

## Table of contents

<b><a href="#"><u>Transition-metal-catalyzed reactions starting from 2,3-substitutedquinoline derivatives</u></a></b>		1
<i>Morteza Shiri, Saideh Rajai-Daryasarei</i>		
1. Introduction		
2. Intramolecular cyclization		
3. Arylation		
4. Alkynylation, alkenylation and carbonylation		
5. Carbon-heteroatom bond formation		
6. Amidation		
7. Reduction		
8. Conclusion		
Acknowledgements		
References		
<b><a href="#"><u>Carbonylative synthesis of heterocyclic compounds using CO surrogates</u></a></b>		22
<i>Jun Ying, Xinxin Qi, Xiao-Feng Wu</i>		
1. Introduction		
2. Metal carbonyls		
3. Formic acid		
4. Formates		
5. Aldehydes		
6. Conclusion		
Acknowledgement		
References		
<b><a href="#"><u>Synthesis, reactivity and applications of 1,2-oxathiane 2,2-dioxides</u></a></b>		33
<i>Orlando D. C. C. de Azevedo, B. Mark Heron, Dimitrios Zonidis</i>		
1. Introduction		
2. Synthesis		
2.1. 1,2-Oxathiane 2,2-dioxides		
2.2. Dihydro-1,2-oxathiine 2,2-dioxides		
2.2.1. 3,4-Dihydro-1,2-oxathiine 2,2-dioxides		
2.2.2. 3,6-Dihydro-1,2-oxathiine 2,2-dioxides		
2.2.3. 5,6-Dihydro-1,2-oxathiine 2,2-dioxides		
2.3. 1,2-Oxathiine 2,2-dioxides		
3. Reactivity and applications		
3.1. 1,2-Oxathiane 2,2-dioxides		
3.2. Dihydro-1,2-oxathiine 2,2-dioxides		
3.3. 1,2-Oxathiine 2,2-dioxides		
4. Concluding remarks		
References		
<b><a href="#"><u>Recent synthetic approaches towards selenophene scaffolds</u></a></b>		57
<i>Luana Bettanin, Roberta Cargnelutti, Ricardo F. Schumacher, Eder J. Lenardão</i>		
1. Introduction		
2. New approaches to the synthesis of selenophenes		
2.1. Starting from alkynes bearing an organoselenium substituent		
2.2. Starting from alkynes and an external selenium source		
2.3. Starting from vinyl bromides bearing an organoselenium substituent		
2.4. Starting from vinyl bromides and an external selenium source		
2.5. C-H bond functionalization of (hetero)arenes by an external selenium source		

- 3. Reactivity and application of selenophenes
  - 3.1. Pd-catalyzed C-H bond functionalization
  - 3.2. Preparation of selenophene-based heteroacenes
- 4. Conclusion
- Acknowledgements
- References

## **Synthesis of heterocyclic substituted phosphonates, phosphonic and phosphinic acids**

84

*Tomasz K. Olszewski*

- 1. Introduction
- 2. Preparation of heterocyclic substituted phosphinic acids
  - 2.1. Synthesis of heterocyclic mono- and bis( $\alpha$ -hydroxymethyl)phosphinic acids
  - 2.2. Synthesis of heterocyclic  $\alpha$ -aminomethylphosphinic acids
- 3. Towards the synthesis of heterocyclic aminophosphonates and phosphonic acids
  - 3.1. Cleavage of the C-P bond in derivatives of thiazole-2, quinoline-2 and -4, and imidazole-2
- 4. Asymmetric synthesis of heterocyclic substituted phosphonates and phosphonic acids
  - 4.1. The use of (*R,R*)-TADDOL *H*-phosphonate as easily available chiral auxiliary
  - 4.2. Asymmetric synthesis of phosphonates and phosphonic acids derivatives of hexahydroquinoxalin-2(1*H*)-one
- 5. Conclusion
- Acknowledgement
- References

## **Catalytic enantioselective synthesis of C-3-substituted dihydrocoumarins**

109

*Thomas Martzel, Sifeddine Aouina, Vincent Levacher, Sylvain Oudeyer, Jean-François Brière*

- 1. Introduction
- 2. Enantioselective synthesis of C3-substituted dihydrocoumarins
  - 2.1. Catalytic syntheses involving an enantioselective protonation reaction
  - 2.2. Catalytic syntheses involving an enantioselective alkylation reaction
  - 2.3. Catalytic syntheses involving enantioselective annulation processes
- 3. Enantioselective catalytic synthesis of C3-disubstituted dihydrocoumarins
  - 3.1. Metal-promoted radical alkylation reaction
  - 3.2. Metal-catalyzed alkylation reaction
  - 3.3. Organocatalyzed alkylation reaction
  - 3.4. Miscellaneous
- 4. Conclusions
- Acknowledgement
- References

## **Recent advances in oxidative alkenylation of five- and six-membered heterocyclic ring systems**

130

*Nabil El Brahmi, Jamal Koubachi, Gérald Guillaumet, Saïd El Kazzouli*

- 1. Introduction
- 2. Alkenylation of five-membered heterocyclic ring systems
  - 2.1. Oxidative alkenylation of thiophene and furan
  - 2.2. Oxidative alkenylation of pyrrole
  - 2.3. Oxidative alkenylation of azole derivatives: pyrazole, thiazole, oxazole, isoxazole, isothiazole, triazole
- 3. Alkenylation of six-membered heterocyclic ring systems: pyridine and derivatives
- 4. Conclusion and outlook
- References

**Exploiting the ambiphilic nature of  $\alpha$ -arylpalladium species in the synthesis of heterocycles: a personal account** 158

*Daniel Solé*

1. Introduction
2. Pd-catalyzed intramolecular coupling of amino-tethered aryl halides and ketones
  - 2.1.  $\alpha$ -Arylation
  - 2.2. Carbonyl addition
3. Pd-catalyzed intramolecular coupling of amino-tethered aryl halides and esters
  - 3.1.  $\alpha$ -Arylation
  - 3.2. Sequential  $\alpha$ -arylation/Diels Alder reaction
  - 3.3. Acylation
4. Pd-catalyzed intramolecular coupling of amino-tethered aryl halides and amides
  - 4.1.  $\alpha$ -Arylation
  - 4.2. Acylation
5. Pd-catalyzed intramolecular coupling of amino-tethered aryl halides and aldehydes
  - 5.1. Acylation
  - 5.2. Nucleophilic addition
6. Pd-catalyzed intramolecular coupling of amino-tethered aryl/vinyl halides and  $\beta,\gamma$ -unsaturated nitronates
7. Pd-catalyzed intramolecular  $\alpha$ -arylation of amino-tethered aryl halides and sulfonyl derivatives
  - 7.1. Domino reactions leading to tetrahydroisoquinolines
  - 7.2. Domino reactions leading to indoles
8. Conclusion

Acknowledgement

References

**Use of sulfonium salts in the synthesis of oxygen heterocycles**

178

*Camilo Mahecha-Mahecha, Laura Adarve-Cardona, Diego Gamba-Sánchez*

1. Introduction
2. Preparation of sulfonium salts
3. Pummerer-type cyclizations
  - 3.1. Intramolecular cyclizations with oxygen nucleophiles
  - 3.2. Intramolecular cyclizations with carbon nucleophiles
4. Cyclizations with sulfonium salts
  - 4.1. Additive Pummerer cyclizations
  - 4.2. Epoxidations
  - 4.3. Formation of five-, six- and seven-membered rings
5. Sulfonium salts as electrophile sources: induction of cyclization
6. Sulfonium salts in the functionalization of oxygen heterocycles
  - 6.1. Functionalizations using photocatalysis
  - 6.2. Functionalizations by electrophilic activation or direct coupling
7. Conclusion

Acknowledgements

References

**The total synthesis of pyrrole-containing and related marine natural products**

208

*Martin G. Banwell, Ping Lan*

1. Introduction
2. The longamides and related brominated pyrrole-2-carboxamides
3. The lamellarins and related compounds
4. Halitulin
5. The discoipyrroles
6. The marinoquinolines

7. The tambjamines
8. A new method for the synthesis of pyrroles
9. Conclusions
- Acknowledgements
- References

### **Recent advances in the asymmetric synthesis of chromane derivatives**

227

*Renato Dalpozzo, Raffaella Mancuso, Yan-Kai Liu*

1. Introduction
2. DFT studies on the reaction mechanisms
3. Cyclization of hydroxystyrene derivatives
  - 3.1. From 2-nitrovinylphenols
  - 3.2. From chalcones
  - 3.3. From 2'-hydroxycinnamaldehyde
  - 3.4. From other derivatives
4. Cycloaddition of *ortho*-quinone methides
5. Asymmetric alkylation
6. Desymmetrization
7. Reaction of phenols with activated alkenes
8. Reduction of chromones
9. Spiro, fused and bridged chromane-indoles
10. Miscellaneous
11. Examples of total syntheses
12. Conclusion
- References and notes

### **Recent progress in the synthesis of imidazole derivatives via cyclization of alkynes and nitrogen compounds**

275

*Jose S. S. Neto, Gilson Zeni*

1. Introduction
2. Synthesis of imidazoles
  - 2.1. Transition metal-catalyzed synthesis of imidazoles
    - 2.1.1. Copper-catalyzed synthesis of imidazoles
    - 2.1.2. Gold-catalyzed synthesis of imidazoles
    - 2.1.3. Lanthanum-catalyzed synthesis of imidazoles
    - 2.1.4. Palladium-catalyzed synthesis of imidazoles
    - 2.1.5. Rhodium-catalyzed synthesis of imidazoles
    - 2.1.6. Samarium-catalyzed synthesis of imidazoles
    - 2.1.7. Silver-catalyzed synthesis of imidazoles
    - 2.1.8. Titanium-catalyzed synthesis of imidazoles
    - 2.1.9. Ytterbium-catalyzed synthesis of imidazoles
  - 2.2. Transition metal-free synthesis of imidazoles
3. Synthesis of imidazolidines
  - 3.1. Transition metal-catalyzed synthesis of imidazolidines
    - 3.1.1. Copper-catalyzed synthesis of imidazolidines
    - 3.1.2. Palladium-catalyzed synthesis of imidazolidines
  - 3.2. Transition metal-free synthesis of imidazolidines
4. Synthesis of imidazolines
  - 4.1. Transition metal-free synthesis of imidazolines
5. Conclusion
- Acknowledgements
- References

**Recent advances in the synthesis of five- and six-membered selena-heterocycles**

290

*Damiano Tanini, Antonella Capperucci*

1. Introduction
2. Synthesis of heterocyclic systems containing selenium
3. Synthesis of heterocyclic systems containing selenium and nitrogen
4. Synthesis of heterocyclic systems containing selenium and other heteroatoms (O, S, P)
5. Conclusions and future outlook

Acknowledgements

References

**Selenium chemistry: a powerful tool for heterocycles synthesis and functionalization**

319

*Claudio Santi, Luca Sancinetto*

1. General introduction
2. Electrophilic organoselenium reagents
  - 2.1. Electrophilically promoted C-O bond formation in the synthesis of oxygenated heterocycles
  - 2.2. Electrophilically promoted C-N bond formation in the synthesis of nitrogenated heterocycles
3. Bioinspired oxidative oxa-cyclizations
4. Selenium containing heterocycles

References

**Synthesis of highly functionalized nitrogen heterocycles from 2-hydroxycyclobutanones and aromatic amines**

334

*Francesco Secci, Angelo Frongia*

1. Introduction
2. Synthesis of tryptamines
3. Synthesis of 2-alkoxy-; 2-phenylthio-; 2-phenoxy-; 2-halogen- and 2-trifluoroacetoxy-ethyl-indoles
4. Synthesis of 2,2-bis(2-pyridylamino)cyclobutanols and 5-(pyridine-2-ylamino)dihydrofuran-2(3H)-ones
5. Synthesis of carbonyl-containing alkyl-substituted benzo[d]imidazoles
6. Conclusions

Acknowledgement

References

**Covalently supported imidazolium salts in catalysis**

347

*Vincenzo Campisciano, Carla Calabrese, Francesco Giacalone, Michelangelo Gruttaduria*

1. Introduction
2. Supported imidazolium salts as metal-free heterogeneous catalysts
3. Supported imidazolium salts as metal-based heterogeneous catalysts
4. Conclusions

Acknowledgement

References

**Recent advances on 1,2,4-oxadiazoles: from synthesis to reactivity and pharmaceutical applications**

377

*Paola Marzullo, Andrea Pace, Ivana Pibiri, Antonio Palumbo Piccionello, Silvestre Buscemi*

1. Introduction
2. Synthesis of 1,2,4-oxadiazoles
3. Reactivity of 1,2,4-oxadiazoles
  - 3.1. Thermal rearrangement reactions
  - 3.2. Photochemical rearrangements
  - 3.3. Nucleophilic aromatic substitutions (SNAr) and ANRORC rearrangements
4. Biological properties of 1,2,4-oxadiazoles
  - 4.1. Antimicrobial agents

- 4.2. Antitumor agents
- 4.3. Anti-inflammatory and analgesic agents
- 4.4. Antidiabetic agents
- 4.5. Read-through promoters
- 4.6. Miscellaneous properties
- 5. Conclusion
- Acknowledgement
- References

## **1,3,5,2-Oxadiazaborinines as a class of fluorescent organoboron dyes**

398

*Mykhaylo A. Potopnyk*

- 1. Introduction
- 2. Pyrazino[1,2-*c*][1,3,5,2]oxadiazaborinines
- 3. [1,3,5,2]Oxadiazaborinino[3,4-*a*][1,8]naphthyridines
- 4. Pyrido[1,2-*c*][1,3,5,2]oxadiazaborinines
- 5. Pyrimido[1,2-*c*][1,3,5,2]oxadiazaborinines
- 6. [1,3,4]Thiadiazolo[3,2-*c*][1,3,5,2]oxadiazaborinines
- 7. (Benzothiazolo[3,2-*c*][1,3,5,2]oxadiazaborinines
- 8. Conclusion
- Acknowledgement
- References

## **Transition-metal-catalyzed functionalization of 1,10-phenanthrolines and their complexes**

419

*Anton S. Abel, Alexei D. Averin, Irina P. Beletskaya, Alla Bessmertnykh-Lemeune*

- 1. Introduction
- 2. Synthesis of halogenophenanthrolines
- 3. Transition-metal-catalyzed functionalization of 1,10-phenanthroline
  - 3.1. C–C coupling
    - 3.1.1. Sonogashira cross-coupling
    - 3.1.2. Suzuki-Miyaura cross-coupling
    - 3.1.3. Stille cross-coupling
    - 3.1.4. Negishi cross-coupling
    - 3.1.5. Kumada cross-coupling
    - 3.1.6. Mizoroki-Heck cross-coupling
    - 3.1.7. Reductive dimerization
  - 3.2. C–Het coupling
    - 3.2.1. Pd- and Cu-catalyzed amination reactions
    - 3.2.2. C–P bond forming reactions
    - 3.2.3. Miyaura-Ishiyama coupling
  - 3.3. Alkoxycarbonylation
  - 3.4. Cyanation
- 4. Functionalization of metal complexes with 1,10-phenanthroline ligands
- 5. Conclusion
- Acknowledgement
- References