Handbook of Reagents for Organic Synthesis

Activating Agents and Protecting Groups

Edited by

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and

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Preface

As stated in its Preface, the major motivation for our undertaking publication of the *Encyclopedia of Reagents for Organic Synthesis* was "to incorporate into a single work a genuinely authoritative and systematic description of the utility of all reagents used in organic chemistry." By all accounts, this reference compendium has succeeded admirably in attaining this objective. Experts from around the globe contributed many relevant facts that define the various uses characteristic of each reagent. The choice of a masthead format for providing relevant information about each entry, the highlighting of key transformations with illustrative equations, and the incoroporation of detailed indexes serve in tandem to facilitate the retrieval of desired information.

Notwithstanding these accomplishments, the editors have since recognized that the large size of this eight-volume work and its cost of purchase have often served to deter the placement of copies of the *Encyclopedia* in or near laboratories where the need for this type of insight is most critically needed. In an effort to meet this demand in a cost-effective manner, the decision was made to cull from the major work that information having the highest probability for repeated consultation and to incorporate same into a set of handbooks. The latter would also be purchasable on a single unit basis.

The ultimate result of these deliberations is the publication of the *Handbook of Reagents for Organic Synthesis* consisting of the following four volumes:

Reagents, Auxiliaries and Catalysts for C–C Bond Formation
Edited by Robert M. Coates and Scott E. Denmark

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Each of the volumes contains a complete compilation of those entries from the original *Encyclopedia* that bear on the specific topic. Ample listings can be found to functionally related reagents contained in the original work. For the sake of current awareness, references to recent reviews and monographs have been included, as have relevant new procedures from *Organic Syntheses*.

The end product of this effort by eight of the original editors of the *Encyclopedia* is an affordable, enlightening set of books that should find their way into the laboratories of all practicing synthetic chemists. Every attempt has been made to be of the broadest synthetic relevance and our expectation is that our colleagues will share this opinion.

Leo A. Paquette
Columbus, Ohio USA

Introduction

The combination of reagents included in this volume reflects the fact that protecting groups and activation procedures are often used in combination, one example being in peptide synthesis, where an amino group of one amino acid component must be blocked before its carboxylic acid is activated for coupling with a second amino acid to form the amide bond. There are many other instances in the synthesis of natural and unnatural products, pharmaceuticals, oligosaccharides, and oligonucleotides, etc., where similar tactics must be employed to prevent undesired activation or reaction of functionality, such as hydroxyl, when more than one such group is present, or to prevent reactive functional groups from entering into unwanted reactions with oxidizing agents, reducing agents, or organometallic reagents commonly employed in organic synthesis. Accordingly, the most important reagents used to protect amines, alcohols, carboxyl, carbonyl and other reactive functional groups are included in this volume.

The selection of activating reagents includes both well known and less traditional ones. Thus, typical peptide coupling reagents that activate carboxylic acids, such as dicyclohexylcarbodiimide, are listed in this volume, in addition to reagents that are not immediately identified as activators. One example of the latter is hexacarbonylchromium, which may be used to activate aromatic substrates toward nucleophilic addition and substitution, via the formation of arenechromium tricarbonyl complexes. Another example is nonacarbonyldiiron, which can serve multiple purposes in activating alkenes and dienes toward nucleophilic attack, or allowing their conversion to cationic allyl- or dienyl- complexes, as well as protecting the same functionality from reactions such as hydroboration, Diels-Alder cycloadditions, etc. Transition metal systems that perform these types of functions could have formed a separate volume if one includes catalytic processes under the heading of activation. To avoid a volume of unmanageable size, the choice of these reagents has been limited to those that are used stoichiometrically, and that are relatively familiar to the organic chemistry community.

Some reagents, such as hexamethylphosphoric triamide (HMPA) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) that "activate" enolates and alkyllithium reagents and increase their nucleophilicity, thereby facilitating their reactions, are also included. A number of Lewis acids appear in this volume, including the alkylaluminum halides and the boron halides, as examples of reagents that activate various functional groups by increasing their electrophilicity. The complete entries for all lewis acids and nucleophilic catalysts (e.g. dimethylaminopyridine) also appear in the volume on Acidic and Basic Reagents.

There are many reagents that may be considered as activating in the broadest sense. The phosphorus halides, for example, can be used to activate hydroxyl groups of alcohols or carboxylic acids by converting them to halide leaving groups for nucleophilic substitution or elimination, while the corresponding sulfonate esters activate alcohols in the more traditional manner. Reagents such as *N,N′*-thiocarbonyldiimidazole and phenyl chlorothionocarbonate, which serve to activate alcohols for subsequent deoxygenation reactions with a trialkyltin hydride reagent, and (methoxycarbonylsulfamoyl)triethylammonium hydroxide, which facilitates the dehydrative elimination of alcohols to alkenes, also qualify as activating reagents in the broadest sense and are included in the present volume. As many examples of activating agents are included in this volume as possible but, again, an effort has been made to produce a work that is not too voluminous in scope.

Finally, there are many reagents that perform functions other than those that are the immediate subject matter of this volume. No attempt has been made to trim the original entries that were prepared for the *Encyclopedia of Reagents for Organic Synthesis*, since we recognize the value of having as much information as possible about each reagent, thus allowing their optimal use in situations where side

reactions might be a problem when limited information is at hand.

In preparing this volume we have been aware of the fact that the original *Encyclopedia* entries were written several years ago, and so may not be completely up to date with regard to literature citations. This is inevitable in a work of this kind, but we have tried to ameliorate the problem as much as possible by including references to relevant articles from *Organic Syntheses*. Volumes 69–75 that either deal with the preparation of a particular reagent or illustrate its application, as well as recent (since 1993) review articles and monographs that focus on various aspects of the subject matter of this particular volume. For this purpose we have included reviews that may not be directly connected with any particular reagent, but that may be useful to the practicing organic chemist in seeking information concerning use of the various technologies described in the present work. Finally, we have also included expanded lists of "Related Reagents" for each entry which will allow the reader to locate additional information about additional related reagents and methods in the original *Encyclopedia*.

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Organic Syntheses References

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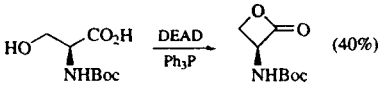
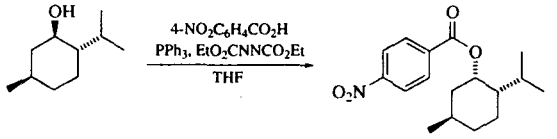
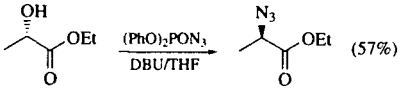
Pansare, S. V.; Arnold, L. D.; Vederas, J. C. "Synthesis of *N-tert*-Butyloxycarbonyl-L-serine β-Lactone and the *p*-Toluenesulfonic Acid Salt of (*S*)-3-Amino-2-oxetanone" **OS**, (1991), *70*, 10.



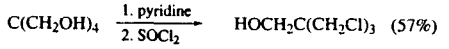
Dodge, J. A.; Nissen, J. S.; Presnell, M. "A General Procedure for Mitsunobu Inversion of Sterically Hindered Alcohols: Inversion of Menthol. (*1S*, *2S*, *5R*)-5-Methyl-2-(1-methylethyl)cyclohexyl 4-Nitrobenzoate" **OS**, (1995), *73*, 110.



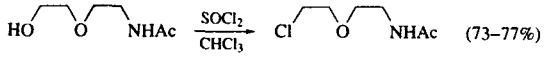
Thompson, A. S.; Hartner, F. W., Jr.; Grabowski, E. J. J. "Ethyl (*R*)-2-Azidopropionate" **OS**, (1997), *75*, 31.



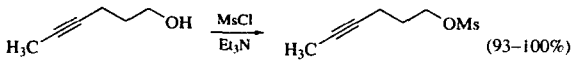
Lynch, K. M.; Dialey, W. P. "3-Chloro-2-(chloromethyl)-1-propene" **OS**, (1997), *75*, 89.



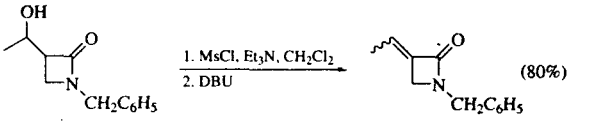
Krakowiak, K. E.; Bradshaw, J. S. "4-Benzyl-10,19-diethyl-4,10,19-triaza-1,7,1,16-tetraoxacycloheneicosane (Triaza-21-Crown-7)" **OS**, (1991), *70*, 129.



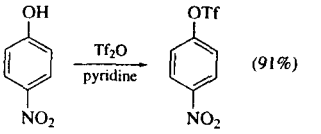
Arnold, H.; Overman, L. E.; Sharp, M. J.; Witschel, M. C. "(*E*)-1-Benzyl-3-(1-iodoethylidene)piperidine: Nucleophile-Promoted Alkyne-Iminium Ion Cyclizations" **OS**, (1991), *70*, 111.



Behrens, C.; Paquette, L. A. "*N*-Benzyl-2,3-azetidinedione" **OS**, (1997), *75*, 106.



Stille, J. K.; Echavarren, A. M.; Williams, R. M.; Hendrix, J. A. "4-Methoxy-4′-nitrobiphenyl" **OS**, (1992), *71*, 97.



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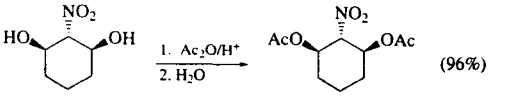
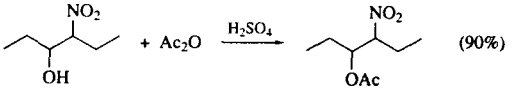
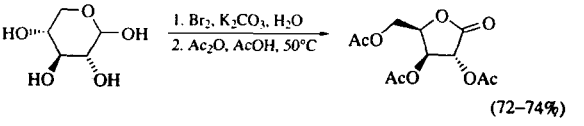
Eberle, M.; Missbach, M.; Seebach, D. "Enantioselective Saponification with Pig Liver Esterase (PLE): (*1S*, *2S*, *3R*)-3-Hydroxy-2-nitrocyclohexyl Acetate" **OS**, (1990), *69*, 19.



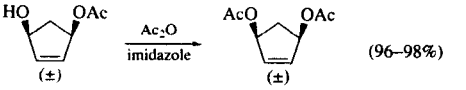
Sessler, J. L.; Mozaffari, A.; Johnson, M. R. "3,4-Diethylpyrrole and 2,3,7,8,12,13,17,18-Octaethylporphyrin" **OS**, (1991), *70*, 68.



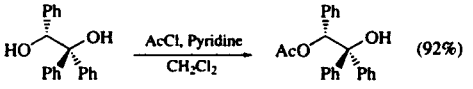
Sun, R. C.; Okabe, M. "(*2S*, *4S*)-2,4,5-Trihydroxypentanoic Acid 4,5-Acetonide Methyl Ester" **OS**, (1993), *72*, 48.



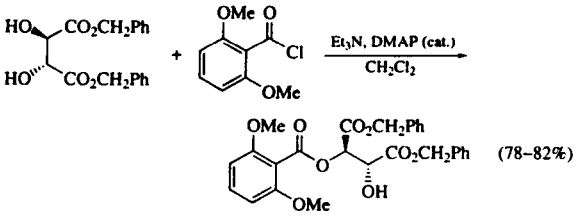
Deardorff, D. R.; Windham, C. Q.; Craney, C. L. "Enantioselective Hyrolysis of *cis*-3,5-Diacetoxycyclopentene: (1*R*, 4*S*)-(+)-4-Hydroxy-2-Cyclopentenyl Acetate" **OS**, (1995), *73*, 25.



Braun, M.; Graf, S.; Herzog, S. "(*R*)-(+)-2-Hydroxy-1,2,2-Triphenylethyl Acetate" **OS**, (1993), *72*, 32.

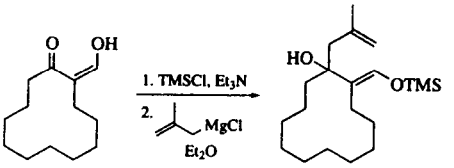


Furuta, K.; Gao, Q.-Z.; Yamamoto, H. "Chiral (Acyloxy)borane Complex-Catalyzed Asymmetric Diels-Alder Reaction: (1*R*)-1,3,4-Trimethyl-3-cyclohexene-1-carboxaldehyde" **OS**, (1993), *72*, 86.

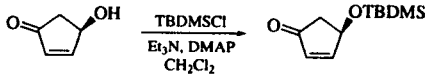


(b) Silylation

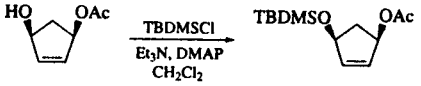
Tius, M. A.; Kannangara, G. S. K. "Benzoannelation of Ketones: 3,4-Cyclodedeceno-1-methylbenzene" **OS**, (1992), *71*, 158.



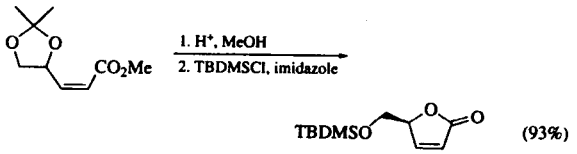
Paquette, L. A.; Earle, M. J.; Smith, G. F. "(4*R*)-(+)-*tert*-Butyldimethylsiloxy-2-cyclopenten-1-one" **OS**, (1995), *73*, 36.



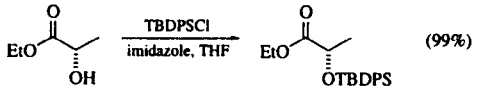
Paquette, L. A.; Heidelbaugh, T. M. "(4*S*)-(−)-*tert*-Butyldimethylsiloxy-2-cyclopenten-1-one" **OS**, (1995), *73*, 44.



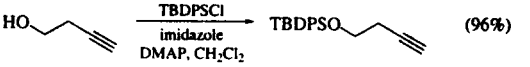
Mann, J.; Weymouth-Wilson, A. C. "Photoinduced-Addition of Methanol to (5*S*)-(5-*O*-*tert*-Butyldimethylsiloxymethyl)furan-2(5*H*)-one: (4*R*, 5*S*)-4-Hydroxymethyl-(5-*O*-*tert*-Butyldimethylsiloxymethyl)furan-2(5*H*)-one" (**OS**, (1997), *75*, 139.



Overman, L. E.; Rishton, G. M. "3-(*S*)-[(*tert*-Butyldiphenylsilyl)oxy]-2-butanone" **OS**, (1992), *71*, 56.



Wipf, P.; Xu, W. Allylic Alcohols by Alkene Transfer from Zirconium to Zinc: 1-[(*tert*-Butyldiphenylsilyl)oxy]-dec-3-en-5-ol" **OS**, (1996), *74*, 205.



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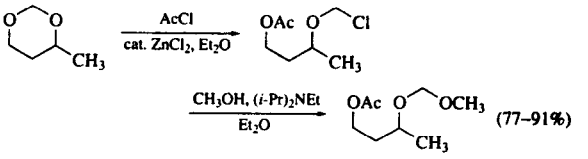
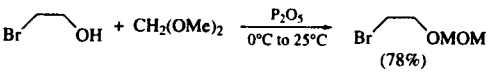
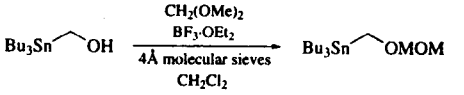
Bailey, W. F.; Carson, M. W.; Zarcone, L. M. J. "Selective Protection of 1,3-Diols at the More Hindered Hydroxy Group: 3-(Methoxymethoxy)-1-Butanol" **OS**, (1997), *75*, 177.



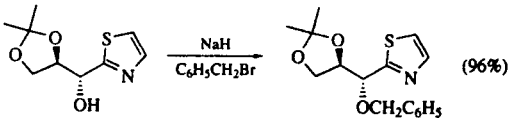
Tamao, K.; Nakagawa, Y.; Ito, Y. "Regio- and Stereoselective Intramolecular Hydrosilylation of α-Hydroxy Enol Ethers: 2,3-*syn*-2-Methoxymethoxy-1,3-nonanediol" **OS**, (1995), *73*, 94.



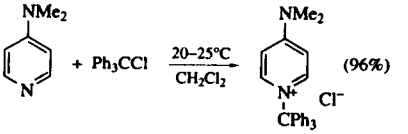
Danheiser, R. L.; Romines, K. R.; Koyama, H.; Gee, S. K.; Johnson, C. R.; Medich, J. R. "A Hydroxymethyl Anion Equivalent: Tributyl[(methoxymethoxy)methyl]stannane" **OS**, (1992), *71*, 133.



Dondoni, A.; Merino, P. "Diastereoselective Homologation of D-(*R*)-Glyceraldehyde Acetonide Using 2-(Trimethylsilyl)thiazole: 2-*O*-Benzyl-3,4-isopropylidene-D-erythrose" **OS**, (1993), *72*, 21.



Bhatia, A. V.; Chaudhary, S. K.; Hernandez, O. "4-Dimethylamino-*N*-triphenylmethylpyridinium Chloride" **OS**, (1997), *75*, 184.



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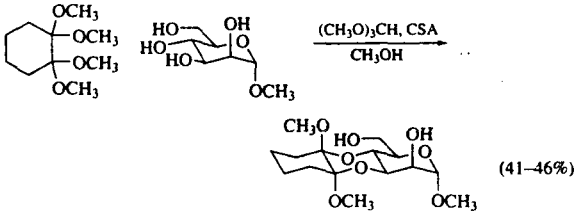
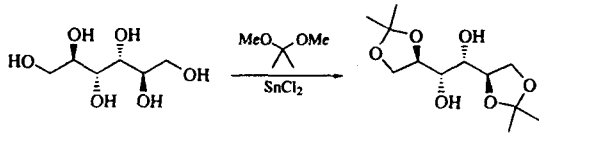
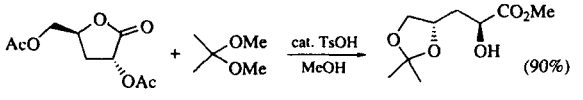
Ley, S. V.; Osborn, H. M. I.; Priepke, H. W. M.; Warriner, S. L.; "(1′*S*, 2′*S*)-Methyl-3*O*,4*O*-(1′, 2′-dimethoxycyclohexane-1′, 2′-diyl)-α-D-mannopyranoside" **OS**, (1997), *75*, 170.



Schmid, C. R.; Bryant, J. D. "D-(*R*)-Glyceraldehyde Acetonide" **OS**, (1993), *72*, 6.

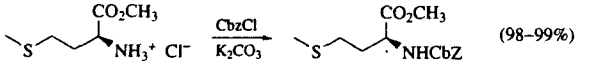


Sun, R. C.; Okabe, M. "(2*S*, 4*S*)-2,4,5-Trihydroxypentanoic Acid 4,5-Acetonide Methyl Ester" **OS**, (1993), *72*, 48.

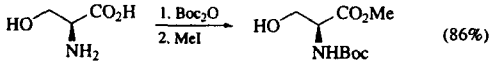


III. Amine Protection

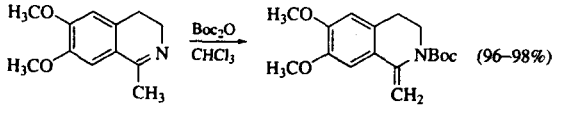
Carrasco, M.; Jones, R. J.; Kamel, S.; Rapoport, H. Truong, T. "*N*-(Benzyloxycarbonyl)-L-vinylglycine Methyl Ester" **OS**, (1991), *70*, 29.



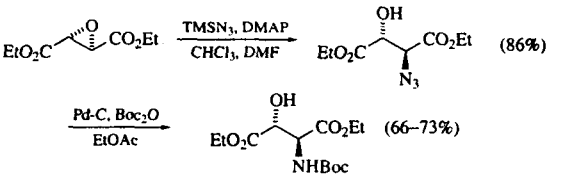
Garner, P.; Park, J. M. "1,1-Dimethylethyl (*S*)- or (*R*)-4-Formyl-2,2-dimethyl-3-oxazolidinecarboxylate: A Useful Serinal Derivative" **OS**, (1991), *70*, 18.



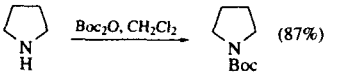
Lenz, G. R. Lessor, R. A. "Tetrahydro-3-benzazepin-2-ones: Lead Tetraacetate Oxidation of Isoquinoline Enamides" **OS**, (1991), *70*, 139.



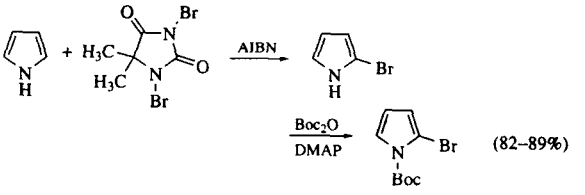
Saito, S.; Komada, K.; Moriwake, T. "Diethyl (2*S*, 3*R*)-2-(*N*-*tert*-Butoxycarbonyl)amino-3-hydroxysuccinate" **OS**, (1995), *73*, 184.



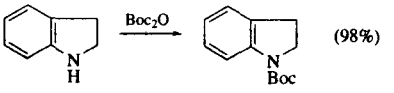
Nikolic, N. A.; Beak, P. "(*R*)-(+)-2-(Diphenylhydroxymethyl)pyrrolidine" **OS**, (1996), *74*, 23.



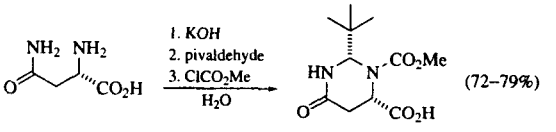
Chen, W.; Stephenson, E. K.; Cava, M. P.; Jackson, Y. A. "2-Substituted Pyrroles from *N*-*tert*-Butyloxycarbonyl-2-bromopyrrole: *N*-*tert*-Butoxy-2-trimethylsilylpyrrole" **OS**, (1991), *70*, 151.



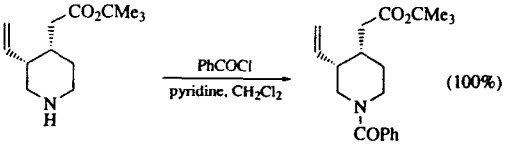
Iwao, M.; Kuraishi, T. "Synthesis of 7-Subtituted Indolines via Directed Lithiation of 1-(*tert*-Butoxycarbonyl)indoline: 7-Indoline: 7-Indolinecarboxaldehyde" **OS**, (1995), *73*, 85.



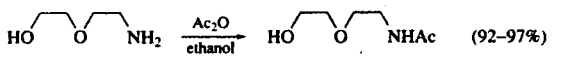
Lakner, F. J.; Chu, K. S.; Negrete, G. R.; Konopelski, J. P. "Synthesis of Enantiomerically Pure β-Amino Acids from 2-*tert*-Butyl-1-carbomethoxy-2,3-dihydro-4(1*H*)-pyrimidinone: (*R*)-3-Amino-3-(*p*-methoxyphenyl)propionic Acid" **OS**, (1995), *73*, 201.



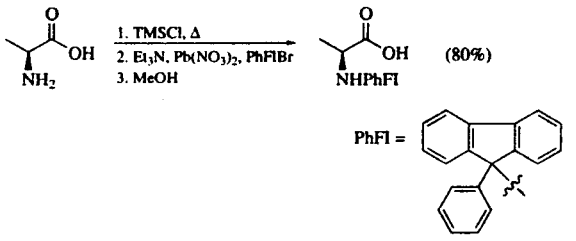
Hutchison, D. R.; Khau, V. V.; Martinelli, M. J.; Nayyar, N. K.; Peterson, B. C.; Sullivan, K. A. "Synthesis of *cis*-4a(*S*),8a(*R*)-Perhydro-6(2*H*)-isoquinolinones from Quinine: 4a(*S*),8a(*R*)-2-Benzoyloctahydro-6(2*H*)-isoquinolinone" **OS**, (1997), *75*, 223.



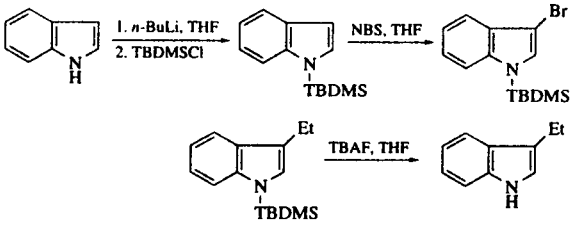
Krakowiak, K. E.; Bradshaw, J. S. "4-Benzyl-10,19-diethyl-4,10,19-triaza-1,7,13,16-tetraoxacycloheneicosane (Triaza-21-Crown-7)" **OS**, (1991), *70*, 129.



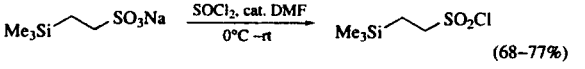
Carrasco, M.; Jones, R. J.; Kamel, S.; Rapoport, H. Truong, T. "*N*-(Benzyloxycarbonyl)-L-vinylglycine Methyl Ester" **OS**, (1991), *70*, 29.



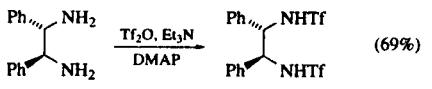
Amat, M.; Hadida, S.; Sathyanarayana, S.; Bosch, J. "Regioselective Synthesis of 3-Substituted Indoles: 3-Ethylindole" **OS**, (1996), *74*, 248.



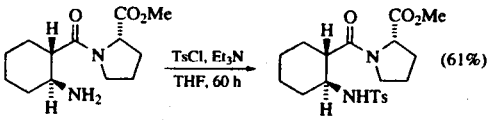
Weinreb, S. M.; Chase, C. E.; Wipf, P.; Venkatraman, S. "2-Trimethylsilylethanesulfonyl Chloride (SES-Cl)" **OS**, (1997), *75*, 161.



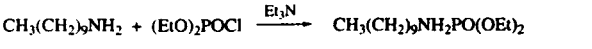
Pikal, S.; Corey, E. J. "Enantioselective, Catalytic Diels-Alder Reaction: (1*S*-*endo*)-3-(Bicyclo[2.2.1]hept-5-en-2-ylcarbonyl)-2-oxazolidinone" **OS**, (1992), *71*, 30.



Schultz, A. G.; Alva. C. W. " Asymmetric Synthesis of *trans*-2-Aminocyclohexanecarboxylic Acid Derivatives from Pyrrolobenzodiazepine-5,11-diones" **OS**, (1995), *73*, 174.

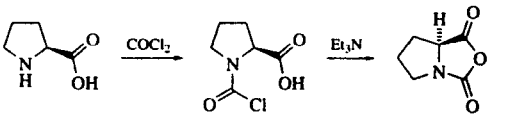


Nikolaides, N.; Schipor, I.; Ganem, B. "Conversion of Amines to Phospho Esters: Decyl Diethyl Phosphate" **OS**, (1993), *72*, 246.

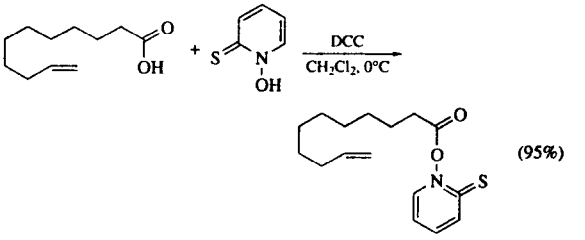


IV. Carboxyl Activation:

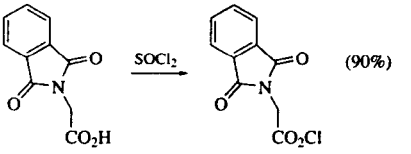
Xavier, L. C.; Mohan, J. J.; Mathre, D. J.; Thompson, A. S.; Carroll, J. D.; Corley, E. G.; Desmond, R. "(*S*)-Tetrahydro-1-methyl-3,3-diphenyl-1*H*, 3*H*-pyrrolo-[1,2,-*c*][1,3,2]oxazaborole-Borane Complex" **OS**, (1996), *74*, 50.



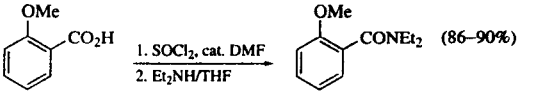
Barton, D. H. R.; MacKinnon, J.; Perchet, R. N.; Tse, C.-L. "Efficient Synthesis of Bromides from Carboxylic Acids Containing a Sensitive Functional Group: Dec-9-enyl Bromide from 10-Undecenoic Acid" **OS**, (1997), *75*, 124.



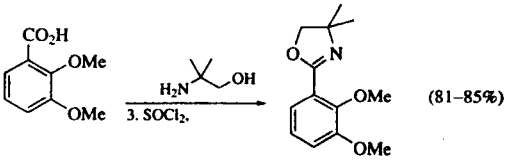
Hubschwerlen, C.; Specklin, J.-L. "(3*S*, 4*S*)-3-Amino-1-(3,4-dimethoxybenzyl)-4-[(*R*)-2,2-dimethyl-1,3-dioxolan-4-yl]-2-azetidinone" **OS**, (1993), *72*, 14.



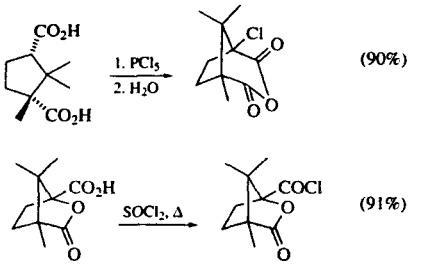
Wang, X.; deSilva, S. O.; Reed, J. N.; Billadeau, R.; Griffen, E. J.; Chan, A.; Snieckus, V. "7-Methoxyphthalide" **OS**, (1993), *72*, 163.



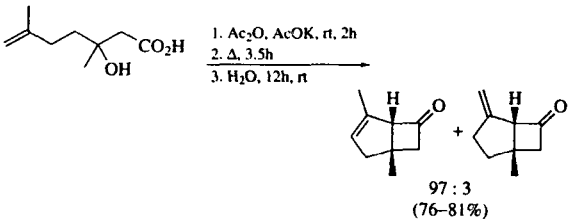
Meyers, A. I.; Flanagan, M. E. "2,2′-Dimethoxy-6-formylbiphenyl" **OS**, (1992), *71*, 107.



Gerlach, H.; Kappes, D.; Boeckman, R. K. Jr.; Maw, G. N. "(−)-(1*S*, 4*R*)-Camphanoyl Chloride" **OS**, (1992), *71*, 48.

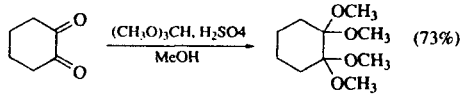


Rosini, G.; Confalonieri, G.; Marotta, E.; Rama, F.; Righi, P. "Preparation of Bicyclo[3.2.0]hept-3-en-6-ones: 1,4-Dimethylbicyclo[3.2.0]hept-3-en-6-one" **OS**, (1996), *74*, 158.

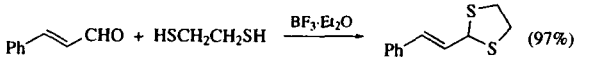


V. Carbonyl Protection:

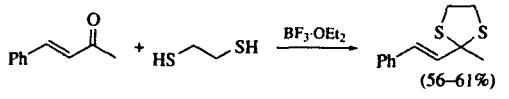
Ley, S. V.; Osborn, H. M. I.; Priepke, H. W. M.; Warriner, S. L. "(1′*S*, 2′*S*)-Methyl-*O*,4*O*-(1′, 2′-dimethyoxycylohexane-1′, 2′-diyl)-α-D-mannopyranoside" **OS**, (1997), *75*, 170.



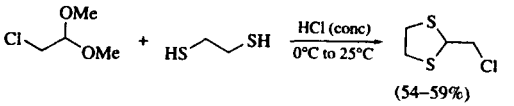
Ni, Z.-J.; Luch, T.-Y. "Nickel-Catalyzed Silylolefination of Allylic Dithioacetals: (*E*, *E*)-Trimethyl(4-phenyl-1,3-butadienyl)silane" **OS**, (1991), *70*, 240.



Yuan, T.-M.; Luh, T.-Y. "Nickel-Catalyzed, Geminal Dimethylation of Allylic Dithioacetals; (*E*)-1-Phenyl-3,3-dimethyl-1-butene" **OS**, (1996), *74*, 187.

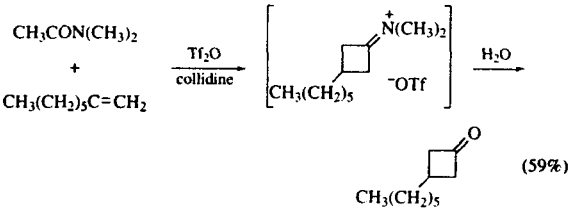


Dahnke, K. R.; Paquette, L. A. "2-Methylene-1,3-dithiolane" **OS**, (1992), *71*, 175.

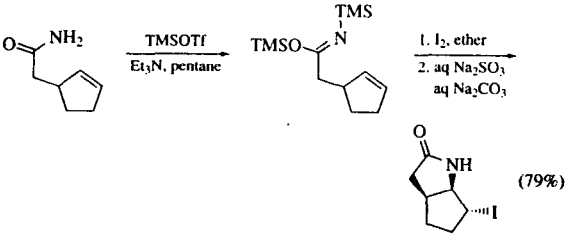


VI. Carbonyl Activation or Functionalization:

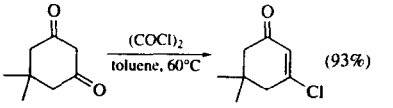
Schmit, C.; Falmagne, J. B.; Escudero, J.; Vanlierde, H.; Ghosez, L. "A General Synthesis of Cyclobutanones from Olefins and Tertiary Amides: 3-Hexylcyclobutanone" **OS**, (1990), *69*, 199.



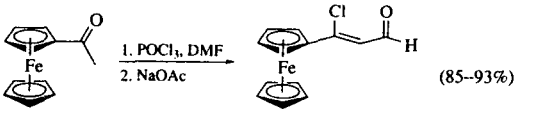
Knapp, S.; Gibson, F. S. "Iodolactamization: 8-*exo*-Iodo-2-azabicyclo[3.3.0]octan-3-one" **OS**, (1991), *70*, 101.



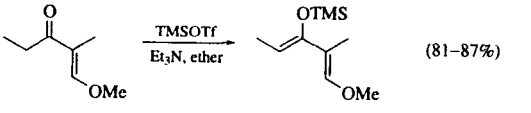
Wender, P. A.; White, A. W.; MacDonald, F. E. "Spiroannelation via Organobis(cuprates): 9,9-Dimethylspiro[4.5]decan-7-one" **OS**, (1991), *70*, 204.



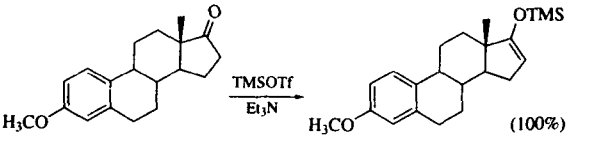
Polin, J.; Schottenberger, H. "Conversion of Methyl Ketones into Terminal Acetylenes: Ethynylferrocene" **OS**, (1995), *73*, 262.



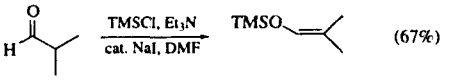
Myles, D. C.; Bigham, M. H. "Preparation of (*E*, *Z*)-1-Methoxy-2-methyl-3-(trimethylsiloxy)-1,3-pentadiene" **OS**, (1991), *70*, 231.



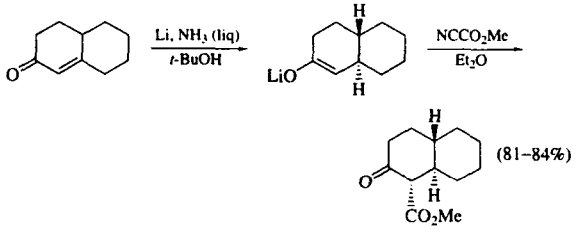
Umemoto, T.; Tomita, K.; Kawada, K. "*N*-Fluoropyridinium Triflate: An Electrophilic Fluorinating Agent" **OS**, (1990), *69*, 129.



Reissig, H.-U.; Reichelt, I.; Kunz, T. "Methoxycarbonylmethylation of Aldehydes via Siloxycyclopropanes: Methyl 3,3-Dimethyl-4-oxobutanoate" **OS**, (1992), *71*, 189.

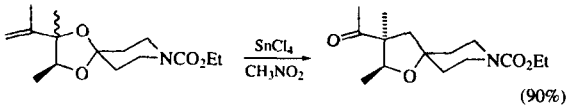


Crabtree S. R.; Mander, L. N.; Sethi, S. P. "Synthesis of β-Keto Esters by C-Acylation of Preformed Enolates with Methyl Cyanoformate: Preparation of Methyl (1α,4aβ,8aα)-2-oxodecahydro-1-naphthoate" **OS**, (1991), *70*, 256.

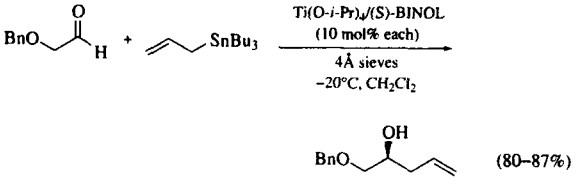


VII. Lewis Acid Promoted Reactions

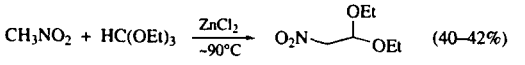
Overman, L. E.; Rishton, G. M. "Stereocontrolled Preparation of 3-Acyltetrahydrofurans from Acid-Promoted Rearrangements of Allylic Ketals: (2*S*, 3*S*)-3-Acetyl-8-carboethoxy-2,3-dimethyl-1-oxa-8-azaspiro[4.5]decane" **OS**, (1992), *71*, 63.



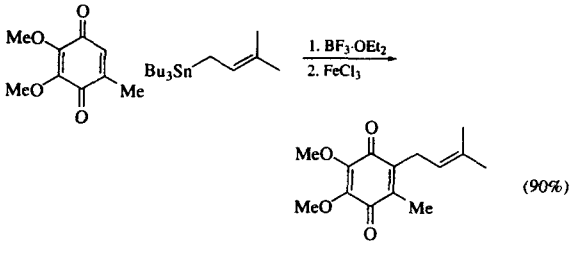
Keck, G. E.; Krishnamurthy, D. "Catalytic Asymmertic Allylation Reactions: (*S*)-1-(Phenylmethoxy)-4-penten-2-ol" **OS**, (1997), *75*, 12.



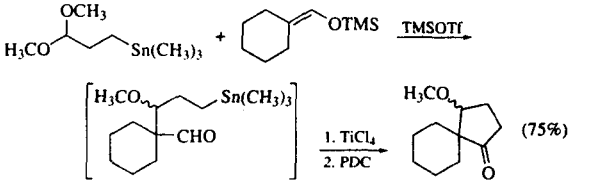
Jager, V.; Poggendorf, P. "Nitroacetaldehyde Diethyl Acetal" **OS**, (1996), *74*, 130.



Naruta, Y.; Maruyama, K. "Ubiquinone-1" **OS**, (1992), *71*, 125.

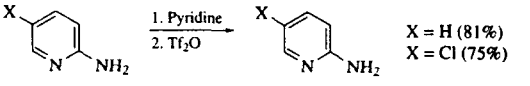


Lee, T. V.; Porter, J. R. "Spiroannelation of Enol Silanes: 2-Oxo-5-methoxyspiro[5.4]decane" **OS**, (1993), *72*, 189.

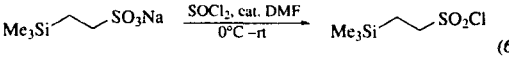


VIII. Sulfonylation Reagents:

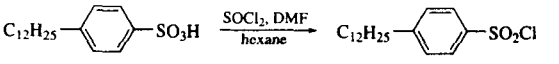
Comins, D. L.; Dehghani, A.; Foti, C. J.; Joseph, S. P. "Pyridine-Derived Triflating Reagents: *N*-(2-Pyridyl)triflimide and *N*-(5-Chloro-2-pyridyl)triflimide" **OS**, (1996), *74*, 77.



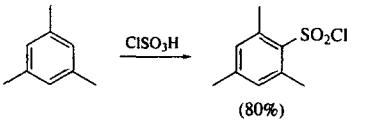
Weinreb, S. M.; Chase, C. E.; Wipf, P.; Venkatraman, S. "2-Trimethylsilylethanesulfonyl Chloride (SES-Cl)" **OS**, (1997), *75*, 161.



Hazen, G. G.; Billinger, F. W.; Roberts, F. E.; Russ, W. K.; Seman, J. J.; Staskiewicz, S. "4-Dodecylbenzenesulfonyl Azides" **OS**, (1995), *73*, 144.

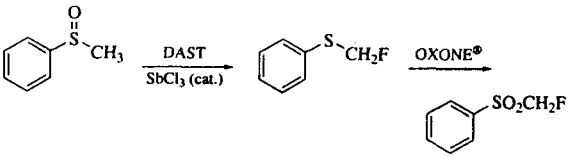


Reid, J. R.; Dufresne, R. F.; Chapman, J. J. "Mesitylenesulfonylhydrazine, and (1α, 2α, 6β)-2,6-Dimethylcyclohexanecarbonitrile and (1α, 2β, 6α)-2,6-Dimethylcyclohexanecarbonitrile as a Racemic Mixture" **OS**, (1996), *74*, 217.



IX. Sulfoxide Activation

McCarthy, J. R.; Matthews, D. P.; Paolini, J. P. "Stereoselective Synthesis of 2,2-Disubstituted 1-Fluoroalkenes: (*E*)-[[Fluoro(2-phenylcyclohexylidene)methyl]sulfonyl] benzene and (*Z*)-[2-(Fluoromethylene)cyclohexyl]benzene" **OS**, (1993), *72*, 209.



Recent Review Articles and Monographs

General Carboxyl and Hydroxyl Activation

Chatgilialoglu, C.; Ferreri, C. Progress of the Barton-McCombie Methodology: From Tin Hydrides to Silanes. *Res. Chem. Intermed.* **1993**, *19*, 755–775.

Norcross, R. D.; Paterson, I. Total Synthesis of Bioactive Marine Macrolides. *Chem. Rev.* **1995**, *95*, 2041–2114.

Hughes, D. L. Progress in the Mitsunobu Reaction. A Review. *Org. Prep. Proc. Int.*, **1996**, *28*, 127–164.

Ryan, T. A. Phosgene and Related Compounds. Elsevier Science: New York, 1996.

Sherif, S. M.; Erian, A. W. The Chemistry of Trichloroacetonitrile, *Heterocycles* **1996**, *43* (5), 1083–1118.

Cotarca, L.; Delogu, P.; Nardelli, A.; Sunjic, V. Bis(trichloromethyl) Carbonate in Organic Synthesis. *Synthesis* **1996**, 553–576.

Dimon, C.; Hosztafi, S.; Makleit, S. Application of the Mitsunobu Reaction in the Field of Alkaloids. *J. Heterocyclic Chem.* **1997**, *34*, 349–365.

Zard, S. Z. On the Trail of Xanthates: Some New Chemistry from an Old Functional Group. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 672–685.

Wisniewski, K.; Koldziejczyk, A. S.; Falkiewicz, B. Applications of the Mitsunobu Reaction in Peptide Chemistry. *J. Peptide Sci.* **1998**, *4*, 1–14.

Peptide Synthesis

Albericio, F.; Carpino, L. A. Coupling reagents and activation. *Method. Enzymol.*, **1997**, *289*, 104–126.

Albericio, F.; Lloyd-Williams, P.; Giralt, E. Convergent solid-phase peptide synthesis. *Method. Enzymol.*, **1997**, *289*, 313–336.

Bodanszky, M. Peptide Chemistry: A Practical Textbook, 2nd ed. Springer-Verlag: Berlin, 1993.

Bodanszky, M. Principles of Peptide Synthesis, 2nd ed. Springer-Verlag: Berlin, 1993.

Bodanszky, M.; Bodanszky, A. The Practice of Peptide Synthesis, 2nd ed. Springer-Verlag: Heidelberg, 1994.

Pennington, M. W.; Dunn, B. M.; Eds. Peptide Synthesis Protocols (In: Methods Mol. Biol. 1994, 35) Humana Press: Totowa, NJ 1994.

Mikhalkin, A. P. The Synthesis, Properties, and Applications of *N*-Acyl-α-aminoacids. *Russ. Chem. Rev.* **1995**, *64* (3), 259–75.

Wipf, P. Synthetic Studies of Biologically Active Marine Cyclopeptides. *Chem. Rev.* **1995**, *95*, 2115–2134.

Gutte, B., Ed. Peptides, Synthesis, Structures, and Applications. Academic Press: San Diego, 1995.

Carpino, L. A; Beyermann, M.; Wenschuh, H.; Bienert, M. Peptide Synthesis via Amino Acid Halides. *Acct. Chem. Res.* **1996**, *29*, 268–274.

Deming, T.J. Polypeptide materials: New synthetic methods and applications. *Adv. Mater.*, **1997**, *9*, 299–311.

Stephanov, V. M. Proteinases as Catalysts in Peptide Synthesis. *Pure Appl. Chem.*, **1996**, *68* (6), 1335–1340.

Ichikawa, J. Fluorine as activator and controller in organic synthesis. *J. Syn. Org. Chem. Jpn.*, **1996**, *54*, 654–664.

North, M. Amines and amides. *Contemp. Org. Synth.*, **1996**, *3*, 323–343.

Humphrey, J. M.; Chamberlin, A. R. Chemical Synthesis of Natural Product Peptides: Coupling Methods for the Incorporation of Noncoded Amino Acids into Peptides. *Chem. Rev.* **1997**, *97*, 2243–2266.

Carbohydrate Activation/Glycosylation

Suzuki, K.; Nagasawa, T. Recent progress in O-glycoside synthesis - methodological aspects. *J. Syn. Org. Chem. Jpn.* **1992**, *50*, 378–390.

Toshima, K.; Tatsuta, K. Recent Progress in *O*-Glycosylation Methods and Its Application to Natural Products Synthesis. *Chem. Rev.*, **1993**, *93*, 1503–1531.

Schmidt, R. R; Kinzy, W. Anomeric-Oxygen Activation for Glycoside Synthesis: The Trichloroacetimidate Method. *Adv. Carbohydrate Chem. Biochem.* **1994**, *50*, 21–123.

Ogawa, T. Haworth Memorial Lecture: Experiments Directed Towards Glycoconjugate Synthesis, CSR **1994**, *23*, 397–407

Wilson, L. J.; Hager, M. W.; El-Kattan, Y.A.; Liotta, D. C. Nitrogen Glycosylation Reactions Involving Pyrimidine and Purine Nucleoside Bases with Furanoside Sugars. Synthesis-Stuttgart **1995**, 1465–1479.

Boons, G.-J. Strategies in Oligosaccharide Synthesis. *Tetrahedron* **1996**, *52*, 1095–1121.

Boons, G.-J. Recent Developments in Chemical Oligosaccharide Synthesis. Contemp. Org. Synth. **1996**, *3*, 173–200.

Danishefsky, S. J.; Bilodeau, M. T. Glycals in Organic Synthesis: The Evolution of Comprehensive Strategies for the Assembly of Oligosaccharides and Glycoconjugates of Biological Consequence. *Angew. Chem. Int. Ed.* **1996**, *35*, 1380–1419.

Voelter, W.; Khan, K. M.; Shekhani, M. S. Anhydro Sugars, Valuable Intermediates in Carbohydrate Syntheses. *Pure Appl. Chem.* **1996**, *68*, 1347–1353.

Khan, S. H.; O'Neill, R. A., Eds. Modern Methods in Carbohydrate Synthesis. Hardwood: Amsterdam, The Netherlands, 1996.

Whitfield, D. M.; Douglas, S. P. Glycosylation reactions: Present status and future directions. *Glycoconjugate J.*, **1996**, *13*, 5–17.

Garegg, P. J. Thioglycosides as Glycosyl Donors in Oligosaccharide Synthesis. *Adv. Carbohydrate Chem. Biochem.* **1997**, *52*, 179–205.

Hanessian, S. Preparative Carbohydrate Chemistry. Marcel Dekker: New York, 1997.

Tsuda, Y. Regioselective manipulation of carbohydrate-hydroxyl groups (selective activation of a hydroxyl group by tin compounds). *J. Synth. Org. Chem. Jpn.* **1997**, 55, 907–919.

Synthesis of Oligonucleotides

Beaucage, S. L.; Iyer, R. P. The Functionalization of Oligonucleotides via Phosphoramidite Derivatives. *Tetrahedron*, **1993**, *49*, 1925–1963.

Beaucage, S. L.; Iyer, R. P. The Synthesis of Modified Oligonucleotides by the Phosphoramidite Approach and Their Applications. *Tetrahedron*. **1993**, *49*, 6123–6194.

Beaucage, S. L.; Iyer, R. P. The Synthesis of Specific Ribonucleotides and Unrelated Phosphorylated Biomolecules by the Phosphoramidite Method. *Tetrahedron*. **1993**, *49*, 10441–10488.

Lesnikowski, Z. J. Stereocontrolled Synthesis of P-Chiral Analogs of Oligonucleotides. *Bioorg. Chem.* **1993**, *21*, 127–155.

Stec, W. J.; Wilk, A. Stereocontrolled Synthesis of Oligo(nucleoside phosphorothioate)s. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 709–722

Activation by Lewis Acids

Otera, J. Transesterification. *Chem. Rev.* **1993**, *93*, 1449–1470.

Oh, T.; Reilly, M. Reagent-Controlled Asymmetric Diels-Alder Reactions. A Review. *Org. Prep. Proced. Int.*, **1994**, *26*, 129–148.

Waldmann, H. Asymmetric Hetero Diels-Alder Reactions. *Synthesis*, **1994**, 535–551.

Suzuki, K. Novel Lewis acid catalysis in organic synthesis. *Pure Appl. Chem.* **1994**, *66*, 1557–1564.

Pons, J.-M.; Santelli, M.; Eds. Lewis acids and selectivity in organic synthesis. CRC Press: Boca Raton, FL, 1996.

Hiroi, K. Transition metal or Lewis acid-catalyzed asymmetric reactions with chiral organosulfur functionality. *Rev. Heteroatom Chem.*, **1996**, *14*, 21–57.

Siling, M. I.; Laricheva, T. N. Titanium compounds as catalysts for esterification and transesterification Reactions. *Russ. Chem. Rev.* **1996**, *65*, 279–286.

Engberts, J. B. F. N.; Feringa, B. L.; Keller, E.; Otto, S. Lewis-acid catalysis of carbon carbon bond forming reactions in water. *Recl. Trav. Chim. Pays-Bas* **1996**, *115*, 457–464.

Holloway, C. E.; Melnik, M. Organoaluminium compounds: classification and analysis of crystallographic and structural data. *J. Organomet. Chem.* **1997**, *543*, 1–37.

Activation by Transition Metal Organometallic Systems

Pearson, A. J.; Woodgate, P. D. Aromatic Compounds of the Transition Elements. Second Supplement to the 2nd Edition of Rodd's Chemistry of Carbon Compounds. Vol. $III^B/III^C/III^D$ (partial): Aromatic Compounds. Sainsbury, M., Ed. Elsevier: Amsterdam, The Netherlands, 1995.

Donaldson, W. A. Preparation and Reactivity of Acyclic (Pentadienyl)iron(1+) Cations: Applications to Organic Synthesis. *Aldrichim. Acta* **1997**, *30*, 17–24.

Grée, R.; Lellouche, J. P. Acyclic Diene Tricarbonyliron Complexes in Organic Synthesis. Advances in Metal-Organic Chemistry. Vol. 4. Liebeskind, L. S., Ed. JAI: Greenwich, Connecticut, 1995.

Donohoe, T. J. Stoichiometric Applications of Organotransition Metal Complexes in Organic Synthesis. *Contemp. Org. Synth.* **1996**, *3*, 1–18.

Reviews of Protecting Group Chemistry

Green, T. W.; Wuts, P. G. M. Protective Groups in Organic Chemistry, 2nd Ed; Wiley: New York, 1991.

Reidel, A.; Waldmann, H. Enzymatic Protecting Group Techniques in Bioorganic Synthesis. *J. Prakt. Chem.* **1993**, *335*, 109–127.

Kocienski, P. J. Protecting Groups. Theime Verlag: Stuttgart, 1994.

Sonveaux, E. Protecting Groups in Oligonucleotide Synthesis. in Methods in Molecular Biology, Vol. 26; Agrawal, S., Ed.; Humana Press: Totowa, NJ, 1994, pp. 1–71.

Wong, C.-H.; Whitesides, G. M. Enzymes in Synthetic Organic Chemistry. Pergamon: Oxford, 1994.

Waldmann, H.; Sebastian, D. Enzymatic Protecting Group Techniques. *Chem. Rev.* **1994**, *94*, 911–937.

Jarowicki, K.; Kocienski, P. Protecting groups. *Contemp. Org. Synth.* **1995**, *2*, 315–336; **1996**, *3*, 397–431; and **1997**, *4*, 454–492.

Donaldson, W. A. Transition Metal Alkene, Diene, and Dienyl Complexes: Complexation of Dienes for Protection. in Comprehensive Organometallic Chemistry II, Vol. 12. Hegedus, L. S., Ed. Elsevier: New York, 1995, pp. 623–635.

Schelhaas, M.; Waldmann, H. Protecting Group Strategies in Organic Synthesis. *Angew. Chem., Int. Ed. Engl.*, **1996**, *35*, 2056–2083.

Nelson, T. D.; Crouch, R. D. Selective Deprotection of Silyl Ethers. *Synthesis*, **1996**, 1031–1069.

Ranu, B. C.; Bhar, S. Dealkylation of Ethers. A Review. *Org. Prep. Proced. Int.* **1996**, *28*, 371–409.

Debenham, J. S.; Rodebaugh, R.; Fraser-Reid, B. Recent Advances in *N*-Protection for Amino Sugar Synthesis. *Liebigs Ann./Recueil* **1997**, 791–802.

El Gihani, M. T.; Heaney, H. The Use of Bis(trimethylsilyl)acetamide and Bis(trimethylsilyl)urea for Protection and as Control Reagents in Synthesis. *Synthesis*, **1998**, 357–375.