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Abstract:
Given the central role of carbonyl compounds in chemical synthesis, considerable effort has been devoted to developing more sustainable and efficient methods for accessing aldehydes and ketones at both laboratory and industrial scales. In recent years electrochemical oxidations of alcohols have seen increased interest in academic settings as a method to removing the toxic and environmentally damaging reagents, such as transition metal catalysts, found in classical alcohol oxidations. This review aims to deliver a concise summary of the current synthetic electrochemical methods available and place them in context of the traditional oxidations they aim to replace.

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Contributors‘ Statement: Conall Molloy: Conceptualization, Data curation, Validation, Visualization, Writing - original draft, Writing - review & editing. Kevin Georges Lam: Funding acquisition, Supervision, Validation, Visualization.

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Non-Transition Metal Mediated Electrochemical Oxidations of Alcohols to Aldehydes and Ketones

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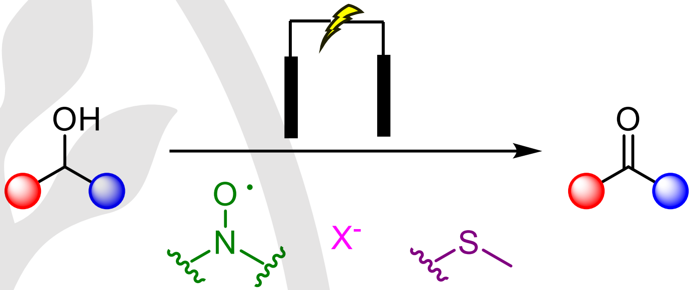

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Abstract Given the central role of carbonyl compounds in chemical synthesis, considerable effort has been devoted to developing more sustainable and efficient methods for accessing aldehydes and ketones at both laboratory and industrial scales. In recent years electrochemical oxidations of alcohols have seen increased interest in academic settings as a method to removing the toxic and environmentally damaging reagents, such as transition metal catalysts, found in classical alcohol oxidations. This review aims to deliver a concise summary of the current synthetic electrochemical methods available and place them in context of the traditional oxidations they aim to replace.

Key words Electrosynthesis, TEMPO, Halide, Oxidation, Alcohols, Ketone, Aldehyde

The oxidation of alcohols to aldehydes and ketones remains a fundamental transformation in organic chemistry, underpinning both fine-chemical synthesis and large-scale industrial manufacturing. Conventional oxidation methods often rely on stoichiometric reagents or precious-metal catalysts, generating waste and limiting sustainability. As the demand for greener chemical processes intensifies, the development of environmentally benign oxidation strategies has become a central objective in modern synthetic research.

Electroorganic synthesis has emerged as a powerful alternative, replacing traditional redox reagents with electric current as a clean, tunable, and inherently sustainable oxidant. This approach eliminates hazardous oxidants while enabling precise control over potential, selectivity, and reaction kinetics. In particular, the electrochemical oxidation of primary and secondary alcohols has gained prominence as a versatile platform for sustainable oxidation chemistry. Among various strategies, mediated (indirect) electrooxidation has proven especially effective: instead of direct substrate oxidation at the electrode, a redox-active mediator is electrochemically generated to perform the oxidation under milder, more selective conditions.

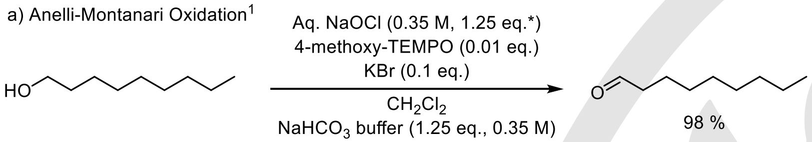
Nitroxyl radicals, halides, and sulfides have emerged as leading mediator systems, each offering distinct mechanistic profiles, operational advantages, and environmental considerations. Despite substantial advances, challenges persist regarding scalability, generality, and mechanistic understanding. This review critically examines the evolution of mediator-enabled electrochemical alcohol oxidation, summarising key mechanistic insights, highlighting landmark studies, and identifying the remaining hurdles and future directions necessary for broad and practical adoption.

Biosketches

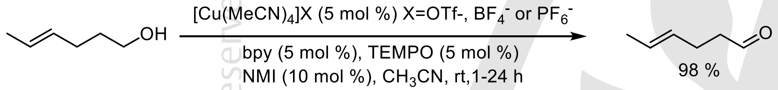
	Kevin Lam obtained his PhD in Medicinal and Synthetic Organic Chemistry from the Catholic University of Louvain (UCLouvain), Belgium, in 2010 under the supervision of Professor István Markó, where he developed a new radical-based deoxygenation reaction now known as the Lam–Markó reaction. Following his doctorate, he joined the University of Vermont, USA, as a postdoctoral researcher, applying analytical and physical electrochemistry alongside spectroscopy to investigate the redox behaviour of organometallic complexes. In 2013, he was appointed Assistant Professor at Nazarbayev University in Astana, Kazakhstan, where he established a new research programme in molecular electrochemistry. He later joined the University of Greenwich in 2017, becoming Reader in Synthetic Electrochemistry, and was promoted to Full Professor in 2023. In 2025, he became Head of C-SMART (Centre for Synthesis, Materials, Analytics and Research in Translational Science). Kevin's research focuses on sustainable electrosynthesis: the development of safe, green, and scalable electrochemical methodologies for generating highly reactive intermediates. His group pioneers novel flow-electrosynthetic platforms that bridge laboratory discovery and industrial implementation, with applications across pharmaceutical, fine chemical, and materials sectors. Collaborations with partners such as GSK, AstraZeneca, and Johnson & Johnson exemplify the translational reach of his work.
Paste photo in this space. 	Conall Molloy was born in Dublin, Ireland and completed his Bachelor's degree in General Chemistry at Trinity College Dublin, where his dissertation focused on the synthesis of ammonium catalysts for PET recycling, contributing to sustainable solutions for plastic waste. In 2024 Conall started his PhD in collaboration with GSK on the development of novel electrochemical methods for the synthesis or aldehydes. He also really likes monkeys.

1.1) Classical Tempo Oxidations

a) Anelli-Montanari Oxidation[1]



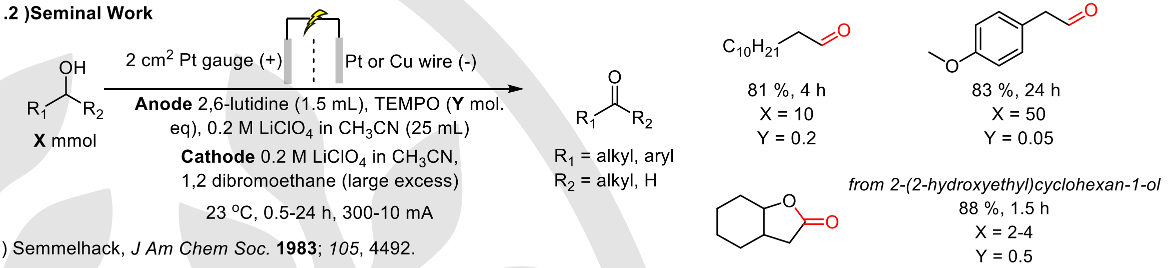
b) Stahl Protocol[2]



1) Anelli, *J. Org. Chem.* **1987**, *52*, 2559.
2) Hoover, *J. Am. Chem. Soc.* **2011**,*133*,16901.

*All equivalents are in molar equivalents

1.2)Seminal Work



Anode 2,6-lutidine (1.5 mL), TEMPO (**Y** mol. eq), 0.2 M $LiClO_4$ in CH_3CN (25 mL)
Cathode 0.2 M $LiClO_4$ in CH_3CN, 1,2 dibromoethane (large excess)
23 °C, 0.5-24 h, 300-10 mA

R_1 = alkyl, aryl
R_2 = alkyl, H

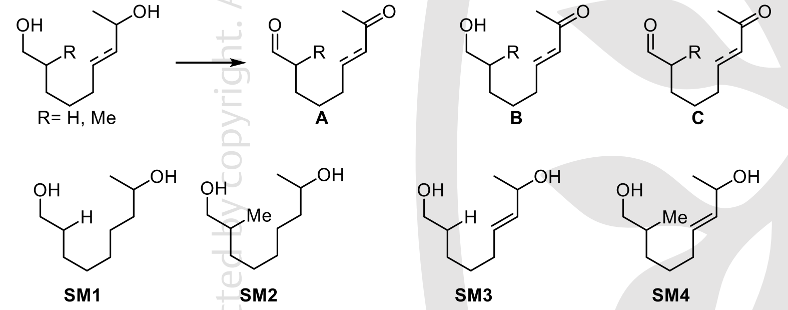
81 %, 4 h
X = 10
Y = 0.2

83 %, 24 h
X = 50
Y = 0.05

from 2-(2-hydroxyethyl)cyclohexan-1-ol
88 %, 1.5 h
X = 2-4
Y = 0.5

3) Semmelhack, *J Am Chem Soc.* **1983**; *105*, 4492.

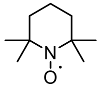
1.3) Steric and Electronic Effects of substrates



See 1.2 for reaction conditions

SM	% Conv	% A	% B	%C
SM1	100	100	0	0
SM2	96	93	7	0
SM3[a]	89	53	13	33
SM3[b]	100	0	7	93
SM3[c]	92	81	0	19
SM4[a]	75	81	3	16
SM4[c]	100	11	0	89

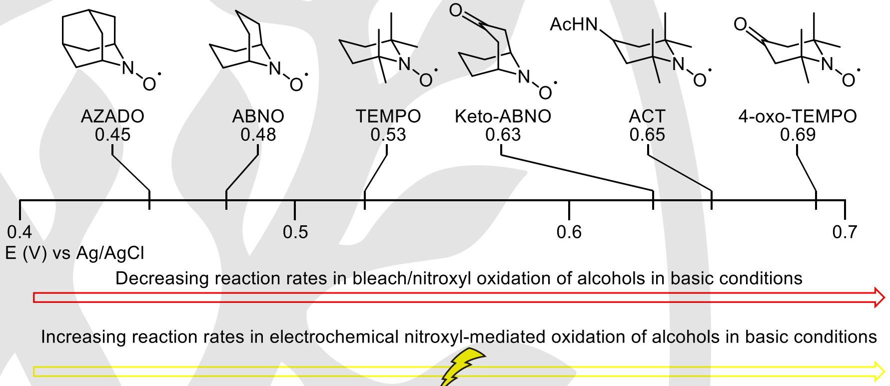
[a] Reaction interrupted after passage of 1 C/mol of diol.
[b] Reaction allowed to proceed until current decayed.
[c] The diol was added to 2 mol. equiv. of preformed **T1** at - 60 °C



T1

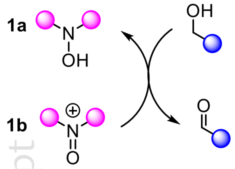
3) Semmelhack, *J Am Chem Soc.* **1983**, *105*, 4492.

1.4) Effect of Catayst Structure[5]



Decreasing reaction rates in bleach/nitroxyl oxidation of alcohols in basic conditions

Increasing reaction rates in electrochemical nitroxyl-mediated oxidation of alcohols in basic conditions

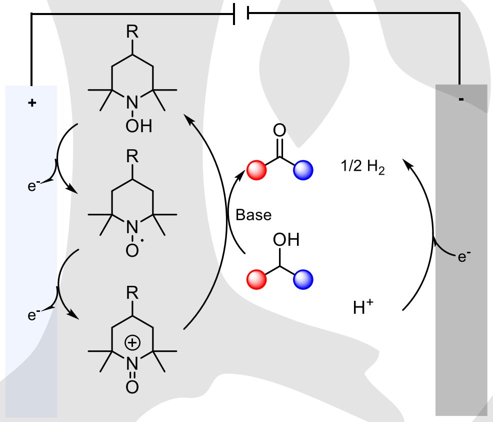


Rate affected by concentration of "active" oxidising species **1b**

Electrodes tuned to redox pot. of nitroxyl catalyst means rate more affected byelectrophilicity of **1b**

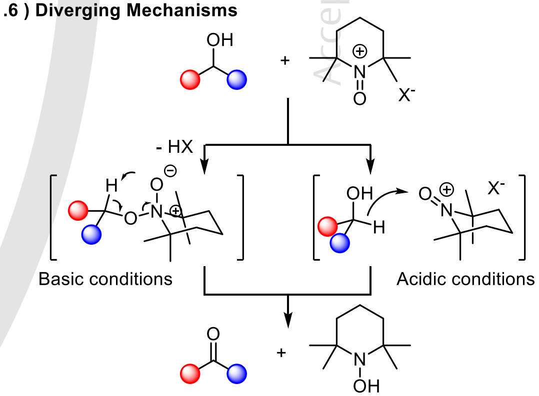
4) Rafiee, *J Am Chem Soc.* **2015**, *137*, 14751.

1.5) Proposed Mechanism



2) and 5) Tsunaga, *Electrochim. Acta.* **1973**, *18*, 241.

1.6) Diverging Mechanisms



6) Bailey, *J Org Chem.* **2007**, *72*, 4504.
7) Bobbitt, *J Org Chem.* **2014**, *79*, 1055.
8) Kishioka, *Chem Lett.* **1998**, *27*, 343

Figure 1 Nitroxyl mediated electrochemical oxidation of alcohols to aldehydes and ketones 1

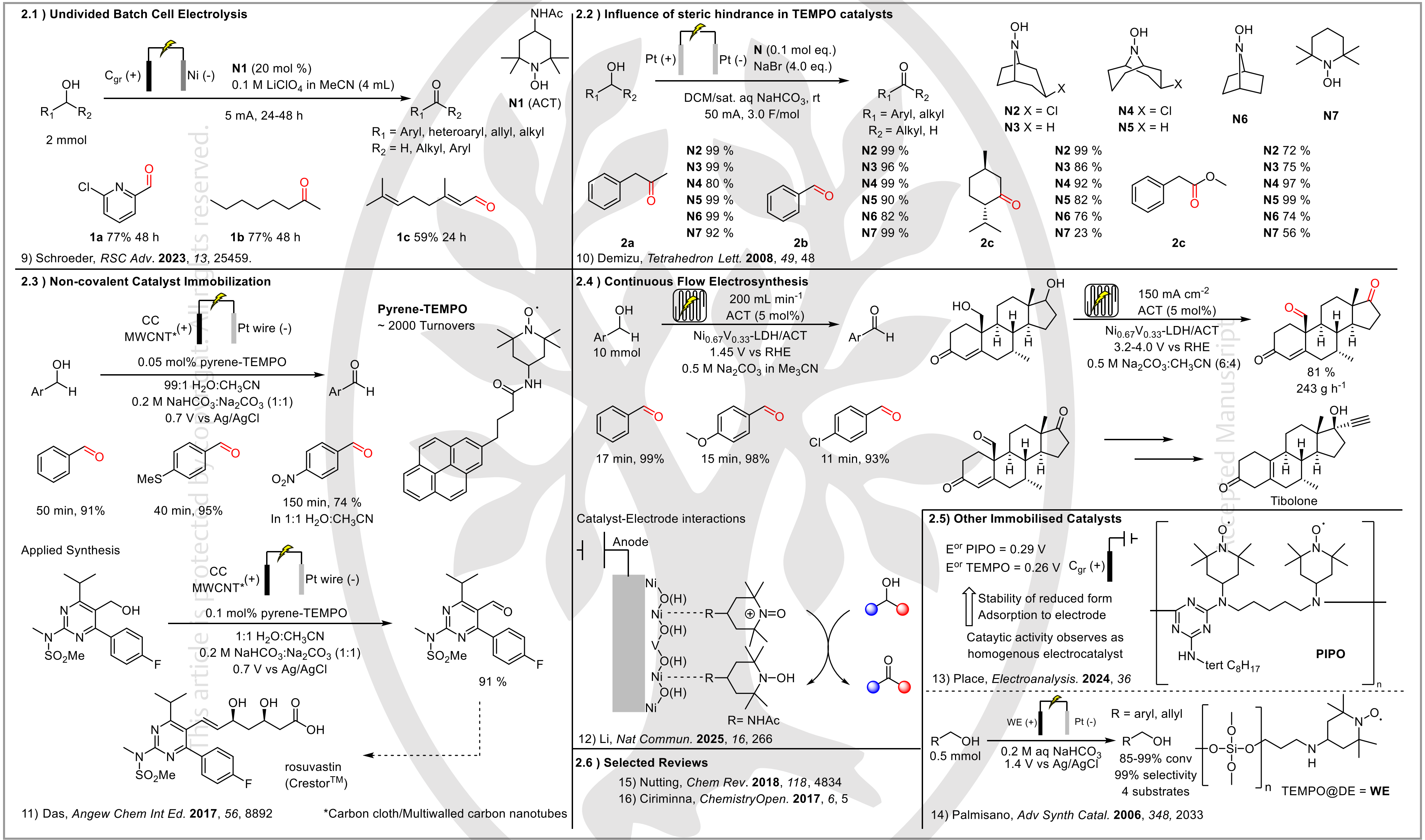


Figure 2 Nitroxyl mediated electrochemical oxidation of alcohols to aldehydes and ketones 2

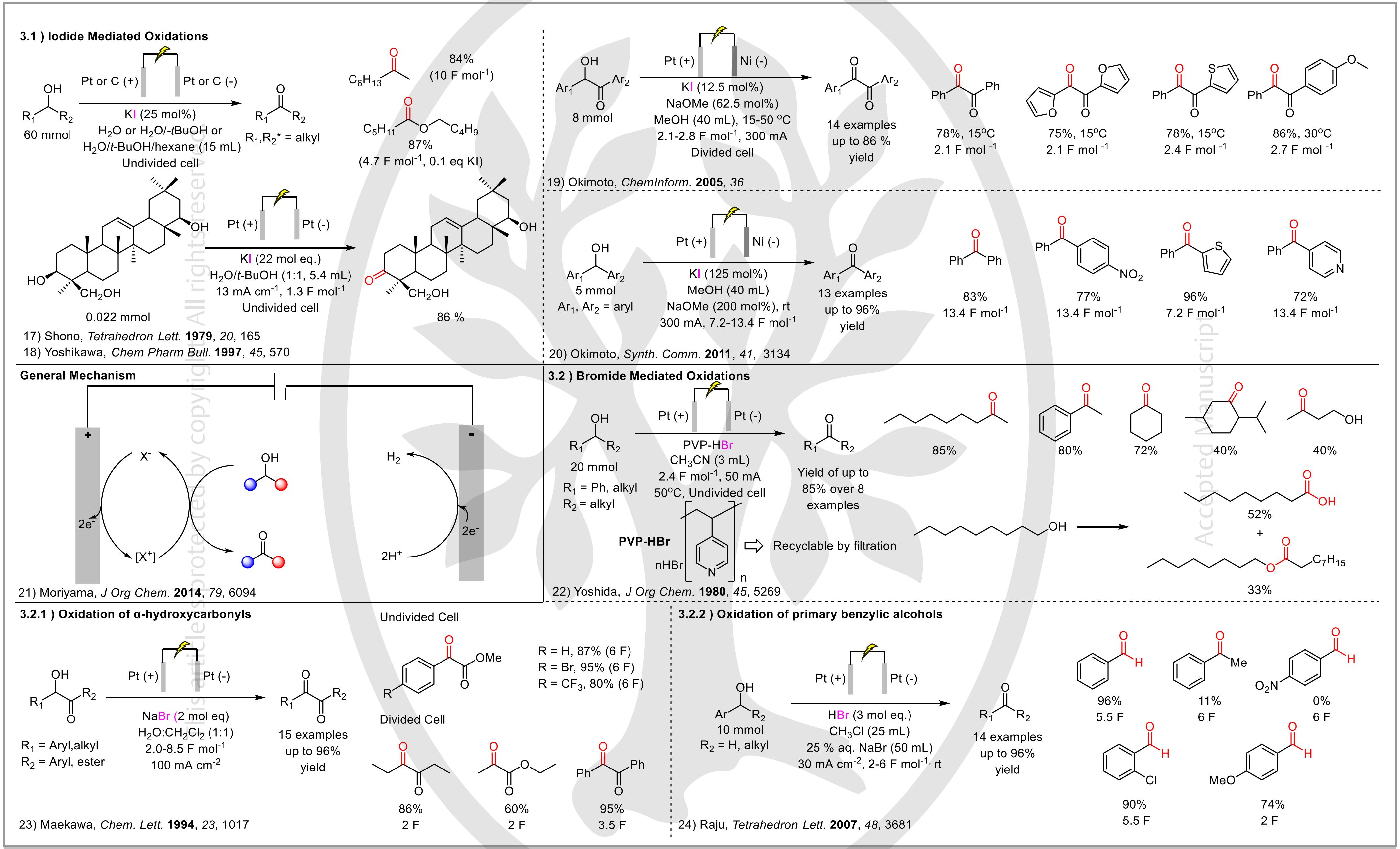
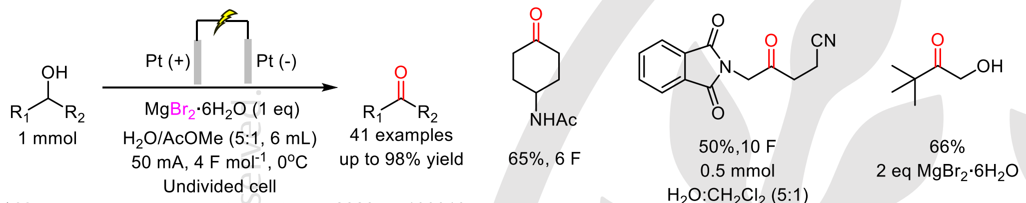


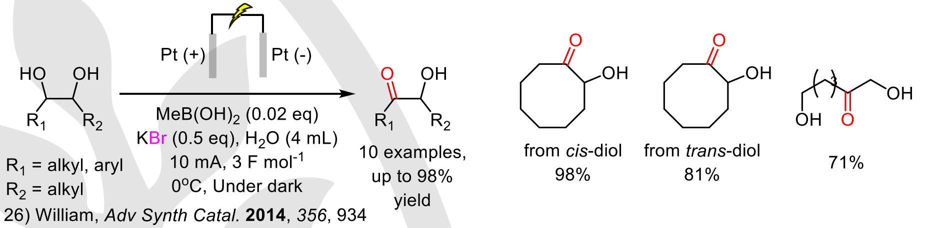
Figure 3 Halide Mediated Oxidations 1

4.1) Bromide Mediated Oxidations continued



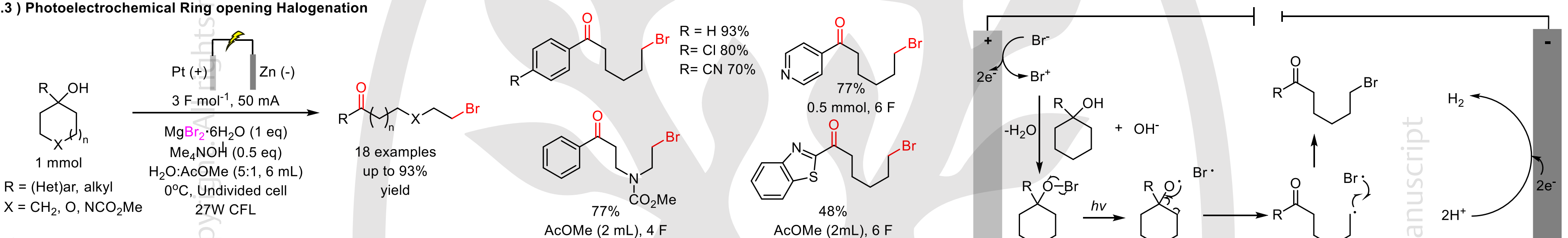
25) Yamamoto, *Tetrahedron Green Chem.* **2023**, *1*, 100010.

4.2) Selective oxidation of 1,2-diols



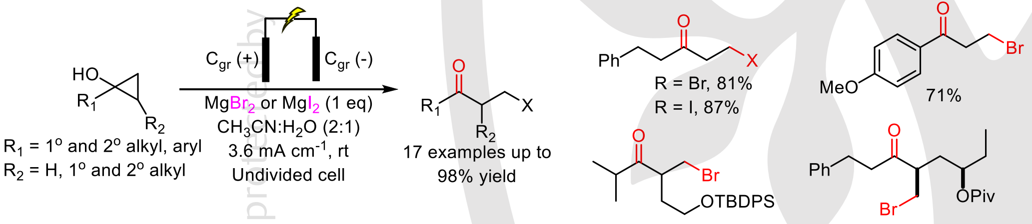
26) William, *Adv Synth Catal.* **2014**, *356*, 934

4.3) Photoelectrochemical Ring opening Halogenation



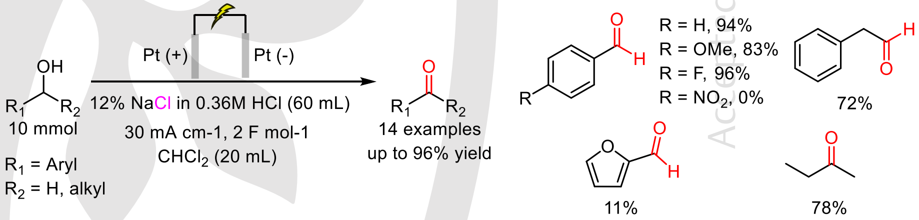
27) Yamamoto, *J Org Chem.* **2021**, *86*, 16177

4.4) Electrochemical Ring Opening Halogenation of Cyclopropanes



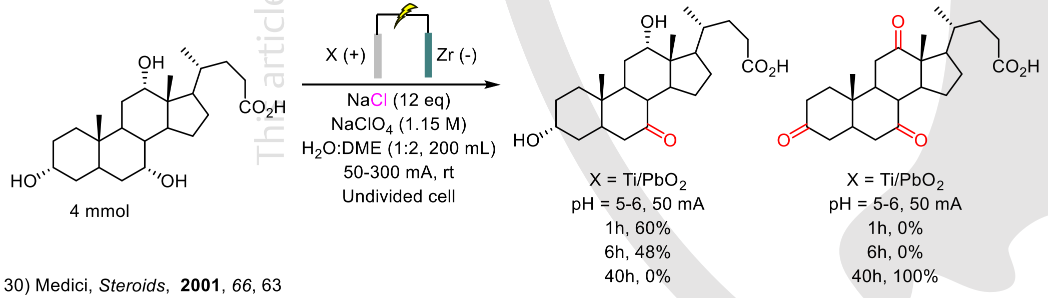
28) Barysevich, *Synlett.* **2021**, *32*, 1934

4.5) Chloride Mediated Oxidations



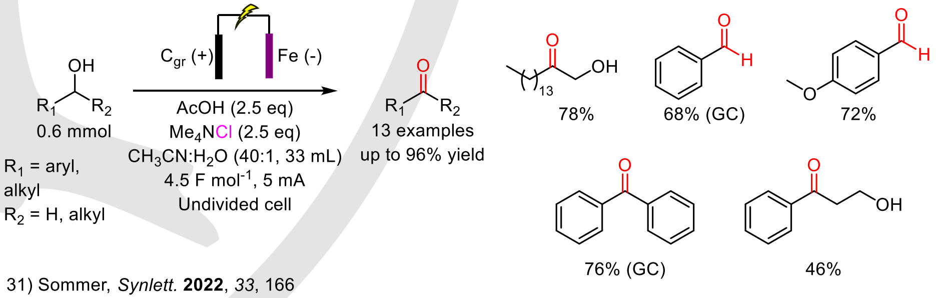
29) Bosco, *J Phys Org Chem.* **2015**, *28*, 591

4.6) Selective Oxidation of Cholic Acid



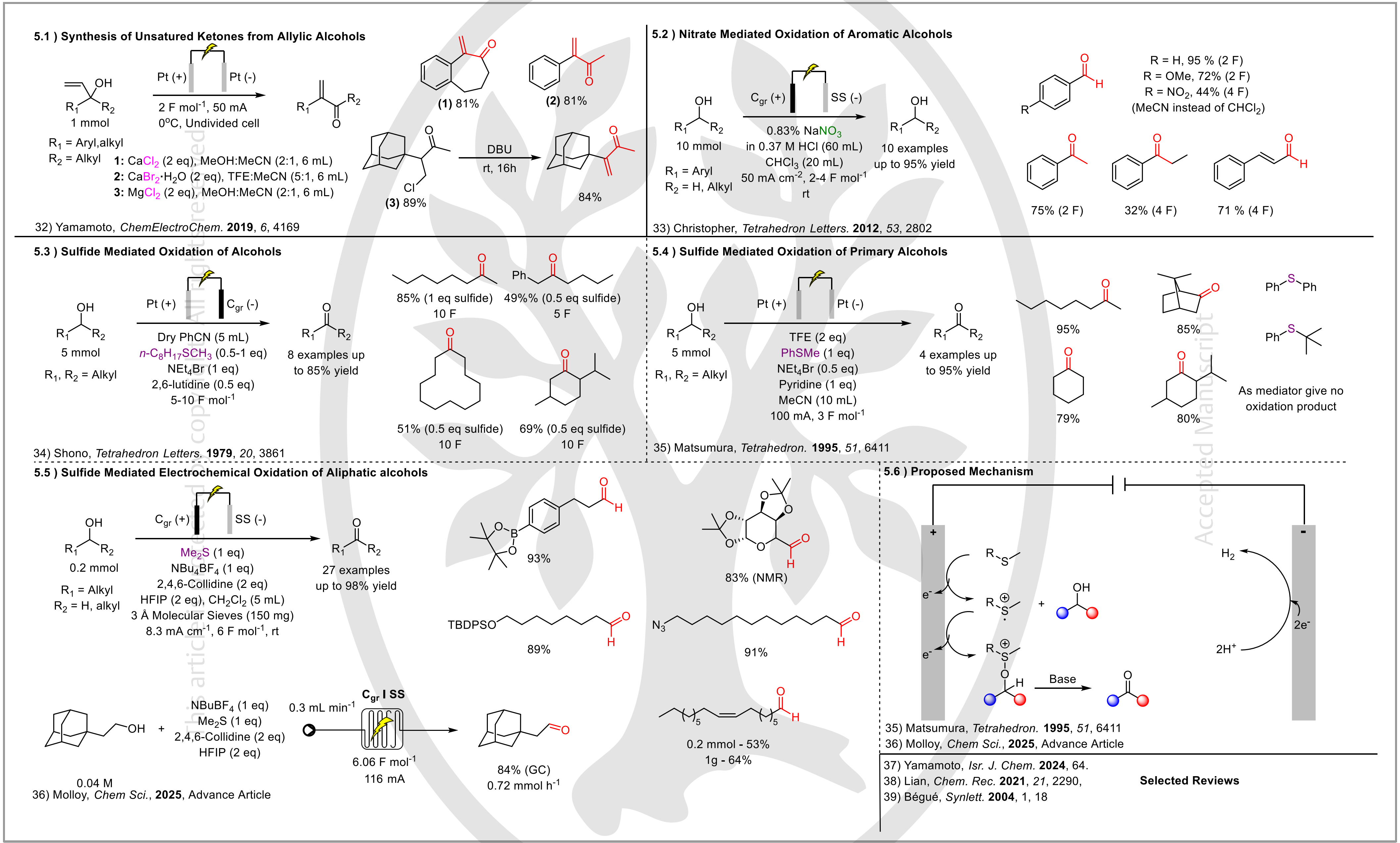
30) Medici, *Steroids*, **2001**, *66*, 63

4.7) Chemoselective oxidation of Secondary Alcohols



31) Sommer, *Synlett.* **2022**, *33*, 166

Figure 4 Halide Mediated Oxidations 2



32) Yamamoto, *ChemElectroChem.* **2019**, *6*, 4169

33) Christopher, *Tetrahedron Letters.* **2012**, *53*, 2802

34) Shono, *Tetrahedron Letters.* **1979**, *20*, 3861

35) Matsumura, *Tetrahedron.* **1995**, *51*, 6411

36) Molloy, *Chem Sci.*, **2025**, Advance Article

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36) Molloy, *Chem Sci.*, **2025**, Advance Article

37) Yamamoto, *Isr. J. Chem.* **2024**, 64.

38) Lian, *Chem. Rec.* **2021**, *21*, 2290,

39) Bégué, *Synlett.* **2004**, 1, 18

Selected Reviews

Figure 5 Halide, nitrate and sulifde mediated oxidations of alcohol

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Conflict of Interest

The authors declare no conflicts of interest.

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