

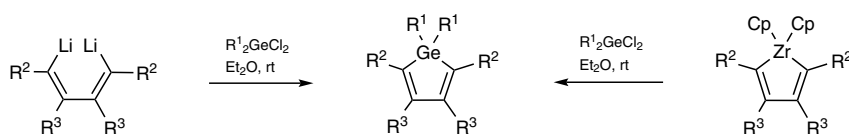
## Abstracts

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5.1.28 **Product Subclass 28: Germoles**T. Müller <sup>1b</sup>

This chapter provides an overview of methods for the synthesis of 1*H*-germoles. It covers the literature from 1959 until 2020. Classical methods involve the cyclization of 1,4-dithiobuta-1,3-dienes and zirconium/germanium exchange in zirconacyclopentadienes, but more-recent approaches such as catalytic double hydrogermylations of butadiynes are included as well. Finally, methods for the preparation of alkali metal salts of 1*H*-germol-1-ides and 1*H*-germole-1,1-diides are summarized.



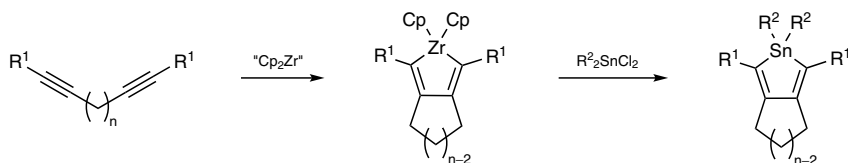
**Keywords:** germoles · anionic reagents · alkynes · butadienes · butadiynes · germanium compounds · germanes · iodo compounds · lithium compounds · zirconocenes

New

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5.2.30 **Product Subclass 30: Stannoles**I.-M. Ramirez y Medina <sup>1b</sup>, W. Kipke, J. Makow, and A. Staubitz

This chapter gives an overview of different methods for the synthesis of classical stannoles and related compounds such as ring-fused stannoles and stannoles containing further heteroatoms. It represents a review of the literature from 1959 to 2019.



**Keywords:** carbon–tin bonds · coupling reactions · cyclization · five-membered rings · fused-ring systems · heterocycles · hydrostannation · lithiation · tin compounds · transmetalation · organoboration · stannoles

2020

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10.4 **Product Class 4: Benzo[*b*]thiophenes**

N. Yoshikai, C. M. Rayner, and M. A. Graham

This chapter is a revision of the earlier *Science of Synthesis* Section 10.4. It describes methods for the synthesis of benzo[*b*]thiophenes and related compounds by ring closure or by modification of existing substituent(s) on the benzo[*b*]thiophene skeleton. Ring-closure methods typically involve the formation of the five-membered ring starting from benzene derivatives bearing substituents such as halogen, alkenyl, alkynyl, or sulfanyl groups at appropriate positions. Ring closure to form the benzene ring can also be

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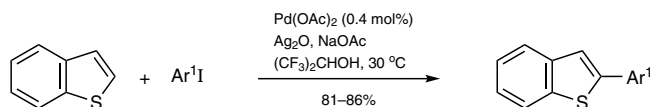
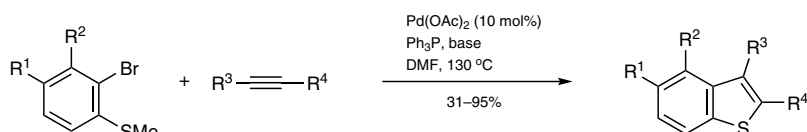
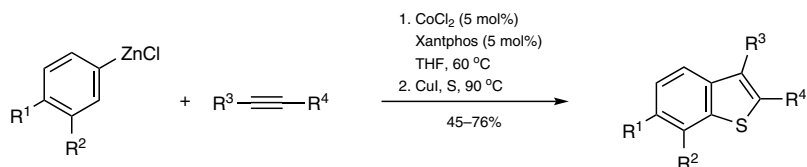
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achieved using suitably substituted thiophene derivatives. In particular, a number of new methods involving metal-catalyzed C–C and C–S bond formation that have been developed since the previous review are included. Recent years have also witnessed substantial progress in the methods available to directly introduce new substituents to the 2- and 3-positions of benzo[*b*]thiophenes through metal-catalyzed C–H bond functionalization, and these are included in this chapter.



**Keywords:** benzo compounds · benzo[*b*]thiophenes · thiophenes · sulfides · alkenes · alkynes · halo compounds · carbonyl compounds · palladium catalysis · copper catalysis · organolithium compounds · cyclization · ring closure · annulation · cross-coupling reactions · C–H activation reactions

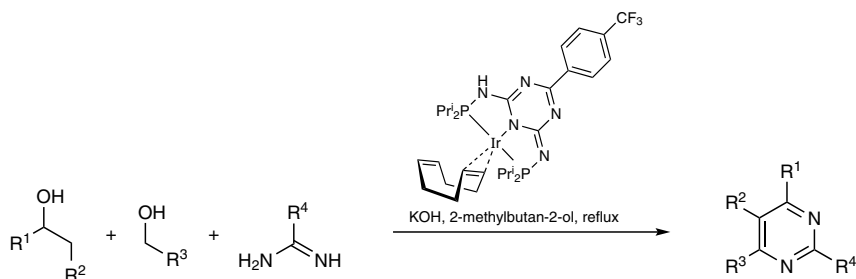
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## 16.12.5 Pyrimidines

J. M. Campagne<sup>1D</sup> and E. Leclerc<sup>1D</sup>

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 16.12) covering the synthesis and substituent modification of pyrimidines. It focuses on the literature published in the period 2012–2019, gathering all the methods reported in this period, but with a particular emphasis on transition-metal-catalyzed synthetic processes.



**Keywords:** pyrimidines · heterocycles · transition-metal catalysis · cyclization · cycloadditions · metalation · substitution

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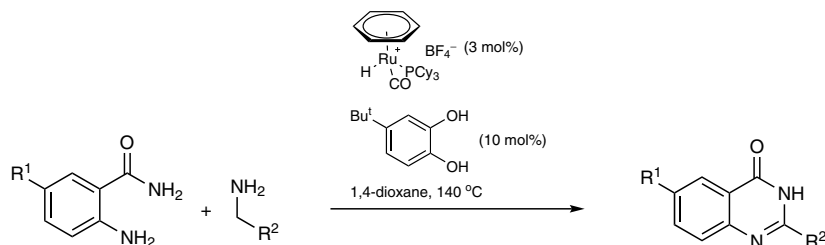
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## 16.13.6 Quinazolines

J. M. Campagne<sup>b</sup> and E. Leclerc<sup>b</sup>

This chapter is an update to the earlier *Science of Synthesis* contributions (Sections 16.13 and 16.13.5) covering the synthesis of quinazolines. It focuses on the literature published in the period 2012–2019, gathering all the methods reported in this period, but with a particular emphasis on transition-metal-catalyzed synthetic processes.



**Keywords:** quinazolines · heterocycles · pyrimidines · transition-metal catalysis · cyclization · cycloadditions · metalation

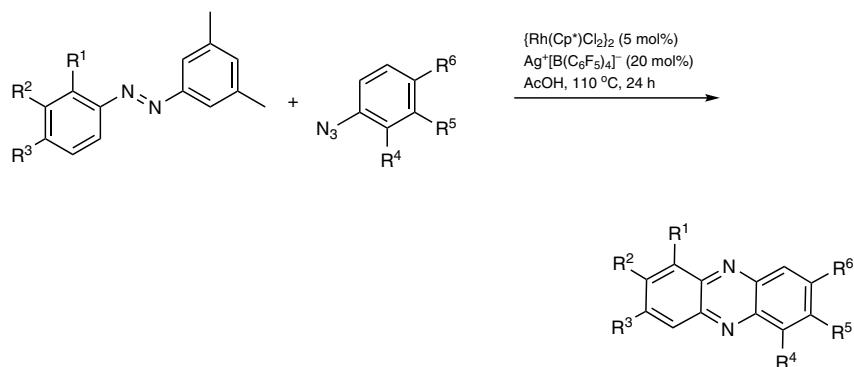
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## 16.16.5 Phenazines

N. B. Ambhaikar

Phenazines are an interesting class of nitrogen-containing heterocycles present in many natural products. This update describes the construction of phenazines through some newer practical synthetic methods that have been reported since the first review on phenazines in *Science of Synthesis* (Section 16.16). For the most part, standard ways of synthesizing phenazine and its derivatives have employed traditional approaches or their variations along the lines of the Wohl–Aue reaction and the Beirut reaction. The current account focuses on modern synthetic tools to construct the phenazine core and includes some of the newer approaches, with recent key methods that have been developed between 2004 and 2019.



**Keywords:** phenazines · phenazine *N*-oxides · electrochemical reduction · C–H activation · oxidative coupling · Fischer carbenes · cyclization · quinoxalines

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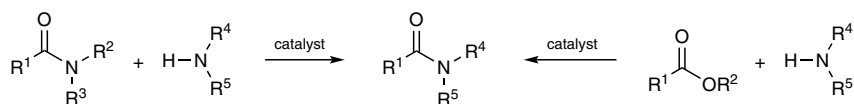
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21.1.8 **Synthesis of Amides by Transamidation and Amidation of Activated Amides and Esters**

G. Li and M. Szostak

This chapter provides a summary of the recent advances in direct transamidation and amidation reactions of activated amides and esters via transition-metal-catalyzed and transition-metal-free C(acyl)–N and C(acyl)–O bond cleavage as a new disconnection for the synthesis of amide bonds.



**Keywords:** amides · esters · transamidation · amidation · N–C cleavage · O–C cleavage · tetrahedral intermediates · nucleophilic addition · cross coupling · palladium–NHC catalysis · nickel catalysis · nitroarenes · anilines · chemoselectivity · reductive coupling · twisted amides · ground-state destabilization · electronic activation

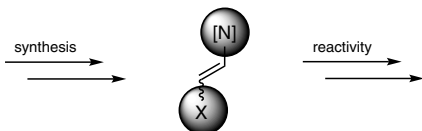
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32.3.4.2 **1-Nitrogen-Functionalized 2-Haloalkenes**

M. L. Tong, K. Kunz, M. Jaschinski, K. Holzschneider, I. E. Celik, and S. F. Kirsch

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 32.3.4) describing general synthetic methods to access 1-nitrogen-functionalized 2-haloalkenes. It puts a new focus on recent synthetic developments for this rather broad class of compounds, covering the literature from 2008 until 2018. The contents are broadly categorized by discussing methods of synthesis first, followed by specific reactivities. The synthetic methods section is arranged according to the number of substituents attached to the alkene core. Due to the vast number of examples in the literature, the current overview represents a selection of methods. In particular, when describing reactivities with 1-nitrogen-functionalized 2-haloalkenes, only archetypical examples are shown, while explicit variants are omitted.

[N] = NR<sup>1</sup><sub>2</sub>, N<sub>3</sub>, NO<sub>2</sub>, NR<sup>1</sup>(SO<sub>2</sub>R<sup>2</sup>); X = F, Cl, Br, I

**Keywords:** alkenes · enamines · haloalkenes · halogenation · cross coupling · elimination reactions · Michael addition · metathesis · Wittig alkenation

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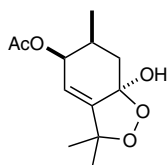
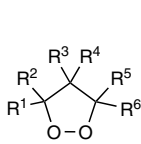
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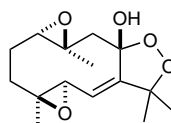
38.8.3.2 **Stable and Unstable 1,2-Dioxolanes: Origin, Synthesis, and Biological Activities**

V. M. Dembitsky and I. A. Yaremenko

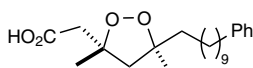
This chapter describes 1,2-dioxolanes, with confirmed biological activity, isolated from various natural sources. The key steps in the formation of the 1,2-dioxolane ring in the total synthesis of some natural peroxides as well as interesting modern procedures for the synthesis of 1,2-dioxolanes are also presented.



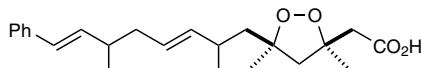
acetylsaturejol



wenjine



andavadoic acid



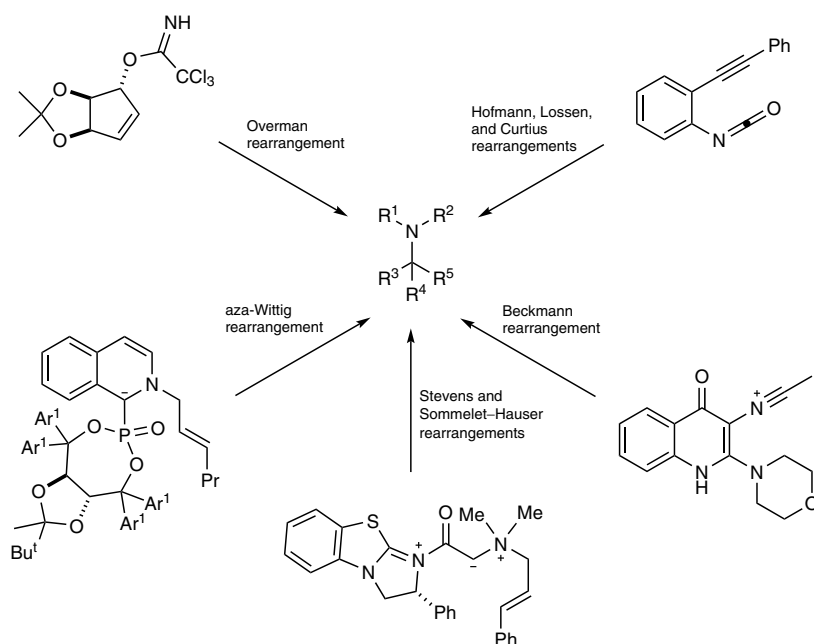
plakinic acid A

**Keywords:** 1,2-dioxolanes · peroxides · oxidation · oxygen · hydrogen peroxide · hydroperoxides · cyclopropanes · acetylenes · carbonyl compounds · ketones · alkenes · enones · ketals · acetals · epoxides · allenes · nitrosoarenes · ozonolysis · antimalarial · antifungal · antiviral · anticancer

40.1.1.4.3 **Synthesis of Amines by Rearrangement**

C. I. Ochoa and U. K. Tambar

The synthesis of amines is one of the most important areas of research in organic chemistry due to the prevalence of nitrogen atoms in many functional molecules, including natural products, pharmaceutical drugs, and agrochemicals. The synthesis of amines through rearrangement reactions has been heavily researched and discussed over the past few decades. One of the most comprehensive reviews of this topic was included in *Science of Synthesis* (Section 40.1.1.4). The purpose of this review is to provide an up-to-date account of new methods and synthetic developments in amine rearrangement reactions within the last decade. Over this period of time, new chemistry has been developed which was not discussed in any particular section in the original account on this topic. Thus, this chapter serves as a supplementary document to the earlier review but is also a source of new synthetic strategies not discussed previously. The chapter is arranged in two sections: rearrangements from carbon to nitrogen, and rearrangements from nitrogen to carbon.



**Keywords:** amines · rearrangements · Stevens rearrangement · Sommelet–Hauser rearrangement · aza-Wittig rearrangement · Overman rearrangement · Beckmann rearrangement · Hofmann rearrangement · Lossen rearrangement · Curtius rearrangement

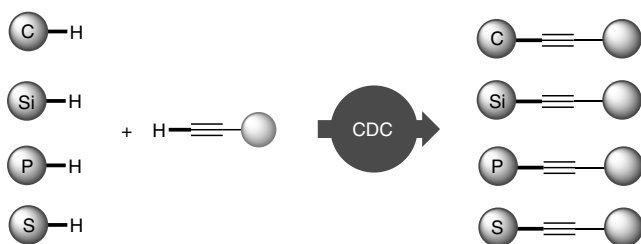
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43.10

**Cross-Dehydrogenative Coupling of Terminal Alkynes***T. Tian and Z. Li*

The construction of C–C and C–X bonds via cross-dehydrogenative coupling (CDC) reactions has made remarkable progress, and the methods developed have reached excellent levels of versatility, selectivity, and efficiency over the past few decades. The oxidative coupling of various C–H or X–H substrates to terminal alkynes can complement the coupling reactions of functionalized starting materials and can minimize waste and allow faster access to functionalized product molecules. These reactions represent a historic breakthrough in alkylation chemistry and have greatly expanded the synthetic routes available for the efficient construction of alkynyl compounds.



**Keywords:** cross-dehydrogenative coupling · terminal alkynes · alkylation · C–C bond formation · C–X bond formation

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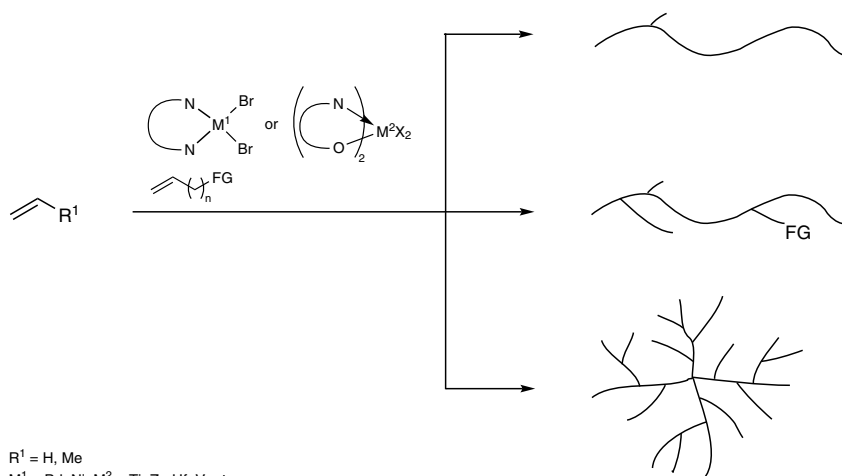
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48.5.5

**Hydrocarbon Polymers**

X.-Y. Wang and X.-L. Sun

X.-Y. Wang and X.-L. Sun This review is an update to the original *Science of Synthesis* chapter (Section 48.5) on hydrocarbon polymers, published in 2009. This update focuses on the typical methods for the synthesis of polyethene and polypropene reported over the past two decades. In addition, it has been supplemented with some general synthesis procedures for copolymers of ethene or propene with polar vinyl monomers as well as typical synthetic methods for other polyalk-1-ene [poly( $\alpha$ -olefin), PAO] products. The methods covered are mainly based on early-transition-metal, non-metallocene catalysts and late-transition-metal catalysts.

R<sup>1</sup> = H, MeM<sup>1</sup> = Pd, Ni; M<sup>2</sup> = Ti, Zr, Hf, V, etc.FG = OH, CO<sub>2</sub>H, CO<sub>2</sub>R<sup>2</sup>, Cl, CN

**Keywords:** coordination polymerization · catalysis · polyalkenes · polyolefins · polymers · copolymers · structure · non-metallocene catalysts · late-transition-metal catalysts

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