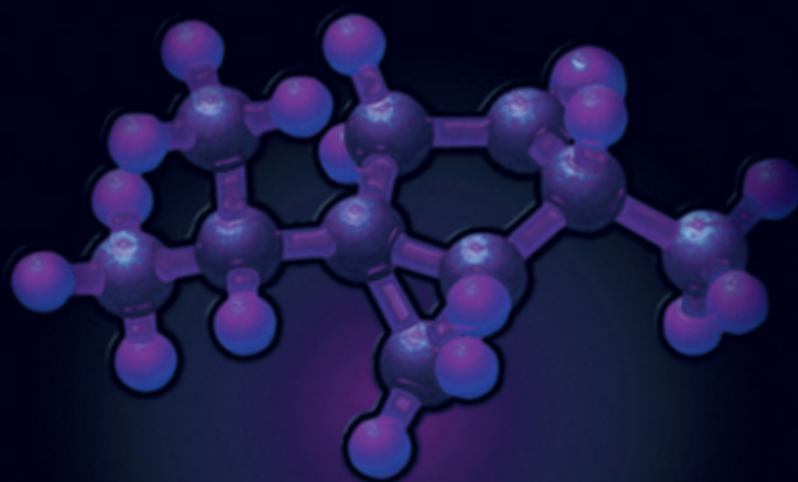




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Edited by
Leo A. Paquette

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*Handbook of Reagents
for Organic Synthesis*

Sulfur-Containing Reagents

Edited by

Leo A. Paquette

The Ohio State University, Columbus, OH, USA



A John Wiley & Sons, Ltd, Publication

This edition first published 2009
© 2009 John Wiley & Sons Ltd

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John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ,
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Library of Congress Cataloging-in-Publication Data

Handbook of reagents for organic synthesis.

p.cm

Includes bibliographical references.

Contents: [1] Reagents, auxiliaries and catalysts for C–C bond formation / edited by Robert M. Coates and Scott E. Denmark [2] Oxidizing and reducing agents / edited by Steven D. Burke and Riek L. Danheiser [3] Acidic and basic reagents / edited by Hans J. Reich and James H. Rigby [4] Activating agents and protecting groups / edited by Anthony J. Pearson and William R. Roush [5] Chiral reagents for asymmetric synthesis / edited by Leo A. Paquette [6] Reagents for high-throughput solid-phase and solution-phase organic synthesis / edited by Peter Wipf [7] Reagents for glycoside, nucleotide and peptide synthesis / edited by David Crich [8] Reagents for direct functionalization of C–H bonds / edited by Philip L. Fuchs [9] Fluorine-Containing Reagents / edited by Leo A. Paquette [10] Catalyst Components for Coupling Reactions / edited by Gary A. Molander [11] Reagents for Radical and Radical Ion Chemistry / edited by David Crich [12] Sulfur-Containing Reagents / edited by Leo A. Paquette

ISBN 0-471-97924-4 (v. 1)	ISBN 0-471-97926-0 (v. 2)
ISBN 0-471-97925-2 (v. 3)	ISBN 0-471-97927-9 (v. 4)
ISBN 0-470-85625-4 (v. 5)	ISBN 0-470-86298-X (v. 6)
ISBN 0-470-02304-X (v. 7)	ISBN 0-470-01022-3 (v. 8)
ISBN 978-0-470-02177-4 (v. 9)	ISBN 978-0-470-51811-3 (v.10)
ISBN 978-0-470-06536-5 (v. 11)	ISBN 978-0-470-74872-5 (v.12)

1. Chemical tests and reagents. QD77.H37 1999 547'.2 dc 21	2. Organic compounds-Synthesis. 98-53088 CIP
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A catalogue record for this book is available from the British Library.

ISBN 13: 978-0-470-74872-5

Set in 9½/11½ pt Times Roman by Thomson Press (India) Ltd., New Delhi.
Printed in Great Britain by Antony Rowe, Chippenham, Wiltshire.

This volume is dedicated to Dr. Gerald Berkelhammer who introduced me to the field of organosulfur chemistry during summer employment (1957) as a fledgling graduate student while working at the American Cyanamid Company in Stamford, Connecticut.

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Contents

Preface	xiii	(4 <i>R</i> ,5 <i>R</i>)-2-Bromo-1,3-bis-(4-methylphenyl sulfonyl)-4,5-diphenyl-1,3,2-diazaborolidine and	
Introduction	xv	(4 <i>S</i> ,5 <i>S</i>)-2-Bromo-1,3-bis-(4-methylphenyl sulfonyl)-4,5-diphenyl-1,3,2-diazaborolidine	91
Short Note on InChIs and InChIKeys	xvi	Bromodifluorophenylsulfanylmethane	98
Organic Syntheses Procedures Featuring the Synthesis of Organosulfur Compounds and Preparative Applications thereof, Volumes 65–85		Bromomethanesulfonyl Phenyl Tetrazole (Chloro)	100
	1	2-(2-Butenylthio)benzothiazole	102
Allyl Triflone	15	<i>tert</i> -Butyl <i>N</i> -Lithio- <i>N</i> -(<i>p</i> -toluenesulfonyloxy)carbamate	103
Aminoiminomethanesulfonic Acid	16	2-[<i>N</i> -(<i>tert</i> -Butyloxycarbonyl)aminophenyl]ethanethiol	104
<i>p</i> -Anisolesulfonyl Chloride	18	<i>tert</i> -Butylsulfonyl Chloride	107
Anthracenesulfonamide	19	<i>tert</i> -Butyltetrazolylthiol	109
1-Benzenesulfinyl Piperidine	21	10-Camphorsulfonyl Chloride	111
Benzenesulfonic Acid, 2-Nitro-, (1-Methylethylidene) hydrazide	23	Carbomethoxysulfonyl Chloride	118
Benzenesulfonic Anhydride	25	Carbon Disulfide	124
Benzenesulfonyl Bromide	26	Cerium(IV) Ammonium Sulfate	128
Benzimidazolium Triflate	27	Cesium Fluoroxysulfate	130
(1 <i>R</i> ,5 <i>R</i>)-2 <i>H</i> -1,5-Benzodithiepin-3(4 <i>H</i>)-one 1,5-Dioxide	29	<i>N</i> -Chloro- <i>N</i> -cyclohexylbenzenesulfonamide	131
3 <i>H</i> -1,2-Benzodithiol-3-one 1,1-Dioxide	31	Chloromethyl <i>p</i> -Tolyl Sulfide	132
Benzothianthrene Oxide	34	Chloromethyl <i>p</i> -Tolyl Sulfone	134
Benzothiazole-2-sulfonyl Chloride	36	4-Chlorophenyl Chlorothionoformate	136
4-Benzyloxazolidine-2-thione	37	4-(4-Chlorophenyl)-3-hydroxy-2(3 <i>H</i>)thiazolethione	137
3-(2-Benzyloxyacetyl)thiazolidine-2-thione	40	<i>N</i> -Chlorosuccinimide–Dimethyl Sulfide	140
Benzyltriethylammonium Tetrathiomolybdate	42	Chloro(heptyl)borane–Dimethyl Sulfide	144
<i>N</i> -Benzyl Triflamide	46	Copper(II) Sulfate	145
4,4'-Bis(2-amino-6-methylpyrimidyl) Disulfide	48	Copper, (2-Thiophenecarboxylato- κ O ₂ , κ S ₁)	152
Bis(2,2'-bipyridyl)silver(II) Peroxydisulfate	49	Copper(II) Toluene sulfonate	157
<i>N,N'</i> -Bis(<i>tert</i> -butoxycarbonyl)- <i>N''</i> -trifluoromethanesulfonylguanidine	50	Copper(I) Trifluoromethanesulfonate	158
[<i>N,N'</i> -[1,2-Bis(3,5-dimethylphenyl)-1,2-ethanediy]bis(1,1,1-trifluoromethanesulfonamidato)]methylaluminum	51	Copper(II) Trifluoromethanesulfonate	181
2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane	52	Dibromoborane–Dimethyl Sulfide	189
2,4-Disulfide	52	Dibutyl(trifluoromethanesulfoxy)stannane	197
2,3-Bis[(4-methylphenyl)thio]-1,3,2,4-dithiadiphosphetane	68	Dicarbonyl(cyclopentadienyl)[(dimethylsulfonium)methyl]iron Tetrafluoroborate	198
2,4-Disulfide	68	Dichloroborane–Dimethyl Sulfide	200
2,4-Bis(methylthio)-1,3,2,4-dithiadiphosphetane	69	2-2-Difluorovinyl <i>p</i> -Toluenesulfonate	205
2,4-Disulfide	69	2,5-Dihydro-2,2-dimethyl-5,5-bis(propylthio)-1,3,4-oxadiazole	206
<i>N</i> -[Bis(methylthio)methylene]- <i>p</i> -toluenesulfonamide	71	2,3-Dihydro-2-phenylimidazo[2,1- <i>b</i>]benzothiazole	207
Bis[<i>N</i> -(<i>p</i> -toluenesulfonyl)]selenodiimide	80	Diisopropyl Methylsulfanyldifluoromethylphosphonate	209
1-[Bis(trifluoromethanesulfonyl)methyl]-2,3,4,5,6-pentafluorobenzene	81	4-(Dimethylamino)pyridinium Chlorosulfite Chloride	211
Bis(4-trimethylsilylphenyl) Disulfide and Bis(4-trimethylsilylphenyl) Diselenide	85	Dimethyl Bis(methylthio)methylphosphonate	212
Boron Trifluoride–Dimethyl Sulfide	86	6,6-Dimethyl-1,4-diseleno-3,7-tetrasulfide	213
4-Bromobenzenesulfonyl Azide	89	<i>N,N</i> -Dimethyldithiocarbamoylacetonitrile	214
4-Bromobenzenesulfonyl Chloride	90	<i>N</i> -(1,1-Dimethylethyl)benzenesulfenamide	215
		<i>N,N</i> -Dimethyl- <i>O</i> -(methylsulfonyl)hydroxylamine	217
		Dimethyl(methylthio)sulfonium Tetrafluoroborate	219
		Dimethyl(methylthio)sulfonium Trifluoromethanesulfonate	225

<i>cis</i> -3-[<i>N</i> -(3,5-Dimethylphenyl)benzenesulfonamido]borneol	230	Mesitylsulfonyl-1 <i>H</i> -1,2,4-triazole	345
Dimethylsuccinimidosulfonium Tetrafluoroborate	231	(<i>R,R</i>)-1,2-(Methanesulfonamido)-cyclohexane	346
Dimethyl Sulfoxide-Iodine	233	Methanesulfonic Anhydride	349
Dimethyl Sulfoxide-Methanesulfonic Anhydride	234	Methanesulfonyl Chloride-Dimethylaminopyridine	350
Dimethyl Sulfoxide-Phosphorus Pentoxide	234	Methoxycarbonylmethanesulfonyl Chloride	351
Dimethyl Sulfoxide-Silver Tetrafluoroborate	235	Methoxycarbonylsulfamoyl Chloride	351
Dimethyl Sulfoxide-Sulfur Trioxide/Pyridine	237	4-Methoxycarbonylthiolan-3-one	352
<i>S,S</i> -Dimethyl- <i>N</i> -(<i>p</i> -toluenesulfonyl)sulfilimine	238	2-(2-Methoxyethoxy)-ethyl 2-(Chlorosulfonyl)-benzoate	354
<i>S,S</i> -Dimethyl- <i>N</i> -(<i>p</i> -toluenesulfonyl)sulfoximine	239	Methoxyphenyl Benzenethiosulfinate	357
2,4-Dinitrobenzenesulfonyl Chloride	240	1-(4-Methoxyphenyl)-2-(4'-methylbenzylthio)ethylamine	358
3,5-Dinitrobenzenesulfonyl Chloride	242	7-Methoxy-3-(phenylsulfonyl)-1(3 <i>H</i>)-isobenzofuranone	361
2,4-Dinitrobenzenesulfonylhydrazide	243	Methoxy(phenylthio)methane	362
2-(1,3-Dioxan-2-yl)ethylsulfonyl Chloride	244	Methoxy(phenylthio)trimethylsilylmethane	364
1,1-Dioxobenzo[<i>b</i>]-thiophene-2-yl Methyloxycarbonyl Chloride	246	2-Methylallyl Phenyl Sulfone	366
Diphenylbis(1,1,1,3,3,3-hexafluoro-2-phenyl-2-propoxy)sulfurane	246	2-Methylbenzothiazole	369
(<i>R,R</i>)-1,2-Diphenyl-1,2-diaminoethane		Methylbis(methylthio)sulfonium Hexachloroantimonate	371
<i>N,N'</i> -Bis[3,5-bis(trifluoromethyl)benzenesulfonamide]	248	Methyl α -Chloro- α -phenylthioacetate	373
<i>N</i> -(Diphenylmethylene)benzenesulfonamide and <i>N</i> -(Diphenylmethylene)-4-methylbenzenesulfonamide	250	Methyl Diethylamidossulfite	374
Diphenyl Sulfoxide	253	Methyl Methanethiosulfonate	374
2,2'-Dipyridyl Disulfide- <i>N,N'</i> -dioxide	258	4-Methyl- <i>N</i> -phenylbenzene Sulfonimidoyl Chloride	377
1,2,4-Dithiazolidine-3,5-dione	262	1-Methyl-2(1 <i>H</i>)-pyridinethione	380
1,3-Dithienium Tetrafluoroborate	266	Methylsulfonyl Trifluoromethanesulfonate	380
<i>trans</i> -1,3-Dithiolane 1,3-Dioxide	267	(+)-(<i>S</i>)- <i>N</i> -Methylsulfonylphenylalanyl Chloride	381
1,4-Dithiothreitol	268	2-Methylsulfonyl-3-phenyl-1-prop-2-enyl Chloroformate	382
<i>tert</i> -Dodecanethiol	269	Methyl Thioglycolate	384
<i>p</i> -Dodecylbenzenesulfonyl Azide	272	Methylthiomaleic Anhydride	385
Ethyl (Dimethylsulfuranylidene)acetate	275	1-(Methylthiomethyl)benzotriazole	386
<i>S</i> -Ethyl Ethanethiosulfinate	279	Methylthiomethyl <i>p</i> -Tolyl Sulfone	387
4-Ethylhexahydro-4-methyl-(4 <i>S</i> ,9 <i>aS</i>)-pyrrolo[1,2- <i>d</i>][1,4]thiazepin-5(4 <i>H</i>)-one	282	(<i>E</i>)-3-Methylthio-2-propenyl <i>p</i> -Tolyl Sulfone	390
5-Ethylthio-1 <i>H</i> -tetrazole	283	2-(Methylthio)tetrahydrofuran	391
2-Fluoro-3,3-dimethyl-2,3-dihydro-1,2-benzisothiazole 1,1-Dioxide	287	5-Methylthio-1 <i>H</i> -tetrazole	391
<i>N</i> -Fluoro- <i>N</i> -(phenylsulfonyl)benzenesulfonamide	288	Methyl <i>N</i> -(<i>p</i> -Toluenesulfonyl)carbamate	392
Fluorosulfuric Acid	291	α -Methyltoluene-2, α -sultam	395
Fluorosulfuric Acid-Antimony(V) Fluoride	294	Methyl <i>p</i> -Toluenethiosulfonate	397
Glyoxylyl Chloride <i>p</i> -Toluenesulfonylhydrazone	299	<i>N</i> -Methyltrifluoromethanesulfonamide	398
2-Hydroxyethyl Phenyl Sulfone	305	Methyltrifluoromethanesulfonate	399
[Hydroxy(tosyloxy)iido]benzene	307	(-)-2- <i>exo</i> -Morpholinoisobornane-10-thiol	408
Isopropylidiphenylsulfonium Tetrafluoroborate	317	<i>o</i> -Nitrobenzenesulfonyl Azide	411
(<i>S</i>)-4-Isopropylthiazolidine-2-thione	318	<i>o</i> -Nitrobenzenesulfonyl Chloride	412
(1 <i>R</i> ,2 <i>S</i>)-1-Lithio-1-phenylsulfonyl-2-[(<i>tert</i> -butyldiphenyl)silyl]oxymethyloxirane	321	<i>o</i> -Nitrobenzenesulfonylhydrazide	415
2-Lithio- <i>N</i> -phenylsulfonylindole	323	<i>p</i> -Nitrobenzenesulfonyl-4-nitroimidazole	417
Lithium Butyl(phenylthio)cuprate	325	<i>p</i> -Nitrobenzenesulfonyloxymethane	418
Lithium Cyclopropyl(phenylthio)cuprate	326	5-Nitro-3 <i>H</i> -1,2-benzoxathiole <i>S,S</i> -Dioxide	419
Lithium (3,3-Diethoxy-1-propen-2-yl)(phenylthio)cuprate	327	Nitrosylsulfuric Acid	420
Lithium 2-Lithiobenzenethiolate	329	1,1,1,2,2,3,3,4,4-Nonafluoro-6-(methanesulfonyl)hexane	422
Lithium 1-Methyl-2-(2-methyl-1-(<i>E</i>)-propenyl)-cyclopropyl(phenylthio)cuprate	330	Oxodimethoxyphosphoranesulfonyl Chloride	425
Lithium Phenylthio(trimethylstannyl)cuprate	333	Pentafluorosulfonyl Chloride	427
Lithium Phenylthio(2-vinylcyclopropyl)cuprate	334	1 <i>H</i> ,1 <i>H</i> ,2 <i>H</i> ,2 <i>H</i> -Perfluorodecanethiol	428
(-)-(1 <i>R</i> ,2 <i>S</i> ,5 <i>R</i>)-Menthyl (<i>S</i>)- <i>p</i> -Toluenesulfinate	337	Peroxydisulfuryl Difluoride	430
6-Mercapto-4-dibenzofuranol	340	Phenyl Chlorothionocarbonate	432
1-(Mesitylene-2-sulfonyl)-3-nitro-1,2,4-triazole (MSNT)	342	1-Phenyl-2-(phenylsulfonyl)ethyl Acetate	434
		4-Phenylsulfonyl-2-butanone Ethylene Acetal	436
		<i>N</i> -(Phenylsulfonyl)(3,3-dichlorocamphoryl)oxaziridine	437
		(2-Phenylsulfonyl)ethoxy Dichlorophosphine	439
		α -Phenylsulfonylethyllithium	440
		(2-Phenylsulfonylethyl)trimethylsilane	444
		Phenylsulfonylfluoromethylphosphonate	445
		(1 <i>S</i> ,6 <i>S</i>)-2-(Phenylsulfonyl)-7-oxabicyclo[4.1.0]hept-2-ene	446

(<i>E,E</i>)- <i>N</i> -Phenylsulfonyl-4-phenyl-1-aza-1,3-butadiene	449	(<i>R</i>)-(+)-3-(<i>p</i> -Tolylsulfinyl)propionic Acid	557
3-(Phenylsulfonyl)propanal Ethylene Acetal	451	Tosyl Azide, Polymer-supported	558
1-Phenylsulfonyl-1 <i>H</i> -tetrazole	452	β -Tosylethylamine	559
(<i>E</i>)-1-Phenylsulfonyl-2-trimethylsilylethylene	453	β -Tosylethylazide	560
1-Phenyl-2-tetrazoline-5-thione	454	6-Tosyl-3-oxa-6-azabicyclo[3.1.0]hexane	561
2-Phenylthioethanol	456	Tri(<i>tert</i> -butoxy)silanethiol	563
(Phenylthio)nitromethane	457	Tricarbonyl[(2,3,4,5,6,7- η)-thiepin-1,1-dioxide]chromium(0)	566
<i>N</i> -Phenylthiophthalimide	459	2,2,2-Trichloroethoxysulfonamide	568
1-Phenylthiovinyl Triphenylphosphonium Iodide	460	2,2,2-Trichloroethyl- <i>N</i> -tosyloxycarbamate	571
<i>Se</i> -Phenyl <i>p</i> -Tolueneselenosulfonate	461	Triethylsilyl Trifluoromethanesulfonate	572
<i>N</i> -Phenyltrifluoromethanesulfonimide	465	Trifluoromethanesulfonic Acid	573
Phthalimidosulfonyl Chloride	469	Trifluoromethanesulfonic Anhydride	581
Potassium <i>tert</i> -Butoxide–Dimethyl Sulfoxide	471	Trifluoromethanesulfonyl Azide	595
Potassium Hydroxide–Dimethyl Sulfoxide	474	Trifluoromethanesulfonyl Chloride	598
Potassium Monoperoxysulfate	475	Trifluoromethanesulfonylmethyl Methyl Sulfone	602
Potassium <i>o</i> -Nitrobenzeneperoxysulfonate	487	<i>S</i> -(Trifluoromethyl)dibenzothiophenium	
Potassium Nitrosodisulfonate	489	Triflate	603
1,3-Propanedithiol Bis(<i>p</i> -toluenesulfonate)	491	Trifluoromethyl Phenyl Sulfone	604
<i>N</i> -Propenoyl Camphor-10,2-sultam	493	{[(Trifluoromethyl)sulfonyl]ethynyl}benzene	606
3-Propionylthiazolidine-2-thione	495	(<i>S</i>)- <i>N</i> -Trifluoromethylsulfonyl-2-isopropylaziridine	607
2-Pyridinesulfonyl Chloride	496	[1,1,1-Trifluoro- <i>N</i> -	
<i>N</i> -(2-Pyridyl)bis(trifluoromethanesulfonimide)	498	[(trifluoromethyl)sulfonyl]methanesulfonamidato-	
Sodium Dodecyl Sulfate	501	κN](triphenylphosphine)	610
<i>N</i> -Sulfinyl- <i>p</i> -toluenesulfonamide	503	1,1,1-Trifluoro- <i>N</i> -[(trifluoromethyl)sulfonyl]- <i>N</i> -	
9-(2-Sulfo)fluorenylmethoxycarbonyl Chloride	505	(trimethylsilyl)methanesulfonamide	613
Sulfonic Acid, Polymer-supported	506	2,4,6-Triisopropylbenzenesulfonyl Azide	616
<i>o</i> -Sulfoperbenzoic Acid	515	2,4,6-Triisopropylbenzenesulfonyl Hydrazide	623
Sulfur Trioxide	516	Triisopropylbenzenesulfonyl Tetrazole	629
<i>N,N,N',N'</i> -Tetrabromobenzene-1,3-disulfonamide		Triisopropylsilylethynyl Triflone	632
(TBBDS)	521	Triisopropylsilyl Trifluoromethanesulfonate	633
Tetrachlorothiophene Dioxide	523	2-Trimethylsilyl-1,3-benzothiazole	635
2,2,4,4-Tetramethylcyclobutan-1-one-3-thione	527	[<i>N</i> -(2-(Trimethylsilyl)ethanesulfonyl)imino]phenyliodane	636
1,1'-(Thiocarbonyl)bis(1 <i>H</i> -benzotriazole)	533	(Trimethylsilyl)methanesulfonyl Chloride–Cesium	
2-Thiono-1,3-dioxol-4-ene	535	Fluoride	638
Thiophenol–Azobisisobutyronitrile	535	2-(Trimethylsilyl)phenyl Triflate	639
Thiophenol, Polymer-supported	536	Triphenylphosphonium 3,3-Dimethyl-1,2,5-	
Thiophosphoryl Chloride	537	thiadiazolidine 1,1-Dioxide	642
2-Thiopyridyl Chloroformate	538	Triphenyl Thioborate	644
Thiourea Dioxide	540	Trityl Thionitrite	645
<i>p</i> -Toluenesulfinic Acid	541		
<i>p</i> -Toluenesulfonyl Bromide	542	List of Contributors	647
<i>p</i> -Toluenesulfonyl Chloride and Related Reagents,			
Polymer-supported	545	Reagent Formula Index	663
<i>O-p</i> -Toluenesulfonylhydroxylamine	548		
[<i>N</i> -(<i>p</i> -Toluenesulfonyl)imino]phenyliodinane	550	Subject Index	669
<i>p</i> -Toluenesulfonylmethylene Triphenylphosphorane	553		
(<i>R</i>)-(+)- <i>p</i> -Tolylsulfinylacetic Acid	555	General Abbreviations	
(<i>R</i>)-(+)- α -(<i>p</i> -Tolylsulfinyl)- <i>N,N</i> -dimethylacetamide	556		

Preface

The eight-volume *Encyclopedia of Reagents for Organic Synthesis (EROS)*, authored and edited by experts in the field, and published in 1995, had the goal of providing an authoritative multivolume reference work describing the properties and reactions of approximately 3000 reagents. With the coming of the Internet age and the continued introduction of new reagents to the field as well as new uses for old reagents, the electronic sequel, *e-EROS*, was introduced in 2002 and now contains in excess of 4000 reagents, catalysts, and building blocks making it an extremely valuable reference work. At the request of the community, the second edition of the encyclopedia, *EROS II*, was published in March 2009 and contains the entire collection of reagents at the time of publication in a 14 volume set.

Although the comprehensive nature of *EROS* and *EROS II* and the continually expanding *e-EROS* render them invaluable as reference works, their very size limits their practicability in a laboratory environment. For this reason, a series of inexpensive one-volume *Handbooks of Reagents for Organic Synthesis (HROS)*, each focused on a specific subset of reagents, was introduced by the original editors of *EROS* in 1999:

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

Edited by Robert M. Coates and Scott E. Denmark

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

This series has continued over the past several years with the publication of another series of *HROS* volumes, each edited by a current or past member of the *e-EROS* editorial board:

Chiral Reagents for Asymmetric Synthesis

Edited by Leo A. Paquette

Reagents for High-Throughput Solid-Phase and Solution-Phase Organic Synthesis

Edited by Peter Wipf

Reagents for Glycoside, Nucleotide, and Peptide Synthesis

Edited by David Crich

Reagents for Direct Functionalization of C–H Bonds

Edited by Philip L. Fuchs

Fluorine-Containing Reagents

Edited by Leo A. Paquette

Catalyst Components for Coupling Reactions

Edited by Gary A. Molander

Reagents for Radical and Radical Ion Chemistry

Edited by David Crich

This series now continues with this volume entitled *Sulfur-Containing Reagents*, edited by Leo Paquette, the originator and longtime guiding light of the *EROS* and *HROS* volumes, in addition to the online version, *e-EROS*. This 12th volume in the *HROS* series, like its predecessors, is intended to be an affordable, practicable compilation of reagents arranged around a central theme that it is hoped will be found at arm's reach from synthetic chemists worldwide. The reagents have been selected to give broad relevance to the volume, within the limits defined by the subject matter of organosulfur reagents. We have enjoyed putting this volume together and hope that our colleagues will find it as much enjoyable and useful to read and consult.

David Crich

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Institut de Chimie des Substances Naturelles
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Introduction

The widespread use of sulfur-containing reagents by synthetic chemists is a reflection of the diversity of properties offered by this broad class of compounds. The enormous divergence in the reactivity of divalent and tetravalent sulfur reagents, the stereochemical issues offered by sulfoxides, and the ionizability of sulfonic acids represent only a few of the many facets of this collective group of reagents. The resulting demands placed on chemists for the appropriate adaptation of a given reagent emerge in many forms, not the least of which bear on one's knowledge of reactivity, availability of building blocks, appreciation of the consequences of associated changes in electronic character, and the like. As a consequence of many recent developments, it was deemed appropriate to incorporate into a single volume a compilation that brings together a large fraction of the more useful organosulfur reagents as well as key sulfur-containing promoters that are currently in vogue. As usual, the compilation has been arranged alphabetically in order to facilitate searching. An added benefit is to foster the scanning for information since proximal arrangements by compound type are not prevalent.

The selection covered in this volume is built on the many important discoveries at the hands of numerous practitioners of our science. These achievements have been realized in conjunction with a very extensive physical organic base.

The featured reagents have been culled from three sources. A minority of the entries appeared initially in the *Encyclopedia of Reagents for Organic Synthesis (EROS)*, which was published in 1995. Since that time, a significant number of entries involving these classical reagents have been updated (*e-EROS*), 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 sulfur-containing compounds. In some instances, groups of reagents coincidentally appear in close proximity, thereby facilitating comparative analysis. Subsets consisting of *meta*- and *para*-nitrobenzenesulfonyl peroxide and of β -tosylethyl amine, hydrazine, and hydroxylamine are exemplary.

Among the opening segments of this volume is a section that illustrates those procedures relevant to the field that have appeared in volumes 65–85 of *Organic Syntheses*. It is hoped that these tried and tested protocols will provide a useful level of added guidance in selecting what course of action one might pursue. All in all, it is hoped that this handbook will prove to be a valued adjunct to researchers experienced in sulfur 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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Short Note on InChIs and InChIKeys

The IUPAC International Chemical Identifier (InChITM) and its compressed form, the InChIKey, are strings of letters representing organic chemical structures that allow for structure searching with a wide range of online search engines and databases such as Google and PubChem. While they are obviously an important development for online reference works, such as *Encyclopedia of Reagents for Organic Reactions* (e-EROS), readers of this volume may be surprised to find printed InChi and InChIKey information for each of the reagents.

We introduced InChi and InChIKey to e-EROS in autumn 2009, including the strings in all HTML and PDF files. While

we wanted to make sure that all users of e-EROS, the second print edition of EROS and all derivative Handbooks would find the same information, we appreciate that the strings will be of little use to the readers of the print editions, unless they treat them simply as reminders that e-EROS now offers the convenience of InChIs and InChIKeys, allowing the online users to make best use of their browsers and perform searches in a wide range of media.

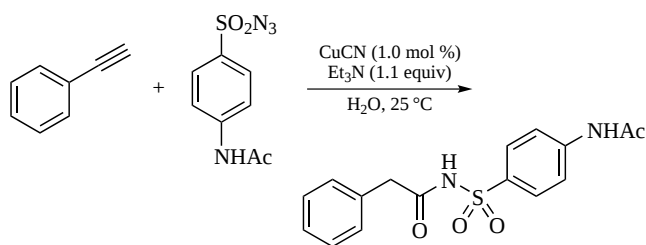
If you would like to know more about InChIs and InChIKeys, please go to the e-EROS website: www.mrw.interscience.wiley.com/eros/ and click on the InChI and InChIKey link.

Organic Synthesis Procedures Featuring the Synthesis of Organosulfur Compounds and Preparative Applications thereof, Volumes 65–85

Synthesis of Organosulfur Compounds

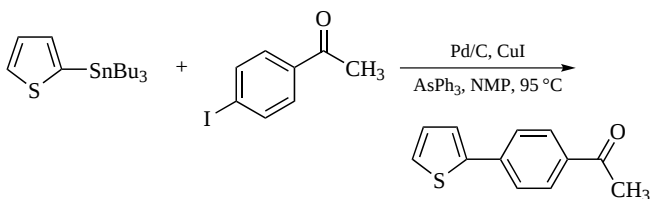
N-(4-Acetamidophenylsulfonyl)-2-phenylacetamide

S. H. Chol, S. J. Hwang, and S. Chang; *Org. Synth.* **2008**, 85, 131.



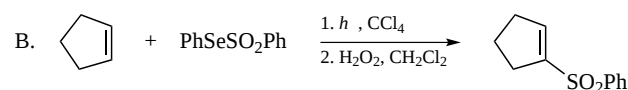
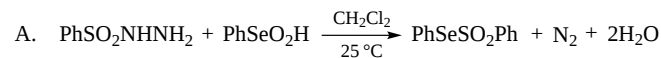
2-(4'-Acetylphenyl)thiophene

L. S. Liebeskind and E. Peña-Cabrera; *Org. Synth.* **2000**, 77, 135.



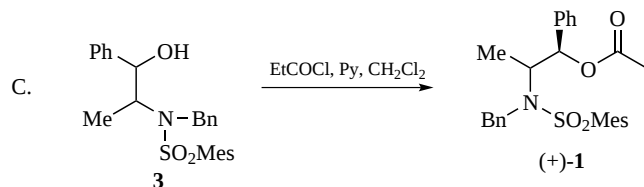
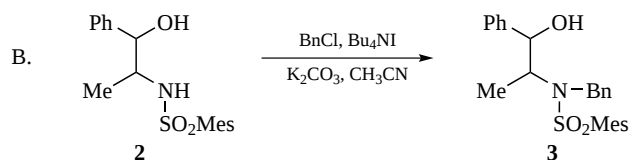
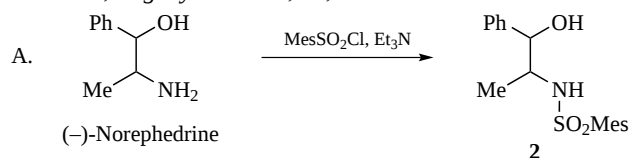
1-(Benzenesulfonyl)cyclopentane

H. S. Lin, M. J. Coghlan, and L. A. Paquette; *Org. Synth.* **1989**, 67, 157.



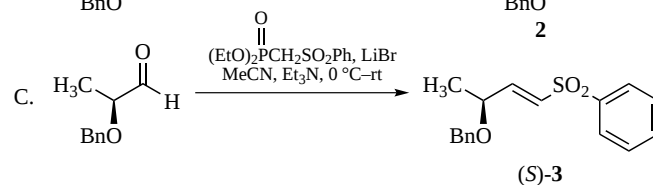
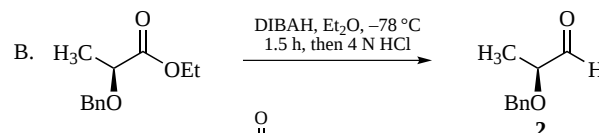
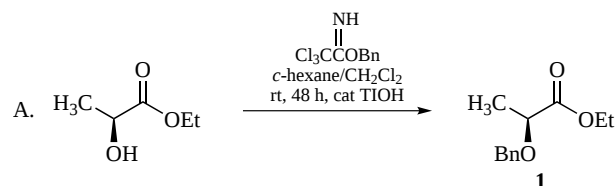
2-(*N*-Benzyl-*N*-mesitylenesulfonyl)amino-1-phenyl-1-propyl Propionate

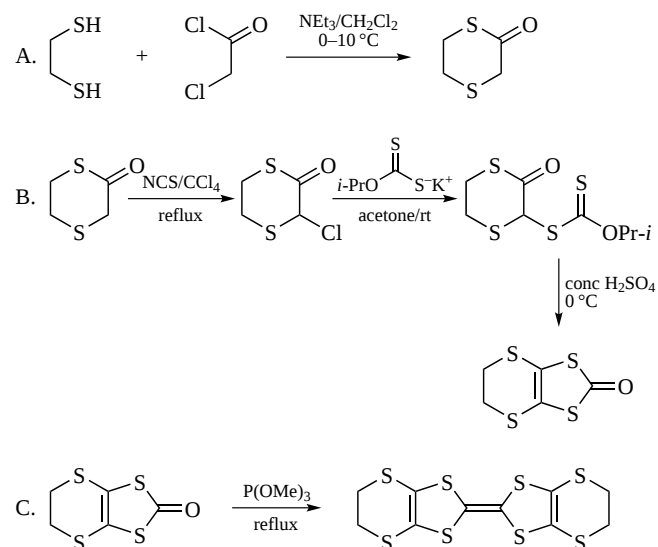
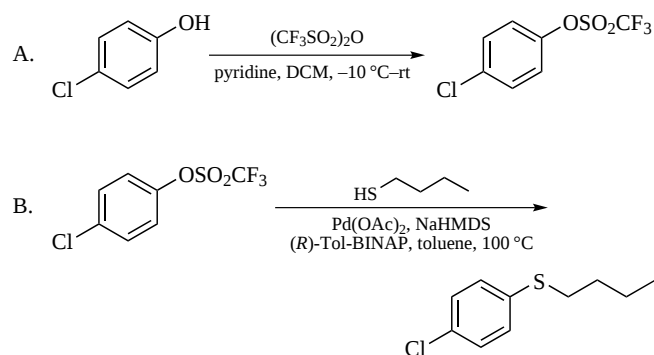
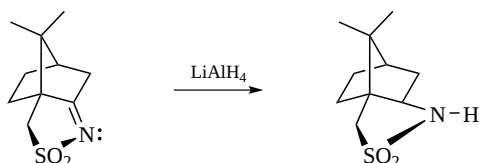
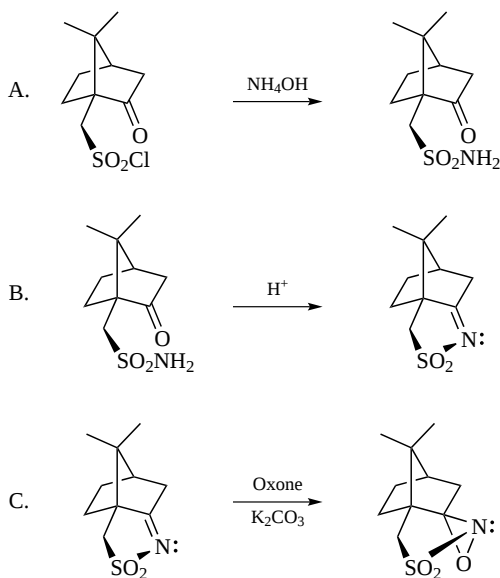
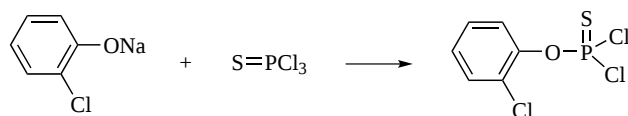
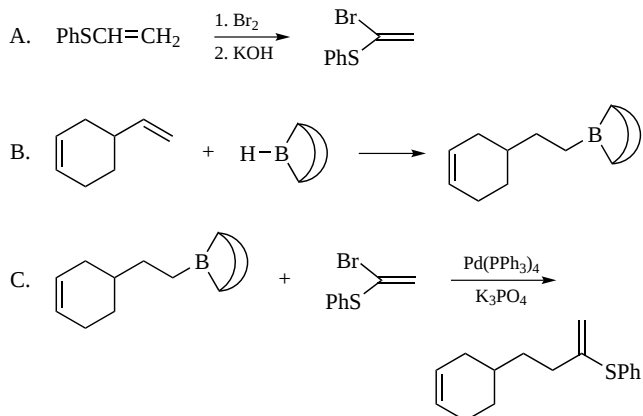
A. Abiko; *Org. Synth.* **2003**, 19, 109.



(-)-(E,S)-3-(Benzyloxy)-1-butenyl Phenyl Sulfone

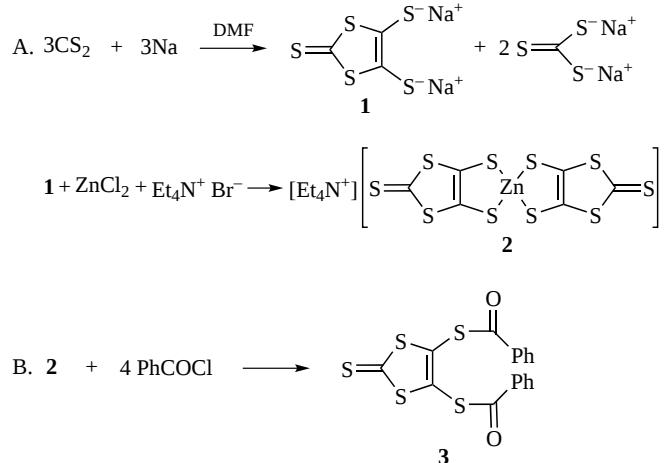
D. Enders, S. Von Berg, and B. Jandeleit; *Org. Synth.* **2002**, 78, 177.



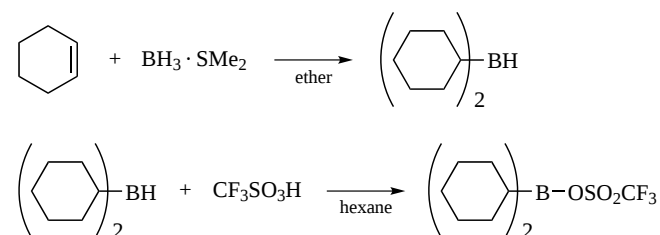
2,2'-Bi-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiinylidene (BEDT-TTF)J. Larsen and C. Lenoir; *Org. Synth.* **1995**, 72, 265.***n*-Butyl 4-Chlorophenyl Sulfide**J. C. McWilliams, F. Fleitz, N. Zheng, and J. D. Armstrong III; *Org. Synth.* **2003**, 79, 43.**(-)-D-2, 10-Camphorsultam**M. C. Weismiller, J. C. Towson, and F. A. Davis; *Org. Synth.* **1990**, 69, 154.**(+)-(2*R*,8*aS*)-10-(Camphorylsulfonyl)oxaziridine**J. C. Towson, M. C. Weismiller, G. S. Lal, A. C. Sheppard, and F. A. Davis; *Org. Synth.* **1990**, 69, 158.**2-Chlorophenyl Phosphorodichloridothioate**V. T. Ravikumar and B. Ross; *Org. Synth.* **1999**, 76, 271.**4-(3-Cyclohexenyl)-2-phenylthio-1-butene**T. Ishiyama, N. Miyaura, and A. Suzuki; *Org. Synth.* **1993**, 71, 89.

4,5-Dibenzoyl-1,3-dithiole-1-thione

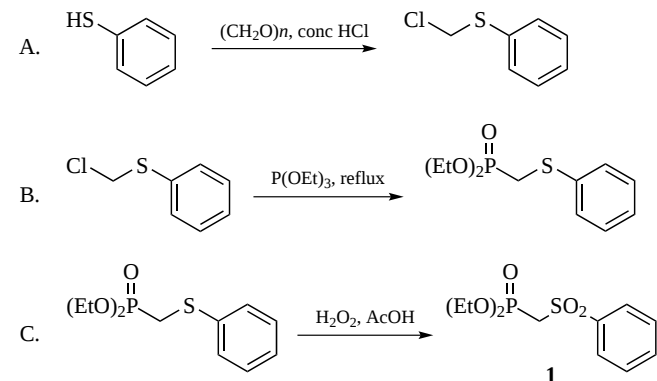
T. K. Hansen, J. Becher, T. Jørgensen, K. S. Varma, R. Khedekar, and M. P. Cava; *Org. Synth.* **1976**, 73, 270.

**Dicyclohexylboron Trifluoromethanesulfonate**

A. Abiko; *Org. Synth.* **2003**, 78, 103.

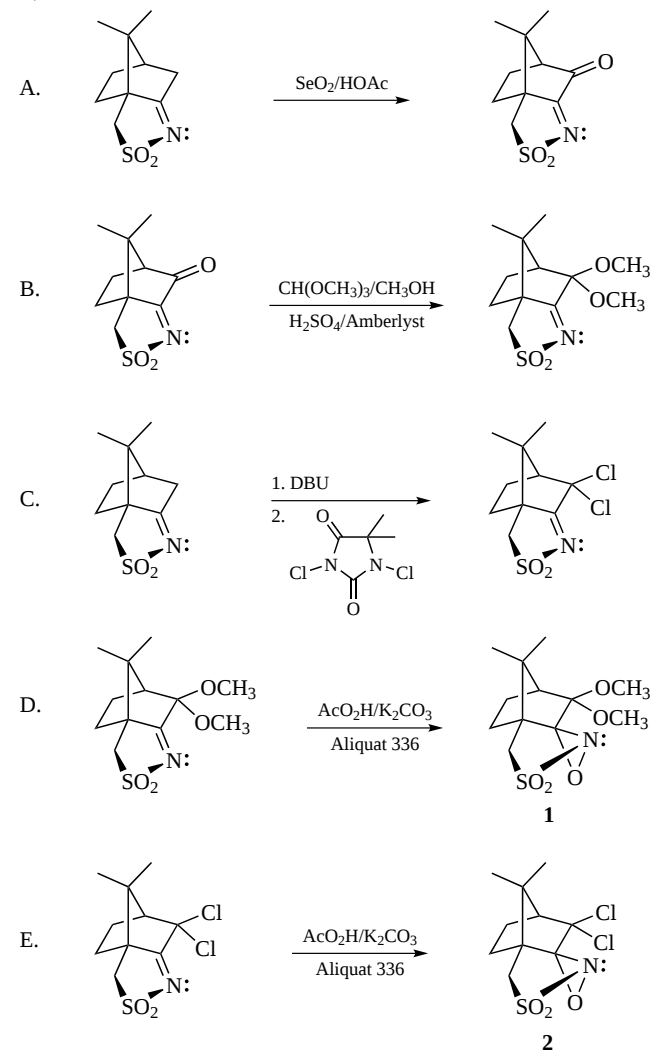
**Diethyl [(Phenylsulfonyl)methyl]phosphonate**

D. Enders, S. von Berg, and B. Jandeleit; *Org. Synth.* **2002**, 78, 169.

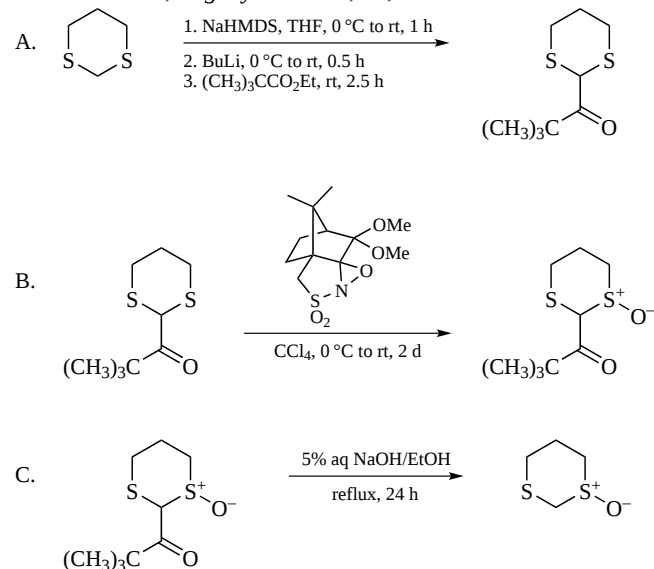
**(+)-(2R,8aR*)-[(8,8-Dimethoxycamphoryl)sulfonyl]oxaziridine and (+)-(2R,8aR*)-[(8,8-Dichlorocamphoryl)sulfonyl]oxaziridine**

B.-C. Chen, C. K. Murphy, A. Kumar, R. T. Reddy, C. Clark, P. Zhou, B. M. Lewis, D. Gala, I. Mergelsberg, D. Scherer,

J. Buckley, D. DiBenedetto, and F. A. Davis; *Org. Synth.* **1995**, 93, 159.

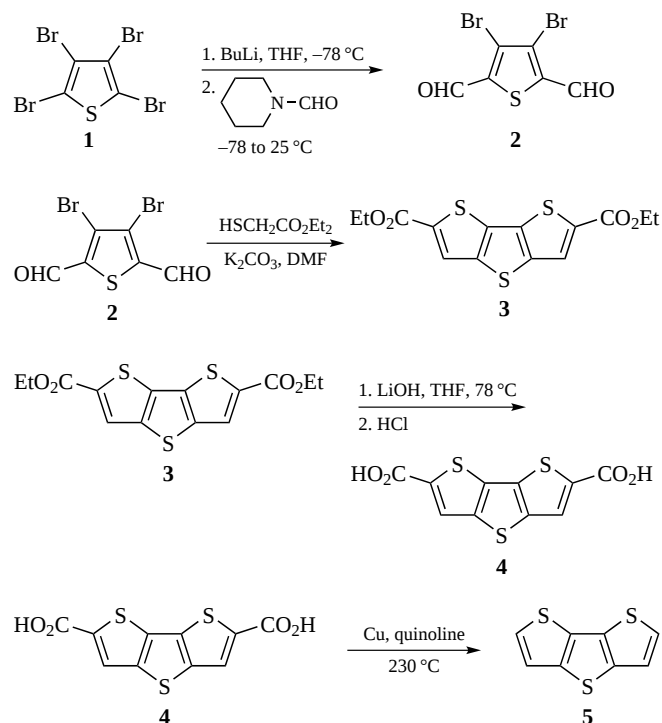
**1S-(−)-1,3-Dithiane 1-Oxide**

P. C. Bulman Page, J. P. Heer, D. Bethell, E. W. Collington, and D. M. Andrews; *Org. Synth.* **1999**, 76, 37.

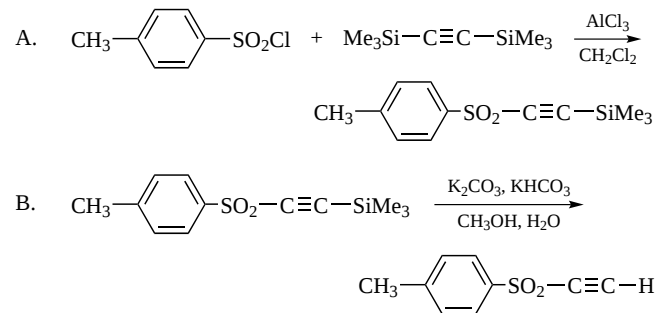


Dithieno[3,2-*b*:2',3'-*d*]thiophene

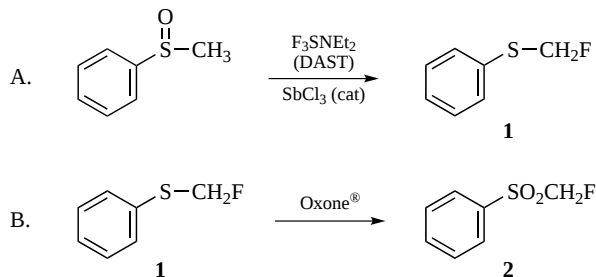
J. Frev, S. Proemmel, M. A. Armitage, and A. B. Holmes; *Org. Synth.* **2006**, 83, 209.

**Ethynyl *p*-Tolyl Sulfone**

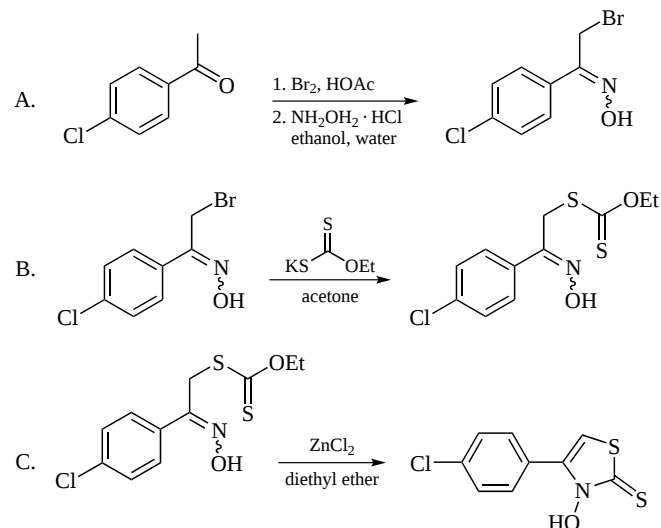
L. Waykole and L. A. Paquette; *Org. Synth.* **1989**, 67, 149.

**Fluoromethyl Phenyl Sulfone**

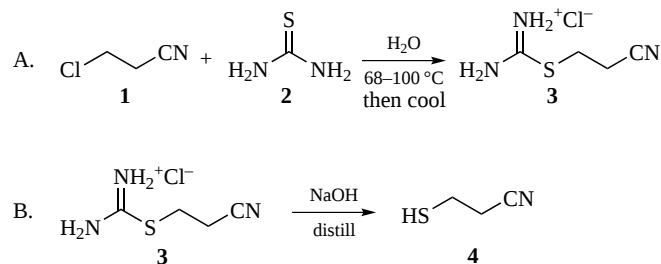
J. R. McCarthy, D. P. Matthews, and J. P. Paolini; *Org. Synth.* **1995**, 72, 209.

***N*-Hydroxy-4-(*p*-chlorophenyl)thiazole-2(3*H*)-thione**

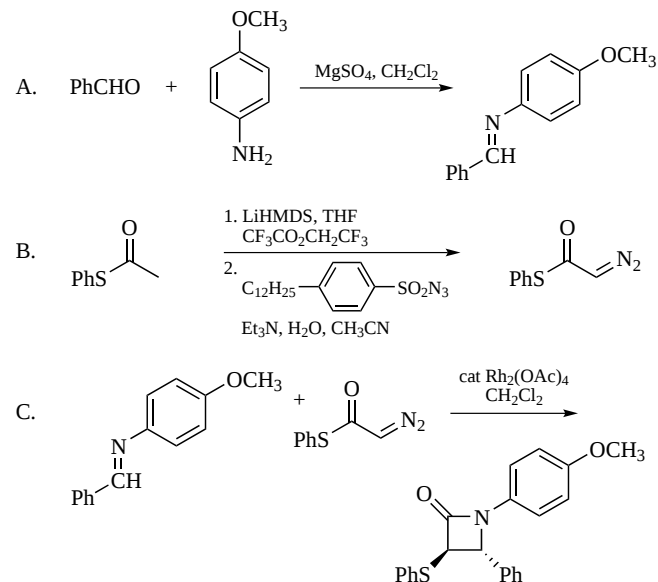
J. Hartung and M. Schwarz; *Org. Synth.* **2003**, 79, 228.

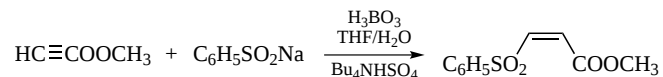
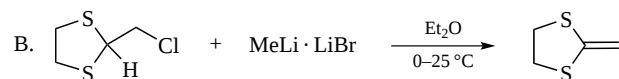
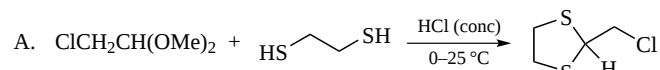
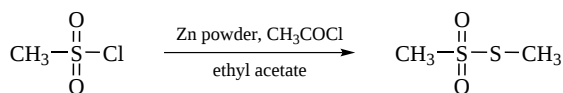
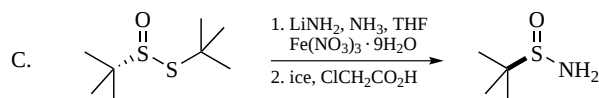
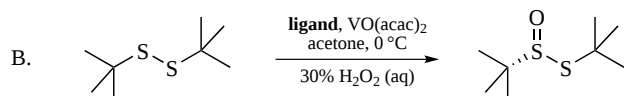
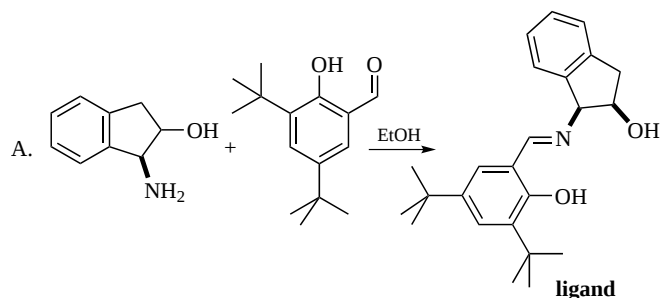
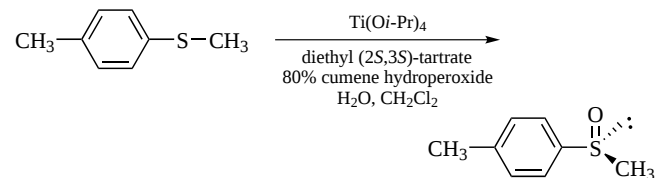
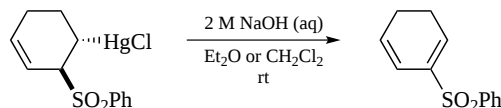
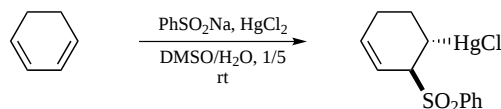
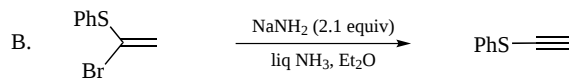
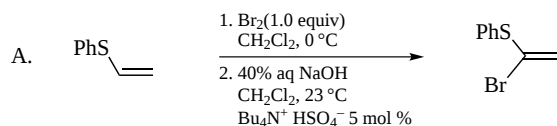
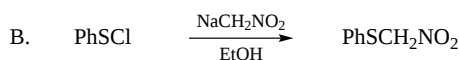
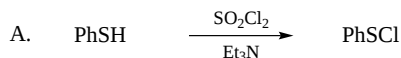
 **β -Mercaptopropionitrile (2-Cyanoethanethiol)**

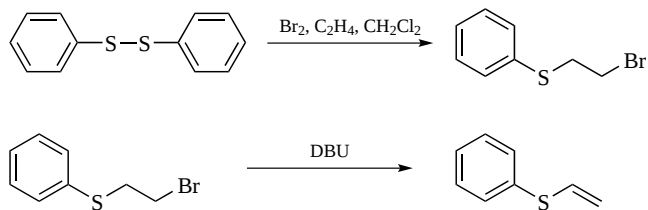
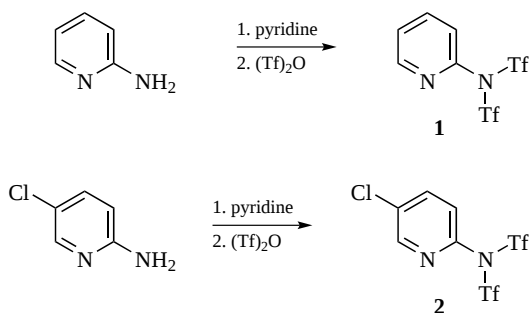
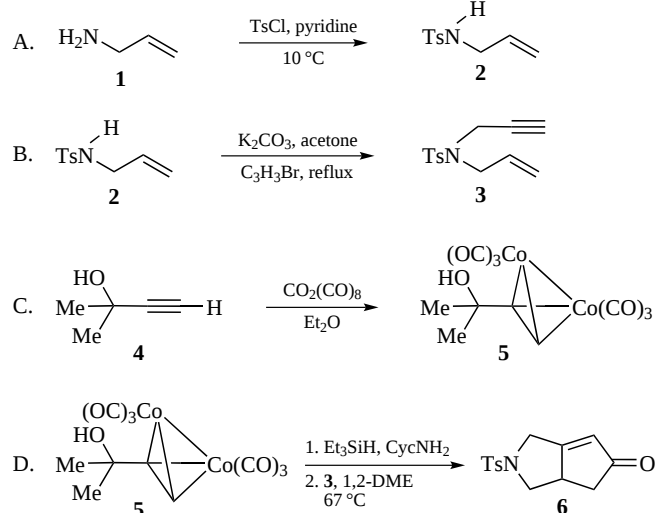
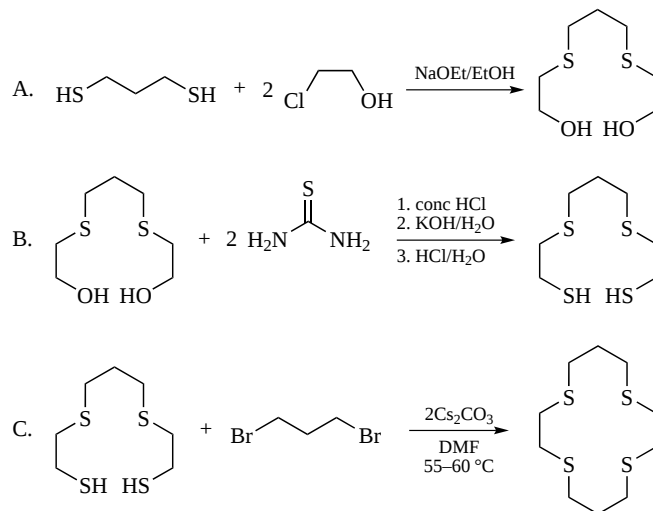
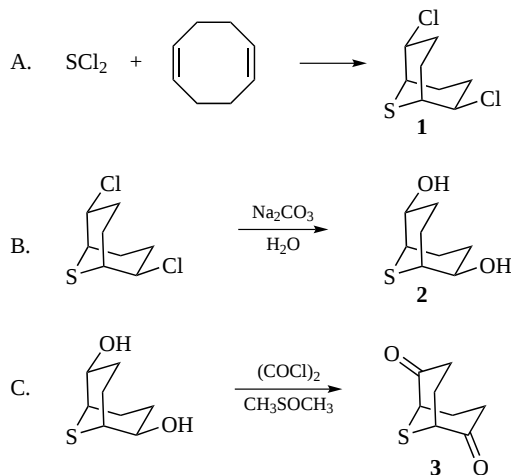
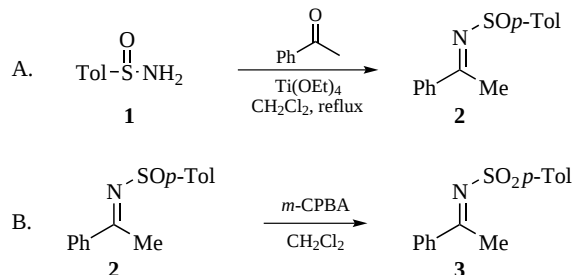
R. E. Gerber, C. Hasbun, L. G. Dubenko, M. F. King, and D. E. Bierer; *Org. Synth.* **2000**, 77, 186.

***trans*-1-(4-Methoxyphenyl)-4-phenyl-3-(phenylthio)azetidin-2-one**

R. L. Danheiser, I. Okamoto, M. D. Lawlor, and T. W. Lee; *Org. Synth.* **2003**, 80, 160.

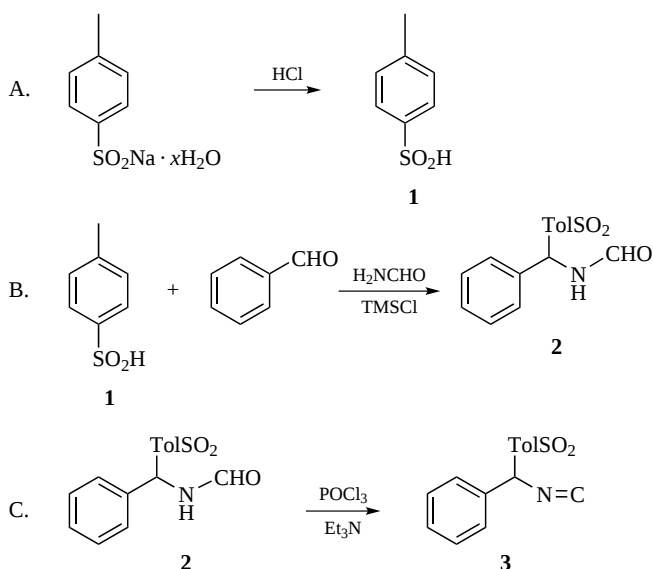


Methyl (Z)-3-(Benzenesulfonyl)prop-2-enoateG. C. Hirst and P. J. Parsons; *Org. Synth.* **1990**, 69, 169.**2-Methylene-1,3-dithiolane**K. R. Dahnke and L. A. Paquette; *Org. Synth.* **1993**, 71, 175.**S-Methyl Methanethiosulfonate**F. Chemla and P. Karoyan; *Org. Synth.* **2002**, 78, 99.**(R_s)-(+)-2-Methyl-2-propanesulfinamide**D. J. Weix and J. A. Ellman; *Org. Synth.* **2005**, 82, 157.**(S)-(-)-Methyl p-Tolyl Sulfoxide**S. H. Zhao, O. Samuel, and H. B. Kagan; *Org. Synth.* **1990**, 68, 49.**2-(Phenylsulfonyl)-1,3-cyclohexadiene**J.-E. Bäckvall, S. K. Juntunen, and O. S. Andell; *Org. Synth.* **1990**, 68, 148.**Phenylthioacetylene**P. A. Magriotis and J. T. Brown; *Org. Synth.* **1995**, 72, 252.**(Phenylthio)nitromethane**A. G. M. Barrett, D. Dhanak, G. G. Graboski, and S. J. Taylor; *Org. Synth.* **1990**, 68, 8.

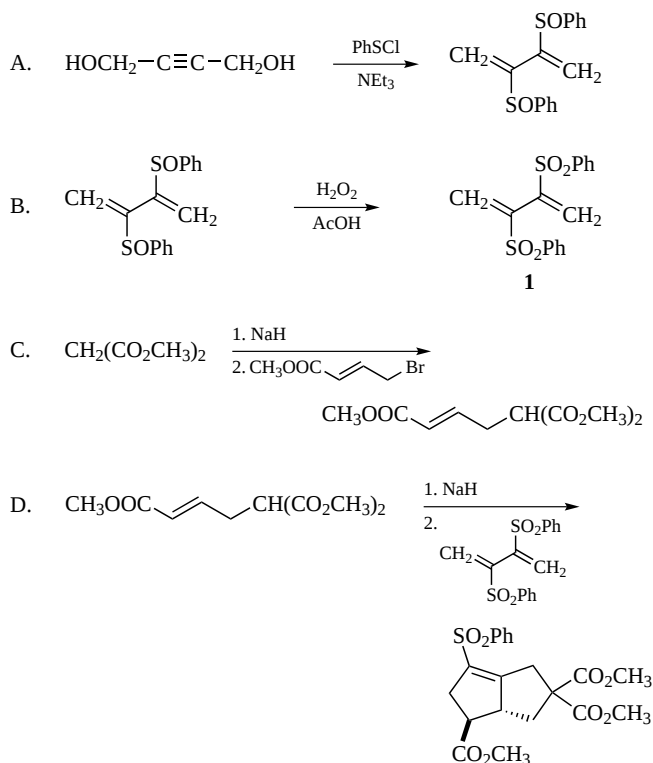
Phenyl Vinyl SulfideD. S. Reno and R. J. Pariz; *Org. Synth.* **1997**, 74, 124.**N-(2-Pyridyl)triflimide and N-(5-Chloro-2-pyridyl)triflimide**D. L. Comins, A. Dehghani, C. J. Foti, and S. P. Joseph; *Org. Synth.* **1997**, 74, 77.**2,3,3 α ,4-Tetrahydro-2-[(4-methylbenzene)sulfonyl]cyclopenta[c]pyrrol-5(1H)-one**M. C. Patel, T. Livinghouse, and B. L. Pagenkopf; *Org. Synth.* **2003**, 80, 93.**1,4,8,11-Tetrathiacyclotetradecane**J. Buter and R. M. Kellogg; *Org. Synth.* **1987**, 65, 150.**9-Thiabicyclo[3.3.1]nonane-2,6-dione**R. Bishop; *Org. Synth.* **1992**, 70, 120.**N-p-Tolylsulfonyl-(E)-1-Phenylethylideneimine**J. L. G. Ruano, J. Aleman, A. Parra, and M. B. Cid; *Org. Synth.* **2007**, 84, 129.

α -Tosylbenzyl Isocyanide

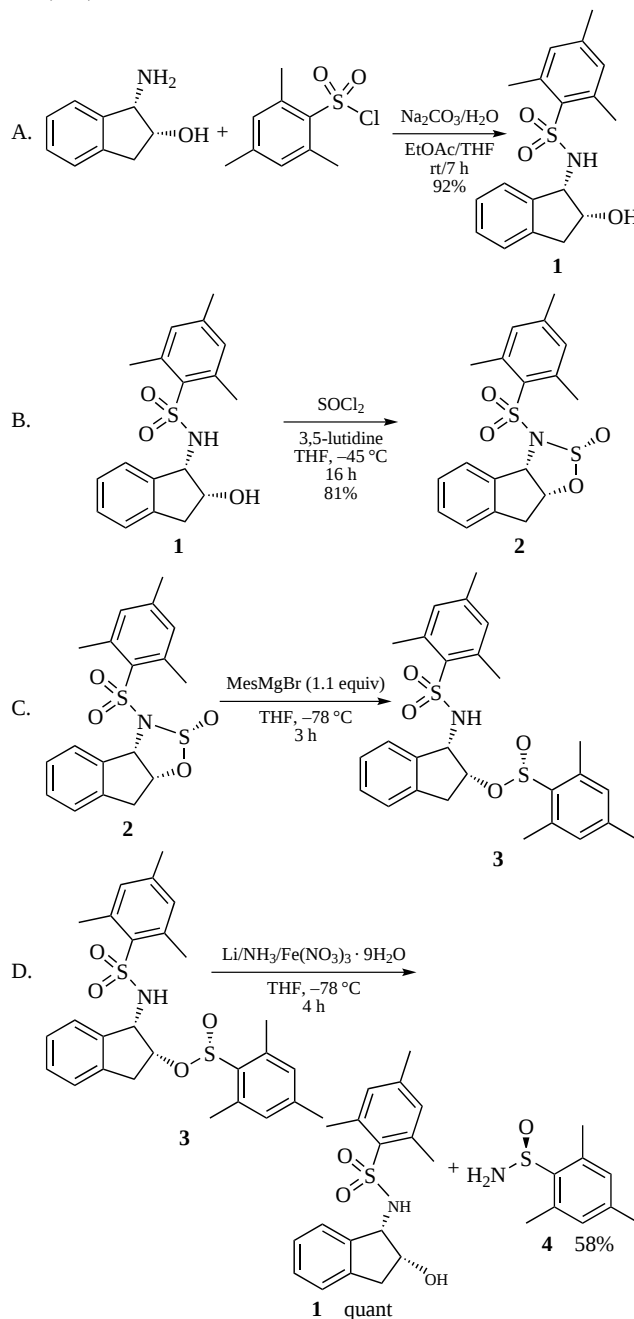
J. Sisko, M. Mellinger, P. W. Sheldrake, and Neil H. Baine; *Org. Synth.* **2000**, 77, 198.

***trans*-4,7,7-Tricarbomethoxy-2-phenylsulfonylbicyclo[3.3.0]oct-1-ene**

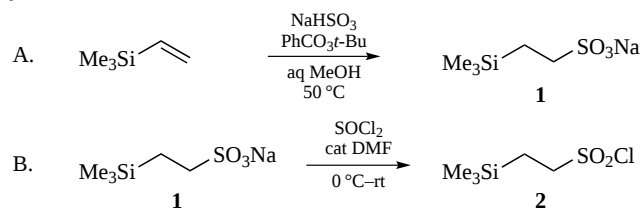
A. Padwa, S. H. Watterson, and Z. Ni; *Org. Synth.* **1997**, 74, 147.

**(S)-(+)-2,4,6-Trimethylbenzenesulfinamide**

T. Ramachandar, Y. Wu, J. Zhang, and F. A. Davis; *Org. Synth.* **2006**, 83, 131.

**2-Trimethylsilylthanesulfonyl Chloride**

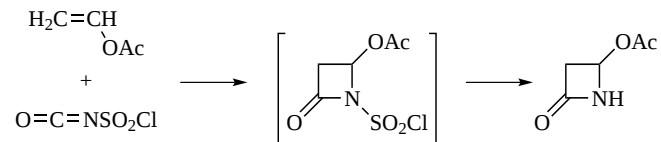
S. M. Weinreb, C. E. Chase, P. Wipf, and S. Venkatraman; *Org. Synth.* **1998**, 75, 161.



Synthetic Applications of Sulfur-Containing Compounds

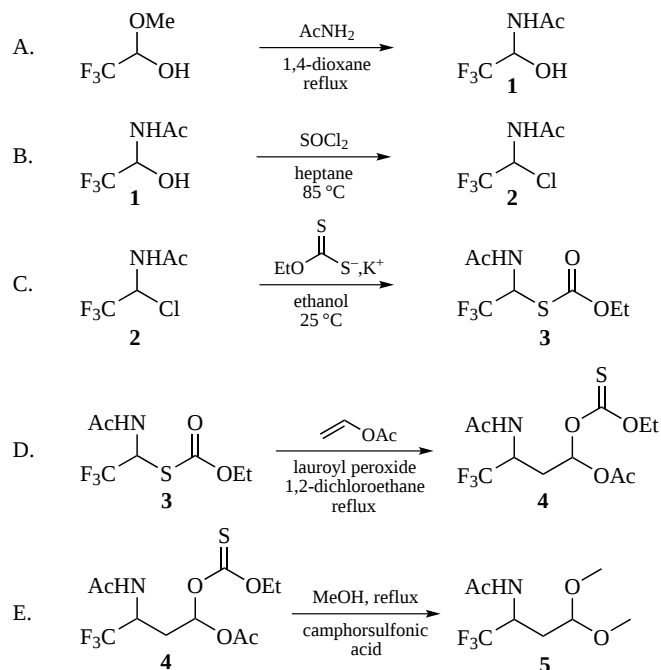
4-Acetoxyazetidin-2-one

S. J. Mickel, C.-N. Hsiao, and M. J. Miller; *Org. Synth.* **1987**, 65, 135.



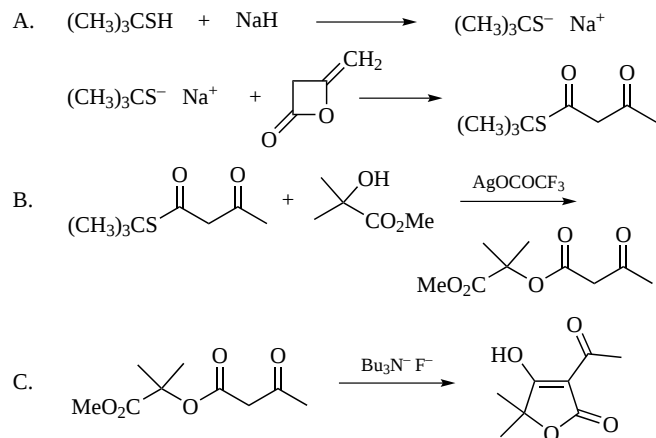
2-(*N*-Acetylamino)-4,4-dimethoxy-1,1,1-trifluorobutane

F. Gagosz and S. Z. Zard; *Org. Synth.* **2007**, 84, 32.



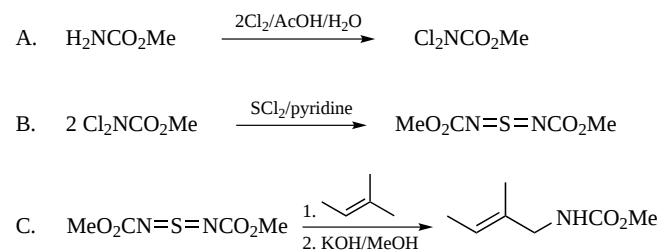
3-Acetyl-4-hydroxy-5,5-dimethylfuran-2(5*H*)-one

C. M. J. Fox and S. V. Ley; *Org. Synth.* **1988**, 66, 108.



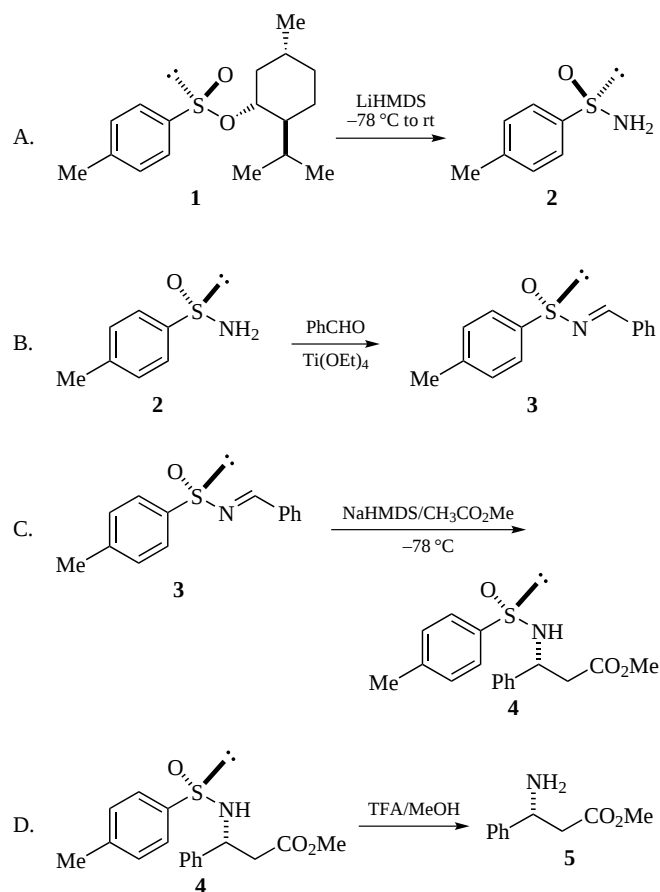
Allylcarbamates by the Aza-ene Reaction: Methyl *N*-(2-methyl-2-butenyl)carbamate

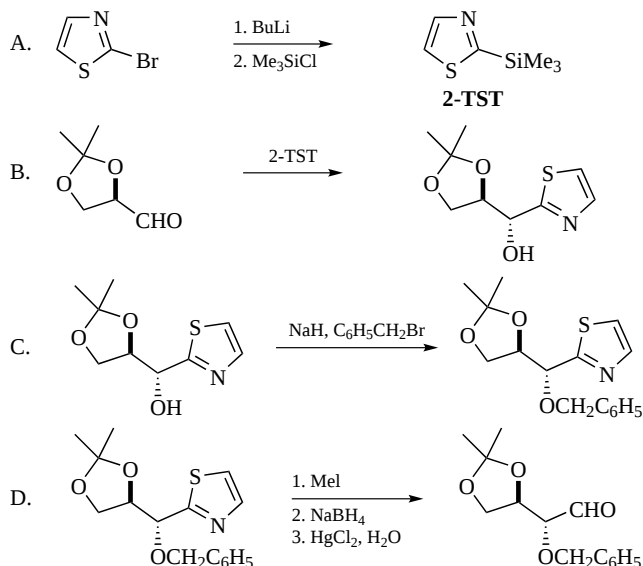
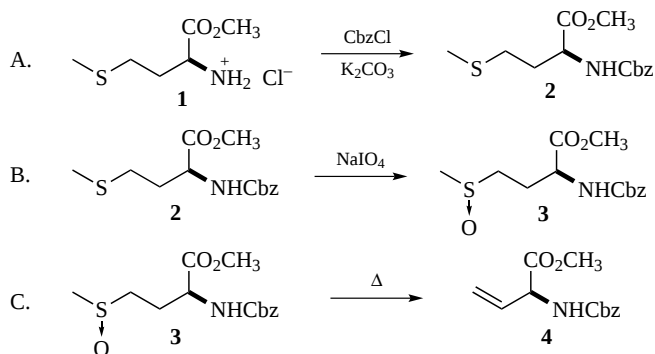
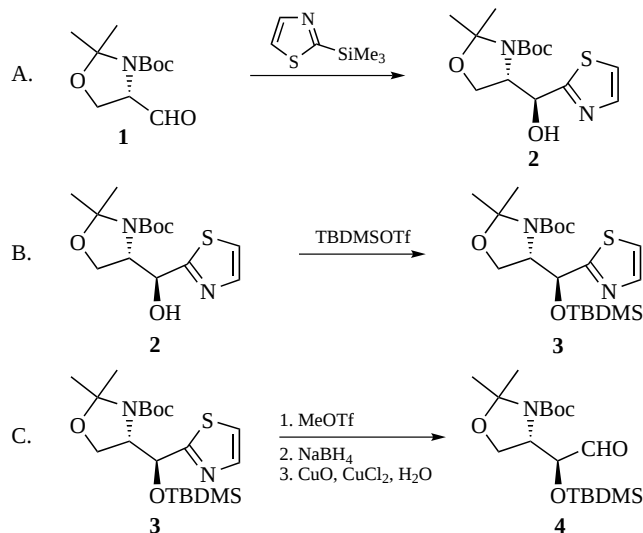
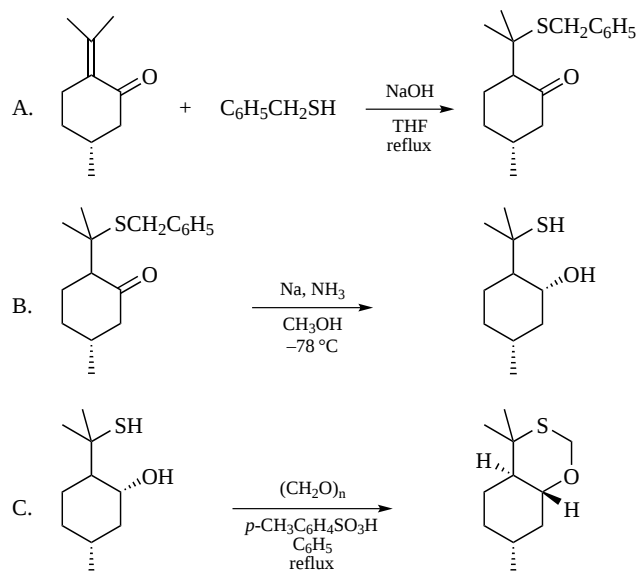
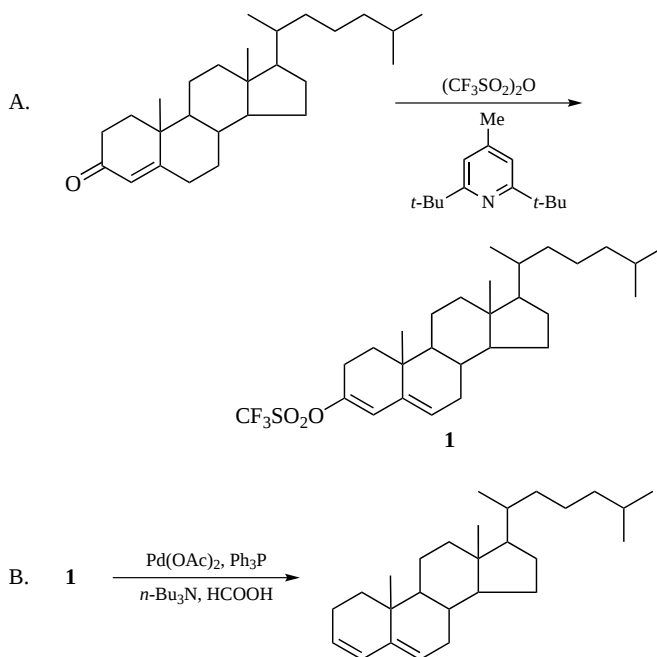
G. Kresze, H. Braxmeier, and H. Münsterer; *Org. Synth.* **1987**, 65, 159.



Asymmetric Synthesis of Methyl (*R*)-(+)- β -Phenylalanate from (*S*)-(+)-*N*-(Benzylidene)-*p*-toluenesulfinamide

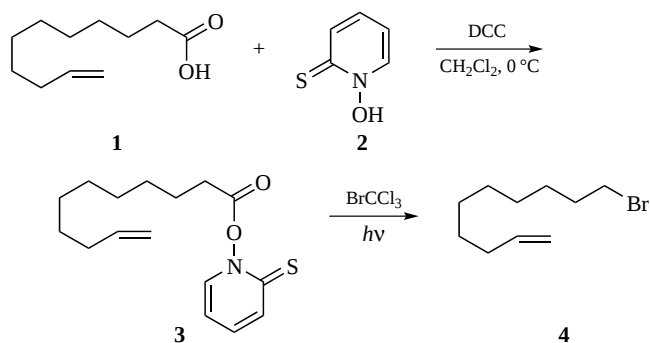
D. L. Fanelli, J. M. Szewczyk, Y. Zhang, G. V. Reddy, D. M. Burns, and F. A. Davis; *Org. Synth.* **2000**, 77, 50.



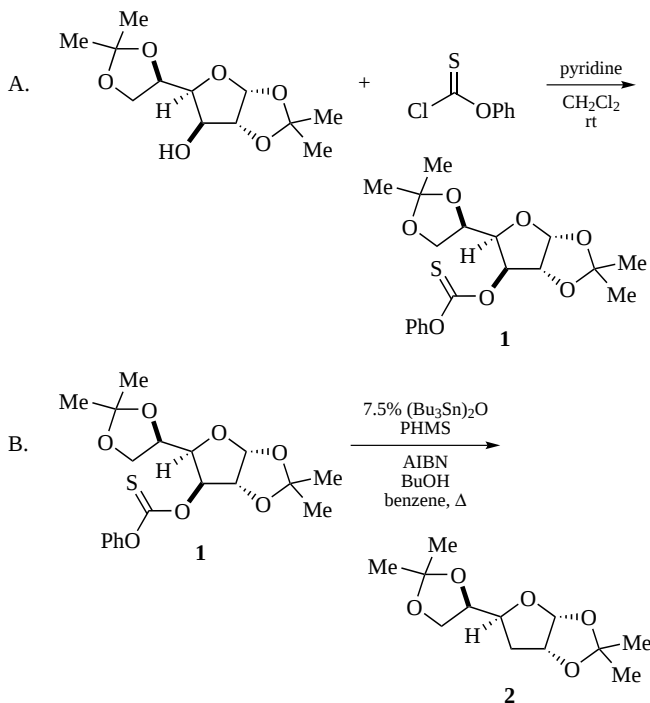
2-O-Benzyl-3,4-isopropylidene-D-erythroseA. Dondoni and P. Merino; *Org. Synth.* **1995**, 72, 21.**N-(Benzyloxycarbonyl)-L-vinylglycine Methyl Ester**M. Carrasco, R. J. Jones, S. Kamel, H. Rapoport; *Org. Synth.* **1992**, 70, 29.**(S)-2-[(4S)-N-tert-Butoxycarbonyl-2,2-dimethyl-1,3-oxazolidinyl]-2-tert-butyl dimethylsiloxyethanal**A. Dondoni and D. Perrone; *Org. Synth.* **2000**, 77, 78.**Chiral 1,3-Oxathiane from (+)-Pulegone: Hexahydro-4,4,7-Trimethyl-4H-1,3-benzoxathiin**E. L. Eliel, J. E. Lynch, F. Kume, and S. V. Frye; *Org. Synth.* **1987**, 65, 215.**Cholesta-3,5-diene**S. Cacchi, E. Morera, and G. Ortar; *Org. Synth.* **1990**, 68, 138.

Dec-9-enyl Bromide from 10-Undecenoic Acid

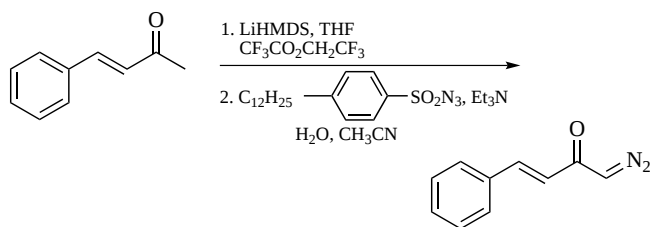
D. H. R. Barton, J. MacKinnon, R. N. Perchel, and C.-L. Tse; *Org. Synth.* **1998**, 75, 124.

**3-Deoxy-1,2:5,6-bis-O-(1-methylethylidene)- α -D-ribohexofuranose**

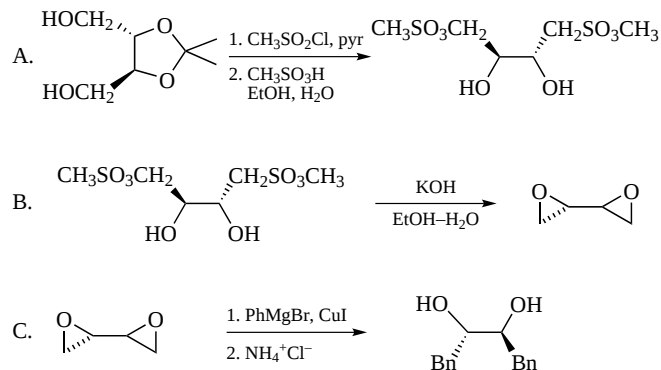
J. Tormo and G. C. Fu; *Org. Synth.* **2002**, 78, 239.

**(E)-1-Diazo-4-phenyl-3-buten-2-one**

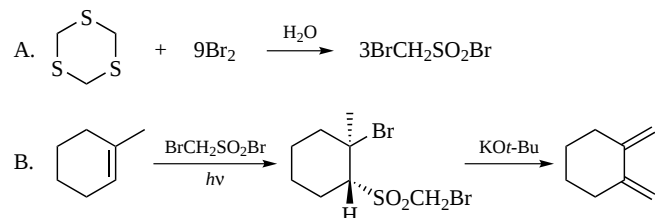
R. L. Danheiser, R. F. Miller, and R. G. Brisbois; *Org. Synth.* **1995**, 73, 134.

**(2S,3S)-Dihydroxy-1,4-diphenylbutane**

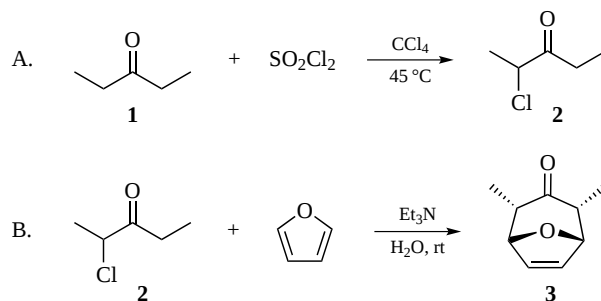
M. A. Robbins, P. N. Devine, and T. Oh; *Org. Synth.* **1999**, 76, 101.

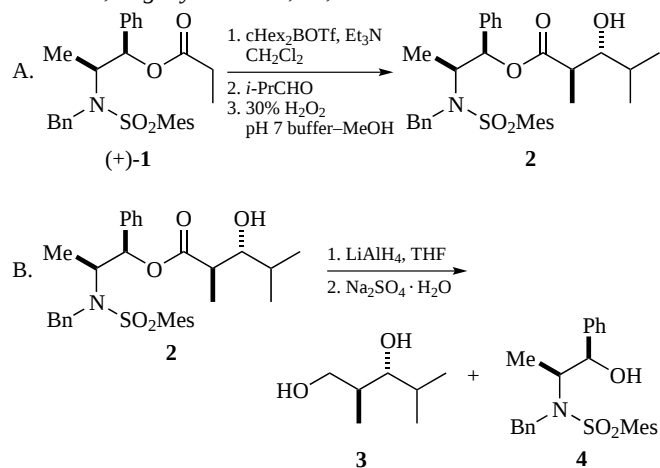
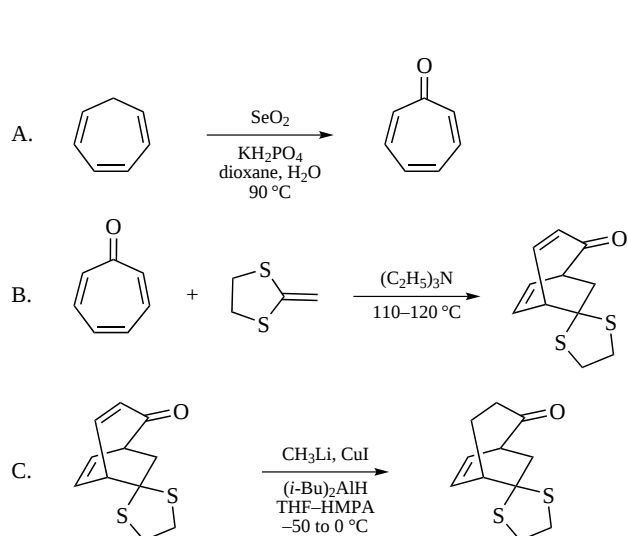
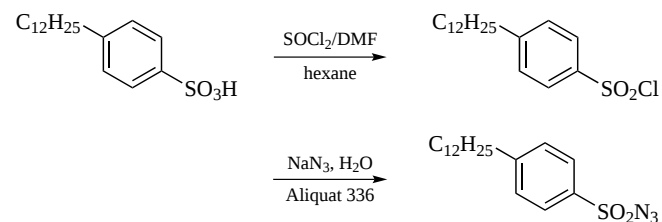
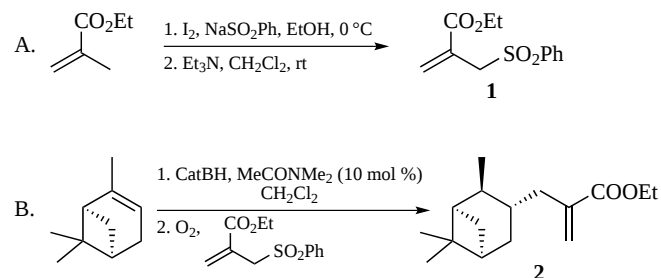
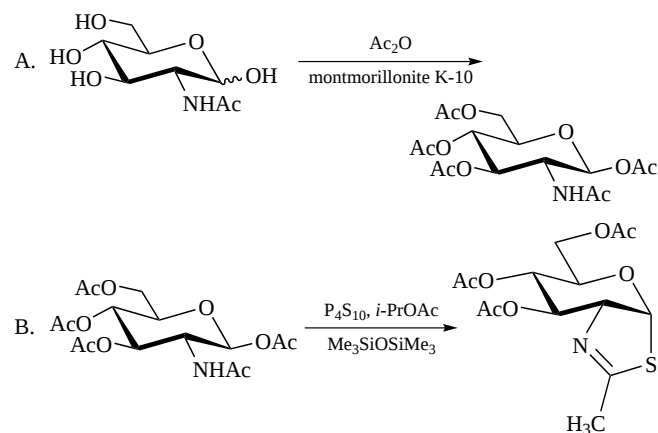
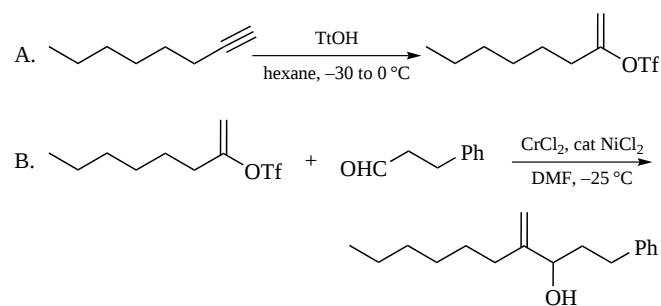
**1,2-Dimethylenecyclohexane**

E. Block and M. Aslam; *Org. Synth.* **1987**, 65, 90.

**2,4-endo,endo-Dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one**

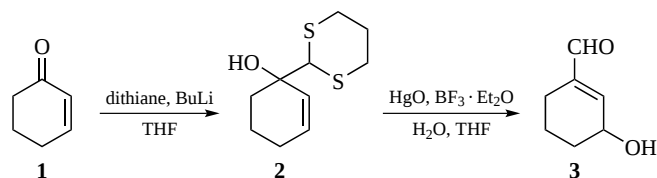
M. Lautens and G. Bouchain; *Org. Synth.* **2003**, 79, 251.



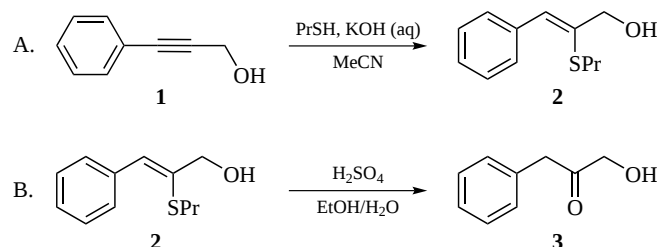
(2S,3R)-2,4-Dimethyl-1,3-pentanediolA. Abiko; *Org. Synth.* **2003**, 79, 116.**9-Dithiolanobicyclo[3.2.2]non-6-en-2-one**K. R. Dahnke and L. A. Paquette; *Org. Synth.* **1993**, 71, 181.**4-Dodecylbenzenesulfonyl Azides**G. G. Hazen, F. W. Bollinger, F. E. Roberts, W. K. Russ, J. J. Seman, and S. Staskiewicz; *Org. Synth.* **1995**, 73, 144.**Ethyl 2-[(1S,2R,3R,5S-2,6,6-Trimethylbicyclo[3.1.1]hept-3-yl)methyl]acrylate**V. Darmency, E. M. Scanlan, A. P. Schaffner, and P. Renaud; *Org. Synth.* **2006**, 83, 24.**GlcNAc-thiazoline Triacetate**S. Knapp, R. A. Huhn, and B. Amorelli; *Org. Synth.* **2007**, 84, 68.**2-Hexyl-5-phenyl-1-penten-3-ol**K. Takai, K. Sakogawa, Y. Kataoka, K. Oshima, and K. Utimoto; *Org. Synth.* **1995**, 72, 180.

3-Hydroxy-1-cyclohexene-1-carboxaldehyde

H. L. Rigby, M. Neveu, D. Pauley, B. C. Ranu, and T. Hudlicky; *Org. Synth.* **1989**, 67, 205.

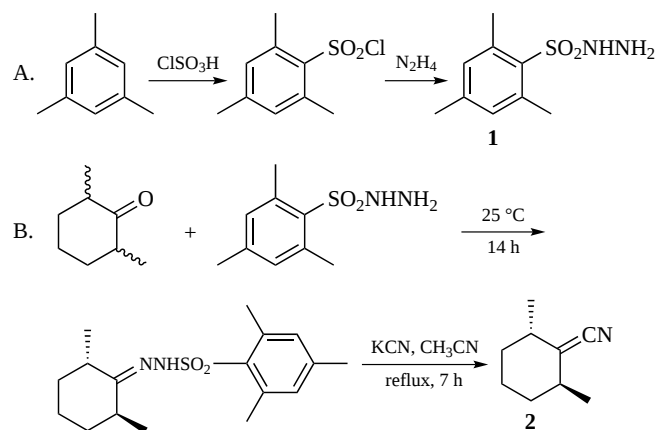
**1-Hydroxy-3-phenyl-2-propanone**

M. S. Waters, K. Snelgrove, and P. Maligres; *Org. Synth.* **2003**, 80, 190.

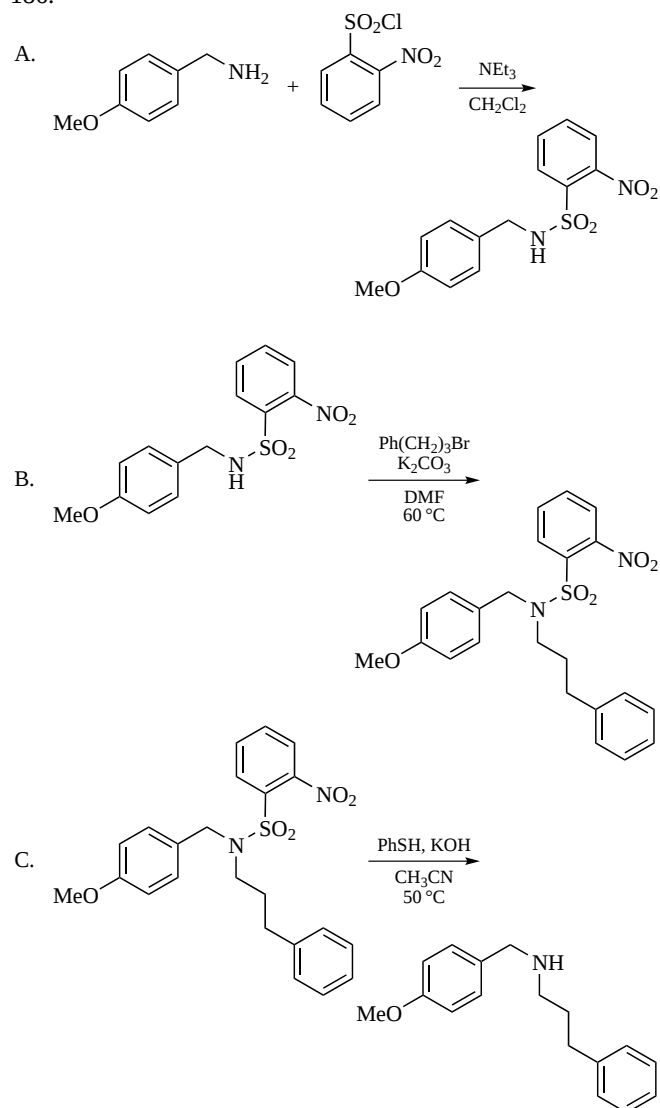


**Mesitylenesulfonylhydrazine, and
(1 α ,2 α ,6 β)-2,6-Dimethylcyclohexanecarbonitrile and
(1 α ,2 β ,6 α)-2,6-Dimethylcyclohexanecarbonitrile as a
Racemic Mixture**

J. R. Reid, R. F. Dufresne, and J. J. Chapman; *Org. Synth.* **1997**, 74, 217.

**N-(4-Methoxybenzyl)-3-phenylpropylamine**

W. Kurosawa, T. Kan, and T. Fukuyama; *Org. Synth.* **2003**, 79, 186.

**5-Methyl-2,2'-bipyridine**

A. P. Smith, S. A. Savage, J. C. Love, and C. L. Fraser; *Org. Synth.* **2002**, 78, 51.

