

Handbook  
of Reagents for  
Organic Synthesis

**Fluorine-Containing  
Reagents**

*Edited by*  
**Leo A. Paquette**

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for Organic Synthesis*  
*Fluorine-Containing Reagents*

Edited by

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*The Ohio State University, Columbus, OH, USA*



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## General Abbreviations

Ac	acetyl	DIEA	= DIPEA
acac	acetylacetonate	DIOP	2,3- <i>O</i> -isopropylidene-2,3-dihydroxy-1,4-bis-(diphenylphosphino)butane
AIBN	2,2'-azobisisobutyronitrile	DIPEA	diisopropylethylamine
Ar	aryl	diphos	=dppe
BBN	borabicyclo[3.3.1]nonane	DIPT	diisopropyl tartrate
BCME	dis(chloromethyl)ether	DMA	dimethylacetamide
BHT	butylated hydroxytoluene (2,6-di- <i>t</i> -butyl- <i>p</i> -cresol)	DMAD	dimethyl acetylenedicarboxylate
BINAL-H	2,2'-dihydroxy-1,1'-binaphthyl-lithium aluminum hydride	DMAP	4-(dimethylamino)pyridine
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl	DME	1,2-dimethoxyethane
BINOL	1,1'-bi-2,2'-naphthol	DMF	dimethylformamide
bipy	2,2'-bipyridyl	dmg	dimethylglyoximate
BMS	borane-dimethyl sulfide	DMPU	<i>N,N'</i> -dimethylpropyleneurea
Bn	benzyl	DMS	dimethyl sulfide
Boc	<i>t</i> -butoxycarbonyl	DMSO	dimethyl sulfoxide
BOM	benzyloxymethyl	DMTSF	dimethyl(methylthio) sulfonium tetrafluoroborate
bp	boiling point	dppb	1,4-bis(diphenylphosphino)butane
Bs	brosyl (4-bromobenzenesulfonyl)	dppe	1,2-bis(diphenylphosphino)ethane
BSA	<i>N,O</i> -bis(trimethylsilyl)acetamide	dppf	1,1'-bis(diphenylphosphino)ferrocene
Bu	<i>n</i> -butyl	dppp	1,3-bis(diphenylphosphino)propane
Bz	benzoyl	DTBP	di- <i>t</i> -butyl peroxide
CAN	cerium(IV) ammonium nitrate	EDA	ethyl diazoacetate
Cbz	benzyloxycarbonyl	EDC	1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide
CDI	<i>N,N'</i> -carbonyldiimidazole	EDCI	= EDC
CHIRAPHOS	2,3-bis(diphenylphosphino)butane	ee	enantiomeric excess
Chx	= Cy	EE	1-ethoxyethyl
cod	cyclooctadiene	Et	ethyl
cot	cyclooctatetraene	ETSA	ethyl trimethylsilylacetate
Cp	cyclopentadienyl	EWG	electron withdrawing group
CRA	complex reducing agent	Fc	ferrocenyl
CSA	10-camphorsulfonic acid	Fmoc	9-fluorenylmethoxycarbonyl
CSI	chlorosulfonyl isocyanate	fp	flash point
Cy	cyclohexyl	Hex	<i>n</i> -hexyl
<i>d</i>	density	HMDS	hexamethyldisilazane
DABCO	1,4-diazabicyclo[2.2.2]octane	HMPA	hexamethylphosphoric triamide
DAST	<i>N,N'</i> -diethylaminosulfur trifluoride	HOBT	1-hydroxybenzotriazole
dba	dibenzylideneacetone	HOBT	=HOBT
DBAD	di- <i>t</i> -butyl azodicarboxylate	HOSu	<i>N</i> -hydroxysuccinimide
DBN	1,5-diazabicyclo[4.3.0]non-5-ene	Im	imidazole (imidazolyl)
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene	Ipc	isopinocampheyl
DCC	<i>N,N'</i> -dicyclohexylcarbodiimide	IR	infrared
DCME	dichloromethyl methyl ether	KHDMS	potassium hexamethyldisilazide
DDO	dimethyldioxirane	LAH	lithium aluminum hydride
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone	LD <sub>50</sub>	dose that is lethal to 50% of test subjects
de	diastereomeric excess		
DEAD	diethyl azodicarboxylate		
DET	diethyl tartrate		
DIBAL	diisobutylaluminum hydride		

LDA	lithium diisopropylamide	PMDTA	<i>N,N,N',N'',N'''</i> -pentamethyldiethylene-triamine
LDMAN	lithium 1-(dimethylamino)naphthalenide	PPA	polyphosphoric acid
LHMDS	= LiHMDS	PPE	polyphosphate ester
LICA	lithium isopropylcyclohexylamide	PPTS	pyridinium <i>p</i> -toluenesulfonate
LiHMDS	lithium hexamethyldisilazide	Pr	<i>n</i> -propyl
LiTMP	lithium 2,2,6,6-tetramethylpiperidide	PTC	phase transfer catalyst/catalysis
LTMP	= LiTMP	PTSA	<i>p</i> -toluenesulfonic acid
LTA	lead tetraacetate	py	pyridine
lut	lutidine		
<i>m</i> -CPBA	<i>m</i> -chloroperbenzoic acid	RAMP	( <i>R</i> )-1-amino-2-(methoxymethyl)pyrrolidine
MA	maleic anhydride	rt	room temperature
MAD	methylaluminum bis(2,6-di- <i>t</i> -butyl-4-methylphenoxide)	salen	bis(salicylidene)ethylenediamine
MAT	methylaluminum bis(2,4,6-tri- <i>t</i> -butylphenoxide)	SAMP	( <i>S</i> )-1-amino-2-(methoxymethyl)pyrrolidine
Me	methyl	SET	single electron transfer
MEK	methyl ethyl ketone	Sia	siamyl (3-methyl-2-butyl)
MEM	(2-methoxyethoxy)methyl	TASF	tris(diethylamino)sulfonium difluorotrimethylsilicate
MIC	methyl isocyanate	TBAB	tetrabutylammonium bromide
MMPP	magnesium monoperoxyphthalate	TBAF	tetrabutylammonium fluoride
MOM	methoxymethyl	TBAD	= DBAD
MoOPH	oxodiperoxomolybdenum(pyridine)-(hexamethylphosphoric triamide)	TBAI	tetrabutylammonium iodide
mp	melting point	TBAP	tetrabutylammonium perruthenate
MPM	= PMB	TBDMS	<i>t</i> -butyldimethylsilyl
Ms	mesyl (methanesulfonyl)	TBDPS	<i>t</i> -butyldiphenylsilyl
MS	mass spectrometry; molecular sieves	TBHP	<i>t</i> -butyl hydroperoxide
MTBE	methyl <i>t</i> -butyl ether	TBS	= TBDMS
MTM	methylthiomethyl	TCNE	tetracyanoethylene
MVK	methyl vinyl ketone	TCNQ	7,7,8,8-tetracyanoquinodimethane
<i>n</i>	refractive index	TEA	triethylamine
NaHDMS	sodium hexamethyldisilazide	TEBA	triethylbenzylammonium chloride
Naph	naphthyl	TEBAC	= TEBA
NBA	<i>N</i> -bromoacetamide	TEMPO	2,2,6,6-tetramethylpiperidinoxyl
nbd	norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)	TES	triethylsilyl
NBS	<i>N</i> -bromosuccinimide	Tf	triflyl (trifluoromethanesulfonyl)
NCS	<i>N</i> -chlorosuccinimide	TFA	trifluoroacetic acid
NIS	<i>N</i> -iodosuccinimide	TFAA	trifluoroacetic anhydride
NMO	<i>N</i> -methylmorpholine <i>N</i> -oxide	THF	tetrahydrofuran
NMP	<i>N</i> -methyl-2-pyrrolidinone	THP	tetrahydropyran; tetrahydropyranyl
NMR	nuclear magnetic resonance	Thx	thexyl (2,3-dimethyl-2-butyl)
NORPHOS	bis(diphenylphosphino)bicyclo[2.2.1]-hept-5-ene	TIPS	triisopropylsilyl
Np	= Naph	TMANO	trimethylamine <i>N</i> -oxide
PCC	pyridinium chlorochromate	TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
PDC	pyridinium dichromate	TMG	1,1,3,3-tetramethylguanidine
Pent	<i>n</i> -pentyl	TMS	trimethylsilyl
Ph	phenyl	Tol	<i>p</i> -tolyl
phen	1,10-phenanthroline	TPAP	tetrapropylammonium perruthenate
Phth	phthaloyl	TBHP	<i>t</i> -butyl hydroperoxide
Piv	pivaloyl	TPP	tetraphenylporphyrin
PMB	<i>p</i> -methoxybenzyl	Tr	trityl (triphenylmethyl)
		Ts	tosyl ( <i>p</i> -toluenesulfonyl)
		TTN	thallium(III) nitrate
		UHP	urea-hydrogen peroxide complex
		Z	= Cbz

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*This volume is dedicated to the memory of my former colleague, Professor Albert L. Henne (1925–1967), whose lifelong commitment to pioneering research in organofluorine chemistry at The Ohio State University was inspirational to the international community at large.*



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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 succeeded admirably in approaching 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 incorporation of detailed indexes serve in tandem to facilitate the retrieval of desired information.

Notwithstanding these accomplishments, the editors came to recognize that the large size of this eight-volume work and its cost of purchase often deterred the placement of copies of the *Encyclopedia* in or near laboratories where the need for this type of information is most critical. 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 the same into a set of handbooks. The latter would also be purchasable on a single unit basis.

The ultimate result of these deliberations was the publication of the *Handbook of Reagents for Organic Synthesis*, the first four volumes of which were published in 1999:

*Oxidizing and Reducing Agents*

Edited by Steven D. Burke and Rick L. Danheiser

*Acidic and Basic Reagents*

Edited by Hans J. Reich and James H. Rigby

*Activating Agents and Protecting Groups*

Edited by Anthony J. Pearson and William R. Roush

*Reagents, Auxiliaries, and Catalysts for C–C Bond Formation*

Edited by Robert M. Coates and Scott E. Denmark

Since then, the fifth, sixth, seventh, and eighth members of this series listed below have made their appearance:

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*Reagents for Glycoside, Nucleotide, and Peptide Synthesis*

Edited by David Crich

*Reagents for Direct Functionalization of C–H Bonds*

Edited by Philip L. Fuchs

Each of the volumes contain a selected compilation of those entries from the original *Encyclopedia* that bear on the specific topic. The coverage of the last four handbooks also extends to the electronic sequel *e-EROS*. 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 present volume entitled *Fluorine-Containing Reagents* constitutes the ninth entry into a continuing series of utilitarian reference works. As with its predecessors, this handbook is intended to be an affordable, enlightening compilation that will hopefully find its way into the laboratories of all practicing synthetic chemists. Every attempt has been made to be of the broadest possible relevance and the expectation is that our many colleagues will share in this opinion.

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# Introduction

With increasing recognition of the desirable and often unique properties intrinsic to fluorine-containing substances has come a dramatically heightened interest in the chemical and biological features of this family of compounds. The resulting demands placed on synthetic, mechanistic, and medicinal chemists emerge in many forms, not the least of which bear on understanding reactivity, controlling the regio- and stereoselectivity associated with introduction of the fluorine atoms, and establishing bioactivity relationships. This flurry of activity has been spurred on by the ever-present need to gain ready access to proper building blocks and to develop an enhanced appreciation of the associated changes in electronic character, Lewis acidity, and bioavailability to name a few. Given the evolution of these many developments, the present time was considered to be appropriate for incorporating into a single volume a compilation that lists a great many of the more important organofluorine reagents, as well as the key fluorine-containing catalysts presently in vogue.

The reagents featured in this volume have been culled from three sources. A minority of the entries appeared initially in the *Encyclopedia of Reagents for Organic Synthesis (EROS)* which issued in 1995. Since that time, a significant number of the entries for these classical reagents have been updated (*eEROS*), and this important add-on information is also found herein in the form of extensions to the original articles. The third pool of reagents is constituted of entirely new entries that detail the chemical and

physical properties of an added subset of fluorinated compounds. In some instances, sets of isomeric agents appear in close proximity in order to facilitate comparative analysis. Subsets consisting of 2-, 3-, and 4-(trifluoromethyl)pyridine and of *o*-, *m*-, and *p*-trifluoromethylacetophenone are exemplary.

The reader may find it beneficial to examine the opening segments of this volume. The first consists of a listing of recent monographs and overviews dealing with different aspects of organofluorine chemistry. Following that, there is a section that illustrates those procedures relevant to the field that have appeared in Volumes 68–82 of *Organic Syntheses*. The body of the reagent compilation is presented in alphabetical order in the anticipation that benefits may be derived from scanning the content of adjoining pages.

Finally, it is hoped that this handbook will prove to be a valued adjunct to researchers experienced in fluorine chemistry, and a particularly useful compilation for others seeking to gain a foothold in the field as expediently as possible. These goals will have been realized if advances materialize from exposure to its contents.

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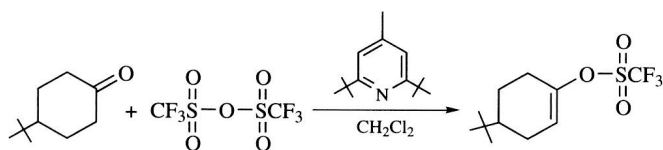


# Organic Syntheses Procedures Featuring the Preparation of Organofluorine End-Products and of Fluorinated Reagents as Promoters, Volumes 68–82

## Synthesis of Organofluorine Compounds

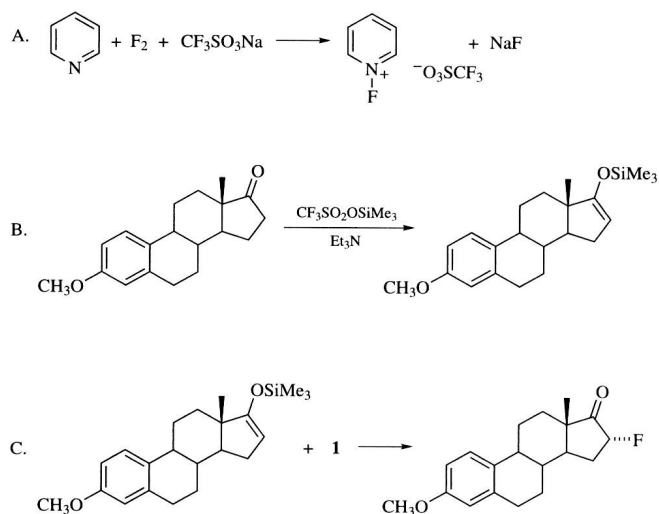
### 4-*tert*-Butylcyclohexen-1-yl Trifluoromethane-sulfonate

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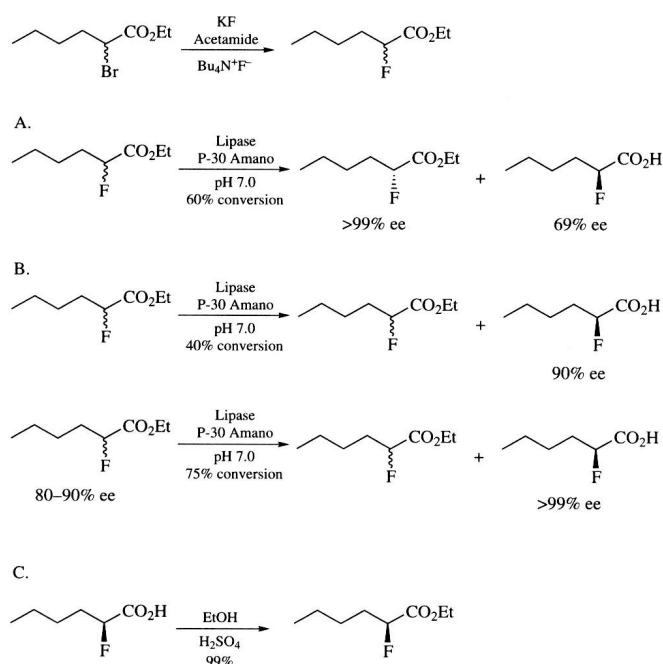
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