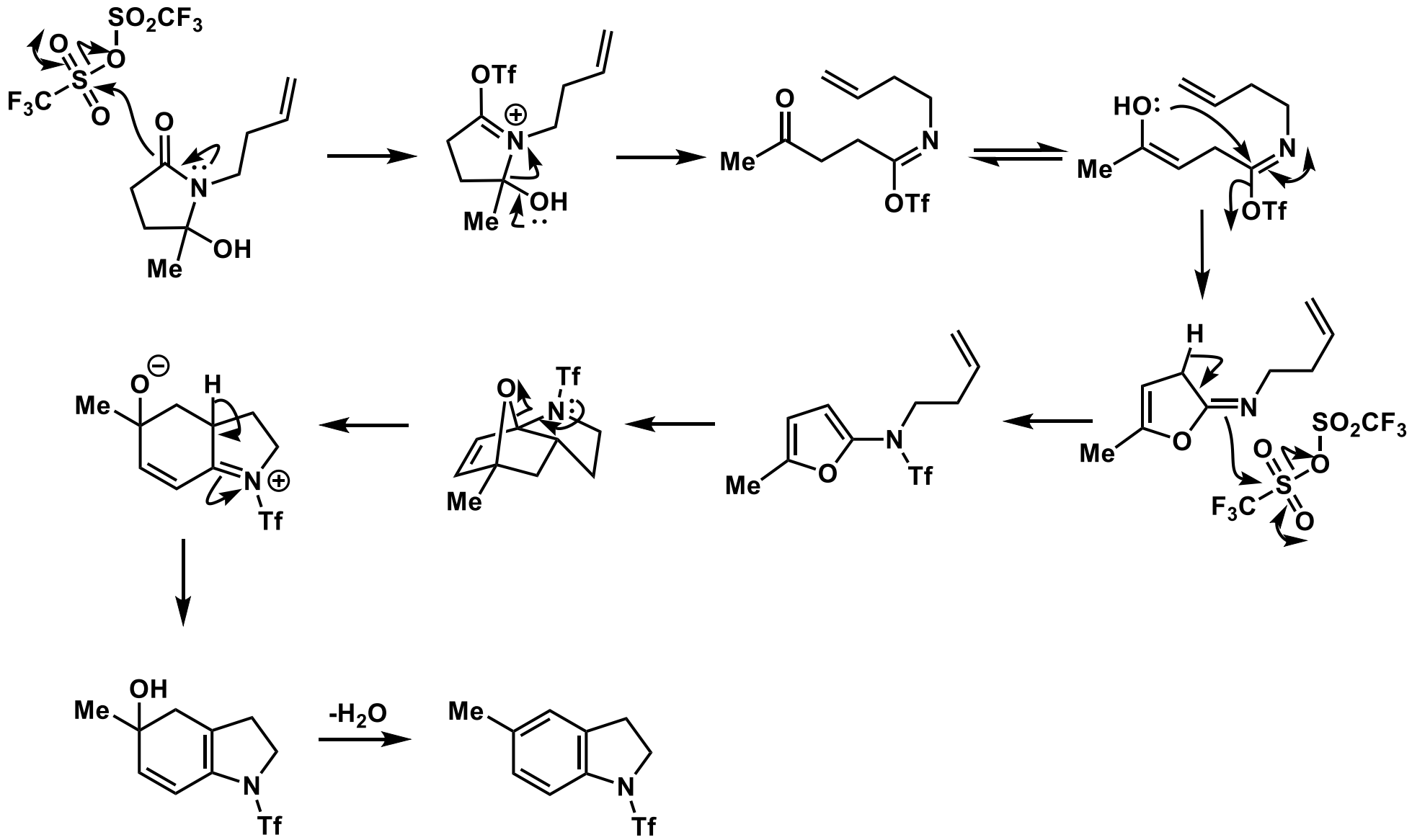
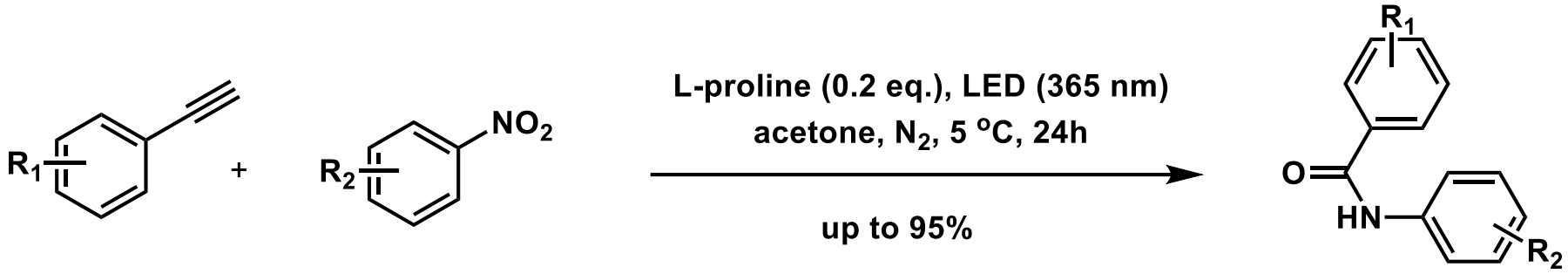
1.



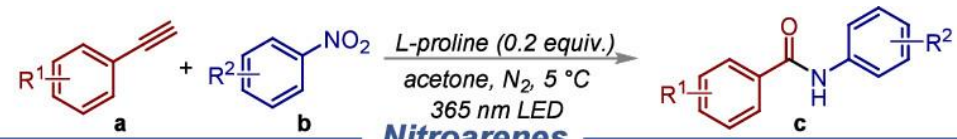
Org. Lett., **2003**, *5*, 189.


SO2CF3
F3C
OTf
Me
OH
HO:
H
Tf
-H2O

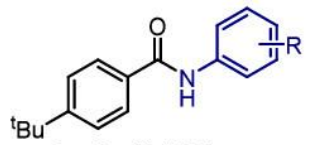
2.



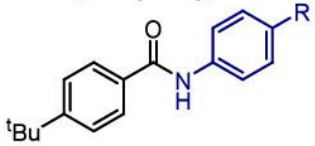
DOI: 10.1021/acs.orglett.4c02636.



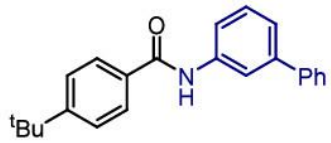
Nitroarenes



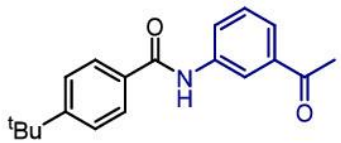
1c, R = H, 73%
2c, R = o-CH_3, 67%
3c, R = m-CH_3, 74%
4c, R = p-CH_3, 72%



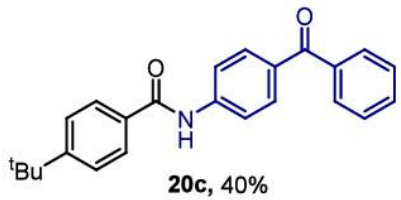
5c, R = ^{t}Bu, 61%
6c, R = CH_2CN, 43%
7c[b], R = OMe, 44%
8c[b], R = OAc, 49%
9c[b], R = OCF_3, 40%
10c, R = F, 47%
11c, R = Cl, 24%
12c, R = Br, 34%
13c, R = CHO, 80%
14c, R = CN, 54%
15c, R = CF_3, 77%
16c, R = COOH, 74%
17c, R = COOEt, 82%



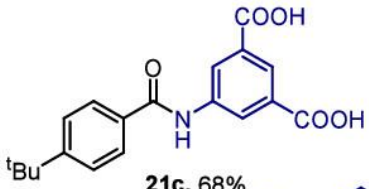
18c, 47%



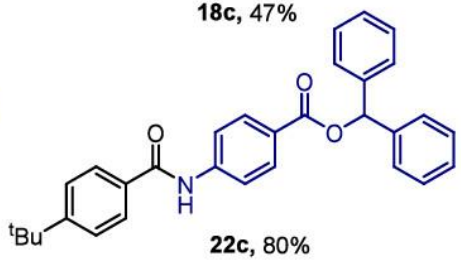
19c, 89%



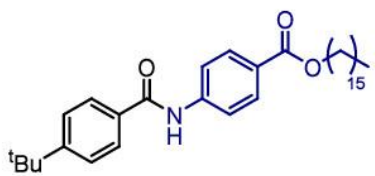
20c, 40%



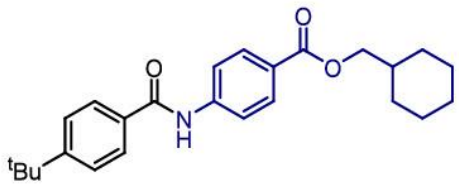
21c, 68%



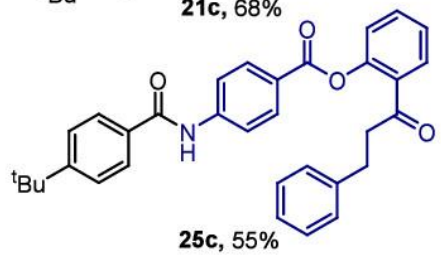
22c, 80%



23c, 63%

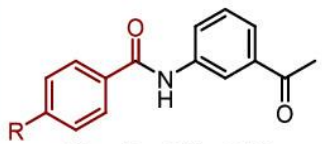


24c, 65%

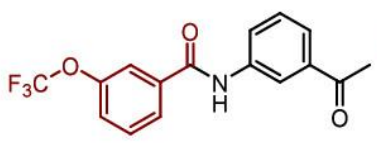


25c, 55%

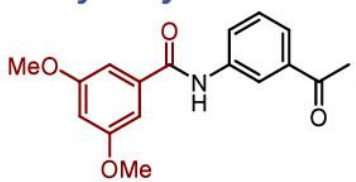
Aryl alkynes



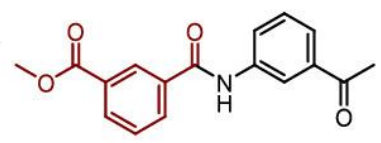
30c, R = CH_3 67%
31c, R = Et 79%
32c, R = ^{i}Pr 84%
33c, R = Ph 54%
34c, R = F 66%
35c, R = Cl 72%
36c, R = Br 73%
37c, R = CN 41%
38c, R = CF_3 49%



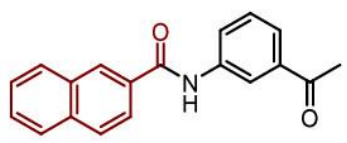
39c, 74%



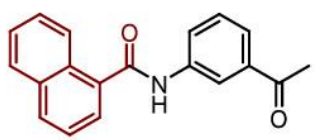
40c, 67%



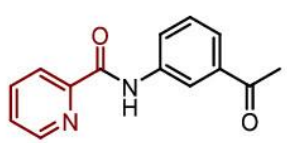
41c, 40%



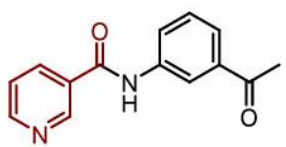
42c, 73%



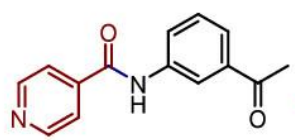
43c, 77%



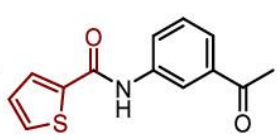
44c, 57%



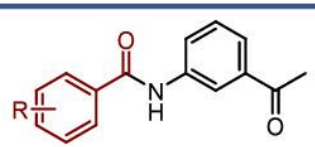
45c, 47%



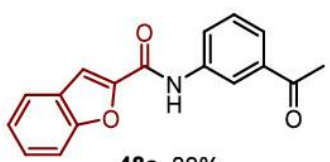
46c, 60%



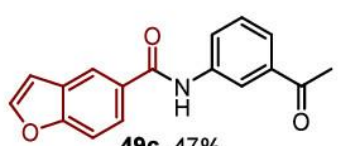
47c, 32%



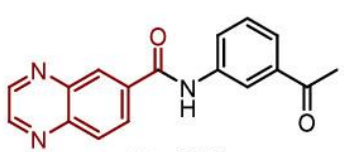
26c, R = H 72%
27c, R = o-OMe 83%
28c, R = m-OMe 69%
29c, R = p-OMe 87%



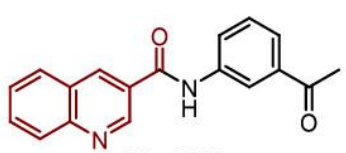
48c, 30%



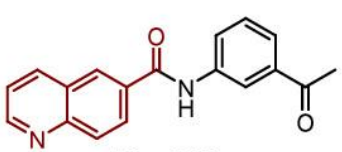
49c, 47%



50c, 53%



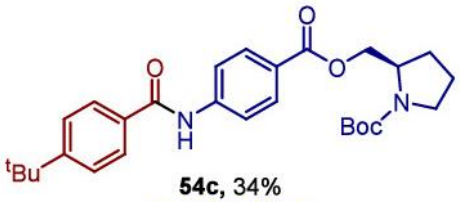
51c, 63%



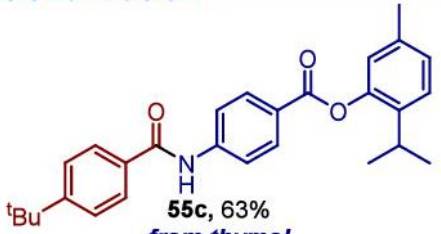
52c, 66%

Late-Stage Functionalization

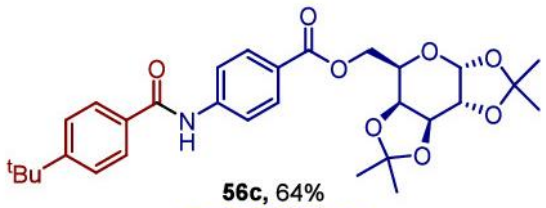
53c, 71%
from tyrosine



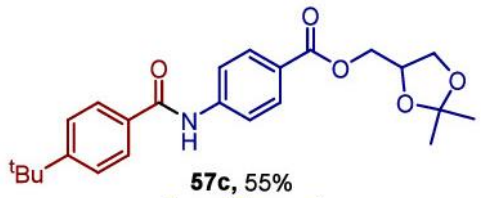
54c, 34%
from prolinol



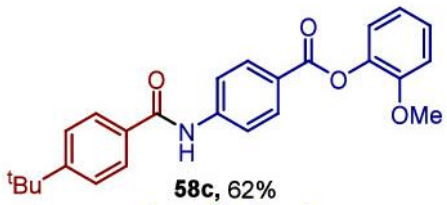
55c, 63%
from thymol



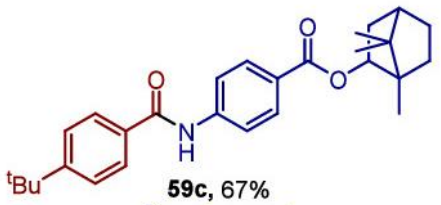
56c, 64%
from Galaclose



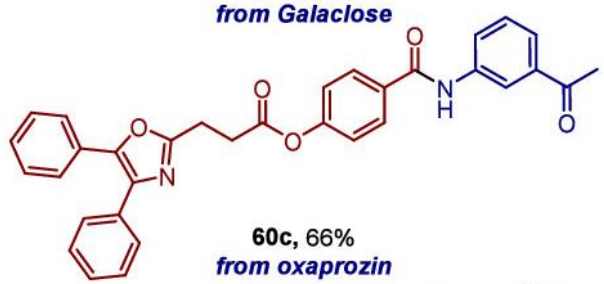
57c, 55%
from Glycerol



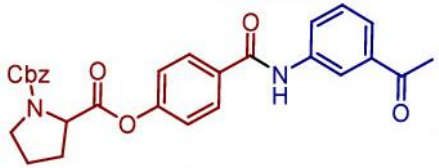
58c, 62%
from Guaiacol



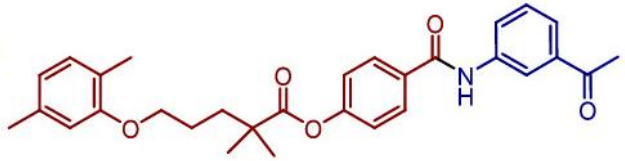
59c, 67%
from borneol



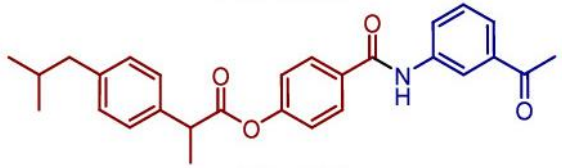
60c, 66%
from oxaprozin



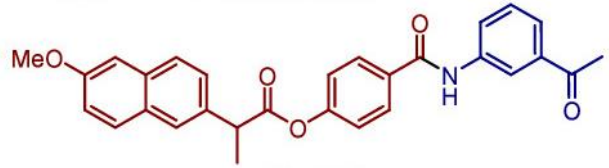
61c, 43%
from L-proline



62c, 69%
from gemfibrozil

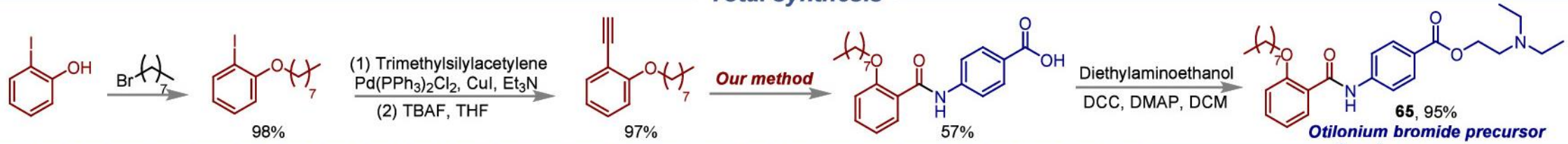


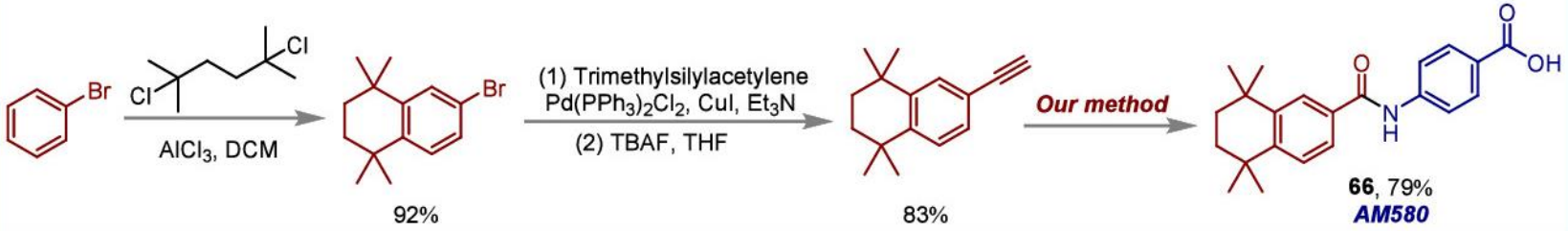
63c, 70%
from Ibuprofen



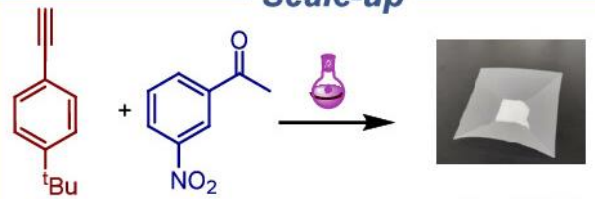
64c, 67%
from naproxen

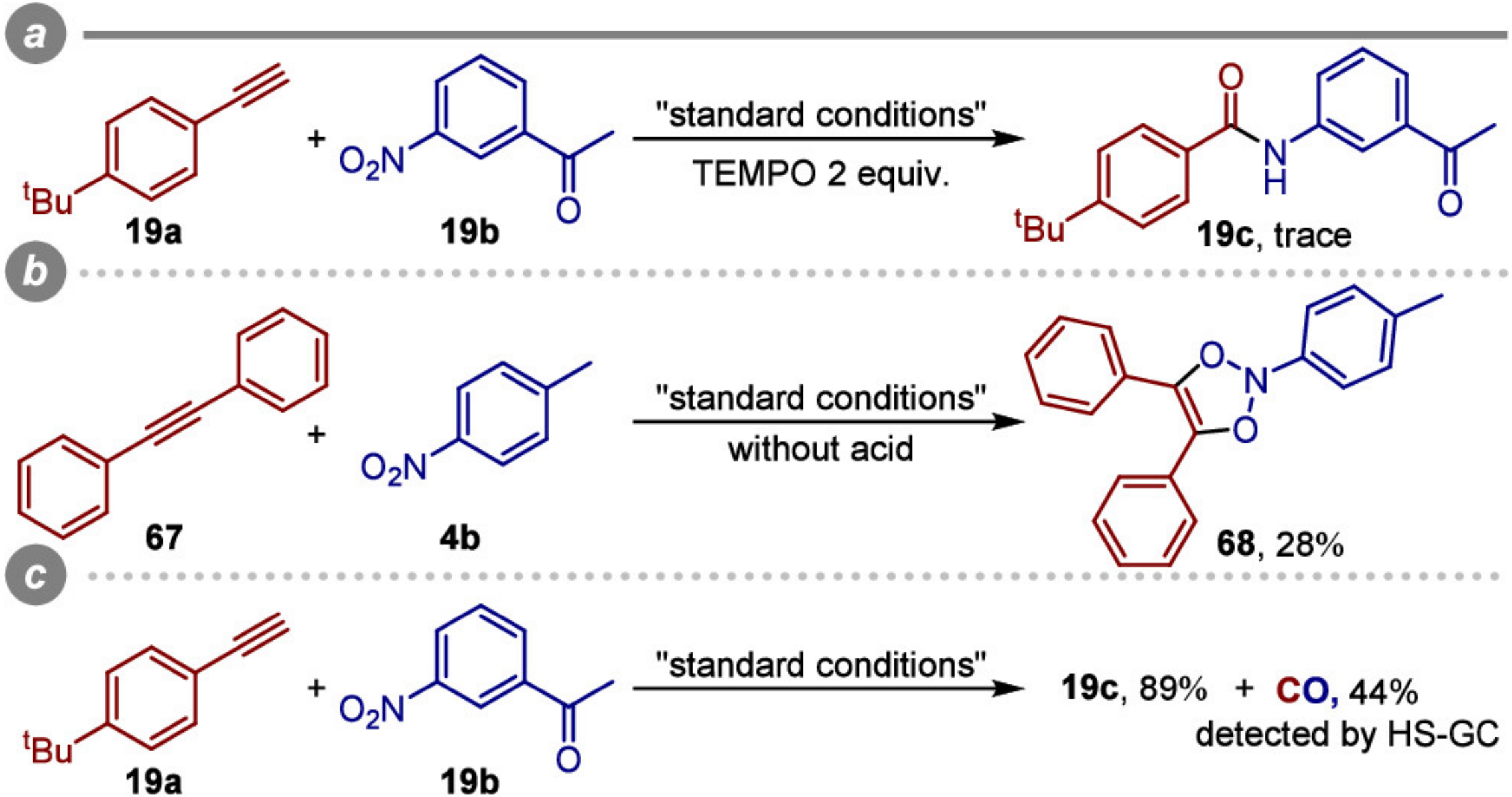
Total synthesis

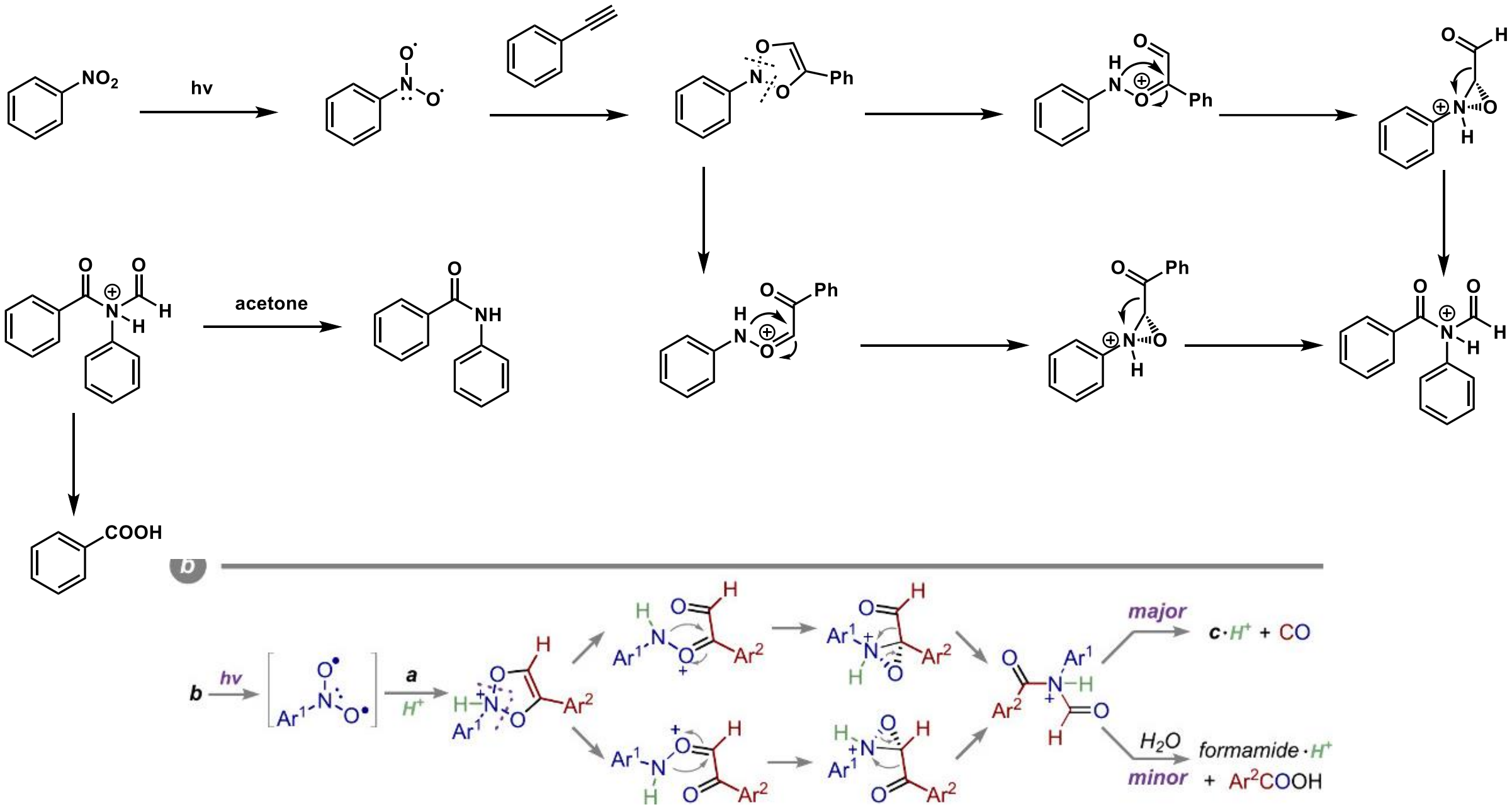


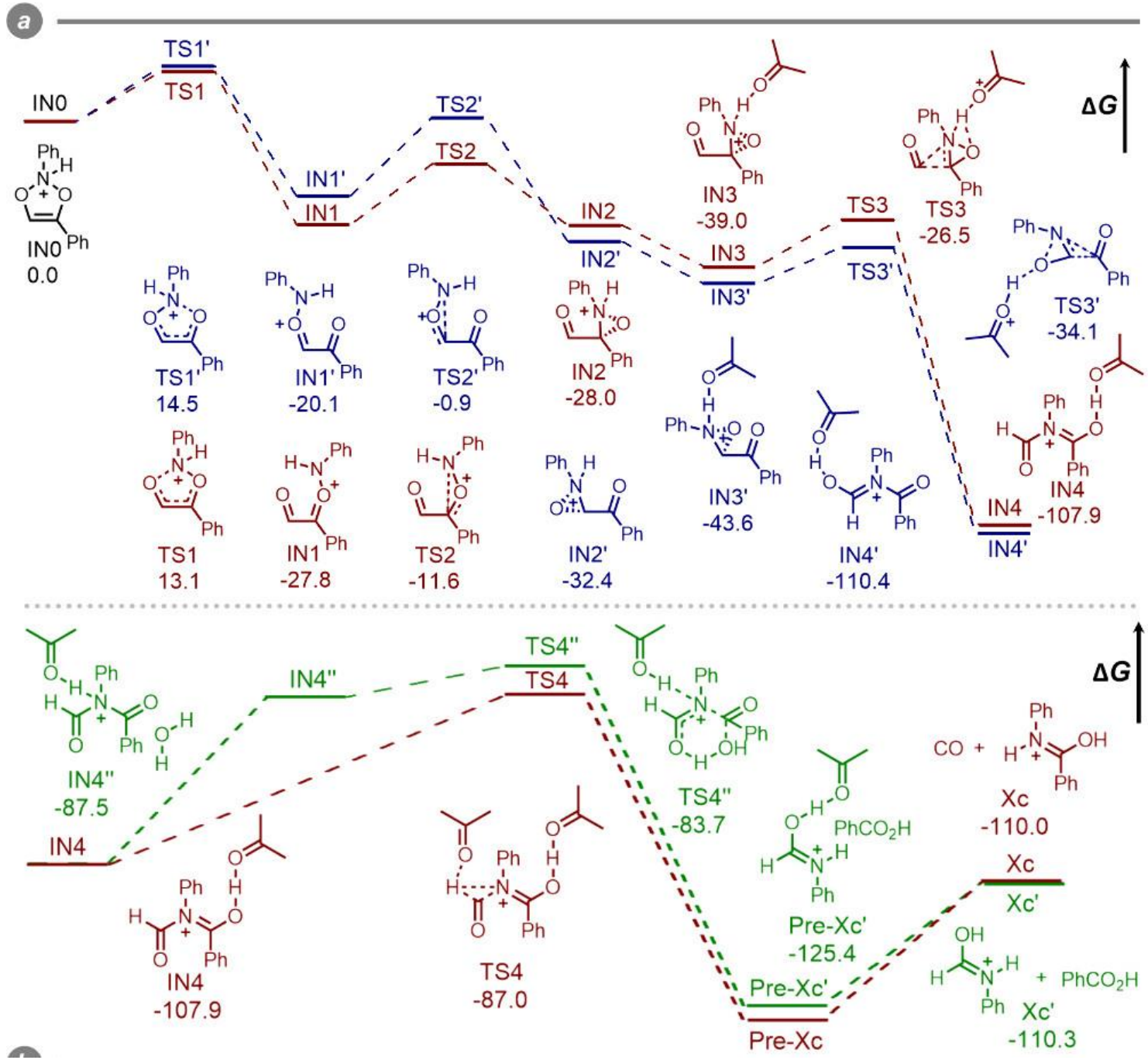


Scale-up




a
tBu
19a
+
O2N
19b
"standard conditions"
TEMPO 2 equiv.
O
N
H
O
tBu
19c, trace
b
67
+
O2N
4b
"standard conditions"
without acid
O
N
O
68, 28%
c
tBu
19a
+
O2N
19b
"standard conditions"
19c, 89% + CO, 44%
detected by HS-GC


hv
acetone
COOH
b
hv
a
H+
major
c·H+ + CO
H2O
minor
formamide·H+
+ Ar2COOH


a
TS1'
TS1
IN0
IN0
0.0
IN1'
IN1
TS2'
TS2
IN2
IN2'
IN3
IN3'
TS3
TS3'
IN4
IN4'
ΔG
TS1'
14.5
IN1'
-20.1
TS2'
-0.9
IN2
-28.0
IN3
-39.0
TS3
-26.5
TS3'
-34.1
IN4
-107.9
TS1
13.1
IN1
-27.8
TS2
-11.6
IN2'
-32.4
IN3'
-43.6
IN4'
-110.4
IN4''
TS4''
TS4
ΔG
IN4''
-87.5
IN4
IN4
-107.9
TS4
-87.0
TS4''
-83.7
Pre-Xc'
-125.4
Pre-Xc
Xc
Xc'
CO +
Xc
-110.0
+ PhCO2H
Xc'
-110.3