Organic Electrochemistry

Untapped Potential for Synthetic Chemists?

Helena Pickford

Literature Review | 17.01.20

Prof. Ed Anderson
Group

Review Outline

Introduction

- Organic Electrochemistry
- Key Milestones
- Underlying theory

Practicalities & Applications

- Experimental Parameters
- Electrolysis Methods
- Applications
  - Industrial Processes
  - Natural Product Synthesis

Break

Methodology

- Anodic Oxidation
- Cathodic Reduction
- Paired Electrolysis
- Asymmetric Electrocatalysis
- Photo-electrochemistry

Electrochemistry

'Electrochemistry relates the flow of electrons to chemical changes'

• last resort • non-standard • sheer desperation • lack of engineering savy • a quandry • tailor made • unpredictable • realm of specialists • expensive • precious metals •

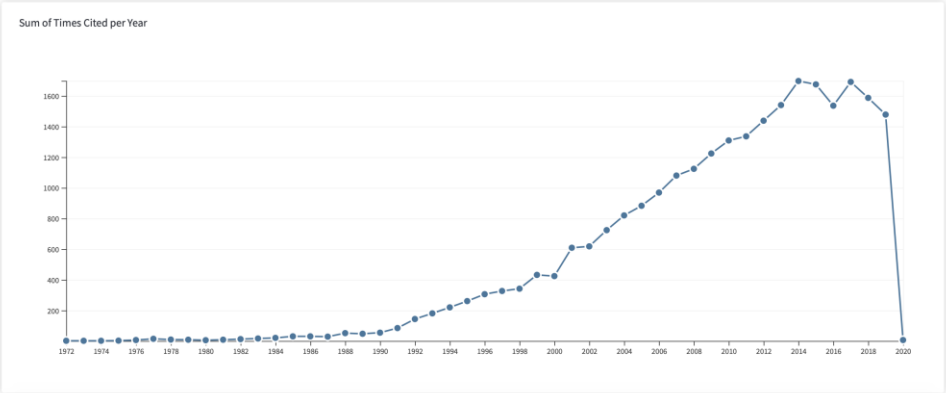
• Intimate • visceral • raw redox-chemistry • do more with less • no reagent approach • dial in oxidative strength • green • precisely controlled • great promise • electrosynthesis gives organic chemists more power • resurgence • surrogate reagent • recyclable electrodes • tunability •

Image: shutterstock.com
N. Elgrishi *et. al.* J. Chem. Educ. **2018**, *95*, 2, 197.

Electrochemistry

‘Many reactions can be accomplished using simple chemical oxidants…’

Could synthetic organic electrochemistry head into a ‘golden era of vibrant utility’?



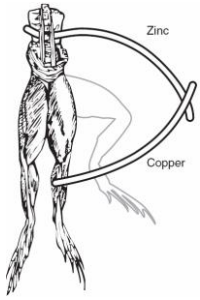
Citation Report: 1945-2019 ‘electrochemistry‘ and ‘synthesis’. Refined by Chemistry Organic. *Web of Science*, 26.11.2019.

Milestones in Electrochemistry

"Each metal has a certain power, which is different from metal to metal, of setting the electric fluid in motion."

Luigi Galvani

Alessandro Volta



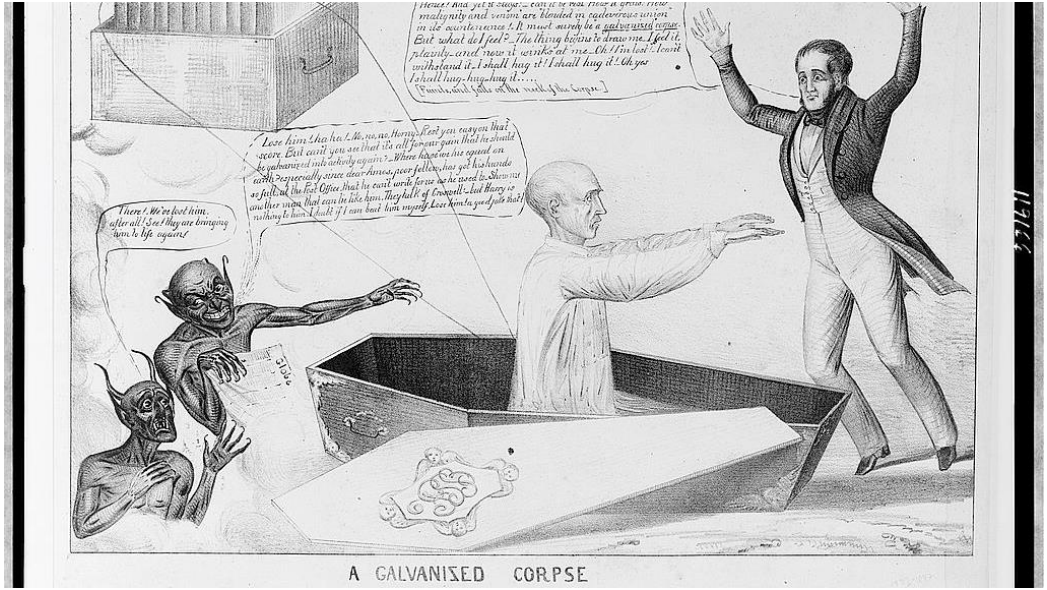
"animal electric fluid"
from the muscles
1786

+ 0.72 V per cell

"metallic electricity"
from connection of two wires
1794-1800

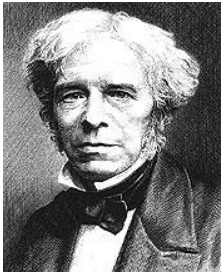
B. Dibner. *Encyclopedia Britannica,* **2019**. Luigi Galvani and Alessandro Volta.
Image source: Electrochemistry encyclopedia, Wikipedia

Milestones in Electrochemistry



Printed & Pub: H.R. Robinson, N.Y., Washington, D.C. **1836**.

A Timeline of Electro-Organic chemistry



"Astonishing how great the precautions that

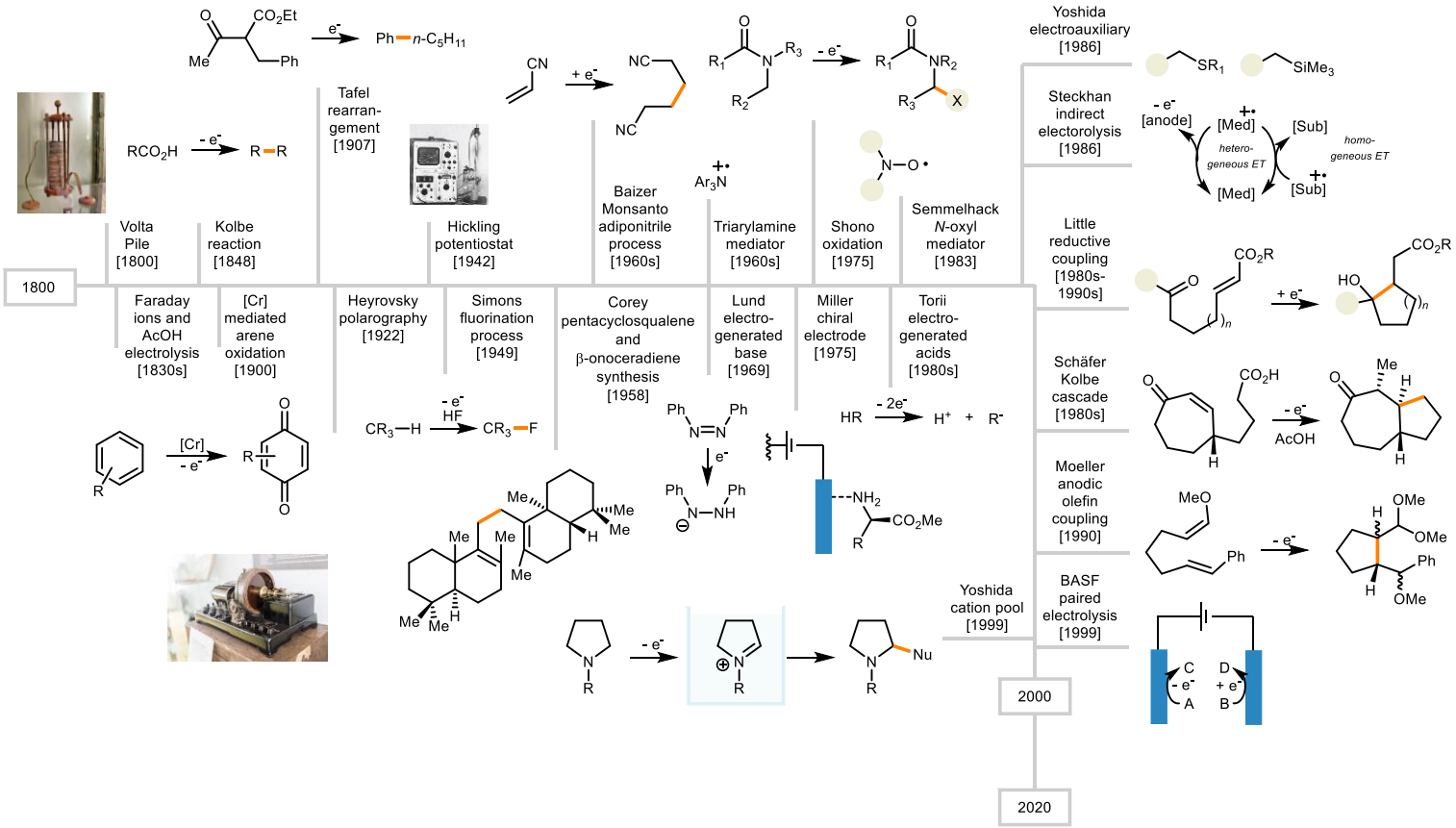
are needed in these delicate

experiments. Patience. Patience."

Michael Faraday

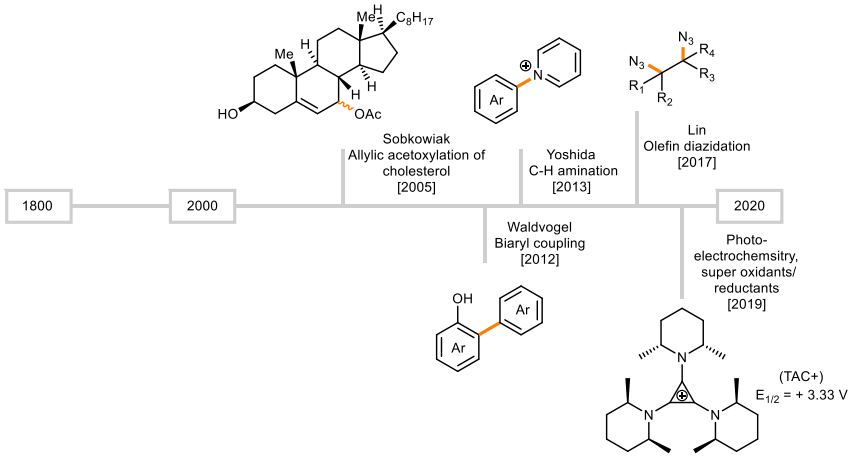
M. Yan *et. al. Chem. Rev.* **2017**, 117, 13230.
Image Source: Wikipedia

A Timeline of Electro-Organic chemistry



M. Yan *et. al. Chem. Rev.* **2017**, 117, 13230.
Image Source: Wikipedia

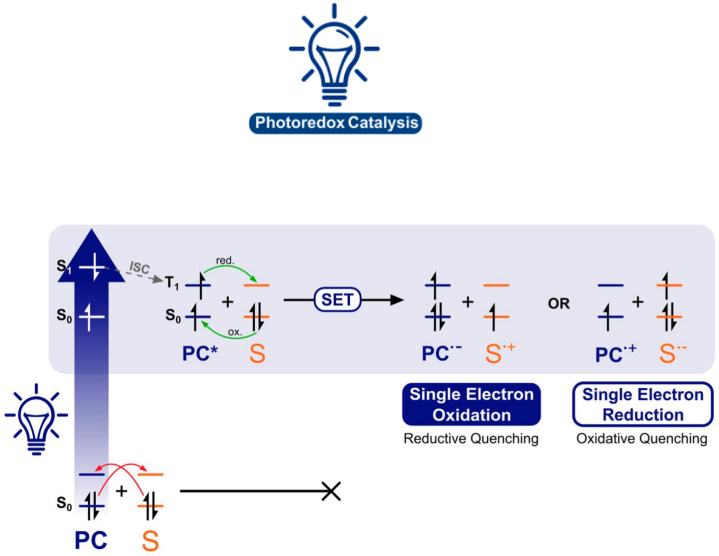
A Timeline of Electro-Organic chemistry

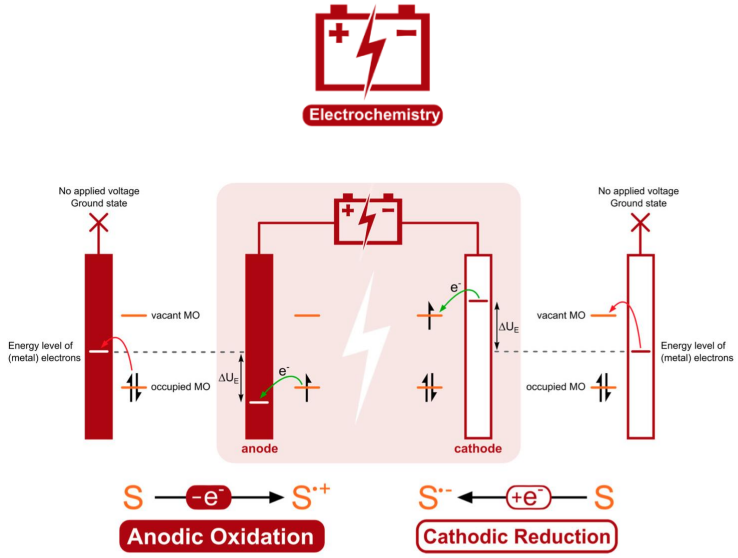


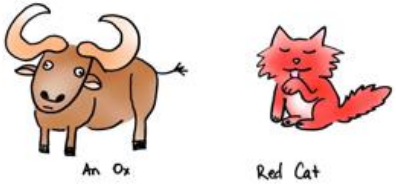
This Literature Review:

Select examples to highlight key transformations and techniques used in electro-organic synthesis

Underlying Theory

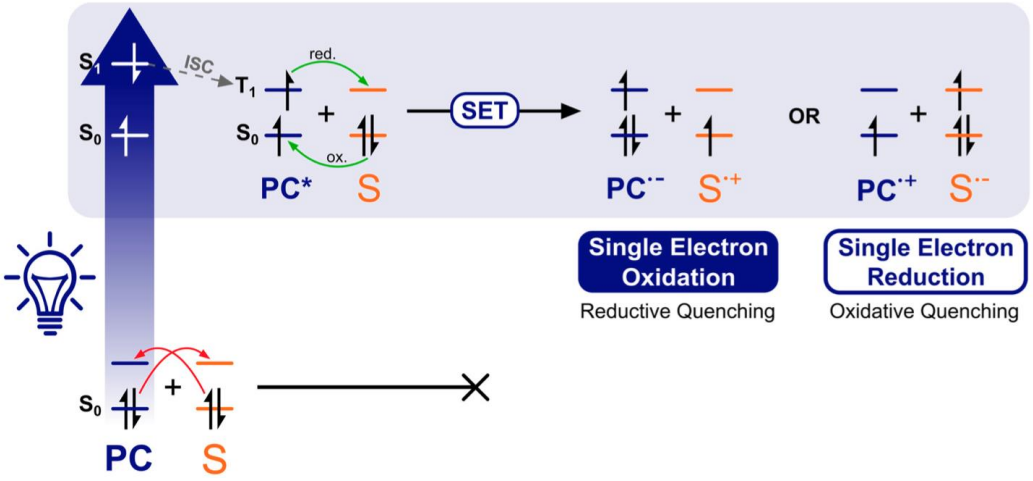






R. H. Verschueren and W. M. De Borggraeve. *Molecules* **2019**, *24*, 2122.

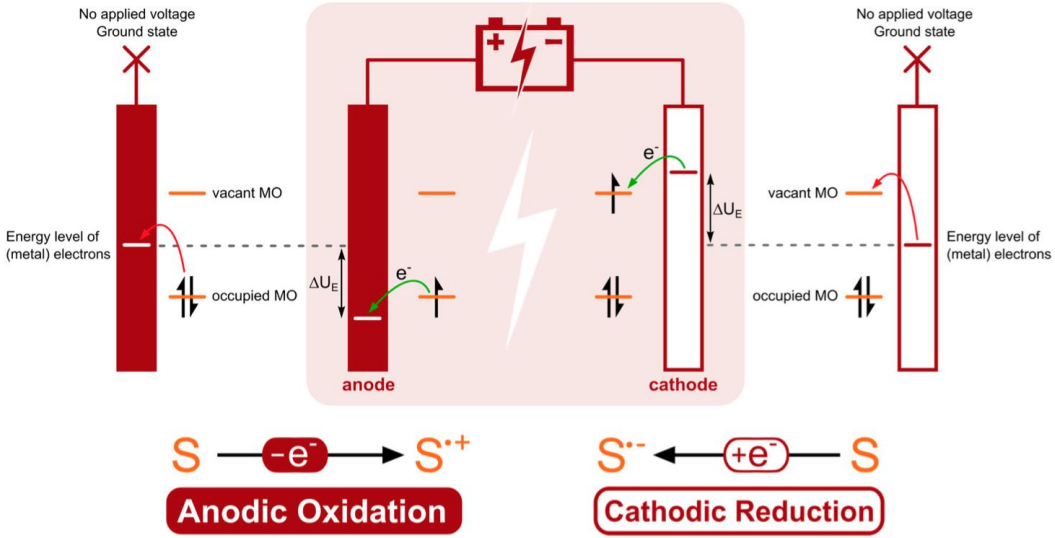
Photoredox Catalysis

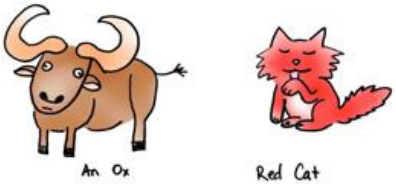


R. H. Verschueren and W. M. De Borggraeve. *Molecules* **2019**, *24*, 2122.

Electrochemistry

*"The **Fermi Level** of a solid-state body is the thermodynamic work required to add one electron to the body."*





R. H. Verschueren and W. M. De Borggraeve. *Molecules* **2019**, *24*, 2122.

A Comparison between Photoredox Catalysis and Electrochemistry

Photoredox Catalysis

- **Electron Transfer -** Homogeneous
- **Half Reactions** - Within once cycle
- **Selectivity** – Catalyst choice
- **Rate** – Loading, light intensity
- **Over reactivity –** Concentration, catalyst
- **Mild & Green & Cost**

Electrochemistry

- **Electron Transfer** - Heterogeneous
- **Half Reactions** - Two distinct locations
- **Selectivity** –Tunable potential, electrode choice
- **Rate –** Current, electrode, electrolyte
- **Over reactivity** – Total charge consumption (F/mol)
- **Mild & Green & Cost**

R. H. Verschueren and W. M. De Borggraeve. *Molecules* **2019**, *24*, 2122.

A Comparison between Photoredox Catalysis and Electrochemistry

Limitations

Photoredox Catalysis

- **Light absorption** - Beer-Lambert-Bouguer Law
- **Sacrificial redox agents**
- **Photon energy limit**

Electrochemistry

- **Solvent potential window**
- **Ohmic drop** – Double layer, diffusion controlled

Beer-Lambert-Bouguer law

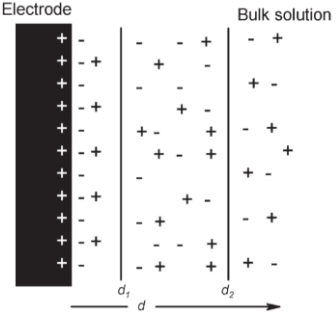
$$A = \varepsilon \cdot c \cdot d = \log \frac{I_0}{I}$$

$A \sim d$ $\quad$ $I \sim 10^{-\varepsilon \cdot c \cdot d}$

Ohmic drop

$$\Delta E_{ohm} = -I \cdot R_{cell} \text{ with } R_{cell} = \frac{d}{\rho \cdot A}$$

$\Delta E_{ohm} \sim d$



R. H. Verschueren and W. M. De Borggraeve. *Molecules* **2019**, *24*, 2122.

Key Equations

Nernst Equation

$$E_{cell} = E^{o}_{cell} - \frac{RT}{nF} \ln Q$$

$$\Delta G = -nF\Delta E_{cell} < 0$$

$$\Delta E^{cell} = E_{reduced} - E_{oxidised} > 0$$

Image Source: Geni.

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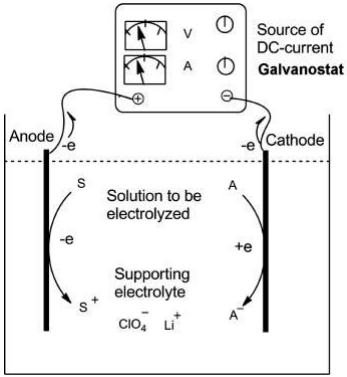
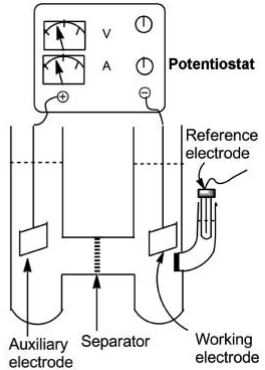
Experimental Parameters

Un-divided Cell



- First choice
- Easy to set up

Divided Cell



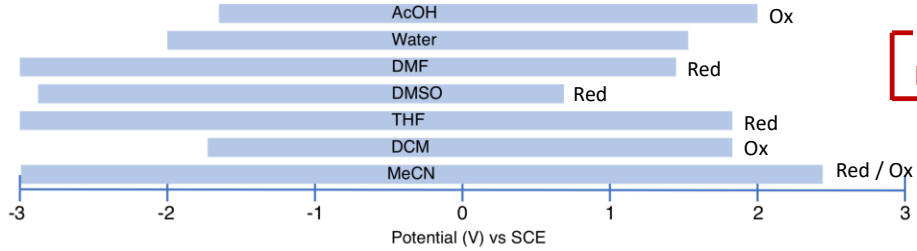
- Higher resistance
- Inconvenient
- Useful when product reacts at opposite electrode

(A) constant current	▪ First choice (2 - 10 mA, 2 - 4 F/mol, 0.1 - 0.3 mmol) ▪ Better conversion, sometimes over-reaction
(V) constant potential	▪ Lower conversion ▪ Higher selectivity

B. A. Frontana-Uribe *et. al. Green Chem.*, **2010**, *12*, 2099.

Experimental Parameters

Solvent Potential Window



Unsuitable Solvents

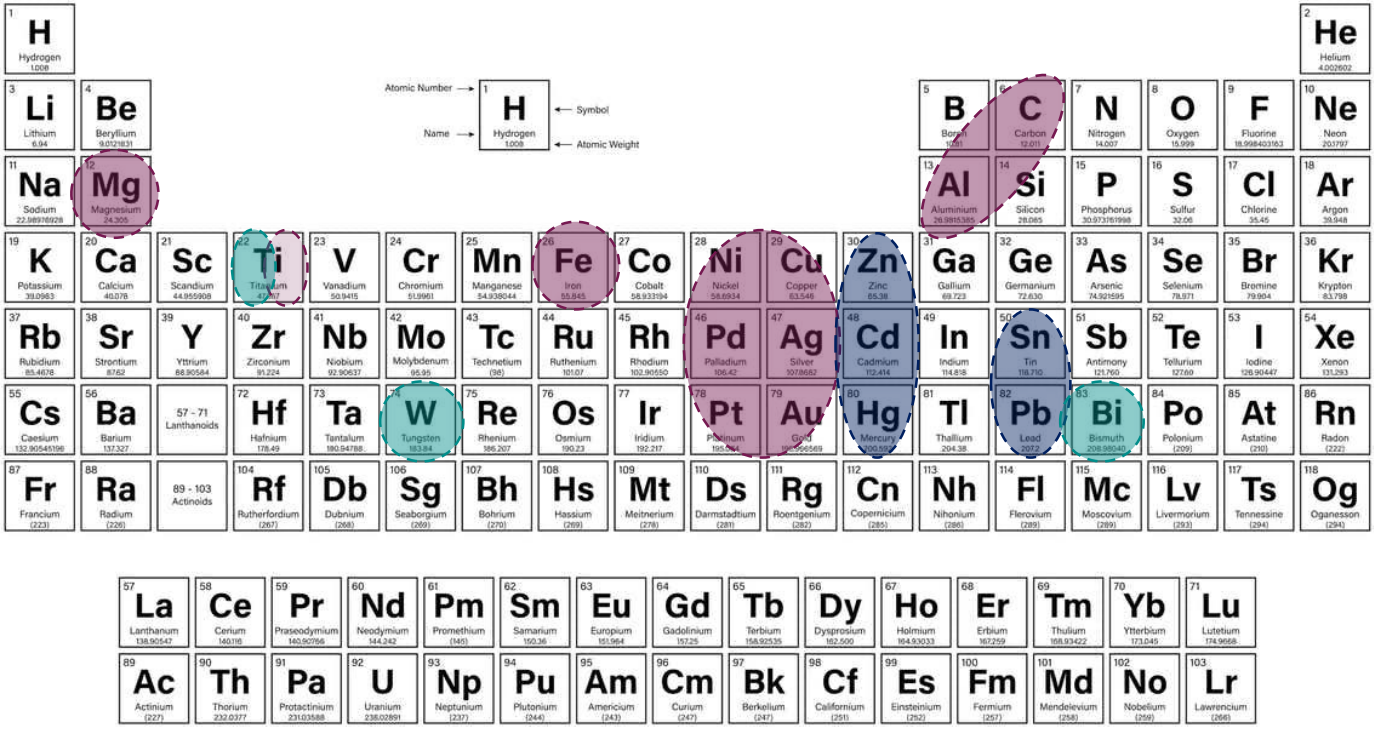
benzene, toluene, hexane

Supporting Electrolyte

Concentration: [0.1 – 0.5 M]
Cation: Li^+ , R_4N^+
Anion: ClO_4^- , BF_4^- , triflate, halide

D. A. Nicewicz *et. al.*. *Synlett*, **2016**, *27*, 714.
T. Fuchigami *et. al.* Fundamentals and Applications of Organic Electrochemistry: Synthesis, Meterials and Devices, John Wiley & Sons, Oxford, **2015.**

Electrode Material



Electrodes

High H_2 overpotential

Photoanodes

Experimental Parameters

Large O_2 overpotential

Anode

• graphite • glassy carbon • boron-doped diamond (BDD) • reticulum vitreous carbon (RVC)

Reduction	Oxidation
Mg Al Fe Ni Sn Pb Cu Hg Ag	Au Pt Carbon-based
Sacrificial anode (dissolve when used)	*Non-sacrificial anode*

Large H_2 overpotential

Cathode

Low H_2 overpotential

Mg Al Fe Sn Pb Hg Carbon-based	Fe Au Ni Pt
Reduction of organic compounds	*When H_2 evolution is needed*

"Electrodes are merely the surfaces or doors by which the electricity enters into or passes out of the substances suffering decomposition."

Michael Faraday, **1833**

D. A. Nicewicz *et. al. Synlett*, **2016**, *27*, 714.

Experimental Parameters

Large O_2 overpotential

Anode

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Cathode

Low H_2 overpotential

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Reduction of organic compounds	*When H_2 evolution is needed*

Reference Electrodes

Standard Hydrogen Electrode (SHE) E = 0.000 V

Saturated Calomel Electrode (SCE) E = 0.241 V

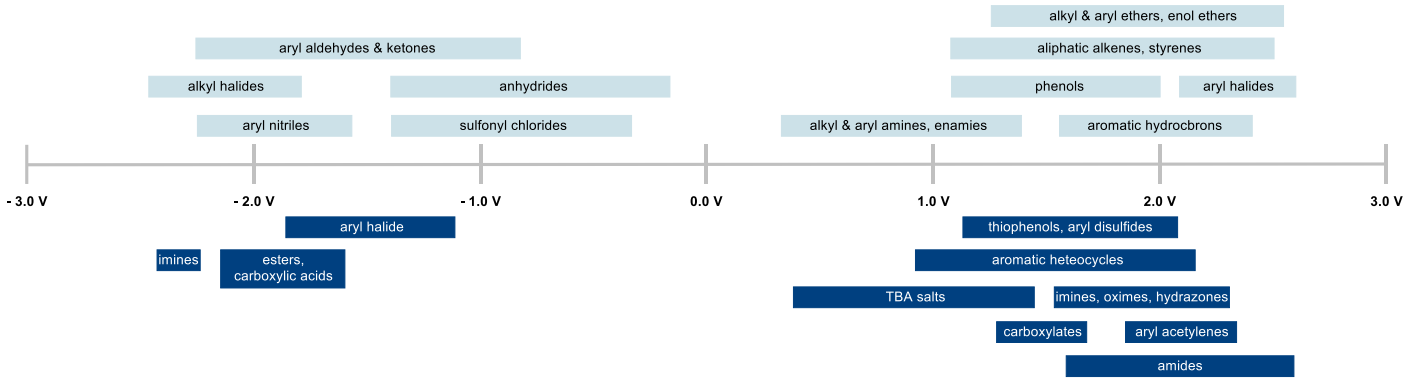
$Cu/CuSO_4$ electrode (CSE) E = 0.314 V

Ag/AgCl electrode E = 0.197 V

D. A. Nicewicz *et. al. Synlett*, **2016**, *27*, 714.

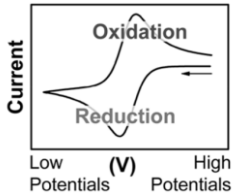
Experimental Parameters

Redox Potentials



Cyclic Voltammetry

IPUAC Convention

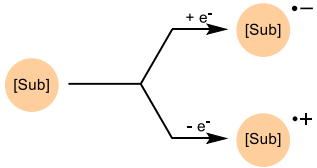


- Measure reduction potentials at a fixed current
- Reversible / Irreversible / Quai-reversible processes
- Ferrocene (Fc / Fc^+ = 0.45 V) internal standard in organic solvents (MeCN)

H. Roth *et. al. Synlett.*, **2016**, *27*, 714.
N. Elgrishi *et. al. J. Chem. Educ.* **2018**, 95, 197.

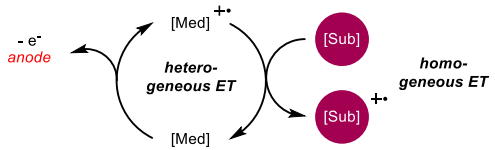
Electrolysis Methods in Organic Chemistry

D Direct Electrolysis



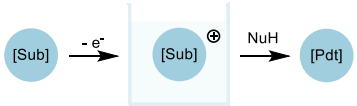
- Direct electrolysis by electrodes
- Heterogeneous electron transfer

M Mediated Electrolysis



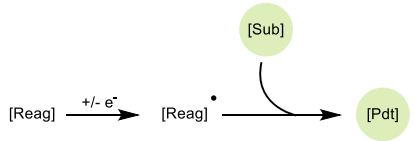
- Mediators act as electron carriers
- Homogeneous electron transfer (photoredox like)
- Increase in reaction rate
- Supporting electrolyte is indispensable

C Cation Pool Method



- Low temperature generates and accumulates reactive species

E Electro-Generated Reagents



M. Yan *et. al. Chem. Rev.* **2017**, 117, 13230.

Industrial Applications of Electrochemistry

Aluminium

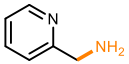
$$2\ Al_2O_3 + 3\ C \xrightarrow[\text{(-) Al}]{\text{(+) C}} 4\ Al + 3\ CO_2$$

Chlor-Alkali Industry

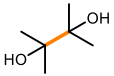
$$2\ NaCl + 2\ H_2O \xrightarrow[\text{(-) Steel/Hg}]{\text{(+) Ti}} Cl_2 + H_2 + 2\ NaOH$$

acetoin
BASF

acetylenedicarboxylic acid
BASF

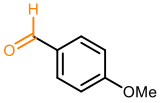


2-aminomethylpyridine
Reilly Tar

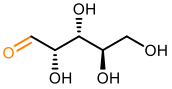


pinacol
BASF

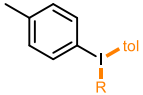
adiponitrile
BASF, Monsanto



***p*-anisaldehyde**
BASF, Monsanto

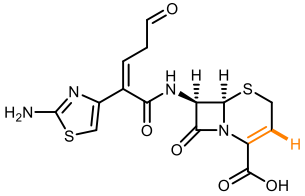


arabinose
Electrosynthesis Co.



ditolyliodonium salts
Eastman Chemical

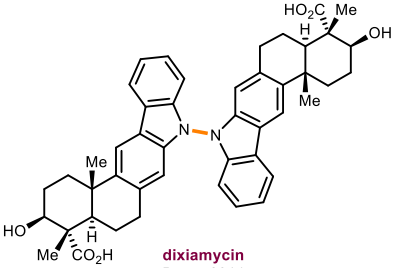
ditolyliodonium salts
BASF



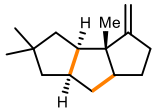
ceftibuten
Electrosynthesis Co.

D.S.P. Cardoso *et. al. Org. Process Res. Dev.* **2017**, *21*, 1213.

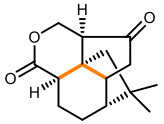
Electrochemistry in Natural Product Synthesis



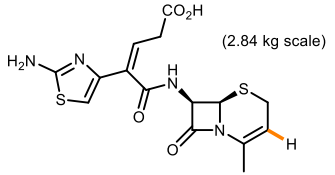
dixiamycin
Baran 2014
N-N dimerization



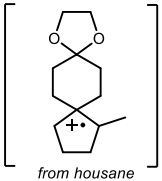
(±)-hirsutene
Little 1981
reduction / oxidation



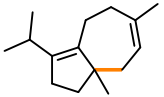
quadrone
Little 1990
reductive cyclization



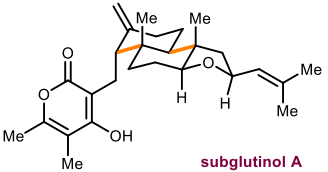
ceftibuten
Zhang 2002
cathodic reduction



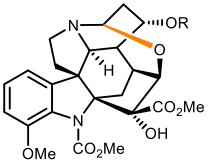
from housane



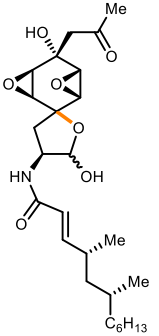
daucene
Little 2009
radcal cation rearrangement



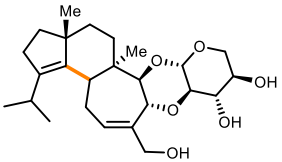
subglutinol A
Baran 2018
snider polyene cyclisation



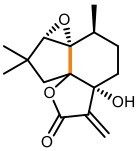
kopsidine A / B
Tan 2001
shono amine oxidation



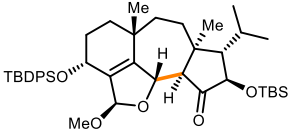
penicimutanolone
Xu 2019
electro-oxidative dearomatization



erinacine
Wright 1999
furan annulation

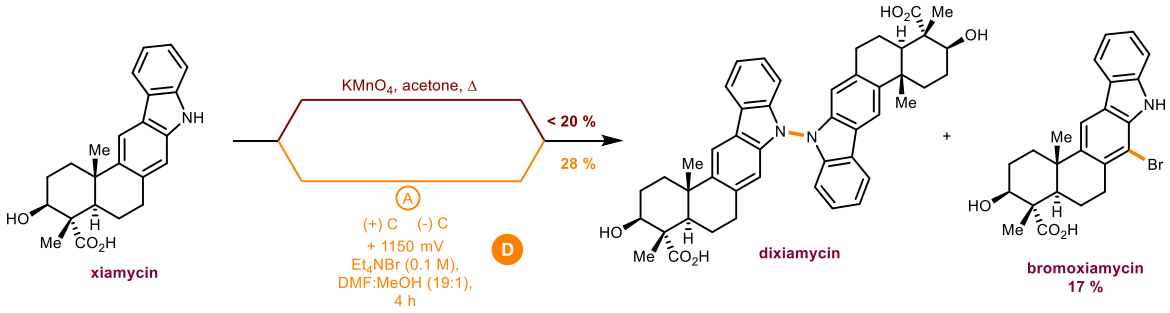


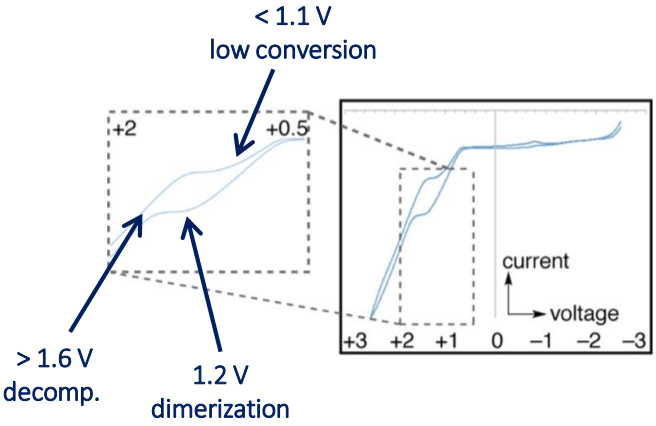
(-)-alliacol
Moeller 2004
furan annulation



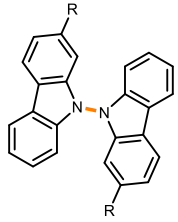
towards guanacastepenes
Trauner 2005
furan annulation

Natural Products: Case Studies

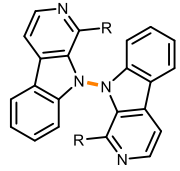




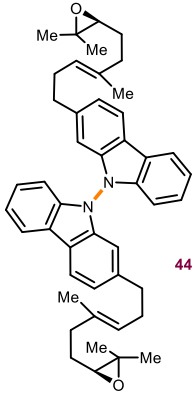
N-N dimerization Scope



CO_2Me	32 %
t-Bu	50 %
SO_2Me	60 %
CF_3	66 %



Me	66 %
H	49 %

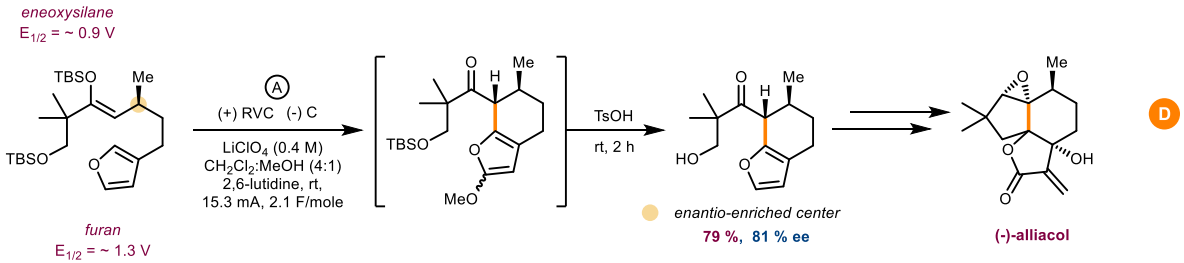


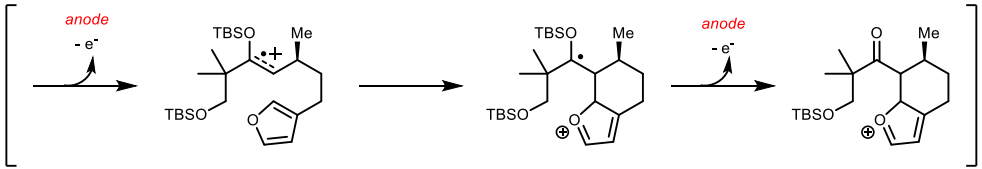
44 %

B. R. Rosen *et. al. J. Am. Chem. Soc.* **2014**, *136*, 5571.

Natural Products: Case Studies

Marasmius alliaceus

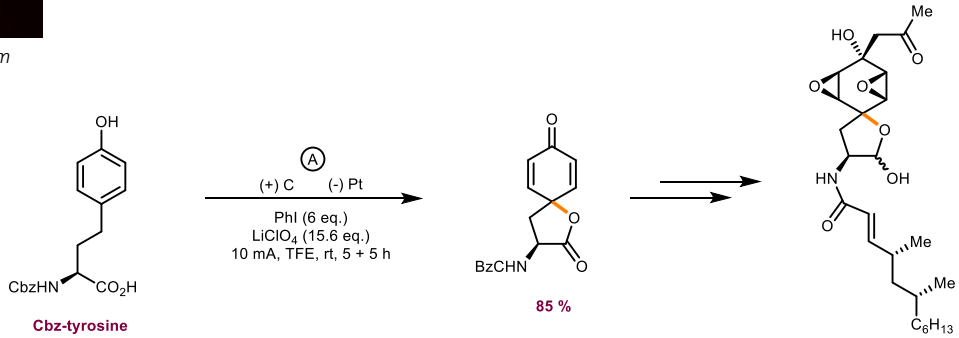




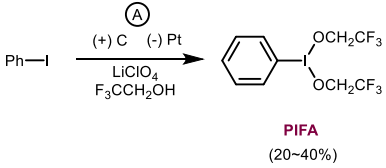
J. Mihelcic, K. D. Moeller. *J. Am. Chem. Soc.* **2004**, *126*, 9106

Natural Products: Case Studies

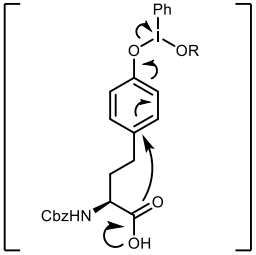
Penicillium purpurogenum



E



electrogenerated hypervalent iodine oxidant



electro-oxidative dearomatisation

Review Outline

Introduction

- Organic Electrochemistry
- Key Milestones
- Underlying theory

Practicalities & Applications

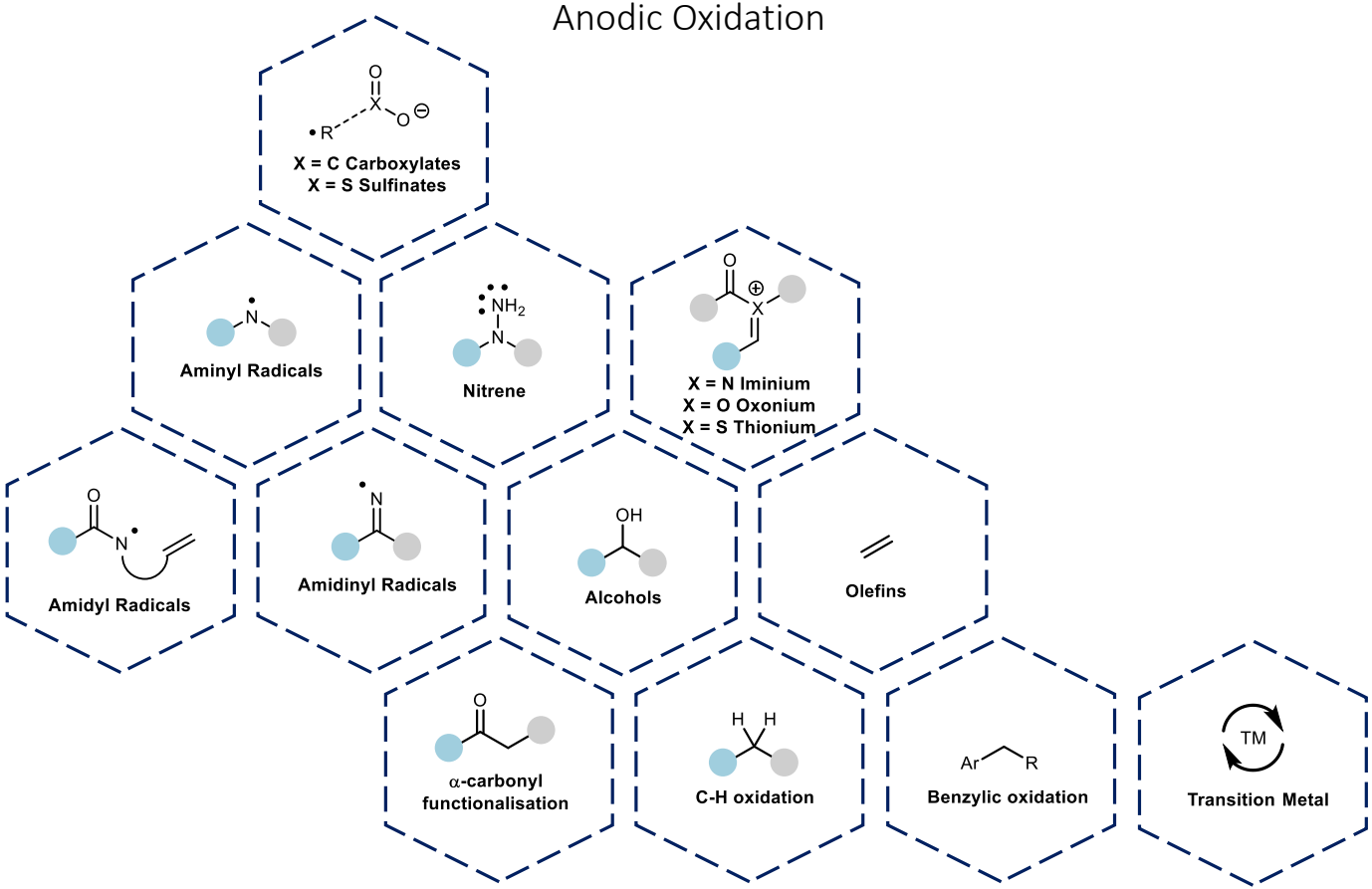
- Experimental Parameters
- Electrolysis Methods
- Applications
  - Industrial Processes
  - Natural Product Synthesis

Break

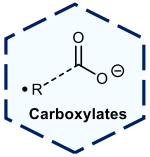
Methodology

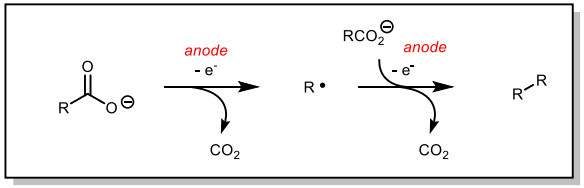
- Anodic Oxidation
- Cathodic Reduction
- Paired Electrolysis
- Asymmetric Electrocatalysis
- Photo-electrochemistry

Anodic Oxidation

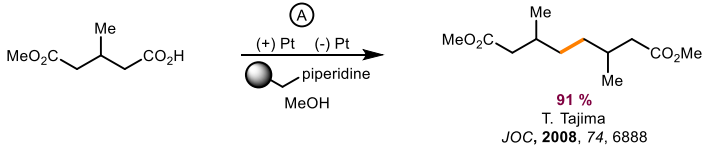


Anodic Oxidation



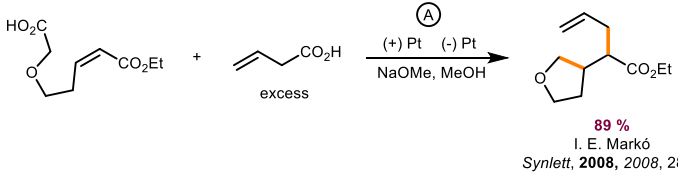


- **Kolbe**



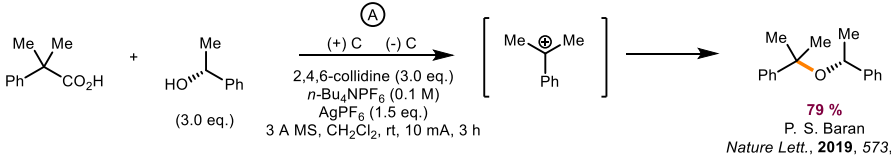
7 examples
44 - 99 %
D

- **Mixed-Kolbe**



15 examples
16 - 90 %
D

- **Non-Kolbe**

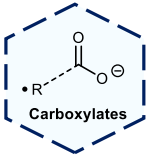


83 examples
14 - 95 %
Nu = KF, CN, CO_2H
D

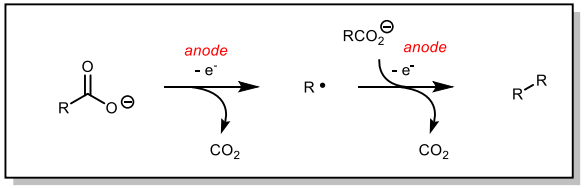
Secondary oxidation to cationic intermediate

• fragmentation • rearrangement • elimination • nucleophilic addition •

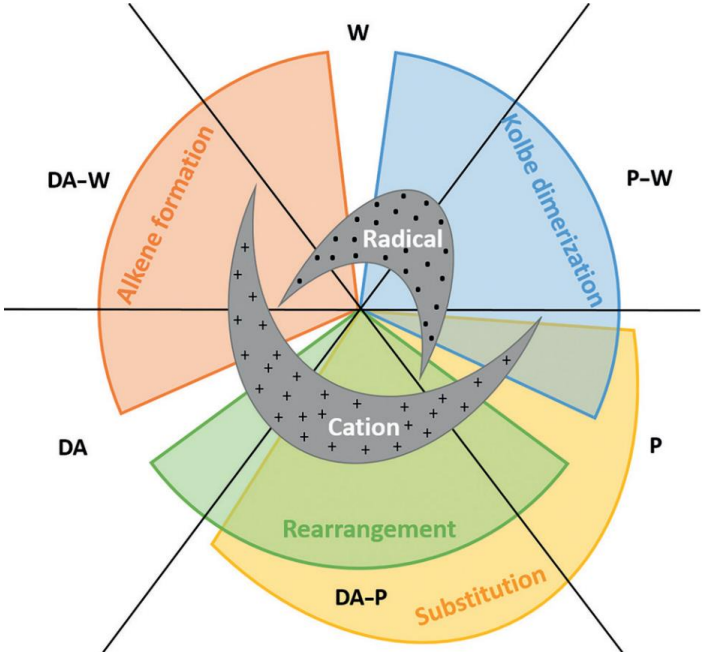
Recent and concise summary on Kolbe processes: *Angew. Chem. Int. Ed.* **2018**, *57*, 5594.



Anodic Oxidation

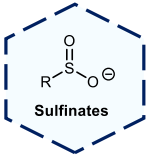


- Solvent effect on reactive intermediate

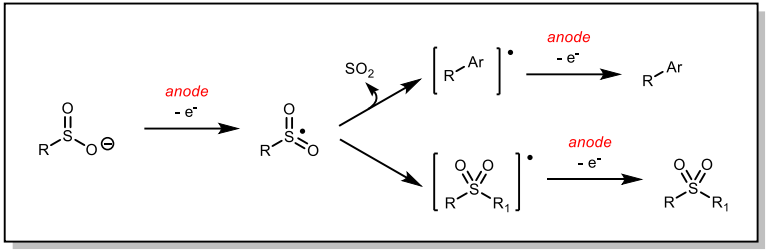


W water
P protic
DA dipolar aprotic

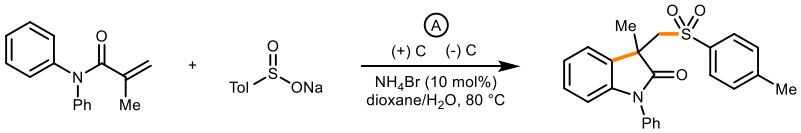
L. Schulz, S. R. Waldvogel, *Synlett*, **2019**, *30*, 275–286



Anodic Oxidation

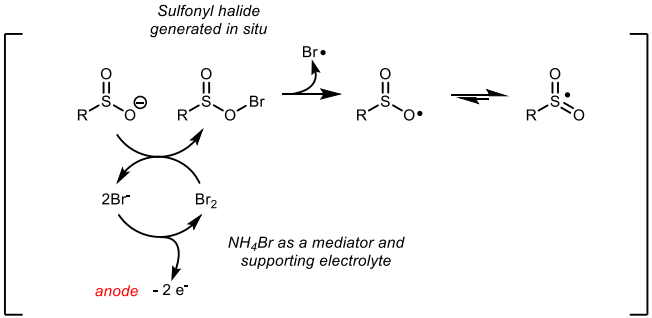


- Sulfonyl radical

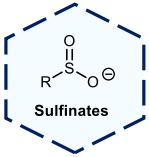


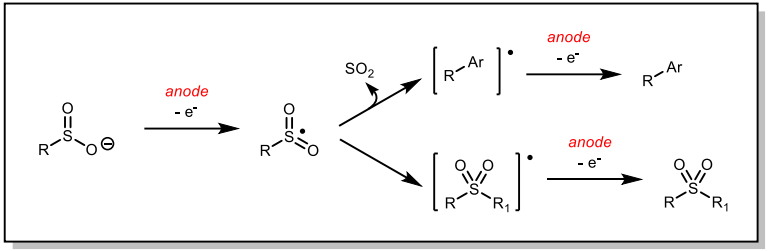
15 examples
48 - 85 %

75 %
B. G. Sun
Green Chem. **2016,** *18*, 6311

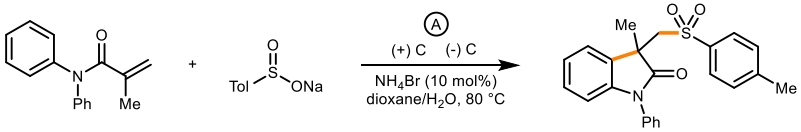


Anodic Oxidation





- Sulfonyl radical

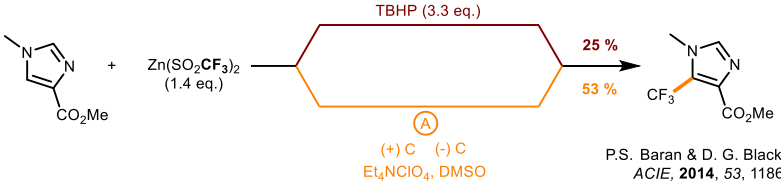


75 %
B. G. Sun
Green Chem. **2016,** *18*, 6311

15 examples
48 - 85 %

M

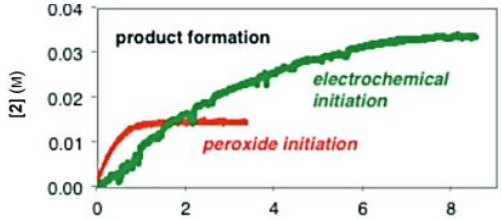
- Alkyl radical



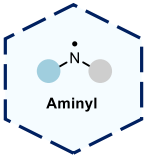
P.S. Baran & D. G. Blackmond
ACIE, **2014**, *53*, 11868

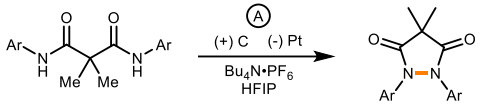
24 examples
15 - 92 %

E



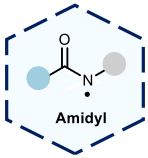
Anodic Oxidation

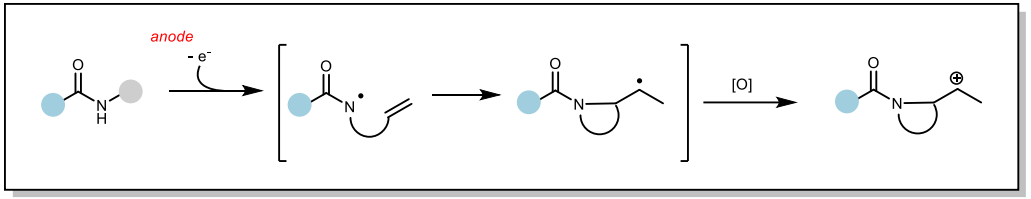




66 %
D. Waldvogel
ACIE, **2016**, *55*, 9437

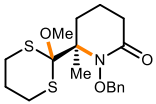
D



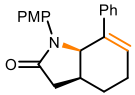


• *elimination* • *nucleophilic addition* • *H-atom abstraction* •

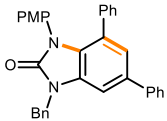
Direct Electrolysis



Nu addition
K. D. Moeller
JOC, **2014**, *79*, 379

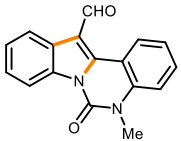


Elimination
H. C Xu
JACS, **2017**,*139*, 2956

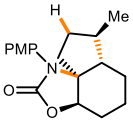


Oxidative
H. C. Xu
ACIE, **2019**, *58*, 9017

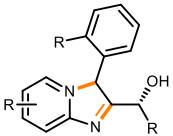
Mediated Electrolysis



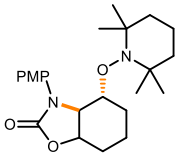
Oxidative
H. C. Xu
ACIE, **2016**, *55*, 9168



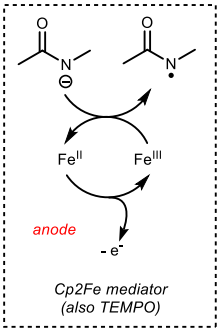
H-atom source
H. C. Xu
ACIE, **2016**, *55*, 2226



Oxidative
H. C. Xu
Beilstein *JOC*. **2019**, *15*, 795

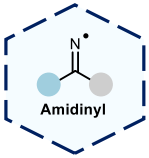


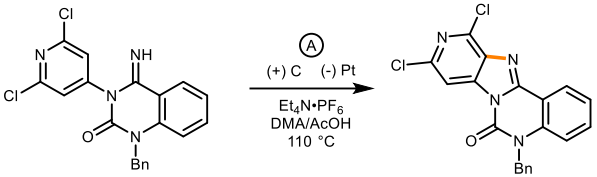
Nu addition
H. C. Xu
Chem. Eur. J. **2014**, *20*, 12740



Cp2Fe mediator
(also TEMPO)

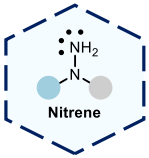
Anodic Oxidation

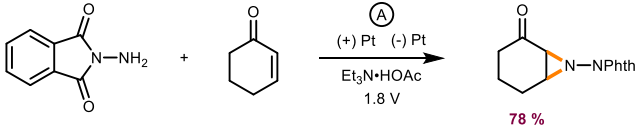




84 %
H. C. Xu
ACIE, **2017**, *56*, 587

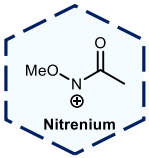
D

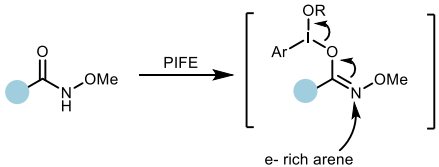




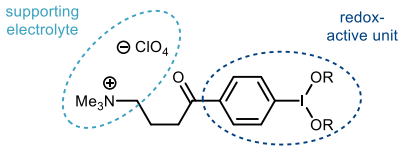
78 %
K. A. Yudin
JACS, **2002**, *124*, 530

D

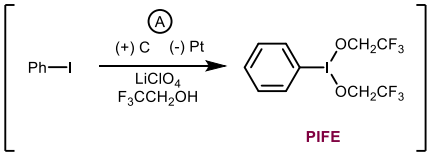




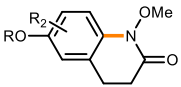
hypervalent iodine as electrogenerated redox mediator



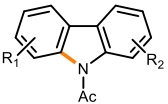
HFIP
Org. Lett. **2016**, *18*, 5896



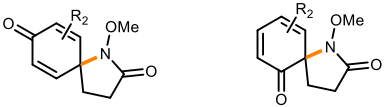
PIFE



quinolines
Org. Lett. **2010**, *12*, 436
Synlett. **2008**, *2008*, 134



carbazoles
Tetrahedron, **2010**, *66*, 9779
Org. Lett. **2016**, *18*, 5896

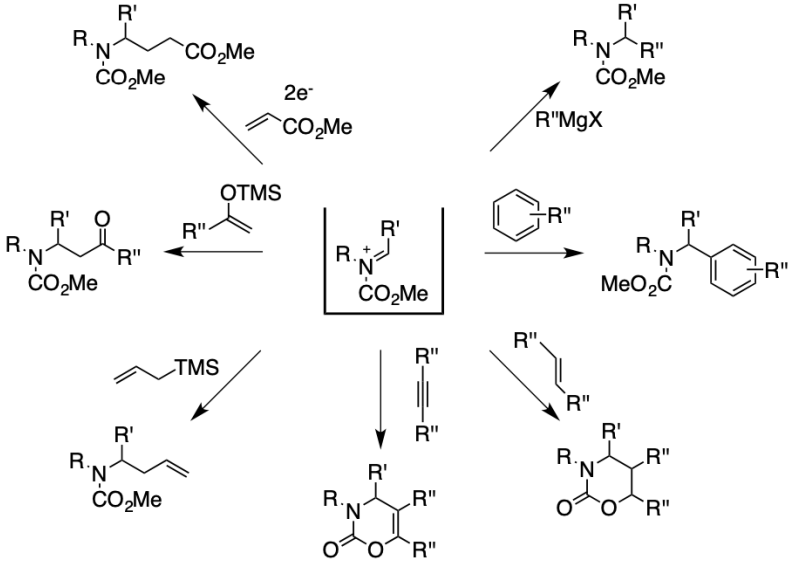


spirocycles
Tet. Lett. **2006**, *47*, 6505

E

Anodic Oxidation

- Shono Oxidation

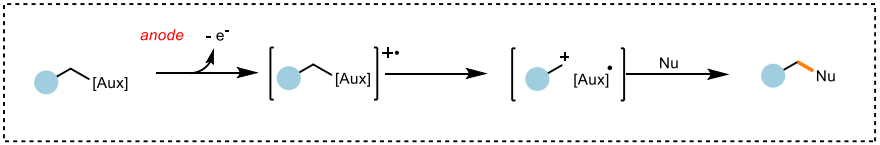


Cation Pool Method

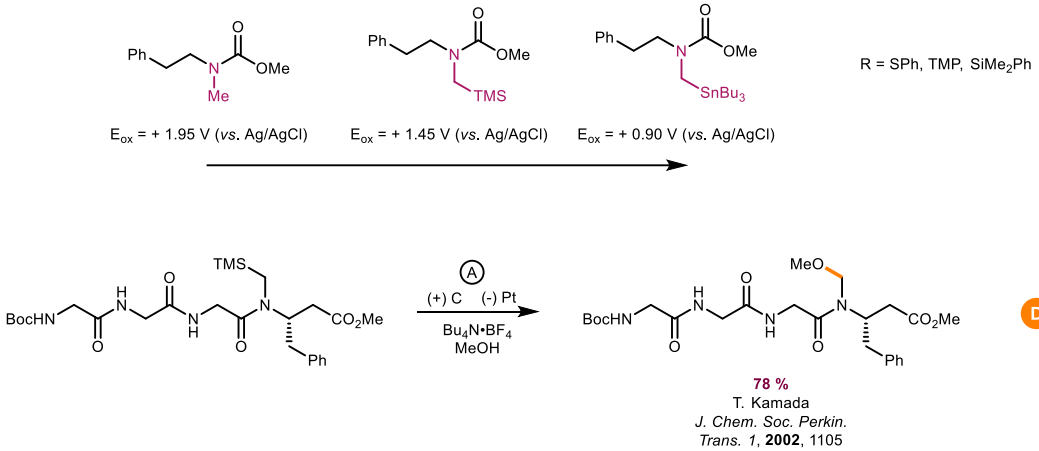
• cryogenic temperatures accumulates cationic intermediates • reduced oxidation of nucleophile • prevents over oxidation of product •

Anodic Oxidation

- Shono Oxidation - electroauxilaries



• lowers redox potential • prevents solvent oxidation • prevents over-oxidation• chemo- and regio- control •

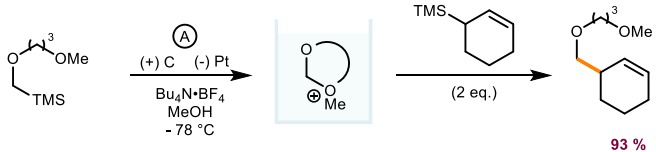


78 %
T. Kamada
J. Chem. Soc. Perkin. Trans. 1, **2002**, 1105

H. Sun *et. al. J. Am. Chem. Soc.*, **2006**, *128*, 1376

Anodic Oxidation

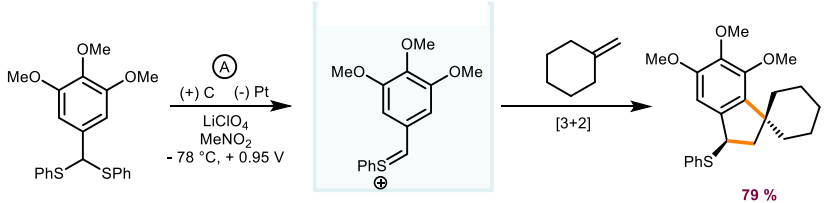
- Related Intermediates



Further stabilisation of the cation pool

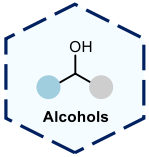
93 %
J. I. Yoshida
Org. Lett. **2005**, *7*, 4717

C



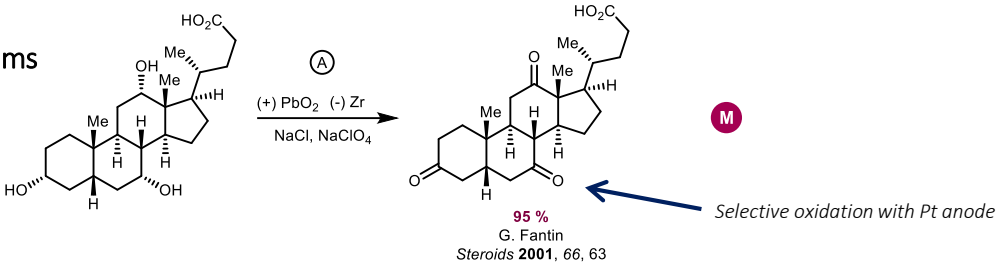
79 %
M. Tada
Org. Lett. **2001**, *3*, 1245

C



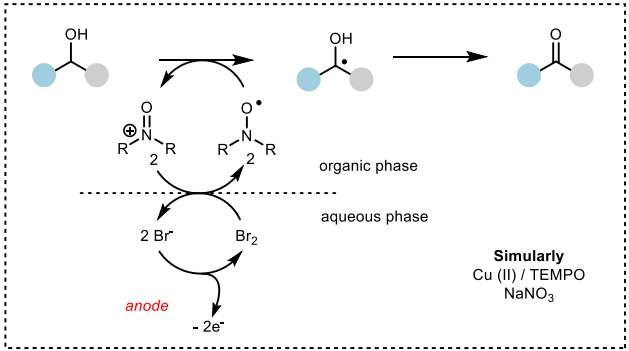
Anodic Oxidation

- Double Mediatory Systems



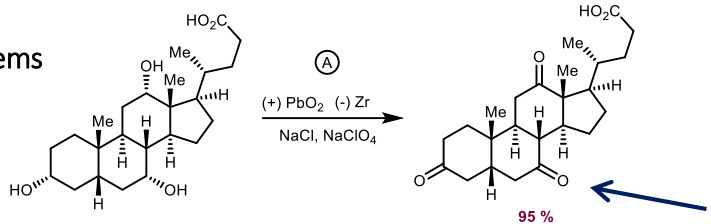
Requires nitroxyl mediators

• sparingly soluble in polar media • double mediatory systems • biphasic solvent mixture / emulsions • polymer support • electrode anchoring •



Anodic Oxidation

- Double Mediatory Systems



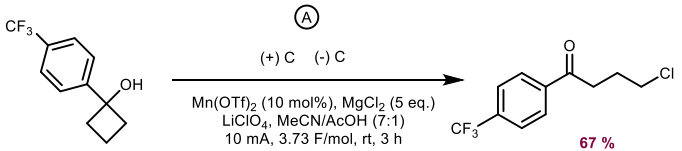
95 %
G. Fantin
Steroids **2001**, *66*, 63

Selective oxidation with Pt anode

Requires nitroxyl mediators

• sparingly soluble in polar media • double mediatory systems • biphasic solvent mixture / emulsions • polymer support • electrode anchoring •

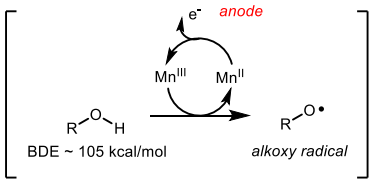
- Alkoxy Radicals



41 examples batch and flow

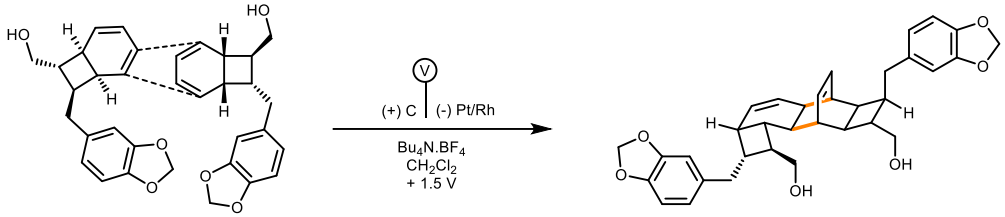
M

67 %
L. C. Morrill
Org. Lett., **2019**, *21*, 9241



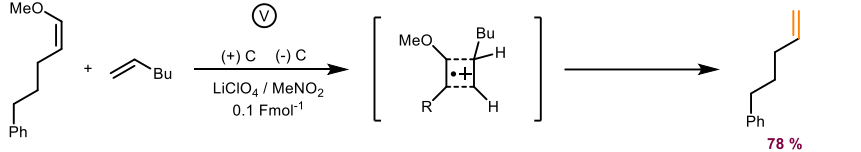
Anodic Oxidation

- Cycloadditions



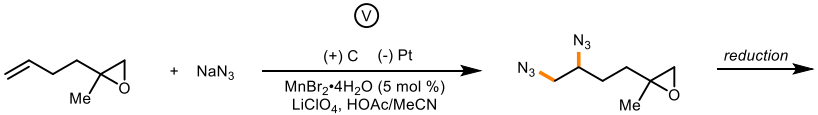
13 %
J. E. Moses
Chem. Commun. **2014**, *50*, 12523

- Cross-Metathesis



78 %
K. Chiba *et. al.*
ACIE, **2006**,*45*, 1461

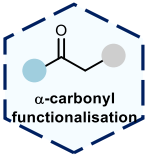
- Diazidiation

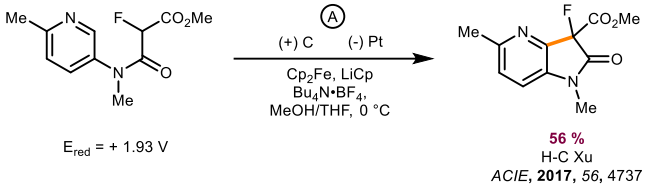


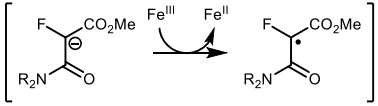
72 %, 1:1 dr
S. Lin
Science, **2017**, *357*, 575

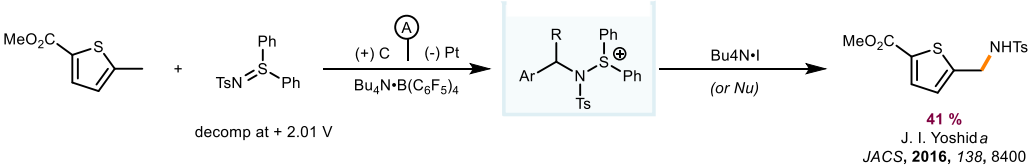
• inexpensive Mn catalyst • potentiostatic conditions allow high chemoselectitivty•

Anodic Oxidation

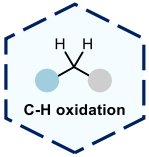






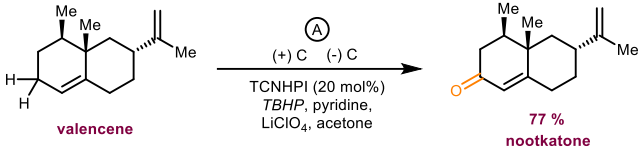


• benzyl cations unstable at – 78 °C (unlike di-aryl cations) •
cation pool prevents overoxidation •

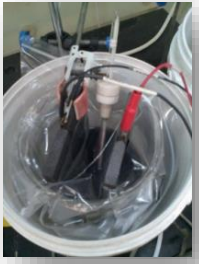


Anodic Oxidation

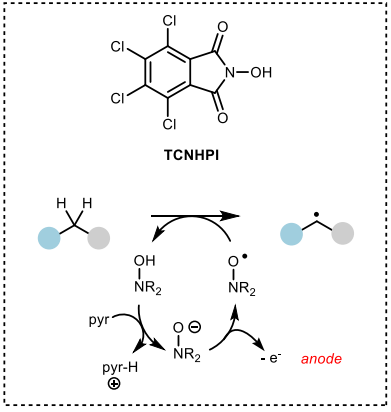
- Allylic C—H

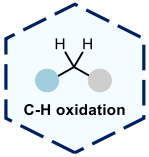


P. S. Baran
Nature, **2016**, 533, 77



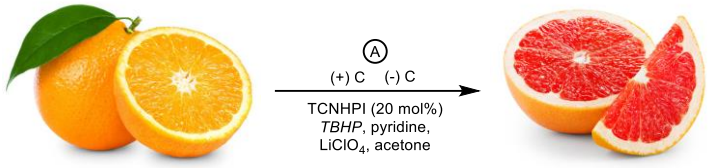
• improved yields over Cr, Rh or Se • up to 100 g scale • 40 examples





Anodic Oxidation

- Allylic C—H

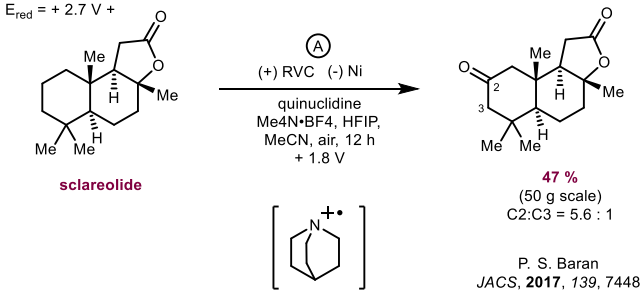


P. S. Baran
Nature, **2016**, 533, 77

400 tonnes of grapefruit = 1 kg

P450 enzymatic oxidation
(Oxford Biotrans)

- Methylene C—H



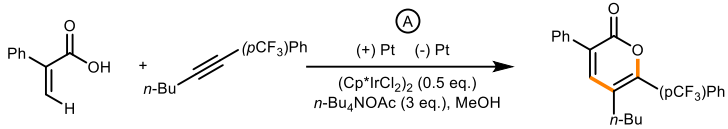
P. S. Baran
JACS, **2017**, *139*, 7448

electricity cost = $2,517
TFDO cat. = $ 9,120
Fe(PDP) cat. = $37,229

• mediator choice important • scalable • selectivity dependent on steric and electronic factors •

Anodic Oxidation

- C—H Functionalisation

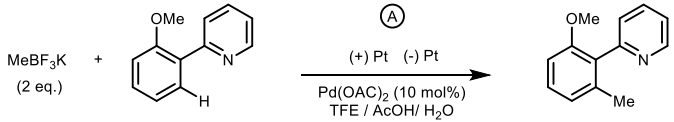


67 examples

Chemical oxidants:
$Cu(OAc)_2$, Ag_2CO_3, $PhI(OAc)_2$
< 18 % yield

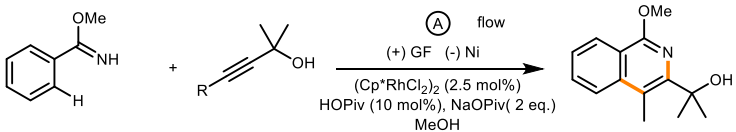
[*anode* Ir^{I} --> Ir^{III} ground state]

90 %
T. S. Mei
JACS, **2019**, *141,18970*



24 examples

64 %
T. S. Mei
Organometallics **2019**, *38*, 1208



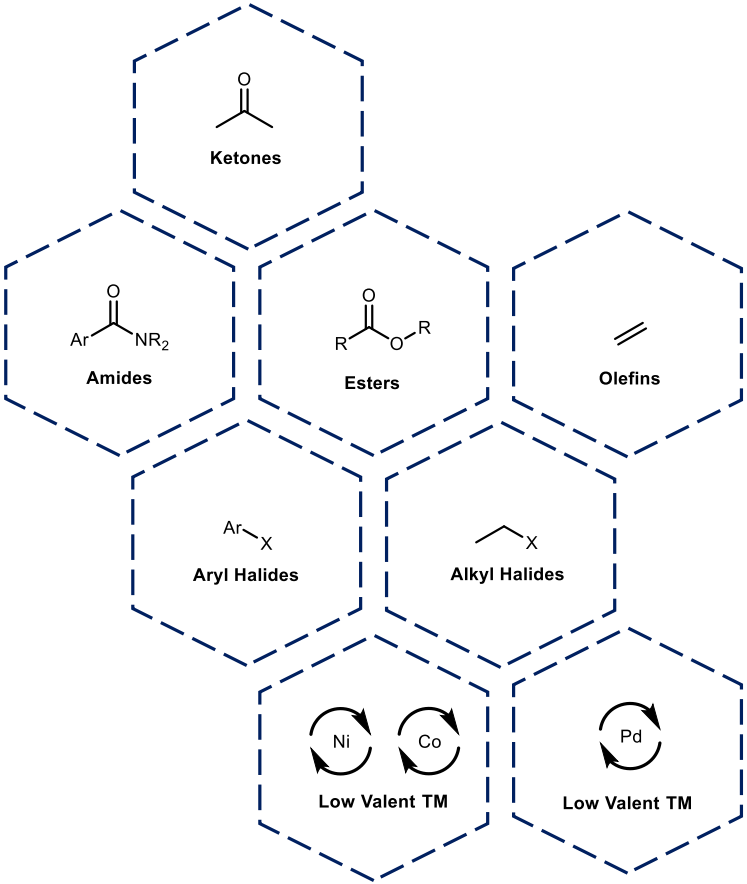
26 examples
35 - 99 %

90 %
L. Auckermann
JACS, **2019**, *141*, 17198

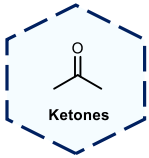
[*anode* Rh^{III} --> Rh^{IV} then Rh^{II} --> Rh^{III}]

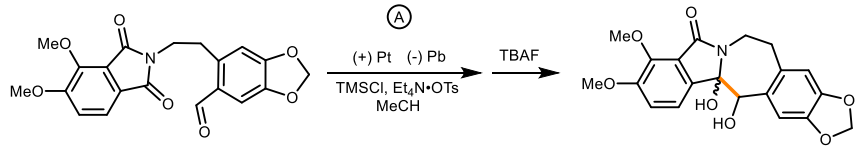
Related example H. C. Xu. *ACIE*, **2019**, *58*, 16770

Cathodic Reduction



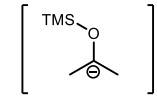
Cathodic Reduction



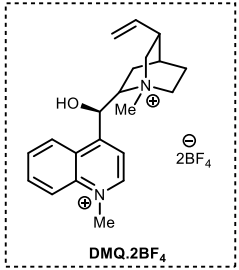


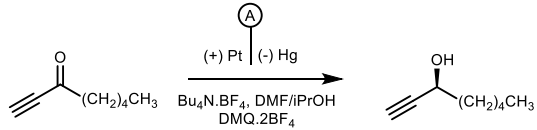
68 %, 1:1 dr

T. Sakurai
JOC. **2011**, *76*, 9856



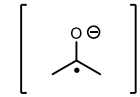
• TMS lowers redox potential •

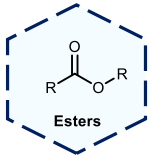




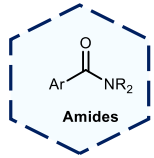
72 %, 70 % ee

P. R. Chhinpa
Tet. Asym. **2003**, *14*, 1079

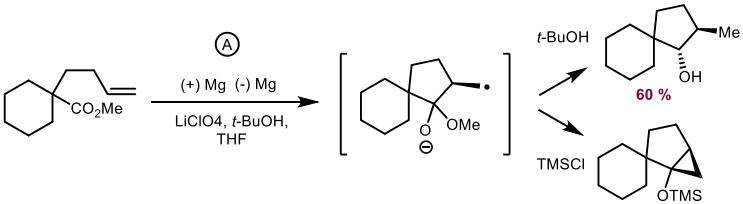




• *not reduced with Zn, Pb, Ni, Cu, Pt or C* •



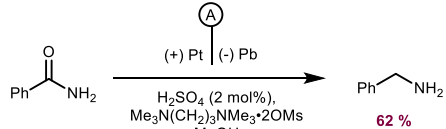
• *requires acidic media* •



60 %

67 %

Shono
JOC, **1922**, *57*,1061

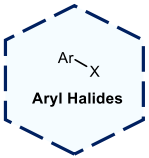


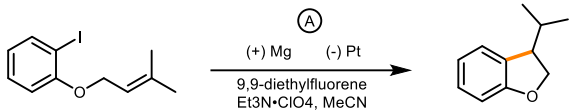
62 %

Waldvogel
EJOC, **2014**, 5144.

10 examples inc. 2° and 3° amines

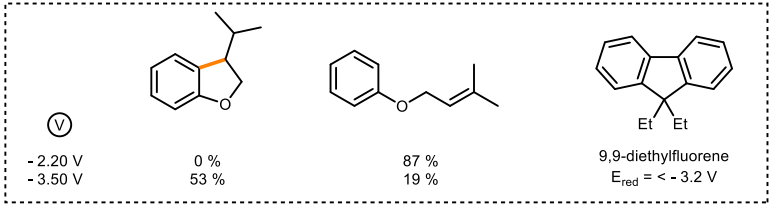
Cathodic Reduction

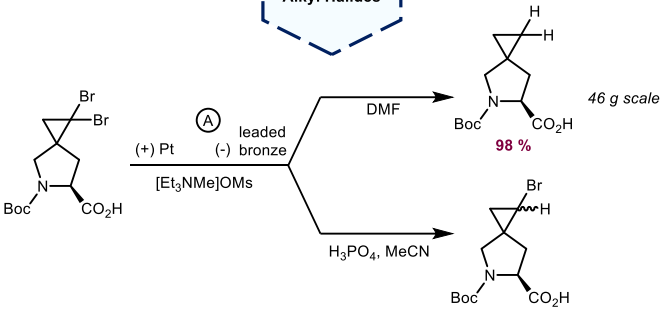




74%

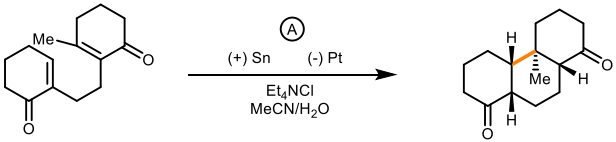
K. Mitsudo.
Electrochim. Acta, **2012**, *82*, 444.



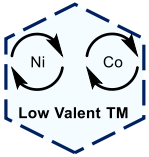


S.R Waldvogel
Chem. Eur. J. **2015**, *21*, 13878

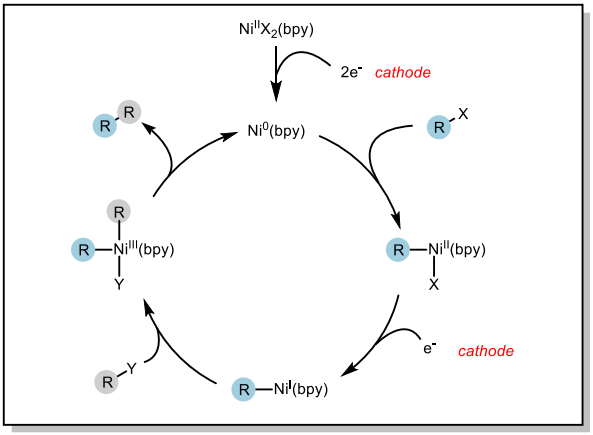
• *leaded bronze higher resistance to corrosion* •
racemisation & ring opening with chemical reagents •



59 %
30 % with SmI_2
Tetrahedron, **2007**, *63*, 1366



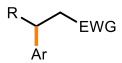
Cathodic Reduction



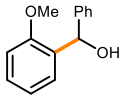
Low valent transition metal species as mediators

• Co(I) • Ni(I) •

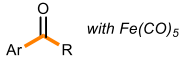
Aryl Halides



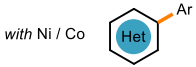
Conjugate addition
C. Ma
Electrochim. Acta, **2015**, *151*, 284



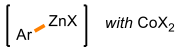
Nozaki-Hiyama-Kishi coupling
J. Perichon
Org. Let. **2001,** *3*, 2073



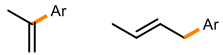
Ketone synthesis
J. Nedelec
Tetrahedron, **2001**, *57*, 525



Heteroaryl haides
J Perichon
Tet. Lett. **2000**, *41*, 201

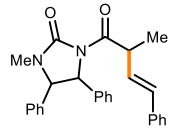


Transmetallation to Zn
J. Perichon
JOC. **2000**, *65*, 6024

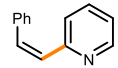


Cross electrophile coupling
J. Perichon
J. Org. Chem. **2003**, *68*, 1142
Tetrahedron, **2003,** *59*, 2999

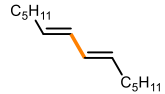
Alkenyl Halides



Alkyl-X



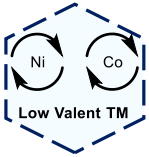
(Het)Ar-X



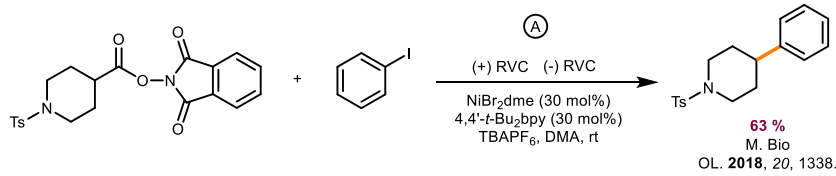
Homocoupling

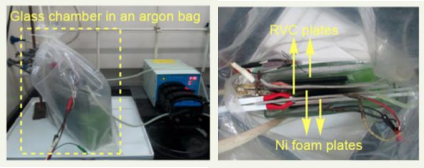
J. Nédélec
JOC, **2000**, *65*, 4575

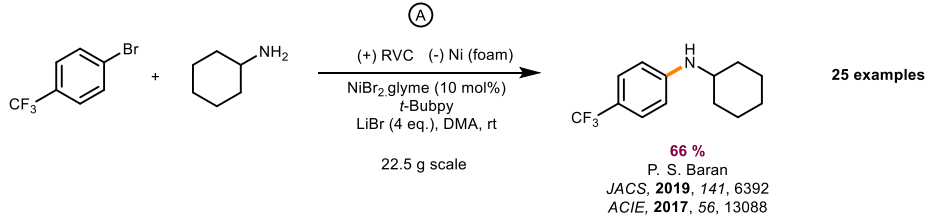
Cathodic Reduction

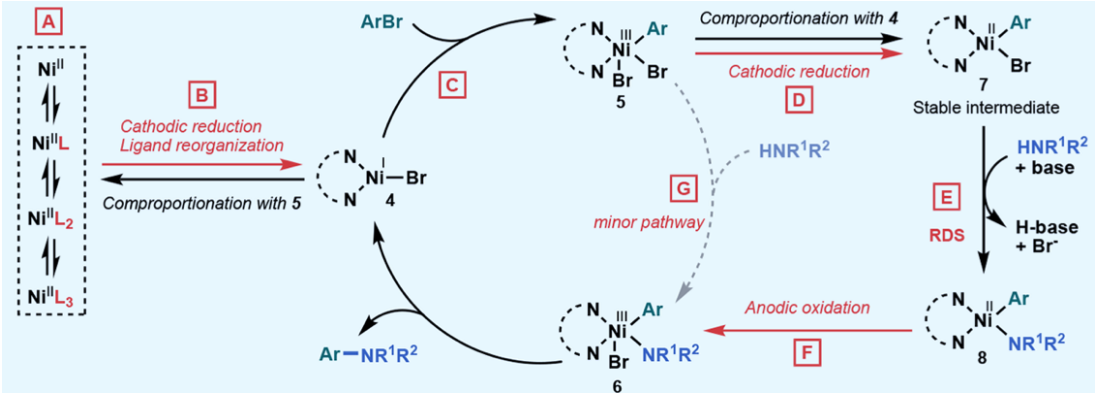


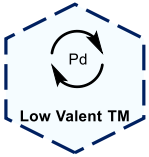
- Recent highlights



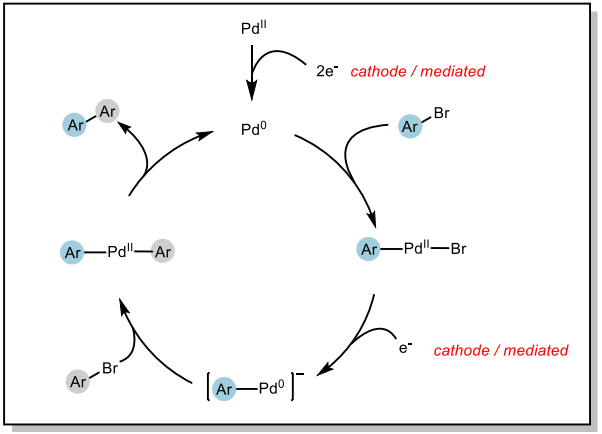


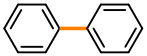




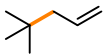


Cathodic Reduction





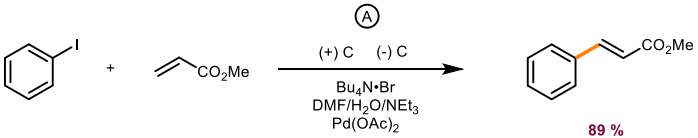
Homocoupling of aryl halides
G. Rothenberg
Adv. Synth. Catal. **2006**, *348*, 1705
H. Tanaka
Tet. Lett. **2013**, *54*, 3666



Allylation of alkyl halides
J. M. Huang
Org. Lett. **2017**, *19*, 2022

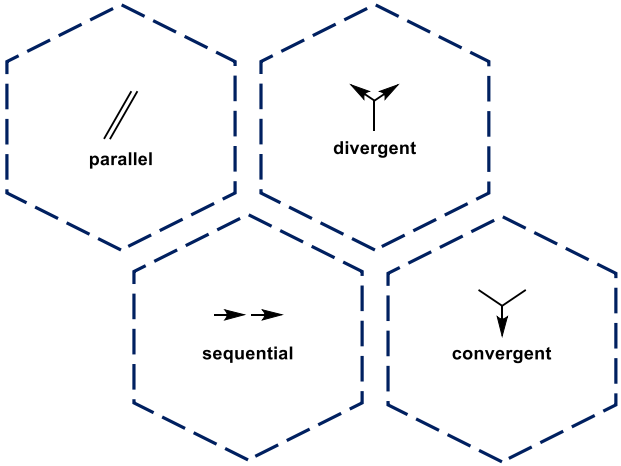
Electrochemically assisted Heck Reaction

• no ligand • no high temperatures •



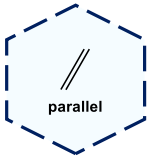
89 %
Moeller
Org. Lett. **2005**, *7*, 5381

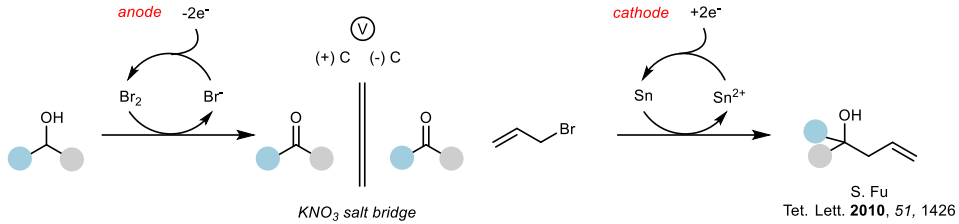
Paired Electrolysis



Paired Electrolysis

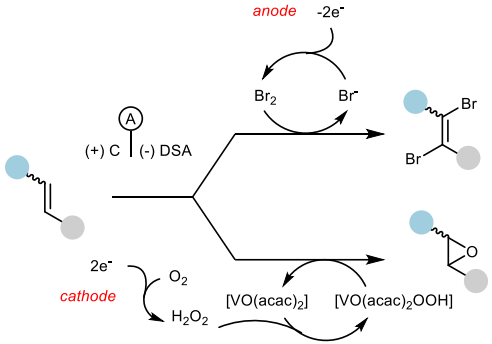
'Choreographed electrochemical processes where two desirable half reactions are preformed simultaneously'





S. Fu
Tet. Lett. **2010**, *51*, 1426

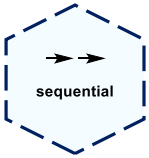
Two simultaneous and non-interfering half reactions

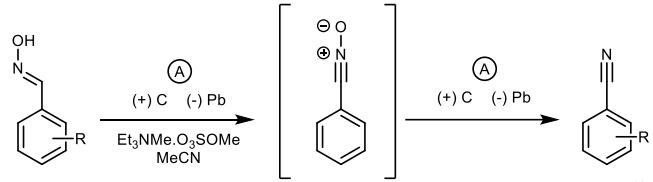


T. Nonaka
Electrochim. Acta, **2003**, *48*, 1041

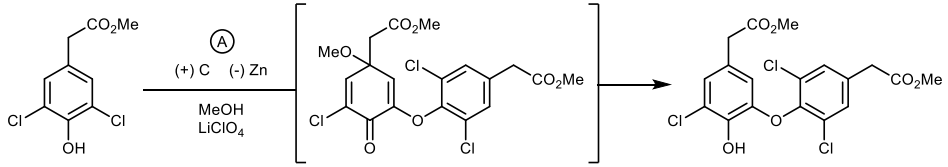
Two alternative reactions at each electrode

Paired Electrolysis



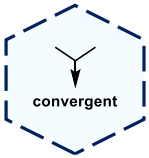


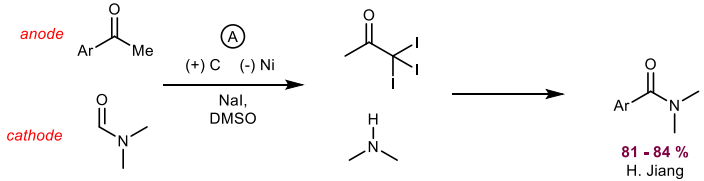
40 - 81 %
S. R. Waldvogel
Chem. Commun. **2015**, *51*, 16346



41 %
M. Atobe
Chem. Lett. **2014**, *43*, 799

Sequential oxidations and reductions

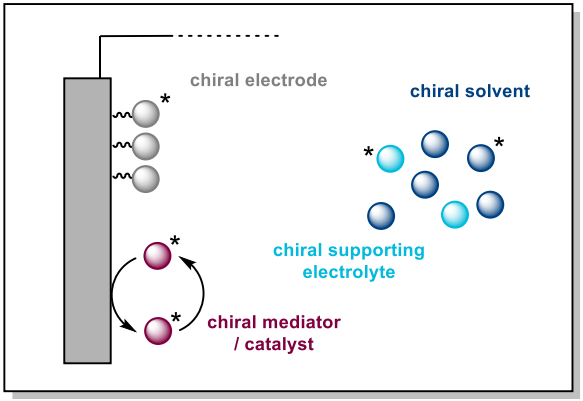




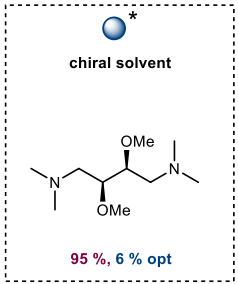
81 - 84 %
H. Jiang
Tet. Lett. **2013**, *54*, 7156

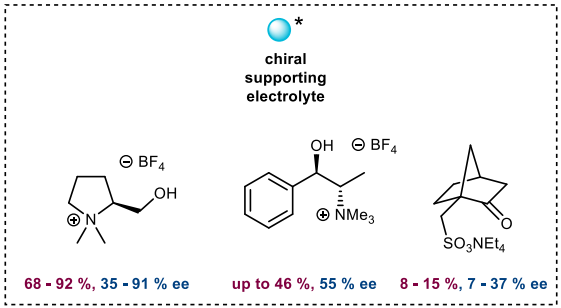
Anodically and cathodically generated intermediates react to afford the product

Asymmetric Electrochemical Catalysis



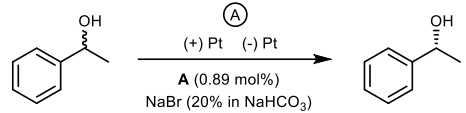
....mostly unsuccessful...
generation of a 'chiral double- layer'



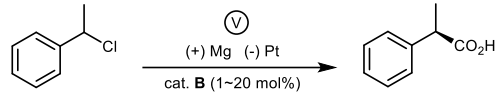


Q. Lin et. al. Chem. Eur. J. **2019**, *25*, 10033.

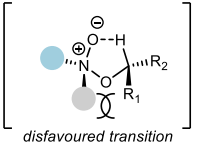
Asymmetric Electrochemical Catalysis



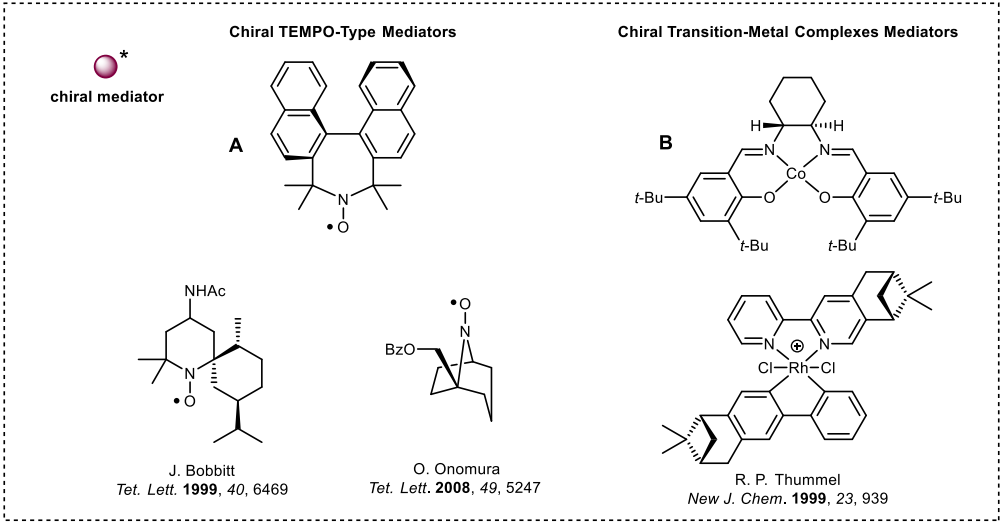
43 %, 91 % ee
H. Tanaka
Tet. Lett. **2000**, *41*,8131



66 %, 83 % ee
J. Lu
Electrochem. Commun. **2014,** *42*,55



disfavoured transition state, slower oxidation



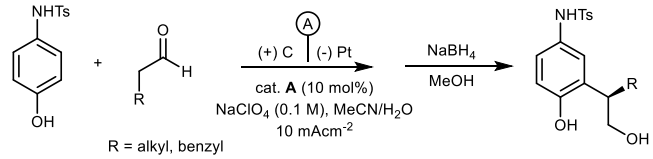
J. Bobbitt
Tet. Lett. **1999**, *40*, 6469

O. Onomura
Tet. Lett. **2008**, *49*, 5247

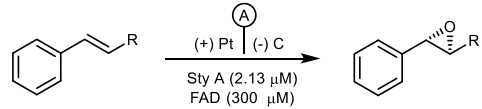
R. P. Thummel
New J. Chem. **1999**, *23*, 939

Q. Lin et. al. Chem. Eur. J. **2019**, *25*, 10033.

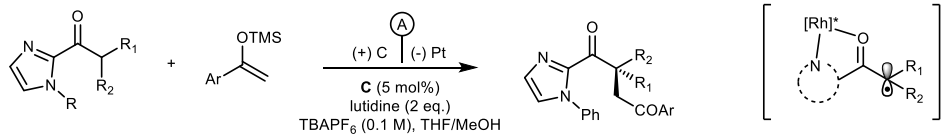
Asymmetric Electrochemical Catalysis



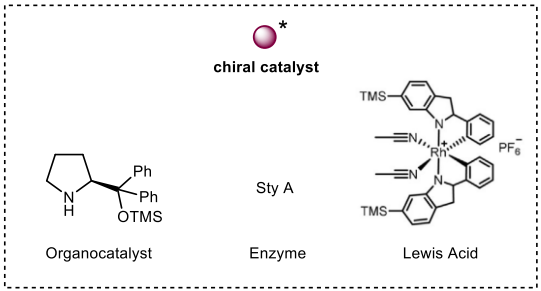
61-75 %, 81-96 % ee
Jorgensen
ACIE, **2010**, *49*, 129.

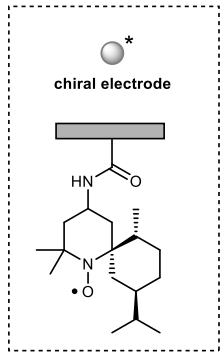


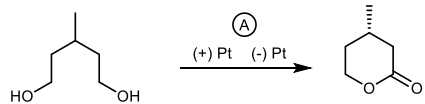
98.1 - 99.9 % ee
A. Schmid
JACS. **2005**, *127*, 6540



42 - 83 %, 96 % ee
E. Meggers
Nat. Catal. **2019**, *2*, 34





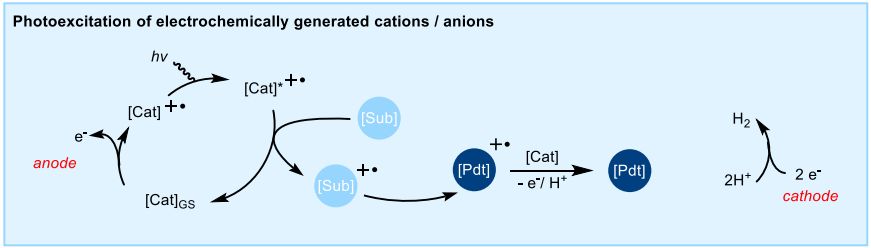


96 %, 98 % ee
J. M. Bobbitt,
Chem. Commun. **2003**, 114

Q. Lin et. al. Chem. Eur. J. **2019**, *25*, 10033.

Photo-Electrochemistry

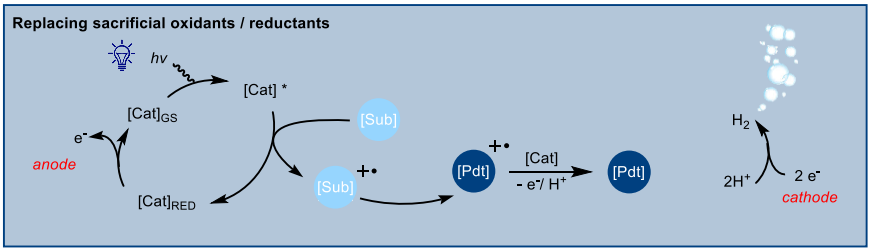
'Cross-pollination between toolboxes' …. 'The dawn of a new alliance'



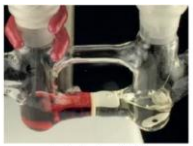
Electron exchange as the common point

• boarder redox window • selectivity • sacrificial oxidant/reductant free

• 'redox energy top-up' •



direct electrolysis (3.0 V)

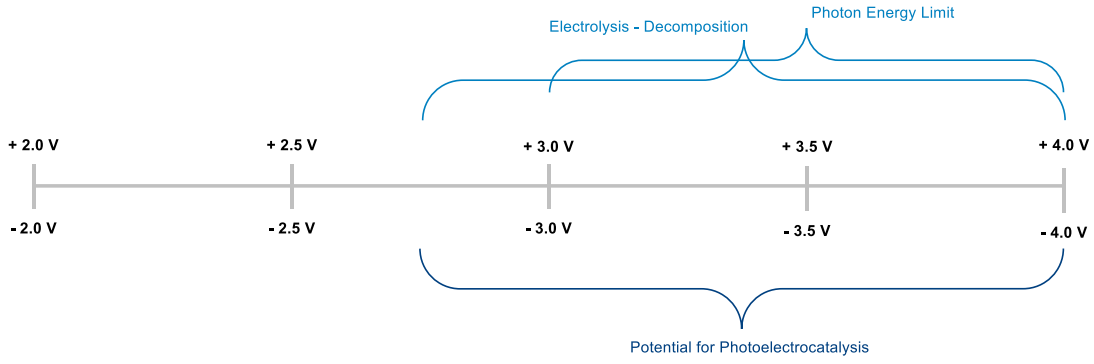


electrophotocatalytic

J. P. Barham and B. Konig. ACIE, **2019**, DOI: 10.1002/anie.201913767

Photo-Electrochemistry

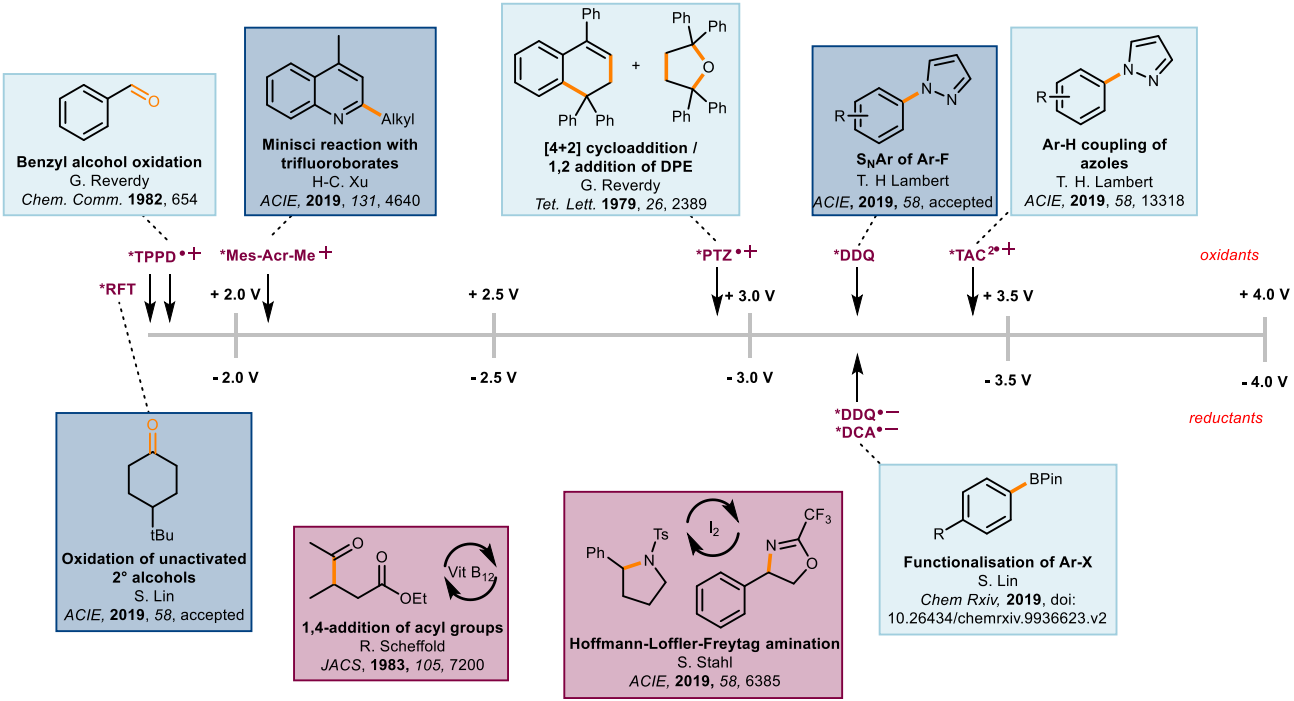
'Cross-pollination between toolboxes' …. 'The dawn of a new alliance'



J. P. Barham and B. Konig. ACIE, **2019**, DOI: 10.1002/anie.201913767

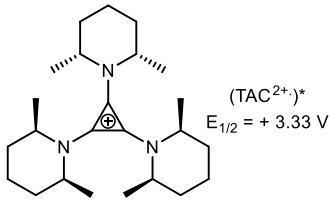
Photo-Electrochemistry

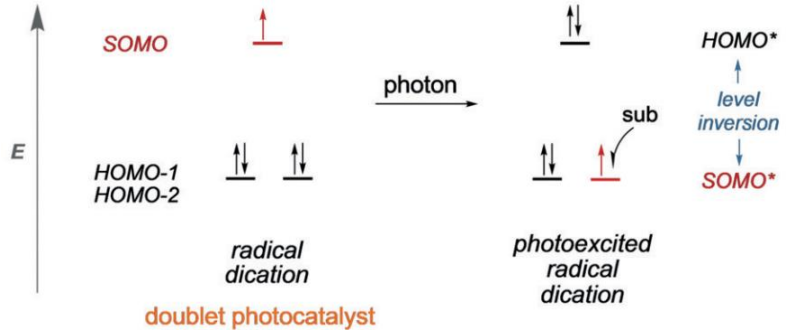
'Cross-pollination between toolboxes' …. 'The dawn of a new alliance'

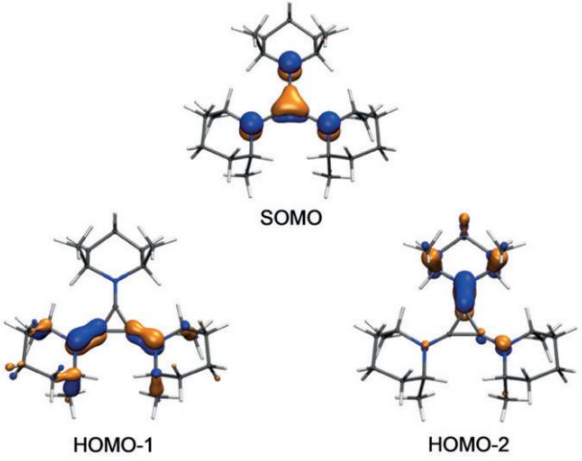


J. P. Barham and B. Konig. ACIE, **2019**, DOI: 10.1002/anie.201913767

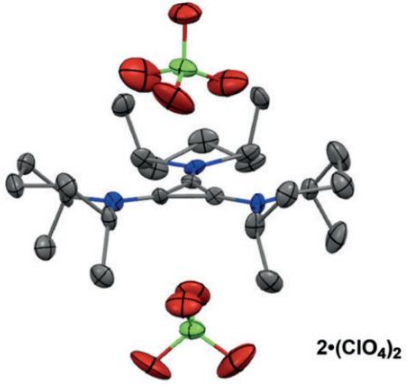
Photo-Electrochemistry: $TAC^{2+\bullet}$

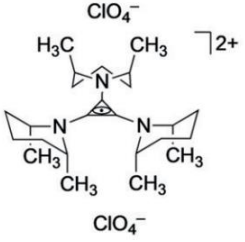






TD-DFT



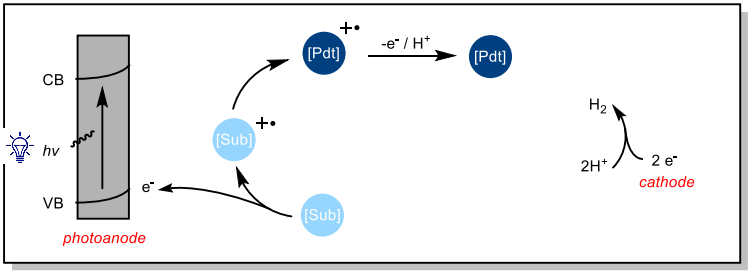


Crystal structure of TAC radical dication

• piperidine α-H orthogonal to TAC π-system protected from deprotonation / abstraction •

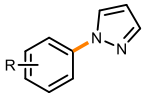
ACIE, **2019**, *58*, 13318

Photoelectrodes



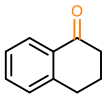
- *One electrode is coated with a photoresposive material* • *'visible light to offset high applied electrode potentials'*

α-Fe_2O_3
VB + 2.30 V



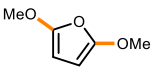
Ar-H coupling with azoles
X. Hu
Nat. Cat., **2019**, *2*, 366.

$BiVO_4$
VB + 0.8 V



Oxidations of small organic compounds
J. Kasahara
Nat. Comm., **2017**, *8*, 1.

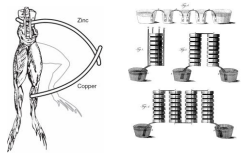
$BiVO_4$ / WO_3



Oxidative dimethoxylation of furan
H. Tatano
Chem. Comm., **2017**, *53*, 4378.

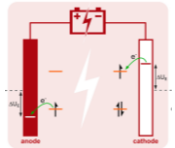
J. P. Barham and B. Konig. ACIE, **2019**, DOI: 10.1002/anie.201913767

Summary and Conclusion



Introduction

- Organic Electrochemistry
- Key Milestones
- Underlying theory



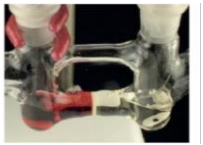
Practicalities & Applications

- Experimental Parameters
- Electrolysis Methods
- Applications
  - Industrial Processes
  - Natural Product Synthesis

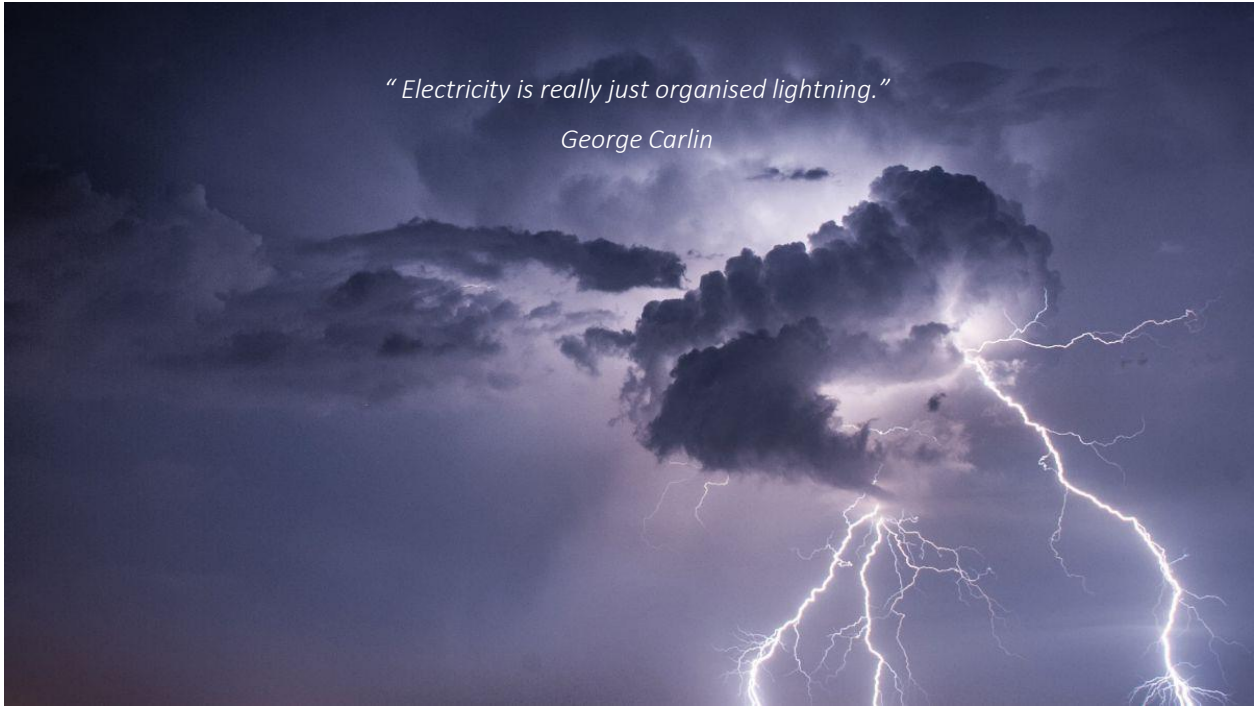
Break

Methodology

- Anodic Oxidation
- Cathodic Reduction
- Paired Electrolysis
- Asymmetric Electrocatalysis
- Photo-electrochemistry



Summary & Conclusion



References

Introduction

- A Practical Beginner's Guide to Cyclic Voltammetry
  J. Chem. Educ. **2018**, 95, 197.
- Luigi Galvani and Alessandro Volta
  Encyclopedia Britannica, **2019**
- Electrochemistry and Photoredox Catalysis: A Comparative Evaluation in Organic Synthesis.
  Molecules **2019***, 24,* 2122.
- Experimental and Calculated Electrochemical Potentials of Common Organic Molecules…
  Synlett, **2016**, *27*, 714
- Organic electrosynthesis: a promising green methodology in organic chemistry
  Green Chem., **2010**, *12*, 2099.
- Fundamentals and Applications of Organic Electrochemistry: Synthesis, Meterials and Device
  T. Fuchigami *et. al. John Wiley & Sons*, Oxford, **2015**

Online Resources

- IKA, Electrosyn 2.0.
  www.ika.com/electrasyn/Fundamentals.html
- Y. Kawamata, presentation
  www.t.co/cLutBb7AZH
- Y. Kawamata, **2016**, presentation
  www.baranlab.org/wp-content/uploads/2018/08/Group-Meeting-61210-ver4.pdf
- B. Rosen, **2014**, presentation
  www.scripps.edu/baran/images/grpmtgpdf/Rosen_2014.pdf
- N. Ambhaikar, **2005**, presentation
  www.scripps.edu/baran/images/grpmtgpdf/Ambhaikar_Dec_05.pdf

Industrial Applications

- Organic Electrosynthesis: From Laboratorial Practice to Industrial Applications.
  Org. Process Res. Dev. **2017**, *21*, 1213.

Natural Products

- Dixiamycin B
  J. Am. Chem. Soc. **2014**, *136*, 5571
- Hirsutene
  J. Am. Chem. Soc. **1981**, *103*, 2744
- Quadrone
  Tet. Lett. **1990**, *31*, 485
- Subglutinol A
  J. Am. Chem. Soc. **2018**, *140*, 7462
- Erinacine
  Org. Lett. **1999**, *1*, 1535
- (−)-Alliacol – A
  J. Am. Chem. Soc. **2004**, *126*, 9106
- Ducane
  Electrochimica Acta, **2009**, ,*54,* 5077
- Guanacastepenes
  Org. Lett. **2005**, 3425
- Ceftibuten
  Org. Process Res. Dev., **2002**, *6*, 178
- Kopsidine
  J. Chem. Soc. Perkin. Trans. **2001**, *1*, 1594
- Penicimutanin
  Chem. Sci., **2019**, DOI: 10.1039/c9sc05252f

Reviews

- Synthetic Organic Electrochemical Methods Since 2000.
  Chem. Rev. **2017**, *117*, 13230
- Benefits of Unconventional Methods in the Total Synthesis of Natural Products.
  ACS Omega, **2018**, *3*, 17326
- Electrifying Organic Synthesis.
  Angew. Chem. Int. Ed. **2018**, *57*, 5594
- Use of Electrochemistry in the Synthesis of Heterocyclic Structures
  Chem. Rev. **2018**, *118*, 4485
- Recent Advances in C–H Functionalization Using Electrochemical Transition Metal Catalysis
  ACS Catal. **2018**, 8, 7179
- Electrochemical Transition-Metal-Catalyzed C–H Bond Functionalization: Electricity as Clean Surrogates of Chemical Oxidants
  ChemSusChem, **2019**,*12*,115
- Chemistry with Electrochemically Generated N-Centered Radicals
  Acc. Chem. Res. **2019**, *52*, 12, 3339
- Modern Strategies in Electroorganic Synthesis
  Chem.Rev. **2008**, *108*, 2265

Assymmetric Electrochemistry

- Asymmetric Electrochemical Catalysis.
  Chem. Eur. J. **2019**, *25*, 10033

Photoelectrochemistry

- Merging Photocatalysis with Electrochemistry
  Angew. Chem. Int. Ed. **2019**, *58*, 17508
- Synthetic Photoelectrochemistry
  Angew. Chem, Int. Ed. **2019**, doi: 10.1002/anie.201913767

Miscellaneous

- Synthetic Organic Electrochemistry: Calling All Engineers
  Angew. Chem. Int. Ed, **2018**, *57*, 4149
- Use of Electroauxiliaries for Introducing N-Acyliminium Ions Into Peptides
  J. Am. Chem. Soc., **2006**, *128,* 1376

Specific examples directly referenced in text.