

Table of contents

Tandem alkyne carbopalladation/Suzuki cross-coupling reaction in the synthesis of heterocyclic compounds **1**

Pratap R. Jagtap, Eliška Matoušová

1. Introduction
2. Formation of five-membered nitrogen heterocycles
 - 2.1. Synthesis of indolines
 - 2.2. Synthesis of oxindoles
 - 2.3. Synthesis of isoindolinones
3. Synthesis of five-membered heterocycles from alkenyl halides
4. Formation of six-membered nitrogen heterocycles
 - 4.1. Synthesis of tetrahydroisoquinolines and tetrahydroquinolines
 - 4.2. Synthesis of dihydroisoquinolinones
5. Formation of medium-sized nitrogen heterocycles
6. Formation of oxygen heterocycles
 - 6.1. Using starting materials with an ether linker
 - 6.2. Using starting materials with an ester linker
7. Formation of heterocycles with other heteroatoms
8. Conclusions
- Acknowledgements
- References

Synthetic routes to P(O)-substituted five-membered aromatic heterocycles (2010-2021) **18**

Yulia Volkova, Mikhail Kozlov, Igor Zavarzin

1. Introduction
2. Pyrroles
 - 2.1. Formal [3+2]-cycloaddition
 - 2.2. Formal [4+1]-cycloaddition
 - 2.3. Cyclization reactions
 - 2.4. Phosphorylation of pyrroles
3. Pyrazoles
 - 3.1. Formal [3+2]-cycloaddition
 - 3.2. Phosphorylation of pyrazoles
4. Imidazoles
 - 4.1. Synthesis of imidazoles from imines
 - 4.2. Phosphorylation of imidazoles
5. 1,2,3-Triazoles
 - 5.1. Azide-alkyne cycloaddition
 - 5.2. Synthesis of 1,2,3-triazoles using the Ohira–Bestmann reagent
 - 5.3. Synthesis of polydentate borophosphonate complexes
 - 5.4. Phosphorylation of 1,2,3-triazoles
6. Isoxazoles
 - 6.1. Formal [3+2]-cycloaddition
 - 6.2. Cyclization of γ -keto and hydroxy vinyl azides
7. Oxazoles
 - 7.1. Formal [3+2]-cycloaddition
 - 7.2. Cyclization of α -isonitrile- β -ketophosphonates
 - 7.3. Cyclization of *N*-acyl-1-phosphoryl-2,2-dichloroethyleneamines
 - 7.4. Phosphorylation of oxazoles
8. Thiazoles
 - 8.1. Formal [3+2]-cycloaddition

- 8.2. Phosphorylation of thiazoles
- 9. Conclusions
- Acknowledgement
- References

Synthetic strategies for the synthesis of benzo[c]chromene scaffold

46

Andrea Temperini, Marco Ballarotto

- 1. Introduction
- 2. Synthetic strategies for 6*H*-benzo[c]chromenes
- 3. Synthesis of the biaryl system and subsequent cyclization to chromene
 - 3.1. Synthesis *via* a chromanone intermediate
 - 3.2. Formation of the ether Csp²-O or Csp³-O linkage of the oxygenated ring
- 4. Starting from arylbenzyl ethers (intramolecular aryl-aryl coupling)
 - 4.1. Metal-catalysed synthesis
 - 4.2. Metal-free synthesis
- 5. Annulation reaction to benzene ring on the [c] side of a chromene system
- 6. Simultaneous formation of the pyranic and benzene ring *via* intramolecular Diels-Alder reaction
- 7. Substituted 6*H*-benzo[c]chromenes *via* an intermolecular Diels-Alder reaction
- 8. Other synthetic paths
- 9. Conclusion
- Acknowledgement
- References

C-3 Functionalization of quinoxalin-2-ones and dihydroquinoxalin-2-ones

70

Jaume Rostoll-Berenguer, Gonzalo Blay, José R. Pedro, Carlos Vila

- 1. Introduction
- 2. C-3 Functionalization of quinoxalin-2-ones
 - 2.1. C–C Bond formation
 - 2.1.1. Alkylation reactions
 - 2.1.2. Fluoroalkylation reactions
 - 2.1.3. Acylation reactions
 - 2.1.4. Arylation reactions
 - 2.2. C–N Bond formation
 - 2.3. C–O Bond formation
 - 2.4. C–Si Bond formation
 - 2.5. C–P Bond formation
 - 2.6. C–S Bond formation
- 3. C-3 Functionalization of dihydroquinoxalin-2-ones
 - 3.1. C–C Bond formation
 - 3.1.1. Alkylation reactions
 - 3.1.2. Fluoroalkylation reactions
 - 3.1.3. Arylation reactions
 - 3.1.4. Alkynylation reactions
 - 3.2. C–N Bond formation
 - 3.3. C–O Bond formation
 - 3.4. C–P Bond formation
- 4. Conclusions
- Acknowledgements
- References

C–H Functionalization of cyclic amines mediated by TEMPO oxoammonium cations

100

Silvano Cruz-Gregorio, Julio Romero-Ibañez, Fernando Sartillo-Piscil

1. Introduction
2. α -C-H Functionalizations
 - 2.1. Tetrahydroisoquinolines (THIQs)
 - 2.2. Dihydroquinolines (DHQs)
 - 2.3. Tetrahydro- β -carbolines (TH β Cs), isoindolines, and dehydropiperidines
3. α,β -C-H Functionalizations
 - 3.1. Pyrrolidines, piperidines, and piperazines
 - 3.1.1. Deconstructive C-C functionalizations
 - 3.2. Indolo[2,3-*a*]quinolizines
4. Triple α,β,γ -C-H functionalization of piperidines
5. In-situ generation of oxoammonium cation by electricity
6. Conclusions
- Acknowledgments
- References

2-Imidazolidinones and epimeric pyrroloimidazolones in asymmetric synthesis: from classical to non-classical chiral auxiliaries 122

Costa Metallinos

1. Introduction
2. *N*-Acetyl-(*S*)-4-isopropyl-1-[(*R*)-1-phenylethyl]imidazolidin-2-ones
3. 2-Imidazolidinones with one chiral center
4. 2-Imidazolidinones with 4,5-chiral centers
5. Hydantoin auxiliaries
6. Epimeric pyrroloimidazolones
 - 6.1. Planar chiral ferrocenes
 - 6.2. η^6 -Arene chromium tricarbonyl complexes
 - 6.3. *N*-Benzyl pyrroloimidazolones
 - 6.4. Cyclohexa-1,4-dienes with quaternary chiral centers
 - 6.5. *N*-Propargyl pyrroloimidazolones and axial chiral allenamides
7. Conclusions
- Acknowledgements
- References

Photochemical access to four membered heterocycles 142

Alessio Porta, Stefano Protti

1. Introduction
2. Photochemical synthesis of oxygen containing four membered rings
 - 2.1. Photochemical synthesis of oxetanes
 - 2.2. Photochemical synthesis of dioxetanes
3. Photochemical synthesis of thietanes
4. Synthesis of four-membered aza-heterocycles
5. Conclusions
- References

A diversity-oriented route to Micrococccins P1 and P2 for medicinal chemistry investigations 154

Hee-Jong Hwang, Marco A. Ciufolini

1. Introduction
2. Retrosynthetic considerations
3. A robust avenue to the pyridine domain
4. Synthesis of a protected version of tripeptide **5**
5. Assembly of the macrocycle and Suzuki-Miyaura reactions thereof
6. Total synthesis of MP1, MP2, and congeners

- 7. Bioactivity data
- 8. A noteworthy chemical property of MP2
- 9. Conclusion
- Acknowledgement
- References

Heterocyclic compounds containing organochalcogen moiety 170

Gelson Perin, Márcio S. Silva, Elton L. Borges, Angelita M. Barcellos, Thiago J. Peglow

- 1. Introduction
- 2. Oxygen-containing heterocycles
- 3. Nitrogen-containing heterocycles
- 4. Sulfur/selenium/tellurium-containing heterocycles
- 5. Conclusion
- Acknowledgement
- References

β -Ketothioamides: versatile precursors towards important heterocyclic frameworks 198

Maya Shankar Singh, Subhasish Ray

- 1. Introduction
- 2. Synthesis of β -ketothioamides
- 3. Reactivity profile of β -ketothioamides
- 4. Functionalization of β -ketothioamides
- 5. Synthetic applications of β -ketothioamides
- 6. Conclusion and outlook
- Acknowledgments
- References

Recent progress in the modification of heterocycles based on the transformation of DMSO 222

Hai-Lei Cui

- 1. Introduction
- 2. DMSO as source of CH
- 3. DMSO as source of CH₂
- 4. DMSO as source of CH₃
- 5. DMSO as source of SCH₃
- 6. DMSO as source of CH₂SCH₃
- 7. DMSO as source of SOCH₃
- 8. DMSO as source of CHO
- 9. DMSO as oxidant
- 10. Halogenation
- 11. Conclusion
- Acknowledgement
- References

Copper-catalyzed arylations and heteroarylations 249

Muhammad Bilal, Moniba Sharif, Nasir Rasool, Iram Kanwal, Gulraiz Ahmad, Peter Langer

- 1. Introduction
- 2. C–N cross-coupling
 - 2.1. Copper halides
 - 2.2. Copper acetate
 - 2.3. Copper triflate
 - 2.4. Copper sulphate
 - 2.5. Copper oxide

- 2.6. Copper MOF
- 3. C-O cross-coupling
 - 3.1. Copper halides
 - 3.2. Copper acetate
- 4. C-S cross-coupling
 - 4.1. Copper halide
 - 4.2. Copper acetate
 - 4.3. Copper triflate
 - 4.4. Copper oxide
- 5. Conclusions
- Acknowledgement
- References

Cooperative dual catalysis: combining organocatalysis and transition-metal catalysis to access heterocyclic compounds 278

Bojan Vulovic, Radomir N. Saicic

- 1. Introduction
- 2. Combining amine and transition metal catalysis
 - 2.1. Intramolecular reactions of carbonyl compounds
 - 2.2. Annulations
 - 2.3. Reactions of enals and dynamic kinetic asymmetric transformations
 - 2.4. Multicomponent reactions
 - 2.5. Miscellaneous reactions
- 3. Combining phosphine and transition metal catalysis
- 4. Combining hydrogen-bond and transition metal catalysis
- 5. Combining chiral phosphoric acids and transition metal catalysis
 - 5.1. Etherifications, oxidative etherifications and aminations
 - 5.2. Reactions with carbenes
 - 5.3. C-H activations
 - 5.4. Miscellaneous and domino reactions
- 6. Combining *N*-heterocyclic carbenes and transition metal catalysis
 - 6.1. Reactions of NHC-bound enol intermediates
 - 6.2. Reactions of NHC-bound homoenolate intermediates
 - 6.3. Dynamic kinetic asymmetric transformation and kinetic resolution
- 7. Conclusion
- Acknowledgement
- References

Thermal heterocyclization in pyrolytic reactions: synthetic and mechanistic study 313

Nouria Al-Awadi, Asaad S. Mohamed, Osama M. Habib

- 1. Introduction
- 2. Thermal heterocyclization
 - 2.1. FVP of cinnolines
 - 2.2. FVP of [1,2,3]-triazines
 - 2.3. FVP of [1,2,4]-triazines
- 3. Pyrolysis of acetylenic compounds
 - 3.1. Acetylenic ethers
 - 3.2. Acetylenic esters
 - 3.2.1. Propiolate esters with β -hydrogen(s)
 - 3.2.2. Propiolate esters without β -hydrogen
 - 3.3. Acetylenic alcohols
 - 3.4. Acetylenic amides

4. Conclusion
5. References

Recent advances in selective functionalization of the quinazoline scaffold 330

Thiago dos Santos, Gabriel de P. Bueno, Thais R. Arroio, Giuliano C. Clososki

1. Introduction
2. Functionalization of the quinazoline scaffold
 - 2.1. Nucleophilic aromatic substitution (S_NAr)
 - 2.2. C–H functionalization reactions
 - 2.3. Cross-coupling reactions
 - 2.4. Selective functionalization *via* metalation
 - 2.5. Photocatalyzed reactions and electrochemical functionalization
3. Conclusions
- Acknowledgment
- References

Synthesis of heterocycles in non-conventional media: the case of ionic liquids 356

Salvatore Marullo, Francesca D'Anna

1. Introduction
2. Synthesis of 5- and 6-membered heterocycles
3. Synthesis of benzofused and bicyclic heterocycles
4. Synthesis of polycyclic and spirocyclic heterocycles
5. Conclusions
- Acknowledgement
- References

3-Acylamino-2H-pyran-2-ones as dienes in Diels-Alder reactions 378

Krištof Kranjc

1. Introduction
2. 3-Acylamino-2H-pyran-2-ones as dienes in Diels-Alder reactions: General reaction pathways
 - 2.1. Alkynes as dienophiles in cycloadditions with 3-acylamino-2H-pyran-2-ones
 - 2.2. Alkenes as dienophiles in cycloadditions with 3-acylamino-2H-pyran-2-ones
3. Adjusting reaction conditions of 3-acylamino-2H-pyran-2-one cycloadditions with alkenes to yield various types of products
 - 3.1. Favouring the formation of 4-acylamino-2-oxabicyclo[2.2.2]oct-5-en-3-ones: high pressure conditions
 - 3.2. Favouring the formation of 1-acylaminocyclohexa-1,3-diene systems
 - 3.3. Favouring the formation of 1-acylaminobicyclo[2.2.2]oct-2-enes: Kinetic control
 - 3.4. Favouring the formation of aromatic products: Thermodynamic control
4. Selected examples
 - 4.1. Synthesis of indole derivatives
 - 4.2. Synthesis of boscalid derivatives
 - 4.3. Further transformations of 1-acylaminobicyclo[2.2.2]oct-2-ene systems with nitrogen nucleophiles
 - 4.4. Formation of macrocycles
5. Conclusions
- Acknowledgement
- References

Selenium-containing highly functionalized 1,2,3-triazoles 399

Liane. K. Soares, Gustavo B. Blödorn, Joel S. Reis, Diego Alves

1. Introduction

- 2. Copper catalysis
- 3. Organocatalysis
- 4. Conclusion
- Acknowledgements
- References

Synthesis of dihydropyrone containing natural products

422

Priyanka Choudhary, Ravikant Ranjan, Gulenur N. Khatun, Rodney A. Fernandes

- 1. Introduction
- 2. 2,6-Disubstituted dihydropyrone natural products
 - 2.1. Total synthesis of (+)-hepialone
 - 2.2. Total synthesis of (+)-obolactone and (+)-7,8-dihydroobolactone
 - 2.3. Total synthesis of (+)-7,8-dihydroobolactone
- 3. Highly substituted dihydropyrone natural products
 - 3.1. Total synthesis of (–)-stegobiol and (–)-stegobinone
 - 3.2. Total synthesis of (–)-maurenone
 - 3.3. Total synthesis of (–)-membrenones A, B and C
 - 3.4. Total synthesis of (–)-vallartanones A and B
 - 3.5. Total synthesis of (+)-auripyrones A and B
- 4. Conclusions
- Acknowledgement
- References

Furans and hydroxymethylfurans: sustainable sources of molecular diversity

456

Ana L. Cardoso, Susana M. M. Lopes, Terver John Sasse, Teresa M. V. D. Pinho e Melo

- 1. Introduction
- 2. The Achmatowicz rearrangement
- 3. The Piancatelli rearrangement
 - 3.1. Carbo- and aza-Piancatelli reactions
 - 3.2. The Piancatelli rearrangement in cascade reactions
- 4. Metal-catalysed furan ring-opening reactions
- 5. Acid-catalysed furan ring-opening reactions
- 6. Conclusion
- Acknowledgement
- References

Accessing chiral dihydro- and tetrahydroquinazoline-2,4-diones via [4+2]-cycloadditions: from asymmetric pioneering studies to asymmetric organocatalyzed syntheses

509

Claudio Curti, Enrico Marcantonio, Andrea Sartori, Lucia Battistini, Franca Zanardi

- 1. Introduction
- 2. Synthesis of chiral, racemic dihydro- and tetrahydroquinazoline-2,4-diones via [4+2]-cycloadditions
 - 2.1. [4+2]-Cycloadditions involving metal oQDM dienolates
 - 2.2. [4+2]-Cycloadditions involving oQDM dienamines
- 3. Catalytic, enantioselective synthesis of chiral, dihydro- and tetrahydroquinazoline-2,4-diones
 - 3.1. Aminocatalytic strategies
 - 3.2. NHC-catalyzed [4+2]-transformations
 - 3.3. Noncovalent, bifunctional organocatalytic strategies
- 4. Conclusions
- Acknowledgements
- References

Heterocyclic α -oxoesters (hetaryl glyoxylates): synthesis and chemical transformations. Part 1. 533*Bohdan V. Vashchenko, Oleksandr Geraschenko, Oleksandr O. Grygorenko*

1. Introduction
 2. Synthesis of pyrrolyl, furyl, thienyl glyoxylates and their fused analogues
 - 2.1. Pyrrolyl glyoxylates
 - 2.2. Furyl glyoxylates
 - 2.3. Thienyl glyoxylates
 - 2.4. Indolyl glyoxylates
 - 2.5. Benzofuryl and benzothienyl glyoxylates
 3. Chemical transformations of pyrrolyl, furyl, thienyl glyoxylates and their fused analogs
 - 3.1. Reduction reactions
 - 3.2. Reactions with heteroatom nucleophiles
 - 3.3. Reactions with C-nucleophiles
 - 3.4. Heterocyclizations
 4. Conclusions
- Acknowledgement
- References