



**Science of
Synthesis**

Knowledge Updates 2017/2

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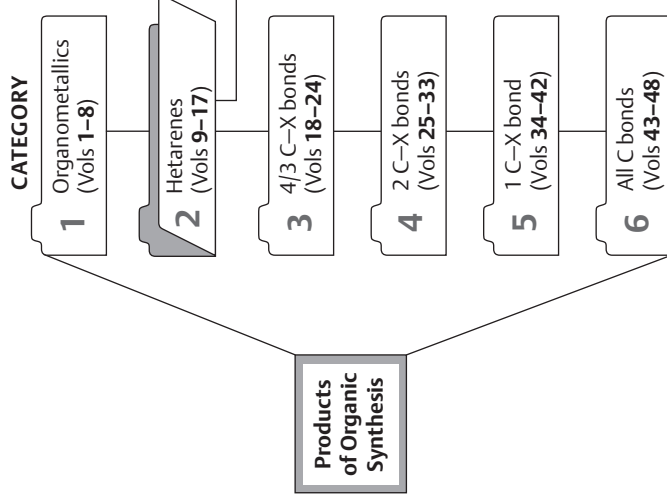
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Organizational Structure of Science of Synthesis*



Classification is **based on the product**, with all products belonging to one of six broad-ranging categories. All products occupy a strict hierarchical position in Science of Synthesis, defined according to the classification principles*. Products in Categories 3–6 are organized according to oxidation state, with products containing the greatest number of carbon–heteroatom (C–X) or C–C π -bonds to a single carbon occupying the highest positions (e.g., carboxylates, enolates, and alcoholates are covered in Categories 3, 4, and 5, respectively).

Each category is subdivided into volumes (see opposing page), each of which is devoted to discrete groupings of compounds called **product classes** (e.g., “Thiophenes” is Product Class 10 of Volume 9). Product classes may be further subdivided into **product subclasses**, (e.g., “Thiophene 1,1-Dioxides” is Product Subclass 3 of Product Class 10 of Volume 9). Consequently, the relationship between heading name and heading number varies below product class level within individual volumes.

For each product class or subclass, a number of methods are described for synthesizing the general product type. Often there are variations on a method given. Both methods and variations contain experimental procedures with relevant background information and literature references. **Selected products and reactions** display the scope and limitations of the methods.

* A complete description of the full classification principles can be found in the **Science of Synthesis Guidebook**.

CATEGORY

UPDATED VOLUMES

1 Organometallics (Vols 1-8)	1	2	3	4	5	6	7	8a	8b
2 Heteroarenes (Vols 9-17)	9	10	11	12	13	14	15	16	17
3 4/3 C-X bonds (Vols 18-24)	18	19	20a	20b	21	22	23	24	
4 2 C-X bonds (Vols 25-33)	25	26	27	28	29	30	31a	31b	32
5 1 C-X bond (Vols 34-42)	34	35	36	37	38	39	40a	40b	41
6 All C bonds (Vols 43-48)	43	44	45a	45b	46	47a	47b	48	

17 Six-Membered Heteroarenes with Two Unlike or More than Two Heteroatoms and Fully Unsaturated Larger-Ring Heterocycles

34 Fluorine

40 Amines and Ammonium Salts

* Detailed listings of product classes and subclasses, methods, and variations can be found in the **Table of Contents** sections of every volume.

Science of Synthesis

Science of Synthesis is the authoritative and comprehensive reference work for the entire field of organic and organometallic synthesis.

Science of Synthesis presents the important synthetic methods for all classes of compounds and includes:

- Methods critically evaluated by leading scientists
- Background information and detailed experimental procedures
- Schemes and tables which illustrate the reaction scope



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Preface

As the pace and breadth of research intensifies, organic synthesis is playing an increasingly central role in the discovery process within all imaginable areas of science: from pharmaceuticals, agrochemicals, and materials science to areas of biology and physics, the most impactful investigations are becoming more and more molecular. As an enabling science, synthetic organic chemistry is uniquely poised to provide access to compounds with exciting and valuable new properties. Organic molecules of extreme complexity can, given expert knowledge, be prepared with exquisite efficiency and selectivity, allowing virtually any phenomenon to be probed at levels never before imagined. With ready access to materials of remarkable structural diversity, critical studies can be conducted that reveal the intimate workings of chemical, biological, or physical processes with stunning detail.

The sheer variety of chemical structural space required for these investigations and the design elements necessary to assemble molecular targets of increasing intricacy place extraordinary demands on the individual synthetic methods used. They must be robust and provide reliably high yields on both small and large scales, have broad applicability, and exhibit high selectivity. Increasingly, synthetic approaches to organic molecules must take into account environmental sustainability. Thus, atom economy and the overall environmental impact of the transformations are taking on increased importance.

The need to provide a dependable source of information on evaluated synthetic methods in organic chemistry embracing these characteristics was first acknowledged over 100 years ago, when the highly regarded reference source **Houben–Weyl Methoden der Organischen Chemie** was first introduced. Recognizing the necessity to provide a modernized, comprehensive, and critical assessment of synthetic organic chemistry, in 2000 Thieme launched **Science of Synthesis, Houben–Weyl Methods of Molecular Transformations**. This effort, assembled by almost 1000 leading experts from both industry and academia, provides a balanced and critical analysis of the entire literature from the early 1800s until the year of publication. The accompanying online version of **Science of Synthesis** provides text, structure, substructure, and reaction searching capabilities by a powerful, yet easy-to-use, intuitive interface.

From 2010 onward, **Science of Synthesis** is being updated quarterly with high-quality content via **Science of Synthesis Knowledge Updates**. The goal of the **Science of Synthesis Knowledge Updates** is to provide a continuous review of the field of synthetic organic chemistry, with an eye toward evaluating and analyzing significant new developments in synthetic methods. A list of stringent criteria for inclusion of each synthetic transformation ensures that only the best and most reliable synthetic methods are incorporated. These efforts guarantee that **Science of Synthesis** will continue to be the most up-to-date electronic database available for the documentation of validated synthetic methods.

Also from 2010, **Science of Synthesis** includes the **Science of Synthesis Reference Library**, comprising volumes covering special topics of organic chemistry in a modular fashion, with six main classifications: (1) Classical, (2) Advances, (3) Transformations, (4) Applications, (5) Structures, and (6) Techniques. Titles will include *Stereoselective Synthesis*, *Water in Organic Synthesis*, and *Asymmetric Organocatalysis*, among others. With expert-evaluated content focusing on subjects of particular current interest, the **Science of Synthesis Reference Library** complements the **Science of Synthesis Knowledge Updates**, to make **Science of Synthesis** the complete information source for the modern synthetic chemist.

The overarching goal of the **Science of Synthesis** Editorial Board is to make the suite of **Science of Synthesis** resources the first and foremost focal point for critically evaluated information on chemical transformations for those individuals involved in the design and construction of organic molecules.

Throughout the years, the chemical community has benefited tremendously from the outstanding contribution of hundreds of highly dedicated expert authors who have devoted their energies and intellectual capital to these projects. We thank all of these individuals for the heroic efforts they have made throughout the entire publication process to make **Science of Synthesis** a reference work of the highest integrity and quality.

The Editorial Board

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Abstracts

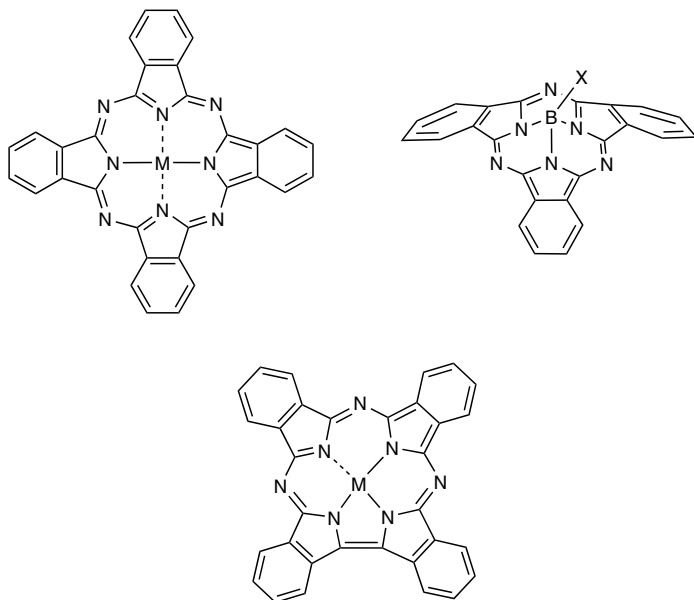
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17.9.24 Phthalocyanines and Related Compounds

M. S. Rodríguez-Morgade and T. Torres

This review updates the original *Science of Synthesis* chapter (Section 17.9) on phthalocyanines and various ring-fused, ring-contracted, and ring-expanded analogues. It adds some recently published methods, examples, and variations on the synthesis of unsubstituted phthalocyanines and metal phthalocyanines, as well as identically and nonidentically substituted phthalocyanine derivatives. Besides peripheral substitution, axial functionalization is also discussed, but attention is focused only on those methods that represent appreciable progress for a particular type of metal coordination and axial functionalization, provide phthalocyanines with specific features such as chirality, or allow the functionalization of phthalocyanines with entities that are difficult to introduce at the peripheral sites. This account also includes sections on new types of phthalocyanine derivatives and analogues that were not covered in the original chapter, as well as the progress made in the synthesis of some of these families in the decade since 2003.



Keywords: phthalocyanines · phthalocyanine–metal complexes · porphyrazines · tetraazaporphyrins · naphthalocyanines · phenanthrenocyanines · triphenylenocyanines · anthracenocyanines · pyrenocyanines · benzoperylenocyanines · helicenocyanines · azulenocyanines · tetraazachlorins · tetraazabacteriochlorins · azaphthalocyanines · triazacorroles · subphthalocyanines · subporphyrazines · superazaporphyrins · pyrenocyanines · phthalonitriles · phthalic anhydrides · phthalic acids · phthalimides · isoindolinediimines · condensation reactions · substituent modification · ligand substitution

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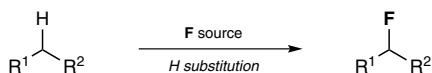
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34.1.1.8 **Synthesis of Fluoroalkanes by Substitution of Hydrogen**

M. Rueda-Becerril and G. M. Sammis

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 34.1.1) describing methods for the synthesis of fluoroalkanes by substitution of hydrogen. The increasing importance of fluorine-containing molecules in the health, pharmaceutical, and agrochemical sectors has resulted in the rapid development of more-selective, more-controlled, and safer methods for the insertion of a fluorine atom into structurally diverse molecules. Herein, the most synthetically useful methods reported from 2006 until mid-2016 to achieve such transformations are described.



Keywords: fluorination · hydrogen substitution · alkanes · cycloalkanes · fluorine compounds · fluorine transfer · Selectfluor · photocatalysis · organometallic reagents

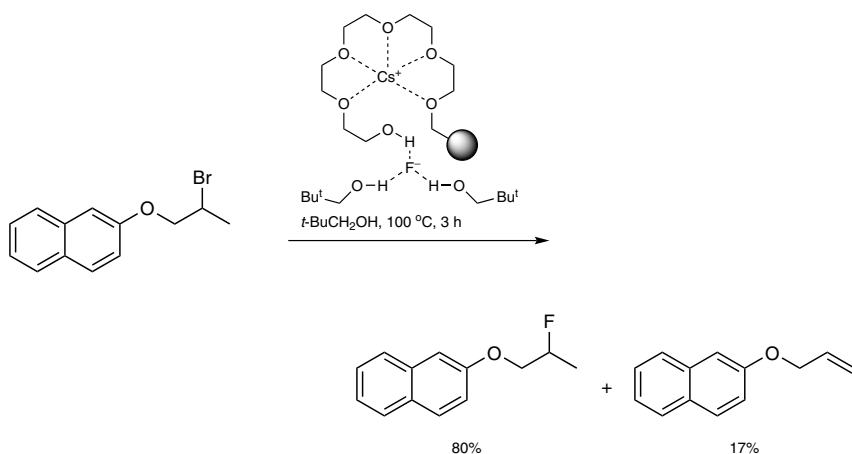
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34.1.4.1 **Synthesis of Fluoroalkanes by Substitution of a Halogen**

T. P. Lequeux

This chapter is a revision of the earlier *Science of Synthesis* contribution describing methods for the synthesis of fluoroalkanes by substitution of a halogen atom. It includes additional methods published up until 2016. Newer approaches involve the use of fluoride complex reagents and the use of solvent effects to avoid competitive elimination reactions.



Keywords: fluoroalkanes · nucleophilic substitution · fluorides · halides · alkanes · cycloalkanes · nucleosides · amines · steroids · ammonium compounds · copper complexes

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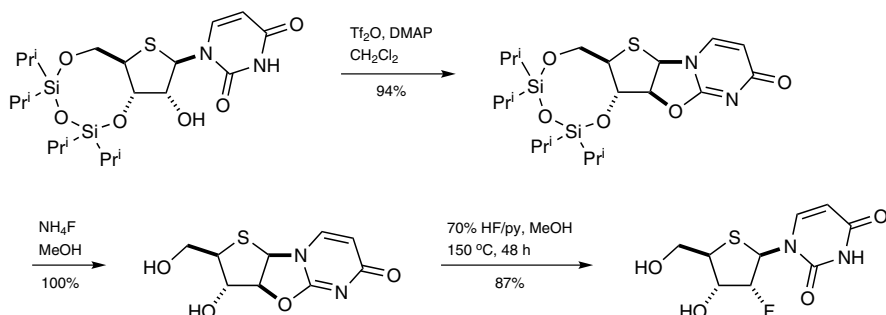
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34.1.4.3 **Synthesis of Fluoroalkanes by Substitution of Oxygen and Sulfur Functionalities**

T. P. Lequeux

This chapter is a revision of the earlier *Science of Synthesis* contribution describing methods for the synthesis of fluoroalkanes by substitution of oxygen and sulfur functionalities. It now includes the literature published up until 2016. The additional material focuses on new reagents and their applications. For example, the effect of an ionic liquid on the rate of the displacement of sulfonates by cesium fluoride, and expeditious synthesis of nucleoside derivatives are described.



Keywords: fluoroalkanes · nucleophilic substitution · fluorides · sulfonates · alkanes · cycloalkanes · pyrans · nucleosides · carbohydrates · steroids · sulfur compounds · copper complexes

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34.1.6.4 **Synthesis of Fluoroalkanes with Retention of the Functional Group**

T. Yamazaki

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 34.1.6) describing methods for the synthesis of monofluorinated compounds with a $\text{C}(\text{sp}^3)\text{—F}$ bond by way of a wide variety of transformations of molecules already bearing the key C—F bond. The focus is on methods published in the period 2005–2015.



Keywords: alkylation · crossed aldol reactions · conjugate addition · $\text{S}_{\text{N}}2'$ reactions · hydrogenation · reduction · cycloadditions · iodolactonization

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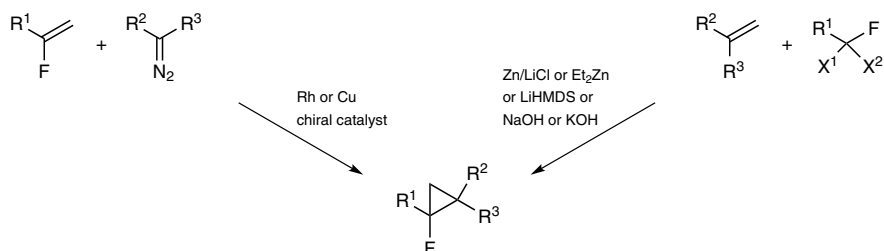
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34.2.2 Fluorocyclopropanes

P. Jubault, T. Poisson, and X. Pannecoucke

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 34.2) describing methods for the synthesis of fluorocyclopropanes. The most important breakthrough described in this update is the development of asymmetric syntheses of fluorocyclopropanes based on various approaches, such as the use of chiral fluorinated scaffolds or the development of catalytic enantioselective sequences. This review focuses on the contributions published between 2005 and 2016.



Keywords: fluorocyclopropanes · cyclopropanes · fluorine compounds · conjugate addition · carbenoids · diazo compounds · asymmetric catalysis · alkenes

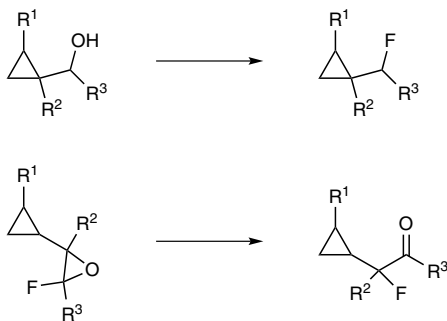
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34.3.2 (Fluoromethyl)cyclopropanes

P. Jubault, T. Poisson, and X. Pannecoucke

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 34.3) describing methods for the synthesis of (fluoromethyl)cyclopropanes. In this review, new methods, published since 2006, by means of direct or two-step fluorodehydroxylation and by rearrangement of fluoroepoxides are described.



Keywords: (fluoromethyl)cyclopropanes · cyclopropanes · fluorine compounds · nucleophilic fluorination · carbenoids · rearrangement

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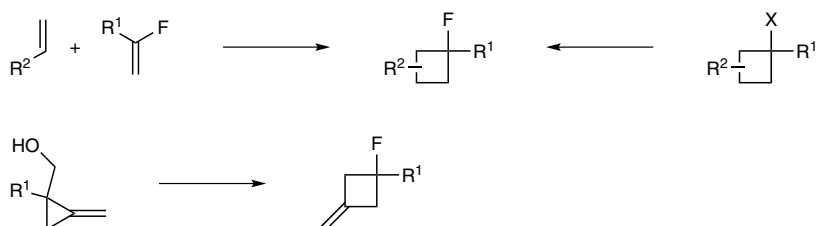
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34.4.2 Fluorocyclobutanes

T. Poisson, P. Jubault, and X. Pannecoucke

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 34.4) describing methods for the synthesis of fluorocyclobutanes. In this review, progress made in the field since 2006 is reported. The use of cycloaddition reactions as well as rearrangement reactions to access the fluorocyclobutane motif are significant advances in this area.



Keywords: fluorocyclobutanes · cyclobutanes · fluorine compounds · nucleophilic fluorination · [2 + 2] cycloaddition · rearrangement

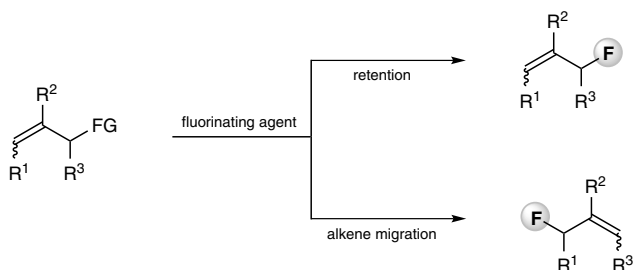
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34.7.4 Allylic Fluorides

C. R. Pitts and T. Lectka

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 34.7) regarding the synthesis of allylic monofluorides. Herein, literature from 2005–2015 is discussed. Advancements during this time period include the employment of milder fluorinating reagents, methods that favor alkene migration or retention, tactics for catalytic and asymmetric reactions, and the introduction of a creative array of functional-group interconversions.



FG = OR⁴, SR⁴, SiR⁴₃, Br, Cl, H, etc.

Keywords: fluorination · halogenation · allylic fluorides · carbon–halogen bonds · allylic substitution · electrophilic fluorination · nucleophilic fluorination · asymmetric fluorination · regioselectivity

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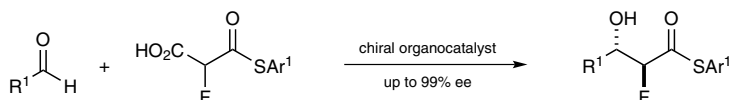
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34.9.3

 β -Fluoro Alcohols

K. Shibatomi

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 34.9) describing methods for the synthesis of β -fluoro alcohols. It focuses on enantioselective synthetic approaches, and includes methods based on the α -fluorination of carbonyl compounds and subsequent reduction.



Keywords: β -fluoro alcohols · fluorine compounds · asymmetric fluorination · decarboxylation · decarbonylation · aldol reaction · reduction · enantioselectivity · Lewis acid catalysts · chiral amine catalysts

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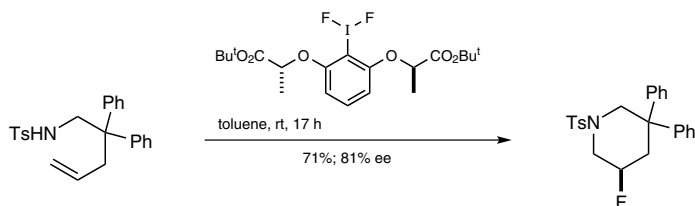
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34.10.5

 β -Fluoroamines

L. Hunter

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 34.10) describing methods for the synthesis of β -fluoroamines. This topic has continued to attract significant attention from the synthetic community, largely due to the medicinal importance of this class of compounds. A wide variety of new methods have been developed, and this review focuses on examples that were published between 2005 and 2015.



Keywords: aminofluorination · carbon–fluorine bonds · electrophilic fluorination · nucleophilic fluorination · radical fluorination · stereoselective reactions

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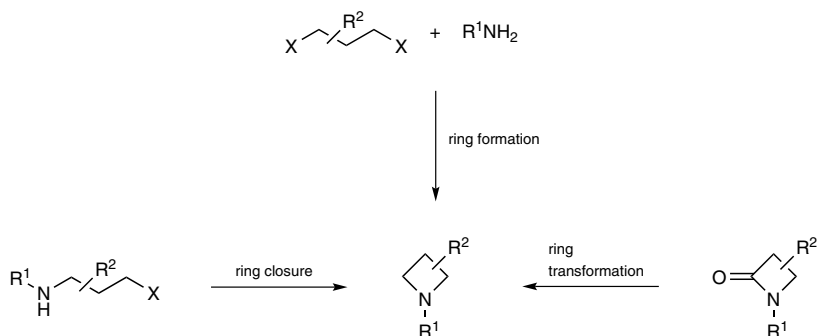
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40.1.6.2 Azetidines

F. Couty

This chapter is an update to the earlier *Science of Synthesis* contribution (Section 40.1.6) describing methods for the synthesis of azetidines. This review focuses on contributions in this field published between 2008 and 2015 (with some exceptions of papers published as early as 2006, which were not covered in the earlier review). This period has witnessed an impressive breakthrough of pharmaceutical agents bearing an azetidine ring in medicinal chemistry and the first examples of organocatalyzed enantioselective syntheses of nonracemic azetidines.



Keywords: azetidines · small rings · ring strain · nitrogen heterocycles · ring closure · ring contraction · β-lactams

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