

C-1 Building Blocks in Organic Synthesis

To selectively expand the structure of a growing molecule is one of the most important and demanding tasks for the synthetic organic chemist. In particular, the addition of one carbon atom (C-1) to the target substrate is of key interest for several reasons: first of all, C-1 building blocks are typically of lower cost. Secondly, when C-1 addition is combined with transition metal catalysis, it can achieve high chemoselectivity under mild conditions. Thirdly, although the range of available C-1 building blocks can be considered somewhat limited, there is a wide choice of methods for incorporating them. These are all factors that have made C-1 manipulation of molecules a very attractive approach, not only for research purposes but also in the industrial production of advanced intermediates and commodities. Although comprehensive review articles for the individual areas of C-1 installation methods are available, a collection of the most general approaches has been lacking up to now. The two-volume publication *C-1 Building Blocks in Organic Synthesis* (part of the *Science of Synthesis* series) takes on this challenge with success. In contrast to the general literature in the area, these two books do not classify C-1 additions according to the method used, but instead by C-1 elongation of a specific functionality, as clearly stated by the editor Piet W. N. M. van Leeuwen: "...how one can add a C-1 unit to a certain functional group?" Finally, in order to be included in this work, the C-1 addition has to be part of a carbon-carbon bond-forming reaction, as this collection does not cover carbon-heteroatom bond-forming transformations. Volume 1 covers C-1 addition to alkenes, alkynes, and carbonyl compounds. Volume 2 is an extension of Volume 1, and covers alkenations, cross-couplings, insertions, substitutions, and halomethylations on different functionalities. In all, 54 authors have contributed, each within a field of their own expertise, thus giving the reader an up-to-date view on each topic. However, the large number of authors has resulted in variations between the chapters. Some authors include a detailed discussion of mechanistic considerations and additive effects, whereas others are more focused on the transformational overview itself. It is not obvious whether this inconsistency is due to the sheer volume of information on certain topics or to the freedom allowed to the individual authors. With that said, all chapters are well written with very few mistakes, and each provides a good overview including references up to the year 2012. Every chapter begins with a short introduction to the topic (1–2 pages) before describing methods and reaction

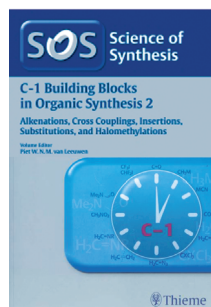
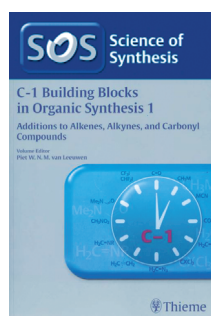
conditions, all presented concisely with reaction schemes and tables. Each sub-topic ends with typical experimental details, providing the reader with an insight into the reaction/reactor setup. Apart from one sub-chapter (industrial applications of hydroformylation), nearly all the experimental examples are for the laboratory (mmol) scale. Although this experimental information is valuable, it would have been useful to also describe examples of larger-scale production, especially in the chapters where industrial applications are known (hydroformylations, reductive carbonylations, hydrocyanations, etc.).

The first 200 pages of Volume 1 are focused on the hydroformylation of alkenes, and are divided into five sub-chapters, with contributions from 13 different authors. This very comprehensive part of the book covers all aspects of classical and modern hydroformylation reactions, including classes of starting materials, catalysts with different metal-ligand combinations, asymmetric and tandem hydroformylations, alternative reaction media, and finally industrial applications. This section is by far the largest in the book, undoubtedly due to its industrial relevance. However, the likewise industrially important topic of hydrocyanation of alkenes takes up only 30 pages in the excellent chapter by M. E. Tauchert. Despite this considerably shorter chapter size, Tauchert manages to cover the majority of applicable catalysts, ligands, and additive effects in a precise manner. His discussion returns several times to the hydrocyanation of butadiene yielding the 1,6-nylon precursor adiponitrile, and this gives continuity for the reader.

As the editor explains, the book is limited to carbon-carbon bond-forming reactions, and consequently only two carbon dioxide C-1 addition reactions are covered. Both chapters are written by J. Takaya and N. Iwasawa, and they describe the addition of CO₂ to acyclic hydrocarbons such as alkenes, alkynes, allenes, etc., as well as the more classical carboxylation of organometallic compounds, including transition-metal-catalyzed versions. Both chapters include discussions of catalytic cycles and stable intermediates such as nickel metallacycles, and are well illustrated with schemes and tables.

Apart from the more dominant chapters, room has also been left for more specialized C-1 additions. For example, in Volume 2 a 13-page chapter by H. Ibrahim deals with the ring expansion of aziridine derivatives by insertion of carbon monoxide (CO) forming four- to six-member lactams, using cobalt, rhodium, and palladium organometallic catalysts.

Given that these volumes cover a very broad diversity of different C-1 addition methods, there are no particular topics that are obviously missing.



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However, one could have wished that the editor had enforced a more streamlined approach to each chapter, ensuring that every author included a more detailed discussion of reaction mechanisms.

I thoroughly recommend *C-1 Building Blocks in Organic Synthesis* as a work that provides a broad and detailed overview of an otherwise difficult-to-cover field of organic chemistry. The stringent approach whereby C-1 additions are treated, not in terms of the specific method, but from the viewpoint of "...how one can add a C-1 unit to a certain functional group?" works exceptionally well. Especially as the chapters include an up-to-date collection of literature references, these

books will serve as a comprehensive reference source for years to come. Finally, as every chapter includes numerous experimental details, the books could also be used for applications in teaching. These volumes should be part of every research and development chemist's book collection.

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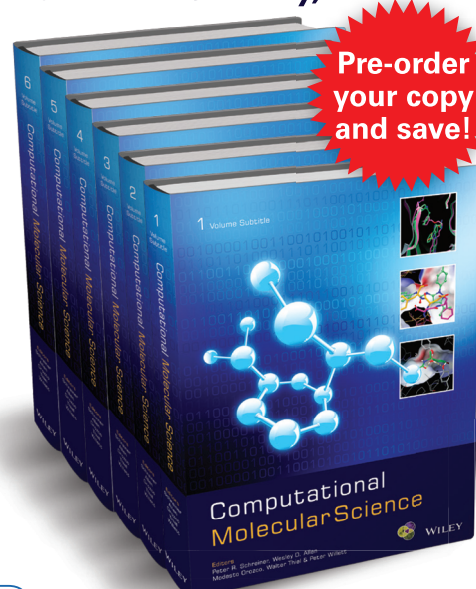
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