Deoxygenative Transformation of Carbonyl and Carboxyl Compounds Using gem-Diborylalkanes

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For aldehydes & ketones

For carboxylic acid derivatives

via B–O elimination

Thiadiazoloquinoxalines

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Max Planck Institute for Polymer Research, Germany

Thiadiazoloquinoxalines made soluble and core-extended
Controlled-Coupling of Quinone Monoacetals by New Activation Methods: Regioselective Synthesis of Phenol-Derived Compounds

T. Kamitanaka
K. Morimoto
T. Dohi
Y. Kita*
Ritsumeikan University, Japan

Various nucleophiles (Nu) react with quinone monoacetals (QMA) to afford ortho-substituted phenols, biaryls, dihydrobenzofurans, and \( \alpha \)-aryl carbonyls.

Cluster Cover Page

Cluster Preface: Electrochemical Synthesis and Catalysis
Recent Advances in Electrochemical Oxidative Cross-Coupling for the Construction of C–S Bonds

C. Song
K. Liu
X. Dong
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A. Lei*
Wuhan University, P. R. of China

Metallaelectro-Catalyzed C–H Activation by Weak Coordination

Y. Qiu
J. Struwe
L. Ackermann*
Georg-August-Universität Göttingen, Germany

Electrochemical Synthesis of 2-Hydroxy-para-terphenyls by Dehydrogenative Anodic C–C Cross-Coupling Reaction

S. Lips
R. Franke
S. R. Waldvogel*
Johannes Gutenberg University Mainz, Germany
**Electrochemical C(sp³)–H Fluorination**

**Y. Takahira**
**M. Chen**
**Y. Kawamata**
**P. Mykhailiuk**
**H. Nakamura**
**B. K. Peters**
**S. H. Reisberg**
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**T. Hoshikawa**
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**P. S. Baran**

The Scripps Research Institute, United States

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* >20 examples
* unactivated 2° & 3° C(sp³)–H
* mild conditions
* scalable
* comparison with lit. methods

**Electrochemical C(sp³)–H fluorination**

**Efficient Flow Electrochemical Alkoxylation of Pyrrolidine-1-carbaldehyde**

**N. Amri**
**R. A. Skilton**
**D. Guthrie**
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Cardiff University, UK

**DOI**: 10.1055/s-0037-1611774

6 examples
≤ 94% conversion to monoalkoxy product
≤ 83% conversion to dialkoxy product

**Phthalocyanines as a π–π Adsorption Strategy to Immobilize Catalyst on Carbon for Electrochemical Synthesis**

**K. J. Klunder**
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**DOI**: 10.1055/s-0037-1611792

**π–π Adsorption**

Graphitic Carbon
**A Flow Microreactor Approach to a Highly Efficient Diels–Alder Reaction with an Electrogenated o-Quinone**

K. Tanaka  
H. Yoshizawa  
M. Atobe*  
Yokohama National University, Japan

A microreactor setup is shown, with an anode and a cathode. The yield comparison is given:

- Batch type reactor: 13% yield
- Flow microreactor: up to 75% yield

**Three-Component Chlorophosphinoylation of Alkenes via Anodically Coupled Electrolysis**

L. Lu  
N. Fu  
S. Lin*  
Cornell University, USA

The reaction scheme is shown with catalytic Mn electrolysis:

- 22 examples, 41–92% yield
- (R1 = aryl, alkyl; R2 = alkyl, H; R3 = alkyl, H; R4 = aryl, alkoxy; X = Cl, N₃)

**Diastereodivergent Synthesis of Bromoiminolactones: Electrochemical and Chemical Bromoiminolactonization of α-Allylmalonamides**

K. Yamamoto  
K. Ishimaru  
S. Mizuta  
D. Minato  
M. Kuriyama  
O. Onomura*  
Nagasaki University, Japan

The synthesis involves both electrochemical and chemical conditions:

- Up to >99:1 dr
- 14 examples
- Excellent yields and diastereoselectivity for both conditions
1,10-Phenanthroline- or Electron-Promoted Cyanation of Aryl Iodides

K. Mitsudo*  
K. Yoshioka  
T. Hirata  
H. Mandal  
K. Midorikawa  
S. Suga*  
Okayama University, Japan

1,10-phenanthroline or electroreduction

R_ArCN  
1,10-phenanthroline  
electroreduction

10 examples ≤ 78% yield

Cathodic Reduction of Caffeine: Synthesis of an Amino-Functionalized Imidazole from a Biobased Reagent

F. Pandolfi  
I. Chiarotto  
L. Mattiello  
D. Rocco  
M. Feroci*  
Sapienza University, Italy

Electrochemical

Chemical  
1) NaOH/water, reflux, 2 h
2) HCO2H/(CH3CO)2O, 55 °C, 2 h, rt, 12 h (literature)

51% (one step)

29% (two steps)

Electrochemical Deoxygenation of N-Heteroaromatic N-Oxides

P. Xu  
H.-C. Xu*  
Xiamen University, P. R. of China

Et4NPF6 (0.2 equiv)  
MeCN/H2O (4:1), 80 °C  
undivided cell

14 examples up to 80% yield
Oxidative Cyclization of Naphtholic Sulfonamides Mediated by a Chiral Hypervalent Iodine Reagent: Asymmetric Synthesis versus Resolution

N. Jain  
J. E. Hein*  
M. A. Ciufolini*  
The University of British Columbia, Canada

Synlett 2019, 30, 1222–1227  
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**Oxidative Cyclization**

Equation:

\[
\begin{align*}
\text{MCPBA, CH}_2\text{Cl}_2, -20 ^\circ\text{C} \\
\end{align*}
\]

- \(R\)-configuration
- Best results with \(R^1 = \text{Me}, R^2 = \text{Cl}\)
- \(11–87\%\) ee; \(\approx 20\%\) yield
- Crystallizes as a conglomerate
- Coupled Preferential Crystallization (CPC) enables the resolution of large amounts of racemate starting with 3–4 mg of \(>99\%\) ee material

Asymmetric Synthesis of cis-(S,R)-3-Amino-4-fluoro-1-methylpyrrolidine

Z. Fei  
X. Xiong  
C. Cheung  
W. Liu  
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Synlett 2019, 30, 1228–1230  
DOI: 10.1055/s-0037-1611553

**Asymmetric Synthesis**

Equation:

\[
\begin{align*}
\text{DAST, DCM} \\
-60 ^\circ\text{C} \text{ to rt, 16 h} \text{ 86\%}
\end{align*}
\]

- Complete retention
- Complete inversion

One-Pot Synthesis of Spiro-2H-pyrroles from \(N\)-Propargylic \(\beta\)-Enaminones

E. Karadeniz  
M. Zora*  
Middle East Technical University, Turkey

Synlett 2019, 30, 1231–1236  
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**One-Pot Synthesis**

Equation:

\[
\begin{align*}
\text{Cs}_2\text{CO}_3, \text{DMSO, 80 } ^\circ\text{C} \\
8 \text{ examples} \text{ up to 75\% yield}
\end{align*}
\]
Intramolecular Aldol Ring Closures of Cysteine Derivatives Leading to Densely Functionalised Pyroglutamates

H. Almahli
N. C. Jimenez
M. G. Moloney*
The University of Oxford, UK

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R1 = t-Bu, i-Pr, Ph, o-FC6H4, o-CF3C6H4; R2 = H, MeO, CH2=CHCH2-; p-BrC6H4; R3 = H, Me

Amino Acid Salt Catalyzed Asymmetric Addition Reaction of Acetylacetone to Maleimides and 2-(2-Oxindolin-3-ylidene)malononitriles

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H. Liu
J. Li
X. Li*
H.-P. Xiao
J. Jiang*
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J. Jiang*
Wenzhou University, P. R. of China

n = 1, X = H, 24% yield, 0% ee
n = 2, X = Ba, up to 99% yield, 76% ee

Synthesis of 3-Halo-7-azaindoles through a 5-endo-dig Electrophilic Cyclization Reaction

A. Philips
C. Cunningham
K. Naran
T. Kesharwani*
University of West Florida, USA

Synthesis of 3-Halo-7-azaindoles through a 5-endo-dig Electrophilic Cyclization Reaction

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University of West Florida, USA

(X = Cl, Br, I)
Yield 55–75%

R = alkyl, aryl, vinyl
Yield 45–97%