« Sodium chlorite beyond Pinnick oxidation »

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« Reduction of azides to primary amines »

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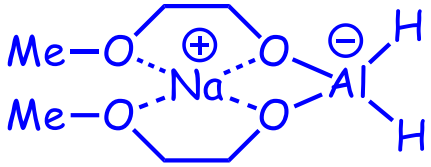
CHEMATEK

CEISAM
Chimie et Interdisciplinarité Synthèse, Analyse, Modélisation



SDMA (Synhydrid, Red-Al, Vitride): A Chemoselective and Safe Solution for Reduction Reactions

Chiara Colletto, Arnaud Tessier, Jacques Lebreton

ORGANIC PROCESS RESEARCH & DEVELOPMENT
OPR&D
Accepted, ID op-2025-00114m.

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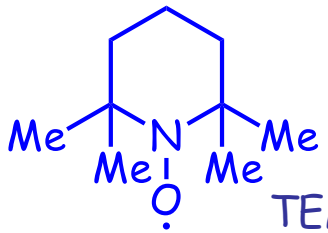
" Oxidation of alcohols to the corresponding carbonyl derivatives: keep the TEMPO up ! "

AtlanChimPharma Scientific Letter, 7, July, 2012.



TEMPO
(2,2,6,6-Tetramethylpiperidinyloxy)

https://www.atlanchimpharma.com/fr/

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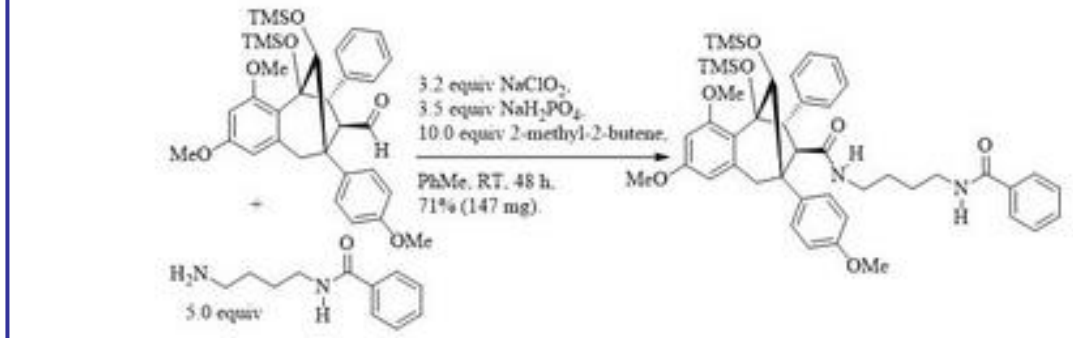
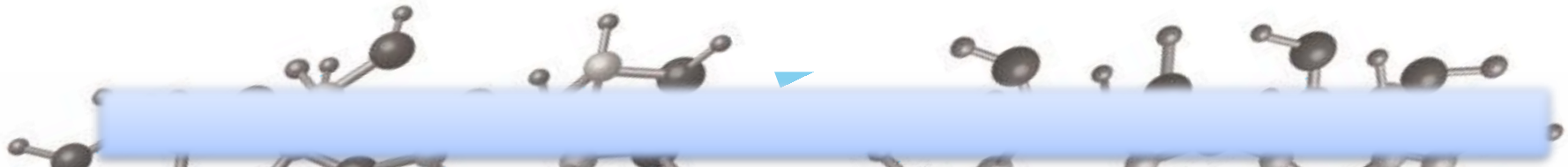
LinkedIn



#TheMinuteOfChemistry "Oxidative amidation with sodium chlorite"

Summary



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Summary

Generalities

Sodium chlorite

CAS [7758-19-2]

Molecular weight: 90.44 g

Melting-point: decomposes at 180-200 °C.

Soluble in water: 390 g/l at 17 °C.

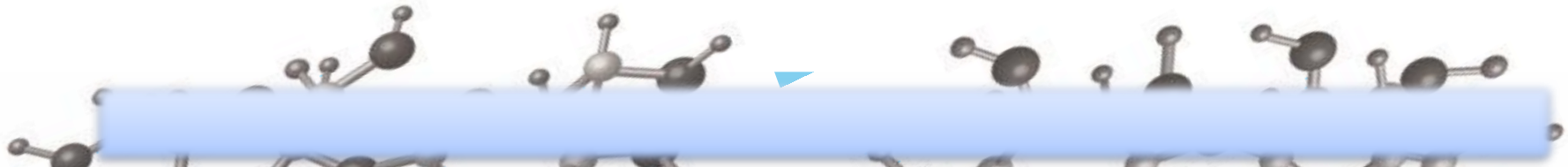
1 kg ~ 150 €

➡ Stable in the absence of oxidizable organic material.

➡ Can explode in response to physical shock.*

*N. Langerman, *ACS Chem. Health Saf.* **2021**, *28*, 402-409.

Summary



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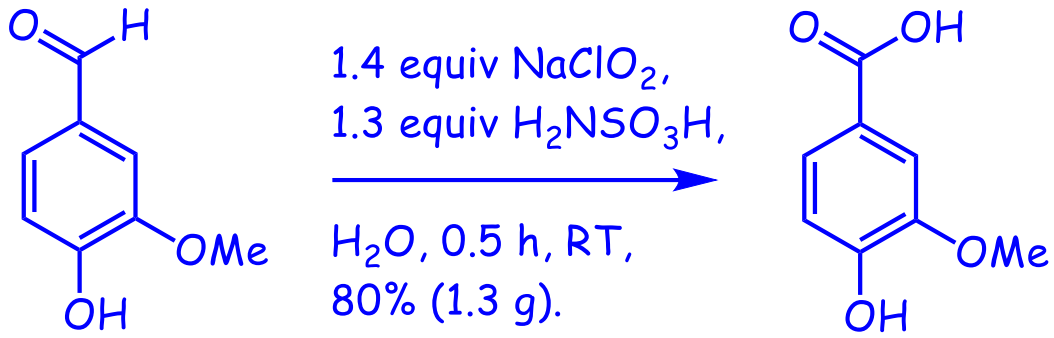
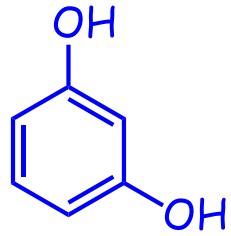
Pinnick oxidation



Vanillin

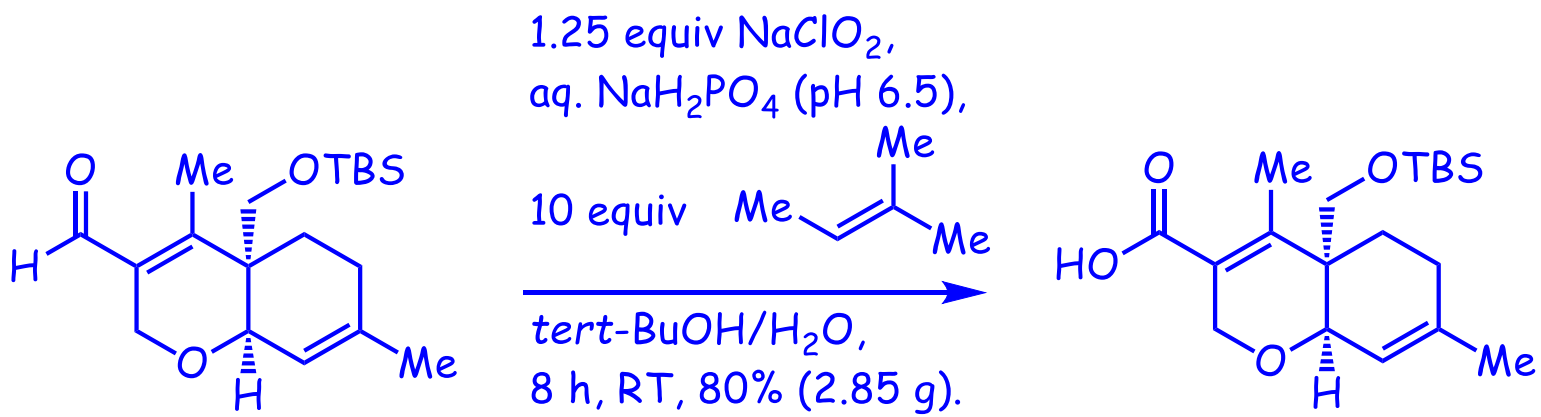
Vanillinic acid

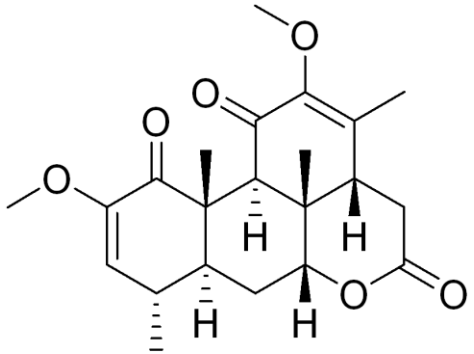


Resorcinol

B. O. Lindgren, T. Nilsson, *Acta Chem. Scand.* **1973**, *27*, 888-890.

Pinnick oxidation



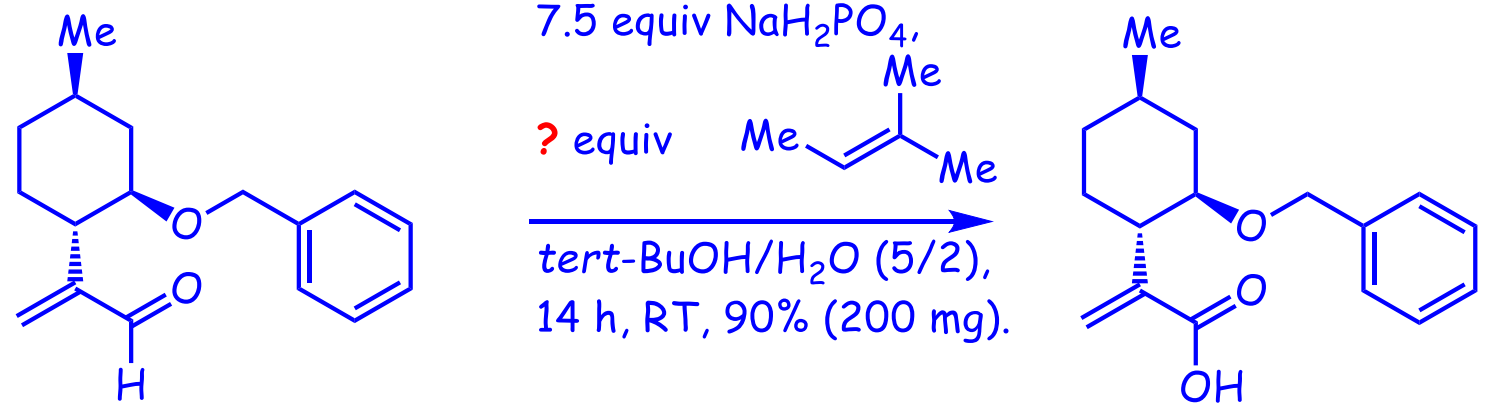


Quassinoids

G. A. Kraus, M. J. Taschner , *J. Org. Chem.* **1980**, *45*, 1175-1176.

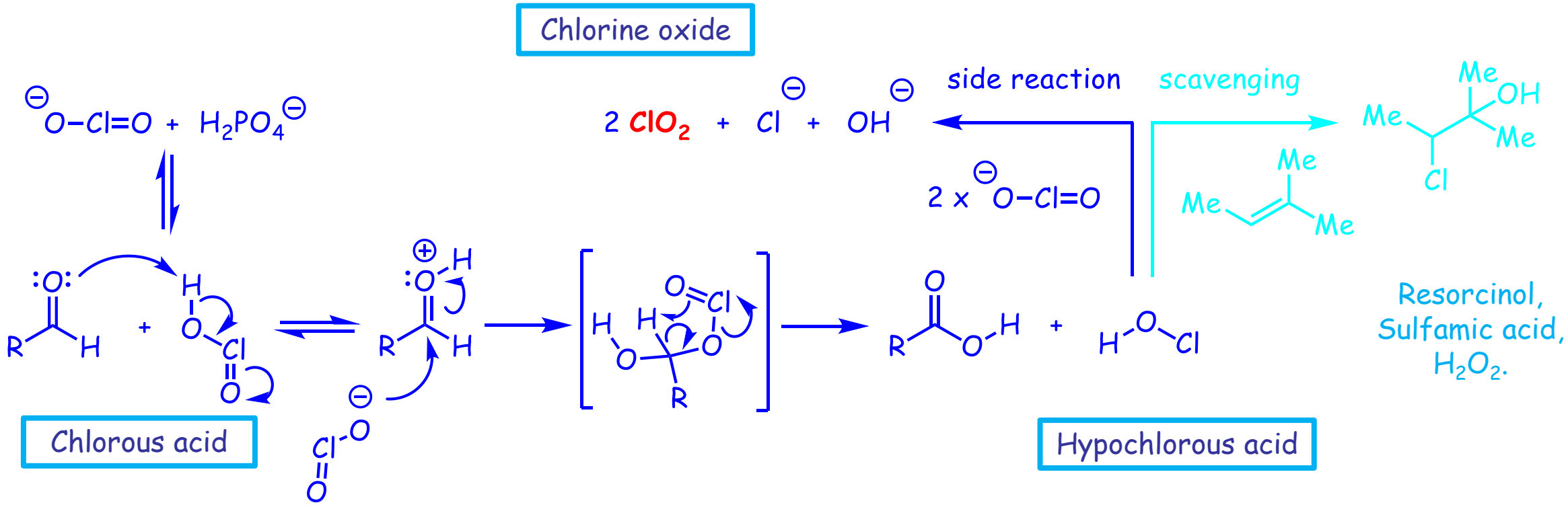
Pinnick oxidation

Harrold W. Pinnick
(1947-2021)



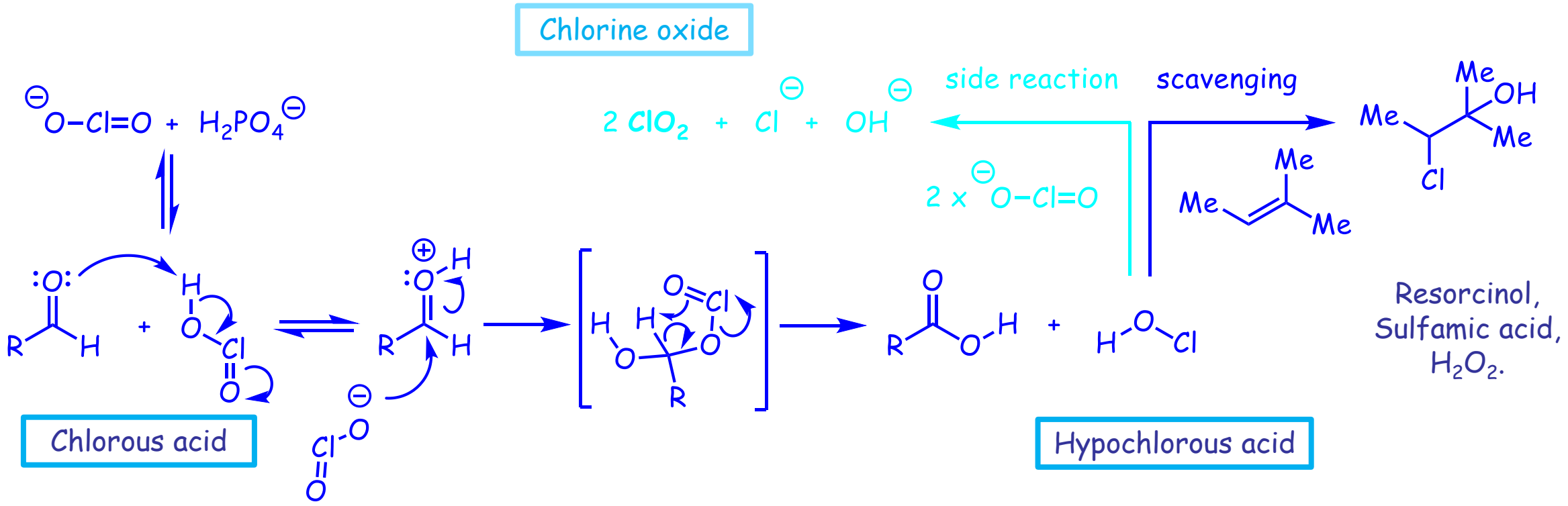
P. S. Bal, W. E. Childers, H. W. Pinnick, *Tetrahedron* **1981**, *37*, 2091-2096.

Pinnick oxidation



A. A. Hussein et al., R. Soc. open sci. **2020**, 7, 191568.

Pinnick oxidation

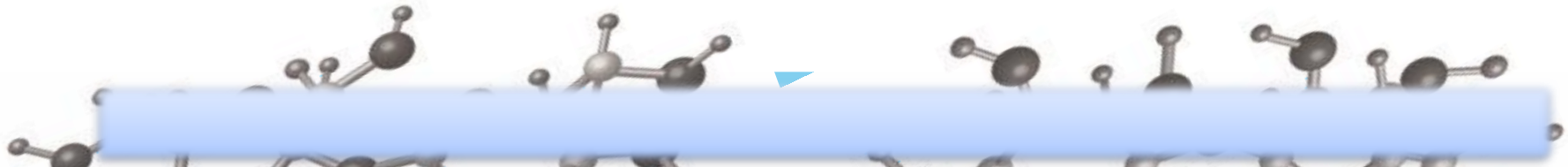


A. A. Hussein et al., R. Soc. open sci. **2020**, 7, 191568.

Pinnick oxidation

Typical procedure

Aldehyde in *tert*-BuOH in combination with another solvent such as THF or H_2O, large excess of the scavenger followed by dropwise addition of the aqueous solution of sodium dihydrogen phosphate buffer and then sodium chlorite at room temperature.



Pinnick oxidation

Key points

To ensure a constant pH value (~6.5), the use of several equivalents of sodium dihydrogen phosphate is recommended.

Due to the instability of the sodium chlorite in acidic medium in the presence of metal salts, the use of a steel needle for the addition of the oxidant should be avoided.

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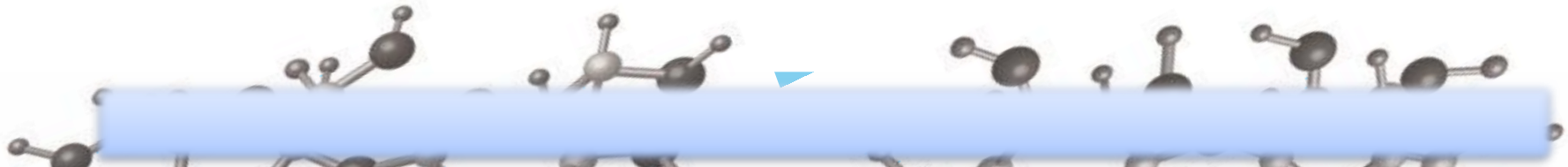
Advantages

Stereocenters at the a-position of aldehydes are unaffected.

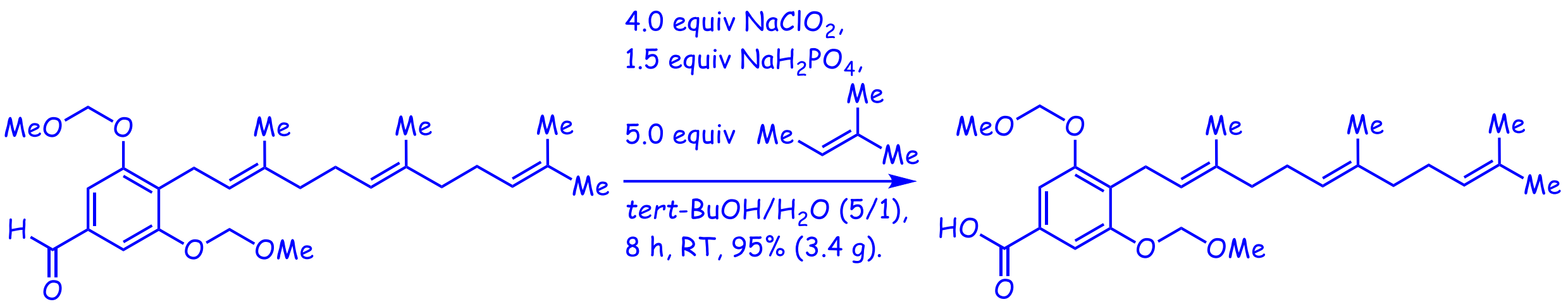
Excellent functional group tolerance.

Good reactivity with sterically hindered aldehydes.

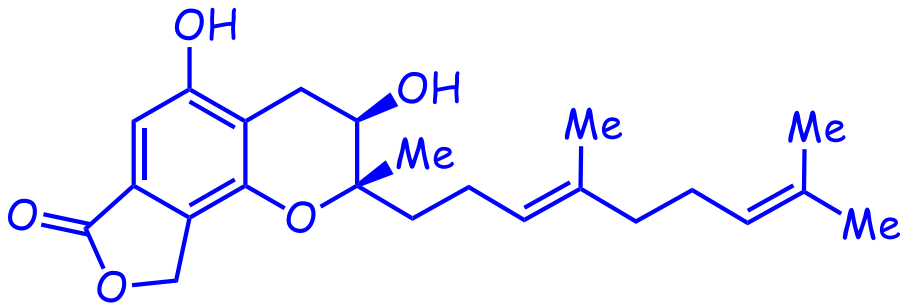
Relatively low cost of the reagents.



Pinnick oxidation



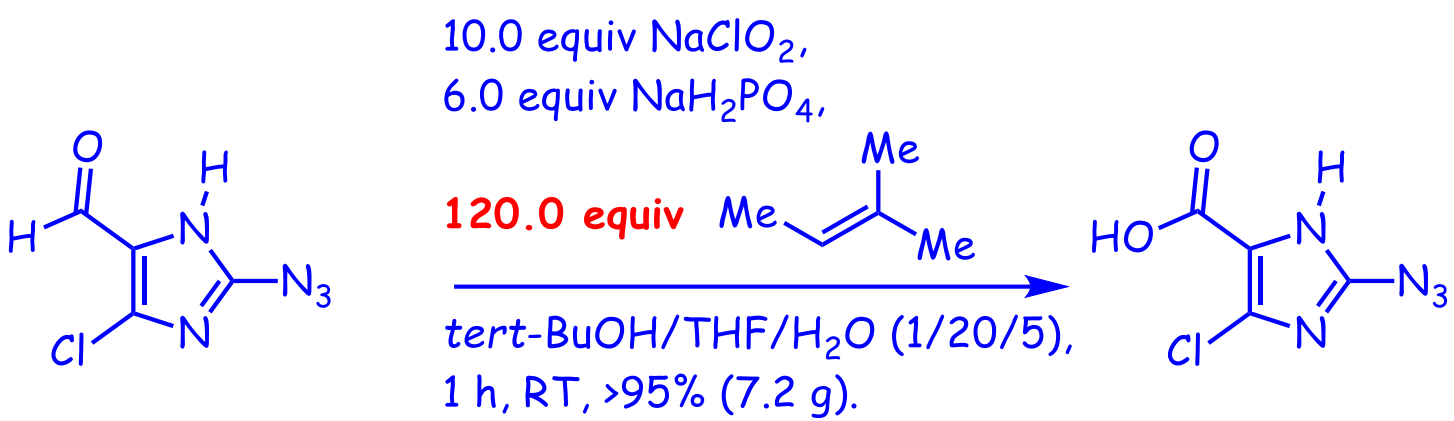
Stachybotrys microspora

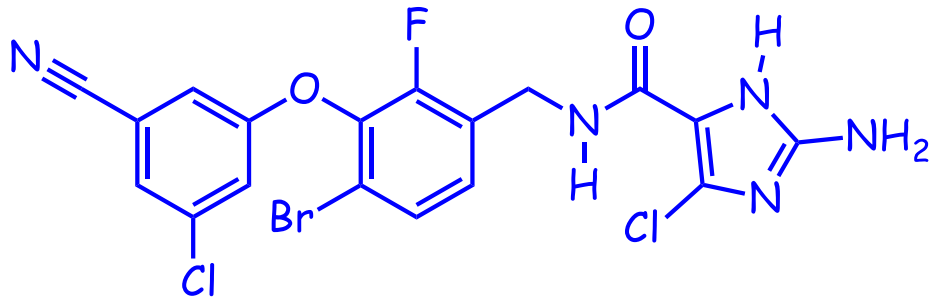


NG-121

M. Singh, P. Argade, *Synthesis* **2012**, *44*, 3797-3804.

Pinnick oxidation

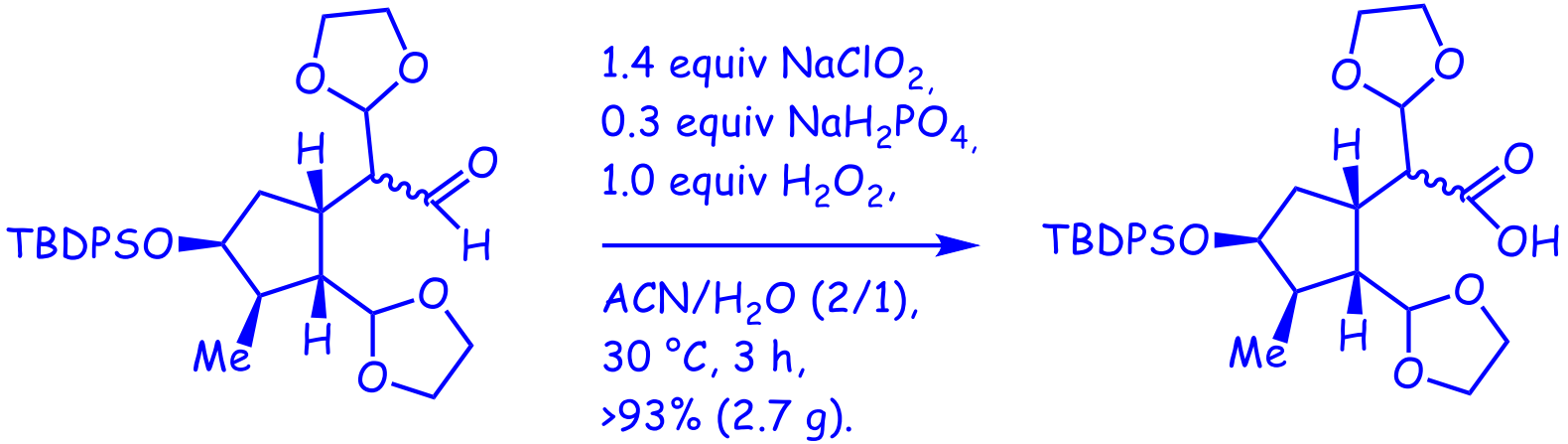


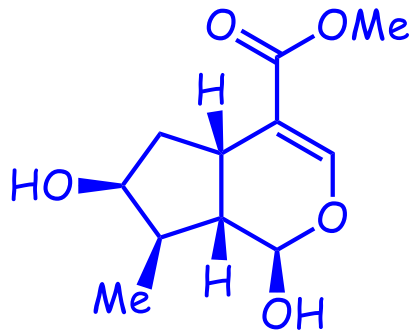


Non-nucleoside inhibitors of HIV-1 reverse transcriptase

A. Peat *et al.*, *J. Med. Chem.* **2012**, *55*, 10601-10609.

Pinnick oxidation



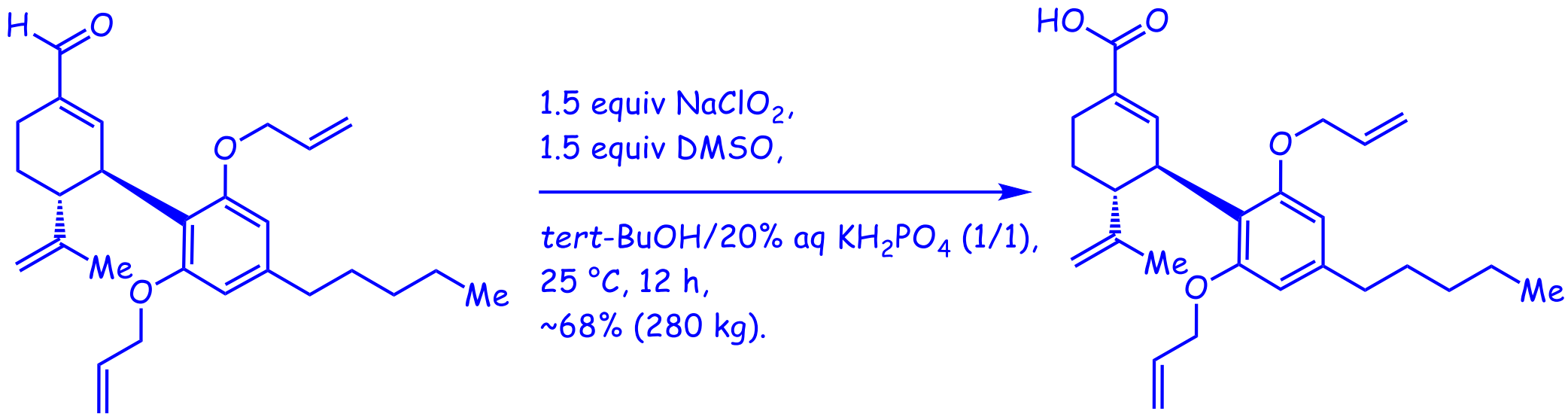


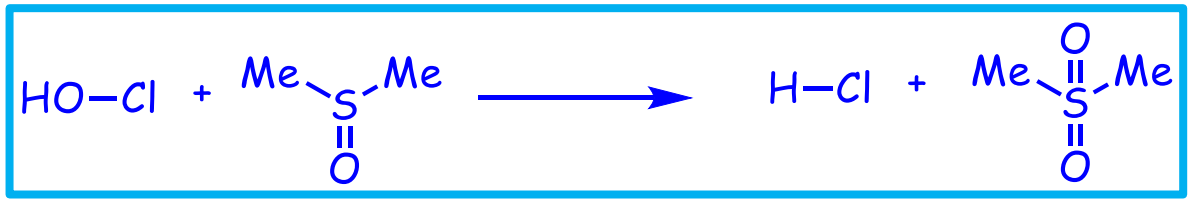
Loganetin

E. Dalcanale, F. Montanari, *J. Org. Chem.* **1986**, *51*, 567-569.

B. Wang *et al.*, *J. Org. Chem.* **2023**, *88*, 5844-5851.

Pinnick oxidation





H. Straker *et al.*, *Org. Process Res. Dev.* **2024**, *28*, 2708-2723.

Summary

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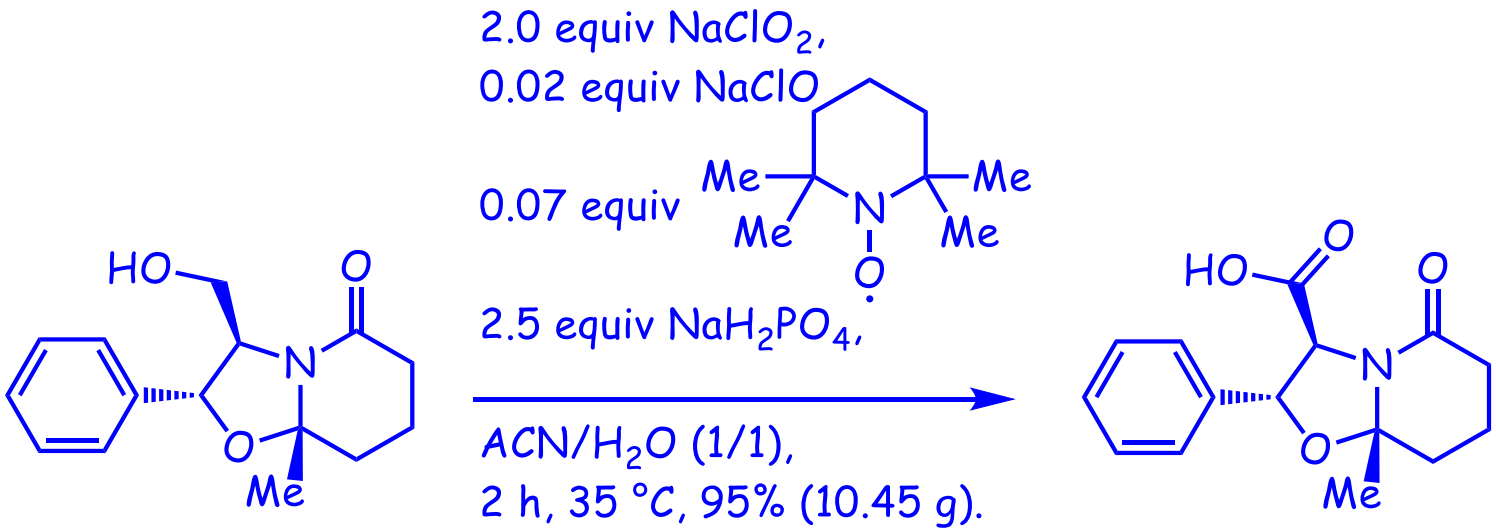
One-pot oxidation of RCH_2OH to RCO_2H

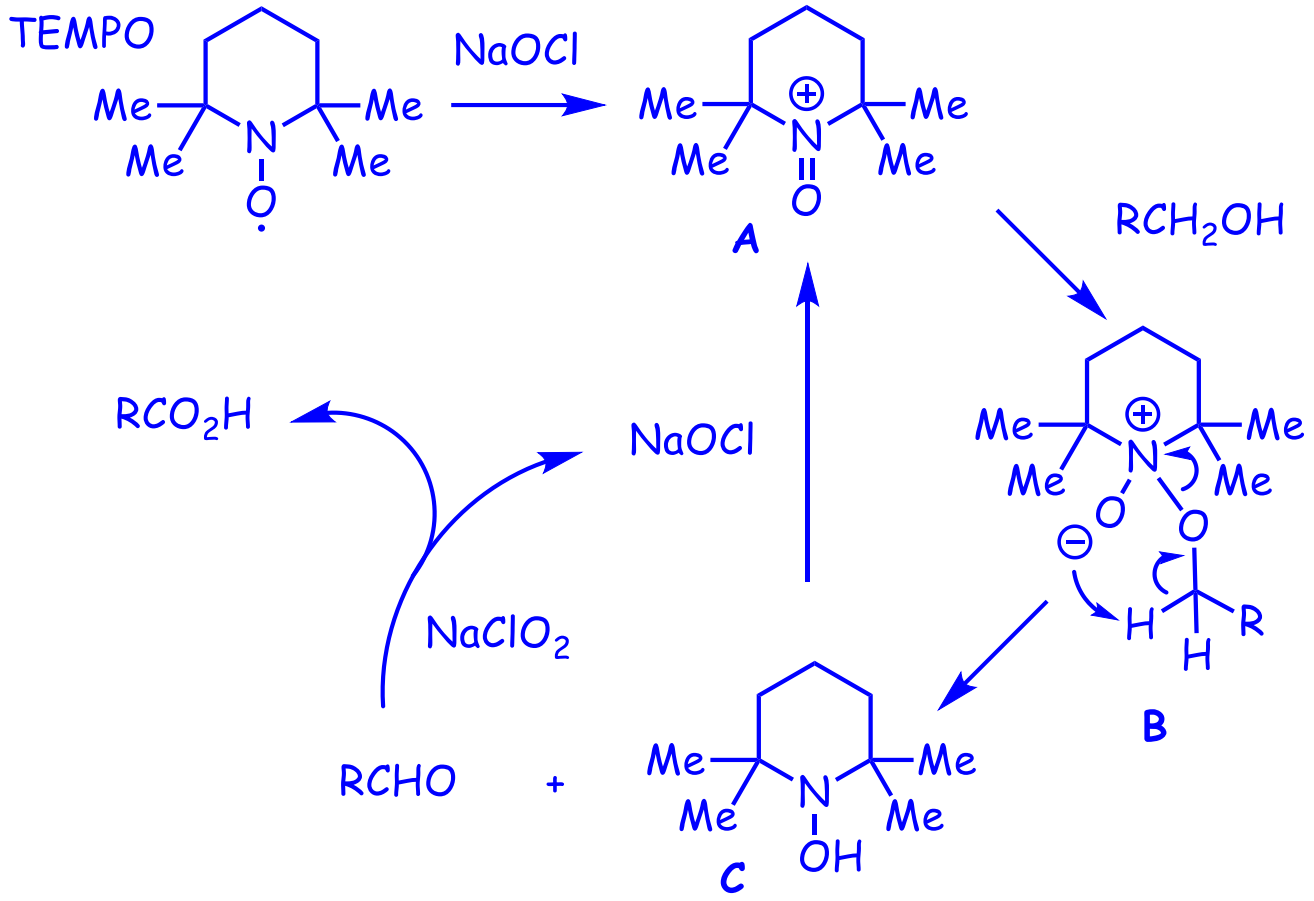
Typical procedure



M. Zhao *et al.*, *J. Org. Chem.* **1999**, *64*, 2564-2566.

One-pot oxidation of RCH_2OH to RCO_2H

Catalytic cycle for the TEMPO/ NaOCl-catalyzed oxidation



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One-pot oxidation of RCH_2OH to RCO_2H

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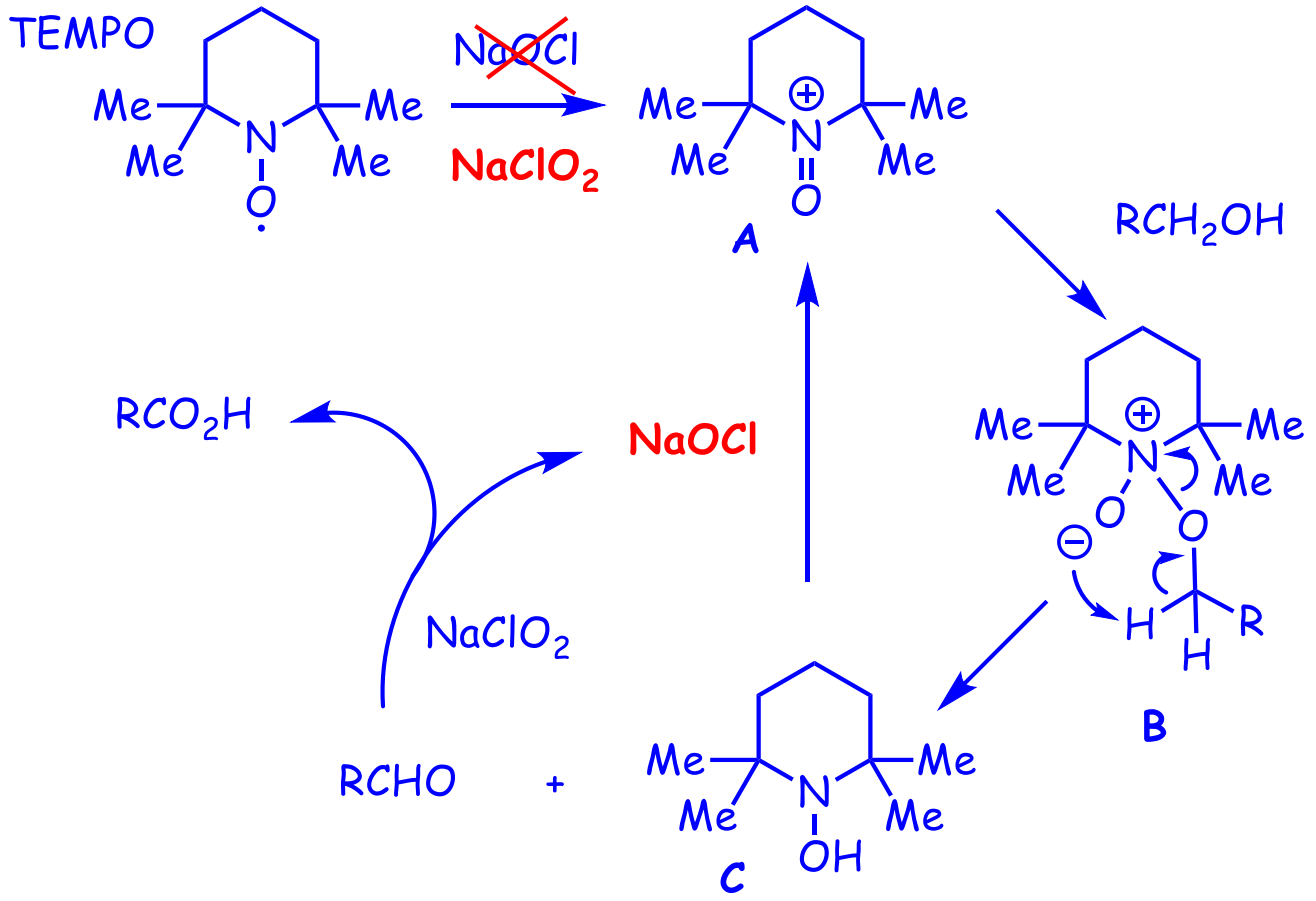
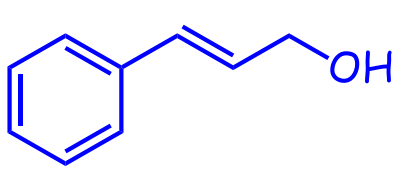
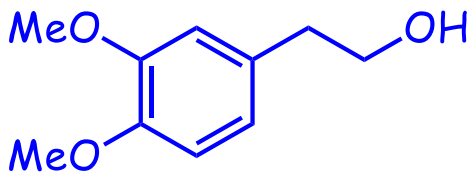


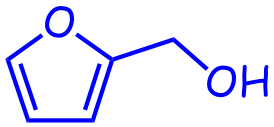
M. Zhao *et al.*, *J. Org. Chem.* **1999**, 64, 2564-2566.

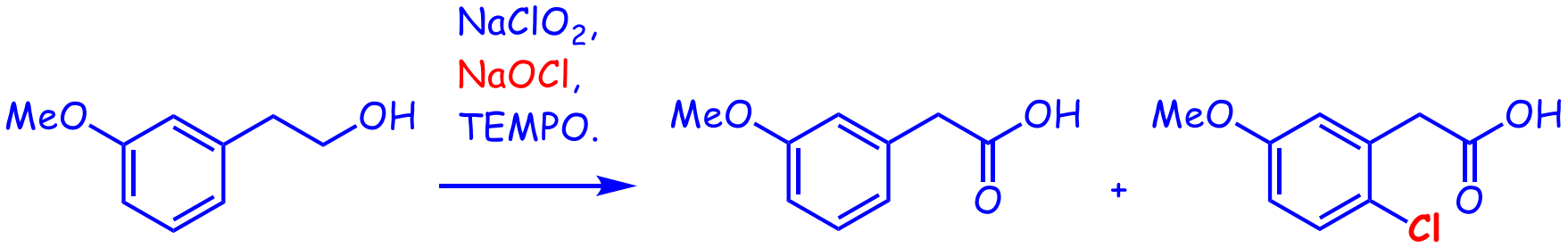
One-pot oxidation of RCH_2OH to RCO_2H

Limitations



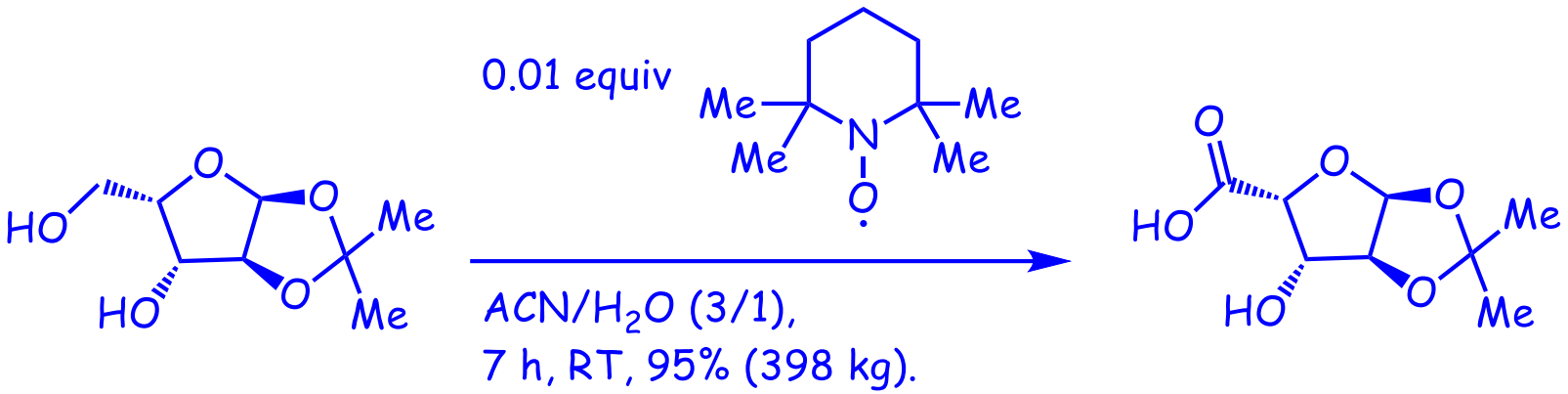




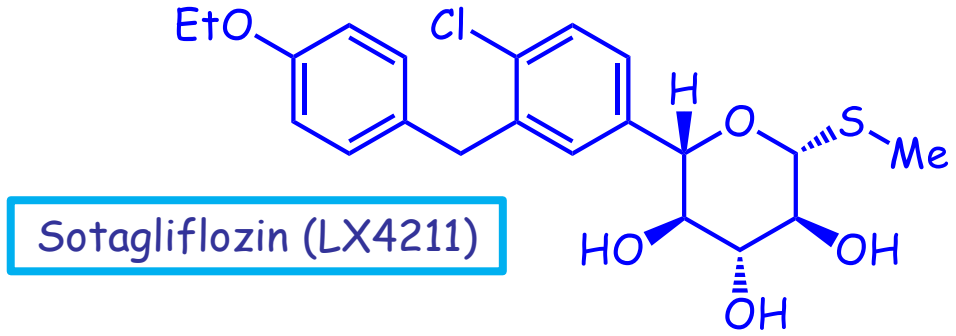


M. Zhao *et al.*, *J. Org. Chem.* **1999**, *64*, 2564-2566.

One-pot oxidation of RCH_2OH to RCO_2H



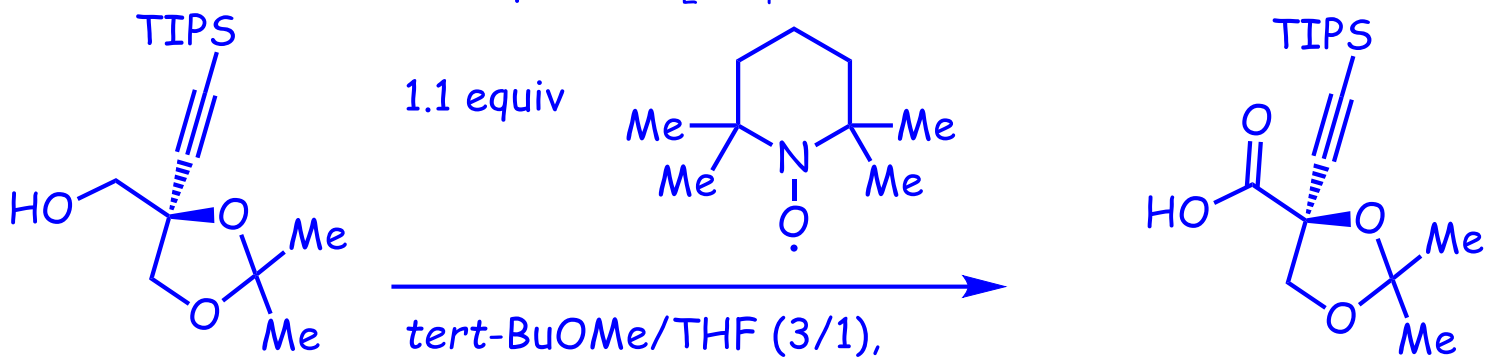
Isolated as crystalline morpholine salt



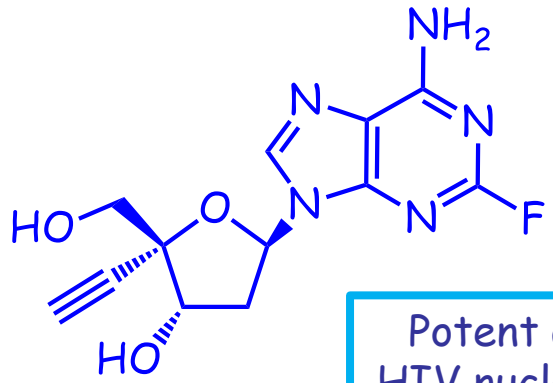
Sotagliflozin (LX4211)

M. M. Zhao *et al.*, *Org. Process Res. Dev.* **2020**, *24*, 2689-2701.

One-pot oxidation of RCH_2OH to RCO_2H



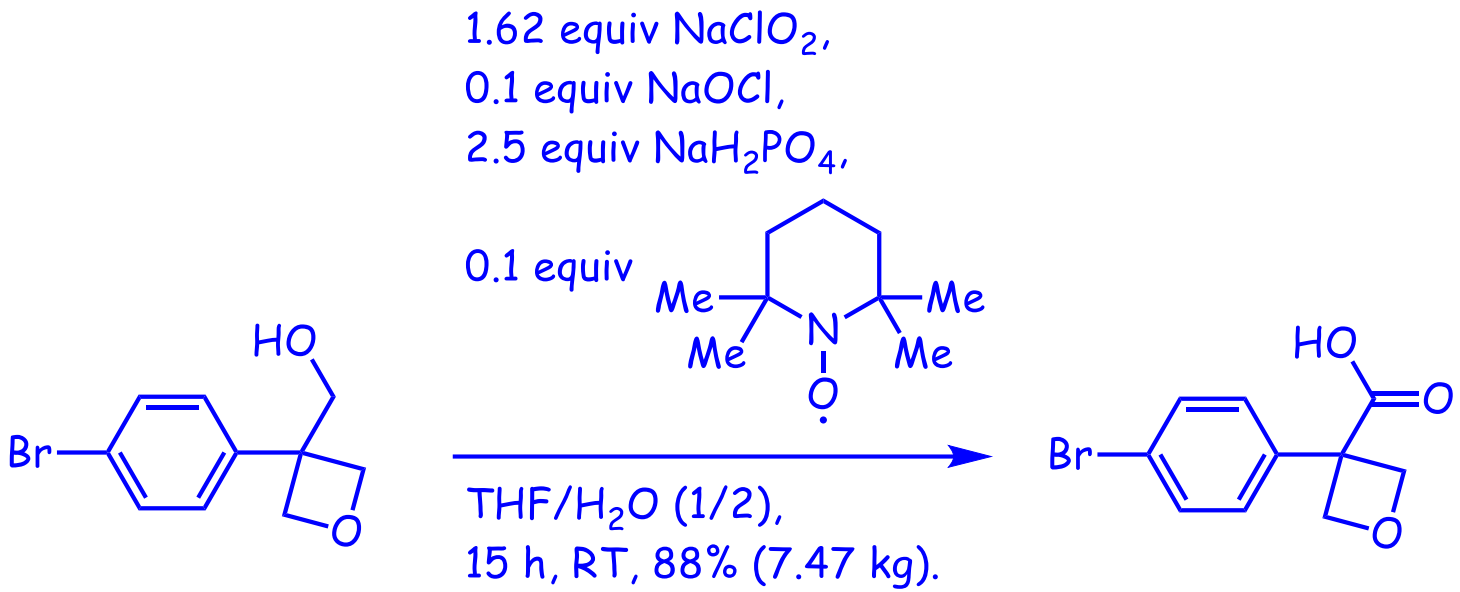
TIPS = $(iso\text{-}Pr)_3Si$



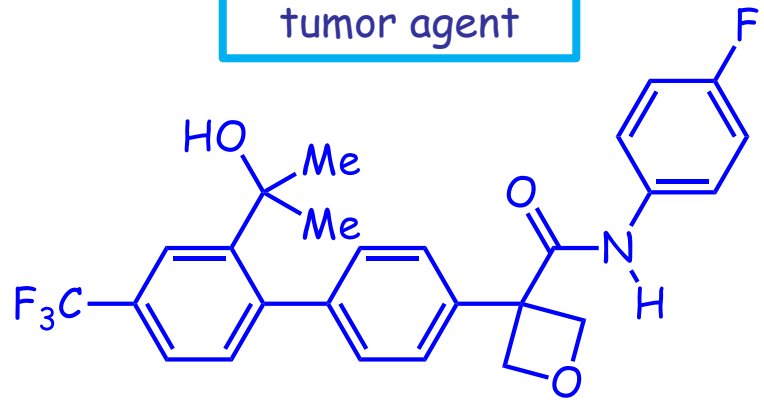
Potent anti-HIV nucleoside

M. McLaughlin *et al.*, *Org. Lett.* **2017**, *19*, 926-929.

One-pot oxidation of RCH_2OH to RCO_2H



Potent anti-tumor agent



D. Li, D. L. Sloman *et al.*, *J. Med. Chem.* **2022**, *65*, 6001-6016.

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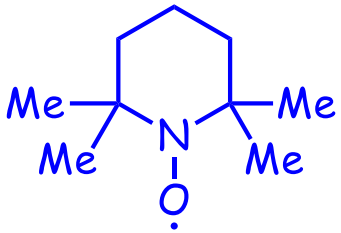
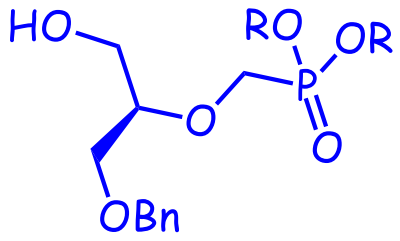
One-pot oxidation of RCH_2OH to RCO_2H

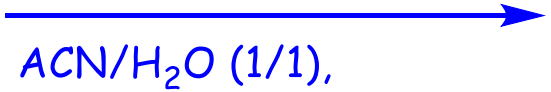
2.0 equiv $NaClO_2$,
0.5 equiv NaOCl,
2.0 equiv NaH_2PO_4,

0.1 equiv

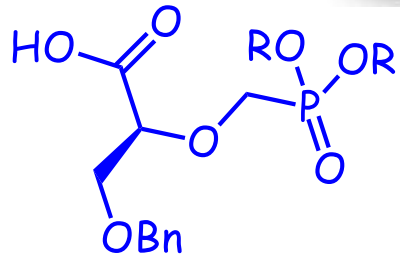


R = *iso*-Pr

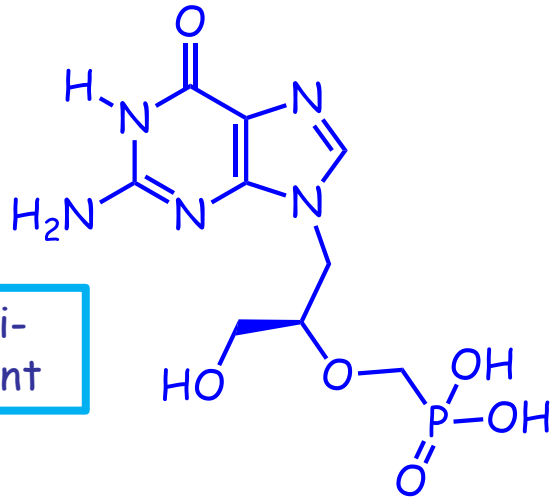




ACN/H_2O (1/1),
48 h, 40 °C, 88% (13.2 g).



Potent anti-malaria agent



L. W. Guddat, Z. Janeba *et al.*, *ChemMedChem* **2015**, *10*, 1707-1723.

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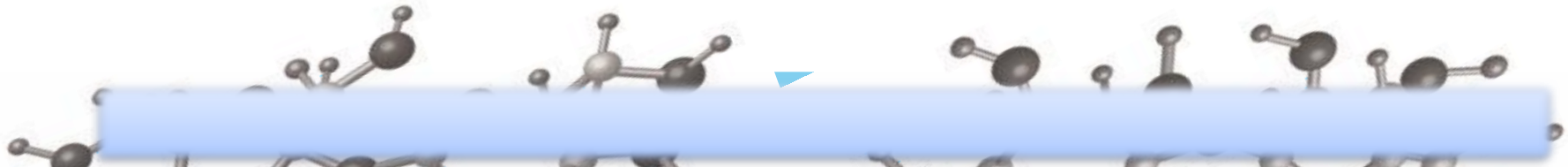
Summary



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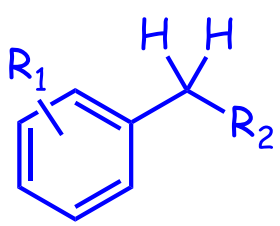
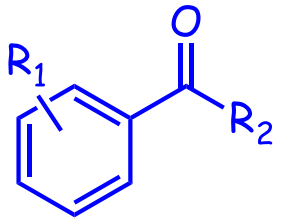
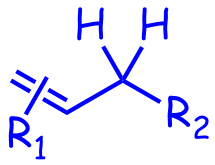
Allylic and benzylic oxidation

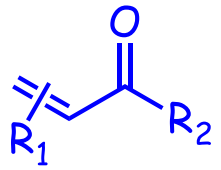


CrO_3-pyridine complex,
CrO_3 and 3,5-dimethylpyrazole,
pyridinium chlorochromate (PCC),
pyridinium dichromate (PDC),

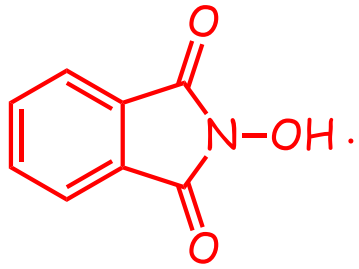


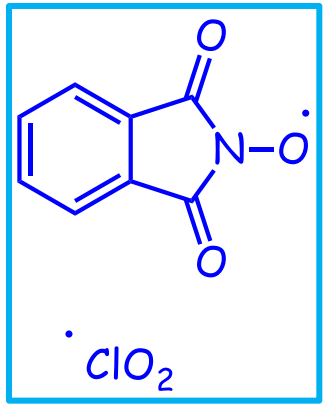


MnO_2, $KMnO_4$, SeO_2,
H_2O_2/metal catalyts,



$NaClO_2$, cat

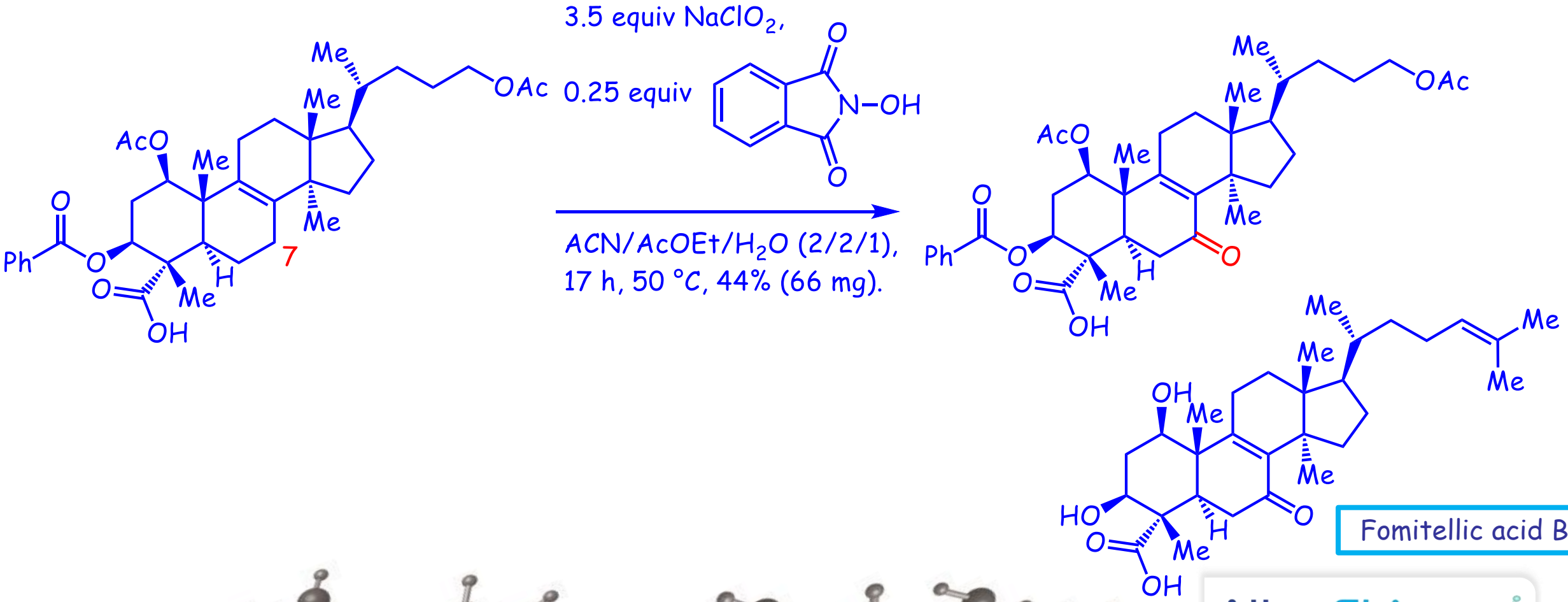




See N. C. O. Tomkinson *et al*, *J. Org. Chem.* **2024**, *89*, 7933-7945.

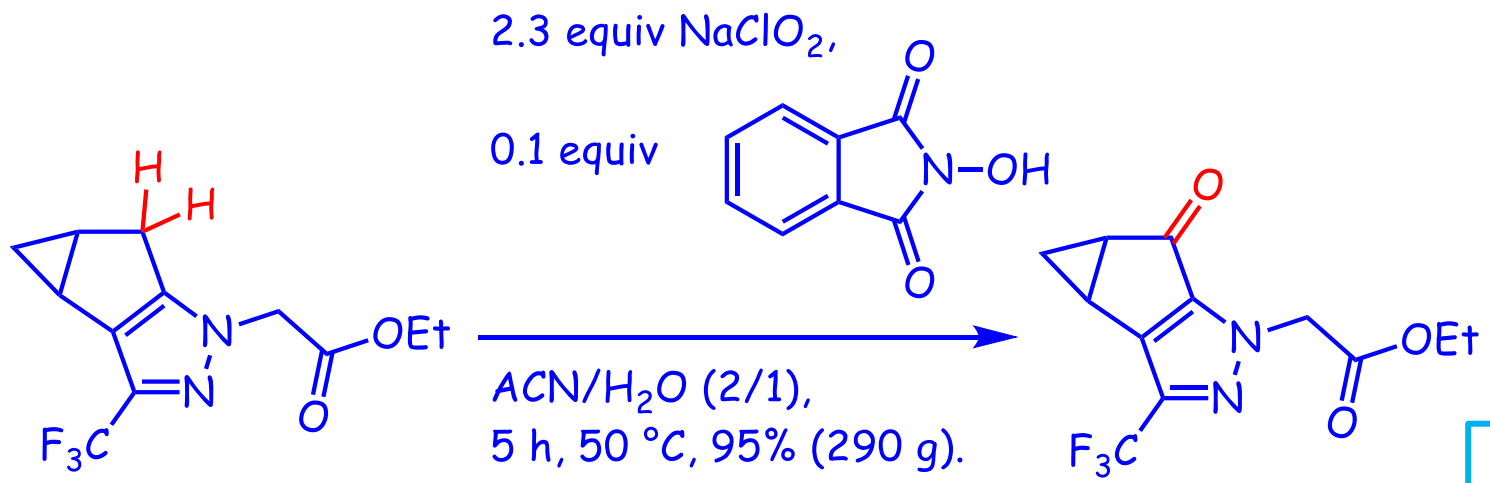
See S. M. Silvestre, J. A. R. Salvador, *Tetrahedron* **2007**, *63*, 2439–2445.

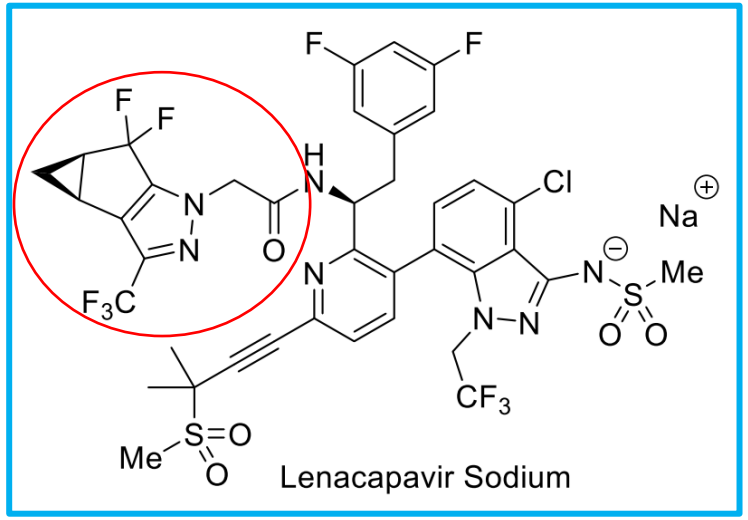
Allylic and benzylic oxidation



M. Yamaoka, A. Nakazaki, S. Kobayashi, *Tetrahedron Lett.* **2009**, *50*, 6764–6768.

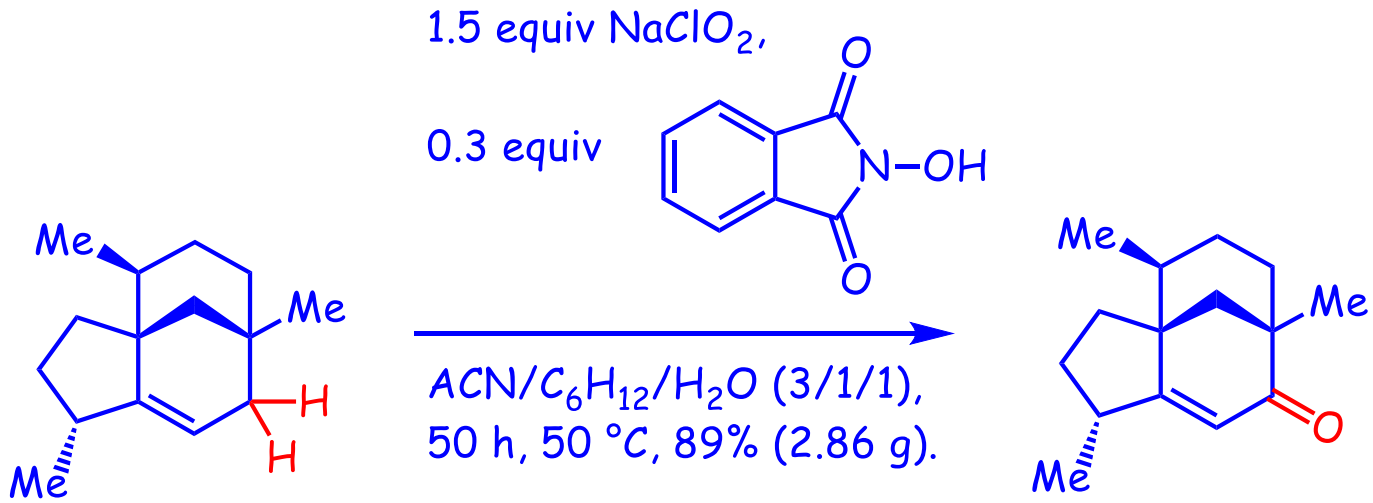
Allylic and benzylic oxidation





N. Kadunce, O. St-Jean *et al.*, *Org. Process Res. Dev.* **2024**, *28*, 3368-3381.

Allylic and benzylic oxidation



P. L. Türtscher, G. Brunner, A. Goeke, *Helv. Chim. Acta* **2024**, *107*, e202300205.

Summary

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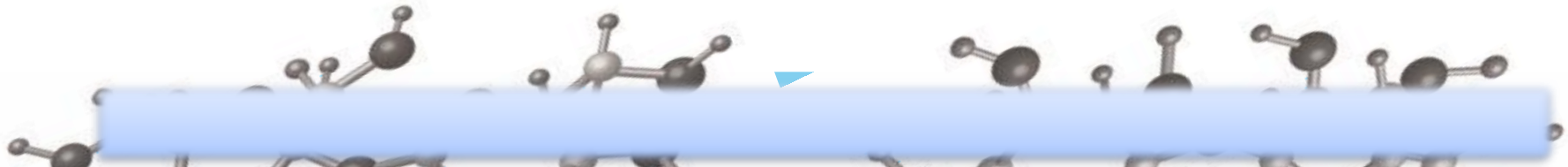

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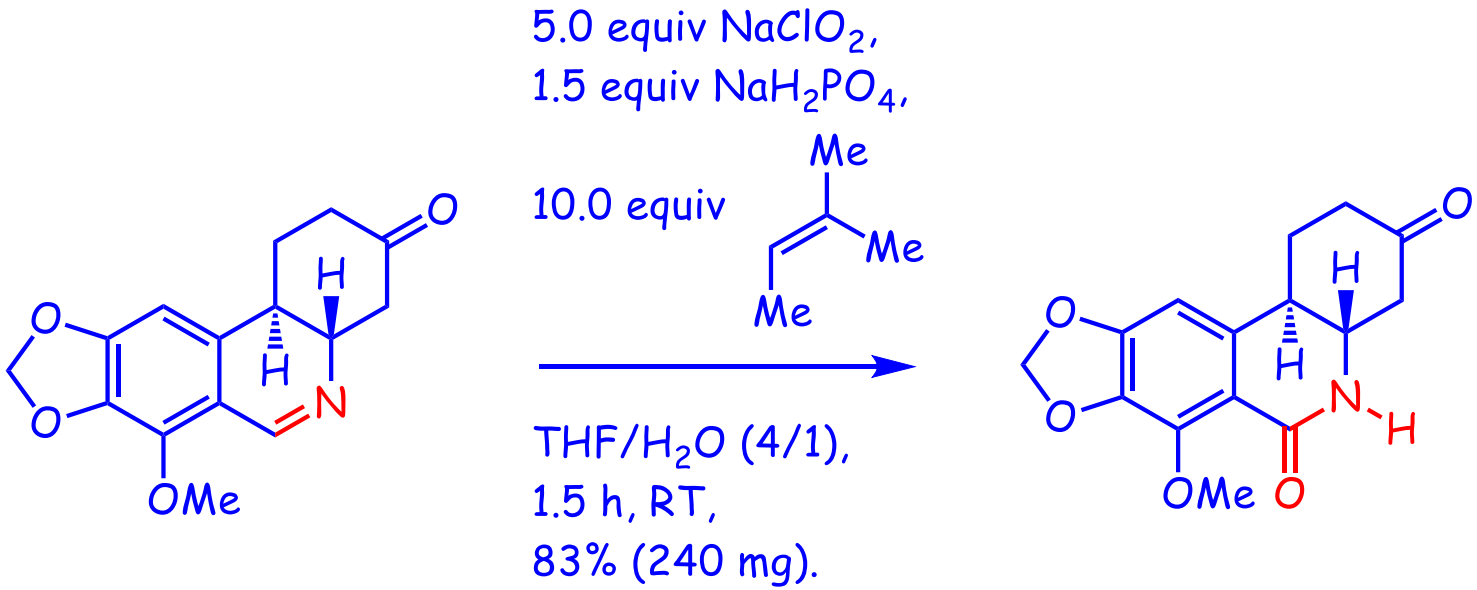
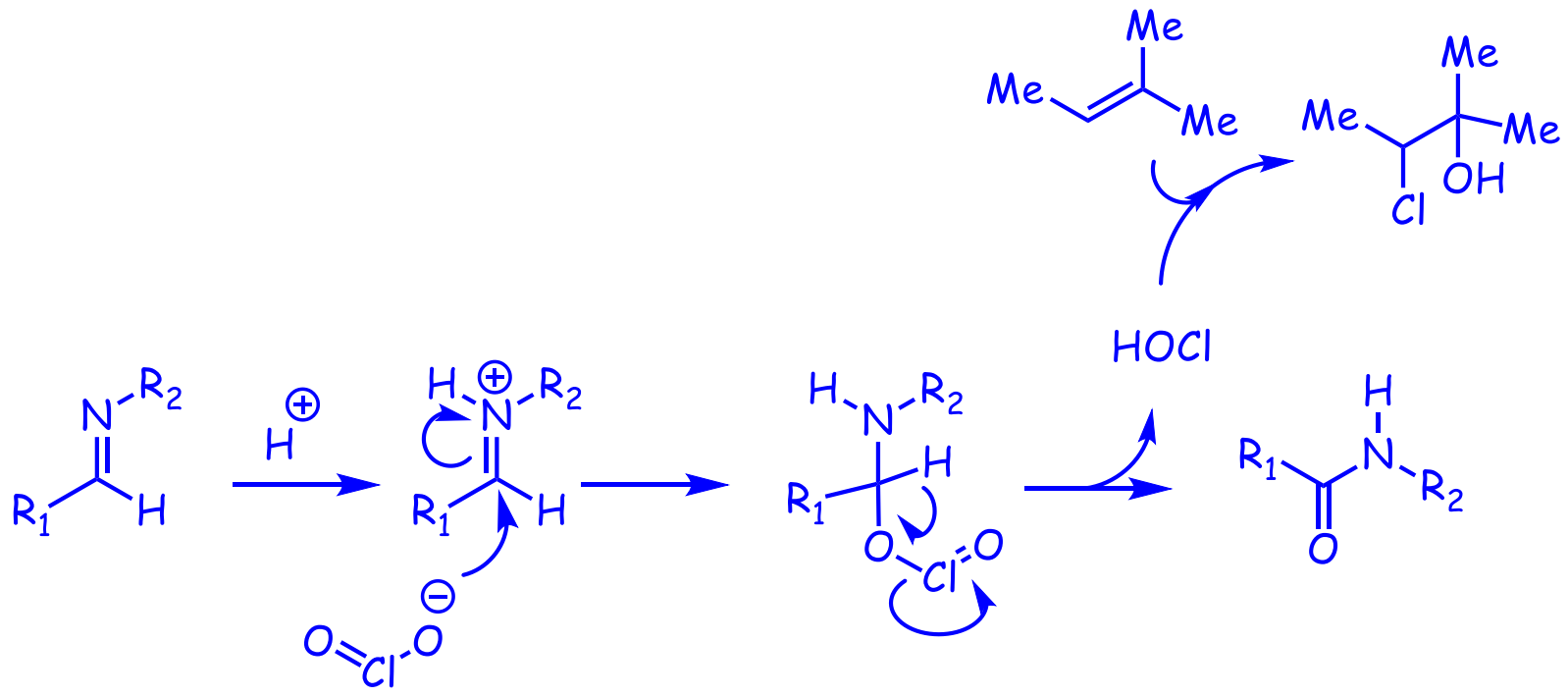
Imine oxidation to amide



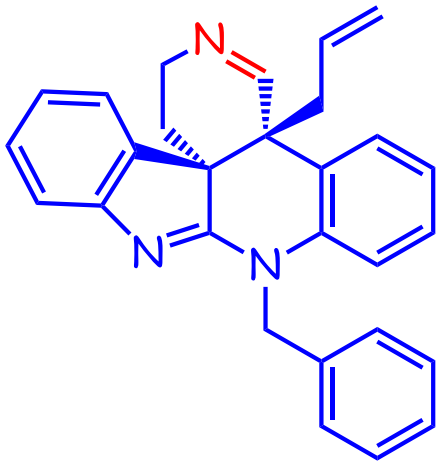
M. A. Mohamed, K.-i. Yamada, K. Tomioka, *Tetrahedron Lett.* **2009**, *50*, 3436–3438.

Imine oxidation to amide

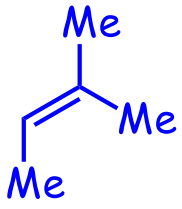


M. A. Mohamed, K.-i. Yamada, K. Tomioka, *Tetrahedron Lett.* **2009**, *50*, 3436–3438.

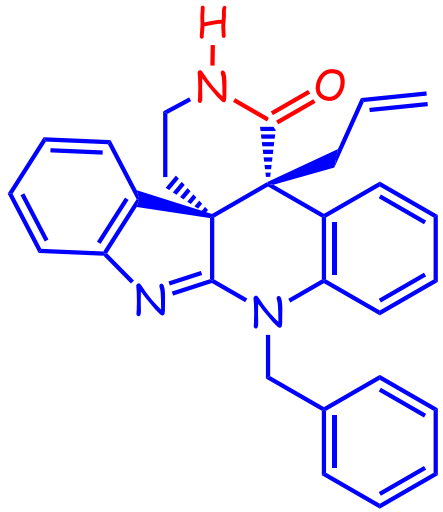
Imine oxidation to amide



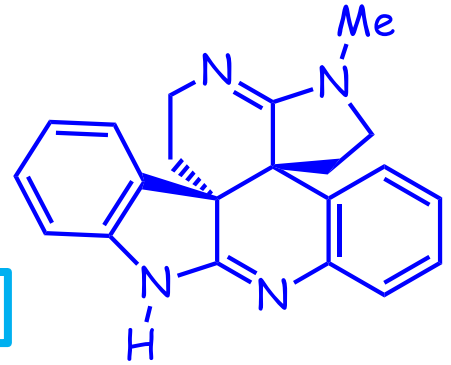
5.0 equiv $NaClO_2$,
2.5 equiv NaH_2PO_4,

10.0 equiv 

THF/H_2O (3/2),
3 h, RT,
58% (102 mg).

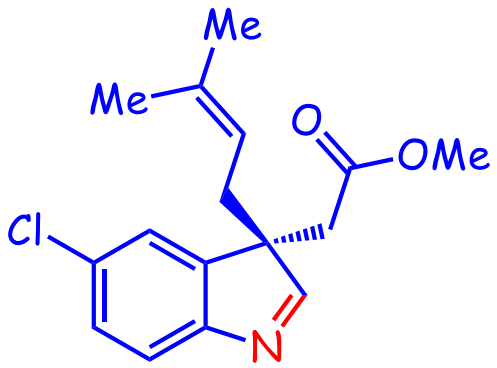


Dehaloperophoramidine

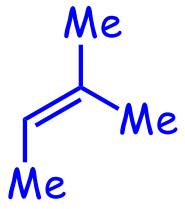


N. J. Westwood *et al.*, *Chem. Commun.* **2016**, *52*, 10747-10750.

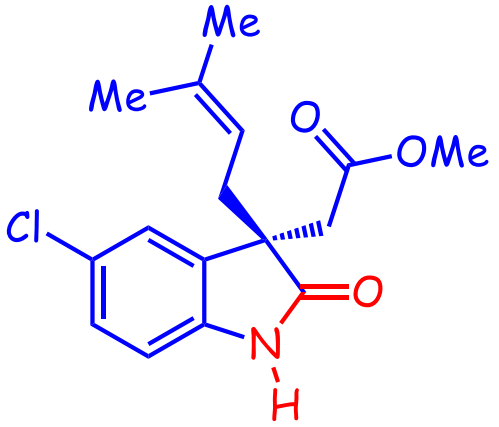
Imine oxidation to amide



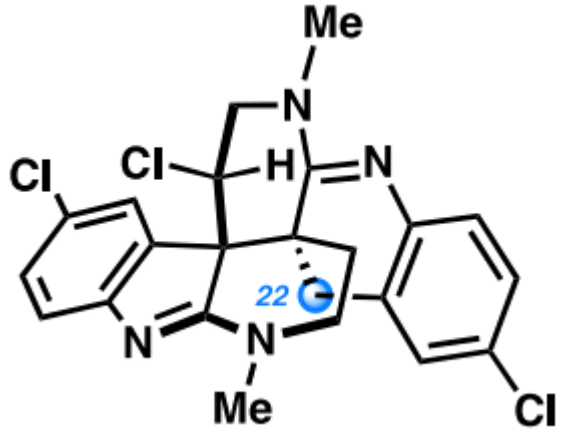
5.7 equiv $NaClO_2$,
1.7 equiv NaH_2PO_4,

11.0 equiv 

THF, 1 h, RT,
96% (90.2 mg).



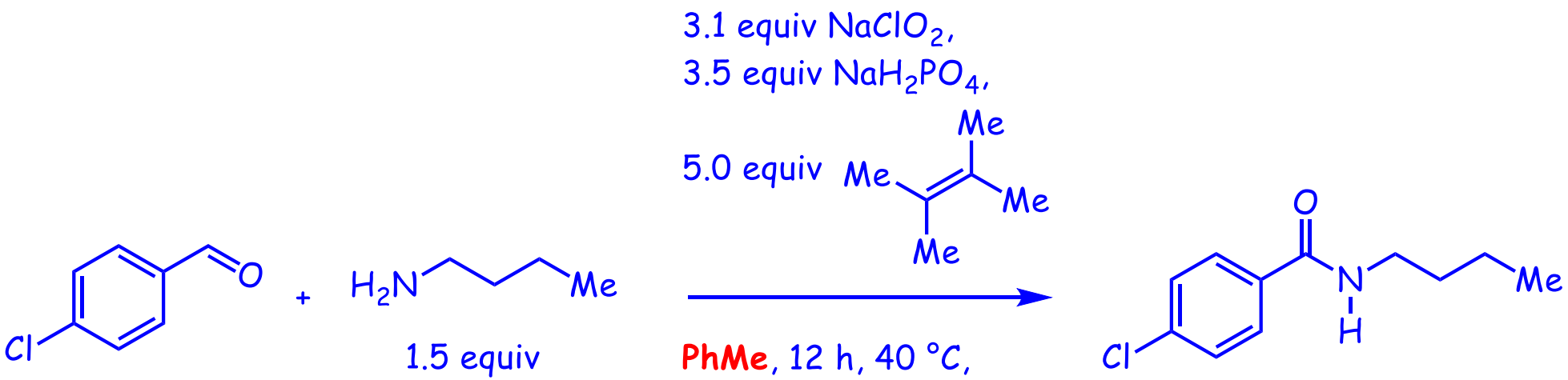
(–)-Caulamidine A



Z. Zhu, T. J. Maimone, *J. Am. Chem. Soc.* **2023**, *145*, 14215-14220.

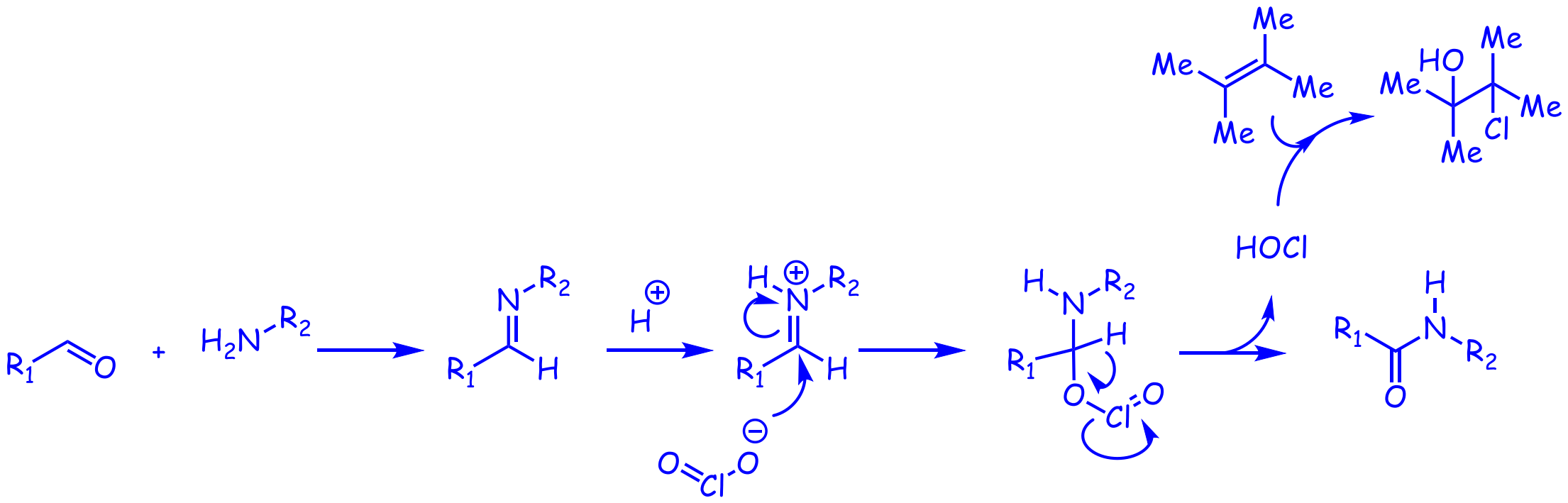
Summary

Oxidative amidation of aldehydes



K. S. Goh, C.-H. Tan, *RSC Advances* **2012**, *2*, 5536-5538.

Oxidative amidation of aldehydes



K. S. Goh, C.-H. Tan, *RSC Advances* **2012**, *2*, 5536-5538.

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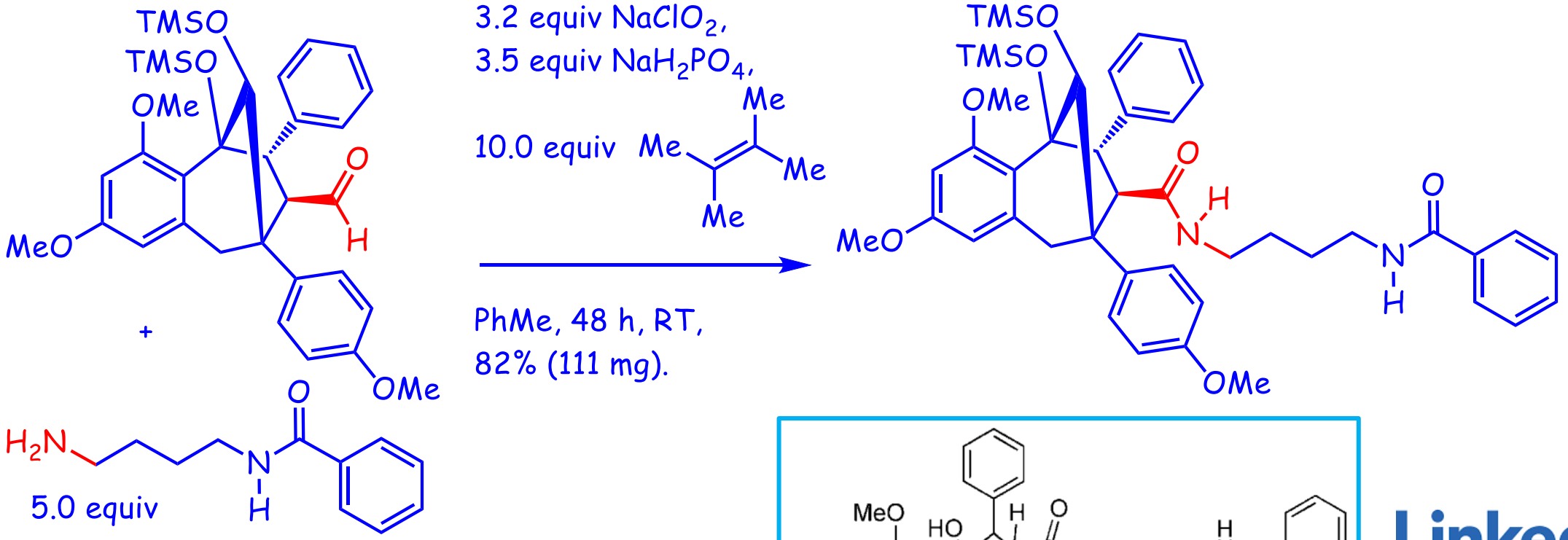
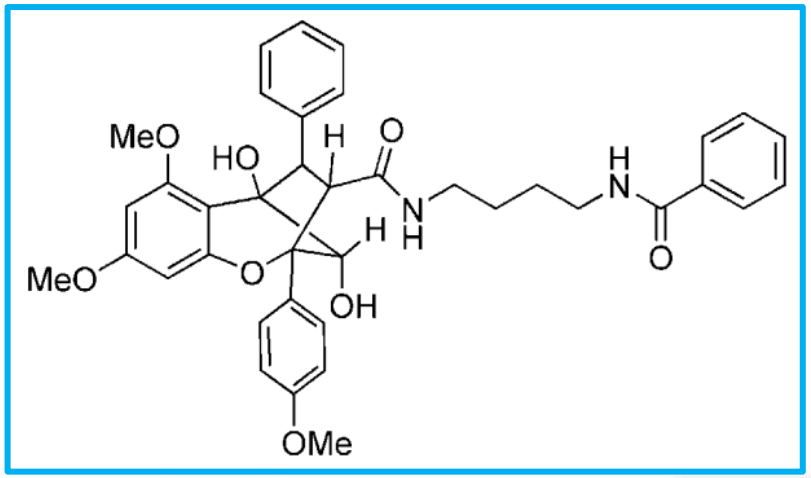
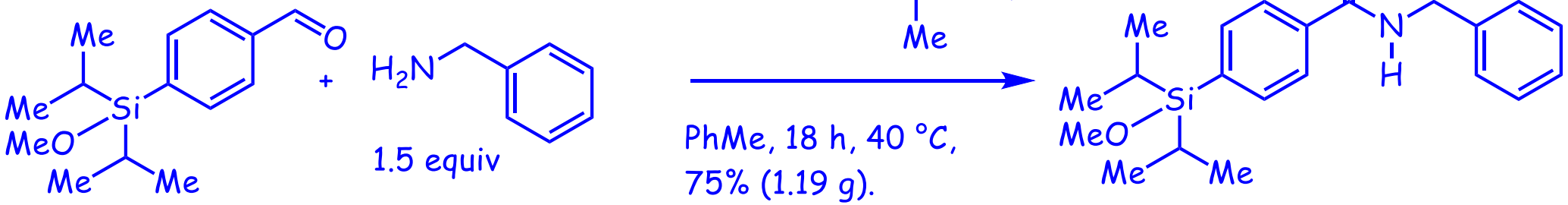


Foveoglin A



J. A. Porco et al., *Angew. Chem. Int. Ed.* **2017**, *56*, 14479-14482.

Oxidative amidation of aldehydes



1) Pinnick oxidation.

2) Peptide coupling,
<50%.

S. D. Lepore *et al.*, *J. Org. Chem.* **2017**, *82*, 2329-2335.

Summary

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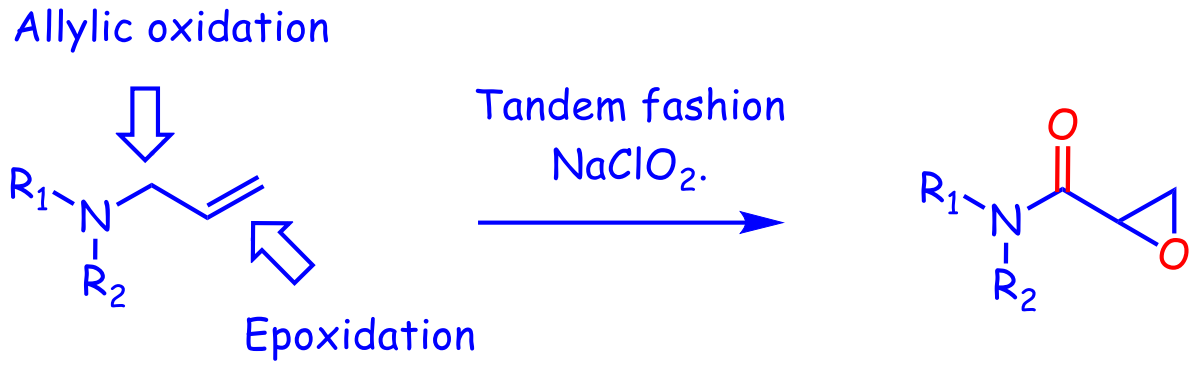
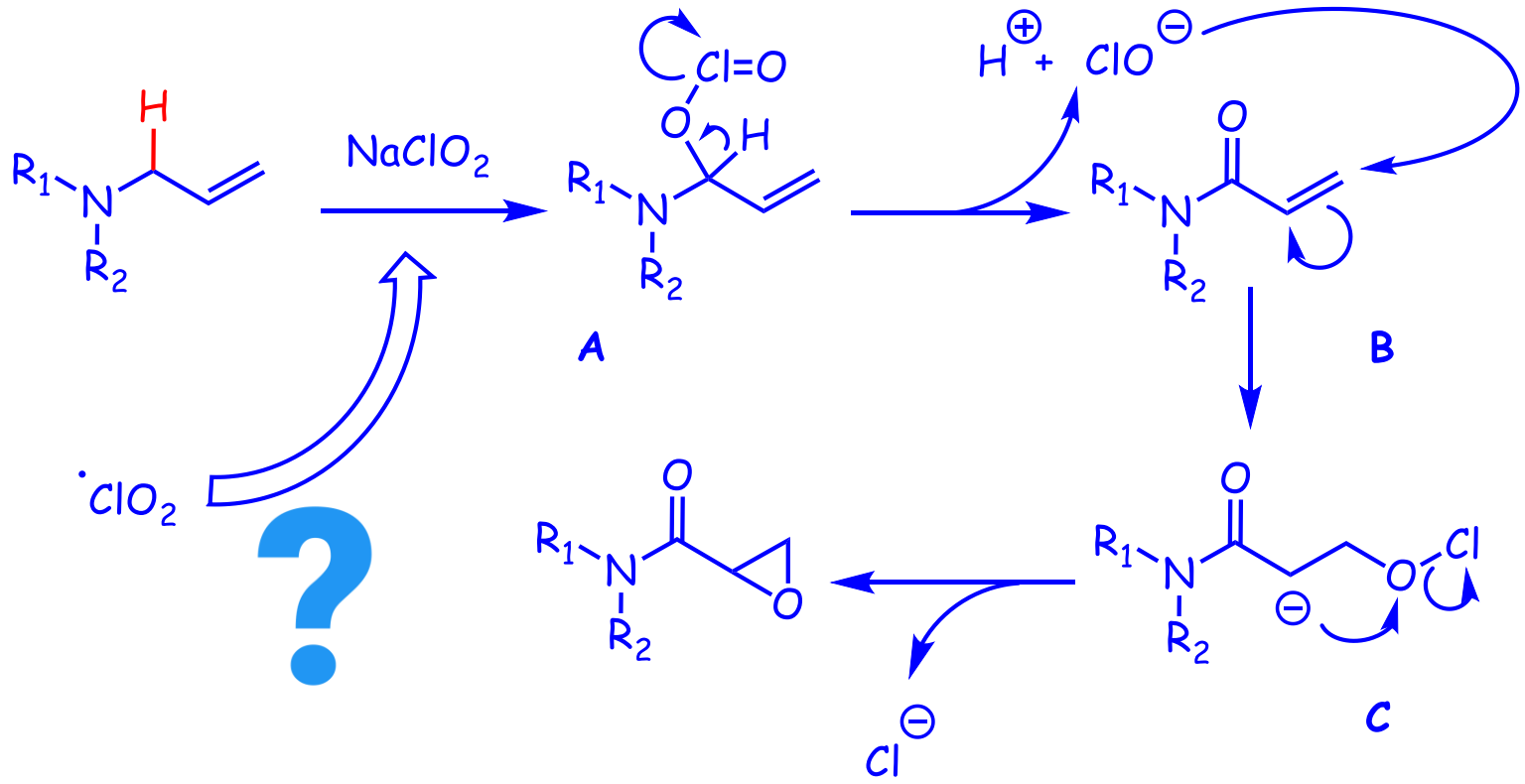
Direct method for preparing 2,3-epoxyamides



R_1 and R_2 = Alkyl, allyl and benzyl

L. Fuentes, F. Sartillo-Piscil *et al.*, *J. Org. Chem.* **2012**, *77*, 5515-5524.

Direct method for preparing 2,3-epoxyamides



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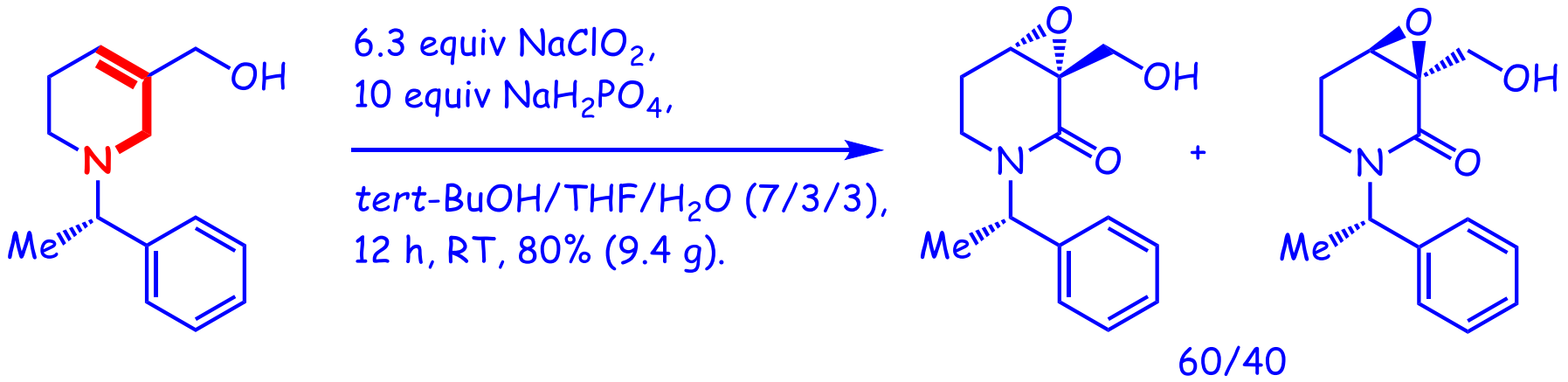
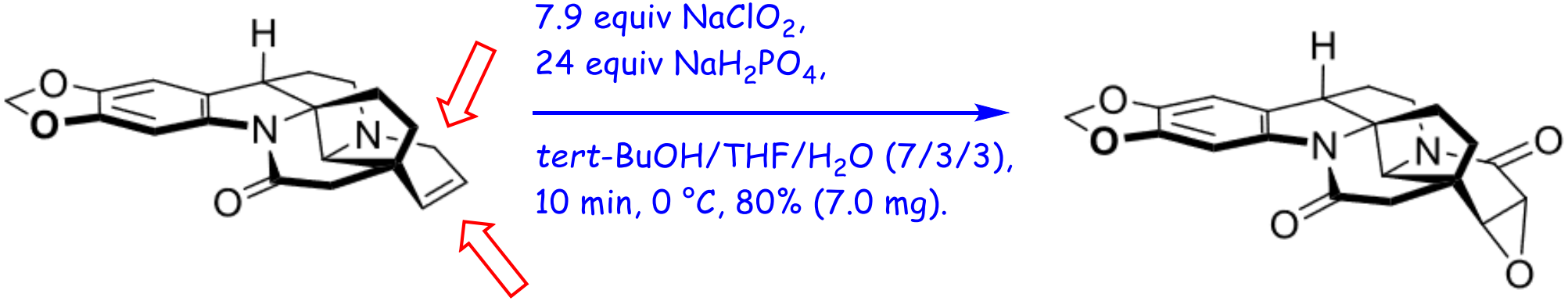


60/40

L. Fuentes, F. Sartillo-Piscil *et al.*, *Tetrahedron Lett.* **2015**, *56*, 5607-5607.

Direct method for preparing 2,3-epoxyamides



M. Zhang *et al.*, *J. Am. Chem. Soc.* **2021**, *143*, 19975-19982.

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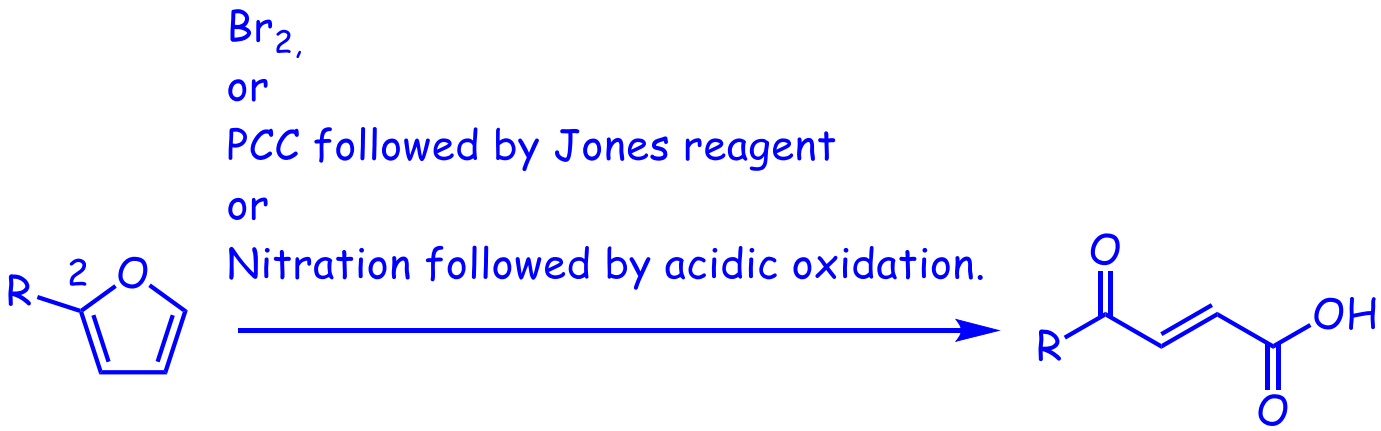
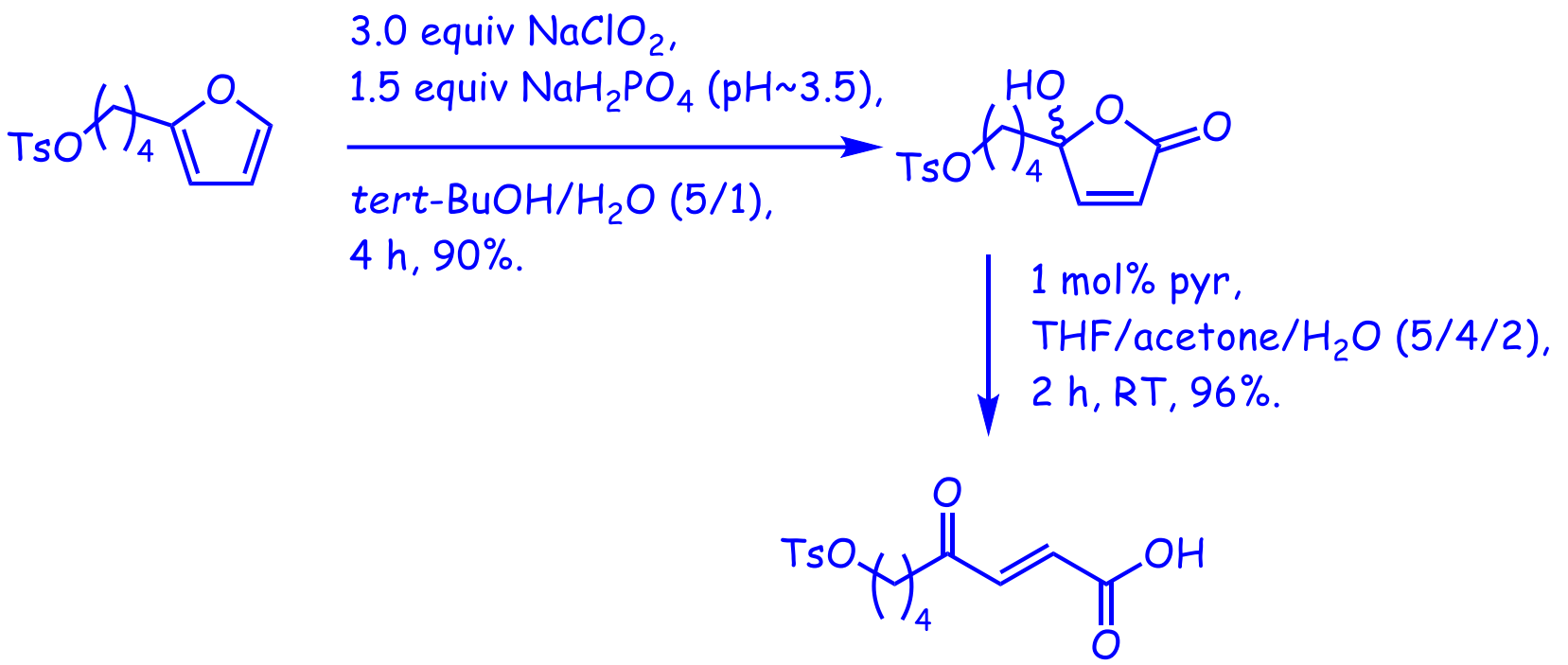
Furan ring oxidation



See R. G. Salomon *and al.*, *Synlett* **2005**, 1468-1470.

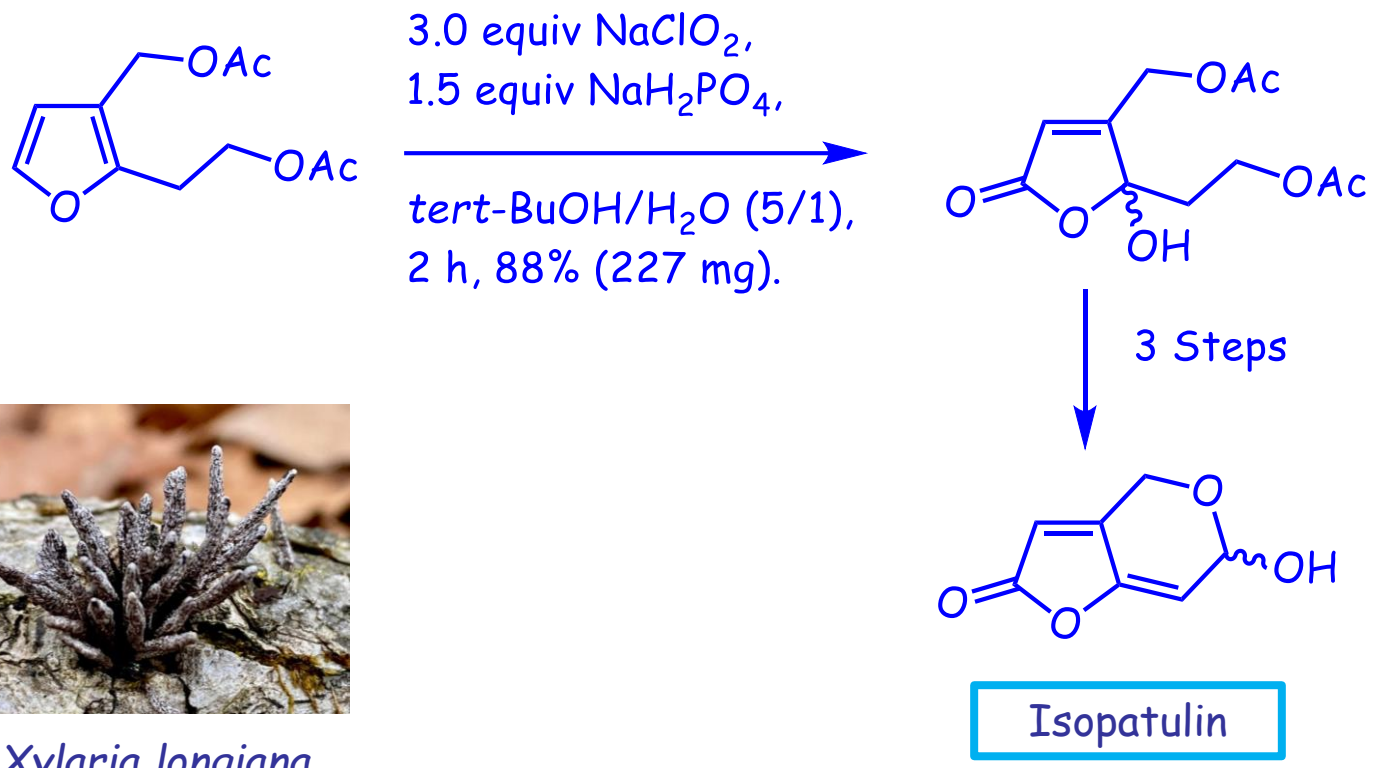
Furan ring oxidation



D. L. J. Clive, L. Ou, *Tetrahedron Lett.* **2002**, *43*, 4559-4563.

S. P. Annangudi, M. Sun, R. G. Salomon, *Synlett* **2005**, 1468-1470.

Furan ring oxidation

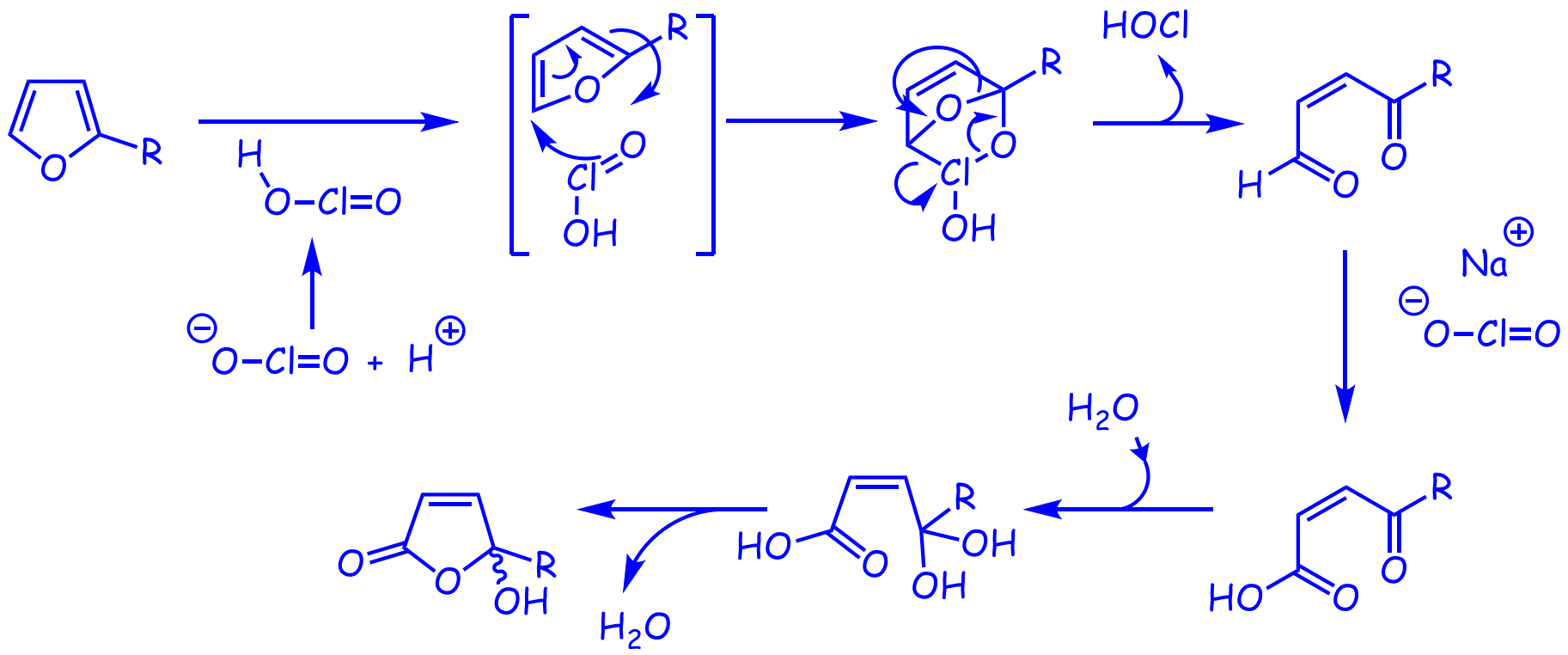


Xylaria longiana.

Isopatulin

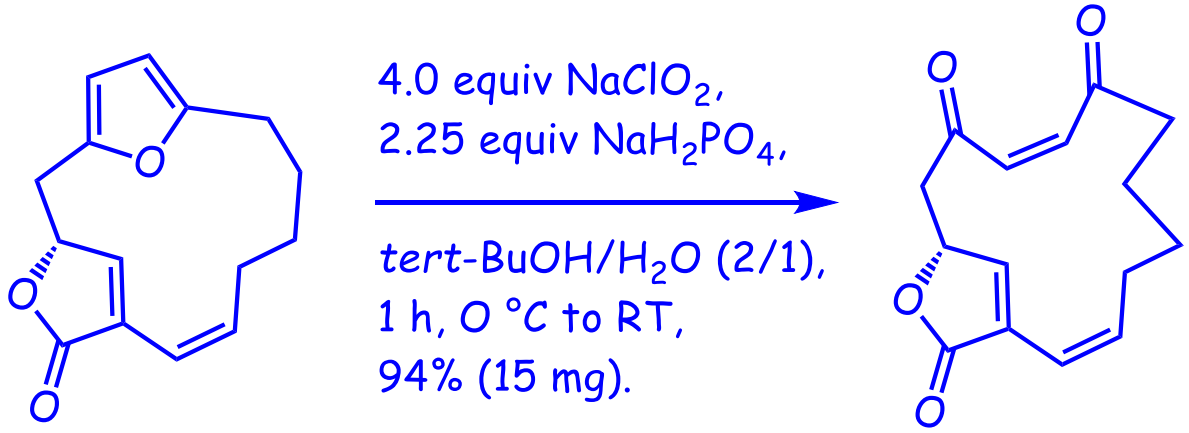
I. N. Lykakis, I.-P. Zaravinos, C. Raptis, M. Stratakis, *J. Org. Chem.* **2009**, *74*, 6339-6342.

Furan ring oxidation



Z.-M. Zhang, J. Zhang, Q. Cai, *Chem. Sci.* **2023**, *14*, 12598–12605.

Furan ring oxidation



L. Vasamsetty, F. A. Khan , G. Mehta, *Tetrahedron Lett.* **2014**, *55*, 7068–7071.

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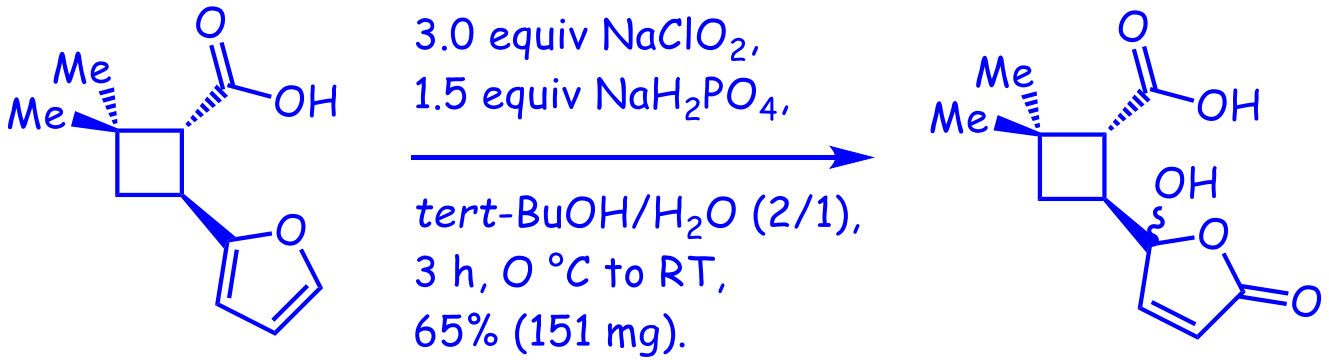
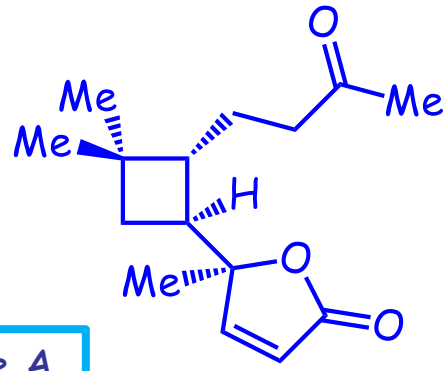
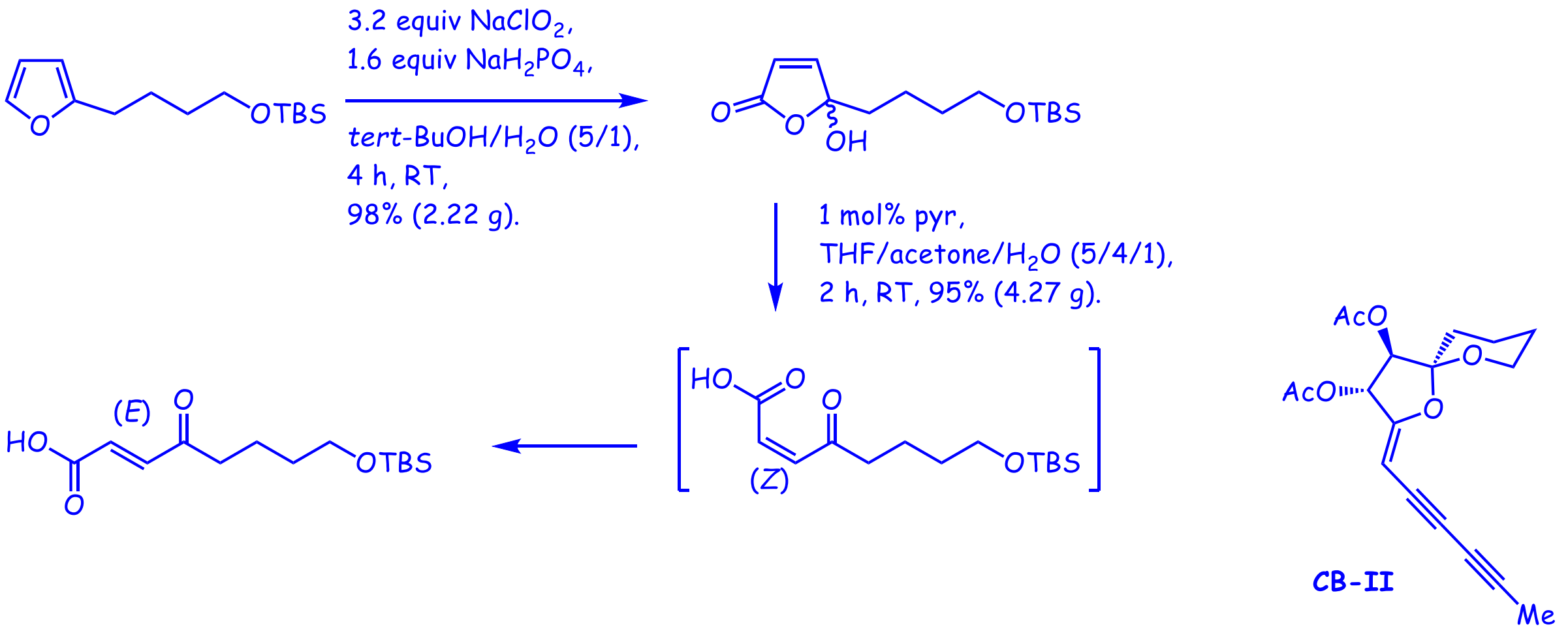




(+)-Rumphellaone A

J. C. Beck, C. R. Lacker, L. M. Chapman, S. E. Reisman, *Chem. Sci.* **2019**, *10*, 2315-2319.

Furan ring oxidation



B. Wu, G. C. Feast, A. L. Thompson, J. Robertson, *J. Org. Chem.* **2012**, *77*, 10623-10630.

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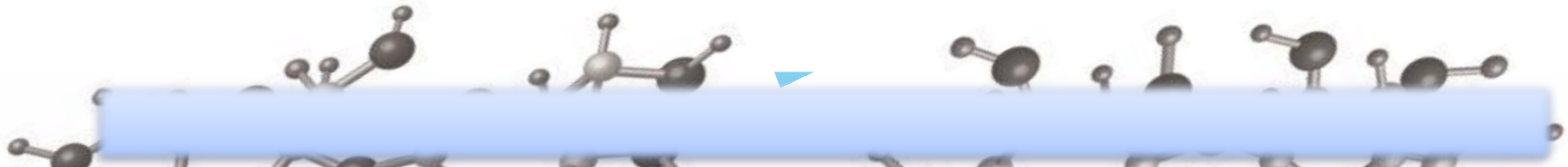

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Conclusion


Na
O
Cl
O


Sodium Chlorite 80%
NaClO2
CAS 7758-19-2
5 Lbs.
5.1
OXIDIZER
UN1496
CHEMICALSTORE.COM


SODIUM CHLORITE
TECHNICAL GRADE 31% MIN
CAS# 7758-19-2
UN 1908

Conclusion

More than 2200 contracts achieved since our creation 20 years ago.

Important scientific watch, in particular with our
Scientific Letters, Webinars and "Minute of Chemistry".

Strong expertise in synthesis of labelled products with
more than 350 compounds prepared and synthesis of impurities from API.

AtlanChim Pharma

Contact us…….

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Acknowledgement

Sylvie ARCHAMBAUD PhD

Aude VIBERT PhD

Hervé PORAS PhD

Jean-Yves GOUJON PhD

DO YOU HAVE ANY QUESTIONS ?

Open-ended question : please feel free to ask

CONTACT US

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jacques.lebreton@atlanchimpharma.com